Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Synthesis and Properties of B,N-Bridged *p*-Terphenyls

Dong-Mei Chen,[†] Qian Qin,[†] Zuo-Bang Sun,[†] Qian Peng,[‡] and Cui-Hua Zhao*[,†]

School of Chemistry and Chemical Engineering, Shandong University, Shanda Nanlu 27, Jinan 250100, People's Republic of China, and Key Laboratory of Organic Solids, Beijing National Laboratory for Molecular Science (BNLMS), Beijing 100190, People's Republic of China

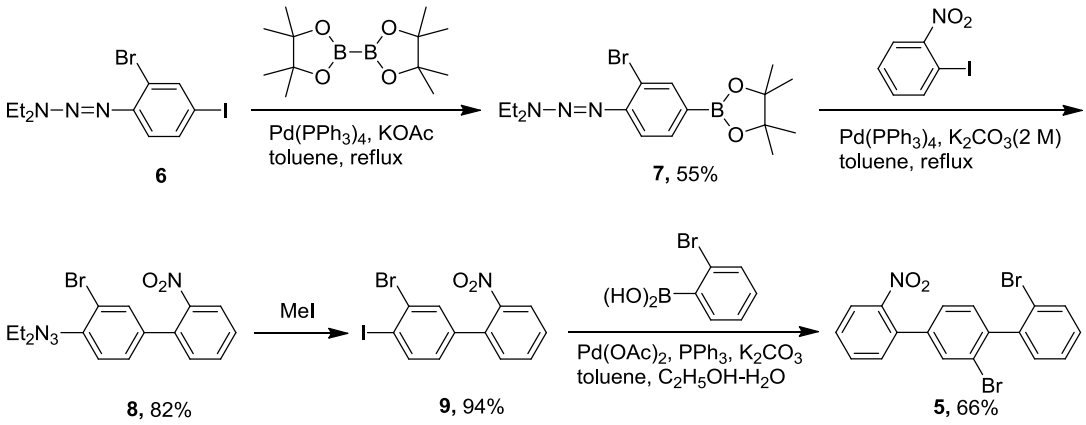
Table of Contents

General. Melting points (mp) were measured on a Tektronix XT-4 instrument. ^{1}H and ^{13}C NMR spectra were recorded with a Bruker 300 spectrometer or a Bruker 400 spectrometer in $CDCl_3$. UV-vis absorption spectra and fluorescence spectra measurement were performed with a Hitachi UV-4100 spectrometer and a Hitachi F-4500 spectrometer, respectively. All reactions were carried out under nitrogen atmosphere. Compounds **6**,[1] **11**[2] were prepared according to the literature.

Synthesis

Synthesis of B,N-Bridged *p*-Terphenyls

Scheme S-1



3-Bromo-4-(3,3-dimethyl-1-trizeno)phenyl pinacol boronic ester (7): To a mixture of **6** (4.48 g, 12.5 mmol), bis(pinacolato)diboron (3.17 g, 12.5 mmol), $Pd(PPh_3)_4$ (144 mg, 0.13mmol) and KOAc (12.3 g, 125mmol) was added degassed toluene (60 mL) under a stream of nitrogen. The resulting mixture was refluxed overnight. The mixture was cooled to room temperature and then extracted with CH_2Cl_2 (3 times). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting crude product was subjected to a silica gel column chromatography (5/1 petroleum ether/CH_2Cl_2, R_f = 0.29) to afford 2.63 g (6.88

mmol) of **7** in 55% yield as yellow solids: mp 112–113 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (br, 18H), 3.81 (q, *J* = 7.2 Hz, 4 H), 7.36 (d, *J* = 7.8 Hz, 1H), 7.62 (dd, *J* = 1.2, 7.8 Hz, 1H) , 8.01 (d, *J* = 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 10.8, 14.5, 24.9, 42.0, 49.3, 83.9, 117.8, 119.7, 134.1, 139.5, 150.7; HRMS (ESI): 382.1311 ($[M+H]^+$); Calcd for $C_{16}H_{26}{}^{11}BBrN_3O_2$: 382.1301.

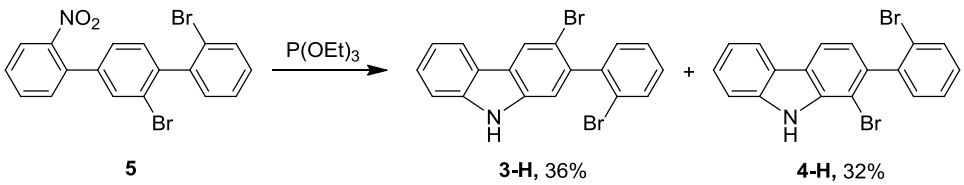
3'-Bromo-4'-(3,3-diethyltriazeno)-2-nitro-[1,1']biphenyl (8): To a solution of **7** (9.92 g, 10.3 mmol), 2-nitroiodobenzene (2.56 g, 10.3 mmol) and $Pd(PPh_3)_4$ (119 mg, 0.1 mmol) in degassed toluene (95 mL) was added a degassed solution of K_2CO_3 (20 mL, 2.0M) under a steam of nitrogen. The reaction mixture was refluxed overnight. The mixture was cooled to room temperature and then extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (2/1 petroleum ether/CH_2Cl_2, R_f = 0.39) to afford 3.16 g (8.40 mmol) of **8** in 82% yield as yellow solids: mp 70–71 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.33 (br, 6H), 3.82 (q, *J* = 7.2 Hz, 4H), 7.15 (dd, *J* = 1.8, 8.1 Hz, 1H), 7.43–7.50 (m, 3H), 7.57–7.63 (m, 2H), 7.84 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 10.9, 14.5, 42.1, 49.3, 118.4, 119.9, 124.2, 127.4, 128.2, 131.9, 132.3, 134.8, 135.0, 148.4, 149.1; HRMS (ESI): 377.0633 ($[M+H]^+$); Calcd for $C_{16}H_{18}BrN_4O_2$: 377.0613.

3'-Bromo-4'-iodo-2-nitro-[1,1']biphenyl (9): A solution of triazene derivative **8** (2.30 g, 6.1 mmol) in iodomethane (21.4 mL, 343 mmol) was placed in a 100 mL Schlenk tube under a steam of N_2 and stirred overnight at 135 ^{o}C. The reaction mixture was cooled to room temperature and the solvent was removed by vacuum evaporation. The resulting crude product was purified by silica gel column chromatography (4/1 petroleum ether/CH_2Cl_2, R_f = 0.56) to afford 2.31 g (5.73 mmol) of **9** in 94% yield as white solids: mp 137–138 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.93 (dd,

J = 2.1, 8.1 Hz, 1H), 7.38 (dd, *J* = 1.2, 7.5 Hz, 1H), 7.51 (td, *J* = 1.5, 7.8 Hz, 1H), 7.59 (d, *J* = 2.1 Hz, 1H), 7.62 (td, *J* = 0.9, 7.5 Hz, 1H), 7.88 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 101.1, 124.5, 128.0, 129.1, 130.1, 131.7, 131.9, 132.8, 134.1, 139.2, 140.3, 148.6; HRMS (EI): 402.8704 (M^+); Calcd for $C_{12}H_7BrINO_2$: 402.8705.

2,2'-Dibromo-2"-nitro-[1,1':4',1"]terphenyl (5): To a mixture of **9** (2.21 g, 5.4 mmol), 2-bromophenylboronic acid (1.30 g, 6.5 mmol), K_2CO_3 (2.98 g, 21.6 mmol), PPh_3 (212 mg, 0.8 mmol) and $Pd(OAc)_2$ (60 mg, 0.27 mmol) were added degassed toluene (60 mL) and a 1/1 C_2H_5OH/H_2O (12 mL) degassed mixed solvent under a steam of nitrogen. The reaction mixture was refluxed overnight. The mixture was cooled to room temperature and then extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (5/1 petroleum ether/CH_2Cl_2, R_f = 0.31) to afford 1.54 g (3.57 mmol) of **5** in 66% yield as white solids: mp 160–162 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30–7.32 (m, 4H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.50–7.57 (m, 2H), 7.65–7.70 (m, 3H), 7.93 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 123.4, 123.7, 124.4, 126.8, 127.2, 128.9, 129.6, 131.0, 131.9, 132.0, 132.6, 132.7, 134.7, 138.8, 141.5, 141.8, 149.0; HRMS (EI): 430.9155 (M^+); Calcd for $C_{18}H_{11}Br_2NO_2$: 430.9157.

Scheme S-2

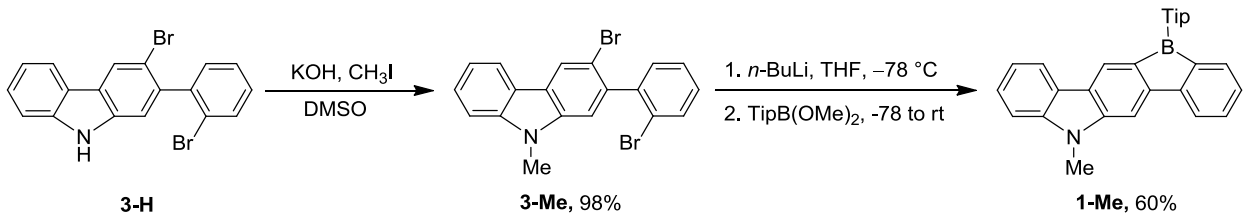


5 **3-H**, 36% **4-H**, 32%

3-Bromo-2-(2-bromophenyl)-9*H*-carbazole (3-H)

1-Bromo-2-(2-bromophenyl)-9*H*-carbazole (4-H): A solution of **5** (1.38 g, 3.2 mmol) in triethylphosphite (10 mL, 58.3 mmol) was placed in a 100 mL Schlenk tube under a steam of nitrogen and stirred overnight at 160 ^{o}C. The solvent was removed under reduced pressure. The resulting crude product was purified by silica gel column chromatography (5/1 petroleum ether/CH_2Cl_2) to afford 457 mg of **3-H** (R_f = 0.28) and 406 mg of 4-H (R_f = 0.40) as white solids in 36% and 32% yields, respectively. **3-H:** mp > 300 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.25–7.50 (m, 7H), 7.68 (dd, *J* = 0.9, 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 1H), 8.09 (s, 1H), 8.35 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 110.9, 112.7, 113.6, 120.1, 120.7, 122.2, 124.0, 124.1, 124.8, 126.8, 127.1, 129.3, 131.4, 132.5, 138.2, 139.0, 140.2, 142.8; HRMS (EI): 398.9254 (M^+); Calcd for $C_{18}H_{11}Br_2N$: 398.9258. **4-H:** mp 221–222 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.12 (d, *J* = 8.1 Hz, 1H), 7.26–7.54 (m, 6H), 7.71 (dd, *J* = 0.9, 7.8 Hz, 1H), 8.04–8.10 (m, 2H), 8.36 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 105.3, 111.1, 118.9, 120.3, 120.9, 122.0, 123.7, 124.0, 126.6, 127.1, 129.3, 131.5, 132.6, 138.4, 138.8, 139.5, 142.1; HRMS (EI): 398.9257 (M^+); Calcd for $C_{18}H_{11}Br_2N$: 398.9258.

Scheme S-3



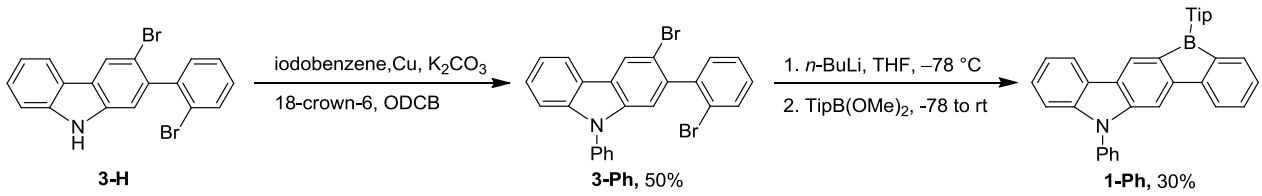
3-H **3-Me**, 98% **1-Me**, 60%

4-Bromo-3-(2-bromophenyl)-9-methyl-*9H*-carbazole (3-Me): To a mixture of **3-H** (482 mg, 1.2 mmol), KOH (677 mg, 12.1 mmol) in a 100 mL Schlenk tube were added DMSO (5 mL) and iodomethane (0.15 mL, 2.4 mmol) under a steam of nitrogen. The reaction mixture was stirred

overnight at 110 ^{o}C. The solvent was removed under reduced pressure. The resulting crude product was purified by silica gel column chromatography (petroleum ether, R_f = 0.24) to afford 485 mg (1.17 mmol) of **3-Me** in 98% yield as white solids: mp 158–160 ^{o}C; ^{1}H NMR of ($CDCl_3$, 400 MHz): δ 3.86 (s, 3H), 7.27–7.44 (m, 6H), 7.52 (t, *J* = 7.6 Hz, 1H),7.71 (d, *J* = 8.0 Hz, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 8.39 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 29.3, 108.7, 110.6, 113.0, 119.5, 120.6, 121.6, 123.9, 124.0, 124.1, 126.6, 127.1, 129.3, 131.4, 132.5, 138.8, 139.8, 141.7, 143.1; HRMS (EI): 412.9414 (M^+); Calcd for $C_{19}H_{13}Br_2N$: 412.9415.

5,11-Dihydro-5-methyl-11-(2,4,6-triisopropylphenyl)benzoborolo[3,2-*b*]carbazole (1-Me): To a solution of **3-Me** (242 mg, 0.6 mmol) in anhydrous THF (10 mL) was added a hexane solution of *n*-BuLi (0.48 mL, 2.5 M, 1.2 mmol) dropwise by syringe at –78 ^{o}C under a steam of nitrogen. The mixture was stirred at the same temperature for 1 h. Dimethoxytripylborane (331 mg, 0.36 mL, 1.2 mmol) in anhydrous THF (6 mL) was added to the reaction mixture via syringe. The reaction mixture was warmed to room temperature and stirred overnight. The reaction was quenched with saturated solution of NaCl and the aqueous layer was extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (petroleum ether, R_f = 0.15) to afford 195 mg (0.37 mmol) of **1-Me** in 60% yield as yellow solids: mp 218–220 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.14 (d, *J* = 6.9 Hz, 12H), 1.34 (d, *J* = 6.9 Hz, 6H), 2.57 (septet, *J* = 6.9 Hz, 2H), 2.94 (septet, *J* = 6.9 Hz, 1H), 3.89 (s, 3H), 7.06–7.09 (m, 3H), 7.16 (td, *J* = 1.5, 8.1 Hz, 1H), 7.31–7.42 (m, 5H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 8.09 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.1, 24.7, 29.2, 34.3, 35.5, 100.7, 108.9, 119.2, 119.9, 120.10, 120.14, 122.8, 123.9, 125.4, 128.3, 128.6, 133.6, 134.1, 135.4, 141.4, 145.5, 145.9, 148.5, 150.1, 151.9, 153.1; HRMS (MALDI/DHB): 468.2964 (M^+); Calcd for $C_{34}H_{36}{}^{10}BN$: 468.2972.

Scheme S-4

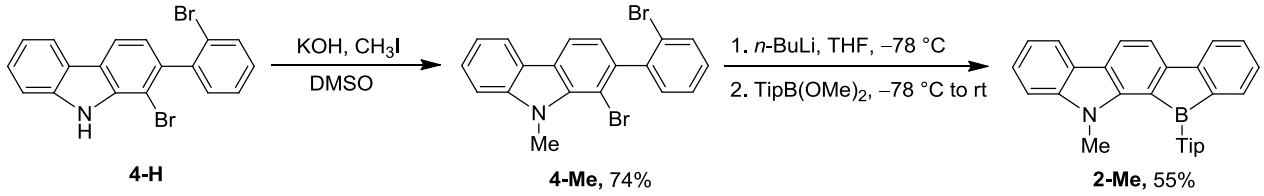


4-Bromo-3-(2-bromophenyl)-9-phenyl-*9H*-carbazole (3-Ph): To a mixture of **3-H** (365 mg, 0.91 mmol), iodobenzene (0.31 mL, 2.74mmol), Cu (116 mg, 1.83 mmol), K_2CO_3 (506 mg, 3.66 mmol) and 18-crown-6 (24 mg, 0.09 mmol) was added 1,2-dichlorobenzene (7.5 mL) under a steam of nitrogen. The reaction mixture was stirred at 150 ^oC for 12 h. The mixture was cooled to room temperature. After removal of the solvent under reduced pressure, the mixture was poured into water and extracted with CH_2Cl_2. The combined organic layer was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The resulting mixture was subjected to a silica gel column chromatography (10/1 petroleum ether/CH_2Cl_2, R_f = 0.35) to afford 217 mg (0.46 mmol) of **3-Ph** in 50% yield as white solids: mp 80–82 ^oC; ^1H NMR ($CDCl_3$, 300 MHz): δ 7.27–7.47 (m, 8H), 7.54–7.61 (m, 4H), 7.65 (d, J = 8.7 Hz, 1H), 8.11 (d, J = 7.8 Hz, 1H), 8.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 110.1, 111.9, 114.0, 120.5, 120.6, 122.1, 123.9, 124.1, 124.7, 126.8, 127.0, 127.1, 127.8, 129.3, 130.0, 131.4, 132.5, 137.2, 139.1, 139.7, 141.7, 142.9; HRMS (EI): 474.9575 (M^+); Calcd for $C_{24}H_{15}Br_2N$: 474.9571.

