Sterically controlled C-H/C-H homocoupling of arenes via C-H borylation

Supporting Information

Table of Contents

1. General experimental details

All (hetero)arenes were purchased from commercial sources and used without further purification. $[Ir(COD)OMe]_2$ and 4,4'-*di*-*tert*-butylbipyridine (dtbpy) were obtained from Sigma-Aldrich Chemicals and used as received. $[Ir(COD)OMe]_2$ was stored in the nitrogen-filled glovebox. C-H borylation reactions were conducted under a nitrogen atmosphere and carried out on Radleys carousel reactors. The homocoupling reactions were carried out under an atmosphere of air or oxygen. Anhydrous solvents were obtained from solvent purification system (Innovative Technology). Thin-layer chromatography (TLC) was carried on pre-coated glass plates with 0.2mm silica gel using UV, potassium permanganate ($KMnO_4$) or I_2 visualization. Preparative TLC (HF 254/GF 254, 20 × 20 cm and 0.9 - 1.0 mm) were purchased from commercial vendors and used directly. Flash column chromatography was performed using Silica gel 60 (200 - 400 mesh) with specified eluents. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were recorded on Brüker Avance 400 MHz or 600 MHz spectrometers. Chemical shifts are reported in ppm relative to a residual solvent peak ($CDCl_3$ = 7.26 ppm for ^{1}H NMR and 77.16 ppm for ^{13}C NMR; $(CD_3)_2SO$ = 2.50 ppm for ^{1}H NMR and 39.52 ppm for ^{13}C NMR). ^{1}H NMR coupling constants (*J*) are reported in Hertz (Hz). The following abbreviations were used in reporting multiplicities: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), q (quartet), p (pentet) and m (multiplet). High resolution mass spectrometry (HRMS) data were recorded on Q Exactive HF (Q Exactive™ HF/UltiMate™ 3000 RSL Cnano) using electron spray ionization (ESI) in positive mode. Low resolution mass spectra were recorded on a GCMS-QP2010 S mass spectrometer (EI); Agilent 6230 LC-TOF mass spectrometer using electrospray ionization (ESI) in positive mode.

2. General procedures

(a) General Procedure for the Conversion of Arenes to Biaryl Arenes (Procedure A):

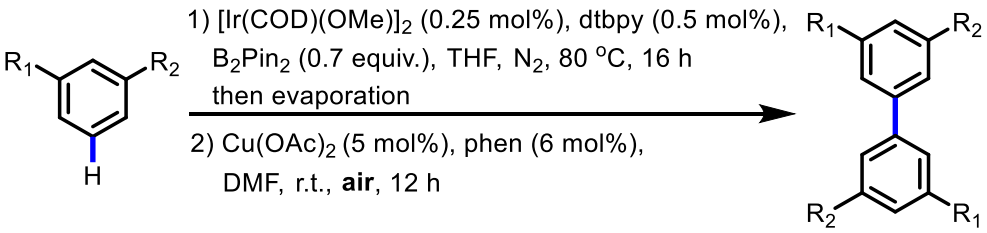
$[Ir(COD)(OMe)]_2$ (1.65 mg, 0.25 mol%), dtbpy (1.35 mg, 0.5 mol%) and B_2Pin_2 (178 mg, 0.70 mmol) were taken in an oven-dried round bottom flask under an atmosphere of nitrogen. Anhydrous THF (2.0 mL) was added to the flask using a syringe. The dark red solution formed on stirring was purged with nitrogen for two minutes. The solution was transferred into a nitrogen filled reaction tube containing the arene (1.0 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere for over 24 hours on the carousel reactor. The reaction was monitored either by TLC or NMR. After the completion of the reaction, the solvent was removed under reduced pressure. $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 1,10-phenanthroline (phen) (10.8 mg, 0.06 mmol) and DMF (2 mL) were added to a reaction vial loaded with a stir bar, then the concentrated borylation product was transferred into this reaction vial, and the reaction was stirred at room temperature under air for 12 hours. After the completion of the reaction, the reaction mixture was filtered and the residue was washed with EtOAc. The resulting filtrate was poured into water and extracted with EtOAc three times. The organic layers were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum. The concentrated crude product was purified by silica gel column chromatography eluting with a mixture of petroleum ether (bp: 60-90 ^oC) and EtOAc.

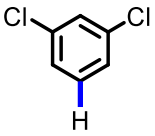
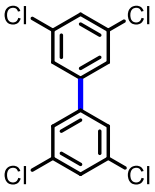
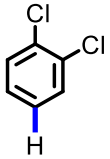
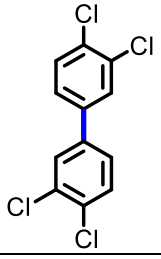
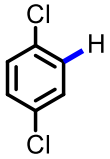
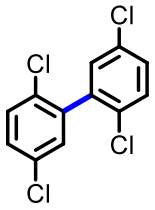
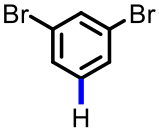
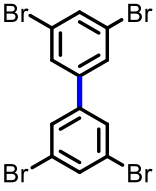
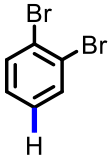
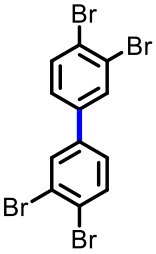
(b) General Procedure for the Conversion of Heteroarenes to Biaryl Heteroarenes (Procedure B):

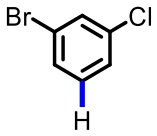
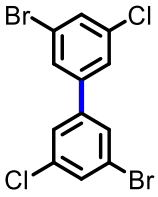
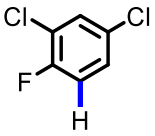
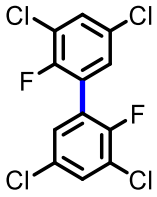
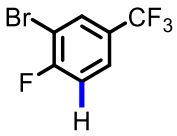
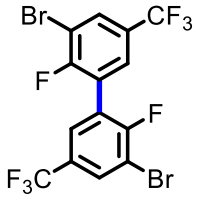
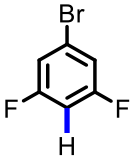
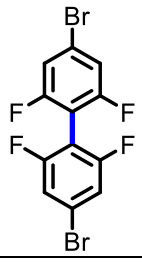
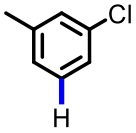
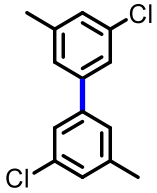
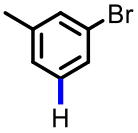
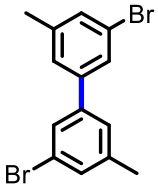
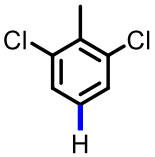
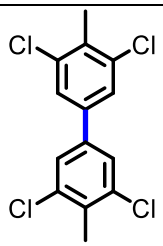
$[Ir(COD)(OMe)]_2$ (4.95 mg, 0.75 mol%) and dtdpy (4.05 mg, 1.5 mol%) were taken in an oven-dried round bottom flask under an atmosphere of nitrogen. Anhydrous THF (2.0 mL) was added to the flask using a syringe. The dark red solution formed on stirring was purged with nitrogen for two minutes. The solution was transferred into a fnitrogen filled reaction tube containing the arene (1.0 mmol). The mixture was stirred at 80 °C under nitrogen atmosphere for over 24 hours on the carousel reactor. The reaction was monitored either by TLC or NMR. After the completion of the reaction, the solvent was removed under reduced pressure. $Cu(OTf)_2$ (36.2 mg, 0.1 mmol), bipyridine (18.7 mg, 0.12 mmol) and DMF (2 mL) were added to a reaction vial with a stir bar, followed by the addition of the concentrated borylation product. The reaction was stirred at room temperature under an atmosphere of oxygen for 12 hours. After the completion of the reaction, the reaction mixture was filtered and the residue was washed with EtOAc. The resulting filtrate was poured into water and extracted with EtOAc three times. The organic layers were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum. The concentrated crude product was purified by silica gel column chromatography eluting with a mixture of petroleum ether (bp: 60-90 ^oC) and EtOAc.

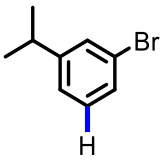
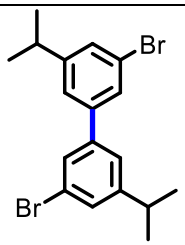
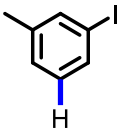
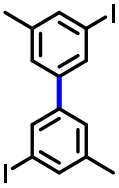
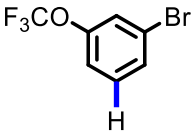
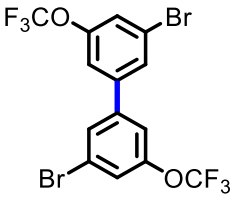
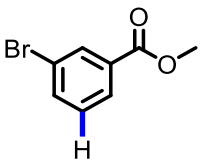
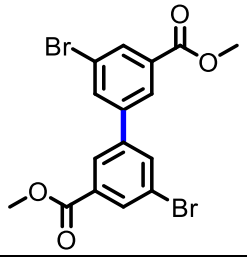
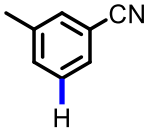
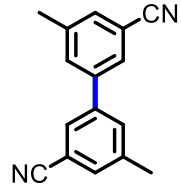
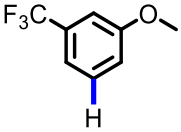
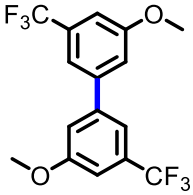
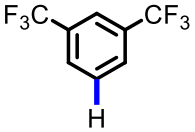
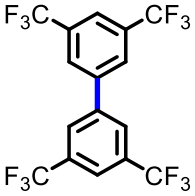
3. Table of (hetero)arenes used in this study

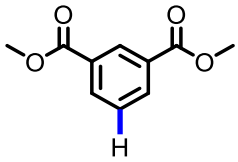
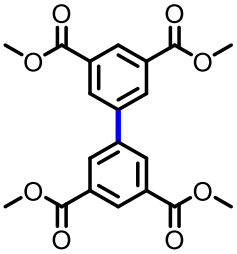
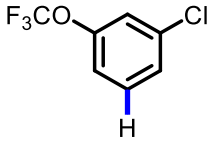
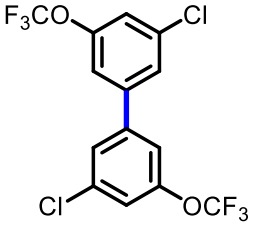
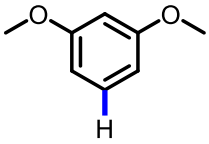
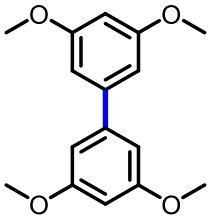
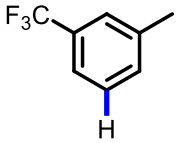
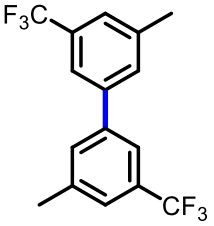
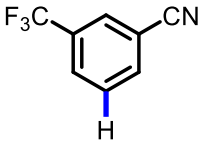
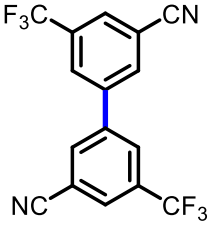
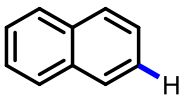
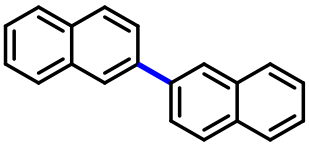
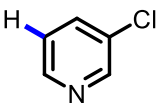
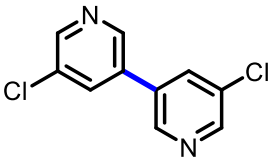
Table 1: General scheme to prepare the homocoupling symmetrical biarlys from arenes

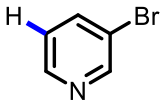
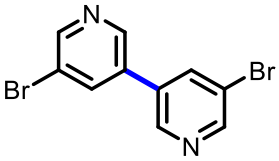
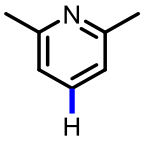
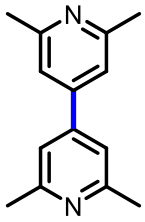
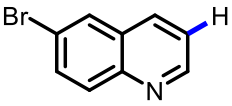
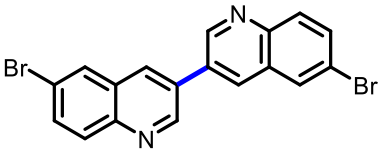
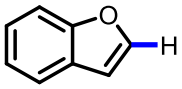
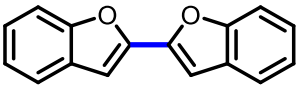
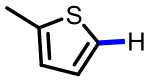
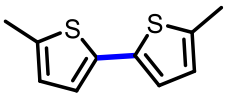
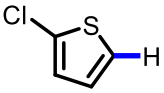
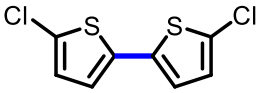
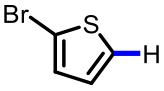
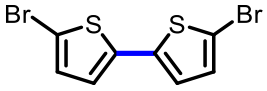


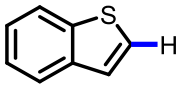
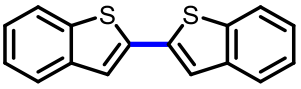
Product ID	Arenes	Biaryls	Isolated yield (%)
2a[a]			**92**
2b[a]			**92**
2c[a]			**88**
2d[a]			**93**
2e[a]			**93**

2f[a]			**82**
2g[a]			**81**
2h[a]			**91**
2i[a]			**92**
2j[a]			**85**
2k[a]			**85**
2l[a]			**79**

2m[a]			**80**
2n[a]			**80**
2o[a]			**73**
2p[a]			**70**
2q[a]			**62**
2r[a]			**58**
2s[a]			**56**

2t[a]			**67**
2u[a]			**70**
2v[a]			**68**
2w[a]			**72**
2x[a]			**79**
2y[a]			**20**
4a[b]			**67**

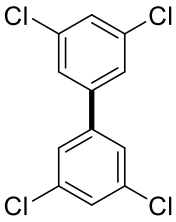
4b[b]			**76**
4c[b]			**50**
4d[b]			**63**
4e[b]			**55**
4f[b]			**62**
4g[b]			**52**
4h[b]			**60**

4i[*b*]			**60**

(*a*) Prepared according to the general procedure **A** (*b*) Prepared according to the general procedure **B**

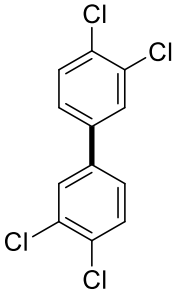
4. Characterization of symmetrical biaryls

3,3',5,5'-Tetrachloro-1,1'-biphenyl (2a) [1]



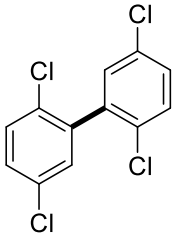
Synthesized according to the general procedure **A**, the title product was obtained from 1,3-dichlorobenzene (0.114 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2a** (0.134 g, 92%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 1.6 Hz, 4H), 7.40 (t, *J* = 1.7 Hz, 2H). ^{1}H NMR data matches with the literature data. [1]

3,3',4,4'-Tetrachloro-1,1'-biphenyl (2b) [2]



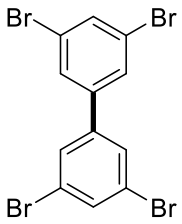
Synthesized according to the general procedure **A**, the titled product was obtained from 1,2-dichlorobenzene (0.113 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2b** (0.134 g, 92%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 2.1 Hz, 2H), 7.52 (d, *J* = 8.3 Hz, 2H), 7.37 (dd, *J* = 8.3, 1.9 Hz, 2H). ^{1}H NMR data matches with the literature data. [2]

2,2',5,5'-Tetrachloro-1,1'-biphenyl (2c) [3]



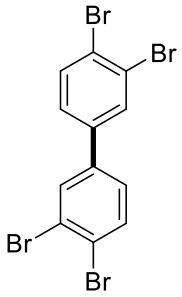
Synthesized according to general procedure **A**, the titled product was obtained from 1,4-dichlorobenzene (0.118 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2c** (0.128 g, 88%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.6 Hz, 2H), 7.34 (dd, *J* = 8.6, 2.5 Hz, 2H), 7.26 (s, 2H) (coincident with $CHCl_3$). ^{1}H NMR data matches with the literature data. [3]

3,3',5,5'-Tetrabromo-1,1'-biphenyl (2d) [4]



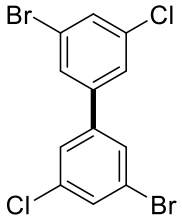
Synthesized according to the general procedure **A**, the titled product was obtained from 1,3-dibromobenzene (0.121 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2d** (0.218 g, 93%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.70 (t, *J* = 1.7 Hz, 2H), 7.59 (d, *J* = 1.7 Hz, 4H). ^{1}H NMR data matches with the literature data. [4]

3,3',4,4'-Tetrabromo-1,1'-biphenyl (2e)



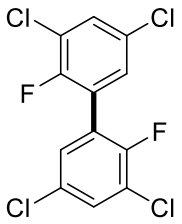
Synthesized according to the general procedure **A**, the titled product was obtained from 1,2-dibromobenzene (0.121 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2e** (0.218 g, 93%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 (d, *J* = 2.1 Hz, 2H), 7.68 (d, *J* = 8.3 Hz, 2H), 7.33 (dd, *J* = 8.3, 2.2 Hz, 2H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 139.5, 134.3, 132.1, 127.1, 125.7, 124.9; **GC-MS** (EI) *m/z*: 465.5.

3,3'-Dibromo-5,5'-dichloro-1,1'-biphenyl (2f)



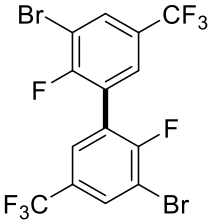
Synthesized according to the general procedure **A**, the titled product was obtained from 1-bromo-3-chlorobenzene (0.117 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2f** (0.156 g, 82%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dt, *J* = 3.8, 1.5 Hz, 4H), 7.45 (t, *J* = 1.6 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 141.7, 135.9, 131.3, 128.6, 126.2, 123.5; **GC-MS** (EI) *m/z*: 377.6.

3,3',5,5'-Tetrachloro-2,2'-difluoro-1,1'-biphenyl (2g)



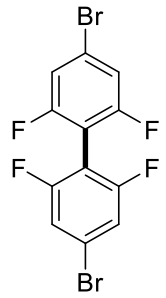
Synthesized according to the general procedure **A**, the titled product was obtained from 2,4-dichloro-1-fluorobenzene (0.117 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2g** (0.133 g, 81%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.51 - 7.48 (m, 2H), 7.27 - 7.24 (m, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 155.5 – 152.8 (m), 131.1, 129.7, 129.4, 124.1 (dd, $J_{C\text{-}F}$ = 10.9, 5.4 Hz), 123.1 (dd, $J_{C\text{-}F}$ = 13.5, 6.2 Hz); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.9 (p, *J* = 3.2 Hz); **GC-MS** (EI) *m/z*: 325.7.

3,3'-Dibromo-2,2'-difluoro-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (2h)



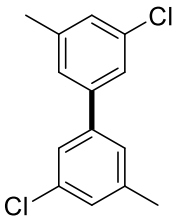
Synthesized according to the general procedure **A**, the titled product was obtained from 2-bromo-1-fluoro-4-(trifluoromethyl)benzene (0.142 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2h** (0.220 g, 91%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96 (s, 2H), 7.62 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 158.3 (d, $J_{C\text{-}F}$ = 256.9 Hz), 132.1 - 131.9 (m), 128.5 - 128.1 (m), 127.9 - 127.7 (m), 123.7 - 123.5 (m), 122.7 (q, $J_{C\text{-}F}$ = 273.7 Hz), 111.2 - 110.9 (m); **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.2, -101.2; **GC-MS** (EI) *m/z*: 481.6.

4,4'-Dibromo-2,2',6,6'-tetrafluoro-1,1'-biphenyl (2i) [5]



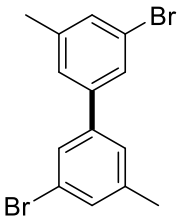
Synthesized according to the general procedure **A**, the titled product was obtained from 1-bromo-3,5-difluorobenzene (0.115 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2i** (0.177 g, 92%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.24 - 7.21 (m, 4H). ^{1}H NMR data matches with the literature data. [5]

3,3'-Dichloro-5,5'-dimethyl-1,1'-biphenyl (2j) [6]



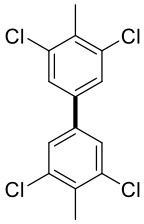
Synthesized according to the general procedure **A**, the titled product was obtained from 1-chloro-3-methylbenzene (0.118 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2j** (0.107 g, 85%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (s, 2H), 7.23 (s, 2H), 7.16 (s, 2H), 2.39 (s, 6H). ^{1}H NMR data matches with the literature data. [6]

3,3'-Dibromo-5,5'-dimethyl-1,1'-biphenyl (2k) [6]



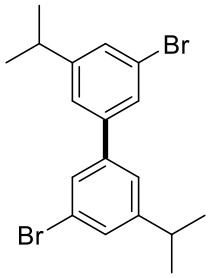
Synthesized according to the general procedure **A**, the titled product was obtained from 1-bromo-3-methylbenzene (0.121 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2k** (0.145 g, 85%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 (s, 2H), 7.32 (s, 2H), 7.26 (s, 2H) (coincident with $CHCl_3$), 2.39 (s, 6H). ^{1}H NMR data matches with the literature data. [6]

3,3',5,5'-Tetrachloro-4,4'-dimethyl-1,1'-biphenyl (2l)



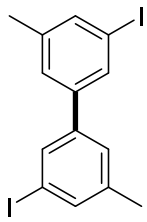
Synthesized according to the general procedure **A**, the titled product was obtained from 1,3-dichloro-2-methylbenzene (0.128 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2l** (0.126 g, 79%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.45 (s, 4H), 2.50 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 137.9, 136.2, 134.2, 126.1, 17.4; **GC-MS** (EI) *m/z*: 317.8.

3,3'-Dibromo-5,5'-diisopropyl-1,1'-biphenyl (2m)



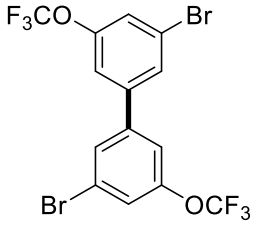
Synthesized according to the general procedure **A**, the titled product was obtained from 1-bromo-3-isopropylbenzene (0.155 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2m** (0.158 g, 80%) as a white solid. **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.49 (t, *J* = 1.7 Hz, 2H), 7.36 (t, *J* = 1.5 Hz, 2H), 7.29 (t, *J* = 1.3 Hz, 2H), 2.94 (p, *J* = 6.9 Hz, 2H), 1.29 (d, *J* = 6.9 Hz, 12H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.7, 142.3, 128.9, 127.8, 124.4, 123.0, 34.3, 24.0; **GC-MS** (EI) *m/z*: 393.8.

3,3'-Diiodo-5,5'-dimethyl-1,1'-biphenyl (2n) [7]



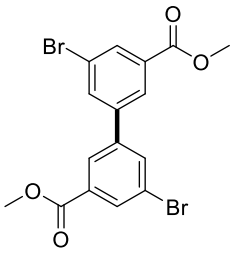
Synthesized according to the general procedure **A**, the titled product was obtained from 1-iodo-3-methylbenzene (0.128 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2n** (0.174 g, 80%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.66 (s, 2H), 7.53 (s, 2H), 7.28 (s, 2H), 2.36 (s, 6H). ^{1}H NMR data matches with the literature data. [7]

3,3'-Dibromo-5,5'-bis(trifluoromethoxy)-1,1'-biphenyl (2o)



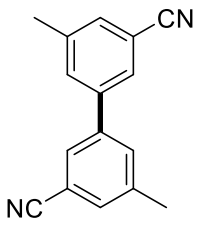
Synthesized according to the general procedure **A**, the titled product was obtained from 1-bromo-3-(trifluoromethoxy)benzene (0.150 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) followed by preparative TLC (100% petroleum ether) to give **2o** (0.175 g, 73%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (t, *J* = 1.6 Hz, 2H), 7.44 (s, 2H), 7.31 (s, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.1 (q, J_{C-F} = 1.7 Hz), 141.9, 128.9, 124.3 - 124.2 (m), 123.6, 120.4 (q, J_{C-F} = 259.6 Hz), 118.8; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.8; **GC-MS** (EI) *m/z*: 477.7.

Dimethyl 5,5'-dibromo-[1,1'-biphenyl]-3,3'-dicarboxylate (2p)



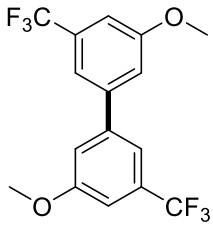
Synthesized according to the general procedure **A**, the titled product was obtained from methyl 3-bromobenzoate (0.215 g, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **2p** (0.150 g, 70%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (t, *J* = 1.6 Hz, 2H), 8.18 (t, *J* = 1.5 Hz, 2H), 7.91 (t, *J* = 1.8 Hz, 2H), 3.97 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.5, 141.0, 134.4, 132.8, 132.3, 127.0, 123.3, 52.8; **GC-MS** (EI) *m/z*: 425.7.

5,5'-Dimethyl-[1,1'-biphenyl]-3,3'-dicarbonitrile (2q)



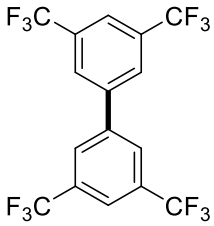
Synthesized according to the general procedure **A**, the titled product was obtained from 3-methylbenzonitrile (0.120 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **2q** (0.072 g, 62%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (s, 2H), 7.57 (s, 2H), 7.50 (s, 2H), 2.48 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.4, 140.4, 132.5, 132.3, 128.0, 118.7, 113.4, 21.4; **MS** (ESI): $[M+Na]^+$ *m/z* = 255.09 (Calculated for $C_{16}H_{12}N_2Na$: 255.09).

3,3'-Dimethoxy-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (2r)



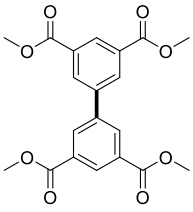
Synthesized according to the general procedure **A**, the titled product was obtained from 1-methoxy-3-(trifluoromethyl)benzene (0.176 mg, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 20:1) to give **2r** (0.102 g, 58%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.25 (s, 2H), 7.15 (s, 2H), 3.92 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 160.4, 142.2, 132.7 (q, J_{C-F} = 32.4 Hz), 124.0 (q, J_{C-F} = 272.6 Hz), 116.8 - 116.7 (m), 116.5 (q, J_{C-F} = 3.8 Hz), 110.2 (q, J_{C-F} = 3.8 Hz), 55.9; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.7; **GC-MS** (EI) *m/z*: 349.9.

3,3',5,5'-Tetrakis(trifluoromethyl)-1,1'-biphenyl (2s) [8]



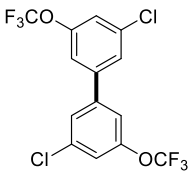
Synthesized according to the general procedure **A**, the titled product was obtained from 1,3-bis(trifluoromethyl)benzene (0.156 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2s** (0.119 g, 56%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.03 (s, 4H), 7.99 (s, 2H). ^{1}H NMR data matches with the literature data. [8]

Tetramethyl [1,1'-biphenyl]-3,3',5,5'-tetracarboxylate (2t) [9]



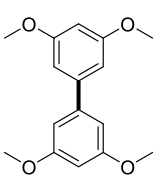
Synthesized according to the general procedure **A**, the titled product was obtained from dimethyl isophthalate (0.194 g, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **2t** (0.129 g, 67%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (t, *J* = 1.4 Hz, 2H), 8.52 (d, *J* = 1.5 Hz, 4H), 4.00 (s, 12H). ^{1}H NMR data matches with the literature data. [9]

3,3'-Dichloro-5,5'-bis(trifluoromethoxy)-1,1'-biphenyl (2u)



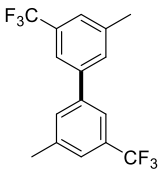
Synthesized according to the general procedure **A**, the titled product was obtained from 1-chloro-3-(trifluoromethoxy)benzene (0.143 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2u** (0.137 g, 70%) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.47 (t, *J* = 1.6 Hz, 2H), 7.29 (d, *J* = 5.4 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.2 (d, $J_{C\text{-}F}$ = 1.9 Hz), 141.7, 136.2, 126.0, 121.4, 120.5 (q, $J_{C\text{-}F}$ = 259.6 Hz), 118.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.9; **GC-MS** (EI) *m/z*: 389.8.

