

Silicon-Containing COFs and MOFs for CO₂ Capture

Okpara Sergeant Bull

Imperial College London
Department of Chemistry

A thesis Submitted for the Degree of Doctor of Philosophy

September, 2018

Declarations

Declaration of Originality

The work described in this thesis was conducted in the Department of Chemistry, Imperial College London, between November 2014 and July 2018. Other than cited references or acknowledgements, the entire body of work is mine, and has not been previously submitted for a degree at this or any other university.

Copyright Declaration

The copyright of this thesis rests with the author and is made available under a Creative Commons Attribution Non-commercial No Derivatives licence. Researchers are free to copy, distribute or transmit the thesis on the condition that they attribute it, that they do not use it for commercial purposes and that they do not alter, transform or build upon it. For any reuse or redistribution, researchers must make clear to others the licence terms of this work.

Acknowledgement

I wish to thank very specially my supervisors: Prof. Paul Lickiss and Dr. Rob Davies for all the support they gave me throughout my studentship period. God bless both of you richly.

Many thanks to other members of the Paul Lickiss and Rob Davies research groups. Thanks to Dr. Andrew White for solving most of the X-ray crystal structures in this thesis as well as David Pugh, and Peter Horton of the UK National Crystallographic Service who solved some of the MOF structures. Additionally, I thank Pete Haycock and Lisa Haigh for running the NMR and Mass spectrometry services respectively. Furthermore I thank Stephen Boyer of London Metropolitan University for carrying out elemental analysis of my samples.

I acknowledge and appreciate most greatly the indefatigable efforts and supports of my lovely wife (Mrs. Ibiso Bull) and those of my children (Olem-Odinami Bull, Ella Bull, Nissi Bull, Lisa Bull and James Bull) throughout the period of this programme. God will bless all of you real good.

Abstract

This work was conducted in order to explore the potential of novel silicon-based Covalent Organic Frameworks (COFs) and Metal-Organic Frameworks (MOFs) for CO₂ capture. A Lewis acid, cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane (**3**) was synthesized and complexed with a variety of Lewis bases such as 4,4'-bipyridine (**L**₁), 1,2-di(pyridin-4-yl)ethane (**L**₂), 1,2-di(pyridin-4-yl)ethene (**L**₃), 1,3-di(pyridin-4-yl)propane (**L**₄), 1,2-di(pyridin-4-yl)sulfane (**L**₅), 1,2-di(pyridin-4-yl)diazene (**L**₆), 1,4-di(pyridin-4-yl)benzene (**L**₇), 3,5-di(pyridin-3-yl)-1,2,4-thiadiazole (**L**₈) and 3,5-di(pyridin-4-yl)-1,2,4-thiadiazole (**L**₉) to afford a range of 1-D polymers such as [Ph₆B₂Si₂O₄].L₁ (**4**), [Ph₆B₂Si₂O₄].L₂ (**5**), [Ph₆B₂Si₂O₄].L₃ 0.5(CH₂Cl₂) (**6**), [Ph₆B₂Si₂O₄].L₄ (**7**), [Ph₆B₂Si₂O₄].L₅ (**8**), [Ph₆B₂Si₂O₄].2L₉.2[PhB(OH)₂] (**14**) as well as a short polymeric structure [Ph₆B₂Si₂O₄].L₈ (**13**). In addition, other compounds such as Ph₈B₄Si₂O₆.L₆ (**9**), 4(C₁₂H₁₂O₂Si).3(C₁₀H₈N₄) (**10**), Ph₄Si₂(OH)₄.2L₇ (**11**) and Ph₈B₄Si₂O₆.L₇ (**12**) were formed due to ring contraction readiness of compound (**3**). These compounds displayed extended inter- and intra-molecular π - π and other forms of π -interactions as well as hydrogen bonding in their crystal packings. Furthermore, novel silicon-based tetrakis-, tris- and di- aryl-pyridine linkers such as tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L**₁₀), tri(4-(pyridine-4-vinyl)phenyl)methylsilane (**L**₁₁), bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (**L**₁₂) tetrakis(4-(pyridine-4-vinyl)biphenyl)silane (**L**₁₃), tri(4-(pyridine-4-vinyl)biphenyl)methylsilane (**L**₁₄), as well as aryl-carboxylic acid linkers such as silane tetrakis(biphenyl-4-carboxylic acid) (**L**₁₅) and silane tris(biphenyl-4-carboxylic acid) (**L**₁₆) have been synthesized from their corresponding aryl-bromine precursors. Treatment of (**L**₁₀) with Zn(CH₃COO)₂ and Zn(NO₃)₂.6H₂O give a 2-D (MOF) (**17**) and a 3-D MOF (**18**) respectively. While (**L**₁₅) solvothermally formed MOF (**19**) after treatment with Zn(NO₃)₂.6H₂O in solvent mixture of H₂O/DMA. MOF (**17**) possesses a pore size of 18.5 Å

with no interpenetration of channels while **(18)** exhibits a five-fold interpenetration of channels as well as two types of pores with length and width of 31.42 and 24.62 Å for the big pores and 15.70 and 12.20 Å for the small pores respectively. MOF **(19)** exhibits a pore diameter of 17.06 Å.

List of Figures, Schemes and Tables

CHAPTER 1

Figure 1.0: Global energy balance on annual-average basis (Figure adapted from ref. ¹).....	1
Figure 1.1: Global temperature and carbon dioxide; Global data average and adjusted to early industrial baseline (1881-1910), Source: NASA GISS, NOAA NCEI, ESRL.....	2
Figure 1.2: Technology for CO ₂ Storage; Source: Intergovernmental Panel on Climate Change (IPCC). ²⁶	4
Figure 1.3: Three methods for CO ₂ capture from power generation plan. (Adapted from refs. ^{26,27}).....	6
Figure 1.4: Materials for CO ₂ capture in the context of pre-combustion, post-combustion and oxy-fuel captures (adapted from refs. ²³⁻²⁵).....	7
Figure 1.5: Schematic diagram of the Carbozyme permeation process.(adapted from ref. ⁷⁰)...16	
Figure 1.6: Structures of (i) Cyclo-boratrissiloxane; (ii) Cyclo-diboratetrasiloxane; (iii) 1:1 adduct of a boroxine; (iv) 1:1 adduct of a cyclo-diboratetrasiloxane; (v) 10-membered cyclo-boratetrasiloxane; (vi) 12-membered cyclo-diboratetrasiloxane. ^{83,85}	18
Figure 1.7: Potential route for COF/MOF formation and CO ₂ sorption.....	25
Scheme 1.0: Equations (1) production of syngas (2) production of further H ₂	5
Scheme 1.1: Reaction of CO ₂ and aqueous amine solution.....	8
Scheme 1.2: Pathways interaction of CO ₂ and amine.....	9
Scheme 1.3: Hydrolysis of carbamate to bicarbonate.....	9
Scheme 1.4: Base catalysed hydration of CO ₂ to bicarbamate.....	9
Scheme 1.5: Formation of a carbamate and bicarbonate via the reaction of CO ₂ and inorganic metal hydroxide [MOH is an inorganic Metal hydroxide (a base)].....	11
Scheme 1.6: Reaction of CO ₂ with alkaline earth metal oxides.....	12
Scheme 1.7: Equations (3) adsorption of CO ₂ on CaO to give CaCO ₃ (4) decomposition of CaCO ₃ to liberate CO ₂	13
Scheme 1.8: A two-step pathway for the formation of carbamate from amines and CO ₂	14
Scheme 1.9: Pathways for the syntheses of cyclic 8- and 6-membered ring Si-O-B compounds.....	19
Scheme 1.10: Self-condensation of boronic acids. ⁹⁴	20

Scheme 1.11: Adduct formation of boronate esters and boroxines with N-donor ligands NR ₃	21
Scheme 1.12: Formation of a macrocycle via condensation reaction ^{107,114}	22
Scheme 1.13: Formation of calix[3] arene-like macrocycle (b). ¹⁰⁷	22
Scheme 1.14: Formation [4+4] condensation product from arylboronic acids. ¹¹⁵	22
Scheme 1.15: Formation of tetrameric ¹¹³ and pentameric macrocycles. ¹¹⁶	23
Scheme 1.16: Syntheses of 1-D polymer and macrocycle from their respective monomers. ¹¹⁷	23

CHAPTER 2

Figure 2.0: self- and co-condensation reaction of boronic acids to boroxine and boronate esters.....	29
Figure 2.1: Monomers with different geometries for the design of boron-based COFs.....	35
Figure 2.2: Monomers used for the construction of CTFs of different dimensions.....	53
Figure 2.3: Some monomers used for constructing imine-based COFs.....	66
Figure 2.4: Conventional two-component [1+1] and multiple-component [1+2] or [1+3] strategies for the design and synthesis of COFs. Adapted from refs. ^{135,239,240}	67
Figure 2.5: Schematic method of the aims of this project.....	77
Figure 2.6: Linkers used in this work.....	79
Figure 2.7: 1-D Crystal structure of Compound (4). Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms are omitted for clarity.....	81
Figure 2.8: An ellipsoid view of a fragment of [Ph ₆ B ₂ Si ₂ O ₄].L ₁ (4) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms omitted for clarity.....	82
Figure 2.9: Two polymer chains with C-H... π (2.731 Å) & π ... π (3.409 Å) interaction in the crystal packing. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O and white = H. Disordered solvent and most H atoms are omitted for clarity.....	83
Figure 2.10: Crystal packing in [Ph ₆ B ₂ Si ₂ O ₄].L ₁ (4) with four polymeric chains running parallel to the a-axis leading to formation of channels. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms and disordered solvents are omitted for clarity.....	84

Figure 2.11: 1-D polymeric structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (5) connecting two eight membered rings. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O and white = H. Most H atoms are omitted for clarity.....	85
Figure 2.12: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (5) with some atom labelling, H atoms omitted for clarity except ethane H atoms. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms omitted for clarity.....	86
Figure 2.13: Two polymer chains with C-H... π (2.779 Å), C-H...O(2.439 Å) interactions in the crystal packing of compound (5). Colour identity, pink = B, green = Si, grey = C, blue = N, red= O and white = H. Most H atoms are omitted for clarity.....	87
Figure 2.14: Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (5) with potential channels of 6.945 Å. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms are omitted for clarity.....	88
Figure 2.15: 1-D polymeric structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (6) connecting two eight membered rings. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O and white = H. The 0.5 (CH_2Cl_2) and all H atoms are omitted except the ones on the ethene for clarity.....	89
Figure 2.16: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (6) with some atom labelling, H atoms are omitted for clarity except ethene H atoms.....	90
Figure 2.17: Two polymer chains running parallel to the c-axis with C-H...O (2.098 Å) interactions in the crystal packing of Compound (6). Colour identity, pink = B, green = Si, light green = Cl, grey = C, blue = N, red= O. H atoms are omitted for clarity.....	92
Figure 2.18: Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (6), [A] four individual polymer chains, viewed from a-axis, and [B] four polymer chains leading to formation of solvent filled channels (11.441 Å), viewed from b-axis. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms and solvents are omitted for clarity.....	93
Figure 2.19: 1-D structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (7) connecting two eight membered rings via L4. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O and white = H. Most H atoms are omitted for clarity.....	94
Figure 2.20: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (7) with some atom labelling, H atoms omitted for clarity except propane H atoms. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O and white = H. Most H atoms are omitted for clarity.....	95
Figure 2.21: Two polymer chains of (7) with C-H... π (2.640 Å), C-H... π (2.730 Å) and π ... π (3.376 Å) interaction in the crystal packing. . Colour identity, pink = B, green = Si, grey = C, blue = N, red= O. H atoms omitted for clarity. Viewed from b axis.....	97

Figure 2.22: Crystal packing in (7) five individual polymer with solvent filled channels. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O.H atoms are omitted for clarity. Viewed from b axis.....	98
Figure 2.23: Polymeric structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_5$ (8) connecting four eight membered rings via four L_5 . Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity.....	99
Figure 2.24: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_5$ (8) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O, yellow = sulphur. H atoms are omitted for clarity. H atoms omitted for clarity.....	100
Figure 2.25: Crystal packing of compound (8) with intra-noncovalent interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O, yellow = sulphur, white = H. Most H atoms are omitted for clarity.....	102
Figure 2.26: An ellipsoid view of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_6$ (9) with some atom numbering. Colour identity, pink = B, green = Si, grey = C, blue = N, and red= O. H atoms are omitted for clarity.....	103
Figure 2.27: Crystal packing in $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_6$ (9) with six individual dimer. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O, white = H. Most H atoms are omitted for clarity.....	105
Figure 2.28: An ellipsoid view of $4(\text{Ph}_2\text{Si}(\text{OH})_2)$, $3(\text{C}_{10}\text{H}_8\text{N}_4)$ (10) with $\text{H}\cdots\text{O}$ and $\text{H}\cdots\text{N}$. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O, light grey = H. All H atoms except the ones involved in hydrogen bonding are omitted for clarity.....	107
Figure 2.29: Crystal packing in $4(\text{Ph}_2\text{Si}(\text{OH})_2)$, $3(\text{C}_{10}\text{H}_8\text{N}_4)$ (10) with hydrogen bonding and other forms of inter- and intra-rings interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O, light grey = H. Most H atoms are omitted for clarity.....	108
Figure 2.30: Structure of $2[\text{Ph}_2\text{Si}(\text{OH})_2]\cdot 2\text{L}_7$ (11) with hydrogen bonding. Colour identity, green = Si, grey = C, blue = N, red = O, light grey = H. Most H atoms are omitted for clarity.....	109
Figure 2.31: The crystal packing of $\text{Ph}_4\text{Si}_2(\text{OH})_4\cdot 2\text{L}_7$ (11) with intermolecular non-covalent $\text{C}-\text{H}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{O}$ interaction in its crystal packing. A and B indicate centroids. Colour identity, green = Si, grey = C, blue = N, red = O, light grey = H. Most H atoms are omitted for clarity.....	110

- Figure 2.32:** An ellipsoid view of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_8$ (**13**) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity.....113
- Figure 2.33:** Non-bonded interactions in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_8$ (**13**) units with intramolecular C-H $\cdots\pi$, C-H $\cdots\text{N}$, C-H $\cdots\text{O}$ and $\pi\cdots\pi$ interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H. Most H atoms are omitted for clarity.....115
- Figure 2.34:** Crystal packing of two individual $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_8$ (**13**) connected by intermolecular C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions. Colour identity, pink = B green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H, colour solid circles = centroid. Most H atoms are omitted for clarity.....115
- Figure 2.35:** Figure 2: 1-D Polymeric structure of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) showing hydrogen bonding as pale blue bonds between phenylboronic acids and linkers. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H, Most H atoms are omitted for clarity.....117
- Figure 2.36:** 1-D chain structure of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (**14**), pale blue bonds, hydrogen bonding (H $\cdots\text{O}$) and linker (H $\cdots\text{N}$). Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H, Most H atoms are omitted for clarity.....118
- Figure 2.37:** An ellipsoid view of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity.....118
- Figure 2.38:** Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) with intramolecular C-H $\cdots\pi$, C-H $\cdots\text{N}$, C-H $\cdots\text{O}$ and H $\cdots\text{B}$ interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H. black dot = centroid. Most H atoms are omitted for clarity.....120
- Figure 2.39:** Crystal packing of three individual $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) chains connected by intermolecular C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions. Colour identity, pink = B green = Si, black and purple = C, blue = N, red = O, yellow = sulphur, light grey = H, colour solid circles = centroid. Most H atoms are omitted for clarity.....121
- Figure 2.40:** Other di- and tri-connected Lewis acids.....121

Figure 2.41: An ellipsoid view of (Ph ₄ Si ₂ O ₃ B)C ₆ H ₅ (Ph ₄ Si ₂ O ₃ B) (3a) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, red= O. H atoms are omitted for clarity.....	123
Figure 2.42: Non-covalent C-H··· π , C-H···B and B··· π in the crystal packing of (3a); H atoms omitted for clarity.....	124
Figure 2.43: Crystal structure of (3b) with some atom labels. (Adapted from Ref. ⁸⁴), Colour identity, pink = B, green = Si, grey = C, red= O. H atoms are omitted for clarity.....	126
Scheme 2.0: Synthesis of COF-1 and COF-5. ¹⁸¹	30
Scheme 2.1: Synthetic scheme and proposed structure for COF-18Å. ¹⁸²	31
Scheme 2.2: Synthesis of COF-66. ¹⁴⁵	32
Scheme 2.3: Synthesis OF COF TDCOF-5. ¹⁸⁴	33
Scheme 2.4: Synthesis of 3-D COFs (COFs- 102 and 103) with <i>ctn</i> topology. ⁷⁷	36
Scheme 2.5: Synthesis of 3-D boron-based COF-108, with bor topology. ⁷⁷	37
Scheme 2.6: Synthesis of 2-D triazine-based COF (CTF-1). ¹²²	38
Scheme 2.7: Trimerization of 1,3,5-tricyanobenzene to CTF-0. ¹⁹⁰	39
Scheme 2.8: Synthesis of (PCTF-1 & PCTF-2). ¹⁹¹	39
Scheme 2.9: Synthesis of porous covalent triazine-based frameworks (PCTF-3 - PCTF-7). ¹⁹²	41
Scheme 2.10: Structures of PCTF-1, PCTF-2, PCTF-3 & PCTF-4. ¹⁹⁴	42
Scheme 2.11: Synthesis of CTF-1 and perfluorinated covalent triazine-based framework (FCTF-1). ¹⁹⁶	44
Scheme 2.12: Synthesis pathway for fl-CTFs. ¹⁹⁸	46
Scheme 2.13: Synthetic pathway for the MCTP networks. ⁴⁰	47
Scheme 2.14: Synthesis of the CTFs CTF1 (top), pym-CTF(middle), lut-CTF (bottom left), and bipy CTF (bottom right). ¹⁷²	48
Scheme 2.15: Synthesis of CTF-FUM and CTF-DCN. ²⁰⁴	49
Scheme 2.16: Triazine formation in the synthesis of CTF-HUST. "HUST" = "Huanzhong University of Science and Technology". ²⁰⁵	50
Scheme 2.17: Synthesis of CTF- HUSTs (a) CTF-HUST-1 (b) CTF-HUST-2; the different coloured circles represent two types of pores. ²⁰⁵	51

Scheme 2.18: Synthesis of CTF-HUSTs (c) CTF-HUST-3 (d) CTF-HUST-4; the different coloured circles represent two types of pores. ²⁰⁵	52
Scheme 2.19: Synthesis of CUPor-BPDC COF. ²¹⁰	54
Scheme 2.20: Synthesis of TpPa-1 and TpPa-2 by combined reversible and irreversible reactions. ²¹¹	55
Scheme 2.21: Synthesis of TpPa-COF (MW). ²¹³	57
Scheme 2.22: Synthesis of ILCOF-1. ²¹⁸	58
Scheme 2.23: The synthesis of ACOF-1. ²²⁰	59
Scheme 2.24: The synthesis of COFJLU2. ²²¹	60
Scheme 2.25: synthesis of HEX and HEX-COF1. ²²⁷	61
Scheme 2.26: The room-temperature polyimine condensation to form RT-COF-1. ²²⁸	62
Scheme 2.27: Synthesis of [N=N]x% -TAPH-COFs with azobenzene group and [C=C]x% -TAPH COFs with stilbene group via nucleophilic substitution reaction from [HO]x% -TAPH-COFs (X = 25, 50, 75, 100). ²²⁹	64
Scheme 2.28: Synthesis pathway for three 2-D squaraine-bridge COFs. ²³⁰	65
Scheme 2.29: Synthesis of NTU-COF-2 involving the formation of two kinds of covalent bonds from orthogonal reactions. ²³⁹	68
Scheme 2.30: Synthesis and structures of typical [1 + 2] hexagonal MC-COFs. ¹³⁵	69
Scheme 2.31: Synthesis and ordered structure of MC-COF-TP-E ₁ E ₃ E ₇ .	71
Scheme 2.32: Synthesis of tetragonal [1+2] MC-NiPc-E ₁ E ₇ . ¹³⁵	72
Scheme 2.33: Preparation of (Ph ₆ B ₂ Si ₂ O ₄) (3)	77
Scheme 2.34: Synthesis of [Ph ₆ B ₂ Si ₂ O ₄].L ₁ (4)	80
Scheme 2.35: The synthesis of [Ph ₆ B ₂ Si ₂ O ₄].L ₂ (5)	84
Scheme 2.36: The synthesis of [Ph ₆ B ₂ Si ₂ O ₄].L ₃ (6)	88
Scheme 2.37: The synthesis of [Ph ₆ B ₂ Si ₂ O ₄].L ₄ (7)	94
Scheme 2.38: Reaction method for the synthesis of [Ph ₆ B ₂ Si ₂ O ₄].L ₅ (8)	98
Scheme 2.39: The synthesis of Ph ₈ B ₄ Si ₂ O ₆ (9). For (10) see Scheme 2.40	102
Scheme 2.40: The synthesis of 4[Ph ₂ Si(OH) ₂].3(C ₁₀ H ₈ N ₄) (10). For (9) see Scheme 2.39	104
Scheme 2.41: Reaction scheme for the synthesis of 2[Ph ₂ Si(OH) ₂].2L ₇ (11). For (12) see Scheme 2.42	109

Scheme 2.42: Reaction scheme for the synthesis of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_7$ (12). For (11) see Scheme 2.41	111
Scheme 2.43: The synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_8$ (13).....	112
Scheme 2.44: Reaction scheme for the synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (14)....	116
Scheme 2.45: Reaction method for the synthesis of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_5(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (3a).....	122
Scheme 2.46: Reaction scheme for the synthesis of $[\text{B}(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3\text{B}]$ (3b).....	125

Table 2.0: Summary of pore sizes, BET and CO_2 uptake 1 and 55 bars of some boron-based COFs.....	32
Table 2.1: S_{BET} , density and CO_2 uptake capacities of some 3-D boron-based COFs.....	37

CHAPTER 3

Figure 3.0: Examples of metal ions and linkers used to give 1-,2- or 3-D structures with porosity for gas adsorption.....	128
Figure 3.1: Timeline of the most common synthetic methods used for the synthesis of MOFs. ²⁸¹	135
Figure 3.2: Some ditopic carboxylate linkers used for the synthesis of MOFs.....	152
Figure 3.3: Some tritopic carboxylate linkers used for the preparation of MOFs.....	154
Figure 3.4: Symmetry elements of a T_d symmetry.....	155
Figure 3.5: Pictorial representation of some topologies associated with MOFs by the combination of tetrahedral linkers and SBUs (adapted from ref. ⁴³⁷).....	156
Figure 3.6: Some tetratopic carboxylate linkers used for the synthesis of MOFs.....	159
Figure 3.7: Some hexatopic carboxylate linkers used for the construction of MOFs.....	161
Figure 3.8: Some octatopic carboxylate linkers used for the construction of MOFs.....	162
Figure 3.9: The bridging angles in (a) metal Im (b) zeolites. ⁴⁵³	163
Figure 3.10: Some N-heterocyclic linkers used for the construction of MOFs.....	166
Figure 3.11: Schematic method of the for making of linkers and MOFs.....	167
Figure 3.12: Single crystal X-ray structure of (L12). Colour identity, green = Si, grey = C, blue = N, white = H.....	174

Figure 3.13: Non-covalent intermolecular interaction in the crystal packing of (L ₁₂). Most H atoms are omitted for clarity.....	175
Figure 3.14: Crystal structure of compound (3d). Colour identity, pink = B, green = Si, grey = C, blue = N, red= O, light grey = H.....	176
Figure 3.15: (A) a 2-D coordination of Zn(OAc) ₂ and linker (L ₁₀) to give tetrakis (4-(pyridine-4-vinyl)phenyl)silane MOF (17). (B) a novel 2,4-connected net topology. Colour identity, green Si, purple Zn, blue N, grey C, and red O. H atoms are omitted for clarity.....	186
Figure 3.16: (A) 2-D network with pores as viewed along the c-axis, (B) Interleave leaved layers. Colour identity on (A), green Si, purple Zn, blue N, grey C, and red O. H atoms omitted for clarity.....	186
Figure 3.17: Space-filled 2-D structure of (17) with mean pore size of 18. 5 Å, viewed down the c-axis. Colour identity, green Si, purple Zn, blue N, grey C, pink H, and red O. solvent omitted for clarity.....	187
Figure 3.18: Diamond-like crystals with dimensions of ca. 0.190×0.100×0.030 mm ³ of MOF(18).....	188
Figure 3.19: (A) 3-D connection of four (L ₁₀) and two H ₂ O around each zinc atom in the framework of MOF (18) viewed along the b-axis; (B) a 4,4-connected net of pts topology. Colour identity, green Si, purple Zn, blue N, grey C, and red O, and pink H. All H atoms are omitted for clarity except those found in H ₂ O.....	189
Figure 3.20: Space-filled crystal packing of MOF (18) with two types of pore sizes viewed along the b-axis. Colour identity, green Si, purple Zn, blue N, grey C, red O, and pink H.....	190
Figure 3.21: Space filled crystal structure of MOF (18) with five-fold network interpenetration as well as pores, viewed from the c-axis.....	190
Figure 3.22: Connection of one silane tetrakis(biphenyl-4-carboxylate with 4 disordered zinc centres.....	192
Figure 3.23: 3-D connection of (L ₁₅) and zinc atoms in the framework of MOF (19) viewed along the a-axis. Disorder at Zn was hard to resolve and so is included in the Figure. Colour identity, green Si, purple Zn, grey C, and red O. All H atoms are omitted for clarity.....	192
Figure 3.24: Space-filled structure of MOF (19) with 17.06 Å pore size, viewed from the a-axis. Colour identity, green Si, purple Zn, grey C, red O, and pink H.....	193
Figure 3.25: Perspective view of network channels along the a-axis.....	193

Scheme 3.0: Preparation of a chiral MOF via slow diffusion. ³⁴⁵	151
Scheme 3.1: Pathway for the synthesis of tetrakis(4-bromophenyl)silane (C).....	168
Scheme 3.2: Pathway for the synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (L₁₀)...	169
Scheme 3.3: Pathway for the synthesis of tri(4-bromophenyl)methylsilane (E).....	170
Scheme 3.4: Pathway for the synthesis of tri(4-(pyridine-4-vinyl)phenyl)methylsilane (L₁₁)	171
Scheme 3.5: Method for the preparation of [(Methylsilanetriyl)tris(benzene-4,1)]triboronic acid (3c).....	172
Scheme 3.6: Pathway for the synthesis of di(4-bromophenyl)dimethylsilane (F).....	173
Scheme 3.7: Synthesis of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L₁₂).....	173
Scheme 3.8: Method for the preparation of [(Dimethylsilanediy)bis(4,1-phenylene)]diboronic acid (3d).....	175
Scheme 3.9: Multi-step synthetic method for the preparation of tris(-bromophenyl)chlorsilane (G), adapted from reference. ⁴⁸⁴	177
Scheme 3.10: Reaction method for the preparation of compound (G).....	177
Scheme 3.11: Reaction scheme for the preparation of compound (J).....	178
Scheme 3.12: Synthesis of tetrakis(4-(pyridine-4vinyl)biphenyl)silane (L₁₃).....	179
Scheme 3.13: Synthesis of tri(4-bromobiphenyl)methylsilane (K).....	180
Scheme 3.14: Pathway for the making of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (L₁₄).....	181
Scheme 3.15: Pathway for the synthesis of silane tetrakis(biphenyl-4-carboxylic acid) (L₁₅).....	182
Scheme 3.16: Pathway for the synthesis of methylsilane tris(biphenyl-4-carboxylic acid) (L₁₆).....	183
Scheme 3.17: Synthesis of MOF (17) via layering and slow diffusion.....	185
Scheme 3.18: Pathway for the preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18).....	187
Scheme 3.19: Pathway for the preparation of MOF (19).....	191

Table 3.0: Selected MOFs and some of their relevant material characteristics enabled by scCO ₂ activation.....	139
--	-----

List of abbreviations

COFs	Covalent Organic Frameworks
MOFs	Metal Organic Frameworks
GHGs	Greenhouse Gases
CCS	Carbon Capture and Storage
MEA	Monoethanolamine
DEA	Diethanolamine
MDEA	Methyldiethanolamine
S_{BET}	Brunauer-Emmett-Teller Surface Area

Table of Contents

Silicon-Containing COFs and MOFs for CO ₂ Capture.....	i
Declarations	i
Acknowledgement.....	ii
Abstract	iii
List of Figures, Schemes and Tables.....	v
List of abbreviations	xvi
Chapter 1	1
1.0 INTRODUCTION.....	1
1.1. Global Warming.....	1
1.2. Carbon Capture and Storage (CCS).....	3
1.3. Amine Based Absorbents.....	7
1.4. Porous Materials for Adsorption	10
1.5. Compounds Derived from Borosilicate/Organoboron Lewis Acids and Pyridines.....	17
1.6. Aim and Objective of Thesis	24
Chapter 2	26
2.0 COVALENT ORGANIC FRAMEWORKS (COFs)	26
2.1 Introduction.....	26
2.2 COF Design	27
2.2.1 Dynamic Covalent Chemistry of COFs.....	27
2.2.2 Structure of Building Units	28
2.3 Building Blocks for COFs	29
2.3.1 Boron-based COFs.....	29
2.3.2 Triazine-based COFs (CTF)	38
2.3.3 Imine-based COFs.....	53

2.3.4 Multiple-component COFs.....	67
2.4 Synthetic Methods Used in the preparation of COFs.....	73
2.4.1 Solvothermal Synthesis of COFs.....	73
2.4.2 Ionothermal Synthesis of COFs.....	75
2.4.3 Microwave-assisted Synthesis of COFs	75
2.5 Challenges in the synthesis of COFs.....	76
2.6.0 Synthetic Methods, Results and Discussion.....	77
2.6.1 Synthesis of $Ph_6B_2Si_2O_4$ (3).....	77
2.6.2 Synthesis of $[Ph_6B_2Si_2O_4].L_1$ (4)	80
2.6.2.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_1$ (4).....	80
2.6.3 Synthesis of $[Ph_6B_2Si_2O_4].L_1$ (5)	84
2.6.3.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_2$ (5).....	85
2.6.4 Synthesis of $[Ph_6B_2Si_2O_4].L_3$ 0.5(CH_2Cl_2) (6)	88
2.6.4.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_3$ (6).....	89
2.6.5 Synthesis of $[Ph_6B_2Si_2O_4].L_4$ (7)	93
2.6.5.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_4$ (7)	94
2.6.6 Synthesis of $[Ph_6B_2Si_2O_4].L_5$ (8)	98
2.6.6.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_5$ (8)	98
2.6.7 Synthesis of $Ph_8B_4Si_2O_6.L_6$ (9)	102
2.6.7.1 Spectral and crystal description of $Ph_8B_4Si_2O_6$ (9)	102
2.6.8 Synthesis of $4(Ph_2Si(OH)_2), 3(C_{10}H_8N_4)$ (10).....	106
2.6.8.1 Crystal description of $4(C_{12}H_{12}O_2Si), 3(C_{10}H_8N_4)$ (10)	106
2.6.9 Synthesis of $2Ph_2Si(OH)_2].2L_7$ (11)	108
2.6.10 Synthesis of $2[Ph_4B_2SiO_3].L_7$ (12)	111
2.6.11 Synthesis of $[Ph_6B_2Si_2O_4].2L_8$ (13)	112
2.6.11.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].2L_8$ (13)	112
2.6.12 Synthesis of $[Ph_6B_2Si_2O_4].2L_9, 2[PhB(OH)_2]$ (14).....	116

2.6.12.1 Spectral and crystal description of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (14)	116
2.6.13.1 Spectral and crystal description of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_5(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (3a)....	122
2.7. Summary and Outlook.....	127
Chapter 3	128
3.0 METAL-ORGANIC FRAMEWORKS (MOFs).....	128
3.1 Introduction	128
3.2 Synthesis of Metal-Organic Frameworks (MOFs)	129
3.2.1 <i>Hydro (solvo) thermal methods</i>	129
3.2.2 <i>Microwave (MW) Assisted Methods</i>	131
3.2.3 <i>Sonochemical Method</i>	132
3.2.4 <i>Electrochemical Method</i>	132
3.2.5 <i>Mechanochemical (Mechanosynthesis) Method</i>	133
3.2.6 <i>Slow Diffusion Method</i>	134
3.2.7 <i>Solvent evaporation and ionothermal Method</i>	135
3.3. Activation of Metal-Organic Frameworks (MOFs).....	136
3.3.1 <i>Conventional Activation</i>	137
3.3.2 <i>Activation by Solvent-Exchange</i>	137
3.3.3 <i>The Use of scCO_2</i>	138
3.3.4 <i>Activation by Freeze-drying</i>	140
3.3.5 <i>Activation by chemical treatment</i>	141
3.4 Characterisation of Metal-Organic Frameworks MOFs).....	142
3.4.1 <i>Single crystal X-ray Diffraction (XRD)</i>	143
3.4.2 <i>Powder X-ray Diffraction (PXRD)</i>	144
3.4.3 <i>Elemental Analysis</i>	145
3.4.4 <i>Thermogravimetric Analysis (TGA)</i>	145
3.4.5 <i>Surface Area Measurements (N_2 Adsorption & Desorption Isotherms)</i>	146
3.4.6 <i>Nuclear Magnetic Resonance (NMR) Spectroscopy</i>	148

3.4.7 Gas Adsorption Measurements	149
3.5.0 Organic Linkers	150
3.5.1 Ditopic Carboxylate Linkers	150
3.5.2 Tritopic Carboxylate Linkers	153
3.5.2 Tetratopic Carboxylate Linkers	155
3.5.3 Hexatopic and Octatopic Carboxylate Linkers.....	160
3.5.4 N-Heterocyclic Linkers	163
3.6.0 Synthetic Methods, Results and Discussion	167
3.6.1 Synthesis of tetrakis(4-bromophenyl)silane (C).....	167
3.6.2 Synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (L₁₀)	168
3.6.3 Synthesis of tris(4-bromophenyl)methylsilane (E).....	170
3.6.4 Synthesis of tris(4-(pyridine-4-vinyl)phenyl)methylsilane (L₁₁)	171
3.6.6 Synthesis of di(4-bromophenyl)dimethylsilane (F).....	173
3.6.7 Synthesis of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L₁₂)	173
3.6.7.1 Spectral and crystal description of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L₁₂).....	174
3.6.9 Synthesis of tris(4-bromophenyl)chlorosilane (G).....	176
3.6.10 Synthesis of tetrakis(4-bromobiphenyl)silane (J)	178
3.6.11 Synthesis of tetrakis(4-(pyridine-4-vinyl)biphenyl)silane (L₁₃)	179
3.6.13 Synthesis of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (L₁₄)	181
3.6.14 Synthesis of silane tetrakis(biphenyl-4-carboxylic acid) (L₁₅).....	182
3.6.15 Synthesis of methylsilane tris(biphenyl-4-carboxylic acid) (L₁₆).....	183
3.6.16 Synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)	185
3.6.16.1 Spectral and crystal description of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)	186
3.6.17 Synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18).....	188
3.6.17.1 Spectral and crystal description of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18)	190

3.6.18 Synthesis of silane tetrakis(biphenyl-4-carboxylate MOF (19)	192
3.7. Summary	195
Chapter 4	197
4.0 CONCLUSION	197
Chapter 5	200
5.0 EXPERIMENTAL	200
Preparation of $\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4$ (3)	200
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].\text{L}_1$ (4)	201
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].\text{L}_2$ (5)	202
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].\text{L}_3$ 0.5(CH_2Cl_2) (6)	202
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].\text{L}_4$ (7)	203
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].\text{L}_5$ (8)	204
Preparation of $[\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6].\text{L}_6$ (9)	204
Preparation of $4(\text{C}_{12}\text{H}_{12}\text{O}_2\text{Si})$, $3(\text{C}_{10}\text{H}_8\text{N}_4)$ (10)	205
Preparation of $\text{Ph}_4\text{Si}_2(\text{OH})_4.2\text{L}_7$ (11)	205
Preparation of $[\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6].\text{L}_7$ dimer (12)	206
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_8$ (13)	207
Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_9$. $2[\text{PhB}(\text{OH})_2]$ (14)	208
Preparation of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_4(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (3a)	208
Preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (L₁₀)	209
Preparation of tris(4-bromophenyl)methylsilane (E)	210
Preparation of tri(4-(pyridine-4-vinyl)phenyl)methylsilane (L₁₁)	211
Preparation of di(4-bromophenyl)dimethylsilane (F)	212
Preparation of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L₁₂)	212
Preparation of tris(4-bromophenyl)chlorosilane (G)	214
Preparation of tetrakis(4-bromobiphenyl)silane (J)	214
Preparation of tetrakis(4-(pyridine-4-vinyl)biphenyl)silane (L₁₃)	215

<i>Preparation of tri(4-bromobiphenyl)methylsilane (K)</i>	216
<i>Preparation of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (L₁₄)</i>	217
<i>Preparation of silane tetrakis(biphenyl-4-carboxylic acid) (L₁₅)</i>	218
<i>Preparation of methylsilane tris(biphenyl-4-carboxylic acid) (L₁₆)</i>	218
<i>Preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)</i>	219
<i>Preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18)</i>	220
<i>Preparation of silane tetrakis(biphenyl-4-carboxylate MOF (19))</i>	220
Chapter 6	221
6.0 References	221
Supplementary Information (S ₁ -S ₈₂) for Silicon-Containing COFs and MOFs for CO ₂ Capture.....	i
Crystallographic Data and Crystallographic Experimental	xlvi
Appendix 1	xlvi

Chapter 1

1.0 INTRODUCTION

1.1. Global Warming

The sun is the major source of energy for the Earth's climate system compared to other sources of energy. An equilibrated climate system of the earth in terms of energy and concentration of greenhouse gases (GHGs) - carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O), water vapour and other trace gases in the atmosphere implies that the amount of solar energy reaching the Earth's surface should be the same as the sum of the reflected solar radiation and infrared long-wave radiation leaving the surface of the earth. A disruption of this global radiation arrangement and concentration of GHGs, be it natural or by human activities, brings about a radiation imbalance because GHGs are known to absorb infrared electromagnetic radiation and retain it on the surface of the Earth thus making the surface of the Earth warmer than it would otherwise be **Figure 1.0**.¹⁻

3

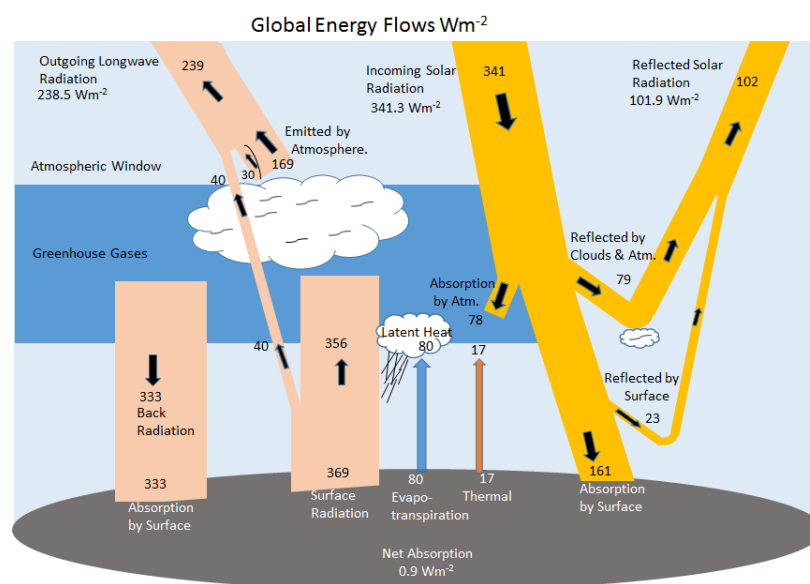


Figure 1.0: Global energy balance on annual-average basis (Figure adapted from ref.¹)

Globally, 85% of energy for domestic and industrialised application is generated using fossil fuels (crude oil, coal, natural gas) or fossil fuel power plants.⁴⁻⁶ When fossil fuels are combusted in air for the purpose of generating energy, CO₂, H₂O and other greenhouse gases are also produced. Since the industrial revolution in ca. 1750,⁷ there has been the large scale use of fossil fuels and, of late, large scale deforestation which have caused an imbalance in the energy circle. The average Earth surface temperature has increased by more than 0.8 °C, an effect which has been most pronounced in the last four decades.^{1,8} Scientists believe that the major cause of the warmer surface of the Earth (global warming) is CO₂, whose concentration in the atmosphere has been increasing steadily from the early years of the twenty-first century with a growth rate of ca. 2 ppm/year as well as increasing overall from 270 ppm at the beginning of the industrial revolution to about 403 ppm at present.⁹⁻¹¹ **Figure 1.1**

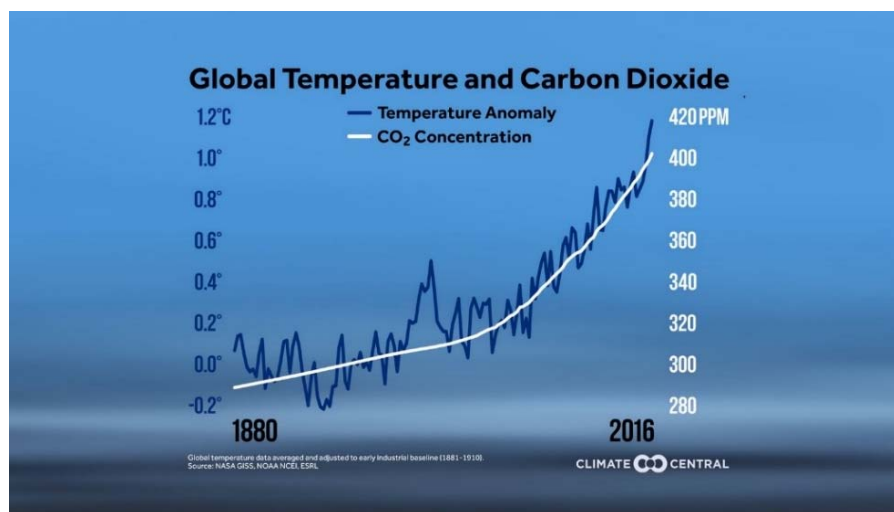


Figure 1.1: Global temperature and carbon dioxide; Global data average and adjusted to early industrial baseline (1881-1910), Source: NASA GISS, NOAA NCEI, ESRL

As can be seen in **Figure 1.1** above, as the global concentration of CO₂ increases the global temperature of the Earth's surface also increases. The increase of CO₂ concentration in the atmosphere influences the balance of incoming and outgoing atmospheric energy of the Earth's system. The increase in CO₂ concentration and warmer surface of the Earth are widely believed to

be due to anthropogenic activities such as the use of fossil fuels as a major source of energy which burns in air to give off CO₂, as well deforestation and biomass decay. Deforestation clears natural sinks for CO₂ uptake whereas biomass decay leads to methane production and eventually CO₂. The production of hydrogen from hydrocarbons via steam conversion and partial oxidation, has also contributed to CO₂ concentration.^{12–17} Deforestation and the emission of these greenhouse gases into the atmosphere does not only lead to global warming, but are also associated with drought as well as serious health problems to humans and farm animals.^{18,19}

Thus, globally it has become a task to reduce CO₂ emissions while generating energy, chemical products, services, buildings and public infrastructure for the continuously rising population that is estimated to exceed nine billion by 2050.^{20–22} With this in mind, CO₂ chemistry, in particular with respect to its capture and storage, has attracted a great deal of attention in the past two and half decades in industry, the academic world, and the scientific community in general. Worldwide concerted efforts are being made toward steadying CO₂ concentration in the atmosphere. Some of these efforts include carbon mitigation technologies to moderate sources of CO₂ emission and to promote carbon dioxide sinks. Some such approaches adopted so far include: increasing the efficiency of means of energy conversions and utilization, energy conservation in buildings by means of insulation and the use of alternative energy sources such as renewable energies (hydroelectric-power, wind, solar, biofuels etc.) and nuclear energy. Other methods are the expansion of natural carbon sinks such as forests and soils to enhance their CO₂ absorption capacities, as well as carbon sequestration.

1.2. Carbon Capture and Storage (CCS)

Carbon Capture and Storage (CCS) from flue gas has gained growing interest in recent years in a bid to create a benign and sustainable energy economy. CCS is a three-part process: CO₂ capture,

CO₂ separation from other flue gases, and transportation to a storage site or permanent storage. The technologies for conveyance and storage of CO₂ are moderately mature and an increasing number of fully integrated CCS projects have got to the pilot and demonstration phases prior to commercialization.^{23–25} Among the technologies used for CO₂ storage are mineral sequestrations, in which the CO₂ captured is pressurized and made to react with minerals underground and thus become part of the rock formation, or geological storage in which the CO₂ captured is permanently stored in large underground stores as a gas as depicted in **Figure 1.2**.²⁶

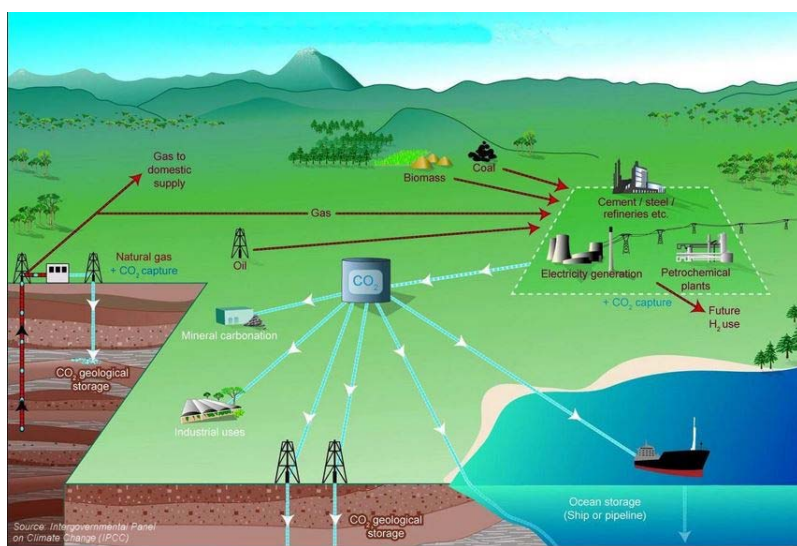
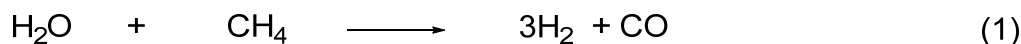


Figure 1.2: Technology for CO₂ Storage; Source: Intergovernmental Panel on Climate Change (IPCC).²⁶

However, before the storage process, the CO₂ has to be captured or separated from other flue gases. The capture of CO₂ from source after the combustion of fossil fuels seems to be the most effective strategy for controlling anthropogenic CO₂ release. In general, based on the fundamental chemical processes involved in fossil fuels combustion, the main CO₂ capture possibilities are: pre-combustion, oxy-fuel combustion and post combustion capture.^{4,27}

In pre-combustion capture, a primary fuel (e.g. natural gas) reacts with oxygen or air at high temperature and pressure to give CO, CO₂ and H₂. In some cases however, the produced gas mixture is mainly made up of CO and H₂ (Synthesis gas) also known as syngas. The CO is further

treated with steam in a catalytic reactor (shift converter) to produce more H₂ (**Equations 1 & 2 in Scheme 1.0**)



Scheme 1.0: Equations (1) production of syngas, (2) production of further H₂

The separation of CO₂ and H₂ can thereafter be achieved by other technologies. One of the advantages of pre-combustion capture is that the higher component concentrations and elevated pressures reduce the energy penalty of the process to about 10-16% which is about half that of post-combustion CO₂ capture.²⁸ Furthermore pre-combustion capture technology produces a H₂-rich fuel, which can be used as a feedstock, in a fuel cell for power generation or in the improvement of a hydrogen economy.

Oxy-fuel combustion on the other hand requires the use of nearly pure oxygen instead of air for the combustion of fuels. Oxy-fuel combustion produces nearly pure CO₂ which can be stored directly. However, one of the drawbacks of this technique is that it requires pure oxygen and the pure oxygen is usually obtained from the separation of air or by other means.

Post-combustion capture requires the stripping-off of CO₂ from other flue gas comprising mainly N₂ and CO₂ before release into the atmosphere. This method of CO₂ capture is the most feasible in the short time scale because most of the proposed technologies can be retrofitted to the existing fossil fuel consuming power plants. One of the new methodologies involves the use of cooled and CO₂-rich flue gases to feed the bioreactor to produce microbial biomass that would be utilised as a biofuel. In post-combustion capture even if the CO₂ capture unit is shut down due to an emergency, electricity can still be generated. This is not possible with pre-combustion and oxy-fuel combustion captures. The post-combustion capture method has been deployed commercially and primarily for the separation of minor contaminants such as Hg, SO_x/NO_x gases, however, the

sorbent for CO₂ removal requires some modification of the power plant with respect to high preparation and regeneration cost. **Figure 1.3**^{4,25,27} is a diagrammatic representation of the three methods for CO₂ capture from power generation plant.

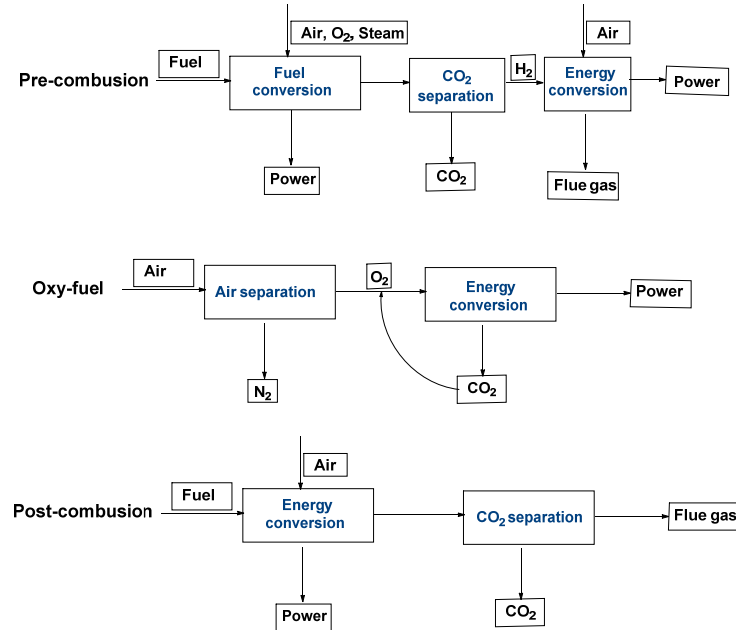


Figure 1.3: Three methods for CO₂ capture from power generation plan. (Adapted from refs. ^{26,27})

However, within the three methods for CO₂ capture described above, there are further techniques for the separation of CO₂ from other light gases. These subheadings fall into five different approaches. These approaches are cryogenic distillation, membrane purification, absorption with liquids, adsorption based on solid materials and chemical looping, **Figure 1.4**.^{23–25}

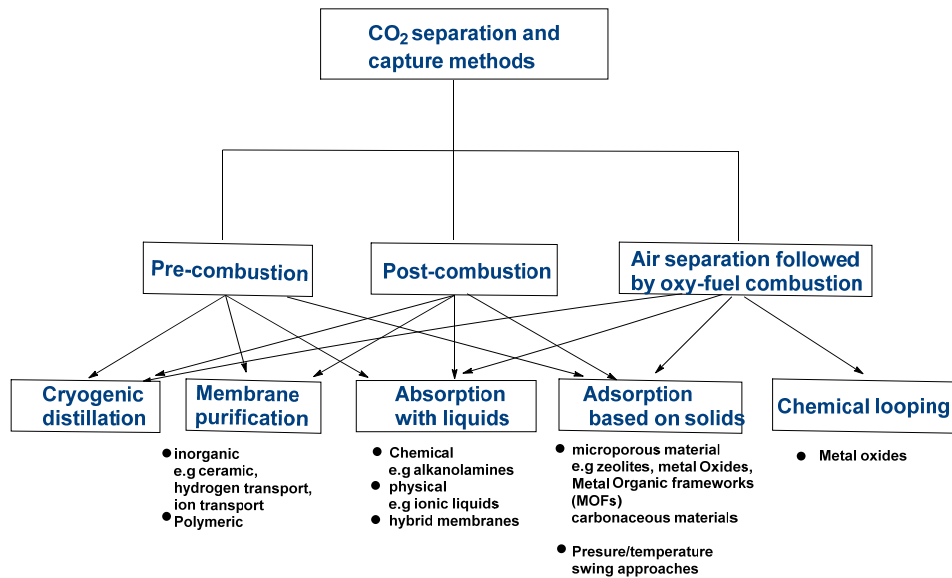


Figure 1.4: Materials for CO₂ capture in the context of pre-combustion, post-combustion and oxy-fuel captures (adapted from refs.^{23–25})

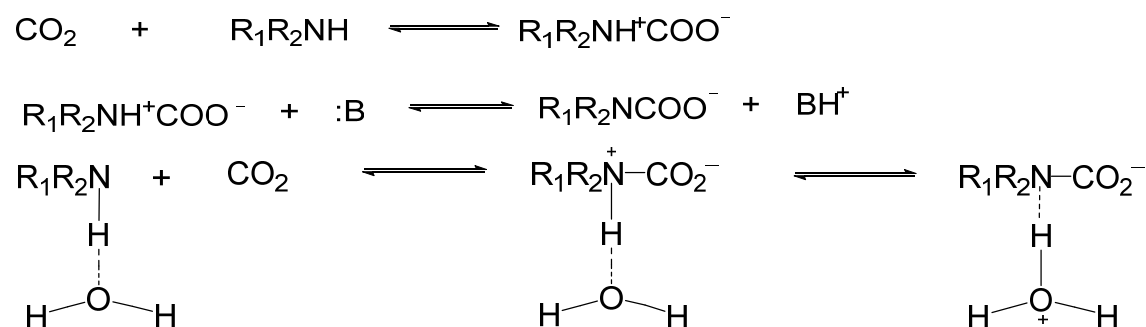
Cryogenic distillations are widely used for other gas separations but are not practically viable for CO₂ separations from flue gases because of the high energy cost.¹⁰

For relatively concentrated sources of CO₂, e.g. from natural gas deposits, extensive studies have been done (e.g. the use of membranes).¹¹ Membranes are most effective as mass-separation agents when the species that are to pass through them are in high concentration. Thus, in pre-combustion capture in which CO₂ is well known to be a minor component of the off-gases, membranes are not likely to be good candidates for efficient separation. However, for processes such as post-combustion capture in which there is a relatively high concentration of CO₂ stream at elevated temperature, membranes are good candidates.

1.3. Amine Based Absorbents

Absorption of CO₂ with liquids is usually carried out with solvents containing aqueous amine solutions such as monoethanolamine (MEA), diethanolamine (DEA) or methyldiethanolamine (MDEA). They are considered to be state-of-the-art due to their efficiency of up to 98% CO₂ capture from flue gases. These aqueous amine solutions provide high absorption rates and

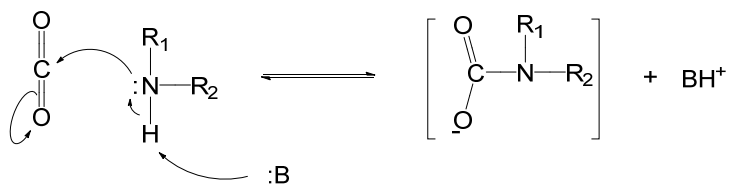
capacities for CO₂ through the nucleophilic attack of the amine ⁹ functional group on CO₂ to give a carbamate or bicarbonate molecule as shown below in **Scheme 1.1**.^{29–31} The reaction mechanism for the reaction between CO₂ and primary or secondary amine based solvents begin with the formation of a zwitterion followed by the attack of a base [:B] to abstract a proton (H⁺) from the zwitterion. The base molecule could be water, hydroxyl ion or an amine functional group while R₁ and R₂ are substituents such as alkyl or hydrogen.



Scheme 1.1: Reaction of CO₂ and aqueous amine solution

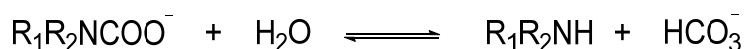
This mechanism implies that, in the first step; CO₂ interacts with the hydrated amine molecule via hydrogen bonding of the oxygen of water to form the intermediate zwitterion. The zwitterion is weakly bonded to the water molecule, hence in the second step, a base molecule attacks to deprotonate the zwitterion. The zwitterion is thus an intermediate species formed by this proposed mechanism.³² One of the assumptions of this mechanism is that a hydrogen bonding is formed between the amine and the base (H₂O) followed by the reaction of the CO₂.

However, others have proposed a single step termolecular mechanism as shown below in **Scheme 1.2**.³³ This pathway implies that no zwitterion is formed and the breaking and formation of old and new bonds between CO₂, amine and the base (B) all take place in a concerted manner.



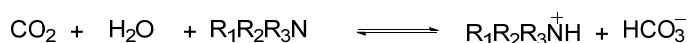
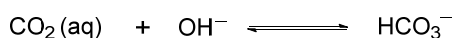
Scheme 1.2: Pathways interaction of CO₂ and amine

However, be it through the zwitterion or termolecular mechanisms discussed above, a carbamate is formed. The carbamate formed undergoes a hydrolysis to give bicarbonate, **Scheme 1.3**.



Scheme 1.3: Hydrolysis of carbamate to bicarbonate

Tertiary amine solvents on the other hand do not react directly with CO₂ to give carbamates the way primary and secondary amine solvents do. This is because, tertiary amine solvents lack a reactive N-H group. They usually react by acting as a base to catalyse the hydration of CO₂ in the presence of H₂O to give a bicarbonate as exemplified with an alkanolamine shown below in **Scheme 1.4**.



Scheme 1.4: Base catalysed hydration of CO₂ to bicarbonate

The reaction involves the lone pair of electrons on the nitrogen acting as a Lewis base enabling the alkanolamine to be bonded to the water molecule via hydrogen bonding and thus driving the reaction between the water and CO₂ to give hydrogen carbonate. Since pK_a plays an important role in the absorption of CO₂ by amine based solvents, tertiary amines such as triethanolamine (pK_a = 7.76 at 25 °C) will most likely decrease the absorption capacity of this amine solvent compared to primary amine solvents. However, it has been reported that tertiary amines require less energy for their regeneration as well as remaining intact after several regeneration cycles.^{34,35}

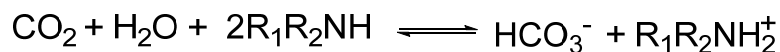
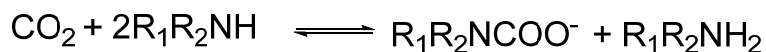
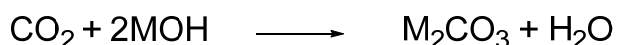
In the post-combustion removal of CO₂ from the flue gas stream in the natural gas industry, the most widely used amine based solvent system is the MEA absorption process. In this absorption process, the MEA solution is required to be in contact with the flue gas in an absorber column, reacting with CO₂ to form MEA carbamate in solution. The CO₂ rich MEA solution is then sent to a stripper where the solution is reheated to regenerate pure CO₂.³⁶ However, this process is capital intensive as it requires a high energy input for absorbent regeneration as well as large process units. The heating cost during the solvents' regeneration is estimated to be up to 70% of the total cost of operating a CO₂ capture plant.^{37,38} In view of all the difficulties associated with amine based absorption solvents, better CO₂ capture systems are rapidly required for advancing CCS technologies.

1.4. Porous Materials for Adsorption

Adsorption processes for gases using solid adsorbent are well known.^{23,24,39-45} At a low pressure, CO₂ behaves like N₂ and Ar in terms of its adsorption on non-porous solid surfaces, following closely to the Langmuir model. Thus in theory, a solid-state adsorbent with a high Brunauer-Emmett-Teller (BET) surface area will have a high CO₂ adsorption capacity as well as a high adsorption aptitude for other gases like N₂, H₂O and other flue gases due to non-selective adsorption. This implies that the adsorption capability of an adsorbent toward CO₂ will be reduced significantly if the amount of CO₂ in a mixture of gases is low. The percentages of CO₂ in a typical flue gas from coal-fired or gas-fired station are only approximately 13% and 8% respectively.⁴⁶ In a bid to attain a high CO₂ separation efficiency, adsorbents for post-combustion capture need to have a high selectivity for CO₂ over N₂ and H₂O present in the gas stream. Two common strategies are employed in a bid to design proficient adsorbents for CO₂. These strategies are: targeting the

physical property of CO₂ in terms of its molecular dimensions, and exploiting its chemical properties.

Size exclusion can be used to separate CO₂ from flue gas stream. This is based on the variance in molecular dimensions of the gas components in the flue gas mixture.^{7,47} Size exclusion takes advantage of the permeability theory and is mainly applied to separate larger molecules in the liquid phase, such as dialysis for the purification of biomolecules.⁴⁷ But its application in the separation for CO₂ depends greatly on the size, shape, connectivity and topography of the pores of an adsorbent solid to create a stronger interface towards a specific target component in the mixture due to the close proximity of the surface to the target gas molecules.⁴⁸ One family of microporous crystalline materials known as zeolites have been extensively used for this purpose due to their unique pore size/structure. Other microporous materials such as carbon nanomaterials and Metal-Organic Frameworks (MOFs) possessing distinctive pore dimensions are also capable of this kind of separation.⁴⁹ Advantage can also be taken from the chemical properties of CO₂ for selective adsorption. Carbon dioxide can be considered as a weak acid. As a weak acid it can react readily with a base to give carbamates and bicarbonates as shown in **Scheme 1.5**.



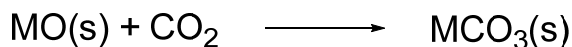
Scheme 1.5: Formation of a carbamate and bicarbonate via the reaction of CO₂ and inorganic metal hydroxide [MOH is an inorganic Metal hydroxide (a base)]

In a flue gas stream components such as N₂, unreacted O₂, H₂O and hydrocarbons are neutral, as such, adsorbents of basic functionalities can selectively adsorb acidic gas such as CO₂. However, in a typical flue gas stream, CO₂ is not the only acidic component, other components such as SO₂

(a major component if the flue gas has a high sulphur content) and NO_x are also acidic. Thus, increasing the concentration of these two acidic gases in the flue gas stream will reduce the efficiency of the CO₂ separation. In addition, the adsorption strength of the CO₂ onto the basic adsorbents should not be too strong as this would cause problems for the downstream removal of CO₂ and the regeneration of the adsorbents' active sites.³⁷

The adsorption of CO₂ on solid materials works through weak physisorption or chemisorption interaction and is mostly employed in cyclic, multi-module processes of adsorption and desorption in which desorption is induced by pressure or temperature swing.⁹ Activated carbons, alkaline earth metal-oxides, hydrotalcites,⁵⁰ supported amines,^{30,51} zeolites,⁴⁸ Covalent Organic Frameworks (COFs)^{52,53} as well as MOFs^{49,54,55} are all examples of this class of adsorbents.^{56,57} Activated carbons have been reported to have a CO₂ uptake of 4 mmol/g and a selectivity of CO₂/N₂ near 10 at room temperature and 1 bar.⁴¹ However, activated carbons are negatively affected by the presence of moisture. This is because of water's ability to competitively adsorb with respect to CO₂. Although most activated carbons with hydrophobic features reduce these effects, under humid conditions their adsorption capacities are still reduced due to gradual oxidation of the carbon surface brought about by the presence of water.

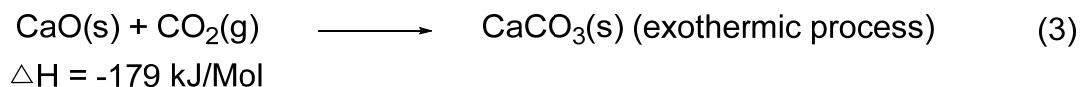
Alkaline earth metal oxides are also known to adsorb CO₂. A mole of the metal oxide has the ability to react with a stoichiometric equivalent of CO₂ exothermically to give a metal carbonate as shown below in **Scheme 1.6**.



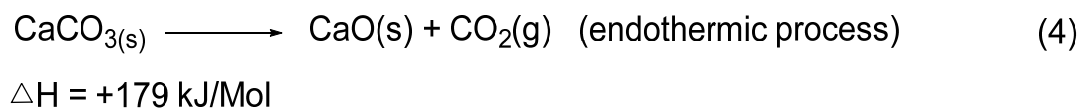
Where M = Mg, Ca, Sr, or Ba.

Scheme 1.6: Reaction of CO₂ with alkaline earth metal oxides

The calcium minerals are the most abundant of all the alkaline earth metal oxides in nature. They occur commonly in nature in the form of carbonates such as limestone or dolomite and when heated to high temperature they liberate CO₂ and form calcium oxide. Hence CaO represents an already available CO₂ adsorbent as shown below (**Equation 3 Scheme 1.7**) (unfortunately however, it releases CO₂ when it is formed).



the decomposition of the CaCO₃(s) liberates CO₂ as shown in (**Equation 4**):



Scheme 1.7: Equations (3) absorption of CO₂ on CaO to give CaCO₃ (4) decomposition of CaCO₃ to liberate CO₂

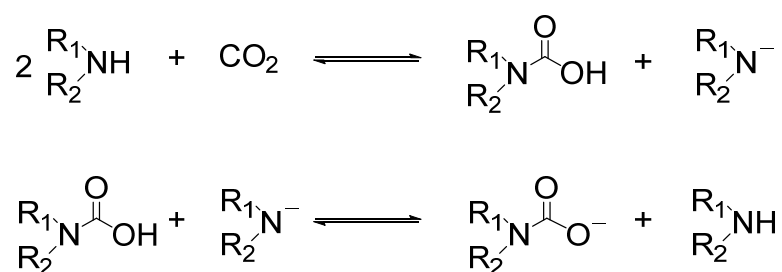
In general the uptake capacity of alkaline earth metal oxides is based on a stoichiometric reaction. For basic absorbents using neutralization, the maximum CO₂ uptake capacity can also be estimated stoichiometrically if 100% efficiency is assumed. For instance, the CO₂ adsorption capacity of calcium oxide CaO in the equation above can be estimated using the formula:

$$\text{CO}_2 \text{ adsorption capacity (mmol/g)} = \frac{\text{sorbent/CO}_2 \text{ stoichiometric ratio}}{\text{formula weight of sorbent}} \times 1000$$

Thus the maximum theoretical amount of CO₂ adsorbed by CaO is 17.8 mmol/g. However, typical capacities reported in the literature (e.g. 13.4 mmol/g for micrometer-sized particles (10 μm))⁵⁸ are much lower than this ideal value.⁹ The CO₂ adsorptions by CaO and MgO are approximately 17.86 and 25 mmol/g of sorbent respectively but the regeneration of the latter requires less energy.³⁷

Thus, using this method, the maximum theoretical capacity of all bases - liquids or solids can be estimated. For ammonium hydroxide solution (≈30% w/w) the maximum CO₂ adsorption capacity

is 8.8 mmol/g, while beryllium oxide (BeO) solid is 37.0 mmol/g, which is probably the material with the highest theoretical CO₂ adsorption capacity via neutralization. Unfortunately, these estimations assume a 100% stoichiometric reaction which is unlikely to occur, particularly for solid, and non-porous adsorbents such as CaO, due to the accessibility of sites. Therefore, the experimental values are usually much lower. In the case of amine adsorbents, the assumption is usually made, that two amine groups will react with one molecule of CO₂ to form the more stable carbamate species as shown in **Scheme 1.8**.



Scheme 1.8: A two-step pathway for the formation of carbamate from amines and CO₂

Thus, the ratio of nitrogen/carbon dioxide (N₂/CO₂) gives a certain degree of indication on how efficient an amine-based adsorbent is. But the efficiency of CO₂ uptake capacity of an adsorbent can be determined from the experimental and theoretical maximum adsorption capacity as follows:

$$\text{adsorption efficiency (\%)} = \frac{\text{experimental capacity}}{\text{theoretical maximum capacity}} \times 100$$

Such calculations and estimations give indication of how many basic sites, such as the number of amine groups on an adsorbent, are actively interacting with CO₂ molecules.

Hydrotalcites, have a general formula Mg₆Al₂CO₃(OH)₁₆·4(H₂O) and are generally anionic clays that are also suitable sorbents for CO₂ in temperature ranges of 400-500 °C. Impregnation of the hydrotalcite materials with K₂CO₃ has been reported to improve their CO₂ sorption.^{59,60}

Both alkaline earth metal oxides and hydrotalcite materials degrade after several cycles. However, the regeneration of hydrotalcites can be enhanced via some variation in the calcination step.⁶¹

Oxides of lithium such as Li_2ZrO_3 and Li_4SiO_4 have also been reported to show great prospects for high temperature CO_2 uptake.^{62,63}

Zeolite materials have also been reported to adsorb CO_2 in greater capacities than activated carbons.^{64–66} Zeolites are natural or synthetic hydrated aluminosilicate minerals made from linked tetrahedra of alumina (AlO_4) and silica (SiO_4) that have relatively porous three-dimensional crystalline structures.⁶⁷ Generally zeolites contain alkali or alkaline-earth metals with a general chemical composition of $\text{M}_{\text{nx/n}}\text{Si}_{1-\text{x}}\text{Al}_\text{x}\text{O}_2 \cdot \text{yH}_2\text{O}$, where M could be Na^+ , K^+ , Li^+ , Ag^+ , NH_4^+ , H^+ , Ca^{2+} , Ba^{2+} etc. Zeolite 13X (a bench-mark zeolite) has a CO_2 uptake of up to 7.4 mmol/g with a higher selectivity of CO_2 over N_2 than activated carbons.^{45,68} However, zeolites also have the problem of requiring higher regeneration temperatures.^{41,69}

Enzyme-based systems have also been reported to have potential for CO_2 capture. Carbozyme Inc. has developed biomimetic technology in which a 0.5 m² Carbozyme permeator fed with 15.4% CO_2 feed stream successfully separated 85% of the CO_2 .⁷⁰ Thus is a significant improvement over the use of amine-based solvents for CO_2 absorption process. This strategy of CO_2 uptake derives its origin from natural occurring reactions of CO_2 in living organisms.^{71,72} A biological-based system mimics the mechanism of the mammalian respiratory system to capture CO_2 and release as shown in **Figure 1.5**.

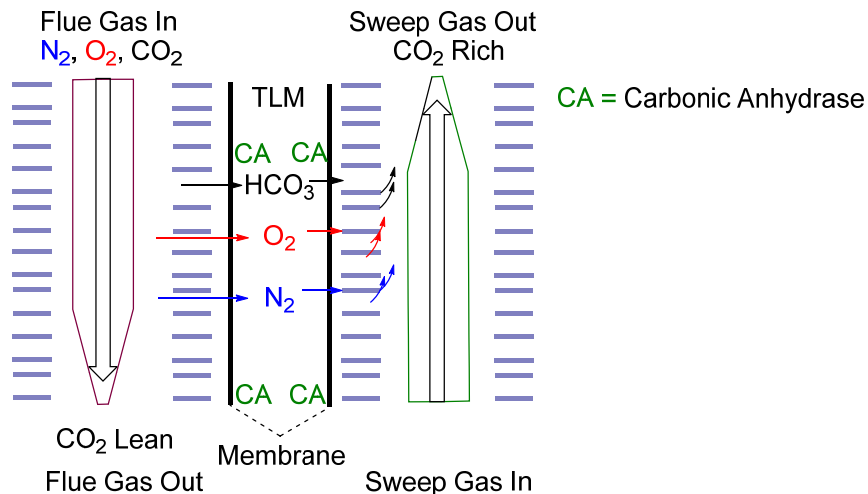


Figure 1.5: Schematic diagram of the Carbozyme permeation process.(adapted from ref.⁷⁰)

The Carbozyme permeator is made up of three key components: (a) a rapid catalyst (CA = Carbonic Anhydrase), (b) a high efficiency mass transfer hollow fiber and (c) and low energy (low energy steam).^{25,70} The two hollow fiber chambers are separated by a microporous membrane which contains a thin liquid membrane (TLM). The CA is attached to the wall of the hollow fiber to ensure that all CO₂ entering the hollow fiber gets in contact with the CA at the gas liquid interface to obtain the highest conversion efficiency. The resistance encountered by the gases as they travel through the microporous membrane is low. This implies that CO₂ faces minimal diffusion resistance before its conversion to bicarbonate at the feed side. The rate at which CO₂ dissolves in water is hindered by its aqueous hydration. In addition, the CO₂ carrying capacity of water is also limited by the buffering capacity of water. Thus the addition of the enzyme CA to the solution speeds up the rate at which carbonic acid is formed.⁷³ This means that CA serves as a catalyst by facilitating the conversion of CO₂ to carbonate while the liquid film restricts the entrance of nitrogen and oxygen.

Experimentally, one molecule of CA has been found to have the capacity to catalyze the hydration of 600,000 molecules of CO₂ per second compared to a theoretical 1,400,000 maximum rate.²⁵ Thus the quantity of enzymes needed for this process is small as a result of the turnover rate. It has

been reported that CA process has a low heat of absorption. This implies that the energy penalty associated with biological-based CO₂ absorption processes is reduced compared to MEA-based solvent processes. The Carbozyme biomimetic process looks promising; but the use of enzyme based systems has some technical challenges such as membrane boundary layer, poor mass transfer, instant backward dehydration, pore wetting, surface fouling, loss of enzyme activity over long time operation, and problems associated with scaling-up.^{25,74,75}

Covalent-Organic Frameworks (COFs) (for a detailed discussion see Chapter 2) have been reported as porous materials with promising applications in areas such as gas storage and adsorption where lightweight materials are desired.⁷⁶ COF-108⁷⁷ for example has been reported to have a density as low as 0.17 g/cm³ as well as possessing 4.7 nm diameter hexagonal pores.⁷⁸ In addition, MOFs such as MOF-210 (surface area 6240 m²/g) and MOF-177 (surface area of 4500 m²/g) have been reported to possess a CO₂ uptake potential of 2870 mg/g at 298 K/55 bar, and 33.5 mmol/g at 32 bar respectively.^{37,79,80} MOFs are made of metal based nodes connected by organic bridging ligands or “struts” and assemble principally by strong co-ordinate bonds under mild conditions which results in crystalline 1, 2, or 3-D materials^{81,82} with uniform pore diameters typically in the range of 3 - 20 Å. A detailed discussion of MOFs is given in Chapter 3 of this report.

1.5. Compounds Derived from Borosilicate/Organoboron Lewis Acids and Pyridines

Si-O-B and O-B-O containing compounds abound in the literature⁸³ and the Si-O, B-O and C-O bond energies are 452, 536 and 358 kJ/mol respectively. Thus the Si-O and the B-O bonds are stronger than typical C-O bond energy. A good number of these compounds possess and display unusual high elasticity when a stress is suddenly applied, as well as high plasticity when the stress is applied slowly.⁸⁴ These Si-O-B and O-B-O containing compounds exist in the form of

metaboric, boronic acid, six-, eight- or ten-membered cages, cyclo-borosiloxane derivatives or borosilicate cage as well as large rings as shown in **Figure 1.6**.^{83,85}

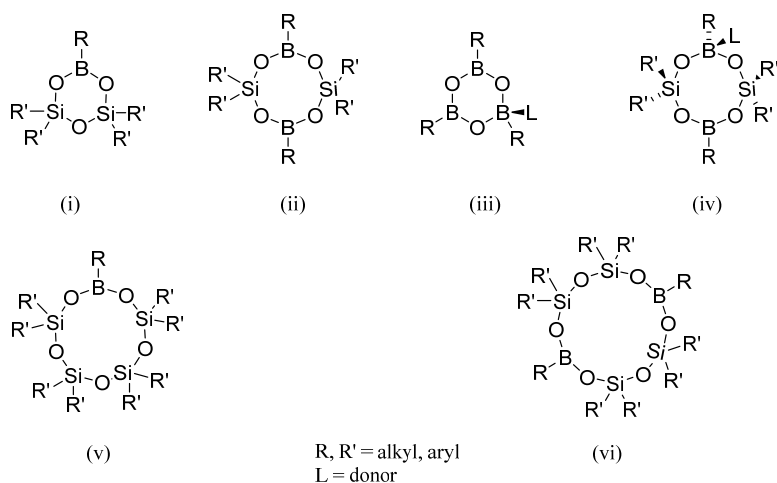


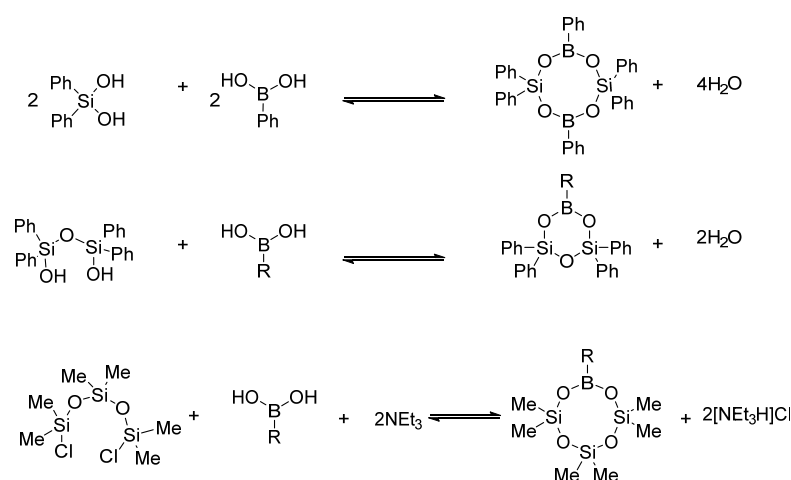
Figure 1.6: Structures of (i) Cyclo-boratrissiloxane; (ii) Cyclo-diboratetrasiloxane; (iii) 1:1 adduct of a boroxine; (iv) 1:1 adduct of a cyclo-diboratetrasiloxane; (v) 10-membered cyclo-boratetrasiloxane; (vi) 12-membered cyclo-diboratetrasiloxane.^{83,85}

Borosilicate scaffolds have promising applications as building blocks in supramolecular chemistry. However, they have only been marginally exploited. For example, Yaghi⁸⁶ and Severin⁸⁷ reported the use of a 8-membered borosilicate cage whose nodes were used for the synthesis of a 3-D system (COF-202) and macrocycles respectively. Wenjun *et al.*⁸⁸ used the same principle for the synthesis of π -extended polymeric borosilicate cages used as sensors for volatile organic amines. Palanisami *et al.*⁸⁹ reported the synthesis, structure, photophysical and other calculations on series of eight-membered cyclic-borarasiloxanes wherein the crystal packing pattern displayed non-covalent interactions. Recently, the synthesis of cyclic and cage-like borosilicates based on boronic acid and potential application in assemblies of triphenylboroxine and piperazine was reported.^{90,91}

Irrespective of the myriad of applications of borosilicates and borosilicate adducts, only a few synthetic strategies for cyclic and cagelike molecular borosilicates and adducts are known. The reason for this may mainly be as a result of: (I) the number of commercially available silanols are

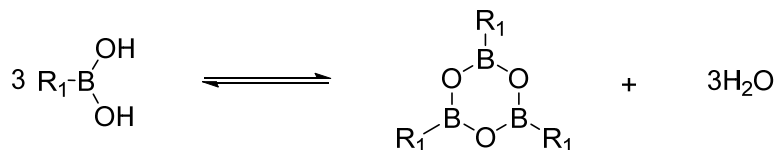
few, (II) structural modifications of these compounds are difficult, (III) issues associated with stability.⁹⁰

The basic methods used in the syntheses of these borasiloxanes rings involve the cyclocondensation reaction of appropriate organoboronic acids and Si-containing precursors such as dihydroxysiloxanes, diethoxysilanes, and α,ω -dihydrosiloxanes as well as the condensation of dichlorophenylborane with dihydroxysilanes.^{83,92,93} Solvents used include dry toluene, triethylamine, sodiumdriedbenzene or a mixture of solvents under a nitrogen atmosphere in which water is continuously removed by the use of a Dean-Stark apparatus as these reactions are readily reversible. Some reactions for the syntheses of these compounds are shown in **Scheme 1.9**.



Scheme 1.9: Pathways for the syntheses of cyclic 8- and 6-membered ring Si-O-B compounds

However, in the absence of diols, boronic acids also undergo self-condensation reaction. The reversible reaction nature of boronic acids that lead to the formation of boroxines enables formation of reversible molecular assemblies.⁹⁴ For example, the self-condensation of boronic acids to give boroxines of 6-membered ring B_3O_3 structures is a powerful tool for the building of molecular assembly,⁹⁴ as shown in **Scheme 1.10**.

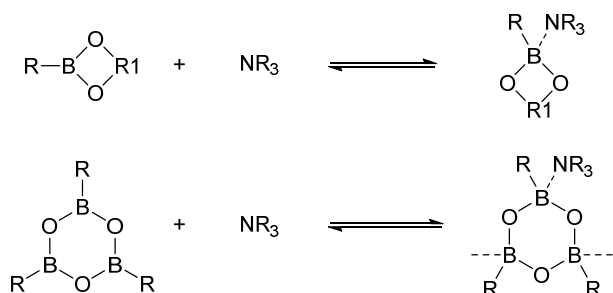


Scheme 1.10: Self-condensation of boronic acids.⁹⁴

Apart from the fact that boronic acids can form covalent bonds via condensation, they also have the potential to interact non-covalently via hydrogen bonding. Thus, hydroxyl functional group in boronic acids can act as hydrogen bond donors which enables the formation of supramolecular self-assembly in the solid state.

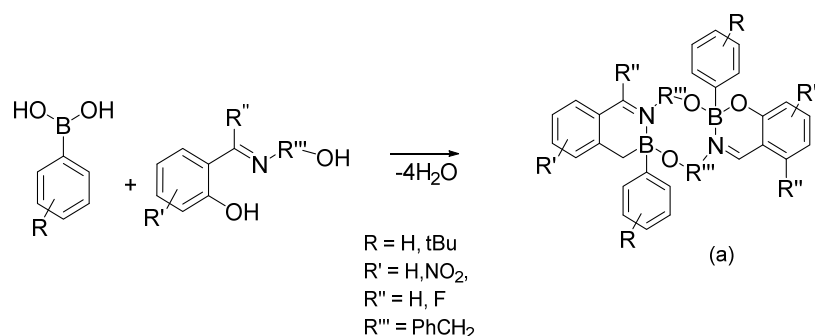
Most of these boron-based compounds in the literature contain three coordinated B centres in which the boron has a vacant p-orbital and as such are Lewis acidic in character. Gutman and co-workers³⁸ described a quantitative parameter called acceptor number (AN) as a measure of solvent Lewis acidity. The acceptor number scale arbitrarily assigns fixed points 0 and 100 to hexane and SbCl₅ respectively. On the same scale BF₃ has a value of 89.⁹⁵ Thus the relative reactivity of Lewis bases such as amines toward boratrisiloxanes and diboratetrasiloxanes is dependent on the acceptor number which has a close relationship with the electronic environment. Cyclo-diboratetrasiloxanes have acceptor number values between 46-62 and are termed as moderately strong Lewis acids comparable to triorganoboroxines with acceptor numbers of approximately 50.⁹² On the other hand cyclo-boratrisiloxanes have considerably lower AN values, ranging from 22-28 which are comparable to trialkylorthoborate esters with ANs in the range (18-30).⁹⁵ Thus, the AN plays a pivotal role in determining whether a B-O-Si containing compound can form an isolable adduct on reaction with a Lewis base such as amines or not. For example whereas triorganoboroxines (AN approximately 50) forms isolable amine (cyclohexylamine, 4-methylpyridine, 3-methylpyridine, piperidine, morpholine, isobutylamine, methylamine)⁹⁶ adducts, trialkylorthoborate esters AN (18-30) generally do not form isolable amine adducts.⁹⁷

The Lewis acidity of borasiloxane ring systems depend on the degree of electron density offered to the B from adjacent O atom and on the organic substituent on the B atom. The boron in these O-B-O compounds is sp^2 hybridized, and can bind with Lewis bases (N-donors, O-donors)^{98,99} as ligands as shown **Scheme 1.11**.



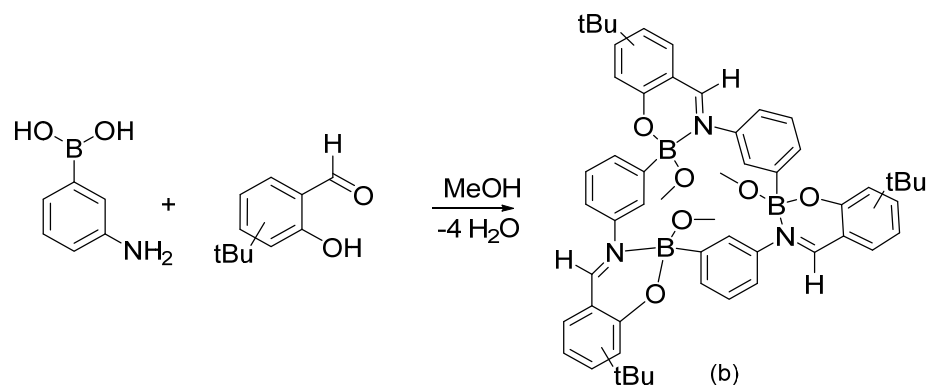
Scheme 1.11: Adduct formation of boronate esters and boroxines with N-donor ligands NR_3

However, the $B \cdots N$ bonds are less stable than the corresponding B-O covalent bonds. For adducts of boronate esters, the N-B bond energy is approximately 15 to 25 kJ/mol,¹⁰⁰ whereas a computational estimated value of 13 kJ/mol has been reported by Stefan *et al.*¹⁰¹ That notwithstanding, the formation of tetracoordinated boron adducts is important in non-polar organic solvents.¹⁰² The N-B bond has been employed in recognition processes¹⁰³ as well as in the construction of macrocycles,^{104–108} polymeric-systems,^{109,110} rotaxanes¹¹¹ and lately organic cage compounds.^{94,112} For instance, the reaction of boronic acids with tridentate imine ligands derived from salicylaldehyde and aminoalcohols has been reported in the literature to give macrocycles^{107,113,114} **Scheme 1.12**.



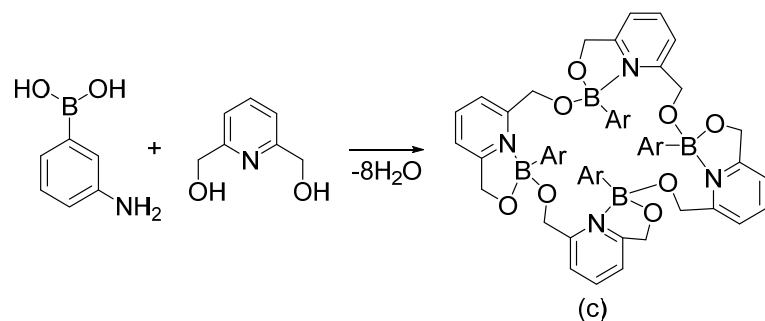
Scheme 1.12: Formation of a macrocycle via a condensation reaction.^{107,114}

The reactions of 3-aminophenylboronic acid with substituted salicylaldehyde, 2-hydroxyacetatophenone or 2-hydrobenzophenone have also been reported to give a calix[3] arene-like macrocycles¹⁰⁷ such as the one in **Scheme 1.13**.



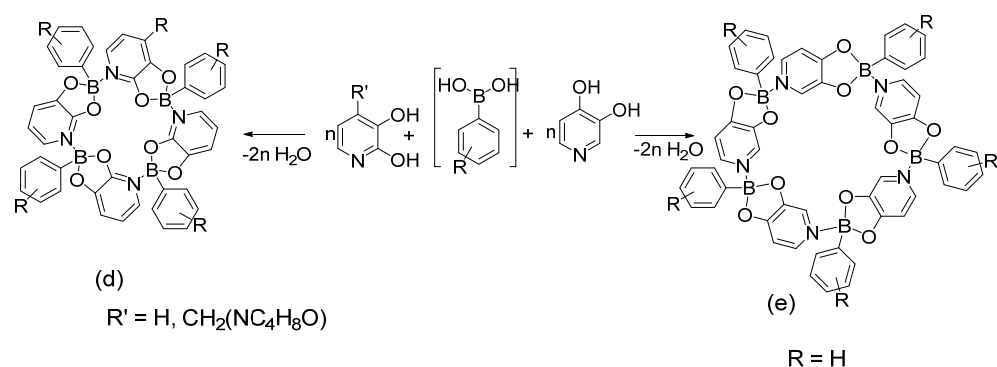
Scheme 1.13: Formation of calix[3] arene-like macrocycle (b).¹⁰⁷

Arylboronic acids have also been reported¹¹⁵ to react with 2,6-dimethylethanolpyridine to give [4+4] condensation products as shown in **Scheme 1.14**.



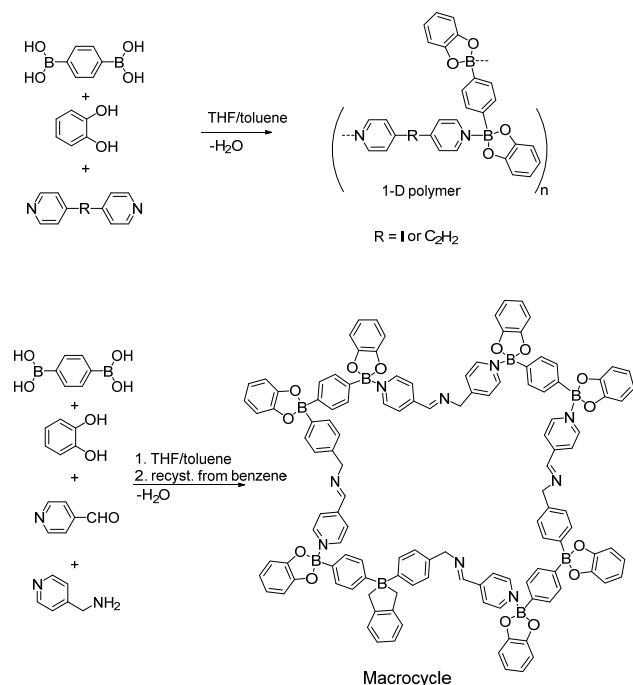
Scheme 1.14: Formation [4+4] condensation product from arylboronic acids.¹¹⁵

These macrocycles - (a), (b) and (c), are all made up of covalent organic frameworks with O-B-O connections. However, boronate ester reactions can also result in macro-cyclisation initiated by B-N bonds. For example, the reaction of boronic acids with 2,3- or 3,4-dihydroxypyridine ligands give tetrameric (d)¹¹³ and pentameric (e)¹¹⁶ macrocycles respectively as shown in **Scheme 1.15**.



Scheme 1.15: Formation of tetrameric¹¹³ and pentameric macrocycles.¹¹⁶

Furthermore, Severin and coworkers¹¹⁷ obtained a 1-D polymer, connected via a dative B-N bond and a macrocycle by the condensation of pyridyl ligands alongside other precursors and 1,4-bis(benzodioxaborole)benzenes as shown in **Scheme 1.16**.



Scheme 1.16: Syntheses of 1-D polymer and macrocycle from their respective monomers.¹¹⁷

2-D and 3-D structures with these type of assemblies based on literature search have not been prepared. In addition, borosilicate ring compounds have been studied little for the formation of 1-D, 2-D or 3-D polymeric structures.

1.6. Aim and Objective of Thesis

This work describes studies to make adducts of cyclo-diboradisiloxanes with amines as well as preparation of MOFs using novel rigid silicon-based tetra-, tri- and di-dentate ligands (aryl-pyridine and aryl-carboxylic acids). In particular, this project aims:

- (1) to synthesise Lewis Acids (LA) using simple synthetic methods and cheap diphenylsilanediol and boronic acids (aryl and non-aryl) as starting materials via condensation reactions to give rigid cyclic- or non-cyclic-borasiloxane compounds with 2 or 3 boron centres (C2 and C3 connectors). Borasiloxane rings give uncommon high elasticity as well as serve as building blocks in supramolecular chemistry
- (2) preparation of novel rigid silicon-centred Lewis Bases (LB) tetra-, tri- and di-aryl-pyridine and aryl-carboxylic acids which will give rigidity to framework materials. Tetra- and tri-dentate geometry linkers could lead to 2- or 3-D COF/MOFs. Furthermore the silicon-based linkers are easy to make via metathesis compared to their carbon-centred analogues
- (3) to combine the LA and LB (novel and commercially available ones) to produce 1-D, 2-D or 3-D COF materials with permanent porosity/potential channels, low density, high thermal and chemical stabilities, tunable pore size and structure, columnar π -stacking structures as well as versatilities in covalent combination of building units with potential application such as gas adsorption/separation and optoelectronics and photovoltaics etc.
- (4) to characterize the new materials prepared as well as their precursors and then to carry out CO₂ sorption studies

(5) prepare silicon-based MOFs with the silicon-based linkers and metal ions such as Zn^{2+} , Fe^{3+} , Mg^{2+} , Ca^{2+} , Zr^{4+} , Ni^{2+} , Co^{2+} , Al^{3+} or Cu^{2+}

(6) characterize these MOFs and carry out CO_2 sorption studies if possible. The work is summarized below in **Figure 1.7**

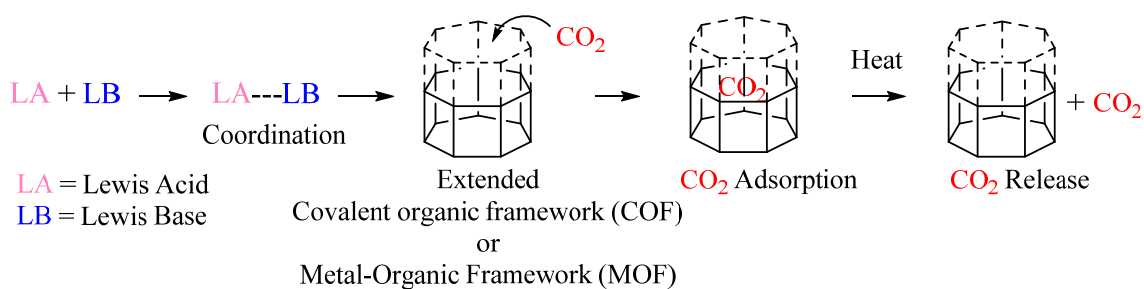


Figure 1.7: Potential route for COF/MOF formation and CO_2 sorption

Chapter 2

2.0 COVALENT ORGANIC FRAMEWORKS (COFs)

2.1 Introduction

Covalent-Organic Frameworks (COFs) are made by the linking of well-defined organic building units with diverse functionalities through strong covalent bonding to give 1-D, 2-D or 3-D structures. Research in this area of chemistry was initially not very promising due to difficulties associated with the synthesis of crystalline COFs for X-ray characterization.⁷⁶ However, the shortcomings of COFs' crystallinity has been partly overcome by modifying synthetic methods and the emergence and application of reticular chemistry, which makes use of topologically designed building units for the construction of crystalline COFs via the use of boronic acids or boronate esters as precursors.¹¹⁸ Yaghi and co-workers used topological design principles to successfully prepare the first examples of COFs in 2005.¹¹⁹ With this breakthrough, there has been rapid progress in COF chemistry in many parts of the globe as COFs display great potential for functional applications.

COFs are constructed by using well defined organic building blocks, containing bonds such as C-C, C-O, C-N, C=N, C-Si, B-O and B-N.^{119–121} The reactions leading to the formation of COFs are usually reversible condensation reactions, such as the formation of B-O bonds as seen in boronate, boroxines and borosilicate,^{77,86} C-N bonds formed in triazine and imidazation,^{122–126} B-N bonds formed in boraxines,^{127,128} C=N bonds formed in imine, hydrazine and squaraine,^{129–133} as well as N-N bonds formed in azodioxides.¹³⁴ In comparison to other porous materials (zeolites and MOFs), COFs have the advantage of low density, high thermal and chemical stabilities, permanent porosity, tunable pore size and structure, columnar π -stacking structures as well as versatilities in covalent combination of building units.^{135–138} The columnar stacking structure in some COFs

provides a unique avenue to constructing ordered π -systems that are difficult if not impossible to achieve with conventional covalent or non-covalent approaches. These unique features of COFs have attracted considerable interests amongst scientists, engineers and industrialists thus making COFs novel materials for important applications such as gas adsorption,^{76,139–144} optoelectronics and photovoltaics,^{120,145–150} gas separation,^{151–153} catalysis,^{154–159} proton conductivity,^{160–163} chemical sensor,^{164–166} drug delivery,¹⁶⁷ energy storage^{168,169} as well as in chromatographic separations.¹⁷⁰

In recent times, great efforts have been directed towards the enhancement of COFs for CO₂ capture and rapid research and advancement has been reported.^{52,171–173} However, there is still more to be done concerning COFs for CO₂ capture and purification as well as construction of COFs with large CO₂ adsorption and selectivity over other gases in the flue gas stream.⁵² In addition to the progress made in COF chemistry for CO₂ adsorption, the need for high thermal and chemical stabilities and the recyclability of COF materials without loss of performance in air are still major problems. Thus, new synthetic strategies, enhancement of crystallinity, stability and porosity, and CO₂ capture efficiency as well as improved selectivity with respect to other flue gas are all factors of COFs that need improvement.

2.2 COF Design

2.2.1 Dynamic Covalent Chemistry of COFs

Kinetic control of reactions leading to the synthesis of polymeric material is key to irreversible formation of COFs (containing mainly covalent bonds).¹⁷⁴ It has always been a challenge to crystallize linked organic polymers into solids by means of irreversible reactions.^{129,175} However, dynamic covalent chemistry which involves the breaking /formation bonds leads to the reversible formation of covalent bonds. Dynamic covalent bond chemistry is thermodynamically driven, as

a result, it offers reversible reactions process with “error checking” as well as “proof reading” features and thus leads to the formation of the most thermodynamically stable products. Thus, the application of dynamic covalent chemistry in COFs enables the polymer skeleton formation to occur alongside the crystallization process, while self-healing feedback reduces the incidence of structural defects and helps the formation of an ordered structure.^{118,135,176,177} The end effect of the dynamic covalent chemistry is that the final COF product has an ordered crystalline structure having high thermodynamic stability. To design and synthesise a COF, two key factors must be considered in order to achieve thermodynamic control in reversible reactions.^{118,174} These factors are: the functionality and structure of the building units, and the synthetic methodology (consideration of the reaction media and the reaction conditions are important).

2.2.2 Structure of Building Units

The structure of the building unit for COF construction must meet two requirements. Firstly, the reaction leading to the formation of the COF material should be a reversible reaction. This implies that the building units should be ones that undergo dynamic covalent bond formation. That is, there should be no irreversible reactions and the reaction system should contain only monomers, oligomers and polymers that are interchangeable under thermodynamic conditions. Secondly, the geometry of the secondary building units should be retained in the COF. This means that rigid building units as well as discrete directional bond formation are required.

In a bid to satisfy the first requirement, the chemistry of boronic acids, triazines and imines has been explored for successful COFs syntheses.^{118,173,178–180}

2.3 Building Blocks for COFs

2.3.1 Boron-based COFs

A large number of known COFs depend on boron chemistry because boronic acids can undergo condensation reaction through either self-condensation or co-condensation with diols to give six-membered boroxine and five-membered boronate ester rings as shown **Figure 2.0**.

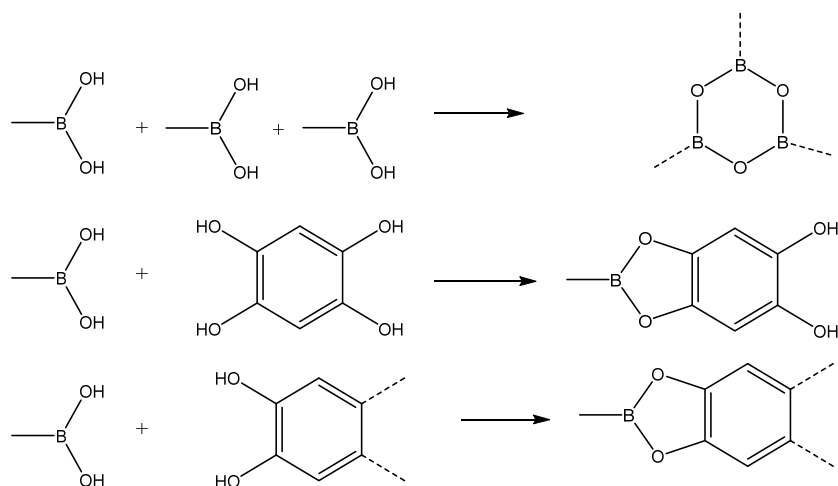
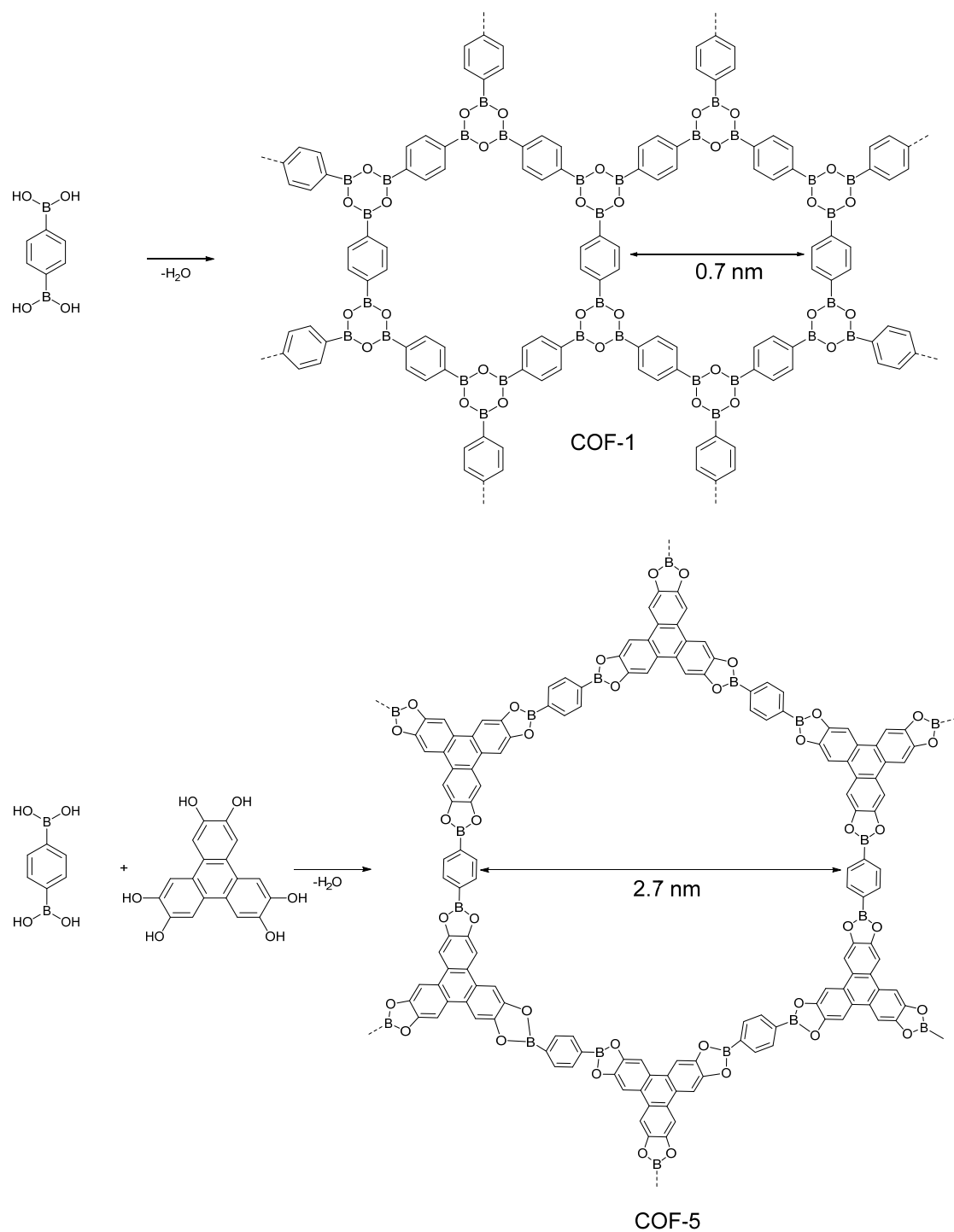


Figure 2.0: self- and co-condensation reaction of boronic acids to boroxine and boronate esters

Boron-based COFs were among the first group of COFs designed and synthesised.¹¹⁹

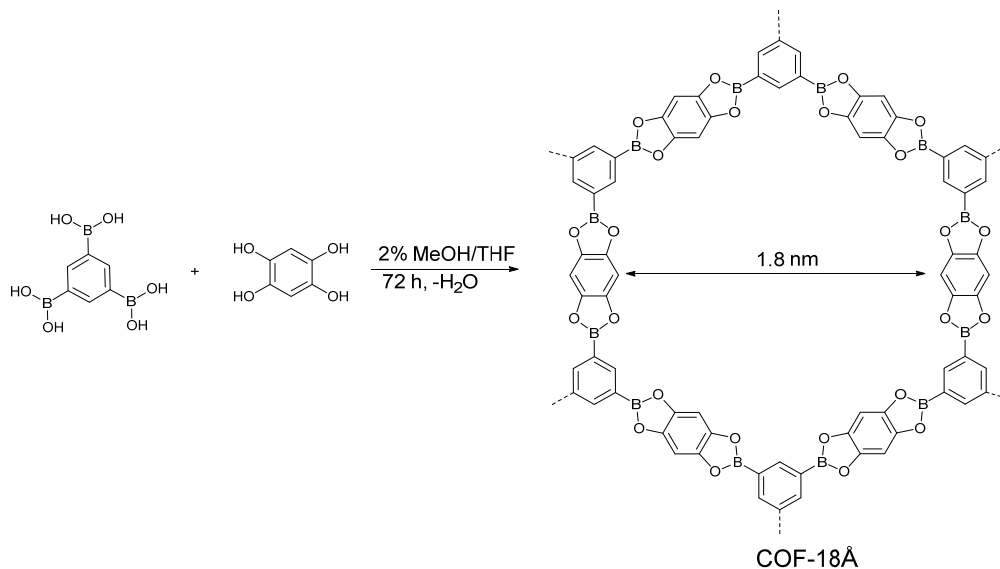
COF-1 and COF-5 are boron-based 2-D COFs that were synthesised under solvothermal conditions using a mixture of dioxane and mesitylene as solvents. COF-1 was obtained through the self-condensation of 1,4-benzene diboronic acid (BDDBA) with the removal of water to give a planar 6-membered B_3O_3 ring (boroxine).¹¹⁹ The co-condensation reaction of BDDBA and 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) formed COF-5 alongside the release of water as by-product. COF-5 contains a 5-membered $\text{C}_2\text{O}_2\text{B}$ ring (boronate group).¹⁸¹ The synthesis of COF-1 and COF-5 are shown below **Scheme 2.0**.



Scheme 2.0: Synthesis of COF-1 and COF-5.¹⁸¹

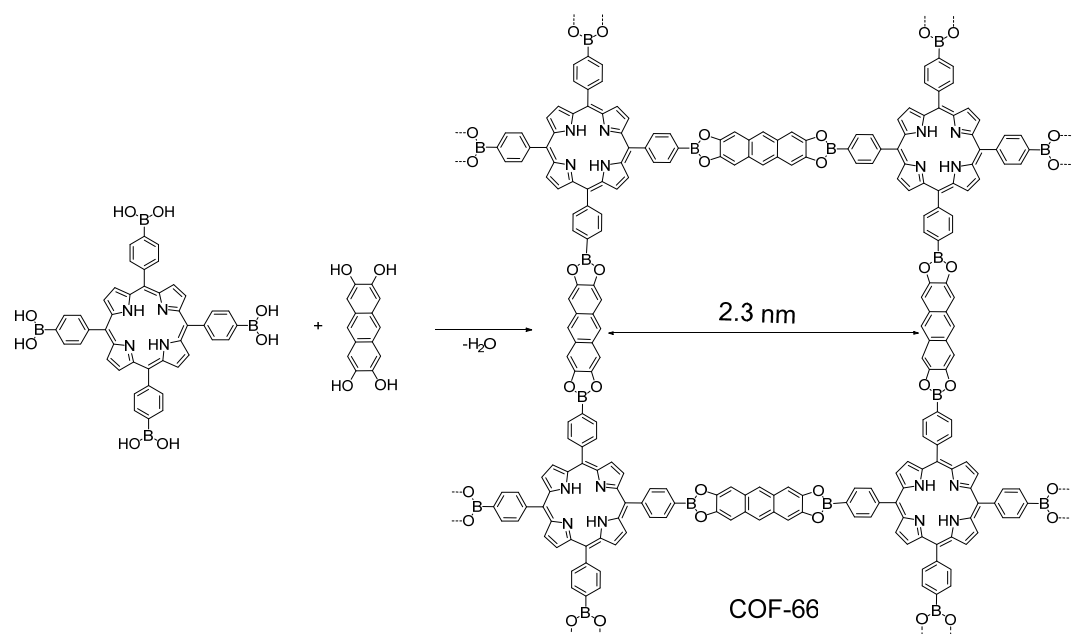
In addition, COF-18Å,¹⁸² a poly(boronate ester)-based COF, was synthesised via the condensation reaction of 1,3,5-benzenetriboronic acid and 1,2,4,5-tetrahydroxybenzene in 2% methanol/THF at reflux as shown in **Scheme 2.1**. COF-18Å, was reported to possess ester linkages that formed

infinite 2-D hexagonally porous sheets. Furthermore, it was reported that COF-18Å, the ester-linked sheets atoms that are adjacent to the layers overlapped with each other to form a hexagonal array structure with 1.8 nm pores. In addition, COF-18Å was reported to exhibit thermal stability of up to 500 °C as well as a Brunauer-Emmett- Teller Surface Area (S_{BET}) and micropore volume of 1260 m²/g and 0.29 cm³/g respectively.



Scheme 2.1: Synthetic scheme and proposed structure for COF-18Å.¹⁸²

These reactions prompted other researchers to apply the principle of dynamic covalent chemistry (DCC) reactions to prepare other 2-D COFs such as COF-6, COF-8, COF-10 and COF-66. COF-6, COF-8, COF-10 were formed via the co-condensation of (1,3,5-benzenetriboronic acid (BTBA), and HHTP, (1,3,5-tris [(4-dihydroxyborylphenyl)]benzene (TDBPB), and HHTP, and (4,4'-biphenyldiboronic acid (BPDBA), and HHTP respectively.¹⁸³ COF-66 was made via the co-condensation of 5,10,15,20-tetrakis(4-dihydroxylborylphenyl)porphyrin (TDBPP) and anthracene-2,3,6,7-tetraol (TPH) **Scheme 2.2.**¹⁴⁵



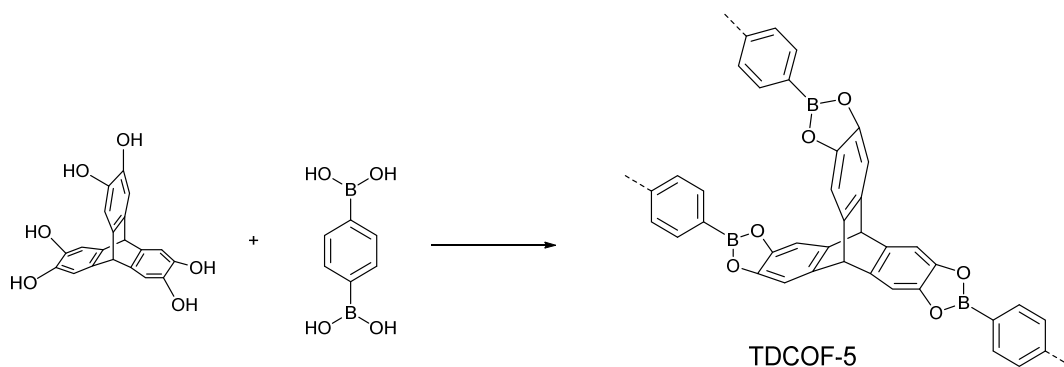
Scheme 2.2: Synthesis of COF-66.¹⁴⁵

On the basis of pore size distribution, COF-1 and COF-6 are classified as Group 1 comprising 2-D structures with 1-D micropores, while COF-5, COF-8, COF-10 and COF-66 belong to Group 2 comprising of 2-D structures with 1-D mesopores.⁷⁶ COF-1, COF-6 have been reported to have pore sizes of 0.7 nm and 0.9 nm as determined by the Ar gas adsorption isotherm at 87 K. For COF-5, COF-8, COF-10 and COF-66 their pore sizes are 2.7, 1.6, 3.2 and 2.3 nm respectively.^{52,118,145} The S_{BET} surface areas and CO_2 uptake of these 2-D COFs are summarised below in **table 2.0**

Table 2.0: Summary of pore sizes, BET and CO_2 uptake 1 and 55 bars of some boron-based COFs

2-D COFs	Pore size (nm)	BET (m^2/g)	CO_2 Uptake capacity at 273 K/1 bar (mg/g)	CO_2 Uptake capacity at 55 bar 273 K (mg/g)	Ref
COF-1	0.7	750	100	230	76
COF-5	2.7	1670	60.9	870	76
COF-6	0.9	750	167	310	76
COF-8	1.6	1350	64.8	630	76
COF-10	3.2	1760	50	1010	76
COF-66	2.3	366	N/A	N/A	145
TDCOF-5	N/A	2497	92	N/A	184

From the **Table 2.0** above, it can be seen that the S_{BET} of the 2-D COFs decreases in the order: COF-10 > COF-5 > COF-8 > >COF-6 = COF-1 > COF-66. But the CO_2 uptake capacities of these COFs at 273 K/1 bar decreases as follows: COF-6 > COF-1 > COF-8 > COF-5 > COF-10. Thus irrespective of the fact that COF-6 has a pore size of 0.9 nm as well a S_{BET} of 750 m^2/g , it has the highest CO_2 uptake capacity of 167 mg/g at 273 K/ 1bar compared to the other 2-D COF in the **Table 2.0**. This suggests that the CO_2 uptake of the COFs at low pressure depends more on the pore diameter than on the S_{BET} . However, at a higher pressure of 55 bar and 278 K, the order of the CO_2 uptake capacities of these COFs is: COF-10 (1010 mg/g) > COF-5 (870 mg/g) > COF-8 (630 mg/g) > COF-6 (310 mg/g) > COF-1 (230 mg/g). This implies that at high pressures the CO_2 uptake capacities of these COFs is more related to their S_{BET} than on their pore sizes. In addition to the list of 2-D boron-based COFs, Kahvechi *et al.* successfully synthesised a 2-D mesoporous triptycene-derived COF (TDCOF-5) using 1,4-benzenediboronic acid and hexahydroxytriptycene solvothermally to give a boronate as shown in **Scheme 2.3**.¹⁸⁴ The S_{BET} and pore volume reported for TDCOF-5 were 2497 m^2/g and 1.3 cm^3/g at p/p_o of 0.9. The S_{BET} for TDCOF-5 is higher than that of COF-5 (1670 m^2/g).^{52,76,178} The reported CO_2 adsorption capacity of TDCOF-5 was 92 mg/g at 273 K/ 1 bar.¹⁸⁴



Scheme 2.3: Synthesis OF COF TDCOF-5.¹⁸⁴

The rigid conformation of the building units drives the topological design of the COFs. The rigid nature as well as discrete bonding direction of arene molecules makes aromatic π -systems good building units. The diversity of π -aromatic systems allows the combination of various building units which, results in the formation of COFs with very variable molecular design.¹¹⁸ Some building blocks used for the synthesis of boron-based COFs are summarised below **Figure 2.1**. These building blocks can be classified as either 2-D or 3-D on the basis of the directional symmetry of the coordinating groups. The geometry of the building units determines the final structure of the COF. There are fewer 3-D COFs than 2-D COFs due to the limited number of building blocks available. Thus the self-condensation of tetrahedral nodes (3D-T4) or co-condensation of tetrahedral nodes with linear 2D-C₃ or triangular 2D-C₃ building units can lead to the construction of 3-D COFs with different crystalline space groups. However, a combination of 2-D (2D-C₂ + 2D-C₃, 2D-C₃ + 2D-C₃, or 2D-C₂ + 2D-C₄) will lead to formation of 2-D COFs.¹¹⁸

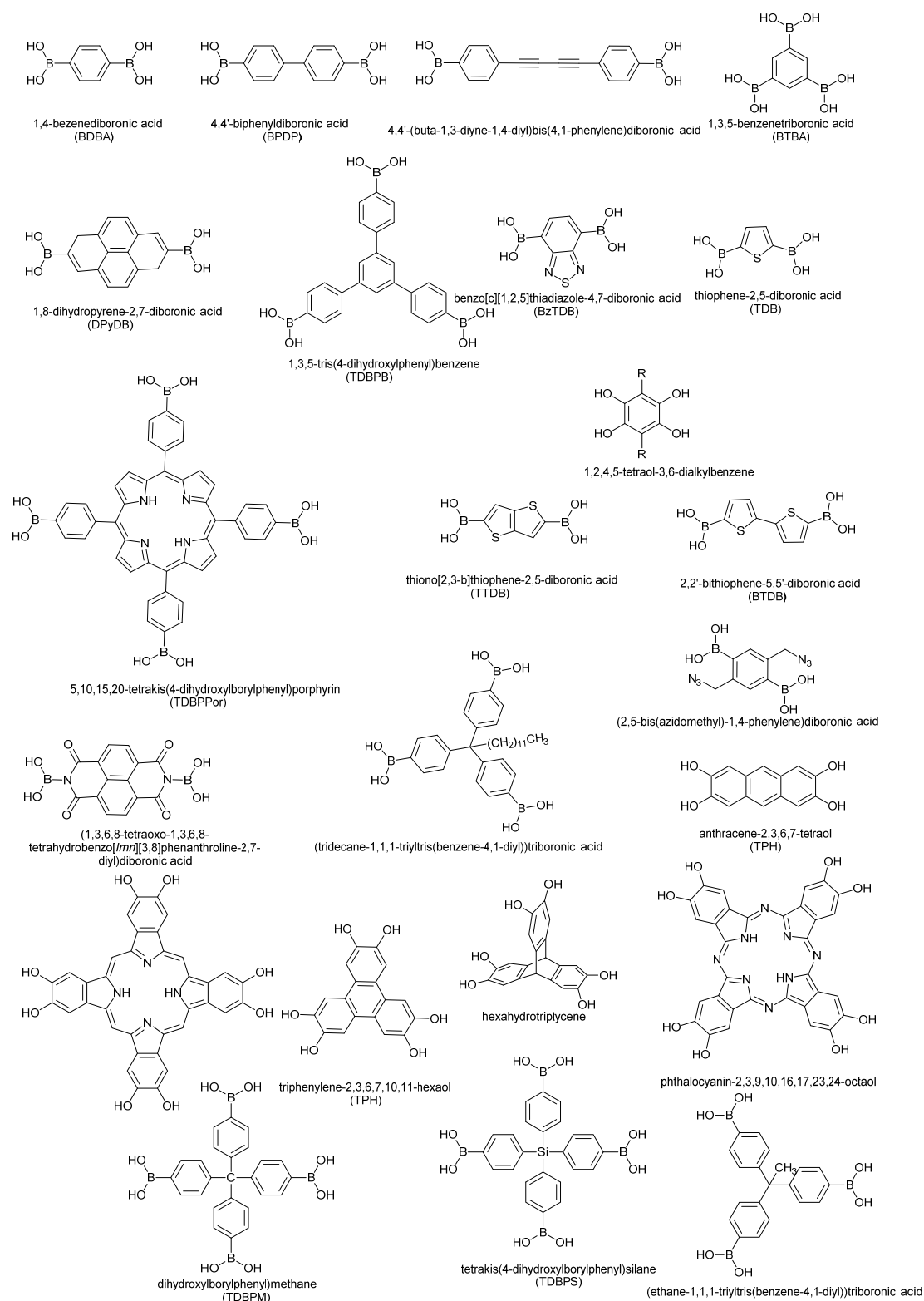
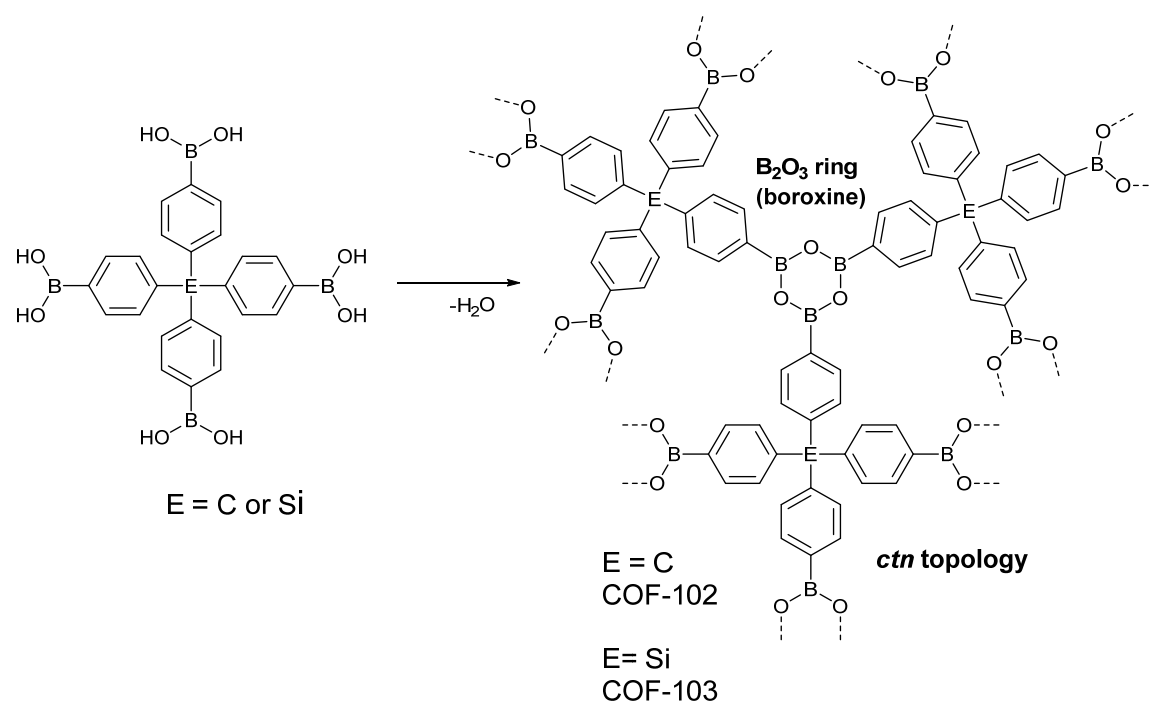


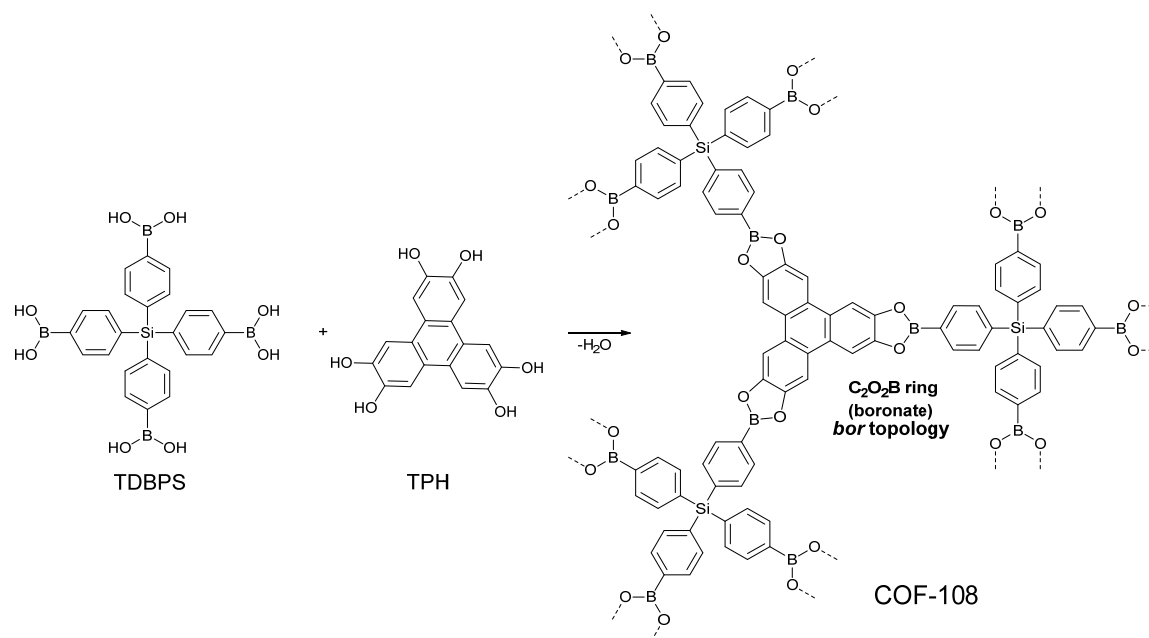
Figure 2.1: Monomers with different geometries for the design of boron-based COFs

Cote *et al.* pioneered the construction of 3-D COFs (COF-102 and COF-103) from tetrakis(4-dihydroxyborylphenyl)methane (TDBPM) and tetrakis(4-dihydroxyborylphenyl)silane (TDBPS) as four connector nodes. Both COFs have *ctn* topology and are formed via dehydration of the boronic acid to give B_3O_3 rings as shown in **Scheme 2.4**.⁷⁷



Scheme 2.4: Synthesis of 3-D COFs (COFs- 102 and 103) with *ctn* topology.⁷⁷

Another boron-based 3-D COF is COF-108 with a *bor* topology and a pore size of 3.1 nm and low density of 0.17 g/cm^3 .^{52,77,118} COF-108 was synthesised via the co-condensation of tetrakis(4-dihydroxyborylphenyl)silane (TDBPS) and triphenylene-2,3,6,7,10,11-hexaol (TPH) as shown below in **Scheme 2.5**.⁷⁷



Scheme 2.5: Synthesis of 3-D boron-based COF-108, with bor topology⁷⁷

The S_{BET} , densities and CO₂ uptake capacities at low pressure of these 3-D COFs are summarised in **Table 2.1**.

Table 2.1: S_{BET} , density and CO₂ uptake capacities of some 3-D boron-based COFs

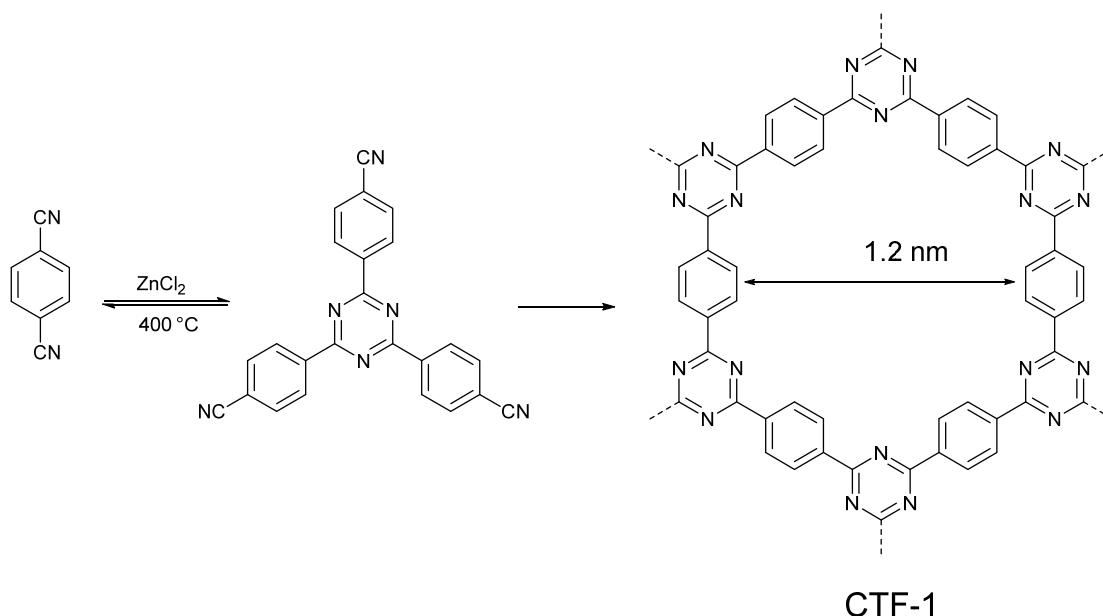
Boron-based COFs	3-D	S_{BET} (m ² /g)	Density (g/cm ³)	CO ₂ Uptake capacity at 55 bar, 273 K	Ref
COF-102		3427	0.41	1200	77
COF-103		4210	0.38	1190	76
COF-108		N/A	0.17	N/A	76

From the **Table 2.1**, it can be seen that COF-103 has higher S_{BET} than COF-102. However, the density of COF-102 as well as its CO₂ uptake capacity is higher than that of COF-103. The boron-based 2-D COFs (COF-1, COF-5, COF-6, COF-8, COF-10, COF-66, TDCOF-5) and 3-D COFs (COF-102, COF-103, and COF-108) have good crystallinity, low densities, large S_{BET} , high thermal and chemical stabilities as well as diversity in structure. Other boron-based COFs reported in the literature include ZnPcPy COFs,¹⁸⁵ thiophene-containing COFs (TCOFs),¹⁸⁶ ZnP-COF,¹⁸⁷ 100%N₃-COF-5, 50%ACTrz-COF-5 and 100%Trz-COF-5.¹⁸⁸ However, some shortcomings associated with boron-based COFs that limit their applications as CO₂ capture porous materials

are: their low CO₂ uptake at low pressures and their instability in moist air or aqueous environments.¹⁸⁹ Thus further research on COFs using other building blocks such as triazines has been carried out.

2.3.2 Triazine-based COFs (CTF)

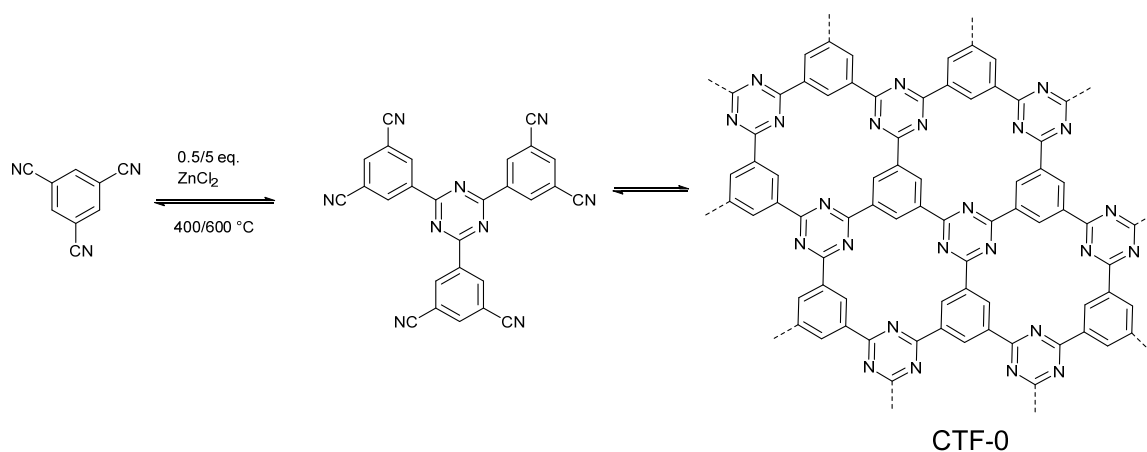
The pioneers of the use of cyano-aromatic compounds for the synthesis of triazine-based crystalline COF (COF-CTF-1) were Thomas and co-workers (2008).¹²² The synthesis of CTF-1 was done by the reversible cyclotrimerization reaction of aromatic nitrile building unit (1,4-dicyanobenzene) in the presence of ZnCl₂ which served as a catalyst as well as a solvent at 400 °C as shown in **Scheme 2.6**.¹²²



Scheme 2.6: Synthesis of 2D triazine-based COF (CTF-1).¹²²

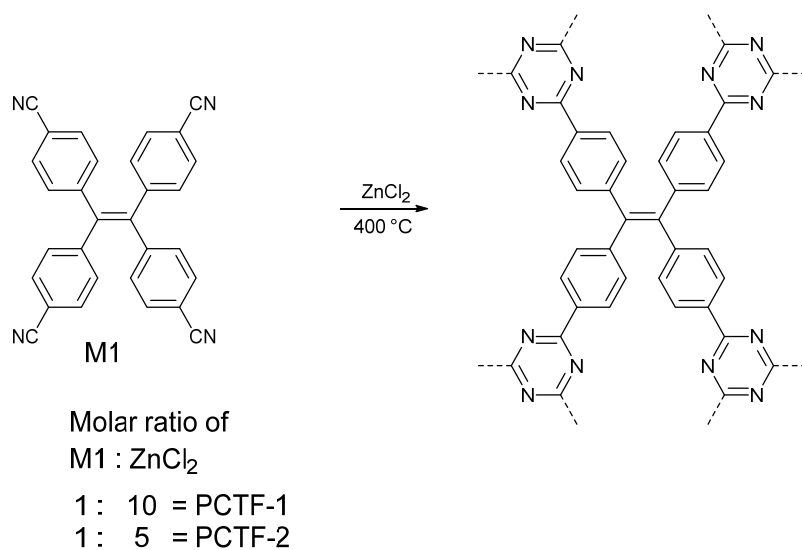
CTF-1 has a 2-D hexagonal COF structure with pore size of 1.2 nm, 1-D pore channels and S_{BET} of ca. 1000 m²/g. In addition, Thomas and co-workers¹⁹⁰ also synthesised CTF-0 via the trimerization of 1,3,5-tricyanobenzene in molten ZnCl₂ as shown in **Scheme 2.7**. It was reported that the crystalline framework (CTF-0) possessed a S_{BET} of 500 m²/g and CO₂ uptake capacity of

186 mg/g at 273 K, while CTF-0 derivatives obtained at higher temperatures had an increased S_{BET} of 2000 m^2/g .



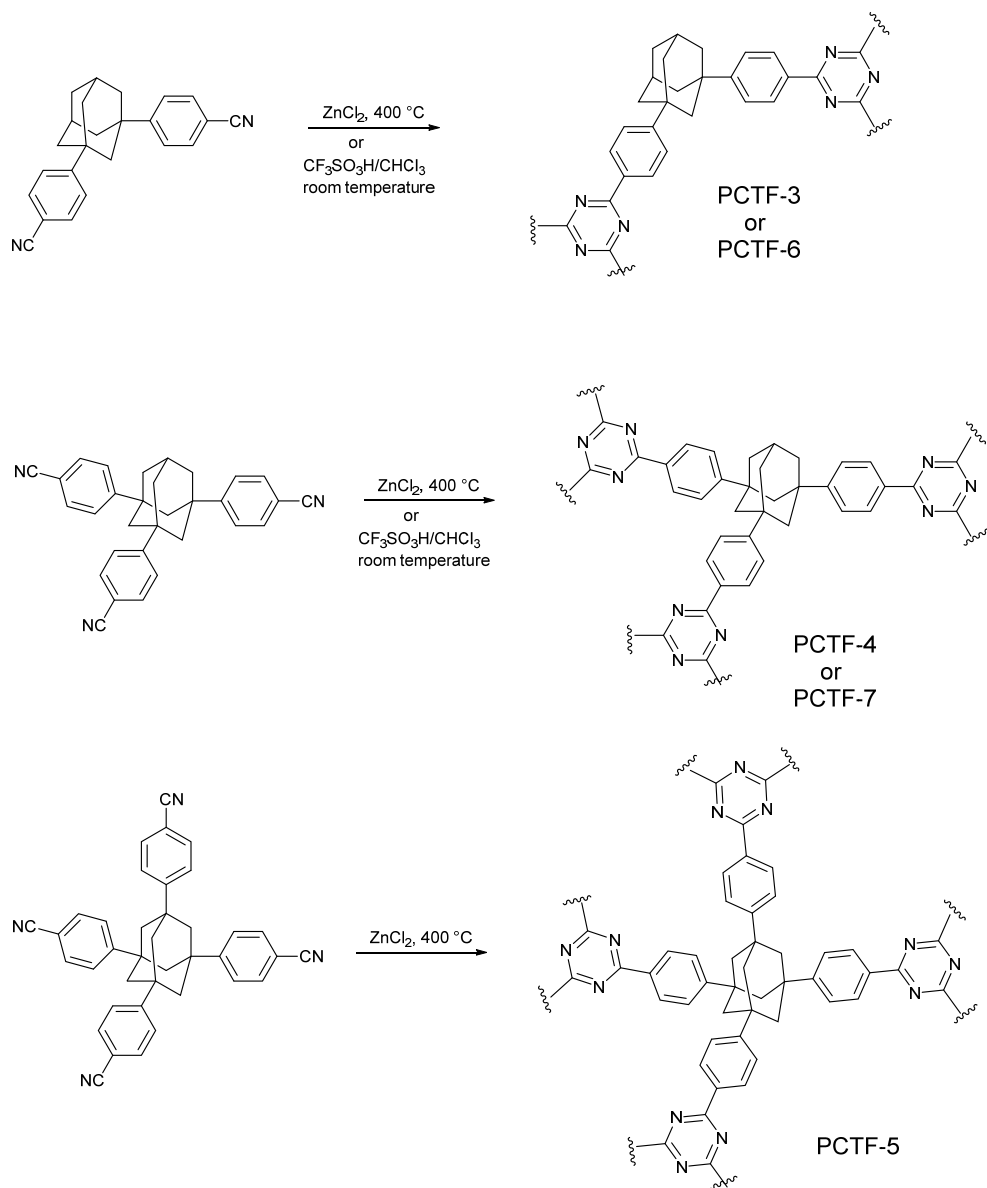
Scheme 2.7: Trimerization of 1,3,5-tricyanobenzene to CTF-0.¹⁹⁰

The transformation of tetrakis(4-cyanophenyl)ethylene under Lewis acidic (ZnCl_2) conditions at 400 °C was studied for different ratios of tetrakis(4-cyanophenyl)ethylene and ZnCl_2 to give two porous covalent triazine-based frameworks (PCTF-1 & PCTF-2, which have the same overall structure but a different porosity dependent on the reaction conditions) with S_{BET} of 2235 and 784 m^2/g respectively¹⁹¹ **Scheme 2.8**.



