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Sequential In-Catalyzed Intramolecular Hydroarylation and Pd-Catalyzed Cross-Coupling Reactions Using Bromopropargyl Aryl Ethers and Amines

Lorena Alonso-Marañón, Luis A. Sarandeses, M. Montserrat Martínez,* and José Pérez Sestelo*

Centro de Investigaciones Científicas Avanzadas (CICA) and Departamento de Química Fundamental, Universidade da Coruña, E-15071 A Coruña, Spain

Contents

General methods. All reactions were carried out in flame-dried glassware, under argon atmosphere, using standard gastight syringes, cannula and septa. Toluene and THF were distilled from sodium/benzophenone. Dichloromethane was distilled from calcium hydride. Dry acetone, DMF and MeOH and other commercially available reagents were used as received. Reaction temperatures refer to external bath temperatures. Butyllithium was titrated prior to use. Indium(III) iodide (99.998%), indium(III) bromide (99%), indium(III) chloride (99.99%) were purchased and used as received under argon. Triorganoindium reagents were prepared according to previously published methods by treatment of the corresponding organolithium reagents (3.0 eq, ~0.5 M in dry THF) with a solution of $InCl_3$ (1.0 eq, ~0.1 M in dry THF) at –78 °C and warming to room temperature and were used without isolation.[1b] NBS was recrystallized from water. Reactions were monitored by TLC using pre-coated silica gel plates (Xtra SIL G/UV_{254}, 0.20 mm thick), UV light as the visualizing agent and ethanolic phosphomolybdic acid as the developing agent. Organic extracts were dried with anhydrous $MgSO_4$, filtered, and concentrated by using a rotary evaporator under reduced pressure. Flash column chromatography was performed with 230–400 mesh silica gel packed in glass columns. ^1H, ^{13}C NMR and DEPT-135 spectra were recorded in $CDCl_3$ at 300 MHz and 75 MHz, respectively at ambient temperature, and calibrated to the solvent peak. DEPT data were used to assign carbon types. Chemical shifts are reported in ppm (δ) relative to the solvent. Data are reported as follows: chemical shift (multiplicity [singlet (s), doublet (d), triplet (t), quartet (q), broad (br) and multiplet (m)], coupling constant [Hz], integration). The low and high resolution mass spectra were measured by electronic impact at 70 eV data were recorded using a double-focusing magnetic sector analyzer. IR spectra were taken with ATR ("attenuated total reflectance"). Melting points are uncorrected.

1 I. Pérez, J. Pérez Sestelo and L. A. Sarandeses, *J. Am. Chem. Soc.*, 2001, **123**, 4155–4160

6-Methoxy-4-phenyl-2*H*-chromene (3a).[2] According to the general procedure, the reaction of **2a** (100 mg, 0.415 mmol) with triphenylindium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.5 mg, 0.021 mmol) afforded **3a** (87.0 mg, 88%) as a white solid after purification by column chromatography (5% EtOAc/hexanes); mp: 62–64 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42–7.34 (m, 5H), 6.86 (d, J = 8.7 Hz, 1H), 6.73 (dd, J = 8.7, 3.0 Hz, 1H), 6.59 (d, J = 3.0 Hz, 1H), 5.85 (t, J = 4.0 Hz, 1H), 4.80 (d, J = 4.0 Hz, 2H), 3.67 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 153.9 (C), 148.6 (C), 138.1 (C), 137.2 (C), 128.6 (2 × CH), 128.4 (2 × CH), 127.8 (C), 124.5 (C), 120.8 (CH), 116.6 (CH), 114.1 (CH), 111.6 (CH), 65.1 (CH_2), 55.7 (CH_3); IR (ATR) ν_{max} 3061, 2933, 2829, 1731, 1608, 1579, 1488, 1300, 1247 cm^{-1}; MS (EI) m/z 238 $[M]^+$ (100); HRMS (EI) calcd for $C_{16}H_{14}O_2$ $[M]^+$ 238.0988, found 238.0988.

6-Methoxy-4-(2-thienyl)-2*H*-chromene (3b). According to the general procedure, the reaction of **2a** (100 mg, 0.415 mmol) with tri(2-thienyl)indium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.5 mg, 0.021 mmol) afforded **3b** (89.2 mg, 89%) as a green oil after purification by column chromatography (2% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (dd, J = 5.0, 1.3 Hz, 1H), 7.13 (dd, J = 3.6, 1.3 Hz, 1H), 7.08 (dd, J = 5.1, 3.5 Hz, 1H), 6.95 (d, J = 3.0 Hz, 1H), 6.87 (d, J = 8.7 Hz, 1H), 6.76 (dd, J = 8.7, 3.0 Hz, 1H), 6.03 (t, J = 4.2 Hz, 1H), 4.74 (d, J = 4.2 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1 (C), 148.7 (C), 139.7 (C), 130.5 (C), 127.3 (CH), 126.3 (CH), 125.0 (CH), 123.9 (C), 121.7 (CH), 116.8 (CH), 114.6 (CH), 111.3 (CH), 64.8 (CH_2), 55.8 (CH_3); IR (ATR) ν_{max} 3434, 3105, 3072, 2933, 2831, 1731, 1486, 1423 cm^{-1}; MS (EI) m/z 244 $[M]^+$ (100); HRMS (EI) calcd for $C_{14}H_{12}O_2S$ $[M]^+$ 244.0553, found 244.0545.

6-Methoxy-4-(phenylethynyl)-2*H*-chromene (3c).[2] According to the general procedure the reaction of **2a** (100 mg, 0.415 mmol) with triphenylethynylindium (0.207 mmol) and $Pd(dppf)Cl_2$ (15.4 mg, 0.021 mmol) afforded **3c** (72.9 mg, 67%) as a brown oil after purification by column

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chromatography (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.55–7.51 (m, 2H), 7.39–7.34 (m, 3H), 7.13 (d, J = 2.6 Hz, 1H), 6.76–6.73 (m, 2H), 6.24 (t, J = 4.1 Hz, 1H), 4.82 (d, J = 4.1 Hz, 2H), 3.81 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.3 (C), 147.6 (C), 131.7 (2 × CH), 128.6 (2 × CH), 128.5 (CH), 128.4 (CH), 122.8 (C), 122.2 (C), 119.5 (C), 116.5 (CH), 114.9 (CH), 111.1 (CH), 92.2 (C), 84.7 (C), 65.3 (CH_2), 55.8 (CH_3); IR (ATR) ν_{max} 2955, 2923, 2855, 1623, 1560, 1492, 1432 cm^{-1}; MS (EI) *m*/*z* 262 $[M]^+$ (10); HRMS (EI) calcd for $C_{18}H_{14}O_2$ $[M]^+$ 262.0988, found 262.0983.

4-Butyl-6-methoxy-2*H*-chromene (3d). According to the general procedure, the reaction of **2a** (100 mg, 0.415 mmol) with tributylindium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.5 mg, 0.021 mmol) afforded **3d** (54.4 mg, 60%) as a colorless oil after purification by column chromatography (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.78–6.75 (m, 2H), 6.67 (dd, J = 8.8, 2.8 Hz, 1H), 5.62 (t, J = 3.8 Hz, 1H), 4.67 (dt, J = 3.8, 1.5 Hz, 2H), 3.78 (s, 3H), 2.37 (td, J = 7.5, 1.1 Hz, 2H), 1.58–1.48 (m, 2H), 1.46–1.34 (m, 2H), 0.94 (t, J = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.0 (C), 148.4 (C), 134.5 (C), 124.7 (C), 118.4 (CH), 116.2 (CH), 113.0 (CH), 109.6 (CH), 65.3 (CH_2), 55.8 (CH_3), 31.0 (CH_2), 30.0 (CH_2), 22.5 (CH_2), 13.9 (CH_3); IR (ATR) ν_{max} 2957, 2928, 2832, 1574, 1482, 1429 cm^{-1}; MS (EI) *m*/*z* 218 $[M]^+$ (100); HRMS (EI) calcd for $C_{14}H_{18}O_2$ $[M]^+$ 218.1301, found 218.1301.

Palladium-catalyzed cross-coupling of $PhSnBu_3$ with 4-bromo-6-methoxy-2*H*-chromene (2a) (Table 1, entry 6). A solution of $PhSnBu_3$ (0.335 g, 0.913 mmol) in dry toluene (2 mL) was added to a solution of **2a** (100 mg, 0.415 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) in dry toluene (5 mL) in a Schlenk tube. The reaction mixture was heated at 100 °C for 48 h and was allowed to cool down to room temperature. The solvent was removed *in vacuo*. The residue was diluted with EtOAc (10 mL) and poured into a separatory funnel with water (10 mL). The product was extracted with EtOAc (3 × 10 mL) and the combined organic layers were washed with brine (15 mL), dried,

filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5% EtOAc/hexanes) to afford **3a** (29.7 mg, 30%) as a white solid after concentration and high vacuum drying.

Palladium-catalyzed cross-coupling of PhZnCl with 4-bromo-6-methoxy-2*H*-chromene (2a) (Table 1, entry 7). A solution of *n*-BuLi (0.882 mL, 1.826 mmol) was added dropwise to a cooled (–78 °C) solution of bromobenzene (0.175 mL, 1.66 mmol) in dry THF (5 mL). After 15 min, $ZnCl_2$ (1.0 M in Et_2O, 1.66 mL, 1.66 mmol) was slowly added and the resulting mixture was allowed to warm up to room temperature. After 30 min, the THF solution of the freshly prepared PhZnCl was added to a solution of **2a** (100 mg, 0.415 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) in toluene (10 mL). The reaction mixture was heated at 80 °C for 48 h and was allowed to cool down to room temperature. The reaction was quenched with saturated aqueous NH_4Cl (10 mL) and the mixture was poured into a separatory funnel. The phases were extracted with Et_2O (3 × 10 mL), washed with saturated aqueous NaCl (15 mL), dried ($MgSO_4$), filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5% EtOAc/hexanes) to afford **3a** (39.6 mg, 40%) as a white solid after concentration and high vacuum drying.

Palladium-catalyzed cross-coupling of phenylboronic acid with 4-bromo-6-methoxy-2*H*-chromene (2a) (Table 1, entry 8). Na_2CO_3 (0.264 g, 2.49 mmol), $PhB(OH)_2$ (0.111 g, 0.914 mmol) and EtOH (6 mL) were added to a solution of **2a** (100 mg, 0.415 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) in toluene (6 mL) in a Schlenk tube. The reaction mixture was heated at 80 °C for 24 h and was allowed to cool down to room temperature. The solvent was removed *in vacuo*. The residue was diluted with EtOAc (20 mL) and poured into a separatory funnel with water (20 mL). The product was extracted with EtOAc (2 × 20 mL) and the combined organic layers were washed with saturated aqueous NaCl (30 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5% EtOAc/hexanes) to afford **3a** (86 mg, 87%) as a white solid after concentration and high vacuum drying.

6-Methoxy-4-phenyl-2*H*-chromene (3a).[2] Following the general procedure, reaction of **1a** (100.0 mg, 0.415 mmol), $InCl_3$ (4.6 mg, 0.021 mmol), triphenylindium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.021 mmol) afforded **3a** (93.9 mg, 95%) as a white solid after purification by column chromatography (5% EtOAc/hexanes).

6-Methoxy-4-(2-thienyl)-2*H*-chromene (3b). Following the general procedure, reaction of **1a** (100.0 mg, 0.415 mmol), $InCl_3$ (4.6 mg, 0.021 mmol), tri(2-thienyl)indium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.021 mmol) afforded **3b** (86.2 mg, 85%) as a green oil after purification by column chromatography (5% EtOAc/hexanes).

6-Methoxy-4-(phenylethynyl)-2*H*-chromene (3c).[2] Following the general procedure, reaction of **1a** (100.0 mg, 0.415 mmol), $InCl_3$ (4.6 mg, 0.021 mmol), tri(phenylethynyl)indium (0.207 mmol) and $Pd(dppf)Cl_2$ (15.4 mg, 0.021 mmol) afforded **3c** (78.4 mg, 72%) as a brown oil after purification by column chromatography (5% EtOAc/hexanes).

4-Butyl-6-methoxy-2*H*-chromene (3d). Following the general procedure, reaction of **1a** (100.0 mg, 0.415 mmol), $InCl_3$ (4.6 mg, 0.021 mmol), tributylindium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.021 mmol) to afford **3d** (63.4 mg, 70%) as a white oil after purification by column chromatography (10% EtOAc/hexanes).

6-Methoxy-4-methyl-2*H*-chromene (3e).[2] Following the general procedure, reaction of **1a** (100.0 mg, 0.415 mmol), $InCl_3$ (4.6 mg, 0.021 mmol), trimethylindium (0.207 mmol) and $Pd(PPh_3)_2Cl_2$ (14.7 mg, 0.021 mmol) afforded **3e** (65.0 mg, 89%) as a light yellow oil after purification by column chromatography (5% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.77–6.66 (m, 3H); 5.62 (dd, J = 3.6, 1.8 Hz, 1H), 4.68 (dd, J = 3.5, 1.8 Hz, 2H), 3.77 (s, 3H), 2.02 (dd, J = 3.3, 1.7 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 154.1 (C), 148.1 (C), 130.3 (C), 125.2 (C), 119.4 (CH), 116.0 (CH), 113.3 (CH), 109.7 (CH), 65.3 (CH_2), 55.8 (CH_3), 17.9 (CH_3); IR (ATR) ν_{max} 2943, 2919,

2832, 2733, 1577, 1490, 1425 cm^{-1}; MS (EI) *m*/*z* 176 $[M]^+$ (62), 161 $[M - CH_3]^+$ (87); HRMS (EI) calcd for $C_{11}H_{12}O_2$ $[M]^+$ 176.0832, found 176.0827.

***N*-(3-Bromoprop-2-ynyl)-*N*-(4-methoxyphenyl)-4-methylbenzenesulfonamide (4).** According to the general procedure, starting from *N*-(4-methoxyphenyl)-4-methyl-*N*-(prop-2-ynyl)-benzenesulfonamide (1.0 g, 3.17 mmol), compound **4** (1.01 g, 81%) was prepared, after purification by column chromatography (30% EtOAc/hexanes), as a pale yellow solid; mp: 102–104 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H), 7.25 (d, J = 8.1 Hz, 2H), 7.10 (d, J = 8.9 Hz, 2H), 6.82 (d, J = 8.7 Hz, 2H), 4.41 (s, 2H), 3.79 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.4 (C), 143.6 (C), 135.7 (C), 132.0 (C), 129.9 (2 × CH), 129.2 (2 × CH), 128.1 (2 × CH), 114.3 (2 × CH), 74.7 (C), 55.4 (CH_3), 45.3 (C), 42.6 (CH_2), 21.6 (CH_3); IR (ATR) ν_{max} 2962, 2846, 2226, 1595, 1510, 1344, 1252 cm^{-1}; MS (EI) *m*/*z* 395 [M, ^{81}Br]$^+$ (40), 393 [M, ^{79}Br]$^+$ (38), 238 [M, ^{81}Br – $C_7H_7SO_2$]$^+$ (98), 236 [M, ^{79}Br – $C_7H_7SO_2$]$^+$ (100); HRMS (EI) calcd for $C_{17}H_{16}O_3NBrS$ $[M]^+$ 393.0029, found 393.0029.

***N*-(3-Bromoprop-2-ynyl)-4-methyl-*N*-phenylbenzenesulfonamide (5).** According to the general procedure, starting from 4-methyl-*N*-phenyl-*N*-(prop-2-ynyl)-benzenesulfonamide (0.904 g, 3.17 mmol), compound **5** (0.958 g, 83%) was prepared, after purification by column chromatography (20% EtOAc/hexanes), as a yellow solid; mp: 99–102 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, J = 8.3 Hz, 2H); 7.34–7.30 (m, 3H); 7.27–7.22 (m, 4H); 4.46 (s, 2H); 2.43 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.7 (C), 139.6 (C), 135.6 (C), 129.2 (2 × CH), 129.1 (2 × CH), 128.2 (2 × CH), 128.1 (CH), 128.0 (2 × CH), 74.5 (C), 45.5 (C), 42.3 (CH_2), 21.6 (CH_3); IR (ATR) ν_{max} 3058, 2971, 2225, 1651, 1499 cm^{-1}; MS (EI) *m*/*z* 365 [M, ^{81}Br]$^+$ (25), 363 [M, ^{79}Br]$^+$ (24), 210 [M, ^{81}Br – $C_7H_7SO_2$]$^+$ (90), 208 [M, ^{79}Br – $C_7H_7SO_2$]$^+$ (86); HRMS (EI) calcd for $C_{16}H_{14}O_2NBrS$ $[M]^+$ 362.9923, found 362.9905.

***N*-(3-Bromoprop-2-ynyl)-*N*-(3-5-dimethoxyphenyl)-4-methylbenzenesulfonamide (6).** According to the general procedure, starting from *N*-(3,5-dimethoxyphenyl)-4-methyl-*N*-(prop-2-ynyl)-benzenesulfonamide (1.10 g, 3.17 mmol), compound **6** (0.766 g, 57%) was prepared as a white solid after purification by column chromatography (20% EtOAc/hexanes); mp: 81–83 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4, 2H), 7.25 (d, J = 8.0 Hz, 2H), 6.41 (s, 3H); 4.43 (s, 2H), 3.71 (s, 6H), 2.42 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.7 (2 × C), 143.7 (C), 141.3 (C), 135.7 (C), 129.2 (2 × CH), 128.1 (2 × CH), 106.2 (2 × CH), 100.6 (CH), 74.6 (C), 55.4 (2 × CH_3), 45.5 (C), 42.3 (CH_2), 21.6 (CH_3); IR (ATR) ν_{max} 2931, 2840, 2219, 1539, 1458, 1427 cm^{-1}; MS (EI) *m*/*z* 344 [M – Br]$^+$ (16), 240 [M, ^{81}Br – $C_8H_{10}SO_3$]$^+$ (17), 238 [M, ^{79}Br – $C_8H_{10}SO_3$]$^+$ (15); HRMS (EI) calcd for $C_{18}H_{18}O_4NSBr$ [M]$^+$ 423.0134, found 423.0118.

4-Bromo-6-methoxy-1-tosyl-1,2-dihydroquinoline (7). In a Schlenk tube filled with argon, a solution of $InCl_3$ (7.4 mg, 0.021 mmol) and **4** (0.164 mg, 0.415 mmol) in toluene (5 mL) was heated at 100 ºC for 2 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (10% EtOAc/hexanes) to afford **7** (0.155 g, 95%) as a white solid after concentration and high vacuum drying; mp: 140–142 ºC (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.60 (d, J = 8.7 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 6.94–6.87 (m, 2H), 5.85 (t, J = 4.5 Hz, 1H), 4.36 (d, J = 4.5 Hz, 2H), 3.84 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.5 (C), 143.8 (C), 135.3 (C), 130.2 (C), 129.3 (2 × CH), 128.7 (CH), 128.3 (C), 127.3 (2 × CH), 126.2 (CH), 118.7 (C), 114.4 (CH), 112.3 (CH), 55.6 (CH_3), 47.0 (CH_2), 21.5 (CH_3); IR (ATR) ν_{max} 2923, 2851, 1728, 1600, 1568, 1479 cm^{-1}; MS (EI) *m*/*z* 395 [M, ^{81}Br]$^+$ (12), 393 [M, ^{79}Br]$^+$ (11), 238 [M, ^{81}Br – $C_7H_7SO_2$]$^+$ (68), 236 [M, ^{79}Br – $C_7H_7SO_2$]$^+$ (67), 159 [M – $C_7H_7SO_2Br$]$^+$ (100); HRMS (EI) calcd for $C_{17}H_{16}O_3NBrS$ [M]$^+$ 393.0029, found 393.0027.

4-Bromo-1-tosyl-1,2-dihydroquinoline (8). In a Schlenk tube filled with argon, a solution of $InBr_3$ (7.4 mg, 0.021 mmol) and **5** (0.151 g, 0.415 mmol) in toluene (5 mL) was heated at 100 ºC for 2 h.

The solvent was removed *in vacuo* and the residue purified by flash chromatography on silica gel (10% EtOAc/hexanes) to afford **8** (0.133 g, 88%) as a yellow solid after concentration and high vacuum drying; mp: 108–110 ºC (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.68 (dd, J = 7.9, 1.2 Hz, 1H), 7.41 (dd, J = 7.6, 1.7 Hz, 1H), 7.36 (dd, J = 7.7, 1.7 Hz, 1H), 7.29 (dd, J = 7.6, 1.4 Hz, 1H), 7.27–7.24 (m, 2H), 7.11 (d, J = 8.0 Hz, 2H), 5.87 (t, J = 4.5 Hz, 1H), 4.40 (d, J = 4.5 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.9 (C), 135.5 (C), 135.4 (C), 129.4 (CH), 129.3 (2 × CH), 129.0 (C), 127.2 (2 × CH), 127.2 (CH), 127.1 (CH), 126.8 (CH), 125.7 (CH), 118.8(C), 46.8 (CH_2), 21.5 (CH_3); IR (ATR) ν_{max} 3064, 2923, 2856, 1620, 1597, 1476, 1450 cm^{-1}; MS (EI) *m/z* 365 [M, ^{81}Br]$^{+}$ (20), 363 [M, ^{79}Br]$^{+}$ (19), 210 [M, ^{81}Br – $C_7H_7SO_2$]$^{+}$ (100), 208 [M, ^{79}Br – $C_7H_7SO_2$]$^{+}$ (98); HRMS (EI) calcd for $C_{16}H_{14}O_2NBrS$ [M]$^{+}$ 362.9923, found 362.9907.

4-Bromo-5,7-dimethoxy-1-tosyl-1,2-dihydroquinoline (9). In a Schlenk tube filled with argon, a solution of InI_3 (10.4 mg, 0.021 mmol) and **6** (0.176 g, 0.415 mmol) in toluene (5 mL) was heated at 100 ºC for 2 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography on silica gel (20% EtOAc/hexanes), to afford **9** (0.132 g, 75%) as a yellow solid after concentration and high vacuum drying; mp: 114–115 ºC (EtOAc/hexanes). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 6.96 (d, J = 2.4 Hz, 1H), 6.38 (d, J = 2.4 Hz, 1H), 5.68 (t, J = 5.3 Hz, 1H), 4.19 (d, J = 5.3 Hz, 2H), 3.88 (s, 3H), 3.78 (s, 3H), 2.36 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.6 (C), 157.1 (C), 143.8 (C), 139.2 (C), 136.1 (C), 129.5 (2 × CH), 127.1 (2 × CH), 124.7 (CH), 113.9 (C), 111.8 (C), 103.4 (CH), 98.7 (CH), 55.7 (2 × CH_3), 46.9 (CH_2), 21.5 (CH_3); IR (ATR) ν_{max} 2940, 2842, 1605, 1565, 1462 cm^{-1}; MS (EI) *m/z* 425 [M, ^{81}Br]$^{+}$ (23), 423 [M, ^{79}Br]$^{+}$ (22), 270 [M, ^{81}Br – $C_7H_7SO_2$]$^{+}$ (43), 268 [M, ^{79}Br – $C_7H_7SO_2$]$^{+}$ (44); HRMS (EI) calcd for $C_{18}H_{18}O_4NSBr$ [M]$^{+}$ 423.0134, found 423.0127.

6-Methoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (10a).[3] Following the general procedure, the reaction of **4** (0.164 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), triphenylindium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **10a** as a yellow solid (0.150 g, 92%) after purification by column chromatography (10% EtOAc/hexanes); mp: 190–192 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (d, J = 8.8 Hz, 1H), 7.33 (d, J = 8.3 Hz, 2H), 7.26–7.19 (m, 3H), 7.03 (d, J = 8.0 Hz, 2H), 6.87 (dd, J = 8.8, 2.9 Hz, 1H), 6.72–6.69 (m, 2H), 6.40 (d, J = 2.9 Hz, 1H), 5.57 (t, J = 4.4 Hz, 1H), 4.51 (d, J = 4.4 Hz, 2H), 3.69 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.0 (C), 143.3 (C), 138.6 (C), 137.9 (C), 136.1 (C), 135.2 (C), 132.0 (C), 129.0 (2 × CH), 128.8 (CH), 128.5 (2 × CH), 128.0 (2 × CH), 127.7 (2 × CH), 127.6 (CH), 122.2 (CH), 113.0 (CH), 111.8 (CH), 55.4 (CH_3), 45.6 (CH_2), 21.3 (CH_3); IR (ATR) ν_{max} 3002, 2927, 2833, 1732, 1599, 1481, 1342 cm^{-1}; MS (EI) m/z 391 $[M]^+$ (5), 236 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{23}H_{21}O_3NS$ $[M]^+$ 391.1237, found 391.1229.

6-Methoxy-4-(2-thienyl)-1-tosyl-1,2-dihydroquinoline (10b). Following the general procedure, the reaction of **4** (0.164 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), tri(2-thienyl)indium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **10b** (0.142 g, 86%) as an orange solid after purification by column chromatography (20% EtOAc/hexanes); mp: 166–170 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, J = 8.8 Hz, 1H), 7.39 (d, J = 8.3 Hz, 2H), 7.18 (dd, J = 5.1, 1.1 Hz, 1H), 7.01 (d, J = 8.0 Hz, 2H), 6.93–6.88 (m, 2H), 6.74 (d, J = 2.9 Hz, 1H), 6.55 (dd, J = 3.5, 1.1 Hz, 1H), 5.67 (t, J = 4.5 Hz, 1H), 4.45 (d, J = 4.5 Hz, 2H), 3.75 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1 (C), 143.4 (C), 139.4 (C), 135.8 (C), 131.6 (C), 131.5 (C), 129.1 (2 × CH), 128.9 (CH), 128.4 (C), 127.4 (2 × CH), 126.7 (CH), 126.5 (CH), 125.0 (CH), 123.3 (CH), 113.5 (CH), 111.4 (CH), 55.4 (CH_3), 45.4 (CH_2), 21.4 (CH_3); IR (ATR) ν_{max} 2923, 2850, 1600, 1568, 1484 cm^{-1}; MS (EI) m/z 397 $[M]^+$ (10), 242 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{21}H_{19}O_3NS_2$ $[M]^+$ 397.0801, found 397.0801.

3 K. Komeyama, R. Igawa and K. Takaki, *Chem. Commun.*, 2010, **46**, 1748–1750.

6-Methoxy-4-(phenylethynyl)-1-tosyl-1,2-dihydroquinoline (10c). Following the general procedure, the reaction of **4** (0.164 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), triphenylethynylindium (0.291 mmol) and $Pd(dppf)Cl_2$ (15.4 mg, 0.021 mmol) afforded **10c** (0.112 g, 65%) as a brown-orange oil after purification by column chromatography (10% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.63 (d, J = 8.8 Hz, 1H), 7.44–7.38 (m, 2H), 7.37–7.32 (m, 3H), 7.28 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 2.9 Hz, 1H), 6.90 (dd, J = 8.8, 2.9 Hz, 1H), 5.90 (t, J = 4.5 Hz, 1H), 4.45 (d, J = 4.5 Hz, 2H), 3.85 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.4 (C), 143.7 (C), 135.5 (C), 131.5 (2 × CH), 130.0 (C), 129.3 (CH), 129.2 (2 × CH), 128.6 (CH), 128.5 (CH), 128.4 (2 × CH), 127.7 (C), 127.4 (2 × CH), 122.7 (C), 120.4 (C), 113.6 (CH), 111.0 (CH), 91.5 (C), 84.5 (C), 55.5 (CH_3), 45.7 (CH_2), 21.5 (CH_3); IR (ATR) ν_{max} 2921, 2840, 1598, 1568 cm^{-1}; MS (EI) m/z 415 $[M]^+$ (5), 260 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{25}H_{21}O_3NS$ $[M]^+$ 415.1237, found 415.1218.

4-Butyl-6-methoxy-1-tosyl-1,2-dihydroquinoline (10d). Following the general procedure, the reaction of **4** (0.164 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), tributylindium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **10d** (92.5 mg, 60%) was obtained as a white solid after purification by column chromatography (10% EtOAc/hexanes); mp: 67–70 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65 (d, J = 8.8 Hz, 1H), 7.25 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.1 Hz, 2H), 6.83 (dd, J = 8.8, 2.9 Hz, 1H), 6.66 (d, J = 2.9 Hz, 1H), 5.33 (t, J = 4.2 Hz, 1H), 4.33 (d, J = 4.2 Hz, 2H), 3.82 (s, 3H), 2.31 (s, 3H), 1.97–1.91 (m, 2H), 1.20–1.08 (m, 2H), 0.87–0.77 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.1 (C), 143.0 (C), 136.5 (C), 135.8 (C), 132.1 (C), 129.0 (2 × CH), 128.6 (CH), 128.2 (C), 127.4 (2 × CH), 119.9 (CH), 111.9 (CH), 109.4 (CH), 55.4 (CH_3), 45.4 (CH_2), 31.1 (CH_2), 29.9 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 14.0 (CH_3); IR (ATR) ν_{max} 2925, 2860, 1606, 1569, 1482 cm^{-1}; MS (EI) m/z 371 $[M]^+$ (5), 216 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{21}H_{25}O_3NS$ $[M]^+$ 371.1550, found 371.1535.

6-Methoxy-4-methyl-1-tosyl-1,2-dihydroquinoline (10e). Following the general procedure, the reaction of **4** (0.164 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), trimethylindium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) compound **10e** was isolated (98.4 mg, 72%) as an orange solid after purification by column chromatography (20% EtOAc/hexanes); mp: 132–135 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.84 (dd, J = 8.8, 2.9 Hz, 1H), 6.64 (d, J = 2.9 Hz, 1H), 5.31–5.28 (m, 1H) 4.30 (dd, J = 4.2, 1.7 Hz, 2H), 3.83 (s, 3H), 2.33 (s, 3H), 1.52 (dd, J = 3.2, 1.6 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.3 (C), 143.0 (C), 136.1 (C), 132.8 (C), 131.3 (C), 128.8 (2 × CH), 128.5 (CH), 128.1 (C), 127.5 (2 × CH), 120.8 (CH), 112.0 (CH), 109.4 (CH), 55.5 (CH_3), 45.4 (CH_2), 21.4 (CH_3), 17.6 (CH_3); IR (ATR) ν_{max} 2921, 2850, 1650, 1602, 1484 cm^{-1}; MS (EI) m/z 329 $[M]^+$ (9), 174 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{18}H_{19}O_3NS$ $[M]^+$ 329.1080, found 329.1074.

4-Phenyl-1-tosyl-1,2-dihydroquinoline (11a).[4] Following the general procedure, the reaction of **5** (0.151 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), triphenylindium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol). After purification by column chromatography (10% EtOAc/hexanes) **11a** was obtained as a white solid (0.138 g, 92%); mp: 169–170 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (dd, J = 8.0, 1.1 Hz, 1H), 7.36–7.32 (m, 3H); 7.27–7.22 (m, 3H); 7.15 (dt, J = 7.6, 1.3 Hz, 1H), 7.03 (d, J = 8.0 Hz, 2H), 6.87 (dd, J = 7.8, 1.4 Hz, 1H), 6.73–6.70 (m, 2H), 5.58 (t, J = 4.5 Hz, 1H), 4.55 (d, J = 4.5 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.4 (C), 138.7 (C), 138.1 (C), 136.2 (C), 135.6 (C), 131.0 (C), 129.1 (2 × CH), 128.5 (2 × CH), 128.2 (CH), 128.0 (2 × CH), 127.57 (CH), 127.55 (2 × CH), 126.6 (CH), 126.0 (CH), 121.6 (CH), 45.5 (CH_2), 21.3 (CH_3); IR (ATR) ν_{max} 3066, 2920, 2849, 1634, 1493, 1478 cm^{-1}; MS (EI) m/z 361 $[M]^+$ (12), 206 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{22}H_{19}O_2NS$ $[M]^+$ 361.1131, found 361.1123.

