Electronic Supplementary Information

Metal Ion Detection by Luminescent 1,3-bis(dimethylaminomethyl)phenyl Receptor-Modified Chromophores and Cruciforms

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List of Supporting Information Figures:

Experimental section:

General: Reagents were obtained from Acros, Aldrich Chemical Co., TCI America, or Alfa Aesar and used as received from the suppliers without further purification. All the solvents used, were purified by passage through alumina column under a N_2 atmosphere employing an MBraun solvent purification system. All the air sensitive reactions were performed in an MBraun dry box or using standard Schlenk techniques under N_2 atmosphere. Proton, carbon-13 and phosphorus-31 NMR spectra were acquired on a Bruker ARX 300 spectrometer operating at 300, 75 and 121 MHz, respectively. All spectra were collected at 25 °C and referenced to TMS or residual solvent peak for proton and carbon-13. Absorption spectra were recorded using Varian Cary-50 spectrophotometer and photoluminescence (PL) data were recorded using Varian Eclipse spectrofluorimeter in quartz cuvettes of path length 1 cm in THF. Quantum yield (Φ) were calculated for all the compounds relative to quinine bisulfate in 0.1 M H_2SO_4 (aq) ($\Phi = 0.546$).

Synthesis of 3,5-bis(bromomethyl)-bromobenzene (2): 5-bromo-*m*-xylene **1** (20.00 g, 105.8 mmol), N-bromosuccinamide (41.50 g, 233.0 mmol) and benzoylperoxide (BPO) (2.470 g, 10.20 mmol) were dissolved in chloroform (600 mL) and refluxed overnight. After cooling to room temperature, reaction mixture was extracted with water (3 × 100 mL) and organic layer was removed under reduced pressure. White crystalline solid was precipitated out while keeping the yellow oil residue on room temperature. Remaining oil was decanted out; 5 mL of methanol was added into it and left for recrystallization. White solid was washed with methanol (3 × 5 mL) (10 g, 27%). Observed Melting point 97.5 °C; Literature melting point 95-98 °C. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 4.426$ (s, 4H; CH_2), 7.359 (s, 1H; Aromatic), 7.495 (d, 2H; J =1.5 Hz, Aromatic).

Synthesis of 3,5-bis[(dimethylamino) methyl] bromobenzene (3): 3,5-bis(bromomethyl)-bromobenzene **2** (5.00 g, 14.5 mmol) was dissolved in THF (20 mL) and dimethyl amine (6.60 g. 145

mmol) was added into it. Reaction mixture was stirred at room temperature for 2 d. Dimethylammonium bromide salt was filtered off and volatiles were removed under reduced pressure, yielding colorless oil. Dichloromethane (50 mL) was added and solution was washed by saturated aq. Na_2CO_3 (3 × 50 mL). Organic layer was collected, dried over Na_2SO_4 and removed under reduced pressure, yielding a viscous colorless oil (2.00 g, 50.0%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.245$ (s, 12H; N-C*H*$_3$), 3.385 (s, 4H; N-C*H*$_2$), 7.191 (s, 1H; Aromatic), 7.382 (d, 2H; *J* = 1.2, Aromatic).

Synthesis of 1,4-bis(hexyloxy) benzene (5): Hydroquinone **4** (25.0 g, 227 mmol) was dissolved in acetonitrile (300 mL) and K_2CO_3 (80.5 g, 582 mmol) was added into it. Hexylbromide (112 g, 681 mmol) was added dropwise to the heated solution and refluxed overnight. While the reaction was hot, K_2CO_3 was filtered off and volatiles were removed under reduced pressure. Residue was dissolved in minimum amount of DCM and added dropwise into 400 mL of methanol and left for recrystallization. Solid was filtered off and recrystallized again yielding pure off white solid flakes (38 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.946$ (t, 6H; *J* = 6.9 Hz, 2 × CH_3), 1.514 - 1.323 (m, 12H; 6 × CH_2), 1.818 (q, 4H; *J* = 6.6 Hz, 2 × CH_2), 3.941 (t, 4H; *J* = 6.6 Hz, 2 × O-C*H*$_2$), 6.840 (s, 4H; Aromatic).

Synthesis of 2-Bromo-1,4-bis(hexyloxy) benzene (6): 1,4-bis(hexyloxy) benzene **5** (10 g, 36 mmol) was dissolved in $CHCl_3$ (120 mL) and 2 mL bromine (6.3 g, 39.6 mmol) in $CHCl_3$ (8 mL) was added dropwise into it through syringe pump for 12 h at room temperature. Reaction mixture was quenched with saturated Na_2SO_3 solution followed by extraction with H_2O (4 × 100 mL). Organic layer was collected, dried over Na_2SO_4 and removed under reduced pressure, yielding viscous oil. Column chromatography was done in pure hexane to purify the crude (4.2 g, 33%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.93$ (t, 6H; *J* = 7.0 Hz, 2 × CH_3), 1.54 - 1.32 (m, 12H; 6 × CH_2), 1.87 – 1.72 (m, 4H; 2 × CH_2), 3.90 (t, 2H; *J* = 6.0 Hz, O-C*H*$_2$), 3.97 (t, 2H; *J* = 6.0 Hz, O-C*H*$_2$), 6.86 – 6.78 (m, 2H; Aromatic), 7.13 (d, 1H;

J = 2.0 Hz, Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 25.6, 29.2, 29.2, 31.5, 31.5, 68.8, 70.2, 112.7, 114.3, 114.7, 119.4, 149.7, 153.5.

Synthesis of 2,5-diBromo-1,4-bis(hexyloxy) benzene (9): Compound **5** (20.0 g, 72.0 mmol) was dissolved in DCM (150 mL) and reaction mixture was cooled to 0 °C. Br_2 (25.4 g, 158 mmol) was added dropwise into it and stirred overnight at room temperature. Excess of bromine was quenched with saturated Na_2SO_3 solution followed by extraction with H_2O (4 × 100 mL). Organic layer was collected, dried over Na_2SO_4 and removed under reduced pressure, yielding off white solid (28 g, 89%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.926 (t, 6H; *J* = 6.9 Hz, 2 × CH_3), 1.550 - 1.332 (m, 12H; 6 × CH_2), 1.820 (q, 4H; *J* = 6.9 Hz, 2 × CH_2), 3.965 (t, 4H; *J* = 6.6 Hz, 2 × O-CH_2), 7.104 (s, 2H; Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.5, 25.6, 29.0, 31.4, 70.3, 111.1, 118.4, 150.0.

Synthesis of 1,4-bis(hexyloxy)-2,5-bis(2-(trimethylsilyl)ethynyl) benzene (10): Under nitrogen, compound **9** (2.0 g, 4.6 mmol) was dissolved in toluene (20 mL) followed by addition of tetrakis(triphenylphosphine) palladium(0) (0.58 g, 0.60 mmol) and copper iodide (0.10 g, 0.60 mmol). Trimethylsilylacetylene (1.8 g, 18 mmol) was dissolved in triethylamine (20 mL) separately and added dropwise into the reaction mixture and stirred for 48 h at 85 °C. Reaction mixture was passed through silica, followed by washing with ether (50 mL). Organic layer was extracted with sat. sodium bicarbonate solution (4 × 100 mL), dried over sodium sulfate and removed under reduced pressure. Residue was washed with methanol (20 mL), yielding dark solid (1.5 g, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.27 (s, 18H; 6 × Si-CH_3), 0.93 (t, 6H; *J* = 9.0 Hz, 2 × CH_3), 1.55 – 1.33 (m, 12H; 6 × CH_2), 1.80 (q, 4H; *J* = 6.0 Hz, 2 × CH_2), 3.96 (t, 4H; *J* = 6.0 Hz, 2 × O-CH_2), 6.91 (s, 2H; Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0, 14.0, 22.6, 25.7, 29.2, 31.6, 69.4, 100.0, 101.0, 113.9, 117.1, 153.9. Small resonances attributable to residual triphenylphosphine oxide were observed in the NMR spectra

(Figures S14-15); these impurities were removed (by methanol rinse) after deprotection to form compound **11** (*vide infra*).

Synthesis of 1,4-diethynyl-2,5-bis(hexyloxy) benzene (11): Compound **10** (1.9 g, 4.1 mmol), was dissolved in THF (100 mL) followed by the addition of methanol (40 mL) and 20 % aqueous NaOH solution (20 mL) and stirred for 2 h at room temperature. Ether (50 mL) was added into it, and reaction mixture was extracted with water (4 × 50 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure. Methanol (20 mL) was added into crude residue and stirred for 20 min. Solid ppt. was filtered and washed with methanol, yielding off white solid (1.2 g, 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, 6H; *J* = 6.0 Hz, 2 × CH_3), 1.51 – 1.33 (m, 12H; 6 × CH_2), 1.82 (q, 4H; *J* = 6.0 Hz, 2 × CH_2), 3.35 (s, 2H; C≡C*H*), 3.99 (t, 2H; *J* = 6.0 Hz, 2 × O-CH_2), 6.97 (s, 2H; Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.5, 25.5, 29.0, 31.5, 69.6, 79.7, 82.4, 113.2, 117.7, 154.0.

Synthesis of 2-bromo-9,9-dihexyl-9-*H*-fluorene (13): Compound **12** (6.80 g, 27.8 mmol) was dissolved in DMSO (20 mL) and KOH (15.6 g, 278 mmol) was added into it. Hexylbromide (11.0 g, 66.8 mmol) was added dropwise to the heated solution and refluxed overnight. Reaction mixture was dissolved in water (400 mL) and extracted with ethyl acetate (3 × 50 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure yielding yellow color oil. Column chromatography, in pure hexane, was done on this compound yielding light yellow color oil (8.2 g, 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.61 (b, 6H; 2 × CH_3), 1.12 – 0.74 (m, 16H; 8 × CH_2), 1.96, (b, 4H; 2 × CH_2), 7.34 (m, 3H; Aromatic), 7.47 (m, 2H; Aromatic), 7.56 (m, 1H; Aromatic), 7.69 (m, 1H; Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 23.7, 29.7, 31.5, 40.3, 55.4, 119.7, 121.0, 121.0, 122.8, 126.1, 126.9, 127.5, 129.9, 140.0, 140.1, 150.3, 153.0.

Synthesis of (2-(9,9-dihexyl-9-*H*-fluorene-2-yl) ethynyl)trimethylsilane (14): Under nitrogen, compound **13** (2.0 g, 4.8 mmol) was dissolved in diisopropylamine (70 mL) followed by addition of tetrakis(triphenylphosphine) palladium(0) (0.32 g, 0.30 mmol) and copper iodide (0.057 g, 0.30 mmol). Trimethylsilyl acetylene (1.0 g, 9.7 mmol) was added into the reaction mixture dropwise and stirred at room temperature for 2 h and then heated at 85 °C for 48 h. Reaction mixture was passed through silica, followed by washing with ether (50 mL). Organic layer was extracted with sat. sodium bicarbonate solution (4 × 100 mL), dried over sodium sulfate and removed under reduced pressure. Column chromatography, in pure hexane, was done on this compound yielding light yellow color oil (1.4 g, 64%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.31 (s, 9H; 3 × Si-CH_3), 0.59 (b, 6H; 2 × CH_3), 0.76 – 1.16 (m, 16H; 8 × CH_2), 1.96 (t, 4H; J = 8.8 Hz, 2 × CH_2), 7.37 – 7.33 (m, 3H; Aromatic), 7.49 – 7.45 (m, 2H; Aromatic), 7.72 – 7.62 (m, 2H; Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.1, 14.0, 22.6, 23.7, 29.7, 31.5, 40.4, 53.4, 55.1, 93.8, 106.3, 119.5, 120.0, 121.2, 122.9, 126.2, 126.8, 127.5, 131.1, 140.4, 141.7, 150.6, 151.0.

Synthesis of 2-ethynyl-9,9-dihexyl-9-*H*-fluorene (15): Compound **14** (0.70 g, 1.6 mmol), was dissolved in THF (60 mL) followed by addition of methanol (30 mL) and 20 % aqueous NaOH solution (30 mL) and stirred for 2 h at room temperature. Ether (50 mL) was added into it, and reaction mixture was extracted with water (4 × 50 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure, yielding light yellow color oil (0.58 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.55 – 0.65 (m, 4H; 2 × CH_3), 0.76 – 1.16 (m, 18H; 8 × CH_2 and 2H from CH_3), 1.94 – 1.99 (m, 4H; 2 × CH_2), 3.16 (s, 1H; C≡C*H*), 7.36 – 7.34 (m, 3H; Aromatic), 7.51 – 7.48 (m, 2H; Aromatic), 7.72 – 7.65 (m, 2H; Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0, 22.6, 23.7, 29.7, 31.5, 40.3, 55.1, 68.0, 84.8, 119.6, 120.1, 120.1, 122.9, 126.5, 126.9, 127.6, 131.1, 140.2, 141.9, 150.7, 151.0.

Synthesis of Compound 17: Compound **16** (10 g, 0.038 mol), *N*-bromosuccinimide (15 g, 0.084 mol) and azobisisobutyronitrile (AIBN) (1.3 g, 0.0076 mol) were dissolved in CCl_4 (250 mL) refluxed for 8 h. After cooling to room temperature, reaction mixture was washed with water (3 × 100 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure. Residue was recrystallized in ethanol yielding white crystalline solid (9.0 g, 56%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.53 (s, 4H; 2 × CH_2), 7.68 (s, 2H; Aromatic).

Synthesis of 4-hexyloxy benzaldehyde (19): Compound **18** (5.0 g, 41 mmol) was dissolved in acetonitrile (70 mL) and K_2CO_3 (11 g, 82 mmol) was added into it. Hexylbromide (8.3 g, 51 mmol) was added dropwise to the heated solution and refluxed overnight. H_2O (200 mL) was added into the reaction mixture and extracted with ether (3 × 50 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure (8.1 g, 96%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.952 – 0.896 (b, 3H; CH_3), 1.562 - 1.330 (m, 6H; 3 × CH_2), 1.832 (q, 2H; J = 6.0 Hz, CH_2), 4.056 (t, 2H; J = 6.6 Hz, 2 × O-CH_2), 7.030 (dd, 2H; J_1 = 8.7 Hz, J_2 = 1.8 Hz, Aromatic), 7.858 (dd, 2H; J_1 = 8.7 Hz, J_2 = 1.8 Hz, Aromatic), 9.890 (s, 1H; CHO).

Synthesis of Compound 20: Compound **17** (6.20 g, 14.7 mmol) and triethylphosphite (12.2 g, 73.5 mmol) were heated up to 90 °C for 3 h under nitrogen atmosphere. After completion, reaction mixture was vacuum distilled to remove excess triethylphosphite. Residue was triturated with pentane (10 ml) yielding white solid (7.6 g, 95%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (t, 12H; J = 9.0 Hz, 4 × CH_3), 3.36 (dd, 4H; J_1 = 30.0 Hz, J_2 = 6.0 Hz, 2 × (O)PCH_2), 4.10 (m, 8H; 4 × CH_2), 7.65 (d, 2H; J = 3.0 Hz, Aromatic). ^{31}P NMR (121 MHz, $CDCl_3$): δ = 24.7. This product was contaminated with a small amount of nonvolatile P-containing impurities present in the triethylphosphite starting material (see Figure S31); we elected to remove the impurities by aqueous extraction following the next step.

Synthesis of 3,5-bis[(dimethylamino) methyl] phenyl trimethylsilyl acetylene (26): Under nitrogen, compound **3** (2.0 g, 7.4 mmol) was dissolved in toluene (10 mL) followed by addition of tetrakis(triphenylphosphine) palladium(0) (0.50 g, 0.50 mmol) and copper iodide (85 mg, 0.50 mmol). Trimethylsilylacetylene (1.8 g, 18 mmol) was dissolved in triethylamine (15 mL) separately and added dropwise to the reaction mixture and stirred for 24 h at 85 °C. Ether (20 mL) was added into the reaction mixture and extracted with sat. sodium bicarbonate solution (4 × 50 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure. Residue was triturated with hexane (20 mL) and hexane layer was removed under reduced pressure, yielding yellow viscous oil (1.3 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.251 (s, 9H; Si-C*H*$_3$), 2.241 (s, 12H; N-C*H*$_3$), 3.385 (s, 4H; N-C*H*$_2$), 7.237 (s, 1H; Aromatic), 7.352 (d, 2H; *J* =1.2 Hz, Aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.0, 45.4, 63.9, 94.0, 105.2, 122.9, 130.0, 131.3, 139.2.

Synthesis of 3,5-bis[(dimethylamino) methyl] phenylacetylene (27): Compound **26** (0.60 g, 2.1 mmol) was dissolved in THF (20 mL) followed by addition of tetrabutylammonium fluoride trihydrate (5.4 g, 21 mmol) and stirred for 2 h at room temperature. Volatiles were removed under reduced pressure and dissolved in ether (30 mL). Solution was extracted with sat. bicarbonate solution (4 × 50 mL). Organic layer was collected, dried over sodium sulfate and removed under reduced pressure, yielding brown viscous oil (0.2 g crude). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 12H; N-C*H*$_3$), 3.05 (s, 1H; C≡C*H*), 3.40 (s, 4H; N-C*H*$_2$), 7.37 (m, 3H; aromatic). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 45.3, 63.8, 76.8, 83.7, 121.8, 130.6, 131.4, 139.1.

