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Location, Location, Location - strategic positioning of 2,1,3-benzothiadiazole units within trigonal quaterfluorene-truxene star-shaped structures

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The fused, bicyclic molecule, 2,1,3-benzothiadiazole (BT), has become a key ingredient in the design of new organic semiconductors for light emission and energy harvesting applications. Here, we report the synthesis of a series of trigonal, star-shaped compounds comprising a truxene core and three quater-dialkylfluorene arms into each of which a BT unit is inserted sequentially at each possible position (T4BT-A to T4BT-E). Analysis of the resulting electronic properties shows that as a consequence of conjugative coupling to the core and the resulting symmetry there are three distinct locations for the BT unit and we discuss the influence that these locations have on light emission and other spectroscopic characteristics. The systematic variation in photophysical properties for the different structural isomers helps to clarify the influence of BT unit addition to 9,9-dialkylfluorene chains. It also helps to establish a design template for the construction of donor-acceptor conjugated materials with targeted properties. For T4BT-E with a BT unit at the terminal position of each arm the photoluminescence quantum efficiency is significantly reduced and

we do not observe amplified spontaneous emission under typical pumping conditions. Theoretical calculations assist in understanding the variation in behaviors among the T4BT-X family of compounds, especially in relation to their photoluminescence decay times and the Raman scattering intensities of their dominant BT-unit-centred molecular vibrations.

1. Introduction

One of the great strengths of organic electronics is the possibility of chemically tuning materials to produce new compounds tailored for specific applications. Organic light emitting diodes (OLEDs) have been the first devices to be commercialised, featuring in highly regarded active matrix (AMOLED) mobile phone displays. The pursuit of solution-processed approaches to these applications has given rise to the design and synthesis of complex materials incorporating a variety of chemical moieties and chain architectures to enhance charge injection and transport, emission efficiency and color definition, and device lifetime and manufacturability.^[1-3] Large area passive matrix structures for lighting or optical gain structures for amplification and lasing represent, in many ways, even more challenging targets for these complex emission materials.^[4] In the latter case, it should be noted that not all materials that show good performance in OLEDs show efficient optical gain at low pump thresholds.^[5] Working with well-defined chemical systems helps to better understand the requirements and this has motivated our development of star-shaped molecules composed of a central truxene unit from which emanate three short conjugated arms. We have previously reported on the properties of the blue light emission mono-, bi-, ter- and quater-dialkylfluorene (**T1-T4**) arm / truxene core compounds.^[6,7] We have also previously reported detailed studies of related hexa-dialkylfluorene substituted truxene/triazatruxene core and quater-dialkylfluorene substituted pyrene core compounds, including OLED, optical gain and lasing performance.^[8] These previous studies have allowed us to investigate the influence of arm length, arm number and core type from among a wide range of star-shaped molecule parameters. We now report (see Figure 1) novel **T4**-based structures where fused bicyclic 2,1,3-benzothiadiazole (BT) units are sequentially inserted at each of the five possible positions within the quater-dialkylfluorene arms. This yields compounds **T4BT-A**, **T4BT-B**, **T4BT-C**, **T4BT-D** and **T4BT-E**, beginning with BT adjacent to the truxene core (**T4BT-A**)

and moving this unit stepwise to position the heterocycle at the termini of the arms (**T4BT-E**). The development of these compounds represents the introduction of an additional degree of freedom into the design of star-shaped molecules.^[9]

The BT unit is a fascinating fused heterocycle that was first introduced into fluorene-based copolymer light emitting diode material systems by E. P. Woo and colleagues at the Dow Chemical Company.^[10] It has been used since to great effect in the design of new organic semiconductors for light emission and energy harvesting applications. If it is embedded in simple conjugated structures, BT's electron-deficient character serves to stabilize and spatially localize the lowest unoccupied molecular orbital (LUMO).^[11] This has allowed the generation of efficient copolymer green emission materials, such as poly(9,9-dioctylfluorene-co-benzothiadiazole) (**F8BT** see Figure 1)^[12,13] with advantageously lowered electron injection barriers.^[14,15] Subsequent optimization for OLEDs has been achieved by blending **F8BT** with poly(9,9-dioctylfluorene) (PFO) and/or fluorene-arylamine copolymers, the latter with advantageously lowered hole injection barriers.^[16,17] The final step has been to make complex copolymers containing a mixture of BT, arylamine and fluorene constituents, as for example found in the proprietary LumationTM green and other polymers.^[18,19]

Red emission materials can also be achieved by linking BT with thiophene-based structures. The three-component thiophene-benzothiadiazole-thiophene chromophore is a particularly common structure in this regard, again one that was introduced by the Dow Chemical Company in their development of red emission fluorene copolymers, like Dow Red F and more recent proprietary LumationTM red materials.^[14, 20-22] The three-component thiophene-benzothiadiazole-thiophene sequence is also used in a variety of energy harvesting materials for solar cells including the well-known poly[2,6-(4,4-bis-(2-ethylhexyl)-4*H*-cyclopenta[2,1-*b*;3,4-*b'*]-dithiophene)-*alt*-4,7-(2,1,3-benzothiadiazole)] (**PCDTBT**) polymer.^[23] BT has, moreover, been combined with other thiophene based units to achieve smaller optical gap solar cell polymers and molecular light absorbers for dye-sensitized solar cells.^[24-27]

A greater understanding of the electronic interplay between the BT and neighboring units in a given structure would be highly beneficial to the organic electronics community - particularly at the most fundamental level in the structural design of new semiconductors. To this end, the series of structural isomers **T4BT-A** to **T4BT-E** allows a thorough investigation

of the effect of subtle variations in environment on the influence of BT addition to a 9,9-dialkylfluorene chain. Importantly, unlike 9,9-dialkylfluorene/BT copolymer studies with varying fractions of BT inclusion^[28] the molecular architecture here is precisely defined; each of the isomers can be studied as a separate entity. In the copolymers, the distribution of BT units within each chain in a sample is much less well defined and subtle effects will then be averaged out over the ensemble. The trigonal structure also provides a defined symmetry that helps us to explain the observed electronic properties. Our **T4BT-X** series are, moreover, highly efficient green emitters with excellent solubility and film-forming properties. The new materials have been characterized by absorption, emission (photoluminescence (PL) and amplified spontaneous emission (ASE)) and Raman spectroscopy. Symmetry plays an important role for absorption and PL spectra with a pair-wise equivalence of the **T4BT-A** and **-D** and **T4BT-B** and **-C** structures. **T4BT-E** represents a distinct situation where placement of the BT unit at the terminal position of the tetra(9,9-dialkylfluorene) arm leads to significant alterations in behavior. It is these two pairs and the terminal position that represent the three *locations* of the paper title (see also the table of contents graphic).

As shown below, however, a more detailed description is needed to explain the subtle trends in Raman intensity for BT-centred vibrations at ≈ 1360 and ≈ 1547 cm^{-1} and in PL decay times. Density functional theory/time dependent density functional theory (DFT/TD-DFT) calculations match well to the experimental results for Raman intensity and also do a very fair job of predicting the oscillator strengths for the longest wavelength (≈ 455 nm) absorption peak without requiring any variation in torsional angle for the BT unit. The key factor is the distribution of the HOMO/occupied Natural Transition Orbital (NTO) amplitude along the arm and specifically the proportion of the wavefunction present on the BT unit. PL decay times are harder to rationalise and one has to factor in the influence of non-radiative decay processes. The precision in the chemical structure of these compounds relative to 9,9-dialkylfluorene/BT copolymers allows a consideration of the role of BT location in isolation from other factors; there is no ensemble averaging over a range of different chemical structures and chain architectures for the **T4BT-X** family. In particular, this allows us to shed new light on the literature discussion of BT torsion angles within the chain. Our experimental observations and supporting calculations indicate that changes in BT Raman intensity are seemingly not a specific signature of changes in torsion angle.

2. Results

2.1. Absorption

Figure 2 shows the absorption and normalized PL emission spectra for thin film samples of **T4BT-A**, **-B**, **-C**, **-D** and **-E** on Spectrosil B substrates. The corresponding spectra for thin film samples of **F8BT** (65 nm film) and **T4** (50 nm film) are shown in Figure 1 for reference. A number of features are immediately evident. The **T4** absorption spectrum, as previously reported,^[29] closely resembles the spectrum for poly(9,9-dihexylfluorene) with two main features close to 220 and 370 nm corresponding in a simplified description to localized-localized (corresponding to feature I in Figure 2) and delocalized-delocalized (corresponding to feature II in Figure 2) (highest occupied molecular orbital (HOMO) to LUMO) π - π^* transitions of the 9,9-dihexylfluorene arms/truxene core. The alternating copolymer **F8BT** has a similar high-energy localized-localized (feature I) π - π^* transition peak near 220 nm but two longer wavelength peaks close to 330 nm and 455 nm that are understood to involve, respectively, transitions between the HOMO and higher lying delocalized unoccupied molecular orbitals (feature II) (similar to the delocalized-delocalized transition of **T4**) and between the HOMO and LUMO (corresponding to feature III in Figure 2), with the LUMO now spatially localized on the BT unit.^[11, 28] In some respects, compounds **T4BT-A**, **-B**, **-C**, **-D** and **-E** have absorption spectra that interpolate between the two reference materials (**T4** and **F8BT**). As expected, all five compounds have the high-energy localized-localized π - π^* transition peak near 220 nm (feature I). Interestingly, however, the absorption spectrum of **T4BT-E** provides no clear evidence for the presence of BT units within the chemical structure. It has a single long wavelength peak that aligns with the 370 nm peak in **T4** (feature II), although it is slightly broadened and does show a weak short-wavelength shoulder that if present in **T4** is not so clearly resolved. We discuss this compound further below but first we focus on the other four. A closer examination of Figure 2 suggests there is a pair-wise correspondence of the spectra for (i) **T4BT-A** and **T4BT-D** and (ii) **T4BT-B** and **T4BT-C** that can be rationalized in terms of the chemical structures on the basis that the arms conjugatively couple to one effective 9,9-dihexylfluorene unit within the truxene core (highlighted in Figure 1). We then have pairs of equivalent conjugated segments comprising (i) F6'-BT-F6-F6-F6-F6 (**T4BT-A**) and F6'-F6-F6-F6-BT-F6 (**T4BT-D**) and (ii) F6'-F6-BT-F6-F6-F6 (**T4BT-B**) and F6'-F6-F6-BT-F6-F6 (**T4BT-C**) where F6 signifies a 9,9-

dihexylfluorene unit and F6' the effective 9,9-dihexylfluorene unit within the truxene core. For the **T4BT-A** and **T4BT-D** pair, transitions between the HOMO and higher lying delocalized unoccupied molecular orbitals (feature II) are split into two components, a clear peak at ~ 362 nm and 370 nm, respectively, with a well-defined shoulder at ~ 320 nm. For the **T4BT-B** and **T4BT-C** pair, these transitions (feature II) show a peak at ~ 356 nm with the suggestion of a shorter wavelength (unresolved) shoulder again around 320 nm. The main peak position and splitting appear to correlate with the uninterrupted lengths of F6/F6' sequences either side of the BT unit. For the **T4BT-A** and **T4BT-D** pair we have one and four 9,9-dihexylfluorenes whereas for the **T4BT-B** and **T4BT-C** pair it is two and three - this explains both why the main peak (feature II) is more red-shifted for the **T4BT-A** and **T4BT-D** pair and the splitting, between the main peak and the shoulder, is greater. The most red-shifted peaks are found for **T4BT-E** and **T4** where there is a five F6/F6' sequence involved in their (feature II) transitions.

The fitted peak wavelengths, λ_{III} , for the HOMO-LUMO transition III of each compound are reported in Table 1. For the **T4BT-A** and **T4BT-D** pair $\lambda_{\text{III}} \approx 445$ nm with an associated peak absorption coefficient (α_{III} in Table 1) 38 ± 1 % that of transitions II between the HOMO and delocalized unoccupied molecular orbitals centred on F6/F6' units. For the **T4BT-B** and **T4BT-C** pair $\lambda_{\text{III}} \approx 440$ nm with a peak absorption coefficient 41 ± 1 % that of transitions II. As already noted above, in **F8BT** the HOMO-LUMO transition III is at ~ 455 nm and has an absorption coefficient that is, if anything, marginally stronger than that of transitions II. The somewhat weaker HOMO-LUMO transition III we find for the present set of compounds is consistent with results from an earlier report on $\text{F8}_{(1-x)}\text{BT}_{(x)}$ copolymers with varying fractions of BT incorporation ($x = 0.06$ to 0.5).^[28] The argument given there was that the HOMO-LUMO oscillator strength increases as the spatial overlap of molecular orbitals increases and hence the $\sim 17\%$ BT conjugated structures in **T4BT-A**, **-B**, **-C**, **-D** and **-E** would indeed be expected to have weaker transitions III than the 50% BT (**F8BT**) copolymer. The anomalous behavior of **T4BT-E** in this regard, with no evident transition III, is noted again. Our multipeak fitting procedure (see SI for details) was unable to fit a physically meaningful oscillator in the 445 nm region of the **T4BT-E** spectrum, and so we are forced to conclude that if there is a transition present here, it must have extremely small oscillator strength.

2.2. Photoluminescence Measurements

As noted for the absorption spectra, there is also a pair-wise correspondence of PL spectra (Figure 2, dotted lines, excitation at λ_{II} in Table 1) for (i) **T4BT-A** and **T4BT-D** and (ii) **T4BT-B** and **T4BT-C**, although the differences between the pairs are more subtle than was the case for absorption. The **T4BT-B** and **T4BT-C** pair has the more red-shifted PL (562 nm peak) and a slightly more structured line shape with an unresolved shorter-wavelength shoulder. The **T4BT-A** and **T4BT-D** pair has an essentially featureless, weakly blue-shifted PL (553 nm and 546 nm respectively). In all four cases the PL spectra are similar to the spectrum for **F8BT**, albeit in each case somewhat blue shifted from the **F8BT** 569 nm peak. It is also noteworthy that, unlike the case for BT-fluorene co-polymers^[28] with similar BT fractions, we observe no (fluorene localized) blue light emission from either thin-film samples or solutions (data not shown) of **T4BT-A**, **-B**, **-C** and **-D**. **T4BT-E** is again anomalous with a strongly blue-shifted PL spectrum (507 nm peak) but not possessing the vibronically structured, blue (417 nm peak) PL of **T4**. In this sense, the PL spectra more clearly reveal the difference in chemical structure between **T4BT-E** and **T4**. In addition, the observed large Stokes shift between absorption and PL emission peaks for **T4BT-E** suggests that there may be a significant geometric relaxation following excitation of this compound via transition II. Again, this is discussed in more detail below.

The subtle PL spectral changes among **T4BT-A**, **-B**, **-C** and **-D** have essentially no effect on their PLQY values (Figure 3(a)). However, as also found for **F8BT**,^[30] their PLQY values do depend on which of the absorption transitions II or III is optically pumped. A higher efficiency is achieved for direct excitation at transition III (open circle data points, $\Phi_{PL} = 55 \pm 7 \%$), rather than cascaded excitation via transition II (filled circle data points, $\Phi_{PL} = 40 \pm 4 \%$). Figure 3(b) (upper panel) further shows this wavelength dependence by comparison of PLE (solid line) and absorption (dotted line) spectra; the data shown are for **T4BT-A** with peak normalization at transition II. The relative enhancement of PLE (grey shaded area) in the spectral vicinity of transition III is evident. Similar enhancements were found for **T4BT-B**, **-C** and **-D** (not shown). **T4BT-E** again stands out; this time by virtue of having a significantly lower PLQY ($\Phi_{PL} = 27 \pm 4 \%$) than the other members of the **T4BT-X** family (Figure 3(a)) and through its PLE and absorption spectra rather closely matching each other

(Figure 3(b), lower panel). The apparent long wavelength tail in the absorption spectrum of **T4BT-E** is also revealed to be most likely the consequence of scattering and/or reflection rather than true absorption since excitation at those wavelengths does not generate PL. This latter observation, taken together with the absorption peak fitting results (cf. SI) supports the deduction that transition III, if present, can only be very weak for compound **T4BT-E** and/or is much more blue-shifted than theoretically predicted (*vide infra*) so that it strongly overlaps with transition II.

PL transients were measured for 50 nm thickness films of each of the **T4BT-X** compounds following 1 MHz, 70 ps pulse excitation at 405 nm. Figure 4(a) displays the data for **T4BT-D** and **T4BT-E**, representing the decay time extrema (see Figure 4(b)). The transient for **T4BT-D** follows an almost straight-line (i.e. mono-exponential) decay when plotted, as here, on a semi-logarithmic scale. The same is true for **T4BT-A**, **-B** and **-C**, allowing us to adopt a numerical convolution approach to extract the excited state lifetime for each of these compounds: The experimental traces were best-fitted to the convolution of the recorded excitation response and a single exponential function of varying duration. The same procedure was used for the **T4BT-E** decay transient even though it is not truly mono-exponential. The deduced decay times are shown in Figure 4(b). Other forms of fitting, including a statistical first moment measure, revealed the same trend with $\approx 8\%$ or less variation in absolute values. Compared to the parent truxene **T4** ($\tau \approx 0.6$ ns) and **F8BT** alternating copolymer ($\tau \approx 2$ ns), **T4BT-A**, **-B**, **-C** and **-D** have longer PL decay times, consistent with the reduced oscillator strength of their lowest energy optical absorption peaks (Figure 2). The pair-wise correspondence noted above for the absorption and PL spectra only partially holds for PL transients; compounds **T4BT-B** and **-C** have very similar decay times ($\tau \approx 3.6$ ns) but **T4BT-A** and **-D** do not. **T4BT-D** exhibits the slowest decay ($\tau \approx 4$ ns) of all compounds, almost 20% slower than **T4BT-A** ($\tau \approx 3.4$ ns). Both our multipeak fitting of the absorption spectra (see SI) and DFT calculations (*vide infra*) indicate that transition III for **T4BT-D** has the lowest oscillator strength amongst **T4BT-A**, **-B**, **-C** and **-D**, consistent with the recorded longer decay time but not quantitatively so. Further studies will be required to fully understand this behavior and would benefit from measuring the decay transients following selective excitation of transitions II and III rather than mixed excitation as here.

T4BT-E has the fastest ($\tau \approx 3.3$ ns) decay, consistent at first sight with PL emission following excitation via the larger oscillator strength transition II (see PLE data in Figure 3(b), lower panel). However, as suggested by a lack of vibronic structure in the PL spectrum and a large Stokes shift between absorption and emission peaks, and indeed by our own TD-DFT simulations (*vide infra*), the emissive excited state appears to have charge transfer character and to involve a significant geometry relaxation following excitation. This plausibly explains why the decay time is longer than for the parent **T4** truxene compound despite having a lower PLQY ($\Phi_{\text{PL}} \approx 27\%$ for **T4BT-E** versus 43% for **T4**); the transient PL further evidences the difference in chemical structure between **T4BT-E** and **T4**. Compared to the other **T4BT-X** compounds, where the variation in τ is proportionately smaller than the variation in PLQY, it is noteworthy that although **T4BT-E** has a shortened decay time, its significantly lower PLQY (Figure 3(a)) suggests that it may, in fact, have the longest radiative lifetime; fully consistent with a significant charge transfer character^[31] and implying the importance of non-radiative decay processes, as also indicated by the non-mono-exponential decay (c.f. Figure 4).

2.3. Theoretical Models of Electronic Structure

Density functional theory (DFT) and semi-empirical methods have been used on several occasions to study the electronic structure of linear chain molecules containing covalently linked BT and 9,9-dioctylfluorene units^[11,30,32] and BT and 6,6,12,12-tetraoctylindenofluorene units.^[33] The conjugated bonding interaction between 9,9-dialkylfluorene and BT moieties leads to the appearance of two main HOMO-originating optical transitions. The lowest energy of these (labelled III in Figure 2) involves a LUMO that is spatially localized on the BT unit and it is generally considered to possess a degree of charge-transfer character^[28,30] though not as much as the HOMO-LUMO transition in solar cell materials wherein the BT is flanked by more strongly electron donating thiophene containing moieties.^[23-26] The second (labelled II in Figure 2) links the HOMO to higher lying delocalized unoccupied molecular orbitals that are reported either to be centred on 9,9-dialkylfluorene units^[11] or more fully delocalized, involving the BT unit as well.^[30] This transition is similar in character to the delocalized-delocalized π - π^* HOMO-LUMO transition of **T4** and poly(9,9-dialkylfluorene)s.^[11]

We have undertaken further DFT/TD-DFT calculations to gain a clearer insight into the specific electronic structure of our **T4BT-X** compounds. These star-shaped molecules differ from the related linear chain **F8BT** and **F8_(1-x)BT_(x)**^[28] copolymers in having only a single BT unit within each conjugated sequence and a precisely defined chemical structure with no polydispersity and no isomeric mixtures. Turning first to their physical structure, we find from ground state geometry optimization calculations on the proxy structures (single arm attached to truxene core with 9,9-dihydrogen rather than 9,9-dialkyl substituents for theoretical simplicity) that the torsion angle, θ , between the BT unit and its F6 neighbours is $36 \pm 1^\circ$ (see Table 1) for all five of the **T4BT-X** isomers under study - an observation that has significance for the discussions presented later.

For the electronic description and following the calculation of molecular orbitals we transform to a representation based on NTOs^[32] such that an occupied NTO will correspond to the state from which an electron is excited for a certain transition while a virtual NTO can be regarded as the unoccupied state to which the electron transfers. Each of the five proxy structures was modelled in turn and the results for the absorption transition intensities in the spectral range $\approx 320 - 520$ nm are shown superimposed on the experimental spectra in Figure 2; calculated wavelengths and oscillator strengths of the main transitions visible are also listed in Table 2. Two dominant transitions corresponding to experimental peaks II and III are observed. The molecular orbitals calculated to be involved in the higher energy of these are found to be delocalized along the fluorene arm as previously found for the linear chain **F8BT** and **F8_(1-x)BT_(x)** copolymer structures.^[11,28,30] In the case of the lower energy peak, again there is good agreement, with the transition being one that links a delocalized HOMO (spread along the fluorene arm) to a LUMO that is spatially localized on the BT unit. This is true for all five of the proxy structures. The DFT/TD-DFT predictions of the transition wavelengths are in reasonable agreement with experiment, with 12 - 17 nm red shift for transition II and 63 - 78 nm for transition III. The larger deviations in the latter case are understandable as our theoretical approach is less reliable for the calculation of charge transfer state energies.^[33] Encouragingly the pair-wise association, first suggested from the molecular structure and measured absorption and PL spectra, between **T4BT-A** and **-D** and **T4BT-B** and **-C** also emerges clearly in the theoretical data. For example the transition II wavelengths for the **T4BT-B** and **T4BT-C** pair exhibit a blue shift compared to those found for the **T4BT-A** and

T4BT-D pair. Furthermore, the increased separation between transitions II and III for the **T4BT-B** and **T4BT-C** pair, which as noted earlier enhances the visibility of their transition III in Figure 2, is also faithfully reproduced by the calculations.

Figure 5 shows the TD-DFT calculated probability density distributions of the occupied (blue bars) and unoccupied (red bars) NTOs associated with the lowest energy optical transition of the **T4BT-X** proxy structures (corresponding to transition III). The bar charts are plotted as a function of site position, moving (from left to right) away from the truxene core-based F'6 site and presented so as to emphasise the pair-wise associations. Panel (a) shows the results for the **T4BT-A/-D** pair, panel (b) for the **T4BT-B/-C** pair and panel (c) for **T4BT-E**. Also shown in panel (c) is the iso-surface plot for the occupied NTO wavefunction (iso-surface values ± 0.02 shown in green/purple). The localization of the unoccupied NTO on the BT unit is evident as are the relative strengths of the overlaps between the occupied and unoccupied NTOs; weakest for **T4BT-E** and strongest for the **T4BT-B/-C** pair.

Additional key results for the **T4BT-E** proxy include the prediction of both a lower energy transition II and an increase in its oscillator strength in comparison to the other members of the family; both these traits are consistent with experimental observations (Figure 2 and Table 1). The expected character of transition III is also reasonably well described but with greatly reduced oscillator strength and a smaller separation from transition II compared to the rest of the **T4BT-X** series. A major factor behind this weaker transition strength is the small fraction of the occupied NTO (HOMO) residing on the BT unit compared to that found for the other **T4BT-X** compounds (c.f. Figure 5); as a consequence the calculated overlap integral with the unoccupied NTO (LUMO), which is still localized on and around the BT unit, is significantly reduced. These calculations do not directly shed light, however, on the observed PL decay time since the weaker oscillator strength for transition III would be expected to yield a longer radiative decay time. We note however that the low PLQY for **T4BT-E** points to the importance of non-radiative decay processes following excitation of transition II. These need to be better understood.

2.4. Raman Spectra

He-Ne laser (632.8 nm) excited Raman scattering measurements were performed for compounds **T4BT-A**, **-B**, **-C**, **-D** and **-E** and the results are reported in Figure 6(a). The

Raman spectra are dominated by two carbon-carbon ring stretching modes at $\approx 1608\text{ cm}^{-1}$ and $\approx 1547\text{ cm}^{-1}$ and are typical of conjugated structures containing 9,9-dialkylfluorene and BT moieties with the lower wavenumber peak characteristic of BT-centred ring stretching and the higher wavenumber peak characteristic of the corresponding ring stretching for the 9,9-dialkylfluorene unit;^[34-37] all other modes having substantially smaller amplitudes. The 1608 cm^{-1} peak was used for normalization since the same number of 9,9-dialkylfluorene units is present in each of the **T4BT-X** compounds. The spectra were peak fitted to determine mode magnitude and wavenumber (see results in Table 1 and SI for further details). From the fitting we observe that the **T4BT-A**, **-B**, **-C** and **-D** compounds all share common Raman shifts for the 9,9-dialkylfluorene (1608 cm^{-1}) and BT (1547 cm^{-1}) ring stretch modes, within the nominal $\pm 1\text{ cm}^{-1}$ instrument resolution. The BT ring stretch mode softens more dramatically (by $\approx 9\text{ cm}^{-1}$) to 1538 cm^{-1} for **T4BT-E**. This observation can be rationalized on the basis that the local mechanics of the BT ring stretch mode is largely unperturbed within the sequence of compounds **T4BT-A** to **-D** since each BT unit has an F6 or F6' attached on both sides. In the case of **T4BT-E**, however, there is a 9,9-dialkylfluorene unit attached to only one side, removing a substantial restoring force and resulting in a softening of the mode. Figure 6(b) compares the corresponding dependence of experimental (filled squares data points) and calculated (empty triangles data points) Raman intensities for the BT ring stretch mode.

We observe that as the BT unit moves out from the core to the end of the arm (i.e. **T4BT-A** to **-E**) the Raman intensity rises slightly, peaking at the **-B/-C** location before falling off rapidly for the **-D** (by a factor of ≈ 1.5) and **-E** (by a factor of ≈ 6 theoretically and ≈ 13 experimentally) positions. The experimental trend is faithfully reproduced by the DFT calculations. The strength of Raman scattering depends upon the modulus squared of the equilibrium (zero displacement) polarizability gradient, $d\alpha/dr$, with α the polarizability and r the normal coordinate of the vibration.^[38] Hence, whilst the polarizability gradient for the BT ring stretch mode is approximately constant for **T4BT-A**, **-B** and **-C**, it clearly falls when the BT unit is placed at positions **-D** and especially **-E**. We re-iterate that the calculations were performed with a fixed torsion angle ($36 \pm 1^\circ$) so changes in the calculated intensities cannot be a consequence of twisting of the BT unit relative to neighboring F6 units.

The weaker Raman scattering in the $1200 - 1500\text{ cm}^{-1}$ spectral range also depends on the BT unit position, most notably for the $\approx 1360\text{ cm}^{-1}$ peak that has previously been used to

characterize the torsion angle of the **BT** unit within **F8BT**.^[39] In the case of **T4BT-A** to **-E**, this peak displays a similar trend to that found earlier for the $\approx 1547\text{ cm}^{-1}$ BT ring stretch (Figure 6(b)) as perhaps might be expected given its similar BT unit^[28,37] origin.

2.5. Amplified Spontaneous Emission

Amplified Spontaneous Emission (ASE) measurements were carried out for thin film samples of each member of the **T4BT-X** family in order to probe their ability to provide optical gain. It is worth recalling that both of the reference materials, **F8BT** and **T4** have been previously shown to provide significant optical gain, supporting amplification and lasing.^[12, 29] Representative results, for **T4BT-B**, are presented in Figure 7 (a). Pumping the sample with increasing incident energy causes the PL spectrum to collapse into a line-narrowed peak - typical behavior for amplified spontaneous emission. The ASE spectrum (solid line) peaks at the PL (dotted line) maximum, somewhat shorter in wavelength (561 nm) than for **F8BT** where the ASE peaks at 575 nm.^[12] The power dependence of the ASE is presented in the Figure 7 (b). The onset of a super-linear region just above $\sim 60\text{ }\mu\text{J cm}^{-2}$ is coincident with the spectral width reducing to around half its initial PL value and is frequently assigned as the onset of ASE (or ASE threshold). ASE saturation is also visible for pump energy densities above $\approx 200\text{ }\mu\text{J cm}^{-2}$. For comparison we note that for **F8BT** the energy density typically required for the onset of ASE is $\approx 40\text{ }\mu\text{J cm}^{-2}$. Similar results to those for **T4BT-B** were obtained for **T4BT-A**, **-C** and **-D**. However, for **T4BT-E** there was no evidence of ASE for incident pump energy densities up to the $500\text{ }\mu\text{J cm}^{-2}$ limit of our pump laser system. The absence of ASE in the **T4BT-E** compound is intriguing and has yet to be fully understood. The observed PLQY and emission decay time results do not obviously suggest that ASE should be absent - for comparison, blends of 20 wt% regioregular poly(3-hexylthiophene) with 80 wt% **F8BT** have similar PLQY values ($\Phi_{\text{PL}} \approx 25\%$) and shorter decay times but still show efficient ASE and lasing.^[40] PL spectra generally map the emission following excited state relaxation (Kasha's Rule)^[41] and as long as the processes involved in the relaxation occur rapidly enough to not overlap in time with the emissive decay they can be largely ignored or, if competing with the formation of the emissive state, can be considered simply as part of an average non-radiative decay rate. In ASE (and lasing), however, the radiative decay time is drastically reduced due to emission stimulation and as a

consequence processes involved in the excited state relaxation may then directly compete with the emission. Clearly a more detailed examination is required to unravel the likely contributing factors but we note the evidence already discussed above for significant excited state relaxation in this compound.

3. Discussion

A summary of the key experimental observations for the **T4BT-X** family of compounds is presented in Table 3. In an effort to focus on the positional role of the BT unit the results from each technique are discussed in terms of the pairings identified earlier through consideration of the molecular geometry (Figure 1) and supported by the calculated NTOs (Figure 5).

Considering first the basic optical properties of our materials, the pair-wise correspondence appears compelling. The three groupings, i.e. **T4BT-A/-D**, **T4BT-B/-C** and **T4BT-E**, each give rise to distinct characteristics in both absorption and PL spectra. Geometry optimized DFT/TD-DFT studies provide further support for this grouping in regard of the relative trends in (computed) transition energies. In the case of transitions between the HOMO and higher-lying delocalized unoccupied molecular orbitals (cf. transition II region of Figure 2) we find that those for **T4BT-B/-C** are most blue-shifted, followed by **T4BT-A/-D**, with the lowest energy arising for the **T4BT-E** structure. The trend to lower energies is entirely consistent with the size of the longest sequence of adjacent F6/F6' units in the arm; determined by the BT unit location this ranges from 3 F6/F6' units for **T4BT-B/-C** to 5 for **T4BT-E**. Moreover, the computed energy splitting between transitions II and III follows a similar vein (i.e. largest for **T4BT-B/-C** smallest for **T4BT-E**) and again is consistent with observations for the measured absorption spectra, e.g. the greater visibility of transition III for the **T4BT-B/-C** pair arising from a larger energy splitting.

However, not all properties mirror this behavior. Specifically, PL decay transients show a significantly different variation with BT position (c.f. Figure 4 inset). **T4BT-B/-C** exhibit very similar decay times ($\tau \approx 3.6$ ns) i.e. they do still appear to behave as a pair but **T4BT-A** ($\tau \approx 3.4$ ns) and **-D** ($\tau \approx 4.0$ ns) are quite distinct from each other and taking into account their PLQYs to estimate their radiative decay times enhances rather than diminishes the difference. **T4BT-D** has noticeably the longest decay time of all five compounds, qualitatively consistent

with its smaller calculated transition III oscillator strength (Figure 6(b)), albeit tempered by the excitation wavelength (405 nm) overlapping in part with transition II. **T4BT-E** has the shortest observed decay time ($\tau \approx 3.3$ ns) but this is for pumping predominantly via transition II rather than III. Transition III is expected to have much smaller oscillator strength (there is little overlap between occupied and unoccupied NTOs (Figure 5)) and is not in fact resolved as a separate peak in the absorption (Figure 2) or PLE (Figure 3(b)) spectra. **T4BT-E** also has a substantially smaller PLQY ($\Phi_{\text{PL}} \approx 27\%$) than the other compounds and as such may not be directly comparable - non-radiative processes clearly play a greater role for this compound (recall also its non-mono-exponential decay transient). The molecular symmetry of the arm does not therefore provide a full picture for the PL decays; the discussion needs also to consider the *absolute* placement of the BT unit within the arm. One could, for example, imagine that the tendency for BT moieties to interact with like units on neighboring molecules would depend on distance from the truxene core.

Comparison of the Raman spectra in Figure 6 also shows that whilst the position of the BT unit is still a factor, it is no longer the case that there is a strict pairing of positions; this is true for both experimental and DFT calculated scattering intensities (Figure 6(b)). With this in mind, we return again to the interpretation of the results from Raman spectroscopy, drawing on a number of previous studies on the **F8BT** copolymer system.

Previous Raman studies in the literature, concerned with the BT unit in the polymer **F8BT**, have generally correlated the degree of planarization of the BT and neighboring F8 units (i.e. the torsion angle between aromatic rings in the conjugated backbone tending to zero) with the relative intensities of the in-plane modes.^[31,37,39] Donley *et al*^[39] reported that planarization leads to a relative decrease in the Raman intensity for the 1360 cm^{-1} BT peak and Schmidtke *et al*^[37] that the relative strength of the 1547 cm^{-1} BT ring stretching mode should increase with planarization. Examining our data (Figure 6) we find that *both* of these modes reduce in intensity when the BT unit is moved to the **-D** position and diminish further for the **-E** position. Our observation that both peaks decrease in relative intensity as the unit moves towards the arm-end position is then seemingly at odds with the literature reports for **F8BT**, at least in respect of the proposed correlation. It is rather difficult to accept the arguments made in those publications in relation to the BT unit torsion angle in light of this behavior. Our theoretical modelling, moreover, yields the same torsion angle for the BT unit of $36 \pm 1^\circ$

for *all* of the proxy structures. Yet these same calculations faithfully reproduce the observed reduction in the BT ring stretching mode intensity (Figure 6(b)); we do not need to invoke a change in torsion angle to explain the observed changes. Also shown in this graph (right ordinate) are the calculated oscillator strengths for transition (III) and the experimentally determined absorption integrals; they closely mimic the trend displayed by the Raman scattering intensities, suggesting that changes in wavefunction most likely play the major role. Reminding ourselves that geometry-optimized calculations are routinely, as here, carried out in the gas phase,^[31,37,39] we should recognise that the ignored packing interactions between molecules in the solid state may well affect the absolute torsion angles. One might also imagine that such interactions would be most pronounced for BT moieties at the end of a truxene arm, i.e. **T4BT-D** and **T4BT-E** but it seems likely that any such changes do not substantially contribute to the variation in Raman intensities.

Finally, in relation to the optical gain properties of these **T4BT-X** compounds (examined via ASE studies), we find that placing the BT unit at the end of the 9,9-dialkylfluorene arms has a detrimental effect. It would be interesting to know if the same applies to linear chain alternating copolymer **F8BT**^[12] and/or statistical copolymer **F8_(1-x)BT_(x)**^[28] samples. The detailed nature of the behavior that limits optical gain will need further investigation.

4. Conclusions

In summary, we have presented the synthesis and detailed characterization of a series of structural isomers of trigonal star-shaped molecules comprising a truxene core with quaterdialkylfluorene arms appended that contain BT moieties placed in each possible position along the arm (Figure 1: **T4BT-A**, **-B**, **-C**, **-D** and **-E**). These compounds are, in the main, efficient green light emitters with excellent solubility and film-forming properties and good thermal stability. The optical absorption and PL spectral properties may be adequately described in terms of three different locations for the BT unit, corresponding to a **T4BT-A/-D** pair, a **T4BT-B/-C** pair and **T4BT-E**, rationalised on the basis of molecular symmetry. A more detailed description is needed, however, to explain the trends in Raman intensity for BT-centred vibrations at ≈ 1357 and ≈ 1547 cm⁻¹ and in PL decay times for which **-A** and **-D** no longer behave as a pair. This is achieved by optimized geometry DFT/TD-DFT calculations of Raman scattering intensity and transition III oscillator strength that are shown to be consistent with the observed trends. The missing/very weak transition III absorption,

strongly blue-shifted PL and very weak 1360 and 1547 cm^{-1} BT-centred Raman scattering intensities of **T4BT-E** can be plausibly explained as a direct consequence of the weak HOMO/occupied NTO amplitude on the BT unit at the end of the arm. However, it would also appear that formation of the emissive excited state involves a fast relaxation from the Franck-Condon (vertical transition) state created by photon absorption, resulting in a low PLQY ($\Phi_{\text{PL}} \approx 27\%$) and absence of ASE when optically pumped at upto 500 $\mu\text{J cm}^{-2}$ energy density.

The precision in the chemical structure of these compounds relative to 9,9-dialkylfluorene/BT copolymers allows a consideration of the role of BT location in isolation from other factors - there is no ensemble averaging over a range of different chemical structures and chain architectures for the **T4BT-X** family. In particular, this allows us to shed new light on the literature discussion of BT torsion angles within the chain. Our experimental observations and supporting calculations indicate that changes in BT Raman intensity are not a specific signature of changes in torsion angle; any effect that alters the ground state polarizability gradient is relevant and here we tune it by proximity of the BT unit to the end of a chain.