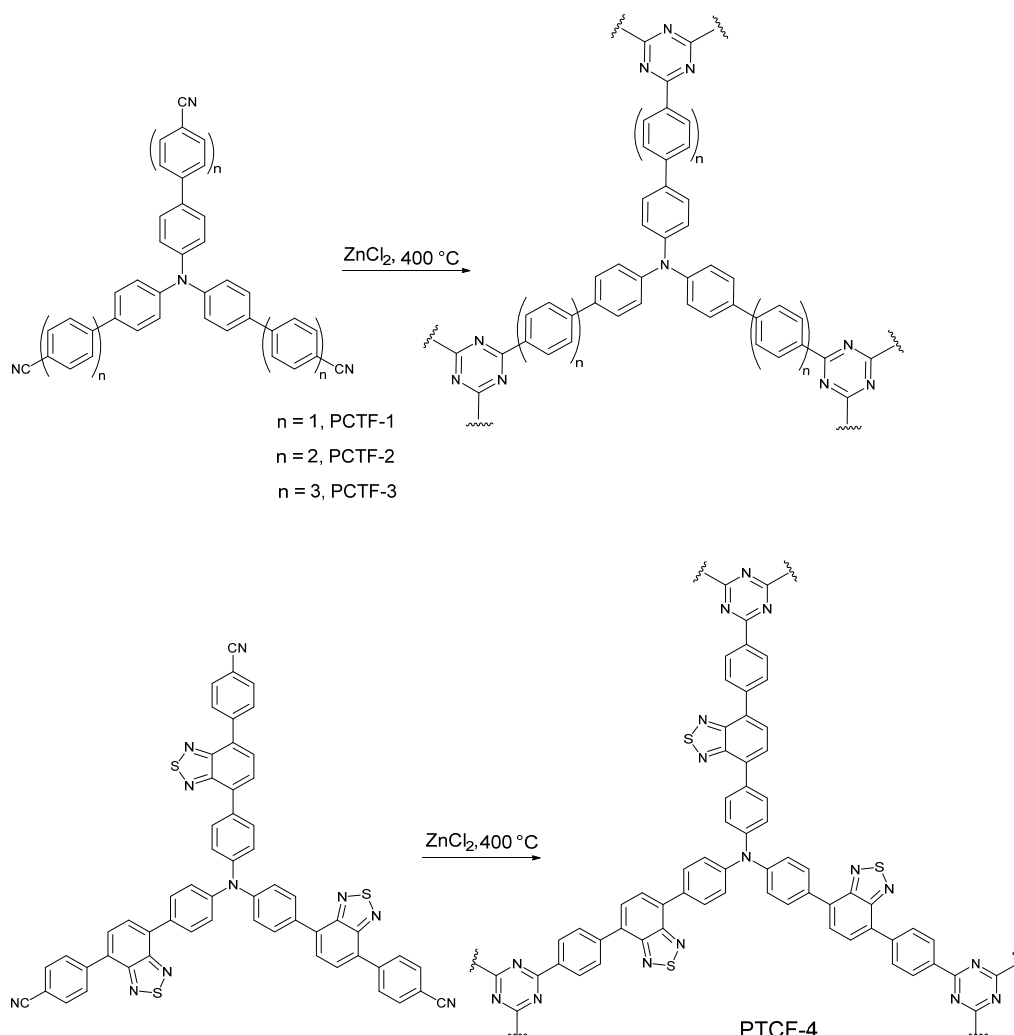
Scheme 2.8: Synthesis of (PCTF-1 & PCTF-2).¹⁹¹

In addition to triazine-based COFs, PCTF-3, PCTF-4 & PCTF-5 were constructed by Janiak and co-workers.¹⁹² These COFs were built by using adamantane cages bearing two to four 4-cyanophenyl groups which resulted in the formation of a series of porous covalent triazine-based framework (PCTF) structures. Thus, PCTFs (PCTF-3, PCTF-4 & PCTF-5) were respectively obtained by the trimerization reaction of 1,3-bis-, 1,3,5-tris- and 1,3,5,7-tetrakis(4-cyanophenyl)adamantane, in the presence of ZnCl_2 which acted as Lewis acid and $\text{CF}_3\text{SO}_3\text{H}$ which served as strong Brønsted acid as shown in **Scheme 2.9**.¹⁹² The conditions in which the Lewis acid (ZnCl_2) were used were thus different to those used for the strong Brønsted acid reported to produce higher S_{BET} as against the use of strong Brønsted acid ($\text{CF}_3\text{SO}_3\text{H}$). Thus, PCTF-5, which was obtained from the trimerization reaction of 1,3-bis-, 1,3,5-tris- and 1,3,5,7- tetrakis(4-cyanophenyl)adamantane, in the presence of ZnCl_2 was reported to have the highest S_{BET} of 1183 m^2/g as well as CO_2 uptake capacity of 114 mg/g at 273/ 1 bar when compared to other CTFs that gave CO_2 uptake capacities ranging from 39 - 183 mg/g at 273 K/ 1bar.^{122,190,191,193} In terms of selectivity for CO_2 uptake over other gases, PCTF-5 was also reported to have CO_2/N_2 and CO_2/CH_4 of 32 and 7 respectively.^{52,192}



Scheme 2.9: Synthesis of porous covalent triazine-based frameworks (PCTF-3 - PCTF-7).¹⁹²

Following the work of Janiak and co-workers,¹⁹¹ Gu *et al.* synthesised another four triazine –based frameworks (PCTF-1, PCTF-2, PCTF-3 PCTF-4) using triphenylamine as the core and aromatic nitriles under the catalysis of ZnCl_2 .¹⁹⁴ The triphenylamine and C_3N_3 triazine rings linked with each other through covalent bonds which gave rise to (PCTF-1, PCTF-2, PCTF-3 PCTF-4)¹⁹⁴ as shown in **Scheme 2.10**.



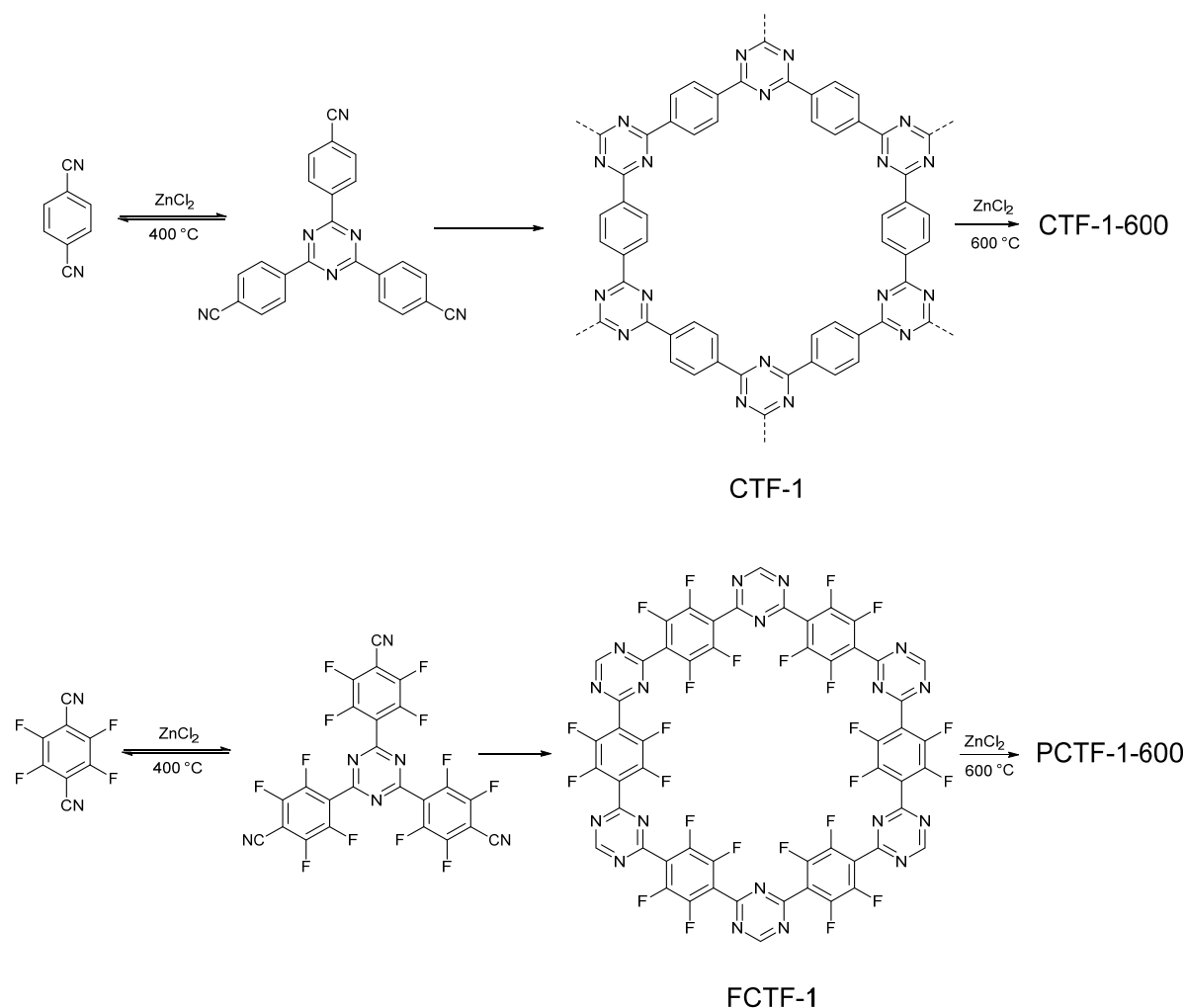
Scheme 2.10: Structures of PCTF-1, PCTF-2, PCTF-3 & PCTF-4.¹⁹⁴

The S_{BET} of these four triazine-based COFs was reported to decrease as the length of the branched arm elongates. Thus PCTF-1 (containing biphenyl as the branched arm), PCTF-2 with terphenyl branched arm and PCTF-3 with four-phenyl branched arm have S_{BET} 853, 811 and 395 m^2/g , respectively. It was reported that PCTFs containing monomers with longer branches packed more efficiently, which resulted in higher density and lower surface areas. However, comparing PCTF-4 containing benzothiadiazole in the place of the central benzene in PCTF-2, the N_2 adsorption isotherms showed its S_{BET} to be 1404 m^2/g , which ranked highest among the PCTFs, almost twice that of PCTF-2. The three nitrogen atoms in the C_3N_3 triazine rings in them, which

are reported to be responsible for the high affinity of these frameworks toward the adsorption of CO₂. The CO₂ uptake capacity reported for PCTF-4 was 205 mg/g at 273 K/ 1 bar, one of the highest reported for this class of CTF materials. The high CO₂ adsorption capacity of PCTF-4 is attributed to the presence of the benzothiadiazole in the framework. The benzothiadiazole served as a polar group that enhanced the affinity of the framework toward CO₂.

This observation suggests that the incorporation of strong polar groups such as benzothiadiazole into the framework of a microporous polymer could improve the binding affinity of CO₂ molecules towards the polymer. PTCF-4, was also reported to have CO₂/N₂ and CO₂/CH₄ selectivity ratios ranging from 14–56 and 11–20 respectively, at 273 K.¹⁹⁴

Hydrocarbons containing fluorine atoms are more hydrophobic and lipophilic than corresponding hydrocarbons lacking fluorine and show stronger affinity toward CO₂ than hydrocarbons without fluorine substituents. Similar observations of the positive effects concerning fluorine atoms in framework materials were reported by Smaldone and co-workers¹⁹⁵ who reported that increasing the ratio of non-fluorinated to fluorinated monomers led to significant improvement in both crystallinity and porosity of TFx-COFs.¹⁹⁵ With this in mind, Han and co-workers¹⁹⁶ designed and constructed two triazine-based covalent frameworks (CTF-1 & FCTF-1) as shown in **Scheme 2.11**.¹⁹⁶ The target for synthesis of FCTF-1 was to prepare a material with high water tolerance and a strong preferences for binding CO₂.¹⁹⁶



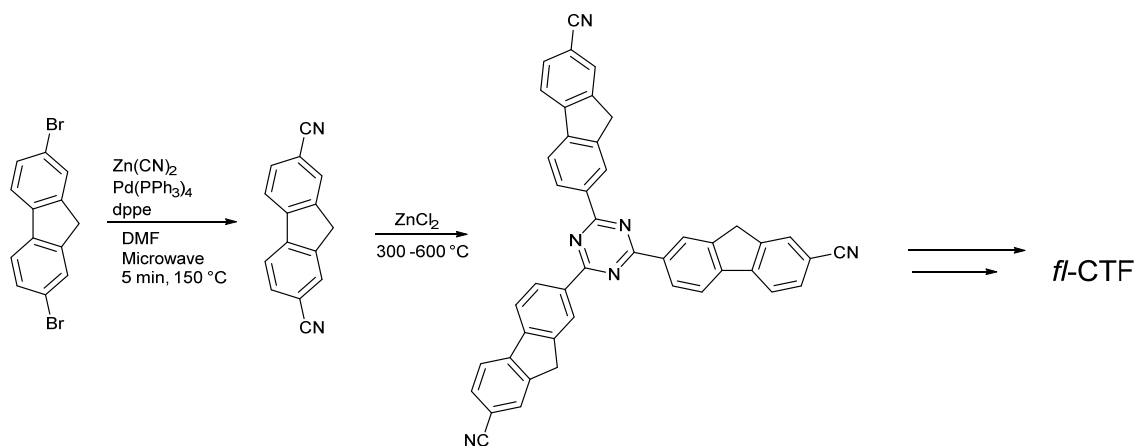
Scheme 2.11: Synthesis of CTF-1 and perfluorinated covalent triazine-based framework (FCTF-1)¹⁹⁶

The addition of fluorine in FCTF-1 was reported to create an F-rich framework which enhanced the CO₂ adsorption capacity of FCTF-1 in comparison to CTF-1 without fluorine atoms. The fluorine atoms in the framework are highly electronegative and thus produce strong polar covalent C-F bonds which increase CO₂ electrostatic interactions. In addition, it was reported that the presence of F atoms in the PCTF-1 compared to CTF-1 reduced the pore size considerably to <0.5 nm, thus increasing the high CO₂ uptake capacity as well as the kinetic selectivity for CO₂/N₂ separation. In the mixed-gas breakthrough experiments, FCTF-1 was reported to display a remarkable CO₂/N₂ selectivity ratio of 77 under kinetic flow conditions. The ratio 77 is much higher than predicted selectivity ratio of 31 from single-gas equilibrium uptake data. Most

framework materials tend to perform poorly in their adsorption of CO₂ in the presence of moisture. However, the performance of FCTF-1 in terms of CO₂ adsorption was also reported to remain excellent even in the presence of moisture in the flue gas stream. This was attributed to the hydrophobic nature of the C-F groups.^{52,196}

Although, both CTF-1 and FCTF-1 were reported to have poor crystallinity, they were heated at 600 °C to give CTF-1-600 and PCTF-1-600 respectively. However, no fluorine atoms were detected in FCTF-1-600, which suggested that F species had been removed from the polymer framework by thermal decomposition at high temperatures. At 600 °C both FCTF-1 and FCTF-1-600 were reported to display type-I isotherms. The CO₂ adsorption isotherms for CTF-1, PCTF-1, CTF-1-600, and PCTF-1-600 were determined, their uptake capacities at 273 K/1bar was stated to be in the order: FCTF-1-600 (243.6 mg/g) > FCTF-1 (206 mg/g) > CTF-1-600 (169 mg/g) > CTF-1 (108 mg/g). FCTF-1 showed the highest initial isosteric heat of adsorption (Q_{st}) value of 35.0 kJ/mol at low coverage, demonstrating the moderate affinity to CO₂. The CO₂/N₂ (10:90 v/v) selectivity established on single-gas adsorption isotherms at 298 K/1 bar, for these triazine-based COFs using ideal adsorption solution theory (IAST)¹⁹⁷ was also stated to decline as follows: 31 (FCTF-1) > 20 (CTF-1) > 19 (FCTF-1-600) > 13 (CTF-1-600).⁵²

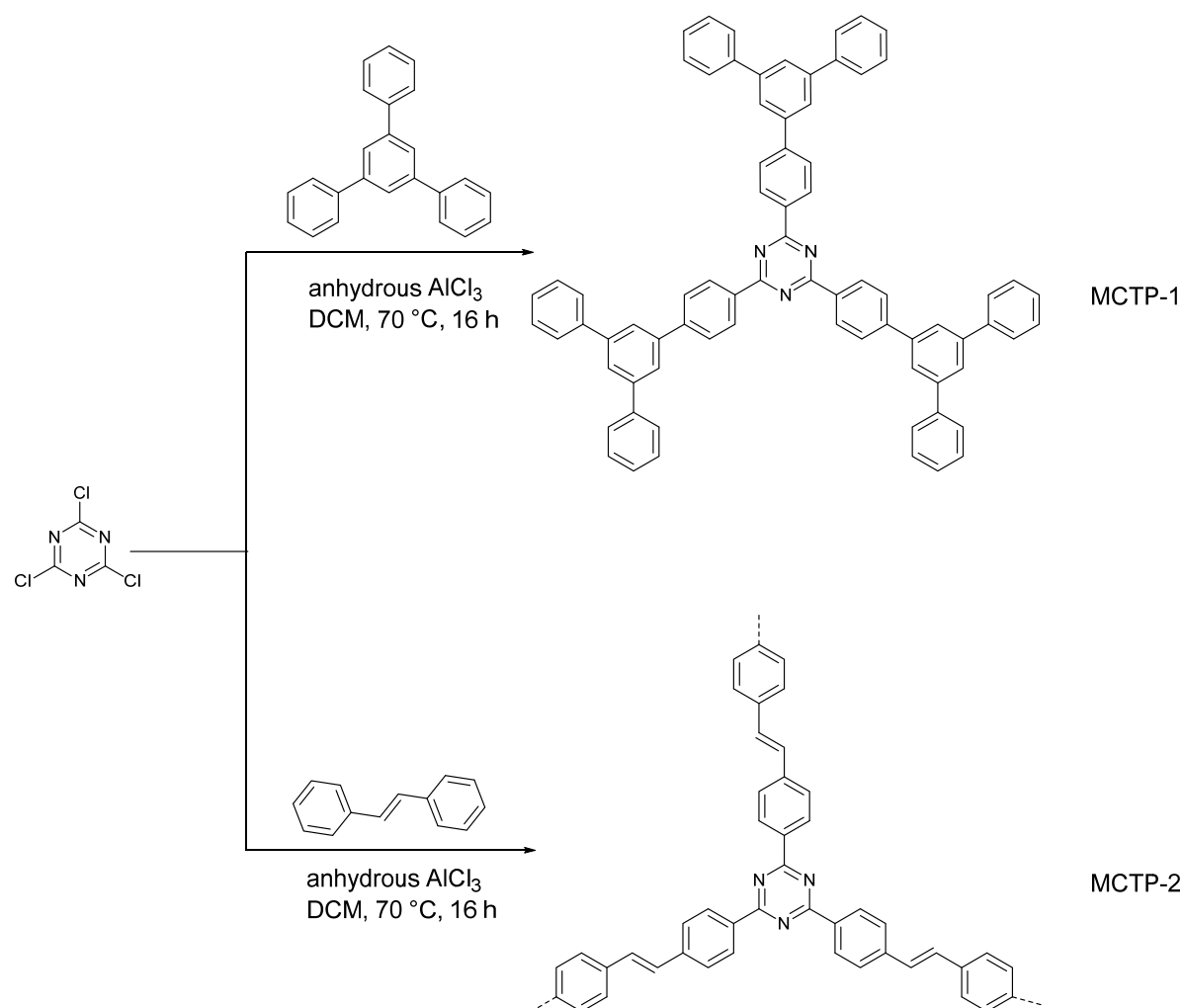
Other covalent triazine-based frameworks (CTFs) containing fluorene building blocks (*fl*-CTF300, *fl*-CTF350, *fl*-CTF400, *fl*-CTF500, *fl*-CTF600) have been synthesised by Lotsch and co-workers as shown in **Scheme 2.12**.¹⁹⁸



Scheme 2.12: Synthesis pathway for fl-CTFs.¹⁹⁸

However, the CTFs obtained at lower temperatures were reported mainly to possess ultramicropores and moderate surface areas of 297 m²/g at 300 °C. But the porosities of *fl*-CTFs materials obtained at higher temperatures were reported to increase significantly, giving rise to surface areas in excess of 2800 m²/g.¹⁹⁸ The COF *fl*-CTF-350 was reported to have a high CO₂/N₂ selectivity ratio of 37 as well as possess the highest fraction of micropores and moderate S_{BET} of 1235 m²/g. However, the adsorption value for *fl*-CTF-350 (188 mg/g) is lower than the reported value for FCTF-1 (205–243 mg/g)⁵² but higher than values reported for other CTF materials such as CTF-0 (186 mg/g)¹⁹⁰, CTF-1 (109–168 mg/g)¹⁹⁶, CTF-P2–P6 (82.7–149 mg/g)¹⁹³ CTF-P1M–P6 M (41.44–184.8 mg/g)¹⁹³, MCTF300–500 (99–139 mg/g)¹⁹⁹, PCTF-1–7 (81–142 mg/g)^{191,192} and TPI-1–7 (29.9–107.8 mg/g).²⁰⁰ In addition, the CO₂ adsorption capacity of *fl*-CTF-350 is higher than the uptake capacities of various Microporous Organic Polymers (MOPs) such as covalent organic frameworks (COFs; 53.2–169.8 mg/g),^{76,201} microporous polyimides (MPIs; 99–167.6 mg/g)²⁰² and hyper-cross-linked organic polymers (HCPs; 84–172.5 mg/g).^{43,203}

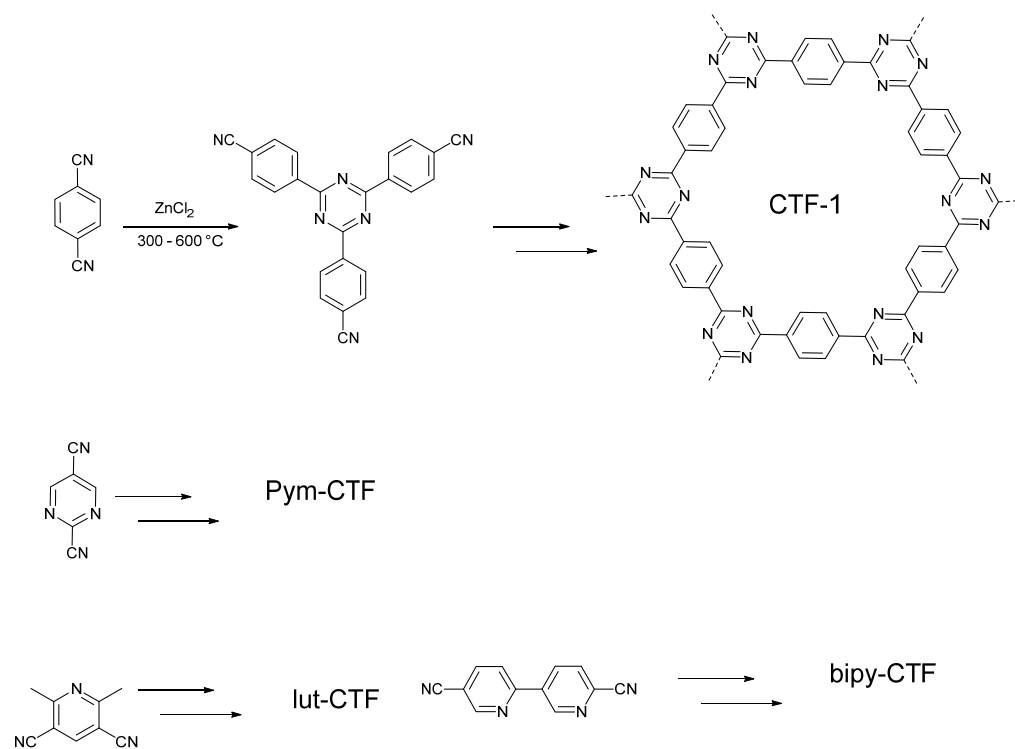
The synthesis of microporous covalent triazine-based organic polymers MCTP-1 and MCTP-2 was conducted by Ahn and coworkers⁴⁰ using cyanuric chloride with 1,3,5-triphenylbenzene/trans-stilbene via Friedel-Craft reaction shown in **Scheme 2.13**.



Scheme 2.13: synthetic pathway for the MCTP networks.⁴⁰

These materials (MCTP-1 and MCTP-2) were reported to possess high S_{BET} s of 1452 and 859 m^2/g respectively. The reported CO_2 adsorption capacity for MCTP-1 is 204.3 mg/g at 273 K/1 bar as well a moderate CO_2/N_2 selectivity ratio of 54.4. However, MCTP-2 was reported to show a moderate CO_2 uptake of 160 mg/g at 273 K/1 bar with a moderately high CO_2/N_2 selectivity ratio of 68.6 compared to 54.4 for MCTP-1. In a bid to obtain new functionalized COF materials for gas capture, Hug *et al.*¹⁷² synthesized nitrogen rich covalent triazine frameworks (CTFs) based on lutidine, pyrimidine, bipyridine and phenyl units in order to study their CO_2 adsorption capacities. These materials were synthesized via ionothermal synthesis at different temperatures as shown in **Scheme 2.14**. These porous organic polymers (POPs) were reported to display high gas uptakes

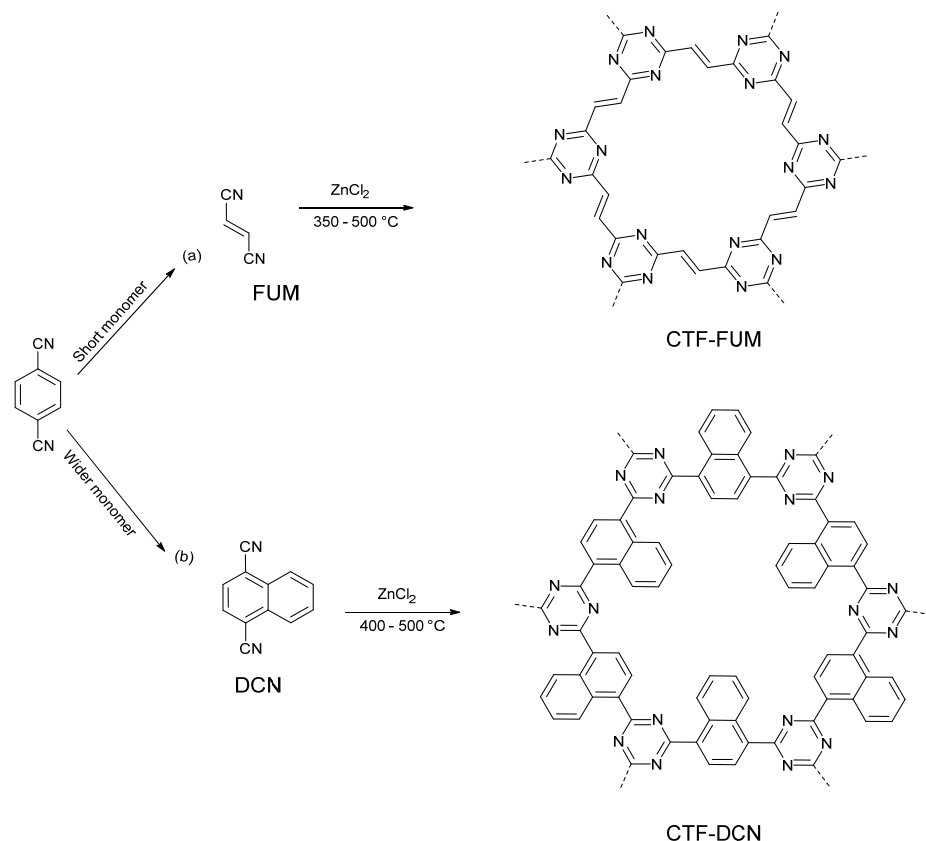
and exceptionally high CO₂/N₂ selectivity ratios. The CO₂ adsorption capacity of bipy-CTF-600 (BP-CTF-600) was reported to be the highest in the family of CTFs synthesized, with CO₂ uptake capacity of 245.5 mg/g at 278 K and CO₂/N₂ selectivity ratio of 20.1; while pyrimidine-based CTF-500 (Py-CTF-500) which contained the highest nitrogen content was reported to possess the highest CO₂/N₂ selectivity ratio of 50.2 based on IAST but with a lower CO₂ capture capacity of 185 mg/g.



Scheme 2.14: Synthesis of the CTFs CTF1 (top), pym-CTF (middle), lut-CTF (bottom left), and bipy CTF (bottom right).¹⁷²

In addition, Hug, *et al.*¹⁷² also reported that the trends in the gas adsorption behaviour within the CTF family and nitrogen-containing POPs, revealed the dominant role of the micropore volume for maximum CO₂ uptake performance, while the N-content is a secondary factor for improving the CO₂ adsorption capacity. However, the nitrogen content in the frameworks was stated to be a key contributor to the high CO₂/N₂ selectivity ratios of the produced CTFs.¹⁷²

Zhong and coworkers²⁰⁴ also designed and synthesized two covalent triazine-based frameworks with both ultramicropores and high nitrogen content for the purpose of CO₂ capture. They successfully synthesized two covalent triazine-based frameworks (CTF-FUM and CTF-DCN) with ultramicropores of width less than 7 Å using fumaronitrile (FUM) and 1,4-dicyanonaphthalene (DCN) as shown in **Scheme 2.15**.

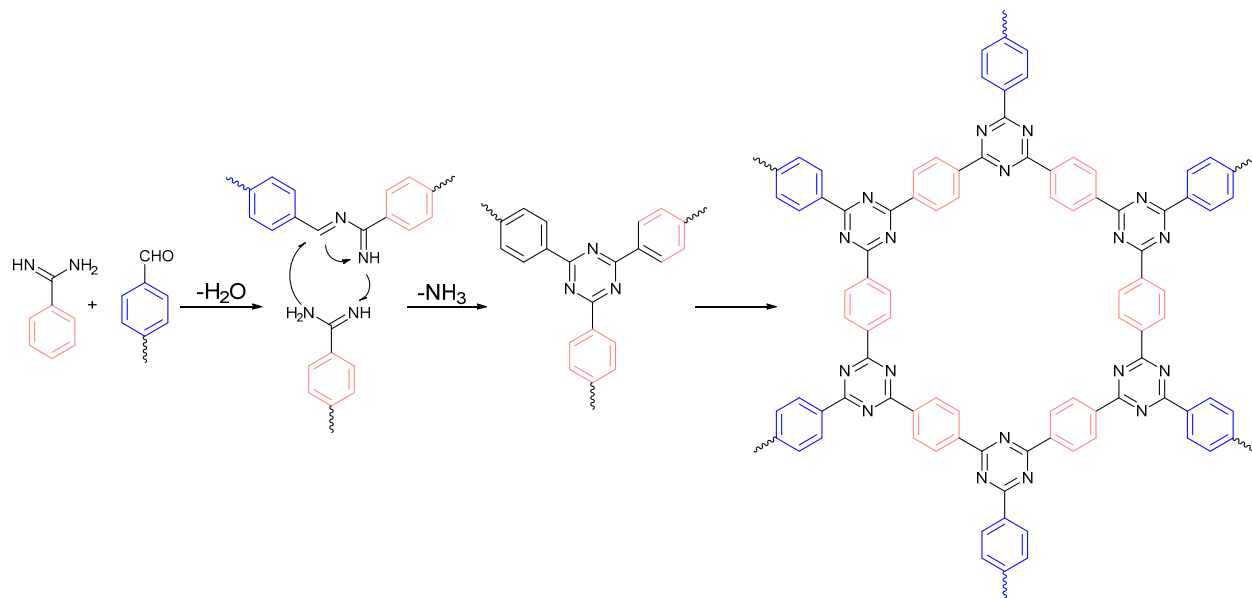


Scheme 2.15: Synthesis of CTF-FUM and CTF-DCN.²⁰⁴

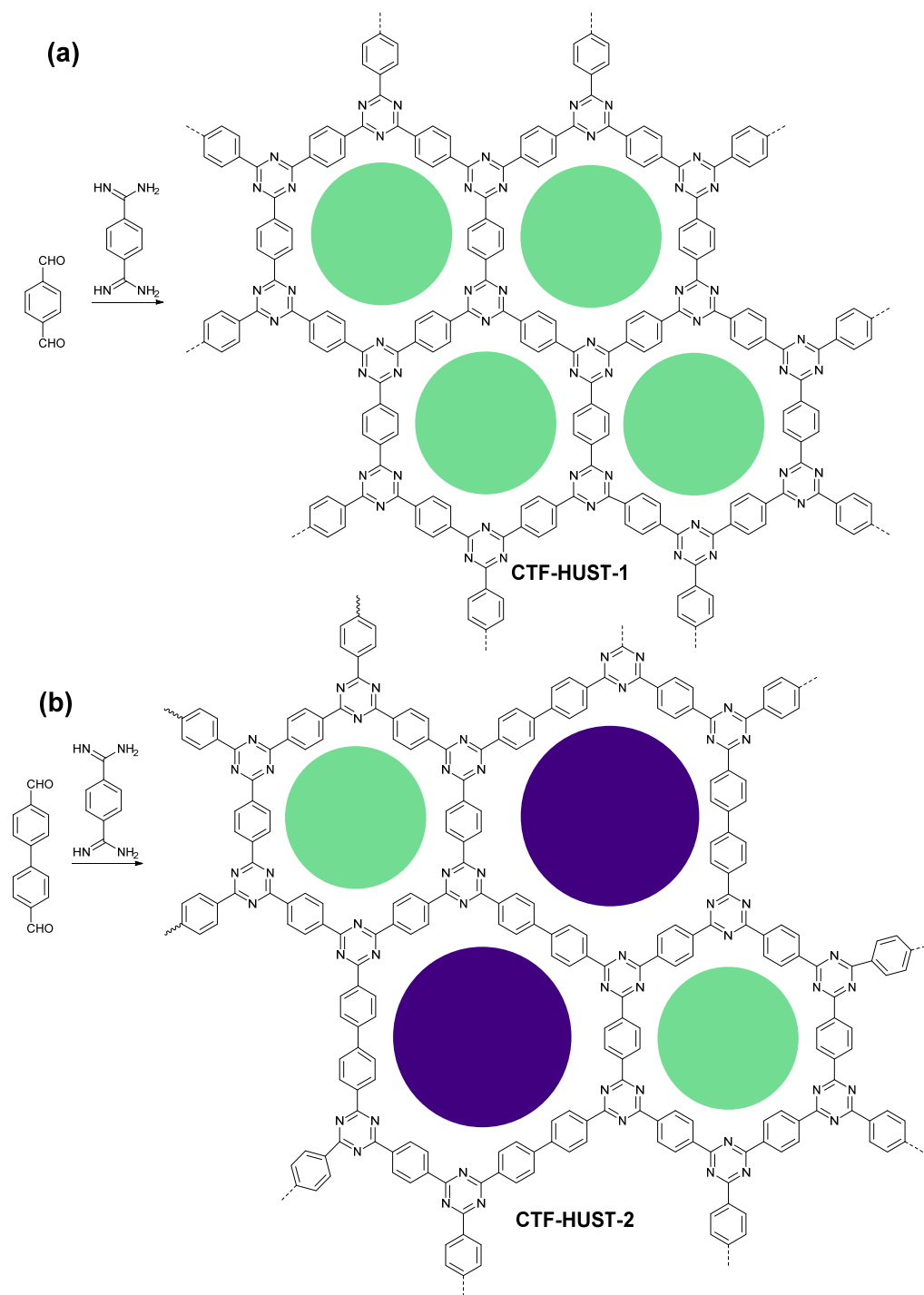
Both CTF-FUM and CTF-DCN were reported to have excellent chemical and thermal stability with ultra-micro-pores of 5.2 and 5.4 Å width respectively. These CTFs were also reported to have excellent abilities to selectively adsorb CO₂ because of the ultra-micro-porous nature of the materials as well as their rich nitrogen content.²⁰⁴ CTF-FUM-350 which contained the highest nitrogen content of 27.4% was reported to display the highest CO₂ adsorption capacity of 112.4

mg/g at 298 K and CO₂/N₂ and CO₂/CH₄ selectivity ratios of 102.4 and 20.5 respectively at 298 K for CTF-FUM and CTF-DCN.

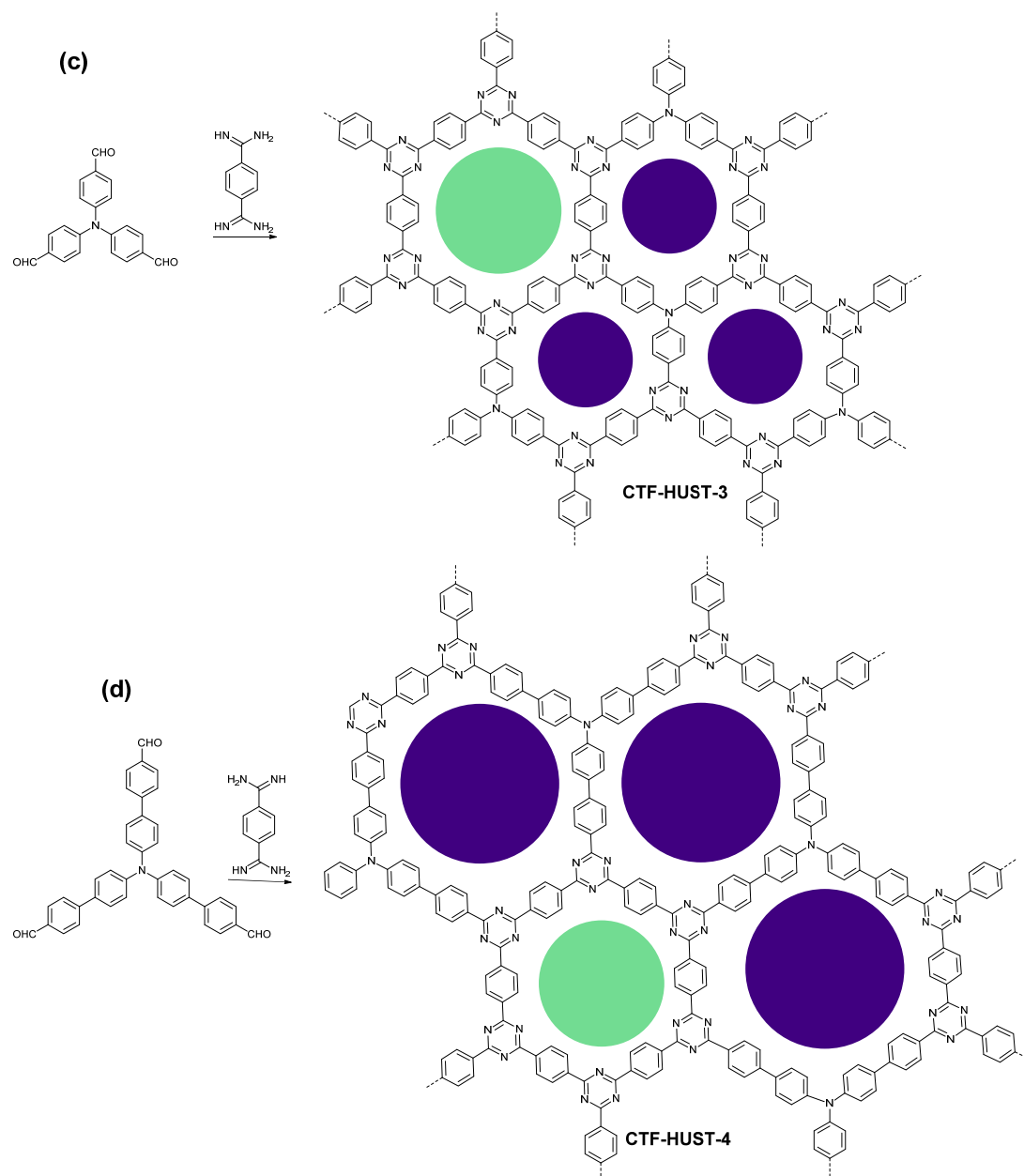
Recently Jin and co-workers²⁰⁵ reported the synthesis of triazine COFs (CTF-HUST) via polycondensation reactions that allowed the synthesis of CTFs under mild conditions (low-temperature) using a variety of building blocks as shown in **Schemes (2.16, 2.17 and 2.18)**.



Scheme 2.16: Triazine formation in the synthesis of CTF-HUST. "HUST" = "Huanzhong University of Science and Technology".²⁰⁵



Scheme 2.17: Synthesis of CTF- HUSTs (a) CTF-HUST-1 (b) CTF-HUST-2; the different coloured circles represent two types of pores.²⁰⁵



Scheme 2.18: Synthesis of CTF-HUSTs (c) CTF-HUST-3 (d) CTF-HUST-4; the different coloured circles represent two types of pores.²⁰⁵

The CTF-HUST materials were reported to display good performance in the fields of photocatalyst, gas separations as well as in sodium ion batteries.²⁰⁵

Building units such as dicyano- and / or multicyno-, pyridine and thiadiazole compounds^{206–209} are the main monomers used for the construction of various 2-D CTFs. Some of these building units are shown in **Figure 2.2**.

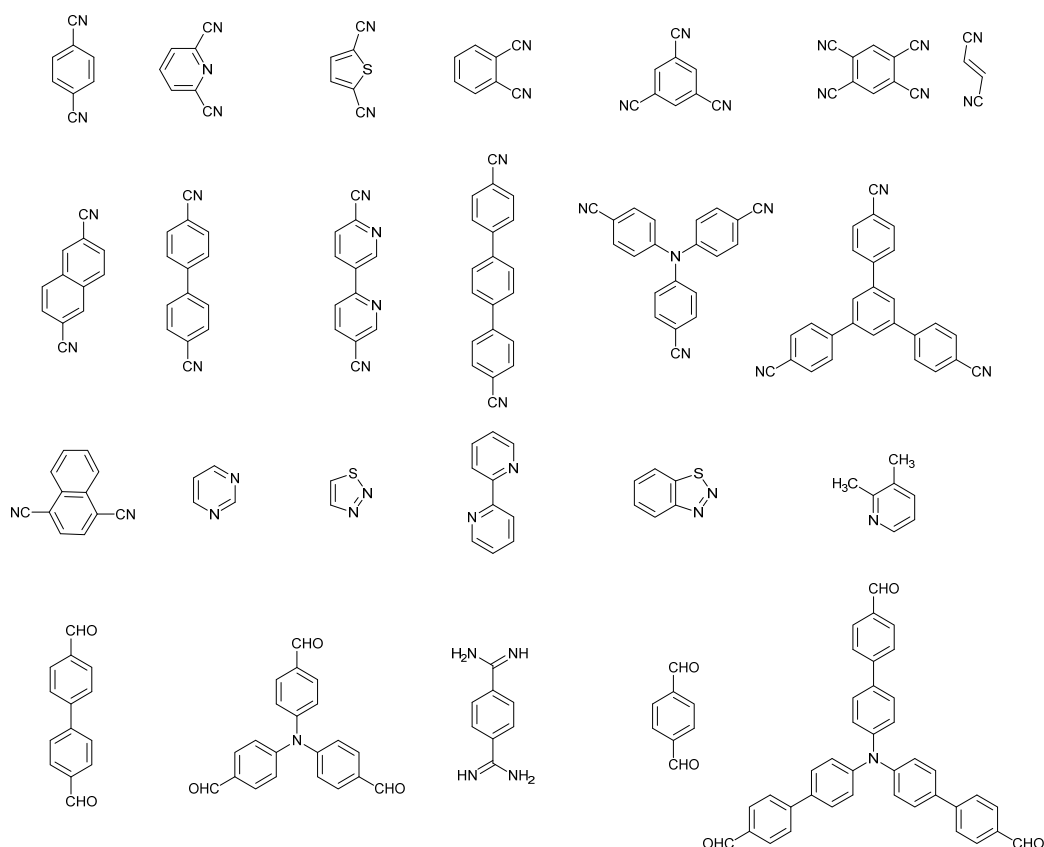


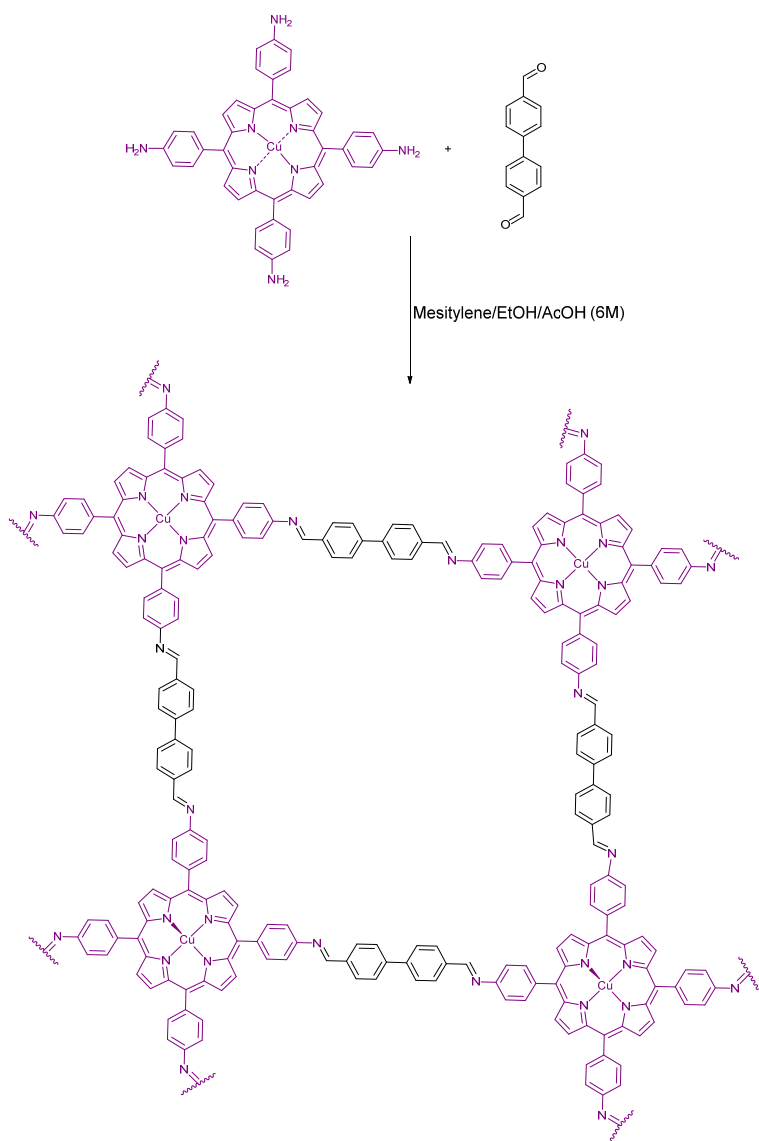
Figure 2.2: Monomers used for the construction of CTFs of different dimensions

Triazine-based COFs show better thermal and chemical stability when compared to boron-based COFs, although they show poor crystallinity and porosity, as well as poor structural integrity. Irrespective of these shortcomings, CTFs show high CO₂ uptake capacities and selectivity as well as being reported to show good reusability after several regenerations without loss of their CO₂ adsorption abilities even in the presence of water vapour.⁵²

2.3.3 Imine-based COFs

Imine-based COFs were first investigated by Yaghi and coworkers¹³¹ and are crystalline porous polymeric material containing C=N bonds. The Yaghi group applied the principles of dynamic covalent chemistry for the construction of imine based COFs. These COFs were of a “Schiff base” type formed by the co-condensation of aldehydes and amines or a “hydrazine” type that was made by the co-condensation of aldehydes and hydrazides. An imine-linked porous porphyrin polymer

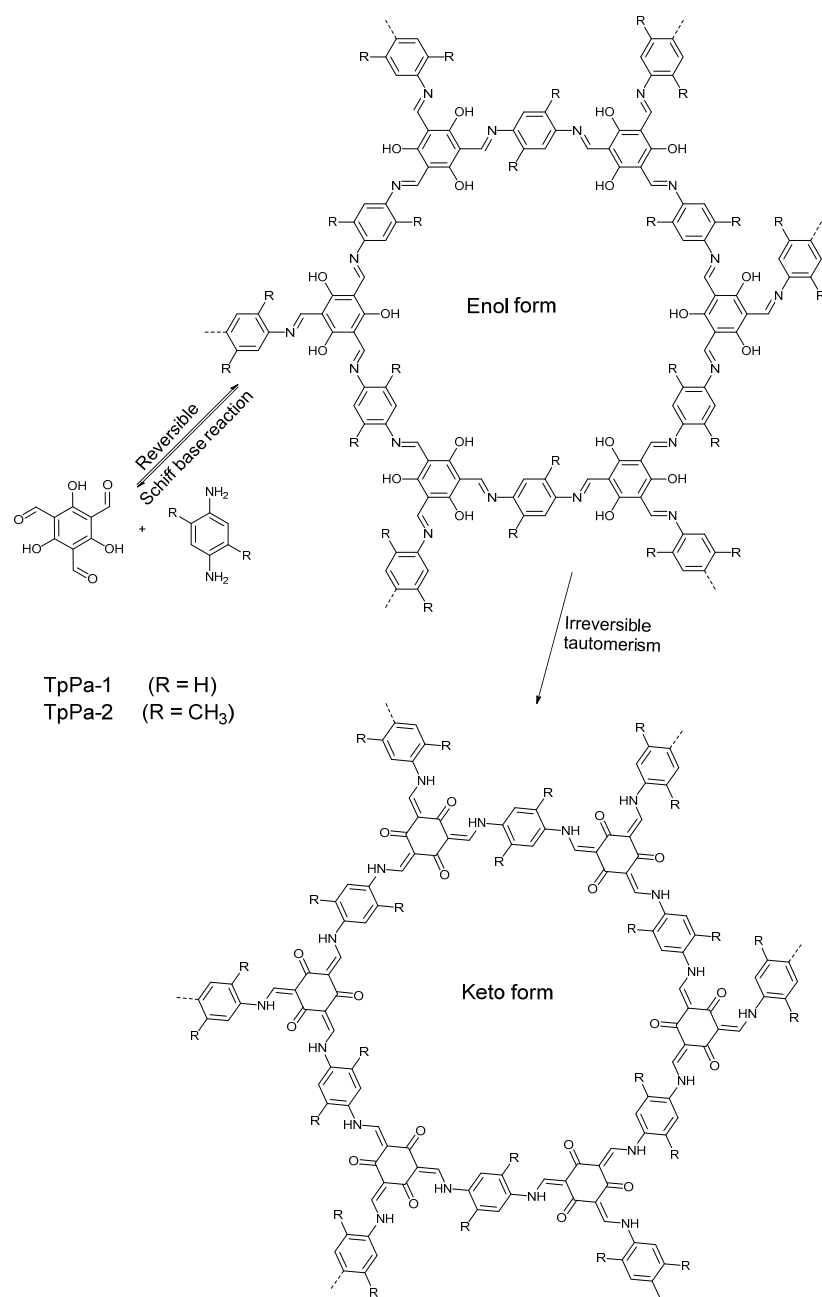
CuPor-BPDC was also synthesized by Neti *et al.*²¹⁰ using a Schiff base condensation reaction between 5,10,15,20-terakis (*p*-aminophenyl) porphyrin Cu(II) and 4,4'-biphenyl dicarboxaldehyde as shown in **Scheme 2.19**.



Scheme 2.19: Synthesis of CuPor-BPDC COF.²¹⁰

CuPor-BPDC was reported to display a S_{BET} of 442 m²/g and high thermal stability of up to 400 °C. In addition, CuPor-BPDC also showed CO₂ uptake capacity of 55 mg/g at 273 K/1 bar as well as a CO₂/CH₄ selectivity ratio of 5.6 at 273 K/1 bar.

Two other 2-D imine-based COFs, TpPa-1 and TpPa-2,²¹¹ were synthesised by the combination of reversible and irreversible reaction of 1,3,5-triformylphloroglucinol (TP) with *p*-phenylenediamine (PaP-1) and 2,5-dimethyl-*p*-phenylenediamine (PaP-2) respectively as shown on **Scheme 2.20**.

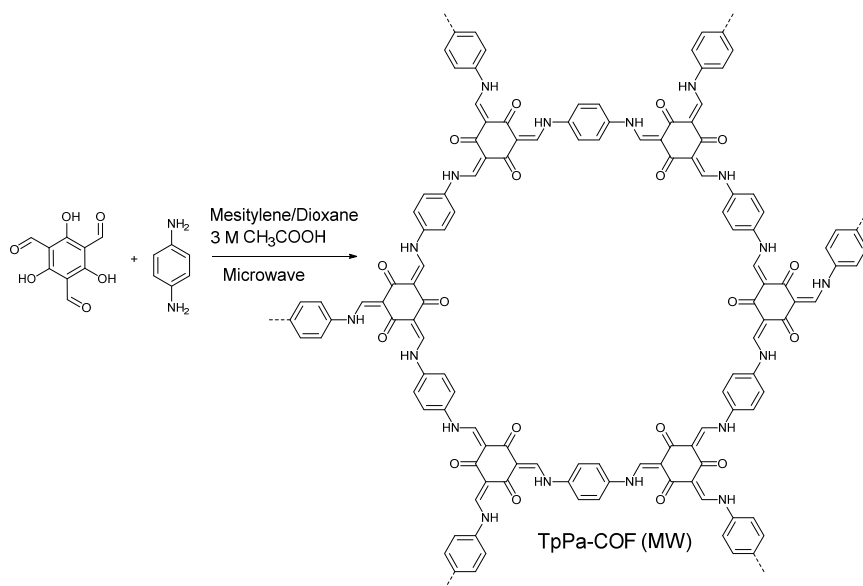


Scheme 2.20: Synthesis of TpPa-1 and TpPa-2 by combined reversible and irreversible reactions.²¹¹

It was reported that TpPa-1 and TpPa-2 showed strong resistance to acid (9 N HCl) as well as boiling water as a result of the irreversible tautomerism from the enol-imine (OH) form to the keto-enamine form. In addition, TpPa-2 was reported to show excellent stability in base (9 N NaOH). The pore size and S_{BET} reported for TpPa-1 are 1.25 nm and 535 m^2/g respectively; whereas TpPa-2 possessed 1.32 nm pore size and S_{BET} of 339 m^2/g as determined from N_2 adsorption isotherms at 237 K. The CO_2 adsorption capacities of TpPA-1 and TpPa-2 were reported to be 15 and 126 mg/g at 273 K/1 bar respectively.

Another synthetic method (mechanochemical grinding) was employed in the synthesis of other TP COFs (TpPa-1) (MC), (TpPa-2 (MC) and TpBD using Tp and other amines as building units. These COFs were synthesised via room temperature solvent free mechanochemical grinding using a Schiff base aldehyde-amine condensation reaction. In addition TpBD was also synthesised solvothermally and the CO_2 uptake of TpBD obtained via solvothermal method was reported to be 84.5 mg/g at 273 K/ 1 bar which is comparable with TpPa-1 (153 mg/g) and TpPa-2 (128 mg/g) obtained by Banerjee and co-workers.²¹¹ By way of expanding Tp COFs, Chandra *et al.*²¹² used the same Tp organic linkers with other amines to synthesise more COFs and measured their CO_2 uptake capacities at 273 K/ 1 bar. They reported the trend to decrease in the order: TpPa-1 > TpPa-NO₂ (143.4 mg/g) > TpPa-2 (126 mg/g) > TpBD-(NO₂)₂ (102 mg/g) > TpBD (85.5 mg/g) > TpBDMe₂ (72.7 mg/g) > TpPa-F₄ (68.8 mg/g) > TpBD-(OMe) (53 mg/g).

To expand further the methods for the making of Tp COFs, Yang and co-workers²¹³ synthesised the same TpPa by using a rapid microwave-assisted solvothermal synthesis method to obtain TpPa-COF (MW) as shown on **Scheme 2.21**.



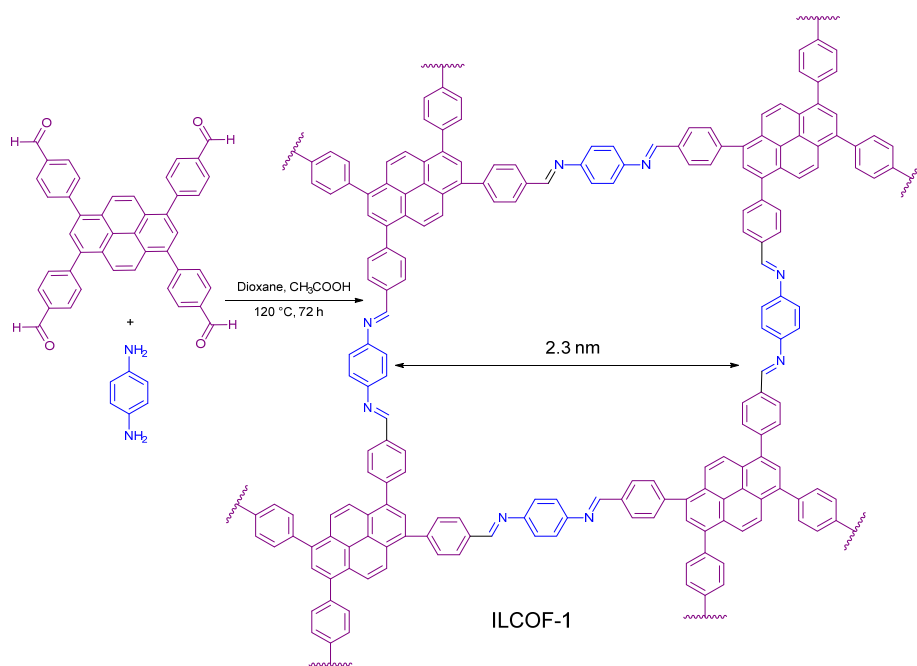
Scheme 2.21: Synthesis of TpPa-COF (MW).²¹³

TpPa-COF (MW) was reported to possess a higher S_{BET} of $725 \text{ m}^2/\text{g}$ as well as better crystallinity than TpPa-COF (CE) synthesised by the simple solvothermal method. TpPa-COF (MW) is rich in N-H sites on its pore wall; these N-H sites were reported to interact more strongly with polarizable CO_2 molecules via hydrogen bonding interactions. These interactions were proposed to be responsible for the CO_2/N_2 adsorption selectivity ratio of 32 recorded for TpPa-COF (MW). In addition, the CO_2 uptake capacity for TpPa-COF (MW) was reported to be 218 mg/g at $273 \text{ K}/1 \text{ bar}$.²¹³

Other researchers, such as Biswal *et al.*²¹⁴ targeted the incorporation of chemically stable isorecticular COFs (TpPa-1 and TpPa-2) as the active phase at 50% loading within the substituted polybenzimidazole (PBI-Bul) matrix to produce self-supported TpPA-1(50)@PBI-Bul and TBD(50)@PBI-Bul crossbreed membranes. It was reported that the permeability of TpBD(50)@PBI-Bul hydrid ($P_{\text{CO}_2} = 14.8$) performed better than some commonly used gas separation membrane materials such as Matrimid, Polysulfones (PSF) and Polycarbonate (PC).²¹⁴ Furthermore, it was reported that the CO_2/CH_4 selectivity ratio of TpBD(50)@PBI-Bul-based

membranes materials (48.7) was higher than that of Matrimid (36), PSF (22) and PC (19).^{215,216} In addition, the TpBD(50)@PBI-Bul-based membrane material was also reported to demonstrate a better CO₂ and CH₄ permeability ($P_{CO_2} = 14.8$ and $P_{CH_4} = 0.3$) with marginally higher CO₂/CH₄ selectivity ratio of 48.7 than Z₃₀@PBI-Bul ($P_{CO_2} = 5.23$ and $P_{CH_4} = 0.12$) and CO₂/CH₄ selectivity ratio of 43.6. However, the CO₂/N₂ selectivity ratio for TpBD(50)@PBI-Bul-based membrane was reported to be 23.²¹⁷

As a follow up, Elkaderi and co-workers²¹⁸ synthesised the mesoporous imine-linked COF (ILCOF-1) by the condensation reaction of 1,3,6,8-tetraakis (4'-formyl-phenyl)-pyrene and p-phenylenediamine in 1,4-dioxane containing aqueous acetic acid as shown in **Scheme 2.22**.

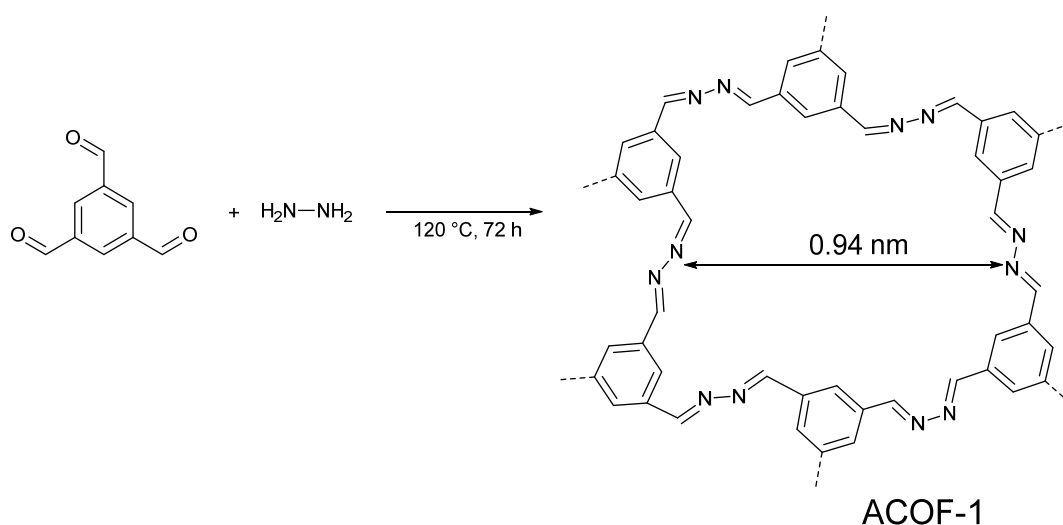


Scheme 2.22: Synthesis of ILCOF-1.²¹⁸

ILCOF-1 was reported to have a high S_{BET} of 2723 m²/g. In addition, ILCOF-1 was also reported to be stable up to 400 °C under air as well as possessing a pore size distribution centred at around 2.3 nm. The CO₂ uptake capacity reported for ILCOF-1 was 60.9 mg/g at 273 K/1 bar.^{52,218} However, the CO₂ uptake capacity at 298 K and 40 bar reported in the literature was 1289 mg/g.²¹⁸

A comparison of this value to other values in the literature shows that it surpasses most of the reported CO₂ adsorption capacities of many 2-D and 3-D COFs including some hyper-branched conjugated polymers such as HCPs (467.5 – 589 mg/g) at 298 K/ 35 bar.⁴³ However, 1289 mg/g is close to the value reported for PAF-1 (1300 mg/g) at 298 K/40 bar.²¹⁹ The CO₂ uptake performance of ILCOF-1 was attributed to the presence of nitrogen-functionalized pore walls, which enhance CO₂ adsorption via N $\cdots$ CO₂ interaction.

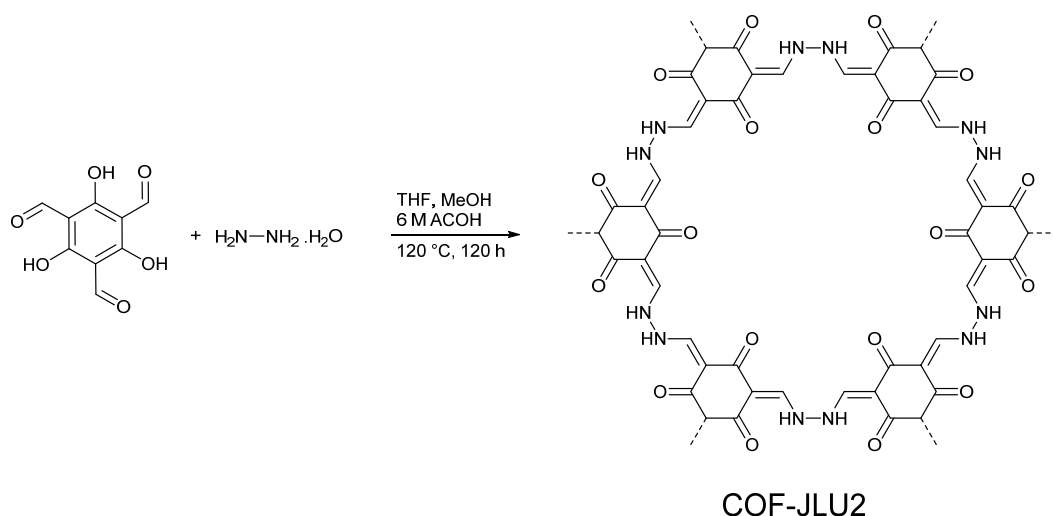
An azine-linked 2-D COF (ACOF-1) was designed and synthesised by Lui and co-workers²²⁰ using the condensation reaction of hydrazine hydrate and 1,3,5-triformylbenzene under solvothermal conditions as shown in **Scheme 2.23**.



Scheme 2.23: The synthesis of ACOF-1.²²⁰

ACOF-1 was reported to possess an S_{BET} and pore size of 1176 m²/g and 0.94 nm respectively. In addition, it was reported that the CO₂ uptake capacity of ACOF-1 was 177 mg/g at 273 K/1 bar as well as a CO₂/N₂ selectivity of 40 at 273 K in the very low pressure range of 0 – 0.1 bar.

Another 2-D azine-linked COF is COF-JLU2, reported by Li *et al.*²²¹ also used a condensation reaction of hydrazine hydrate and 1,3,5-triformylphloroglucinol under solvothermal conditions as shown in **Scheme 2.24**.

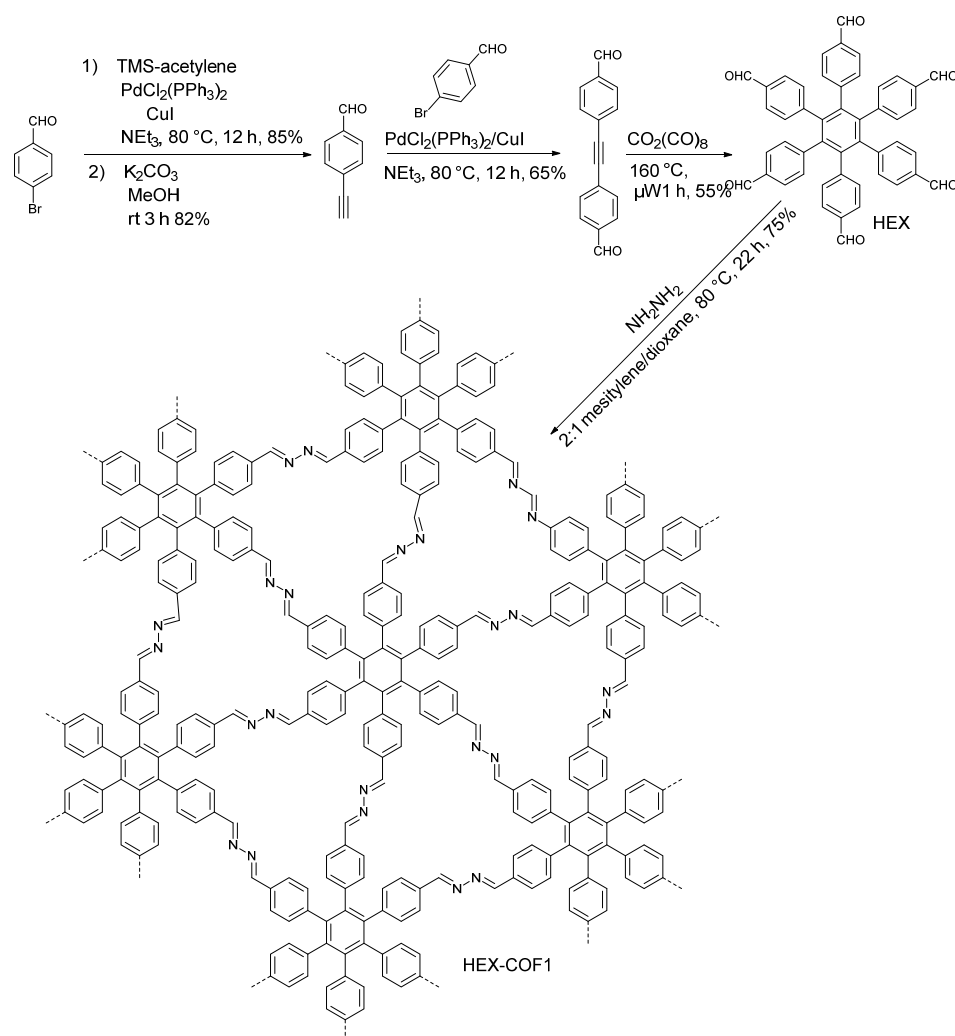


Scheme 2.24: The synthesis of COFJLU2.²²¹

COF-JLU2 contains many heteroatom sites in its skeleton, which are believed to enhance its functionality. COF-JLU2 was reported to be highly crystalline and to possess a moderate S_{BET} and pore size of 410 m^2/g at 77 K and 0.96 nm respectively as well as display good chemical (towards acid and base) and thermal stability. In addition, the CO_2 adsorption capacity reported for COF-JLU2 was 216 mg/g at 273 K/1 bar. This CO_2 uptake capacity value is higher than adsorption capacity values for some other COFs in the literature such as COF-103 (76.6 mg/g),⁷⁶ TDCOF-5 (92 mg/g)¹⁸⁴ and ACOF-1 (177 mg/g).²²⁰ Nevertheless, the uptake capacity of COF-JLU2 (216 mg/g at 273 K/1 bar) is comparable to uptake capacities of some amorphous COFs such as porous organic polymer CPOP-1 (212 mg/g)²²², azo-linked polymer ALP-1 (267 mg/g)²²³ and imine-linked porous polymer PPF-1 (269 mg/g).²²⁴ The reported CO_2 uptake capacity of COF-JLU2, was ascribed to the in-built micro-porosity of the network and the pore walls which are nitrogen- and oxygen-rich. The reported CO_2/N_2 selectivity ratio for COF-JLU2 was 77 which is higher than the CO_2/N_2 selectivity ratio for ACOF-1 (40)²²⁰ and PPFs (21).²²⁴ However, this same value (77) is less than CO_2/N_2 selectivity ratio for some microporous organic polymers (MOPs) such as tetraphenyladamantane-based polycyanurate network PCN-AD (112)²²⁵ and benzimidazole-

linked polymer BILP-2 (113).²²⁶ In addition, the reported CO₂/CH₄ selectivity ratio for COF-JLU2 at temperatures of 273 K and 298 K were 4.1 and 3.2 respectively.²²¹ These two selectivity values are comparable to values reported in the literature for other microporous organic polymers (MOPs).^{222–224}

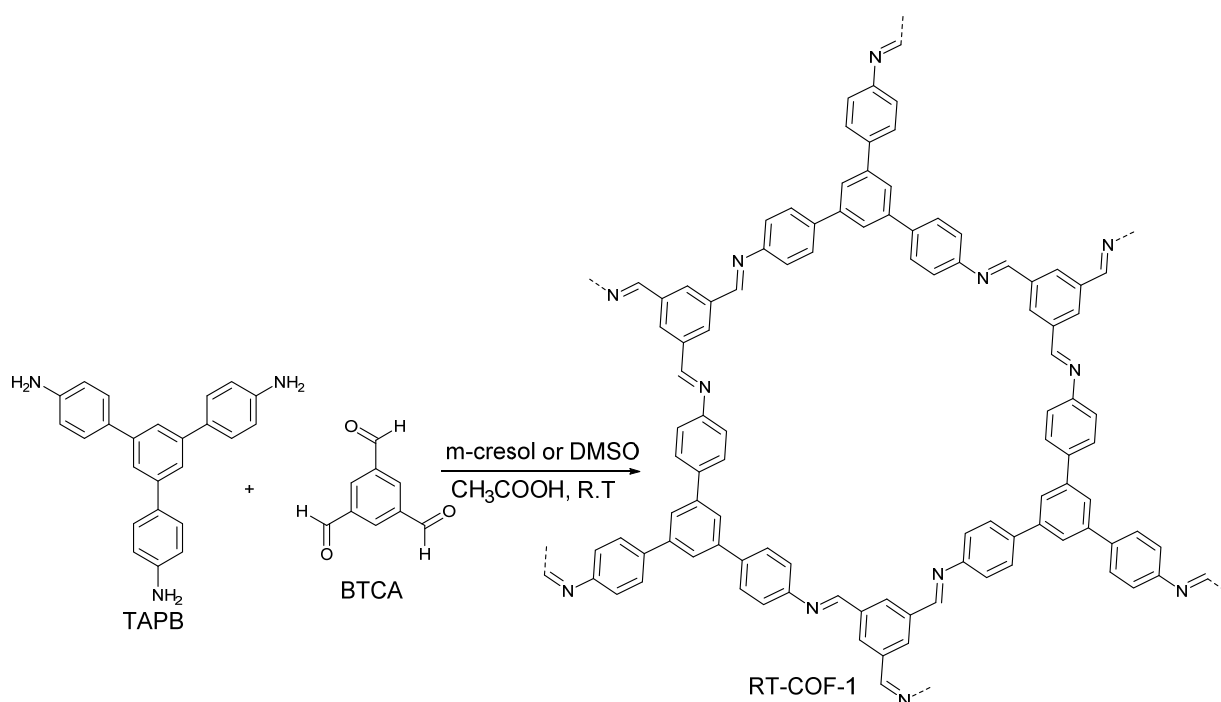
Another group of researchers, Smaldone and co-workers²²⁷ also reported the synthesis of an azine-linked COF containing a six-fold symmetric hexaphenylbenzene (HEX) monomer functionalized with aldehyde groups which was thereafter treated with hydrazine to give HEX-COF1 as shown in **Scheme 2.25**.



Scheme 2.25: synthesis of HEX and HEX-COF1.²²⁷

HEX-COF-1 was reported to have a mean pore size of 1 nm and a surface area in excess of 1200 m²/g as well as to demonstrate outstanding CO₂ uptake capacity of 200 mg/g at 273 K and 1 atmosphere pressure.

In addition, the design and construction of a laminar COF (RT-COF-1) from the reaction of 1,3,5-tris(4-aminophenyl)benzene (TAPB) and 1,3,5-benzenetricarbaldehyde (BTCA) through a Schiff base reaction at room temperature in air was conducted by Zamora and co-workers²²⁸ as shown in **Scheme 2.26**.



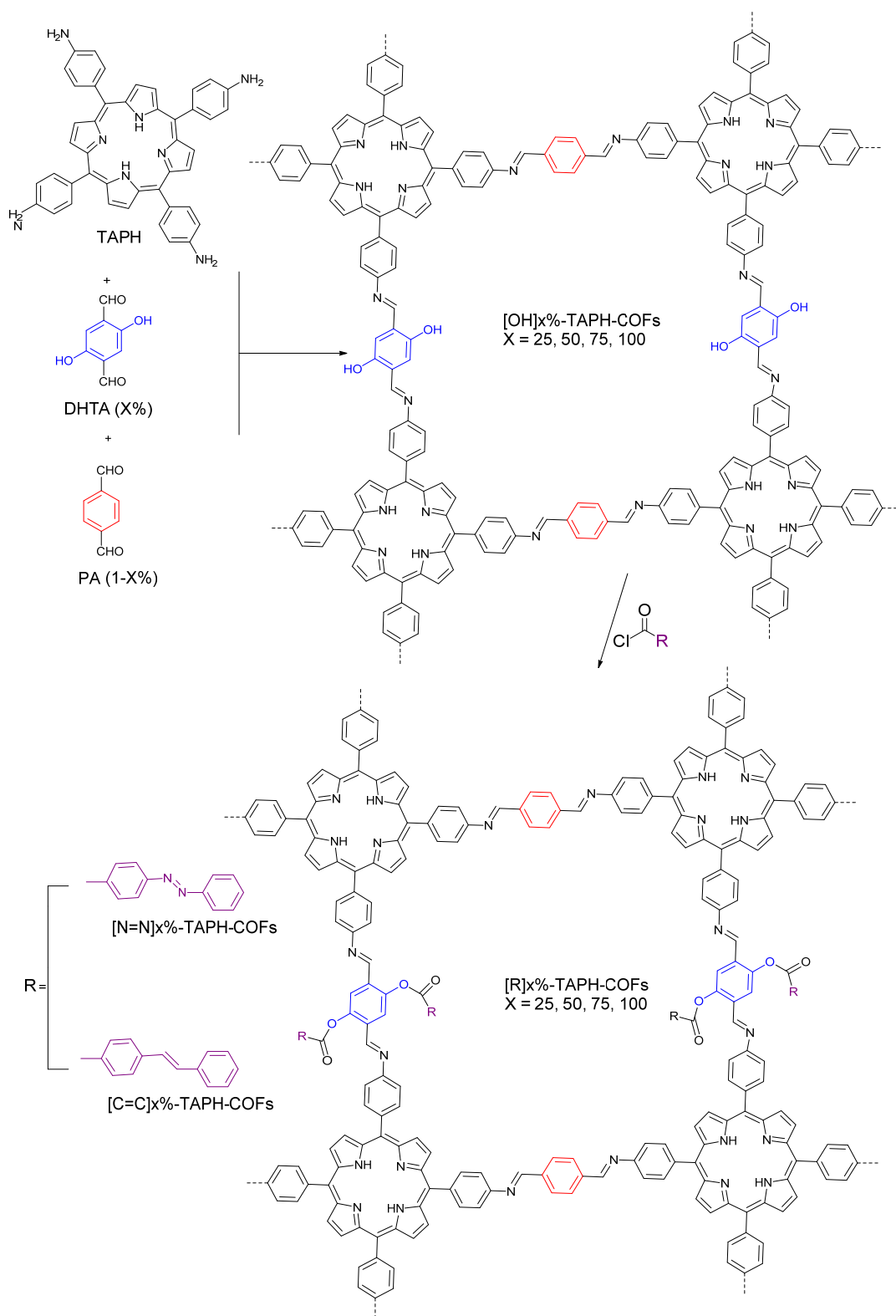
Scheme 2.26: The room-temperature polyimide condensation to form RT-COF-1.²²⁸

The S_{BET} and pore volume reported for RT-COF-1 at N₂ isotherm of 77 K were 329 m²/g and 0.224 cm³/g respectively.²²⁸ Furthermore, it was reported that activated RT-COF-1 adsorbed ca. 86 mg/g of CO₂ at 273 K/1 bar.²²⁸

Furthermore, Gao and co-workers¹⁷¹ synthesized an azo-based COF, COF-Tpazo via a Schiff base condensation reaction of 4,4'-azodianiline (Azo) and 1,3,5-triformylphloroglucinol (Tp). COF-Tpazo was reported to have an S_{BET} of 1552 m²/g and a pore volume of 0.97 cm³/g as well

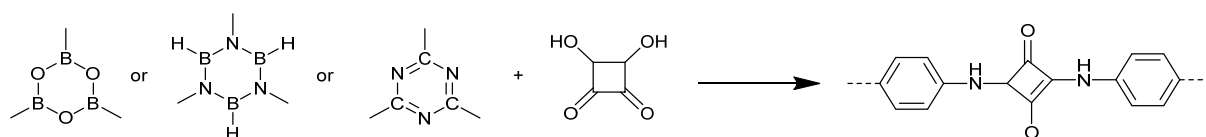
as a CO₂ uptake capacity of 112 and 68 mg/g at 273 and 298 K/1 bar respectively. In addition, COF-Tpazo was also found to exhibit a high CO₂/N₂ selectivity ratio of 127 at 273 K; while the CO₂/N₂ selectivity ratio recorded at 298 K was 45. However, the CO₂/CH₄ selectivity ratios at 273 and 298 K, were reported to be 39 and 43 respectively. The CO₂-philic and N₂-phobic ends of COF-Tpazo were proposed to be responsible for the reported properties of the material.¹⁷¹

Furthermore, Gao and Co-workers also synthesised a range of tailored COFs, i.e [N=N]_{x%}-TAPH-COFs and [C=C]_{x%}-TAPH-COFs by post-modification of [OH]_{x%}-TAPH-COFs with 4-phenylazobenzoyl chloride and stilbenecarbonyl chloride (PhStil),²²⁹ respectively as shown in **Scheme 2.27**. These COFs were reported to possess moderate surface areas, narrow pore sizes as well as good physicochemical stability. The [N=N]_{x%}-TAPH-COFs were reported to show higher CO₂ adsorption capacity of up to 207 mg/g at 273 K/1 bar and CO₂/N₂ selectivity ratio of 78 at 273 K than the corresponding [C=C]_{x%}-TAPH-COFs (16-27).²²⁹ The differences in properties between these two groups of COFs were attributed to the dipole interaction between the azo group and the CO₂ as well as the N₂-phobic behaviour of the azo group.



Scheme 2.27: Synthesis of $[N=N]_x\%$ -TAPH-COFs with azobenzene group and $[C=C]_x\%$ -TAPH COFs with stilbene group via nucleophilic substitution reaction from $[OH]_x\%$ -TAPH-COFs (X = 25, 50, 75, 100).²²⁹

Three hypothetical 2-D squaraine-bridge covalent organic polymers (SQ-COP-1, SQ-COP-2 and SQ-COP-3) were proposed by Huang and Cao²³⁰ by the use of linear squaraine unit and heterocyclic molecules such as $(\text{CH}_3)_3\text{B}_3\text{O}_3$, $\text{H}_3\text{B}_3\text{N}_3$ and $(\text{CH}_3)_3\text{C}_3\text{N}_3$ as shown in Scheme 2.28 as well as the use of grand canonical Monte Carlo (GCMC) simulations.



Scheme 2.28: Synthesis pathway for three 2-D squaraine-bridge COFs.²³⁰

These 2-D squaraine COFs (SQ-COP-1, SQ-COP-2 and SQ-COP-3) were calculated to exhibit exceptional high S_{BET} of 8686, 8938 and 8585 m^2/g respectively. The high S_{BET} s associated with these 2-D squaraine COFs were attributed to the presence of the extended squaraine linkage in the framework materials. These exceptionally high S_{BET} s are however, smaller than those of some microporous coordination polymers MCPs (10436 – 10577 m^2/g)²³¹ but higher than those of MOF-210 (6240 m^2/g),²³² PAF-1 (5460 m^2/g)²¹⁹ and Nu-110SP (7800 m^2/g).⁸⁰ The CO_2 uptake capacities of SQ-COP-1, SQ-COP-2 and SQ-COP-3 were also estimated to be 990, 737 and 833 mg/g at 298 K/50 bar respectively. Nevertheless, it was reported that at 298 K /30 bar, the CO_2 uptake capacities for SQ-COP-1, SQ-COP-2 and SQ-COP-3 were 804, 575 and 633 mg/g respectively which is significantly higher than the value 326 mg/g reported for a benchmark zeolite 13X.⁶⁸ In addition, SQ-COPs COFs were reported to display a good selective adsorption of CO_2 over N_2 , CH_4 , and H_2 . For example, the calculated CO_2/N_2 of SQ-COP-1 is comparable to that of PAF-302 (3-4)²³³ and AlBDC MOF (4.3).²³⁴ Other imine-based COFs have also reported in the literature.^{235–}

237

The results described above show that imine-based COFs possess better crystallinity as well as structural regularity which can be tuned to achieve desired pore size more easily than triazine-

based COFs (CTFs). In addition, imine-based COFs have better stability in water as well as in most organic solvents when compared with boron-based and triazine-based COFs. A summary of the main building units used for the construction of imine-based COFs is depicted below in **Figure 2.3**.

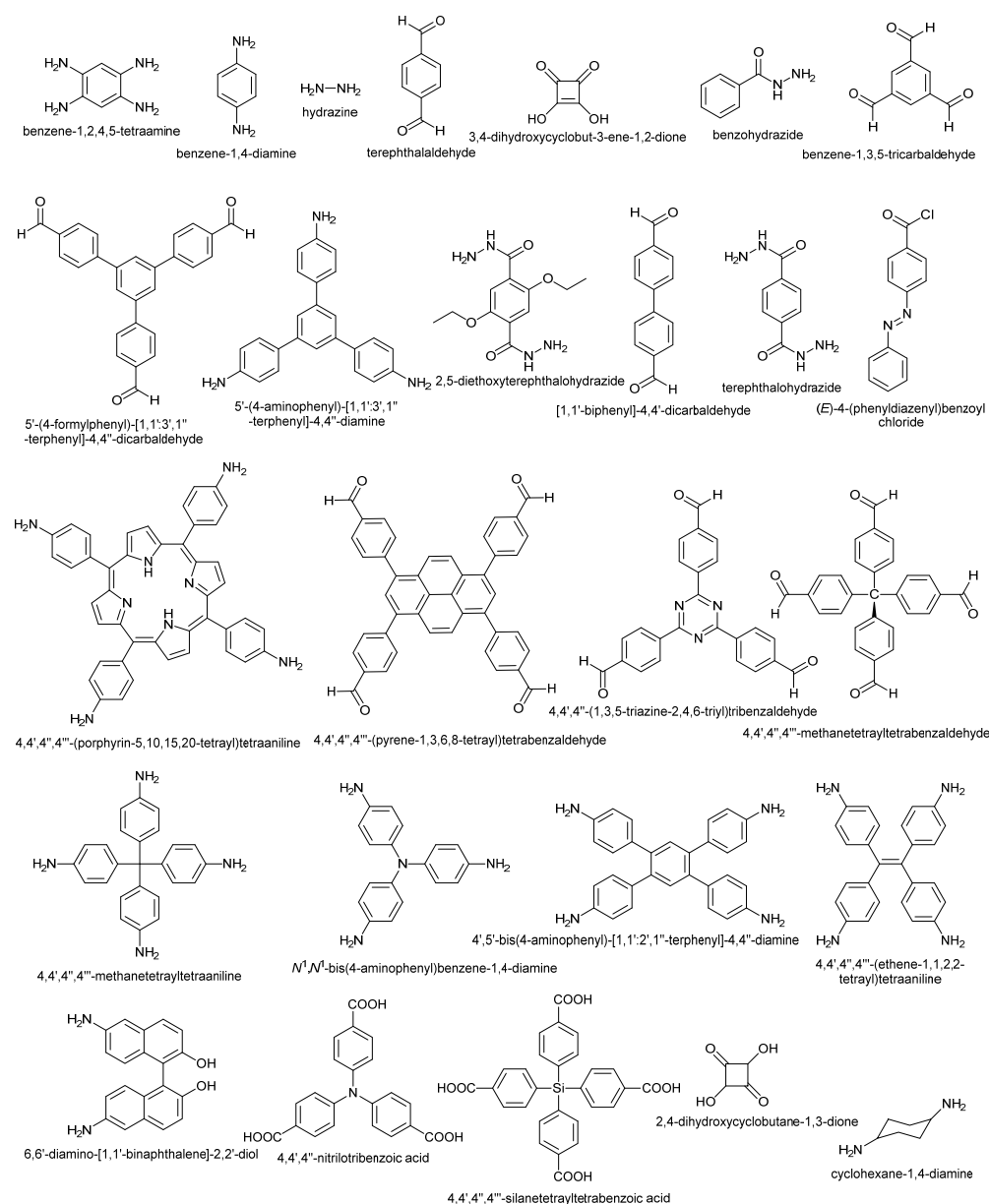


Figure 2.3: Some monomers used for constructing imine-based COFs.

The boron-, triazine- and imine-linked COFs discussed above make use of a conventional two-component [1 + 1] condensation design scheme. The design and synthesis of these COFs as well

as new ones largely depends on the exploration of new nodes and linkers which can be difficult, time consuming and often do not give the desired results. In contrast to conventional two [1 + 1] design systems, multiple-component (MC) COF design makes use of three [1 + 2] i.e. one node and two linker units or four [1 + 3] i.e. one node and three linker units for their synthesis.¹³⁵

2.3.4 Multiple-component COFs

Multiple-component COFs (MC-COFs) feature asymmetric tiling of organic building units into anisotropic skeletons with uncommon shaped pores. Thus the application of the MC method has enabled the expansion of structural complexity of framework materials and their pores as well as the enhancement of their structural diversity. In addition, the multiple-component strategy has also provided new platforms for considerable expansion and design of functionalized structures of porous organic materials. The design and synthesis of both hexagonal and trigonal COF topologies using two-component [1 + 1] copolymerisation of a C_3 - or C_4 -symmetric node and a C_2 -symmetric linker^{179,185,188,235,236,238} as shown in **Figure 2.4 a**, and three- or four-component systems **Figure 2.4 b** using one node and two or three dissimilar linkers.^{135,239,240}

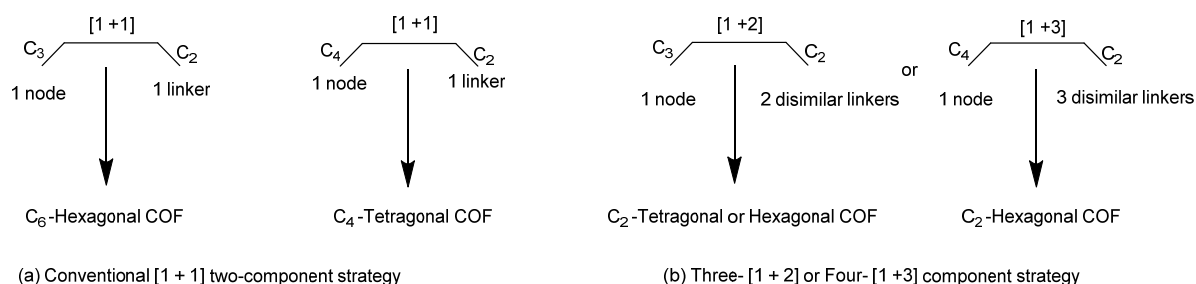
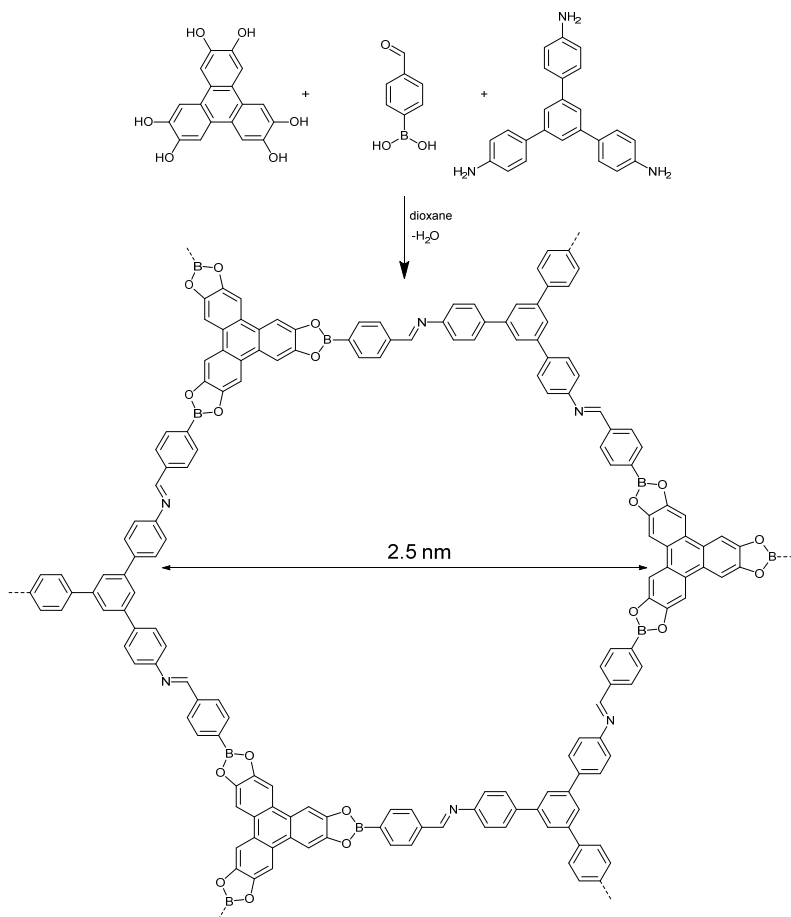


Figure 2.4: Conventional two-component [1+1] and multiple-component [1+2] or [1+3] strategies for the design and synthesis of COFs. Adapted from refs.^{135,239,240}

In a bid to enhance and expand the research of COF materials using multiple-component orthogonal reaction strategies, Zhao and co-workers used 4-formylphenyl boronic acid (a bifunctional linker) for the synthesis of MC-COF (NTU-COF-2). NTU-COF-2 was reported to consist of two dissimilar boronate and imine linkages in its skeleton that are not accessible for

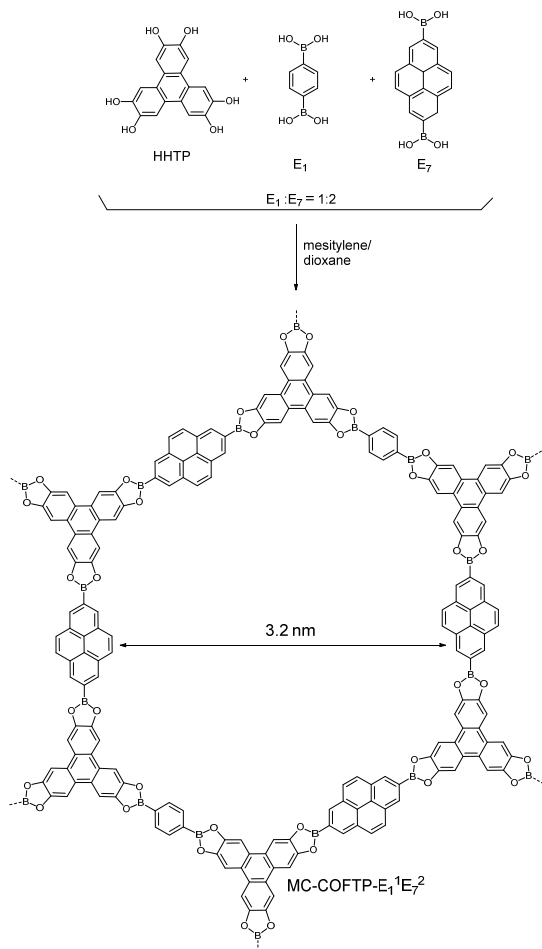
conventional [1 + 1] based COFs.²³⁹ By way of using different starting materials, Zhao and co-workers also designed a new three [1 + 2] multiple-component COF (NTU-COF-2) with the use of 2,3,6,7,10,11-hexahydroxytriphenylene (HHTP) which served as node while 4-formylphenylboronic acid (FPBA) and 1,3,5-tris(4-amino-phenyl)-benzene (TAPB) acted as the linkers to give an imine group and a C₂O₂B boronate ring as shown in **Scheme 2.29**.



Scheme 2.29: Synthesis of NTU-COF-2 involving the formation of two kinds of covalent bonds from orthogonal reactions.²³⁹

NTU-COF-2 was reported to have pore volume of 0.86 cm³/g and CO₂ uptake capacity of 102 mg/g at 273 K/1 bar. In addition, an S_{BET} of 1619 m²/g was reported for NTU-COF-2; this S_{BET} value is larger than those reported for other COFs such as COF-5 (1590 m²/g),²³⁸ DZnPcANDI-COF (1410 m²/g), and TCOF-1 (927 m²/g)¹⁸⁶ and smaller than the S_{BET}s reported for COF-10

(1760 m²/g),⁷⁶ ZnP-COF (1742 m²/g)¹⁸⁷ and TT-COF(1810 m²/g).¹⁴⁷ In a manner similar to Zhao and co-workers,²³⁹ Jiang and co-workers¹³⁵ also applied a multiple-component strategy with two or three dissimilar linkers to obtain hexagonal MC-COFs (MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹) as shown in **Scheme 2.30**. E₁¹E₇² and E₁²E₇¹ are defined as the 1:2 and 2:1 molar ratio respectively, for the E₁ and E₇ in the units in the COF.

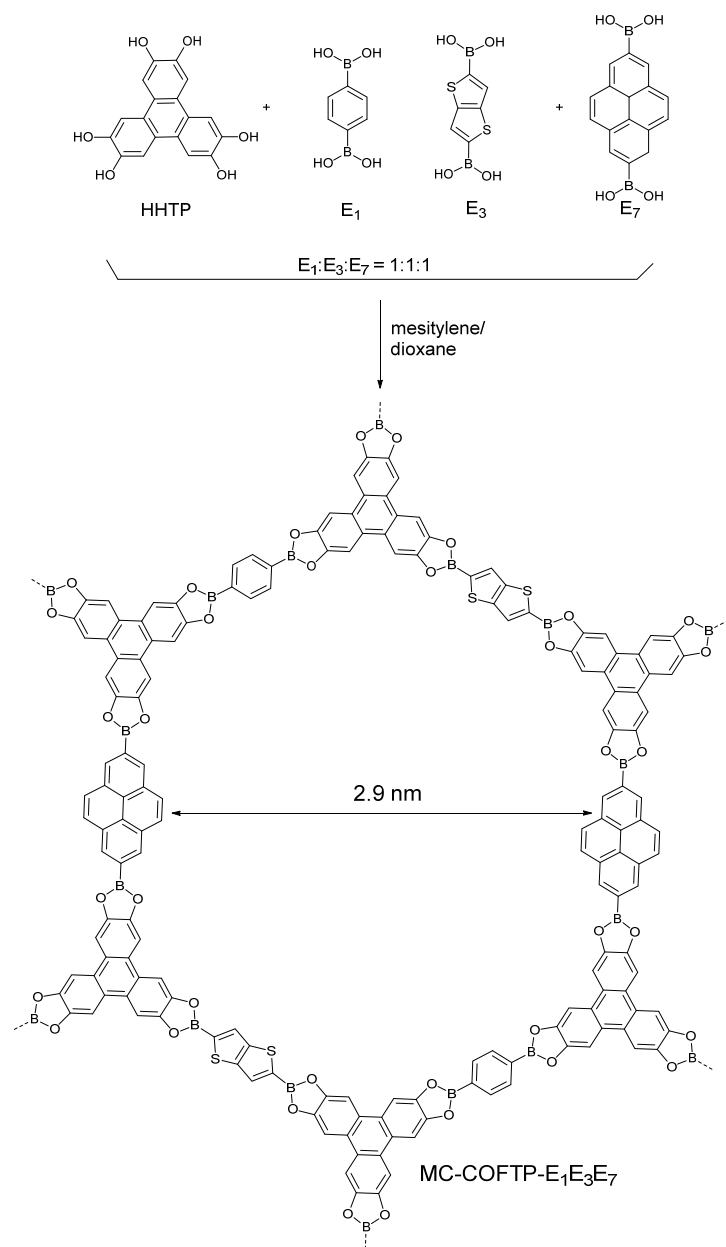


Scheme 2.30: Synthesis and structures of typical [1 + 2] hexagonal MC-COFs.¹³⁵

The syntheses of MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹ were carried out by the application of three [1 + 2] component solvothermal copolymerisation of HHTP as node with a short linker (E₁) and longer linker (E₇) (molar ratio of 1:2 or 2:1) in a mixture of mesitylene and dioxane. These two MC-COFs (MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹) were reported to possess S_{BET} of

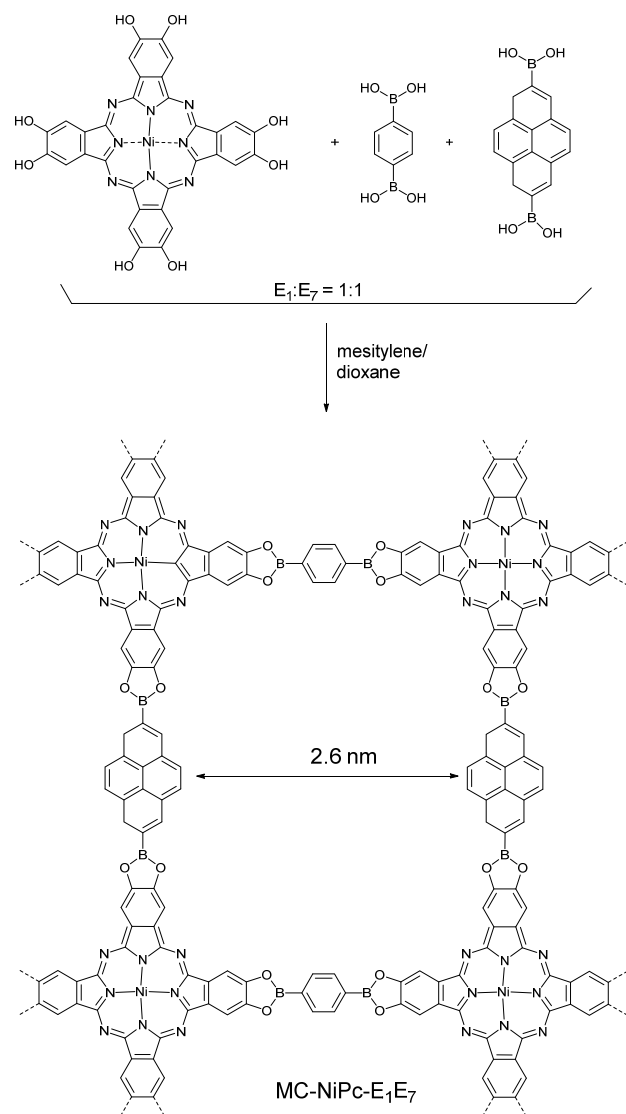
1892 and 1534 m²/g respectively. In addition, these MC-COFs were reported to be highly porous with a type-IV sorption isotherm profile as well possessing only one type of mesopore overall with pore sizes for MC-COF-TP-E₁¹E₇² and MC-COF-TP-E₁²E₇¹ of 3.2 and 2.9 nm respectively. These pore sizes are similar to those of other similar [1+1] COFs such as COF-5 (2.7 nm)²³⁸ and TPCOF (3.2 nm).¹²⁰

Furthermore, the same researchers used the MC synthetic strategy for the design and synthesis of four [1+3] component hexagonal MC-COFs (MC-COF-TP-E₁E₃E₇).¹³⁵ MC-COF-TP-E₁E₃E₇ was constructed with one node (HHTP) and three linkers (E₁, E₃ and E₇) using the same molar ratio of node and linkers of 2:1:1:1 as shown in **Scheme 2.31**. The S_{BET} and mesopore size reported for MC-COF-TP-E₁E₃E₇ were 1887 m²/g and 2.9 nm respectively.



Scheme 2.31: Synthesis and ordered structure of MC-COF-TP-E₁E₃E₇

The same research¹³⁵ group used the MC/COF strategy with a [1+2] component reaction for the construction of tetragonal MC-COF (NiPc-E₁E₇) by the use of nickel phthalocyanine (NiPc) as the knot and two linkers (E₁ and E₇) as depicted in **Scheme 2.32**. It was reported that NiPc-E₁E₇ contained only one type of mesopore with pore size of 2.6 nm and S_{BET} of 672 m²/g.



Scheme 2.32: Synthesis of tetragonal [1+2] MC-NiPc-E₁E₇.¹³⁵

The MC strategy of constructing COFs make use of a selective combination of three or more blocks (usually the building units used for the making of boron-, triazine- and imine-based COFs) consisting of one node and two or three linkers leading to the formation of hexagonal and tetragonal COFs. The MC strategy has opened new insight for the expansion and construction of structurally complex frameworks via asymmetric tiling of building units with provision for platforms for further construction of anisotropic π -columnar arrays and unconventional shaped pores.

2.4 Synthetic Methods Used in the preparation of COFs

In addition to the building units for the construction of COFs the synthesis conditions are also important to regulate the thermodynamic equilibrium involved in the formation of covalent bonds. Thus, the reaction media and conditions (temperature, pressure as well as presence or absence of template) are crucial factors for the formation of thermodynamically stable crystalline polymeric products. Since the pioneering work of Yaghi and co-workers,¹¹⁹ many other researchers globally have exploited and expanded the synthetic possibilities by developing mixed solvent systems and molten metal salts that have provided platforms such as solvothermal, ionothermal, microwaves and room temperature methods for COF synthesis.

2.4.1 Solvothermal Synthesis of COFs

Most of the reported COFs were obtained through solvothermal synthetic methods. A typical solvothermal method for synthesising COFs involves the mixing of monomers with a suitable solvent or a mixture of solvents and then putting the monomer mixture in a Pyrex or Parr-autoclave followed by degassing with several freeze-pump-thaw cycles. Following the degassing process, the tube or the autoclave is sealed and heated to a given temperature (usually 80 °C and above) for some reaction time (usually 1- 9 days). This treatment of monomers usually leads to the formation of precipitates. The precipitates are collected and washed with suitable solvent followed by drying under vacuum to give the COF material (usually a powder product). Factors such as solvent combination and ratios as well temperature and duration of reaction processes are crucial when designing a solvothermal reaction process for COFs synthesis, due to issues such as solubility, reaction rate, crystal nucleation and crystal growth as well as ‘self-healing’ of structures during the formation of COFs.

Solvent combination and ratios are important points to consider for the purpose of forming crystalline framework materials. For example, the influence of solvents on the crystallinity of a

COF materials was demonstrated by Jiang and co-workers¹⁸⁷ who found that co-condensation of zinc(II) 5,10,15,20-tetrakis(4-(dihydroxyboryl)phenyl)porphyrin and 1,2,4,5-tetrahydroxybenzene in a mixture of mesitylene and dioxane (1/1, v/v) produced amorphous solids. On the other hand, when the v/v ratio of mesitylene/dioxane was changed to 19/1 or 9/1, COF materials with high crystallinity were obtained. Furthermore, in the formation of boronate ester and boroxine-linked COFs, mesitylene/dioxane,^{119,241} DMAc-*o*-dichlorobenzene,¹⁶² and THF/methanol¹⁸² have been used as solvent combinations. In the formation of borosilicate COFs, dioxane/toluene solvent mixtures have been used.⁸⁶ Dioxane/aqueous acetic acid was used as solvent mixture in some imine-based COFs.¹²⁹ Mesitylene /dioxane/acetic acid solvent mixture²⁴² was used as solvent mixture in the synthesis of some hydrazone-linked COFs.¹³¹ Recently Zhao and co-workers used a mixture of mesitylene/dimethylacetamide/AcOH (6M, aqueous) (5:5:1 by volume) which was heated in a sealed glass ampoule at (120 °C for 3 days) to produce COF-BTA-DAB and COF-BTA-BZ.²⁴³

A suitable temperature appropriate to the solvent used is also important to ensure the reversibility of the reaction. In general, most reported COFs in the literature were prepared in the temperature range 80 - 120 °C depending on the chemical reactivity of the building units. A closed reaction system enhances the retention of any water molecules that could trigger a reverse reaction in the system. The final products of solvothermal methods are often powdered COF materials which may limit their practical applications under certain circumstance, e.g. interfaced incorporation into devices. To this end, Dichtel and co-workers²⁴⁴ developed a solvothermal method for producing 2-D COF materials as thin films on single-layer graphene. It was reported that the obtained COF materials exhibited improved crystallinity in comparison with the powder samples.²⁴⁴

2.4.2 Ionothermal Synthesis of COFs

Ionothermal synthesis involves the growing of single crystals from an ionic liquid in an autoclave at high temperature (300-600 °C) and pressure. Thomas and co-workers were the first to apply ionothermal method to produce crystalline porous COFs.¹²² As mentioned in **Section 2.3.2**, they used reversible cyclotrimerisation of nitrile building units (1,4-dicyanobenzene) in molten ZnCl₂ to generate covalent triazine-based frameworks (CTFs) with high crystallinity alongside outstanding chemical and thermal stabilities. The molten ZnCl₂ functioned both as a solvent and as a catalyst for the reversible cyclotrimerisation reaction that lead to the formation CTFs. A comparison of COF materials obtained through solvothermal methods, and CTF polymers obtained from ionothermal method can be made; CTF polymers have the drawback of lack of crystallinity control because the reversible cyclotrimerisation reaction takes place under harsh reaction conditions that often lead to the formation of amorphous materials that lack long-range molecular order.¹¹⁸ In addition, the constraint of high reaction temperature limits the choice of suitable building units.²⁴⁵ Based on these limitations, ionothermal methods at present have limited application.¹⁷⁹

2.4.3 Microwave-assisted Synthesis of COFs

Microwave heating has many applications in accelerating chemical reactions.²¹³ Cooper and co-workers developed a rapid microwave-assisted protocol for the synthesis of boronate ester linked COFs.²⁴⁶ For example, 2-D (COF-5) and 3-D (COF-102) COFs could be synthesised using microwave heating in 20 minutes.²¹³ The syntheses of these COFs were achieved by conventional solvothermal methods in 72 h.^{119,247} Thus the microwave-assisted synthesis is 200 times faster than the solvothermal method. In addition, the S_{BET} obtained for the product under microwave was reported to be 2019 m²/g; whereas the S_{BET} of the same material but obtained via solvothermal

means was reported to be 1590 m²/g.²⁴⁶ Thus by way of comparison, it can be seen that (1) Microwave-assisted synthesis can produce COFs more rapidly than solvothermal methods. (2) In microwave-assisted syntheses, the methods for the removal of solvent and residual impurities trapped in the frameworks are more efficient than in solvothermal methods, and thus microwave-assisted syntheses enhance the formation of materials with better porosity.¹¹⁸

2.5 Challenges in the synthesis of COFs.

Boron-, triazine- and imine-based COFs that are obtained via condensation, Schiff-base reaction, Friedel-Crafts reactions, cyclotrimerization and post-synthesis exfoliation have all opened many opportunities for exploring novel functional materials using existing building units.^{53,76,173,179,180,248,249} However, some major challenges that are yet to be fully addressed are: further improvement on how to achieve the combined properties of stability and crystallinity as well as porosity in COF materials; the growing of extended and high quality crystalline molecular materials; and the design of COF materials with flexible monomers. Despite these challenges large SBETs and pore volumes as well as better structural integrity with low CO₂ adsorption capacities at low pressures have been reported for boron-, boron/imine-, triazine and imine-based COFs.^{52,138,180} However, in terms of chemical/water stability as well diversity for different applications, further work is still needed. Ways forward to solving these challenges in COF synthesis are: (1) The development of new synthetic methodologies to improve the stability of COF materials, (2) The construction of COFs with more flexible monomers as well as diverse 3-D architectures for high-pressure CO₂ uptake. (3) Development of room temperature methods for the synthesis of COFs. In a bid to provide some solutions to the challenges associated with the synthesis of COFs, this report describes new methodologies and strategies for their synthesis.

2.6.0 Synthetic Methods, Results and Discussion.

This section describes the synthesis of adducts of cyclo-diboradisiloxanes with amines. In the literature, simple adducts of cyclo-diboradisiloxanes (Lewis acids) and amines (Lewis bases) have been reported.^{85,102,250} However, the methods for the syntheses of the cyclo-diboratetrasiloxanes as well as adducts are modified in this project to achieve new results. Thus this section aims: to synthesize C₂ or C₃ Lewis Acids (LA) and then combine the C₂ or C₃ connectors with Lewis Bases (LB) to produce 1-D, 2-D or 3-D COFs, and to characterize these new materials with the intention to use them to capture CO₂ as depicted in **Figure 2.5** below

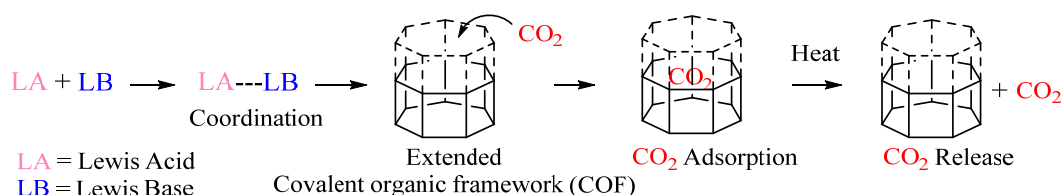
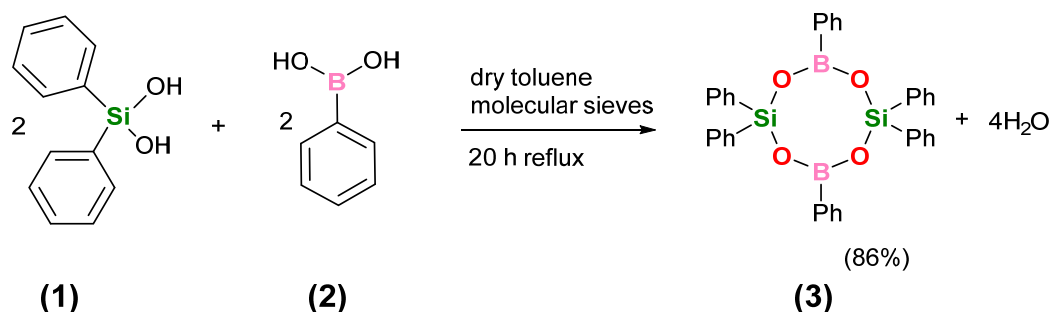


Figure 2.5: Schematic method of the aims of this project

2.6.1 Synthesis of Ph₆B₂Si₂O₄ (3).

In the literature the synthesis of cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane (Ph₆B₂Si₂O₄) (3) has been reported using diphenylsilanediol (1) and phenylboronic acid (2) and a Dean-Stark apparatus for the removal of water, with a reported 87% yield of (3).⁸⁵ However, in the current research molecular sieves were used for the removal of water as shown in **Scheme 2.33**.



Scheme 2.33: Preparation of (Ph₆B₂Si₂O₄) (3)

The eight-membered borasiloxane, **(3)** was characterised using standard analytical and spectroscopic methods. Compound **(3)** is a colourless crystalline solid and readily soluble in non-polar organic solvents. The ^1H NMR spectrum of compound **(3)** shows well resolved resonances with aromatic proton signals found within the range of $\delta = 7.32 - 8.17$ ppm, comparable to values reported in the literature.^{83,85,89} The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **(3)** shows signals for the aromatic carbons in the range of 127.93-135.65 ppm which are also in agreement with the literature values.^{83,85,89} The $^{11}\text{B}\{^1\text{H}\}$ NMR of compound **(3)** shows a broad singlet at 25.69 ppm which is indicative of a single boron chemical environment. In the same way, the ^{29}Si NMR of compound **(3)** show a singlet at -45.00 ppm. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound **(3)** are provided as Supplementary information (**S1-S4** respectively).

In addition, the IR spectrum obtained from compound **(3)** showed strong absorption peaks in the regions: $\nu(\text{cm}^{-1})$ 3023, C-H aromatic; 1349, B-O; 1307, Si-C stretch; 1071, Si-O stretch).¹⁰²

Compound **(3)** was thereafter treated with a variety of pyridine linkers shown in **Figure 2.6** below (**L1-9**) and the tri- and tetra-dentate linkers.

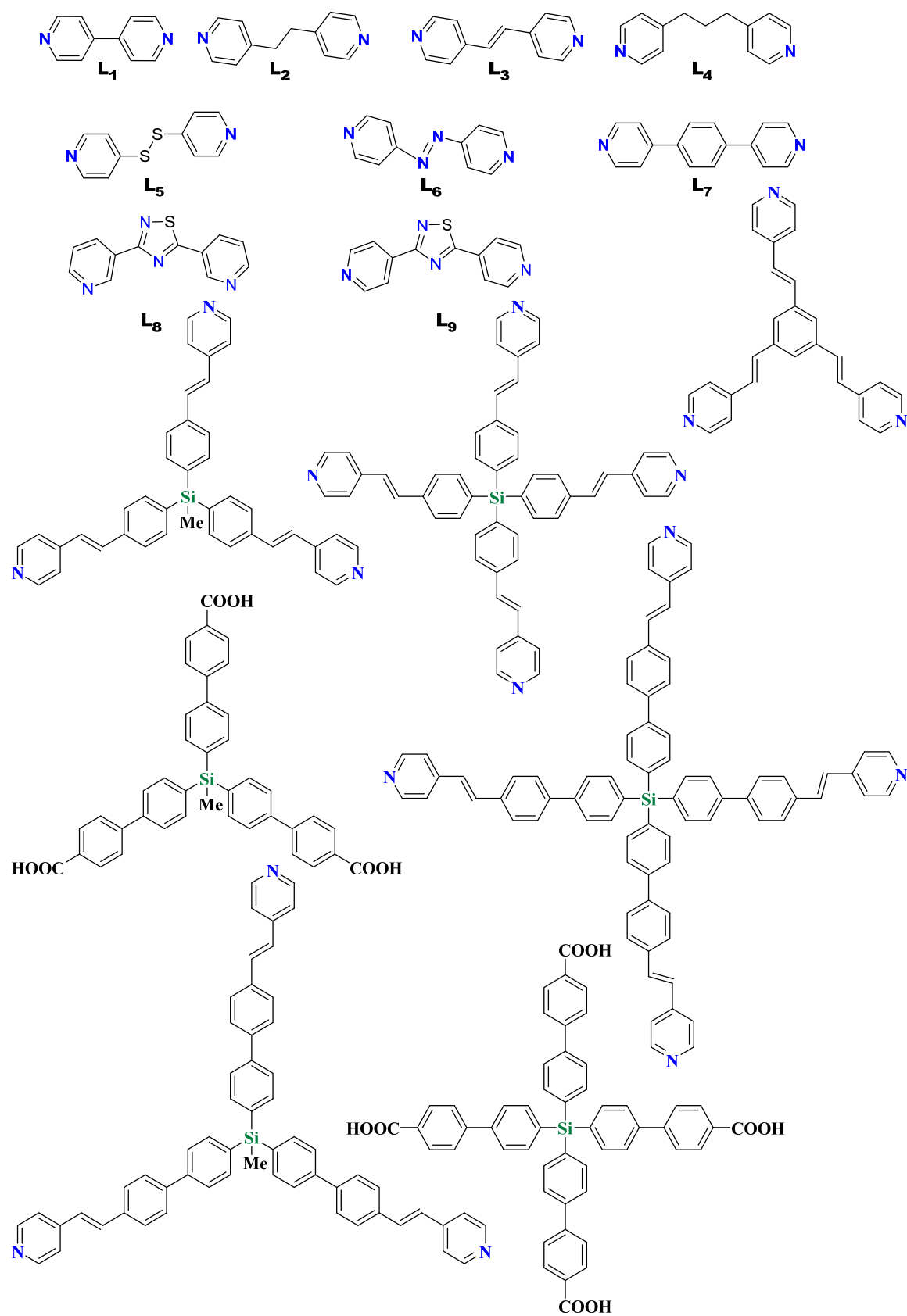
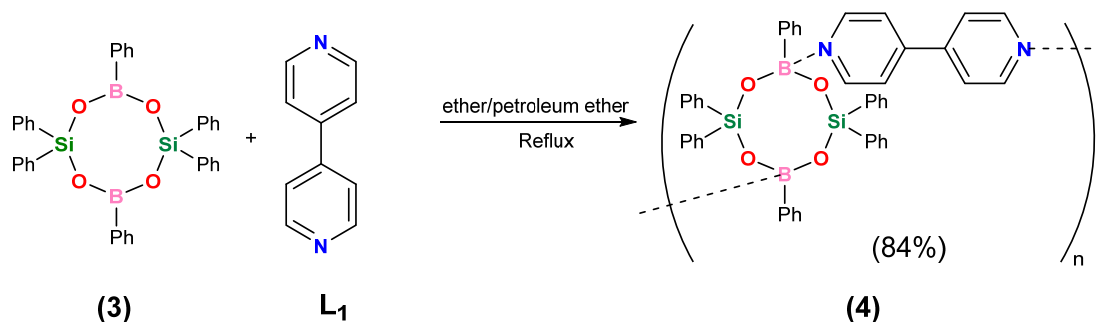


Figure 2.6: Linkers used in this work.

2.6.2 Synthesis of $[Ph_6B_2Si_2O_4].L_1$ (**4**)

Compound (**3**) was treated with 4,4'-bipyridine (**L₁**) in a mixture of solvents at reflux as shown in **Scheme 2.34**



Scheme 2.34: Synthesis of $[Ph_6B_2Si_2O_4].L_1$ (**4**)

2.6.2.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_1$ (**4**).

Compound (**4**) is a 1-D borasiloxane/bipyridine polymer obtained as colourless crystals from solution after a slow evaporation of some of the solvent from the reaction mixture. At room temperature the compound (**4**) was soluble in organic solvents such as dichloromethane, ether, toluene and acetone. Elemental analysis for C, H and N reveals (**4**) as a 1:1 adduct. The $^{11}B\{^1H\}$ NMR spectrum of compound (**4**) showed a singlet at 20.91 ppm typical of 4-coordinate boron, whereas that of the starting material, compound (**3**) was 25.69 ppm typical of 3-coordinate B. Similarly, the $^{29}Si\{^1H\}$ NMR spectrum of compound (**4**) showed a singlet at -45.16 ppm and compound (**3**) was -45.00 ppm. The NMR (^1H , $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{29}Si\{^1H\}$) spectra of compound (**4**) are provided as Supplementary Information (**S₅-S₈** respectively).

Data obtained from a single crystal X-ray diffraction study shows that compound (**4**) consists of eight-membered ring structure derived from (**3**) with the two B atoms coordinated to the 4,4'-bipyridine (**L₁**), resulting in the formation of a 1-D polymer as shown in **Figure 2.7**.

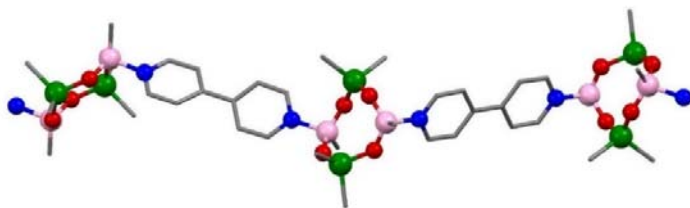


Figure 2.7: 1-D Crystal structure of Compound **(4)**. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms are omitted for clarity.

The B-O-Si angles in compound **(4)** range from 133.44(19) to 147.0(2)° with an average value of 139.19(2) and display some distortion at the O atoms as revealed in the ellipsoid plot **Figure 2.8**, and when compared to the B-O-Si angles of compound **(3)** (145.3(3) and 160.9(3)).⁸⁵ The four B-O distances in **(4)** are 1.426(4) Å (B1-O2), 1.427(4) Å (B1-O8), 1.437(4) Å (B5-O4), and 1.433(4) Å (B5-O6), and are longer than the B-O lengths for the tri-coordinated B in compound **(3)** (Si₂B₂O₄) which range from (1.36-1.39 Å)^{84,89,102} However the values reported here are similar to other B-O distances for tetrahedrally coordinated B in compounds such as N(CH₂CH₂O)B [1.43(1) Å],²⁵¹ Ph₂BOCH₂CH₂NH₂ [1.484(3) Å],²⁵² and Ph(OSiR₂R')B{OCH₂CH₂N}[1.439 (4) Å and 1.461(3) Å],²⁵⁰ (R or R' = Ph or CH₃) and [Bu^tSi(OPhBO)₃SiBu^t].NC₅H₅ [1.457 (18) Å and 1.469 (18) Å]¹⁰² wherein the B is directly bonded to two O atoms, a phenyl group and the N atom. The observed longer bond length at the tetrahedrally bonded B site compared to the tri-coordinated B may be linked to a reduction in any B-O π-bonding component on changing from trigonal to tetrahedral coordination geometry at the B.

In addition, the four Si-O bond lengths in **(4)** range from 1.606(2) to 1.614(2) Å, and are relatively short compared to literature bond lengths for Si-O for a tetra-coordinate Si bonded to two O atoms and two carbon atoms with a mean value of 1.645 Å.^{89,102} However, some similar Si-O bond distances to those reported here have been observed in the literature (1.585 to 1.634 Å).^{102,250} The shorter Si-O distances associated with **(4)** suggest an electron density increase in the Si-O bond which is also consistent with the decrease in the B-O electron density.

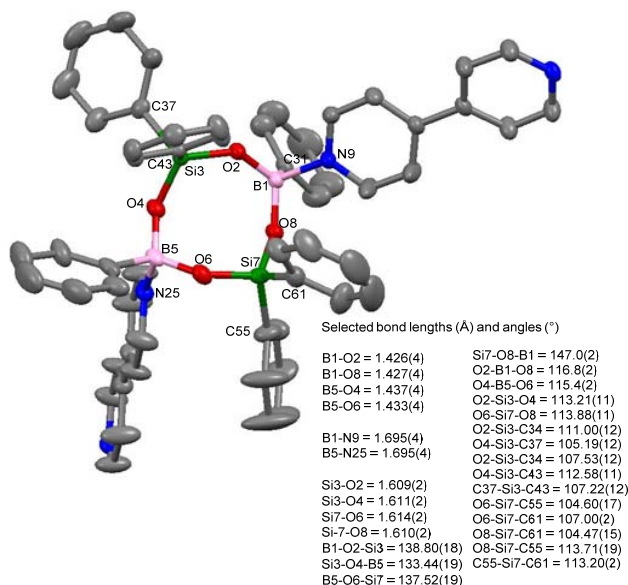


Figure 2.8: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_1$ (**4**) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms omitted for clarity.

The B-N bond lengths in (**4**) are 1.695(4) Å and 1.708(4) Å with an average value of 1.702(4) Å. For a simple borosiloxane such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or R' = Ph or CH₃) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t]\cdot\text{NC}_5\text{H}_5$,¹⁰² the B-N distances reported were 1.639 Å and 1.655 Å respectively. However, values of 1.556 Å, 1.651 Å, 1.653 Å, 1.654 Å, 1.676 Å, 1.679 Å, 1.681 Å, and 1.688 Å have been reported elsewhere in the literature for B-N bond length in boroxine adducts for which the B atoms were also tetra-coordinated.^{110,117,121,252–255} The Si-C bond lengths in (**4**) range from 1.866(3) to 1.885(3) Å with an average of bond distance of 1.877(3) Å. These are as expected for single Si-C bonds.^{89,102,250}

The internal ring angles O2-B1-O8 and O4-B5-O6 are 116.8(2)° and 115.4(2)° respectively with a mean value of 116.1(2)°. These angles in compound (**4**) at the B centres are higher than 109.5° expected for a tetrahedral geometry but a similar observation has been reported in the literature.¹⁰² Similarly, the O2-Si3-O4 and O6-Si7-O8 angles are 113.21(11)° and 113.88(11)° respectively with a mean value of 113.6(11)° which is also slightly higher than 109.5° expected for a tetrahedral

silicon. The bond angles at the Si centre as well as the Si-C bonds are comparable to other borasiloxane compounds and simple adducts in the literature.^{89,102,256}

In addition to the covalent and dative bonds found in **(4)**, the crystal packing of the compound also shows inter- and intra-molecular non-covalent interactions C-H $\cdots$ π (2.731 Å) and $\pi\cdots\pi$ (3.409 Å) as shown in **Figure 2.9**. Similar non-covalent interactions have been reported in cycloborasiloxane of eight membered rings.⁸⁹

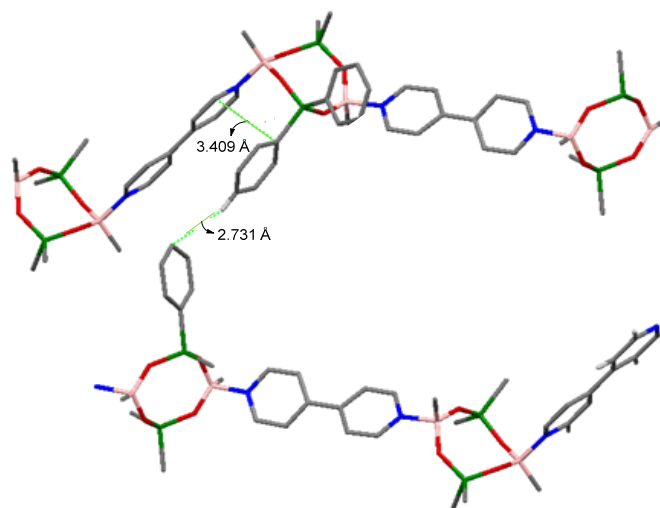


Figure 2.9: Two polymer chains with C-H $\cdots$ π (2.731 Å) & $\pi\cdots\pi$ (3.409 Å) interaction in the crystal packing. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O and white = H. Disordered solvent and most H atoms are omitted for clarity

The various inter- and intra-molecular interactions give rise to the chains running parallel to the *a*-axis and cross linking to form potential channels as shown in **Figure 2.10**. The channels are occupied by disordered solvent molecules (dichloromethane)

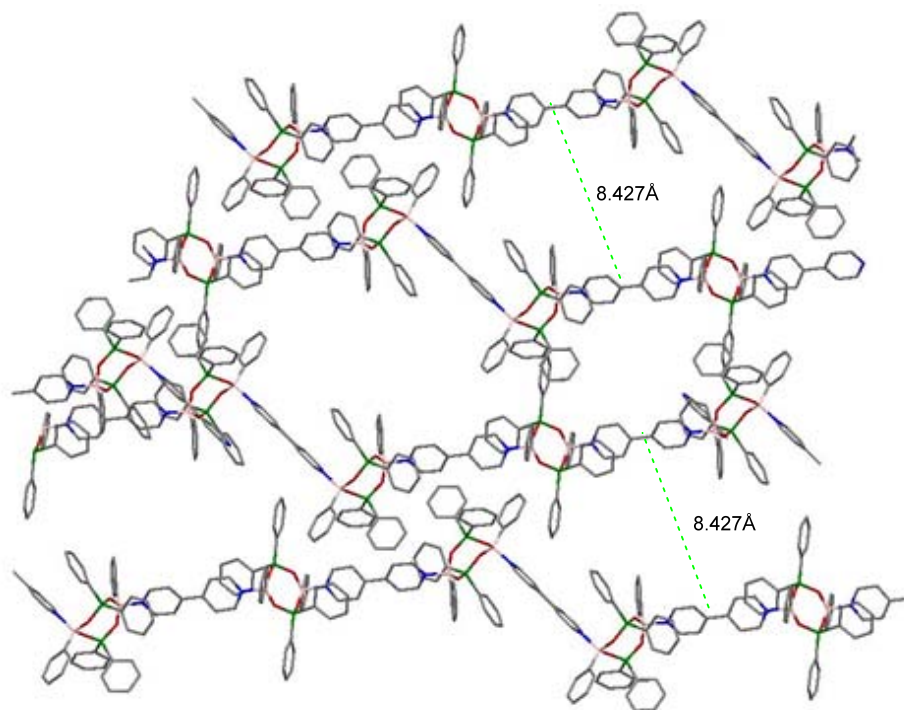
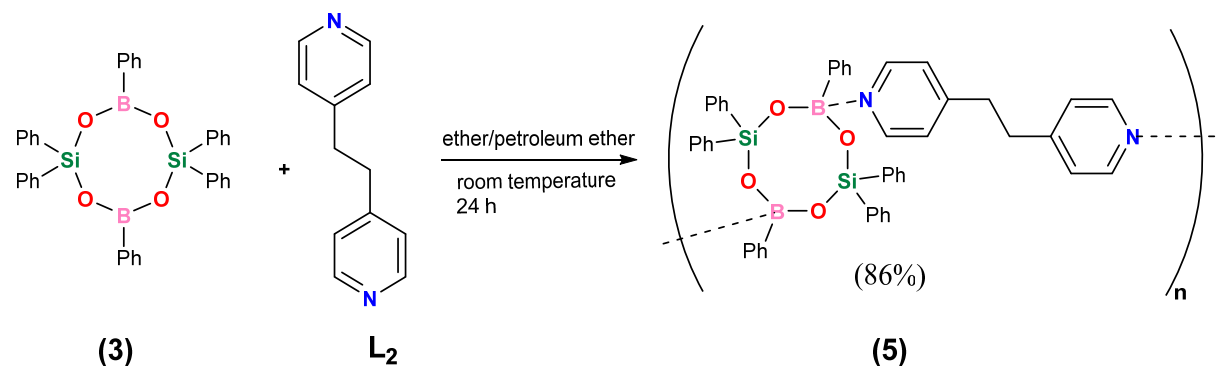


Figure 2.10: Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_1$ (**4**) with four polymeric chains running parallel to the a-axis leading to formation of channels. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms and disordered solvent molecule are omitted for clarity.

The crystallographic data for compound (**4**) are provided as Appendix 1

2.6.3 Synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_1$ (**5**)

Treatment of compound (**3**) with an ether/petroleum ether solution of bis(pyridyl)ethane (**L**₂) as shown in **Scheme 2.35**, afforded a colourless powder which was recrystallized from CH_2Cl_2 -ether (2:1) via slow evaporation to give colourless crystals of (**5**).



Scheme 2.35: The synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (**5**)

2.6.3.1 Spectral and crystal description of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (**5**).

The $^{11}\text{B}\{^1\text{H}\}$ NMR and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound (**5**) showed singlets at 19.86 ppm and -45.60 ppm respectively. The NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) of compound (**5**) are provided as Supplementary information (S9-S12 respectively).

Data obtained via single crystal X-ray diffraction studies reveal that compound (**5**) comprises the eight-membered ring structure (**3**) and linker L_2 as shown in **Figure 2.11**.

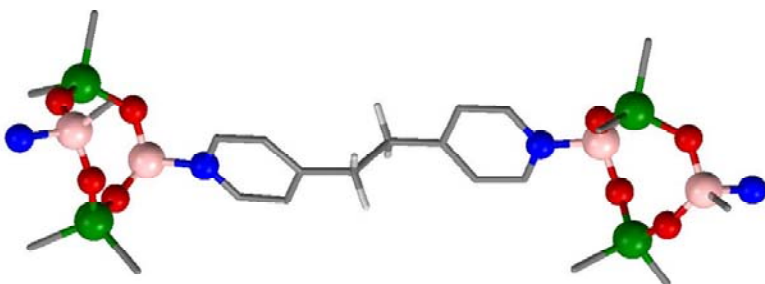


Figure 2.11: 1-D polymeric structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (**5**). Colour identity, pink = B, green = Si, grey = C, blue = N, red = O and white = H. Most H atoms are omitted for clarity.

The two B atoms are tetra-coordinate, and each is bonded to two O atoms, one C atom from a phenyl ring and one N via a coordination (dative bond) to the bis(pyridyl)ethane (L_2), to give a 1-D polymeric structure (**5**).

The B-O-Si angles of compound (**5**) range from 133.24(12) to 143.93(13) $^\circ$ with an average value of 139.69(13) which are comparable to those of compound (**4**), and show distortion at the O atoms in the ring as revealed in the ellipsoid plot **Figure 2.12**, compared to compound (**3**).

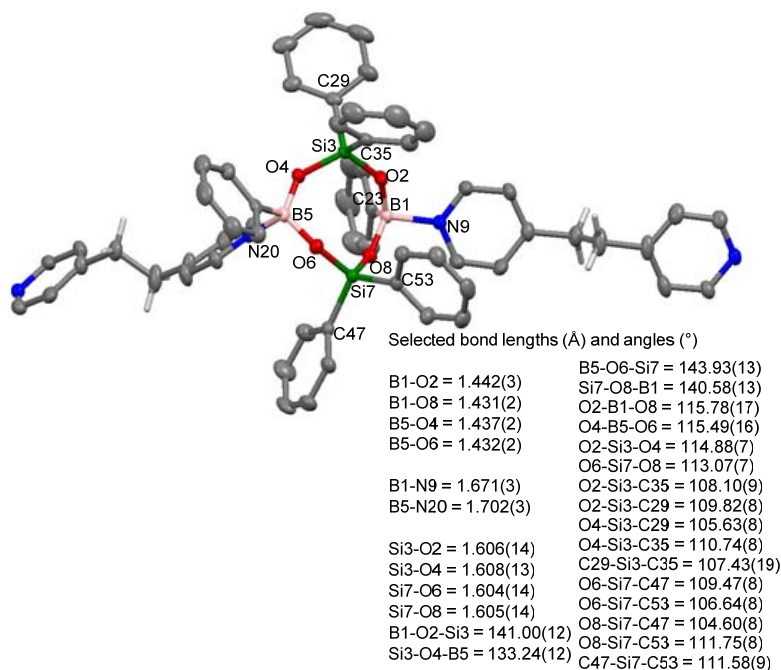


Figure 2.12: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (**5**) with some atom labelling, H atoms omitted for clarity except ethane H atoms. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms omitted for clarity

The four B-O distances in (**5**) range from 1.321(2) to 1.442(3) Å with a mean value of 1.436 Å. These B-O bond distances are longer than B-O length for a tri-coordinated B in $\text{Si}_2\text{B}_2\text{O}_4$ rings which range from (1.36-1.39 Å)^{84,89,102} but similar to those of compound (**4**) discussed earlier. The observed longer bond length at the tetrahedrally bonded B site compared to the tri-coordinated B may be linked to a reduction in the B-O π -bonding component on changing from trigonal to tetrahedral coordination geometry at the B.

Furthermore, the four Si-O bond lengths in (**5**) range from 1.604(14) to 1.618(13) Å which are similar to those found in compound (**4**).

The B-N bond lengths in (**5**) are 1.671(3) Å and 1.702(3) Å with an average value of 1.686(3) Å. Just like compound (**4**), the B-N bond length for compound (**5**) are slightly longer than those of simple borosiloxane such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or R' = Ph or CH_3) and

[Bu^tSi(OPhBO)₃SiBu^t].NC₅H₅.¹⁰² The Si-C bond lengths in **(5)** range 1.866(2) Å to 1.871(2) Å with an average of bond distance of 1.868(2) Å.

The ring angles O2-B1-O8 and O4-B5-O6 are 115.78(17)° and 115.49(16)° respectively with a mean value of 115.64(16)°. The mean internal ring angle of compound **(5)** is higher than the 109°.5 expected for a tetrahedral geometry but similar to compound **(4)** as well as the reported observation in the literature.¹⁰² Similarly, the ring angles at the silicon; O2-Si3-O4 and O6-Si7-O8 are 114.88(7)° and 113.07(7)° respectively with a mean value of 113.98(7)° which is also slightly higher than 109.5° for a tetrahedral silicon. The other bond angles at Si as well as the Si-C bonds lengths are comparable to compound **(4)** as well as other borasiloxane compounds and simple adducts in the literature.^{89,102,256}

Besides the covalent and dative bonds found in **(5)**, the crystal packing of the compound also displays non-covalent interactions C-H... π (2.779 Å) and C-H...O (2.439 Å) as shown in **Figure 2.13**. These two interactions differ from those observed in compound **(4)**.

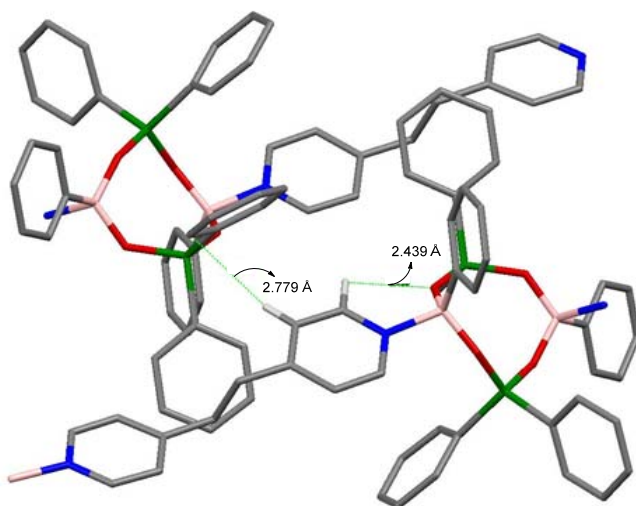


Figure 2.13: Two polymer chains with C-H... π (2.779 Å), C-H...O(2.439 Å) interactions in the crystal packing of compound **(5)**. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O and white = H. Most H atoms are omitted for clarity.

The individual chains of the polymer **(5)** which run parallel to the c-axis continue to interact with one another to create solvent filled channels of 6.954 Å, as depicted with two individual polymeric chains in **Figure 2.14**.

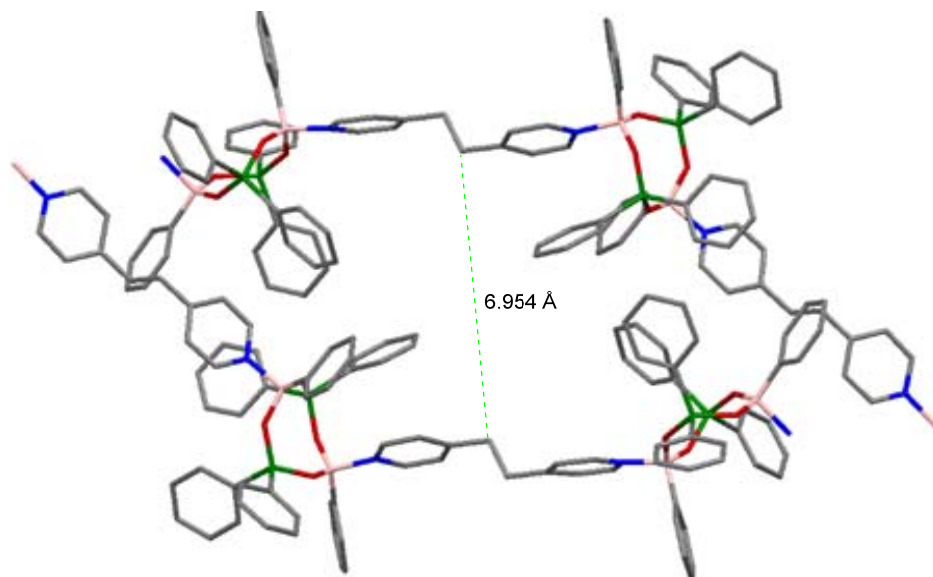
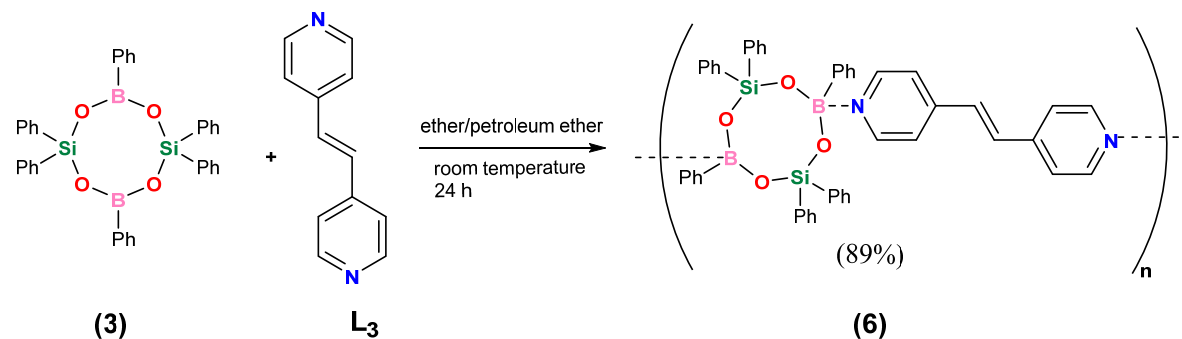


Figure 2.14: Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (**5**), with potential channels of 6.945 Å. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms and solvent molecules are omitted for clarity

The crystallographic data for compound **(5)** are provided as Appendix 2

2.6.4 Synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3\cdot 0.5(\text{CH}_2\text{Cl}_2)$ (**6**)

Compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3\cdot 0.5(\text{CH}_2\text{Cl}_2)$ (**6**) was prepared by the reaction of **(3)** and bis(pyridyl)ethene(**L**₃) in ether/petroleum ether solution as shown in **Scheme 2.36**.



