Electronic Supplementary Material (ESI) for RSC Advances.


# Supporting Information

## Synthesis, structure and properties of polysubstituted benzo[g]chrysene by $FeCl_3$-promoted from diphenylacetypene and phenylacetaldehyde derivatives

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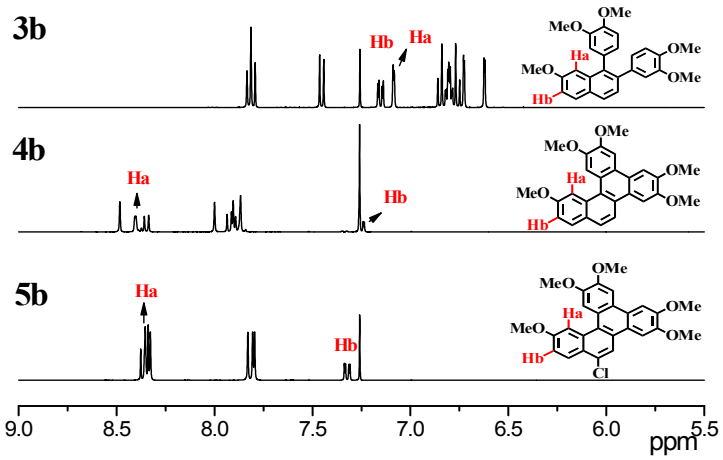


Figure S1. $^{1}$H NMR spectral of **3b**, **4b** and **5b** in $CDCl_3$

The DSC traces of the BgCh derivatives with hexyloxy alkoxy chains are shown in figure s2 and the heating / cooling rate is 10 °C /min under nitrogenatmosphere in commonly. The phase transition temperatures and enthalpy changes for studying compounds are summarized in Table S1. The peak temperatures are given in °C and the numbers in square brackets indicate the transition enthalpy ($\Delta H$) in kJ mol$^{-1}$.

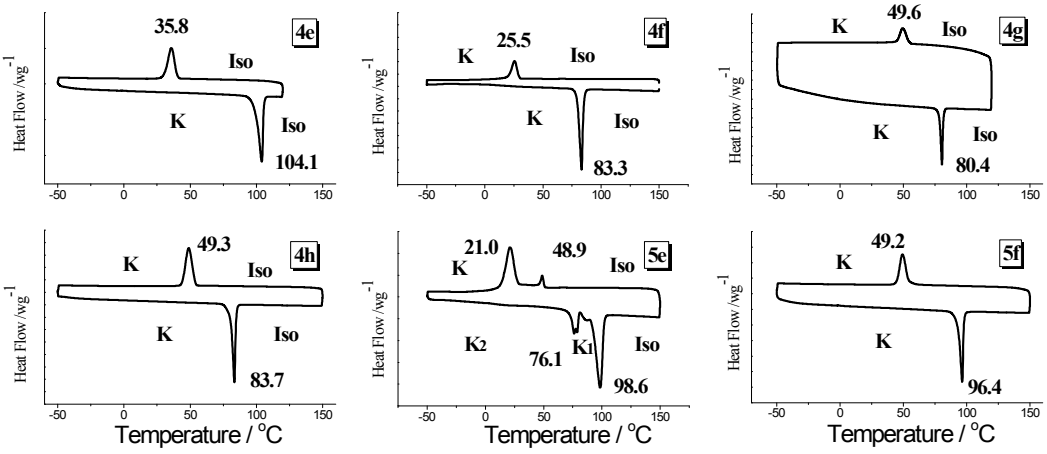


Figure S2. The DSC trances of the BgCh [4e~4h, 5e, 5f] with hexyloxy alkoxy chains. All the solid lines, except 5bd-2, were recorded on the second heating and first cooling circles at 10 °C / min.

Table S1 Transition temperatures and associated enthalpy values of the BgCh derivatives with hexyloxy alkoxy chains [4e~4h, 5e~5h].

| compounds | Transitions[ab] T/°C [$\Delta H$ / kJ mol$^{-1}$] | |
|---|---|---|
| | Heating | Cooling |
| 4e | K – 104.1 [68.2] – Iso | Iso – 35.8 [41.5] – K |
| 4f | K – 83.3 [61.3] – Iso | Iso – 25.5 [29.6] – K |
| 4g | K – 80.4 [50.8] – Iso | Iso – 49.6 [33.8] – K |
| 4h | K – 83.7 [63.9] – Iso | Iso – 49.3 [52.5] – K |
| 5e | $K_2$ – 76.1 [10.7] – $K_1$ – 98.6 [31.9] – Iso | Iso – 48.9 [2.2] – $Col_h$ – 21.0 [25.3] – K |
| 5f | K – 96.4 [55.2] – Iso | Iso – 49.2 [41.5] – K |
| 5g | K - 91.5 [61.2] – Iso | Iso – 36.4 [11.5] – K |
| | | Iso – 34.3 [2.7] – Sp – -2.23 – g[c] |
| 5h | $Col_{rp}$ – 44.3 [11.6] – $K_2$ – 57.6 [32.7] – $K_1$ – 86.0 [55.8] – $Col_h$ – 115.5 [4.5] – Iso | Iso – 112.4 [4.4] – $Col_h$ – 35.3 [5.9] – $Col_{rp}$ |
| | K - 88.9 [63.7] – $Col_h$ – 115.5 [4.2] – Iso[d] | |

[a] K = Crystal; $Col_h$ = hexagonal columnar phase; $Col_{rp}$ = Rectangular Columnar plastic phase; Iso = Isotropic Liquid; Sp = spherulite. [b] Transitions determined by DSC (peak temperature) during the second heating and first cooling at 10 °C / min. [c] The cooling rate is 25 °C / min. [d] DSC trance on the first heating at 10 °C / min.

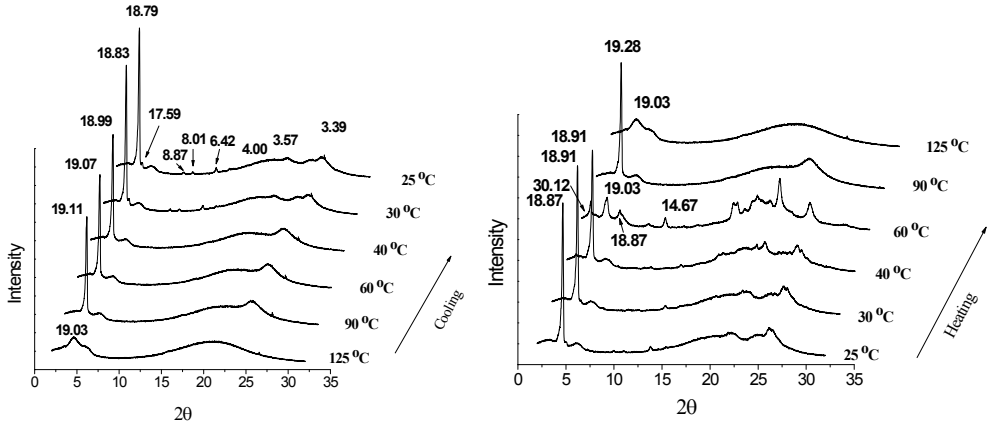


Figure S3. Temperature-dependent XRD diffraction of 5h scans from 25 to 130 °C on heating and cooling.

## Molecular Geometry and Energy of the Electron-deficient Compound 4a

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Using Gaussian 09, Revision A02, Gaussian, Inc., Wallingford C. T, 2009.

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# B3LYP/6-31G* opt(noeigen) freq=noraman test

#N Geom=AllCheck Guess=TCheck SCRF=Check Test GenChk UB3LYP/6-31G(d) Freq

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Charge = 1 Multiplicity = 2

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Optimization completed.

| Item | Value | Threshold | Converged? |
|---|---|---|---|
| Maximum Force | 0.000009 | 0.000450 | YES |
| RMS Force | 0.000002 | 0.000300 | YES |
| Maximum Displacement | 0.001605 | 0.001800 | YES |
| RMS Displacement | 0.000347 | 0.001200 | YES |

Predicted change in Energy=-9.759886D-09

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| Center Number | Atomic Number | Atomic Type | Coordinates (Angstroms) X | Y | Z |
|---|---|---|---|---|---|
| 1 | 6 | 0 | -0.320374 | 3.863488 | -0.738412 |
| 2 | 6 | 0 | 0.698948 | 2.953786 | -0.732121 |
| 3 | 6 | 0 | 0.497736 | 1.606325 | -0.310933 |
| 4 | 6 | 0 | -0.846456 | 1.178704 | -0.010040 |
| 5 | 6 | 0 | -1.853190 | 2.201152 | 0.237168 |
| 6 | 6 | 0 | -1.602637 | 3.539510 | -0.194120 |
| 7 | 6 | 0 | 1.591994 | 0.679973 | -0.187665 |
| 8 | 6 | 0 | -1.131341 | -0.226440 | -0.022769 |
| 9 | 6 | 0 | -0.055068 | -1.169844 | 0.052568 |
| 10 | 6 | 0 | 1.329623 | -0.692267 | 0.080136 |
| 11 | 6 | 0 | -0.364160 | -2.524869 | 0.070875 |
| 12 | 1 | 0 | 0.407116 | -3.281511 | 0.144668 |
| 13 | 6 | 0 | -1.676299 | -3.015210 | -0.034880 |
| 14 | 6 | 0 | -2.745354 | -2.080942 | -0.228488 |
| 15 | 6 | 0 | -2.451141 | -0.732460 | -0.210996 |
| 16 | 1 | 0 | 1.672530 | 3.259767 | -1.094304 |
| 17 | 6 | 0 | 2.943627 | 1.109607 | -0.251580 |
| 18 | 6 | 0 | 4.012757 | 0.255443 | -0.049809 |
| 19 | 6 | 0 | 3.743329 | -1.118146 | 0.245618 |
| 20 | 6 | 0 | 2.408272 | -1.545960 | 0.298149 |
| 21 | 1 | 0 | 3.156289 | 2.154384 | -0.425597 |
| 22 | 1 | 0 | 2.266938 | -2.595183 | 0.526749 |
| 23 | 6 | 0 | -2.582577 | 4.535263 | -0.015297 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 6 | 0 | -3.041227 | 1.964964 | 0.968683 |
| 25 | 6 | 0 | -3.980544 | 2.969809 | 1.166375 |
| 26 | 6 | 0 | -3.770372 | 4.253606 | 0.644505 |
| 27 | 1 | 0 | -2.381394 | 5.540072 | -0.376686 |
| 28 | 1 | 0 | -4.873573 | 2.760321 | 1.747529 |
| 29 | 1 | 0 | -4.513197 | 5.031866 | 0.789249 |
| 30 | 8 | 0 | -3.976334 | -2.600649 | -0.458831 |
| 31 | 8 | 0 | -1.765503 | -4.345449 | 0.003295 |
| 32 | 8 | 0 | 4.633448 | -2.086501 | 0.489130 |
| 33 | 8 | 0 | 5.315351 | 0.631547 | -0.093033 |
| 34 | 6 | 0 | -5.064025 | -1.712249 | -0.714533 |
| 35 | 1 | 0 | -5.241798 | -1.050085 | 0.141076 |
| 36 | 1 | 0 | -4.882278 | -1.115586 | -1.616075 |
| 37 | 1 | 0 | -5.933750 | -2.351098 | -0.868231 |
| 38 | 6 | 0 | -2.997354 | -5.096126 | 0.033364 |
| 39 | 1 | 0 | -2.678044 | -6.125226 | 0.197531 |
| 40 | 1 | 0 | -3.636127 | -4.761193 | 0.852255 |
| 41 | 1 | 0 | -3.526395 | -5.007860 | -0.916018 |
| 42 | 6 | 0 | 6.064387 | -1.916816 | 0.509414 |
| 43 | 1 | 0 | 6.432950 | -1.593724 | -0.465310 |
| 44 | 1 | 0 | 6.361360 | -1.201790 | 1.278039 |
| 45 | 1 | 0 | 6.446486 | -2.909471 | 0.748271 |
| 46 | 6 | 0 | 5.633185 | 1.990207 | -0.390696 |
| 47 | 1 | 0 | 5.236020 | 2.666292 | 0.375928 |
| 48 | 1 | 0 | 6.722021 | 2.042575 | -0.392704 |
| 49 | 1 | 0 | 5.250088 | 2.277884 | -1.377084 |
| 50 | 1 | 0 | -3.244552 | -0.030584 | -0.420136 |
| 51 | 1 | 0 | -3.199754 | 1.002218 | 1.439394 |
| 52 | 1 | 0 | -0.147046 | 4.873300 | -1.100149 |

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Statistical Thermodynamic Analysis

Temperature= 298.150 Kelvin Pressure= 1.00000 Atm

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SCF Done: *E*(B3LYP) = -1304.663571

Sum of electronic and zero-point Energies= -1304.244290

Sum of electronic and thermal Energies= -1304.218253

Sum of electronic and thermal Enthalpies= -1304.217308

Sum of electronic and thermal Free Energies= -1304.301474

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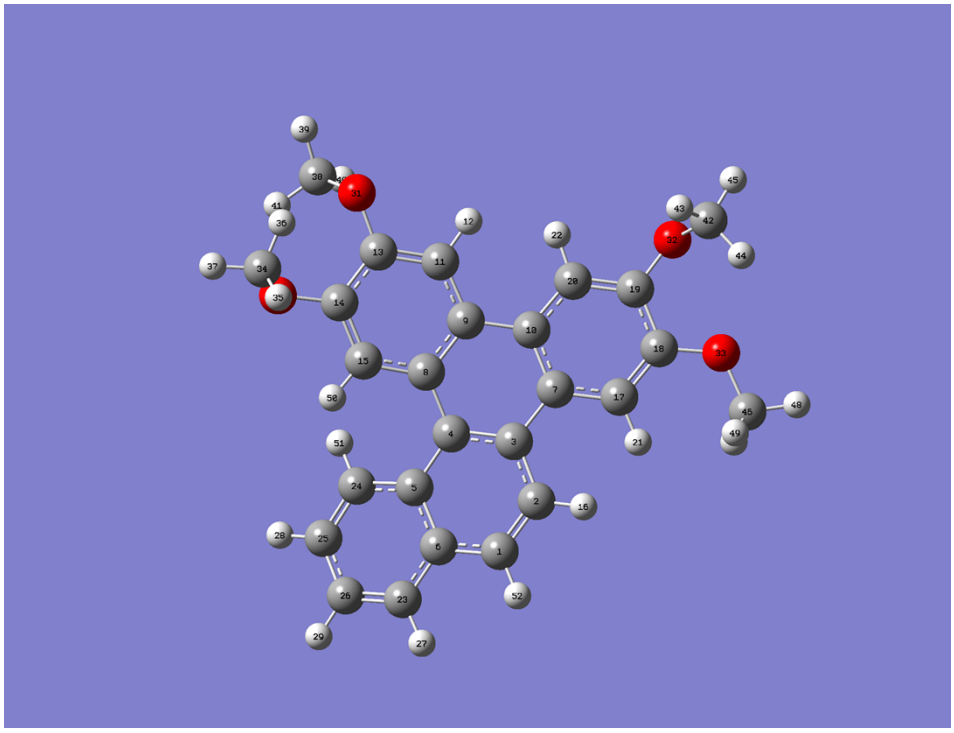
Frequencies -- 19.8648 27.6147 39.7156



Natural Population

| Atom | No | Natural Charge | Core | Valence | Rydberg | Total |
|---|---|---|---|---|---|---|
| C | 1 | -0.19317 | 1.99904 | 4.17434 | 0.01979 | 6.19317 |
| C | 2 | -0.20925 | 1.99907 | 4.19142 | 0.01876 | 6.20925 |
| C | 3 | -0.02930 | 1.99902 | 4.01163 | 0.01865 | 6.02930 |
| C | 4 | 0.00335 | 1.99902 | 3.97878 | 0.01885 | 5.99665 |
| C | 5 | -0.03605 | 1.99902 | 4.01882 | 0.01820 | 6.03605 |
| C | 6 | -0.05551 | 1.99902 | 4.03768 | 0.01881 | 6.05551 |
| C | 7 | -0.01966 | 1.99904 | 4.00140 | 0.01922 | 6.01966 |
| C | 8 | -0.04247 | 1.99903 | 4.02531 | 0.01813 | 6.04247 |
| C | 9 | -0.02384 | 1.99904 | 4.00607 | 0.01873 | 6.02384 |
| C | 10 | -0.04668 | 1.99903 | 4.02906 | 0.01860 | 6.04668 |
| C | 11 | -0.24166 | 1.99899 | 4.22447 | 0.01820 | 6.24166 |
| H | 12 | 0.23904 | 0.00000 | 0.75984 | 0.00112 | 0.76096 |
| C | 13 | 0.30927 | 1.99862 | 3.66357 | 0.02854 | 5.69073 |
| C | 14 | 0.29617 | 1.99861 | 3.67687 | 0.02836 | 5.70383 |
| C | 15 | -0.24399 | 1.99900 | 4.22583 | 0.01916 | 6.24399 |
| H | 16 | 0.22394 | 0.00000 | 0.77515 | 0.00091 | 0.77606 |
| C | 17 | -0.30021 | 1.99903 | 4.28522 | 0.01597 | 6.30021 |
| C | 18 | 0.34325 | 1.99867 | 3.63194 | 0.02614 | 5.65675 |
| C | 19 | 0.31252 | 1.99867 | 3.65893 | 0.02988 | 5.68748 |
| C | 20 | -0.22580 | 1.99900 | 4.20876 | 0.01804 | 6.22580 |

| | | | | | | |
|---|---|---|---|---|---|---|
| H | 21 | 0.22756 | 0.00000 | 0.77129 | 0.00115 | 0.77244 |
| H | 22 | 0.23919 | 0.00000 | 0.75970 | 0.00111 | 0.76081 |
| C | 23 | -0.20503 | 1.99906 | 4.18672 | 0.01925 | 6.20503 |
| C | 24 | -0.21427 | 1.99908 | 4.19583 | 0.01936 | 6.21427 |
| C | 25 | -0.22757 | 1.99908 | 4.20812 | 0.02037 | 6.22757 |
| C | 26 | -0.22453 | 1.99907 | 4.20513 | 0.02033 | 6.22453 |
| H | 27 | 0.22821 | 0.00000 | 0.77111 | 0.00068 | 0.77179 |
| H | 28 | 0.23296 | 0.00000 | 0.76656 | 0.00047 | 0.76704 |
| H | 29 | 0.23215 | 0.00000 | 0.76738 | 0.00047 | 0.76785 |
| O | 30 | -0.63352 | 1.99975 | 6.61875 | 0.01502 | 8.63352 |
| O | 31 | -0.63258 | 1.99975 | 6.61778 | 0.01505 | 8.63258 |
| O | 32 | -0.62326 | 1.99975 | 6.60814 | 0.01538 | 8.62326 |
| O | 33 | -0.60859 | 1.99973 | 6.59330 | 0.01555 | 8.60859 |
| C | 34 | -0.23460 | 1.99943 | 4.21842 | 0.01675 | 6.23460 |
| H | 35 | 0.18748 | 0.00000 | 0.81139 | 0.00113 | 0.81252 |
| H | 36 | 0.20143 | 0.00000 | 0.79695 | 0.00163 | 0.79857 |
| H | 37 | 0.20365 | 0.00000 | 0.79580 | 0.00055 | 0.79635 |
| C | 38 | -0.23496 | 1.99943 | 4.21876 | 0.01677 | 6.23496 |
| H | 39 | 0.20431 | 0.00000 | 0.79515 | 0.00054 | 0.79569 |
| H | 40 | 0.18738 | 0.00000 | 0.81147 | 0.00115 | 0.81262 |
| H | 41 | 0.20211 | 0.00000 | 0.79627 | 0.00162 | 0.79789 |
| C | 42 | -0.23120 | 1.99943 | 4.21511 | 0.01667 | 6.23120 |
| H | 43 | 0.18116 | 0.00000 | 0.81761 | 0.00123 | 0.81884 |
| H | 44 | 0.20152 | 0.00000 | 0.79729 | 0.00119 | 0.79848 |
| H | 45 | 0.20422 | 0.00000 | 0.79523 | 0.00055 | 0.79578 |
| C | 46 | -0.23772 | 1.99945 | 4.21947 | 0.01880 | 6.23772 |
| H | 47 | 0.19092 | 0.00000 | 0.80777 | 0.00130 | 0.80908 |
| H | 48 | 0.21518 | 0.00000 | 0.78442 | 0.00040 | 0.78482 |
| H | 49 | 0.18659 | 0.00000 | 0.81209 | 0.00132 | 0.81341 |
| H | 50 | 0.25128 | 0.00000 | 0.74752 | 0.00120 | 0.74872 |
| H | 51 | 0.24155 | 0.00000 | 0.75760 | 0.00085 | 0.75845 |
| H | 52 | 0.22905 | 0.00000 | 0.77029 | 0.00066 | 0.77095 |

## Experimental Section

**General methods:**

$^{1}H$ NMR and $^{13}C$ NMR spectra were recorded at room temperature on a Varian 400 spectrometer. Chemical shifts are given in ppm (δ) relative to tetramethylsilane (TMS). The NMR data of compounds 4a~4h were achieved from method two and the NMR chemical shift data and spectra of compounds 4a~4h from method one as shown at the end of the detail experiment section. Multistage mass was run on Thermal LCQ fleet with ion trap. Elemental analysis was carried out on an EA3000 CHN analyzer. The liquid crystalline properties were studied using an Olympus BX41 polarising optical microscopy (POM) with crossed polarizers and a Linkam T95-PE hot stage. Differential scanning calorimetry was performed on TA 100, and the X-ray diffraction (XRD) was carried out on a Rigaku Smart Lab (3) with a hot accessory. UV/Vis absorption spectra were recorded on a Perkin Elmer Lambda 850 spectrophotometer. Fluorescence spectra were recorded on a HORIBA Fluoromax-4p.

The intermediate materials of diphenylacetylene and phenylacetaldehyde derivatives were synthesized according to literatures procedure. All solvents were of AR quality, and chemicals were used as received.

**General synthesis procedure for 3a-3h**

1 equiv diphenylacetypene derivatives (**1a~1b**) and 1.2 equiv hyacinthin derivatives (**2a~2e**) were dissolved in DCE, then 0.6-2 equiv $FeCl_3$ was added and the mixture was stirred at room temperature until the derivatives of diphenylacetypene disappeared by thin layer chromatography (TLC) detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization.

**Compound 3a**. 1, 2-bis(3,4-dimethoxyphenyl)ethyne **1a** (268 mg, 0.9 mmol), 2-phenylacetal dehyde **2a** (132 mg, 1.1 mmol), $FeCl_3$ (179 mg, 1.1 mmol) and DCE 11 mL. Yield: 245 mg (68%) of light yellow powder. $^{1}H$ NMR (400MHz, $CDCl_3$): 7.91 (d, $J$ = 8.4Hz, 2H), 7.77 (d, $J$ = 8.4 Hz, 1H), 7.60 (d, $J$ = 8.4 Hz, 1H), 7.48 (td, $J$ = 7.4 Hz, $J$ = 0.8 Hz, 1H), 7.42 (td, $J$ = 7.6 Hz, $J$ = 1.2 Hz 1H), 6.76- 6.87 (m, 4H), 6.72 (sd, $J$ = 1.6 Hz, 1H), 6.64 (sd, $J$ = 2.0 Hz, 1H), 3.91 (s, 3H), 3.86 (s, 3H), 3.68 (s, 3H), 3.61 (s, 3H). $^{13}C$ NMR (100MHz, $CDCl_3$): 148.5, 147.9, 147.8, 147.4, 137.9, 137.1, 134.7, 132.8, 132.7, 131.7, 128.2, 127.8, 127.5, 126.7, 126.2, 125.5, 123.7, 122.1, 114.8, 113.6, 110.7, 110.47, 55.8, 55.7, 55.6. Mass (APCI, m/z), calcd for $C_{26}H_{24}O_4$: 400.17. Found: $[M+H]^+$, 401.10. Anal. Calcd for $C_{26}H_{24}O_4$: C, 77.98; H, 6.04. Found: C, 77.86; H, 5.80.

**Compound 3b**. 1,2-bis(3,4-dimethoxyphenyl)ethyne **1a** (314 mg, 1.05 mmol), 2-(4-methoxy phenyl)acetaldehyde **2b** (189 mg, 1.26 mmol), $FeCl_3$ (205 mg, 1.26 mmol), DCE 8 mL. Yield: 293 mg (65%) of light yellow powder. $^1$H NMR (400MHz, $CDCl_3$): 7.79-7.84 (m, 2H), 7.45 (d, *J* = 8.4Hz, 1H), 7.15 (dd, *J* = 8.8 Hz, *J* = 2.6Hz, 1H), 7.09 (sd, *J* = 2.4Hz 1H), 6.75-6.86 (m, 4H), 6.72 (sd, *J*= 2Hz, 1H), 6.62 (sd, *J* = 2Hz, 1H), 3.90 (s, 3H), 3.85 (s, 3H), 3.73 (s, 3H), 3.68 (s, 3H), 3.61 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 158.0, 148.6, 147.9, 147.7, 147.4, 138.6, 136.0, 135.0, 134.1, 132.0, 129.4, 128.3, 127.23, 126.1, 123.6, 122.1, 118.1, 114.8, 113.7, 110.8, 110.5, 105.4, 55.9, 55.8, 55.8, 55.6, 55.2. Mass (APCI, m/z), calcd for $C_{27}H_{26}O_5$: 430.18. Found: $[M+H]^+$, 431.26. Anal. Calcd for $C_{27}H_{26}O_5$: C, 75.33; H, 6.09. Found: C, 75.05; H, 6.07.

**Compound 3c**. 1, 2-bis(3,4-dimethoxyphenyl)ethyne **1a** (596 mg, 2.0 mmol), 2-(4-(hexyloxy) phenyl) acetaldehyde **2c** (528 mg, 2.4 mmol), $FeCl_3$ (390 mg, 2.4 mmol), DCE 15 mL. Yield: 610 mg (61%) of light yellow powder. $^1$H NMR (400MHz, $CDCl_3$): 7.78-7.83 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.15 (dd, *J* = 9.0 Hz, *J* = 2.2 Hz, 1H), 7.06 (sd, *J* = 2.0 Hz, 1H), 6.80-6.86 (m, 4H), 6.72 (sd, *J* = 1.2 Hz, 1H), 6.61 (sd, *J* = 1.6 Hz, 1H), 3.91 (s, 3H), 3.84-3.87 (m, 5H), 3.68 (s, 3H), 3.60 (s, 3H), 1.72-1.76 (m, 2H), 1.40-1.44 (m, 2H), 1.29-1.32 (m, 4H), 0.89 (t, *J* = 6.8 Hz, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.5, 148.6, 147.9, 147.7, 147.4, 138.5, 135.9, 135.0, 134.1, 132.0, 129.3, 128.2, 127.2, 125.9, 123.6, 122.1, 118.4, 114.8, 113.7, 110.8, 110.5, 106.2, 67.9, 55.9, 55.8, 55.7, 55.6, 31.6, 29.1, 25.8, 22.6, 14.0. Mass (APCI, m/z), calcd for $C_{32}H_{36}O_5$: 500.26. Found: $[M+H]^+$, 501.31. Anal. Calcd for $C_{32}H_{36}O_5$: C, 76.77; H, 7.25. Found: C, 76.57; H, 7.21.

**Compound 3d**. 1, 2-bis(3, 4-dimethoxyphenyl)ethyne **1a** (298 mg, 1.0 mmol), 2-(3,4-dimethoxy phenyl) acetaldehyde **2d** (216 mg, 1.2 mmol), $FeCl_3$ (195 mg, 1.2 mmol), DCE 10 mL. Yield: 285 mg (62%) of light yellow powder. $^1$H NMR (400MHz, $CDCl_3$): 7.75 (d, *J* = 8.4 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 1H), 7.19 (s, 1H), 7.09 (s, 1H), 6.73-6.86 (m, 5H), 6.61 (s, 1H), 4.04 (s, 1H), 3.91 (s, 1H), 3.86 (s, 1H), 3.77 (s, 1H), 3.68 (s, 1H), 3.61 (s, 1H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.5, 149.2, 148.5, 147.8, 147.6, 147.2, 136.5, 135.8, 135.1, 132.1, 128.7, 128.4, 126.6, 125.9, 123.5, 122.0, 114.6, 113.6, 110.7, 110.4, 106.2, 105.6, 55.9, 55.8, 55.8, 55.8, 55.7, 55.6. Mass (APCI, m/z), calcd for $C_{28}H_{28}O_6$: 460.19. Found: $[M+H]^+$, 461.28. Anal. Calcd for $C_{28}H_{28}O_6$: C, 73.03; H, 6.13. Found: C, 72.73; H, 6.08.

**Compound 3e**. 1, 2-bis(3, 4-bis(hexyloxy)phenyl)ethyne **1b** (289 mg, 0.5 mmol), 2-phenyl acetaldehyde **2a** (72 mg, 0.6 mmol), $FeCl_3$ (78 mg, 0.48 mmol), DCE 4 mL. Yield: 218 mg (64%) of light yellow oil. $^1$H NMR (400MHz, $CDCl_3$): 7.88 (dd, *J* = 8.8 Hz, *J* =

2.8 Hz, 1H), 1.76 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.4 Hz, 1H), 7.46 (t, *J* = 7.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 1H), 6.73-6.84 (m, 4H), 6.70 (s, 1H), 6.65 (s, 1H), 3.93-4.02 (m, 4H), 3.66-3.84 (m, 4H), 1.67-1.83 (m, 8H), 1.25-1.49 (m, 24H), 0.86-0.92 (m, 12H). $^{13}$C NMR (100MHz, $CDCl_3$): 148.6, 148.1, 147.9, 147.6, 138.0, 137.2, 134.8, 133.0, 132.7, 131.8, 128.4, 127.8, 127.3, 126.9, 126.1, 125.4, 123.8, 122.3, 117.3, 116.2, 113.1, 113.0, 69.2, 69.1, 31.7, 31.6, 31.5, 29.4, 29.3, 29.2, 29.1, 25.8, 25.7, 25.6, 22.6, 14.0. Mass (APCI, m/z), calcd for $C_{46}H_{64}O_4$: 680.48. Found: $[M+H]^+$, 681.37. Anal. Calcd for $C_{46}H_{64}O_4$: C, 81.13; H, 9.47. Found: C, 80.92; H, 9.27.

**Compound 3f**. 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (289 mg, 0.5 mmol), 2-(4-methoxy phenyl)acetaldehyde **2b** (90 mg, 0.6 mmol), $FeCl_3$ (87 mg, 0.54 mmol), DCE 4 mL. Yield: 264 mg (74%) of light yellow oil. $^1$H NMR (400MHz, $CDCl_3$): 7.77-7.81 (m, 2H), 7.44 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.08 (sd, *J* = 2.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 6.72-6.74 (m, 4H), 6.64 (s, 1H), 3.80-4.01 (m, 4H), 3.66-3.86 (m, 7H), 1.76-1.87 (m, 4H), 1.65-1.72 (m, 4H), 1.58 (s, 2H), 1.44-1.50 (m, 4H), 1.29-1.40 (m, 22H), 0.87-0.94 (m, 12H). $^{13}$C NMR (100MHz, $CDCl_3$): 156.8, 147.6, 147.0, 146.8, 146.5, 137.6, 135.1, 134.0, 133.1, 131.0, 128.3, 127.1, 126.0, 125.1, 122.7, 121.2, 116.9, 116.1, 115.1, 112.2, 112.0, 104.4, 68.1, 68.0, 54.1, 30.7, 30.6, 28.7, 28.4, 28.3, 28.2, 28.1, 24.8, 24.7, 24.6, 21.6, 21.5, 13.0. Mass (APCI, m/z), calcd for $C_{47}H_{66}O_5$: 710.49. Found: $[M+H]^+$, 711.53. Anal. Calcd for $C_{47}H_{66}O_5$: C, 79.39; H, 9.36. Found: C, 79.05; H, 9.25.

**Compound 3g**. 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (192 mg, 0.33 mmol), 2-(4-(hexyloxy)phenyl) acetaldehyde **2c** (108 mg, 0.49 mmol), $FeCl_3$ (43 mg, 0.26 mmol), DCE 4 mL. Yield: 167 mg (65%) of light yellow oil. $^1$H NMR (400MHz, $CDCl_3$): 7.77-7.80 (m, 2H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.13 (dd, *J* = 8.8 Hz, *J* = 2.0 Hz, 1H), 7.06 (s, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 6.71-6.74 (m, 4H), 6.64 (s, 1H), 3.66-4.01 (m, 10H), 1.67-1.84 (m, 10H), 1.31-1.50 (m, 30H), 0.89-0.94 (m, 15H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.3, 148.5, 147.9, 147.6, 147.4, 138.5, 136.0, 135.0, 134.1, 132.0, 129.2, 128.1, 127.0, 126.0, 123.7, 122.2, 118.3, 116.8, 115.9, 113.0, 112.8, 106.1, 69.1, 69.0, 68.9, 67.8, 31.7, 31.6, 29.4, 29.3, 29.2, 29.1, 29.0, 25.8, 25.7, 25.6, 22.6, 14.1, 14.0. Mass (APCI, m/z), calcd for $C_{52}H_{76}O_5$: 780.57. Found: $[M+H]^+$, 781.66. Anal. Calcd for $C_{52}H_{76}O_5$: C, 79.95; H, 9.81. Found: C, 79.68; H, 9.67.

