Supporting Information

Synthesis of Oligo(phenyleneethynylene) with Dendrimer "Shell" for Molecular Electronics

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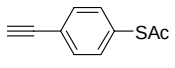
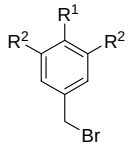
Content

General Procedure. All anhydrous reactions were carried out avoiding moisture by standard procedure under argon atmosphere. Commercial available reagents were used as received. The solvents were dried by distillation over the appropriate drying agents. Petroleum ether (bp 60–90 °C) was used for column chromatography. Reactions were monitored by TLC inspection on silica gel GF254 plates. Column chromatography was generally performed on silica gel (200–300 mesh). IR spectra were recorded on a Nicolet AVATAR 360 FT–IR spectrophotometer and reported in wave number (cm^{-1}). UV-Vis spectra were recorded on a T6 spectrophotometer by quartz cells with path length of 1.0 cm. Fluorescence spectra were recorded on a Perkin Elmer LS-55 spectrophotometer. Melting point was measured on a Reichert Microscope apparatus and uncorrected. ^1H, ^{13}C NMR and DEPT 135 were recorded on a Mercury Plus–400 spectrometer or a Mercury Plus–300 spectrometer. The chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz and relative to TMS (δ 0.00) for ^1H NMR (s, d, t, m and br s mean single, double, ternary, multiple and broad single respectively) and chloroform (δ 77.0) and carbon tetrachloride (δ 96.5) for ^{13}C NMR. Mass spectra (ESI) and mass spectra (EI) were obtained on an ABI Mariner-ESI-TOF (or Fisons VG Autospec in Bielefeld) and an HP–5988 mass spectrometers, respectively. High resolution mass spectral data (HRMS) were obtained on a Bruker APEX II FT-MS mass spectrometer. Elemental analysis was carried out by Elementar Vario EL.

Structure of compound 7 and dendrimers as materials.

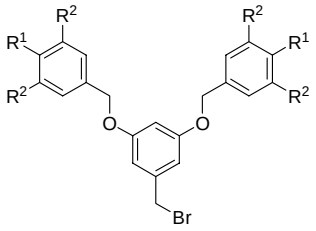


7



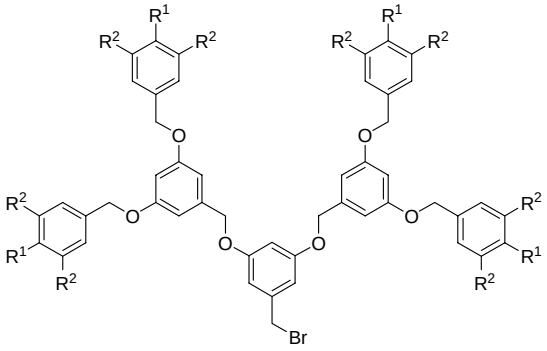
8, R^1 = *t*-Bu, R^2 = H

11, R^1 = H, R^2 = *t*-Bu



9, R^1 = *t*-Bu, R^2 = H

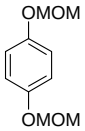
12, R^1 = H, R^2 = *t*-Bu



10, R^1 = *t*-Bu, R^2 = H

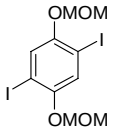
13, R^1 = H, R^2 = *t*-Bu

1,4-Bis(methoxymethoxy)benzene (3)[1]



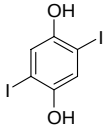
To a stirred suspension of K_2CO_3 (11.06 g, 80.02 mmol) and hydroquinone (**2**) (2.20 g, 19.98 mmol) in acetone (50 mL) was added MOMCl (1.67 mL, 22.00 mmol). The mixture was refluxed for 12 h, then water (2 mL) was added and stirred for another 1 h at rt. The mixture was filtered through a plug (silica gel, acetone), and concentrated *in vacuo*. The residue was purified by chromatography (petroleum ether/AcOEt, 20:1) to provide **3** (2.97 g, 75%) as a colorless oil: ^1H NMR (300 MHz, CCl_4) δ: 3.80 (s, 6 H), 5.42 (s, 4 H), 7.26 (s, 4 H); ^{13}C NMR (75 MHz, CCl_4) δ: 55.6, 94.9, 117.3, 152.6. MS (EI) *m*/*z*: 198 (M^+).

2,5-Bis(methoxymethoxy)-1,4-diiodobenzene (4)



To a stirred solution of **3** (3.96 g, 19.98 mmol) in CH_2Cl_2 (200 mL) were added $Hg(OAc)_2$ (15.93 g, 49.99 mmol) and I_2 (12.69 g, 50.00 mmol). The reaction mixture was stirred overnight at rt, formed slurry was filtered through a plug (silica gel, CH_2Cl_2). The filtrate was washed with $Na_2S_2O_3$ (10% aq.), $NaHCO_3$ (saturated), water, brine, dried ($MgSO_4$), concentrated *in vacuo* and recrystallized from ethanol to afford **4** (7.20 g, 80%) as colorless flakes: mp 124–125 °C. ^1H NMR (300 MHz, $CDCl_3$) δ: 3.52 (s, 6 H), 5.16 (s, 4 H), 7.46 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 56.5, 87.0, 95.7, 125.2, 151.9. IR (KBr) *v*: 2962, 1464, 978, 739. MS (ESI) *m*/*z*: 473 ($[M+Na]^+$). Anal. Calcd for $C_{10}H_{12}I_2O_4$: C, 26.69; H, 2.69. Found: C, 26.72; H, 2.55.

2,5-Diiodo-l,4-hydroquinone (**5**)

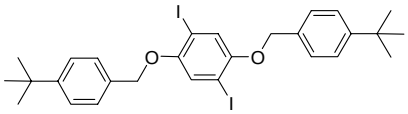


To a solution of **4** (6.75 g, 15.00 mmol) in methanol (50 mL) was added HCl (concd. 2.0 mL). The mixture was refluxed for 4 h. After the most solvent was removed *in vacuo*, water (30 mL) was added. The solid was collected by filter and recrystallized from water to afford product **5** (5.16 g, 95%): mp 194–197 °C (lit.[2] 195–197 °C). MS (EI) *m*/*z*: 362 (M^+).

The general procedure for 6a–6h

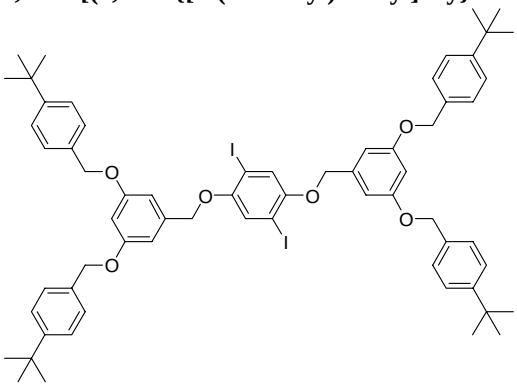
To a solution of **5** and RBr (**8**, **9**, **10**, **11**, **12**, **13,** benzyl bromide or isoamyl bromide) in DMF (10 mL) was added potassium carbonate. The mixture was stirred at 50 °C for 4 h. After the most solvent was removed *in vacuo*, the residue was washed with CH_2Cl_2 three times. The combined organic phase was washed with brine, dried ($MgSO_4$), concentrated *in vacuo* and purified by chromatography (petroleum ether/CH_2Cl_2, 1:1) to provide product (**6a**–**6h**).

2,5-Bis{[(4-tertbutyl)benzyl]oxy}-1,4-diiodobenzene (6a)



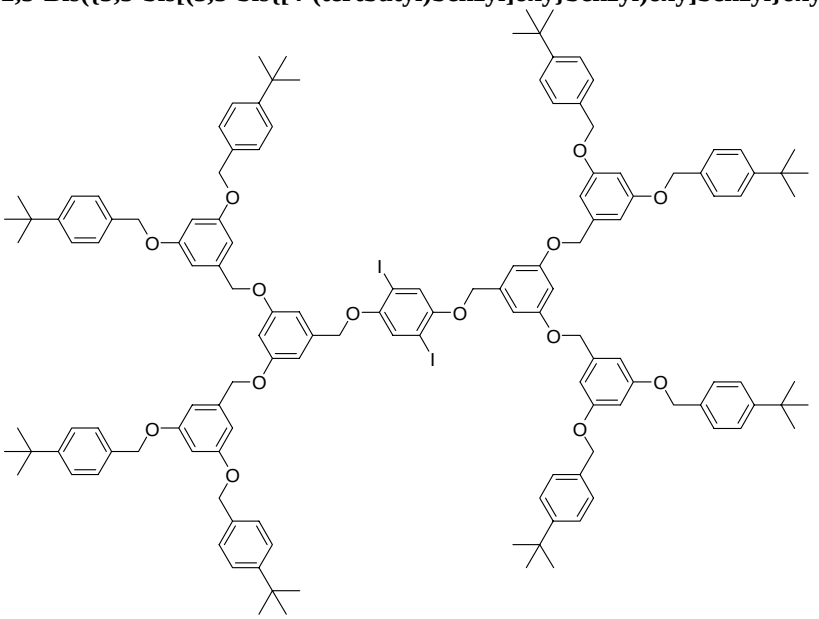
From **5** (0.11 g, 0.30 mmol), **8** (0.15 g, 0.66 mmol) and K_2CO_3 (0.25 g, 1.81 mmol) was afforded **6a** (0.16 g, 81%) as a white solid: mp 191–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.33 (s, 18 H), 5.02 (s, 4 H), 7.29 (s, 2 H), 7.42 (s, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.3 (CH_3), 34.6 (C), 71.9 (CH_2), 86.5 (C), 123.5 (CH), 125.5 (CH), 127.0 (CH), 133.2 (C), 151.0 (C), 152.8 (C). IR (KBr) *v*: 2955, 1481, 1354, 1204, 1062, 848, 813. HRMS (ESI) Calcd for $C_{28}H_{32}I_2NaO_2$ $[M+Na]^+$ 677.0384, found: 677.0381. Anal. Calcd for $C_{28}H_{32}I_2O_2$: C, 51.39; H, 4.93. Found: C, 51.11; H, 4.62.

2,5-Bis[(3,5-bis{[4-(tertbutyl)benzyl]oxy}benzyl)oxy]-1,4-diiodobenzene (6b)



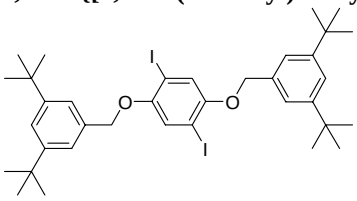
From **5** (72 mg, 0.20 mmol), **9** (0.22 g, 0.44 mmol) and K_2CO_3 (0.17 g, 1.23 mmol) was afforded **6b** (0.20 g, 84%) as a white solid: mp 198–201 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 36 H), 4.98 (s, 4 H), 5.02 (s, 8 H), 6.59 (s, 2 H), 6.75 (s, 4 H), 7.25 (s, 2 H), 7.36 (d, *J* = 8.7, 8 H), 7.41 (d, *J* = 8.7, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.3 (CH_3), 34.6 (C), 70.0 (CH_2), 71.7 (CH_2), 86.5 (C), 101.8 (CH), 105.8 (CH), 123.3 (CH), 125.5 (CH), 127.5 (CH), 133.8 (C), 138.5 (C), 151.0 (C), 152.7 (C), 160.3 (C). IR (KBr) *v*: 3442, 2958, 1597, 1355, 1159, 822, 682. HRMS (ESI) Calcd for $C_{64}H_{72}I_2NaO_6$ $[M+Na]^+$ 1213.3310, found: 1213.3316. Anal. Calcd for $C_{64}H_{72}I_2O_6$: C, 64.54; H, 6.09. Found: C, 64.35; H, 5.98.

2,5-Bis({3,5-bis[(3,5-bis{[4-(tertbutyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)-1,4-diiodobenzene (6c)



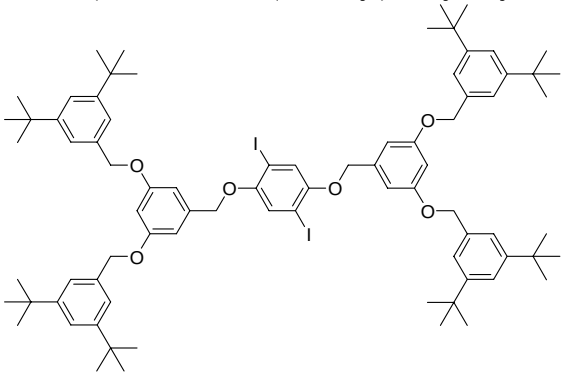
From **5** (36 mg, 0.10 mmol), **10** (0.23 g, 0.22 mmol) and K_2CO_3 (83 mg, 0.60 mmol) was afforded **6c** (0.19 g, 84%) as a white solid: mp 81–84 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (s, 72 H), 4.97-5.00 (m, 28 H), 6.58 (s, 6 H), 6.69 (s, 8 H), 6.74 (s, 4 H), 7.23 (s, 2 H), 7.35 (d, *J* = 8.1, 16 H), 7.39 (d, *J* = 8.1, 16 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.3 (CH_3), 34.5 (C), 69.9 (CH_2), 69.9 (CH_2), 71.5 (CH_2), 86.4 (C), 101.4 (CH), 101.7 (CH), 105.8 (CH), 106.1 (CH), 123.1 (CH), 125.5 (CH), 127.6 (CH), 133.6 (C), 138.6 (C), 139.1 (C), 151.0 (C), 152.5 (C), 160.0 (C), 160.2 (C). IR (KBr) *v*: 2958, 1597, 1155, 1053, 822, 680. Anal. Calcd for $C_{136}H_{152}I_2O_{14}$: C, 72.13; H, 6.77. Found: C, 71.93; H, 6.52.

2,5-Bis{[3,5-bis(tertbutyl)benzyl]oxy}-1,4-diiodobenzene (6d)



From **5** (0.11 g, 0.30 mmol), **11** (0.19 g, 0.67 mmol) and K_2CO_3 (0.25 g, 1.81 mmol) was afforded **6d** (0.18 g, 78%) as a white solid: mp 261–262 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.28 (s, 36 H), 5.00 (s, 4 H), 7.25 (s, 2 H), 7.29–7.32 (m, 6 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.5 (CH_3), 34.9 (C), 72.5 (CH_2), 86.6 (C), 121.6 (CH), 121.9 (CH), 123.6 (CH), 135.2 (C), 150.9 (C), 152.8 (C). IR (KBr) *v*: 2955, 2360, 1484, 1354, 1216, 1060, 861, 827, 707. HRMS (ESI) Calcd for $C_{36}H_{48}I_2NaO_2$ $[M+Na]^+$ 789.1636, found: 789.1659. Anal. Calcd for $C_{36}H_{48}I_2O_2$: C, 56.40; H, 6.31. Found: C, 56.14; H, 6.05.