Scheme 2.36: The synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (**6**)

2.6.4.1 Spectral and crystal description of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (**6**).

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound (**6**) and the $^{29}\text{Si}\{^1\text{H}\}$ NMR showed singlets at 21.97 and -44.90 ppm respectively, and are as expected and similar to those of compounds (**4**) and (**5**). The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (**6**) are provided as Supplementary Information (**S13-S16** respectively).

Compound (**6**) consists of the eight-membered ring structure (**3**), the linker L_3 and half an equivalent of dichloromethane. The chain grows parallel to the c-axis leading to the formation of 1-D polymer as shown in **Figure 2.15**.

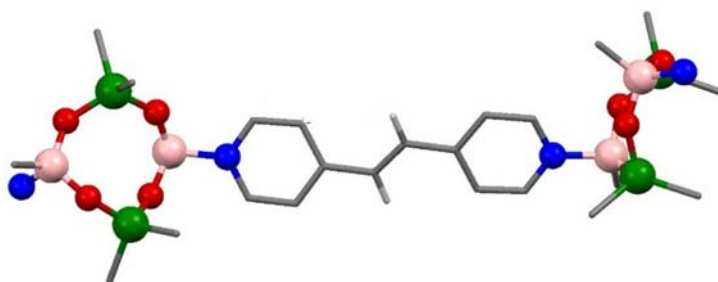


Figure 2.15: 1-D polymeric structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (**6**) connecting two eight membered rings. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O and white = H. The 0.5 (CH_2Cl_2) and all H atoms are omitted except the ones on the ethene for clarity.

Just like compounds (**4**) and (**5**) discussed above, the two B atoms in compound (**6**) are tetra-coordinate, and each is bonded to two O atoms, one C atom from a phenyl ring and one N via a coordinate covalent bond from the bis(pyridyl)ethene (L_3) alongside half a mole of dichloromethane to give a 1-D polymer compound (**6**).

The B-O-Si angles of compound (**6**) range from $135.55(11)$ to $142.12(12)^\circ$ with an average value of $140.11(12)^\circ$ which is comparable to those of compounds (**4**) and (**5**). There are some distortion at the O atoms in the ring as revealed in the ellipsoid plot **Figure 2.16**, compared to those of compound (**3**).

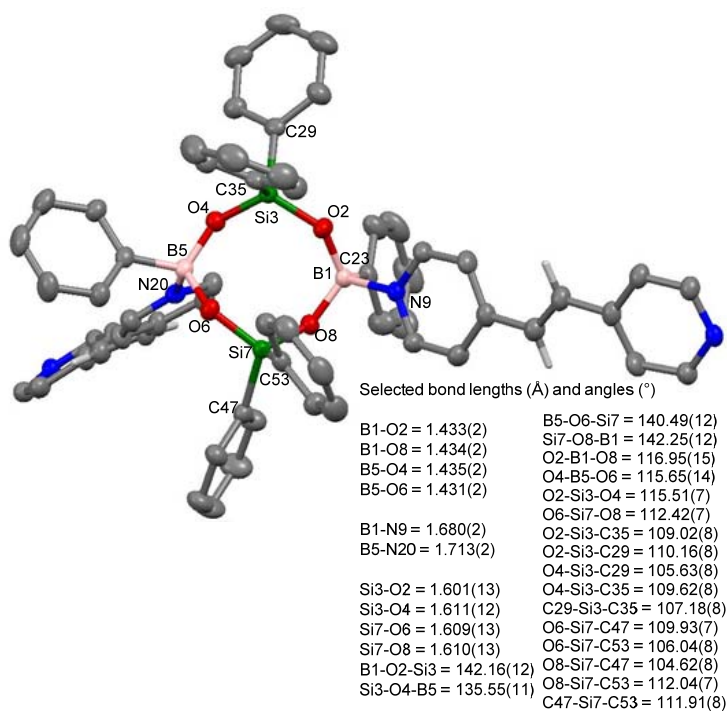


Figure 2.16: An ellipsoid view of a fragment of the $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (**6**) polymer with some atom labelling, H atoms are omitted for clarity except ethene H atoms.

The four B-O distances in (**6**) range from 1.431(2) Å (B5-O6) to 1.435(2) Å (B5-O4) and are longer than B-O lengths for tri-coordinated B in other $\text{Si}_2\text{B}_2\text{O}_4$ rings which range from (1.36-1.39 Å)^{84,89,102} but similar to those of compounds (**4**) and (**5**) discussed earlier. The observed longer bond lengths at the tetrahedrally bonded B site compared to the tri-coordinated B may be related to the reduction in B-O π -bonding component on shifting from trigonal to tetrahedral coordination geometry at the B.

In addition, the four Si-O bond length in (**6**) range from 1.610(13) to 1.611(13) Å which are similar to those found in compound (**4**) and (**5**). However, in the literature longer bond lengths for Si-O for a four-coordinate Si to two O atoms and C have a mean value is 1.645 Å.^{89,102} However, similar Si-O bond distances to those reported here have been reported in the literature (1.585 to 1.643 Å).^{102,250} The shorter Si-O distances associated with (**6**) suggest an electron density increase in the

Si-O bond which is consistent with the decrease in the B-O electron density, just as in compounds **(4)** and **(5)**.

The B-N bond lengths in **(6)** are 1.680(2) Å and 1.713(2) Å with an average value of 1.696(2) Å and are comparable to those found in compounds **(4)** and **(5)**, but a bit smaller than those found in the literature in compounds such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or R' = Ph or CH₃) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t].\text{NC}_5\text{H}_5^{102}$ where the B-N distances reported were 1.639 Å and 1.655 Å respectively. However, values of 1.556 Å, 1.646 Å, 1.651 Å, 1.654 Å, 1.676 Å, 1.679 Å, 1.681 Å, and 1.688 Å have been reported elsewhere in the literature for B-N bond length in boroxine adducts for which the B atoms were also tetra-coordinated.^{110,117,121,253–255} The Si-C bond lengths in **(6)** ranges 1.866(19) Å to 1.876(18) Å, which are comparable to those of compounds **(4)** and **(5)** as well as consistent with those in the literature.^{89,102,250}

The ring angles O2-B1-O8 and O4-B5-O6 are 116.95(15)° and 115.65(14)° respectively. The average internal ring angles of compound **(6)** at the B centres is higher than 109.5° expected for a tetrahedral geometry but similar to compounds **(4)** and **(5)** as well as those reported in the literature.¹⁰² Similarly, the ring angles, O2-Si3-O4 and O6-Si7-O8 are 115.51(7)° and 112.42(7)° respectively with a mean value of 113.96(7)° which is also slightly higher than 109.5° for a tetrahedral silicon. The Si centre thus shows slightly distorted tetrahedral geometry just as compounds **(4)** and **(5)**. The Si-C bonds lengths are comparable to those of compounds **(4)** and **(5)** as well as other borasiloxane compounds and simple adducts in the literature.^{89,102,256}

Besides the covalent and dative bonds found in **(6)**, the crystal packing of the compound also displays non-covalent interaction such as C-H $\cdots$ O (2.098 Å) may be responsible for the wide difference in B-N bond distance (1.680(2) Å and 1.713(2) Å) of as shown in **Figure 2. 17**.

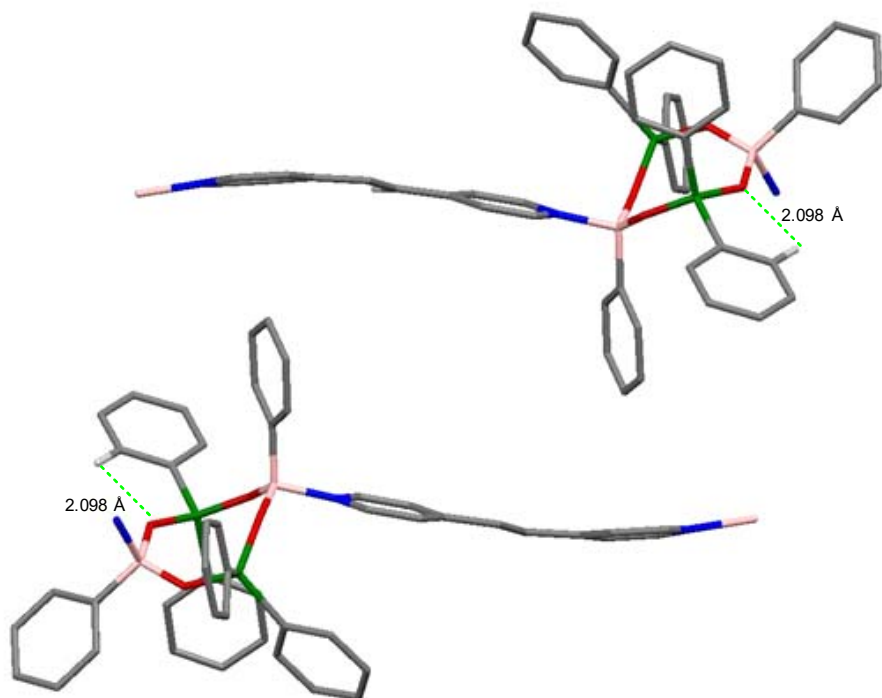
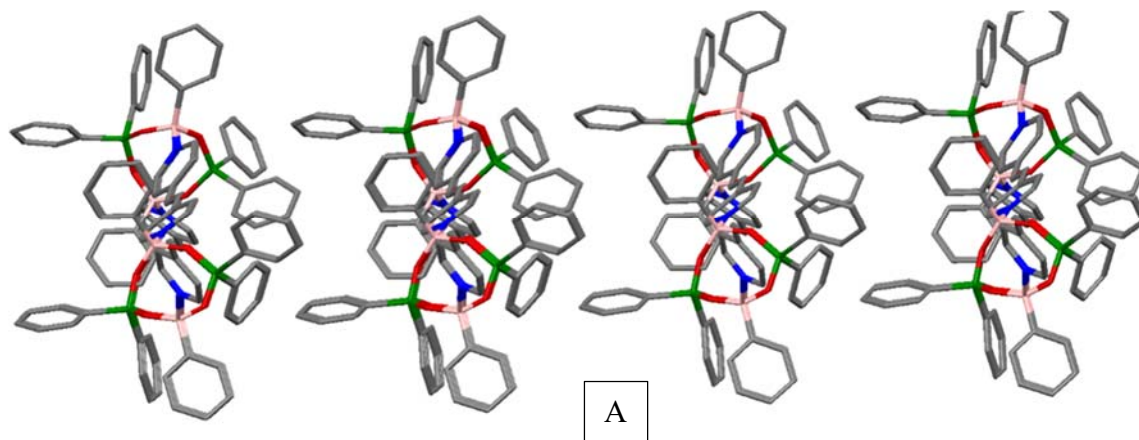


Figure 2.17: Two polymer chains running parallel to the c-axis with C-H...O (2.098 Å) interaction in the crystal packing of Compound (6). Colour identity, pink = B, green = Si, light green = Cl, grey = C, blue = N, red = O. H atoms are omitted for clarity.

The individual chains of the 1-D polymer **(6)** interact with one another to create potential channels. For example, **Figure 2.18** below show **(A)** chains of four individual polymers and **(B)** four polymers with channels 11.441 Å. The channels in the polymeric chains are occupied by dichloromethane.



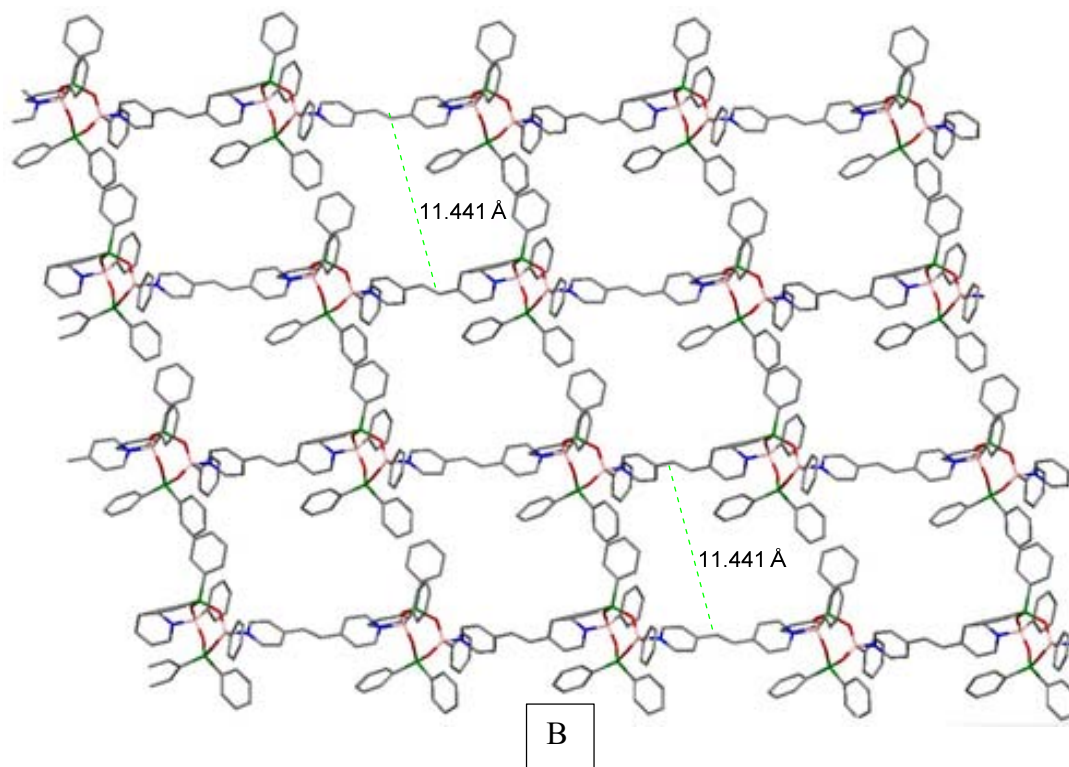
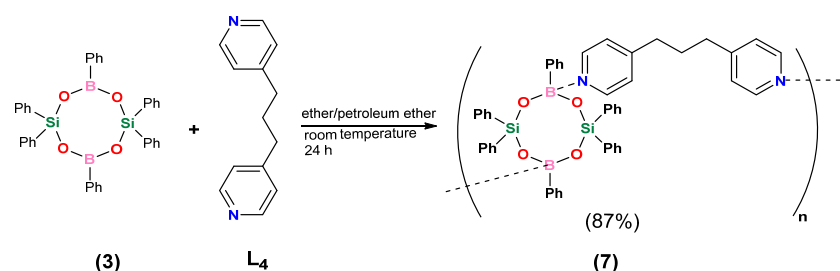


Figure 2.18: Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3$ (**6**), [A] four individual polymer chains, viewed down the a-axis, and [B] four polymer chains leading to formation of solvent filled channels (11.441 Å), viewed down the b-axis. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms and solvents are omitted for clarity.

The crystallographic data for compound (**6**) are provided as Appendix 3

2.6.5 Synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (**7**)

Compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (**7**) was synthesised by combining an ether solution of (**3**) with an ether solution of 1,3-bis(4-pyridyl)propane (**L4**) as shown in **Scheme 2.37**. Removal of ether/petroleum ether via filtration afforded colourless powder which was recrystallized from CH_2Cl_2 -ether to give colourless crystals of (**7**) in 87% yield.



Scheme 2.37: The synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (**7**)

2.6.5.1 Spectral and crystal description of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (**7**)

The $^{11}\text{B}\{^1\text{H}\}$ NMR and $^{29}\text{Si}\{^1\text{H}\}$ NMR of compound (**7**) showed singlets at 20.83 and -45.60 ppm respectively. These values are as expected and comparable to those of compounds (**4**), (**5**) and (**6**) but differ from those of compound (**3**). The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (**7**) are provided as Supplementary Information (S₁₇-S₂₀ respectively).

Compound (**7**) just like compounds 1-D polymers (**4**), (**5**) and (**6**) discussed earlier, consists of the eight-membered ring structure (**3**) and the linker **L**₄. The chains grow parallel to the c-axis leading to the formation of 1-D polymer as shown in **Figure 2.19**.

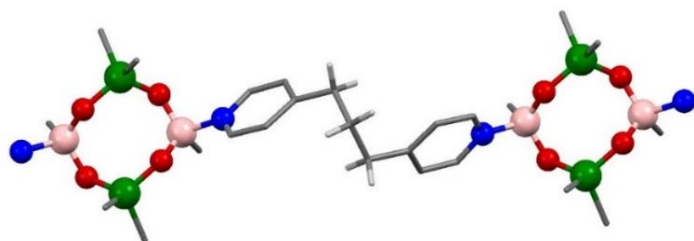


Figure 2.19: 1-D structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (**7**) connecting two eight membered rings via **L**₄. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O and white = H. Most H atoms are omitted for clarity.

However, unlike compounds (**4**), (**5**) and (**6**) discussed above, in compound (**7**) both boron atoms are crystallographically equivalent. Each B is bonded to two O atoms, one C atom from a phenyl ring and one N coordination to the 1,3-bis(4-pyridyl)propane (**L**₄) to give a 1-D polymeric structure (**7**). In addition, the Si₃ centres as well as the linker (**L**₄) and phenyl rings in compound (**7**) repeats in the ring and along the polymer chain. The B-O-Si angles of compound (**7**) are

128.3(3)° and 134.3(3)° with a mean value of 131.3(3)° which is smaller than that of compound (3) (153.1(3)°).⁸⁵ This shows a notable distortion at the O atoms in the ring of (7) as revealed in the ellipsoid plot **Figure 2.20**. The average B-O-Si angle in compound (7) is different from those found in compounds (4), (5) and (6), which are 139.19(2), 139.69(13) and 140.11(12)° respectively.

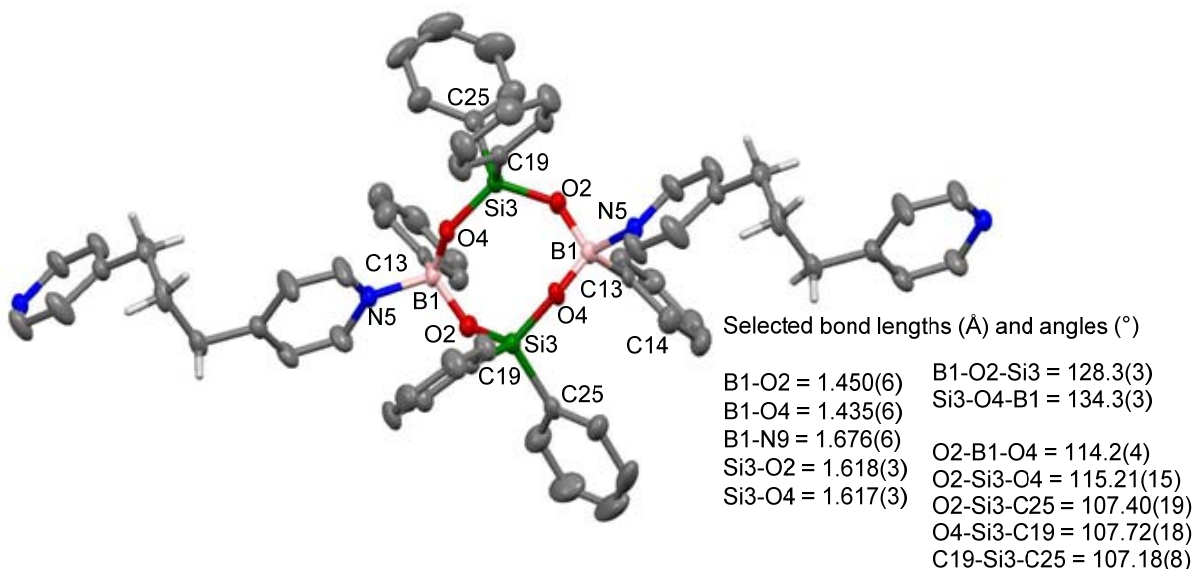


Figure 2.20: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (7) with some atom labelling, H atoms omitted for clarity except propane H atoms. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O and white = H. Most H atoms are omitted for clarity.

The two B-O bond lengths are 1.435(6) Å (B1-O2) and 1.450(6) Å (B1-O4) and these are similar to those found in compounds (4), (5) and (6) but are longer than B-O lengths for a tri-coordinated B in compound (3) ring which range from (1.36-1.39 Å).^{84,89,102} However the values reported here are similar to other B-O distances for tetrahedrally coordinated B in compounds such as $\text{N}(\text{CH}_2\text{CH}_2\text{O})\text{B}$ [1.43(1) Å],²⁵¹ $\text{Ph}_2\text{BOCH}_2\text{CH}_2\text{NH}_2$ [1.484(3) Å],²⁵² and $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}$ [1.439 (4) Å and 1.461(3) Å],²⁵⁰ (R or R' = Ph or CH₃) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t]\cdot\text{NC}_5\text{H}_5$ [1.457 (18) Å and 1.469 (18) Å]¹⁰² wherein the B is directly bonded to two O atoms, a phenyl group and the N atom. The observed longer bond length at the

tetrahedrally bonded B site compared to the tri-coordinated B may be linked to a reduction in B-O π -bonding component on changing from trigonal to tetrahedral coordination geometry at the B. In addition, the two Si-O bond lengths in (7) are 1.618(3) Å (Si3-O2) and 1.617(3) Å (Si3-O4) which are similar to those found in compounds (4), (5) and (6). However, as stated in the discussion of compound (4), in the literature longer bond lengths for Si-O for a tetra-coordinate Si to two O atoms with mean a value is 1.645 Å.^{89,102} But similar Si-O bond distances to those reported here have been observed in the literature.^{102,250} The shorter Si-O distances associated with (7) suggest an electron density increase in the Si-O bond which is consistent with the decrease in the B-O electron density just as in compounds (4), (5) and (6).

Furthermore, unlike in compounds (4), (5) and (6) which have a range of B-N bond lengths, compound (7) have only one type of B-N bond length in the 1-D polymer chain and the value is 1.676 (6) Å. This value is slightly lower than the B-N distance found in compounds (4), (5) and (6) as well as a bit higher than to those reported for simple borosiloxane such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or R' = Ph or CH₃) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t].\text{NC}_3\text{H}_5$ ¹⁰² where the B-N distances reported were 1.639 Å and 1.655 Å respectively. However, values of 1.556 Å, 1.646 Å, 1.651 Å, 1.654 Å, 1.676 Å, 1.679 Å, 1.681 Å, and 1.688 Å have been reported elsewhere in the literature for B-N bond length in boroxine adducts for which the B atoms were also tetra-coordinated.^{110,117,121,253–255} The two Si-C bond lengths in (7) are 1.868(5) Å (Si3-C19) and 1.875(5) Å (Si3-C25) and are as expected, and comparable to those of compounds (4), (5) and (6). The dihedral angle O2-B1-C13-C14 in compound (7) is -13.1°, which is smaller than 8.6° reported for (3), but comparable to the dihedral angle of -13.5° reported for a six-membered Si₂BO₃ ring.⁸⁵ The internal ring angle of compound (7) at the B centres O2-B1-O4 is 114.2(4)° is higher than expected 109.5° for a tetrahedral planar geometry but comparable to those of compounds (4), (5)

and (6) as well as values reported in the literature.¹⁰² Similarly, the ring angle at silicon (O2-Si3-O4), in compound (7) is 115.21(17)° which is also slightly higher than 109.5° for a tetrahedral silicon. The Si centre also show slight distorted tetrahedral geometry just as compounds (4), (5) and (6). Each Si is bonded to two O and two C atoms and the bond angles as well as the Si-C bonds lengths are comparable to those of compounds (4), (5) and (6) as well as other borasiloxane compounds and simple adducts in the literature.^{89,102,256}

Apart from the covalent and dative bonds found in (7), the crystal packing of the compound also exhibit non-covalent interactions such as C-H... π (2.640 Å), C-H...O (2.293 Å) and π ... π (3.376 Å) as shown in **Figure 2.21**, and these are comparable to those found in the literature.⁸⁹

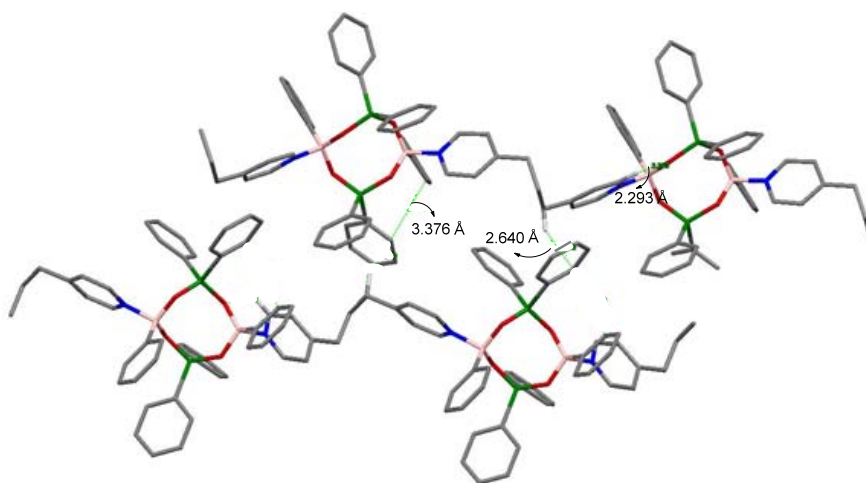


Figure 2.21: Two polymer chains of (7) with C-H... π (2.640 Å), C-H... π (2.730 Å) and π ... π (3.376 Å) interaction in the crystal packing. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O. H atoms omitted for clarity. Viewed from the b axis.

The covalent bonds, dative bonds and all the other non-covalent interactions in the compounds contribute to the nature of the 1-D polymer. The distance between two polymeric chains is 6.221 Å as depicted with five polymeric chains below in **Figure 2.22**.

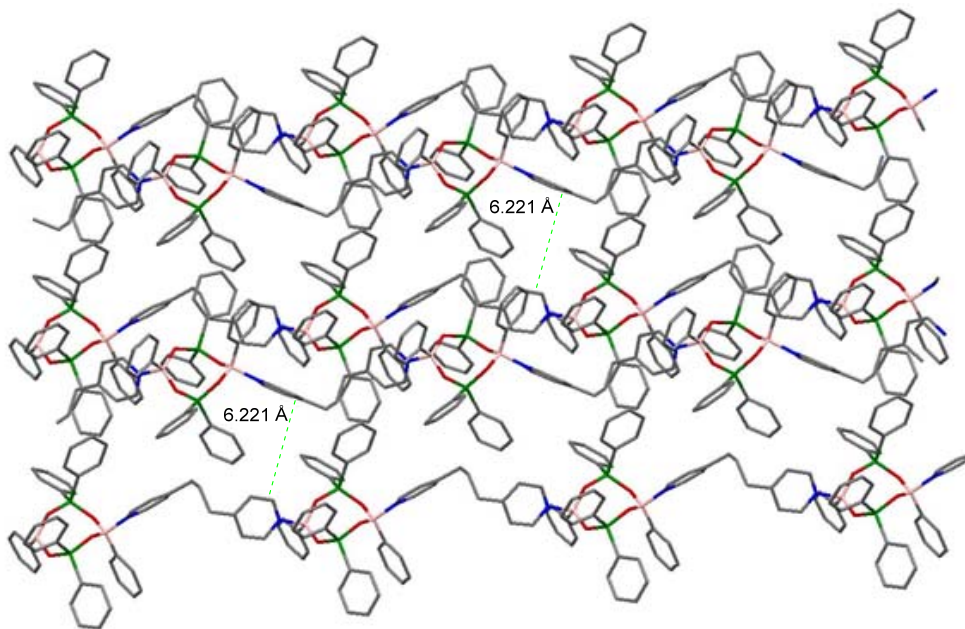
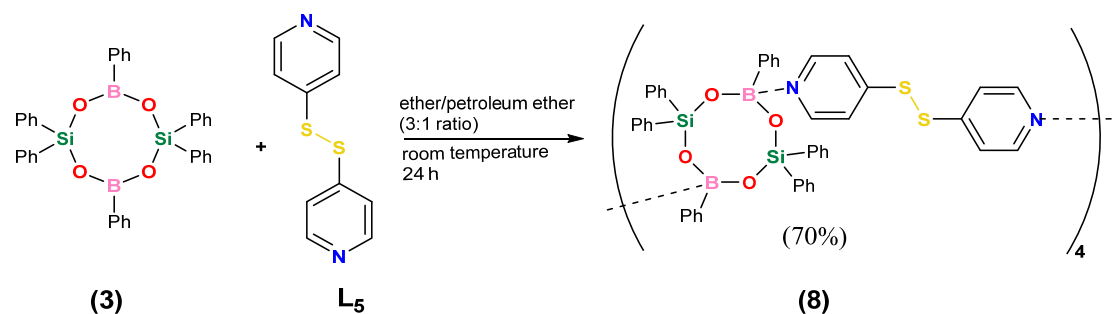


Figure 2.22: Crystal packing in **(7)** five individual polymer with solvent filled channels. Colour identity, pink = B, green = Si, grey = C, blue = N, red= O.H atoms are omitted for clarity. Viewed from the b axis.

The crystallographic data of compound **(7)** are provided as Appendix 4

2.6.6 Synthesis of $[Ph_6B_2Si_2O_4].L_5$ (**8**)

Compound **(8)** was synthesised by the treatment of **(3)** with 4,4-dithiobis(pyridine) (**L₅**) in ether /petroleum ether solution as shown in **Scheme 2.38**.



Scheme 2.38: Reaction method for the synthesis of $[Ph_6B_2Si_2O_4].L_5$ (**8**)

2.6.6.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].L_5$ (**8**)

The $^{11}B\{^1H\}$ NMR spectrum of compound **(8)** showed a singlet at 20.64 ppm, while the $^{29}Si\{^1H\}$ NMR spectrum showed a singlet at -44.28 ppm, and these are similar to those found in compounds

(4), (5), (6) and (7). The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra show some impurities which may be due to some unreacted starting materials. Several purification attempts yielded no improvement of the spectra. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (8) are provided as Supplementary information (S21-S24 respectively).

Data obtained from single crystal X-ray diffraction studies show that compound (8), unlike 1-D polymers (4), (5), (6) and (7) discussed above, is a short chain oligomer with four repeating units. It consists of structure (3), and the linker L_5 and the oligomeric chain grows parallel to the c-axis leading to the formation of the structure shown in **Figure 2.23**.

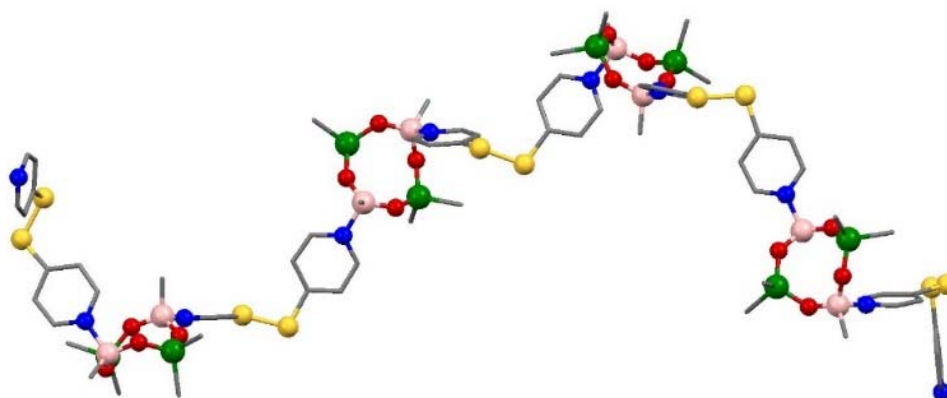


Figure 2.23: Polymeric structure of compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_5$ (8) connecting four eight membered rings via four L_5 . Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity.

The asymmetric unit of compound (8) is made up of two of (3) and two linkers (L_5) as shown in the ellipsoid plot in **Figure 2.24**. Thus, the B atoms (B1, B5, B23, and B27) are different from one another but are repeated in the other remaining part of the short 4 unit oligomer. Each B atom in the asymmetric unit is bonded to four atoms (two O atoms, one C atom from a phenyl ring and one N atom from the 1,2-di(pyridin-4-yl)disulfane linker (L_5)). The bond connecting B atoms to the linkers in (8) are all dative bonds as in compounds (4), (5), (6) and (7) discussed above.

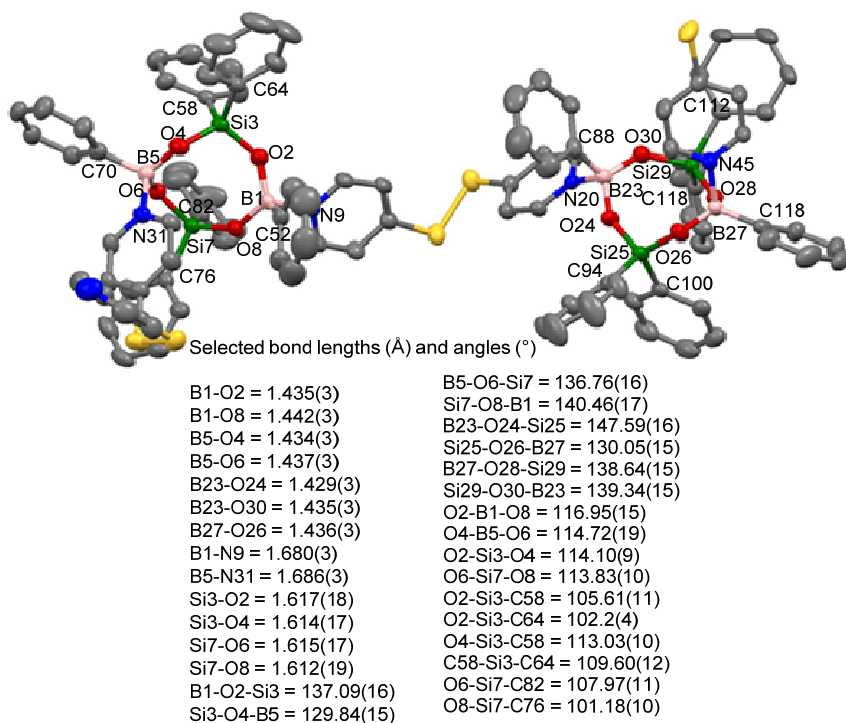


Figure 2.24: An ellipsoid view of a fragment of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_5$ (**8**) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity

The B-O-Si angles of compound (**8**) range from $129.84(15) - 147.59(16)^\circ$ with a mean value of $137.47(16)$, which is higher than that of compound (**7**), but lower than those of compounds (**4**), (**5**), and (**6**). The B-O distances in (**8**) are longer than B-O length for a tri-coordinated B in compound (**3**) ring ($\text{Si}_2\text{B}_2\text{O}_4$) which range from $(1.36\text{-}1.39 \text{ \AA})^{84,89,102}$ but similar to those of compounds (**4**), (**5**), (**6**) and (**7**) discussed earlier. However, the values observed in compound (**8**) are also similar to other B-O distances for tetrahedrally coordinated B in compounds such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or $\text{R}' = \text{Ph}$ or CH_3) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t]\cdot\text{NC}_5\text{H}_5^{102}$ wherein the B is directly bonded to two O atoms, a phenyl group and the N atom. The observed longer bond length at the tetrahedrally bonded B site compared to the tri-coordinated B may be linked with the removal of some B-O π -bonding component on transiting from trigonal to tetrahedral coordination geometry at the B.

Similarly, the eight Si-O bond length in **(8)** range from 1.607(17) to 1.622(19) Å which are similar to those found in compounds **(4)**, **(5)**, **(6)** and **(7)**. However, in the literature longer bond lengths for Si-O for a four-coordinate Si to two O and two C atoms with mean value is 1.645 Å.^{89,102} But similar Si-O bond distances to those reported here have been observed in the literature.^{102,250} The shorter Si-O distances associated with **(8)** suggest an electron density increase in the Si-O bond which is consistent with the decrease in the B-O electron density just as in compounds **(4)**, **(5)**, **(6)** and **(7)**.

The B-N bond lengths in **(8)** range from 1.680(3) to 1.703(3) Å, with an average value of 1.688(3) Å. Just like compounds **(4)**, **(5)**, **(6)** and **(7)**, the B-N bond lengths in compound **(8)** are comparable to those of simple borosiloxane such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or R' = Ph or CH₃) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t]$. NC_5H_5 ¹⁰² where the B-N distances reported were 1.639 Å and 1.655 Å respectively. The Si-C bond lengths in **(8)** range from 1.861(2) to 1.897(2) Å, and are as expected and consistent with those of compounds **(4)**, **(5)**, **(6)** and **(7)**.

The O-B-O angles have an average value of 115.4(2)° which is higher than the 109.5° expected for a tetrahedral geometry, but similar to compounds **(4)**, **(5)**, **(6)** and **(7)** as well as those reported in the literature.¹⁰² The Si centre also shows a slightly distorted tetrahedral geometry just as compounds **(4)**, **(5)**, **(6)** and **(7)**. Each Si is bonded to two O and two C atoms with angles and bond lengths at Si being comparable to those of compounds **(4)**, **(5)**, **(6)** and **(7)** as well as other borosiloxane compounds and simple adducts in the literature.^{89,102,256}

In contrast to compounds **(4)**, **(5)**, **(6)** and **(7)**, which showed some non-covalent interactions in their crystal packing, compound **(8)** showed only very few areas of intra-chain non-covalent interactions such as C-H $\cdots$ O (2.689 Å) and C-H $\cdots$ S (2.726 Å & 2.838 Å) as shown in **Figure 2.25**.

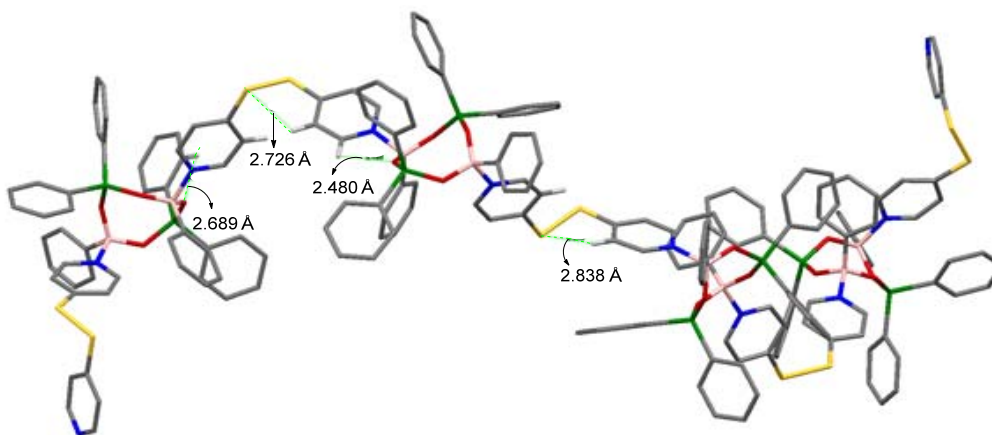
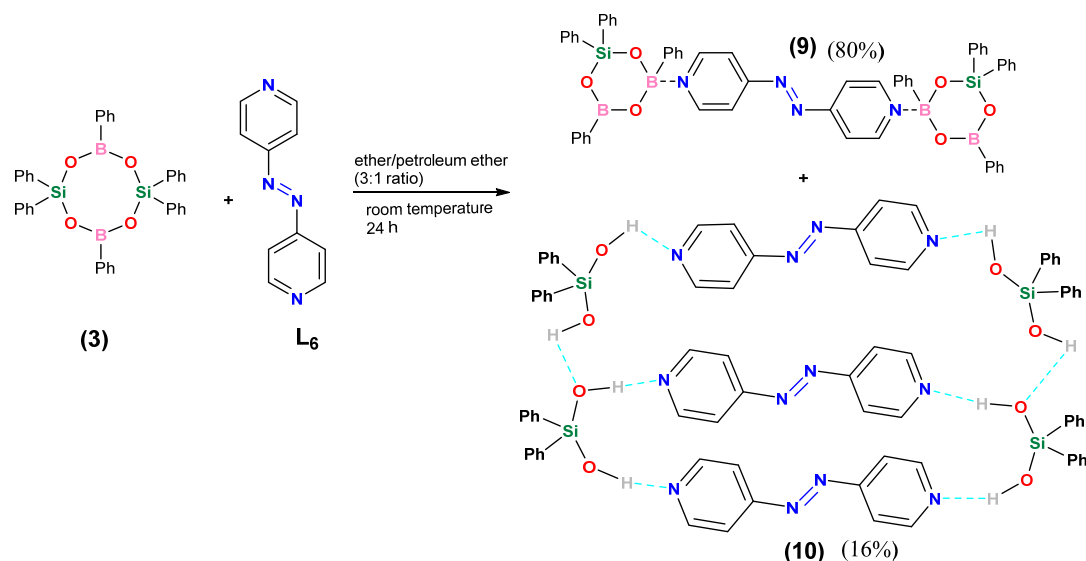


Figure 2.25: Crystal packing of compound **(8)** with intra-noncovalent interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, white = H. Most H atoms are omitted for clarity

The crystallographic data of compound **(8)** are provided as Appendix 5

2.6.7 Synthesis of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6 \cdot \text{L}_6$ (**9**)

Compound $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6 \cdot \text{L}_6$ (**9**) was prepared by the treatment of **(3)** with 4, 4'-azopyridine (**L**₆) in ether/petroleum ether as shown in **Scheme 2.39**.



Scheme 2.39: The synthesis of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6$ (**9**). For **(10)** see **Scheme 2.40**

2.6.7.1 Spectral and crystal description of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6$ (**9**)

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound **(9)** showed two singlets at 29.52 and 22.36 ppm, while the $^{29}\text{Si}\{^1\text{H}\}$ NMR of **(9)** showed a singlet at -45.04 ppm. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$), and

$^{29}\text{Si}\{^1\text{H}\}$ spectra of compound **(9)** are provided as Supplementary information (**S₂₅**–**S₂₈** respectively).

The crystal structure confirms compound **(9)** as a dimer instead of a 1-D polymer like **(4)**, **(5)**, **(6)** and **(7)** or oligomer as **(8)** discussed above. Also, in the reaction leading to the formation of compound **(9)**, the eight-membered ring **(3)** has contracted into a six-membered ring ($\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3$) together with $\text{Ph}_2\text{Si}(\text{OH})_2$. The $\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3$ thereafter reacted with the linker (**L₆**) to form **(9)**, while the $\text{Ph}_2\text{Si}(\text{OH})_2$ interacted with the linker (**L₆**) via hydrogen bonding to give compound **(10)** discussed in detail below (Section 2.6.8).

The ellipsoid plot with atom numbering shown in **Figure 2.26** shows that the B1 and B3 atoms are tetra- and tri-coordinated respectively. The linker (**L₆**) bridges the two B_2SiO_3 rings via a dative bond at the two B1 atoms.

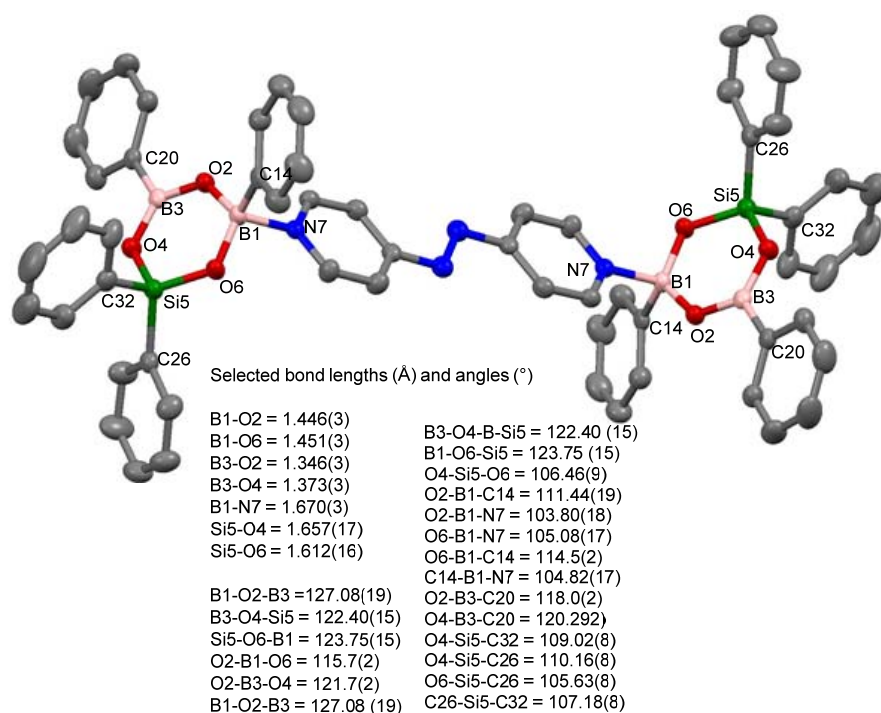


Figure 2.26: An ellipsoid view of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6 \cdot \text{L}_6$ (**9**) with some atom numbering. Colour identity, pink = B, green = Si, grey = C, blue = N, and red = O. H atoms are omitted for clarity

The B1-O2 and B1-O6 distances in **(9)** are 1.451(3) Å and 1.446(3) Å respectively, whereas at the trigonal boron atoms (B3), the B3-O2 and B3-O4 bond lengths are 1.346(3) Å and 1.373(3) Å respectively. Thus, the B-O bond lengths associated with the tetrahedrally coordinated B1 are longer than those of the tri-coordinate B3 in **(9)**, consistent with stronger $B_{\pi} \cdots O_{\pi}$ interactions with O atoms bound to B_{sp^2} -O than B_{sp^3} -O. The trigonally bonded boron in B-O distance in **(9)** is comparable to tri-coordinated B-O distance of 1.374(7) Å, reported for $Ph_5Si_2BO_3$ ring,⁸⁵ as well as to other tri-coordinated B-O distances in other $Si_2B_2O_4$ rings which ranges from (1.36-1.39 Å).^{84,89,102} However the values reported here are comparable to other B-O distances for tetrahedrally coordinated B in compounds such as $N(CH_2CH_2O)B$ [1.43(1) Å],²⁵¹ $Ph_2BOCH_2CH_2NH_2$ [1.484(3) Å],²⁵² and $Ph(OSiR_2R')B\{OCH_2\}_3N\}$ [1.439 (4) Å, and 1.461(3) Å],²⁵⁰ (R or R' = Ph or CH₃) and $[Bu^tSi(OPhBO)_3SiBu^t].NC_5H_5$ [1.457 (18) Å, and 1.469 (18) Å]¹⁰² wherein the B is directly bonded to two O atoms, a phenyl group and the N atom.

The Si-O bond lengths in **(9)** are 1.657(17) Å (Si5-O4) and 1.612(16) Å (Si5-O6), which are similar to those found in compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)** as well as comparable to bond lengths for Si-O for a four-coordinate Si to two O atoms with mean value is 1.645 Å.^{89,102,102,250} The shorter Si5-O6 distances associated with **(9)** suggest an electron density increase in the Si5-O6 bond which consistent with the decrease in the B-O electron density just as in compound **(4)**, **(5)**, **(6)**, **(7)** and **(8)**.

The B1-N9 bond length **(9)** is 1.670(3) Å which is similar to those found in compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)**, but a bit longer than those of simple borosiloxane such as $Ph(OSiR_2R')B\{OCH_2\}_3N\}$ ²⁵⁰ (R or R' = Ph or CH₃) and $[Bu^tSi(OPhBO)_3SiBu^t].NC_5H_5$ ¹⁰² where the B-N distances reported were 1.639 Å and 1.655 Å respectively. The two Si-C bond lengths in

(9) are 1.845(2) Å (Si5-C26) and 1.868(3) Å (Si5-C32) and are similar to those of compounds (4), (5), (6), (7) and (8).

The ring angles O2-B1-O6 and O2-B3-O4 are 115.7(2)° and 121.7(2)° respectively. The internal ring angle of compound (9) at the tetrahedrally coordinated B (B1) is higher than 109.5° expected for a tetrahedral geometry but similar to compounds (4), (5), (6), (7) and (8) as well as reported observation in the literature.¹⁰² However, the ring angle O2-B3-O4 for three coordinate B (B3) is higher than that of the tetra-coordinated boron centre but similar to other compounds in the literature.^{89,102,255,256} Similarly, the O4-Si5-O6 angle is 106.46(9)° which is lower than 109.5° for a tetrahedral silicon but is comparable to literature values.⁸³ The bond angles at Si as well as the Si-C bonds lengths are comparable to those of compounds (4), (5), (6), (7) and (8) as well as other borasiloxane compounds and simple adducts in the literature.^{89,102,256} Besides the covalent and dative bonds found in (9), the crystal packing of the compound also displays non-covalent interactions such as C-H $\cdots$ π (2.853 Å), C-H $\cdots$ N (2.461 Å) and $\pi \cdots$ B3 (3.527 Å) as shown in **Figure 2.27**.

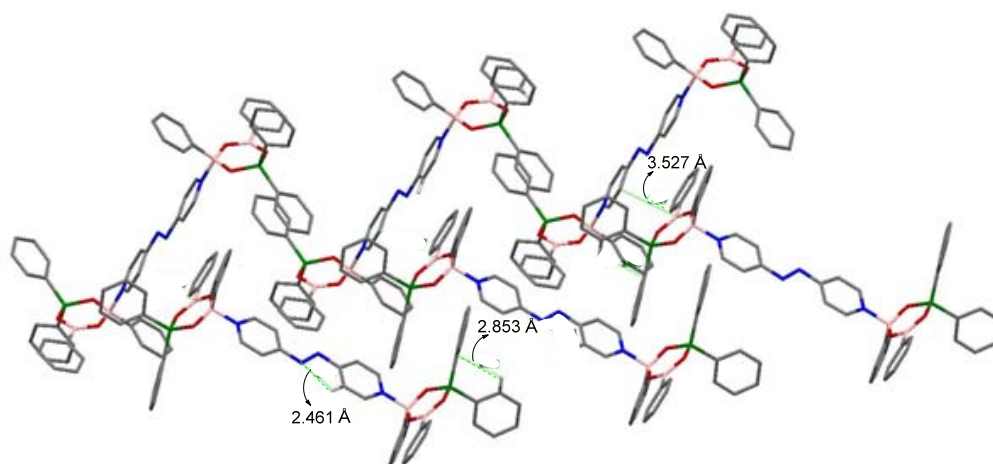
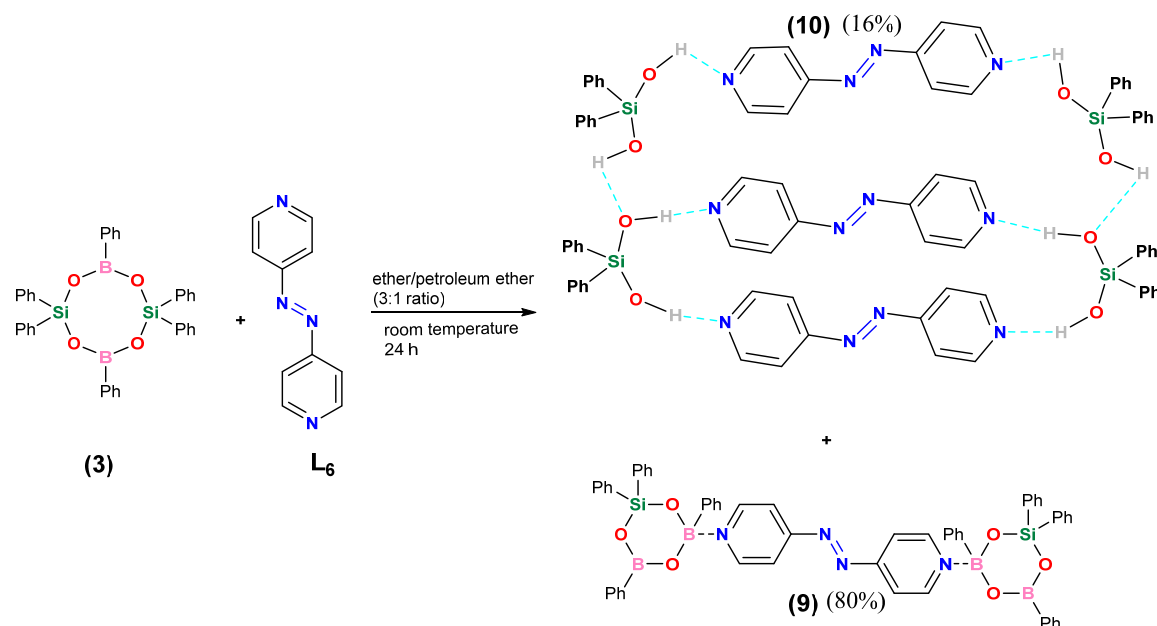


Figure 2.27: Crystal packing in $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_6$ (9) with six individual dimer. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, white = H. Most H atoms are omitted for clarity

The crystallographic data of compound (9) are provided as Appendix 6.

2.6.8 Synthesis of $4(\text{Ph}_2\text{Si}(\text{OH})_2)_3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**)

Compound $4[\text{Ph}_2\text{Si}(\text{OH})_2] \cdot 3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**) was prepared combining ether/petroleum ether solutions of (**3**) and 4, 4'-azopyridine (**L₆**) as shown in **Scheme 2.40**.



Scheme 2.40: The synthesis of $4[\text{Ph}_2\text{Si}(\text{OH})_2] \cdot 3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**). For (**9**) see **Scheme 2.39**

2.6.8.1 Crystal description of $4(\text{C}_{12}\text{H}_{12}\text{O}_2\text{Si})_3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**)

Compound (**10**) is a combination of (**L₆**) and the other part of the product $[\text{Ph}_2\text{Si}(\text{OH})_2]$ from the preparation of compound (**9**), wherein (**3**) contracted into a six-membered ring ($\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3$) and $\text{Ph}_2\text{Si}(\text{OH})_2$ as described above. As the crystals of compounds (**9**) and (**10**) have different morphologies and shapes, compound (**10**) was isolated by hand-picking from that of (**9**) but in low yield. The $\text{Ph}_2\text{Si}(\text{OH})_2$ and linker (**L₆**) crystal structure that gave $4[\text{Ph}_2\text{Si}(\text{OH})_2] \cdot 3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**) is shown in **Figure 2.28**. The $\text{Ph}_2\text{Si}(\text{OH})_2$ and the linker (**L₆**) interact via hydrogen bonding ($\text{H} \cdots \text{O}$ and $\text{H} \cdots \text{N}$) as shown in **Figure 2.28**.

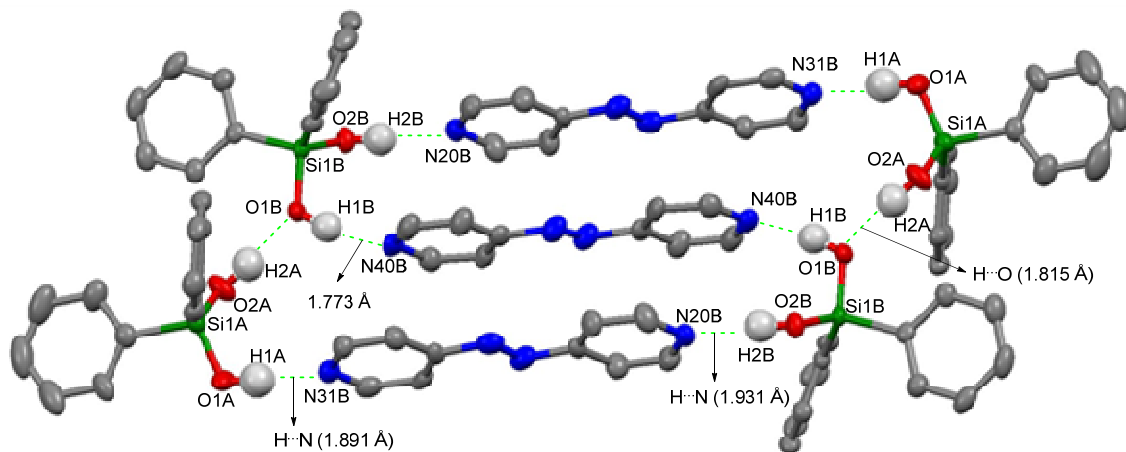


Figure 2.28: An ellipsoid view of $4(\text{Ph}_2\text{Si}(\text{OH})_2)$, $3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**) with $\text{H}\cdots\text{O}$ and $\text{H}\cdots\text{N}$. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, light grey = H. All H atoms except the ones involved in hydrogen bonding are omitted for clarity.

As can be seen from **Figure 2.28**, the H atoms bonding with O atoms in the molecule are $\text{H2A}\cdots\text{O1B}$ (1.815 Å) and $\text{H2A}\cdots\text{O1A}$ (1.815 Å), while H1A and H2B hydrogen bonded with N31B ($\text{H1A}\cdots\text{N31B}$) (1.891 Å) and N20B ($\text{H2B}\cdots\text{N20B}$) (1.931 Å) respectively. H1B atoms hydrogen bonded with another molecule of (**L₆**) at N40B ($\text{H1B}\cdots\text{N40B}$) (1.773 Å). Thus, the three linker (**L₆**) molecules bonding with the four $\text{Ph}_2\text{Si}(\text{OH})_2$ molecules are parallel to one another. In addition to the hydrogen bonding displayed by (**10**), the crystal packing of the compound also show other forms of inter- and intra-non-covalent ($\text{C-H}\cdots\text{N}$, $\text{C-H}\cdots\text{O}$, $\text{C-H}\cdots\pi$, and $\pi\cdots\pi$) interactions as depicted in **Figure 2.29**. The ring angle from O1A-Si1A-O2A and O1B-Si1B-O2B are 113.68° and 113.40° which are larger than those of (**9**) [$106.46(9)^\circ$] but comparable to those of compounds (**4**), (**5**), (**6**), (**7**), and (**8**). Furthermore individual molecules of (**10**) interact intermolecularly via $\text{C-H}\cdots\text{N}$ (3.330 Å).

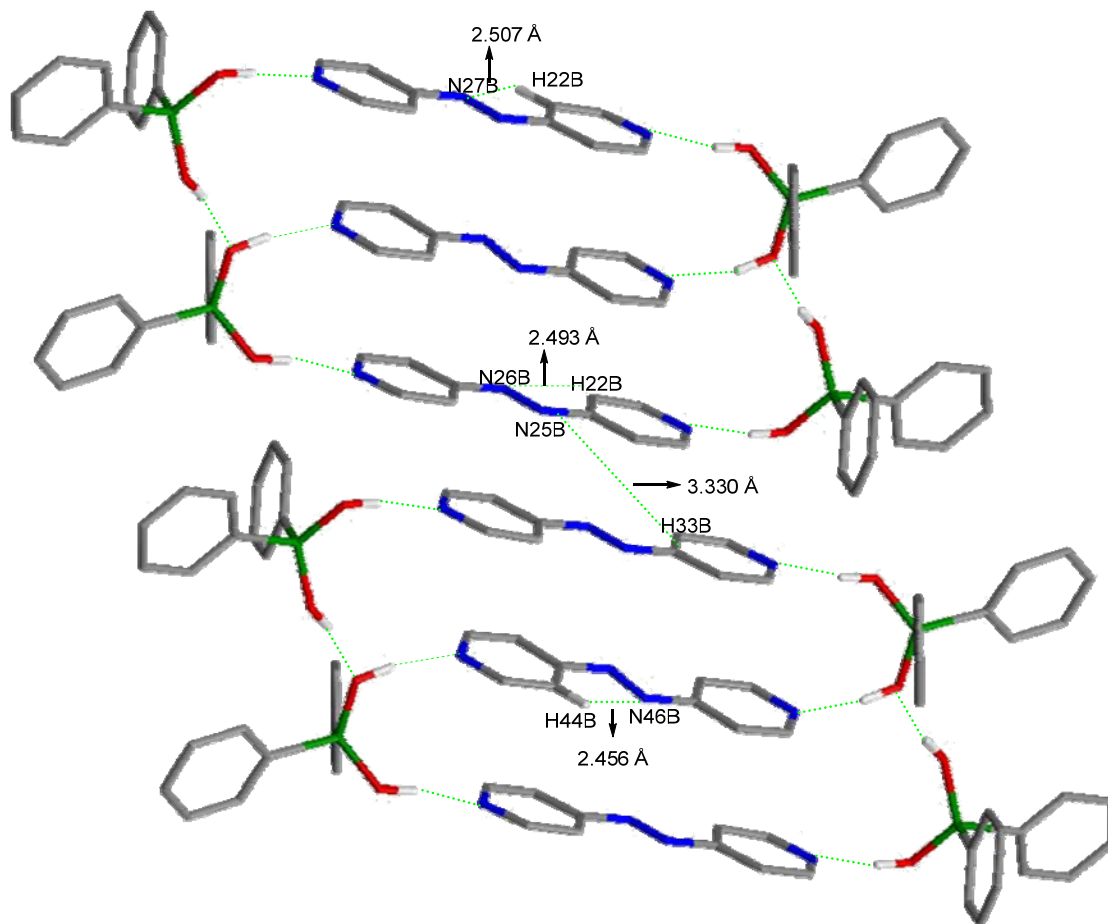


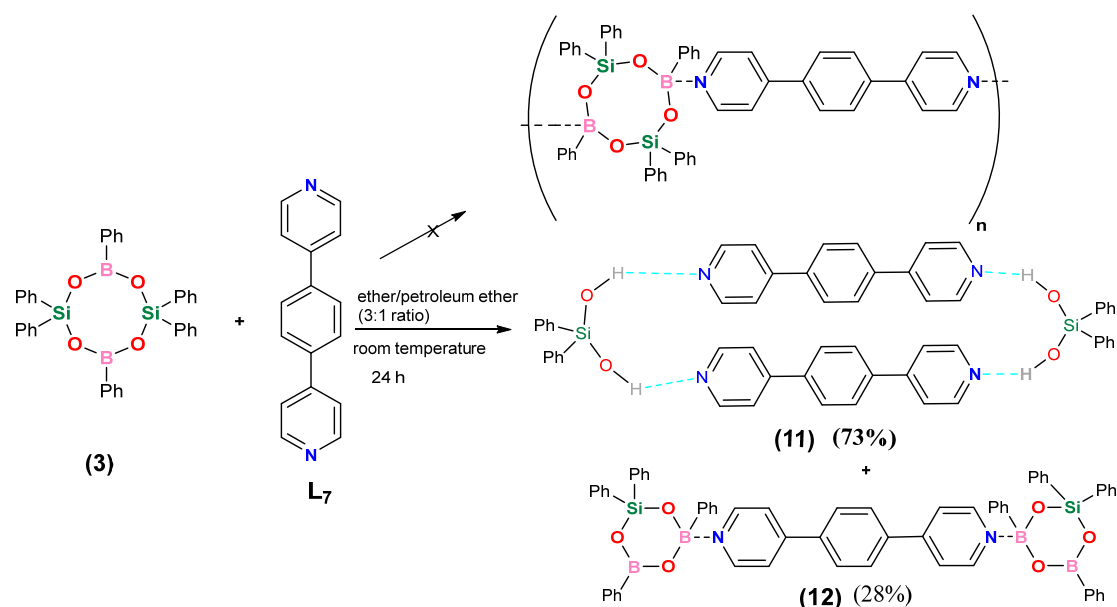
Figure 2.29: Crystal packing in $4(\text{Ph}_2\text{Si}(\text{OH})_2)_3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**) with hydrogen bonding and other forms of inter- and intra-rings interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, light grey = H. Most H atoms are omitted for clarity.

The sum of all these interactions and as well as the stability of the products (**9**) and (**10**) as well as the basicity of (**L₆**) may be the reason for the contraction of (**3**) ring to $(\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3)$ and $\text{Ph}_2\text{Si}(\text{OH})_2$, which thereafter reacted with the linker (**L₆**) to give compounds (**9**) and (**10**) respectively.

The crystallographic data of compound (**10**) are provided as Appendix 7.

2.6.9 Synthesis of $2\text{Ph}_2\text{Si}(\text{OH})_2 \cdot 2\text{L}_7$ (**11**)

Compound $2[\text{Ph}_2\text{Si}(\text{OH})_2] \cdot 2\text{L}_7$ (**11**) formed as a product from the reaction of (**3**) and 4,4'-(1,4-phenylene)bispyridine (**L₇**) as shown in **Scheme 2.41**.



Scheme 2.41: Reaction scheme for the synthesis of $2[\text{Ph}_2\text{Si}(\text{OH})_2] \cdot 2\text{L}_7$ (**11**). For (**12**) see Scheme 2.42

The formation of compound (**11**) is similar to the processes that lead to the formation of compounds (**9**) and (**10**) discussed above. Prior to the formation of compound (**11**) there was a contraction of (**3**) ring into a six-membered ring ($\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3$) and $\text{Ph}_2\text{Si}(\text{OH})_2$. The $\text{Ph}_2\text{Si}(\text{OH})_2$ and the linker (**L**₇) in solution interact via hydrogen bonding with N ($\text{H1} \cdots \text{N20}$ and $\text{H2} \cdots \text{N35}$) to form compound (**11**) as shown in the **Figure 2.30**. Crystals of (**11**) were separated from those (**12**) by visual inspection and hand picking as they possessed different crystallographic morphologies.

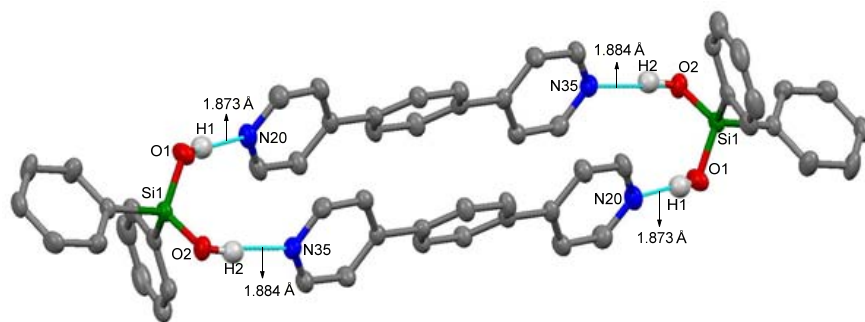


Figure 2.30: Structure of $2[\text{Ph}_2\text{Si}(\text{OH})_2] \cdot 2\text{L}_7$ (**11**) with hydrogen bonding. Colour identity, green = Si, grey = C, blue = N, red = O, light grey = H. Most H atoms are omitted for clarity.

Compound (**11**) is thus a dimer containing two molecule each of $\text{Ph}_2\text{Si}(\text{OH})_2$ and the linker (**L**₇) thereby forming a 34-membered macrocycle. The O2-Si1-O2 angle is 114.95° which is similar to

those of compounds (4), (5), (6), (7), (8) and (10). But unlike in compound (10), where three linkers bonded with four $\text{Ph}_2\text{Si}(\text{OH})_2$ groups via hydrogen bonding using H, O and N, in compound (11), only H and N are involved in the hydrogen bonding. The bond lengths of the hydrogen bonding with N in compound (11) are 1.873 Å ($\text{H1}\cdots\text{N20}$) and 1.884 Å ($\text{H2}\cdots\text{N35}$) respectively. In addition, compound (11) also displays some intermolecular short distance non-covalent interactions in its crystal packing as revealed in **Figure 2.31**.

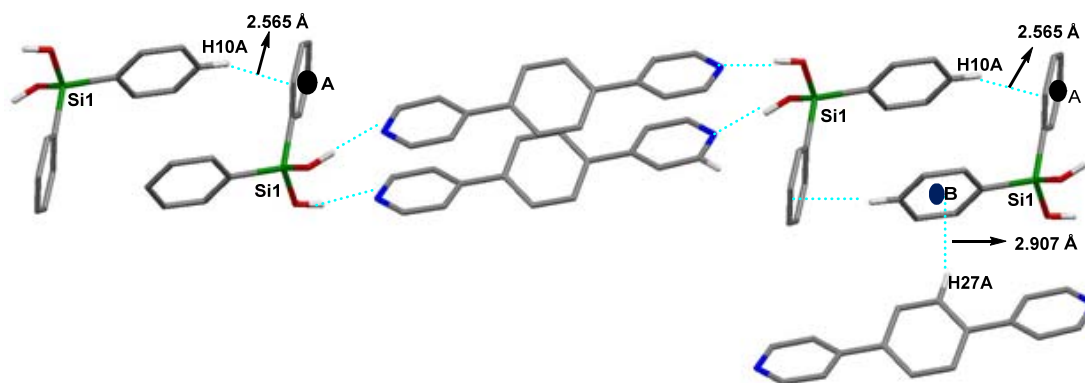


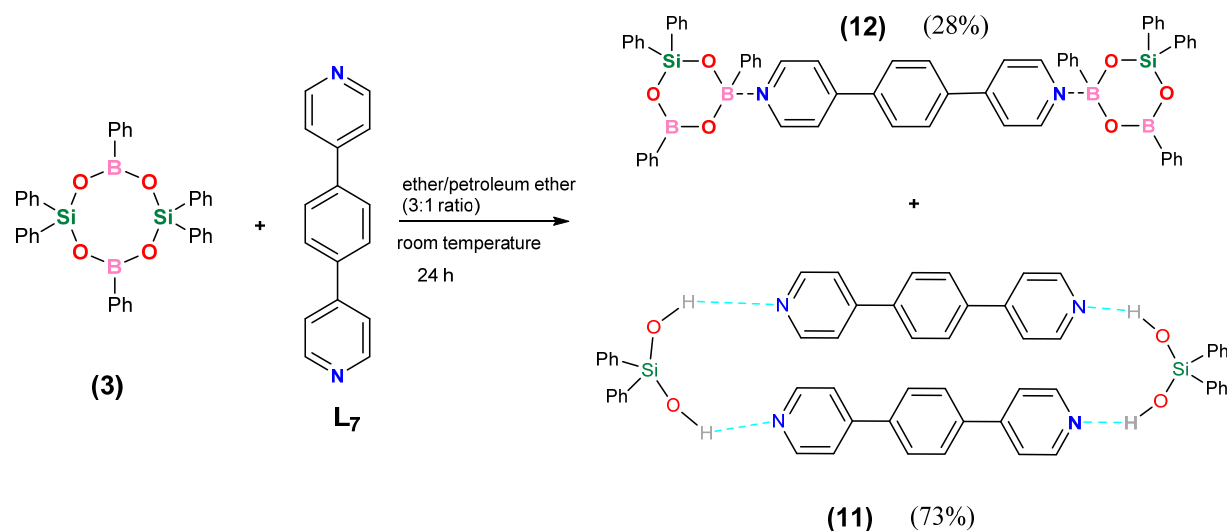
Figure 2.31: The crystal packing of $\text{Ph}_4\text{Si}_2(\text{OH})_4.2\text{L}_7$ (11) with intermolecular non-covalent $\text{C-H}\cdots\pi$ and $\text{C-H}\cdots\text{O}$ interaction in its crystal packing. A and B indicate ring centroids. Colour identity, green = Si, grey = C, blue = N, red = O, light grey = H. Most H atoms are omitted for clarity

Thus from **Figure 2.31** above, it can be seen that in addition to the classical hydrogen bonding found in compound (11), the crystal packing of the compound also shows other forms of interesting intermolecular non-covalent interaction that are weaker than the hydrogen bonding. These interactions include: $\text{C-H10A}\cdots\pi$ centroid $\bullet^A$ (2.565 Å), $\text{C-H27A}\cdots\pi$ centroid $\bullet^B$ (2.907 Å), $\text{C-H36A}\cdots\text{O1}$ (2.455 Å) and $\text{C-H21A}\cdots\text{O2}$ (2.696 Å). The sum of all these interactions further enhances the stability of (11). In the literature values of $\text{C-H}\cdots\pi$ centroid bond as high as 3.26 Å, 3.27 Å, and 3.80 Å for similar compounds have been reported.²⁵⁵ In other work, $\text{C-H}\cdots\pi$ values ranging from 2.665–3.71 Å and $\pi\cdots\pi$ distances range of 3.649 – 4.053 Å have been reported.⁸⁹ Hence, the non-covalent interactions observed in interactions (11) are within previously reported ranges.

All the crystallographic data about **(11)** are provided as Appendix 8.

2.6.10 Synthesis of $2[\text{Ph}_4\text{B}_2\text{SiO}_3]\cdot\text{L}_7$ (**12**)

The product $2[\text{Ph}_4\text{B}_2\text{SiO}_3]\cdot\text{L}_7$ (**12**) resulted from the reaction of $(\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3)$ and the linker (**L**₇) as shown in **Scheme 2.42**. Compound (**12**) was separated from (**11**) by visual inspection, and hand-picking of (**11**).

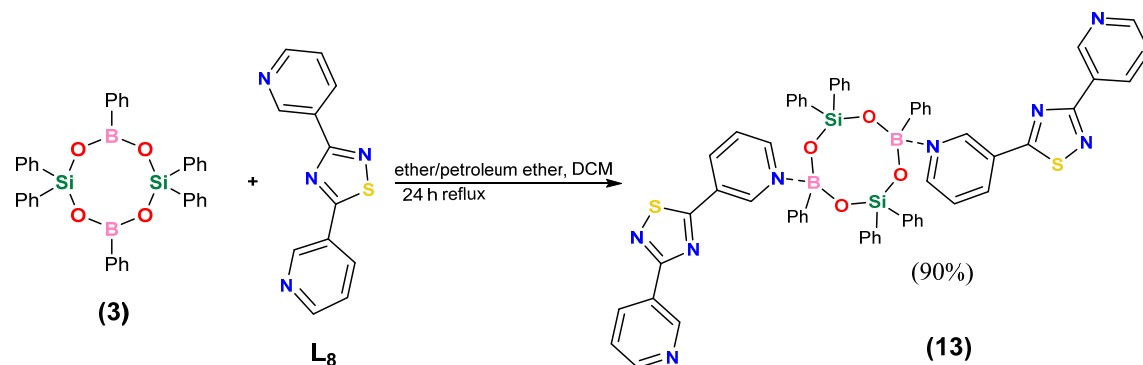


Scheme 2.42: Reaction scheme for the synthesis of $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_7$ (**12**). For (**11**) see **Scheme 2.41**

The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of compound $2[\text{Ph}_4\text{B}_2\text{SiO}_3]\cdot\text{L}_7$ (**12**) showed a singlet at 20.90 ppm and the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of (**12**) showed a singlet at -45.39 ppm. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (**12**) are provided as Supplementary information (**S**₂₉-**S**₃₂ respectively). Although many attempts were made to get a crystal structure of (**12**), all were unsuccessful. However, based on the NMR data, elemental analysis and IR spectrum, it can be concluded that (**12**) is likely product from the contraction of compound (**3**) into $(\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3)$ and $\text{Ph}_2\text{Si}(\text{OH})_2$. The $(\text{Ph}_2\text{B}_2\text{Ph}_2\text{SiO}_3)$ then interacted with (**L**₇) to give (**12**), and the $\text{Ph}_2\text{Si}(\text{OH})_2$ interacted with the (**L**₇) to give compound (**11**) as discussed above.

2.6.11 Synthesis of $[Ph_6B_2Si_2O_4].2L_8$ (**13**)

Compound $[Ph_6B_2Si_2O_4].2L_8$ (**13**) was synthesised by combining ether/petroleum ether solution of (**3**) and 3,5-di-(3-pyridyl)-1,2,4-thiadiazole (**L₈**) in dichloromethane as shown in **Scheme 2.43**.

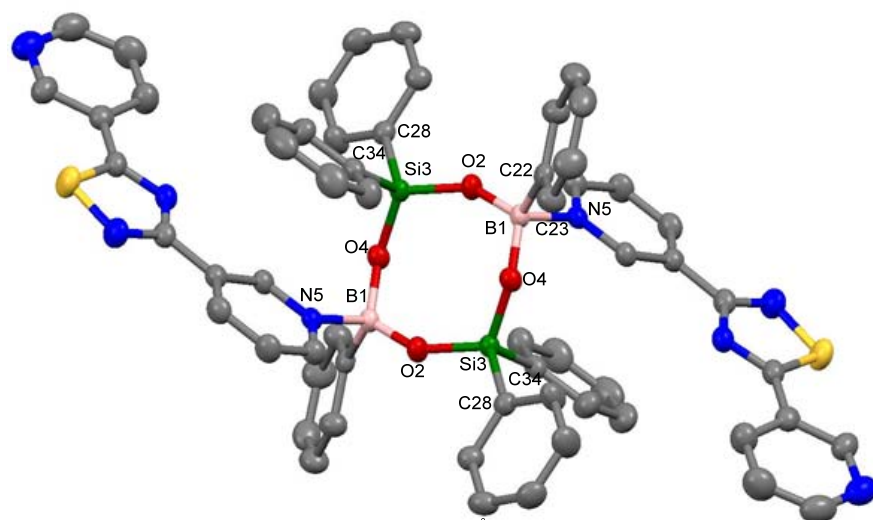


Scheme 2.43: The synthesis of $[Ph_6B_2Si_2O_4].2L_8$ (**13**)

2.6.11.1 Spectral and crystal description of $[Ph_6B_2Si_2O_4].2L_8$ (**13**)

At room temperature compound (**13**) was soluble in organic solvents such dichloromethane, ether, toluene and acetone. Chemical analysis for C, H and N reveals (**13**) as a 1:2 adduct. The ^1H NMR spectrum of compound (**13**) showed well resolved resonances with aromatic proton signals found within the range of $\delta = 7.28$ -8.87 ppm, while the $^{13}C\{^1H\}$ NMR spectrum showed signals for the aromatic carbons in the range of 121.00-186.69 ppm. In addition, the $^{11}B\{^1H\}$ NMR of compound (**13**) showed a singlet at 22.82 ppm, and the $^{29}Si\{^1H\}$ NMR of (**13**) showed a singlet at -45.17 ppm. The NMR (^1H , $^{13}C\{^1H\}$, $^{11}B\{^1H\}$, and $^{29}Si\{^1H\}$) spectra of compound (**13**) are consistent with the compound and are provided as supplementary information (S₃₃-S₃₆ respectively).

Data obtained from single crystal X-ray diffraction studies of compound (**13**) show that the (**13**) is a short chain oligomer consisting of (**3**) and only two linkers (**L₈**) connected at the two boron (B1) centres as shown by the ellipsoid plot in **Figure 2.32**.



Selected bond lengths (Å) and angles (°)

B1-O2 = 1.431(3)	O2-B1-N5 = 102.06(17)
B1-O4 = 1.436(3)	O4-B1-C22 = 111.63(19)
B1-N5 = 1.699(3)	C22-B1-N5 = 106.42(16)
Si3-O2 = 1.607(16)	O2-B1-O4 = 116.93(19)
Si3-O4 = 1.612(16)	O2-Si3-O4 = 113.53(9)
	O2-Si3-C28 = 107.18(10)
	O2-Si3-C34 = 110.35(10)
B1-O2-Si3 = 143.47(15)	O4-Si3-C34 = 110.16(9)
B1-O4-Si3 = 142.70(15)	O4-Si3-C28 = 106.84(9)
O2-B1-C22 = 113.12(19)	C28-Si3-C34 = 108.57(10)

Figure 2.32: An ellipsoid view of (13) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity

Unlike compounds (4), (5) and (6) discussed above, in (13) one end of each of the Lewis base linkers is not connected to any other molecule. The two B-O distances in (13) are 1.431(3) Å (B1-O2) and 1.436(3) Å (B1-O4) respectively, and are longer than B-O length for the tri-coordinated B in (3) which range from (1.36-1.39 Å)^{84,89,102} but similar to those of compounds (4), (5), (6), (7) and (8) discussed earlier. However, the B-O bond lengths in compound (13) are also similar to other B-O distances for tetrahedrally coordinated B in compounds such as $\text{Ph}(\text{OSiR}_2\text{R}')\text{B}\{\text{OCH}_2\}_3\text{N}\}^{250}$ (R or R' = Ph or CH₃) and $[\text{Bu}^t\text{Si}(\text{OPhBO})_3\text{SiBu}^t] \cdot \text{NC}_5\text{H}_5^{102}$ wherein the B is directly bonded to two O atoms, a phenyl group and the N atom. The observed longer bond length at the tetrahedrally bonded B centres compared to the tri-coordinated B, as for the other compound discussed above, may be connected with the reduction of some B-O π -bonding component on changing from trigonal to tetrahedral coordination geometry at the B centres.

The two Si-O bond lengths in **(13)** are 1.6074(16) Å (Si3-O2) and 1.6120(16) Å (Si3-O4) respectively. These two Si-O bond lengths are comparable to those found in compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)**. However, the literature reports a mean value of 1.645 Å^{89,102} for Si-O, for a four-coordinate Si to two O and two C atoms. But similar Si-O bond distances reported here have been observed in the literature.^{102,250} The shorter Si-O distances associated **(13)** suggest an electron density increase in the Si-O bond which is consistent with the decrease in the B-O electron density just as in compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)**.

The B-N bond length in **(13)** is 1.699(3) Å (B1-N5), as in compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)**, the B-N bond lengths in **(13)** are comparable to those of simple borosiloxane such as Ph(OSiR₂R')B{OCH₂)}₃N²⁵⁰ (R or R' = Ph or CH₃) and [Bu^tSi(OPhBO)₃SiBu^t]. NC₅H₅¹⁰² where the B-N distances reported were 1.639 Å and 1.655 Å respectively. The Si-C bond lengths in **(13)** are 1.867(2) Å (Si3-C28) and 1.881(2) Å (Si3-C34) and are as expected as well as consistent with those of **(4)**, **(5)**, **(6)**, **(7)** and **(8)**.

The dihedral angle O2-B1-C22-C23 in **(13)** is 2.85° which is lower than 8.6° reported for compound **(3)**⁸⁵ while the ring angle at the B centre (O2-B1-O4) is 116.93°. Thus the ring angles of compound **(13)** at the two B centres are higher than 109.5° expected for a tetrahedral geometry but similar to those of compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)** as well as those reported in the literature.¹⁰² Similarly, the ring angle of O2-Si3-O4 is 113.53(9)° which is higher than 109.5° for a tetrahedral silicon. The bond angles at the Si centres as well as the Si-C bond distances in **(13)** are comparable to those of compounds **(4)**, **(5)**, **(6)**, **(7)** and **(8)** as well as other borasiloxane compounds and simple adducts in the literature.^{89,102,256}

Compound **(13)**, shows intra- molecular non-covalent (C-H $\cdots$ π , C-H $\cdots$ N, C-H $\cdots$ O, C-H $\cdots$ S and $\pi\cdots\pi$) interactions in its crystal packings as depicted in **Figure 2.33**

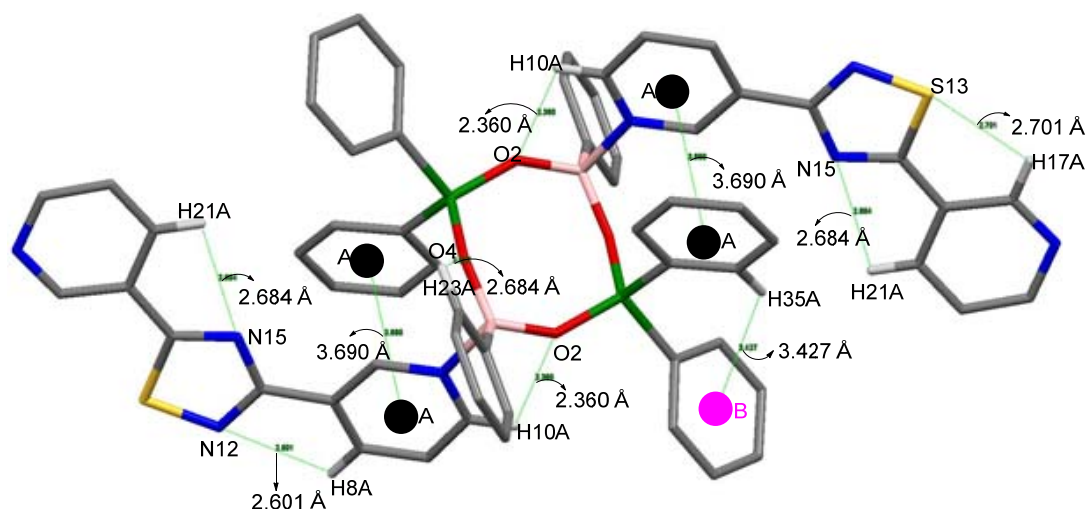


Figure 2.33: Non-bonded interactions in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_8$ (**13**) units with intramolecular C-H $\cdots\pi$, C-H $\cdots\text{N}$, C-H $\cdots\text{O}$ and $\pi\cdots\pi$ interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H. Most H atoms are omitted for clarity.

In addition, compound (**13**) also displays some intermolecular short distance non-covalent interactions in its crystal packing such as $\bullet^{\text{A}}\pi$ centroid $\cdots\pi$ centroid $\bullet^{\text{A}}$ (3.805 Å) and C-H17A $\cdots\pi$ centroid $\bullet^{\text{B}}$ (3.112 Å), as depicted in **Figure 2.34**.

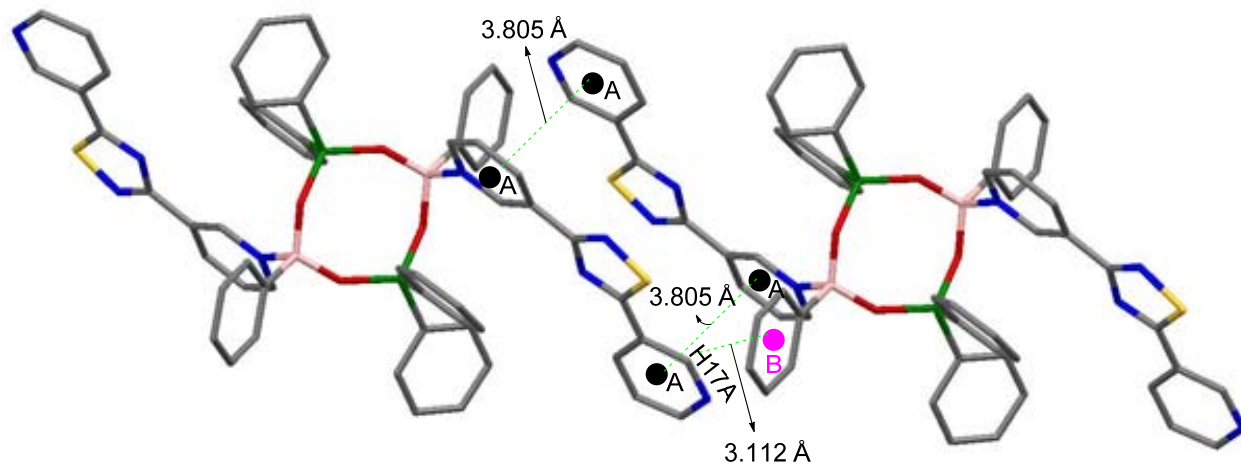
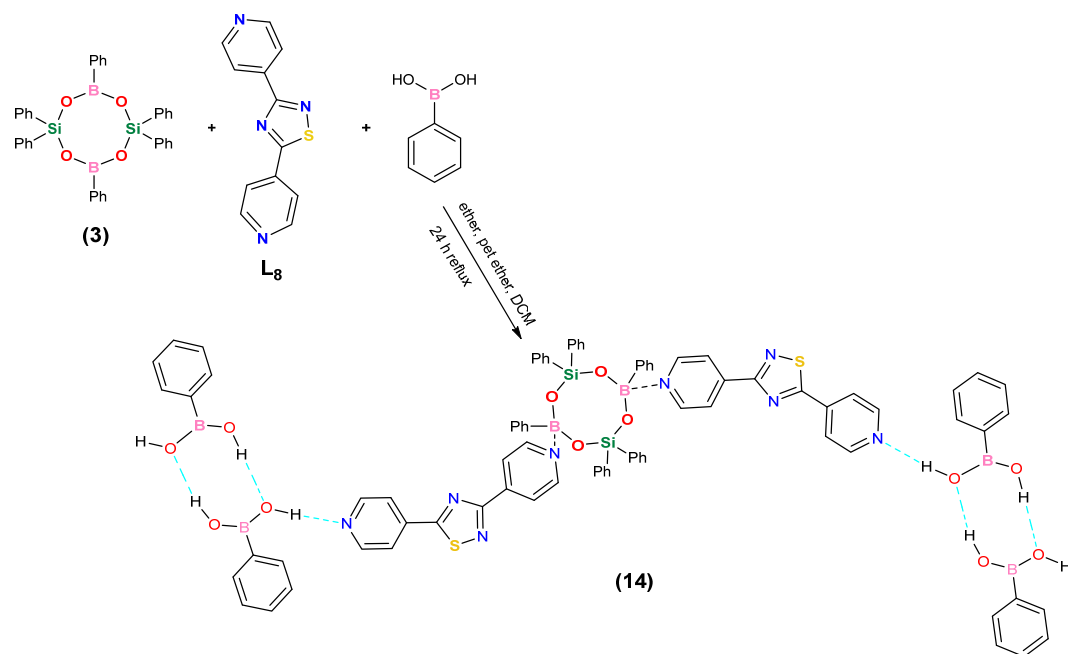


Figure 2.34: Crystal packing of two individual $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_8$ (**13**) connected by intermolecular C-H $\cdots\pi$ and $\pi\cdots\pi$ interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H, colour solid circles = centroid. Most H atoms are omitted for clarity.

Detailed crystallographic data for compound (**13**) are provided as Appendix 9.

2.6.12 Synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_9.2[\text{PhB}(\text{OH})_2]$ (**14**)

Compound $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_9.2[\text{PhB}(\text{OH})_2]$ (**14**) was synthesised by stirring a mixture of (**3**), 3,5-di-(4-pyridyl)-1,2,4-thiadiazole (**L**₉) and $\text{PhB}(\text{OH})_2$ (**2**), in dichloromethane/ ether/petroleum ether solution as shown in **Scheme 2.44**.



Scheme 2.44: Reaction scheme for the synthesis of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_9.2[\text{PhB}(\text{OH})_2]$ (**14**)

2.6.12.1 Spectral and crystal description of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_9.2[\text{PhB}(\text{OH})_2]$ (**14**)

The ^1H NMR spectrum of compound (**14**) shows well resolved resonances with aromatic proton signals found within the range of $\delta = 7.28$ -9.66 ppm, while the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows signals for the aromatic carbons in the range of 123.80-185.37 ppm. The $^{11}\text{B}\{^1\text{H}\}$ NMR and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of (**14**) showed singlets at 21.53 ppm and -45.17 ppm respectively. The NMR spectra (^1H , ^{13}C , ^{11}B , and ^{29}Si) of compound (**14**) are provided as Supplementary information (S₃₇-S₄₀ respectively).

The compound crystallizes in the triclinic space group *P*-1 and single -crystal X-ray diffraction analysis showed an interesting 1-D polymeric assembly, in which each eight-membered ring is

bound to two (**L9**) nitrogen atoms via coordinate covalent bonds ($N \rightarrow B$). The other two nitrogens are connected to phenylboronic acid molecules via hydrogen bonding as shown in **Figure 2.35**.

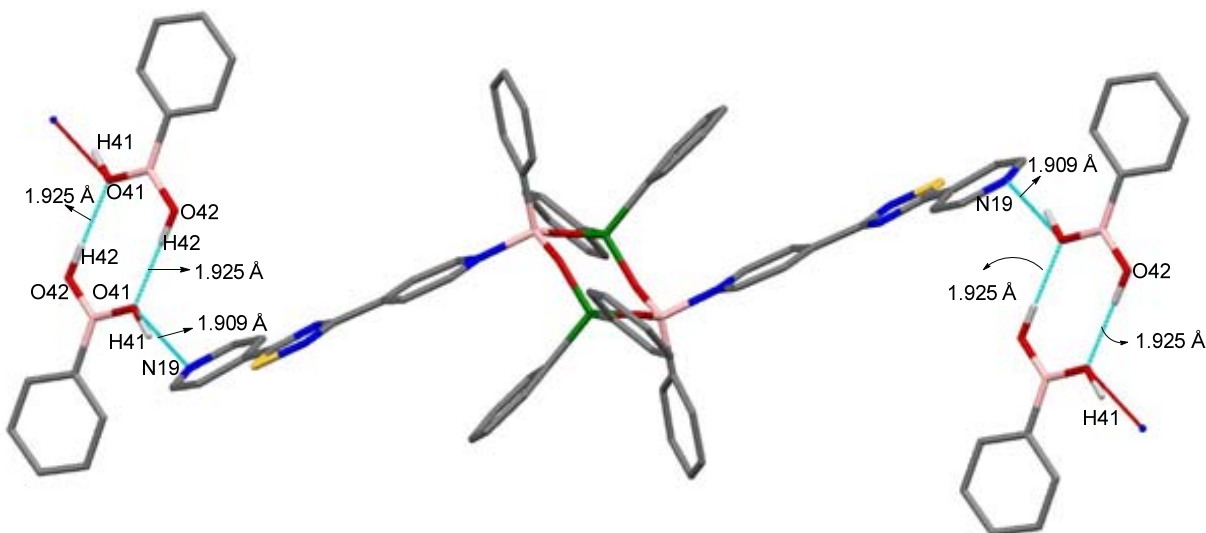


Figure 2.35: Figure 3:1-D polymeric structure of $[Ph_6B_2Si_2O_4].2L_9.2[PhB(OH)_2]$ (**14**) showing hydrogen bonding as pale blue bonds between phenylboronic acids and linkers. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H, Most H atoms are omitted for clarity

As can be seen from **Figure 2.35** above, only one OH group of each phenylboronic acids (OH41) is connected to the linker (**L9**) (N19) via hydrogen bonding, leaving the other OH group (H42 and O41) available for further H-bonding. The H42 and O41 are connected with another molecule of phenylboronic acid through hydrogen bonding with oxygen to give an 8-membered ring of phenylboronic acids as shown in **Figure 2.35**. The hydrogen bonding bond lengths in compound (**14**) are 1.909 Å ($H41 \cdots N19$) and 1.925 Å ($H42 \cdots O41$) respectively.

Furthermore, as can be seen from **Figure 2.36** below, the other hydrogen atoms in the hydrogen bonded ring are then connected with the linker (**L9**) via further hydrogen bonding to give a 1-D polymeric structure.

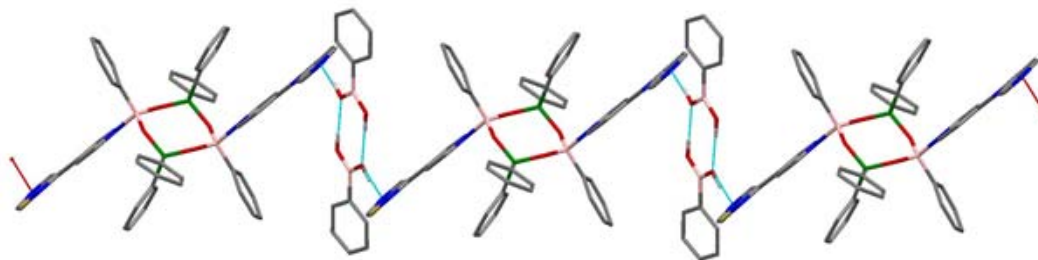


Figure 2.36: 1-D chain structure of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4] \cdot 2\text{L}_9 \cdot 2[\text{PhB}(\text{OH})_2]$ (**14**), pale blue bonds, hydrogen bonding ($\text{H} \cdots \text{O}$) and linker ($\text{H} \cdots \text{N}$). Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H, Most H atoms are omitted for clarity

An ellipsoid plot with atom numbering is shown in **Figure 2.37**

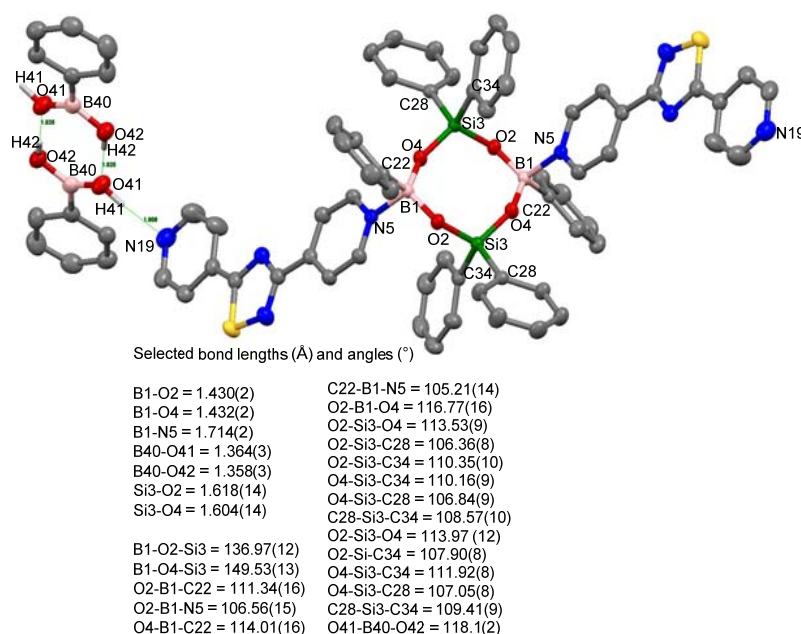


Figure 2.37: An ellipsoid view of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4] \cdot 2\text{L}_9 \cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur. H atoms are omitted for clarity

As revealed in **Figure 2.37**, compound (**14**) is similar to compound (**13**) but with extra hydrogen bonding that results in the formation of a 1-D polymer. Thus, there are two types of boron atoms (B1 and B40) in (**14**). The B1 atoms are tetrahedrally coordinated whereas the B40 atoms are tri-coordinated. The two tetrahedrally coordinated B atoms are bonded to two O atoms (O2 & O4), one C (C22) atom from a phenyl ring and one N (N5) from the linker (**L9**) via a dative bond. Unlike in compound (**13**) discussed above, where some of the linker (**L8**) nitrogens were not

bonded to any other molecule or atom, in **(14)** these N atoms (N19) atoms connect to other phenylboronic acids through hydrogen bonding (H41 $\cdots$ N19). In addition, two other hydrogen bonds are formed between two phenylboronic acids (H42 $\cdots$ O42), and the other H41 from the phenylboronic acid hydrogen bonds to another linker (**L9**).

The two B-O distances in **(14)** are 1.430(2) Å (B1-O2) and 1.432(2) Å (B1-O4) respectively, which are longer than B-O lengths for the tri-coordinated B in **(3)** ring which range from (1.36-1.39 Å)^{84,85,89,102} but are similar to those of compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)** and **(13)**. However, the B-O bond lengths in compound **(14)** are also similar to other B-O distances for tetrahedrally coordinated B in compounds such as Ph(OSiR₂R')B{OCH₂)}₃N²⁵⁰ (R or R' = Ph or CH₃) and [Bu^tSi(OPhBO)₃SiBu^t]. NC₅H₅.¹⁰² However, the trigonally coordinated boron atoms (B40) in **(14)** have B-O bond lengths of 1.364(3) Å (B40-O41) and 1.358(3) Å (B40-O42). Thus the four-coordinate B-O bond distances in **(14)** are longer than the tri-coordinate B-O lengths. But these are comparable with a tri-coordinated B in Si₂B₂O₄ which ranges from (1.36-1.39 Å).^{84,89,102}

The two Si-O bond lengths in **(14)** are 1.6177(14) (Si3-O2) and 1.6041(14) Å (Si3-O4) respectively. These two Si-O bond lengths are similar to those found in compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)** and **(13)** but shorter than Si-O for a four-coordinate Si to two O atoms in the literature which have mean value is 1.645 Å.^{89,102} However, some similar Si-O bond distances reported here have been observed in the literature.^{102,250} The shorter Si-O distances observed in **(14)** suggest an electron density increase in the Si-O bond which is also consistent with the decrease in the B-O electron density just as in compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)** and **(13)**.

The B1-N5 bond length in **(14)** is 1.714(2) Å and is comparable to those of compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)** and **(13)**. The Si-C bond lengths in **(14)** are 1.868(2) Å (Si3-C28) and 1.858(2) Å (Si3-C34) and are as expected.

The ring angle of **(14)** at the B centre (O2-B1-O4) is 116.77° which is higher than 109.5° expected for a tetrahedral geometry but similar to compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)** and **(13)** as well as those reported in the literature.¹⁰² Similarly, the ring angle of O2-Si3-O4 is $113.97(9)^\circ$ which is higher than 109.5° for a tetrahedral silicon but it is comparable to the value found for compound **(13)**. The bond angles as well as the Si-C bond lengths in **(14)** are comparable to those of compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)** and **(13)** as well as other borasiloxane compounds and simple adducts in the literature.^{89,102,256}

The crystal packing of **(14)** also shows intra-molecular non-covalent (C-H $\cdots$ π , C-H $\cdots$ N, C-H $\cdots$ O, C-H $\cdots$ S and H $\cdots$ B) interactions as depicted in **Figure 2.38**.

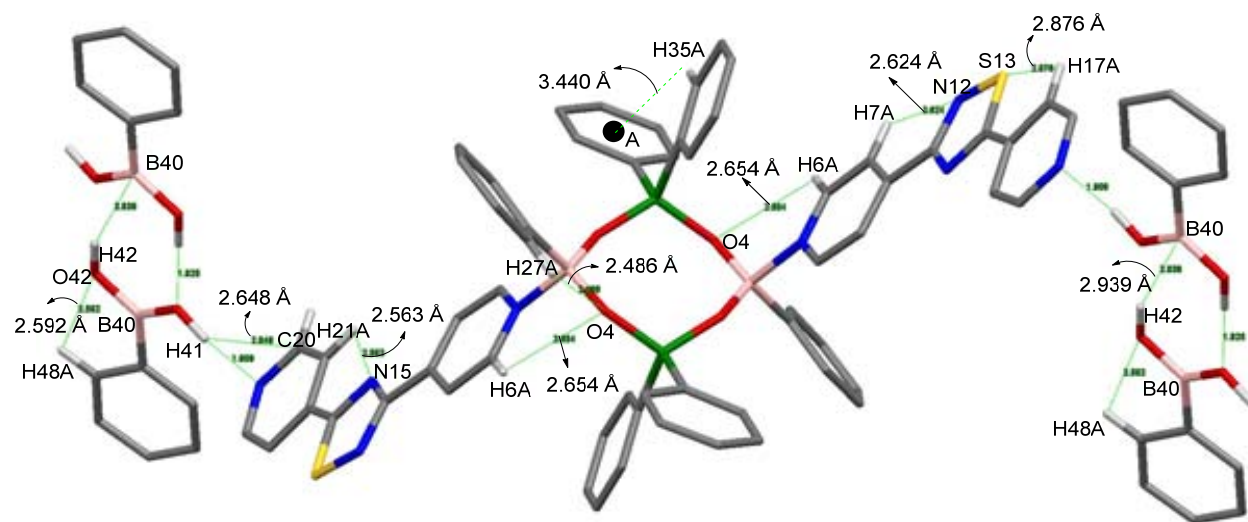


Figure 2.38: Crystal packing in $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4].2\text{L}_9.2[\text{PhB}(\text{OH})_2]$ (**14**) with intramolecular C-H $\cdots$ π , C-H $\cdots$ N, C-H $\cdots$ O and H $\cdots$ B interactions. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, yellow = sulphur, light grey = H. black dot = centroid. Most H atoms are omitted for clarity

Interestingly, **(14)** also exhibits short intermolecular non-covalent interactions in its crystal packing such as $\pi \cdots \pi$, (3.362 Å) (C14 $\cdots$ C36) and (3.243 Å) (C11 $\cdots$ C37), (CH $\cdots$ π) 2.587 Å (CH37A $\cdots$ π C38), and H7A $\cdots$ O42 (2.452 Å) as depicted in **Figure 2.39**

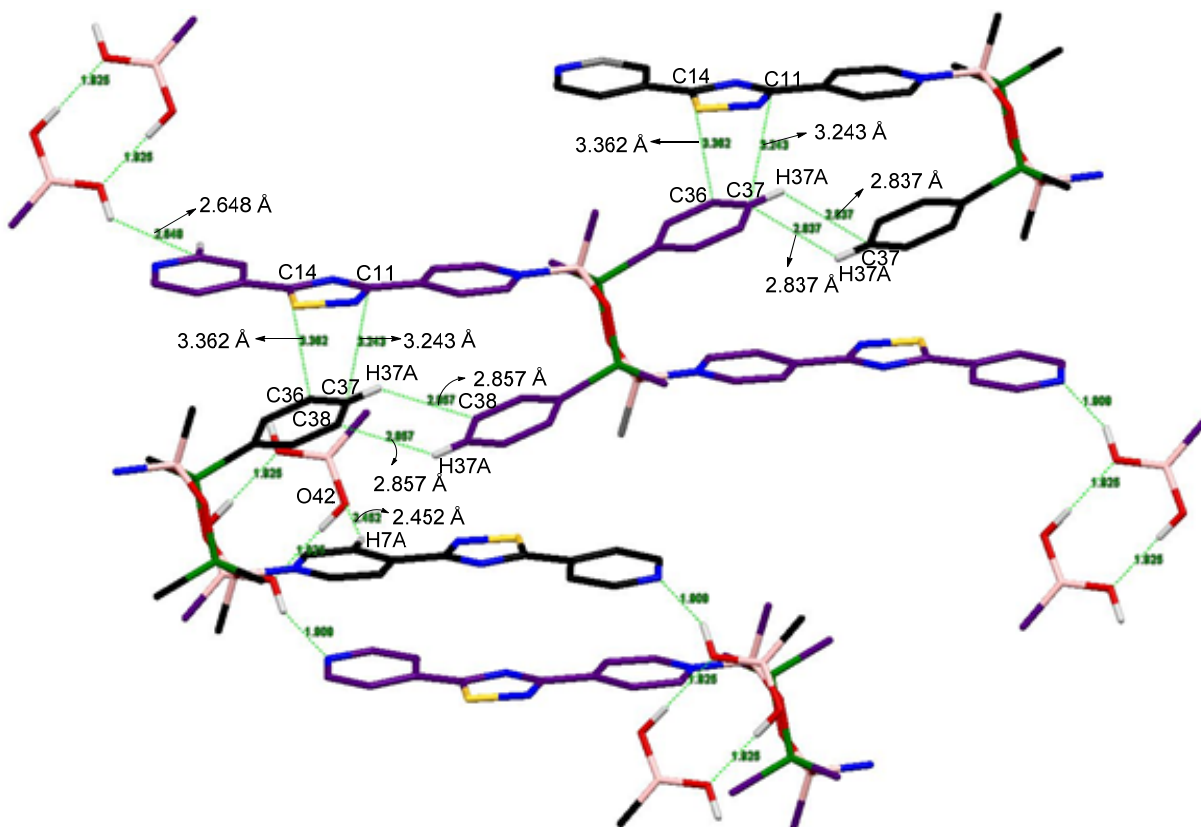


Figure 2.39: Crystal packing of three individual $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4] \cdot 2\text{L}_9 \cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) chains connected by intermolecular C-H... π and π ... π interactions. Colour identity, pink = B green = Si, black and purple = C, blue = N, red = O, yellow = sulphur, light grey = H, colour solid circles = centroid. Most H atoms are omitted for clarity.

The detailed crystallographic data for compound (**14**) are provided as Appendix 10.

In addition to compound (**3**), other Lewis acids such as (**3a**, **3b**, **3c** and **3d**) shown in **Figure 2.40** were also synthesised as potential components of COFs.

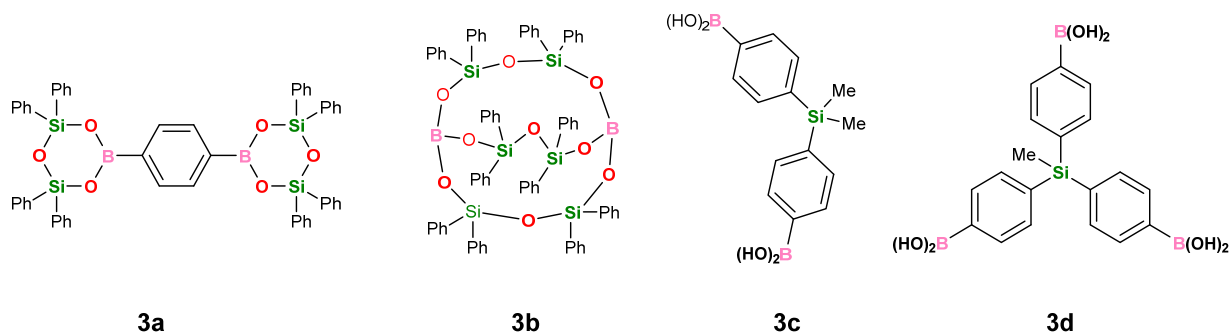
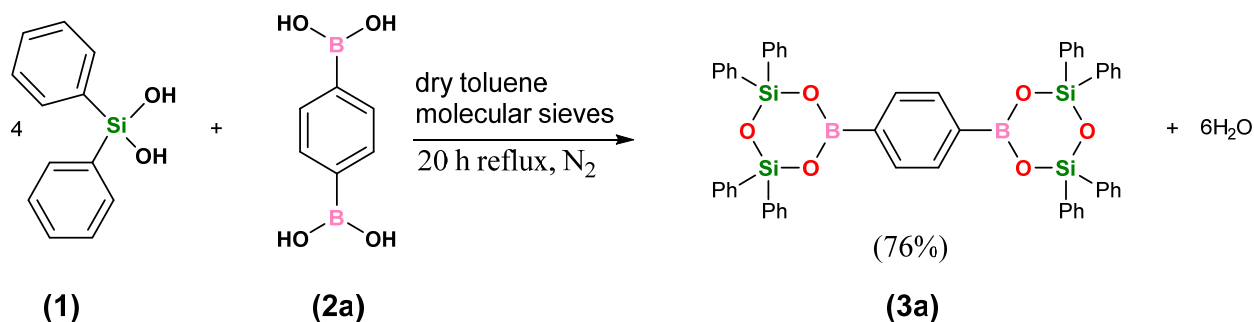


Figure 2.40: Other di- and tri-connected Lewis acids.

2.6.13 Synthesis of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_4(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (**3a**).

The preparation of 1,4-bis(2,2,4,4-tetraphenyl-1,3,5,2,4,6-trioxadisialborinan-6-yl)benzene $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_4(\text{BO}_3\text{Ph}_4\text{Si}_2)$ (**3a**) is similar to the making of compound (**3**) discussed in section 2.6.1 and is shown in **Scheme 2.45**.

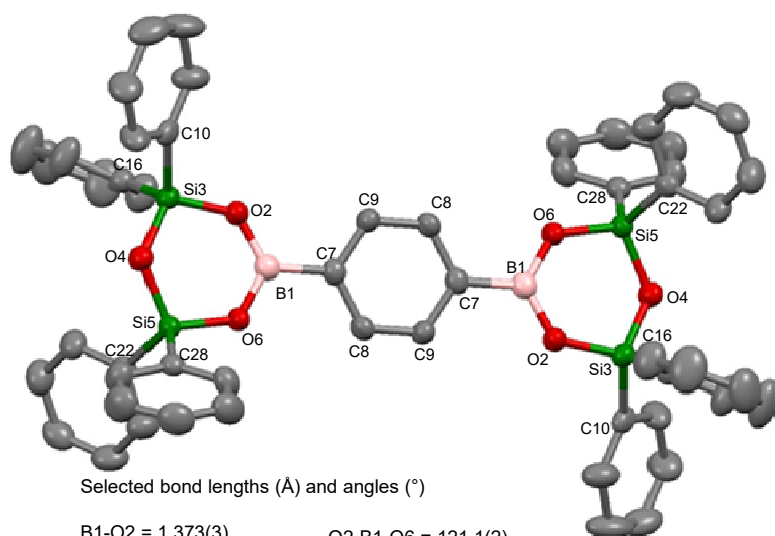


Scheme 2.45: Reaction method for the synthesis of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_5(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (**3a**).

2.6.13.1 Spectral and crystal description of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_5(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (**3a**).

Compound (**3a**) is a colourless crystalline material at room temperature and is readily soluble in organic solvents such dichloromethane, ether, toluene and acetone. The ^1H NMR spectrum of compound (**3a**) shows resolved resonances with aromatic proton signals found within the range of $\delta = 7.35$ -8.10 ppm. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**3a**) shows signals for the aromatic carbons in the range of 127.57-134.32 ppm. The $^{11}\text{B}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound (**3a**) showed broad peak around 28.79 and a singlet at -31.19 ppm respectively. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (**3a**) are provided as Supplementary information (**S41-S44** respectively).

In addition to the NMR data, the preparation of (**3a**) was confirmed by data obtained from single crystal X-ray diffraction studies as shown by the ellipsoid plot with numbering in **Figure 2.41**.



Selected bond lengths (Å) and angles (°)

B1-O2 = 1.373(3)	O2-B1-O6 = 121.1(2)
B1-O6 = 1.371(3)	O2-B1-C7 = 120.6(2)
B1-C7 = 1.554(3)	O6-B1-C7 = 118.3(3)
Si3-O2 = 1.6468(16)	O2-Si3-C10 = 110.41(17)
Si3-O4 = 1.6405(17)	O2-Si3-C16 = 108.0(4)
Si5-O4 = 1.6341(16)	O4-Si3-C10 = 110.95(17)
Si5-O6 = 1.6426(16)	O4-Si3-C16 = 109.47(10)
Si3-C10 = 1.857(2)	C10-Si3-C16 = 111.14(15)
Si3-C16 = 1.853(2)	O4-Si5-C22 = 108.91(9)
Si5-C22 = 1.850(2)	O4-Si5-C28 = 110.64(9)
Si5-C28 = 1.853(2)	O6-Si5-C22 = 108.79(9)
	O6-Si5-C28 = 107.78(10)
	C22-Si5-C28 = 113.53(10)
B1-O2-Si3 = 128.79(16)	
Si3-O4-Si5 = 125.69(10)	
Si5-O6-B1 = 128.42(15)	

Figure 2.41: An ellipsoid view of $(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_5(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})$ (**3a**) with some atom labelling. Colour identity, pink = B, green = Si, grey = C, red = O. H atoms are omitted for clarity.

Compound (**3a**) contains two six-membered cyclic $\text{Ph}_4\text{Si}_2\text{O}_3\text{B}$ groups connected by an aromatic ring at B1 and C7 as shown in the ellipsoid plot view. The B1 atoms are three-coordinate with the angles O2-B1-O6, O2-B1-C7 and O6-B1-C7, 121.1(2), 120.6(2) and 118.3(3)° respectively. The sum of the angles at the B in compound (**3a**) is 360° confirming the trigonal planar geometry at the B centres. The mean B-O and Si-O bond lengths in compound (**3a**) 1.372 Å and 1.641(16) Å respectively, which are shorter than the covalent radii range in some literature (B-O, 1.43-154 Å and Si-O, 1.66-1.91 Å)^{84,257} and those of compounds (**4**), (**5**), (**6**), (**7**), (**8**), (**13**) and (**14**) but comparable to (B-O, of 1.361-1.369 Å and Si-O of 1.621-1.636 Å)⁸⁹ as well as those found in (**3**) (B-O, 1.348(5) and Si-O, 1.615(3) and 1.627(3))⁸⁵ and compound (**9**). The short B-O and Si-O bond lengths in compound (**3a**) are indicative of some π -bonding interactions within the ring.

The Si centres show slight distorted tetrahedral geometry with angles ranging from 107.789(10)-113.53(10)° with a mean angle of 109.96°. The bond distances and bond angles are comparable to those found in (PhBO)₂(Ph₂SiO)^{83,258} Ph₂Si[OBArO]₂SiPh₂ (Ar = 4-EtC₆H₄, 2-PhC₆H₄ and β-C₁₀H₇ (Nap)]⁸⁹ as well as those in compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)**, **(13)** and **(14)**. The B-O-Si angles range from 125.69(10)-128.79(16)° and are smaller than those found in compounds **(4)**, **(5)**, **(6)**, **(7)**, **(8)**, **(13)** and **(14)** but comparable to those of compound **(9)** which range from 122.40(25)-127.08(19)°.

The crystal packing of compound **(3a)** shows non-covalent intermolecular interactions (C-H...π = 2.880 Å; C-H...B = 2.869 Å and B...π = 3.463 Å) as shown in **Figure 2.42**. In the literature values ranging from (2.655-4.032 Å)^{89,259} have been reported for similar interactions in borasilicate and other related ring systems.

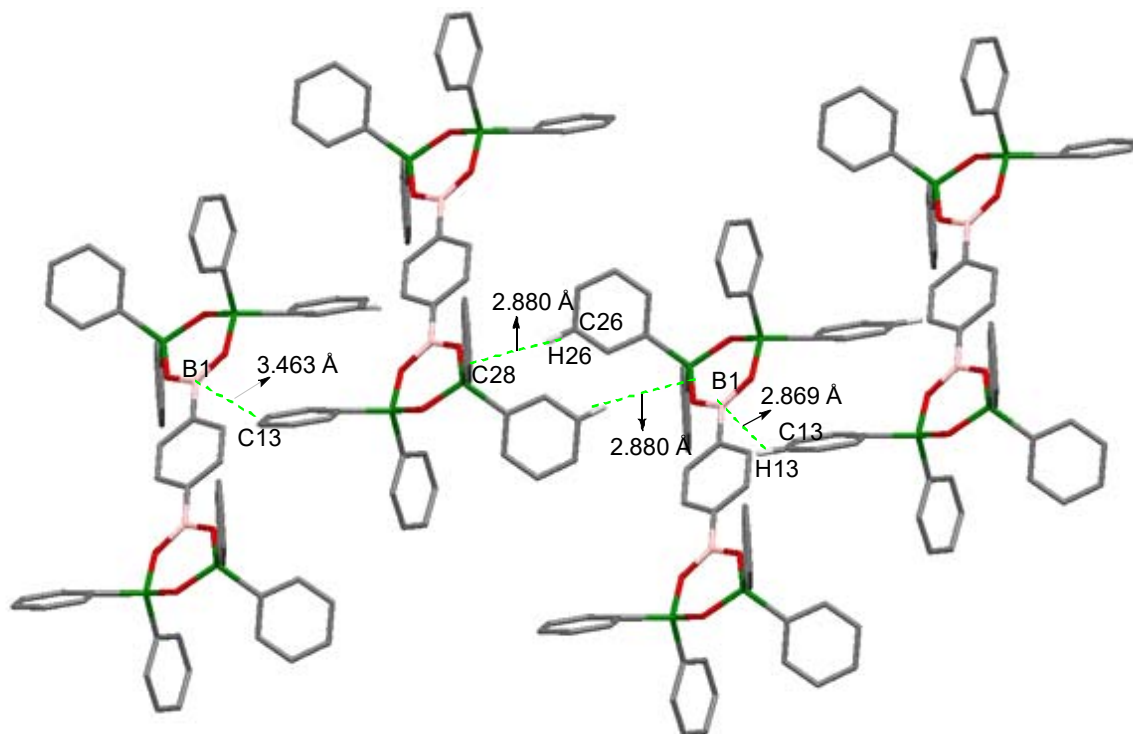
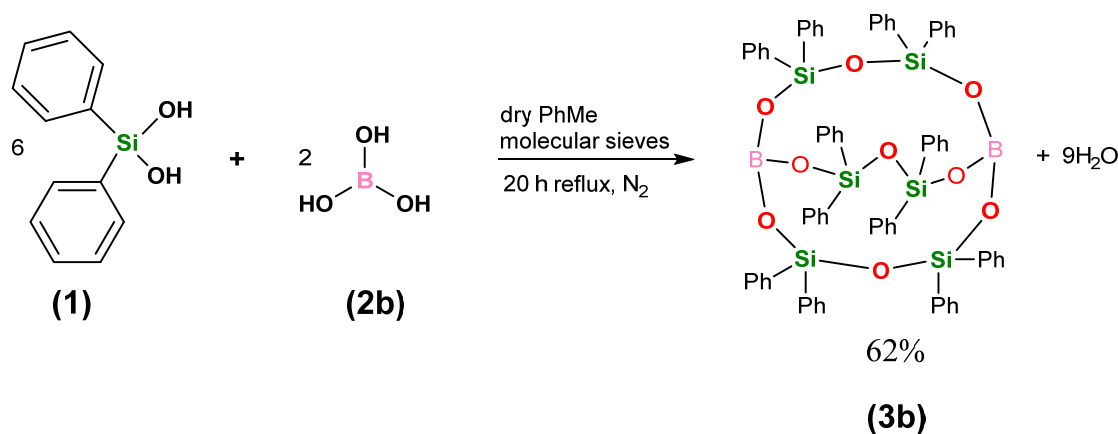


Figure 2.42: Non-covalent C-H...π, C-H...B and B...π interactions in the crystal packing of **(3a)**; H atoms omitted for clarity.

The crystallographic data of compound **(9)** are provided as Appendix 11.

2.6.14 Synthesis of $[B(OSiPh_2OSiPh_2O)_3B]$ (**3b**).

The making of compound (**3b**) is similar to the preparation of compounds (**3**) and (**3a**) except that boric acid (**2b**) was combined with (**1**) in dry toluene at reflux under N_2 and activated molecular sieves for water sorption as shown in **Scheme 2.46** below.



Scheme 2.46: Reaction scheme for the synthesis of $[B(OSiPh_2OSiPh_2O)_3B]$ (**3b**)

Although compound (**3b**) is a known compound prepared by the use of tetraphenyldisiloxanediol and boric acid with 44.9% yield.⁸⁴ Compound (**3b**) was prepared in this project as colourless powder in 62% yield. Block-like crystals of (**3b**) were obtained by recrystallization from CH_2Cl_2 -heptane, and a single crystal X-ray diffraction study using a pre-unit-cell scan ($a = 23.3473(11)$ Å, $b = 13.877(9)$ Å, $c = 20.356(11)$ Å, $v = 6505(6)$ Å³; $\alpha = 90.03(5)^\circ$, $\beta = 98.34(4)^\circ$, $\gamma = 90.02(4)^\circ$) confirmed that (**3b**) is the same compound (HAXPIX) made by Ferguson and co-workers,⁸⁴ of which the crystal structure is shown in **Figure 2.43**

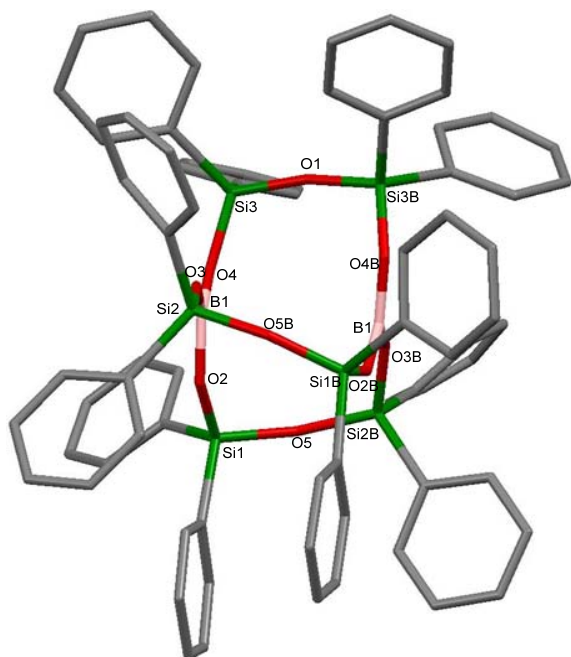


Figure 2.43: Crystal structure of (**3b**) with some atom labels. (Adapted from Ref.⁸⁴), Colour identity, pink = B, green = Si, grey = C, red = O. H atoms are omitted for clarity.

A detailed crystallographic description of the structure of compound (**3b**) was given by Ferguson and co-workers.⁸⁴

The synthesis of compounds **3c** and **3d** are discussed in sections 3.6.5 and 3.6.8 respectively in this report.

All the treatments carried out on compound (**3**) with varieties of Lewis bases, whose results have been discussed, were also conducted with compounds **3a**, **3b**, **3c** and **3d**. Unfortunately, none of the experiments performed with these Lewis acids (**3a**, **3b**, **3c** and **3d**) and the Lewis bases (**L1-9**) gave crystalline materials but instead gave only oil or starting materials. In addition, in a bid to make 2- and 3-D framework materials, the other tri- and tetra-dentate ligands in **Figure 2.6** were treated with compounds (**3**, **3a**, **3b**, **3c** and **3d**) the same way (**L1-9**) were treated with the Lewis acids. But all the reactions were unsuccessful as proton NMR spectra of the reaction products showed starting material with no difference in chemical shifts. Several other attempts with modification of the solvent mixture (e.g. addition of dichloromethane) were also unproductive.

2.7. Summary and Outlook

This chapter has reviewed the literature concerning COFs, in particular those based on boron, triazine and imine components. The successes made so far as well as challenges that require the development of new synthetic strategies were identified.

Based on this, new synthetic methods have been developed to prepare boron-based Lewis acids and a variety novel of 1-D polymers, by connecting a Lewis acid, cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane ($\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4$) (**3**) with pyridine Lewis bases. In some experiments, ring contraction of (**3**) occurred instead of COF formation and single hydrogen bonded adducts were formed. The contraction of compound (**3**) in some of the experiments may be as a result of differences in the basicity of the Lewis bases. In addition to basicity, the stability of the products formed after the contraction may also have influenced the outcome of the reaction. For the reactions that lead to the formation of short polymers or oligomers, the orientation of the Lewis bases may be responsible so as to reduce straining of the overall compounds. CO_2 adsorption studies using these 1-D polymers and the other molecular structures were not attempted because the polymers are not 2-D or 3-D and lack porosity.

Lewis acid - Lewis base reaction in this chapter have provided a range of 1-D polymers with simple pyridine-based linkers. However, preliminary work with more complicated tri- or tetra-dentate aryl pyridine and carboxylate did not lead to 2-D or 3-D being formed. Such polydentate linkers should be investigated further for preparing framework materials. This has been successful with metal ions as nodes as described in **Chapter 3**.

Chapter 3

3.0 METAL-ORGANIC FRAMEWORKS (MOFs)

3.1. Introduction

Metal-Organic Frameworks (MOFs)^{44,54,260} are ordered structures consisting of inorganic and organic components. Most MOFs reported in the literature consist of transition metal ions (node), single or in clusters, interconnected by organic struts or ligands. A successful approach to obtaining a MOF depends on the choice of the building units which have significant influence on the topological structure and functionality of MOFs. Bridging ligands are important building units in the construction of MOFs. Hence, to control the structure of a MOF material, the selection of rigid, organic linkers is one of the most crucial decisions. For this reason, most of the organic linkers used in the construction of MOFs are usually molecules containing aromatic groups that give rigidity to the MOF network. The aromatic groups are in turn terminated or contain functional groups which are capable of coordinating with metal ions to give 1-, 2-, or 3-D networks as shown in **Figure 3.0**.

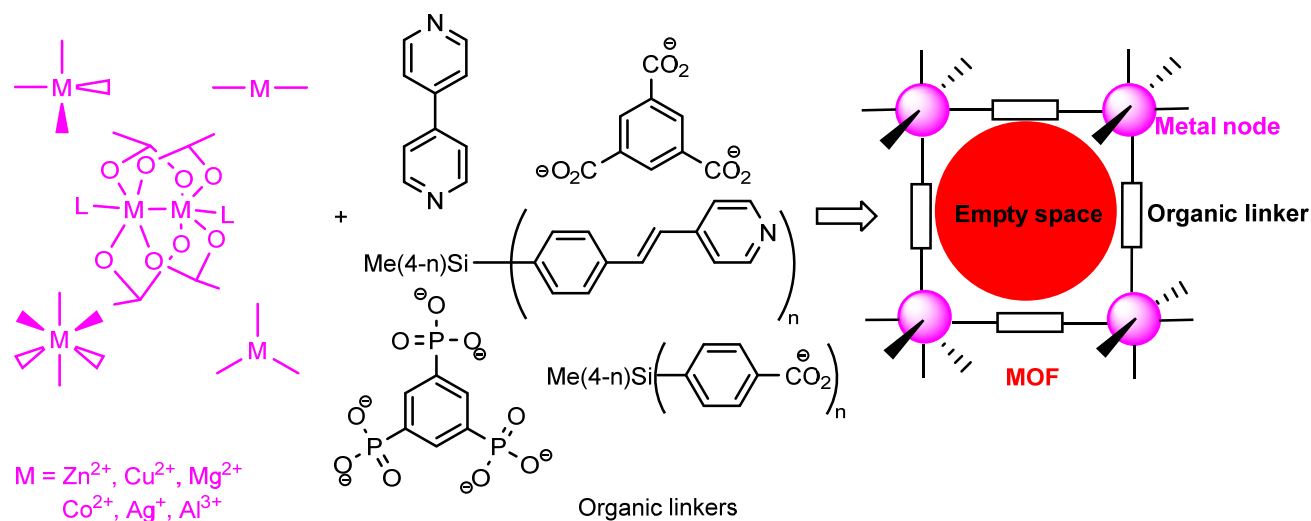


Figure 3.0: Examples of metal ions and linkers used to give 1-, 2- or 3D structures with porosity for gas adsorption.

The functional groups in the aromatic organic ligand could be carboxylic acid,^{261–267} heterocyclic aromatic rings containing N atoms (pyridine)^{267–272} or other coordinating functional groups such as phosphonates^{273–277} and sulfonate.^{278,279} The nodes are usually made of one or more metal ions such as Zn^{2+} , Fe^{3+} , Mg^{2+} , Ca^{2+} , Zr^{4+} , Ni^{2+} , Co^{2+} , Al^{3+} or Cu^{2+} . A good number of MOFs display nanoscale porosity, high S_{BET} and high thermal stability. One unique feature of MOFs over other solid porous adsorbents is that MOF materials can be tuned to carry out task specific jobs by varying of the pore size using judicious selection of the building blocks used in their synthesis.

3.2. Synthesis of Metal-Organic Frameworks (MOFs)

New MOF materials may be obtained when diverse influencing factors such as preservation of structural framework of the building units, optimal conditions of reaction, and metal ion type, as well as the type of organic ligand are considered. In a bid to prepare novel MOFs, significant attention has been devoted to the synthesis of new organic ligands for linkers and optimal conditions for the development of metal-organic ligand linkages. The structure of a MOF material as well as the geometry attained by a metal ion in a given MOF is greatly influenced by the characteristic features of the ligand such as its length, the number of connecting units on the ligand and their relative positions (linear, bent, trigonal or tetrahedral), bulkiness and any chirality present.²⁸⁰ As well as trial-and-error methods, many systematic studies involving hydro (solvo) thermal, microwave, sonochemical, electrochemical, mechanochemical, slow diffusion, solvent evaporation/ionothermal synthetic methods have all been reported.^{280–282}

3.2.1 Hydro (solvo) thermal methods

In general, the formation of a crystalline structural MOF material depends on factors such as solvent/solvent mixture, types of metal ion centres, ligand type as well as reaction temperature. Variations in solvent/solvent mixtures can result in the formation of different framework materials

due to templating effects of the solvent molecule which have the capability of occupying the pores within the synthesised MOFs. Solvents usually used for the synthesis MOF materials include: DMF (dimethylformamide), DMA (dimethylacetamide), and DEF (diethylformamide). These solvent have relatively high boiling points and are also thermally stable. Hence, they are frequently used for the preparation of MOFs under extreme thermal conditions. Lower boiling point solvents such as water, methanol, and ethanol have also been used. However, if the heating of such solvents is anticipated to take place at temperatures above their boiling point, then the reactant solution is put in specially designed high pressure vessels such as a Parr autoclave. These solvents can also coordinate with metal centres and be incorporated in MOF structures.²⁸³ In solvothermal methods of MOFs synthesis the heterogeneous reaction takes place in sealed containers with autogenous pressure and temperature higher than the boiling point of the solvent.^{81,284} Thus, when making a choice for the reaction vessel (typically a screw-top vial), the scale of the reaction and the volume of solvent needed as well as the anticipated temperature range of the reaction are given consideration to ensure that sufficient headspace is left to give room for potential pressure build-up. In some situations, for example when the metal-ligand bond energies are relatively high, a modulator is used to hinder the rapid precipitation of amorphous material.^{285–289} Modulators are non-structural mono-topic linkers such as acetic acid, benzoic acid and hydrochloric acid which can form dynamic bonds with the metal precursor and assist in slowing down the formation of structural bonds by competing with the linkers for metal coordination sites. Modulators have been essential for the preparation of Zr-MOFs which contain strong Zr(IV)-O bonds. The concentration and chemical composition of a modulator influence defect corrections in the MOF structure as well as playing key a role on the MOF crystal size, habit and topology.²⁹⁰ Solvothermal MOFs synthesis is appealing for two reasons: (a) the problems of solubility of large organic molecules

under these solvothermal experimental conditions are minimised and (b) the process of nucleation can be initiated more rapidly for the formation of complexes under the same conditions.^{291,292} The sealed reaction mixture is usually put in electrically heated ovens. The oven heating and cooling temperatures are controlled in order allow crystal growth defects to be resolved as the organic ligand continues to bind reversibly in a MOF thus promoting the growth and size of the crystals formed. The size of the crystals formed is very important for the purpose of characterization, as very small crystals may be unsuitable for single crystal X-ray crystallographic study. Although, this method enables the growth of bigger crystals the heating is usually done over hours or days, and thus is quite time consuming.

3.2.2 Microwave (MW) Assisted Methods

The application of electromagnetic radiation such as MW in synthetic organic and inorganic chemistry is well known.^{293–296} MOFs such as IRMOF-2, IRMOF-3, MOF-5 and HKUST-1 have been synthesised within seconds to minutes under microwave assisted conditions.^{297–299} The surface area of HKUST-1 obtained through this method was reported to be 1820 m²/g, which is higher than that reported for the same HKUST-1 obtained via solvothermal synthetic route (1550 m²/g).³⁰⁰ The MW method relies on the interaction of electromagnetic radiation with polar molecules in a solvent or conducting ions in a solid. In contrast to solvothermal methods, where thermal energy is transferred from the source of heat to the solution through the reaction container, in MW synthesis the interaction is directly with the reactants. The direct interaction of radiation with polar solvents develops hot spots which result in more efficient and faster heating. Furthermore, in MW assisted MOF synthesis crystallisation happens at the hot spots that form as a result of the direct heating of the solvent, as opposed to the wall of the reactor vessel associated with conventional heating methods. The precursors for the MOF synthesis are put in a microwave

oven and heated, this results in rapid heating and short time for the formation of the MOF ranging between seconds to a few minutes. Consequently, MW assisted synthesis is much faster and results in a smaller particle size.²⁸¹ Other than time saving benefits, microwave-assisted MOF synthesis also affords the synthesis of MOF crystals under variable reaction conditions.^{298,301} However, microwave-assisted MOF synthesis does not give good crystals large enough to obtain good structural data.^{295,297}

3.2.3 Sonochemical Method

This method of MOF synthesis is facile, efficient and inexpensive. Ultrasound in the frequency range of 20 kHz–10 MHz,^{280,302} causes changes in pressure which generate cavities (small bubbles) in the solvent. Over time, these bubbles grow and collapse (cavitation). Thus, the formation and collapse of bubbles (cavitation) leads to local pressures and temperatures in excess of 1000 atm and 5000 K within the liquid. The hot spots which evolve lead to superior heating and cooling rates which accelerate the formation of MOFs. Examples of small crystalline MOFs that had been made by this method include Mg-MOF-74,³⁰³ MOF-177,³⁰⁴ MOF-5^{305,306} and MIL-53(Fe).³⁰⁷ One advantage of this method over solvothermal synthesis is the avoidance of long reaction times as well as high heating temperatures.³⁰⁸ However, this method of MOFs synthesis usually produces materials with small crystal size that are unsuitable for single crystal crystallographic studies.

3.2.4 Electrochemical Method

Electrochemical synthesis is also an alternative way of synthesising MOF materials with precise process control.³⁰⁹ This method is fast and the purity of the products is high because of the absence of counter ions such as nitrates, perchlorate or chloride from metal salts.²⁸⁰ In this method ions are placed at the anode while the organic ligand is placed at the cathode and the electrochemical cell is filled with a conducting salt solution. Mueller and co-workers (BASF) pioneered the use of this

method to synthesis Cu-MOF,³⁰⁹ which was made electrochemically by the use of a copper plate as the anode and 1,3,5-benzenetricarboxylic acid dissolved in methanol served as the cathode. The resulting electrochemical process gave a greenish blue precipitate of Cu-MOF (HKUST-1) within 150 minutes with a voltage and current of 12-19 V and 1.3 A respectively.³⁰⁹ BASF has also reported in the literature Al-fum MOF (Basolite A520) which can now be prepared in tonne-scale by the use of a water-based reaction system.³¹⁰ This method has been used to make other MOFs such as $[\text{Cu}_2(\text{BTC})_3(\text{H}_2\text{O})_3]$,³¹¹ and $[\text{Cu}_3(\text{BTC})_2]$.³¹² In the literature other researchers have applied electrochemistry in the preparation of different types of MOFs for varieties of applications.^{313–320} In addition, several review articles have described the successes and shortcomings associated with this synthesis method.^{281,282,321}

3.2.5 Mechanochemical (Mechanosynthesis) Method

Contrary to the other methods so far discussed above that involve the use of solvents for the synthesis of MOFs, mechanochemical synthesis of MOFs is a solvent free method.^{280,322} The application of mechanical force on reactant species is capable of inducing both physical and chemical changes, which cause mechanochemical or solvent free synthesis of MOFs. Although this technique is well known in metallurgy and mineral processing it has only recently expanded rapidly into diverse areas of chemistry such as inorganic chemistry and pharmaceutical synthesis.^{323,324} In this method, chemical reactions occur by milling or grinding solids without any or with very little solvent.^{281,325,326} Thus with this method, the conventional solvothermal MOF reactors are substituted with mortar and pestle or a mechanical process by automated ball mills.³²⁷ In addition to no solvent wastes, this method MOF allows precursors with low solubility such as oxides, hydroxides and carbonates of metals to be used.²⁸¹ Although, the method is a ‘solvent-free’ process, the purification stage may, however still require solvent. The major limitation associated

with mechano-synthesis is scaling-up of the reaction, since the process is fundamentally a batch handling technique with a comparatively low rate of production.³²² Nevertheless, from a green chemistry view point, this approach is an environmentally friendly means of preparation MOFs with a significant reduction in the cost of production.^{328,329}

Mechanosynthesis has three different approaches for the synthesis of MOFs. These approaches are: (1) Solvent-Free Grinding (SFG), that avoid completely the use of solvent;^{330–334} (2) Liquid-Assisted Grinding, which is more versatile and faster as it uses small amount of liquid phases that enhance the mobility of the reagent,^{335–340} and (3) Ion-and-Liquid Assisted Grinding (ILAG),³⁴¹ that makes use of a small liquid containing a small amount of salt additives to enhance the formation of MOF.^{327,342} One disadvantage of this method is that, crystals obtained through this means are unsuitable for single crystal X-ray diffraction studies.

3.2.6 Slow Diffusion Method

The mixing of solutions of metal salts and organic ligands without heating does not usually give MOF materials. However, there are some specific cases where the mixing of metal ions and ligand solution result in the formation of microcrystalline powder, which is not good for single crystal X-ray diffraction study. In a bid to solve the problem of formation of polycrystalline powder materials, slow diffusion of solvents is applied.^{343–345} The slow, gentle and steady diffusion of two solutions (of metal ion and of organic linker) in appropriate solvents generates larger and better quality crystals that tend to be suitable for single crystal X-ray diffraction analysis. In a typical slow diffusion method, the formation of the crystals occur in three different discrete layers of the layered solvents. For instance, Bunz and co-workers³⁴⁶ used this method to prepare a series of interpenetrated MOFs with anisotropic pore structures from a tetrahedral pyridine ligand. The bottom solvent layer contained the organic layer, while the upper solvent layer contained the metal

ions. The middle solvent layer separated the organic linker solution from the metal ion solution for the slow diffusion to occur. In course of the slow movement of solvents from one layer into other layers, the actual growth of the crystals occurs at the boundary of the layers.

3.2.7 Solvent evaporation and ionothermal Method

In this synthetic method, crystals are formed by slow increase in concentration of mother liquor. The reactants are mixed in a suitable solvent and stirred continuously until the formation of a clear solution. The clear solution is thereafter transferred into a beaker and sealed. The formation of MOF crystals is usually initiated by either saturating the solution, or by the cooling of the solution, or by the removal of excess solvent. For example, Zheng *et al.* used this method to synthesise a variety of copper(II)-lanthanide(III) framework materials.³⁴⁷ In addition, Liao and co-workers used an ionic liquid as solvent for the synthesis and crystallization of a coordination polymer: [EMIM][Cd(BTC)] [where (EMIM) is 1-ethyl-3-methylimidazolium, and (BTC) is 1,3,5-Benzenetricarboxylate] through the application of this method.³⁴⁸ This approach was also employed by other researchers to synthesise 3-D MOFs.³⁴⁹

In addition to these method discussed so far above, other approaches found in the literature²⁸¹ include, template, atomic layer deposition, spray dryer, sol gel, supercritical²⁹⁰ and flow chemistry³⁵⁰ as shown in **Figure 3.1**,²⁸¹ timeline for the most common approaches used for the production of MOFs.

