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Supporting Information

N-Heterocyclic Carbene Copper(I) Complex-Catalyzed Synthesis of 2-Aryl Benzoxazoles and Benzothiazoles.

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1. General Information

All reagents were used as purchased from commercial sources without further purification. All reactions were performed under an air atmosphere in standard dried glassware and monitored by thin-layer chromatography using E. Merck silica gel 60 F254 pre-coated plates (0.25 mm). Flash chromatography was performed using silica gel (230-400 mesh, Merck). ^{1}H and ^{13}C NMR spectra were recorded on BRUKER AVANCE III HD-400 (11.74 T, 400 MHz to ^{1}H and 126 MHz to ^{13}C) NMR spectrometers using the residual proton or the carbon signal of the deuterated solvent as an internal standard.

2. Experimental Procedures and Characterization Data

2.1 Synthesis of (IPr)CuCl (2).[1]

A mixture of 1,3-bis(2,6-diisopropylphenyl)imidazolium chloride **1** (200 mg, 0.47 mmol) and Cu_2O (50 mg, 0.35 mmol) in dioxane (8 mL) was stirred at 100 °C for 16 hours. The reaction mixture was cooled to room temperature and the remaining Cu_2O was removed by filtration. After evaporation of the solvent, complex **2** was obtained as a light brown solid (172 mg, 75%); mp 295-296 °C (lit.[2] >300 °C); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (t, *J* = 7.7 Hz, 2H), 7.29 (d, *J* = 7.7 Hz, 4H), 7.13 (s, 2H), 2.49-2.63 (m, *4*H), 1.30 (d, *J* = 6.8 Hz, 12H), 1.22 (d, *J* = 6.8 Hz, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.6, 134.4, 130.6, 124.2, 123.1, 28.7, 24.8, 23.9.

2.2 Synthesis of amides

General procedure for synthesis of amides. To a solution of *ortho*-haloaniline (1.0 equiv.) in dry THF at room temperature was added acyl chloride (1.1 equiv.) and dry triethylamine (1.0 equiv.) The reaction mixture was stirred for 24 h, diluted with ethyl acetate, washed with 5% $NaHCO_3$, brine and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel to give the desired amide.

***N*-(2-Iodophenyl)benzamide (3I)** 2-Iodoaniline (800 mg, 3.65 mmol, 1.0 equiv.), benzoyl chloride (0.47 mL, 4.02 mmol, 1.1 equiv.), THF (9 mL), triethylamine (0.50 mL, 3.65 mmol, 1.0 equiv.). Yield: 91% (1.08 g, 3.34 mmol); white solid; mp 132-133 °C (lit.[3] 133-134 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.30 (s br, 1H), 7.98 (td, *J* = 4.0, 2.4 Hz, 2H), 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.62 – 7.47 (m, 3H), 7.40 (td, *J* = 8.2, 1.5 Hz, 1H), 6.88 (td, *J* = 7.7, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30, 138.8, 138.3, 134.5, 132.2, 129.4, 129.0, 127.2, 126.1, 121.8, 90.3.

***N*-(2-Bromophenyl)benzamide (3Br)** 2-Bromoaniline (760 mg, 4.41 mmol, 1.0 equiv.), benzoyl chloride (0.56 mL, 4.84 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.41 mmol, 1.0 equiv.). Yield: 82% (1.0 g, 3.62 mmol); white solid; mp 108-109 °C (lit.[3] 107-108 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.47 (s br, 1H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.63-7.48 (m, 4H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 135.8, 134.6, 132.3, 132.2, 129.0, 128.6, 127.1, 125.3, 121.8, 113.8.

***N*-(2-Chlorophenyl)benzamide (3Cl)** 2-Chloroaniline (1.0 g, 7.84 mmol, 1.0 equiv.), benzoyl chloride (1.0 mL, 8.62 mmol, 1.1 equiv.), THF (10 mL), triethylamine (1.10 mL, 7.84 mmol, 1.0 equiv.). Yield: 69% (1.0 g, 3.62 mmol); white solid; mp 98 °C (lit.[3] 97-98).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.46 (s br, 1H), 7.93 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.63 - 7.47 (m, 3H), 7.42 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.34 (td, *J* = 8.2, 1.4 Hz, 1H), 7.08 (td, *J* = 7.7, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 134.8, 134.6, 132.2, 129.0, 128.9, 127.9, 127.1, 124.8, 123.1, 121.5.

***N*-(2-Iodo-4-methylphenyl)benzamide (5aI)** 2-Iodo-4-methylaniline (1.0 g, 4.29 mmol, 1.0 equiv.), benzoyl chloride (0.67 mL, 5.15 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.29 mmol, 1.0 equiv.). Yield: 96% (956 mg, 4.1 mmol); white solid; mp 151-152 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 8.3, Hz, 1H), 8.21 (s br, 1H), 7.97 (d, *J* = 7.8 Hz, 2H), 7.65 (s, 1H), 7.63 – 7.46 (m, 3H), 7.21 (d, *J* = 8.3, 1H), 2.31 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 139.0, 136.1, 135.8, 134.7, 132.1, 130.2, 130.1, 128.9, 128.5, 127.2, 121.7, 90.4, 20.4.

***N*-(2-Bromo-4-methylphenyl)benzamide (5aBr)** 2-Bromo-4-methylaniline (1.0 g, 5.37 mmol, 1.0 equiv.), benzoyl chloride (0.77 mL, 5.91 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.75 mL, 5.37 mmol, 1.0 equiv.). Yield: 79% (1.24 g, 4.3 mmol); white solid; mp 148-149 °C (lit.[3] 149-150 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 8.5, Hz, 1H), 8.15 (s br, 1H), 7.93 (d, *J* = 7.5 Hz, 1H), 7.60 – 7.48 (m, 3H), 7.40 (s, 1H), 7.17 (d, *J* = 8.4, 1H), 2.32 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 135.4, 134.7, 133.3, 132.5, 132.1, 129.2, 128.9, 127.1, 121.7, 113.7, 20.6.

***N*-(4-Chloro-2-iodophenyl)benzamide (5bI)** 4-Chloro-2-iodoaniline (1.0 g, 3.95 mmol, 1.0 equiv.), benzoyl chloride (0.57 mL, 4.34 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.55 mL, 3.95 mmol, 1.0 equiv.). Yield: 89% (1.25 g, 3.5 mmol); white solid; mp 97-98 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.8, Hz, 1H), 8.26 (s br, 1H), 7.96 (d, *J* = 7.6 Hz, 2H), 7.65 – 7.45 (m, 4H), 7.39 (d, *J* = 8.8, Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 137.9, 137.1, 134.2, 133.8, 132.4, 130.2, 129.5, 129.0, 128.5, 127.2, 122.1.

***N*-(4-Chloro-2-bromophenyl)benzamide (5bBr)** 4-Chloro-2-bromoaniline (1.0 g, 4.80 mmol, 1.0 equiv.), benzoyl chloride (0.61 mL, 5.3 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.67 mL, 4.80 mmol, 1.0 equiv.). Yield: 79% (1.18 g, 3.8 mmol); white solid; mp 125 °C (lit.[3] 122-124).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (d, *J* = 8.9, Hz, 1H), 8.41 (s br, 1H), 7.92 (d, *J* = 7.9 Hz, 2H), 7.64 - 7.44 (m, 4H), 7.35 (d, *J* = 8.9, Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 134.6, 134.3, 133.7, 132.4, 131.7, 130.2, 129.6, 129.0, 128.7, 128.5, 127.1, 122.3.

***N*-(4-Cyano-2-iodophenyl)benzamide (5c)** 4-Amino-3-iodobenzonitrile (700 mg, 2.87 mmol, 1.0 equiv.), benzoyl chloride (0.4 mL, 3.15 mmol, 1.1 equiv.), THF (8 mL), triethylamine (0.40 mL, 2.87 mmol, 1.0 equiv.). Yield: 92% (920 mg, 2.64 mmol); white solid; mp 141-142 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.75 (d, *J* = 8.7 Hz, 1H), 8.56 (s br, 1H), 7.86 - 7.79 (m, 2H), 7.25 (d, *J* = 1.9 Hz, 1H), 7.10 – 6.88 (m, 2H), 6.70 – 6.55 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.30, 138.8, 134.6, 133.9, 132.6, 132.2, 131.9, 128.9, 127.0, 123.0, 121.1, 116.8, 107.1.

***N*-(4-Fluoro-2-iodophenyl)benzamide (5d)** 4-Fluoro-2-iodoaniline (800 mg, 3.38 mmol, 1.0 equiv.), benzoyl chloride (0.5 mL, 4.05 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.47 mL, 3.38 mmol, 1.0 equiv.). Yield: 88% (920 mg, 2.99 mmol); white solid; mp 152-153 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (dd, *J* = 9.1, 1.5 Hz, 1H), 8.15 (s br, 1H), 7.94 (dd, *J* = 7.4, 1.6 Hz, 2H), 7.62 - 7.50 (m, 4H), 7.17 – 7.10 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 158.6, 134.9, 134.2, 132.3, 129.0, 127.1, 125.3, 122.8, 116.2, 90.0.

***N*-(2-Iodo-4-nitrophenyl)benzamide (5e)** 2-Iodo-4-nitroaniline (310 mg, 1.17 mmol, 1.0 equiv.), benzoyl chloride (0.15 mL, 1.29 mmol, 1.1 equiv.), THF (6 mL), triethylamine (0.16 mL, 1.17 mmol, 1.0 equiv.). Yield: 90% (386 mg, 1.05 mmol); white solid; mp 177 °C (lit.[4] 177-178.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (dd, *J* = 9.1, 1.6 Hz, 1H), 8.71 (d, *J* = 2.5 Hz, 1H), 8.60 (s br, 1H), 8.25 (dd, *J* = 9.3, 2.4 Hz, 1H), 7.96 (d, *J* = 6.5 Hz, 2H), 7.64 - 7.50 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.5, 144.2, 143.7, 134.3, 133.8, 133.1, 129.5, 127.4, 127.3, 125.3, 119.7, 88.0.

4-Chloro-*N*-(2-iodophenyl)benzamide (5fI) 2-Iodoaniline (1.0 g, 4.57 mmol, 1.0 equiv.), 4-chlorobenzoyl chloride (0.64 mL, 5.02 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.57 mmol, 1.0 equiv.). Yield: 73% (1.2 g, 3.35 mmol); white solid; mp 151 °C (lit.[3] 150-151).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 8.2, Hz, 1H), 8.22 (s br, 1H), 7.91 (d, *J* = 7.7 Hz, 2H), 7.82 (d, *J* = 8.0, Hz, 1H), 7.50 (d, *J* = 7.7, Hz, 2H), 7.41 (td, *J* = 8.2, 1.5 Hz, 1H), 6.90 (td, *J* = 8.2, 1.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.3, 138.9, 138.6, 138.0, 132.9, 131.0, 129.5, 129.3, 128.6, 121.8, 90.4.

4-Chloro-*N*-(2-bromophenyl)benzamide (5fBr) 2-Bromoaniline (1.0 g, 5.81 mmol, 1.0 equiv.), 4-chlorobenzoyl chloride (0.8 mL, 6.39 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.80 mL, 5.81 mmol, 1.0 equiv.). Yield: 69% (1.31 g, 3.99 mmol); white solid; mp 133-134 °C (lit.[3] 135-136).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.5, 1.3 Hz, 1H), 8.23 (s br, 1H), 7.93 (d, *J* = 8.4 Hz, 2H), 7.80 (dd, *J* = 8.4, 1.3 Hz, 1H) 7.50 (d, *J* = 8.4 Hz, 2H) 7.41 (td, *J* = 8.4, 1.3 Hz, 1H), 6.88 (td, *J* = 7.9, 1.4 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.2, 138.9, 138.6, 138.1, 132.8, 131.2, 129.5, 129.3, 128.5, 121.7, 90.5.

***N*-(2-Iodophenyl)-4-methoxybenzamide (5gI)** 2-Iodoaniline (1.0 g, 4.57 mmol, 1.0 equiv.), 4-methoxybenzoyl chloride (0.68 mL, 5.02 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.57 mmol, 1.0 equiv.). Yield: 67% (1.08 g, 3.06 mmol); white solid; mp 152-153 °C (lit.[3] 151-152).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 8.2, Hz, 1H), 8.26 (s br, 1H), 8.02 - 7.95 (m, 2H), 7.83 (d, *J* = 8.0, Hz, 1H), 7.42 (td, *J* = 8.2, 1.4, Hz, 1H), 7.09 – 7.02 (m, 2H), 6.90 (td, *J* = 8.1, 1.4 Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 162.8, 138.9, 138.5, 132.6, 129.5, 129.1, 125.8, 121.8, 114.2, 90.4, 55.5.

