Supporting Information

Transition-Metal-Free Borylation of Aryltriazene Mediated by BF_3•OEt_2

*Chuan Zhu, Motoki Yamane**

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore.

yamane@ntu.edu.sg

Table of contents

I. General information

^{1}H NMR spectra were recorded at 400 MHz in $CDCl_3$ [using $(CH_3)_4Si$ (for ^{1}H, δ= 0.00) as internal standard]. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ [using $CDCl_3$ (for ^{13}C, δ= 77.0) as internal standard]. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, m = multiplet, br = broad. IR spectra were recorded on a Shimazu IR Prestige-21 FT-IR Spectrometer. High-resolution mass spectra were obtained with a Finnigan MAT 95 XP mass spectrometer (Thermo Electron Corporation). Melting points were uncorrected and were recorded on a Buchi B-54 melting point apparatus. Flash column chromatography was performed using Merck silica gel 60 with distilled solvents. HPLC was performed using a Shimadzu LC-20AD series HPLC system fitted with a Chiralpak IB column, eluting with hexane/isopropylalcohol (98 : 2).

II. Materials

Commercially available reagents and solvents were used without further purification. **1a, 1f, 1g, 1k, 1o, 1q,**[1] **1j**,[2] **1n**,[3] **1o,**[4] **1q,**[5] and **1s**[6] were prepared from corresponding aniline by the literature method.

General procedure for the preparation of aryltriazene **1b, 1c, 1d, 1e, 1h, 1i, 1l, 1r, 1t, 1u** and **1v**. A solution of corresponding aniline (5.0 mmol) in 2.0 mL of conc. HCl was cooled in an ice bath while a solution of $NaNO_2$ (366 mg, 5.3 mmol) in cold water (10 mL) was added dropwise. The resulting solution of the diazonium salt was stirred at 0 °C for 30 min and then added to a solution of pyrrolidine (2.57 g, 36.2 mmol) and K_2CO_3 (12.51 g, 90.5 mmol) in 1:2 acetonitrile/water (25 mL) by one portion. The

reaction mixture was allowed to warm to room temperature and stirred for 30 min. The aqueous phase was extracted with EtOAc (3 × 15 mL). The organic phase was washed twice with brine, dried with $MgSO_4$, and concentrated under reduced pressure. The crude product was purified by flash column chromatography over silica gel giving the corresponding aryltriazene.

1-[2-(3-methoxyphenyl)diazen-1-yl]pyrrolidine (1b)

Orange solid; mp 48-49 °C; Yield: 74% (759 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.26-7.19 (m, 1H), 7.02-6.99 (m, 2H), 6.69 (dd, J = 8.0, 2.4 Hz, 1H), 3.82 (s, 3H), 3.79 (br, 4H), 2.02 (t, J = 6.8 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 160.2, 152.8, 129.4, 113.2, 111.5, 105.1, 55.2, 23.8; IR (neat) cm^{-1} 3053, 2982, 2876, 1597, 1410, 1315, 1265; ESI-HRMS: Found: m/z 206.1293. Calcd for $C_{11}H_{16}N_3O$: $(M+H)^+$ 206.1289.

1-[2-(2-methoxyphenyl)diazen-1-yl]pyrrolidine (1c)

Pale yellow solid; mp 39-40 °C; Yield: 97% (995 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.30 (d, J = 8.0 Hz, 1H), 7.11 (dd, J = 8.0, 8.0 Hz, 1H), 6.93-6.89 (m, 2H), 3.90 (s, 3H), 3.83 (br, 4H), 2.01 (br, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 152.8, 140.9, 126.0, 120.9, 118.6, 111.7, 56.0, 23.8; IR (neat) cm^{-1} 3051, 2980, 2874, 1587, 1491, 1412, 1317, 1265; ESI-HRMS: Found: m/z 206.1296. Calcd for $C_{11}H_{16}N_3O$: $(M+H)^+$ 206.1293.

1-[2-[4-(benzylsulfanyl)phenyl]diazen-1-yl]pyrrolidine (1d)

Pale yellow solid; mp 113-114 °C; Yield: 90% (1.34 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32-7.18 (m, 9H), 4.05 (s, 2H), 3.76 (br, 4H), 1.99 (t, J = 6.8 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 150.3, 137.8, 131.7, 131.6, 128.8, 128.3, 127.0, 120.7, 40.0, 23.7; IR (neat) cm^{-1} 3053, 2984, 2831, 1422, 1339, 1265; ESI-HRMS: Found: m/z 298.1376.

Calcd for $C_{17}H_{20}N_3S$: $(M+H)^+$ 298.1378.

9-{4-[2-(pyrrolidin-1-yl)diazen-1-yl]phenyl}-9H-carbazole (1e)

Pale yellow solid; mp 143-144 °C; Yield: 77% (1.31 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.13 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 7.41-7.39 (m, 4H), 7.29-7.23 (m, 2H), 3.84 (br, 4H), 2.07 (br, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 150.6, 141.1, 134.3, 127.6, 125.8, 123.2, 121.5, 120.2, 119.7, 109.8, 23.8; IR (neat) cm^{-1} 3053, 2982, 2876, 1506, 1427, 1404, 1315, 1265; ESI-HRMS: Found: m/z 341.1769. Calcd for $C_{22}H_{21}N_4$: $(M+H)^+$ 341.1766.

1-[2-(2-methylphenyl)diazen-1-yl]pyrrolidine (1h)

Red oil; Yield: 90% (851 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.34 (d, *J* = 7.8 Hz, 1H), 7.20-7.14 (m, 2H), 7.05 (dd, *J* = 7.8, 7.2 Hz, 1H), 3.80 (br, 4H), 2.43 (s, 3H), 2.03 (t, *J* = 6.8 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 149.2, 132.3, 130.5, 126.2, 125.0, 116.5, 23.8, 17.6; IR (neat) cm^{-1} 3065, 3020, 2972, 2868, 1483, 1415, 1319, 1223; ESI-HRMS: Found: m/z 190.1343. Calcd for $C_{11}H_{16}N_3$: $(M+H)^+$ 190.1344.

1-[2-(4-tert-butylphenyl)diazen-1-yl]pyrrolidine (1i)

Pale yellow solid; mp 74-75 °C; Yield: 95% (1.10 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.35 (m, 4H), 3.78 (br, 4H), 2.01 (m, 4H), 1.33 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 149.0, 148.0, 125.6, 119.8, 34.4, 31.4, 23.8; IR (neat) cm^{-1} 3053, 2964, 2872, 1246, 1319, 1265; ESI-HRMS: Found: m/z 232.1816. Calcd for $C_{14}H_{22}N_3$: $(M+H)^+$ 232.1814.

1-{4-[2-(pyrrolidin-1-yl)diazen-1-yl]phenyl}ethan-1-one (1l)

Pale yellow solid; mp 115-116 °C; Yield 95% (1.03 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.93 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 3.83 (d, *J* = 102.8 Hz, 4H), 2.58 (s,

3H), 2.05 (br, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 197.4, 155.2, 133.7, 129.6, 120.2, 51.3, 46.5, 26.5, 23.7; IR (neat) cm^{-1} 3053, 2982, 2876, 1672, 1595, 1420, 1355, 1224; ESI-HRMS: Found: m/z 218.1289. Calcd for $C_{12}H_{16}N_3O$: $(M+H)^+$ 218.1293.

(*E*)-methoxy(1-{4-[2-(pyrrolidin-1-yl)diazen-1-yl]phenyl}ethylidene)amine (1m)

To a solution of **1l** (1.09 g, 5.0 mmol) in H_2O/EtOH (15 mL, 3/1) $MeONH_2$•HCl (1.13 g, 13.5 mmol) and NaOAc (1.80 g, 22.0 mmol) were added. The resulting mixture was heated at 70°C for 2 h. After cooling to room temperature, the mixture was extracted with EtOAc (3 × 25 mL). The combined organic phase was dried with $MgSO_4$ and concentrated under reduced pressure. The crude residue was purified by flash column chromtography over silica gel to afford **1m** as pale yellow solid; mp 99-100 °C; Yield: 15% (185 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.63 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.4 Hz, 2H), 3.99 (s, 3H), 3.79 (br, 4H), 2.22 (s, 3H), 2.00 (br, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 154.4, 151.9, 133.0, 126.5, 120.2, 61.7, 23.7, 12.4; IR (neat) cm^{-1} 3053, 2984, 2876, 1205, 1422, 1400, 1315, 1265; ESI-HRMS: Found: m/z 247.1557. Calcd for $C_{13}H_{19}N_4O$: $(M+H)^+$ 247.1559.

1-[2-(3-bromo-4-methoxyphenyl)diazen-1-yl]pyrrolidine (1s)

Pale yellow solid; mp 82-83 °C; Yield: 95% (1.35 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.68 (d, J = 2.4 Hz, 1H), 7.32 (dd, J = 8.4, 2.4 Hz, 1H), 6.86 (d, J = 8.4 Hz, 1H), 3.88 (s, 3H), 3.76 (br, 4H), 2.03-1.99 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 153.4, 145.9, 124.3, 120.8, 111.9, 111.8, 56.4, 23.7; IR (neat) cm^{-1} 3053, 2984, 2876, 1423, 1339, 1265; ESI-HRMS: Found: m/z 284.0402. Calcd for $C_{11}H_{15}BrN_3O$: $(M+H)^+$ 284.0398.

1-[2-(4-iodo-2-methylphenyl)diazen-1-yl]pyrrolidine (1t)

Pale orange oil; Yield: 86% (1.35 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.51 (s, 1H), 7.43 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 3.78 (br, 4H), 2.35 (s, 3H), 2.02 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 148.9, 139.0, 135.1, 134.8, 118.3, 89.1, 23.8, 17.2; IR (neat) cm^{-1} 2970, 2920, 2868, 1470, 1415, 1315, 1267, 1225; ESI-HRMS: Found: m/z 316.0311. Calcd for $C_{11}H_{15}IN_3$: $(M+H)^+$ 316.0311.

1-[2-(3-iodo-4-methoxyphenyl)diazen-1-yl]pyrrolidine (1u)

Pale yellow solid; mp 69-70 °C; Yield: 100% (1.65 g); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.89 (d, *J* = 2.4 Hz, 1H), 7.35 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 1H), 3.86 (s, 3H), 3.75 (br, 4H), 2.00 (t, *J* = 7.6 Hz, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 155.6, 146.3, 130.4, 121.8, 110.7, 86.1, 56.6, 23.7; IR (neat) cm^{-1} 3051, 2978, 2874, 1485, 1422, 1391, 1337, 1265; ESI-HRMS: Found: m/z 332.0263. Calcd for $C_{11}H_{15}IN_3O$: $(M+H)^+$ 332.0260.

1-[2-(3-methylphenyl)diazen-1-yl]pyrrolidine (1v)

Pale yellow slid; mp 34-35 °C; Yield: 95% (899 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.23-7.20 (m, 3H), 6.95 (dd, *J* = 4.0, 4.0 Hz, 1H), 3.79 (br, 4H), 2.35 (s, 3H), 2.04-2.00 (m, 4H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 151.4, 138.5, 128.6, 126.0, 120.9, 117.5, 23.8, 21.4; IR (neat) cm^{-1} 3051, 2978, 2874, 1410, 1319, 1265; ESI-HRMS: Found: m/z 190.1349. Calcd for $C_{11}H_{16}N_3$: $(M+H)^+$ 190.1344.

III. Spectroscopic Data of Products

General procedure for the preparation of arylboronic esters 2a–u. 4,4,5,5-tetramethyl-2-(tetra--methyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (194 mg, 0.75 mmol), aryltriazene **1a–u** (0.5 mmol) were added to a 25 ml two-neck

round bottom flask which was purged thoroughly with N_2. Anhydrous MeCN (2 mL) was added via syringe and the reaction mixture was cooled to 0 °C in an ice-water bath. Then BF_3•OEt_2 (63 μL, 0.5 mmol) was added dropwise. The resulting reaction mixture was allowed to stir for 5-120 min at 0-60 °C. The solution was then concentrated under reduced pressure and the crude residue was purified by flash column chromatography over silica gel to afford corresponding arylboronic ester **2a–u**.

2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2a)[7]

Pale yellow oil; Yield: 73% (85 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.76 (d, J = 8.4 Hz, 2H), 6.90 (d, J = 8.4 Hz, 2H), 3.83 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 162.1, 136.5, 113.3, 85.5, 55.1, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.2.

2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2b)[8]

Pale orange oil; Yield: 50% (58 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.42 (m, 1H), 7.35 (m, 1H), 7.31 (m, 1H), 7.02(m, 1H), 3.84(s, 3H), 1.36(s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 159.0, 128.9, 127.2, 118.7, 117.9, 83.8, 55.2, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ=30.7.

2-[4-(benzylsulfanyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2d)

Pale yellow solid; mp 48-49 °C; Yield: 62% (101 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.68 (d, J = 8.0 Hz, 2H), 7.34-7.22 (m, 7H), 4.16 (s, 2H), 1.33 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 140.7, 137.0, 135.1, 128.8, 128.5, 127.4, 127.2, 83.8, 37.8, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.6; IR (neat) cm^{-1} 3053, 2982, 1597, 1393, 1360, 1265, 1144, 1101; ESI-HRMS: Found: m/z 327.1592. Calcd for $C_{19}H_{24}BO_2S$: $(M+H)^+$ 327.1590.

9-[4-(tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]-9*H*-carbazole (2e)

Orange solid; mp 167-168 °C; Yield: 52% (96 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.17 (d, *J* = 7.6 Hz, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.50-7.42 (m, 4H), 7.34-7.30 (m, 2H), 1.44 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 140.6, 140.4, 136.4, 126.0, 125.9, 123.5, 120.3, 120.0, 109.8, 84.0, 24.9; ^{11}B (96 MHz, $CDCl_3$) δ =30.4; IR (neat) cm^{-1} 3051, 2982, 2682, 1605, 1452, 1362, 1265, 1144, 1088; ESI-HRMS: Found: m/z 370.1979. Calcd for $C_{24}H_{25}BNO_2$: $(M+H)^+$ 370.1978.

4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane (2f)[8]

Orange oil; Yield: 36% (37 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.83 (d, *J* = 6.8 Hz, 2H), 7.47 (t, *J* = 8.4 Hz, 1H), 7.38 (dd, *J* = 6.8, 7.6 Hz, 2H), 1.36 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 134.7, 131.2, 127.7, 83.7, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ =30.9.

4,4,5,5-tetramethyl-2-(4-methylphenyl)-1,3,2-dioxaborolane (2g)[9]

Pale orange oil; Yield: 75% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.70 (d, *J* = 8.0 Hz, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 2.37 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 141.3, 134.8, 128.5, 83.6, 24.8, 21.7; ^{11}B (96 MHz, $CDCl_3$) δ = 31.0.

4,4,5,5-tetramethyl-2-(2-methylphenyl)-1,3,2-dioxaborolane (2h)[8]

Orange oil; Yield: 83% (90 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.76 (d, *J* = 6.8 Hz, 1H), 7.32 (dd, *J* = 7.6, 7.2 Hz, 1H), 7.17-7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ = 144.8, 135.8, 130.8, 129.8, 124.7, 83.4, 24.9, 22.2; ^{11}B (96 MHz, $CDCl_3$) δ = 30.2.

2-(4-tert-butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2i)[7]

Pale orange solid; mp 134-135 °C; Yield: 71% (92 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ

= 7.78 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 1.35 (s, 12H), 1.34 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 154.5, 134.7, 124.7, 83.6, 34.9, 31.2, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.7.

trimethyl({2-[4-(tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethynyl})silane (2j)[10]

Pale yellow solid; mp 152-153 °C; Yield: 53% (79 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ =7.72 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 1.34 (s, 12H), 0.25 (s, 9H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 134.4, 131.1, 125.7, 105.2, 95.5, 83.9, 24.9, -0.1; ^{11}B (96 MHz, $CDCl_3$) δ= 30.4.

4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (2k)[8]

Red solid; mp 54-55 °C; Yield: 65% (82 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.43 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 6.8 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.59 (dd, *J* = 8.0, 6.8 Hz, 1H), 7.52 (dd, *J* = 8.0, 6.8 Hz, 2H), 1.47 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 136.9, 135.6, 133.2, 131.6, 128.4, 128.3, 126.3, 125.4, 124.9, 83.7, 24.9; ^{11}B (96 MHz, $CDCl_3$) δ= 31.5.

(*E*)-methoxy({1-[4-(tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]ethylidene})amine (2m)

Orange solid; mp 40-41 °C; Yield: 70% (96 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.80 (d, *J* = 8.0 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 4.01 (s, 3H), 2.23 (s, 3H), 1.35 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 154.5, 139.1, 134.8, 125.2, 83.8, 61.9, 24.8, 12.5; ^{11}B (96 MHz, $CDCl_3$) δ= 30.2; IR (neat) cm^{-1} 3051, 2982, 2818, 1601, 1396, 1265, 1144, 1049; ESI-HRMS: Found: m/z 276.1775. Calcd for $C_{15}H_{23}BNO_3$: $(M+H)^+$ 276.1771.

2-(4-fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2n)[10]

Brown oil; Yield: 54% (60 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.81-7.79 (m, 2H), 7.05 (m, 2H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 166.3, 163.8, 137.0, 136.9, 114.9, 114.7, 83.9, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.5.

2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2o)[9]

Orange solid; mp 52-53 °C; Yield: 44% (52 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.43 (d, J = 8.4, Hz, 2H), 7.34 (d, J = 8.4Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 137.5, 136.1, 128.0, 84.0, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.7.

2-(4-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2p)[8]

Orange solid; mp 68-69 °C; Yield: 44% (62 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.66 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 136.3, 130.9, 126.2, 84.0, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ=30.6.

2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2q)[11]

Red oil; Yield: 30% (42 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.93 (d, J = 1.2 Hz, 1H), 7.71 (d, J = 7.6 Hz, 1H), 7.59-7.56 (m, 1H), 7.24 (dd, J = 7.6, 8.0 Hz, 1H), 1.34 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 137.5, 134.2, 133.1, 129.5, 122.4, 84.1, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ=30.3.

2-(3-bromo-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2r)

White solid; mp 75-76 °C; Yield: 72% (112 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.98 (s, 1H), 7.71 (d, J = 8.0 Hz, 1H), 6.88 (d, J = 8.0 Hz, 1H), 3.92 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 158.2, 139.7, 135.5, 111.5, 111.2, 83.9, 56.1, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.1; IR (neat) cm^{-1} 3051, 2980, 2843, 1597, 1389, 1265, 1142, 1098; ESI-HRMS: Found: m/z 335.0430. Calcd for $C_{13}H_{18}BBrO_3Na$: $(M+Na)^+$

335.0430.

2-(4-iodophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2s)[8]

Orange solid; mp 90-91 °C; Yield: 34% (56 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.72 (d, J = 8.0 Hz, 2H), 7.50 (d, J = 8.0 Hz, 2H), 1.33 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 136.9, 136.3, 98.8, 84.0, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ=30.8.

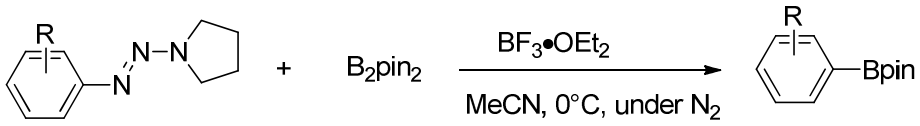
2-(4-iodo-2-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2t)

Orange oil; Yield: 62% (107 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 7.56 (s, 1H), 7.51 (d, J = 8.0 Hz, 1H), 7.45 (d, J = 8.0 Hz, 1H), 2.48 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 146.9, 138.6, 137.2, 133.9, 98.4, 83.6, 24.9, 21.8; ^{11}B (96 MHz, $CDCl_3$) δ= 31.3; IR (neat) cm^{-1} 3051, 2980, 1578, 1344, 1265, 1145, 1063; ESI-HRMS: Found: m/z 345.0531. Calcd for $C_{13}H_{19}BIO_2$: $(M+H)^+$ 345.0528.