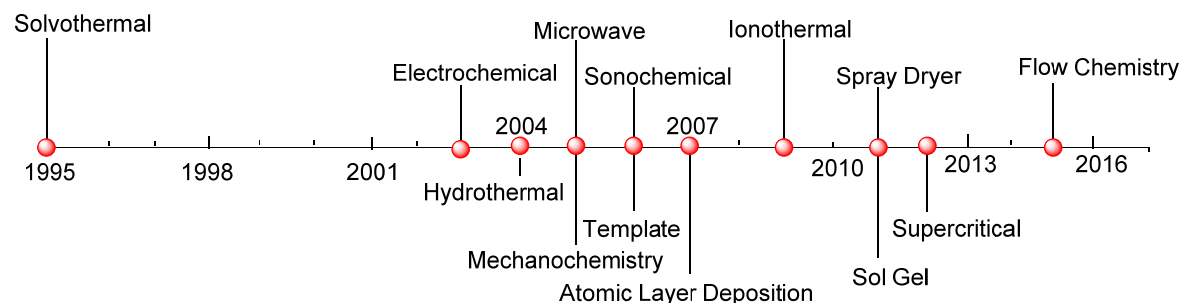


Figure 3.1: Timeline of the most common synthetic methods used for the synthesis of MOFs.²⁸¹

3.3 Activation of Metal-Organic Frameworks (MOFs)

MOFs may be categorized either as rigid or flexible. Rigid MOF materials possess a comparatively stable and robust porous framework with permanent porosity comparable to that of zeolites. Flexible MOFs are framework materials that respond to factors such as temperature and pressure as well as guest molecules.^{351,352} The sensitivity of some MOFs toward temperature or pressure makes them outstanding for temperature/pressure molecular sieving which other traditional adsorbent like zeolites and activated carbons lack. Thus the intense current research efforts towards the industrial application of MOFs in gas separation and storage as well as catalysis can be attributed to their robustness, unique structural properties such as high thermal and chemical stability, unprecedented internal surface areas of up to 5000 m²/g and above, high void volumes of 55-90%, as well as low density from 0.21-1.00 g/cm³, which can be sustained upon the removal of guest molecules such as H₂O from the pores.

When MOFs are being synthesised, solvent molecules or modulators used during the synthesis or sometimes excess organic linkers for example in the case of the synthesis of Cr-MIL-101³⁵³ may be unavoidably trapped in the pores or coordinate to the framework material.³⁵⁴ In order to access the permanent porosity and high surface areas of many framework structures, the trapped solvent molecules or the excess linkers in the pores of the framework materials must be removed. The process by which these trapped solvents are evacuated from the pores of the framework materials is termed activation. If the aim of an activation process is to obtain a MOF material with the highest possible surface area and porosity, then care must be taken during the activation of the MOF.³⁵⁵ Approaches used for the careful activation of MOFs include: conventional heating and vacuum; solvent-exchange; use of supercritical CO₂ (scCO₂); freeze-drying; and chemical treatments.

3.3.1 Conventional Activation

Conventional activation involves the removal of solvent and other guest molecules in the pores of MOFs by the application of heat and vacuum. This means of activation of MOFs is similar to the strategies used for the activation of zeolites and carbons. For example MOFs Cr-MIL-101 $[\text{Cr}_3\text{F}(\text{H}_2\text{O})_2(\text{bdc})_3]^{353}$ and UiO-66 $[\text{Zr}_6(\text{O})_4(\text{OH})(\text{bdc})_{12}]^{356}$ have been activated successfully via this approach, (bdc = benzene dicarboxylate). The surface areas of Cr-MIL-101 and UiO-66 are $4100 \text{ m}^2/\text{g}$ and $1070 \text{ m}^2/\text{g}$ respectively. Both MIL-101 and UiO-66 have remarkable thermal and chemical stability that permits the application of conventional activation to them. But the application of this activation strategy for the purpose of accessing the complete porosity of many other MOFs is limited as a result of complete loss of crystallinity or lack of porosity at the end of the activation exercise.^{343,355,357} The loss of crystallinity and porosity maybe attributed to the fact that the solvent within the MOF pore changes from a liquid phase to a gaseous phase boundary, substantial surface tension and capillary forces are generated that cannot be counterbalanced by the moderate coordination bond energies in many MOF. As a result of this, other ways of MOFs activation are required in order to fully access the large internal surface areas of a large number of MOF materials.

3.3.2 Activation by Solvent-Exchange

Solvent-exchange entails the swapping of a high-boiling solvent such as DMF with a lower boiling point solvent such as trichloromethane followed by a milder activation under vacuum. Lower boiling point solvents are known to have weaker intermolecular interactions which results in the minimization of surface tension and capillary forces in the course of activation. Yaghi and co-workers were the first to use this strategy for the activation of MOFs.^{261,358} The iconic framework material, MOF-5 (IRMOF-1), $[\text{Zn}_4\text{O}(\text{BDC})_3]$ was prepared in DMF-chlorobenzene. The structure

could be retained and subsequently activated after switching the DMF-chlorobenzene for CHCl_3 . The result of the solvent exchange gave a microporous material with a Langmuir surface area of $2900 \text{ m}^2/\text{g}$.^{261,359} Hupps and co-worker carried out further studies on IRMOFs by using conventional activation and solvent-exchanged activation.³⁶⁰ The IRMOF-3 activated conventionally displayed a surface area of $10 \text{ m}^2/\text{g}$ while the same study on IRMOF-16 showed no N_2 uptake. However, when DMF was exchanged for CHCl_3 or THF, the surface areas of IRMOF-3 and IRMOF-16 increased to $1800 \text{ m}^2/\text{g}$ and $470 \text{ m}^2/\text{g}$ respectively,³⁶⁰ although, higher surface areas were expected for IRMOF-3 and IRMOF-16 based on computational calculations.³⁶¹ Thus, even though solvent exchange activation improves porosity, in some cases it still leads to materials with porosity less than expected from computational and single-crystal structure estimation.³⁶⁰ Solvent exchange with acetone coupled with heating cycles under vacuum was used to activate and increase the porosity of a series of isostructural MOFs NOTT-100, NOTT-101, NOTT-102, NOTT-103, NOTT-104, NOTT-105, NOTT-106, NOTT-107, NOTT-108 and NOTT-109 (NOTT = University of Nottingham).³⁶² The S_{BET} of 8 of these MOFs (except those of NOTT-104 and NOTT-108) after activation were reported to be: 1640, 2316, 2942, 2929, 2387, 1855, 1822 and $1718 \text{ m}^2/\text{g}$, respectively.³⁶²

3.3.3 The Use of scCO_2

The use of supercritical carbon dioxide (scCO_2) for the activation of MOFs is an extension of solvent-exchange; in that scCO_2 is used for the activation instead of solvent-switch such as CHCl_3 or THF for DMF.²⁹⁰ The use of scCO_2 is a milder activation approach compared to both conventional activation and solvent exchange activation, both of which may cause framework collapse.^{359,360} This is true in that the use of scCO_2 for activation of MOFs circumvents the liquid-to-gaseous phase change of guest solvent molecules and instead goes through a supercritical phase

directly which bypasses the negative effect of surface tension and capillary forces associated with liquid-to-gaseous phase.³⁵⁹ The surface tension of liquid CO₂, ethanol (EtOH), methanol (MeOH), acetone, dichloromethane (DCM), N,N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO) and water are 0.6, 22.0, 22.1, 23.0, 27.8, 34.4, 42.9 and 72.7 dynes/cm respectively.³⁶³ Although Nelson *et al.* were unable to obtain S_{BET} for IRMOF-16 using conventional methods, when these MOFs which contained Zn₄O nodes and carboxylic acid organic linkers were activated with scCO₂, IRMOF-3 displayed an S_{BET} of 2850 m²/g which represent a 258-fold increase over conventional activation and 1.6-fold increase over solvent-exchange. The S_{BET} observed for IRMOF-16 was reported as 1910 m²/g which represent a 4-fold increase over the same material when activated by solvent exchange.³⁶⁴ Although, the use of scCO₂ for activation has been reported not to give the desired result in some cases,^{277,365,366} a good number of successes have been reported for the activation of MOFs.^{80,367–371} The driving force behind the intense interest in the use of scCO₂ for activation of MOF materials maybe due to its low cost as well as the ease to scaling-up. **Table 3.0** below depicts interesting results obtained via the use of scCO₂ for activation. The MOFs are reported to display the largest S_{BET}, pore volume, extreme pore and aperture sizes, encapsulated reactive species and dynamic structural features.

Table 3.0: Selected MOFs and some of their relevant material characteristics enabled by scCO₂ activation.

MOF	S _{BET} (m ² /g)	Pore Volume (cm ³ /g)	Ref.
Nu-110	7140	4.40	80
MOF-210	6240	3.60	232
SNU-70'	5290	2.17	372
[Co ₆ (btb) ₄ (bp) ₃]	5200	2.10	373
UMCM-9	4970	1.80	374
Bio-MOF-100	4300	4.30	375
FJI-1	4043	1.43	376
DUT-13	2532	1.98	377
IRMOF-74XI	1760	3.41	378
P11-16/1	1009	N/A	379

The concept of “flowing” scCO₂ activation has also been applied in columns containing MOF samples.³⁷⁴ The scCO₂ is made to pass through the MOF sample in the column and effectively displaces the guest solvent molecules. One benefit of this “applied scCO₂ flowing technique” is that guest solvent molecules such as DMF in a MOF can be removed with ease without exchange of the DMF for CO₂ in the pores.³⁸⁰ EtOH has been reported as a useful solvent used in the place of DMF because DMF damages some equipment components.^{359,360}

3.3.4 Activation by Freeze-drying

Although this approach is relatively new,³⁸¹ several research groups have applied it to the activation of MOF with various functionalities.^{359,382–386} The technique involves the exchange of the guest with another solvent following freezing-thaw cycles. For example, Lin and co-workers use this technique to activate two isorecticular Cu paddlewheel based MOFs ([Cu₂(L)(H₂O)₂]) (L = methanetetra(*p*-benzoic acid)).³⁸² The guest solvent molecules were exchanged for benzene and the sample left in benzene. Following this treatment, the sample was frozen at 0 °C, and then put under vacuum, and then warmed back to room temperature three times. At the end of the freeze-thaw cycles, the samples were put under vacuum at a temperature and pressure lower than the triple point of the solvent. Finally the sample was warmed under reduced pressure, wherein the benzene sublimed. The sublimation of the benzene by-passed the liquid phase and avoided the detrimental effects of surface tension and capillary forces.³⁸² The resulting S_{BET} values of the two isorecticular ([Cu₂(L)(H₂O)₂]) MOFs after the freeze-drying activation were reported to increase significantly in comparison to the same MOF sample but subjected to solvent exchange activation. In addition, it was also reported that the X-ray diffraction pattern of the guest-solvent sample differed from the benzene-freeze-dried sample.

Benzene is known to be carcinogenic, as a result, Zhang and co-workers³⁸⁷ used cyclohexane (non-carcinogenic) in the place benzene for the activation of MOF [Zn₂L(Im)]·7(DMF) (FIR-3; L = Tris((4-carboxyl)-phenylduryl)amine, Im = imidazole; FIR denotes Fujian Institute of Research). The conventionally activated material gave an S_{BET} of 24 m²/g, while the cyclohexane-freeze-dried material exhibited an S_{BET} of 497 m²/g

Li *et al.*³⁸⁸ reported the use of a gel-like freeze-drying strategy for the synthesis of hierarchically porous polyoxometalate-based MOFs (NENU-(HP-I), NENU-(HP-II), NENU-(HP-III), NENU-(HP-IV) and NENU-(HP-V) catalyst. It was reported that the freeze-drying process enabled the preparation of the material with high stability, large mesopore sizes as well as high pore volume.

3.3.5 Activation by chemical treatment

MOFs are also activated by treatment with chemicals (acid treatment). All the activation techniques discussed above are centred on guest solvent molecules that are neutral species. However, if the guest solvent molecules are ionic species or high boiling point solvents such as DMF, DEF or DMSO,³⁸⁹ then such molecules cannot be removed from a cavity or a coordination site of an evacuated MOF by mere heating since they have low volatility or, in the case of ions, they are not volatile.^{364,390–392} Hence, in cases where solvent molecules such as benzoic acid or other ionic species are coordinated in MOFs during synthesis (for example as modulators) then chemical treatment maybe the best option. For example, some Zr₆-based node MOFs are known to possess excellent stability both in aqueous and acid solution.³⁵⁶ However, in most cases during synthesis a copious amount of acid (benzoic acid) is used to enhance and modulate the nucleation and growth into MOFs. At the end of the synthesis, the acid is removed via rigorous washing or by chemical treatment. It has been observed,³⁹¹ that for a tetracarboxylate-porphyrin-based MOF such as PCN-222 (also referred to as MOF-545)³⁹⁰ that treatment with concentrated HCl followed

by activation under vacuum and heat resulted in the formation of material with increased pore volume.³⁹¹ However, the specific function of the concentrated HCl was not given. Similarly, tetracarboxylate-pyrene-and Zr₆-containing MOF (NU-1000) studied by Hupp and co-workers revealed that HCl cleaved the coordinated benzoate from the Zr₆ node. The resulting effect of the cleavage was a material with meso-porosity. Jeong and co-workers used chemical treatment dichloromethane for the activation of open metal sites in the copper- containing MOF materials (HKUST-1 and Cu-MOF-2).³⁹³ However, it was reported that strongly coordinated solvent molecules, such as DMF, were difficult to evacuate completely by the activation with DCM.^{389,393} Following this observation, Bae *et al.*³⁸⁹ applied this approach for the activation of open-metal sites in MOFs. They used a multiple coordination exchange (CE) process starting with acetonitrile (MeCN), MeOH, EtOH and finally with DCM to obtain complete activation of open coordination sites (OCSs). In addition, MOF-74 (Ni) was also activated with a multiple CE process.³⁸⁹

3.4 Characterisation of Metal-Organic Frameworks MOFs)

The most important means for the characterisation of MOFs are: (1) single crystal X-ray diffraction (XRD) which provides absolute structural information about the MOF; (2) powder X-ray diffraction (PXRD) to establish crystallinity and phase purity of the bulk; (3) elemental analysis (4) thermogravimetric analysis (TGA) for the determination of the thermal behaviour of MOF and in some cases for the estimation of pore volume; (5) surface area measurement which provides information about the capability of a porous material for gas adsorption; (6) gas adsorption study which estimates the sum of the pore volume of MOFs; (7) infra-red spectroscopy which can be employed to determine the presence or absence of IR active functional group in the frame works; (8) scanning electron microscope (SEM) which measures the crystal size and morphology which

can be coupled with energy dispersive X-ray spectroscopy (EDX); and (10) inductive coupled plasma optical emission spectroscopy (ICP-OES).

3.4.1 Single crystal X-ray Diffraction (XRD)

XRD is the best and most effective single method of characterisation of MOF materials to determine unambiguously its structure, i.e. information about the identity and arrangement of atoms in a single crystal. However, some major limitations are associated with XRD. For example, the collection of reliable data which is a function of the size (50 μm and above) and quality of the crystal. This can be challenging as the general procedures used to obtain large and high quality MOF crystals may not be adequate.^{290,394} In addition, MOF crystals usually have large amount of disordered solvents in their pores. SQUEEZE is the commonly used software for the processing of data due to disordered solvent in the pores of MOF structures.³⁹⁵ Although, the collection of data for MOFs is better at low temperature, the presence of disordered solvent means that the collection of data at higher temperature can sometimes yield better diffraction data as disordered solvent freely tumble (i.e. become highly disordered) and contributes less to the diffraction peaks.^{80,290} Furthermore, un-activated MOFs tend to diffract better than activated ones. Symmetry mismatches are another major challenge associated with MOF refinement. That is the symmetry mismatches between lattice of metal nodes (usually higher symmetry) and those of lattice of organic connectors (usually lower symmetry). Thus, MOF structures with higher symmetry linkers are less troublesome to refine than those with low symmetry organic connectors. In addition, interpenetration in MOF structures may also pose problems in the crystallographic characterisation of MOFs even though, interpenetrated MOF materials frequently display better diffraction patterns because they are more dense and possess less empty space.^{396–398}

3.4.2 Powder X-ray Diffraction (PXRD)

PXRD is used for the characterisation of MOFs, principally if the crystals are too small for single-crystal X-ray diffraction. The powder X-ray diffraction patterns provide information about the crystallinity of MOFs (since sharp diffraction peaks are indicators of crystallinity of the bulk MOFs material) and can be used to obtain unit cell parameters and determination of the bulk crystallinity after de-solvation. Powder patterns can be predicted from the single crystal structure and compared with experimental powder patterns or through the use of computational modelling^{399–401} to verify product identity.

One common method for the preparation of sample for PXRD analysis involves the loading of finely ground powdered sample onto a flat plastic, glass or aluminium disc sample holder. The sample can either be dry-loaded onto the sample holder or attached using oil or volatile solvents. This method of sample preparation works well for most MOF samples but sometimes plate or needle morphology crystals tend to deposit with preferred orientation when MOF samples are prepared by this way. The calculation of simulated powder patterns is based on the assumption that crystallites are randomly oriented.²⁹⁰ Based on this assumption, there may be significant differences in peak intensities between simulated and experimental PXRD patterns. To circumvent problems linked with preferred orientation, MOF samples are usually rotated continually during data collection in a conventional sample holder or in a capillary tube. The spinning of the sample enables the orientation of the crystallites to align in a nearly random with respect to the detector. Overly broad diffraction peaks are features of undersized crystallites and associated Scherrer broadening instead of poor crystallinity. It is difficult to solve a structure from powder data although it has been done in some cases.^{394,402,403}

3.4.3 Elemental Analysis

Elemental analysis is also a very useful tool for the determination of the composition/purity of MOF frameworks. It measures the percentage of carbon, hydrogen and nitrogen in a sample which can then be compared with the molecular formula of the MOF provided by the single-crystal X-ray diffraction. Thus the experimentally determined elemental analysis result can be compared with expected result based on the molecular formula generated from the single-crystal X-ray diffraction. This comparison gives an indication of the purity of the MOF in terms of composition and the possible presence of additional solvent molecule(s).

3.4.4 Thermogravimetric Analysis (TGA)

TGA is used to determine the thermal stability as well as the decomposition characteristics of a given MOF by observing its weight loss as a function of temperature, usually from room temperature to several hundreds of degrees centigrade until the organic component is lost.^{264,358,404–}
⁴⁰⁶ The weight loss can be used to determine the amount of solvent in the pores and how the MOF decomposes at different temperatures. With this information the percentage weight loss of different components and stages can be calculated. Thus, in a typical TGA trace one will see several “segments” which correspond to the loss or decomposition of different components of the MOF framework. The mass that remains after the heating is usually the oxidized metal species such as the carbonate or the metal-oxide if air is used.^{358,404,405} Although the loss mass does not necessarily mean structural changes. Complementary measurements are worth taking to verify the thermal stability of a MOF with temperature variation including in situ PXRD^{290,407,408} and /or sorption measurement carried out on samples subjected to changing temperatures.⁴⁰⁹

3.4.5 Surface Area Measurements (N_2 Adsorption & Desorption Isotherms)

Adsorption isotherms for inert gases at cryogenic temperatures can be used for the determination/estimation of apparent surface areas of MOFs. Surface area measurement is a vital means of estimating the gas storage capability of porous materials.^{410,411} For example MIL-101 and MOF-177 have S_{BET} of 4100 m²/g and 4500 m²/g respectively based on N_2 adsorption isotherm while zeolite Y and activated carbons have surface areas of 904 m²/g and 2000 m²/g respectively.⁴¹² Adsorption of gases by MOFs is primarily due to interactions of guest gas molecules with atoms of the adsorbent wall. Therefore it is logical that a large surface area either per unit mass or per unit volume is desirable for high gas uptake. The gas adsorption of different MOFs falls into three regimes according to Frost *et al.*⁴¹³; (i) at low pressure a MOF's adsorption of H_2 or CO_2 correlate with heat of adsorption (ii) at intermediate pressure gas uptake by MOFs correlates with a MOF's surface area and (iii) at high pressure a MOF's uptake of H_2 or CO_2 correlates with the void volume available in the MOF.^{413,414} But some MOFs show exceptions in that at low pressure the pores are filled thereby shifting the MOF volume to the high pressure regime.

The N_2 gas adsorption at 77 K is the most commonly used strategy for the estimation of the surface area of MOFs. The measurement starts with the activation of the MOF material before the isotherm can be collected. If the MOF material is not properly activated, then the information obtained from the N_2 desorption isotherm may not be reliable. Information about the quantity of sample used for the analysis is vital in that, as a rule-of thumb, the amount of sample (mass) multiplied by the specific surface area (m²/g) of the sample should be equal to 100 m² or more in order to obtain data that are reliable.²⁹⁰ In addition, the choice of data analysis protocol can also contribute to

obtaining reliable data from a N₂ desorption isotherm. An incorrect data analysis may either overestimate or underestimate the apparent surface areas of a given MOF sample.^{290,415–417}

Two general methods commonly applied for calculating the surface area of porous materials are the Langmuir surface area equation method⁴¹⁸ and the BET theory method.⁴¹⁹ The interaction of the gas molecules with MOFs is dependent upon the metal atoms as well as the organic strut. The Langmuir surface area measurement equation is usually applied to porous materials with (i) uniform surfaces, (ii) surfaces in which there is no interaction between the adsorbate and adsorbed molecules as well as (iii) surfaces which form a monolayer with adsorbates and as a result, tends to overvalue the apparent surface areas of most MOFs (in some cases by 50% or more).²⁹⁰ Whereas the BET surface area measurement takes into considerations porous materials that have multilayer interactions. Adsorption surface area measurements by Langmuir equation and BET surface area measurements differ a bit in that the calculation from the former is usually larger than that from the latter.

Currently the BET theory is used for apparent surface area calculations of MOF materials because the pore size of most MOFs supports multilayer adsorption.²⁹⁰ Thus using the BET equation below:

$$\frac{P/P_o}{n(1-P/P_o)} = \frac{1}{n_m C} + \frac{C-1}{n_m C} \left(P/P_o \right)$$

Where n = amount of N₂ gas adsorbed, P = pressure of N₂, P_o = saturation pressure of N₂

C = BET constant and n_m = monolayer capacity.

A plot of $\frac{P/P_o}{n(1-P/P_o)}$ VS (P/P_o)

will give a straight line graph with intercept = $1/n_m C$, and slope = $C-1/n_m C$.

The apparent surface area of a MOF can then be estimated using the plot. A linear region is selected based on Rouquerol *et al.*⁴²⁰ proposed criteria which are (a) the “C” must be positive,

(b) $n(1-P/P_0)$ should increase in a monotonic manner with (P/P_0) , the monolayer capacity (n_m) should correspond to pressure within the limit of the data, and (d) the calculated value for the monolayer formation $[1/(\sqrt{C} + 1)]$ should be approximately equal to (P/P_0) at the monolayer capacity.

Thus from such a plot, the intercept and slope from the linear region as well as the BET area (apparent surface area), n_m and “C” can be obtained. In some publications, the empirical explanation for the application of BET theory with MOF has been detailed, including some computationally made isotherms for flawless (in silico) MOF structures in which absolute S_{BET} can be independently calculated or estimated.^{48,290,415–417}

Information such as pore volume and pore size distribution of a MOF can also be obtained from such an isotherm although with some caution.^{290,411,421} The pore volume and pore size distribution of a MOF can be analysed using models such as density functional theory (DFT) or the Barrett-Joyner-Halenda method⁴²² amongst others.

3.4.6 Nuclear Magnetic Resonance (NMR) Spectroscopy

NMR spectroscopy can also be utilized for the determination of the purity of MOF, linker- metal ratio, unused modulators as well as the presence or absence of solvent after activation.³⁵⁴ Many MOFs are known to be insoluble in common NMR solvents and so for the analysis of a MOF sample, the sample must first be digested before a spectrum can be obtained.⁴²³ The conventionally used approach for the digestion of a MOF for the purpose of NMR analysis involves the addition of D_2SO_4 (5-10 drops) to the sample (1-2 mg) followed by sonication of the mixture until the sample disperses in the acid. Following the sample digestion process, about 0.5 ml of $DMSO-d_6$ can be added to the mixture to dilute and completely dissolve the sample. Sometimes sonication and heating may be required after the addition of $DMSO-d_6$. For the analysis of the data collected

to have meaning, the sample must be completely dissolved.⁴²⁴ However, if poor dissolution of MOF sample is observed following the procedure described, then less MOF sample and more acid can be used as necessary. Alternatively, instead of using D₂SO₄, 0.1 M NaOD (dilution of 40 wt % NaOD with D₂O), hydrofluoric acid diluted with D₂O can be used also for the digestion of MOF materials for NMR spectroscopy analysis.⁴²⁵

Solid-State NMR (SS-NMR) spectroscopy has also been utilized for the analysis of MOFs, especially in a bid to investigate the local chemical environment in a MOF.^{426,427} The SS-NMR technique has been successfully used for the qualitative analysis of the chemical state of some functional group such as the oxidation state of phosphorus atom inside a MOF.^{428–432} The method can also be used to gain insight about the supramolecular interactions as well as kinetics of small molecular species docking inside a MOF.⁴³³

3.4.7 Gas Adsorption Measurements

One problem associated with carbon capture and storage (CCS) is that the saturated adsorption measurement of CO₂ near room temperature or at room temperature and high pressure are directly connected to the maximum capacity of adsorption of MOFs for CO₂.⁴⁴ The sum of the pore volume of MOFs is fundamentally proportional to the volume of CO₂ that can be adsorbed at high pressure which strongly correlates with the S_{BET} of MOFs as discussed above.

Gravimetric and volumetric methods can both be used for the measurement of gas adsorption in MOFs.^{24,139,409,413,434} The gravimetric method involves calculation in terms of mass differences between the mass of adsorbed gas in MOFs by means of highly-sensitive balances^{355,435,436} whereas the volumetric technique entails the measurement of pressure changes as the MOF adsorbs gases in a fixed volume.^{139,435} Both techniques have their pros and cons. For example, the result from the gravimetric technique can be affected drastically by impurities stemming from the gas source

whereas the volumetric method suffers mostly from accumulative errors.^{139,435} However, the volumetric method has the advantage of easy operation as well as availability of equipment.

3.5 Organic Linkers

The synthesis of MOFs requires the presence of an organic ligand that coordinates with metal ions. The organic connectors are typically carboxylate (ditopic, tritopic, tetratopic, hexatopic or octatopic), heterocyclic-pyridyl linkers (ditopic and polytopic)⁴³⁷ or phosphonate linkers.²⁷⁶

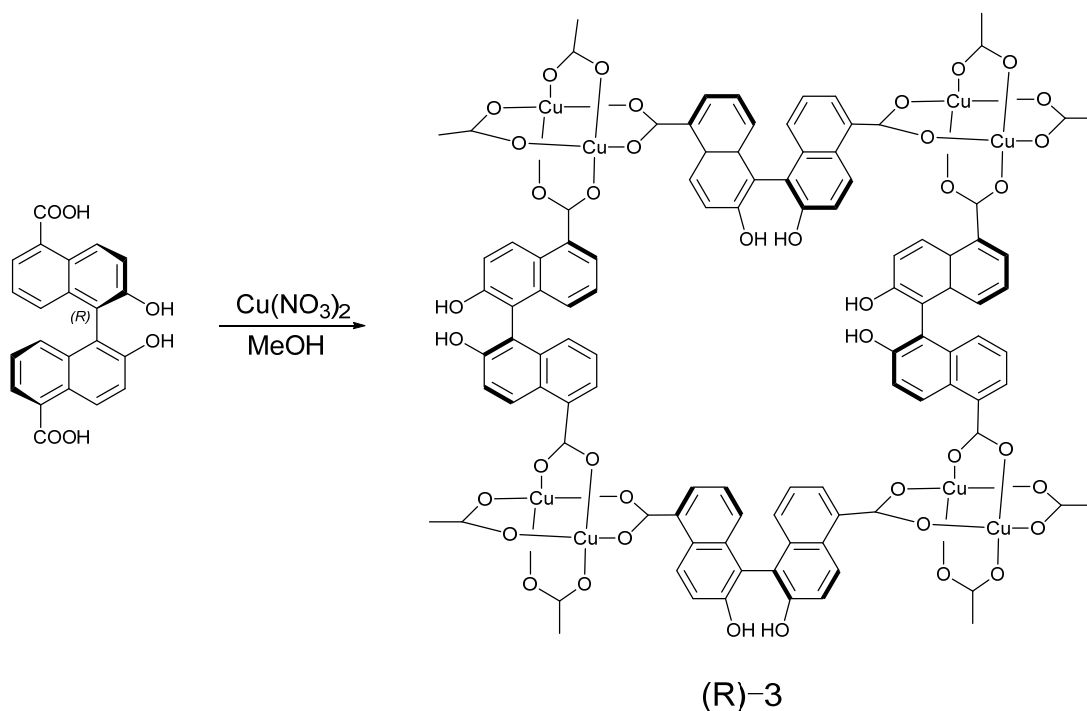
3.5.1 Ditopic Carboxylate Linkers

Ditopic carboxylate connectors have been used extensively for the synthesis of MOFs because of their ready accessibility and well defined structures in combination with secondary building units (SBUs). Ditopic carboxylate linkers can form a variety of structural units such as 4-connected paddle-wheel clusters, octahedral clusters, trigonal-prismatic clusters, 12-connected clusters, and infinite chain clusters.

The same reaction starting materials (metal ions and organic linkers) can give rise to different crystal structures due to variations in reaction conditions. For example, MOF-5 [$\text{Zn}_4\text{O}(\text{BDC})_3(\text{DMF})_8(\text{C}_6\text{H}_5\text{Cl})$] was solvothermally synthesised by the reaction of a ditopic organic linker – 1,4-benzenedicarboxylate (BDC) with zinc nitrate - $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.²⁶¹ But when trimethylamine-toluene was slowly allowed to diffuse at room temperature into an N,N'-dimethylformamide (DMF)-toluene solution containing $\text{Zn}(\text{NO}_3)_2$, and BDC, colourless prism-shaped crystals of $\text{Zn}(\text{BDC})(\text{DMF})(\text{H}_2\text{O})$ was obtained instead of MOF-5.³⁴³ The $\text{Zn}(\text{BDC})(\text{DMF})(\text{H}_2\text{O})$ is a 2-D sheet whereas MOF-5 is a 3-D framework structure.

Examples of a ditopic linker incorporated into 4-connected paddle wheel clusters are found in MOF-118 and MOF-601.⁴³⁸ MOF-118 is a 2-D sheet synthesised by the use of a ditopic linker - 4,4'-biphenyldicarboxylate (BPDC) and copper (II) acetate [$\text{Cu}_2(\text{CH}_3\text{COO})_4$] as the source of the

metal ion. Copper acetate has the capability to assume the paddle-wheel structure with two solvent molecules completing its coordination sphere. MOF-601 is a 3-D MOF obtained using 2,2'-dicyano-4,4'-biphenyldicarboxylate (CNBPDC). Furthermore, 2,2'-dihydroxy-1,1'-binaphthalene-5,5'-dicarboxylate (5,5'-BDA) was used by Tanaka and co-workers³⁴⁵ for the preparation of a chiral MOF $[\text{Cu}_2(5,5'\text{-BDA})_2(\text{H}_2\text{O})_2]\cdot\text{MeOH}\cdot 2\text{H}_2\text{O}$, using $\text{Cu}(\text{NO}_3)_2$ in aqueous MeOH solution by the slow diffusion method of MOF synthesis as shown below in **Scheme 3.0**.



Scheme 3.0: Preparation of a chiral MOF via slow diffusion.³⁴⁵

Some of the ditopic ligands used in the literature for the synthesis of MOFs are shown in **Figure 3.2**.

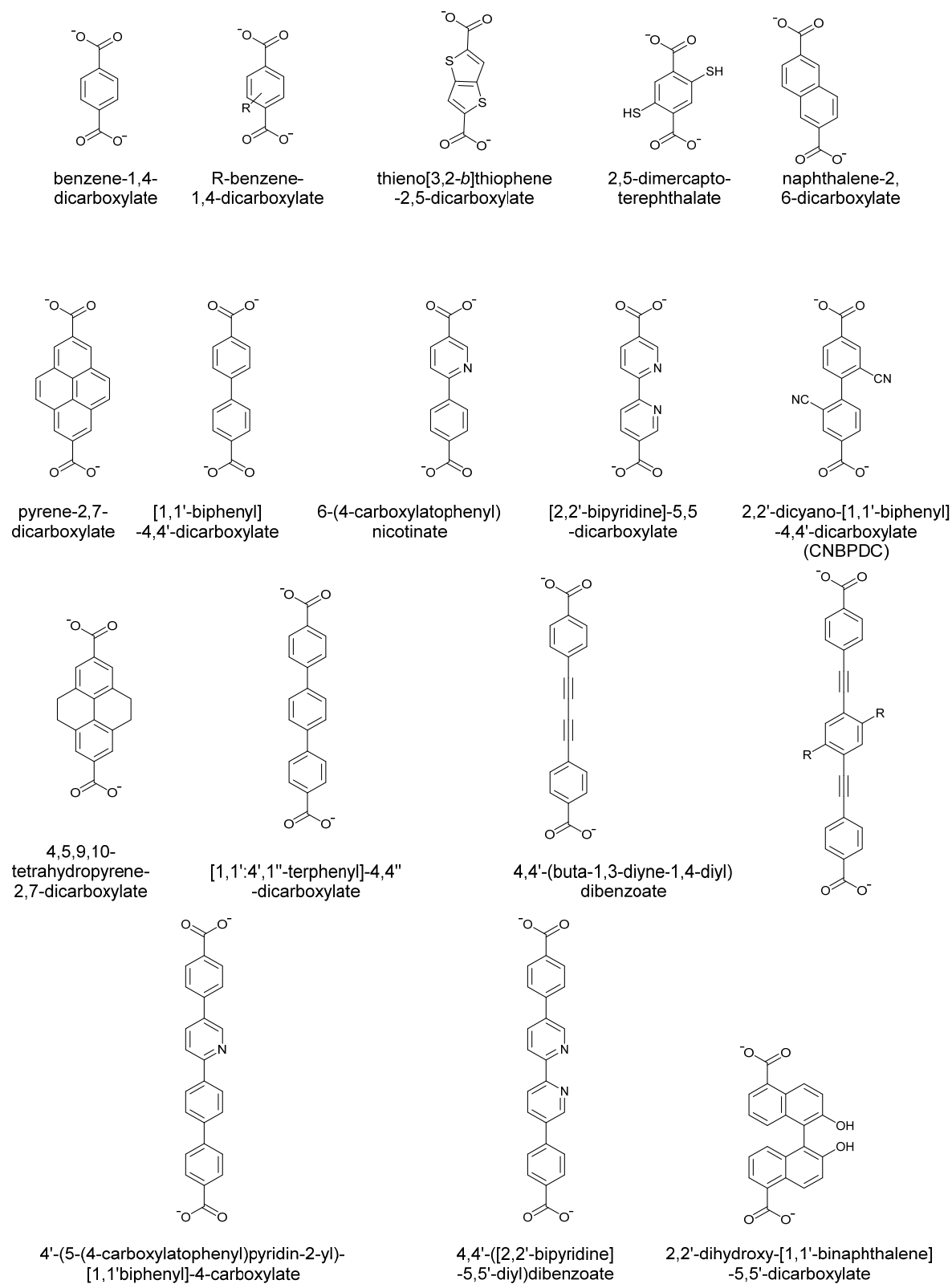


Figure 3.2: Some ditopic carboxylate linkers used for the synthesis of MOFs

3.5.2 Tritopic Carboxylate Linkers

A variety of tritopic carboxylate linkers such as those shown in **Figure 3.3** have been used for the synthesis of MOFs. For example, MOF-177 with S_{BET} of 4,500 m^2/g was synthesised solvothermally using the octahedral $\text{Zn}_4\text{O}(\text{CO}_2)_6$ cluster with the 1,3,5-benzenetricarboxylate (BTC) linker.⁴¹² While MIL-100(Cr) was assembled with $\text{Cr}_3\text{O}(\text{CO}_2)_6$ cluster and BTC.⁴³⁹ The network of MIL-100 was reported to possess two kinds of mesoporous cages with accessible cage diameters of 25 and 29 Å. HKUST-1 (also known as MOF-199)⁴⁴⁰ with $S_{\text{BET}} = 692.2 \text{ m}^2/\text{g}$ was also synthesised with BTC and a dicopper paddle wheel SBU as the metal node.⁴⁰⁶ A good number of isorecticular MOFs have also been prepared using elongated tritopic carboxylate linkers. For example, meso-MOF-1 was synthesised using 4,4',4''-s-triazine-1,3,5-triyltri-*p*-aminobenzoate (TATAB) as linker.⁴⁴¹ PCN-6 was prepared with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and 4,4',4''-s-triazine-2,4,6-triyl-tribenzoate (TATB).⁴⁴² MOF-399 has a void fraction of (94%) and density of ($0.126 \text{ g}/\text{cm}^3$) the second lowest after (NU-1301 = $0.124 \text{ g}/\text{cm}^3$),⁴⁴³ was prepared by the use of a tritopic carboxylate linker (BBC) and $\text{Cu}_2(\text{CO}_2)_4$ cluster.⁴⁴⁰ MOF-143 and MOF-338 were synthesised with BTB and TAPB respectively using the $\text{Cu}_2(\text{CO}_2)_4$ cluster.⁴⁴⁰ Furthermore, MOF-180 (porosity = 89%) and MOF-200 (porosity = 90%) were prepared by the use of BTE and BBC respectively.²³² Biphenyl-3,4',5-tricarboxylate (BHTC) has been used for the synthesis of UMCM-150 (UMCM = University of Michigan crystalline material) with $\text{Cu}_3(\text{CO}_2)_6$ cluster as the source of metal node.⁴⁴⁴ The UMCM-150 was reported to have an apparent S_{BET} of 2300 m^2/g and Langmuir surface area of 3100 m^2/g as well as a CO_2 uptake of 4.68 mmol/g at 273 K/ 1 bar.⁴⁴⁴ Duan *et al.* prepared NJU-Bai3,⁴⁴⁵ by the use of 5-(4-carboxybenzoylamino)-isophthalate (CAIA) as a tritopic carboxylate linker and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ as the source of metal ion. It was reported that the presence of the amide group in CAIA extended the length of the cell as well as providing amide groups on the

surfaces of the pores of NJU-Bai3, which enhanced the uptake (6.21 mmol/g at 273 K/ 1 bar) and selectivity of CO₂ over other flue gas molecules.

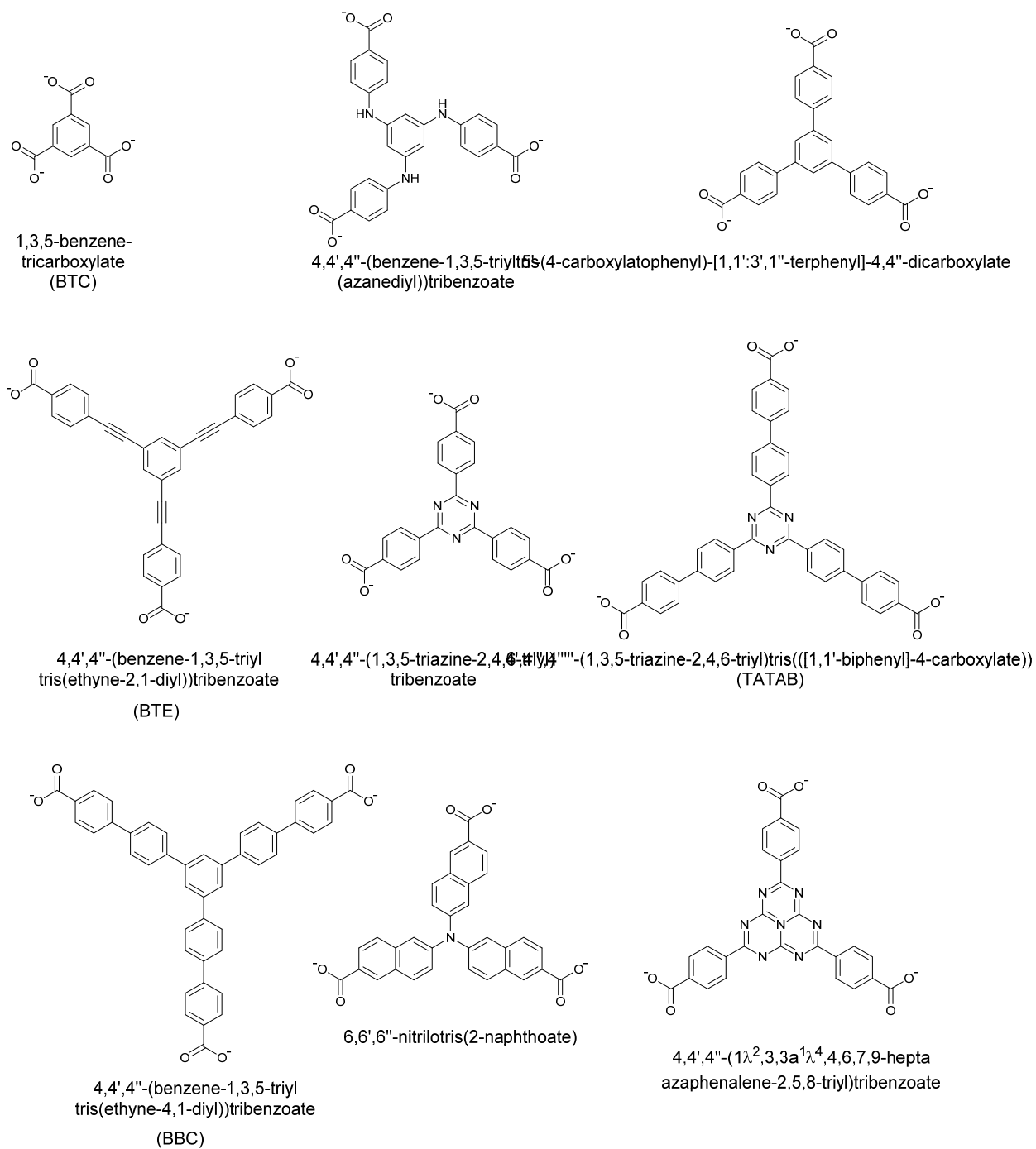


Figure 3.3: Some tritopic carboxylate linkers used for the preparation of MOFs

3.5.2 Tetratopic Carboxylate Linkers

Tetratopic carboxylate connectors are good building units used for the construction of many MOFs, particularly those with tetrahedral geometry. Tetrahedral linkers are becoming more popular in the construction of MOFs because they possess full T_d symmetry, the highest symmetry in a linker that is currently attainable through organic synthesis.⁴³⁷ High-symmetry, building units are preferred in the construction of MOFs for several reasons. Some of these reasons are: (I) they expedite the packing process of repeating units during the formation of crystallites,^{437,446–448} (II) tetrahedral connectors may assume the geometry of any T_d subdivision such as T, C_3 , C_2 , C_s , and C_1 ^{437,449} as shown in **Figure 3.4**, and as such give diversity in the structures of MOF materials, (III) the tetrahedral linkers by nature are 3-dimensional; hence, when they are used in the construction of framework materials, wide channels and/or large pores are likely to form.

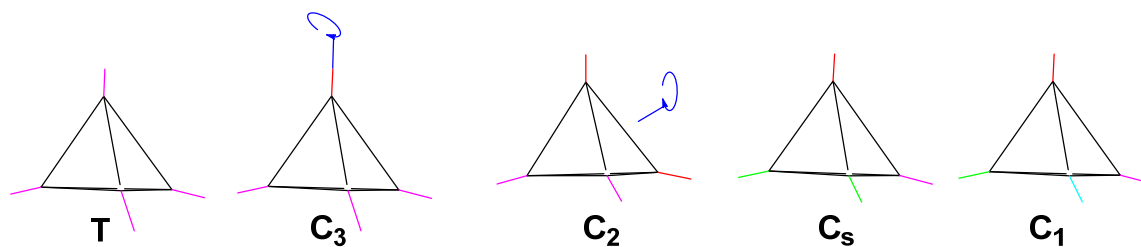


Figure 3.4: Symmetry elements of a T_d symmetry.

The porosity, stability and the possibility of interpenetration in MOF materials are closely related to their topology.^{448,450,451} MOFs constructed by the combination of tetrahedral linkers, square planar linkers and (SBUs) such as hexagonal bipyramid clusters of metals are usually associated with network topologies such as fluorite (**flu**), platinum sulfide (**pts**) and **alb/p** as shown in **Figure 3.5**.⁴³⁷ These network topologies have the possibility of high porosity. The **flu** topology represents the combination of a tetrahedral linker with 8-connected cubic SBUs in the ratio of 2:1. The **flu** topology is potentially useful in MOFs because of its large cavity and non-interpenetrating

nature.⁴⁵² A framework containing **flu** topology does not suffer from self-interpenetration even when extended organic linkers are used.^{437,453}

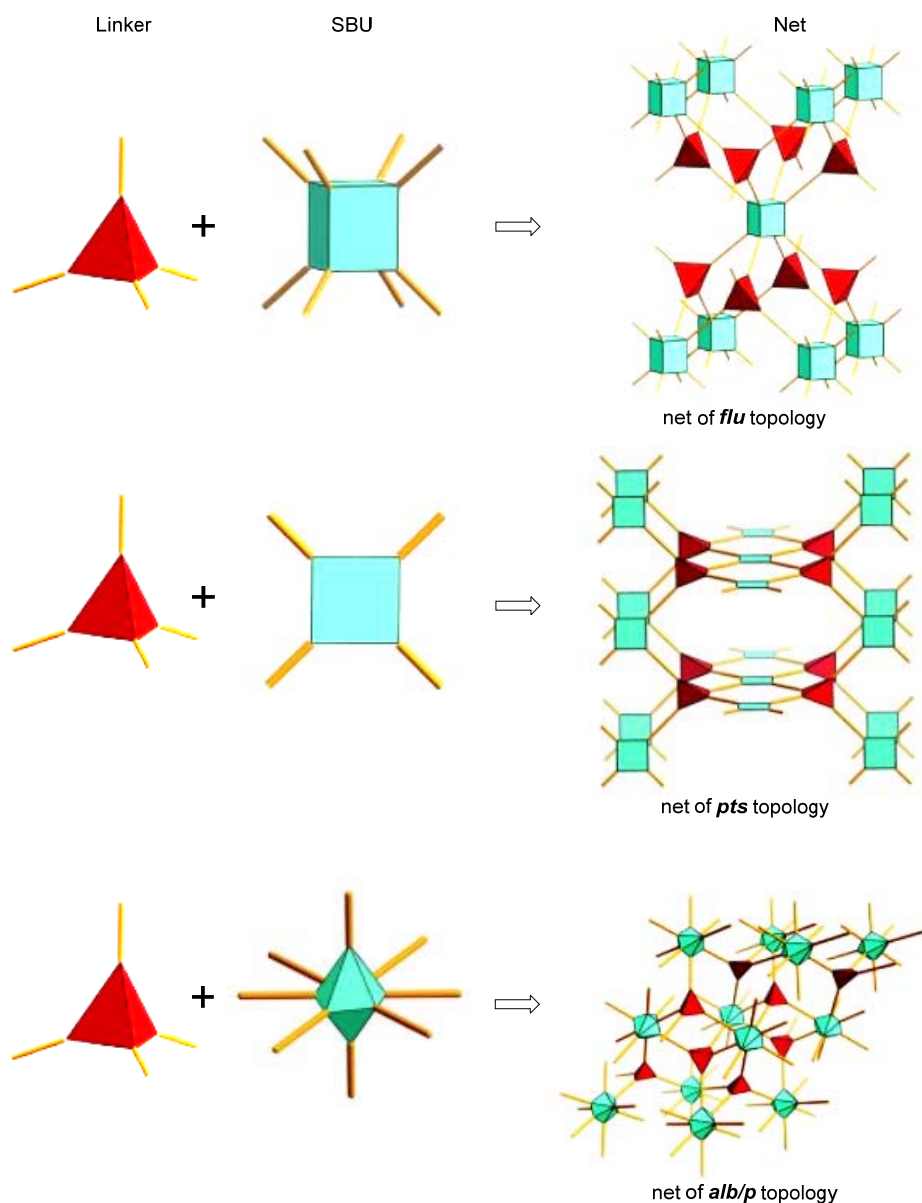


Figure 3.5: Pictorial representation of some topologies associated with MOFs by the combination of tetrahedral linkers and SBUs (adapted from ref.⁴³⁷)

The **pts** topology on the other hand is by default the preferred topology formed by the combination of a 4-connected tetrahedral linker and a 4-connected square planar SBU in a 1: 1 ratio. For example, the combination of a dinuclear paddle-wheel SBU and a rigid tetrahedral connector generally leads to the formation of framework materials with pts topology.^{437,446} The alb/p

topology involves the combination of 4-connected tetrahedral linker and 8-connected hexagonal bipyramidal SBUs.⁴⁴⁹ Unlike the flu topology, frameworks containing alb/p topology usually suffer from self-interpenetration.^{266,437}

The combination of tetratopic carboxylate linkers such as 4,4',4'',4'''-methanetetrayltetrabiphenyl-4-carboxylate (MTBC) and 8-connected Zr_6 clusters as SBU gave (M-TMBC, M = Zr or Hf),⁴⁵⁴ and PCN-521,⁴⁵² The S_{BET} of PCN-521 was reported to be 3411 m²/g and are amongst the most porous MOFs assembled from tetratopic carboxylate linkers.⁴⁵² MOF-11 [Cu₂(ATC)·6H₂O] was prepared by Yaghi and co-workers via hydrothermal reaction of Cu(NO₃)₂ and a tetrahedral carboxylate linker, 1,3,5,7-adamantane tetracarboxylate (ATC).⁴⁵⁵ MOF-11 was reported to possess a permanent porosity as well as a Langmuir surface area and pore volume of 650 m²/g and 0.20 cm³/g respectively. However, when 4,4',4'',4'''-methanetetrayltetrabenzoate (MTB) which is a longer tetrahedral connector was solvothermally reacted with a di-zinc paddle-wheel as SBU, MOF-36 [Zn₂(MTB)(H₂O)₂·(DMF)₆(H₂O)₅] was formed.⁴⁵⁶

A tetratopic carboxylate linker based with silicon as the central atom has also been used for the synthesis of MOFs. For example, IMP-8Cd [Cd₂(L)(H₂O)₂·(DMA)], IMP-8Mn [Mn₂(L)(H₂O)₂·(DMA)_{2.5}], IMP-9 [Cu₂(L)(H₂O)₂·(DMA)₁₂], IMP-10 [Me₂NH₂]₂[Cd₃(L)₂(H₂O)₂·(DMA)₈(H₂O)₈], IMP-11 [Me₂NH₂]₂[Zn₃(L)₂·(DMF)₆], and IMP-12 [Me₂NH₂]₂[Zn₃(L)₂·(DMF)₃] were prepared solvothermally by Davies and co-workers²⁶⁵ by the use of 4,4',4'',4'''-tetrakis-carboxylatephenylsilane (L = TCPS) with appropriate SBUs and solvent combination. In addition, PCN-512 was prepared by solvothermal method using TCPS and copper nitrate [Cu(NO₃)₂·2.5H₂O].⁴⁴⁹ The PCN-512 was reported to exhibit 72.7% calculated solvent accessibility volume and an S_{BET} of 601 m²/g. Furthermore, TCPS also reacted solvothermally with zinc nitrate in DEF at 85 °C to give PCN-511, Zn₃(HTCPS³⁻)₂,⁴⁴⁹ with an

S_{BET} of 702 m^2/g and a solvent accessible volume of 45.6%. PCN-511/IMP-11 were reported to possess a solvent accessible volume and S_{BET} of 48.4%²⁶⁵ and 1284 m^2/g ⁴³⁷ respectively after activation using a freeze-drying approach. A semi-rigid tetratopic carboxylate linker N,N,N',N'-tetrakis(4-carboxyphenyl)-1,4-phenylenediamine (TCPPDA) also reacted under solvothermal conditions with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in dimethyl sulfoxide (DMSO) resulting in the formation of a MOF with pts topology.⁴⁵⁷ The Langmuir surface area of this MOF was reported to be 627 m^2/g and to have a hydrogen storage capacity of 14 mg/g at 77 K/ 1 bar. Furthermore, PCN-46 was synthesised using 5,5'-(buta-1,3-diyne-1,4-diyl)diisophthalate (BDIP) and a copper salt.⁴⁵⁸ The S_{BET} and pore volume of PCN-46 were reported to be 2500 m^2/g and 1.012 cm^3/g respectively. MOF PCN-14 was synthesised with another tetratopic carboxylate linker [5,5'-(anthracene-9,10-diyl)diisophthalate (ADIP)] and a dicopper paddlewheel cluster.^{459,460} The PCN-14 was reported to possess an S_{BET} and density of 2000 m^2/g and 0.829 g/cm^3 respectively.⁴⁶¹ PCN-12 was synthesised under solvothermal reaction conditions by Wang *et al.*⁴⁶² using a tetratopic carboxylate linker 5,5'-methylene-di-isophthalate (MDIP) with $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ in DMA. PCN-12 was reported to possess a hydrogen uptake of 3.05 wt.% at 77 K and 1 bar. Furthermore, Wenzel *et al.* also used 5,5'-(dimethylsilanediyl)diisophthalate (DMSDIP) a tetratopic carboxylate linker for the construction of UHM-3 (PCN-12-Si).²⁷⁷ The PCN-12-Si was reported to have a S_{BET} of 2430 m^2/g as well as a H_2 uptake of 2.6 wt at 77K and 1 bar. In addition, Frahm *et al.* used an extended silicon-based tetratopic linker 4',4''-(dimethylsilanediyl)bis([1,1'-biphenyl]-3,5-dicarboxylate) (SBBIP) and a copper paddle-wheel motif for the synthesis of UHM-6.⁴⁶³ MOF UHM-6 was reported to possess a S_{BET} and specific microporous volume of 1200 m^2/g and 0.48 cm^3/g respectively. In addition, UHM-6 was reported to show a CO_2 uptake of 3.3 mmol/g at 273 K and 1 bar after activation.

Some tetratopic carboxylate connectors used for the synthesis of MOFs are depicted in **Figure 3.6**.

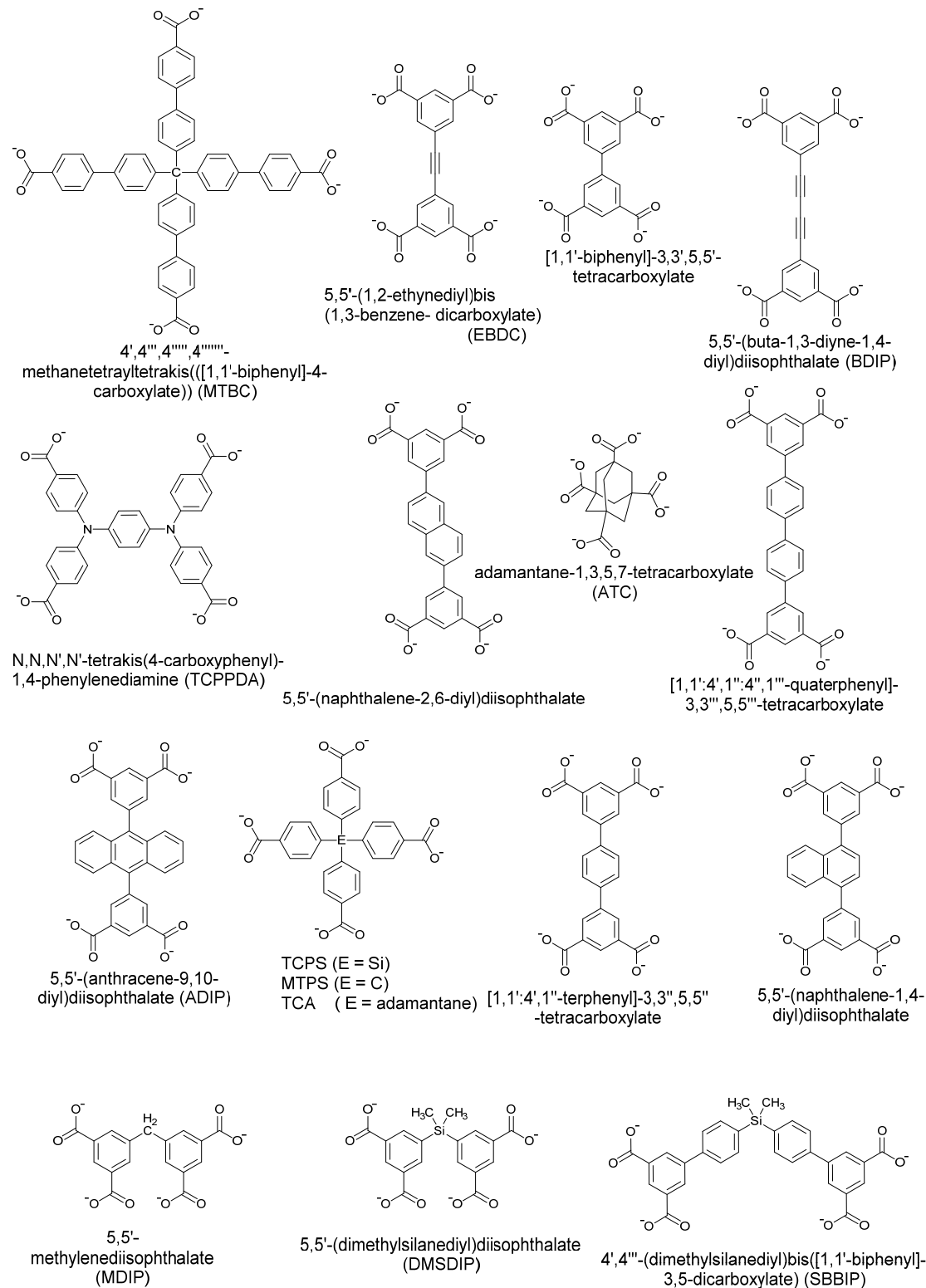


Figure 3.6: Some tetratopic carboxylate linkers used for the synthesis of MOFs

3.5.3 Hexatopic and Octatopic Carboxylate Linkers

Hexa-topic, octa-topic and other carboxylate linkers have been also used for the synthesis of MOFs.⁴³⁷ For example, a semi-rigid hexatopic linker 5,5',5''-[1,3,5-Benzene-triyltris(carbonylimino)]tris-1,3-benzenedicarboxylate was used in the construction of a MOF consisting of a (3, 24)-network topology.⁴⁶⁴ In addition, a series of isorecticular MOFs such as (PCN-61, -66, -69 and -610) were constructed using hexatopic carboxylate linkers [5,5',5''-benzene-1,3,5-triyltris(1-ethynyl-2-isophthalate) (BTEI) and 5,5',5''-(4,4',4''-nitrilotris(benzene-4,1-diyl)tris(ethyne-2,1-diyl))triisophthalate (NTEI)] and other similar linkers with a dicopper paddle-wheel precursors.^{465–467} MOF NU-110E was constructed solvothermally by the reaction of 5,5',5''-(((benzene-1,3,5-triyl-tris(ethyne-2,1-diyl))-tris(benzene-4,1-diyl))tris(ethyne-2,1-diyl))triisophthalate (TTEI) and Cu(NO₃)₂ in DMF-EtOH-HCl at 75 °C.⁸⁰ The NU-110E was reported to show a high experimental S_{BET} of 7140 m²/g.⁸⁰

MOFs constructed using octatopic carboxylate linkers are rare as a result of synthetic challenges. Frameworks constructed with long linkers often prefer to form interpenetrated structures,^{437,446} but construction using octahedral connectors seems to discourage interpenetration possibly as a result of connectivity. Irrespective of these observations, MOFs such as UTSA-33a,⁴⁶⁸ and UTSA-33b,⁴⁶⁹ were constructed by octatopic carboxylate linkers (4',5'-bis(3,5-dicarboxylatophenyl)-[1,1':2',1''-terphenyl]-3,3'',5,5''-tetracarboxylate) (BDPPC) and zinc and dicopper paddle-wheel clusters respectively. In addition, Fang and co-workers⁴⁷⁰ used an octadentate carboxylate linker 5,5',5'',5'''-silanetetrayltetraisophthalate (STIP) with different metal ions to give three different MOFs which possessed interesting structures and properties. Furthermore, Tan *et al.*⁴⁷¹ used extended tetrahedral octatopic carboxylate linkers 4',4''',4''''',4''''''-methanetetrayltetrakis([1'',1'''-biphenyl]-3,5-dicarboxylate)) (MTBPC) to construct MOF NOTT-140.⁴⁷¹ The estimated apparent S_{BET} of

NOTT-140 was reported to be 2620 m²/g. Some hexatopic and octatopic carboxylate linkers used for the construction of MOFs are shown in **Figures 3.7** and **3.8**

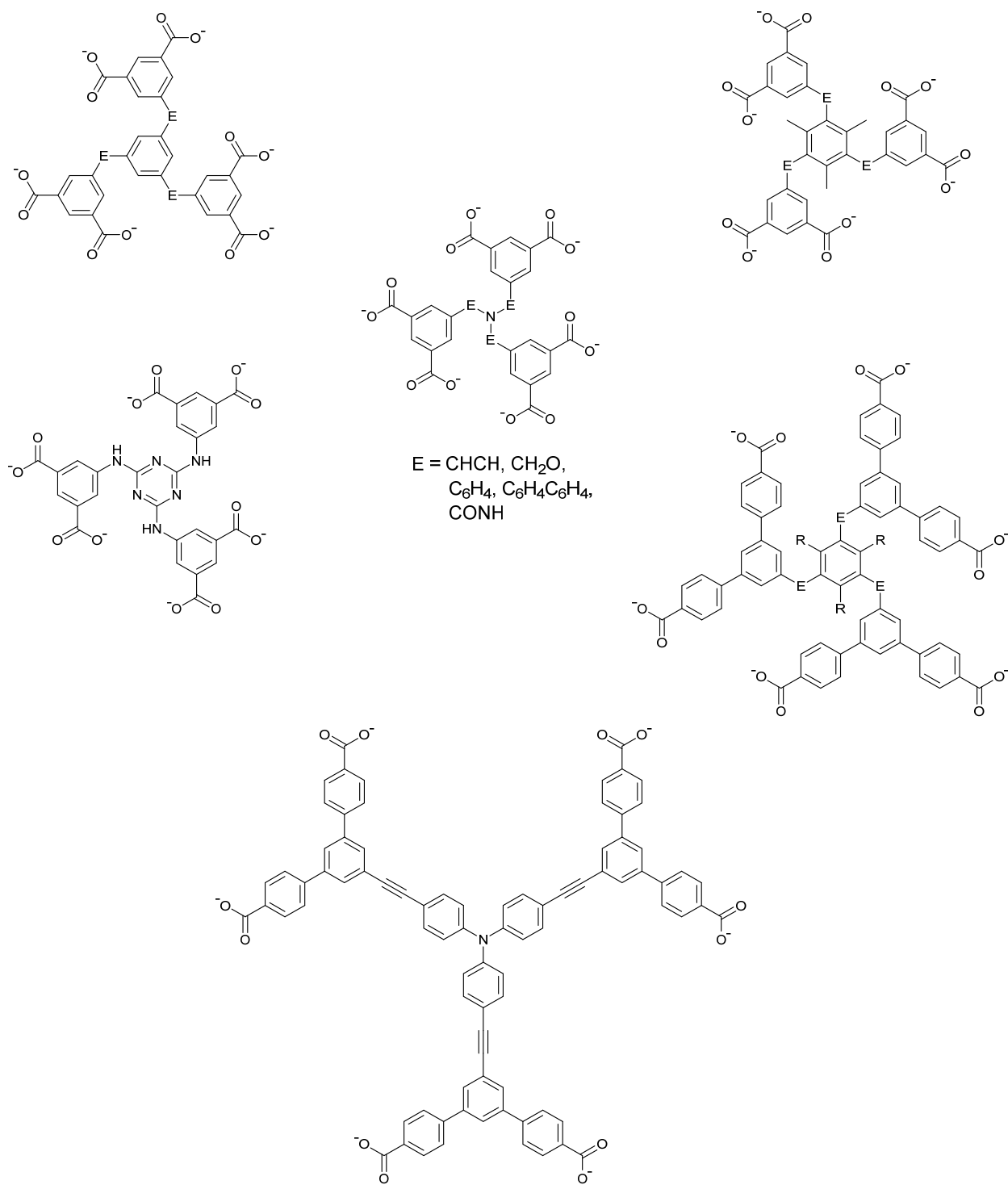


Figure 3.7: Some hexatopic carboxylate linkers used for the construction of MOFs

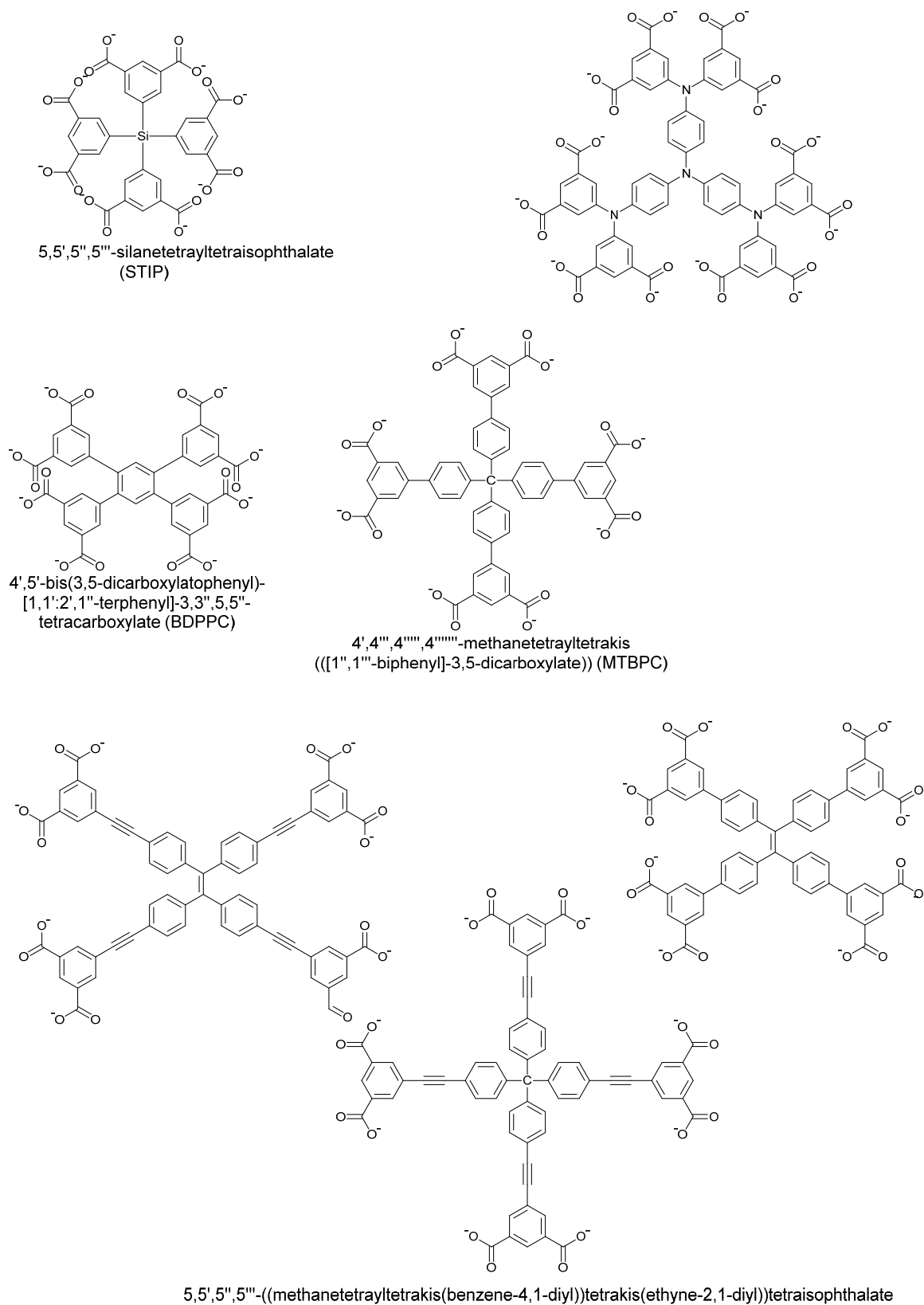


Figure 3.8: Some octatopic carboxylate linkers used for the construction of MOFs

3.5.4 N-Heterocyclic Linkers

The strength of the bond formed between nitrogen and transition metal ions is strong.⁴⁷² Thus, organic linkers containing N donor(s) (azole and pyridine) derivatives have been employed in the synthesis of MOFs. The N-heterocyclic linkers may be ditopic, tritopic, tetratopic or polytopic. Azole-based linkers are used for the construction of MOFs because of their ability to bind strongly with metal ions. The azoles are five-membered aromatic N-heterocycles such as imidazoles, pyrazoles, 1, 2,4-triazole, 1,2,3-triazole and tetrazole. The deprotonation of azoles through the decomposition of amide solvents such as N,N-dimethylformamide (DMF) or N,N-diethylformamide (DEF) used in solvothermal reactions gives rise to azolates.^{437,473,474} When metal ions react with azolates, Metal-Azolate-Metal bonds are formed.⁴⁷³ Metal-Imidazolate Frameworks (also known as Zeolitic Imidazolate Frameworks (ZIFs), ZIF-1, ZIF-2, ZIF-3 to ZIF-12 series are examples of MOFs obtained from N-heterocyclic linkers with metal ions.⁴⁷³ Many ZIFs have been constructed with metal ions such as Fe^{2+} , Co^{2+} , Cu^{2+} , or Zn^{2+} which resulted in the formation of frameworks that are topologically isomorphous to zeolites.⁴⁷³ For example, it has been reported that when two metal ions react with imidazoles (Im) to form (M-Im-M), the bridging angle between the imidazolate and the metals is coincidentally similar to the Si-O-Si angle found in zeolites (145°) aluminosilicate-based materials,^{473,474} as shown in **Figure 3.9**.

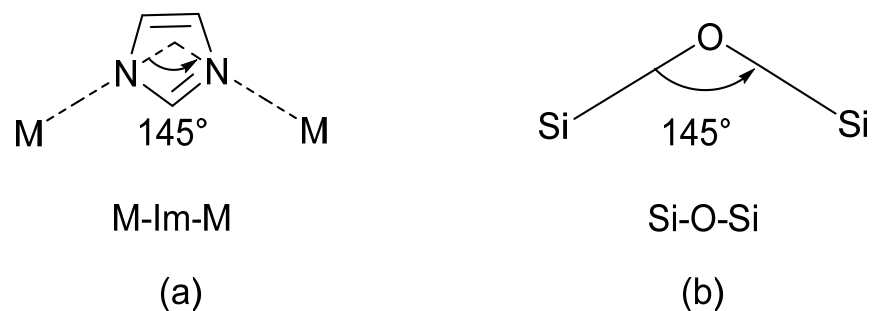


Figure 3.9: The bridging angles in (a) metal Im (b) zeolites.⁴⁵³

For example, ZIF-8 $[\text{Zn}(\text{MeIm})_2]$ and ZIF-11 $[\text{Zn}(\text{PIm})_2]$ were constructed by the use of 2-methylimidazolate and benzimidazolate respectively. These two ZIFs were reported to display permanent porosity and exceptional thermal stability up to 500 °C. In addition, ZIF-8 was reported to show outstanding chemical stability at reflux in organic solvents as well as in aqueous alkaline solutions.⁴⁷⁴ ZIF-95 $[\text{Zn}(\text{cbIm})_2]$ and ZIF-100 $[\text{Zn}_{20}(\text{cbIm})_{39}(\text{OH})]$, (cbIM = chlorobenzimidazolate) are also MOFs obtained from N-heterocyclic linkers.⁴⁷⁵ ZIF-95 and ZIF-100 were reported to have permanent porosity as well as Langmuir surface areas of 1240 and 780 m^2/g respectively. 3,3,5,5-Tetramethyl-4,4-bipyrzolate (Me_4Bpz) was utilized for the construction of MOF $\text{Ag}_2(\text{Me}_4\text{bpz})$ ⁴⁷⁶ which was reported to show reversible sorption properties as well as possess an S_{BET} of 240 m^2/g .

One of the limitations associated with the use of azolates for the construction of MOFs is their short bridging lengths. Thus, longer pyrazole-based linkers are also used in the construction of MOF materials. For example, four pyrazolate-bridged MOFs $\text{M}_3(\text{btp})_2$, where $\text{M} = \text{Ni}, \text{Cu}, \text{Zn}$ and Co have been constructed using 1,3,5-tris(1H-pyrazol-4-yl)benzene as a source of N-heterocyclic linker.⁴⁷⁷ it was reported that the S_{BET} s of these four MOFs after activation were 1650, 1860, 930 and 1027 m^2/g respectively. In addition, $\text{Zn}_3(\text{btp})_2$ was reported to show high thermal stability up to 500 °C as well as chemical stability in boiling aqueous solution. The Tritopic tetrazolate linker 1,3,5-benzenetristetrazolate (BTT) has also been employed for the construction of a series of MOF materials.^{478–480} In these MOFs, the BTT coordinated with the metal ions through its two middle N atoms. Furthermore, Long and co-workers, treated CuCl_2 with a tetrahedral N-heterocyclic linker tetrakis(4-tetrazolylphenyl)methane) (ttpm) which resulted in the formation of MOF $\text{Cu}_4(\text{ttpm})_2 \cdot 0.7\text{CuCl}_2$, which upon activation using solvent exchange approach exhibited an S_{BET} of 2506 m^2/g .⁴⁸¹ Davies and co-workers have also used tetrahedral tetrakis(4-

tetrazolylphenyl)silane ligand (H_4TTPS) and $CuCl_2 \cdot 2H_2O$ for the synthesis of $[H(Cu_4Cl)(ttps)_2(DMF)_4] \cdot 18DMF$ (IMP-16).⁸²

Dipyridyl linkers have also been used in the literature for the synthesis of MOF materials. However, as they are neutral components, another anionic ligand or counterion is required to balance out the positive charge on the metal centres. For example, Bunz and co-workers constructed a series of MOFs using the tetrahedral pyridine linker [tetrakis(4-(pyridin-4-ylethynyl)phenyl)silane].³⁴⁶ This series of MOFs was reported to show a variety of topologies, interpenetrations as well as porosities. Mandal and co-workers used a carboxylate silicon-based linker, 4,4'-bipyridine as a co-connector and Mn(II) paddle-wheel subunit to construct $\{[Mn_2(O_2CC_6H_4Si(CH_3)_2C_6H_4CO_2)_2(4,4'-bpy)]\}_n$.⁴⁸² Mocanu *et al.*²⁷² used 1,3,5,7-tetrakis{4-(4-pyridyl)phenyl}adamantane) and copper (II) ions to construct a 3-D MOF $[CuL^1(H_2O)_2](BF_4)_2 \cdot 8H_2O$. This MOF was reported to show a 4-fold interpenetration with a **pts** topology. A zinc(II) MOF $[Zn_2(1\text{-}4\text{-}o\text{-}pda)_2(1\text{-}abpy)]_n$ based on flexible *o*-phenylenediacetate and rigid 4,4'-azobis(pyridine) ligands was constructed by Tabak and co-workers.²⁷¹ This MOF was reported to be thermally stable up to 300 °C. **Figure 3.10**, shows some of the N-heterocyclic linkers used for the synthesis of MOF materials.

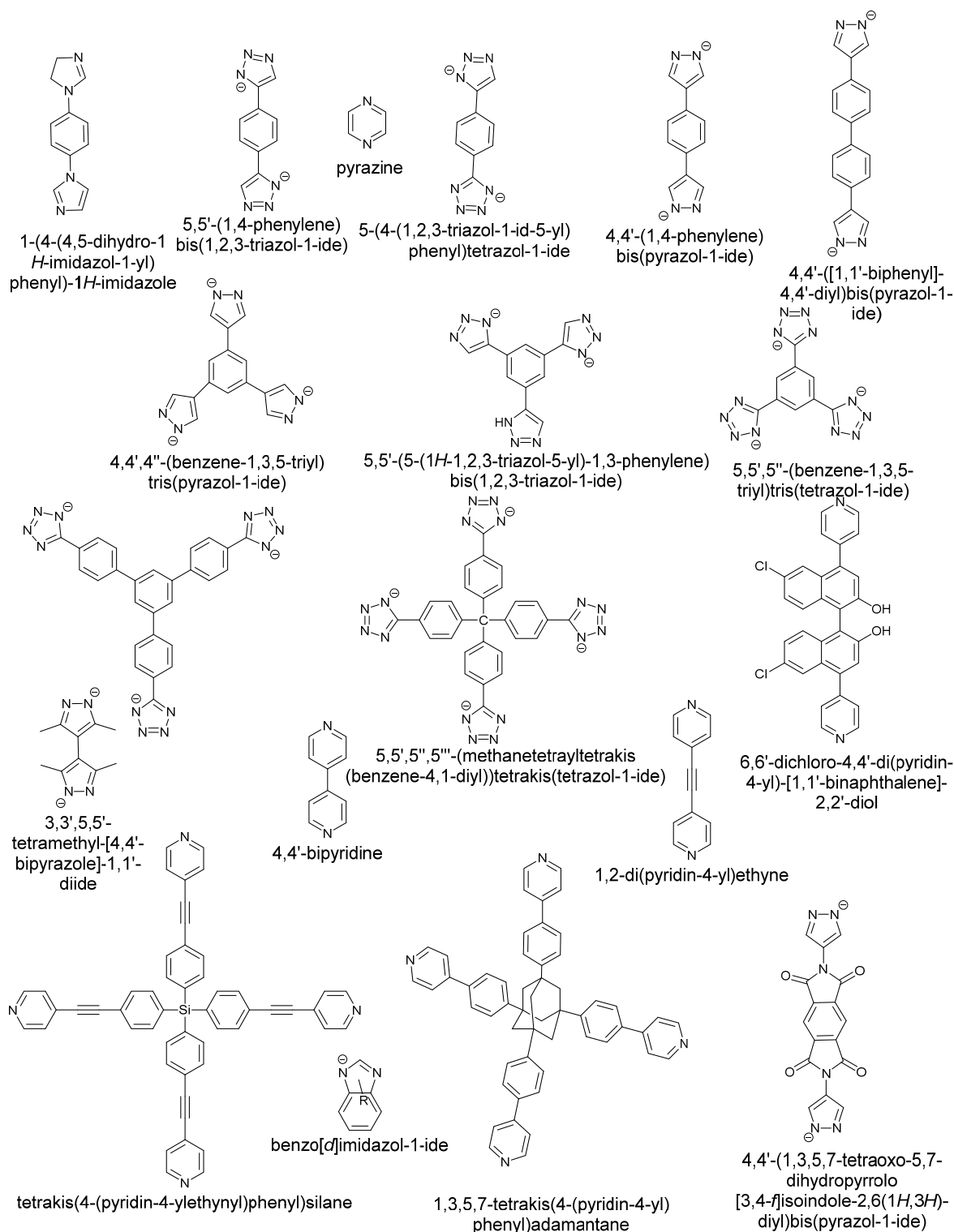


Figure 3.10: Some N-heterocyclic linkers used for the construction of MOFs

Most of the carboxylate and N-heterocyclic linkers used for the construction of MOF materials are based on carbon centres as well as commercially available connectors. Silicon-based connecting

units are scarce compared to their carbon analogues but silicon-centred linkers are more convenient to prepare through metathesis compared to their carbon analogues.⁴⁸³ To this end, it is still desirable to design novel linkers with tailored dimensionality or pendant functional groups so as to have a control of the physicochemical properties of the resultant framework materials. Several synthetic routes have been employed for the syntheses of varieties of rigid aryl systems based on silicon or boron centres with carboxylate or pyridyl pendants.^{262,265,489–493,273,277,449,484–488}

3.6.0 Synthetic Methods, Results and Discussion

This section describes the synthesis (using simpler methods) and characterisation of new linkers (pyridyl and carboxylate) based on silicon centres followed by ligation with metal ions for the preparation of MOFs with the intent to capture CO₂ as depicted in **Figure 3.11**, below

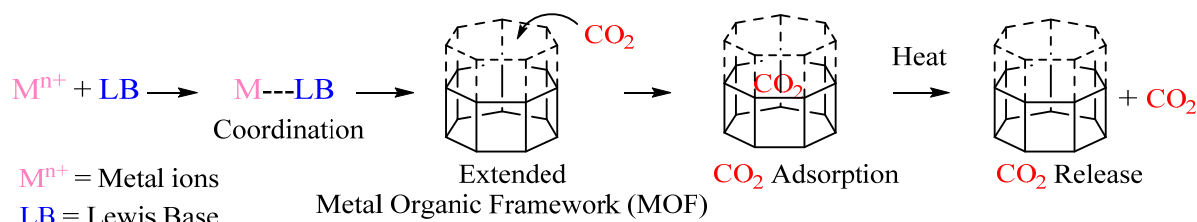
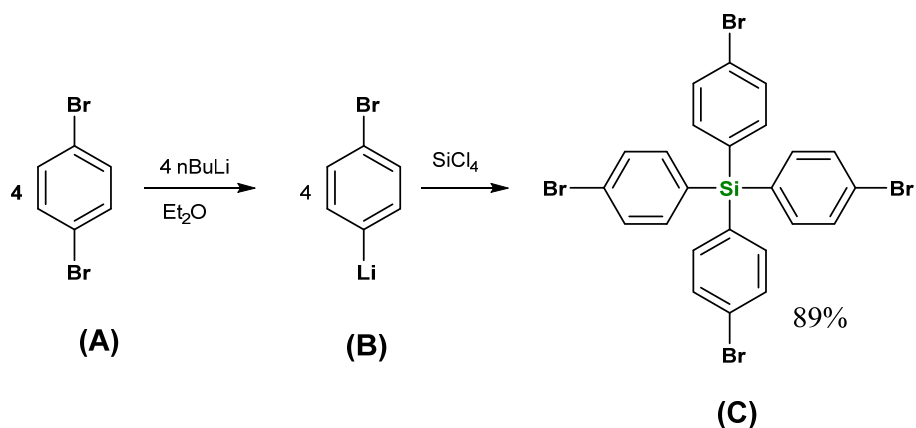


Figure 3.11: Schematic method of the for making of linkers and MOFs

3.6.1 Synthesis of tetrakis(4-bromophenyl)silane (C)

The number of commercially available tetrahedral linkers with silicon-based pyridyl connectors is small compared to their carbon-based counterparts. In order to increase the availability of these linkers, a new approach was attempted using tetrakis(4-bromophenyl)silane (C). The synthesis of (C) followed literature preparations with some modifications^{493–495} The preparation method is shown in **Scheme 3.1**.

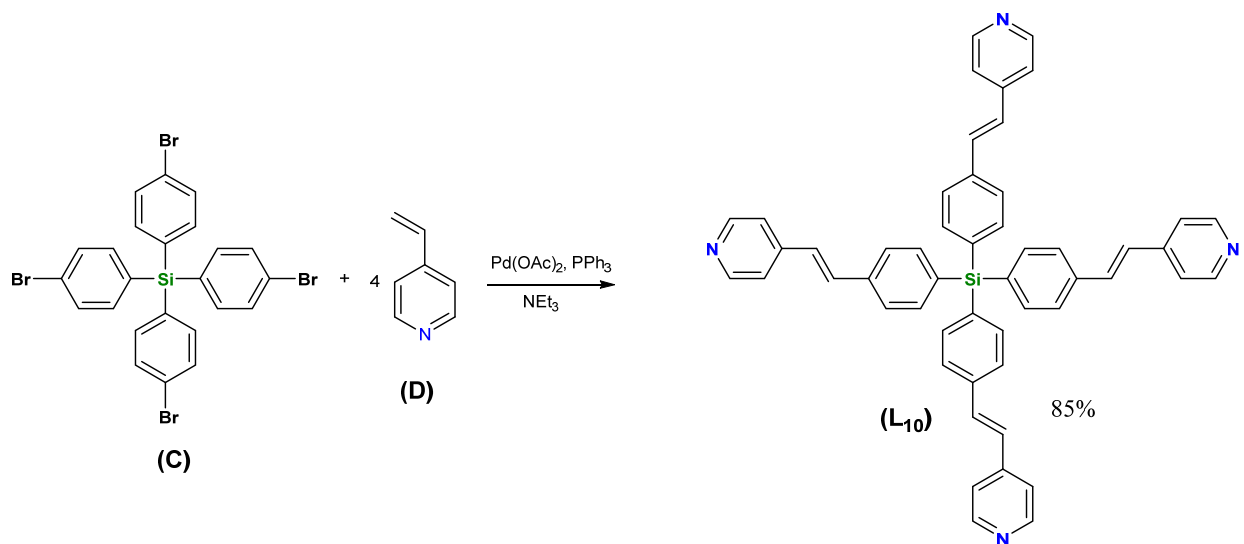


Scheme 3.1: Pathway for the synthesis of tetrakis(4-bromophenyl)silane (**C**)

Thus, the preparation of compound (**C**) started with the dissolution of 1,4-dibromobenzene (**A**) in dry ether (cooled -76°C using dry ice and acetone) followed by the addition of *n*-BuLi which resulted in the in situ formation of the 1-bromo-4-lithiobenzene (**B**) intermediate. After stirring, the reaction mixture was slowly allowed to warm-up to room temperature in order to drive only the desired lithiation reaction to completion without the formation of unwanted by-product; followed by re-cooling to -76°C . Tetrachlorosilane (SiCl_4) was added to the lithiation product, which resulted in the formation of colourless powder product after aqueous workup of 89% yield of tetrakis(4-bromophenyl)silane (**C**) (lit. yields 52.6%, 69%, 85%).^{484,493,494} Compound (**C**) was characterised using standard analytical and spectroscopic methods. For example, the ^1H NMR spectrum of the compound showed the expected doublets in the aromatic region as shown in Supplementary Information (**S45**) and is comparable to literature spectra.^{484,493,494}

3.6.2 Synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L10**)

Tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L10**) is a novel potential linker and was prepared following a literature procedure for similar reactions,^{490,496} (standard Heck reaction⁵⁰¹) as shown in **Scheme 3.2**.



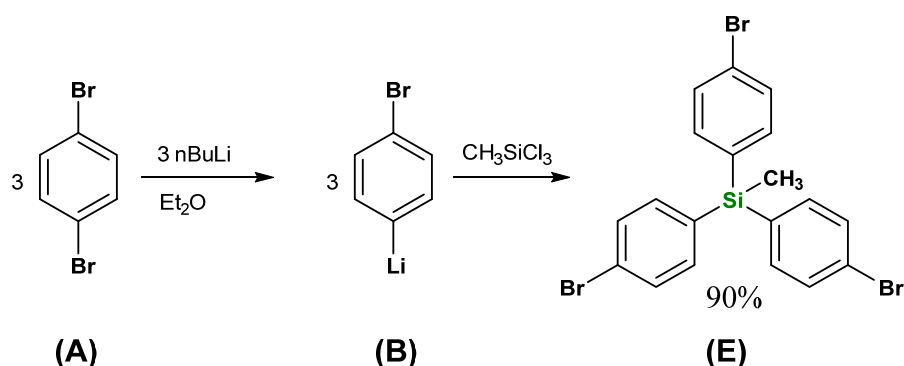
Scheme 3.2: Pathway for the synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L₁₀**)

At the end of the reaction, the reaction mixture was partitioned between aqueous and organic layer (dichloromethane) to give a brown powder which was washed with ethyl acetate to give (**L₁₀**) as a brown powder in 85% yield. The ^1H NMR spectrum of (**L₁₀**) showed well resolved resonances with the aromatic proton signals found within $\delta = 7.09 - 8.59$ ppm which are consistent with aromatic vinylpyridine compounds (7.14 – 8.63 ppm) in the literature.⁴⁹⁰ The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**L₁₀**) shows signals for the aromatic carbons in the range of 120.90-150.25 ppm which are consistent with the literature values.⁴⁹⁰ In addition, the $^{29}\text{Si}\{^1\text{H}\}$ NMR of compound (**L₁₀**) shows a singlet at -14.79 ppm, which is consistent with single Si environment (-14.70, -14.36 ppm)⁴⁸⁵ in the literature. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (**L₁₀**) are provided as Supplementary Information (**S46-S48** respectively). When two or more nodes form linkages with rod-like ligands, the resulting complex networks do not stack densely but rather causes the formation of free volume after network interpenetration. High connectivity building units are used in the preparation of framework materials to permit only the formation of desired framed framework.^{497,498} In contrast to this (**L₁₀**) is a low connectivity building block which fosters interpenetration of networks to produce pore structures and further enhances the stabilization of

the pyridine frameworks and can also prevent interpenetration depending on the nature of the metal ion. In terms of coordination chemistry, (**L10**) is closely related to tetra(4-pyridyl)methane⁴⁹⁹ as well as tetrakis(4-(pyridin-4-ylethynyl)-phenyl)silane.³⁴⁶ However, the additional phenyl-ethene units change the length of the linker and makes (**L10**) resemble the latter more than the former. Compound (**L10**) was used as a linker for the construction of a MOF structures which have been discussed in sections (3.6.16 and 3.6.17) of this report.

3.6.3 Synthesis of tris(4-bromophenyl)methylsilane (**E**)

The preparation of tris(4-bromophenyl)methylsilane (**E**) is similar to the described procedure used for the synthesis of compound (**C**) above and as shown in **Scheme 3.3** below.

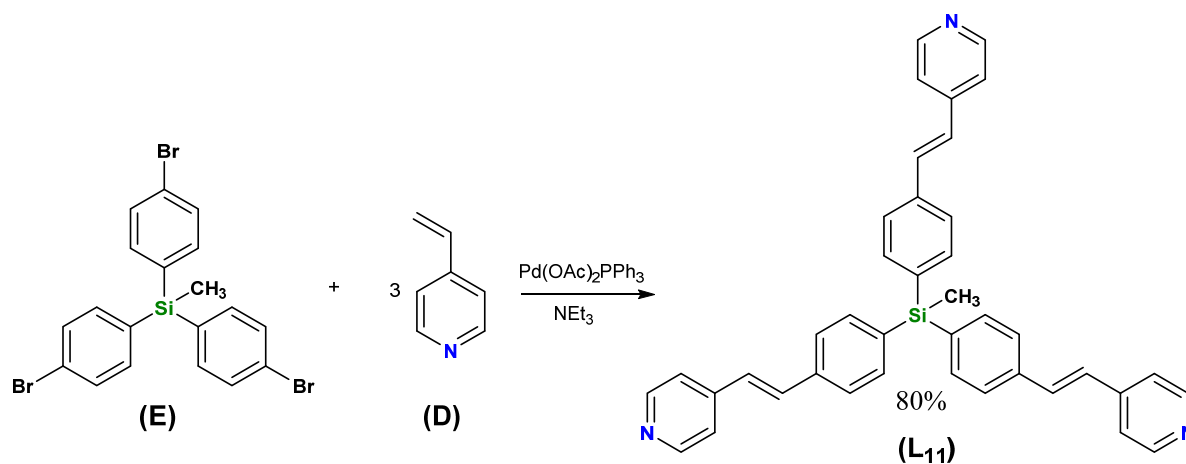


Scheme 3.3: Pathway for the synthesis of tri(4-bromophenyl)methylsilane (**E**)

Trichloro(methyl)silane (CH_3SiCl_3) was added to the lithiation product, which resulted in the formation of (**E**) as a colourless powder product after aqueous workup in 90% yield of the compound (lit. 82%, 83.5%)^{493,494} Compound (**E**) was characterised using standard analytical and spectroscopic methods. For example, the ^1H NMR spectrum of the compound is comparable to the literature,^{484,493,494} and showed well resolved resonances with aromatic proton signals found within the range $\delta = 7.30 - 7.50$ ppm, while the non-aromatic methyl protons are found at 0.79 ppm as shown in Supplementary Information (**S49**)

3.6.4 Synthesis of tris(4-(pyridine-4-vinyl)phenyl)methylsilane (**L₁₁**)

The preparation of tris(4-(pyridine-4-vinyl)phenyl)methylsilane (**L₁₁**) (a novel linker), was analogous to the synthetic procedure followed for the preparation of compound (**L₁₀**), as shown in **Scheme 3.4**.



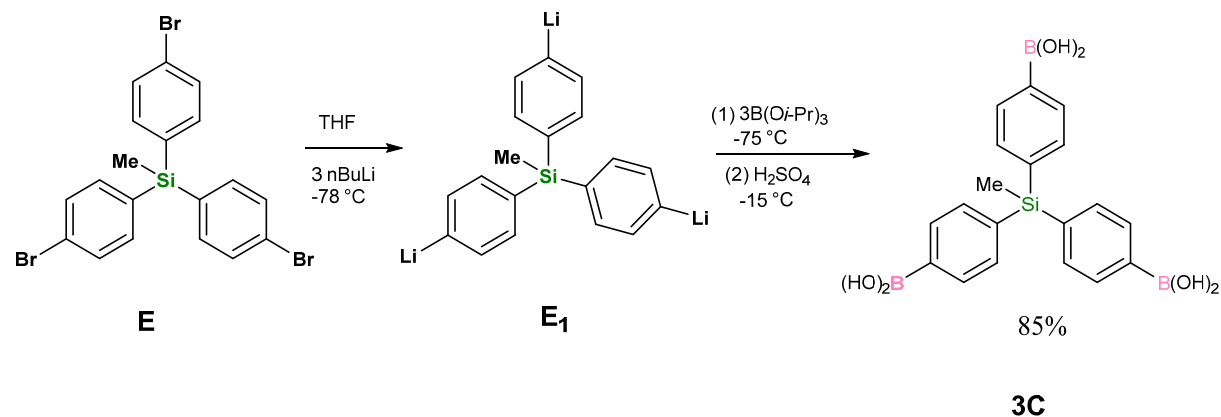
Scheme 3.4: Pathway for the synthesis of tri(4-(pyridine-4-vinyl)phenyl)methylsilane (**L₁₁**)

At the end of the reaction, the reaction mixture was partitioned between aqueous and organic layers to give brown powder which was washed with ethyl acetate to give an 80% yield of (**L₁₁**) as brown powder. The ^1H NMR spectrum of compound (**L₁₁**) displayed well resolved resonances with aromatic proton signals found within $\delta = 7.07 - 8.58$ ppm, which are consistent with aromatic vinylpyridine compounds (7.14 – 8.63 ppm) in the literature,⁴⁹⁰ while the non-aromatic methyl protons were found at 0.89 ppm, (starting material **(E)** = 0.79 ppm), (lit. 0.94 ppm for similar Si-CH_3 ⁴⁹³). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**L₁₁**) shows signals for the aromatic carbons in the range of 120.90-150.24 ppm, which are consistent with the literature values,⁴⁹⁰ whereas the methyl carbon signal was found at -3.45 ppm, which is also consistent with similar compounds in the literature with values such as [-4.3 ppm, for tris(4-bromophenyl)(methyl)silane,⁴⁹⁵ and -2.7 ppm, for tri(3,5-difluorophenyl)methylsilane.⁴⁸⁹] Furthermore, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of

compound (**L**₁₁) shows a singlet at -11.09 ppm. The NMR (¹H, ¹³C{¹H} and ²⁹Si{¹H}) spectra of compound (**L**₁₁) are provided as Supplementary Information (**S**₅₀-**S**₅₂ respectively).

3.6.5 Synthesis of [(methylsilanetriyl)tris(benzene-4,1-)]triboronic acid (**3c**).

The preparation of (**3c**) is analogous to the literature procedure for the same compound,⁴⁸⁹ but with some modifications. The method is as shown in **Scheme 3.5**.

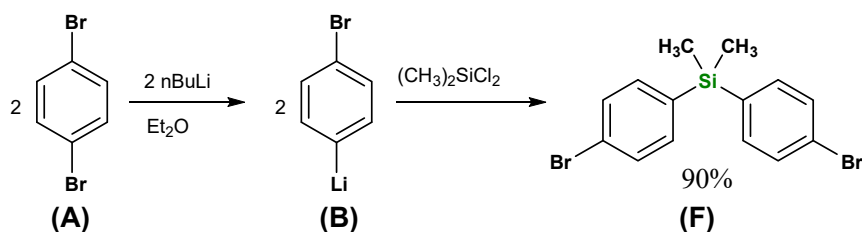


Scheme 3.5: Method for the preparation of [(Methylsilanetriyl)tris(benzene-4,1)]triboronic acid (**3c**)

At the end of the reaction and subsequent removal of solvent gave a crude colourless powder which was recrystallized with aqueous NaOH and HCl to give an 85% yield of (**3c**) as colourless crystals. The ¹H NMR spectrum of compound (**3c**) shows the aromatic protons signals within the range δ = 7.50 - 7.87 ppm, while the non-aromatic methyl protons were found at 0.82 ppm, (starting material (**E**) = 0.79 ppm), (lit. 0.79 ppm).⁴⁸⁹ The ¹³C{¹H} NMR spectrum of (**3c**) shows signals for the aromatic carbons in the range of 131.85-137.89 ppm, which are consistent with the literature values,⁴⁸⁹ whereas the methyl carbons signal was found at -3.65 ppm. Furthermore, the ¹¹B{¹H} and ²⁹Si{¹H} NMR spectra of compound (**3c**) showed singlets at 29.18 ppm and -11.11 ppm respectively. The NMR (¹H, ¹³C{¹H}, ¹³B{¹H} and ²⁹Si{¹H}) spectra of compound (**3c**) are provided as Supplementary information (**S**₅₃-**S**₅₆ respectively).

3.6.6 Synthesis of di(4-bromophenyl)dimethylsilane (**F**)

The preparation of di(4-bromophenyl)dimethylsilane (**F**), followed the same reaction procedure for the making of compounds (**C**) and (**D**). The method for the synthesis of (**F**) is shown in **Scheme 3.6** below.

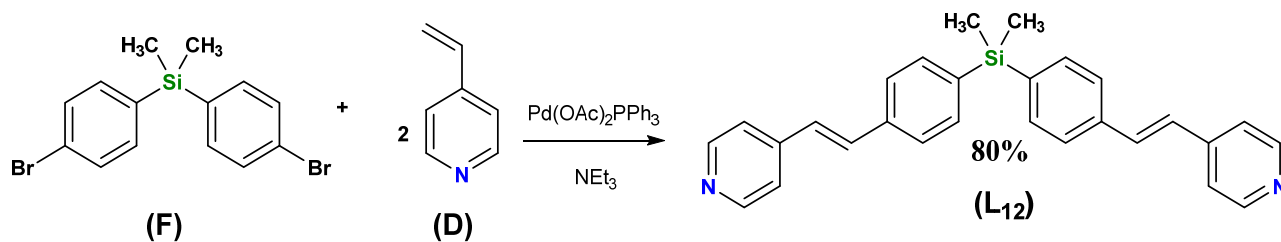


Scheme 3.6: Pathway for the synthesis of di(4-bromophenyl)dimethylsilane (**F**)

The product (**F**) was isolated as a colourless powder product after aqueous workup in 90% yield (lit. yields 55%, 78.5%)^{493,495} The ^1H NMR spectrum of the compound (**F**) showed well resolved resonances with aromatic proton signal found within the range $\delta = 7.34 - 7.49$ ppm, while the non-aromatic methyl protons are found at 0.51 ppm as shown in Supplementary Information (**S57**), and are comparable to those of the literature (0.55 ppm).^{484,493,494}

3.6.7 Synthesis of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (**L₁₂**)

The preparation of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (**L₁₂**) followed the described procedure for the synthesis of compounds (**L₁₀**) and (**L₁₁**). The route for the synthesis of compound (**L₁₂**) is depicted in **Scheme 3.7**.



Scheme 3.7: Synthesis of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (**L₁₂**)

3.6.7.1 Spectral and crystal description of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L_{12})

At the end of the reaction, the reaction mixture was partitioned between aqueous and organic layers to give brown powder which was washed with ethyl acetate to give an 80% yield of (L_{12}) as brown powder. The ^1H NMR spectrum of compound (L_{12}) displayed well resolved resonances with aromatic proton signals found within the range $\delta = 7.07 - 8.58$ ppm, which are consistent with aromatic vinylpyridine compounds (7.14 – 8.63 ppm) in the literature,⁴⁹⁰ while the non-aromatic methyl protons were found at 0.57 ppm, (starting material (**F**) = 0.51 ppm). The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (L_{12}) shows signals for the aromatic carbons in the range of 120.83-150.05 ppm, which are consistent with the literature values,⁴⁹⁰ whereas the methyl carbon signal was found at -2.54 ppm. Furthermore, the $^{29}\text{Si}\{^1\text{H}\}$ NMR of compound (L_{12}) shows a singlet at -7.83 ppm. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (L_{12}) are provided as Supplementary information (S58-S60 respectively).

A single crystal suitable for X-ray diffraction study was grown in ethyl acetate and was found to have the structure of compound (L_{12}) shown in **Figure 3.12**.

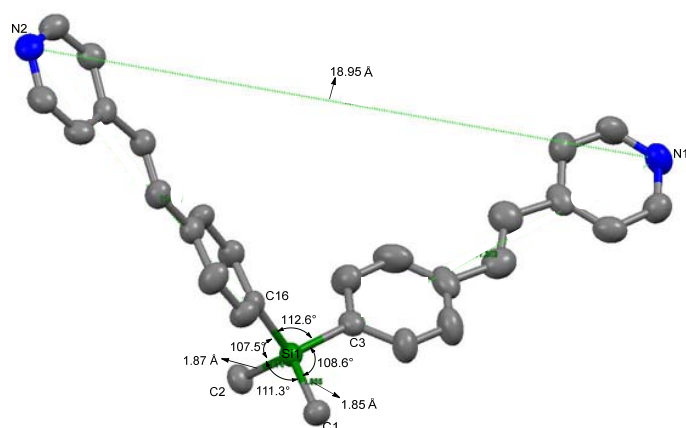


Figure 3.12: Single crystal X-ray structure of (L_{12}). Colour identity, green = Si, grey = C, blue = N, white = H

The distance between the two nitrogen atoms (N1 and N2) in the molecule of (L_{12}) is 18.95 Å. The crystal packing of the potential ditopic linker also exhibits intermolecular non-covalent

interactions. For example, there is an intermolecular (C-H $\cdots$ N) C18-H18 $\cdots$ N2 (2.645 Å) as shown in **Figure 3.13**.

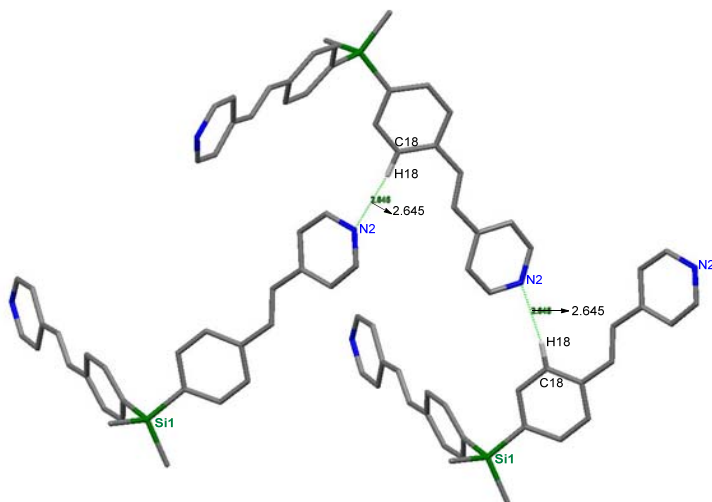
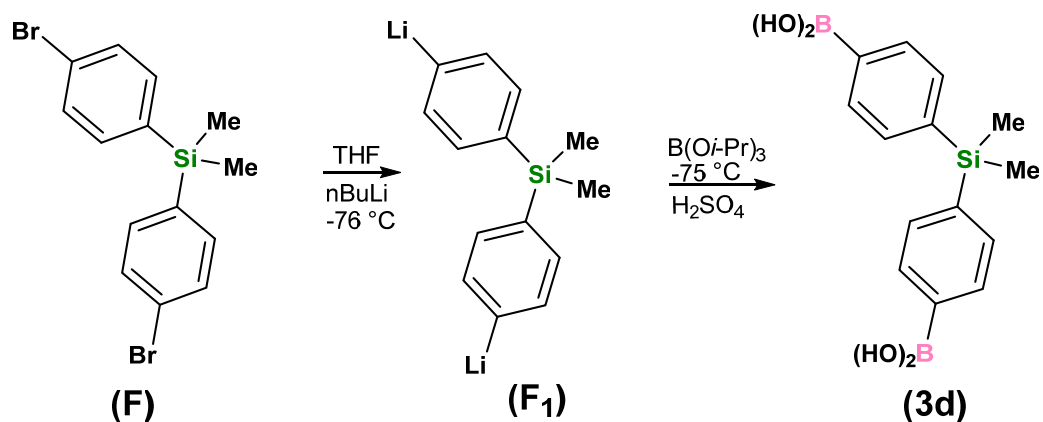


Figure 3.13: Non-covalent intermolecular interaction in the crystal packing of (**L**₁₂), Most H atoms are omitted for clarity.

The crystallographic data for (**L**₁₂) are provided as Appendix 12.

3.6.8 Synthesis of [(dimethylsilanediyl)bis(1,4-phenylene)]diboronic acid (**3d**).

The preparation of (**3d**) is analogous to the preparation of compound (**3c**) and the literature procedure for the same compound,⁴⁸⁹ but with some modifications. The method is as shown in **Scheme 3.8**.



Scheme 3.8: Method for the preparation of [(Dimethylsilanediyl)bis(4,1-phenylene)]diboronic acid (**3d**)

A crude colourless powder was isolated from the reaction and treated with aqueous NaOH and HCl to give an 87% yield of **(3d)** as colourless crystals. The ^1H NMR spectrum of compound **(3d)** shows the aromatic protons signals within the range $\delta = 7.20 - 7.85$ ppm, while the non-aromatic methyl protons were found at 0.56 ppm, (starting material **(F)** = 0.51 ppm), (lit. 0.55 ppm).⁴⁸⁹ The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **(L11)** shows signals for the aromatic carbons in the range of 134.20-141.00 ppm, which are consistent with the literature values,⁴⁸⁹ whereas the methyl carbons signal was found at -2.50 ppm. Furthermore, the $^{11}\text{B}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra of compound **(3d)** showed singlets at 29.20 ppm and -8.50 ppm respectively. The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound **(3d)** are provided as Supplementary information (**S61-S64** respectively).

A single crystal X-ray diffraction study independent of this project (Lickiss and Davies research group unpublished work) revealed the structure of **(3d)** as shown in **Figure 3.14**.

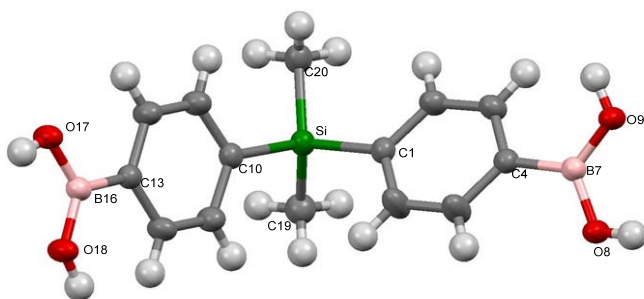
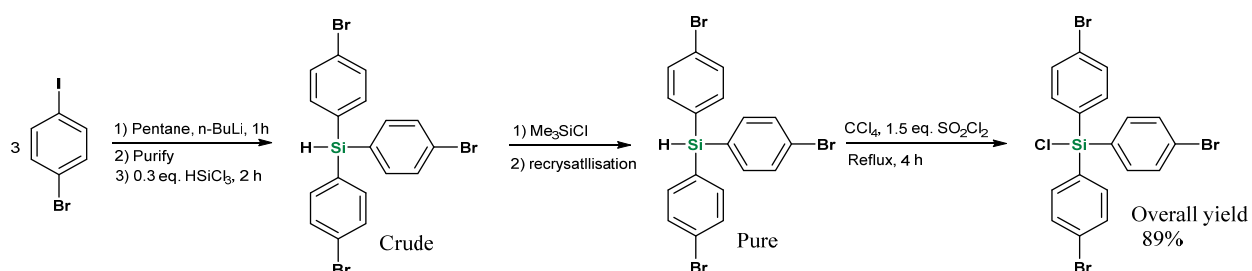


Figure 3.14: Crystal structure of compound **(3d)**. Colour identity, pink = B, green = Si, grey = C, blue = N, red = O, light grey = H

The crystallographic data of compound **(3d)** are provided as Appendix 13.

3.6.9 Synthesis of tris(4-bromophenyl)chlorosilane (**G**)

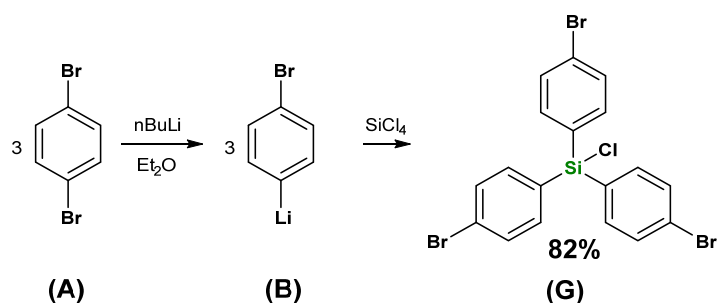
Tris(4-bromophenyl)chlorosilane (**G**) is a compound usually utilised as a precursor for the formation of a rigid core carbosilane dendrimers. In the literature⁴⁸⁴ the preparation of compound **(G)** was carried out using several steps that involved the formation tris(4-bromophenyl)silane followed by the addition of the other reagents to give the compound **(G)** as shown in **Scheme 3.9**.



Scheme 3.9: Multi-step synthetic method for the preparation of tris(4-bromophenyl)chlorosilane (**G**), adapted from reference.⁴⁸⁴

The tris(4-bromophenyl)silane was thereafter chlorinated using reagents such as Cl₂, PCl₅, CCl₄ or SO₂Cl₂, to give (**G**). In addition to being a multi-step synthetic route which is time consuming, the starting material, 1-bromo-4-iodo benzene, as well as some of the other reagents used in this protocol are expensive.

In this report a straight-forward and less expensive method is used for the synthesis of compound (**G**) as shown in **Scheme 3.10**.



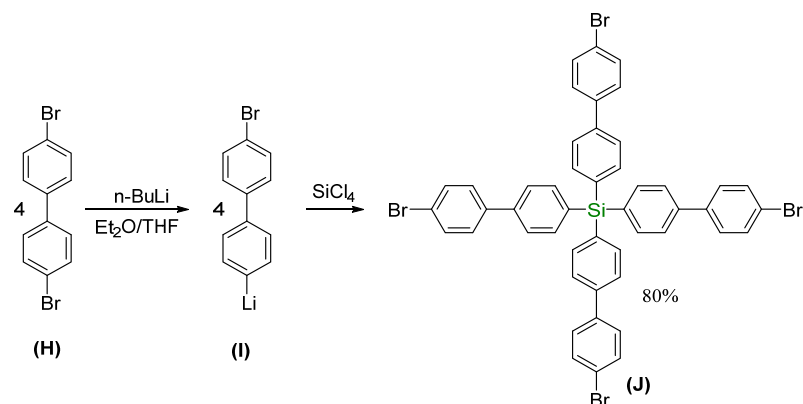
Scheme 3.10: Reaction method for the preparation of compound (**G**)

The reaction pathway for the synthesis of compound (**G**) is similar to the procedure followed for the synthesis of compounds (**C**), (**E**) and (**F**), but with some modifications in the workup process. The workup for the making of compounds (**C**), (**E**) and (**F**) required the quenching of the reaction with water (details in experimental section) whereas in the making of compound (**G**) the reaction was not quenched with water (to avoid hydrolysis of the remaining Si-Cl group) rather, more dry ether was added to partition all of the product into the organic layer and the formation of colourless precipitate.

The precipitate formed at the end of the reaction was filtered off and the volatiles removed using a rotary evaporator to give a colourless powder. The powder was recrystallized from hexane which resulted in the formation of compound **(G)** in 82% (M.p = 123.4 °C) (lit. overall yield, 89%, M.p = 123 °C).⁴⁸⁴ The ¹H NMR of the compound **(G)** showed well resolved resonances with aromatic proton signals found within the range δ = 7.44 - 7.58 ppm. The ¹³C{¹H} NMR spectrum of **(G)** show signals for the aromatic carbons in the range of 126.46-136.33 ppm. Furthermore, the ²⁹Si{¹H} NMR of compound **(G)** shows a singlet at (1.47 ppm), (lit. 1.48 ppm).⁴⁸⁴ The NMR (¹H, ¹³C{¹H} and ²⁹Si{¹H}) spectra of compound **(G)** are provided as Supplementary information (**S65-S67** respectively).

3.6.10 Synthesis of tetrakis(4-bromobiphenyl)silane (**J**)

The preparation of tetrakis(4-bromobiphenyl)silane **(J)** (also a novel compound when it was made) is analogous to the preparations described for the other bromophenylsilanes described above. Although the making of compound **(J)** required some modifications of the solvents used (a mixture of Et₂O and THF) as shown in **Scheme 3.11**.



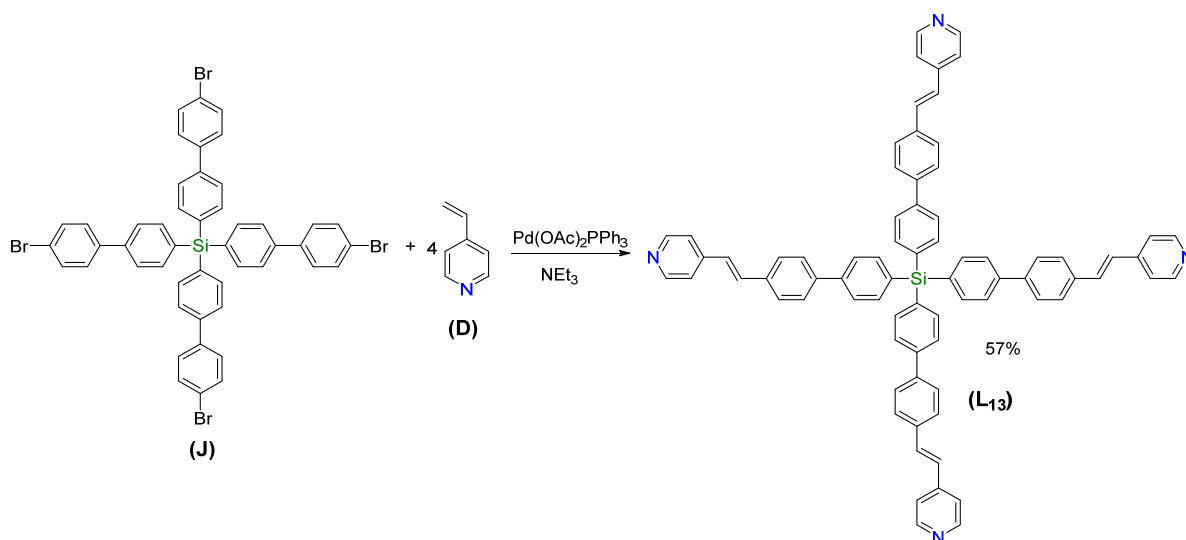
Scheme 3.11: Reaction scheme for the preparation of compound **(J)**

A powder was isolated from the reaction and washed with warmed acetone to give pure compound **(J)** in 80% yield. The ¹H NMR spectrum of the compound **(J)** showed well resolved resonances with aromatic proton signals found between δ = 7.49 - 7.71 ppm. The ¹³C{¹H} NMR spectrum of

(**J**) shows signals for the aromatic carbons in the range of 121.94-141.26 ppm. In addition, the $^{29}\text{Si}\{^1\text{H}\}$ NMR of compound (**J**) shows a singlet at (-14.28 ppm), (lit. -14.36 ppm).⁴⁸⁵ The NMR (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$) spectra of compound (**J**) are provided as Supplementary Information (S₆₈-S₇₀ respectively).

3.6.11 Synthesis of tetrakis(4-(pyridine-4-vinyl)biphenyl)silane (**L₁₃**)

The preparation of tetrakis(4-(pyridine-4vinyl)biphenyl)silane (**L₁₃**) (a new linker) followed a similar procedure for the synthesis of other linkers (**L₁₀**, **L₁₁** and **L₁₂**) discussed earlier and is shown in **Scheme 3.12**.



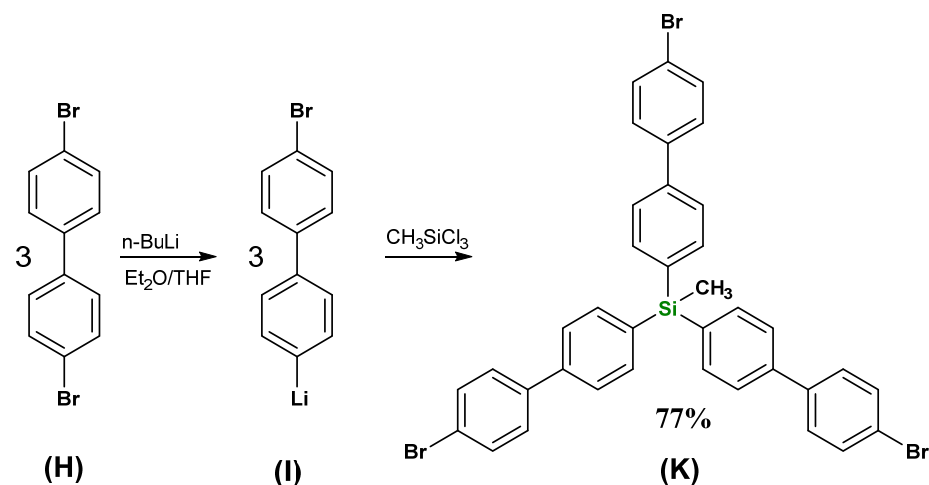
Scheme 3.12: Synthesis of tetrakis(4-(pyridine-4vinyl)biphenyl)silane (**L₁₃**)

One equivalent of tetrakis(4-bromobiphenyl)silane (**J**) was coupled with 4 equivalents of 4-vinylpyridine (**D**). At the end of the reaction, the reaction mixture was partitioned between water and dichloromethane to give crude brown powder which was washed with warmed acetone and hexane to give pale yellow powder in 57% yield of (**L₁₃**). The ^1H NMR spectrum of the compound showed aromatic proton signals between $\delta = 7.04 - 8.59$ ppm which are consistent with aromatic vinylpyridine compounds (7.14 – 8.63 ppm) in the literature⁴⁹⁰ as well as those of compounds (**L₁₀**,

L₁₁ and **L**₁₂). The ¹³C{¹H} NMR spectrum of (**L**₁₃) shows signals for the aromatic carbons in the range of 120.80-150.15 ppm which are consistent with the literature values.⁴⁹⁰ In addition, the ²⁹Si{¹H} NMR spectrum of compound (**L**₁₃) shows a singlet at -14.40 ppm, which is consistent with a single Si environment (-14.70, -14.36 ppm)⁴⁸⁵ in the literature. The NMR (¹H, ¹³C{¹H} and ²⁹Si{¹H}) spectra of compound (**L**₁₃) are provided as Supplementary information (**S**₇₁-**S**₇₃ respectively). However, the elemental analysis result was slightly inconsistent with the compound, which is an indication of the presence of impurities. Several purification attempts to get a better analysis result were unsuccessful.

3.6.12 Synthesis of tri(4-bromobiphenyl)methylsilane (**K**)

The synthesis of tris(4-bromobiphenyl)methylsilane (**K**) followed the procedure for the making of compound (**J**). The preparation method is depicted in **Scheme 3.13**.



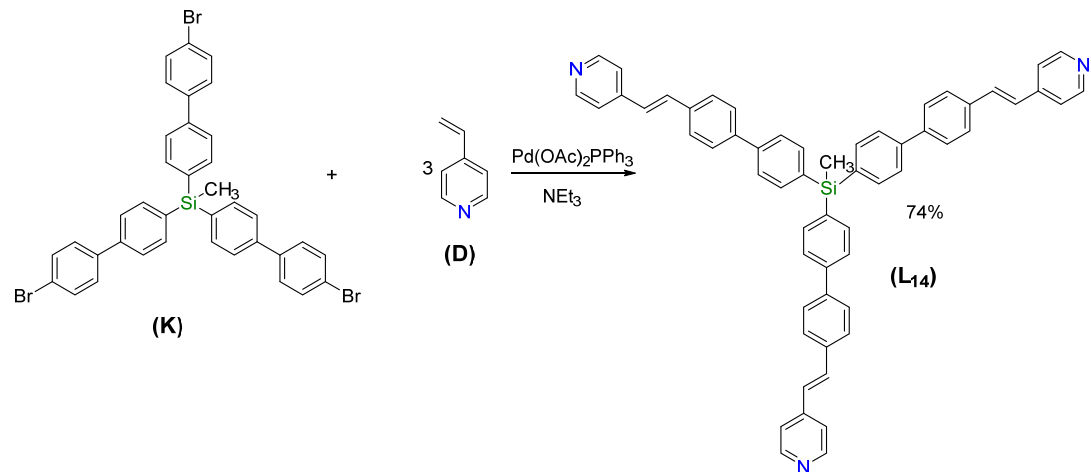
Scheme 3.13: Synthesis of tri(4-bromobiphenyl)methylsilane (**K**)

Trichloro(methyl)silane (CH_3SiCl_3) was added to the lithiation product (**I**). After 24 h of stirring, the reaction mixture was quenched with water followed by aqueous workup which gave crude colourless powder. Washing of the powder with warmed acetone gave pure compound (**J**) in 77% yield. The ¹H NMR spectrum of (**J**) showed aromatic proton signals between $\delta = 7.48 - 7.64$ ppm, while the non-aromatic proton (CH_3) signal was found at 0.93 ppm. The ¹³C{¹H} NMR spectrum

of (**J**) showed signals for the aromatic carbons in the range of 121.45-141.04 ppm, while the non-aromatic carbon (CH₃) was found at -3.31 ppm. In addition, the ²⁹Si{¹H} NMR of compound (**J**) showed a singlet at -10.28 ppm. The NMR (¹H, ¹³C{¹H} and ²⁹Si{¹H}) spectra of compound (**J**) are provided as Supplementary Information (S74-S76 respectively).

3.6.13 Synthesis of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (**L**₁₄)

The preparation of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (**L**₁₄) (a novel linker) followed a similar procedure for the making of linker (**L**₁₃) discussed earlier. The method for the preparation of linker (**L**₁₄) is shown in **Scheme 3.14**.



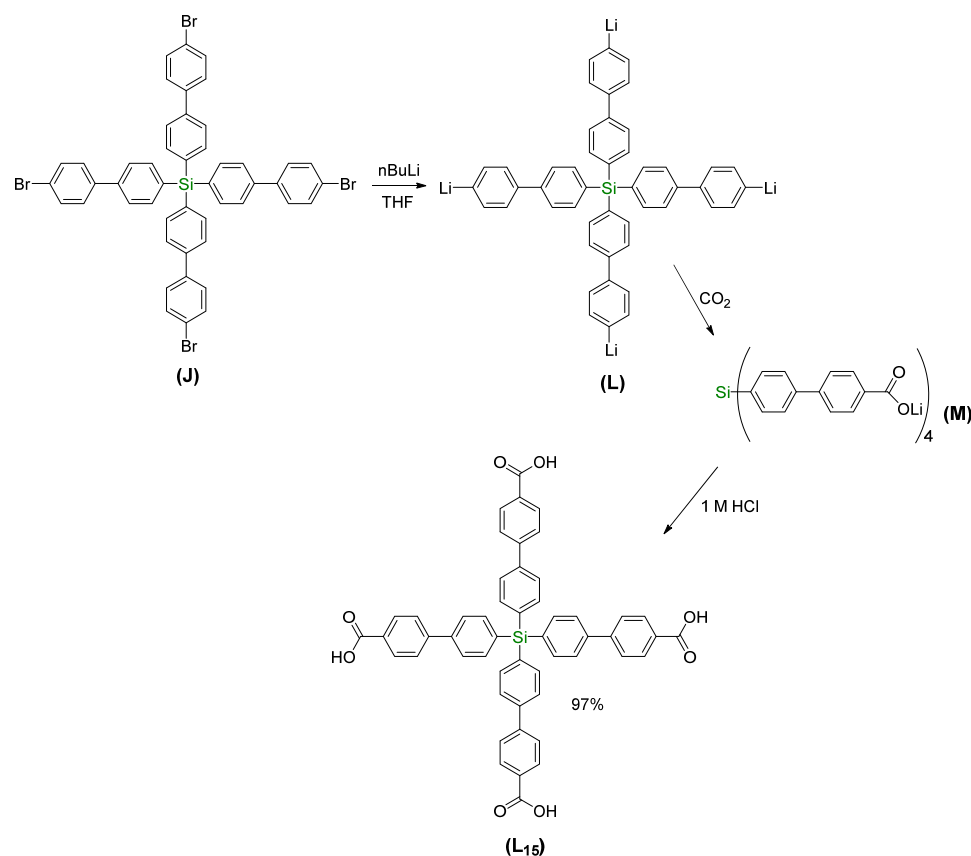
Scheme 3.14: Pathway for the making of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (**L**₁₄)

One equivalent of (**K**) was coupled with 3 equivalents of (**D**) as shown above. At the end of the reaction, and following aqueous workup, a crude brown powder product was obtained which was washed with warmed acetone and hexane to give (**L**₁₄) as a pale yellow powder in 74% yield. The ¹H NMR spectrum of the compound showed well resolved resonances with aromatic proton signal found between $\delta = 7.09 - 8.58$ ppm which are consistent with aromatic vinylpyridine compounds (7.14 – 8.63 ppm) in the literature⁴⁹⁰ as well as those of compounds (**L**₁₀, **L**₁₁ and **L**₁₂) as well as 0.94 ppm for the CH₃ protons. The ¹³C{¹H} NMR spectrum of (**L**₁₄) showed signals for the aromatic carbons in the range of 120.80-150.15 ppm which are consistent with the literature

values,⁴⁹⁰ while the non-aromatic carbon was found at -3.30 ppm. In addition, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound (**L14**) showed a singlet at -10.95 ppm, which is as expected and comparable to that of compound (**L11**) (-11.09 ppm). The NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$) of compound (**L14**) are provided as Supplementary Information (**S77-S79** respectively).

3.6.14 Synthesis of silane tetrakis(biphenyl-4-carboxylic acid) (**L15**)

The preparation of silane tetrakis(biphenyl 4-carboxylic acid) (**L15**) (a novel linker) followed procedures for the making of arylcarboxylic acid linkers in the literature,^{81,277,491,495} with some modifications. The pathway for the synthesis of linker (**L15**) is shown in **Scheme 3.15**.



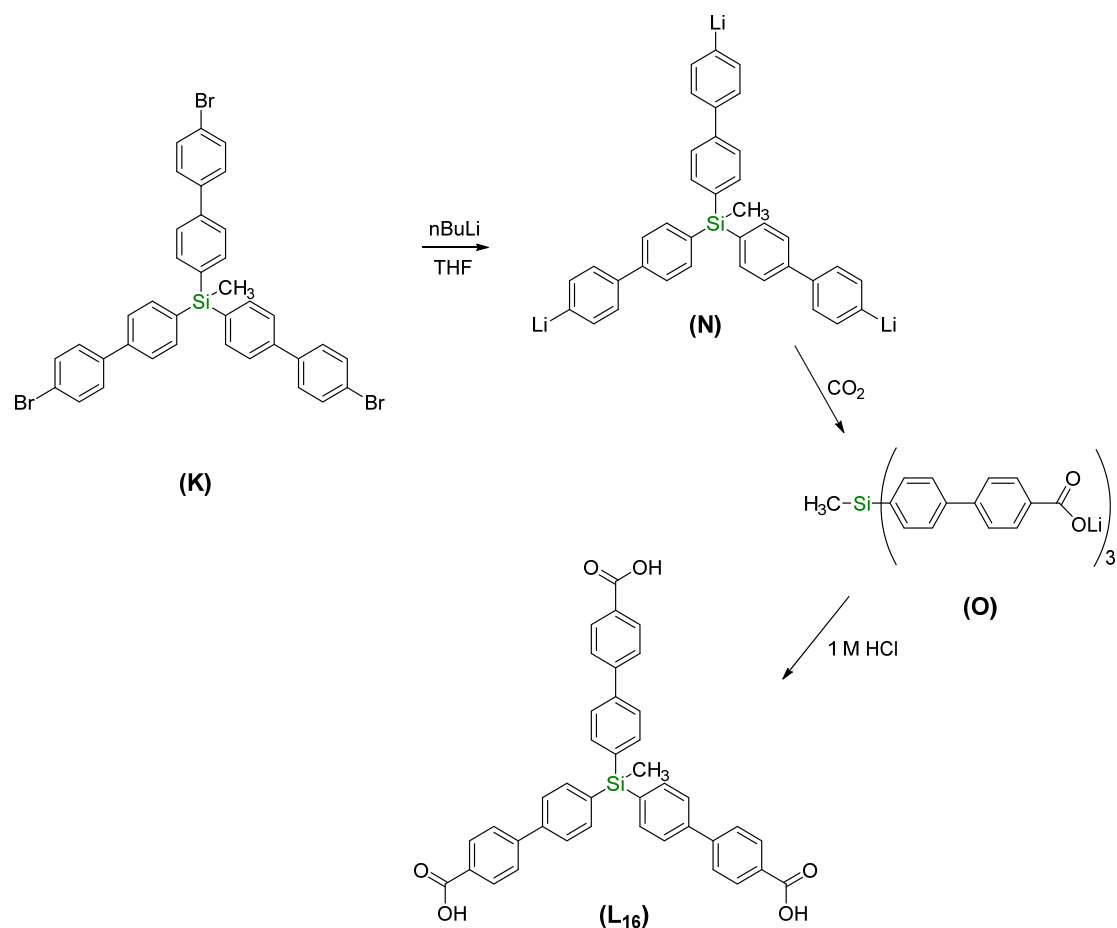
Scheme 3.15: Pathway for the synthesis of silane tetrakis(biphenyl-4-carboxylic acid) (**L15**)

After the carboxylation step in **Scheme 3.15**, an aqueous workup gave a colourless powder which was washed with warmed hexane/ ethyl acetate to give (**L15**) in 97% yield. Compound (**L15**) was characterised using standard analytical and spectroscopic techniques. The ^1H NMR spectrum of

(**L15**) showed well resolved resonances with aromatic proton signals found between $\delta = 7.71 - 8.04$ ppm, while the CO₂H signal was found at 12.94 ppm. In addition, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**L15**) showed signals for the aromatic carbons in the range of 126.83-144.81 ppm, while those of the carbonyl carbon was found at 167.15 ppm. Furthermore, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound (**L15**) showed a singlet at -14.87 ppm. These data are consistent with the expected linker (**L15**), as well different from those of the starting material (**J**). The NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$) of (**L15**) are provided as Supplementary Information (**S80-S82** respectively).

*3.6.15 Synthesis of methylsilane tris(biphenyl-4-carboxylic acid) (**L16**)*

The preparation protocol for methylsilane tris(biphenyl-4-carboxylic acid (**L16**)) is analogous to that of compound (**L15**) discussed above. The pathway for the synthesis of (**L16**) is shown in **Scheme 3.16**.



Scheme 3.16: Pathway for the synthesis of methylsilane tris(biphenyl-4-carboxylic acid (**L₁₆**))

After the carboxylation step in **Scheme 3.16**, an aqueous workup gave a colourless powder which was washed with warmed hexane/ ethyl acetate to give (**L₁₆**) in 84% yield. The ^1H NMR spectrum of (**L₁₆**) showed well resolved resonances with aromatic proton signal found within $\delta = 7.66 - 8.05$ ppm, while the CO_2H signal was found at 12.98 ppm. In addition, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of (**L₁₆**) showed signals for the aromatic carbons in the range of 126.62-143.99 ppm, while the carbonyl carbon was found at 167.12 ppm. Furthermore, the $^{29}\text{Si}\{^1\text{H}\}$ NMR spectrum of compound (**L₁₆**) showed a singlet at -11.24 ppm. These data are consistent with the expected linker (**L₁₆**), and comparable to those of compound (**L₁₅**) but different from those of the starting material

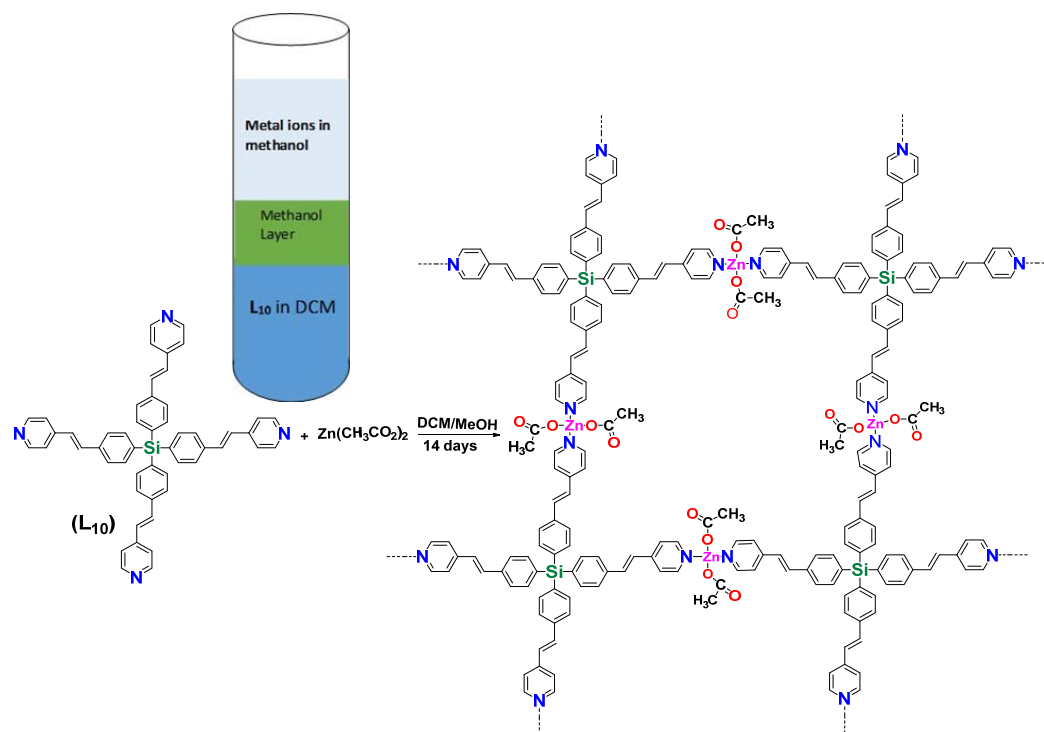
(K). The NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$) of (**L₁₆**) are provided as Supplementary Information (S83-S85 respectively).

The modified synthetic methods used to prepare the described precursors and their corresponding linkers were quite straight-forward and simple. The yield of the precursors as well as the linkers in most cases were better than those of the literature. The method may be applied to other starting materials to give more complex polyaryl rigid-core carbosilane dendrimers as well as poly pyridyl and carboxylate linkers. Most of the linkers reported here are novel, rigid and have the potential to form MOFs with metal ions.

3.6.16 Synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)

In a bid to utilise the linkers prepared for the making of MOFs with metal ions; the linkers were treated with metal ions using various reaction conditions. The preparation of MOFs (**17**), (**18**) and (**19**) were some of the successful attempts made.

The preparation of tetrakis (4-(pyridine-4-vinyl)phenyl)silane MOF (**17**) followed the layering and slow diffusion method of MOF synthesis used by Bunz and co-workers.³⁴⁶ The MOF (**17**) crystallised in a vial after the dissolution of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L₁₀**) in DCM, followed by the careful layering of methanol on top of the DCM solution of (**L₁₀**). In another test tube an equivalent volume of methanol to that of DCM used for the dissolution of (**L₁₀**) was utilised for the dissolution of zinc acetate $[\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}]$. Then the methanol solution of $[\text{Zn}(\text{CH}_3\text{CO}_2)_2 \cdot 2\text{H}_2\text{O}]$ was carefully layered on top of the methanol in vial and then sealed for two weeks, within which period crystals of MOF (**17**) formed. The method is depicted as shown in **Scheme 3.17**.



Scheme 3.17: Synthesis of MOF (17) via layering and slow diffusion

3.6.16.1 Spectral and crystal description of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)

The reaction between (**L**₁₀) and Zn(CH₃CO₂)₂·2H₂O gave colourless blocky needle crystals, which were found to be a 2-D MOF. The tetratopic linker (**L**₁₀) as well as the Zn²⁺ centre, have tetrahedral geometries as shown in **Figure 3.15(A)**. The resulting crystal has potential pores with a ca. void volume of 1653 Å³ (41.8% of the unit cell volume). In addition, the structure has a point symbol for the net of {8⁴.12²} {8²} and shows a novel 2,4-connected topology net as shown in **Figure 3.15(B)**.

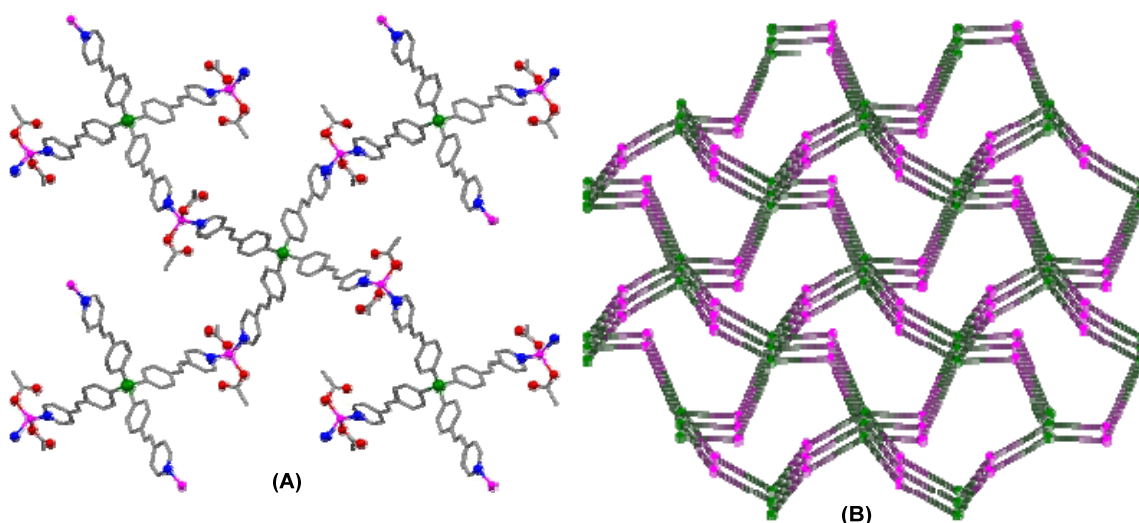


Figure 3.15: (A) a 2-D coordination of $\text{Zn}(\text{OAc})_2$ and linker (L_{10}) to give tetrakis (4-(pyridine-4-vinyl)phenyl)silane MOF (**17**). (B) a novel 2,4-connected net topology. Colour identity, green Si, purple Zn, blue N, grey C, and red O. H atoms are omitted for clarity.

Each Zn^{2+} cation coordinates to two acetates and two pyridine groups resulting in a 2-D intercorrugated sheet network as shown in **Figure 3.16(A)**. The layers do not interpenetrate and are not connected to one another, rather they interleave as shown by the red and the green layers in **Figure 3.16(B)**.

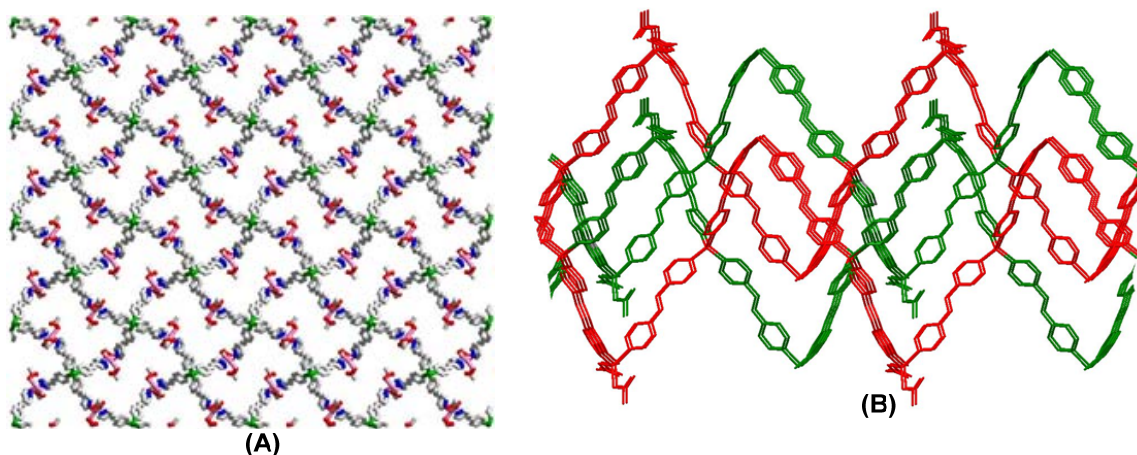


Figure 3.16: (A) 2-D network with pores as viewed along the c-axis, (B) Interleave leaved layers. Colour identity on (A), green Si, purple Zn, blue N, grey C, and red O. H atoms omitted for clarity

The void space is brought about by the parallel alignment of the non-interconnected channels when viewed from the c-axis. The void space is occupied by methanol, and the mean pore size of the

pores is 18.5 Å as shown in **Figure 3.17**.