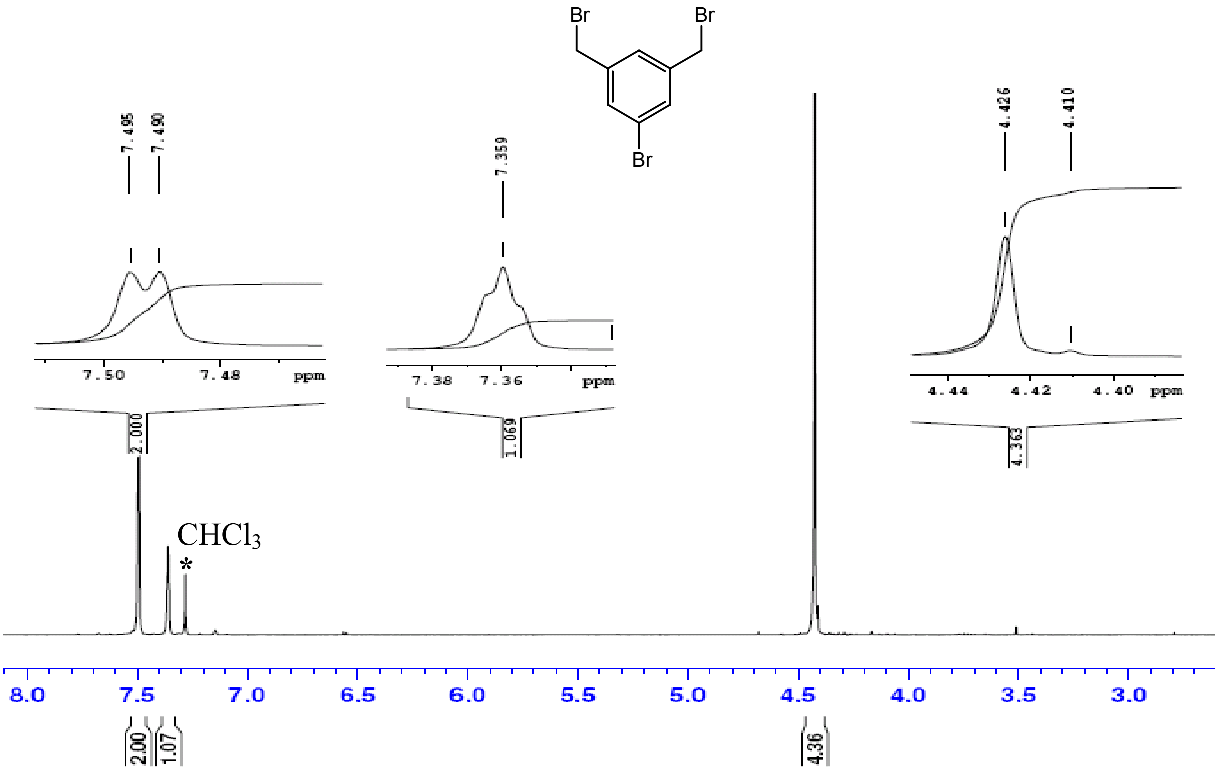


Figure S1. Proton NMR spectrum of **2** (300 MHz, $CDCl_3$)

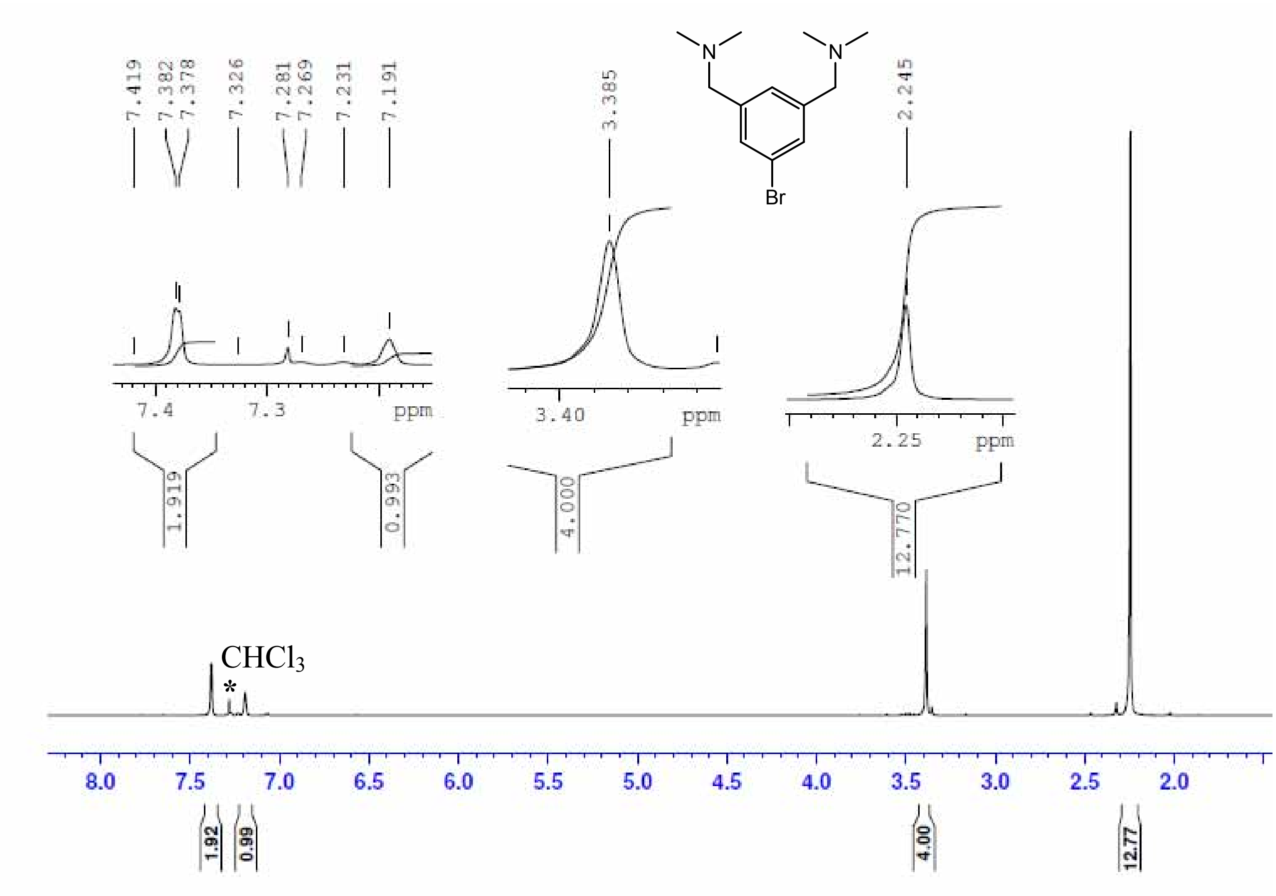


Figure S2. Proton NMR spectrum of **3** (300 MHz, $CDCl_3$)

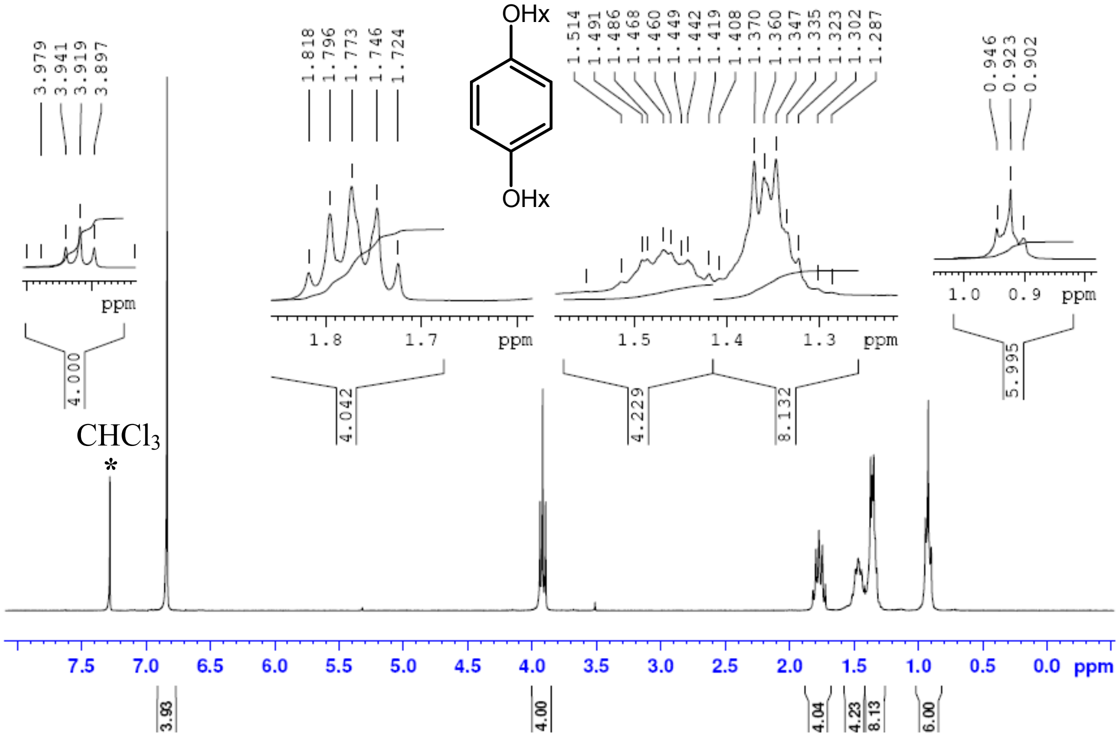


Figure S3. Proton NMR spectrum of **5** (300 MHz, $CDCl_3$)

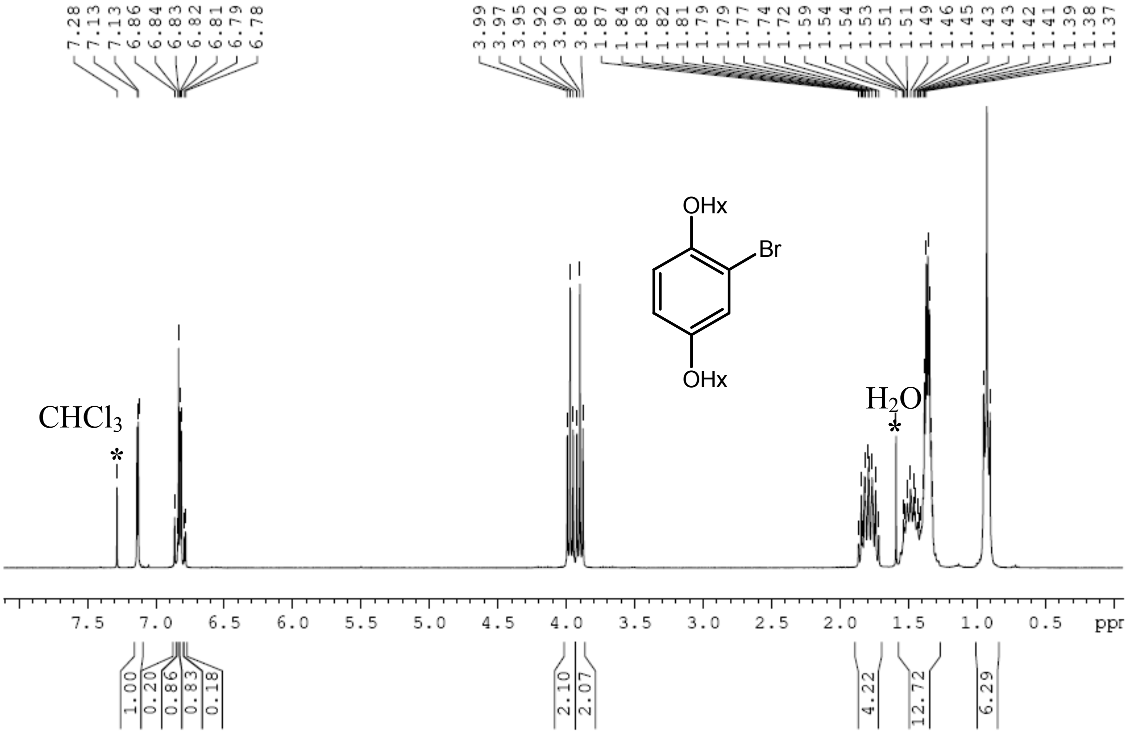


Figure S4. Proton NMR spectrum of **6** (300 MHz, $CDCl_3$)

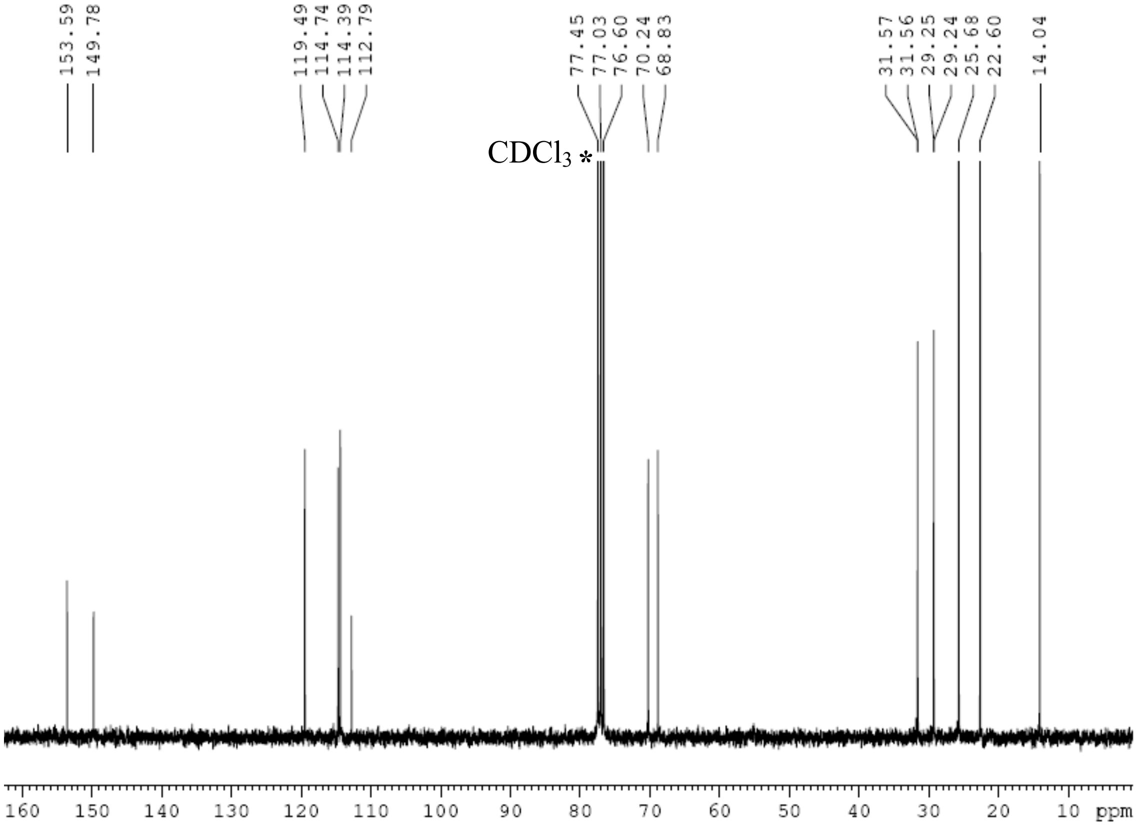


Figure S5. Carbon-13 NMR spectrum of **6** (75 MHz, $CDCl_3$)

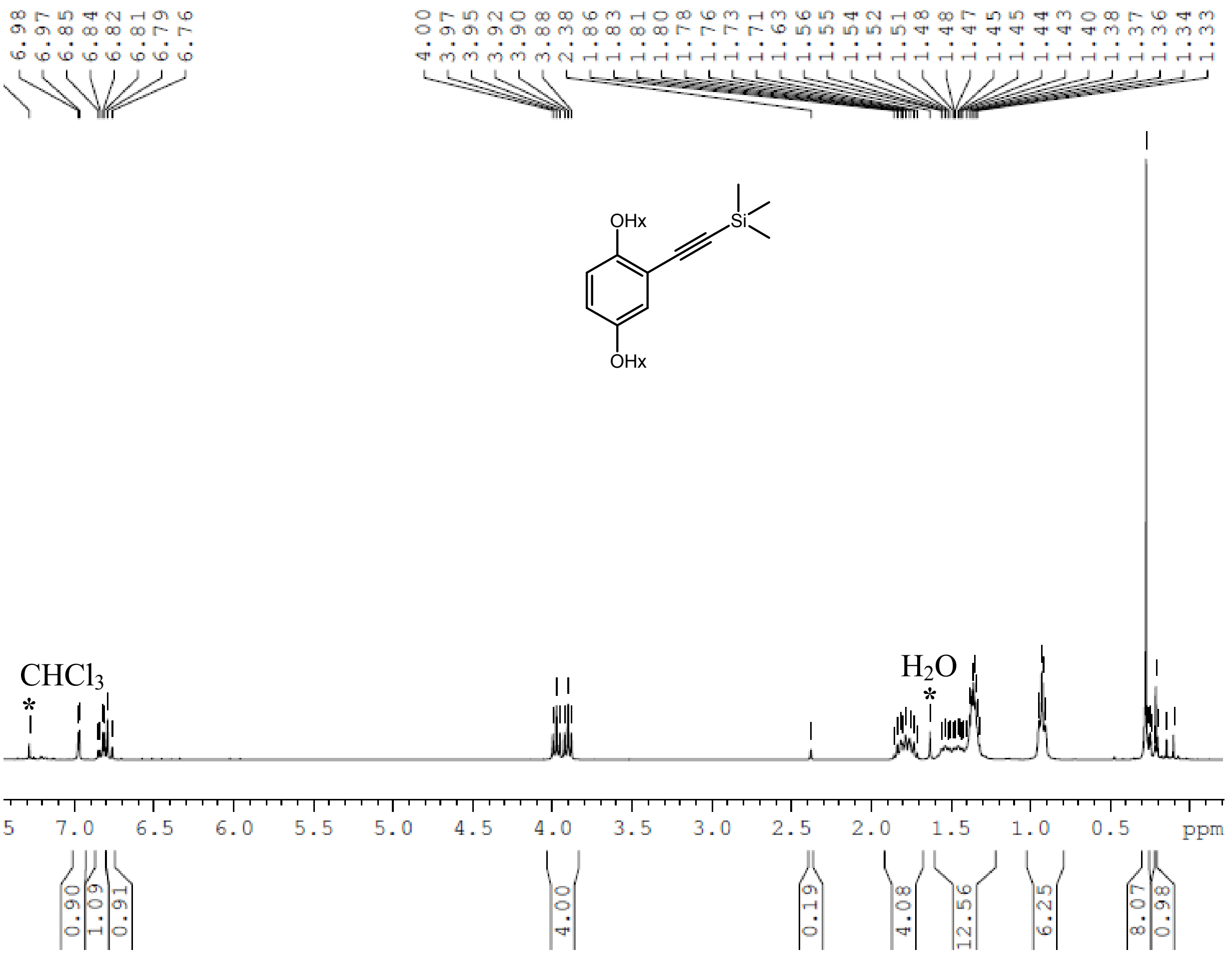


Figure S6. Proton NMR spectrum of **7** (300 MHz, $CDCl_3$)

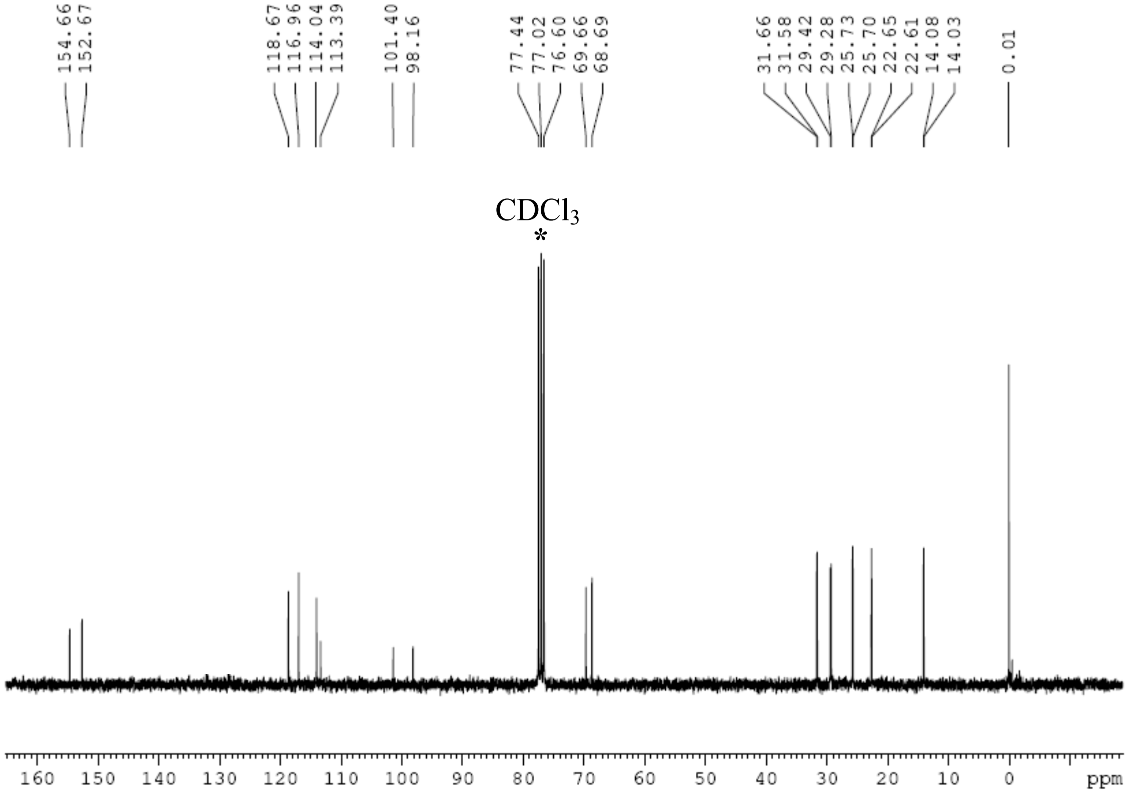


Figure S7. Carbon-13 NMR spectrum of **7** (75 MHz, $CDCl_3$)