5,11-Dihydro-5-phenyl-11-(2,4,6-triisopropylphenyl)benzoborolo[3,2-*b*]carbazole (1-Ph): This compound was prepared essentially in the same manner as described for **1-Me** using **3-Ph** (151 mg, 0.32 mmol), *n*-BuLi (0.44 mL, 1.6 M, 0.7 mmol), dimethoxytripylborane (166 mg, 0.20 mL, 0.6 mmol) and anhydrous THF (10 mL). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.21) afforded 48 mg (0.17 mmol) of **1-Ph** in 30% yield as yellow solids: mp 190–191 ^oC; ^1H NMR ($CDCl_3$, 300 MHz): δ 1.17 (t, J = 7.2 Hz, 12H), 1.36 (d, J = 6.9 Hz, 6H),

2.59 (septet, J = 6.9 Hz, 2H), 2.94 (septet, J = 6.9 Hz, 1H), 7.01 (t, J = 7.2 Hz, 1H), 7.09 (s, 2H), 7.20–7.37 (m, 7H), 7.52–7.69 (m, 5H), 7.96 (d, J = 7.8 Hz, 1H), 8.14 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ 24.0, 24.6, 34.2, 35.5, 101.8, 110.0, 119.3, 119.9, 120.0, 120.8, 123.2, 124.2, 125.5, 127.4, 128.0, 128.2, 128.5, 130.0, 133.5, 134.1, 137.0, 141.5, 145.4, 148.5, 150.1, 152.0, 152.9; HRMS (MALDI/DHB): 530.3121 (M^+); Calcd for $C_{39}H_{38}{}^{10}BN$: 530.3128.

Scheme S-5



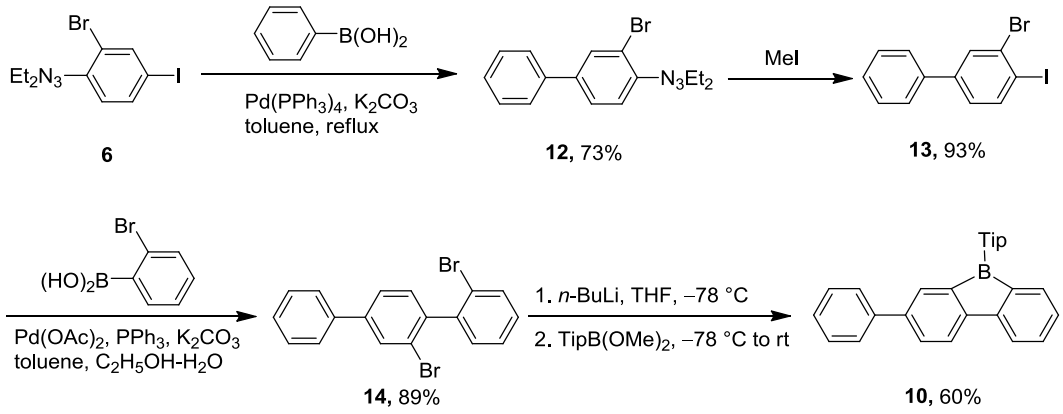
2-Bromo-3-(2-bromophenyl)-9-methyl-*9H*-carbazole (4-Me): This compound was prepared essentially in the same manner as described for **3-Me** using **4-H** (199 mg, 0.50 mmol), iodomethane (0.06 mL, 1.0 mmol), KOH (270 mg, 5.0 mmol) and DMSO (2 mL). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.28) afforded 153 mg (0.37 mmol) of **4-Me** in 74% yield as white solids: mp 133–134 ^{o}C; ^{1}H NMR of ($CDCl_3$, 300 MHz): δ 4.31 (s, 1H), 7.08 (dd, J = 2.7, 7.8 Hz, 1H), 7.25–7.34 (m, 3H), 7.39–7.46 (m, 2H),7.50 (t, J = 7.2 Hz, 1H), 7.70 (d, J = 7.8 Hz, 1H), 8.06–8.10 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 32.7, 104.6, 109.2, 118.9, 119.9, 120.1, 121.7, 122.1, 124.2, 125.4, 126.5, 127.0, 129.1, 131.4, 132.5, 137.9, 140.7, 142.6, 143.4; HRMS (EI): 412.9412 (M^+); Calcd for $C_{19}H_{13}Br_2N$: 412.9415.

11,12-Dihydro-11-methyl-12-(2,4,6-triisopropylphenyl)benzoborolo[2,3-*a*]carbazole (2-Me): This compound was prepared essentially in the same manner as described for **1-Me** using **4-Me** (220 mg, 0.53 mmol), *n*-BuLi (0.75 mL, 1.6 M, 1.20 mmol), dimethoxytripylborane (292 mg, 0.32 mL, 1.06 mmol) and anhydrous THF (10 mL). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.24) afforded 154 mg (0.33 mmol) of **2-Me** in 55% yield

as orange solids: mp 196–198 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.11 (d, *J* = 6.6 Hz, 6H), 1.13 (d, *J* = 6.6 Hz, 6H), 1.31 (d, *J* = 6.9 Hz, 6H), 2.55 (septet, *J* = 6.6 Hz, 2H), 2.88 (septet, *J* = 6.9 Hz, 1H), 3.29 (s, 3H), 6.98 (d, *J* = 7.2 Hz, 1H), 7.03 (s, 2H), 7.13–7.42 (m, 7H), 7.95 (d, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 7.5 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 23.7, 24.2, 25.1, 32.0, 34.4, 35.7, 108.8, 111.6, 119.0, 119.7, 119.8, 120.2, 122.7, 123.2, 125.9, 126.1, 127.0, 128.3, 133.8, 134.4, 138.5, 142.5, 144.0, 146.7, 148.9, 149.2, 152.6, 154.0; HRMS (MALDI/DHB): 468.2970 (M^+); Calcd for $C_{34}H_{36}{}^{10}BN$: 468.2972.

Synthesis of Related Compound 10

Scheme S-6



3-Bromo-4-(3,3-diethyltriazeno)-[1,1']biphenyl (12): This compound was prepared essentially in the same manner as described for **8** using **6** (1.90 g, 5.0 mmol), phenylboronic acid (671 mg, 5.5 mmol), $Pd(PPh_3)_4$ (58 mg, 0.05 mmol), K_2CO_3 (10 mL, 2M) and toluene (50 mL). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.42) afforded 1.21 g (3.65 mmol) of **12** in 73% yield as brown oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 1.34 (t, *J* = 6.9 Hz, 6H), 3.82 (q, *J* = 6.9 Hz, 4H), 7.32–7.37 (m, 1H), 7.41–7.49 (m, 4H), 7.57–7.61 (m, 2H), 7.85 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 11.1, 14.4, 42.2, 49.3, 118.6, 120.2, 126.4, 126.8, 127.3, 128.8, 131.4, 139.0,

139.7, 147.6; HRMS (ESI): 332.0745 ($[M+H]^+$); Calcd for $C_{16}H_{19}BrN_3$: 332.0762.

3-Bromo-4-iodo-[1,1']biphenyl (13): This compound was prepared essentially in the same manner as described for **9** using **12** (1.23 g, 3.7 mmol), and MeI (6.93 mL, 111 mmol). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.83) afforded 1.23 g (3.44 mmol) of **13** in 93% yield as colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.19 (dd, *J* = 2.1, 8.4 Hz, 1H), 7.31–7.48 (m, 3H), 7.53–7.55 (m, 2H), 7.85 (d, *J* = 2.1 Hz, 1H), 7.90 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 99.5, 126.9, 127.2, 128.2, 129.0, 130.2, 131.2, 138.7, 140.5, 142.9; HRMS (EI): 357.8856 (M^+); Calcd for $C_{12}H_8BrI$: 357.8854.

2,2'-Dibromo-[1,1':4',1"]terphenyl (14): This compound was prepared essentially in the same manner as described for **5** using **13** (716 mg, 2.0 mmol), 2-bromophenylboronic acid (480 mg, 2.4 mmol), K_2CO_3 (1.13 g, 8 mmol), PPh_3 (79 mg, 0.3 mmol) and $Pd(OAc)_2$ (22 mg, 0.1 mmol), degassed toluene (60 mL) and 1/1 C_2H_5OH/H_2O (5 mL). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.80) afforded 687 mg (1.78 mmol) of **14** in 89% yield as white solids: mp 119–121 ^{o}C; ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.28–7.33 (m, 3H), 7.37–7.50 (m, 4H), 7.59–7.64 (m, 3H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.91 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 123.6, 123.9, 125.8, 127.1, 128.0, 128.9, 129.4, 131.1, 131.1, 131.2, 132.6, 139.3, 140.8, 141.8, 142.6; HRMS (EI): 385.9303 (M^+); Calcd for $C_{18}H_{12}Br_2$: 385.9306.

2-Phenyl-9-(2,4,6-triisopropylphenyl)dibenzoborole (10): This compound was prepared essentially in the same manner as described for **10** using **14** (463 mg, 1.20 mmol), *n*-BuLi (1.2 mL, 2.5 M, 3.00 mmol), dimethoxytripylborane (0.45 mL, 1.50 mmol) and anhydrous THF (30 mL). The purification by a silica gel column chromatography (petroleum ether, R_f = 0.35) afforded 320 mg (0.76 mmol) of **10** in 60% yield as yellow solids: mp 172–174 ^{o}C; ^{1}HNMR ($CDCl_3$, 300 MHz):

δ 1.14 (d, *J* = 6.6 Hz, 6H), 1.16 (d, *J* = 6.6 Hz, 6H), 1.31 (d, *J* = 6.9 Hz, 6H), 2.45 (septet, *J* = 6.6 Hz, 2H), 2.88 (septet, *J* = 6.9 Hz, 1H), 7.03 (s, 2H), 7.05 (t, *J* = 7.2 Hz, 1H), 7.27–7.62 (m, 10H), 7.68 (s, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ 24.1, 24.6, 24.8, 34.3, 35.8, 119.6, 119.8, 120.1, 126.7, 127.3, 128.4, 128.7, 133.5, 134.4, 134.9, 140.9, 141.4, 143.8, 144.3, 148.9, 150.0, 152.1, 152.8; HRMS (MALDI/DHB): 441.2867 (M^+); Calcd for $C_{33}H_{35}B$: 441.2863.

X-ray Crystal Structure Analysis for the Decomposed Compound of 2-Me. Single crystals of the decomposed compound of **2-Me** suitable for X-ray crystal analysis were obtained by recrystallization from a hexane/CH_2Cl_2 mixed solvent. Intensity data were collected at 293 K on a Bruker SMART CCD X-ray Diffractometer (APEX II) with Mo Kα radiation (λ = 0.71073 Å) and graphite monochrometer. A total of 7100 reflections were measured at a maximum 2θ angle of 50.0˚, of which 4953 were independent reflections (R_{int} = 0.0373). The structure was solved by direct methods (SHELXS-97[4]) and refined by the full-matrix least-squares on F^2 (SHELEXL-97[4]). All non-hydrogen atoms were refined anisotropically and all hydrogen atoms except for those of the disordered solvent molecules were placed using AFIX instructions. The crystal data are as follows: $C_{34}H_{38}BNO$; FW = 487.46, crystal size 0.15 × 0.12 × 0.1 mm^3, Triclinic, P–1, a = 9.963(3) Å, b = 11.105(3) Å, c = 13.816(4) Å, V = 1424.1(7) $Å^3$, Z = 2, D_c = 1.137 g cm^{-3}. The refinement converged to R_1 = 0.0686, wR_2 = 0.2242 ($I > 2\sigma(I)$), GOF = 0.969.

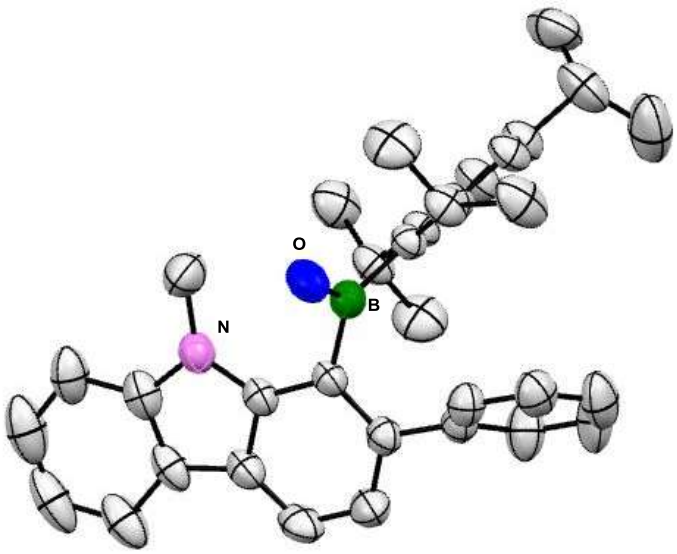


Figure S-1. ORTEP drawing for the docomposed compound of **2-Me**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Theoretical Calculations

The geometries of compounds B,N-bridged p-terphenyls **1**–**2** and related compounds **10**–**11** in the ground state were optimized using density functional theory (DFT) at the B3LYP/6-31G(d) level of theory by Gaussian 09 program.[3] The time-dependent density functional theory (TD-DFT) calculations were conducted at the B3LYP/6-31G(d) level of theory. The NICS values of B,N-bridged *p*-terphenyls **1**–**2** were obtained with the gauge-independent atomic orbital (GIAO) method at the B3LYP/6–31++G(d,p) level of theory.

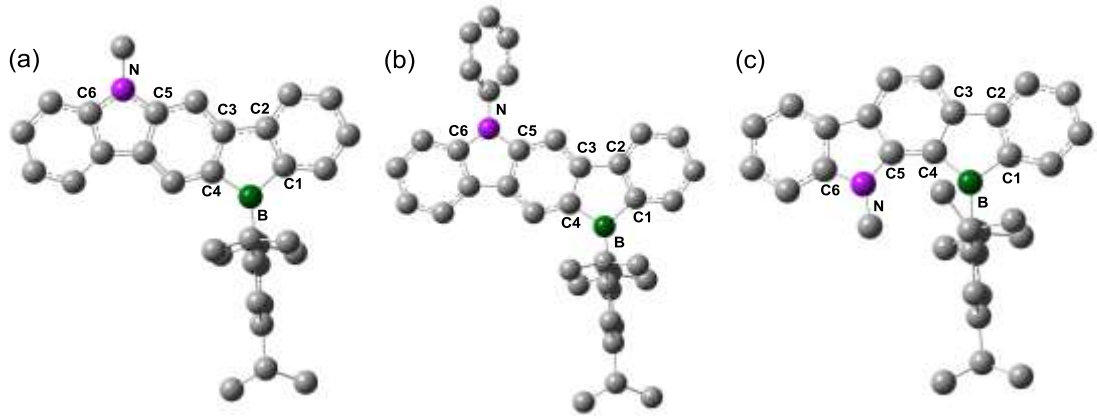


Figure S-2. Ball-and-Stick representation of the optimized geometry of B,N-bridged *p*-terphenyls (a) **1-Me**; (b) **1-Ph** and (c) **2-Me**, calculated at the B3LYP/6-31G(d) level of theory. Hydrogens are omitted for clarity.

Table S-1. Selected bond lengths [Å] and angles [^{o}] for B,N-bridged *p*-terphenyls.