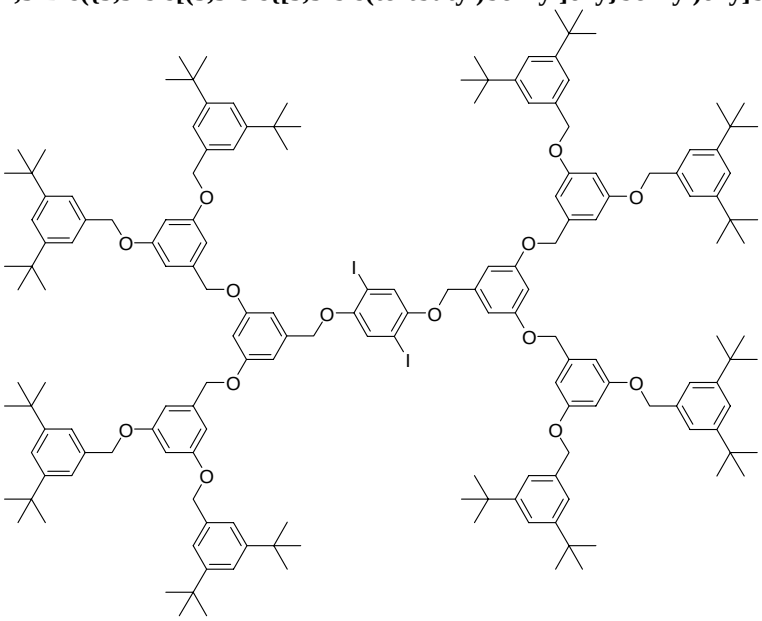
2,5-Bis[(3,5-bis{[3,5-bis(tertbutyl)benzyl]oxy}benzyl)oxy]-1,4-diiodobenzene (6e)



From **5** (72 mg, 0.20 mmol), **12** (0.27 g, 0.44 mmol) and K_2CO_3 (0.17 g, 1.23 mmol) was afforded **6e** (0.22 g, 78%) as a white solid: mp 259–260 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 72 H), 4.95 (s, 12 H), 6.58 (s, 2 H), 6.73 (d, *J* = 1.2, 4 H), 7.22

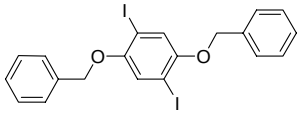
(s, 10 H), 7.33 (s, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.5 (CH_3), 34.8 (C), 71.0 (CH_2), 71.8 (CH_2), 86.5 (C), 101.7 (CH), 105.9 (CH), 122.4 (CH), 122.4 (CH), 123.3 (CH), 135.6 (C), 138.4 (C), 151.0 (C), 152.7 (C), 160.4 (C). IR (KBr) *v*: 3432, 2961, 2903, 2869, 2360, 1594, 1480, 1460, 1380, 1350, 1321, 1250, 1211, 1164, 1052, 1014, 876, 813, 707. HRMS (ESI) Calcd for $C_{80}H_{104}I_2NaO_6$ $[M+Na]^+$ 1437.5814, found: 1437.5804. Anal. Calcd for $C_{80}H_{104}I_2O_6$: C, 67.88; H, 7.41. Found: C, 67.68; H, 7.12.

2,5-Bis({3,5-bis[(3,5-bis{[3,5-bis(tertbutyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)-1,4-diiodobenzene (6f)



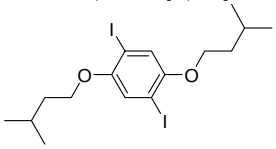
From **5** (36 mg, 0.10 mmol), **13** (0.28 g, 0.22 mmol) and K_2CO_3 (83 mg, 0.60 mmol) was afforded **6f** (0.21 g, 77%) as a white solid: mp 56–58 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (s, 144 H), 4.90–4.95 (m, 28 H), 6.54–6.56 (m, 6 H), 6.64–6.69 (m, 12 H), 7.18–7.20 (m, 18 H), 7.30–7.32 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 31.4 (CH_3), 34.8 (C), 70.1 (CH_2), 71.0 (CH_2), 71.6 (CH_2), 86.5 (C), 101.4 (CH), 101.8 (CH), 105.8 (CH), 106.3 (CH), 122.3 (CH), 122.3 (CH), 123.2 (CH), 135.6 (C), 138.6 (C), 139.1 (C), 151.0 (C), 152.6 (C), 160.1 (C), 160.4 (C). IR (KBr) *v*: 2961, 1596, 1158, 757, 711. Anal. Calcd for $C_{168}H_{216}I_2O_{14}$: C, 74.37; H, 8.02. Found: C, 74.02; H, 7.86.

2,5-Bis[(benzyl)oxy]-1,4-diiodobenzene (6g)[3]



From **5** (0.11 g, 0.30 mmol), benzyl bromide (0.08 mL, 0.66 mmol) and K_2CO_3 (0.25 g, 1.81 mmol) afforded **6g** (0.12 g, 74%) as a white solid: ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.06 (s, 4 H), 7.28 (s, 2 H), 7.31–7.43 (m, 6 H), 7.49 (d, *J* = 6.9, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 72.0, 86.5, 123.5, 127.2, 128.0, 128.6, 136.2, 152.7. IR (KBr) *v*: 3031, 1479, 1350, 1009, 845, 793.

2,5-Bis[(isoamyl)oxy]-1,4-diiodobenzene (6h)



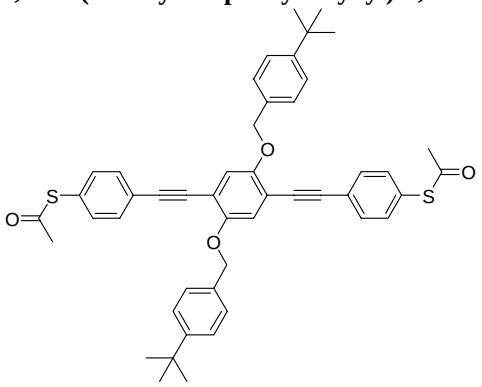
From **5** (0.11 g, 0.30 mmol), isoamyl bromide (0.08 mL, 0.66 mmol) and K_2CO_3 (0.25 g, 1.81 mmol) was afforded **6h** (0.12 g, 80%) as a white solid: mp 115–116 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.96 (d, *J* = 5.4, 12 H), 1.67–1.74 (m, 4 H), 1.90–1.95 (m, 2 H), 3.95 (t, *J* = 6.0, 4 H), 7.18 (s, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.6 (CH_3), 25.0 (CH), 37.9 (CH_2), 68.7 (CH_2), 86.2 (C), 122.7 (CH), 152.9 (C). IR (KBr) *v*: 2953, 1487, 1458, 1347, 1211, 1058, 978, 856, 781. MS (ESI) *m*/*z*: 525 ($[M+Na]^+$). Anal. Calcd for $C_{16}H_{24}I_2O_2$: C, 38.27; H, 4.82. Found: C, 37.95; H, 4.58.

The general procedure for 1a–1i

A mixture of diiodide (**6a**–**6h** or **4)**, bis(triphenylphosphine)palladium(II) chloride, and CuI was placed in a flask and

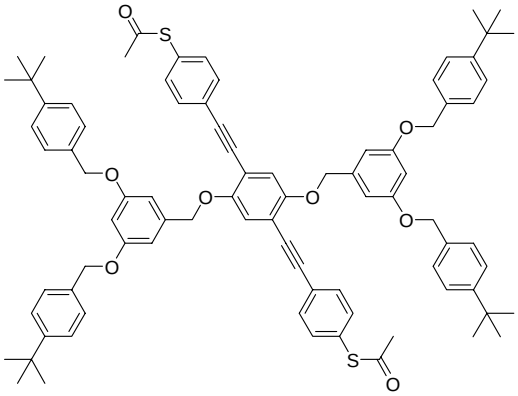
H_2-degassed, then a solution of diisopropylamine (DIEA) in H_2-degassed THF (10 mL) was added. After the mixture was stirred for 1 h, a solution of acetylene **7** in H_2-deggased THF (10 mL) was added. The reaction mixture was stirred under hydrogen atmosphere for 24–48 h at 50 °C, then concentrated *in vacuo* and purified by chromatography (1:10 CH_2Cl_2/petroleum ether slowly increased to CH_2Cl_2) to provide cross-coupled product (**1a**–**1i**).

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis{[(4-tertbutyl)benzyl]oxy}benzene (1a)



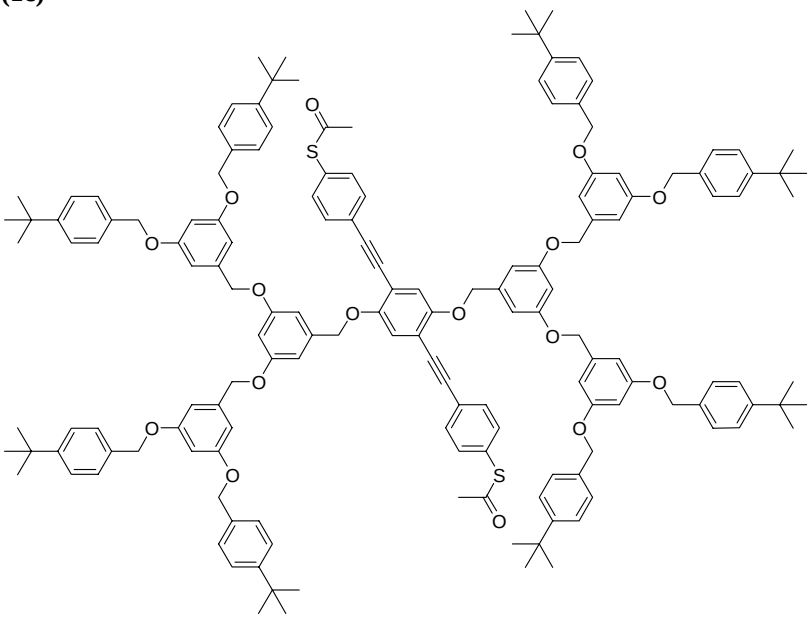
From diiodide **6a** (0.13 g, 0.20 mmol), CuI (4 mg, 0.021 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.010 mmol), DIEA (0.5 mL) and **7** (0.10 g, 0.57 mmol) was afforded **1a** (83 mg, 55%) as a primrose yellow solid: mp 177–181 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 18 H), 2.43 (s, 6 H), 5.12 (s, 4 H), 7.13 (s, 2 H), 7.37 (d, *J* = 8.4, 4 H), 7.44 (d, *J* = 7.5, 8 H), 7.53 (d, *J* = 8.4, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.3 (CH_3), 31.3 (CH_3), 34.6 (C), 71.2 (CH_2), 87.5 (C), 94.6 (C), 114.4 (C), 117.6 (CH), 124.5 (C), 125.4 (CH), 126.9 (CH), 128.0 (C), 132.1 (CH), 133.8 (C), 134.1 (CH), 150.8 (C), 153.7 (C), 193.5 (C). IR (KBr) *v*: 3394, 2922, 2385, 2303, 1648, 1384, 1119, 1068, 969. MS (ESI) *m*/*z*: 751 ($[M+H]^+$). Anal. Calcd for $C_{48}H_{46}O_4S_2$: C, 76.77; H, 6.17. Found: C, 76.58; H, 5.96.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis[(3,5-bis{[4-(tertbutyl)benzyl]oxy}benzyl)oxy]benzene (1b)



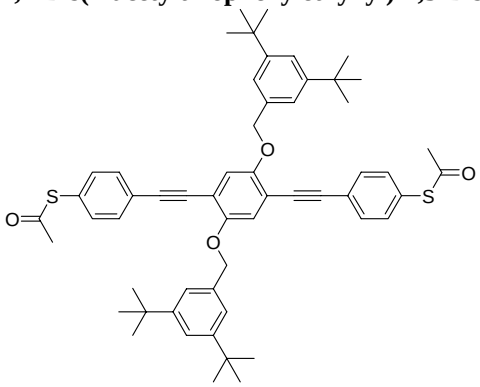
From diiodide **6b** (0.12 g, 0.10 mmol), CuI (2 mg, 0.010 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg, 0.0057 mmol), DIEA (0.5 mL) and **7** (88 mg, 0.50 mmol) was afforded **1b** (54 mg, 42%) as a primrose yellow solid: mp 215–218 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 36 H), 2.41 (s, 6 H), 4.95 (s, 8 H), 5.11 (s, 4 H), 6.58 (s, 2 H), 6.82 (s, 4 H), 7.12 (s, 2 H), 7.26 (d, *J* = 8.1, 4 H), 7.31 (d, *J* = 8.1, 8 H), 7.39 (d, *J* = 8.1, 8 H), 7.56 (d, *J* = 8.1, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.2 (CH_3), 31.3 (CH_3), 34.6 (C), 69.9 (CH_2), 71.0 (CH_2), 87.4 (C), 94.7 (C), 101.2 (CH), 105.6 (CH), 114.3 (C), 117.4 (CH), 124.4 (C), 125.5 (CH), 127.6 (CH), 128.1 (C), 132.2 (CH), 133.6 (C), 134.2 (CH), 139.2 (C), 151.0 (C), 153.5 (C), 160.2 (C), 193.3 (C). IR (KBr) *v*: 3391, 2923, 2392, 2288, 1644, 1384, 1067, 965. MS (ESI) *m*/*z*: 1287 ($[M+H]^+$). Anal. Calcd for $C_{84}H_{86}O_8S_2$: C, 78.35; H, 6.73. Found: C, 78.19; H, 6.52.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis({3,5-bis[(3,5-bis{[4-(tertbutyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzene (1c)



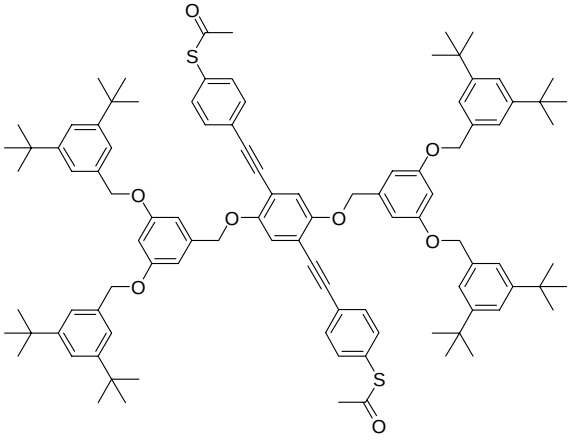
From diiodide **6c** (0.11 g, 0.048 mmol), CuI (1 mg, 0.0052 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg, 0.0028 mmol), DIEA (0.5 mL) and **7** (88 mg, 0.50 mmol) was afforded **1c** (47 mg, 41%) as a primrose yellow solid: mp 78–80 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.31 (s, 72 H), 2.31 (s, 6 H), 4.93 (s, 8 H), 4.96 (s, 16 H), 5.10 (s, 4 H), 6.58 (s, 6 H),6.65 (s, 8 H), 6.81 (s, 4 H), 7.10 (s, 2 H), 7.20 (d, *J* = 8.4, 4 H), 7.34 (d, *J* = 8.1, 16 H), 7.39 (d, *J* = 8.1, 16 H), 7.55 (d, *J* = 8.4, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.2 (CH_3), 31.3 (CH_3), 34.5 (C), 69.9 (CH_2), 70.0 (CH_2), 70.4 (CH_2), 87.4 (C), 94.8 (C), 101.1 (CH), 101.5 (CH), 105.6 (CH), 106.3 (CH), 114.3 (C), 117.2 (CH), 124.2 (C), 125.5 (CH), 127.6 (CH), 128.3 (C), 132.1 (CH), 133.6 (C), 134.2 (CH), 139.0 (C), 139.3 (C), 151.0 (C), 153.5 (C), 160.0 (C), 160.2 (C), 193.3 (C). IR (KBr) *v*: 3400, 2923, 2392, 2281, 1646, 1384, 1120, 969. MS (ESI) *m*/*z*: 2360 ($[M+H]^+$). Anal. Calcd for $C_{156}H_{166}O_{16}S_2$: C, 79.36; H, 7.09. Found: C, 79.35; H, 6.80.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis{[3,5-bis(tertbutyl)benzyl]oxy}benzene (1d)