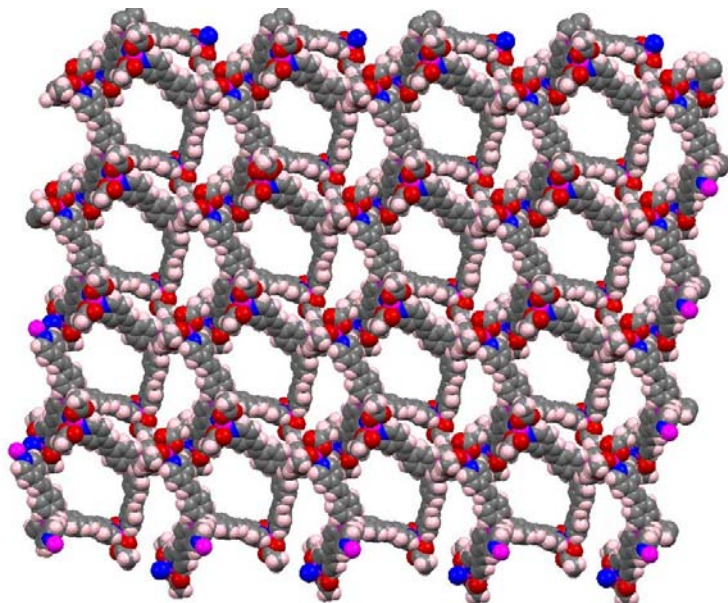
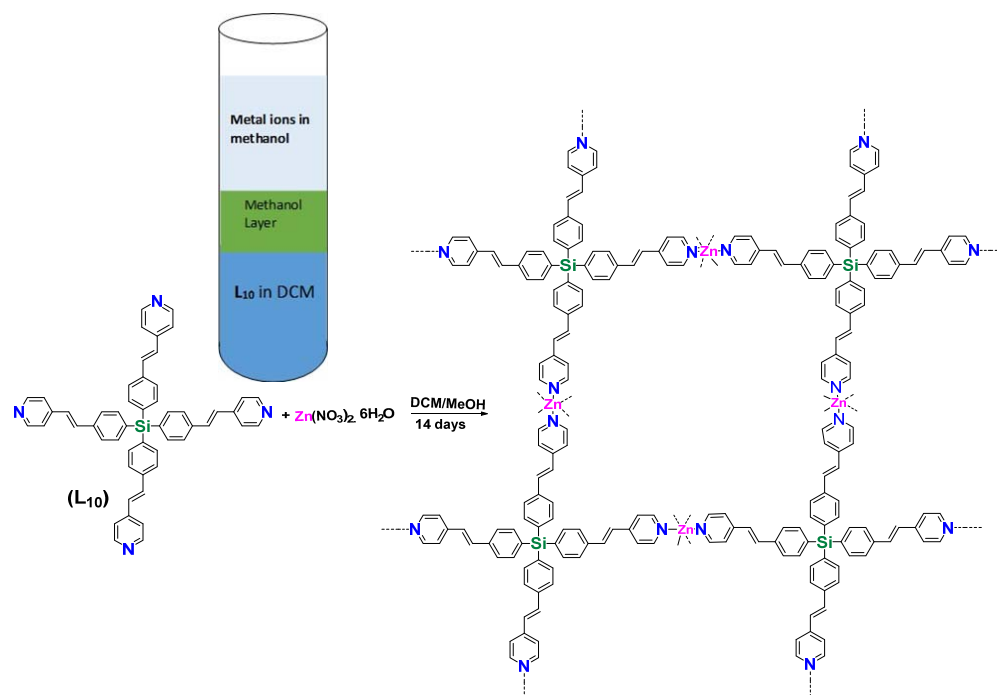


Figure 3.17: Space-filled 2-D structure of **(17)** with mean pore size of 18.5 Å, viewed down the c-axis. Colour identity, green Si, purple Zn, blue N, grey C, pink H, and red O. solvent omitted for clarity.

The acetates are strongly coordinated to the inner sphere of the zinc thus making them difficult to move to the second coordination sphere. A 2-D MOFs is expected to form the zinc acetates as against a 3-D MOF if were nitrates, and is consistent with literature report for similar MOF structure with zinc acetate and pyridine ligand.³⁴⁶ The stacking of the 2-D networks is much more space efficient and the void space of the tunnels remain intact even with the dense stacking of the sheets onto each other as a result of the long strut of the linker (**L₁₀**). The crystallographic data of MOF **(17)** are provided as Appendix 14.

3.6.17 Synthesis of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18)

The making of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF **(18)** is analogous to the procedure used in the preparation of MOF **(17)**, except that instead of the use of zinc acetate as the source of metal ions, zinc nitrate was used. This was done as NO₃⁻ is less strongly coordinating than OAc⁻ and therefore a different MOF (3-D) was anticipated. Therefore, zinc nitrate was used in the making of **(18)** as shown in **Scheme 3.18**.



Scheme 3.18: Pathway for the preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18)

At the end of fourteen days diamond-like crystals as shown in **Figure 3.18** were obtained.

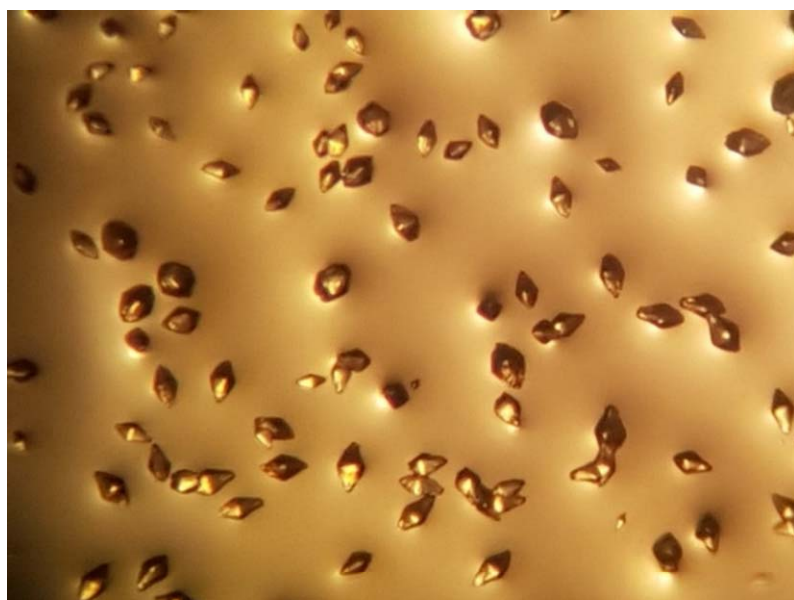


Figure 3.18: Diamond-like crystals with dimensions of ca. $0.190 \times 0.100 \times 0.030 \text{ mm}^3$ of MOF (18)

3.6.17.1 Spectral and crystal description of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18)

Although the data refinement for the structure was poor, the basic connections of the building units are demonstrated in the structure shown in **Figure 3.19(A)** consisting of a point symbol for the net of $\{4^2.8^4\}$ and 4,4-connection net of **pts** topology as shown in **Figure 3.19(B)**

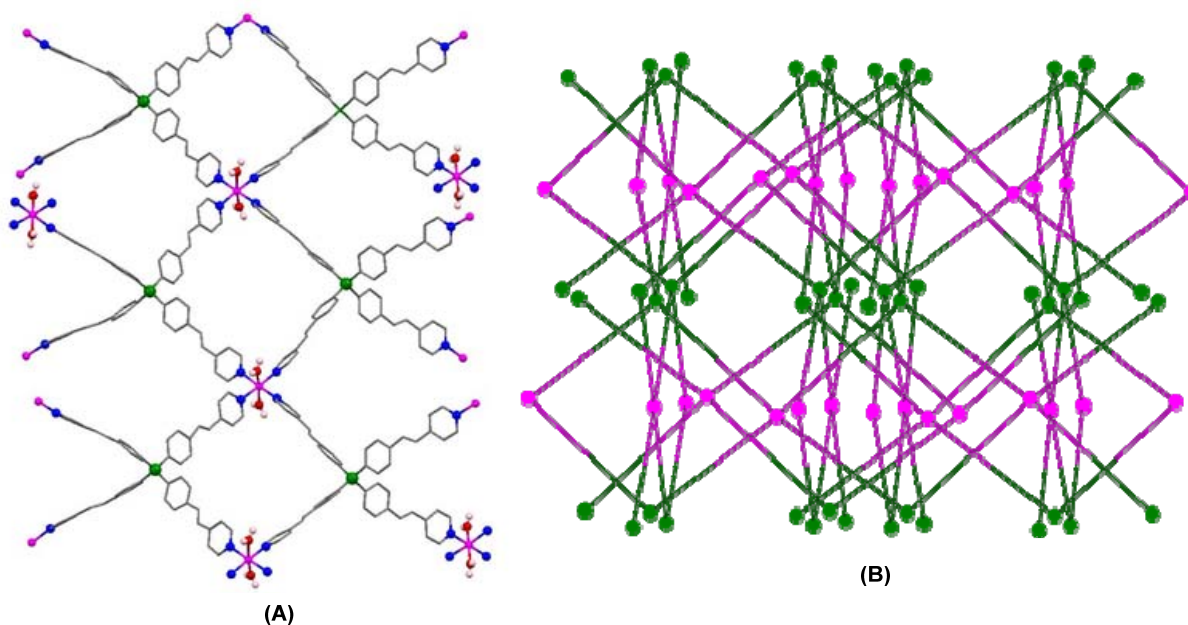


Figure 3.19: (A) 3-D connection of four L_{10} and two H_2O around each zinc atom in the framework of MOF (18) viewed along the b-axis; (B) a 4,4-connected net of **pts** topology. Colour identity, green Si, purple Zn, blue N, grey C, and red O, and pink H. All H atoms are omitted for clarity except those found in H_2O .

The Zn atom is hexa-connected with four N atoms from L_{10} and two water molecules and the connectivity continues to build a 3-D framework with a ca void volume of $11603.8 \text{ \AA}^3$ (43.7% of the unit cell volume). Thus unlike MOF (17) which is a 2-D network, MOF (18) is a 3-D framework structure. Also the NO_3^- as expected is not coordinated to the Zn. There are two types of pores in the framework of MOF (18) as revealed in **Figure 3.20**. The length and width of the big pores are 31.42 and 24.62 $\text{\AA}$ respectively, while that of the small pores are 15.50 and 12.20 $\text{\AA}$.

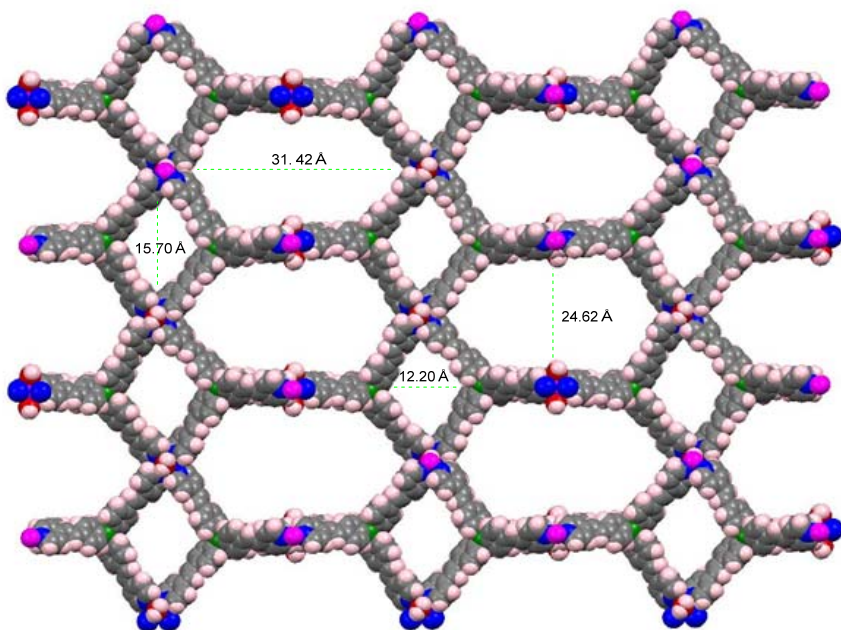


Figure 3.20: Space-filled crystal packing of MOF (18) with two types of pore sizes viewed along the b-axis. Colour identity, green Si, purple Zn, blue N, grey C, red O, and pink H.

In addition, the framework exhibits a remarkable five-fold interpenetration of nets as shown in

Figure 3.21; viewed from c-axis

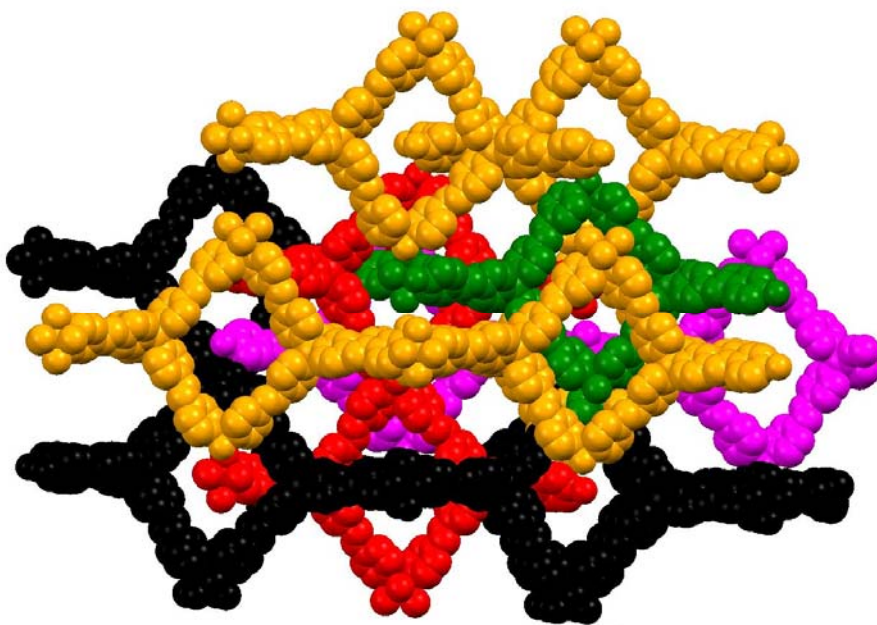
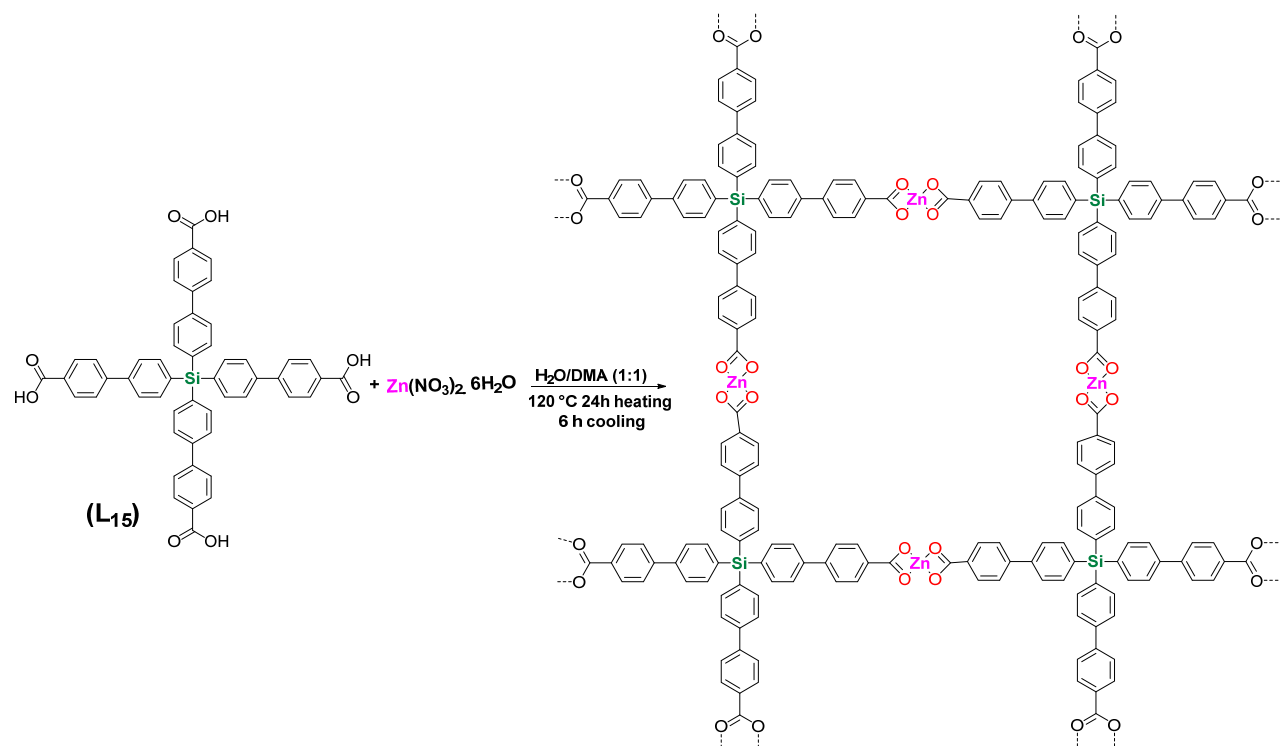


Figure 3.21: Space filled crystal structure of MOF (18) with five-fold network interpenetration as well as pores, viewed from the c-axis

This five-fold interpenetration is unusual as the similar pyridine linker, tetrakis(4-(pyridin-4-ylethynyl)-phenylsilane,³⁴⁶ to (**L10**) gave a two-fold interpenetrated MOF with Cu(II) nitrate. (**L10**) formed crystalline solids with a variety of metal ions (transition and s-block elements), but the structures discussed above were the only ones that were successfully determined by X-ray diffraction study. The crystallographic data for MOF (**18**) are provided as Appendix 15.

3.6.18 Synthesis of silane tetrakis(biphenyl-4-carboxylate MOF (19)

MOF (**19**) was prepared solvothermally by the reaction of silane tetrakis(biphenyl-4-carboxylic acid) (**L15**) and zinc nitrate using a solvent mixture of H₂O and DMA as shown in **Scheme 3.19**.



Scheme 3.19: Pathway for the preparation of MOF (**19**)

At the end of the reaction, colourless needle-shaped crystals of ca. dimension 0.320 x 0.025 x 0.015 mm³ were obtained. Although the crystal structure is disordered, around the metal, it can be seen from **Figure 3.22** that each linker connects to four metal centres.

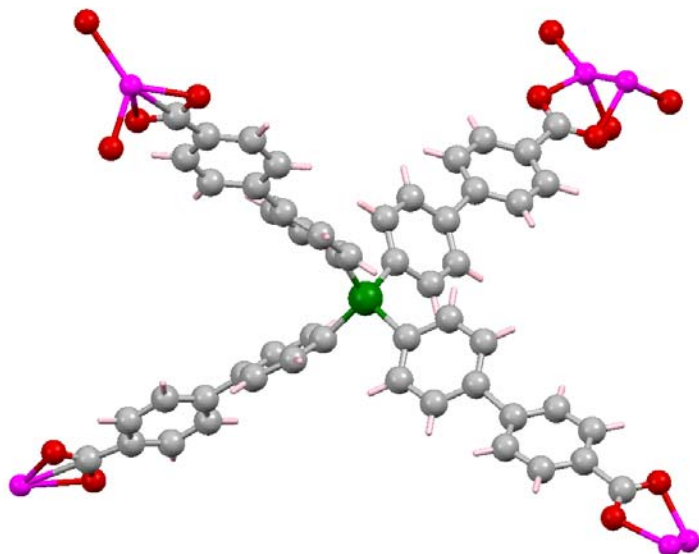


Figure 3.22: Connection of one silane tetrakis(biphenyl-4-carboxylate with 4 disordered zinc centres

Each zinc centre is connected via a deprotonated carboxylic acid and a dative bond from the carbonyl group of the carboxylic acid resulting to the formation of a 3-D MOF structures as shown below in **Figure 3.23**.

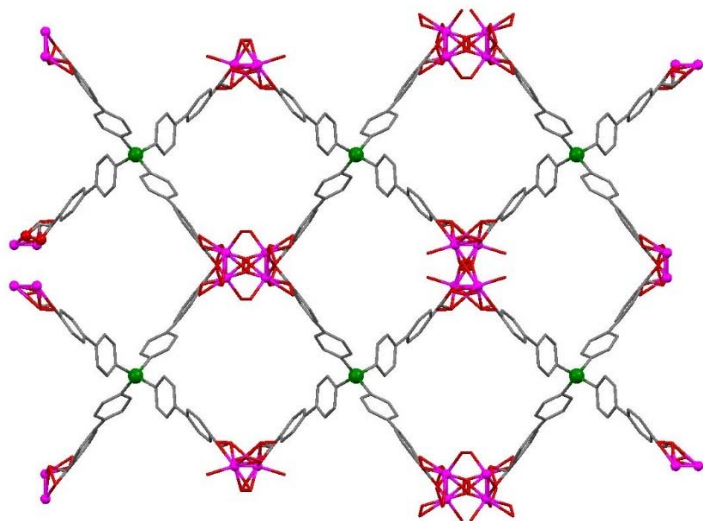


Figure 3.23: 3-D connection of (L_{15}) and zinc atoms in the framework of MOF (19) viewed along the a-axis. Disorder at Zn was hard to resolve and so is included in the Figure. Colour identity, green Si, purple Zn, grey C, and red O. All H atoms are omitted for clarity

The network has a pore size of 17.06 Å as revealed by the space-filled structure in **Figure 3.24**.

Figure 3.25 shows a perspective view of network channels along the a-axis

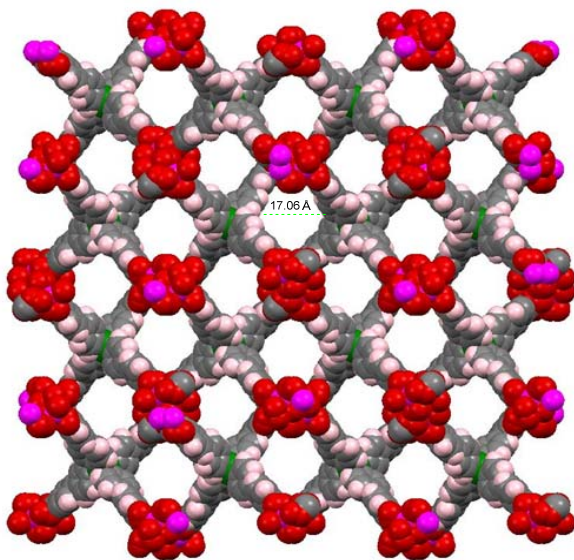


Figure 3.24: Space-filled structure of MOF (19) with 17.06 Å pore size, viewed from the a-axis. Colour identity, green Si, purple Zn, grey C, red O, and pink H.

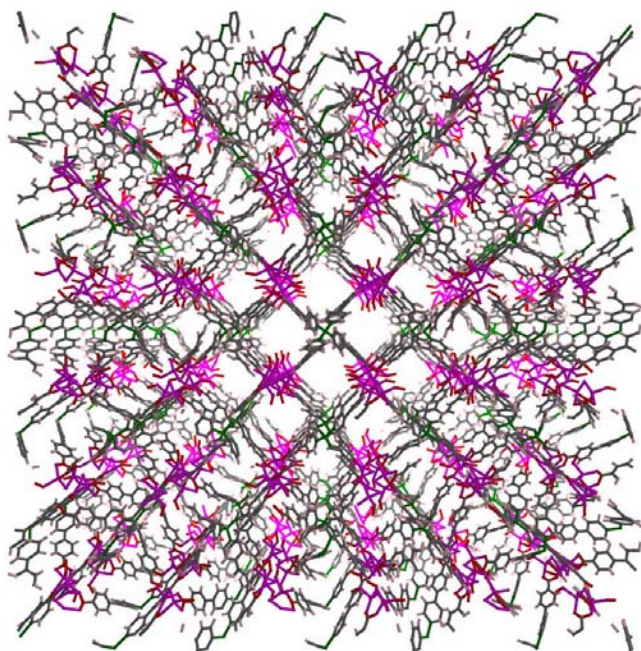


Figure 3.25: Perspective view of network channels along the a-axis

The crystallographic data for MOF (19) are provided as Appendix 16.

3.7. Summary

In this chapter, a survey of MOF literature has been carried out. Novel di-, tri- and tetra-dentate aryl-pyridine and carboxylate ligands based on silicon centres have been prepared and characterised. The synthetic methods used for the preparation of precursors and their corresponding linkers are quite straight forward and easy to replicate, and can be applied to other precursors to give more complex polyaryl rigid-core carbosilane dendrimers, polypyridyl and carboxylic connectors.

Most of the N-heterocyclic and carboxylic linkers for the construction of MOF materials are based on carbon centres as well as commercially available linkers. In contrast, silicon-based connecting units are scarce when compared with their carbon counterparts; however, the silicon-based linkers are more convenient to synthesise through metathesis compared to their carbon analogues. The linkers reported in this project contain aromatic groups which have the capability to give rigidity to MOF networks. In addition, these ligands contain functional groups which can coordinate with metal ions to give 1-, 2-, or 3-D networks. The pyridyl-based ones are neutral components and as such will require another anionic ligand or counter ion to balance the charge on metal centres. In addition, the linkers have long struts which can lead to either non-interpenetrated or interpenetrated networks. Some of the ligands, tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L₁₀**) and silane tetrakis(biphenyl 4-carboxylic acid) (**L₁₅**) have been used to prepare 2-D MOF (**17**) and 3-D MOFs (**18**) and (**19**). MOFs (**17**) and (**18**) were made using zinc acetate and zinc nitrate respectively. MOF (**17**) showed no interpretation of networks, however, MOF (**18**) showed a five-fold network interpenetration. In **Chapter 2**, preliminary experiments to make 2- or 3-D materials with tri- and tetra-dent ligand were unsuccessful. The use of metal ions in place of boron was envisaged to give 2-or 3-D network material. This has been achieved in this section. These MOFs

show better porosity than the 1-D polymers discussed in **Chapter 2**. Although, these materials have better porosity in their frameworks, due to difficulties associated with their characterisation using X-ray diffraction and PXRD studies, CO₂ adsorption studies were not carried out.

Chapter 4

4.0 CONCLUSION

In this project Lewis acids such as cyclo-1,3,3,5,7,7-hexaphenyl-1,5-dibora-3,7-disiloxane ($\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4$) (**3**), 1,4-bis(2,2,4,4-tetraphenyl-1,3,5,2,4,6-trioxadisilaborinan-6-yl)benzene ($(\text{Ph}_4\text{Si}_2\text{O}_3\text{B})\text{C}_6\text{H}_4(\text{BO}_3\text{Ph}_4\text{Si}_2)$) (**3a**), $[\text{B}(\text{OSiPh}_2\text{OSiPh}_2\text{O})_3\text{B}]$ (**3b**), [(methylsilanetriyl)tris(benzene-1,4)]triboronic acid (**3c**) and [(dimethylsilanediy)bis(1,4-phenylene)]diboronic acid (**3d**) have been synthesised successfully and the structures confirmed by standard analytical and spectroscopic techniques. Following this, a variety of aryl-pyridines which acted as Lewis bases such as 4,4'-bipyridine, 1,2-di(pyridin-4-yl)ethane, *trans*-1,2-di(pyridin-4-yl)ethene, 1,3-di(pyridin-4-yl)propane, 1,2-di(pyridin-4-yl)sulfane, 1,2-di(pyridin-4-yl)diazene, 1,4-di(pyridin-4-yl)benzene, 3,5-di(pyridin-3-yl)-1,2,4-thiadiazole and 3,5-di(pyridin-4-yl)-1,2,4-thiadiazole were complexed with (**3**) to give a series of 1-D polymeric structures such as $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_1$ (**4**), $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_2$ (**5**), $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_3\cdot 0.5(\text{CH}_2\text{Cl}_2)$ (**6**), $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_4$ (**7**), $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot\text{L}_5$ (**8**) and $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_9\cdot 2[\text{PhB}(\text{OH})_2]$ (**14**) These polymeric materials were characterised by standard analytical and spectroscopy methods. Some of the polymers have channels in their packing as well as show inter- and intra-molecular π - π and other forms of π -interactions as well as hydrogen bonding.

Other than the 1-D polymers, in some cases there was ring contraction of compound (**3**) that gave rise to the formation of other products such as $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_6$ (**9**), $4(\text{C}_{12}\text{H}_{12}\text{O}_2\text{Si})\cdot 3(\text{C}_{10}\text{H}_8\text{N}_4)$ (**10**), $\text{Ph}_4\text{Si}_2(\text{OH})_4\cdot 2\text{L}_7$ (**11**) and $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_7$ (**12**) which also displayed interesting intra-molecular π - π and other forms of π -interactions as well as hydrogen bonding. These novel 1-D COFs as well as the other COF materials reported in this project should be explored more deeply for various application such as photoluminescence, charge carriers and stability. In addition, the methods used

for the preparation of these materials should be used with tri-, tetra- and multidentate aryl-pyridines so as to obtain 2-D, or 3-D COFs.

All the experiments performed using compound **(3)** with the varieties of Lewis bases, were also conducted with compounds **3a**, **3b**, **3c** and **3d**. Unfortunately, all these experiments performed with **3a**, **3b**, **3c** and **3d** and the Lewis bases (**L**₁₋₉) were unsuccessful after several attempts.

Furthermore, a number of novel silicon-based di-, tri- and tetra- topic pyridine linkers such as tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L**₁₀), tri(4-(pyridine-4-vinyl)phenyl)methylsilane (**L**₁₁), bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (**L**₁₂) and tetrakis(4-(pyridine-4-vinyl)biphenyl)silane (**L**₁₃), tri(4-(pyridine-4-vinyl)biphenyl)methylsilane (**L**₁₄), as well as and carboxylic acid linkers such as silane tetrakis(biphenyl-4-carboxylic acid) (**L**₁₅) and silane tris(biphenyl-4-carboxylic acid) (**L**₁₆) have been synthesised successfully from the corresponding dibromo-aryl precursor. These linkers have been characterised using standard analytical and spectroscopic methods. In addition, tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L**₁₀) was found to give crystalline materials with zinc acetate and zinc nitrate. The linker (**L**₁₀) reacts with zinc acetate to give a 2-D MOF while with zinc nitrate, a 3-D MOF was formed. These two MOFs have pores in their structure. Furthermore, linker (**L**₁₀) also give crystalline materials with a variety of other metal ions but crystal structures were not obtained as a result of the sizes of the crystals. These are worthy of exploring further to open possibilities for the construction of interesting framework materials with multi-interpenetration of networks. The silane tetrakis(biphenyl-4-carboxylic acid) (**L**₁₅) was also used to construct MOF (**19**), but because of problems associated with characterisation by single crystal X-ray diffraction studies, further studies of this MOF and linkers are needed. Furthermore, the methods used for the preparation of these various precursors as well as the linkers should be explored. The linkers reported here are all novel and should be used for

the construction of COFs and MOFs for the purpose of gas adsorption and other applications such as catalysis. The expanded networks constructed using (**L₁₀**) and (**L₁₅**) linkers are stabilized via interpenetration of networks which give rise to intriguing pore structure in the crystals that deserve further studies.

Chapter 5

5.0 EXPERIMENTAL

Methods

Chemicals and Reagents: All chemicals, reagents and solvents were purchased from Sigma Aldrich or Alfa Aesar and used as received unless otherwise stated. Molecular sieves (1.6 mm rods and 0.4 nm pores) were preheated to dryness in the oven at 120 °C for two weeks before use.

Spectroscopy: ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{11}\text{B}\{^1\text{H}\}$ and $^{29}\text{Si}\{^1\text{H}\}$ NMR spectra were recorded on Bruker AVANCE III HD 400 MHz or 500 MHz spectrometers in CDCl_3 solvent unless stated otherwise. The chemical shifts (δ) for ^1H and $^{13}\text{C}\{^1\text{H}\}$, $^{29}\text{Si}\{^1\text{H}\}$, and $^{11}\text{B}\{^1\text{H}\}$, are quoted in ppm with reference to Me_4Si and BF_3OEt_2 respectively. Coupling constants are reported in Hz. Infrared spectra were obtained on a Perkin Elmer Spectrum 100 FTIR Spectrometer operating in ATR mode. Mass spectra (EI 70) were recorded by Imperial College Department of Chemistry Mass Spectrometry Service: MALDI TOFESI (m/z). All the crystal structures reported in this work were collected and solved by Dr. Andrew White of Imperial College London except those of (**L**₁₂) and MOFs (**18**, **19**) which were collected and solved by Dr. David Pugh of Imperial College London and Peter Horton of the UK National Crystallographic Service respectively.

*Preparation of $\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4$ (**3**)*

Diphenylsilanediol (**1**) 1.082 g, (5.0 mmol) was mixed with 0.609 g (5.0 mmol) of phenylboronic acid (**2**) in dry toluene (50 ml) and 0.5 g molecular sieves in a round bottom flask containing a magnetic stirrer bar. The mixture was refluxed under N_2 for 20 h. Thereafter, the round bottom flask and its contents were allowed to cool to room temperature. The cooled reaction mixture was filtered and the filtrate collected. The molecular sieves were washed with dry toluene (3 x 25 ml). The filtrates were combined and concentrated under reduced pressure, and the solid residue

recrystallized from diethyl ether and petroleum ether (3:1 ratio) to give **(3)** 1.30 g, 86% (lit. 87%)⁸⁵; M.p. 162 -163 °C (lit.161-162 °C)⁸⁵. ¹H NMR: δ (CDCl₃ 500 MHz) 7.31-7.54 (m, 18H, *m, p*-C₆H₅); 7.73-7.75 (m, 8H *o*-C₆H₅Si); 8.08-8.10 (m, 4H, *o*-C₆H₅B). ¹³C NMR: δ (CDCl₃, 125 MHz) 127.93, 128.06, 130.60, 131.74, 133.40, 134.12, 135.65 ppm (C₆H₅Si, C₆H₅B). ¹¹B NMR: δ (CDCl₃, 160 MHz) 25.69 ppm. ²⁹Si{¹H}, NMR: δ (CDCl₃, 99MHz) -45.00ppm. Mass spectrum (70 eV, EI): *m/z* 604 (M⁺), 527 (M-Ph)⁺, 423 (M-Ph-PhBO)⁺, 406 (M-Ph₂SiO)⁺. IR: ν (cm⁻¹) 3023, C-H aromatic; 1349, B-O; 1307, Si-C stretch; 1071, Si-O stretch).

*Preparation of [Ph₆B₂Si₂O₄].L₁ (**4**)*

In a round bottom flask, [Ph₆B₂Si₂O₄] (**3**), (0.25 g 0.415 mmol) was added to 4,4'-bipyridine (**L₁**) (0.065 g 0.415 mmol) and a mixture of solvents (diethyl ether 21 ml and petroleum ether 7 ml). The mixture was heated at reflux while stirring for 4 h. The resultant solution was allowed to cool to room temperature followed by filtration. The filtrate was transferred into a vial and covered with perforated Parafilm and stored in the fumehood for slow evaporation of the solvent. Colourless crystals were obtained from the solvent after 12 h to give [Ph₆B₂Si₂O₄].L₁ (**5**) (0.27 g, 84% yield; M.p 184 °C); found: C, 72.78%, H, 5.33%, N, 3.61%. Calc. for C₅₆H₄₄N₂Si₂B₂: C, 72.57%, H, 5.78%, N, 3.68%; IR: ν (3067 cm⁻¹, C-H aromatic; 1429 cm⁻¹ B-O; 1324 cm⁻¹ C-N aromatic; 1059 cm⁻¹ Si-O stretch); ¹H NMR: δ (CDCl₃ 500 MHz) 7.32-7.56 (m, 18H, *m, p*-C₆H₅); 7.62- 7.64 (m, 4H, *m*-C₅H₄N); 7.73-7.78 (m, 8H, *o*-C₆H₅Si) 8.09-8.17 (m, 4H, *o*-C₆H₅B); 8.80-8.82 (m, 4H, *o*-C₅H₄N). ¹³C{¹H}, NMR: δ (CDCl₃, 125 MHz) 149.96, 145.87, 135.36, 134.30, 134.10, 133.72, 131.32, 127.94, 127.94, 127.82, 121.59 ppm; ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 20.91 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -45.16 ppm.

Preparation of [Ph₆B₂Si₂O₄].L₂ (5)

In a round bottom flask, [Ph₆B₂Si₂O₄] (**3**) (0.125 g 0.208 mmol) was dissolved in ether (20 ml) and stirred with a magnetic stirrer bar. In another round bottom flask, 1,2-bis(pyridyl)ethane (**L**₂) (0.038 g, 0.208 mmol) was dissolved in ether (20 ml) and stirred. The [Ph₆B₂Si₂O₄] solution was added to the bis(pyridyl)ethane (**L**₂) while stirring. The reaction mixture was stirred for 24 h during which time a milky solution formed. Removal of ether via filtration afforded a colourless powder. Recrystallisation from CH₂Cl₂-ether (2:1) via slow evaporation gave colourless crystals after 24 h of [Ph₆B₂Si₂O₄].L₂ (**5**) (0.14 g, 87% yield; M.p 196 – 197 °C); found: C, 72.82%, H, 5.47% N, 3.41% Calc. for (C₄₈H₄₂B₂N₂O₄Si₂)_n: C, 73.03%, H, 5.33%, N, 3.55%; IR: ν (3017 cm⁻¹ C-H aromatic; 1477 cm⁻¹ CH₂ scissor; 1412 cm⁻¹ B-O; 1379 cm⁻¹ C-N; 1251 cm⁻¹ CH₂ rock; 1114 cm⁻¹ CH₂ wag; 1073 cm⁻¹ Si-O); ¹H NMR: δ (CDCl₃ 500 MHz) 2.94 (s, 4H, CH₂CH₂); 7.09-7.10 (m, 4H, *m*-C₅H₄N); 7.31-7.49 (m, 18H, *m*, *p*-C₆H₅); 7.68-7.70 (m, 8H, *o*-C₆H₅Si); 8.02-8.04 (m, 4H, *o*-C₆H₅B); 8.55-8.56 (m, 4H, *o*-C₅H₄N). ¹³C NMR: δ (CDCl₃, 125 MHz) 150.64, 148.36, 135.27, 134.32, 134.12, 133.88, 133.59, 131.17, 130.33, 127.90, 127.79, 127.51, 124.06, 33.52 ppm; ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 19.86 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -45.60 ppm.

Preparation of [Ph₆B₂Si₂O₄].L₃ 0.5(CH₂Cl₂) (6)

In a round bottom flask, [Ph₆B₂Si₂O₄] (**3**) (0.25 g, 0.415 mmol) was dissolved in ether (21 ml), petroleum ether (7 ml) and stirred with a magnetic stirrer bar. In another round bottom flask, 1,2-bis(4-pyridyl)ethene (**L**₃) (0.076 g, 0.415 mmol) was dissolved in ether (20 ml), petroleum ether (7 ml) and stirred. The solution of (**3**) was added to that of (**L**₃) while stirring. The reaction mixture was stirred for 24 h during which time a milky solution formed. Removal of solvents via filtration afforded colourless powder. Recrystallisation from CH₂Cl₂-ether (1:1) gave (**6**) (0.29 g, 89%) after 24 h; M.p 204 - 205 °C; found: C, 71.05%, H, 5.24%, N, 3.29% Calc. for (C₄₈H₄₀B₂N₂O₄Si₂),

0.5(CH₂Cl₂): C, 70.92%, H, 5.07%, N, 3.38%; IR: ν (3066 cm⁻¹ C-H aromatic; 3004 cm⁻¹ =C-H; 1624 cm⁻¹ C=C; 1436 cm⁻¹ B-O; 1336 C-N aromatic; 1289 cm⁻¹ Si-C stretch; 1059 cm⁻¹ Si-O); ¹H NMR: δ (CDCl₃ 400 MHz) 5.30 (s, 0.25H, CH₂Cl₂); 7.27-7.30 (m, 4H, *m*-C₅H₄N); 7.30-7.48 (m, 18H, *m*, *p*-C₆H₅); 7.64-7.74 (m, 8H, *o*-C₆H₅Si); 7.95-8.09 (m, 4H, *o*-C₆H₅B); 8.61-8.68 (m, 4H, *o*-C₅H₄N). ¹³C NMR: δ (CDCl₃, 125 MHz) 149.40, 143.84, 135.19, 134.30, 134.10, 133.93, 131.05, 130.70, 130.26, 127.86, 127.75, 121.32 ppm; ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 21.97 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -44.90 ppm.

Preparation of [Ph₆B₂Si₂O₄].L₄ (7)

In a round bottom flask, **(3)** (0.25 g, 0.415 mmol) was dissolved in ether (20 ml) and stirred with a magnetic stirrer bar. In another round bottom flask, 1,3-bis(4-pyridyl)propane (**L₄**) (0.082 g, 0.415 mmol) was dissolved in ether and stirred. The mixture of **(3)** was added to that of **(L₄)** while stirring. The reaction mixture was stirred for 24 h during which time a milky solution formed. Removal of solvents via filtration afforded colourless powder. Recrystallisation of the powder from CH₂Cl₂-ether (2:1) gave **(7)** (0.14 g, 87%) yield; M.p 152 - 153 °C; found: C, 73.15%, H, 5.54% N, 3.52% Calc. for C₄₉H₄₄B₂N₂O₄Si₂: C, 73.26%, H, 5.48%, N, 3.49%; IR: ν (3014 cm⁻¹ C-H aromatic, 2968 cm⁻¹ CH₂ asym stretch; 1485 cm⁻¹ CH₂ scissor; 1412 cm⁻¹ B-O; 1330 cm⁻¹ C-N; 1249 cm⁻¹ CH₂ rock; 1112 cm⁻¹ CH₂ wag; 1059 cm⁻¹ Si-O); ¹H NMR: δ (CDCl₃ 500 MHz) 1.89 - 1.99 (s, 4H, CH₂-**CH₂**-CH₂); 2.59 -2.66 (m, 2H, -**CH₂**CH₂**CH₂**-); 7.05-7.10 (m, 4H, *m*-C₅H₄N); 7.24-7.45 (m, 18H, *m*, *p*-C₆H₅); 7.56-7.79 (m, 8H, *o*-C₆H₅Si); 7.91-8.02 (m, 4H, *o*-C₆H₅B); 8.50-8.55 (m, 4H, *o*-C₅H₄N). ¹³C{¹H}, NMR: δ (CDCl₃, 125 MHz) 149.82, 146.62, 133.18, 132.42, 128.85, 128.35, 126.04, 125.93, 122.26, 32.69, 28.56 ppm; ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 20.83 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -45.60 ppm.

*Preparation of [Ph₆B₂Si₂O₄].L₅ (**8**)*

In a round bottom flask, (**3**) (0.25 g, 0.415 mmol) was dissolved in ether (20 ml) and then stirred with a magnetic stirrer bar. In another round bottom flask, 4,4' - dithiobis(pyridine) (**L₅**) (0.091 g, 0.415 mmol) was dissolved in ether (20 ml) and stirred. The solutions were combined while stirring. The reaction mixture was stirred for another 24 h, during which time a colourless solution formed but no crystals or powder. The mixture was transferred into a vial and sealed with perforated Parafilm. After about 30 - 50% of the solvent had slowly evaporated, colourless crystals of (**8**) formed, (70% yield; M.p 65-66°C); found: C, 65.57%, H, 4.76%, N, 4.28%. Calc. for (C₁₉₄H₁₆₀N₁₀O₁₆Si₁₀Si₈B₈+C₁₀H₈N₂S₂,C₄H₁₀O): C, 65.45%, H, 4.67%, N, 4.40%; IR: ν (3067 cm⁻¹ C-H aromatic; 1428 cm⁻¹ B-O; 1399 C-N aromatic; 1280 cm⁻¹ Si-C stretch; 1055 cm⁻¹ Si-O); ¹H NMR: δ (CDCl₃ 500 MHz) 7.23-7.24(m, 4H, *o*-C₅H₄N); 7.36-7.39 (m, 18H, *m*, *p*-C₆H₅); 7.68-7.73 (m, 8H, *o*-C₆H₅Si); 8.03-8.07 (m, 4H, *o*-C₆H₅B); 8.53-8.55 (m, 4H, *o*-C₅H₄N). ¹³C{¹H}, NMR: δ (CDCl₃, 125 MHz) 149.34, 148.99, 135.45, 134.31, 134.28, 134.19, 133.58, 130.77, 130.18, 128.31, 127.92, 127.74, 127.53, 124.95, 120.14 ppm; ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 20.64 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -44.28 ppm.

*Preparation of [Ph₆B₄Si₂O₆].L₆ (**9**)*

In a round bottom flask, [Ph₆B₂Si₂O₄] (**3**) (0.25 g, 0.415 mmol) was dissolved in ether (20 ml) and then stirred with a magnetic stirrer bar. In another round bottom flask, 4,4'-azopyridine (**L₆**) (0.076 g, 0.415 mmol) was dissolved in ether (20 ml) and stirred. The solution of (**3**) was added to (**L₆**) solution while stirring. The reaction mixture was stirred for 24 h during which time an orange-brown precipitate formed. Removal of solvents via filtration afforded an orange-brown powder. Recrystallization of the powder from CH₂Cl₂-ether (1:1) gave (**9**) as orange crystals after 24 h, (0.33 g, 80% yield; M.p 194 – 195 °C); found: C, 69.84%, H, 4.94% ; N, 5.70%. Calc. for

$C_{58}H_{48}B_4N_4O_6Si_2$: C, 69.91%, H, 4.86%, N, 5.62%; IR: $\nu(3071\text{ cm}^{-1}$ C-H aromatic; 3004 cm^{-1} =C-H; 1624 cm^{-1} C=C; 1436 cm^{-1} B-O; 1340 cm^{-1} C-N aromatic; 1289 cm^{-1} Si-C stretch; 1063 cm^{-1} Si-O); ^1H NMR: δ ($CDCl_3$ 400 MHz) 7.27-7.36 (m, 8H, *m*- C_6H_5Si); 7.49-7.55 (m, 4H, *p*- C_6H_5Si); 7.68-7.74 (m, 8H, *o*- C_6H_5Si); 7.76-7.78 (m, 2H, *p*- C_6H_5B); 7.84-7.87 (m, 4H, *m*- C_6H_5B); 8.04-8.10 (m, 4H, *o*- C_6H_5B); 8.11-8.18 (m, 4H, *m*- C_6H_4N); 8.94-8.97 (m, 4H, *o*- C_5H_4N). $^{13}C\{^1H\}$, NMR: δ ($CDCl_3$, 125 MHz) 156.95, 150.13, 135.57, 135.02, 134.37, 134.08, 133.80, 133.40, 131.64, 130.53, 129.98, 128.06, 128.00, 127.87, 127.62, 116.90 ppm; $^{11}B\{^1H\}$, NMR: δ ($CDCl_3$, 160 MHz) 29.52, 22.36 ppm; $^{29}Si\{^1H\}$, NMR: δ ($CDCl_3$, 99 MHz) -45.04 ppm.

Preparation of 4($C_{12}H_{12}O_2Si$), 3($C_{10}H_8N_4$) (10)

In a round bottom flask, $[Ph_6B_2Si_2O_4]$ (**3**) (0.25 g, 0.415 mmol) was dissolved in ether/petroleum ether (2:1) (20 ml) and then stirred with a magnetic stirrer bar. In another round bottom flask, 4,4'-azopyridine (0.076 g, 0.415 mmol) was dissolved in ether/petroleum ether (2:1) (20 ml) and stirred. The solution of (**3**) was added to 4,4'-azopyridine solution while stirring. The reaction mixture was stirred for 24 h wherein orange-brown precipitate formed. Removal of solvents via filtration afforded orange-brown powder. Recrystallization of the powder from CH_2Cl_2 -ether (1:1) gave (**10**) as orange crystals of after 24 h. As the crystals of compounds (**9**) and (**10**) have different morphologies and shapes, compound (**10**) was isolated by hand-picking from that of (**9**) but in low yield; (0.012 g, 16% yield; Mp 190 -193 °C); found: C, 68.47%; H, 4.69%; N, 6.06%; Calc. for $C_{66}H_{64}N_8O_8Si_4$: C, 66.21%, H, 5.23%, N, 9.08%;

Preparation of $Ph_4Si_2(OH)_4 \cdot 2L_7$ (11)

In a round bottom flask, $[Ph_6B_2Si_2O_4]$ (**3**) (0.125 g 0.208 mmol) was dissolved in ether (20 ml) and stirred with a magnetic stirrer bar. In another round bottom flask, (0.038 g, 0.208 mmol) (**L7**) was dissolved in ether (20 ml) and stirred. The solution of (**3**) was added to that of (**L7**) while

stirring. The reaction mixture was stirred for 24 h during which time a milky solution formed. Removal of ether via filtration afforded a colourless powder. Recrystallisation from CH₂Cl₂-ether (1:1 ratio) gave colourless crystals after 24 h of [diphenylsilanediol]-4,4'-(1,4-phenylene)bispyridine dimer (**11**) which were separated from (**12**) by hand picking as compound (**11**) possessed different crystallographic morphologies, (0.17 g, 73% yield; M.p 167-168 °C); found: C, 74.69%, H, 4.84% N, 5.78%, Calc. for C₅₆H₄₈N₄O₄Si₂: C, 74.97%; H, 5.39%; N, 6.24%; IR: ν (3254 cm⁻¹ intermolecular H-bonding 3075 cm⁻¹ C-H aromatic; 1627 cm⁻¹ C=C; 1602 cm⁻¹ N-H bending; 1346 C-N aromatic; 1281 cm⁻¹ Si-C stretch; 1069 cm⁻¹ Si-O); ¹H NMR: δ (CDCl₃ 400 MHz) 7.31-7.41 (m, 12H, *m*, *p*-C₆H₅Si); 7.54-7.56 (m, 8H, *m*-C₅H₄N); 7.57-7.73 (m, 8H, *o*-C₆H₅Si); 7.74-7.78 (s, 8H, C₆H₄); 8.72-8.80 (m, 8H, *o*-C₅H₄N); ¹³C{¹H}, NMR: δ (CDCl₃, 125 MHz) 148.52, 138.44, 135.07, 134.30, 134.24, 133.57, 127.85, 127.81, 127.59 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -45.92 ppm.

*Preparation of [Ph₈B₄Si₂O₆].L₇dimer (**12**)*

In a round bottom flask, [Ph₆B₂Si₂O₄] (**3**) (0.125 g 0.208 mmol) was dissolved in ether (20 ml) and stirred with a magnetic stirrer bar. In another round bottom flask, (0.038 g, 0.208 mmol) (**L₇**) was dissolved in ether (20 ml) and stirred. The solution of (**3**) was added to the solution (**L₇**) while stirring. The reaction mixture was stirred for 24 h during which time a milky solution formed. Removal of the ether via filtration afforded a white powder. Recrystallisation from CH₂Cl₂-ether (2:1) gave colourless crystals after 24 h of 2,2,4,6-tetraphenyl,1,3,5-trioxo-2-sila-4-6-diboracychexanyl-4-bis-4,4'-(1,4-phenylene)bispyridine dimer (**12**) which were separated from those of (**11**) due differences in crystallographic morphologies (0.07g, 28% yield); M.p 206 – 207 °C ; found: C, 73.16%; H, 5.60%; N, 3.37 Calc. for C₆₄H₅₂B₄N₂O₆Si₂: C, 73.59%, H, 5.02%, N, 2.68%; IR: ν (3066 cm⁻¹ C-H aromatic; 1625 cm⁻¹ C=C; 1429 cm⁻¹ B-O; 1338 C-N aromatic;

1295 cm^{-1} Si-C stretch; 1064 cm^{-1} Si-O); ^1H NMR: δ (CDCl_3 400 MHz) 7.27-7.30 (m, 4H, *m*- $\text{C}_5\text{H}_4\text{N}$); 7.34-7.43 (m, 10H, *m*, *p*- $\text{C}_6\text{H}_5\text{Si}$); 7.44-7.47 (m, 2H, *p*- $\text{C}_6\text{H}_5\text{B}$); 7.51-7.57 (m, 4H, *o*- $\text{C}_6\text{H}_5\text{B}$); 7.65-7.71 (m, 8H, *o*- $\text{C}_6\text{H}_5\text{Si}$); 7.74-7.76 (s, 4H, C_6H_4); 7.97-8.04 (m, 4H, *o*- $\text{C}_6\text{H}_5\text{B}$); 8.66-8.76 (m, 4H, *o*- $\text{C}_5\text{H}_4\text{N}$); $^{13}\text{C}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 125 MHz) 149.11, 148.13, 138.60, 135.07, 134.13, 130.83, 130.19, 127.82, 127.75, 127.71 ppm; ^{11}B NMR: δ (CDCl_3 , 160 MHz) 20.19 ppm; $^{29}\text{Si}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 99 MHz) -45.39 ppm.

*Preparation of $[\text{Ph}_6\text{B}_2\text{Si}_2\text{O}_4]\cdot 2\text{L}_8$ (**13**)*

In a round bottom flask, $[(\text{C}_6\text{H}_5\text{BO})_2(\text{Ph}_2\text{SiO})_2]$ (**3**), (0.25 g 0.415 mmol) was added to 3,5-di(3-pyridyl)-1,2,4-thiadiazole (0.10 g 0.415 mmol) (**L₈**) and a mixture of solvents (diethyl ether 21 ml, petroleum ether 7 ml and dichloromethane 7ml). The mixture was heated at reflux while stirring for 24 h. The resultant solution was allowed to cool to room temperature. After 48 h colourless crystals of compound (**13**) were obtained (0.365 g, 90% yield; M.p 110.6-111.7 $^\circ\text{C}$); found: C, 66.45%, H, 4.31 %, N, 9.63%, Calc. for $(\text{C}_{60}\text{H}_{46}\text{B}_2\text{N}_8\text{O}_4\text{S}_2\text{Si}_2, 2(\text{C}_6\text{H}_7\text{BO}_2))$: C, 66.42%, H, 4.27%, N, 10.33%; ^1H NMR: δ (CDCl_3 500 MHz) 7.28-7.42 (m, 18H, *m*, *p*- C_6H_5); 7.48- 7.52 (m, 4H, *m*- $\text{C}_5\text{H}_4\text{N}$); 7.70-7.73 (m, 8H, *o*- $\text{C}_6\text{H}_5\text{Si}$); 8.03-8.07 (m, 4H, *o*- $\text{C}_6\text{H}_5\text{B}$); 8.34 (dd, $J = 4.0$ Hz, $J' = 2.0$ Hz, 2H, *p*- $\text{C}_5\text{H}_4\text{N}$); 8.36 (dd, $J = 4.0$ Hz, $J' = 2.0$ Hz, 2H, *p*- $\text{C}_5\text{H}_4\text{N}$); 8.64-8.65 (t, 2H, *m*- $\text{C}_5\text{H}_4\text{N}$); 8.66-8.67 (t, 2H, *m*- $\text{C}_5\text{H}_4\text{N}$); 8.76 (dd, $J = 6.8$ Hz, $J' = 1.6$ Hz, 2H, *o*- $\text{C}_5\text{H}_4\text{N}$); 8.80 (dd, $J = 6.8$ Hz, $J' = 2.0$ Hz, 2H, *o*- $\text{C}_5\text{H}_4\text{N}$); 9.27 (dd, $J = 2.4$ Hz, $J' = 0.8$ Hz, 2H, *o*- $\text{C}_5\text{H}_4\text{N}$); 9.65 (d, $J = 2.4$ Hz, 2H, *o*- $\text{C}_5\text{H}_4\text{N}$); $^{13}\text{C}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 125 MHz) 185.53, 171.27, 152.67, 150.45, 149.00, 148.31, 135.94, 135.32, 134.31, 134.09, 133.74, 133.00, 131.26, 130.36, 127.91, 127.80, 127.60, 121.16; $^{11}\text{B}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 160 MHz) 22.82 ppm; $^{29}\text{Si}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 99 MHz) -45.17 ppm.

*Preparation of [Ph₆B₂Si₂O₄].2L₉. 2[PhB(OH)₂] (**14**)*

In a round bottom flask, [(C₆H₅BO)₂(Ph₂SiO)₂] (**3**), (0.25 g 0.415 mmol) was added to 3,5-di(4-pyridyl)-1,2,4-thiadiazole (**L₉**) (0.10 g 0.415 mmol), phenylboronic acid (0.10 g, 0.830 mmol) and a mixture of solvents (diethyl ether 21 ml, petroleum ether 7 ml and dichloromethane 7ml). The mixture was heated at reflux while stirring for 24 h. The resultant solution was allowed to cool to room temperature. After 72 h colourless crystals were obtained from the solvent to give compound (**14**) (0.365 g, 85% yield; M.p 124.0-125.0 °C); found: C, 64.65%, H, 4.51 %, N, 8.41%. Calc. for (C₆₀H₄₆B₂N₈O₄S₂Si₂, 2(C₆H₇BO₂)): C, 65.02%, H, 4.51%, N, 8.43%; ¹H NMR: δ (CDCl₃ 500 MHz) 7.29-7.42 (m, 18H, *m*, *p*-C₆H₅); 7.65-7.74 (m, 8H, *o*-C₆H₅Si); 7.89- 7.92 (m, 8H, *m*-C₅H₄N); 7.99-8.06 (m, 4H, *o*-C₆H₅B); 8.24-8.27 (m, 8H, *m*-C₅H₄N); 8.84-8.87 (m, 16H, *p*-C₅H₄N); ¹³C{¹H}, NMR: δ (CDCl₃, 125 MHz) 186.69, 171.92, 151.11, 150.02, 139.40, 136.81, 135.35, 134.10, 133.63, 130.39, 127.93, 127.57, 122.30, 121.00 ppm; ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 21.53 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99 MHz) -45.17 ppm.

*Preparation of (Ph₄Si₂O₃B)C₆H₄(Ph₄Si₂O₃B) (**3a**).*

4.33 g, (20.0 mmol) of diphenylsilanediol (**1**) was mixed with 0.83 g (5.0 mmol) of 1,4-phenylenediboronic acid (**2a**) in dry toluene (50 ml) and 0.5 g molecular sieves (0.4 nm rods) in a round bottom flask containing a magnetic stirrer bar. The mixture was refluxed under N₂ for 20 h. Thereafter, the round bottom flask and its contents were allowed to cool to room temperature. The cooled reaction mixture was filtered and the filtrate collected. The molecular sieves were washed with dry toluene (3 x 25 ml). The filtrates were combined and concentrated under reduced pressure, and the solid residue recrystallized from dichloromethane and heptane via slow diffusion method (3:1 ratio) to give (**3a**) 3.51 g, 76%; M.p. 182 -183 °C, Found: C, 72.32%, H, 5.38%, Calc. for (C₅₄H₄₄B₂O₆Si₄): C, 70.88%, H, 4.81%; ¹H NMR: δ (CDCl₃ 500 MHz) 7.44-7.47 (m, 16H,

m-C₆H₅Si); 7.66-7.69 (m, 8H *p*-C₆H₅Si), 7.73-7.75 (m, 8H *o*-C₆H₅Si); 8.08-8.09 (m, 4H, *o*-C₆H₄B). ¹³C{¹H}, NMR: δ (CDCl₃, 125 MHz) 127.57, 127.70, 127.95, 130.81, 132.90, 134.16, 134.32 ppm (C₆H₅Si, C₆H₄B); ¹¹B{¹H}, NMR: δ (CDCl₃, 160 MHz) 28.79 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 99MHz) -31.19 ppm.

Preparation of tetra(4-bromophenyl)silane (C)

In a round three-neck bottom flask equipped with a magnetic stirrer bar, 1,4-dibromobenzene (**A**) (8.28 g, 35.1 mmol) was dissolved in dry Et₂O (100 ml) under N₂ and then degassed. The degassed solution was cooled to -76 °C. ⁿBuLi (2.5 M) in hexane (14.04 ml, 35.1 mmol) was added to the solution dropwise while stirring. After the addition of the ⁿBuLi the solution was slowly raised to room temperature and stirred for another 1 h. The solution was thereafter cooled again to -76 °C and then tetrachlorosilane (1.32 g, 0.89 ml, 7.8 mmol) was added slowly keeping the temperature between -70 to -75 °C. At the end of the addition, the reaction mixture was slowly raised to room temperature again and stirred overnight. The next day; the reaction was quenched with 30 ml of H₂O. Some white precipitates were observed and these were removed via filtration. The filtrate was transferred into a separatory funnel wherein the organic and the aqueous layers were separated. The aqueous layer was washed with 30 ml Et₂O twice and then combined with the first portion. The organic layer was washed with brine followed by drying over anhydrous MgSO₄ and filtered off. Removal of the solvent using a rotary evaporator gave a colourless powder which was washed with hexane to give the desired product (4.09, 89%) yield, ¹H NMR (400 MHz, chloroform-d, δ, ppm) 7.33 (d, *J* = 8.4 Hz, 8H), 7.53 (d, *J* = 8.4 Hz, 8H).

Preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane (L10)

In a clean dry round bottom flask, a mixture of tetra(4-bromophenyl)silane (**C**) (2.94 g, 5 mmol), 4-vinylpyridine (**D**) (2.16 g, 20.5 mmol), triethylamine (NEt₃) (2.08 g, 2.87 ml, 20.5 mmol),

palladium acetate [Pd(OAc)₂] (0.045 g, 0.20 mmol), triphenylphosphane (PPh₃) (0.105 g, 0.40 mmol) and magnetic stirrer bar were mixed under N₂ and then degassed. The degassed mixture was heated under an N₂ flow refluxed at 100 °C for 48 h. The resultant solid mass was partitioned between CH₂Cl₂ and water. The organic layer was separated and evaporated to dryness. The crude product was washed with warmed ethyl acetate to give 82% yield of (**L**₁₀) as a brown powder. Mp: 217-218 °C; Found: C, 82.51%, H, 5.56% N, 6.65% Calc. for (C₅₂H₄₀N₄Si): C, 83.39%, H, 5.38%, N, 7.48%; ¹H NMR: δ (CDCl₃ 400 MHz) 7.13 (d, *J* = 16 Hz, 4H, CHCH), 7.32-7.33 (d, *J* = 16 Hz, 4H, CHCH), 7.36-7.38 (m, 8H, *m*-C₅H₄N), 7.56-7.60 (m, 8H, *m*-C₄H₄), 7.60-7.67 (m, 8H, *o*-C₄H₄), 8.57-8.59 (m, 8H *o*-C₅H₄N), ¹³C {¹H}, NMR: δ (CDCl₃, 100.61 MHz) 120.90, 126.54, 127.09, 132.79, 134.38, 136.78, 137.59, 144.31, 150.25 ppm; ²⁹Si {¹H}, NMR: δ (CDCl₃, 79.5 MHz) - 14.79 ppm.

Preparation of tris(4-bromophenyl)methylsilane (E)

In a clean dry three-neck round bottom flask equipped with magnetic stirrer bar, 1,4-dibromobenzene (7.5 g, 30 mmol) was dissolved in dry ether (100 ml) and the mixture stirred and cooled to -76 °C under N₂. ⁿBuLi (2.5 M in hexanes, 12 ml, 30 mmol) was added into the solution dropwise while stirring. At the end of the addition, the mixture was slowly raised to room for 1 h. The mixture was cooled to -76 °C and then methyltrichlorosilane (1.18 ml, 10 mmol) was added dropwise. At the end of the addition, the reaction mixture was slowly raised to room temperature and stirred for 24 h. The reaction was then quenched by 30 ml H₂O and the organic layer was separated. The water layer was washed by 30 ml of Et₂O twice. The organic layer layers were combined, washed with brine and then dried over anhydrous MgSO₄ and then filter. Removal of the solvents under vacuum gave crude product which was recrystallized in hexane to give

colourless crystals 90% yield ^1H NMR (400 MHz, chloroform- d , δ , ppm) 0.79 (s, 3H, CH_3), 7.30 (d, 6H, $J = 8.4$ Hz), 7.50 (d, 6H, $J = 8.4$ Hz).

*Preparation of tri(4-(pyridine-4-vinyl)phenyl)methylsilane (**L11**)*

In a clean dry round bottom flask, a mixture of tri(4-dibromophenyl)methylsilane (**E**) (1.70 g, 3.33 mmol), 4-vinylpyridine (**D**) (1.32 g, 12.53 mmol, 1.35 ml), trimethylamine (1.27 g, 12.53 mmol, 1.75 ml), $[\text{Pd}(\text{OAc})_2]$ (0.023 g, 0.10 mmol), PPh_3 (0.053 g, 0.20 mmol) and magnetic stirrer bar were mixed under N_2 and then degassed. The degassed mixture was heated under N_2 flow refluxed at 100°C for 48 h. The resultant solid mass was partitioned between CH_2Cl_2 and water. The organic layer was separated and evaporated to dryness. The crude brown coloured product was recrystallized from acetone to give 80% brown product; Mp: $169.4\text{--}170.2^\circ\text{C}$; ^1H NMR: δ (CDCl_3 400 MHz), 0.89 (s, 3H, CH_3), 7.07 (d, $J = 16$ Hz, 3H, CHCH), 7.31 (d, $J = 16$ Hz, 3H, CHCH), 7.35–7.37 (m, 6H, $m\text{-C}_5\text{H}_4\text{N}$), 7.54 (s, 12H, $o,m\text{-C}_4\text{H}_4$), 8.46–8.58 (m, 8H $o\text{-C}_5\text{H}_4\text{N}$); $^{13}\text{C}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 100.61 MHz) -3.45, 120.90, 126.49, 126.83, 132.91, 135.74, 136.54, 137.31, 144.40, 150.24 ppm; $^{29}\text{Si}\{^1\text{H}\}$, NMR: δ (CDCl_3 , 79.5 MHz) -11.09 ppm.

*Preparation of [(methylsilanetriyl)tris(benzene-1,4-)] triboronic acid (**3c**).*

$n\text{BuLi}$ (2.5 M in hexane; 6.3 ml, 0.0158 mmol) was added to dry THF (20 ml) at -78°C . Then a solution of $\text{MeSi}(\text{4-C}_6\text{H}_4\text{Br})_3$ (**E**) (2.31 g, 0.0045 mole) in THF (5 ml) was added while the temperature was kept below -75°C . The resulting mixture was stirred for 1 h, then $\text{B}(\text{Oi-Pr})_3$ (3.7 ml, 0.0158 mmol) was added. The resulting mixture was stirred for 30 min and hydrolysed with H_2SO_4 (1.5 M aq, 20 ml) at -15°C . The organic phase was separated, and the solvents were evaporated under reduced pressure to give crude powder which was dissolved in 60 ml of 1 M NaOH solution and stirred, followed by filtration. The filtrate was treated with 40 ml of 2.5 M HCl solution. White precipitates were formed which were further washed with small portion of 2.5 M

HCl solution followed by rinsing with water. The precipitates were air dried to give (2.54 g, 85% yield), Mp: > 300 °C; ^1H NMR: δ (acetone- D_6 , 400 MHz) 0.82 (s, 3H, CH_3), 4.15 (br, 6H, OH) 7.50 (d, $J = 7.6$ Hz, 6H, $o\text{-C}_5\text{H}_4\text{Si}$); 7.87 (d, $J = 7.6$ Hz, 6H, $m\text{-C}_5\text{H}_4\text{Si}$), $^{13}\text{C}\{^1\text{H}\}$, NMR: δ (acetone- d_6 , 100.61 MHz) -3.65, 131.85, 134.24, 135.10, 137.89 ppm; $^{11}\text{B}\{^1\text{H}\}$, NMR: δ (acetone- D_6 , 160 MHz) 29.18 ppm; $^{29}\text{Si}\{^1\text{H}\}$, NMR: δ (acetone- D_6 , 79.5 MHz) -11.11 ppm.

Preparation of di(4-bromophenyl)dimethylsilane (F)

In a clean dry three-neck round bottom flask equipped with a magnetic stirrer bar, 1,4-dibromobenzene (7.50 g, 30 mmol) was dissolved in dry ether (100 ml) and the mixture stirred and cooled to -76 °C under N_2 . $^n\text{BuLi}$ (2.5 M in hexanes, 12 ml, 30 mmol) was added into this solution dropwise while stirring. At the end of the addition, the mixture was slowly raised to room for 1 h. The mixture was cooled to -76 °C and then dimethyldichlorosilane (1.8 ml, 15 mmol) was added dropwise. At the end of the addition, the reaction mixture was slowly raised to room temperature and stirred for 24 h. The reaction was then quenched by 30 ml H_2O and the organic layer was separated. The water layer was washed by 30 ml of Et_2O twice. The organic layer layers were combined, washed with brine and then dried over anhydrous MgSO_4 and then filter. Removal of the solvents under vacuum gave crude product which was recrystallized in hexane to give colourless crystals 90% yield ^1H NMR (400 MHz, CDCl_3 , δ , ppm) 0.51 (s, 6H, CH_3), 7.34 (d, 4H, $J = 8.4$ Hz), 7.49 (d, 4H, $J = 8.4$ Hz). Mass spectrum (70 eV EI): m/z 370 (M^+), 357 (M-CH) $^+$ 355 (M-CH_3) $^+$.

Preparation of bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L₁₂)

In a clean dry round bottom flask, a mixture of di(4-dibromophenyl)dimethylsilane (3.70 g, 10 mmol), 4-vinylpyridine (2.64 g, 25.07 mmol, 2.70 ml), triethylamine (2.54 g, 25.07 mmol, 3.5 ml), palladium acetate (0.045 g, 0.20 mmol), PPh_3 (0.105 g, 0.40 mmol) and a magnetic stirrer bar were

mixed under N₂ and then degassed. The degassed mixture was heated under reflux at 100 °C for 48 h. The resultant solid mass was partitioned between CH₂Cl₂ and water. The organic layer was separated and evaporated to dryness. The crude brown product was recrystallized from acetone to give 80% brown product. Mp: 158-160 °C found: C, 80.30%; H, 6.25%; N, 6.68%, Calc. for (C₂₈H₂₆N₂Si): C, 80.34%, H, 6.26%, N, 6.69%; ¹H NMR: δ (CDCl₃ 400 MHz) 0.57 (s, 6H, CH₃), 7.03 (d, *J* = 16 Hz, 2H, CHCH), 7.31 (d, *J* = 16 Hz, 2H, CHCH), 7.34-7.35 (m, 4H, *m*-C₅H₄N), 7.53-7.57 (m, 4H, *o*-C₄H₄), 7.50-7.53 (m, 4H, *m*-C₄H₄), 8.53-8.55 (m, 4H, *o*-C₅H₄N); ¹³C{¹H}, (100.61 MHz) -2.54, 120.83, 126.31, 132.98, 134.60, 136.79, 138.90, 144.44, 150.05 ppm; ²⁹Si{¹H}, NMR (CDCl₃ 79.5 MHz), -7.83 ppm.

Preparation of [(Dimethylsilanediyl)bis(1,4-phenylene)] diboronic acid (3d)

ⁿBuLi (2.5 M in hexane; 5.8 ml, 0.0145 mmol) was added to dry THF (20 ml) at -78 °C. Then a solution of Me₂Si(4-C₆H₄Br)₂ (**E**) (2.7 g, 0.0073 mole) in THF (5 ml) was added while the temperature was kept below -76 °C. The resulting mixture was stirred for 1 h, then B(Oi-Pr)₃ (3.4 ml, 0.0145 mol) was added. The resulting mixture was stirred for 30 min and hydrolysed with H₂SO₄ (1.5 M aq, 20 ml) at -15 °C. The organic phase was separated, and the solvents were evaporated under reduced pressure to give crude powder which was dissolved in 60 ml of 1 M NaOH solution and stirred followed by filtration. The filtrate was treated with 40 ml of 2.5 M HCl solution. White precipitates were formed which were further washed with small portions of 2.5 M HCl solution followed by rinsing with water. The precipitates were air dried to give (1.92 g, 88% yield), Mp: > 300 °C; ¹H NMR: δ (acetone-D₆, 400 MHz) 0.56 (s, 6H, CH₃), 7.20 (s, 4H, OH), 7.54 (d, *J* = 8.0 Hz, 4H Ph), 7.85 (d, *J* = 8.0 Hz, 4H, Ph) ppm; ¹³C{¹H}, NMR (acetone-D₆ 101 MHz): -2.50, 134.0, 134.2, 141.2 ppm; ¹¹B{¹H}, NMR (acetone-D₆, 128 MHz), 29.2 ppm; ²⁹Si{¹H}, NMR (acetone-D₆, 79.5 MHz), -8.5 ppm

Preparation of tris(4-bromophenyl)chlorosilane (G)

In a three neck round bottom flask equipped with a magnetic stirrer bar, 1,4-dibromobenzene (14.16 g, 60 mmol) was dissolved in dry Et₂O (100 ml) under N₂ and then degassed. The degassed solution was cooled to -76 °C. ⁿBuLi (2.5 M) in hexane (24 ml, 60 mmol) was added to the solution dropwise while stirring. After the addition of the ⁿBuLi the solution was slowly raised to room temperature and stirred for another 1 h. The solution was then cooled again to -75 °C and then tetrachlorosilane (3.4 g, 2.3 ml, 20 mmol) was added slowly keeping the temperature in range -70 to -75 °C. At the end of the addition, the reaction mixture was slowly raised to room temperature again and stirred overnight. The next day 30 ml of dry Et₂O was added to the reaction mixture. Some white precipitates were observed (LiCl) and these were removed via filtration by the use of a Buchner funnel. The precipitate on the Buchner funnel was rinsed with (25 ml x 4) of dry Et₂O. The filtrate was transferred into a round bottom flask and the solvent removed using a rotary evaporator to give a crude powder product which was recrystallized from hexane (-40 to -50 °C) to give colourless powder which was stored under dry N₂ at 4 °C (8.73 g, 82%) yield (lit, 95%)⁴⁸⁴, Mp: 123.4 °C (lit, 123 °C)⁴⁸⁴; Anal. Calc for C₁₈H₁₂ClBr₃Si: C, 40.67; H, 2.28; found: C, 40.80; H, 2.26; ¹H NMR: δ (CDCl₃ 400 MHz) 7.44 (d, *J* = 8.4 Hz, 6H, Ar-H), 7.58 (d, *J* = 8.4 Hz, 6H, Ar-H); ¹³C{¹H}, NMR: δ (CDCl₃, 101 MHz) 126.46, 130.66, 131.61, 136.53 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 79.5 MHz) 1.47 ppm.

Preparation of tetrakis(4-bromobiphenyl)silane (J)

In a three neck round bottom flask equipped with a magnetic stirrer bar, 4,4-dibromobiphenyl (10.95 g, 35.1 mmol) was dissolved in a mixture of dry Et₂O and THF (8:2 respectively) (100 ml) under N₂ and then degassed. The degassed solution was cooled to -78 °C. ⁿBuLi (2.5 M) in hexane (14.04 ml, 35.1 mmol) was added in this solution dropwise while stirring. After the addition of the

ⁿBuLi the solution was stirred for 1 h and then slowly raised to (-10 to 0 °C) and stirred for another 1 h. The solution was cooled again to -76 °C and then tetrachlorosilane (1.32 g, 0.89 ml, 7.8 mmol) was added slowly keeping the temperature in the range -70 to -75 °C. At the end of the addition, the reaction mixture was slowly raised to room temperature and stirred overnight. The next day the reaction was quenched with 30 ml of H₂O. A lot of white precipitate was observed and this was removed via filtration. The precipitate is the desired product and was washed with another 60 ml of water twice followed by washing with warmed acetone to give (4.50 g, 65%) of colourless powder. The filtrate was transferred into a separatory funnel wherein the organic and the aqueous layers were separated. The aqueous layer was washed with 30 ml Et₂O twice and combined with the first portion. The organic layer was washed with brine followed by drying over anhydrous MgSO₄ and filtered off. Removal of the solvent using a rotary evaporator gave colourless powder products which were washed with warmed acetone to give a further (1.13 g, 15%) of the desired product. Total product obtained (6.0 g, 80.0% combined yield); Mp: 149 -150 °C; found: C, 60.46%, H, 3.5%; Calc. for (C₄₈H₃₂Br₄Si): C, 60.28%, H, 3.37%; ¹H NMR: δ (CDCl₃ 400 MHz) 7.49 (d, *J* = 8.0 Hz, 8H), 7.58 (d, *J* = 8.0 Hz, 8H), 7.61 (d, *J* = 8.0 Hz, 8H), 7.71 (d, *J* = 8.0 Hz, 8H); ¹³C {¹H}, NMR: δ (CDCl₃, 101 MHz) 121.94, 126.49, 128.71, 131.97, 133.06, 136.94, 139.67, 141.26 ppm; ²⁹Si {¹H}, NMR: δ (CDCl₃, 79.5 MHz) -14.28 ppm.

Preparation of tetrakis(4-(pyridine-4-vinyl)biphenyl)silane (L₁₃)

In a clean dry round bottom flask, a mixture of tetra(4-bromobiphenyl)silane (4.78 g, 5 mmol), 4-vinylpyridine (2.16 g, 20.5 mmol), triethylamine (2.08 g, 2.87 ml, 20.5 mmol), palladium acetate (0.045 g, 0.20 mmol), PPh₃ (0.105 g, 0.40 mmol) and magnetic stirrer bar were sealed under N₂ and then degassed. The degassed mixture was heated under reflux at 100 °C for 48 h. The resultant solid mass was partitioned between CH₂Cl₂ and water. The organic layer was separated

and evaporated to dryness. The crude product was washed with warmed acetone and then warmed hexane to give a pale yellow product (3.0 g, 57% yield); Mp: > 300 °C; found: C, 83.73%; H, 5.54%; N, 4.42%; Calc. for (C₇₆H₅₆N₄Si): C, 86.66%; H, 5.36%; N, 5.32%; ¹H NMR: δ (CDCl₃, 400 MHz) 7.07 (d, J = 16 Hz, 4H, CHCH), 7.35(d, J = 16 Hz, 4H, CHCH), 7.39 (d, J = 8.0 Hz, 8H, *m*-C₅H₄N), 7.64 (d, J = 8.0 Hz, 8H, Ar-C₅H₄), 7.69 (d, J = 8.0 Hz, 8H, Ar-C₄H₄), 7.71 (d, J = 8.0, 8H, Ar-C₄H₄), 7.77 (d, J = 8.0 Hz, 8H, Ar-C₄H₄), 8.59 (d, J = 8.0 Hz, 8H, *o*-C₅H₄N); ¹³C {¹H}, NMR: δ (CDCl₃, 101 MHz) 120.81, 126.70, 127.53, 128.82, 131.94, 132.54, 133.13, 135.47, 136.93, 140.95, 141.55, 144.48, 150.15 ppm; ²⁹Si {¹H}, NMR: δ (CDCl₃, 79.5 MHz) -14.40 ppm.

Preparation of tri(4-bromobiphenyl)methylsilane (K)

In a round three neck bottom flask equipped with a magnetic stirrer bar, 4,4-dibromobiphenyl (8.21 g, 26.4 mmol) was dissolved in a mixture of dry Et₂O and THF (8:2 respectively) (100 ml) under N₂ and then degassed. The degassed solution was cooled to -76 °C. ⁿBuLi (2.5 M) in hexane (10.56 ml, 28.4 mmol) was added in this solution dropwise while stirring. After the addition of the ⁿBuLi the solution was stirred for 1 h and then slowly raised to (-10 to 0 °C) and stirred for another 1 h. The solution was the cooled again to -76 °C and then methyltrichlorosilane (1.32 g, 1.04 ml, 8.8 mmol) was added slowly keeping the temperature in the range -70 to -75 °C. At the end of the addition, the reaction mixture was slowly raised to room temperature and stirred overnight. The next day the reaction was quenched with 30 ml of H₂O. A lot of white precipitate was formed and these were removed through filtration. The precipitate was washed with another 60 ml of water twice followed by washing with warmed acetone to give (4.87 g, 75% yield) of colourless powder. The filtrate was transferred into a separatory funnel wherein the organic and the aqueous layers were separated. The aqueous layer was washed with 30 ml Et₂O twice and combined with the first portion. The organic layer was washed with brine followed by drying over anhydrous MgSO₄ and

filtered off. Removal of the solvent using a rotary evaporator gave colourless powder which was washed with warmed acetone to give a further desired product of (0.13 g, 2% yield). Total product obtained (5.0 g, 77% combined yield), Mp 289 -291 °C; found: C, 60.17%; H, 3.74%; Calc. for (C₃₇H₂₇Br₃Si): C, 60.05%, H, 3.68%, ¹H NMR: δ (CDCl₃ 400 MHz) 0.93 (s, 3H), 7.48 (d, *J* = 8.0 Hz, 6H), 7.56 (d, *J* = 8.0 Hz, 6H), 7.58 (d, *J* = 8.0 Hz, 6H), 7.64 (d, *J* = 8.0 Hz, 6H); ¹³C{¹H}, NMR: δ (CDCl₃, 101 MHz) -3.31, 121.85, 126.45, 128.72, 131.94, 135.08, 135.87, 139.77, 141.04 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 79.5 MHz) -10.95 ppm.

Preparation of tris(4-(pyridine-4-vinyl)biphenyl)methylsilane (L₁₄)

In a clean dry round bottom flask, a mixture of tris(4-bromobiphenyl)methylsilane (1.85 g, 3.33 mmol), 4-vinylpyridine (0.99 g, 12.53 mmol), triethylamine (0.95 g, 1.75 ml, 12.53 mmol), palladium acetate (0.023 g, 0.10 mmol), PPh₃ (0.053 g, 0.20 mmol) and magnetic stirrer bar were mixed under N₂ and then degassed. The degassed mixture was heated under reflux at 100 °C for 48 h. The resultant solid mass was partitioned between CH₂Cl₂ and water. The organic layer was separated and evaporated to dryness. The crude product was washed with warmed acetone and then warmed hexane to give pale yellow product (1.59 g, 74% yield. Mp: > 300 °C; found: C, 85.68%, H, 5.48%, N, 5.13%, Calc. for (C₅₈H₄₅N₃Si): C, 85.78%, H, 5.59%, N, 5.17%; ¹H NMR: δ (CDCl₃ 400 MHz) 0.94 (s, 3H), 7.05-7.09 (m, 3H, CHCH), 7.20-7.21 (m, 3H, CHCH), 7.36-7.38 (m, 6H, *m*-C₅H₄N), 7.67-7.62 (m, 24H, *o,m*-C₄H₄), 8.57-8.59 (m, 6H *o*-C₅H₄N); ¹³C{¹H}, NMR: δ (CDCl₃, 100.61 MHz) -3.30, 120.80, 126.07, 126.40, 126.61, 127.84, 128.62, 131.87, 132.56, 135.82, 141.07, 144.50, 150.15 ppm; ²⁹Si{¹H}, NMR: δ (CDCl₃, 79.5 MHz) -10.92 ppm. MS: (70 eV EI): *m/z* 812(M⁺)

Preparation of silane tetrakis(biphenyl-4-carboxylic acid) (L₁₅)

In a round bottom three neck flask equipped with a magnetic stirrer bar, tetrakis(4-dibromobiphenyl)silane (0.82 g, 0.86 mmol) was dissolved in dry THF (100 ml) under N₂ and then degassed. The degassed solution was cooled to -76 °C. ⁿBuLi (2.5 M) in hexane (1.72 ml, 4.3 mmol) was added to the solution dropwise while stirring. After the addition of the ⁿBuLi the solution was slowly raised to room temperature and stirred for another 1 h. The solution was then cooled again to -75 °C and then CO₂ gas was bubbled through the solution for 2 h. The reaction mixture was slowly raised to room temperature again and stirred under N₂ overnight. The next day the reaction was quenched with 30 ml aqueous HCl. The organic and aqueous layers were separated using a separatory funnel. The aqueous layer was washed with 10 ml THF twice and then the organic fractions were combined. The organic layer was washed with brine and dried over MgSO₄. The organic layer was then filtered and its volume reduced under pressure to give the crude product which was washed with warmed hexane / ethyl acetate to give a colourless powder (0.68 g, 97% yield) Mp: above 300 °C; Calc for C₅₂H₃₆O₈Si: C, 76.45; H, 4.44; found: C, 76.39; H, 4.53, ¹H NMR: δ (DMSO-D₆ 400 MHz) 7.71 (d, *J* = 8.0 Hz, 8H, Ar-H), 7.90-7.80 (16H, Ar-H), 8.04 (d, *J* = 8.0 Hz, 8H, Ar-H), 12.94 (4H, CO₂H); ¹³C{¹H}, NMR: δ (DMSO, 100.61 MHz) 126.83, 126.98, 129.95, 135.29, 136.61, 140.56, 144.81, 167.15 ppm; ²⁹Si{¹H}, NMR: δ (DMSO-D₆, 79.5 MHz) -14.87 ppm; Mass spectrum (ES⁻): *m/z* 815(M-H)⁻

Preparation of methylsilane tris(biphenyl-4-carboxylic acid) (L₁₆)

In a round bottom three neck flask equipped with a magnetic stirrer bar, tri(4-bromobiphenyl)methylsilane (2.77g, 3.75 mmol) was dissolved in dry THF (100 ml) under N₂ and then degassed. The degassed solution was cooled to -76 °C. ⁿBuLi (2.5 M) in hexane (5.0 ml, 12.5 mmol) was added in this solution dropwise while stirring. After the addition of the ⁿBuLi, the

solution was slowly raised to room temperature and stirred for another 1 h. The solution was then cooled again to -75 °C and then CO₂ gas was bubbled through the solution for 2 h. The reaction mixture was slowly raised to room temperature again and stirred under N₂ overnight. The next day the reaction was quenched with 30 ml aqueous HCl. The organic and aqueous layers were separated via filtration by the use of a separatory funnel. The aqueous layer was washed with 10 ml THF twice and then combined. The organic layer was washed with brine and dried over MgSO₄. The organic layer was then filtered and its volume reduced under pressure to give crude product which was washed with warmed hexane / ethyl acetate to give a colourless powder (2.0 g, 84%) yield Mp: above 300 °C; Calc. for C₄₀H₃₀O₆Si: C, 75.69; H, 4.76; found: C, 75.59; H, 4.84; ¹H NMR: δ (DMSO-D₆ 400 MHz) 0.92 (s, 3H, CH₃), 7.66 (d, *J* = 8.0 Hz, 6H, Ar-H,) 7.87-7.73 (12H, Ar-H) 8.05 (d, *J* = 8.0 Hz, 6H, Ar-H), 12.98 (3H, CO₂H); ¹³C {¹H}, (100.61 MHz) -3.86, 126.62, 126.91, 128.97, 130.00, 135.63, 140.20, 143.99, 167.12 ppm; ²⁹Si {¹H}, (79.5 MHz), -11.24 ppm. Mass spectrum (ES⁻): *m/z* 633(M-H)⁻

Preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)

Tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L**₁₀) (18.5 mg, 25 μmol) was put into a 1.0 cm internal diameter vial and dissolved in 2.0 ml DCM. Then, 1 ml methanol was carefully layered on top of the DCM solution. Zn(CH₃COO)₂·2H₂O (9.2 mg, 50 μmol) was dissolved in 2.0 ml methanol and layered on top of the methanol in the vial. Then vial was sealed and positioned upright in a rack which was put in a dark and vibration free cupboard over a period of 14 days for crystallisation. After this period of time, colourless blocky needle crystals of 0.12 g, 86% yield based on the metal were obtained.

Preparation of tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (18)

Tetrakis(4-(pyridine-4-vinyl)phenyl)silane (**L₁₀**) (18.5 mg, 25 μ mol) was put into 1.0 cm internal diameter vial and dissolved in 2.0 ml DCM. Then, 1 ml methanol was carefully layered on top of the DCM solution. In another clean vial, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (15 mg, 50 μ mol) was dissolved in 2.0 ml methanol and layered on top of the methanol in the vial. Then vial was sealed and positioned upright in a rack which was put in a dark and vibration free cupboard over a period of 14 days for crystallisation. After this period of time, colourless blocky diamond-like crystals were obtained in 0.23 g, 84% based on the metal.

Preparation of silane tetrakis(biphenyl-4-carboxylate MOF (19)

MOF (**19**) was prepared solvothermally using a mixture of DMA (5ml)/water (5ml) with 2.5 mmol (0.4953 g) of silane tetrakis(biphenyl-4-carboxylic acid) (**L₁₅**) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 1.0 mmol (0.236 g) which was put in a clean vial and then stirred for 10 minutes using a magnetic stirrer bar. The resulting solution was transferred into a Teflon lined autoclave and firmly sealed. The autoclave was put in to an oven and heated at 120 °C for 24 h and allowed to cool slowly for 6 h to obtain colourless needle crystals at the bottom of the autoclave. The solvent in the autoclave was decanted and the crystals collected. The percentage yield based on the metal salt is 40%, 1.8 g.

Chapter 6

6.0 References

- 1 J. H. Seinfeld, *Am. Inst. Chem. Eng. J.*, 2011, **57**, 3259–3284.
- 2 K. E. Trenberth, *Phys. Soc.*, 2009, **38**, 11–16.
- 3 K. E. Trenberth, J. T. Fasullo, J. Kiehl, K. E. Trenberth, J. T. Fasullo and J. Kiehl, *Bull. Am. Meteorol. Soc.*, 2009, **90**, 311–324.
- 4 S. A. Rackley, *Carbon Capture and Storage*, Elsevier, 2010.
- 5 D. P. Hanak, E. J. Anthony and V. Manovic, *Energy Environ. Sci.*, 2015, **8**, 2199–2249.
- 6 L. Riboldi and O. Bolland, *Int. J. Greenh. Gas Control*, 2015, **39**, 1–16.
- 7 J. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H. Jeong, P. B. Balbuena and H. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791–1823.
- 8 I. Held, *Nat. Geosci.*, 2012, **5**, 236–237.
- 9 S. Choi, J. H. Drese and C. W. Jones, *ChemSusChem*, 2009, **2**, 796–854.
- 10 M. R. Raupach, G. Marland, P. Ciais, C. Le Quere, J. G. Canadell, G. Klepper and C. B. Field, *Proc. Natl. Acad. Sci. U.S.A.*, 2007, **104**, 10288–10293.
- 11 K. S. Lackner, *Environ. Sci. Technol.*, 2010, **29**, 1–40.
- 12 J. R. Rostrup-Nielsen and T. Rostrup-Nielsen, *Cattech*, 2002, **6**, 150–159.
- 13 C. M. Kalamaras and A.M. Efstathiou, in *Hydrogen Production Technologies: Current State and Future Developments*, 2012, vol. 2013, pp. 1–9.
- 14 M. Balat and M. Balat, *Int. J. Hydrogen Energy*, 2009, **34**, 3589–3603.
- 15 A. Konieczny, K. Mondal, T. Wiltowski and P. Dydo, *Int. J. Hydrogen Energy*, 2008, **33**, 264–272.
- 16 M. Onozaki, K. Watanabe, T. Hashimoto, H. Saegusa and Y. Katayama, *Fuel*, 2006, **85**, 143–149.
- 17 N. Z. Muradov, *Int. J. Hydrogen Energy*, 1993, **18**, 211–215.
- 18 N. Li, M. Hao, R. F. Phalen, W. C. Hinds and A. E. Nel, *Clin. Immunol.*, 2003, **109**, 250–265.
- 19 J. C. Slaughter, E. Kim, L. Sheppard, J. H. Sullivan, T. V Larson and C. Claiborn, *J. Expo. Anal. Environ. Epidemiol.*, 2005, **15**, 153–9.

- 20 United Nations / Department of Economic and Social Affairs, *Popul. Newsl.*, 2009, **87**, 1–20.
- 21 United Nations: Department of Social and Economic Affairs, *Popul. Div. 2013. Accessed 16th July, 2018, 2.00pm*, <http://esa.un.org/unpd/wpp/Excel-Data/population>.
- 22 United Nations: Department of Social and Economic Affairs, *World Population Prospects*, 2008 revision.
- 23 D. M. D'Alessandro, B. Smit and J. R. Long, *Angew. Chem. Int. Ed.*, 2010, **49**, 6058–6082.
- 24 J. R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H. K. Jeong, P. B. Balbuena and H. C. Zhou, *Coord. Chem. Rev.*, 2011, **255**, 1791–1823.
- 25 J. D. Figueroa, T. Fout, S. Plasynski, H. McIlvried and R. D. Srivastava, *Int. J. Greenh. Gas Control*, 2008, **2**, 9–20.
- 26 I. Panel and C. Change, in *IPCC Special Report*, 2005.
- 27 C. A. Feron, P. H. M., & Hendriks, *Oil Gas Sci. Technol.*, 2005, **60**, 451–459.
- 28 L. I. Eide and D. W. Bailey, *Oil Gas Sci. Technol. – Rev. IFP*, 2005, **60**, 475–484.
- 29 G. T. Rochelle, *Science*, 2009, **325**, 1652–1654.
- 30 C. H. Yu, C. H. Huang and C. S. Tan, *Aerosol Air Qual. Res.*, 2012, **12**, 745–769.
- 31 F. Shakerian, K. H. Kim, J. E. Szulejko and J. W. Park, *Appl. Energy*, 2015, **148**, 10–22.
- 32 M. Caplow, *J. Am. Chem. Soc.*, 1968, **90**, 6795–6803.
- 33 J. E. Crooks and J. P. Donnellan, *J. Chem. Soc. Perkin Trans. 2*, 1989, **2**, 331–333.
- 34 J. Reza and A. Trejo, *Chem. Eng. Commun.*, 2006, **193**, 129–138.
- 35 S. H. Lin and C. T. Shyu, *Environ. Technol.*, 2000, **21**, 1245–1254.
- 36 C. Stewart and M. A. Hessami, *Energy Convers. Manag.*, 2005, **46**, 403–420.
- 37 L. Espinal and B. D. Morreale, *MRS Bull.*, 2012, **37**, 431–438.
- 38 R. Idem, M. Wilson, P. Tontiwachwuthikul, A. Chakma, A. Veawab, A. Aroonwilas and D. Gelowitz, *Ind. Eng. Chem. Res.*, 2006, **45**, 2414–2420.
- 39 N. Rangnekar, N. Mittal, B. Elyassi, J. Caro and M. Tsapatsis, *Chem. Soc. Rev.*, 2015, **44**, 7128–7154.
- 40 P. Puthiaraj, S.-M. Cho, Y.-R. Lee and W.-S. Ahn, *J. Mater. Chem. A*, 2015, **3**, 6792–6797.
- 41 K. Berlier and M. Frère, *J. Chem. Eng. Data*, 1996, **41**, 1144–1148.
- 42 S. Cavenati, *J. Chem. Eng. Data*, 2004, **49**, 1095–1101.
- 43 C. F. Martín, E. Stöckel, R. Clowes, D. J. Adams, A. I. Cooper, J. J. Pis, F. Rubiera and C.

- Pevida, *J. Mater. Chem.*, 2011, **21**, 5475–5483.
- 44 J. Li, J. Sculley and H. Zhou, *Chem. Rev.*, 2012, **112**, 869–932.
- 45 J. Merel, M. Clausse and F. Meunier, *Ind. Eng. Chem. Res.*, 2008, **47**, 209–215.
- 46 M. M. F. Hasan, R. C. Baliban, J. A. Elia and C. A. Floudas, *Ind. Eng. Chem. Res.*, 2012, **51**, 15642–15664.
- 47 G. Sneddon, A. Greenaway and H. H. P. Yiu, *Adv. Energy Mater.*, 2014, **4**, 1–19.
- 48 R. Krishna and J. M. van Baten, *J. Memb. Sci.*, 2010, **360**, 323–333.
- 49 W. M. Verdegaa, K. Wang, J. P. Sculley, M. Wriedt and H. C. Zhou, *ChemSusChem*, 2016, **9**, 636–643.
- 50 L. K. G. Bhatta, S. Subramanyam, M. D. Chengala, U. M. Bhatta and K. Venkatesh, *Ind. Eng. Chem. Res.*, 2015, **54**, 10876–10884.
- 51 F. Shakerian, K.-H. Kim, J. E. Szulejko and J.-W. Park, *Appl. Energy*, 2015, **148**, 10–22.
- 52 A. A. Olajire, *Biochem. Pharmacol.*, 2017, **17**, 137–161.
- 53 U. Diaz and A. Corma, *Coord. Chem. Rev.*, 2016, **311**, 85–124.
- 54 H. Zhou; J. R. Long; O. M. Yaghi, *Am. Chem. Soc.*, 2012, **112**, 673–674.
- 55 R. Sabouni, H. Kazemian and S. Rohani, *Environ. Sci. Pollut. Res.*, 2014, **21**, 5427–5449.
- 56 K. Sumida, D. L. Rogow, J. A. Mason, T. M. McDonald, E. D. Bloch, Z. R. Herm, T. H. Bae and J. R. Long, *Chem. Rev.*, 2012, **112**, 724–781.
- 57 H. Li, K. Wang, Y. Sun, C. T. Lollar, J. Li and H. C. Zhou, *Mater. Today*, 2017, **21**, 108–121.
- 58 R. Barker, *J. Appl. Chem. Biotechnol.*, 1974, **24**, 221–227.
- 59 B. Feng, H. An and E. Tan, *Energy and Fuels*, 2007, **21**, 426–434.
- 60 N. D. Hutson, S. a. Speakman and E. A. Payzant, *Chem. Mater.*, 2004, **16**, 4135–4143.
- 61 M. K. R. Reddy, Z. P. Xu, G. Q. Lu and J. C. D. da Costa, *Ind. Eng. Chem. Res.*, 2006, **45**, 7504–7509.
- 62 E. Ochoa-Fernández, M. Rønning, T. Grande and D. Chen, *Chem. Mater.*, 2006, **18**, 6037–6046.
- 63 M. Kato, K. Nakagawa, K. Essaki, Y. Maezawa, S. Takeda, R. Kogo and Y. Hagiwara, *Int. J. Appl. Ceram. Technol.*, 2005, **2**, 467–475.
- 64 K. T. Chue, J. N. Kim, Y. J. Yoo, S. H. Cho and R. T. Yang, *Ind. Eng. Chem. Res.*, 1995, **34**, 591–598.

- 65 L. Hauchhum and P. Mahanta, *Int. J. Energy Environ. Eng.*, 2014, **5**, 349–356.
- 66 P. Langlois, I. Pentchev, I. Hinkov, F. D. Lamari, P. Langlois, M. Dicko, C. Chilev and I. Pentchev, *J. Chem. Technol. Metall.*, 2016, **51**, 609–627.
- 67 R. Xu, W. Pang, J. Yu and J. Chen, *Chemistry of zeolites and related porous materials: synthesis and structure*, John Wiley and Sons, Inc, Singapore, 2007.
- 68 B. Yuan, D. Ma, X. Wang, Z. Li, Y. Li, H. Liu and D. He, *Chem. Commun.*, 2012, **48**, 1135–1137.
- 69 J. a Dunne, M. Rao, S. Sircar, R. J. Gorte and a L. Myers, *Langmuir*, 1996, **12**, 5896–5904.
- 70 M. C. Trachtenberg, R. M. Cowan, D. A. Smith, D. A. Horazak, M. D. Jensen, J. D. Laumb, A. P. Vucelic, H. Chen, L. Wang and X. Wu, *Energy Procedia*, 2009, **1**, 353–360.
- 71 S. Lindskog and J. E. Coleman, *Proc. Natl. Acad. Sci. U. S. A.*, 1973, **70**, 2505–2508.
- 72 D. N. Silverman and S. Lindskog, *Acc. Chem. Res.*, 1988, **21**, 30–36.
- 73 A. Y. Shekh, K. Krishnamurthi, S. N. Mudliar, R. R. Yadav, A. B. Fulke, S. S. Devi and T. Chakrabarti, *Crit. Rev. Environ. Sci. Technol.*, 2012, **42**, 1419–1440.
- 74 L. Bao and M. C. Trachtenberg, *J. Memb. Sci.*, 2006, **280**, 330–334.
- 75 R. R. Yadav, K. Krishnamurthi, S. N. Mudliar, S. S. Devi, P. K. Naoghare, A. Bafana and T. Chakrabarti, *J. Basic Microbiol.*, 2014, **54**, 472–481.
- 76 H. Furukawa and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 8875–8883.
- 77 H. M. El-Kaderi, J. R. Hunt, J. L. Mendoza-Cortés, A. P. Côté, R. E. Taylor, M. O’Keeffe and O. M. Yaghi, *Science*, 2007, **316**, 268–272.
- 78 E. L. Spitler, B. T. Koo, J. L. Novotney, J. W. Colson, F. J. Uribe-Romo, G. D. Gutierrez, P. Clancy and W. R. Dichtel, *J. Am. Chem. Soc.*, 2011, **133**, 19416–19421.
- 79 A. R. Millward and O. M. Yaghi, *J. Am. Chem. Soc.*, 2005, **127**, 17998–17999.
- 80 O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. Ö. Yazaydin and J. T. Hupp, *J. Am. Chem. Soc.*, 2012, **134**, 15016–15021.
- 81 R. P. Davies, P. D. Lickiss, K. Robertson and A. J. P. White, *CrystEngComm*, 2012, **14**, 758.
- 82 I. Timokhin, J. Baguña Torres, A. J. P. White, P. D. Lickiss, C. Pettinari and R. P. Davies, *Dalton Trans.*, 2013, **42**, 13806–8.
- 83 I. M. Daniel A. Foucher, Alan J. Lough, *Inorg. Chem.*, 1992, **31**, 3034–3043.

- 84 A. T. O'Dowd, T. R. Spalding, G. Ferguson, J. F. Gallagher and D. Reed, *J. Chem. Soc. Chem. Commun.*, 1993, **634**, 1816–1817.
- 85 B. J. Brisdon, M. F. Mahon, K. C. Molloy and P. J. Schofield, *J. Organomet. Chem.*, 1992, **436**, 11–22.
- 86 J. R. Hunt, C. J. Doonan, J. D. Levangie and A. P. Co, *J. Am. Chem. Soc.*, 2008, **130**, 11872–11873.
- 87 R. S. and K. S. Mirela Pascu, Albert Ruggi, *Chem. Commun.*, 2013, **49**, 45–47.
- 88 W. Liu, M. Pink and D. Lee, *J. Am. Chem. Soc.*, 2009, **131**, 8703–8707.
- 89 M. Gopalakrishnan, K. Thirumoorthy, N. S. P. Bhuvanesh and N. Palanisami, *RSC Adv.*, 2016, **6**, 55698–55709.
- 90 V. J. Aarón Torres-Huerta, Miriam de J. Velásquez-Hernández, Lillian G. Ramírez-Palma, Fernando Cortés-Guzmán, Diego Martínez-Otero, Uvaldo Hernández-Balderas, *Inorg. Chem.*, 2017, **56**, 10032–10043.
- 91 A. Torres-Huerta, M. De Jesu, D. Mart, H. Ho and V. Jancik, *Cryst. Growth Des.*, 2017, **17**, 2438–2452.
- 92 M. A. Beckett, D. E. Hibbs, M. B. Hursthouse, K. M. A. Malik, P. Owen and K. S. Varma, *J. Organomet. Chem.*, 2000, **595**, 241–247.
- 93 M. A. Beckett, G. C. Strickland, S. K. Varma, D. E. Hibbs, M. B. Hursthouse and A. K. M. Malik, *J. Organomet. Chem.*, 1997, **535**, 33–41.
- 94 B. Icli, E. Sheepwash, T. Riis-Johannessen, K. Schenk, Y. Filinchuk, R. Scopelliti and K. Severin, *Chem. Sci.*, 2011, **2**, 1719–1721.
- 95 M. a. Beckett, G. C. Strickland, J. R. Holland and K. S. Varma, *Polym. Commun.*, 1996, **37**, 4629–4631.
- 96 M. A. Beckett, G. C. Strickland, K. S. Varma, D. E. Hibbs, M. B. Hursthouse and K. M. A. Malik, *Polyhedron*, 1995, **14**, 2623–2630.
- 97 M. F. Lappert, *Chem. Rev.*, 1956, **56**, 959–1064.
- 98 J. Kua, M. N. Fletcher and P. M. Iovine, *J. Phys. Chem. A*, 2006, **110**, 8158–8166.
- 99 H. Höpfl, *J. Organomet. Chem.*, 1999, **581**, 129–149.
- 100 L. I. Bosch, T. M. Fyles and T. D. James, *Tetrahedron*, 2004, **60**, 11175–11190.
- 101 S. Franzen, W. Ni and B. Wang, *J. Phys. Chem. B*, 2003, **107**, 12942–12948.
- 102 G. Ferguson, S. E. Lawrence, L. A. Neville, B. J. O'Leary and T. R. Spalding, *Polyhedron*,

- 2007, **26**, 2482–2492.
- 103 N. A. Celis, C. Godoy-Alcántar, J. Guerrero-Álvarez and V. Barba, *Eur. J. Inorg. Chem.*, 2014, **2014**, 1477–1484.
 - 104 E. Sheepwash, K. Zhou, R. Scopelliti and K. Severin, *Eur. J. Inorg. Chem.*, 2013, **14**, 2558–2563.
 - 105 V. Barba, P. Ramos, D. Jiménez, A. Rivera and A. Meneses, *Inorg. Chem. Acta*, 2013, **401**, 30–37.
 - 106 D. Salazar-Mendoza, J. Guerrero-Alvarez and H. Höpfl, *Chem. Commun.*, 2008, **48**, 6543.
 - 107 V. Barba, H. Hopfl, N. Farfan, R. Santillan, H. I. Beltran and L. S. Zamudio-Rivera, *Chem. Commun.*, 2004, **24**, 2834–2835.
 - 108 V. Barba and I. Betanzos, *J. Organomet. Chem.*, 2007, **692**, 4903–4908.
 - 109 N. Christinat, E. Croisier, R. Scopelliti, M. Cascella, U. Röthlisberger and K. Severin, *Eur. J. Inorg. Chem.*, 2007, **33**, 5177–5181.
 - 110 E. Sheepwash, V. Krampl, R. Scopelliti, O. Sereda, A. Neels and K. Severin, *Angew. Chem. Int. Ed.*, 2011, **50**, 3034–3037.
 - 111 N. Christinat, R. Scopelliti and K. Severin, *Chem. Commun.*, 2008, **31**, 3660.
 - 112 A. Dhara and F. Beuerle, *Chem. Eur. J.*, 2015, **21**, 17391–17396.
 - 113 V. Barba, E. Gallegos, R. Santillan and N. Farfán, *J. Organomet. Chem.*, 2001, **622**, 259–264.
 - 114 M. Sa, R. Santillan and S. Rojas-lima, *Chem. Eur. J.*, 2002, **8**, 612–621.
 - 115 R. Santillan, A. Gutie and V. Barba, *Inorg. Chim. Acta*, 2005, **358**, 2996–3002.
 - 116 N. Christinat, R. Scopelliti and K. Severin, *J. Org. Chem.*, 2007, **72**, 2192–2200.
 - 117 B. Icli, E. Solari, B. Kilbas, R. Scopelliti and K. Severin, *Chem. Eur. J.*, 2012, **18**, 14867–14874.
 - 118 X. Feng, X. Ding and D. Jiang, *Chem. Soc. Rev.*, 2012, **41**, 6010–6022.
 - 119 N. W. Ockwig, A. P. Cote, M. O. Keeffe, A. J. Matzger and O. M. Yaghi, *Science*, 2005, **310**, 1166–1170.
 - 120 S. Wan, J. Guo, J. Kim, H. Ihee and D. Jiang, *Angew. Chem. Int. Ed.*, 2008, **47**, 8826–8830.
 - 121 S. Saha, R. Kumar, T. K. Panda, K. Harms, S. Dehnen and H. Pada, *J. Organomet. Chem.*, 2013, **745–746**, 329–334.
 - 122 P. Kuhn, M. Antonietti and A. Thomas, *Angew. Chem. Int. Ed.*, 2008, **48**, 3450–3453.

- 123 J. M. Chem, S. Hug, M. E. Tauchert, S. Li, E. Pachmayr and B. V Lotsch, *J. Mater. Chem.*, 2012, **22**, 13956–13964.
- 124 S. Lin, Y. Hou, X. Deng, H. Wang, S. Sun and X. Zhang, *RSC Adv.*, 2015, **5**, 41017–41024.
- 125 W. Zhang, F. Liang, C. Li, L. Qiu, Y. Yuan, F. Peng, X. Jiang, A. Xie, Y. Shen and J. Zhu, *J. Hazard. Mater.*, 2011, **186**, 984–990.
- 126 Q. Fang, Z. Zhuang, S. Gu, R. B. Kaspar, J. Zheng and J. Wang, *Nat. Commun.*, 2014, **5**, 1–8.
- 127 K. T. Jackson, T. E. Reich and H. M. El-Kaderi, *Chem. Commun.*, 2012, **48**, 8823–8825.
- 128 E. L. Spitler and W. R. Dichtel, *Nat. Chem.*, 2010, **2**, 672–677.
- 129 F. J. Uribe-Romo, J. R. Hunt, H. Furukawa, C. Klotz, M. O. Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2009, **131**, 4570–4571.
- 130 S. Jin, X. Ding, X. Feng, M. Supur, K. Furukawa, S. Takahashi, M. Addicoat, M. E. El-Khouly, T. Nakamura, S. Irle, S. Fukuzumi, A. Nagai and D. Jiang, *Angew. Chem. Int. Ed.*, 2017, **52**, 2017–2021.
- 131 F. J. Uribe-Romo, C. J. Doonan, H. Furukawa, K. Oisaki and O. M. Yaghi, *J. Am. Chem. Soc.*, 2011, **133**, 11478–11481.
- 132 T. Zhou, S. Xu, Q. Wen, Z. Pang and X. Zhao, *J. Am. Chem. Soc.*, 2014, **136**, 15885–15888.
- 133 Y. Zhang, J. Su, H. Furukawa, Y. Yun, F. Ga, A. Duong, X. Zou and O. M. Yaghi, *J. Am. Chem. Soc.*, 2013, **135**, 16336–16339.
- 134 D. Beaudoin, T. Maris and J. D. Wuest, *Nat. Chem.*, 2013, **5**, 830–834.
- 135 N. Huang, L. Zhai, D. E. Coupry, M. A. Addicoat, K. Okushita, K. Nishimura, T. Heine and D. Jiang, *Nat. Commun.*, 2016, **7**, 1–12.
- 136 F. Auras, L. Ascherl, A. H. Hakimiooun, J. T. Margraf, F. C. Hanusch, S. Reuter, D. Bessinger, M. Döblinger, C. Hettstedt, K. Karaghiosoff, S. Herbert, P. Knochel, T. Clark and T. Bein, *J. Am. Chem. Soc.*, 2016, **138**, 16703–16710.
- 137 I. Hisaki, N. Q. Emilya Affendy and N. Tohnai, *CrystEngComm*, 2017, **19**, 4892–4898.
- 138 Q. Gao, X. Li, G.-H. Ning, K. Leng, B. Tian, C. Liu, W. Tang, H.-S. Xu and K. P. Loh, *Chem. Commun.*, 2018, **54**, 2349–2352.
- 139 R. Babarao and J. Jiang, *Energy Environ. Sci.*, 2008, **1**, 139.
- 140 C. J. Doonan, D. J. Tranchemontagne, T. G. Glover, J. R. Hunt and O. M. Yaghi, *Nat. Chem.*, 2010, **2**, 235–238.

- 141 J. L. Mendoza-Cortés, S. S. Han and W. A. Goddard, *J. Phys. Chem.*, 2012, **116**, 1621–31.
- 142 J.-T. Yu, Z. Chen, J. Sun, Z.-T. Huang and Q.-Y. Zheng, *J. Mater. Chem.*, 2012, **22**, 5369–5373.
- 143 S. J. Yang, X. Ding and B. H. Han, *Macromolecules*, 2018, **51**, 947–953.
- 144 D. Cui, J. M. MacLeod, M. Ebrahimi and F. Rosei, *CrystEngComm*, 2017, **19**, 4927–4932.
- 145 S. Wan, G. Felipe, L. Liao, M. W. Ambrogio, Y. Y. Botros, X. Duan, S. Seki, J. F. Stoddart and O. M. Yaghi, *Chem. Mater.*, 2011, **23**, 4094–4097.
- 146 N. Huang, X. Ding, J. Kim, H. Ihee and D. Jiang, *Angew. Chem. Int. Ed.*, 2015, **54**, 8704–8707.
- 147 M. Dogru, M. Handloser, F. Auras, T. Kunz, D. Medina, A. Hartschuh, P. Knochel and T. Bein, *Angew. Chem. Int. Ed.*, 2013, **52**, 2920–2924.
- 148 D. Jiang, *J. Am. Chem. Soc.*, 2014, **136**, 9806–9809.
- 149 X. Liu, C. Guan, D. Wang and L. Wan, *Adv. Mater.*, 2014, **26**, 6912–6920.
- 150 M. Calik, F. Auras, L. M. Salonen, K. Bader, I. Grill, M. Handloser, D. D. Medina, M. Dogru, F. Lo, D. Trauner, A. Hartschuh and T. Bein, *J. Am. Chem. Soc.*, 2014, **136**, 17802–17807.
- 151 H. Oh, S. B. Kalidindi, Y. Um, S. Bureekaew, R. Schmid, R. A. Fischer and M. Hirscher, *Angew. Chem. Int. Ed.*, 2013, **52**, 13219–13222.
- 152 G. Ma, Heping; Ren, Hao; Meng, Shuang; Yan, Zhuojun; Zhao, Huanyu; Sun, Fuxing; Zhu, *Chem. Commun.*, 2013, **49**, 9773–9775.
- 153 Y. Lan, M. Tong, Q. Yang and C. Zhong, *CrystEngComm*, 2017, **19**, 4920–4926.
- 154 S. Ding, J. Gao, Q. Wang, Y. Zhang, W. Song, C. Su and W. Wang, *J. Am. Chem. Soc.*, 2011, **133**, 19816–19822.
- 155 E. Article, L. Stegbauer and B. V Lotsch, *Chem. Sci.*, 2014, **5**, 2789–2793.
- 156 S. Lin, C. S. Diercks, Y. Zhang, N. Kornienko, O. M. Yaghi and C. J. Chang, *Science*, 2015, **349**, 1208–1213.
- 157 T. He, L. Liu, G. Wu and P. Chen, *J. Mater. Chem. A*, 2015, **3**, 16235–16241.
- 158 Q. Fang, S. Gu, J. Zheng, Z. Zhuang, S. Qiu and Y. Yan, *Angew. Chem. Int. Ed.*, 2014, **53**, 2878–2882.
- 159 P. Pachfule, A. Acharjya, J. Roeser, T. Langenhahn, M. Schwarze, R. Schomaecker, A. Thomas and J. Schmidt, *J. Am. Chem. Soc.*, 2018, **140**, 1423–1427.

- 160 S. M. Kunjir and R. Banerjee, *J. Am. Chem. Soc.*, 2014, **136**, 6570–6573.
- 161 J. Li, Z. Wu, H. Li, H. Liang and S. Li, *New J. Chem.*, 2018, **42**, 1604–1607.
- 162 X. Ding, J. Guo, X. Feng, Y. Honsho, J. Guo, S. Seki, P. Maitarad, A. Saeki, S. Nagase and D. Jiang, *Angew. Chem. Int. Ed.*, 2011, **50**, 1289–1293.
- 163 H. Guo, J. Wang, Q. Fang, Y. Zhao, S. Gu, J. Zheng and Y. Yan, *CrystEngComm*, 2017, **19**, 4905–4910.
- 164 S. Dalapati, S. Jin, J. Gao, Y. Xu, A. Nagai and D. Jiang, *J. Am. Chem. Soc.*, 2013, **135**, 17310–17313.
- 165 G. Das, B. P. Biswal, V. Kandambeth, Sharath Venkatesh, G. Kaur, M. Addicoat, T. Heine, S. Verma and R. Banerjee, *Chem. Sci.*, 2015, **6**, 3931–3939.
- 166 A. Nagai, X. Chen, X. Feng, X. Ding, Z. Guo and D. Jiang, *Angew. Chem. Int. Ed.*, 2013, **125**, 3858–3862.
- 167 H. Guo, S. Qiu and Y. Yan, *J. Am. Chem. Soc.*, 2015, **137**, 8352–8355.
- 168 C. R. Deblase, K. E. Silberstein, T. Truong, H. D. Abruña and W. R. Dichtel, *J. Am. Chem. Soc.*, 2013, **135**, 16821–16824.
- 169 F. Xu, H. Xu, X. Chen, D. Wu, Y. Wu, H. Liu, C. Gu and R. Fu, *Angew. Chem. Int. Ed.*, 2015, **54**, 6814–6818.
- 170 C. Yang, C. Liu, Y. Cao and X. Yan, *Chem. Commun.*, 2015, **51**, 12254–12257.
- 171 R. Ge, D. Hao, Q. Shi, B. Dong, W. Leng, C. Wang and Y. Gao, *J. Chem. Eng. Data*, 2016, **61**, 1904–1909.
- 172 S. Hug, L. Stegbauer, H. Oh, M. Hirscher and B. V. Lotsch, *Chem. Mater.*, 2015, **27**, 8001–8010.
- 173 Y. Zeng, R. Zou and Y. Zhao, *Adv. Mater.*, 2016, **28**, 2855–2873.
- 174 C. S. Diercks and O. M. Yaghi, *Science*, 2017, **355**, 923–931.
- 175 C. Qian, Q. Y. Qi, G. F. Jiang, F. Z. Cui, Y. Tian and X. Zhao, *J. Am. Chem. Soc.*, 2017, **139**, 6736–6743.
- 176 N. Huang, P. Wang and D. Jiang, *Nat. Rev. Mater.*, 2016, **1**, 2058–8437.
- 177 B. J. Smith, L. R. Parent, A. C. Overholts, P. A. Beaucage, R. P. Bisbey, A. D. Chavez, N. Hwang, C. Park, A. M. Evans, N. C. Gianneschi and W. R. Dichtel, *ACS Cent. Sci.*, 2017, **3**, 58–65.
- 178 U. Díaz and A. Corma, *Coord. Chem. Rev.*, 2016, **311**, 85–124.

- 179 W. W. San-Yuan Ding, *Chem Soc Rev*, 2013, **42**, 548–568.
- 180 F. Beuerle and B. Gole, *Angew. Chem. Int. Ed.*, 2018, **57**, 2–31.
- 181 N. W. Ockwig, A. P. Co, M. O. Keeffe, A. J. Matzger and O. M. Yaghi, 2005, **310**, 1166–1171.
- 182 R. W. Tilford, W. R. Gemmill, H. C. Zur Loye and J. J. Lavigne, *Chem. Mater.*, 2006, **18**, 5296–5301.
- 183 A. P. Côté, H. M. El-Kaderi, H. Furukawa, J. R. Hunt and O. M. Yaghi, *J. Am. Chem. Soc.*, 2007, **129**, 12914–12915.
- 184 Z. Kahveci, T. Islamoglu, G. A. Shar, R. Ding and H. M. El-Kaderi, *CrystEngComm*, 2013, **15**, 1524–1527.
- 185 E. L. Spitler, J. W. Colson, F. J. Uribe-Romo, A. R. Woll, M. R. Giovino, A. Saldivar and W. R. Dichtel, *Angew. Chem. Int. Ed.*, 2012, **51**, 2623–2627.
- 186 G. H. V. Bertrand, V. K. Michaelis, T.-C. Ong, R. G. Griffin and M. Dinca, *Proc. Natl. Acad. Sci. U.S.A.*, 2013, **110**, 4923–4928.
- 187 X. Feng, L. Chen, Y. Dong and D. Jiang, *Chem. Commun.*, 2011, **47**, 1979–1981.
- 188 A. Nagai, Z. Guo, X. Feng, S. Jin, X. Chen, X. Ding and D. Jiang, *Nat. Commun.*, 2011, **2**, 536–538.
- 189 B. J. Smith, A. C. Overholts, N. Hwang and W. R. Dichtel, *Chem. Commun.*, 2016, **52**, 3690–3693.
- 190 P. Katekomol, J. Roeser, M. Bojdys, J. Weber and A. Thomas, *Chem. Mater.*, 2013, **25**, 1542–1548.
- 191 A. Bhunia, V. Vasylyeva and C. Janiak, *Chem. Commun.*, 2013, **49**, 3961–3963.
- 192 A. Bhunia, I. Boldog, A. Moller and C. Janiak, *J. Mater. Chem. A*, 2013, **1**, 14990–14999.
- 193 S. Ren, M. J. Bojdys, R. Dawson, A. Laybourn, Y. Z. Khimyak, D. J. Adams and A. I. Cooper, *Adv. Mater.*, 2012, **24**, 2357–2361.
- 194 C. Gu, D. Liu, W. Huang, J. Liu and R. Yang, *Polym. Chem*, 2015, **6**, 7410–7417.
- 195 S. B. Alahakoon, G. Occhialini, G. T. McCandless, A. A. K. Karunathilake, S. O. Nielsen and R. A. Smaldone, *CrystEngComm*, 2017, **19**, 4882–4885.
- 196 Y. Zhao, K. X. Yao, B. Teng, T. Zhang and Y. Han, *Energy Environ. Sci.*, 2013, **6**, 3684.
- 197 J. A. O'Brien and A. L. Myers, *Ind. Eng. Chem. Res.*, 1988, **27**, 2085–2092.
- 198 S. Hug, M. B. Mesch, H. Oh, N. Popp, M. Hirscher, J. Senker and B. V. Lotsch, *J. Mater.*

- Chem. A*, 2014, **2**, 5928–5936.
- 199 X. Liu, H. Li, Y. Zhang, B. Xu, S. A, H. Xia and Y. Mu, *Polym. Chem.*, 2013, **4**, 2445–2445.
 - 200 M. R. Liebl and J. Senker, *Chem. Mater.*, 2013, **25**, 970–980.
 - 201 R. Dawson, E. Stöckel, J. R. Holst, D. J. Adams and A. I. Cooper, *Energy Environ. Sci.*, 2011, **4**, 4239–4245.
 - 202 G. Li and Z. Wang, *Macromolecules*, 2013, **46**, 3058–3066.
 - 203 Y. Luo, S. Zhang, Y. Ma, W. Wang and B. Tan, *Polym. Chem.*, 2013, **4**, 1126–1131.
 - 204 K. Wang, H. Huang, D. Liu, C. Wang, J. Li and C. Zhong, *Environ. Sci. Technol.*, 2016, **50**, 4869–4876.
 - 205 K. Wang, L. M. Yang, X. Wang, L. Guo, G. Cheng, C. Zhang, S. Jin, B. Tan and A. Cooper, *Angew. Chem. Int. Ed.*, 2017, **56**, 14149–14153.
 - 206 L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peters and S. Hecht, *Nat. Nanotechnol.*, 2007, **2**, 687–691.
 - 207 P. Kuhn, A. Forget, D. Su, A. Thomas and M. Antonietti, *J. Am. Chem. Soc.*, 2008, **130**, 13333–13337.
 - 208 P. Kuhn, A. Forget, J. Hartmann, A. Thomas and M. Antonietti, *Adv. Mater.*, 2009, **21**, 897–901.
 - 209 M. J. Bojdys, J. Jeromenok, A. Thomas and M. Antonietti, *Adv. Mater.*, 2010, **22**, 2202–2205.
 - 210 V. S. P. K. Neti, X. Wu, S. Deng and L. Echegoyen, *Polym. Chem.*, 2013, **4**, 4566–4569.
 - 211 S. Kandambeth, A. Mallick, B. Lukose, M. V. Mane, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2012, **134**, 19524–19527.
 - 212 S. Chandra, S. Kandambeth, B. P. Biswal, B. Lukose, S. M. Kunjir, M. Chaudhary, R. Babarao, T. Heine and R. Banerjee, *J. Am. Chem. Soc.*, 2013, **135**, 17853–17861.
 - 213 H. Wei, S. Chai, N. Hu, Z. Yang, L. Wei and L. Wang, *Chem. Commun.*, 2015, **51**, 12178–12181.
 - 214 B. P. Biswal, H. D. Chaudhari, R. Banerjee and U. K. Kharul, *Chem. Eur. J.*, 2016, **22**, 4695–4699.
 - 215 L. M. Robeson, *J. Memb. Sci.*, 2008, **320**, 390–400.
 - 216 W. F. Yong, F. Y. Li, Y. C. Xiao, P. Li, K. P. Pramoda, Y. W. Tong and T. S. Chung, *J.*

- Memb. Sci.*, 2012, **407–408**, 47–57.
- 217 A. Bhaskar, R. Banerjee and U. Kharul, *J. Mater. Chem. A*, 2014, **2**, 12962–129.
- 218 M. G. Rabbani, A. K. Sekizkardes, Z. Kahveci, T. E. Reich, R. Ding and H. M. El-Kaderi, *Chem. Eur. J.*, 2013, **19**, 3324–3328.
- 219 T. Ben, H. Ren, S. Ma, D. Cao, J. Lan, X. Jing, W. Wang, J. Xu, F. Deng, J. M. Simmons, S. Qiu and G. Zhu, *Angew. Chem. Int. Ed.*, 2009, **121**, 9621–9624.
- 220 Z. Li, X. Feng, Y. Zou, Y. Zhang, H. Xia, X. Liu and Y. Mu, *Chem. Commun.*, 2014, **50**, 13825–13828.
- 221 Z. Li, Y. Zhi, X. Feng, X. Ding, Y. Zou, X. Liu and Y. Mu, *Chem. Eur. J.*, 2015, **21**, 12079–12084.
- 222 Q. Chen, M. Luo, Hammershøj, D. Zhou, Y. Han, B. W. Laursen, C. G. Yan and B. H. Han, *J. Am. Chem. Soc.*, 2012, **134**, 6084–6087.
- 223 P. Arab, M. G. Rabbani, A. K. Sekizkardes, T. Islamoğlu and H. M. El-Kaderi, *Chem. Mater.*, 2014, **26**, 1385–1392.
- 224 Y. Zhu, H. Long and W. Zhang, *Chem. Mater.*, 2013, **25**, 1630–1635.
- 225 C. Shen, H. Yu and Z. Wang, *Chem. Commun.*, 2014, **50**, 11238.
- 226 M. G. Rabbani and H. M. El-Kaderi, *Chem. Mater.*, 2012, **24**, 1511–1517.
- 227 S. B. Alahakoon, C. M. Thompson, A. X. Nguyen, G. Occhialini, G. T. McCandless and R. A. Smaldone, *Chem. Commun.*, 2016, **52**, 2843–2845.
- 228 A. Delapeñaruigómez, D. Rodríguez-San-Miguel, K. C. Stylianou, M. Cavallini, D. Gentili, F. Liscio, S. Milita, O. M. Roscioni, M. L. Ruiz-González, C. Carbonell, D. MasPOCH, R. Mas-Ballesté, J. L. Segura and F. Zamora, *Chem. Eur. J.*, 2015, **21**, 10666–10670.
- 229 S. Zhao, B. Dong, R. Ge, C. Wang, X. Song, W. Ma, Y. Wang, C. Hao, X. Guo and Y. Gao, *RSC Adv.*, 2016, **6**, 38774–38781.
- 230 L. Huang and G. Cao, *Chem. Sel.*, 2016, **1**, 533–538.
- 231 J. K. Schnobrich, K. Koh, K. N. Sura and A. J. Matzger, *Langmuir*, 2010, **26**, 5808–5814.
- 232 H. Furukawa, N. Ko, Y. B. Go, N. Aratani, S. B. Choi, E. A. Choi, O. A. Yazaydin, R. Q. Snurr, M. O’Keeffe, J. Kim and O. M. Yaghi, *Science*, 2010, **329**, 424–428.
- 233 Z. Yang, X. Peng and D. Cao, *J. Phys. Chem. C*, 2013, **117**, 8353–8364.
- 234 T. Sun, J. Hu, X. Ren and S. Wang, *Sep. Sci. Technol.*, 2015, **50**, 874–885.
- 235 L. Ascherl, T. Sick, J. T. Margraf, S. H. Lapidus, M. Calik, C. Hettstedt, K. Karaghiosoff,

- M. Döbblinger, T. Clark, K. W. Chapman, F. Auras and T. Bein, *Nat. Chem.*, 2016, **8**, 310–316.
- 236 H. Furukawa, Z. Liu, H. Zhu, C. Zhu and K. Suenaga, *Science*, 2016, **351**, 365–369.
- 237 L. Zou, X. Yang, S. Yuan and H. Zhou, *CrystEngComm*, 2017, **19**, 4868–4871.
- 238 N. W. Ockwig, A. P. Co, M. O. Keeffe, A. J. Matzger and O. M. Yaghi, 2005, **310**, 1166–1171.
- 239 Y. Zeng, R. Zou, Z. Luo, H. Zhang, X. Yao, X. Ma, R. Zou and Y. Zhao, *J. Am. Chem. Soc.*, 2015, **137**, 1020–1023.
- 240 X. Chen, M. Addicoat, E. Jin, H. Xu, T. Hayashi, F. Xu, N. Huang, S. Irle and D. Jiang, *Sci. Rep.*, 2015, **5**, 1–19.
- 241 J. W. Colson and W. R. Dichtel, *Nat. Chem.*, 2013, **5**, 453–465.
- 242 S. Kandambeth, V. Venkatesh, D. B. Shinde, S. Kumari, A. Halder, S. Verma and R. Banerjee, *Nat. Commun.*, 2015, **6**, 6786–7786.
- 243 Y. Tian, S.-Q. Xu, R.-R. Liang, C. Qian, G.-F. Jiang and X. Zhao, *CrystEngComm*, 2017, **19**, 4877–4881.
- 244 J. W. Colson, A. R. Woll, A. Mukherjee, M. P. Levendorf, E. L. Spitler, V. B. Shields, M. G. Spencer, J. Park and W. R. Dichtel, *Science (80-.)*, 2011, **332**, 228–232.
- 245 H. Ren, T. Ben, E. Wang, X. Jing, M. Xue, B. Liu, Y. Cui, S. Qiu and G. Zhu, *Chem. Commun.*, 2010, **46**, 291–293.
- 246 N. L. Campbell, R. Clowes, L. K. Ritchie and A. I. Cooper, *Chem. Mater.*, 2009, **21**, 204–206.
- 247 L. K. Ritchie, A. Trewin, A. Reguera-Galan, T. Hasell and A. I. Cooper, *Microporous Mesoporous Mater.*, 2010, **132**, 132–136.
- 248 W. Zhao, L. Xia and X. Liu, *CrystEngComm*, 2018.
- 249 M. Tong, Q. Yang, Y. Xiao and C. Zhong, *Phys. Chem. Chem. Phys.*, 2014, **16**, 15189–98.
- 250 G. Ferguson, A. J. Lough, J. P. Sheehan and T. R. Spalding, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 1991, **47**, 379–381.
- 251 L. Vol and G. Britain, *Inorg. Nucl. Chem. Lett.*, 1971, **7**, 509–512.
- 252 S. J. Rettig and J. Trotter, *Can. J. Chem.*, 1973, **51**, 1288–1294.
- 253 A. G. Orpen, L. Brammer, F. H. Allen, O. Kennard, D. G. Watson and R. Taylor, *J. Chem. Soc. Perkin Trans. II*, 1987, **2**, 1–19.

- 254 W. Clegg, A. J. Scott, F. E. S. Souza and T. B. Marder, *Acta Crystallogr. Sect. C Cryst. Struct. Commun.*, 1999, **55**, 1885–1888.
- 255 J. Cruz-Huerta, G. Campillo-Alvarado, H. Höpfl, P. Rodríguez-Cuamatzi, V. Reyes-Márquez, J. Guerrero-Álvarez, D. Salazar-Mendoza and N. Farfán-García, *Eur. J. Chem.*, 2016, **3**, 355–365.
- 256 D. A. Foucher, J. Alan and I. Manners, *Inorg. Chem.*, 1992, **31**, 3034–3043.
- 257 M. A. Beckett, D. E. Hibbs, M. B. Hursthouse, K. M. A. Malik, P. Owen and K. S. Varma, *J. Organomet. Chem.*, 2000, **595**, 241–247.
- 258 L. A. Neville and G. F. Spalding, Trevor R, *Angew. Chem. Int. Ed.*, 2000, **39**, 3598–3601.
- 259 M. Nishio, *CrystEngComm*, 2004, **27**, 130–158.
- 260 N. L. Rosi, M. Eddaoudi, J. Kim, M. O’Keeffe and O. M. Yaghi, *CrystEngComm*, 2002, **4**, 401–404.
- 261 H. Li, M. Eddaoudi, M. O’Keeffe and O. M. Yaghi, *Nature*, 1999, **402**, 276–279.
- 262 C.-Y. Liu, Y.-Q. Ma, H.-R. Tian, C.-Y. Gao, Y.-H. Li and Z.-M. Sun, *Chinese J. Struct. Chem. J. Struct. Chem.*, 2017, **36**, 654–660.
- 263 A. Vlad, M.-F. Zaltariov, S. Shova, G. Novitchi, C. Train and M. Cazacu, *RSC Adv.*, 2016, **6**, 37412–37423.
- 264 R. P. Davies, R. J. Less, P. D. Lickiss and A. J. P. White, *Dalton Trans.*, 2007, **3**, 2528–2535.
- 265 R. P. Davies, R. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Cryst. Growth Des.*, 2010, **10**, 4571–4581.
- 266 L. Wen, P. Cheng and W. Lin, *Chem. Sci.*, 2012, **3**, 2288–2292.
- 267 T. Guo, X. Yang, R. Li, X. Liu, Y. Gao and Z. Dai, *J. Solid Chem.*, 2017, **253**, 129–138.
- 268 S. S. Chen, R. Qiao, L. Q. Sheng, S. Yang and Z. Di Liu, *CrystEngComm*, 2013, **639**, 1808–1814.
- 269 D. M. L. Goodgame, P. D. Lickiss, S. J. Rooke, A. J. P. White and D. J. Williams, *Inorganica Chim. Acta*, 2003, **343**, 61–73.
- 270 D. M. L. Goodgame, P. D. Lickiss, S. J. Rooke, A. J. P. White and D. J. Williams, *Inorganica Chim. Acta*, 2001, **324**, 218–231.
- 271 G. Günay, O. Z. Yeşilel, H. Erer, S. Keskin and A. Tabak, *Polyhedron*, 2015, **100**, 108–113.

- 272 T. Mocanu, L. Pop, S. Shova, I. Grosu and M. Andruh, *CrystEngComm*, 2017, **19**, 27–31.
- 273 A. Schütrumpf, E. Kirpi, A. Bulut, F. L. Morel, M. Ranocchiari, E. Lork, Y. Zorlu, S. Grabowsky, G. Yücesan and J. Beckmann, *Cryst. Growth Des.*, 2015, **15**, 4925–4931.
- 274 J. Ai, X. Min, C.-Y. Gao, H.-R. Tian, S. Dang and Z.-M. Sun, *Dalton Trans.*, 2017, **46**, 6756–6761.
- 275 J. K. Zaręba, *Inorg. Chem. Commun.*, 2017, **86**, 172–186.
- 276 A. D. G. Firmino, F. Figueira, J. P. C. Tomé, F. A. A. Paz and J. Rocha, *Coord. Chem. Rev.*, 2018, **355**, 133–149.
- 277 S. E. Wenzel, M. Fischer, F. Hoffmann and M. Fröba, *Inorg. Chem.*, 2009, **48**, 6559–6565.
- 278 Y. Liu, J. Su, W. Li and J. Wu, *Inorg. Chem.*, 2005, **44**, 3890–3895.
- 279 A. P. Côté and G. K. H. Shimizu, *Inorg. Chem.*, 2004, **43**, 6663–6673.
- 280 K. K. Gangu, S. Maddila, S. B. Mukkamala and S. B. Jonnalagadda, *Inorganica Chim. Acta*, 2016, **446**, 61–74.
- 281 M. Rubio-Martinez, C. Avci-Camur, A. W. Thornton, I. Imaz, D. MasPOCH and M. R. Hill, *Chem. Soc. Rev.*, 2017, **46**, 3453–3480.
- 282 J. Ren, X. Dyosiba, N. M. Musyoka, H. W. Langmi, M. Mathe and S. Liao, *Coord. Chem. Rev.*, 2017, **352**, 187–219.
- 283 J. Fan, M.-H. Shu, T. Okamura, Y.-Z. Li, W.-Y. Sun, W.-X. Tang and N. Ueyama, *New J. Chem.*, 2003, **27**, 1307–1309.
- 284 A. T. Çolak, G. Pamuk, O. Z. Yeilel and F. Yüksel, *Solid State Sci.*, 2011, **13**, 2100–2104.
- 285 A. Schaate, P. Roy, A. Godt, J. Lippke, F. Waltz, M. Wiebcke and P. Behrens, *Chem. Eur. J.*, 2011, **17**, 6643–6651.
- 286 F. Vermoortele, B. Bueken, G. Le Bars, B. Van De Voorde, M. Vandichel, K. Houthoofd, A. Vimont, M. Daturi, M. Waroquier, V. Van Speybroeck, C. Kirschhock and D. E. De Vos, *J. Am. Chem. Soc.*, 2013, **135**, 11465–11468.
- 287 H. Wu, Y. S. Chua, V. Krungleviciute, M. Tyagi, P. Chen, T. Yildirim and W. Zhou, *J. Am. Chem. Soc.*, 2013, **135**, 10525–10532.
- 288 G. C. Shearer, S. Chavan, S. Bordiga, S. Svelle, U. Olsbye and K. P. Lillerud, *Chem. Mater.*, 2016, **28**, 3749–3761.
- 289 M. J. Katz, Z. J. Brown, Y. J. Colón, P. W. Siu, K. A. Scheidt, R. Q. Snurr, J. T. Hupp and O. K. Farha, *Chem. Commun.*, 2013, **49**, 9449–9451.

- 290 A. J. Howarth, A. W. Peters, N. A. Vermeulen, T. C. Wang, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 26–39.
- 291 S. Natarajan, S. Mandal, P. Mahata, V. K. Roa, P. Ramaswamy, A. Banerjee, A. K. Paul and K. V. Ramya, *J. Chem. Sci.*, 2006, **118**, 525–536.
- 292 T. A. Mulyati, R. Ediati and M. Nadjib, *IPTEK J. Proceeding Ser.*, 2014, **1**, 2354–6026.
- 293 D. M. P. Mingos and D. R. Baghurst, *Chem. Soc. Rev.*, 1991, **20**, 1–47.
- 294 C. Oliver Kappe, *Chem. Soc. Rev.*, 2008, **37**, 1127–1139.
- 295 J. Klinowski, A. F. A. Paz, P. Silva and J. Rocha, *Dalton Trans.*, 2011, **40**, 321–330.
- 296 M. A. Surati, S. A. Jauhari and K. R. Desai, *Arch. Appl. Sci. Res.*, 2012, **4**, 645–661.
- 297 Z. Ni and R. I. Masel, *J. Am. Chem. Soc.*, 2006, **128**, 12394–12395.
- 298 C. McKinsty, E. J. Cussen, A. J. Fletcher, S. V. Patwardhan and J. Sefcik, *Chem. Eng. J.*, 2017, **326**, 570–577.
- 299 J. Y. Choi, J. Kim, S. H. Jhung, H. Kim, J. Chang and H. K. Chae, *Bull. Korean Chem. Soc. Chem. Soc.*, 2006, **27**, 1523–1524.
- 300 M. Taddei, D. A. Steitz, J. A. Van Bokhoven and M. Ranocchiari, *Chem. Eur. J. Eur. J.*, 2016, **22**, 3245–3249.
- 301 N. Abhyankar, M. Lee, M. Foley, E. S. Choi, G. Strouse, H. W. Kroto and N. S. Dalal, *Phys. Status Solid Rapid Res. Lett.*, 2016, **10**, 600–605.
- 302 K. Akhbari, A. Morsali and P. Retailleau, *Ultrason. Sonochem.*, 2013, **20**, 1428–1435.
- 303 D.-A. Yang, H.-Y. Cho, J. Kim, S.-T. Yang and W.-S. Ahn, *Energy Environ. Sci.*, 2012, **5**, 6465–6473.
- 304 D.-W. Jung, D.-A. Yang, J. Kim, J. Kim and W.-S. Ahn, *Dalton Trans.*, 2010, **39**, 2883–2887.
- 305 W.-J. Son, J. Kim, J. Kim and W.-S. Ahn, *Chem. Commun.*, 2008, **47**, 6336–6338.
- 306 V. Pezeshkpour, S. A. Khosravani, M. Ghaedi, K. Dashtian, F. Zare, A. Sharifi, R. Jannesar and M. Zoladl, *Ultrason. Sonochem.*, 2018, **40**, 1031–1038.
- 307 E. Haque, N. Khan, H. J. Park and S. H. Jhung, *Chem. Eur. J.*, 2010, **16**, 1046–1052.
- 308 O. Abuzalat, D. Wong, M. Elsayed, S. Park and S. Kim, *Ultrason. Sonochem.*, 2018, **45**, 180–188.
- 309 U. Mueller, M. Schubert, F. Teich, H. Puetter, K. Schierle-Arndt and J. Pastré, *J. Mater. Chem.*, 2006, **16**, 626–636.