**Compound 3h**. 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (289 mg, 0.5 mmol), 2-(3,4-bis (hexyloxy)phenyl) acetaldehyde **2e** (192 mg, 0.6 mmol), $FeCl_3$ (81 mg, 0.5 mmol), DCE 10 mL. Yield: 255 mg (58%) of light yellow oil. $^1$H NMR (400MHz, $CDCl_3$): 7.69

(d, $J$ = 8.4 Hz, 1H), 7.42 (d, $J$ = 8.4 Hz, 1H), 7.16 (s, 1H), 7.06 (s, 1H), 6.82 (d, $J$ = 8.4 Hz, 1H), 6.70-6.73 (m, 4H), 6.62 (s, 1H), 4.14 (t, $J$ = 4.6 Hz, 2H), 3.92-4.01 (m, 4H), 3.65-3.86 (m, 6H), 1.75-1.92 (m, 12H), 1.25-1.54 (m, 36H), 0.87-0.94 (m, 18H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.3, 149.1 148.4, 147.9, 147.6, 147.2, 136.3, 135.8, 135.2, 132.2, 128.6, 128.5, 126.5, 125.6, 123.6, 122.1, 116.8, 116.0, 112.9, 112.8, 107.6, 107.3, 69.1, 69.0, 68.9, 68.8, 68.6, 31.7, 31.6, 29.4, 29.3, 29.2, 29.0, 28.9, 25.7, 25.6, 22.6, 14.1, 14.04. Mass (APCI, m/z), calcd for $C_{58}H_{88}O_6$: 880.66. Found: $[M+H]^+$, 881.75. Anal. Calcd for $C_{58}H_{88}O_6$: C, 79.04; H, 10.06. Found: C, 79.31; H, 9.97.

**General synthesis procedure for 4a-4h**

**Method one**

1 equiv diphenylacetypene derivatives (**1a-1b**) and 1.2-1.5 equiv hyacinthin derivatives (**2a-2e**) were dissolved in DCE, then 3-5 equiv $FeCl_3$ was added and the mixture was stirred at room temperature until the derivatives of diphenylacetypene disappeared by TLC detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization.

**Method two**

1 equiv 1, 2-dibenzylnaphthalene derivatives **3a-3h** was dissolved in DCE, then 3-5 equiv $FeCl_3$ was added and the mixture was stirred at room temperature until the derivatives of **3a-3h** was disappeared by TLC detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization.

**Compound 4a**.

Method one: 1,2-bis(3,4-dimethoxyphenyl)ethyne **1a** (150 mg, 0.5 mmol), 2-phenylacetaldehyde **2a** (72 mg, 0.6 mmol), $FeCl_3$ (406 mg, 2.5 mmol), DCE 10 mL. Yield: 110 mg (55%) of yellow powder.

Method two: **3a** (120 mg, 0.3 mmol), $FeCl_3$ (195 mg, 1.2 mmol), DCE 4 mL. Yield: 84 mg (71%) of yellow powder. $^1$H NMR (400MHz, $CDCl_3$): 8.98 (d, $J$ = 8.4 Hz, 1H), 8.47 (d, $J$ = 8.8 Hz, 1H), 8.41 (s, 1H), 8.00-8.02 (m, 2H), 7.95 (d, $J$ = 8.8 Hz, 1H), 7.88 (s, 1H), 7.86 (s, 1H), 7.56-7.63 (m, 2H), 4.17 (s, 3H), 4.16 (s, 3H), 4.15 (s, 3H), 4.06 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.5, 149.1, 148.8, 147.9, 133.1, 130.2, 128.28, 127.6, 126.9, 126.6, 126.0, 125.7, 125.5, 125.2, 124.1, 123.6, 123.5, 120.8, 110.9, 104.9, 104.2, 103.8, 56.1, 56.0. Mass (APCI, m/z), calcd for $C_{26}H_{22}O_4$: 398.15. Found: $[M+H]^+$, 399.16. Anal. Calcd for $C_{26}H_{22}O_4$: C, 78.37; H, 5.57. Found: C, 78.52; H, 5.35.

**Compounds 4b**.

Method one: 1,2-bis(3,4-dimethoxyphenyl)ethyne **1a** (298 mg, 1.0 mmol), 2-(4-methoxyphenyl) acetaldehyde **2b** (180 mg, 1.2 mmol), $FeCl_3$ (813 mg, 5 mmol), DCE 10 mL. Yield: 175 mg (41%) of yellow powder.

Method two: 3ab (143 mg, 0.33 mmol), $FeCl_3$ (244 mg, 1.5 mmol), DCE 4 mL. Yield: 114 mg (81%) of yellow powder. $^1$H NMR (400MHz, $CDCl_3$): 8.48 (s, 1H), 8.40 (sd, $J$ = 2.0 Hz, 1H), 8.35 (d, $J$ = 9.2 Hz, 1H), 8.00 (s, 1H), 7.87-7.94(m, 4H), 7.25 (dd, $J$ = 8.0 Hz, $J$ = 2.4 Hz, 1H), 4.14-4.18 (m, 9H), 4.07 (s, 3H), 3.98 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 158.0, 149.5, 149.1, 148.7, 147.7, 131.4, 129.8, 128.2, 127.6, 126.4, 125.3, 125.2, 124.2, 123.8, 123.7, 118.6, 116.9, 110.0, 108.1, 105.0, 104.3, 103.8, 56.2, 56.1, 56.0, 55.5. Mass (APCI, m/z), calcd for $C_{27}H_{24}O_5$: 428.16. Found: $[M+H]^+$, 429.19. Anal. Calcd for $C_{27}H_{24}O_5$: C, 75.68; H, 5.65. Found: C, 75.31; H, 5.69.

**Compounds 4c**.

Method one: 1,2-bis(3,4-dimethoxyphenyl)ethyne **1a** (298 mg, 1.0 mmol), 2-(4-(hexyloxy)phenyl) acetaldehyde **2c** (264 mg, 1.2 mmol), $FeCl_3$ (813 mg, 5 mmol), DCE 15 mL. Yield: 214 mg (43%) of yellow powder.

Method two: 3ac (100 mg, 0.2 mmol), $FeCl_3$ (130 mg, 0.8 mmol), DCE 5 mL. Yield: 78 mg (78%) of yellow powder. $^1$H NMR (400MHz, $CDCl_3$): 8.48 (s, 1H), 8.39 (d, $J$ = 1.6 Hz, 1H), 8.33 (d, $J$ = 8.8 Hz, 1H), 7.99 (s, 1H), 7.86-7.92 (m, 4H), 7.24 (dd, $J$ = 8.8 Hz, $J$ = 2.0 Hz, 1H), 4.18 (s, 3H), 4.16 (s, 3H), 4.10-4.14 (m, 5H), 4.06 (s, 3H), 1.85-1.89 (m, 2H), 1.49-1.55 (m, 2H), 1.35-1.38 (m, 4H), 0.90-0.93 (m, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.6, 149.5, 149.8, 148.6, 147.7, 131.4, 129.7, 128.1, 127.5, 126.4, 125.3, 125.1, 124.1, 123.8, 123.7, 118.5, 117.3, 110.1, 108.9, 105.0, 104.3, 103.8, 68.4, 56.1, 56.0, 31.6, 29.4, 25.8, 22.6, 14.0. Mass (APCI, m/z), calcd for $C_{32}H_{34}O_5$: 498.24. Found: $[M+H]^+$, 499.32. Anal. Calcd for $C_{32}H_{34}O_5$: C, 77.08; H, 6.87. Found: C, 77.32; H, 6.84.

**Compounds 4d**.

Method one: 1,2-bis(3,4-dimethoxyphenyl)ethyne **1a** (149 mg, 0.5 mmol), 2-(3,4-dimethoxyphenyl) acetaldehyde **2d** (108 mg, 0.6 mmol), $FeCl_3$ (325 mg, 2.0 mmol), DCE 7 mL. Yield: 78 mg (34%) of yellow powder.

Method two: 3ad (262 mg, 0.57 mmol), $FeCl_3$ (397 mg, 2.44 mmol), Yield: 172 mg (66%) of yellow powder. $^1$H NMR ($CDCl_3$, 400MHz): 8.40 (s, 1H), 8.35-8.37 (m, 2H), 7.97 (s, 1H), 7.89 (s, 1H), 7.81-7.83 (m, 2H), 7.33 (s, 1H), 4.17 (s, 3H), 4.15 (s, 3H), 4.14 (s, 3H), 4.09 (s, 3H), 4.06 (s, 3H), 4.05 (s, 3H). $^{13}$C NMR ($CDCl_3$, 100MHz): 149.2, 149.1, 148.9, 148.6, 147.6, 128.8, 126.2, 125.5, 125.4, 125.3, 125.2, 123.9, 123.6, 123.5, 119.3, 110.0,

108.0, 107.4, 104.7, 104.4, 103.8, 56.1, 56.0, 55.9. Mass (APCI, m/z), calcd for $C_{28}H_{26}O_6$: 458.17. Found: $[M+H]^+$, 459.29. Anal. Calcd for $C_{28}H_{26}O_6$: C, 73.35; H, 5.72. Found: C, 73.18; H, 5.68.

**Compounds 4e**.

Method one: 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (145 mg, 0.25 mmol), 2-phenylacetaldehyde **2a** (36 mg, 0.3 mmol), $FeCl_3$ (203 mg, 1.25 mmol), DCE 4 mL. Yield: 41 mg (24%) of light yellow powder.

Method two: **3e** (119 mg, 0.17 mmol), $FeCl_3$ (85 mg, 0.52 mmol). Yield: 78 mg (68%) of light yellow powder. $^1H$ NMR (400MHz, $CDCl_3$): 8.96 (d, $J$ = 8.0 Hz, 1H), 8.46 (d, $J$ = 7.2 Hz, 1H), 8.39 (s, 1H), 8.02 (s, 1H), 8.00 (dd, $J$ = 8.0 Hz, $J$ = 1.6 Hz, 1H), 7.90-7.93 (m, 3H), 7.54-7.62 (m, 2H), 4.24-4.31 (m, 6H), 4.18 (t, $J$ = 6.4 Hz, 2H), 1.91-2.00 (m, 8H), 1.53-1.62 (m, 8H), 1.37-1.44 (m, 16H), 0.90-0.96 (m, 12H). $^{13}C$ NMR (100MHz, $CDCl_3$): 149.6, 149.2, 148.9, 148.0, 133.0, 130.3, 128.0, 127.4, 127.0, 126.3, 126.1, 125.6, 125.4, 125.3, 124.4, 123.8, 123.6, 121.0, 113.1, 107.2, 106.8, 106.5, 69.6, 69.4, 69.3, 31.7, 29.4, 29.3, 25.9, 25.8, 22.7, 14.1. Mass (APCI, m/z), calcd for $C_{46}H_{62}O_4$: 678.46. Found: $[M+H]^+$, 679.38. Anal. Calcd for $C_{46}H_{62}O_4$: C, 81.37; H, 9.20. Found: C, 81.11; H,9.03.

**Compounds 4f**.

Method one: 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (145 mg, 0.25 mmol), 2-(4-methoxyphenyl) acetaldehyde **2b** (45 mg, 0.3 mmol), $FeCl_3$ (163 mg, 1.0 mmol), DCE 4 mL. Yield: 35 mg (20%) of light yellow powder.

Method two: **3f** (264 mg, 0.37 mmol), $FeCl_3$ (202 mg, 1.24 mmol). Yield: 186 mg (71%) of light yellow powder. $^1H$ NMR ($CDCl_3$, 400MHz): 8.46 (s, 1H), 8.31-8.39 (m, 2H), 8.01 (s, 1H), 7.86-7.92 (m, 4H), 7.23 (dd, $J$ = 8.8 Hz, $J$ = 2.0 Hz, 1H), 4.23-4.31 (m, 6H), 4.16 (t, $J$ = 6.6 Hz, 2H), 3.97 (s, 3H), 1.90-1.99 (m, 8H), 1.51-1.59 (m, 8H), 1.25-1.41 (m, 16H), 0.90-0.96 (m, 12H). $^{13}C$ NMR ($CDCl_3$, 100MHz): 157.8, 149.6, 149.2, 148.7, 147.9, 131.4, 129.7, 128.2, 127.6, 126.4, 126.2, 125.3, 124.4, 123.9, 123.8, 118.7, 116.8, 112.2, 108.1, 107.3, 107.0, 106.6, 69.6, 69.4, 55.5, 55.4, 31.7, 31.6, 29.4, 29.3, 25.8, 22.7, 14.1. Mass (APCI, m/z), calcd for $C_{47}H_{64}O_5$: 708.48. Found: $[M+H]^+$, 709.39. Anal. Calcd for $C_{47}H_{64}O_5$: C, 79.62; H, 9.10. Found: C, 79.75; H, 8.93.

**Compounds 4g**.

Method one: 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (193 mg, 0.33 mmol), 2-(4-(hexyloxy) phenyl)acetaldehyde **2c** (88 mg, 0.4 mmol), $FeCl_3$ (217 mg, 1.34 mmol), DCE 10 mL. Yield: 36 mg (14%) of light yellow powder.

Method two: **3g** (163 mg, 0.21 mmol), $FeCl_3$ (103 mg, 0.63 mmol). Yield: 128 mg (78%)

of light yellow powder. $^{1}$H NMR ($CDCl_3$, 400MHz): 8.46 (s, 1H), 8.38 (sd, *J* = 2.0 Hz, 1H), 8.31 (d, *J* = 7.2 Hz, 1H), 8.01 (s, 1H), 7.88-7.91 (m, 3H), 7.85 (d, *J* = 7.2 Hz, 1H), 7.22 (dd, *J* = 8.8 Hz, *J* = 2.4Hz, 1H), 4.23-4.31 (m, 6H), 4.16 (t, *J* = 6.6 Hz, 2H), 4.11 (t, *J* = 6.4 Hz, 2H), 1.90-1.99 (m, 10H), 1.51-1.61 (m, 10H), 1.35-1.43 (m, 20H), 0.90-0.96 (m, 15H). $^{13}$C NMR ($CDCl_3$, 100MHz): 157.5, 149.6, 149.2, 148.5, 147.9, 131.5, 129.6, 128.1, 127.6, 126.2, 125.3, 125.2, 124.3, 123.9, 123.8, 118.6, 117.2, 112.0, 108.7, 107.3, 106.8, 106.5, 69.6, 69.6, 69.4, 69.3, 68.3, 31.7, 31.6, 29.4, 29.3, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0. Mass (APCI, m/z), calcd for $C_{52}H_{74}O_5$: 778.55. Found: $[M+H]^+$, 779.52. Anal. Calcd for $C_{52}H_{74}O_5$: C, 80.16; H, 9.57. Found: C, 79.79; H, 9.46.

**Compounds 4h**.

Method one: 1,2-bis(3,4-bis(hexyloxy)phenyl)ethyne **1b** (193 mg, 0.33 mmol), 2-(3,4-bis(hexyloxy) phenyl)acetaldehyde **2e** (128 mg, 0.4 mmol), $FeCl_3$ (215 mg, 1.32 mmol), DCE 10 mL. Yield: 30 mg (10%) of light yellow powder.

Method two: **3h** (77 mg, 0.09 mmol), $FeCl_3$ (50 mg, 0.31 mmol). Yield: 55 mg (72%) of light yellow powder. $^{1}$H NMR ($CDCl_3$, 400MHz): 8.40 (s, 1H), 8.37 (s, 1H), 8.32 (d, *J* = 9.2 Hz, 1H), 7.99 (s, 1H), 7.91 (s, 1H), 7.87 (s, 1H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.30 (s, 1H), 4.23-4.30 (m, 6H), 4.20 (t, *J* = 6.8 Hz, 2H), 4.14 (td, *J* = 6.8 Hz, *J* = 1.6 Hz, 4H), 1.91-1.97 (m, 12H), 1.52-1.61 (m, 12H), 1.35-1.42 (m, 24H), 0.92-0.96 (m, 18H). $^{13}$C NMR ($CDCl_3$, 100MHz): 149.2, 149.2, 148.9, 148.5, 147.8, 128.9, 126.0, 125.4, 125.3, 124.1, 123.8, 119.1, 112.0, 109.9, 108.7, 107.1, 106.9, 106.8, 69.7, 69.6, 69.4, 69.3, 69.2, 68.8, 31.7, 31.7, 31.6, 29.4, 29.3, 29.2, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0. Mass (APCI, m/z), calcd for $C_{58}H_{86}O_6$: 878.64. Found: $[M+H]^+$, 879.58. Anal. Calcd for $C_{58}H_{86}O_6$: C, 79.22; H, 9.86. Found: C, 78.97; H, 9.75.

**General synthesis procedure for benzo[g]chrysene derivatives 5a-5h**

1 equiv of 1, 2-dibenzylnaphthalene derivatives 3aa-3bd was dissolved in DCE, then 7-10 equiv $FeCl_3$ was added and the mixture was stirred at room temperature until the derivatives of 3aa-3bd was disappeared by TLC detected. The solvent was removed under vacuum and the residue was purified by column chromatography on silica gel. The final product was obtained from recrystallization.

**Compound 5a**. **3a** (100 mg, 0.25 mmol), $FeCl_3$ (406 mg, 2.5 mmol), DCE 10 mL. Yield: 78 mg (72%) of yellow powder. $^{1}$H NMR (400MHz, $CDCl_3$): 8.89 (d, *J* = 7.2 Hz, 1H), 8.46 (s, 1H), 8.43 (dd, *J* = 8.0 Hz, *J* = 1.6 Hz, 1H), 8.22 (s, 1H), 7.78 (s, 2H), 7.77 (s, 1H), 7.59-7.67 (m, 2H), 4.13 (s, 3H), 4.12 (s, 3H), 4.11 (s, 3H), 4.00 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.8, 149.2, 149.0, 148.0, 131.3, 130.1, 130.0, 127.9, 126.8, 126.3,

126.2, 125.3, 125.2, 124.8, 124.3, 122.9, 122.6, 121.1, 110.7, 104.5, 104.1, 103.7, 56.1, 56.0. Mass (APCI, m/z), calcd for $C_{26}H_{21}ClO_4$: 432.11. Found: $[M+H]^+$, 433.19. Anal. Calcd for $C_{26}H_{21}ClO_4$: C, 72.14; H, 4.89. Found: C, 72.18; H, 4.85.

**Compound 5b**. **3b** (130 mg, 0.3 mmol), $FeCl_3$ (498 mg, 3.06 mmol), DCE 5 mL. Yield: 113 mg (81%) of light yellow powder. $^1H$ NMR (400MHz, $CDCl_3$): 8.33-8.38 (m, 4H), 7.83 (s, 1H), 7.80 (d, *J* = 4.4 Hz, 2H), 7.32 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 4.16 (s, 1H), 4.15 (s, 1H), 4.14 (s, 1H), 4.04 (s, 1H), 3.97 (s, 1H). $^{13}C$ NMR (100MHz, $CDCl_3$): 158.4, 149.8, 149.2, 148.8, 147.9, 132.7, 130.2, 127.6, 126.5, 125.2, 125.1, 124.5, 124.3, 123.2, 122.7, 118.9, 117.3, 110.0, 108.7, 104.7, 104.3, 103.7, 56.1, 56.0, 55.6. Mass (APCI, m/z), calcd for $C_{27}H_{23}ClO_5$: 462.12. Found: $[M+H]^+$, 463.20. Anal. Calcd for $C_{27}H_{23}ClO_5$: C, 70.05; H, 5.01. Found: C, 70.13; H, 4.97.

**Compound 5c**. **3c** (100 mg, 0.2 mmol), $FeCl_3$ (326 mg, 2.01 mmol), DCE 5 mL. Yield: 72 mg (68%) of light yellow powder. $^1H$ NMR (400MHz, $CDCl_3$): 8.34-8.37 (m, 4H), 7.84 (s, 1H), 7.81 (d, J = 4.4 Hz, 2H), 7.32 (dd, *J* = 9.2 Hz, *J* = 2.4Hz, 1H), 4.16 (s, 3H), 4.15 (s, 3H), 4.14 (s, 3H), 4.11 (t, *J* = 6.8 Hz, 2H), 4.04 (s, 3H), 1.85-1.88 (m, 2H), 1.48-1.58 (m, 2H), 1.35-1.38 (m, 4H), 0.91 (t, *J* = 6.8Hz, 3H). $^{13}C$ NMR (100MHz, $CDCl_3$): 158.1, 149,8, 149.2, 148.8, 147.8, 132.7, 130.2, 127.5, 126.4, 125.2, 125.0, 124.4, 124.3, 123.2, 122.7, 118.7, 117.7, 110.0, 109.3, 104.7, 104.3, 103.7, 68.4, 56.1, 56.0, 31.5, 29.3, 25.8, 22.6, 14.0. Mass (APCI, m/z), calcd for $C_{32}H_{33}ClO_5$: 532.20. Found: $[M+H]^+$, 533.29. Anal. Calcd for $C_{32}H_{33}ClO_5$: C, 72.10; H, 6.24. Found: C, 71.91; H, 6.17.

**Compound 5d**. **3d** (71 mg, 0.15 mmol), $FeCl_3$ (171 mg, 1.05 mmol), DCE 5 mL. Yield: 56 mg (74%) of light yellow powder. $^1H$ NMR (400MHz, $CDCl_3$): 8.41 (s, 1H), 8.34 (s, 1H), 8.29 (s, 1H), 7.86 (s, 1H), 7.83 (s, 1H), 7.82 (s, 1H), 7.76 (s, 1H), 4.15-4.18 (m, 12H), 4.06 (s, 3H), 4.04 (s, 3H). $^{13}C$ NMR (100MHz, $CDCl_3$): 149.5, 149.3, 149.2, 149.1, 148.8, 147.7, 129.0, 126.4, 126.2, 125.8, 125.3, 124.5, 123.7, 123.0, 122.8, 119.4, 109.9, 108.3, 104.4, 104.3, 103.7, 56.1, 56.0. Mass (APCI, m/z), calcd for $C_{28}H_{25}ClO_6$: 492.13. Found: $[M+H]^+$, 493.22. Anal. Calcd for $C_{28}H_{25}ClO_6$: C, 68.22; H, 5.11. Found: C, 67.95; H, 5.01.

**Compound 5e**. **3e** (90 mg, 0.13 mmol), $FeCl_3$ (148 mg, 0.91 mmol), DCE 5 mL. Yield: 72 mg (77%) of light yellow powder. $^1H$ NMR (400MHz, $CDCl_3$): 8.95 (dd, *J* = 7.2 Hz, *J* = 2.0 Hz, 1H), 8.53 (s, 1H), 8.46 (dd, *J* = 7.2 Hz, *J* = 2.4 Hz, 1H), 8.28 (s, 1H), 7.87-7.90 (m, 3H), 7.64-7.68 (m, 2H), 4.25-4.31 (m, 6H), 4.16 (t, *J* = 6.2 Hz, 2H), 1.95-1.98 (m, 8H), 1.55-1.62 (m, 8H), 1.36-1.43 (m, 16H), 0.92-0.96 (m, 12H). $^{13}C$ NMR (100MHz, $CDCl_3$): 149.9, 149.4, 149.2, 148.2, 131.4, 130.0, 128.1, 126.9, 126.2, 125.6, 125.5, 125.4, 124.7, 124.5, 123.1, 122.8, 121.2, 113.2, 113.1, 106.8, 106.5, 69.6, 69.4, 31.7, 31.6, 29.4,

29.3, 25.9, 25.8, 22.7, 14.1. Mass (APCI, m/z), calcd for $C_{46}H_{61}ClO_4$: 712.43. Found: $[M+H]^+$, 713.27. Anal. Calcd for $C_{46}H_{61}ClO_4$: C, 77.44; H, 8.62. Found: C, 77.29; H, 8.45.

**Compound 5f**. **3f** (116 mg, 0.16 mmol), $FeCl_3$ (182 mg, 1.12 mmol), DCE 5 mL. Yield: 92 mg (76%) of light yellow powder. $^1H$ NMR ($CDCl_3$, 400MHz): 8.35-838 (m, 4H), 7.89 (s, 1H), 7.88 (s, 1H), 7.86 (s, 1H), 7.31 (dd, $J$ = 7.2Hz, $J$ = 2.4Hz, 1H), 4.24-4.30 (m, 6H), 4.14 (t, $J$ = 6.6 Hz, 2H), 3.97 (s, 3H), 1.89-1.99 (m, 8H), 1.57-1.61 (m, 8H), 1.25-1.42 (m, 16H), 0.93-0.96 (m, 12H). $^{13}C$ NMR ($CDCl_3$, 100MHz): 158.3, 149.9, 149.4, 148.9, 148.1, 132.8, 130.1, 127.7, 126.4, 125.4, 125.1, 124.6, 124.5, 123.3, 122.9, 119.0, 117.4, 112.2, 108.6, 106.9, 106.5, 69.6, 69.4, 55.5, 31.7, 31.6, 29.4, 29.3, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0. Mass (APCI, m/z), calcd for $C_{47}H_{63}ClO_5$: 742.44. Found: $[M+H]^+$, 743.21. Anal. Calcd for $C_{47}H_{63}ClO_5$: C, 75.93; H, 8.54. Found: C, 75.67; H, 8.42.

**Compound 5g**. **3g** (71 mg, 0.09 mmol), $FeCl_3$ (103 mg, 0.63 mmol), DCE 5 mL. Yield: 53 mg (74%) of light yellow powder. $^1H$ NMR ($CDCl_3$, 400MHz): 8.34-8.37 (m, 4H), 7.89 (s, 1H), 7.87 (s, 1H), 7.86 (s, 1H), 7.30 (dd, $J$ = 9.2Hz, $J$ = 2.4 Hz, 1H), 4.24-4.30 (m, 6H), 4.10-4.16 (m, 4H), 1.84-1.99 (m, 10H), 1.56-1.61 (m, 10H), 1.35-1.42 (m, 20H), 0.92-0.96 (m, 15H). $^{13}C$ NMR ($CDCl_3$, 100MHz): 158.0, 149.9, 149.4, 148.8, 148.1, 132.8, 130.1, 127.7, 126.3, 125.4, 125.0, 124.6, 124.5, 123.3, 122.9, 118.9, 117.8, 112.1, 109.3, 107.0, 106.8, 106.5, 69.7, 69.6, 69.5, 69.4, 68.4, 31.7, 31.6, 29.4, 29.3, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0. Mass (APCI, m/z), calcd for $C_{52}H_{73}ClO_5$: 812.51. Found: $[M+H]^+$, 813.39. Anal. Calcd for $C_{52}H_{73}ClO_5$: C, 76.77; H, 9.04. Found: C, 76.88; H, 8.88.

**Compound 5h**. **3h** (80 mg, 0.09 mmol), $FeCl_3$ (100 mg, 0.62 mmol), DCE 5 mL. Yield: 61 mg (73%) of light yellow powder. $^1H$ NMR ($CDCl_3$, 400MHz): 8.40 (s, 1H), 8.35 (s, 1H), 8.30 (s, 1H), 7.88 (s, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.73 (s, 1H), 4.24-4.30 (m, 8H), 4.10-4.16 (m, 4H), 1.88-1.99 (m, 12H), 1.50-1.60 (m, 12H), 1.35-1.42 (m, 24H), 0.93-0.96 (m, 18H). $^{13}C$ NMR ($CDCl_3$, 100MHz): 149.5, 149.4, 149.3, 149.2, 148.7, 148.0, 128.9, 126.5, 126.1, 125.8, 125.4, 124.7, 124.0, 123.3, 123.2, 119.3, 112.0, 112.0, 110.1, 106.9, 106.7, 106.6, 105.4, 69.7, 69.5, 69.4, 69.3, 69.2, 68.9, 31.7, 31.6, 29.4, 29.3, 29.2, 29.1, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0. Mass (APCI, m/z), calcd for $C_{58}H_{85}ClO_6$: 912.60. Found: $[M+H]^+$, 913.55. Anal. Calcd for $C_{58}H_{85}ClO_6$: C, 76.24; H, 9.38. Found: C, 76.06; H, 9.14.

## The NMR data of compounds 4a-4h from method one.

**4a (method one)**

$^1$H NMR (400MHz, $CDCl_3$): 8.97 (d, *J* = 8.0 Hz, 1H), 8.47 (d, *J* = 9.2 Hz, 1H), 8.40 (s, 1H), 7.99-8.02 (m, 2H), 7.93 (d, *J* = 8.8 Hz, 1H), 7.87 (s, 1H), 7.85 (s, 1H), 7.57-7.61 (m, 2H), 4.17 (s, 3H), 4.14 (s, 3H), 4.06 (s, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.7, 149.0, 148.8, 147.8, 133.0, 130.2, 128.3, 127.6, 126.9, 126. 6, 126.0, 125.6, 125.5, 125.2, 124.1, 123.6, 123.4, 120.8, 110.8, 104.8, 104.0, 103.7, 56.1, 56.0.

**4b (method one)**

$^1$H NMR (400MHz, $CDCl_3$): 8.48 (s, 1H), 8.40 (sd, *J* = 2 Hz, 1H), 8.34 (d, *J* = 9.2 Hz, 1H), 8.00 (s, 1H), 7.86-7.94 (m, 4H), 7.25 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 4.18 (s, 3H), 4.17 (s, 3H), 4.14 (s, 3H), 4.07 (s, 1H), 3.08 (s, 1H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.9, 149.5, 149.0, 148.6, 147.7, 131.4, 129.8, 128.2, 127.5, 126.4, 125.3, 125.1, 124.1, 123.7, 123.6, 118.6, 116.9, 110.0, 108.0, 104.9, 104.3, 103.7, 56.1, 56.0, 55.5.

**4c (method one)**

$^1$H NMR (400MHz, $CDCl_3$): 8.48 (s, 1H), 8.39 (sd, *J* = 1.2 Hz, 1 H), 8.00 (s, 1H), 7.87-7.93 (m, 4H), 7.24 (dd, *J* = 6.6 Hz, *J* = 2.4 Hz, 1 H), 4.18 (s, 3H), 4.17 (s, 3H), 4.15 (s, 3H), 4.12 (t, *J* = 6.6 Hz, 2H), 4.07 (s, 3H), 1.84-1.90 (m, 2H), 1.49-1.52 (m, 2H), 1.34-1.38 (m, 4H), 0.89-0.93 (m, 3H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.6, 149.5, 149.0, 148.6, 147.6, 131.4, 129.7, 128.1, 127.5, 126.4, 125.2, 125.1, 124.1, 123.8, 123.7, 118.5, 117.3, 110.0, 108.8, 104.9, 104.2, 103.7, 68.3, 56.1, 56.1, 56.0, 31.6, 29.4, 25.8, 22.6, 14.1.

**4d (method one)**

$^1$H NMR (400MHz, $CDCl_3$): 8.42 (s, 1H), 8.37-8.39 (m, 2H), 7.99 (s, 1H), 7.90 (s, 1H), 7.83-7.86 (m, 2H), 7.34 (s, 1H), 4.18 (s, 1H), 4.16 (s, 1H), 4.15 (s, 1H), 4.10 (s, 1H), 4.06 (s, 1H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.2, 149.0, 148.9, 148.6, 147.6, 128.8, 126.1, 125.5, 125.4, 125.2, 125.2, 123.9, 123.6, 123.5, 119.2, 109.9, 108.0, 107.4, 104.7, 104.4, 103.8, 56.1, 56.0, 55.9.

**4e (method one)**

$^1$H NMR (400MHz, $CDCl_3$): $^1$H NMR (400MHz, $CDCl_3$): 8.96 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 7.2 Hz, 1H), 8.39 (s, 1H), 7.99-8.02 (m, 2H), 7.89-7.93 (m, 3H), 7.54-7.63 (m, 2H), 4.24-4.31(m, 6H), 4.18 (t, *J* = 6.6 Hz, 2H), 1.95-1.98 (m, 8H), 1.59-1.60 (m, 8H), 1.37-1.41 (m, 16H), 0.94 (t, *J* = 7.2 Hz, 18H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.6, 149.2,

148.9, 148.0, 133.0, 130.2, 128.1, 127.7, 127.0, 126.4, 126.0, 125.5, 125.4, 125.3, 124.4, 123.8, 123.6, 120.9, 113.1, 107.2, 106.9, 106.6, 69.6, 31.7, 31.6, 29.4, 29.3, 25.9, 25.8, 22.7, 14.1.