3,3',5,5'-Tetramethoxy-1,1'-biphenyl (2v) [4]



Synthesized according to the general procedure **A**, the titled product was obtained from 1,3-dimethoxybenzene (0.131 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **2v** (0.093 g, 68%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.72 (d, *J* = 2.3 Hz, 4H), 6.48 (t, *J* = 2.2 Hz, 2H), 3.85 (s, 12H). ^{1}H NMR data matches with the literature data. [4]

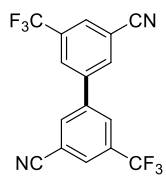
3,3'-Dimethyl-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (2w)



Synthesized according to the general procedure **A**, the titled product was obtained from 1-methyl-3-(trifluoromethyl)benzene (0.160 g, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2w** (0.115 g, 72%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 2H), 7.56 (s, 2H), 7.46 (s, 2H), 2.50 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.9, 139.7, 131.5 (q, $J_{C\text{-}F}$ = 32.3 Hz), 131.4 – 131.3 (m), 125.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 124.3 (q, $J_{C\text{-}F}$ = 273.7 Hz), 121.3 (q, $J_{C\text{-}F}$ = 3.8 Hz), 21.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.6; **GC-MS** (EI) *m/z*: 317.9.

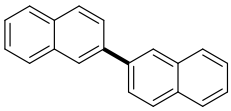
5,5'-Bis(trifluoromethyl)-[1,1'-biphenyl]-3,3'-dicarbonitrile (2x)

Synthesized according to the general procedure **A**, the titled product was obtained from 3-(trifluoromethyl)benzonitrile



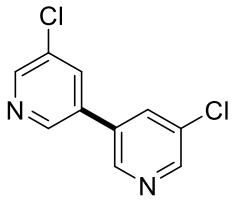
(0.134 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 30:1) to give **2x** (0.134 g, 79%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (s, 2H), 8.04 (d, J = 5.3 Hz, 4H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 140.1, 134.0, 133.6 (q, $J_{C\text{-}F}$ = 34.3 Hz), 129.4 (q, $J_{C\text{-}F}$ = 3.7 Hz), 128.3 (q, $J_{C\text{-}F}$ = 3.5 Hz), 122.7 (q, $J_{C\text{-}F}$ = 274.7 Hz), 116.7, 115.2; **^{19}F NMR** (376 MHz, $CDCl_3$) δ -63.1; **GC-MS** (EI) *m/z*: 339.8.

2,2'-Binaphthalene (2y) [4]



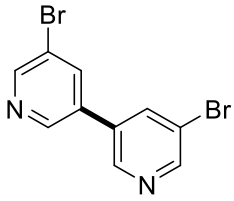
Synthesized according to the general procedure **A**, the titled product was obtained from naphthalene (0.128 g, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2y** (0.025 g, 20%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 2H), 7.96 (t, J = 9.1 Hz, 4H), 7.93 – 7.86 (m, 4H), 7.57 – 7.48 (m, 4H). ^{1}H NMR data matches with the literature data. [4]

5,5'-Dichloro-3,3'-bipyridine (4a) [10]



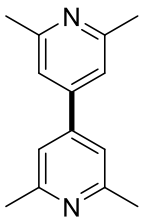
Synthesized according to the general procedure **B**, the titled product was synthesized from 3-chloropyridine (0.096 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **4a** (0.075 g, 67%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.72 (d, J = 1.9 Hz, 2H), 8.66 (d, J = 2.2 Hz, 2H), 7.87 (t, J = 2.1 Hz, 2H). ^{1}H NMR data matches with the literature data. [10]

5,5'-Dibromo-3,3'-bipyridine (4b)



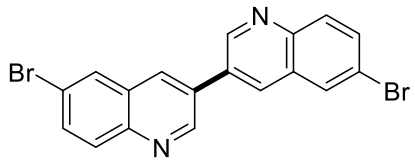
Synthesized according to the general procedure **B**, the titled product was obtained from 3-bromopyridine (0.096 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C):ethyl acetate = 10:1) to give **4b** (0.119 g, 76%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.75 (dd, J = 3.3, 2.1 Hz, 4H), 8.02 (t, J = 2.0 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 151.1, 146.3, 137.1, 133.8, 121.4; **HRMS** (ESI): $[M+H]^+$ *m/z* = 312.8969 (calculated for $C_{10}H_7Br_2N_2$: 312.8971).

2,2',6,6'-Tetramethyl-4,4'-bipyridine (4c) [11]



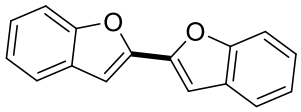
Synthesized according to the general procedure **B**, the titled product was obtained from 2,6-dimethylpyridine (0.116 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 3:1 and add 0.1% Et_3N) to give **4c** (0.053 g, 50%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.17 (s, 4H), 2.60 (s, 12H). ^{1}H NMR data matches with the literature data. [11]

6,6'-Dibromo-3,3'-biquinoline (4d)



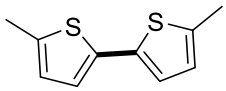
Synthesized according to the general procedure **B**, the titled product was obtained from 6-bromoquinoline (0.134 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **4d** (0.130 g, 63%) as a lightly yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.87 (d, *J* = 2.7 Hz, 2H), 8.01 (d, *J* = 8.9 Hz, 2H), 7.89 (d, *J* = 2.1 Hz, 2H), 7.76 (dd, *J* = 9.0, 2.1 Hz, 2H), 7.56 (d, *J* = 2.7 Hz, 2H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 150.7, 145.3, 144.1, 132.3, 131.3, 129.8, 129.3, 122.1, 120.3; **HRMS** (ESI): $[M+H]^+$ *m/z* = 412.9281 (calculated for $C_{18}H_{11}Br_2N_2$: 412.9284).

2,2'-Bibenzofuran (4e) [4]



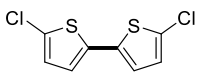
Synthesized according to the general procedure **B**, the titled product was obtained from benzofuran (0.108 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **4e** (0.064 g, 55%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.7 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.37 - 7.32 (m, 2H), 7.29 (d, *J* = 7.4 Hz, 2H), 7.17 (s, 2H). ^{1}H NMR data matches with the literature data. [4]

5,5'-Dimethyl-2,2'-bithiophene (4f) [12]



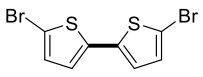
Synthesized according to the general procedure **B**, the titled product was obtained from 2-methylthiophene (0.097 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **4f** (0.060 g, 62%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.87 (d, *J* = 3.5 Hz, 2H), 6.63 (dd, *J* = 3.4, 1.0 Hz, 2H), 2.47 (s, 6H). ^{1}H NMR data matches with the literature data. [12]

5,5'-Dichloro-2,2'-bithiophene (4g) [13]



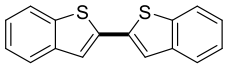
Synthesized according to the general procedure **B**, the titled product was obtained from 2-chlorothiophene (0.092 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **4g** (0.061 g, 52%) as a yellow solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.85 (d, *J* = 3.9 Hz, 2H), 6.82 (d, *J* = 3.8 Hz, 2H). ^{1}H NMR data matches with the literature data. [13]

5,5'-Dibromo-2,2'-bithiophene (4h) [14]



Synthesized according to the general procedure **B**, the titled product was obtained from 2-bromothiophene (0.097 mL, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **4h** (0.097 g, 60%) as a white solid. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.96 (d, *J* = 3.8 Hz, 2H), 6.85 (d, *J* = 3.8 Hz, 2H). ^{1}H NMR data matches with the literature data. [14]

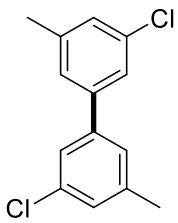
2,2'-Bibenzo[b]thiophene (4i) [15]



Synthesized according to the general procedure **B**, the titled product was obtained from benzo[b]thiophene (0.134 g, 1.0 mmol). The crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **4i** (0.080 g, 60%) as a white solid. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.83 – 7.75 (m, 4H), 7.52 (s, 2H), 7.39 – 7.31 (m, 4H). ^{1}H NMR data matches with the literature data. [15]

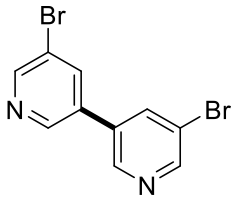
5. Procedure for the scale up reaction (10 mmol)

3,3'-Dichloro-5,5'-dimethyl-1,1'-biphenyl (2j)



The catalyst $[Ir(COD)(OMe)]_2$ (16.5 mg, 0.025 mol), dtbpy (13.5 mg, 0.050 mol) and B_2Pin_2 (1.78 g, 7.0 mmol) were taken in an oven dried round bottom flask under an atmosphere of nitrogen. Anhydrous THF (20 mL) was added to the flask using a syringe. The dark red solution formed was degassed by purging with nitrogen for two minutes. The solution formed was later transferred into a nitrogen filled reaction tube containing the 1-chloro-3-methylbenzene (1.18 mL, 10 mmol) and the mixture was stirred at 80 °C under an atmosphere of nitrogen for 24 hours on the carousel reactor. The solvent was removed *in vacuo*. $Cu(OAc)_2$ (90.8 mg, 0.5 mmol), 1,10-phenanthroline (phen) (108.1 mg, 0.6 mmol) and DMF (20 mL) were added to a round bottom flask with a stir bar, followed by the addition of the concentrated borylation product. The reaction was stirred at room temperature under air for 12 hours. After that, the reaction was filtered and the residue was washed with EtOAc. Then the filtrate was poured into water and extracted with EtOAc three times. The organic layers were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum. The concentrated crude product was purified by silica gel chromatography (100% petroleum ether, 60-90 °C) to give **2j** (1.0 g, 80%).

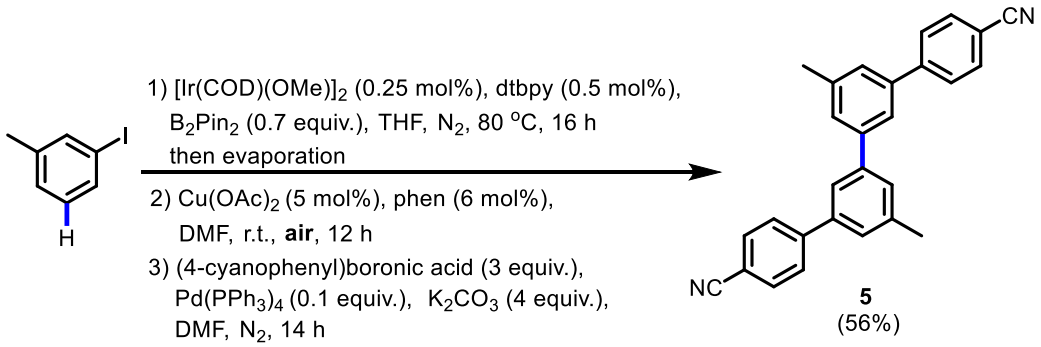
5,5'-Dibromo-3,3'-bipyridine (4b)



$[Ir(COD)(OMe)]_2$ (49.5 mg, 0.075 mol), dtbpy (40.5 mg, 0.150 mol) and B_2Pin_2 (1.78 g, 7.0 mmol) were taken in an oven dried round bottom flask under an atmosphere of nitrogen. Anhydrous THF (20 mL) was added to the flask using a syringe. The red solution formed was degassed by purging with nitrogen for two minutes and transferred into a nitrogen filled reaction tube containing the 3-bromopyridine (0.96 mL, 10 mmol). The mixture was stirred at 80 °C under an atmosphere of nitrogen for 24 hours on the carousel reactor. The solvent was removed *in vacuo*. $Cu(OTf)_2$ (361.7 mg, 1 mmol), bipyridine (187.4 mg, 1.2 mmol) and DMF (20 mL) were added to a round bottom flask with a stir bar, followed by the addition of the concentrated borylation product. The reaction was stirred at room temperature under an atmosphere of oxygen for 12 hours. The reaction was filtered and the residue was washed with EtOAc. The filtrate was poured into water and then extracted with EtOAc three times. The organic layers were combined and washed with brine, dried over anhydrous Na_2SO_4, filtered and the solvent was removed under vacuum.

The concentrated crude product was purified by silica gel chromatography (petroleum ether (60-90 °C): ethyl acetate = 10:1) to give **4b** (1.1 g, 70%).

6. Procedure for one pot C-H borylation/Cu-catalyzed homocoupling/Suzuki sequence:



One pot preparation of the Suzuki product (**5**) from the arene. The reaction was performed on 1.0 mmol scale.

5',5''-dimethyl-[1,1':3',1'':3'',1'''-quaterphenyl]-4,4'''-dicarbonitrile (5)

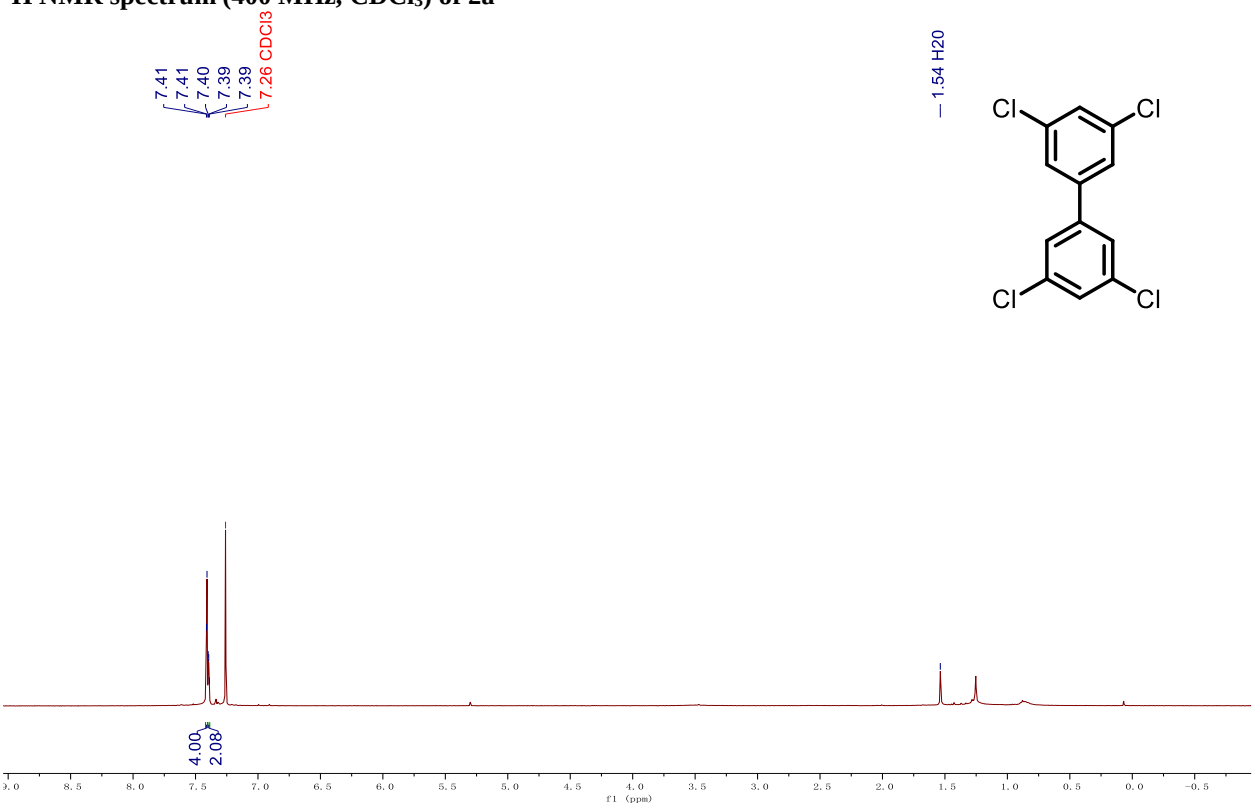
$[Ir(COD)(OMe)]_2$ (1.65 mg, 0.25 mol%), dtbpy (1.35 mg, 0.5 mol%) and B_2Pin_2 (178 mg, 0.70 mmol) were taken in an oven dried round bottom flask under an atmosphere of nitrogen. Anhydrous THF (2 mL) was added to the flask using a syringe. The dark red solution formed on stirring was degassed by purging with nitrogen for two minutes, and the solution was transferred into a nitrogen filled reaction tube containing the 1-iodo-3-methylbenzene (0.128 mL, 1.0 mmol). The mixture was stirred at 80 °C under an atmosphere of nitrogen for 24 hours on the carousel reactor after that the solvent was removed *in vacuo*. $Cu(OAc)_2$ (9.1 mg, 0.05 mmol), 1,10-phenanthroline (phen) (10.8 mg, 0.06 mmol) and DMF (2 mL) were added to a round bottom flask with a stir bar, followed by the addition of the concentrated borylation product. The reaction was stirred at room temperature under air for 12 hours. Then (4-cyanophenyl)boronic acid (220.4 mg, 1.5 mmol), K_2CO_3 (276.4 mg, 2 mmol) and DMF (1 mL) were added to the crude reaction mixture followed by degassing by purging with nitrogen for three times. Then the catalyst $Pd(PPh_3)_4$ (57.8 mg, 0.05 mmol) was added to the nitrogen filled reaction tube immediately. The reaction mixture was degassed by purging with again nitrogen for another three times. The reaction was stirred at 80 °C for 14 hours under nitrogen atmosphere. Then the solvents were evaporated under reduced pressure and the crude product was purified by silica gel chromatography (100% petroleum ether (60-90 °C):ethyl acetate = 30:1) to give **5** (0.108 g, 56%) as a lightly brown-red solid. **^{1}H NMR** (600 MHz, DMSO-d_6) δ 8.02 (d, J = 8.2 Hz, 4H), 7.95 (d, J = 8.2 Hz, 4H), 7.89 (s, 2H), 7.68 (s, 2H), 7.59 (s, 2H), 2.48 (s, 6H); **^{13}C NMR** (101 MHz, $CDCl_3$) δ 145.8, 141.9, 140.0, 139.6, 132.7, 128.5, 128.0, 127.4, 123.6, 119.0, 111.2, 21.7; **MS** (ESI): $[M+Na]^+$ m/z = 407.15 (Calculated for $C_{28}H_{20}N_2Na$: 407.15).

7. References

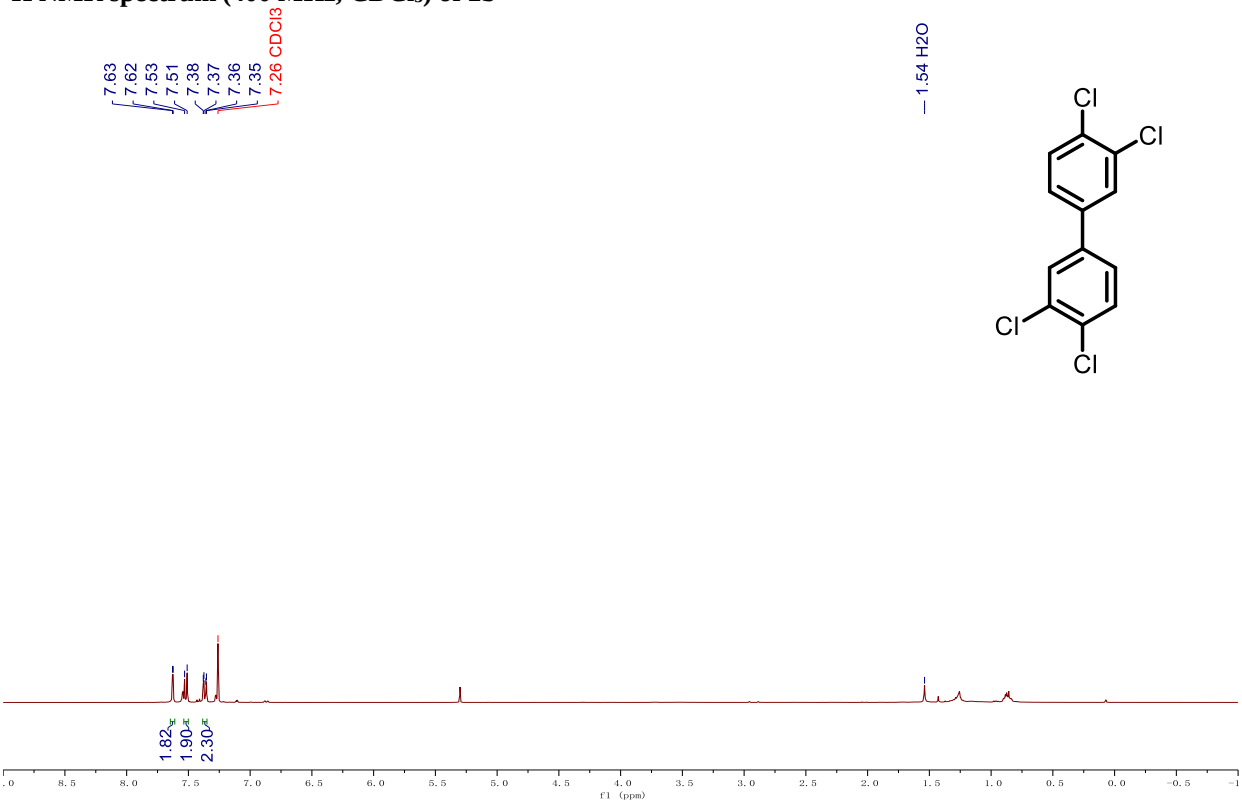
[1] X. Li, D.-J. Li, Y.-N. Bai, C.-X. Zhang, H.-H. Chang, W.-C. Gao and W.-L. Wei, *Tetrahedron*, 2016, **72**, 6996.
[2] J. A. V. Er, A. G. Tennyson, J. W. Kamplain, V. M. Lynch and C. W. Bielawski, *Eur. J. Inorg. Chem.*, 2009, **2009**, 1729.
[3] D. Welti and D. Sissons, *Org. Magn. Reson.*, 1972, **4**, 309.
[4] N. Kirai and Y. Yamamoto, *Eur. J. Org. Chem.*, 2009, **2009**, 1864.
[5] F. Leroux, T. U. Hutschenreuter, C. Charrière, R. Scopelliti and R. W. Hartmann, *Helv. Chim. Acta*, 2003, **86**, 2671.
[6] F. Pu, L.-Y. Zhang, Z.-W. Liu and X.-Y. Shi, *Adv. Synth. Catal.*, 2018, **360**, 2644.
[7] W. Huang, M. Wang, C. Du, Y. Chen, R. Qin, L. Su, C. Zhang, Z. Liu, C. Li and Z. Bo, *Chem. - Eur. J.*, 2011, **17**, 440.
[8] H. Tran, T. McCallum, M. Morin and L. Barriault, *Org. Lett.*, 2016, **18**, 4308.
[9] M. Mazik and A. König, *J. Org. Chem.*, 2006, **71**, 7854.
[10] H. Muratake, M. Tonegawa and M. Natsume, *Chem. Pharm. Bull.*, 1998, **46**, 400.
[11] T. Ohmura, Y. Morimasa and M. Suginome, *J. Am. Chem. Soc.*, 2015, **137**, 2852.
[12] T. Korenaga, K. Nitatori, H. Muraoka, S. Ogawa and K. Shimada, *J. Org. Chem.*, 2018, **83**, 4835.
[13] H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc.*, 2009, **131**, 17052.
[14] J. P. Brand and J. Waser, *Angew. Chem. Int. Ed.*, 2010, **49**, 7304.
[15] S. Ostrowska, S. Rogalski, J. Lorkowski, J. Walkowiak and C. Pietraszuk, *Synlett*, 2018, **29**, 1735.

8. NMR Spectra

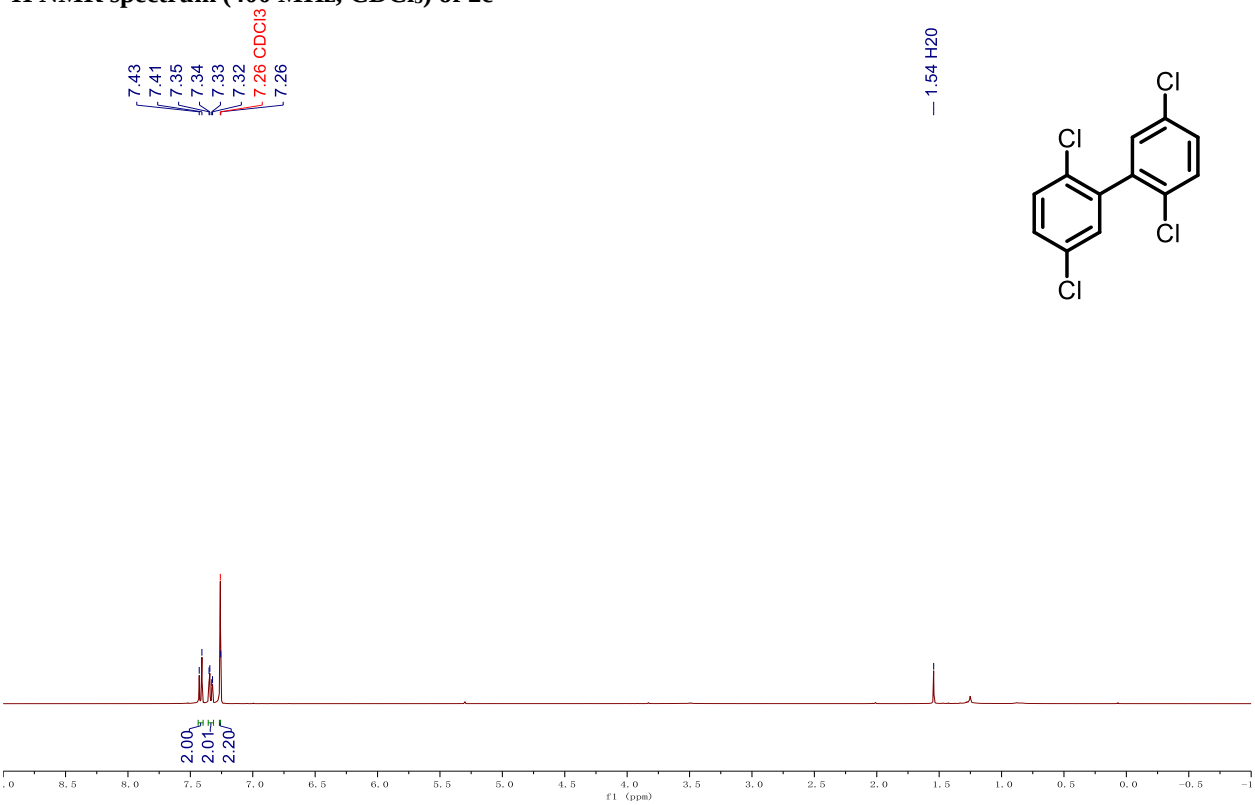
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2a



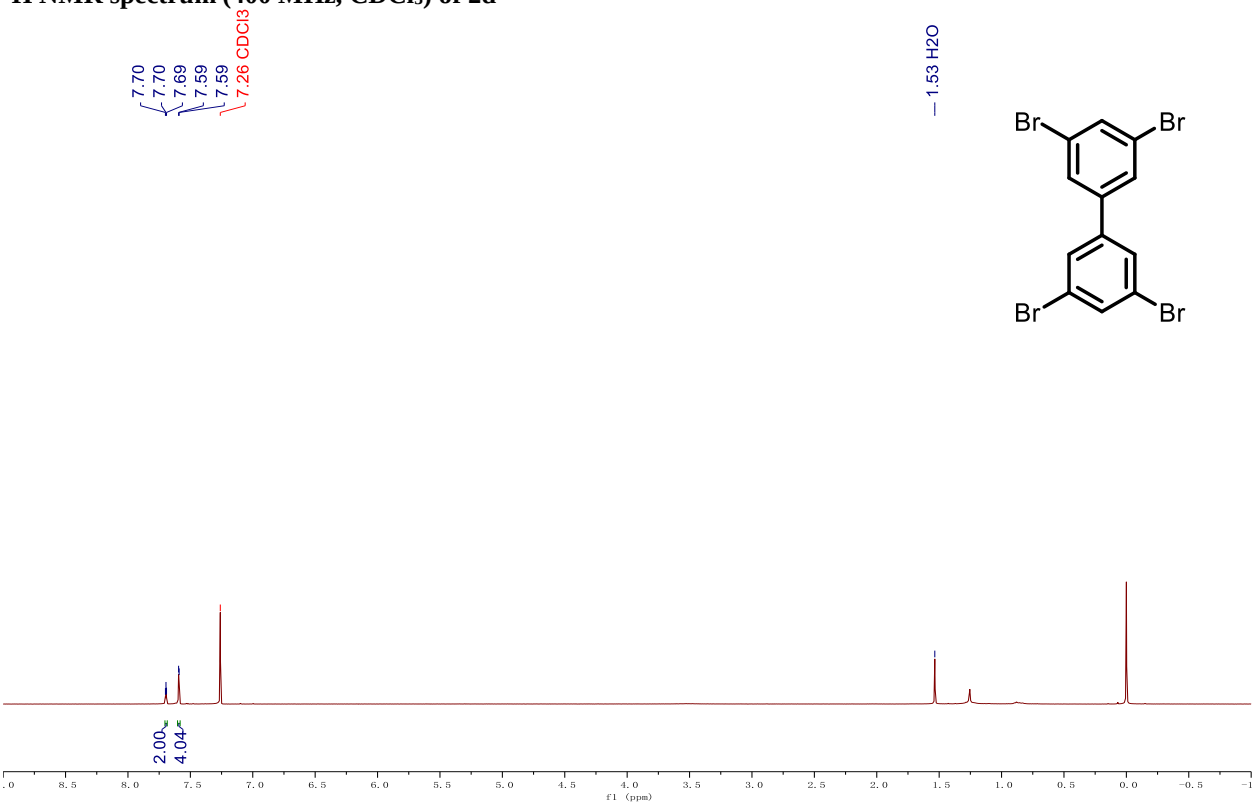
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2b