5. Experimental

Synthesis: The synthetic strategy for creating the **T4BT-A** to **T4BT-E** series of C_3 symmetric star-shaped conjugated systems is presented in Scheme 1. To synthesise the first member (**T4BT-A**) it was found convenient to couple truxenetricboronic ester **1** with bromo(tetradialkylfluorenyl)benzothiadiazole **F4BTBr** for two reasons: 1) to avoid another conversion of bromide **F4BTBr** to boronic ester and 2) to achieve a more efficient coupling by using a more electrophilic bromo-compound. The ester **1** was synthesized from tribromohexahexyltruxene **2** (See Scheme S1, Supporting Information (SI)), via lithiation with n-BuLi, followed by quenching with triisopropylborate and hydrolysis in acidic conditions. Due to the poor solubility of the polymeric anhydrous forms of the triboronic acid **2a**, the latter was converted to the ester **1**.

The other members of the series (**T4BT-B**, **T4BT-C**, **T4BT-D** and **T4BT-E**) were obtained by coupling the corresponding boronic esters **F3BTBE**, **F2BTBE**, **F1BTBE** and **BTBE** with oligodialkylfluorene truxene core compounds bromo-substituted in the terminal positions, respectively **T1Br**, **T2Br**, **T3Br** and **T4Br**. We synthesized the **TnBr** compounds

by bromination of the corresponding tris(oligodialkylfluorene)truxene substituted with terminal trimethylsilyl substituents **T1Si** - **T4Si** under mild conditions (0°C, Br₂/CH₃COONa) (Scheme S2, SI). Convergent and semi-convergent strategies were used for the synthesis of **T1Si** - **T3Si** and **T4Si**, respectively, using both Suzuki and Negishi coupling protocols. We found that a modified Suzuki protocol using Ba(OH)₂ as a base gave almost quantitative yields for **T1Si-T4Si**. To increase the yield of the oligofluorene-truxene core compounds **T1Si-T4Si** in both Suzuki and Negishi coupling protocols, it was essential to increase the equivalents of the precursor arms (boronic acid or organozinc compound) relative to the core compound **2** or **T2Br** to a ratio of 5: 1 (instead of the 3.45 : 1 ratio that was used in our original publication [6]).

2,7-Dibromo-9,9-dihexyl-9H-fluorene **3** (see Scheme S3, SI) was used not only for the conversion of trimethylsilylboronic acids **SiF₁B** – **SiF₂B** to the corresponding bromooligodialkylfluorenes of the next generation **SiF₂Br** – **SiF₃Br** but also as a starting compound for the synthesis of the first member of trimethylsilyl functionalized boronic acids **SiF₁B** (Scheme S3, SI). In contrast to the known two-step procedure [42], the synthesis of the latter was performed in one pot, with the following sequence: lithiation - trimethylsilylation - lithiation - boronation. Not only does this approach provide access to trimethylsilylsubstituted monobromooligodialkylfluorenes, desilylation under acidic conditions (CF₃COOH/CH₂Cl₂) quantitatively afforded monobrominated non-substituted oligodialkylfluorenes. The advantage of using compound **3** instead of monobrominated or monoiodinated 9,9-dihexyl-9H-fluorene is a much simpler approach to large-scale synthesis, due to easier purification and handling. The synthesis of arm precursors **F₁BTBE** - **F₃BTBE** (Scheme S4, SI) was performed by coupling the corresponding bromide **F₁BTBr** - **F₃BTBr** with bis(pinacolato)diboron in the presence of a weak base (CH₃COOK). Monobrominated oligodialkylfluorenylbenzothiadiazoles were synthesized by coupling of the corresponding oligodialkylfluorenyl boronic ester with a 3-fold excess of dibromobenzothiadiazole **BTBr₂** using an anhydrous modified Suzuki protocol with K₃PO₄ as base and DMF as solvent (to provide better solubility of **BTBr₂**).

Each of the resulting **T4BT-A** to **T4BT-E** compounds is readily soluble in common organic solvents such as dichloromethane and dichlorobenzene. The **T4BT-A** to **T4BT-E** series also demonstrates good thermal stability. The onsets of decomposition measured by

TGA are all in the temperature range 414 - 428 °C (Figure S1, SI). DSC also reveals good morphological stability with $T_g = 107 - 112$ °C for all compounds (Figure S2, SI) and no obvious crystallization. These are attractive characteristics for device application.

Sample Preparation: Thin films of the **T4BT** compounds with thicknesses 30 nm, 50 nm and 120 nm ($\pm 10\%$ tolerance, Tencor Alphastep 200 profilometer) were spin-coated at 2000 rpm from filtered (0.2 μm Millipore), 10 - 40 mg/ml *o*-dichlorobenzene solutions onto pre-cleaned (10 min sonication in acetone then 2-propanol followed by 5 min, 80 W oxygen plasma exposure) Spectrosil B (quartz) substrates.

Absorption Measurements: The absorption spectra for both 50 nm and 120 nm thickness films of each **T4BT** compound were measured using a Shimadzu UV2550 spectrophotometer. Absorption coefficients were evaluated via the Beer-Lambert law and gave consistent results (within 10%) for the two film thicknesses. The corresponding refractive index spectra were derived from the absorption spectra using a Kramers-Kronig analysis [43] with reference data from a **T4** truxene sample [29] (see SI for details).

Photoluminescence Measurements: Room temperature Photoluminescence (PL) spectra were measured - using a Jobin-Yvon Fluoromax-3 spectrofluorimeter - for the 30 nm thickness films of each **T4BT** compound, thereby limiting self-absorption effects. For each material the excitation wavelength was selected to match the absorption maximum, i.e. feature II indicated in Figure 2; also see Table 1 for further details. PL Excitation (PLE) spectra were measured by recording the PL emission intensity (cf. Table 1 for PL maximum wavelength) as the excitation wavelength was scanned from 250 to 530 nm. PLQY measurements were performed within an integrating sphere, as described by de Mello *et al* [44] with excitation performed at both absorption features II and III for **T4BT-A**, **-B**, **-C** and **-D** and feature II only for **-E** (no significant PL was detected when exciting within the feature III wavelength range). Transient PL decay measurements used a 405 nm pulsed diode laser (1 MHz, 70 ps pulses) as excitation source, focussed onto the sample with an $\times 20$ microscope objective. This wavelength lies between the feature II and III peaks such that absorption by both is likely to contribute to the measured dynamics. The resultant photoluminescence was collected using the same microscope objective and focussed into a Chromex 250 IS imaging spectrograph, fibre coupled to a Hamamatsu C4334 Streakscope detector. The temporal scan length was set to 50 ns and scans of 40000 photon counts were taken at three different spatial

locations on each sample; the transients reported below are averages. For each **T4BT** compound both 30 nm and 120 nm thickness films were studied with no significant variation detected in decay transient or extracted decay time.

Amplified Spontaneous Emission Measurements: 120 nm thickness **T4BT** compound films on Spectrosil B substrates were stripe-pumped ($4.1 \text{ mm} \times 42 \text{ }\mu\text{m}$ excitation area defined with a cylindrical lens) using 6 - 7 ns, 10 Hz, third harmonic (355 nm) pulses from a Q-switched Nd:YAG laser. The incident pump energy density was varied between 5 and $500 \text{ }\mu\text{J cm}^{-2}$ using neutral density filters inserted into the optical path. The edge-emitted, gain-guided light output was collected with a microscope objective and coupled via a liquid light guide into a spectrograph equipped with a charge-coupled device (CCD) detector.

DFT Calculations: Density Functional Theory (DFT) and Time Dependent Density Functional Theory (TD-DFT) calculations were undertaken to gain a clearer insight into the electronic structure of the **T4BT-X** family of compounds. We used Becke's three-parameter hybrid exchange functional and Lee, Yang and Parry's correlation functional (B3LYP) together with Pople's double zeta split basis sets (6-31g*). For computational expediency we modelled simplified proxy structures comprising a truxene core with only a single arm attached, and replaced hexyl substituents with hydrogens. We justify this approach on the basis of the C3 symmetry of the **T4BT-X** compounds and the absence of conjugation through their truxene cores. To check the consequences of this simplification we used the same methods to optimize the full structure and compared the lowest excited state energies to those of the proxies and found that they differed by less than 1%. We therefore conclude that while we expect the system to be degenerate, there is no significant effect on the molecular orbital energies. Each compound was considered in turn and the geometry in the ground state was optimized and used to compute both electronic absorption and Raman (*vide infra*) activity. Excited state calculations were carried out with TD-DFT, all others with DFT. In order to gain a clear description of the various electronic excitations we adopted a Natural Transition Orbital (NTO) representation - obtained from diagonalizing the transition density matrix [32] - to represent the "electron" and "hole" states involved in the principal ground- and excited-state transitions.

Raman Measurements: Unpolarized Raman spectra were excited in a backscattering geometry using the 632.8 nm line of a HeNe laser focussed on the sample with a $\times 100$

microscope objective. Spectra were collected in the 1200 to 1700 cm^{-1} range using a Renishaw micro Raman system equipped with a CCD detector. A 10 s integration time was used and the signal was averaged over 3 separate scans. After each measurement (10 mW incident power), the samples were visually inspected through the microscope to confirm that there were no signs of laser damage.

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Supporting Information is available online from Wiley InterScience. Synthetic procedures and characterization for all novel compounds, NMR, TGA, DSC, UV-Vis, Kramers Kronig analysis and Raman fitting, (Figures S1-S56; Schemes S1-S4; Tables S1-S4) (PDF).

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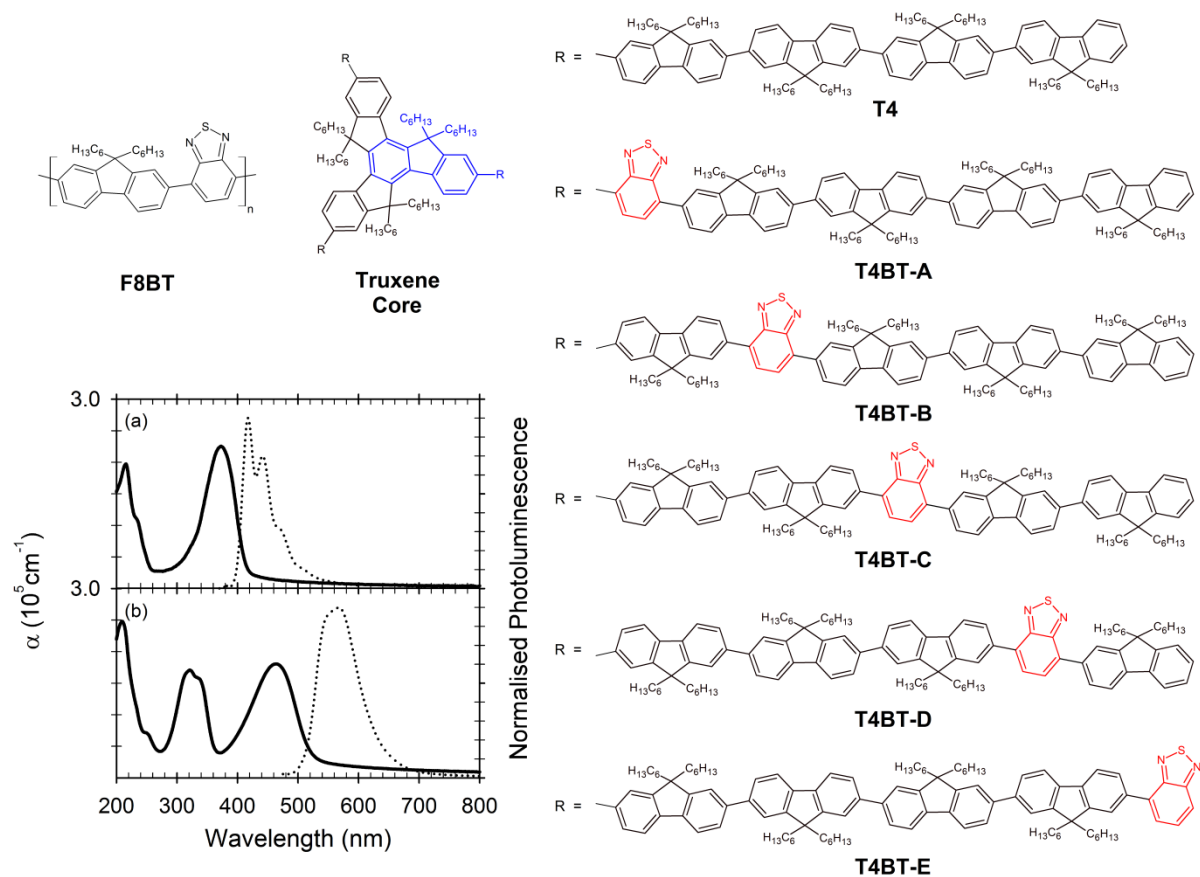


Figure 1. Chemical structures of truxene-cored starburst compounds **T4BT-A**, **-B**, **-C**, **-D** and **-E**, the parent **T4** truxene (R = tetra(9,9-dihexylfluorene)) and the alternating copolymer **F8BT**. The highlighted part of the truxene core (blue) identifies an effective 9,9-dihexylfluorene unit to which the attached arm is conjugatively coupled. BT units are highlighted in red. Also shown for reference are the absorption (solid lines) and PL (dotted lines) for the **T4** truxene (panel (a)) and **F8BT** polymer (panel (b)).

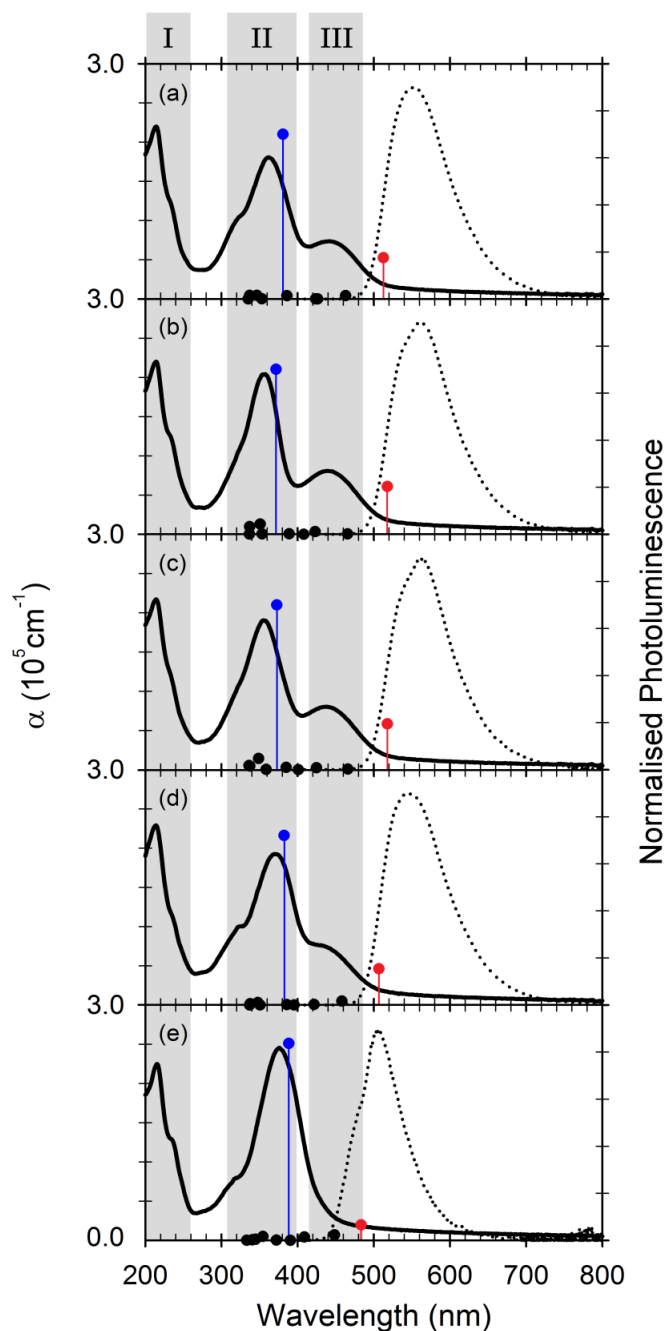


Figure 2. Absorption coefficient (α , 10^5 cm^{-1}) (solid lines, left ordinate) and normalised photoluminescence emission (dotted lines, right ordinate) spectra for thin film samples of (a) **T4BT-A**, (b) **-B**, (c) **-C**, (d) **-D** and (e) **-E**. The absorption features I, II and III described in the text are highlighted by the grey shaded areas. The absorption data shown here were obtained for $50 \pm 5 \text{ nm}$ thickness films while the PL spectra were recorded for $30 \pm 7 \text{ nm}$ films in order to limit self-absorption effects. The TD-DFT calculated oscillator strengths (discrete circles data and vertical lines) for the many, low-lying optical transitions are also plotted. The oscillator strengths for transitions II and III are highlighted in blue and red respectively.

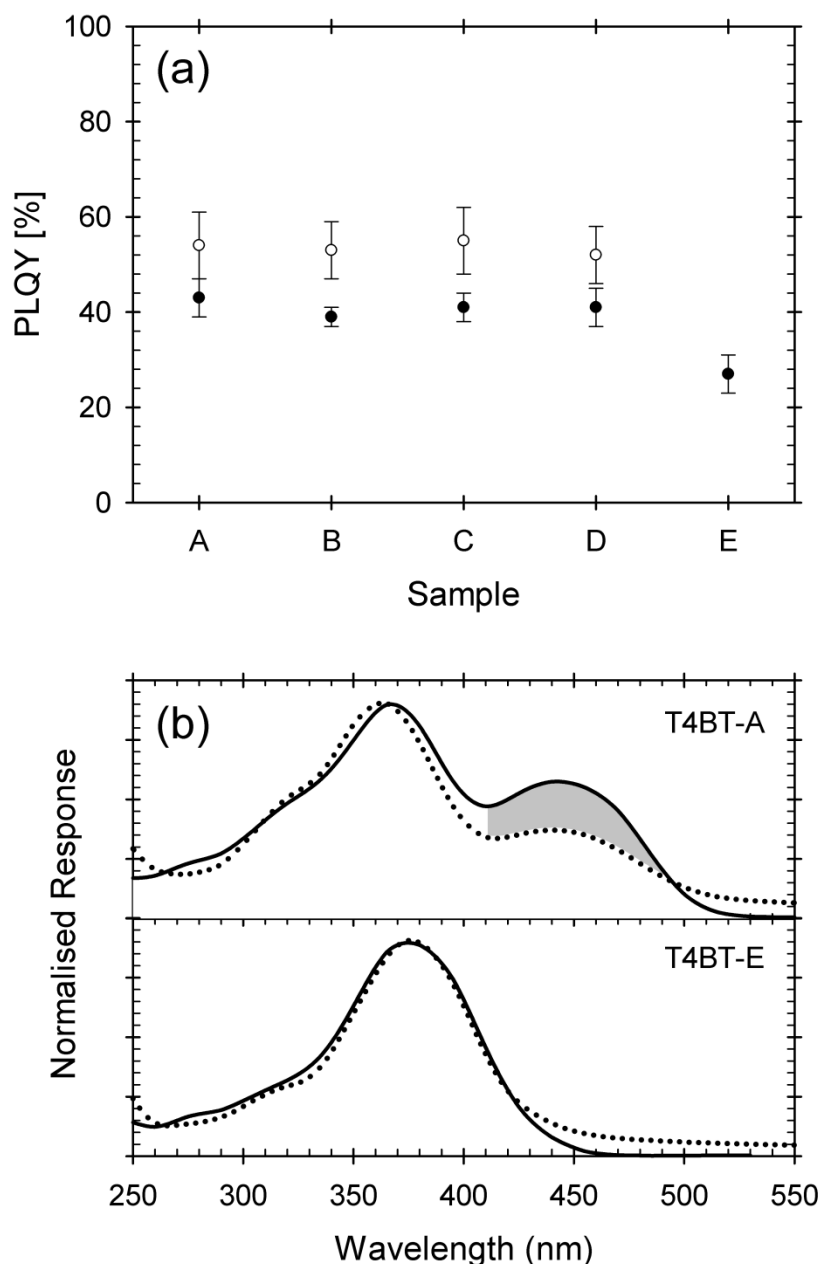


Figure 3. (a) PLQY values for **T4BT-A**, **-B**, **-C**, **-D** and **-E** for excitation at transitions II (filled circles) and III (empty circles) (c.f. Figure 2). (b) Photoluminescence excitation (PLE) spectra (solid lines, peak normalised at transition II) for **T4BT-A** (600 nm PL detection, upper panel) and **T4BT-E** (550 nm PL detection, lower panel). The corresponding absorption spectra (dotted lines, peak normalised at transition II) are included for comparison. The increase in PLQY as the excitation wavelength is moved from transition II to transition III for **T4BT-A** manifests as a relative increase (shaded area) in the PLE signal strength compared to the underlying absorption.

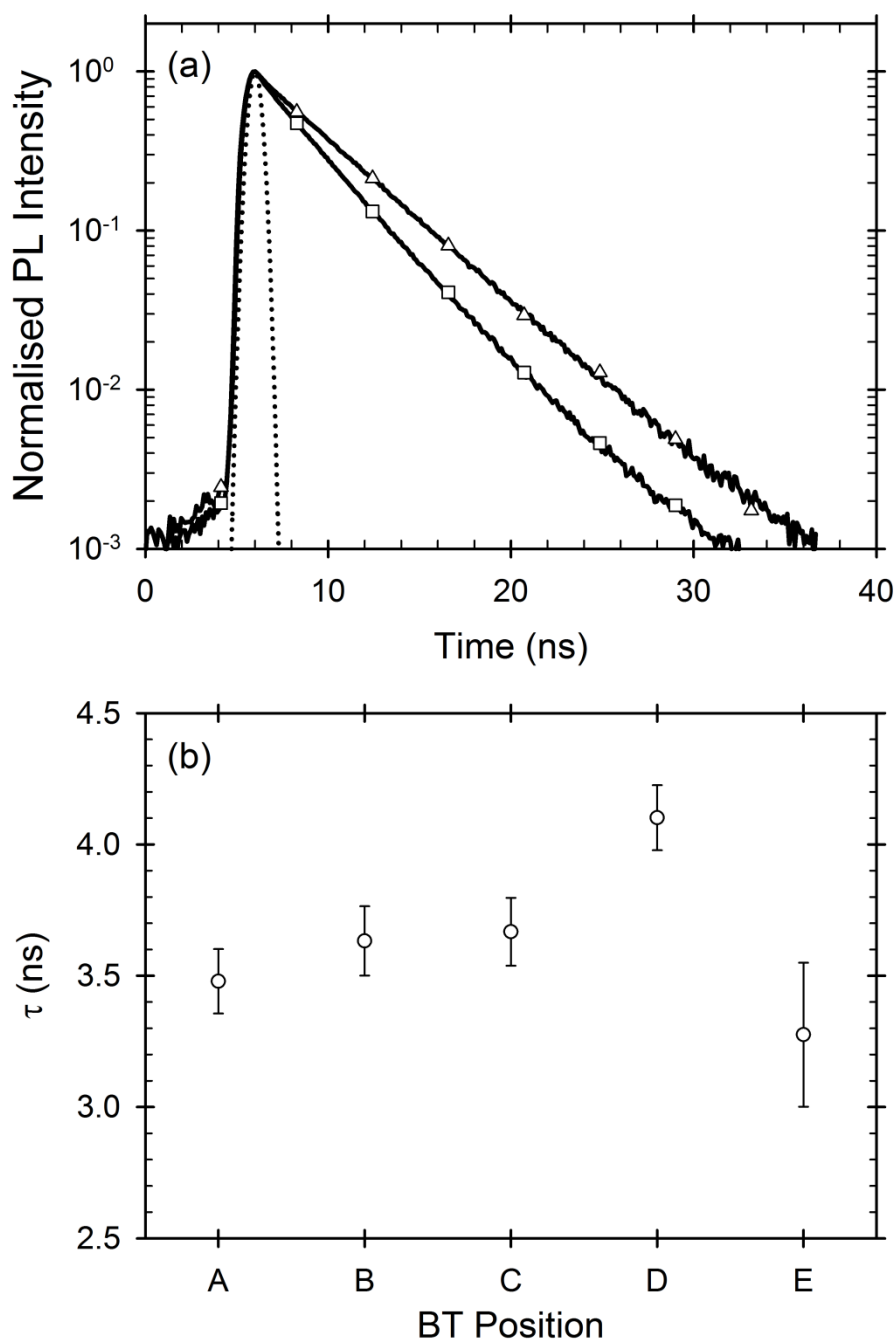


Figure 4. (a) Normalised PL decay transients for **T4BT-D** (open triangles) and **T4BT-E** (open squares) under 405 nm pulsed excitation (70 ps, 1MHz laser diode excitation). The dotted line shows the instrument response function. (b) Lifetimes for **T4BT-A**, **-B**, **-C**, **-D** and **-E**, extracted by fitting the convolution of a mono-exponential decay with the instrument response.

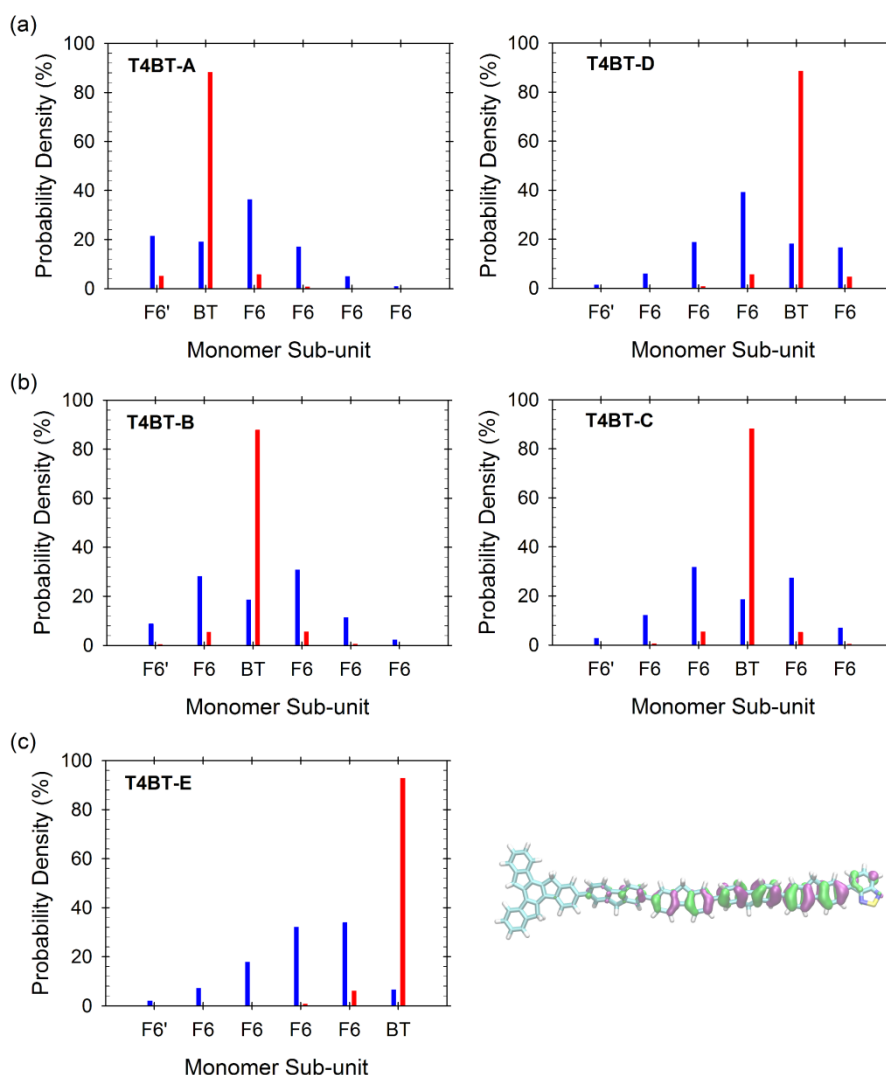


Figure 5. TD-DFT calculated probability density distributions for the occupied (blue bars) and unoccupied (red bars) NTOs associated with the lowest energy optical transition for the proxy structures of the **T4BT-X** compounds. Panel (a) shows the results for the **T4BT-A/-D** pair, panel (b) for the **T4BT-B/-C** pair and panel (c) for **T4BT-E** (Left). The iso-surface plot for the occupied NTO wavefunction (iso-surface values ± 0.02 shown in green/purple) for **T4BT-E** is shown in panel (c) (Right) for comparison.

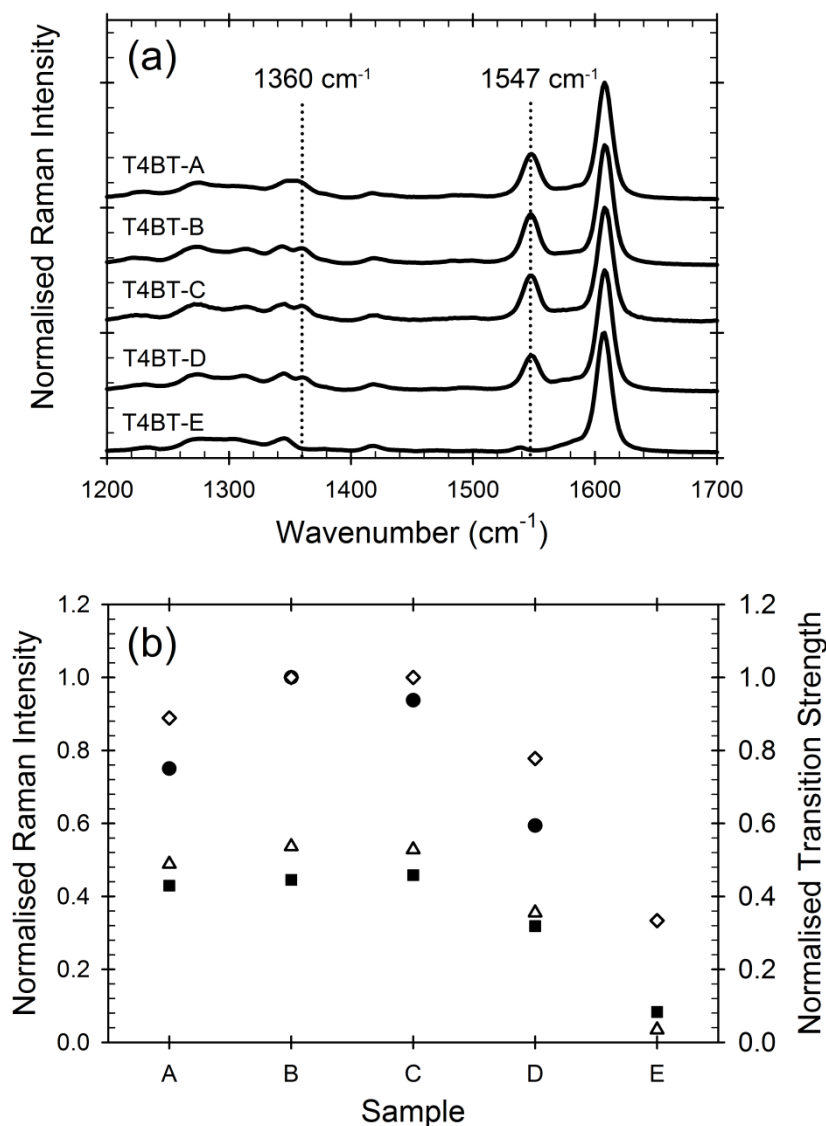


Figure 6. (a) Normalised Raman scattering spectra for **T4BT-A**, **-B**, **-C**, **-D** and **-E**. The usual BT-centred C-C (1360 cm⁻¹) and ring stretching (1547 cm⁻¹) mode frequencies are highlighted by vertical dotted lines. (b) Comparison between experimental (filled squares, left ordinate) and calculated (open triangles, left ordinate) intensities for the ≈ 1547 cm⁻¹ Raman peak for compounds **T4BT-A**, **-B**, **-C**, **-D** and **-E**. Both data sets are normalized to the 1608 cm⁻¹ 9,9-dialkylfluorene ring stretch mode intensity. The scattering cross sections were calculated using an orbital analysis on simplified proxy structures (single arm, hydrogen substituents). Also shown are the experimental (filled circles, right ordinate) integrated absorption strengths (S_{III}) and calculated (open diamonds, right ordinate) oscillator strengths (f_{III}) of transition III for compounds **T4BT-A**, **-B**, **-C**, **-D** and **-E** (data from Tables 2 and 3).

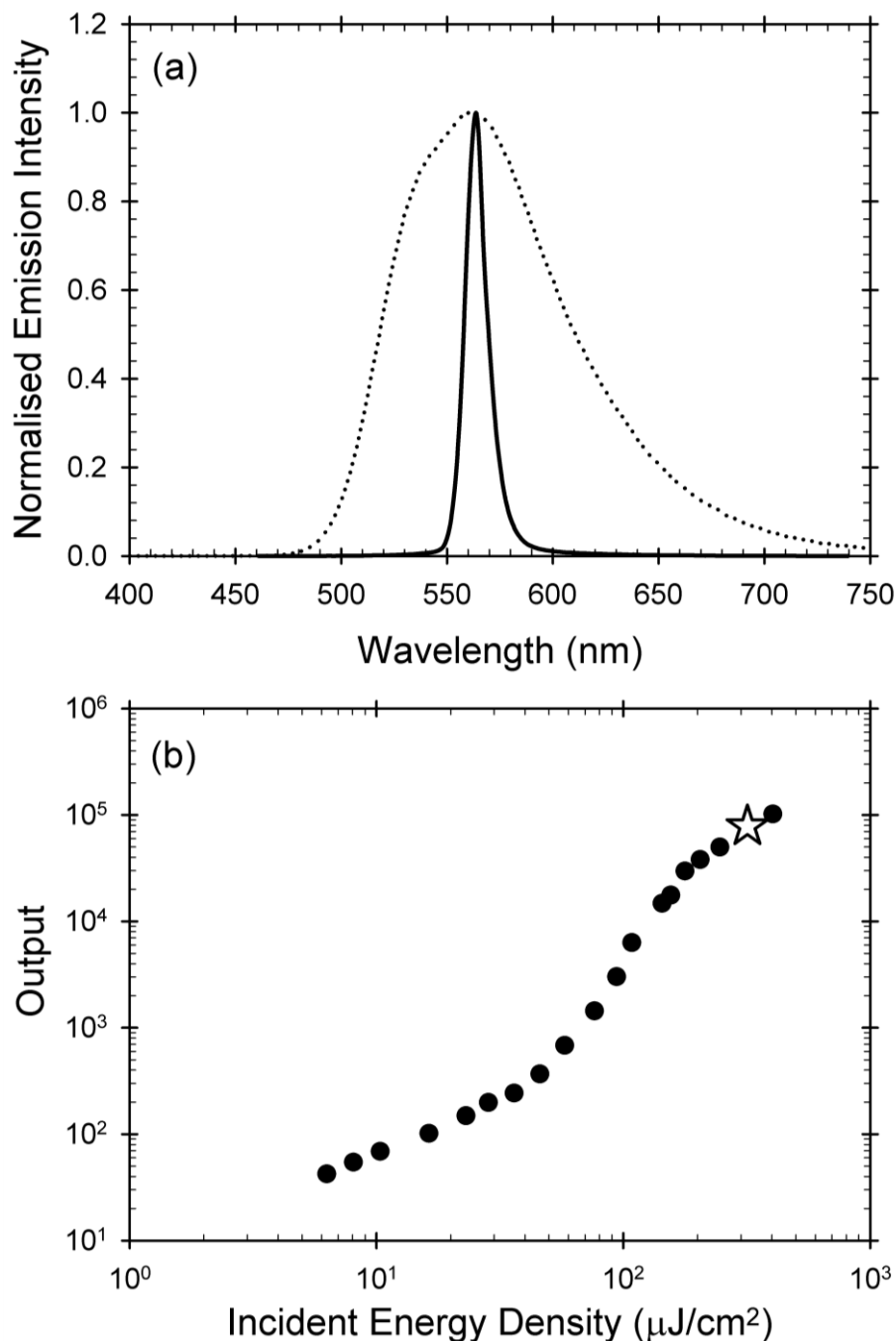
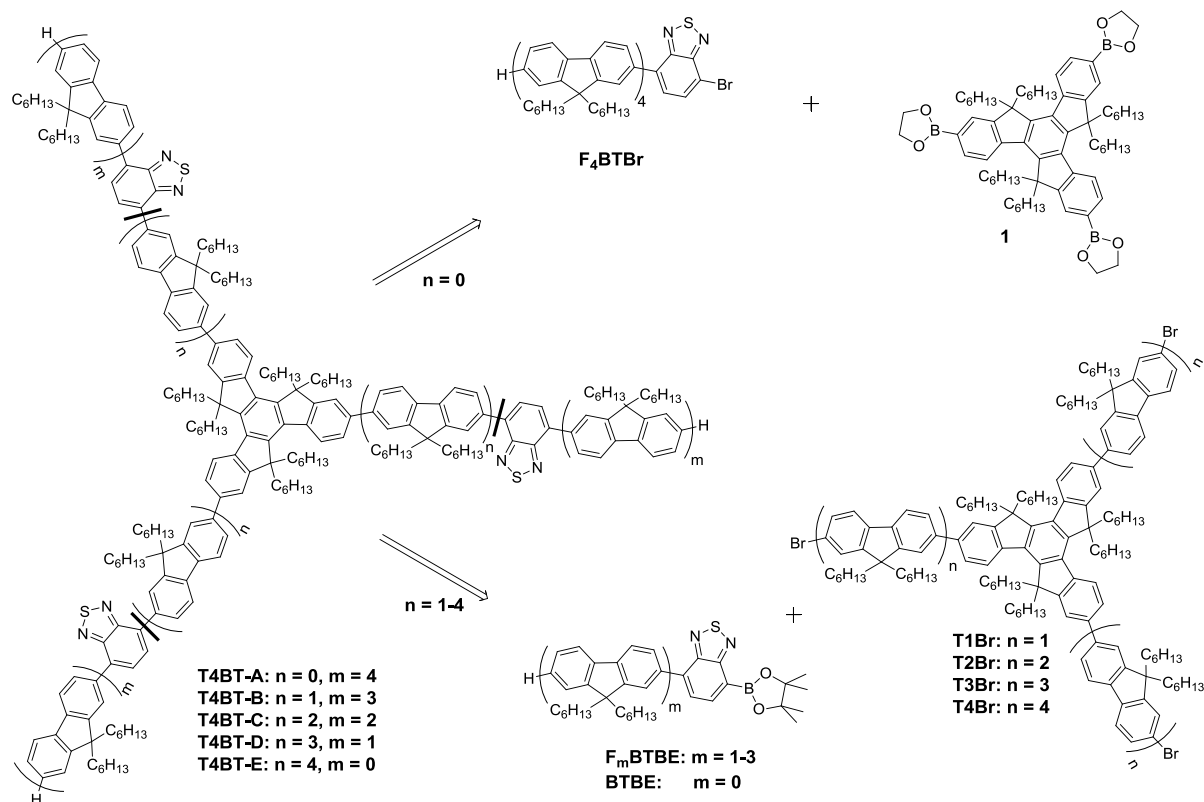


Figure 7. (a) Normalised amplified spontaneous emission (ASE) spectrum (solid line) for a **T4BT-B** film (120 ± 10 nm) at an incident pump energy density of $320 \mu\text{J cm}^{-2}$. A normalised PL spectrum (dotted line) is also shown for reference. (b) Incident pump energy density dependence of the ASE (filled circles data); the data point highlighted by a star indicates $320 \mu\text{J cm}^{-2}$ excitation, corresponding to the ASE spectrum plotted in (a).