***N*-(2-Bromophenyl)-4-methoxybenzamide (5gBr)** 2-Bromoaniline (1.0 g, 5.81 mmol, 1.0 equiv.), 4-methoxybenzoyl chloride (0.87 mL, 6.39 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.80 mL, 5.81 mmol, 1.0 equiv.). Yield: 59% (1.04 g, 3.40 mmol); white solid; mp 148 °C (lit.[3] 147-148).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 8.1, 8.4 Hz, 1H), 8.50 (s br, 1H), 7.95 - 7.90 (m, 2H), 7.56 (dd, *J* = 8.0, 8.1 Hz, 1H), 7.36 (td, *J* = 8.1, 1.4, Hz, 1H), 7.05 - 6.95 (m, 3H), 3.86 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 162.8, 135.9, 132.2, 132.4, 128.9, 128.5, 126.6, 125.0, 121.8, 114.2, 113.7, 113.6, 55.5.

***N*-(2-Iodophenyl)-3,4-dimethoxybenzamide (5h)** 2-Iodoaniline (1.0 g, 4.57 mmol, 1.0 equiv.), 3,4-dimethoxybenzoyl chloride (0.68 mL, 5.02 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.57 mmol, 1.0 equiv.). yield: 67% (1.08 g, 3.06 mmol); white solid; mp 154 °C (lit.[4] 154-155).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 8.2 Hz, 1H), 8.25 (s br, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 2H), 7.40 (t, *J* = 7.7, Hz, 1H), 3.98 (s, 3H), 3.96 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.8, 152.4, 149.2, 138.7, 138.5, 129.5, 126.9, 126.0, 122.0, 119.9, 110.7, 110.5, 90.4, 56.0, 56.1.

***N*-(2-Iodophenyl)-4-methylbenzamide (5iI)** 2-Iodoaniline (1.0 g, 4.57 mmol, 1.0 equiv.), 4-methylbenzoyl chloride (0.66 mL, 5.02 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.57 mmol, 1.0 equiv.). Yield: 84% (1.29 g, 3.82 mmol); white solid; mp 112-113 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 8.4, 1.2 Hz, 1H), 8.29 (s br, 1H), 7.90 (d, *J* = 8.0 Hz, 2H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.38 (d, *J* = 8.0, Hz, 2H), 6.88 (td, *J* = 7.6, 1.2 Hz, 1H), 2.45 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 142.6, 138.8, 131.7, 130.4, 129.9, 129.4, 129.2, 127.1, 121.5, 90.2, 21.4.

***N*-(2-Bromophenyl)-4-methylbenzamide (5iBr)** 2-Bromoaniline (1.0 g, 5.81 mmol, 1.0 equiv.), 4-methylbenzoyl chloride (0.66 mL, 5.02 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.80 mL, 5.81 mmol, 1.0 equiv.). Yield: 79% (1.33 g, 4.58 mmol); white solid; mp 68 °C. (lit.[5] 69-71).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (dd, *J* = 8.3 Hz, 1.3 1H) 8.45 (s, br, 1H), 7.82 (d, *J* = 7.9 Hz, 2H), 7.57 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.38 (m, 3H) 7.02 (td, *J* = 7.8, 1.2 Hz, 1H), 2.44 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3, 142.9, 136.0, 132.4, 131.9, 129.7, 128.7, 127.3, 127.2, 125.2, 121.9, 121.8, 113.8, 21.7.

***N*-(2-Iodophenyl)-2-methylbenzamide (5jI)** 2-Iodoaniline (1.0 g, 4.57 mmol, 1.0 equiv.), 2-methylbenzoyl chloride (0.65 mL, 5.02 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.60 mL, 4.57 mmol, 1.0 equiv.). Yield: 90% (1.39 g, 4.12 mmol); white solid; mp 124-125 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 7.9 Hz, 1H) 8.03 (s, br, 1H), 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.47 - 7.23 (m, 5H), 6.87 (td, *J* = 7.9, 1.4 Hz, 1H), 2.58 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.9, 138.9, 138.5, 137.0, 135.8, 131.5, 130.6, 129.3, 126.8, 126.2, 126.1, 122.1, 90.3, 20.18.

***N*-(2-Bromophenyl)-2-methylbenzamide (5jBr)** 2-Bromoaniline (1.0 g, 5.81 mmol, 1.0 equiv.), 2-methylbenzoyl chloride (0.83 mL, 6.39 mmol, 1.1 equiv.), THF (10 mL), triethylamine (0.80 mL, 5.81 mmol, 1.0 equiv.). Yield: 89% (1.39 g, 5.17 mmol); white solid; mp 120-121 °C. (lit.[5] 121-123).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (d, *J* = 8.1 Hz, 1H) 8.03 (s, br, 1H), 7.56 (dd, *J* = 8.0, 7.7 Hz, 1H), 7.45 - 7.22 (m, 5H), 7.02 (td, *J* = 8.0, 7.7 Hz, 1H), 2.55 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.5, 137.0, 136.1, 132.4, 131.8, 130.6, 128.7, 127.0, 126.0, 125.4, 122.3, 113.7, 14.5.

2.2 Synthesis of thioamides

General procedure for synthesis of thioamides. To a solution of amide (1.0 equiv.) in dry toluene at room temperature was added Lawesson's reagent (0.6 equiv.). The reaction mixture was refluxed for 3 h, then the solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel to give the desired thioamide.

***N*-(2-Iodophenyl)benzothioamide (7aI)** N-(2-Iodophenyl)benzamide (300 mg, 0.92 mmol, 1.0 equiv.), Lawesson's reagent (225 mg, 0.56 mmol, 0.6 equiv.), toluene (10 mL). Yield: 91% (200 mg, 0.59 mmol); yellow solid; mp 132-133 °C (lit.[3] 133-134 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.11 (s br, 1H), 8.25 (s br, 1H), 8.06 - 7.86 (m, 3H), 7.60 - 7.34 (m, 4H), 7.03 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.44, 142.41, 139.9, 139.4, 131.58, 129.4, 129.0, 128.8, 128.7, 128.0, 127.2, 127.0, 126.7, 95.1.

***N*-(2-Bromophenyl)benzothioamide (7aBr)** N-(2-Bromophenyl)benzamide (500 mg, 1.81 mmol, 1.0 equiv.), Lawesson's reagent (439 mg, 1.09 mmol, 0.6 equiv.), toluene (12 mL). Yield: 73% (386 mg, 1.32 mmol); yellow solid; mp 82-83 °C (lit.[3] 83-85 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (s br, 1H), 8.53 (s br, 1H), 7.91 (d, *J* = 6.5 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.31 (m, 4H), 7.16 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 142.1, 137.0, 132.9, 131.6, 128.7, 128.2, 127.9, 126.97, 125.9, 118.1.

***N*-(2-Chlorophenyl)benzothioamide (7aCl**) N-(2-Chlorophenyl)benzamide (400 mg, 1.73 mmol, 1.0 equiv.), Lawesson's reagent (419 mg, 1.04 mmol, 0.6 equiv.), toluene (12 mL). Yield: 68% (290 mg, 1.17 mmol); yellow solid; mp 134-135 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.10 (s br, 1H), 8.48 (s br, 1H), 7.67 (d, *J* = 6.0 Hz, 2H), 7.27 (m, 4H), 7.14 (t, *J* = 6.9 Hz, 1H), 7.07 - 6.98 (m, 1H), 7.16 (t, *J* = 7.7 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.0, 135.8, 131.5, 129.6, 128.7, 127.6, 127.4, 127.1, 126.9, 125.1, 99.9.

***N*-(2-Iodo-4-methylphenyl)benzothioamide (7b)** N-(2-Iodo-4-methylphenyl)benzamide (450 mg, 1.34 mmol, 1.0 equiv.), Lawesson's reagent (325 mg, 0.80 mmol, 0.6 equiv.), toluene (12 mL). Yield: 62% (292 mg, 0.83 mmol); yellow solid; mp 93-95 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (s br, 1H), 7.88 (s br, 1H), 7.74 (d, *J* = 6.4 Hz, 2H), 7.53 (s, 1H), 7.29 (d, *J* = 6.4 Hz, 1H), 7.24 (d, *J* = 6.8 Hz, 2H), 7.03 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.6, 139.2, 137.5, 131.5, 129.6, 128.7, 127.0, 126.4, 20.7.

***N*-(4-Chloro-2-iodophenyl)benzothioamide (7c)** N-(4-Chloro-2-iodophenyl)benzamide (500 mg, 1.40 mmol, 1.0 equiv.), Lawesson's reagent (339 mg, 0.84 mmol, 0.6 equiv.), toluene (15 mL). Yield: 55% (288 mg, 0.77 mmol); yellow solid; mp 125-127 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79 (s, 1H), 8.02 (s, 1H), 7.71 (d, *J* = 3.8 Hz, 2H), 7.67 (s, 1H), 7.35 - 7.27 (m, 2H), 7.20 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.7, 138.5, 133.0, 131.7, 129.0, 128.8, 128.2, 127.2, 126.9, 126.9, 94.9.

***N*-(4-Fluoro-2-iodophenyl)benzothioamide (7d)** N-(4-Fluoro-2-iodophenyl)benzamide (450 mg, 1.32 mmol, 1.0 equiv.), Lawesson's reagent (320 mg, 0.79 mmol, 0.6 equiv.), toluene (12 mL). Yield: 58% (273 mg, 0.76 mmol); yellow solid; mp 132-134 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.11 (s, 1H), 7.94 (d, *J* = 7.5, 2H), 7.63 (dd, *J* = 7.6, 2.3 Hz, 1H), 7.53 (m, 1H), 7.45 (m, 2H), 7.16 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.7, 159.2, 142.1, 136.5, 131.7, 130.8, 128.7, 128.1, 127.9, 127.0, 126.2, 126.0, 116.1, 115.9, 95.2.

4-Chloro-*N*-(2-bromophenyl)benzothioamide (7e) 4-Chloro-N-(2-bromophenyl)benzamide (450 mg, 1.13 mmol, 1.0 equiv.), Lawesson's reagent (273 mg, 0.68 mmol, 0.6 equiv.), toluene (10 mL). Yield: 72% (264 mg, 0.81 mmol); yellow solid; mp 133-134 °C.
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.51 (s, 1H), 7.84 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 3H), 7.19 (dd, *J* = 15.7, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.8, 141.0, 137.8, 136.8, 132.9, 128.9, 128.3, 128.2, 127.9, 125.6, 117.8.

***N*-(2-Bromophenyl)-4-methoxybenzothioamide (7f)** N-(2-Bromophenyl)-4-methoxybenzamide (400 mg, 1.30 mmol, 1.0 equiv.), Lawesson's reagent (317 mg, 0.78 mmol, 0.6 equiv.), toluene (10 mL). Yield: 89% (375 mg, 1.16 mmol); yellow solid; mp 125-126 °C (lit.[3] 124-126 °C).
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.20 (s, 1H), 8.60 (s, 1H), 8.00-7.94 (m, 2H), 7.69 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.45 (td, *J* = 8.2, 1.4 Hz, 1H), 7.20 (td, *J* = 8.1, 1.4 Hz, 1H), 7.06 - 6.93 (m, 2H), 3.88 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.2,162.7, 136.9, 132.7, 128.9, 127.6, 128.0, 126.0, 118.2, 114.2, 114.0, 55.5.