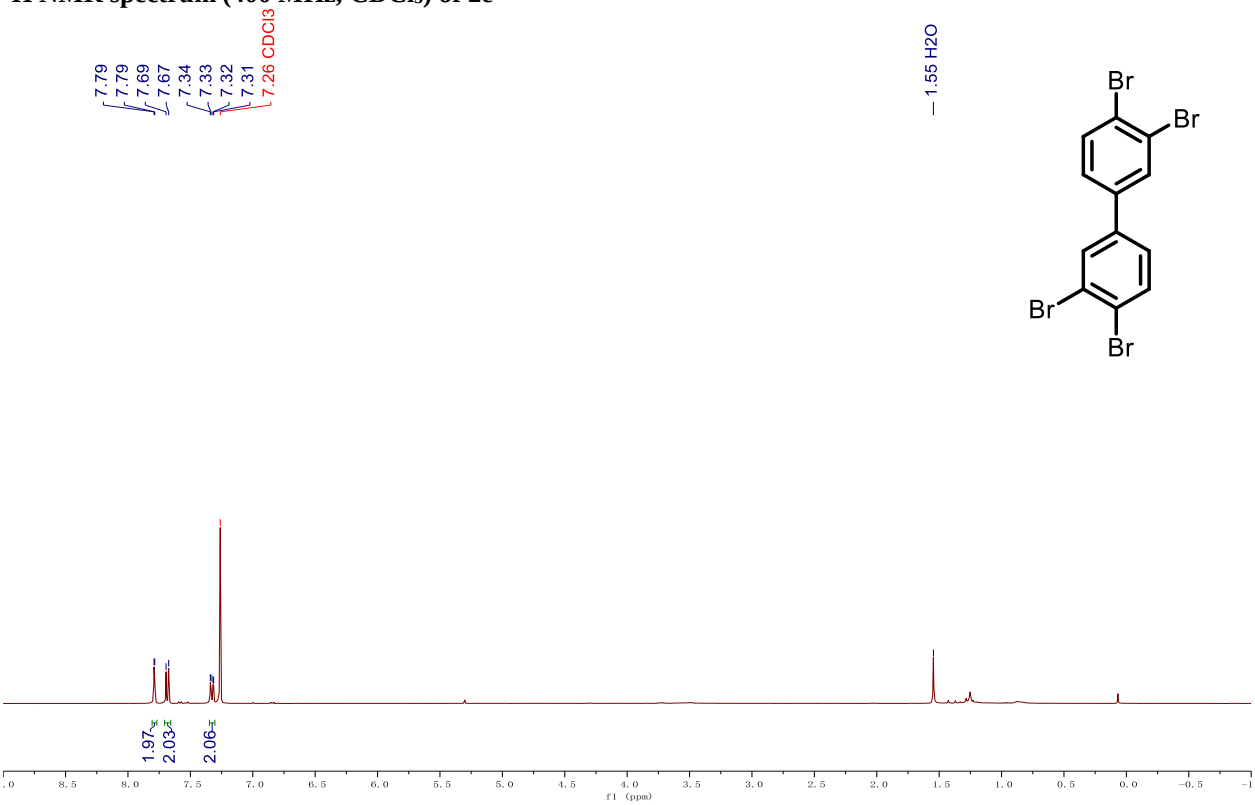
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2c



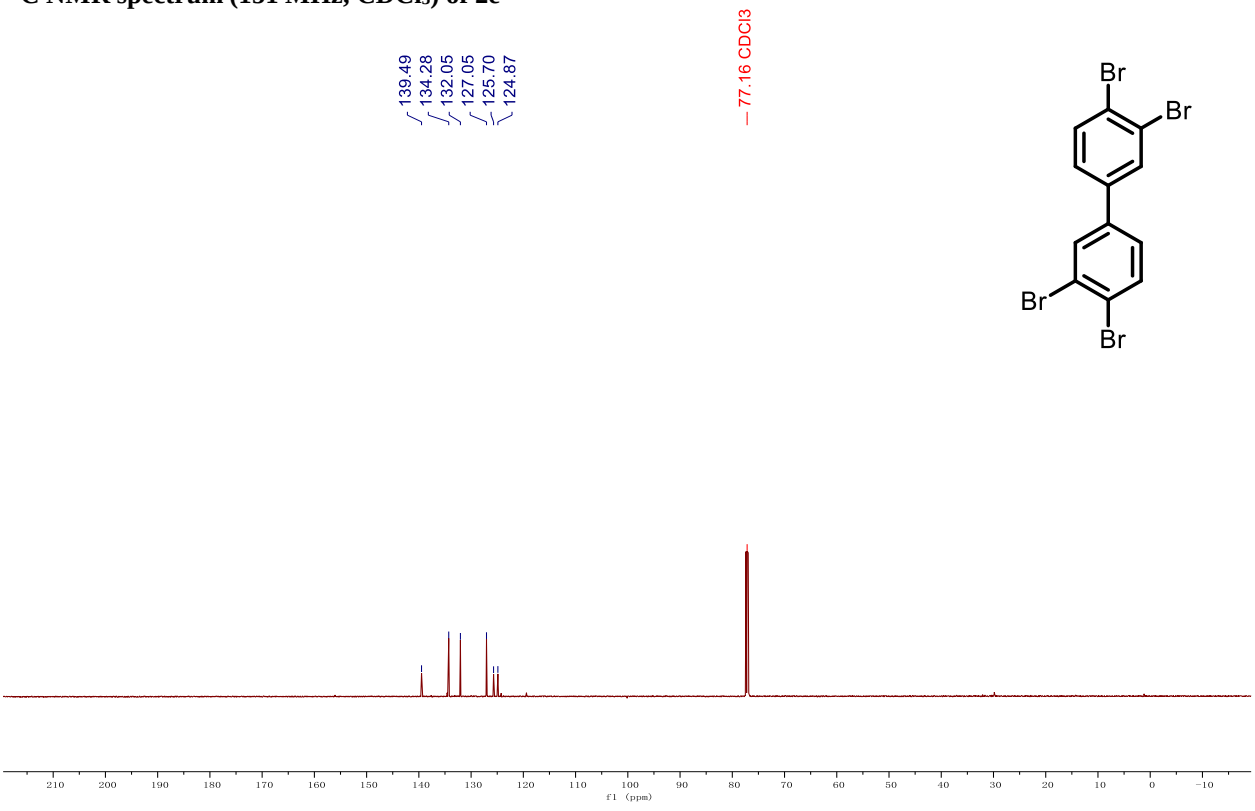
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2d



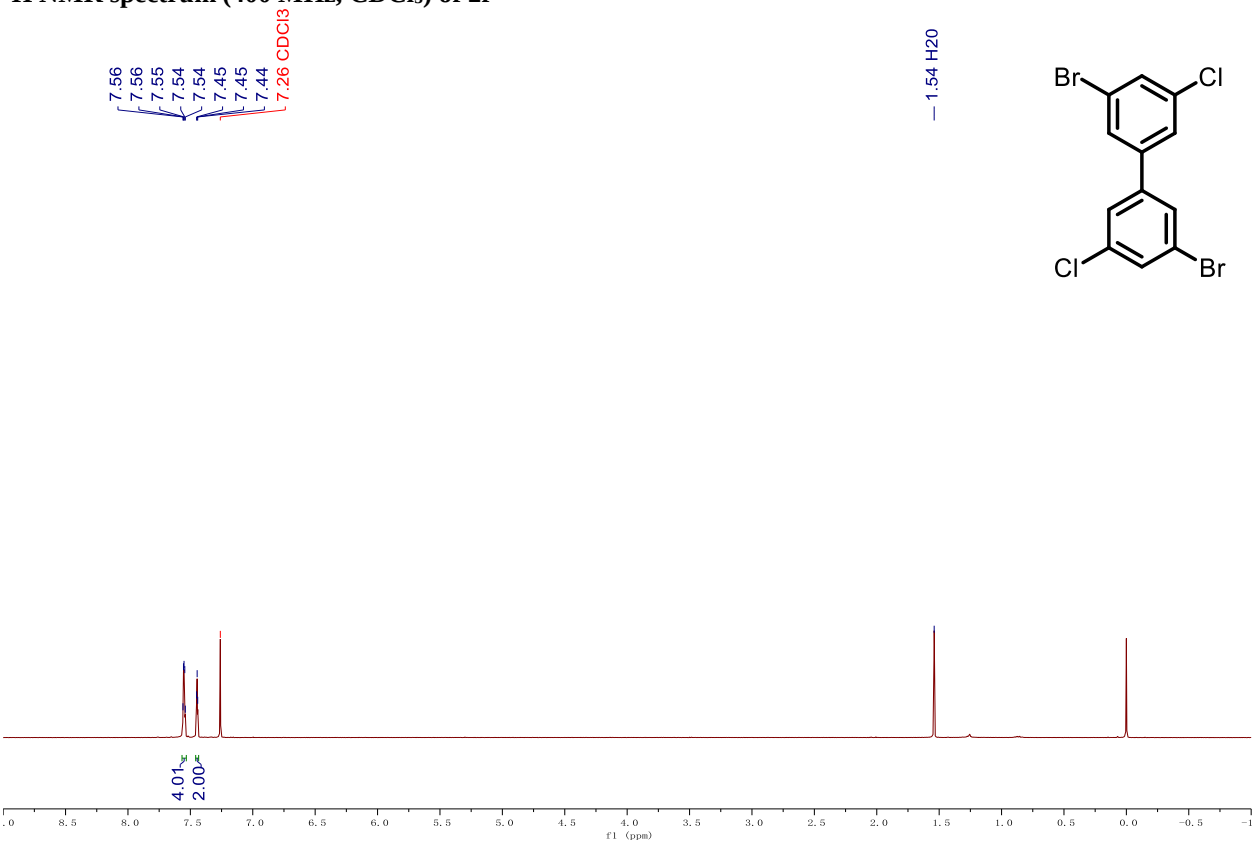
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2e



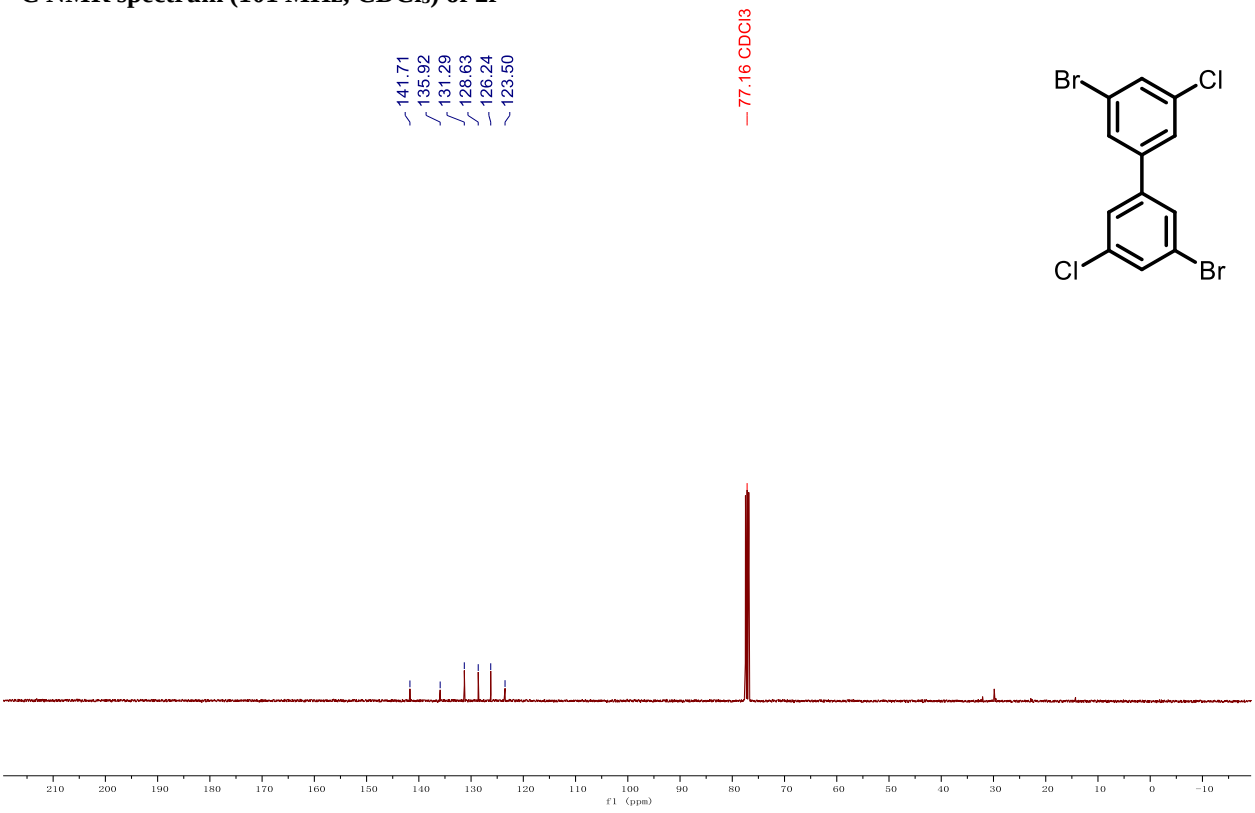
^{13}C NMR spectrum (151 MHz, $CDCl_3$) of 2e



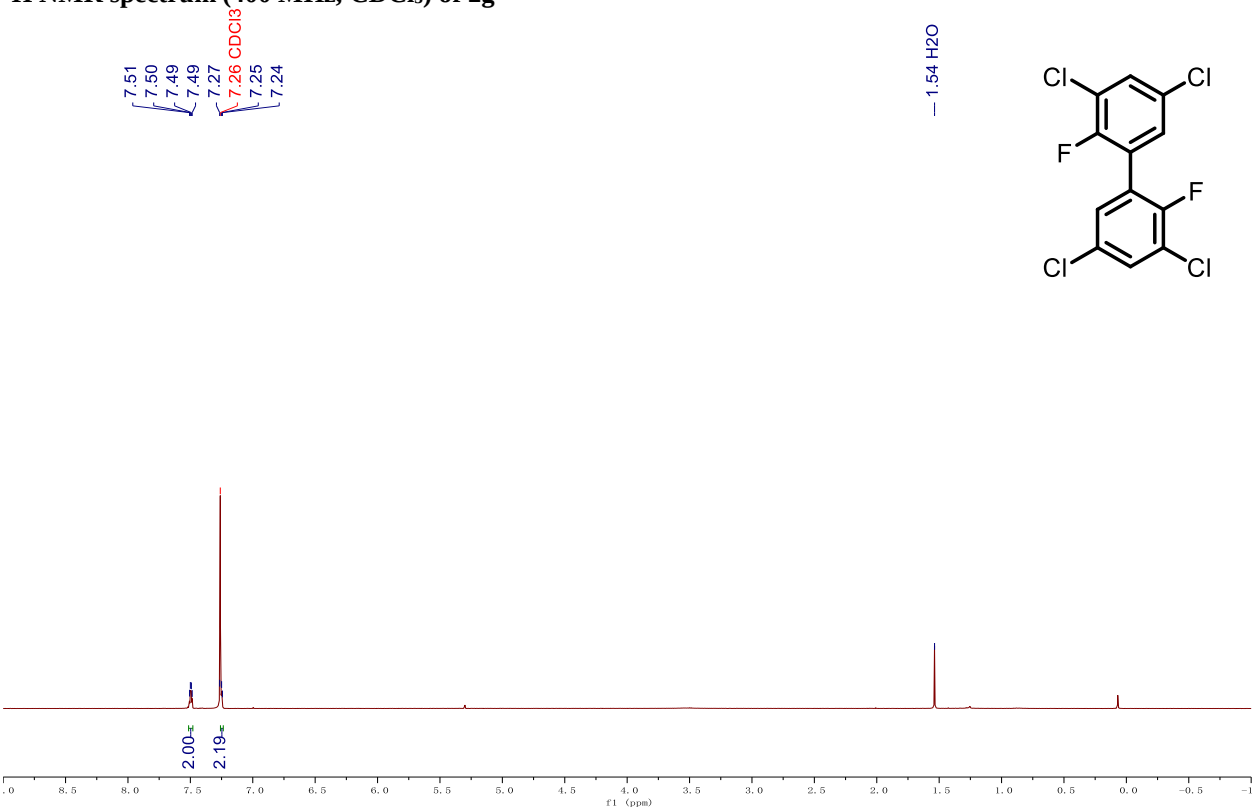
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2f



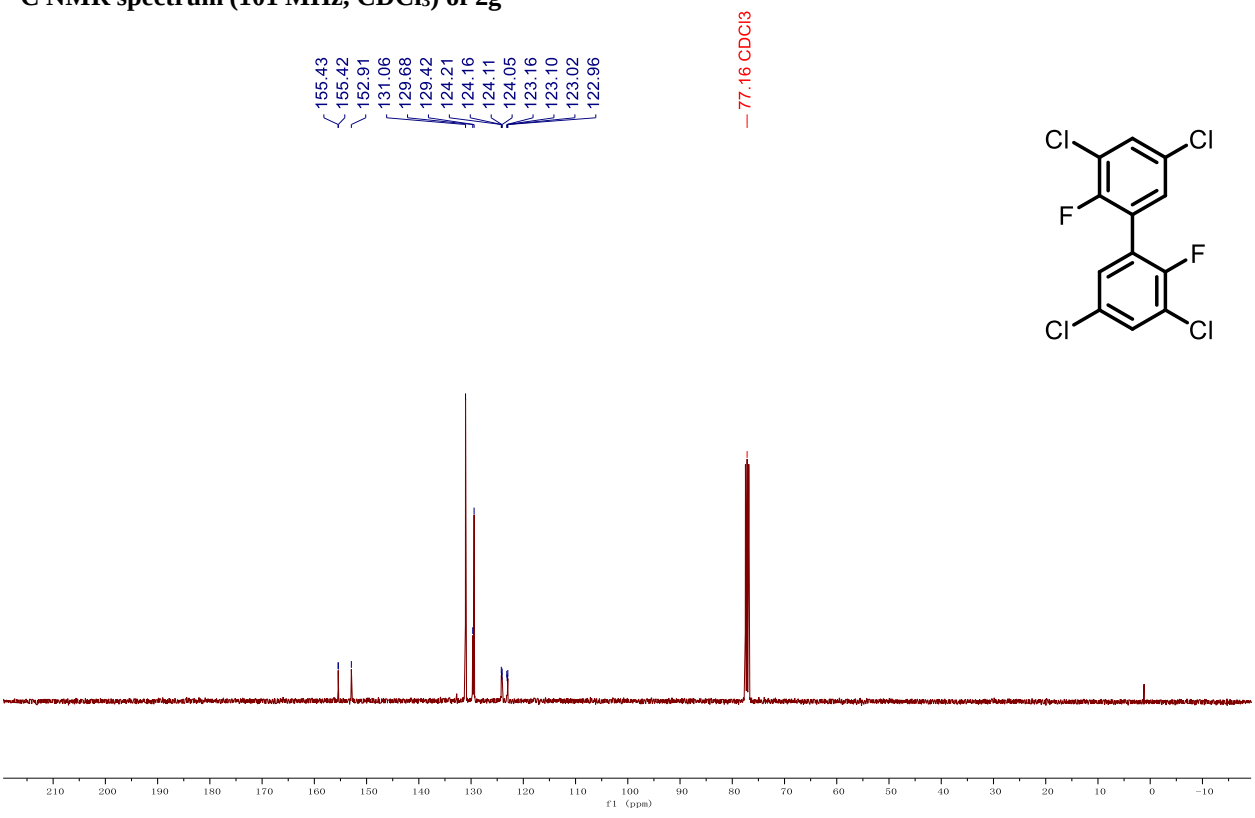
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2f



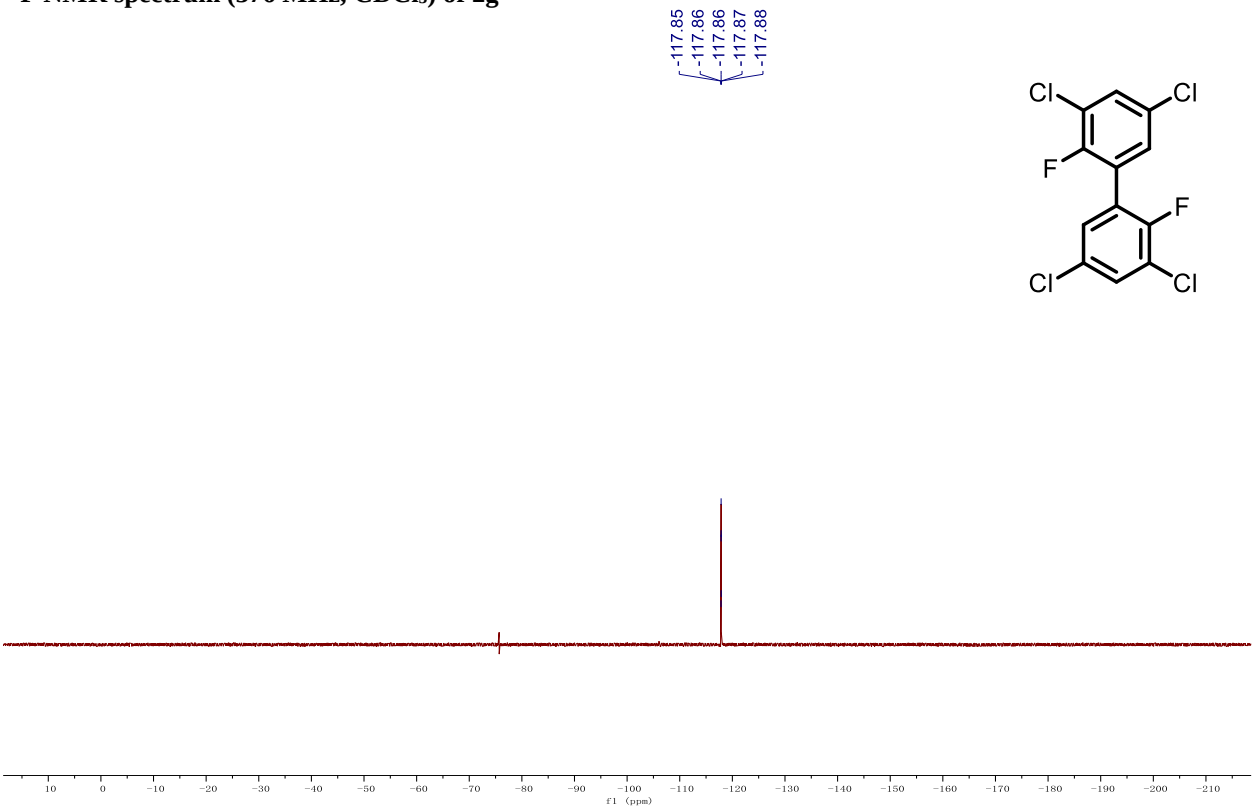
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2g



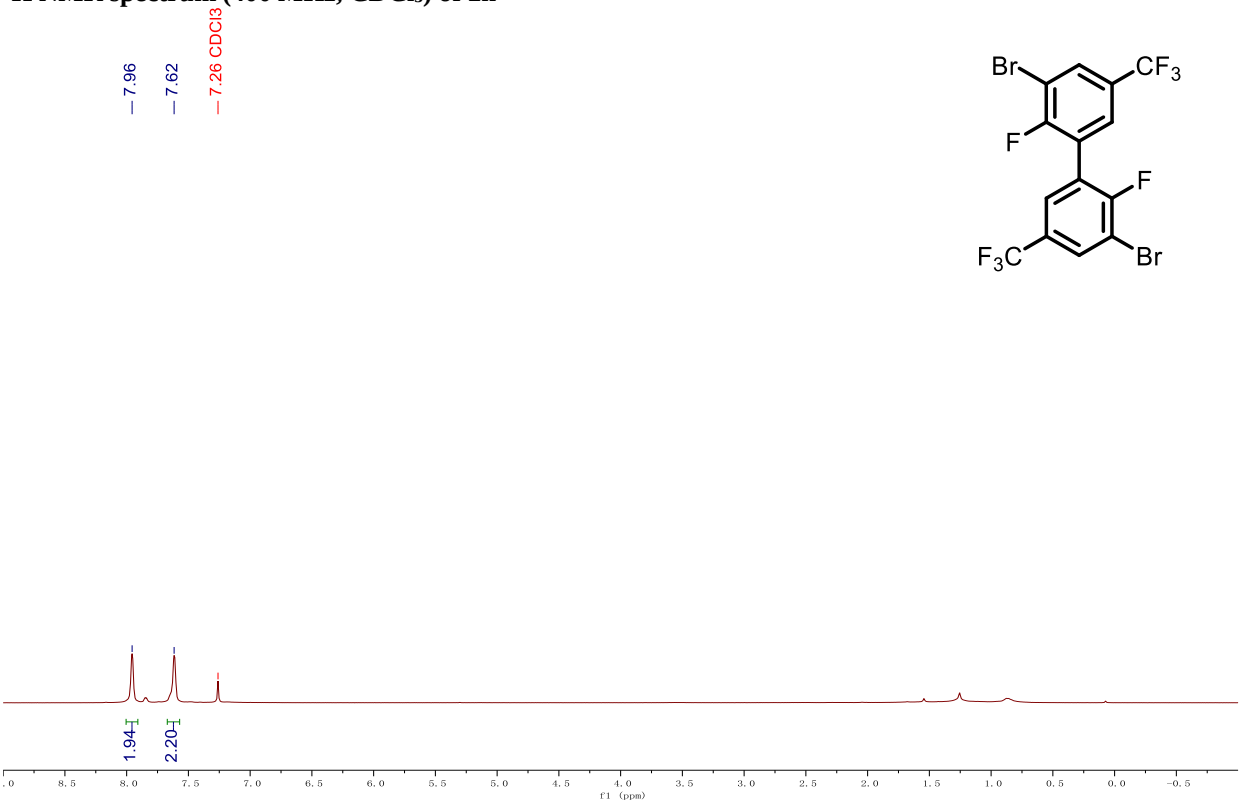
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2g