Scheme 1. Retrosynthetic scheme for the **T4BT-X** family of compounds. Bold lines represent the disconnection sites.

Table 1. Numerical values for selected physical properties of the **T4BT-X** family. λ_{II} and λ_{III} are, respectively, the peak wavelengths deduced from fitting transitions II and III and α_{II} and α_{III} the corresponding peak absorption coefficients; S_{II} and S_{III} are the related absorption integrals defined as $S = \int \alpha(E) dE$, where $\alpha(E)$ is the absorption coefficient (modelled as a Gaussian oscillator) and E the photon energy; $\lambda_{PL \max}$ is the peak of the photoluminescence spectrum; $\Phi_{PL}(\lambda_{II} \text{ ex})$ and $\Phi_{PL}(\lambda_{III} \text{ ex})$ are the PL quantum yields for excitation at transitions II and III respectively; $\langle \tau \rangle$ is the first temporal moment of the transient decay; $n(\lambda_{PL \max})$ is the refractive index evaluated at $\lambda_{PL \max}$; $\nu_{F6 \text{ Ph}}$ is the fitted peak wavenumber for 9,9-dialkylfluorene phenyl ring stretching; $\nu_{BT \text{ Ph}}$ and $\nu_{BT \text{ C-C}}$ are the fitted peak wavenumbers for BT phenyl ring stretching and C-C stretching respectively, with $A_{BT \text{ Ph}}$ and $A_{BT \text{ C-C}}$ the corresponding amplitudes.

Property	T4BT-A	T4BT-B	T4BT-C	T4BT-D	T4BT-E
λ_{II} [nm]	364	357	358	372	376
α_{II} [10^5 cm^{-1}]	1.8	2	1.9	1.9	2.4
S_{II} [10^4 eV cm^{-1}]	7.7	7.3	7.8	8.0	11.1
λ_{III} [nm]	445	440	440	444	—
α_{III} [10^5 cm^{-1}]	0.7	0.8	0.8	0.7	—
S_{III} [10^4 eV cm^{-1}]	2.4	3.2	3.0	1.9	—
$\lambda_{PL \max}$ [nm]	553	561	562	546	507
$\Phi_{PL}(\lambda_{II} \text{ ex})$ [%]	43 ± 4	39 ± 2	41 ± 3	41 ± 4	27 ± 4
$\Phi_{PL}(\lambda_{III} \text{ ex})$ [%]	54 ± 7	53 ± 6	55 ± 7	52 ± 6	—
$\langle \tau \rangle$ [ns]	3.4	3.6	3.6	4.0	3.3
$n(\lambda_{PL \max})$	1.75	1.75	1.75	1.76	1.78
$\nu_{F6 \text{ Ph}}$ [cm^{-1}]	1608	1608	1608	1608	1607
$\nu_{BT \text{ Ph}}$ [cm^{-1}]	1547	1547	1547	1547	1538
$A_{BT \text{ Ph}}$	0.289	0.326	0.300	0.225	0.031
$\nu_{BT \text{ C-C}}$ [cm^{-1}]	1360	1361	1361	1362	—
$A_{BT \text{ C-C}}$	0.086	0.101	0.080	0.080	—

Table 2. Parameters extracted from DFT modelling and geometry optimization of proxy structures (Figure 1) for the **T4BT-X** family. λ'_{II} and λ'_{III} are the calculated absorption wavelengths for transitions II and III, f'_{II} and f'_{III} are the corresponding oscillator strengths (dimensionless) and θ is the torsion angle between the BT unit and adjacent F6/F6' units.

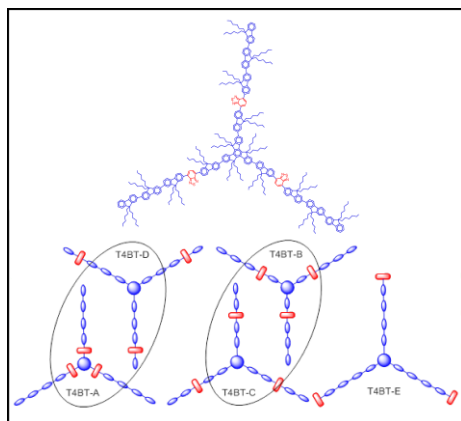
Parameter	T4BT-A	T4BT-B	T4BT-C	T4BT-D	T4BT-E
λ'_{II} [nm]	381	372	373	382	388
f'_{II}	3.3	3.3	3.3	3.4	3.9
λ'_{III} [nm]	513	518	518	507	483
f'_{III}	0.8	0.9	0.9	0.7	0.3
θ [°]	35	37	37	35	36

Table 3. Summary of experimental results characterising the properties of **T4BT-X** compounds.

Technique	Results Summary
Absorption Spectra	- Pairwise correspondence between T4BT-B and -C and T4BT-A and -D absorption spectra. - Only transition (II) observable for T4BT-E.
PL Spectra	- Pairwise correspondence between T4BT-B and -C and T4BT-A and -D PL emission spectra; associated with absorption transition III. T4BT-E emission appears at considerably shorter wavelength; associated with absorption transition II but showing a large Stokes shift and negligible vibronic structure in contrast to the spectra for T4.
PL Quantum Yields	- Similar PLQY for T4BT-A, -B, -C and -D, with excitation at transition III exhibiting a higher Φ_{PL} value than excitation at transition II. - PLQY reduced for T4BT-E and only excited via transition II. - PLE spectra show consistent enhancement of transition III spectral region for T4BT-A, -B, -C and -D.
PL Decay Transients	- Pairwise correspondence between T4BT-B and -C is preserved. - Divergence between T4BT-A and -D behaviors - qualitatively consistent with calculated weaker transition III for T4BT-D. T4BT-E exhibits shortened, non-mono-exponential decay time.
ASE	- Amplified spontaneous emission readily observed for T4BT-A, -B, -C and -D. - No ASE for T4BT-E up to 500 $\mu\text{J}/\text{cm}^2$ pump energy density.
Raman Scattering	- All T4BT-X compounds have very similar Raman spectra. - Intensity of BT-centred vibrational modes increases from T4BT-A to -B, to -C then decreases from T4BT-C to -D, to -E. - Calculated Raman intensities show analogous behavior.

Location, Location, Location - strategic positioning of 2,1,3-benzothiadiazole units within trigonal quaterfluorene-truxene star-shaped structures

Colin R. Belton, Alexander L. Kanibolotsky, James Kirkpatrick, Clara Orofino, Saadeldin E. T. Elmasly, Paul N. Stavrinou, Peter J. Skabara* and Donal D. C. Bradley*



2,1,3-benzothiadiazole (BT) units are systematically incorporated into star-shaped trigonal molecules comprising a truxene core and three quaterfluorene arms. Five isomers are synthesised corresponding to the symmetric insertion of a single BT unit into each of the possible positions within the arms. Three BT *locations* are identified (see figure) by comparison of absorption and photoluminescence (PL) spectra, supported by theoretical calculations. Additional experimental and theoretical characterisations reveal the influence of BT position on Raman, photoluminescence and stimulated emission properties.

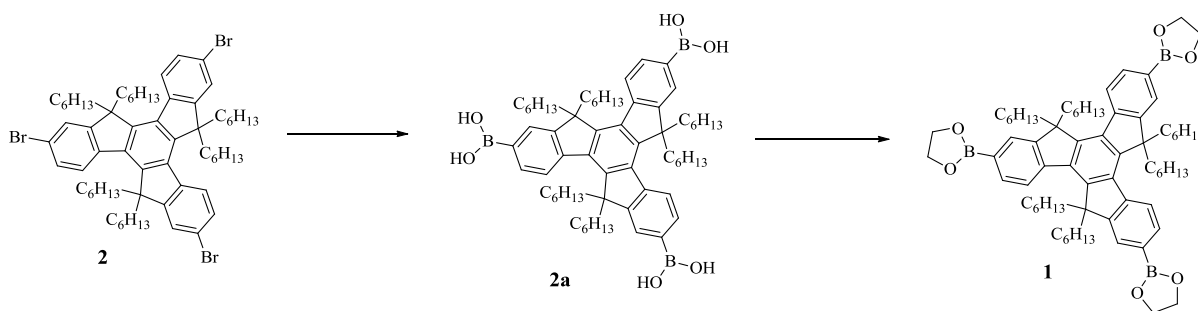
Keyword: Supramolecular Materials, Molecular Electronics, Photoluminescence, Photonics, Structure Property Relationships

Supporting Information

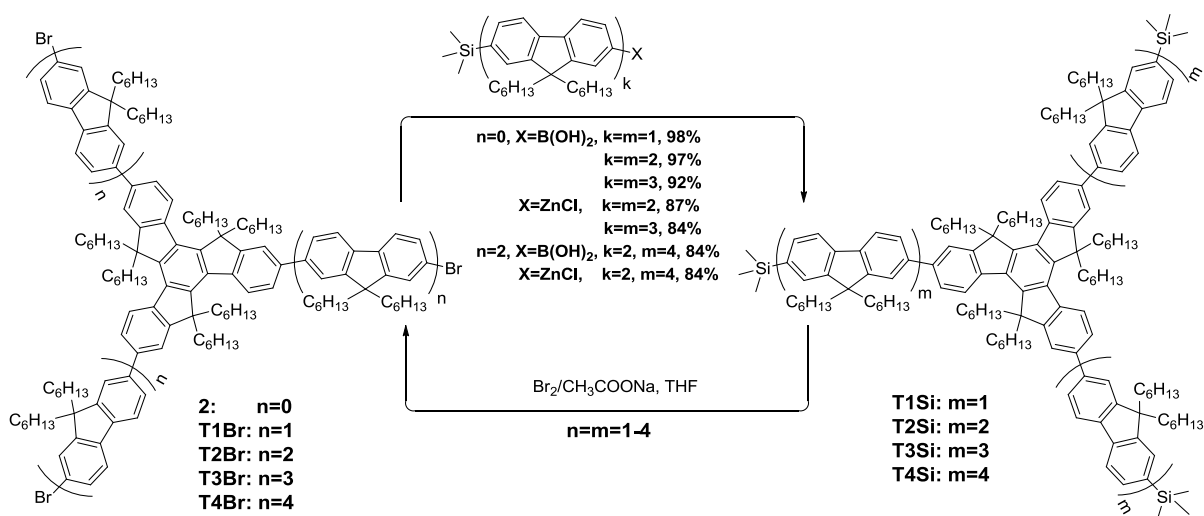
Table of Contents

Synthesis of T4BT materials	S-2
Thermal Analyses	S-12
Absorption Spectra with Peak Fitting	S-13
Refractive Index Measurements (Kramers-Kronig Analysis)	S-17
Raman Spectra with Peak Fitting	S-18
¹ H and ¹³ C NMR Spectra of Newly Synthesised Compounds	S-22

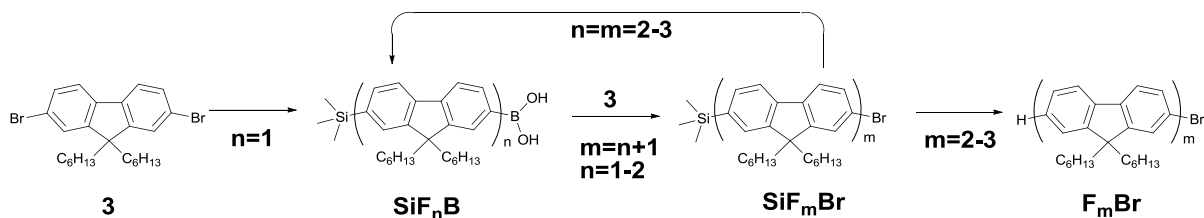
Synthesis of T4BT Materials



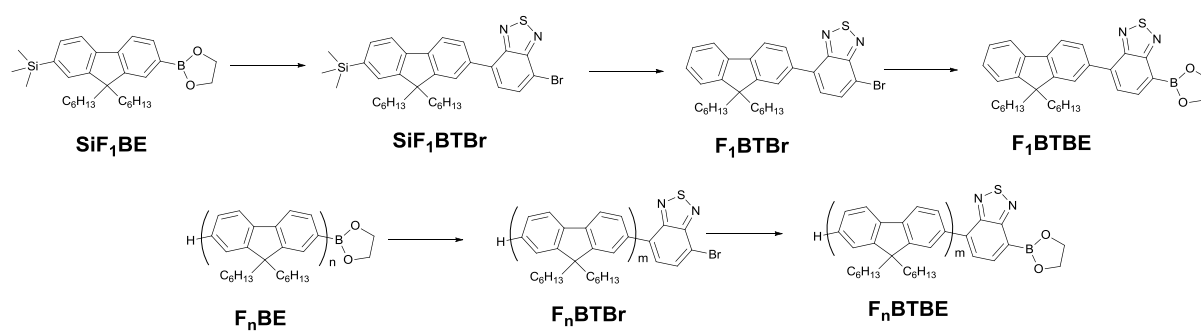
Scheme S1- Synthesis of the truxenetriboronic ester **1**.



Scheme S2- Synthesis of **T1Si-T4Si** by modified Suzuki coupling and bromination in mild conditions.



Scheme S3- Synthesis of the oligofluorene arm precursors.



Scheme S4- Synthesis of the oligofluorene-BT arm precursors F₁BTBE - F₃BTBE.

2,2',2''-(5,5,10,10,15,15-hexamethyl-10,15-dihydro-5H-diindeno[1,2-a:1',2'-c]fluorene-2,7,12-triyl)tris(1,3,2-dioxaborolane) (1)

A solution of 1.0 g (922 μmol) of tribromohexahexyltruxene **2** in 98 mL of THF was cooled to $-100\text{ }^{\circ}\text{C}$ and 1.6 mL (3.77 mmol) of butyl lithium solution in hexane (2.36 M) was added. The reaction mixture was allowed to reach $-80\text{ }^{\circ}\text{C}$ over 30 min and cooled to $-100\text{ }^{\circ}\text{C}$. 2.8 mL (12.1 mmol) of triisopropyl borate was added, the bath removed, and the reaction mixture stirred for another 20 h. Acidic aqueous work up afforded the crude product which was washed with 3 x 25 mL of hexane to give 914 mg of triboronic acid **2a**. To the latter 240 mL of toluene and 190 μL of ethylene glycol was added and the mixture refluxed for 16 hours. After evaporating the solvent and recrystallisation from hexane the yield of the white solid was 806 mg (83 %)

1, MALDI-TOF MS: m/z 1056.3 (M^+), 971.3($(\text{M}-\text{C}_6\text{H}_{13})^+$). Anal. Calcd for $\text{C}_{69}\text{H}_{99}\text{B}_3\text{O}_6$: C, 78.41; H, 9.44 %. Found: C, 78.47; H, 9.38%.

^1H NMR (CDCl_3 , δ , 400 MHz) 8.40 (1H, d, $^3J = 8\text{ Hz}$), 7.89 (1 H, s), 7.87 (1H, d, $^3J = 8\text{ Hz}$), 4.46 (4H, s), 3.4–2.86 (2H, m), 2.04–2.23 (2H, m), 1.00–0.70 (12H, m), 0.57 (6H, t, $^3J = 8\text{ Hz}$), 0.55–0.55 (4H, m).

^{13}C NMR (CDCl_3 , δ , 101 MHz) 152.95, 146.81, 143.55, 138.44, 133.00, 128.55, 124.30, 66.25, 55.90, 37.03, 31.63, 29.60, 24.09, 22.40, 13.99.

9,9-dihexyl-7-trimethylsilylfluorene-2-ylboronic acid (SiF₁B)

To a solution of 5.56 g (11.3 mmol) of 2,7-dibromo-9,9-dihexylfluorene in 90 mL of THF at $-80\text{ }^{\circ}\text{C}$ a solution of butyl lithium (2.48 M) in hexane (4.6 mL, 11.4 mmol) was added dropwise over 40 min under N_2 . The reaction was cooled to $-100\text{ }^{\circ}\text{C}$ and 1.5 mL (11.9 mmol) of chlorotrimethylsilane was added. The reaction mixture was allowed to reach room temperature before being cooled to $-85\text{ }^{\circ}\text{C}$ and the second portion (5.5 mL, 13.6 mmol) of butyl lithium solution added slowly, not allowing to warm the mixture to a temperature higher than $-78\text{ }^{\circ}\text{C}$. The reaction mixture was cooled to $-100\text{ }^{\circ}\text{C}$ and 8.0 mL (34.7 mmol) of triisopropyl borate was added and after removing the bath the stirring continued for another 18 h. The solution was poured onto 500 mL of cold de-ionized water, which was extracted with 7 x 100 mL of diethyl ether. The combined ether extracts were washed with an

additional 500 mL of de-ionized water, dried over MgSO_4 , and the solvent evaporated yielding 5.73 g of crude material. The product was purified by column chromatography on silica gel, eluting first with toluene to remove by-products then with ether to isolate the product. Yield 4.48 g, 88%¹.

^1H NMR (500 MHz, δ , CDCl_3): 8.30 (1H, d, $J=7.5$ Hz), 8.23 (1H, s), 7.89 (1H, d, $J=7.5$ Hz), 7.80 (1H, d, $J=7.7$ Hz), 7.56 (1H, d, $J=6.7$ Hz), 7.54 (1H, s), 2.07-2.13 (4H, m), 1.06-1.15 (12H, m), 0.77 (4H, m), 0.77 (6H, t, $J=6.6$ Hz), 0.35 (9H, s).

General procedure for the synthesis SiF_2Br and SiF_3Br . To a solution of 2,7-dibromo 9,9-dihexylfluorene (**3**) (3 mol) and tetrakis(triphenylphosphine)palladium (0) (0.03 mol) in toluene a solution of boronic acid (SiF_3B , SiF_2B) (1mol) in toluene was added, followed by addition of 2M aqueous Na_2CO_3 solution (2 mol). The mixture was degassed, heated to 80 °C and stirred at this temperature for 20 h. The toluene layer was separated, the aqueous layer being extracted with CH_2Cl_2 . The combined organic layers were washed with water, and after drying over MgSO_4 the solvent removed under vacuum to afford the crude mixture. The latter was purified on a silica column using petrol ether as the eluent for compound SiF_2Br . In the case of compound SiF_3Br eluents were petrol ether to remove excess of 2,7-dibromo 9,9-dihexylfluorene (**3**) and petrol : toluene, 10:1 to elute the product. The yields were: 75% for SiF_2Br ¹ and 82% for SiF_3Br .

SiF_3Br , MALDI-TOF MS: m/z 1148 (M^+). Anal. Calcd for $\text{C}_{78}\text{H}_{105}\text{BrSi}$: C, 81.42; H, 9.20; Br, 6.94 %. Found: C, 81.34; H, 9.12; Br, 6.97%.

^1H NMR (400 MHz, δ , CDCl_3): 7.88-7.70 (5H, m), 7.70-7.57 (9H, m), 7.56-7.44 (4H, m), 2.30-1.80 (12H, m), 1.25-1.10 (36H, m), 0.92-0.60 (30H, m), 0.33 (9H, s)

^{13}C NMR (CDCl_3 , δ , 101 MHz) 153.42, 151.98, 151.92, 151.86, 151.27, 150.33, 141.56, 141.20, 140.77, 140.48, 140.43, 140.32, 140.05, 140.01, 139.36, 139.15, 132.00, 130.15, 127.79, 126.43, 126.37, 126.32, 126.17, 121.67, 121.60, 121.22, 121.13, 120.13, 119.16, 55.69, 55.48, 55.26, 40.48, 40.44, 40.28, 31.60, 31.51, 29.78, 29.72, 23.98, 23.88, 22.70, 22.63, 14.15, -0.70.

General procedure for the synthesis of boronic acids SiF_2B , SiF_3B . The solution of the corresponding bromoderivative (SiF_2Br or SiF_3Br) (1 mol) in THF (12 mL per gram) was cooled to -95°C under nitrogen, and 1.6-2.5 M of n-butyl lithium solution (1.3 mol) added, not allowing the temperature to rise above -80°C. The reaction mixture was stirred at -80°C for another 15 min before cooling to -100 °C and adding triisopropylborate. The mixture was allowed to reach room temperature for 12 h and quenched with deionized water. The product was extracted with diethyl ether, washed with deionized water, then dried over MgSO_4 . After evaporating the ether the product was subjected to column chromatography on silica gel eluting first with toluene to remove non-boronated by-products and then with ether to elute the boronic acid. The yields were: 87% for SiF_2B ¹ and 90% for SiF_3B .

SiF_3B , MALDI-TOF MS: m/z 1114.44 (M^+), Anal. Calcd for boronic anhydride $\text{C}_{78}\text{H}_{105}\text{SiBOSi}$: C, 85.36; H, 9.64 %. Found: C, 85.13; H, 9.86%.

^1H NMR (500 MHz, δ , CDCl_3): 8.40 (1H, d, $^3J=7.5$ Hz), 8.31 (1H, s), 7.98 (1H, d, $^3J=7.5$ Hz), 7.95 (1H, d, $^3J=8.0$ Hz), 7.87 (1H, d, $^3J=8.0$ Hz), 7.86 (1H, d, $^3J=7.5$ Hz), 7.82 (1H, d, $^3J=7.5$ Hz), 7.78-7.63 (9H, m),

7.54 (1H, d, $^3J=7.5$ Hz), 7.53 (1H, s), 2.00-2.35 (12H, m), 1.05-1.25 (36H, m), 0.65-0.95 (30H, m), 0.35 (9H, s)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 152.61, 151.96, 151.87, 150.62, 150.34, 141.57, 140.79, 140.56, 140.09, 139.15, 132.00, 127.79, 126.40, 126.18, 121.69, 120.16, 119.16, 55.51, 55.39, 55.26, 40.51, 40.29, 31.68, 31.62, 31.51, 29.90, 29.82, 29.73, 24.02, 23.88, 22.72, 22.64, 14.17, -0.69.

General procedure for the synthesis of trimethylsilyl terminated oligofluorene-truxenes **T2Si, **T3Si** and **T4Si** by Negishi cross-coupling.** A solution of the corresponding bromooligofluorene (**SiF₂B**, **SiF₃B**) (1 mol) in THF (14-17 mL per gram) was cooled to -95-100°C under nitrogen, and 2.5 M of n-butyl lithium solution (1-1.03 mol) added, not allowing the temperature to rise above -80°C. The reaction mixture was stirred at -80°C for another 15 min before cooling to -100 °C and adding a solution of zinc chloride (1.1 mol) in THF (20-40 mL per gram). The cooling bath was removed, allowing the reaction mixture to warm up to room temperature. The obtained solution of organozinc compound was syringed (or cannulated, depending on the scale of the reaction) to a degassed solution of the corresponding bromo-substituted core compound (**2** in the case of **T2Si** and **T3Si** synthesis or **T2Br** in the case of **T4Si** synthesis) (0.20-0.21 mol), tetrakis(triphenylphosphine)palladium (0) (0.04 mol) in THF (30 mL per gram of **2** or 15 mL per gram of **T2Br**), and the rest of the organozinc compound was washed from the wall of the flask with an additional amount of THF (15 mL per gram of the core compound). The reaction was finally flashed with nitrogen and refluxed at 80°C for 20 h before basic aqueous work up. The crude product was purified by column chromatography on silica gel eluting with petrol : toluene (10:1) for **T2Si** (yield 87%), with petrol : toluene (7:1) ramping to petrol : toluene (3:1) for **T3Si** (yield 84%), with petrol : CH_2Cl_2 (1:7) for **T4Si** (yield 84%).

General procedure for the synthesis of trimethylsilyl terminated oligofluorene-truxenes **T1Si, **T2Si**, **T3Si** and **T4Si** by Suzuki cross-coupling.** To a mixture of the corresponding bromo-substituted core compound (**2** in the case of **T1Si**, **T2Si** and **T3Si** synthesis or **T2Br** in the case of **T4Si** synthesis) (1 mol), tetrakis(triphenyl phosphine)palladium (0) (0.2), the corresponding boronic acid (**SiF₁B**, **SiF₂B** or **SiF₃B**) (5 mol), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (7.5-8.0 mol) in DME (30-40 mL per gram of the core compound) H_2O (2.1 mL per gram of the base) was added and the reaction mixture degassed and stirred at 80°C for 20 h. After aqueous work up the crude product was subjected to column chromatography on silica gel, eluting with petrol : toluene (30:1) ramping to petrol : toluene (10:1) (yield 98%) for **T1Si**. The column purification of the **T2Si** – **T4Si** was performed as described above. The yields were: 97% for **T2Si**, 92% for **T3Si** and 84% for **T4Si**.

T1Si, MALDI-TOF MS: m/z 2060 (M^+). Anal. Calcd for $\text{C}_{147}\text{H}_{210}\text{Si}_3$: C, 85.65; H, 10.27 %. Found: C, 85.66; H, 10.38%.

^1H NMR (500 MHz, δ , CDCl_3): 8.52 (1H, d, $^3J=8.5$ Hz), 7.85 (1H, d, $^3J=7.5$ Hz), 7.83-7.67 (5H, m), 7.55 (1H, dd, $^3J = 7.8$ Hz, $^4J = 0.5$ Hz), 7.54 (1H, s), 3.20-3.00 (2H, m), 2.35-2.15 (2H, m), 2.09 (4H, t, $^3J=8.3$ Hz), 1.24-0.88 (24H, m), 0.88-0.72 (10H, m), 0.72-0.6 (10H, m), 0.36 (9H, s)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.56, 151.90, 150.34, 145.32, 141.65, 140.54, 140.41, 139.75, 139.68, 139.14, 138.30, 132.01, 127.80, 126.11, 125.38, 125.07, 121.47, 120.67, 120.22, 119.17, 56.01, 55.31, 40.39, 37.31, 31.71, 31.54, 29.77, 29.74, 24.21, 23.90, 22.66, 22.49, 14.16, 14.07, -0.68.

T2Si, (AK352, ^1H only) MALDI-TOF MS: m/z 2995 ($[\text{M}-\text{C}_6\text{H}_{14}+\text{Na}]^+$), 2975 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). $\text{C}_{147}\text{H}_{210}\text{Si}_3$: C, 87.16; H, 10.08 %. Found: C, 87.40; H, 10.36%.

^1H NMR (500 MHz, δ , CDCl_3): 8.52 (1H, d, $^3J=8.5$ Hz), 7.88 (1H, d, $^3J=7.5$ Hz), 7.85 (1H, d, $^3J=8.0$ Hz), 7.84-7.76 (5H, m), 7.74 (1H, d, $^3J=7.5$ Hz), 7.72-7.63 (4H, m), 7.53 (1H, d, $^3J=8.0$ Hz), 7.51 (1H, s), 3.20-3.00 (2H, m), 2.35-1.95 (10H, m), 1.24-0.60 (66H, m), 0.34 (9H, s)

^{13}C NMR (CDCl_3 , δ , 101 MHz) 154.60, 152.02, 151.94, 151.88, 150.36, 145.36, 141.59, 140.83, 140.76, 140.48, 140.29, 140.21, 139.79, 139.70, 139.15, 138.34, 132.01, 127.81, 126.34, 126.25, 126.19, 125.41, 125.12, 121.71, 121.49, 120.70, 120.18, 120.13, 119.17, 56.04, 55.54, 55.28, 40.63, 40.30, 37.34, 31.73, 31.65, 31.52, 29.88, 29.74, 24.24, 24.04, 23.90, 22.74, 22.64, 22.50, 14.17, 14.09, -0.69.

T3Si, MALDI-TOF MS: m/z 3968 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{297}\text{H}_{402}\text{Si}_3$: C, 87.93; H, 9.99 %. Found: C, 87.95; H, 9.82%.

^1H NMR (500 MHz, δ , CDCl_3): 8.53 (1H, bd, $^3J=7.5$ Hz), 8.00-7.60 (18H, m), 7.53 (1H, d, $^3J=8.0$ Hz), 7.51 (1H, s), 3.25-2.95 (2H, m), 2.40-1.90 (14H, m), 1.25-0.55 (88H, m), 0.34 (9H, s)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.61, 152.02, 151.97, 151.87, 150.35, 145.36, 141.58, 140.80, 140.73, 140.69, 140.47, 140.29, 140.24, 140.21, 140.14, 139.79, 139.69, 139.14, 138.33, 132.00, 127.80, 126.32, 126.26, 126.18, 125.41, 125.13, 121.69, 121.49, 120.70, 120.16, 120.13, 119.16, 56.04, 55.54, 55.49, 55.26, 40.63, 40.53, 40.29, 37.34, 31.73, 31.65, 31.62, 31.51, 29.88, 29.83, 29.76, 29.73, 24.24, 24.02, 23.89, 22.75, 22.71, 22.64, 22.51, 14.18, 14.10, -0.69.

T4Si, MALDI-TOF MS: (AK368) m/z 5052 (M^+), 4967 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{372}\text{H}_{498}\text{Si}_3$: C, 88.40; H, 9.93 %. Found: C, 88.69; H, 9.93%.

^1H NMR (500 MHz, δ , CDCl_3): 8.54 (1H, bd, $^3J=6.5$ Hz), 8.00-7.60 (24H, m), 7.53 (1H, d, $^3J=8.0$ Hz), 7.51 (1H, s), 3.25-2.95 (2H, m), 2.40-1.90 (18H, m), 1.30-0.60 (110H, m), 0.34 (9H, s)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.61, 151.98, 151.86, 150.34, 145.37, 141.58, 140.72, 140.47, 140.28, 140.20, 139.80, 139.14, 138.34, 132.00, 127.79, 126.32, 126.18, 121.69, 121.49, 120.15, 119.16, 56.04, 55.55, 55.50, 55.26, 40.53, 40.29, 37.33, 31.73, 31.66, 31.62, 31.51, 29.88, 29.83, 29.76, 29.73, 24.02, 23.88, 22.75, 22.72, 22.64, 22.51, 14.19, -0.69.

General procedure for the synthesis of T1Br, T2Br, T3Br and T4Br. To a mixture of the corresponding trimethylsilyl substituted oligofluorene-truxene compound (**T1Si**, **T2Si**, **T3Si**, **T4Si**) (1 mol) and sodium acetate (3 mol), in THF (30-33 ml per gram of **TnSi**) at 0°C , was added bromine (7 mol) under protection from light and the reaction mixture stirred at this temperature for 30 min and quenched with triethylamine followed by addition of aqueous Na_2SO_3 . The product was extracted with CH_2Cl_2 , washed with NaHCO_3 and dried over MgSO_4 . After evaporation of the solvent the product was dissolved in toluene and passed through a plug of silica. Evaporation of toluene and re-precipitation from CH_2Cl_2 -methanol afforded the product as an off-white solid in quantitative yields.

T1Br, MALDI-TOF MS: m/z 2077 (M^+), 2014 ($[\text{M}-\text{C}_6\text{H}_{14}+\text{Na}]^+$), 1992 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{138}\text{H}_{183}\text{Br}_3$: C, 79.62; H, 8.86; Br 11.52%. Found: C, 79.63; H, 8.93; Br 12.30%.

^1H NMR (500 MHz, δ , CDCl_3): 8.51 (1H, d, $^3J=8.5$ Hz), 7.81 (1H, d, $^3J=7.5$ Hz), 7.80-7.75 (3H, m), 7.72 (1H, s), 7.63 (1H, d, $^3J=8.0$ Hz), 7.52 (1H, d, $^4J=1.5$ Hz), 7.51 (1H, d, $^3J=7.9$ Hz, $^4J=1.75$ Hz), 3.20-3.00 (2H, m), 2.34-2.18 (2H, m), 2.18-1.96 (4H, m), 1.24-0.86 (24H, m), 0.86-0.71 (10H, m), 0.71-0.58 (10H, m)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.58, 151.40, 150.31, 145.39, 140.76, 140.05, 139.85, 139.48, 138.28, 130.17, 126.37, 125.41, 125.09, 121.39, 121.24, 121.16, 120.67, 120.22, 56.02, 55.73, 40.54, 37.28, 31.68, 31.63, 29.82, 29.71, 24.19, 23.92, 22.74, 22.47, 14.15, 14.06.

T2Br, MALDI-TOF MS: m/z 3016 ($[\text{M}-\text{C}_6\text{H}_{14}+\text{Na}]^+$), 2994 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{213}\text{H}_{279}\text{Br}_3$: C, 83.08; H, 9.13. Found: C, 83.38; H, 9.14.

^1H NMR (400 MHz, δ , CDCl_3): 8.52 (1H, d, $^3J=8.0$ Hz), 7.95-7.55 (12H, m), 7.55-7.45 (2H, m), 3.20-3.00 (2H, m), 2.45-1.85 (10H, m), 1.26-0.50 (66H, m)

^{13}C NMR (CDCl_3 , δ , 101 MHz) 154.59, 153.43, 151.99, 151.29, 145.36, 141.21, 140.48, 140.37, 140.20, 140.01, 139.79, 139.66, 139.38, 138.32, 130.17, 126.45, 126.38, 126.27, 125.41, 125.11, 121.68, 121.62, 121.49, 121.23, 121.14, 120.70, 120.22, 120.17, 56.03, 55.70, 55.54, 40.60, 40.45, 37.33, 31.72, 31.62, 29.86, 29.78, 29.75, 24.23, 24.03, 23.91, 22.72, 22.50, 14.16, 14.09.

T3Br, MALDI-TOF MS: m/z 4076.26 (M^+). Anal. Calcd for $\text{C}_{288}\text{H}_{375}\text{Br}_3$: C, 84.85; H, 9.27; Br 5.88%. Found: C, 84.92; H, 9.41; Br 5.34%.

^1H NMR (500 MHz, δ , CDCl_3): 8.53 (1H, d, $^3J=7.5$ Hz), 7.95-7.55 (18H, m), 7.55-7.45 (2H, m), 3.20-3.00 (2H, m), 2.40-1.90 (14H, m), 1.26-0.50 (88H, m)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.60, 153.43, 152.01, 151.97, 151.28, 145.36, 141.20, 140.78, 140.69, 140.47, 140.32, 140.26, 140.11, 140.01, 139.79, 139.69, 139.38, 138.33, 130.16, 126.44, 126.34, 125.42, 125.11, 121.70, 121.61, 121.49, 121.23, 121.14, 120.69, 120.17, 56.04, 55.69, 55.54, 55.50, 40.63, 40.50, 40.44, 37.33, 31.73, 31.65, 31.61, 29.88, 29.81, 29.77, 24.24, 24.01, 23.90, 22.74, 22.71, 22.50, 14.17, 14.09.

T4Br, MALDI-TOF MS: m/z 5074 (M^+), 4987 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{363}\text{H}_{471}\text{Br}_3$: C, 85.92; H, 9.36; Br, 4.72%. Found: C, 85.95; H, 9.37; Br, 4.97%.

^1H NMR (500 MHz, δ , CDCl_3): 8.53 (1H, bd, $^3J=5.4$ Hz), 7.95-7.55 (24H, m), 7.55-7.45 (2H, m), 3.25-2.95 (2H, m), 2.45-1.85 (18H, m), 1.26-0.50 (110H, m)

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.61, 153.42, 151.98, 151.28, 145.37, 141.20, 140.72, 140.46, 140.31, 140.01, 139.68, 139.38, 138.33, 130.16, 126.34, 121.70, 121.61, 121.23, 121.13, 120.16, 56.04, 55.69, 55.55, 55.50, 40.51, 37.37, 31.73, 31.61, 29.88, 29.82, 29.78, 24.24, 24.02, 23.90, 22.75, 22.72, 22.51, 14.18, 14.10.

General procedure for the synthesis of SiF_2BTBr and $\text{F}_2\text{BTBr}-\text{Fl}_4\text{BTBr}$. A mixture of BTBr_2 (3-3.3 mol), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.22-0.24 mol), SiF_2BE (1 mol) and K_3PO_4 (1.7-1.8 mol) in DMF (30-40 mL per 1 g of BTBr_2) was degassed and stirred under nitrogen at 80 °C for 24 – 32 h. After aqueous work up the reaction mixture was subjected to column chromatography on silica gel eluting with CH_2Cl_2 : Petrol (3:7).

SiF_2BTBr , brown-orange oil. Yield: 90 %. MALDI-TOF MS: m/z 618.10 (M^+).

^1H NMR (CDCl_3 , δ , 400 MHz) 7.95 (1H, d, $^3J = 7.6$ Hz), 7.91 (1 H, dd, $^3J = 7.6$ Hz, $^4J = 1.6$ Hz), 7.88 (1H, s), 7.85 (1H, d, $^3J = 8$ Hz), 7.74 (1H, d, $^3J = 7.2$ Hz), 7.64 (1H, d, $^3J = 7.6$ Hz), 7.57-7.47 (2 H, m), 2.05-1.97 (4H, m), 1.18-1.02 (12 H, m), 0.76 (10H, t, $^3J = 6.8$ Hz), 0.33 (9H, s).

^{13}C NMR (CDCl_3 , δ , 101 MHz) 154.12, 153.50, 151.57, 150.60, 141.88, 141.20, 139.77, 135.46, 134.79, 132.44, 132.06, 128.21, 128.12, 127.81, 124.08, 120.04, 119.43, 112.81, 55.32, 40.18, 31.51, 29.73, 23.91, 22.63, 14.15, 0.73.