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2. V. Jurkauskas, J. P. Sadighi, S. L. Buchwald, *Org. Lett.*, 2003, **5**, 2417
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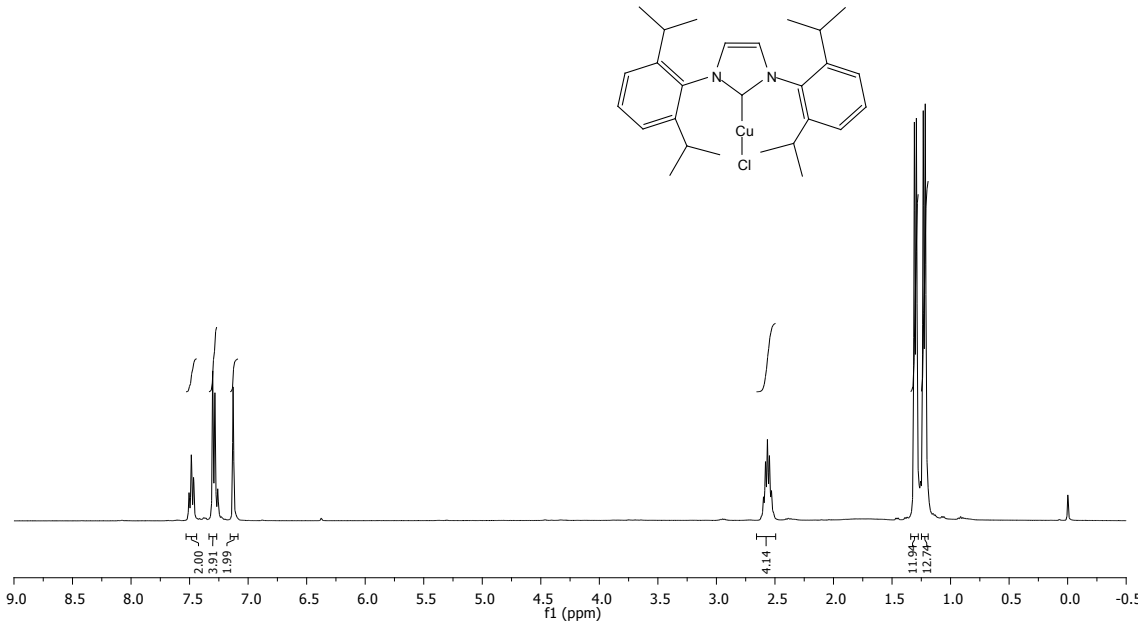
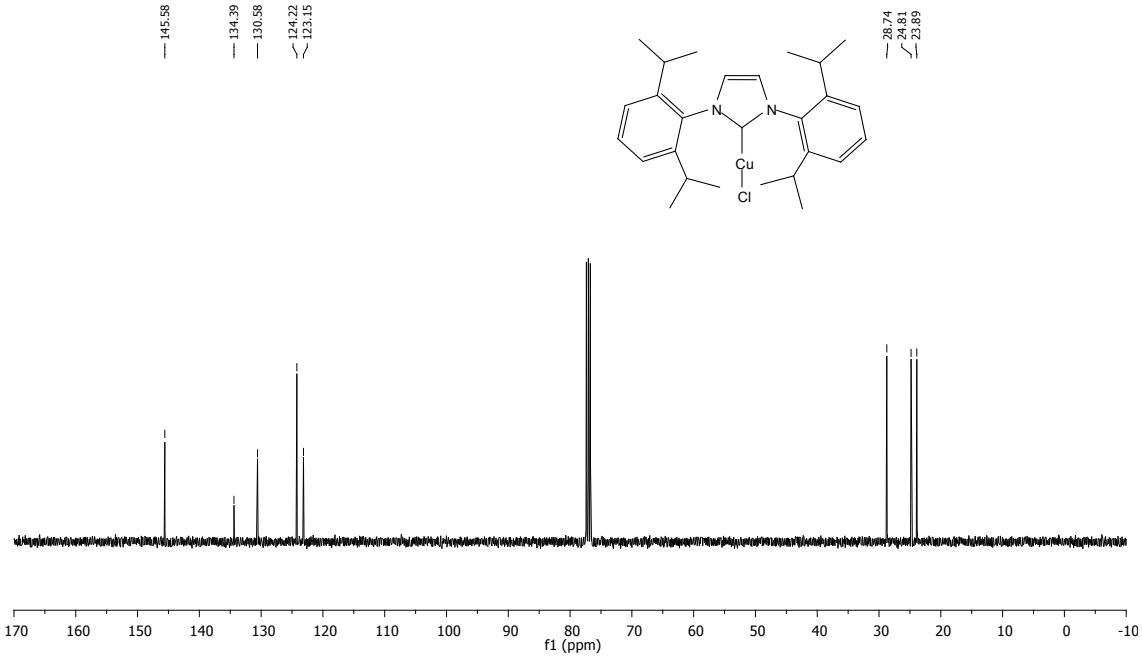
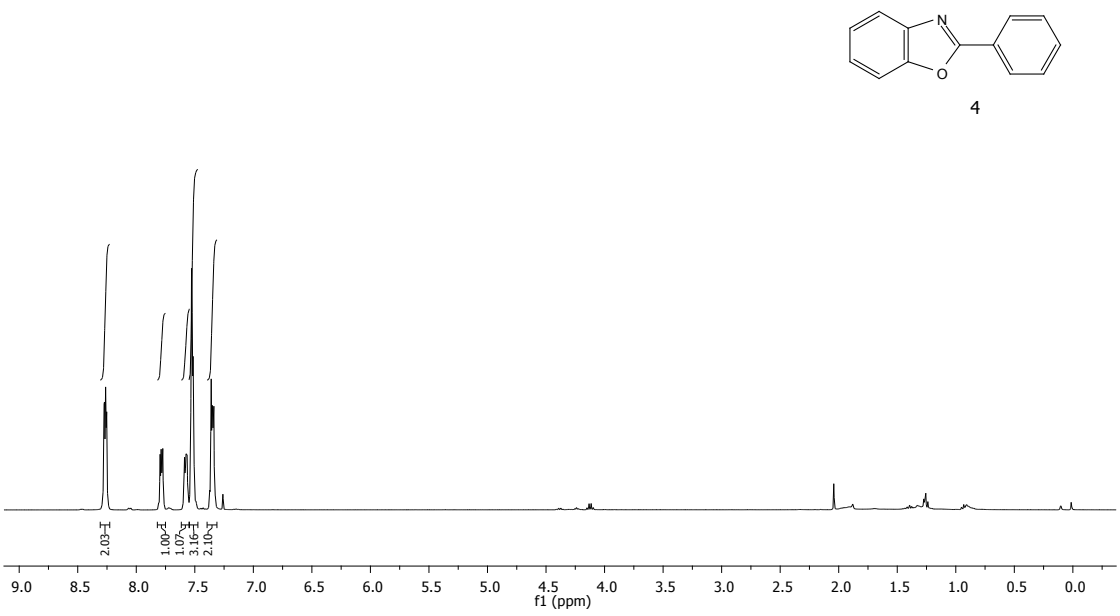
3. NMR Spectra of Catalyst, Benzoxazoles and Benzothiazole Products.

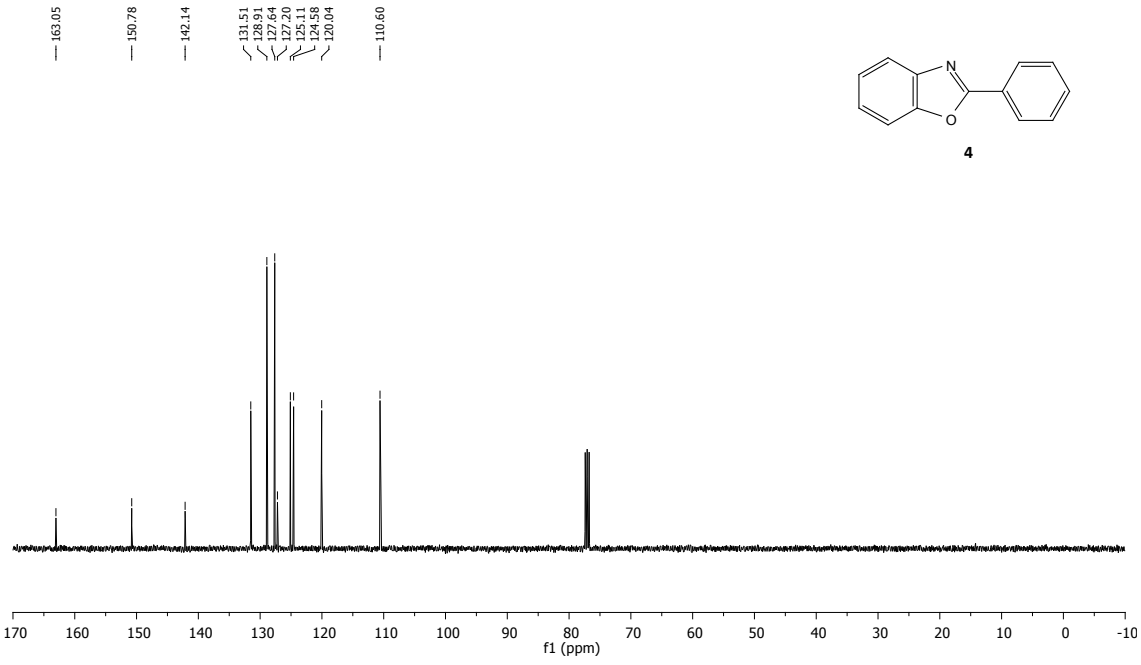
(IPr)CuCl (2)



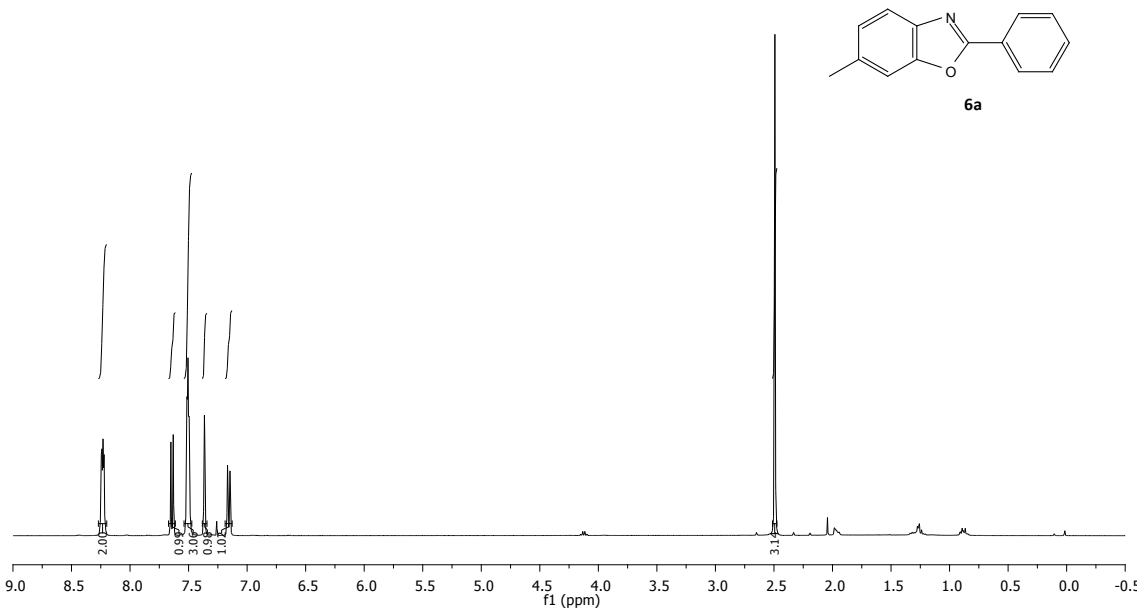


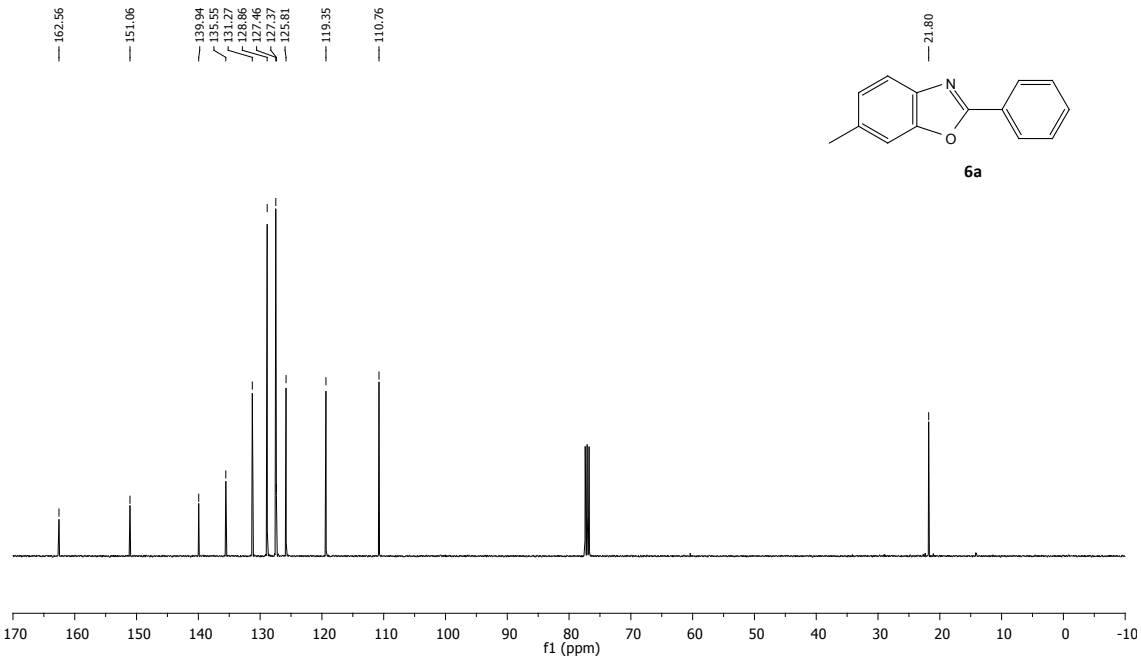
2-Phenylbenzoxazole (4)



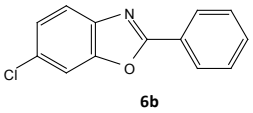


6-Methyl-2-phenylbenzoxazole (6a)