Compound	B-C1	B-C4	C1-C2	C2-C3	C3-C4	N-C5	N-C6	C1-B-C4
1-Me	1.574	1.559	1.421	1.486	1.433	1.384	1.394	103.7
1-Ph	1.573	1.560	1.422	1.486	1.434	1.392	1.403	103.6
2-Me	1.572	1.582	1.414	1.484	1.432	1.391	1.393	104.0

Table S-2. Calculated Kohn-Sham molecular orbital energy levels and the first excited-state energies for B,N-bridged *p*-terphenyls **1**–**2** and related compounds **10**–**11**.

compound	HOMO/eV	LUMO/eV	HOMO–LUMO gap/eV	Transition energy/eV (λ/nm)[a]	f[b]
1-Me	–5.33	–1.85	3.48	2.74 (452)	0.0030
1-Ph	–5.34	–1.86	3.48	2.74 (452)	0.0048
2-Me	–5.32	–2.04	3.28	2.57 (483)	0.0053
10	–5.61	–2.14	3.47	2.73 (454)	0.0147
11	–5.37	–0.94	4.43	3.83 (323)	0.0277

[a] The first excited-state transition energy. [b] Oscillator strength.

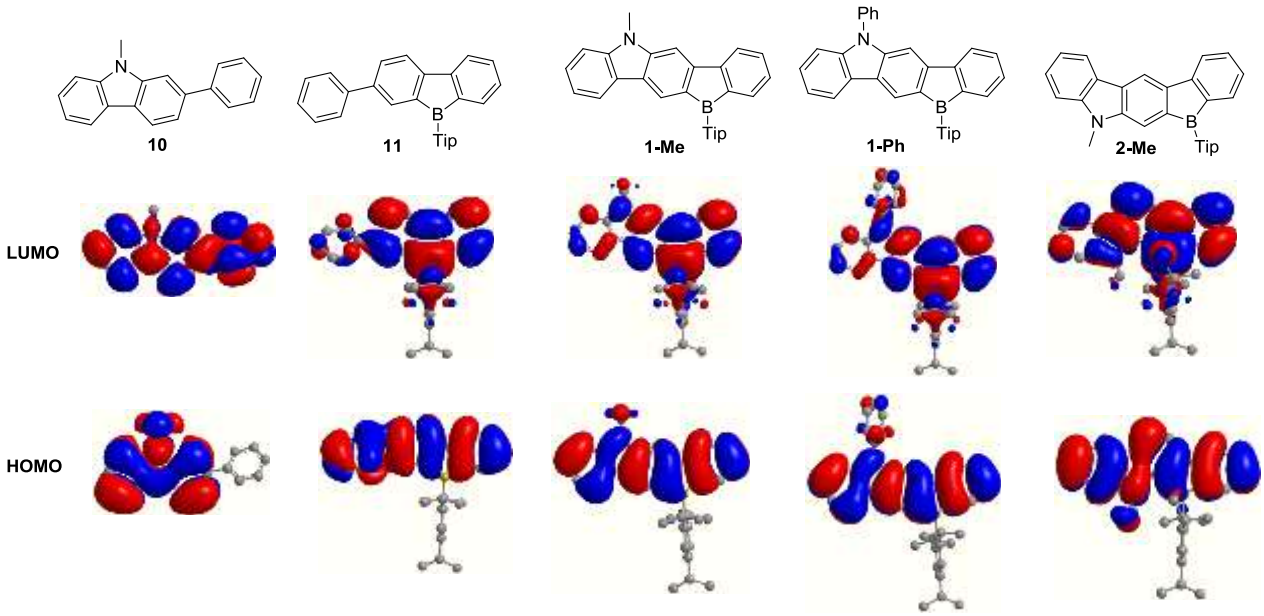


Figure S-3. Pictorial represnetation of the Kohn-Sham HOMOs and LUMOs of B,N-bridged p-terphenyls **1**–**2** and related compounds **10**–**11**, calcualted at the B3LYP/6-31G(d) level of theory.

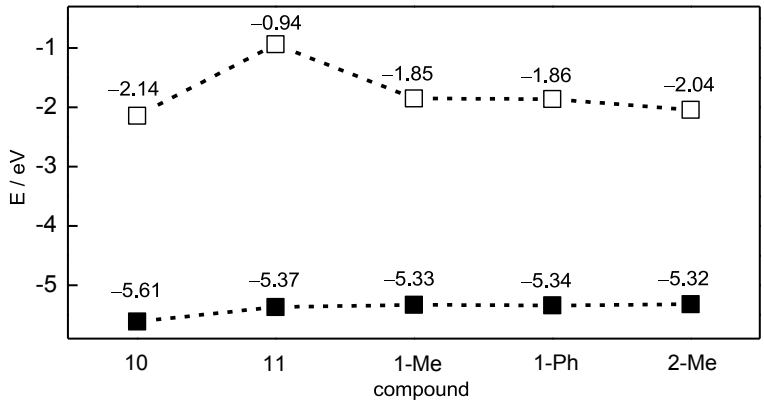


Figure S-4. Kohn-Sham HOMO and LUMO energy levels for B,N-bridged p-terphenyls **1**–**2** and related compounds **10**–**11**.

Photophysical Properties

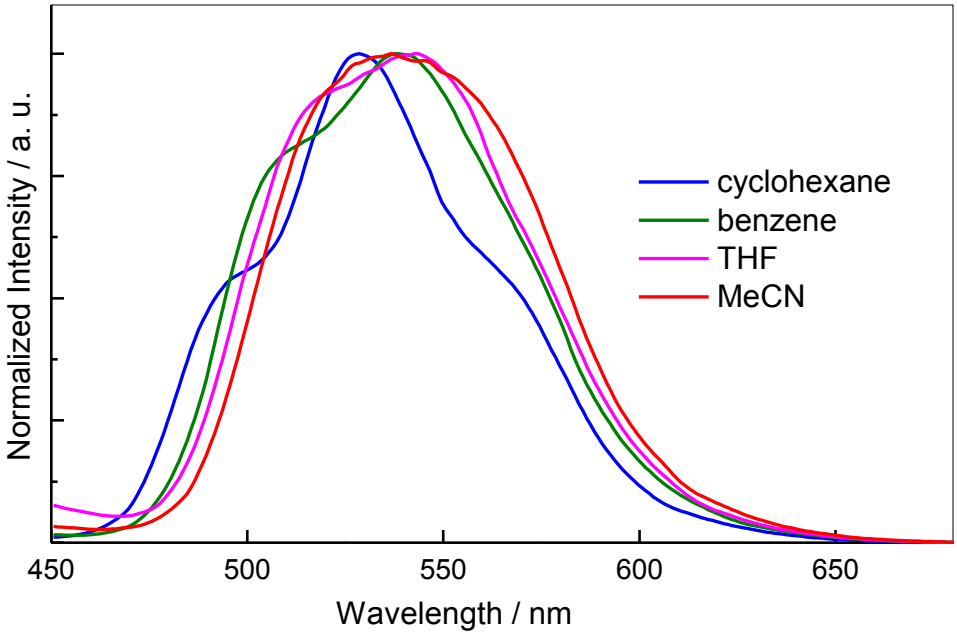


Figure S-5. Emission spectra of **1-Me** in various solvents.

Table S-3. Absorption and fluorescence data of B,N-bridged *p*-terphenyls **1**–**2** and related compounds **10**–**11**.

compound	solvent	absorption	Fluorescence		Excited-state dynamics	
		λ_{abs}/nm[a] (lgε)	λ_{em}/nm[c] (Φ_F[d])	τ_s/nm	k_r/s^{-1}	K_{nr}/s^{-1}
	cyclohexane	430[b] (3.28)	529 (0.21)	82.5	2.5×10^6	9.6×10^6
1-Me	benzene	430[b] (3.56)	538 (0.22)			
	THF	430[b] (3.40)	543 (0.22)			
	MeCN	435[b] (3.35)	540 (0.17)			
1-Ph	cyclohexane	430[b] (3.27)	527 (0.36)			
2-Me	cyclohexane	451 (4.03)	537, 567 (0.13)			
10	cyclohexane	442 (2.76)	503, 523 (0.47)	73.4	6.4×10^6	7.2×10^6
11	cyclohexane	340[b] (3.89)	366, 380 (0.96)	8.7	1.1×10^8	4.6×10^6

[a] Only the longest maxima are shown. [b] Observed as shoulder. [c] Excited at the longest absorption maxima. [d] Calculated using fluorescein as standard.

Electrochemical Properties

Electrochemical Measurements: Cyclic voltammetry (CV) was performed using a BSA 100W instrument with a scan rate of 100 mV/ s. A three-electrode configuration was used for the measurements: a platinum electrode as the working electrode, a platinum wire as the counter electrode, and an Ag/Ag+electrode as the reference electrode. A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in THF was used as the supporting electrolyte. The ferrocene/ferrocenium (Fc/Fc+) couple was used as the internal standard.

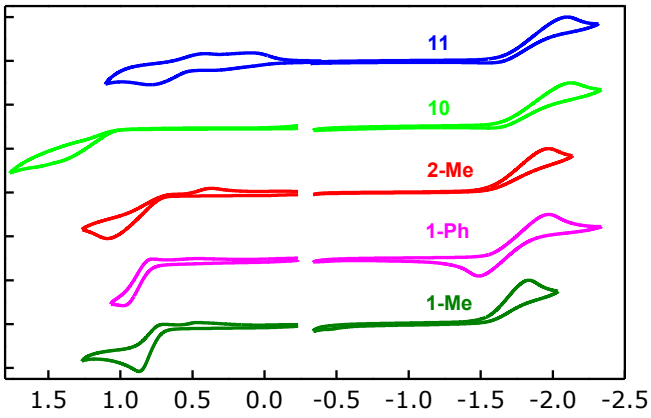


Figure S-6. Cyclic voltammograms of B,N-bridged *p*-terphenyls **1**–**2** and related compounds **10**–**11** (1 mM), measured with TBAP (0.1 M) as the supporting electrolyte as a scan rate of 100 mV/s.

References

(1) Hirose, K.; Miura, S.; Senda, Y.; Tobe, Y. *Chem. Commun.* **2012**, *48*, 6052.

(2) Quasdorf, K. W.; Antoft-Finch, A.; Liu, P.; Silberstein, A. L.; Komaromi, A.; Blackburn, T.; Ramgren, S. D.; Houk, K. N.; Snieckus, V.; Garg, N. K. *J. Am. Chem. Soc.* **2011**, *133*, 6352.

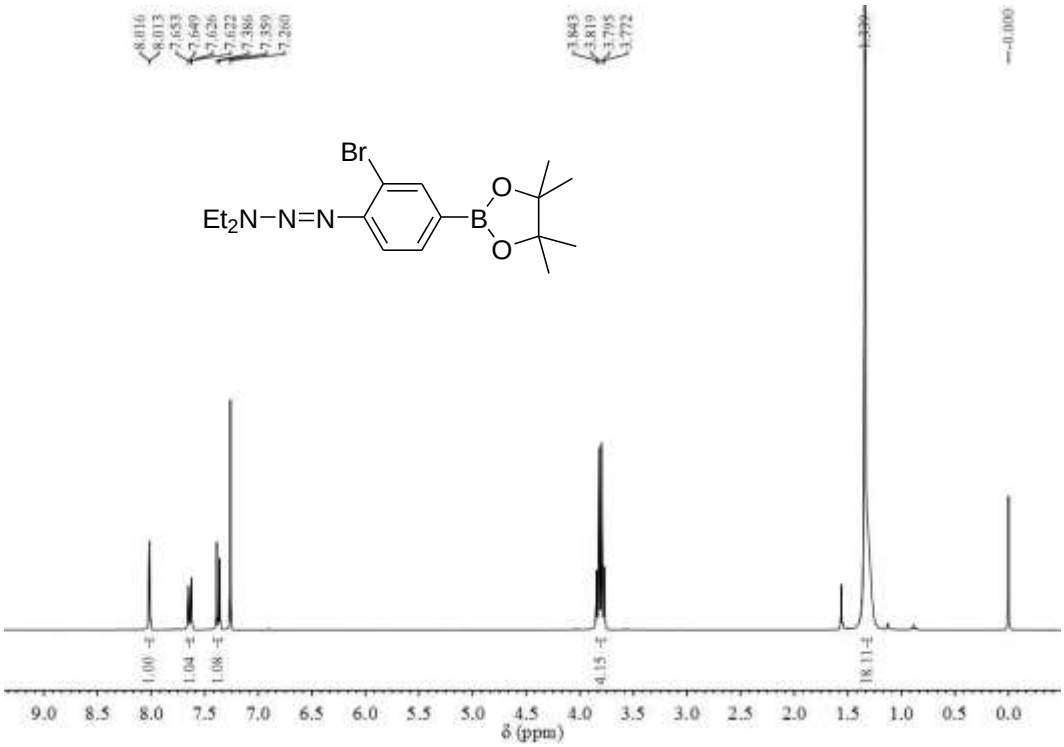
(3) Gaussian 09, Revision A.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.;

Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, Jr. J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G. ; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, **2009**.

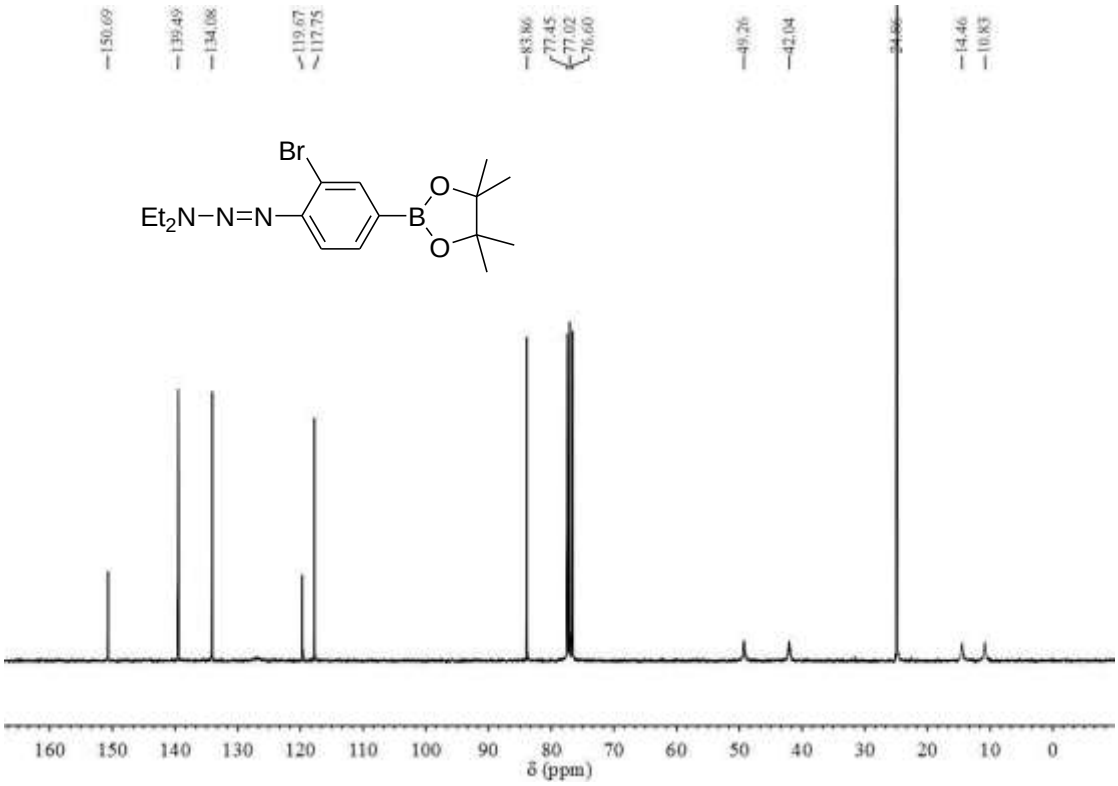
(4) SHELX-97, Program for the Refinement of Crystal Structure, G. M. Sheldrick, University of Götingen, Götingen (Germany), 1997.

