Copper and Cobalt Co-Catalyzed Aerobic Oxidative Cross-Dehydrogenative Coupling Reaction of (Benzo)Azoles

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Supporting Information

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1. General Information

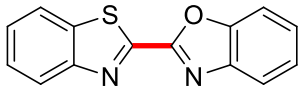
All the solvents and commercially available reagents were purchased from commercial sources and used directly. Thin layer chromatography (TLC) was performed on EMD precoated plates (silica gel 60 F254, Art 5715). Visualization of TLC was achieved by the use of UV light (254 nm). Column chromatography was performed on silica gel (300-400 mesh) using a forced flow of 0.5–1.0 bar. ^{1}H NMR was recorded on FT AM 400 (400 MHz). Chemical shifts were reported in parts per million (ppm) referenced to the appropriate solvent peak or 0.0 ppm for tetramethylsilane. The following abbreviations were used to describe peak splitting patterns: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, td = triplet of doublet, ddd = doublet of doublet of doublet, m = multiplet. Coupling constants, J, were reported in hertz (Hz). The fully decoupled ^{13}C NMR was recorded on FT AM 400 (100 MHz). Infrared (IR) spectra were recorded on a Nicolet 6700 spectrophotometer and reported as wave number (cm^{-1}). High resolution mass spectra were obtained by using the UHD Accurate-Mass Q-TOF.

2. Experimental Section

2.1 General Procedure For the Objective Product

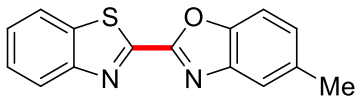
A 35 mL oven-dried pressure tube was charged with **1a** benzothiazole (27.0 mg, 0.2 mmol), **2a** benzo[d]oxazole (35.8 mg, 0.3 mmol), $Cu(OAc)_2$ •H_2O (8 mg, 0.04 mmol), $Co(NO_3)_2$ •$6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), and 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL). The tube was then sealed and stirred vigorously at 130 ˚C for 18 h. Then cooled to room temperature, diluted with ethyl acetate, filtered through a celite pad and concentrated under reduced pressure. The residue was purified by silica gel chromatography (dichloromethane/hexane: 1/1, v/v) to give the desired product **(benzo[d]thiazol-2-yl)benzo[d]oxazole** (**3a**, 45 mg, 73% yield). The R_f values of TLC for **3a**, self-coupling products 2,2'-bibenzothiazole **4a** and 2,2'-bibenzoxazole **5a** are 0.36, 0.54 and 0.27, respectively.

2-(benzo[d]thiazol-2-yl)benzo[d]oxazole (3a)



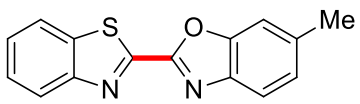
White solid, m.p.: 185-186 ºC, 37 mg, yield: 73%. (known compound[1]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, *J* = 8.1 Hz, 1H), 8.02 (d, *J* = 7.9 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.65-7.53 (m, 2H), 7.49 (dd, *J* = 17.5, 8.7 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.04, 154.45, 153.68, 151.03, 141.42, 136.86, 127.14, 127.12, 127.07, 125.50, 124.76, 121.94, 121.01, 111.43. IR (neat) ν 3015, 2969, 2942, 2853, 1738, 1465, 1446, 1318, 1216, 931, 848, 760, 669. HRMS (ESI, m/z): calcd. for $C_{14}H_9N_2OS(M+H)^+$: 253.0430, found: 253.0433.

2-(benzo[d]thiazol-2-yl)-5-methylbenzo[d]oxazole (3b)



White solid, m.p.: 197-198 ºC, 38 mg, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.65-7.54 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.06, 154.58, 153.72, 149.41, 141.66, 135.47, 128.31, 127.05, 126.98, 124.68, 121.90, 120.71, 110.75, 21.53. IR (neat) ν 3015, 2969, 2855, 2379, 1428, 1365, 1228, 1120, 910, 807, 668. HRMS (ESI, m/z): calcd. for $C_{15}H_{10}N_2NaOS(M+Na)^+$: 289.0406, found: 289.0404.

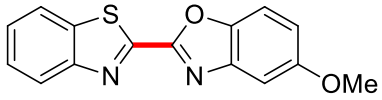
2-(benzo[d]thiazol-2-yl)-6-methylbenzo[d]oxazole (3c)



White solid, m.p.: 185-186 ºC, 40 mg, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.65-7.54 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 2.50 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 156.55, 154.64, 153.64, 151.32, 139.26, 137.93, 135.74,

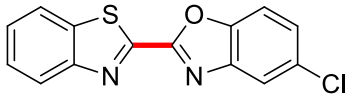
127.06, 126.96, 126.91, 124.64, 121.89, 120.30, 111.38, 21.99. IR (neat) ν 3022, 2967, 2851, 2375, 1615, 1455, 1373, 1313, 1228, 1017, 756, 728, 699. HRMS (ESI, m/z): calcd. for $C_{15}H_{10}N_2NaOS(M+Na)^+$: 289.0406, found:289.0405.