F₂BTBr, as a yellow solid. Yield: 74%. MALDI-TOF MS: m/z 878.40 (M^+). Anal. Calcd for $\text{C}_{56}\text{H}_{67}\text{BrN}_2\text{S}$: C, 76.42; H, 7.67; N, 3.18; Br, 9.08; S, 3.64%. Found: C, 76.36; H, 7.67; N, 3.07; Br, 8.71; S, 3.59%.

^1H NMR (CDCl_3 , δ , 500 MHz) 7.99- 7.82 (5H, m), 7.79 (1 H, d, $^3J = 8$ Hz), 7.75 (1 H, d, $^3J = 7.3$ Hz), 7.71-7.61(5H, m), 7.40-7.29 (3H, m), 2.20-1.80 (8H, m), 1.20-1.00 (24 H, m), 0.95-0.60 (20H, m).

^{13}C NMR (CDCl_3 , δ , 101 MHz) 154.12, 153.50, 152.22, 151.65, 151.14, 141.59, 141.16, 140.88, 140.56, 140.50, 139.74, 135.32, 134.74, 132.45, 128.35, 128.11, 127.17, 126.94, 126.40, 126.20, 124.05, 123.06, 121.68, 121.58, 120.42, 120.05, 120.00, 119.88, 112.82, 55.53, 55.31, 40.52, 40.40, 31.61, 29.83, 24.02, 23.91, 22.71, 14.17.

F₃BTBr, as a yellow solid. Yield: 79%. MALDI-TOF MS: m/z 1210 (M^+). Anal. Calcd for $\text{C}_{81}\text{H}_{99}\text{BrN}_2\text{S}$: C, 80.23; H, 8.23; N, 2.31; Br, 6.59; S, 2.64%. Found: C, 80.18; H, 7.79; N, 2.41; Br, 6.11; S, 3.01%.

^1H NMR (CDCl_3 , δ , 500 MHz) 7.99- 7.93 (2H, m), 7.93-7.87 (2 H, m), 7.87-7.77 (4 H, m), 7.75 (1H, d, $^3J = 7.5$ Hz), 7.73-7.60 (9H, m), 7.40-7.29 (3H, m), 2.19-1.97 (12 H, m), 1.25-1.00 (36H, m), 0.96-0.65 (30 H, m).

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.15, 153.53, 152.26, 151.97, 151.93, 151.67, 151.63, 151.16, 141.61, 141.18, 140.94, 140.76, 140.64, 140.54, 140.49, 140.28, 140.08, 139.79, 135.36, 134.78, 132.46, 128.37, 128.11, 127.14, 126.94, 126.42, 126.32, 126.18, 124.09, 123.08, 121.71, 121.68, 121.59, 120.44, 120.12, 120.03, 119.86, 112.86, 55.56, 55.48, 55.32, 40.52, 40.42, 31.62, 29.84, 29.81, 24.05, 23.99, 23.93, 22.70, 14.16.

F₄BTBr, as a yellow solid. Yield: 84%. MALDI-TOF MS: m/z 1543 (M^+). Anal. Calcd for $\text{C}_{106}\text{H}_{131}\text{BrN}_2\text{S}$: C, 82.40; H, 8.55; N, 1.81; Br, 5.17; S, 2.08%. Found: C, 82.46; H, 8.64; N, 1.81; Br, 4.95; S, 2.17%.

^1H NMR (CDCl_3 , δ , 400 MHz) 8.00-7.61 (24H, m), 7.40-7.29 (3 H, m), 2.20-1.95 (16 H, m), 1.25-1.00 (48H, m), 0.95-0.65 (40 H, m).

^{13}C NMR (CDCl_3 , δ , 101 MHz) 154.02, 153.40, 152.13, 151.83, 151.55, 151.50, 151.03, 141.48, 141.04, 140.81, 140.58, 140.51, 140.42, 140.35, 140.15, 140.06, 139.99, 139.67, 135.23, 134.64, 132.34, 128.24, 127.99, 127.01, 126.81, 126.30, 126.18, 126.05, 123.96, 122.95, 121.54, 120.32, 119.99, 119.90, 119.74, 112.73, 55.43, 55.36, 55.19, 40.39, 40.30, 31.49, 29.72, 29.69, 23.93, 23.87, 23.80, 22.58, 14.05.

General procedure for protolytic desilylation of SiF_2BTBr , $\text{SiF}_2\text{Br-SiF}_3\text{Br}$.

To solution of the corresponding trimethylsilylated compound in CH_2Cl_2 (17-100 mL per 1 g of the compound) trifluoroacetic acid (1/10 of CH_2Cl_2 volume) was added, and the mixture stirred for

another 2 h. Aqueous work up afforded the pure compound in 92 % for compound **F₁BTBr** and in quantitative yield for compounds **F₂Br-F₃Br**¹.

F₁BTBr, brown-orange oil, MALDI-TOF MS: *m/z* 618.10 (M⁺).

¹H NMR (CDCl₃, δ, 400 MHz) 7.95 (1H, d, ³J = 7.6 Hz), 7.91 (1H, d, ³J = 7.6 Hz, ⁴J = 1.6 Hz), 7.88 (1H, d, ⁴J = 1.2 Hz), 7.84 (1H, d, ³J = 8 Hz), 7.80-7.74 (1H, m), 7.65 (1H, d, ³J = 7.6 Hz), 7.41-7.30 (3H, m), 2.15-1.9 (4H, m), 1.2-1.0 (12H, m), 0.90-0.60 (10H, m).

¹³C NMR (CDCl₃, δ, 101 MHz) 154.08, 153.46, 151.41, 151.32, 141.87, 140.58, 135.32, 134.73, 132.40, 128.22, 128.07, 127.57, 127.02, 123.97, 123.10, 120.15, 119.91, 112.78, 55.36, 40.41, 31.60, 29.83, 23.94, 22.69, 14.15.

General procedure for converting of **Fl₁BTBr – Fl₃BTBr** to **Fl₁BTBE – Fl₃BTBE**

A mixture of **Fl_nBTBr** (1 mol), [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium (0.03-0.10 mol), bis(pinacolato)diboron (1.3-1.4 mol), potassium acetate (3.7-3.9 mol) in dioxane (15-16 mL per 1 g of **Fl_nBTBr**) was stirred at 105°C for 21 h. After cooling and aqueous work up the crude product was subjected to column chromatography on silica gel, using as eluent ethyl acetate : hexane mixture first in a ration of 1:10 and then 1:5.

Fl₁BTBE (brownish-yellow tarry solid). Yield 81%. MALDI-TOF MS: *m/z* 594.3 (M⁺). Anal. Calcd for C₃₇H₄₇BN₂O₂S: C, 74.73; H, 7.97; N, 4.71; S 5.39 %. Found: C, 74.37; H, 7.74; N, 4.86; S, 5.12%.

¹H NMR (CDCl₃, δ, 400 MHz) 8.28 (1H, d, ³J = 7.2), 7.97 (1H, dd, ³J = 8 Hz, ⁴J = 1.6 Hz), 7.93 (1H, d, ⁴J = 1.2 Hz), 7.84 (1H, d, ³J = 8 Hz), 7.80-7.54 (1H, m), 7.76(1H, d, ³J = 7.2 Hz), 7.45-7.30 (3H, m), 2.11-1.94 (4H, m), 1.47 (12H, s), 1.18-1.02 (12H, m), 0.84-0.68 (4H, m), 0.76 (6H, t, ³J = 7).

¹³C NMR (CDCl₃, δ, 101 MHz) 158.42, 153.60, 151.50, 151.18, 141.81, 140.69, 139.30, 137.99, 136.09, 128.48, 127.48, 126.95, 124.23, 123.10, 120.13, 119.79, 84.43, 55.35, 40.37, 31.59, 29.83, 25.06, 23.94, 22.69, 14.15.

Fl₂BTBE (yellow solid). Yield 85%. MALDI-TOF MS: *m/z* 926 (M⁺). Anal. Calcd for C₆₂H₇₉BN₂O₂S: C, 80.31; H, 8.59; N, 3.02; S, 3.46%. Found: C, 80.54; H, 8.53; N, 3.06; S, 3.54%.

¹H NMR (CDCl₃, δ, 500 MHz) 8.29 (1H, d, ³J = 8.3), 8.00 (1H, dd, ³J = 7.8, ⁴J = 1.5), 7.97 (1H, d, ⁴J = 1.5), 7.88 (1H, d, ³J = 7.8 Hz), 7.84 (1H, d, ³J = 7.8 Hz), 7.82-7.77 (2H, m), 7.74 (1H, d, ³J = 7.1 Hz), 7.72-7.60 (4H, m), 7.42-7.28 (3H, m), 2.19-1.97 (8H, m), 1.48 (12H, s), 1.20-1.03 (24H, m), 0.92-0.66 (20H, m).

¹³C NMR (CDCl₃, δ, 126 MHz) 158.46, 153.64, 152.32, 151.62, 151.52, 151.16, 141.53, 141.08, 140.93, 140.59, 140.54, 139.87, 139.31, 137.99, 136.11, 128.60, 127.14, 126.94, 126.36, 126.21, 124.35, 123.07, 121.70, 121.61, 120.39, 120.03, 119.87, 84.46, 55.53, 55.32, 40.52, 40.36, 31.60, 29.83, 25.08, 24.04, 23.92, 22.70, 14.15.

Fl₃BTBE (yellow solid). Yield 75%. MALDI-TOF MS: *m/z* 1258 (M⁺). Anal. Calcd for C₈₇H₁₁₁BN₂O₂S: C, 82.95; H, 8.88; N, 2.22; S, 2.55%. Found: C, 82.77; H, 8.92; N, 2.15; S, 2.35%.

^1H NMR (CDCl_3 , δ , 500 MHz) 8.29 (1H, d, $^3J = 7$), 8.01 (1H, dd, $^3J = 7.8$, $^4J = 1.5$), 7.98 (1H, s), 7.89 (1H, d, $^3J = 7.8$), 7.88-7.77 (5H, m), 7.75 (1H, d, $^3J = 7.4$ Hz), 7.72-7.61 (8H, m), 7.40-7.29 (3H, m), 2.20-1.90 (12H, m), 1.48 (12H, s), 1.20-1.04 (36H, m), 0.93-0.67 (30H, m).

^{13}C NMR (CDCl_3 , δ , 126 MHz) 158.47, 153.64, 152.34, 151.94, 151.62, 151.53, 151.16, 141.53, 141.07, 140.95, 140.72, 140.65, 140.60, 140.48, 140.23, 140.11, 139.91, 139.31, 137.99, 136.13, 128.62, 127.13, 126.96, 126.94, 126.37, 126.33, 126.30, 126.18, 124.36, 123.07, 121.70, 121.58, 120.42, 120.11, 120.03, 119.86, 84.46, 55.54, 55.47, 55.32, 40.52, 40.38, 31.60, 29.84, 29.80, 25.09, 24.05, 23.99, 23.93, 22.70, 14.16.

T4BT-A. To a solution of **F4BTBr** (470 mg, 304 μmol) and $(\text{Ph}_3\text{P})_4\text{Pd}$ (18 mg) in a mixture of 5 mL of THF and 10 mL of DME* **TrBE** (77.9 mg, 73.7 μmol) has been added, followed by $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (136 mg) and H_2O (0.28 mL). The mixture was stirred at 80°C for 41 h. Aqueous work up afforded 546 mg of the crude mixture. After two columns on silica using as eluents CH_2Cl_2 :Petrole 3:7 and CH_2Cl_2 :Petrole 1:4 respectively, excess of **F4BTBr** (177 mg, 71.4%) was recovered and **T4BT-A** isolated as a bright yellow solid with a yield of 251 mg, 65 %.

MALDI-TOF MS: m/z 5241 ($[\text{M}+\text{H}]^+$), 5158 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{381}\text{H}_{480}\text{N}_6\text{S}_3$: C, 87.33; H, 9.23; N, 1.60; S 1.84 %. Found: C, 87.05; H, 9.04; 1.89; 2.13%.

^1H NMR (CDCl_3 , δ , 500 MHz) 8.7–8.55 (1H, d, broad), 8.30–8.16 (2 H, m), 8.14–8.04 (3H, m), 8.03–7.94 (2H, m), 7.93–7.79 (6H, m), 7.78–7.60 (13H, m), 7.44–7.30 (3H, m), 3.40–2.90 (2H, m), 2.50–1.90 (18H, m), 1.34–0.62 (110H, m).

^{13}C NMR (CDCl_3 , δ , 126 MHz) 154.69, 154.55, 152.32, 151.97, 151.63, 151.17, 146.23, 141.24, 140.96, 140.73, 140.66, 140.49, 140.19, 140.04, 138.38, 136.37, 135.67, 133.84, 133.37, 128.46, 128.14, 127.14, 126.94, 126.32, 126.19, 124.22, 123.08, 121.69, 121.60, 120.40, 120.14, 120.04, 119.87, 56.18, 55.57, 55.49, 55.33, 40.52, 31.78, 31.67, 31.63, 29.92, 29.83, 24.34, 24.13, 24.01, 23.94, 22.76, 22.71, 22.56, 14.21, 14.17.

*Using THF as a sole solvent requires more time (64 h) for the reaction to be completed.

General procedure for the synthesis of **T4BT-B** - **T4BT-E**.

A mixture of tribromoligofluoreneotruxene core compound (**T1Br-T3Br**, **T4Br**)(1 mol), $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.33-0.58 equiv), boronic ester (**F₃BTBE-F₁BTBE**, **BTBE²**)(5.1-5.7 mol), $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (14-17 mol) in DME (70-90 mL per g of **TnBr**) and water (3-5 % v/v) was stirred for 24 h at 80°C . After aqueous work-up the crude product was subjected to column chromatography on silica gel, eluting with DCM :Petrol 1:3 for **T4BT-B**, DCM :Petrol 2:7 for **T4BT-C**, DCM :Toluene:Petrol 1:3:7 for **T4BT-D**, DCM :Hex 1:2 for **T4BT-E**.

T4BT-B: Yield 82.4%. MALDI-TOF MS: m/z 5155 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$). Anal. Calcd for $\text{C}_{381}\text{H}_{480}\text{N}_6\text{S}_3$: C, 87.33; H, 9.23; N, 1.60; S 1.84 %. Found: C, 87.10; H, 9.17; N, 1.64; S, 2.04%.

^1H NMR (CDCl_3 , δ , 400 MHz) 8.60-8.48 (1H, d, broad), 8.15-8.01 (4H, m), 8.00-7.60 (22H, m), 7.43-7.29 (3H, m), 3.20-3.02 (2H, s, broad), 2.38-2.08 (18H, m), 1.30-0.60 (110H, m).

¹³C NMR (CDCl₃, δ, 101 MHz) 154.56, 152.34, 151.95, 151.59, 151.15, 141.19, 140.97, 140.70, 140.59, 140.47, 140.22, 140.10, 140.00, 139.61, 136.35, 133.78, 128.42, 128.09, 126.93, 126.32, 126.17, 123.07, 56.03, 55.58, 55.53, 55.47, 55.31, 40.52, 31.74, 31.69, 31.66, 31.62, 29.95, 29.90, 29.84, 29.82, 29.76, 24.10, 23.98, 23.92, 22.79, 22.76, 22.72, 22.51, 14.22, 14.18, 14.12.

T4BT-C: Yield 84.2%. MALDI-TOF MS: *m/z* 5243 ([M+H]⁺), 5278 ([M+Na]⁺), 5157([M-C₆H₁₃]⁺). Anal. Calcd for C₃₈₁H₄₈₀N₆S₃: C, 87.33; H, 9.23; N, 1.60; S 1.84 %. Found: C, 87.34; H, 9.20; N, 1.54; S, 1.76%.

¹H NMR (CDCl₃, δ, 500 MHz) 8.59-8.48 (1H, s, broad), 8.12-8.00 (4H, m), 8.00-7.58 (22H, m), 7.42-7.28 (3H, m), 3.20-3.00 (2H, s, broad), 2.40-1.90 (18H, m), 1.30-0.60 (110H, m).

¹³C NMR (CDCl₃, δ, 126 MHz) 154.58, 152.28, 152.03, 151.60, 151.18, 141.21, 141.02, 140.95, 140.62, 140.54, 140.30, 139.99, 139.68, 136.34, 133.79, 128.42, 128.07, 127.16, 126.95, 126.39, 126.22, 124.19, 123.08, 121.73, 121.62, 120.36, 120.20, 120.05, 119.96, 199.88, 56.04, 55.55, 55.34, 40.65, 40.54, 40.48, 31.73, 31.66, 29.89, 29.86, 29.76, 24.11, 23.94, 22.75, 22.51, 14.20, 14.16, 14.10.

T4BT-D: Yield 70.4%. MALDI-TOF MS: *m/z* 5241 ([M+H]⁺), 5157([M-C₆H₁₃]⁺). Anal. Calcd for C₃₈₁H₄₈₀N₆S₃: C, 87.33; H, 9.23; N, 1.60; S 1.84 %. Found: C, 87.27; H, 9.32; N, 1.56; S, 1.66%.

¹H NMR (CDCl₃, δ, 400 MHz) 8.65-8.45 (1H, s, broad), 8.15-7.62 (26H, m), 7.45 7.30 (3H, m), 3.30-2.90 (2H, m), 2.40-1.90 (18H, m), 1.30-0.60 (110H, m).

¹³C NMR (CDCl₃, δ, 101 MHz) 154.54, 152.30, 151.98, 151.59, 151.48, 151.27, 141.50, 141.17, 140.97, 140.81, 140.72, 140.23, 140.03, 139.66, 136.33, 133.80, 133.74, 128.41, 128.29, 128.06, 127.42, 127.00, 126.34, 124.17, 124.08, 123.11, 121.71, 121.48, 120.37, 120.16, 120.11, 119.95, 119.86, 55.54, 55.50, 55.37, 40.48, 31.73, 31.66, 29.90, 29.84, 29.76, 24.10, 24.02, 22.78, 22.75, 22.51, 14.20, 14.10.

T4BT-E: Yield 79%. MALDI-TOF MS: *m/z* 5244 ([M+H]⁺), 5159([M-C₆H₁₃]⁺). Anal. Calcd for C₃₈₁H₄₈₀N₆S₃: C, 87.33; H, 9.23; N, 1.60; S 1.84 %. Found: C, 86.99; H, 9.36; N, 1.55; S 1.75%.

¹H NMR (CDCl₃, δ, 500 MHz) 8.60-8.45 (1H, d, broad), 8.05-7.62 (29H, m), 3.20-3.00 (2H, m), 2.40-1.90 (18H, m), 1.25-0.76 (100H, m), 0.76-0.62 (10H, m).

¹³C NMR (CDCl₃, δ, 126 MHz) 155.91, 154.60, 153.88, 152.26, 151.98, 151.56, 145.36, 141.27, 141.01, 140.71, 140.64, 140.24, 140.19, 139.98, 139.79, 138.33, 136.16, 135.30, 129.84, 128.45, 127.59, 126.33, 124.17, 121.70, 121.49, 120.38, 120.15, 119.91, 56.04, 55.54, 55.50, 40.52, 40.46, 37.33, 31.73, 31.63, 29.88, 29.83, 29.76, 24.24, 24.02, 22.72, 22.51, 14.18.

¹The syntheses of SiF1B, SiF2B, SiF2Br, F2Br, F3Br, F4Br by different methods reported elsewhere:

- Tavasli, M.; Bettington, S.; Bryce, M. R.; Al Attar, H. A.; Dias, F. B.; King, S.; Monkman, A. P. *J. Mater. Chem.* **2005**, *15*, 4963.

- Kanibolotsky, A. L.; Berridge, R; Skabara, P. J.; Perepichka, I. F.; Bradley, D. D. C.; Koeberg, M. *J. Am. Chem. Soc.* **2004**, *126*, 13695.

²The synthesis of BTBE reported elsewhere:

- Anant, P.; Lucas, N.T.; Jacob, J. *Org. Lett.* **2008**, *10*, 5533.

Thermal Analyses

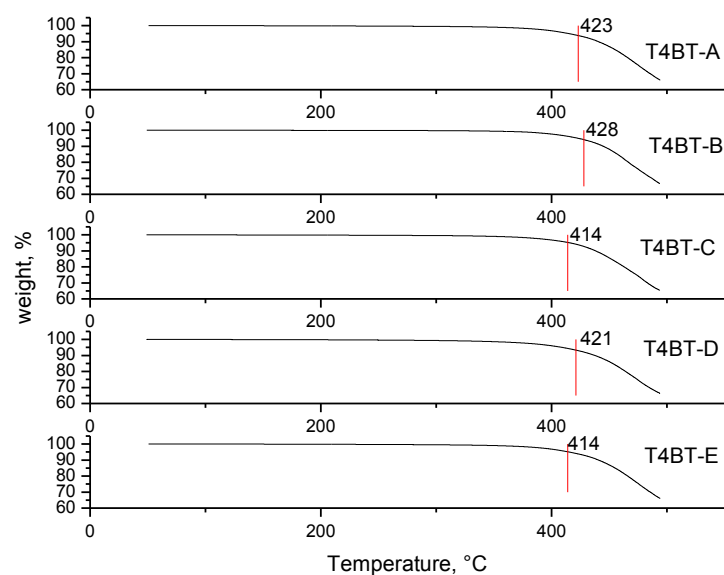


Figure S1-Thermogravimetric analysis of the truxene-oligofluorene-BT series.

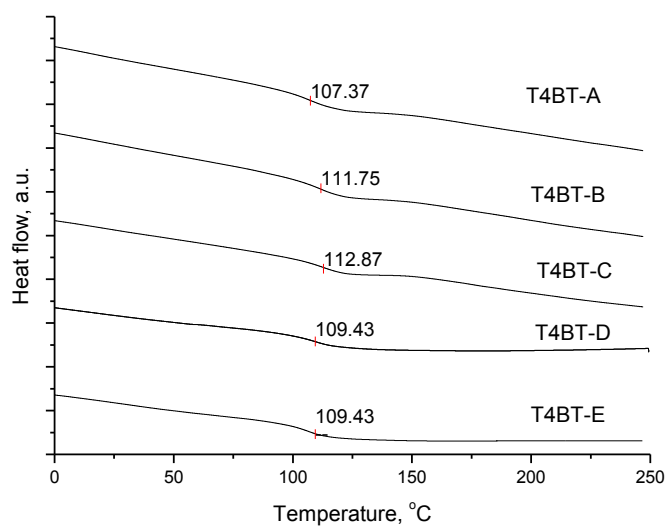


Figure S2 - DSC analysis of the truxene-oligofluorene-BT series.

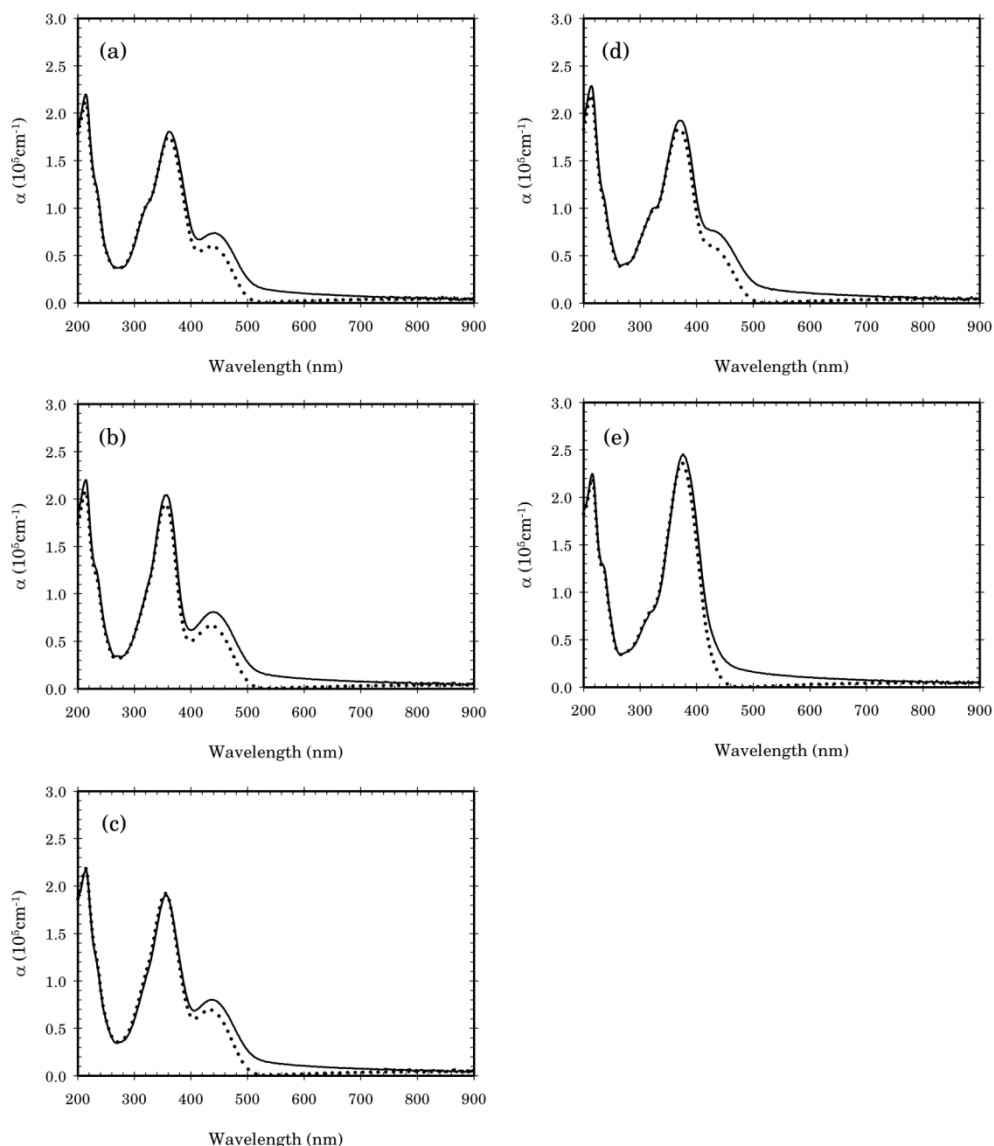


Fig. S3. Absorption spectra for (a) T4BT-A, (b) T4BT-B, (c) T4BT-C, (d) T4BT-D and (e) T4BT-E. For each material the spectra were recorded for 50 ± 5 nm films (solid lines) and 120 ± 10 nm films (dotted lines).

Absorption Spectra with Peak Fitting

Absorption spectra were measured for thin film samples of T4BT-A, -B, -C, -D and -E on quartz substrates using a Shimadzu UV2550 spectrophotometer. For all data, a clean quartz substrate was used as reference, to remove the contribution to the signal caused by reflections at the air quartz interface. After the absorption was measured the thin films were scored using a blunt metal edge and the film thickness was measured using a Tencor Alphastep 200. The absorption coefficient at each wavelength $\alpha(\lambda)$ was then extracted using the relation $\alpha(\lambda) = A \ln(10)/d$ where A was the measured absorbance and d the film thickness. The results obtained are shown in figure S3 for T4BT-A, -B, -C, -D, and -E for thin films of 50 ± 5 nm (solid lines) and 120 ± 10 nm films (dotted lines). The absorption spectra extracted from the two different film thicknesses are consistent within the estimated experimental error ($\sim 10\%$). We note that there is some variation in the magnitude

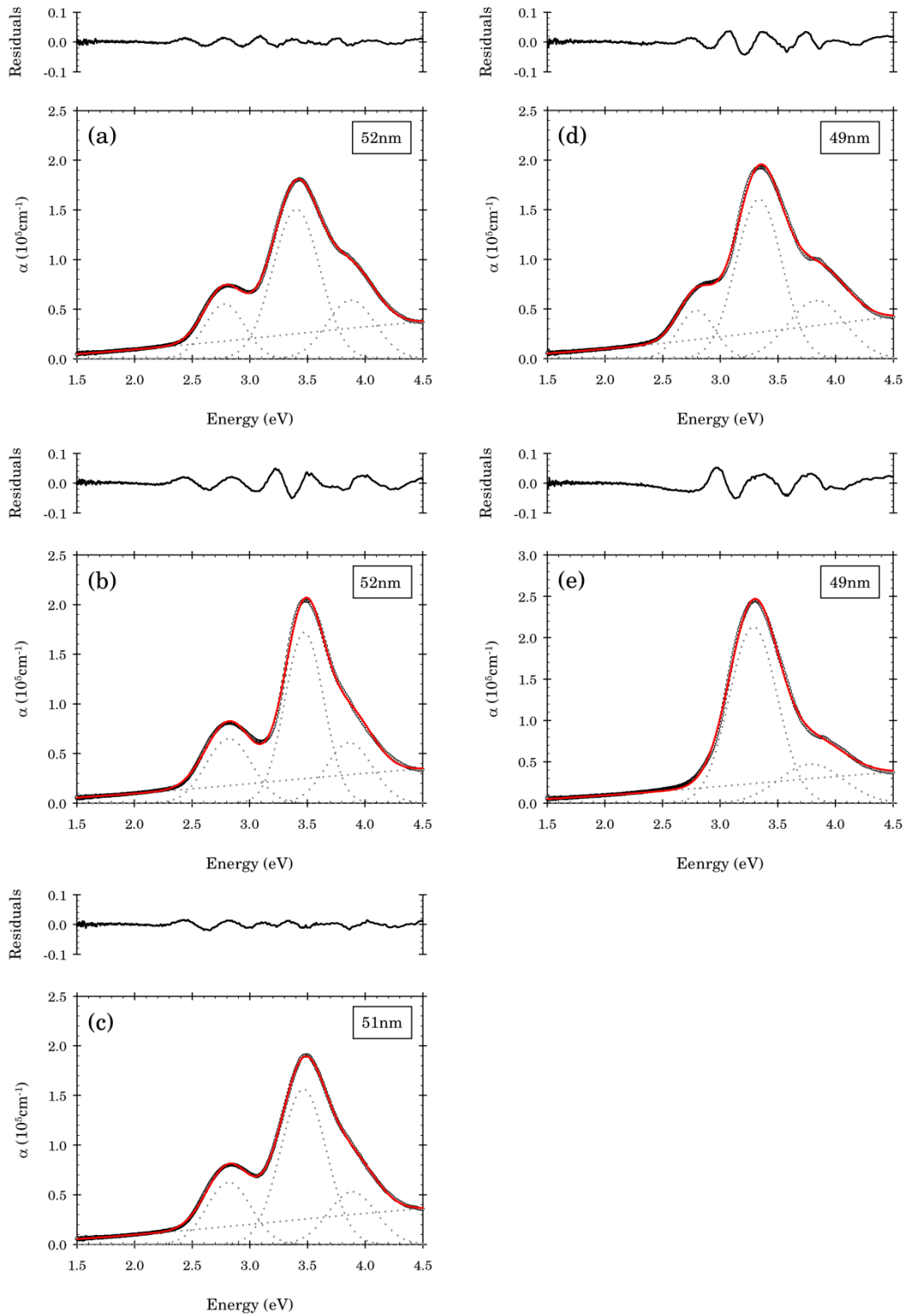


Fig. S4. Results from peak fitting (Gaussian functions) to the absorption spectra of 50 ± 5 nm films for (a) T4BT-A, (b) T4BT-B, (c) T4BT-C, (d) T4BT-D and (e) T4BT-E. The experimental data (empty circles) are fitted to a combination of Gaussian peaks (red line), with each individual contributing Gaussian shown by dotted lines. The residual from each fit is shown above each spectrum black line. In the case of (e) when we attempted to model the data with a transition III (i.e. Placing a peak with an initial transition energy at 2.8 eV) the peak either tended towards unphysical

negative values or moved to considerably lower energies during the regression without any significant improvement in R^2 .

of the absorption at ~440nm for the 50 nm and 120 nm film thicknesses, as well as a clear difference in the long wavelength absorption tail. We attribute this to thin film reflectivity effects.

As discussed in the main text, the absorption spectra are composed of a number of transitions (most notably transitions II and III) whose variation with isomer structure needs to be monitored. In order to extract information regarding the transition energy and absorption strength, the data were modelled using the following equation:-

$$\alpha_{model}(E) = A_0 + \sum_{i=1}^k A_i e^{-\frac{(E_i-E)^2}{2\sigma_i^2}}$$

Eqn. S1

Table S1. Results of the fitting procedure for 50 ± 5 nm films. The parameters A_0 , A_i , E_i and σ_i for $k = 4$ are obtained by fitting equation S1 to the data. The uncertainties provided are the standard deviations returned by a Levenberg-Marquardt non-linear least squares fitting routine. The R^2 fitting coefficients are also provided. The parameters corresponding to Transition II (grey shading) and Transition III (red shading) discussed in the main text are highlighted

	T4BT-A	T4BT-B	T4BT-C	T4BT-D	T4BT-E
A_0	-8836 ± 572	-7041 ± 861	-7810 ± 571	-6495 ± 407	-6707 ± 452
A_1	53703 ± 543	48355 ± 677	50865 ± 462	57724 ± 386	51988 ± 391
E_1	6 ± 0	6 ± 0	6 ± 0	6 ± 0	6 ± 0
s_1	2.72 ± 0.04	2.75 ± 0.05	2.74 ± 0.04	2.52 ± 0.02	2.62 ± 0.03
A_2	59080 ± 403	60967 ± 1515	52939 ± 756	58547 ± 532	47180 ± 683
E_2	3.878 ± 0.003	3.865 ± 0.007	3.888 ± 0.005	3.837 ± 0.006	3.79 ± 0.01
s_2	0.209 ± 0.002	0.201 ± 0.003	0.209 ± 0.003	0.249 ± 0.004	0.28 ± 0.01
A_3	150652 ± 383	172030 ± 261	156269 ± 809	160716 ± 882	213207 ± 1566
E_3	3.403 ± 0.001	3.475 ± 0.001	3.465 ± 0.002	3.335 ± 0.001	3.289 ± 0.002
s_3	0.204 ± 0.001	0.169 ± 0.002	0.199 ± 0.001	0.199 ± 0.001	0.208 ± 0.001
A_4	55106 ± 121	64911 ± 252	62345 ± 114	48521 ± 255	0 ± 0
E_4	2.781 ± 0.001	2.821 ± 0.002	2.818 ± 0.001	2.795 ± 0.002	0 ± 0
s_4	0.173 ± 0.001	0.199 ± 0.001	0.192 ± 0.001	0.158 ± 0.001	0 ± 0
R^2	0.9998	0.9993	0.9998	0.9995	0.9993
S_{II} [10^4 eV/cm]	7.7 ± 0.1	7.3 ± 0.1	7.8 ± 0.1	8.0 ± 0.1	11.1 ± 0.1
S_{III} [10^4 eV/cm]	2.39 ± 0.01	3.24 ± 0.03	3.01 ± 0.02	1.92 ± 0.03	0 ± 0

where $\alpha_{model}(E)$ represents the model to be fit to the data, A_0 is the magnitude of a constant background function. In addition, the function is then made up of k Gaussian peaks for $i = 1$ to k of amplitude A_i set at centre energies E_i (these parameters are then converted to wavelength so that parameters λ_{II} and λ_{III} can be reported in Table 1 of main text) and with width σ_i . The results of this fitting procedure are plotted in Figure S4 and tabulated in Table S1. Transition II corresponds to $i = 3$ (Table S1 grey shaded rows) and transition III to $i = 4$ (Table S1 pink shaded rows). All other oscillator peaks were included in order to model the background due to reflection and/or higher energy peaks. We note that we are able to obtain good fits to all data sets ($R^2 > 0.999$ in all cases). In the case of T4BT-E, we are unable to fit a physically meaningful transition III peak to the data.

The purpose of the fitting procedure was to obtain experimentally determined parameters that could be compared with the values of the oscillator strength calculated using Density Functional Theory. Oscillator strengths can be calculated from absorption spectra provided the number density of absorbing species is known. This parameter is not known for our materials and so instead of extracting oscillator strengths we determine for a given inhomogeneously broadened transition, i , the absorption integral

$$S_i = \int_{-\infty}^{\infty} \alpha_i(E) dE = A_i \sigma_i \sqrt{2\pi} \quad \text{Eqn. S2}$$

This expression allows us to use the values obtained from the regression of the model (Eqn, S1) to extract values of S_i for each absorption transition. These absorption integrals for Transition II and III are summarised in Table S1 for each member of the T4BT series. Provided that the molecular packing density of all our materials is approximately the same, then the experimentally determined S parameter values may be qualitatively compared with the calculated oscillator strength, f , for each transition. Such a comparison is shown below, where we consider the case of transitions II (figure S5 (a)) and III (figure S5(b)). Here we observe that the trend seen for the absorption integrals of the Gaussians fitted to the experimental data is reproduced by the DFT calculations of the oscillator strength. For transition II the strength of the transition is largely the same for samples T4BT-A to -D, while a significant increase is both predicted by the modelling (empty diamonds) and observed (to

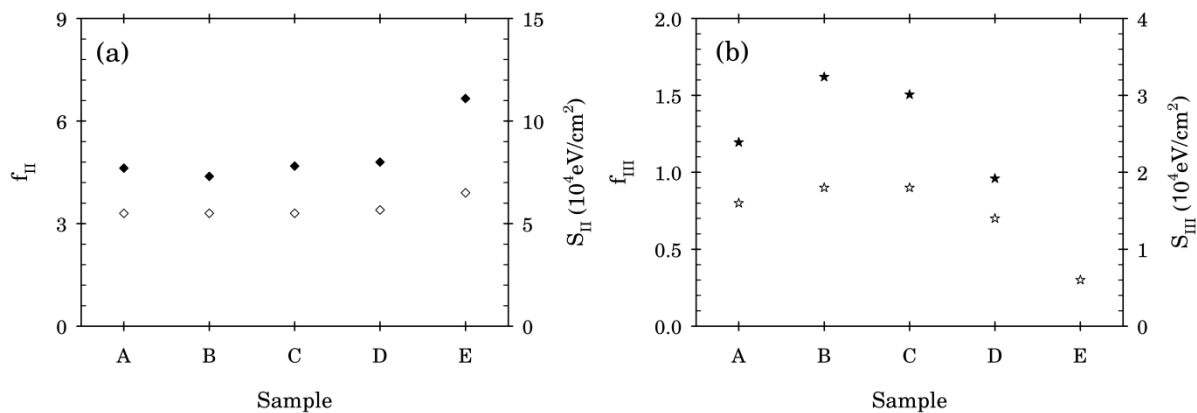


Figure S5. Comparison between DFT calculated oscillator strengths, f (left abscissae, open symbols), and experimentally derived absorption integrals S (right abscissae, filled symbols) for transition II (panel (a)) and transition III (panel (b)).

an even greater degree) in the experimentally derived data (filled diamonds) for the T4BT-E sample. We note however that the relative increase in the absorption integral for the experimental data is greater than that predicted by the calculations of the oscillator strength (see figure S5 (a)).