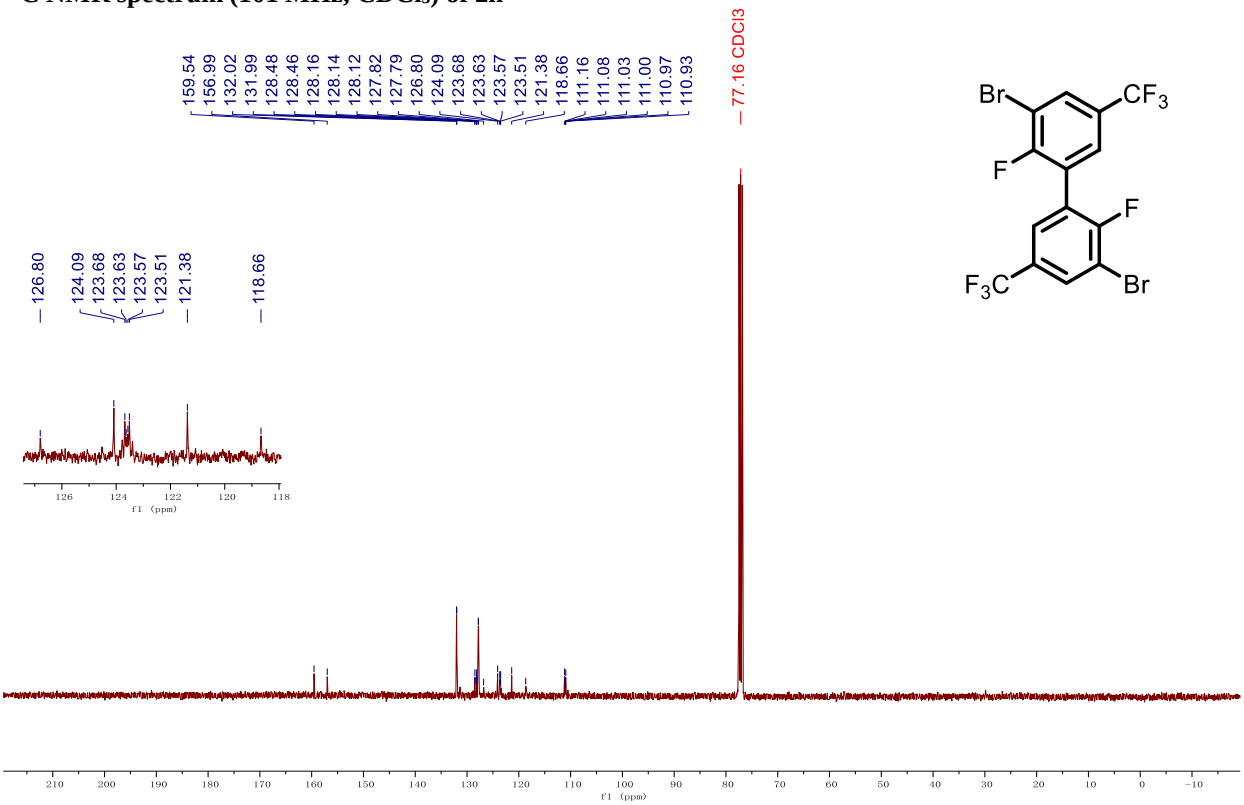
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2g



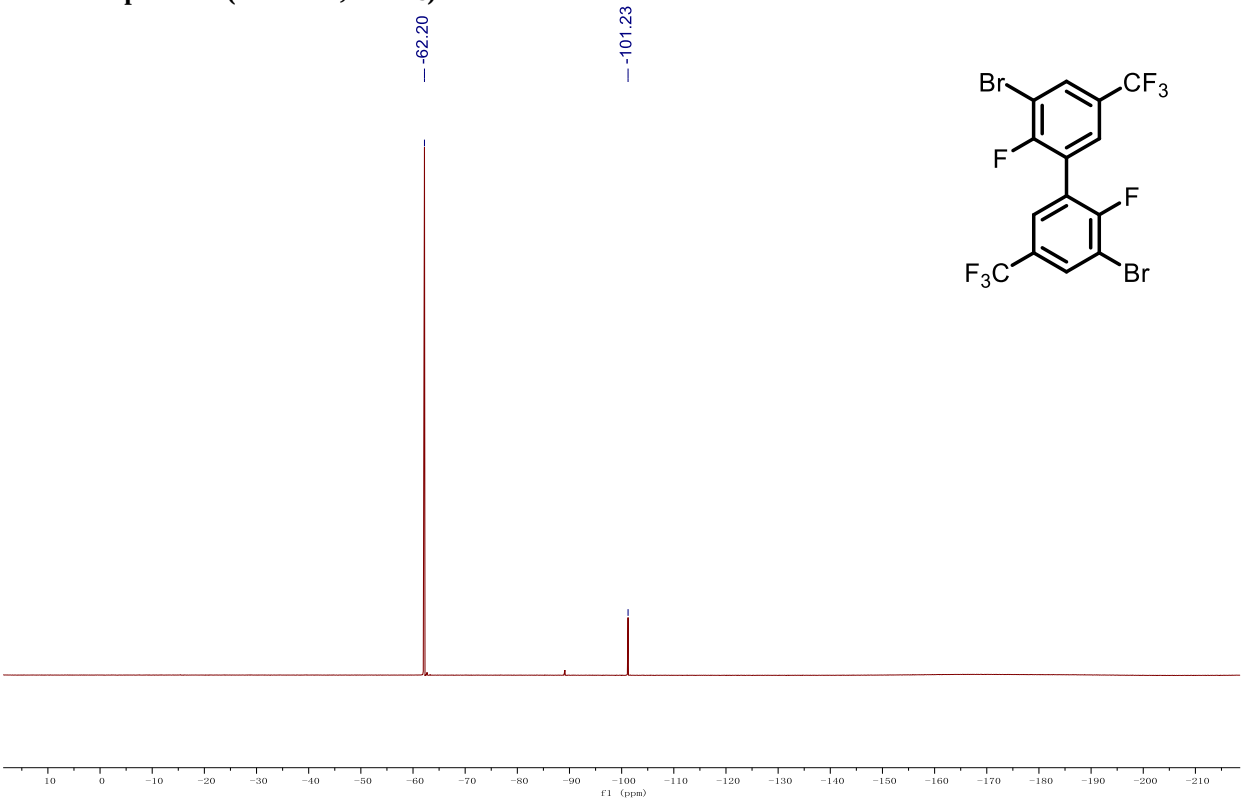
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2h



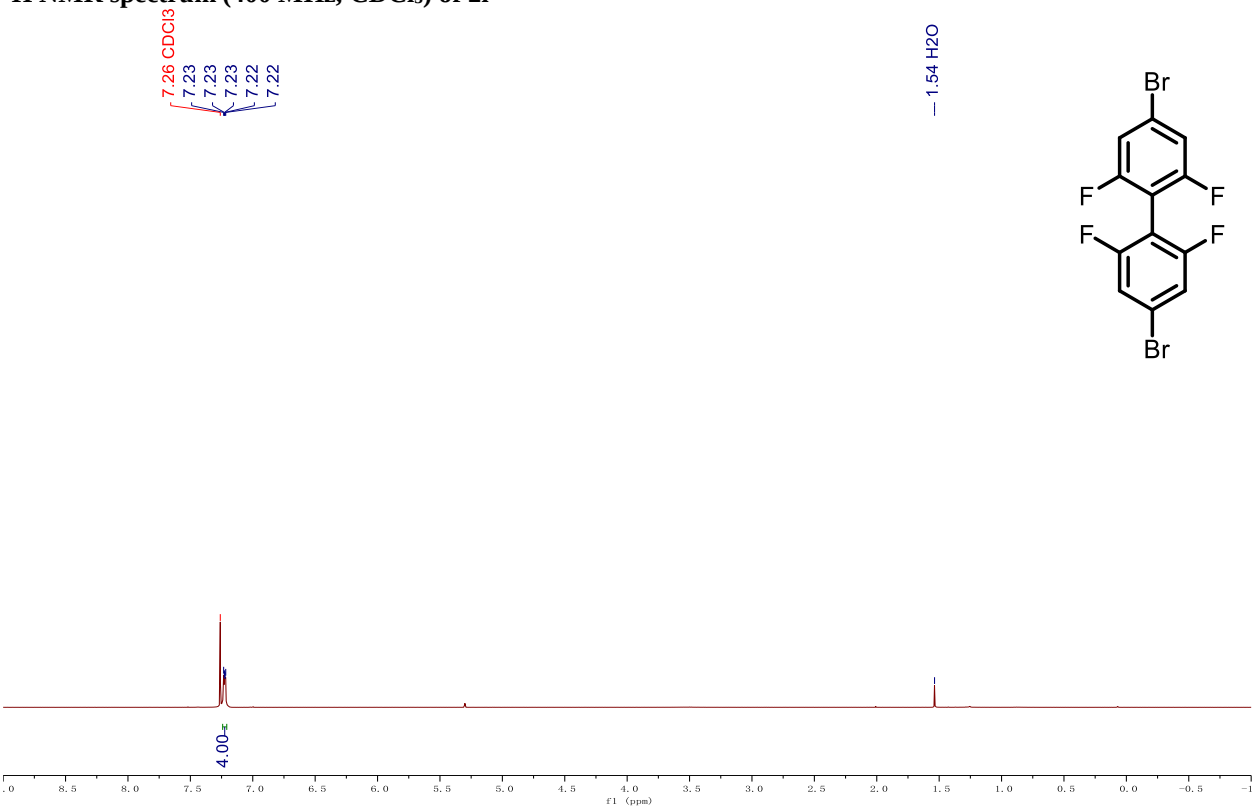
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2h



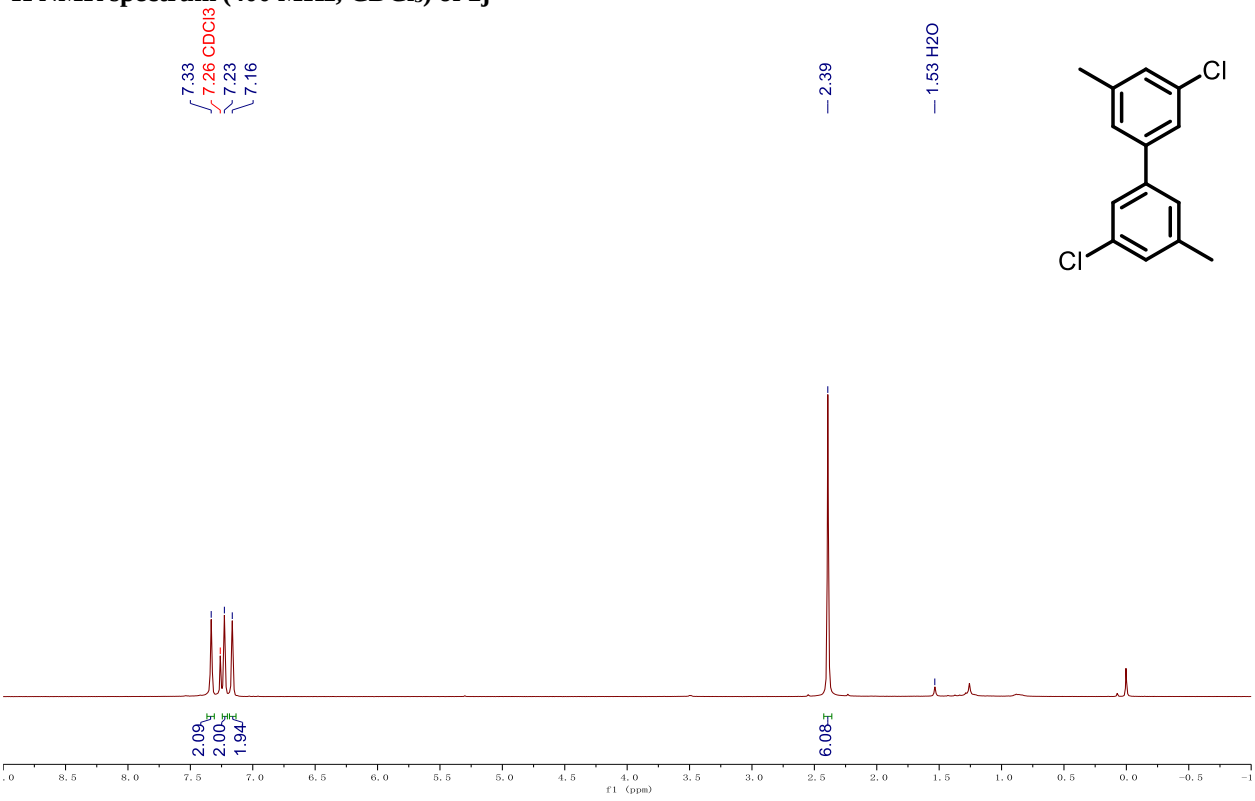
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2h



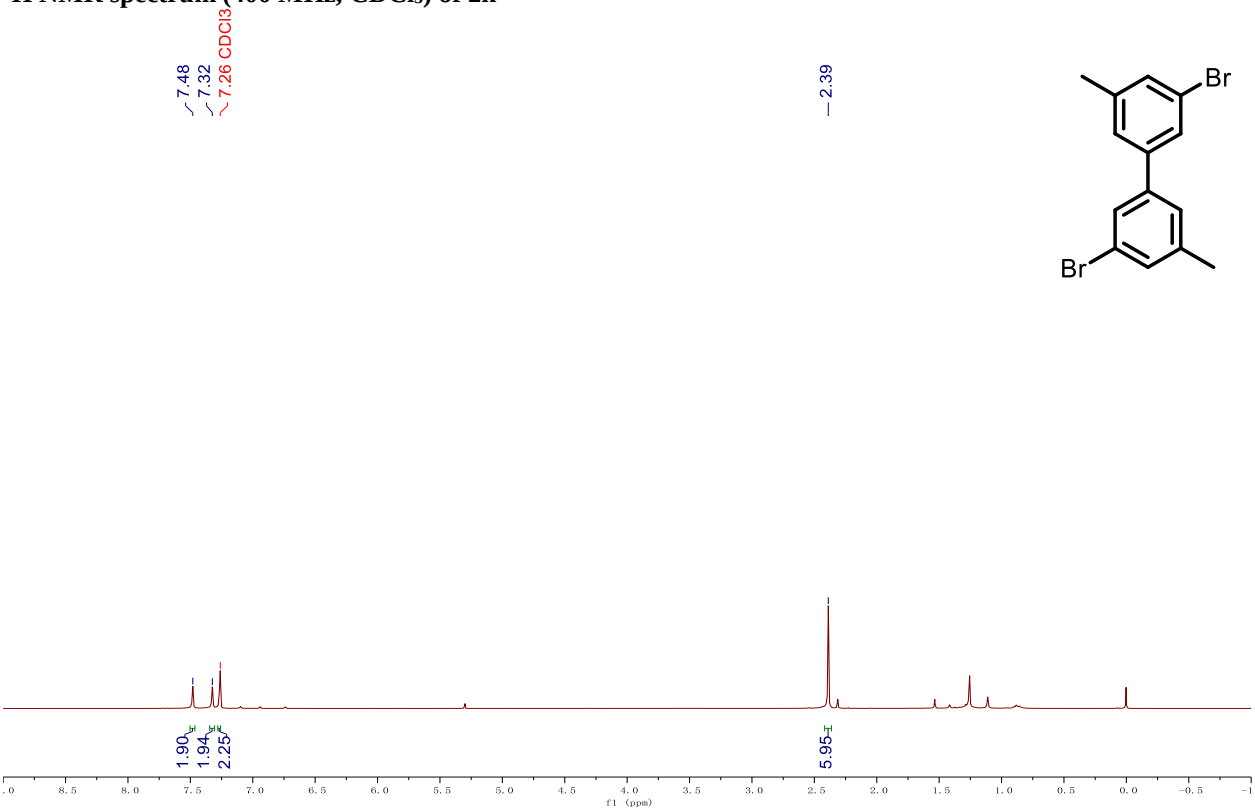
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2i



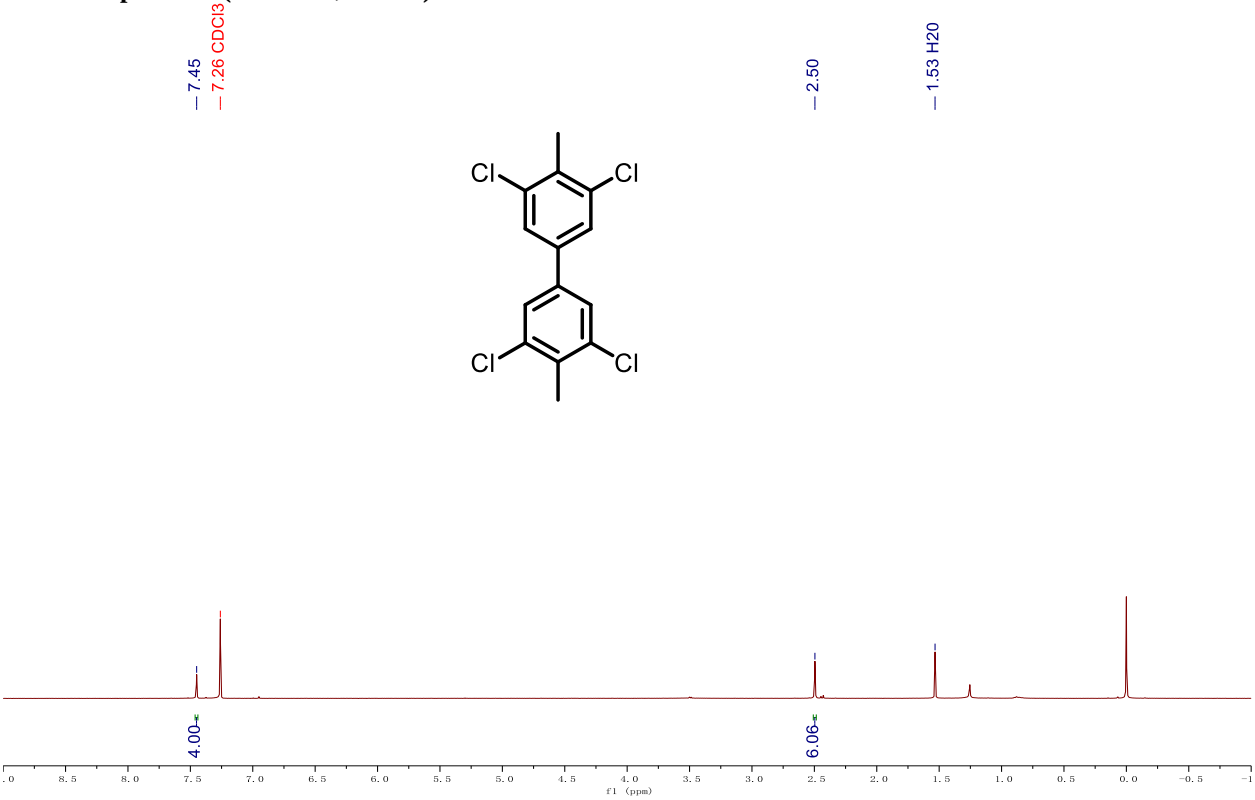
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2j



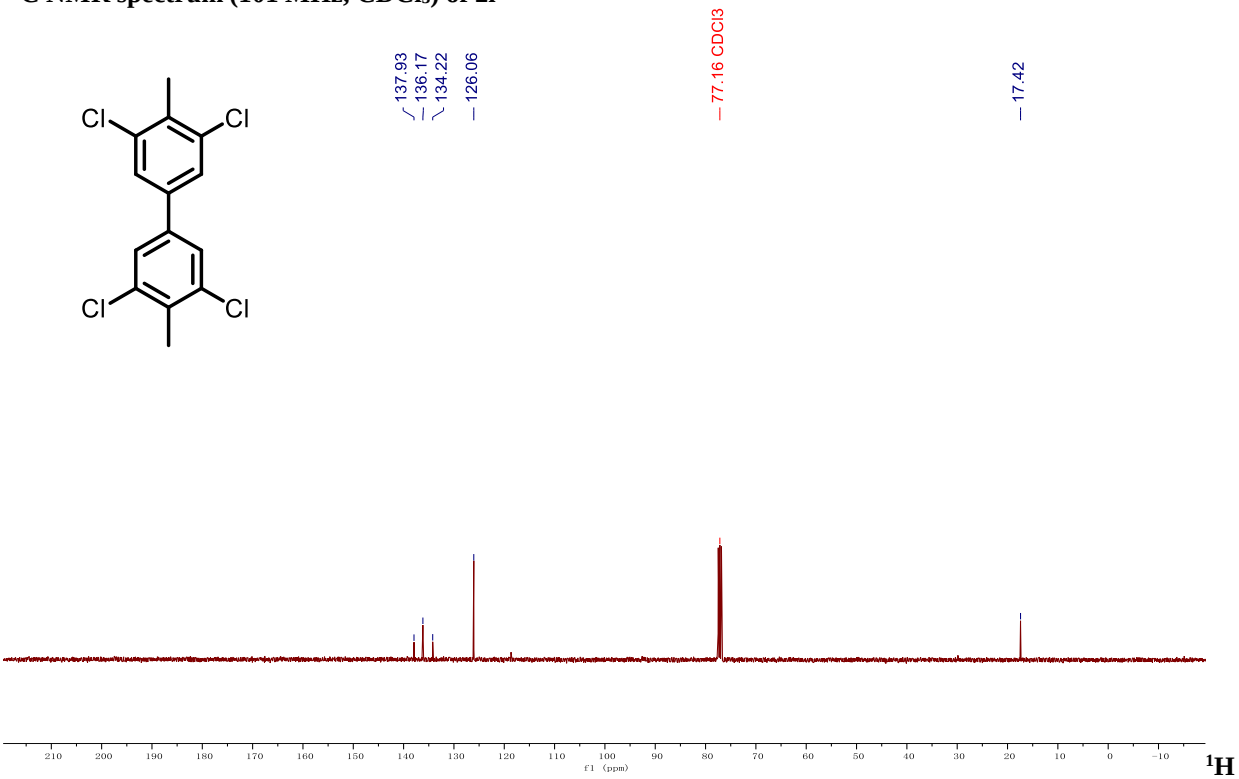
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2k



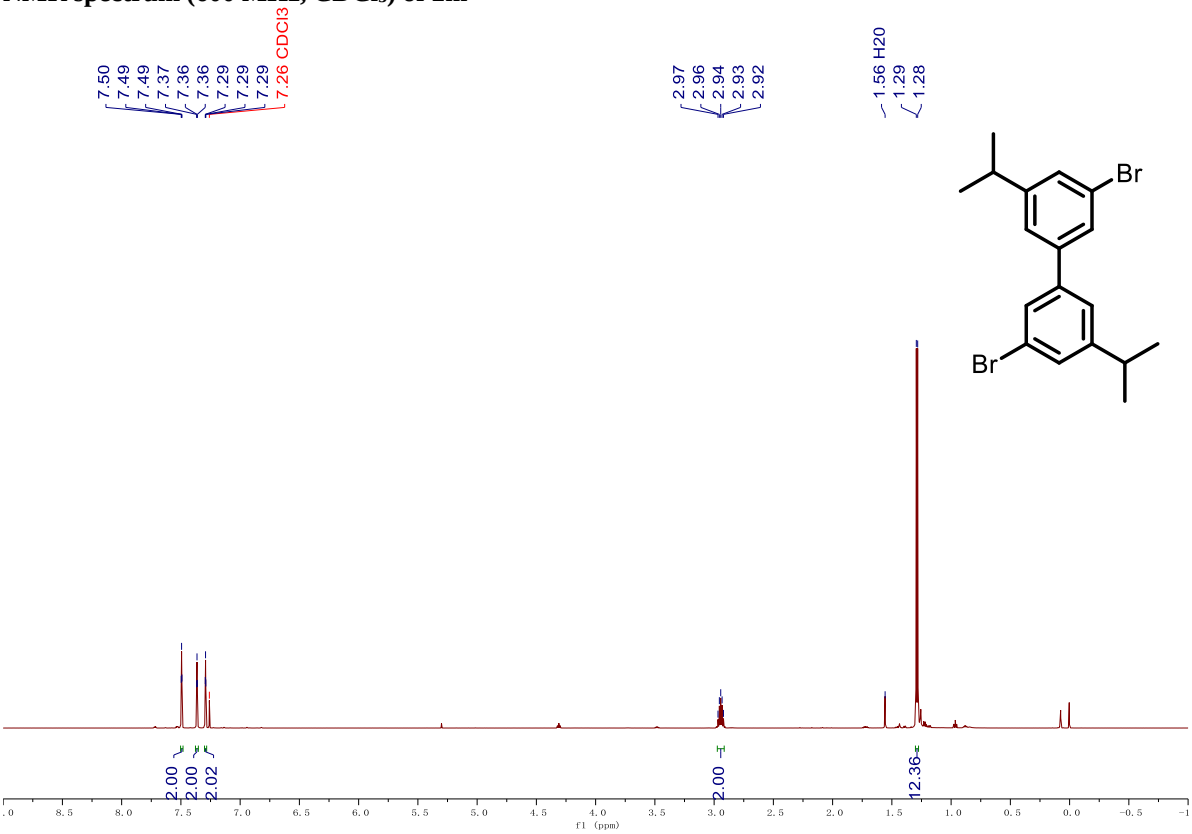
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2l



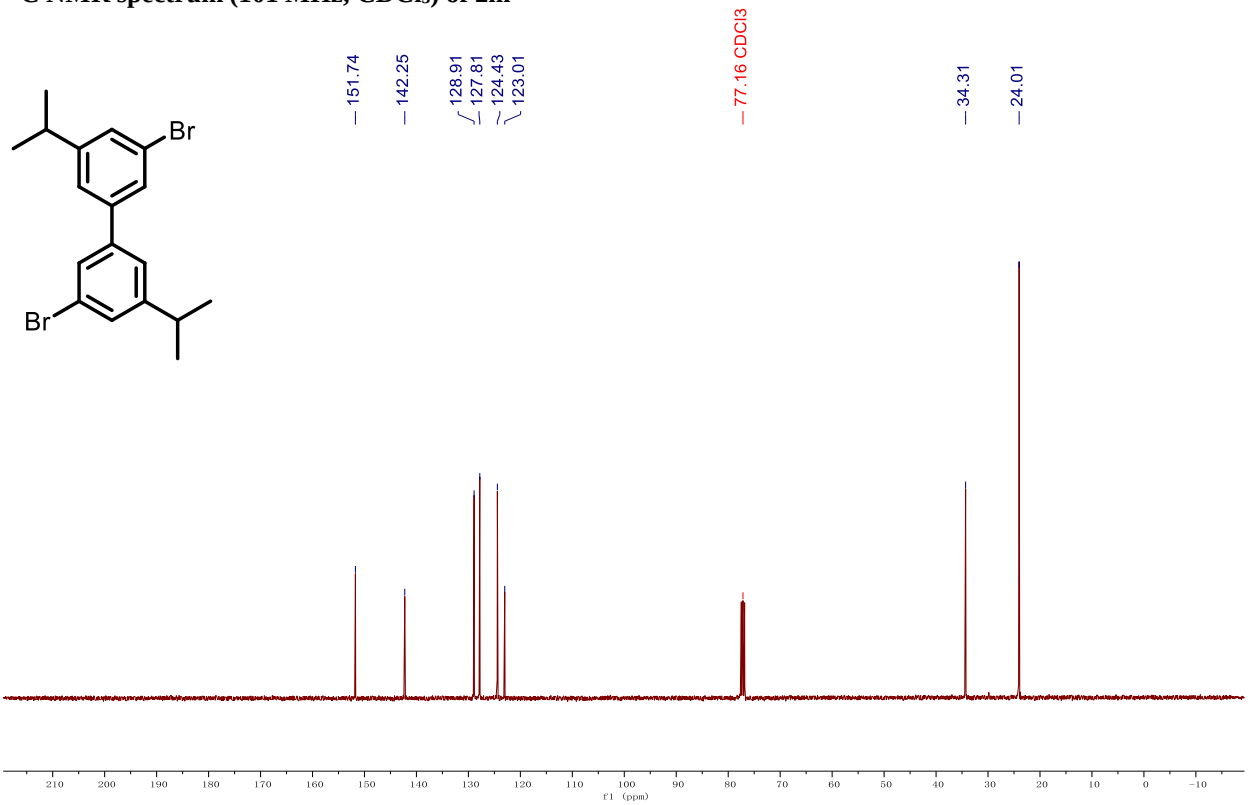
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2l