**4f (method one)**

$^{1}$H NMR (400MHz, $CDCl_3$): 8.46 (s, 1H), 8.39 (sd, *J* = 2 Hz, 1H), 8.32 (d, *J* = 8.8 Hz, 1H), 8.00 (s, 1H), 7.84-7.92 (m, 4H), 7.23 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 4.23-4.31 (m, 6H), 4.16 (t, *J* = 6.6 Hz, 2 H), 3.07 (s, 3H), 1.90-1.99 (m, 8H), 1.56-1.61 (m, 8H), 1.35-1.43 (m, 16 H), 0.90-0.96 (m, 12H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.8, 149.6, 149.2, 148.6, 147.9, 131.4, 129.7, 128.2, 127.6, 126.2, 125.3, 124.3, 123.9, 123.8, 118.7, 116.8, 112.1, 108.0, 107.3, 106.9, 106.5, 69.6, 69.5, 69.3, 55.4, 31.7, 31.6, 29.7, 29.4, 29.3, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0.

**4g (method one)**

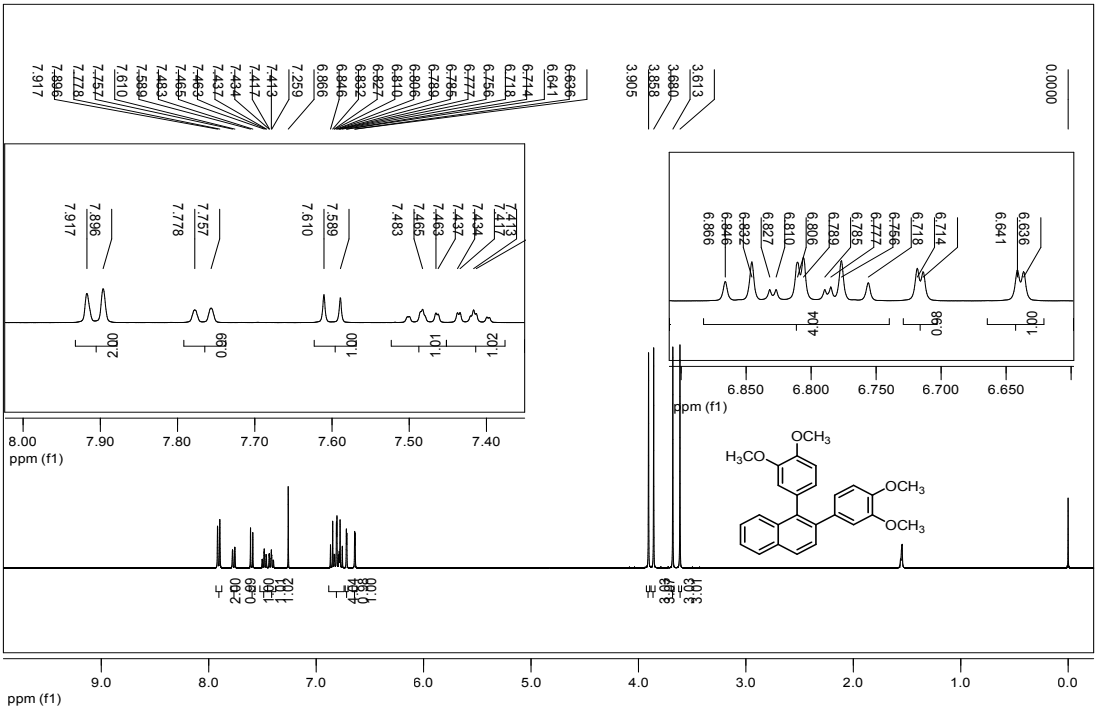
$^{1}$H NMR (400MHz, $CDCl_3$): 8.57 (s, 1H), 8.38 (sd, *J* = 2 Hz, 1H), 8.31 (d, *J* = 9.2 Hz, 1H), 8.00 (s, 1H), 7.88-7.91 (m, 3H), 7.84 (d, *J* = 8.8 Hz, 1H), 7.22 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 1H), 4.23-4.32 (m, 6H), 4.16 (t, *J* = 6.6 Hz, 2H), 4.11 (t, *J* = 6.8 Hz, 2H), 1.86-2.00 (m, 10H), 1.51-1.61 (m, 10 H), 1.35-1.42 (m, 20H), 0.90-0.96 (m, 15H). $^{13}$C NMR (100MHz, $CDCl_3$): 157.5, 149.6, 149.2, 148.6, 147.9, 131.5, 129.6, 128.1, 127.6, 126.2, 125.3, 124.3, 123.9, 123.8, 118.6, 117.2, 112.1, 108.8, 107.4, 106.9, 106.6, 69.7, 69.6, 69.4, 69.3, 68.2, 31.7, 31.6, 29.5, 29.4, 29.3, 25.9, 25.8, , 22.7, 22.6, 14.0, 14.0.

**4h (method one)**

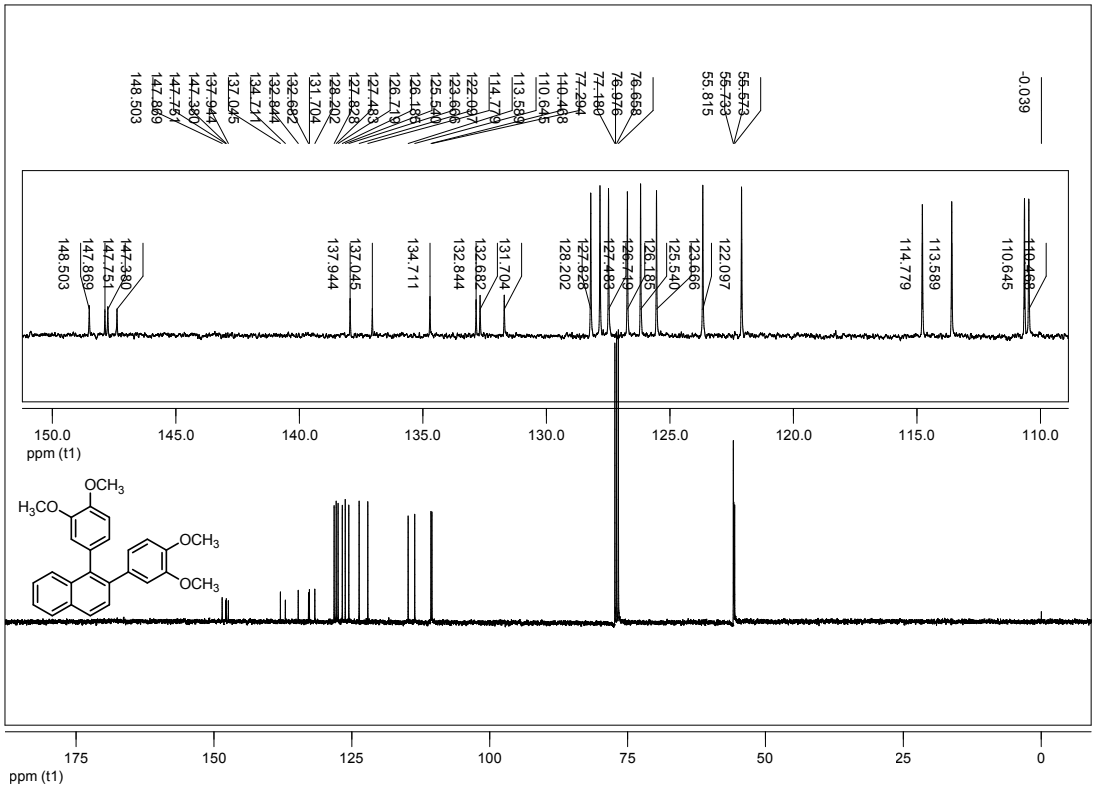
$^{1}$H NMR (400MHz, $CDCl_3$): 8.40 (s, 1H), 8.42 (s, 1H), 8.37 (d, *J* = 7.2 Hz, 1H), 8.04 (s, 1H), 7.96 (s, 1H), 7.92 (s, 1H), 7.82 (d, *J* = 8.8 Hz, 1H), 7.35 (s, 1H), 8.18-8.30 (m, 8H), 4.12-4.16 (m, 4H), 1.91-1.97 (m, 12H), 1.57-1.59 (m, 12H), 1.35-1.43 (m, 24H), 0.89-0.96 (m, 18H). $^{13}$C NMR (100MHz, $CDCl_3$): 149.2, 149.1, 148.8, 148.4, 147.8, 128.8, 126.0, 125.4, 125.3, 125.2, 124.1, 123.8, 123.7, 119.1, 111.9, 109.8, 108.6, 107.0, 106.8, 106.7, 69.7, 69.5, 69.3, 69.2, 69.1, 68.8, 31.7, 31.6, 29.4, 29.3, 29.2, 25.9, 25.8, 22.7, 22.6, 14.1, 14.0.

# The original NMR spectra

## 3a

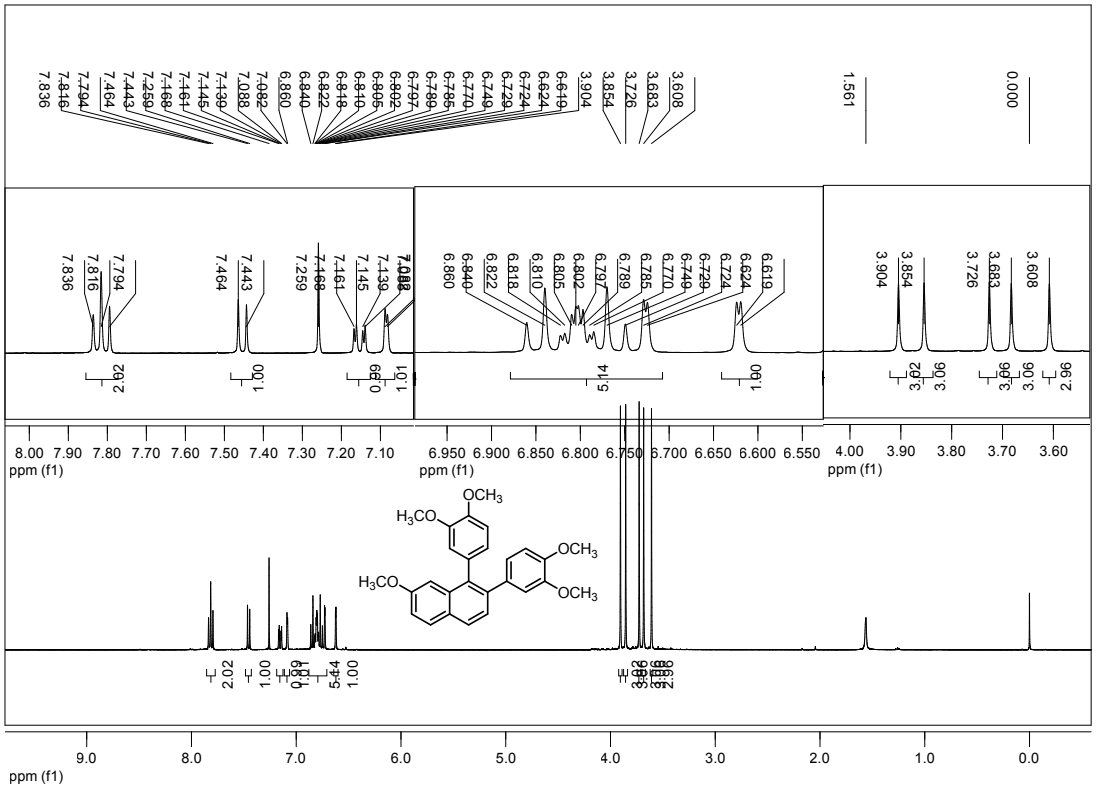



The $^{1}H$ NMR spectra of compound 3a.

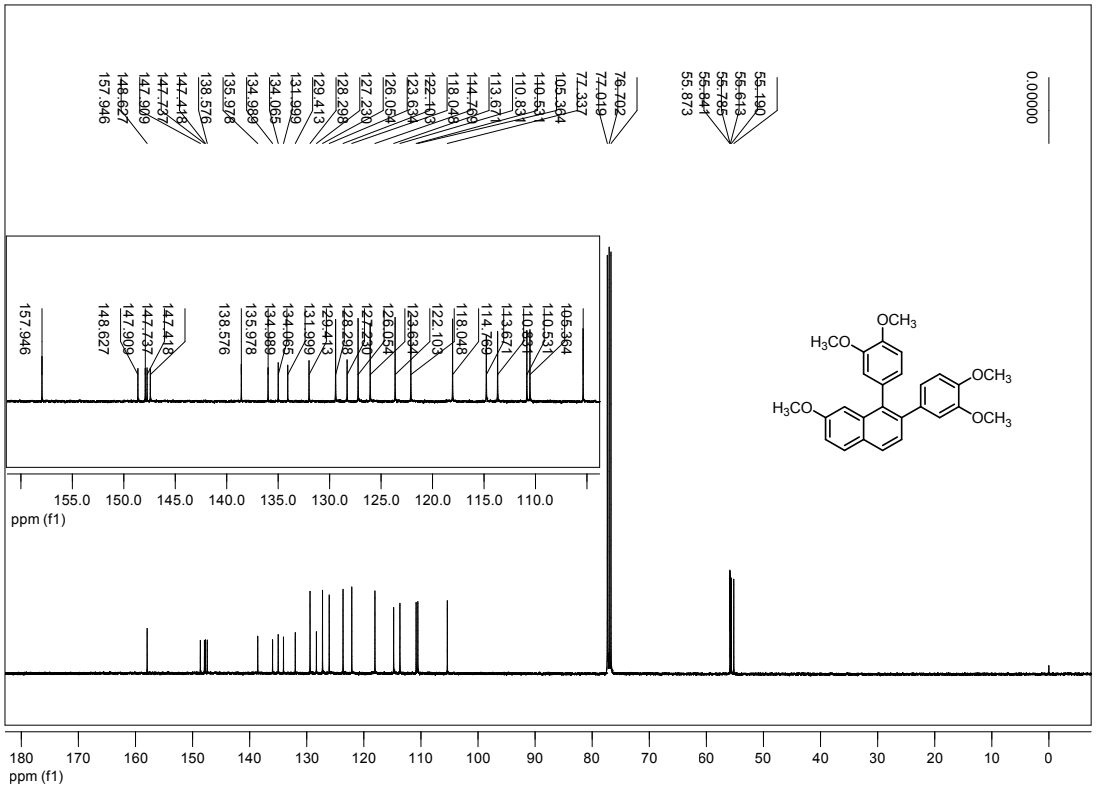



The $^{13}C$ NMR spectra of compound 3a.

## 3b

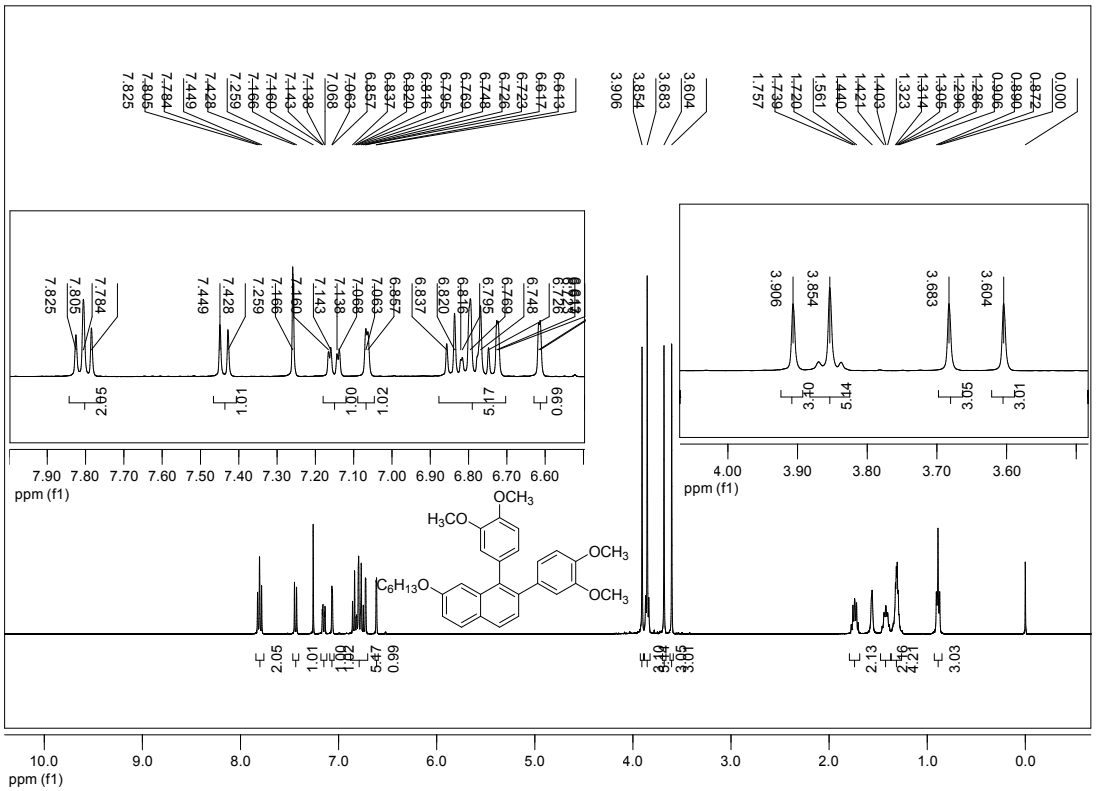



The $^{1}H$ NMR spectra of compound 3b.

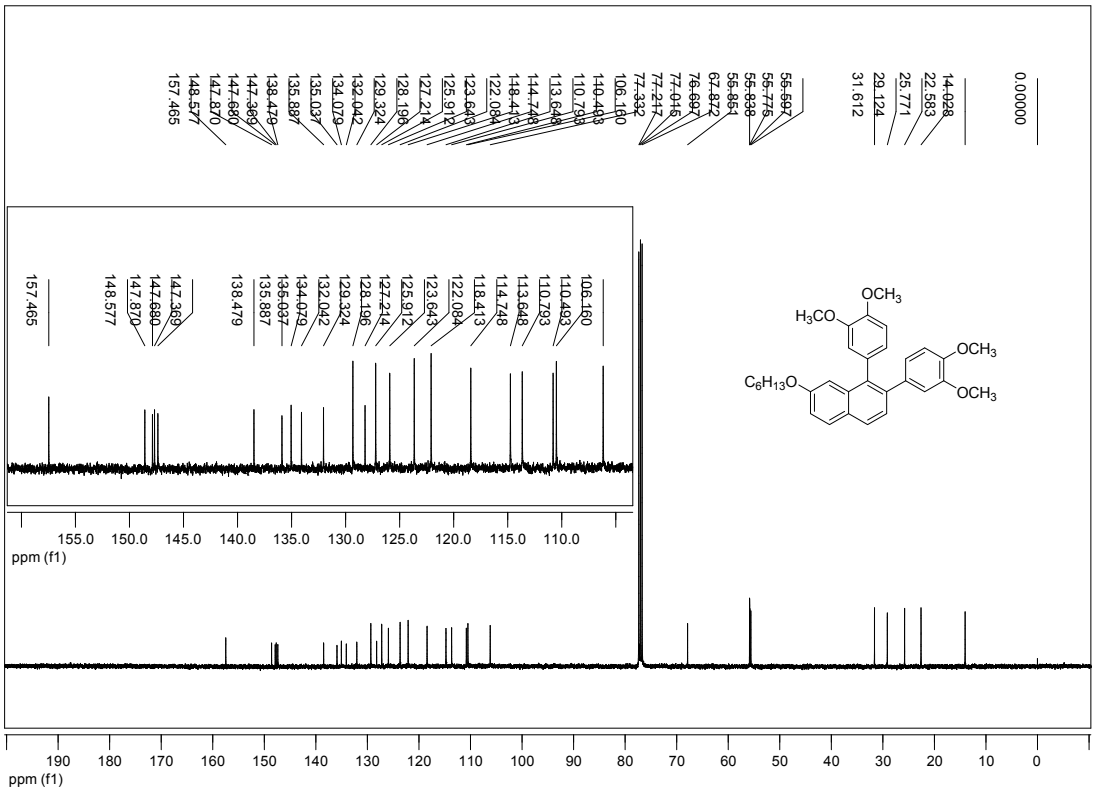



The $^{13}C$ NMR spectra of compound 3b.

## 3c

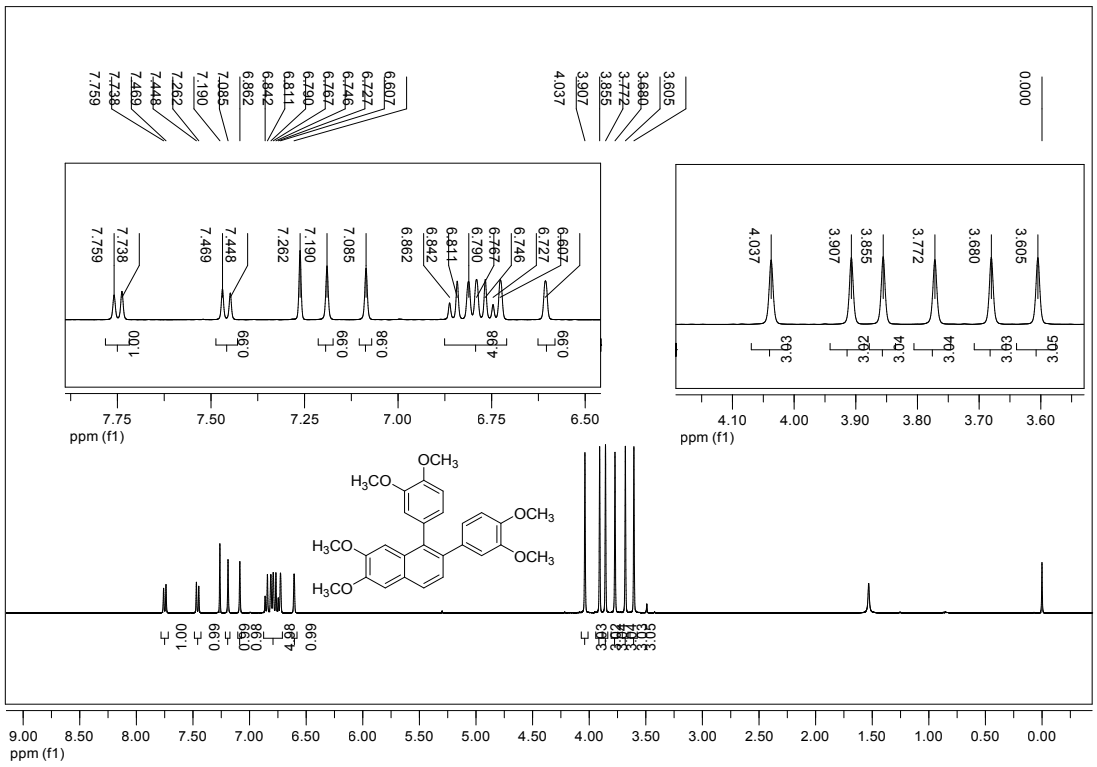



The $^{1}H$ NMR spectra of compound 3c.

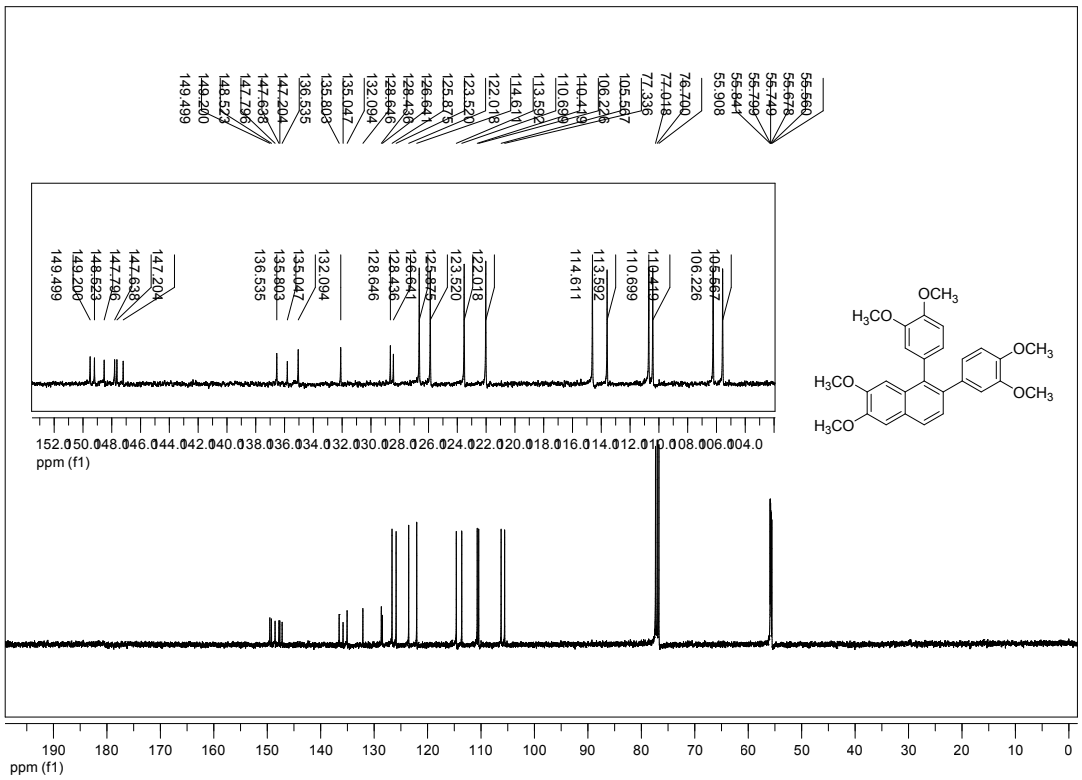



The $^{13}C$ NMR spectra of compound 3c.

## 3d

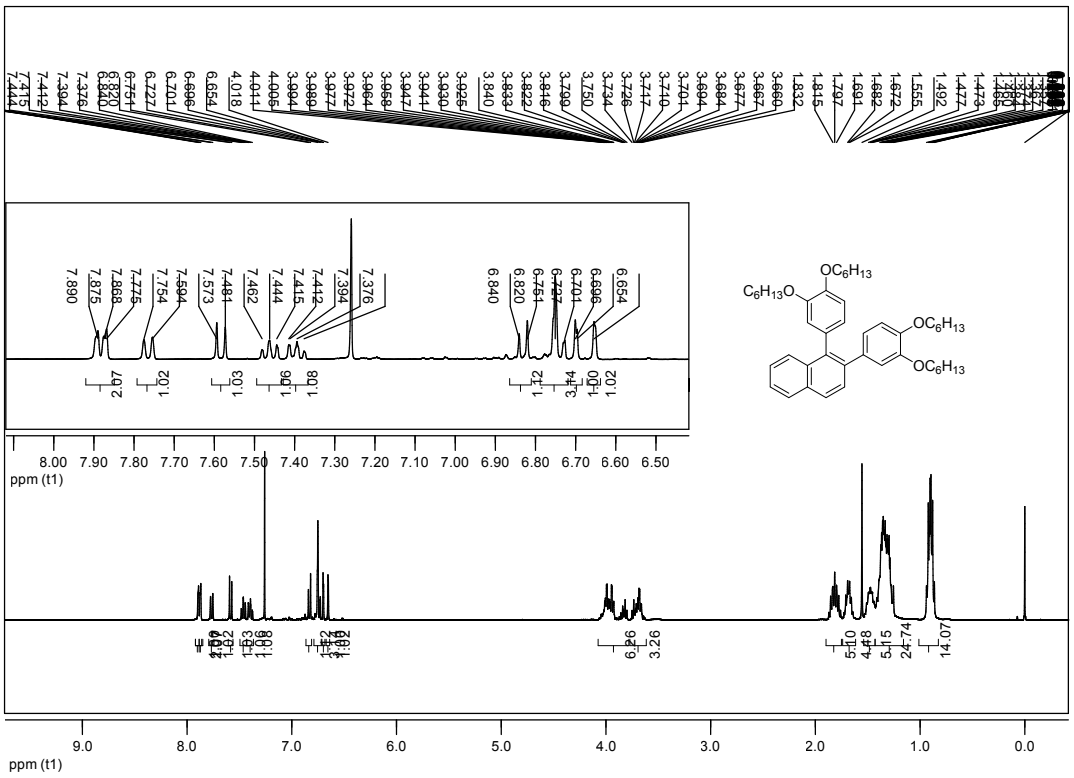


The $^{1}H$ NMR spectra of compound 3d.

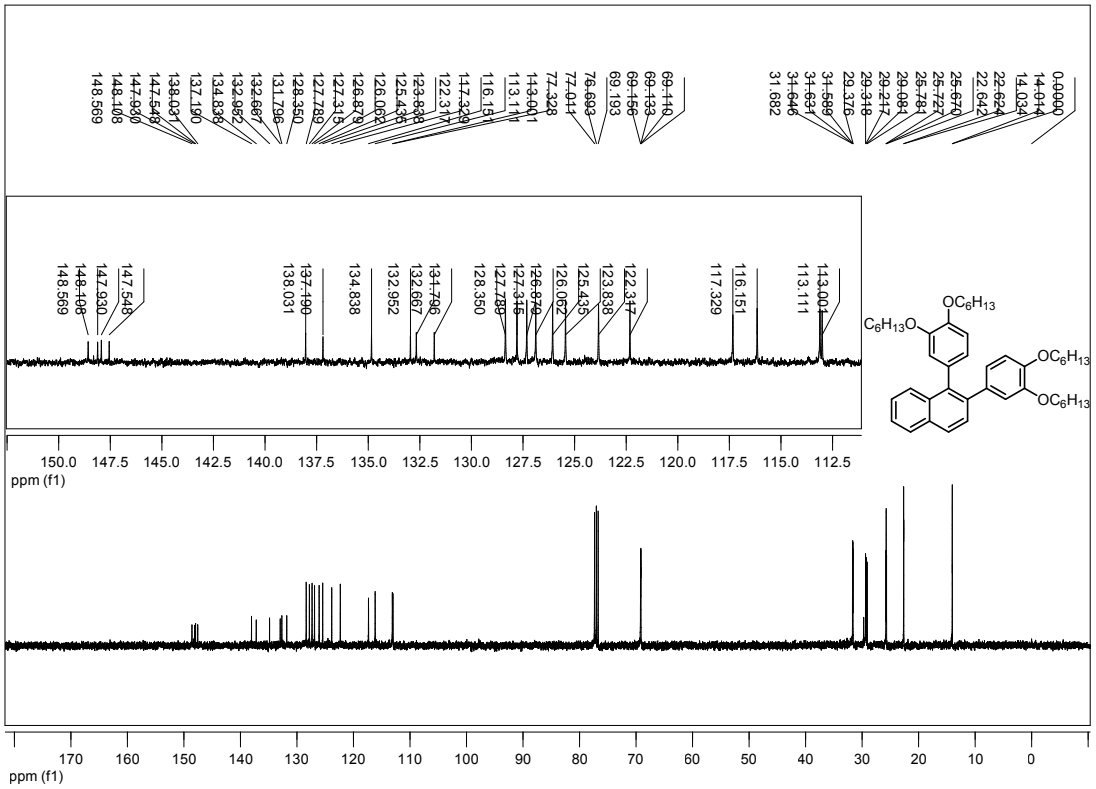


The $^{13}C$ NMR spectra of compound 3d.