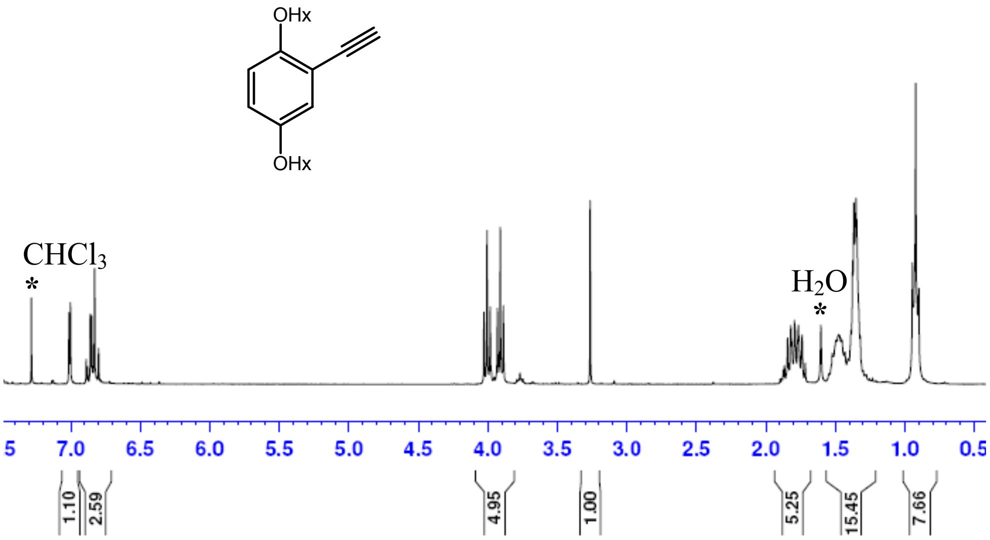


Figure S8. Proton NMR spectrum of **8** (300 MHz, $CDCl_3$)

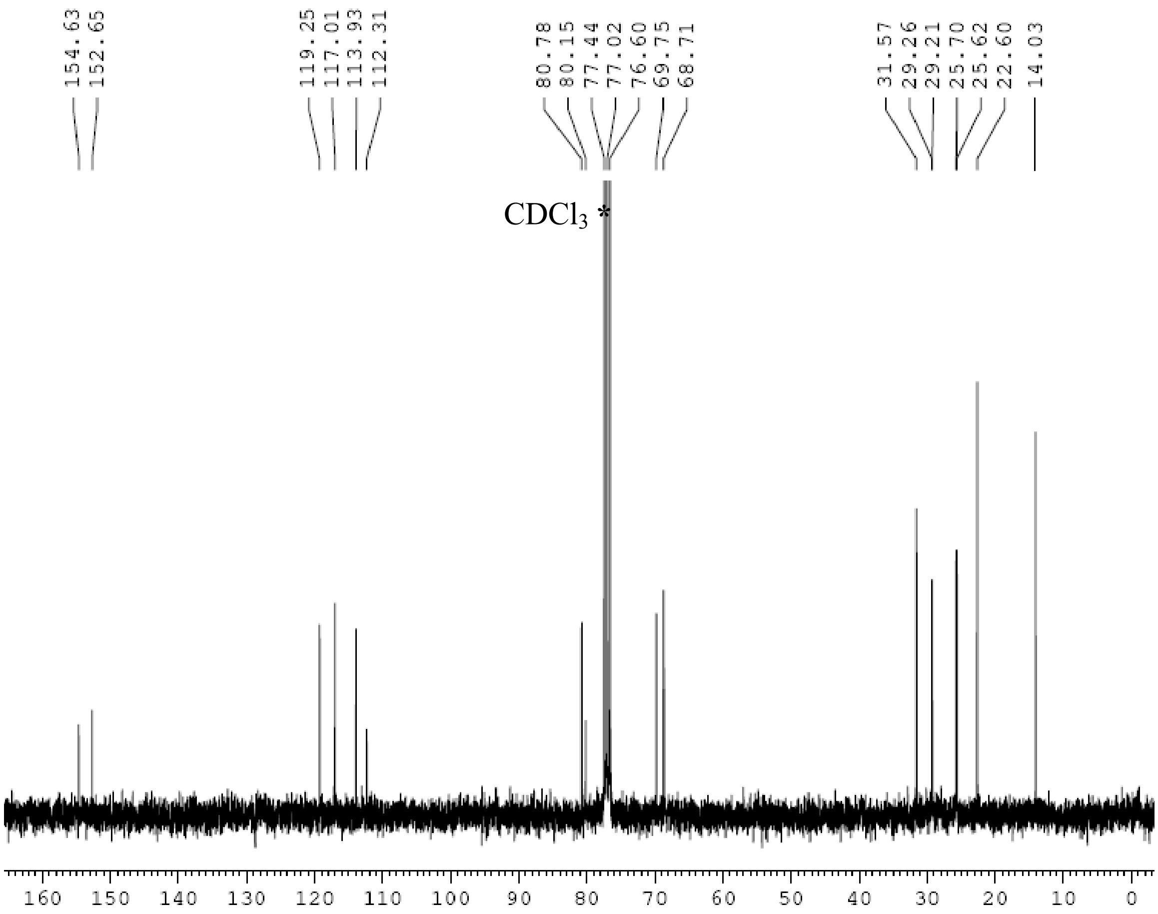


Figure S9. Carbon-13 NMR spectrum of **8** (75 MHz, CDCl$_3$)

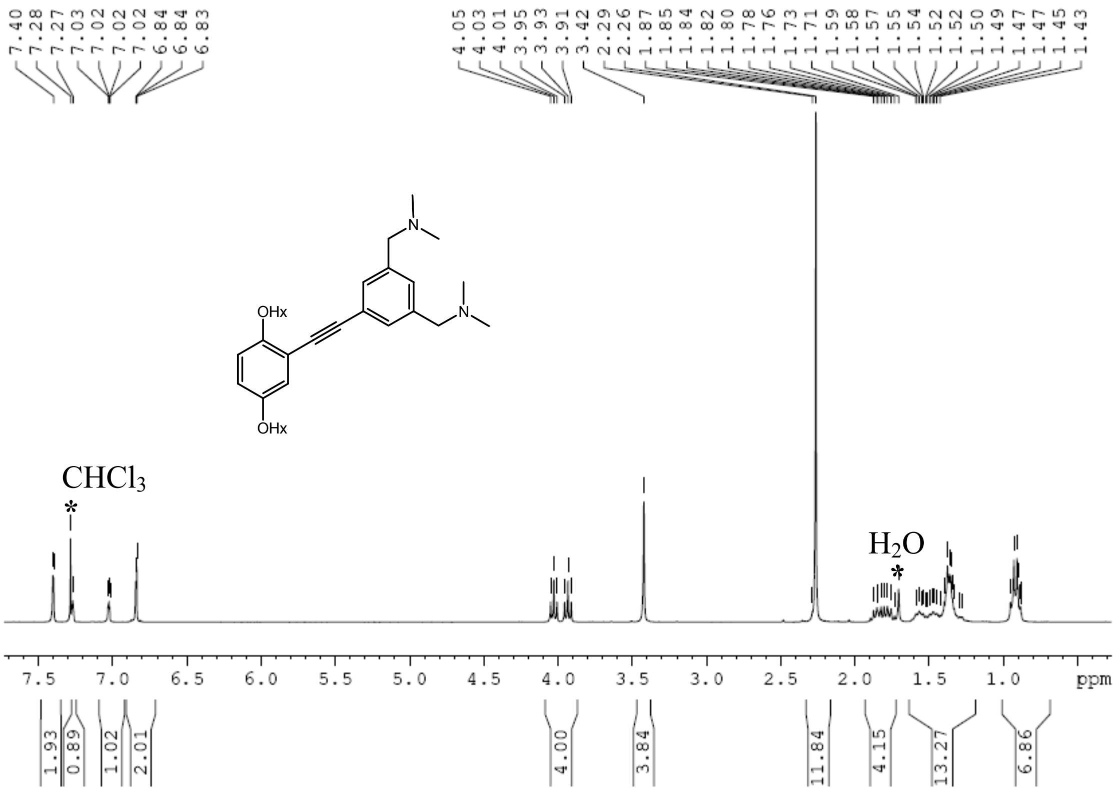
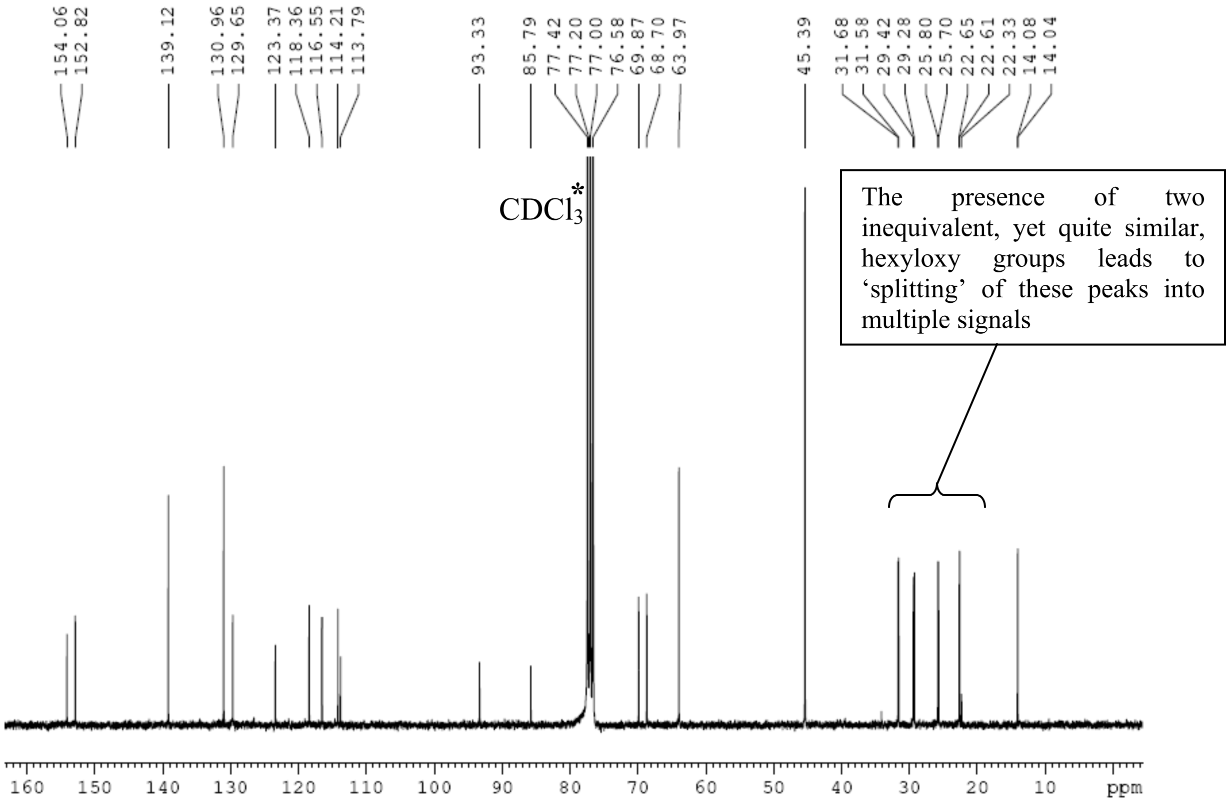


Figure S10. Proton NMR spectrum of **A** (300 MHz, $CDCl_3$)



The presence of two inequivalent, yet quite similar, hexyloxy groups leads to ‘splitting’ of these peaks into multiple signals

Figure S11. Carbon-13 NMR spectrum of **A** (75 MHz, $CDCl_3$)

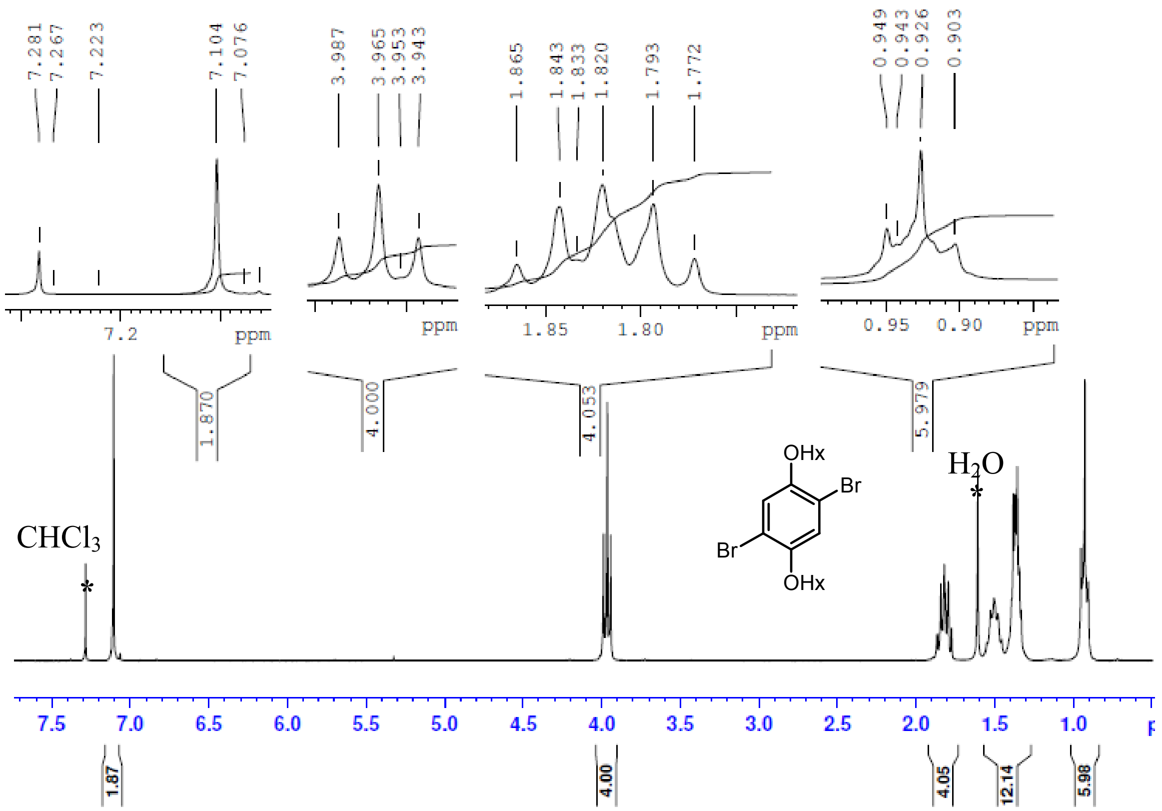


Figure S12. Proton NMR spectrum of **9** (300 MHz, $CDCl_3$)

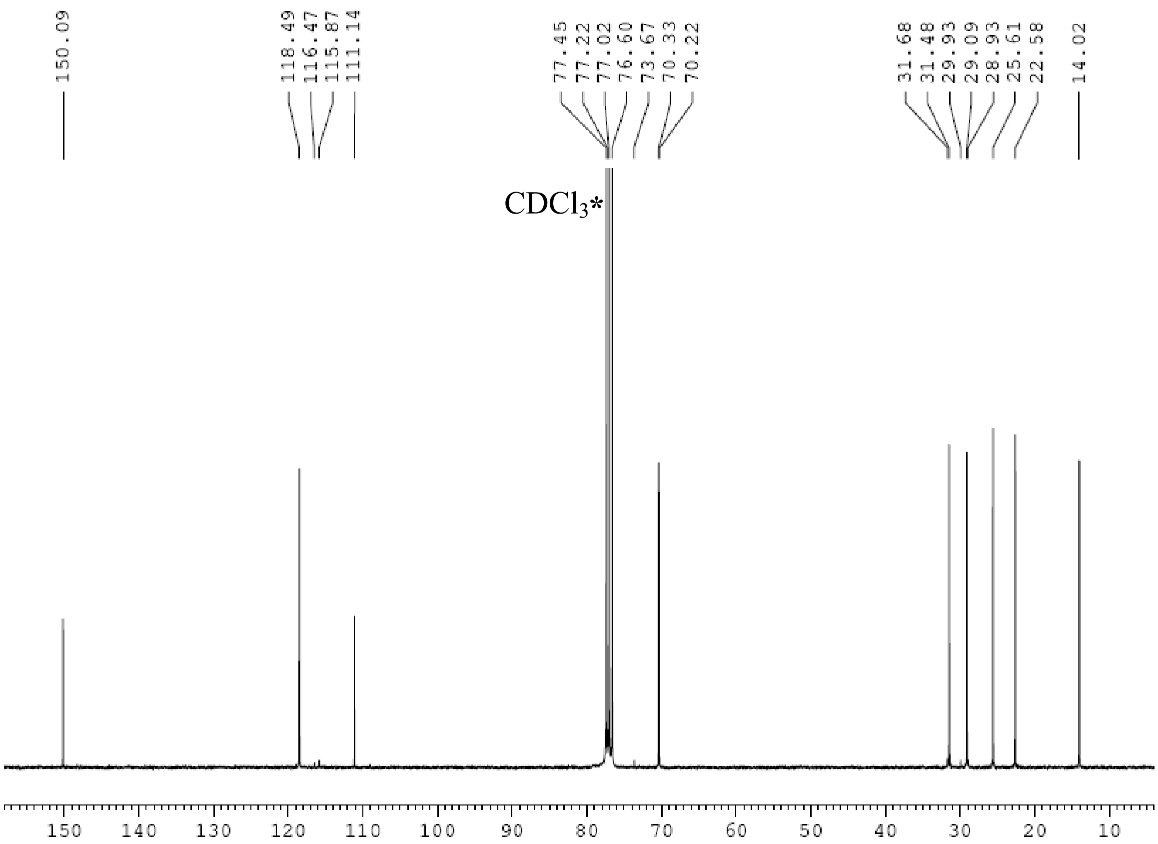
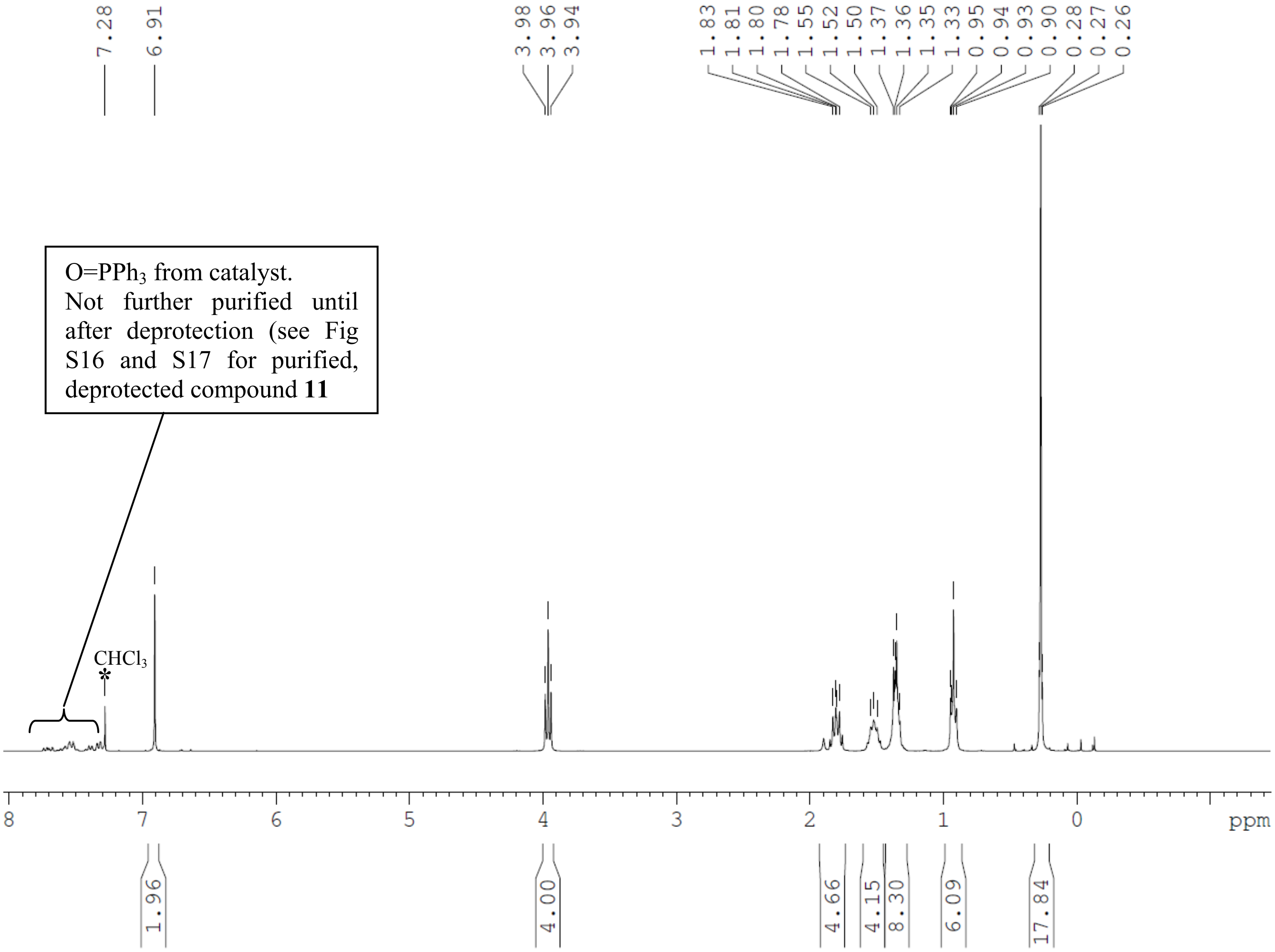