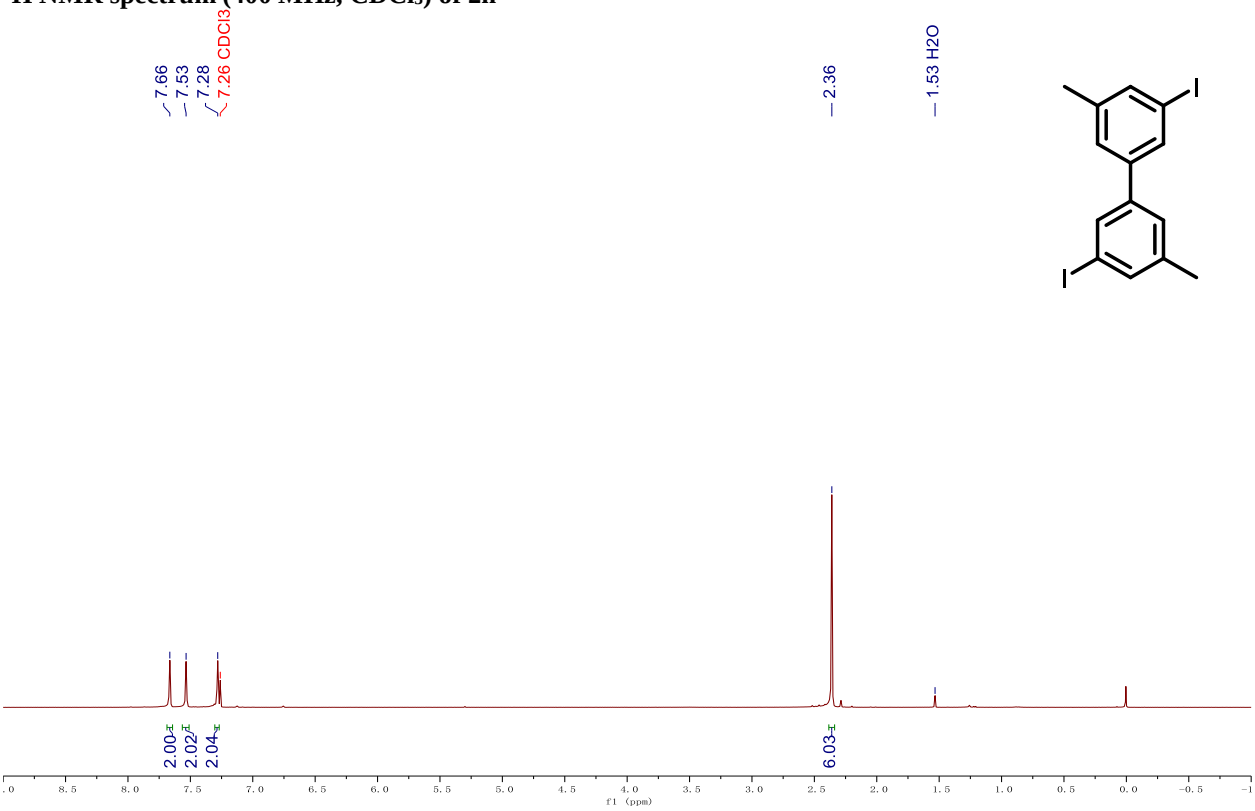
^{1}H NMR spectrum (600 MHz, $CDCl_3$) of 2m



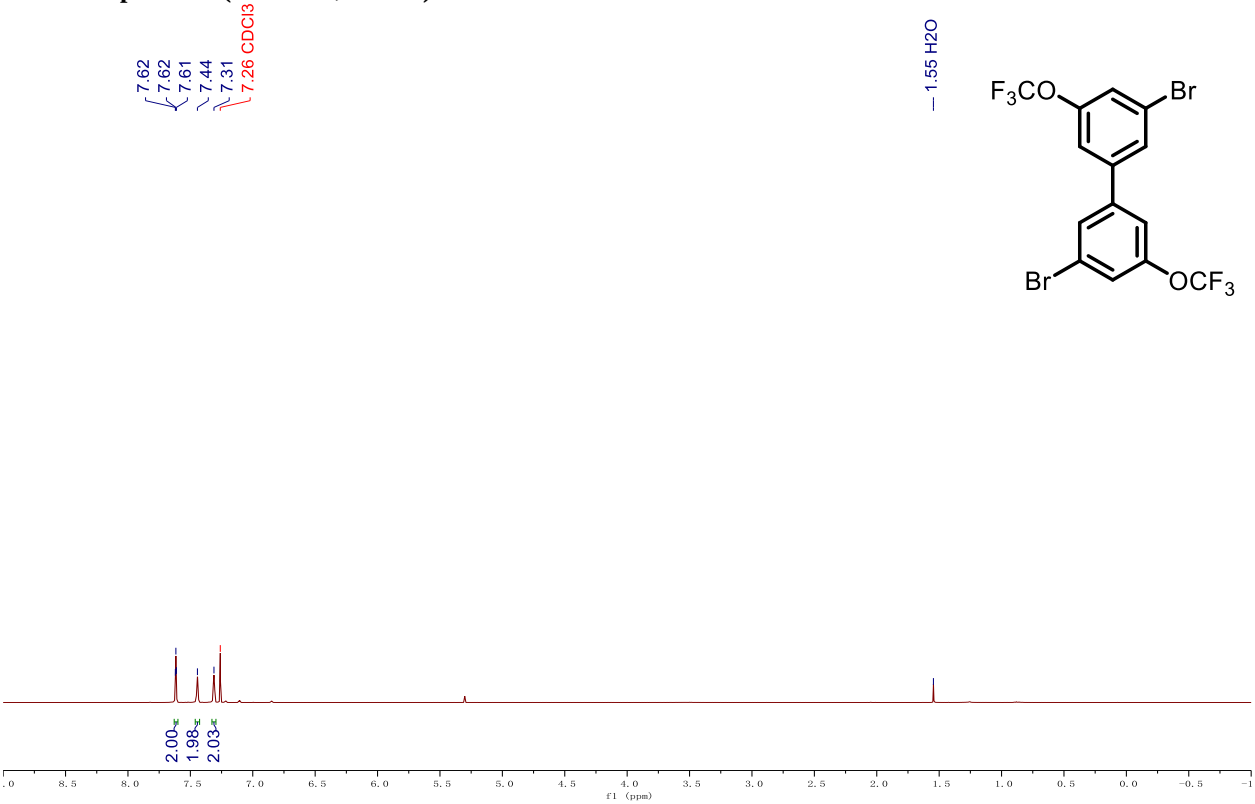
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2m



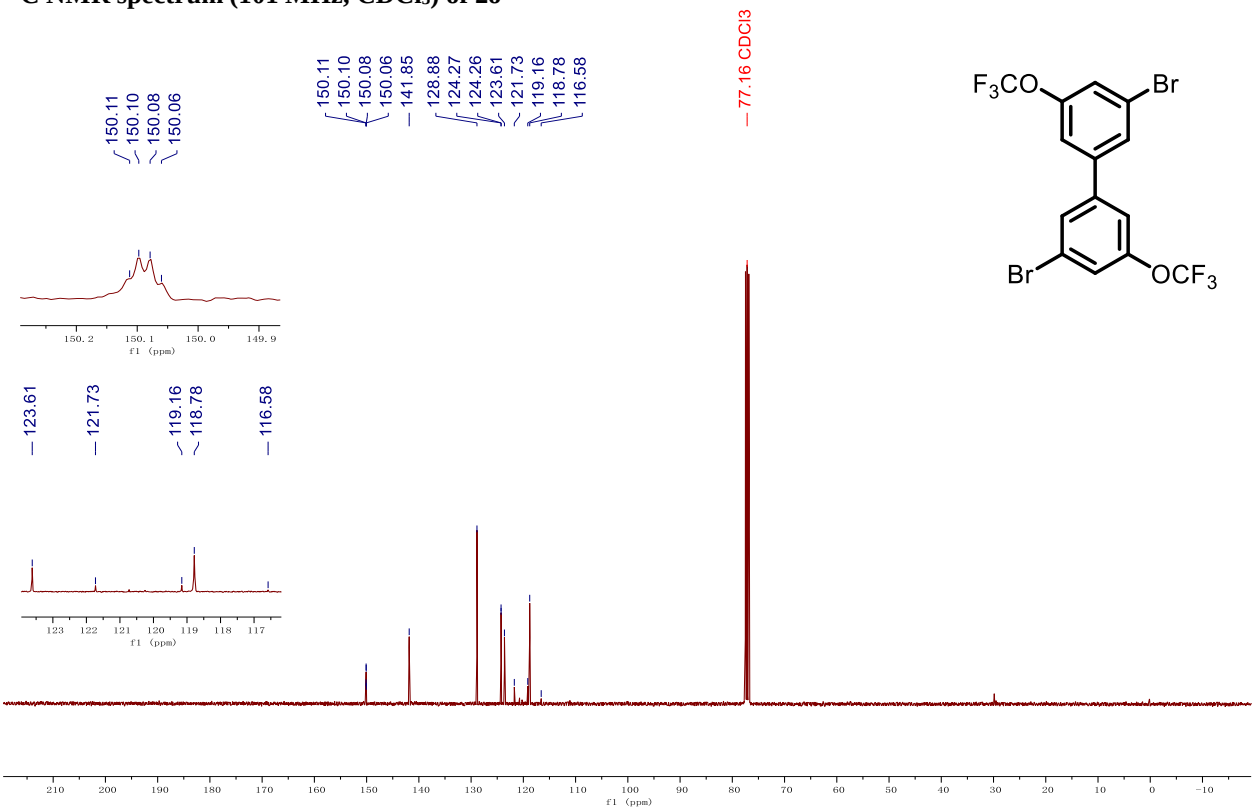
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2n



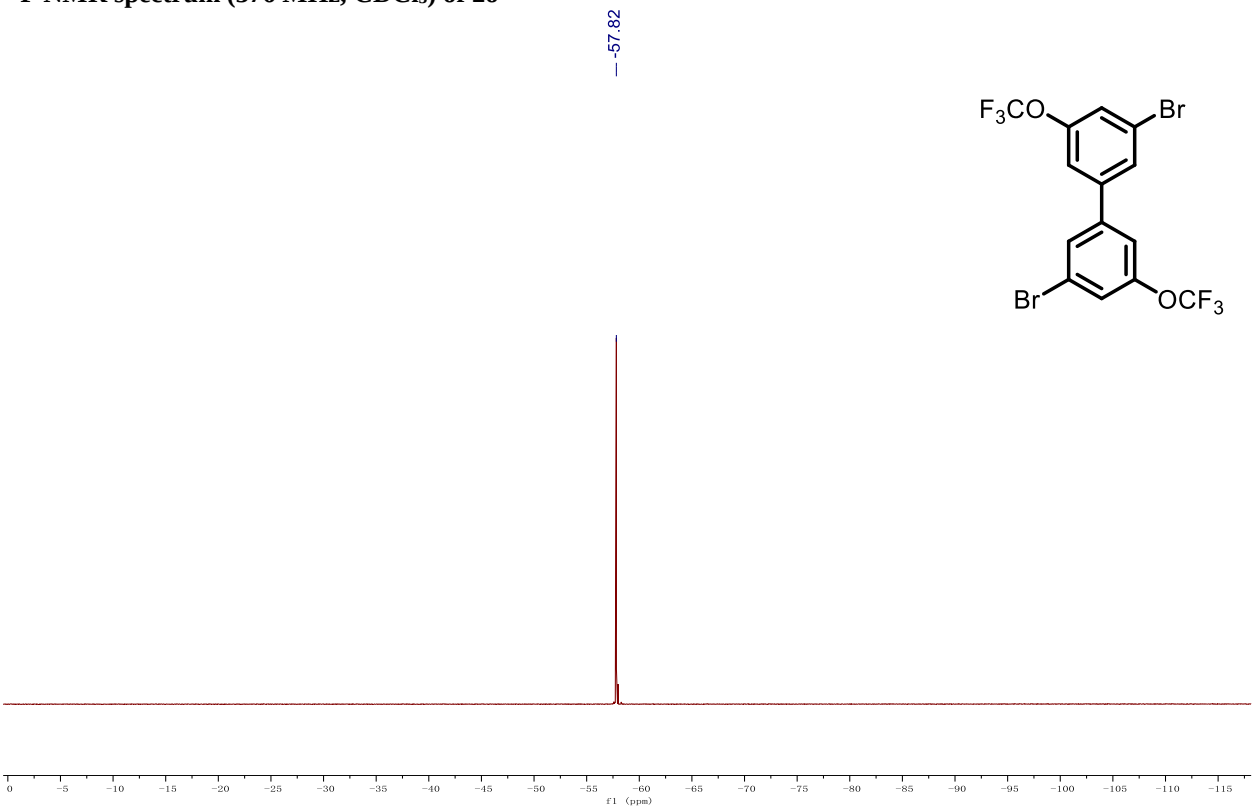
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2o



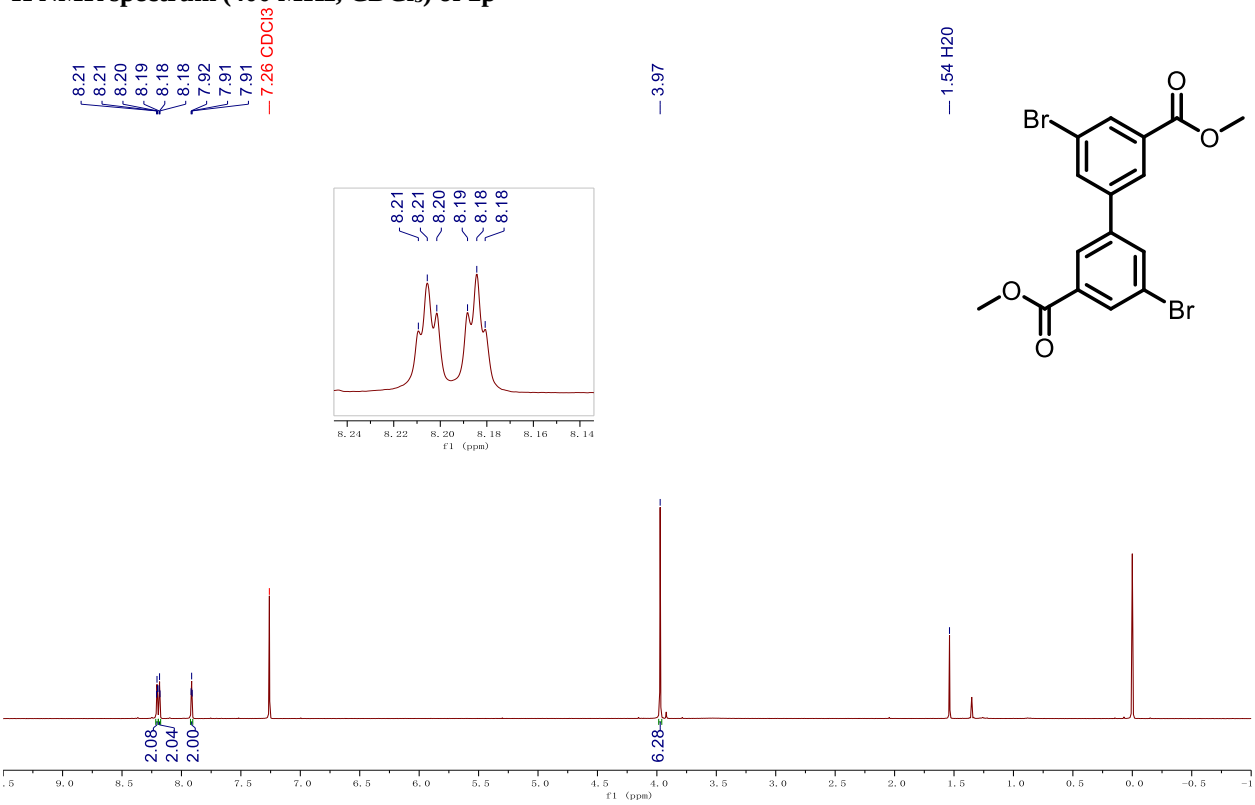
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2o



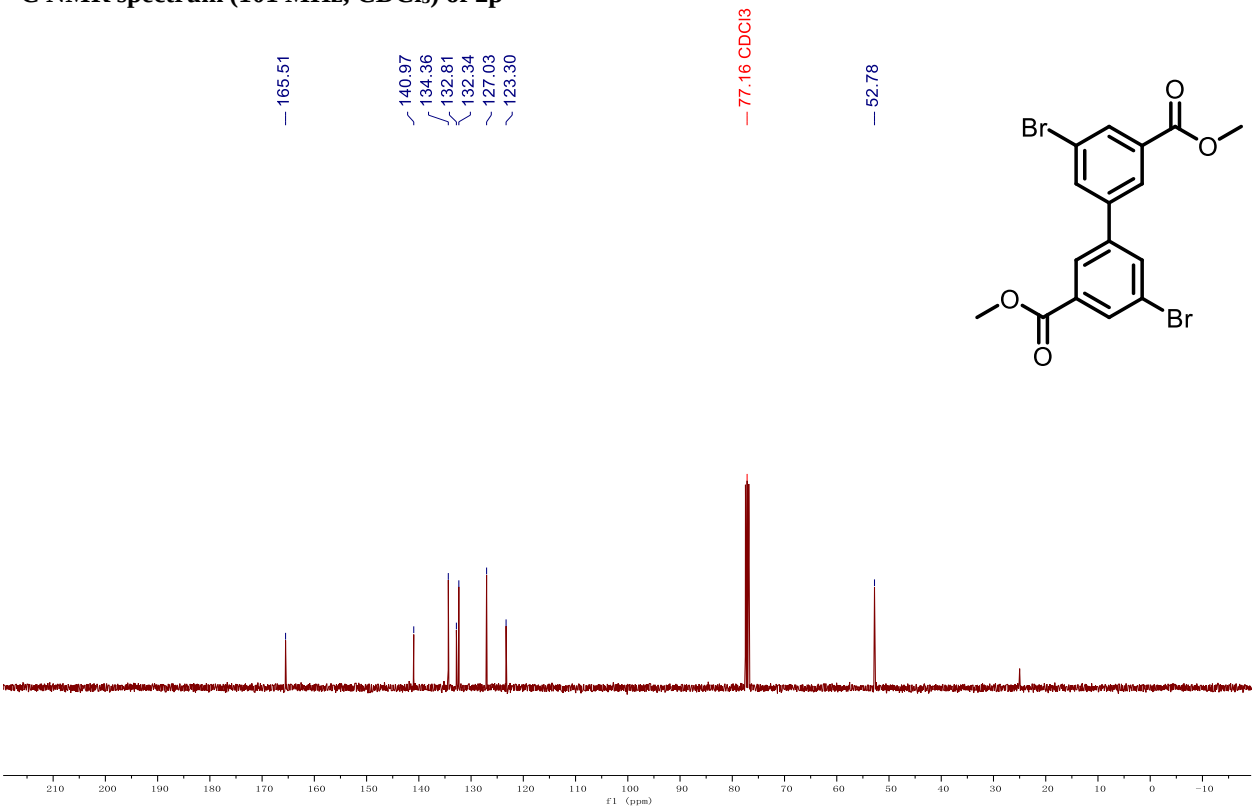
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2o



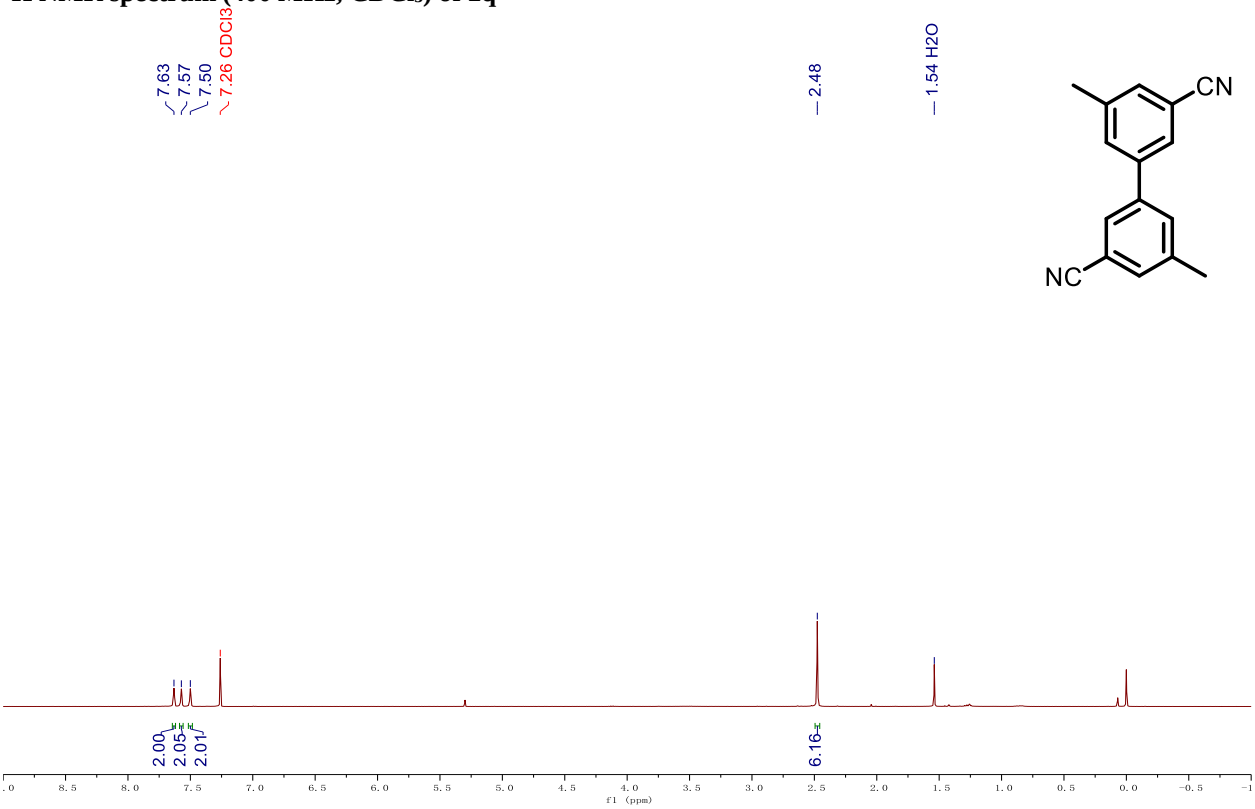
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2p



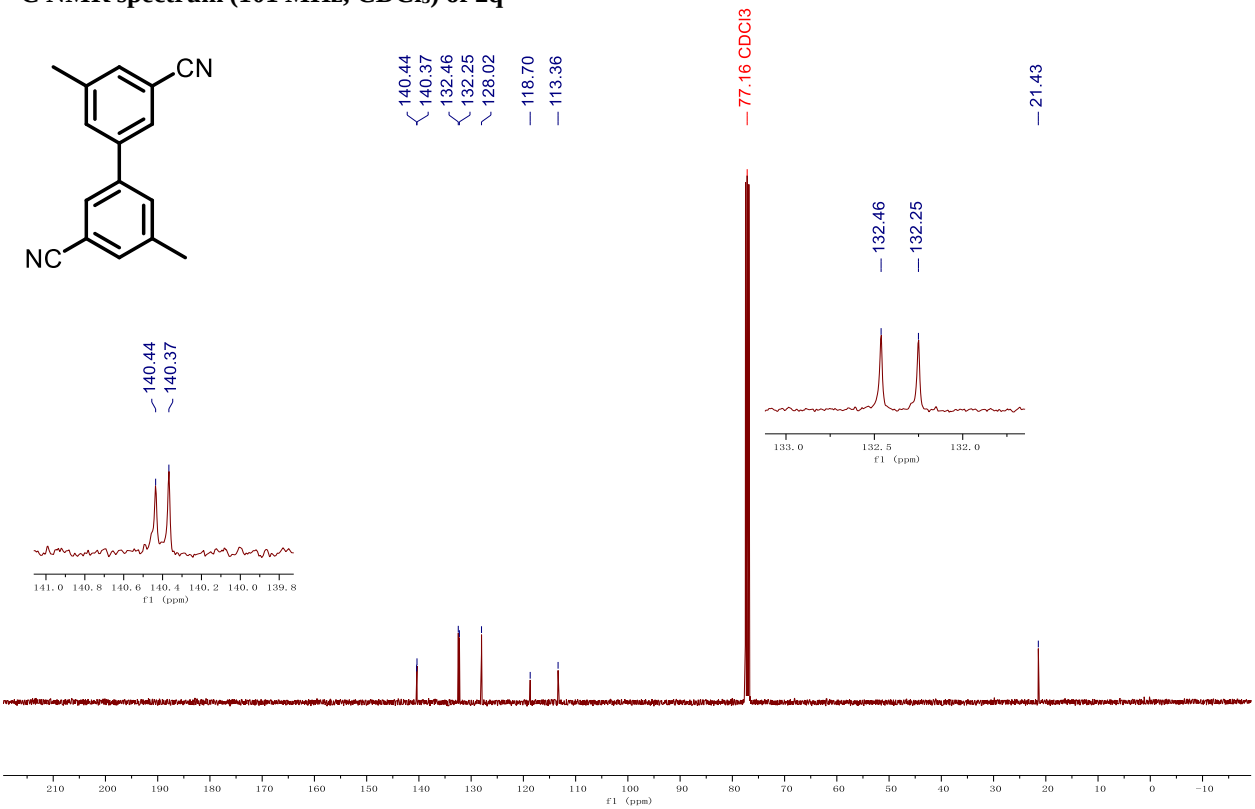
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2p



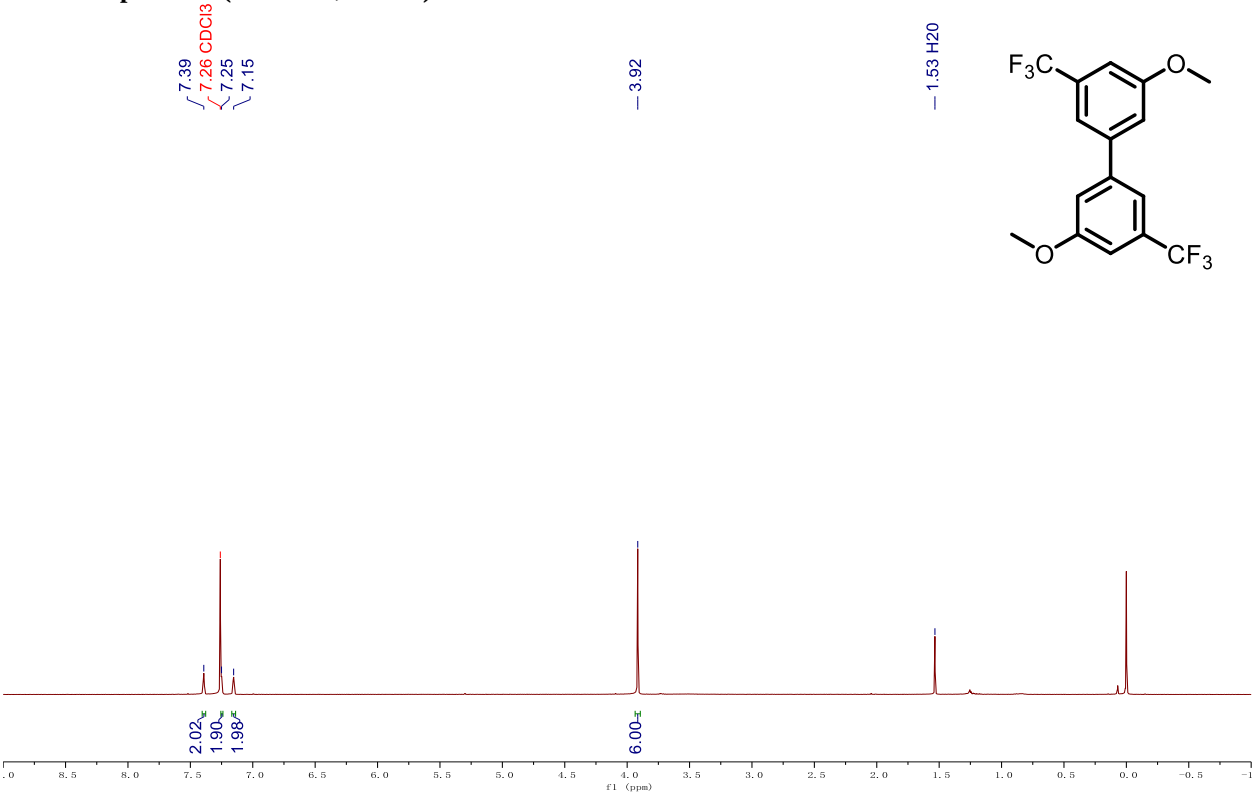
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2q