2-(benzo[d]thiazol-2-yl)-5-methoxybenzo[d]oxazole (3d)



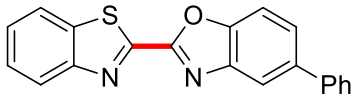
White solid, m.p.: 178-179 ºC, 44 mg, yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 7.9 Hz, 1H), 7.59 (t, *J* = 8.7 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 1H), 7.31 (d, *J* = 2.3 Hz, 1H), 7.08 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.89 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.03, 157.63, 154.46, 153.65, 145.70, 142.27, 135.77, 127.09, 127.01, 124.69, 121.90, 116.32, 111.60, 103.08, 55.95. IR (neat) ν 3079, 3004, 2922, 2951, 1484, 1426, 1275, 1150, 933, 812, 715. HRMS (ESI, m/z): calcd. for $C_{15}H_{10}N_2NaO_2S(M+Na)^+$: 305.0355, found: 305.0353.

2-(benzo[d]thiazol-2-yl)-5-chlorobenzo[d]oxazole (3e)



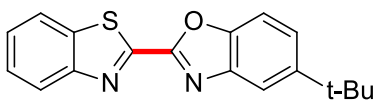
White solid, m.p.: 195-196 ºC, 35 mg, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 7.9 Hz, 1H), 7.85 (s, 1H), 7.62 (t, *J* = 8.4 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.7 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.20, 153.83, 153.59, 149.53, 142.43, 135.89, 131.10, 127.44, 127.37, 127.30, 124.87, 122.00, 120.85, 112.19. IR (neat) ν 2969, 2375, 2014, 1961, 1743, 1646, 1507, 1216, 1081, 736, 668, 591. HRMS (ESI, m/z): calcd. for $C_{14}H_8ClN_2OS(M+H)^+$: 287.0040, found: 287.0041.

2-(benzo[d]thiazol-2-yl)-5-phenylbenzo[d]oxazole (3f)



White solid, m.p.: 195-196 ºC, 45 mg, yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, *J* = 7.9 Hz, 1H), 8.14-7.98 (m, 2H), 7.75 (dd, *J* = 18.9, 8.1 Hz, 2H), 7.66 (d, *J* = 7.1 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 1H), 7.57 (d, *J* = 7.5 Hz, 1H), 7.51 (t, *J* = 6.9 Hz, 2H), 7.43 (d, *J* = 6.5 Hz, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.59, 154.36, 153.67, 150.52, 142.04, 140.59, 139.49, 135.86, 128.97, 127.57, 127.50, 127.20, 127.18, 126.79, 124.80, 121.97, 119.28, 111.44. IR (neat) ν 3015, 2969, 2851, 2377, 1738, 1365, 1216, 1018, 816, 699, 668, 587. HRMS (ESI, m/z): calcd. for $C_{20}H_{12}N_2NaOS(M+Na)^+$: 351.0563, found: 351.0561.

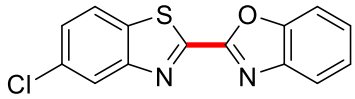
2-(benzo[d]thiazol-2-yl)-5-(tert-butyl)benzo[d]oxazole (3g)



White solid, m.p.: 156-157 ºC, 46 mg, yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 8.1 Hz, 1H), 8.00 (t, *J* = 8.5 Hz, 1H), 7.90 (d, *J* = 1.4 Hz, 1H), 7.66-7.58 (m, 2H), 7.58-7.51 (m, 2H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.14, 154.67, 153.67, 149.20, 149.06, 141.36,

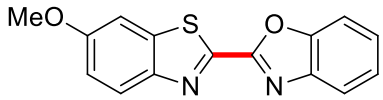
135.80, 127.09, 127.01, 125.07, 124.69, 121.91, 117.30, 110.57, 35.06, 31.70. IR (neat) ν 2922, 2846, 2322, 1922, 1646, 1456, 1216, 1076, 668, 589, 526, 469. HRMS (ESI, m/z): calcd. For $C_{18}H_{16}N_2NaOS(M+Na)^+$: 331.0876, found: 331.0877.