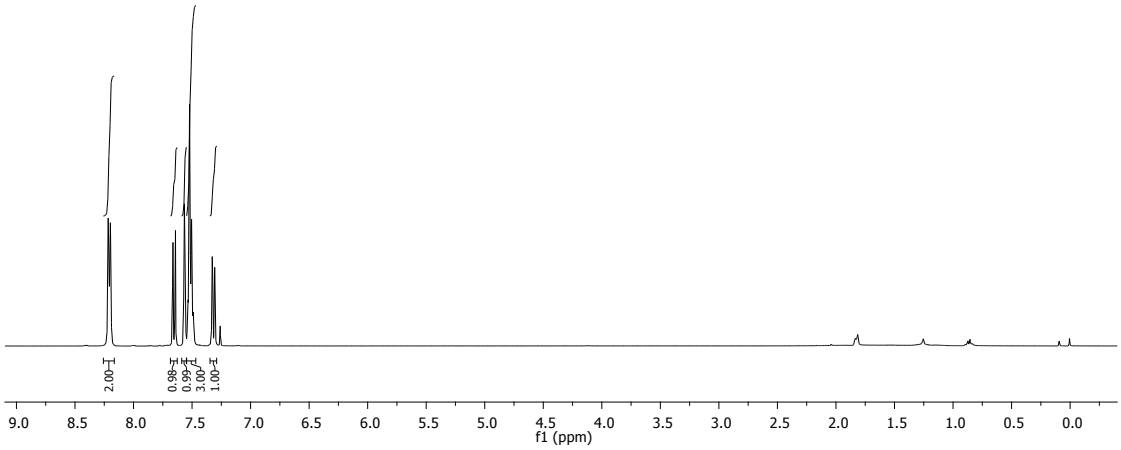


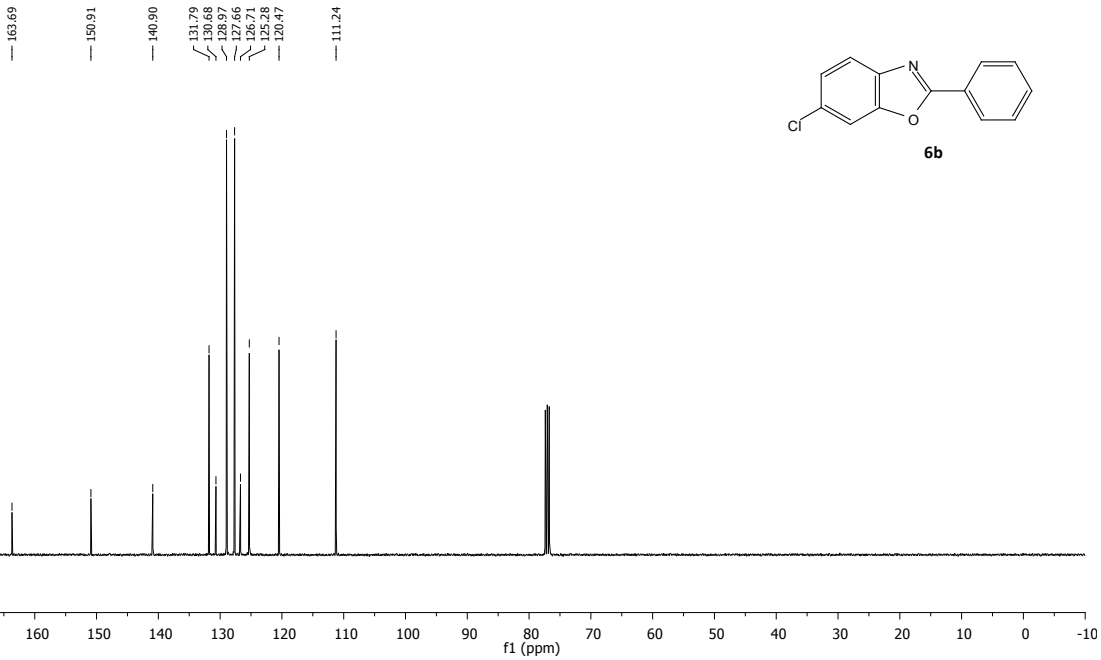


6-Chloro-2-phenylbenzoxazole (6b)



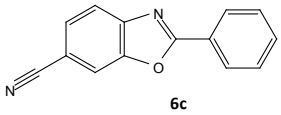
6b





6b

6-Cyano-2-phenylbenzoxazole (6c)



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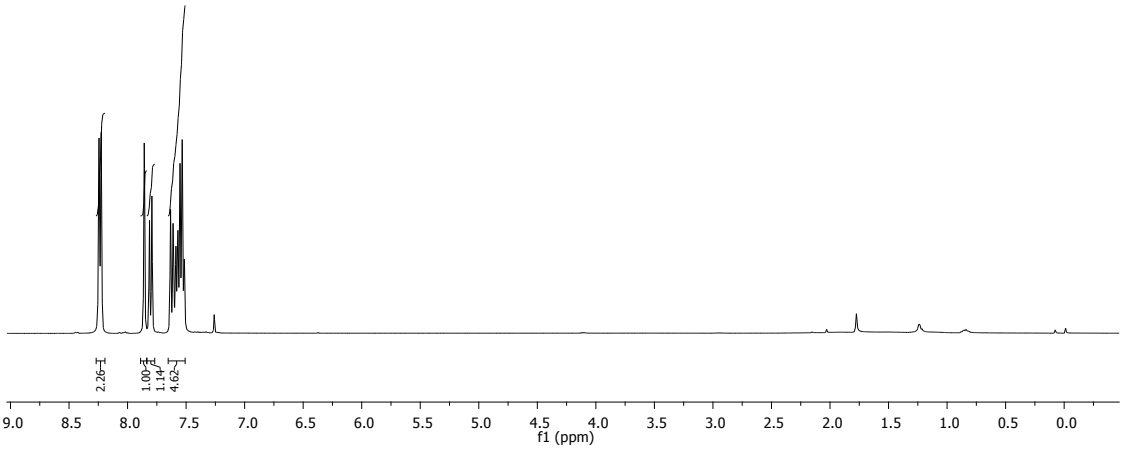
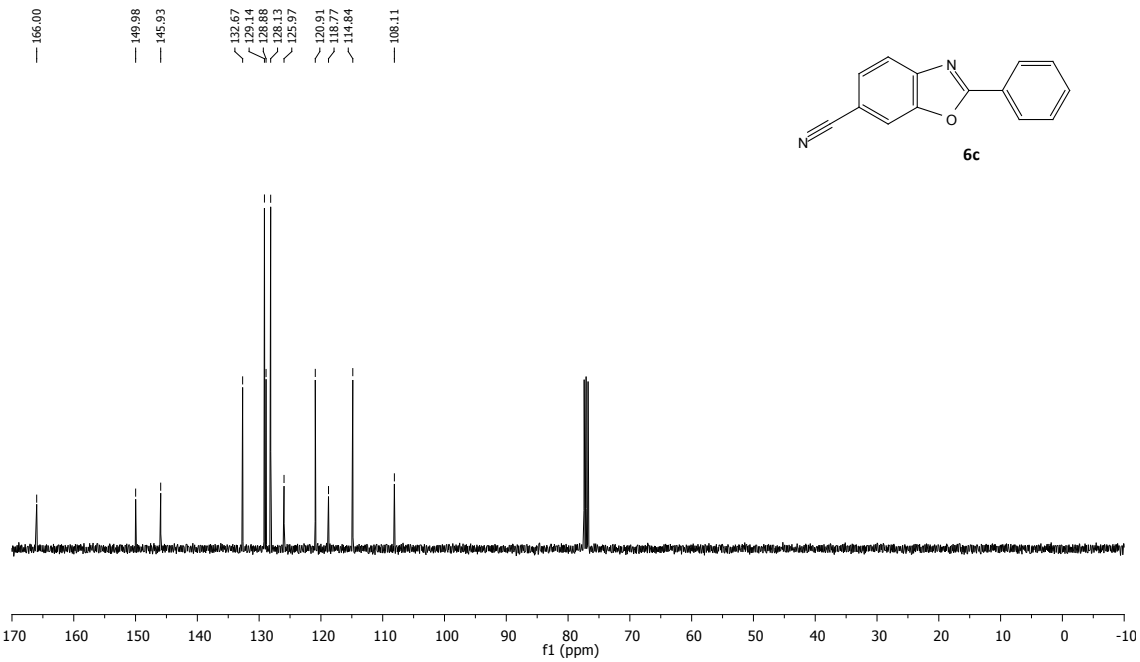
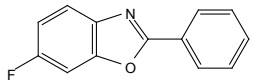


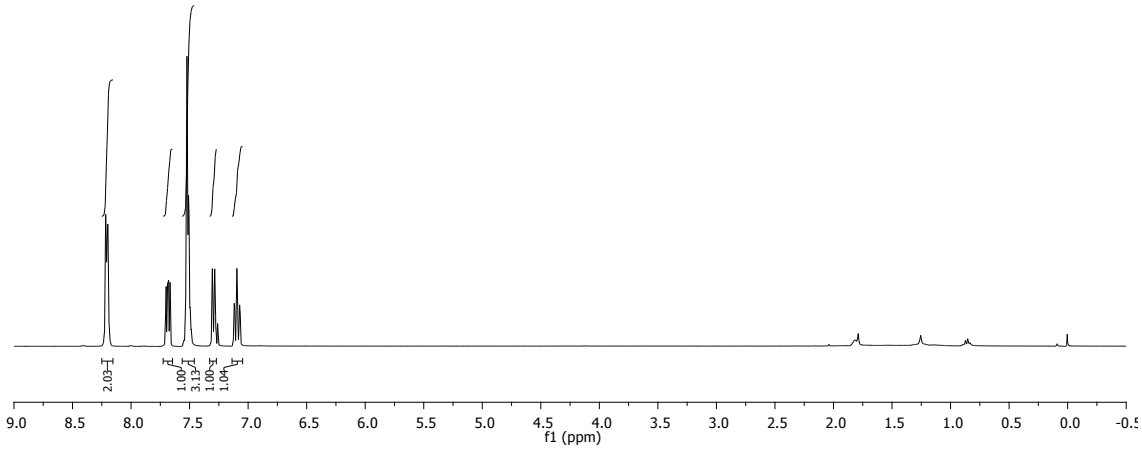


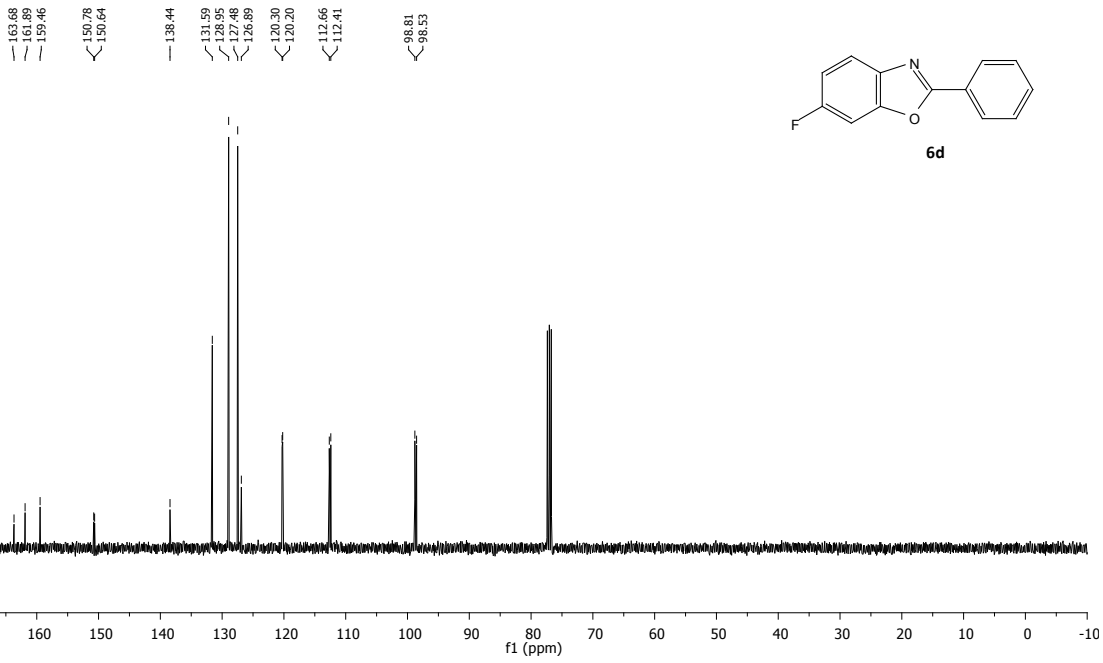
6c

6-Fluoro-2-phenylbenzoxazole (6d)