## 3e

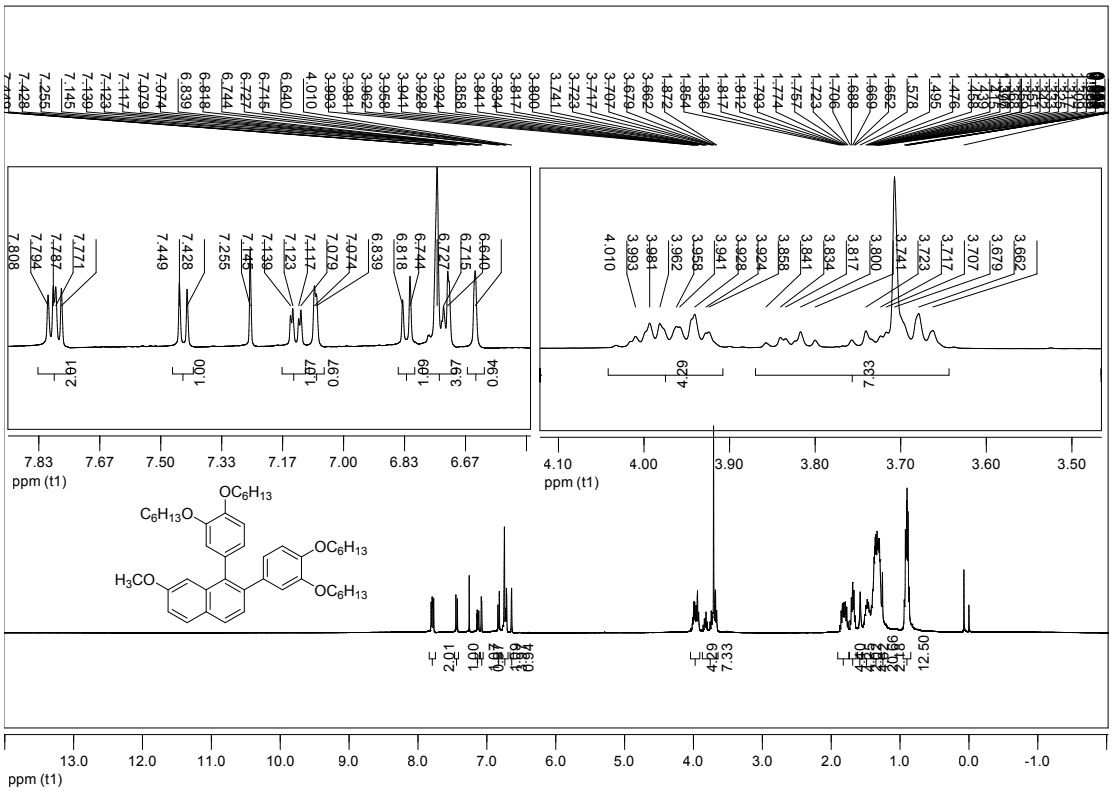



The $^{1}H$ NMR spectra of compound 3e.

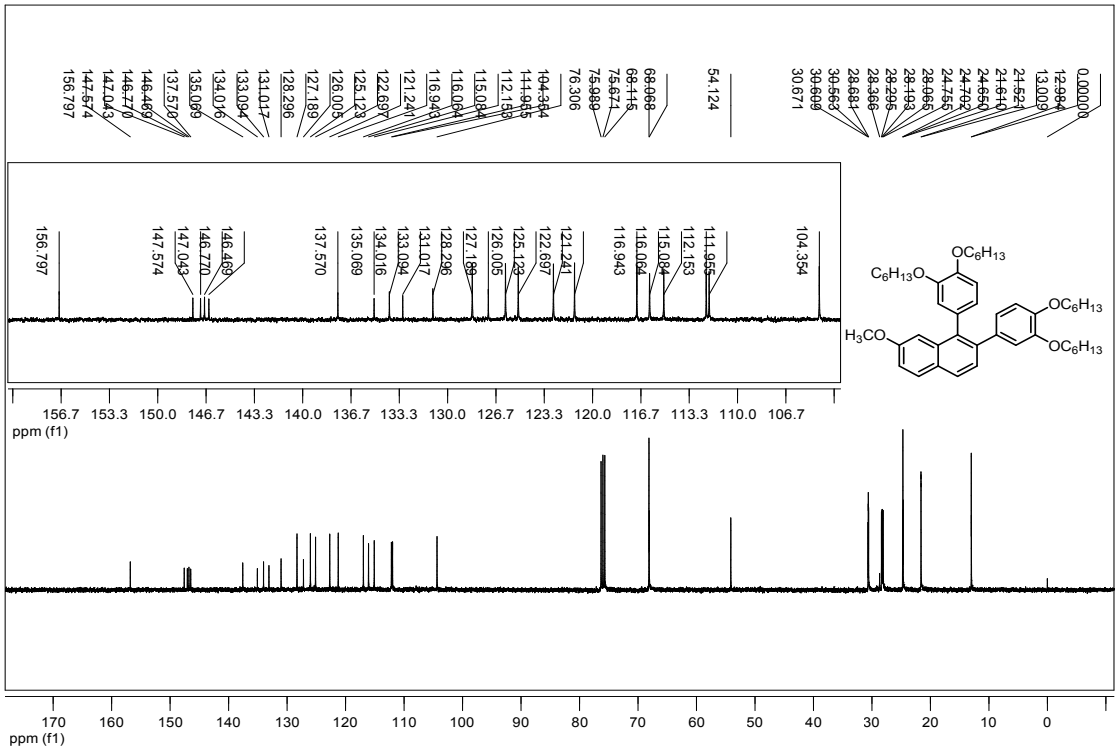



The $^{13}C$ NMR spectra of compound 3e.

# 3f

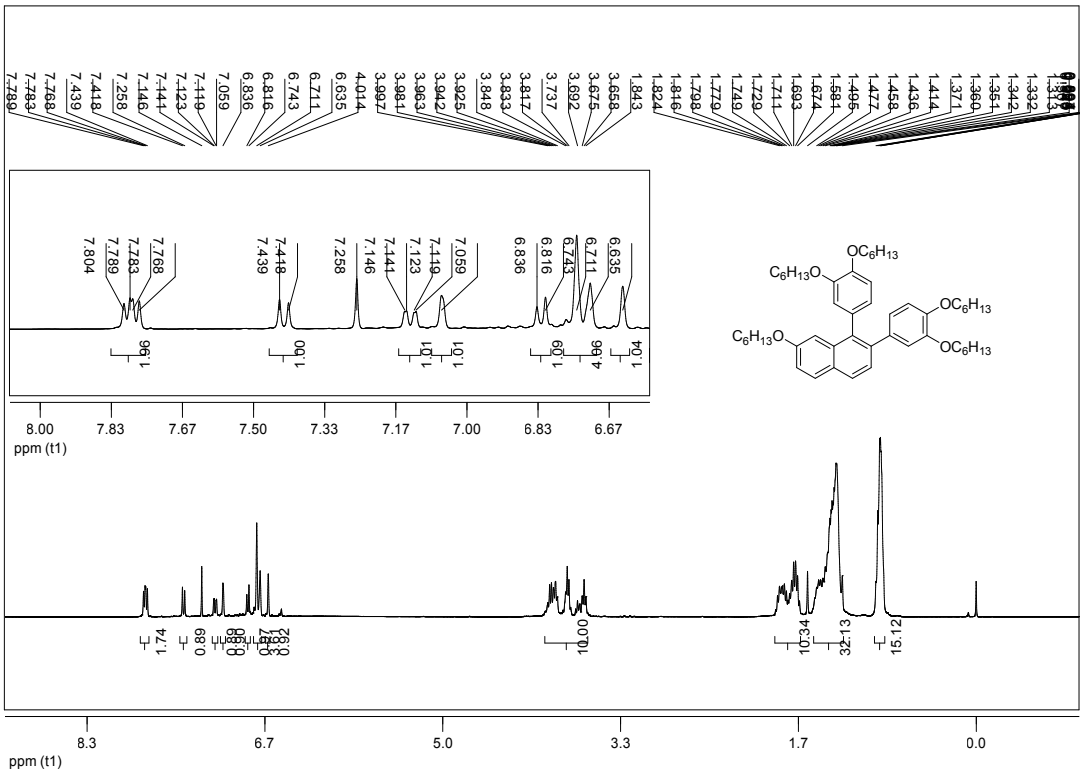



The $^{1}H$ NMR spectra of compound 3f.

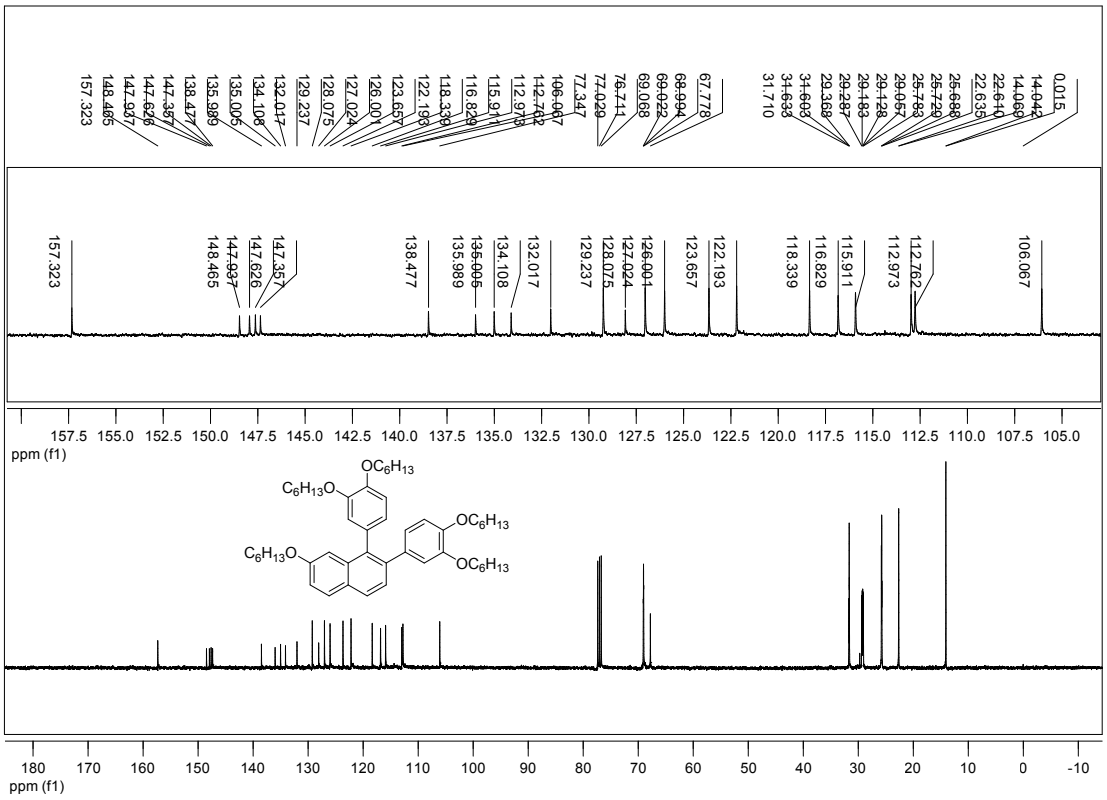



The $^{13}C$ NMR spectra of compound 3f.

# 3g

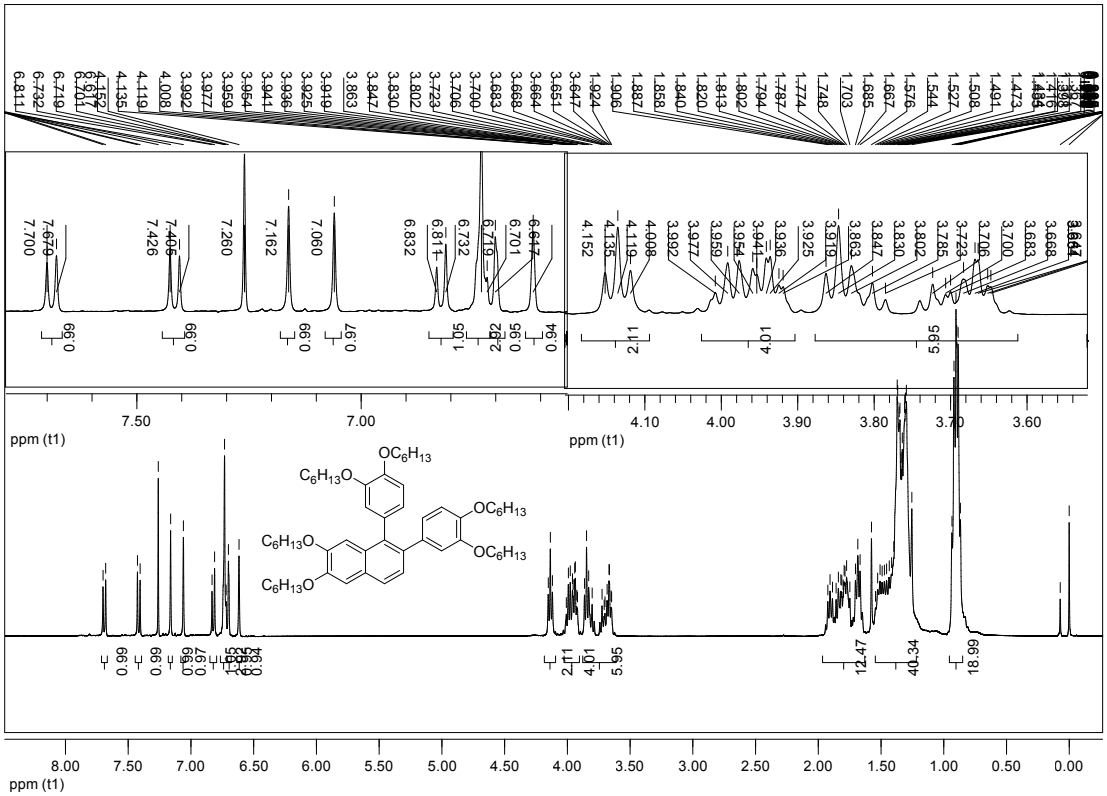


The $^{1}H$ NMR spectra of compound 3g.

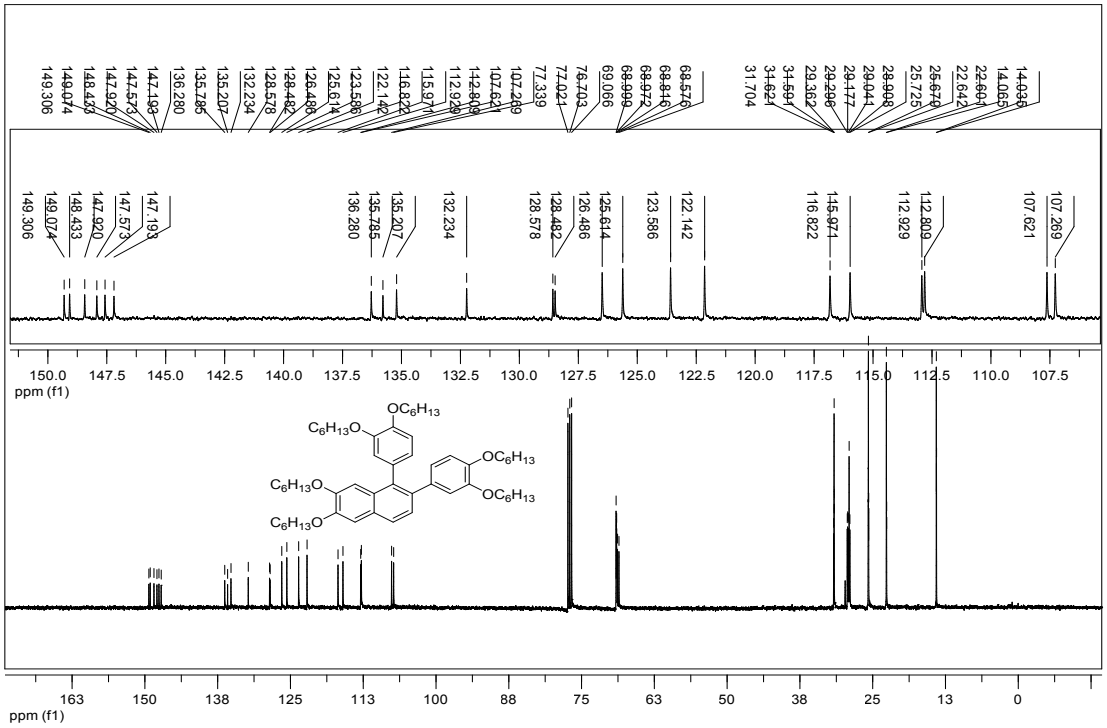


The $^{13}C$ NMR spectra of compound 3g.

## 3h

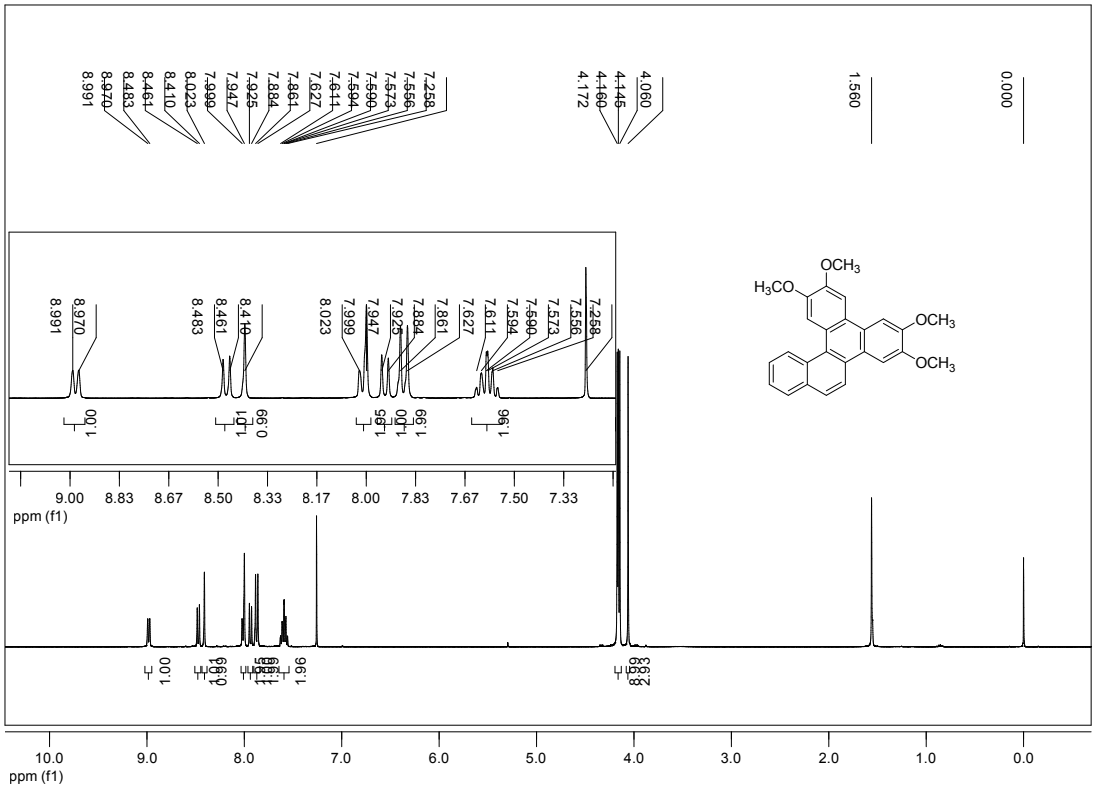



The $^{1}H$ NMR spectra of compound 3h.

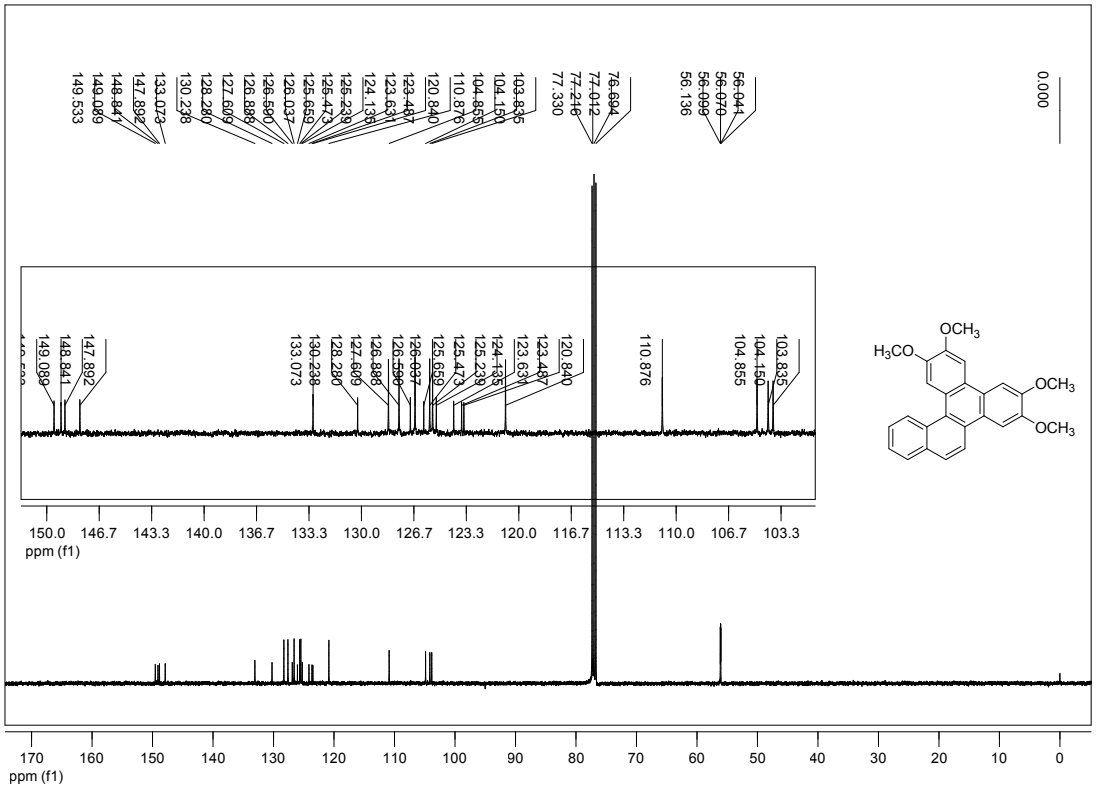



The $^{13}C$ NMR spectra of compound 3h.

## 4a (method two)

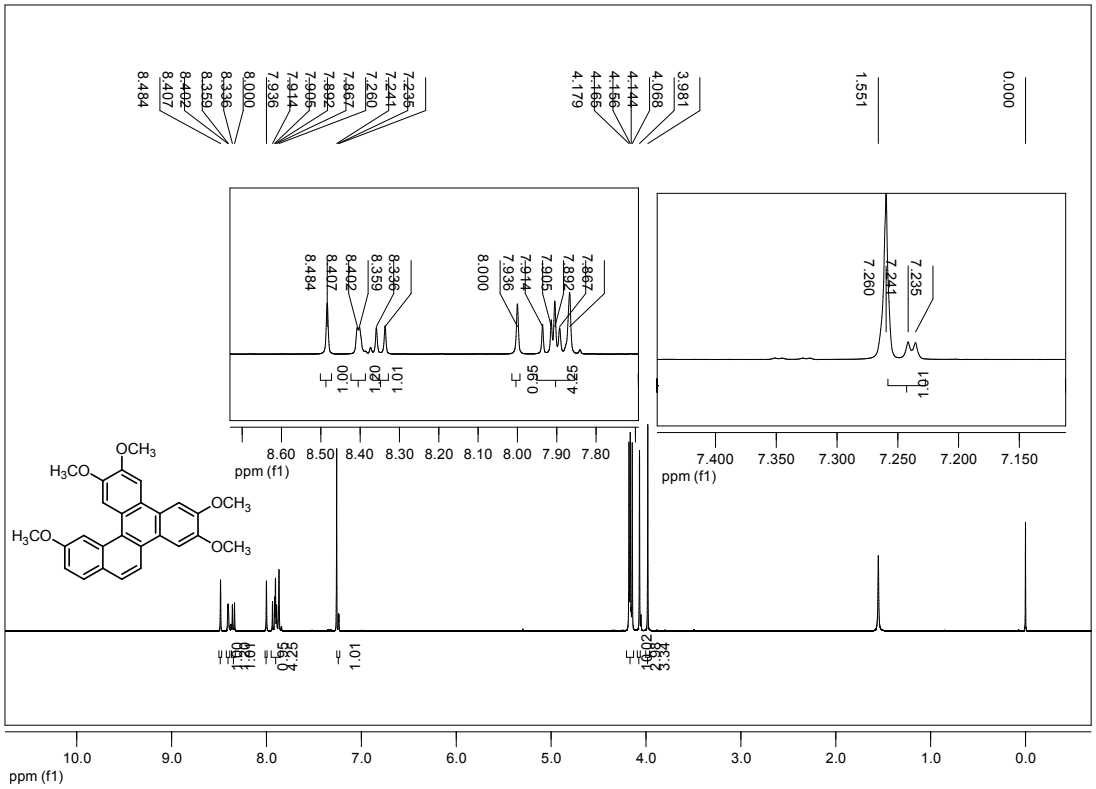



The $^{1}H$ NMR spectra of compound 4a which was prepared using method two.

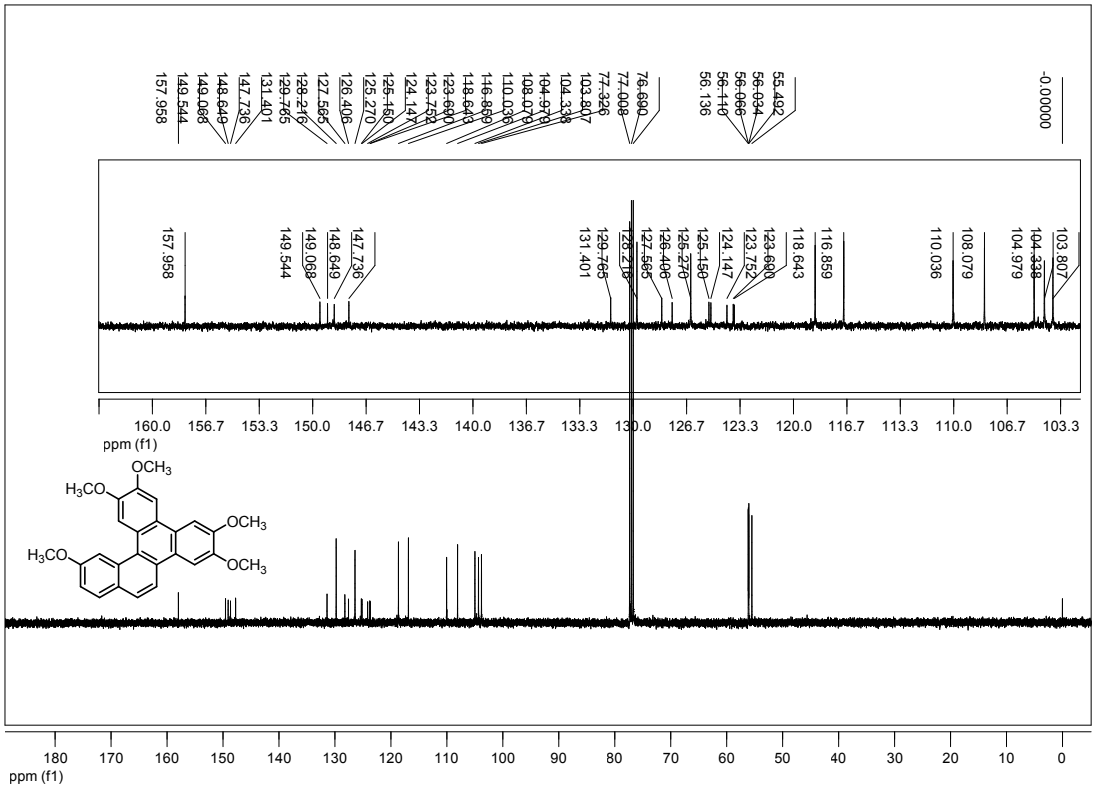



The $^{13}C$ NMR spectra of compound 4a which was prepared using method two

## 4b (method two)

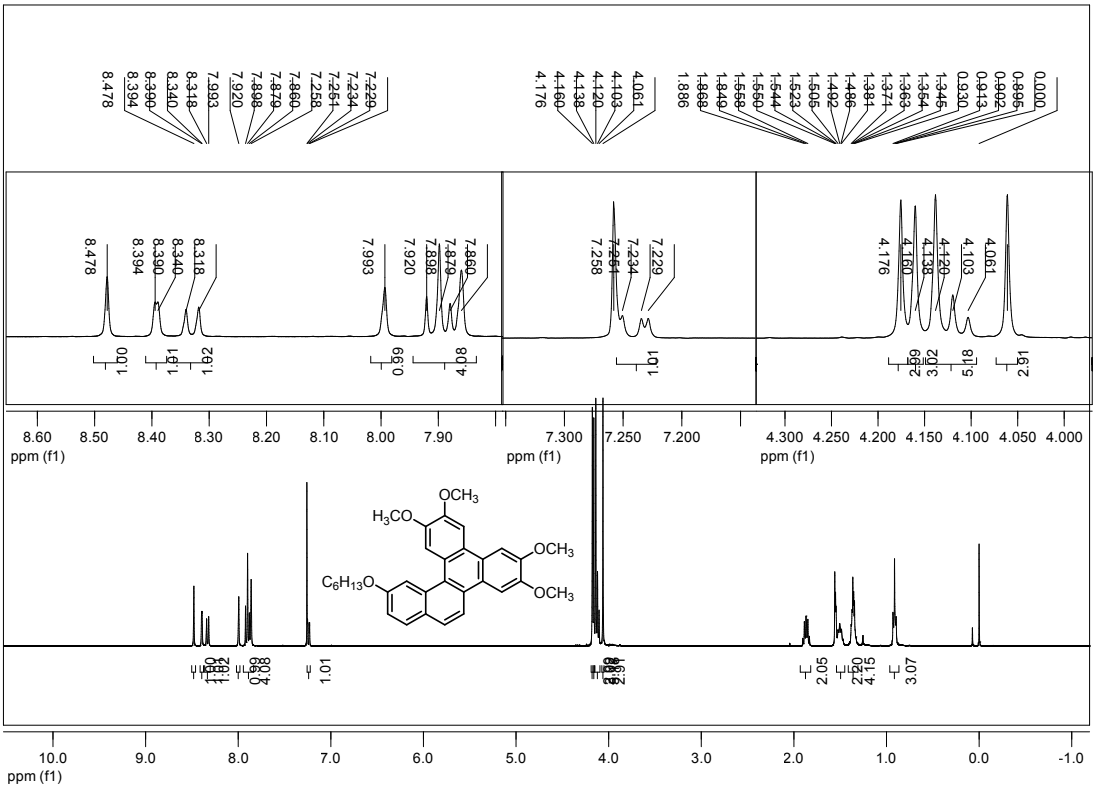



The $^{1}H$ NMR spectra of compound 4b which was prepared using method two.