2-(5-chlorobenzo[d]thiazol-2-yl)benzo[d]oxazole (3h)



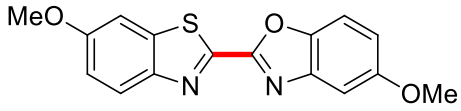
White solid, m.p.: 211-212 ºC, 41 mg, yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.3 Hz, 1H), 7.88 (dd, *J* = 16.7, 8.1 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 1H), 7.54-7.40 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.58, 156.21, 154.42, 151.00, 141.31, 134.05, 133.31, 127.66, 127.31, 125.62, 124.30, 122.64, 121.09, 111.46. IR (neat) ν 3022, 2969, 2377, 1507, 1365, 1216, 910, 802, 737, 668, 517. HRMS (ESI, m/z): calcd. For $C_{14}H_8ClN_2OS(M+H)^+$: 287.0040, found: 287.0037.

2-(6-methoxybenzo[d]thiazol-2-yl)benzo[d]oxazole (3i)



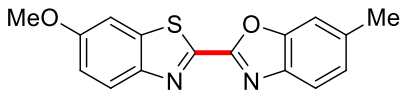
White solid, m.p.: 217-218 ºC, 38 mg, yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 8.1 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.65-7.54 (m, 3H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.28 (s, 1H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.33, 157.20, 151.67, 150.93, 148.29, 141.46, 137.65, 126.79, 125.39, 125.34, 120.81, 117.32, 111.33, 103.67, 55.89. IR (neat) ν 3015, 2969, 2944, 1738, 1434, 1365, 1228, 1216, 1091, 910, 787, 668. HRMS (ESI, m/z): calcd. for $C_{15}H_{11}N_2O_2S(M+H)^+$: 283.0536, found: 283.0535.

5-methoxy-2-(6-methoxybenzo[d]thiazol-2-yl)benzo[d]oxazole (3j)



White solid, m.p.: 212-213 ºC, 45 mg, yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 9.0 Hz, 1H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.30 (d, *J* = 2.3 Hz, 1H), 7.19 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.06 (dd, *J* = 8.9, 2.4 Hz, 1H), 3.93 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.25, 157.97, 157.81, 151.69, 148.29, 145.63, 142.32, 137.59, 125.27, 117.24, 115.91, 111.49, 103.66, 103.05, 55.96, 55.87. IR (neat) ν 2936, 2859, 2373, 1738, 1569, 1476, 1365, 1081, 826, 668, 527.HRMS (ESI, m/z): calcd. for $C_{16}H_{13}N_2O_3S^+(M+H)^+$: 313.0641, found: 313.0640.

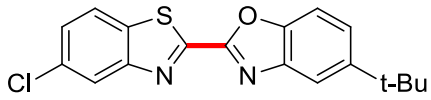
2-(6-methoxybenzo[d]thiazol-2-yl)-6-methylbenzo[d]oxazole (3k)



White solid, m.p.: 217-218 ºC, 38 mg, yield: 63%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.8 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 25.5 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 7.0 Hz, 1H), 3.95 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.23, 137.64, 126.78, 125.26, 120.18, 117.20, 111.40, 103.76, 55.89, 21.99. IR (neat) ν 3026, 2922, 2373, 1567, 1481,

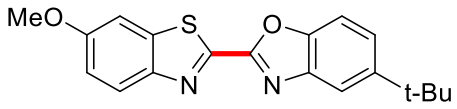
1373, 1228, 1022, 830, 668, 518. HRMS (ESI, m/z): calcd. For $C_{16}H_{13}N_2O_2S(M+H)^+$: 297.0692, found: 297.0691.

5-(tert-butyl)-2-(5-chlorobenzo[d]thiazol-2-yl)benzo[d]oxazole (3l)



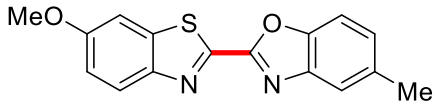
Light yellow solid, m.p.: 230-231 °C, 35 mg, yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (s, 1H), 7.95-7.89 (m, 2H), 7.64 (d, *J* = 8.7 Hz, 1H), 7.58 (d, *J* = 8.7 Hz, 1H), 7.51 (d, *J* = 8.6 Hz, 1H), 1.43 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.70, 156.46, 154.46, 149.38, 149.08, 141.28, 134.02, 133.28, 127.61, 125.39, 124.27, 122.66, 117.37, 110.64, 35.09, 31.69. IR (neat) ν 2973, 2926, 2379, 1743, 1456, 1334, 1216, 1022, 830, 718, 668, 518. HRMS (ESI, m/z): calcd. For $C_{18}H_{15}ClN_2NaOS(M+Na)^+$: 365.0486, found: 365.0478.