2-(3-iodo-4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (2u)

White solid; mp 110-111 °C; Yield: 64% (115 mg); ^{1}H NMR (400 MHz, $CDCl_3$) δ= 8.21 (s, 1H), 7.73 (d, J = 8.0 Hz, 1H), 6.80 (d, J = 8.0 Hz, 1H), 3.90 (s, 3H), 1.33 (s, 12H); ^{13}C NMR (100MHz, $CDCl_3$) δ= 160.3, 145.9, 136.5, 110.3, 85.9, 83.9, 56.2, 24.8; ^{11}B (96 MHz, $CDCl_3$) δ= 30.3; IR (neat) cm^{-1} 3053, 2984, 1591, 1352, 1265, 1142; ESI-HRMS: Found: m/z 361.0471. Calcd for $C_{13}H_{19}BIO_3$: $(M+H)^+$ 361.0472.

IV. Hammett Study



R = 4-H, 4-Me, 3-Me, 4-OMe, 3-OMe, 4-^{t}Bu

4,4,5,5-tetramethyl-2-(tetra--methyl-1,3,2-dioxaborolan-2-yl)-1,3,2-dioxaborolane (0.75 mmol), hexafluorobenzene (internal standard, 0.35 mmol, 40 μL), aryltriazene (0.5 mmol) were added to a 25 ml two-neck round bottom flask which was purged thoroughly with N_2. Anhydrous acetonitrile (2 mL) was added via syringe and the reaction mixture was cooled to 0 °C in an ice-water bath. Then BF_3•OEt_2 was added by one portion. About 2 μL reaction mixture was taken via capillary tube, then quenched by 1500 μL 0.05 mol/L acetonitrile solution of triethylamine and analyzed via HPLC (UV detector 230 nm). Substrate area/internal standard area was converted to absolute concentration by a calibration curve.

At first, initial kinetic data of borylation of 1-(phenyldiazenyl)pyrrolidine **3f** showed the apparent first-order kinetics of this reaction (Figure 1). Then reaction constants *k* of 4-OMe, 3-OMe, 4-Me, 3-Me, and 4-^{t}Bu substituted substrates were determined based on first order kinetics (Figure 2). At last, Hammett plot of logarithm of *k*rel vs. σ was shown in figure 3. Negative slope (ρ) indicating positive charge buildup on rate-determining step.[12]

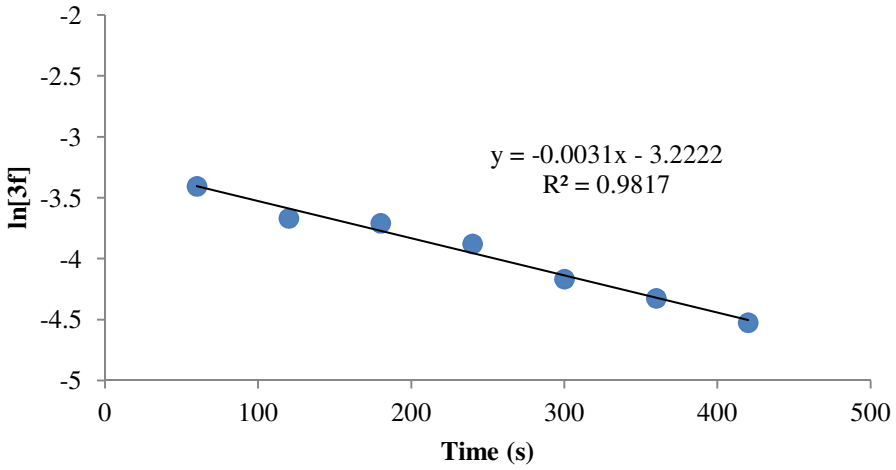


Figure 1. Initial kinetic data of borylation of 1-(phenyldiazenyl)pyrrolidine

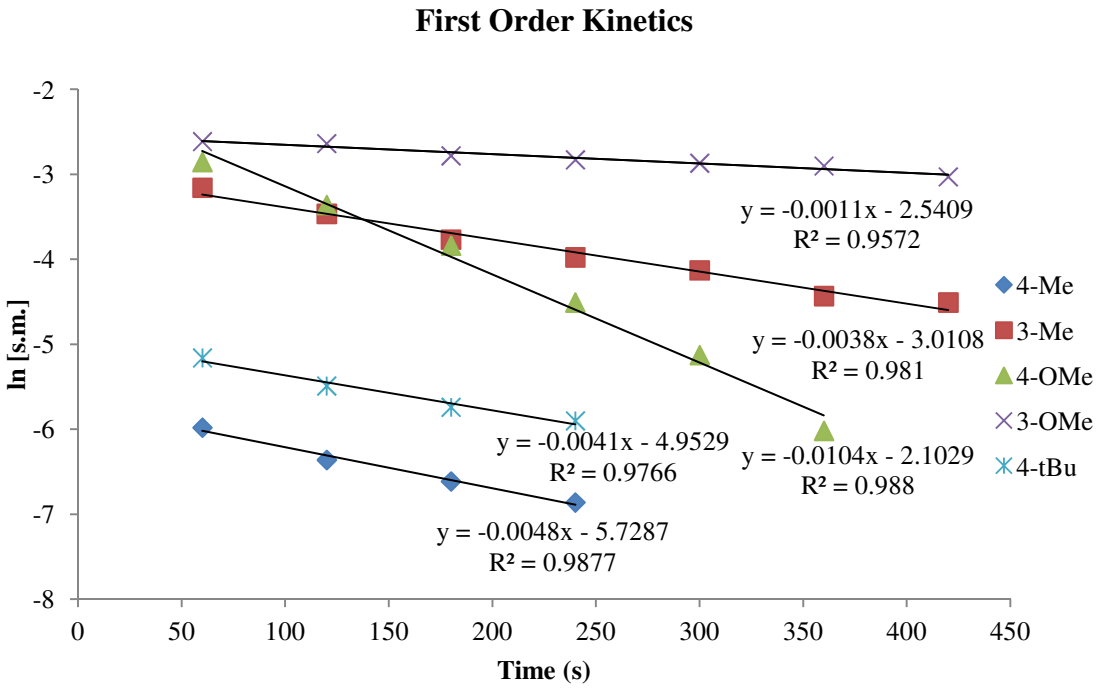


Figure 2. Remainder of Substrates for Hammett Plot

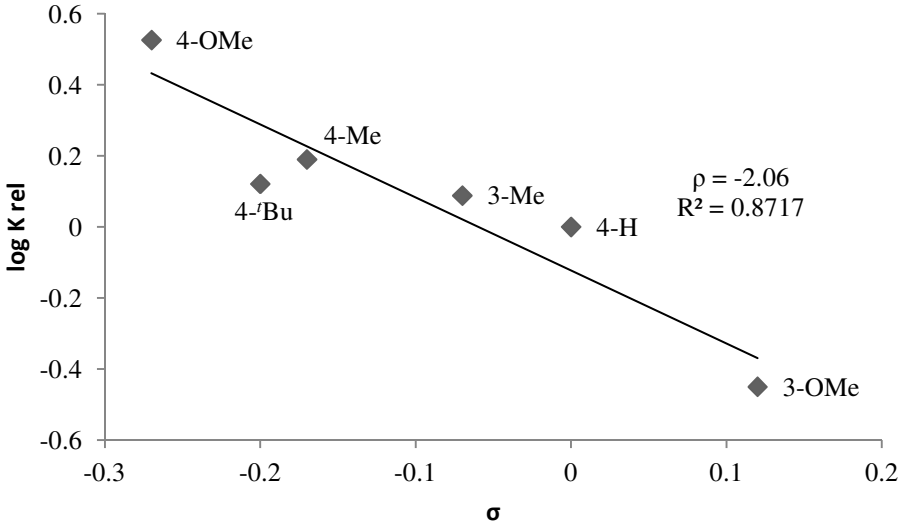


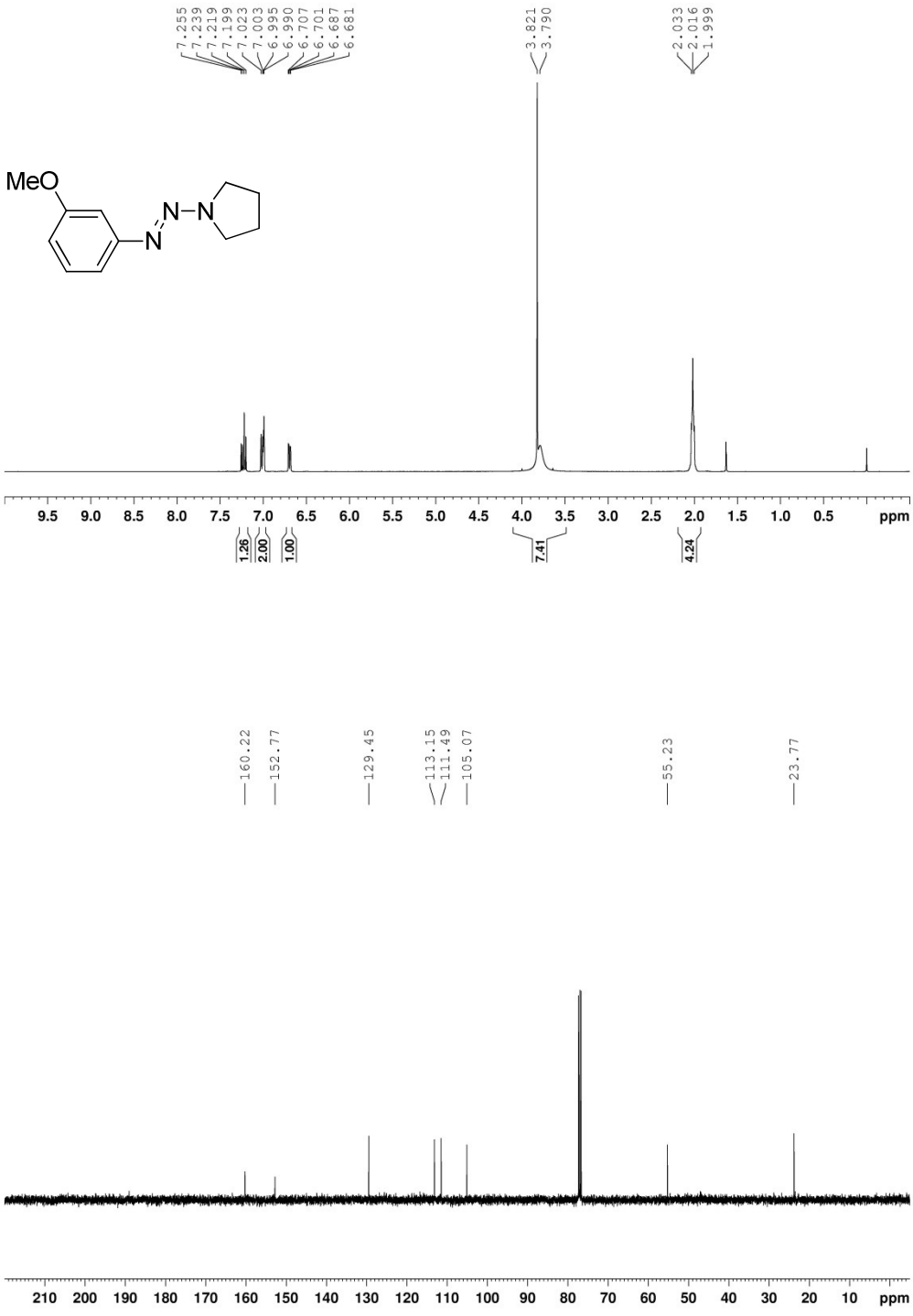
Figure 3. Hammett plot

V. Reference

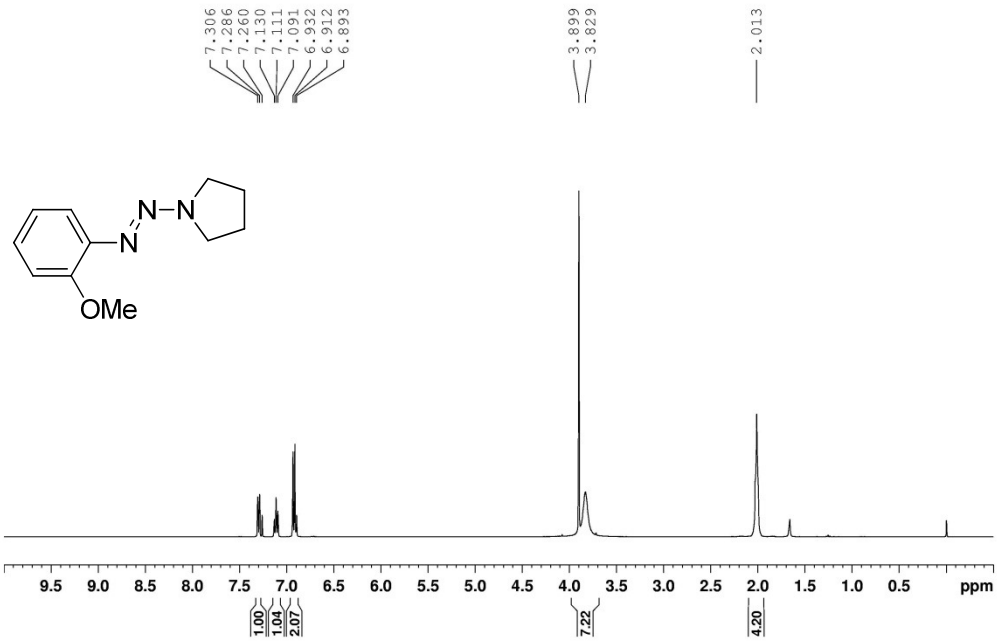
1. Nan, G. M.; Ren, F.; Luo, M. M. *Beilstein J. Org. Chem.* **2010,** 6.
2. Godt, A. *J. Org. Chem.* **1997,** *62*, 7471.
3. Disli, A.; Yildirir, Y. *Org. Prep. Proced. Int.* **1998,** *30*, 349.
4. Gescher, A.; Turnbull, C. P.; Stevens, M. F. G. *Journal of the Chemical Society-Perkin Transactions 1* **1977**, 2078.
5. Gross, M. L.; Blank, D. H.; Welch, W. M. *J. Org. Chem.* **1993,** *58*, 2104.
6. Liu, C.-Y.; Knochel, P. *Org. Lett.* **2005,** *7*, 2543.
7. Yamamoto, T.; Morita, T.; Takagi, J.; Yamakawa, T. *Org. Lett.* **2011,** *13*, 5766.
8. Zhu, W.; Ma, D. *Org. Lett.* **2005,** *8*, 261.
9. Mo, F.; Jiang, Y.; Qiu, D.; Zhang, Y.; Wang, J. *Angew. Chem. Int. Ed.* **2010,** *49*, 1846.
10. Browne, D. L.; Baumann, M.; Harji, B. H.; Baxendale, I. R.; Ley, S. V. *Org. Lett.* **2011,** *13*, 3312.
11. Jiang, Q.; Ryan, M.; Zhichkin, P. *J. Org. Chem.* **2007,** *72*, 6618.
12. (a) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991,** *91*, 165; (b) Shukla, K. H.; DeShong, P. *J. Org. Chem.* **2008,** *73*, 6283; (c) Schmink, J. R.; Krska, S. W. *J. Am. Chem. Soc.* **2011,** *133*, 19574.

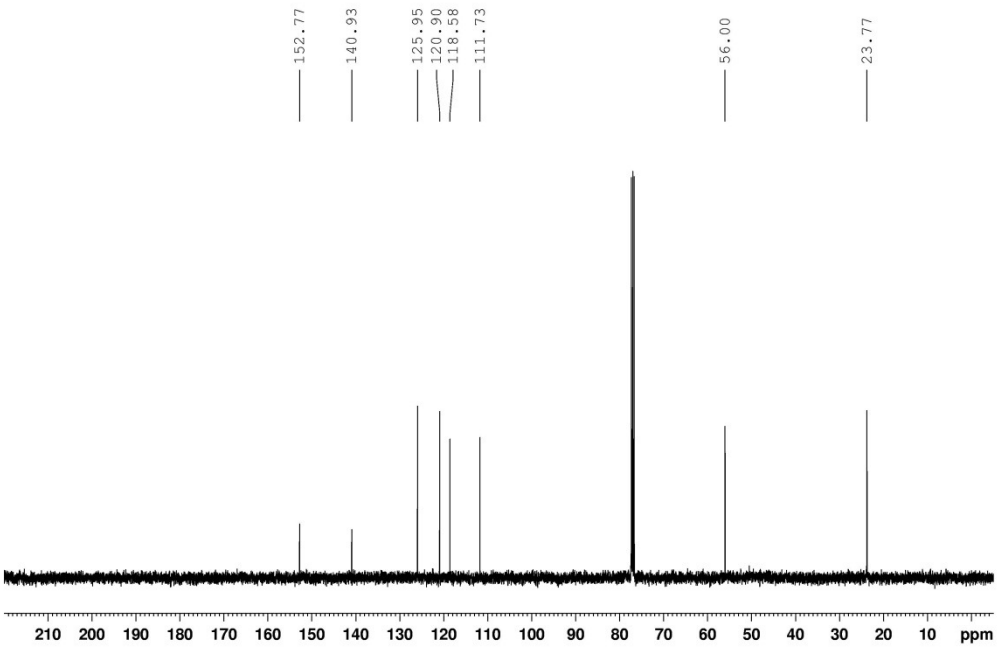
VI. Copies of ^{1}H and ^{13}C NMR Spectra