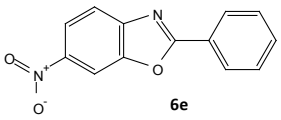
6d



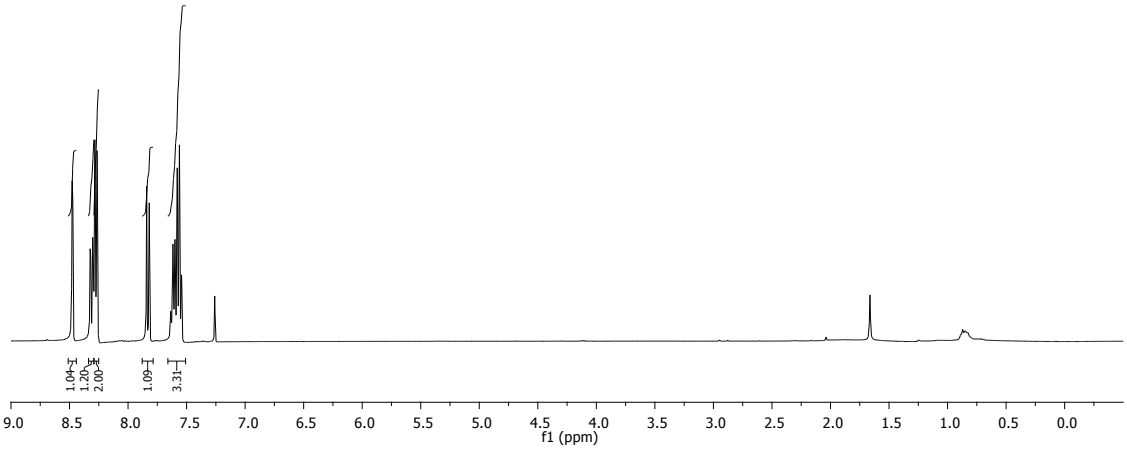


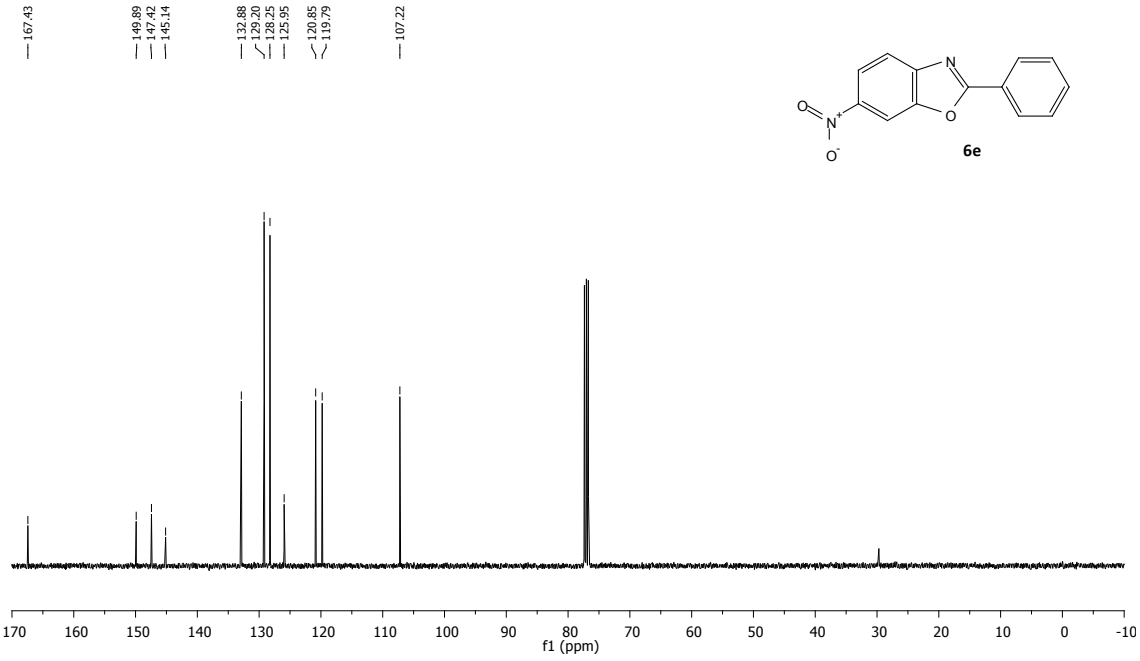
6d

6-Nitro-2-phenylbenzoxazole (6e)



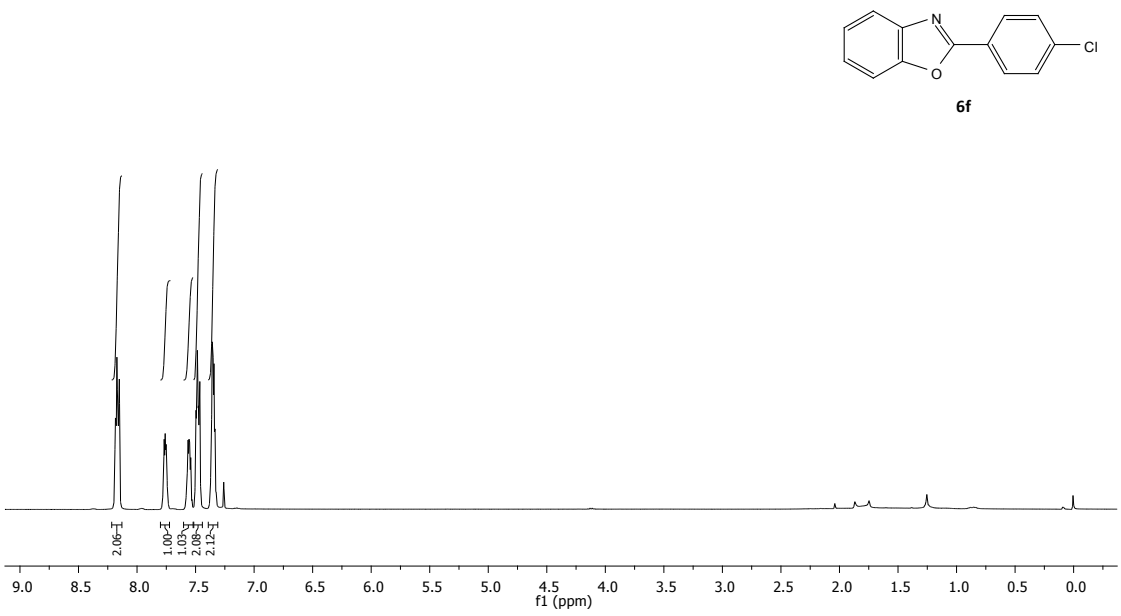
6e

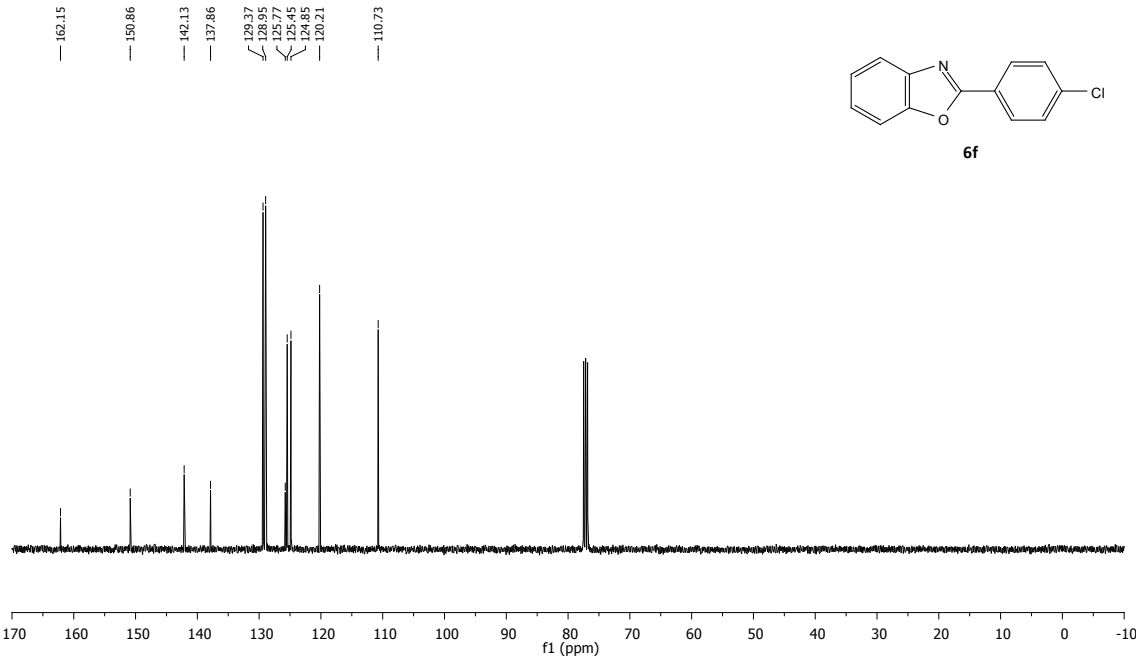




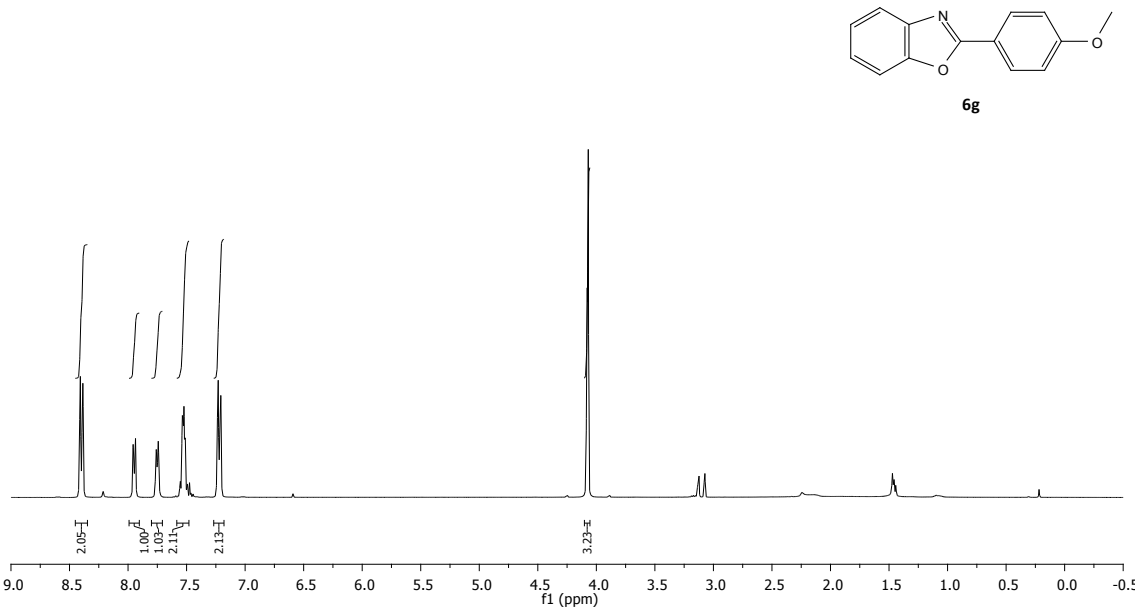
6e

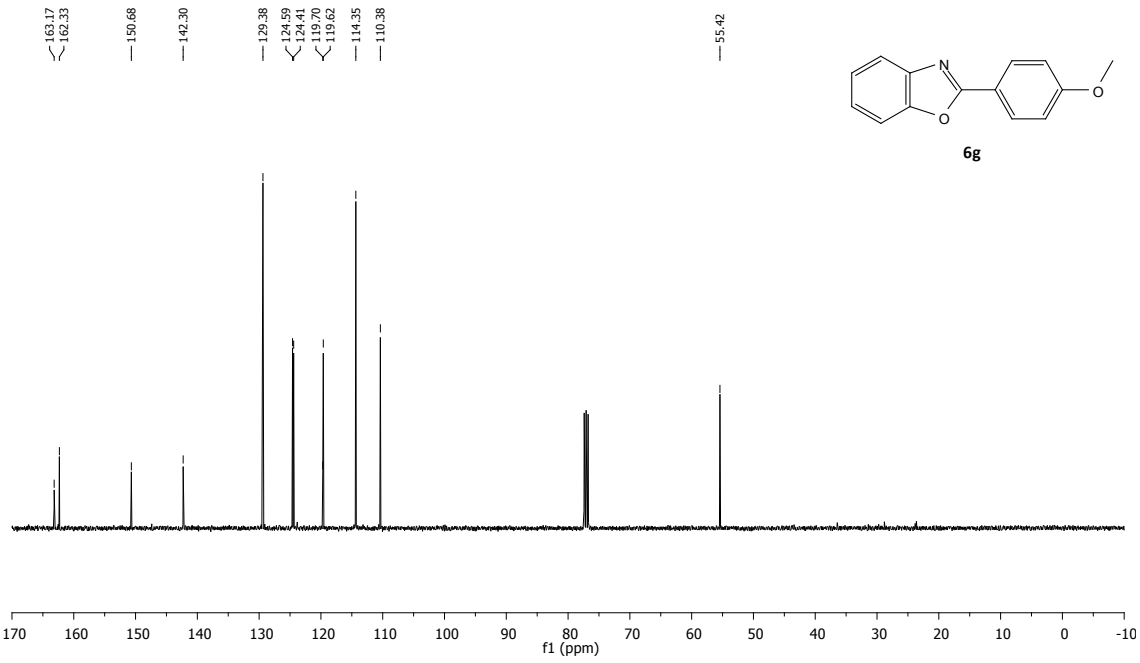
2-(4-Chlorophenyl)-benzoxazole (6f)