5-(tert-butyl)-2-(6-methoxybenzo[d]thiazol-2-yl)benzo[d]oxazole (3m)



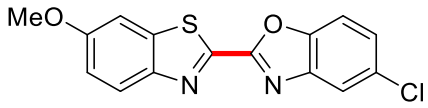
White solid, m.p.: 153-154 °C, 51 mg, yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 1H), 7.86 (d, *J* = 1.5 Hz, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.52 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.16 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.90 (s, 3H), 1.40 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.19, 157.25, 151.83, 149.02, 148.96, 148.24, 141.36, 137.56, 125.23, 124.74, 117.21, 117.11, 110.45, 103.58, 55.84, 35.03, 31.70. IR (neat) ν 2944, 2865, 2824, 1508, 1456, 1260, 1091, 930, 820, 668, 610, 516. HRMS (ESI, m/z): calcd. For $C_{19}H_{18}N_2NaO_2S(M+Na)^+$: 361.0981, found: 361.0984.

2-(6-methoxybenzo[d]thiazol-2-yl)-5-methylbenzo[d]oxazole (3n)



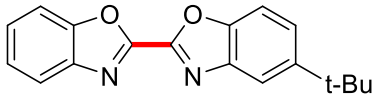
White solid, m.p.: 210-211 °C, 44 mg, yield: 73%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 7.55 (d, *J* = 8.4 Hz, 1H), 7.41 (d, *J* = 2.3 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.92 (s, 3H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.23, 157.22, 151.80, 149.18, 148.26, 141.65, 137.57, 135.36, 128.02, 125.26, 120.55, 117.23, 110.65, 103.63, 55.86, 21.55. IR (neat) ν 2965, 2920, 2848, 1478, 1373, 1264, 1079, 802, 668, 592, 443. HRMS (ESI, m/z): calcd. for $C_{16}H_{12}N_2NaO_2S(M+Na)^+$: 319.0512, found: 319.0514.

5-chloro-2-(6-methoxybenzo[d]thiazol-2-yl)benzo[d]oxazole (3o)



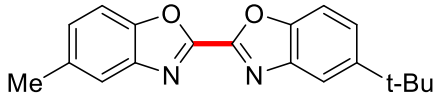
White solid, m.p.: 209-210 °C, 40 mg, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.0 Hz, 1H), 7.84 (d, *J* = 1.9 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.45 (dd, *J* = 6.8, 2.1 Hz, 2H), 7.22 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.96 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.52, 158.40, 151.00, 149.49, 148.27, 142.54, 137.80, 130.98, 127.11, 125.48, 120.68, 117.55, 112.06, 103.63, 55.91. IR (neat) ν 3022, 2924, 2846, 2371, 1507, 1472, 1456, 1373, 1200, 1079, 875, 592. HRMS (ESI, m/z): calcd. for $C_{15}H_{10}ClN_2O_2S(M+H)^+$: 317.0146, found: 317.0146.

5-(tert-butyl)-2,2'-bibenzo[d]oxazole (3p)



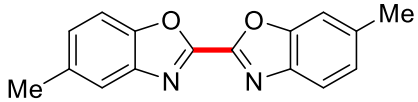
White solid, m.p.: 197-198 °C, 39 mg, yield: 66%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.87 (m, 2H), 7.70 (d, *J* = 7.7 Hz, 1H), 7.63-7.56 (m, 2H), 7.52-7.43 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.91, 150.96, 149.46, 149.04, 141.18, 141.15, 127.39, 125.67, 125.59, 121.43, 117.67, 111.43, 110.60, 35.06, 31.67. IR (neat) ν 2969, 2932, 2855, 2371, 1529, 1437, 1355, 1216, 1116, 668, 527. HRMS (ESI, m/z): calcd. for $C_{18}H_{16}N_2NaO_2(M+Na)^+$: 315.1104, found: 315.1105.

5-(tert-butyl)-5'-methyl-2,2'-bibenzo[d]oxazole (3q)



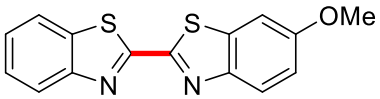
White solid, m.p.: 172-173 °C, 44 mg, yield: 71%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 1.4 Hz, 1H), 7.68 (s, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.60-7.56 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 1H), 2.52 (s, 3H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.03, 149.40, 149.24, 148.99, 141.37, 141.16, 135.74, 128.71, 125.49, 121.08, 117.63, 110.78, 110.57, 35.06, 31.68, 21.54. IR (neat) ν 2969, 1738, 1364, 1228, 1216, 1102, 867, 824, 761, 672, 527. HRMS (ESI, m/z): calcd. for $C_{19}H_{18}N_2NaO_2(M+Na)^+$: 329.1260, found: 329.1264.

5,6'-dimethyl-2,2'-bibenzo[d]oxazole (3r)



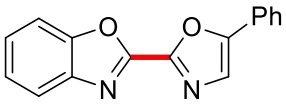
White solid, m.p.: 188-189 °C, 37 mg, yield: 69%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 7.9 Hz, 1H), 7.66 (s, 1H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.47 (s, 1H), 7.30 (s, 1H), 7.25 (s, 1H), 2.53 (s, 3H), 2.50 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.01, 151.46, 151.26, 149.21, 141.36, 139.04, 138.33, 135.71, 128.65, 127.12, 121.04, 120.72, 111.35, 110.73, 21.98, 21.51. IR (neat) ν 2969, 2946, 2133, 1739, 1435, 1365, 1228, 1216, 899, 538, 527, 515. HRMS (ESI, m/z): calcd. for $C_{16}H_{12}N_2NaO_2(M+Na)^+$: 287.0791, found: 287.0793.