NMR Spectra

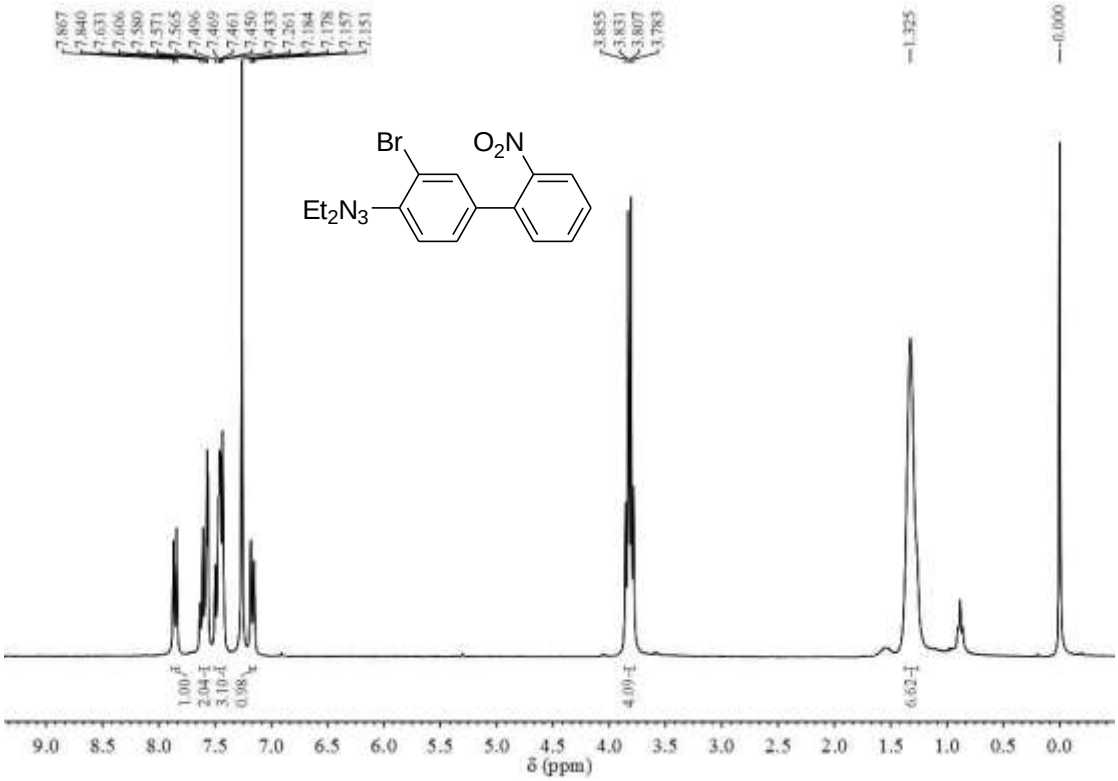
^{1}H NMR of **7** (300 MHz, $CDCl_3$)



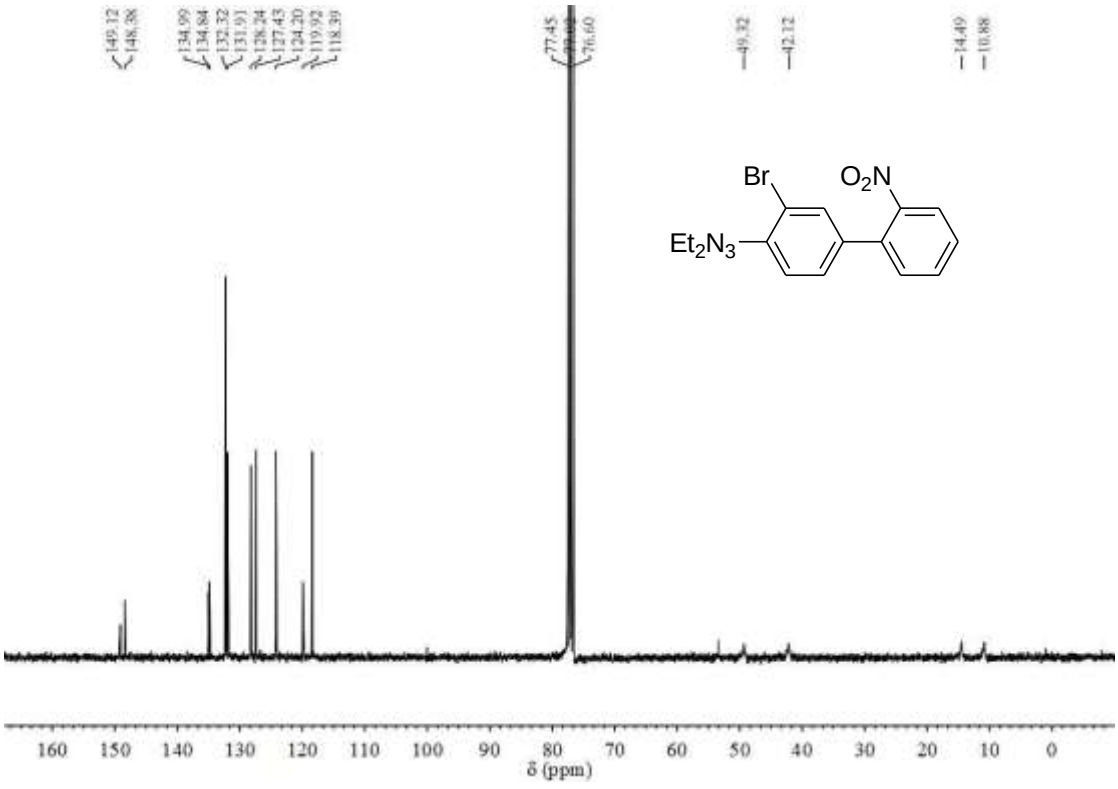
^{13}C NMR of **7** (75 MHz, $CDCl_3$)



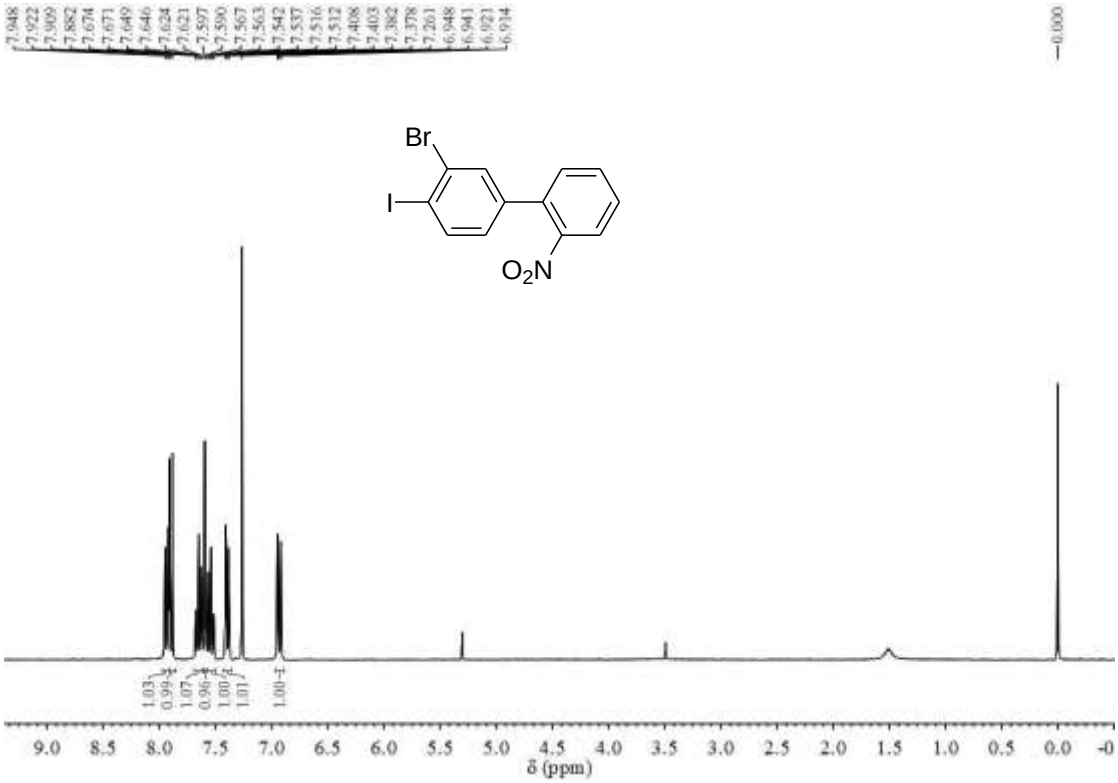
^{1}H NMR of **8** (300 MHz, $CDCl_3$)



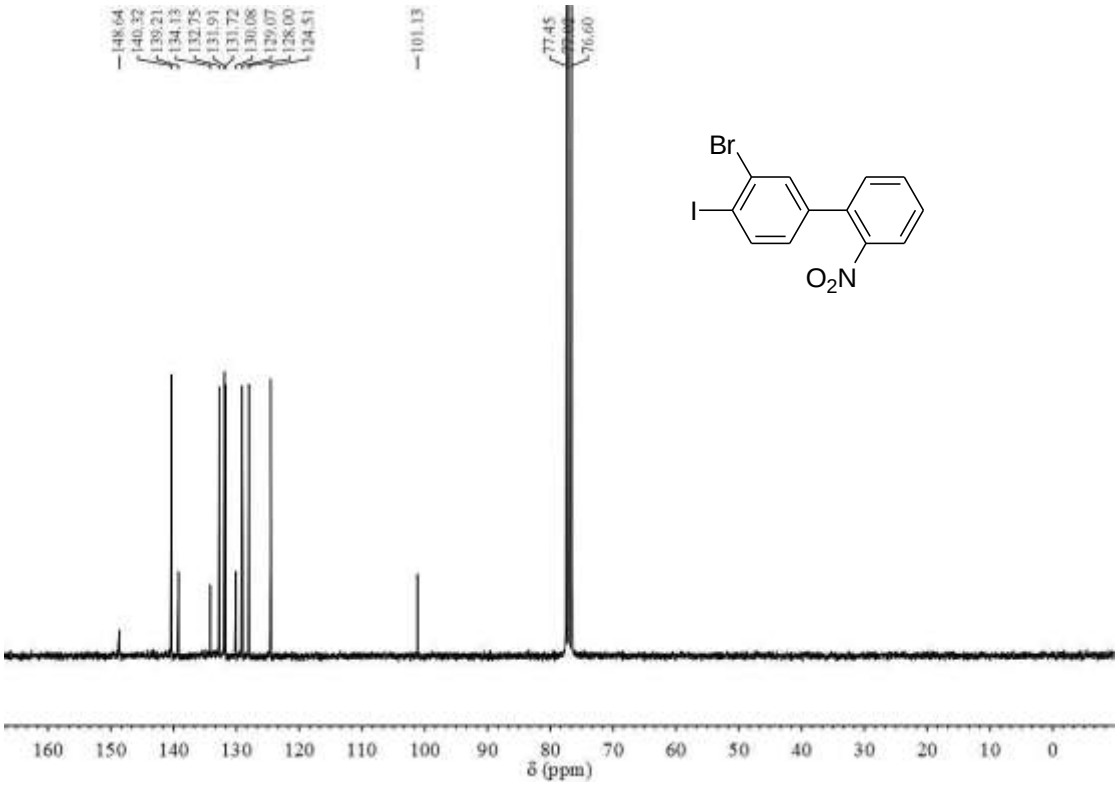
^{13}C NMR of **8** (75 MHz, $CDCl_3$)



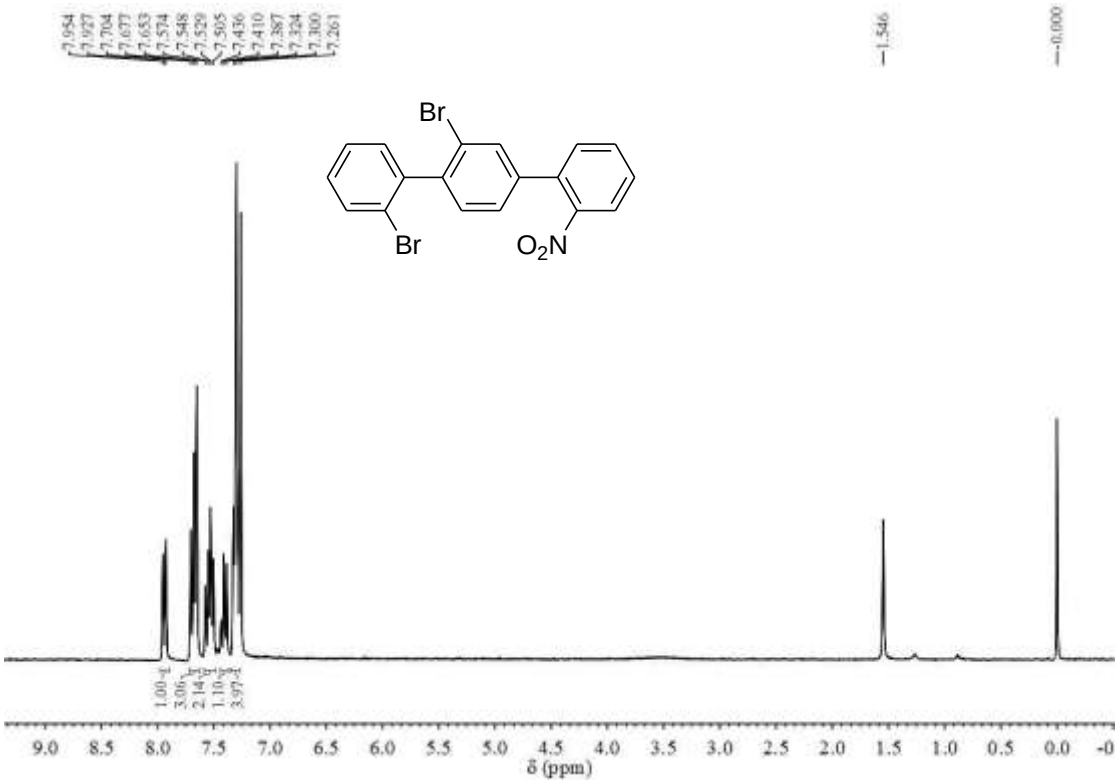
^{1}H NMR of **9** (300 MHz, $CDCl_3$)



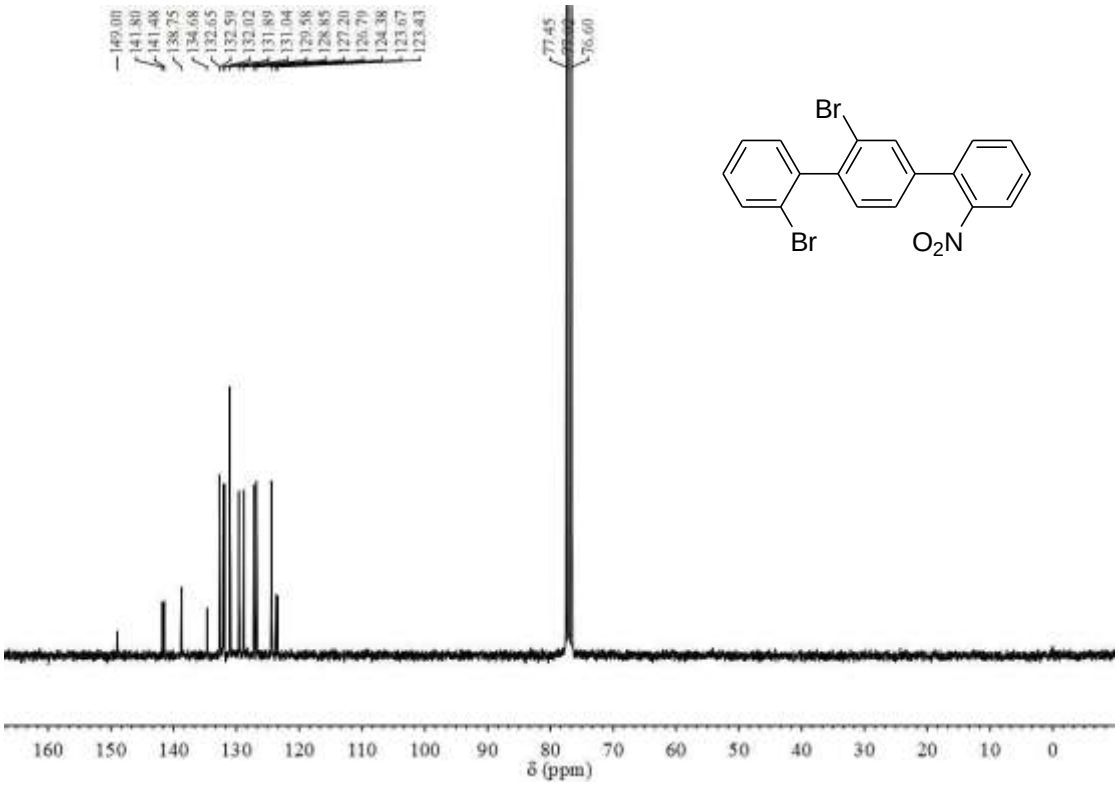
^{13}C NMR of **9** (75 MHz, $CDCl_3$)