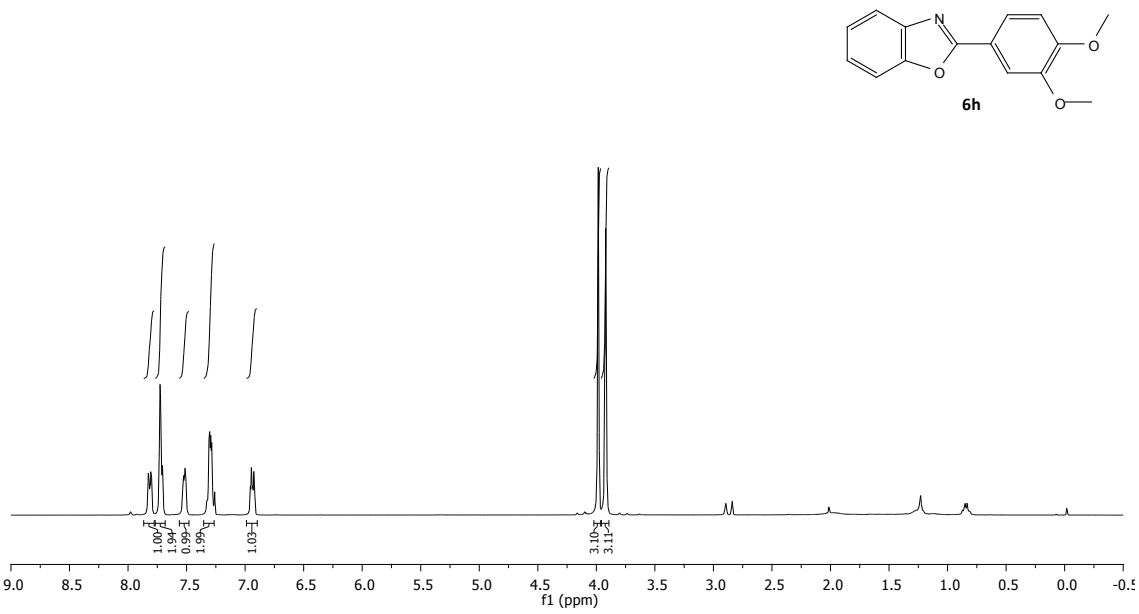


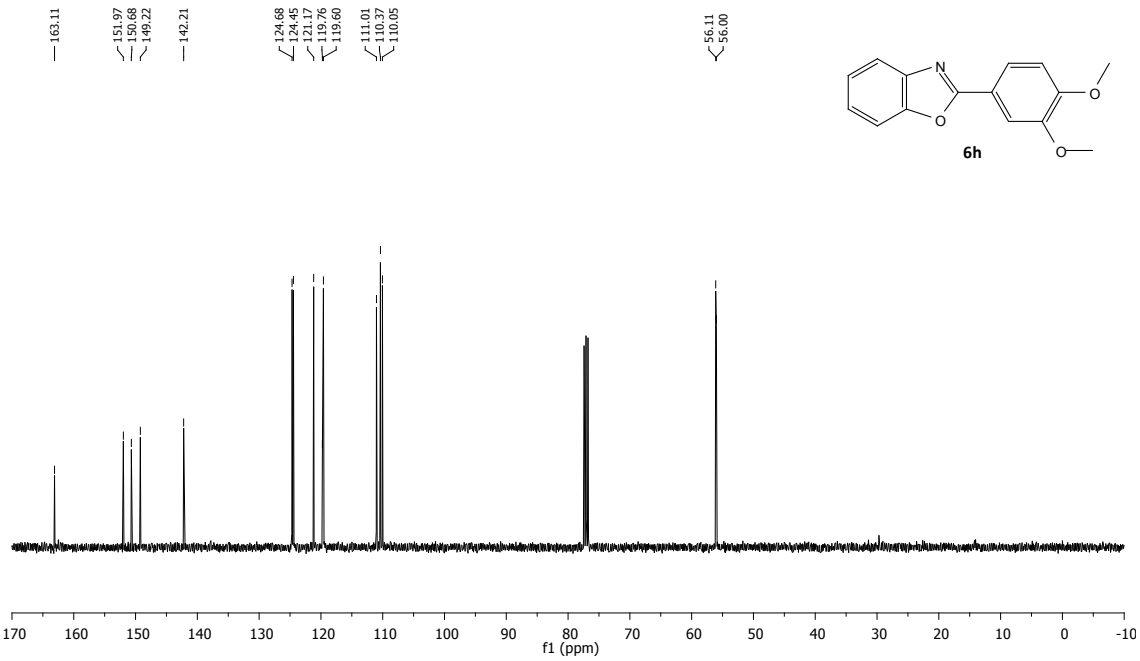
2-(4-Methoxyphenyl)-benzoxazole (6g)



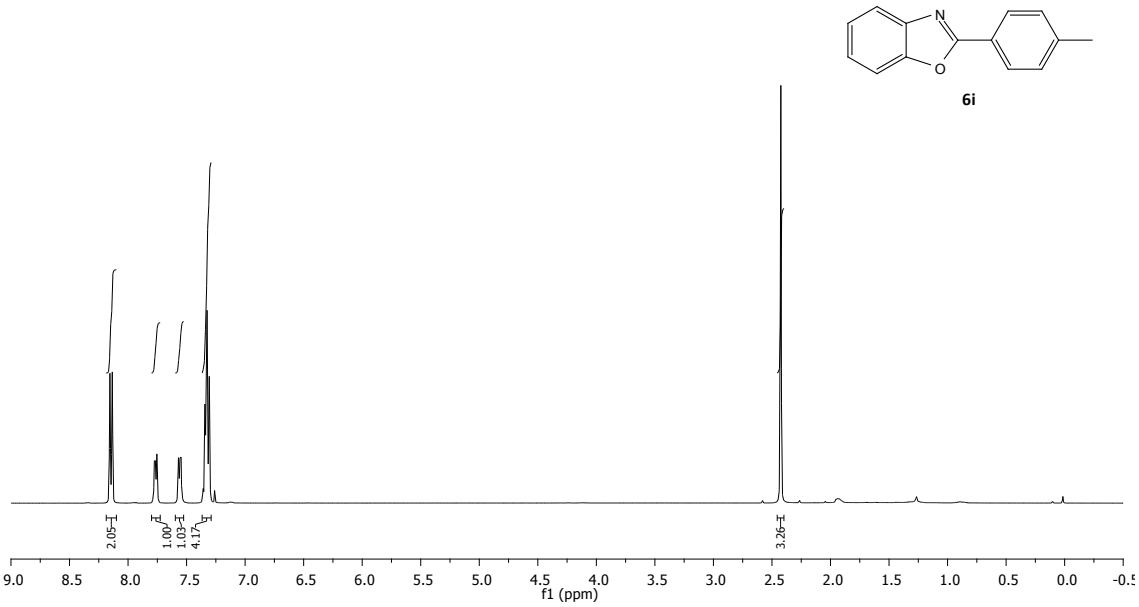


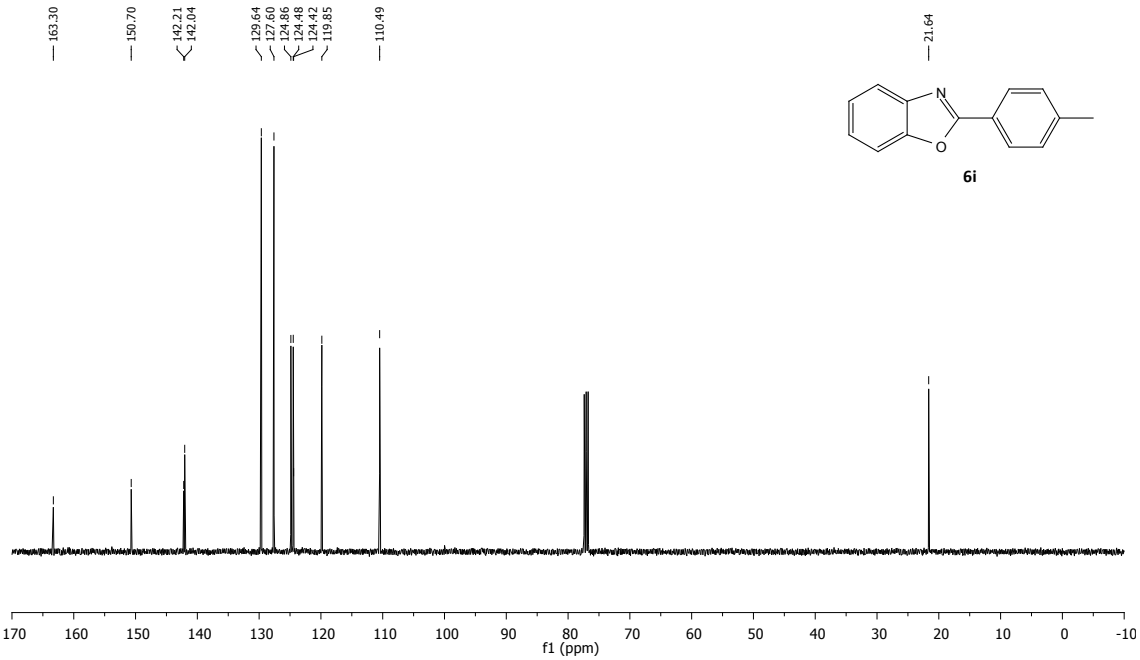
2-(3,4-Dimethoxyphenyl)-benzoxazole (6h)