4 P. Kothandaraman, S. J. Foo and P. W. H. Chan, *J. Org. Chem*. 2009, **74**, 5947–5952.

4-(2-Thienyl)-1-tosyl-1,2-dihydroquinoline (11b). Following the general procedure, the reaction of **5** (0.151 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), tri(2-thienyl)indium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **11b** as an pale yellow solid (0.149 g, 98%) after purification by column chromatography (20% EtOAc/hexanes); mp: 157–159 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 7.9 Hz, 1H), 7.39–7.33 (m, 1H), 7.30 (d J = 8.3 Hz, 2H), 7.21–7.18 (m, 3H), 7.01 (d, J = 8.0 Hz, 2H), 6.93 (dd, J = 5.1, 3.5 Hz, 1H), 6.55 (dd, J = 3.5. 1.0 Hz, 1H), 5.68 (t, J = 4.6 Hz, 1H), 4.49 (d, J = 4.6 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.5 (C), 139.6 (C), 135.9 (C), 135.6 (C), 131.6 (C), 130.4 (C), 129.1 (2 × CH), 128.6 (CH), 127.6 (CH), 127.3 (2 × CH), 126.7 (2 × CH), 126.5 (CH), 125.8 (CH), 125.0 (CH), 122.8 (CH), 45.2 (CH_2), 21.4 (CH_3); IR (ATR) ν_{max} 3062, 2847, 1597, 1483, 1449 cm^{-1}; MS (EI) m/z 367 $[M]^+$ (9), 212 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{20}H_{17}O_2NS_2$ $[M]^+$ 367.0695, found 367.0691.

4-Phenylethynyl-1-tosyl-1,2-dihydroquinoline (11c). Following the general procedure, the reaction of **5** (0.151 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), triphenylethynylindium (0.291 mmol) and $Pd(dppf)Cl_2$ (15.4 mg, 0.021 mmol) afforded **11c** as an orange solid (0.125 g, 78%) after purification by column chromatography (10% EtOAc/hexanes); mp: 93–94 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.9, 1.2 Hz, 1H), 7.52 (dd J = 7.5, 1.7 Hz, 1H), 7.44–7.39 (m, 2H), 7.36–7.26 (m, 7H), 7.11 (d, J = 8.1 Hz, 2H), 5.93 (t, J = 4.6 Hz, 1H), 4.50 (d, J = 4.6 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.8 (C), 135.6 (C), 134.8 (C), 131.5 (2 × CH), 129.2 (2 × CH), 128.8 (CH), 128.8 (CH), 128.7 (C), 128.6 (CH), 128.4 (2 × CH), 127.3 (2 × CH), 127.1 (CH), 126.9 (CH), 125.6 (CH), 122.7 (C), 120.4 (C), 91.5 (C), 84.6 (C), 45.5 (CH_2), 21.5 (CH_3); IR (ATR) ν_{max} 3061, 2921, 1596, 1485, 145 cm^{-1}; MS (EI) m/z 385 $[M]^+$ (5), 230 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{24}H_{19}O_2NS$ $[M]^+$ 385.1131, found 385.1133.

4-Butyl-1-tosyl-1,2-dihydroquinoline (11d). Following the general procedure, the reaction of **5** (0.151 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), tributylindium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **11d** as a white solid (0.105 mg, 74%) after purification by column chromatography (10% EtOAc/hexanes); mp: 65–67 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (dd, J = 7.9, 1.4 Hz, 1H), 7.33–7.26 (m, 3H), 7.22 (dd, J = 7.6, 1.4 Hz, 1H), 7.14 (dd, J = 7.6, 1.6 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 5.36 (t, J = 4.3 Hz, 1H), 4.38 (d, J = 4.3 Hz, 2H), 2.33 (s, 3H), 2.04–1.99 (m, 2H), 1.23–1.10 (m, 2H), 0.91–0.81 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.0 (C), 136.7 (C), 135.9 (C), 135.4 (C), 130.9 (C), 129.0 (2 × CH), 127.6 (CH), 127.4 (2 × CH), 126.5 (CH), 123.1 (CH), 119.3 (CH), 45.3 (CH_2), 31.1 (CH_2), 30.0 (CH_2), 22.7 (CH_2), 21.4 (CH_3), 14.0 (CH_3); IR (ATR) ν_{max} 2069, 2958, 2932, 2861, 1598, 1485, 1450, 1185 cm^{-1}; MS (EI) m/z 341 $[M]^+$ (20), 186 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{20}H_{23}O_2NS$ $[M]^+$ 341.1444, found 341.1428.

4-Methyl-1-tosyl-1,2-dihydroquinoline (11e).[5] Following the general procedure, the reaction of **5** (0.151 g, 0.415 mmol), $InBr_3$ (7.4 mg, 0.021 mmol), trimethylindium (0.291 mmol) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afford **11e** as an pale yellow solid (0.105 g, 85%) after purification by column chromatography (20% EtOAc/hexanes); mp: 108–110 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dd, J = 7.8, 1.4 Hz, 1H), 7.33–7.21 (m, 4H), 7.11 (dd J = 7.6, 1.6 Hz, 1H), 7.06 (d, J = 8.1 Hz, 2H), 5.33-5.30 (m, 1H), 4.34 (dd, J = 4.2, 1.7 Hz, 2H), 2.33 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.1 (C), 136.2 (C), 135.2 (C), 131.6 (C), 131.4 (C), 128.8 (2 × CH), 127.8 (CH), 127.4 (2 × CH), 127.2 (CH), 126.7 (CH), 123.3 (CH), 120.3 (CH), 45.3 (CH_2), 21.4 (CH_3), 17.7 (CH_3); IR (ATR) ν_{max} 2847, 1595, 1484, 1452 cm^{-1}; MS (EI) m/z 299 $[M]^+$ (19), 144 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{17}H_{17}O_2NS$ $[M]^+$ 299.0975, found 299.0971.

5 C. Theeraladanon, M. Ariswa, A. Nishida and M. Nakagama, *Tetrahedron* 2004, **60**, 3017–3035.

5,7-Dimethoxy-4-phenyl-1-tosyl-1,2-dihydroquinoline (12a). Following the general procedure, the reaction of **6** (0.176 g, 0.415 mmol), InI_3 (10.4 mg, 0.021 mmol), triphenylindium (0.207 mmol, 0.5 equiv) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **12a** as an orange solid (0.131 g, 75%) after purification by column chromatography (20% EtOAc/hexanes); mp: 71–73 °C (EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (d, J = 8.3 Hz, 2H), 7.12-7.09 (m, 4H), 6.96 (d, J = 7.5 Hz, 2H), 6.96 (dd, J = 7.6, 1.9 Hz, 2H), 6.31 (d, J = 2.5 Hz, 1H), 5.45 (t, J = 5.0 Hz, 1H), 4.41 (d, J = 5.0 Hz, 2H), 3.90 (s, 3H), 3.29 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1 (C), 157.0 (C), 143.3 (C), 140.7 (C), 139.0 (C), 137.2 (C), 136.5 (C), 129.1 (2 × CH), 127.4 (2 × CH), 126.9 (2 × CH), 126.4 (2 × CH), 126.2 (CH), 120.1 (CH), 113.5 (C), 103.4 (CH), 98.6 (CH), 55.7 (CH_3), 55.2 (CH_3), 45.6 (CH_2), 21.3 (CH_3); IR (ATR) ν_{max} 2937, 2842, 1603, 1566 cm^{-1}; MS (EI) m/z 421 $[M]^+$ (35), 266 $[M - C_7H_7SO_2]^+$ (100); HRMS (EI) calcd for $C_{24}H_{23}O_4NS$ $[M]^+$ 421.1342, found 421.1324.

5,7-Dimethoxy-4-(2-thienyl)-1-tosyl-1,2-dihydroquinoline (12b). Following the general procedure, **12b** was prepared from **6** (0.176 g, 0.415 mmol), InI_3 (10.4 mg, 0.021 mmol), tri(2-thienyl)indium (0.207 mmol, 0.5 equiv) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol). After purification by column chromatography (20% EtOAc/hexanes) **12b** was obtained as an orange oil (97.9 mg, 55%); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 (d, J = 8.3 Hz, 2H), 7.06 (d, J = 2.4 Hz, 1H), 7.03 (dd, J = 5.1, 1.1 Hz, 1H), 6.98 (d, J = 8.1 Hz, 2H), 6.78 (dd, J = 5.1, 3.5 Hz, 1H), 6.34–6.32 (m, 2H), 5.55 (t, J = 5.2 Hz, 1H), 4.35 (d, J = 5.2 Hz, 2H), 3.90 (s, 3H), 3.43 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (C), 157.1 (C), 143.5 (C), 142.8 (C), 138.9 (C), 136.4 (C), 130.3 (C), 129.2 (2 × CH), 127.2 (2 × CH), 125.7 (CH), 124.2 (CH), 123.1 (CH), 121.0 (CH), 113.2 (C), 103.4 (CH), 98.6 (CH), 55.7 (CH_3), 55.4 (CH_3), 45.3 (CH_2), 21.4 (CH_3); IR (ATR) ν_{max} 2922, 2851, 1601, 1564 cm^{-1}; MS (EI) m/z 427 $[M]^+$ (25), 272 $[M - C_7H_8SO_2]^+$ (100); HRMS (EI) calcd for $C_{22}H_{21}O_4NS_2$ $[M]^+$ 427.0907, found 427.0901.

5,7-Dimethoxy-4-methyl-1-tosyl-1,2-dihydroquinoline (12e). Following the general procedure, the reaction of **6** (0.176 g, 0.415 mmol), InI_3 (10.4 mg, 0.021 mmol), trimethylindium (0.207 mmol, 0.5 equiv) and $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) afforded **12e** as an orange oil (100 mg, 67%) after purification by column chromatography (20% EtOAc/hexanes); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 (d, J = 8.3 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 6.94 (d, J = 2.5 Hz, 1H), 6.36 (d, J = 2.5 Hz, 1H), 5.10–5.06 (m, 1H), 4.16 (dd, J = 4.8, 1.4 Hz, 2H), 3.87 (s, 3H), 3.72 (s, 3H), 2.34 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.2 (C), 157.5 (C), 143.1 (C), 138.3 (C), 136.7 (C), 132.2 (C), 128.8 (2 × CH), 127.5 (2 × CH), 118.3 (CH), 115.0 (C), 103.6 (CH), 98.3 (CH), 55.6 (CH_3), 55.4 (CH_3), 45.2 (CH_2), 21.4 (CH_3), 20.9 (CH_3); IR (ATR) ν_{max} 2924, 2842, 1603, 1567, 1455, 1421, 1347, 1311, 1201, 1159, 1128, 1070 cm^{-1}; MS (EI) m/z 359 $[M]^+$ (36), 204 $[M - C_7H_7SO_2]^+$ (100), 204 $[M - C_8H_{10}SO_2]^+$ (46); HRMS (EI) calcd for $C_{19}H_{21}O_4NS$ $[M]^+$ 359.1186, found 359.1170.

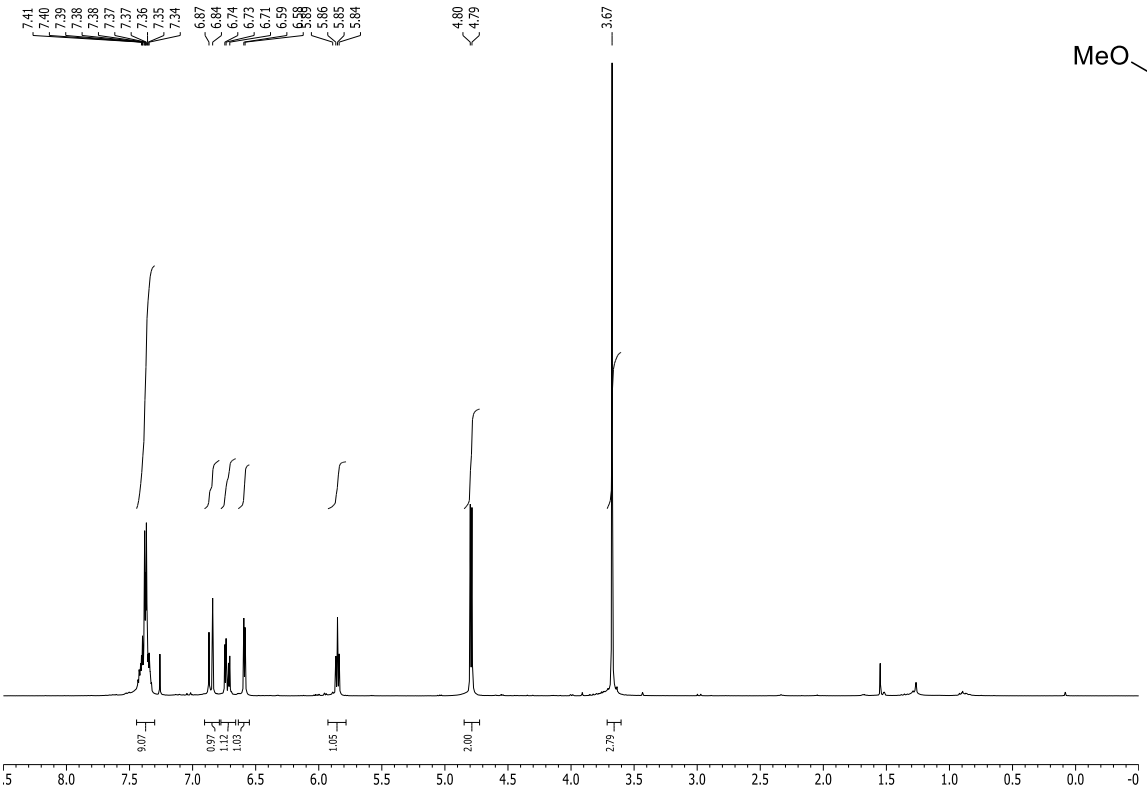
S**equential IMHA-Negishi coupling reaction (Table 2, entry 8).** In a Schlenk tube filled with argon, a solution of $InCl_3$ (0.021 mmol) and 4-methoxyphenyl-(3-bromoprop-2-ynyl)ether (**1a**, 0.415 mmol) in toluene (6 mL) were heated at 60 ºC until the starting material had been consumed (TLC). Then, $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) and a freshly prepared solution of PhZnCl (4.0 equiv, 1.66 mmol, ~0.22 M in THF) were added and the mixture heated at 80 °C until the starting material had been consumed (TLC). The mixture was allowed to cool down to room temperature, quenched with saturated aqueous NH_4Cl (10 mL) and poured into a separating funnel. The product was extracted with Et_2O (3 × 10 mL) and the combined organic phases were washed with brine (15 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5% EtOAc/hexanes) to afford **3a** (39.6 mg, 40%) after concentration and high vacuum drying.

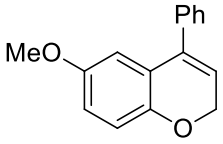
Sequential IMHA-Stille coupling reactions (Table 2, entry 9 and Table 3 entry 11). In a Schlenk tube filled with argon, InX_3 (0.021 mmol) and **1a** or **4** (0.021 mmol) in toluene (6 mL) were added. The solution was stirred at the corresponding temperature until the starting material

was consumed (TLC). $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol) and a solution of $PhSnBu_3$ (0.335 g, 0.913 mmol) in toluene (2 mL) were added and the reaction mixture heated at 100 °C for 48 h. The mixture was allowed to cool down to room temperature and the solvent was removed *in vacuo*. The residue was diluted with EtOAc (10 mL) and poured into a separating funnel with water (10 mL). The product was extracted with EtOAc (3 × 10 mL) and the combined organic phases were washed with saturated aqueous NaCl (15 mL), dried, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel to afford, after concentration and high vacuum drying, **3a** (38.5 mg, 40%) from **1a** or **10a** (61.8 mg, 38%) from **4**.

Sequential IMHA-Suzuki coupling reactions (Table 2, entry 10 and Table 3, entry 12). In a Schlenk tube filled with argon a solution of InX_3 (0.021 mmol) and **1a** or **4** (0.415 mmol) in toluene (6 mL) was prepared. The solution was heated at the corresponding reaction temperature until the starting material had been consumed (TLC). $Pd(PPh_3)_4$ (24.3 mg, 0.021 mmol), Na_2CO_3 (263.9 mg, 2.49 mmol), phenylboronic acid (111 mg, 0.913 mmol) and EtOH (3 mL) were added and the reaction mixture heated at 80 °C for 48 h. The mixture was allowed to cool down to room temperature and the solvent was removed *in vacuo*. The residue was diluted with EtOAc (20 mL) and poured into a separating funnel with water (20 mL). The product was extracted with EtOAc (2 × 20 mL) and the combined organic phases were washed with brine (30 mL). The organic phase was dried with $MgSO_4$, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (5% EtOAc/hexanes) to afford, after concentration and high vacuum drying, **3a** from **1a** (86.0 mg, 87%) or **10a** from **4** (0.130 g, 80%).

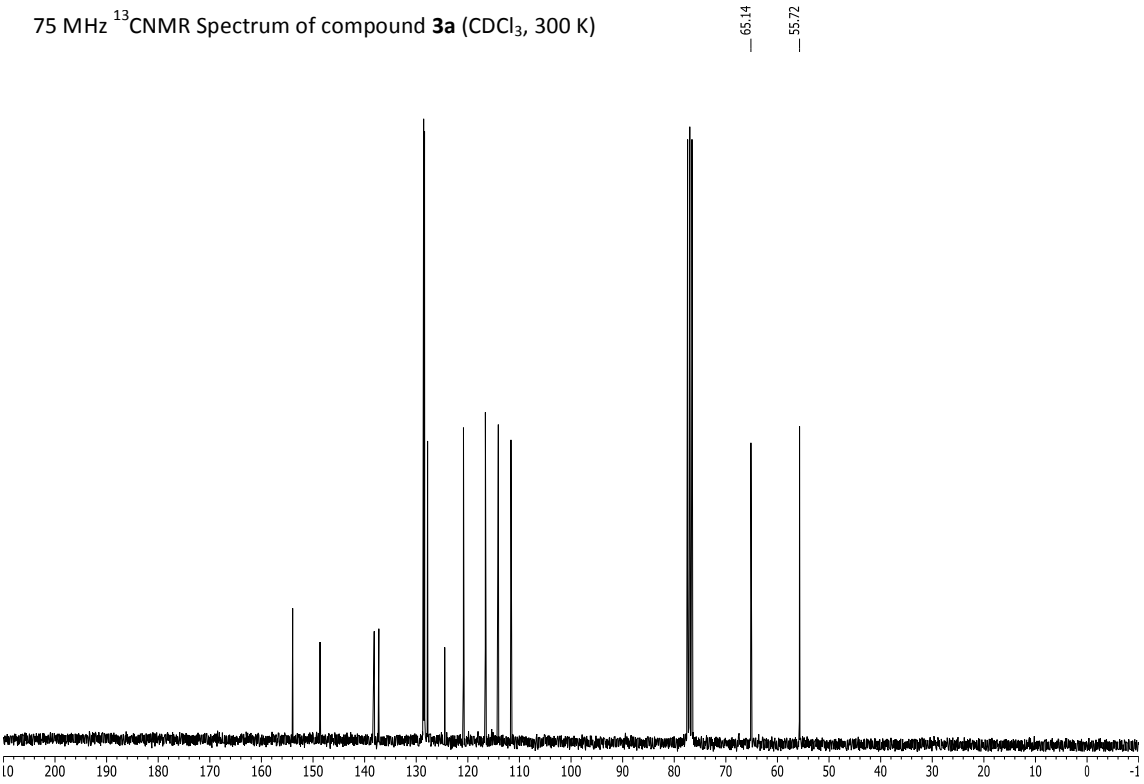
300 MHz ^{1}HNMR Spectrum of compound **3a** ($CDCl_3$, 300 K)



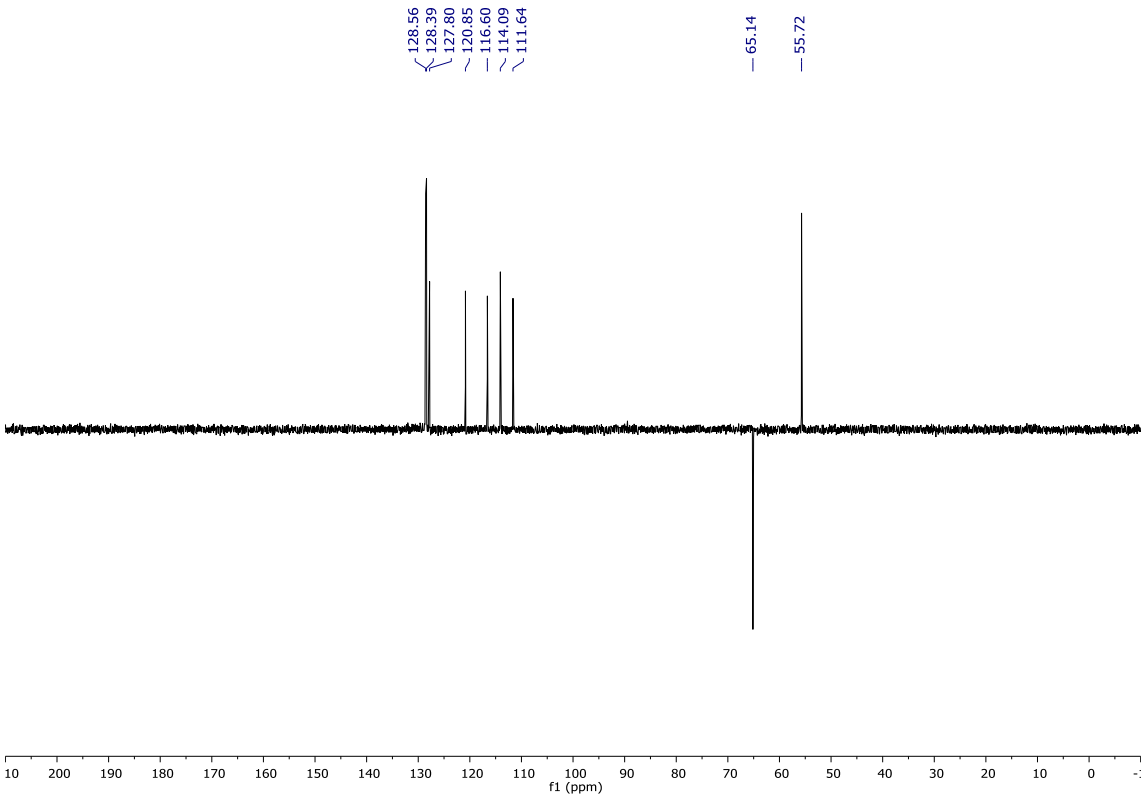


3a

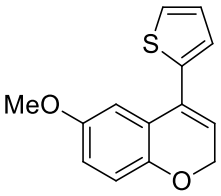
75 MHz ^{13}CNMR Spectrum of compound **3a** ($CDCl_3$, 300 K)



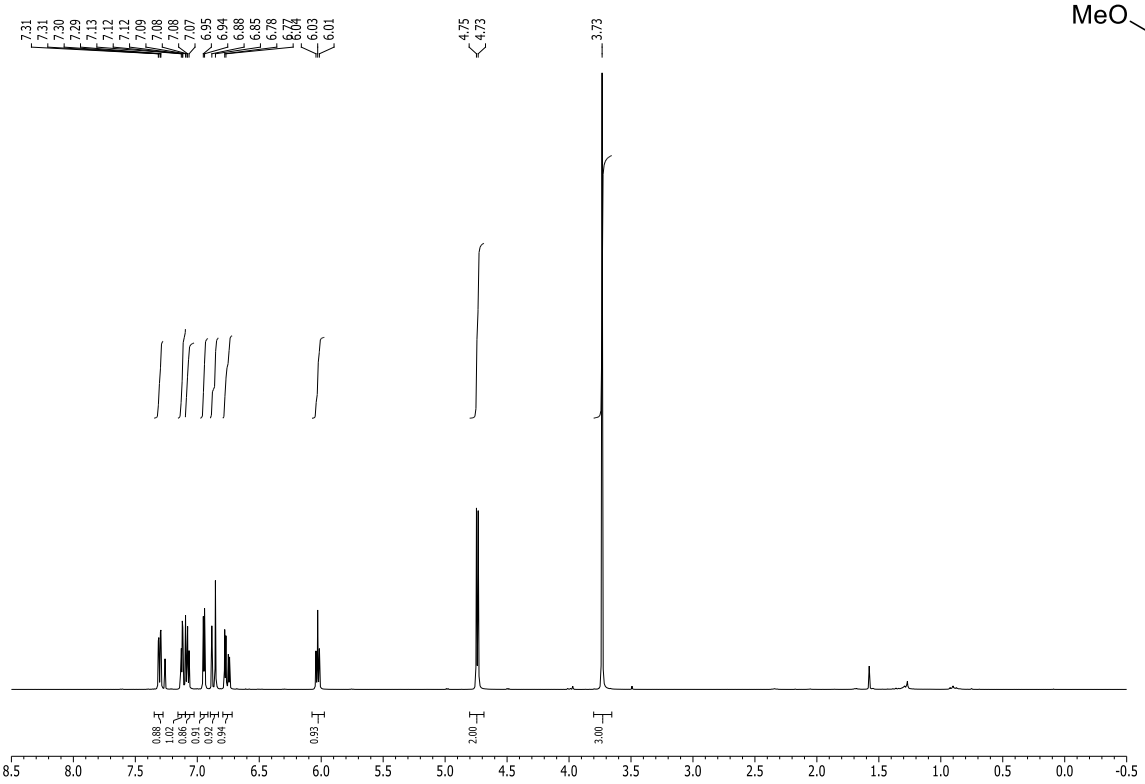
75 MHz DEPT-135 Spectrum of compound **3a** ($CDCl_3$, 300 K)



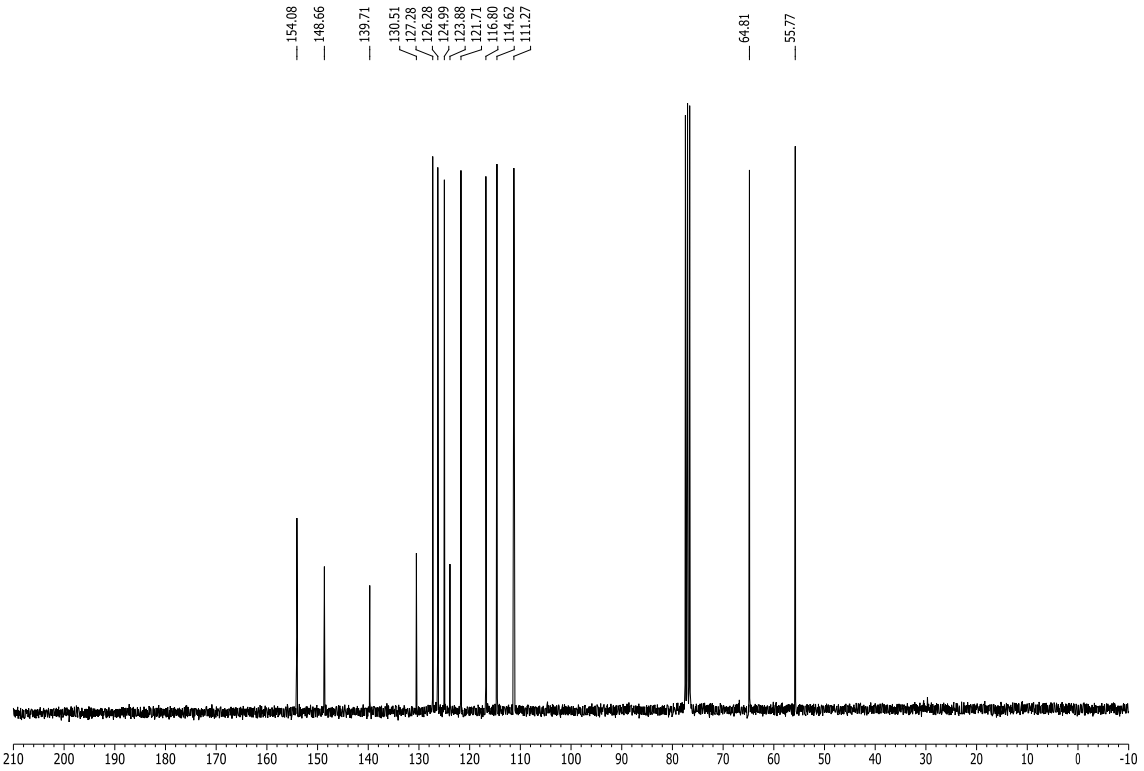
300 MHz ^{1}HNMR Spectrum of compound **3b** ($CDCl_3$, 300 K)



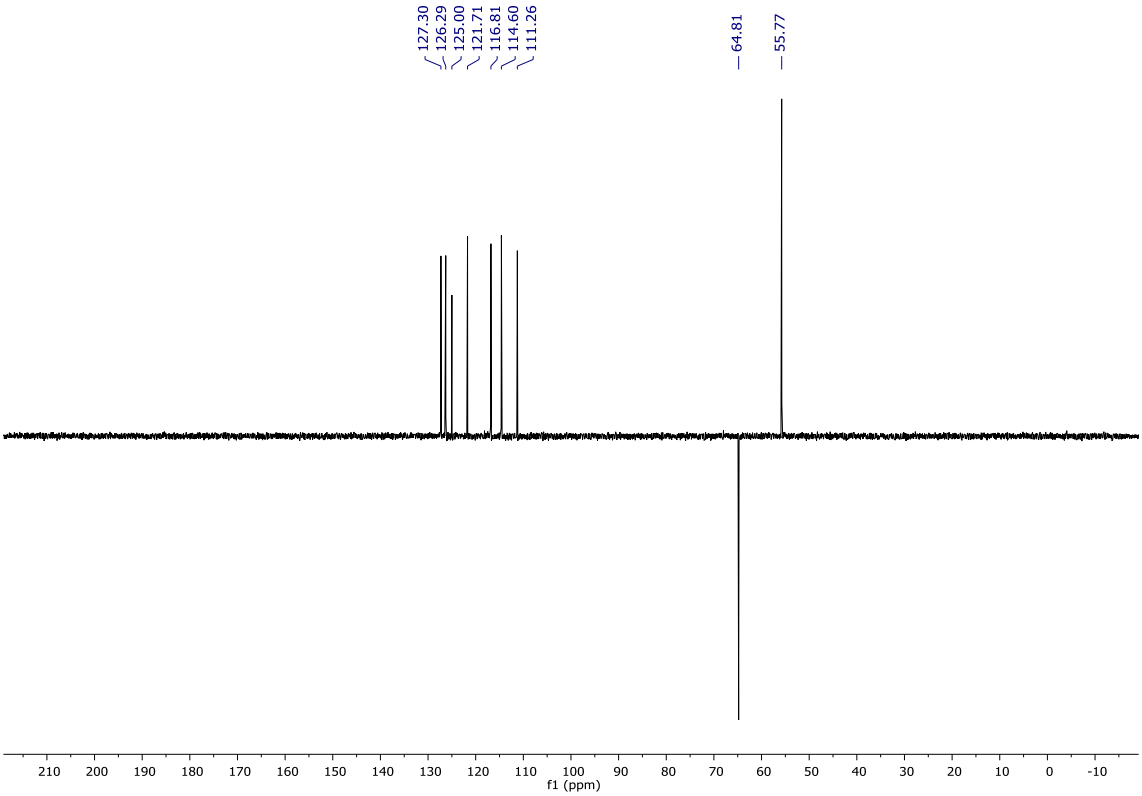
3b



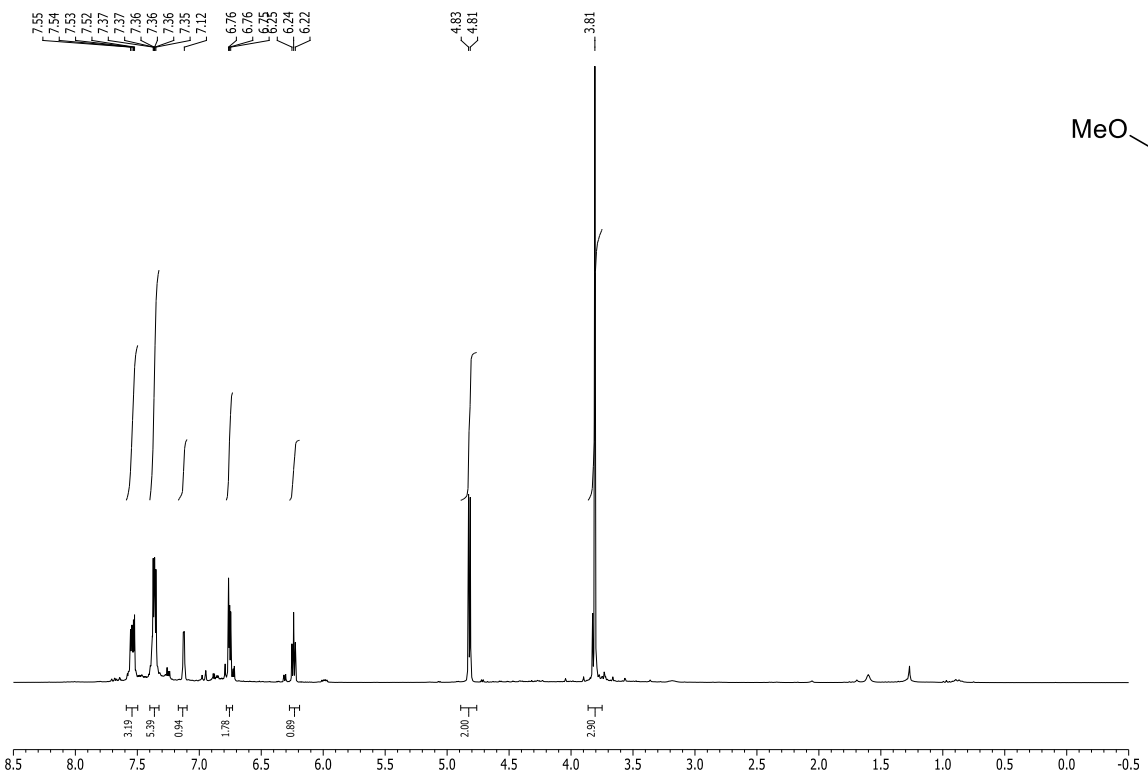
75 MHz ^{13}CNMR Spectrum of compound **3b** ($CDCl_3$, 300 K)