Figure S13. Carbon-13 NMR spectrum of **9** (75 MHz, $CDCl_3$)



O=PPh$_3$ from catalyst.
Not further purified until after deprotection (see Fig S16 and S17 for purified, deprotected compound **11**

Figure S14. Proton NMR spectrum of **10** (300 MHz, CDCl$_3$)

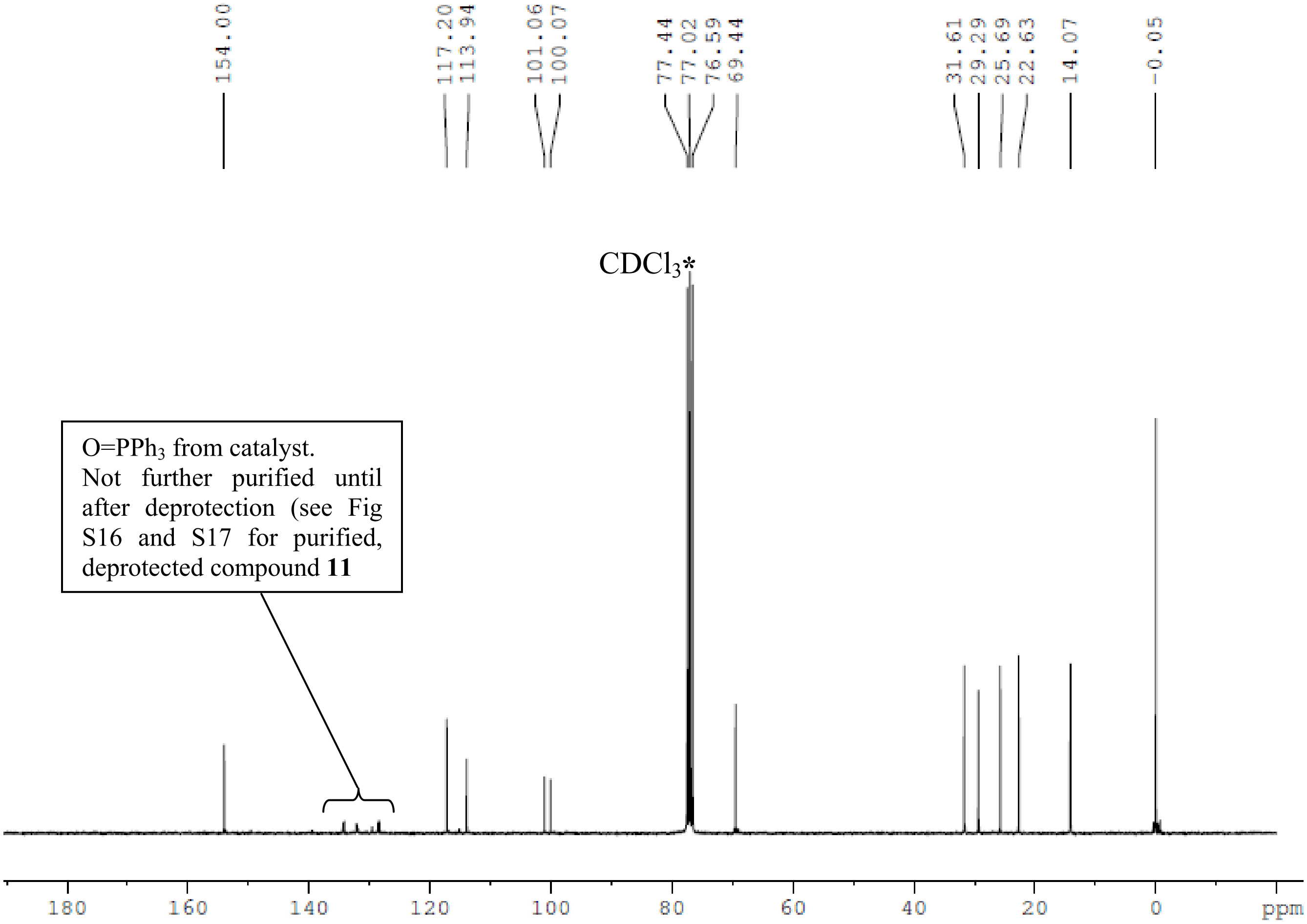


Figure S15. Carbon-13 NMR spectrum of **10** (75 MHz, $CDCl_3$)

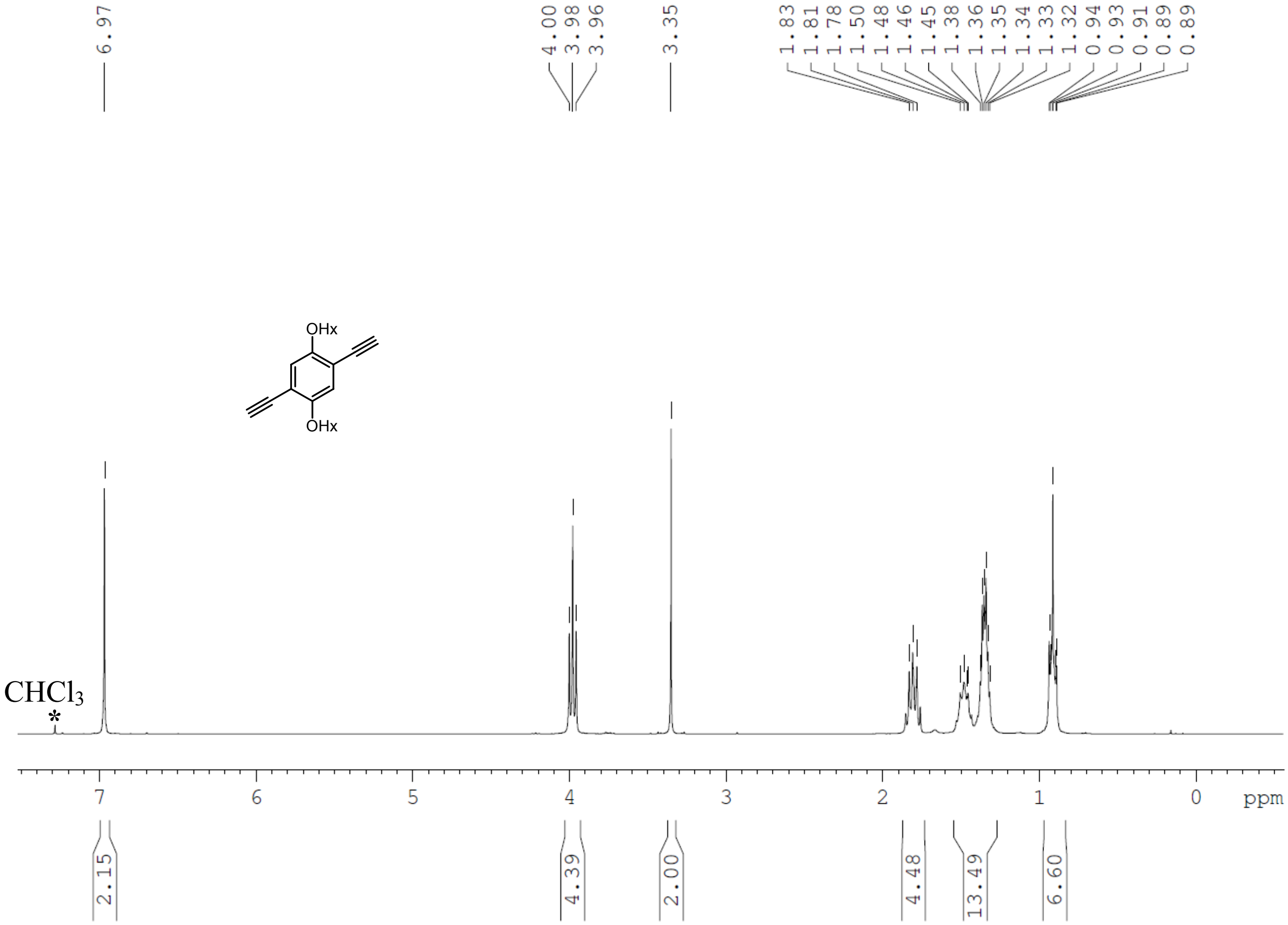


Figure S16. Proton NMR spectrum of **11** (300 MHz, $CDCl_3$)

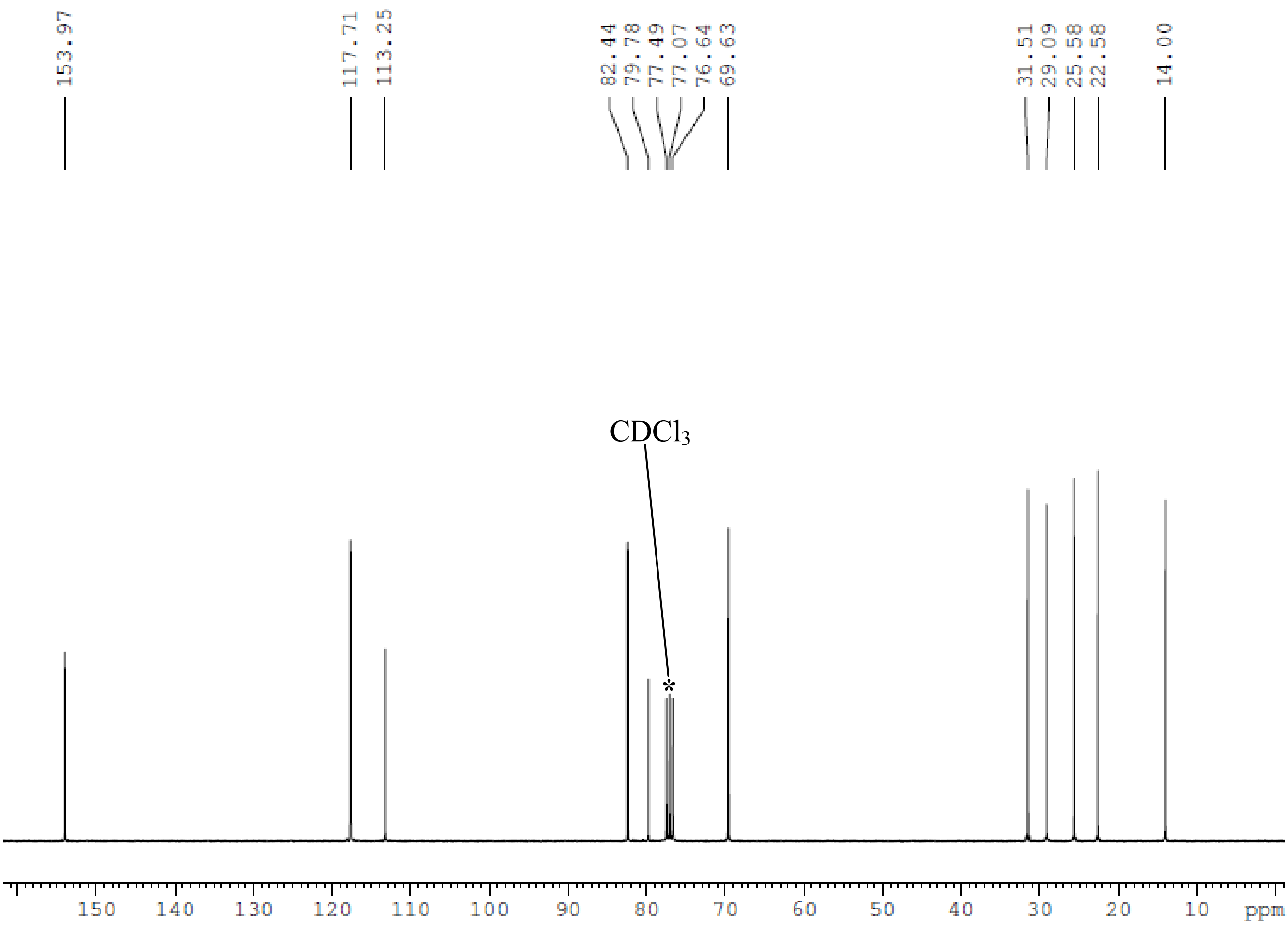


Figure S17. Carbon-13 NMR spectrum of **11** (75 MHz, $CDCl_3$)

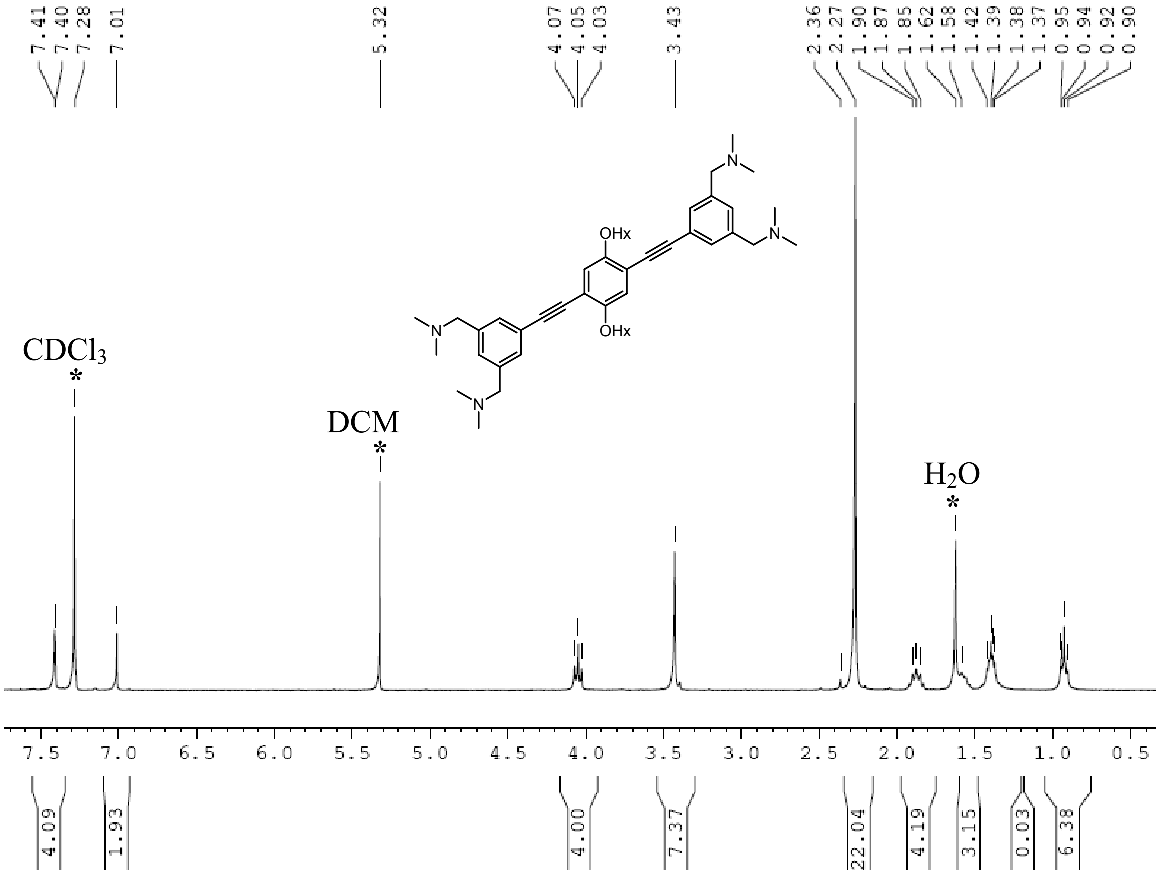


Figure S18. Proton NMR spectrum of **B** (300 MHz, $CDCl_3$)

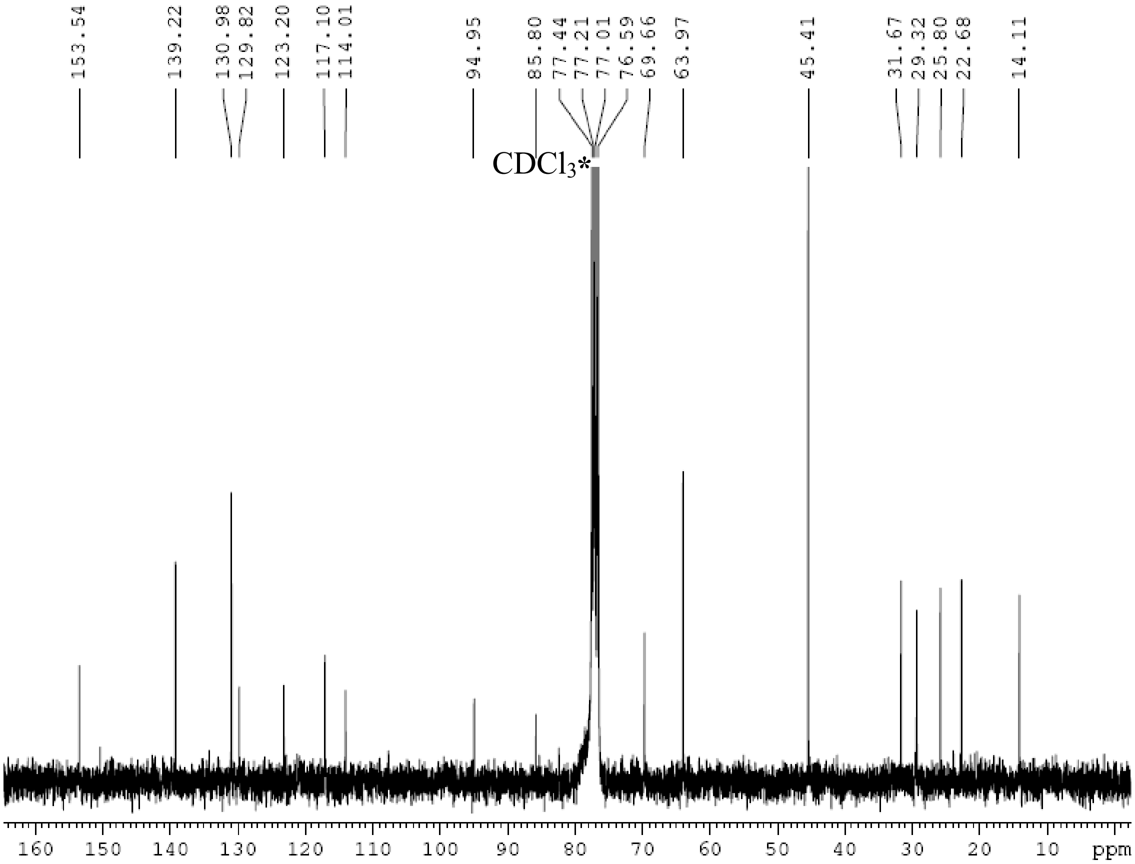


Figure S19. Carbon-13 NMR spectrum of **B** (75 MHz, $CDCl_3$)