6-methoxy-2,2'-bibenzo[d]thiazole (3s)



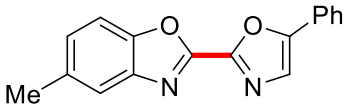
White solid, m.p.: 220-221 °C, 43 mg, yield: 71%. (known compound[2]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 9.0 Hz, 1H), 7.99 (d, *J* = 7.9 Hz, 1H), 7.56 (d, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 2.3 Hz, 1H), 7.18 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.67, 158.93, 158.83, 153.55, 148.16, 137.53, 135.61, 126.74, 126.39, 124.68, 123.87, 121.98, 116.83, 103.90, 55.86. HRMS (ESI, m/z): calcd. IR (neat) ν 3015, 2969, 2942, 2848, 1434, 1365, 1228, 1216, 1091, 895, 754. for $C_{20}H_{12}N_2NaOS(M+H)^+$: 299.0307, found: 299.0306.

2-(5-phenyloxazol-2-yl)benzo[d]oxazole (3t)



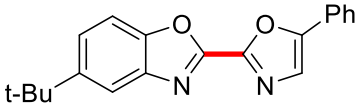
White solid, m.p.: 160-161 °C, 32 mg, yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94-7.89 (m, 1H), 7.88-7.82 (m, 2H), 7.70 (dd, *J* = 7.1, 1.7 Hz, 1H), 7.66 (s, 1H), 7.53-7.49 (m, 2H), 7.49-7.45 (m, 2H), 7.44 (dd, *J* = 5.4, 1.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 154.05, 151.75, 150.64, 150.51, 141.22, 129.67, 129.10, 126.89, 126.74, 125.51, 125.00, 124.38, 121.13, 111.29. IR (neat) ν 3015, 2969, 1738, 1561, 1447, 1365, 1228, 909, 761, 686, 257. HRMS (ESI, m/z): calcd. for $C_{16}H_{10}N_2O_2(M+Na)^+$: 285.0634, found: 285.0636.

5-methyl-2-(5-phenyloxazol-2-yl)benzo[d]oxazole (3u)



White solid, m.p.: 164-165 °C, 30 mg, yield: 53%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 2H), 7.66 (s, 1H), 7.62 (s, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.41 (d, *J* = 7.1 Hz, 1H), 7.28 (d, *J* = 2.4 Hz, 1H), 2.51 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.88, 151.77, 150.63, 148.90, 141.40, 135.48, 129.58, 129.06, 128.13, 126.75, 124.95, 124.31, 120.83, 110.61, 21.55. IR (neat) ν 2969, 2946, 2125, 1739, 1434, 1365, 1228, 1091, 899, 538, 515. HRMS (ESI, m/z): calcd. For $C_{17}H_{15}N_2O_2^+(M-H)^+$: 277.0972, found: 277.0969.

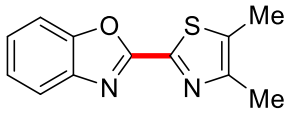
5-(tert-butyl)-2-(5-phenyloxazol-2-yl)benzo[d]oxazole (3v)



White solid, m.p.: 164-165 °C, 40 mg, yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.63 (s, 1H), 7.59 (d, *J* = 8.7 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 1.42 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.89, 151.81, 150.64, 149.14, 148.69, 141.18, 129.56, 129.06, 126.78, 124.93, 124.84, 124.30, 117.40,

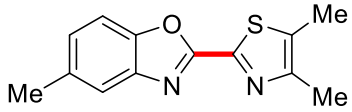
110.39, 35.03, 31.70. IR (neat) ν 2946, 2133, 1739, 1435, 1216, 1092, 899, 792, 760, 685, 674. HRMS (ESI, m/z): calcd. For $C_{20}H_{18}N_2NaO_2(M+Na)^+$: 341.1260, found: 341.1261.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.83 (d, *J* = 7.5 Hz, 2H), 7.63 (s, 1H), 7.56 (dd, *J* = 20.9, 8.7 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.40 (t, *J* = 7.3 Hz, 1H), 1.42 (s, 9H).