^{1}H and ^{13}C NMR spectra of compound of **1b**

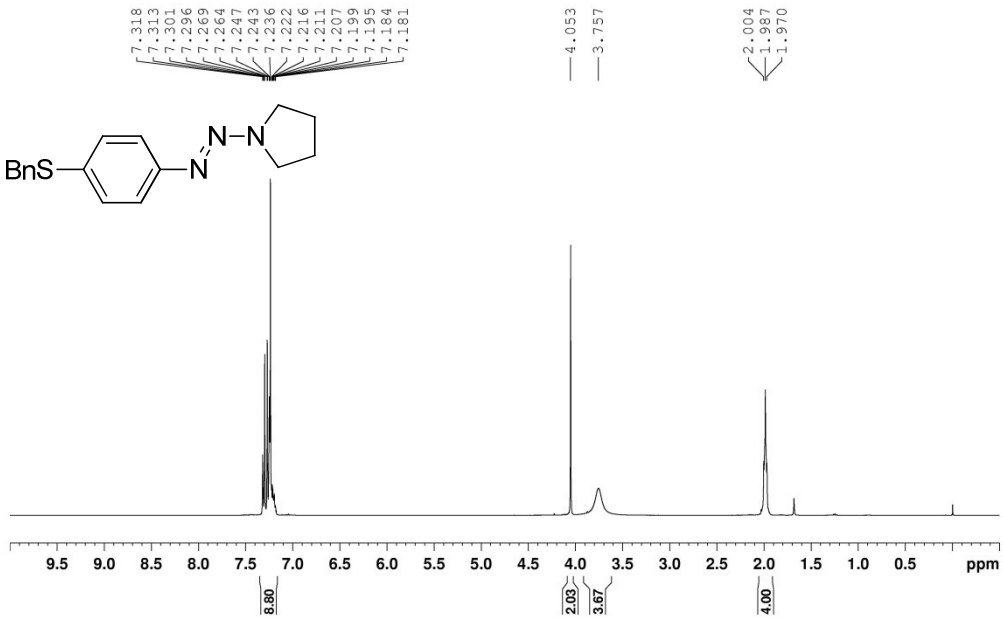


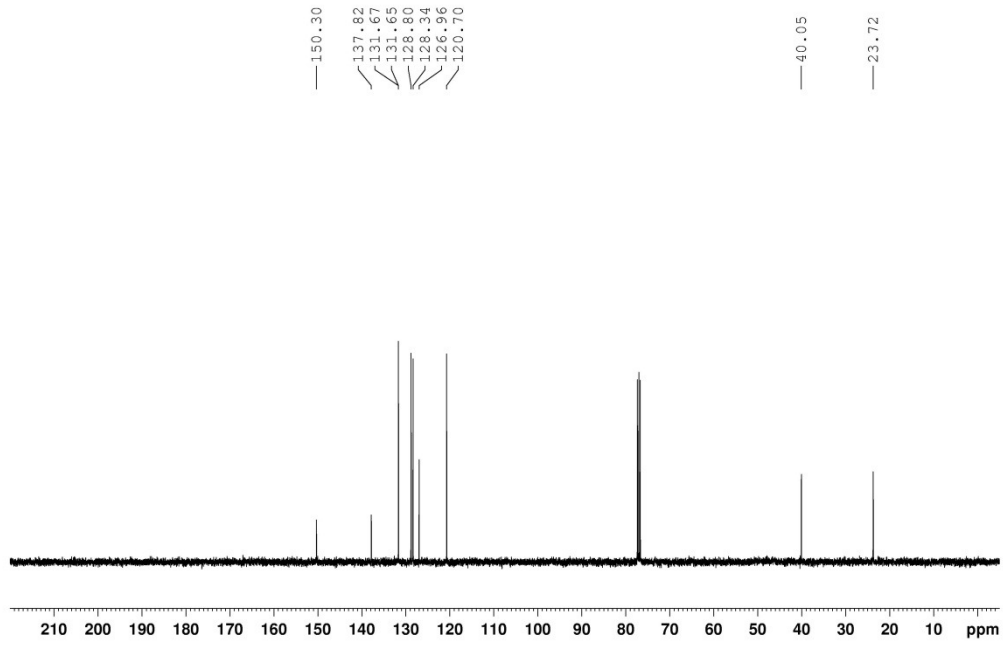
^{1}H and ^{13}C NMR spectra of compound **1c**



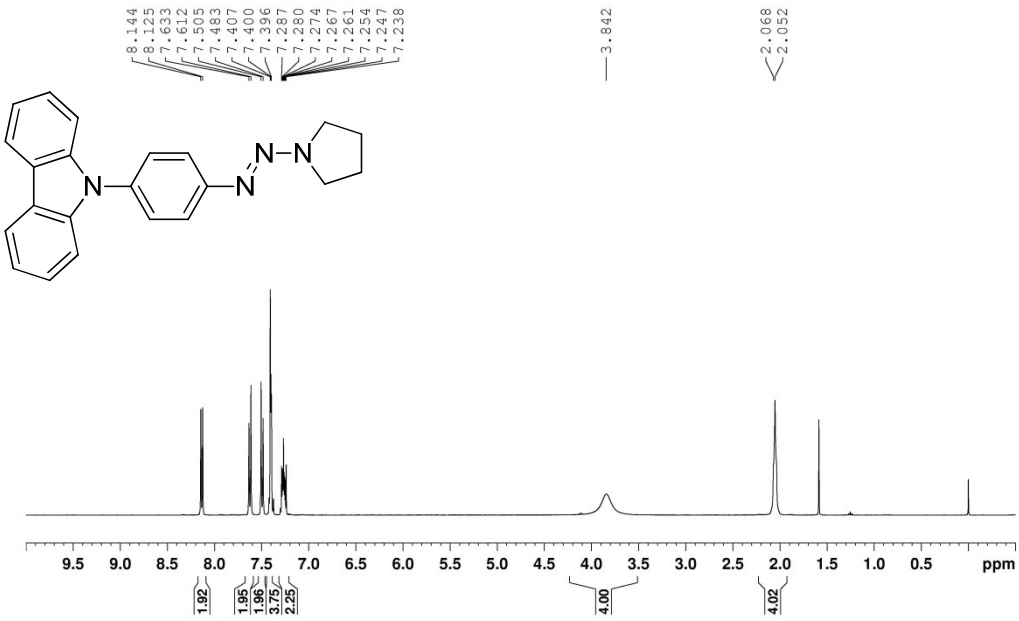


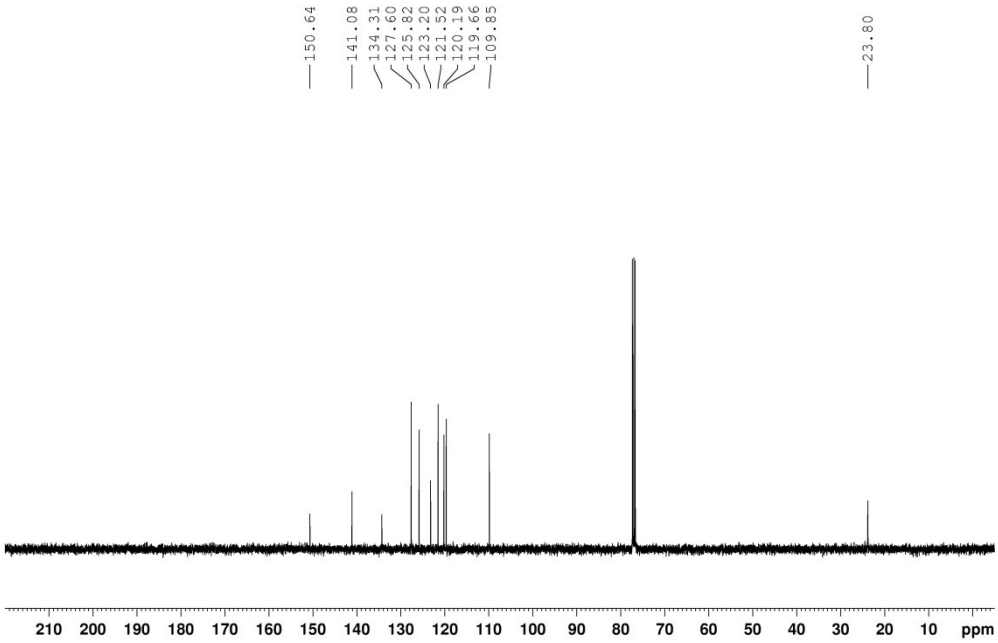
^{1}H and ^{13}C NMR spectra of compound **1d**



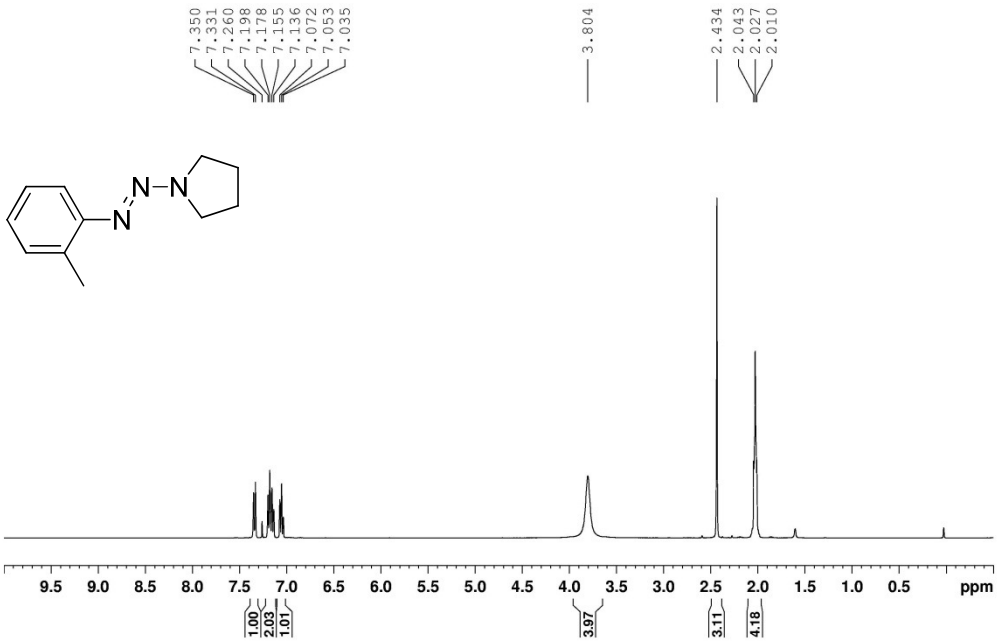


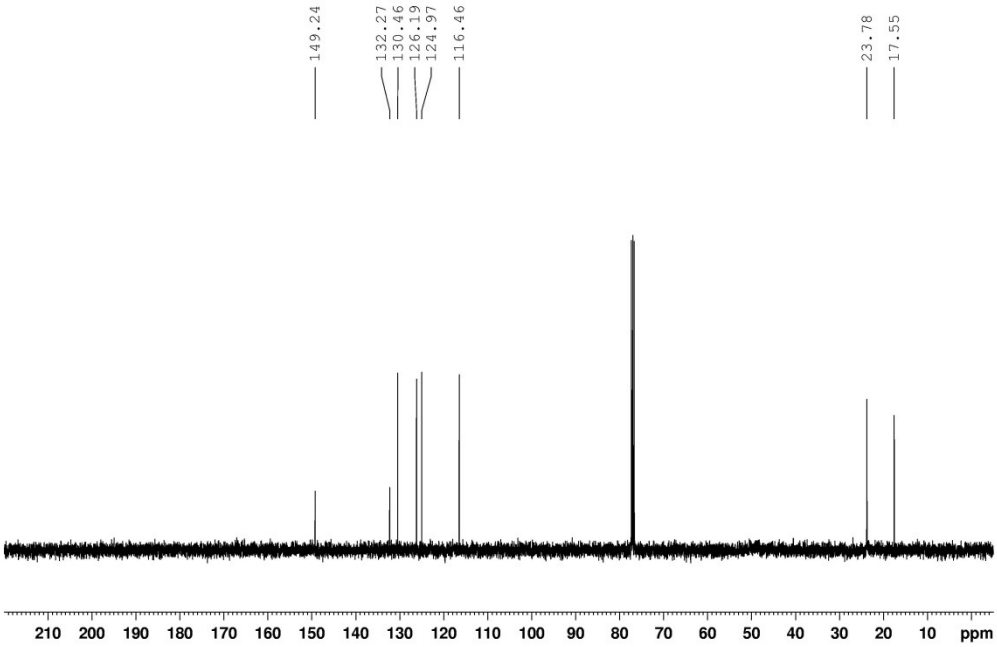
^{1}H and ^{13}C NMR spectra of compound **1e**



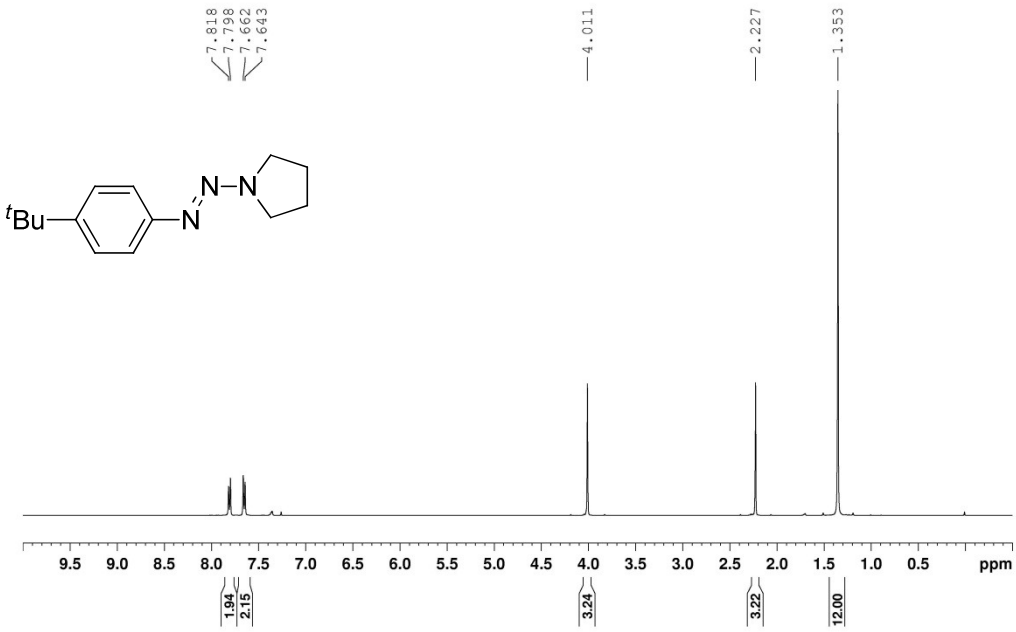


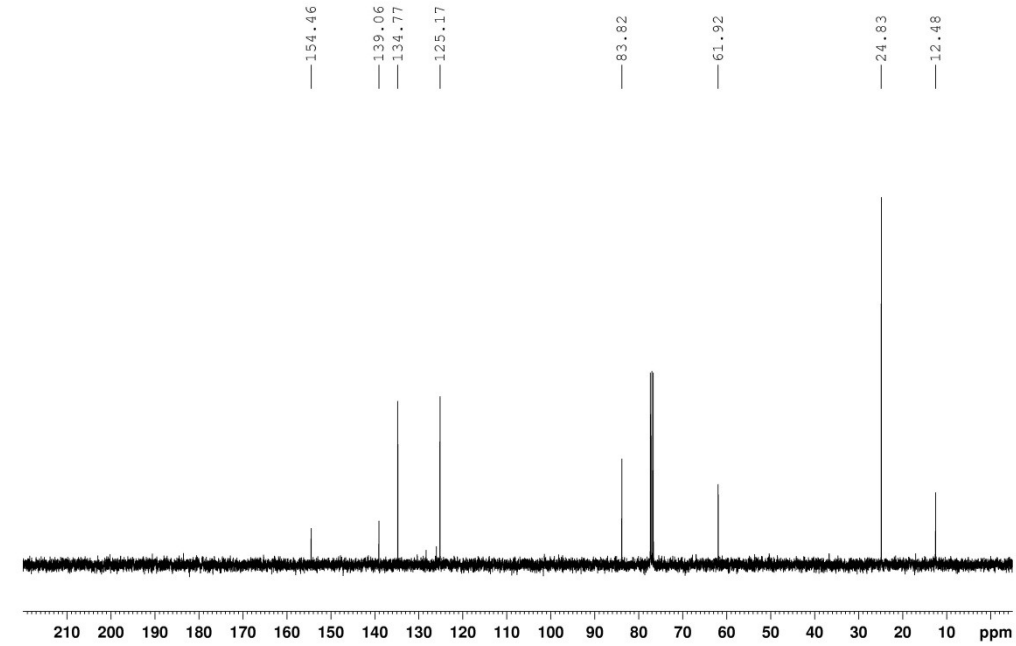
^{1}H and ^{13}C NMR spectra of compound **1h**



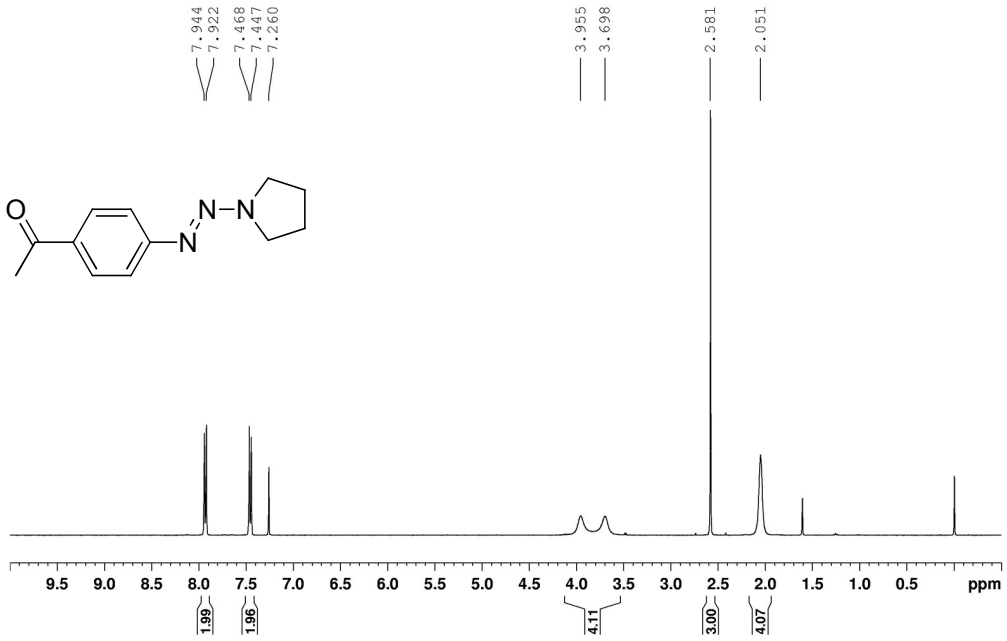


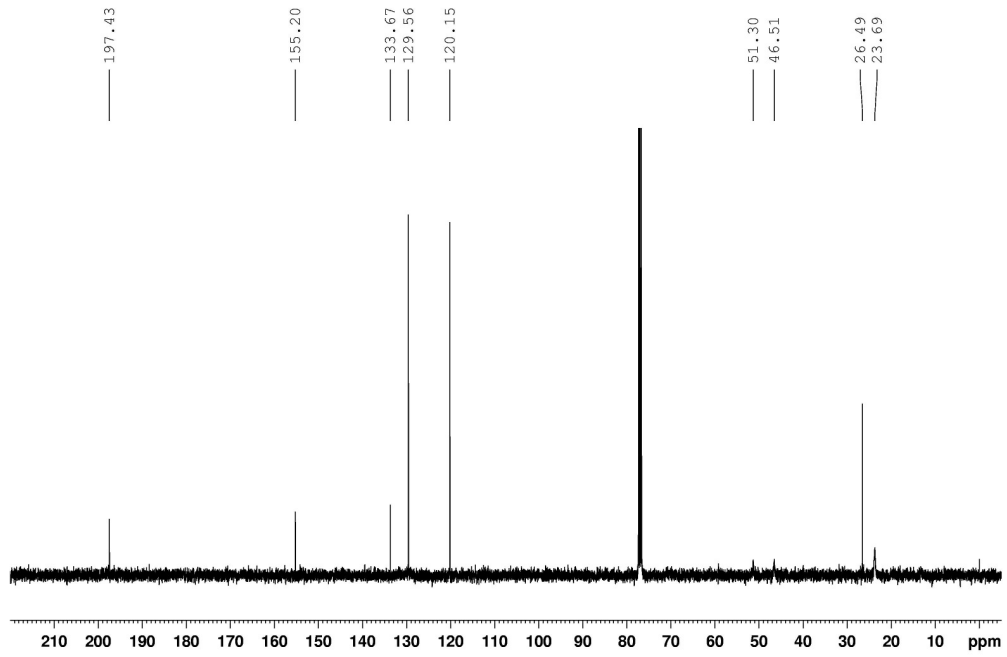
^{1}H and ^{13}C NMR spectra of compound **1i**