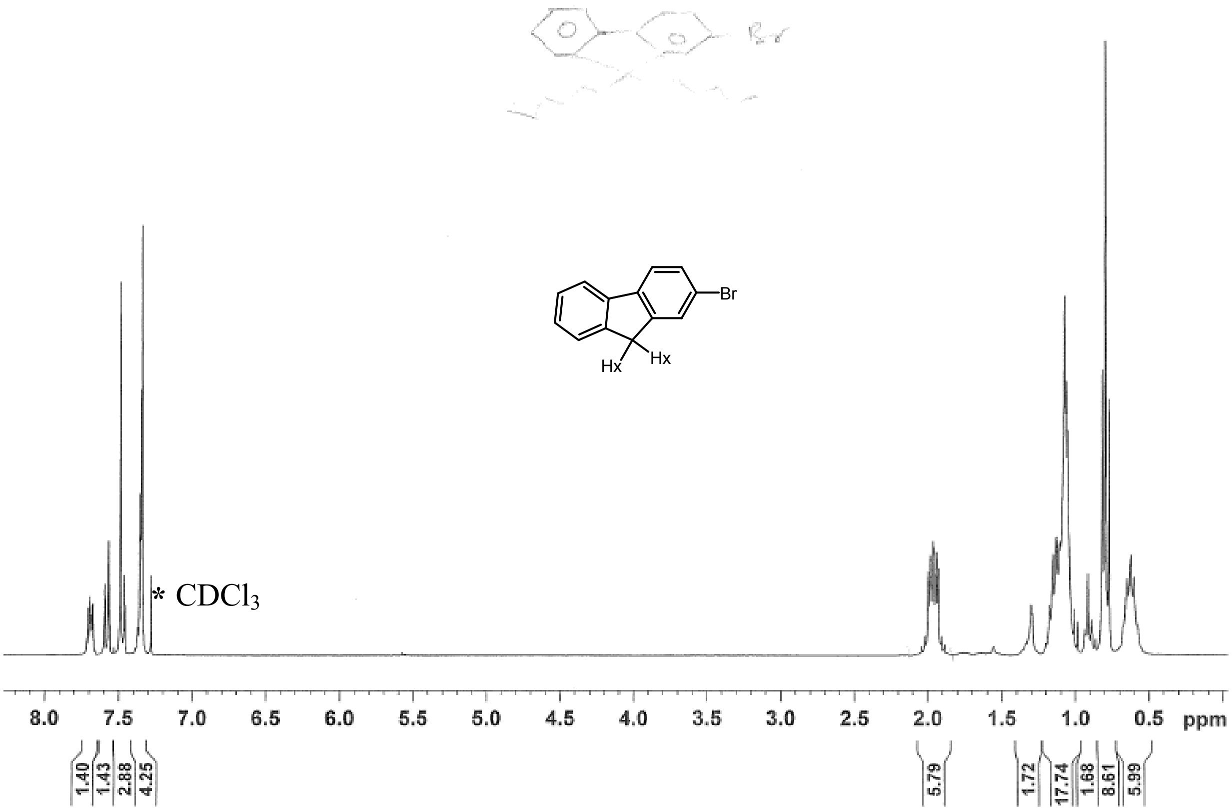


Figure S20. Proton NMR spectrum of **13** (300 MHz, $CDCl_3$)

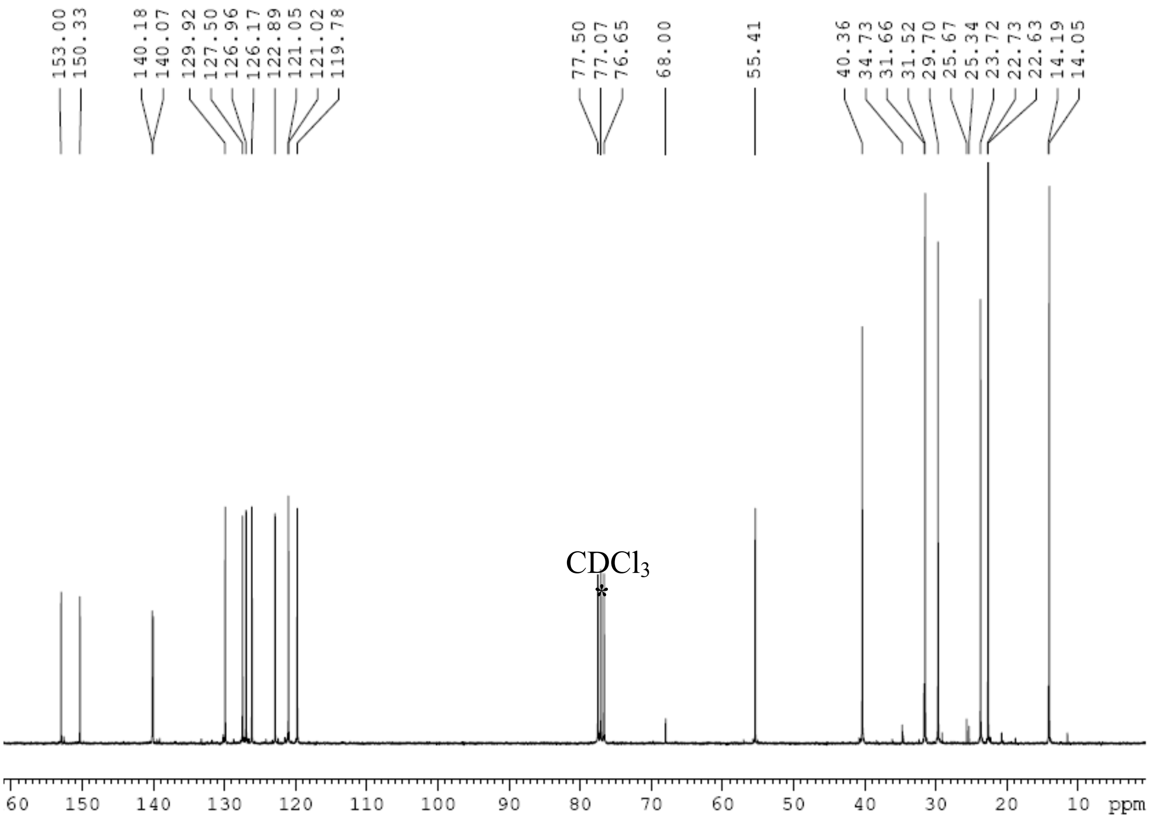


Figure S21. Carbon-13 NMR spectrum of **13** (75 MHz, $CDCl_3$)

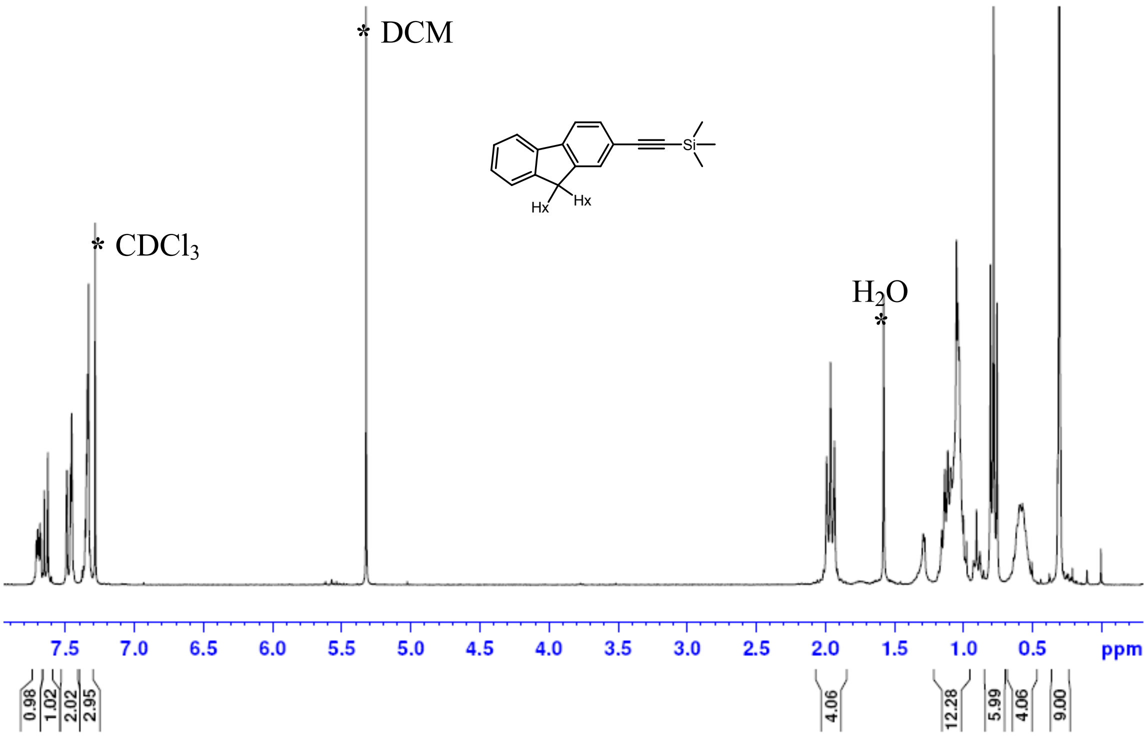


Figure S22. Proton NMR spectrum of **14** (300 MHz, $CDCl_3$)

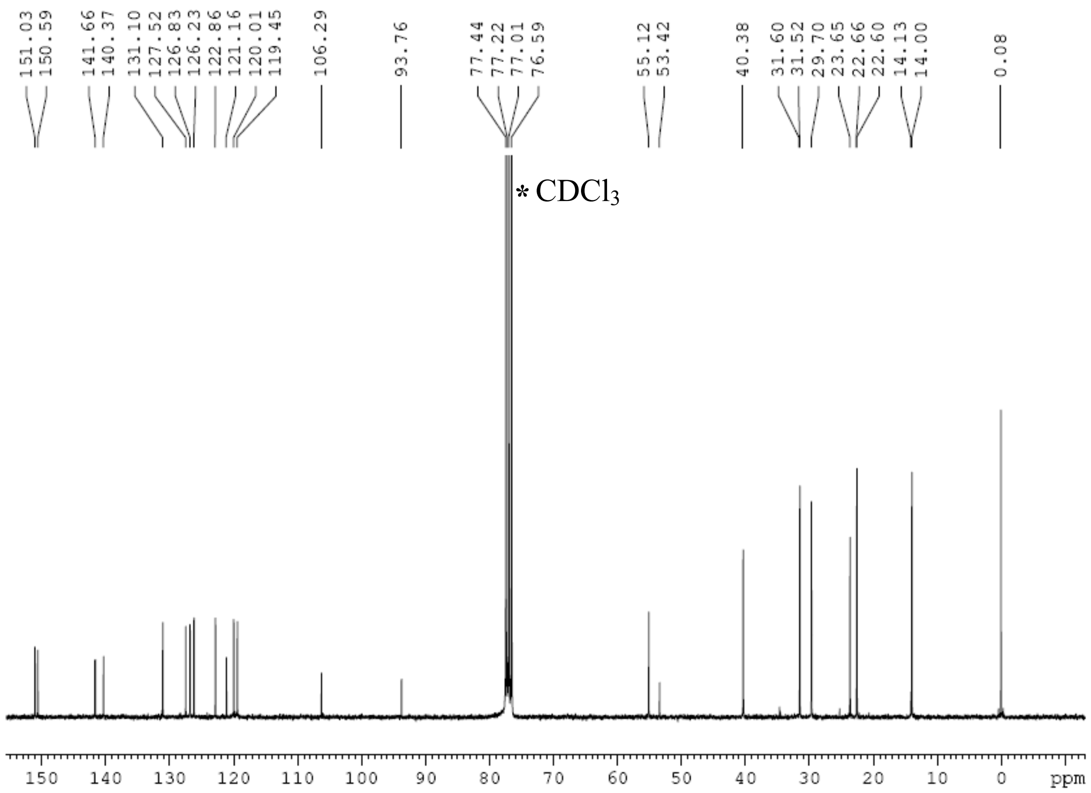


Figure S23. Carbon-13 NMR spectrum of **14** (75 MHz, $CDCl_3$)

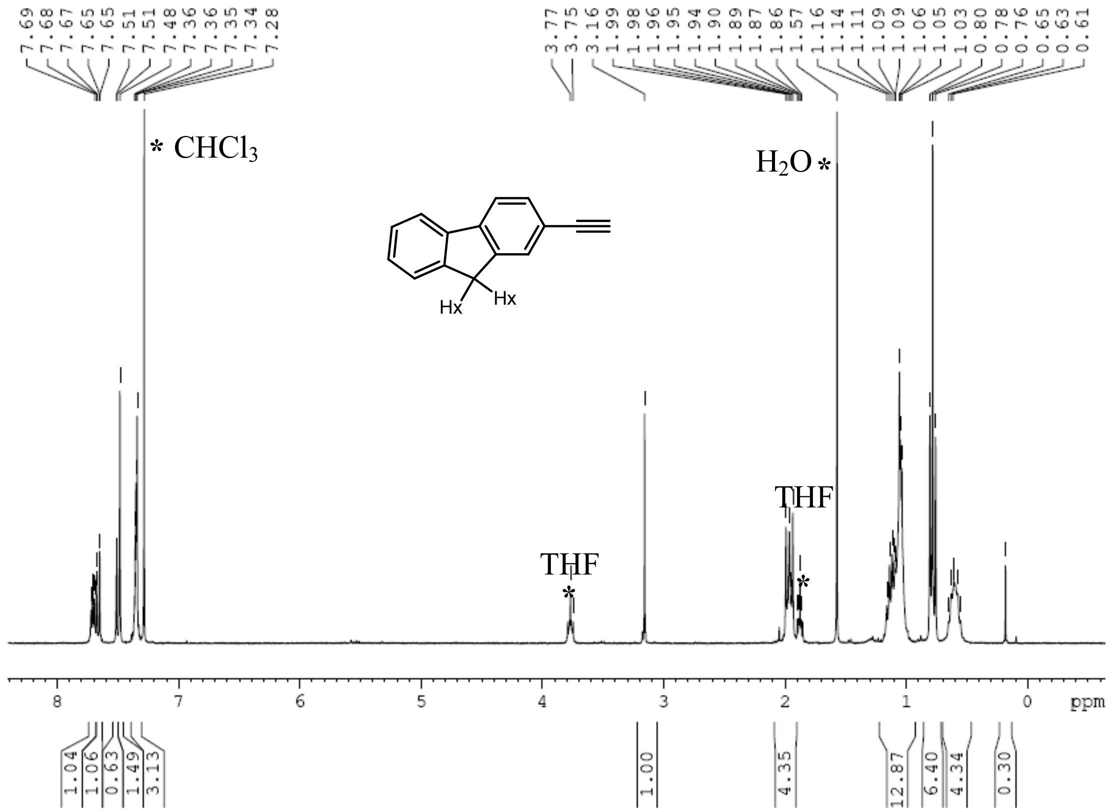


Figure S24. Proton NMR spectrum of **15** (300 MHz, $CDCl_3$)

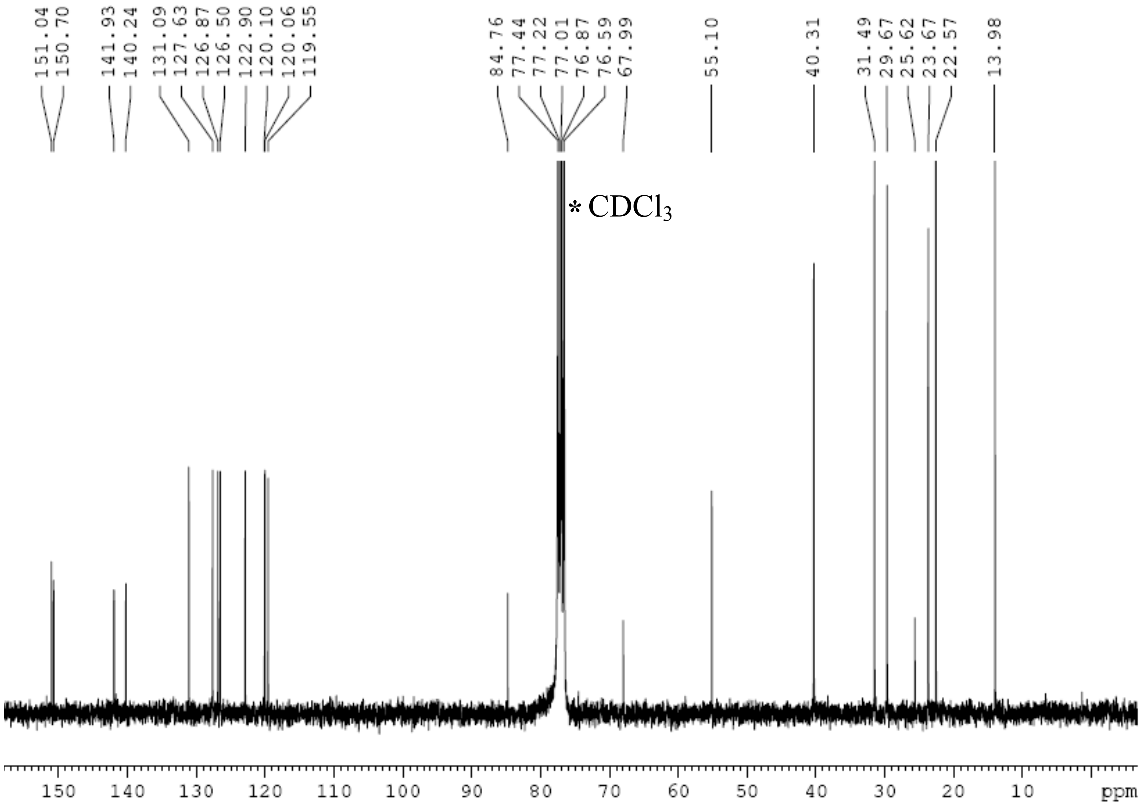


Figure S25. Carbon-13 NMR spectrum of **15** (75 MHz, $CDCl_3$)