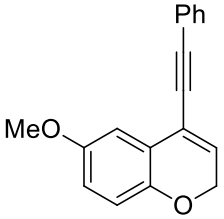


75 MHz DEPT-135 Spectrum of compound **3b** ($CDCl_3$, 300 K)



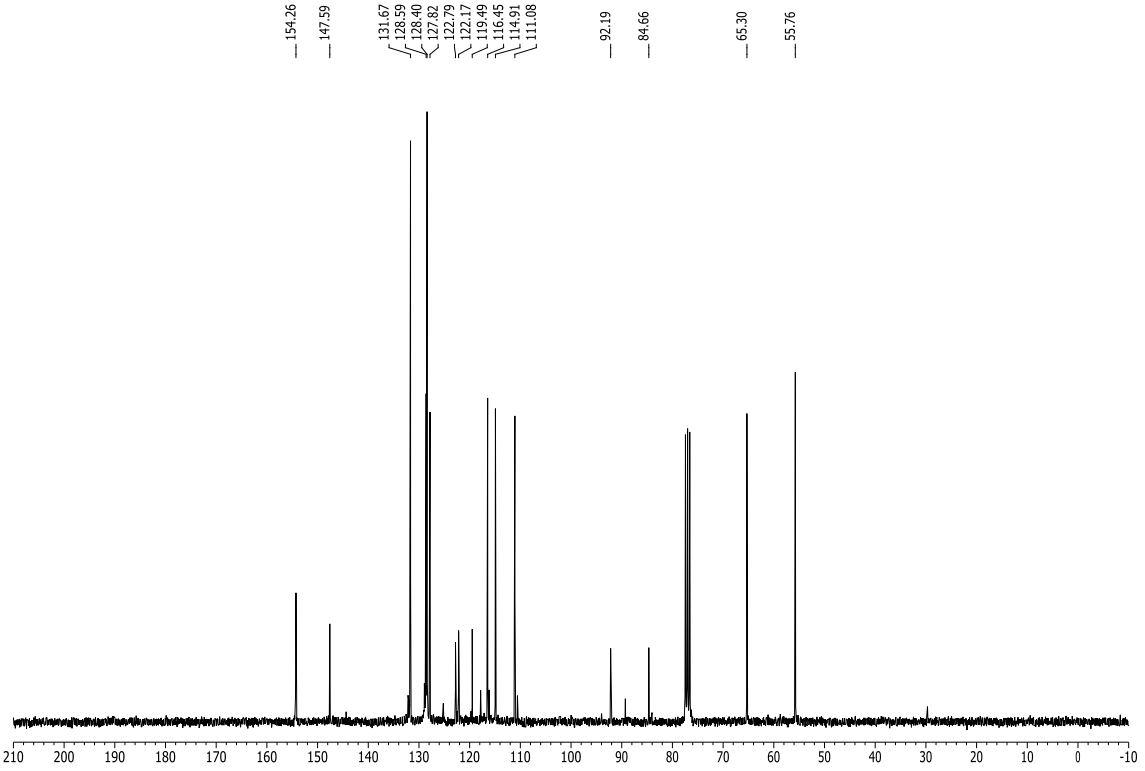
300 MHz ^{1}HNMR Spectrum of compound **3c** ($CDCl_3$, 300 K)



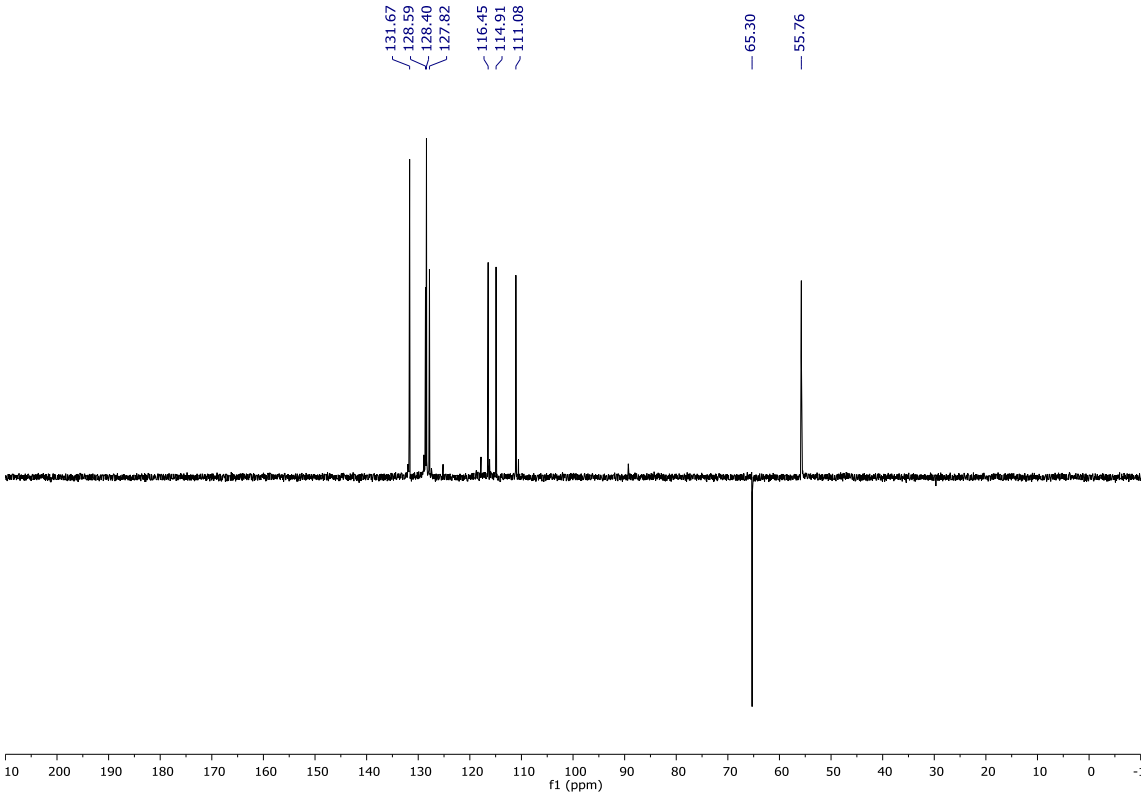


3c

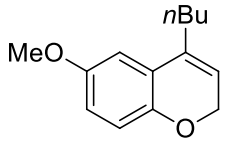
75 MHz ^{13}CNMR Spectrum of compound **3c** ($CDCl_3$, 300 K)



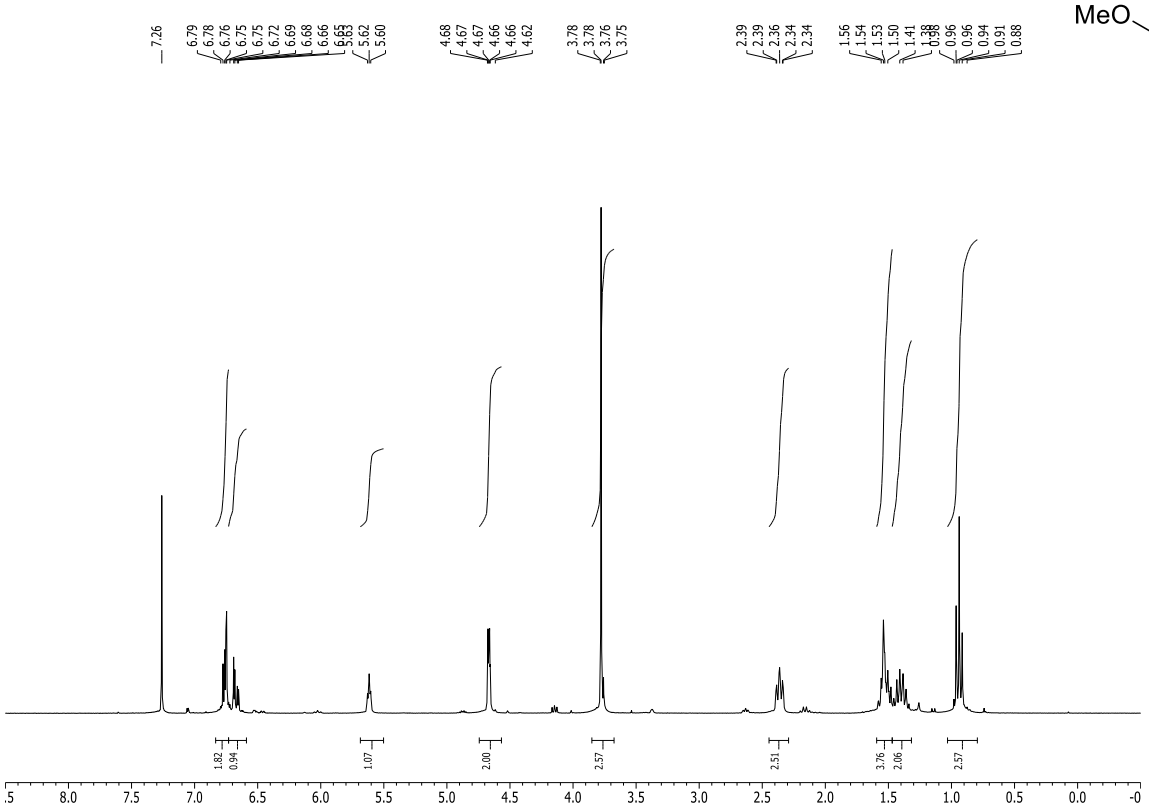
75 MHz DEPT-135 Spectrum of compound **3c** ($CDCl_3$, 300 K)



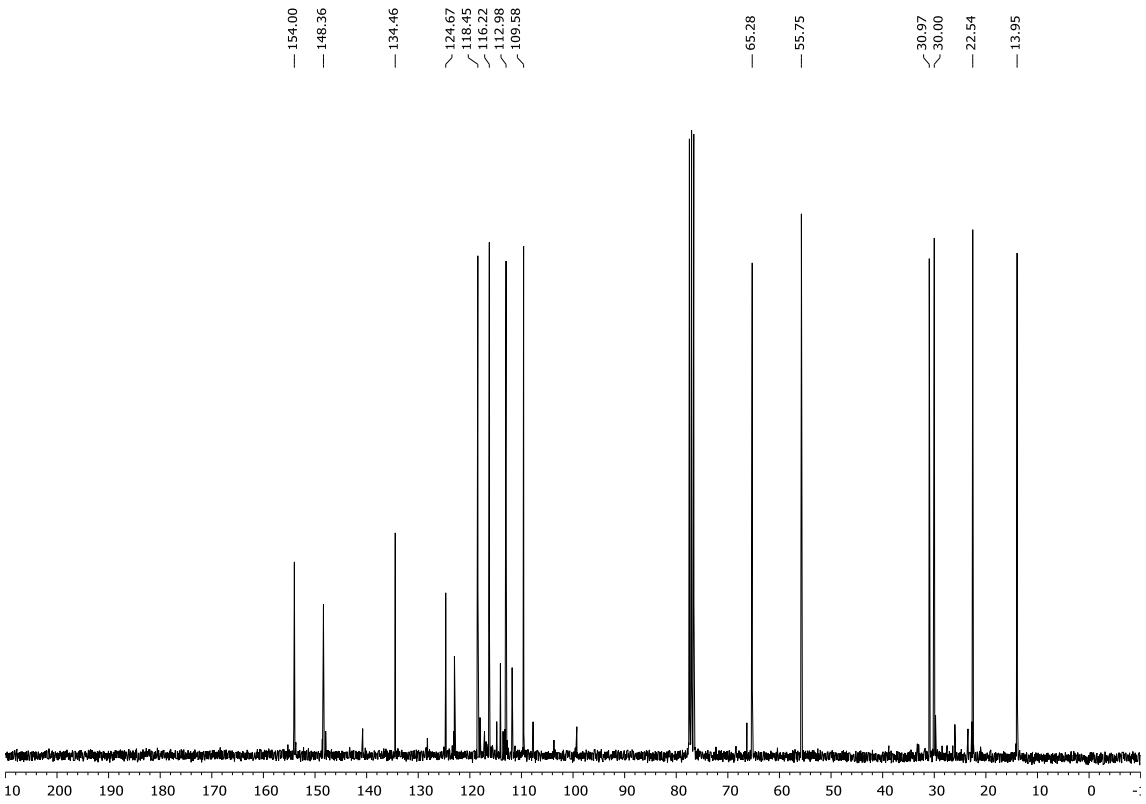
300 MHz ^{1}HNMR Spectrum of compound **3d** ($CDCl_3$, 300 K)



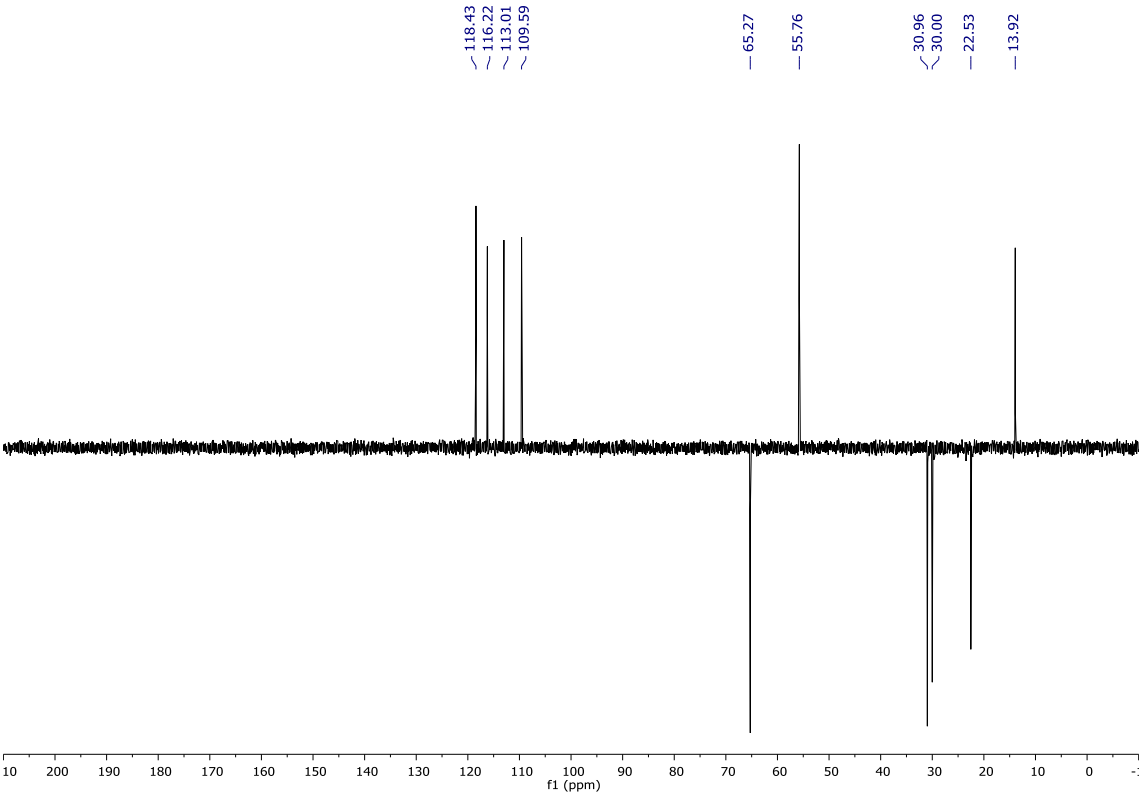
3d



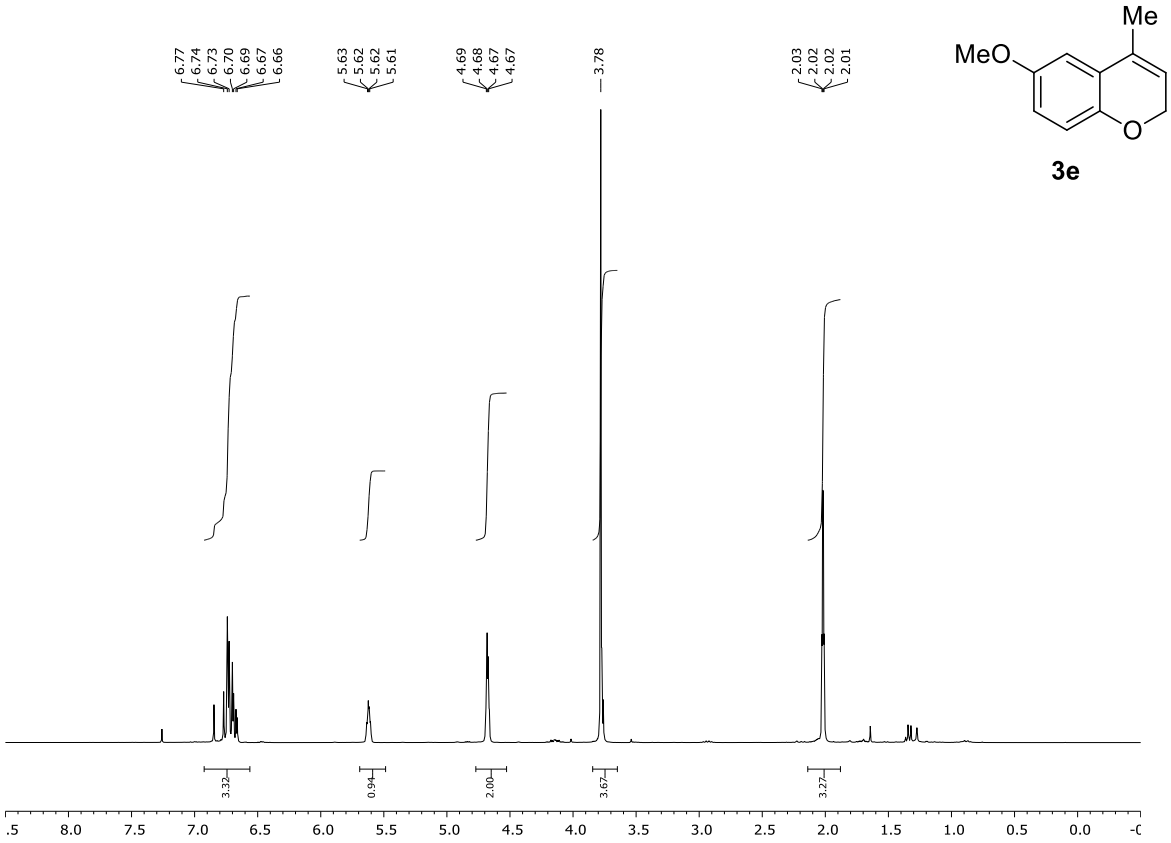
75 MHz ^{13}CNMR Spectrum of compound **3d** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **3d** ($CDCl_3$, 300 K)

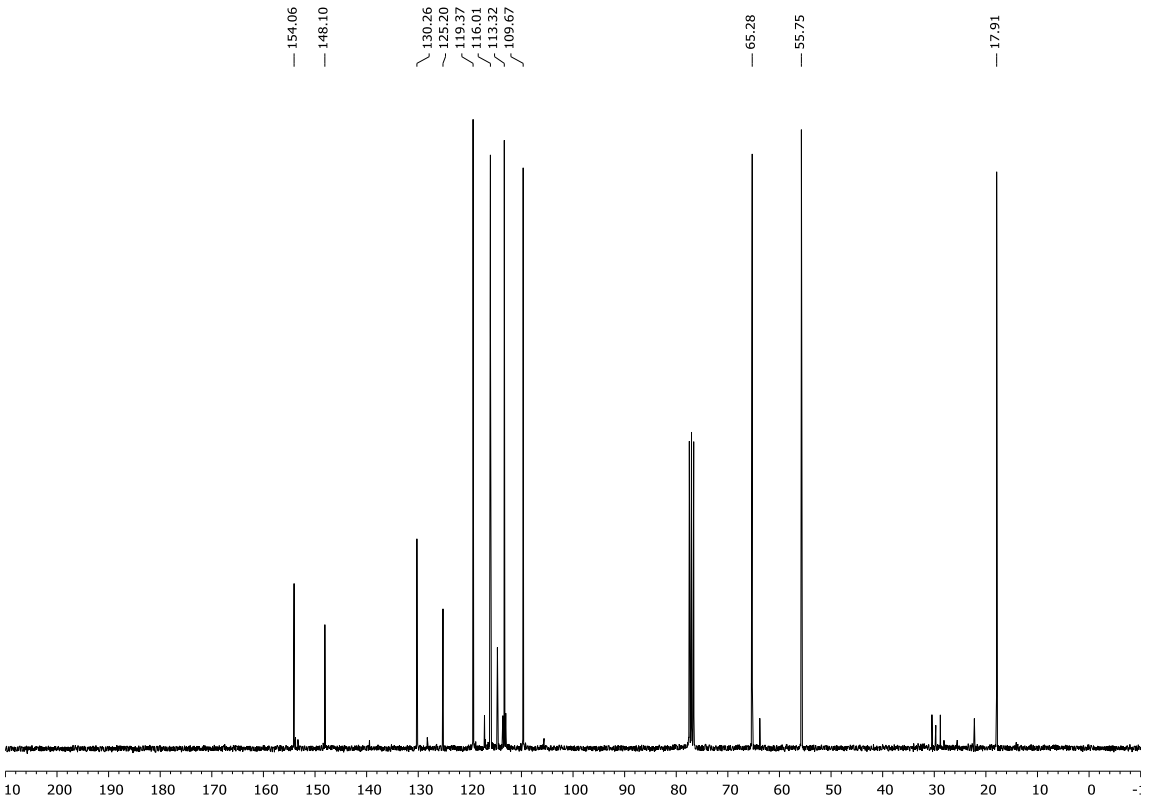


300 MHz ^{1}HNMR Spectrum of compound **3e** ($CDCl_3$, 300 K)

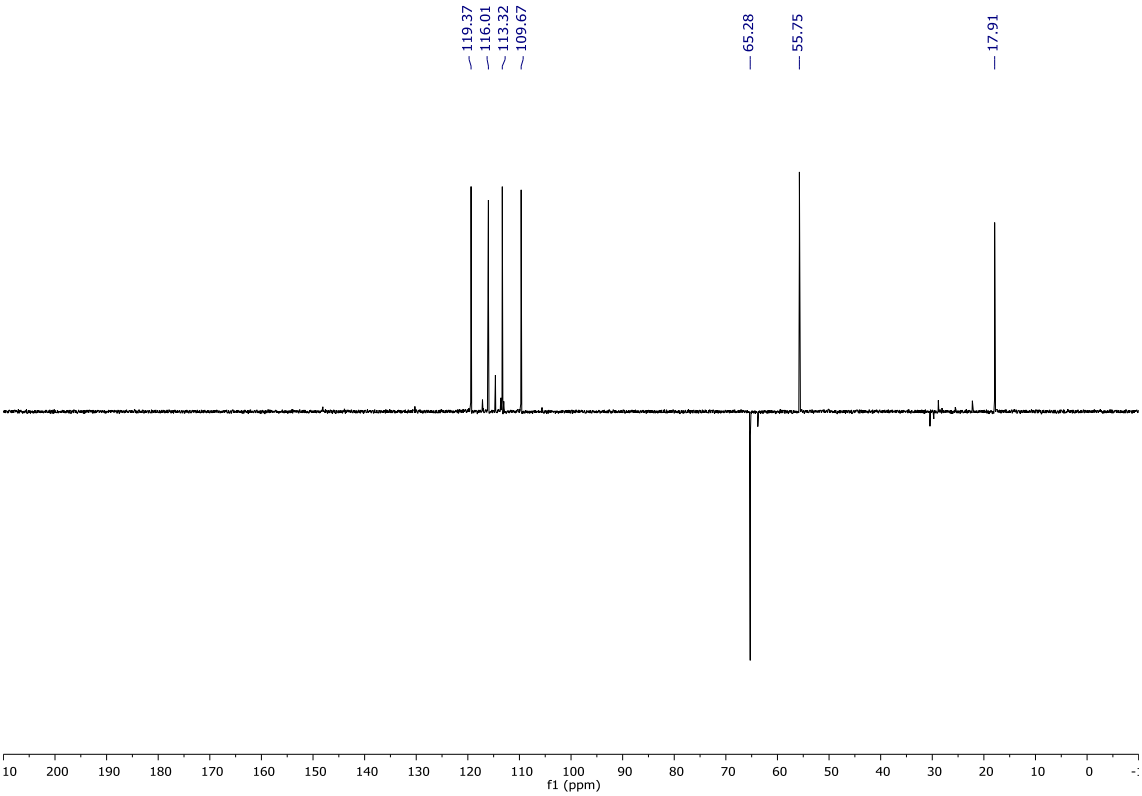


3e

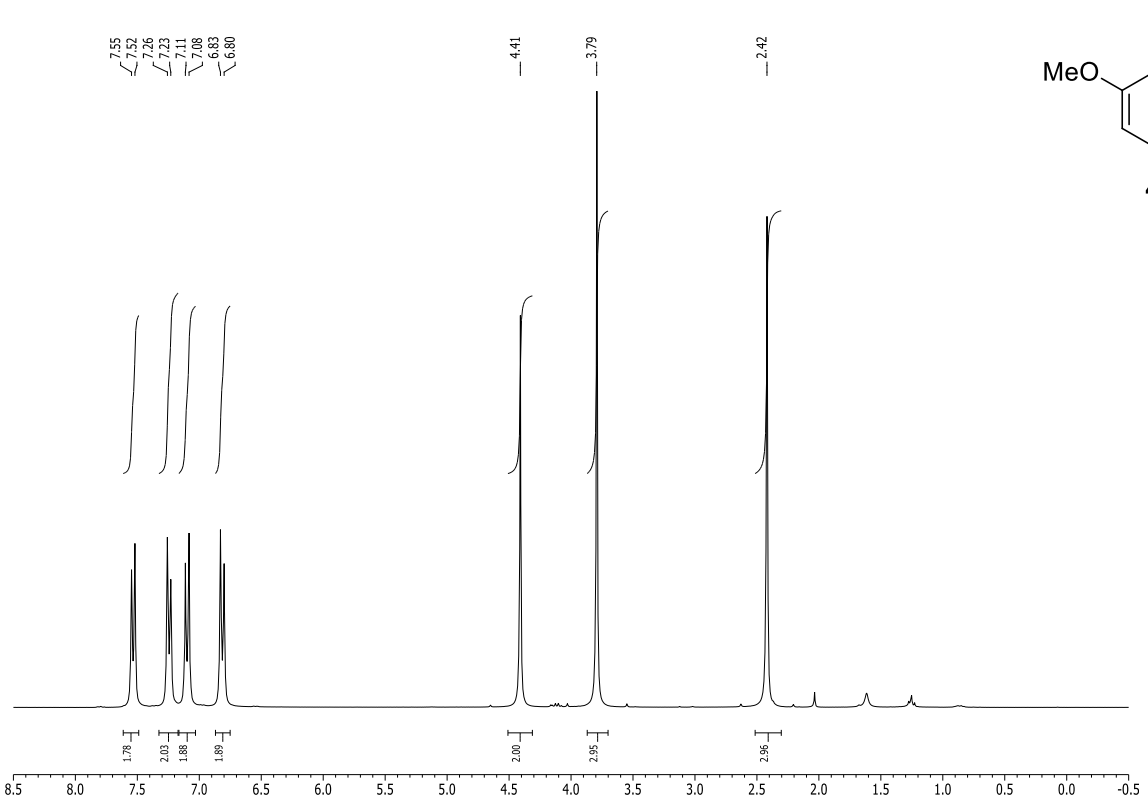
75 MHz ^{13}CNMR Spectrum of compound **3e** ($CDCl_3$, 300 K)

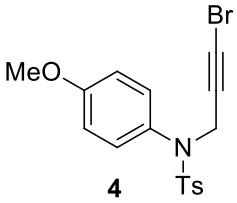


75 MHz DEPT-135 Spectrum of compound **3e** ($CDCl_3$, 300 K)



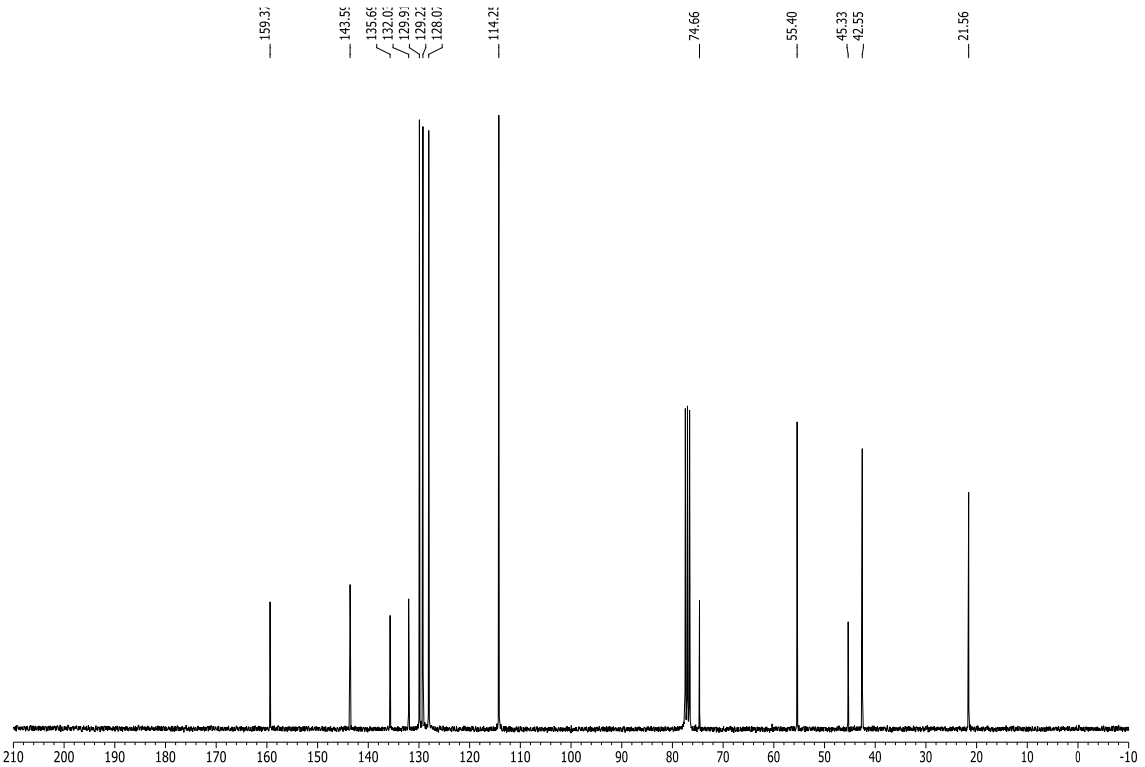
300 MHz ^{1}HNMR Spectrum of compound **4** ($CDCl_3$, 300 K)