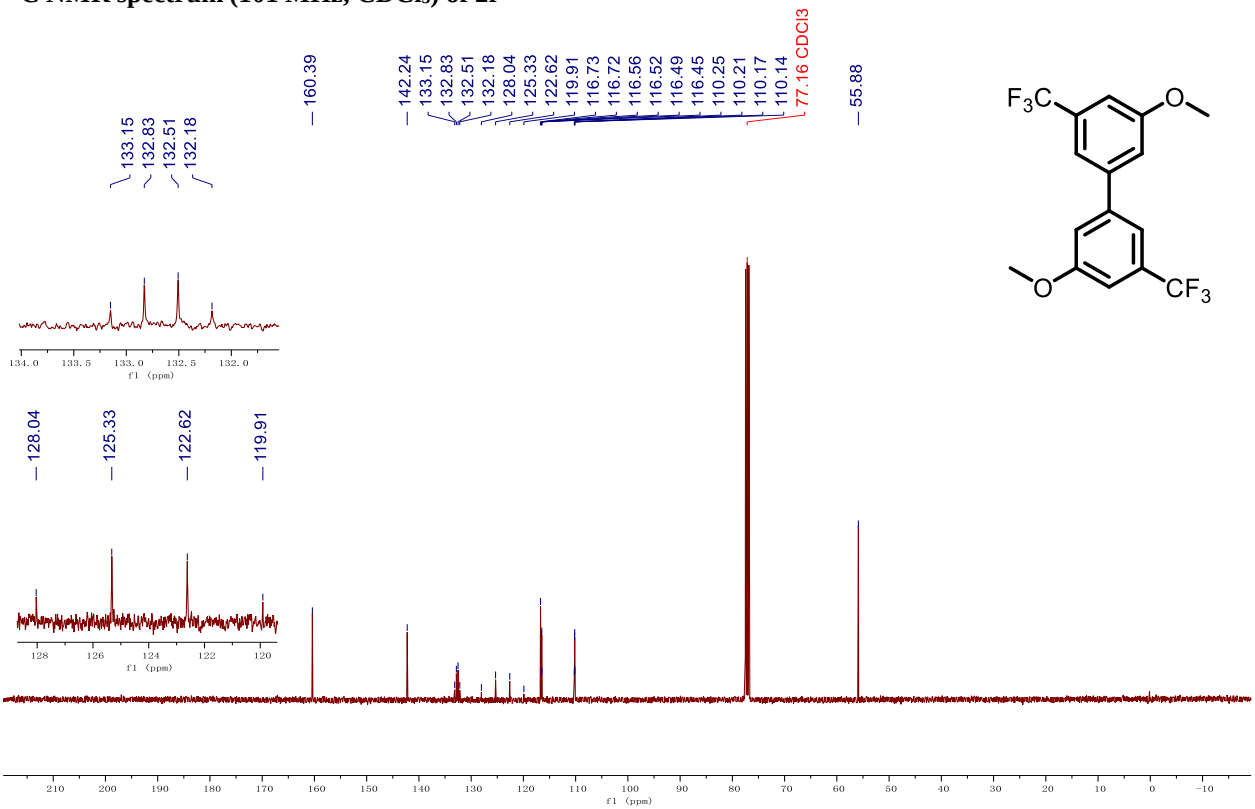
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2q



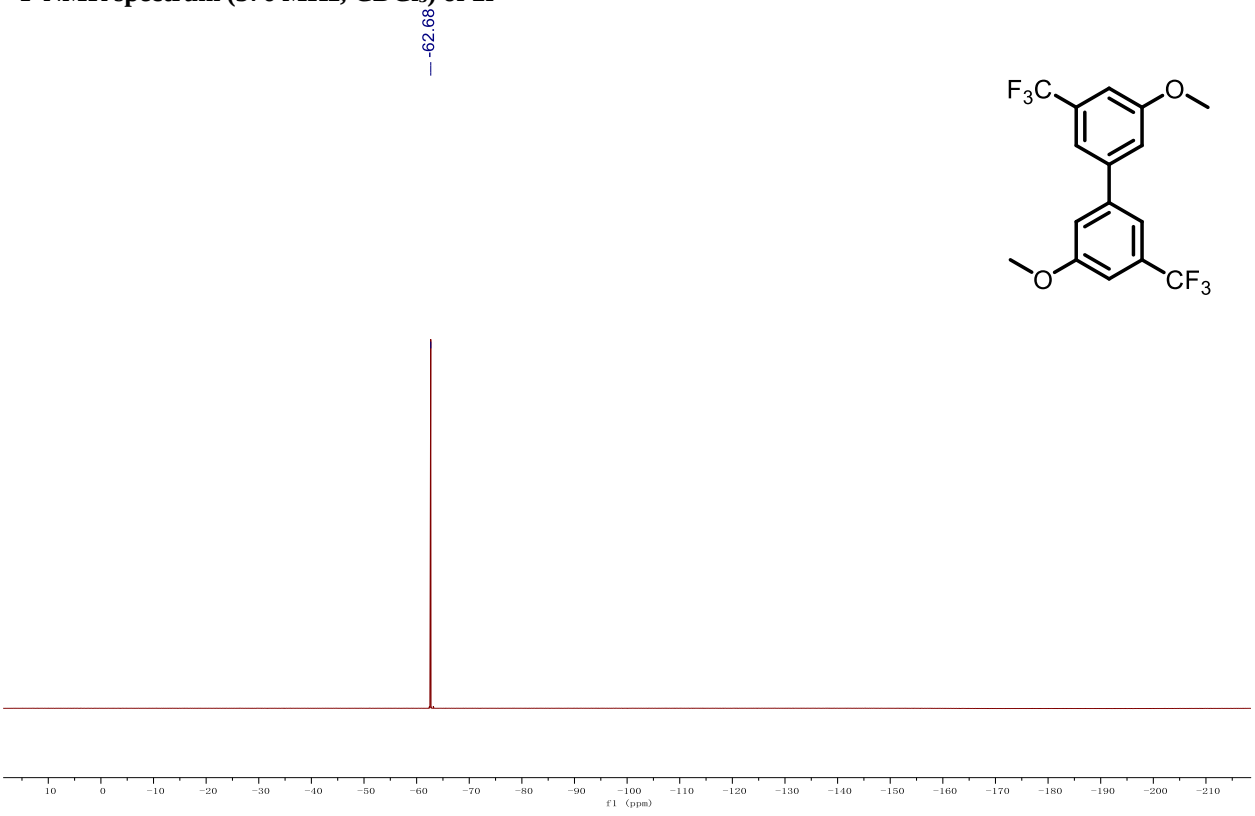
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2r



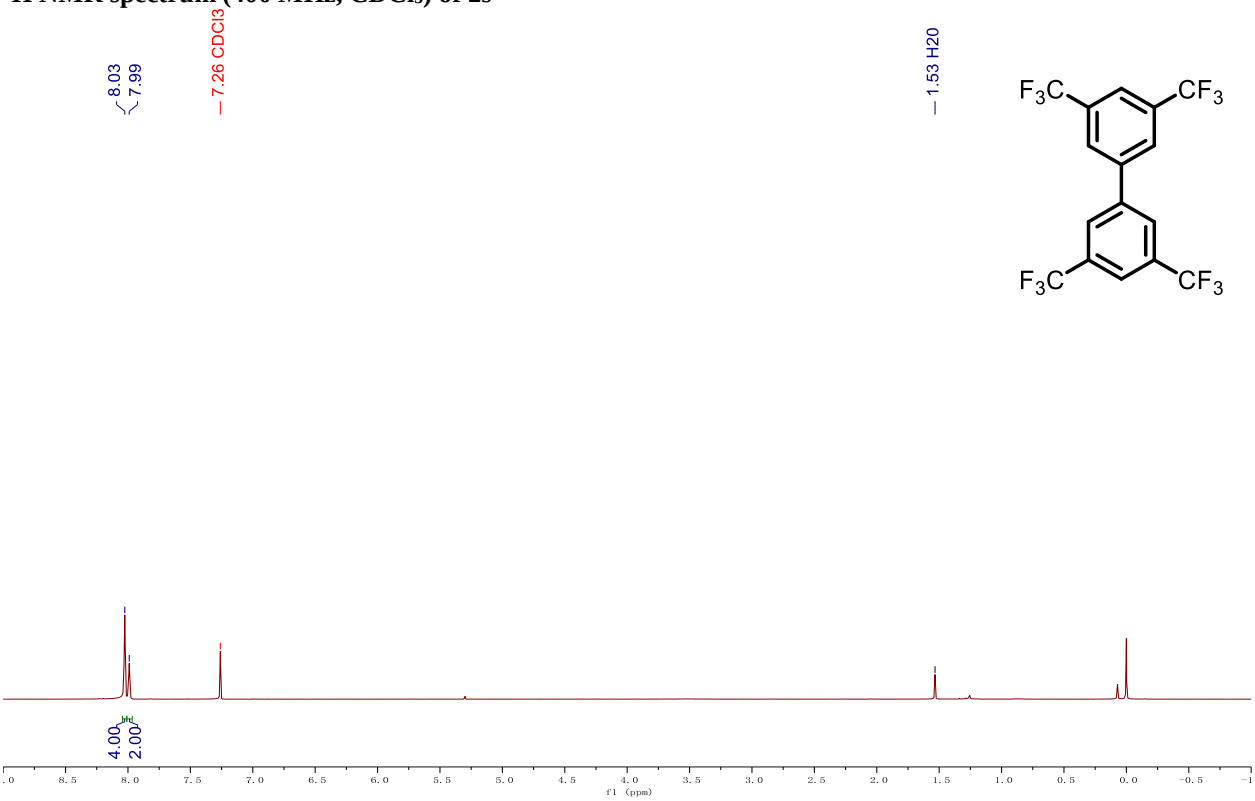
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2r



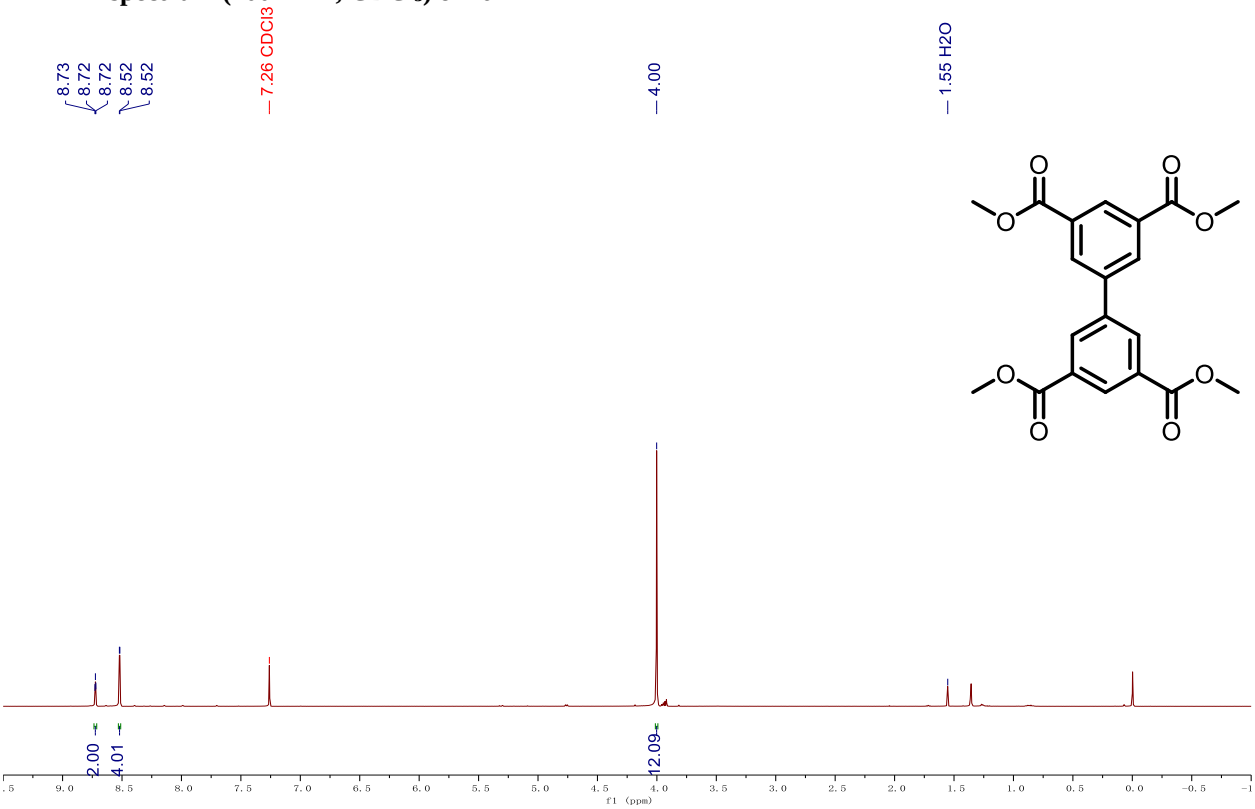
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2r



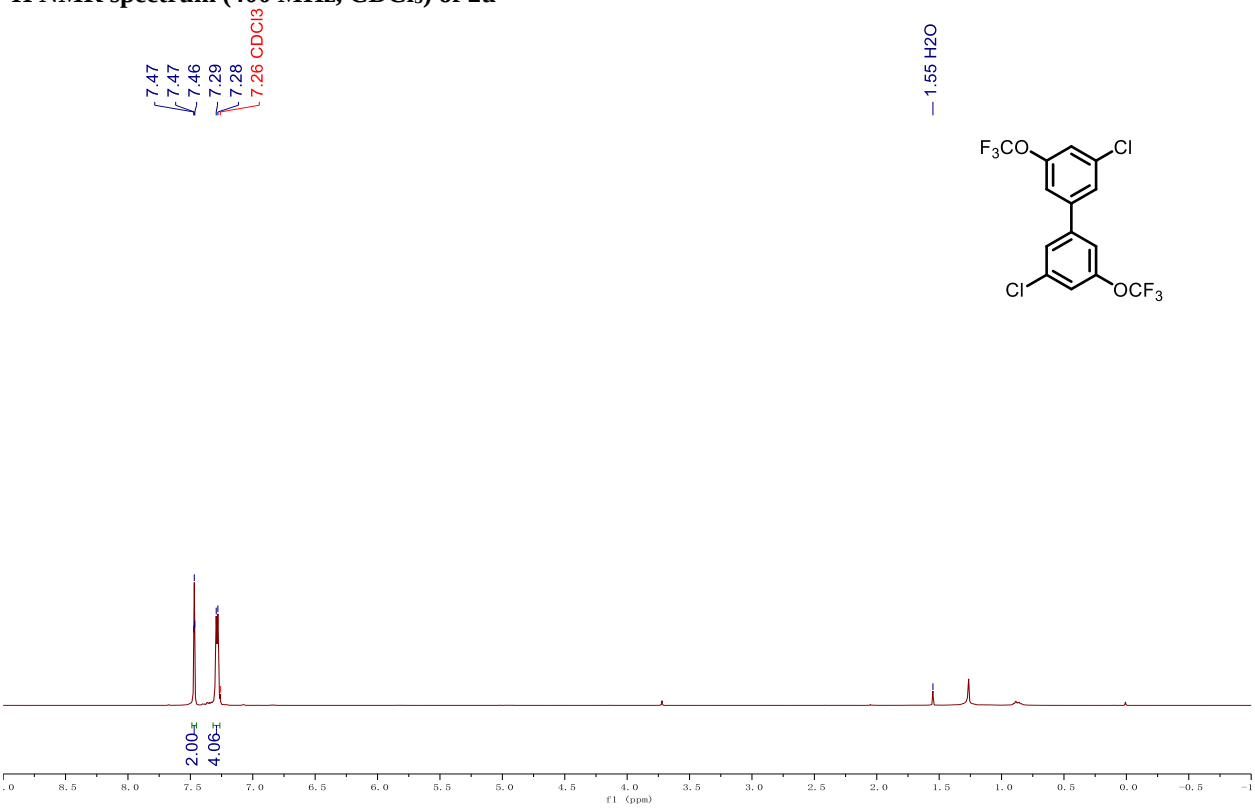
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2s



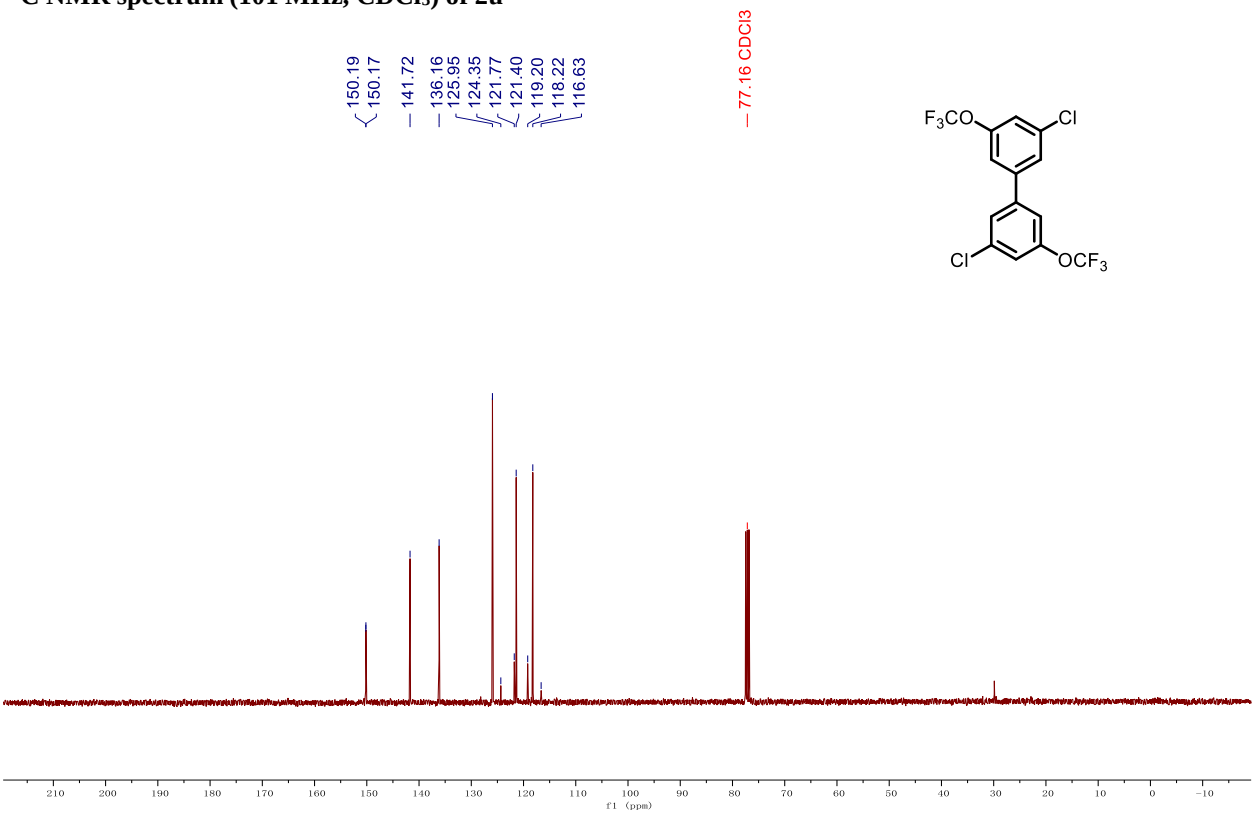
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2t



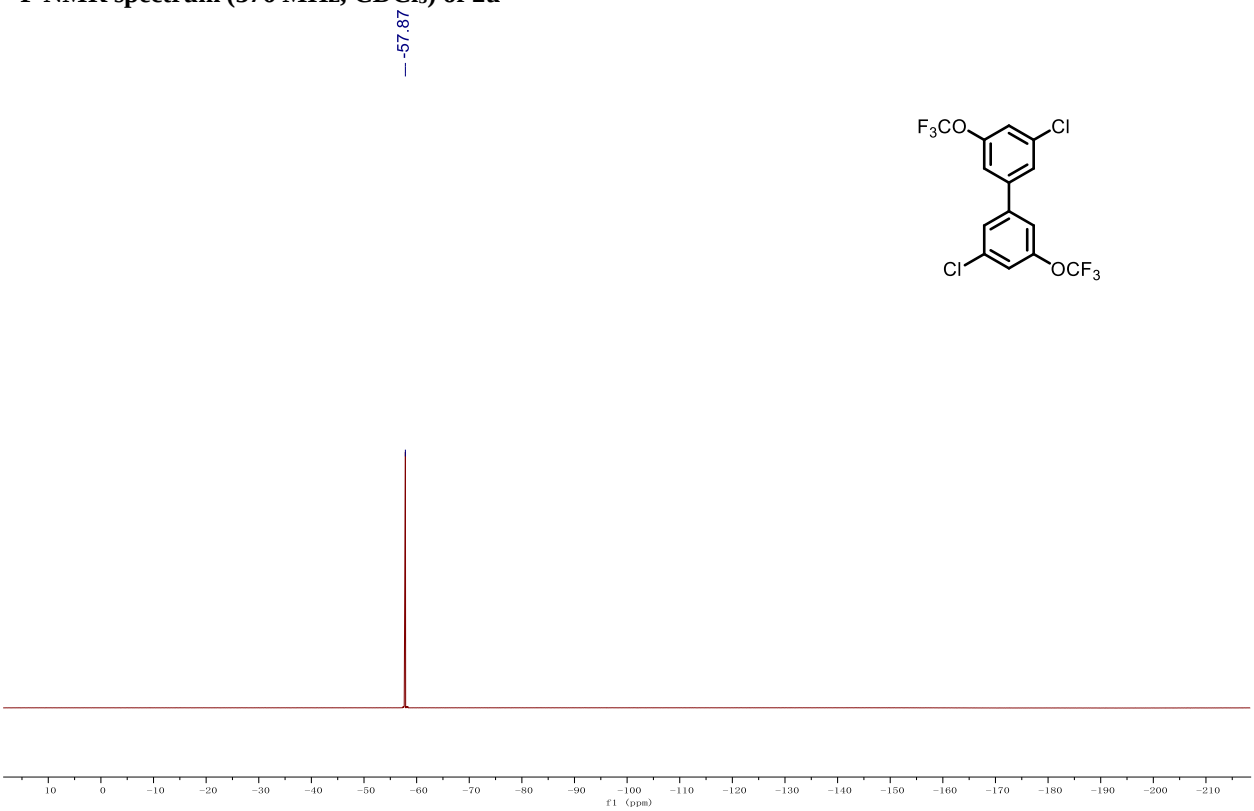
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2u



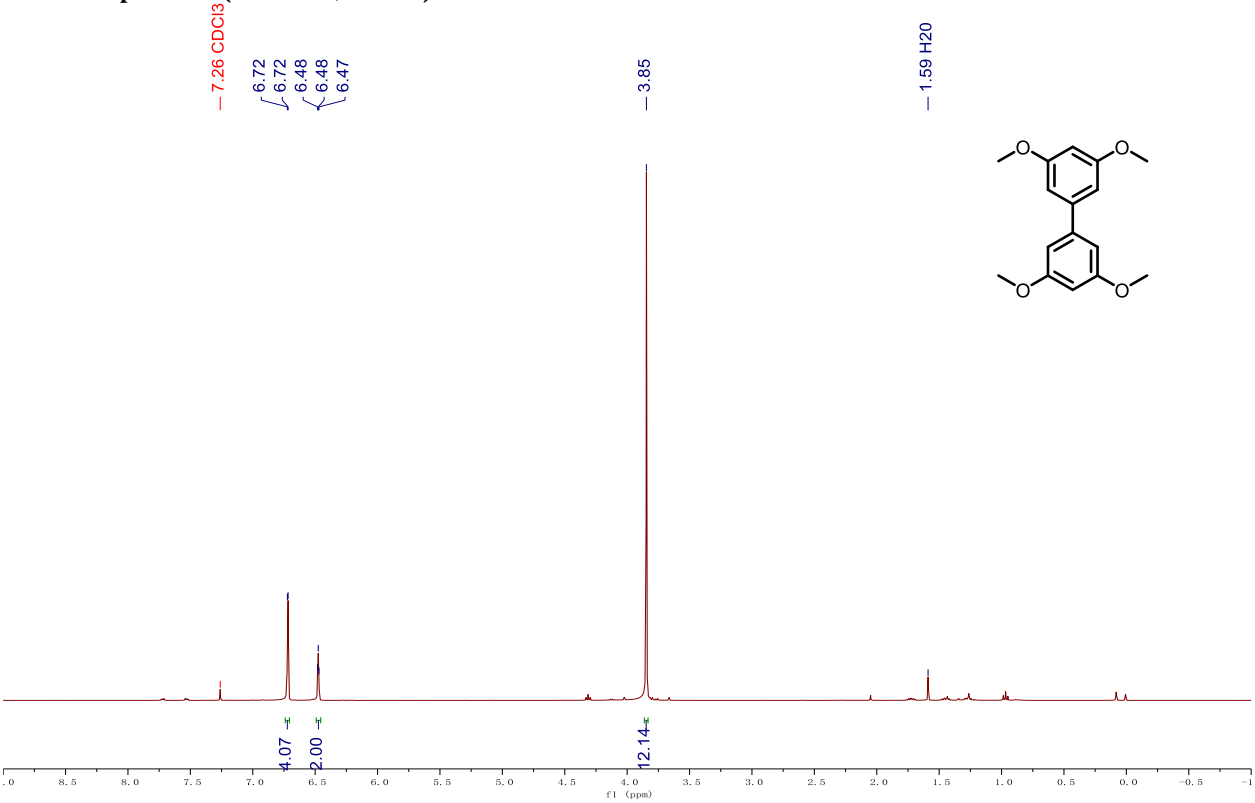
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2u



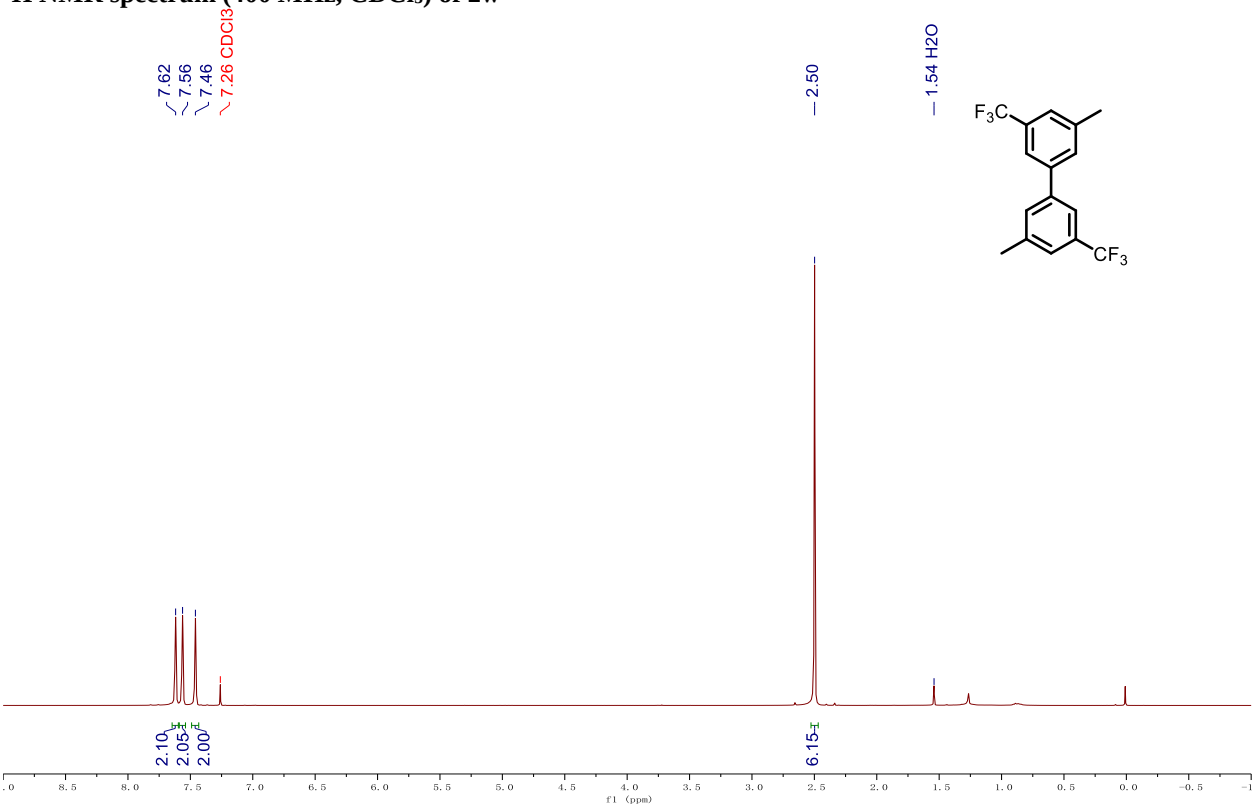
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2u