- 310 M. Gaab, N. Trukhan, S. Maurer, R. Gummaraju and U. Müller, *Microporous Mesoporous Mater.*, 2012, **157**, 131–136.
- 311 M. Schlesinger, S. Schulze, M. Hietschold and M. Mehring, *Microporous Mesoporous Mater.*, 2010, **132**, 121–127.
- 312 M. Hartmann, S. Kunz, D. Himsl, O. Tangermann, S. Ernst and A. Wagener, *Langmuir*, 2008, **24**, 8634–8642.
- 313 H. M. Yang, X. L. Song, T. L. Yang, Z. H. Liang, C. M. Fan and X. G. Hao, *RSC Adv.*, 2014, **4**, 15720–15726.
- 314 A. Martinez Joaristi, J. Juan-Alcañiz, P. Serra-Crespo, F. Kapteijn and J. Gascon, *Cryst. Growth Des.*, 2012, **12**, 3489–3498.
- 315 N. Campagnol, E. R. Souza, D. E. De Vos, K. Binnemans and J. Fransaer, *Chem. Commun.*, 2014, **50**, 12545–12547.
- 316 H. Zhu, H. Liu, I. Zhitomirsky and S. Zhu, *Mater. Lett.*, 2015, **142**, 19–22.
- 317 M. Li and M. Dincă, *Chem. Sci.*, 2014, **5**, 107–111.
- 318 P. Schäfer, M. A. van der Veen and K. F. Domke, *Chem. Commun.*, 2016, **52**, 4722–4725.
- 319 H. Al-Kutubi, J. Gascon, E. J. R. Sudhölter and L. Rassaei, *ChemElectroChem*, 2015, **2**, 462–474.
- 320 M. Li and M. Dincă, *J. Am. Chem. Soc.*, 2011, **133**, 12926–12929.
- 321 W.-J. Li, M. Tu, R. Cao and R. A. Fischer, *J. Mater. Chem. A*, 2016, **4**, 12356–12369.
- 322 D. E. Crawford and J. Casaban, *Adv. Mater.*, 2016, **28**, 5747–5754.
- 323 A. L. Garay, A. Pichon and S. L. James, *Chem. Soc. Rev.*, 2007, **36**, 846–855.
- 324 T. Friščić, *Chem. Soc. Rev.*, 2012, **41**, 3493–3510.
- 325 V. V. Boldyrev, *Solid State Ionics North Holl.*, 1993, **63–65**, 537–543.
- 326 A. Stolle, T. Szuppa, S. E. S. Leonhardt and B. Ondruschka, *Chem. Soc. Rev.*, 2011, **40**, 2317–2329.
- 327 T. Friščić, *J. Mater. Chem.*, 2010, **20**, 7599–7605.
- 328 S. L. James, C. J. Adams, C. Bolm, D. Braga, P. Collier, T. Friščić, F. Grepioni, K. D. M. Harris, G. Hyett, W. Jones, A. Krebs, J. Mack, L. Maini, A. G. Orpen, I. P. Parkin, W. C. Shearouse, J. W. Steed and D. C. Waddell, *Chem. Soc. Rev.*, 2012, **41**, 413–447.
- 329 D. Braga and F. Grepioni, *Chem. Commun.*, 2005, 3635–3645.
- 330 A. Pichon, A. Lazuen-Garay and S. L. James, *CrystEngComm*, 2006, **8**, 211–214.

- 331 A. Pichon and S. L. James, *CrystEngComm*, 2008, **10**, 1839–1847.
- 332 S. Tanaka, K. Kida, T. Nagaoka, T. Ota and Y. Miyake, *Chem. Commun.*, 2013, **49**, 7884–7886.
- 333 S. K. Niraj, H. . Meennakshi and B. P. Viktor, *Chem. Commun.*, 2012, **48**, 11289–11291.
- 334 K. Leng, Y. Sun, X. Li, S. Sun and W. Xu, *Cryst. Growth Des.*, 2016, **16**, 1168–1171.
- 335 D. Braga, M. Curzi, A. Johansson, M. Polito, K. Rubini and F. Grepioni, *Angew. Chem. Int. Ed.*, 2006, **45**, 142–146.
- 336 T. Friščić and L. Fábián, *CrystEngComm*, 2009, **11**, 743–745.
- 337 M. Klimakow, P. Klobes, A. F. Thünemann, K. Rademann and F. Emmerling, *Chem. Mater.*, 2010, **22**, 5216–5221.
- 338 W. Yuan, A. L. Garay, A. Pichon, R. Clowes, C. D. Wood, A. I. Cooper and S. L. James, *CrystEngComm*, 2010, **12**, 4063–4065.
- 339 K. Užarević, T. C. Wang, S.-Y. Moon, A. M. Fidelli, J. T. Hupp, O. K. Farha and T. Friščić, *Chem. Commun.*, 2016, **52**, 2133–2136.
- 340 D. Prochowicz, K. Sokołowski, I. Justyniak, A. Kornowicz, D. Fairen-Jimenez, T. Friščić and J. Lewiński, *Chem. Commun.*, 2015, **51**, 4032–4035.
- 341 T. Friščić, D. G. Reid, I. Halasz, R. S. Stein, R. E. Dinnebier and M. J. Duer, *Angew. Chem. Int. Ed.*, 2010, **49**, 712–715.
- 342 P. J. Beldon, L. Fábián, R. S. Stein, A. Thirumurugan, A. K. Cheetham and T. Friščić, *Angew. Chem. Int. Ed.*, 2010, **49**, 9640–9643.
- 343 H. Li, M. Eddaoudi, T. L. Groy and O. M. Yaghi, *J. Am. Chem. Soc.*, 1998, **120**, 8571–8572.
- 344 M. Eddaoudi, J. Kim, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2002, **124**, 376–377.
- 345 K. Tanaka, S. Oda and M. Shiro, *Chem. Commun.*, 2008, 820–822.
- 346 F. L. Geyer, F. Rominger, M. Vogtland and U. H. F. Bunz, *Cryst. Growth Des.*, 2015, **15**, 3539–3544.
- 347 W. X. Zhang, Y. Y. Yang, S. B. Zai, W. N. Seik and X. M. Chen, *Eur. J. Inorg. Chem.*, 2008, **2**, 679–685.
- 348 J. H. Liao, P. C. Wu and W. C. Huang, *Cryst. Growth Des.*, 2006, **6**, 1062–1063.
- 349 D. N. Dybtsev, H. Chun and K. Kim, *Chem Commun.*, 2004, **3**, 1594–1595.

- 350 M. Rubio-Martinez, M. P. Batten, A. Polyzos, K. C. Carey, J. I. Mardel, K. S. Lim and M. R. Hill, *Sci. Rep.*, 2014, **4**, 1–5.
- 351 T. D. Bennett, A. K. Cheetham, A. H. Fuchs and F. X. Coudert, *Nat. Chem.*, 2016, **9**, 11–16.
- 352 D. S. Sholl and R. P. Lively, *J. Phys. Chem. Lett.*, 2015, **6**, 3437–3444.
- 353 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040–2042.
- 354 Y. Kalinovsky, N. J. Cooper, M. J. Main, S. J. Holder and B. A. Blight, *Dalton Trans.*, 2017, **46**, 15704–15709.
- 355 J. E. Mondloch, O. Karagiari, O. K. Farha and J. T. Hupp, *Acc. Chem. Res.*, 2013, **43**, 9258–9264.
- 356 J. H. Cavka, U. Olsbye, N. Guillou, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **6**, 1–19.
- 357 B. F. Abrahams, B. F. Hoskins, D. M. Michail and R. Robson, *Nature*, 1994, **369**, 727–729.
- 358 M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O. Keefe, O. M. Yaghi, M. Eddaoudi, J. Kim, N. Rosi and O. M. Yaghi, *Science*, 2002, **295**, 469–472.
- 359 J. E. Mondloch, O. Karagiari, O. K. Farha and J. T. Hupp, *Acc. Chem. Res.*, 2013, **43**, 9258–9264.
- 360 A. P. Nelson, O. K. Farha, K. L. Mulfort and J. T. Hupp, *J. Am. Chem. Soc.*, 2009, **131**, 458–460.
- 361 T. Düren, F. Millange, G. Férey, K. S. Walton and R. Q. Snurr, *J. Phys. Chem. C*, 2007, **111**, 15350–15356.
- 362 X. Lin, I. Telepeni, A. J. Blake, A. Dailly, C. M. Brown, J. M. Simmons, M. Zoppi, G. S. Walker, K. M. Thomas, T. J. Mays, P. Hubberstey, N. R. Champness and M. Schroder, *J. Am. Chem. Soc.*, 2009, **131**, 2159–2171.
- 363 C. L. Yaws and P. C. Richmond, in *Thermophysical Properties of Chemicals and Hydrocarbons*, ed. William Andrew, Norwich, NY, Surface te., 2009, pp. 686–781.
- 364 J. E. Mondloch, O. Karagiari, O. K. Farha and J. T. Hupp, *CrystEngComm*, 2013, **15**, 9258–9264.
- 365 W. Zhuang, S. Ma, X.-S. Wang, D. Yuan, J.-R. Li, D. Zhao and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 5223–5225.

- 366 S. T. Meek, J. J. Perry, S. L. Teich-Mcgoldrick, J. A. Greathouse and M. D. Allendorf, *Cryst. Growth Des.*, 2011, **11**, 4309–4312.
- 367 O. K. Farha, A. Ö. Yazaydin, I. Eryazici, C. D. Malliakas, B. G. Hauser, M. G. Kanatzidis, S. T. Nguyen, R. Q. Snurr and J. T. Hupp, *Nat. Chem.*, 2010, **2**, 944–948.
- 368 Y. S. Bae, D. Dubbeldam, A. Nelson, K. S. Walton, J. T. Hupp and R. Q. Snurr, *Chem. Mater.*, 2009, **21**, 4768–4777.
- 369 A. M. Shultz, A. A. Sarjeant, O. K. Farha, J. T. Hupp and S. T. Nguyen, *J. Am. Chem. Soc.*, 2011, **133**, 13252–13255.
- 370 A. M. Shultz, O. K. Farha, D. Adhikari, A. A. Sarjeant, J. T. Hupp and S. B. T. Nguyen, *Inorg. Chem.*, 2011, **50**, 3174–3176.
- 371 C. E. Wilmer, O. K. Farha, T. Yildirim, I. Eryazici, V. Krungleviciute, A. A. Sarjeant, R. Q. Snurr and J. T. Hupp, *Energy Environ. Sci.*, 2013, **6**, 1158–1163.
- 372 T. K. Prasad and M. P. Suh, *Chem. Eur. J.*, 2012, **18**, 8673–8680.
- 373 X. Song, T. K. Kim, H. Kim, D. Kim, S. Jeong, H. R. Moon and M. S. Lah, *Chem. Mater.*, 2012, **24**, 3065–3073.
- 374 K. Koh, J. D. Van Oosterhout, S. Roy, A. G. Wong-Foy and A. J. Matzger, *Chem. Sci.*, 2012, **3**, 2429–2429.
- 375 J. An, O. K. Farha, J. T. Hupp, E. Pohl, J. I. Yeh and N. L. Rosi, *Nat. Commun.*, 2012, **3**, 604–606.
- 376 D. Han, F.-L. Jiang, M.-Y. Wu, L. Chen, Q.-H. Chen and M.-C. Hong, *Chem. Commun.*, 2011, **47**, 9861–9863.
- 377 R. Grönker, I. Senkovska, R. Biedermann, N. Klein, M. R. Lohe, P. Müller and S. Kaskel, *Chem. Commun.*, 2011, **47**, 490–492.
- 378 H. Deng, S. Gruner, K. E. Cordova, C. Valente, H. Furukawa, M. Hmadeh, F. Gándara, A. C. Whalley, Z. Liu, S. Asahina, H. Kazumori, M. O’Keeffe, O. Terasaki, F. J. Stoddart and O. M. Yaghi, *Science*, 2006, **336**, 1757–1762.
- 379 Z. Zhang, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *J. Am. Chem. Soc.*, 2013, **135**, 5982–5985.
- 380 A. W. Francis, *J. Phys. Chem.*, 1954, **58**, 1099–1114.
- 381 L. Rey, *Nature*, 1990, **345**, 185–186.
- 382 L. Ma, A. Jin, Z. Xie and W. Lin, *Angew. Chem. Int. Ed.*, 2009, **48**, 9905–9908.

- 383 S. Deville, E. Saiz, R. K. Nalla and A. P. Tomsia, *Science*, 2006, **311**, 515–518.
- 384 D. Zhao and M. Cao, *ACS Appl. Mater. Interfaces*, 2015, **7**, 25084–25093.
- 385 Y. Li, Q. Liu, D. Kang, J. Gu, W. Zhang and D. Zhang, *J. Mater. Chem. A*, 2015, **3**, 21016–21022.
- 386 C. Gaudillere, J. Garcia-Fayos and J. M. Serra, *J. Mater. Chem. A*, 2014, **2**, 3828–3833.
- 387 Y. P. He, Y. X. Tan and J. Zhang, *Inorg. Chem.*, 2012, **51**, 11232–11234.
- 388 X. Li, Y. Liu, S. Liu, S. Wang, L. Xu, Z. Zhang, F. Luo, Y. Lu and S. Liu, *J. Mater. Chem. A*, 2018, **6**, 4678–4685.
- 389 J. Bae, J. S. Choi, S. Hwang, W. S. Yun, D. Song, J. Lee and N. C. Jeong, *ACS Appl. Mater. Interfaces*, 2017, **9**, 24743–24752.
- 390 W. Morris, B. Voloskiy, S. Demir, F. Gándara, P. L. McGrier, H. Furukawa, D. Cascio, J. F. Stoddart and O. M. Yaghi, *Inorg. Chem.*, 2012, **51**, 6443–6445.
- 391 D. Feng, Z. Y. Gu, J. R. Li, H. L. Jiang, Z. Wei and H. C. Zhou, *Angew. Chem. Int. Ed.*, 2012, **51**, 10307–10310.
- 392 J. E. Mondloch, W. Bury, D. Fairen-Jimenez, S. Kwon, E. J. Demarco, M. H. Weston, A. A. Sarjeant, S. T. Nguyen, P. C. Stair, R. Q. Snurr, O. K. Farha and J. T. Hupp, *J. Am. Chem. Soc.*, 2013, **135**, 10294–10297.
- 393 H. K. Kim, W. S. Yun, M. B. Kim, J. Y. Kim, Y. S. Bae, J. D. Lee and N. C. Jeong, *J. Am. Chem. Soc.*, 2015, **137**, 10009–10015.
- 394 F. Gándara and T. D. Bennett, *IUCr J.*, 2014, **1**, 563–570.
- 395 A. L. Spek, *Acta Crystallogr. Sect. C Struct. Chem.*, 2015, **71**, 9–18.
- 396 H. Wu, J. Yang, Z. M. Su, S. R. Batten and J. F. Ma, *J. Am. Chem. Soc.*, 2011, **133**, 11406–11409.
- 397 H. Wu, H.-Y. Liu, Y.-Y. Liu, J. Yang, B. Liu and J.-F. Ma, *Chem. Commun.*, 2011, **47**, 1818–1820.
- 398 S. R. Batten and R. Robson, *Angew. Chem. Int. Ed.*, 1998, **37**, 1460–1494.
- 399 C. E. Wilmer, M. Leaf, C. Y. Lee, O. K. Farha, B. G. Hauser, J. T. Hupp and R. Q. Snurr, *Nat. Chem.*, 2012, **4**, 83–89.
- 400 P. D. C. Dietzel, R. E. Johnsen, R. Blom and H. Fjellvåg, *Chem. Eur. J.*, 2008, **14**, 2389–2397.
- 401 M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez, G. Férey and G. Maurin,

- J. Am. Chem. Soc.*, 2009, **131**, 10857–10859.
- 402 L. Bromberg, Y. Diao, H. Wu, S. A. Speakman and T. A. Hatton, *Chem. Mater.*, 2012, **24**, 1664–1675.
- 403 A. A. Yakovenko, J. H. Reibenspies, N. Bhuvanesh and H. C. Zhou, *J. Appl. Crystallogr.*, 2013, **46**, 346–353.
- 404 J. Xu, Z.-S. Bai, M.-S. Chen, Z. Su, S.-S. Chen and W.-Y. Sun, *CrystEngComm*, 2009, **11**, 2728–2733.
- 405 P. D. C. Dietzel, R. Blom and H. Fjellvåg, *Eur. J. Inorg. Chem.*, 2008, **23**, 3624–3632.
- 406 S. S. Y. Chui, S. M. F. Lo, J. P. H. Charmant, G. A. Orpen and I. D. Williams, *Science*, 1999, **283**, 1148–1150.
- 407 M. T. Wharmby, S. Henke, T. D. Bennett, S. R. Bajpe, I. Schwedler, S. P. Thompson, F. Gozzo, P. Simoncic, C. Mellot-Draznieks, H. Tao, Y. Yue and A. K. Cheetham, *Angew. Chem. Int. Ed.*, 2015, **54**, 6447–6451.
- 408 V. N. Vukotic and S. J. Loeb, *Chem. Eur. J.*, 2010, **16**, 13630–13637.
- 409 J. A. Mason, K. Sumida, Z. R. Herm, R. Krishna and J. R. Long, *Energy Environ. Sci.*, 2011, **4**, 3030–3040.
- 410 K. S. Walton and R. Q. Snurr, *J. Am. Chem. Soc.*, 2007, **129**, 8552–8556.
- 411 M. Thommes, K. Kaneko, A. V. Neimark, J. P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol and K. S. W. Sing, *Pure Appl. Chem.*, 2015, **87**, 1051–1069.
- 412 H. Chae, J. Kim and Y. Go, *Nature*, 2004, **427**, 523–527.
- 413 H. Frost, T. Düren and R. Q. Snurr, *J. Phys. Chem. B*, 2006, **110**, 9565–9570.
- 414 Q. Yang, C. Zhong and J.-F. Chen, *J. Phys. Chem. C*, 2008, **112**, 1562–1569.
- 415 Y. S. Bae, A. Ö. Yazaydın and R. Q. Snurr, *Langmuir*, 2010, **26**, 5475–5483.
- 416 D. A. Gómez-Gualdrón, P. Z. Moghadam, J. T. Hupp, O. K. Farha and R. Q. Snurr, *J. Am. Chem. Soc.*, 2016, **138**, 215–224.
- 417 T. C. Wang, W. Bury, D. A. Gómez-Gualdrón, N. A. Vermeulen, J. E. Mondloch, P. Deria, K. Zhang, P. Z. Moghadam, A. A. Sarjeant, R. Q. Snurr, J. F. Stoddart, J. T. Hupp and O. K. Farha, *J. Am. Chem. Soc.*, 2015, **137**, 3585–3591.
- 418 I. Langmuir, *J. Am. Chem. Soc.*, 1918, **40**, 1361–1403.
- 419 S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, 309–319.
- 420 J. Rouquerol, F. Rouquerol, P. Llewellyn, G. Maurin and K. Sing, *Adsorption by Powders*

and Porous Solids: Principles, Methodology and Applications, Academic Press, London, 2nd edn., 2013.

- 421 M. Thommes, *Chem. Ing. Tech.*, 2010, **82**, 1059–1073.
- 422 E. P. Barrett, L. G. Joyner and P. P. Halenda, *J. Am. Chem. Soc.*, 1951, **73**, 373–380.
- 423 T. C. Wang, N. A. Vermeulen, I. S. Kim, A. B. F. Martinson, J. Fraser Stoddart, J. T. Hupp and O. K. Farha, *Nat. Protoc.*, 2016, **11**, 149–162.
- 424 L. L. Keenan, H. A. Hamzah, M. F. Mahon, M. R. Warren and A. D. Burrows, *CrystEngComm*, 2016, **18**, 5710–5717.
- 425 H. Fei, J. Shin, Y. S. Meng, M. Adelhardt, J. Sutter, K. Meyer and S. M. Cohen, *J. Am. Chem. Soc.*, 2014, **136**, 4965–4973.
- 426 H. C. Hoffmann, M. Debowski, P. Müller, S. Paasch, I. Senkovska, S. Kaskel and E. Brunner, *Mater.*, 2012, **5**, 2537–2572.
- 427 A. Sutrisno and Y. Huang, *Solid State Nucl. Magn. Reson.*, 2013, **49–50**, 1–11.
- 428 M. Rimoldi, A. Nakamura, N. A. Vermeulen, J. J. Henkelis, A. K. Blackburn, J. T. Hupp, J. F. Stoddart and O. K. Farha, *Chem. Sci.*, 2016, **7**, 4980–4984.
- 429 C. K. Brozek, V. K. Michaelis, T. C. Ong, L. Bellarosa, N. López, R. G. Griffin and M. Dincă, *ACS Cent. Sci.*, 2015, **1**, 252–260.
- 430 F. Gul-E-Noor, M. Mendt, D. Michel, A. Pöpl, H. Krautscheid, J. Haase and M. Bertmer, *J. Phys. Chem. C*, 2013, **117**, 7703–7712.
- 431 V. N. Vukotic, K. J. Harris, K. Zhu, R. W. Schurko and S. J. Loeb, *Nat. Chem.*, 2012, **4**, 456–460.
- 432 K. Zhu, C. A. O’Keefe, V. N. Vukotic, R. W. Schurko and S. J. Loeb, *Nat. Chem.*, 2015, **7**, 514–519.
- 433 C. Sue, Y.-L. Y. Zhao, L. Liu, Q. Li, W. Zhang, O. S. Miljanic, C. Sue, Y.-L. Y. Zhao, L. Liu, C. B. Knobler, J. F. Stoddart and O. M. Yaghi, *Science*, 2009, **325**, 855–859.
- 434 R. J. Kuppler, D. J. Timmons, Q. R. Fang, J. R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang and H. C. Zhou, *Coord. Chem. Rev.*, 2009, **253**, 3042–3066.
- 435 D. Zhao, D. Yuan and H.-C. Zhou, *Energy Environ. Sci.*, 2008, **1**, 222–.
- 436 L. Hamon, P. L. Llewellyn, T. Devic, A. Ghoufi, G. Clet, V. Guillerm, G. D. Pirngruber, G. Maurin, C. Serre, G. Driver, W. Van Beek, E. Jolimaître, A. Vimont, M. Daturi and G. Férey, *J. Am. Chem. Soc.*, 2009, **131**, 17490–17499.

- 437 W. Lu, Z. Wei, Z.-Y. Gu, T.-F. Liu, J. Park, J. Park, J. Tian, M. Zhang, Q. Zhang, T. Gentle III, M. Bosch and H.-C. Zhou, *Chem. Soc. Rev.*, 2014, **43**, 5561–5593.
- 438 H. Furukawa, J. Kim, N. W. Ockwig, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2008, **130**, 11650–11661.
- 439 G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour and I. Margiolaki, *Angew. Chem. Int. Ed.*, 2004, **43**, 6296–6301.
- 440 H. Furukawa, Y. B. Go, N. Ko, Y. K. Park, F. J. Uribe-Romo, J. Kim, M. O’Keeffe and O. M. Yaghi, *Inorg. Chem.*, 2011, **50**, 9147–9152.
- 441 X. Sen Wang, S. Ma, D. Sun, S. Parkin and H. C. Zhou, *J. Am. Chem. Soc.*, 2006, **128**, 16474–16475.
- 442 S. Ma, D. Sun, M. Ambrogio, J. A. Fillinger, S. Parkin and H. C. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1858–1859.
- 443 P. Li, N. A. Vermeulen, C. D. Malliakas, D. A. Gómez-Gualdrón, A. J. Howarth, B. L. Mehdi, A. Dohnalkova, N. D. Browning, M. O’Keeffe and O. K. Farha, *Science*, 2017, **356**, 624–627.
- 444 A. G. Wong-Foy, O. Lebel and A. J. Matzger, *J. Am. Chem. Soc.*, 2007, **129**, 15740–15741.
- 445 J. Duan, Z. Yang, J. Bai, B. Zheng, Y. Li and S. Li, *Chem. Commun.*, 2012, **48**, 3058–3060.
- 446 D. Zhao, D. J. Timmons, D. Yuan and H. C. Zhou, *Acc. Chem. Res.*, 2011, **44**, 123–133.
- 447 F. A. Almeida Paz, J. Klinowski, S. M. F. Vilela, J. P. C. Tomé, J. A. S. Cavaleiro and J. Rocha, *Chem. Soc. Rev.*, 2012, **41**, 1088–1110.
- 448 M. O’Keeffe and O. M. Yaghi, *Chem. Rev.*, 2012, **112**, 675–702.
- 449 M. Zhang, Y.-P. Chen and H.-C. Zhou, *CrystEngComm*, 2013, **15**, 9544–9552.
- 450 L. Carlucci, G. Ciani and D. M. Proserpio, *Coord. Chem. Rev.*, 2003, **246**, 247–289.
- 451 V. a. Blatov, L. Carlucci, G. Ciani and D. M. Proserpio, *CrystEngComm*, 2004, **6**, 378–395.
- 452 M. Zhang, Y.-P. Chen, M. Bosch, T. Gentle, K. Wang, D. Feng, Z. U. Wang and H.-C. Zhou, *Angew. Chem. Int. Ed.*, 2014, **53**, 815–818.
- 453 O. D. Friedrichs, M. O’Keeffe and O. M. Yaghi, *Solid State Sci.*, 2003, **5**, 73–78.
- 454 P. Ji, K. Manna, Z. Lin, A. Urban, F. X. Greene, G. Lan and W. Lin, *J. Am. Chem. Soc.*, 2016, **138**, 12234–12242.
- 455 B. Chen, M. Eddaoudi, T. M. Reineke, J. W. Kampf, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2000, **122**, 11559–11560.

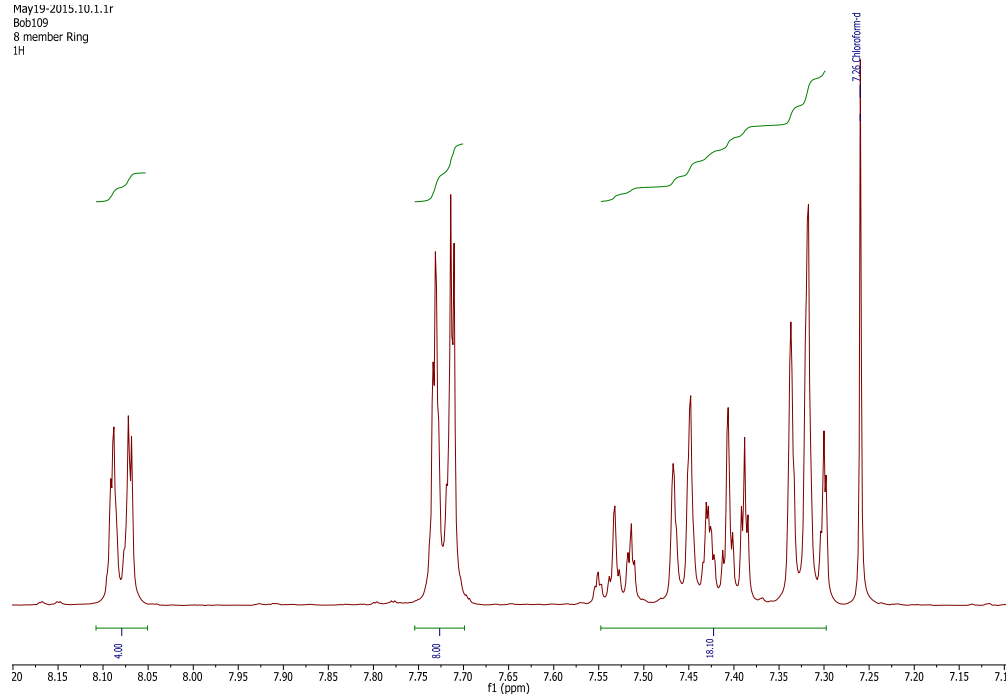
- 456 J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O’Keeffe and O. M. Yaghi, *J. Am. Chem. Soc.*, 2001, **123**, 8239–8247.
- 457 D. Sun, Y. Ke, T. M. Mattox, B. A. Ooro and H.-C. Zhou, *Chem. Commun.*, 2005, **36**, 5447–5449.
- 458 D. Zhao, D. Yuan, A. Yakovenko and H.-C. Zhou, *Chem. Commun.*, 2010, **46**, 4196–4198.
- 459 S. Ma, D. Sun, J. M. Simmons, C. D. Collier, D. Yuan and H. C. Zhou, *J. Am. Chem. Soc.*, 2008, **130**, 1012–1016.
- 460 S. Ma, J. M. Simmons, D. Sun, D. Yuan and H. C. Zhou, *Inorg. Chem.*, 2009, **48**, 5263–5268.
- 461 Y. Peng, V. Krungleviciute, I. Eryazici, J. T. Hupp, O. K. Farha and T. Yildirim, *J. Am. Chem. Soc.*, 2013, **135**, 11887–11894.
- 462 X. Sen Wang, S. Ma, P. M. Forster, D. Yuan, J. Eckert, J. J. López, B. J. Murphy, J. B. Parise and H. C. Zhou, *Angew. Chem. Int. Ed.*, 2008, **47**, 7263–7266.
- 463 D. Frahm, M. Fischer, F. Hoffmann and M. Fröba, *Inorg. Chem.*, 2011, **50**, 11055–11063.
- 464 Y. Zou, M. Park, S. Hong and M. S. Lah, *Chem. Commun.*, 2008, 2340–2342.
- 465 D. Zhao, D. Yuan, D. Sun and H. Zhou, *J. Am. Chem. Soc.*, 2009, **131**, 9186–9188.
- 466 D. Yuan, D. Zhao, D. Sun and H. C. Zhou, *Angew. Chem. Int. Ed.*, 2010, **49**, 5357–5361.
- 467 D. Yuan, D. Zhao and H. C. Zhou, *Inorg. Chem.*, 2011, **50**, 10528–10530.
- 468 Y. He, Z. Zhang, S. Xiang, F. R. Fronczek, R. Krishna and B. Chen, *Chem. Eur. J.*, 2012, **18**, 613–619.
- 469 Y. He, Z. Zhang, S. Xiang, H. Wu, F. R. Fronczek, W. Zhou, R. Krishna, M. O’Keeffe and B. Chen, *Chem. Eur. J.*, 2012, **18**, 1901–1904.
- 470 Y. S. Xue, F. Y. Jin, L. Zhou, M. P. Liu, Y. Xu, H. Bin Du, M. Fang and X. Z. You, *Cryst. Growth Des.*, 2012, **12**, 6158–6164.
- 471 C. Tan, S. Yang, N. R. Champness, X. Lin, A. J. Blake, W. Lewis and M. Schröder, *Chem. Commun.*, 2011, **47**, 4487–4489.
- 472 R. D. Hancock and A. E. Martell, *Chem. Rev.*, 1989, **89**, 1875–1914.
- 473 K. S. Park, Z. Ni, A. P. Côté, J. Y. Choi, R. Huang, F. J. Uribe-Romo, H. K. Chae, M. O’Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 10186–91.
- 474 A. Phan, C. J. Doonan, F. J. Uribe-Romo, C. B. Knobler, M. O’Keeffe and O. M. Yaghi, *Acc. Chem. Res.*, 2010, **43**, 58–67.

- 475 B. Wang, A. P. Côté, H. Furukawa, M. O’Keeffe and O. M. Yaghi, *Nature*, 2008, **453**, 207–211.
- 476 J. P. Zhang, S. Horike and S. Kitagawa, *Angew. Chem. Int. Ed.*, 2007, **46**, 889–892.
- 477 V. Colombo, S. Galli, H. J. Choi, G. D. Han, A. Maspero, G. Palmisano, N. Masciocchi and J. R. Long, *Chem. Sci.*, 2011, **2**, 1311.
- 478 M. Dincă, A. Dailly, Y. Liu, C. M. Brown, D. A. Neumann and J. R. Long, *J. Am. Chem. Soc.*, 2006, **128**, 16876–16883.
- 479 M. Dincă, W. S. Han, Y. Liu, A. Dailly, C. M. Brown and J. R. Long, *Angew. Chem. Int. Ed.*, 2007, **46**, 1419–1422.
- 480 K. Sumida, S. Horike, S. S. Kaye, Z. R. Herm, W. L. Queen, C. M. Brown, F. Grandjean, G. J. Long, A. Dailly and J. R. Long, *Chem. Sci.*, 2010, **1**, 184–191.
- 481 M. Dincă, A. Dailly and J. R. Long, *Chem. Eur. J.*, 2008, **14**, 10280–10285.
- 482 V. Gupta, S. Khullar, S. Kumar and S. K. Mandal, *Dalton Trans.*, 2015, **44**, 16778–16784.
- 483 A. K. Franz and S. O. Wilson, *J. Med. Chem.*, 2013, **56**, 388–405.
- 484 M. Wander, P. J. C. Hausoul, L. A. J. M. Sliedregt, B. J. Van Steen, G. Van Koten and R. J. M. K. Gebbink, *Organometallics*, 2009, **28**, 4406–4415.
- 485 J. H. Baker, N. Bhuvanesh and J. Blümel, *J. Organomet. Chem.*, 2017, **847**, 193–203.
- 486 B. Beele, J. Guenther, M. Perera, M. Stach, T. Oeser and J. Blümel, *New J. Chem.*, 2010, **34**, 2729–2731.
- 487 Y. Yang, B. Beele and J. Blumel, *J. Am. Chem. Soc.*, 2008, **130**, 3771–3773.
- 488 S. Kotha and V. R. Shah, *Amino Acids*, 2008, **35**, 83–88.
- 489 K. Gontarczyk, K. Durka, P. Klimkowski, S. Luliński, J. Serwatowski and K. Woźniak, *J. Organomet. Chem.*, 2015, **783**, 1–9.
- 490 A. J. Amoroso, J. P. Maher, J. A. McCleverty and M. D. Ward, *J. Chem. Soc. Chem. Commun.*, 1994, **3**, 1273–1275.
- 491 L. C. Delmas, P. N. Horton, A. J. P. White, S. J. Coles, P. D. Lickiss and R. P. Davies, *Chem. Commun.*, 2017, **53**, 12524–12527.
- 492 M. S. Deshmukh, A. Chaudhary, P. N. Zolotarev and R. Boomishankar, *Inorg. Chem.*, 2017, **56**, 11762–11767.
- 493 D. Wang, Y. Niu, Y. Wang, J. Han and S. Feng, *J. Organomet. Chem.*, 2010, **695**, 2329–2337.

- 494 K. Gontarczyk, K. Durka, P. Klimkowski, S. Lulinski, J. Serwatowski and K. Wozniak, *J. Organomet. Chem.*, 2015, **783**, 1–9.
- 495 R. P. Davies, R. J. Less, P. D. Lickiss, K. Robertson and A. J. P. White, *Inorg. Chem.*, 2008, **47**, 9958–9964.
- 496 F. R. Heck, *Org. React.*, 1982, **27**, 345–390.
- 497 V. Guillerm, D. Kim, J. F. Eubank, R. Luebke, X. Liu, K. Adil, M. S. Lah and M. Eddaoudi, *Chem. Soc. Rev.*, 2014, **43**, 6141–6172.
- 498 V. Guillerm, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D’Elia, Ł. Wojtas, K. Adil and M. Eddaoudi, *Nat. Chem.*, 2014, **6**, 673–680.
- 499 K. Matsumoto, M. Kannami, D. Inokuchi, H. Kurata, T. Kawase and M. Oda, *Org. Lett.*, 2007, **9**, 2903–2906.

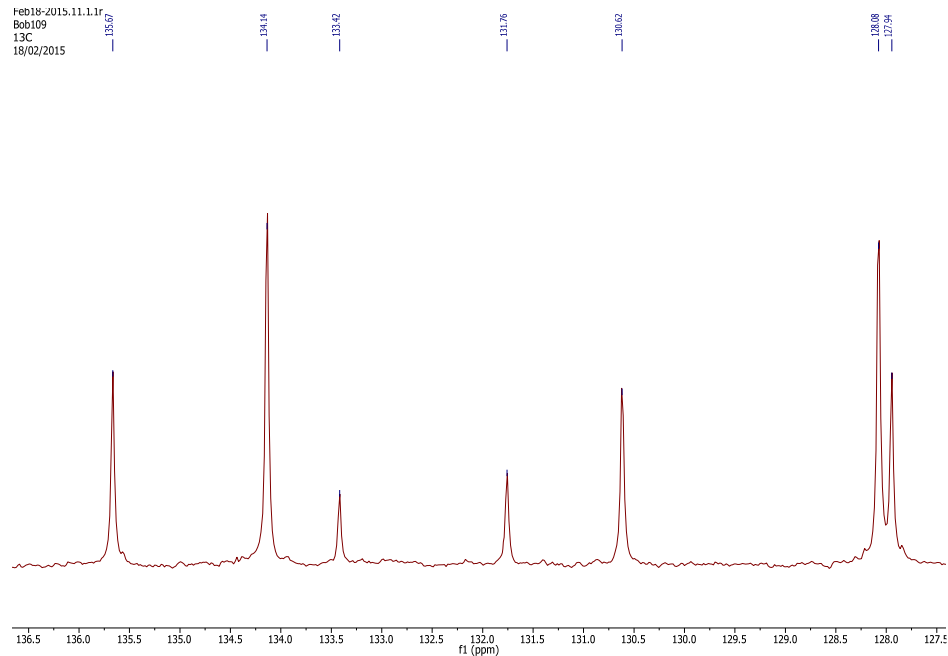
Supplementary Information (S₁-S₈₅) for Silicon-Containing COFs and MOFs for CO₂ Capture.

May19-2015.10.1.1r
Bob109
8 member Ring
1H

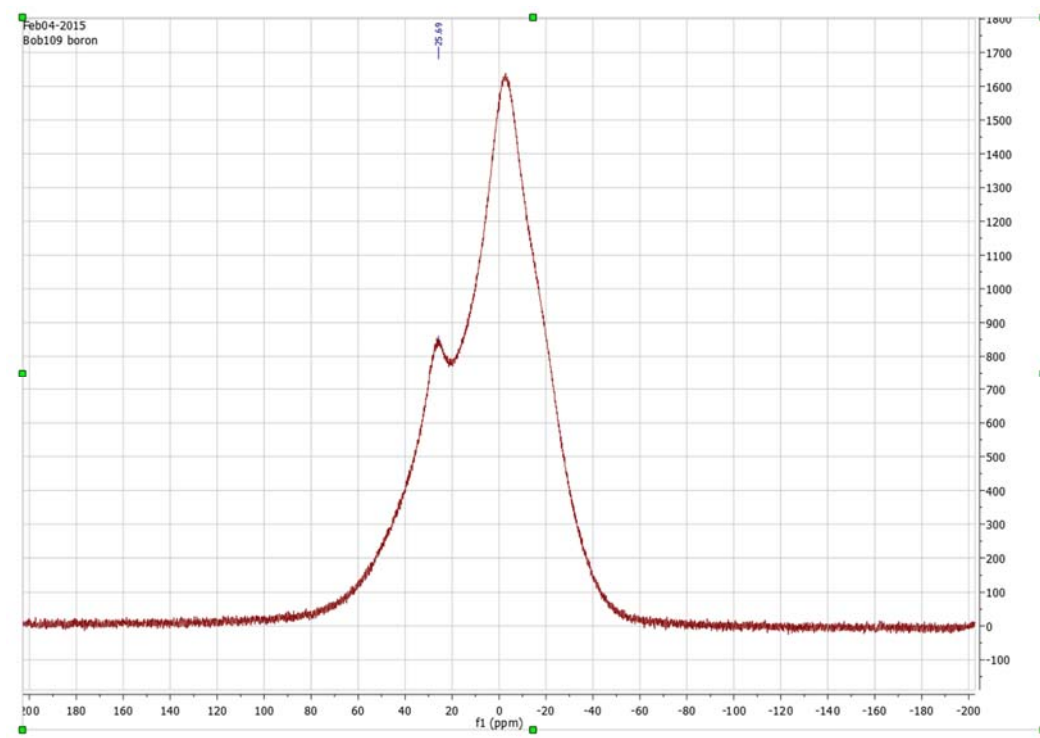


¹H spectrum of compound (3) (S₁)

Feb18-2015.11.1.1r
Bob109
13C
18/02/2015

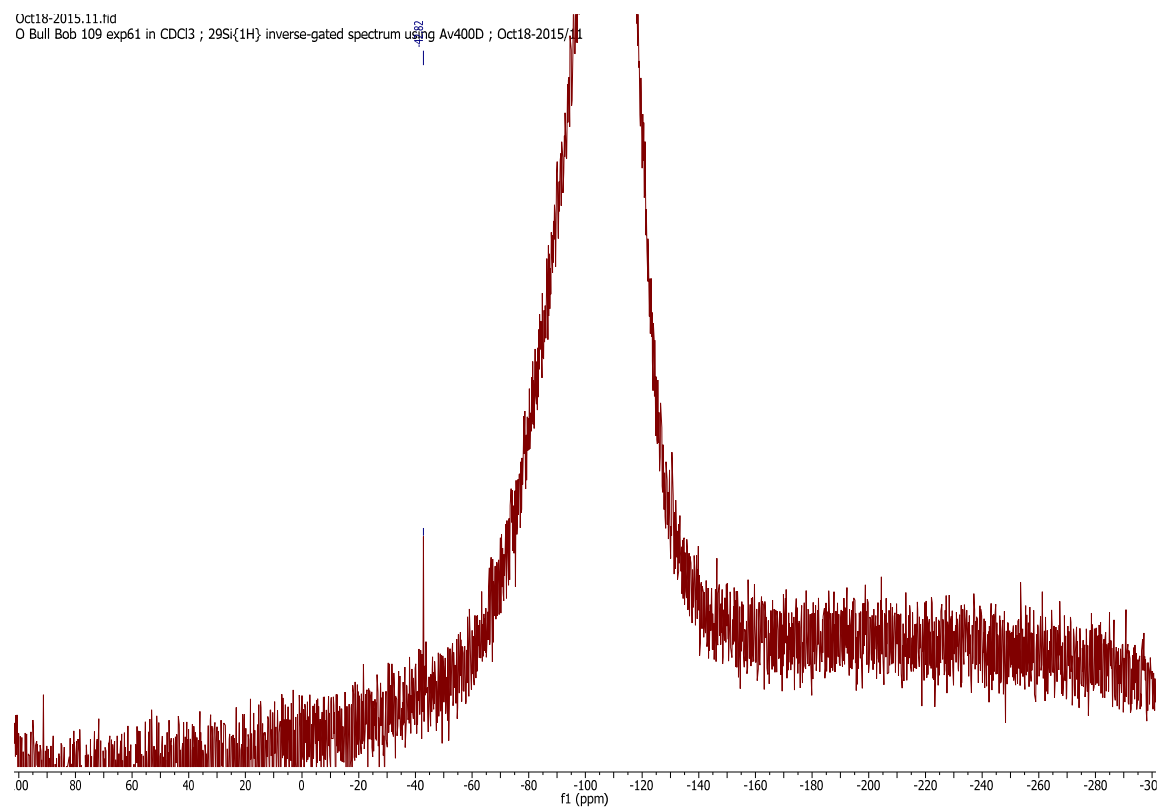


¹³C{¹H} spectrum of compound (3) (S₂)



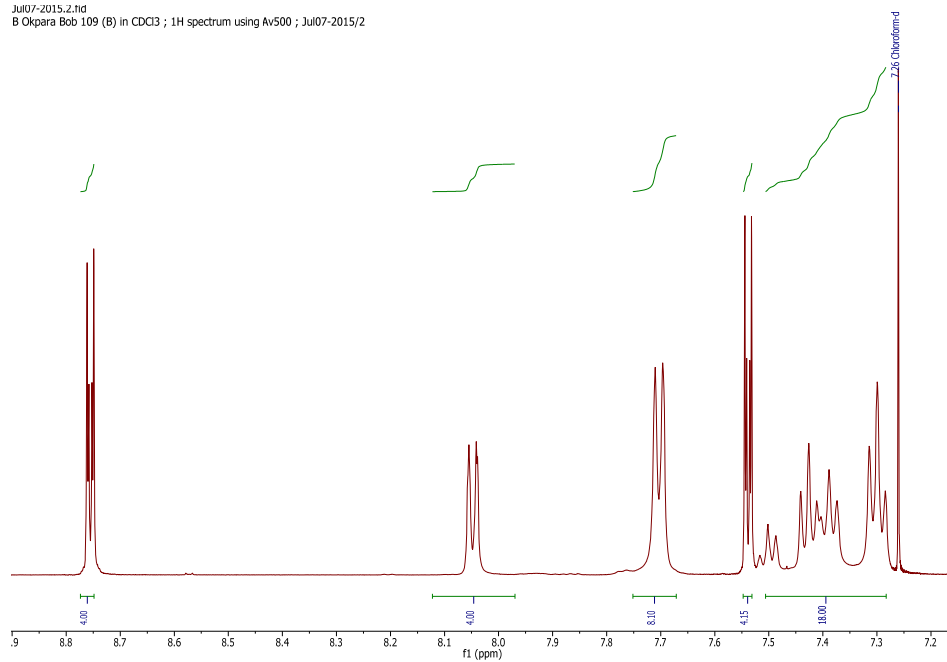
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (3) (S_3)

Oct18-2015.11.h1d
O Bull Bob 109 exp61 in CDCl₃ ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av400D ; Oct18-2015/11



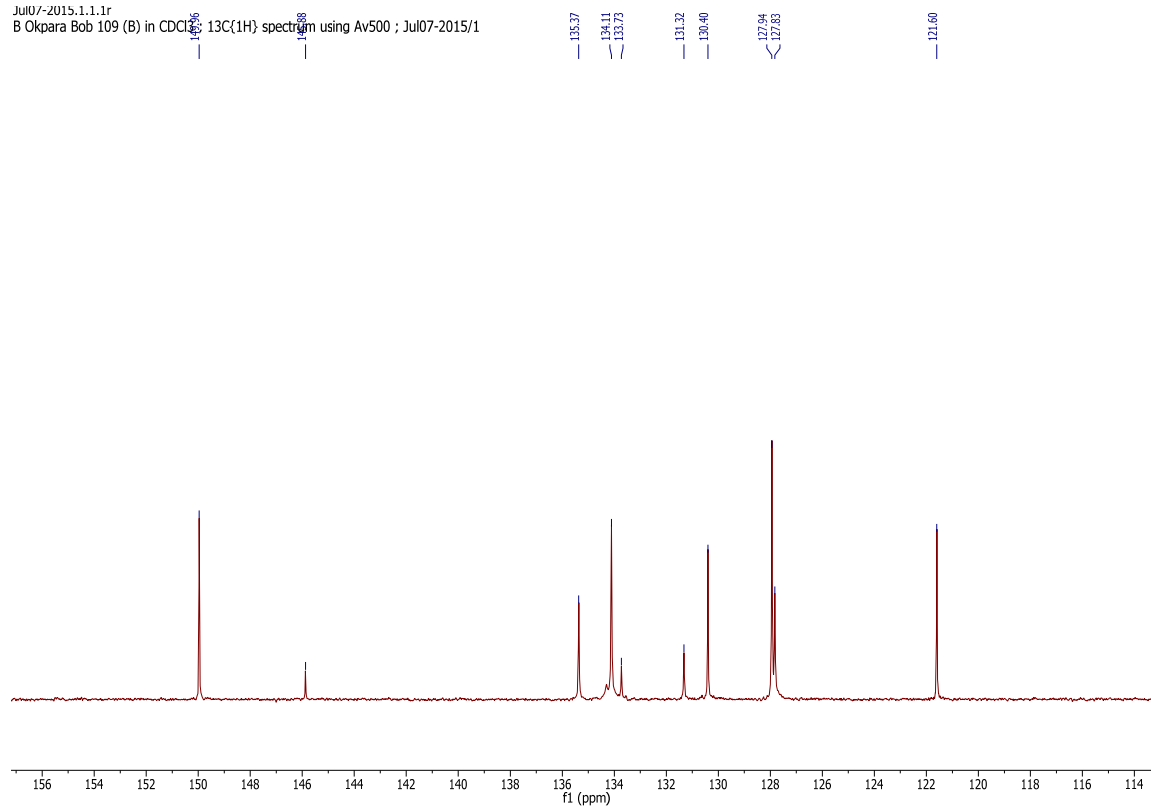
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (3) (S_4)

Jul07-2015.2.hid
B Okpara Bob 109 (B) in CDCl₃ ; ¹H spectrum using Av500 ; Jul07-2015/2



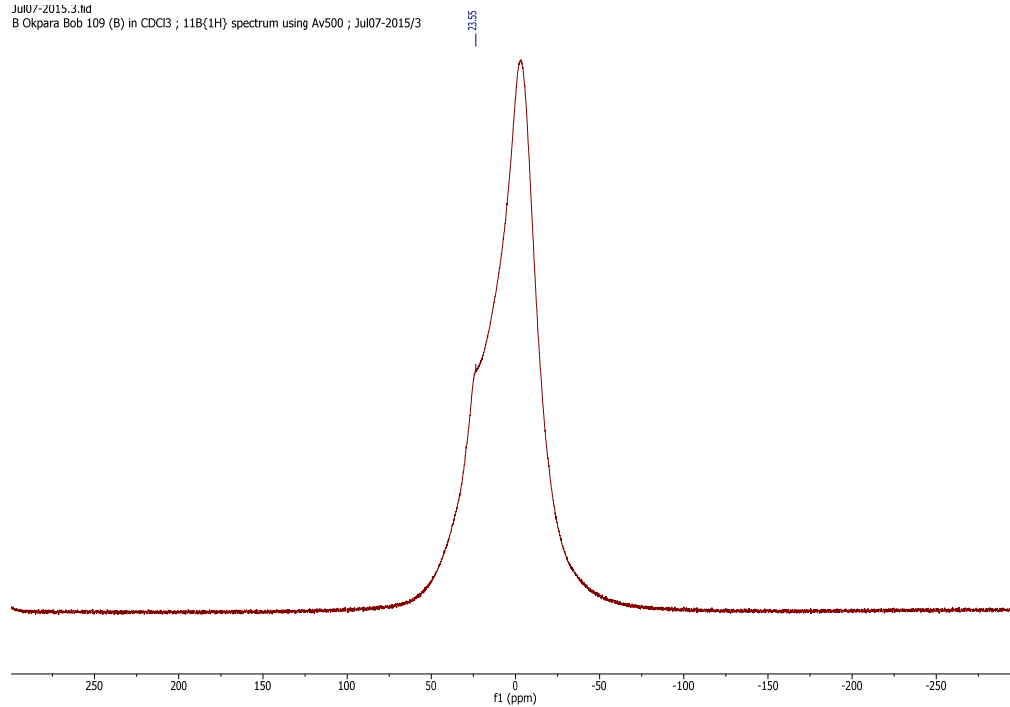
¹H spectrum of compound (4) (S₅)

Jul07-2015.1.1.1r
B Okpara Bob 109 (B) in CDCl₃ ; ¹³C{¹H} spectrum using Av500 ; Jul07-2015/1



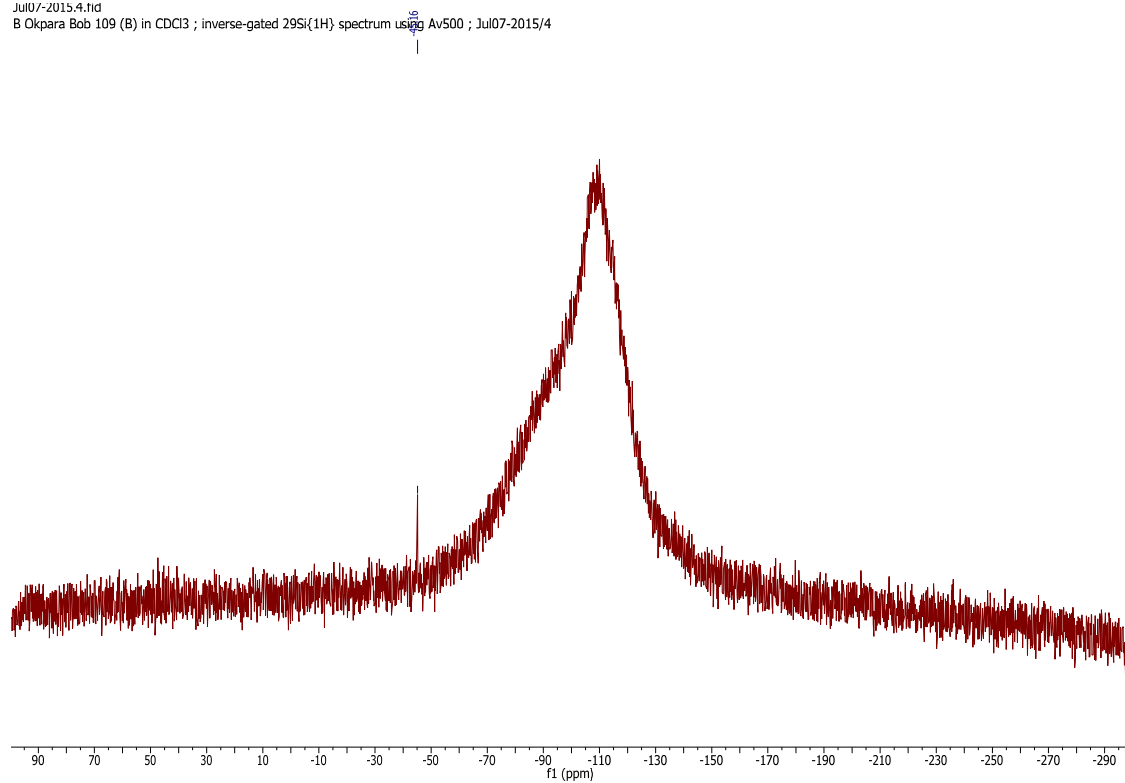
¹³C{¹H} spectrum of compound (4) (S₆)

Jul07-2015.3.fid
B Okpara Bob 109 (B) in CDCl₃ ; ¹¹B{¹H} spectrum using Av500 ; Jul07-2015/3



¹¹B{¹H} spectrum for compound (4) (S₇)

Jul07-2015.4.fid
B Okpara Bob 109 (B) in CDCl₃ ; inverse-gated ²⁹Si{¹H} spectrum using Av500 ; Jul07-2015/4



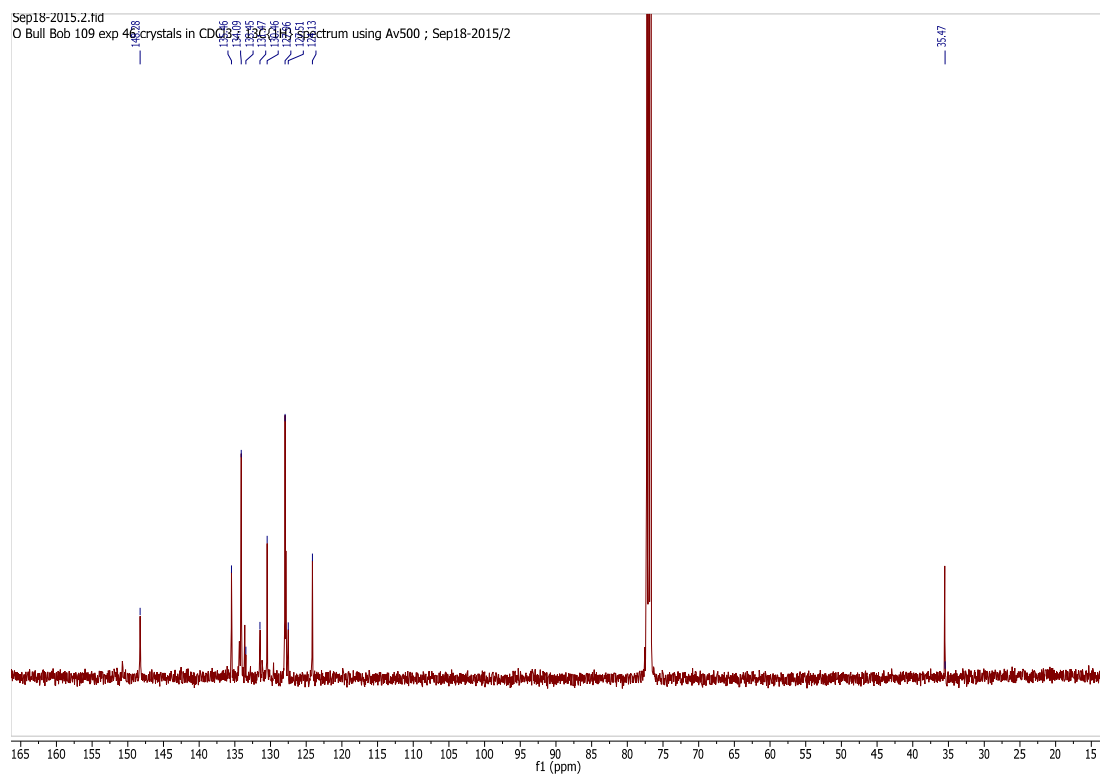
²⁹Si{¹H} spectrum for compound (4) (S₈)

Sep18-2015.1.nd
O Bull Bob 109 exp 46 crystals in CDCl3 ; 1H spectrum using Av500 ; Sep18-2015/1

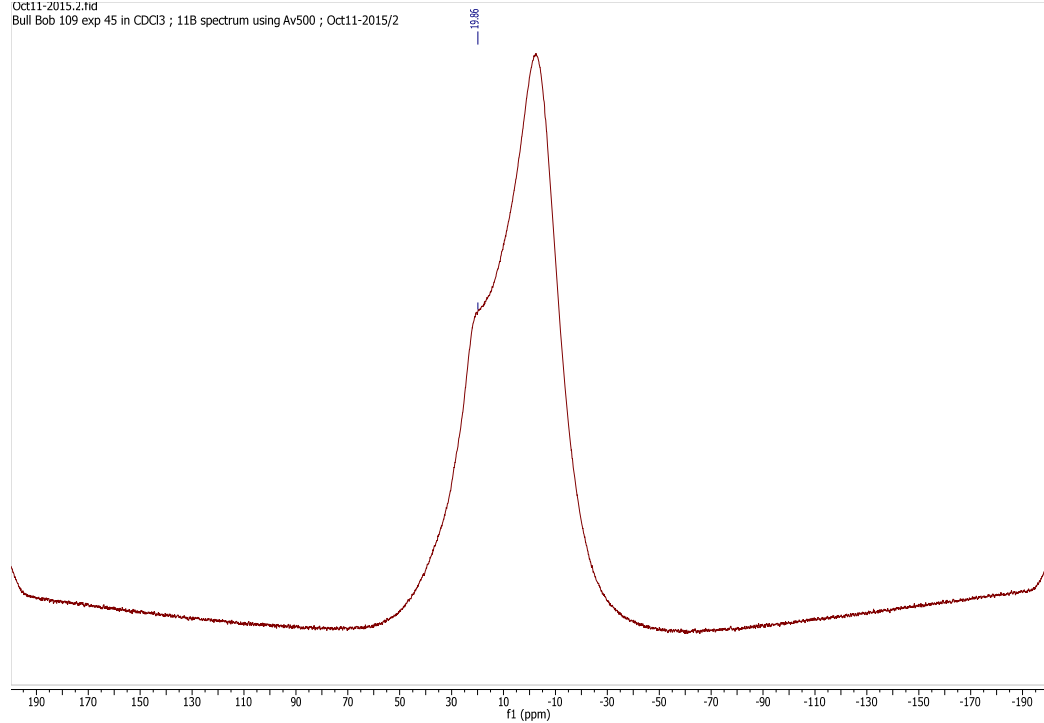
7.26 CDCl₃

4.00
4.10
8.10
11.36
5.20
3.92
4.00

f1 (ppm)

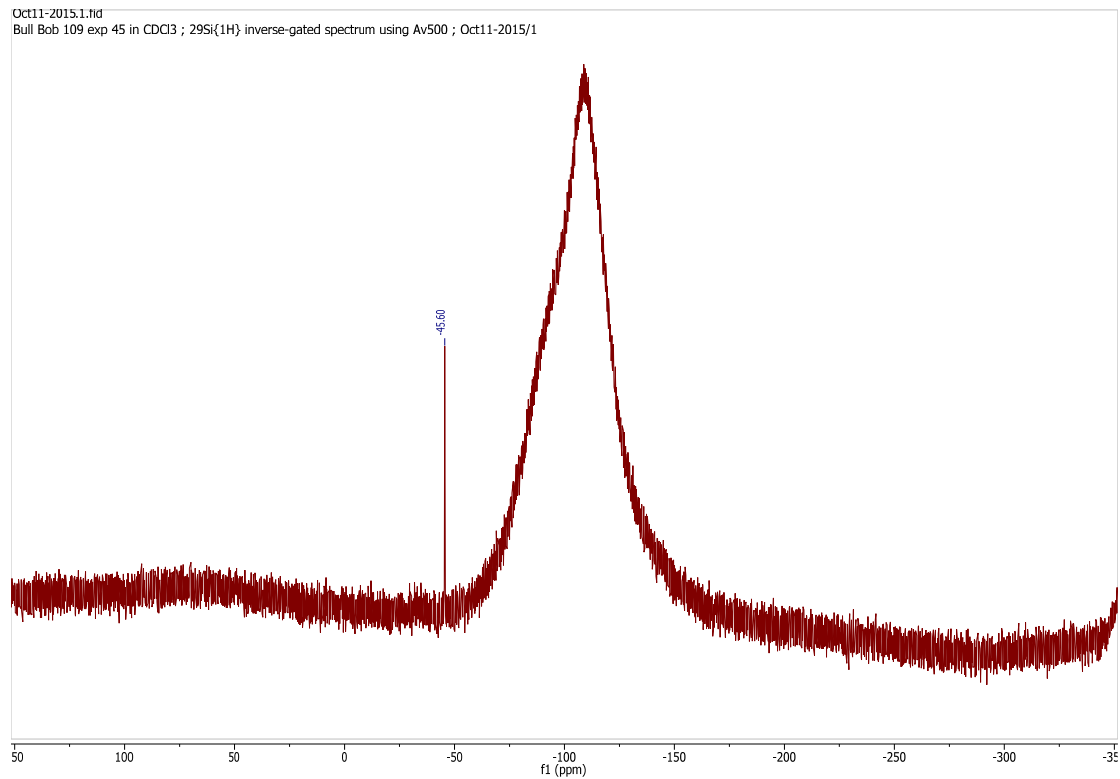
¹H spectrum of compound (5) (S₉) $^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (5) (S_{10})

Oct11-2015.2.fid
Bull Bob 109 exp 45 in CDCl3 ; 11B spectrum using Av500 ; Oct11-2015/2

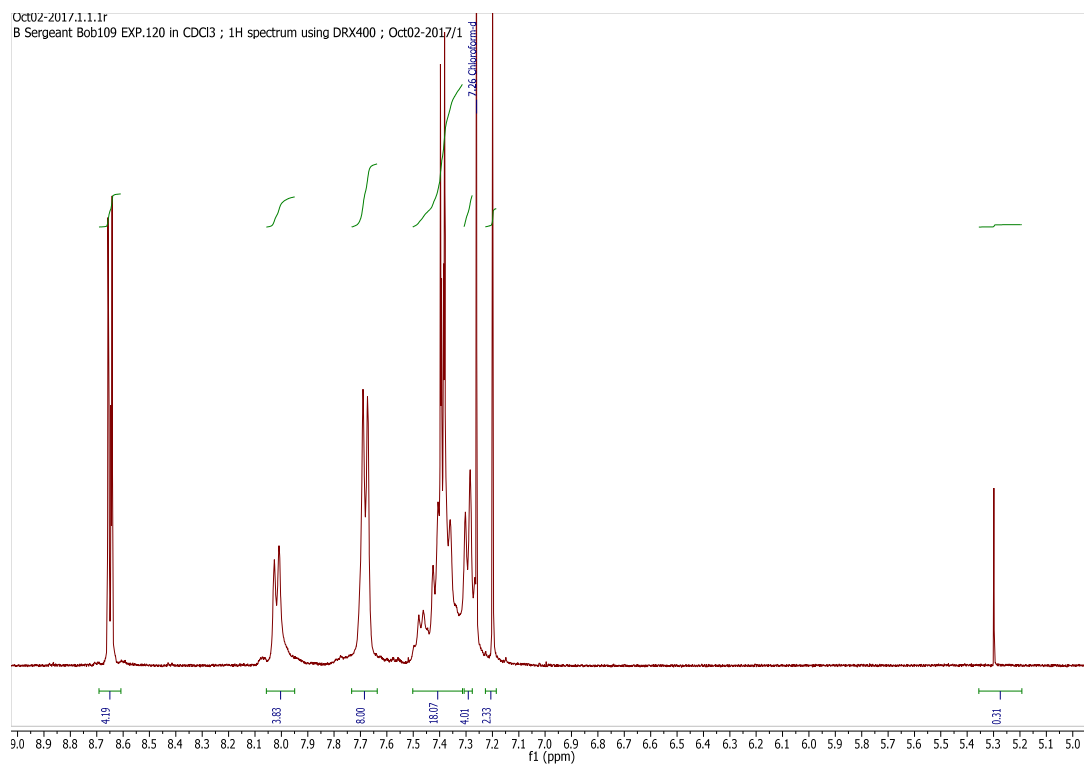


$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (5) (S_{11})

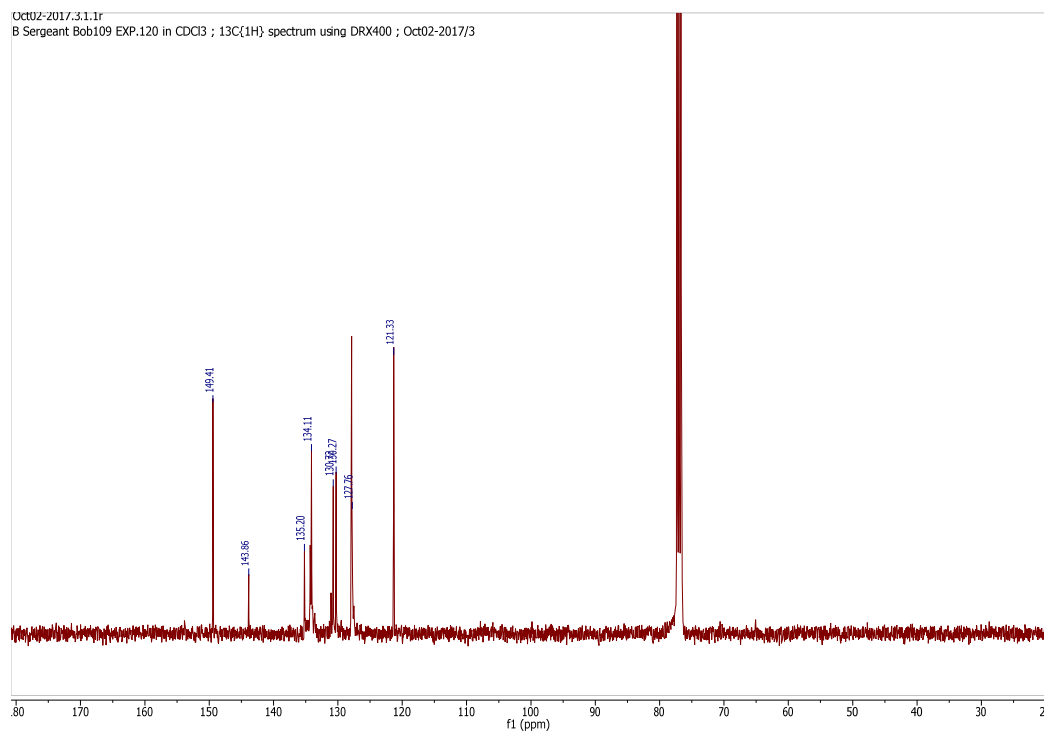
Oct11-2015.1.fid
Bull Bob 109 exp 45 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av500 ; Oct11-2015/1



$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (5) (S_{12})

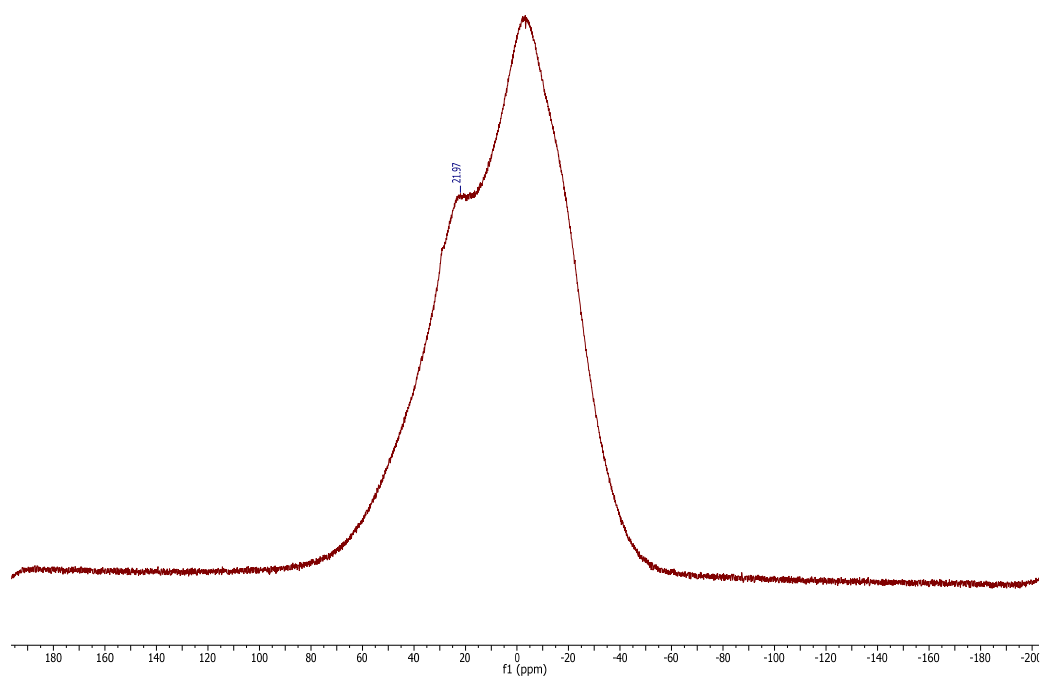


^1H spectrum of compound (6) (S_{13})



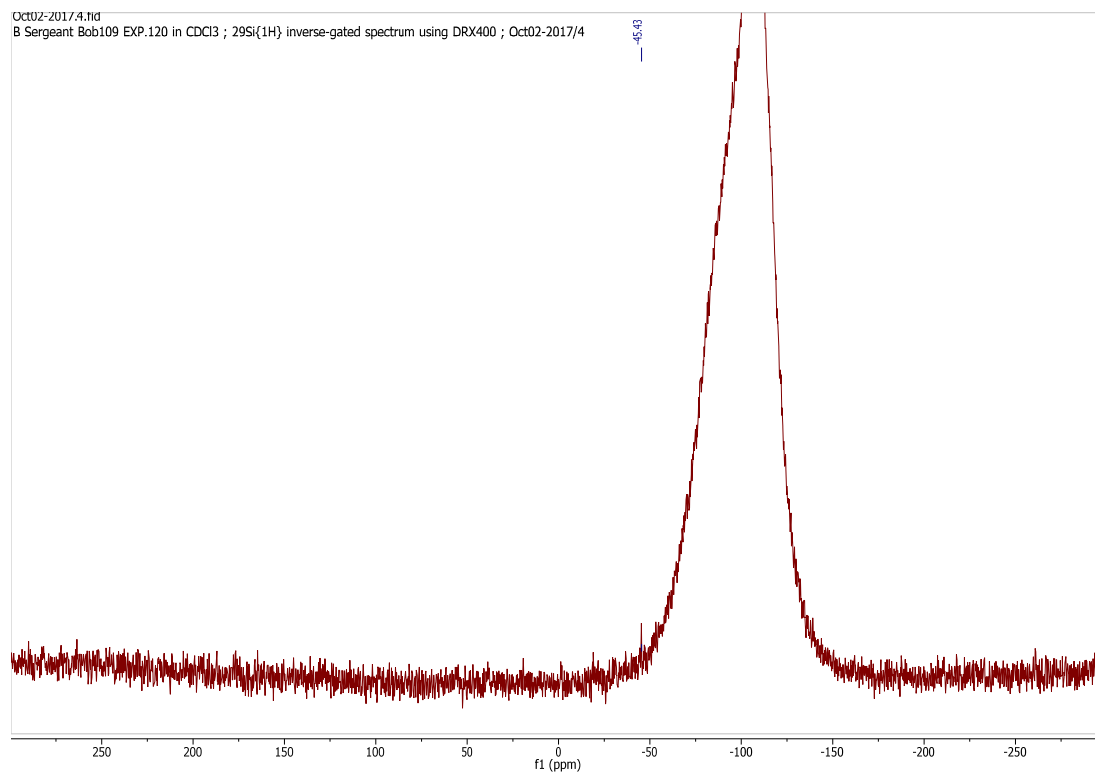
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (6) (S_{14})

Oct02-2017.2.fid
B Sergeant Bob109 EXP.120 in CDCl3 ; 11B spectrum using DRX400 ; Oct02-2017/2



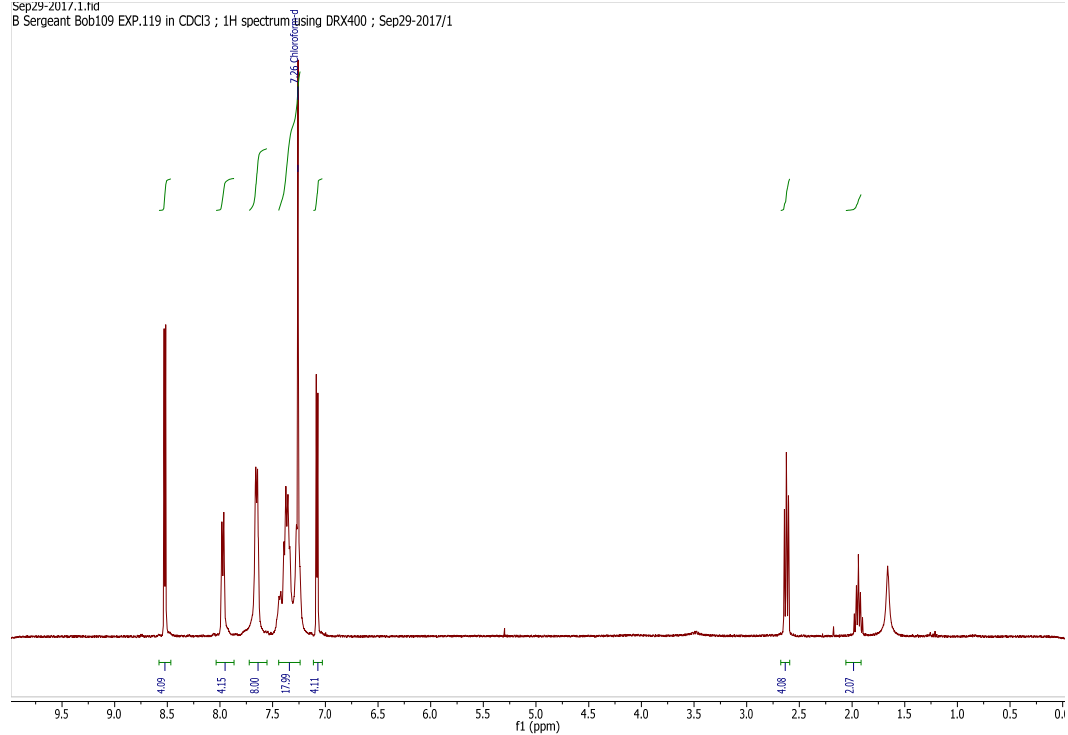
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (6) (S_{15})

Oct02-2017.4.fid
B Sergeant Bob109 EXP.120 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using DRX400 ; Oct02-2017/4



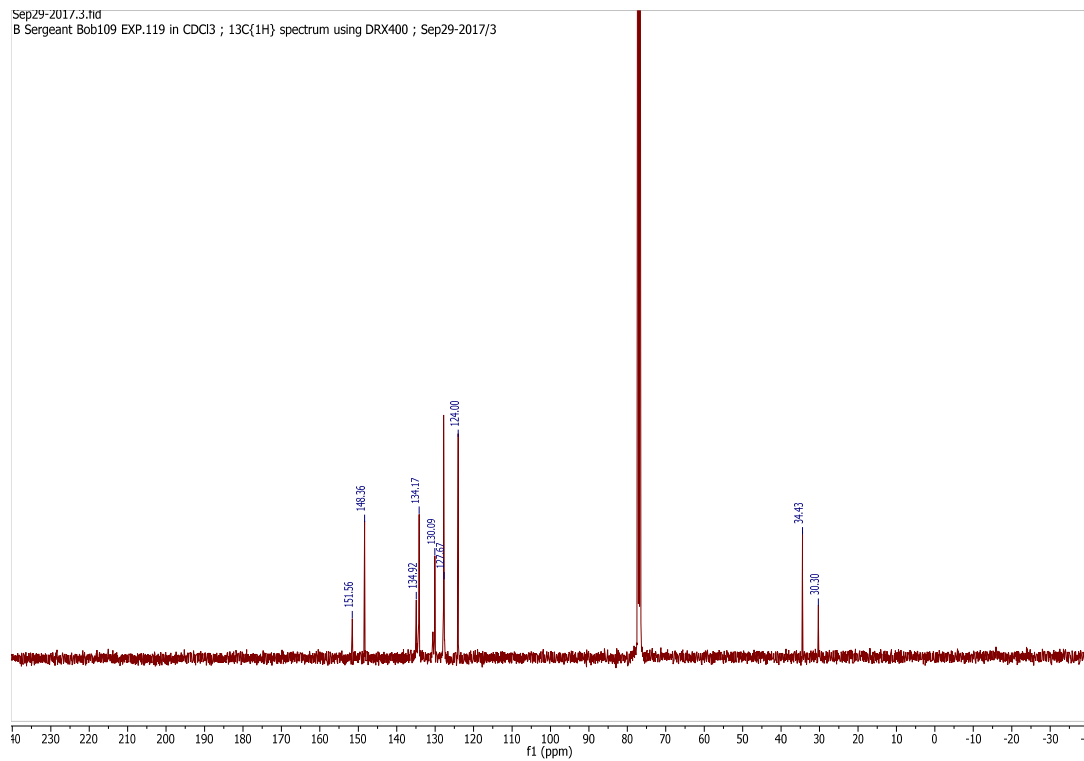
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (6) (S_{16})

Sep29-2017.1.hd
B Sergeant Bob109 EXP.119 in CDCl3 ; 1H spectrum using DRX400 ; Sep29-2017/1



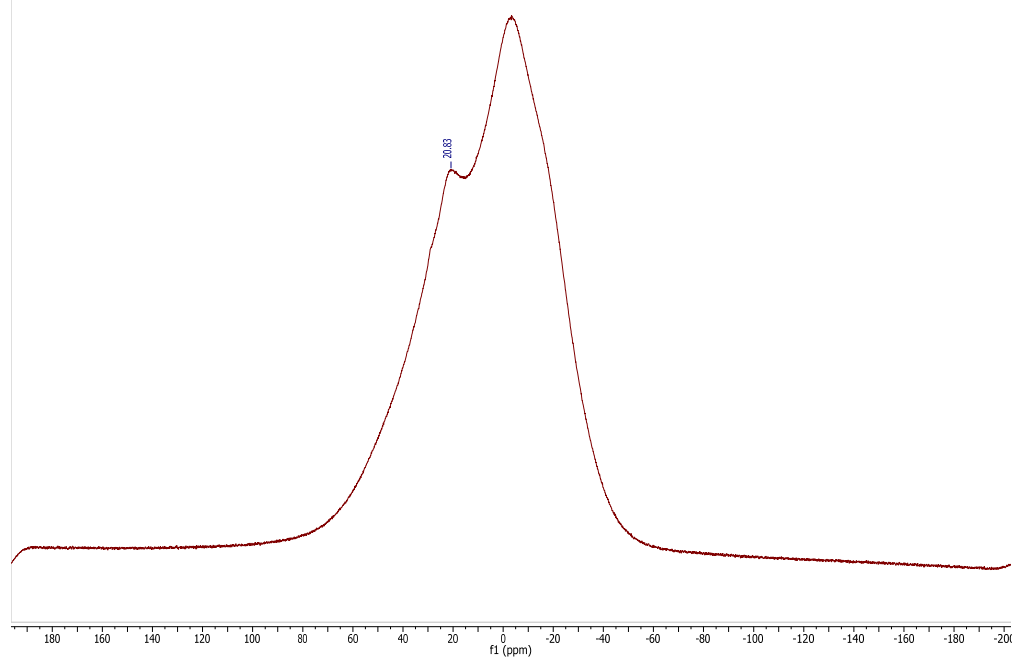
¹H spectrum of compound (7) (S₁₇)

Sep29-2017.3.hd
B Sergeant Bob109 EXP.119 in CDCl3 ; 13C{1H} spectrum using DRX400 ; Sep29-2017/3



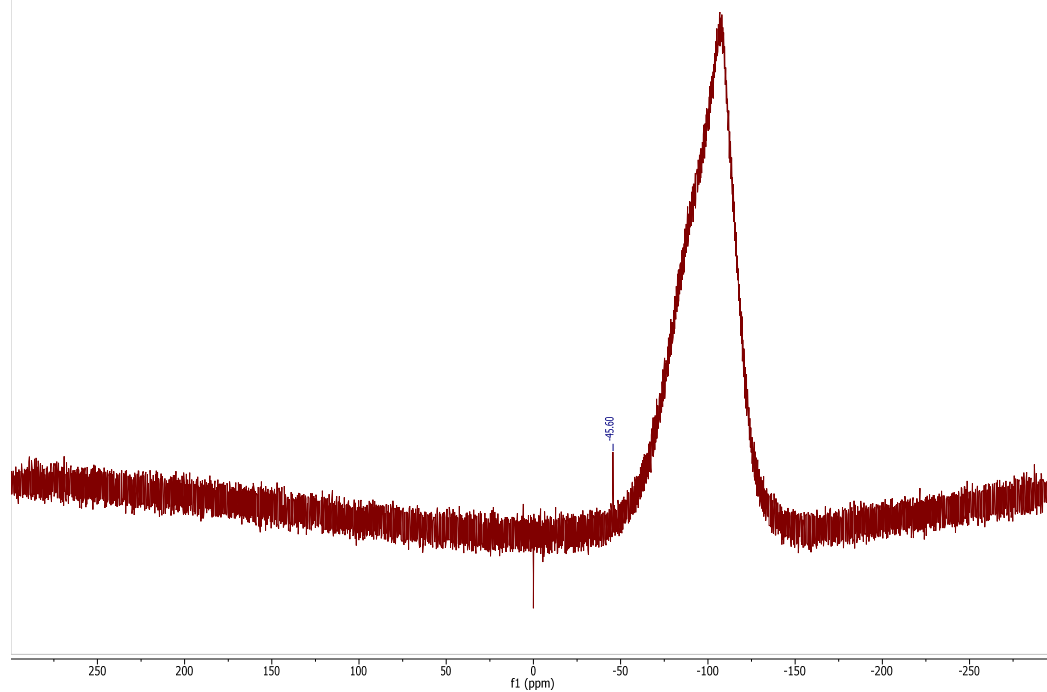
¹³C{¹H} spectrum of compound (7) (S₁₈)

Sep29-2017/2.hid
B Sergeant Bob109 EXP.119 in CDCl3 ; 11B spectrum using DRX400 ; Sep29-2017/2

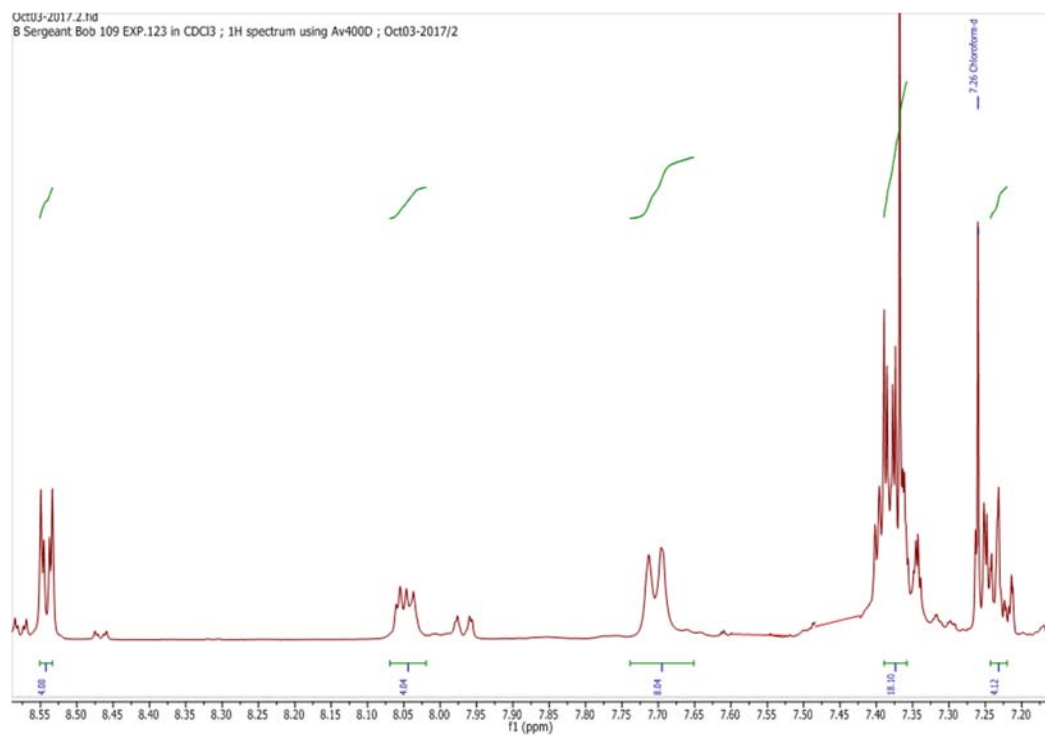


$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (7) (S₁₉)

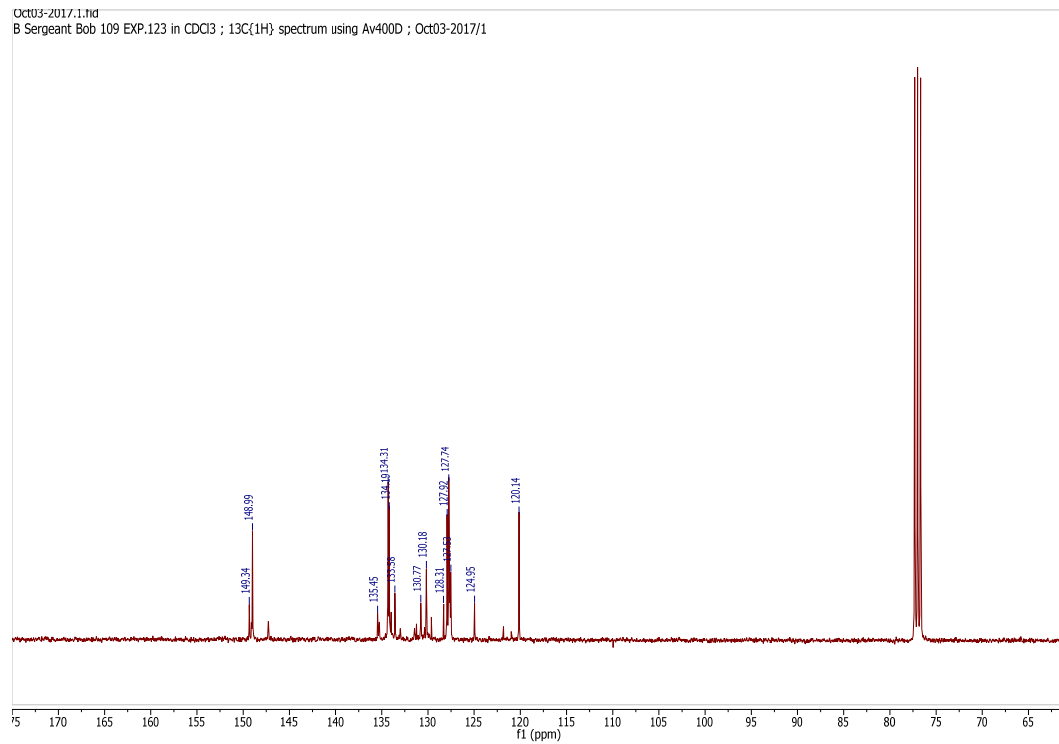
Sep29-2017/4.hid
B Sergeant Bob109 EXP.119 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using DRX400 ; Sep29-2017/4



$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (7) (S₂₀)

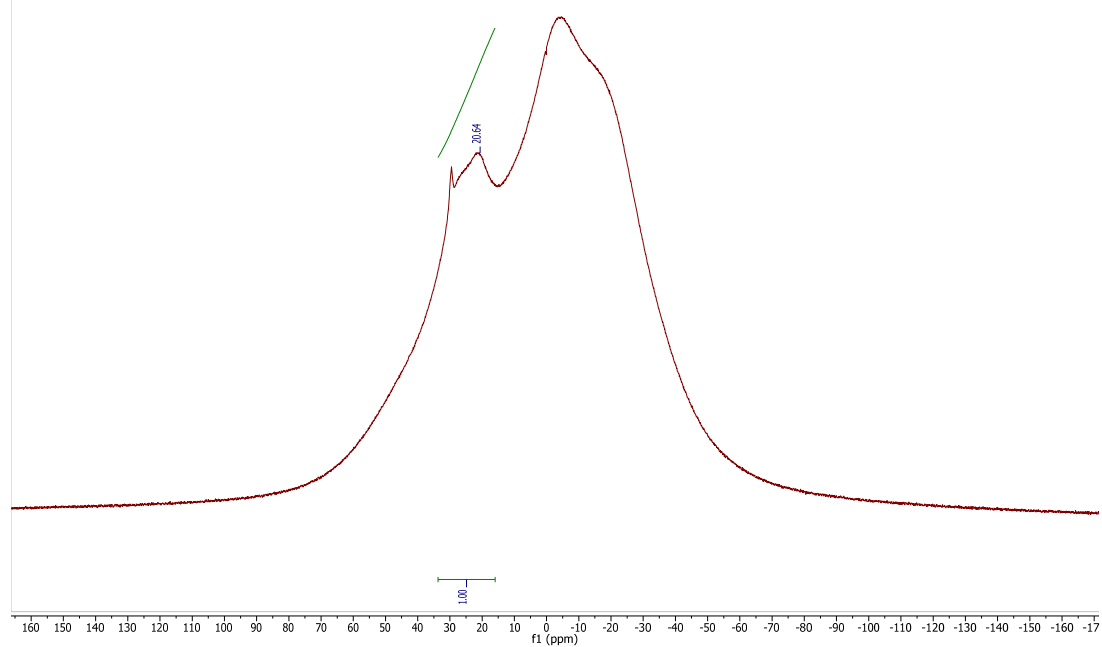


¹H spectrum of compound (8) (S₂₁)



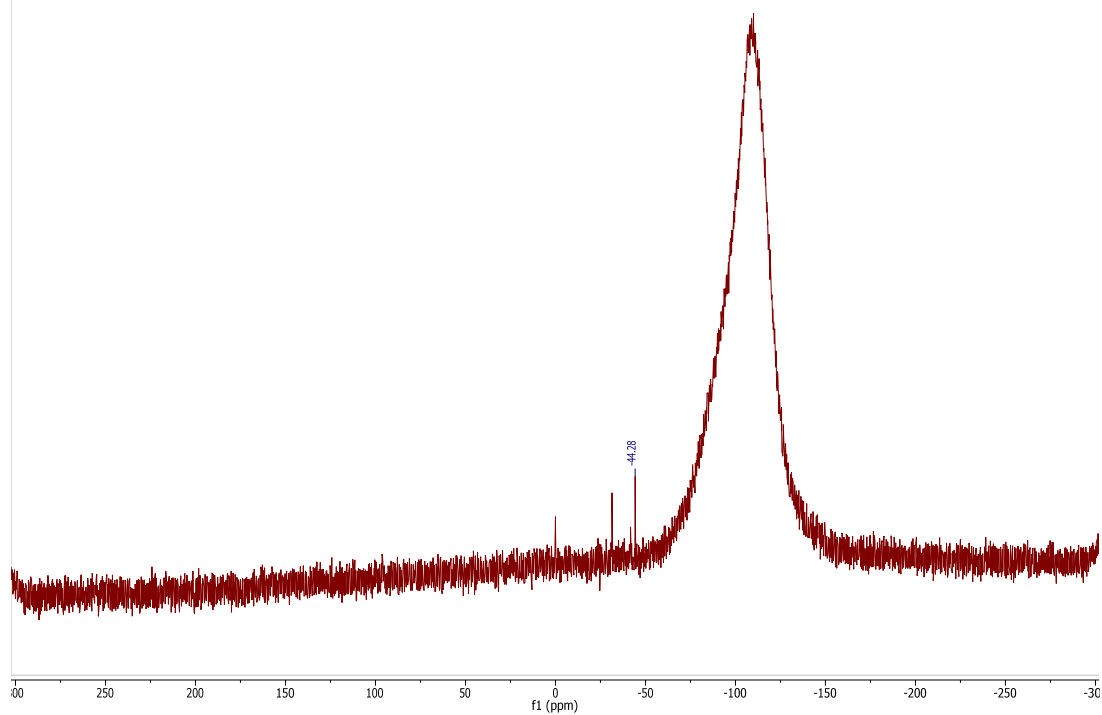
¹³C{¹H} spectrum of compound (8) (S₂₂)

Oct03-2017.3.fid
B Sergeant Bob 109 EXP.123 in CDCl3 ; 11B spectrum using Av400D ; Oct03-2017/3



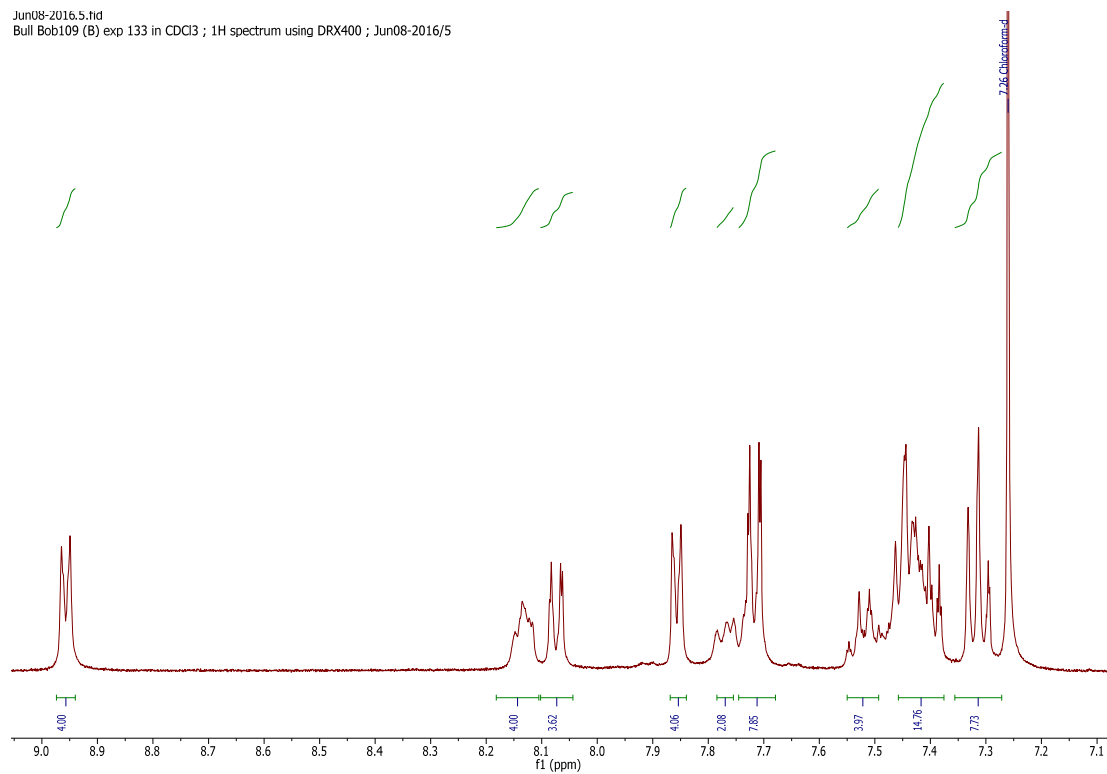
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound **(8)** (S_{23})

Oct03-2017.4.fid
B Sergeant Bob 109 EXP.123 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av400D ; Oct03-2017/4



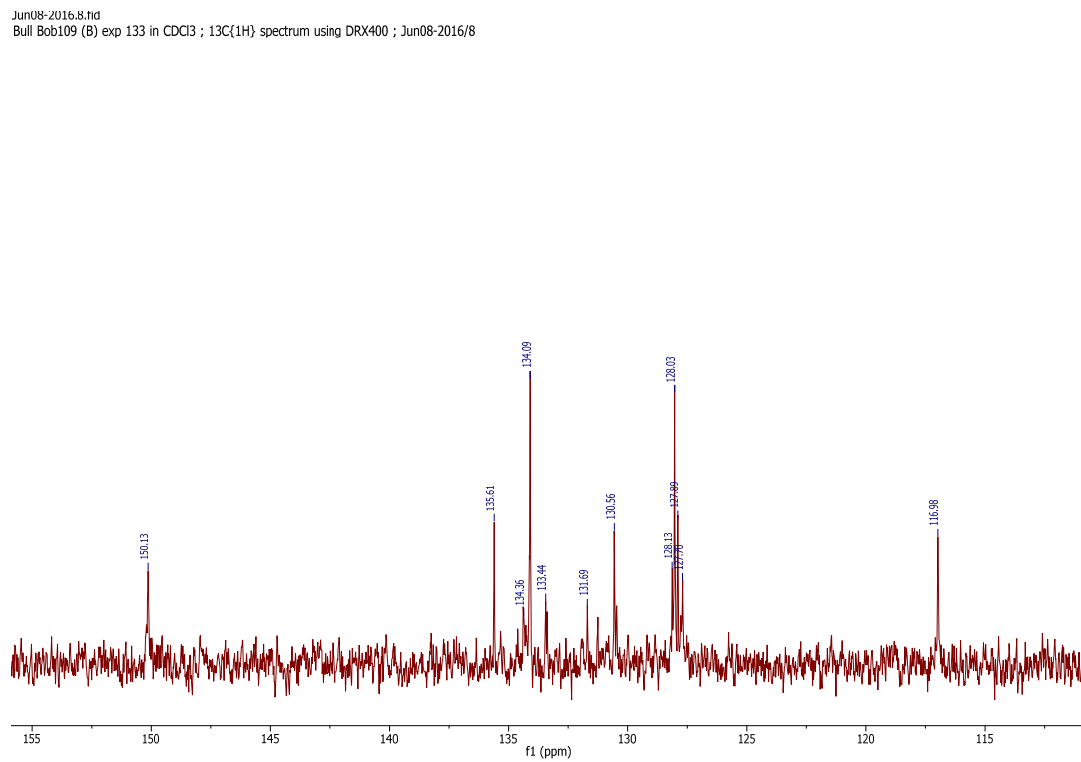
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound **(8)** (S_{24})

Jun08-2016.5.fid
Bull Bob109 (B) exp 133 in CDCl3 ; 1H spectrum using DRX400 ; Jun08-2016/5



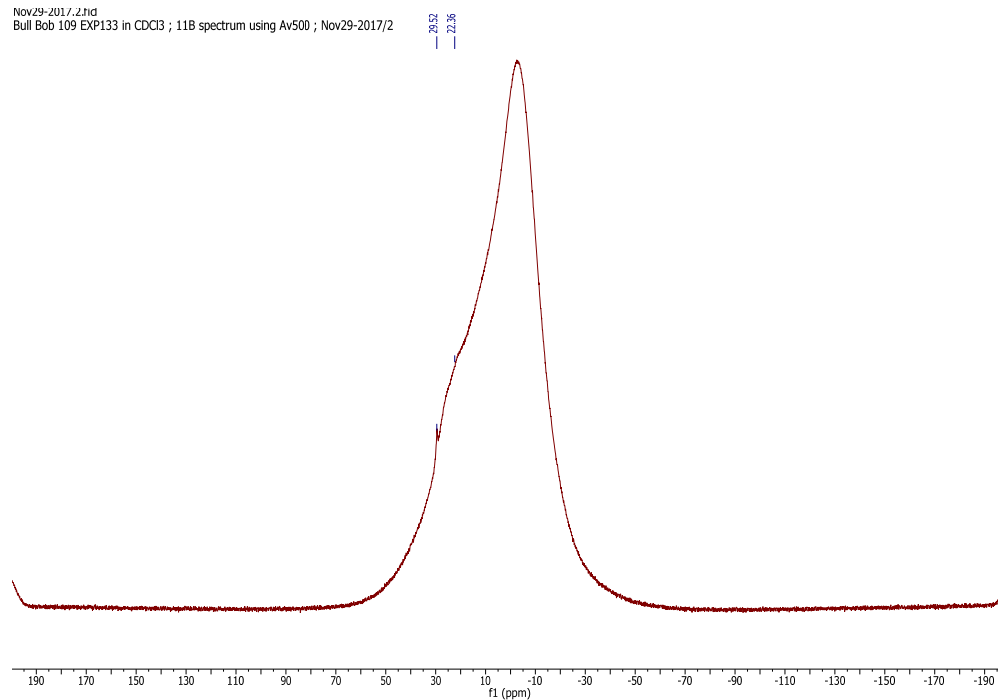
¹H spectrum of compound (9) (S₂₅)

Jun08-2016.8.fid
Bull Bob109 (B) exp 133 in CDCl3 ; 13C{1H} spectrum using DRX400 ; Jun08-2016/8



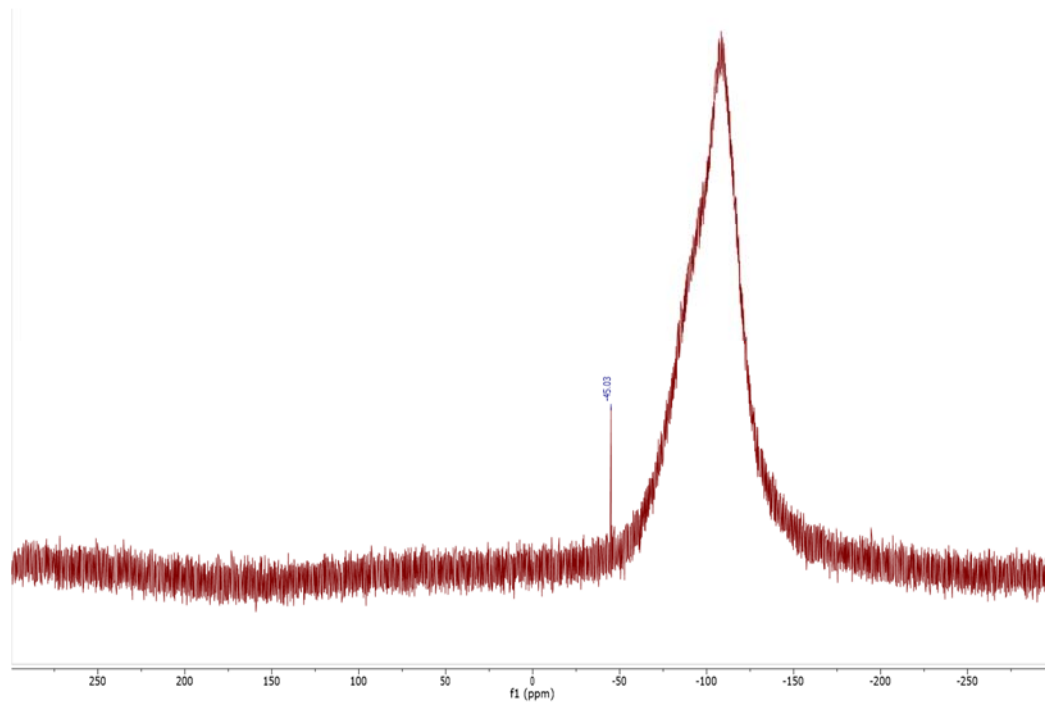
¹³C{¹H} spectrum of compound (9) (S₂₆)

Nov29-2017, 2.11d
Bull Bob 109 EXP133 in CDCl3 ; 11B spectrum using Av500 ; Nov29-2017/2



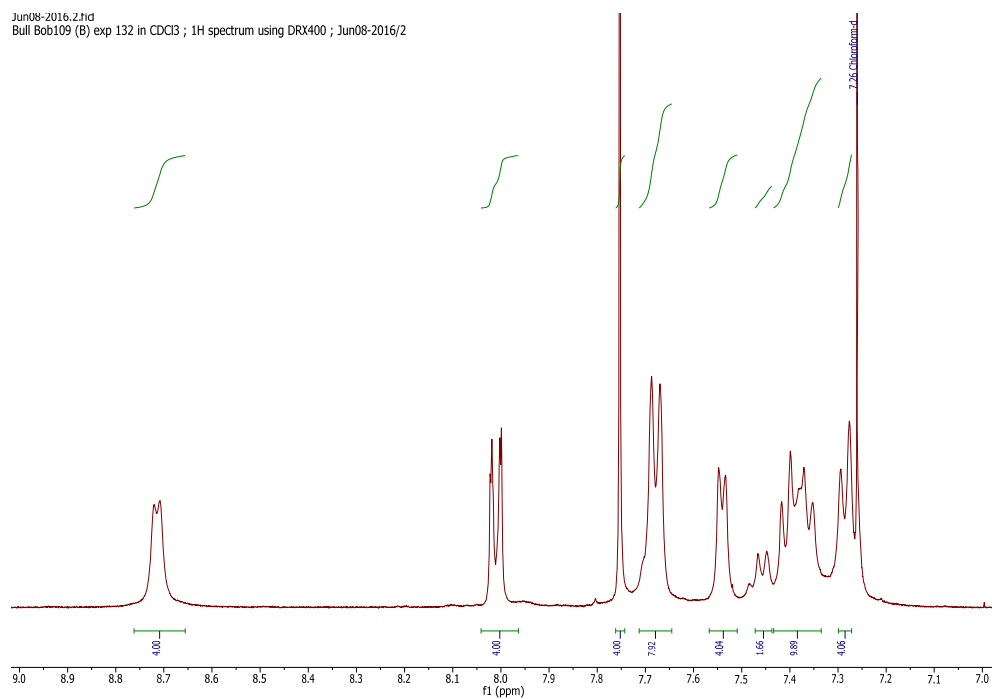
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (9) (S27)

^{29}Si spectrum for compound (7) (S, 20)



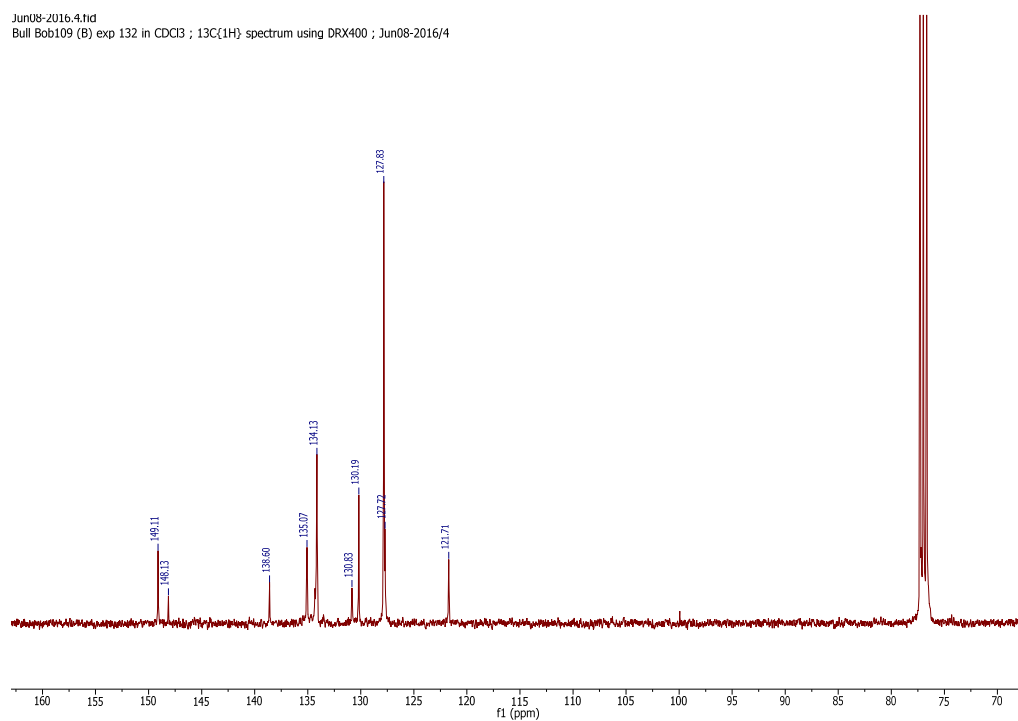
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (9) (S28)

Jun08-2016.2.fid
Bull Bob109 (B) exp 132 in CDCl3 ; ^1H spectrum using DRX400 ; Jun08-2016/2



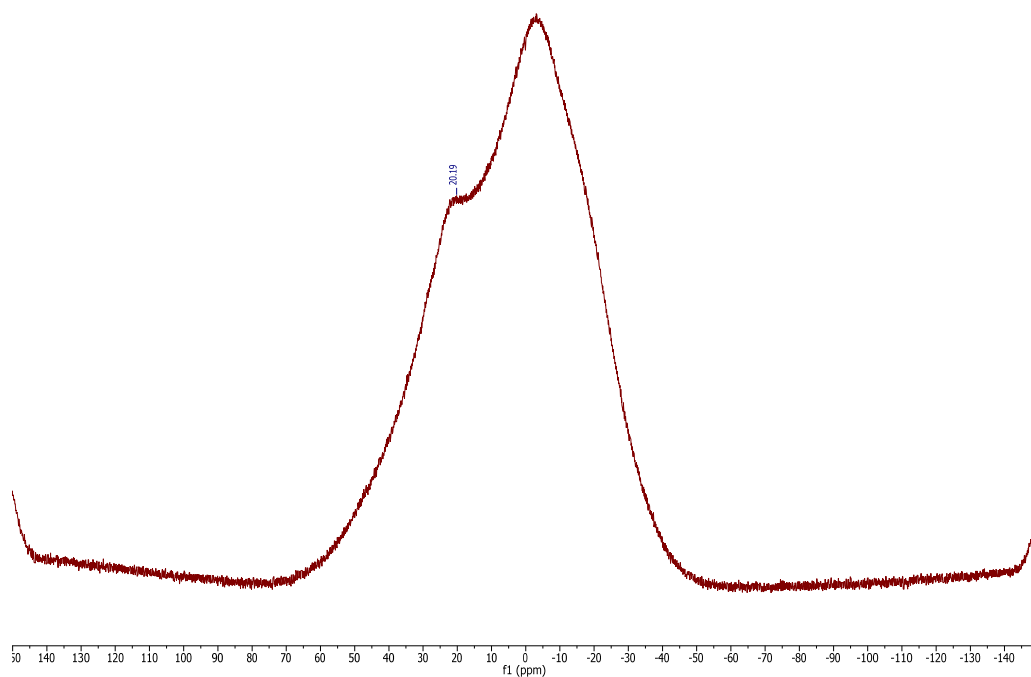
^1H spectrum of compound (12) (S_{29})

Jun08-2016.4.fid
Bull Bob109 (B) exp 132 in CDCl_3 ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using DRX400 ; Jun08-2016/4



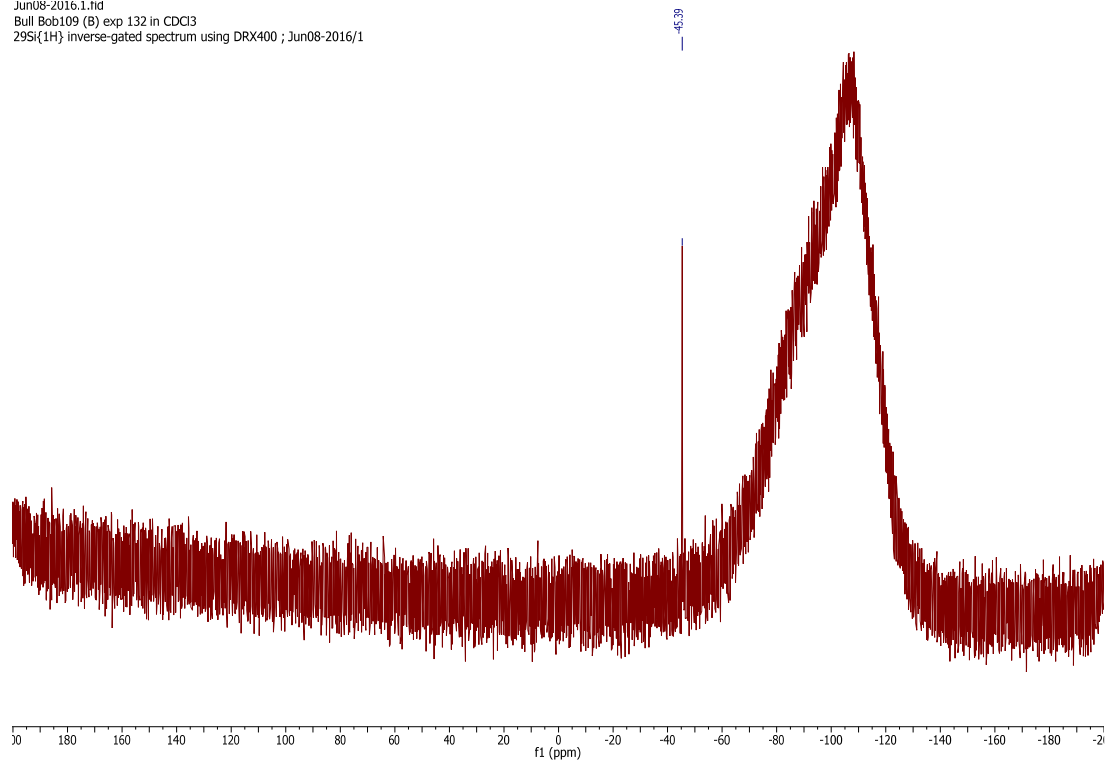
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (12) (S_{30})

Jun08-2016.3.fid
Bull Bob109 (B) exp 132 in CDCl3 ; 11B spectrum using DRX400 ; Jun08-2016/3



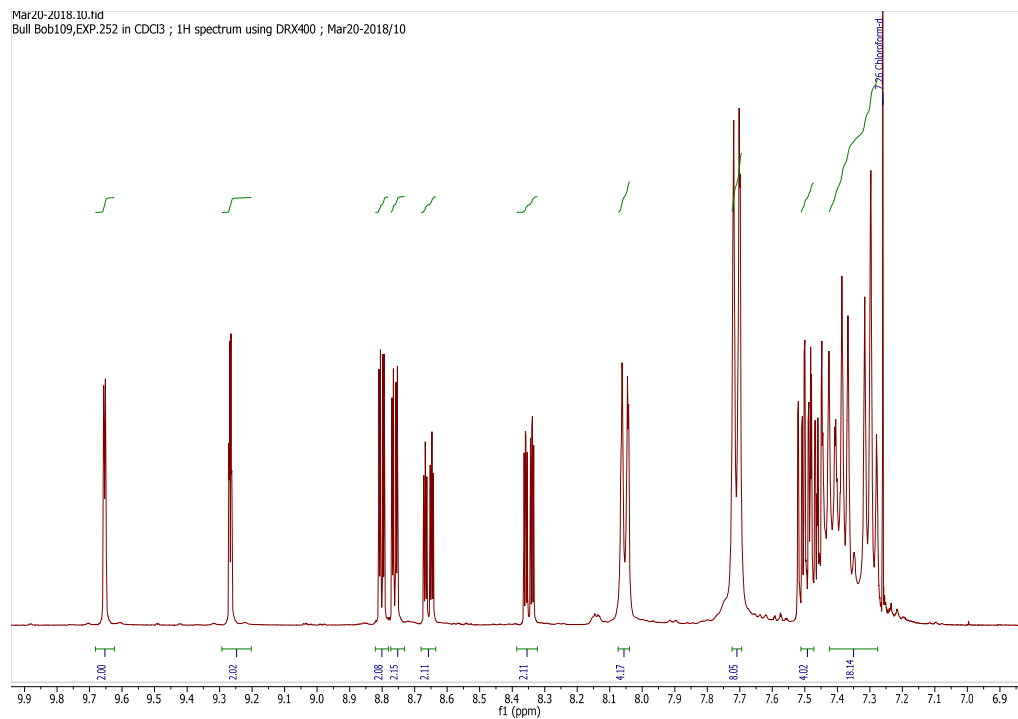
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (12) (S_{31})

Jun08-2016.1.fid
Bull Bob109 (B) exp 132 in CDCl3
29Si{1H} inverse-gated spectrum using DRX400 ; Jun08-2016/1



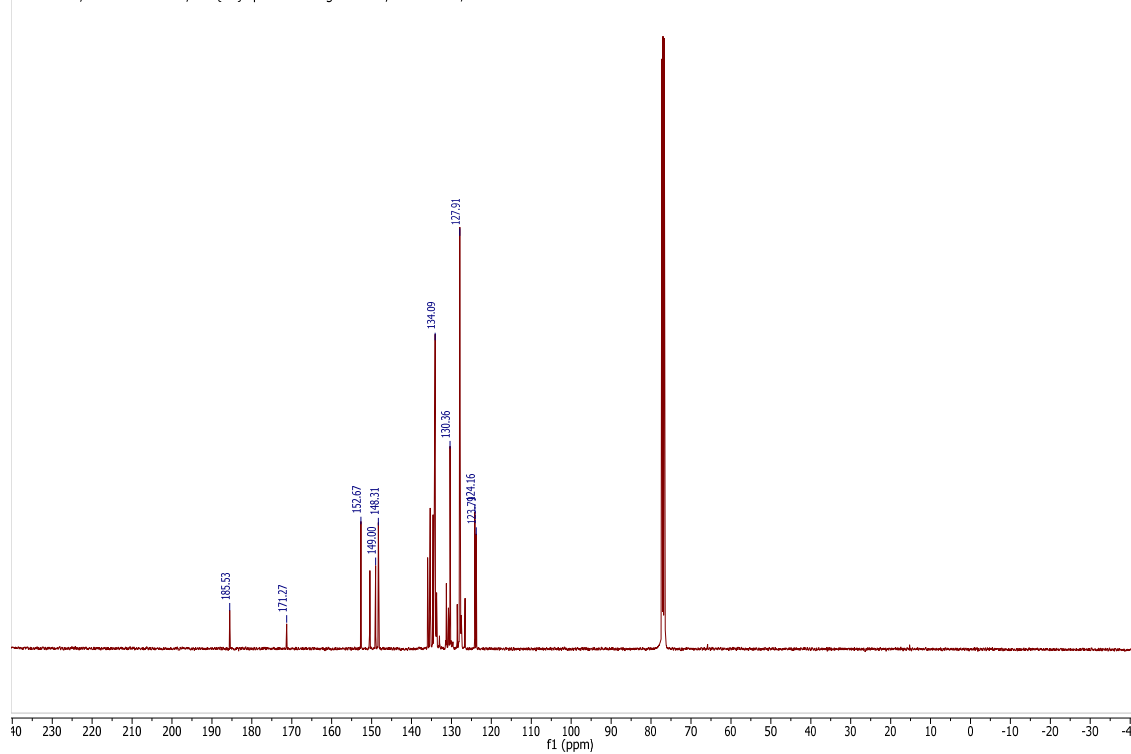
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (12) (S_{32})

Mar20-2018.10.fid
Bull Bob109,EXP.252 in CDCl3 ; 1H spectrum using DRX400 ; Mar20-2018/10



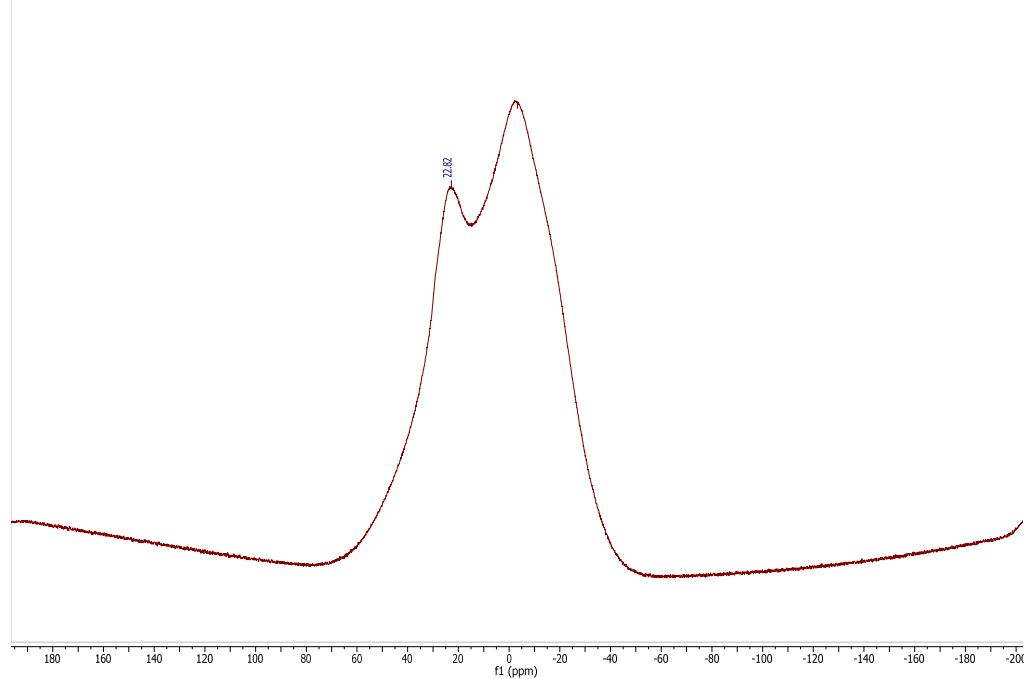
¹H spectrum of compound (13) (S₃₃)

Mar20-2018.11.fid
Bull Bob109,EXP.252 in CDCl3 ; 13C{1H} spectrum using DRX400 ; Mar20-2018/11



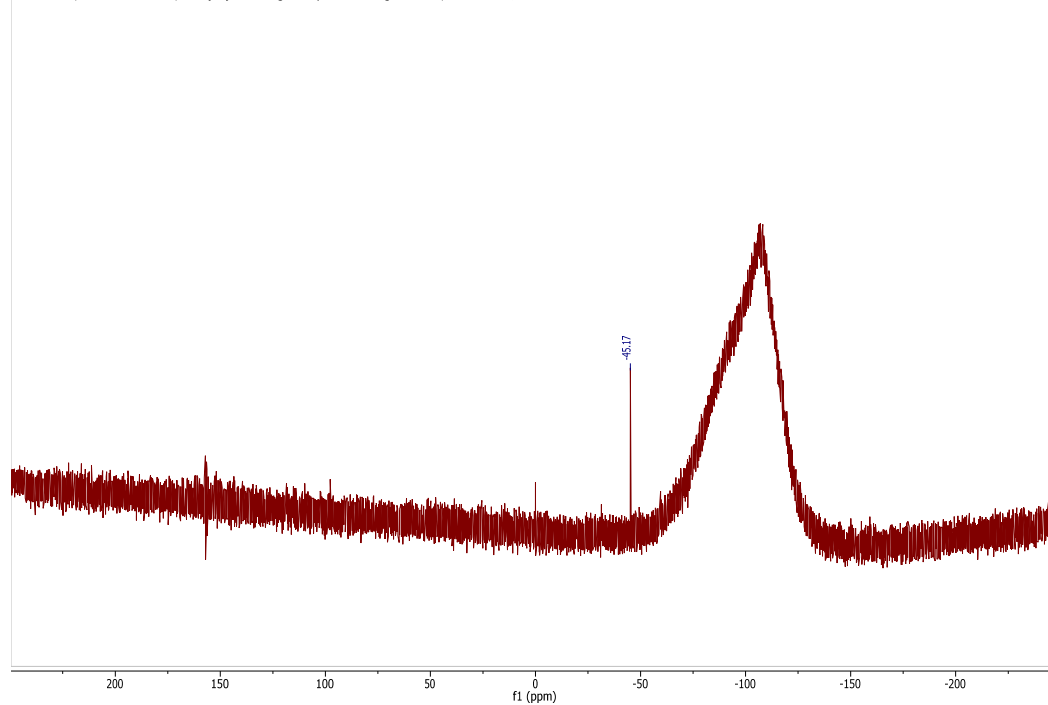
¹³C{¹H} spectrum of compound (13) (S₃₄)

Mar20-2018.12.fid
Bull Bob109,EXP.252 in CDCl3 ; 11B spectrum using DRX400 ; Mar20-2018/12



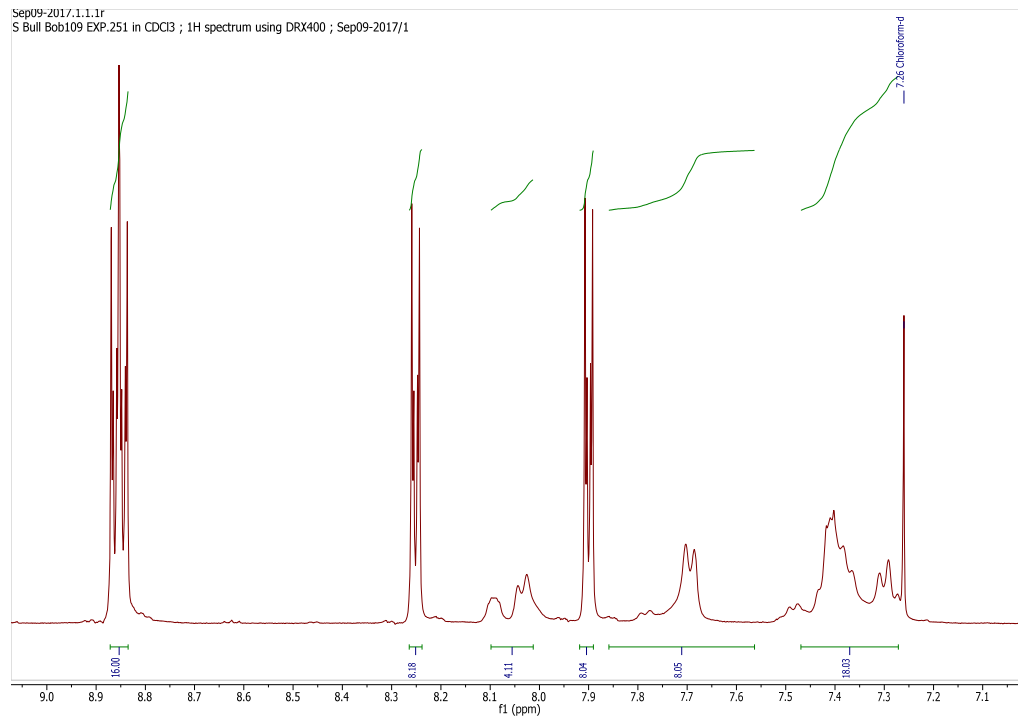
^{11}B spectrum for compound **(13)** (**S₃₅**)

Mar20-2018.13.fid
Bull Bob109,EXP.252 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using DRX400 ; Mar20-2018/13



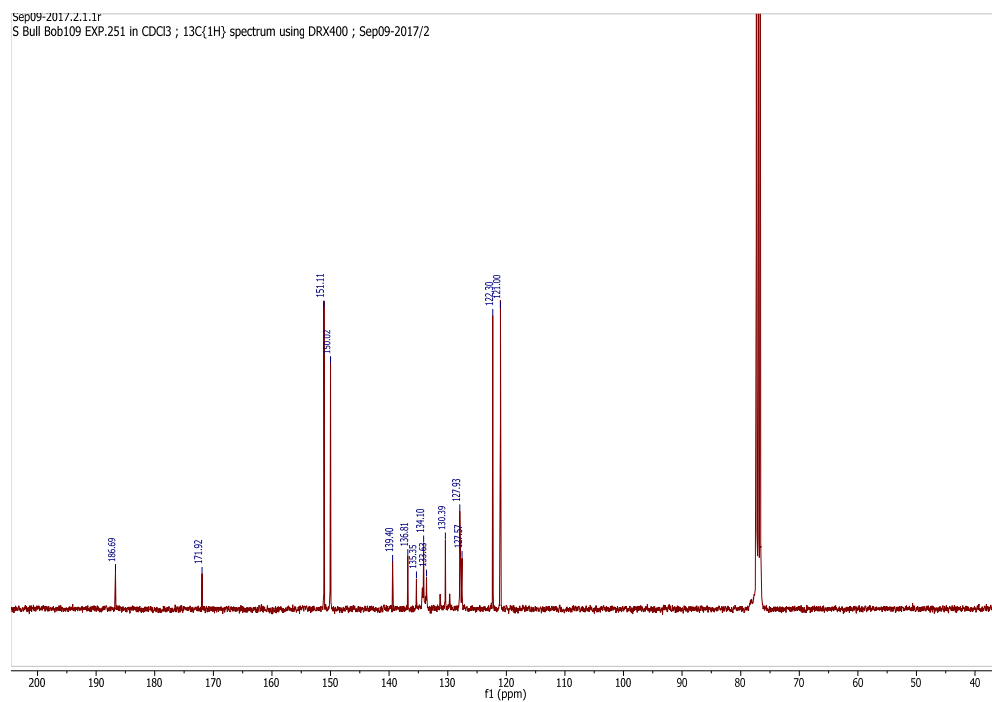
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound **(13)** (**S₃₆**)

Sep09-2017.1.1.1r
S Bull Bob109 EXP.251 in CDCl3 ; 1H spectrum using DRX400 ; Sep09-2017/1

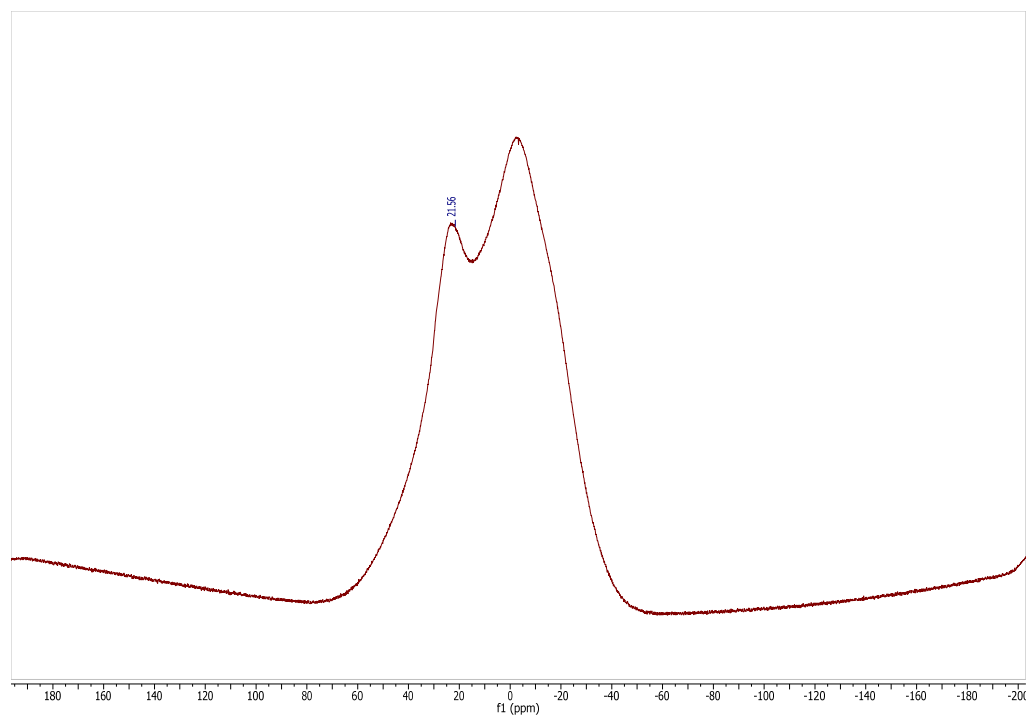


¹H spectrum of compound (14) (S₃₇)

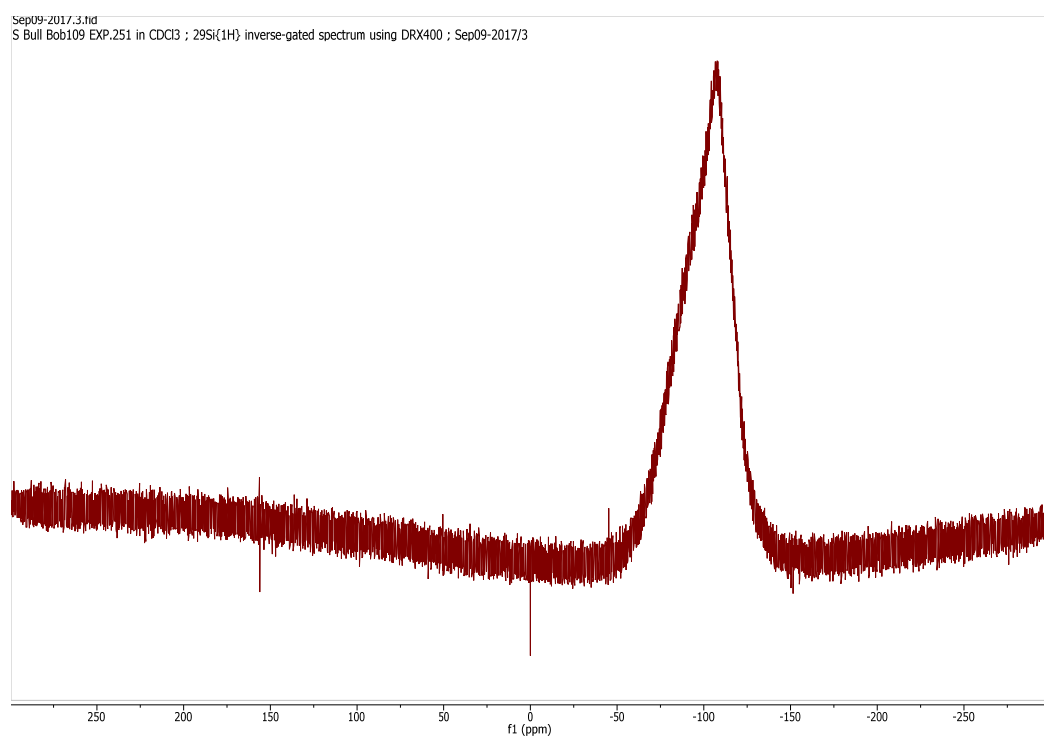
Sep09-2017.2.1.1r
S Bull Bob109 EXP.251 in CDCl3 ; 13C{1H} spectrum using DRX400 ; Sep09-2017/2



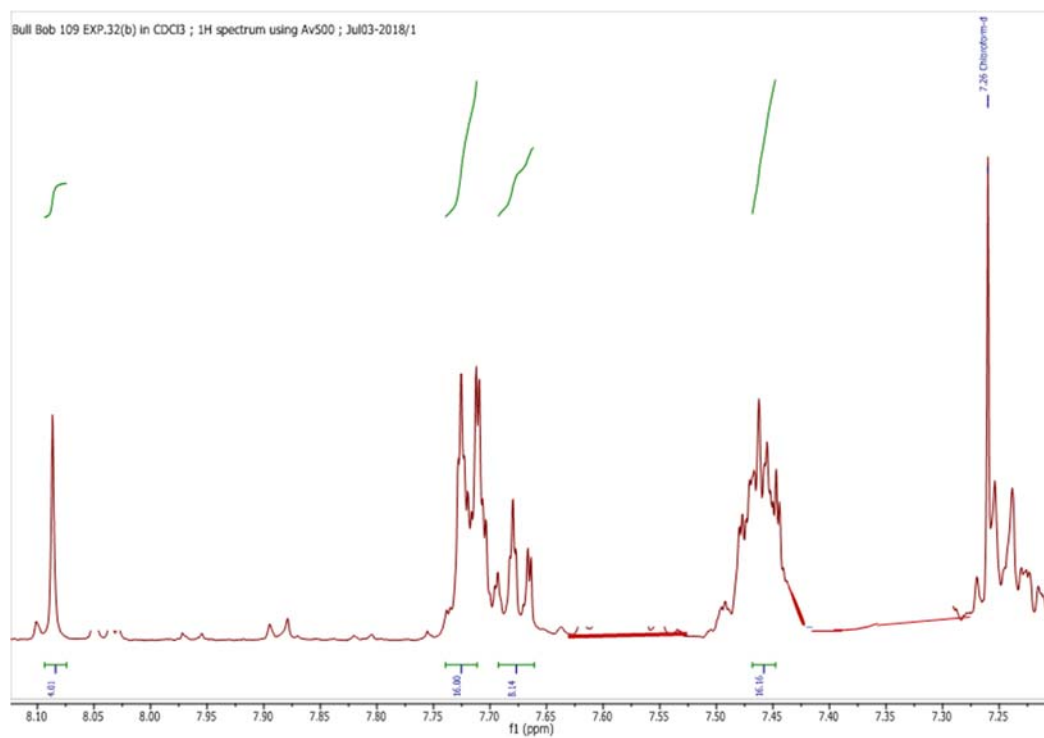
¹³C{¹H} spectrum of compound (14) (S₃₈)



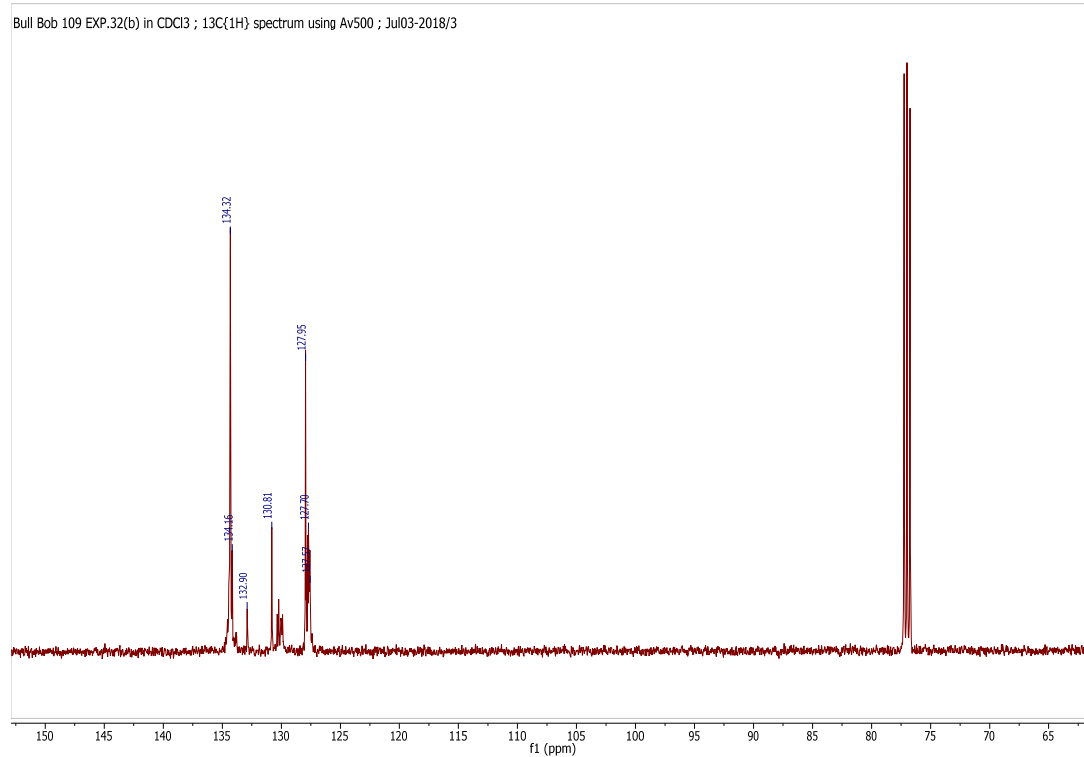
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound **(14)** (*S*₃₉)