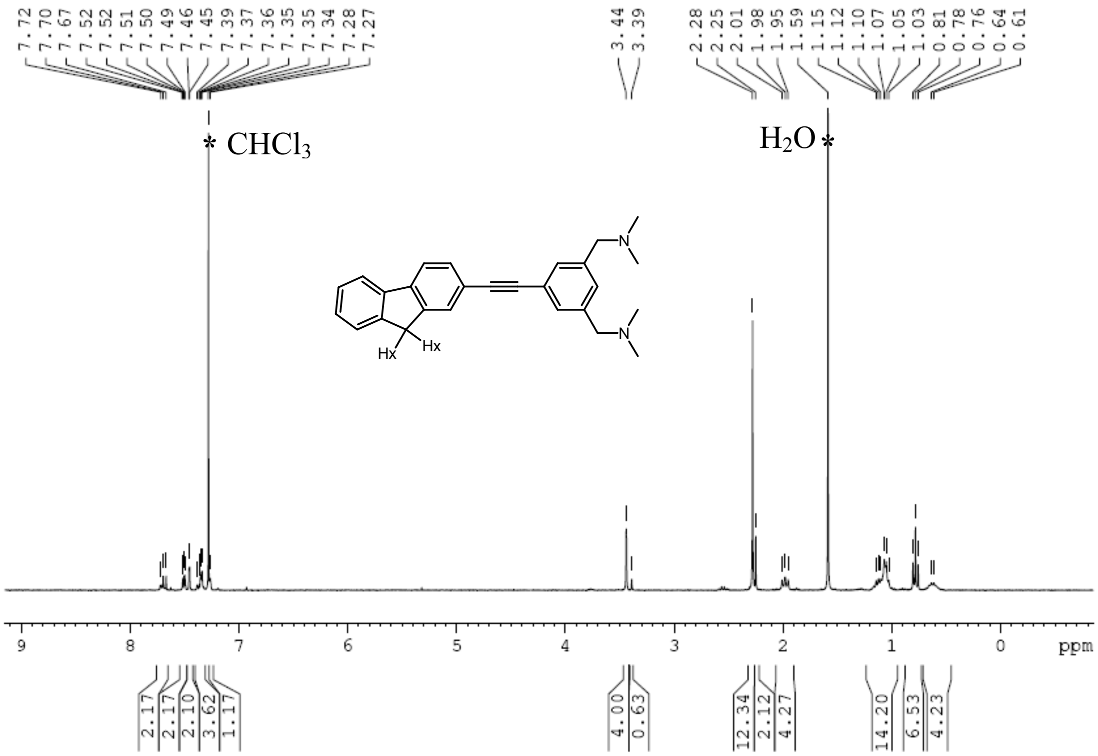


Figure S26. Proton NMR spectrum of **C** (300 MHz, $CDCl_3$)

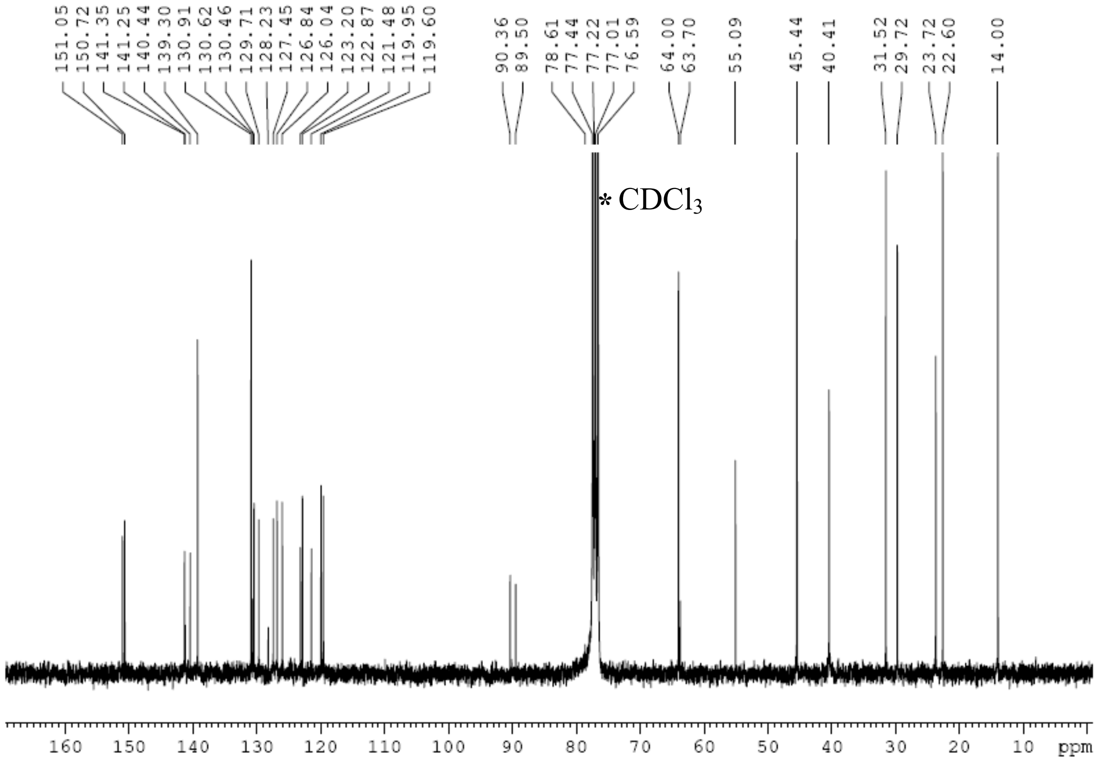


Figure S27. Carbon-13 NMR spectrum of **C** (75 MHz, $CDCl_3$)

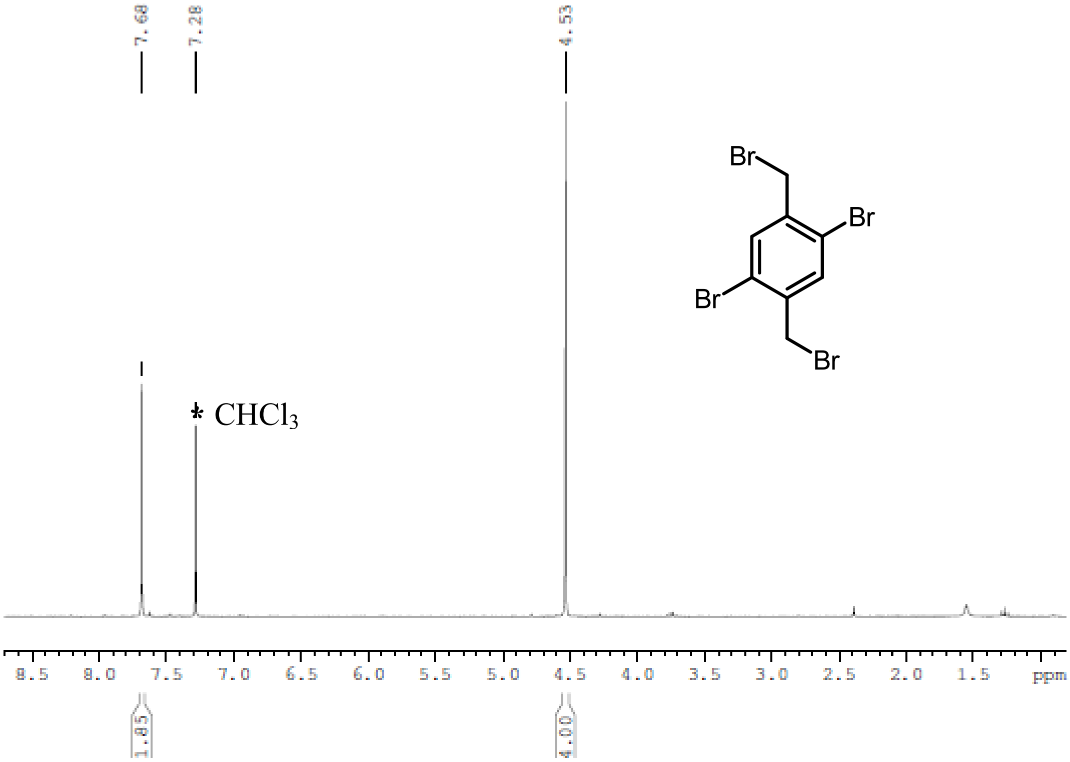


Figure S28. Proton NMR of compound **17** (300 MHz, $CDCl_3$)

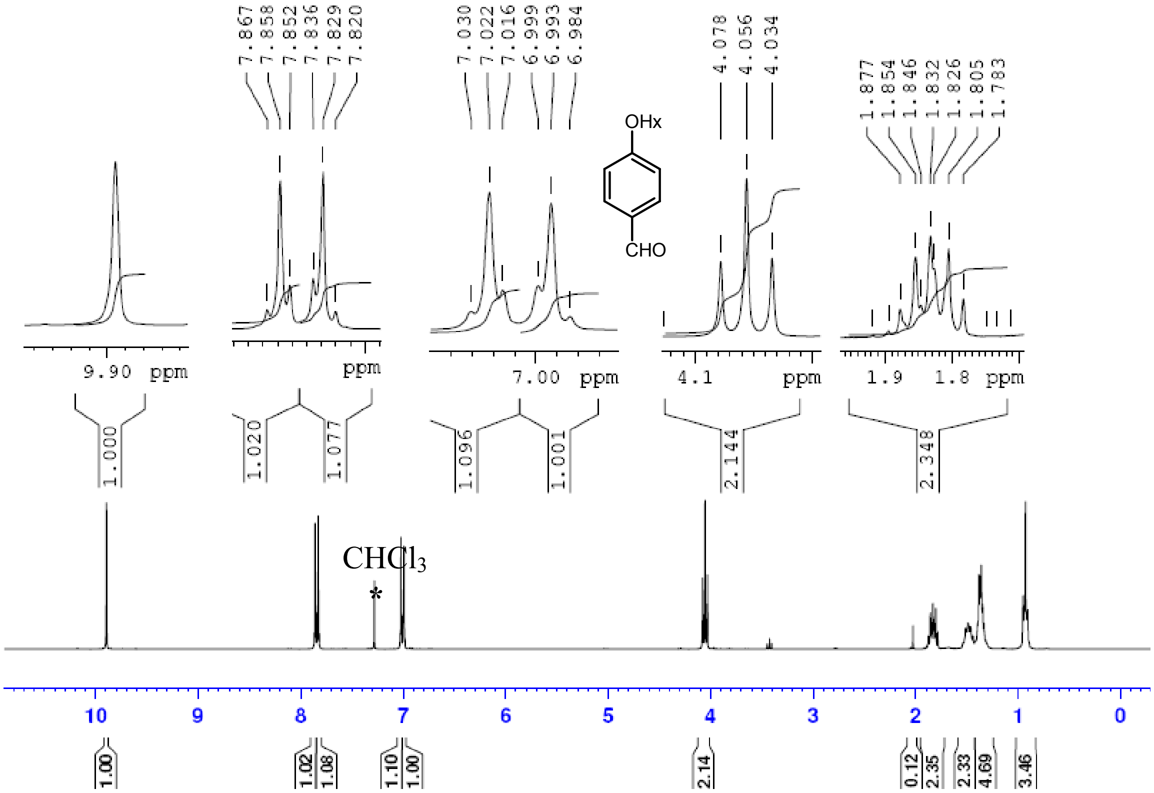


Figure S29. Proton NMR of compound **19** (300 MHz, $CDCl_3$)

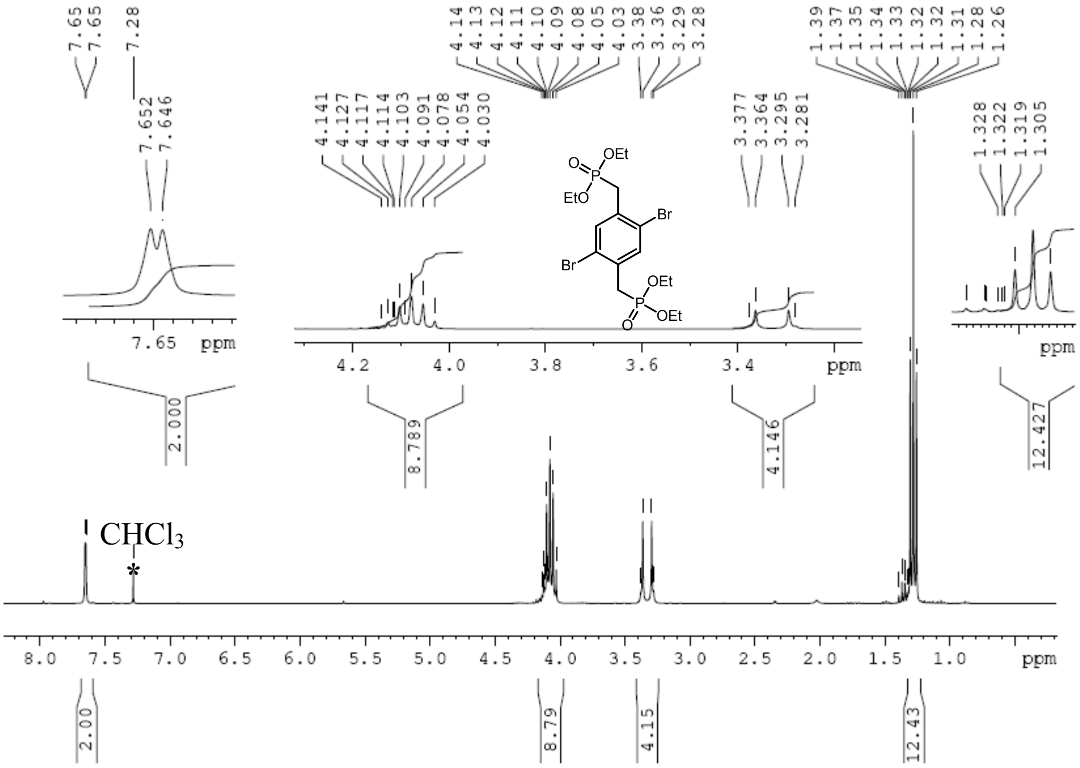
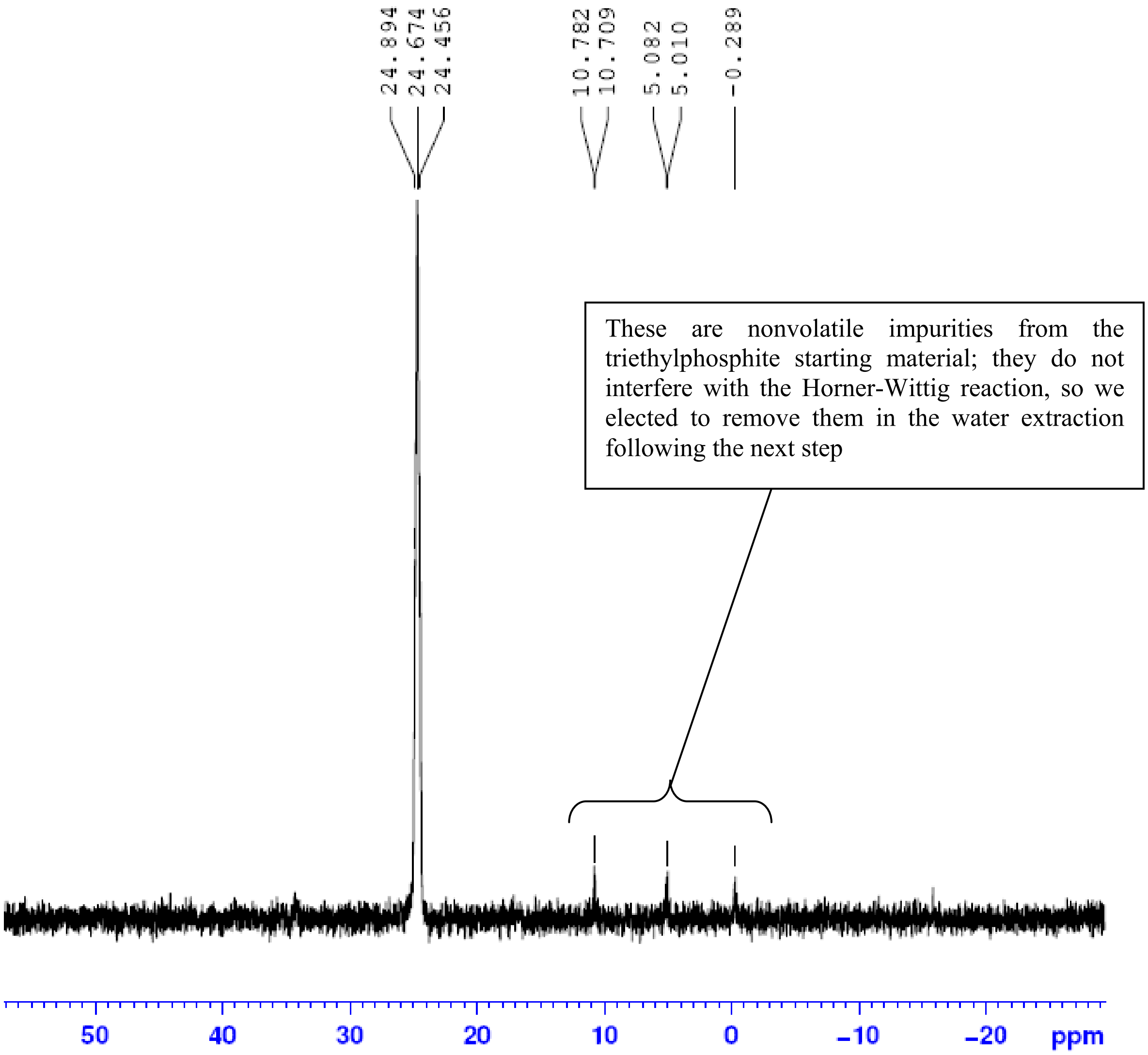


Figure S30. Proton NMR of compound **20** (300 MHz, $CDCl_3$)



These are nonvolatile impurities from the triethylphosphite starting material; they do not interfere with the Horner-Wittig reaction, so we elected to remove them in the water extraction following the next step

Figure S31. Phosphorus-31 NMR of compound **20** (121 MHz, $CDCl_3$)

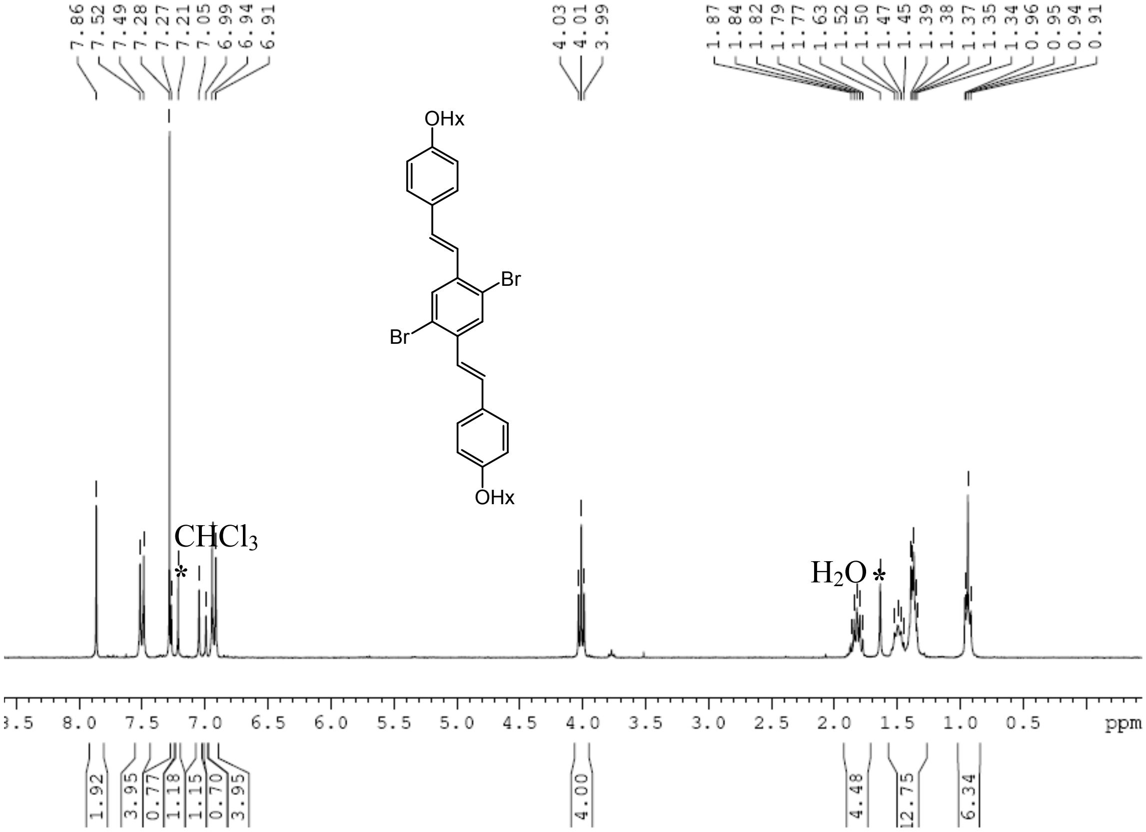


Figure S32. Proton NMR of compound **21** (300 MHz, $CDCl_3$)