For transition III the predicted oscillator strength (empty stars) is slightly lower for the T4BT-A and -D pair ($f \cong 0.7$) while it increases slightly for the T4BT-B and -C pair ($f \cong 0.8$). The anomalous T4BT-E sample is then predicted to display significantly reduced oscillator strength ($f \cong 0.3$) and this trend is again observed in the experimental data (filled stars), although as discussed previously we are unable to resolve this peak at all experimentally. It may well be that for T4BT-E the absorption transition III strongly overlaps with transition II and this may explain why the experimentally observed increase in absorption integral is larger than predicted by the oscillator strength calculations for this transition.

Refractive Index Measurements (Kramers-Kronig Analysis)

We determine the refractive index of the T4BT family using the approach of Stavrinou *et al* (Stavrinou, P. N.; Ryu, G.; Campoy-Quiles, M.; Bradley, D. D. C. *J. Phys.: Condens. Matter* **2007**, *19*, 466107). This involves a semi-empirical calculation, where changes in the refractive index $\Delta n(\omega)$ due to the introduction of a BT unit are treated as a perturbation to that of the parent truxene (T4). This means that the refractive index of materials from the T4BT-X family may be evaluated as $n_{T4BT-X}(\omega) = n_{T4}(\omega) + \Delta n(\omega)$. Assuming that all significant changes in absorption are spectrally localised and occur in the vicinity of the main T4 absorption peaks it is then possible to relate changes in the absorption $\Delta\alpha(\omega) = \alpha_{T4BT-X}(\omega) - \alpha_{T4}(\omega)$ to changes in the refractive index using a Kramers-Kronig relation so that

$$\Delta n(\omega) = \frac{c}{\pi} \wp \int_{\omega_a}^{\omega_b} \frac{\Delta\alpha(\omega')}{(\omega')^2 - \omega^2} d\omega' \quad \text{Eqn. S3}$$

where c is the speed of light and $\wp$ indicates that the principal value of the integral is evaluated. The localised nature of this approach is reflected by the appearance of the integral limits ω_a and ω_b . It is then a straightforward exercise to evaluate the refractive index from the original T4 data and $\Delta n(\omega)$ evaluated from equation S3. The results from applying this approach to the T4BT-X family using refractive index data for T4 obtained from Tsiminis *et al* (Tsiminis, G.; Wang, Y.; Shaw, P. E.; Kanibolotsky, A. L.; Perepichka, I. F.; Dawson, M. D.; Skabara, P. J.; Turnbull, G. A.; Samuel, I. D. W. *Appl. Phys. Lett.* **2009**, *94*, 243304) are outlined in figure S6. It is of particular importance to check that all significant changes of absorption are accounted for between the limits ω_a and ω_b and that differences in thin film reflectivity do not adversely affect the evaluation of the Kramers-Kronig integral. With this in mind we chose to use thin films of 50 ± 5 nm for T4BT-X and T4 to evaluate $\Delta\alpha(\omega)$. An example is shown in figure S6(a) for T4BT-A. This shows that effects due to the thin film reflectivity (see data > 540 nm) are minimal and that the absorption data converge at short wavelengths, indicating the validity of applying our approach. While we note that this approach assumes that there are no changes of absorption outside the region of interest, it can be seen that for frequencies away from the region of interest that the change $\Delta n(\omega)$ rapidly declines and typically falls off as $1/\Delta\omega$, with the difference in optical frequency. The resultant refractive index spectra are shown for T4BT-A, -B, -C, -D and -E in figure S6 (b)-(f) (solid lines) along with the original refractive index data from Tsiminis *et al* for T4. We note that in general the index is increased for the long wavelength spectral region as might be expected due to the proximity of the longer wavelength transition III.

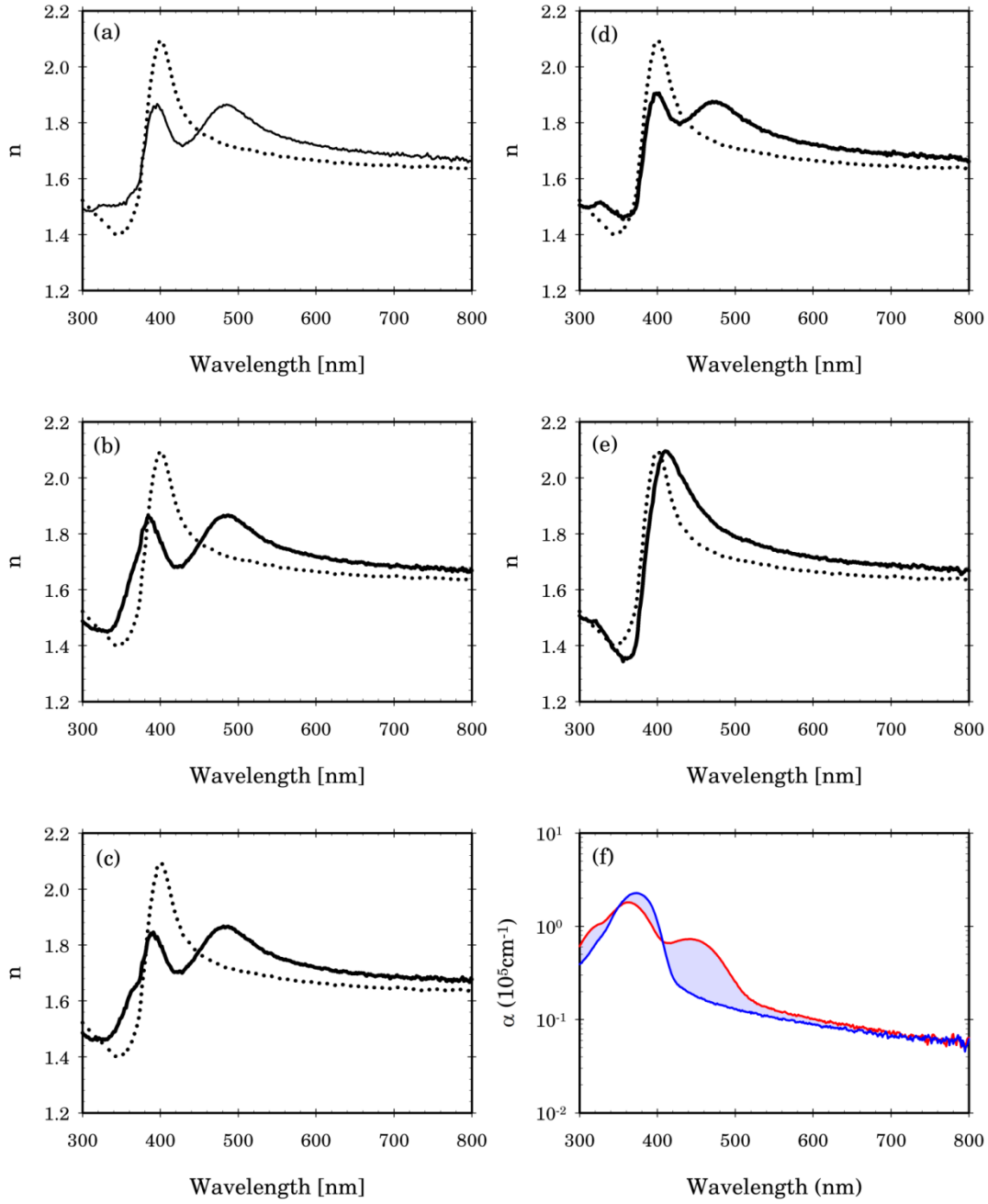


Figure S6. Refractive index, $n_{T4BT-X}(\omega)$ (black line), data for (a) T4BT-A, (b) T4BT-B, (c) T4BT-C, (d) T4BT-D and (e) T4BT-E together with the $n_{T4}(\omega)$ reference index (dotted line). In (f) we show the change in absorption $\Delta\alpha(\omega) = \alpha_{T4}(\omega) - \alpha_{T4BT-A}(\omega)$ (shaded area) between the material under study (red line), here T4BT-A, and T4 (blue line). The Kramers-Kronig integral (see text) was used to determine $\Delta n(\omega)$ from $\Delta\alpha(\omega)$ and hence $n_{T4BT-X}(\omega) = n_{T4}(\omega) + \Delta n(\omega)$ was calculated.

Raman Spectra with Peak Fitting

The T4BT-X Raman spectra were subjected to a multi-peak fitting procedure in order to extract the peak frequencies and intensities. The spectra were fit across two spectral windows (a) 1300 - 1400 cm^{-1} and (b) 1500 - 1700 cm^{-1} , using respectively $k = 5$ and $k = 3$ Gaussian peaks according to:

$$R_{model}(\nu) = A_0 + \sum_{i=1}^k A_i e^{-\frac{(\nu_i - \nu)^2}{2\sigma_i^2}}$$

Eqn. S4

where $R_{model}(\nu)$ represents the modelled Raman scattering intensity, A_0 is the magnitude of a constant background function and k is the number of Gaussian peaks of amplitude A_i placed at centre frequency ν_i and with width σ_i . The results of this analysis are shown in Figure S7 and the parameters from the regression are reported in Tables S2 and S3. The parameters for the C-C stretching mode of the BT moiety are highlighted in green in Table S2 while those corresponding to the BT ring stretching mode and the 9,9-dialkylfluorene ring stretching mode are highlighted in yellow and blue, respectively, in table S3.

Table S2. Peak fitting results for Raman data in the 1300 - 1400 cm⁻¹ wavenumber range for T4BT-X compounds. Standard deviations and R² values are provided. The corresponding fits are shown in Figure S7. Peaks centred at $\nu_i \approx 1360$ cm⁻¹ (highlighted in green) correspond to the C-C stretching mode of the BT moiety discussed in our manuscript; all remaining peaks are not specifically assigned and have been fit to determine the appropriate background.

	T4BT-A			T4BT-B			T4BT-C			T4BT-D			T4BT-E		
A_0	0.0807	±	0.0006	0.0566	±	0.0006	0.099	±	0.001	0.045	±	0.002	0.058	±	0.001
A_1	0.0932	±	0.0008	0.092	±	0.007	0.093	±	0.008	0.094	±	0.002	0.091	±	0.004
ν_1	1304	±	1	1307	±	4	1307	±	5	1302	±	10	1298	±	3
σ_1	31	±	2	25	±	6	24	±	7	29	±	13	26	±	2
A_2	—			0.026	±	0.009	0.02	±	0.01	0.02	±	0.01	0.005	±	0.002
ν_2	—			1315.4	±	0.5	1315.8	±	0.8	1313.3	±	0.3	1306	±	1
σ_2	—			7	±	1	6	±	2	5.4	±	0.9	4	±	2
A_3	0.08	±	0.01	0.099	±	0.007	0.10	±	0.01	0.10	±	0.01	0.080	±	0.002
ν_3	1347	±	1	1343.9	±	0.2	1344.9	±	0.2	1345.3	±	0.2	1345.12	±	0.08
σ_3	7.6	±	0.5	7.0	±	0.2	7.7	±	0.4	7.1	±	0.4	7.0	±	0.1
A_4	0.086	±	0.009	0.101	±	0.005	0.08	±	0.01	0.08	±	0.01	—		
ν_4	1360.1	±	0.9	1360.7	±	0.1	1361.0	±	0.2	1361.7	±	0.2	—		
σ_4	7.1	±	0.6	6.0	±	0.2	5.1	±	0.3	5.2	±	0.2	—		
A_5	0.023	±	0.002	0.025	±	0.003	0.029	±	0.006	0.02	±	0.01	0.012	±	0.001
ν_5	1378.4	±	0.7	1375.5	±	0.8	1372	±	3	1375	±	1	1377.0	±	0.7
σ_5	6.6	±	0.5	7.0	±	0.6	10	±	2	7	±	1	10	±	1
R^2	0.9995			0.9997			0.9986			0.9992			0.9985		

Table S3. Peak fitting results for Raman data in the 1500 - 1700 cm^{-1} wavenumber range for T4BT-X compounds. Standard deviations and R^2 values are provided. The corresponding fits are shown in Figure S7. Peaks centred at $\nu_2 \approx 1547 \text{ cm}^{-1}$ (highlighted in yellow) and $\nu_3 \approx 1608 \text{ cm}^{-1}$ (highlighted in blue) correspond, respectively to the ring stretching modes of the BT and 9,9-dialkylfluorene moieties as discussed in our manuscript; all remaining peaks are not specifically assigned and have been fit to determine the appropriate background.

	T4BT-A	T4BT-B	T4BT-C	T4BT-D	T4BT-E
A_0	0.067 $\pm$ 0.003	0.039 $\pm$ 0.003	0.090 $\pm$ 0.002	0.034 $\pm$ 0.002	0.050 $\pm$ 0.001
A_1	0.289 $\pm$ 0.005	0.326 $\pm$ 0.004	0.300 $\pm$ 0.004	0.225 $\pm$ 0.005	0.031 $\pm$ 0.002
ν_1	1547.4 $\pm$ 0.1	1547.04 $\pm$ 0.09	1547.05 $\pm$ 0.09	1547.4 $\pm$ 0.1	1538.3 $\pm$ 0.4
σ_1	6.4 $\pm$ 0.1	6.2 $\pm$ 0.1	6.2 $\pm$ 0.1	5.9 $\pm$ 0.2	5.8 $\pm$ 0.4
A_2	0.101 $\pm$ 0.003	0.108 $\pm$ 0.003	0.100 $\pm$ 0.003	0.101 $\pm$ 0.003	0.133 $\pm$ 0.003
ν_2	1581 $\pm$ 1	1580 $\pm$ 1	1582 $\pm$ 1	1586 $\pm$ 1	1600.7 $\pm$ 0.2
σ_2	41 $\pm$ 2	42 $\pm$ 1	40 $\pm$ 1	36 $\pm$ 1	20.3 $\pm$ 0.3
A_3	0.832 $\pm$ 0.005	0.863 $\pm$ 0.004	0.815 $\pm$ 0.004	0.869 $\pm$ 0.004	0.821 $\pm$ 0.003
ν_3	1608.12 $\pm$ 0.04	1608.54 $\pm$ 0.03	1608.50 $\pm$ 0.03	1608.14 $\pm$ 0.03	1607.45 $\pm$ 0.02
σ_3	6.14 $\pm$ 0.04	6.14 $\pm$ 0.04	6.22 $\pm$ 0.04	6.20 $\pm$ 0.04	5.76 $\pm$ 0.02
R^2	0.9981	0.9985	0.9990	0.9979	0.9991

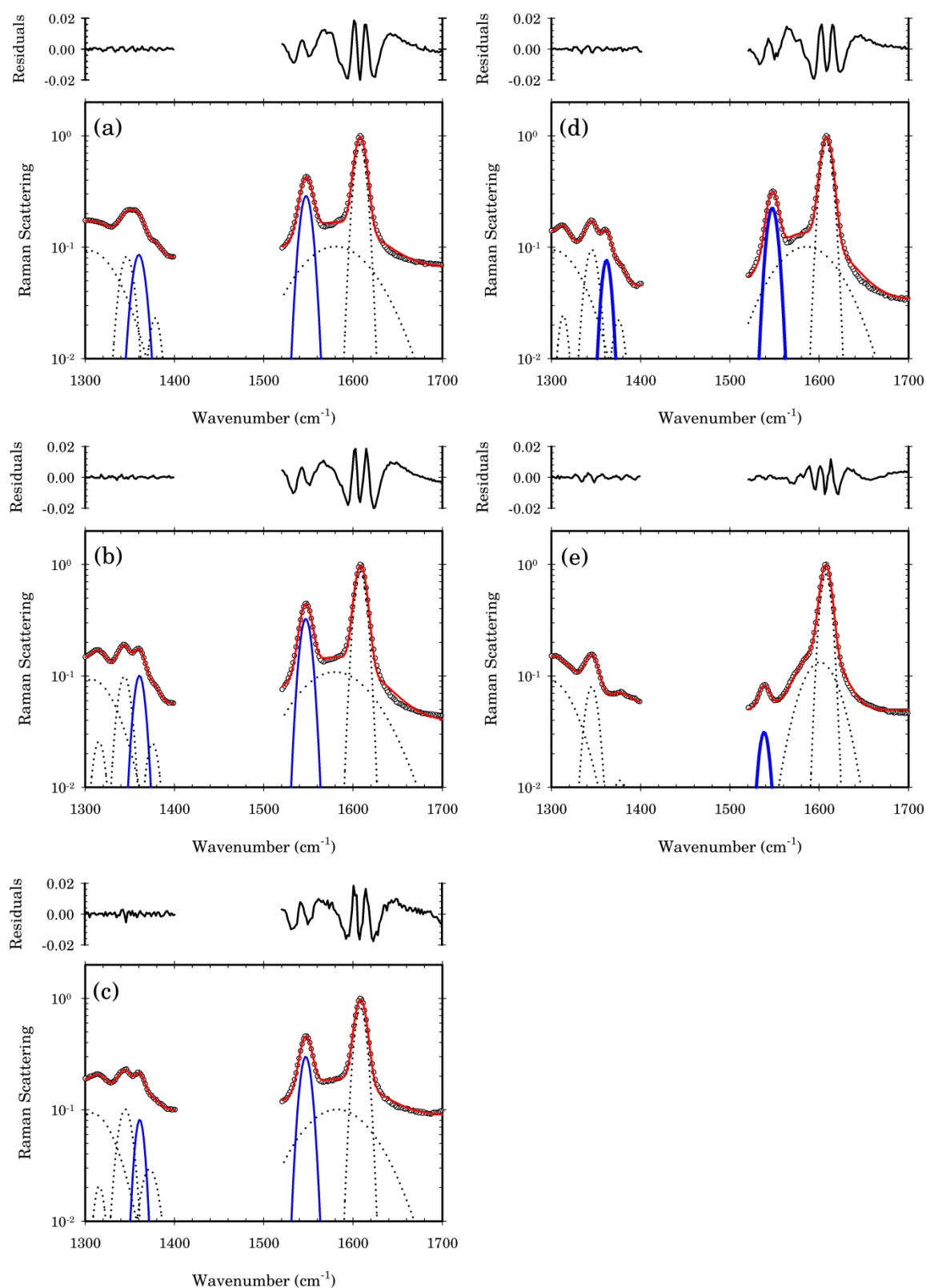


Figure S7. Results from peak fitting (Gaussian functions) to the Raman spectra for (a) T4BT-A, (b) T4BT-B, (c) T4BT-C, (d) T4BT-D and (e) T4BT-E. The fit (red line) is superimposed on the experimental data (empty circles). The deconvoluted peaks are also shown. The two BT-centred Raman modes discussed in detail our manuscript are highlighted in blue; these are the 1360 cm^{-1} BT C-C stretching and 1547 cm^{-1} BT ring stretching vibrations.

1H and 13C NMR Spectra of Newly Synthesised Compounds

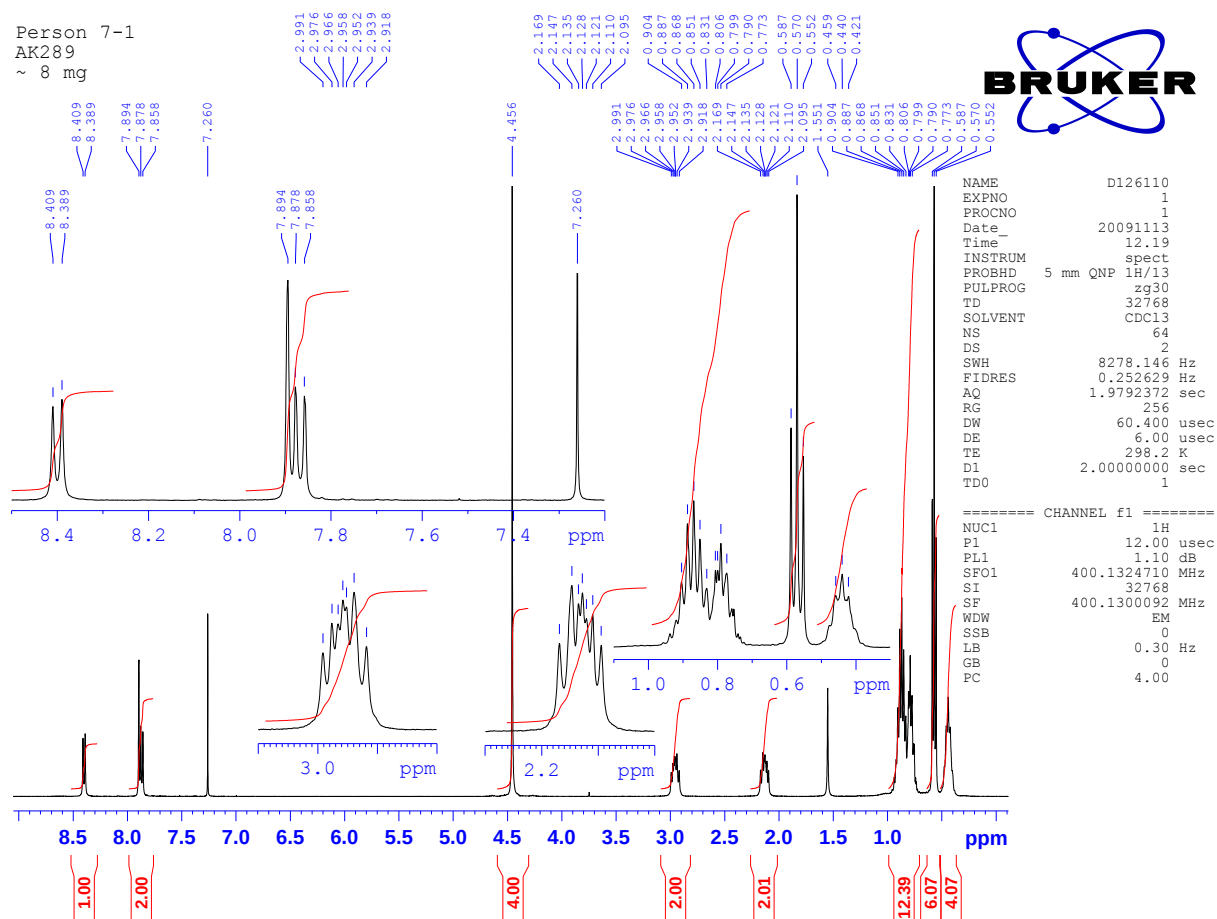


Figure S9- ¹H NMR of compound 1

Person 7-1
AK289
~ 30 mg

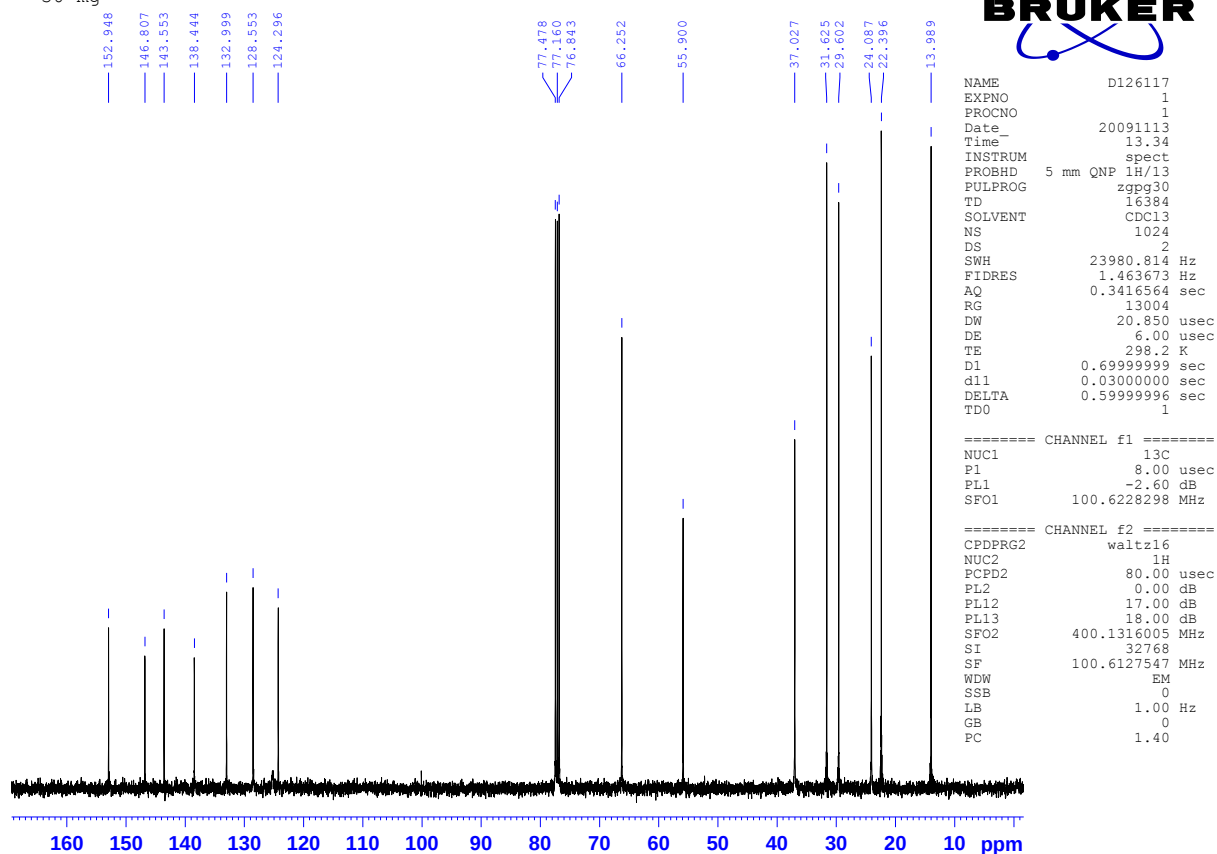


Figure S10- ¹³C NMR of compound 1

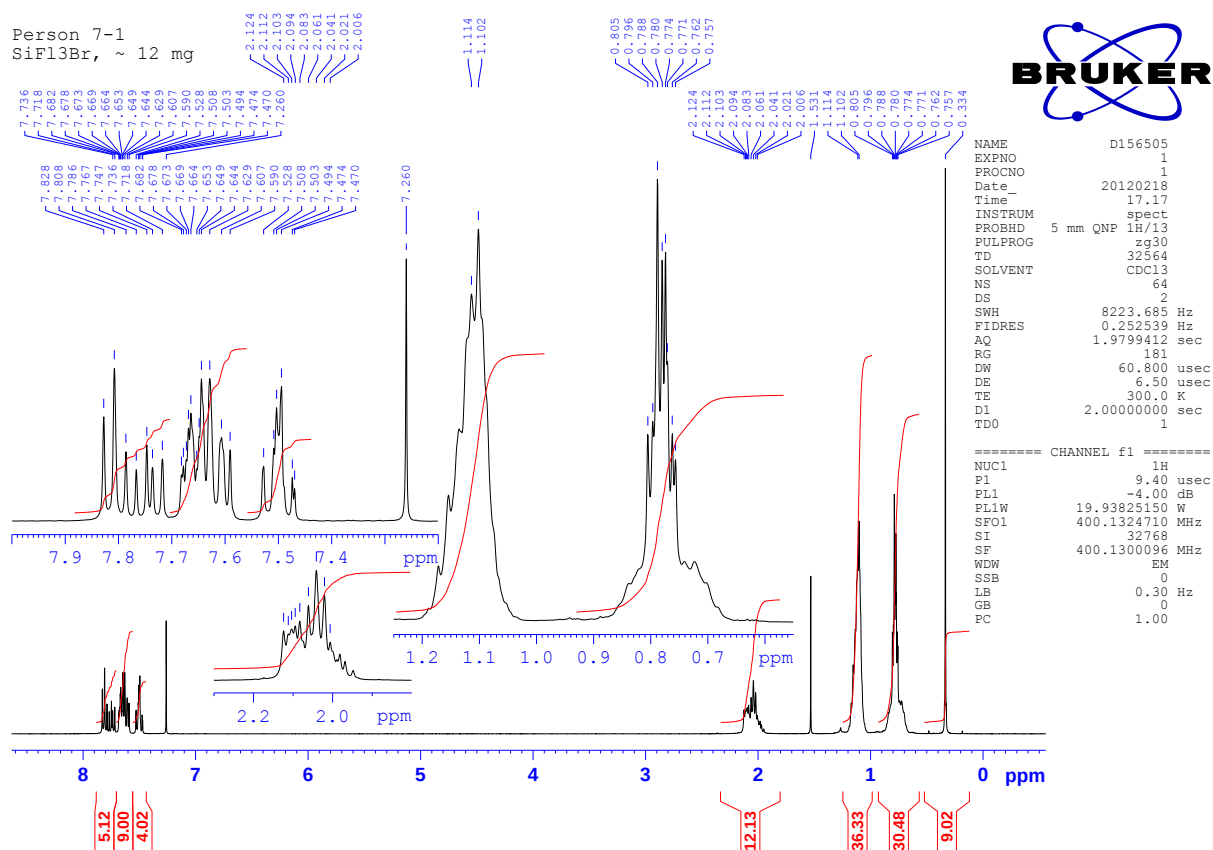


Figure S11- ^1H NMR of compound SiF3Br

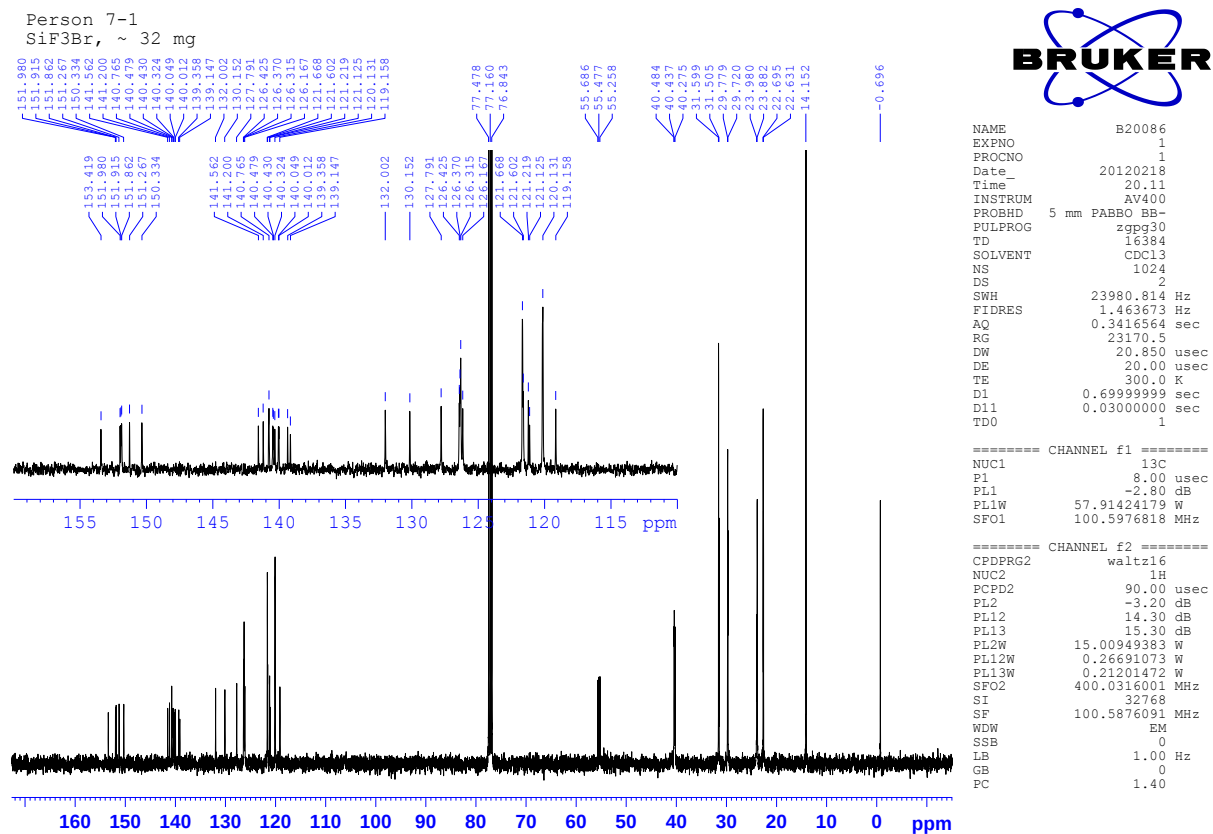


Figure S12 - ¹³C NMR of compound SiF₃Br

person 7-1
SiF3B, ~32 mg

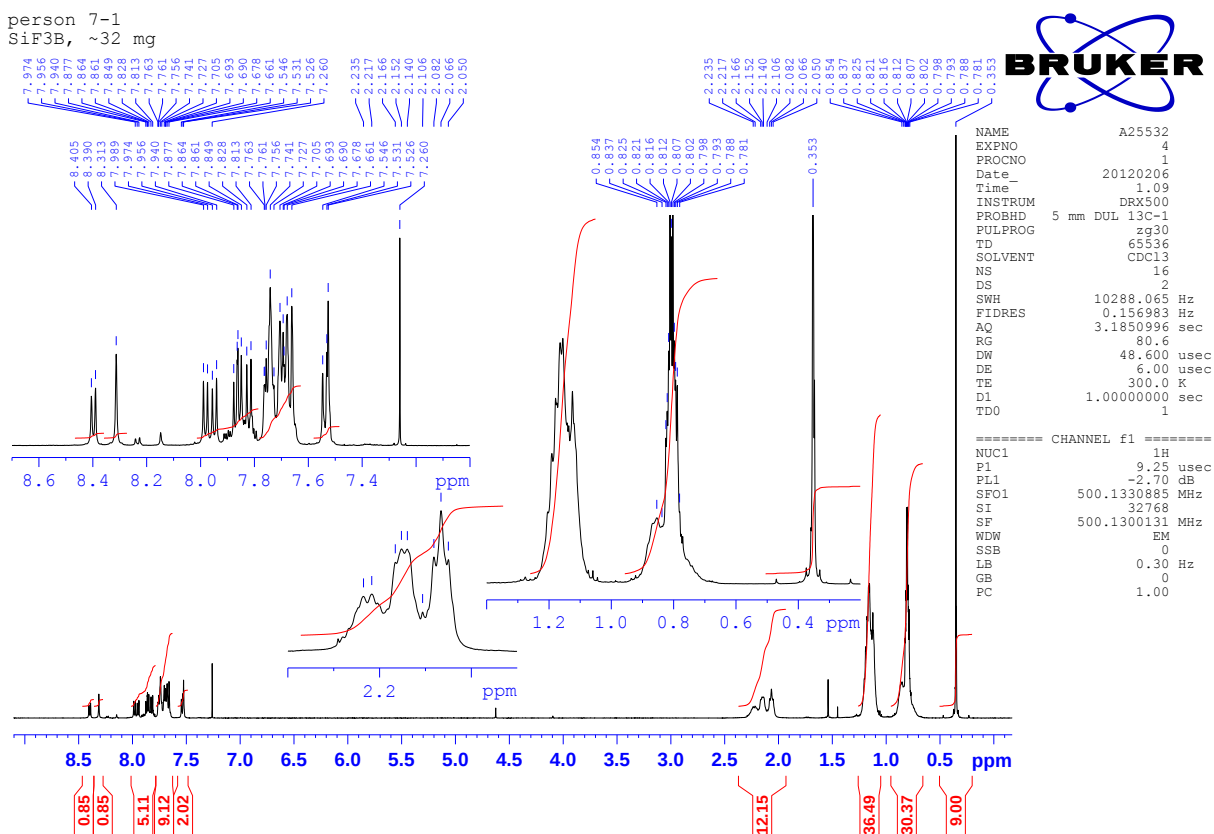
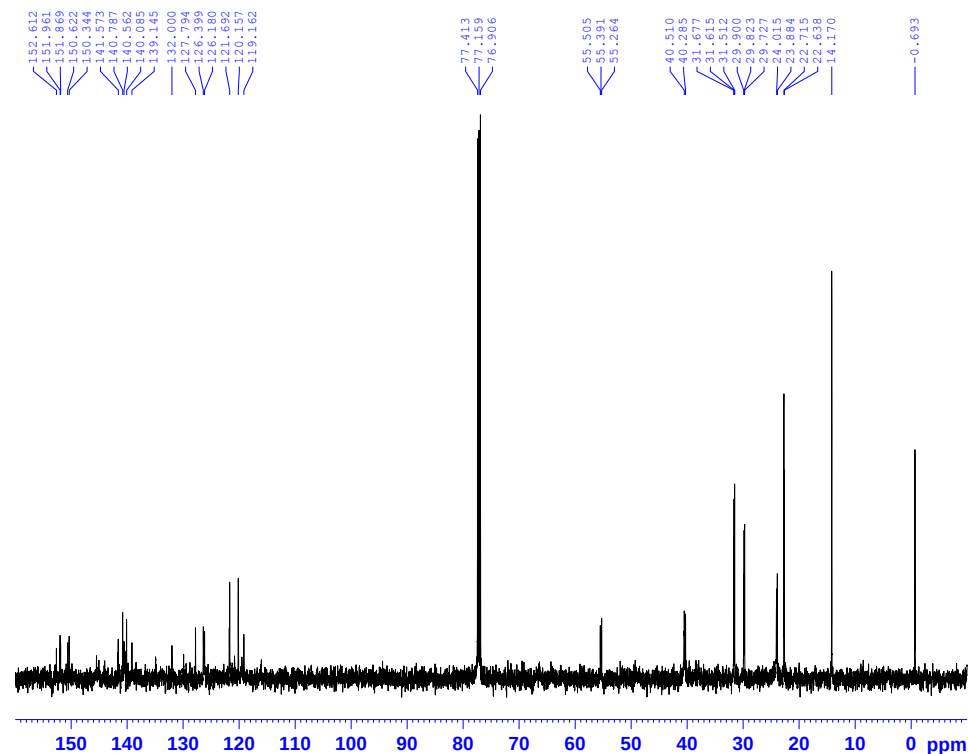