2-(4,5-dimethylthiazol-2-yl)benzo[d]oxazole (3w)



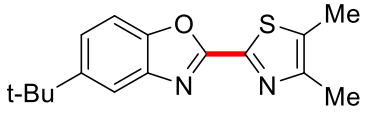
White solid, m.p.: 165-166 °C, 30 mg, yield: 64%. (known compound[3]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.77 (m, 1H), 7.63 (dd, *J* = 6.1, 3.0 Hz, 1H), 7.43-7.37 (m, 2H), 2.48 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.21, 151.48, 150.59, 149.47, 141.50, 131.97, 126.10, 125.10, 120.42, 111.12, 14.91, 11.73. IR (neat) ν 3457, 3015, 2969, 1738, 1436, 1365, 1228, 1216, 1091, 895, 736, 527. HRMS (ESI, m/z): calcd. for $C_{12}H_{10}N_2NaOS(M+Na)^+$: 253.0406, found: 253.0405.

2-(4,5-dimethylthiazol-2-yl)-5-methylbenzo[d]oxazole (3x)



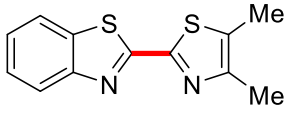
White solid, m.p.: 161-162 °C, 32 mg, yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (s, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 7.20 (dd, *J* = 8.3, 1.0 Hz, 1H), 2.48 (s, 3H), 2.47 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.27, 151.36, 149.62, 148.84, 141.69, 135.01, 131.71, 127.28, 120.22, 110.44, 21.50, 14.89, 11.69. IR (neat) ν 2969, 2922, 2857, 1738, 1425, 1365, 1216, 1091, 910, 806, 716, 665. HRMS (ESI, m/z): calcd. for $C_{13}H_{12}N_2NaOS(M+Na)^+$: 267.0563, found: 267.0565.

5-(tert-butyl)-2-(4,5-dimethylthiazol-2-yl)benzo[d]oxazole (3y)



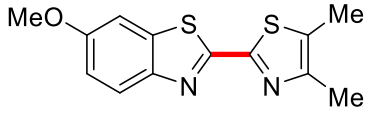
White solid, m.p.:147-148 °C, 39 mg, yield: 67%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 (d, *J* = 1.5 Hz, 1H), 7.53 (d, *J* = 8.6 Hz, 1H), 7.46 (dd, *J* = 8.7, 1.8 Hz, 1H), 2.47 (s, 6H), 1.39 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 157.30, 151.31, 149.69, 148.70, 148.61, 141.40, 131.72, 123.97, 116.80, 110.24, 34.96, 31.71, 14.91, 11.70. IR (neat) ν 2969, 2863, 1891, 1440, 1228, 1128, 1026, 911, 820, 651, 527. HRMS (ESI, m/z): calcd. for $C_{16}H_{18}N_2NaOS(M+Na)^+$: 309.1032, found: 309.1034.

2-(4,5-dimethylthiazol-2-yl)benzo[d]thiazole (3z)



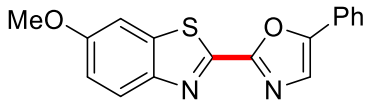
White solid, m.p.:197-198 °C, 34 mg, yield: 68%. (known compound[4,5]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.1 Hz, 1H), 7.91 (d, *J* = 7.9 Hz, 1H), 7.52-7.48 (m, 1H), 7.44-7.38 (m, 1H), 2.45 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.84, 156.39, 153.56, 150.61, 135.12, 130.95, 126.50, 125.80, 123.40, 121.85, 14.89, 11.83. IR (neat) ν 2969, 2375, 1553, 1415, 1228, 1110, 1010, 828, 729, 685, 527. HRMS (ESI, m/z): calcd. for $C_{12}H_{11}N_2S_2(M+H)^+$: 247.0358, found: 247.0359.

2-(4,5-dimethylthiazol-2-yl)-6-methoxybenzo[d]thiazole (3a')



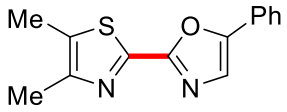
White solid, m.p.: 171-172 °C, 41 mg, yield: 74%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.36 (d, *J* = 2.2 Hz, 1H), 7.10 (dd, *J* = 9.0, 2.4 Hz, 1H), 3.90 (s, 3H), 2.45 (s, 3H), 2.43 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.34, 158.28, 156.61, 150.30, 148.11, 136.68, 130.19, 123.96, 116.16, 104.02, 55.81, 14.86, 11.78. IR (neat) ν 2922, 2851, 1515, 1429, 1268, 1120, 1081, 924, 830, 806, 682, 592. HRMS (ESI, m/z): calcd. for $C_{13}H_{13}N_2OS_2(M+H)^+$: 277.0464, found: 277.0464.