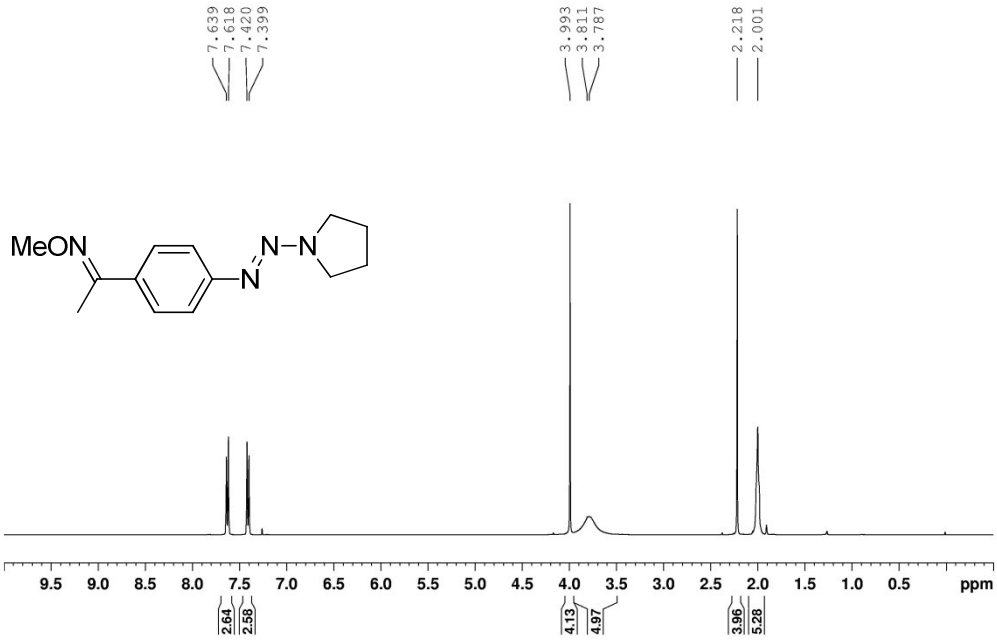


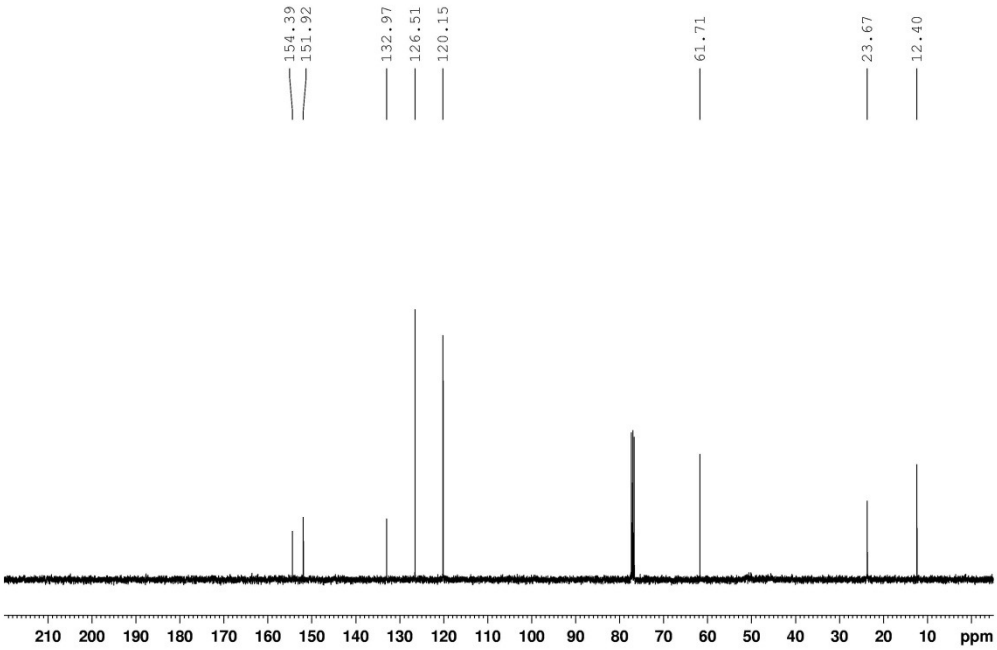
^{1}H and ^{13}C NMR spectra of compound **1l**



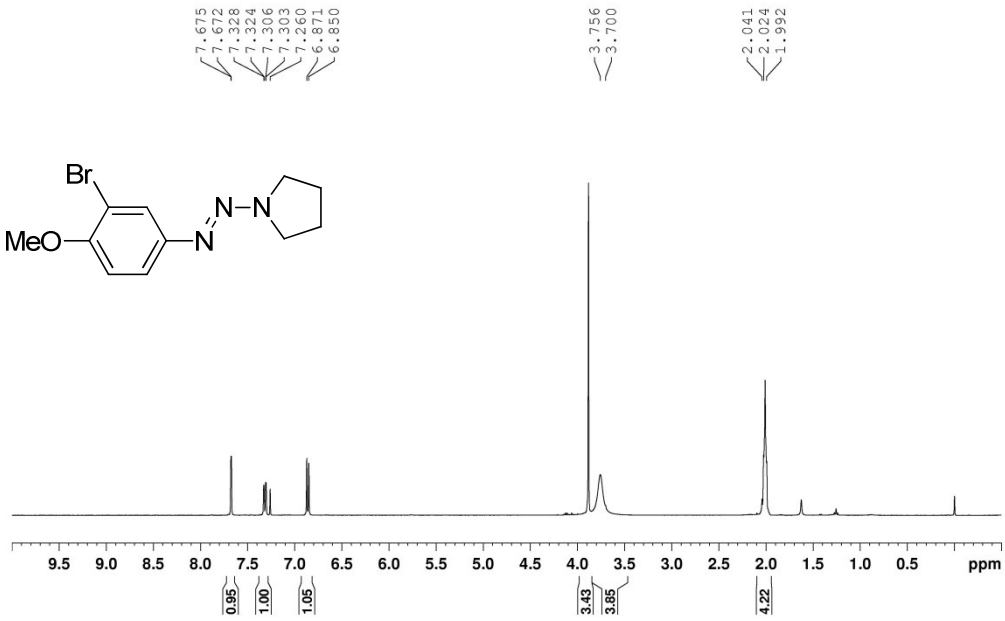


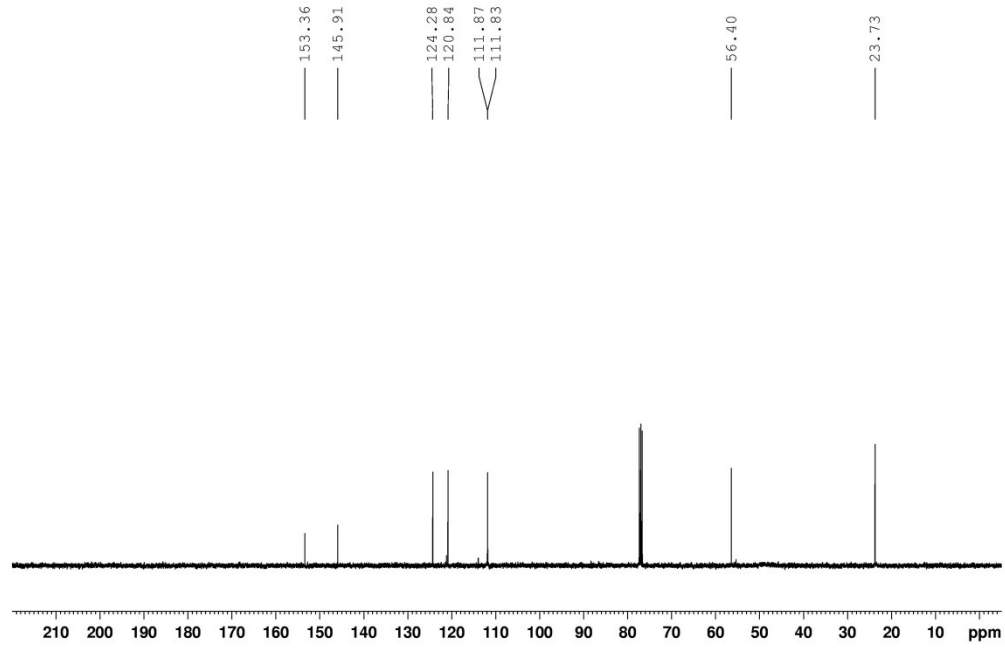
^{1}H and ^{13}C NMR spectra of compound **1m**



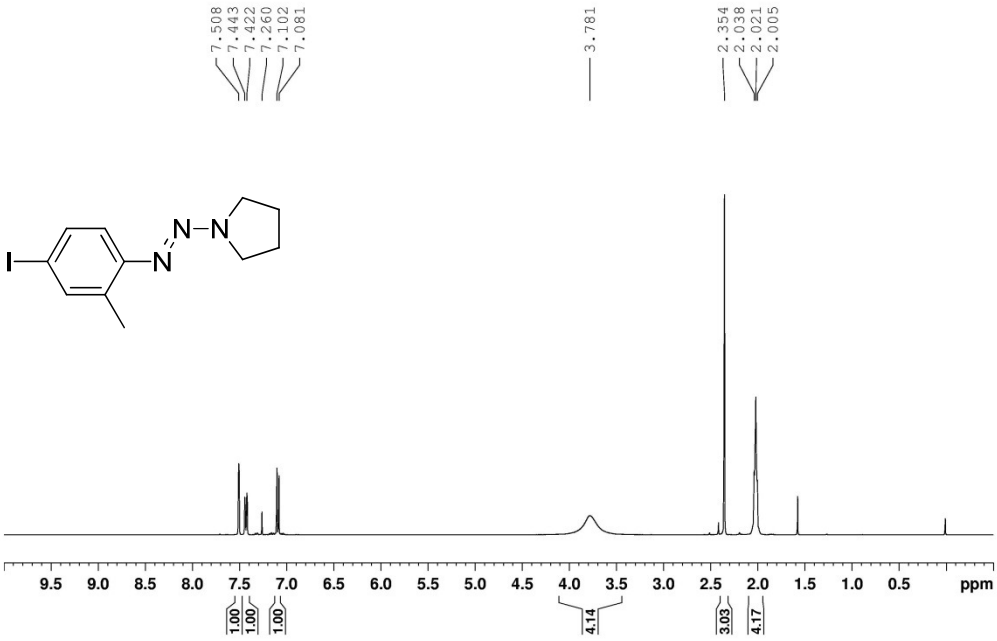


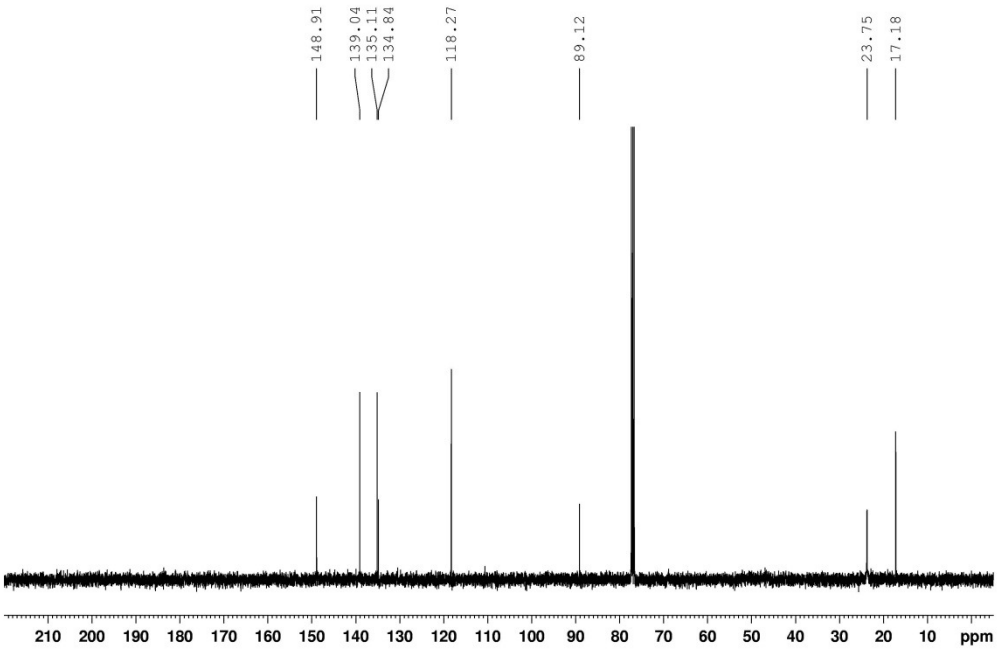
^{1}H and ^{13}C NMR spectra of compound **1r**



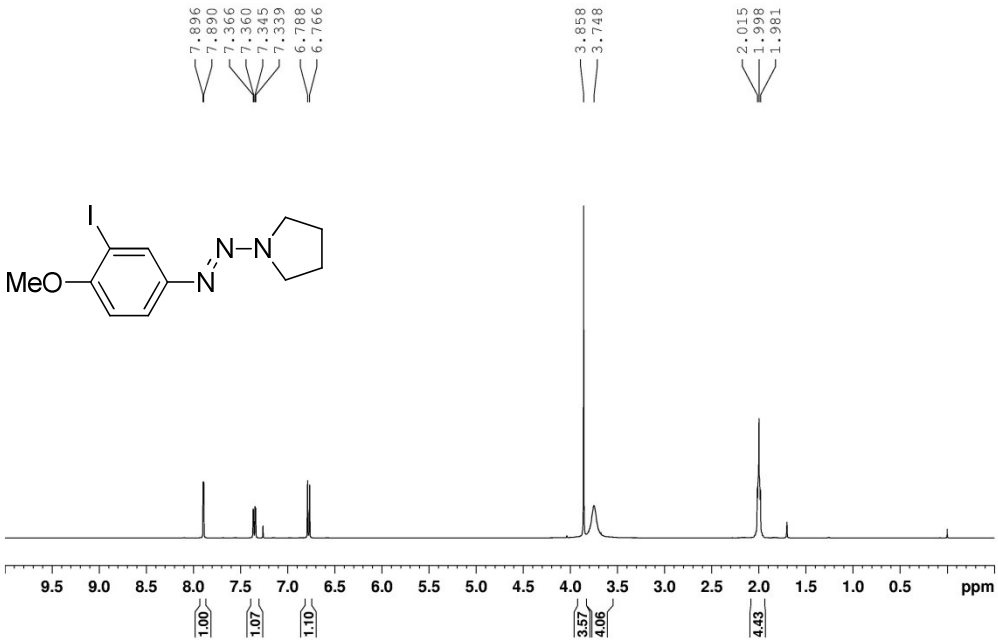


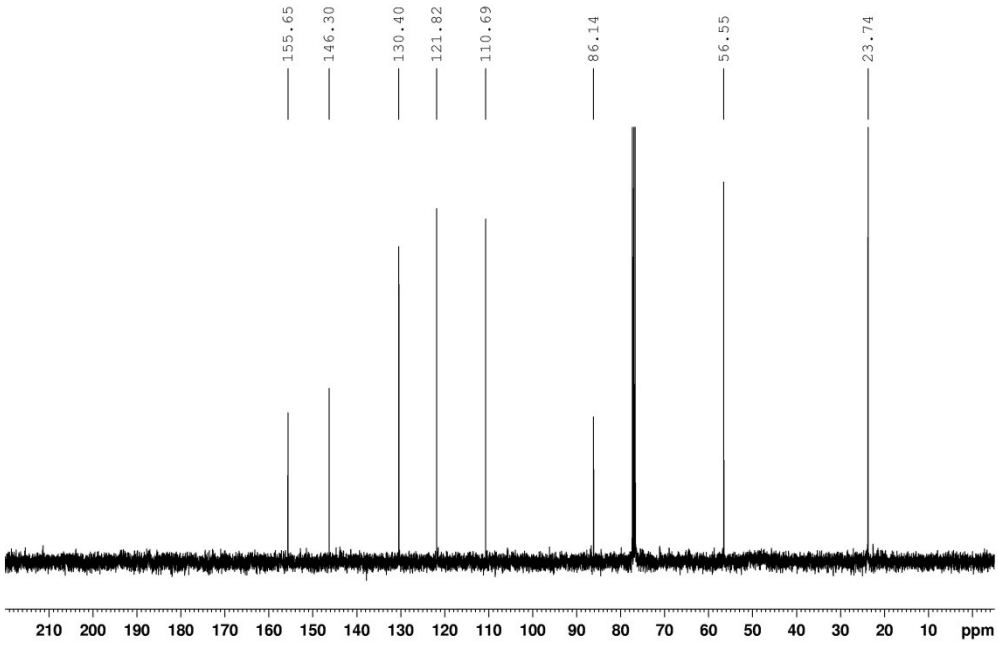
^{1}H and ^{13}C NMR spectra of compound **1t**



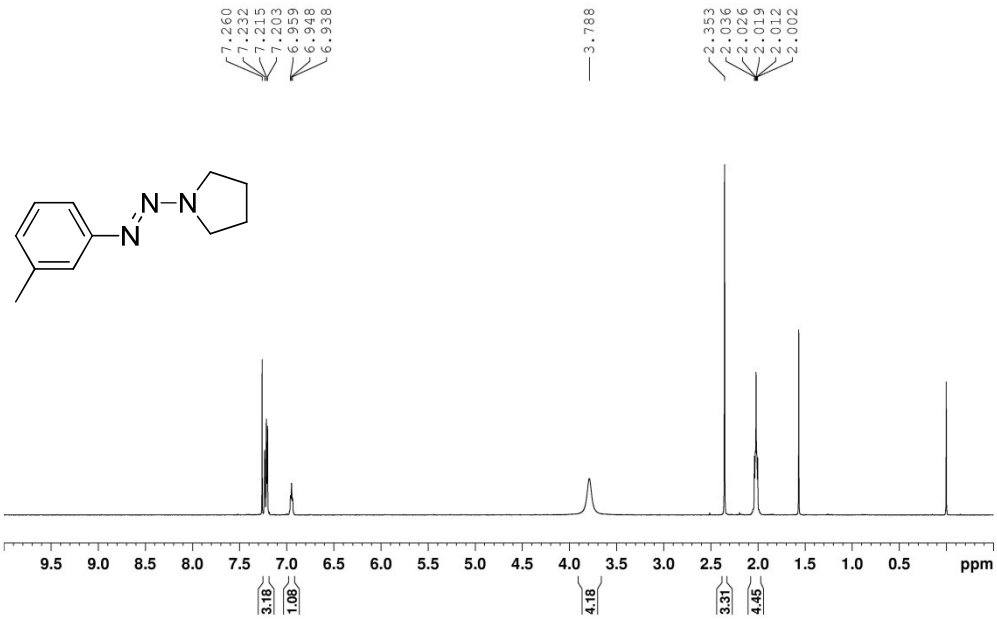


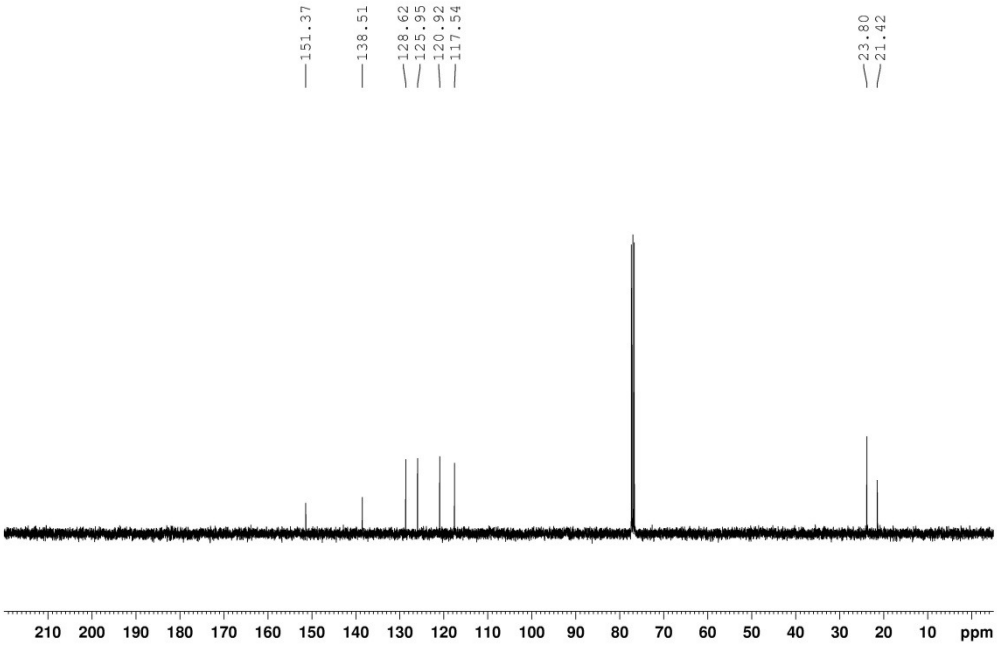
^{1}H and ^{13}C NMR spectra of compound **1u**