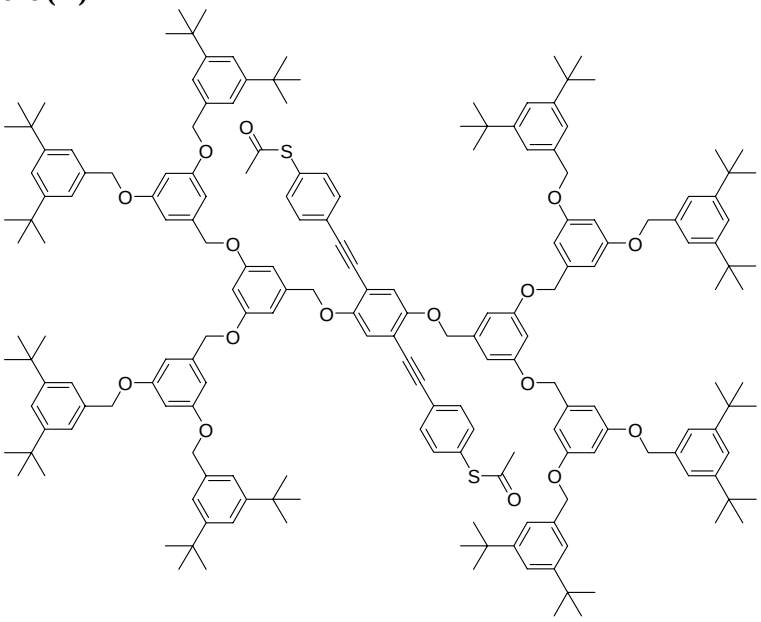
From diiodide **6d** (0.15 g, 0.20 mmol), CuI (4 mg, 0.021 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.010 mmol), DIEA (0.5 mL) and **7** (0.11 g, 0.62 mmol) was afforded **1d** (0.10 g, 58%) as a primrose yellow solid: mp 236–238 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.32 (s, 36 H), 2.44 (s, 6 H), 5.15 (s, 4 H), 7.18 (s, 2 H), 7.35–7.37 (m, 10 H), 7.50 (d, *J* = 6.8, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.2 (CH_3), 31.4 (CH_3), 34.8 (C), 72.4 (CH_2), 87.5 (C), 94.4 (C), 114.5 (C), 118.2 (CH), 121.6 (CH), 121.9 (CH), 124.5 (C), 128.2 (C), 132.2 (CH), 134.1 (CH), 135.8 (C), 151.0 (C), 153.8 (C), 193.3 (C). IR (KBr) *v*: 2958, 2360, 2207, 1701, 1390, 1212, 1012, 750, 616. HRMS (ESI) Calcd for $C_{56}H_{62}NaO_4S_2$ $[M+Na]^+$ 885.3982, found: 885.3963. Anal. Calcd for $C_{56}H_{62}O_4S_2$: C, 77.92; H, 7.24. Found: C, 77.58; H, 6.93.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis[(3,5-bis{[3,5-bis(tertbutyl)benzyl]oxy}benzyl)oxy]benzene (1e)



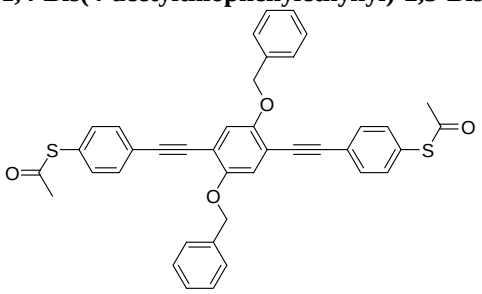
From diiodide **6e** (0.14 g, 0.10 mmol), CuI (2 mg, 0.010 mmol), $Pd(PPh_3)_2Cl_2$ (4 mg, 0.0057 mmol), DIEA (0.5 mL) and **7** (88 mg, 0.50 mmol) was afforded **1e** (60 mg, 40%) as a primrose yellow solid: mp 219–221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.25 (s, 72 H), 2.31 (s, 6 H), 4.91 (s, 8 H), 5.07 (s, 4 H), 6.58 (s, 2 H), 6.79 (d, *J* = 2.0, 4 H), 7.05–7.07 (m, 6 H), 7.19 (s, 8 H), 7.34 (s, 4 H), 7.48 (d, *J* = 8.0, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.2 (CH_3), 31.5 (CH_3), 34.8 (C), 71.1 (CH_2), 71.3 (CH_2), 87.4 (C), 94.8 (C), 101.3 (CH), 105.9 (CH), 114.6 (C), 117.7 (CH), 122.2 (CH), 122.4 (CH), 124.4 (C), 128.2 (C), 132.2 (CH), 134.1 (CH), 135.7 (C), 139.2 (C), 151.0 (C), 153.7 (C), 160.5 (C), 193.1 (C). IR (KBr) *v*: 3427, 2961, 2340, 1711, 1595, 1504, 1364, 1159, 825, 711, 616. HRMS (ESI) Calcd for $C_{100}H_{118}NaO_8S_2$ $[M+Na]^+$ 1533.8160, found: 1533.8168. Anal. Calcd for $C_{100}H_{118}O_8S_2$: C, 79.43; H, 7.87. Found: C, 79.10; H, 7.55.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis({3,5-bis[(3,5-bis{[3,5-bis(tertbutyl)benzyl]oxy}benzyl)oxy]benzyl}oxy)benzene (1f)



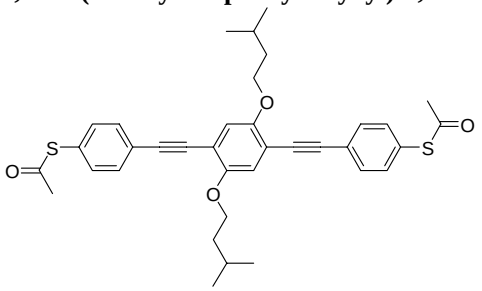
From diiodide **6f** (0.14 g, 0.052 mmol), CuI (1 mg, 0.0052 mmol), $Pd(PPh_3)_2Cl_2$ (2 mg, 0.0028 mmol), DIEA (0.5 mL) and **7** (88 mg, 0.50 mmol) was afforded **1f** (62 mg, 42%) as a primrose yellow solid: mp 100–102 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.34 (s, 144 H), 2.29 (s, 6 H), 4.99 (s, 24 H), 5.12 (s, 4 H), 6.63 (s, 2 H), 6.67 (s, 4 H), 6.71 (s, 8 H), 6.87 (s, 4 H), 7.15 (s, 2 H), 7.21 (d, *J* = 8.4, 4 H), 7.29 (s, 16 H), 7.41 (s, 8 H), 7.56 (d, *J* = 8.4, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 30.1 (CH_3), 31.5 (CH_3), 34.9 (C), 70.2 (CH_2), 71.0 (CH_2), 87.4 (C), 94.9 (C), 101.3 (CH), 101.8 (CH), 105.8 (CH), 106.5 (CH), 114.5 (C), 117.5 (CH), 122.2 (CH), 122.3 (CH), 124.3 (C), 128.4 (C), 132.1 (CH), 134.2 (CH), 135.7 (C), 139.0 (C), 139.4 (C), 151.0 (C), 153.7 (C), 160.2 (C), 160.4 (C), 193.2 (C). IR (KBr) *v*: 3403, 2960, 2199, 1595, 1157, 1053, 733. MS (ESI) *m*/*z*: 2843 ($[M+Cl]^-$). Anal. Calcd for $C_{188}H_{230}O_{16}S_2$: C, 80.36 H, 8.25. Found: C, 80.12; H, 8.02.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis[(benzyl)oxy]benzene (1g)



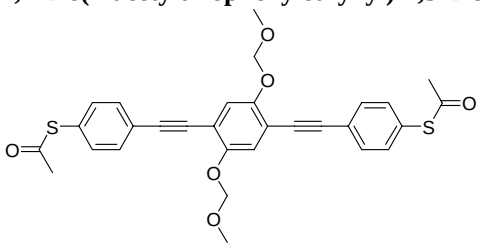
From diiodide **6g** (0.11 g, 0.20 mmol), CuI (4 mg, 0.021 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.010 mmol), DIEA (0.5 mL) and **7** (0.11 g, 0.62 mmol) was afforded **1g** (58 mg, 45%) as a primrose yellow solid: mp 190–192 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 6 H), 5.16 (s, 4 H), 7.12 (s, 2 H), 7.33–7.42 (m, 10 H), 751–7.54 (m, 8 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.3 (CH_3), 71.3 (CH_2), 87.4 (C), 94.7 (C), 114.4 (C), 117.5 (CH), 124.4 (C), 127.0 (CH), 127.9 (CH), 128.1 (C), 128.5 (CH), 132.1 (CH), 134.2 (CH), 136.8 (C), 153.6 (C), 193.5 (C). IR (KBr) *v*: 3397, 2923, 2325, 2203, 1703, 1117, 1068, 957. MS (ESI) *m*/*z*: 639 ($[M+H]^+$). Anal. Calcd for $C_{40}H_{30}O_4S_2$: C, 75.21; H, 4.73. Found: C, 74.91; H, 4.51.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis[(isoamyl)oxy]benzene 1h



From diiodide **6h** (0.10 g, 0.20 mmol), CuI (4 mg, 0.021 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.010 mmol), DIEA (0.5 mL) and **7** (0.11 g, 0.62 mmol) was afforded **1h** (60 mg, 50%) as a primrose yellow solid: mp 119–201 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.99 (d, *J* = 6.9, 12 H), 1.71–1.78 (m, 4 H), 1.89–1.99 (m, 2 H), 2.44 (s, 6 H), 4.06 (t, *J* = 6.3, 4 H), 7.02 (s, 2 H), 7.40 (d, *J* = 8.1, 4 H), 7.55 (d, *J* = 8.1, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 22.7 (CH_3), 25.2 (CH), 30.3 (CH_3), 38.0 (CH_2), 67.9 (CH_2), 87.6 (C), 94.1 (C), 113.7 (C), 116.6 (CH), 124.6 (C), 127.9 (C), 132.1 (CH), 134.2 (CH), 153.6 (C), 193.6 (C). IR (KBr) *v*: 3394, 2924, 2385, 2288, 1648, 1385, 1067, 961. MS (ESI) *m*/*z*: 599 ($[M+H]^+$). Anal. Calcd for $C_{36}H_{38}O_4S_2$: C, 72.21; H, 6.40. Found: C, 71.90; H, 6.00.

1,4-Bis(4-acetylthiophenylethynyl)-2,5-Bis(methoxymethoxy)benzene 1i



From diiodide **4** (90 mg, 0.20 mmol), CuI (4 mg, 0.021 mmol), $Pd(PPh_3)_2Cl_2$ (7 mg, 0.010 mmol), DIEA (0.5 mL) and **7** (0.11 g, 0.62 mmol) was afforded **1i** (67 mg, 61%) as a primrose yellow solid: mp 155–157 °C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.44 (s, 6 H), 3.56 (s, 6 H), 5.25 (s, 4 H), 7.28 (s, 2 H), 7.40 (d, *J* = 8.1, 4 H), 7.57 (d, *J* = 8.1, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ: 30.3 (CH_3), 56.3 (CH_3), 87.1 (C), 94.2 (C), 95.7 (CH_2), 115.1 (C), 120.2 (CH), 124.4 (C), 128.2 (C), 132.2 (CH), 134.2 (CH), 152.5 (C), 193.5 (C). IR (KBr) *v*: 3398, 2918, 2392, 2296, 1647, 1384, 1116, 1067, 969. MS (ESI) *m*/*z*: 569 ($[M+Na]^+$). Anal. Calcd for $C_{30}H_{26}O_6S_2$: C, 65.91; H, 4.79. Found: C, 65.84; H, 4.65.

Fluorescence and UV-Vis Spectroscopy.

Fluorescence spectra were measured on a Perkin Elmer LS-55 spectrophotometer. UV-vis spectra were measured on a T6 spectrophotometer, with dichloromethane as the solvent. For determination of the corresponding quantum yield (¢*f*), qunine sulfate is used as calibration.[4] The quantum yields of **Ia**–**1i** are obtained by the following equation. F denotes fluorescence

intensity at each wavelength and Σ_F is calculated by summation of fluorescence intensity. A is the obsorption intensity of UV-vis at the corresponding excitation wavelength.

$$\phi_f^{(sample)} = \phi_f^{(sample)} \frac{A^{(standard)}}{A^{(sample)}} \frac{\sum F^{(sample)}}{\sum F^{(standard)}}$$

Electrochemical Measurement.