2-(6-methoxybenzo[d]thiazol-2-yl)-5-phenyloxazole (3b')



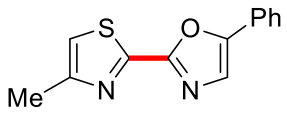
White solid, m.p.: 176-177 °C, 32 mg, yield: 51%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 9.0 Hz, 1H), 7.90-7.81 (m, 2H), 7.57 (s, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.45-7.37 (m, 2H), 7.18 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.88, 155.84, 153.19, 151.78, 148.32, 137.03, 129.30, 129.01, 127.07, 124.90, 124.08, 116.82, 103.77, 77.38, 77.06, 76.75, 55.87. IR (neat) ν 3015, 2969, 2942, 1738, 1365, 1228, 1091, 906, 832, 684, 539, 516. HRMS (ESI, m/z): calcd. for $C_{17}H_{12}N_2O_2S(M+Na)^+$: 331.0512, found: 331.0515.

2-(4,5-dimethylthiazol-2-yl)-5-phenyloxazole (3c')



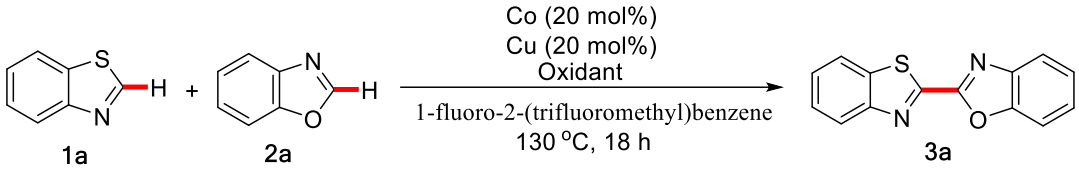
White solid, m.p.: 104-105 °C, 28 mg, yield: 54%. (known compound[2]) ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.73 (m, 2H), 7.46 (dd, *J* = 5.7, 4.6 Hz, 2H), 7.43 (d, *J* = 6.5 Hz, 1H), 7.41-7.32 (m, 1H), 2.46 (d, *J* = 1.3 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.97, 152.14, 150.72, 149.81, 130.0, 128.88, 127.29, 124.9, 124.67, 123.63, 14.90, 11.58. IR (neat) ν 2969, 2924, 2853, 1588, 1448, 1423, 1365, 1228, 1204, 1036, 947, 761, 689. HRMS (ESI, m/z): calcd. for $C_{14}H_{12}N_2OS(M+Na)^+$: 279.0563, found: 279.0562.

2-(4-methylthiazol-2-yl)-5-phenyloxazole (3d')



White solid, m.p.: 106-107 °C, 30 mg, yield: 61%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 5.3, 3.4 Hz, 2H), 7.48 (s, 1H), 7.47-7.41 (m, 2H), 7.36 (m, 1H), 7.06 (d, *J* = 0.6 Hz, 1H), 2.58 (d, *J* = 0.8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.81, 154.95, 153.88, 152.42, 129.05, 128.92, 127.17, 124.73, 123.72, 116.30, 17.23. IR (neat) ν 2922, 2854, 1679, 1486, 1421, 1300, 1041, 909, 720, 690, 546, 502. HRMS (ESI, m/z): calcd. for $C_{13}H_{10}N_2OS(M+Na)^+$: 265.0406, found: 265.0407.

2.2 Aerobic and Anaerobic Control Experiments



Entry	Co source (20 mol %)	Cu source (20 mol %)	Oxidant	Additives	[c]Yield [%]
26[a]	$Co(NO_3)_2{\cdot}6H_2O$	$Cu(OAc)_2{\cdot}H_2O$	O_2	CH_3COONa (1.0 equiv)	56 (22[d], 12[e])
27[b]	$Co(NO_3)_2{\cdot}6H_2O$	$Cu(OAc)_2{\cdot}H_2O$	Ar	CH_3COONa (1.0 equiv)	8 (10[d], 6[e])

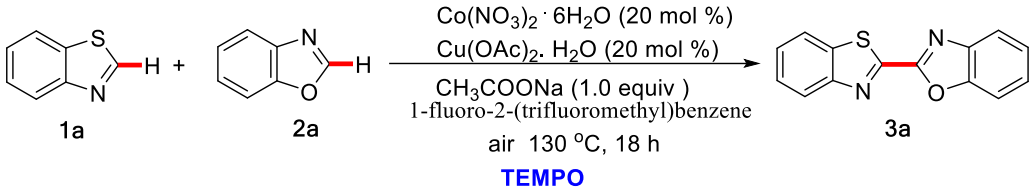
Table S1. Aerobic and Anaerobic Control Experiments

[a]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Co] (0.04 mmol), [Cu] (0.04 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), O_2, 130 °C, 18 h. [b]Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), [Co] (0.04 mmol), [Cu] (0.04 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), Ar, 130 °C, 18 h. [c]Crude ^{1}H NMR yields of desired product **3a** determined by using dibromomethane as an internal standard. [d]Crude ^{1}H NMR yields of self-coupling product **4a** 2,2'-bibenzothiazole determined by using dibromomethane as an internal standard. [e]Crude ^{1}H NMR yields of self-coupling product **5a** 2,2'-bibenzoxazole determined by using dibromomethane as an internal standard and based on **1a**.