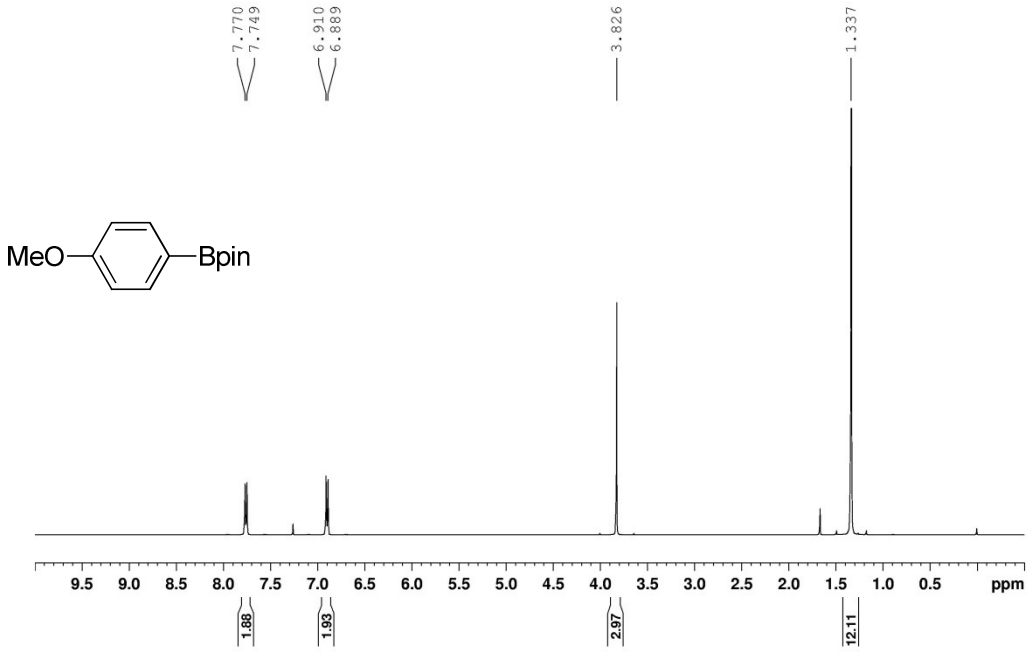


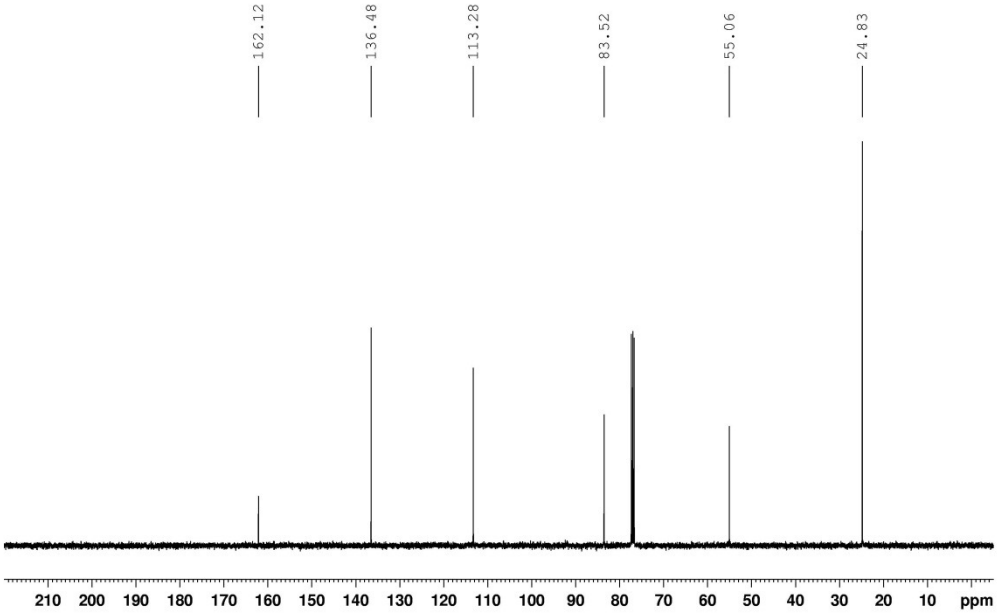
^{1}H and ^{13}C NMR spectra of compound **1v**



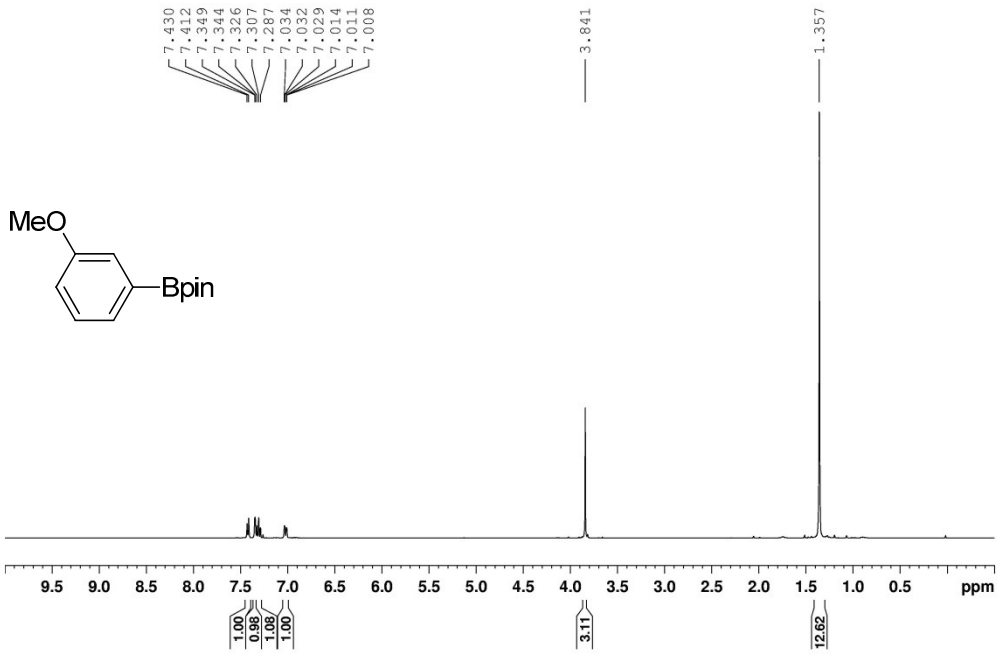


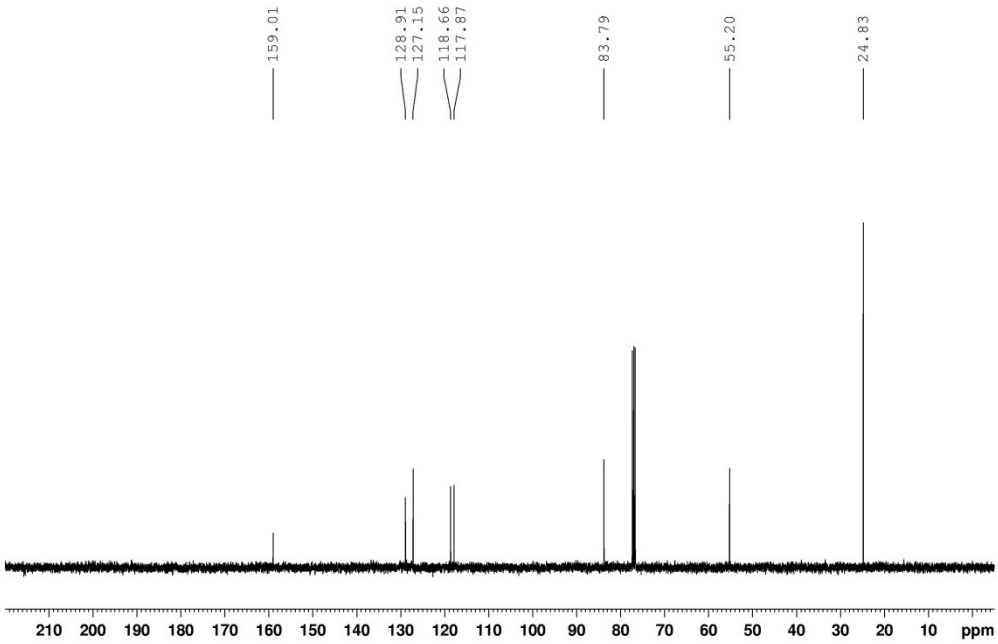
^{1}H and ^{13}C NMR spectra of compound **2a**



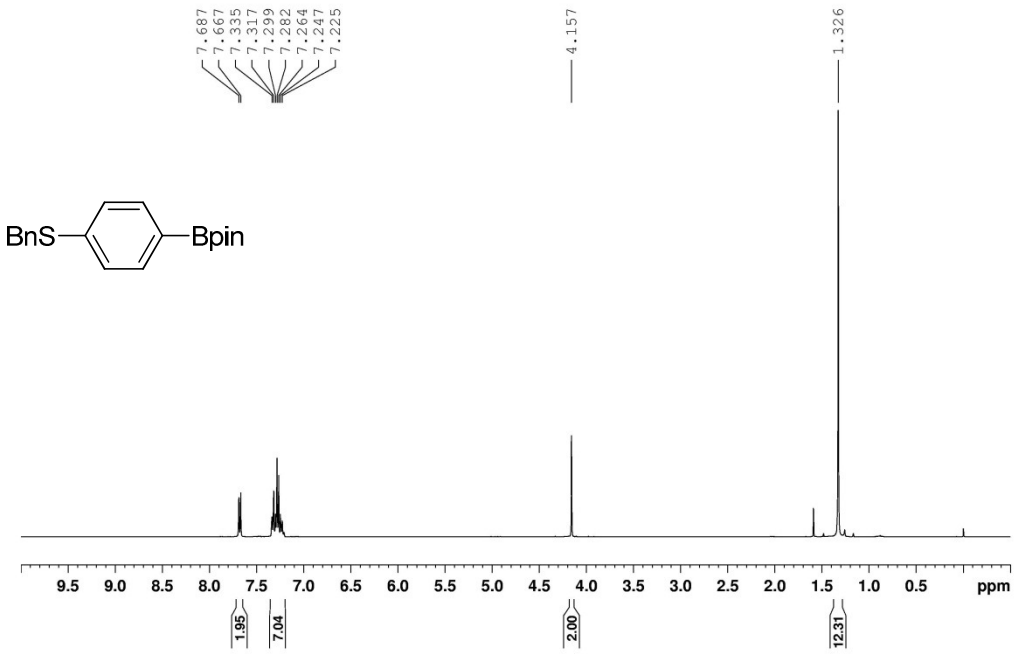


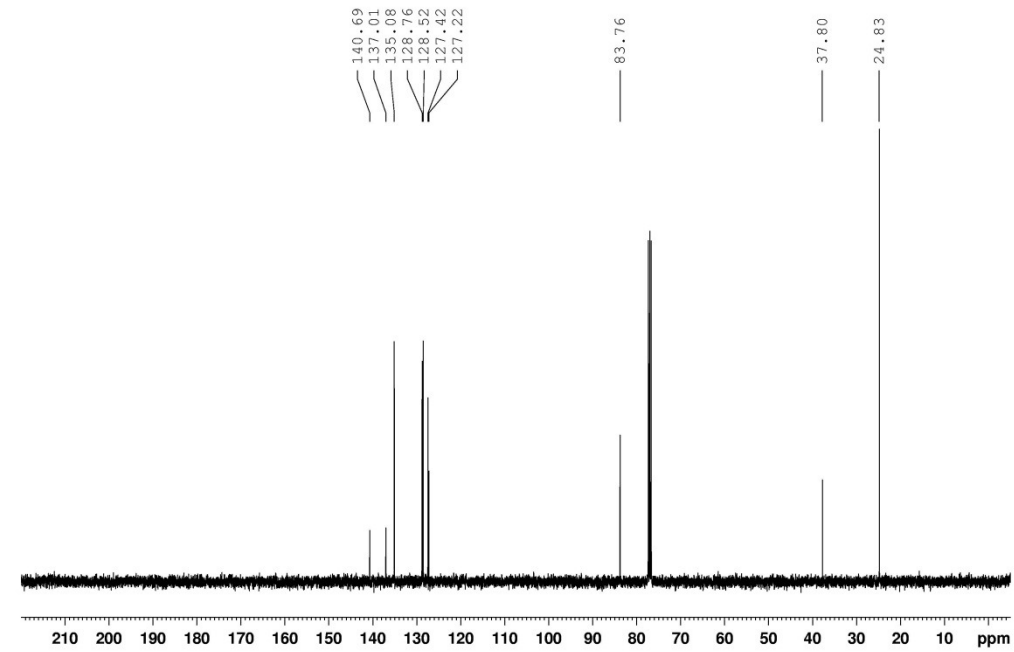
^{1}H and ^{13}C NMR spectra of compound **2b**



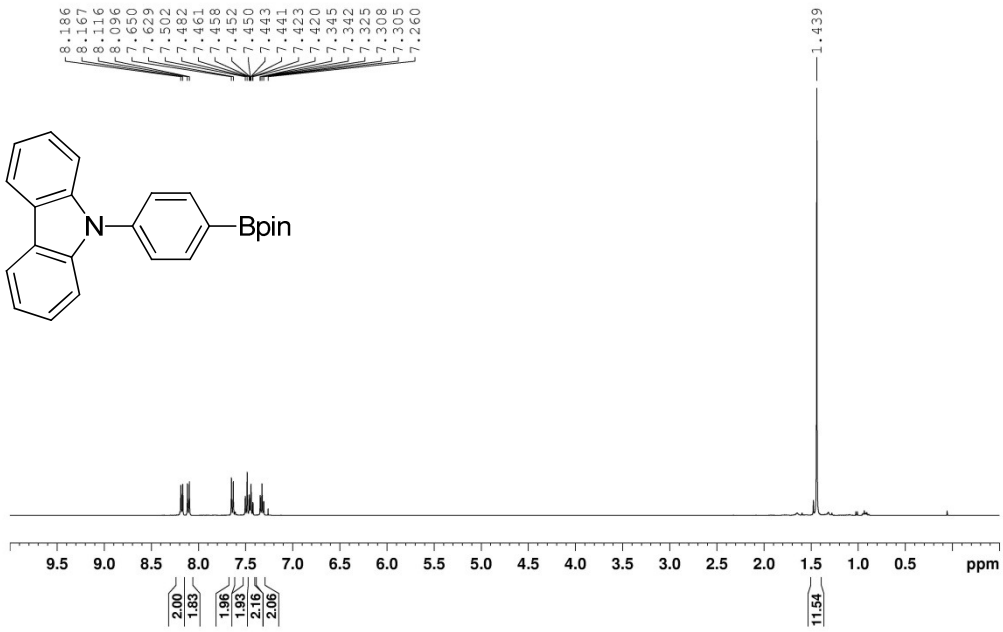


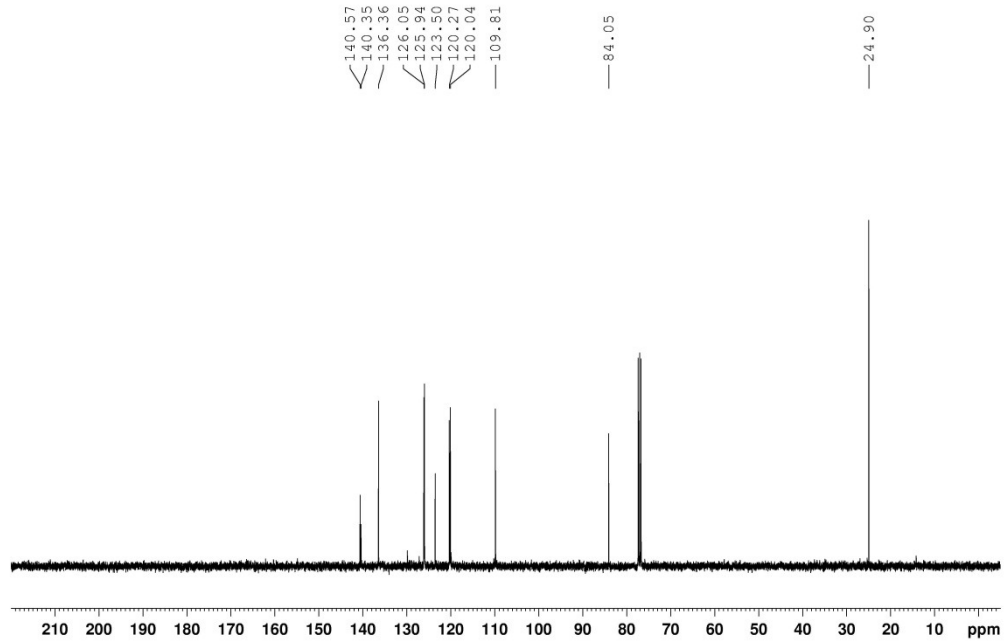
^{1}H and ^{13}C NMR spectra of compound **2d**