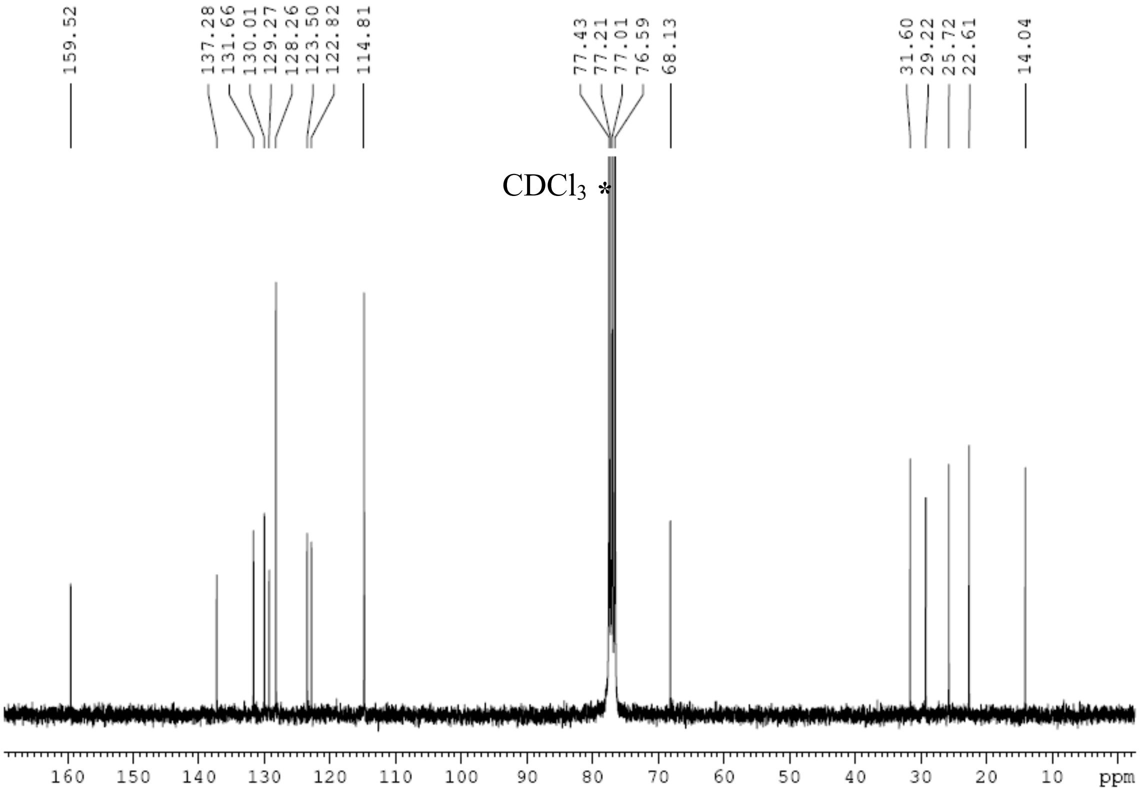


Figure S33. Carbon-13 NMR spectrum of **21** (75 MHz, $CDCl_3$)

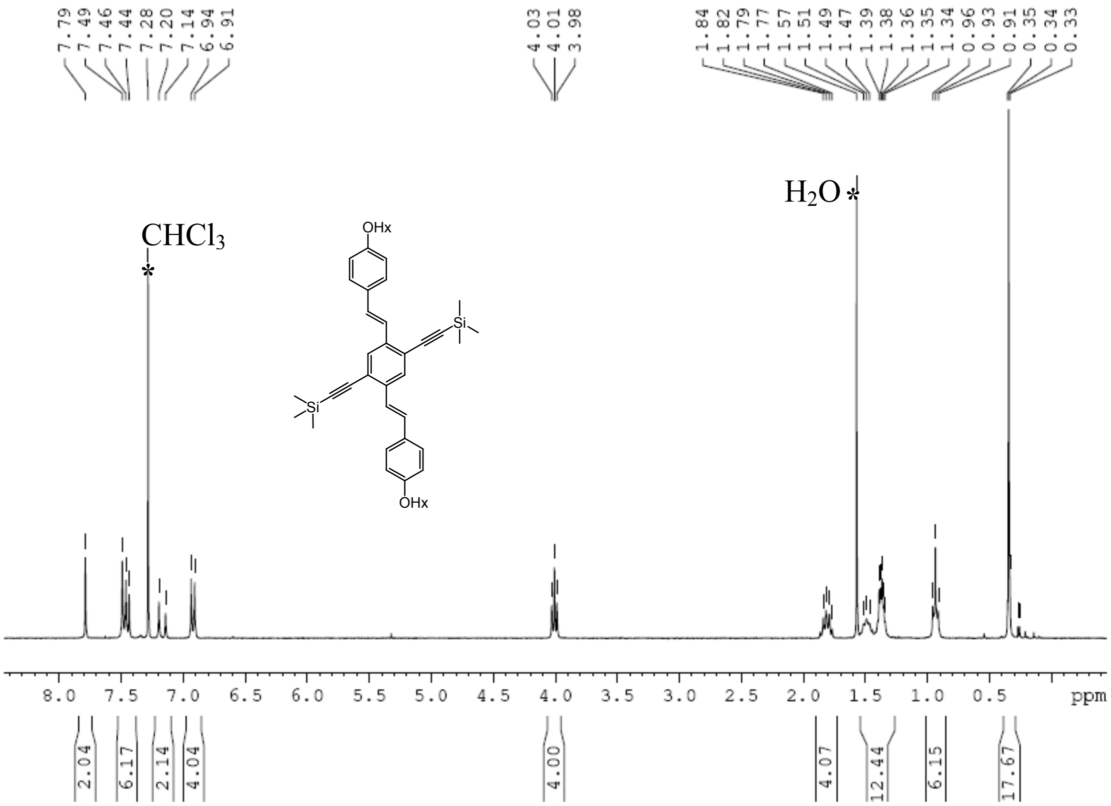


Figure S34. Proton NMR of compound **22** (300 MHz, $CDCl_3$)

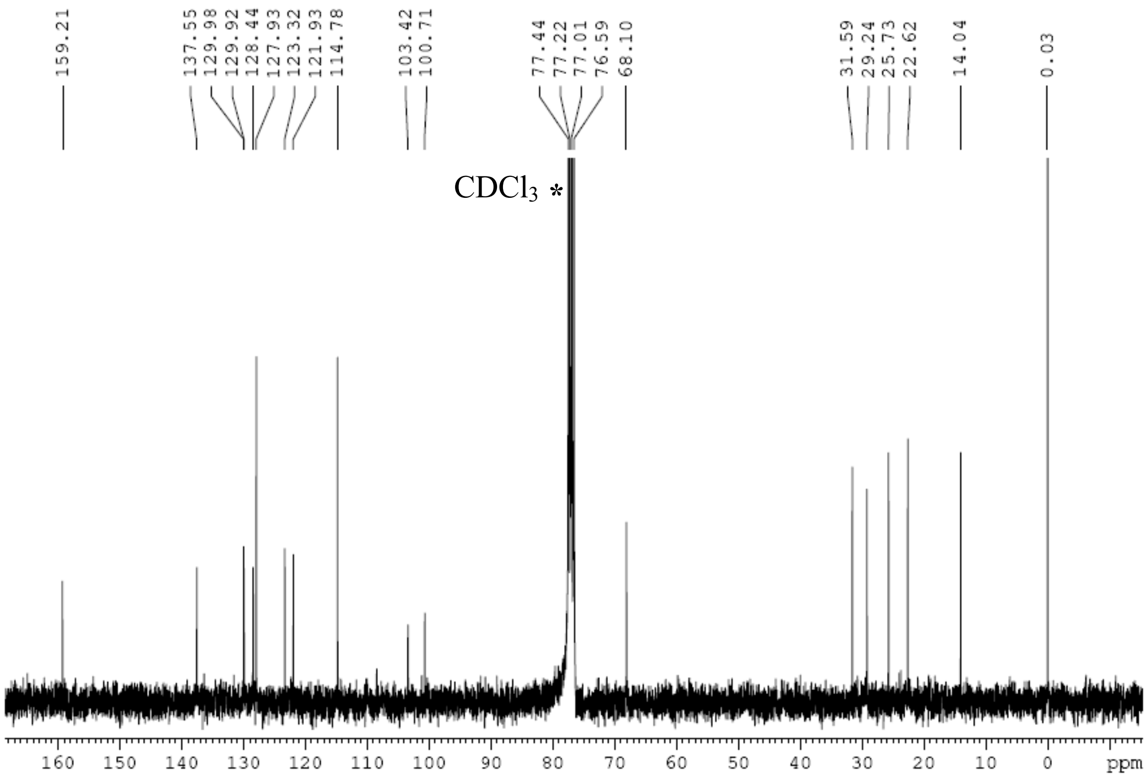


Figure S35. Carbon-13 NMR spectrum of **22** (75 MHz, $CDCl_3$)

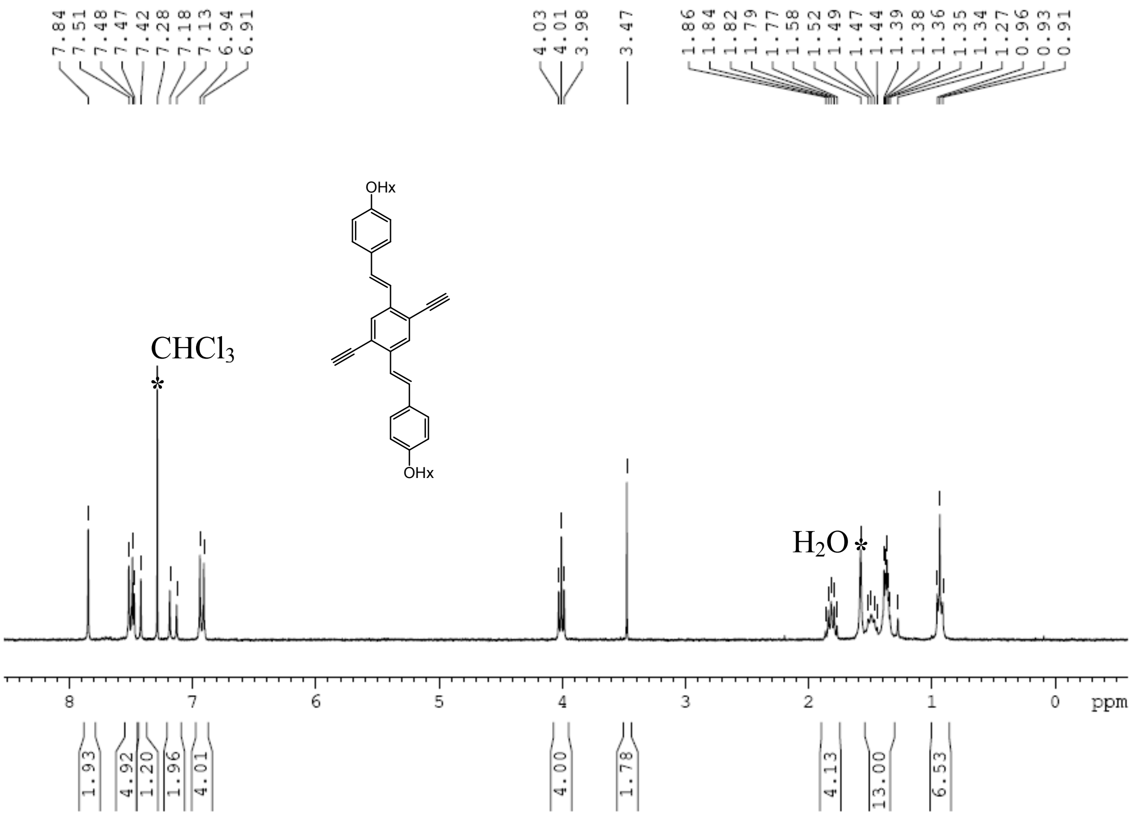


Figure S36. Proton NMR of compound **23** (300 MHz, $CDCl_3$)

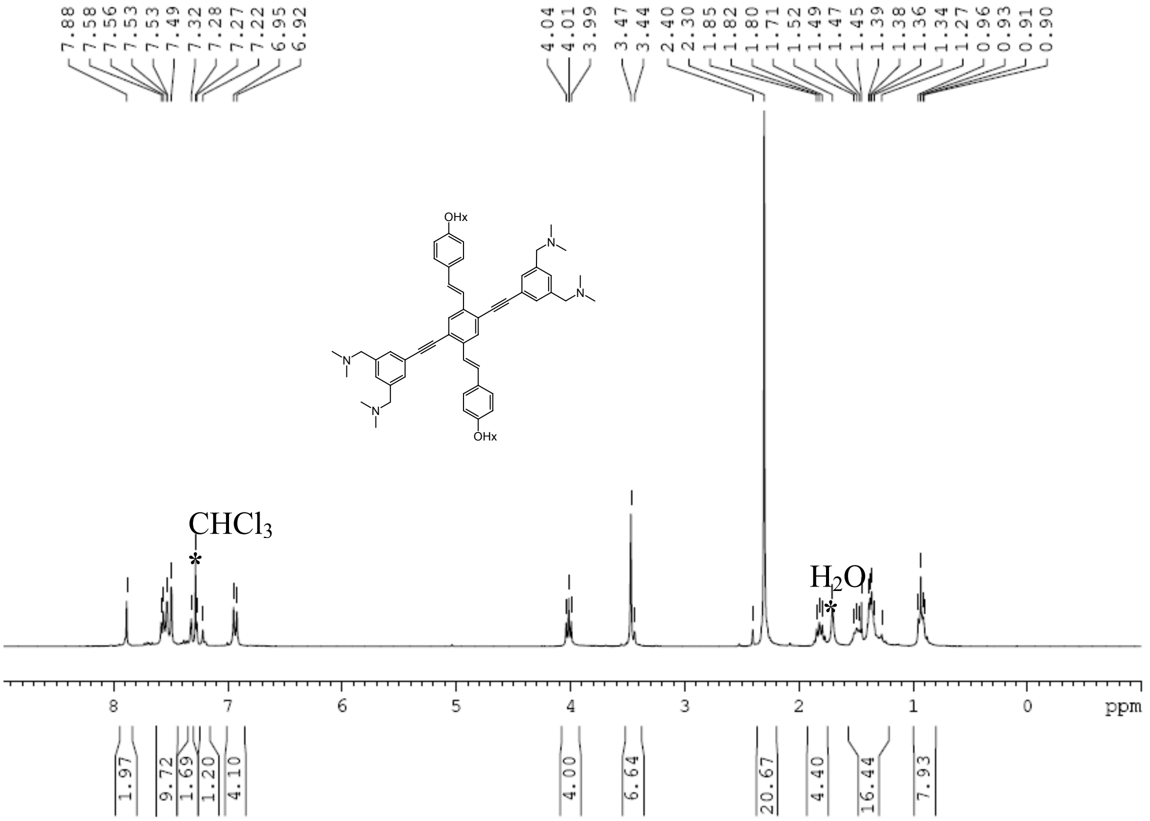


Figure S37. Proton NMR of compound **D** (300 MHz, $CDCl_3$)

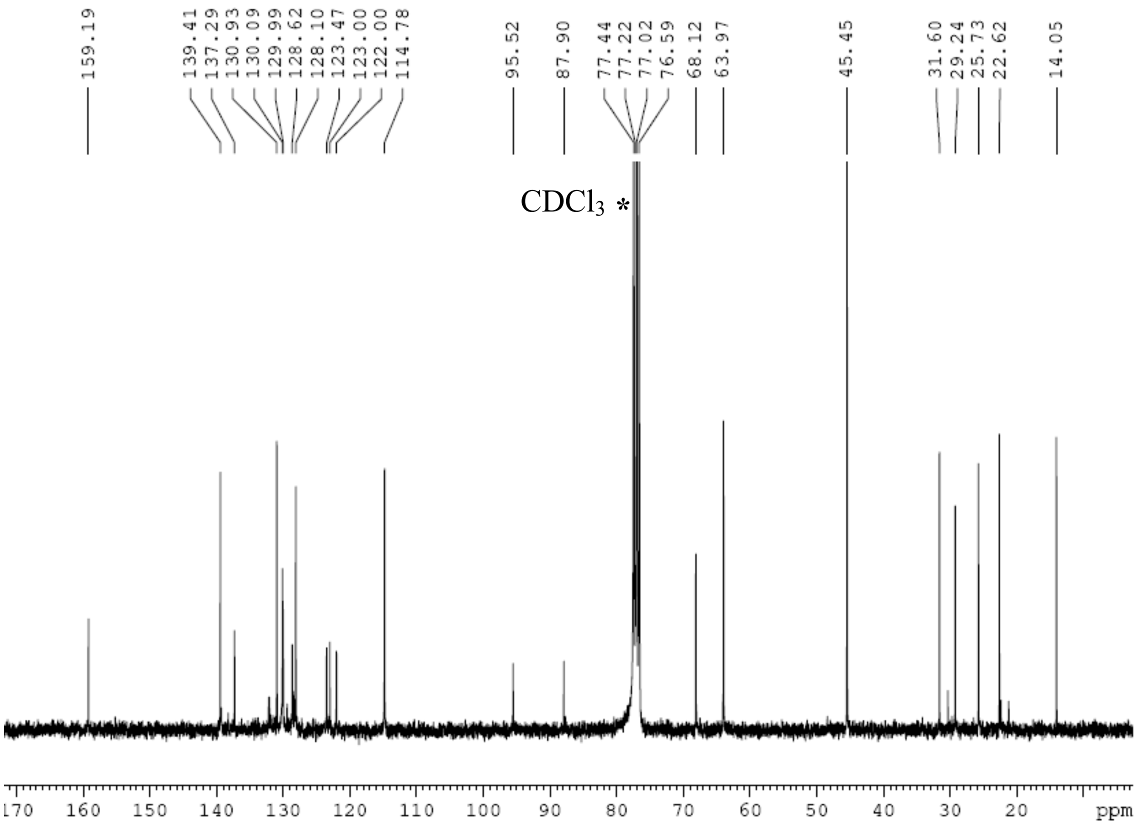


Figure S38. Carbon-13 NMR spectrum of **D** (75 MHz, $CDCl_3$)