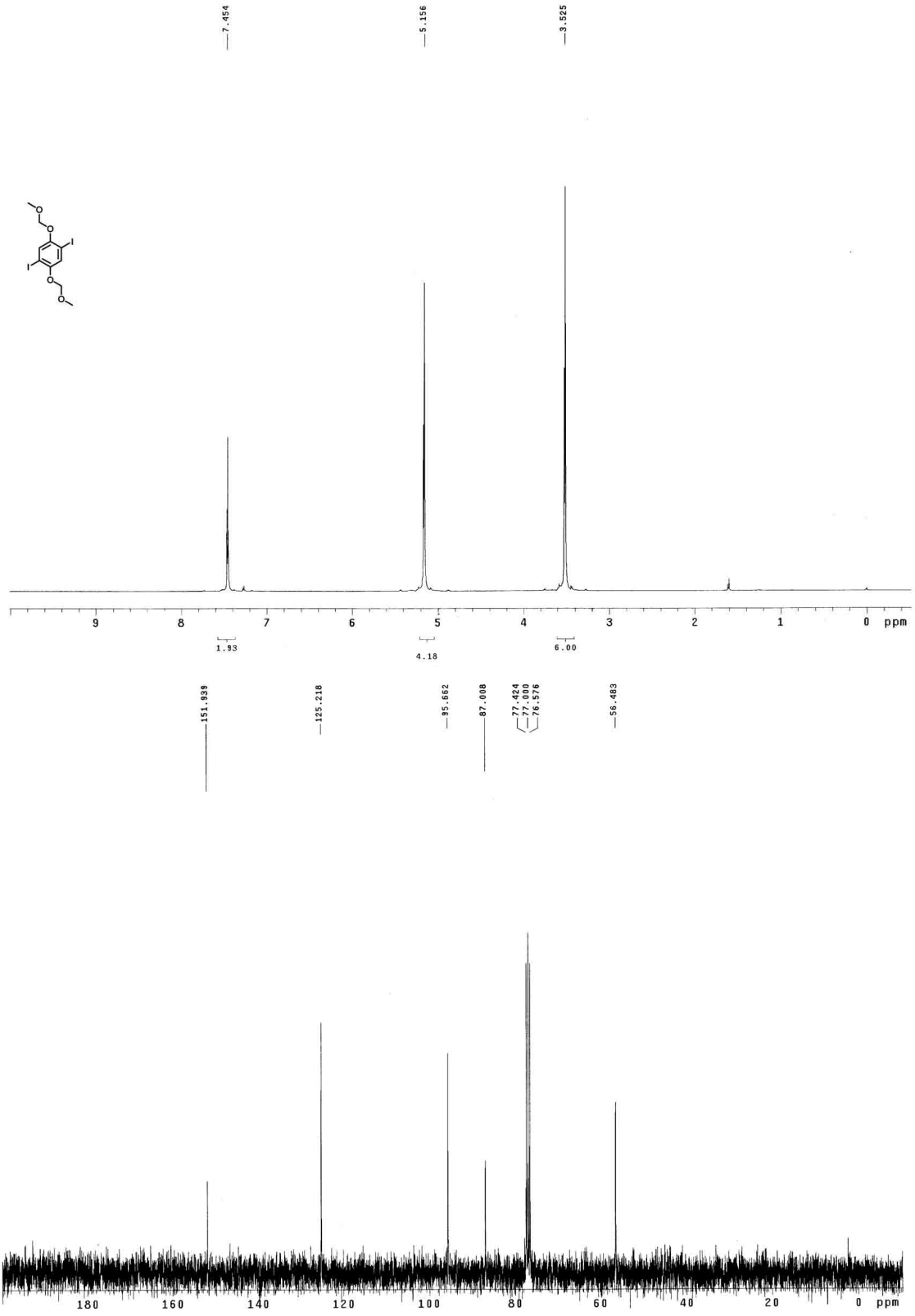
The electrochemical investigations were carried out using a CHI 660B electrochemistry workstation (CHI USA). A standard one-compartment and three-electrode cell was used with an Au disk (1.8 mm in diameter) as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) reference electrode. All potentials reported in this paper are referenced to SCE. AC impedance measurements were performed in the frequency range between 100,000 and 0.01 Hz.
A chemical and potential-assisted assembly method reported by J. M. Tour[5] was used. The molecular wire **1c** (~5 mg) was dissolved in a mixed solvent of CH_2Cl_2/MeOH (2:1, V/V) 20 ml in a 25 ml breaker. Then 250 μL of 98% H_2SO_4 was added, and the solution was incubated for 2 h prior to further treatment in order to deprotect the thiol moiety. Before modification, the electrodes were polished with 0.05 μm alumina slurry on Buehler polishing cloth with distilled water as the lubricant, rinsed with triply distilled water, and sonicated in a water bath for 2 min. After that the electrodes were electrochemically pretreated by scanning between gold redox potentials (from -0.2 to 1.4 V SCE) in 0.5 mol L^{-1} H_2SO_4 aqueous solution with a scan rate of 100 $mV.s^{-1}$. Rinsed with a copious amount of distilled water, and dried in argon flow. After being rinsed with a copious amount of distilled water, and dried in argon flow, the electrode was dipped in OPE **1c** solution immediately. OPE **1c** self-assembled monolayers (SAMs) were deposited on Au electrode by applying a constant potential 0.4 V for 2 h, then rinsed with distilled water and anhydrous ethanol, and blown dry with argon. The modified electrode was used in electrochemical experiments.

References:

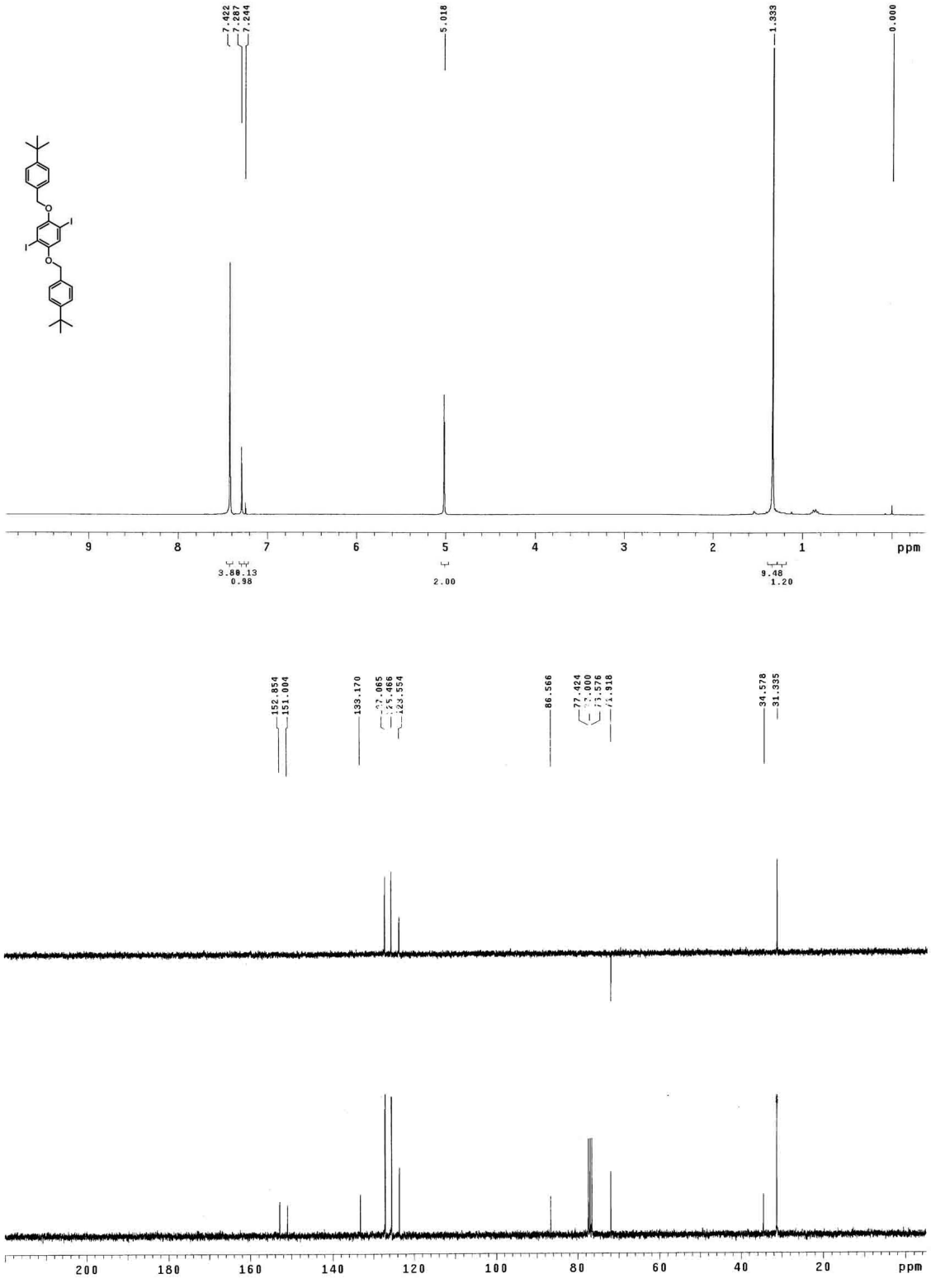
(1) Waterlot, C.; Couturier, D.; Hasiak, B. *J. Chem. Res. Miniprint* **2000**, *3*, 417–429.
(2) Peng, Z.; Gharavi, A. R.; Yu, L. *J. Am. Chem. Soc.* **1997**, *119*, 4622–4632.
(3) Hünig, S.; Baub, R.; Kemmera, M.; Meixnera, H.; Metzenthinb, T.; Karl Petersc; Sinzgera, K.; Gulbisa, J. *Eur. J. Org. Chem.* **1998** *2*, 335–348.
(4) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229–235.
(5) Cai, L. T.; Yao, Y. X.; Yang, J. P.; Price, D. W.; Tour, J. M. *Chem. Mater.* **2002**, *14*, 2905–2909.

^{1}H NMR, ^{13}C NMR and DEPT Spectra

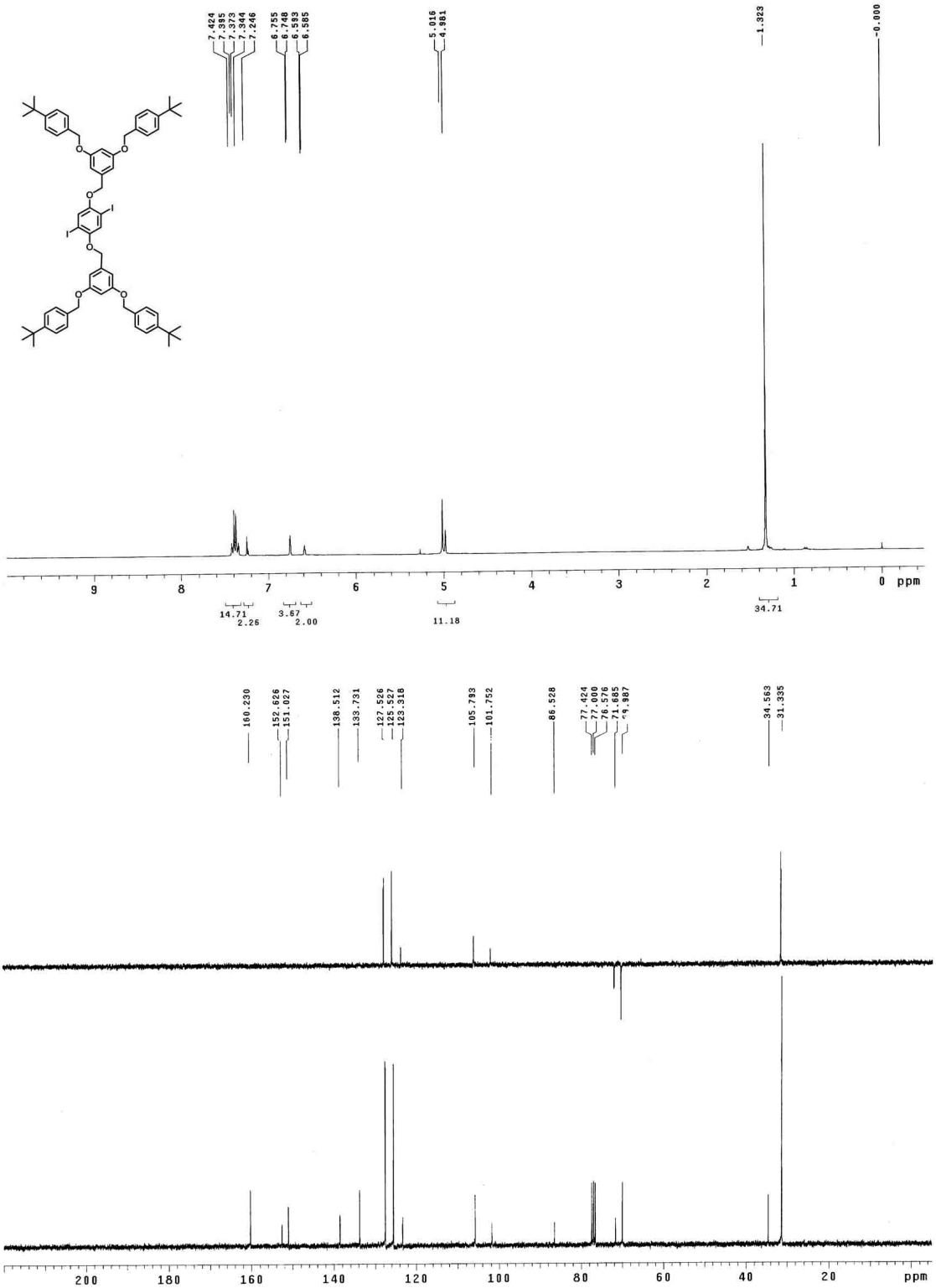
Compound 4 (^{1}H NMR and ^{13}C NMR)



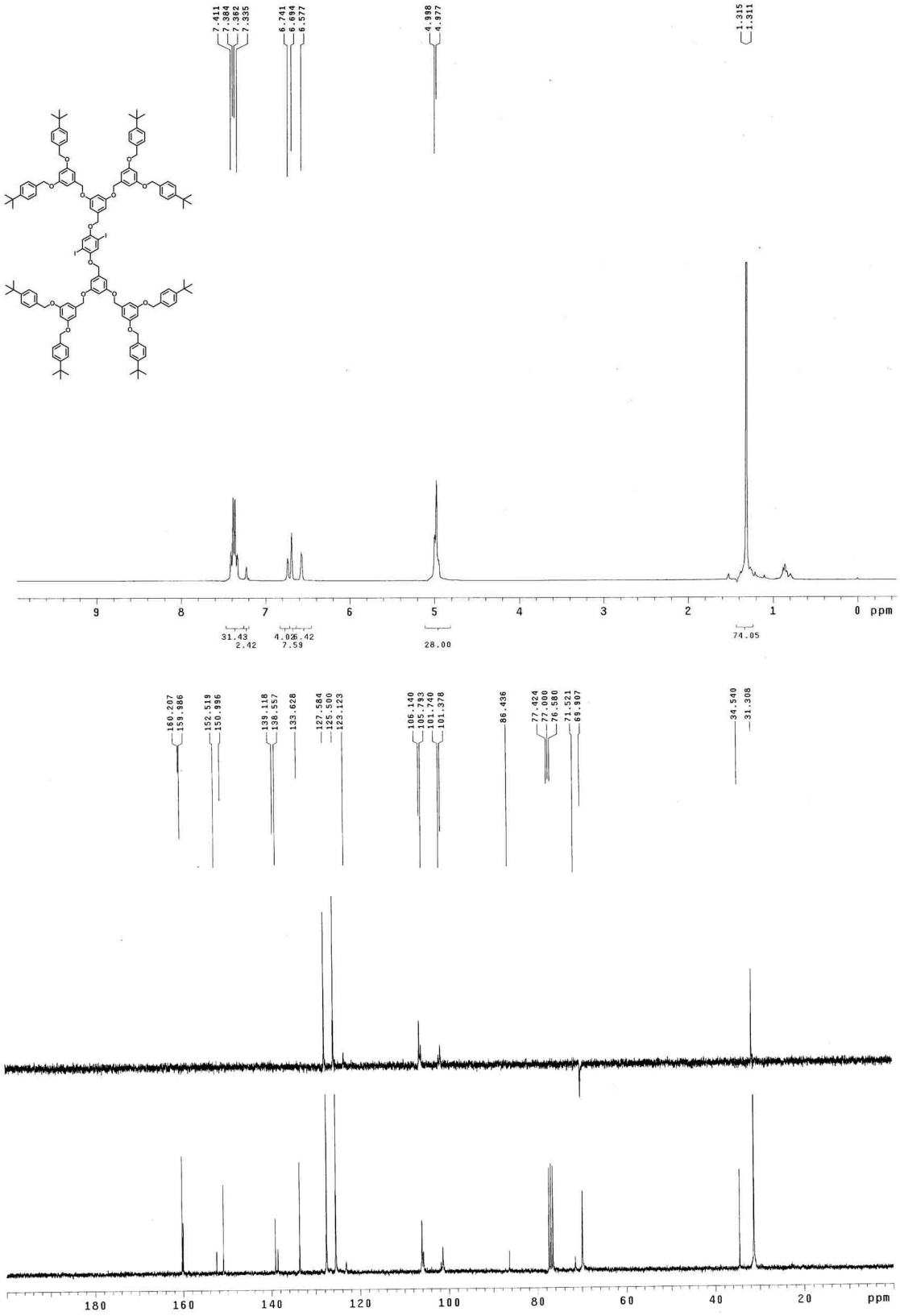
Compound 6a (^{1}H NMR, ^{13}C NMR and DEPT)