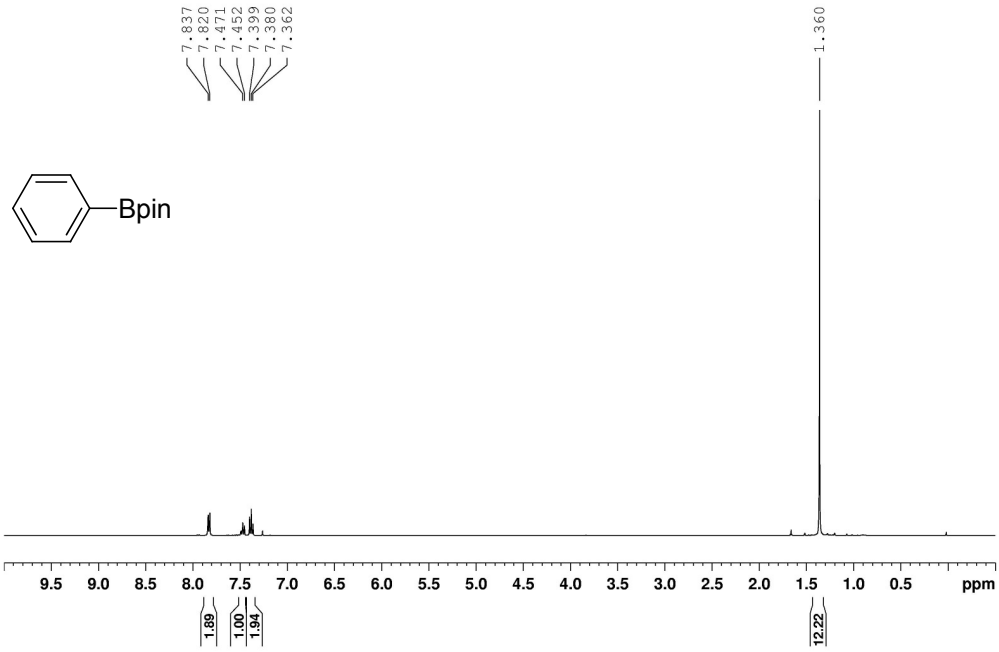


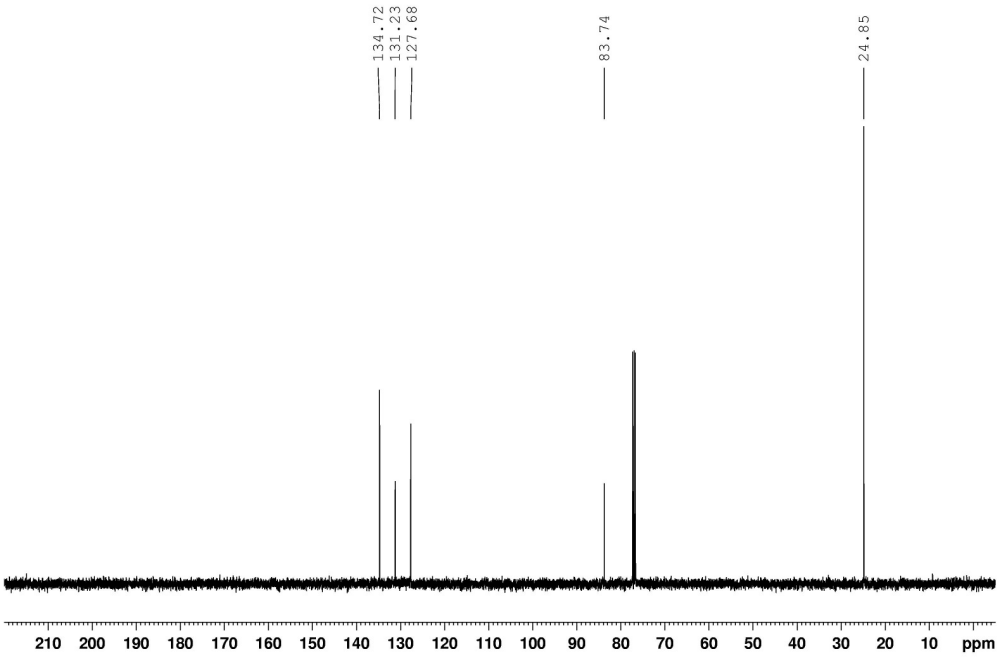
^{1}H and ^{13}C NMR spectra of compound **2e**



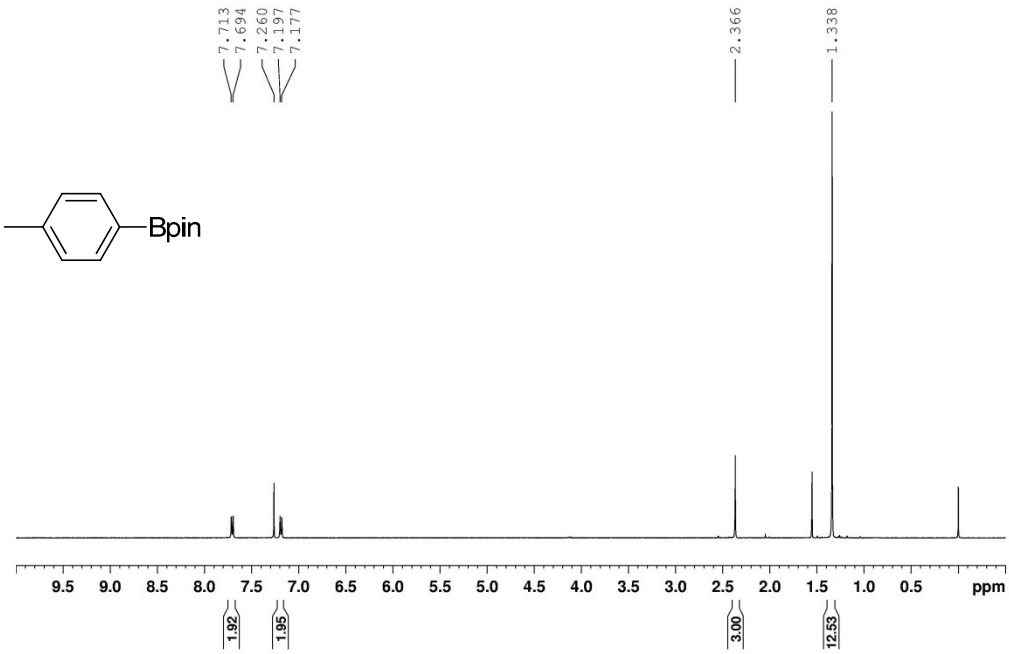


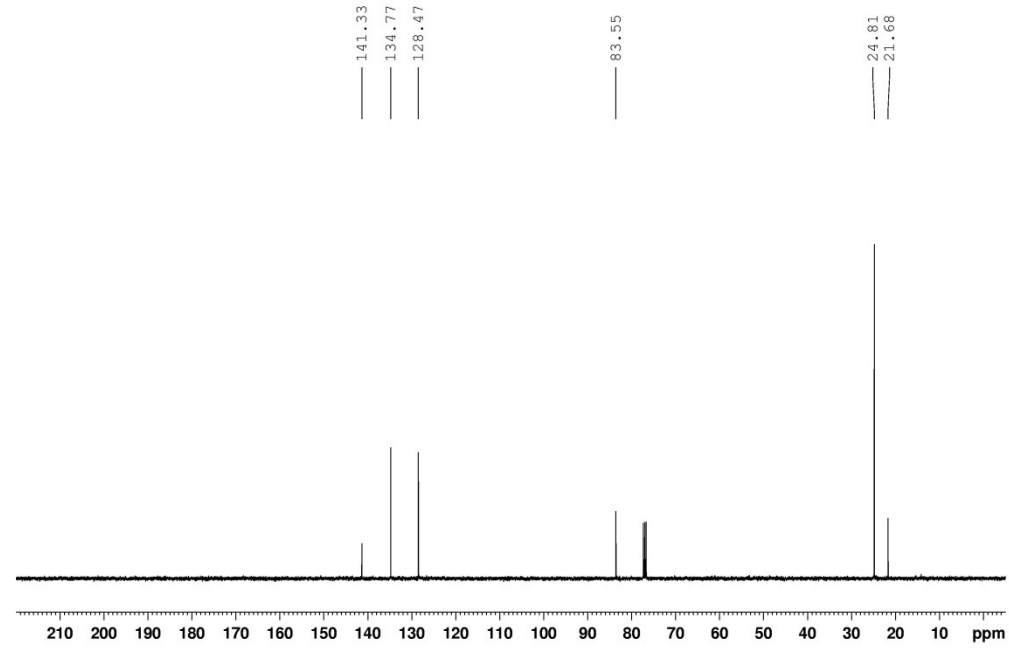
^{1}H and ^{13}C NMR spectra of compound **2f**



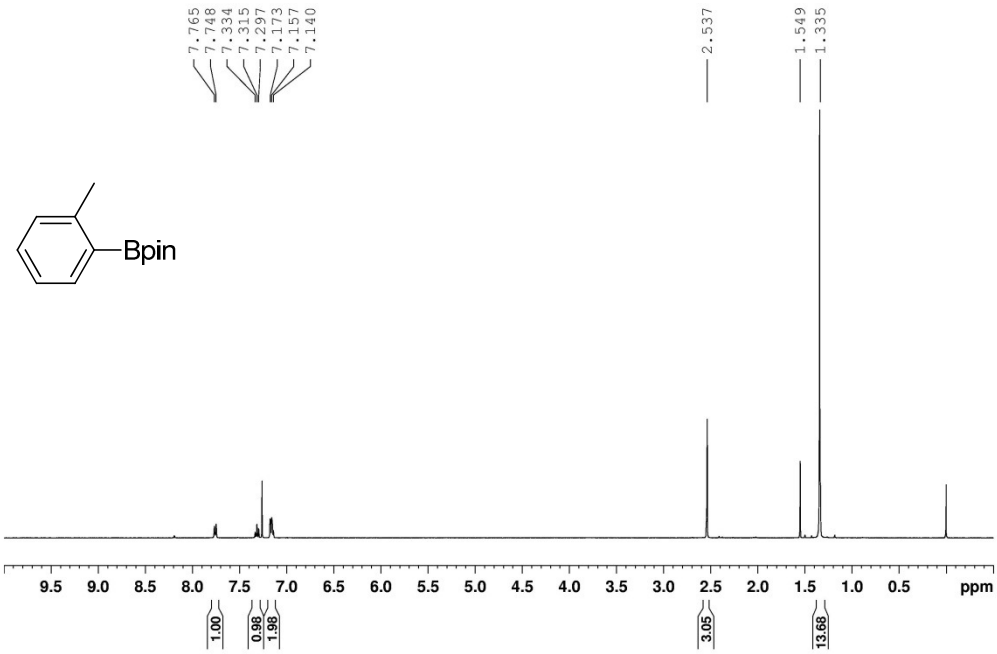


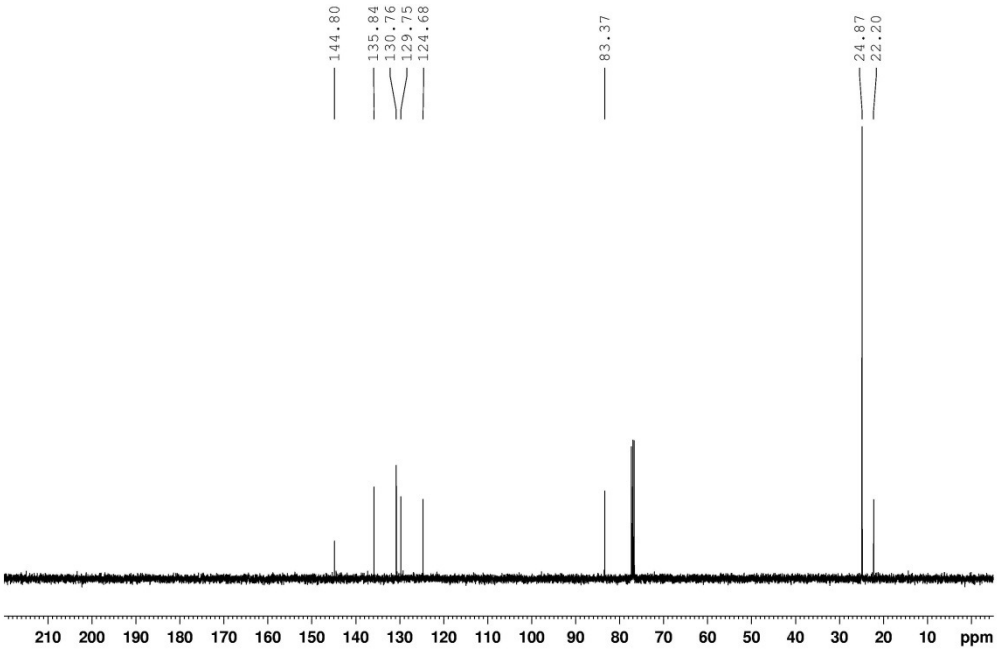
^{1}H and ^{13}C NMR spectra of compound **2g**



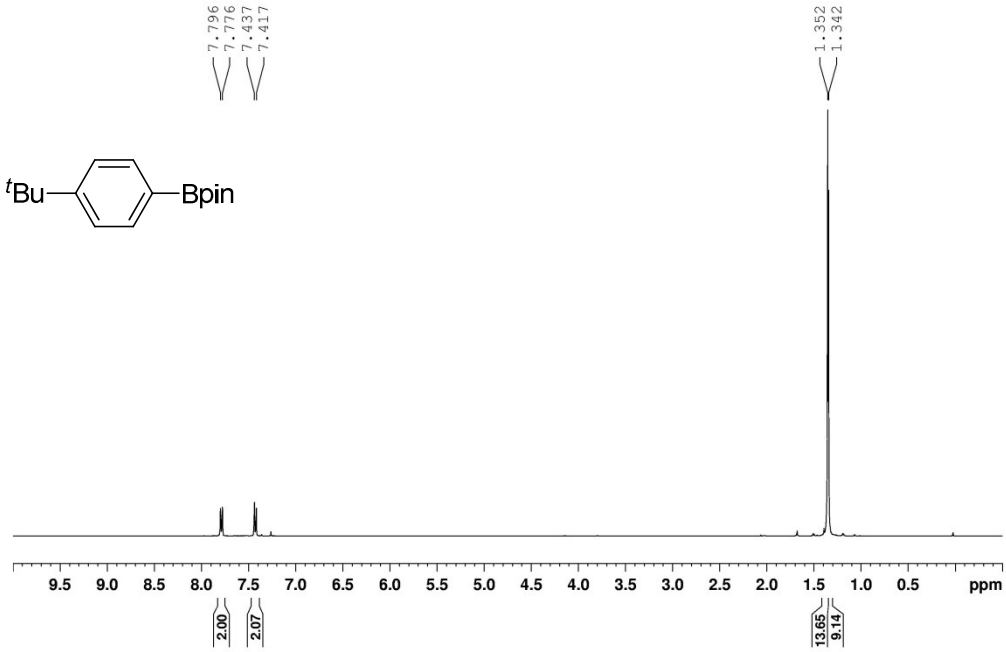


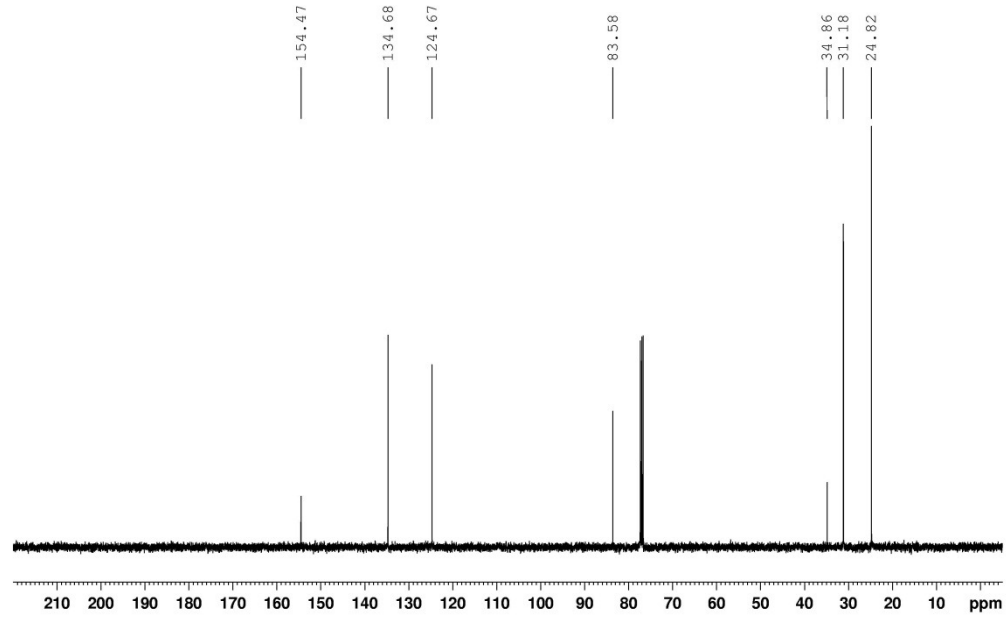
^{1}H and ^{13}C NMR spectra of compound **2h**



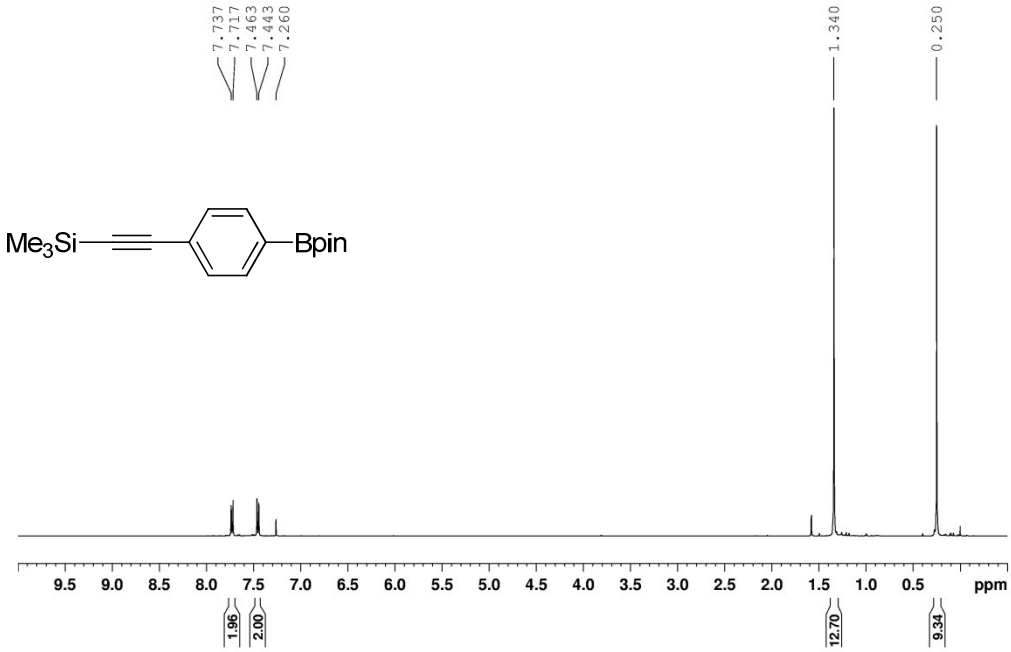


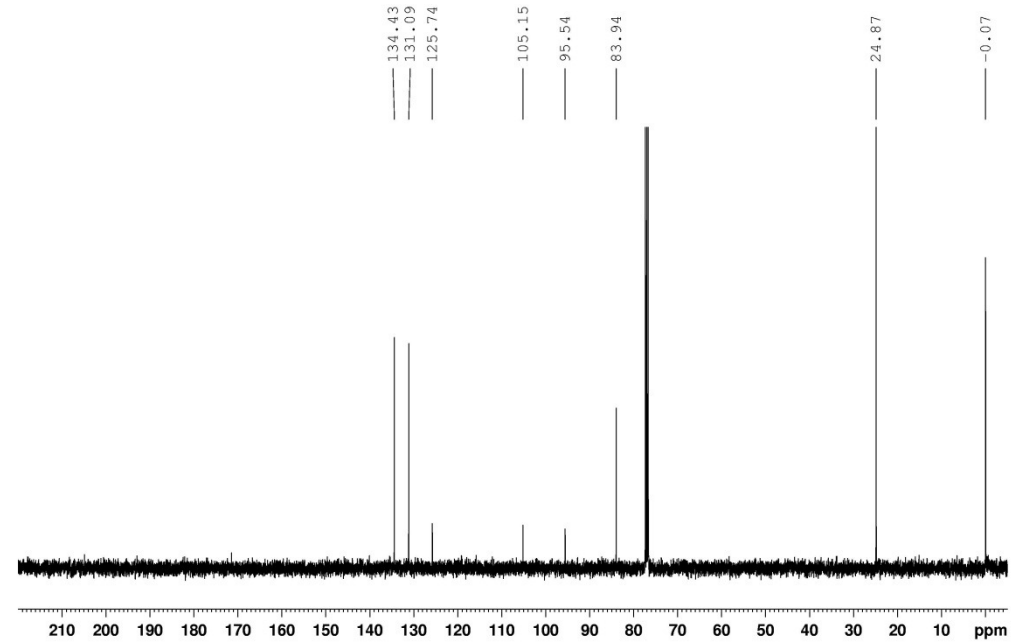
^{1}H and ^{13}C NMR spectra of compound **2i**