Figure S13 - ^1H NMR of compound SiF3B

person 7-1
SiF3B, ~32 mg



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EXPNO     3
PROCNO    1
Date_     20120206
Time      1.03
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PROBHD    5 mm DUL 13C-1
PULPROG   zgpg30
TD         16384
SOLVENT   CDCl3
NS         16384
DS         4
SWH        30120.482 Hz
FIDRES     1.838408 Hz
AQ         0.2720244 sec
RG         10321.3
DW         16.600 usec
DE         6.00 usec
TE         300.0 K
D1         0.69999999 sec
d11        0.03000000 sec
DELTA      0.59999996 sec
TD0        1

===== CHANNEL f1 =====
NUC1       13C
P1         8.00 usec
PL1        -2.30 dB
SFO1       125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2    waltz16
NUC2       1H
PCPD2      80.00 usec
PL2        -2.30 dB
PL12       16.21 dB
PL13       120.00 dB
SFO2       500.1320005 MHz
SI         32768
SF         125.7577720 MHz
WDW        EM
SSB        0
LB         2.00 Hz
GB         0
PC         1.40

```

Figure S14 - ^{13}C NMR of compound SiF3B

person 7-1
AK332_3

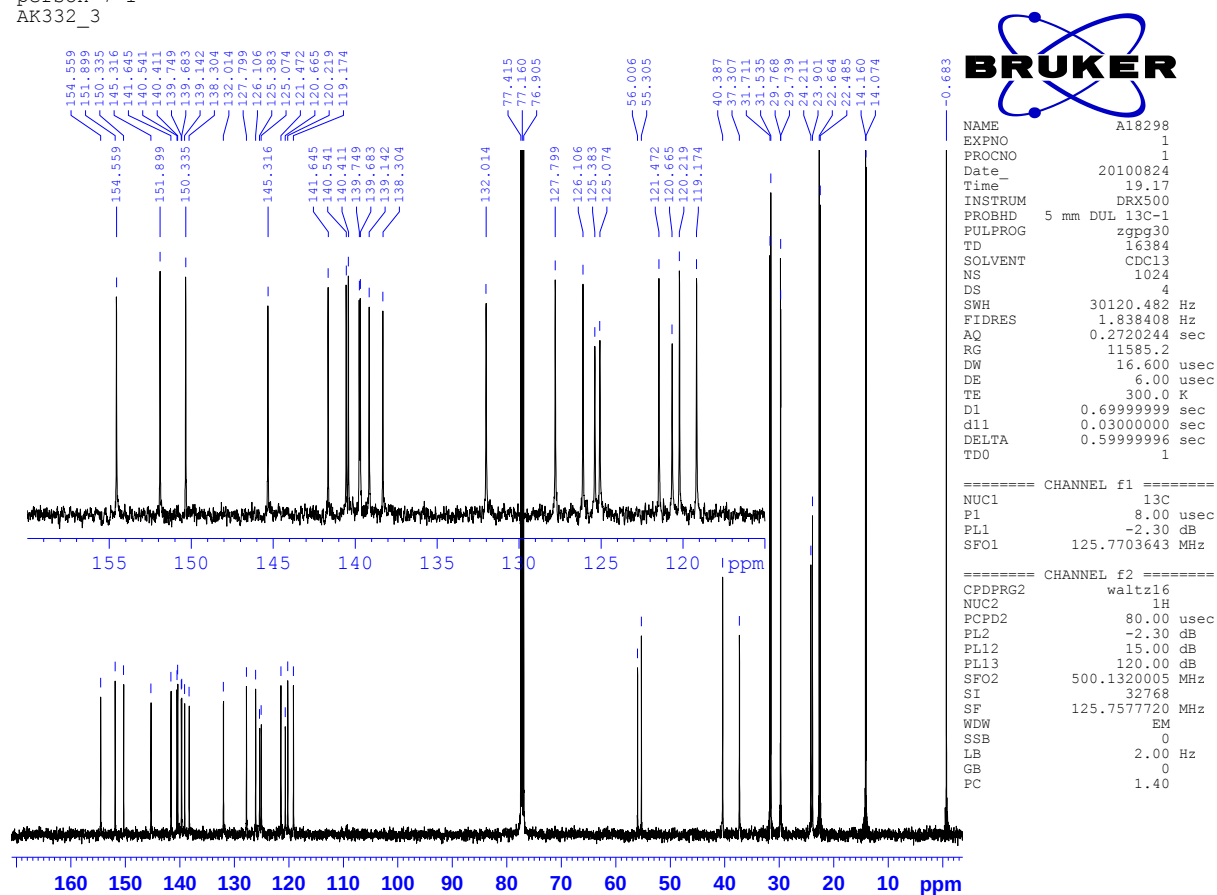


Figure S16 - ^{13}C NMR of compound T1Si

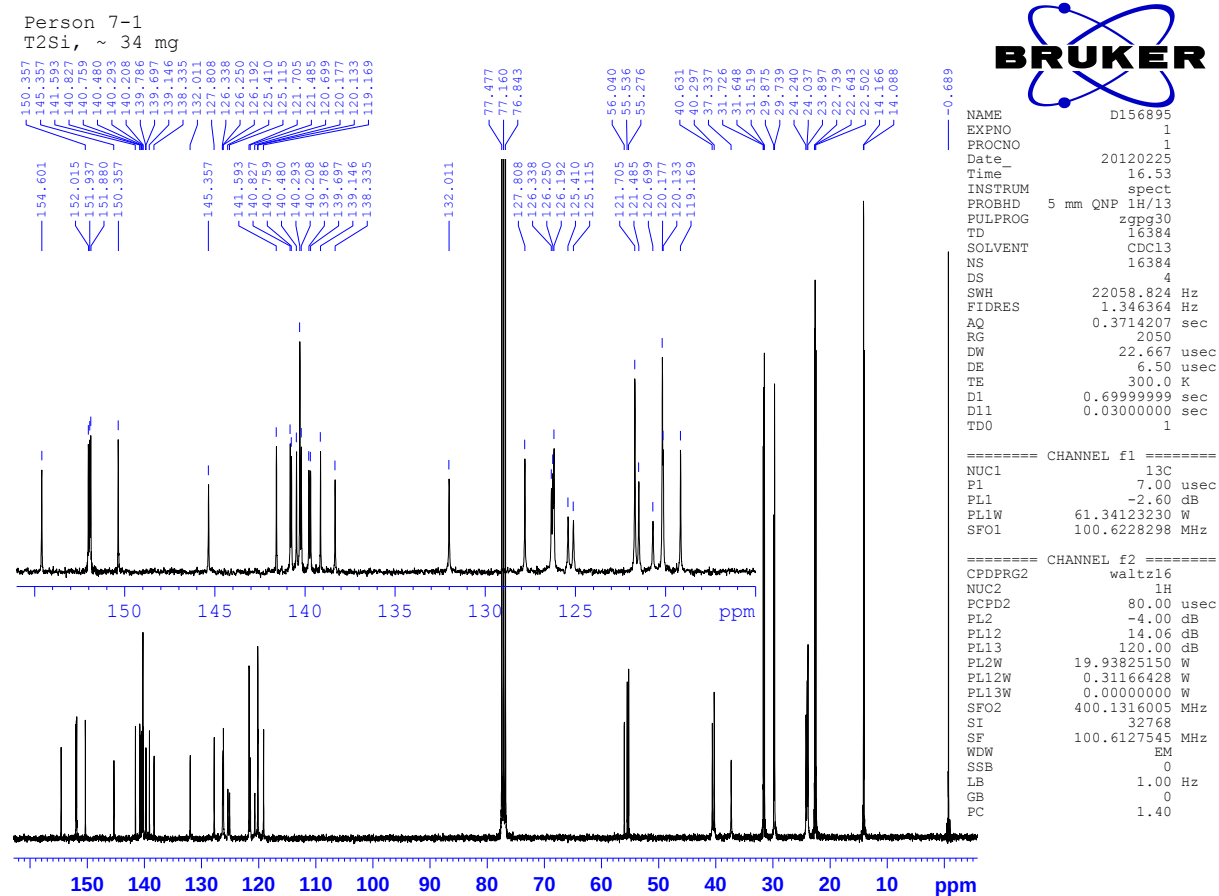


Figure S18 - ^{13}C NMR of compound T2Si

person 7-1
T3Si, ~ 12 mg

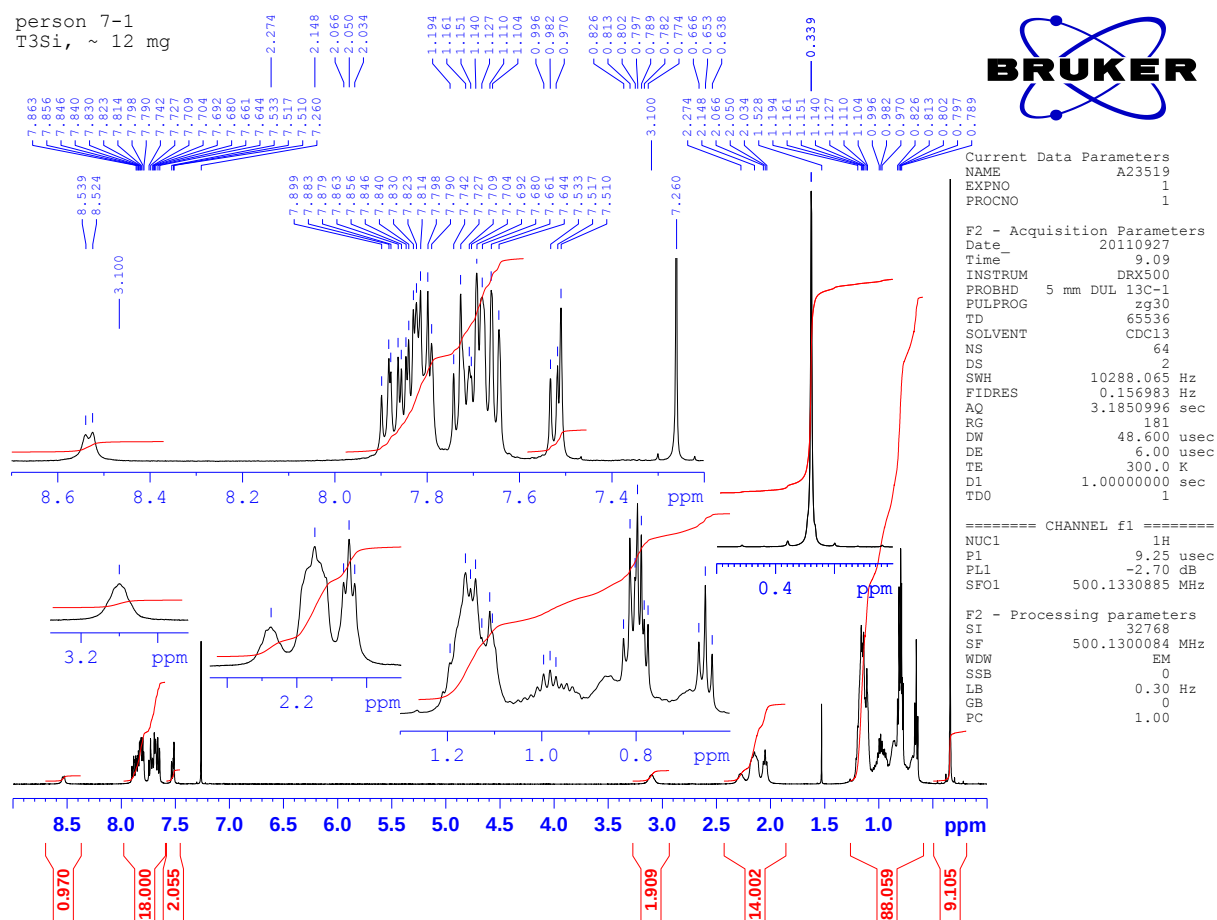
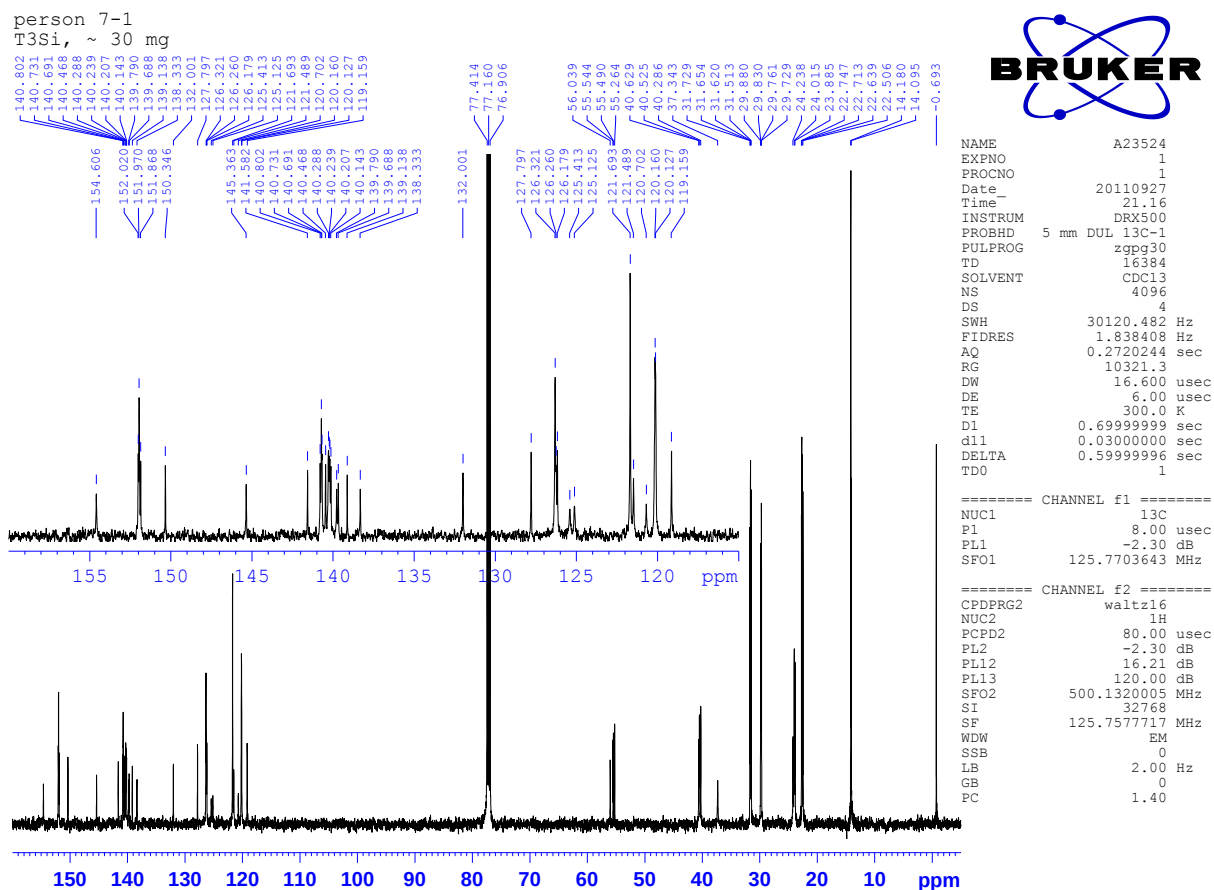


Figure S19 - ^1H NMR of compound T3Si



person 7-1
AK368 (3) 32
~ 12 mg

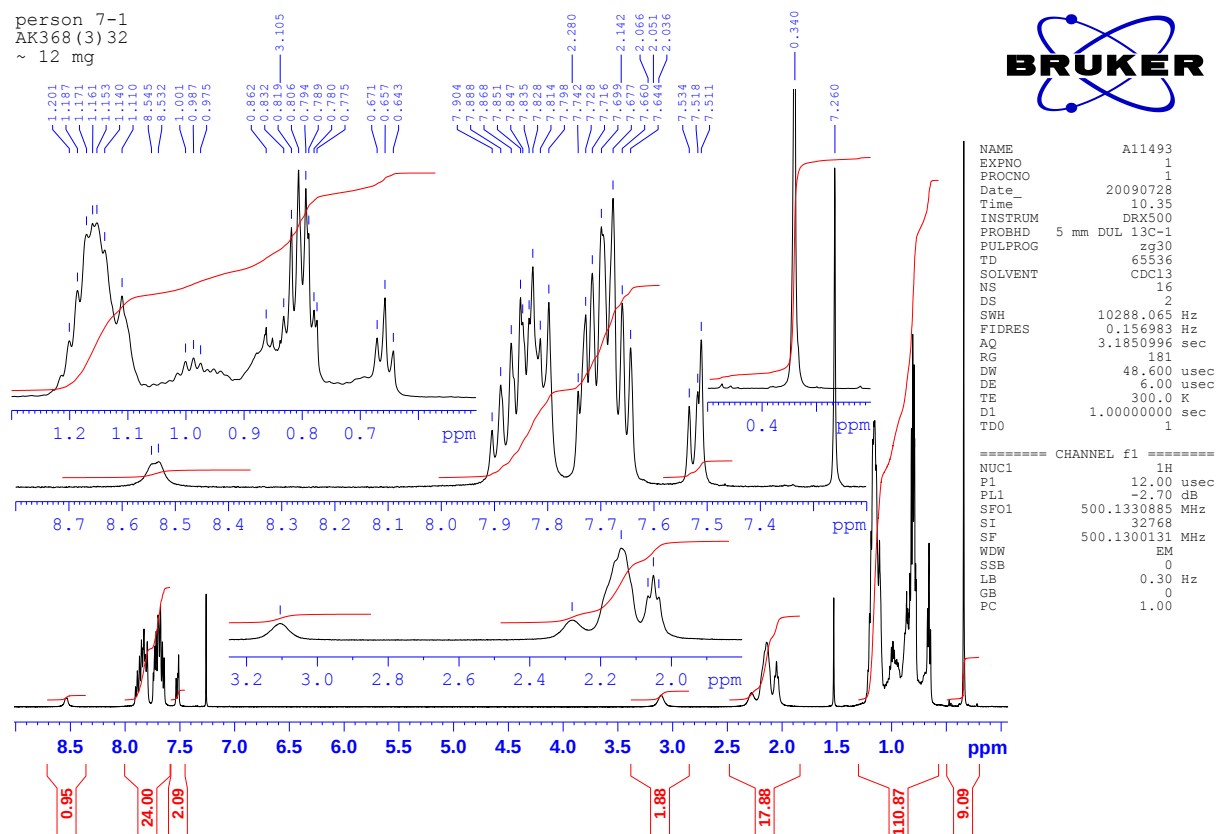
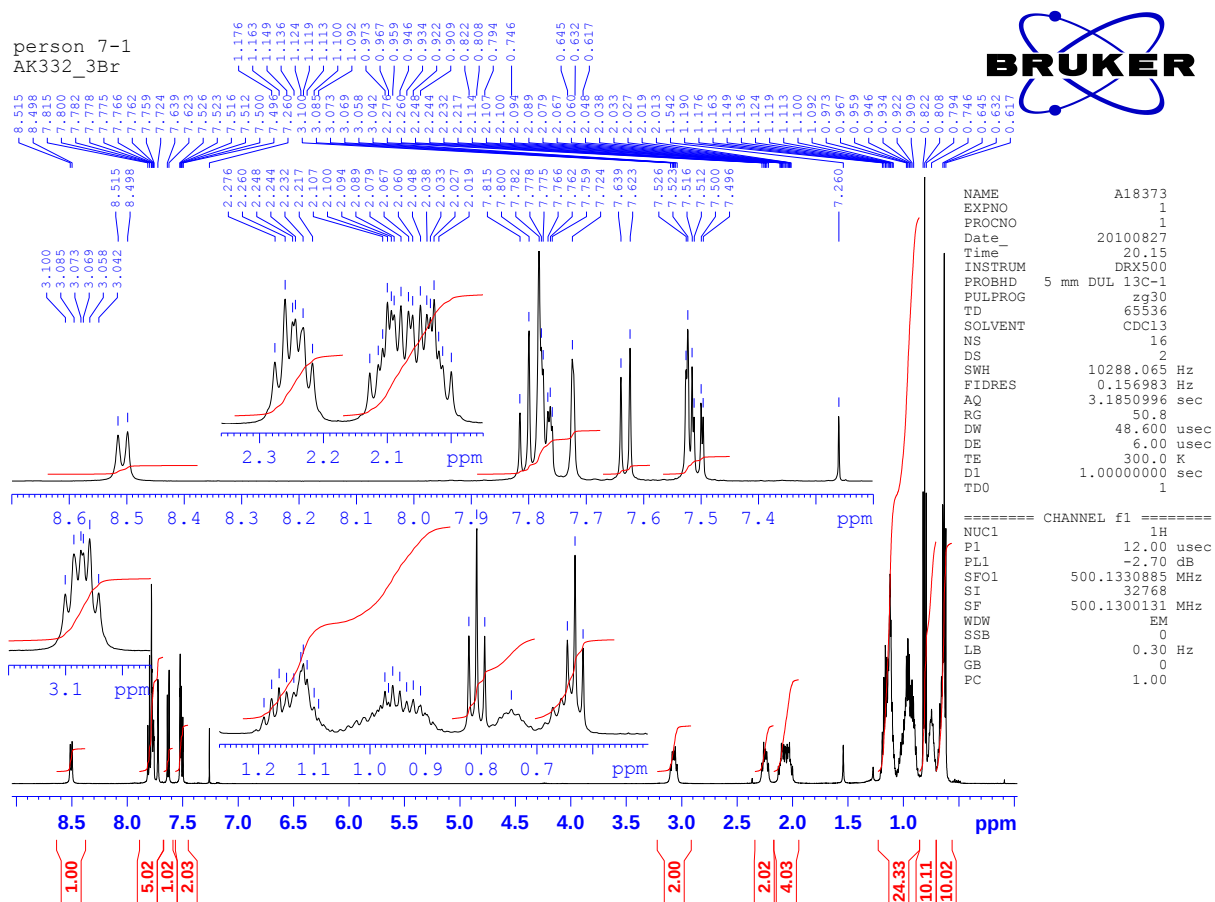


Figure S21 - ^1H NMR of compound T4Si



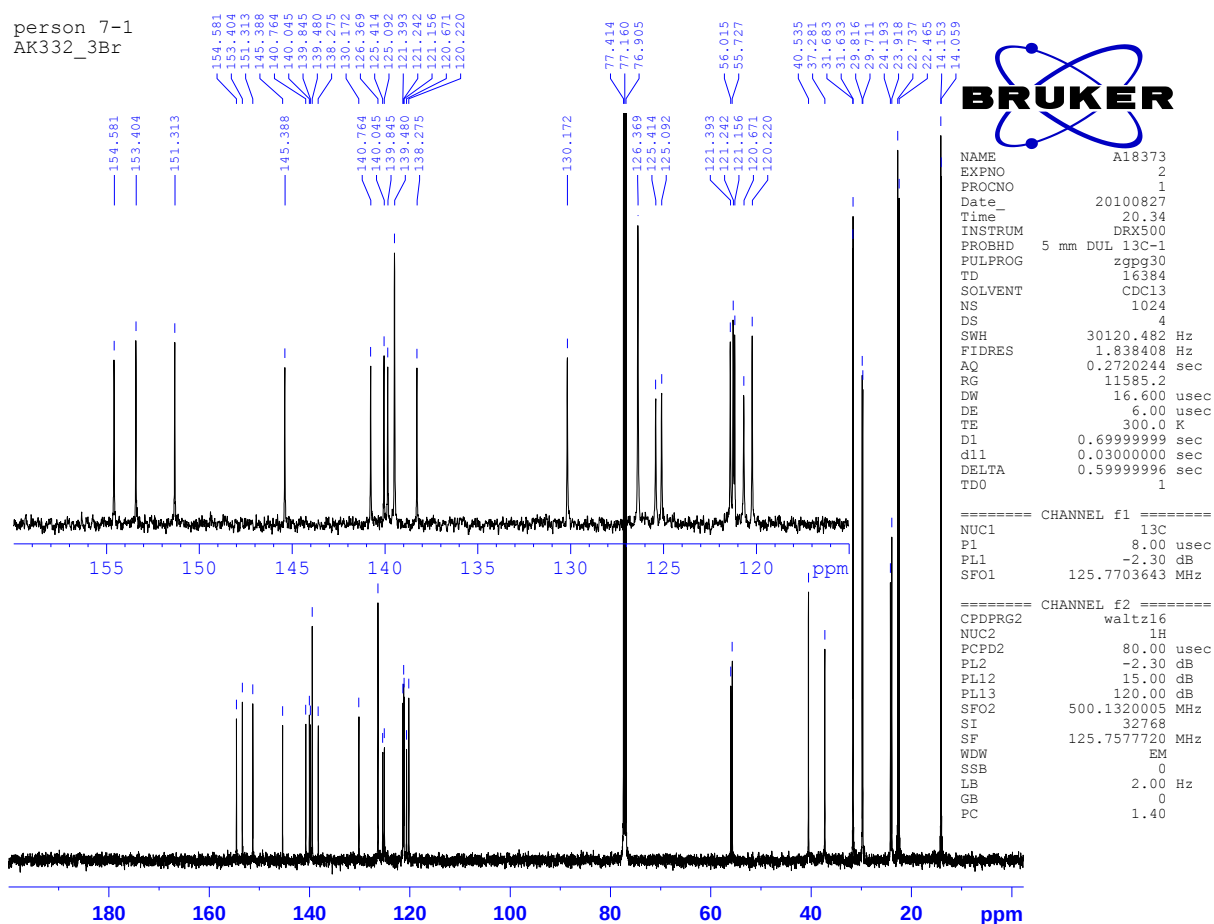


Figure S24 - ^{13}C NMR of compound T1Br

Person 7-1
T2Br, ~ 12 mg

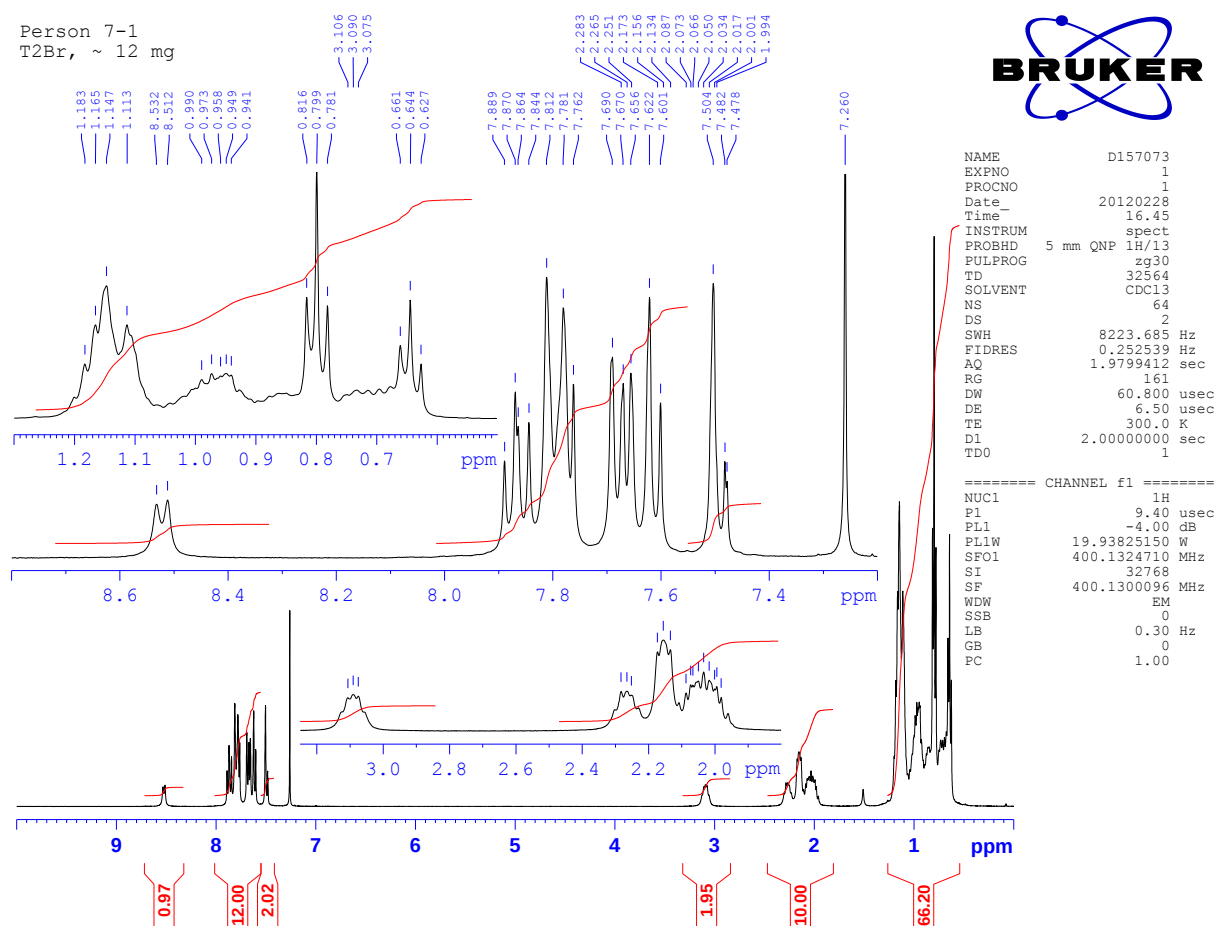


Figure S25 - ^1H NMR of compound T2Br



person 7-1
T3Br, ~ 12 mg

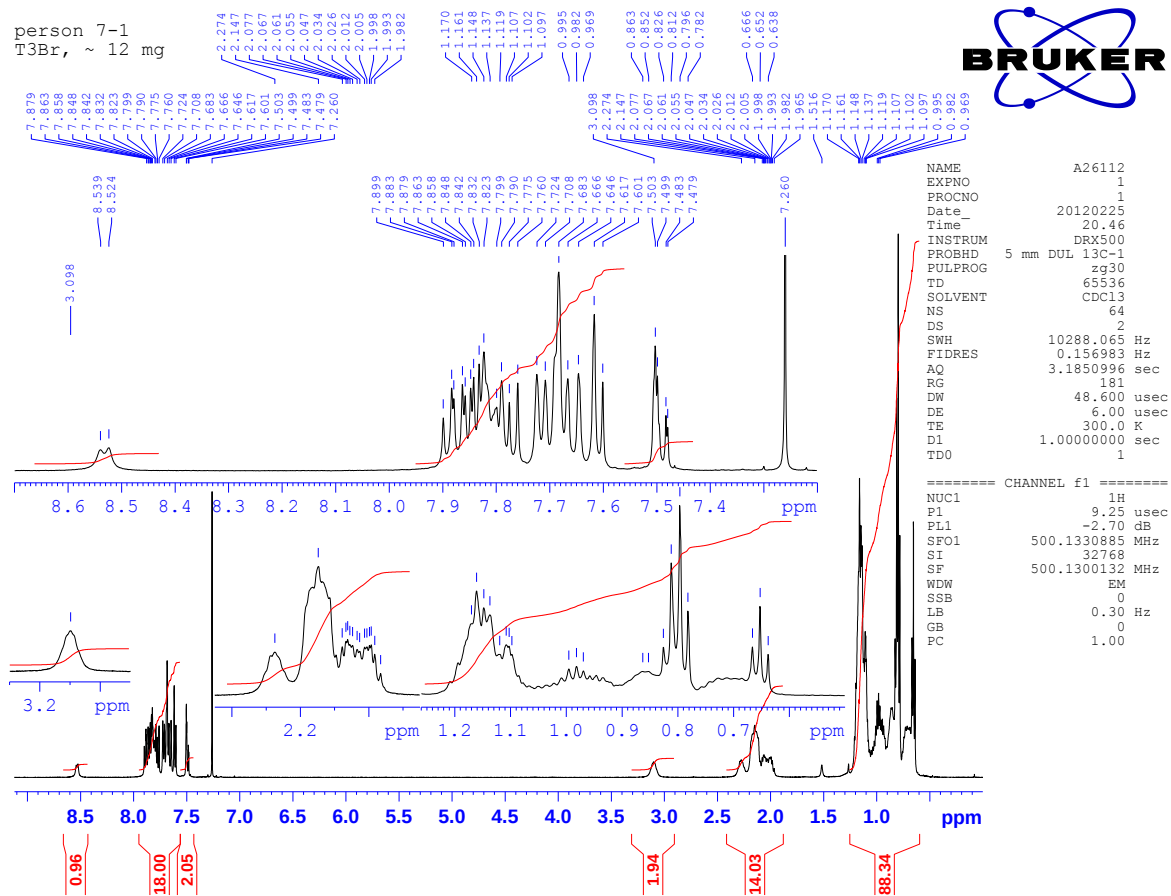


Figure S27 - ^1H NMR of compound T3Br



person 7-1
T4Br, ~ 14 mg

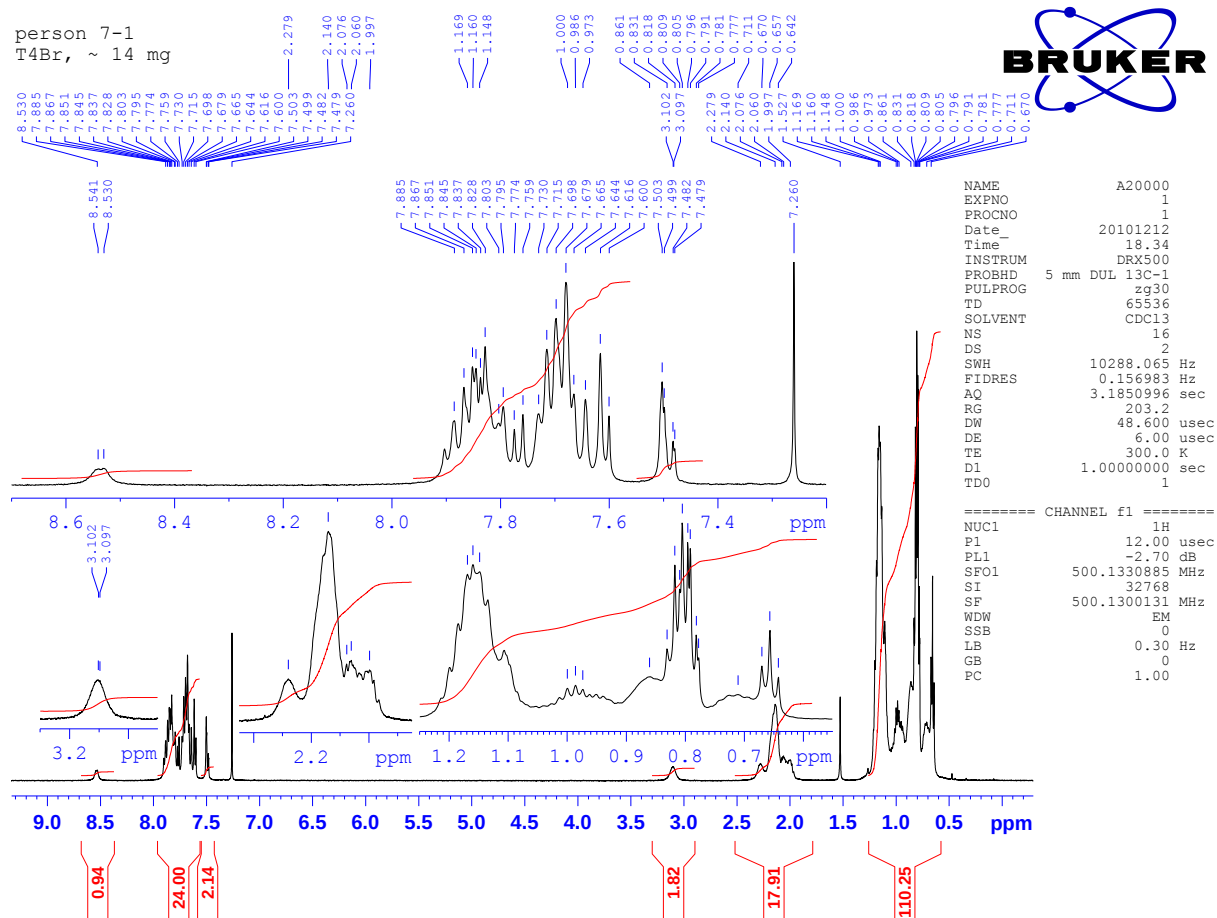


Figure S29 - ^1H NMR of compound T4Br