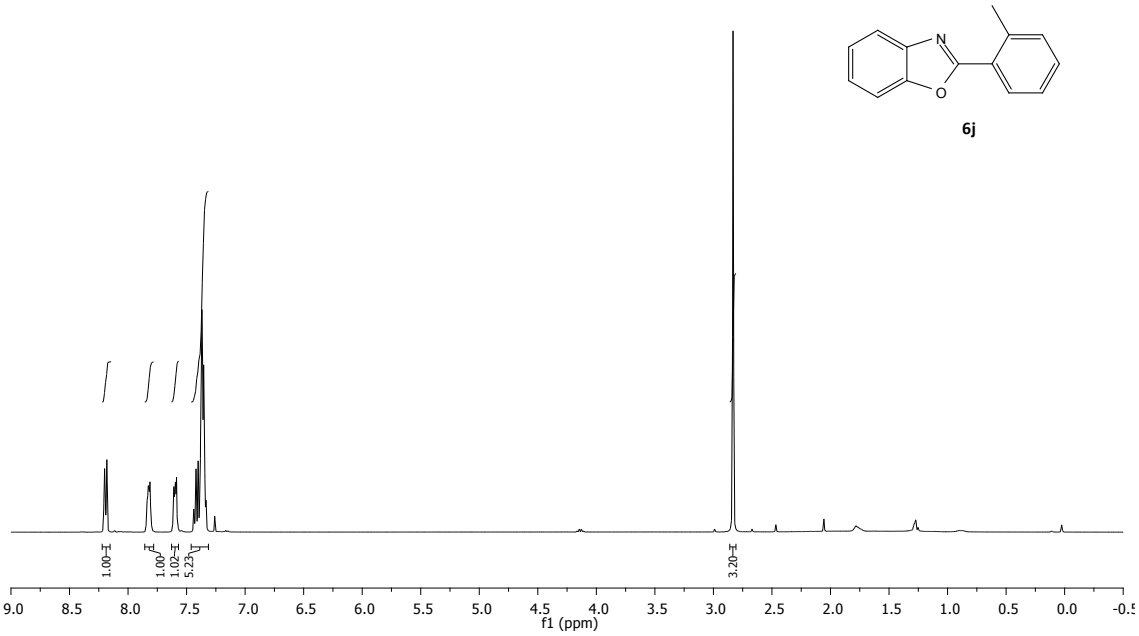


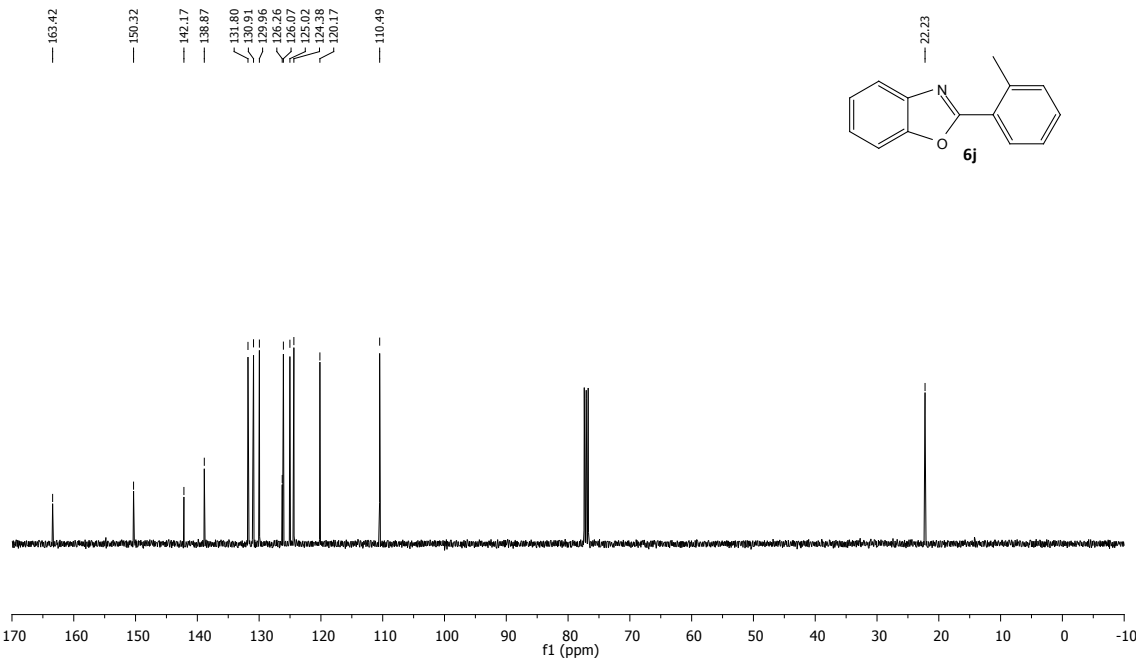
2-(*p*-Tolyl)-benzoxazole (6i)



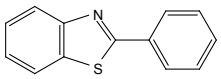


2-(*o*-Tolyl)-benzoxazole (6j)





2-Phenylbenzothiazole (8a)



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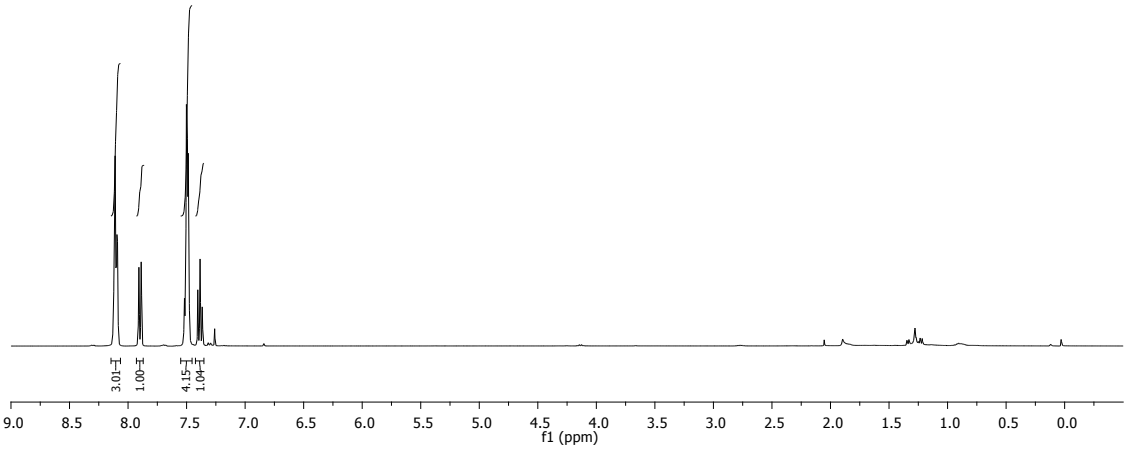
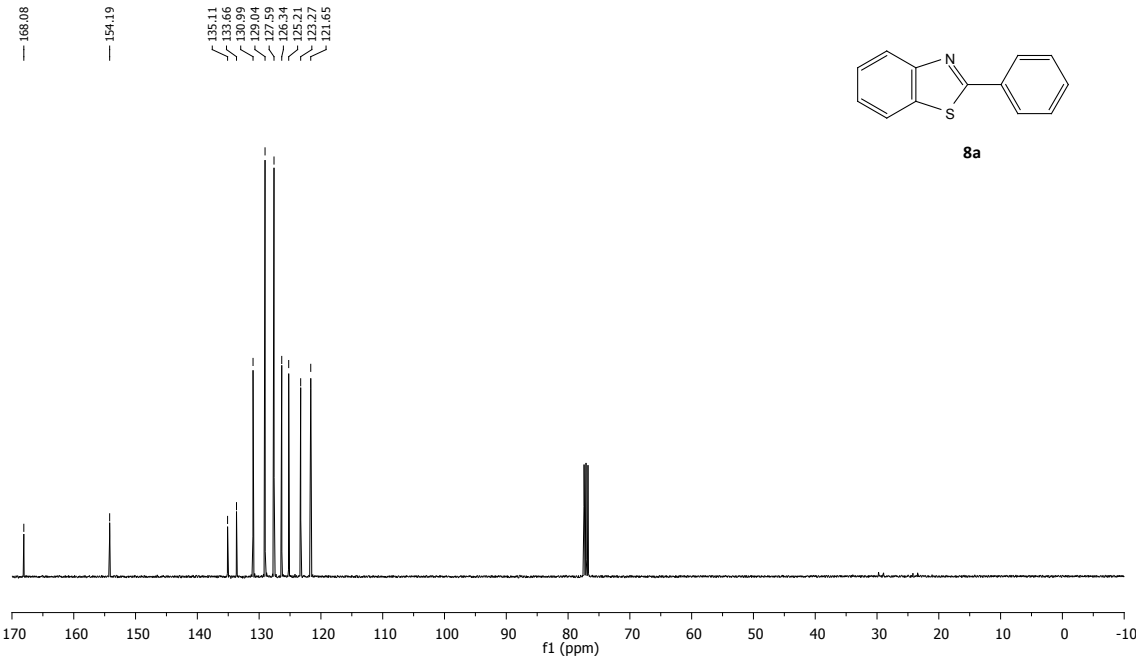
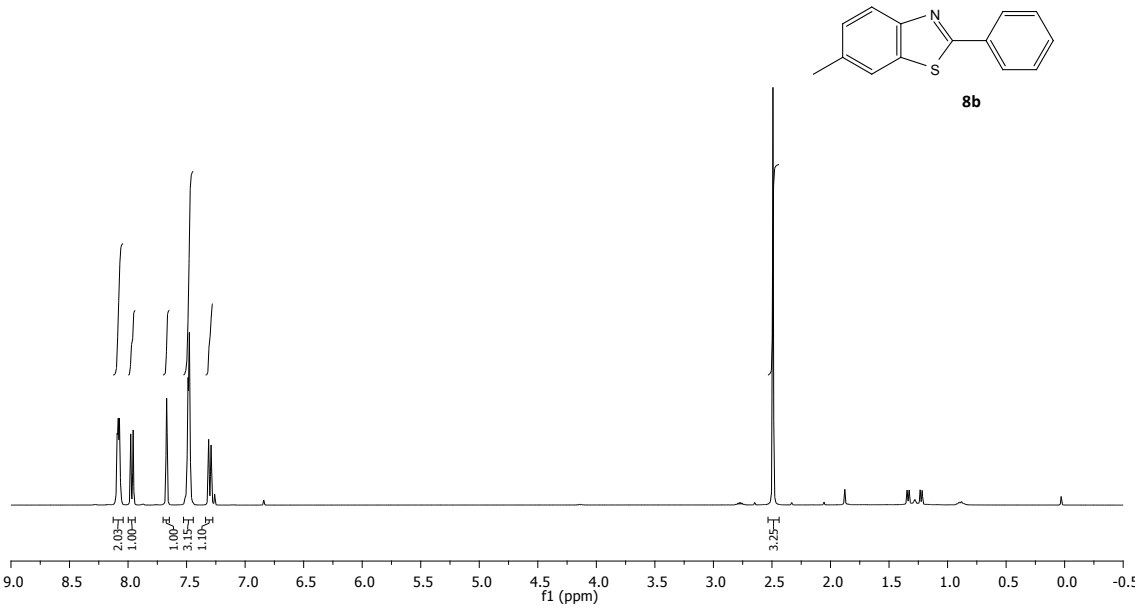
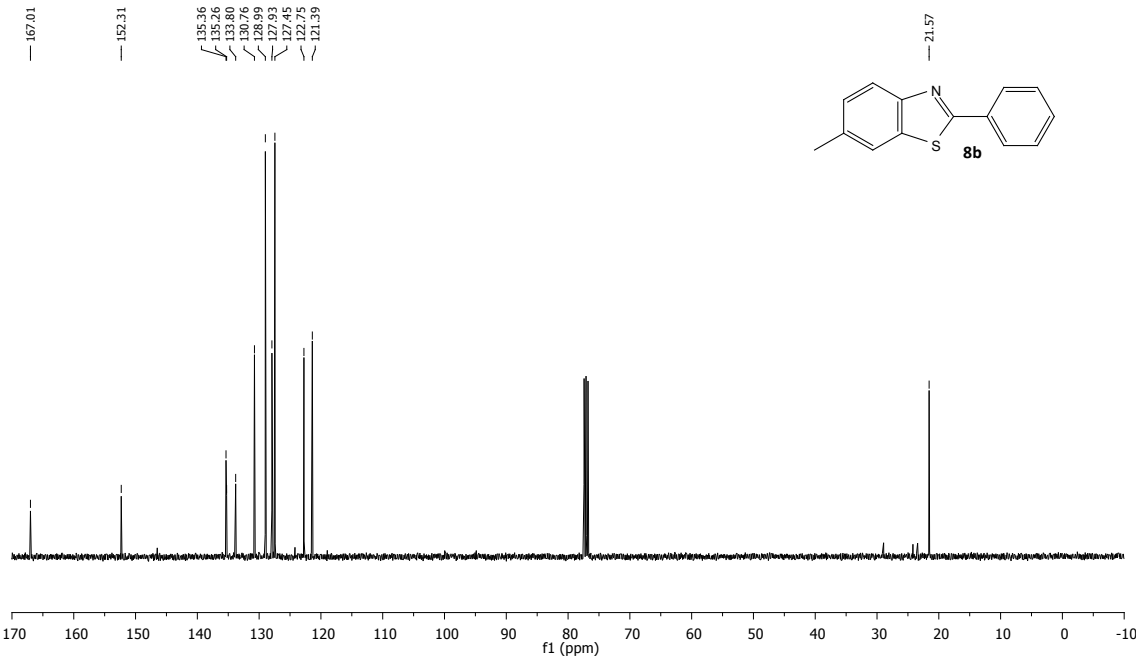