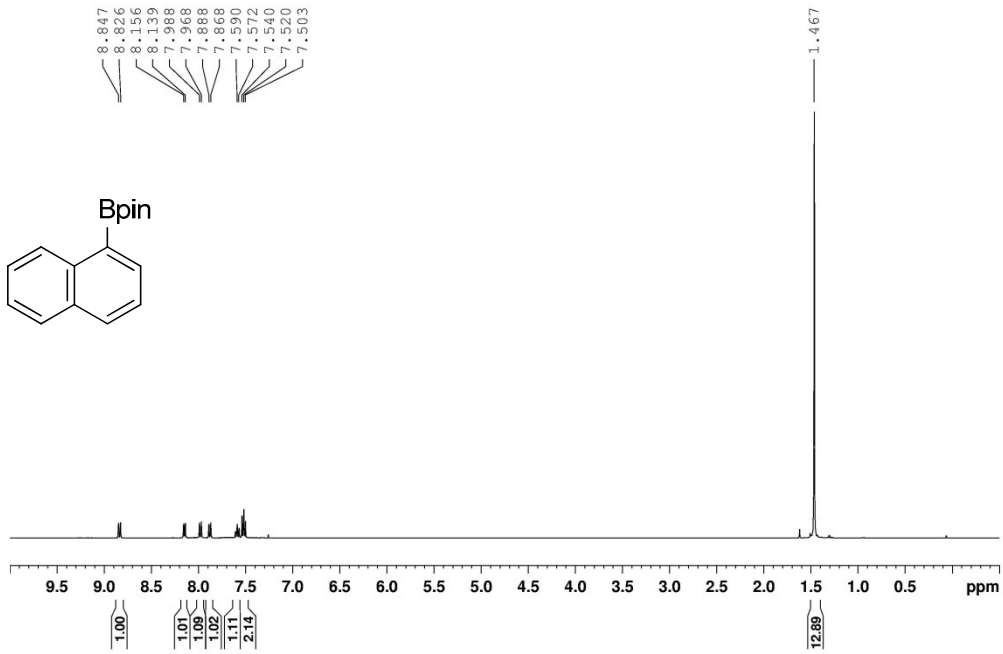


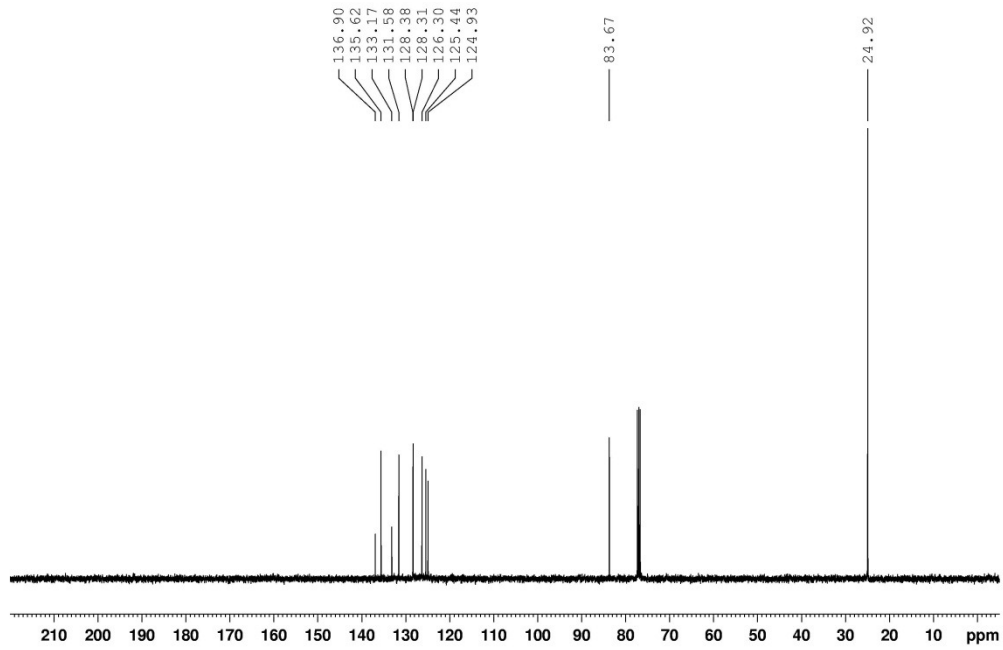
^{1}H and ^{13}C NMR spectra of compound **2j**



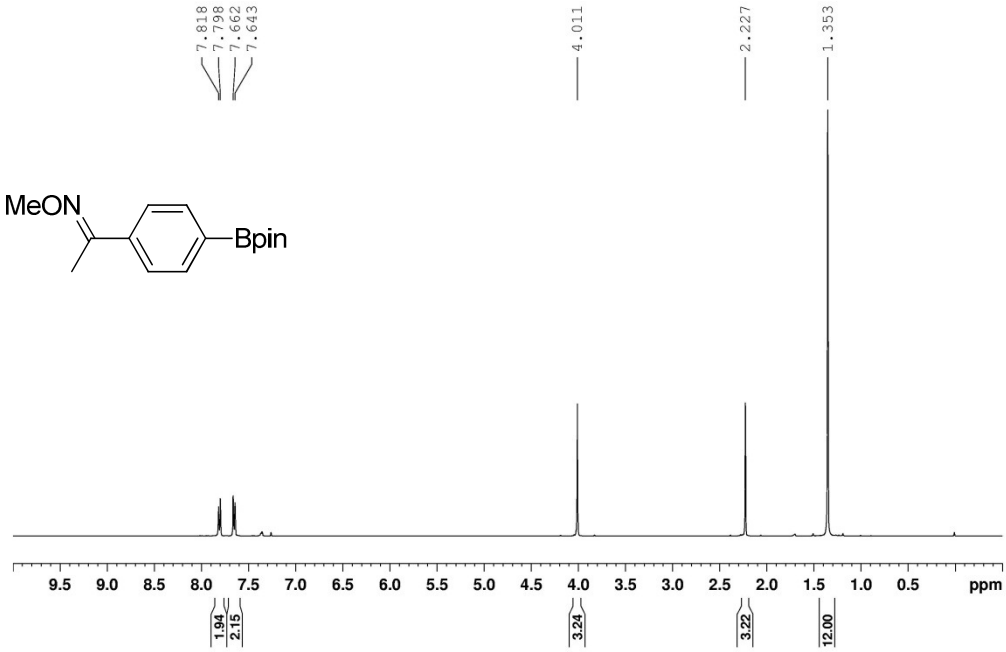


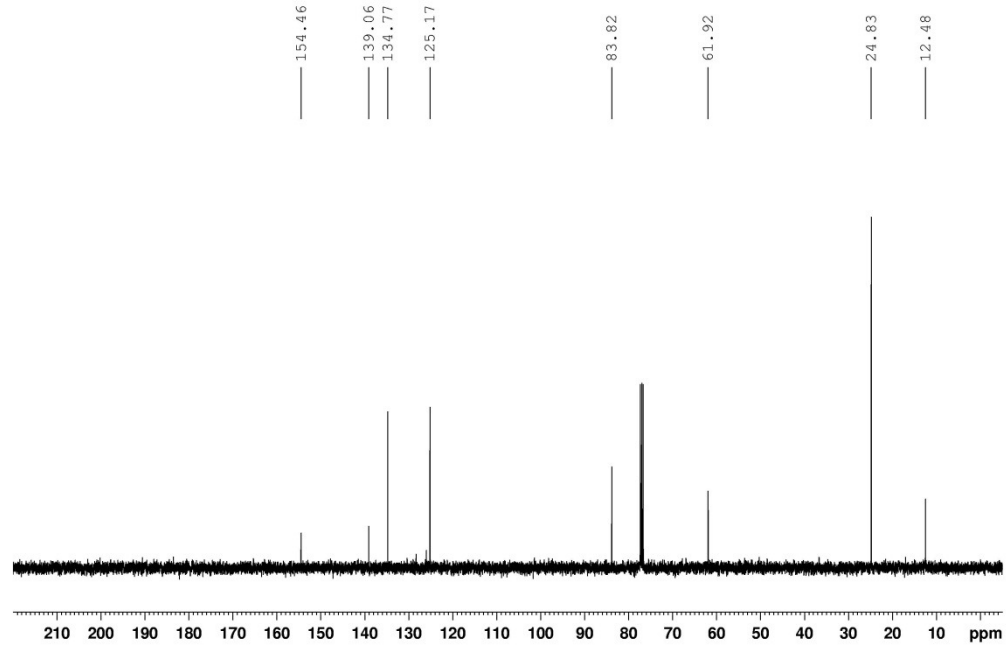
^{1}H and ^{13}C NMR spectra of compound **2k**



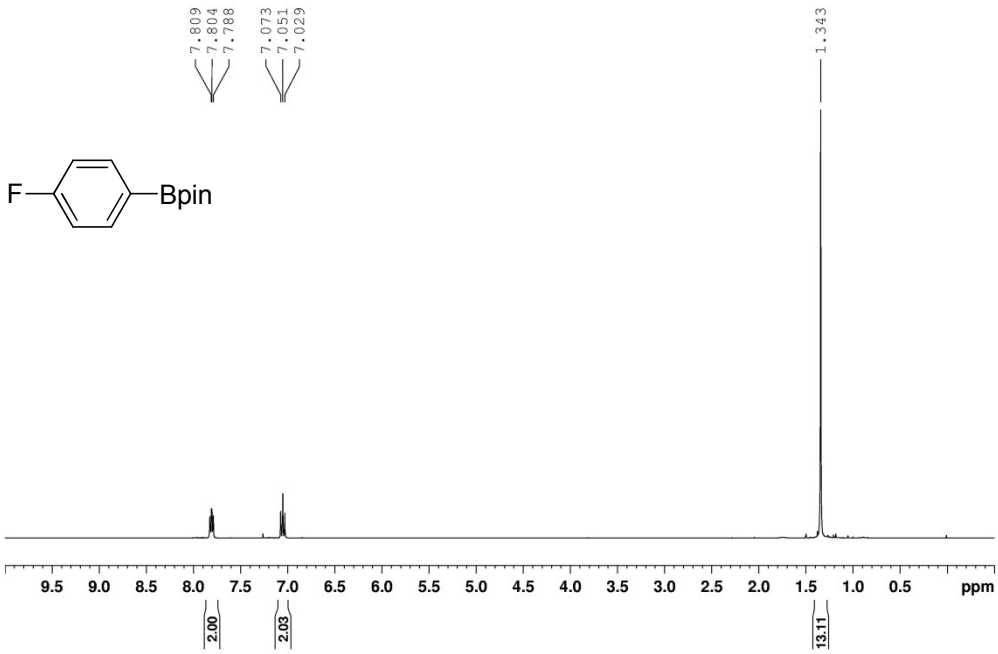


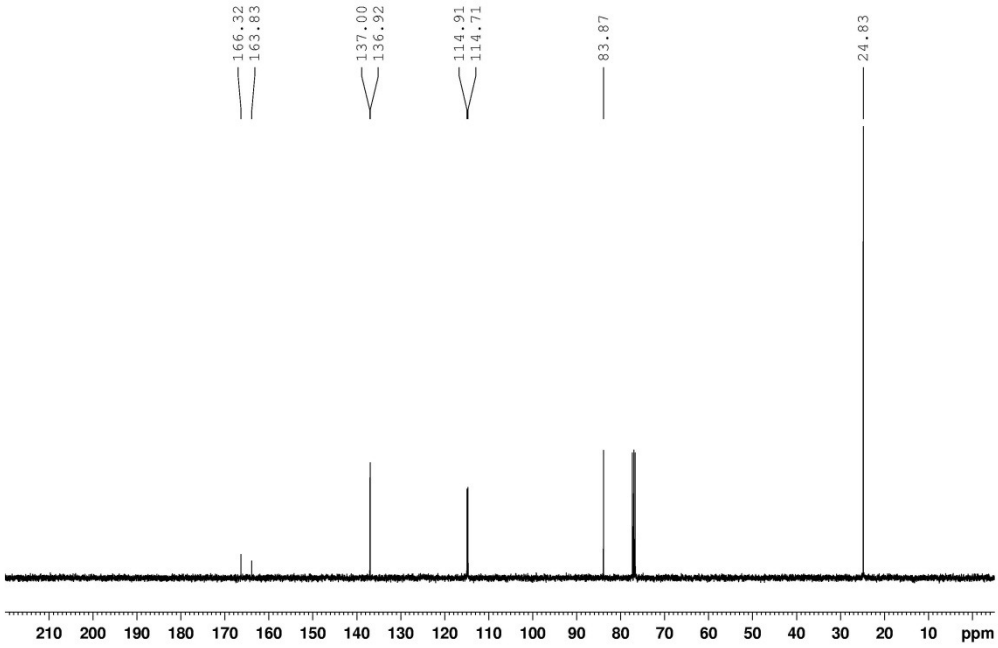
^{1}H and ^{13}C NMR spectra of compound **2m**



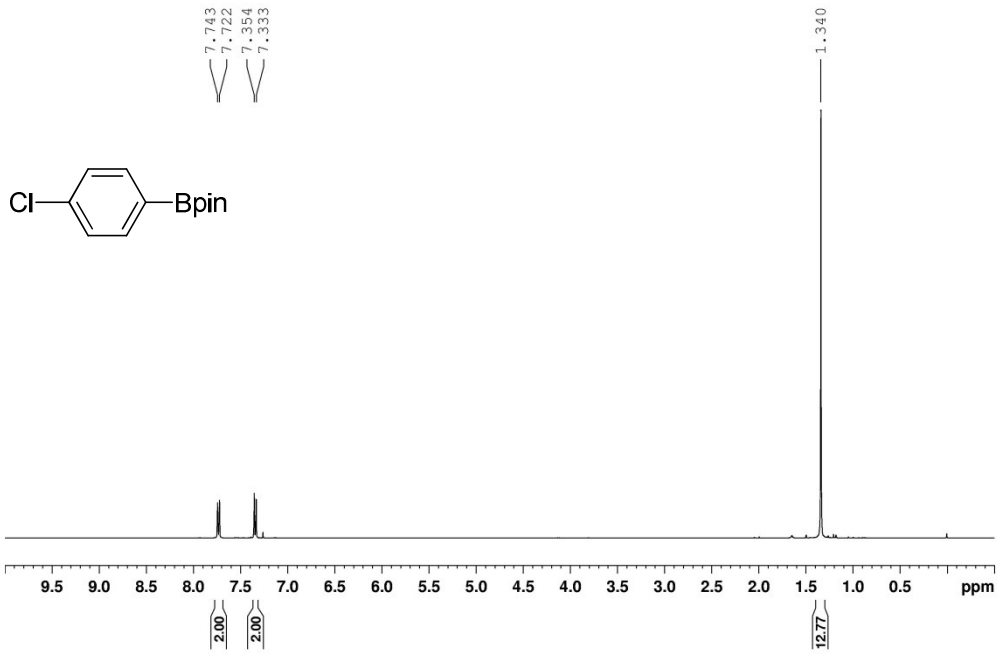


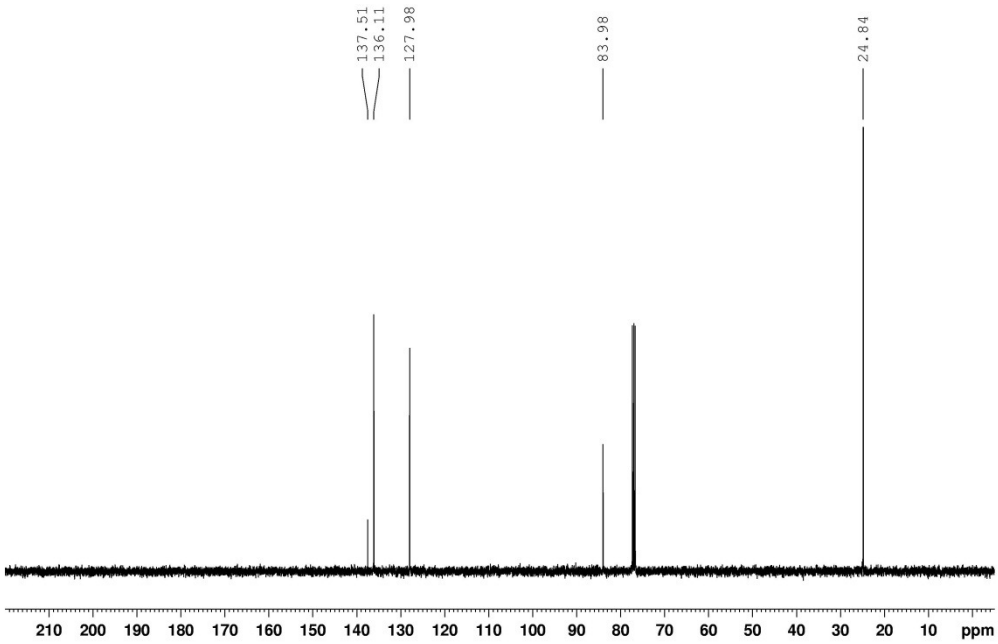
^{1}H and ^{13}C NMR spectra of compound **2n**