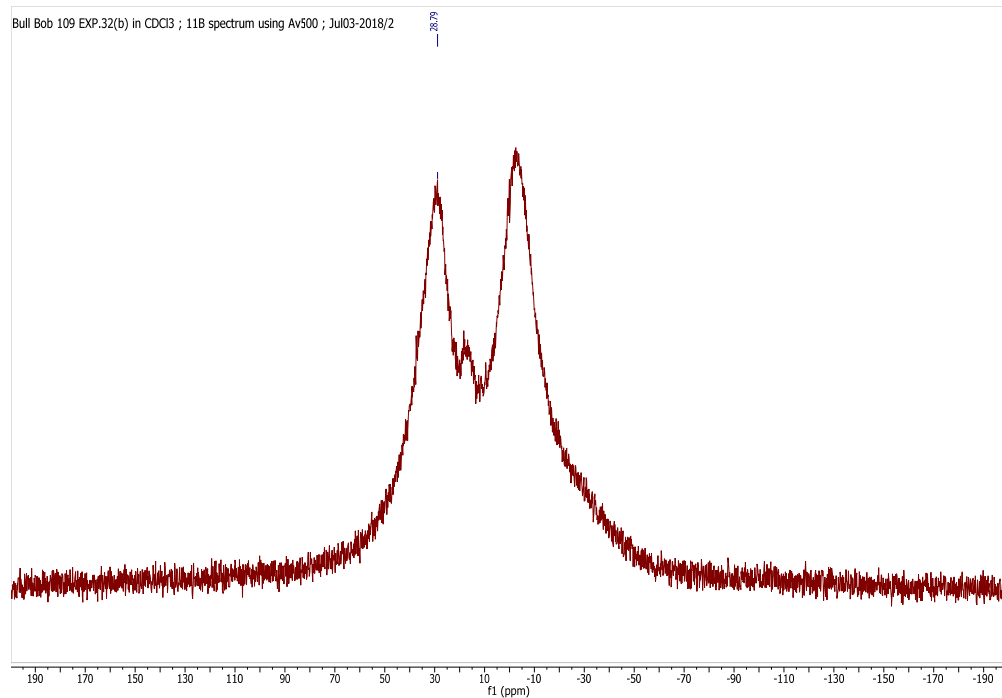
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound **(13)** (*S*₄₀)



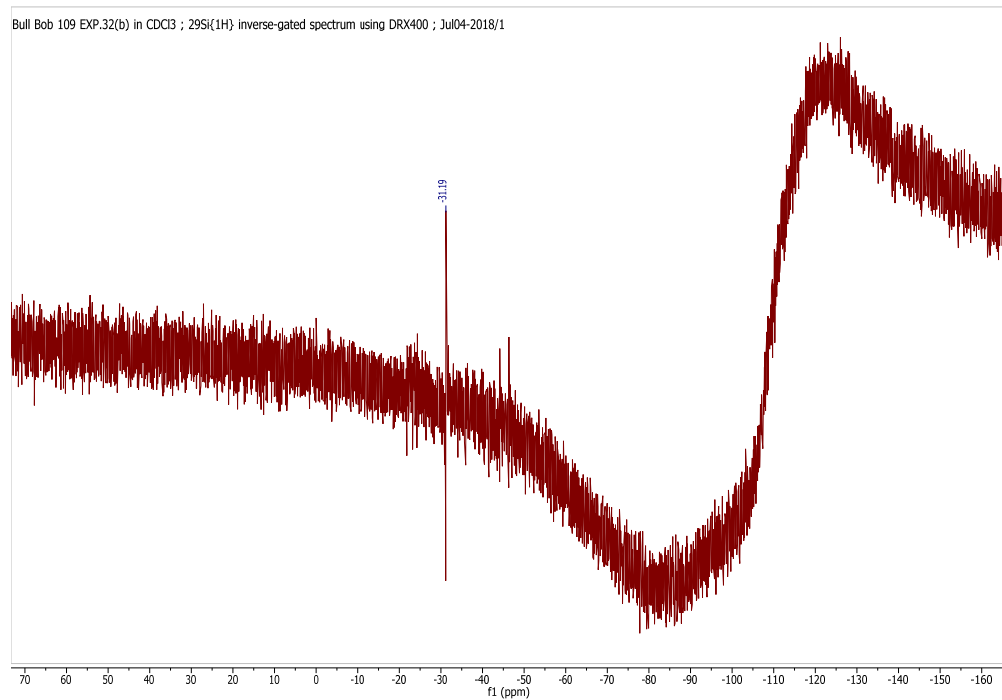
¹H spectrum of compound (**3a**) (S₄₁)



¹³C{¹H} spectrum of compound (**3a**) (S₄₂)

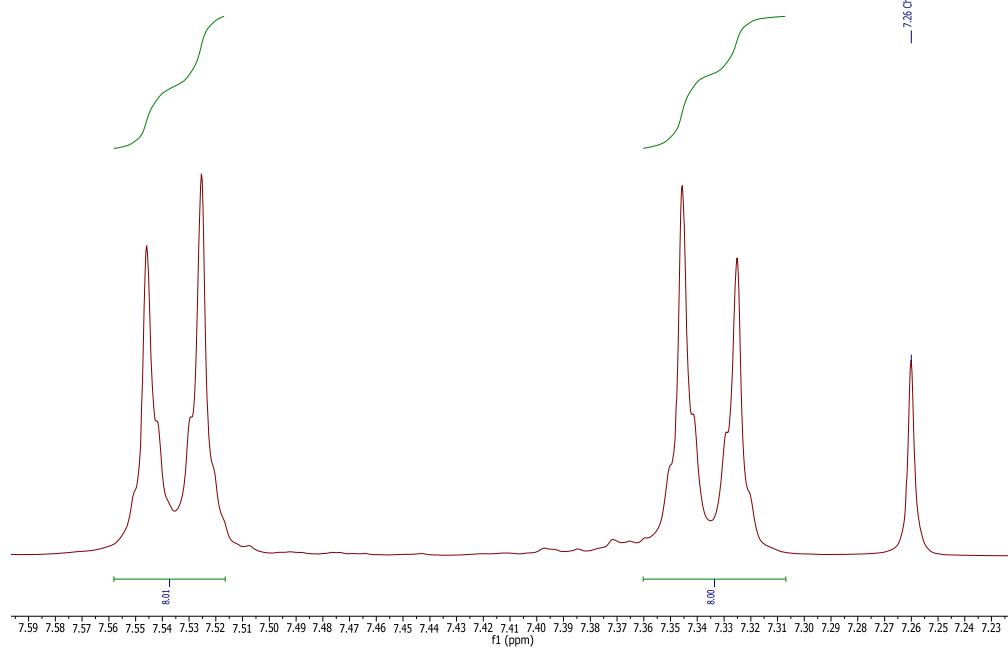


¹¹B spectrum for compound (**3a**) (*S*₄₃)



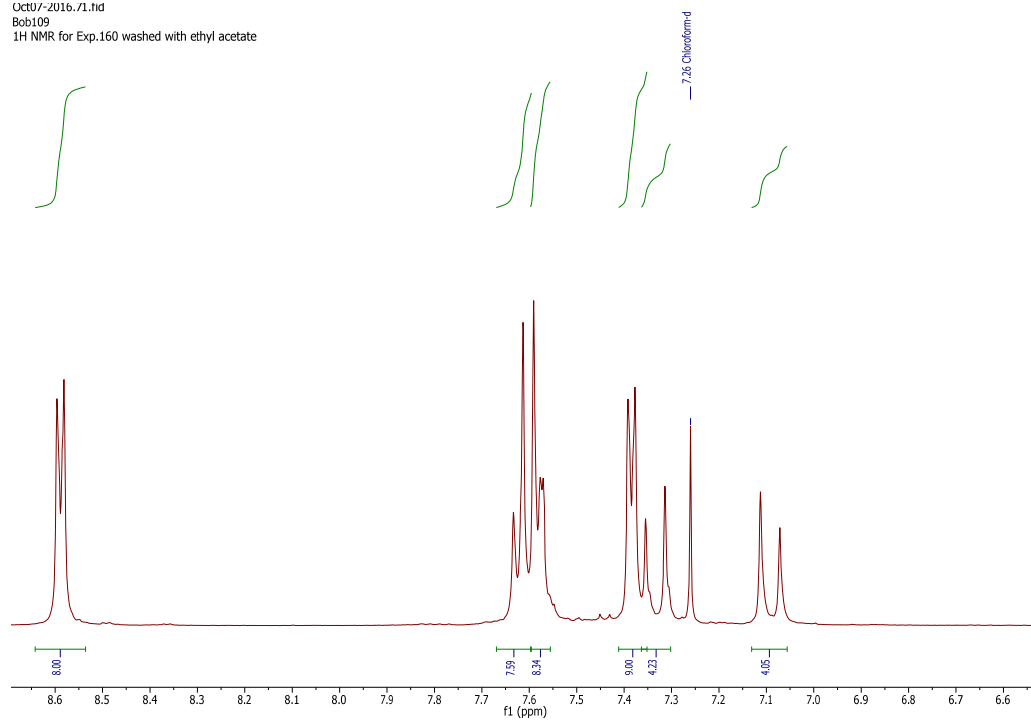
²⁹Si{¹H} spectrum for compound (**3a**) (*S*₄₄)

Sep29-2016.10.hid
Bob109
1H NMR for Exp. 158 crude washed with hexane



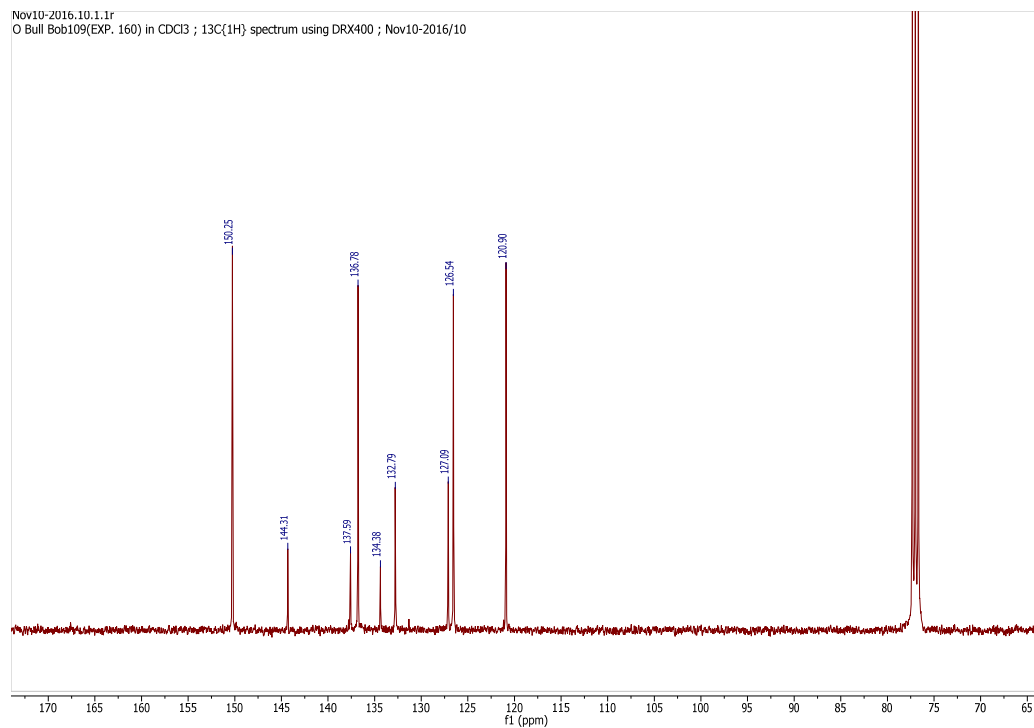
¹H spectrum of compound (C) (S₄₅)

Oct07-2016..71.hid
Bob109
1H NMR for Exp.160 washed with ethyl acetate



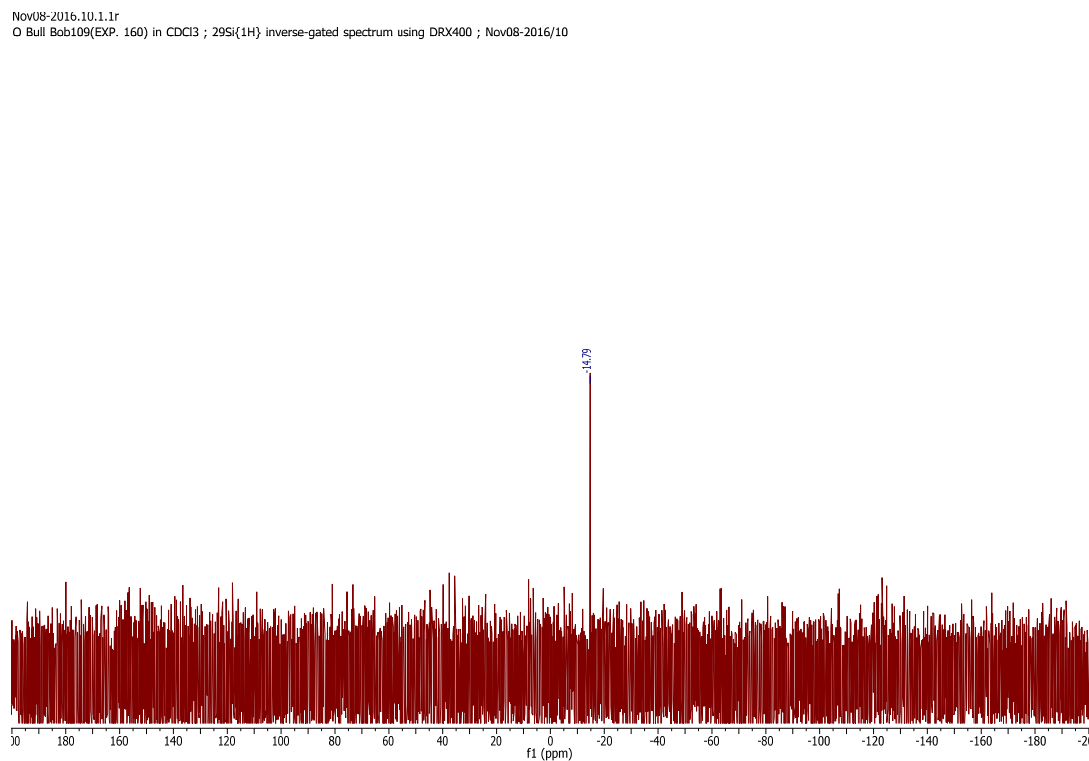
¹H spectrum of compound (L₁₀) (S₄₆)

Nov10-2016.10.1.1r
O Bull Bob109(EXP. 160) in CDCl₃ ; ¹³C{¹H} spectrum using DRX400 ; Nov10-2016/10



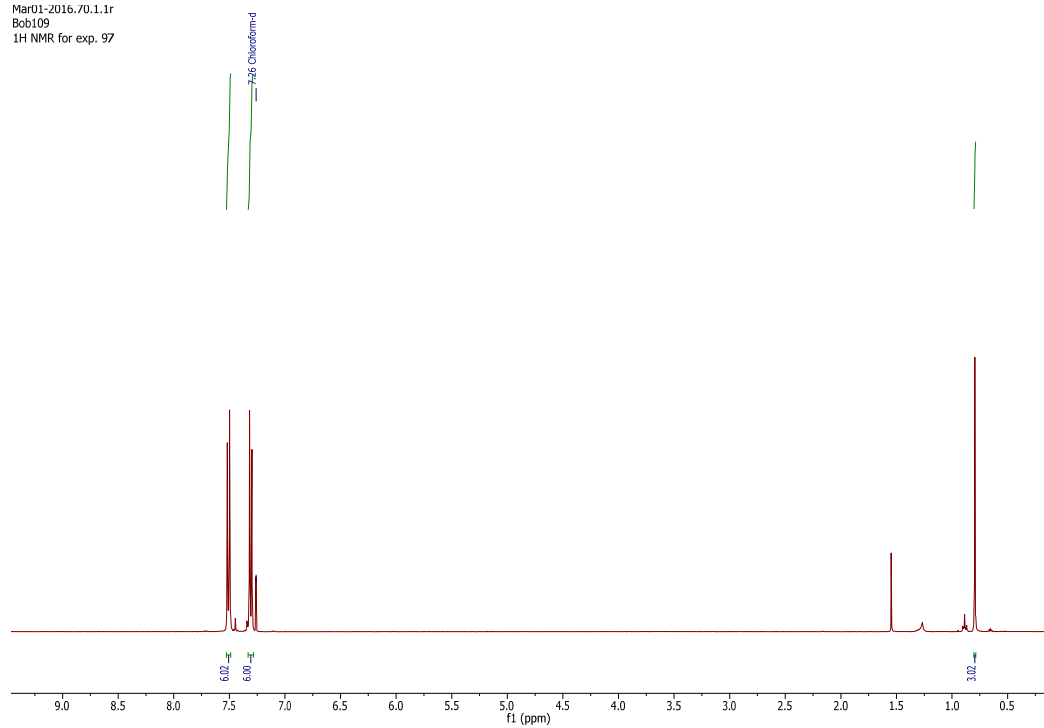
¹³C{¹H} spectrum of compound (L₁₀) (S₄₇)

Nov08-2016.10.1.1r
O Bull Bob109(EXP. 160) in CDCl₃ ; ²⁹Si{¹H} inverse-gated spectrum using DRX400 ; Nov08-2016/10



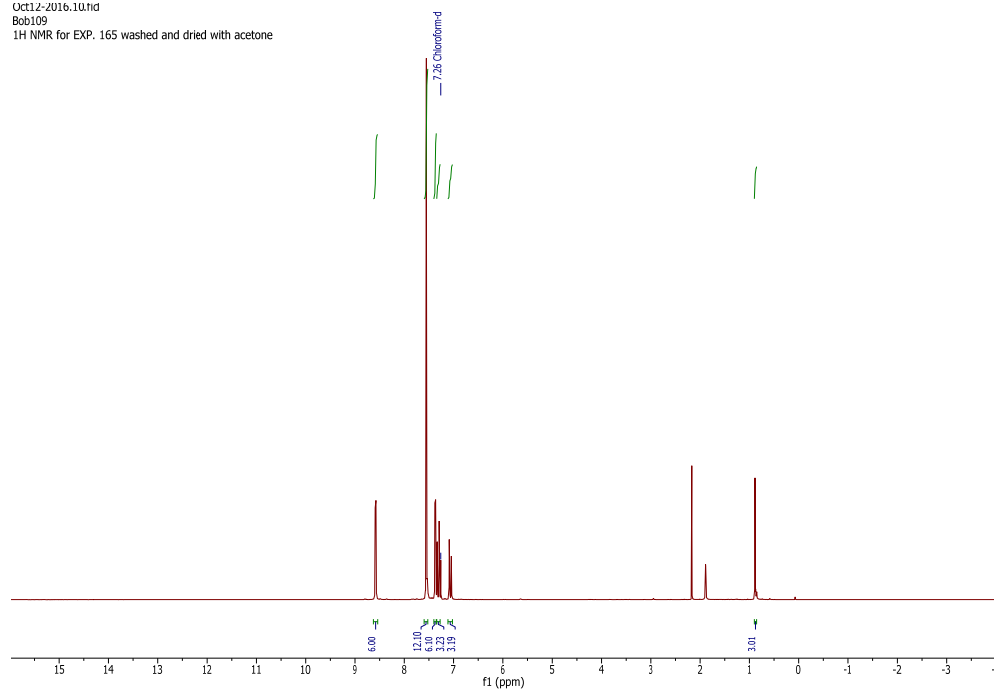
²⁹Si{¹H} spectrum for compound (L₁₀) (S₄₈)

Mar01-2016.70.1.1r
Bob109
1H NMR for exp. 97



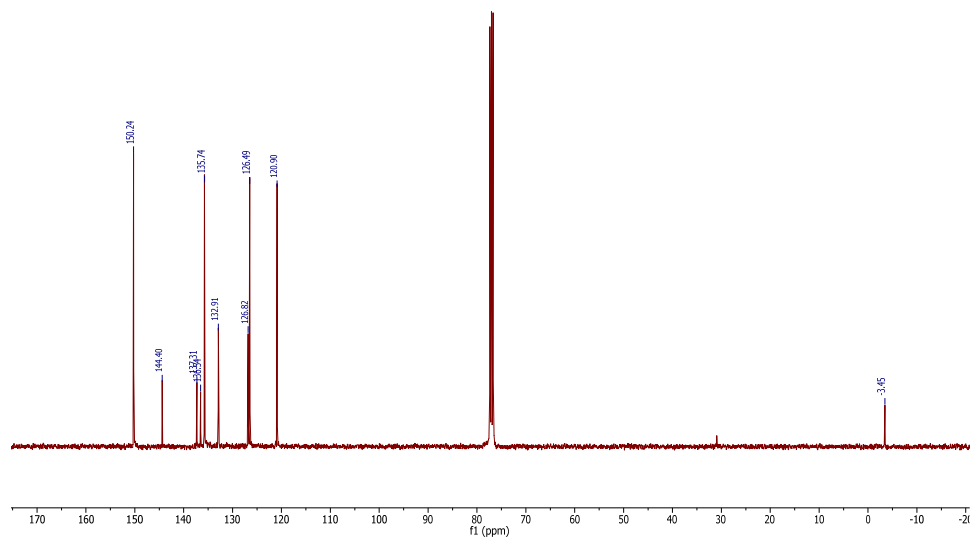
¹H spectrum of compound (E) (S₄₉)

Oct12-2016.10.nd
Bob109
1H NMR for EXP. 165 washed and dried with acetone



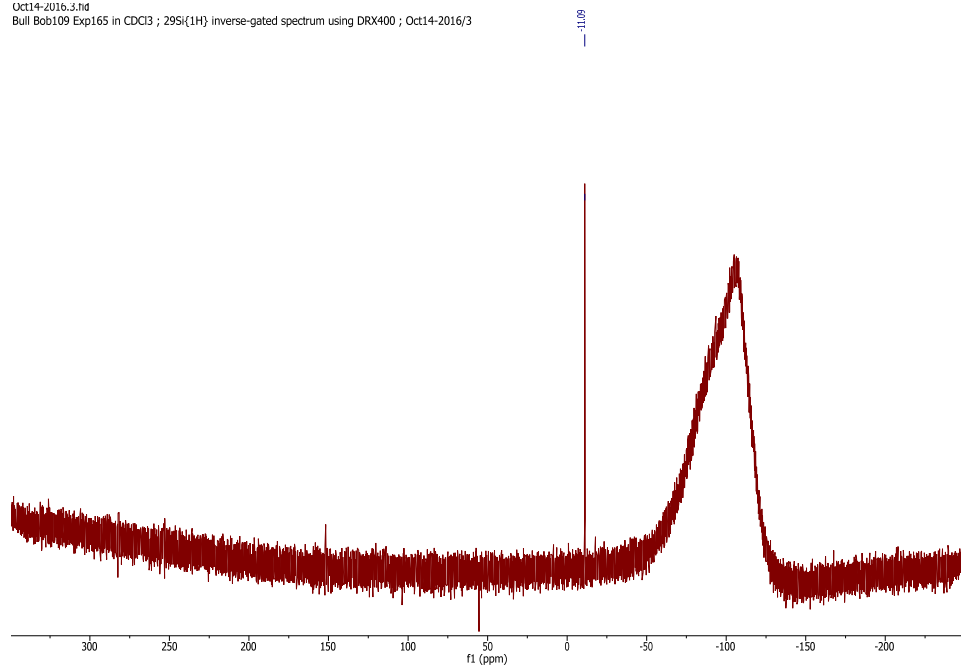
¹H spectrum of compound (L₁₁) (S₅₀)

Oct14-2016.2.fid
Bull Bob109 Exp165 in CDCl3 ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using DRX400 ; Oct14-2016/2



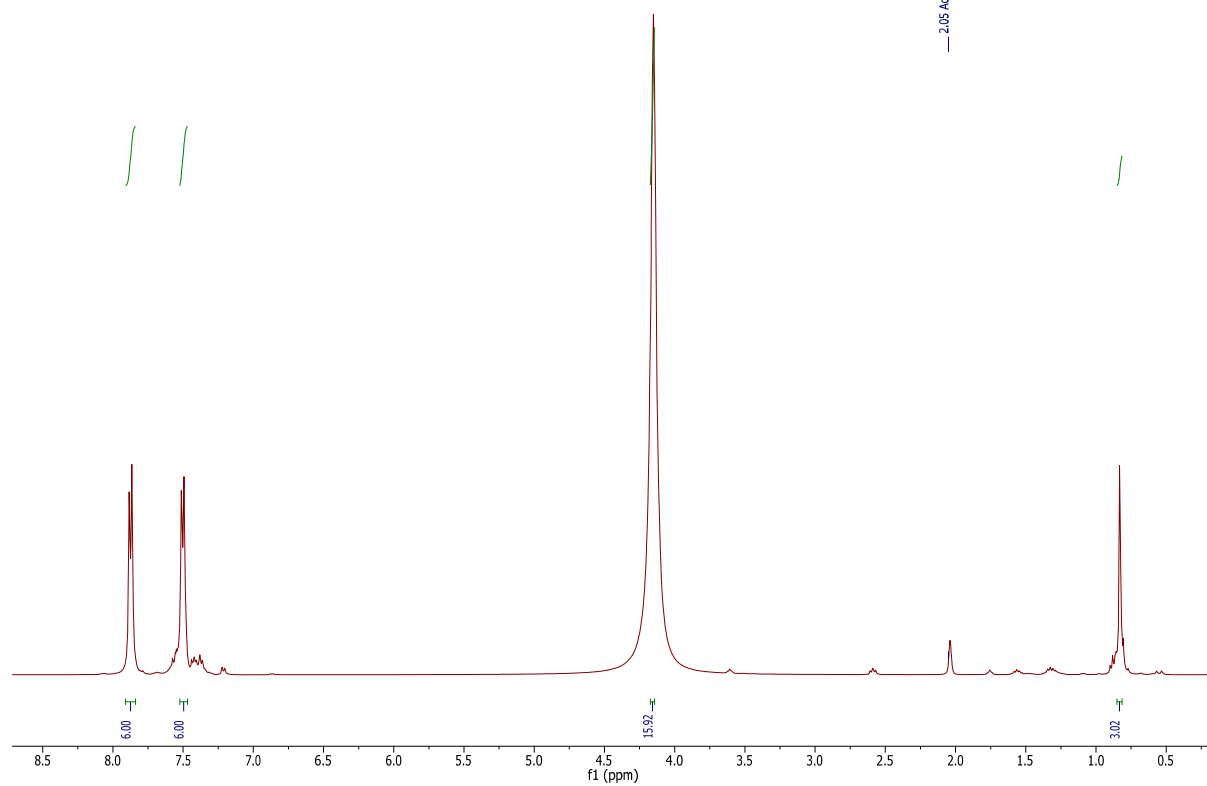
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (L₁₁) (S₅₁)

Oct14-2016.3.fid
Bull Bob109 Exp165 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using DRX400 ; Oct14-2016/3



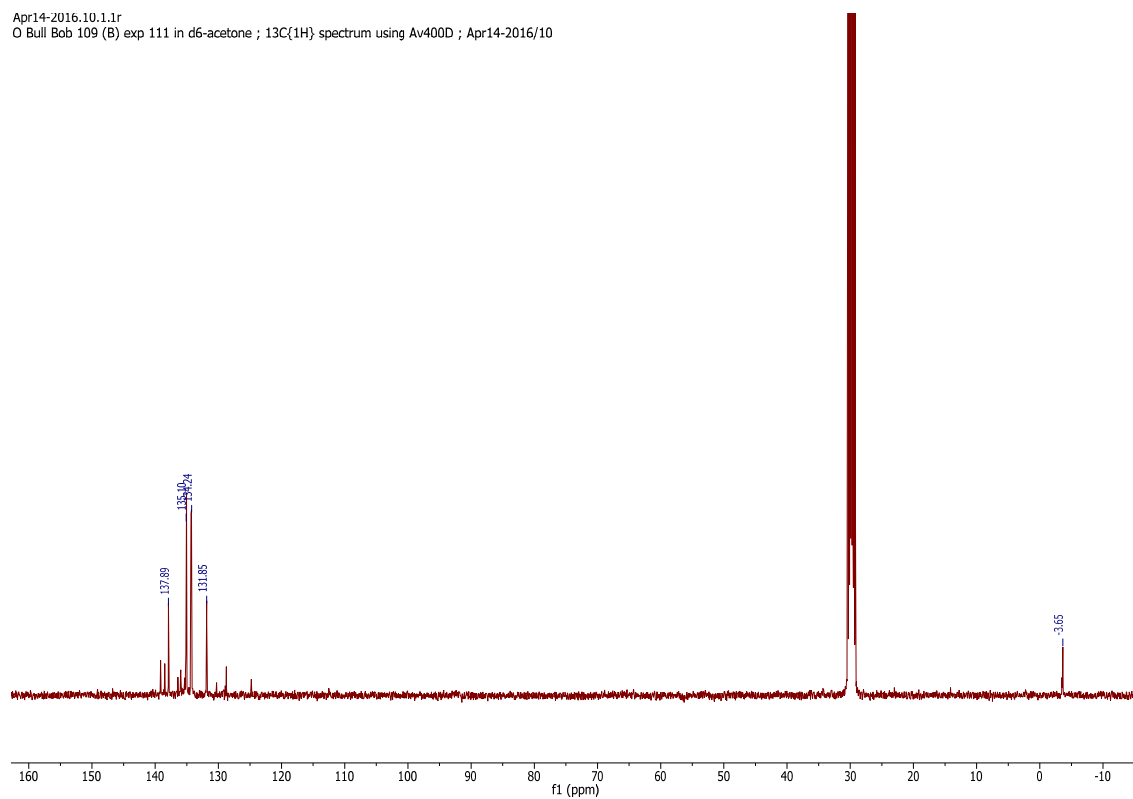
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (L₁₁) (S₅₂)

May13-2016.12.fid
Bob109
1H NMR for Exp. 121 treated



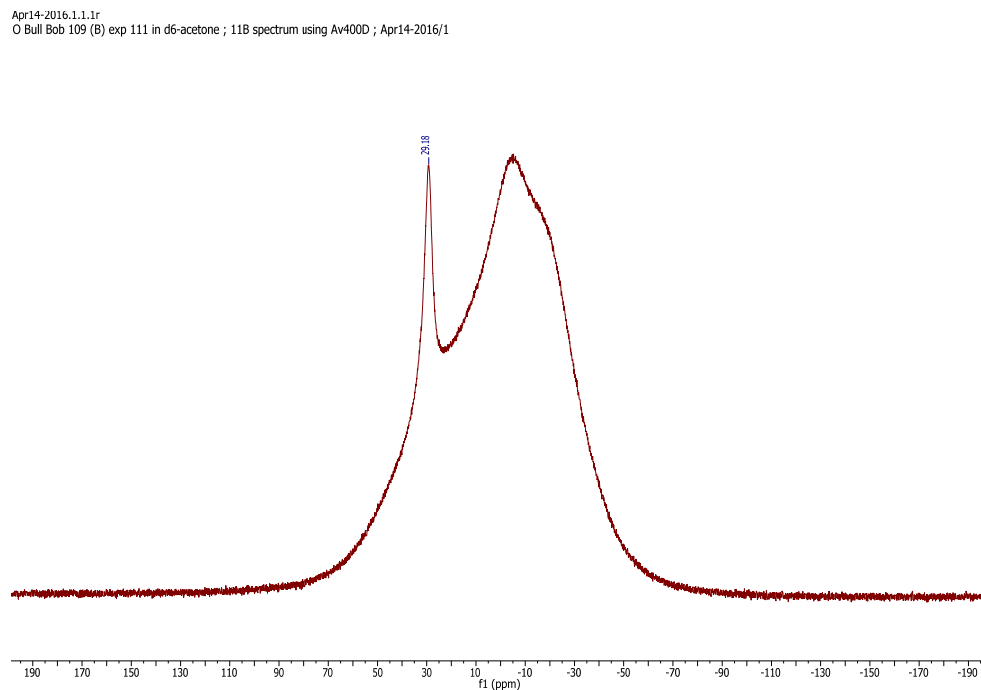
^1H spectrum of compound (3c) (S_{53})

Apr14-2016.10.1.1r
O Bull Bob 109 (B) exp 111 in d6-acetone ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using Av400D ; Apr14-2016/10



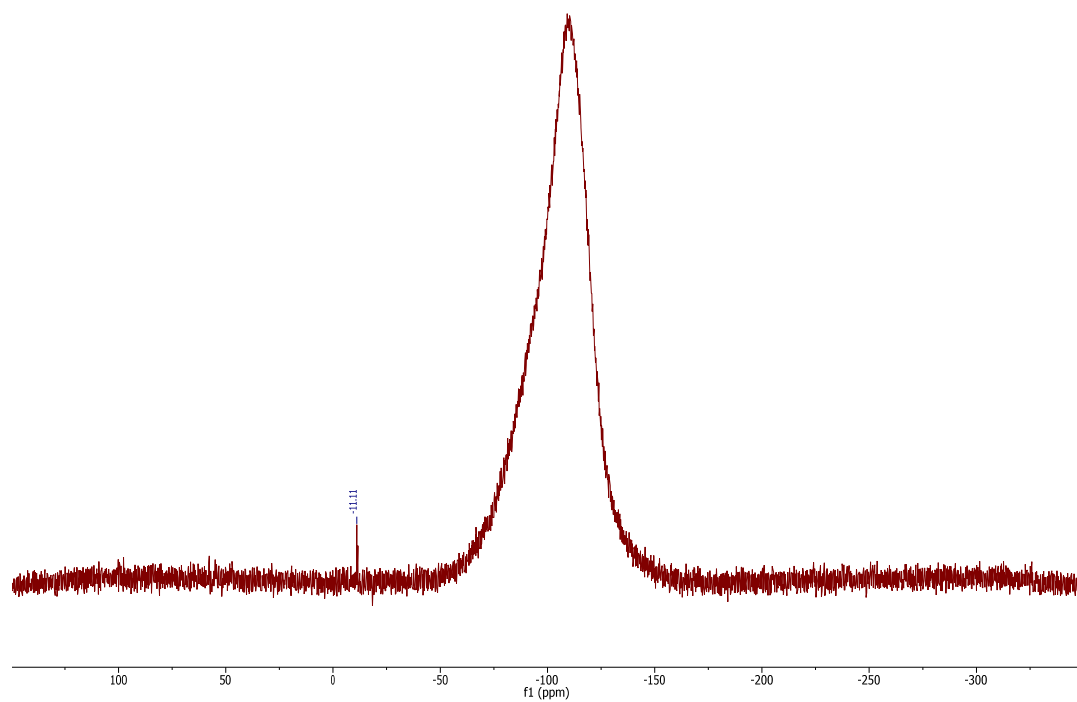
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (3c) (S54)

Apr14-2016.1.1.1r
O Bull Bob 109 (B) exp 111 in d6-acetone ; $^{11}\text{B}\{^1\text{H}\}$ spectrum using Av400D ; Apr14-2016/1



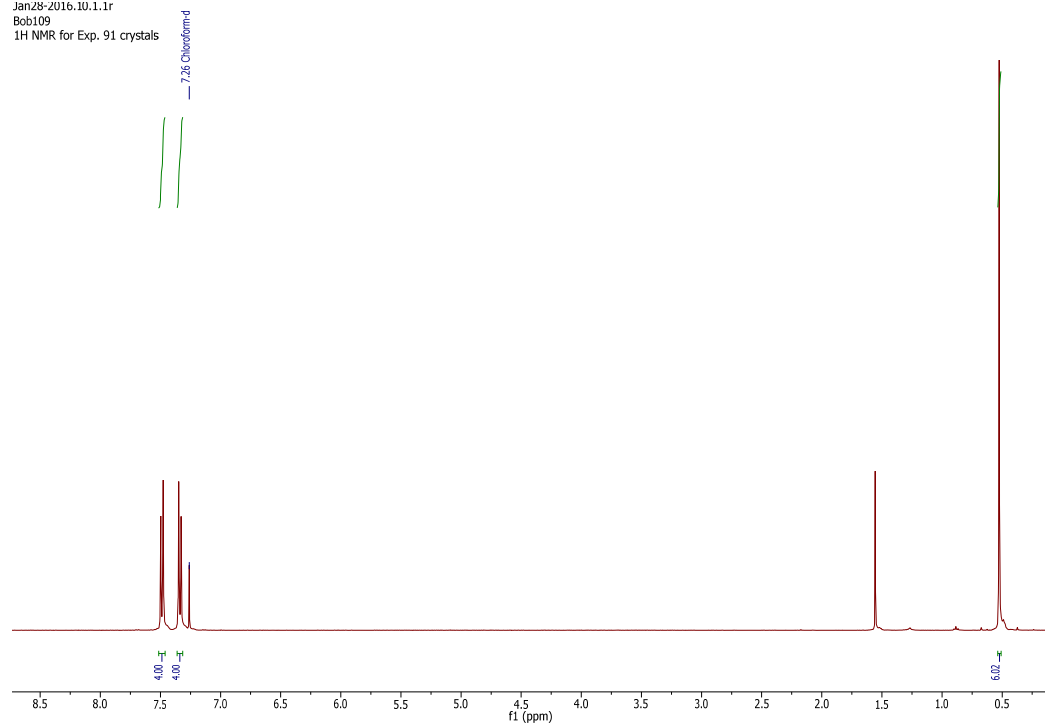
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (3c) (S55)

Apr14-2016.11.1.1r
O Bull Bob 109 (B) exp 111 in d6-acetone ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av400D ; Apr14-2016/11



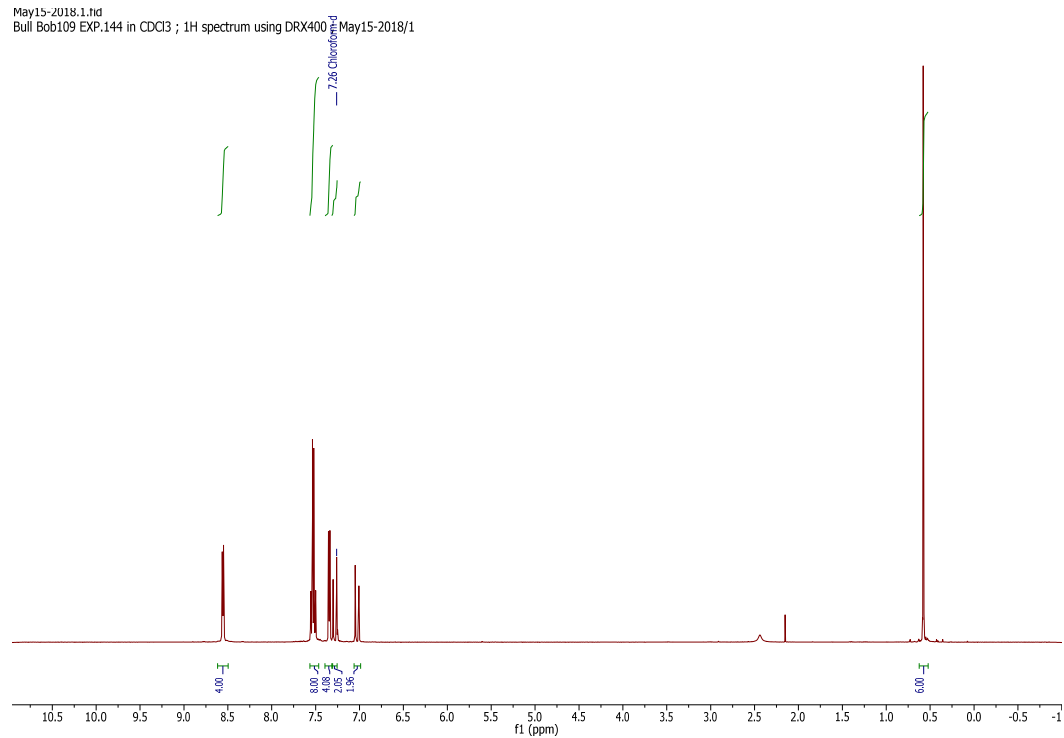
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (3c) (S₅₆)

Jan28-2016.10.1.1r
Bob109
 ^1H NMR for Exp. 91 crystals



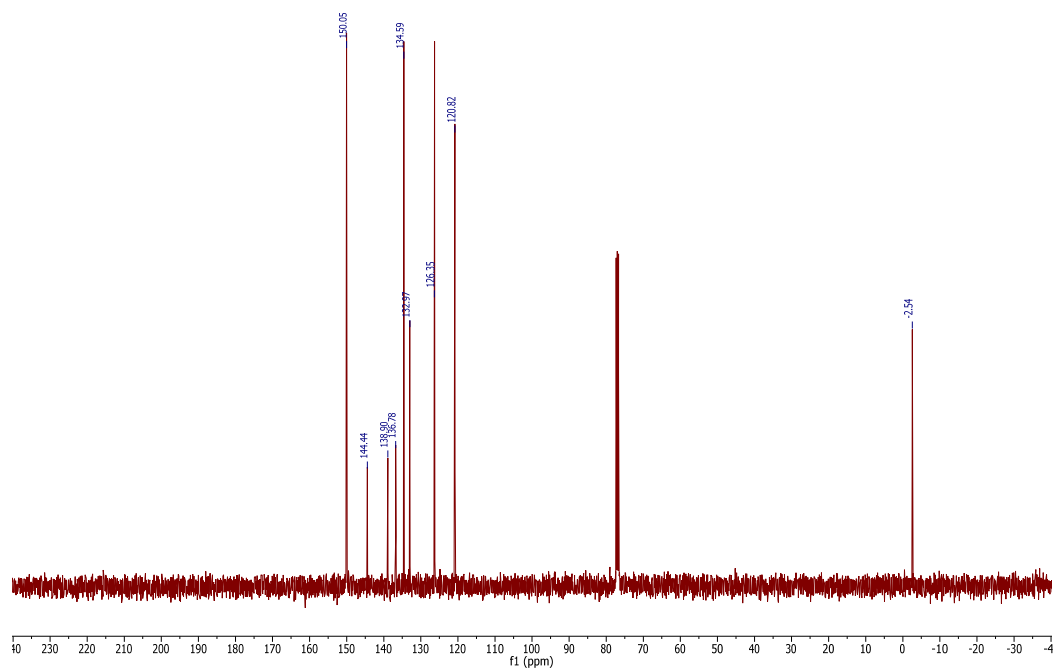
^1H spectrum of compound (F) (S₅₇)

May15-2018.1.nd
Bull Bob109 EXP.144 in CDCl3 ; 1H spectrum using DRX400 May15-2018/1



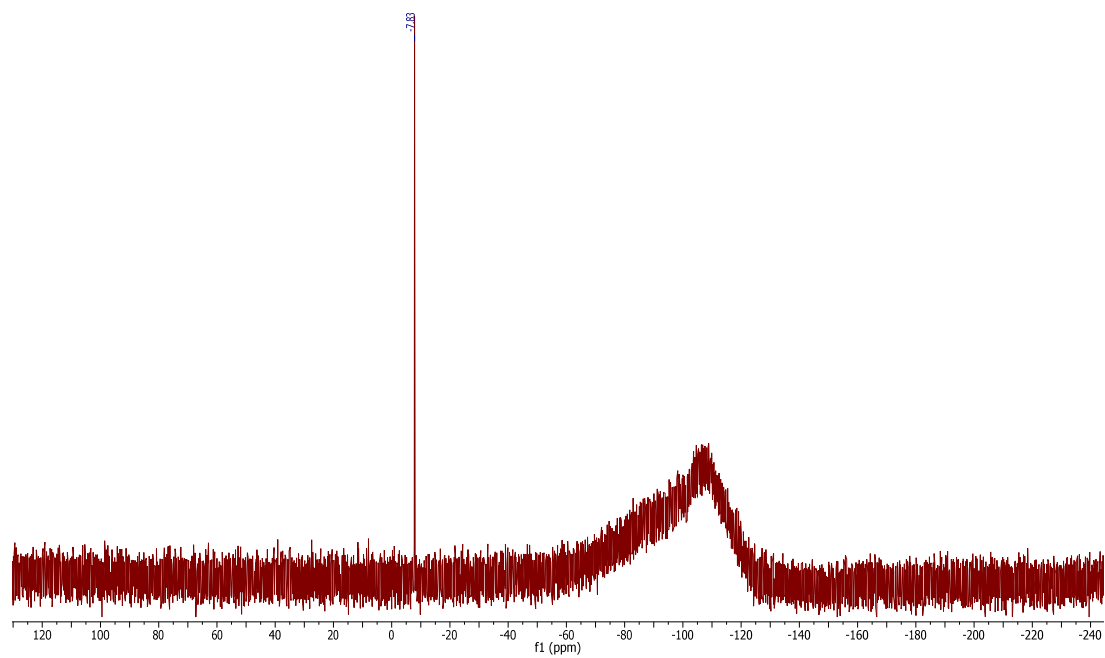
^1H spectrum of compound (L_{12}) (S_{58})

May15-2018.2.fid
Bull Bob109 EXP.144 in CDCl3 ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using DRX400 ; May15-2018/2



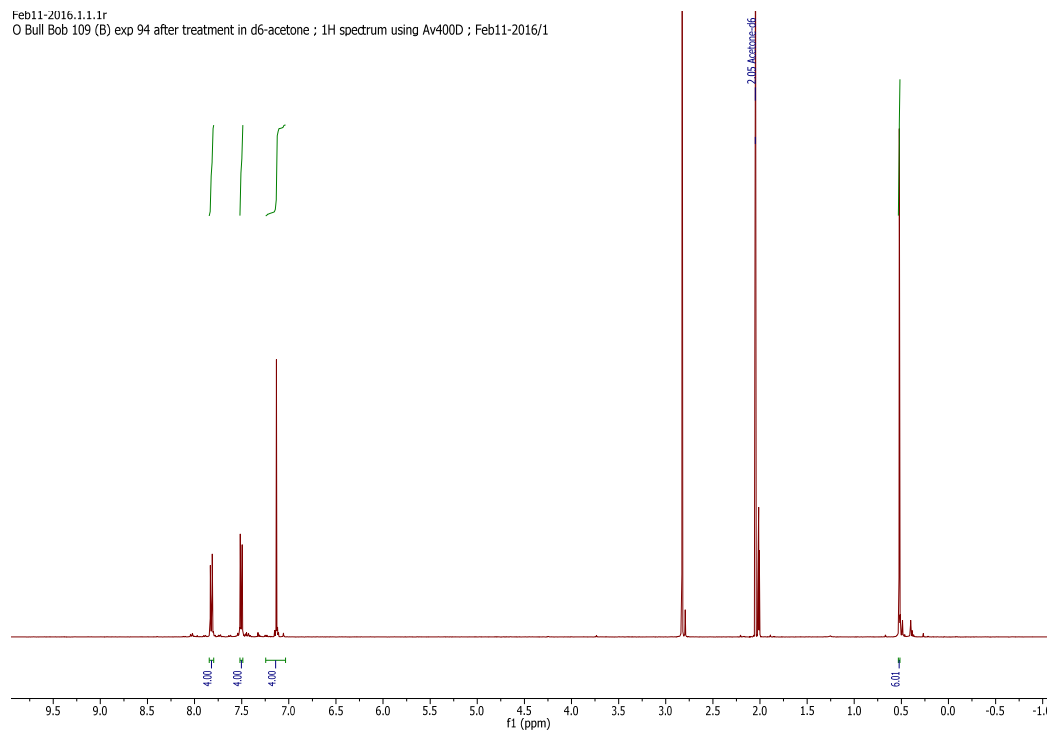
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (L₁₂) (S₅₉)

May15-2018.3.fid
Bull Bob109 EXP.144 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using DRX400 ; May15-2018/3



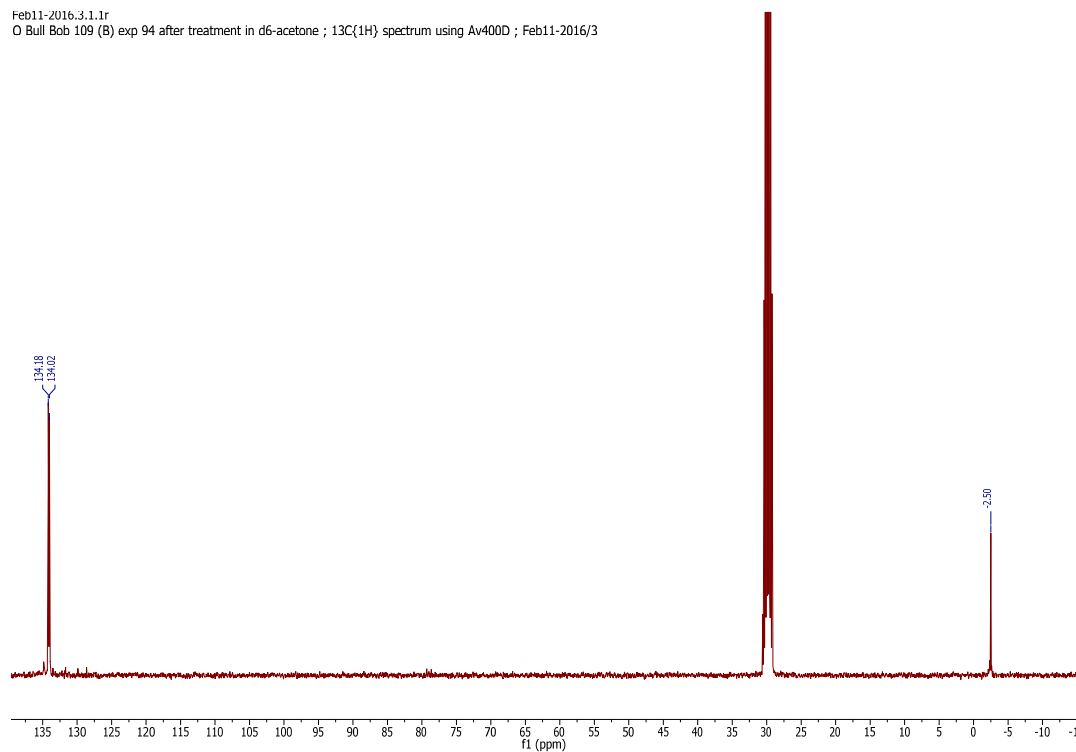
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (L₁₂) (S₆₀)

Feb11-2016.1.1.1r
O Bull Bob 109 (B) exp 94 after treatment in d6-acetone ; ^1H spectrum using Av400D ; Feb11-2016/1



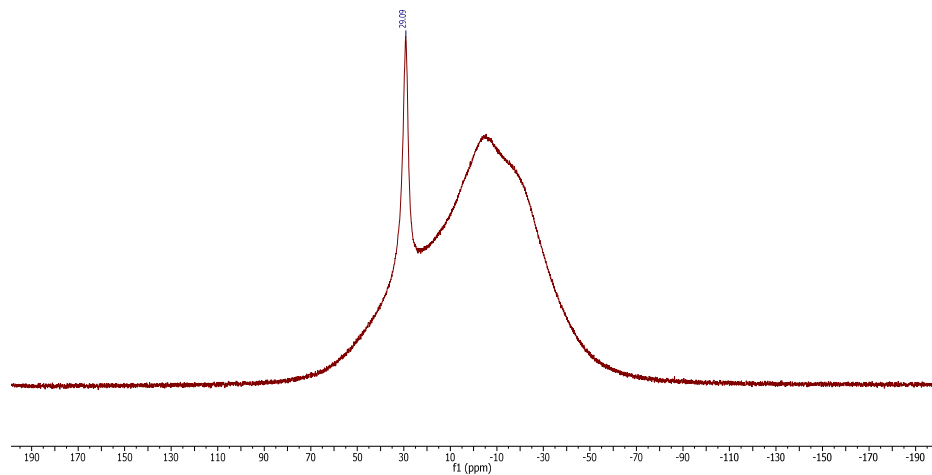
^1H spectrum of compound **(3d)** (S_{61})

Feb11-2016.3.1.1r
O Bull Bob 109 (B) exp 94 after treatment in d6-acetone ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using Av400D ; Feb11-2016/3



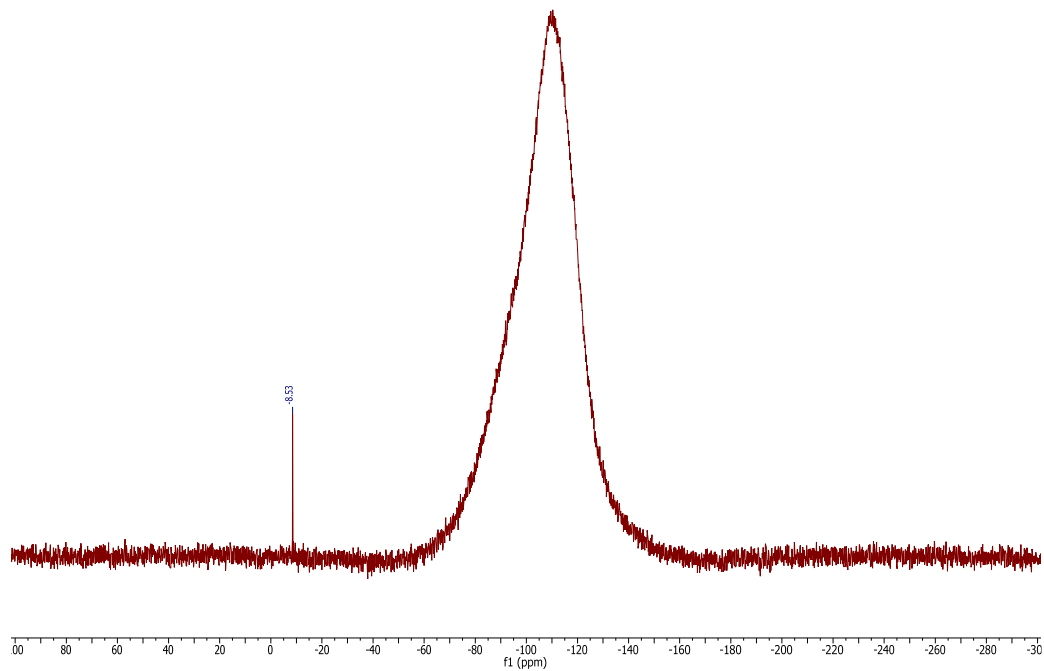
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound **(3d)** (S_{62})

Feb11-2016.2.1d
O Bull Bob 109 (B) exp 94 after treatment in d6-acetone ; 11B spectrum using Av400D ; Feb11-2016/2



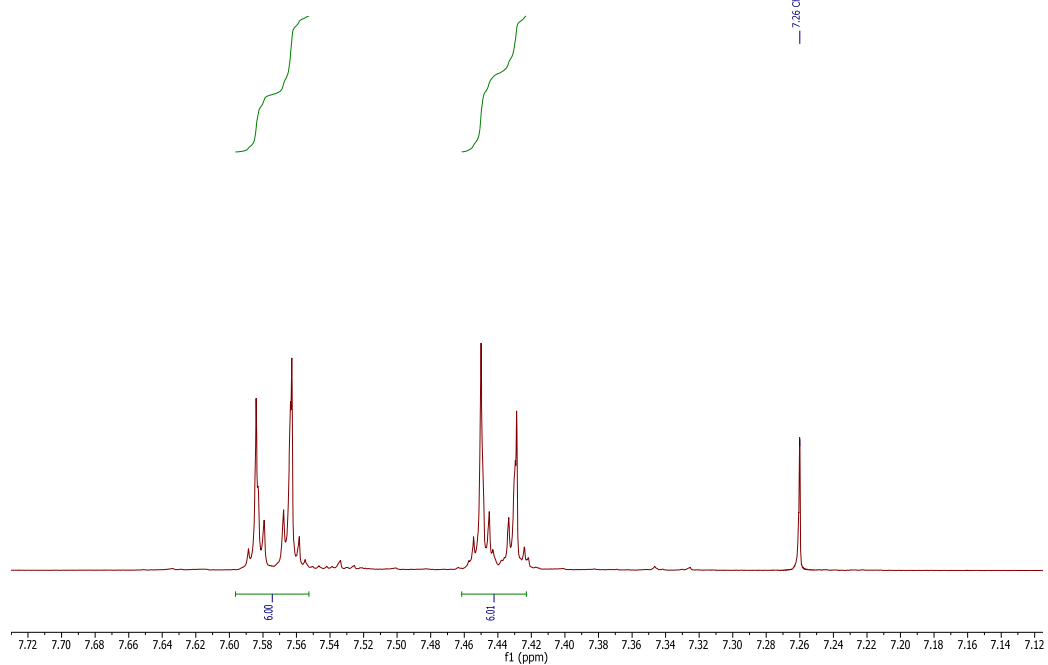
$^{11}\text{B}\{^1\text{H}\}$ spectrum for compound (3d) (S₆₃)

Feb11-2016.4.1.1r
O Bull Bob 109 (B) exp 94 after treatment in d6-acetone
29Si{1H} inverse-gated spectrum using Av400D ; Feb11-2016/4



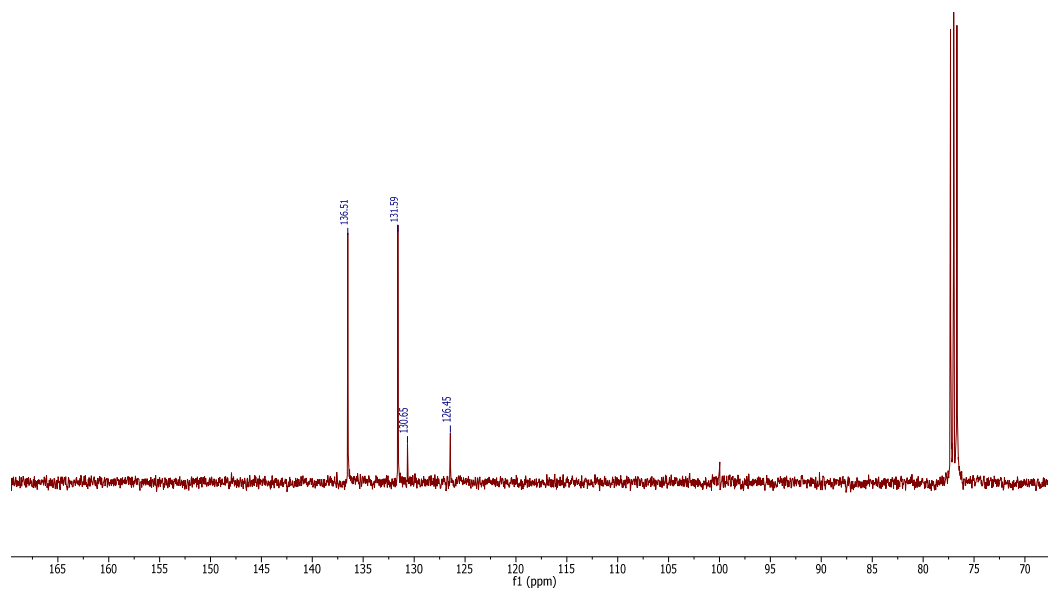
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (3d) (S₆₄)

Dec16-2016.1.hd
O Bull Bob109 EXP.186 in CDCl3 ; 1H spectrum using DRX400 ; Dec16-2016/1



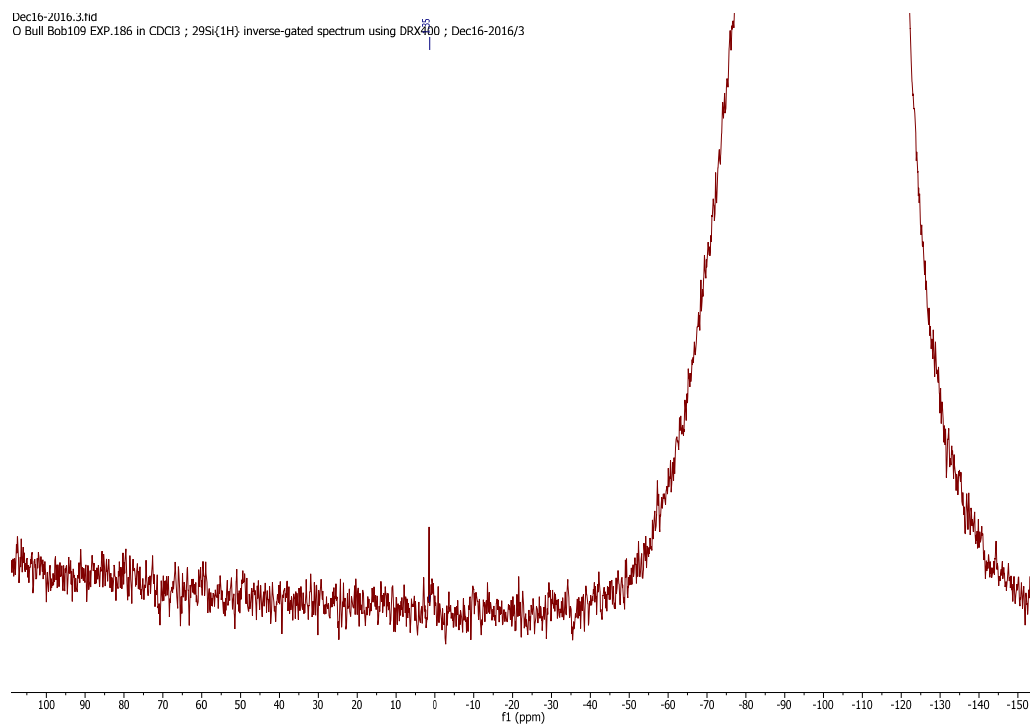
¹H spectrum of compound (G) (S65)

Dec16-2016.2.hd
O Bull Bob109 EXP.186 in CDCl3 ; ¹³C{¹H} spectrum using DRX400 ; Dec16-2016/2



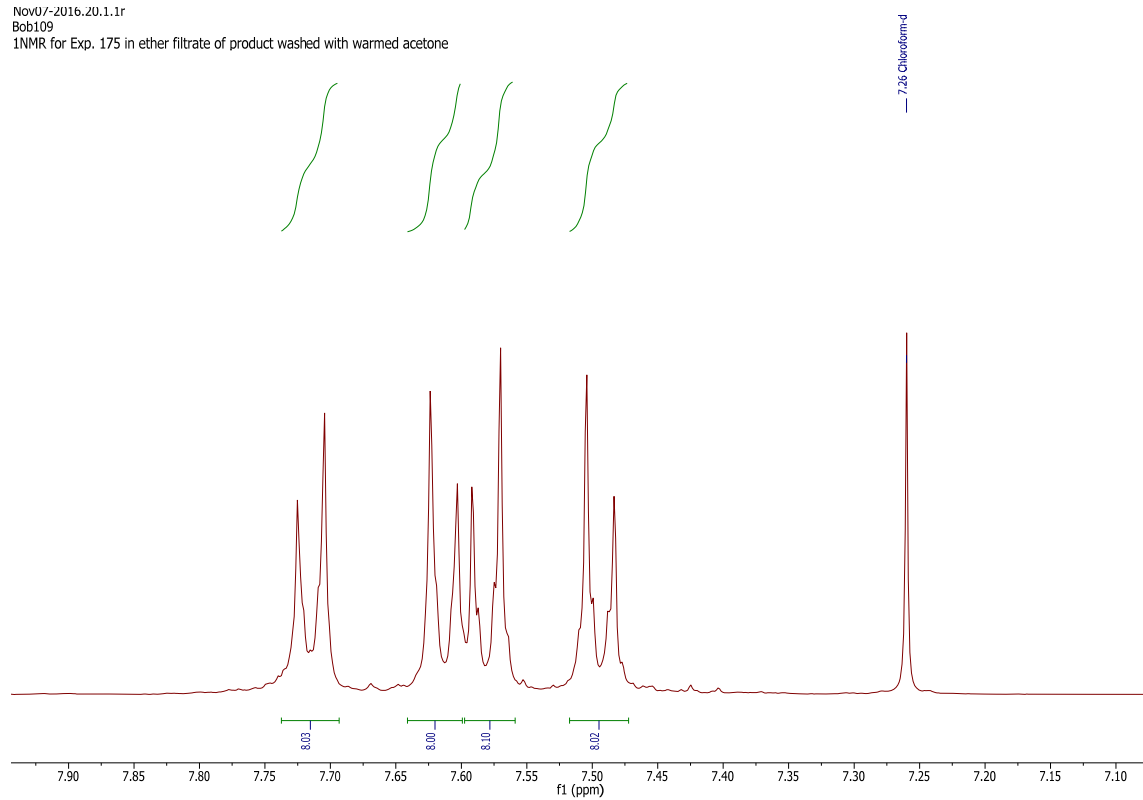
¹³C{¹H} spectrum of compound (G) (S66)

Dec16-2016.3.hrd
O Bull Bob109 EXP.186 in CDCl3 ; 29Si{1H} inverse-gated spectrum using DRX400 ; Dec16-2016/3



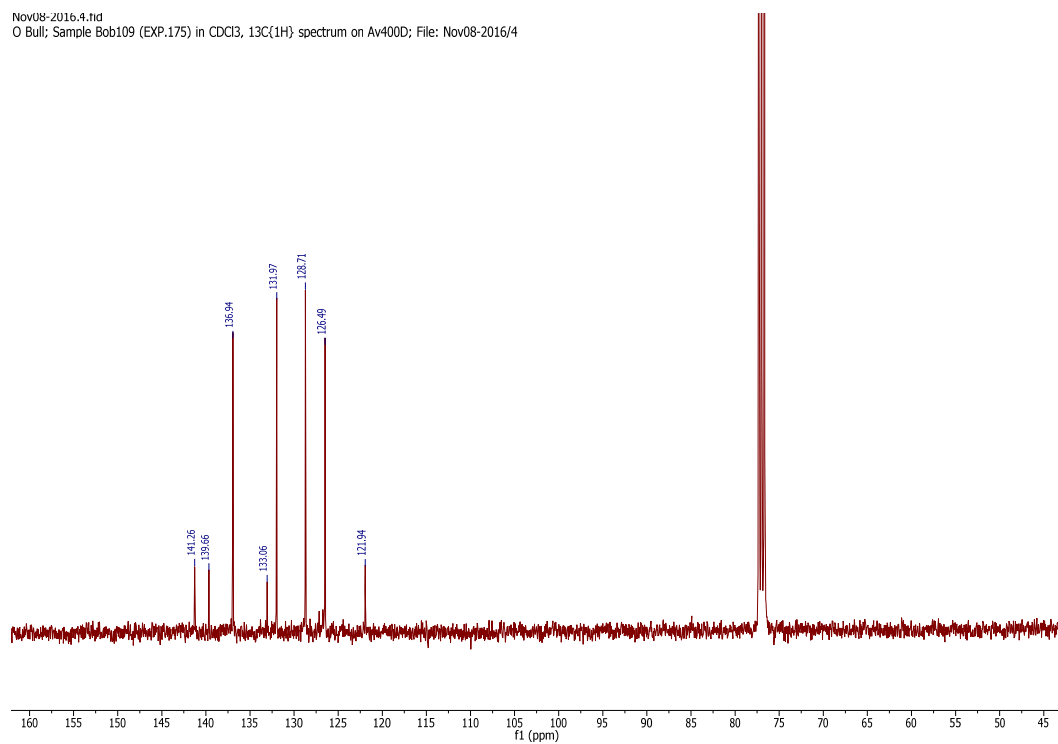
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (G) (S_{67})

Nov07-2016.20.1.1r
Bob109
1NMR for Exp. 175 in ether filtrate of product washed with warmed acetone

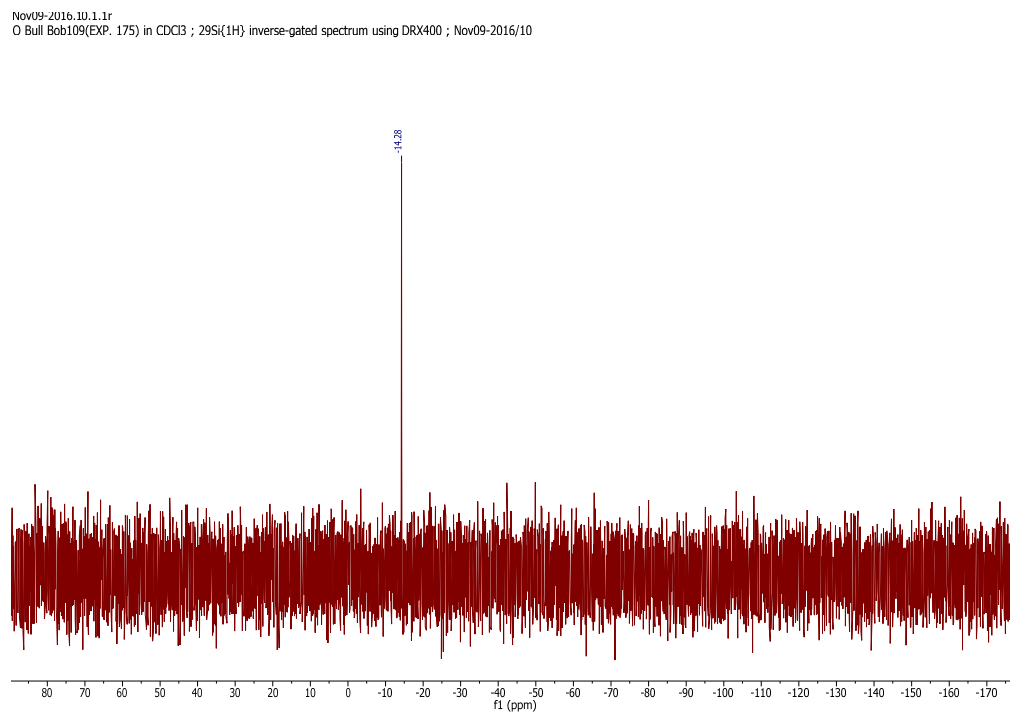


^1H spectrum of compound (J) (S_{68})

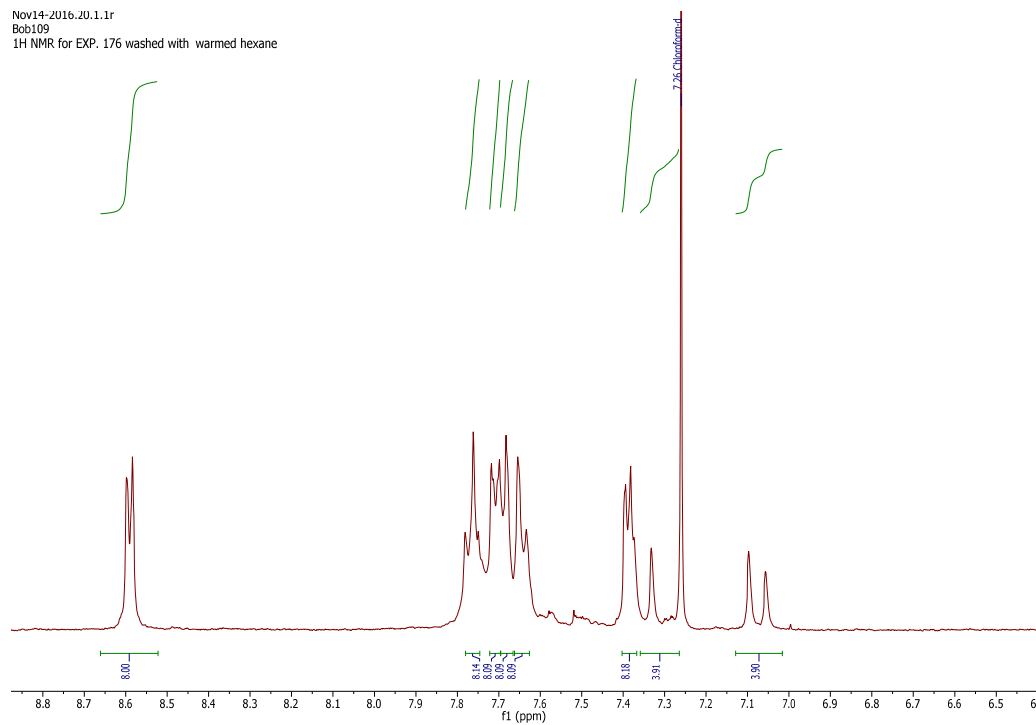
Nov08-2016.4.hd
O Bull; Sample Bob109 (EXP.175) in CDCl₃, ¹³C{¹H} spectrum on Av400D; File: Nov08-2016/4



Nov09-2016.10.1.1r
O Bull Bob109(EXP. 175) in CDCl₃; ²⁹Si{¹H} inverse-gated spectrum using DRX400; Nov09-2016/10

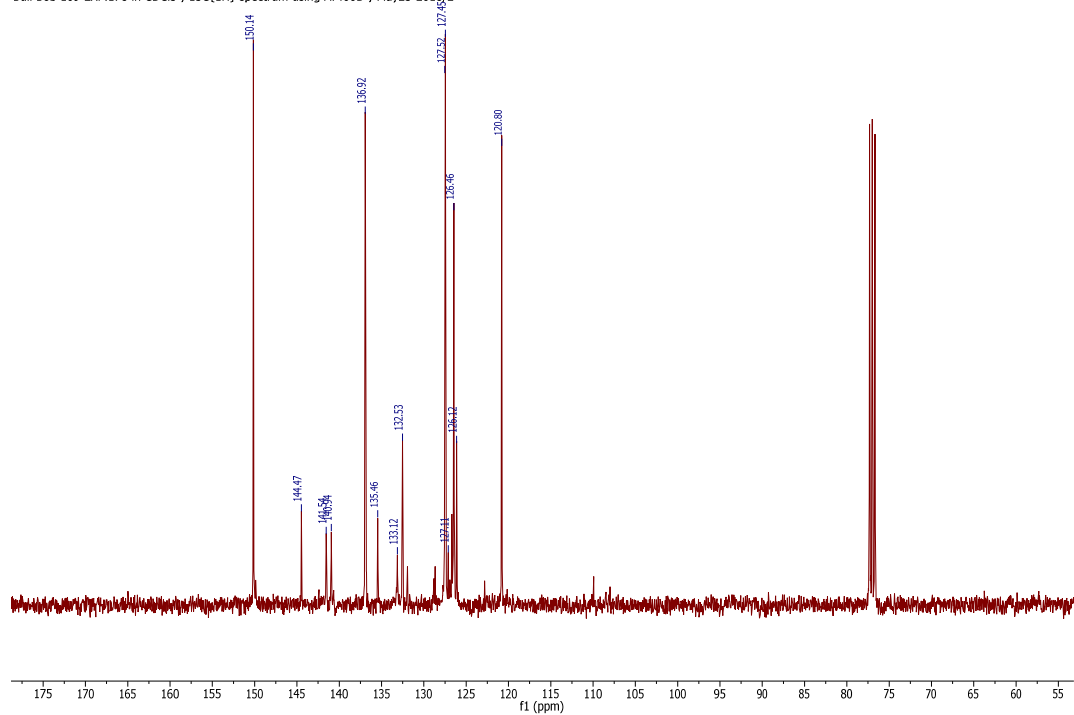


Nov14-2016.20.1.1r
 Bob109
 1H NMR for EXP. 176 washed with warmed hexane



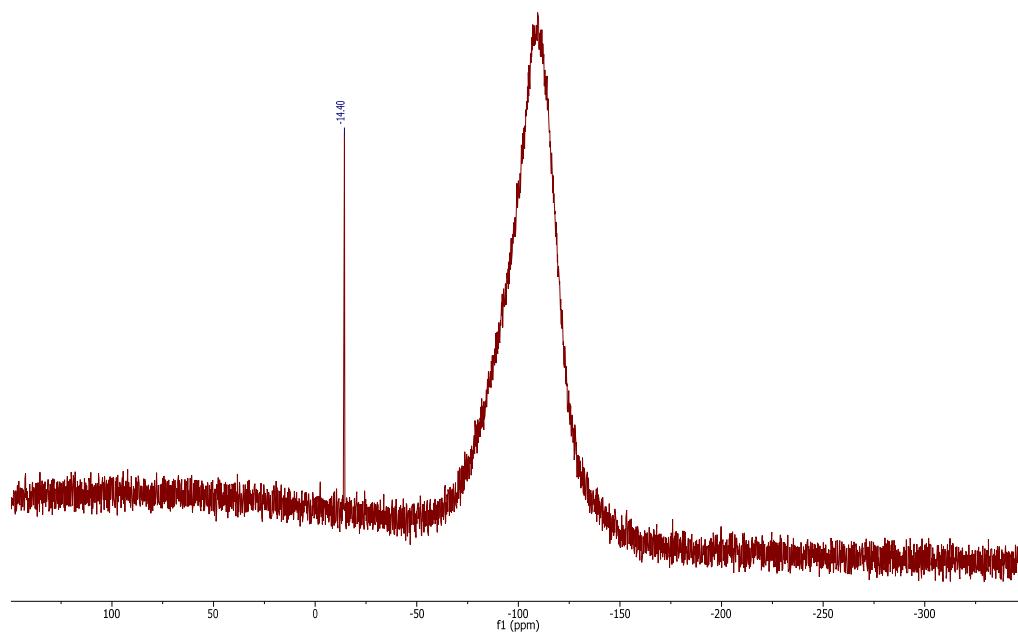
¹H spectrum of compound (L₁₃) (S₇₁)

May23-2018.2.tif
 Bull Bob 109 EXP.178 in CDCl₃ ; 13C{1H} spectrum using Av400D ; May23-2018/2



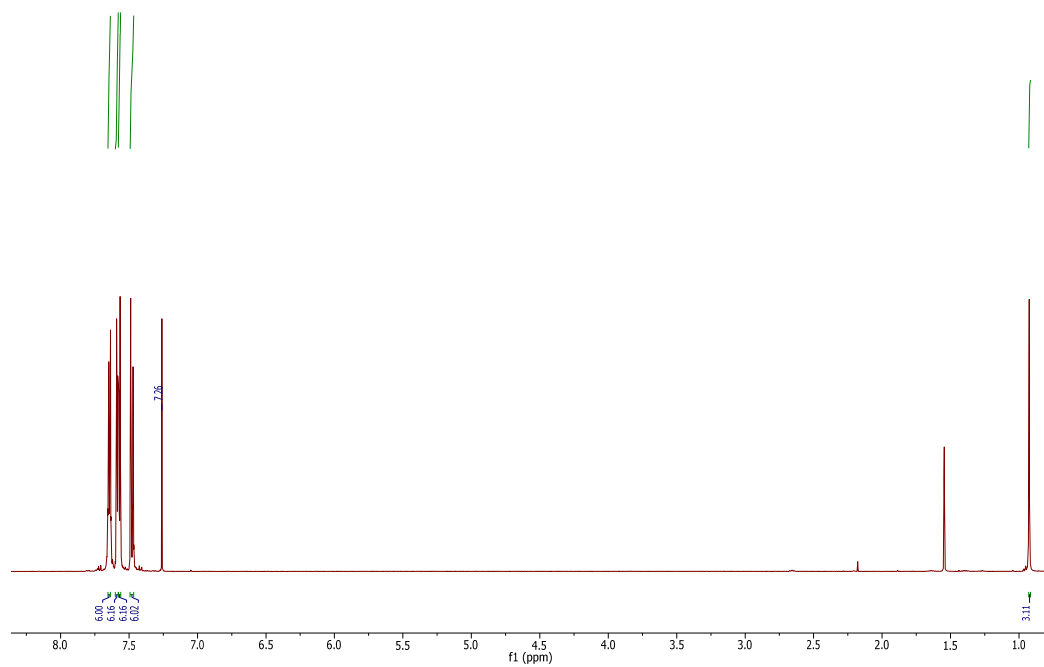
¹³C{¹H} spectrum of compound (L₁₃) (S₇₂)

May23-2018-3.fid
Bull Bob 109 EXP.178 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av400D ; May23-2018/3



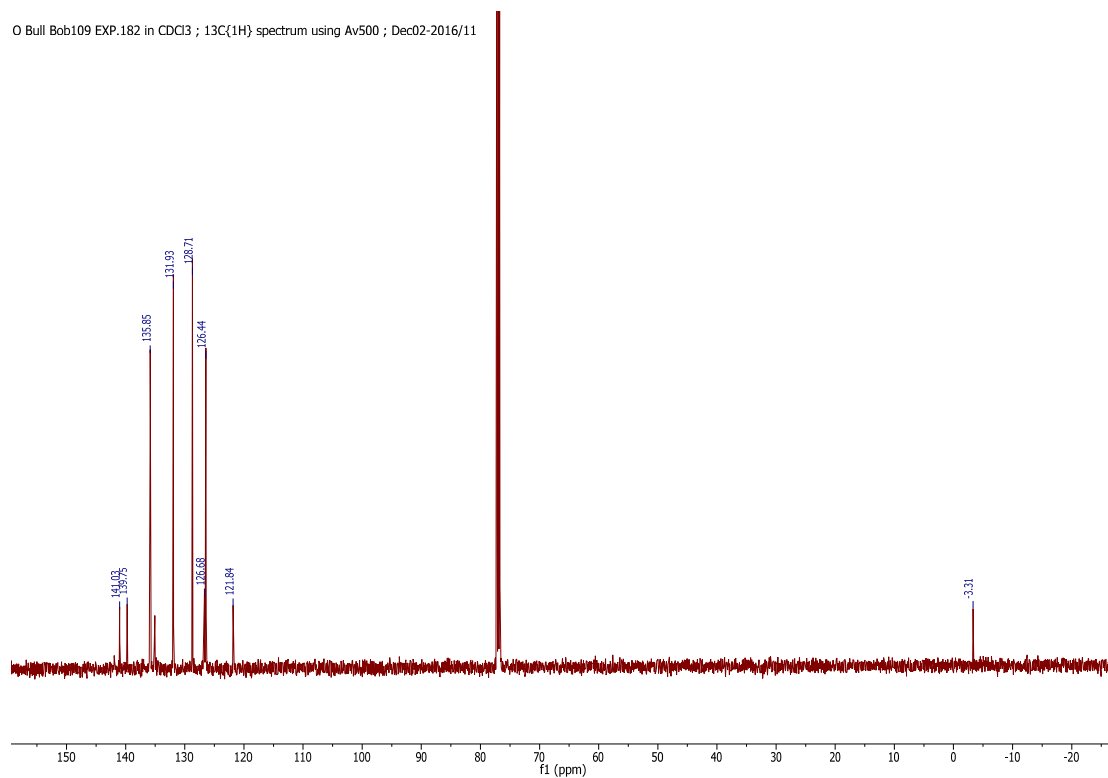
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (L₁₃) (S₇₃)

Dec02-2016-10.fid
O Bull Bob109 EXP.182 in CDCl3 ; ^1H spectrum using Av500 ; Dec02-2016/10



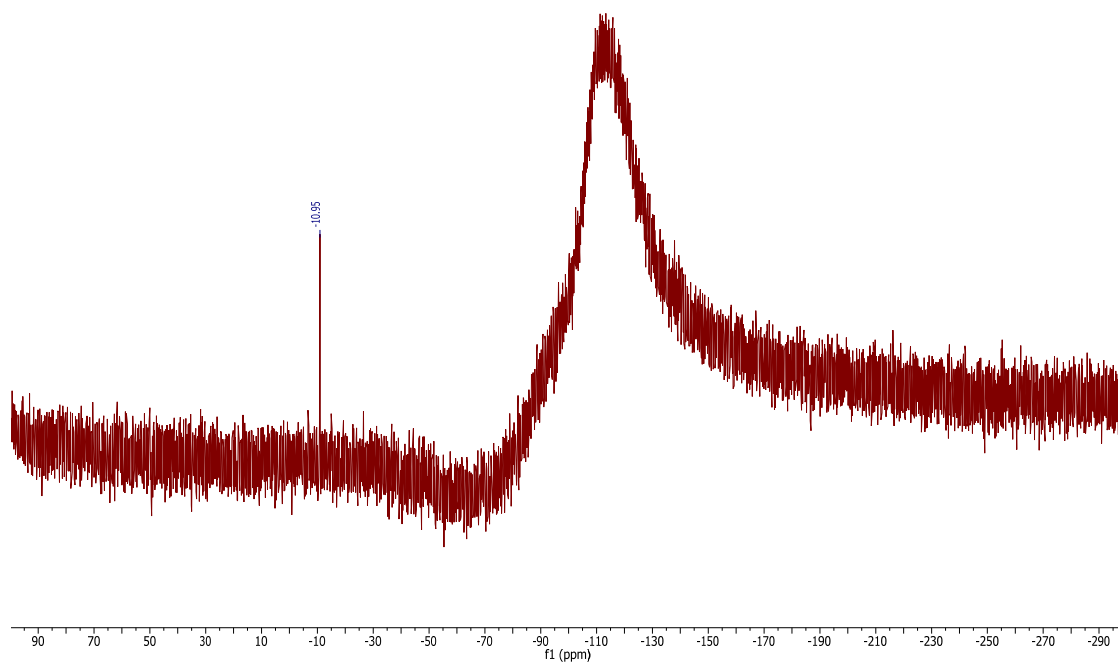
^1H spectrum of compound (K) (S₇₄)

O Bull Bob109 EXP.182 in CDCl₃ ; ¹³C{¹H} spectrum using Av500 ; Dec02-2016/11



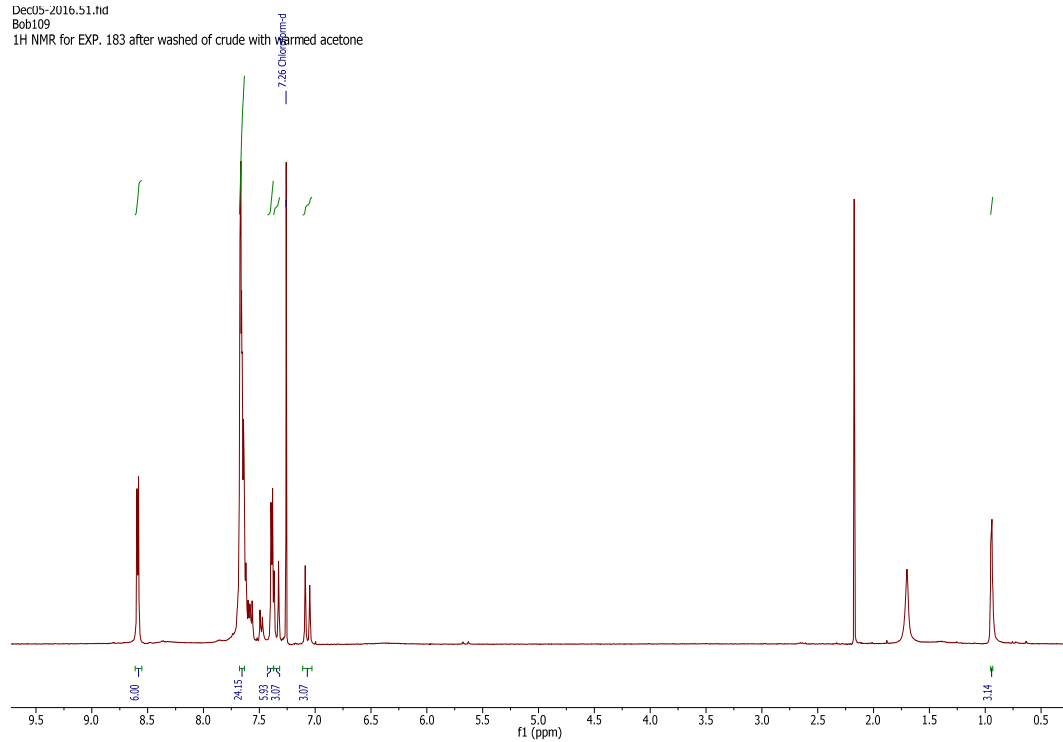
¹³C{¹H} spectrum of compound (K) (S₇₅)

Dec02-2016.12.tld
O Bull Bob109 EXP.182 in CDCl₃ ; ²⁹Si{¹H} inverse-gated spectrum using Av500 ; Dec02-2016/12



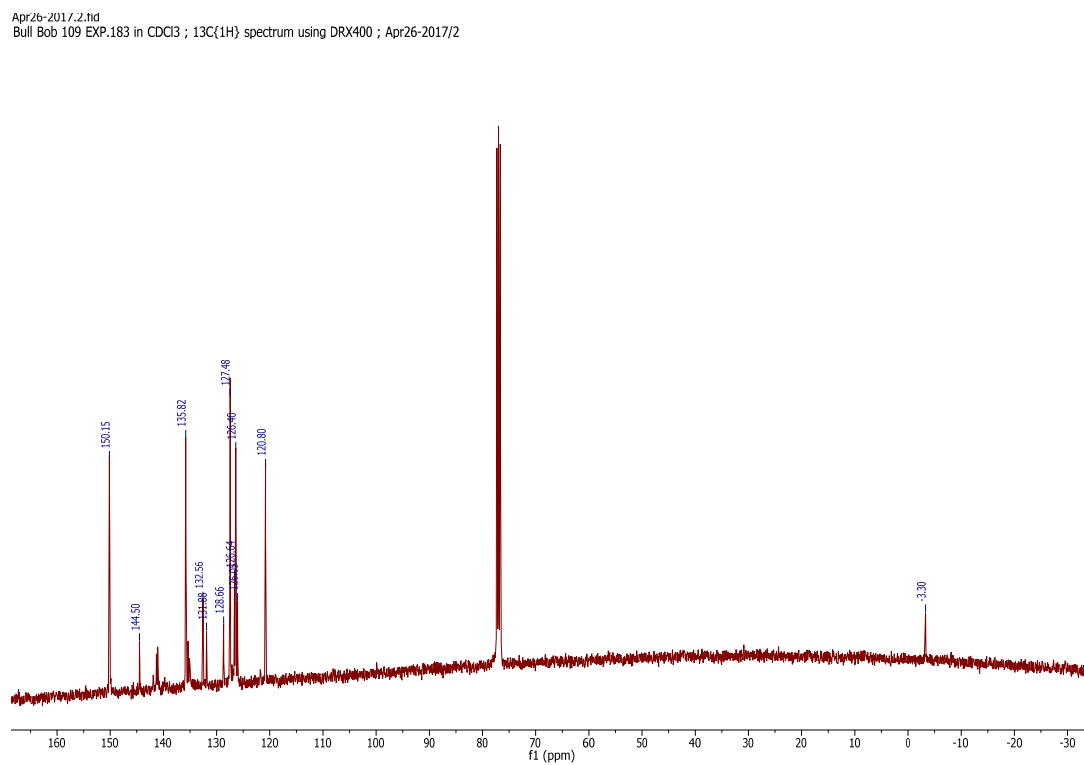
²⁹Si{¹H} spectrum for compound (K) (S₇₆)

Dec05-2016.S1.tif
 Bob109
 1H NMR for EXP. 183 after washed of crude with warmed acetone



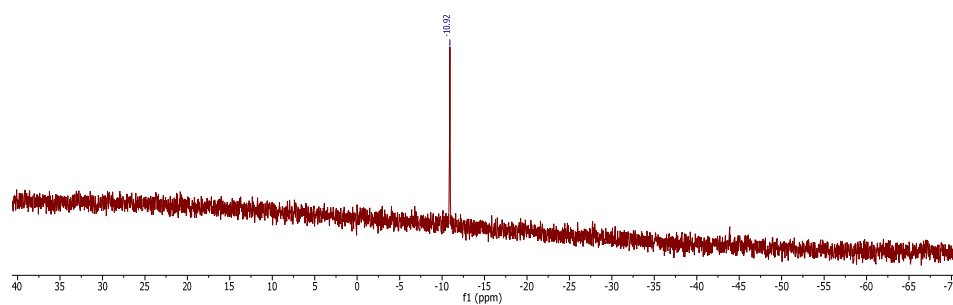
¹H spectrum of compound (L₁₄) (S₇₇)

Apr26-2017.Z.tif
 Bull Bob 109 EXP.183 in CDCl₃ ; ¹³C{¹H} spectrum using DRX400 ; Apr26-2017/2



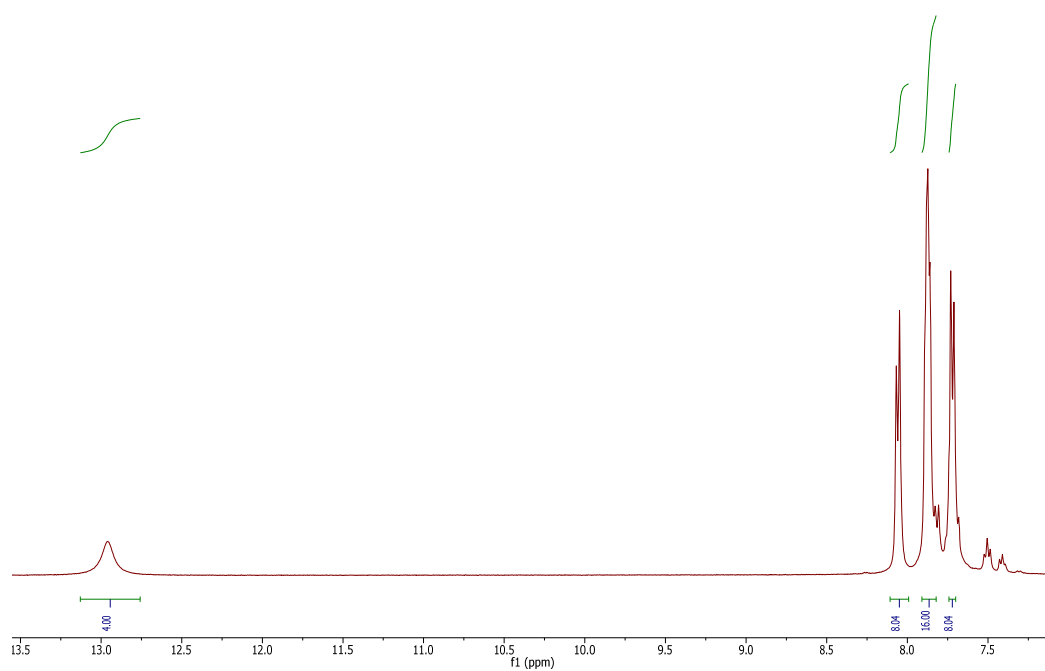
¹³C{¹H} spectrum of compound (L₁₄) (S₇₈)

Apr26-2017.3.fid
Bull Bob 109 EXP.183 in CDCl3 ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using DRX400 ; Apr26-2017/3



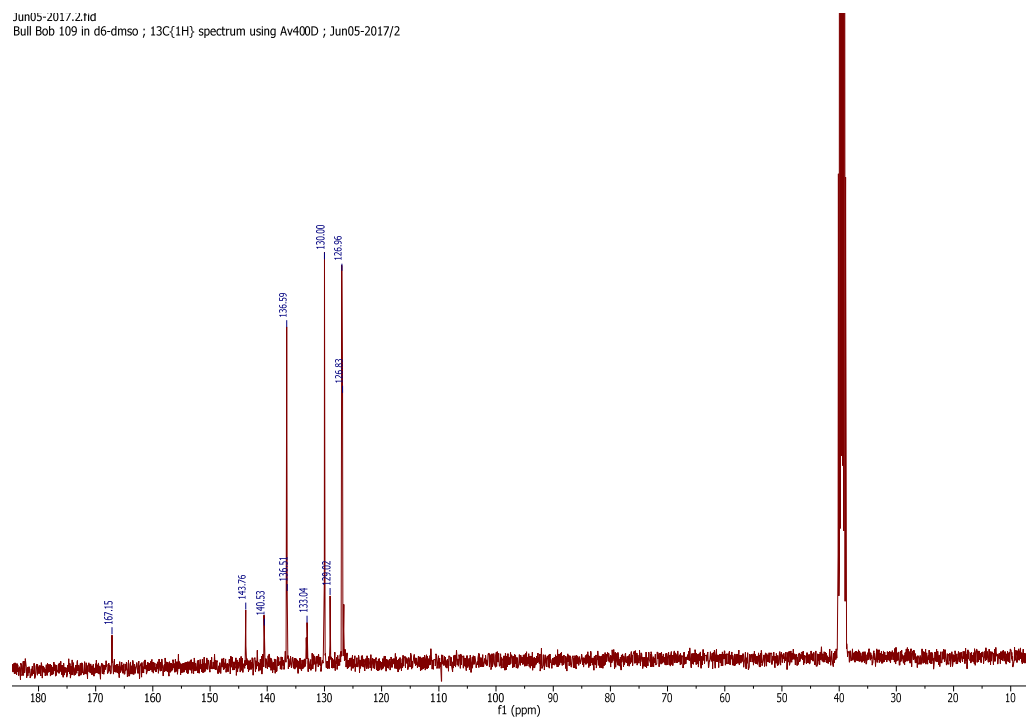
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (K) (*S*₇₉)

Jan25-2017.41.fid
Bob109
 ^1H NMR for EXP. 196 washed with Ethylacetate/hexane



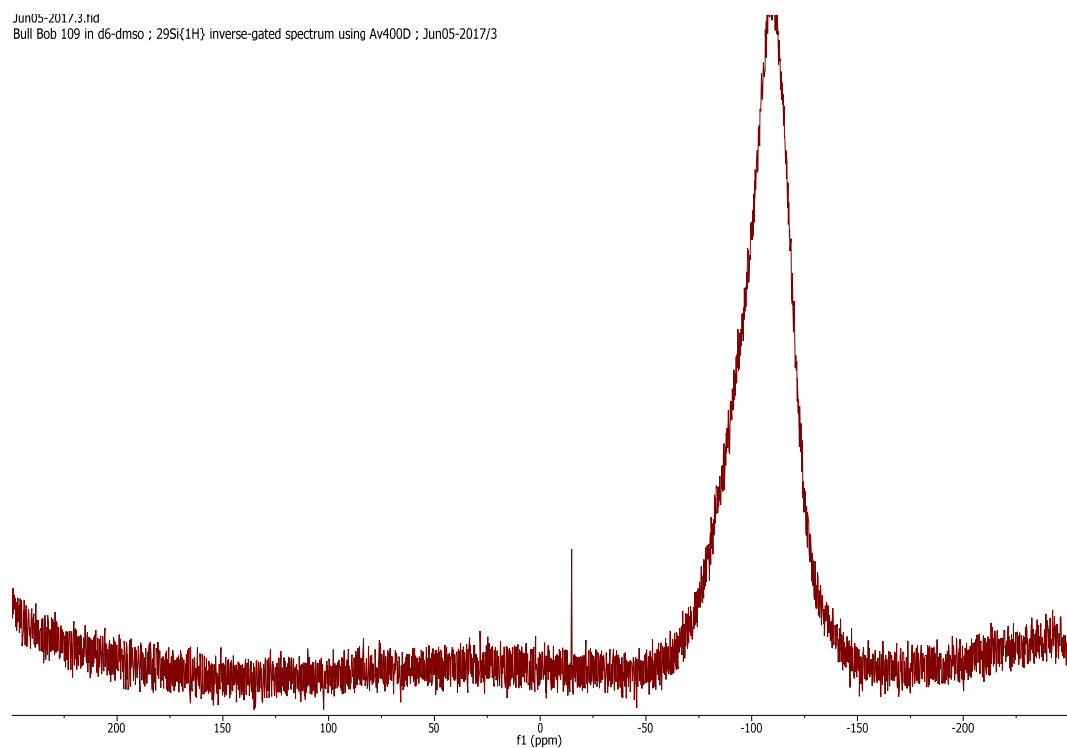
^1H spectrum of compound (*L*₁₅) (*S*₈₀)

Jun05-2017.2.fid
Bull Bob 109 in d6-dmso ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using Av400D ; Jun05-2017/2



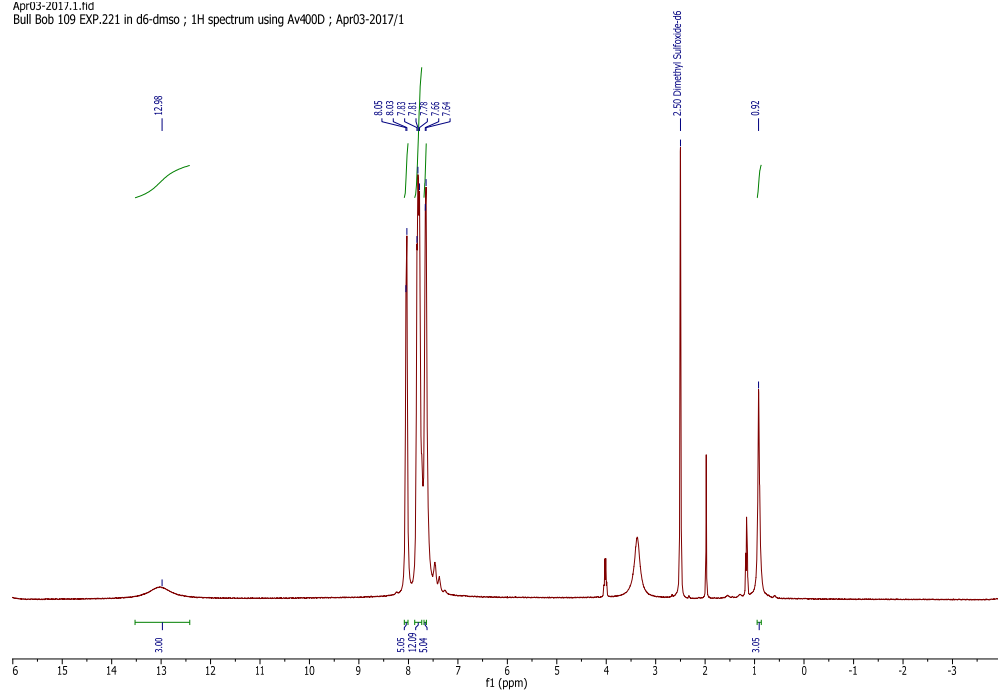
$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (L₁₅) (S₈₁)

Jun05-2017.3.fid
Bull Bob 109 in d6-dmso ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av400D ; Jun05-2017/3



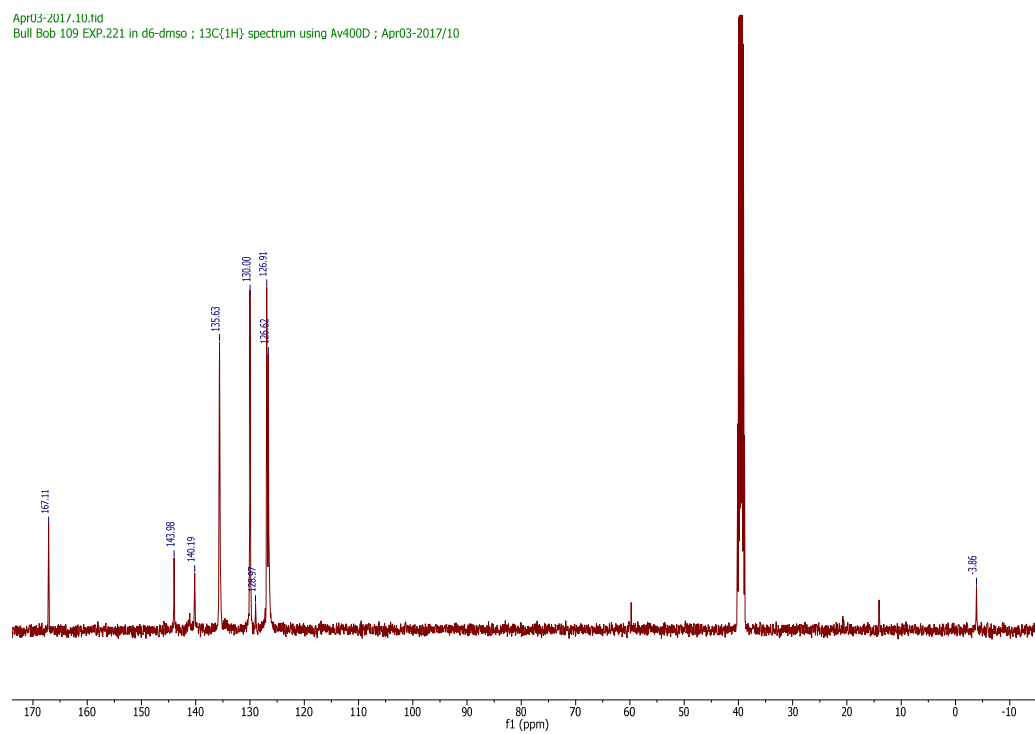
$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (L₁₅) (S₈₂)

Apr03-2017/1.tid
Bull Bob 109 EXP.221 in d6-dmso ; ^1H spectrum using Av400D ; Apr03-2017/1



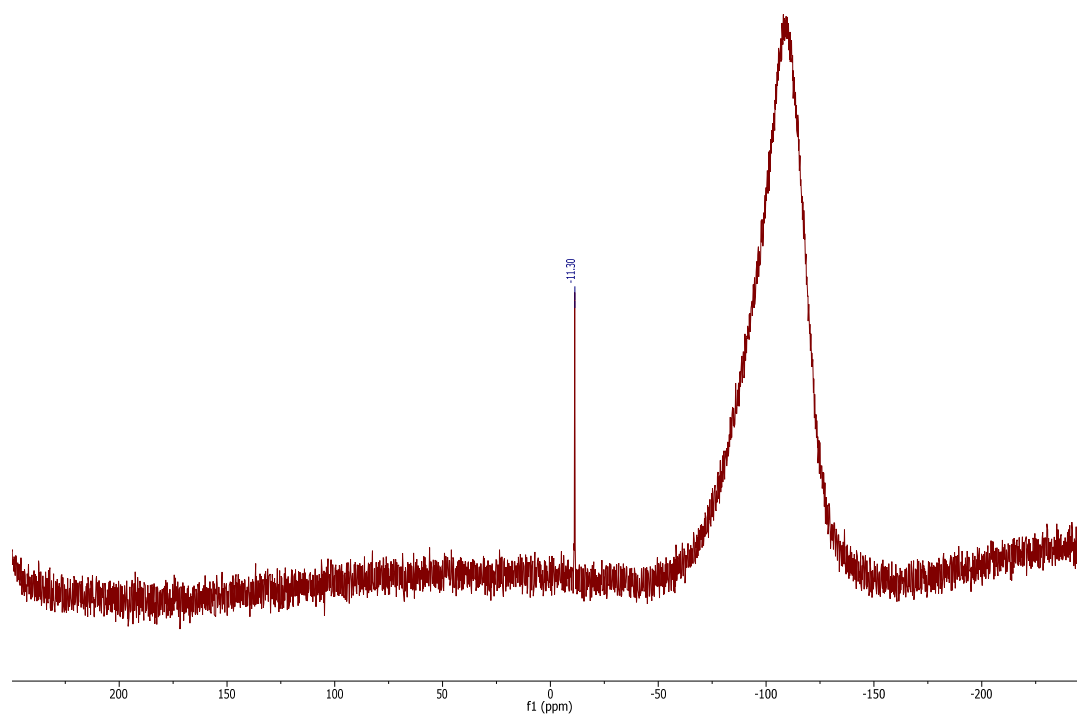
^1H spectrum of compound (L₁₆) (S₈₃)

Apr03-2017/10.tid
Bull Bob 109 EXP.221 in d6-dmso ; $^{13}\text{C}\{^1\text{H}\}$ spectrum using Av400D ; Apr03-2017/10



$^{13}\text{C}\{^1\text{H}\}$ spectrum of compound (L₁₆) (S₈₄)

Apr03-2017.11.fid
Bull Bob 109 EXP.221 in d6-dmso ; $^{29}\text{Si}\{^1\text{H}\}$ inverse-gated spectrum using Av400D ; Apr03-2017/11



$^{29}\text{Si}\{^1\text{H}\}$ spectrum for compound (**L₁₆**) (**S₈₅**)

Crystallographic Data and Crystallographic Experimental

Appendix 1

Compound	[Ph ₆ B ₂ Si ₂ O ₄].L ₁ (4)
Formula	C ₆₉ H ₅₇ B ₃ N ₃ O ₆ Si ₃ O ₆ .6(C ₁₀ H ₈ N ₂ .1.4(C ₄ H ₁₀ O))
Formula weight	1338.35
Temperature	173 K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Triclinic
Space group	P-1
Crystal colour/Morphology	Colourless blocks
Crystal size	0.58 x 0.33 x 0.20 mm ³
Unit cell dimension	a = 10.9372(4) Å α = 70.533(3)° b = 18.4221(6) Å β = 86.476(3)° c = 19.4697(6) Å γ = 88.517(3)°
Volume z	3691.6(2) Å ³ , 2
Density (calculated)	1.204 Mg/m ³
Absorption coefficient	0.122 mm ⁻¹
F(000)	1410
Θ range for data collection	2.393 to 28.211°
Index ranges	-14<=h<=14 -21<=k<=24 -24<=l<=21
Ref1ns collected/unique	21463 / 14525 [R(int) = 0.0185]
Ref1ns observed [F>4σ(F)]	10828
Absorption correction	Analytical
Max. and Min. transmission	0.978 and 0.955
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	14525 / 293 / 909
Goodness-of-fit on F ²	1.033
Final R indices [F>4σ(F)]	R1 = 0.0721, wR2 = 0.1929
R indices (all data)	R1 = 0.0963, wR2 = 0.2143
Largest diff. peak, hole	1.121, -0.903 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.002

Table 2. Bond lengths [Å] and angles [°] for [Ph₆B₂Si₂O₄].L₁ (**4**).

B(1)-O(8)	1.427(4)	O(24)-B(21)#1	1.433(4)	C(56)-C(57)	1.3900
B(1)-O(2)	1.436(4)	N(25)-C(30)	1.322(4)	C(57)-C(58)	1.3900
B(1)-C(31)	1.633(4)	N(25)-C(26)	1.322(4)	C(58)-C(59)	1.3900
B(1)-C(31')	1.665(10)	C(26)-C(27)	1.378(5)	C(59)-C(60)	1.3900
B(1)-N(9)	1.695(4)	C(27)-C(28)	1.370(5)	C(55')-C(56')	1.3900
O(2)-Si(3)	1.609(2)	C(28)-C(29)	1.376(5)	C(55')-C(60')	1.3900
Si(3)-O(4)	1.611(2)	C(28)-C(28)#2	1.490(6)	C(56')-C(57')	1.3900
Si(3)-C(37)	1.866(3)	C(29)-C(30)	1.367(5)	C(57')-C(58')	1.3900
Si(3)-C(43)	1.874(3)	C(31)-C(32)	1.3900	C(58')-C(59')	1.3900
O(4)-B(5)	1.437(4)	C(31)-C(36)	1.3900	C(59')-C(60')	1.3900
B(5)-O(6)	1.433(4)	C(32)-C(33)	1.3900	C(61)-C(62)	1.3900
B(5)-C(49)	1.610(4)	C(33)-C(34)	1.3900	C(61)-C(66)	1.3900
B(5)-N(25)	1.695(4)	C(34)-C(35)	1.3900	C(62)-C(63)	1.3900
O(6)-Si(7)	1.614(2)	C(35)-C(36)	1.3900	C(63)-C(64)	1.3900
Si(7)-O(8)	1.610(2)	C(31')-C(32')	1.3900	C(64)-C(65)	1.3900
Si(7)-C(55)	1.880(3)	C(31')-C(36')	1.3900	C(65)-C(66)	1.3900
Si(7)-C(61)	1.885(3)	C(32')-C(33')	1.3900	C(61')-C(62')	1.3900
Si(7)-C(61')	1.907(7)	C(33')-C(34')	1.3900	C(61')-C(66')	1.3900
Si(7)-C(55')	1.917(10)	C(34')-C(35')	1.3900	C(62')-C(63')	1.3900
N(9)-C(14)	1.319(4)	C(35')-C(36')	1.3900	C(63')-C(64')	1.3900
N(9)-C(10)	1.331(4)	C(37)-C(42)	1.389(4)	C(64')-C(65')	1.3900
C(10)-C(11)	1.373(5)	C(37)-C(38)	1.392(4)	C(65')-C(66')	1.3900
C(11)-C(12)	1.376(5)	C(38)-C(39)	1.398(5)	C(67)-C(72)	1.388(5)
C(12)-C(13)	1.375(4)	C(39)-C(40)	1.386(6)	C(67)-C(68)	1.395(4)
C(12)-C(15)	1.490(4)	C(40)-C(41)	1.354(6)	C(68)-C(69)	1.385(5)
C(13)-C(14)	1.377(4)	C(41)-C(42)	1.386(5)	C(69)-C(70)	1.370(6)
C(15)-C(16)	1.379(4)	C(43)-C(48)	1.395(4)	C(70)-C(71)	1.382(6)
C(15)-C(20)	1.389(4)	C(43)-C(44)	1.396(4)	C(71)-C(72)	1.389(5)
C(16)-C(17)	1.376(4)	C(44)-C(45)	1.389(4)	C(73)-C(74)	1.382(5)
C(17)-N(18)	1.336(4)	C(45)-C(46)	1.381(5)	C(73)-C(78)	1.388(4)
N(18)-C(19)	1.331(4)	C(46)-C(47)	1.376(5)	C(74)-C(75)	1.388(5)
N(18)-B(21)	1.708(4)	C(47)-C(48)	1.388(4)	C(75)-C(76)	1.379(6)
C(19)-C(20)	1.384(4)	C(49)-C(54)	1.384(5)	C(76)-C(77)	1.363(6)
B(21)-O(24)#1	1.433(4)	C(49)-C(50)	1.406(5)	C(77)-C(78)	1.378(5)
B(21)-O(22)	1.438(4)	C(50)-C(51)	1.388(5)	C(79)-C(80)	1.389(4)
B(21)-C(67)	1.609(5)	C(51)-C(52)	1.378(7)	C(79)-C(84)	1.390(5)
O(22)-Si(23)	1.621(2)	C(52)-C(53)	1.377(7)	C(80)-C(81)	1.387(5)
Si(23)-O(24)	1.610(2)	C(53)-C(54)	1.392(5)	C(81)-C(82)	1.368(6)
Si(23)-C(79)	1.872(3)	C(55)-C(56)	1.3900	C(82)-C(83)	1.373(5)
Si(23)-C(73)	1.872(3)	C(55)-C(60)	1.3900	C(83)-C(84)	1.388(5)

O(90)-C(91)	1.365(9)	O(6)-B(5)-N(25)	105.5(2)	C(67)-B(21)-N(18)	102.0(2)
O(90)-C(93)	1.445(9)	O(4)-B(5)-N(25)	102.4(2)	B(21)-O(22)-Si(23)	134.0(2)
C(91)-C(94)	1.490(13)	C(49)-B(5)-N(25)	106.2(2)	O(24)-Si(23)-O(22)	113.68(11)
C(92)-C(93)	1.486(11)	B(5)-O(6)-Si(7)	137.52(19)	O(24)-Si(23)-C(79)	111.01(13)
N(101)-C(102)	1.3900	O(8)-Si(7)-O(6)	113.88(11)	O(22)-Si(23)-C(79)	109.63(11)
N(101)-C(106)	1.3900	O(8)-Si(7)-C(55)	113.71(19)	O(24)-Si(23)-C(73)	106.64(12)
C(102)-C(103)	1.3900	O(6)-Si(7)-C(55)	104.60(17)	O(22)-Si(23)-C(73)	105.51(12)
C(103)-C(104)	1.3900	O(8)-Si(7)-C(61)	104.47(15)	C(79)-Si(23)-C(73)	110.16(13)
C(104)-C(105)	1.3900	O(6)-Si(7)-C(61)	107.0(2)	B(21)#1-O(24)-Si(23)	143.30(19)
C(104)-C(107)	1.441(7)	C(55)-Si(7)-C(61)	113.2(2)	C(30)-N(25)-C(26)	117.7(3)
C(105)-C(106)	1.3900	O(8)-Si(7)-C(61')	103.5(3)	C(30)-N(25)-B(5)	119.4(2)
C(107)-C(108)	1.3900	O(6)-Si(7)-C(61')	115.8(3)	C(26)-N(25)-B(5)	122.8(2)
C(107)-C(112)	1.3900	O(8)-Si(7)-C(55')	106.1(5)	N(25)-C(26)-C(27)	122.0(3)
C(108)-C(109)	1.3900	O(6)-Si(7)-C(55')	108.8(5)	C(28)-C(27)-C(26)	120.8(3)
C(109)-N(110)	1.3900	C(61')-Si(7)-C(55')	108.1(6)	C(27)-C(28)-C(29)	116.2(3)
N(110)-C(111)	1.3900	B(1)-O(8)-Si(7)	147.0(2)	C(27)-C(28)-C(28)#2	122.0(4)
C(111)-C(112)	1.3900	C(14)-N(9)-C(10)	117.5(3)	C(29)-C(28)-C(28)#2	121.8(3)
O(120)-C(123)	1.384(10)	C(14)-N(9)-B(1)	121.4(2)	C(30)-C(29)-C(28)	120.2(3)
O(120)-C(121)	1.404(9)	C(10)-N(9)-B(1)	121.0(2)	N(25)-C(30)-C(29)	123.1(3)
C(121)-C(122)	1.527(9)	N(9)-C(10)-C(11)	122.5(3)	C(32)-C(31)-C(36)	120
C(123)-C(124)	1.492(10)	C(10)-C(11)-C(12)	120.5(3)	C(32)-C(31)-B(1)	118.9(2)
O(8)-B(1)-O(2)	116.8(2)	C(13)-C(12)-C(11)	116.3(3)	C(36)-C(31)-B(1)	121.0(2)
O(8)-B(1)-C(31)	111.9(2)	C(13)-C(12)-C(15)	122.2(3)	C(33)-C(32)-C(31)	120
O(2)-B(1)-C(31)	114.5(2)	C(11)-C(12)-C(15)	121.5(3)	C(32)-C(33)-C(34)	120
O(8)-B(1)-C(31')	111.8(5)	C(12)-C(13)-C(14)	120.2(3)	C(35)-C(34)-C(33)	120
O(2)-B(1)-C(31')	111.0(5)	N(9)-C(14)-C(13)	122.9(3)	C(36)-C(35)-C(34)	120
O(8)-B(1)-N(9)	105.3(2)	C(16)-C(15)-C(20)	117.3(3)	C(35)-C(36)-C(31)	120
O(2)-B(1)-N(9)	103.0(2)	C(16)-C(15)-C(12)	121.2(3)	C(32')-C(31')-C(36')	120
C(31)-B(1)-N(9)	103.5(2)	C(20)-C(15)-C(12)	121.5(3)	C(32')-C(31')-B(1)	121.2(8)
C(31')-B(1)-N(9)	108.1(5)	C(17)-C(16)-C(15)	120.2(3)	C(36')-C(31')-B(1)	118.7(8)
B(1)-O(2)-Si(3)	138.80(18)	N(18)-C(17)-C(16)	122.1(3)	C(31')-C(32')-C(33')	120
O(2)-Si(3)-O(4)	113.21(11)	C(19)-N(18)-C(17)	118.7(3)	C(34')-C(33')-C(32')	120
O(2)-Si(3)-C(37)	111.00(12)	C(19)-N(18)-B(21)	122.5(2)	C(35')-C(34')-C(33')	120
O(4)-Si(3)-C(37)	105.19(12)	C(17)-N(18)-B(21)	118.6(2)	C(34')-C(35')-C(36')	120
O(2)-Si(3)-C(43)	107.53(12)	N(18)-C(19)-C(20)	122.0(3)	C(35')-C(36')-C(31')	120
O(4)-Si(3)-C(43)	112.58(11)	C(19)-C(20)-C(15)	119.7(3)	C(42)-C(37)-C(38)	117.7(3)
C(37)-Si(3)-C(43)	107.22(12)	O(24)#1-B(21)-O(22)	115.8(2)	C(42)-C(37)-Si(3)	121.0(2)
B(5)-O(4)-Si(3)	133.44(19)	O(24)#1-B(21)-C(67)	115.4(2)	C(38)-C(37)-Si(3)	121.2(2)
O(6)-B(5)-O(4)	115.4(2)	O(22)-B(21)-C(67)	113.0(3)	C(37)-C(38)-C(39)	120.8(4)
O(6)-B(5)-C(49)	112.8(3)	O(24)#1-B(21)-N(18)	102.7(2)	C(40)-C(39)-C(38)	119.5(4)
O(4)-B(5)-C(49)	113.2(3)	O(22)-B(21)-N(18)	105.8(2)	C(41)-C(40)-C(39)	120.3(3)

C(40)-C(41)-C(42)	120.3(4)	C(65)-C(66)-C(61)	120	C(105)-C(104)-C(107)	120.9(5)
C(41)-C(42)-C(37)	121.4(4)	C(62')-C(61')-C(66')	120	C(104)-C(105)-C(106)	120.0
C(48)-C(43)-C(44)	117.3(3)	C(62')-C(61')-Si(7)	124.1(6)	C(105)-C(106)-N(101)	120.0
C(48)-C(43)-Si(3)	121.9(2)	C(66')-C(61')-Si(7)	115.8(6)	C(108)-C(107)-C(112)	120.0
C(44)-C(43)-Si(3)	120.8(2)	C(61')-C(62')-C(63')	120	C(108)-C(107)-C(104)	120.1(5)
C(45)-C(44)-C(43)	121.2(3)	C(62')-C(63')-C(64')	120	C(112)-C(107)-C(104)	119.8(5)
C(46)-C(45)-C(44)	120.2(3)	C(65')-C(64')-C(63')	120	C(109)-C(108)-C(107)	120.0
C(47)-C(46)-C(45)	119.7(3)	C(66')-C(65')-C(64')	120	N(110)-C(109)-C(108)	120.0
C(46)-C(47)-C(48)	120.0(3)	C(65')-C(66')-C(61')	120	C(109)-N(110)-C(111)	120.0
C(47)-C(48)-C(43)	121.5(3)	C(72)-C(67)-C(68)	116.0(3)	C(112)-C(111)-N(110)	120.0
C(54)-C(49)-C(50)	117.4(3)	C(72)-C(67)-B(21)	122.9(3)	C(111)-C(112)-C(107)	120.0
C(54)-C(49)-B(5)	122.3(3)	C(68)-C(67)-B(21)	120.9(3)	C(123)-O(120)-C(121)	125.3(16)
C(50)-C(49)-B(5)	120.2(3)	C(69)-C(68)-C(67)	122.5(4)	O(120)-C(121)-C(122)	113.0(11)
C(51)-C(50)-C(49)	121.3(4)	C(70)-C(69)-C(68)	120.0(4)	O(120)-C(123)-C(124)	107.8(14)
C(52)-C(51)-C(50)	119.7(5)	C(69)-C(70)-C(71)	119.3(4)		
C(53)-C(52)-C(51)	120.2(4)	C(70)-C(71)-C(72)	120.0(4)		
C(52)-C(53)-C(54)	119.8(4)	C(67)-C(72)-C(71)	122.2(3)		
C(49)-C(54)-C(53)	121.6(4)	C(74)-C(73)-C(78)	116.5(3)		
C(56)-C(55)-C(60)	120.0	C(74)-C(73)-Si(23)	123.5(2)		
C(56)-C(55)-Si(7)	119.8(3)	C(78)-C(73)-Si(23)	119.9(2)		
C(60)-C(55)-Si(7)	119.7(3)	C(73)-C(74)-C(75)	121.6(3)		
C(57)-C(56)-C(55)	120.0	C(76)-C(75)-C(74)	120.0(4)		
C(58)-C(57)-C(56)	120.0	C(77)-C(76)-C(75)	119.4(3)		
C(57)-C(58)-C(59)	120.0	C(76)-C(77)-C(78)	120.0(4)		
C(60)-C(59)-C(58)	120.0	C(77)-C(78)-C(73)	122.4(3)		
C(59)-C(60)-C(55)	120.0	C(80)-C(79)-C(84)	116.9(3)		
C(56')-C(55')-C(60')	120.0	C(80)-C(79)-Si(23)	120.4(2)		
C(56')-C(55')-Si(7)	114.0(9)	C(84)-C(79)-Si(23)	122.5(2)		
C(60')-C(55')-Si(7)	125.9(9)	C(81)-C(80)-C(79)	121.7(3)		
C(57')-C(56')-C(55')	120.0	C(82)-C(81)-C(80)	120.2(3)		
C(56')-C(57')-C(58')	120.0	C(81)-C(82)-C(83)	119.5(3)		
C(59')-C(58')-C(57')	120.0	C(82)-C(83)-C(84)	120.3(4)		
C(60')-C(59')-C(58')	120.0	C(83)-C(84)-C(79)	121.4(3)		
C(59')-C(60')-C(55')	120.0	C(91)-O(90)-C(93)	113.9(7)		
C(62)-C(61)-C(66)	120.0	O(90)-C(91)-C(94)	116.4(9)		
C(62)-C(61)-Si(7)	119.9(2)	O(90)-C(93)-C(92)	107.8(7)		
C(66)-C(61)-Si(7)	120.0(2)	C(102)-N(101)-C(106)	120		
C(63)-C(62)-C(61)	120.0	N(101)-C(102)-C(103)	120		
C(62)-C(63)-C(64)	120.0	C(104)-C(103)-C(102)	120		
C(63)-C(64)-C(65)	120.0	C(103)-C(104)-C(105)	120		
C(66)-C(65)-C(64)	120.0	C(103)-C(104)-C(107)	119.1(5)		

Symmetry transformations used to generate equivalent atoms: #1 -x,-y+1,-z+2 #2 -x+2,-y,-z+1

Appendix 2

Compound	[Ph ₆ B ₂ Si ₂ O ₄].L ₁ (5)
Formula	C ₄₈ H ₄₂ B ₂ N ₂ O ₄ Si ₂
Formula weight	788.63
Temperature	173 K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Crystal colour/Morphology	Colourless blocks
Crystal size	0.60 x 0.32 x 0.18 mm ³
Unit cell dimension	a = 16.5378(4) Å α = 90° b = 12.6201(3) Å β = 96.689(2)° c = 20.4904(5) Å γ = 90°
Volume z	4247.43(18) Å ³ , 4
Density (calculated)	1.233 Mg/m ³
Absorption coefficient	0.130 mm ⁻¹
F(000)	1656
Θ range for data collection	2.480 to 28.212°
Index ranges	-21 ≤ h ≤ 14 -16 ≤ k ≤ 15 -26 ≤ l ≤ 21
Ref1ns collected/unique	14630 / 8424 [R(int) = 0.0235]
Ref1ns observed [F > 4σ(F)]	6329
Absorption correction	Analytical
Max. and Min. transmission	0.981 and 0.960
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8424 / 0 / 523
Goodness-of-fit on F ²	1.025
Final R indices [F > 4σ(F)]	R1 = 0.0455, wR2 = 0.1070
R indices (all data)	R1 = 0.0682, wR2 = 0.1201
Largest diff. peak, hole	0.767, -0.290 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

B(1)-O(8)	1.431(2)	C(30)-C(31)	1.390(3)	C(35)-Si(3)-C(29)	107.43(9)
B(1)-O(2)	1.442(3)	C(31)-C(32)	1.364(4)	B(5)-O(4)-Si(3)	133.24(12)
B(1)-C(23)	1.608(3)	C(32)-C(33)	1.376(4)	O(6)-B(5)-O(4)	115.49(16)
B(1)-N(9)	1.671(3)	C(33)-C(34)	1.382(3)	O(6)-B(5)-C(41)	111.22(17)
O(2)-Si(3)	1.6057(14)	C(35)-C(40)	1.392(3)	O(4)-B(5)-C(41)	114.24(17)
Si(3)-O(4)	1.6085(13)	C(35)-C(36)	1.397(3)	O(6)-B(5)-N(20)#1	107.20(15)
Si(3)-C(35)	1.866(2)	C(36)-C(37)	1.381(3)	O(4)-B(5)-N(20)#1	101.82(15)
Si(3)-C(29)	1.871(2)	C(37)-C(38)	1.367(4)	C(41)-B(5)-N(20)#1	105.67(14)
O(4)-B(5)	1.437(3)	C(38)-C(39)	1.388(4)	B(5)-O(6)-Si(7)	143.93(13)
B(5)-O(6)	1.432(2)	C(39)-C(40)	1.384(3)	O(6)-Si(7)-O(8)	113.07(7)
B(5)-C(41)	1.603(3)	C(41)-C(42)	1.388(3)	O(6)-Si(7)-C(47)	109.47(8)
B(5)-N(20)#1	1.702(3)	C(41)-C(46)	1.389(3)	O(8)-Si(7)-C(47)	104.60(8)
O(6)-Si(7)	1.6035(14)	C(42)-C(43)	1.388(3)	O(6)-Si(7)-C(53)	106.46(8)
Si(7)-O(8)	1.6047(14)	C(43)-C(44)	1.380(3)	O(8)-Si(7)-C(53)	111.75(8)
Si(7)-C(47)	1.868(2)	C(44)-C(45)	1.375(3)	C(47)-Si(7)-C(53)	111.58(9)
Si(7)-C(53)	1.8689(19)	C(45)-C(46)	1.388(3)	B(1)-O(8)-Si(7)	140.58(13)
N(9)-C(14)	1.335(2)	C(47)-C(48)	1.389(3)	C(14)-N(9)-C(10)	118.07(17)
N(9)-C(10)	1.337(3)	C(47)-C(52)	1.391(3)	C(14)-N(9)-B(1)	120.53(16)
C(10)-C(11)	1.374(3)	C(48)-C(49)	1.387(3)	C(10)-N(9)-B(1)	121.11(16)
C(11)-C(12)	1.384(3)	C(49)-C(50)	1.368(4)	N(9)-C(10)-C(11)	122.2(2)
C(12)-C(13)	1.381(3)	C(50)-C(51)	1.376(4)	C(10)-C(11)-C(12)	120.1(2)
C(12)-C(15)	1.508(3)	C(51)-C(52)	1.387(3)	C(13)-C(12)-C(11)	116.86(19)
C(13)-C(14)	1.368(3)	C(53)-C(54)	1.392(3)	C(13)-C(12)-C(15)	120.9(2)
C(15)-C(16)	1.508(3)	C(53)-C(58)	1.393(3)	C(11)-C(12)-C(15)	122.2(2)
C(16)-C(17)	1.505(3)	C(54)-C(55)	1.386(3)	C(14)-C(13)-C(12)	120.3(2)
C(17)-C(18)	1.378(3)	C(55)-C(56)	1.376(3)	N(9)-C(14)-C(13)	122.4(2)
C(17)-C(22)	1.385(3)	C(56)-C(57)	1.372(3)	C(16)-C(15)-C(12)	111.61(19)
C(18)-C(19)	1.374(3)	C(57)-C(58)	1.388(3)	C(17)-C(16)-C(15)	112.06(19)
C(19)-N(20)	1.339(3)	O(8)-B(1)-O(2)	115.78(17)	C(18)-C(17)-C(22)	116.75(19)
N(20)-C(21)	1.332(3)	O(8)-B(1)-C(23)	110.21(16)	C(18)-C(17)-C(16)	121.3(2)
N(20)-B(5)#2	1.702(3)	O(2)-B(1)-C(23)	116.02(17)	C(22)-C(17)-C(16)	121.9(2)
C(21)-C(22)	1.379(3)	O(8)-B(1)-N(9)	105.17(15)	C(19)-C(18)-C(17)	120.5(2)
C(23)-C(24)	1.388(3)	O(2)-B(1)-N(9)	103.26(15)	N(20)-C(19)-C(18)	122.2(2)
C(23)-C(28)	1.392(3)	C(23)-B(1)-N(9)	104.89(15)	C(21)-N(20)-C(19)	118.08(17)
C(24)-C(25)	1.380(3)	B(1)-O(2)-Si(3)	141.00(12)	C(21)-N(20)-B(5)#2	120.79(16)
C(25)-C(26)	1.382(4)	O(2)-Si(3)-O(4)	114.88(7)	C(19)-N(20)-B(5)#2	121.11(16)
C(26)-C(27)	1.366(4)	O(2)-Si(3)-C(35)	108.10(9)	N(20)-C(21)-C(22)	122.3(2)
C(27)-C(28)	1.384(3)	O(4)-Si(3)-C(35)	110.74(8)	C(21)-C(22)-C(17)	120.2(2)
C(29)-C(34)	1.394(3)	O(2)-Si(3)-C(29)	109.82(8)	C(24)-C(23)-C(28)	116.3(2)
C(29)-C(30)	1.397(3)	O(4)-Si(3)-C(29)	105.63(8)	C(24)-C(23)-B(1)	119.84(19)

C(28)-C(23)-B(1)	123.85(19)	C(55)-C(54)-C(53)	121.7(2)
C(25)-C(24)-C(23)	122.4(2)	C(56)-C(55)-C(54)	119.8(2)
C(24)-C(25)-C(26)	119.6(3)	C(57)-C(56)-C(55)	119.9(2)
C(27)-C(26)-C(25)	119.5(2)	C(56)-C(57)-C(58)	120.1(2)
C(26)-C(27)-C(28)	120.3(2)	C(57)-C(58)-C(53)	121.4(2)
C(27)-C(28)-C(23)	121.8(2)		
C(34)-C(29)-C(30)	116.9(2)		
C(34)-C(29)-Si(3)	122.33(16)		
C(30)-C(29)-Si(3)	120.77(17)		
C(31)-C(30)-C(29)	121.5(2)		
C(32)-C(31)-C(30)	119.9(2)		
C(31)-C(32)-C(33)	120.2(2)		
C(32)-C(33)-C(34)	120.1(2)		
C(33)-C(34)-C(29)	121.4(2)		
C(40)-C(35)-C(36)	117.1(2)		
C(40)-C(35)-Si(3)	120.53(16)		
C(36)-C(35)-Si(3)	122.31(17)		
C(37)-C(36)-C(35)	121.2(2)		
C(38)-C(37)-C(36)	120.4(2)		
C(37)-C(38)-C(39)	120.1(2)		
C(40)-C(39)-C(38)	119.1(2)		
C(39)-C(40)-C(35)	122.0(2)		
C(42)-C(41)-C(46)	116.91(19)		
C(42)-C(41)-B(5)	121.58(19)		
C(46)-C(41)-B(5)	121.50(18)		
C(43)-C(42)-C(41)	122.0(2)		
C(44)-C(43)-C(42)	119.7(2)		
C(45)-C(44)-C(43)	119.7(2)		
C(44)-C(45)-C(46)	120.0(2)		
C(45)-C(46)-C(41)	121.8(2)		
C(48)-C(47)-C(52)	116.96(19)		
C(48)-C(47)-Si(7)	122.74(15)		
C(52)-C(47)-Si(7)	120.20(16)		
C(49)-C(48)-C(47)	121.9(2)		
C(50)-C(49)-C(48)	119.8(2)		
C(49)-C(50)-C(51)	119.9(2)		
C(50)-C(51)-C(52)	120.0(2)		
C(51)-C(52)-C(47)	121.4(2)		
C(54)-C(53)-C(58)	117.03(18)		
C(54)-C(53)-Si(7)	122.11(16)		
C(58)-C(53)-Si(7)	120.67(15)		
Symmetry transformations used to generate equivalent atoms: #1 $x-1/2, -y+1/2, z+1/2$ #2 $x+1/2, -y+1/2, z-1/2$			

Appendix 3

Compound	[Ph ₆ B ₂ Si ₂ O ₄].L ₃ 0.5(CH ₂ Cl ₂) (6)
Formula	C ₄₈ H ₄₀ B ₂ N ₂ O ₄ Si ₂ .0.5(CH ₂ Cl ₂)
Formula weight	829.08
Temperature	173 K
Diffraction wavelength	Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system	Monoclinic
Space group	P 2 ₁ /n
Crystal colour/Morphology	Colourless obelisks
Crystal size	0.32 x 0.12 x 0.11 mm ³
Unit cell dimension	a = 15.8160(2) Å α = 90° b = 13.10732(18) Å β = 98.8090(12)° c = 20.8267(3) Å γ = 90°
Volume z	4266.55(10) Å ³ , 4
Density (calculated)	1.291 Mg/m ³
Absorption coefficient	1.707 mm ⁻¹
F(000)	1732
Θ range for data collection	3.804 to 73.797°
Index ranges	-19<=h<=17 -15<=k<=10 -18<=l<=25
Ref1ns collected/unique	13886 / 8191 [R(int) = 0.0284]
Ref1ns observed [F>4σ(F)]	6675
Absorption correction	Analytical
Max. and Min. transmission	0.882 and 0.746
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8191 / 0 / 550
Goodness-of-fit on F ²	1.023
Final R indices [F>4σ(F)]	R1 = 0.0418, wR2 = 0.1028
R indices (all data)	R1 = 0.0541, wR2 = 0.1135
Largest diff. peak, hole	0.394, -0.609 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°] for [Ph₆B₂Si₂O₄].L₃ 0.5(CH₂Cl₂) (6)

B(1)-O(2)	1.433(2)	C(30)-C(31)	1.390(3)	O(4)-Si(3)-C(29)	105.00(7)
B(1)-O(8)	1.434(2)	C(31)-C(32)	1.376(4)	O(2)-Si(3)-C(29)	110.16(8)
B(1)-C(23)	1.620(3)	C(32)-C(33)	1.386(4)	C(35)-Si(3)-C(29)	107.18(8)
B(1)-N(9)	1.680(2)	C(33)-C(34)	1.389(3)	B(5)-O(4)-Si(3)	135.55(11)
O(2)-Si(3)	1.6114(13)	C(35)-C(40)	1.392(3)	O(6)-B(5)-O(4)	115.65(14)
Si(3)-O(4)	1.6105(12)	C(35)-C(36)	1.401(3)	O(6)-B(5)-C(41)	110.32(15)
Si(3)-C(35)	1.8662(19)	C(36)-C(37)	1.397(3)	O(4)-B(5)-C(41)	114.79(15)
Si(3)-C(29)	1.8761(18)	C(37)-C(38)	1.371(4)	O(6)-B(5)-N(20)#1	107.36(14)
O(4)-B(5)	1.435(2)	C(38)-C(39)	1.384(4)	O(4)-B(5)-N(20)#1	101.26(13)
B(5)-O(6)	1.431(2)	C(39)-C(40)	1.389(3)	C(41)-B(5)-N(20)#1	106.35(13)
B(5)-C(41)	1.609(3)	C(41)-C(46)	1.393(3)	B(5)-O(6)-Si(7)	140.49(12)
B(5)-N(20)#1	1.713(2)	C(41)-C(42)	1.394(3)	O(6)-Si(7)-O(8)	112.42(7)
O(6)-Si(7)	1.6099(13)	C(42)-C(43)	1.398(3)	O(6)-Si(7)-C(47)	109.93(7)
Si(7)-O(8)	1.6101(13)	C(43)-C(44)	1.378(4)	O(8)-Si(7)-C(47)	104.62(8)
Si(7)-C(47)	1.8684(18)	C(44)-C(45)	1.376(4)	O(6)-Si(7)-C(53)	106.04(8)
Si(7)-C(53)	1.8728(17)	C(45)-C(46)	1.391(3)	O(8)-Si(7)-C(53)	112.04(7)
N(9)-C(14)	1.341(2)	C(47)-C(52)	1.396(3)	C(47)-Si(7)-C(53)	111.91(8)
N(9)-C(10)	1.343(2)	C(47)-C(48)	1.398(3)	B(1)-O(8)-Si(7)	142.25(12)
C(10)-C(11)	1.380(3)	C(48)-C(49)	1.394(3)	C(14)-N(9)-C(10)	118.64(15)
C(11)-C(12)	1.392(3)	C(49)-C(50)	1.376(4)	C(14)-N(9)-B(1)	121.48(14)
C(12)-C(13)	1.397(3)	C(50)-C(51)	1.387(4)	C(10)-N(9)-B(1)	119.78(14)
C(12)-C(15)	1.465(3)	C(51)-C(52)	1.387(3)	N(9)-C(10)-C(11)	122.18(17)
C(13)-C(14)	1.383(3)	C(53)-C(58)	1.396(3)	C(10)-C(11)-C(12)	120.00(18)
C(15)-C(16)	1.322(3)	C(53)-C(54)	1.401(3)	C(11)-C(12)-C(13)	117.22(16)
C(16)-C(17)	1.472(3)	C(54)-C(55)	1.391(3)	C(11)-C(12)-C(15)	118.92(18)
C(17)-C(22)	1.388(3)	C(55)-C(56)	1.382(4)	C(13)-C(12)-C(15)	123.79(18)
C(17)-C(18)	1.396(3)	C(56)-C(57)	1.386(3)	C(14)-C(13)-C(12)	119.78(17)
C(18)-C(19)	1.387(3)	C(57)-C(58)	1.390(3)	N(9)-C(14)-C(13)	122.17(17)
C(19)-N(20)	1.338(2)	C(60)-Cl(61)	1.724(9)	C(16)-C(15)-C(12)	126.6(2)
N(20)-C(21)	1.340(3)	C(60)-Cl(62)	1.829(13)	C(15)-C(16)-C(17)	124.01(19)
N(20)-B(5)#2	1.713(2)	O(2)-B(1)-O(8)	116.95(15)	C(22)-C(17)-C(18)	116.99(17)
C(21)-C(22)	1.382(3)	O(2)-B(1)-C(23)	115.25(15)	C(22)-C(17)-C(16)	119.83(18)
C(23)-C(24)	1.392(3)	O(8)-B(1)-C(23)	109.17(14)	C(18)-C(17)-C(16)	123.08(18)
C(23)-C(28)	1.395(3)	O(2)-B(1)-N(9)	103.65(13)	C(19)-C(18)-C(17)	119.95(18)
C(24)-C(25)	1.387(3)	O(8)-B(1)-N(9)	104.34(13)	N(20)-C(19)-C(18)	121.99(19)
C(25)-C(26)	1.376(4)	C(23)-B(1)-N(9)	106.14(13)	C(19)-N(20)-C(21)	118.56(16)
C(26)-C(27)	1.384(4)	B(1)-O(2)-Si(3)	142.16(12)	C(19)-N(20)-B(5)#2	121.23(15)
C(27)-C(28)	1.390(3)	O(4)-Si(3)-O(2)	115.51(7)	C(21)-N(20)-B(5)#2	120.11(14)
C(29)-C(34)	1.396(3)	O(4)-Si(3)-C(35)	109.62(8)	N(20)-C(21)-C(22)	122.32(18)
C(29)-C(30)	1.396(3)	O(2)-Si(3)-C(35)	109.02(8)	C(21)-C(22)-C(17)	119.98(19)