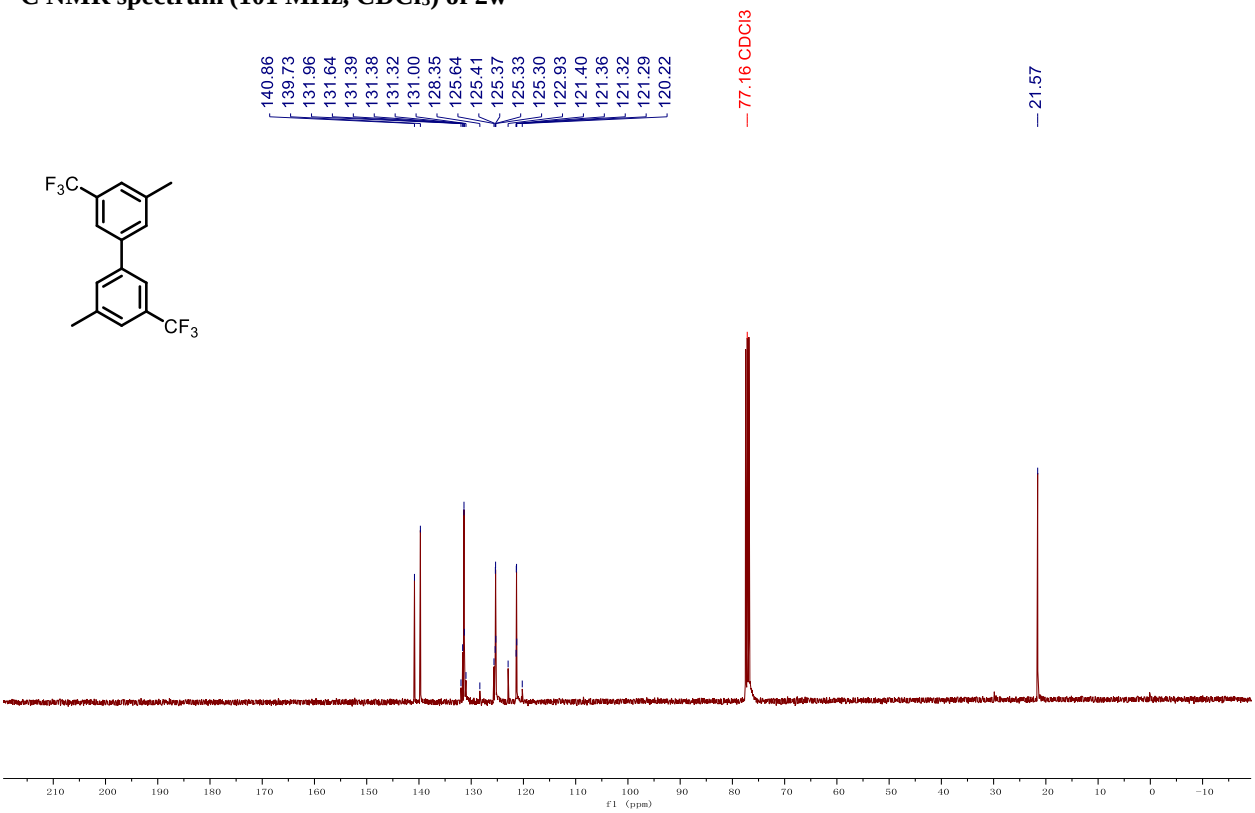
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2v



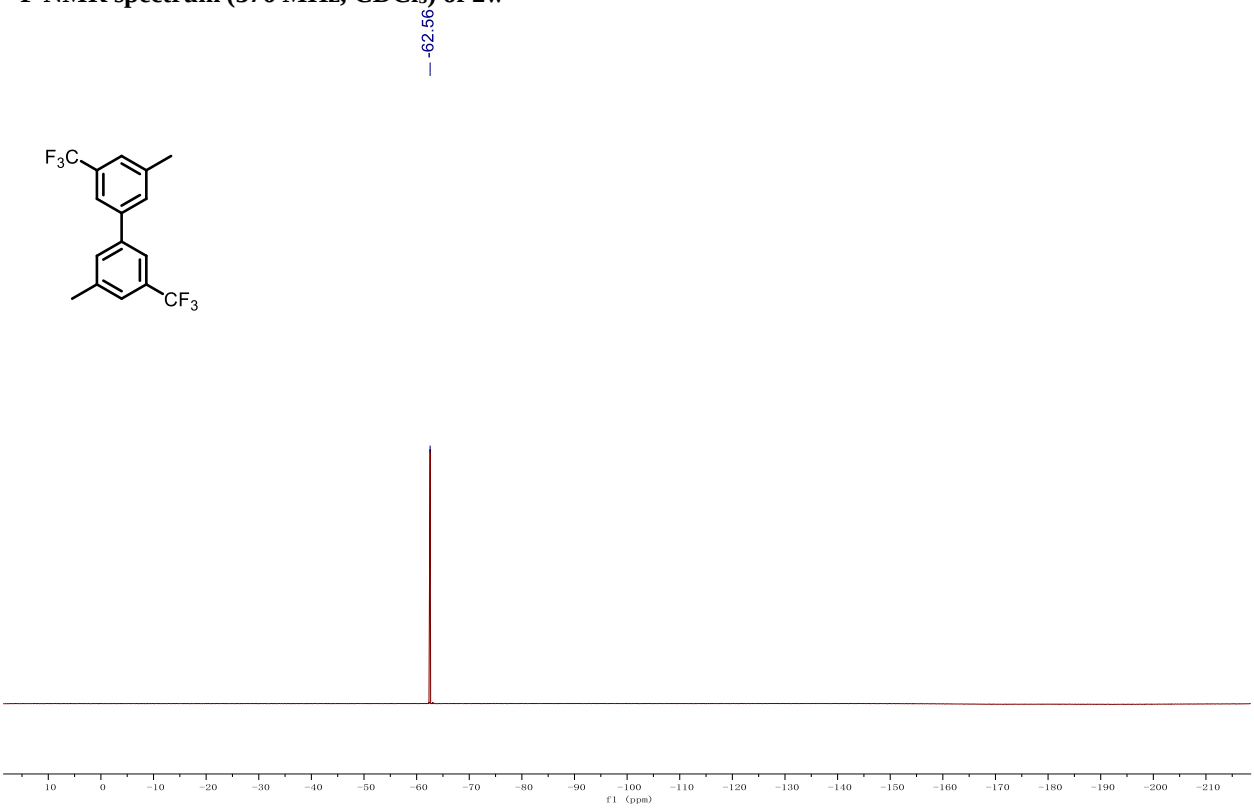
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2w



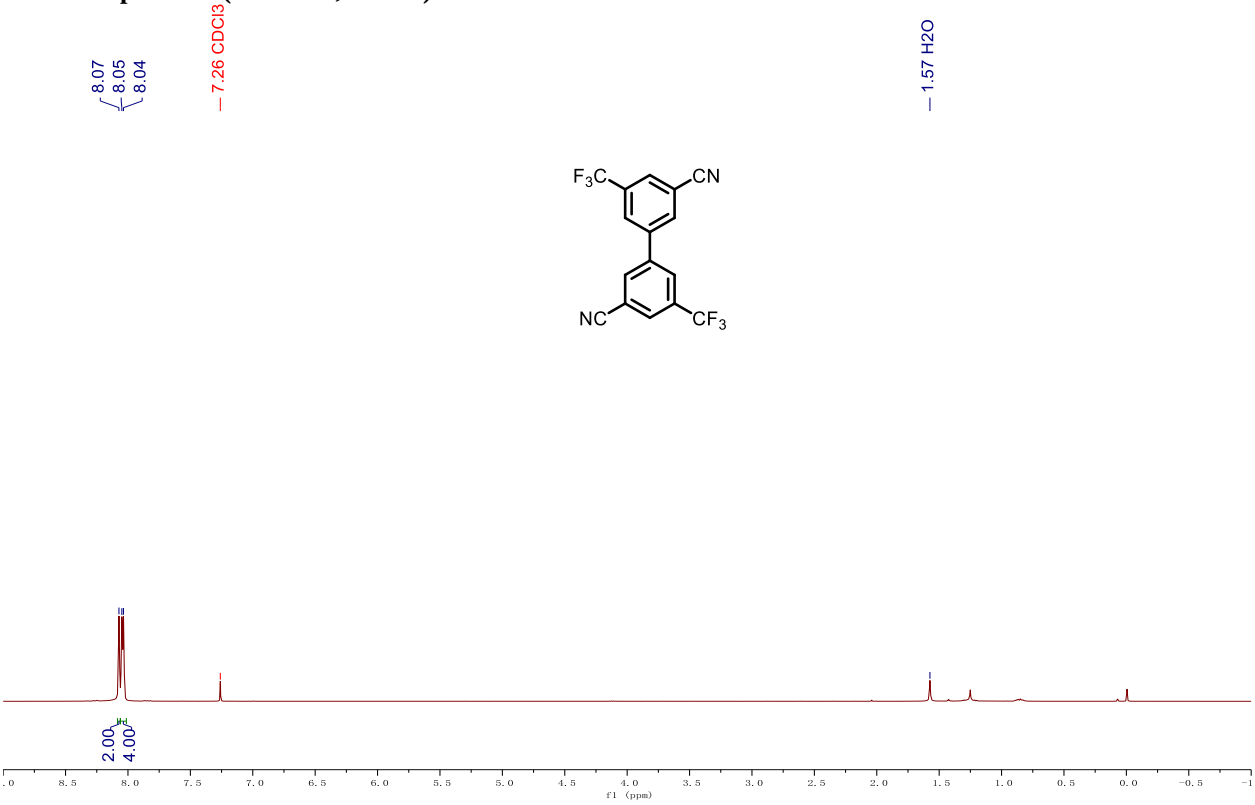
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2w



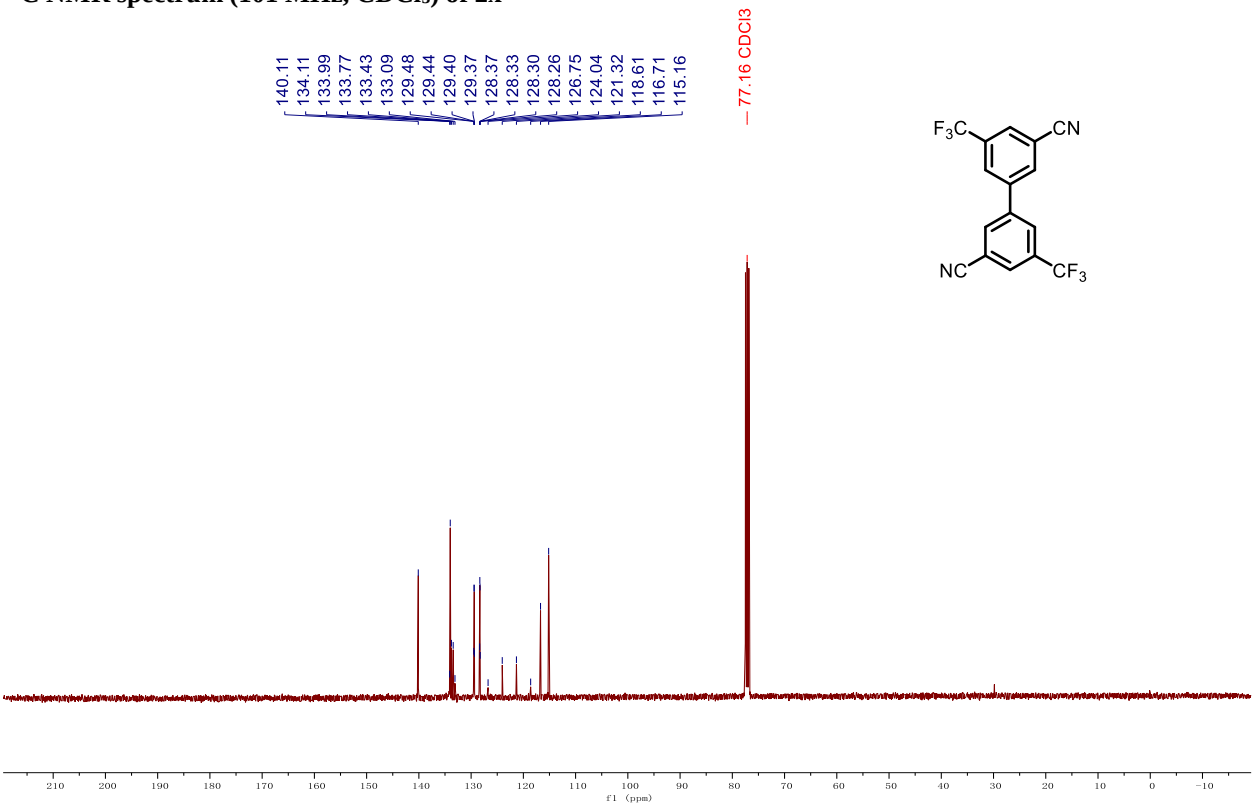
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2w



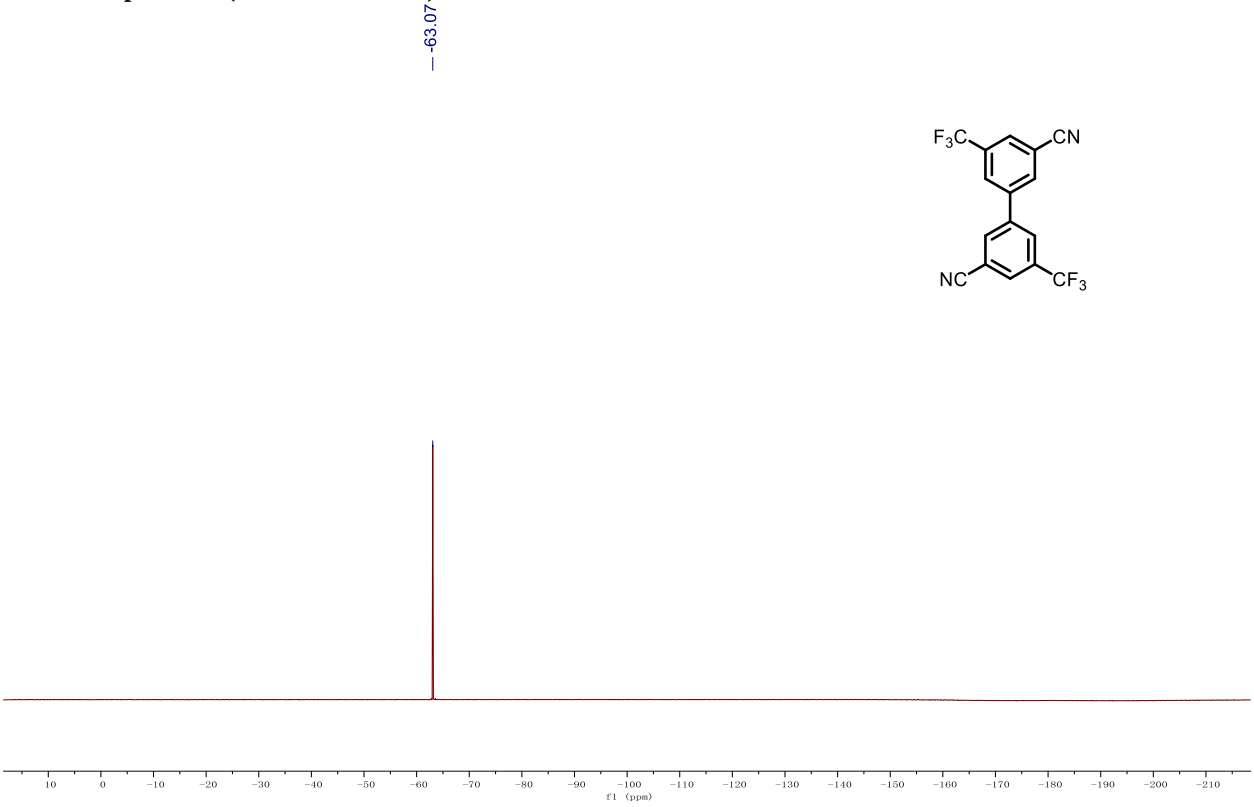
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2x



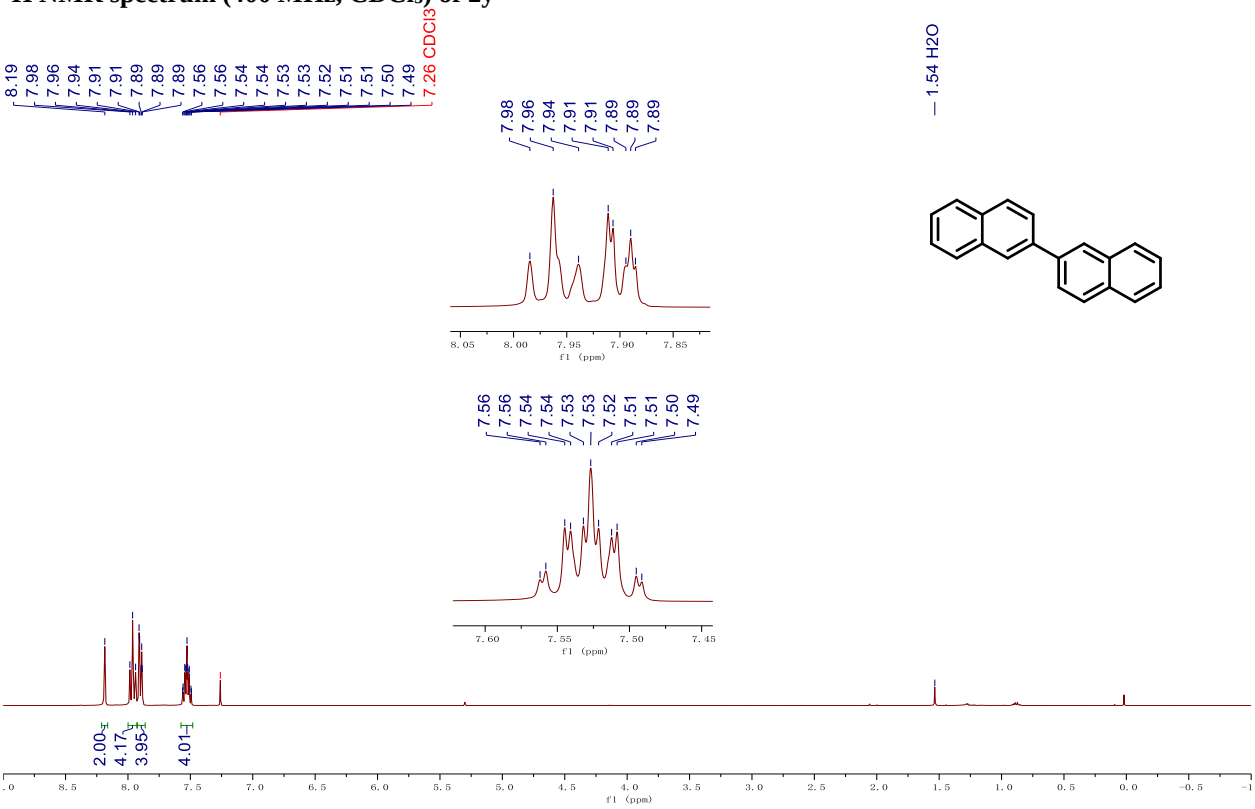
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 2x



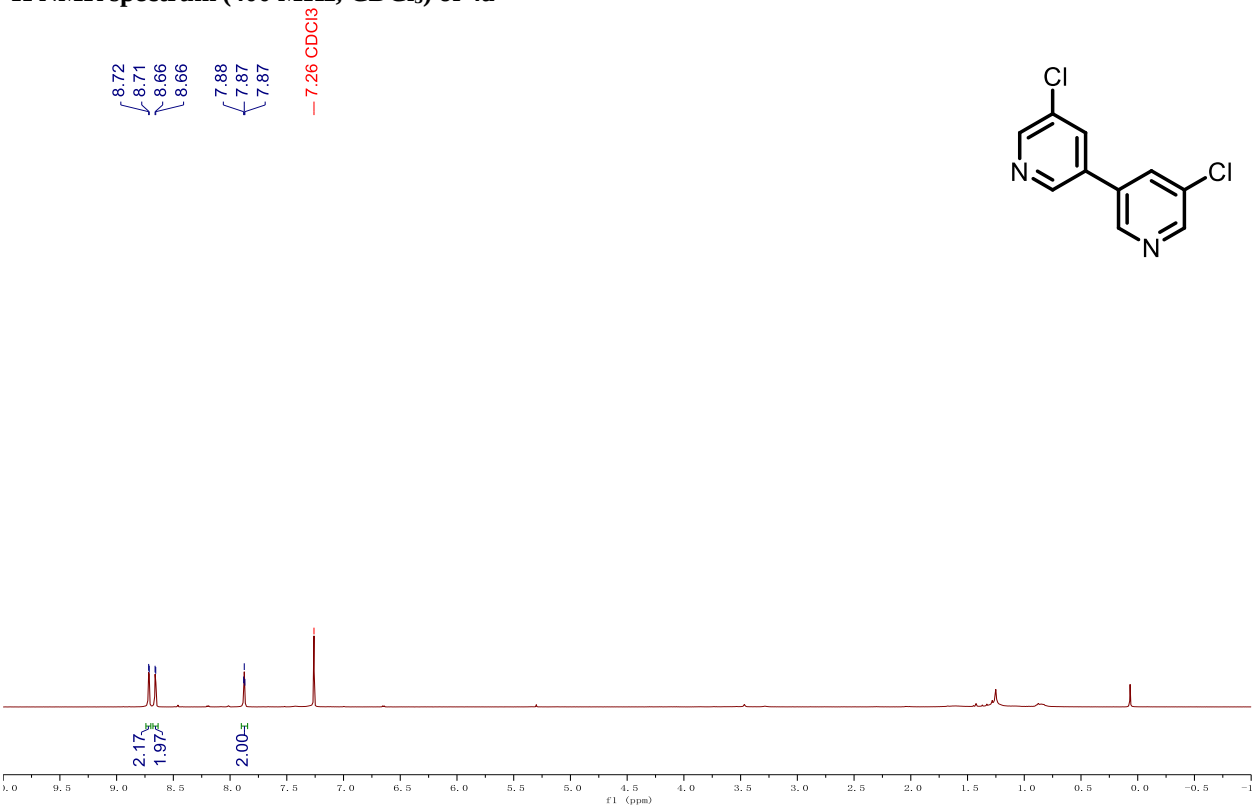
^{19}F NMR spectrum (376 MHz, $CDCl_3$) of 2x



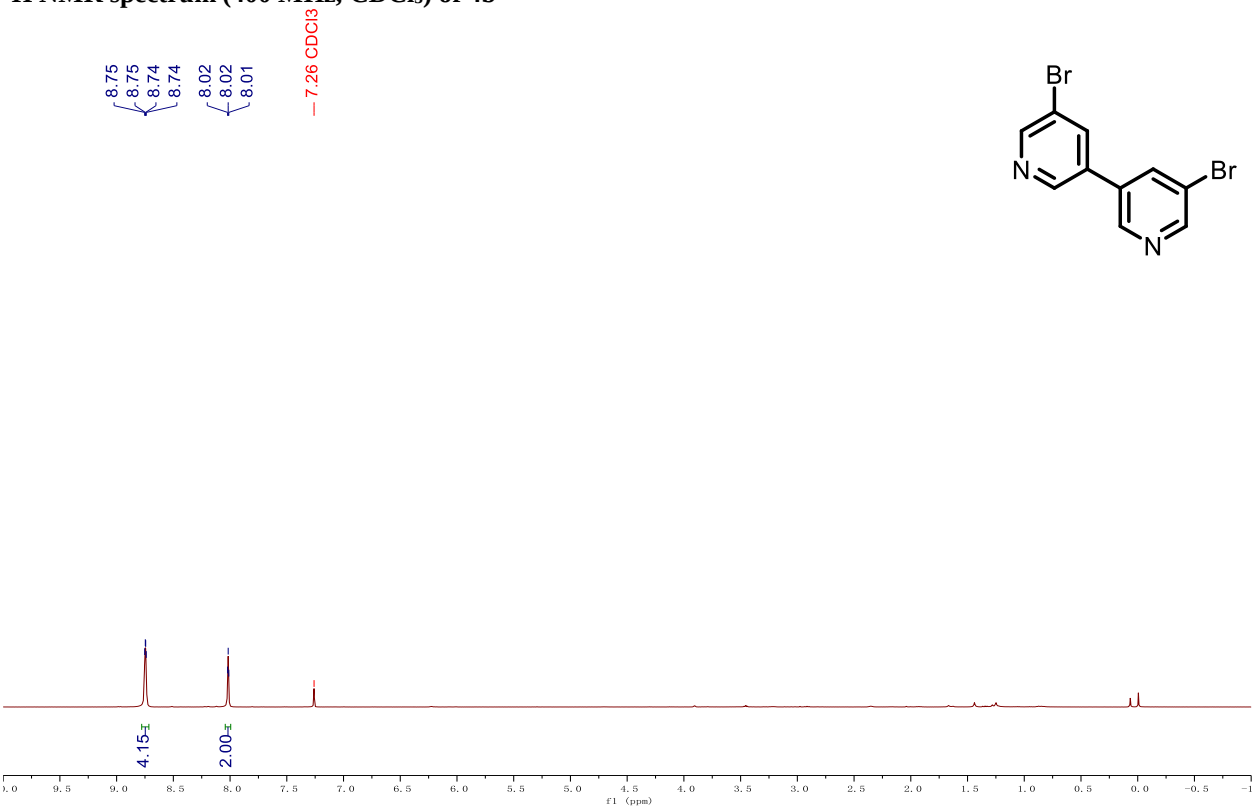
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 2y



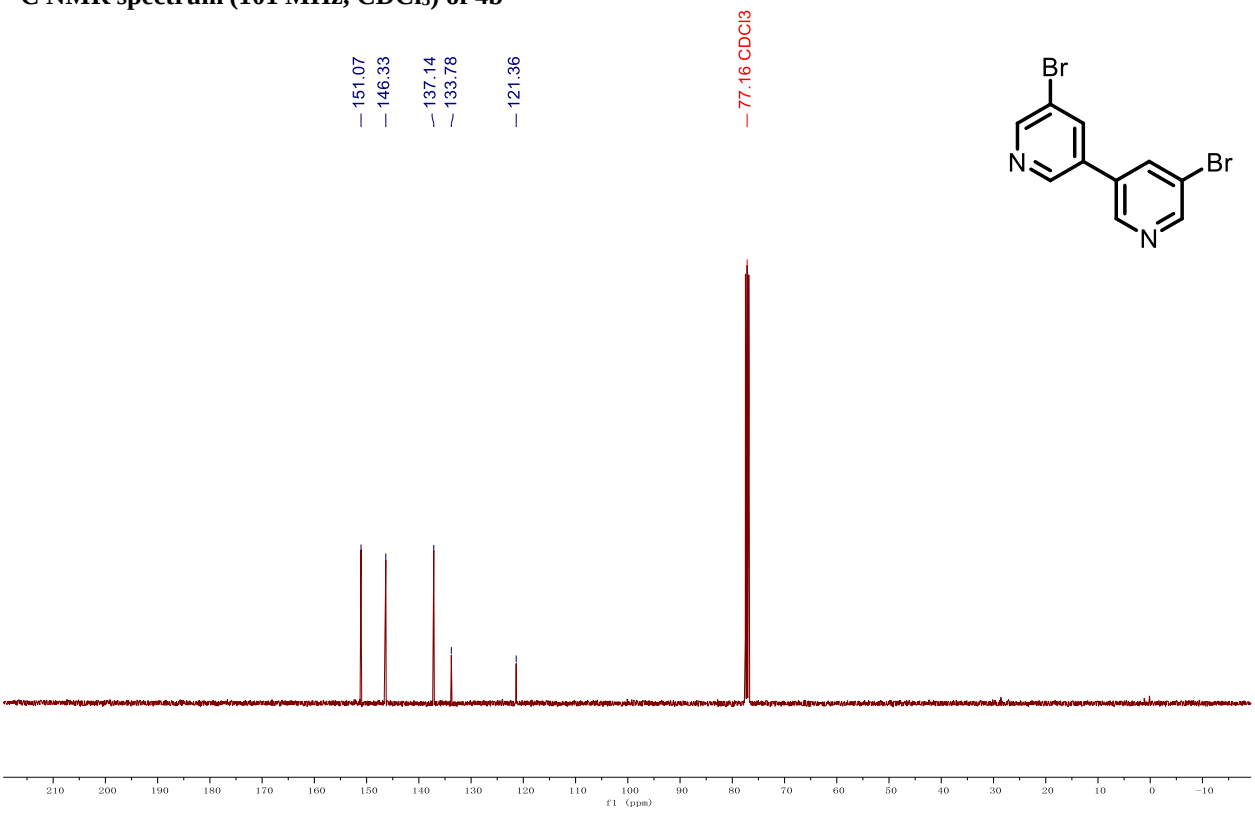
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4a