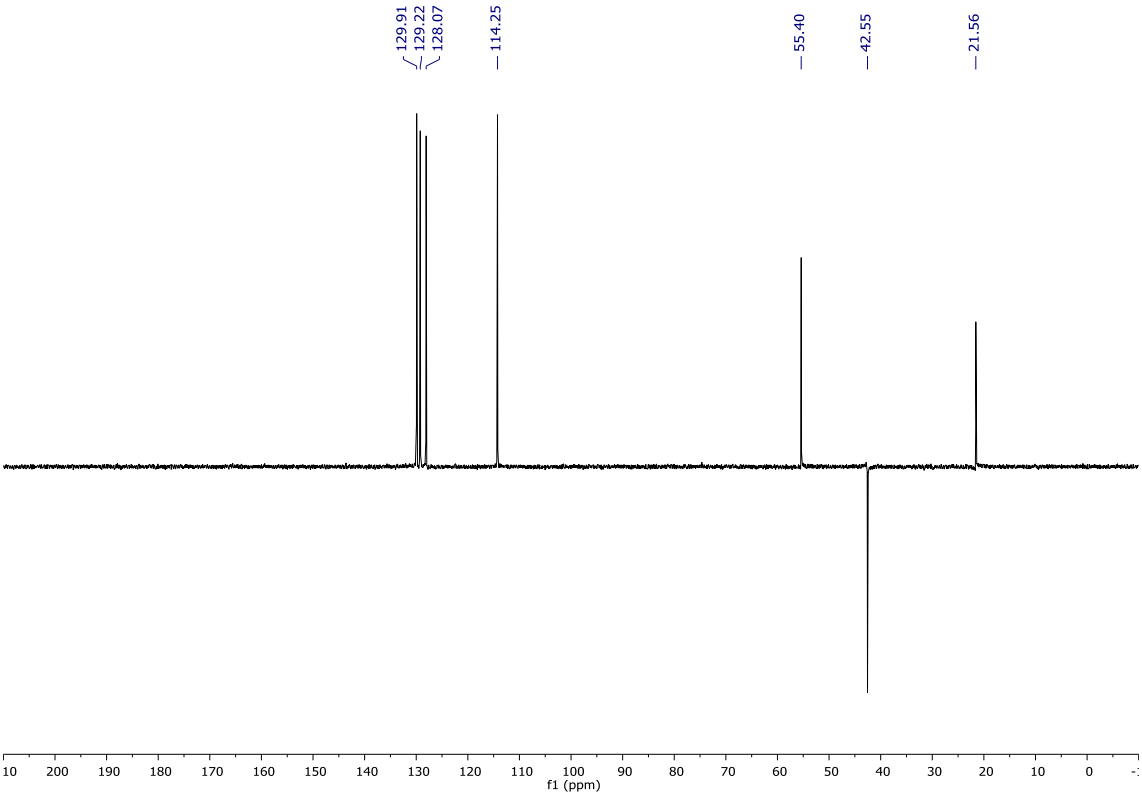


4

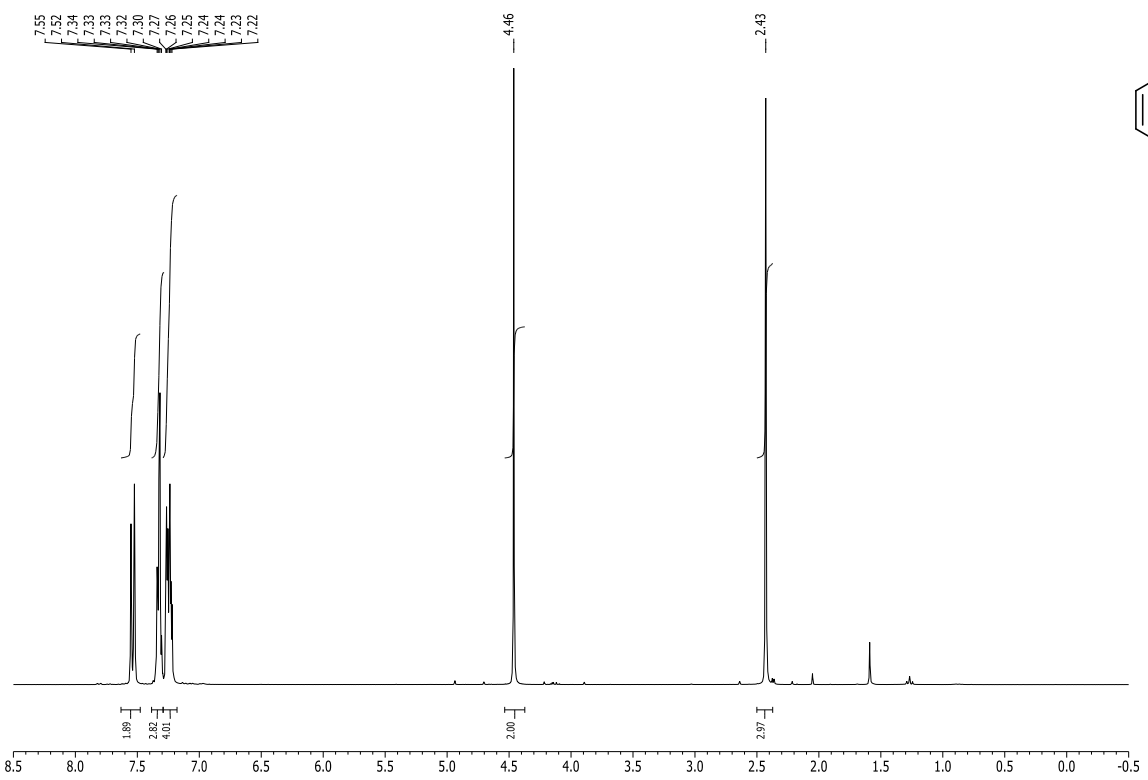
75 MHz ^{13}CNMR Spectrum of compound **4** ($CDCl_3$, 300 K)

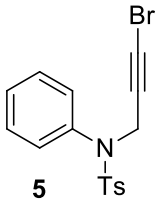


75 MHz DEPT-135 Spectrum of compound **4** ($CDCl_3$, 300 K)

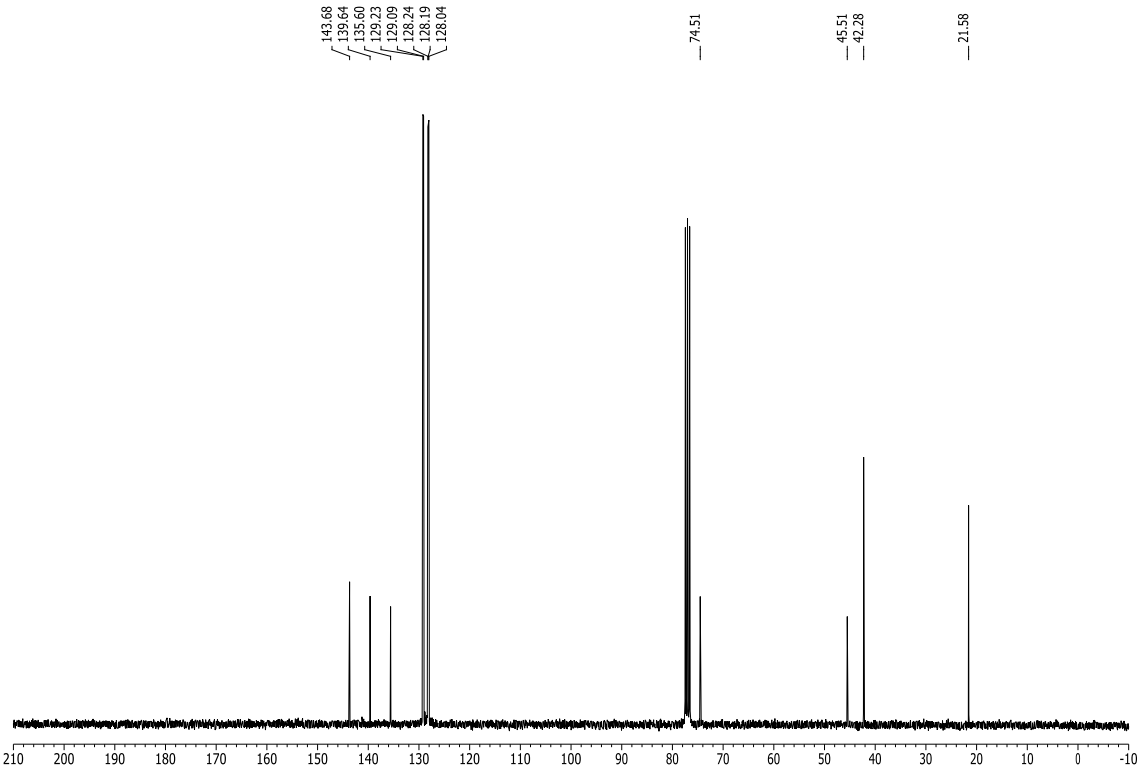


300 MHz ^{1}HNMR Spectrum of compound **5** ($CDCl_3$, 300 K)

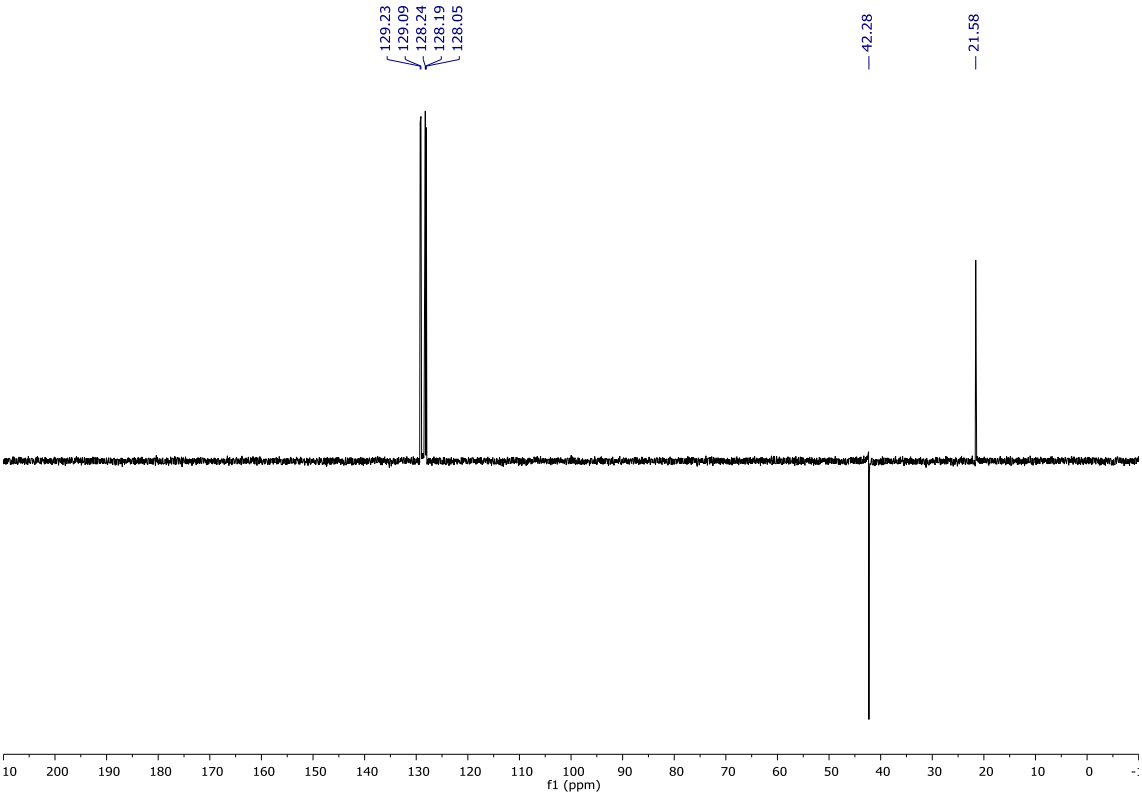




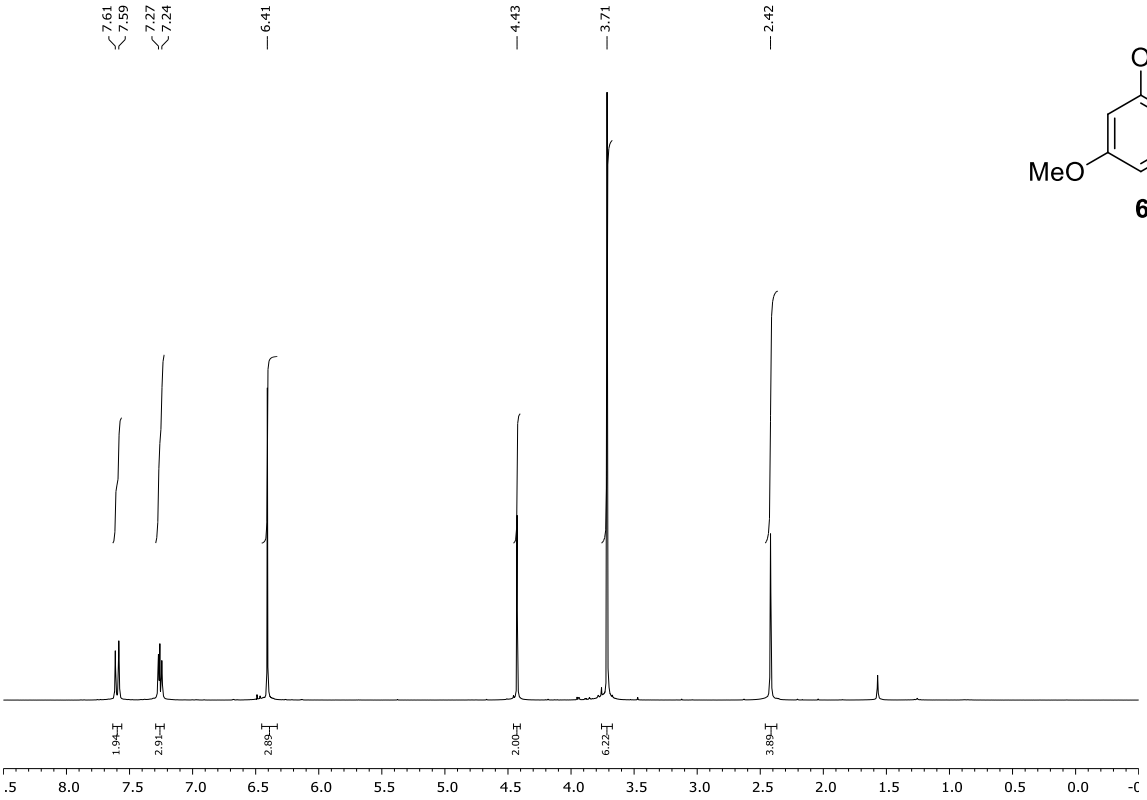
75 MHz ^{13}CNMR Spectrum of compound **5** ($CDCl_3$, 300 K)

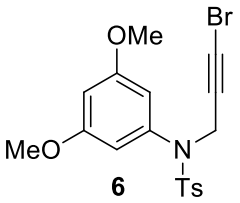


75 MHz DEPT-135 Spectrum of compound **5** ($CDCl_3$, 300 K)



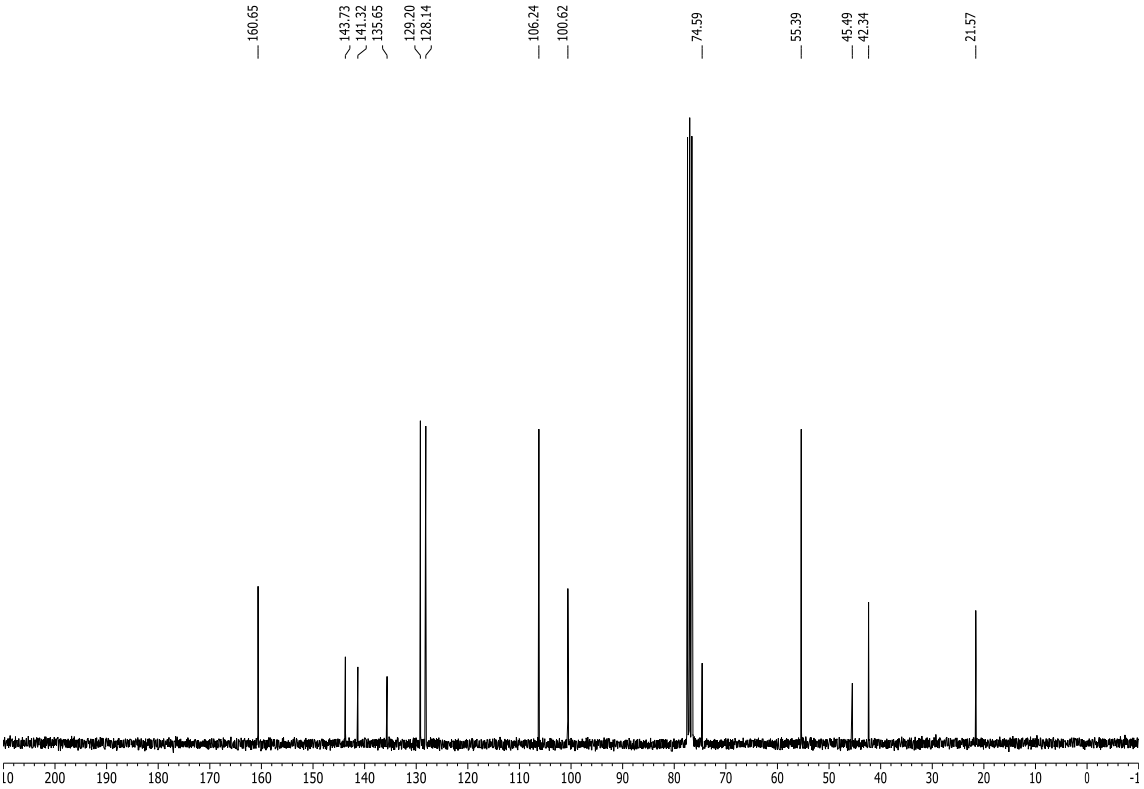
300 MHz ^{1}HNMR Spectrum of compound **6** ($CDCl_3$, 300 K)



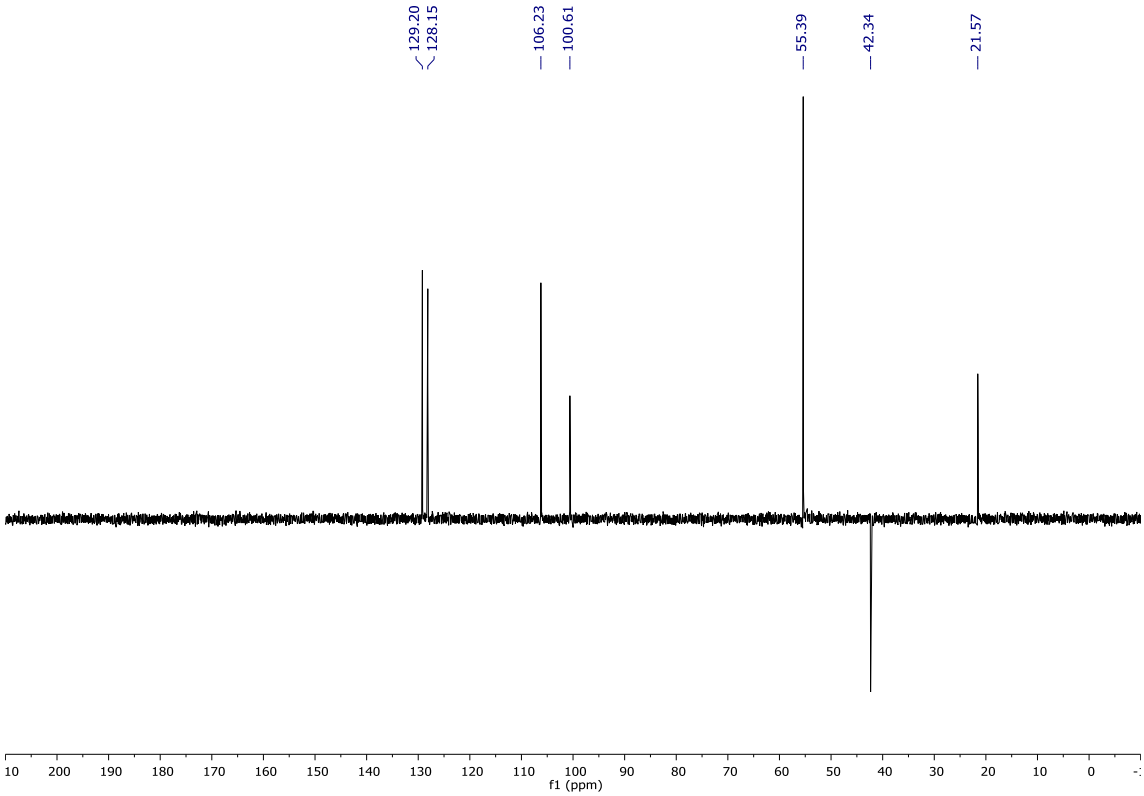


6

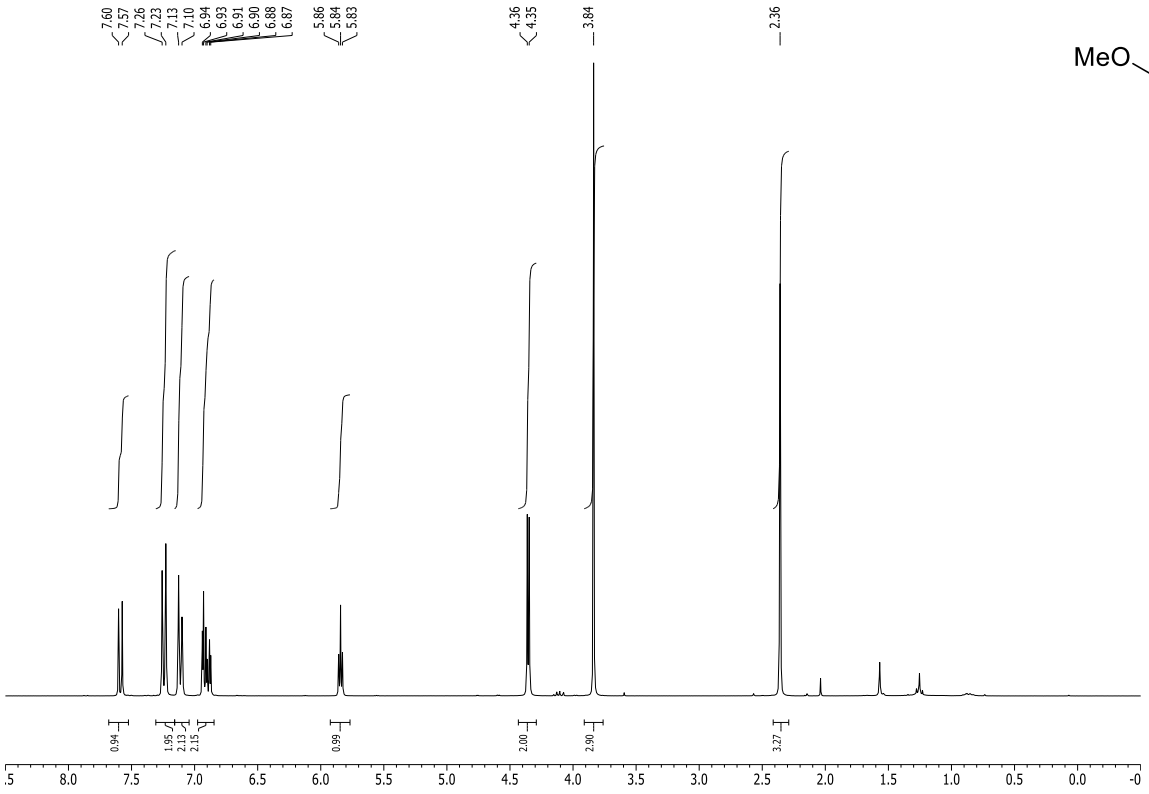
75 MHz ^{13}CNMR Spectrum of compound **6** ($CDCl_3$, 300 K)

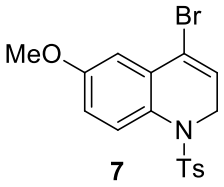


75 MHz DEPT-135 Spectrum of compound **6** ($CDCl_3$, 300 K)



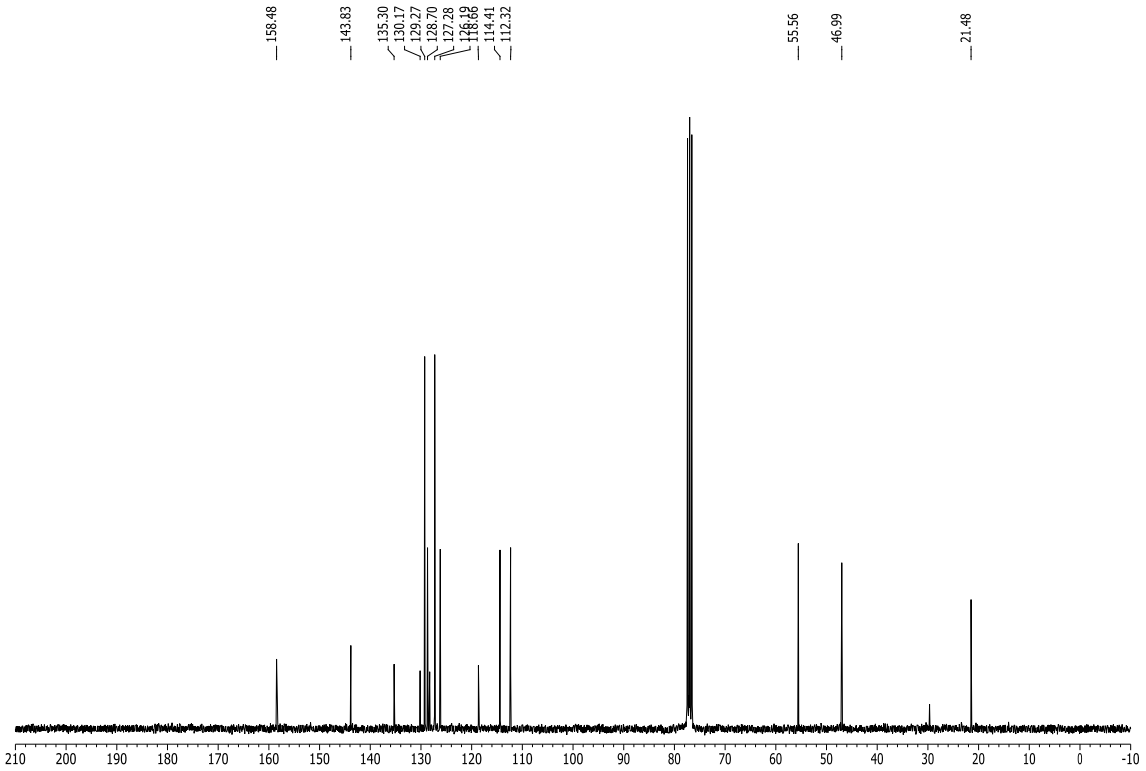
300 MHz ^{1}HNMR Spectrum of compound **7** ($CDCl_3$, 300 K)



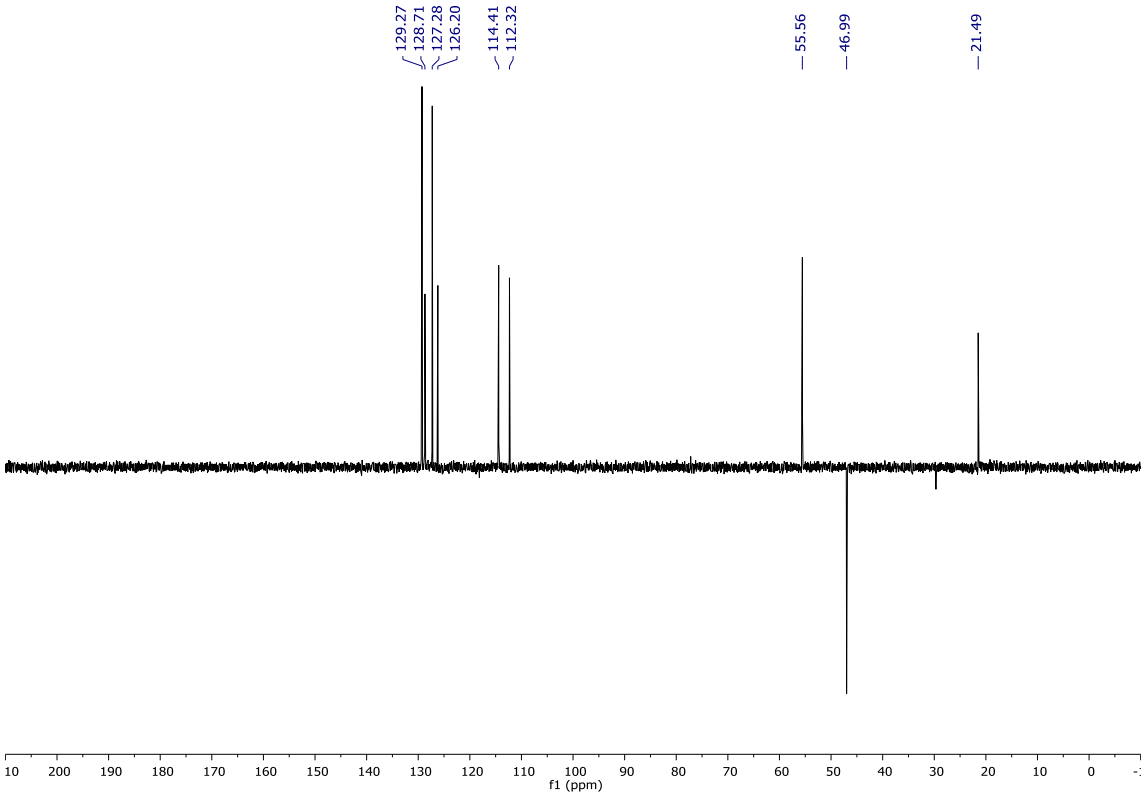


7

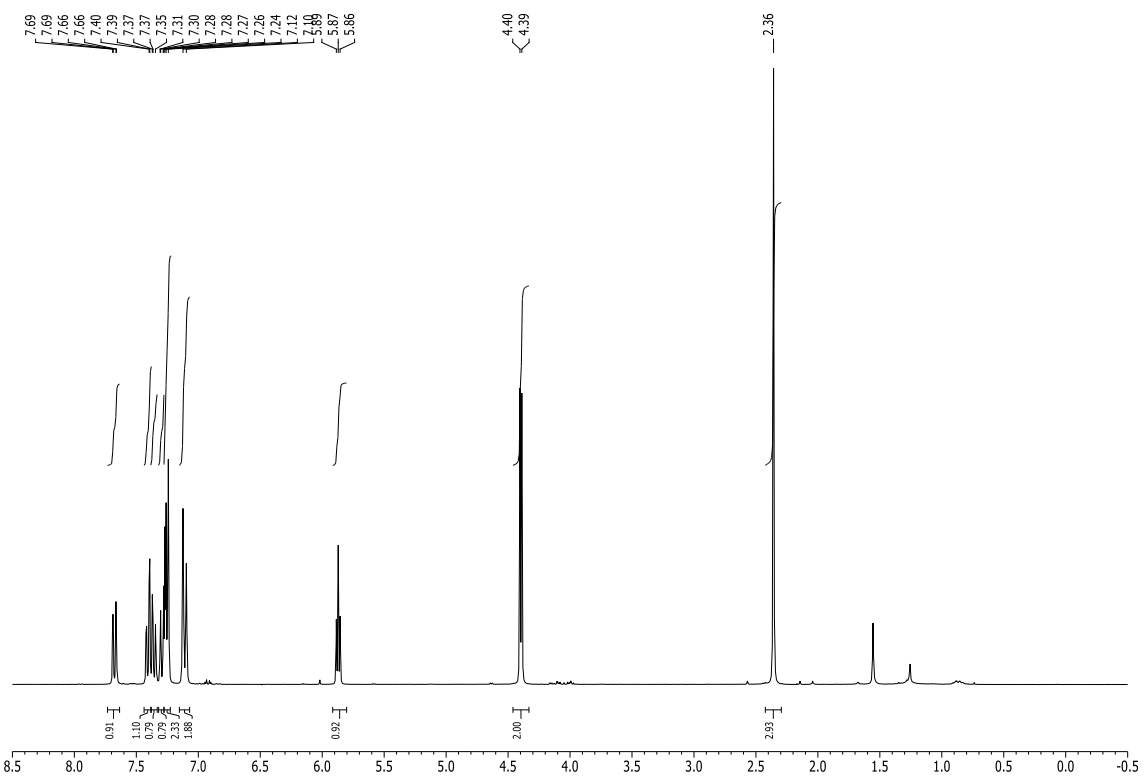
75 MHz ^{13}CNMR Spectrum of compound **7** ($CDCl_3$, 300 K)