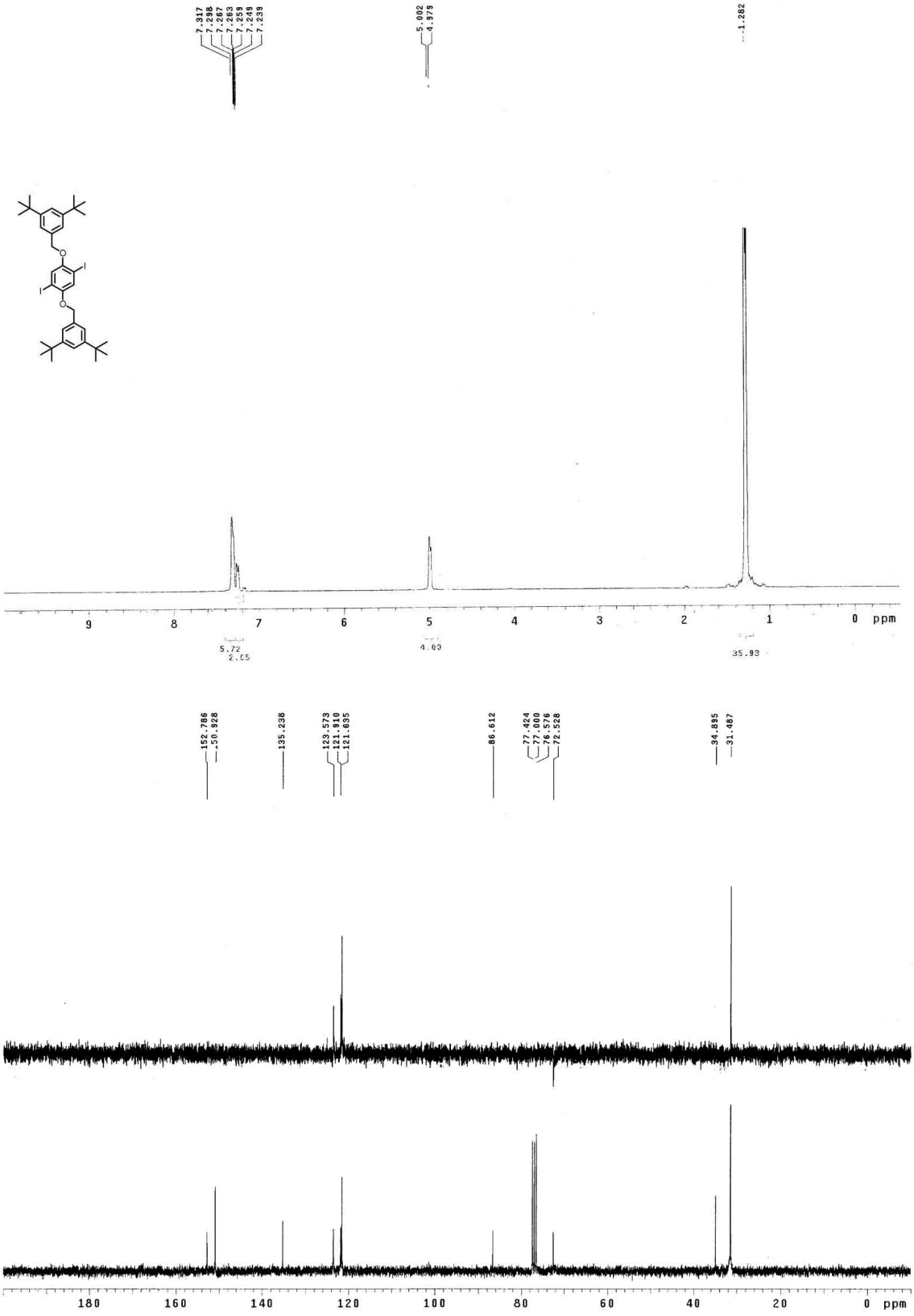
Compound 6b (^{1}H NMR, ^{13}C NMR and DEPT)



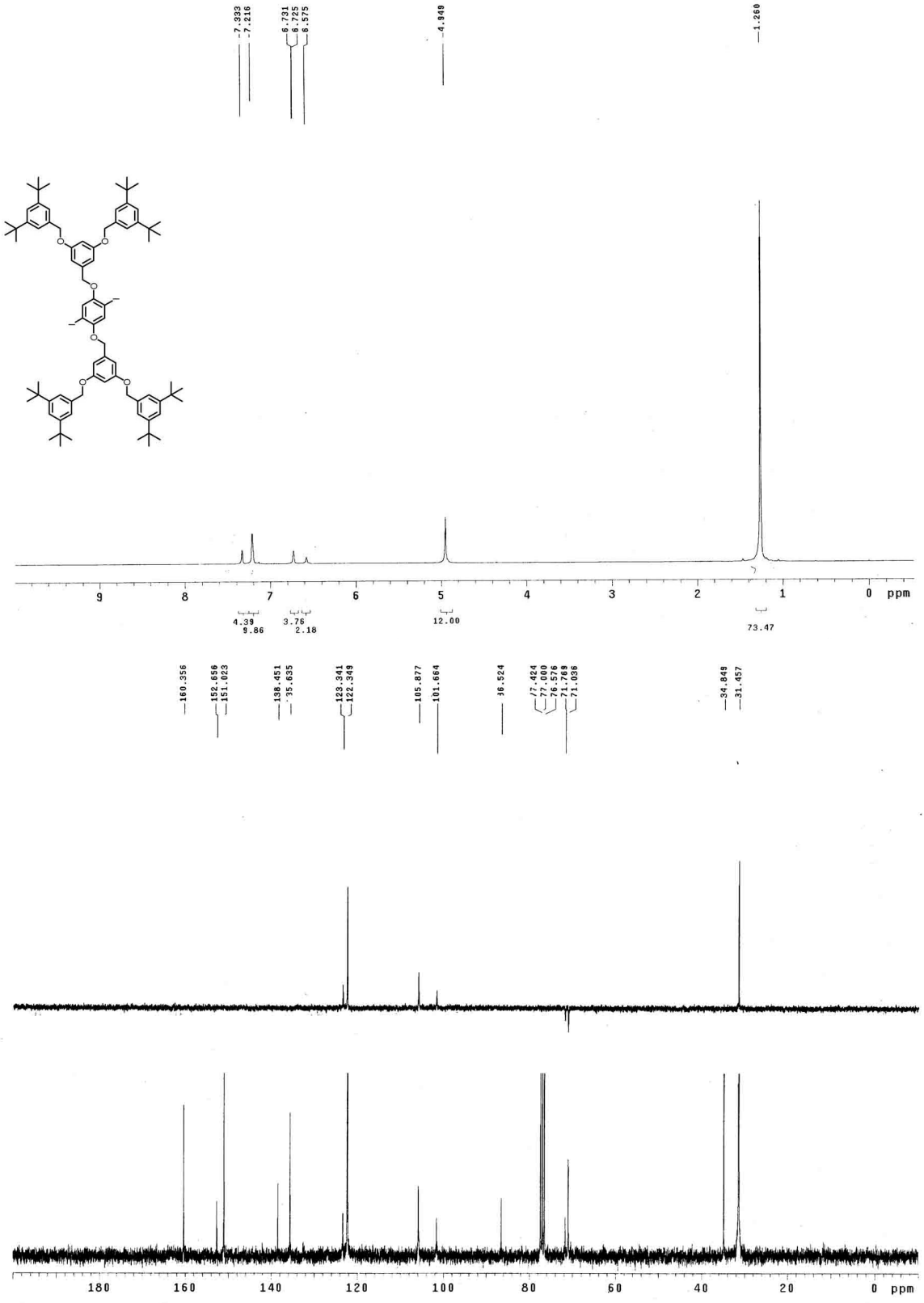
Compound 6c (^{1}H NMR, ^{13}C NMR and DEPT)



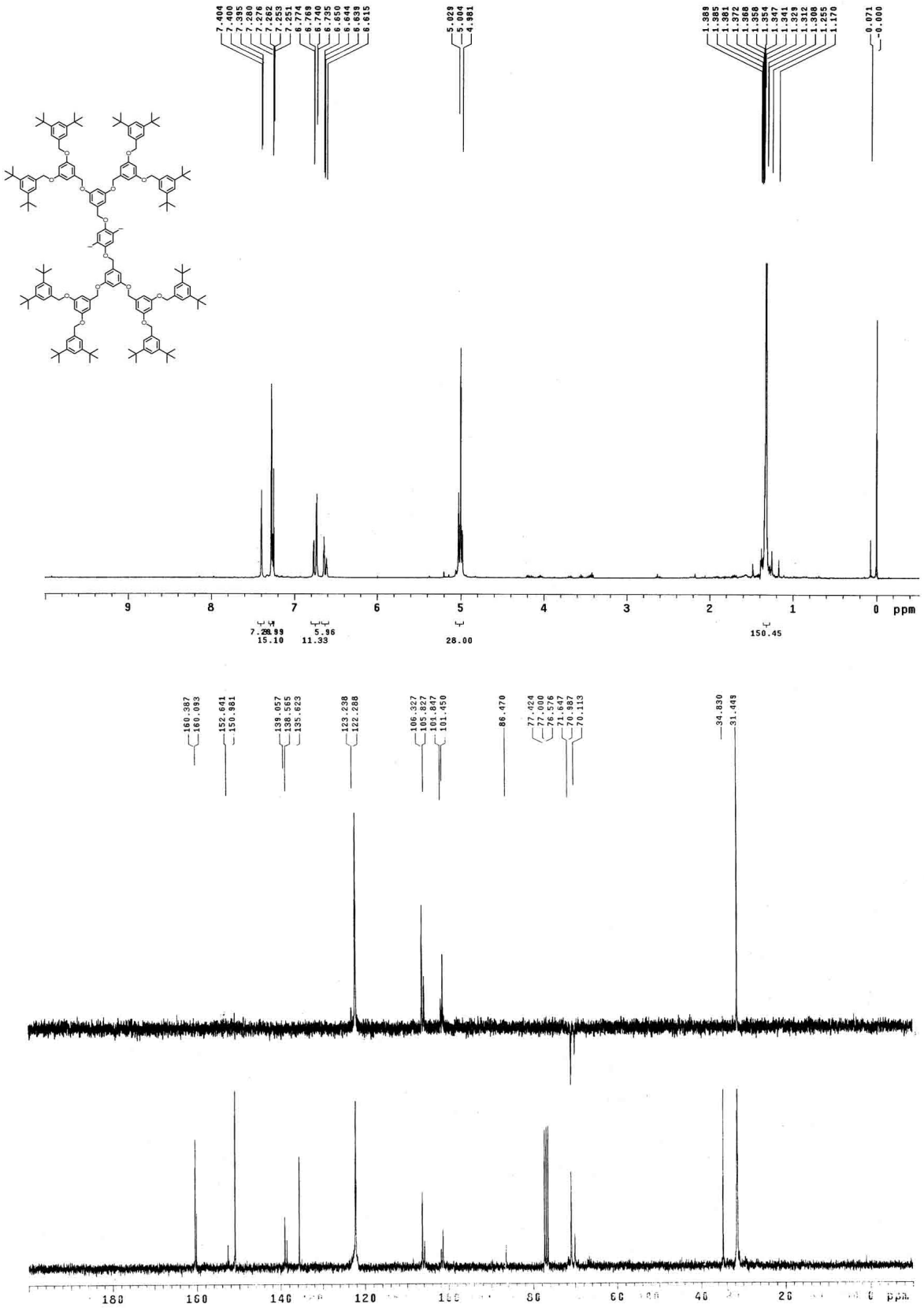
Compound 6d (^{1}H NMR, ^{13}C NMR and DEPT)



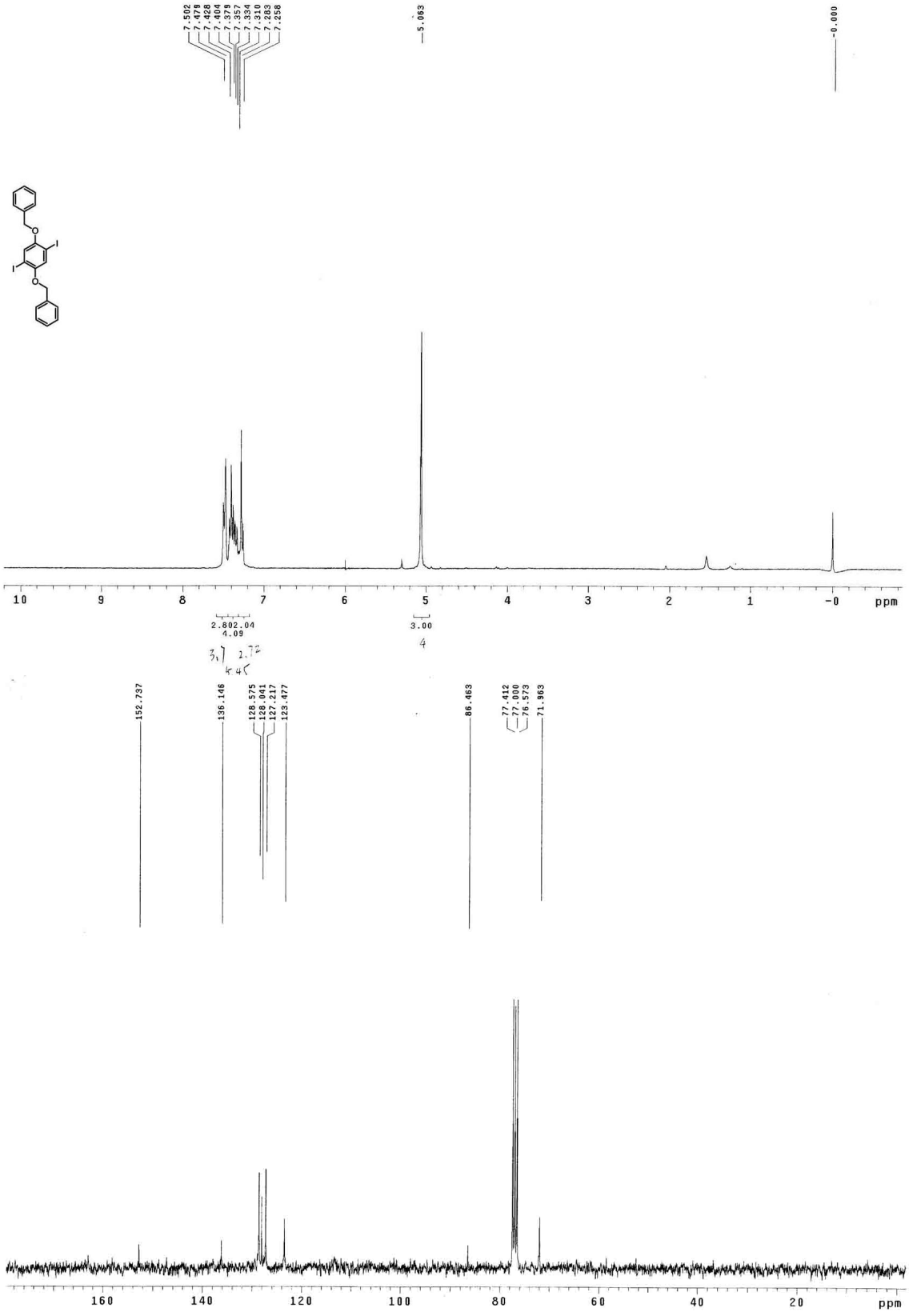
Compound 6e (^{1}H NMR, ^{13}C NMR and DEPT)