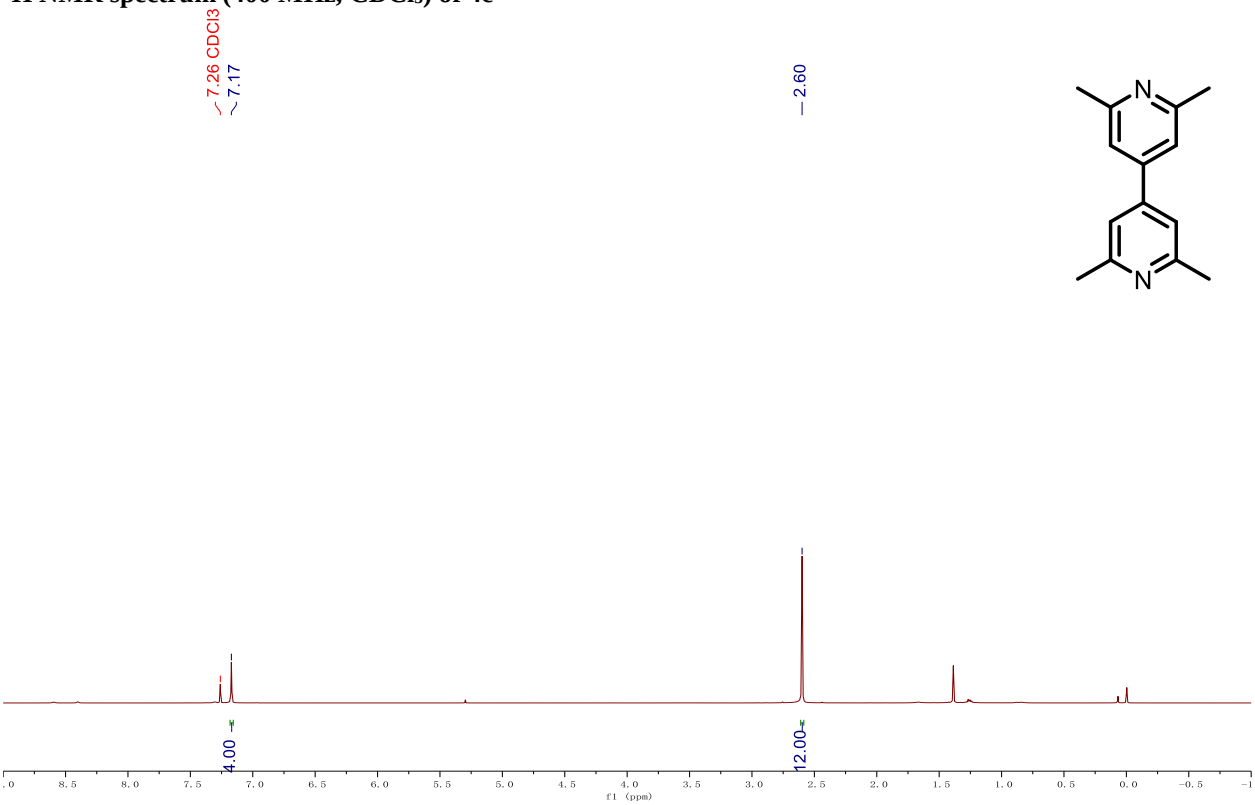
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4b



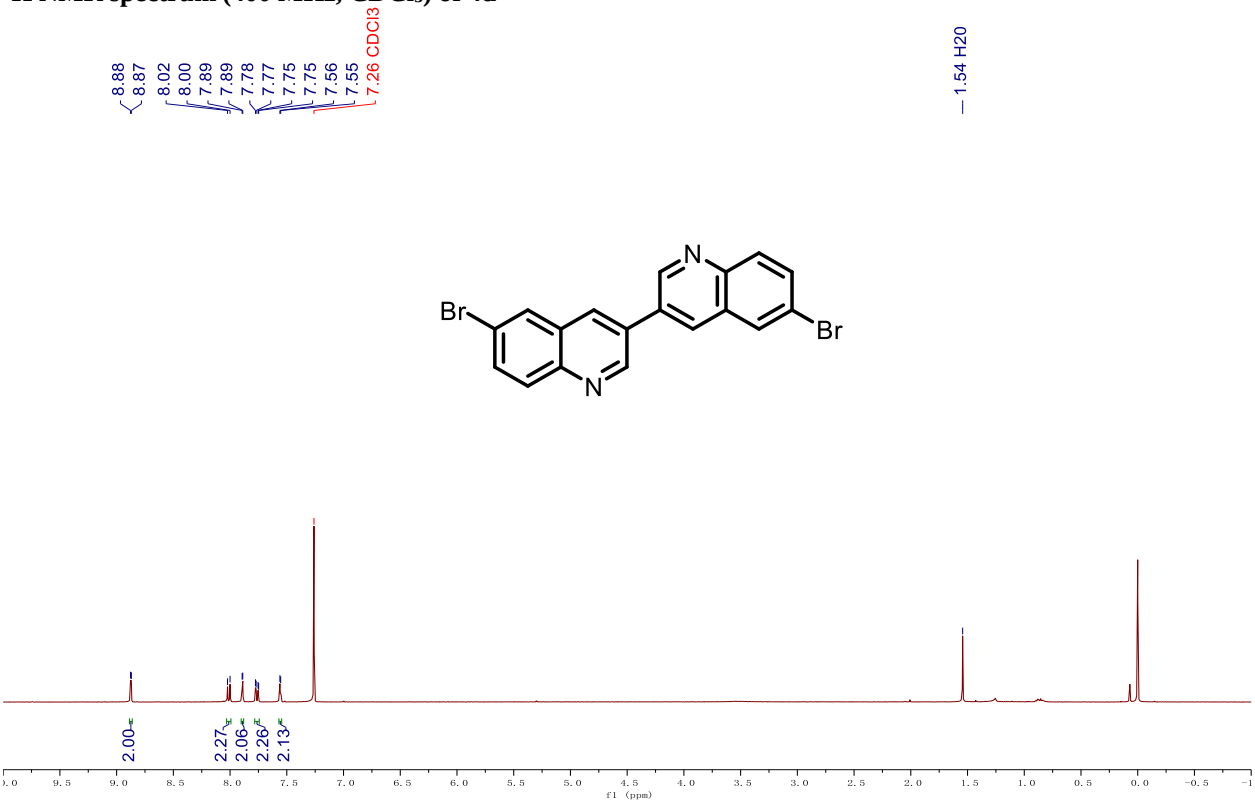
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 4b



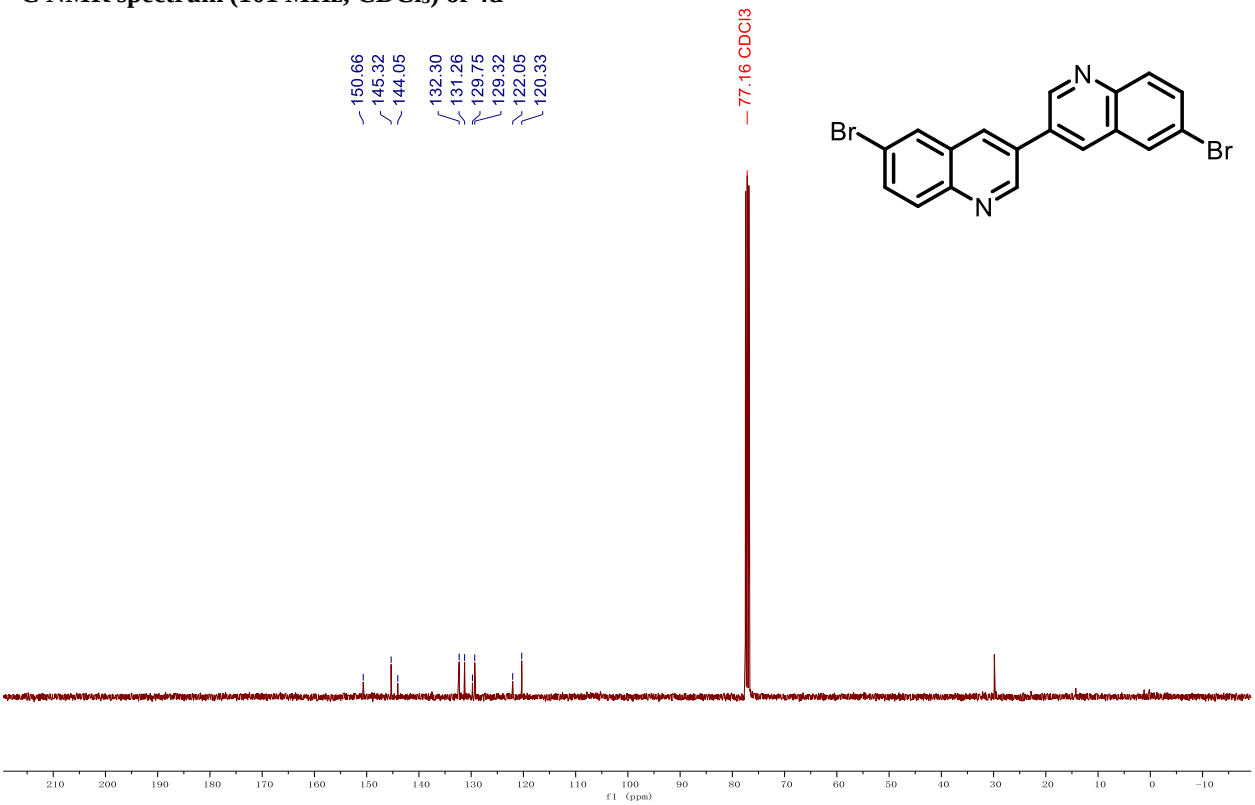
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4c



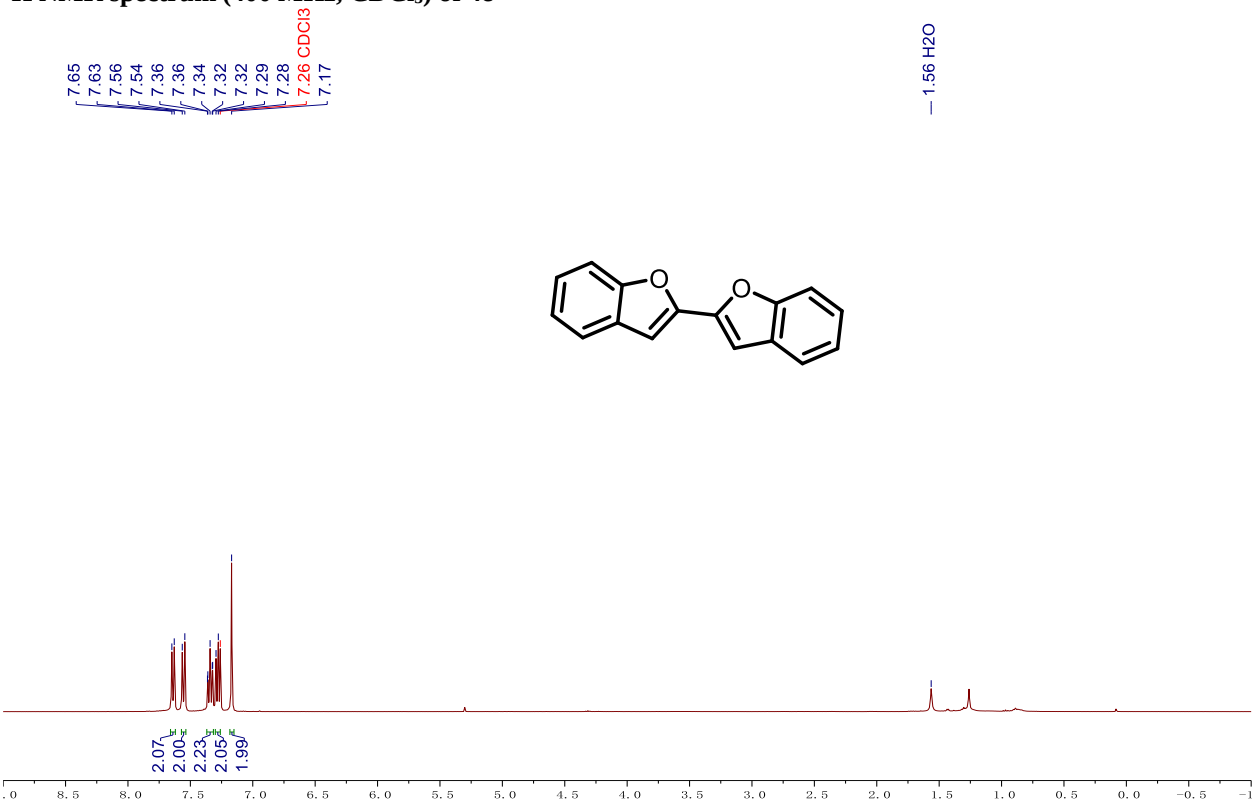
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4d



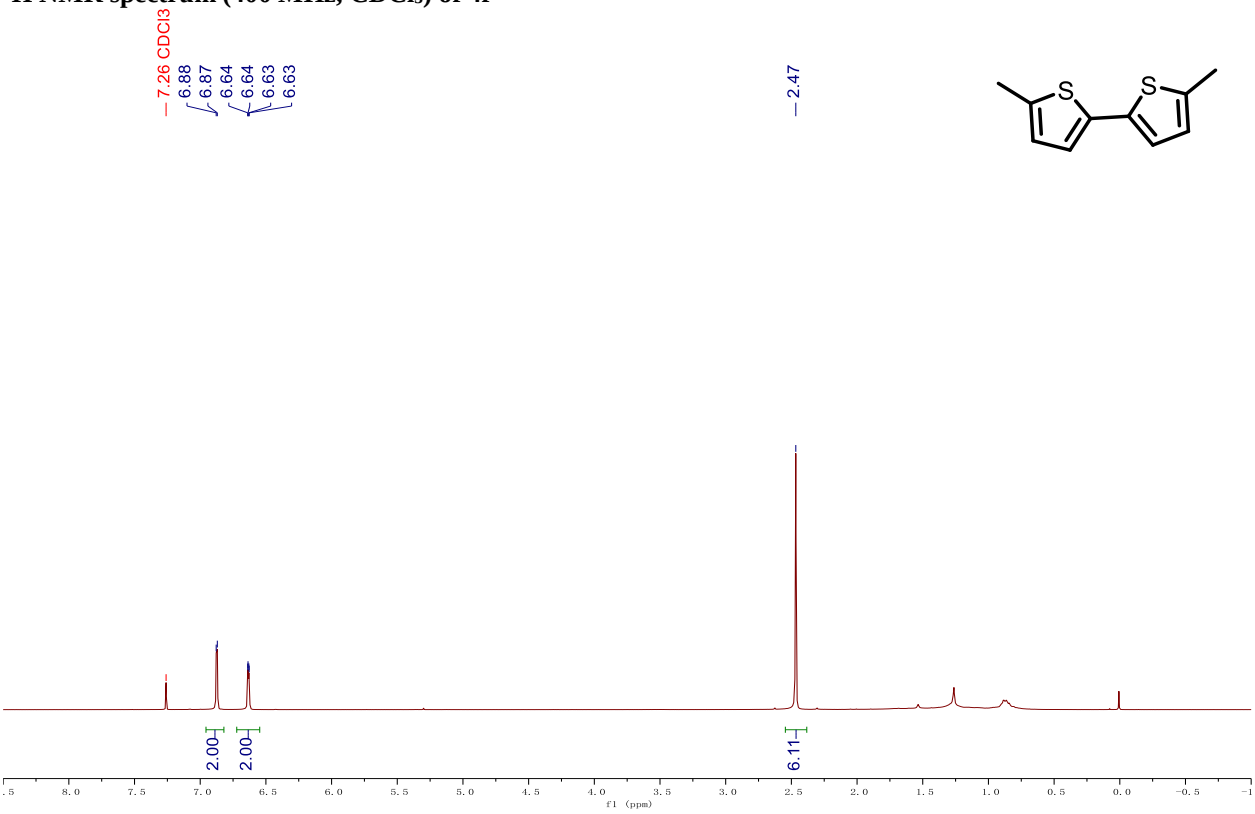
^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 4d



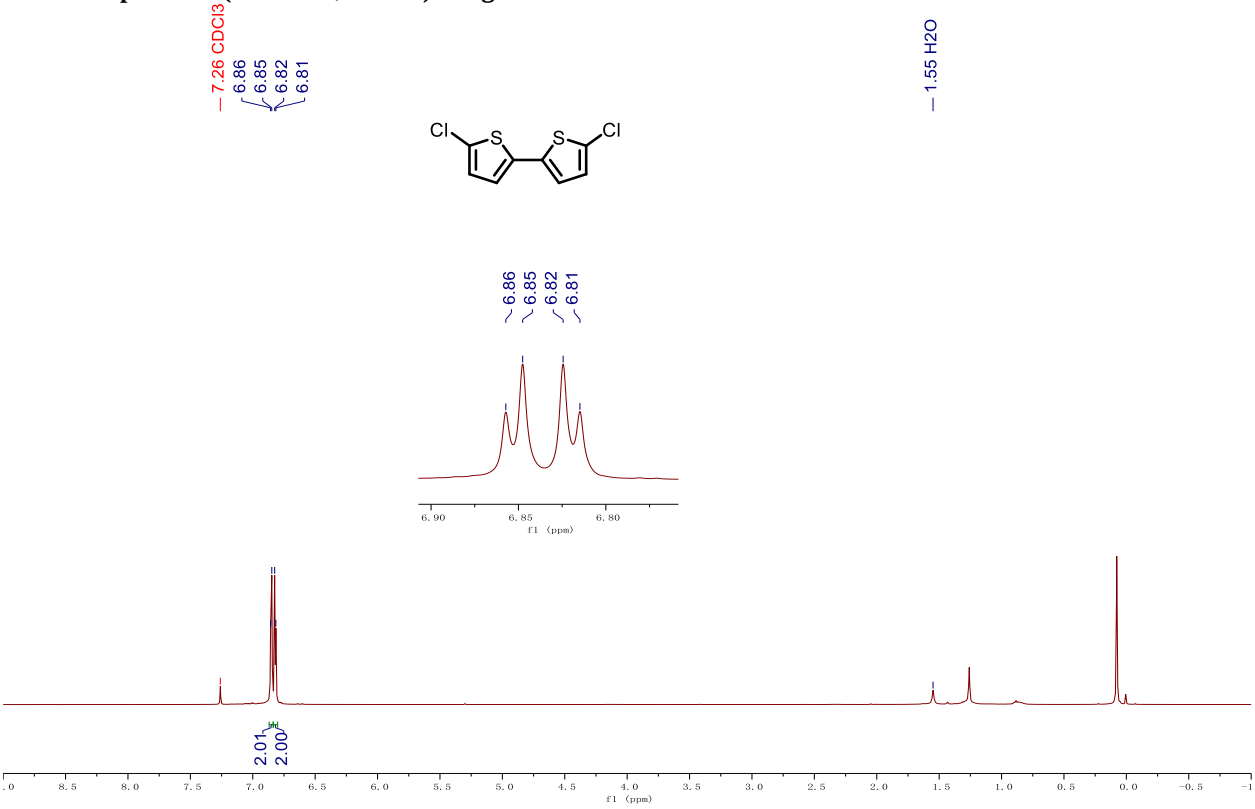
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4e



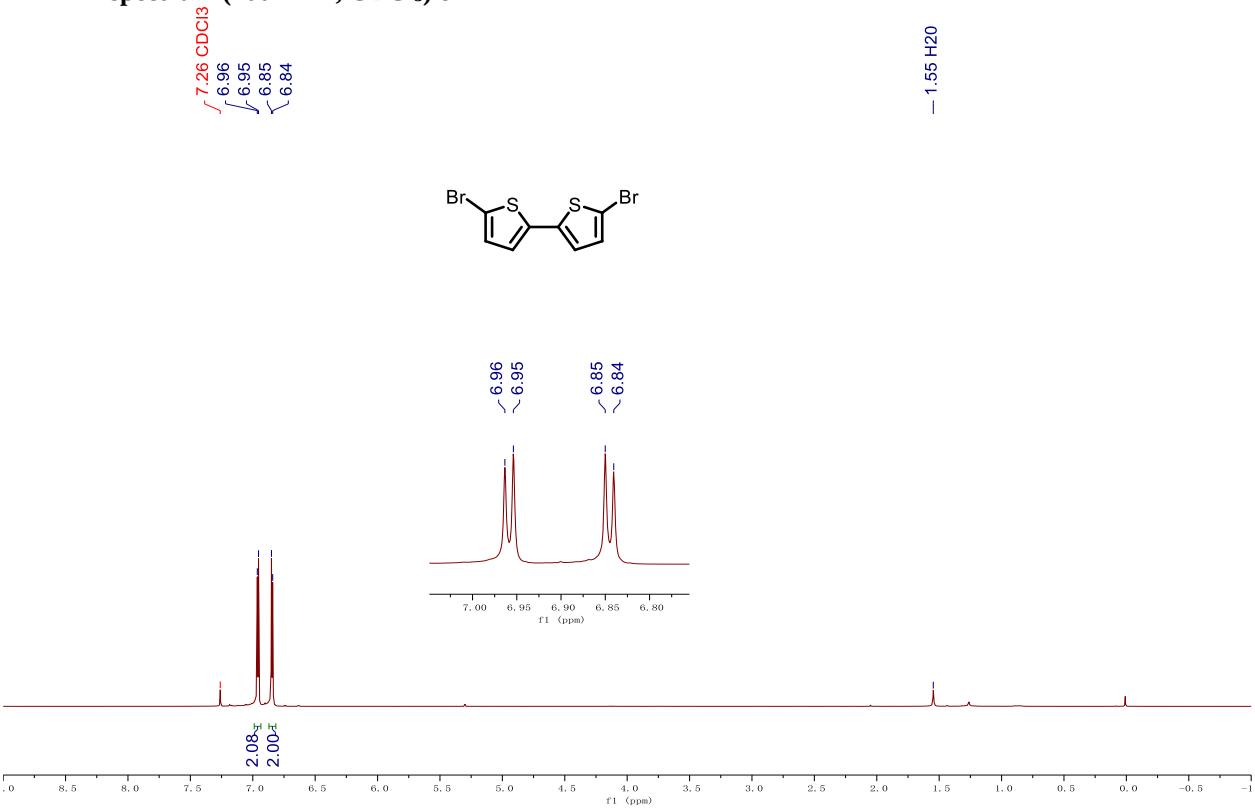
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4f



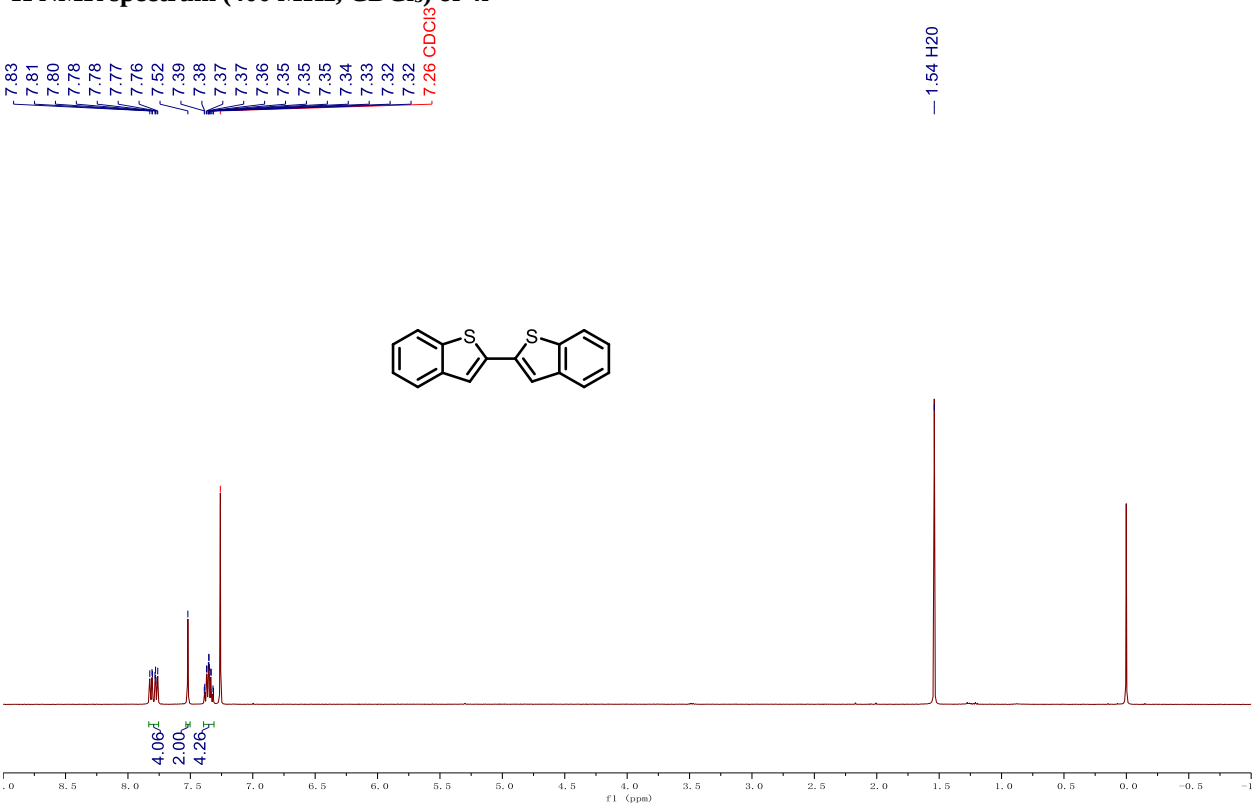
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4g



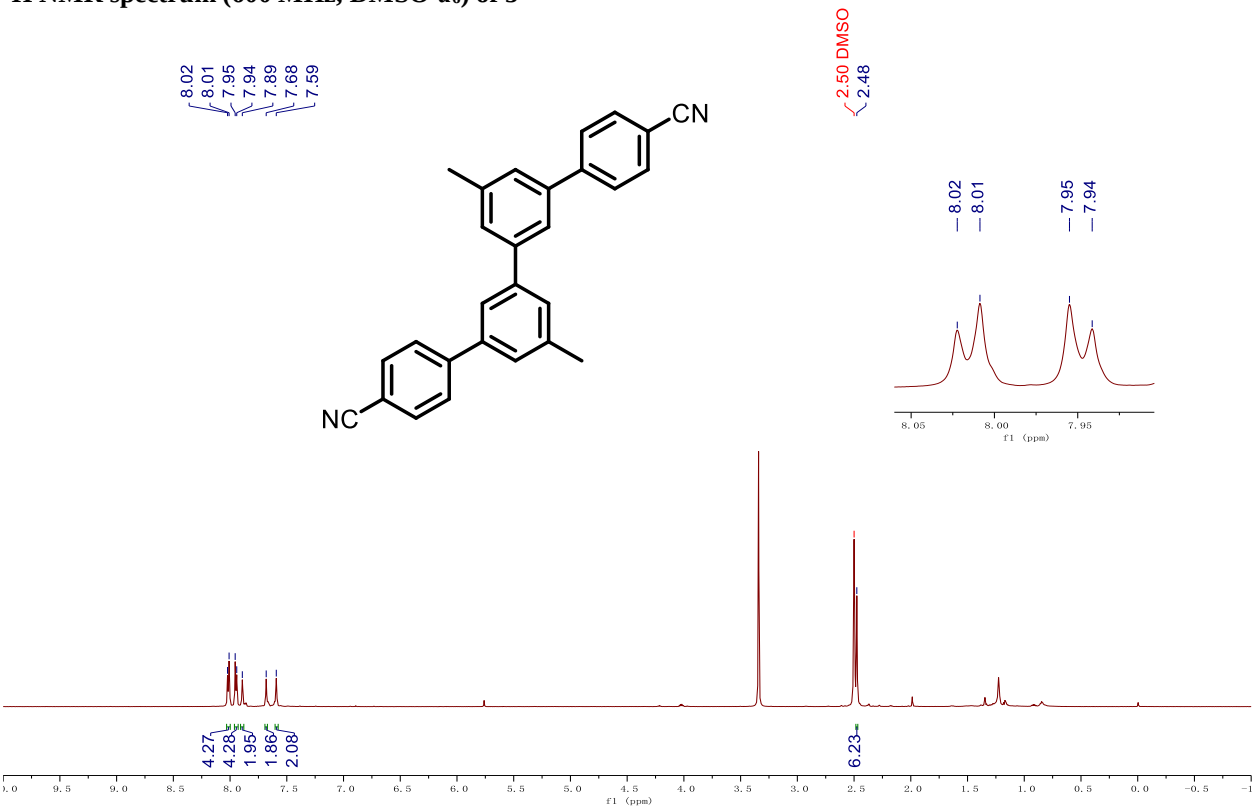
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4h



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of 4i



^{1}H NMR spectrum (600 MHz, DMSO-d_6) of 5



^{13}C NMR spectrum (101 MHz, $CDCl_3$) of 5