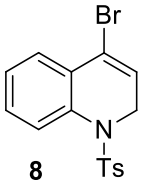


75 MHz DEPT-135 Spectrum of compound **7** ($CDCl_3$, 300 K)



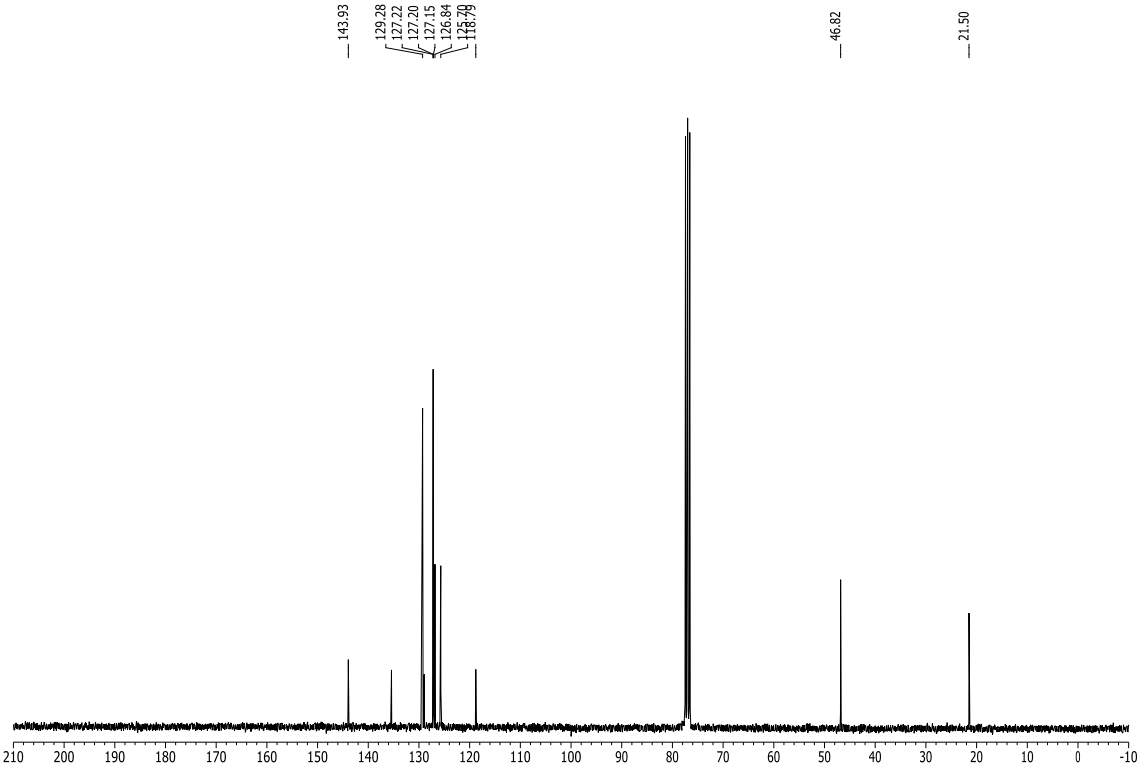
300 MHz ^{1}HNMR Spectrum of compound **8** ($CDCl_3$, 300 K)



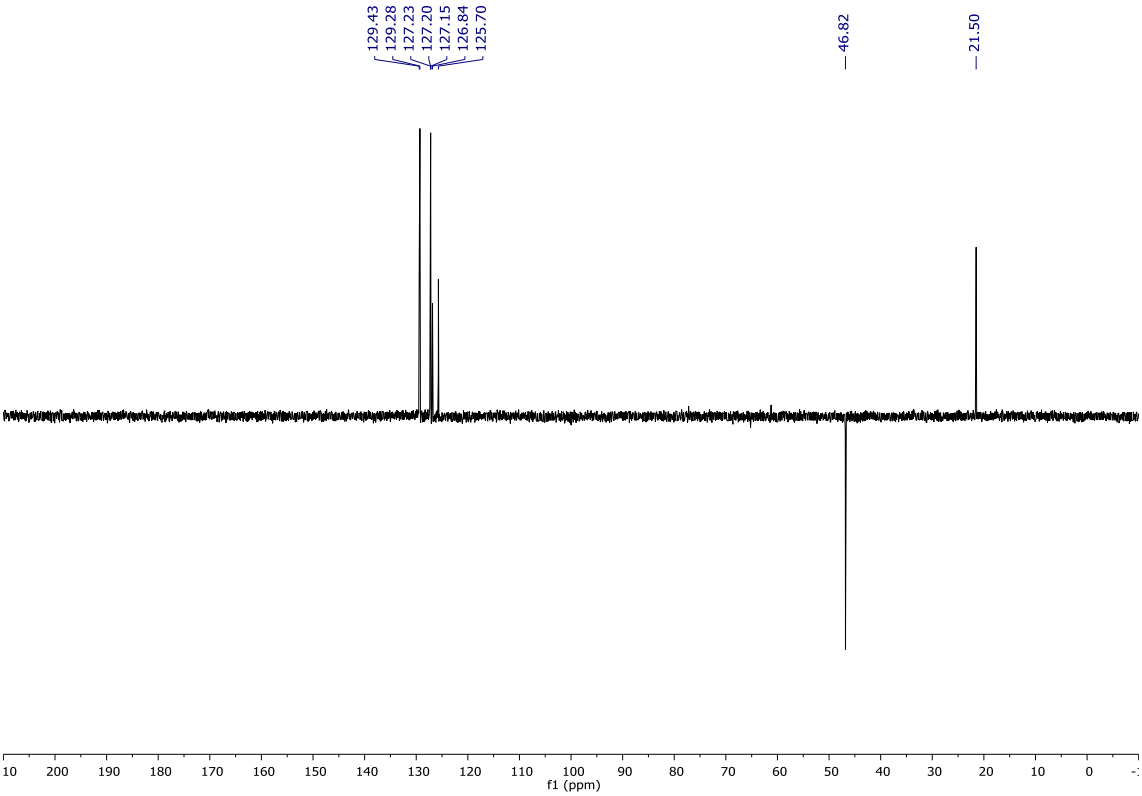


8

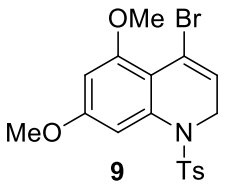
75 MHz ^{13}CNMR Spectrum of compound **8** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **8** ($CDCl_3$, 300 K)

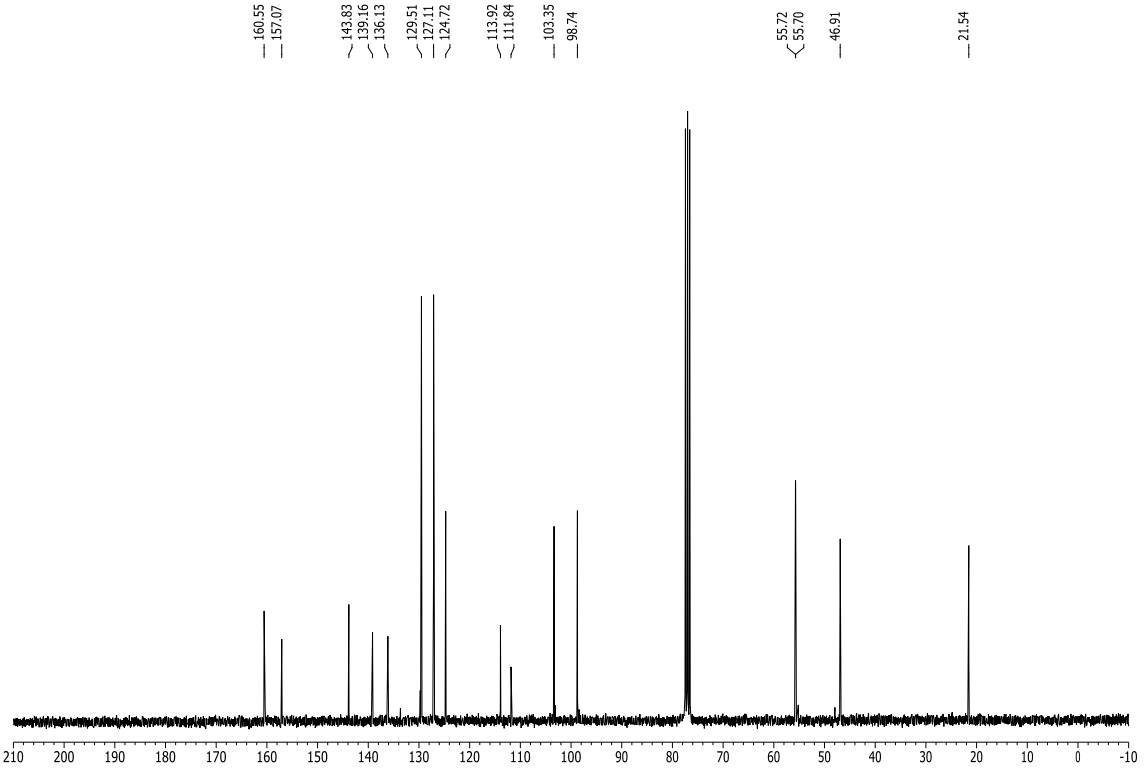


300 MHz ^{1}HNMR Spectrum of compound **9** ($CDCl_3$, 300 K)

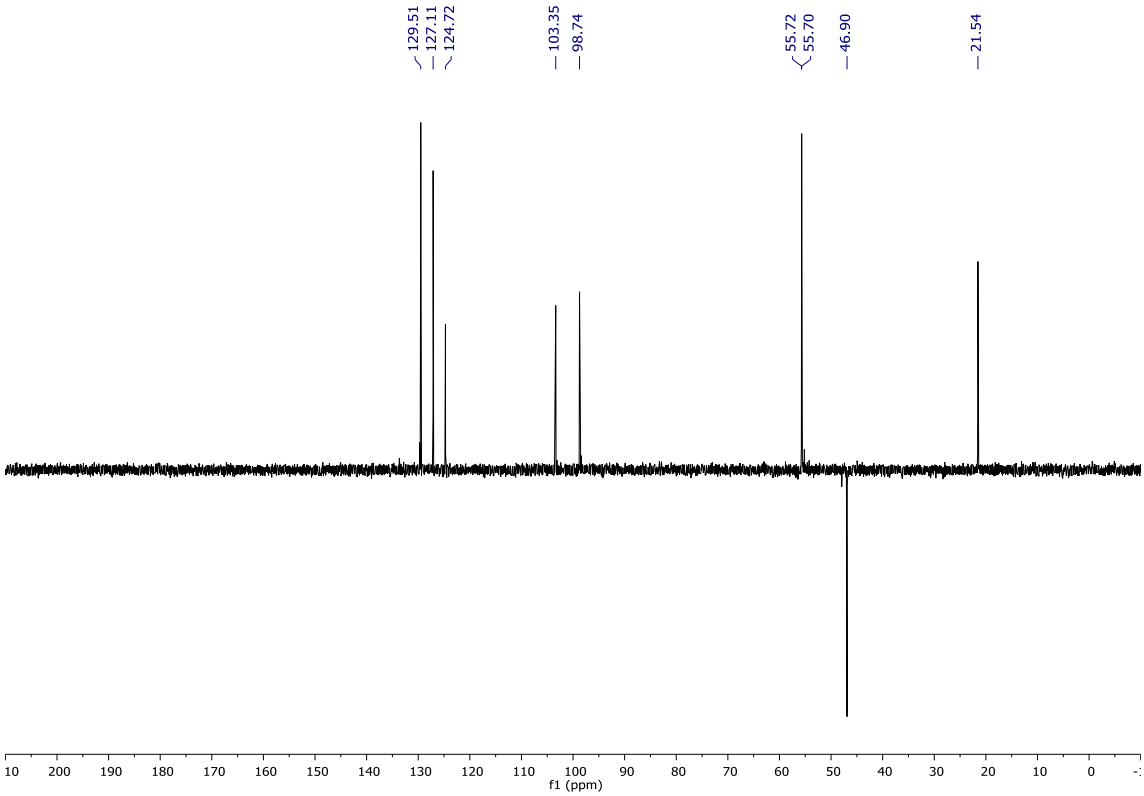


9

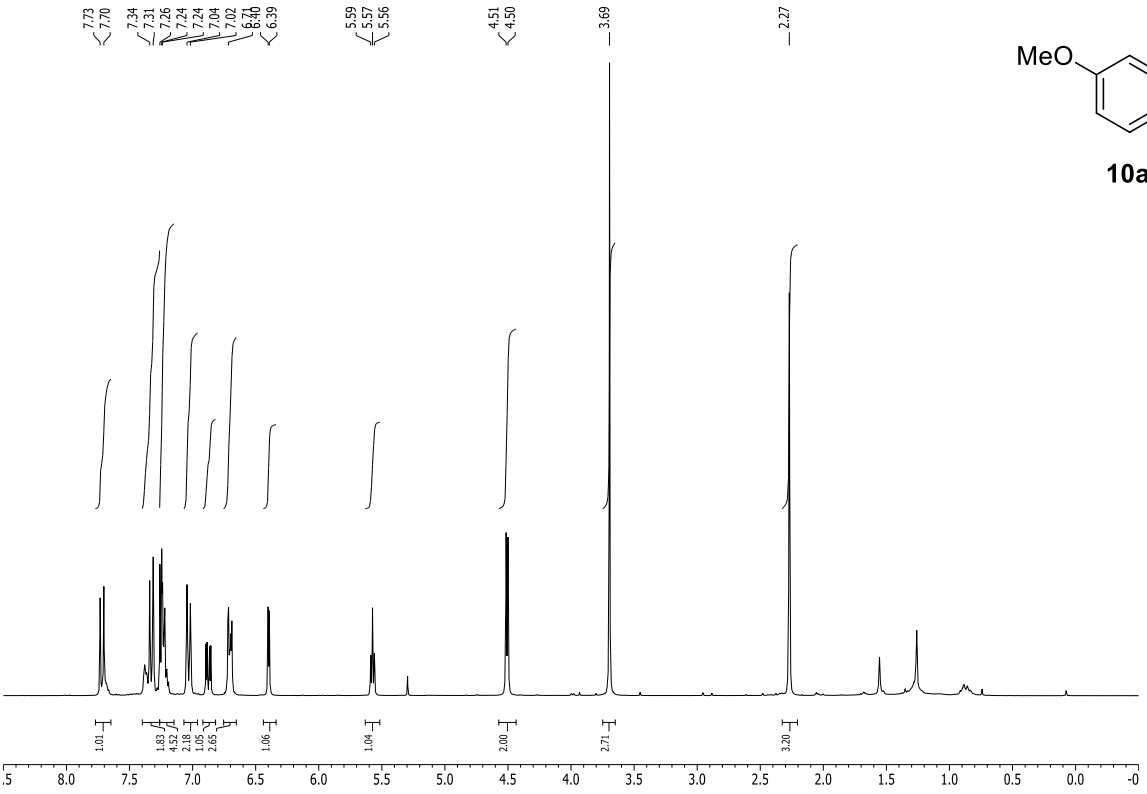
75 MHz ^{13}CNMR Spectrum of compound **9** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **9** ($CDCl_3$, 300 K)

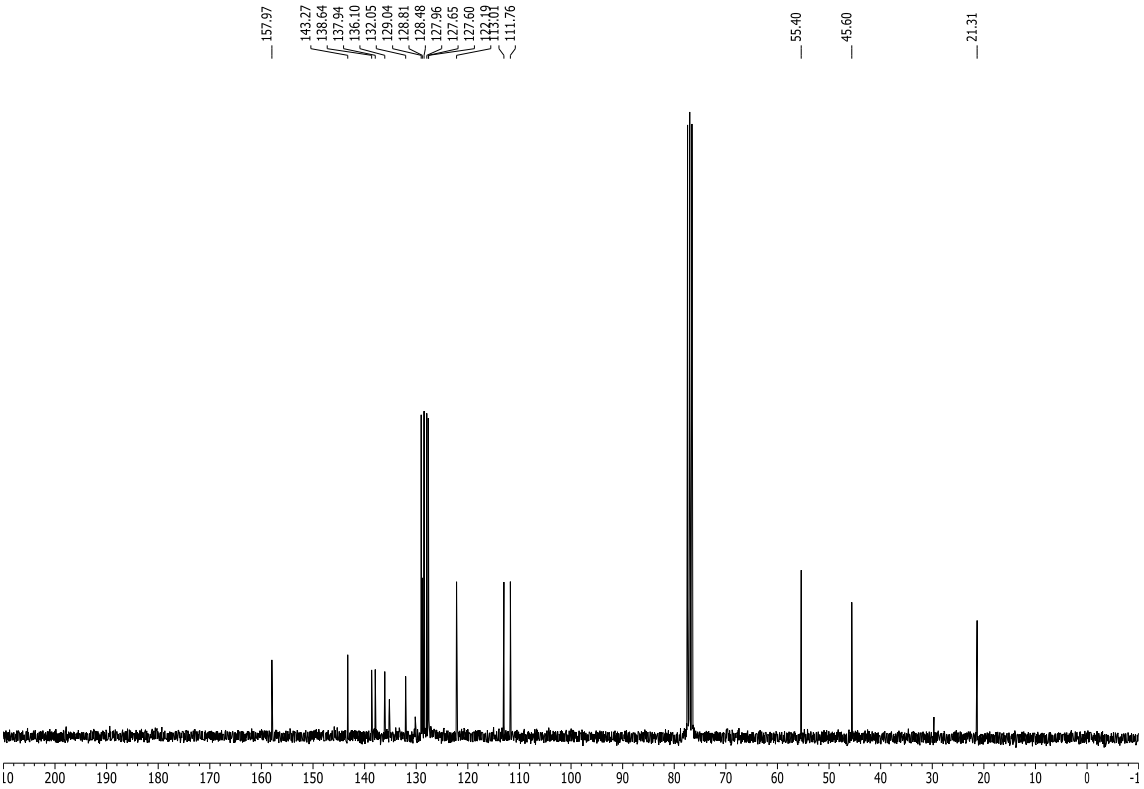


300 MHz ^{1}HNMR Spectrum of compound **10a** ($CDCl_3$, 300 K)

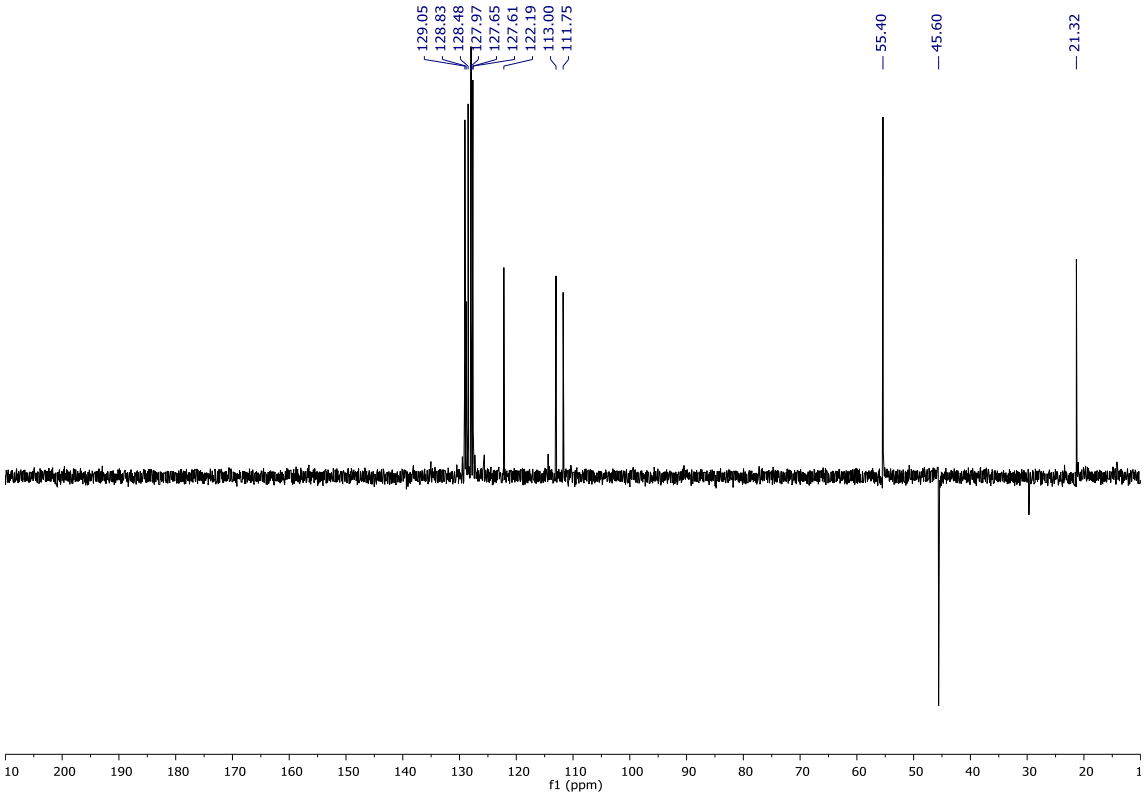


10a

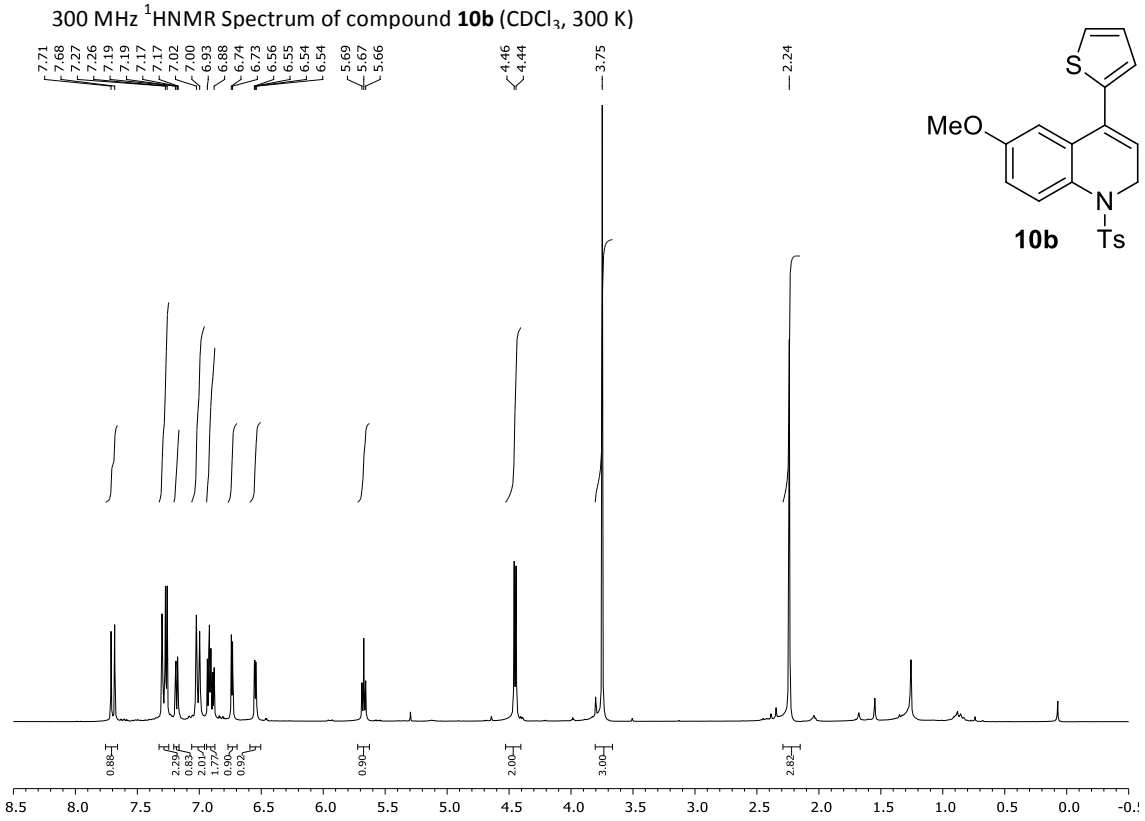
75 MHz ^{13}CNMR Spectrum of compound **10a** ($CDCl_3$, 300 K)



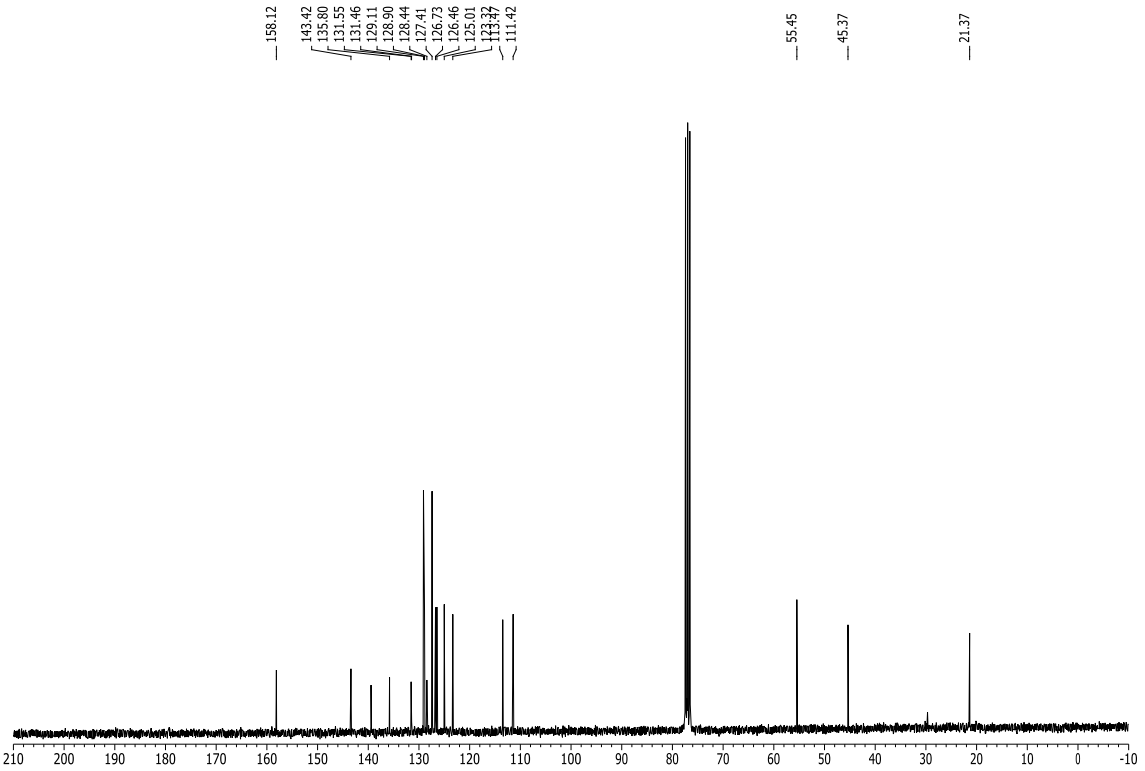
75 MHz DEPT-135 Spectrum of compound **10a** ($CDCl_3$, 300 K)



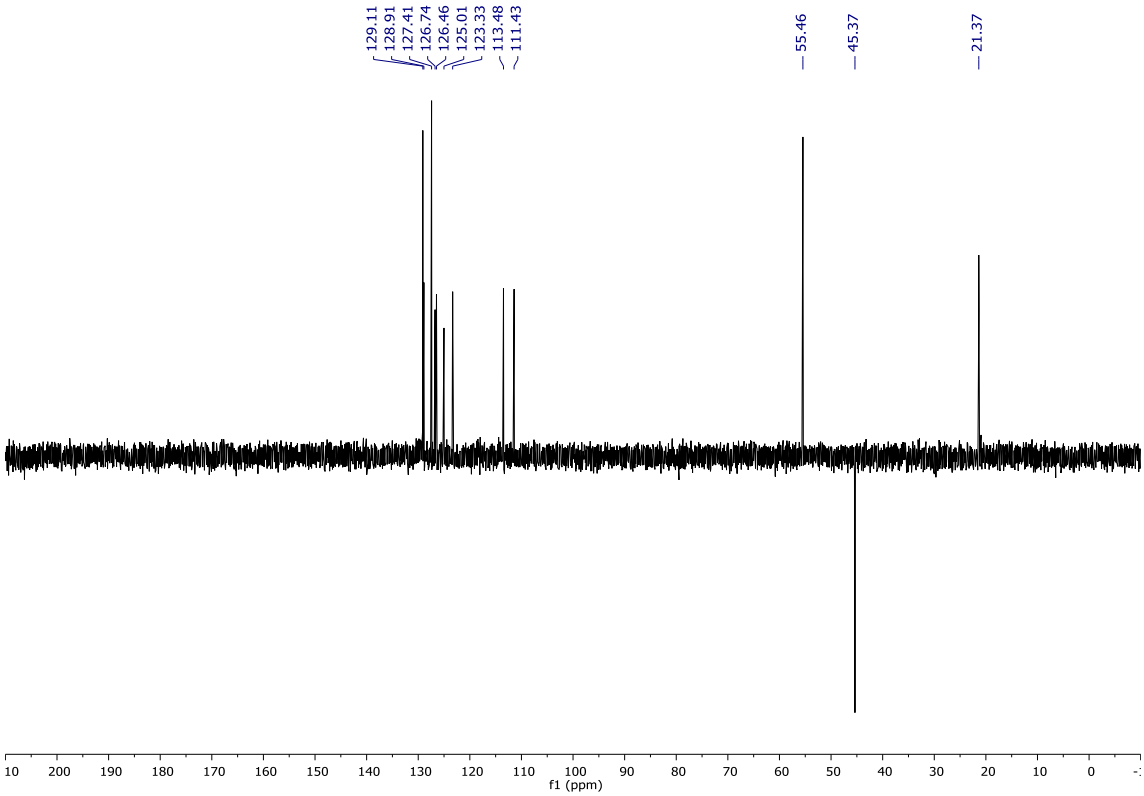
300 MHz ^{1}HNMR Spectrum of compound **10b** ($CDCl_3$, 300 K)