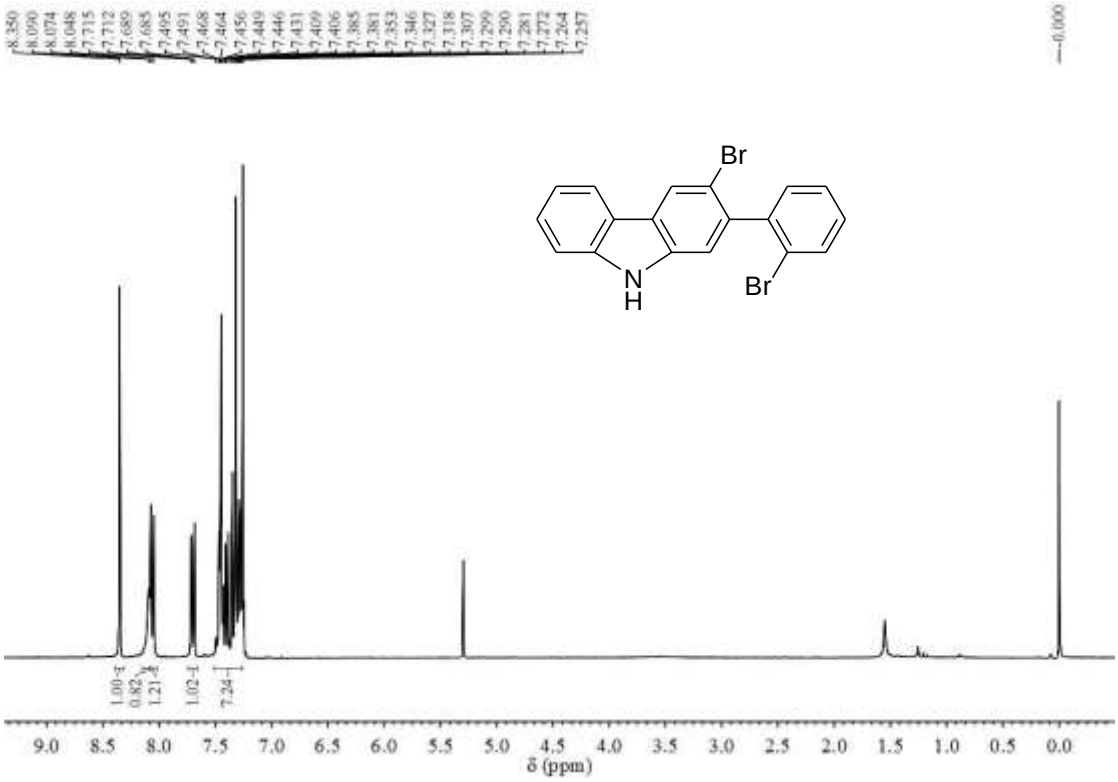
^{1}H NMR of **5** (300 MHz, $CDCl_3$)



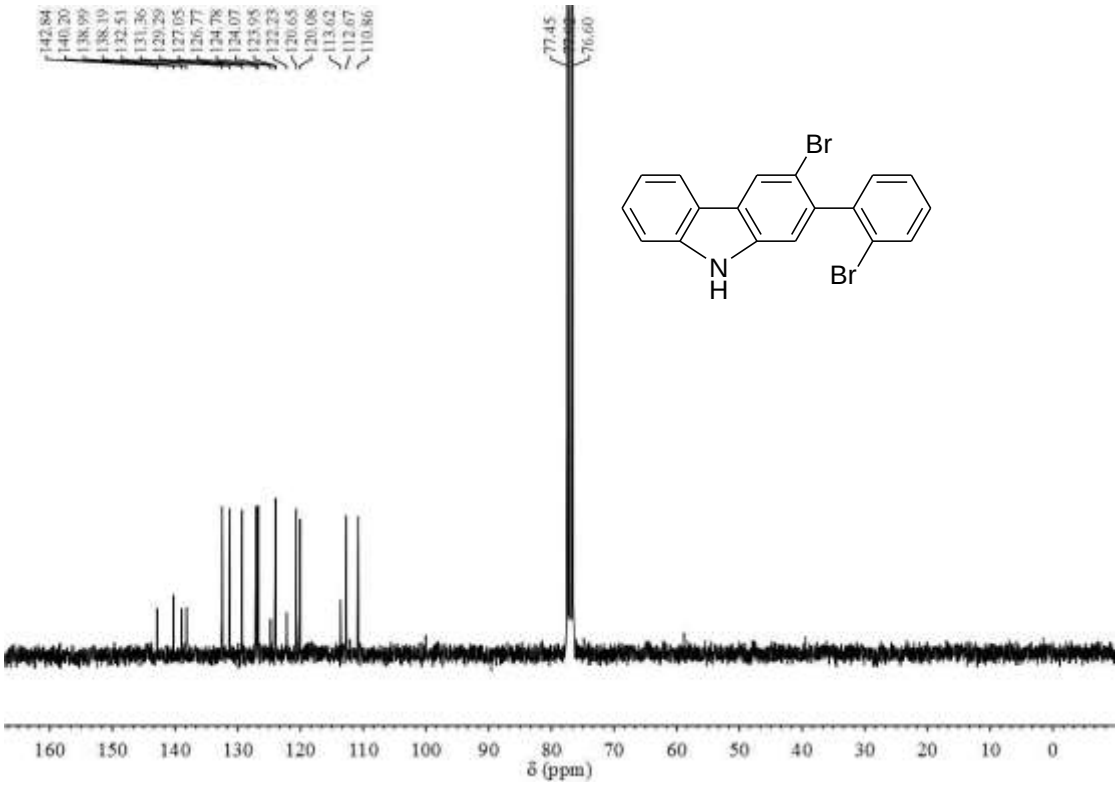
^{13}C NMR of **5** (75 MHz, $CDCl_3$)



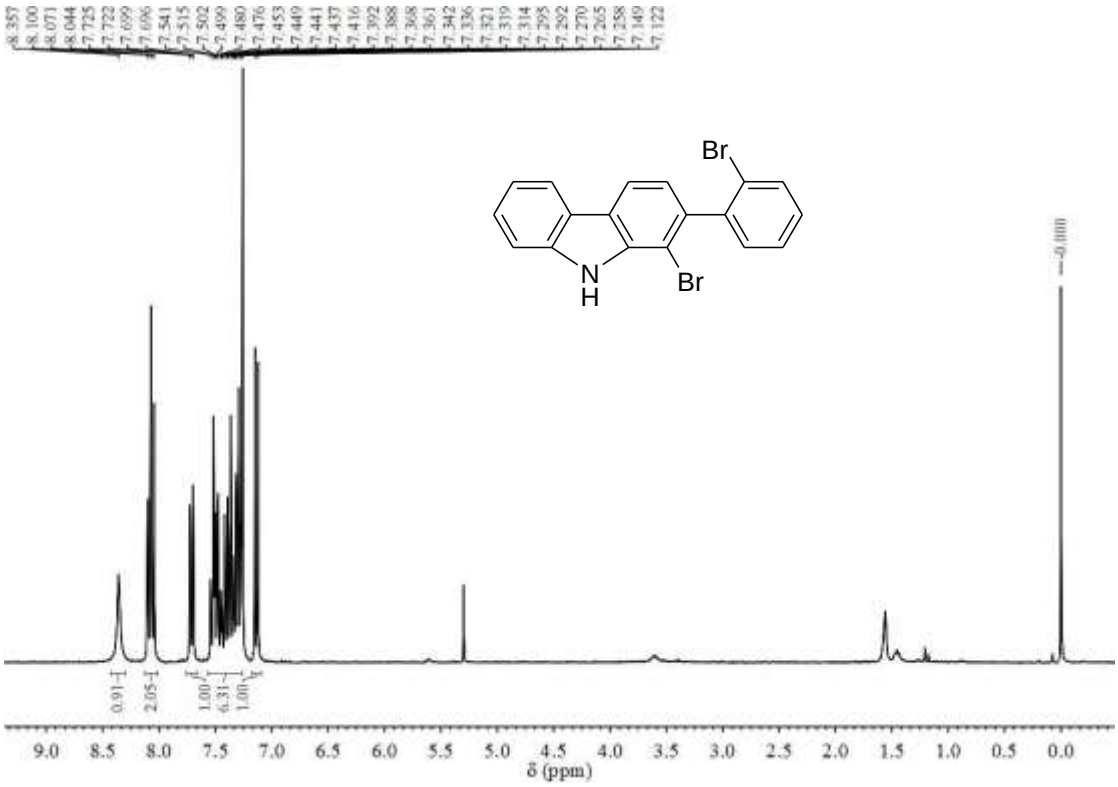
^{1}H NMR of **3-H** (300 MHz, $CDCl_3$)



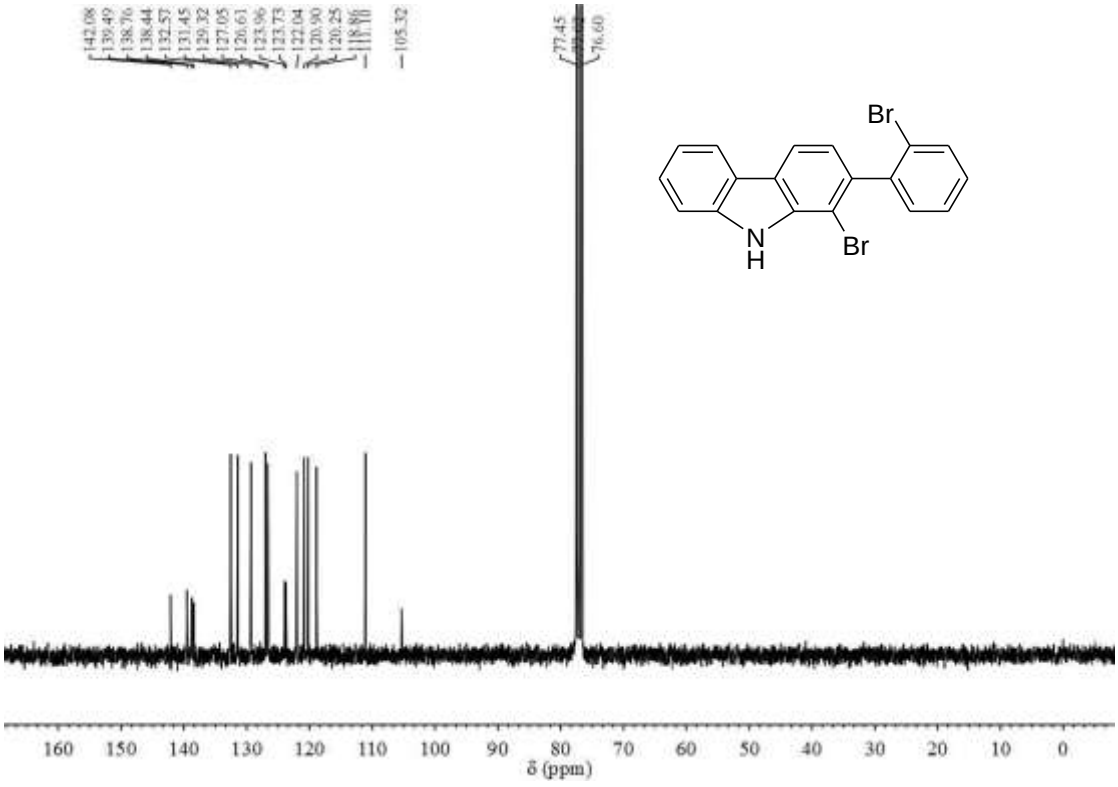
^{13}C NMR of **3-H** (75 MHz, $CDCl_3$)



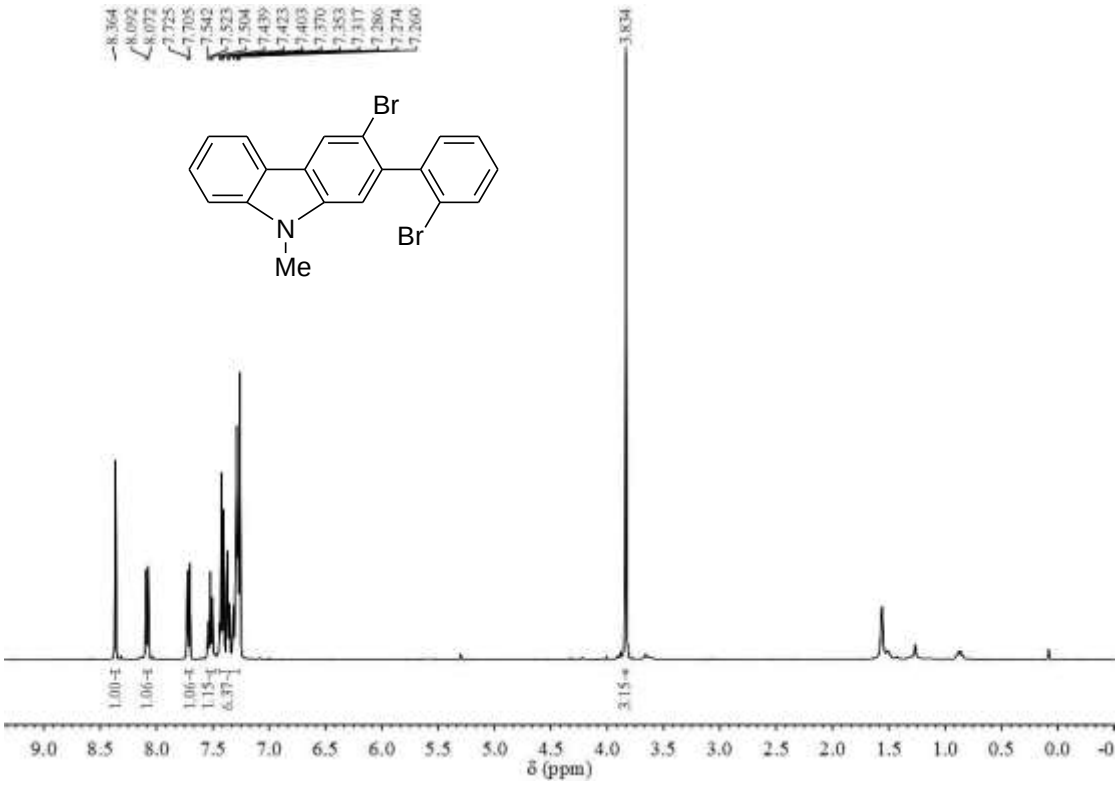
^{1}H NMR of **4-H** (300 MHz, $CDCl_3$)



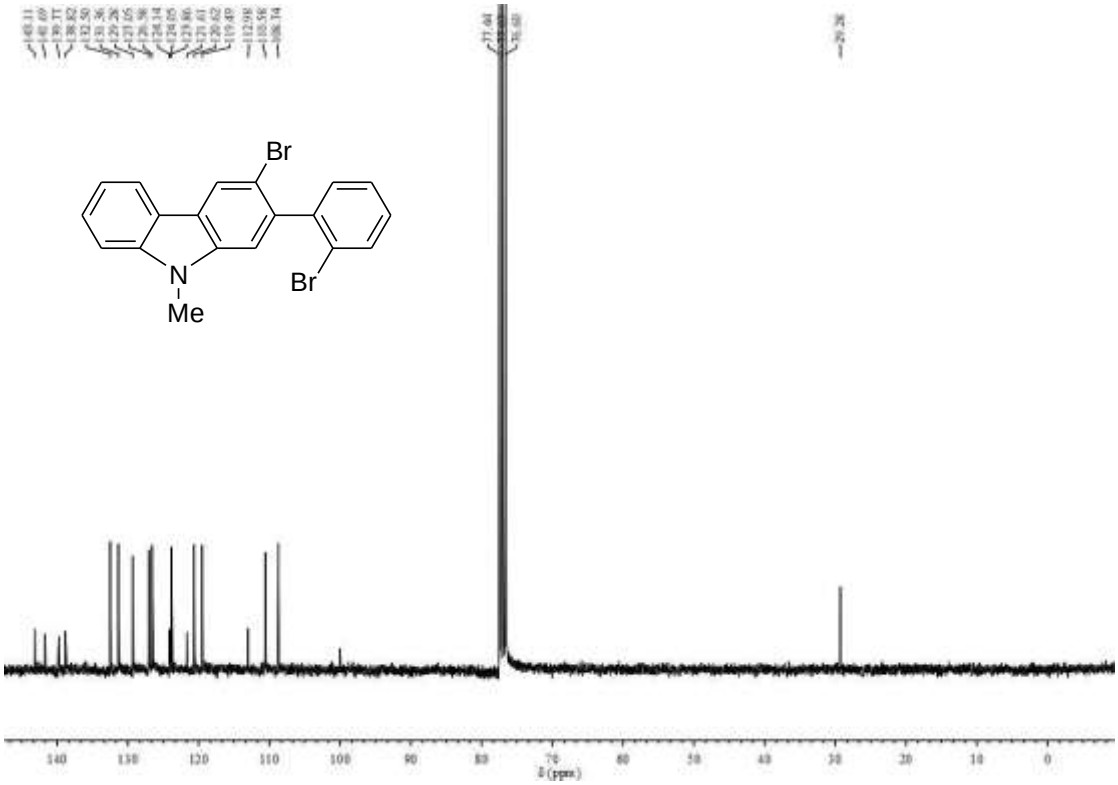
^{13}C NMR of **4-H** (75 MHz, $CDCl_3$)