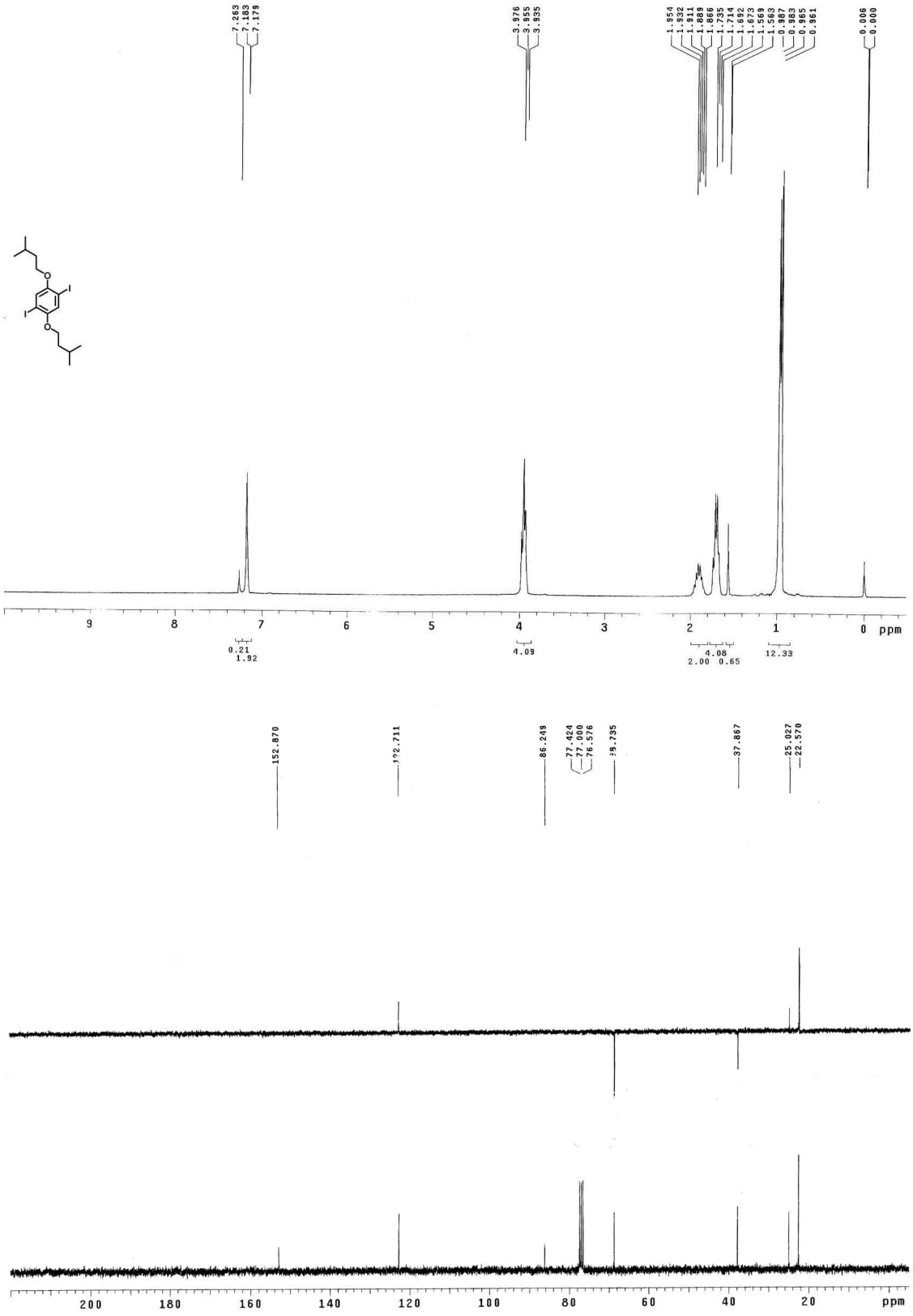
Compound 6f (^{1}H NMR, ^{13}C NMR and DEPT)



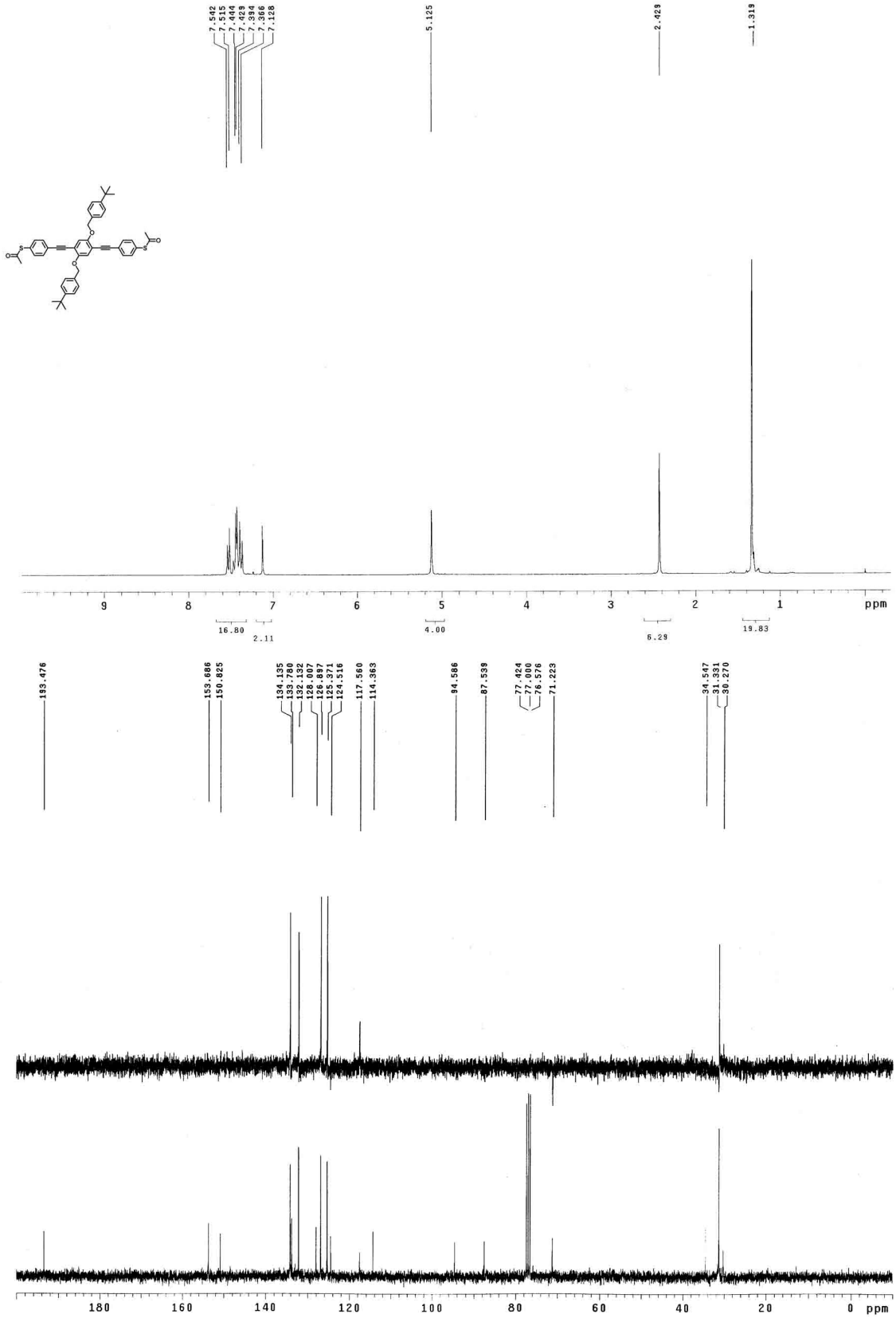
Compound 6g (^{1}H NMR and ^{13}C NMR)



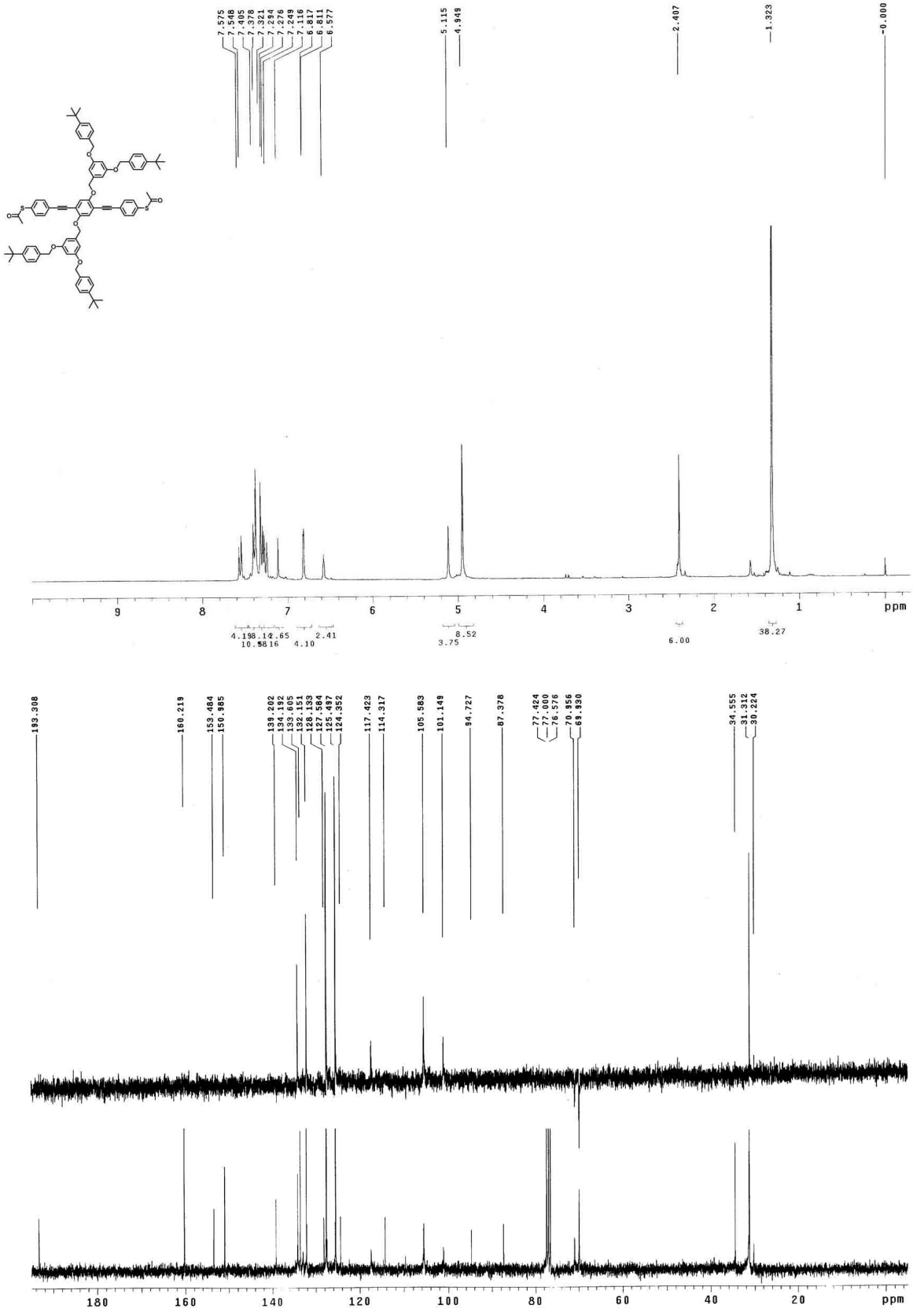
Compound 6h (^{1}H NMR, ^{13}C NMR and DEPT)



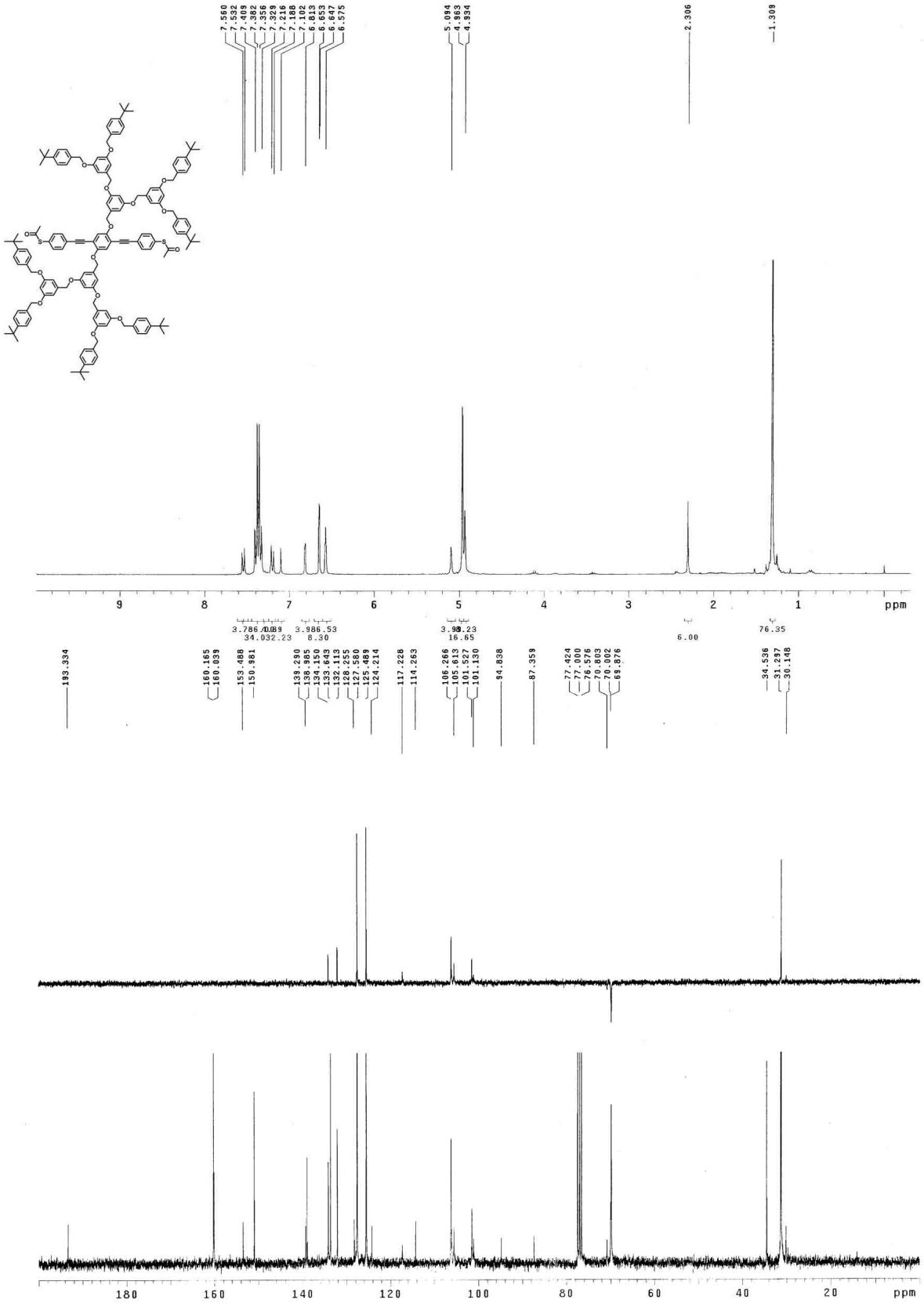
Compound 1a (^{1}H NMR, ^{13}C NMR and DEPT)