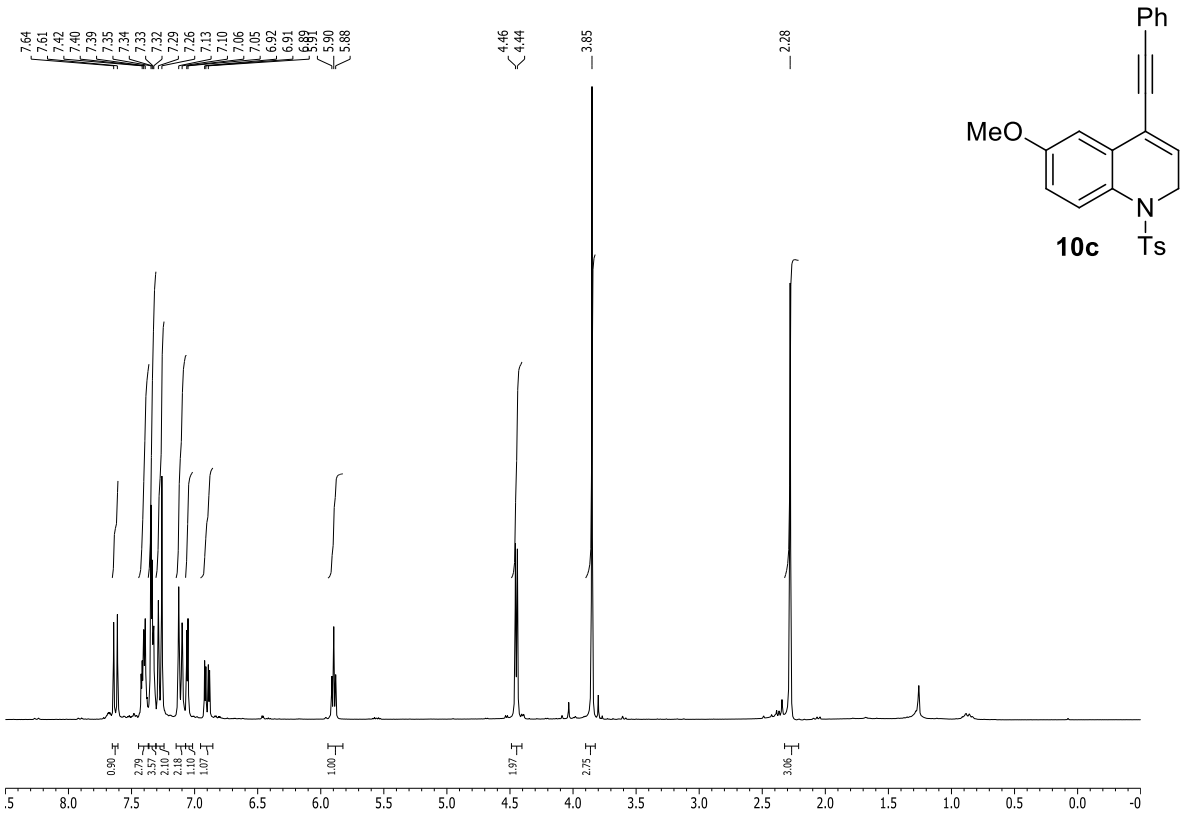
75 MHz ^{13}CNMR Spectrum of compound **10b** ($CDCl_3$, 300 K)



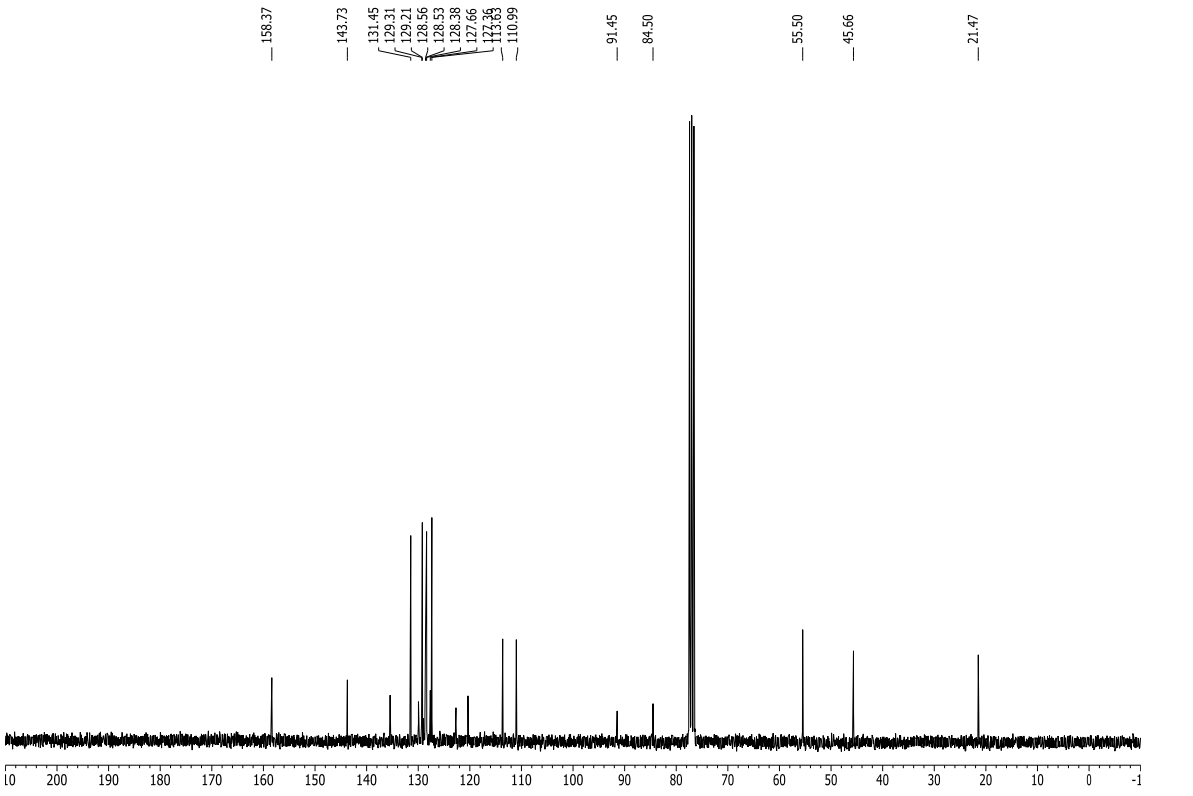
75 MHz DEPT-135 Spectrum of compound **10b** ($CDCl_3$, 300 K)



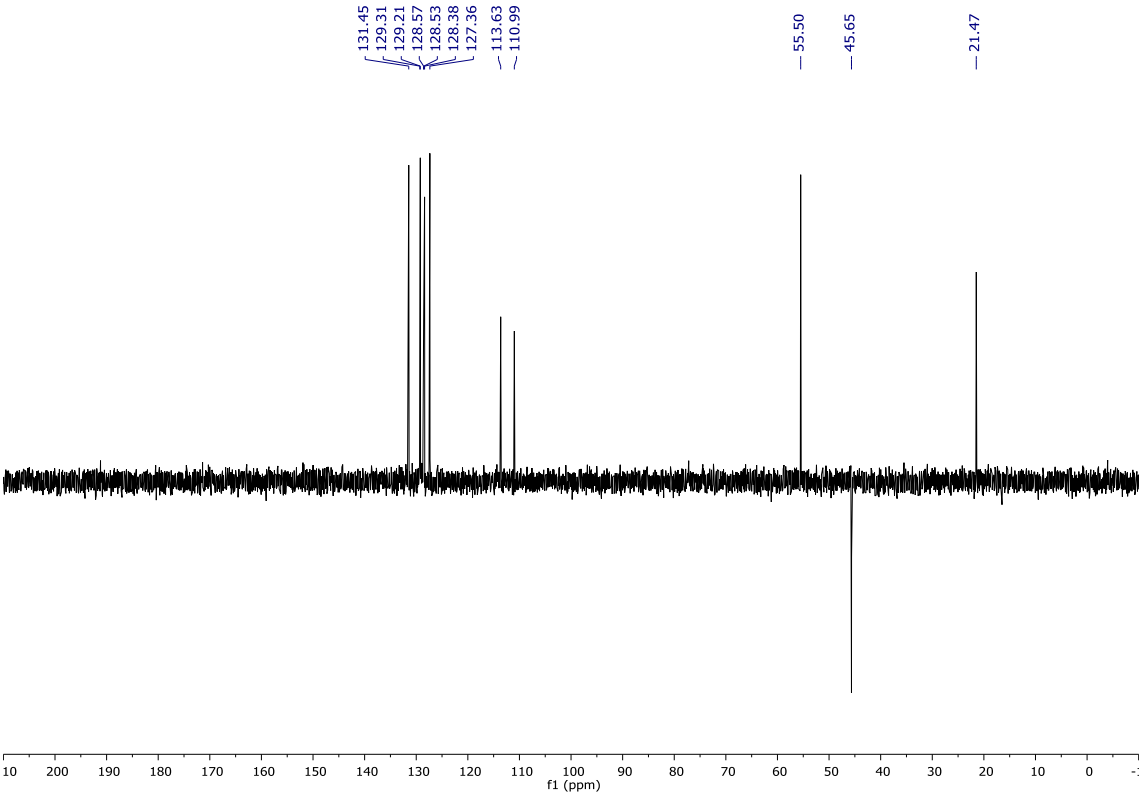
300 MHz ^{1}HNMR Spectrum of compound **10c** ($CDCl_3$, 300 K)



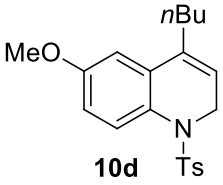
75 MHz ^{13}CNMR Spectrum of compound **10c** ($CDCl_3$, 300 K)



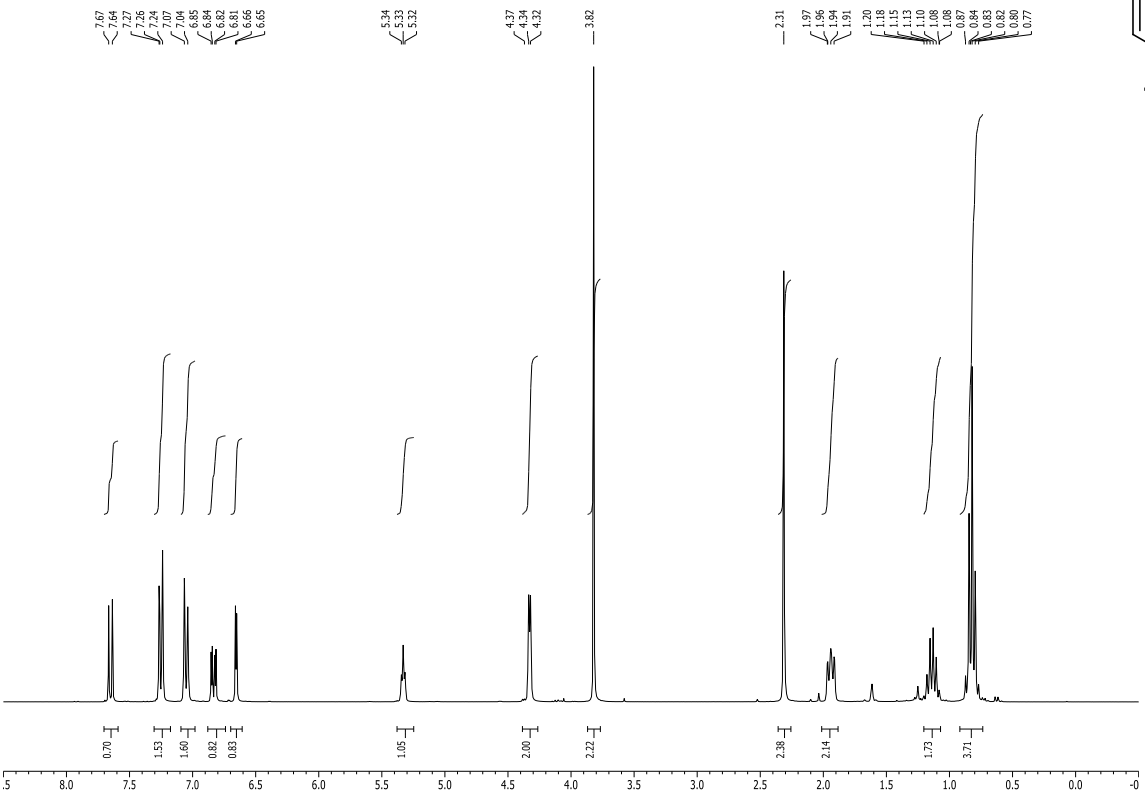
75 MHz DEPT-135 Spectrum of compound **10c** ($CDCl_3$, 300 K)



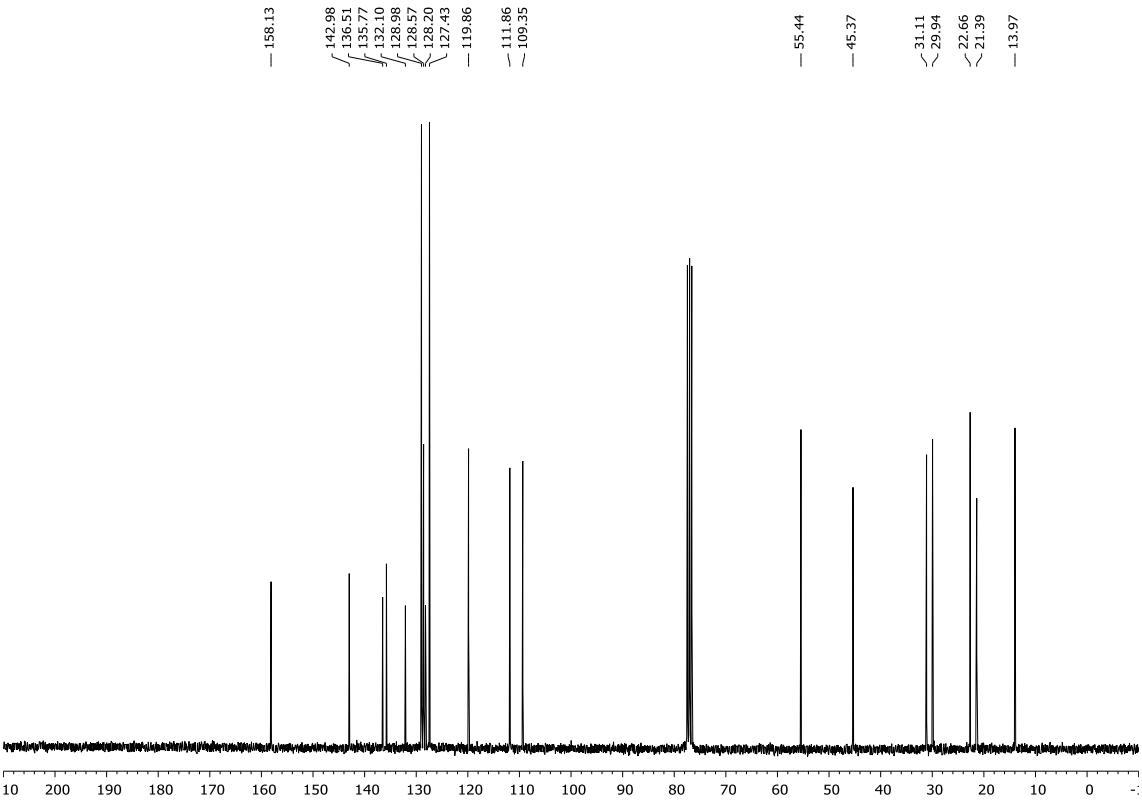
300 MHz ^{1}HNMR Spectrum of compound **10d** ($CDCl_3$, 300 K)



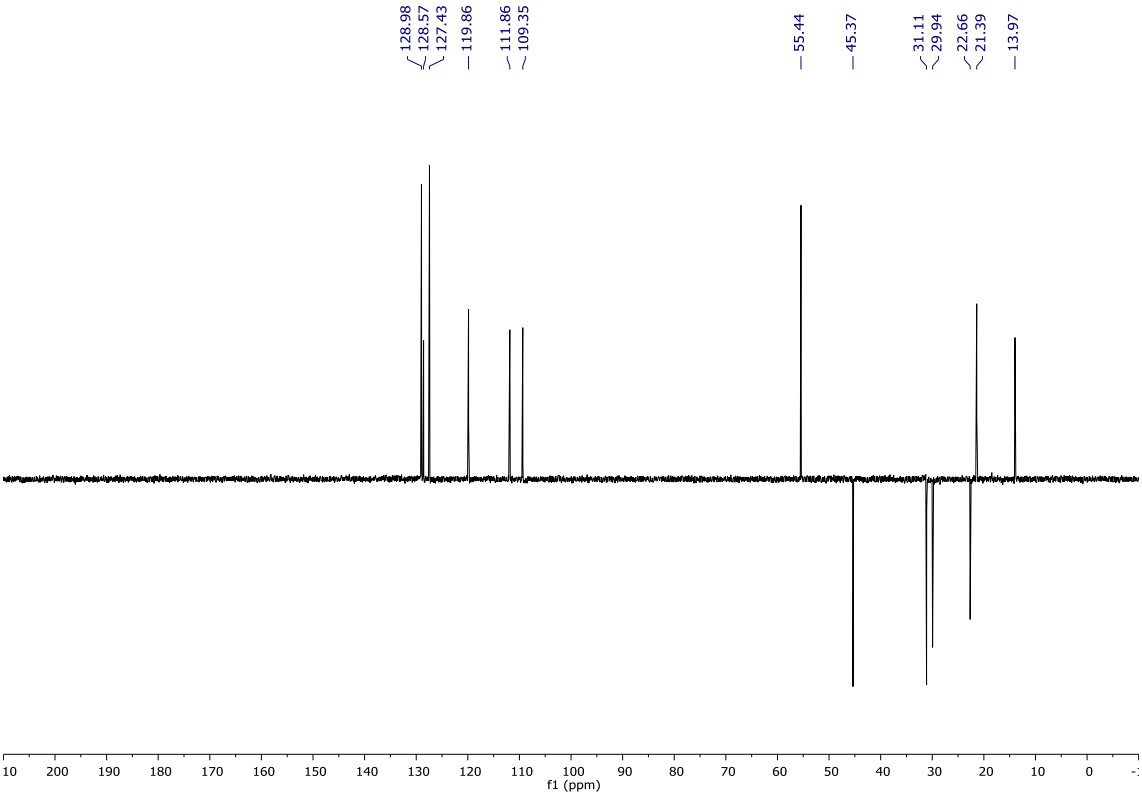
10d



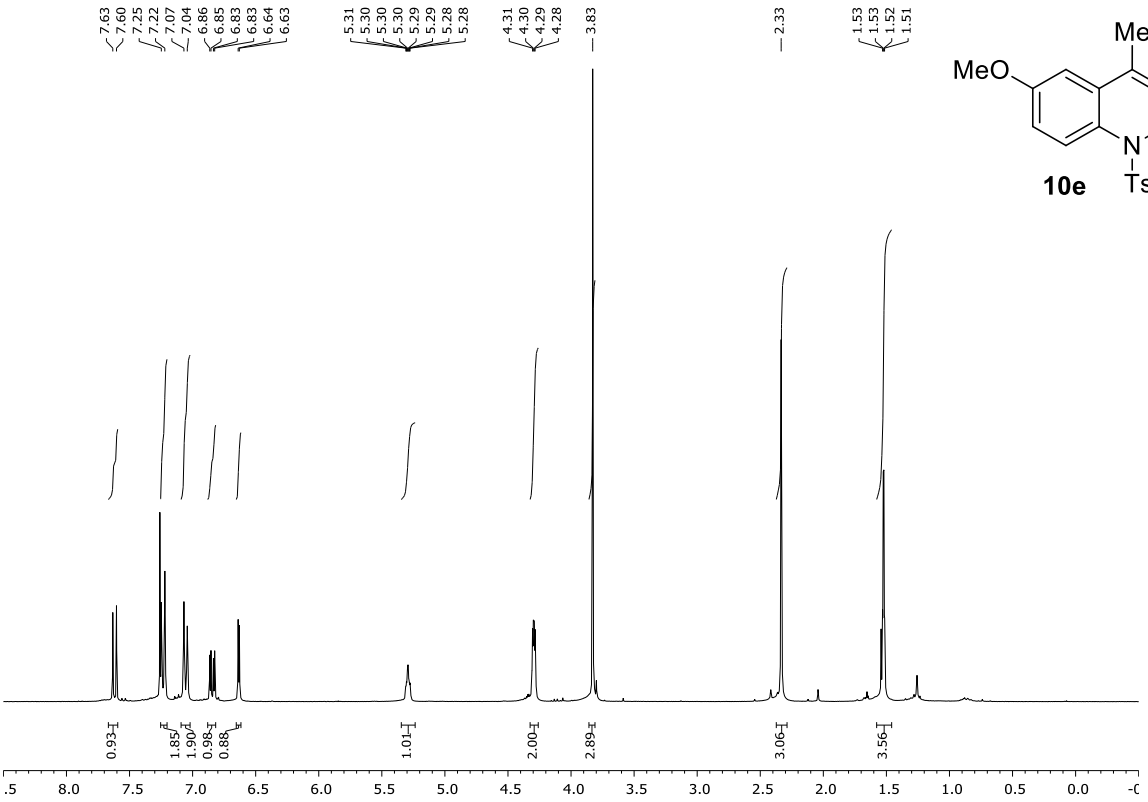
75 MHz ^{13}CNMR Spectrum of compound **10d** ($CDCl_3$, 300 K)



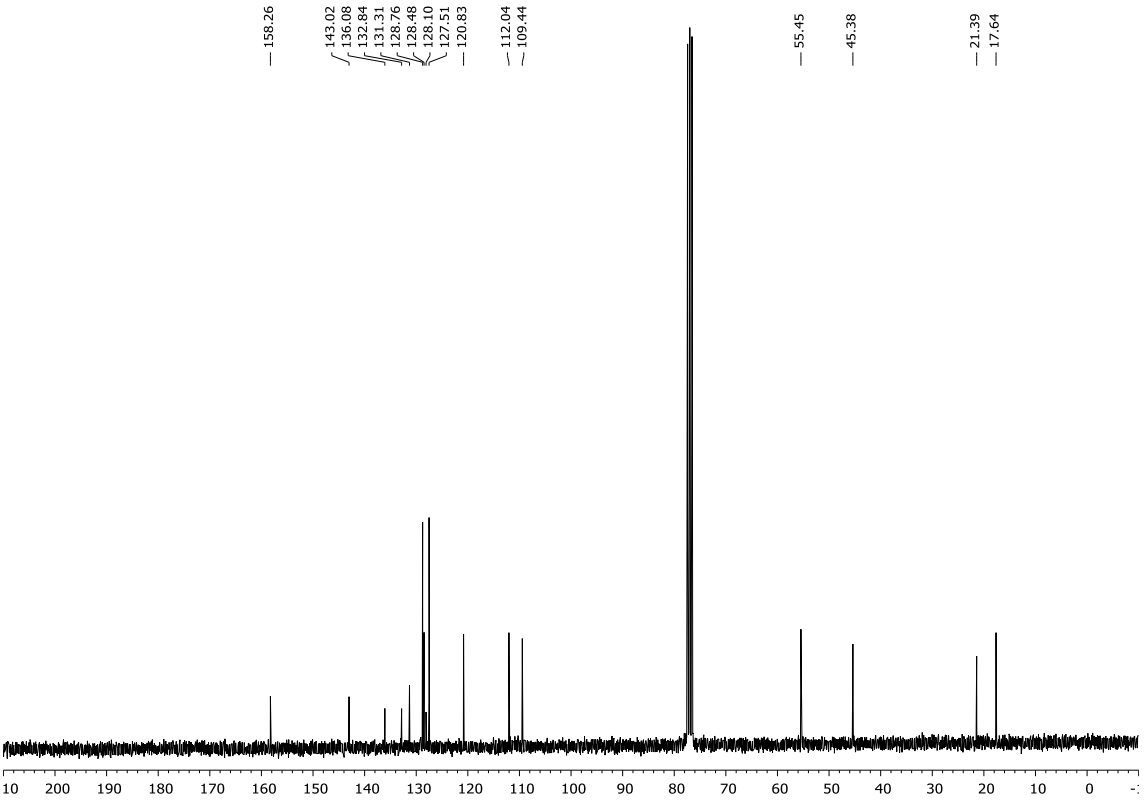
75 MHz DEPT-135 Spectrum of compound **10d** ($CDCl_3$, 300 K)



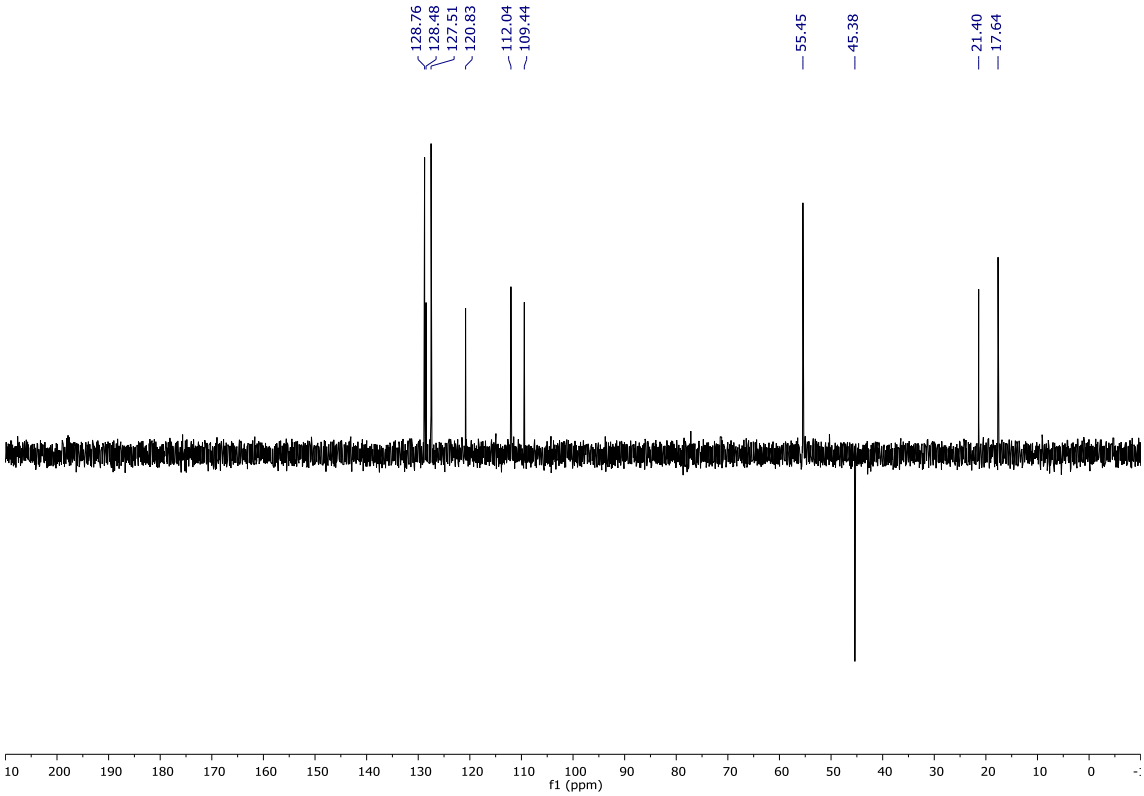
300 MHz ^{1}HNMR Spectrum of compound **10e** ($CDCl_3$, 300 K)



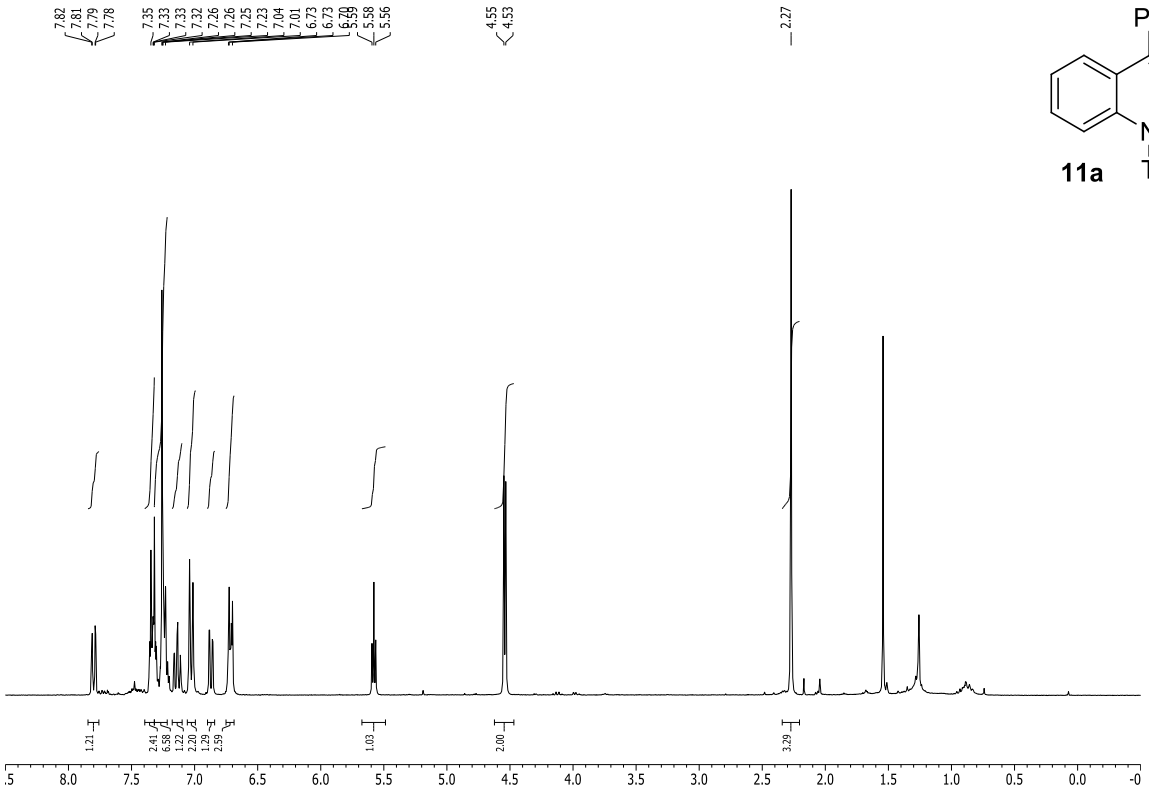
75 MHz ^{13}CNMR Spectrum of compound **10e** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **10e** ($CDCl_3$, 300 K)