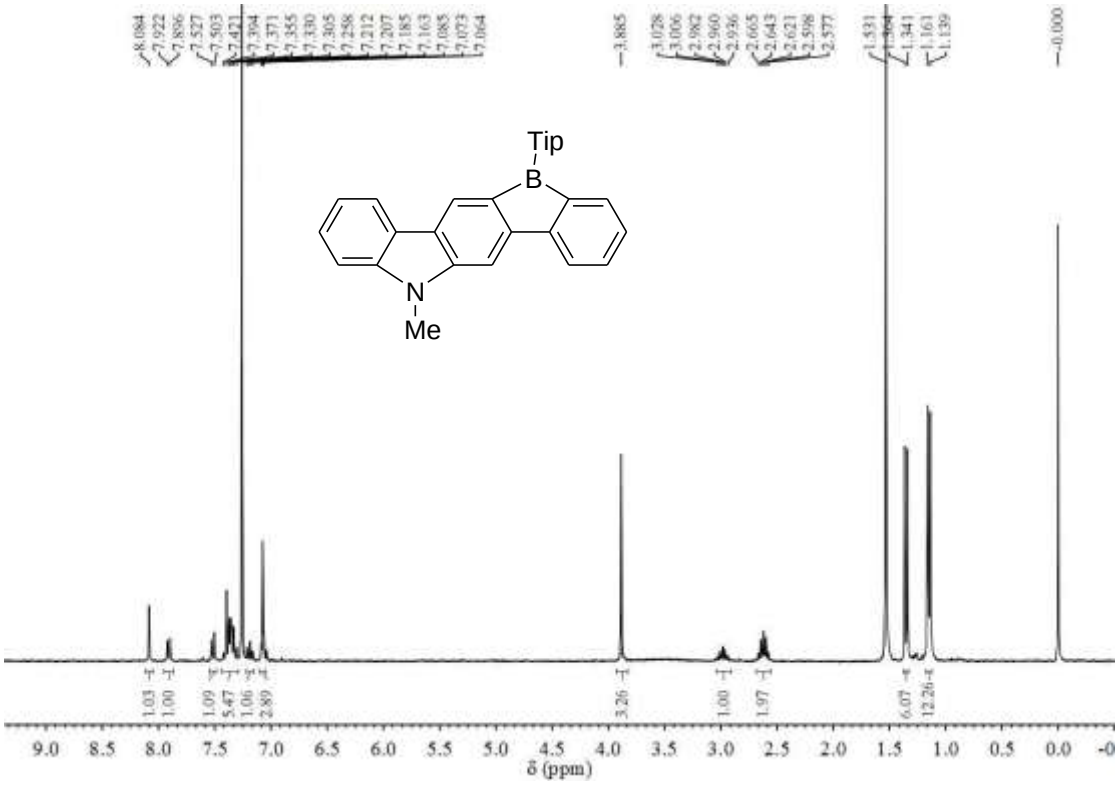
^{1}H NMR of **3-Me** (400 MHz, $CDCl_3$)



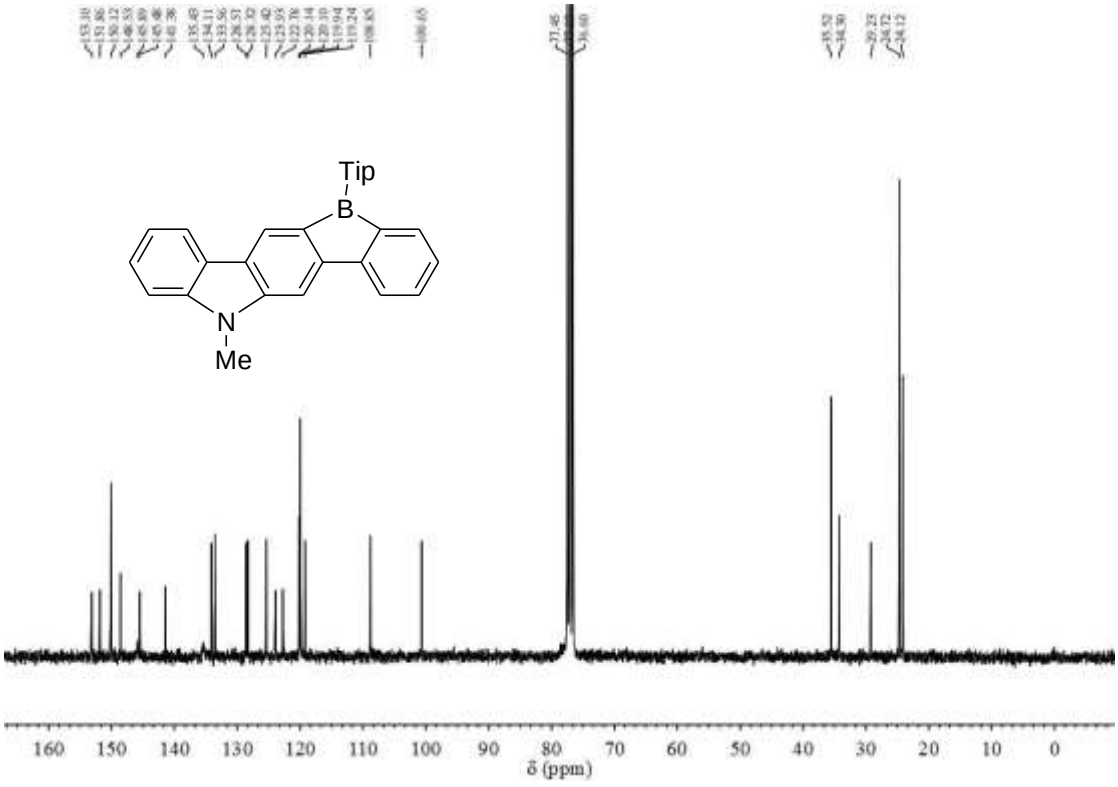
^{13}C NMR of **3-Me** (75 MHz, $CDCl_3$)



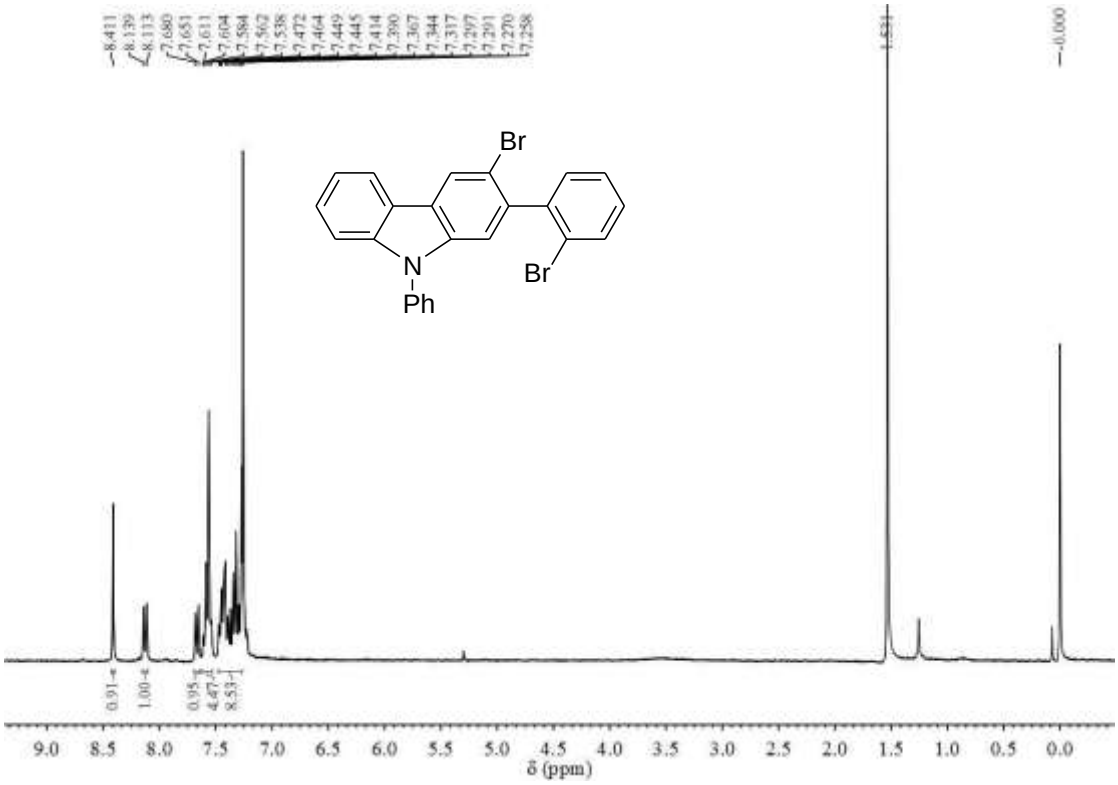
^{1}H NMR of **1-Me** (300 MHz, $CDCl_3$)



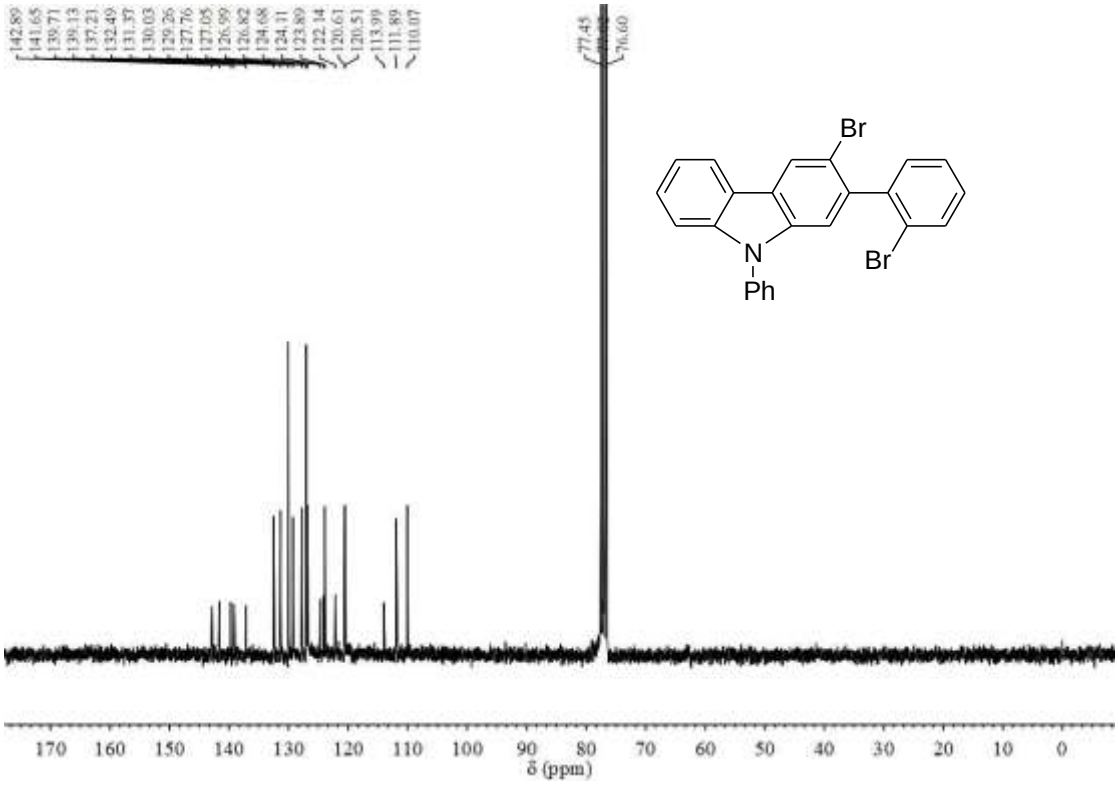
^{13}C NMR of **1-Me** (75 MHz, $CDCl_3$)



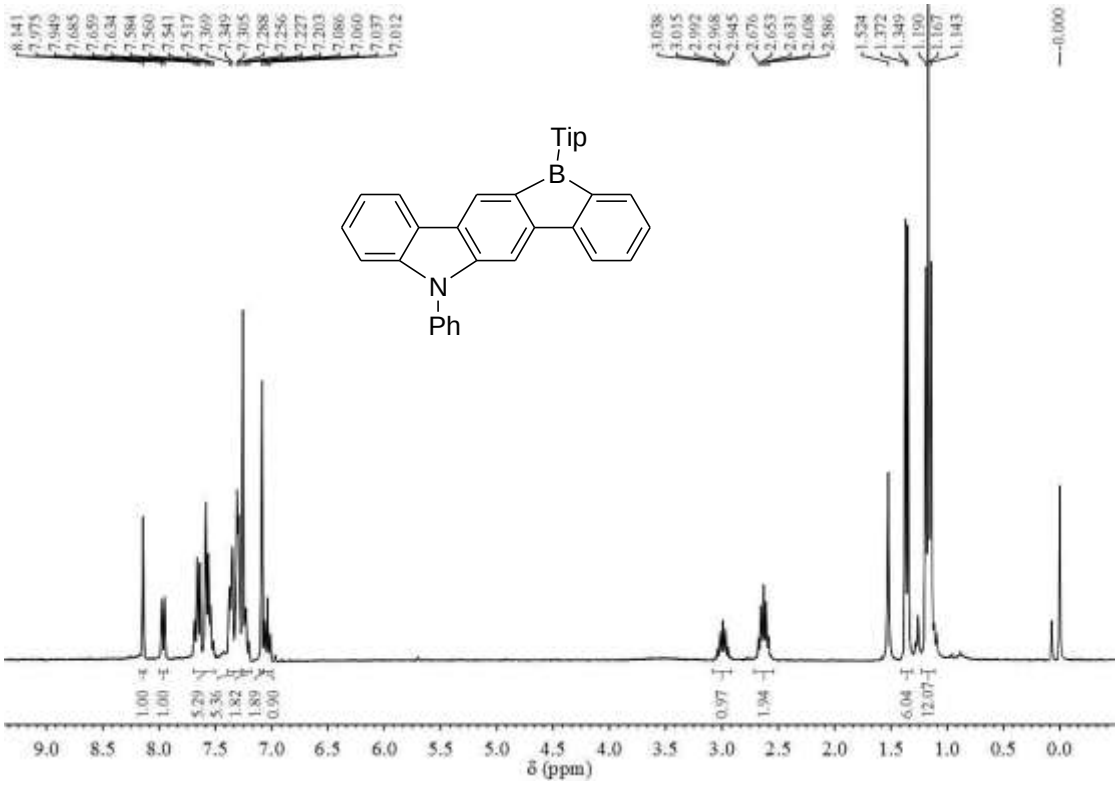
^{1}H NMR of **3-Ph** (300 MHz, $CDCl_3$)



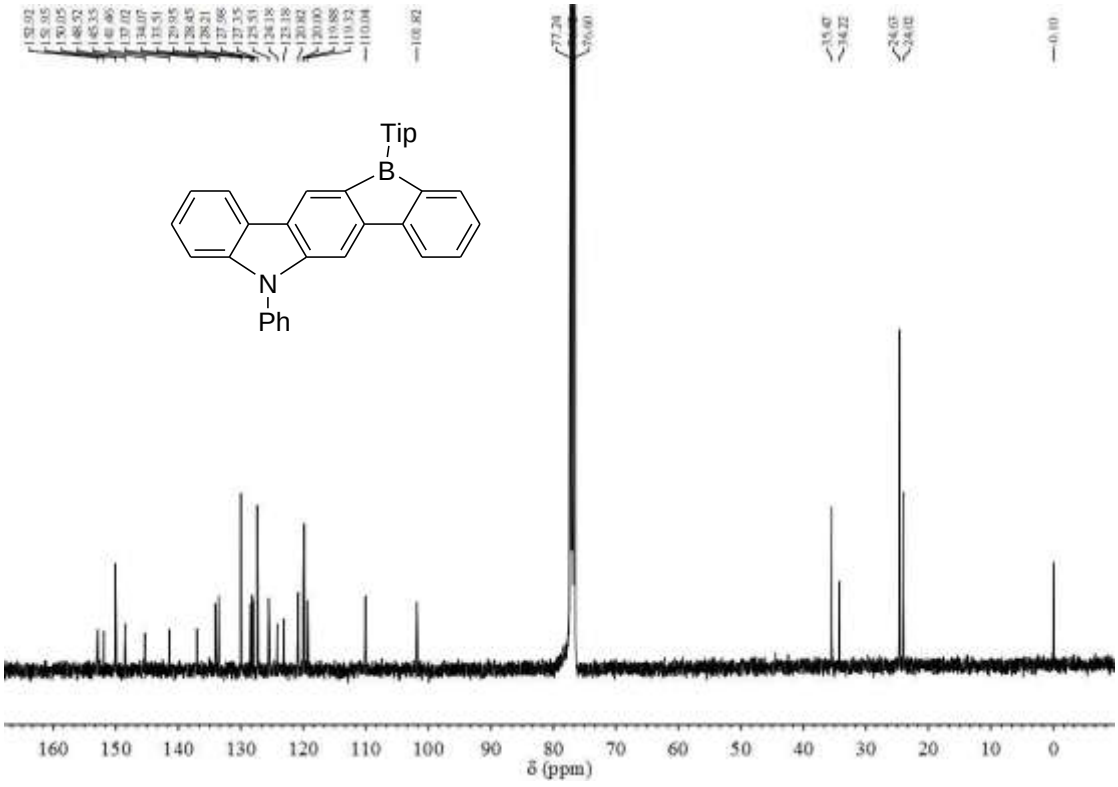
^{13}C NMR of **3-Ph** (75 MHz, $CDCl_3$)