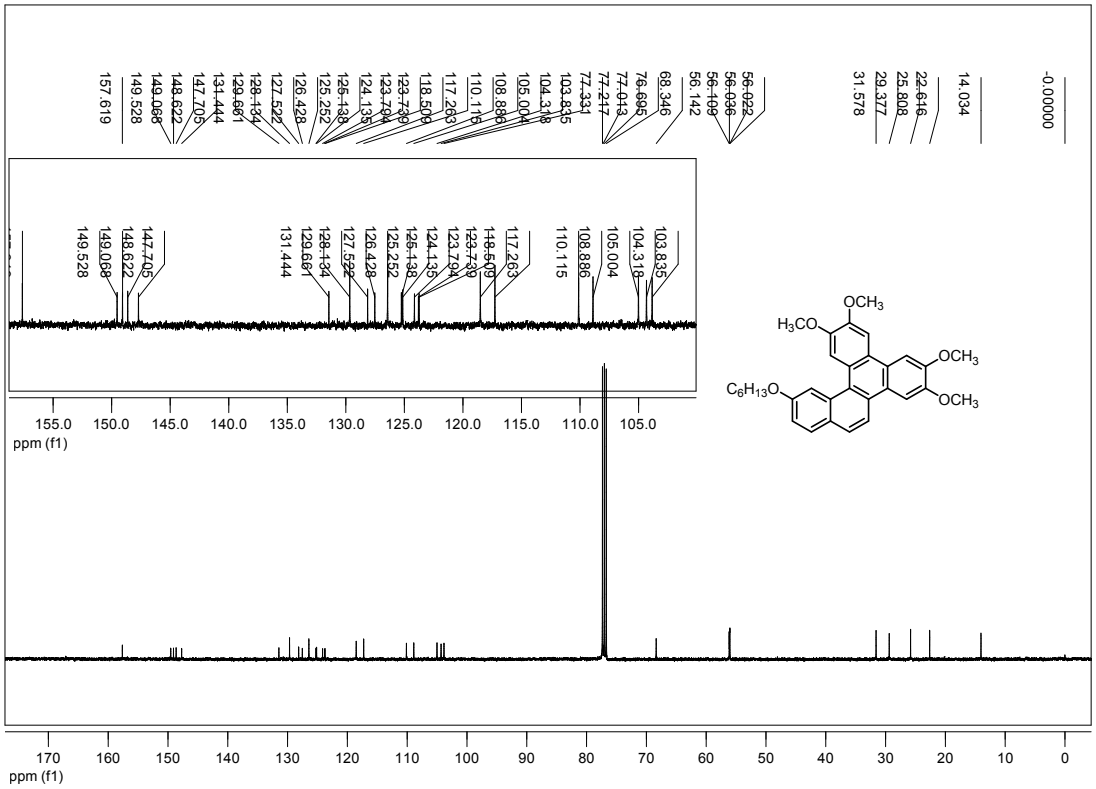



The $^{13}C$ NMR spectra of compound 4b which was prepared using method two

## 4c (method two)

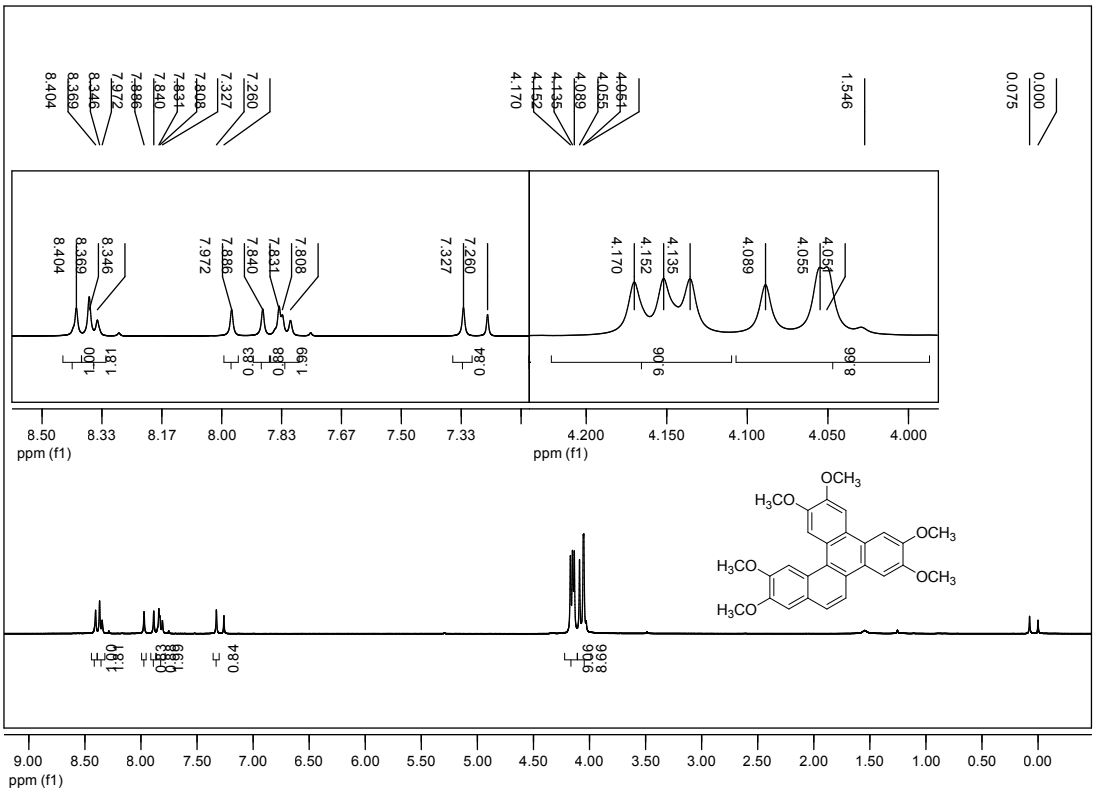



The $^{1}H$ NMR spectra of compound 4c which was prepared using method two.

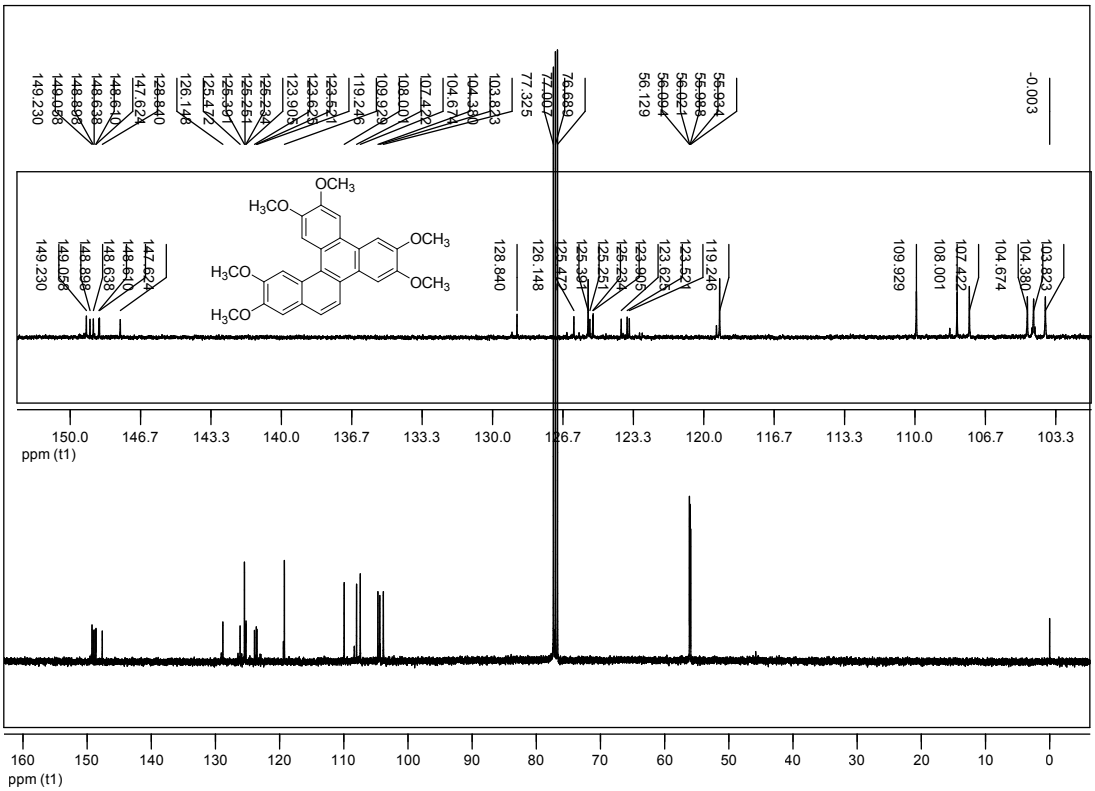



The $^{13}C$ NMR spectra of compound 4c which was prepared using method two

## 4d (method two)

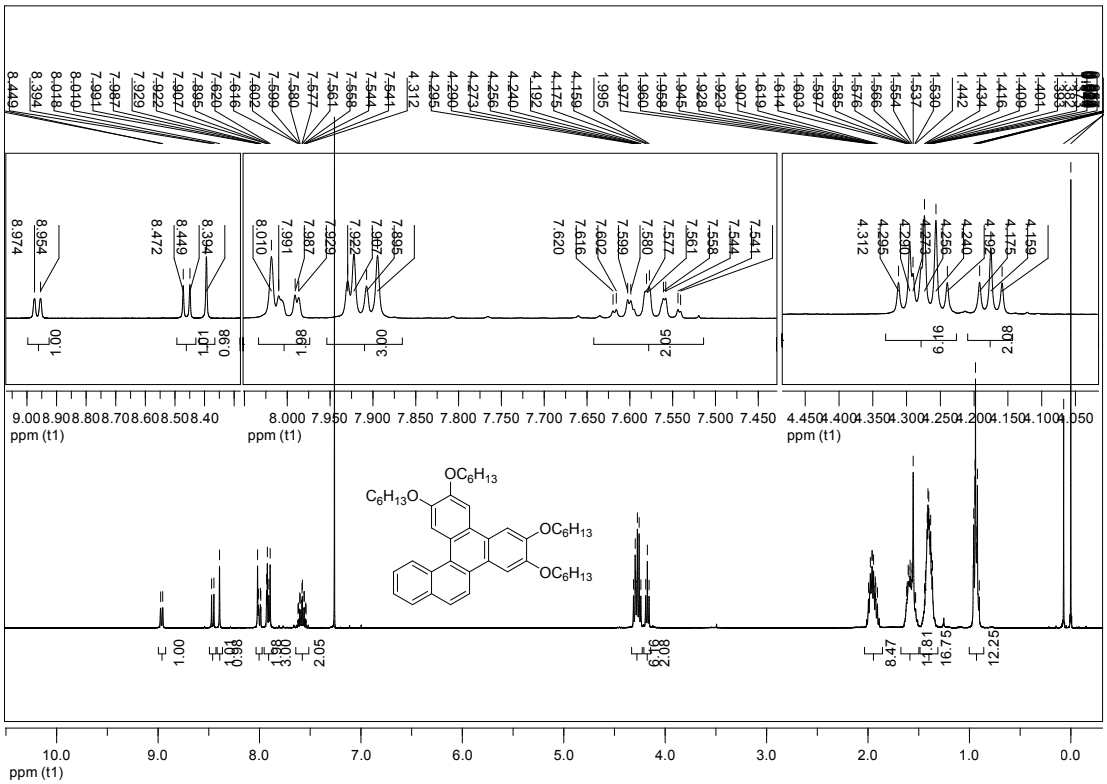


The $^{1}H$ NMR spectra of compound 4d which was prepared using method two.

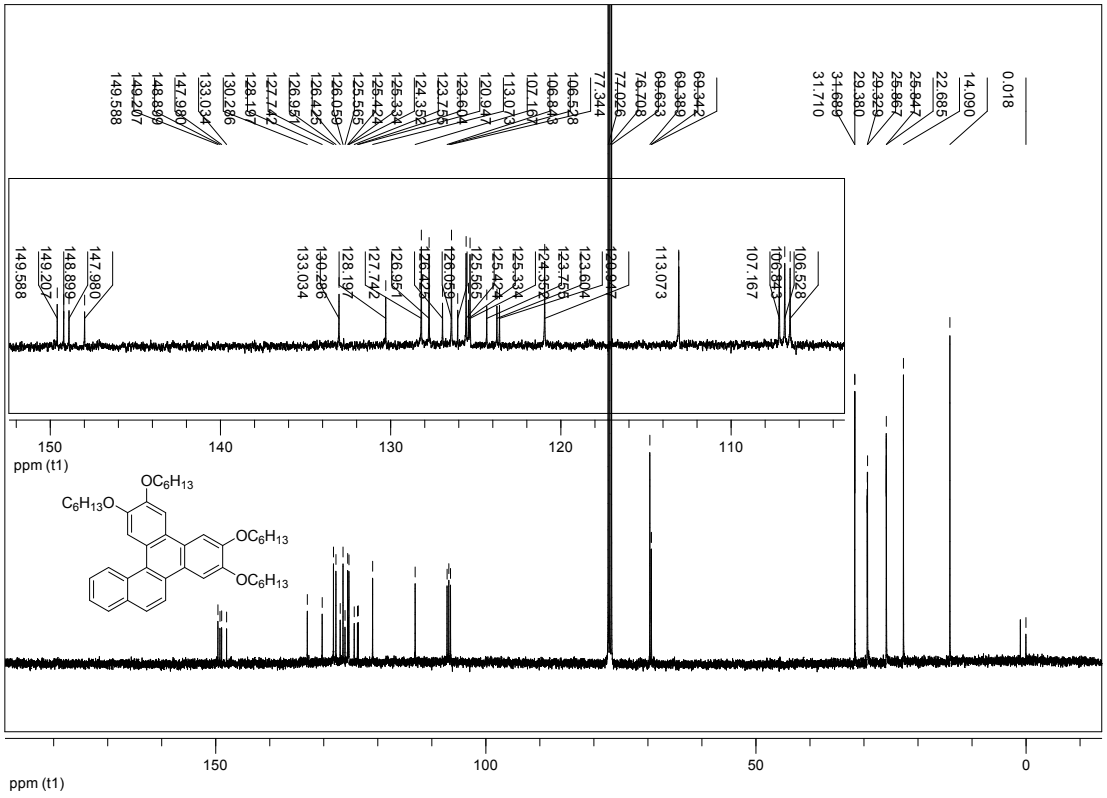


The $^{13}C$ NMR spectra of compound 4d which was prepared using method two

# 4e (method two)

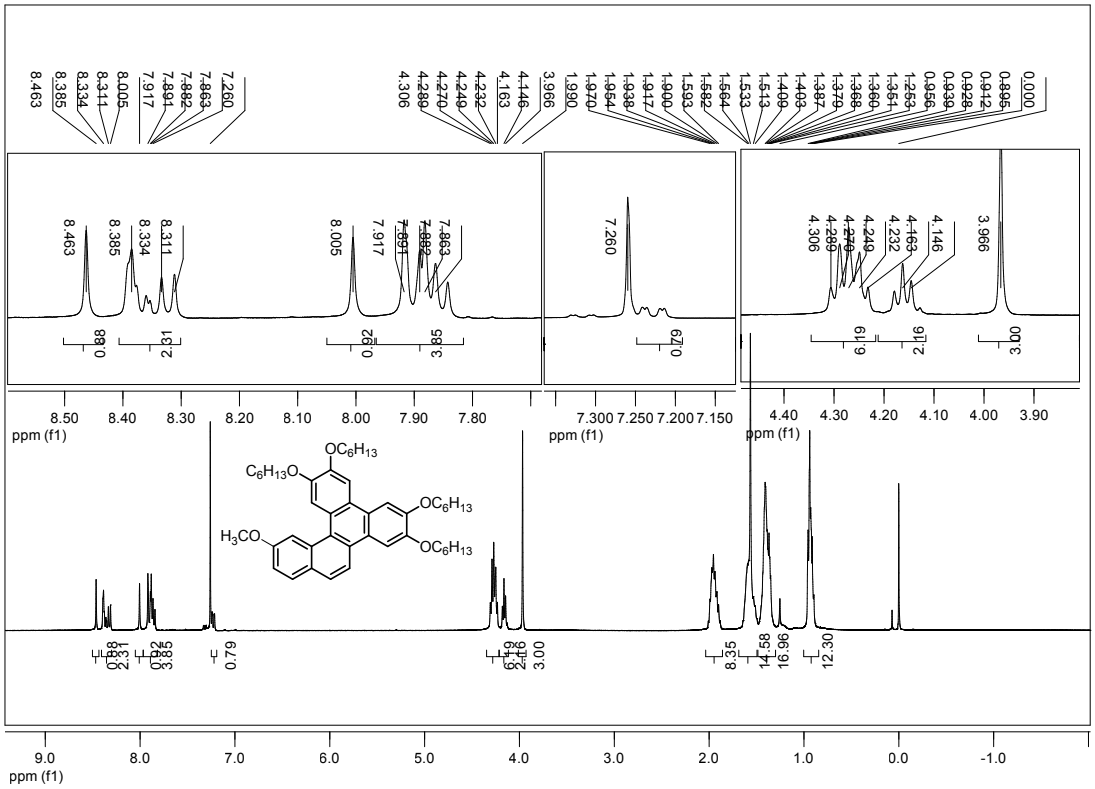


The $^{1}H$ NMR spectra of compound 4e which was prepared using method two.

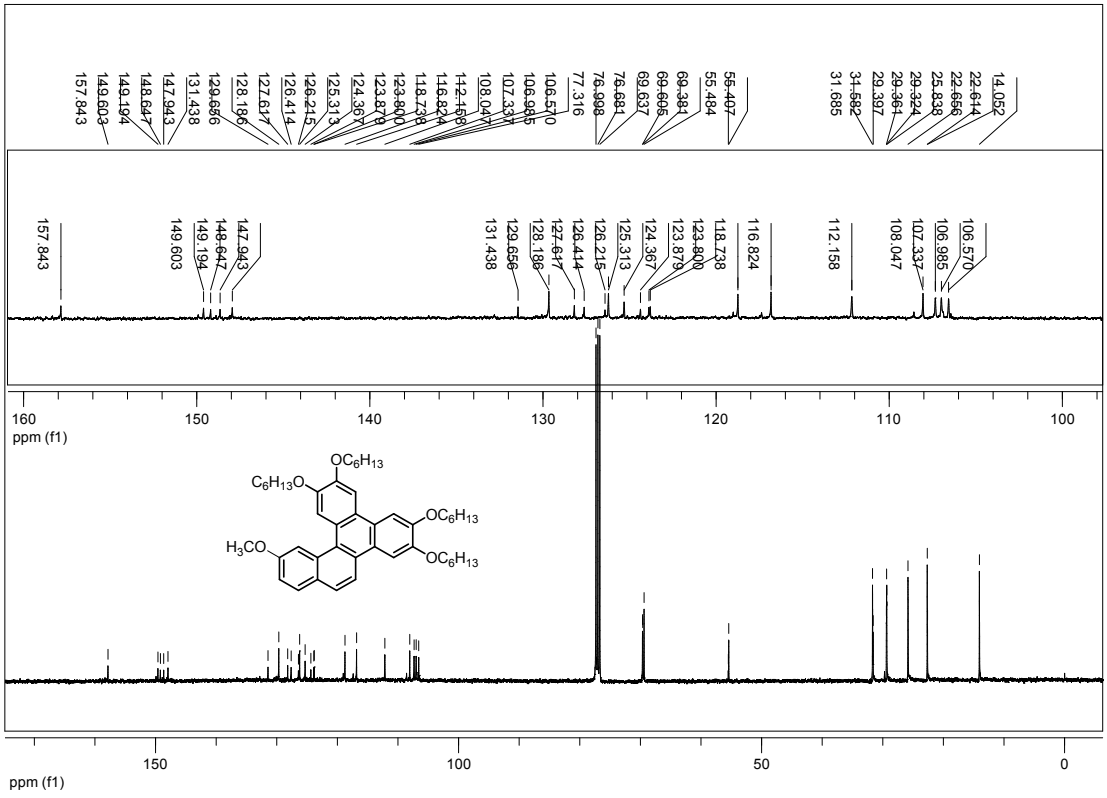


The $^{13}C$ NMR spectra of compound 4e which was prepared using method two

## 4f (method two)

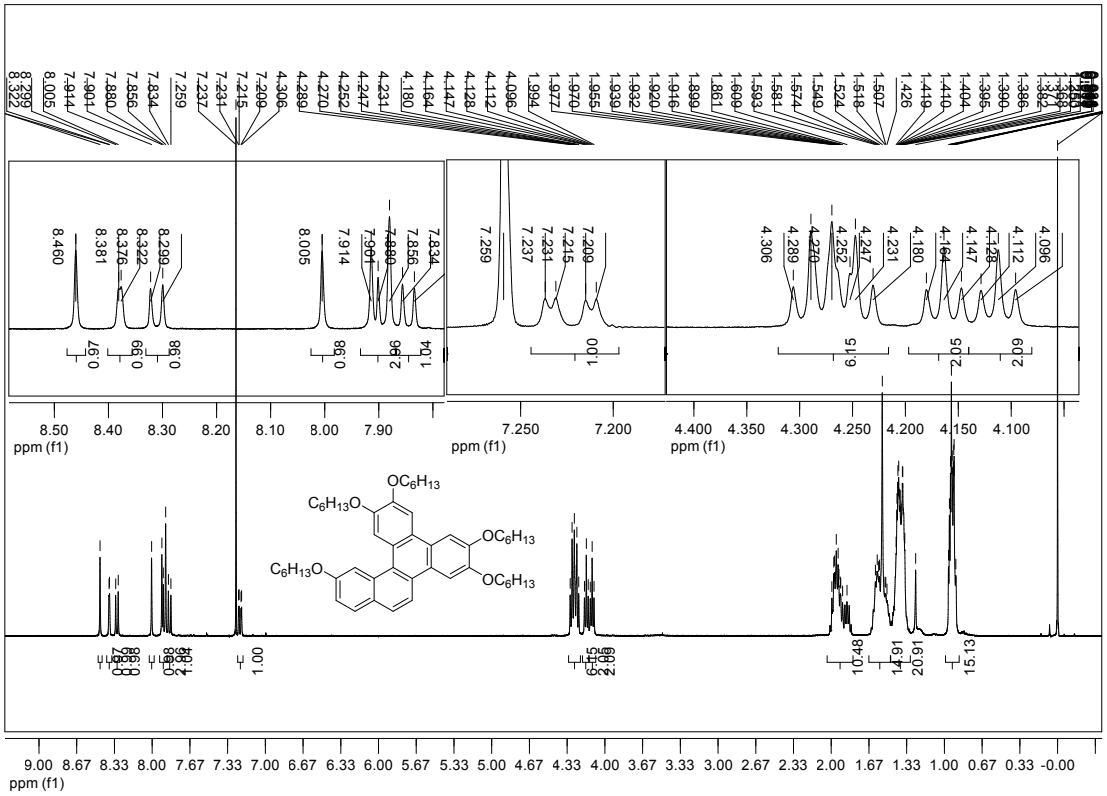



The $^{1}H$ NMR spectra of compound 4f which was prepared using method two.

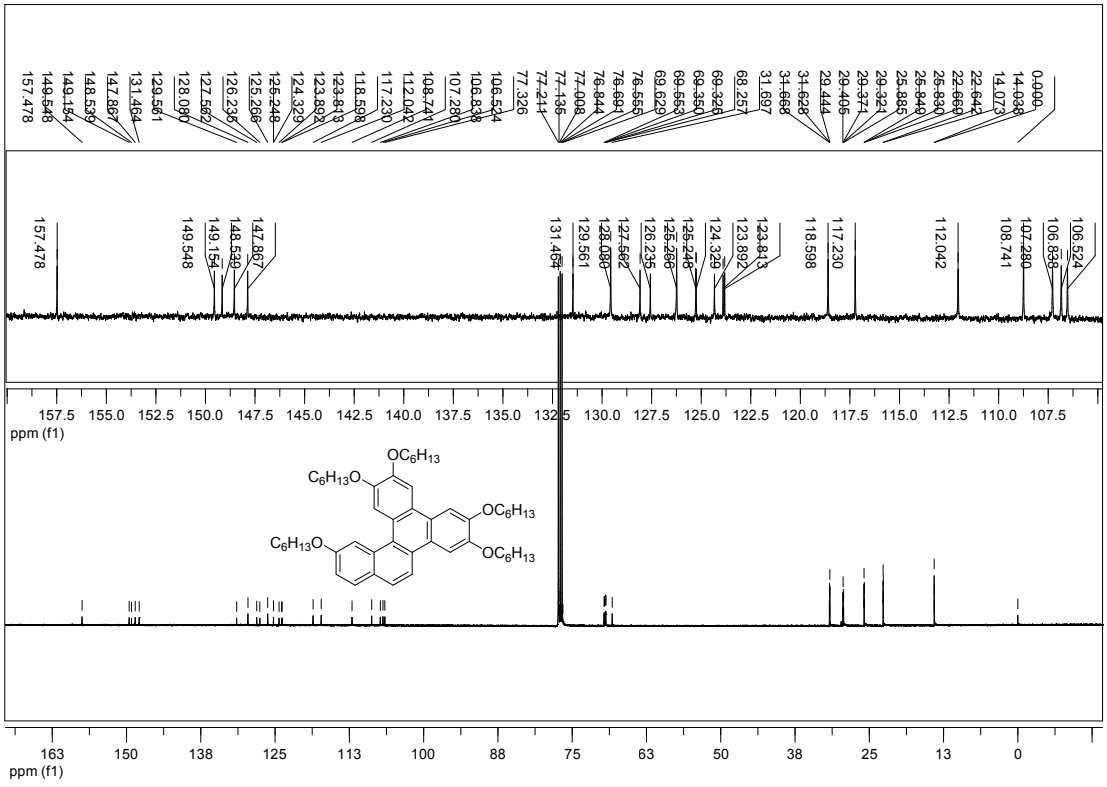



The $^{13}C$ NMR spectra of compound 4f which was prepared using method two

# 4g (method two)

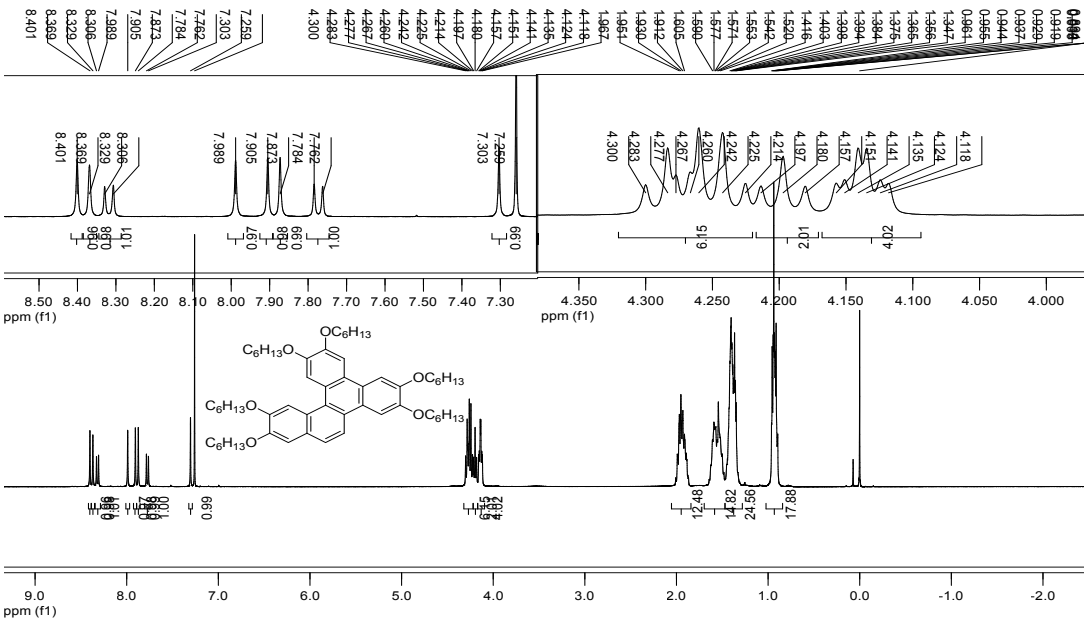


The $^{1}H$ NMR spectra of compound 4g which was prepared using method two.

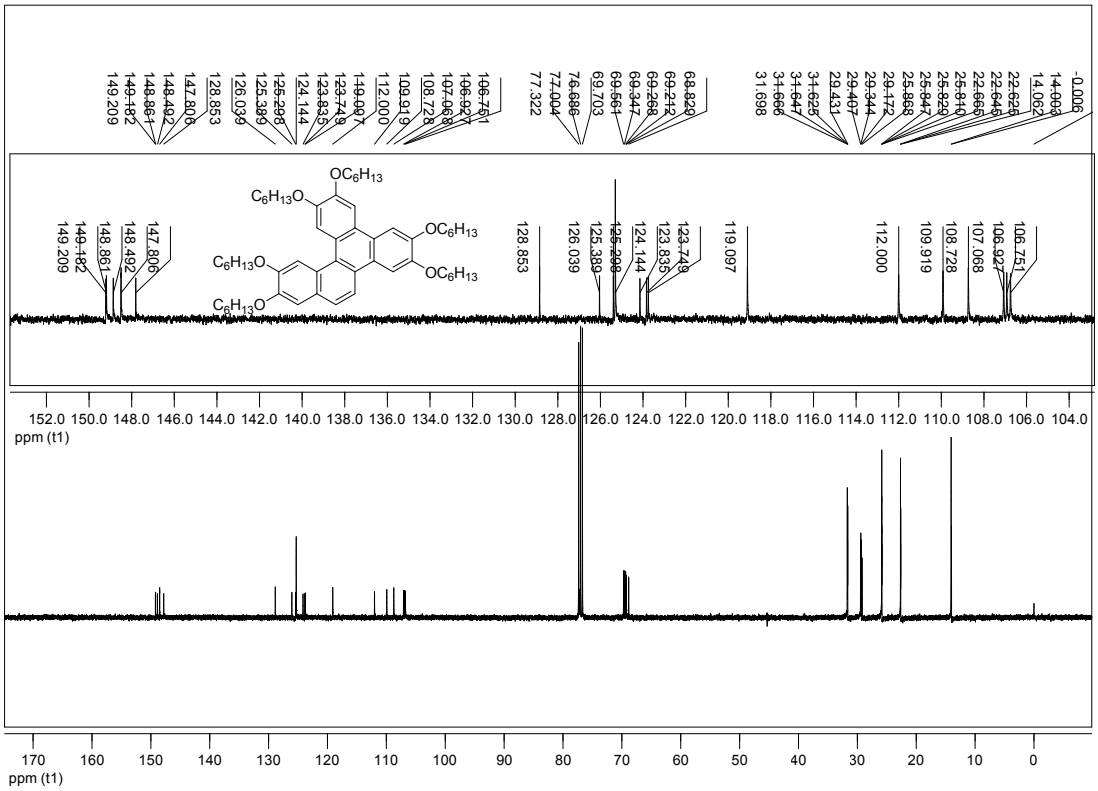


The $^{13}C$ NMR spectra of compound 4g which was prepared using method two

# 4h (method two)

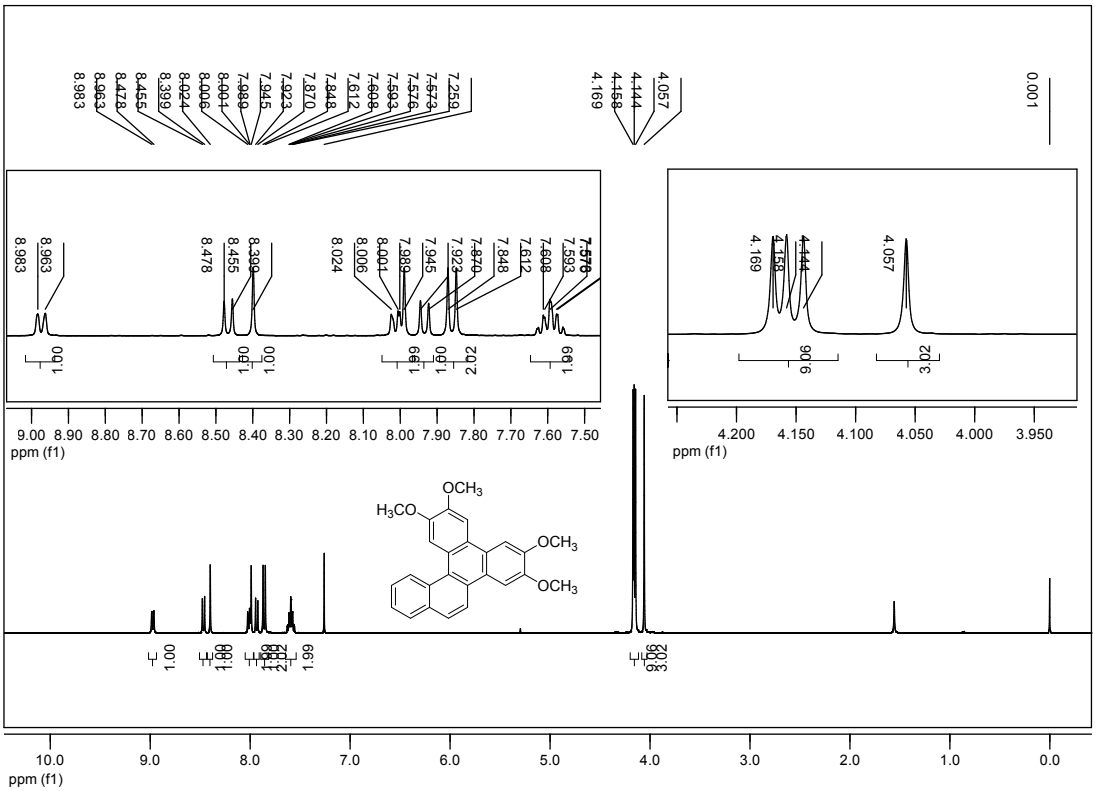


The $^{1}H$ NMR spectra of compound 4h which was prepared using method two.