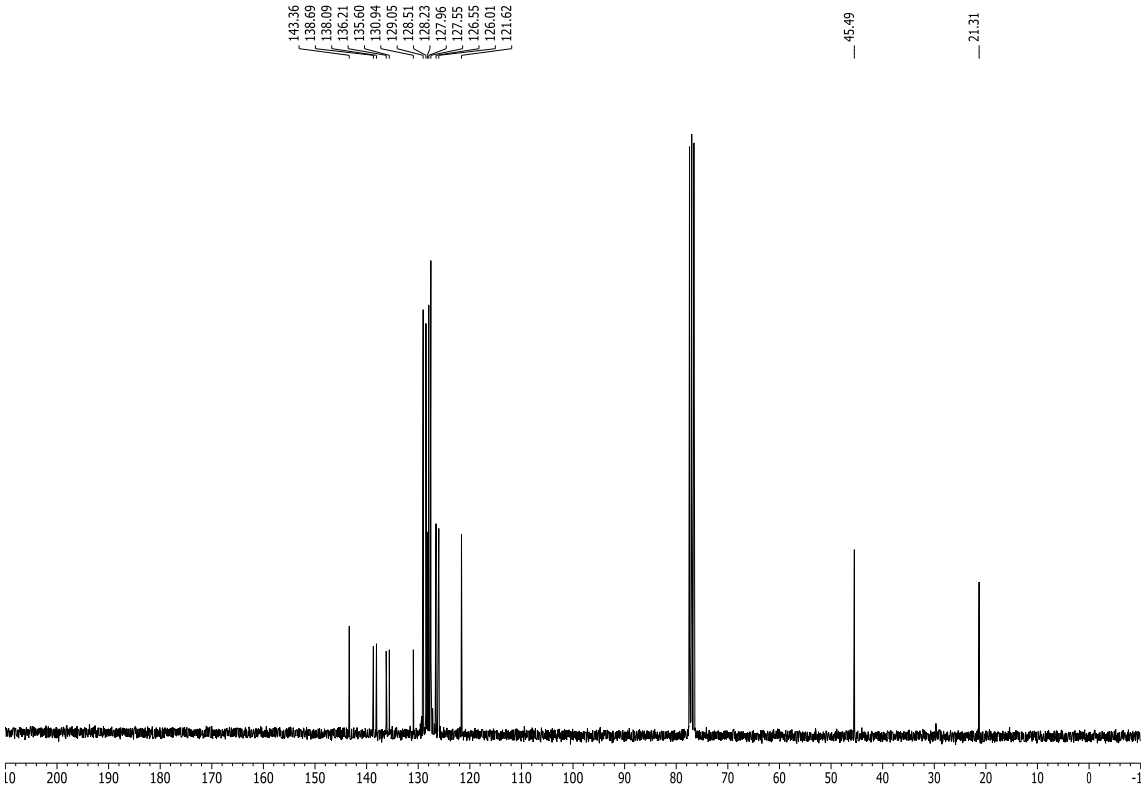


300 MHz ^{1}HNMR Spectrum of compound **11a** ($CDCl_3$, 300 K)

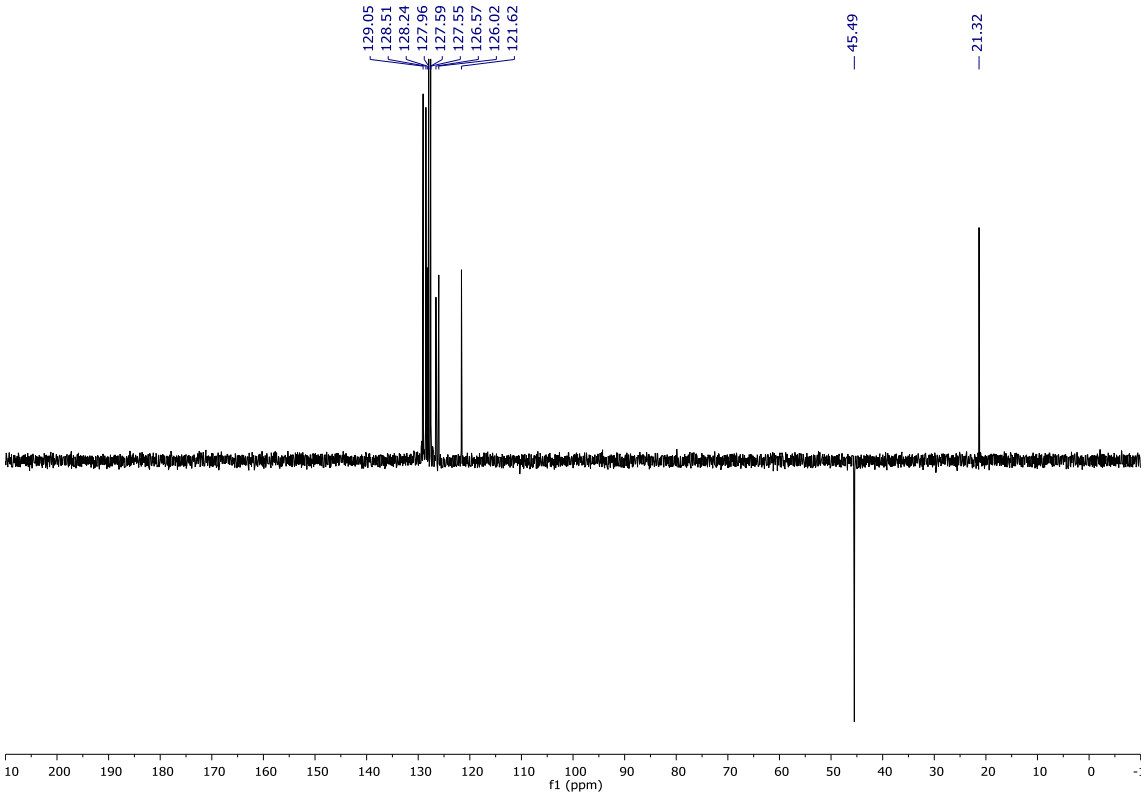


11a

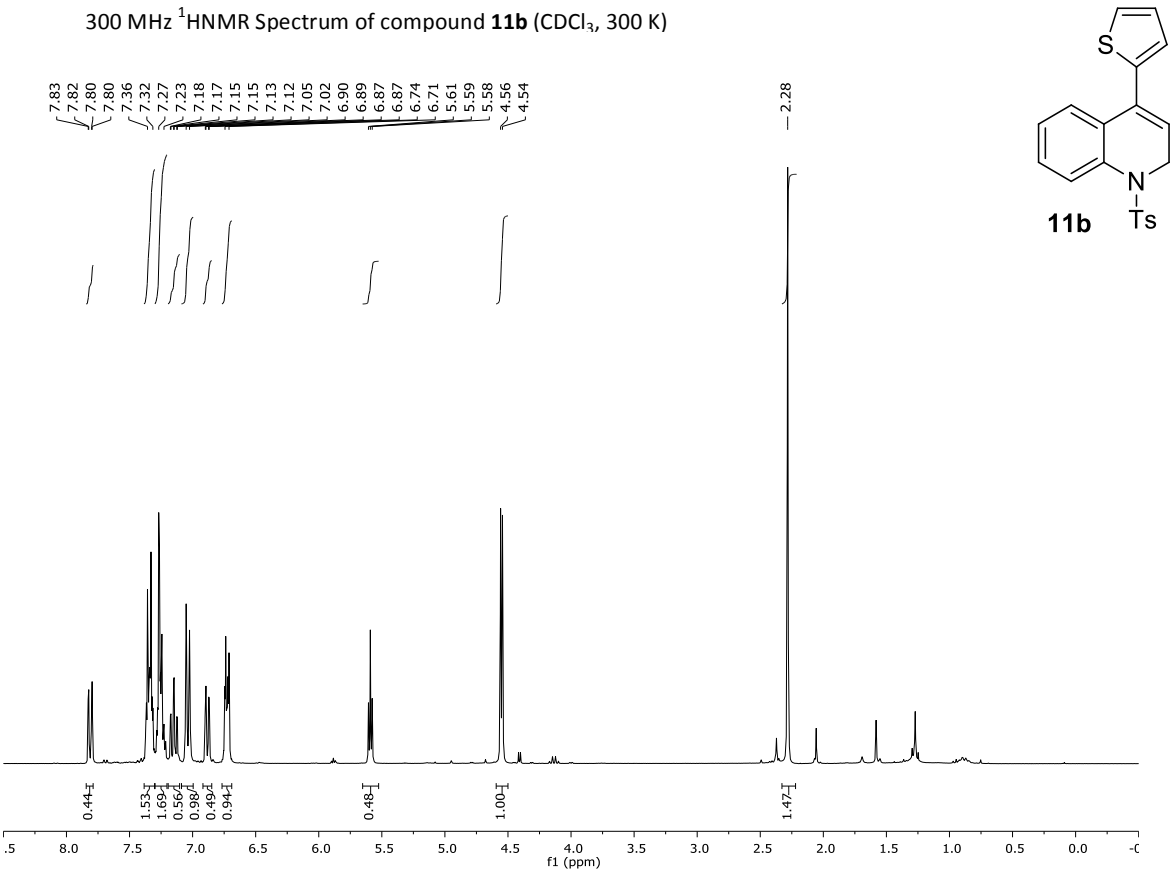
75 MHz ^{13}CNMR Spectrum of compound **11a** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **11a** ($CDCl_3$, 300 K)

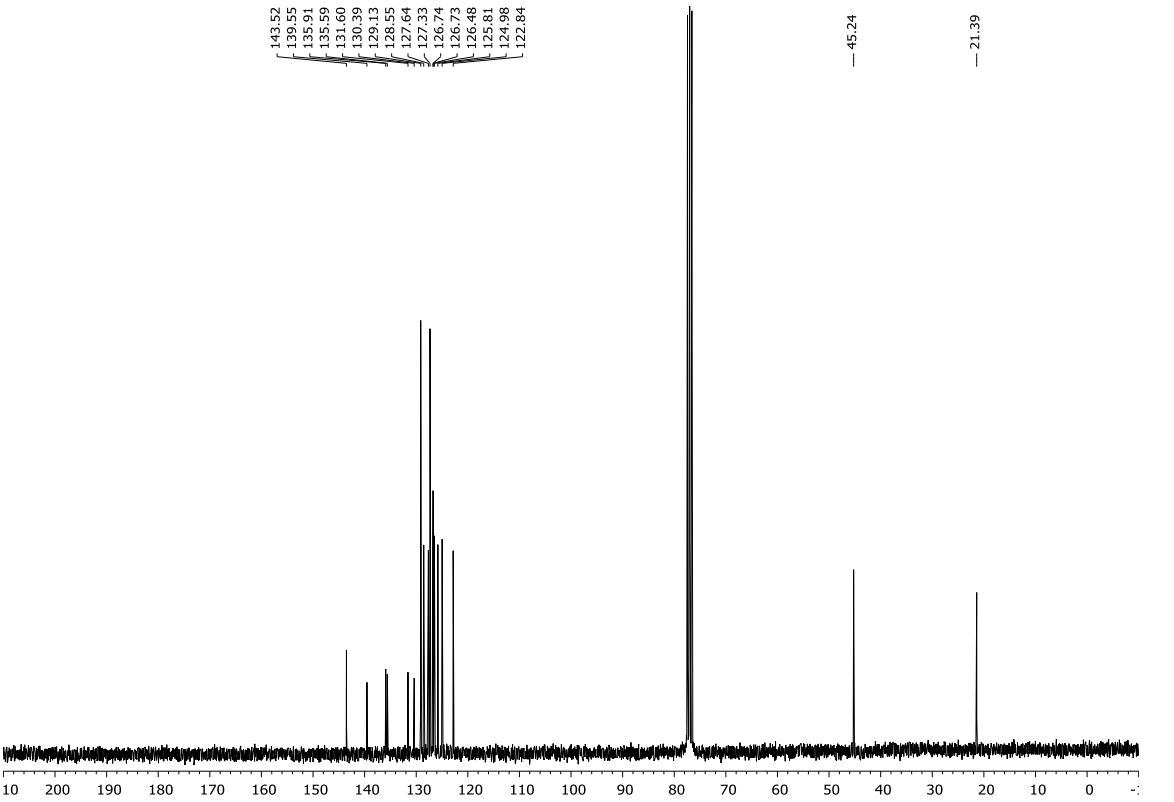


300 MHz ^{1}HNMR Spectrum of compound **11b** ($CDCl_3$, 300 K)

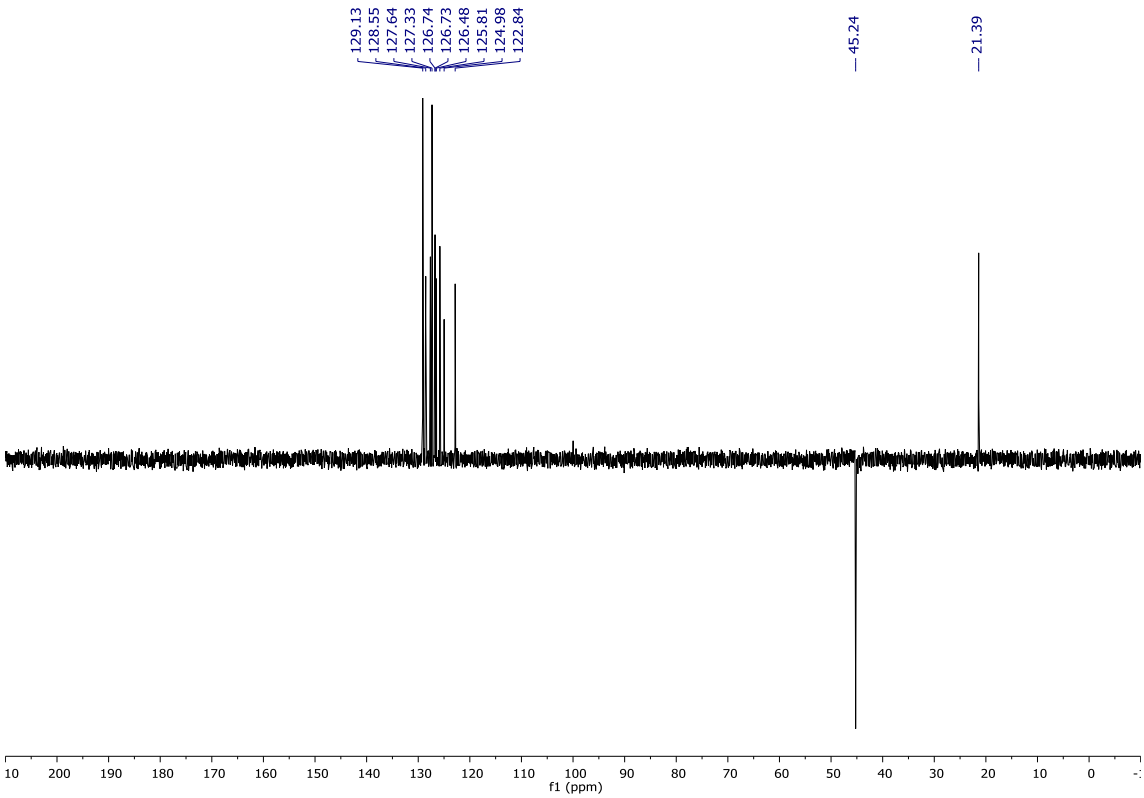


11b

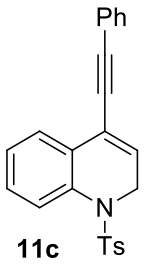
75 MHz ^{13}CNMR Spectrum of compound **11b** ($CDCl_3$, 300 K)



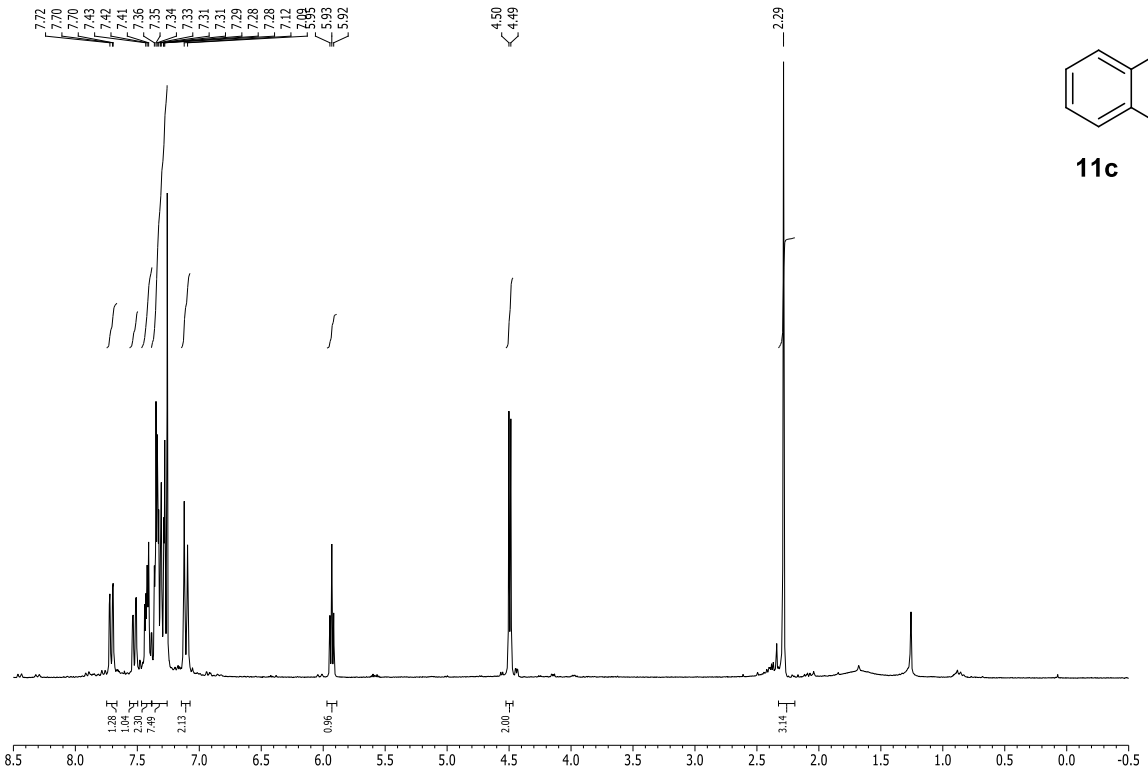
75 MHz DEPT-135 Spectrum of compound **11b** ($CDCl_3$, 300 K)



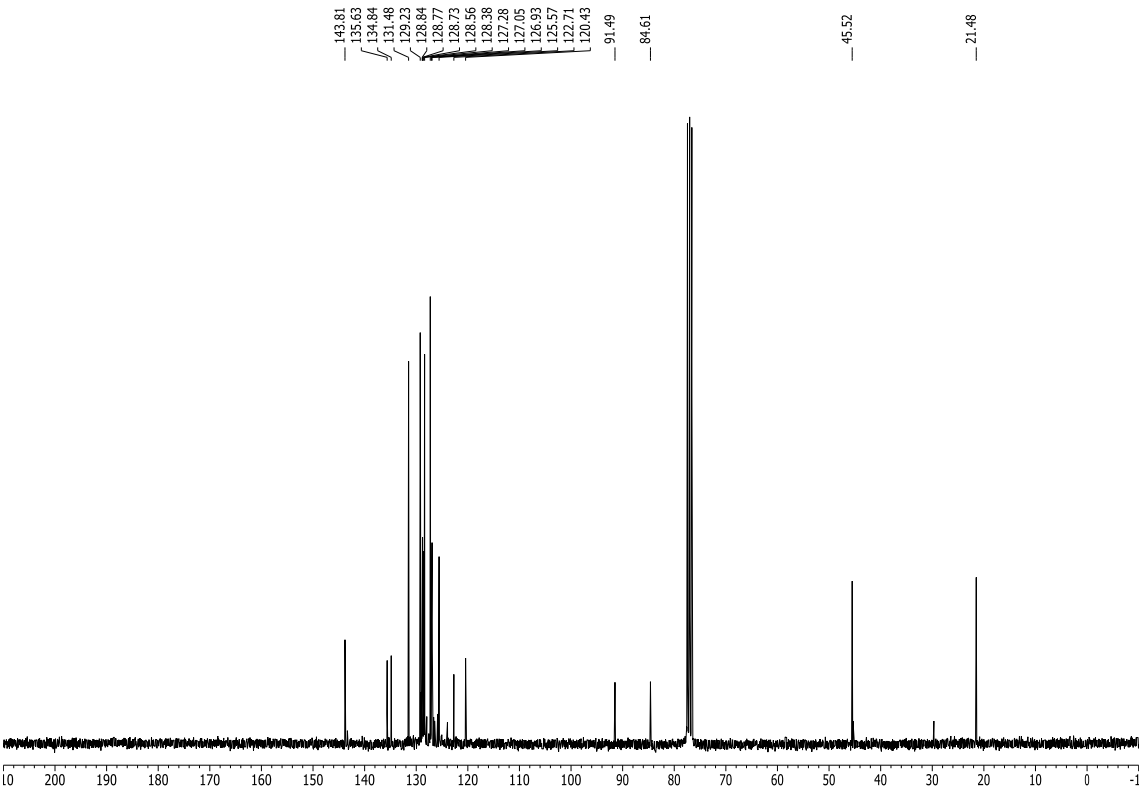
300 MHz ^{1}HNMR Spectrum of compound **11c** ($CDCl_3$, 300 K)



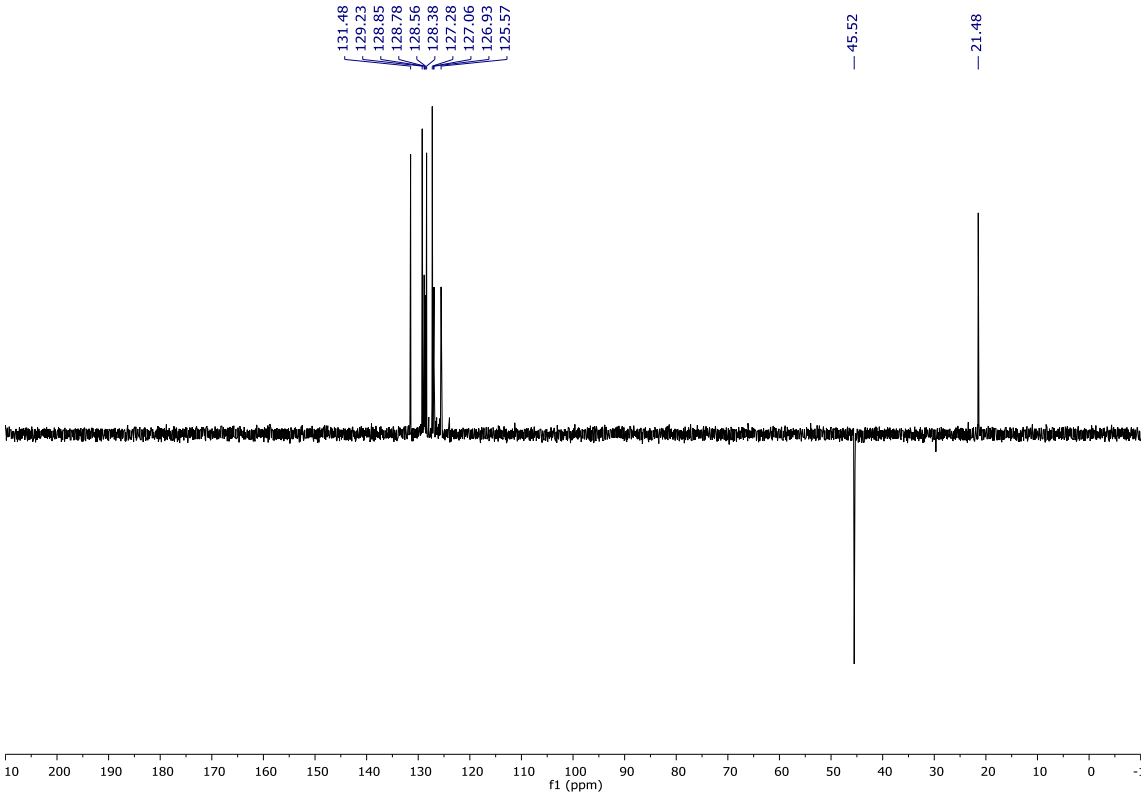
11c



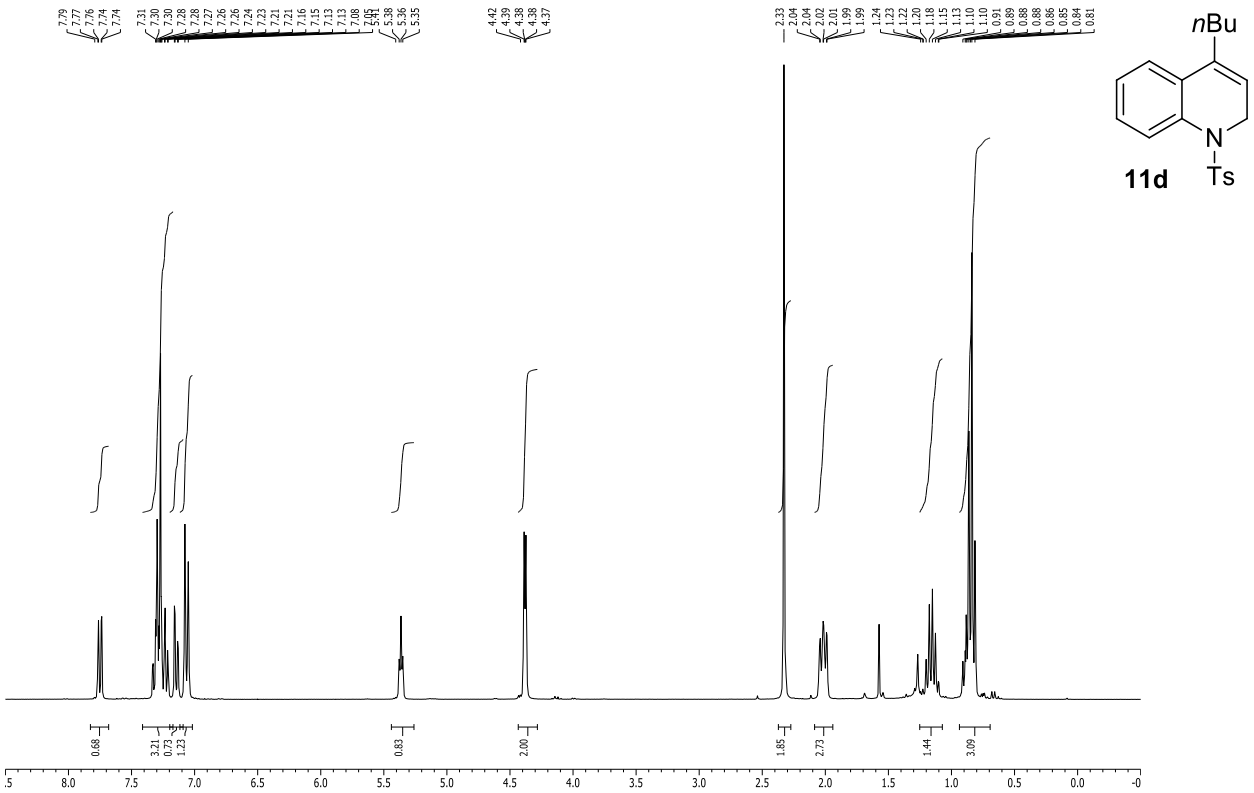
75 MHz ^{13}CNMR Spectrum of compound **11c** ($CDCl_3$, 300 K)



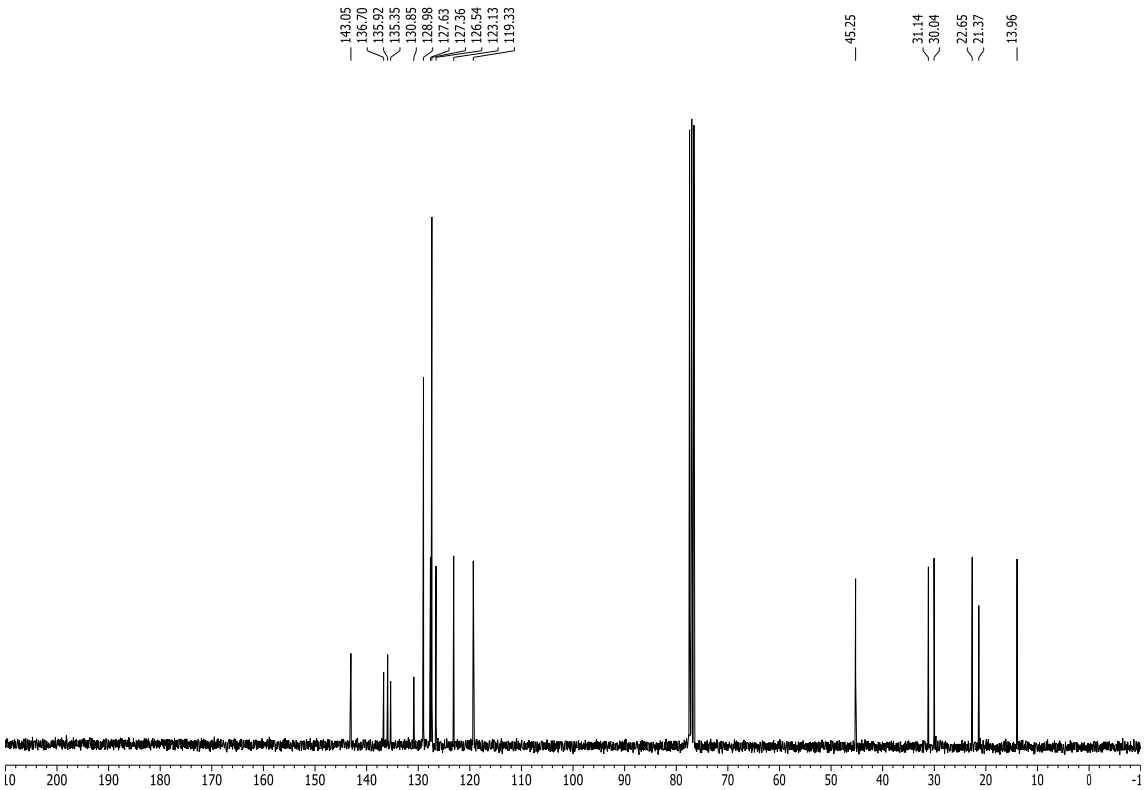
75 MHz DEPT-135 Spectrum of compound **11c** ($CDCl_3$, 300 K)



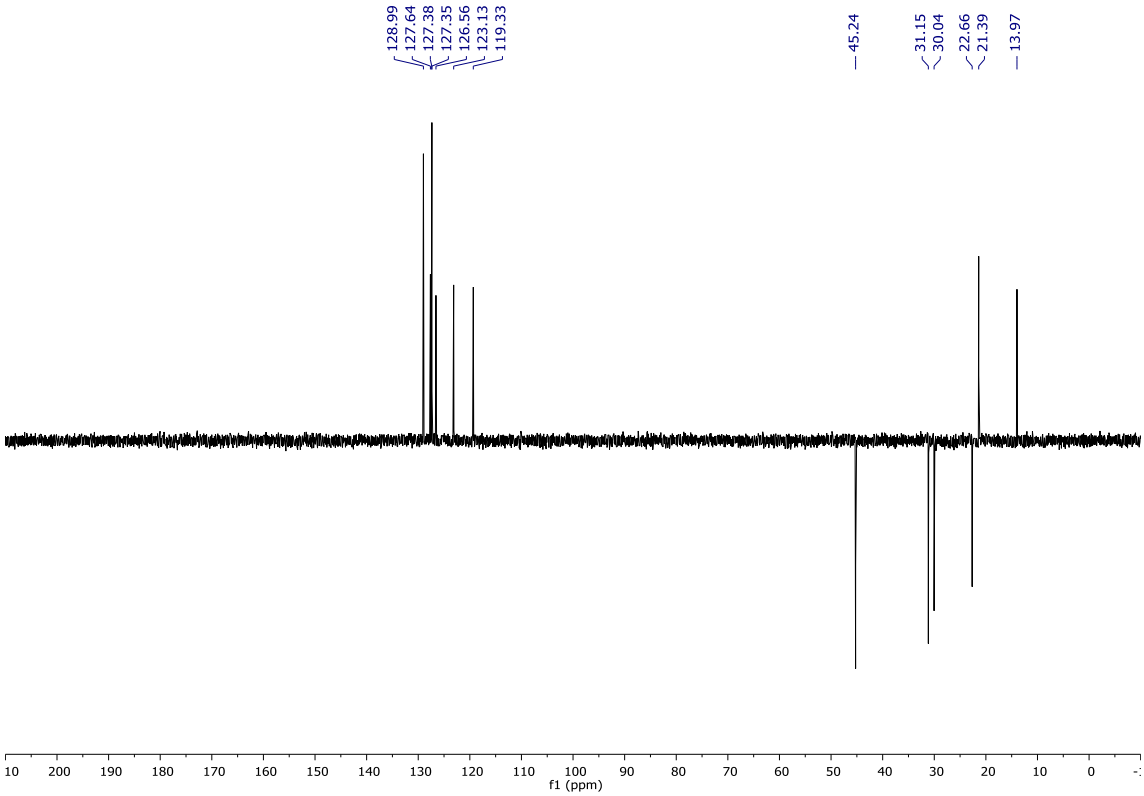
300 MHz ^{1}HNMR Spectrum of compound **11d** ($CDCl_3$, 300 K)