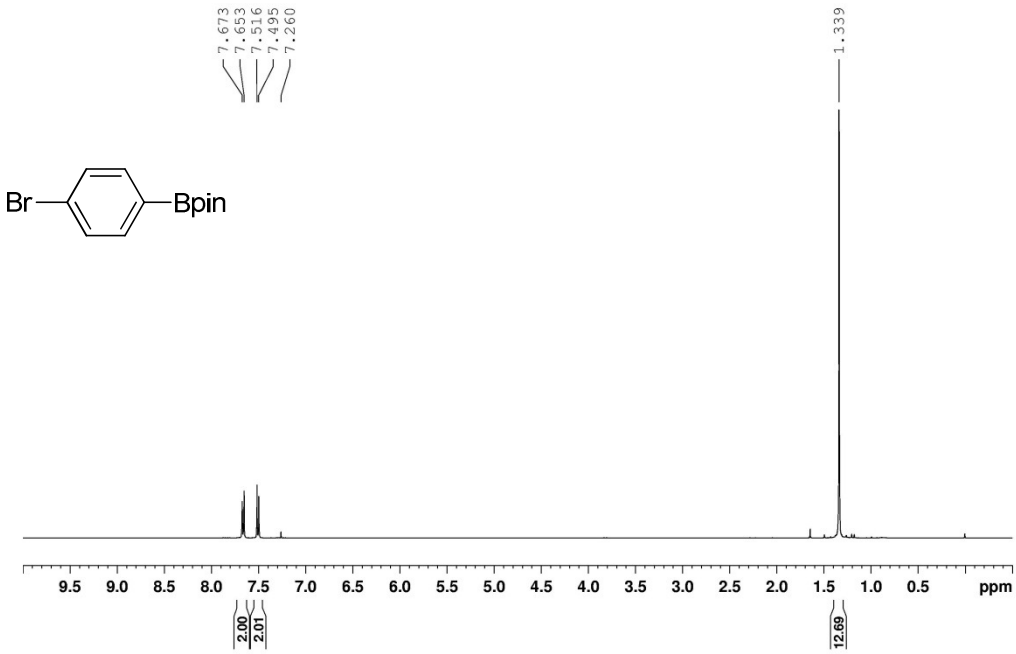


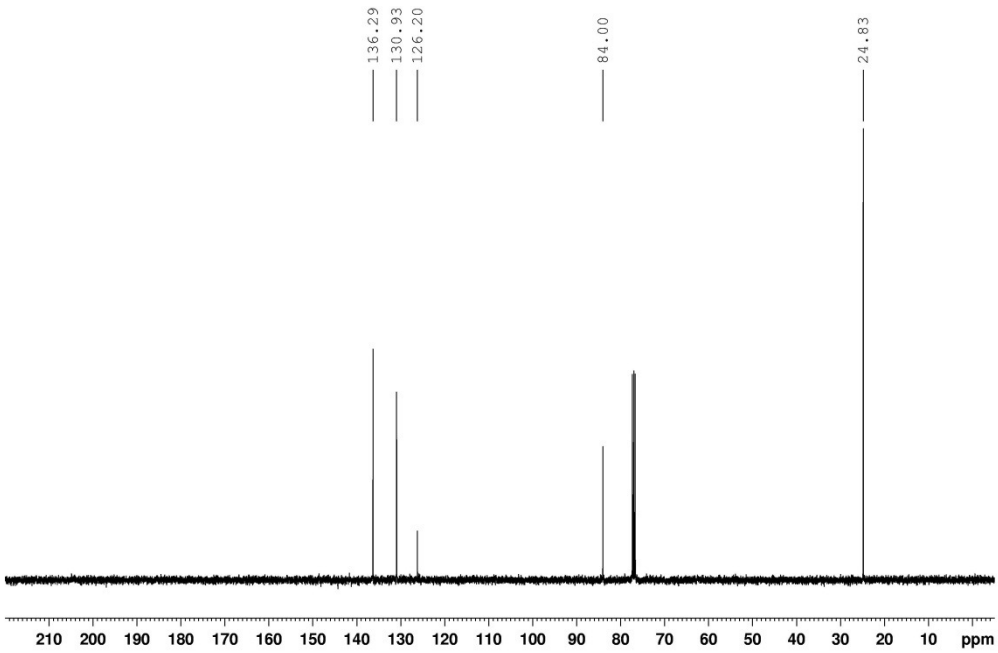
^{1}H and ^{13}C NMR spectra of compound **2o**



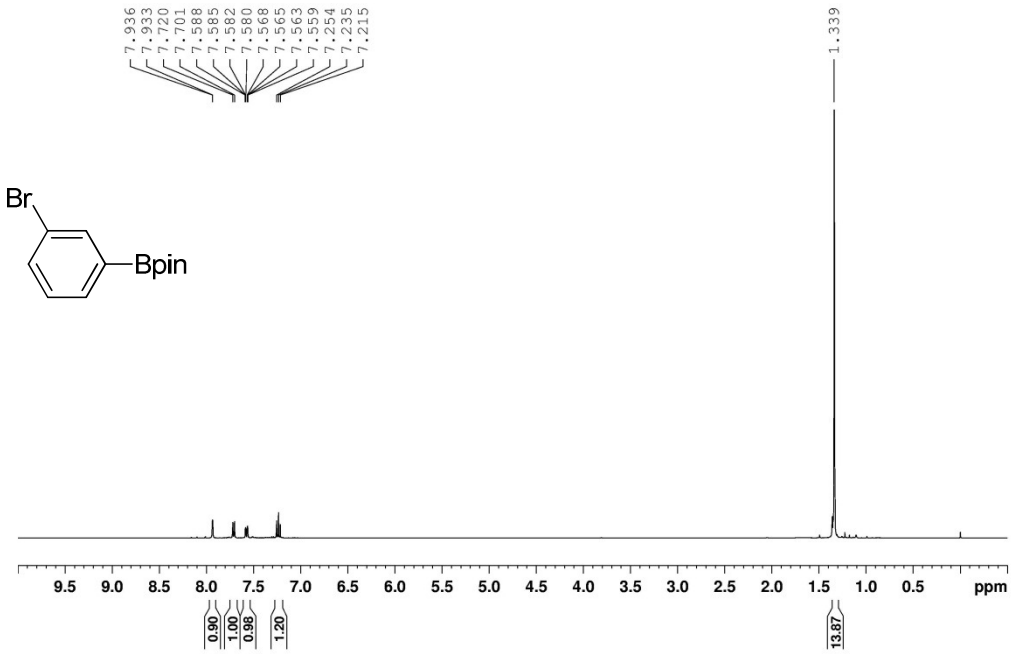


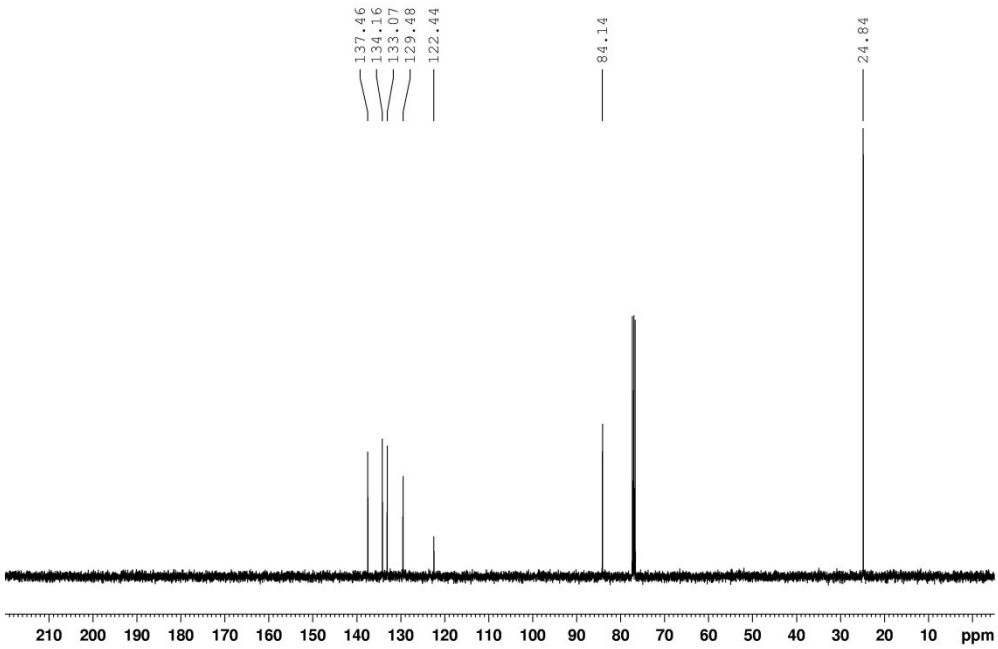
^{1}H and ^{13}C NMR spectra of compound **2p**



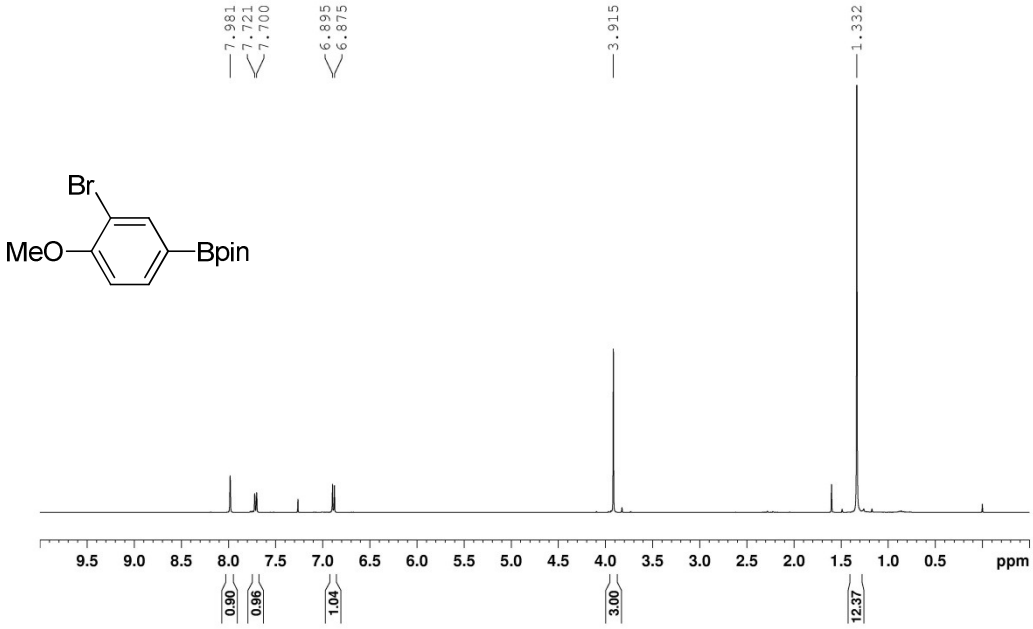


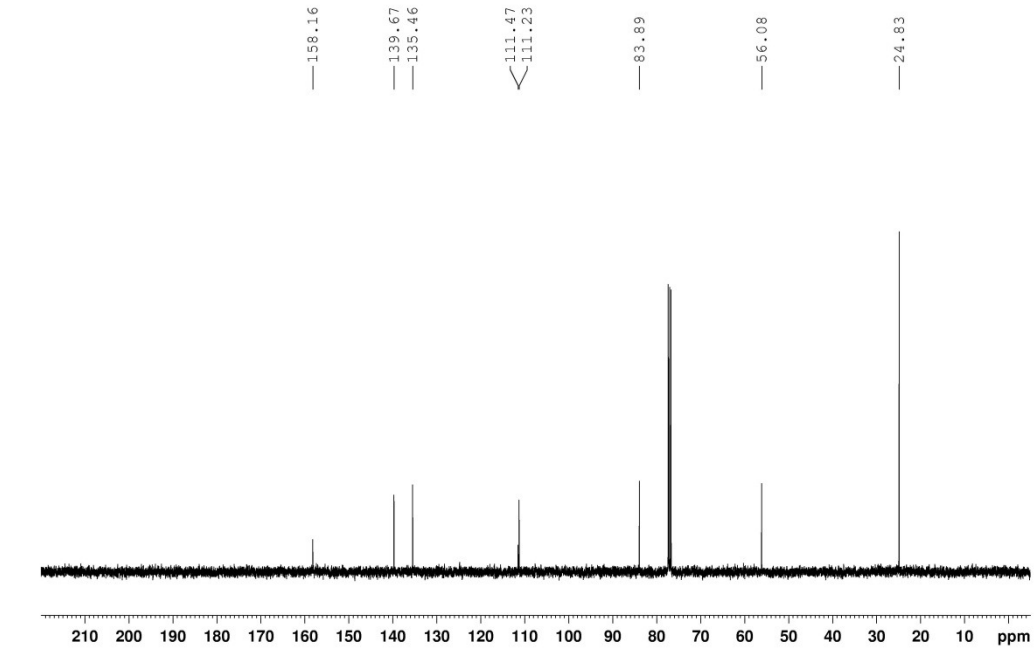
^{1}H and ^{13}C NMR spectra of compound **2q**



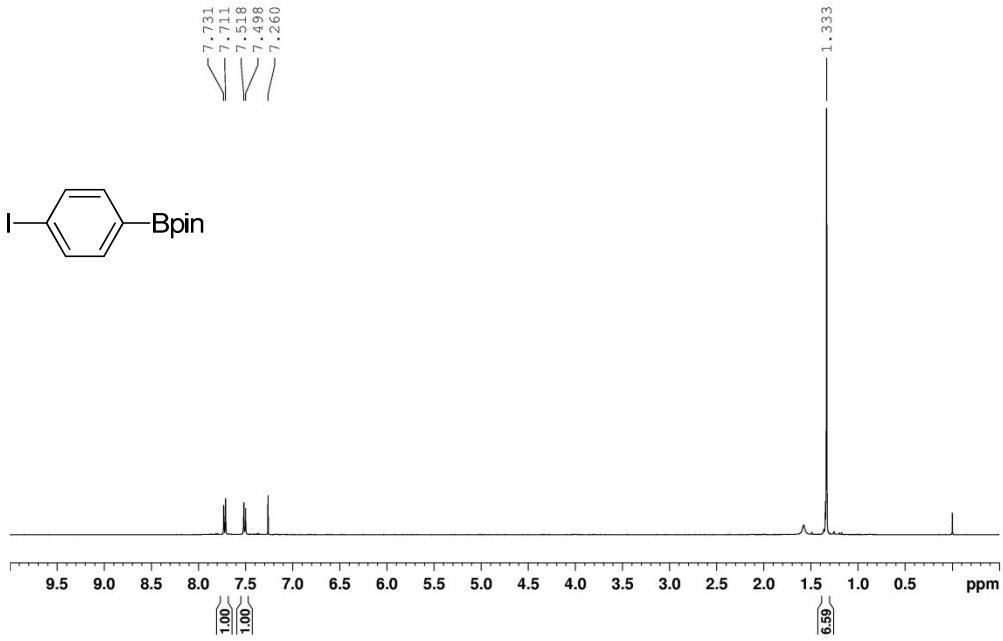


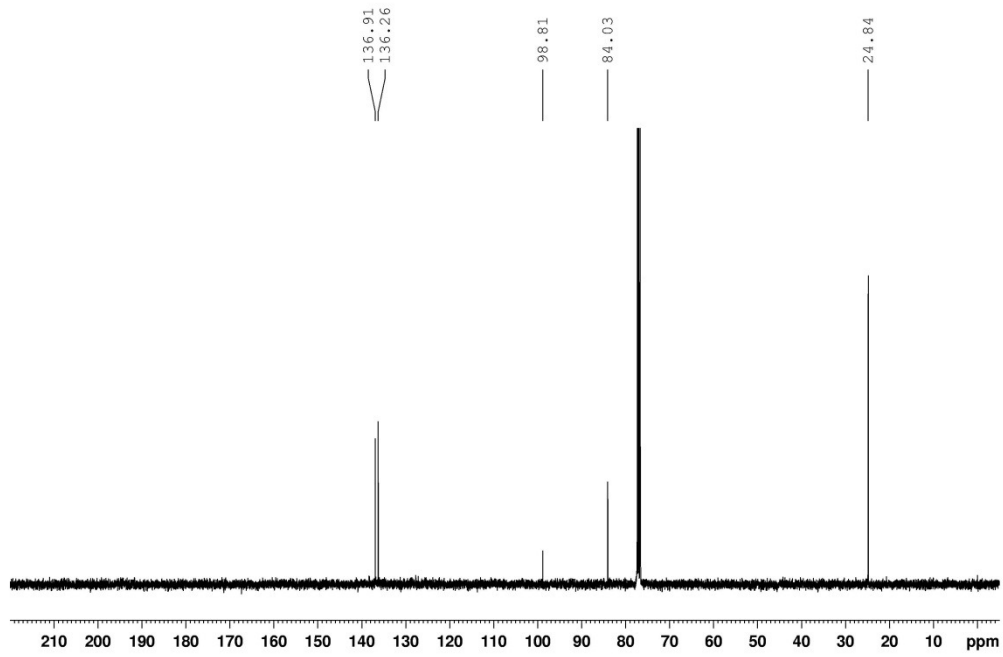
^{1}H and ^{13}C NMR spectra of compound **2r**



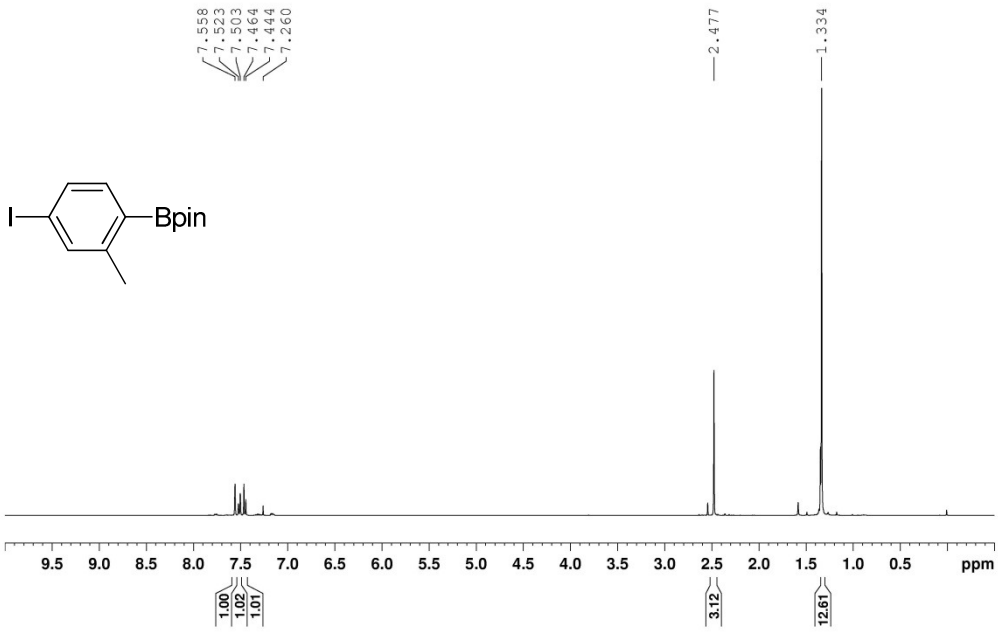


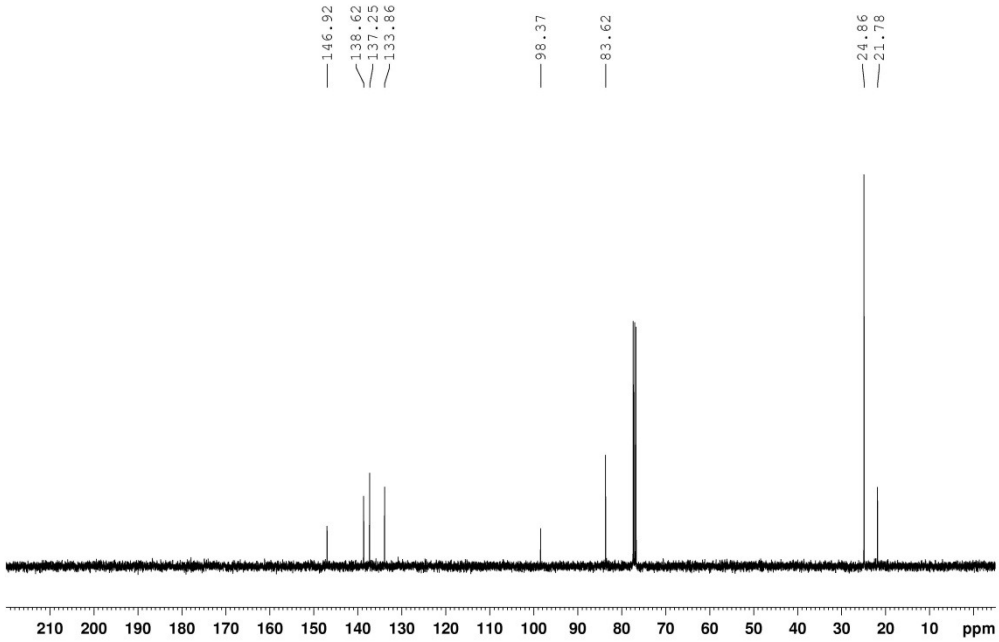
^{1}H and ^{13}C NMR spectra of compound **2s**





^{1}H and ^{13}C NMR spectra of compound **2t**





^{1}H and ^{13}C NMR spectra of compound **2u**