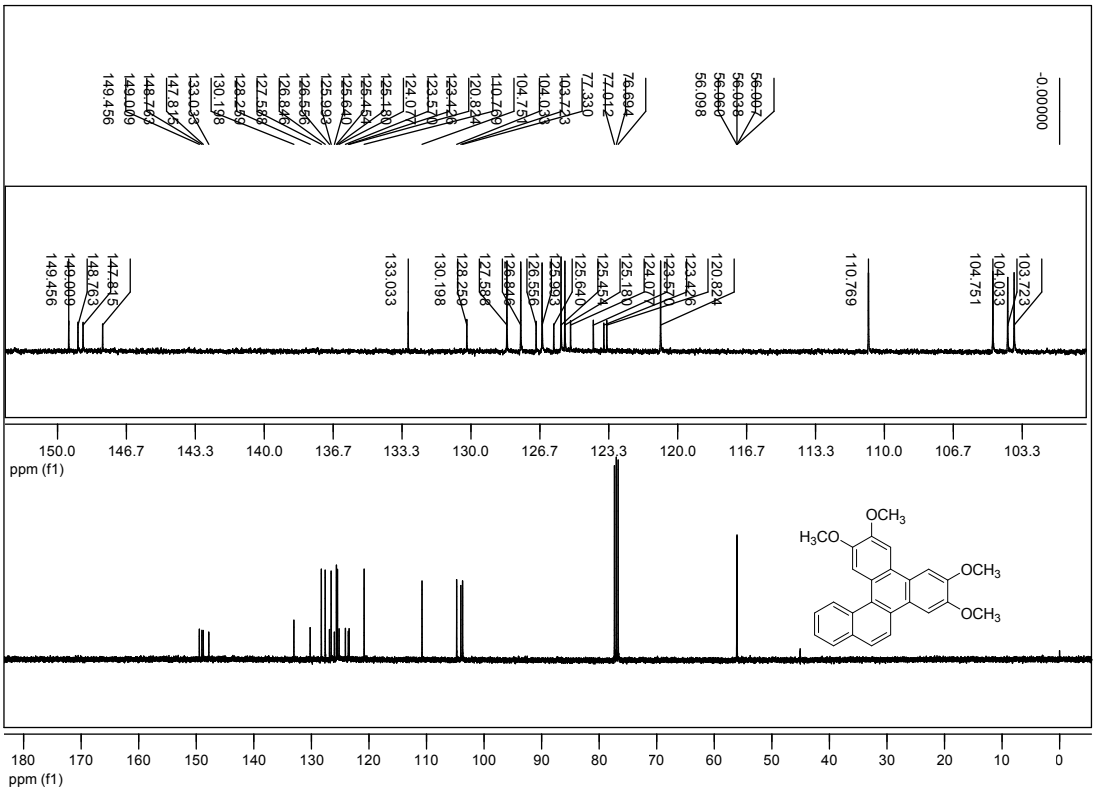


The $^{13}C$ NMR spectra of compound 4h which was prepared using method two

## 4a (method one)

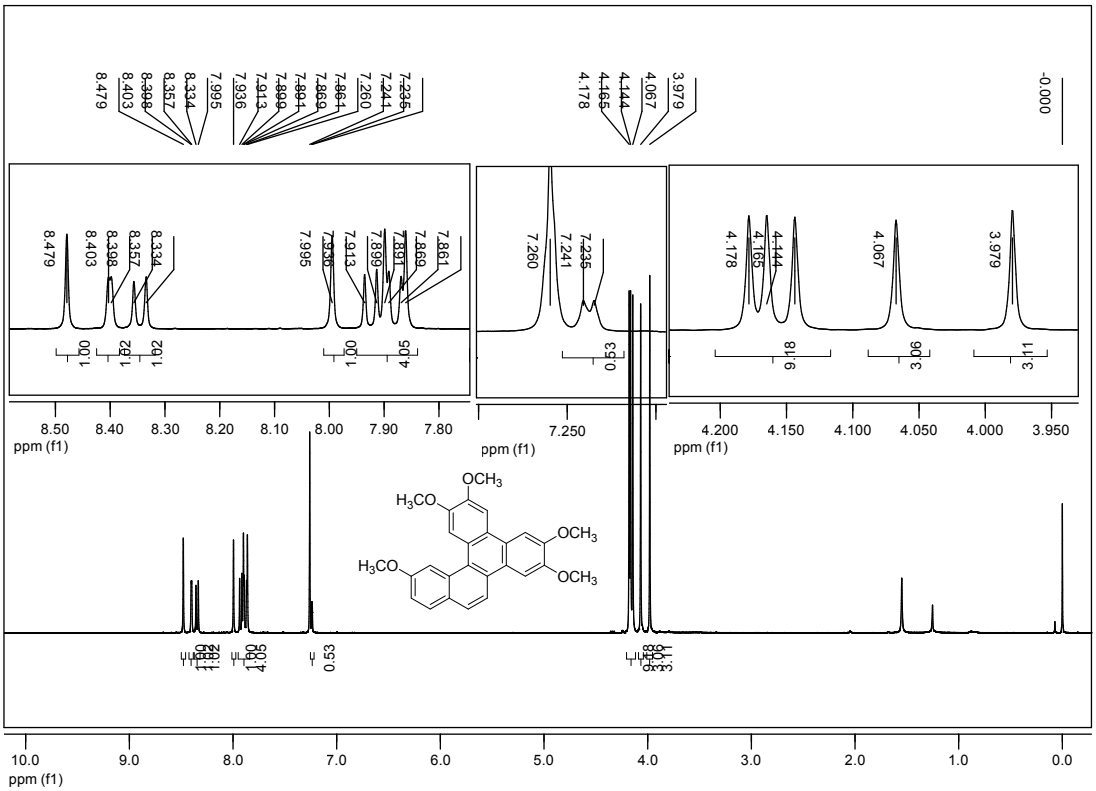



The $^{1}H$ NMR spectra of compound 4a which was prepared using method one

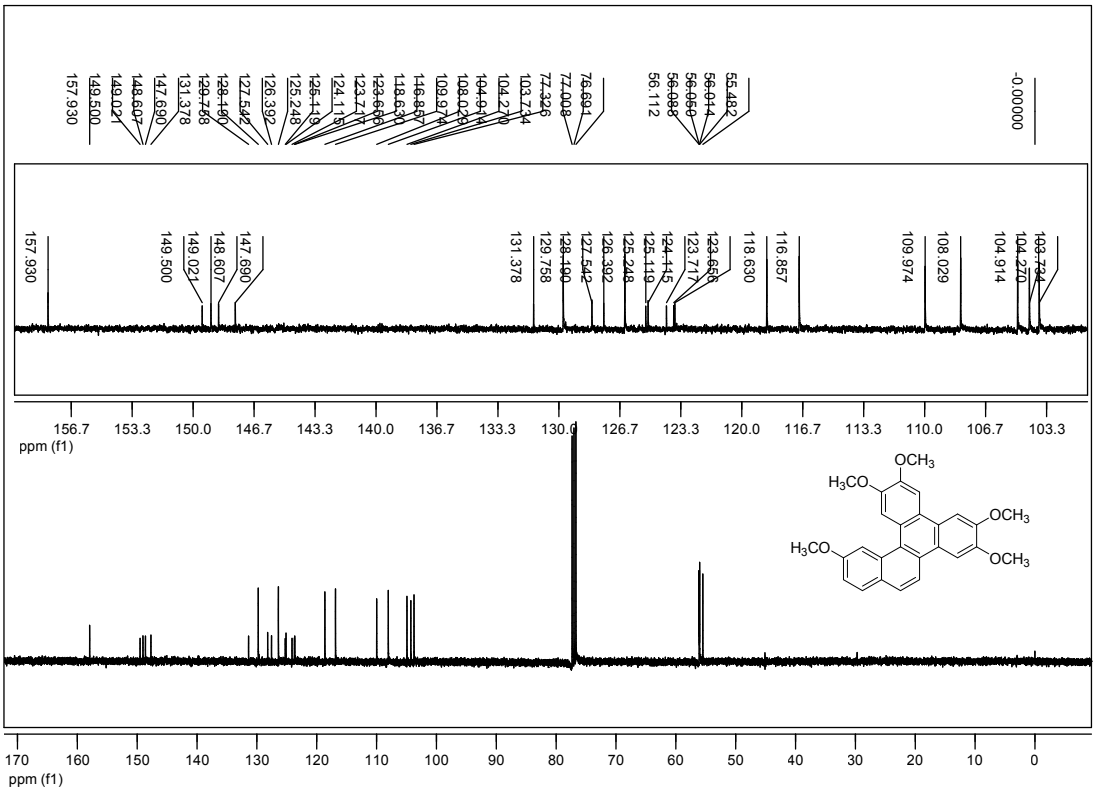



The $^{13}C$ NMR spectra of compound 4a which was prepared using method one

## 4b (method one)

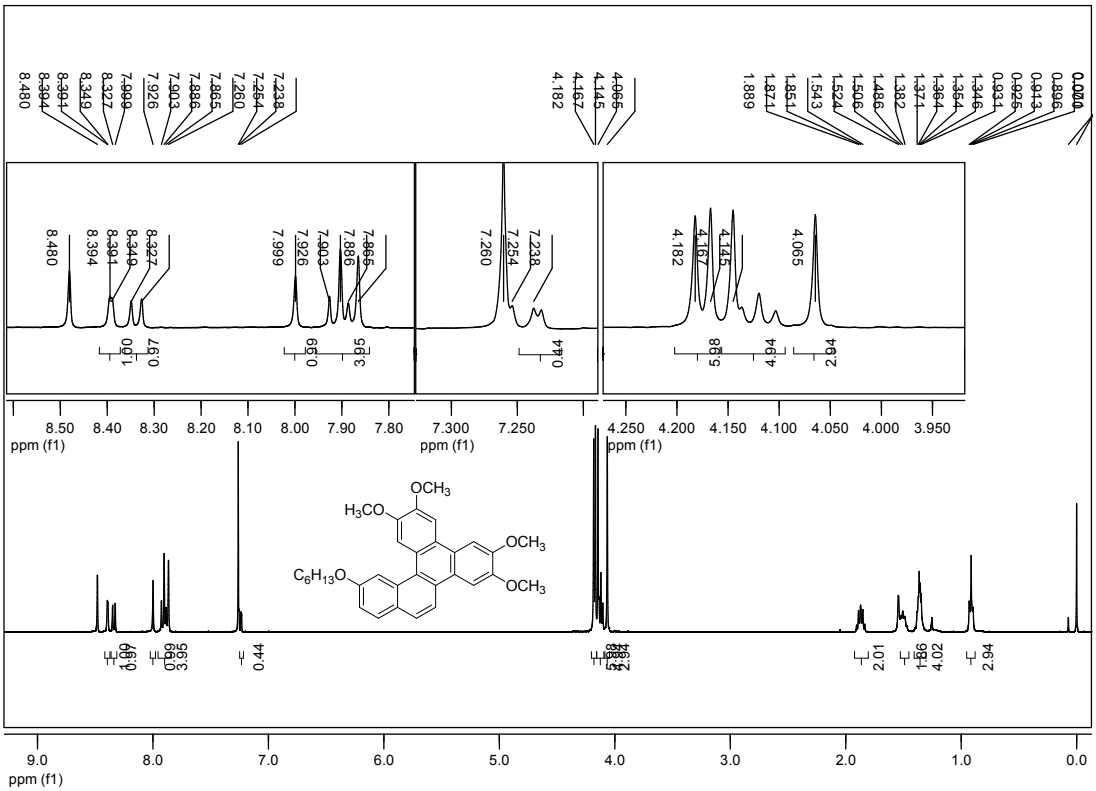



The $^{1}H$ NMR spectra of compound 4b which was prepared using method one

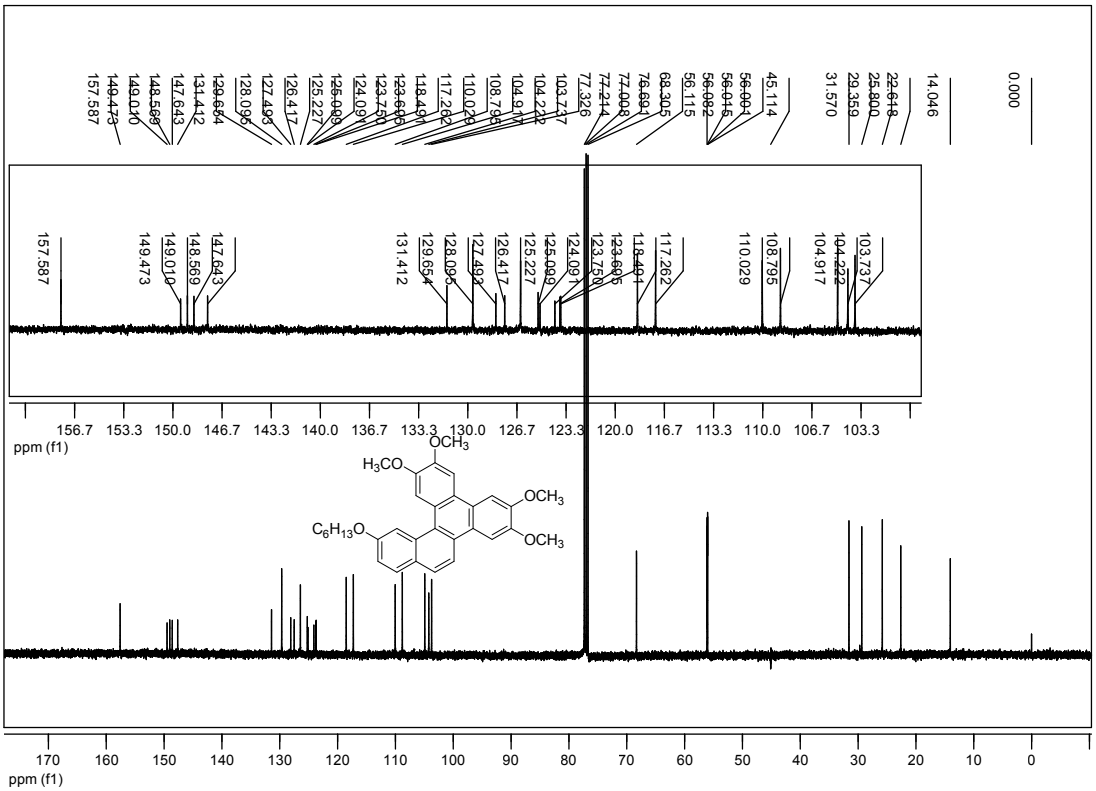



The $^{13}C$ NMR spectra of compound 4b which was prepared using method one

## 4c (method one)

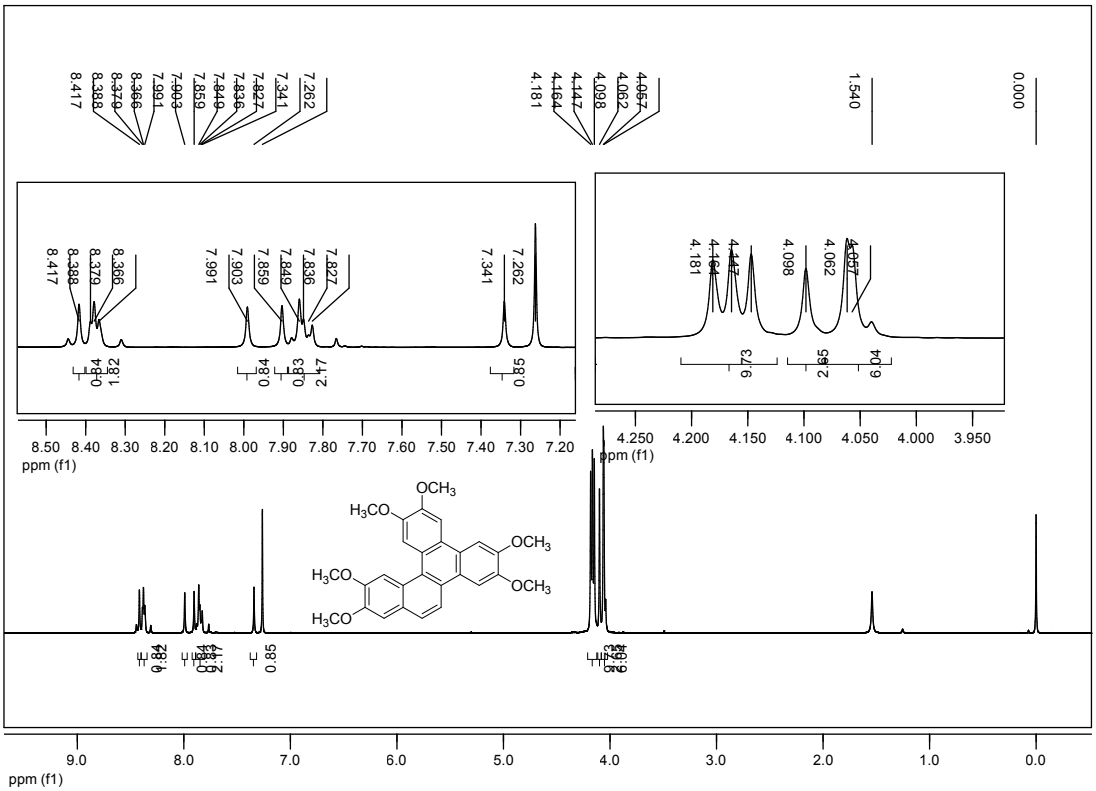


The $^{1}H$ NMR spectra of compound 4c which was prepared using method one

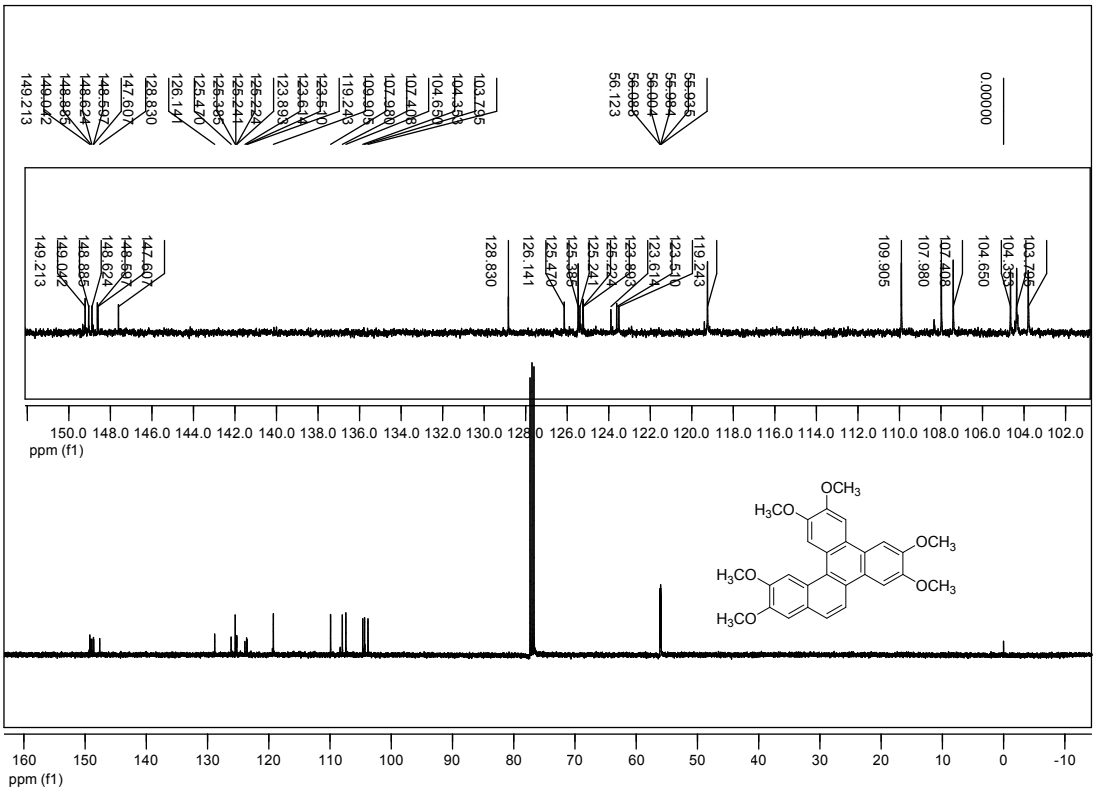


The $^{13}C$ NMR spectra of compound 4c which was prepared using method one

## 4d (method one)

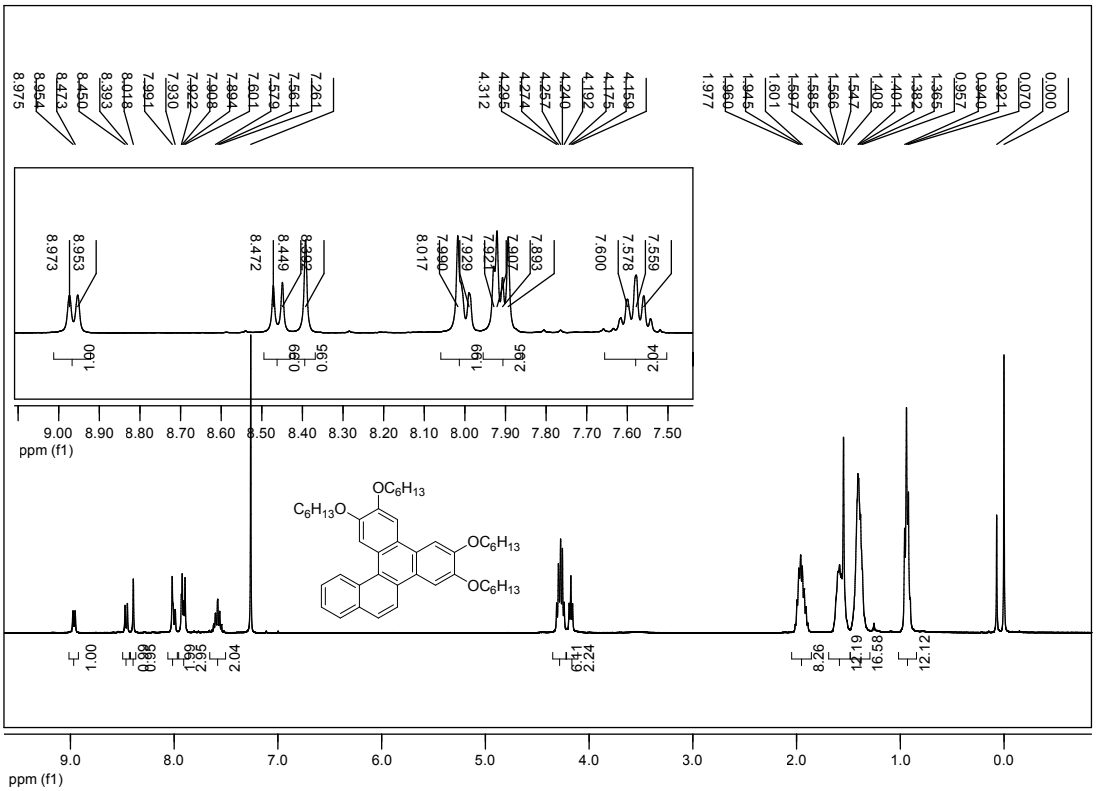



The $^{1}H$ NMR spectra of compound 4d which was prepared using method one

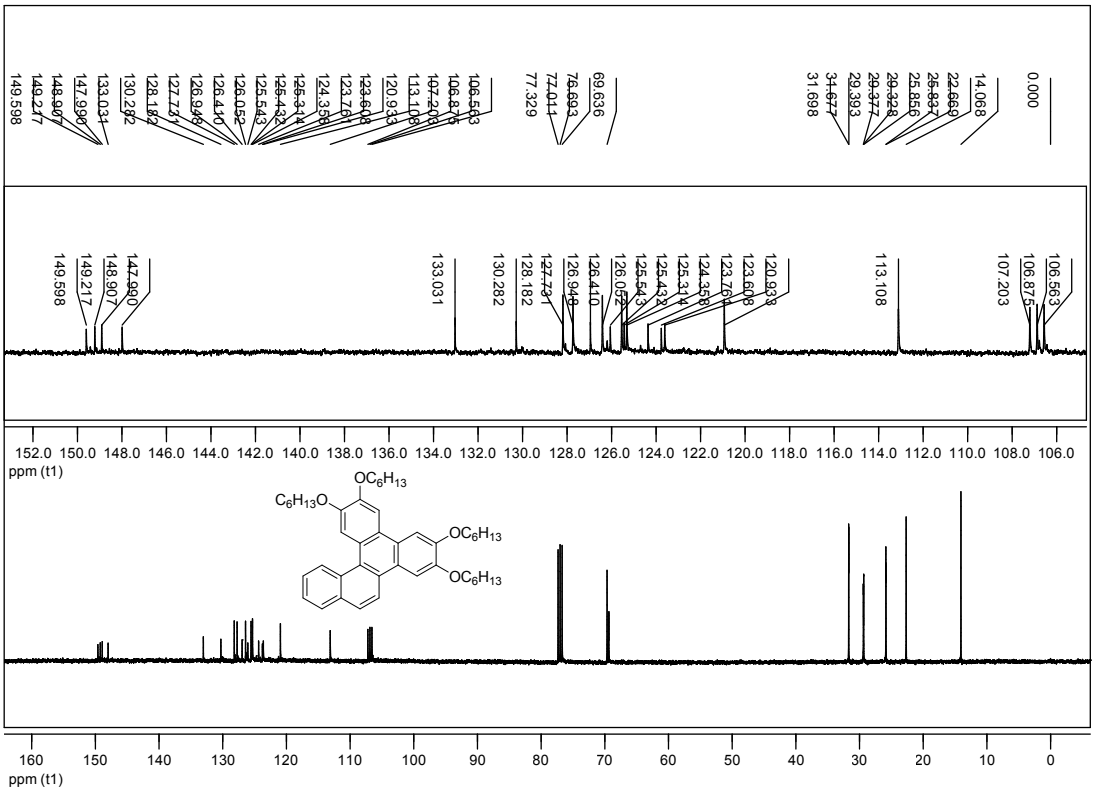



The $^{13}C$ NMR spectra of compound 4d which was prepared using method one

## 4e (method one)

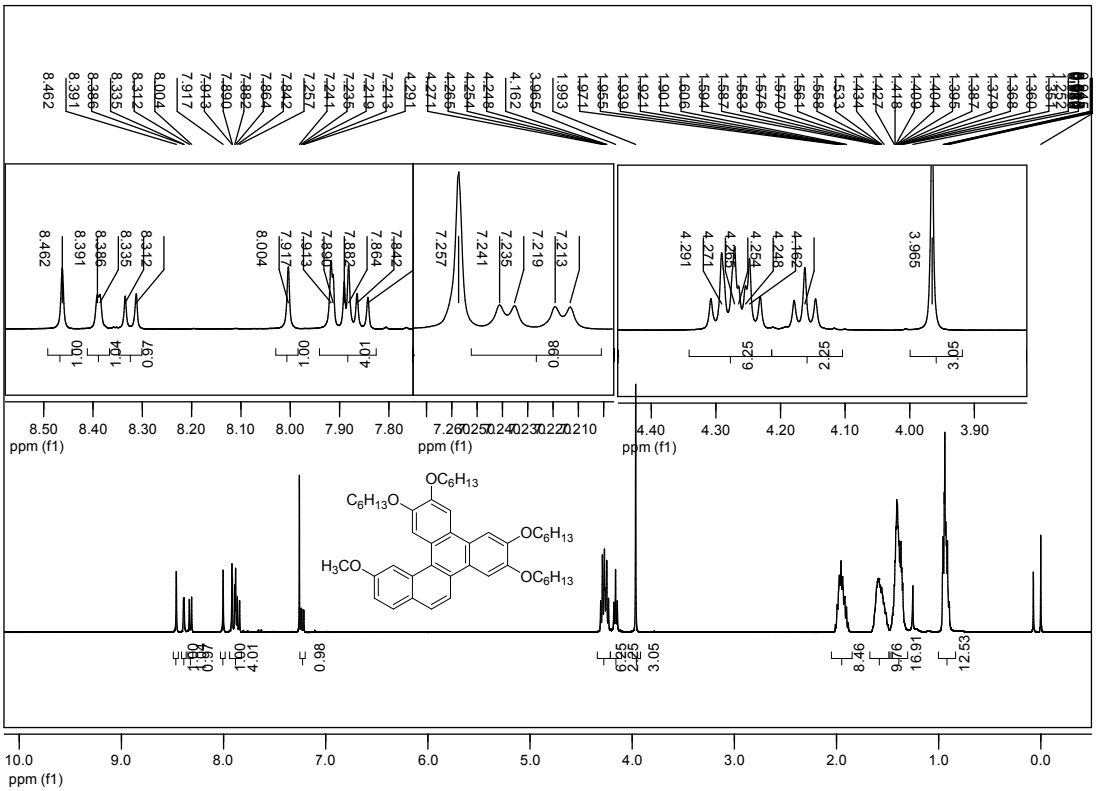



The $^{1}H$ NMR spectra of compound 4e which was prepared using method one

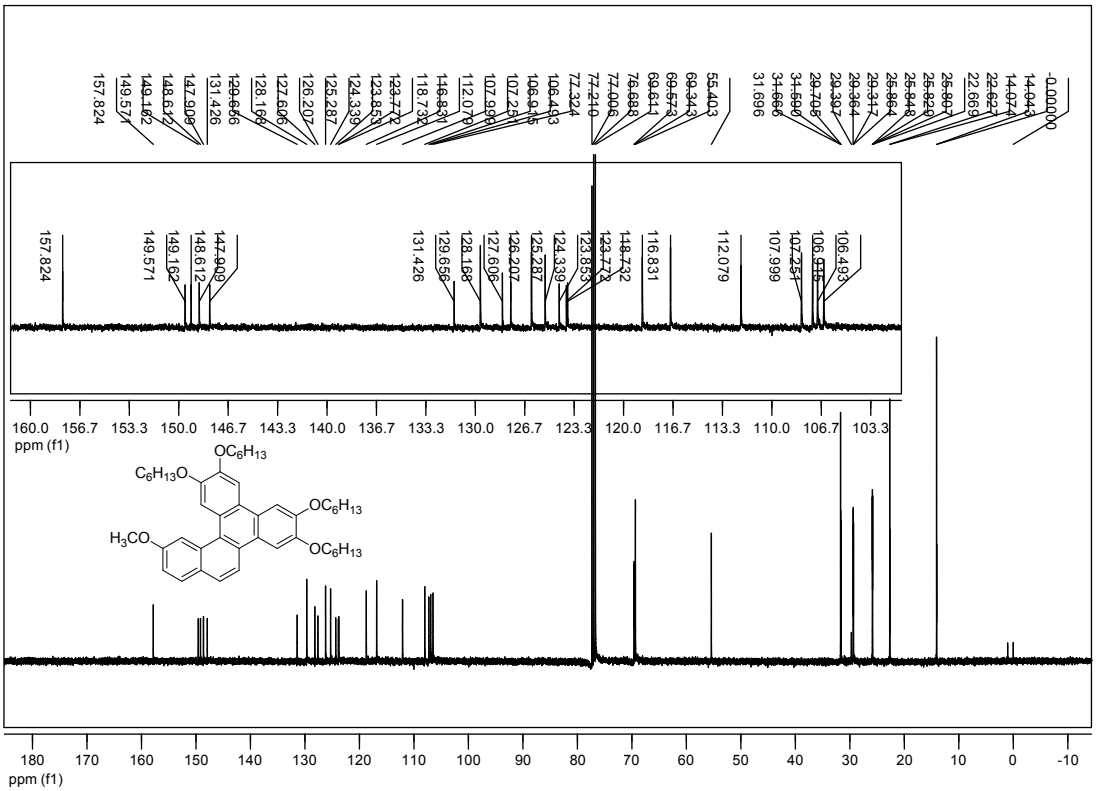