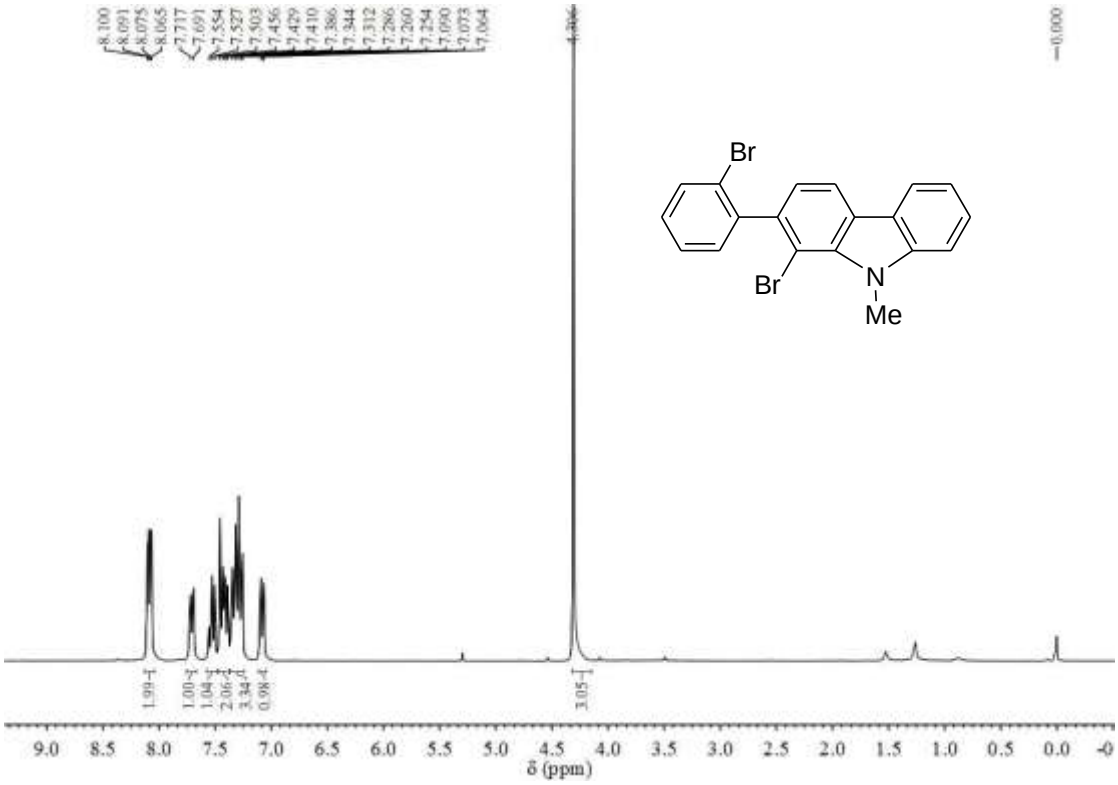
^{1}H NMR of **1-Ph** (300 MHz, $CDCl_3$)



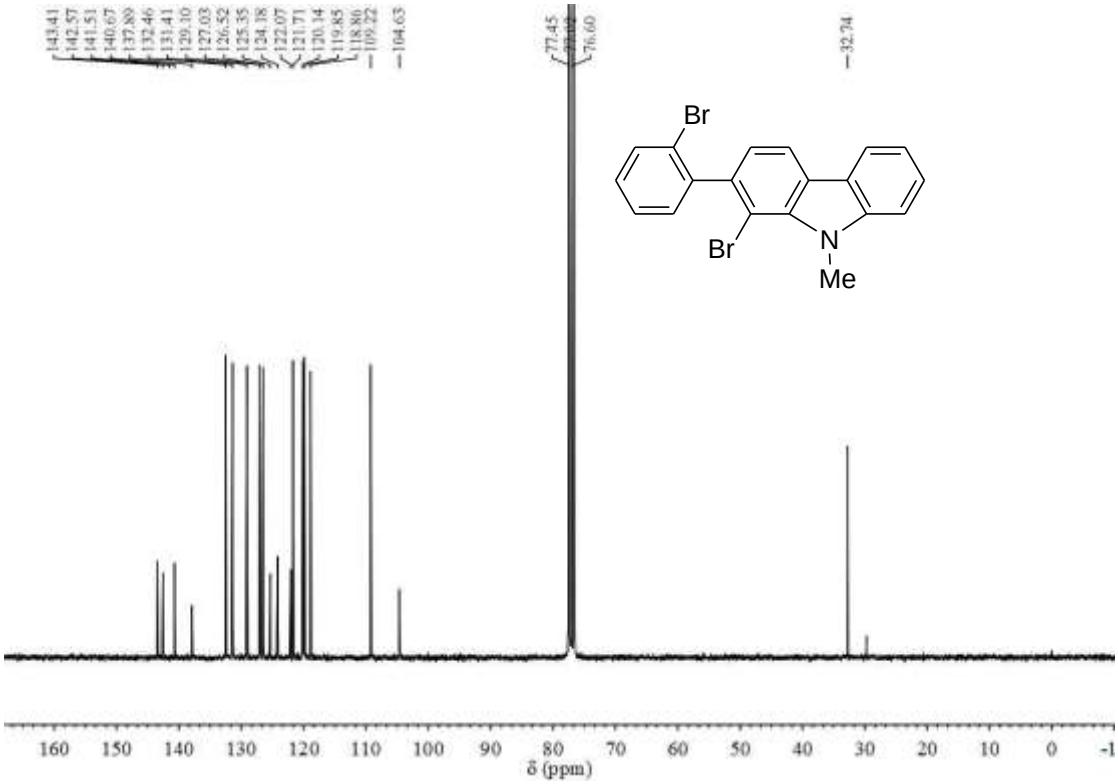
^{13}C NMR of **1-Ph** (100 MHz, $CDCl_3$)



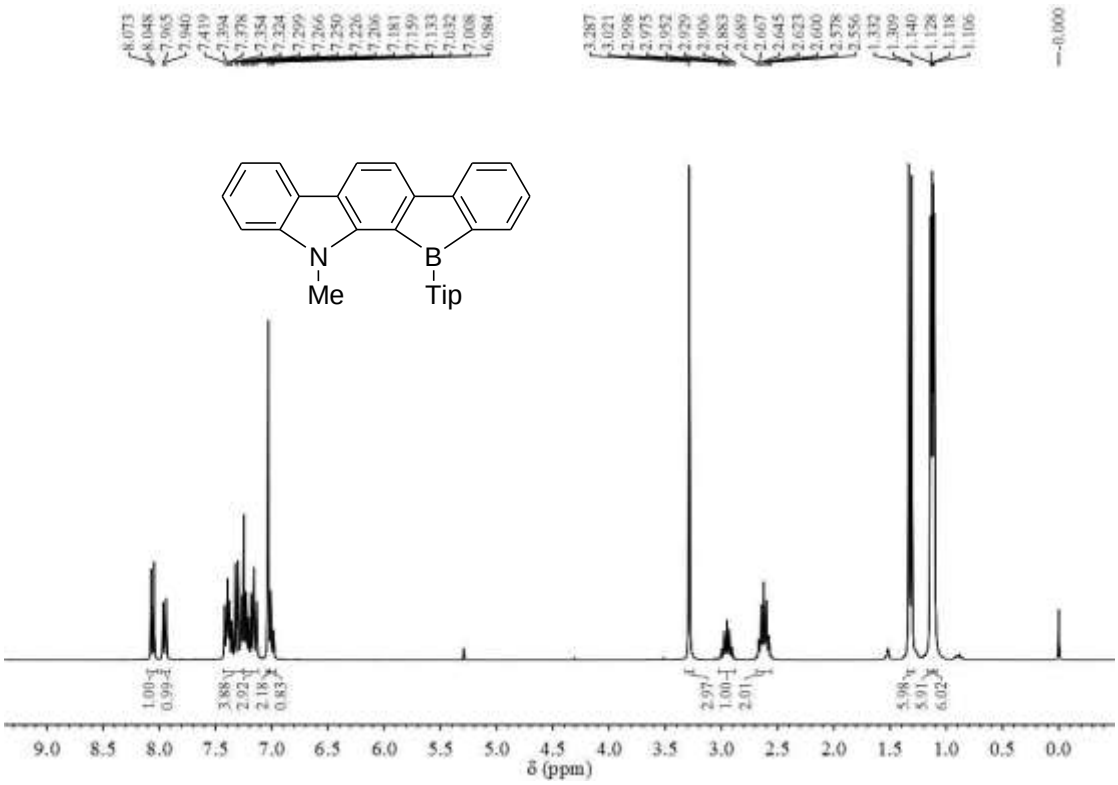
^{1}H NMR of **4-Me** (300 MHz, $CDCl_3$)



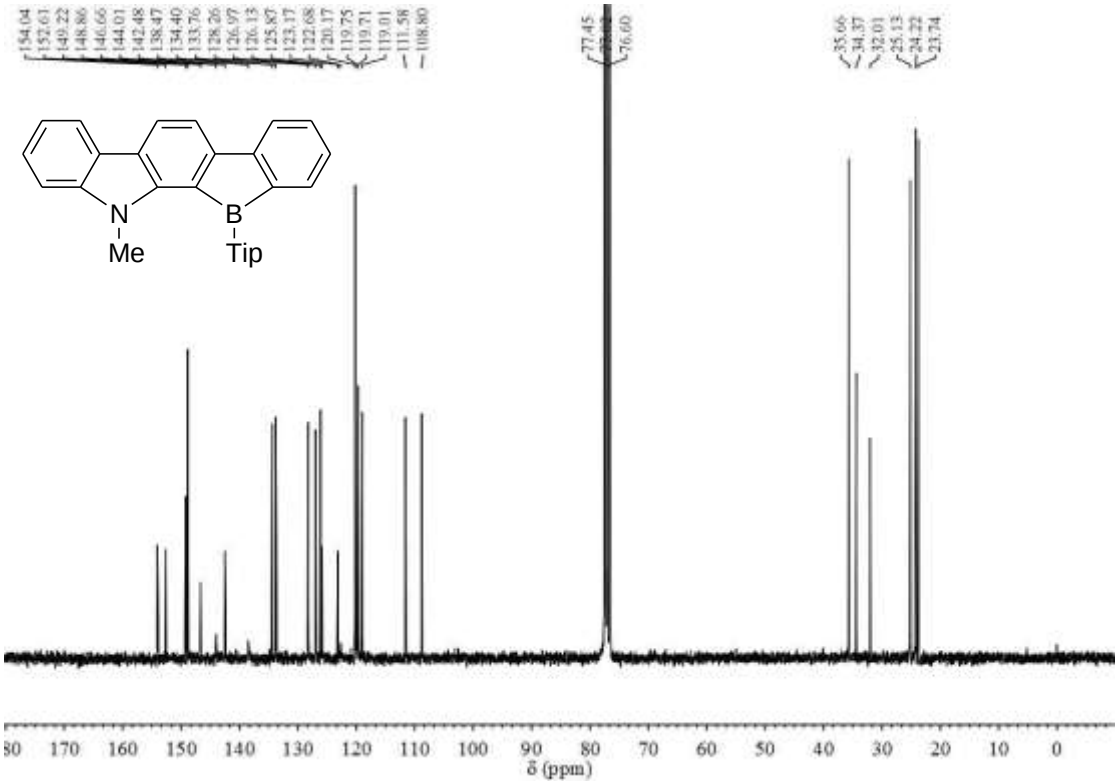
^{13}C NMR of **4-Me** (75 MHz, $CDCl_3$)



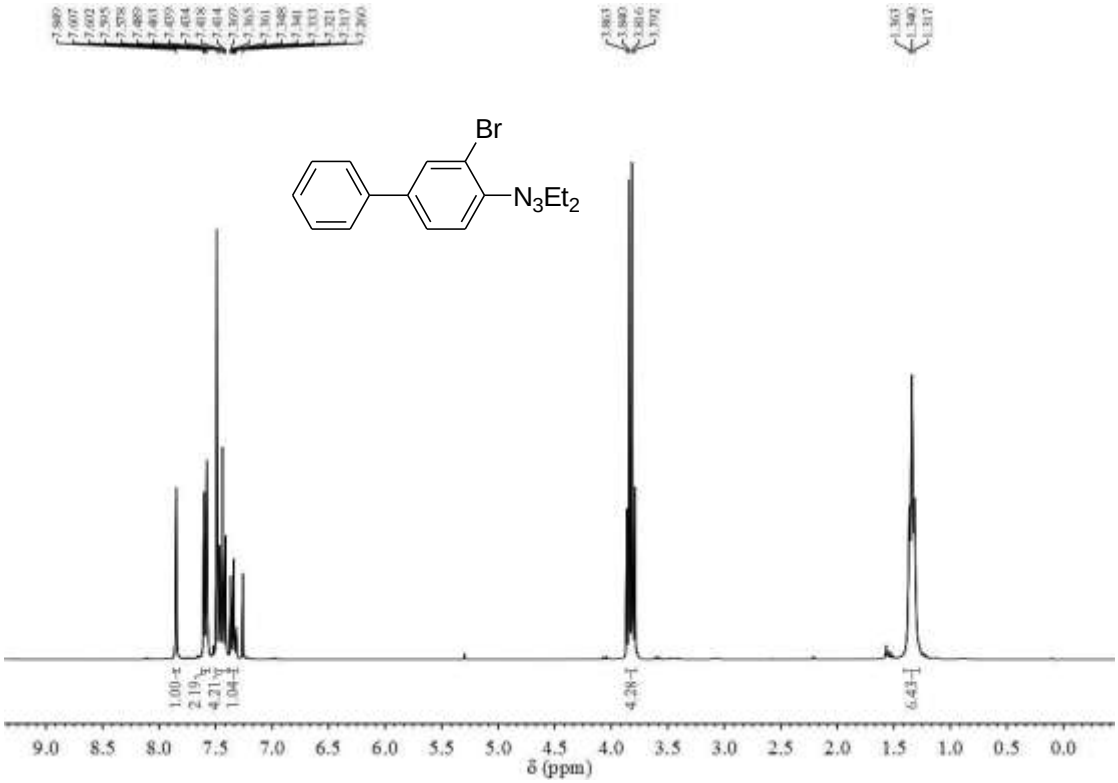
^{1}H NMR of **2-Me** (300 MHz, $CDCl_3$)