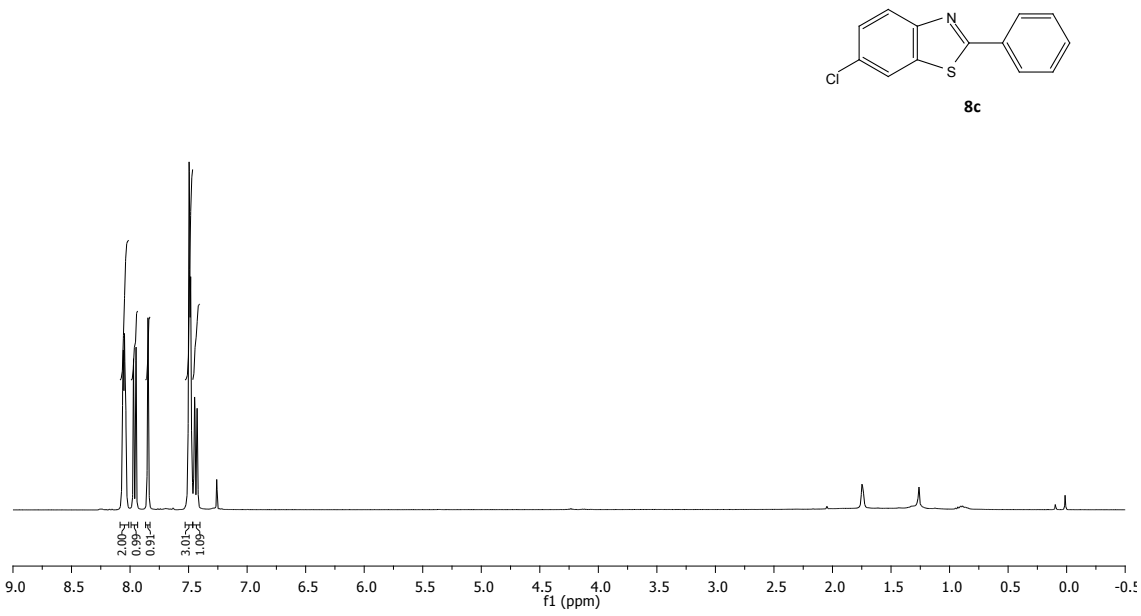
8a

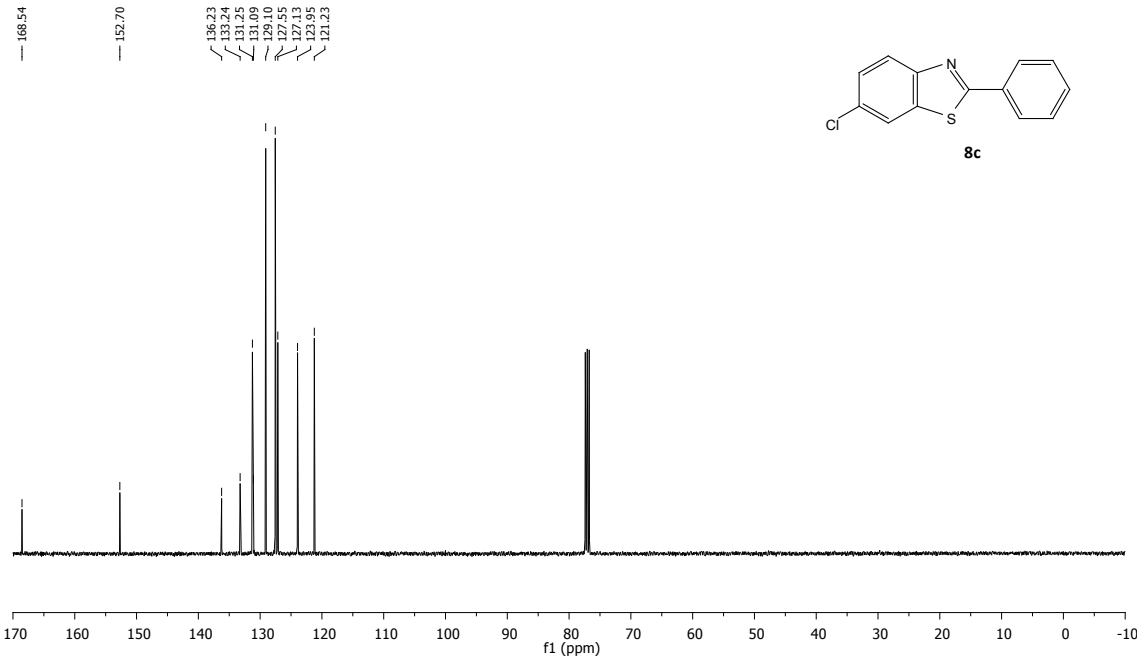
6-Methyl-2-phenylbenzothiazole (8b)





6-Chloro-2-phenylbenzothiazole (8c)





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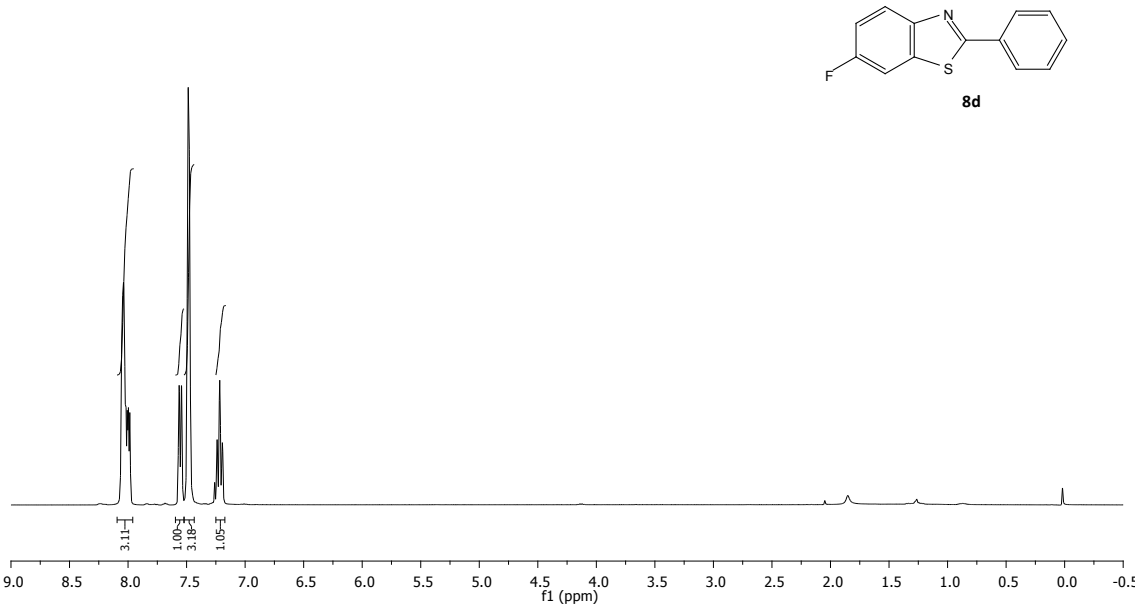
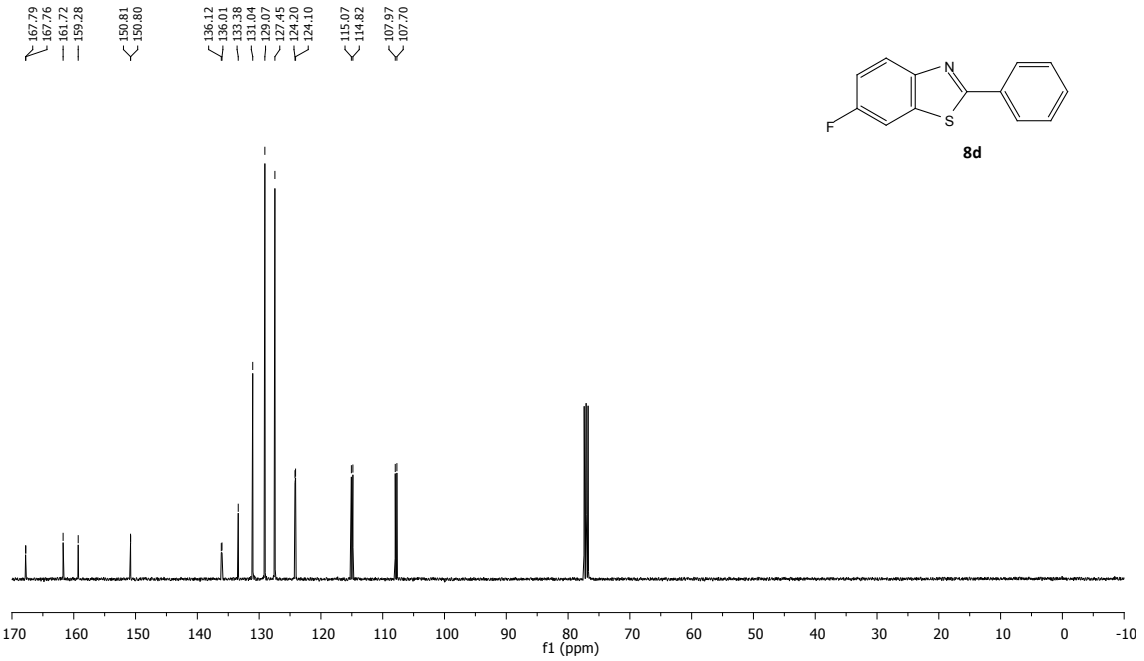
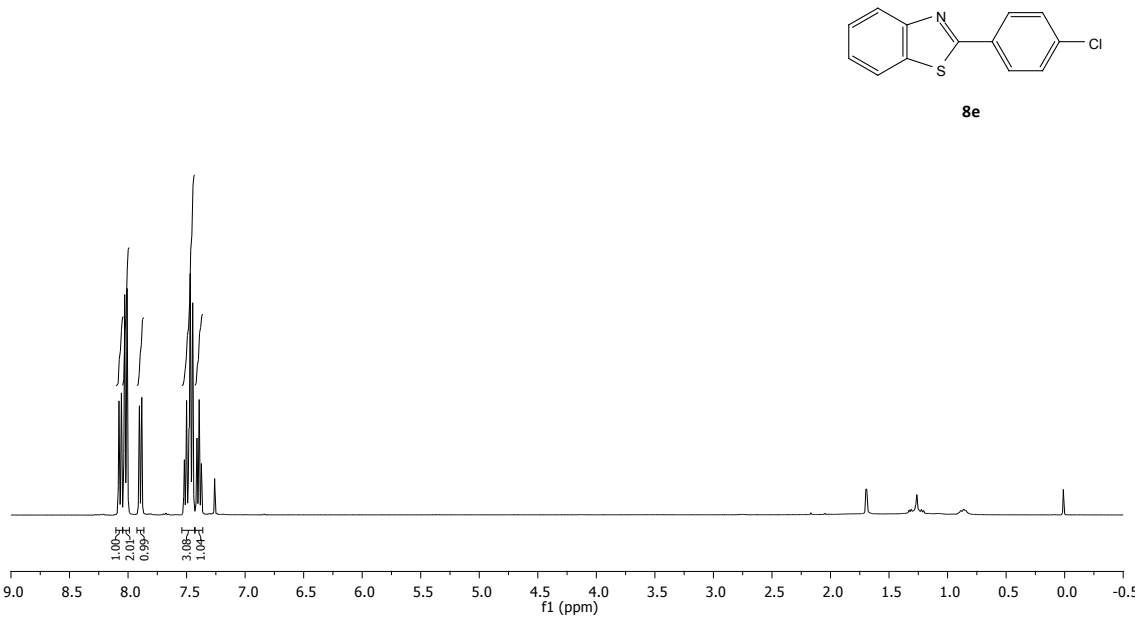
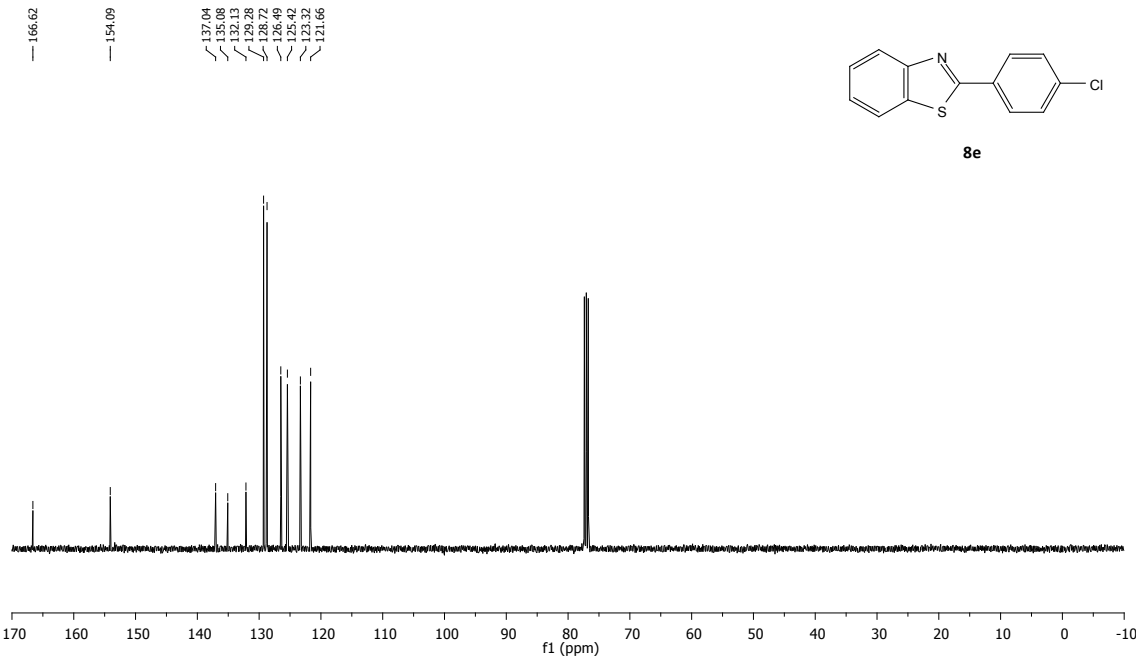




2-(4-Chlorophenyl)-benzothiazole (8e)





2-(4-Methoxyphenyl)-benzothiazole (8f)