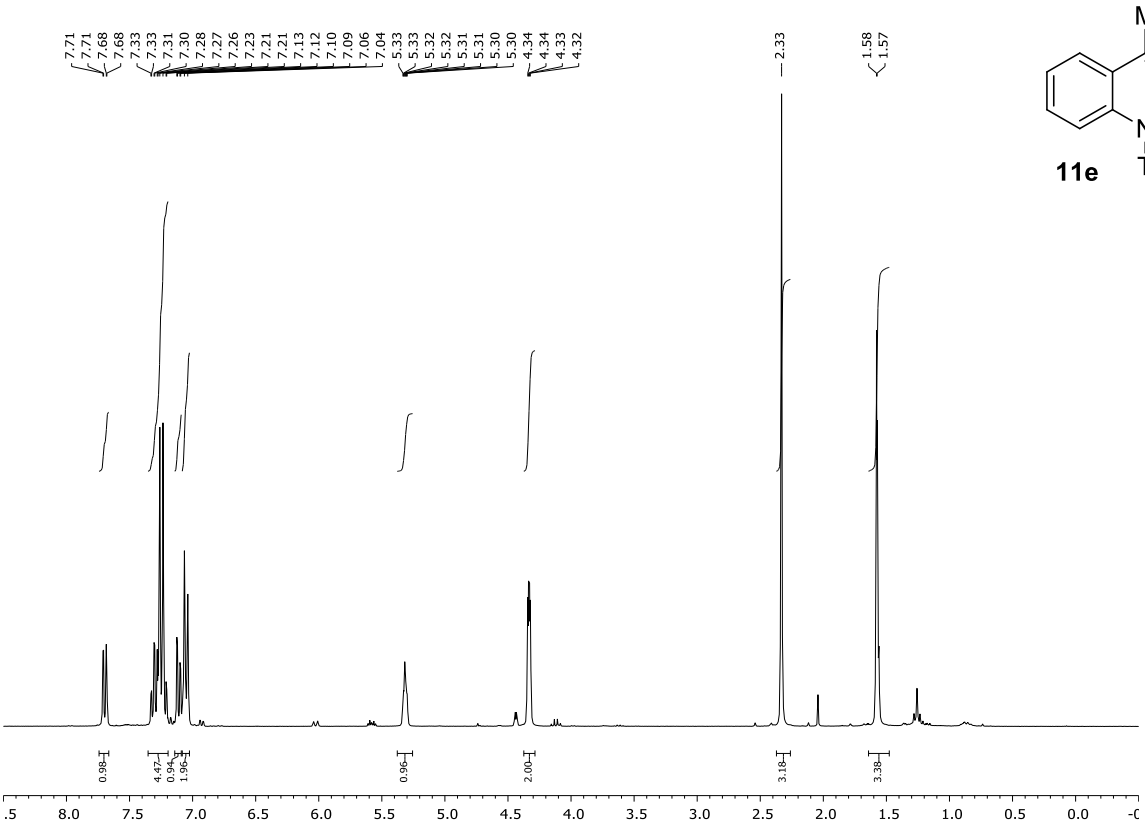
75 MHz ^{13}CNMR Spectrum of compound **11d** ($CDCl_3$, 300 K)



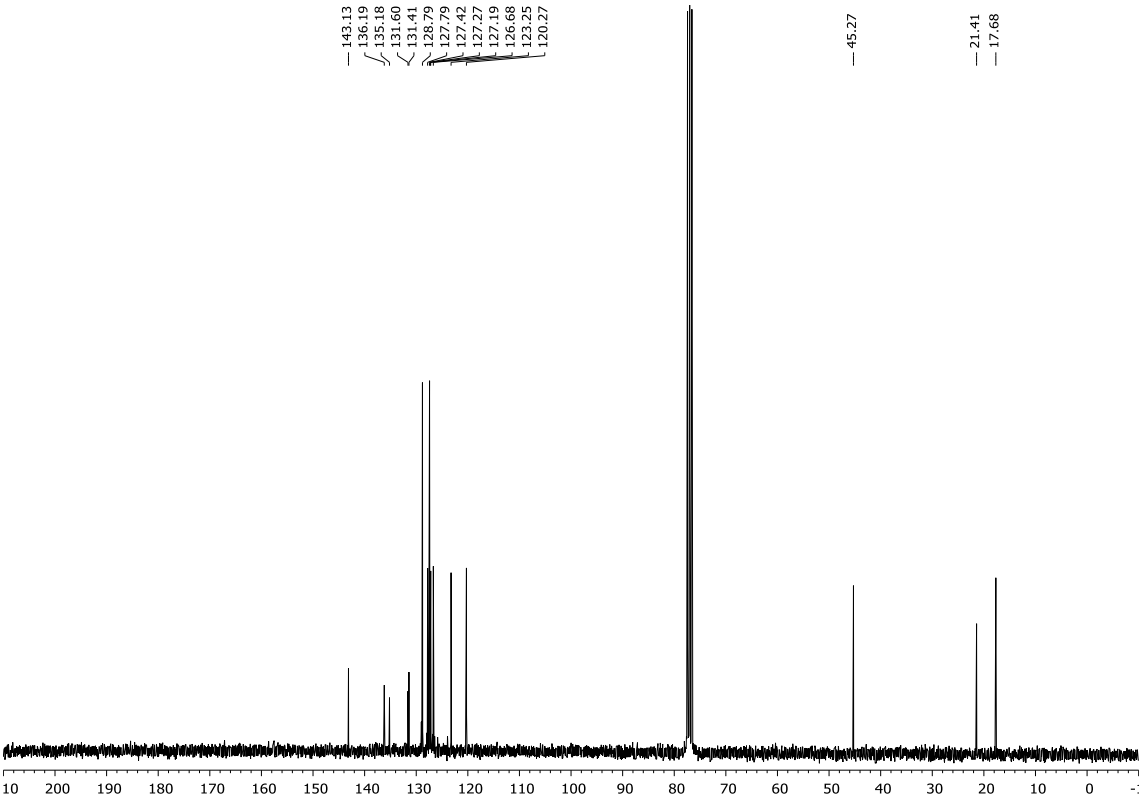
75 MHz DEPT-135 Spectrum of compound **11d** ($CDCl_3$, 300 K)



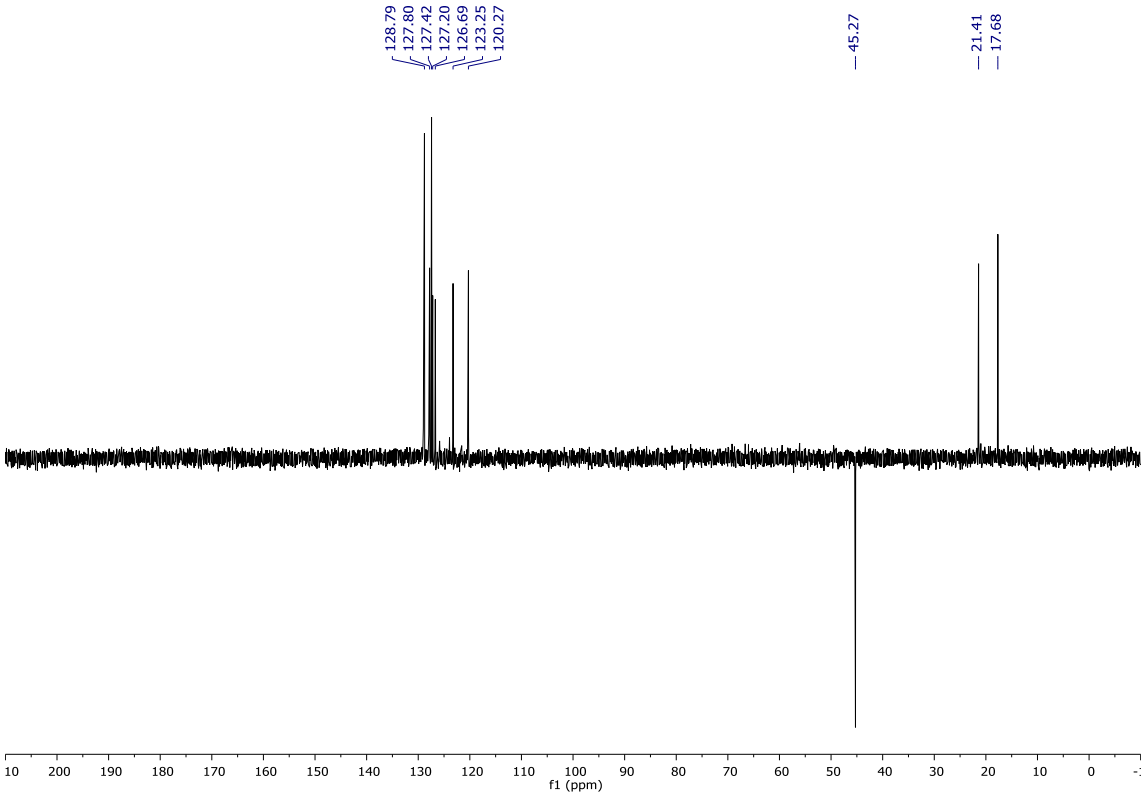
300 MHz ^{1}HNMR Spectrum of compound **11e** ($CDCl_3$, 300 K)



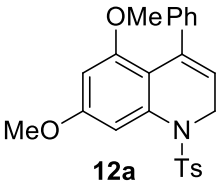
75 MHz ^{13}CNMR Spectrum of compound **11e** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **11e** ($CDCl_3$, 300 K)

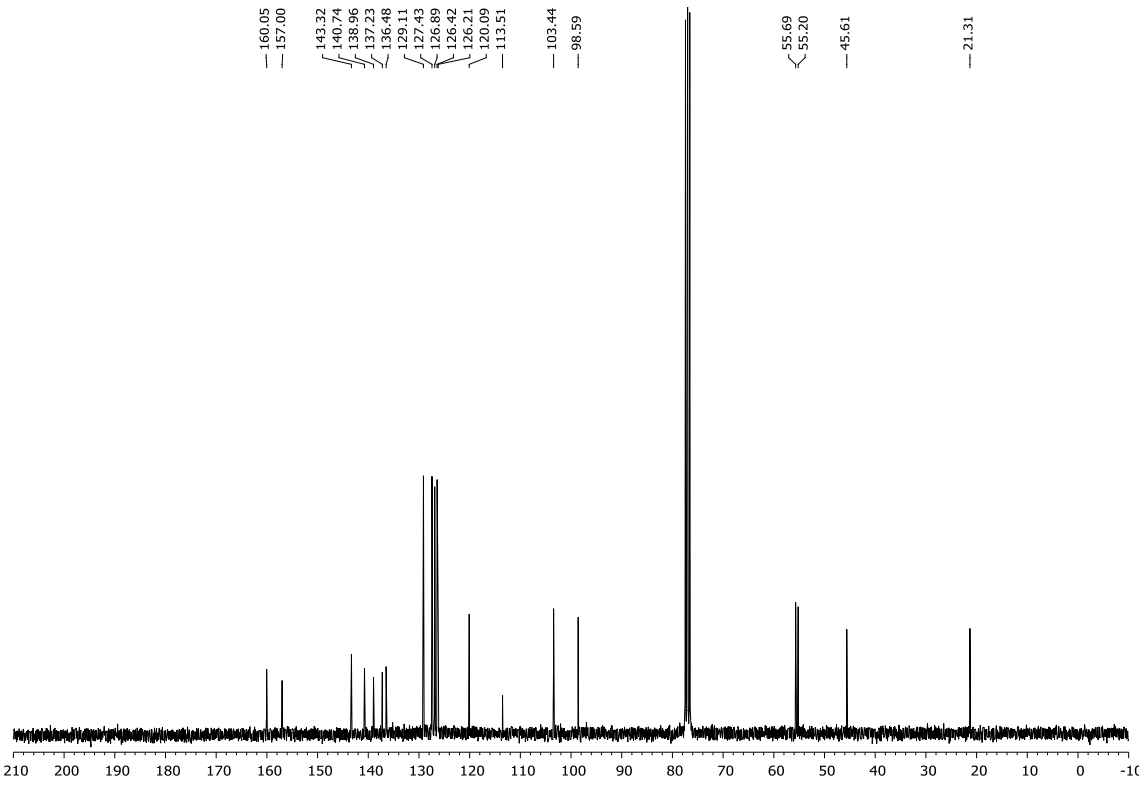


300 MHz ^{1}HNMR Spectrum of compound **12a** ($CDCl_3$, 300 K)

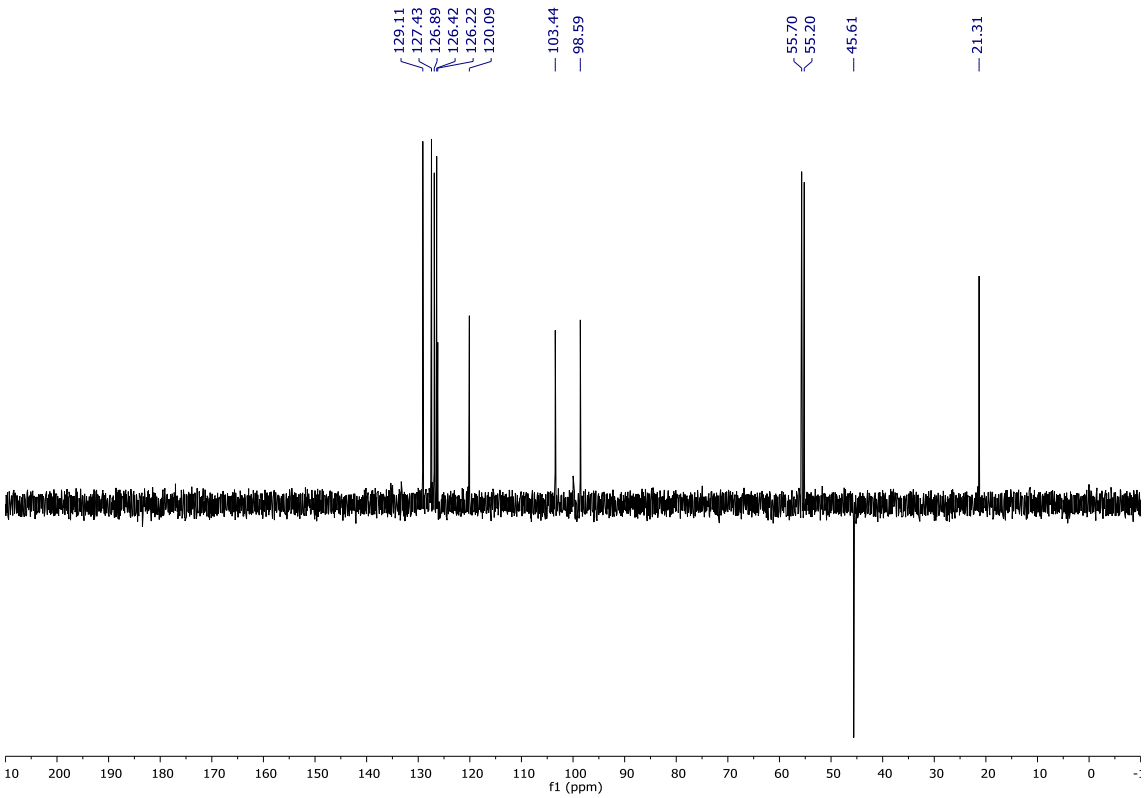


12a

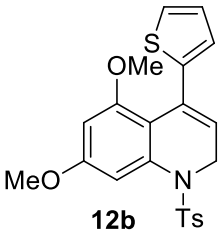
75 MHz ^{13}CNMR Spectrum of compound **12a** ($CDCl_3$, 300 K)



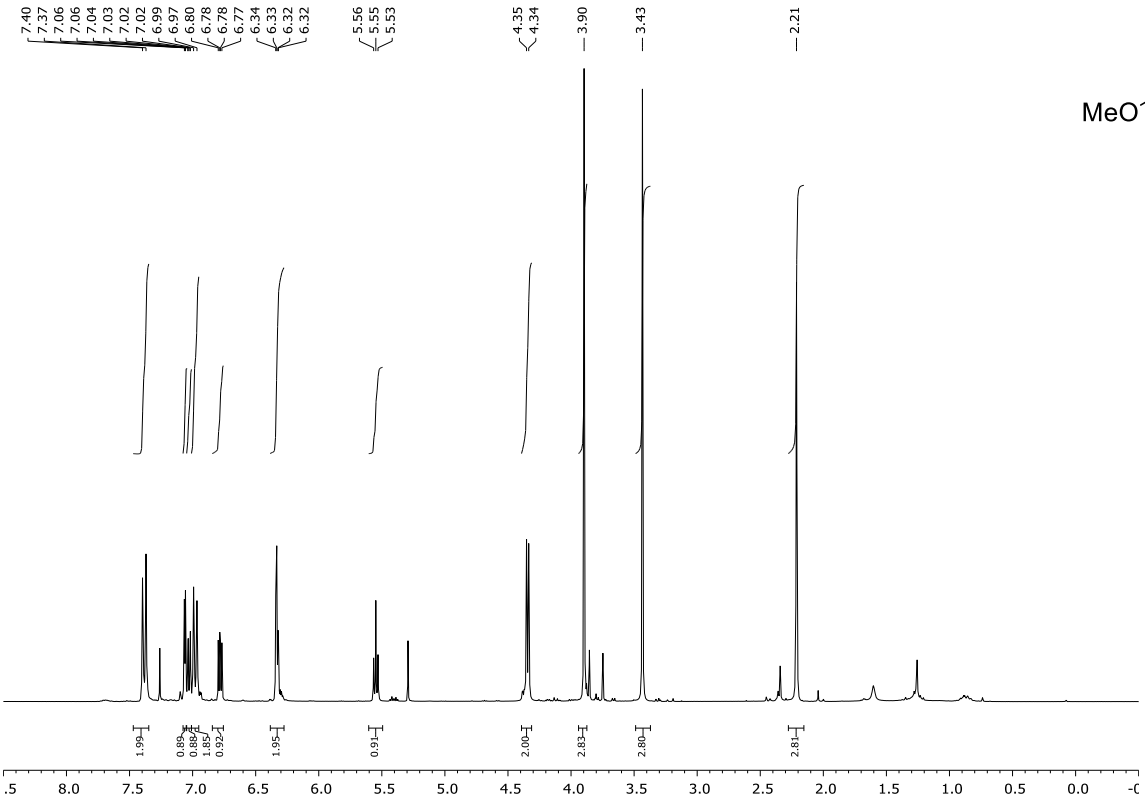
75 MHz DEPT-135 Spectrum of compound **12a** ($CDCl_3$, 300 K)



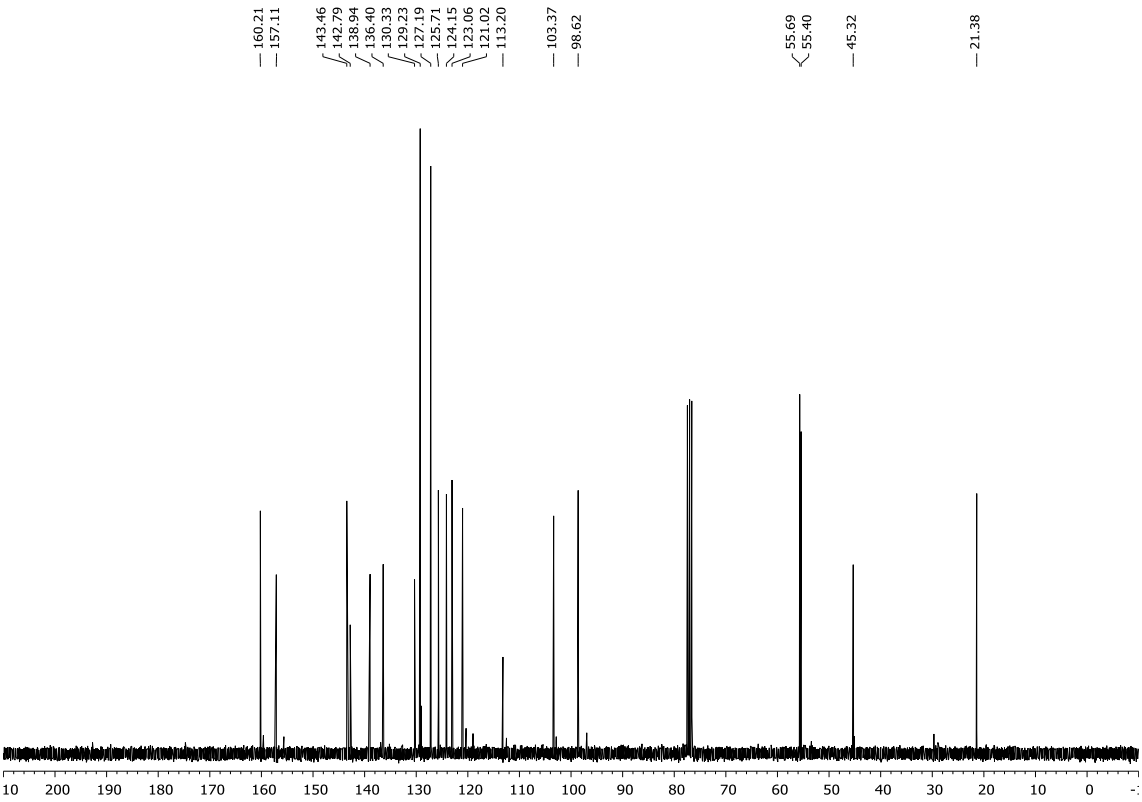
300 MHz ^{1}HNMR Spectrum of compound **12b** ($CDCl_3$, 300 K)



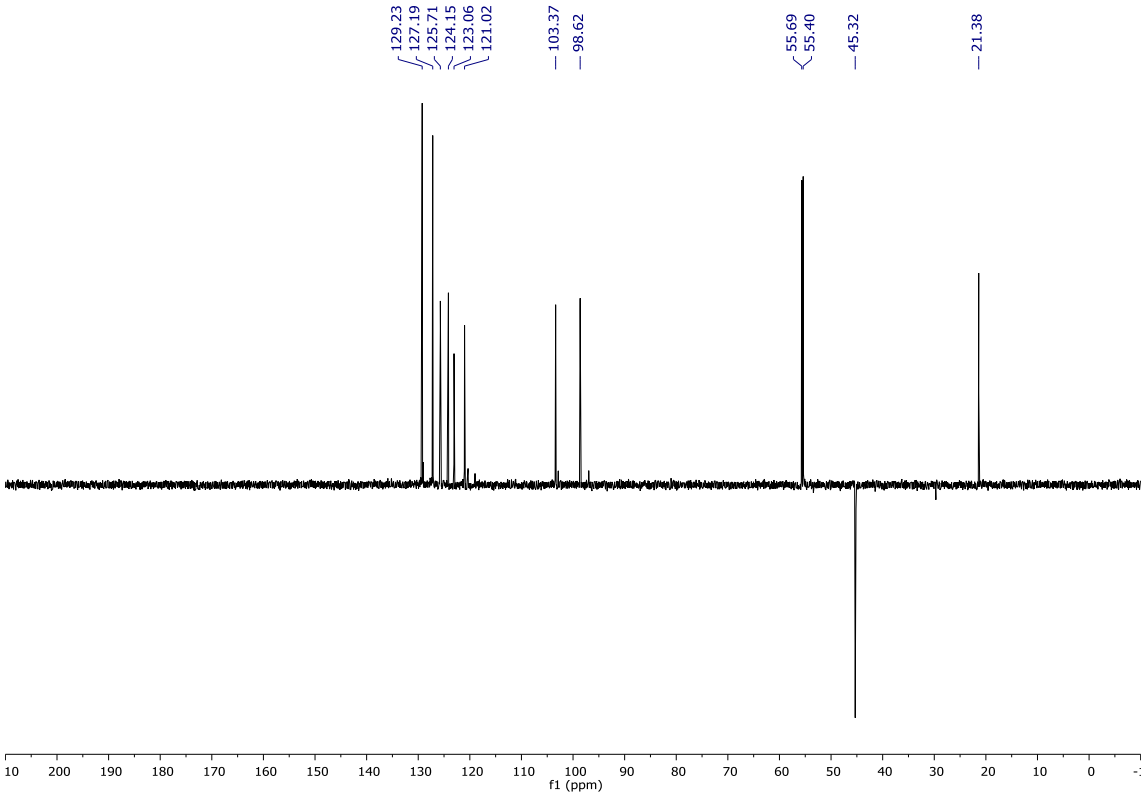
12b



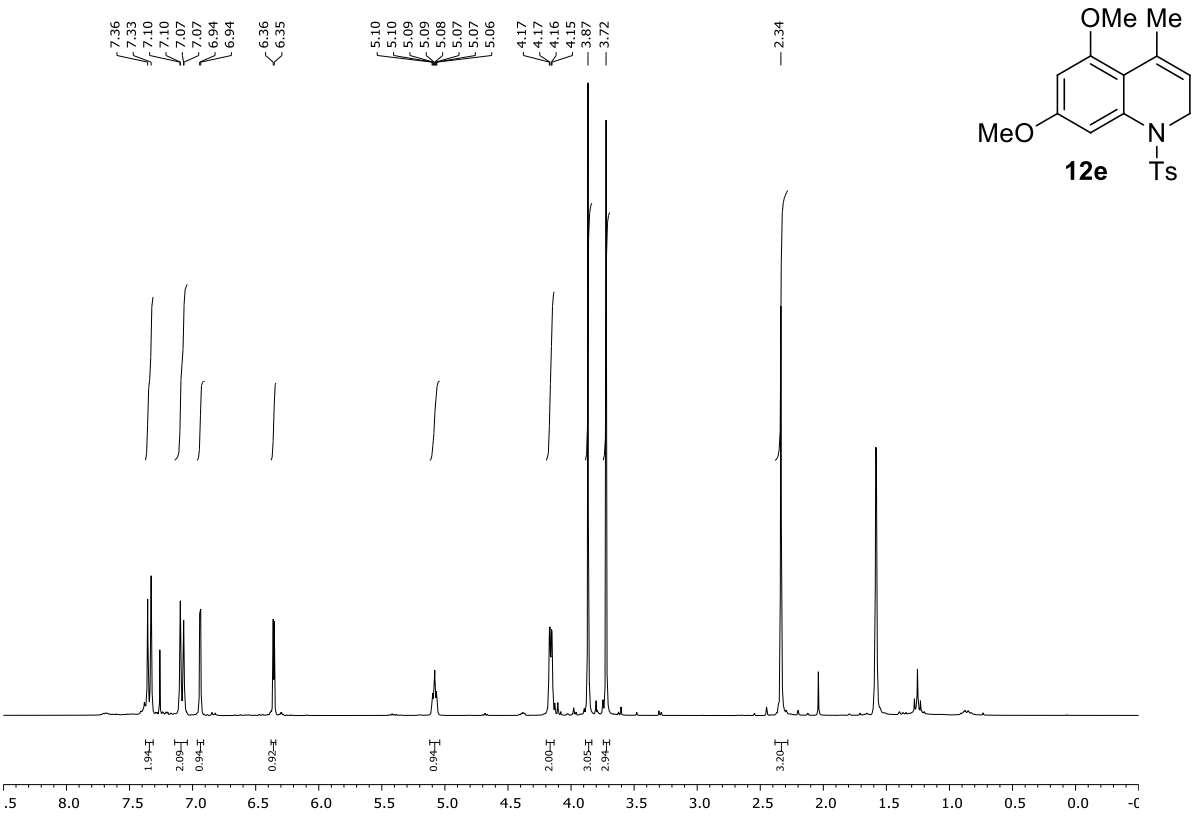
75 MHz ^{13}CNMR Spectrum of compound **12b** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **12b** ($CDCl_3$, 300 K)

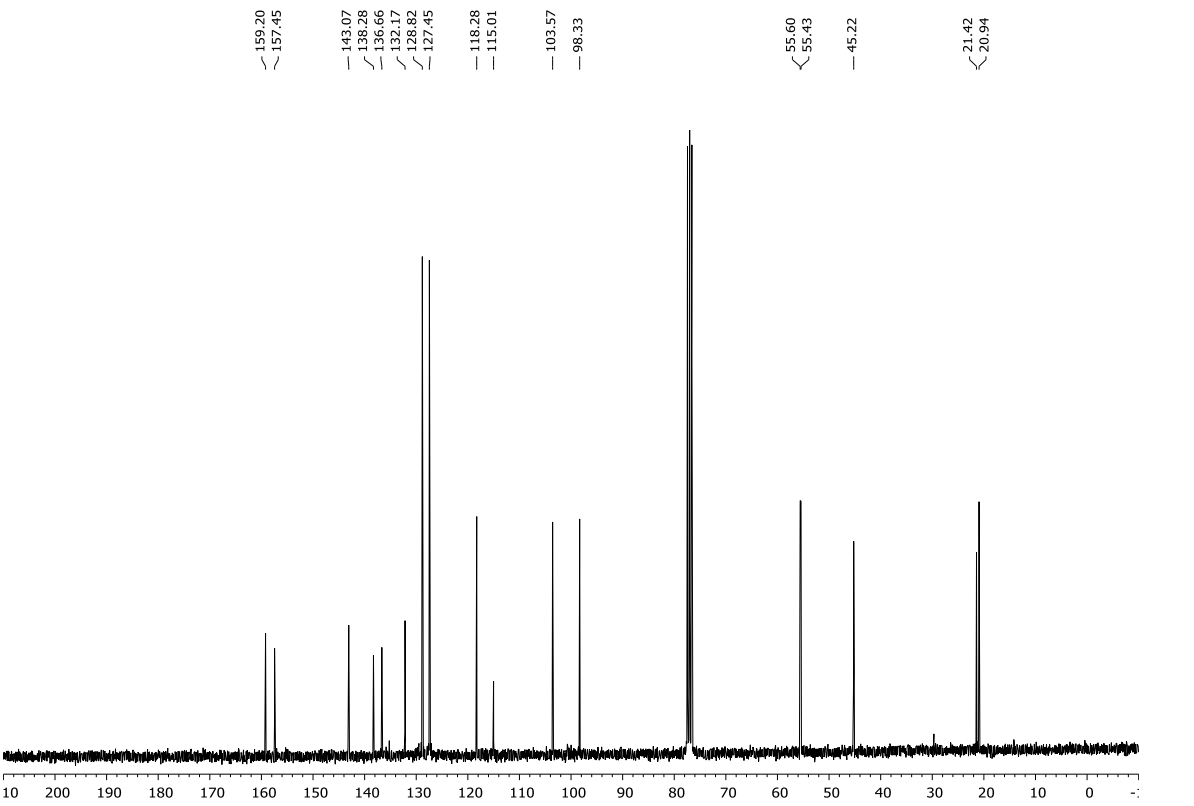


300 MHz ^{1}HNMR Spectrum of compound **12e** ($CDCl_3$, 300 K)



12e

75 MHz ^{13}CNMR Spectrum of compound **12e** ($CDCl_3$, 300 K)



75 MHz DEPT-135 Spectrum of compound **12e** ($CDCl_3$, 300 K)