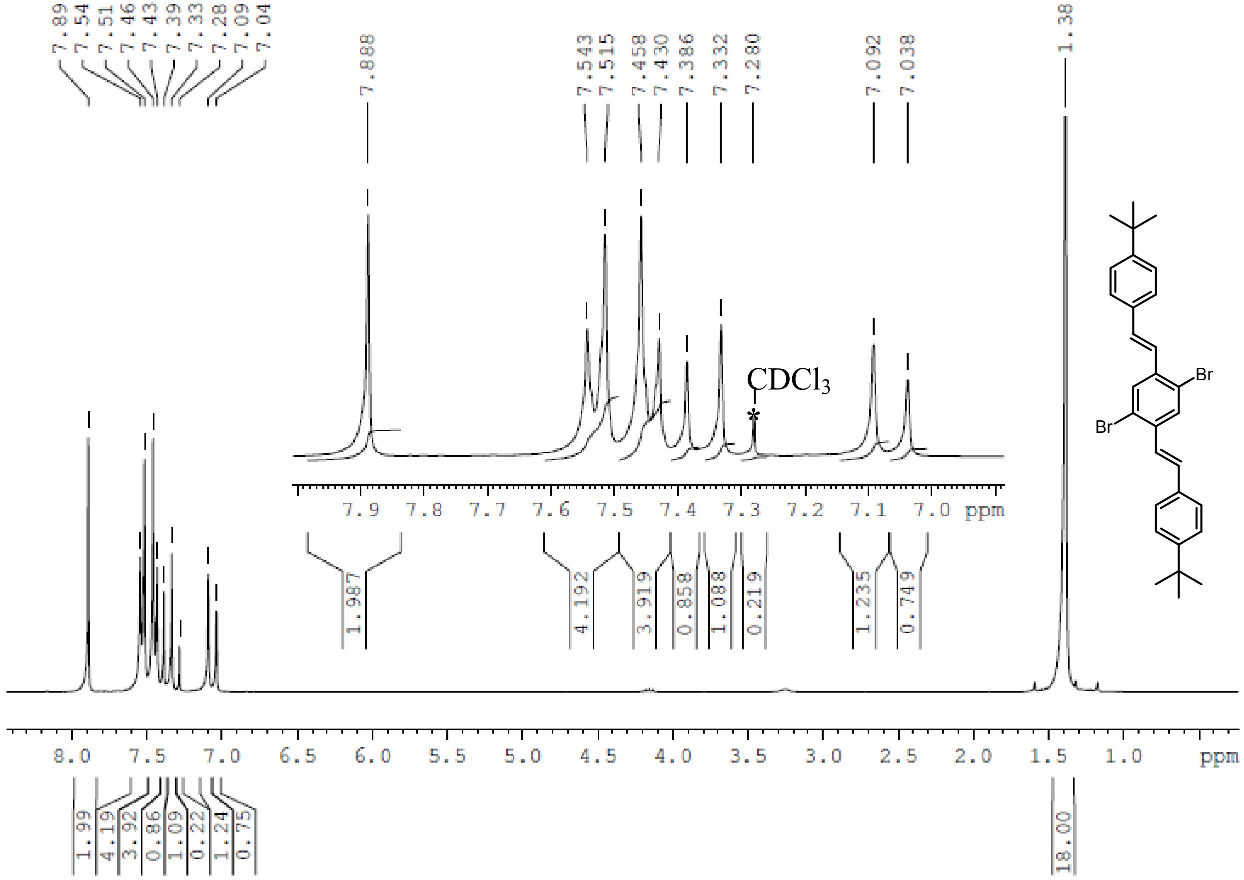


Figure S39. Proton NMR of compound **25** (300 MHz, CDCl$_3$)

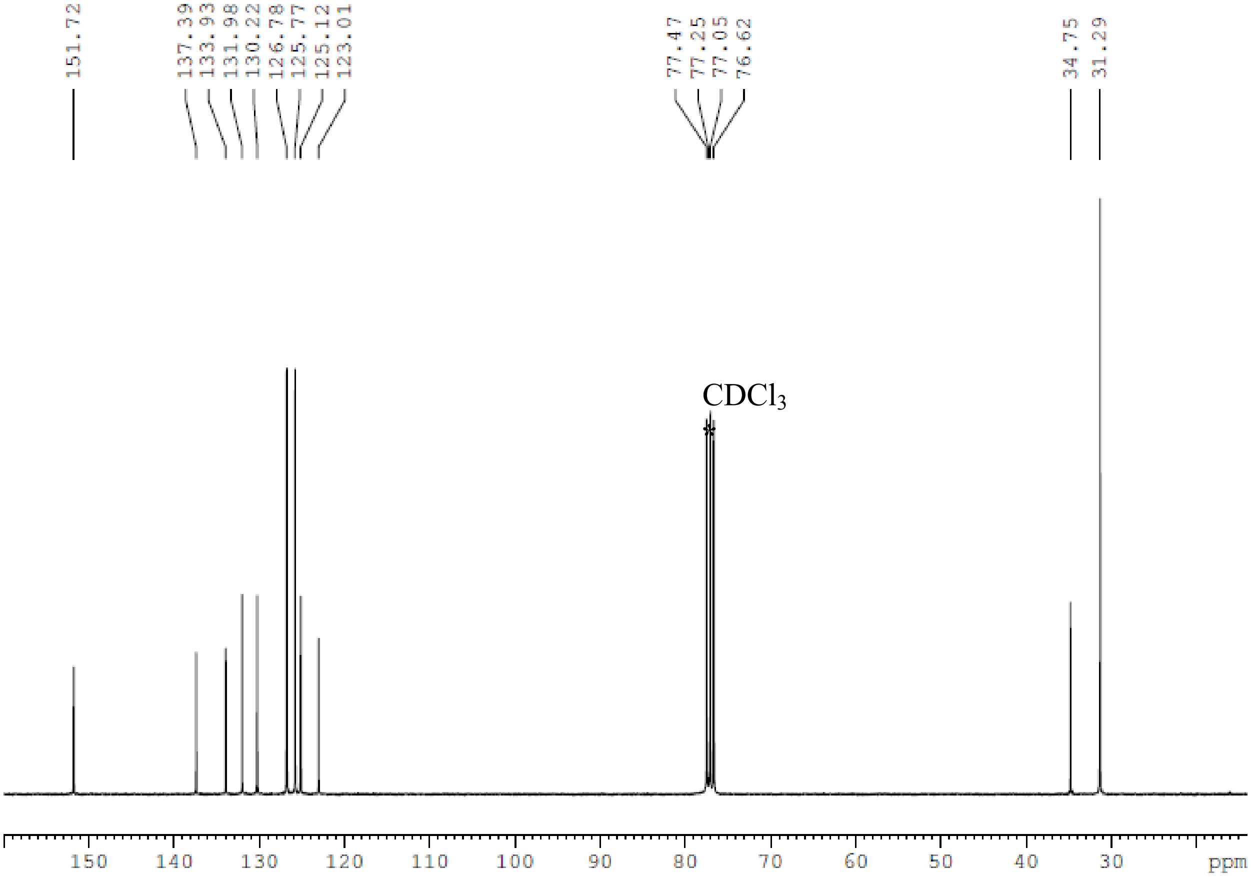


Figure S40. Carbon-13 NMR spectrum of **25** (75 MHz, CDCl$_3$)

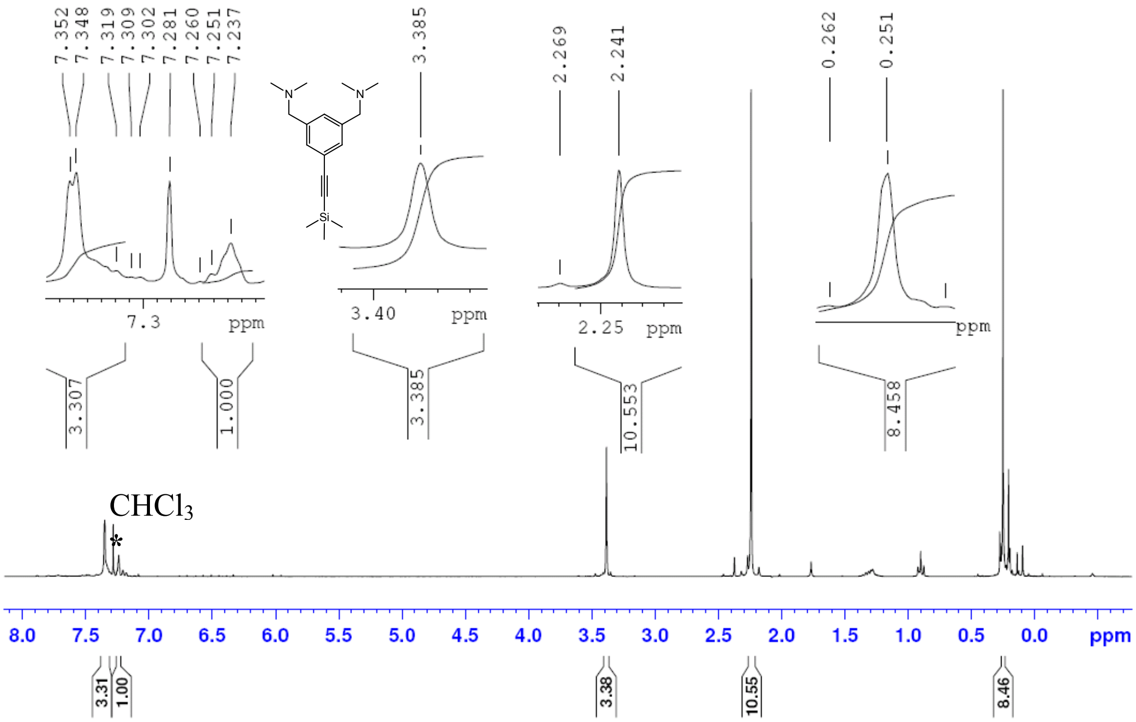


Figure S41. Proton NMR of compound **26** (300 MHz, $CDCl_3$)

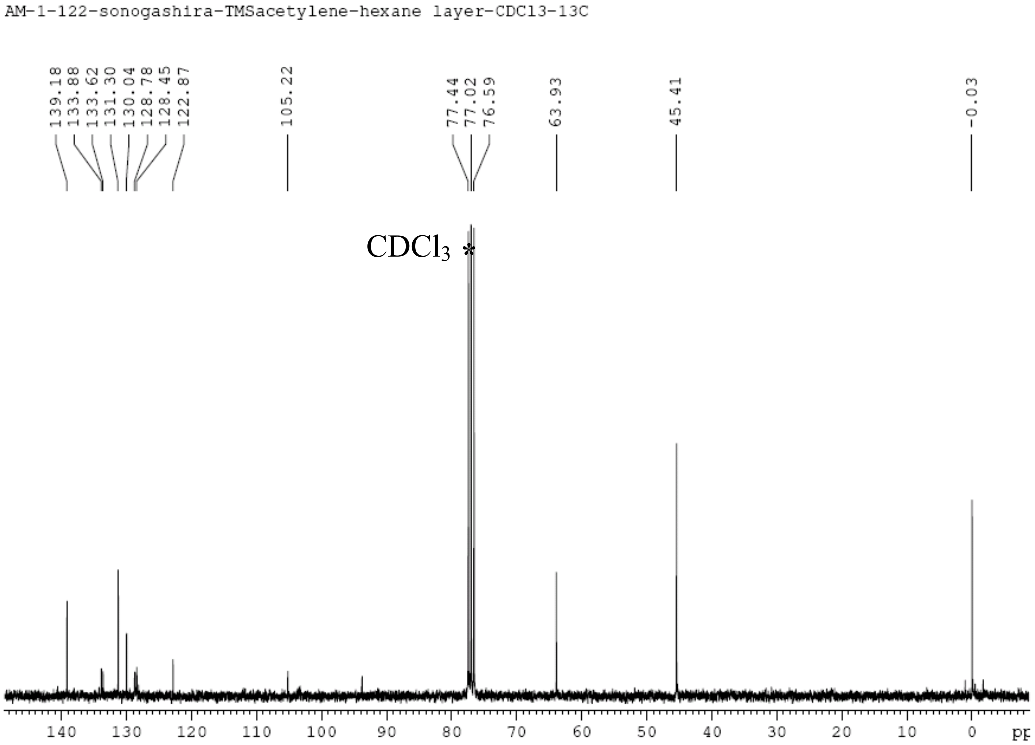


Figure S42. Carbon-13 NMR spectrum of **26** (75 MHz, $CDCl_3$)

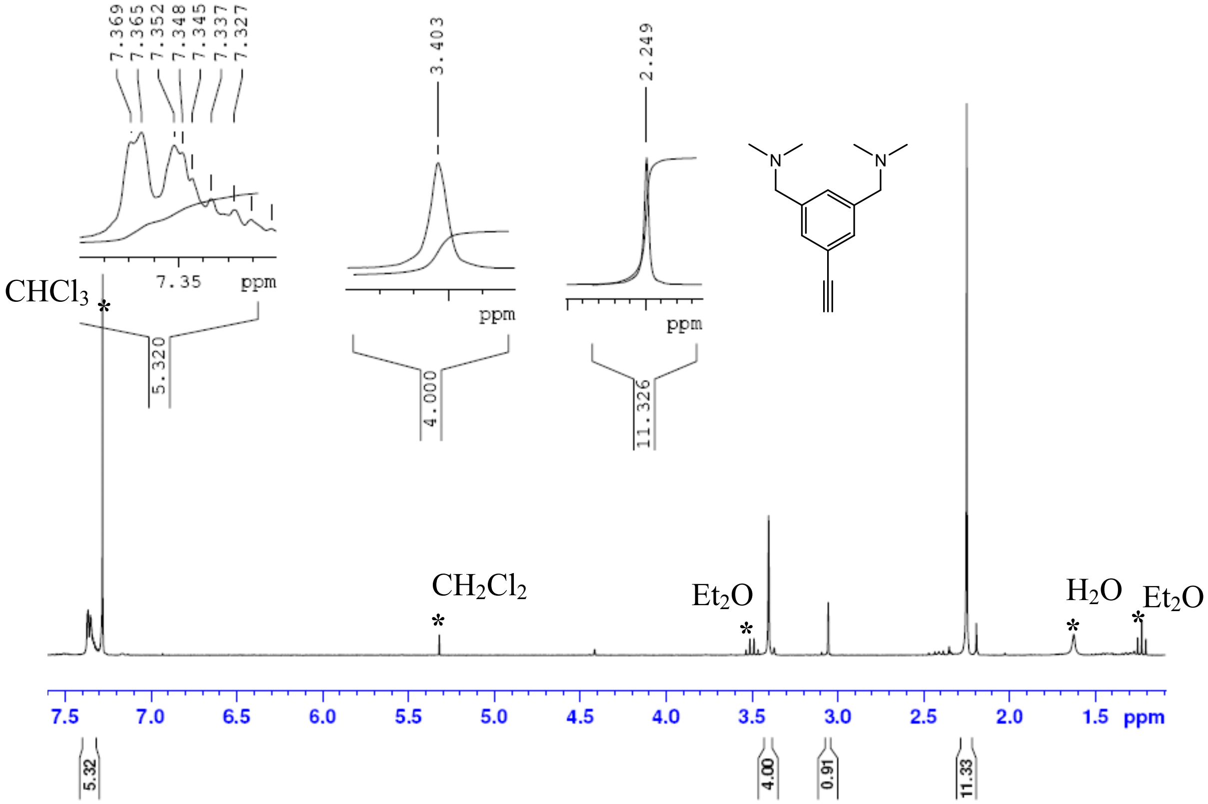


Figure S43. Proton NMR of compound **27** (300 MHz, $CDCl_3$)

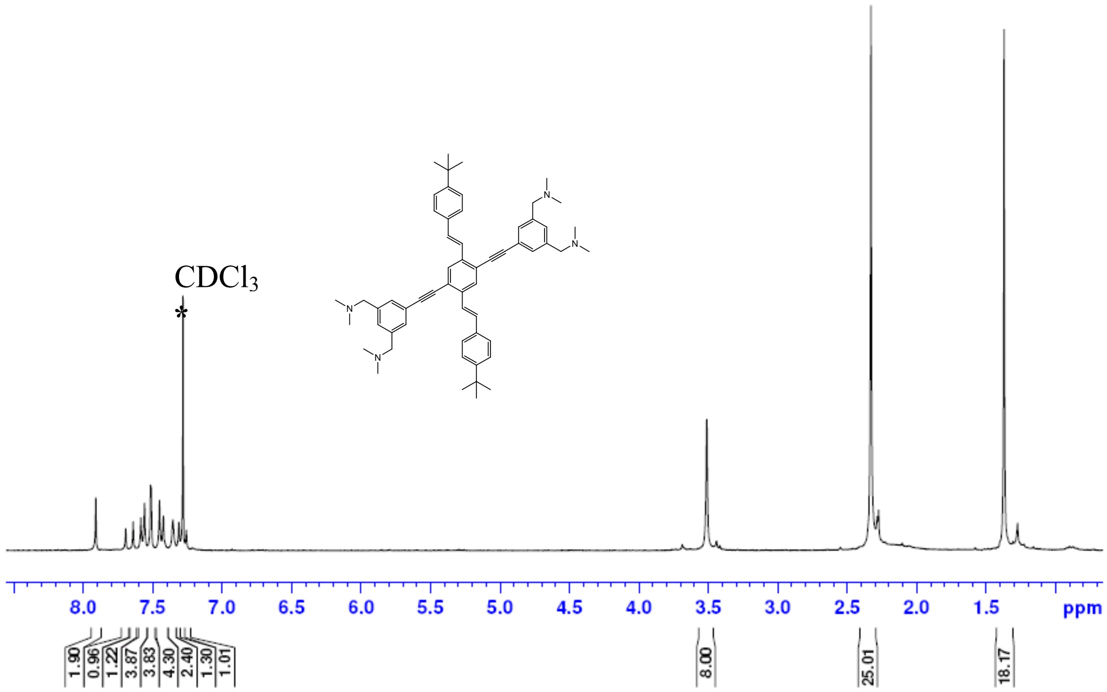


Figure S44. Proton NMR of compound **E** (300 MHz, CDCl$_3$)

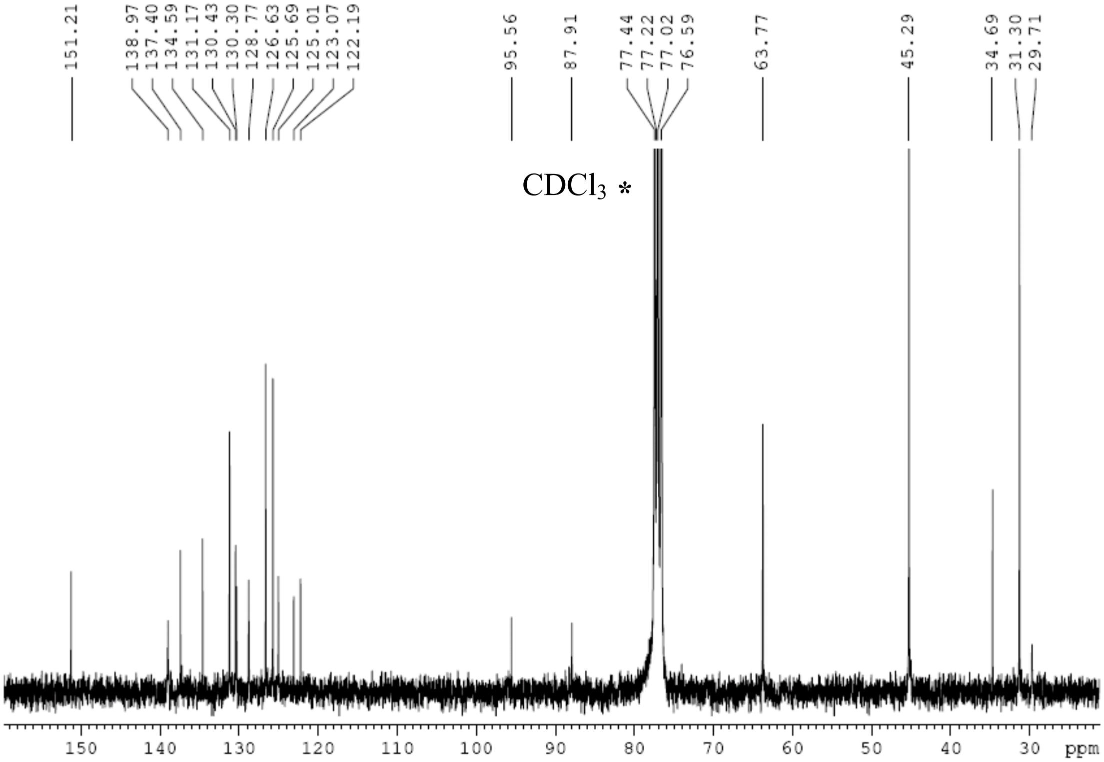


Figure S45. Carbon-13 NMR spectrum of **E** (75 MHz, $CDCl_3$)