person 7-1
T4Br, ~ 32 mg

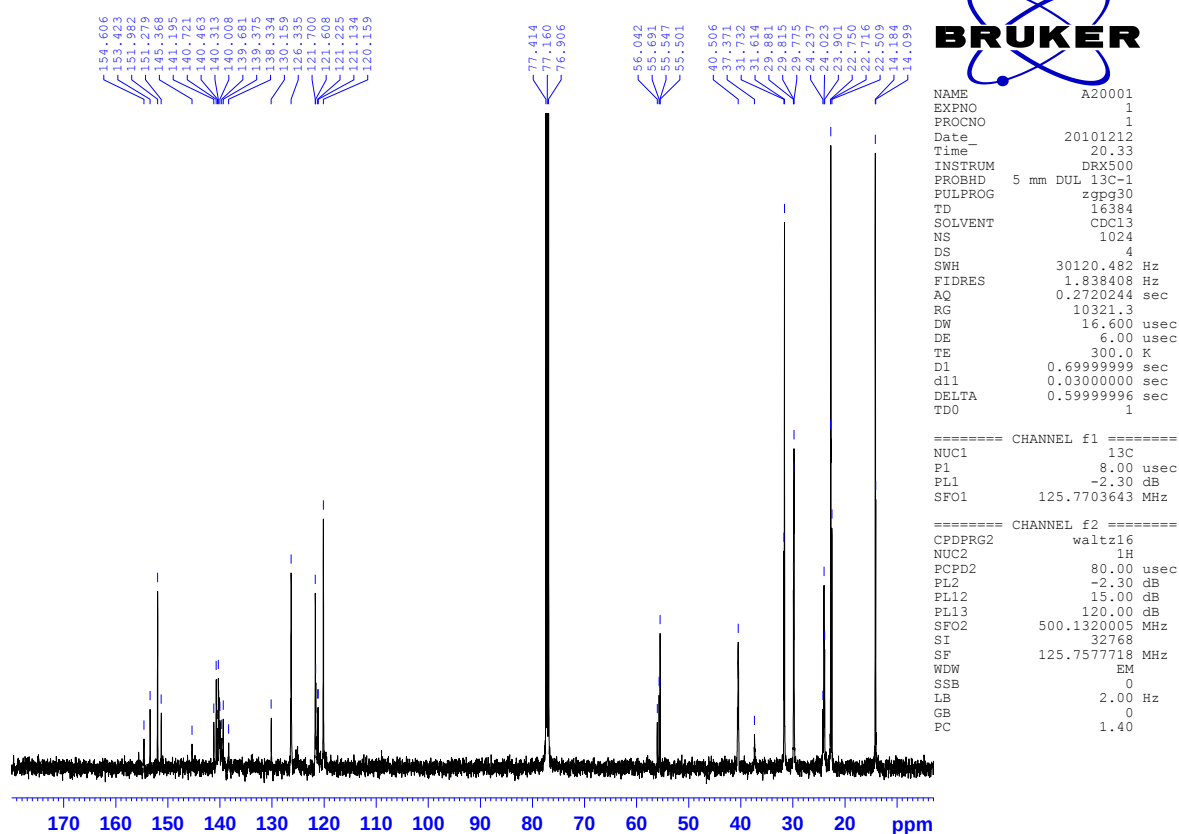


Figure S30 - ^{13}C NMR of compound T4Br

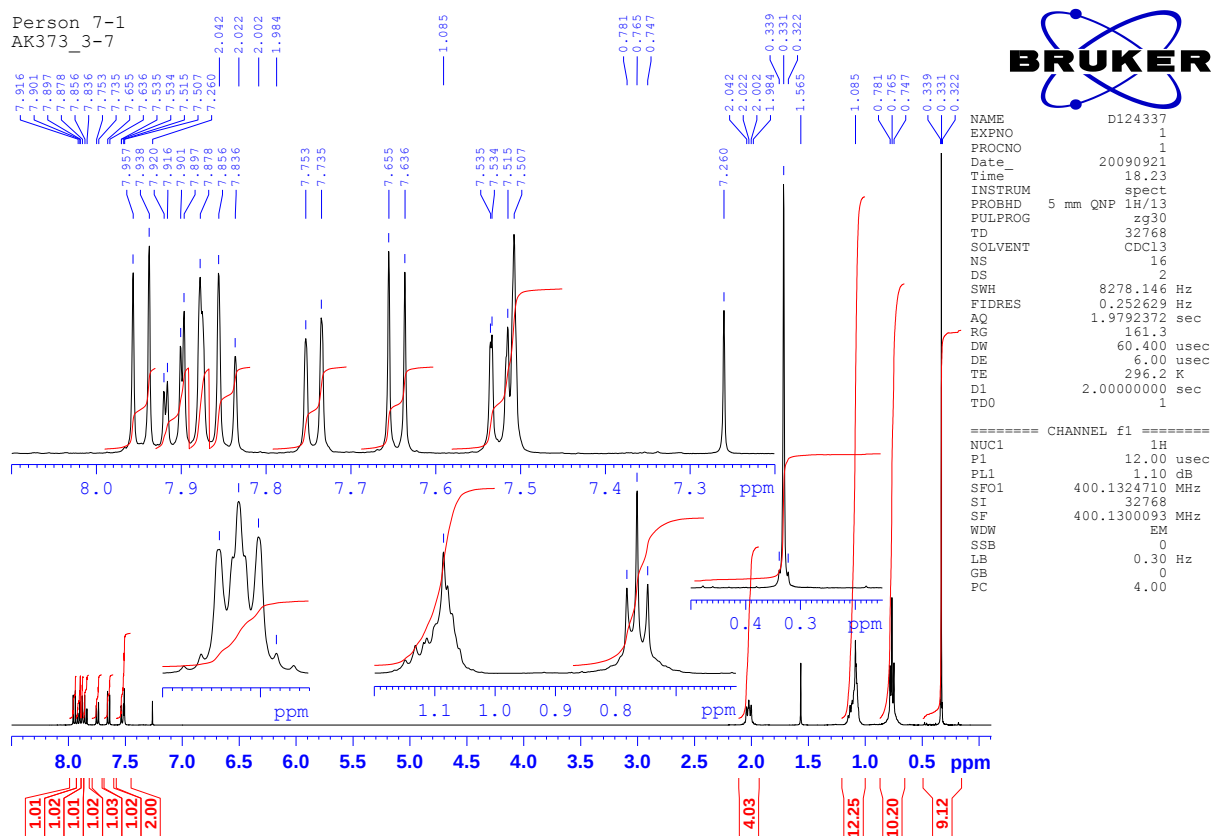


Figure S31 - ^1H NMR of compound SiF_1BTBr

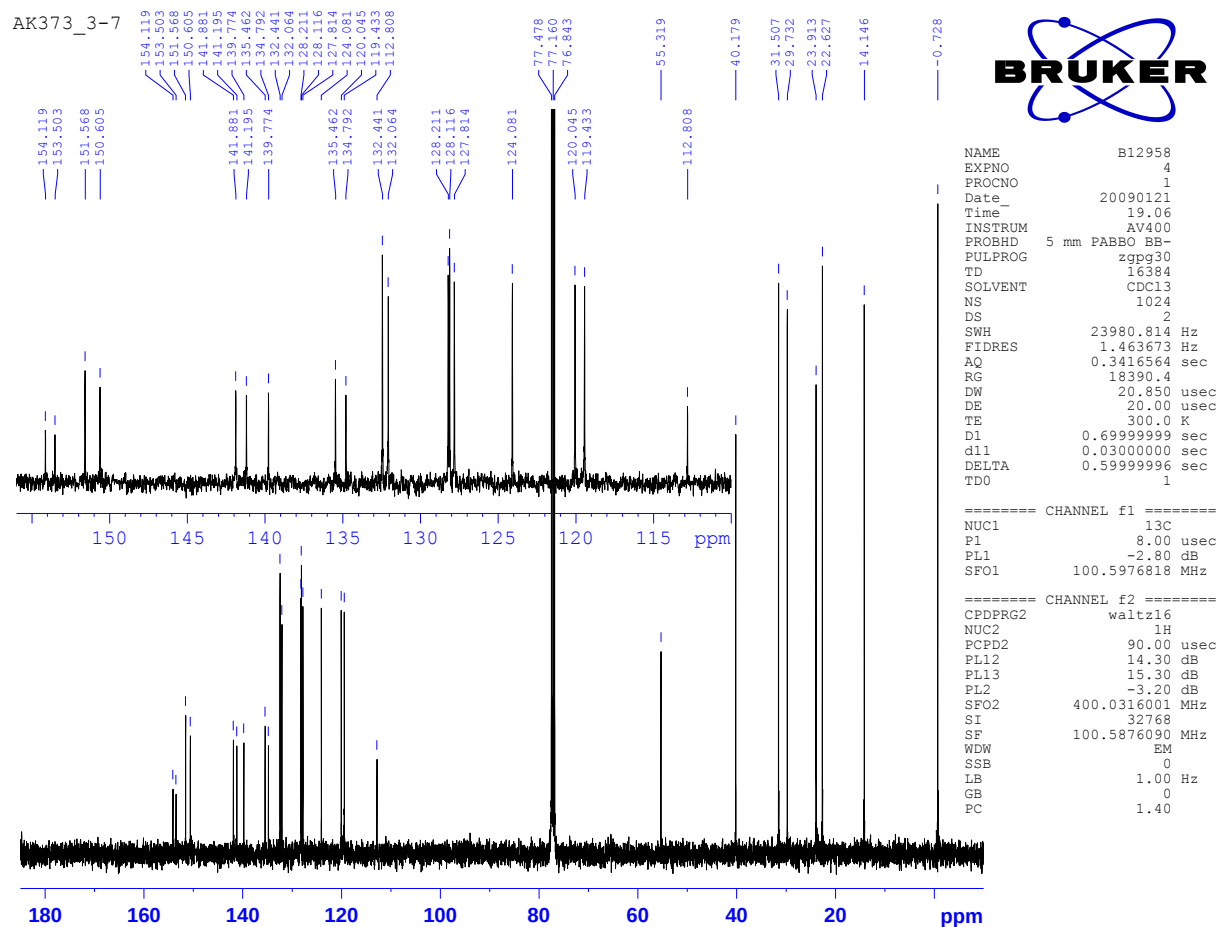


Figure S32 - ^{13}C NMR of compound SiF_3BTBr

person 7-1
AK395_3-8R
~ 15 mg

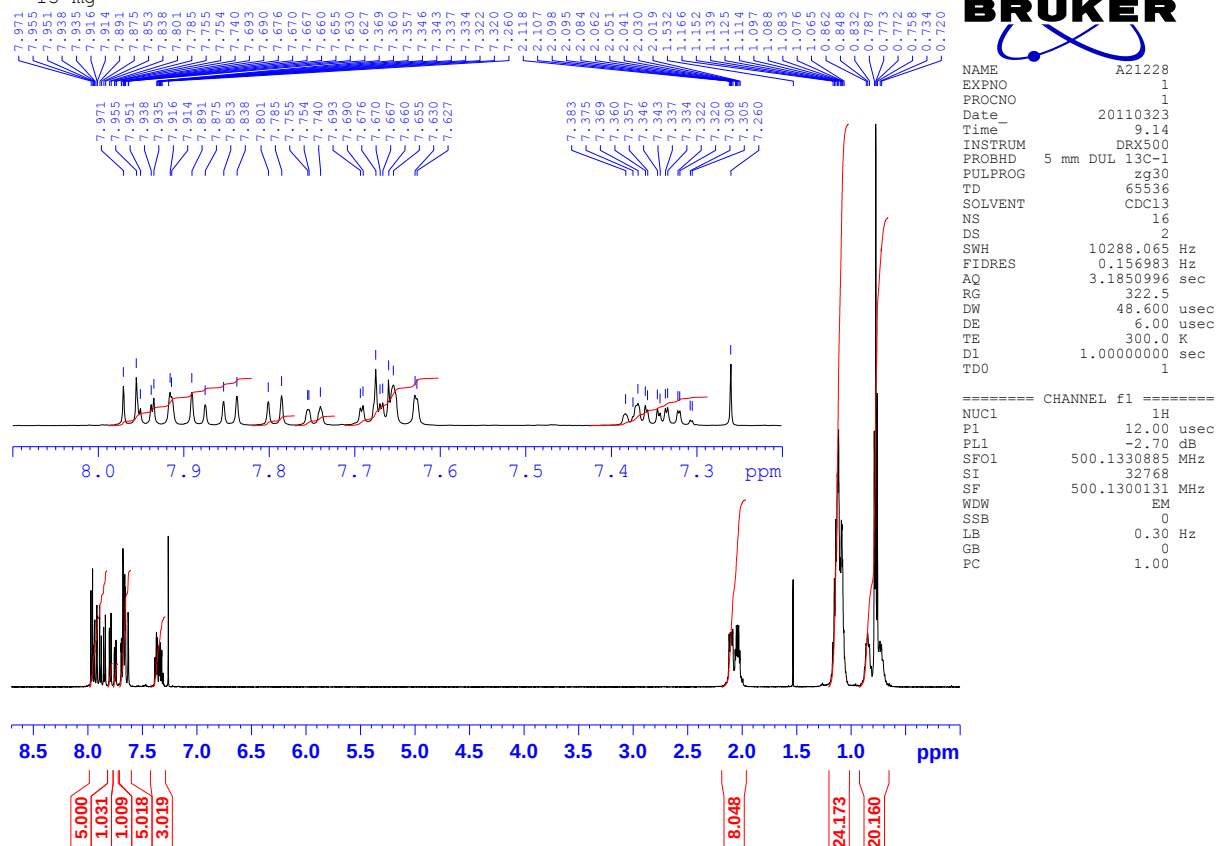


Figure S33 - ^1H NMR of compound F_2BTBr

Person 7-2
AK395_3-8R

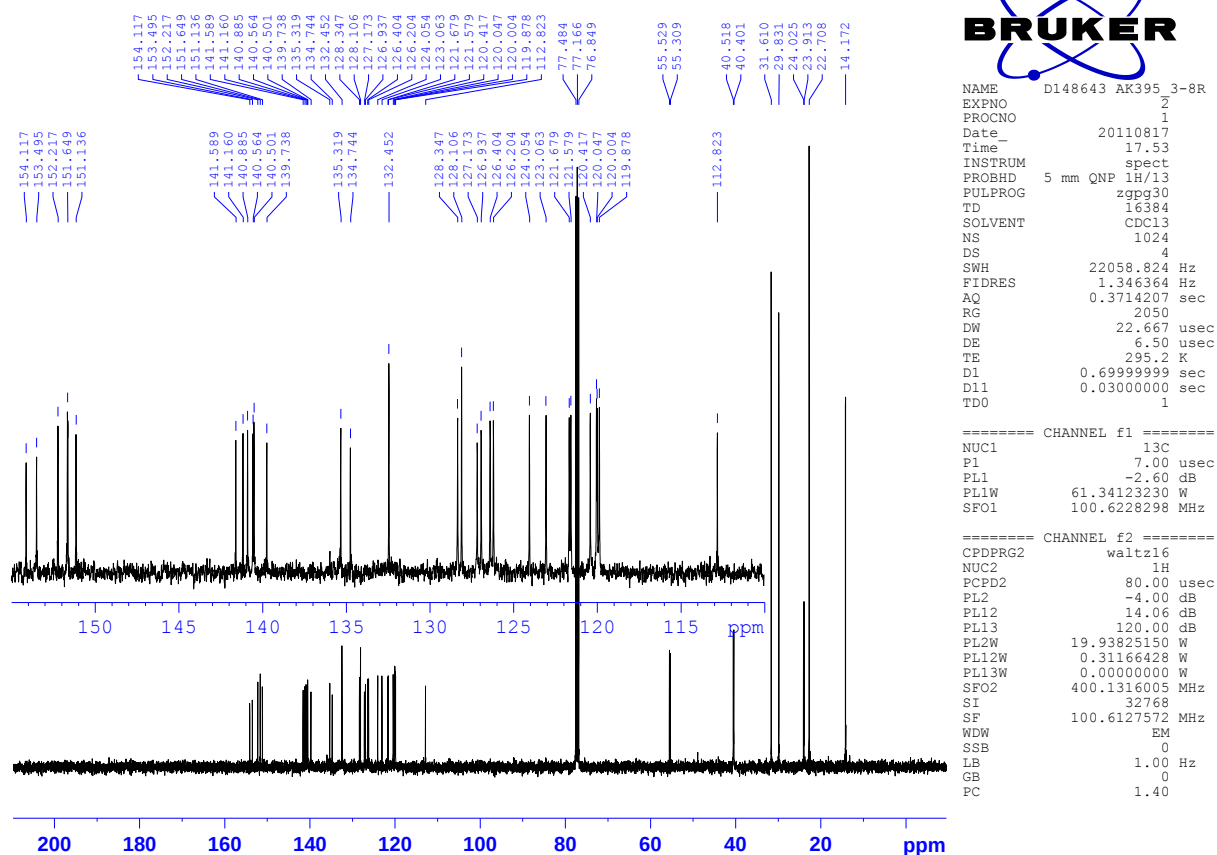


Figure S34 - ^{13}C NMR of compound F_2BTBr

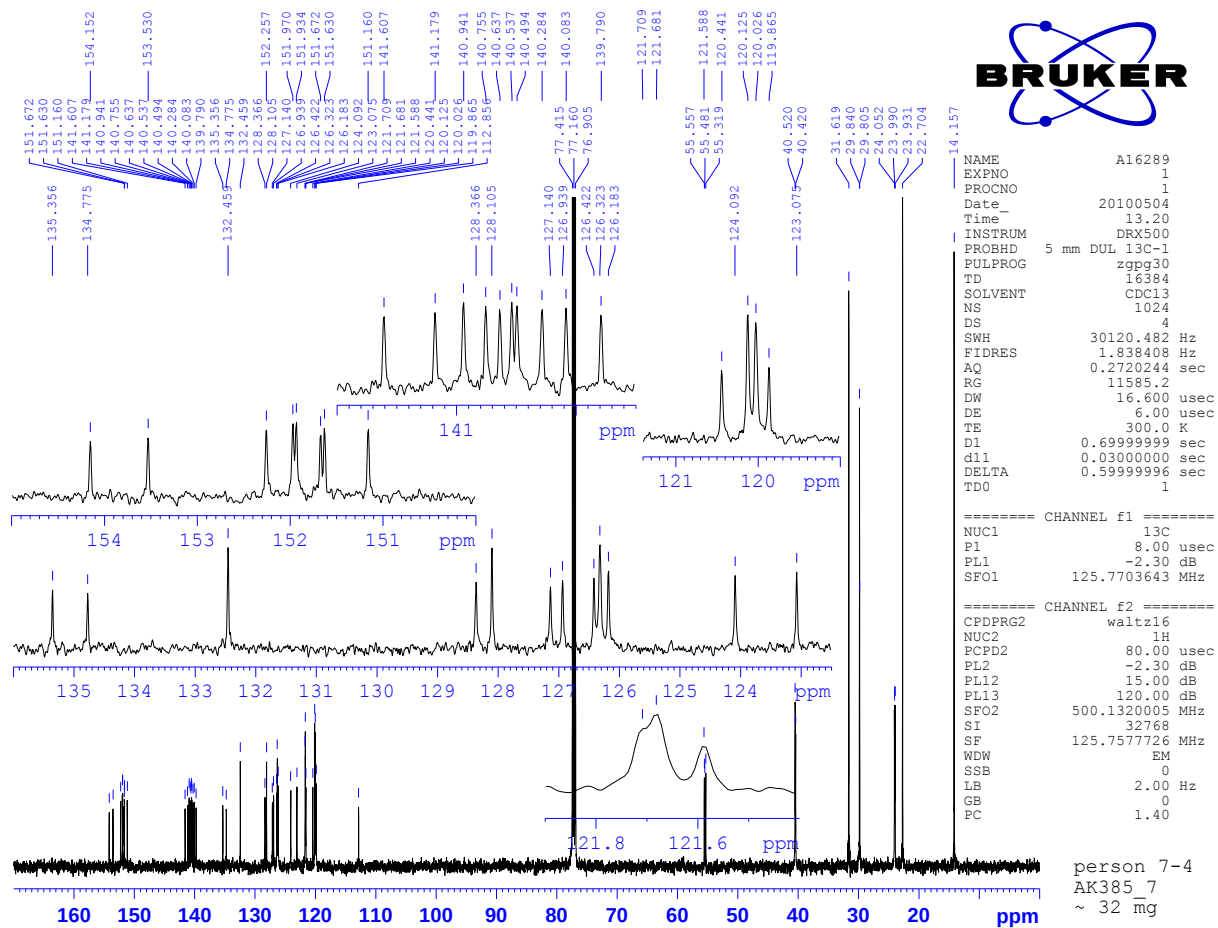


Figure S36 - ^{13}C NMR of compound F_3BTBr

Person 7-1
AK378BT3-4R
 τ 7 mg

Peak Data (ppm)

Chemical Shift (ppm)
7.979
7.960
7.949
7.938
7.924
7.914
7.902
7.884
7.871
7.851
7.844
7.838
7.830
7.824
7.818
7.805
7.796
7.785
7.778
7.771
7.768
7.758
7.744
7.732
7.703
7.684
7.665
7.652
7.632
7.398
7.388
7.377
7.368
7.362
7.345
7.339
7.335
7.332
7.260
2.133
2.116
2.104
2.067
2.055
2.031
2.017
1.536
1.162
1.129
1.125
1.093
0.936
0.926
0.786
0.782
0.779
0.776
0.768
0.758
0.793
0.786
0.782
0.779
0.768
0.764
-0.758

Integration Values: 24.03, 3.01, 16.00, 48.17, 40.20

BRUKER

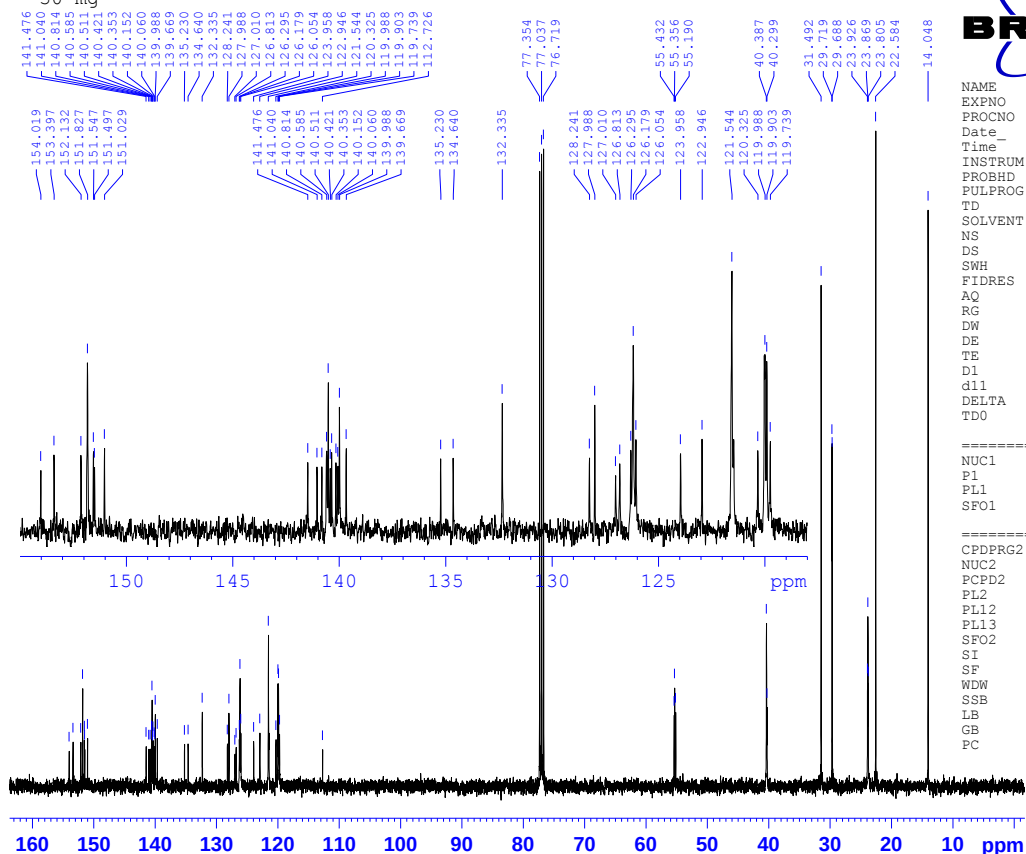
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PROCNO        1
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TD            32768
SOLVENT       CDCl3
NS            64
DS            2
SWH           8278.146 Hz
FIDRES        0.252629 Hz
AQ            1.9792372 sec
RG            406.4
DW            60.400 usec
DE            6.00 usec
TE            298.2 K
D1            2.00000000 sec
TDO           1

===== CHANNEL f1 =====
NUC1          1H
P1            12.00 usec
PL1           1.10 dB
SFO1          400.1324710 MHz
SI            32768
SF            400.1300093 MHz
WDW           EM
SSB           0
LB            0.30 Hz
GB            0
PC            4.00
    
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S-50

Person 7-1
AK378BT3-4R
~ 30 mg