The $^{13}C$ NMR spectra of compound 4e which was prepared using method one

## 4f (method one)

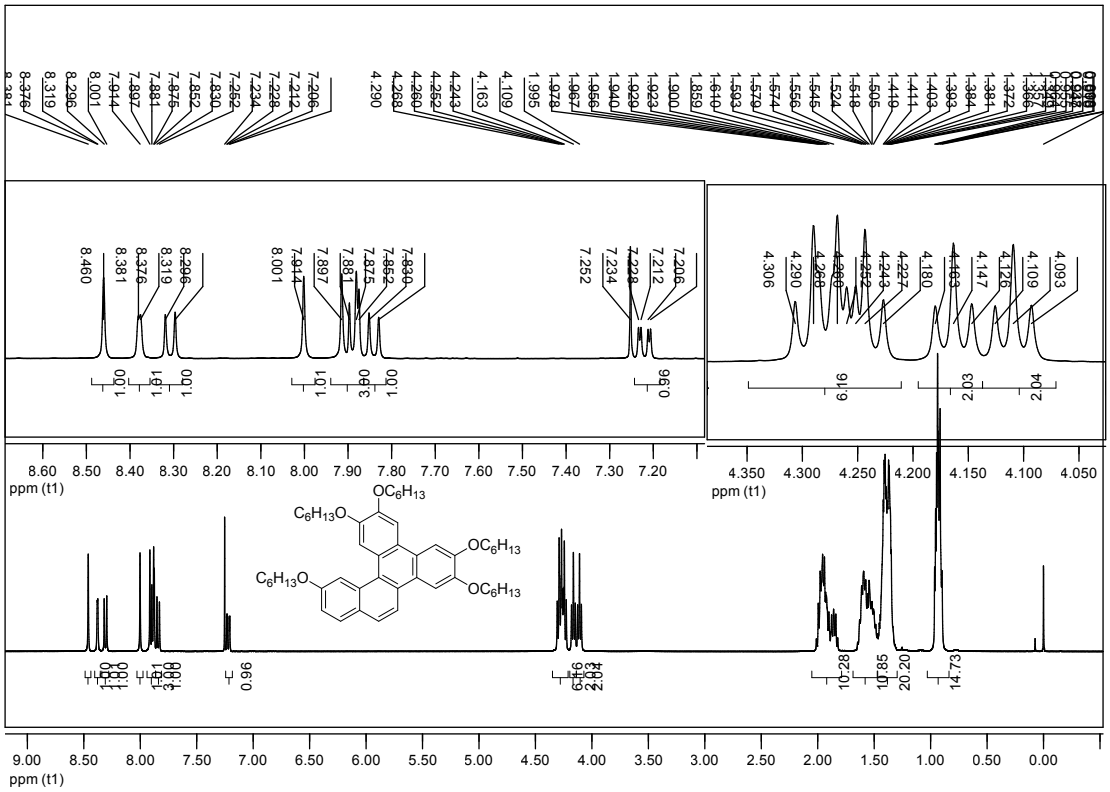



The $^{1}H$ NMR spectra of compound 4f which was prepared using method one

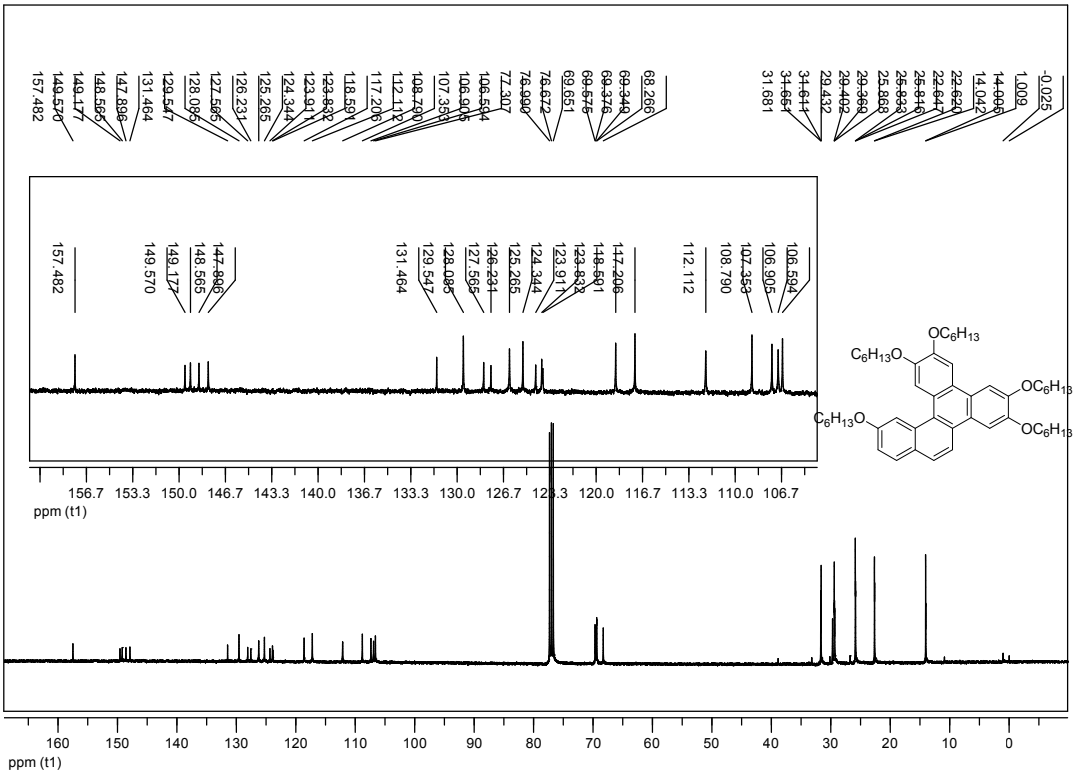



The $^{13}C$ NMR spectra of compound 4f which was prepared using method one

# 4g (method one)

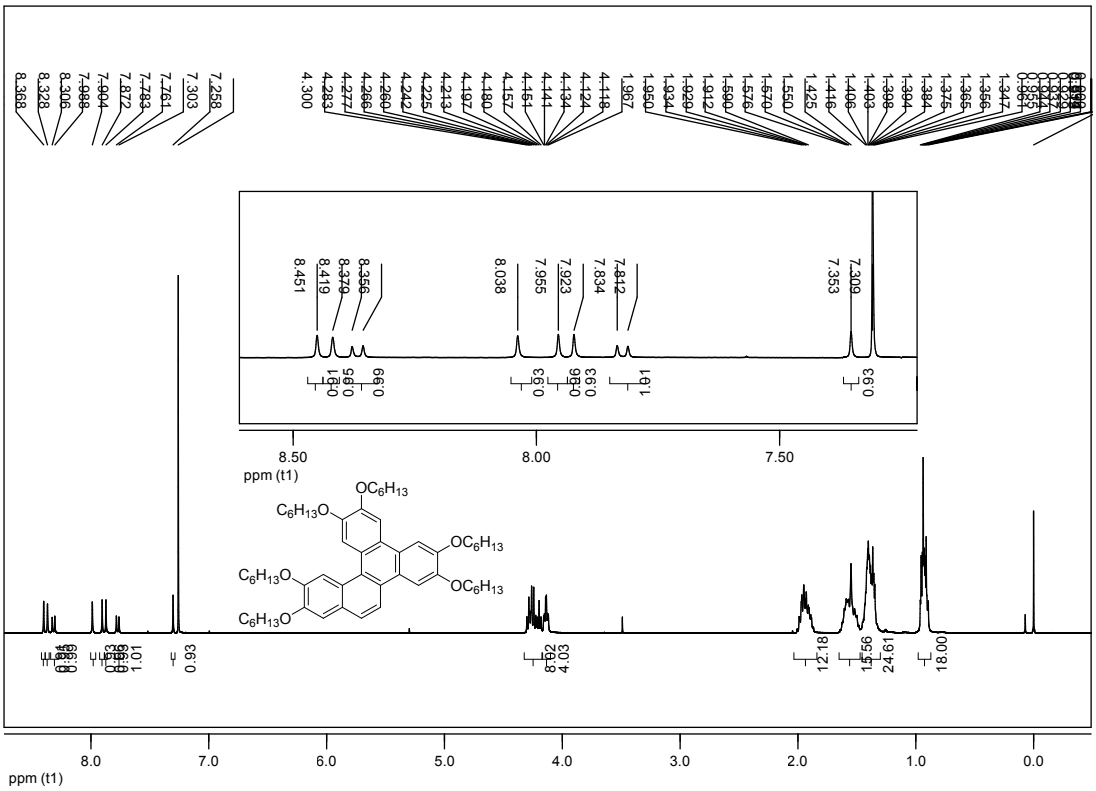


The $^{1}H$ NMR spectra of compound 4g which was prepared using method one

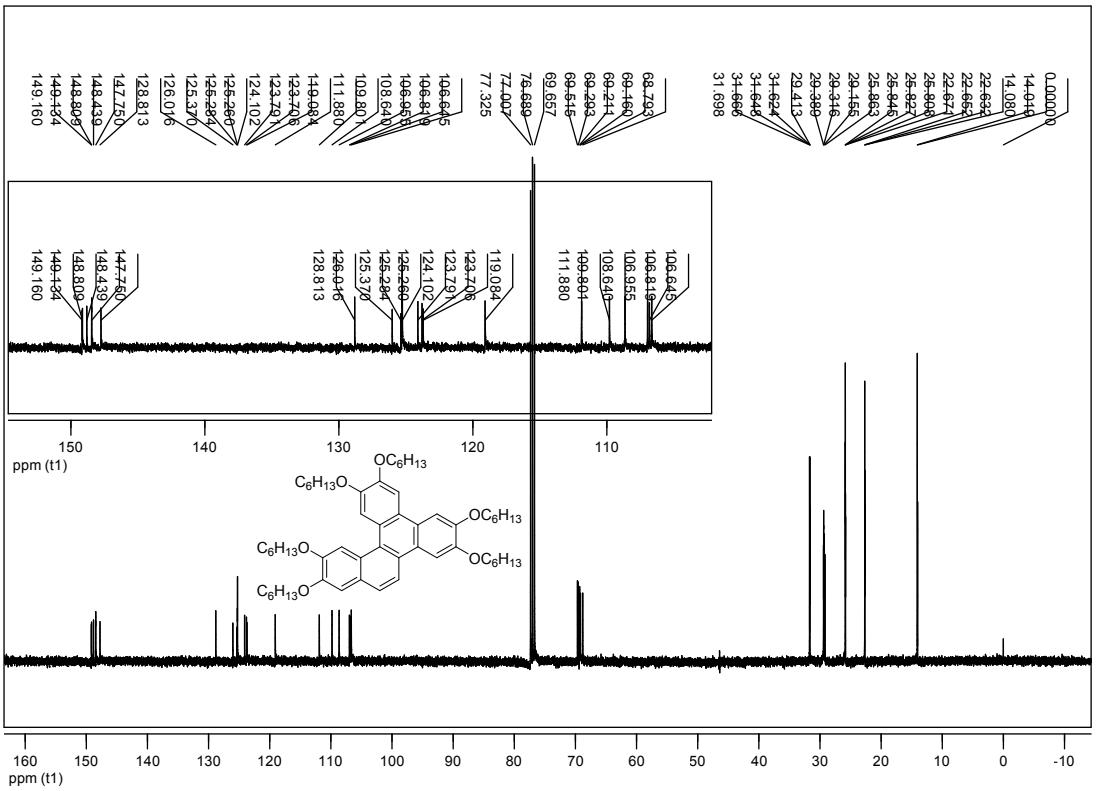


The $^{13}C$ NMR spectra of compound 4g which was prepared using method one

## 4h (method one)

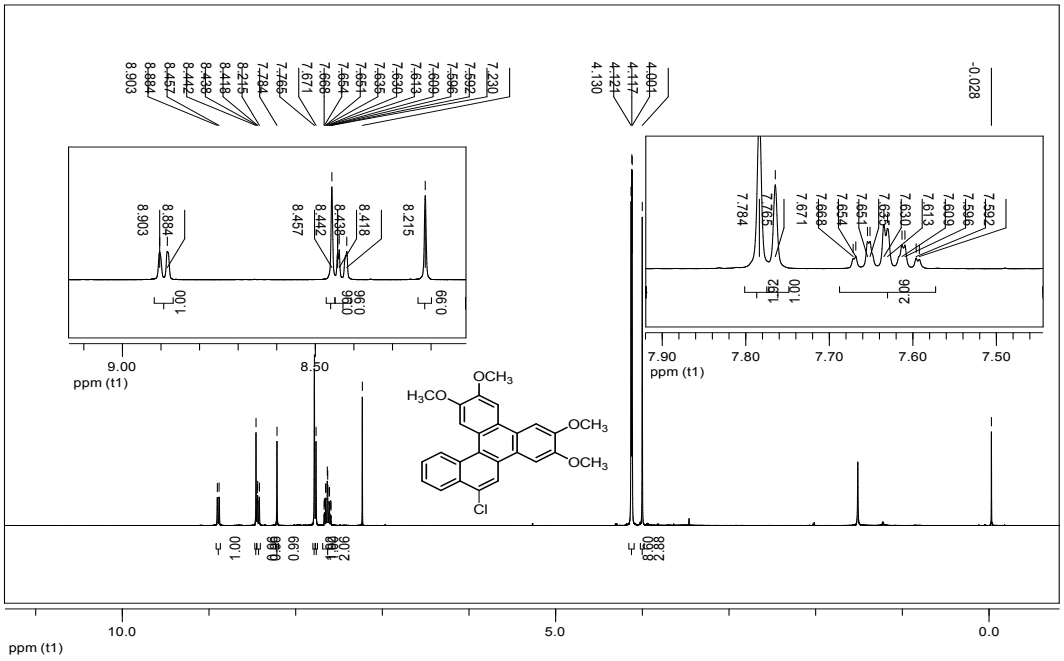



The $^{1}H$ NMR spectra of compound 4h which was prepared using method one

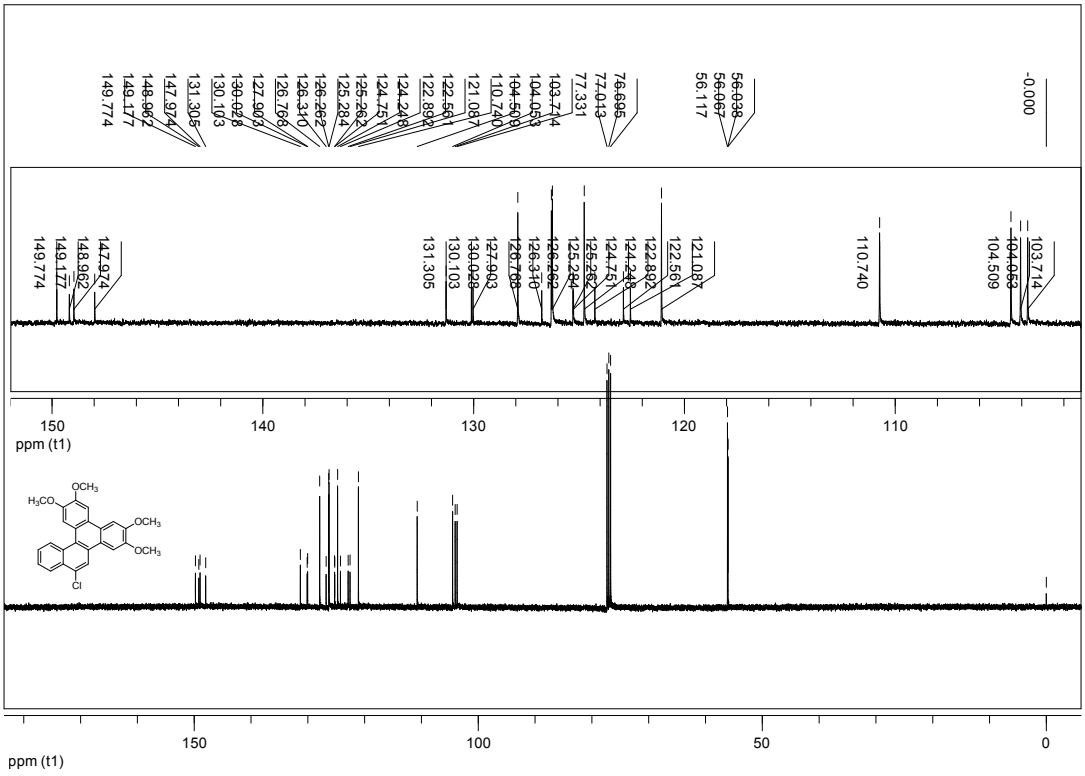



The $^{13}C$ NMR spectra of compound 4h which was prepared using method one

## 5a

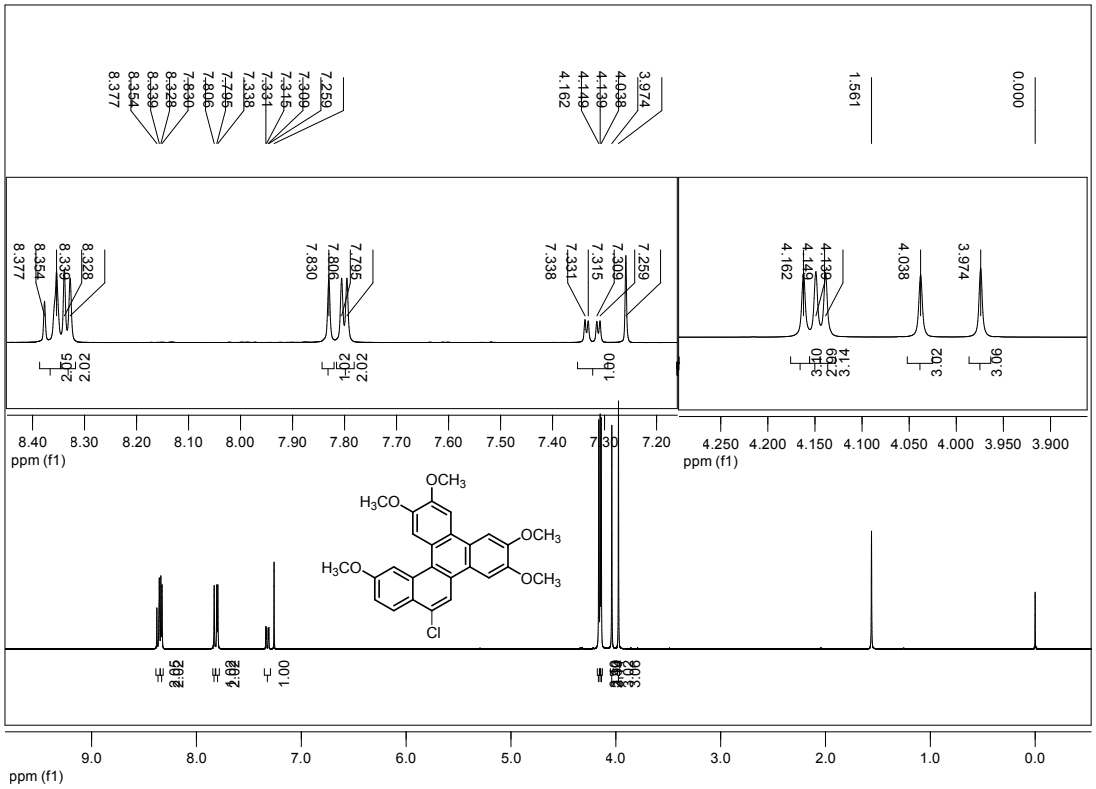



The $^{1}H$ NMR spectra of compound 5a.

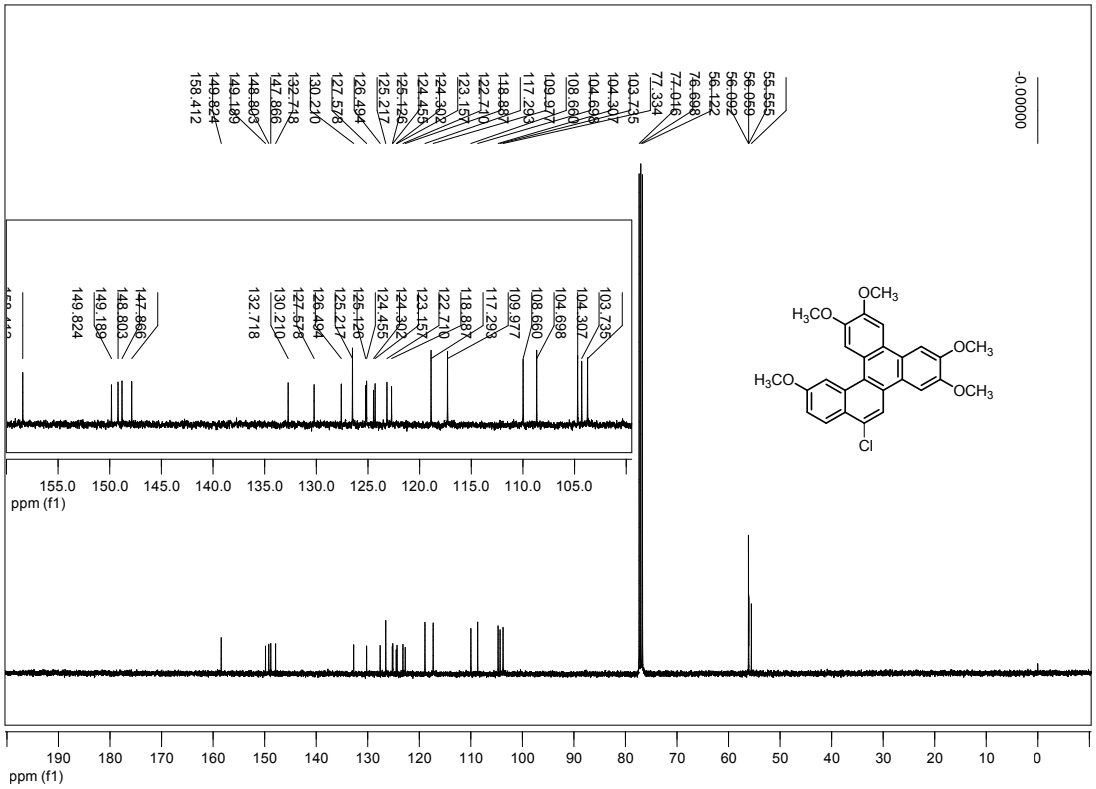



The $^{13}C$ NMR spectra of compound 5a.

## 5b

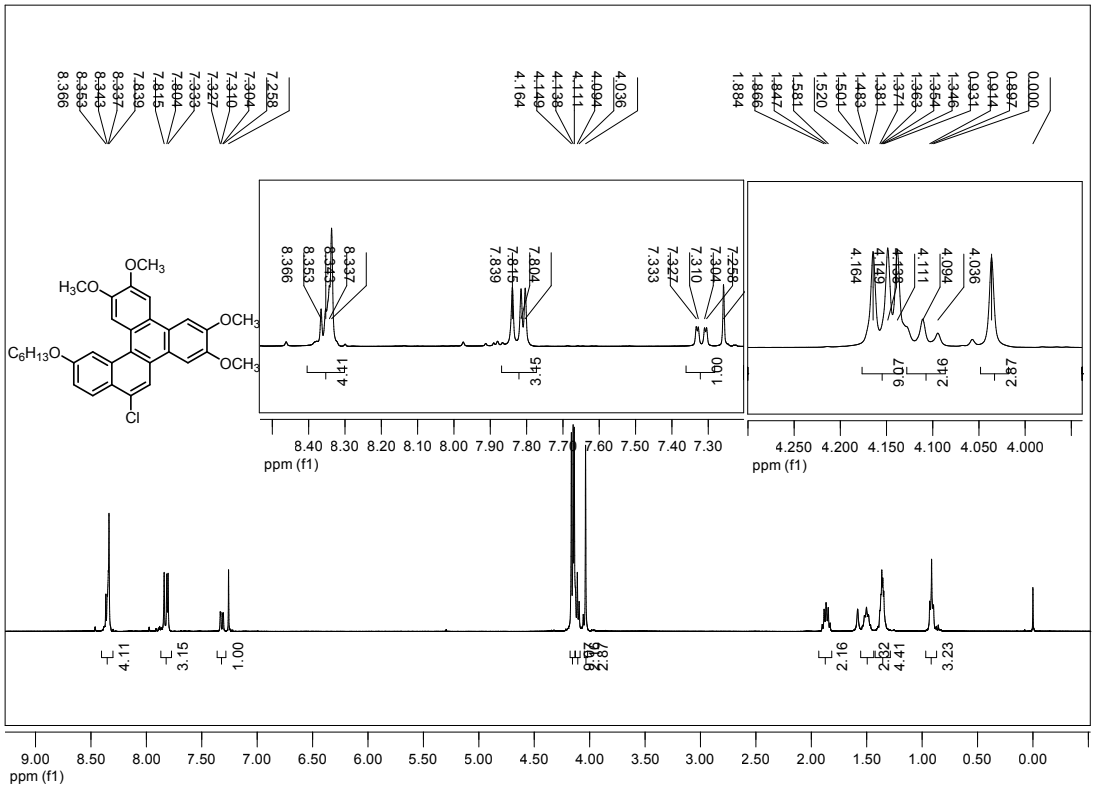



The $^{1}H$ NMR spectra of compound 5b.

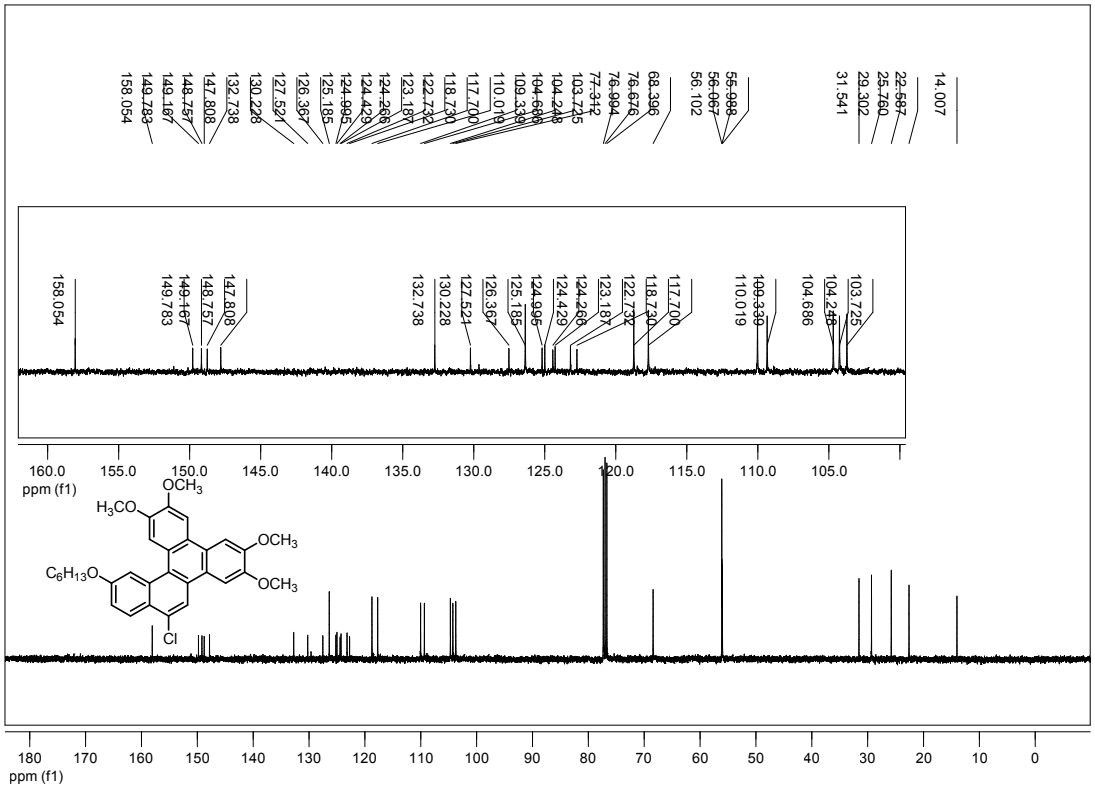



The $^{13}C$ NMR spectra of compound 5b.

## 5c

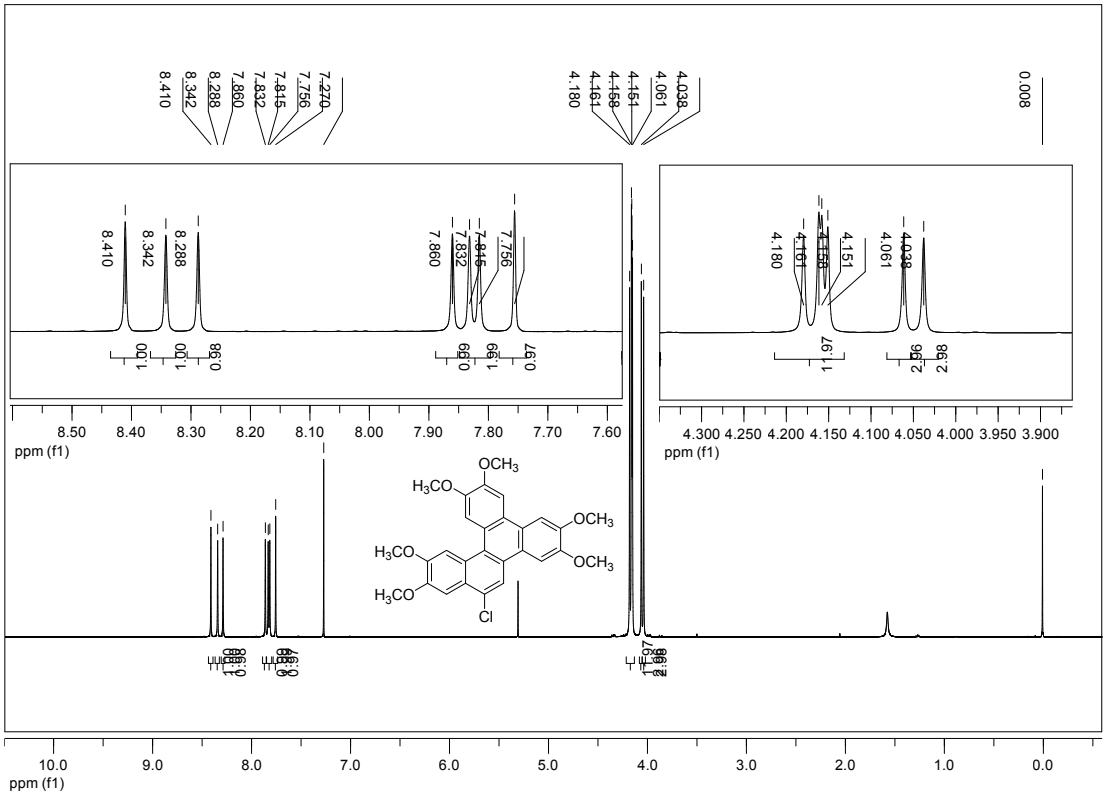


The $^{1}H$ NMR spectra of compound 5c.

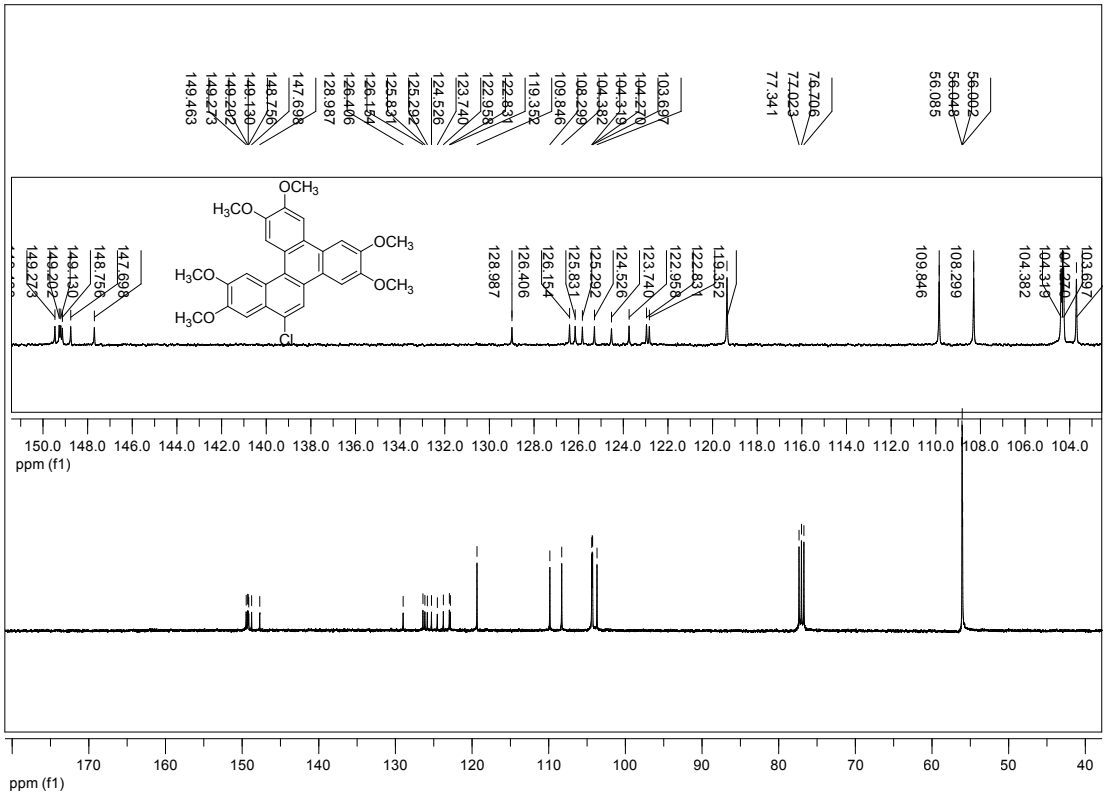


The $^{13}C$ NMR spectra of compound 5c.