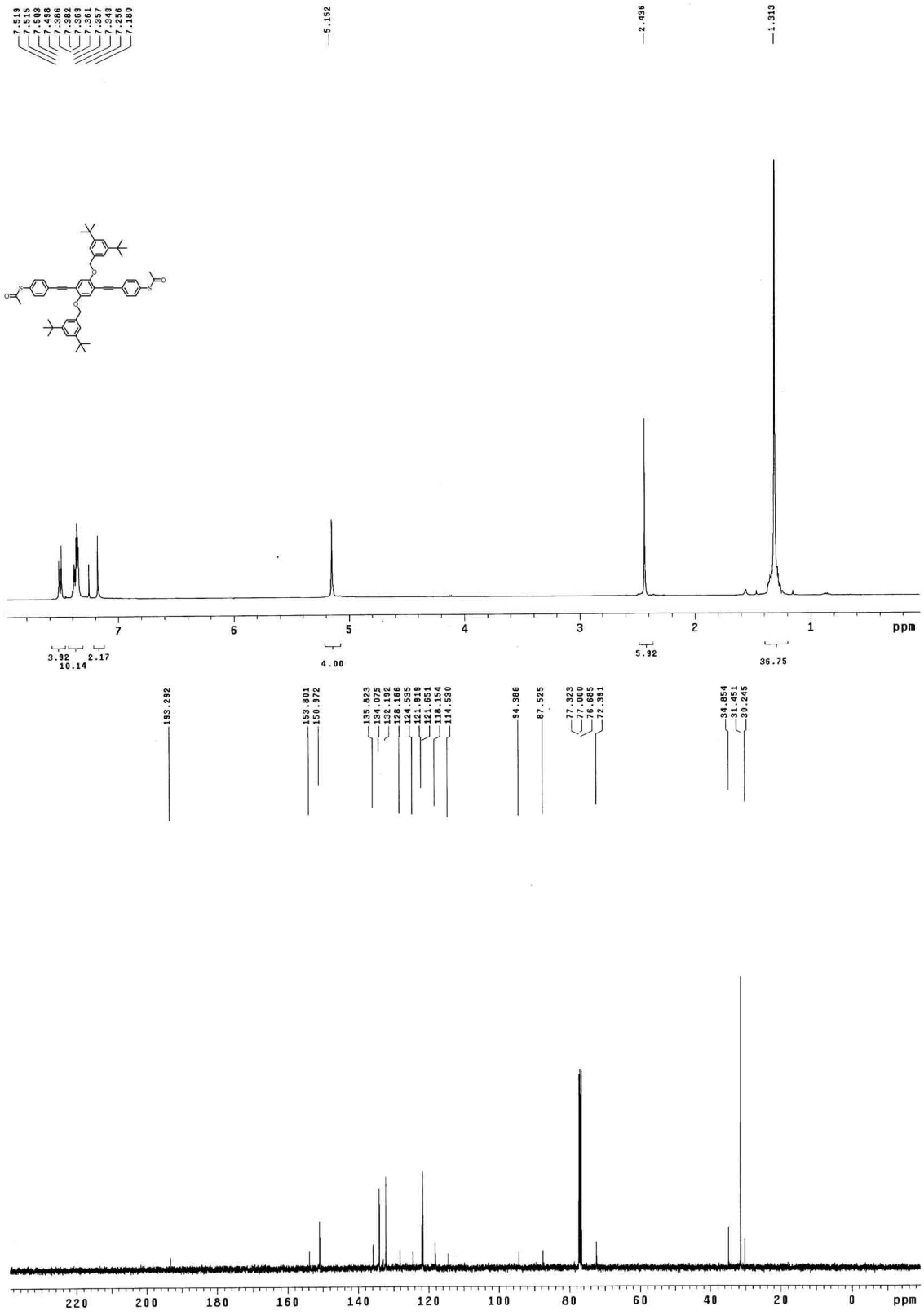
Compound 1b (^{1}H NMR, ^{13}C NMR and DEPT)



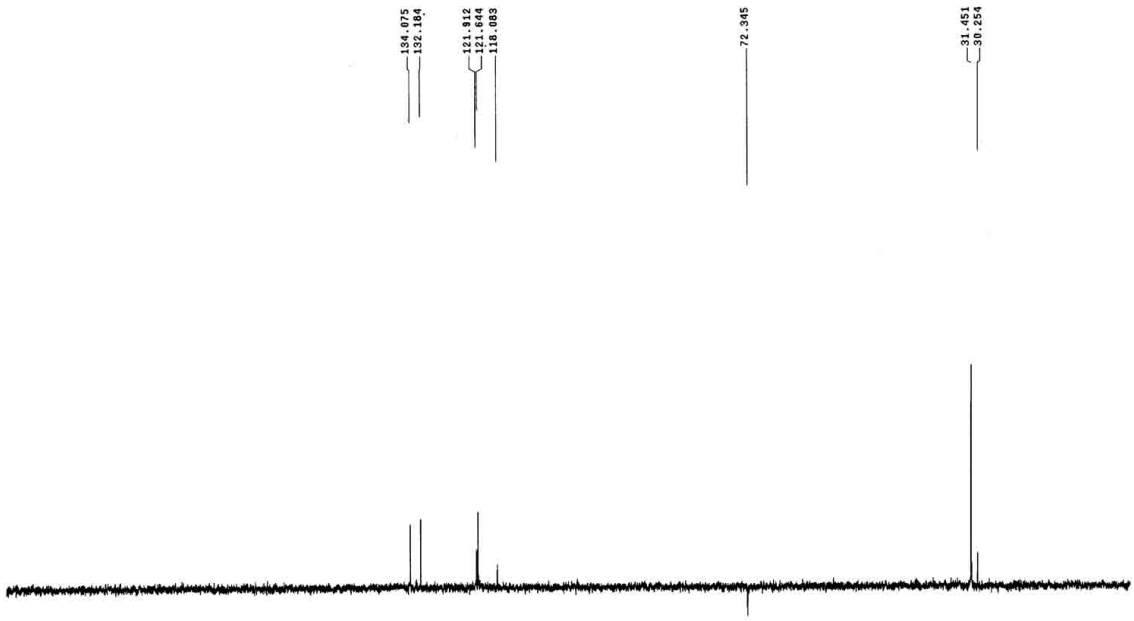
Compound 1c (^{1}H NMR, ^{13}C NMR and DEPT)



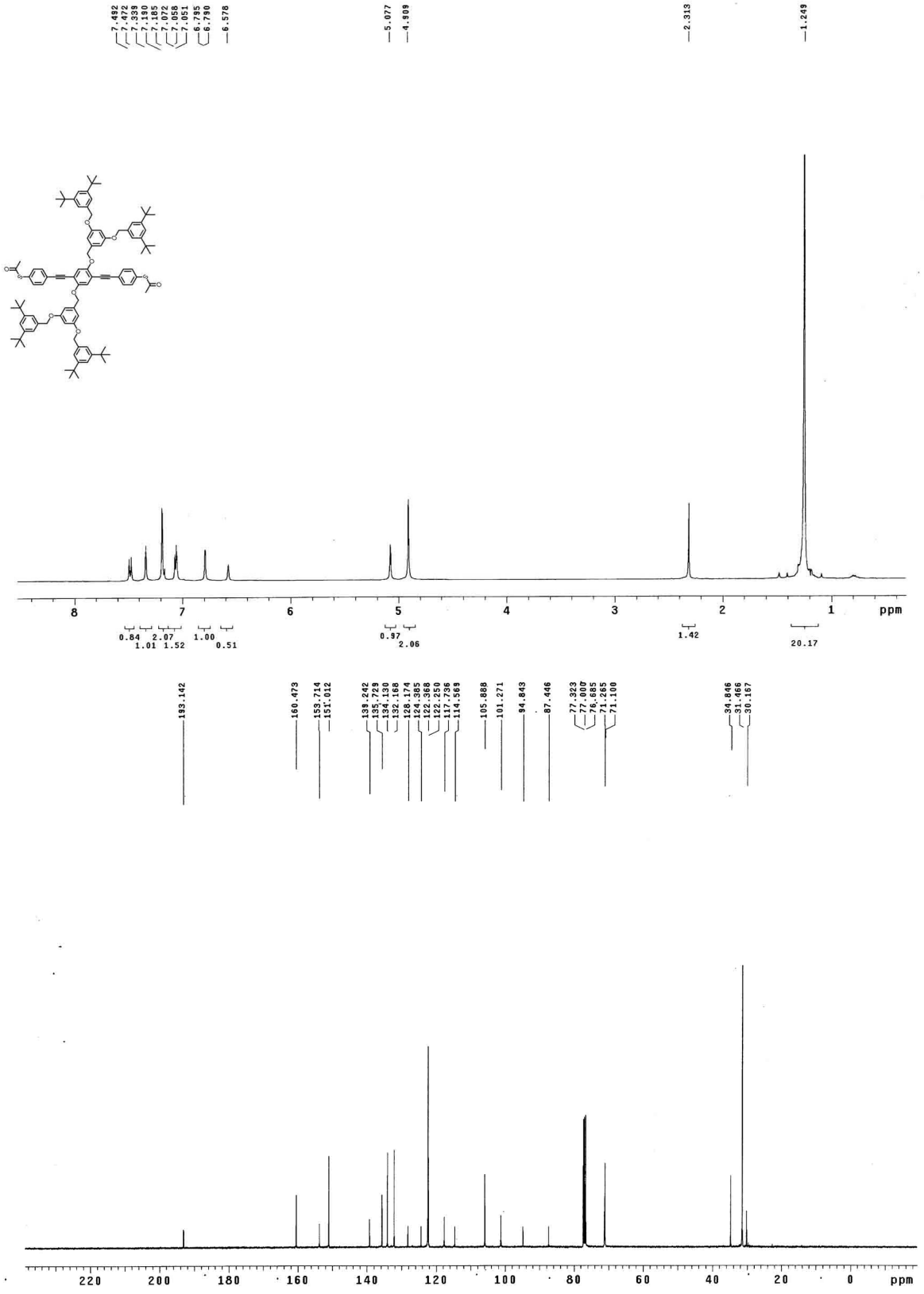
Compound 1d (^{1}H NMR and ^{13}C NMR)



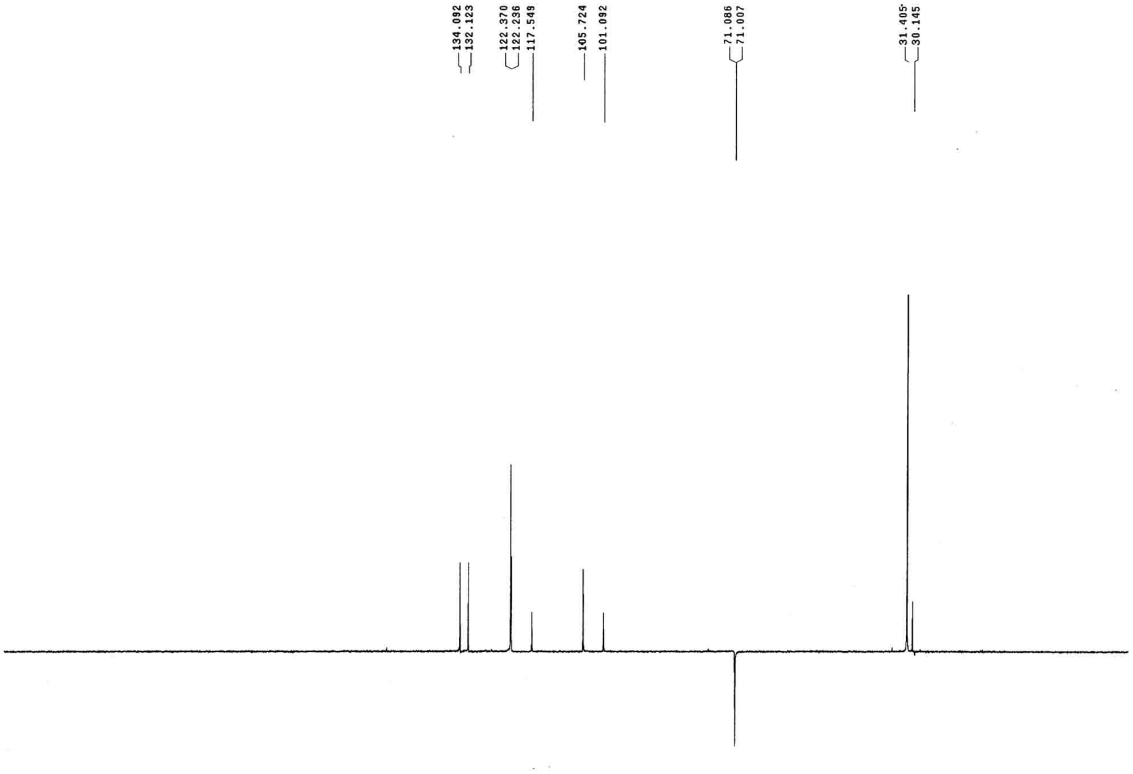
Compound 1d (DEPT)