C(24)-C(23)-C(28)	117.07(19)	C(58)-C(53)-Si(7)	120.43(14)
C(24)-C(23)-B(1)	119.73(16)	C(54)-C(53)-Si(7)	121.75(15)
C(28)-C(23)-B(1)	123.18(18)	C(55)-C(54)-C(53)	121.1(2)
C(25)-C(24)-C(23)	122.0(2)	C(56)-C(55)-C(54)	120.1(2)
C(26)-C(25)-C(24)	119.9(3)	C(55)-C(56)-C(57)	119.93(18)
C(25)-C(26)-C(27)	119.5(2)	C(56)-C(57)-C(58)	119.7(2)
C(26)-C(27)-C(28)	120.3(2)	C(57)-C(58)-C(53)	121.54(19)
C(27)-C(28)-C(23)	121.2(2)	Cl(61)-C(60)-Cl(62)	106.3(5)
C(34)-C(29)-C(30)	117.27(17)		
C(34)-C(29)-Si(3)	121.49(14)		
C(30)-C(29)-Si(3)	121.13(15)		
C(31)-C(30)-C(29)	121.4(2)		
C(32)-C(31)-C(30)	120.1(2)		
C(31)-C(32)-C(33)	119.84(19)		
C(32)-C(33)-C(34)	119.8(2)		
C(33)-C(34)-C(29)	121.58(19)		
C(40)-C(35)-C(36)	117.58(18)		
C(40)-C(35)-Si(3)	118.76(14)		
C(36)-C(35)-Si(3)	123.67(16)		
C(37)-C(36)-C(35)	120.9(2)		
C(38)-C(37)-C(36)	120.0(2)		
C(37)-C(38)-C(39)	120.3(2)		
C(38)-C(39)-C(40)	119.7(2)		
C(39)-C(40)-C(35)	121.5(2)		
C(46)-C(41)-C(42)	116.82(18)		
C(46)-C(41)-B(5)	120.25(16)		
C(42)-C(41)-B(5)	122.92(17)		
C(41)-C(42)-C(43)	121.4(2)		
C(44)-C(43)-C(42)	120.0(2)		
C(45)-C(44)-C(43)	119.9(2)		
C(44)-C(45)-C(46)	119.6(2)		
C(45)-C(46)-C(41)	122.2(2)		
C(52)-C(47)-C(48)	117.25(18)		
C(52)-C(47)-Si(7)	120.83(14)		
C(48)-C(47)-Si(7)	121.81(15)		
C(49)-C(48)-C(47)	121.4(2)		
C(50)-C(49)-C(48)	120.1(2)		
C(49)-C(50)-C(51)	119.6(2)		
C(50)-C(51)-C(52)	120.2(2)		
C(51)-C(52)-C(47)	121.5(2)		
C(58)-C(53)-C(54)	117.53(17)		
Symmetry transformations used to generate equivalent atoms: #1 x+1/2,-y+1/2,z-1/2 #2 x-1/2,-y+1/2,z+1/2			

Appendix 4

Compound	[Ph ₆ B ₂ Si ₂ O ₄].L ₄ (7)
Formula	C ₄₉ H ₄₄ B ₂ N ₂ O ₄ Si ₂
Formula weight	802.66
Temperature	173 K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2
Crystal colour/Morphology	Colourless blocks
Crystal size	0.49 x 0.18 x 0.18 mm ³
Unit cell dimension	a = a = 15.1177(17) Å α = 90° b = 14.1401(18) Å β = 90° c = 9.7259(12) Å γ = 90°
Volume z	2079.1(4) Å ³ , 2
Density (calculated)	1.282 Mg/m ³
Absorption coefficient	0.134 mm ⁻¹
F(000)	844
Θ range for data collection	2.695 to 28.100°
Index ranges	-10<= <i>h</i> <=18 -18<= <i>k</i> <=17 -12<= <i>l</i> <=8
Ref1ns collected/unique	5130 / 3691 [R(int) = 0.0316]
Ref1ns observed [F>4σ(F)]	2905
Absorption correction	Analytical
Max. and Min. transmission	0.978 and 0.959
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3691 / 0 / 267
Goodness-of-fit on F ²	1.061
Final R indices [F>4σ(F)]	R1 = 0.0563, wR2 = 0.1162
R indices (all data)	R1 = 0.0753, wR2 = 0.1279
Absolute structure parameter	-0.4(2)
Largest diff. peak, hole	0.248, -0.457 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°] for [Ph₆B₂Si₂O₄].L₄ (7)

B(1)-O(4)#1	1.435(6)	O(4)-Si(3)-O(2)	115.21(15)
B(1)-O(2)	1.450(6)	O(4)-Si(3)-C(19)	107.72(18)
B(1)-C(13)	1.605(7)	O(2)-Si(3)-C(19)	108.91(18)
B(1)-N(5)	1.676(6)	O(4)-Si(3)-C(25)	109.11(19)
O(2)-Si(3)	1.618(3)	O(2)-Si(3)-C(25)	107.40(19)
Si(3)-O(4)	1.617(3)	C(19)-Si(3)-C(25)	108.32(19)
Si(3)-C(19)	1.868(5)	B(1)#1-O(4)-Si(3)	134.3(3)
Si(3)-C(25)	1.875(5)	C(6)-N(5)-C(10)	117.7(4)
O(4)-B(1)#1	1.435(6)	C(6)-N(5)-B(1)	121.9(4)
N(5)-C(6)	1.318(6)	C(10)-N(5)-B(1)	120.4(4)
N(5)-C(10)	1.334(5)	N(5)-C(6)-C(7)	122.8(5)
C(6)-C(7)	1.381(6)	C(8)-C(7)-C(6)	120.5(5)
C(7)-C(8)	1.378(7)	C(7)-C(8)-C(9)	115.5(4)
C(8)-C(9)	1.387(7)	C(7)-C(8)-C(11)	122.8(5)
C(8)-C(11)	1.511(6)	C(9)-C(8)-C(11)	121.7(4)
C(9)-C(10)	1.367(6)	C(10)-C(9)-C(8)	121.0(5)
C(11)-C(12)	1.512(6)	N(5)-C(10)-C(9)	122.3(5)
C(12)-C(11)#2	1.512(6)	C(8)-C(11)-C(12)	115.0(4)
C(13)-C(14)	1.383(6)	C(11)-C(12)-C(11)#2	113.3(6)
C(13)-C(18)	1.408(6)	C(14)-C(13)-C(18)	116.2(4)
C(14)-C(15)	1.386(7)	C(14)-C(13)-B(1)	121.3(4)
C(15)-C(16)	1.376(7)	C(18)-C(13)-B(1)	122.4(4)
C(16)-C(17)	1.374(8)	C(13)-C(14)-C(15)	122.5(4)
C(17)-C(18)	1.387(7)	C(16)-C(15)-C(14)	120.3(5)
C(19)-C(20)	1.390(6)	C(17)-C(16)-C(15)	119.0(5)
C(19)-C(24)	1.395(6)	C(16)-C(17)-C(18)	120.8(5)
C(20)-C(21)	1.372(7)	C(17)-C(18)-C(13)	121.3(5)
C(21)-C(22)	1.384(7)	C(20)-C(19)-C(24)	115.6(4)
C(22)-C(23)	1.374(7)	C(20)-C(19)-Si(3)	124.7(3)
C(23)-C(24)	1.381(7)	C(24)-C(19)-Si(3)	119.7(4)
C(25)-C(26)	1.385(6)	C(21)-C(20)-C(19)	122.8(5)
C(25)-C(30)	1.386(7)	C(20)-C(21)-C(22)	120.0(5)
C(26)-C(27)	1.392(8)	C(23)-C(22)-C(21)	119.1(5)
C(27)-C(28)	1.378(9)	C(22)-C(23)-C(24)	120.0(5)
C(28)-C(29)	1.367(9)	C(23)-C(24)-C(19)	122.5(5)
C(29)-C(30)	1.380(7)	C(26)-C(25)-C(30)	117.6(5)
O(4)#1-B(1)-O(2)	114.2(4)	C(26)-C(25)-Si(3)	119.4(4)
O(4)#1-B(1)-C(13)	116.5(4)	C(30)-C(25)-Si(3)	123.0(4)
O(2)-B(1)-C(13)	110.8(4)	C(25)-C(26)-C(27)	121.3(6)
O(4)#1-B(1)-N(5)	102.8(3)	C(28)-C(27)-C(26)	119.8(6)
O(2)-B(1)-N(5)	105.6(4)	C(29)-C(28)-C(27)	119.4(6)
C(13)-B(1)-N(5)	105.7(3)	C(28)-C(29)-C(30)	120.7(6)
B(1)-O(2)-Si(3)	128.3(3)	C(29)-C(30)-C(25)	121.1(6)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,z #2 -x+2,-y+1,z

Appendix 5

Compound	[Ph ₆ B ₂ Si ₂ O ₄].L ₅ (8)
Formula	C ₁₉₄ H ₁₆₀ B ₈ N ₁₀ O ₁₆ Si ₈ , C ₁₀ H ₈ N ₂ S ₂ , C ₄ H ₁₀ O
Formula weight	3813.53
Temperature	173 K
Diffraction wavelength	Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system	Orthorhombic
Space group	Pbcn
Crystal colour/Morphology	Colourless blocky needles
Crystal size	0.38 x 0.17 x 0.15 mm ³
Unit cell dimension	a = 22.31341(19) Å α = 90° b = 20.80794(14) Å β = 90° c = 42.3403(3) Å γ = 90°
Volume z	19658.4(2) Å ³ , 4
Density (calculated)	1.289 Mg/m ³
Absorption coefficient	2.234 mm ⁻¹
F(000)	7960
Θ range for data collection	3.577 to 73.858°
Index ranges	-27<=h<=25 -20<=k<=24 -52<=l<=32
Ref1ns collected/unique	39282 / 19091 [R(int) = 0.0276]
Ref1ns observed [F>4σ(F)]	15782
Absorption correction	Analytical
Max. and Min. transmission	0.782 and 0.619
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	19091 / 722 / 1236
Goodness-of-fit on F ²	1.032
Final R indices [F>4σ(F)]	R1 = 0.0514, wR2 = 0.1466
R indices (all data)	R1 = 0.0631, wR2 = 0.1602
Largest diff. peak, hole	0.638, -1.238 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°] for [Ph₆B₂Si₂O₄].L₅ (**8**)

B(1)-O(2)	1.435(3)	Si(25)-C(100)	1.869(3)	C(58)-C(63)	1.394(4)
B(1)-O(8)	1.442(3)	O(26)-B(27)	1.436(3)	C(59)-C(60)	1.378(4)
B(1)-C(52)	1.617(4)	B(27)-O(28)	1.441(3)	C(60)-C(61)	1.384(5)
B(1)-N(9)	1.680(3)	B(27)-C(106)	1.613(3)	C(61)-C(62)	1.375(5)
O(2)-Si(3)	1.6172(18)	B(27)-N(45)	1.703(3)	C(62)-C(63)	1.387(4)
Si(3)-O(4)	1.6140(17)	O(28)-Si(29)	1.6132(16)	C(64)-C(65)	1.3900
Si(3)-C(64')	1.862(7)	Si(29)-O(30)	1.6152(16)	C(64)-C(69)	1.3900
Si(3)-C(58)	1.874(3)	Si(29)-C(12'')	1.849(9)	C(65)-C(66)	1.3900
Si(3)-C(64)	1.8969(19)	Si(29)-C(118)	1.871(2)	C(66)-C(67)	1.3900
O(4)-B(5)	1.434(3)	Si(29)-C(112)	1.8917(19)	C(67)-C(68)	1.3900
B(5)-O(6)	1.437(3)	N(31)-C(32)	1.341(3)	C(68)-C(69)	1.3900
B(5)-C(70')	1.598(10)	N(31)-C(36)	1.341(3)	C(64')-C(65')	1.3900
B(5)-C(70)	1.646(3)	C(32)-C(33)	1.369(3)	C(64')-C(69')	1.3900
B(5)-N(31)	1.686(3)	C(33)-C(34)	1.389(3)	C(65')-C(66')	1.3900
O(6)-Si(7)	1.6152(17)	C(34)-C(35)	1.383(3)	C(66')-C(67')	1.3900
Si(7)-O(8)	1.6125(19)	C(34)-S(37)	1.765(2)	C(67')-C(68')	1.3900
Si(7)-C(82)	1.873(3)	C(35)-C(36)	1.384(3)	C(68')-C(69')	1.3900
Si(7)-C(76)	1.877(2)	S(37)-S(38)	2.0234(9)	C(70)-C(71)	1.3900
N(9)-C(10)	1.338(3)	S(38)-C(39)	1.772(3)	C(70)-C(75)	1.3900
N(9)-C(14)	1.343(3)	C(39)-C(44)	1.382(4)	C(71)-C(72)	1.3900
C(10)-C(11)	1.373(4)	C(39)-C(40)	1.391(4)	C(72)-C(73)	1.3900
C(11)-C(12)	1.394(3)	C(40)-C(41)	1.380(4)	C(73)-C(74)	1.3900
C(12)-C(13)	1.388(3)	C(41)-N(42)	1.314(5)	C(74)-C(75)	1.3900
C(12)-S(15)	1.764(2)	N(42)-C(43)	1.344(5)	C(70')-C(71')	1.3900
C(13)-C(14)	1.378(4)	C(43)-C(44)	1.386(5)	C(70')-C(75')	1.3900
S(15)-S(16)	2.0297(9)	N(45)-C(46)	1.338(3)	C(71')-C(72')	1.3900
S(16)-C(17)	1.766(2)	N(45)-C(50)	1.339(3)	C(72')-C(73')	1.3900
C(17)-C(18)	1.390(3)	C(46)-C(47)	1.378(4)	C(73')-C(74')	1.3900
C(17)-C(22)	1.393(3)	C(47)-C(48)	1.387(4)	C(74')-C(75')	1.3900
C(18)-C(19)	1.375(3)	C(48)-C(49)	1.377(4)	C(76)-C(77)	1.390(4)
C(19)-N(20)	1.339(3)	C(48)-S(51)	1.776(3)	C(76)-C(81)	1.394(4)
N(20)-C(21)	1.342(3)	C(49)-C(50)	1.381(3)	C(77)-C(78)	1.391(4)
N(20)-B(23)	1.685(3)	S(51)-S(51)#1	2.0353(18)	C(78)-C(79)	1.374(5)
C(21)-C(22)	1.376(3)	C(52)-C(53)	1.384(5)	C(79)-C(80)	1.378(5)
B(23)-O(24)	1.429(3)	C(52)-C(57)	1.401(4)	C(80)-C(81)	1.397(4)
B(23)-O(30)	1.435(3)	C(53)-C(54)	1.399(5)	C(82)-C(83)	1.391(4)
B(23)-C(88)	1.615(4)	C(54)-C(55)	1.359(7)	C(82)-C(87)	1.399(5)
O(24)-Si(25)	1.6066(17)	C(55)-C(56)	1.384(7)	C(83)-C(84)	1.391(5)
Si(25)-O(26)	1.6135(16)	C(56)-C(57)	1.392(6)	C(84)-C(85)	1.399(7)
Si(25)-C(94)	1.861(2)	C(58)-C(59)	1.389(4)	C(85)-C(86)	1.377(6)

Si(25)-C(100)	1.869(3)	C(58)-C(63)	1.394(4)	C(86)-C(87)	1.395(5)
O(26)-B(27)	1.436(3)	C(59)-C(60)	1.378(4)	C(88)-C(89)	1.396(4)
B(27)-O(28)	1.441(3)	C(60)-C(61)	1.384(5)	C(88)-C(93)	1.396(4)
B(27)-C(106)	1.613(3)	C(61)-C(62)	1.375(5)	C(89)-C(90)	1.402(4)
B(27)-N(45)	1.703(3)	C(62)-C(63)	1.387(4)	C(90)-C(91)	1.354(6)
O(28)-Si(29)	1.6132(16)	C(64)-C(65)	1.3900	C(91)-C(92)	1.382(6)
Si(29)-O(30)	1.6152(16)	C(64)-C(69)	1.3900	C(92)-C(93)	1.397(5)
Si(29)-C(12'')	1.849(9)	C(65)-C(66)	1.3900	C(94)-C(95)	1.386(4)
Si(29)-C(118)	1.871(2)	C(66)-C(67)	1.3900	C(94)-C(99)	1.387(4)
Si(29)-C(112)	1.8917(19)	C(67)-C(68)	1.3900	C(95)-C(96)	1.378(4)
N(31)-C(32)	1.341(3)	C(68)-C(69)	1.3900	C(96)-C(97)	1.353(5)
N(31)-C(36)	1.341(3)	C(64')-C(65')	1.3900	C(97)-C(98)	1.379(6)
C(32)-C(33)	1.369(3)	C(64')-C(69')	1.3900	C(98)-C(99)	1.383(5)
C(33)-C(34)	1.389(3)	C(65')-C(66')	1.3900	C(100)-C(105)	1.400(4)
C(34)-C(35)	1.383(3)	C(66')-C(67')	1.3900	C(100)-C(101)	1.403(4)
C(34)-S(37)	1.765(2)	C(67')-C(68')	1.3900	C(101)-C(102)	1.387(4)
C(35)-C(36)	1.384(3)	C(68')-C(69')	1.3900	C(102)-C(103)	1.378(5)
S(37)-S(38)	2.0234(9)	C(70)-C(71)	1.3900	C(103)-C(104)	1.383(5)
S(38)-C(39)	1.772(3)	C(70)-C(75)	1.3900	C(104)-C(105)	1.393(4)
C(39)-C(44)	1.382(4)	C(71)-C(72)	1.3900	C(106)-C(111)	1.387(4)
C(39)-C(40)	1.391(4)	C(72)-C(73)	1.3900	C(106)-C(107)	1.389(4)
C(40)-C(41)	1.380(4)	C(73)-C(74)	1.3900	C(107)-C(108)	1.392(4)
C(41)-N(42)	1.314(5)	C(74)-C(75)	1.3900	C(108)-C(109)	1.370(6)
N(42)-C(43)	1.344(5)	C(70')-C(71')	1.3900	C(109)-C(110)	1.375(6)
C(43)-C(44)	1.386(5)	C(70')-C(75')	1.3900	C(110)-C(111)	1.398(4)
N(45)-C(46)	1.338(3)	C(71')-C(72')	1.3900	C(112)-C(113)	1.3900
N(45)-C(50)	1.339(3)	C(72')-C(73')	1.3900	C(112)-C(117)	1.3900
C(46)-C(47)	1.378(4)	C(73')-C(74')	1.3900	C(113)-C(114)	1.3900
C(47)-C(48)	1.387(4)	C(74')-C(75')	1.3900	C(114)-C(115)	1.3900
C(48)-C(49)	1.377(4)	C(76)-C(77)	1.390(4)	C(115)-C(116)	1.3900
C(48)-S(51)	1.776(3)	C(76)-C(81)	1.394(4)	C(116)-C(117)	1.3900
C(49)-C(50)	1.381(3)	C(77)-C(78)	1.391(4)	C(12'')-C(13'')	1.3900
S(51)-S(51)#1	2.0353(18)	C(78)-C(79)	1.374(5)	C(12'')-C(17'')	1.3900
C(52)-C(53)	1.384(5)	C(79)-C(80)	1.378(5)	C(13'')-C(14'')	1.3900
C(52)-C(57)	1.401(4)	C(80)-C(81)	1.397(4)	C(14'')-C(15'')	1.3900
C(53)-C(54)	1.399(5)	C(82)-C(83)	1.391(4)	C(15'')-C(16'')	1.3900
C(54)-C(55)	1.359(7)	C(82)-C(87)	1.399(5)	C(16'')-C(17'')	1.3900
C(55)-C(56)	1.384(7)	C(83)-C(84)	1.391(5)	C(118)-C(119)	1.387(4)
C(56)-C(57)	1.392(6)	C(84)-C(85)	1.399(7)	C(118)-C(123)	1.390(4)
C(58)-C(59)	1.389(4)	C(85)-C(86)	1.377 (6)	C(119)-C(120)	1.391(4)

C(120)-C(121)	1.375(5)	O(6)-B(5)-C(70')	122.1(7)	O(6)-B(5)-C(70')	122.1(7)
C(121)-C(122)	1.371(5)	O(4)-B(5)-C(70)	114.6(2)	O(4)-B(5)-C(70)	114.6(2)
C(122)-C(123)	1.386(5)	O(6)-B(5)-C(70)	110.7(2)	O(6)-B(5)-C(70)	110.7(2)
N(130)-C(131)	1.3900	O(4)-B(5)-N(31)	104.59(18)	O(4)-B(5)-N(31)	104.59(18)
N(130)-C(135)	1.3900	O(6)-B(5)-N(31)	104.96(18)	O(6)-B(5)-N(31)	104.96(18)
C(131)-C(132)	1.3900	C(70')-B(5)-N(31)	104.6(8)	C(70')-B(5)-N(31)	104.6(8)
C(132)-C(133)	1.3900	C(70)-B(5)-N(31)	106.18(18)	C(70)-B(5)-N(31)	106.18(18)
C(133)-C(134)	1.3900	B(5)-O(6)-Si(7)	136.76(16)	B(5)-O(6)-Si(7)	136.76(16)
C(133)-S(136)	1.796(7)	O(8)-Si(7)-O(6)	113.83(10)	O(8)-Si(7)-O(6)	113.83(10)
C(134)-C(135)	1.3900	O(8)-Si(7)-C(82)	114.22(12)	O(8)-Si(7)-C(82)	114.22(12)
S(136)-S(137)	1.982(5)	O(6)-Si(7)-C(82)	105.53(11)	O(6)-Si(7)-C(82)	105.53(11)
S(137)-C(138)	1.779(6)	O(8)-Si(7)-C(76)	105.94(10)	O(8)-Si(7)-C(76)	105.94(10)
C(138)-C(139)	1.3900	O(6)-Si(7)-C(76)	109.18(10)	O(6)-Si(7)-C(76)	109.18(10)
C(138)-C(143)	1.3900	C(82)-Si(7)-C(76)	107.97(11)	C(82)-Si(7)-C(76)	107.97(11)
C(139)-C(140)	1.3900	B(1)-O(8)-Si(7)	140.46(17)	B(1)-O(8)-Si(7)	140.46(17)
C(140)-N(141)	1.3900	C(10)-N(9)-C(14)	118.7(2)	C(10)-N(9)-C(14)	118.7(2)
N(141)-C(142)	1.3900	C(10)-N(9)-B(1)	121.54(19)	C(10)-N(9)-B(1)	121.54(19)
C(142)-C(143)	1.3900	C(14)-N(9)-B(1)	119.6(2)	C(14)-N(9)-B(1)	119.6(2)
O(150)-C(151)#2	1.401(4)	N(9)-C(10)-C(11)	122.1(2)	N(9)-C(10)-C(11)	122.1(2)
O(150)-C(151)	1.401(4)	C(10)-C(11)-C(12)	119.4(2)	C(10)-C(11)-C(12)	119.4(2)
C(151)-C(152)	1.476(6)	C(13)-C(12)-C(11)	118.5(2)	C(13)-C(12)-C(11)	118.5(2)
O(2)-B(1)-O(8)	116.2(2)	C(13)-C(12)-S(15)	125.95(18)	C(13)-C(12)-S(15)	125.95(18)
O(2)-B(1)-C(52)	113.5(2)	C(11)-C(12)-S(15)	115.49(19)	C(11)-C(12)-S(15)	115.49(19)
O(8)-B(1)-C(52)	112.5(2)	C(14)-C(13)-C(12)	118.6(2)	C(14)-C(13)-C(12)	118.6(2)
O(2)-B(1)-N(9)	103.25(18)	N(9)-C(14)-C(13)	122.7(2)	N(9)-C(14)-C(13)	122.7(2)
O(8)-B(1)-N(9)	104.7(2)	C(12)-S(15)-S(16)	105.90(8)	C(12)-S(15)-S(16)	105.90(8)
C(52)-B(1)-N(9)	105.00(19)	C(17)-S(16)-S(15)	104.44(8)	C(17)-S(16)-S(15)	104.44(8)
B(1)-O(2)-Si(3)	137.09(16)	C(18)-C(17)-C(22)	119.0(2)	C(18)-C(17)-C(22)	119.0(2)
O(4)-Si(3)-O(2)	114.10(9)	C(18)-C(17)-S(16)	124.54(18)	C(18)-C(17)-S(16)	124.54(18)
O(4)-Si(3)-C(64')	113.4(4)	C(22)-C(17)-S(16)	116.42(18)	C(22)-C(17)-S(16)	116.42(18)
O(2)-Si(3)-C(64')	102.2(4)	C(19)-C(18)-C(17)	118.2(2)	C(19)-C(18)-C(17)	118.2(2)
O(4)-Si(3)-C(58)	113.05(10)	N(20)-C(19)-C(18)	123.1(2)	N(20)-C(19)-C(18)	123.1(2)
O(2)-Si(3)-C(58)	105.61(11)	C(19)-N(20)-C(21)	118.49(19)	C(19)-N(20)-C(21)	118.49(19)
C(64')-Si(3)-C(58)	107.6(4)	C(19)-N(20)-B(23)	118.84(18)	C(19)-N(20)-B(23)	118.84(18)
O(4)-Si(3)-C(64)	101.98(13)	C(21)-N(20)-B(23)	122.15(18)	C(21)-N(20)-B(23)	122.15(18)
O(2)-Si(3)-C(64)	112.61(13)	N(20)-C(21)-C(22)	122.2(2)	N(20)-C(21)-C(22)	122.2(2)
C(58)-Si(3)-C(64)	109.60(12)	C(21)-C(22)-C(17)	118.9(2)	C(21)-C(22)-C(17)	118.9(2)
B(5)-O(4)-Si(3)	129.84(15)	O(24)-B(23)-O(30)	116.6(2)	O(24)-B(23)-O(30)	116.6(2)
O(4)-B(5)-O(6)	114.72(19)	O(24)-B(23)-C(88)	113.7(2)	O(24)-B(23)-C(88)	113.7(2)
O(4)-B(5)-C(70')	104.1(7)	O(30)-B(23)-C(88)	112.87(19)	O(30)-B(23)-C(88)	112.87(19)
O(6)-B(5)-C(70')	122.1(7)	O(24)-B(23)-N(20)	103.20(17)	O(24)-B(23)-N(20)	103.20(17)

O(30)-B(23)-N(20)	106.31(18)	C(41)-C(40)-C(39)	118.6(3)	C(69')-C(64')-Si(3)	118.0(6)
C(88)-B(23)-N(20)	102.24(17)	N(42)-C(41)-C(40)	125.0(3)	C(64')-C(65')-C(66')	120.0
B(23)-O(24)-Si(25)	147.59(16)	C(41)-N(42)-C(43)	115.8(3)	C(67')-C(66')-C(65')	120.0
O(24)-Si(25)-O(26)	114.46(9)	N(42)-C(43)-C(44)	124.4(3)	C(66')-C(67')-C(68')	120.0
O(24)-Si(25)-C(94)	107.56(11)	C(39)-C(44)-C(43)	118.4(3)	C(69')-C(68')-C(67')	120.0
O(26)-Si(25)-C(94)	105.95(10)	C(46)-N(45)-C(50)	118.4(2)	C(68')-C(69')-C(64')	120.0
O(24)-Si(25)-C(100)	107.69(11)	C(46)-N(45)-B(27)	121.28(19)	C(71)-C(70)-C(75)	120.0
O(26)-Si(25)-C(100)	112.14(10)	C(50)-N(45)-B(27)	120.04(19)	C(71)-C(70)-B(5)	120.85(17)
C(94)-Si(25)-C(100)	108.83(10)	N(45)-C(46)-C(47)	122.4(2)	C(75)-C(70)-B(5)	119.11(17)
B(27)-O(26)-Si(25)	130.05(15)	C(46)-C(47)-C(48)	118.8(2)	C(70)-C(71)-C(72)	120.0
O(26)-B(27)-O(28)	114.07(18)	C(49)-C(48)-C(47)	119.2(2)	C(73)-C(72)-C(71)	120.0
O(26)-B(27)-C(106)	113.29(19)	C(49)-C(48)-S(51)	124.0(2)	C(72)-C(73)-C(74)	120.0
O(28)-B(27)-C(106)	112.6(2)	C(47)-C(48)-S(51)	116.83(19)	C(73)-C(74)-C(75)	120.0
O(26)-B(27)-N(45)	103.89(18)	C(48)-C(49)-C(50)	118.5(2)	C(74)-C(75)-C(70)	120.0
O(28)-B(27)-N(45)	105.75(17)	N(45)-C(50)-C(49)	122.7(2)	C(71')-C(70')-C(75')	120.0
C(106)-B(27)-N(45)	106.23(17)	C(48)-S(51)-S(51)#1	105.29(10)	C(71')-C(70')-B(5)	116.3(9)
B(27)-O(28)-Si(29)	138.64(15)	C(53)-C(52)-C(57)	116.0(3)	C(75')-C(70')-B(5)	123.7(9)
O(28)-Si(29)-O(30)	114.68(9)	C(53)-C(52)-B(1)	121.9(3)	C(70')-C(71')-C(72')	120.0
O(28)-Si(29)-C(12'')	113.8(6)	C(57)-C(52)-B(1)	122.1(3)	C(73')-C(72')-C(71')	120.0
O(30)-Si(29)-C(12'')	104.3(5)	C(52)-C(53)-C(54)	122.3(4)	C(72')-C(73')-C(74')	120.0
O(28)-Si(29)-C(118)	107.45(10)	C(55)-C(54)-C(53)	120.3(4)	C(75')-C(74')-C(73')	120.0
O(30)-Si(29)-C(118)	110.28(10)	C(54)-C(55)-C(56)	119.5(4)	C(74')-C(75')-C(70')	120.0
C(12'')-Si(29)-C(118)	106.1(7)	C(55)-C(56)-C(57)	120.0(4)	C(77)-C(76)-C(81)	117.5(2)
O(28)-Si(29)-C(112)	108.06(16)	C(56)-C(57)-C(52)	121.9(4)	C(77)-C(76)-Si(7)	122.78(19)
O(30)-Si(29)-C(112)	106.24(12)	C(59)-C(58)-C(63)	116.9(2)	C(81)-C(76)-Si(7)	119.6(2)
C(118)-Si(29)-C(112)	110.09(18)	C(59)-C(58)-Si(3)	119.9(2)	C(76)-C(77)-C(78)	121.6(3)
B(23)-O(30)-Si(29)	139.34(15)	C(63)-C(58)-Si(3)	123.22(19)	C(79)-C(78)-C(77)	120.1(3)
C(32)-N(31)-C(36)	118.6(2)	C(60)-C(59)-C(58)	122.1(3)	C(78)-C(79)-C(80)	119.7(3)
C(32)-N(31)-B(5)	118.45(19)	C(59)-C(60)-C(61)	120.1(3)	C(79)-C(80)-C(81)	120.3(3)
C(36)-N(31)-B(5)	122.48(19)	C(62)-C(61)-C(60)	119.0(3)	C(76)-C(81)-C(80)	120.9(3)
N(31)-C(32)-C(33)	122.8(2)	C(61)-C(62)-C(63)	120.6(3)	C(83)-C(82)-C(87)	117.9(3)
C(32)-C(33)-C(34)	118.6(2)	C(62)-C(63)-C(58)	121.3(3)	C(83)-C(82)-Si(7)	121.1(2)
C(35)-C(34)-C(33)	119.0(2)	C(65)-C(64)-C(69)	120.00	C(87)-C(82)-Si(7)	120.9(2)
C(35)-C(34)-S(37)	125.58(19)	C(65)-C(64)-Si(3)	119.68(15)	C(84)-C(83)-C(82)	121.7(3)
C(33)-C(34)-S(37)	115.36(18)	C(69)-C(64)-Si(3)	120.30(15)	C(83)-C(84)-C(85)	119.1(3)
C(34)-C(35)-C(36)	118.9(2)	C(66)-C(65)-C(64)	120.00	C(86)-C(85)-C(84)	120.3(3)
N(31)-C(36)-C(35)	121.9(2)	C(67)-C(66)-C(65)	120.00	C(85)-C(86)-C(87)	119.9(4)
C(34)-S(37)-S(38)	105.63(9)	C(68)-C(67)-C(66)	120.00	C(86)-C(87)-C(82)	121.1(3)
C(39)-S(38)-S(37)	103.31(9)	C(67)-C(68)-C(69)	120.00	C(89)-C(88)-C(93)	115.9(3)
C(44)-C(39)-C(40)	117.9(3)	C(68)-C(69)-C(64)	120.00	C(89)-C(88)-B(23)	121.3(2)
C(44)-C(39)-S(38)	117.6(2)	C(65')-C(64')-C(69')	120.00	C(93)-C(88)-B(23)	122.6(2)
C(40)-C(39)-S(38)	124.6(2)	C(65')-C(64')-Si(3)	121.9(6)	C(88)-C(89)-C(90)	121.8(3)

C(91)-C(90)-C(89)	121.0(3)	C(13'')-C(12'')-C(17'')	120
C(90)-C(91)-C(92)	119.0(3)	C(13'')-C(12'')-Si(29)	118.3(9)
C(91)-C(92)-C(93)	120.3(3)	C(17'')-C(12'')-Si(29)	121.5(9)
C(88)-C(93)-C(92)	122.0(3)	C(14'')-C(13'')-C(12'')	120.0
C(95)-C(94)-C(99)	116.9(2)	C(13'')-C(14'')-C(15'')	120.0
C(95)-C(94)-Si(25)	120.2(2)	C(16'')-C(15'')-C(14'')	120.0
C(99)-C(94)-Si(25)	122.9(2)	C(17'')-C(16'')-C(15'')	120.0
C(96)-C(95)-C(94)	122.8(3)	C(16'')-C(17'')-C(12'')	120.0
C(97)-C(96)-C(95)	119.2(3)	C(119)-C(118)-C(123)	117.1(2)
C(96)-C(97)-C(98)	120.0(3)	C(119)-C(118)-Si(29)	123.54(19)
C(97)-C(98)-C(99)	120.6(4)	C(123)-C(118)-Si(29)	119.3(2)
C(98)-C(99)-C(94)	120.5(3)	C(118)-C(119)-C(120)	121.5(3)
C(105)-C(100)-C(101)	117.5(2)	C(121)-C(120)-C(119)	119.9(3)
C(105)-C(100)-Si(25)	120.76(19)	C(122)-C(121)-C(120)	119.7(3)
C(101)-C(100)-Si(25)	121.7(2)	C(121)-C(122)-C(123)	120.1(3)
C(102)-C(101)-C(100)	120.8(3)	C(122)-C(123)-C(118)	121.6(3)
C(103)-C(102)-C(101)	120.6(3)	C(131)-N(130)-C(135)	120.0
C(102)-C(103)-C(104)	120.0(3)	N(130)-C(131)-C(132)	120.0
C(103)-C(104)-C(105)	119.6(3)	C(131)-C(132)-C(133)	120.0
C(104)-C(105)-C(100)	121.5(3)	C(134)-C(133)-C(132)	120.0
C(111)-C(106)-C(107)	117.0(2)	C(134)-C(133)-S(136)	114.6(6)
C(111)-C(106)-B(27)	121.8(2)	C(132)-C(133)-S(136)	125.3(6)
C(107)-C(106)-B(27)	121.2(2)	C(133)-C(134)-C(135)	120.0
C(106)-C(107)-C(108)	121.7(3)	C(134)-C(135)-N(130)	120.0
C(109)-C(108)-C(107)	119.7(3)	C(133)-S(136)-S(137)	107.7(4)
C(108)-C(109)-C(110)	120.5(3)	C(138)-S(137)-S(136)	106.0(4)
C(109)-C(110)-C(111)	119.2(3)	C(139)-C(138)-C(143)	120.0
C(106)-C(111)-C(110)	121.9(3)	C(139)-C(138)-S(137)	124.7(5)
C(113)-C(112)-C(117)	120.0	C(143)-C(138)-S(137)	115.3(5)
C(113)-C(112)-Si(29)	121.08(16)	C(138)-C(139)-C(140)	120.0
C(117)-C(112)-Si(29)	118.91(16)	C(139)-C(140)-N(141)	120.0
C(114)-C(113)-C(112)	120.0	C(142)-N(141)-C(140)	120.0
C(113)-C(114)-C(115)	120.0	C(143)-C(142)-N(141)	120.0
C(116)-C(115)-C(114)	120.0	C(142)-C(143)-C(138)	120.0
C(115)-C(116)-C(117)	120.0	C(151)#2-O(150)-C(151)	112.4(4)
C(116)-C(117)-C(112)	120.0	O(150)-C(151)-C(152)	110.5(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y,-z+3/2 #2 -x+2,y,-z+1/2

Appendix 6

Compound	Ph₈B₄Si₂O₆.L₆ (9)
Formula	C ₅₈ H ₄₈ B ₄ N ₄ O ₆ Si ₂
Formula weight	996.42
Temperature	173(2) K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Monoclinic
Space group	P2 ₁ /c
Crystal colour/Morphology	Orange-brown plates
Crystal size	0.46 x 0.42 x 0.04 mm ³
Unit cell dimension	a = 11.0879(4) Å α = 90° b = 14.3707(4) Å β = 98.759(3)° c = 16.2697(5) Å γ = 90°
Volume z	2562.20(13) Å ³ , 2
Density (calculated)	1.292 Mg/m ³
Absorption coefficient	0.126 mm ⁻¹
F(000)	1040
Θ range for data collection	2.533 to 28.245°
Index ranges	-13<=h<=9 -16<=k<=18 -13<=l<=21
Ref1ns collected/unique	8564 / 5118 [R(int) = 0.0299]
Ref1ns observed [F>4σ(F)]	3893
Absorption correction	Analytical
Max. and Min. transmission	0.995 and 0.955
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5118 / 0 / 334
Goodness-of-fit on F ²	1.049
Final R indices [F>4σ(F)]	R1 = 0.0570, wR2 = 0.1394
R indices (all data)	R1 = 0.0789, wR2 = 0.1559
Largest diff. peak, hole	0.348, -0.552 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°] for $\text{Ph}_8\text{B}_4\text{Si}_2\text{O}_6\cdot\text{L}_6$ (9)

B(1)-O(6)	1.446(3)	C(34)-C(35)	1.371(5)	C(25)-C(20)-C(21)	117.5(2)
B(1)-O(2)	1.451(3)	C(35)-C(36)	1.390(5)	C(25)-C(20)-B(3)	122.7(2)
B(1)-C(14)	1.614(4)	C(36)-C(37)	1.371(4)	C(21)-C(20)-B(3)	119.8(2)
B(1)-N(7)	1.670(3)	O(6)-B(1)-O(2)	115.7(2)	C(22)-C(21)-C(20)	121.2(3)
O(2)-B(3)	1.346(3)	O(6)-B(1)-C(14)	114.5(2)	C(23)-C(22)-C(21)	120.1(3)
B(3)-O(4)	1.373(3)	O(2)-B(1)-C(14)	111.44(19)	C(24)-C(23)-C(22)	119.9(3)
B(3)-C(20)	1.569(3)	O(6)-B(1)-N(7)	105.08(17)	C(23)-C(24)-C(25)	120.4(3)
O(4)-Si(5)	1.6573(17)	O(2)-B(1)-N(7)	103.80(18)	C(24)-C(25)-C(20)	120.9(2)
Si(5)-O(6)	1.6116(16)	C(14)-B(1)-N(7)	104.82(17)	C(31)-C(26)-C(27)	117.2(2)
Si(5)-C(26)	1.845(2)	B(3)-O(2)-B(1)	127.08(19)	C(31)-C(26)-Si(5)	122.47(19)
Si(5)-C(32)	1.868(3)	O(2)-B(3)-O(4)	121.7(2)	C(27)-C(26)-Si(5)	120.2(2)
N(7)-C(12)	1.338(3)	O(2)-B(3)-C(20)	118.0(2)	C(28)-C(27)-C(26)	121.0(3)
N(7)-C(8)	1.339(3)	O(4)-B(3)-C(20)	120.2(2)	C(29)-C(28)-C(27)	120.3(3)
C(8)-C(9)	1.381(3)	B(3)-O(4)-Si(5)	122.40(15)	C(30)-C(29)-C(28)	119.5(3)
C(9)-C(10)	1.376(3)	O(6)-Si(5)-O(4)	106.46(9)	C(29)-C(30)-C(31)	120.4(3)
C(10)-C(11)	1.387(3)	O(6)-Si(5)-C(26)	113.58(10)	C(30)-C(31)-C(26)	121.5(3)
C(10)-N(13)	1.432(3)	O(4)-Si(5)-C(26)	106.55(10)	C(37)-C(32)-C(33)	117.6(3)
C(11)-C(12)	1.371(3)	O(6)-Si(5)-C(32)	111.02(10)	C(37)-C(32)-Si(5)	120.6(2)
N(13)-N(13)#1	1.238(4)	O(4)-Si(5)-C(32)	108.64(10)	C(33)-C(32)-Si(5)	121.6(2)
C(14)-C(15)	1.382(3)	C(26)-Si(5)-C(32)	110.32(11)	C(34)-C(33)-C(32)	121.8(3)
C(14)-C(19)	1.387(3)	B(1)-O(6)-Si(5)	123.75(15)	C(35)-C(34)-C(33)	119.3(3)
C(15)-C(16)	1.396(4)	C(12)-N(7)-C(8)	119.2(2)	C(34)-C(35)-C(36)	120.3(3)
C(16)-C(17)	1.374(4)	C(12)-N(7)-B(1)	121.12(18)	C(37)-C(36)-C(35)	119.7(3)
C(17)-C(18)	1.372(4)	C(8)-N(7)-B(1)	119.67(19)	C(36)-C(37)-C(32)	121.3(3)
C(18)-C(19)	1.389(4)	N(7)-C(8)-C(9)	121.7(2)		
C(20)-C(25)	1.394(3)	C(10)-C(9)-C(8)	118.8(2)		
C(20)-C(21)	1.398(3)	C(9)-C(10)-C(11)	119.6(2)		
C(21)-C(22)	1.380(4)	C(9)-C(10)-N(13)	116.9(2)		
C(22)-C(23)	1.375(4)	C(11)-C(10)-N(13)	123.6(2)		
C(23)-C(24)	1.373(4)	C(12)-C(11)-C(10)	118.3(2)		
C(24)-C(25)	1.384(4)	N(7)-C(12)-C(11)	122.4(2)		
C(26)-C(31)	1.385(4)	N(13)#1-N(13)-C(10)	112.9(2)		
C(26)-C(27)	1.388(4)	C(15)-C(14)-C(19)	117.1(2)		
C(27)-C(28)	1.379(4)	C(15)-C(14)-B(1)	122.9(2)		
C(28)-C(29)	1.375(4)	C(19)-C(14)-B(1)	119.9(2)		
C(29)-C(30)	1.359(4)	C(14)-C(15)-C(16)	122.0(2)		
C(30)-C(31)	1.379(4)	C(17)-C(16)-C(15)	119.2(3)		
C(32)-C(37)	1.388(4)	C(18)-C(17)-C(16)	120.1(3)		
C(32)-C(33)	1.391(4)	C(17)-C(18)-C(19)	119.9(3)		
C(33)-C(34)	1.379(4)	C(14)-C(19)-C(18)	121.6(2)		
Symmetry transformations used to generate equivalent atoms:					
#1 -x+1, -y, -z					

Appendix 7

Compound	4(Ph₂Si(OH)₂),3(C₁₀H₈N₄) (10)
Formula	4(C ₁₂ H ₁₂ O ₂ Si),3(C ₁₀ H ₈ N ₄)
Formula weight	1417.83
Temperature	173(2) K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Triclinic
Space group	P-1
Crystal colour/Morphology	Orange blocky needles
Crystal size	0.64 x 0.27 x 0.13 mm ³
Unit cell dimension	a = 12.2352(3) Å α = 89.879(3)° b = 15.3274(6) Å β = 89.988(2)° c = 20.0271(6) Å γ = 78.298(3)°
Volume z	3677.7(2) Å ³ , 2
Density (calculated)	1.280 Mg/m ³
Absorption coefficient	0.146 mm ⁻¹
F(000)	1488
Θ range for data collection	2.443 to 28.104°
Index ranges	-12<= <i>h</i> <=15 -20<= <i>k</i> <=18 -25<= <i>l</i> <=25
Ref1ns collected/unique	20569 / 20569 [R(int) = 0.0299]
Ref1ns observed [F>4σ(F)]	12089
Absorption correction	Analytical
Max. and Min. transmission	0.983 and 0.941
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	20569 / 649 / 991
Goodness-of-fit on F ²	0.891
Final R indices [F>4σ(F)]	R1 = 0.0470, wR2 = 0.1013
R indices (all data)	R1 = 0.0891, wR2 = 0.1098
Largest diff. peak, hole	1.037, -0.500 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°] for 4(Ph₂Si(OH)₂),3(C₁₀H₈N₄) (**10**)

Si(1A)-O(2A)	1.6126(18)	C(4C)-C(5C)	1.364(4)	N(20B)-C(21B)	1.342(3)
Si(1A)-O(1A)	1.6176(18)	C(5C)-C(6C)	1.378(4)	C(21B)-C(22B)	1.386(3)
Si(1A)-C(1A)	1.862(3)	C(7C)-C(12C)	1.402(3)	C(22B)-C(23B)	1.366(3)
Si(1A)-C(7A)	1.865(3)	C(7C)-C(8C)	1.404(3)	C(23B)-C(24B)	1.379(4)
C(1A)-C(2A)	1.384(4)	C(8C)-C(9C)	1.387(4)	C(23B)-N(26B)	1.469(3)
C(1A)-C(6A)	1.400(4)	C(9C)-C(10C)	1.383(4)	C(24B)-C(25B)	1.370(4)
C(2A)-C(3A)	1.412(4)	C(10C)-C(11C)	1.368(4)	N(26B)-N(27B)	1.201(3)
C(3A)-C(4A)	1.381(5)	C(11C)-C(12C)	1.374(4)	N(27B)-C(28B)	1.488(3)
C(4A)-C(5A)	1.349(5)	Si(1D)-O(2D)	1.6253(17)	C(28B)-C(29B)	1.360(4)
C(5A)-C(6A)	1.376(4)	Si(1D)-O(1D)	1.6308(16)	C(28B)-C(33B)	1.374(4)
C(7A)-C(12A)	1.394(3)	Si(1D)-C(7D)	1.859(3)	C(29B)-C(30B)	1.382(3)
C(7A)-C(8A)	1.397(3)	Si(1D)-C(1D)	1.867(2)	C(30B)-N(31B)	1.328(3)
C(8A)-C(9A)	1.381(4)	C(1D)-C(6D)	1.391(3)	N(31B)-C(32B)	1.335(3)
C(9A)-C(10A)	1.390(4)	C(1D)-C(2D)	1.397(3)	C(32B)-C(33B)	1.397(3)
C(10A)-C(11A)	1.370(4)	C(2D)-C(3D)	1.377(3)	N(40A)-C(41A)	1.3900
C(11A)-C(12A)	1.387(4)	C(3D)-C(4D)	1.383(3)	N(40A)-C(45A)	1.3900
Si(1B)-O(2B)	1.6218(17)	C(4D)-C(5D)	1.376(4)	C(41A)-C(42A)	1.3900
Si(1B)-O(1B)	1.6314(17)	C(5D)-C(6D)	1.386(3)	C(42A)-C(43A)	1.3900
Si(1B)-C(7B)	1.860(3)	C(7D)-C(12D)	1.401(3)	C(43A)-C(44A)	1.3900
Si(1B)-C(1B)	1.864(2)	C(7D)-C(8D)	1.403(3)	C(43A)-N(46A)	1.515(5)
C(1B)-C(6B)	1.395(3)	C(8D)-C(9D)	1.387(4)	C(44A)-C(45A)	1.3900
C(1B)-C(2B)	1.397(3)	C(9D)-C(10D)	1.373(4)	N(46A)-N(47A)	1.113(5)
C(2B)-C(3B)	1.383(3)	C(10D)-C(11D)	1.385(4)	N(47A)-C(48A)	1.423(5)
C(3B)-C(4B)	1.372(4)	C(11D)-C(12D)	1.374(4)	C(48A)-C(49A)	1.3900
C(4B)-C(5B)	1.379(4)	N(20A)-C(25A)	1.322(3)	C(48A)-C(53A)	1.3900
C(5B)-C(6B)	1.393(3)	N(20A)-C(21A)	1.339(3)	C(49A)-C(50A)	1.3900
C(7B)-C(12B)	1.399(3)	C(21A)-C(22A)	1.377(4)	C(50A)-N(51A)	1.3900
C(7B)-C(8B)	1.401(3)	C(22A)-C(23A)	1.380(4)	N(51A)-C(52A)	1.3900
C(8B)-C(9B)	1.380(4)	C(23A)-C(24A)	1.376(4)	C(52A)-C(53A)	1.3900
C(9B)-C(10B)	1.374(4)	C(23A)-N(26A)	1.452(3)	N(40B)-C(41B)	1.323(3)
C(10B)-C(11B)	1.380(4)	C(24A)-C(25A)	1.369(4)	N(40B)-C(45B)	1.328(3)
C(11B)-C(12B)	1.383(4)	N(26A)-N(27A)	1.205(3)	C(41B)-C(42B)	1.372(3)
Si(1C)-O(2C)	1.6169(18)	N(27A)-C(28A)	1.465(3)	C(42B)-C(43B)	1.367(3)
Si(1C)-O(1C)	1.6183(17)	C(28A)-C(29A)	1.366(4)	C(43B)-C(44B)	1.369(4)
Si(1C)-C(7C)	1.858(3)	C(28A)-C(33A)	1.375(4)	C(43B)-N(46B)	1.451(3)
Si(1C)-C(1C)	1.861(2)	C(29A)-C(30A)	1.374(3)	C(44B)-C(45B)	1.386(3)
C(1C)-C(2C)	1.397(3)	C(30A)-N(31A)	1.329(3)	N(46B)-N(46B)#1	1.219(4)
C(1C)-C(6C)	1.397(3)	N(31A)-C(32A)	1.338(3)	O(2A)-Si(1A)-	113.68(10)
C(2C)-C(3C)	1.384(4)	C(32A)-C(33A)	1.387(3)	O(2A)-Si(1A)-	104.10(10)
C(3C)-C(4C)	1.372(4)	N(20B)-C(25B)	1.323(3)	C(1A)	
				O(1A)-Si(1A)-	105.92(11)
				C(1A)	

O(2A)-Si(1A)-C(7A)	111.02(10)	C(11B)-C(12B)-C(7B)	122.1(2)	C(9D)-C(8D)-C(7D)	121.9(2)
O(1A)-Si(1A)-C(7A)	109.47(11)	O(2C)-Si(1C)-O(1C)	114.25(10)	C(10D)-C(9D)-C(8D)	119.7(3)
C(1A)-Si(1A)-C(7A)	112.50(11)	O(2C)-Si(1C)-C(7C)	110.80(10)	C(9D)-C(10D)-C(11D)	120.1(3)
C(2A)-C(1A)-C(6A)	117.5(3)	O(1C)-Si(1C)-C(7C)	109.19(10)	C(12D)-C(11D)-C(10D)	120.0(3)
C(2A)-C(1A)-Si(1A)	120.6(2)	O(2C)-Si(1C)-C(1C)	103.97(10)	C(11D)-C(12D)-C(7D)	122.0(3)
C(6A)-C(1A)-Si(1A)	121.9(2)	O(1C)-Si(1C)-C(1C)	106.48(10)	C(25A)-N(20A)-C(21A)	116.3(2)
C(1A)-C(2A)-C(3A)	120.7(3)	C(7C)-Si(1C)-C(1C)	112.03(11)	N(20A)-C(21A)-C(22A)	123.9(3)
C(4A)-C(3A)-C(2A)	118.5(3)	C(2C)-C(1C)-C(6C)	116.9(2)	C(21A)-C(22A)-C(23A)	117.8(3)
C(5A)-C(4A)-C(3A)	121.9(3)	C(2C)-C(1C)-Si(1C)	120.50(18)	C(24A)-C(23A)-C(22A)	119.2(2)
C(4A)-C(5A)-C(6A)	119.4(3)	C(6C)-C(1C)-Si(1C)	122.57(19)	C(24A)-C(23A)-N(26A)	114.2(3)
C(5A)-C(6A)-C(1A)	121.9(3)	C(3C)-C(2C)-C(1C)	121.3(3)	C(22A)-C(23A)-N(26A)	126.6(2)
C(12A)-C(7A)-C(8A)	116.7(2)	C(4C)-C(3C)-C(2C)	120.0(3)	C(25A)-C(24A)-C(23A)	118.1(3)
C(12A)-C(7A)-Si(1A)	122.7(2)	C(5C)-C(4C)-C(3C)	120.0(3)	N(20A)-C(25A)-C(24A)	124.6(3)
C(8A)-C(7A)-Si(1A)	120.5(2)	C(4C)-C(5C)-C(6C)	120.4(3)	N(27A)-N(26A)-C(23A)	112.6(2)
C(9A)-C(8A)-C(7A)	121.7(3)	C(5C)-C(6C)-C(1C)	121.3(3)	N(26A)-N(27A)-C(28A)	112.3(2)
C(8A)-C(9A)-C(10A)	120.0(3)	C(12C)-C(7C)-C(8C)	116.6(2)	C(29A)-C(28A)-C(33A)	119.3(2)
C(11A)-C(10A)-C(9A)	119.6(3)	C(12C)-C(7C)-Si(1C)	122.5(2)	C(29A)-C(28A)-N(27A)	115.5(3)
C(10A)-C(11A)-C(12A)	120.0(3)	C(8C)-C(7C)-Si(1C)	120.93(19)	C(33A)-C(28A)-N(27A)	125.3(2)
C(11A)-C(12A)-C(7A)	122.0(3)	C(9C)-C(8C)-C(7C)	121.6(2)	C(28A)-C(29A)-C(30A)	118.4(3)
O(2B)-Si(1B)-O(1B)	113.39(9)	C(10C)-C(9C)-C(8C)	119.5(3)	N(31A)-C(30A)-C(29A)	124.3(3)
O(2B)-Si(1B)-C(7B)	108.40(10)	C(11C)-C(10C)-C(9C)	120.1(3)	C(30A)-N(31A)-C(32A)	116.6(2)
O(1B)-Si(1B)-C(7B)	109.57(10)	C(10C)-C(11C)-C(12C)	120.6(3)	N(31A)-C(32A)-C(33A)	123.2(3)
O(2B)-Si(1B)-C(1B)	107.31(10)	C(11C)-C(12C)-C(7C)	121.6(3)	C(28A)-C(33A)-C(32A)	118.3(2)
O(1B)-Si(1B)-C(1B)	105.81(10)	O(2D)-Si(1D)-O(1D)	113.39(9)	C(25B)-N(20B)-C(21B)	116.5(2)
C(7B)-Si(1B)-C(1B)	112.39(11)	O(2D)-Si(1D)-C(7D)	109.66(10)	N(20B)-C(21B)-C(22B)	123.6(3)
C(6B)-C(1B)-C(2B)	117.0(2)	O(1D)-Si(1D)-C(7D)	109.26(10)	C(23B)-C(22B)-C(21B)	117.9(3)
C(6B)-C(1B)-Si(1B)	123.32(19)	O(2D)-Si(1D)-C(1D)	107.22(10)	C(22B)-C(23B)-C(24B)	119.4(2)
C(2B)-C(1B)-Si(1B)	119.63(19)	O(1D)-Si(1D)-C(1D)	106.43(9)	C(22B)-C(23B)-N(26B)	127.1(2)
C(3B)-C(2B)-C(1B)	121.9(3)	C(7D)-Si(1D)-C(1D)	110.83(11)	C(24B)-C(23B)-N(26B)	113.5(2)
C(4B)-C(3B)-C(2B)	119.8(3)	C(6D)-C(1D)-C(2D)	116.8(2)	C(25B)-C(24B)-C(23B)	118.4(3)
C(3B)-C(4B)-C(5B)	119.9(3)	C(6D)-C(1D)-Si(1D)	123.70(18)	N(20B)-C(25B)-C(24B)	124.1(3)
C(4B)-C(5B)-C(6B)	120.1(3)	C(2D)-C(1D)-Si(1D)	119.53(18)	N(27B)-N(26B)-C(23B)	110.5(2)
C(5B)-C(6B)-C(1B)	121.0(3)	C(3D)-C(2D)-C(1D)	122.2(2)	N(26B)-N(27B)-C(28B)	110.4(2)
C(12B)-C(7B)-C(8B)	116.3(2)	C(2D)-C(3D)-C(4D)	119.8(2)	C(29B)-C(28B)-C(33B)	119.8(2)
C(12B)-C(7B)-Si(1B)	121.98(19)	C(5D)-C(4D)-C(3D)	119.4(2)	C(29B)-C(28B)-N(27B)	114.2(3)
C(8B)-C(7B)-Si(1B)	121.72(18)	C(4D)-C(5D)-C(6D)	120.6(2)	C(33B)-C(28B)-N(27B)	125.9(3)
C(9B)-C(8B)-C(7B)	121.6(2)	C(5D)-C(6D)-C(1D)	121.3(2)	C(28B)-C(29B)-C(30B)	118.2(3)
C(10B)-C(9B)-C(8B)	120.6(3)	C(12D)-C(7D)-C(8D)	116.3(2)	N(31B)-C(30B)-C(29B)	124.2(3)
C(9B)-C(10B)-C(11B)	119.5(3)	C(12D)-C(7D)-Si(1D)	121.8(2)	C(30B)-N(31B)-C(32B)	116.8(2)
C(10B)-C(11B)-C(12B)	119.9(3)	C(8D)-C(7D)-Si(1D)	121.81(18)	N(31B)-C(32B)-C(33B)	123.1(3)

C(28B)-C(33B)-C(32B)	118.0(2)
C(41A)-N(40A)-C(45A)	120.0....
N(40A)-C(41A)-C(42A)	120.0
C(43A)-C(42A)-C(41A)	120.0
C(42A)-C(43A)-C(44A)	120.0
C(42A)-C(43A)-N(46A)	115.3(3)
C(44A)-C(43A)-N(46A)	124.5(3)
C(45A)-C(44A)-C(43A)	120.0
C(44A)-C(45A)-N(40A)	120.0
N(47A)-N(46A)-C(43A)	110.6(4)
N(46A)-N(47A)-C(48A)	112.2(6)
C(49A)-C(48A)-C(53A)	120.0
C(49A)-C(48A)-N(47A)	108.5(4)
C(53A)-C(48A)-N(47A)	131.5(4)
C(48A)-C(49A)-C(50A)	120.0
N(51A)-C(50A)-C(49A)	120.0
C(52A)-N(51A)-C(50A)	120.0
N(51A)-C(52A)-C(53A)	120.0
C(52A)-C(53A)-C(48A)	120.0
C(41B)-N(40B)-C(45B)	117.7(2)
N(40B)-C(41B)-C(42B)	124.0(3)
C(43B)-C(42B)-C(41B)	117.5(3)
C(42B)-C(43B)-C(44B)	120.3(2)
C(42B)-C(43B)-N(46B)	114.7(2)
C(44B)-C(43B)-N(46B)	125.1(2)
C(43B)-C(44B)-C(45B)	117.9(3)
N(40B)-C(45B)-C(44B)	122.6(3)
N(46B)#1-N(46B)-C(43B)	111.6(3)
Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y+1,-z	

Appendix 8

Compound	2Ph ₂ Si(OH) ₂ .2L ₇ (11)
Formula	C ₁₆ H ₁₂ N ₂ , C ₁₂ H ₁₂ O ₂ Si
Formula weight	448.58
Temperature	173(2) K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Triclinic
Space group	P-1
Crystal colour/Morphology	Colourless blocks
Crystal size	0.62 x 0.43 x 0.30 mm ³
Unit cell dimension	a = 9.5309(9) Å α = 81.591(6)° b = 10.9926(7) Å β = 86.658(7)° c = 11.0569(7) Å γ = 85.675(7)°
Volume z	1141.40(15) Å ³ , 2
Density (calculated)	1.305 Mg/m ³
Absorption coefficient	0.132 mm ⁻¹
F(000)	472
Θ range for data collection	2.450 to 28.157°
Index ranges	-11 ≤ h ≤ 11 -13 ≤ k ≤ 10 -14 ≤ l ≤ 14
Ref1ns collected/unique	6616 / 4496 [R(int) = 0.0207]
Ref1ns observed [F > 4σ(F)]	3502
Absorption correction	Analytical
Max. and Min. transmission	0.972 and 0.958
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4496 / 2 / 307
Goodness-of-fit on F ²	1.051
Final R indices [F > 4σ(F)]	R1 = 0.0478, wR2 = 0.1137
R indices (all data)	R1 = 0.0645, wR2 = 0.1288
Largest diff. peak, hole	0.400, -0.380 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°] for **2Ph₂Si(OH)₂.2L₇ (11)**

Si(1)-O(1)	1.6164(15)	C(2)-C(1)-C(6)	117.28(19)
Si(1)-O(2)	1.6254(14)	C(2)-C(1)-Si(1)	120.86(15)
Si(1)-C(7)	1.854(2)	C(6)-C(1)-Si(1)	121.81(16)
Si(1)-C(1)	1.874(2)	C(3)-C(2)-C(1)	121.2(2)
C(1)-C(2)	1.395(3)	C(4)-C(3)-C(2)	120.3(2)
C(1)-C(6)	1.398(3)	C(3)-C(4)-C(5)	119.9(2)
C(2)-C(3)	1.383(3)	C(4)-C(5)-C(6)	119.9(2)
C(3)-C(4)	1.374(4)	C(5)-C(6)-C(1)	121.4(2)
C(4)-C(5)	1.377(4)	C(8)-C(7)-C(12)	116.88(19)
C(5)-C(6)	1.383(3)	C(8)-C(7)-Si(1)	122.06(15)
C(7)-C(8)	1.386(3)	C(12)-C(7)-Si(1)	121.03(16)
C(7)-C(12)	1.393(3)	C(7)-C(8)-C(9)	122.03(19)
C(8)-C(9)	1.390(3)	C(10)-C(9)-C(8)	119.6(2)
C(9)-C(10)	1.385(3)	C(11)-C(10)-C(9)	119.6(2)
C(10)-C(11)	1.371(3)	C(10)-C(11)-C(12)	120.2(2)
C(11)-C(12)	1.388(3)	C(11)-C(12)-C(7)	121.7(2)
N(20)-C(25)	1.334(3)	C(25)-N(20)-C(21)	116.16(18)
N(20)-C(21)	1.335(3)	N(20)-C(21)-C(22)	123.6(2)
C(21)-C(22)	1.381(3)	C(23)-C(22)-C(21)	119.91(19)
C(22)-C(23)	1.381(3)	C(22)-C(23)-C(24)	116.85(19)
C(23)-C(24)	1.385(3)	C(22)-C(23)-C(26)	121.53(18)
C(23)-C(26)	1.483(3)	C(24)-C(23)-C(26)	121.60(18)
C(24)-C(25)	1.382(3)	C(25)-C(24)-C(23)	119.49(19)
C(26)-C(31)	1.391(3)	N(20)-C(25)-C(24)	123.9(2)
C(26)-C(27)	1.393(3)	C(31)-C(26)-C(27)	118.25(19)
C(27)-C(28)	1.382(3)	C(31)-C(26)-C(23)	121.23(18)
C(28)-C(29)	1.395(3)	C(27)-C(26)-C(23)	120.51(18)
C(29)-C(30)	1.392(3)	C(28)-C(27)-C(26)	121.09(19)
C(29)-C(32)	1.477(3)	C(27)-C(28)-C(29)	120.80(19)
C(30)-C(31)	1.391(3)	C(30)-C(29)-C(28)	118.30(19)
C(32)-C(33)	1.387(3)	C(30)-C(29)-C(32)	121.04(18)
C(32)-C(37)	1.390(3)	C(28)-C(29)-C(32)	120.66(18)
C(33)-C(34)	1.387(3)	C(31)-C(30)-C(29)	120.77(19)
C(34)-N(35)	1.330(3)	C(30)-C(31)-C(26)	120.77(19)
N(35)-C(36)	1.334(3)	C(33)-C(32)-C(37)	116.68(19)
C(36)-C(37)	1.381(3)	C(33)-C(32)-C(29)	121.09(17)
O(1)-Si(1)-O(2)	114.95(8)	C(37)-C(32)-C(29)	122.24(18)
O(1)-Si(1)-C(7)	107.15(8)	C(34)-C(33)-C(32)	119.81(18)
O(2)-Si(1)-C(7)	105.70(8)	N(35)-C(34)-C(33)	123.50(19)
O(1)-Si(1)-C(1)	106.90(8)	C(34)-N(35)-C(36)	116.63(18)
O(2)-Si(1)-C(1)	109.08(8)	N(35)-C(36)-C(37)	123.88(18)
C(7)-Si(1)-C(1)	113.22(9)	C(36)-C(37)-C(32)	119.51(19)

Appendix 9

Compound	[Ph₆B₂Si₂O₄].2L₈ (13)
Formula	C ₆₀ H ₄₆ B ₂ N ₈ O ₄ S ₂ Si ₂
Formula weight	1084.97
Temperature	173(2) K
Diffraction wavelength	Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system	Triclinic
Space group	P-1
Crystal colour/Morphology	Colourless needles
Crystal size	0.380 x 0.145 x 0.056 mm ³
Unit cell dimension	a = 9.2619(5) Å α = 111.337(6)° b = 11.6769(8) Å β = 99.104(5)° c = 13.9086(9) Å γ = 102.564(5)°
Volume z	1320.12(16) Å ³ , 1
Density (calculated)	1.365 Mg/m ³
Absorption coefficient	1.817 mm ⁻¹
F(000)	564
Θ range for data collection	3.534 to 73.634°
Index ranges	-11<=h<=9 -14<=k<=13 -17<=l<=15
Ref1ns collected/unique	7555 / 5045 [R(int) = 0.0378]
Ref1ns observed [F>4σ(F)]	3940
Absorption correction	Analytical
Max. and Min. transmission	0.906 and 0.680
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5045 / 0 / 352
Goodness-of-fit on F ²	1.044
Final R indices [F>4σ(F)]	R1 = 0.0470, wR2 = 0.1163
R indices (all data)	R1 = 0.0637, wR2 = 0.1320
Largest diff. peak, hole	0.339, -0.305 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°] for [Ph₆B₂Si₂O₄].2L₈ (**13**)

B(1)-O(2)	1.431(3)	C(34)-C(35)	1.395(3)	C(17)-C(16)-C(14)	120.9(2)
B(1)-O(4)#1	1.436(3)	C(34)-C(39)	1.399(3)	C(21)-C(16)-C(14)	121.4(2)
B(1)-C(22)	1.615(3)	C(35)-C(36)	1.393(4)	N(18)-C(17)-C(16)	124.9(3)
B(1)-N(5)	1.699(3)	C(36)-C(37)	1.380(5)	C(17)-N(18)-C(19)	116.1(3)
O(2)-Si(3)	1.6074(16)	C(37)-C(38)	1.381(5)	N(18)-C(19)-C(20)	123.9(3)
Si(3)-O(4)	1.6120(16)	C(38)-C(39)	1.392(4)	C(21)-C(20)-C(19)	118.6(3)
Si(3)-C(28)	1.867(2)	O(2)-B(1)-O(4)#1	116.93(19)	C(20)-C(21)-C(16)	118.7(3)
Si(3)-C(34)	1.881(2)	O(2)-B(1)-C(22)	113.12(19)	C(23)-C(22)-C(27)	116.5(2)
O(4)-B(1)#1	1.436(3)	O(4)#1-B(1)-C(22)	111.63(19)	C(23)-C(22)-B(1)	122.3(2)
N(5)-C(10)	1.344(3)	O(2)-B(1)-N(5)	102.06(17)	C(27)-C(22)-B(1)	121.1(2)
N(5)-C(6)	1.345(3)	O(4)#1-B(1)-N(5)	105.30(17)	C(24)-C(23)-C(22)	122.0(2)
C(6)-C(7)	1.386(3)	C(22)-B(1)-N(5)	106.42(16)	C(25)-C(24)-C(23)	120.1(3)
C(7)-C(8)	1.394(3)	B(1)-O(2)-Si(3)	143.47(15)	C(26)-C(25)-C(24)	119.2(2)
C(7)-C(11)	1.471(3)	O(2)-Si(3)-O(4)	113.53(9)	C(25)-C(26)-C(27)	120.7(3)
C(8)-C(9)	1.380(4)	O(2)-Si(3)-C(28)	107.18(10)	C(26)-C(27)-C(22)	121.5(2)
C(9)-C(10)	1.388(3)	O(4)-Si(3)-C(28)	106.84(9)	C(33)-C(28)-C(29)	117.5(2)
C(11)-N(12)	1.324(3)	O(2)-Si(3)-C(34)	110.35(10)	C(33)-C(28)-Si(3)	122.06(18)
C(11)-N(15)	1.370(3)	O(4)-Si(3)-C(34)	110.16(9)	C(29)-C(28)-Si(3)	120.43(18)
N(12)-S(13)	1.638(2)	C(28)-Si(3)-C(34)	108.57(10)	C(30)-C(29)-C(28)	121.3(2)
S(13)-C(14)	1.733(2)	B(1)#1-O(4)-Si(3)	142.70(15)	C(31)-C(30)-C(29)	120.0(2)
C(14)-N(15)	1.313(3)	C(10)-N(5)-C(6)	119.38(19)	C(30)-C(31)-C(32)	120.0(2)
C(14)-C(16)	1.457(3)	C(10)-N(5)-B(1)	121.95(18)	C(31)-C(32)-C(33)	119.9(2)
C(16)-C(17)	1.387(4)	C(6)-N(5)-B(1)	118.64(17)	C(32)-C(33)-C(28)	121.4(2)
C(16)-C(21)	1.399(4)	N(5)-C(6)-C(7)	122.0(2)	C(35)-C(34)-C(39)	117.5(2)
C(17)-N(18)	1.330(4)	C(6)-C(7)-C(8)	118.6(2)	C(35)-C(34)-Si(3)	121.25(18)
N(18)-C(19)	1.338(4)	C(6)-C(7)-C(11)	119.7(2)	C(39)-C(34)-Si(3)	121.22(19)
C(19)-C(20)	1.397(5)	C(8)-C(7)-C(11)	121.7(2)	C(36)-C(35)-C(34)	121.7(3)
C(20)-C(21)	1.372(4)	C(9)-C(8)-C(7)	119.3(2)	C(37)-C(36)-C(35)	119.5(3)
C(22)-C(23)	1.396(3)	C(8)-C(9)-C(10)	119.1(2)	C(36)-C(37)-C(38)	120.3(3)
C(22)-C(27)	1.399(3)	N(5)-C(10)-C(9)	121.7(2)	C(37)-C(38)-C(39)	119.9(3)
C(23)-C(24)	1.388(4)	N(12)-C(11)-N(15)	118.9(2)	C(38)-C(39)-C(34)	121.1(3)
C(24)-C(25)	1.380(4)	N(12)-C(11)-C(7)	120.8(2)		
C(25)-C(26)	1.378(4)	N(15)-C(11)-C(7)	120.2(2)		
C(26)-C(27)	1.388(4)	C(11)-N(12)-S(13)	108.19(18)		
C(28)-C(33)	1.396(3)	N(12)-S(13)-C(14)	92.71(11)		
C(28)-C(29)	1.397(3)	N(15)-C(14)-C(16)	125.3(2)		
C(29)-C(30)	1.394(3)	N(15)-C(14)-S(13)	111.10(18)		
C(30)-C(31)	1.379(4)	C(16)-C(14)-S(13)	123.54(18)		
C(31)-C(32)	1.380(4)	C(14)-N(15)-C(11)	109.1(2)		
C(32)-C(33)	1.394(4)	C(17)-C(16)-C(21)	117.8(3)		

Symmetry transformations used to generate equivalent atoms:
#1 -x+1, -y+1, -z+1

Appendix 10

Compound	[Ph₆B₂Si₂O₄].2L₉. 2[PhB(OH)₂] (14)
Formula	C ₆₀ H ₄₆ B ₂ N ₈ O ₄ S ₂ Si ₂ .2(C ₆ H ₇ BO ₂)
Formula weight	1328.82
Temperature	173(2) K
Diffraction wavelength	Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system	Triclinic
Space group	P-1
Crystal colour/Morphology	Colourless blocks
Crystal size	0.237 x 0.134 x 0.039 mm ³
Unit cell dimension	a = 11.6316(7) Å α = 113.649(6)° b = 12.4462(8) Å β = 90.799(5)° c = 12.9148(8) Å γ = 103.151(6)°
Volume z	1656.1(2) Å ³ , 1
Density (calculated)	1.332 Mg/m ³
Absorption coefficient	1.593 mm ⁻¹
F(000)	692
Θ range for data collection	3.763 to 73.725°
Index ranges	-14<= <i>h</i> <=13 -15<= <i>k</i> <=15 -10<= <i>l</i> <=16
Ref1ns collected/unique	9599 / 6324 [R(int) = 0.0325]
Ref1ns observed [<i>F</i> >4σ(<i>F</i>)]	4751
Absorption correction	Analytical
Max. and Min. transmission	0.950 and 0.845
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	6324 / 22 / 450
Goodness-of-fit on <i>F</i> ²	1.019
Final R indices [<i>F</i> >4σ(<i>F</i>)]	R1 = 0.0405, wR2 = 0.0967
R indices (all data)	R1 = 0.0606, wR2 = 0.1096
Largest diff. peak, hole	0.243, -0.302 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°] for [Ph₆B₂Si₂O₄].2L₉. 2[PhB(OH)₂] (**14**)

B(1)-O(2)	1.430(2)	C(30)-C(31)	1.379(3)	C(10)-C(9)-C(8)	119.48(19)
B(1)-O(4)#1	1.432(2)	C(31)-C(32)	1.389(3)	N(5)-C(10)-C(9)	122.36(19)
B(1)-C(22)	1.619(3)	C(32)-C(33)	1.388(3)	N(12)-C(11)-N(15)	118.7(2)
B(1)-N(5)	1.714(2)	C(34)-C(35)	1.389(3)	N(12)-C(11)-C(8)	121.2(2)
O(2)-Si(3)	1.6177(14)	C(34)-C(39)	1.408(3)	N(15)-C(11)-C(8)	120.01(18)
Si(3)-O(4)	1.6041(14)	C(35)-C(36)	1.395(3)	N(15)-C(11)-S(12')	111.0(3)
Si(3)-C(34)	1.858(2)	C(36)-C(37)	1.381(4)	C(8)-C(11)-S(12')	129.0(3)
Si(3)-C(28)	1.868(2)	C(37)-C(38)	1.379(4)	C(11)-N(12)-S(13)	108.0(2)
O(4)-B(1)#1	1.432(2)	C(38)-C(39)	1.388(3)	N(12)-S(13)-C(14)	93.00(16)
N(5)-C(6)	1.340(3)	B(40)-O(42)	1.358(3)	C(11)-S(12')-N(13')	94.8(6)
N(5)-C(10)	1.343(2)	B(40)-O(41)	1.364(3)	C(14)-N(13')-S(12')	106.3(8)
C(6)-C(7)	1.385(3)	B(40)-C(43)	1.578(3)	N(15)-C(14)-N(13')	118.7(5)
C(7)-C(8)	1.392(3)	C(43)-C(48)	1.393(3)	N(15)-C(14)-C(16)	122.41(19)
C(8)-C(9)	1.392(3)	C(43)-C(44)	1.397(3)	N(13')-C(14)-C(16)	118.7(5)
C(8)-C(11)	1.471(3)	C(44)-C(45)	1.390(3)	N(15)-C(14)-S(13)	111.35(16)
C(9)-C(10)	1.378(3)	C(45)-C(46)	1.381(4)	C(16)-C(14)-S(13)	126.24(16)
C(11)-N(12)	1.336(4)	C(46)-C(47)	1.381(4)	C(14)-N(15)-C(11)	108.97(18)
C(11)-N(15)	1.361(3)	C(47)-C(48)	1.391(4)	C(21)-C(16)-C(17)	117.9(2)
C(11)-S(12')	1.631(7)	O(2)-B(1)-O(4)#1	116.77(16)	C(21)-C(16)-C(14)	119.54(19)
N(12)-S(13)	1.637(4)	O(2)-B(1)-C(22)	111.34(16)	C(17)-C(16)-C(14)	122.6(2)
S(13)-C(14)	1.718(2)	O(4)#1-B(1)-C(22)	114.01(16)	C(18)-C(17)-C(16)	119.2(2)
S(12')-N(13')	1.646(12)	O(2)-B(1)-N(5)	106.56(15)	N(19)-C(18)-C(17)	123.2(2)
N(13')-C(14)	1.335(11)	O(4)#1-B(1)-N(5)	101.45(14)	C(20)-N(19)-C(18)	117.1(2)
C(14)-N(15)	1.323(3)	C(22)-B(1)-N(5)	105.21(14)	N(19)-C(20)-C(21)	124.0(3)
C(14)-C(16)	1.472(3)	B(1)-O(2)-Si(3)	136.97(12)	C(20)-C(21)-C(16)	118.6(2)
C(16)-C(21)	1.386(3)	O(4)-Si(3)-O(2)	113.97(8)	C(27)-C(22)-C(23)	116.54(18)
C(16)-C(17)	1.387(3)	O(4)-Si(3)-C(34)	111.92(8)	C(27)-C(22)-B(1)	121.08(18)
C(17)-C(18)	1.384(3)	O(2)-Si(3)-C(34)	107.90(8)	C(23)-C(22)-B(1)	122.34(17)
C(18)-N(19)	1.334(3)	O(4)-Si(3)-C(28)	107.05(8)	C(24)-C(23)-C(22)	122.0(2)
N(19)-C(20)	1.330(3)	O(2)-Si(3)-C(28)	106.38(8)	C(25)-C(24)-C(23)	119.9(2)
C(20)-C(21)	1.382(4)	C(34)-Si(3)-C(28)	109.41(9)	C(26)-C(25)-C(24)	119.4(2)
C(22)-C(27)	1.393(3)	B(1)#1-O(4)-Si(3)	149.53(13)	C(25)-C(26)-C(27)	120.2(2)
C(22)-C(23)	1.397(3)	C(6)-N(5)-C(10)	118.40(17)	C(22)-C(27)-C(26)	121.9(2)
C(23)-C(24)	1.390(3)	C(6)-N(5)-B(1)	121.91(15)	C(33)-C(28)-C(29)	117.12(18)
C(24)-C(25)	1.388(4)	C(10)-N(5)-B(1)	119.68(16)	C(33)-C(28)-Si(3)	121.04(15)
C(25)-C(26)	1.374(4)	N(5)-C(6)-C(7)	122.72(18)	C(29)-C(28)-Si(3)	121.81(15)
C(26)-C(27)	1.396(3)	C(6)-C(7)-C(8)	118.83(19)	C(30)-C(29)-C(28)	121.5(2)
C(28)-C(33)	1.397(3)	C(9)-C(8)-C(7)	118.19(18)	C(31)-C(30)-C(29)	119.8(2)
C(28)-C(29)	1.399(3)	C(9)-C(8)-C(11)	119.52(18)	C(30)-C(31)-C(32)	120.0(2)
C(29)-C(30)	1.397(3)	C(7)-C(8)-C(11)	122.27(19)	C(33)-C(32)-C(31)	119.6(2)

C(32)-C(33)-C(28)	121.9(2)
C(35)-C(34)-C(39)	117.47(19)
C(35)-C(34)-Si(3)	121.47(16)
C(39)-C(34)-Si(3)	120.67(16)
C(34)-C(35)-C(36)	121.5(2)
C(37)-C(36)-C(35)	119.4(2)
C(38)-C(37)-C(36)	120.7(2)
C(37)-C(38)-C(39)	119.5(2)
C(38)-C(39)-C(34)	121.3(2)
O(42)-B(40)-O(41)	118.1(2)
O(42)-B(40)-C(43)	118.2(2)
O(41)-B(40)-C(43)	123.8(2)
C(48)-C(43)-C(44)	117.3(2)
C(48)-C(43)-B(40)	120.2(2)
C(44)-C(43)-B(40)	122.5(2)
C(45)-C(44)-C(43)	121.3(2)
C(46)-C(45)-C(44)	120.3(2)
C(47)-C(46)-C(45)	119.4(2)
C(46)-C(47)-C(48)	120.2(2)
C(47)-C(48)-C(43)	121.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z

Appendix 11

Compound	(Ph ₄ Si ₂ O ₃ B)C ₆ H ₄ (Ph ₄ Si ₂ O ₃ B) (3a)
Formula	C ₅₄ H ₄₄ B ₂ O ₆ Si ₄
Formula weight	922.87
Temperature	173 K
Diffraction wavelength	Agilent Xcalibur 3 E, 0.71073 Å
Crystal system	Triclinic
Space group	P-1
Crystal colour/Morphology	Colourless tabular needles
Crystal size	0.48 x 0.29 x 0.06 mm ³
Unit cell dimension	a = 8.9378(4) Å α = 91.284(4)° b = 10.0148(5) Å β = 104.866(5)° c = 14.2556(8) Å γ = 94.422(4)°
Volume z	1228.46(11) Å ³ , 1
Density (calculated)	1.247 Mg/m ³
Absorption coefficient	0.171 mm ⁻¹
F(000)	482
Θ range for data collection	2.468 to 28.067°
Index ranges	-10 ≤ h ≤ 9 -9 ≤ k ≤ 12 -13 ≤ l ≤ 17
Ref1ns collected/unique	7123 / 4814 [R(int) = 0.0206]
Ref1ns observed [F > 4σ(F)]	3622
Absorption correction	Analytical
Max. and Min. transmission	0.990 and 0.949
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	4814 / 49 / 299
Goodness-of-fit on F ²	1.018
Final R indices [F > 4σ(F)]	R1 = 0.0495, wR2 = 0.1128
R indices (all data)	R1 = 0.0711, wR2 = 0.1278
Largest diff. peak, hole	0.344, -0.279 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°] for (Ph₄Si₂O₃B)₂C₆H₄(Ph₄Si₂O₃B) (**3a**)

B(1)-O(6)	1.371(3)	C(28)-C(29)	1.390(3)	C(11')-C(10')-C(15')	120.0
B(1)-O(2)	1.373(3)	C(28)-C(33)	1.393(3)	C(11')-C(10')-Si(3)	120.1(6)
B(1)-C(7)	1.554(3)	C(29)-C(30)	1.388(4)	C(15')-C(10')-Si(3)	119.8(6)
O(2)-Si(3)	1.6468(16)	C(30)-C(31)	1.362(4)	C(12')-C(11')-C(10')	120.0
Si(3)-O(4)	1.6405(17)	C(31)-C(32)	1.366(4)	C(11')-C(12')-C(13')	120.0
Si(3)-C(10')	1.852(7)	C(32)-C(33)	1.385(4)	C(14')-C(13')-C(12')	120.0
Si(3)-C(16)	1.853(2)	O(6)-B(1)-O(2)	121.1(2)	C(13')-C(14')-C(15')	120.0
Si(3)-C(10)	1.857(2)	O(6)-B(1)-C(7)	118.3(2)	C(14')-C(15')-C(10')	120.0
O(4)-Si(5)	1.6341(16)	O(2)-B(1)-C(7)	120.6(2)	C(21)-C(16)-C(17)	116.9(2)
Si(5)-O(6)	1.6426(16)	B(1)-O(2)-Si(3)	128.79(16)	C(21)-C(16)-Si(3)	119.42(19)
Si(5)-C(22)	1.850(2)	O(4)-Si(3)-O(2)	106.48(8)	C(17)-C(16)-Si(3)	123.55(19)
Si(5)-C(28)	1.853(2)	O(4)-Si(3)-C(10')	104.5(3)	C(16)-C(17)-C(18)	120.7(3)
C(7)-C(8)	1.393(3)	O(2)-Si(3)-C(10')	119.9(4)	C(19)-C(18)-C(17)	120.8(3)
C(7)-C(9)	1.398(3)	O(4)-Si(3)-C(16)	109.47(10)	C(20)-C(19)-C(18)	119.3(3)
C(8)-C(9)#1	1.380(3)	O(2)-Si(3)-C(16)	108.24(10)	C(19)-C(20)-C(21)	120.6(3)
C(9)-C(8)#1	1.380(3)	C(10')-Si(3)-C(16)	108.0(4)	C(16)-C(21)-C(20)	121.8(3)
C(10)-C(11)	1.3900	O(4)-Si(3)-C(10)	110.95(17)	C(27)-C(22)-C(23)	117.1(2)
C(10)-C(15)	1.3900	O(2)-Si(3)-C(10)	110.41(17)	C(27)-C(22)-Si(5)	120.28(18)
C(11)-C(12)	1.3900	C(16)-Si(3)-C(10)	111.14(15)	C(23)-C(22)-Si(5)	122.58(18)
C(12)-C(13)	1.3900	Si(5)-O(4)-Si(3)	125.69(10)	C(24)-C(23)-C(22)	121.5(2)
C(13)-C(14)	1.3900	O(4)-Si(5)-O(6)	106.97(8)	C(25)-C(24)-C(23)	120.0(3)
C(14)-C(15)	1.3900	O(4)-Si(5)-C(22)	108.91(9)	C(26)-C(25)-C(24)	119.5(3)
C(10')-C(11')	1.3900	O(6)-Si(5)-C(22)	108.79(9)	C(25)-C(26)-C(27)	120.4(2)
C(10')-C(15')	1.3900	O(4)-Si(5)-C(28)	110.64(9)	C(26)-C(27)-C(22)	121.4(2)
C(11')-C(12')	1.3900	O(6)-Si(5)-C(28)	107.78(10)	C(29)-C(28)-C(33)	117.1(2)
C(12')-C(13')	1.3900	C(22)-Si(5)-C(28)	113.53(10)	C(29)-C(28)-Si(5)	120.71(18)
C(13')-C(14')	1.3900	B(1)-O(6)-Si(5)	128.42(15)	C(33)-C(28)-Si(5)	122.19(19)
C(14')-C(15')	1.3900	C(8)-C(7)-C(9)	117.4(2)	C(30)-C(29)-C(28)	121.4(3)
C(16)-C(21)	1.377(3)	C(8)-C(7)-B(1)	120.8(2)	C(31)-C(30)-C(29)	120.0(3)
C(16)-C(17)	1.382(4)	C(9)-C(7)-B(1)	121.7(2)	C(30)-C(31)-C(32)	120.2(3)
C(17)-C(18)	1.385(4)	C(9)#1-C(8)-C(7)	121.3(2)	C(31)-C(32)-C(33)	120.1(3)
C(18)-C(19)	1.362(4)	C(8)#1-C(9)-C(7)	121.2(2)	C(32)-C(33)-C(28)	121.2(3)
C(19)-C(20)	1.344(4)	C(11)-C(10)-C(15)	120.0		
C(20)-C(21)	1.380(4)	C(11)-C(10)-Si(3)	119.3(2)		
C(22)-C(27)	1.386(3)	C(15)-C(10)-Si(3)	119.9(2)		
C(22)-C(23)	1.389(3)	C(10)-C(11)-C(12)	120.0		
C(23)-C(24)	1.388(4)	C(13)-C(12)-C(11)	120.0		
C(24)-C(25)	1.377(4)	C(14)-C(13)-C(12)	120.0		
C(25)-C(26)	1.365(4)	C(13)-C(14)-C(15)	120.0		
C(26)-C(27)	1.386(4)	C(14)-C(15)-C(10)	120.0		

Symmetry transformations used to generate equivalent atoms:
#1 -x, -y, -z

Appendix 12

Compound	Bis(4-(pyridine-4-vinyl)phenyl)dimethylsilane (L ₁₂)
Formula	C ₂₈ H ₂₆ N ₂ Si
Formula weight	418.60
Temperature	173.00(10) K
Diffraction wavelength	Agilent Xcalibur 3 E, 1.54184 Å
Crystal system	Orthorhombic
Space group	P 21 21 21
Crystal colour/Morphology	Colourless tabular needles
Crystal size	0.200 x 0.150 x 0.150 mm ³
Unit cell dimension	a = 6.2975(2) Å α = 90° b = 12.3332(3) Å β = 90° c = 29.7641(7) Å γ = 90°
Volume z	2311.73(11) Å ³ , 4
Density (calculated)	1.203 Mg/m ³
Absorption coefficient	1.012 mm ⁻¹
F(000)	888
Θ range for data collection	3.880 to 73.614°.
Index ranges	-6 ≤ h ≤ 7 -14 ≤ k ≤ 13 -36 ≤ l ≤ 35
Ref1ns collected/unique	4810 3608 [R(int) = 0.0362]
Ref1ns observed [F > 4σ(F)]	3622
Absorption correction	Analytical
Max. and Min. transmission	1.00000 and 0.91739
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	3608 / 284 / 282
Goodness-of-fit on F ²	1.030
Final R indices [F > 4σ(F)]	R1 = 0.0514, wR2 = 0.1300
R indices (all data)	R1 = 0.0667, wR2 = 0.1407
Largest diff. peak, hole	0.664 and -0.232 e.Å ⁻³
Mean and maximum shift /error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°] for [bis\(4-\(pyridine-4-vinyl\)phenyl\)dimethylsilane \(L₁₂\)](#)

C(1)-Si1	1.855(5)	C(18)-H(18)	0.95	C(4)-C(5)-H(5)	120.1
C(1)-H(1A)	0.98	C(19)-C(20)	1.377(7)	C(7)-C(6)-C(5)	118.5(5)
C(1)-H(1B)	0.98	C(19)-C(22)	1.481(6)	C(7)-C(6)-C(9)	116.3(5)
C(1)-H(1C)	0.98	C(20)-C(21)	1.394(7)	C(5)-C(6)-C(9)	125.2(6)
C(2)-Si1	1.874(4)	C(20)-H(20)	0.95	C(6)-C(7)-C(8)	121.3(6)
C(2)-H(2A)	0.98	C(21)-H(21)	0.95	C(6)-C(7)-H(7)	119.4
C(2)-H(2B)	0.98	C(22)-C(23)	1.317(7)	C(8)-C(7)-H(7)	119.4
C(2)-H(2C)	0.98	C(22)-H(22)	0.95	C(7)-C(8)-C(3)	122.4(6)
C(3)-C(4)	1.383(7)	C(23)-C(26)	1.473(6)	C(7)-C(8)-H(8)	118.8
C(3)-C(8)	1.393(7)	C(23)-H(23)	0.95	C(3)-C(8)-H(8)	118.8
C(3)-Si1	1.886(4)	C(24)-N(2)	1.330(6)	C(10)-C(9)-C(6)	125.7(6)
C(4)-C(5)	1.410(8)	C(24)-C(25)	1.382(7)	C(10)-C(9)-H(9)	117.1
C(4)-H(4)	0.95	C(24)-H(24)	0.95	C(6)-C(9)-H(9)	117.1
C(5)-C(6)	1.400(9)	C(25)-C(26)	1.388(7)	C(9)-C(10)-C(13)	122.7(6)
C(5)-H(5)	0.95	C(25)-H(25)	0.95	C(9)-C(10)-H(10)	118.6
C(6)-C(7)	1.360(9)	C(26)-C(27)	1.398(7)	C(13)-C(10)-H(10)	118.6
C(6)-C(9)	1.505(8)	C(27)-C(28)	1.381(7)	N(1)-C(11)-C(12)	124.8(5)
C(7)-C(8)	1.374(7)	C(27)-H(27)	0.95	N(1)-C(11)-H(11)	117.6
C(7)-H(7)	0.95	C(28)-N(2)	1.336(7)	C(12)-C(11)-H(11)	117.6
C(8)-H(8)	0.95	C(28)-H(28)	0.95	C(11)-C(12)-C(13)	119.3(5)
C(9)-C(10)	1.276(9)	Si1-C(1)-H(1A)	109.5	C(11)-C(12)-H(12)	120.4
C(9)-H(9)	0.95	Si1-C(1)-H(1B)	109.5	C(13)-C(12)-H(12)	120.4
C(10)-C(13)	1.501(8)	H(1A)-C(1)-H(1B)	109.5	C(12)-C(13)-C(14)	116.5(5)
C(10)-H(10)	0.95	Si1-C(1)-H(1C)	109.5	C(12)-C(13)-C(10)	116.9(5)
C(11)-N(1)	1.321(7)	H(1A)-C(1)-H(1C)	109.5	C(14)-C(13)-C(10)	126.6(6)
C(11)-C(12)	1.376(8)	H(1B)-C(1)-H(1C)	109.5	C(15)-C(14)-C(13)	119.7(5)
C(11)-H(11)	0.95	Si1-C(2)-H(2A)	109.5	C(15)-C(14)-H(14)	120.2
C(12)-C(13)	1.387(8)	Si1-C(2)-H(2B)	109.5	C(13)-C(14)-H(14)	120.2
C(12)-H(12)	0.95	H(2A)-C(2)-H(2B)	109.5	N(1)-C(15)-C(14)	123.5(5)
C(13)-C(14)	1.387(8)	Si1-C(2)-H(2C)	109.5	N(1)-C(15)-H(15)	118.2
C(14)-C(15)	1.387(7)	H(2A)-C(2)-H(2C)	109.5	C(14)-C(15)-H(15)	118.2
C(14)-H(14)	0.95	H(2B)-C(2)-H(2C)	109.5	C(21)-C(16)-C(17)	116.2(4)
C(15)-N(1)	1.332(7)	C(4)-C(3)-C(8)	116.5(4)	C(21)-C(16)-Si1	120.8(4)
C(15)-H(15)	0.95	C(4)-C(3)-Si1	123.4(4)	C(17)-C(16)-Si1	122.9(3)
C(16)-C(21)	1.390(6)	C(8)-C(3)-Si1	120.0(4)	C(16)-C(17)-C(18)	121.8(4)
C(16)-C(17)	1.401(6)	C(3)-C(4)-C(5)	121.5(5)	C(16)-C(17)-H(17)	119.1
C(16)-Si1	1.873(4)	C(3)-C(4)-H(4)	119.3	C(18)-C(17)-H(17)	119.1
C(17)-C(18)	1.408(6)	C(5)-C(4)-H(4)	119.3	C(19)-C(18)-C(17)	120.2(4)
C(17)-H(17)	0.95	C(6)-C(5)-C(4)	119.8(5)	C(19)-C(18)-H(18)	119.9
C(18)-C(19)	1.383(6)	C(6)-C(5)-H(5)	120.1	C(17)-C(18)-H(18)	119.9

C(20)-C(19)-C(18)	118.7(4)
C(20)-C(19)-C(22)	118.5(4)
C(18)-C(19)-C(22)	122.7(4)
C(19)-C(20)-C(21)	120.8(4)
C(19)-C(20)-H(20)	119.6
C(21)-C(20)-H(20)	119.6
C(16)-C(21)-C(20)	122.2(5)
C(16)-C(21)-H(21)	118.9
C(20)-C(21)-H(21)	118.9
C(23)-C(22)-C(19)	127.1(4)
C(23)-C(22)-H(22)	116.5
C(19)-C(22)-H(22)	116.5
C(22)-C(23)-C(26)	125.2(4)
C(22)-C(23)-H(23)	117.4
C(26)-C(23)-H(23)	117.4
N(2)-C(24)-C(25)	123.9(5)
N(2)-C(24)-H(24)	118.1
C(25)-C(24)-H(24)	118.1
C(24)-C(25)-C(26)	120.0(5)
C(24)-C(25)-H(25)	120.0
C(26)-C(25)-H(25)	120.0
C(25)-C(26)-C(27)	116.2(4)
C(25)-C(26)-C(23)	120.0(4)
C(27)-C(26)-C(23)	123.7(4)
C(28)-C(27)-C(26)	119.5(4)
C(28)-C(27)-H(27)	120.3
C(26)-C(27)-H(27)	120.3
N(2)-C(28)-C(27)	124.1(5)
N(2)-C(28)-H(28)	118.0
C(27)-C(28)-H(28)	118.0
C(11)-N(1)-C(15)	116.1(4)
C(24)-N(2)-C(28)	116.3(4)
C(1)-SI1-C(16)	109.8(2)
C(1)-SI1-C(2)	111.3(2)
C(16)-SI1-C(2)	107.5(2)
C(1)-SI1-C(3)	108.6(2)
C(16)-SI1-C(3)	112.65(19)
C(2)-SI1-C(3)	107.0(2)

Appendix 13

Compound	3d
Formula	$C_{14}H_{18}B_2O_4Si \cdot C_4H_8O_2$
Formula weight	388.10
Temperature	293(2) K
Diffraction wavelength	Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system	Triclinic,
Space group	P-1
Crystal colour/Morphology	Colourless blocky needles
Crystal size	0.22 x 0.17 x 0.08
Unit cell dimension	a = 12.0204(4) Å α = 104.653(4)° b = 13.7369(6) Å β = 103.335(3)° c = 15.6587(6) Å γ = 113.053(3)
Volume z	2138.07(18) Å ³ , 4
Density (calculated)	1.206 Mg/m ³
Absorption coefficient	1.218 mm ⁻¹
F(000)	824
Θ range for data collection	3.14 to 72.52°
Index ranges	-14 ≤ h ≤ 13 -16 ≤ k ≤ 16 -19 ≤ l ≤ 18
Ref1ns collected/unique	20680 / 8329 [R(int) = 0.0214]
Ref1ns observed [F > 4σ(F)]	6886
Absorption correction	Analytical
Max. and Min. transmission	0.914 and 0.814
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	8329 / 116 / 573
Goodness-of-fit on F ²	1.073
Final R indices [F > 4σ(F)]	R1 = 0.0419, wR2 = 0.1161
R indices (all data)	R1 = 0.0520, wR2 = 0.1214
Absolute structure parameter	0.08(5)
Largest diff. peak, hole	0.287, -0.299 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.001

Table 2. Bond lengths [Å] and angles [°]

Table 1. Crystal data and structure refinement for compound (**3d**)

Si(1A)-C(20A)	1.856(2)	B(16B)-O(18B)	1.362(2)
Si(1A)-C(19A)	1.8688(19)	B(16B)-O(17B)	1.366(2)
Si(1A)-C(1A)	1.8828(17)	C(30)-C(31)	1.488(6)
Si(1A)-C(10A)	1.8863(17)	C(31)-O(31)	1.218(4)
C(1A)-C(6A)	1.395(2)	C(31)-O(32)	1.324(3)
C(1A)-C(2A)	1.401(2)	O(32)-C(33)	1.486(6)
C(2A)-C(3A)	1.386(2)	C(33)-C(34)	1.478(6)
C(3A)-C(4A)	1.404(2)	C(30')-C(31')	1.483(12)
C(4A)-C(5A)	1.395(2)	C(31')-O(31')	1.244(12)
C(4A)-B(7A)	1.568(2)	C(31')-O(32')	1.329(11)
C(5A)-C(6A)	1.390(2)	O(32')-C(33')	1.446(12)
B(7A)-O(8A)	1.359(2)	C(33')-C(34')	1.497(15)
B(7A)-O(9A)	1.371(2)	C(40)-C(41)	1.497(5)
C(10A)-C(11A)	1.396(2)	C(41)-O(41)	1.200(5)
C(10A)-C(15A)	1.397(2)	C(41)-O(42)	1.334(6)
C(11A)-C(12A)	1.385(2)	O(42)-C(43)	1.464(5)
C(12A)-C(13A)	1.398(2)	C(43)-C(44)	1.461(7)
C(13A)-C(14A)	1.400(2)	C(40')-C(41')	1.452(12)
C(13A)-B(16A)	1.570(2)	C(41')-O(41')	1.241(13)
C(14A)-C(15A)	1.388(2)	C(41')-O(42')	1.315(12)
B(16A)-O(17A)	1.352(2)	O(42')-C(43')	1.469(12)
B(16A)-O(18A)	1.370(2)	C(43')-C(44')	1.512(14)
Si(1B)-C(19B)	1.8575(16)	C(20A)-Si(1A)-C(19A)	111.63(10)
Si(1B)-C(20B)	1.8674(18)	C(20A)-Si(1A)-C(1A)	108.78(9)
Si(1B)-C(1B)	1.8805(16)	C(19A)-Si(1A)-C(1A)	110.22(8)
Si(1B)-C(10B)	1.8871(16)	C(20A)-Si(1A)-C(10A)	109.40(8)
C(1B)-C(6B)	1.395(2)	C(19A)-Si(1A)-C(10A)	110.62(8)
C(1B)-C(2B)	1.398(2)	C(1A)-Si(1A)-C(10A)	106.02(7)
C(2B)-C(3B)	1.386(2)	C(6A)-C(1A)-C(2A)	117.00(15)
C(3B)-C(4B)	1.397(2)	C(6A)-C(1A)-Si(1A)	120.01(13)
C(4B)-C(5B)	1.396(2)	C(2A)-C(1A)-Si(1A)	122.79(12)
C(4B)-B(7B)	1.560(2)	C(3A)-C(2A)-C(1A)	121.47(15)
C(5B)-C(6B)	1.382(2)	C(2A)-C(3A)-C(4A)	121.54(15)
B(7B)-O(8B)	1.369(2)	C(5A)-C(4A)-C(3A)	116.78(15)
B(7B)-O(9B)	1.371(2)	C(5A)-C(4A)-B(7A)	122.31(14)
C(10B)-C(11B)	1.392(2)	C(3A)-C(4A)-B(7A)	120.89(15)
C(10B)-C(15B)	1.392(2)	C(6A)-C(5A)-C(4A)	121.68(15)
C(11B)-C(12B)	1.385(3)	C(5A)-C(6A)-C(1A)	121.52(16)
C(12B)-C(13B)	1.397(2)	O(8A)-B(7A)-O(9A)	116.59(15)
C(13B)-C(14B)	1.389(2)	O(8A)-B(7A)-C(4A)	119.47(14)
C(13B)-B(16B)	1.567(2)	O(9A)-B(7A)-C(4A)	123.91(15)
C(14B)-C(15B)	1.384(2)	C(11A)-C(10A)-C(15A)	116.89(15)

C(11A)-C(10A)-Si(1	120.17(13)	C(15B)-C(10B)-Si(1B)	121.37(12)
C(15A)-C(10A)-Si(1A)	122.65(12)	C(12B)-C(11B)-C(10B)	121.56(16)
C(12A)-C(11A)-C(10A)	121.68(16)	C(11B)-C(12B)-C(13B)	121.89(16)
C(11A)-C(12A)-C(13A)	121.54(15)	C(14B)-C(13B)-C(12B)	116.45(15)
C(12A)-C(13A)-C(14A)	116.79(15)	C(14B)-C(13B)-B(16B)	122.91(14)
C(12A)-C(13A)-B(16A)	119.42(15)	C(12B)-C(13B)-B(16B)	120.63(14)
C(14A)-C(13A)-B(16A)	123.76(15)	C(15B)-C(14B)-C(13B)	121.50(15)
C(15A)-C(14A)-C(13A)	121.56(16)	C(14B)-C(15B)-C(10B)	122.18(15)
C(14A)-C(15A)-C(10A)	121.48(15)	O(18B)-B(16B)-O(17B)	117.26(14)
O(17A)-B(16A)-O(18A)	118.51(16)	O(18B)-B(16B)-C(13B)	125.17(14)
O(17A)-B(16A)-C(13A)	117.67(15)	O(17B)-B(16B)-C(13B)	117.57(14)
O(18A)-B(16A)-C(13A)	123.82(15)	O(31)-C(31)-O(32)	121.2(4)
C(19B)-Si(1B)-C(20B)	112.61(8)	O(31)-C(31)-C(30)	125.4(3)
C(19B)-Si(1B)-C(1B)	110.02(7)	O(32)-C(31)-C(30)	113.3(3)
C(20B)-Si(1B)-C(1B)	108.57(8)	C(31)-O(32)-C(33)	117.2(3)
C(19B)-Si(1B)-C(10B)	108.53(7)	C(34)-C(33)-O(32)	110.0(4)
C(20B)-Si(1B)-C(10B)	108.85(8)	O(31')-C(31')-O(32')	122.2(11)
C(1B)-Si(1B)-C(10B)	108.16(7)	O(31')-C(31')-C(30')	122.5(11)
C(6B)-C(1B)-C(2B)	116.65(15)	O(32')-C(31')-C(30')	115.3(11)
C(6B)-C(1B)-Si(1B)	121.12(12)	C(31')-O(32')-C(33')	121.1(9)
C(2B)-C(1B)-Si(1B)	122.19(12)	O(32')-C(33')-C(34')	107.6(13)
C(3B)-C(2B)-C(1B)	121.62(15)	O(41)-C(41)-O(42)	123.6(5)
C(2B)-C(3B)-C(4B)	121.76(15)	O(41)-C(41)-C(40)	124.6(6)
C(5B)-C(4B)-C(3B)	116.18(15)	O(42)-C(41)-C(40)	111.7(4)
C(5B)-C(4B)-B(7B)	121.48(14)	C(41)-O(42)-C(43)	118.3(4)
C(3B)-C(4B)-B(7B)	122.30(14)	C(44)-C(43)-O(42)	111.4(4)
C(6B)-C(5B)-C(4B)	122.22(14)	O(41')-C(41')-O(42')	115.5(13)
C(5B)-C(6B)-C(1B)	121.44(15)	O(41')-C(41')-C(40')	126.9(14)
O(8B)-B(7B)-O(9B)	116.08(15)	O(42')-C(41')-C(40')	115.1(12)
O(8B)-B(7B)-C(4B)	120.76(14)	C(41')-O(42')-C(43')	117.4(11)
O(9B)-B(7B)-C(4B)	123.13(14)	O(42')-C(43')-C(44')	103.7(11)
C(11B)-C(10B)-C(15B)	116.38(15)		
C(11B)-C(10B)-Si(1B)	122.25(12)		

Appendix 14

Compound	tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)
Formula	C ₃₀ H ₂₆ N ₂ O ₄ Si _{0.5} Zn,5(CH ₄ O)
Formula weight	718.15
Temperature	293(2) K
Diffraction wavelength	Agilent Xcalibur PX Ultra A, 1.54184 Å
Crystal system	Orthorhombic
Space group	P2 ₁ 2 ₁ 2
Crystal colour/Morphology	Colourless blocky needles
Crystal size	0.24 x 0.14 x 0.09 mm ³
Unit cell dimension	a = 24.8316(15) Å α = 90° b = 21.1756(14) Å β = 90° c = 7.5142(4) Å γ = 90°
Volume z	3951.2(4) Å ³ , 4
Density (calculated)	1.207 Mg/m ³
Absorption coefficient	1.421 mm ⁻¹
F(000)	1516
Θ range for data collection	3.560 to 73.441°
Index ranges	-18<=h<=29 -16<=k<=26 -8<=l<=7
Ref1ns collected/unique	9039 / 6576 [R(int) = 0.0735]
Ref1ns observed [F>4σ(F)]	4507
Absorption correction	Analytical
Max. and Min. transmission	0.912 and 0.783
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	6576 / 42 / 359
Goodness-of-fit on F ²	1.023
Final R indices [F>4σ(F)]	R1 = 0.0855, wR2 = 0.1996
R indices (all data)	R1 = 0.1073, wR2 = 0.2137
Absolute structure parameter	0.08(5)
Largest diff. peak, hole	0.945, -0.441 eÅ ⁻³
Mean and maximum shift /error	0.000 and 0.000

Table 2. Bond lengths [Å] and angles [°] for tetrakis(4-(pyridine-4-vinyl)phenyl)silane MOF (17)

Zn(1)-O(52')	1.90(4)	N(32)-Zn(1)#3	2.082(7)	C(5)-C(4)-C(3)	118.2(7)
Zn(1)-O(40)	1.961(10)	C(33)-C(34)	1.405(14)	C(5)-C(4)-C(7)	122.8(8)
Zn(1)-O(50)	1.994(9)	O(40)-C(41)	1.319(16)	C(3)-C(4)-C(7)	119.0(7)
Zn(1)-N(12)	2.061(7)	C(41)-O(42)	1.188(14)	C(4)-C(5)-C(6)	120.8(8)
Zn(1)-N(32)#1	2.082(7)	C(41)-C(43)	1.49(2)	C(1)-C(6)-C(5)	120.8(8)
Zn(1)-O(50')	2.26(4)	O(50)-C(51)	1.245(11)	C(8)-C(7)-C(4)	124.0(8)
Zn(1)-C(51')	2.49(3)	C(51)-O(52)	1.158(10)	C(7)-C(8)-C(9)	124.5(8)
Si(1)-C(21)#2	1.865(8)	C(51)-C(53)	1.488(10)	C(10)-C(9)-C(14)	116.1(9)
Si(1)-C(21)	1.865(8)	O(50')-C(51')	1.306(13)	C(10)-C(9)-C(8)	124.4(10)
Si(1)-C(1)#2	1.902(8)	C(51')-O(52')	1.169(12)	C(14)-C(9)-C(8)	119.5(8)
Si(1)-C(1)	1.902(8)	C(51')-C(53')	1.480(12)	C(9)-C(10)-C(11)	120.5(11)
C(1)-C(2)	1.359(12)	O(52')-Zn(1)-O(40)	150.0(15)	N(12)-C(11)-C(10)	122.4(9)
C(1)-C(6)	1.383(11)	O(40)-Zn(1)-O(50)	116.0(5)	C(13)-N(12)-C(11)	118.0(8)
C(2)-C(3)	1.382(11)	O(52')-Zn(1)-N(12)	92.1(9)	C(13)-N(12)-Zn(1)	125.3(7)
C(3)-C(4)	1.389(12)	O(40)-Zn(1)-N(12)	103.9(4)	C(11)-N(12)-Zn(1)	116.6(6)
C(4)-C(5)	1.360(13)	O(50)-Zn(1)-N(12)	130.9(6)	N(12)-C(13)-C(14)	122.3(10)
C(4)-C(7)	1.491(12)	O(52')-Zn(1)-N(32)#1	106.6(14)	C(9)-C(14)-C(13)	120.5(9)
C(5)-C(6)	1.384(12)	O(40)-Zn(1)-N(32)#1	96.8(3)	C(22)-C(21)-C(26)	116.9(7)
C(7)-C(8)	1.345(13)	O(50)-Zn(1)-N(32)#1	105.4(4)	C(22)-C(21)-Si(1)	125.8(6)
C(8)-C(9)	1.460(13)	N(12)-Zn(1)-N(32)#1	96.5(3)	C(26)-C(21)-Si(1)	116.7(6)
C(9)-C(10)	1.368(14)	O(52')-Zn(1)-O(50')	57.4(9)	C(21)-C(22)-C(23)	121.9(7)
C(9)-C(14)	1.389(14)	O(40)-Zn(1)-O(50')	102.9(7)	C(24)-C(23)-C(22)	120.1(8)
C(10)-C(11)	1.378(16)	N(12)-Zn(1)-O(50')	149.4(8)	C(25)-C(24)-C(23)	118.9(8)
C(11)-N(12)	1.347(14)	N(32)#1-Zn(1)-O(50')	94.7(11)	C(25)-C(24)-C(27)	120.4(8)
N(12)-C(13)	1.305(13)	O(52')-Zn(1)-C(51')	26.9(6)	C(23)-C(24)-C(27)	120.6(8)
C(13)-C(14)	1.391(14)	O(40)-Zn(1)-C(51')	133.1(8)	C(26)-C(25)-C(24)	120.4(8)
C(21)-C(22)	1.377(12)	N(12)-Zn(1)-C(51')	118.5(7)	C(25)-C(26)-C(21)	121.5(8)
C(21)-C(26)	1.423(12)	N(32)#1-Zn(1)-C(51')	97.1(8)	C(28)-C(27)-C(24)	123.4(9)
C(22)-C(23)	1.399(12)	O(50')-Zn(1)-C(51')	31.5(4)	C(27)-C(28)-C(29)	124.6(9)
C(23)-C(24)	1.392(13)	C(21)#2-Si(1)-C(21)	106.8(5)	C(30)-C(29)-C(34)	116.9(10)
C(24)-C(25)	1.387(13)	C(21)#2-Si(1)-C(1)#2	111.0(3)	C(30)-C(29)-C(28)	124.8(10)
C(24)-C(27)	1.492(13)	C(21)-Si(1)-C(1)#2	111.1(3)	C(34)-C(29)-C(28)	118.1(10)
C(25)-C(26)	1.383(13)	C(21)#2-Si(1)-C(1)	111.1(3)	C(29)-C(30)-C(31)	121.0(11)
C(27)-C(28)	1.345(14)	C(21)-Si(1)-C(1)	111.0(3)	N(32)-C(31)-C(30)	121.0(10)
C(28)-C(29)	1.474(14)	C(1)#2-Si(1)-C(1)	105.9(5)	C(33)-N(32)-C(31)	118.2(9)
C(29)-C(30)	1.376(17)	C(2)-C(1)-C(6)	118.4(7)	C(33)-N(32)-Zn(1)#3	121.1(7)
C(29)-C(34)	1.396(16)	C(2)-C(1)-Si(1)	124.9(6)	C(31)-N(32)-Zn(1)#3	118.8(7)
C(30)-C(31)	1.399(17)	C(6)-C(1)-Si(1)	116.2(6)	N(32)-C(33)-C(34)	124.9(10)
C(31)-N(32)	1.344(15)	C(1)-C(2)-C(3)	120.9(7)	C(29)-C(34)-C(33)	117.8(10)
N(32)-C(33)	1.292(13)	C(2)-C(3)-C(4)	120.7(7)	C(41)-O(40)-Zn(1)	107.1(8)

O(42)-C(41)-O(40)	120.5(13)
O(42)-C(41)-C(43)	126.7(15)
O(40)-C(41)-C(43)	112.8(13)
C(51)-O(50)-Zn(1)	112.1(9)
O(52)-C(51)-O(50)	120.0(12)
O(52)-C(51)-C(53)	126.6(14)
O(50)-C(51)-C(53)	113.0(11)
C(51')-O(50')-Zn(1)	84(2)
O(52')-C(51')- O(50')	110(2)
O(52')-C(51')-C(53')	130(3)
O(50')-C(51')-C(53')	108.0(19)
O(52')-C(51')-Zn(1)	47.5(19)
O(50')-C(51')-Zn(1)	64.6(19)
C(53')-C(51')-Zn(1)	162(4)
C(51')-O(52')-Zn(1)	106(2)

Symmetry transformations used to generate equivalent atoms:

#1 $x-1/2, -y+1/2, -z+1$ #2 $-x+1, -y+1, z$ #3 $x+1/2, -y+1/2, -z+1$

Appendix 15

Compound	MOF (18)
Formula	$C_{68}H_{72}N_4O_{18}SiZn_2$
Dcalc./ g cm ⁻³	1.341
ρ /mm ⁻¹	1.617
Formula Weight	1392.12
Colour	colourless
Shape	needle
Size/mm ³	0.320×0.025×0.015
T/K	100(2)
Crystal System	orthorhombic
Flack Parameter	?
Hooft Parameter	0.30(5)
Space Group	I212121
a/Å	7.5726(2)
b/Å	30.1615(8)
c/Å	30.1828(10)
α /°	90
β /°	90
γ /°	90
V/Å ³	30.1828(10)
Z	4
Z'	0.5
Wavelength/Å	1.54184
Radiation type	CuK α
ω min/°	4.144
ω max/°	68.246
Measured Refl.	24377
Independent Refl.	6265
Reflections Used	4549
Rint	0.0446
Parameters	507
Restraints	1633
Largest Peak	0.485
Deepest Hole	-0.273
GooF	1.028
wR2 (all data)	0.2179
wR2	0.1970
R1 (all data)	0.0927
R1	0.0735

Bond lengths in Å for MOF (18)

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O111	1.989(15)	C10	C11	1.3900	C21	C26	1.3900
Zn1	O1 ¹	2.332(14)	C10	C13	1.534(15)	C22	C23	1.3900
Zn1	O1	2.203(15)	C11	C12	1.3900	C23	C24	1.3900
Zn1	O2	2.114(15)	C121	C122	1.3900	C24	C25	1.3900
Zn1	O101 ¹	2.001(13)	C121	C126	1.3900	C25	C26	1.3900
Zn1	O102	1.811(16)	C122	C123	1.3900	C127	C128	1.3900
Zn1	O102 ¹	2.422(15)	C123	C124	1.3900	C127	C132	1.3900
Zn1	O112	2.035(15)	C124	C125	1.3900	C128	C129	1.3900
Zn2	O131	2.020(12)	C124	C127	1.465(13)	C129	C130	1.3900
Zn2	O21 ²	1.964(16)	C125	C126	1.3900	C130	C131	1.3900
Zn2	O22	1.962(15)	C27	C28	1.3900	C130	C133	1.509(15)
Zn2	O121	2.082(11)	C27	C32	1.3900	C131	C132	1.3900
Zn2	O121 ²	2.468(14)	C27	C24	1.599(12)			
Zn2	O122	2.253(17)	C28	C29	1.3900			
Zn2	O132	1.978(11)	C29	C30	1.3900			
Si1	C1 ³	1.898(8)	C30	C31	1.3900			
Si1	C1	1.898(8)	C30	C33	1.542(15)			
Si1	C121	1.880(8)	C31	C32	1.3900			
Si1	C121 ³	1.880(8)	O101	Zn11	2.001(13)			
Si1	C101 ³	1.937(8)	O101	C113	1.268(17)			
Si1	C101	1.936(8)	O102	Zn11	2.422(15)			
Si1	C21	1.928(8)	O102	C113	1.25(2)			
Si1	C21 ³	1.928(8)	O121	Zn22	2.468(14)			
O1	Zn1 ¹	2.332(14)	O121	C133	1.269(17)			
O1	C13	1.271(16)	O122	C133	1.26(2)			
O2	C13	1.19(2)	C101	C106	1.3900			
O21	Zn2 ²	1.965(16)	C101	C102	1.3900			
O21	C33	1.259(17)	C106	C105	1.3900			
O22	C33	1.22(2)	C105	C104	1.3900			
C1	C6	1.3900	C104	C103	1.3900			
C1	C2	1.3900	C104	C107	1.613(11)			
C6	C5	1.3900	C103	C102	1.3900			
C5	C4	1.3900	C107	C108	1.3900			
C4	C3	1.3900	C107	C112	1.3900			
C4	C7	1.482(10)	C108	C109	1.3900			
C3	C2	1.3900	C109	C110	1.3900			
C7	C8	1.3900	C110	C111	1.3900			
C7	C12	1.3900	C110	C113	1.568(15)			
C8	C9	1.3900	C111	C112	1.3900			
C9	C10	1.3900	C113	Zn11	2.546(15)			
			C21	C22	1.3900			

$$^1-3-x,-3/2-y,+z; ^23/2-x,+y,-1-z; ^3+x,-1-y,-3/2-z$$

Bond Angles in ° for MOF (18)

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
O111	Zn1	O11	74.1(7)	C121	Si1	C101	115.6(10)
O111	Zn1	O1	98.5(6)	C121	Si1	C1013	112.5(10)
O111	Zn1	O2	159.7(6)	C1213	Si1	C1013	115.6(10)
O111	Zn1	O1011	94.5(7)	C1213	Si1	C101	112.5(10)
O111	Zn1	O1021	97.8(9)	C101	Si1	C1013	101.6(15)
O111	Zn1	O112	106.4(10)	C21	Si1	C213	111.4(14)
O1	Zn1	O11	131.7(4)	Zn1	O1	Zn11	44.5(3)
O2	Zn1	O11	120.6(6)	C13	O1	Zn11	111.1(9)
O2	Zn1	O1	61.5(5)	C13	O1	Zn1	82.5(10)
O1011	Zn1	O1021	58.5(4)	C13	O2	Zn1	88.3(10)
O1011	Zn1	O112	101.5(8)	C33	O21	Zn22	107.5(10)
O102	Zn1	O111	142.2(8)	C33	O22	Zn2	103.1(10)
O102	Zn1	O1011	100.7(7)	C6	C1	Si1	116.9(12)
O102	Zn1	O1021	63.0(11)	C6	C1	C2	120
O102	Zn1	O112	104.2(9)	C2	C1	Si1	119.8(13)
O112	Zn1	O11	125.7(8)	C1	C6	C5	120
O112	Zn1	O1	102.4(8)	C4	C5	C6	120
O112	Zn1	O2	77.3(9)	C5	C4	C3	120
O112	Zn1	O1021	150.1(9)	C5	C4	C7	120.5(13)
O131	Zn2	O1212	68.0(6)	C3	C4	C7	119.2(13)
O131	Zn2	O121	92.7(7)	C2	C3	C4	120
O131	Zn2	O122	151.7(7)	C3	C2	C1	120
O212	Zn2	O131	97.2(6)	C8	C7	C4	120.7(10)
O212	Zn2	O132	102.1(6)	C8	C7	C12	120
O22	Zn2	O131	133.7(7)	C12	C7	C4	119.3(10)
O22	Zn2	O212	101.9(6)	C9	C8	C7	120
O22	Zn2	O132	118.0(6)	C8	C9	C10	120
O121	Zn2	O1212	128.7(4)	C9	C10	C13	117.5(10)
O121	Zn2	O122	60.8(5)	C11	C10	C9	120
O122	Zn2	O1212	119.2(6)	C11	C10	C13	121.7(10)
O132	Zn2	O131	98.2(7)	C10	C11	C12	120
O132	Zn2	O121	106.7(6)	C11	C12	C7	120
O132	Zn2	O1212	122.4(4)	O1	C13	C10	113.5(15)
O132	Zn2	O122	99.1(7)	O2	C13	O1	127.7(15)
C1	Si1	C13	112.4(14)	O2	C13	C10	118.8(14)
C1	Si1	C213	115.5(11)	C122	C121	Si1	121.0(13)
C1	Si1	C21	101.3(10)	C122	C121	C126	120
C13	Si1	C213	101.3(10)	C126	C121	Si1	119.0(13)
C13	Si1	C21	115.5(11)	C123	C122	C121	120
C121	Si1	C1213	99.6(15)	C122	C123	C124	120
				C123	C124	C125	120

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C123	C124	C127	127.4(18)	C112	C107	C104	120.7(11)
C125	C124	C127	112.6(17)	C107	C108	C109	120.0
C126	C125	C124	120.0	C110	C109	C108	120.0
C125	C126	C121	120.0	C109	C110	C111	120.0
C28	C27	C32	120.0	C109	C110	C113	116.0(11)
C28	C27	C24	123.4(14)	C111	C110	C113	124.0(11)
C32	C27	C24	115.8(14)	C112	C111	C110	120.0
C27	C28	C29	120.0	C111	C112	C107	120.0
C30	C29	C28	120.0	O101	C113	Zn11	50.7(8)
C29	C30	C33	118.8(11)	O101	C113	C110	114.8(14)
C31	C30	C29	120.0	O102	C113	Zn11	69.9(10)
C31	C30	C33	120.8(11)	O102	C113	O101	120.7(15)
C30	C31	C32	120.0	O102	C113	C110	124.5(15)
C31	C32	C27	120.0	C110	C113	Zn11	165.5(12)
O21	C33	C30	118.6(14)	C22	C21	Si1	128.6(12)
O22	C33	O21	126.6(15)	C22	C21	C26	120.0
O22	C33	C30	114.9(15)	C26	C21	Si1	111.4(12)
C113	O101	Zn1 ¹	99.9(10)	C23	C22	C21	120.0
Zn1	O102	Zn1 ¹	45.2(4)	C22	C23	C24	120.0
C113	O102	Zn1	107.2(11)	C23	C24	C27	114.3(16)
C113	O102	Zn1 ¹	81.0(10)	C25	C24	C27	125.4(15)
Zn2	O121	Zn2 ²	49.1(3)	C25	C24	C23	120.0
C133	O121	Zn2	93.1(9)	C24	C25	C26	120.0
C133	O121	Zn2 ²	116.5(10)	C25	C26	C21	120.0
C133	O122	Zn2	85.6(11)	C128	C127	C124	114.7(14)
C106	C101	Si1	122.8(13)	C128	C127	C132	120.0
C106	C101	C102	120.0	C132	C127	C124	121.5(15)
C102	C101	Si1	116.8(13)	C127	C128	C129	120.0
C105	C106	C101	120.0	C128	C129	C130	120.0
C106	C105	C104	120.0	C129	C130	C133	119.1(11)
C105	C104	C107	118.5(14)	C131	C130	C129	120.0
C103	C104	C105	120.0	C131	C130	C133	120.6(11)
C103	C104	C107	121.1(14)	C130	C131	C132	120.0
C104	C103	C102	120.0	C131	C132	C127	120.0
C103	C102	C101	120.0	O121	C133	C130	121.8(15)
C108	C107	C104	119.3(10)	O122	C133	O121	120.5(15)
C108	C107	C112	120.0	O122	C133	C130	117.7(14)

¹-3-x,-3/2-y,+z; ²3/2-x,+y,-1-z; ³+x,-1-y,-3/2-z

Appendix 16

Compound

	MOF (19)
Formula	C ₅₆ H ₆₈ N ₆ O ₁₆ SiZn
$D_{calc.}/\text{g cm}^{-3}$	1.175
μ/mm^{-1}	1.219
Formula Weight	1174.62
Colour	colourless
Shape	plate
Size/mm ³	0.190×0.100×0.030
T/K	100(2)
Crystal System	orthorhombic
Space Group	<i>Pbcn</i>
$a/\text{\AA}$	41.693(3)
$b/\text{\AA}$	36.5521(13)
$c/\text{\AA}$	17.4325(11)
$\alpha/^\circ$	90
$\beta/^\circ$	90
$\gamma/^\circ$	90
$V/\text{\AA}^3$	26566(3)
Z	16
Z'	2
Wavelength/ $\text{\AA}$	1.54184
Radiation type	CuK α
$\theta_{min}/^\circ$	3.002
$\theta_{max}/^\circ$	58.931
Measured Refl.	106852
Independent Refl.	19049
Reflections Used	7198
R_{int}	0.1396
Parameters	893
Restraints	1058
Largest Peak	1.409
Deepest Hole	-0.570
GooF	1.458
wR_2 (all data)	0.5246
wR_2	0.4614
R_1 (all data)	0.2769
R_1	0.1804

Bond lengths in Å for MOF (19)

Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
Zn1	O11	2.339(16)	C21	C22	1.501(9)	C64	C63	1.39
Zn1	O12	1.895(14)	C22	C23	1.3900	C64	C67	1.515(14)
Zn1	N1	2.114(7)	C22	C26	1.3900	C63	C62	1.39
Zn1	N41	2.12(15)	C23	C24	1.3900	C67	C68	1.186(15)
Zn1	N61	2.133(9)	C24	N2	1.3900	C68	C69	1.534(14)
Zn1	N641	2.12(13)	N2	C25	1.3900	C69	C70	1.3900
Zn2	O21	2.115(14)	C25	C26	1.3900	C69	C73	1.3900
Zn2	O22	2.210(15)	C27	C32	1.3900	C70	C71	1.3900
Zn2	N2	2.133(5)	C27	C28	1.3900	C71	N61	1.3900
Zn2	N32	2.12(6)	C32	C31	1.3900	N61	C72	1.3900
Zn2	N623	2.14(12)	C31	C30	1.3900	C72	C73	1.3900
Zn2	N634	2.13(6)	C30	C29	1.3900	C74	C75	1.3900
Si1	C1	1.910(6)	C30	C33	1.535(10)	C74	C79	1.3900
Si1	C14	1.887(5)	C29	C28	1.3900	C75	C76	1.3900
Si1	C27	1.901(6)	C33	C34	1.184(12)	C76	C77	1.3900
Si1	C40	1.871(7)	C34	C35	1.528(11)	C77	C78	1.3900
Si61	C61	1.887(9)	C35	C36	1.3900	C77	C80	1.510(10)
Si61	C74	1.872(6)	C35	C39	1.3900	C78	C79	1.3900
Si61	C87	1.891(6)	C36	C37	1.3900	C80	C81	1.238(12)
Si61	C100	1.909(8)	C37	N3	1.3900	C81	C82	1.523(11)
C1	C2	1.3900	N3	Zn25	2.120(6)	C82	C86	1.3900
C1	C6	1.3900	N3	C38	1.3900	C82	C83	1.3900
C2	C3	1.3900	C38	C39	1.3900	C86	C85	1.3900
C3	C4	1.3900	C40	C41	1.3900	C85	N62	1.3900
C4	C5	1.3900	C40	C45	1.3900	N62	Zn27	2.142(5)
C4	C7	1.511(11)	C41	C42	1.3900	N62	C84	1.3900
C5	C6	1.3900	C42	C43	1.3900	C84	C83	1.3900
C7	C8	1.164(13)	C43	C44	1.3900	C87	C92	1.3900
C8	C9	1.516(12)	C43	C46	1.499(13)	C87	C88	1.3900
C9	C13	1.3900	C44	C45	1.3900	C92	C91	1.3900
C9	C10	1.3900	C46	C47	1.180(14)	C91	C90	1.3900
C13	C12	1.3900	C47	C48	1.497(13)	C90	C89	1.3900
C12	N1	1.3900	C48	C49	1.3900	C90	C93	1.498(11)
N1	C11	1.3900	C48	C52	1.3900	C89	C88	1.3900
C11	C10	1.3900	C49	C50	1.3900	C93	C94	1.212(14)
C14	C15	1.3900	C50	N4	1.3900	C94	C95	1.531(11)
C14	C19	1.3900	N4	Zn16	2.118(8)	C95	C99	1.3900
C15	C16	1.3900	N4	C51	1.3900	C95	C96	1.3900
C16	C17	1.3900	C51	C52	1.3900	C99	C98	1.3900
C17	C18	1.3900	C61	C66	1.3900	C98	N63	1.3900
C17	C20	1.513(9)	C61	C62	1.3900	N63	Zn28	2.131(6)
C18	C19	1.3900	C66	C65	1.3900	N63	C97	1.3900
			C65	C64	1.3900	C97	C96	1.3900

C20	C21	1.252(11)						
Atom	Atom	Length/Å	Atom	Atom	Length/Å	Atom	Atom	Length/Å
C100	C105	1.3900	C102	C101	1.3900	C111	N64	1.3900
C100	C101	1.3900	C106	C107	1.181(14)	N64	Zn16	2.121(10)
C105	C104	1.3900	C107	C108	1.519(14)	N64	C110	1.3900
C104	C103	1.3900	C108	C112	1.3900	C110	C109	1.3900
C103	C102	1.3900	C108	C109	1.3900			
C103	C106	1.531(13)	C112	C111	1.3900			

¹1/2+x,3/2-y,1-z; ²+x,+y,1+z; ³+x,-1+y,+z; ⁴+x,-1+y,1+z;
⁵+x,+y,-1+z; ⁶-1/2+x,3/2-y,1-z; ⁷+x,1+y,+z; ⁸+x,1+y,-1+z

Bond Angles in ° for MOF (19)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
O12	Zn1	O11	174.3(5)	N634	Zn2	N2	178(6)
O12	Zn1	N1	85.0(4)	N634	Zn2	N623	89(6)
O12	Zn1	N4 ¹	89(6)	C14	Si1	C1	113.3(3)
O12	Zn1	N61	93.9(5)	C14	Si1	C27	106.5(3)
O12	Zn1	N64 ¹	86(6)	C27	Si1	C1	110.0(4)
N1	Zn1	O11	92.3(4)	C40	Si1	C1	106.5(3)
N1	Zn1	N4 ¹	174(6)	C40	Si1	C14	110.2(4)
N1	Zn1	N61	89.1(4)	C40	Si1	C27	110.3(4)
N1	Zn1	N64 ¹	89(3)	C61	Si61	C87	108.8(5)
N4 ¹	Zn1	O11	93(6)	C61	Si61	C100	107.7(4)
N4 ¹	Zn1	N61	91(2)	C74	Si61	C61	111.5(5)
N4 ¹	Zn1	N64 ¹	91(4)	C74	Si61	C87	105.0(4)
N61	Zn1	O11	91.1(5)	C74	Si61	C100	111.5(5)
N64 ¹	Zn1	O11	89(6)	C87	Si61	C100	112.2(5)
N64 ¹	Zn1	N61	178(3)	C2	C1	Si1	117.1(4)
O21	Zn2	O22	179.2(3)	C2	C1	C6	120.0
O21	Zn2	N2	93.2(3)	C6	C1	Si1	122.8(4)
O21	Zn2	N3 ²	87(3)	C3	C2	C1	120.0
O21	Zn2	N62 ³	87(5)	C2	C3	C4	120.0
O21	Zn2	N63 ⁴	89(6)	C3	C4	C5	120.0
N2	Zn2	O22	87.4(3)	C3	C4	C7	116.9(8)
N2	Zn2	N62 ³	92(3)	C5	C4	C7	123.1(8)
N3 ²	Zn2	O22	92(3)	C4	C5	C6	120.0
N3 ²	Zn2	N2	87.1(13)	C5	C6	C1	120.0
N3 ²	Zn2	N62 ³	174(5)	C8	C7	C4	129.8(14)
N3 ²	Zn2	N63 ⁴	92(5)	C7	C8	C9	128.4(16)
N62 ³	Zn2	O22	94(5)	C13	C9	C8	119.7(11)
N63 ⁴	Zn2	O22	91(6)	C13	C9	C10	120.0
				C10	C9	C8	120.3(11)

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C12	C13	C9	120.0	C37	C36	C35	120.0
C13	C12	N1	120.0	C36	C37	N3	120.0
C12	N1	Zn1	117.3(7)	C37	N3	Zn25	119.8(5)
C11	N1	Zn1	122.7(7)	C38	N3	Zn25	119.8(5)
C11	N1	C12	120.0	C38	N3	C37	120.0
N1	C11	C10	120.0	N3	C38	C39	120.0
C11	C10	C9	120.0	C38	C39	C35	120.0
C15	C14	Si1	123.6(4)	C41	C40	Si1	118.7(5)
C15	C14	C19	120.0	C41	C40	C45	120.0
C19	C14	Si1	116.2(4)	C45	C40	Si1	121.2(5)
C16	C15	C14	120.0	C40	C41	C42	120.0
C17	C16	C15	120.0	C41	C42	C43	120.0
C16	C17	C18	120.0	C42	C43	C46	117.3(11)
C16	C17	C20	119.6(6)	C44	C43	C42	120.0
C18	C17	C20	120.3(6)	C44	C43	C46	122.5(11)
C19	C18	C17	120.0	C43	C44	C45	120.0
C18	C19	C14	120.0	C44	C45	C40	120.0
C21	C20	C17	124.4(10)	C47	C46	C43	128.1(17)
C20	C21	C22	130.6(10)	C46	C47	C48	120.2(17)
C23	C22	C21	121.2(7)	C49	C48	C47	126.6(14)
C23	C22	C26	120.0	C49	C48	C52	120.0
C26	C22	C21	118.8(7)	C52	C48	C47	113.3(14)
C22	C23	C24	120.0	C50	C49	C48	120.0
N2	C24	C23	120.0	C49	C50	N4	120.0
C24	N2	Zn2	119.1(4)	C50	N4	Zn16	120.7(9)
C24	N2	C25	120.0	C51	N4	Zn16	118.6(9)
C25	N2	Zn2	120.6(4)	C51	N4	C50	120.0
C26	C25	N2	120.0	N4	C51	C52	120.0
C25	C26	C22	120.0	C51	C52	C48	120.0
C32	C27	Si1	120.6(4)	C66	C61	Si61	119.5(6)
C32	C27	C28	120.0	C66	C61	C62	120.0
C28	C27	Si1	118.4(4)	C62	C61	Si61	120.4(6)
C27	C32	C31	120.0	C61	C66	C65	120.0
C32	C31	C30	120.0	C66	C65	C64	120.0
C31	C30	C33	116.4(7)	C65	C64	C63	120.0
C29	C30	C31	120.0	C65	C64	C67	104.1(12)
C29	C30	C33	123.5(7)	C63	C64	C67	135.7(12)
C30	C29	C28	120.0	C62	C63	C64	120.0
C29	C28	C27	120.0	C63	C62	C61	120.0
C34	C33	C30	123.0(12)	C68	C67	C64	115.6(17)
C33	C34	C35	125.1(14)	C67	C68	C69	114.6(18)
C36	C35	C34	114.4(9)	C70	C69	C68	107.8(14)
C36	C35	C39	120.0	C70	C69	C73	120.0
C39	C35	C34	125.3(9)	C73	C69	C68	131.9(14)

Atom	Atom	Atom	Angle [°]	Atom	Atom	Atom	Angle [°]
C69	C70	C71	120.0	C88	C89	C90	120.0
N61	C71	C70	120.0	C89	C88	C87	120.0
C71	N61	Zn1	121.9(7)	C94	C93	C90	125.2(15)
C71	N61	C72	120.0	C93	C94	C95	126.2(15)
C72	N61	Zn1	117.4(7)	C99	C95	C94	125.4(9)
C73	C72	N61	120.0	C99	C95	C96	120.0
C72	C73	C69	120.0	C96	C95	C94	114.4(9)
C75	C74	Si61	117.0(5)	C95	C99	C98	120.0
C75	C74	C79	120.0	N63	C98	C99	120.0
C79	C74	Si61	122.8(5)	C98	N63	Zn28	116.9(5)
C74	C75	C76	120.0	C98	N63	C97	120.0
C75	C76	C77	120.0	C97	N63	Zn28	122.8(5)
C76	C77	C80	120.0(8)	C96	C97	N63	120.0
C78	C77	C76	120.0	C97	C96	C95	120.0
C78	C77	C80	119.9(8)	C105	C100	Si61	124.3(6)
C77	C78	C79	120.0	C105	C100	C101	120.0
C78	C79	C74	120.0	C101	C100	Si61	115.6(6)
C81	C80	C77	123.5(12)	C104	C105	C100	120.0
C80	C81	C82	125.8(12)	C103	C104	C105	120.0
C86	C82	C81	115.5(8)	C104	C103	C102	120.0
C86	C82	C83	120.0	C104	C103	C106	109.9(11)
C83	C82	C81	124.5(8)	C102	C103	C106	129.9(11)
C82	C86	C85	120.0	C103	C102	C101	120.0
N62	C85	C86	120.0	C102	C101	C100	120.0
C85	N62	Zn27	118.6(5)	C107	C106	C103	124.9(18)
C84	N62	Zn27	120.8(4)	C106	C107	C108	128(2)
C84	N62	C85	120.0	C112	C108	C107	123.3(16)
N62	C84	C83	120.0	C112	C108	C109	120.0
C84	C83	C82	120.0	C109	C108	C107	116.3(16)
C92	C87	Si61	121.7(6)	C108	C112	C111	120.0
C92	C87	C88	120	N64	C111	C112	120.0
C88	C87	Si61	118.0(6)	C111	N64	Zn16	122.4(9)
C87	C92	C91	120.0	C110	N64	Zn16	116.9(9)
C90	C91	C92	120.0	C110	N64	C111	120.0
C91	C90	C89	120.0	N64	C110	C109	120.0
C91	C90	C93	116.6(10)	C110	C109	C108	120.0
C89	C90	C93	122.9(10)				

¹1/2+x,3/2-y,l-z; ²+x,+y,l+z; ³+x,-l+y,+z; ⁴+x,-l+y,l+z; ⁵+x,+y,-l+z; ⁶-1/2+x,3/2-y,l-z; ⁷+x,l+y,+z;
⁸+x,l+y,-l+z