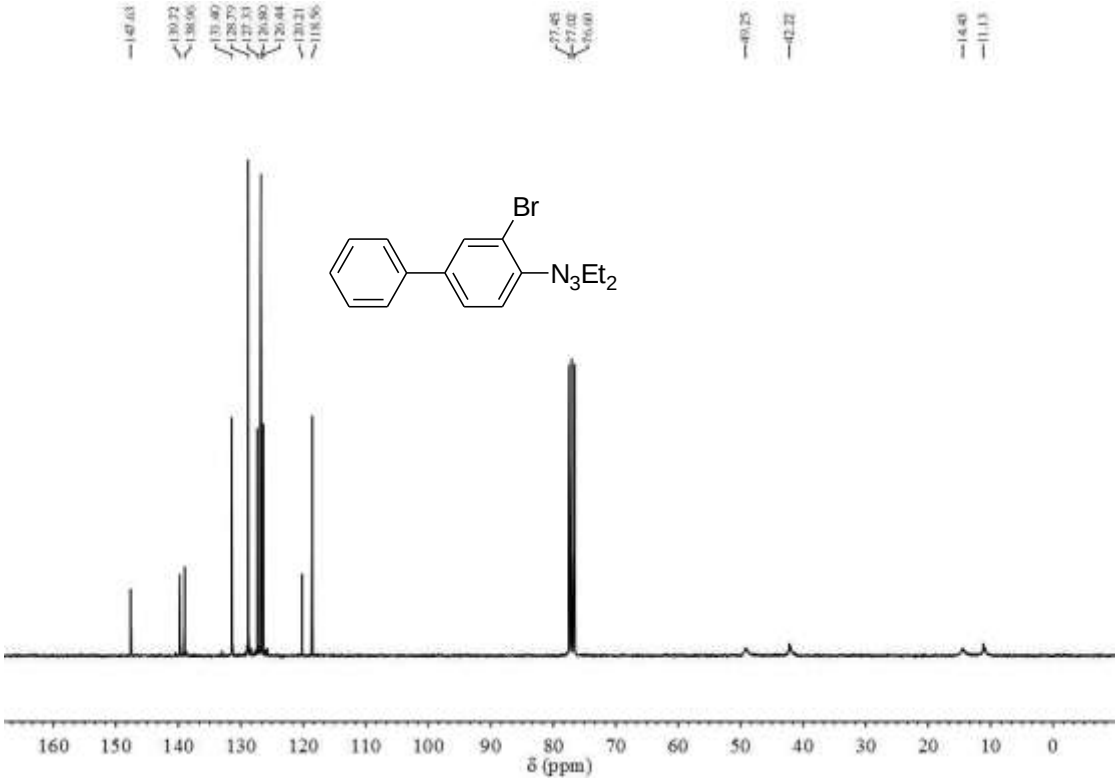
^{13}C NMR of **2-Me** (75 MHz, $CDCl_3$)



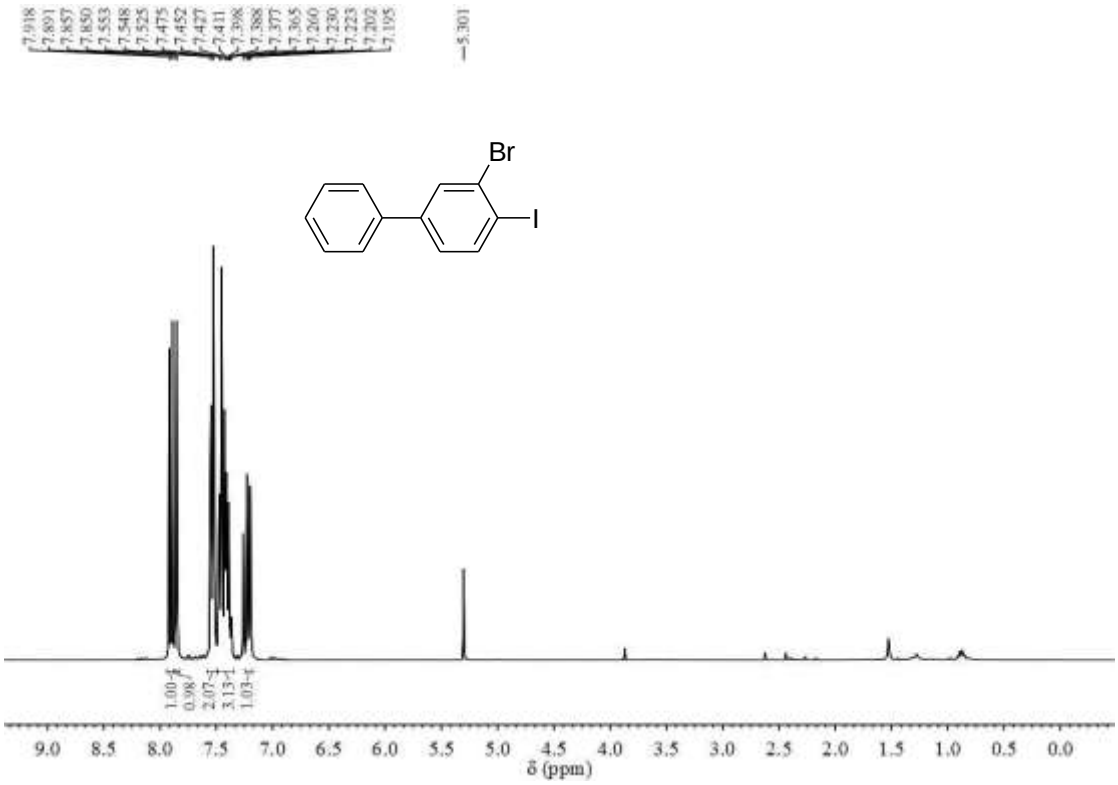
^{1}H NMR of **12** (300 MHz, $CDCl_3$)



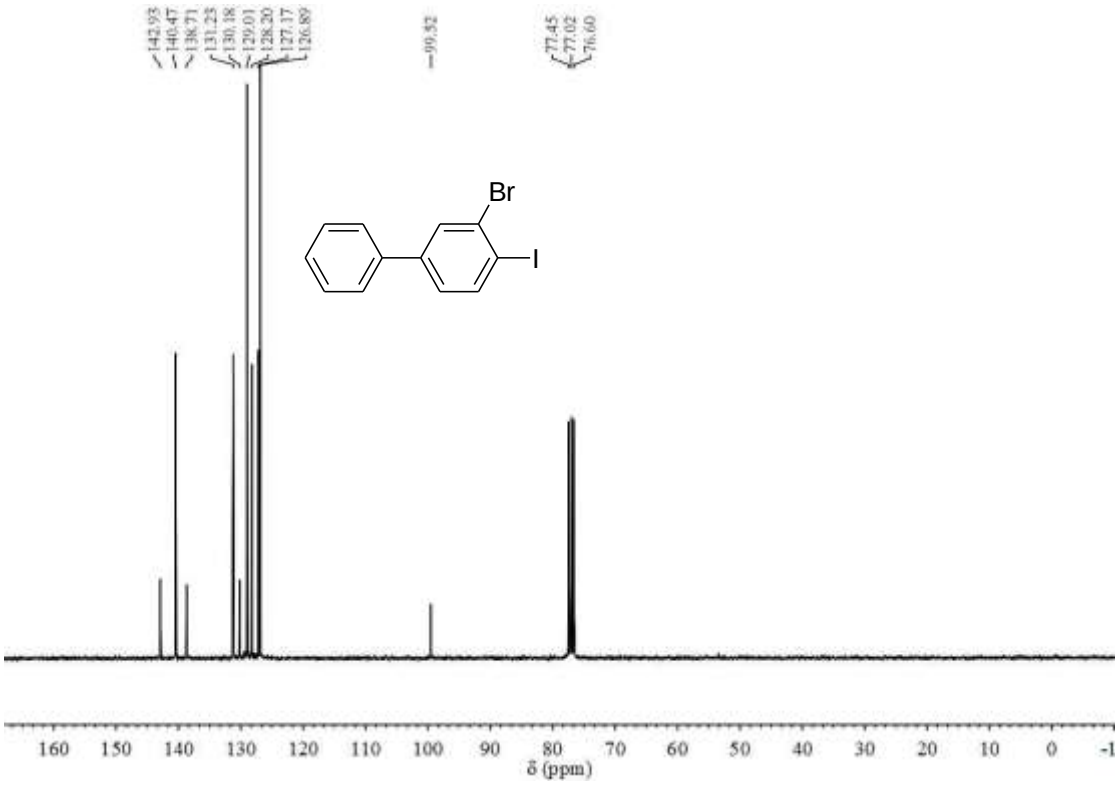
^{13}C NMR of **12** (75 MHz, $CDCl_3$)



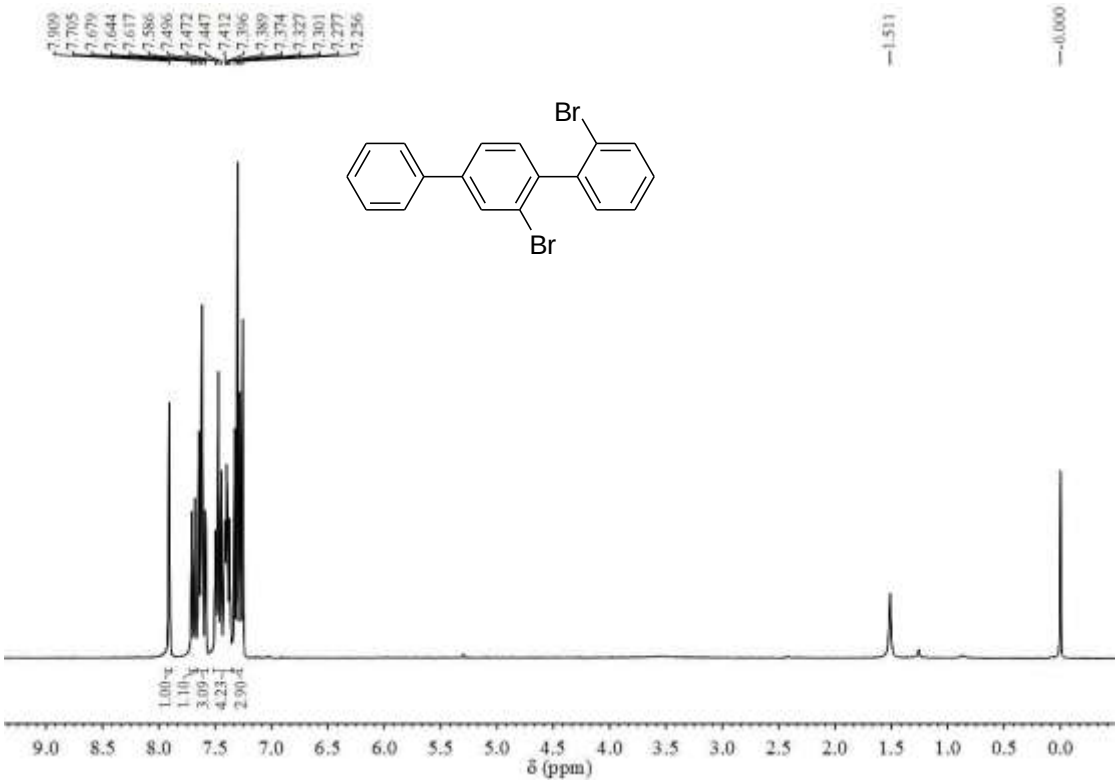
^{1}H NMR of **13** (300 MHz, $CDCl_3$)



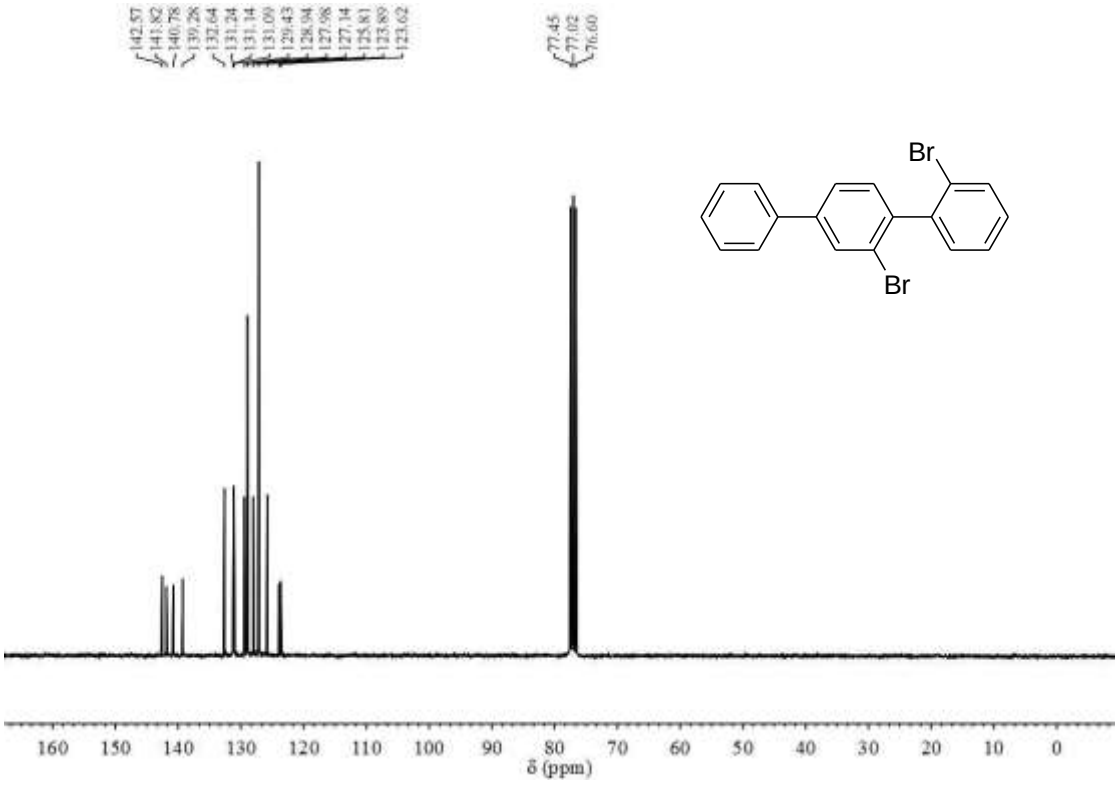
^{13}C NMR of **13** (75 MHz, $CDCl_3$)



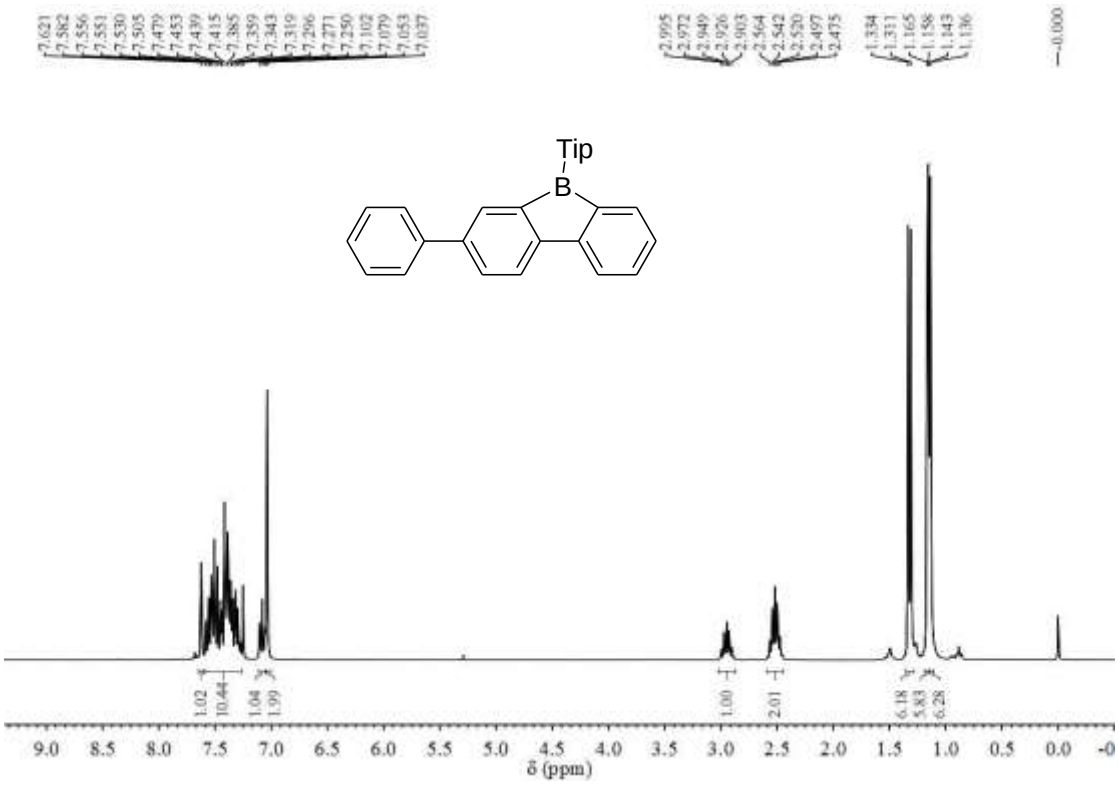
^{1}H NMR of **14** (300 MHz, $CDCl_3$)



^{13}C NMR of **14** (75 MHz, $CDCl_3$)



^{1}H NMR of **10** (300 MHz, $CDCl_3$)



^{13}C NMR of **10** (75 MHz, $CDCl_3$)