```

NAME          D125628
EXPNO         1
PROCNO        1
Date_         20091103
Time_         13.18
INSTRUM       spect
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PULPROG       zgpg30
TD            16384
SOLVENT       CDCl3
NS            1024
DS            2
SWH           23980.814 Hz
FIDRES        1.463673 Hz
AQ            0.3416564 sec
RG            1625.5
DW            20.850 usec
DE            6.00 usec
TE            298.2 K
D1            0.69999999 sec
d11           0.03000000 sec
DELTA         0.59999996 sec
TD0           1

===== CHANNEL f1 =====
NUC1          13C
P1            8.00 usec
PL1           -2.60 dB
SFO1          100.6228298 MHz

===== CHANNEL f2 =====
CPDPRG2       waltz16
NUC2          1H
PCPD2         80.00 usec
PL2           0.00 dB
PL12          17.00 dB
PL13          18.00 dB
SFO2          400.1316005 MHz
SI            32768
SF            100.6127690 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40
  
```

Figure S38 - ^{13}C NMR of compound F_4BTBr

Person 7-1
AK373_3-7DeSi1

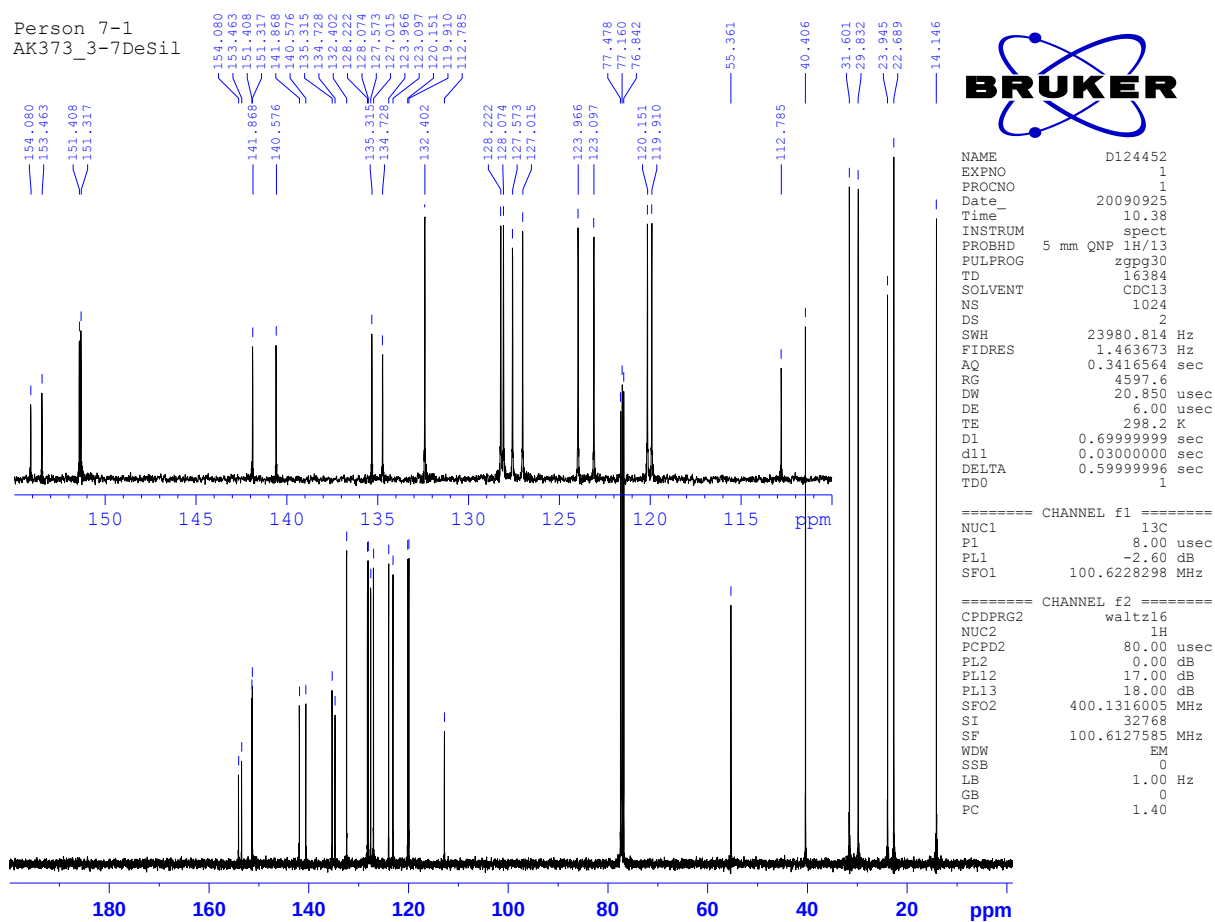


Figure S40 - ^{13}C NMR of compound F_1BTBr

Person 7-1
AK375_3-5PinDr
~ 32 mg

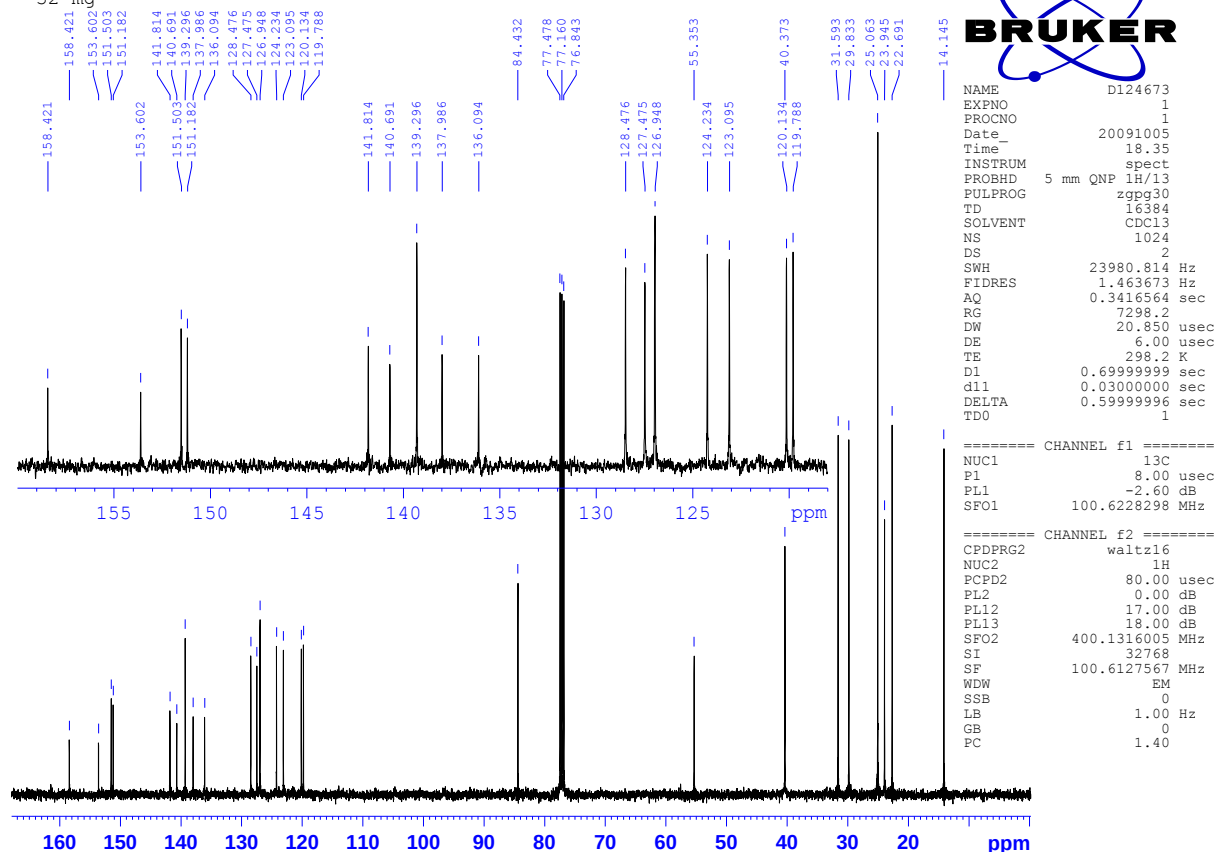
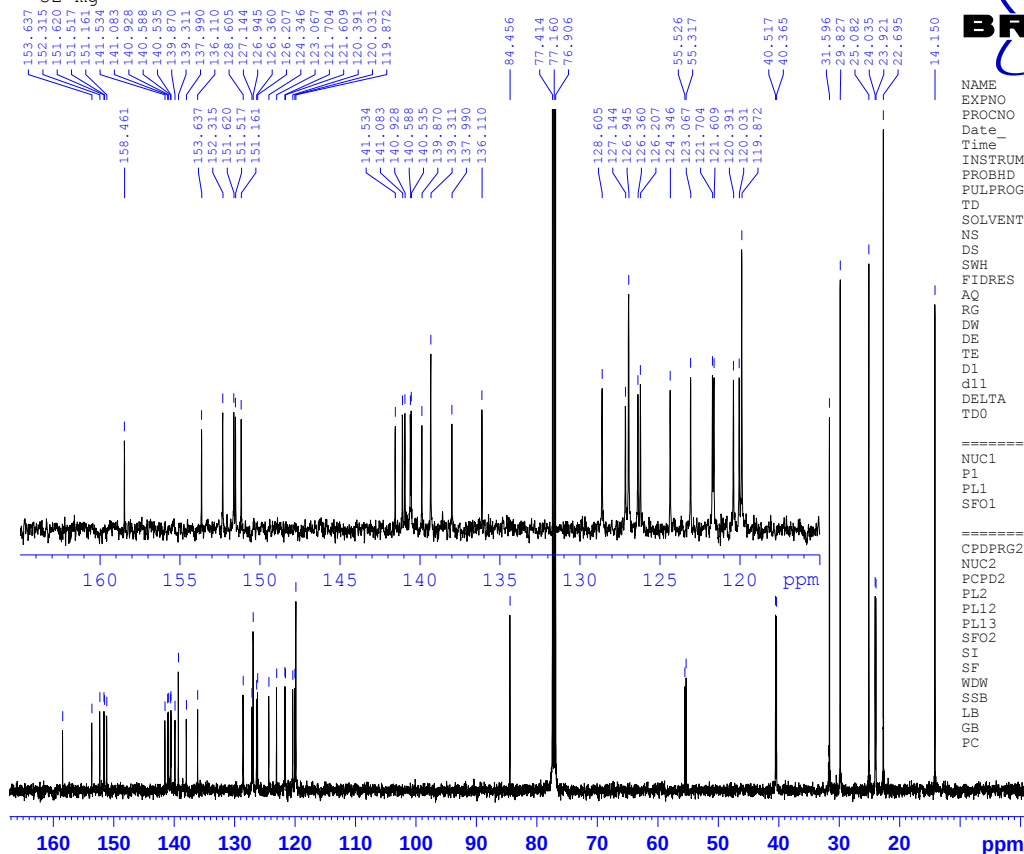


Figure S42 - ^{13}C NMR of compound FI₁BTBE

person 7-1
AK386_3Pin
32 mg



NAME A15851
EXPNO 1
PROCNO 1
Date_ 20100416
Time 18.16
INSTRUM DRX500
PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 16384
SOLVENT CDC13
NS 1024
DS 4
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.2720244 sec
RG 11585.2
DW 16.600 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 -2.30 dB
SFO1 125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.30 dB
PL12 15.00 dB
PL13 120.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577724 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure S44 - ^{13}C NMR of compound FI₂BTBE

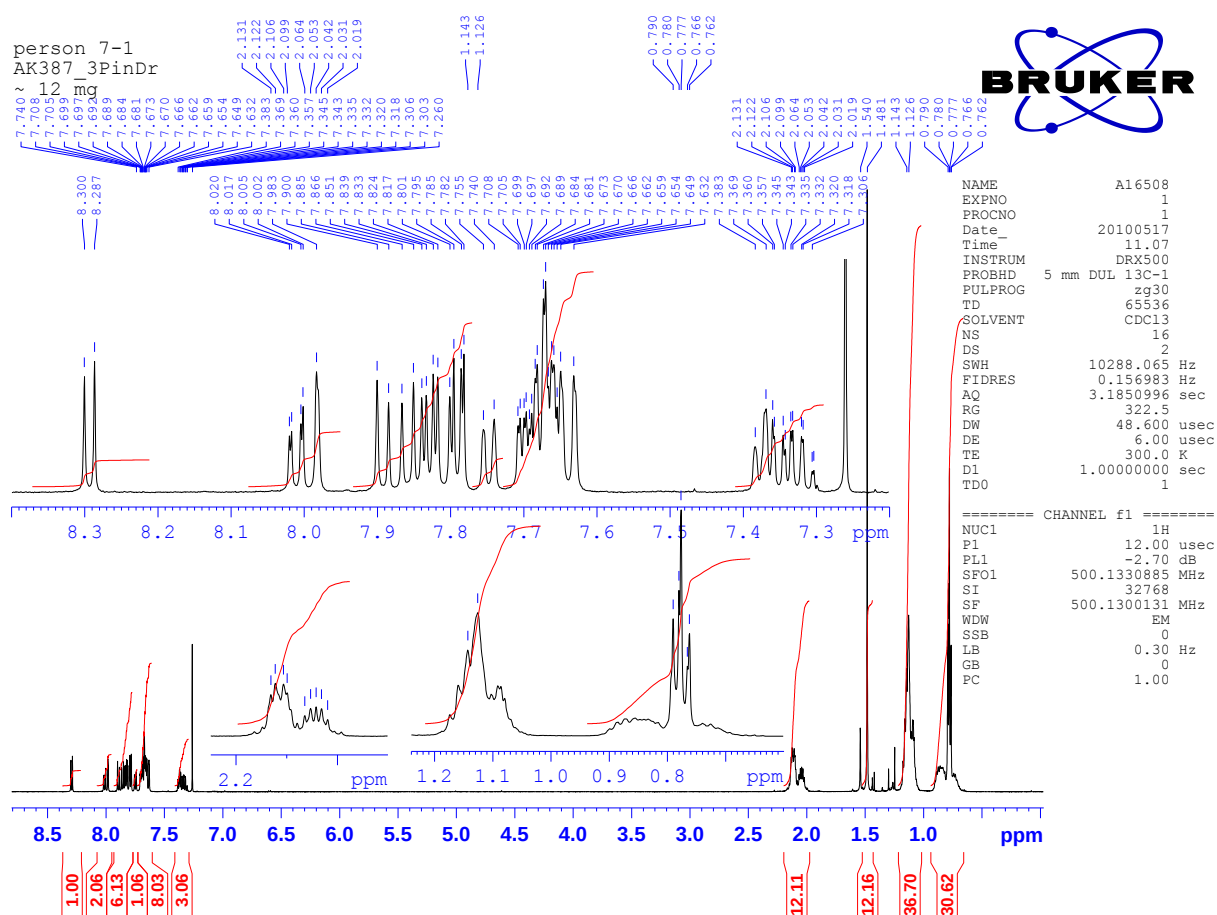
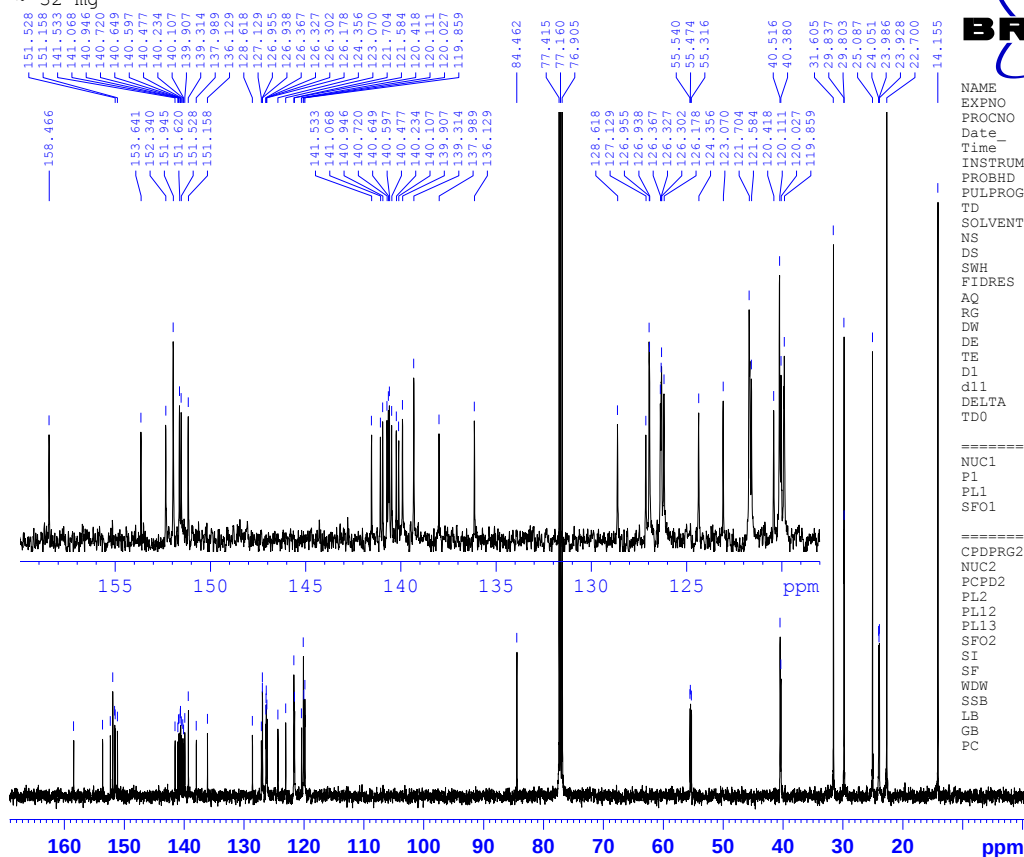


Figure S45 - ^1H NMR of compound FI_3BTBE

person 7-1
AK387_3PinDr
~ 32 mg



NAME A16513
EXPNO 1
PROCNO 1
Date_ 20100517
Time 12.40
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PROBHD 5 mm DUL 13C-1
PULPROG zgpg30
TD 16384
SOLVENT CDC13
NS 1024
DS 4
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.2720244 sec
RG 13004
DW 16.600 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TDO 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 -2.30 dB
SFO1 125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.30 dB
PL12 15.00 dB
PL13 120.00 dB
SFO2 500.1320005 MHz
SI 32768
SF 125.7577724 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure S46 - ^{13}C NMR of compound FI₃BTBE

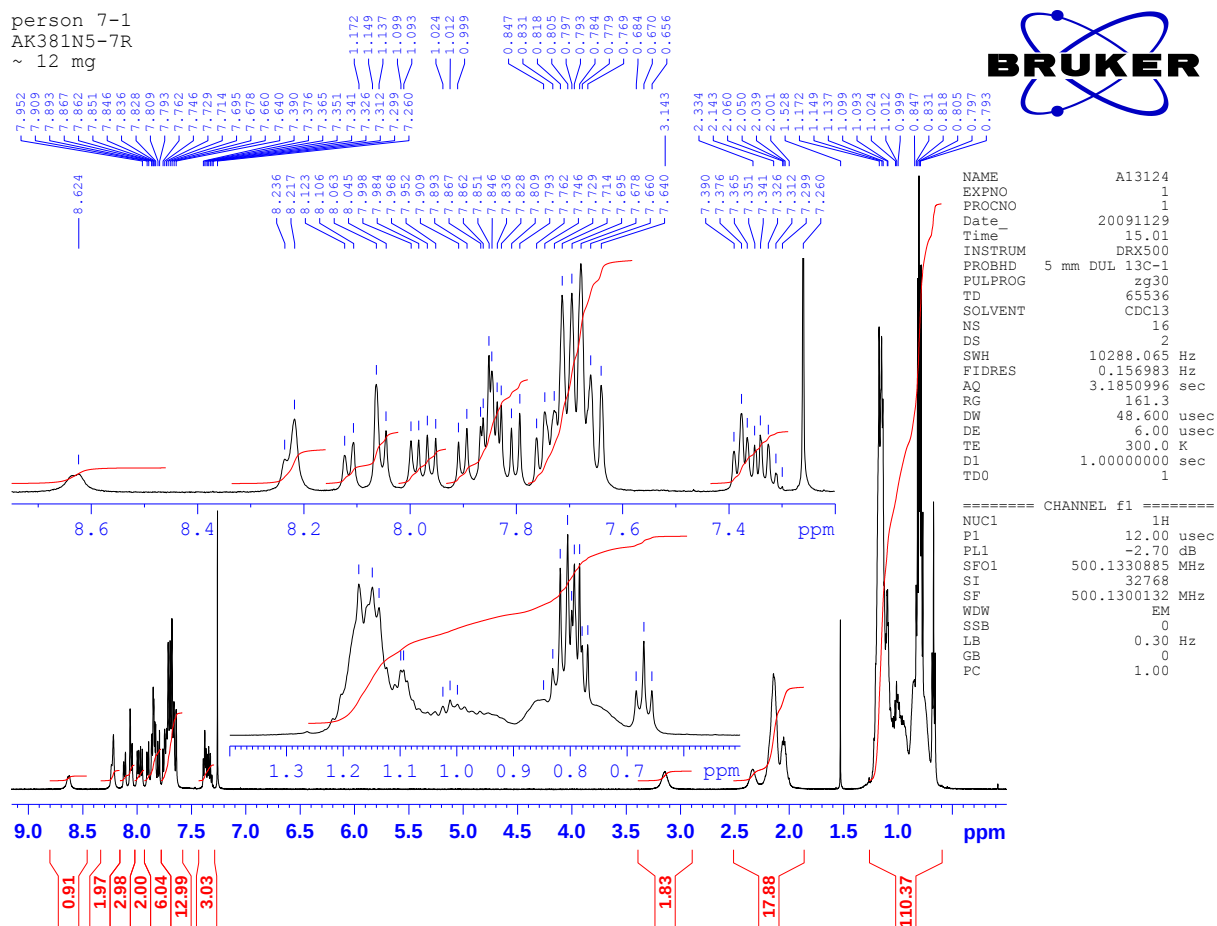


Figure S47 - ^1H NMR of compound T4BTA

person 7-1
AK381N5-7R
~ 32 mg

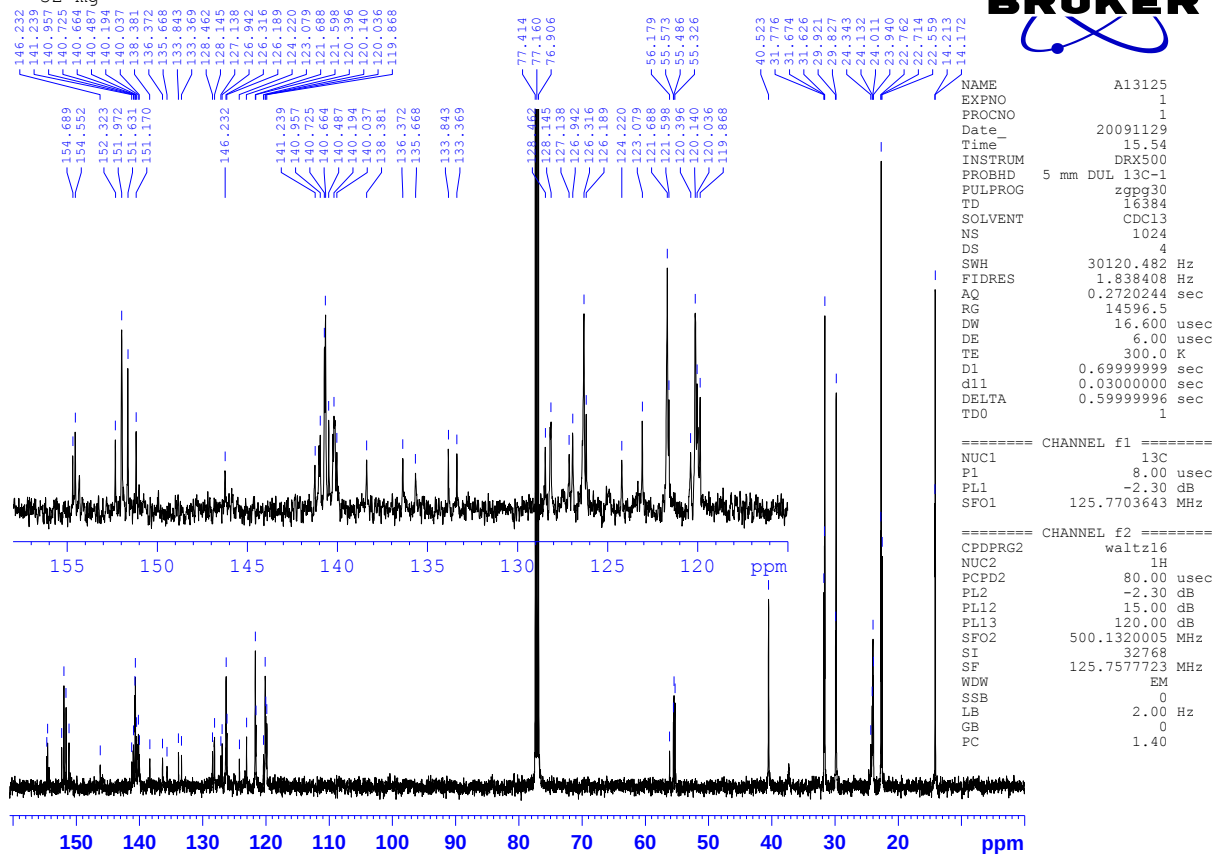


Figure S48 - ^{13}C NMR of compound T4BTA

Person 7-1
AK387BT8

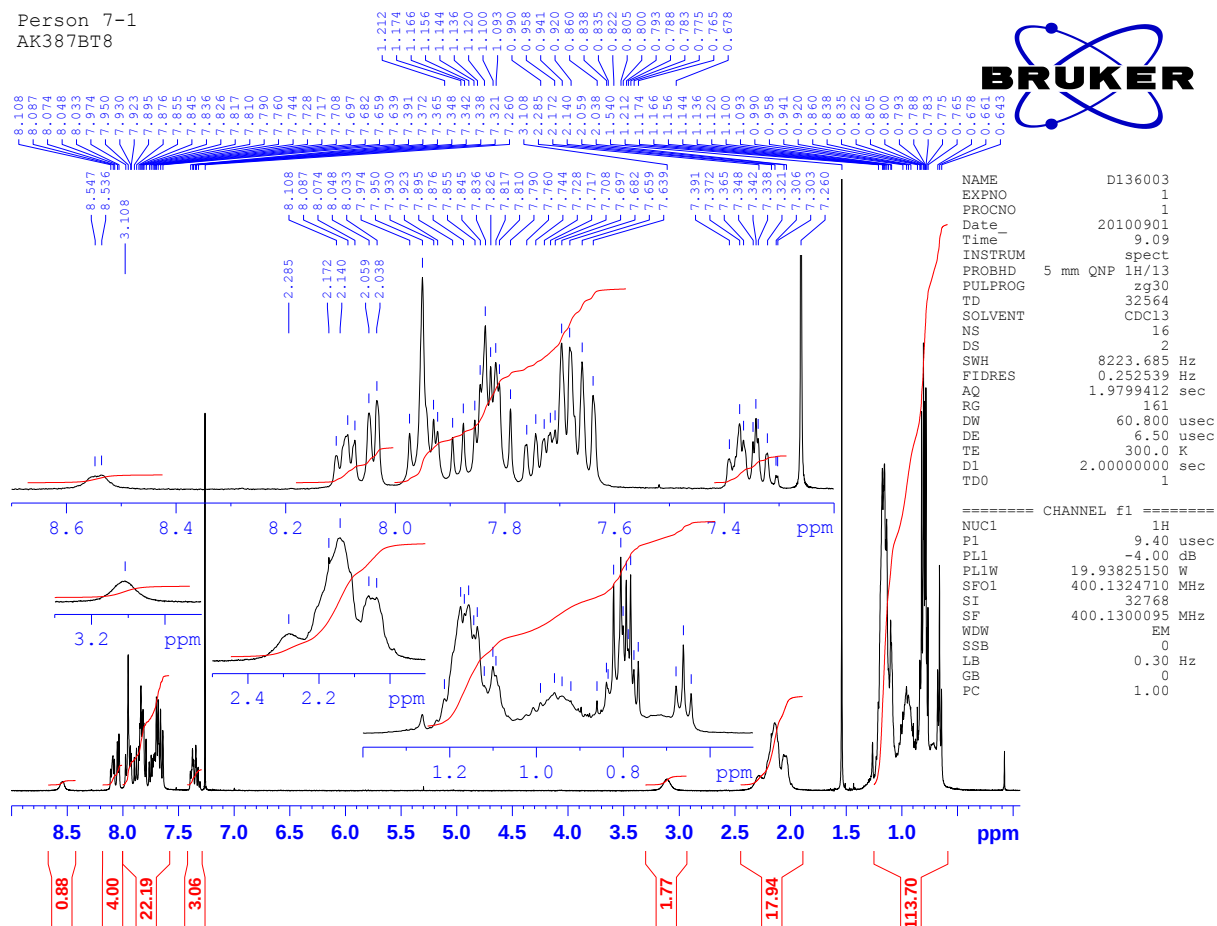


Figure S49 - ^1H NMR of compound T4BTB

Person 7-2
AK401B3F1R

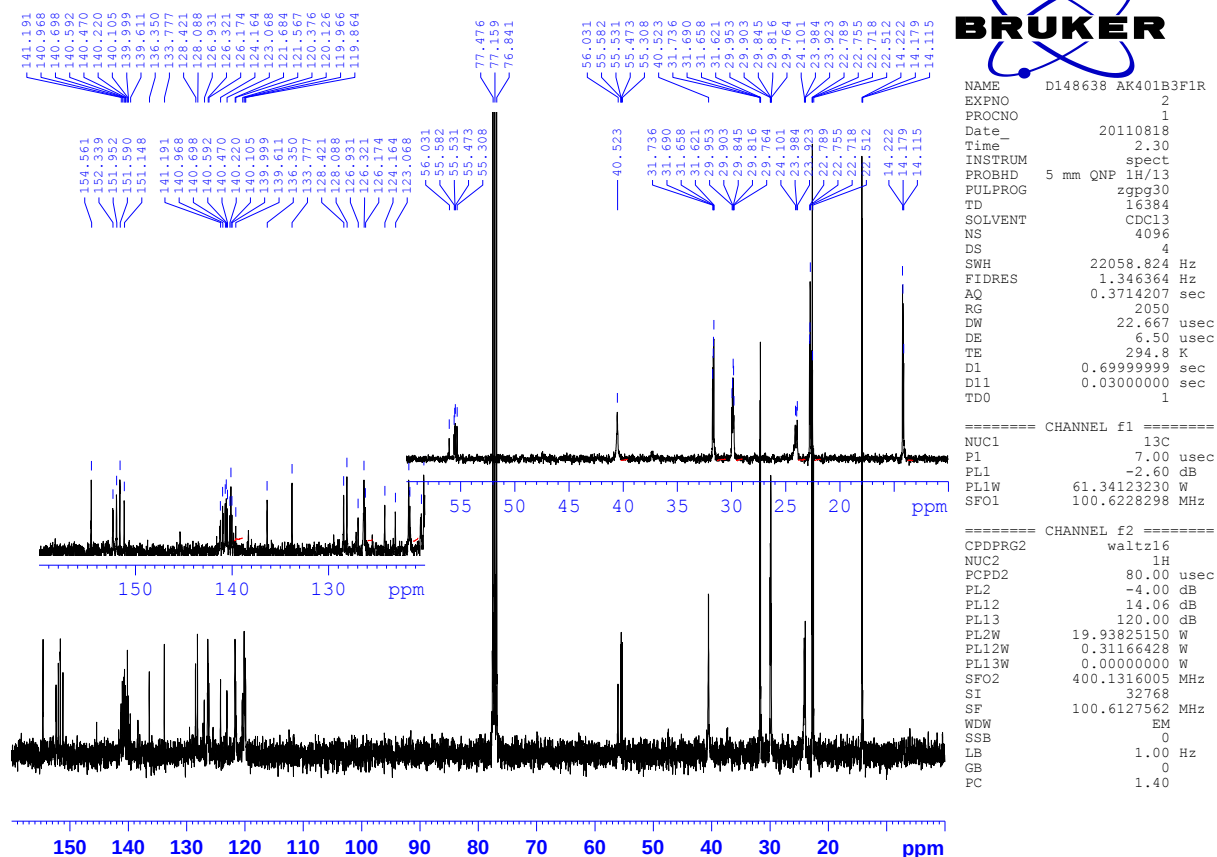


Figure S50 - ^{13}C NMR of compound T4BTB

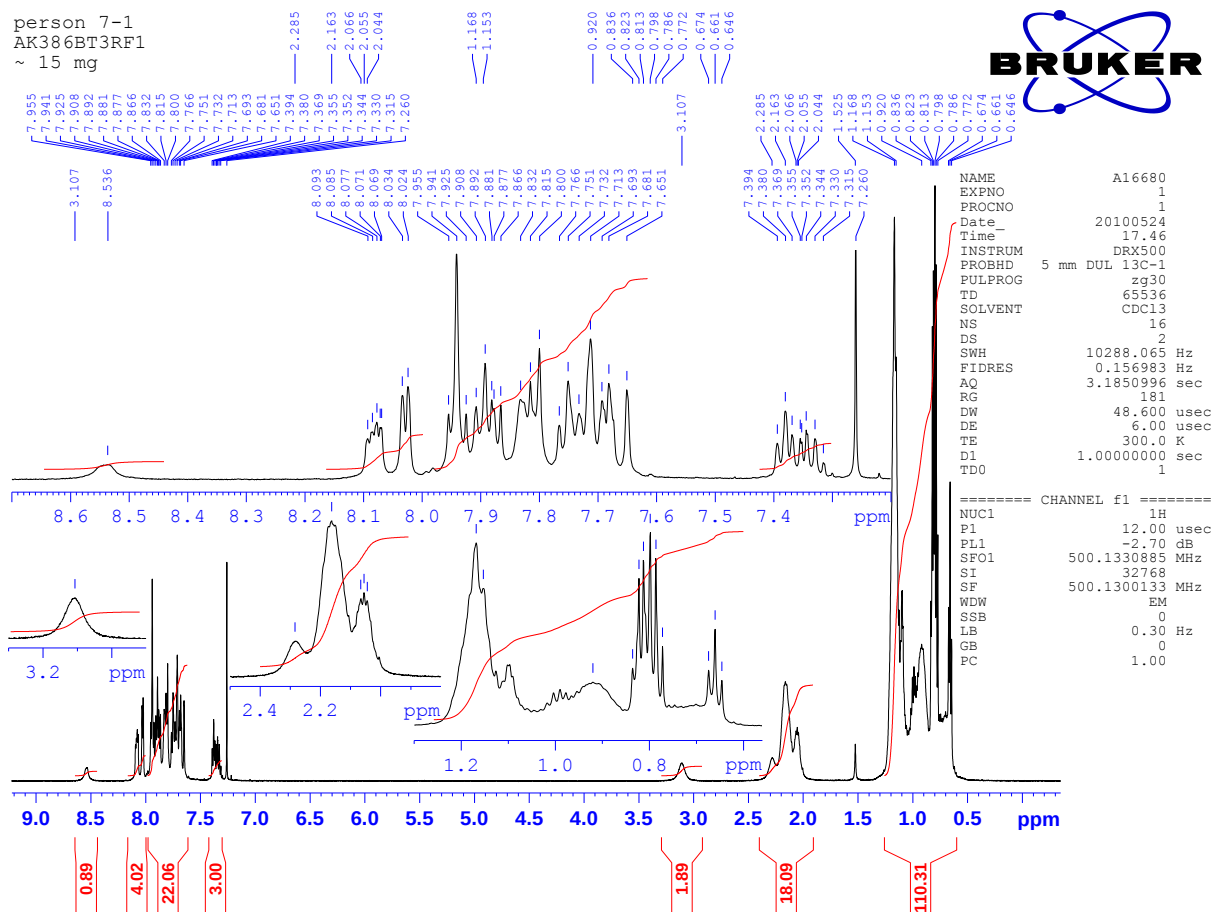


Figure S51 - ^1H NMR of compound T4BTC

person 7-4
AK386BT3RF1
~ 30 mg

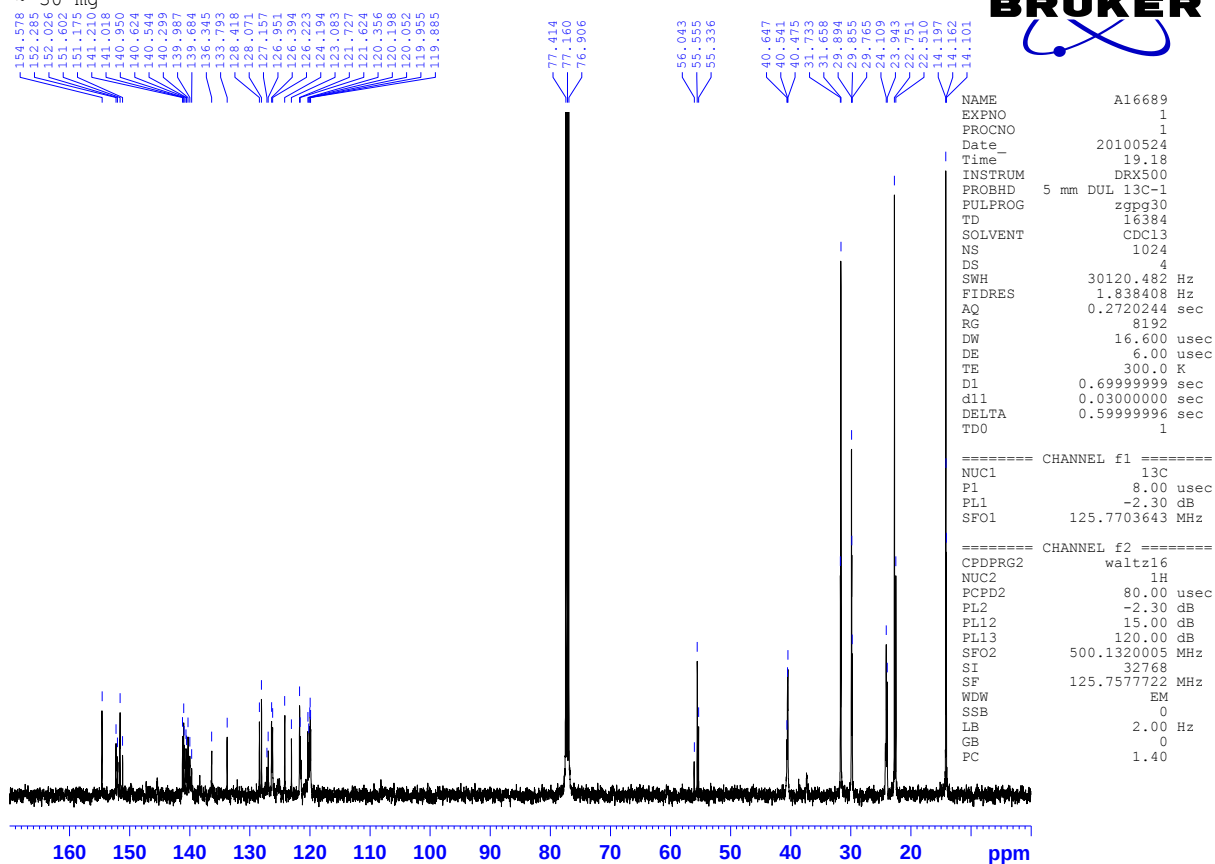


Figure S52 - ^{13}C NMR of compound T4BTC

T4BT-D

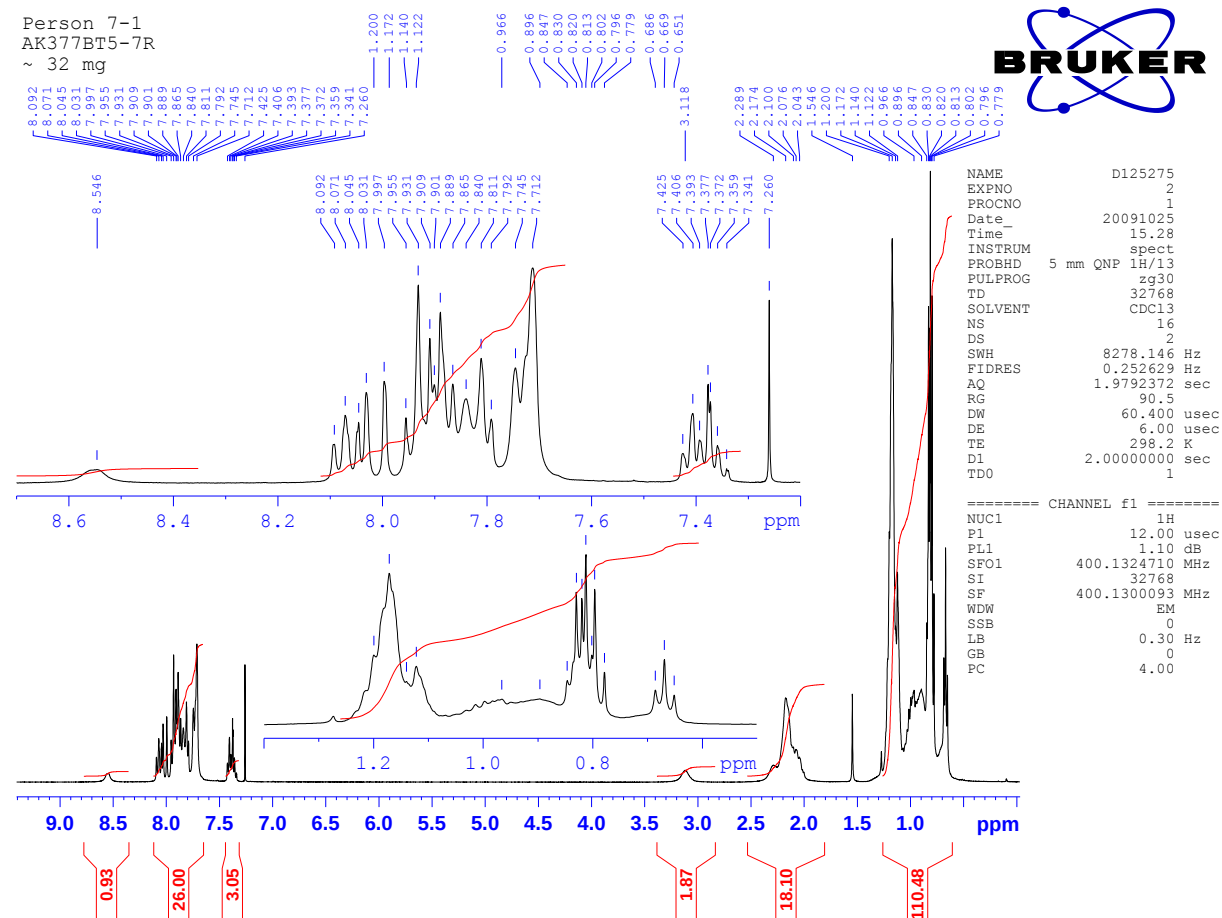


Figure S53 - ^1H NMR of compound T4BT-D

Person 7-1
AK377BT5-7R
~ 32 mg

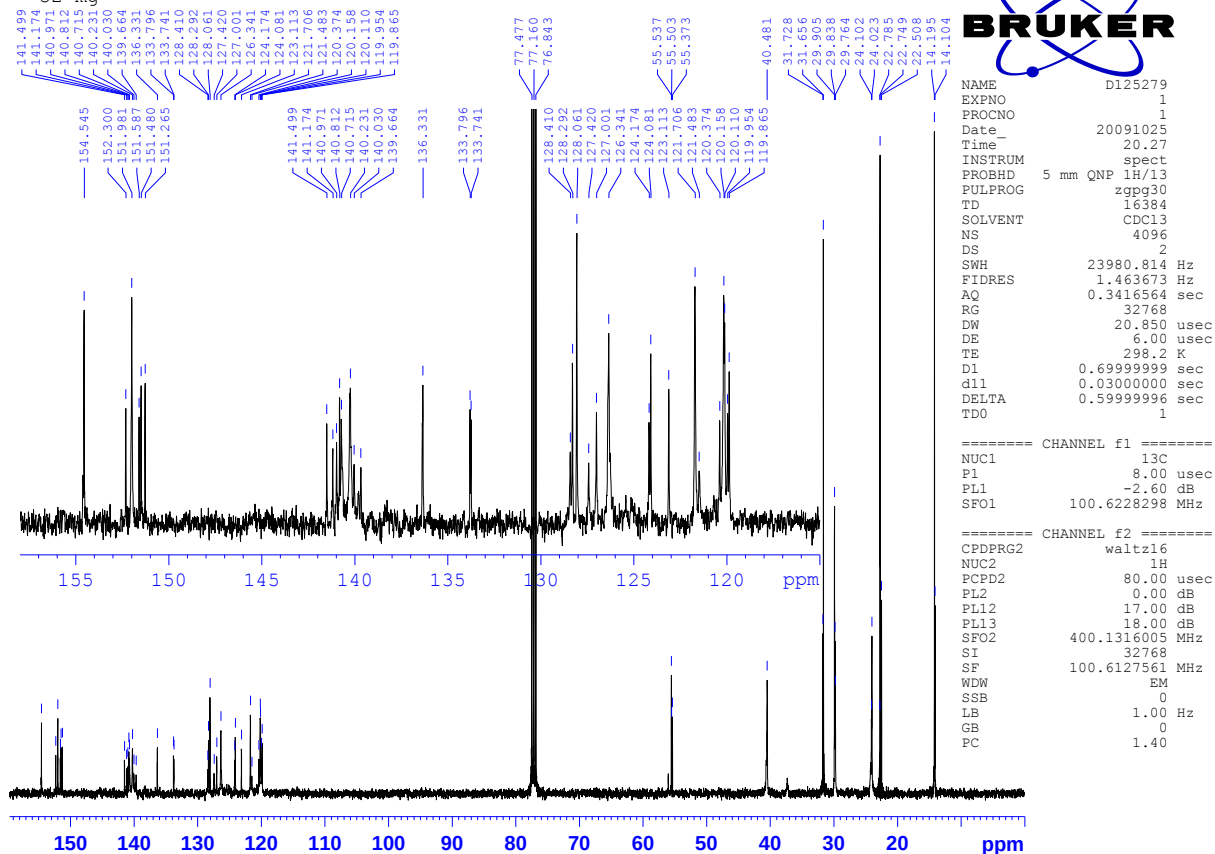


Figure S54 - ¹³C NMR of compound T4BTD

T4BT-E

person 7-1
AK372RC3

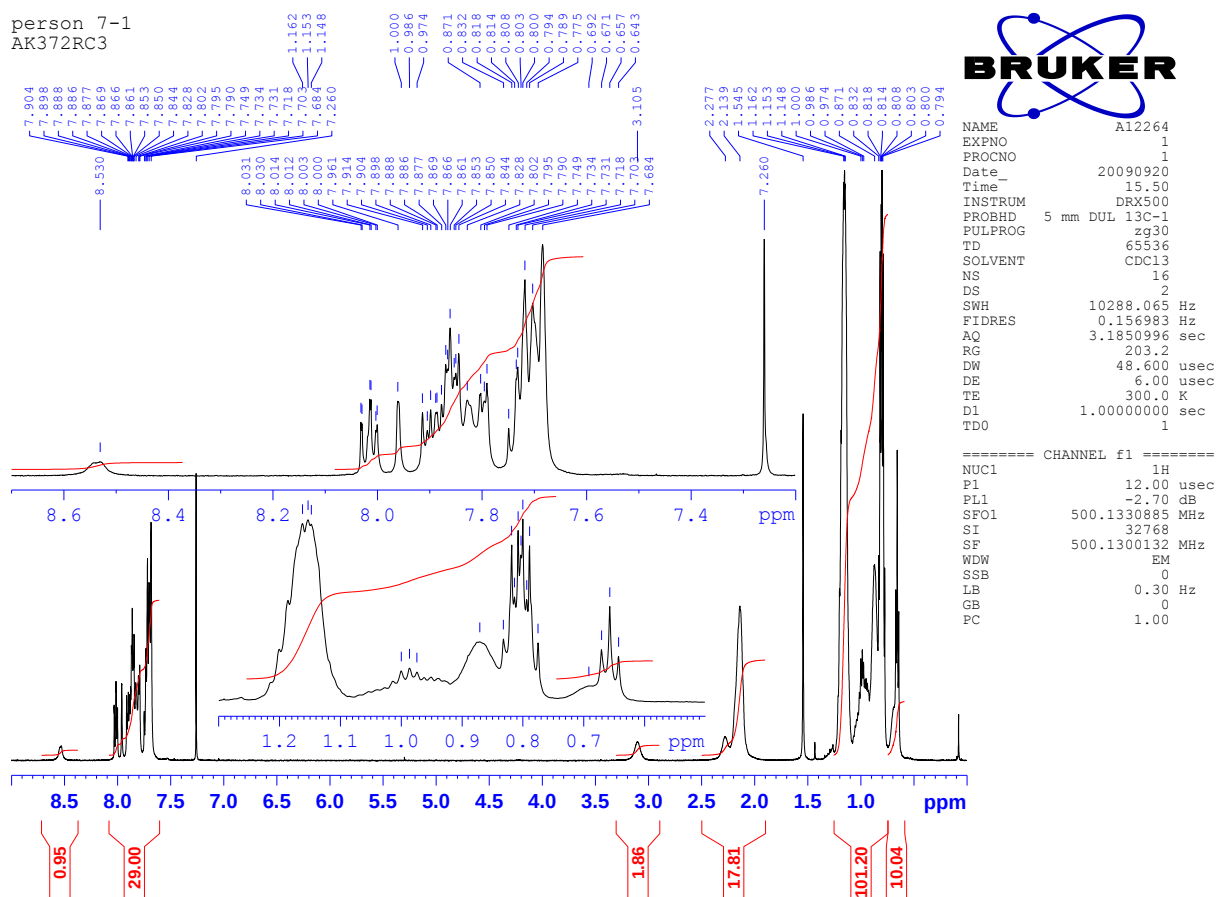
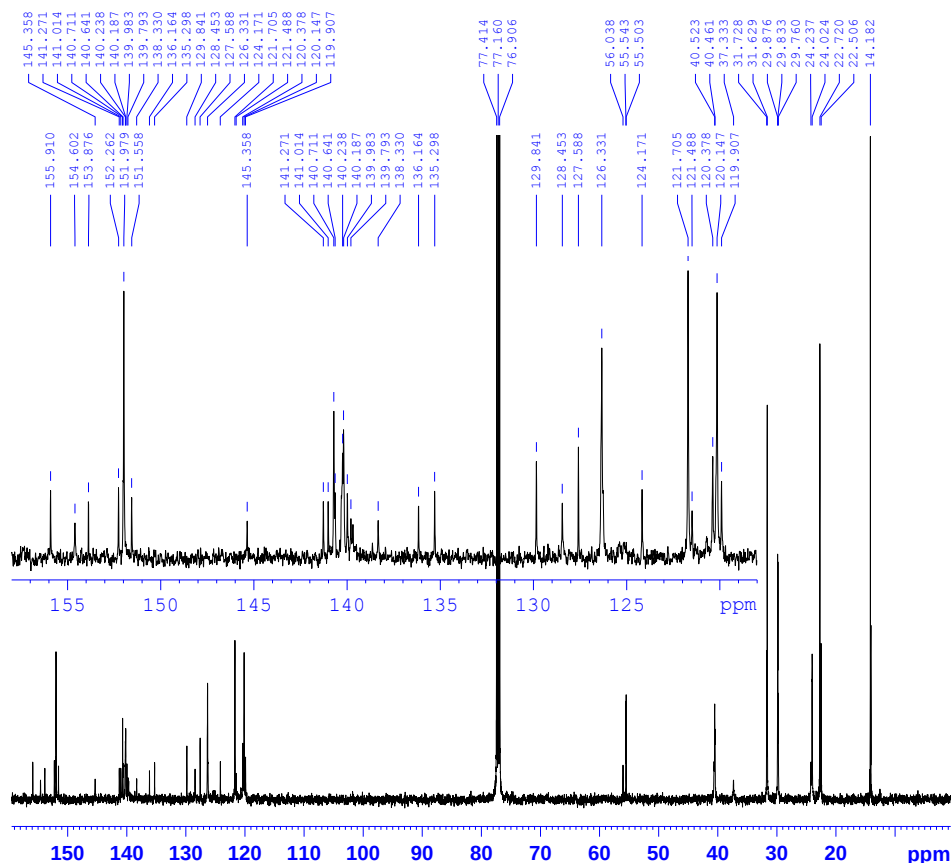


Figure S55 - ^1H NMR of compound T4BTE

person 7-1
AK357C3



Current Data Parameters
NAME A10855
EXPNO 1
PROCNO 1

F2 - Acquisition Parameters
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Time_ 6.37
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PULPROG zgpg30
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SOLVENT CDC13
NS 4096
DS 4
SWH 30120.482 Hz
FIDRES 1.838408 Hz
AQ 0.2720244 sec
RG 6502
DW 16.600 usec
DE 6.00 usec
TE 300.0 K
D1 0.69999999 sec
d11 0.03000000 sec
DELTA 0.59999996 sec
TD0 1

===== CHANNEL f1 =====
NUC1 13C
P1 8.00 usec
PL1 -2.30 dB
SFO1 125.7703643 MHz

===== CHANNEL f2 =====
CPDPRG2 waltz16
NUC2 1H
PCPD2 80.00 usec
PL2 -2.30 dB
PL12 15.00 dB
PL13 120.00 dB
SFO2 500.1320005 MHz

F2 - Processing parameters
SI 32768
SF 125.7577713 MHz
WDW EM
SSB 0
LB 2.00 Hz
GB 0
PC 1.40

Figure S56 - ^{13}C NMR of compound T4BTE