## 5d

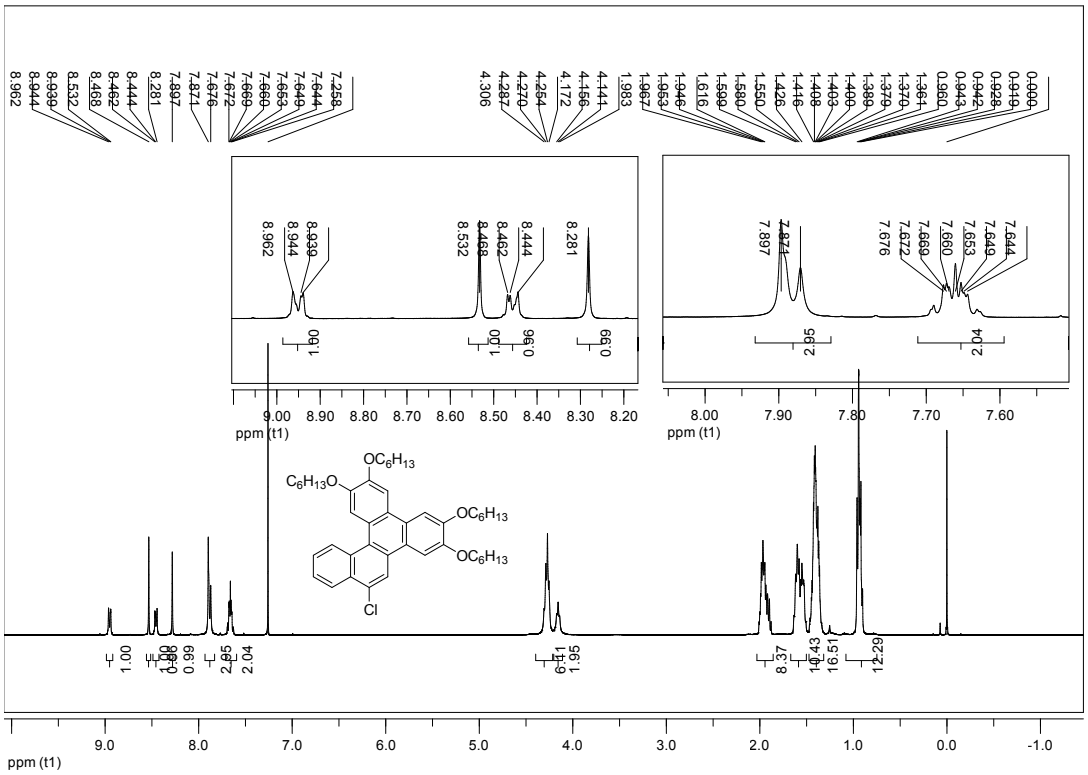



The $^{1}$H NMR spectra of compound 5d.

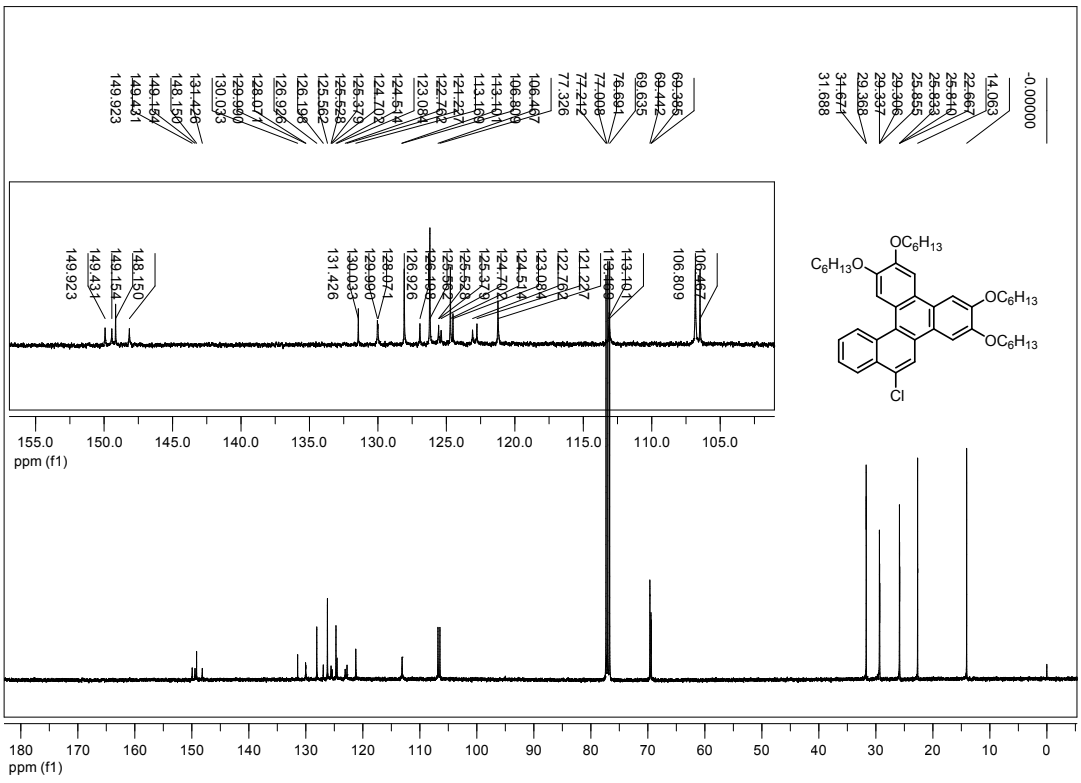



The $^{13}$C NMR spectra of compound 5d.

## 5e

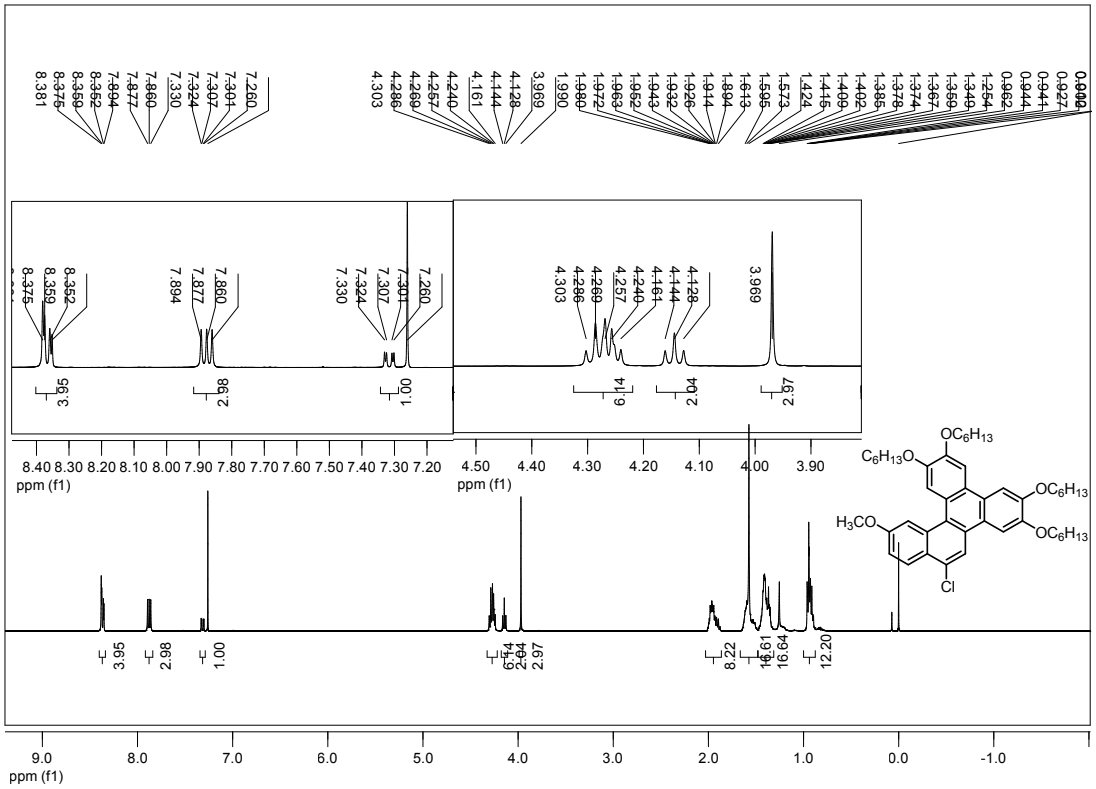



The $^{1}H$ NMR spectra of compound 5e.

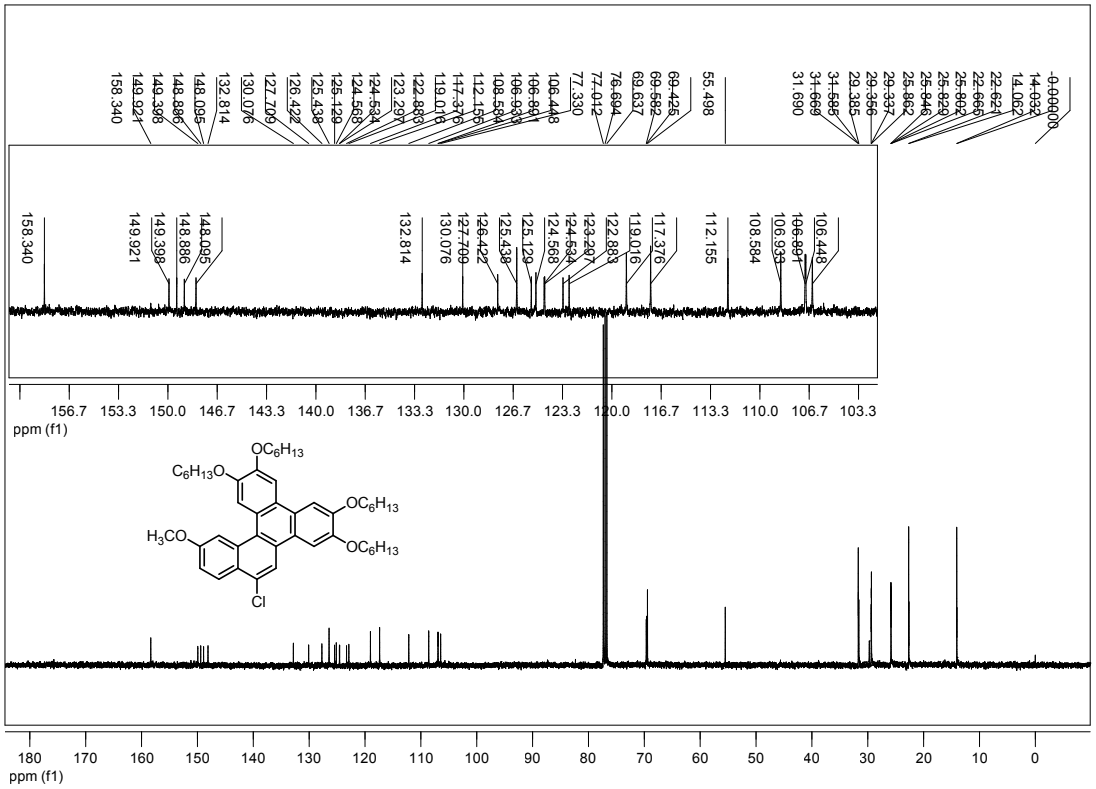



The $^{13}C$ NMR spectra of compound 5e.

**5f**

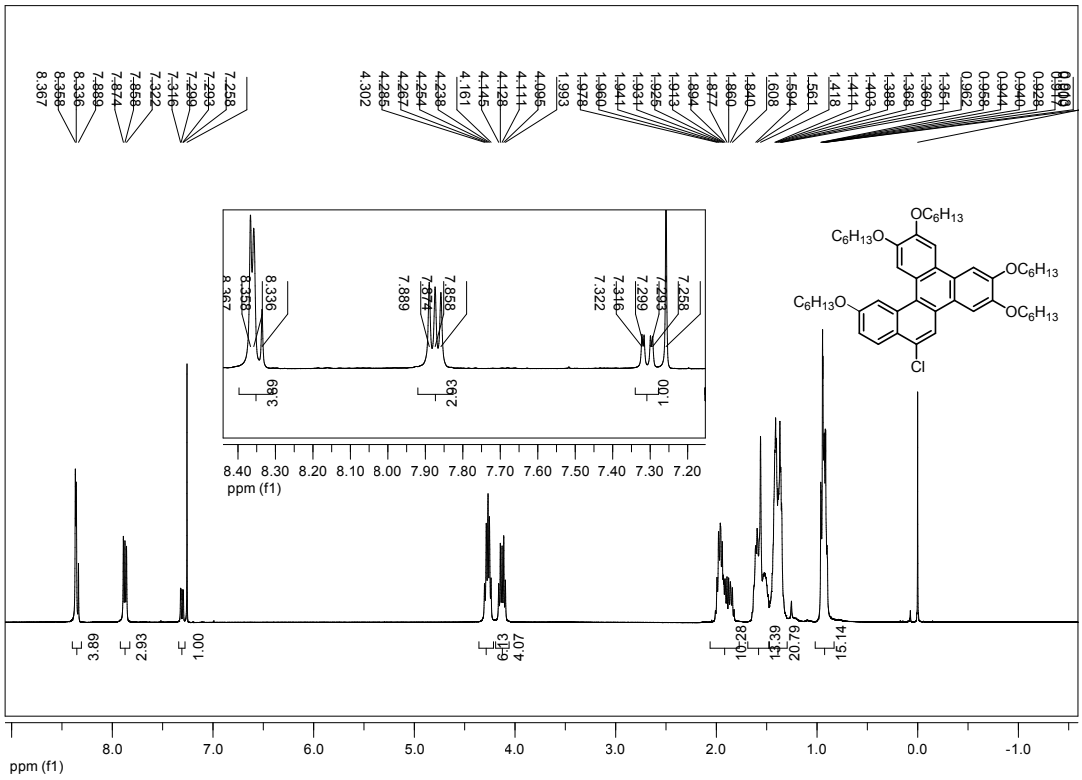



The $^{1}H$ NMR spectra of compound 5f.

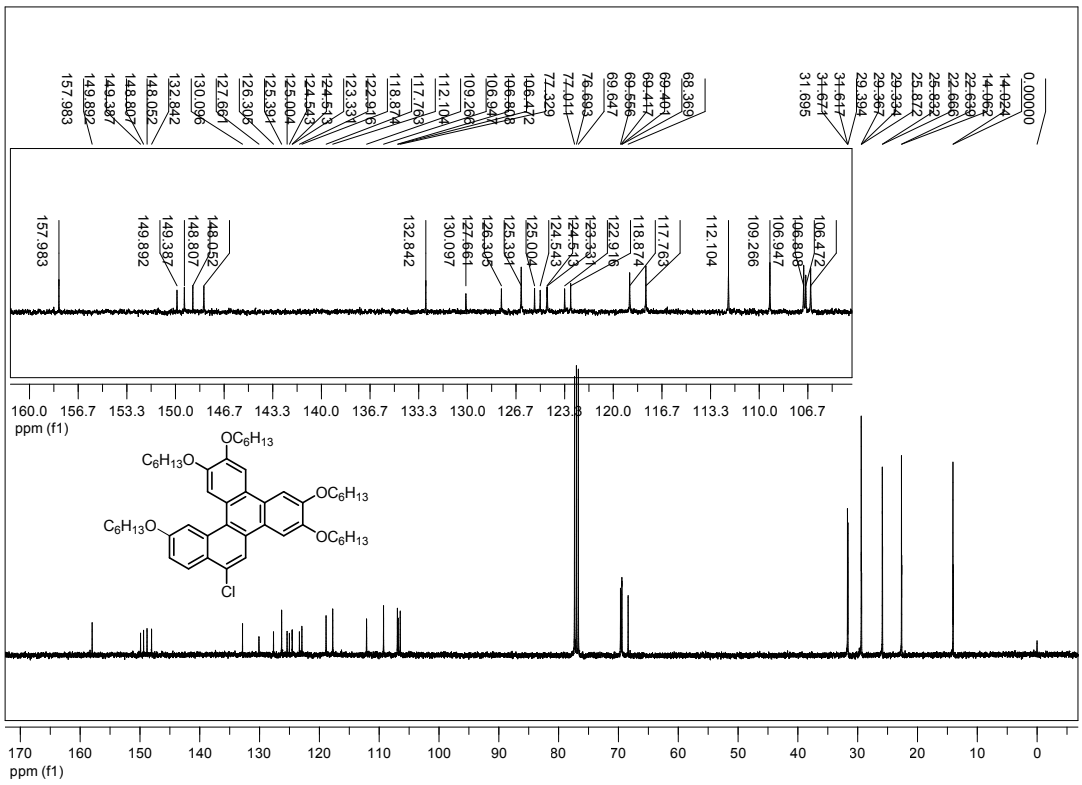



The $^{13}C$ NMR spectra of compound 5f.

## 5g

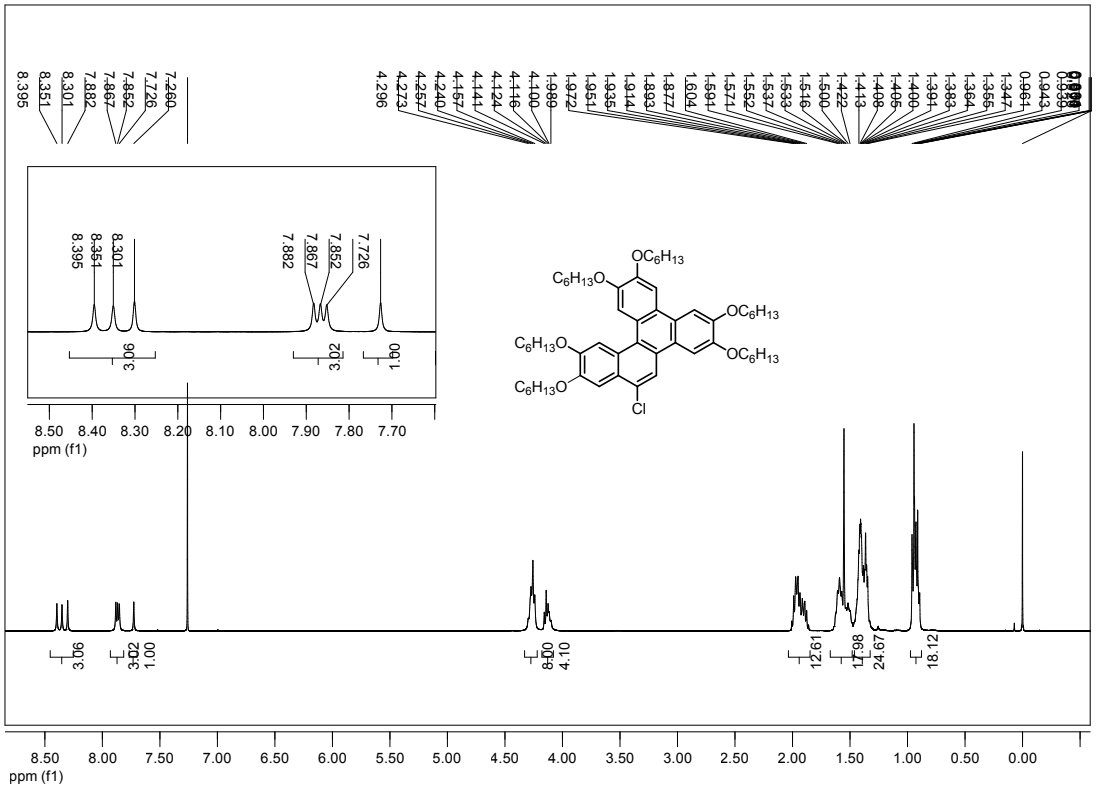


The $^{1}H$ NMR spectra of compound 5g.

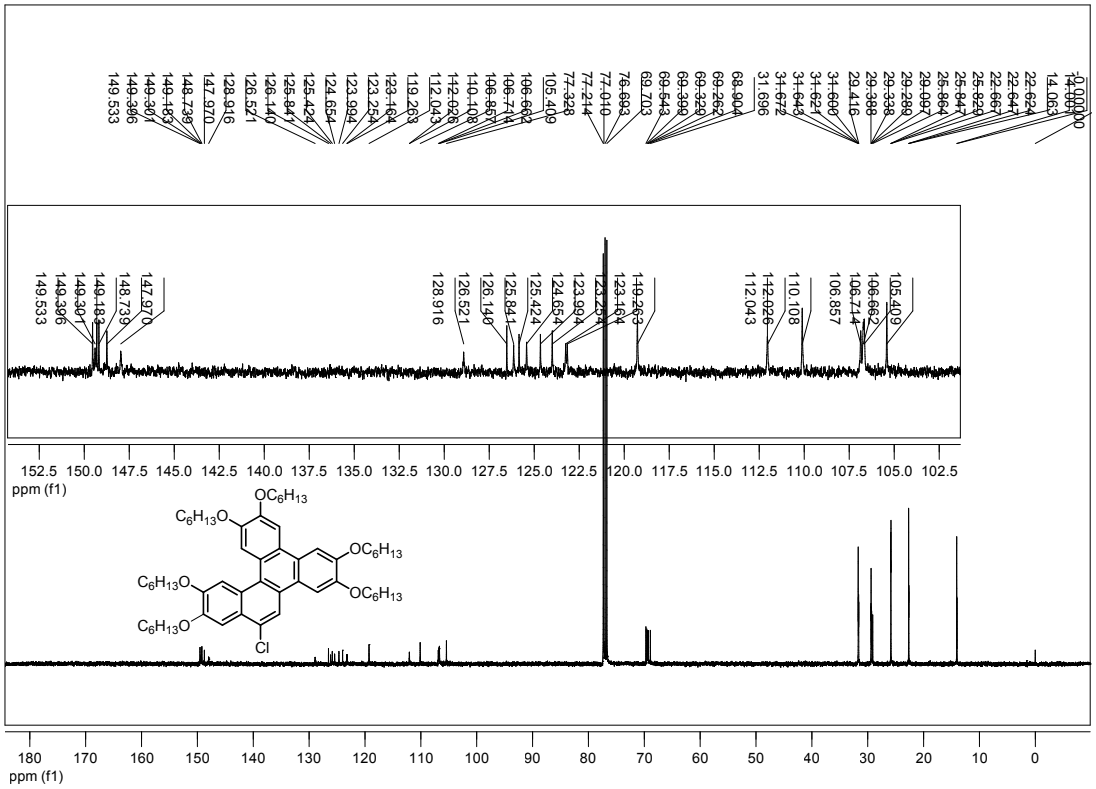


The $^{13}C$ NMR spectra of compound 5g.

## 5h

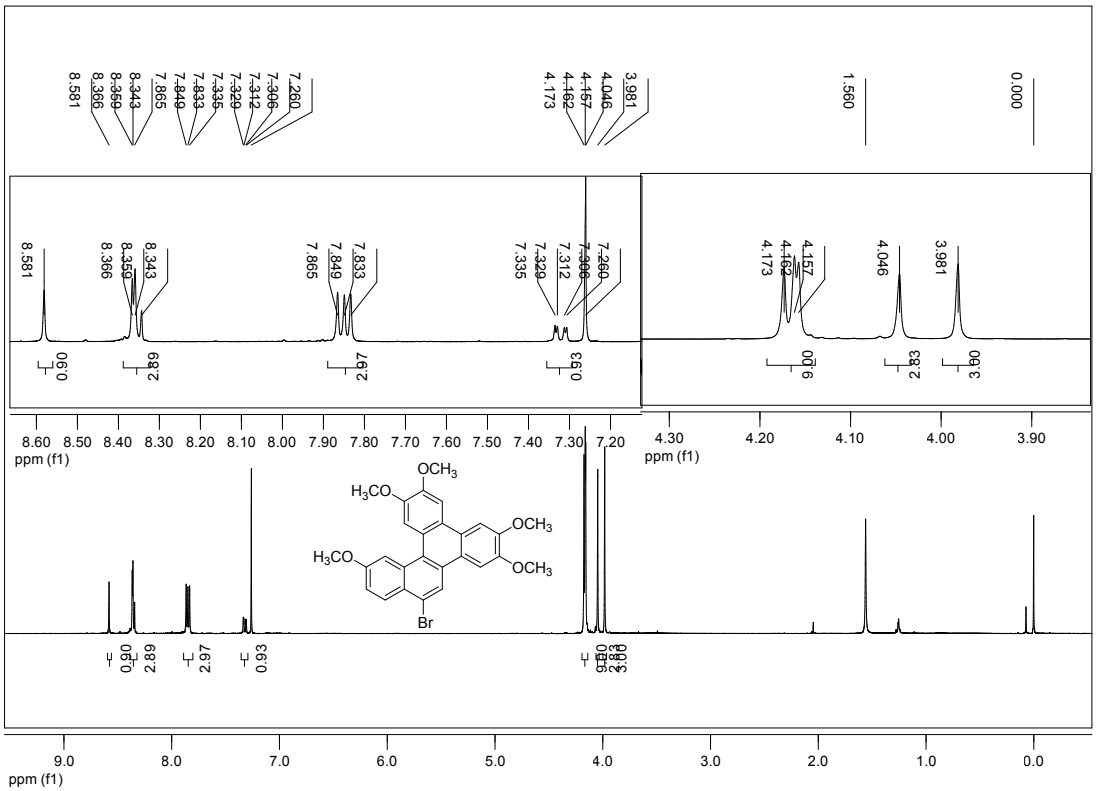


The $^{1}H$ NMR spectra of compound 5h.

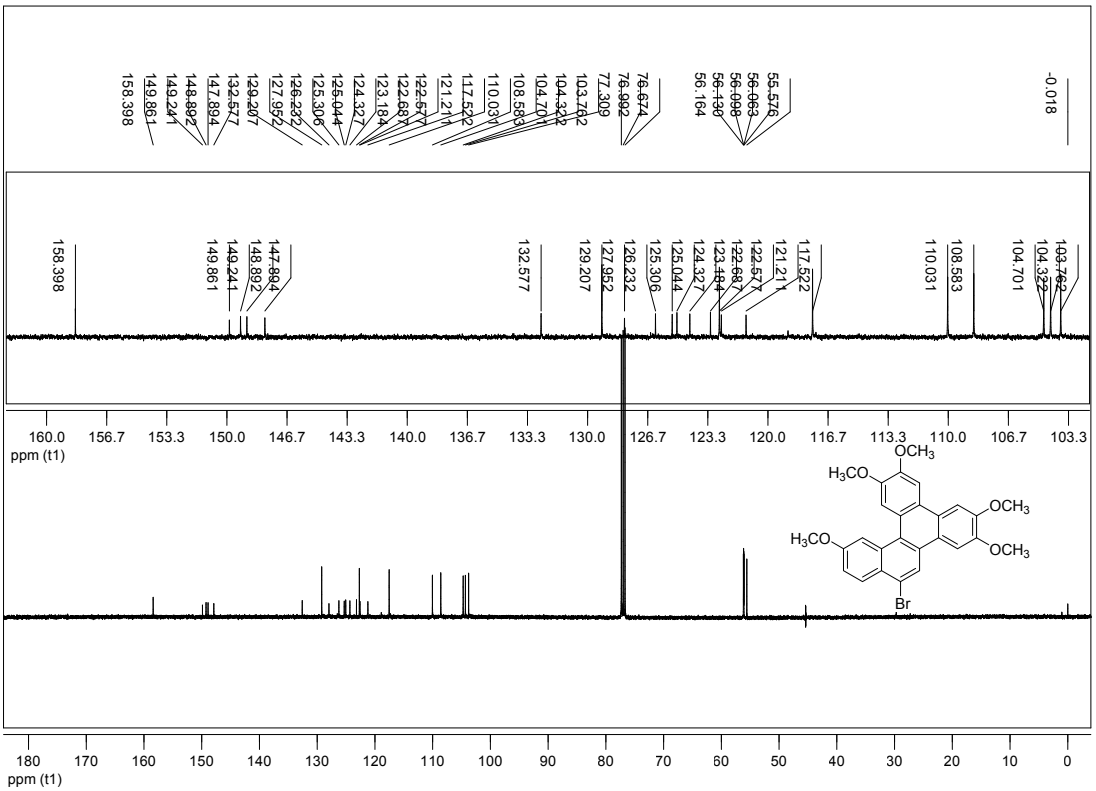


The $^{13}C$ NMR spectra of compound 5h.

**6**

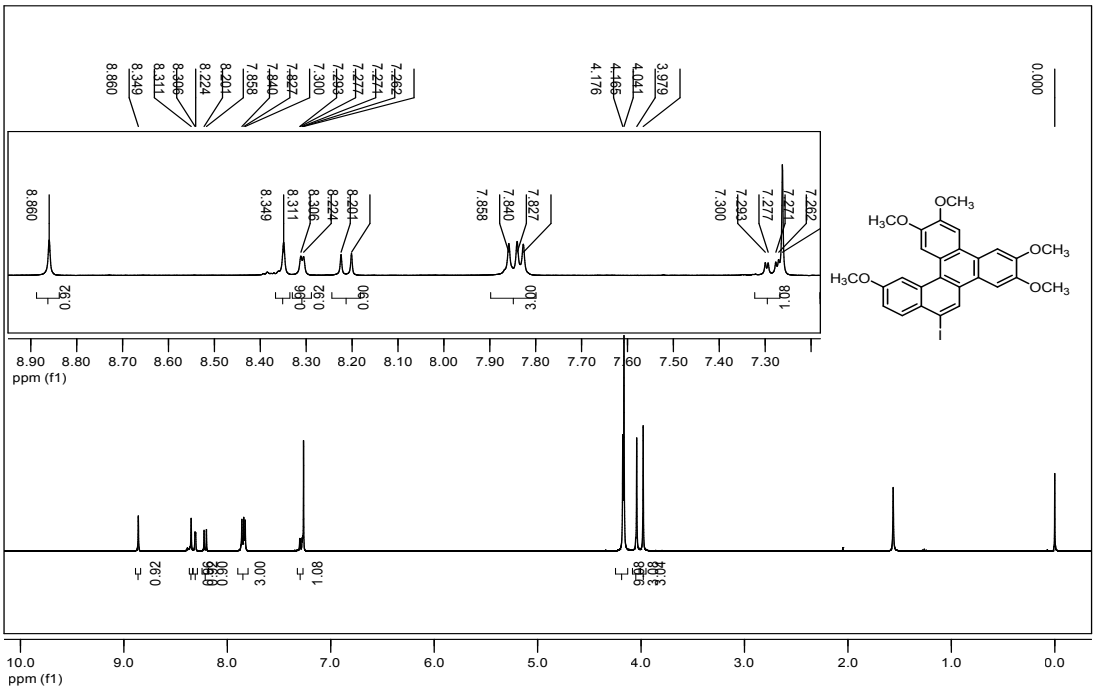



The $^{1}H$ NMR spectra of compound 6.

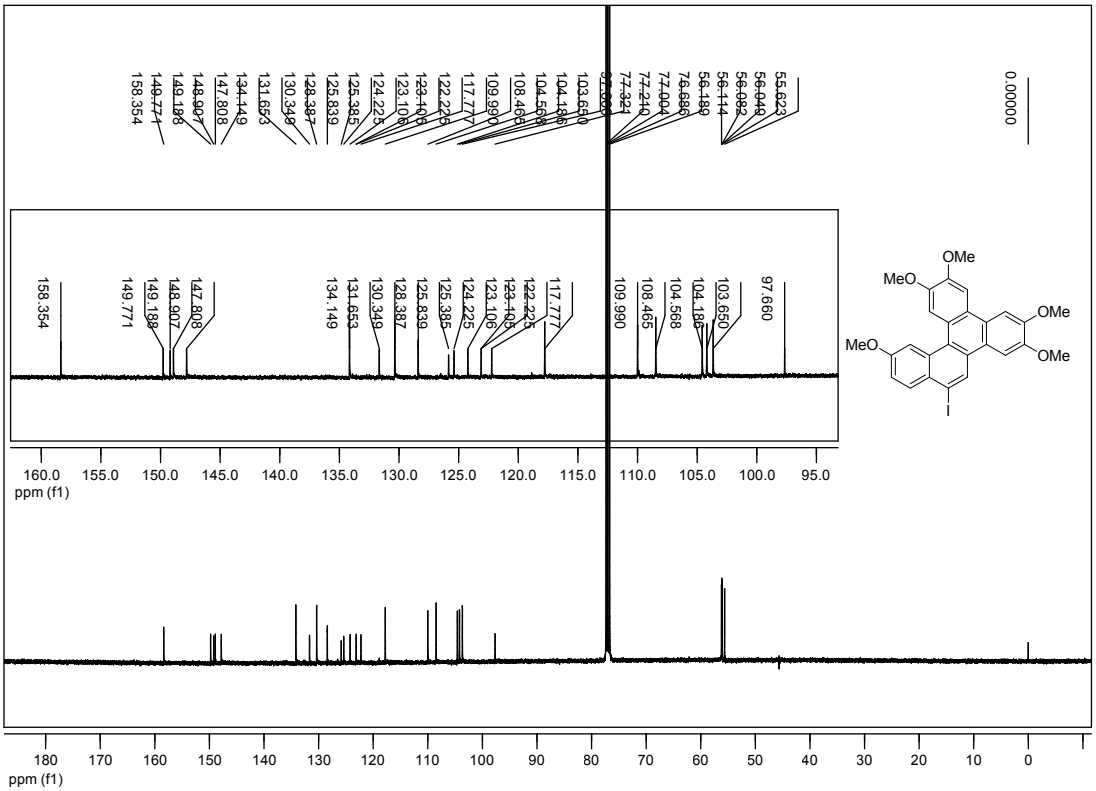



The $^{13}C$ NMR spectra of compound 6.

**7**




The $^{1}H$ NMR spectra of compound 7.




The $^{13}C$ NMR spectra of compound 7.