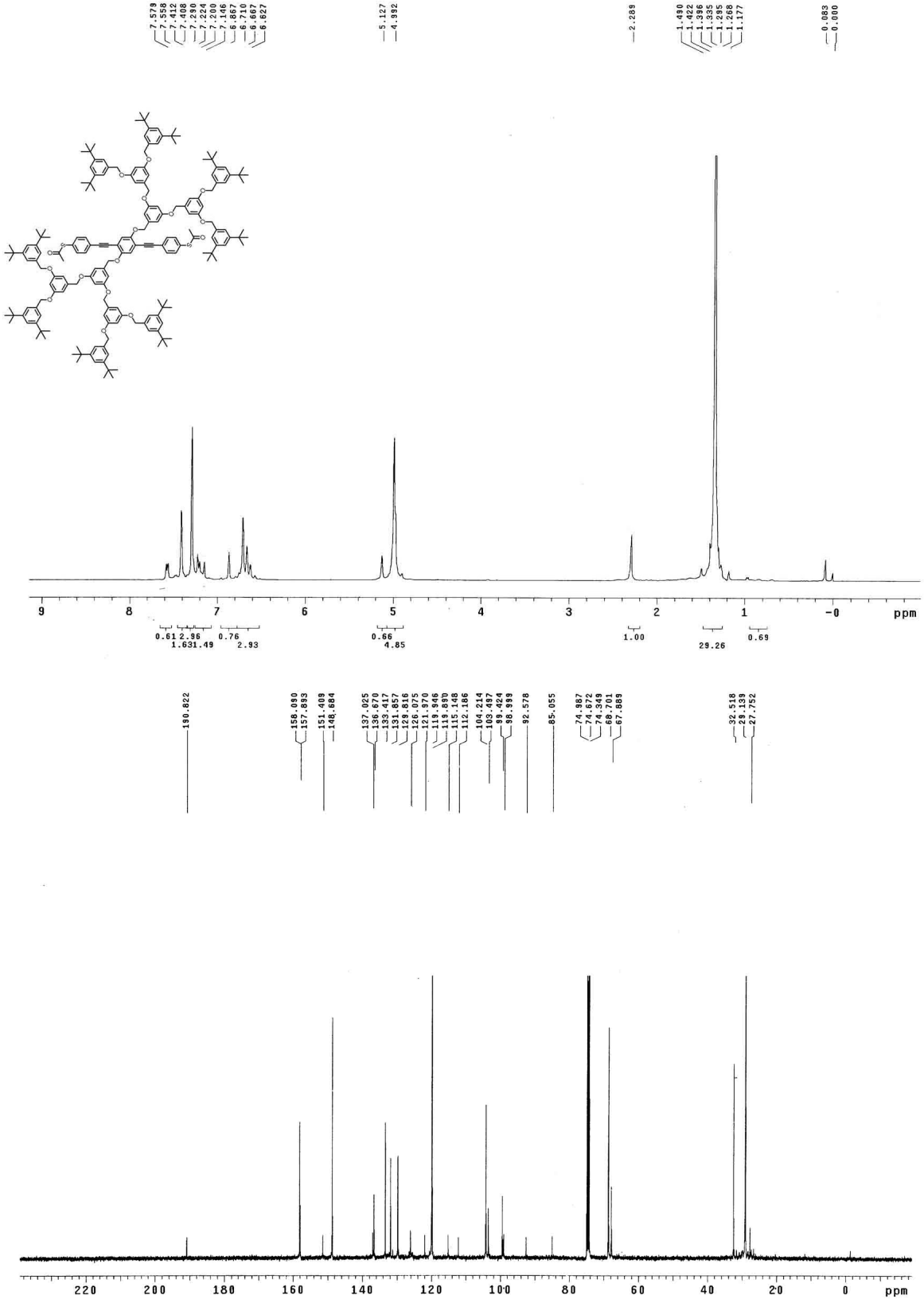
Compound 1e (^{1}H NMR and ^{13}C NMR)



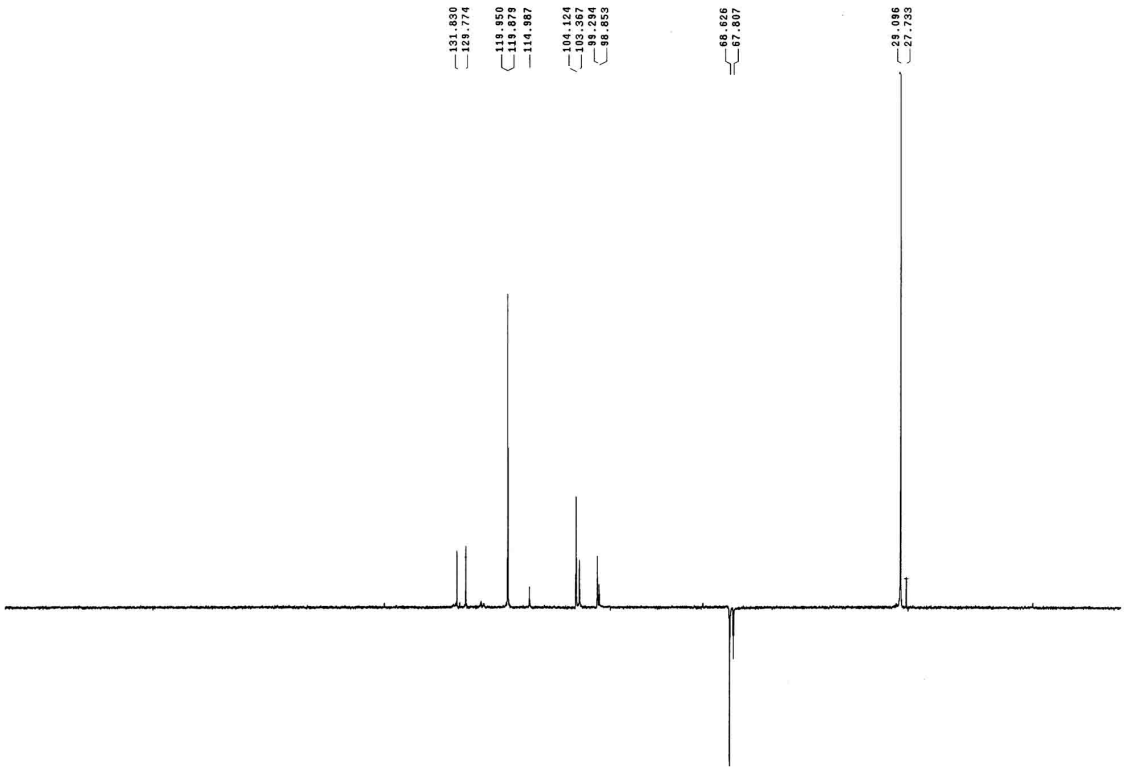
Compound 1e (DEPT)



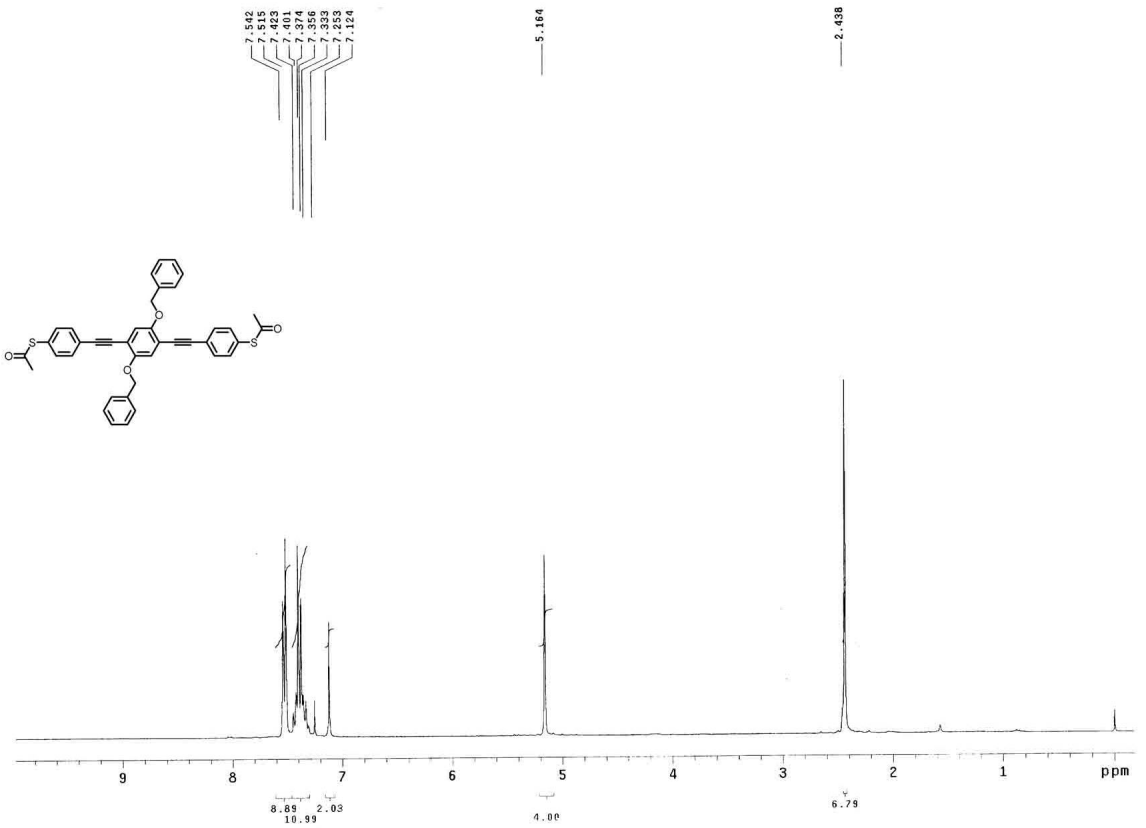
Compound 1f (^{1}H NMR and ^{13}C NMR)

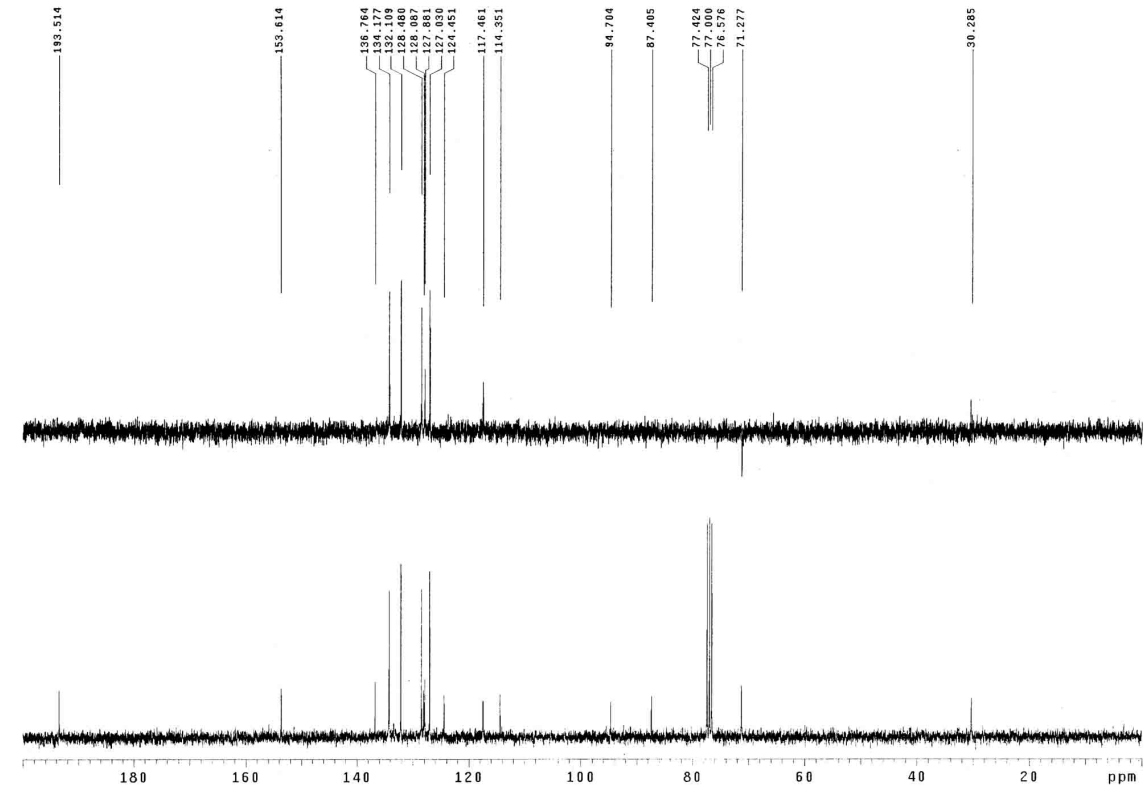


Compound 1f (DEPT)

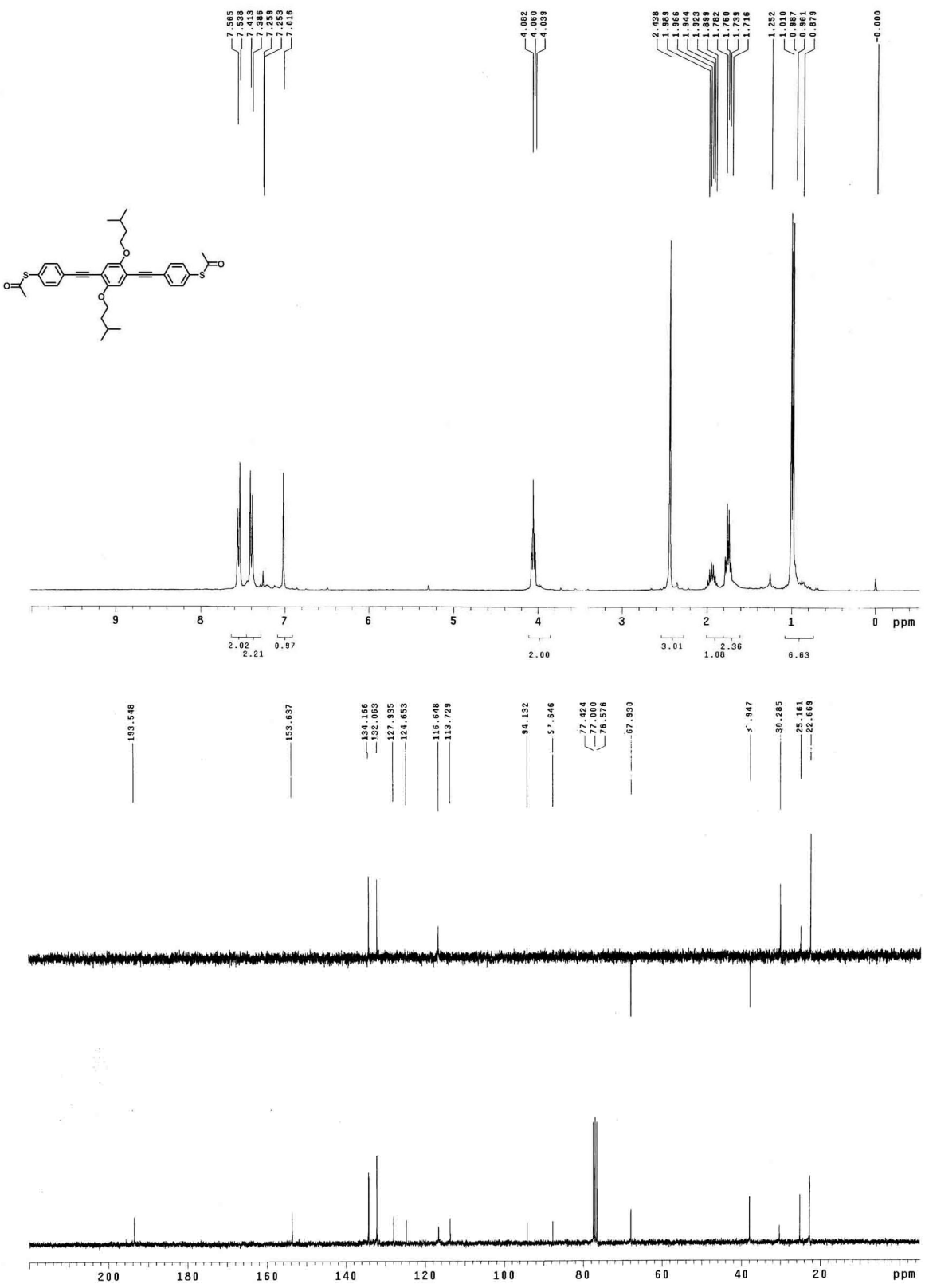


Compound 1g (^{1}H NMR)





Compound 1h (^{1}H NMR)



Compound 1i (^{1}H NMR)