2.3 Radical Trapping Experiment

A 35 mL oven-dried pressure tube was charged with **1a** benzothiazole (27.0 mg, 0.2 mmol), **2a** benzo[d]oxazole (35.8 mg, 0.3 mmol), $Cu(OAc)_2$ •H_2O (8 mg, 0.04 mmol), $Co(NO_3)_2$ •$6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), TEMPO (1.0 equiv./ 2.0 equiv./ 3.0 equiv.) and 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL). The tube was sealed and stirred vigorously at 130 ˚C for 18 h. The reaction mixture was then cooled to room temperature, diluted with EtOAc,

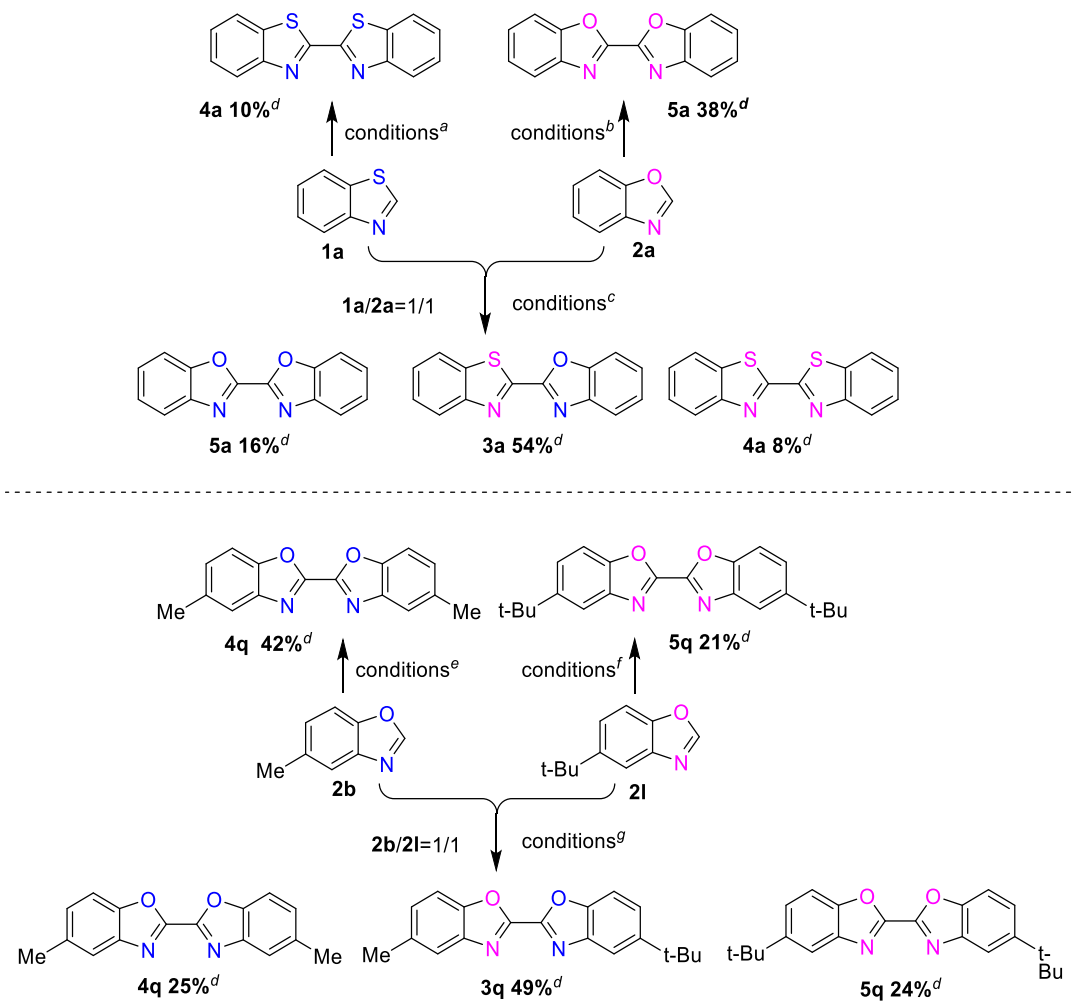
filtered through a celite pad and concentrated under reduced pressure. The crude product was analyzed by ^{1}H NMR in $CDCl_3$ using dibromomethane as internal standard.



		product
enry1	No TEMPO	76%
entry2	TEMPO (1.0 equiv)	68%
entry3	TEMPO (2.0 equiv)	64%
entry4	TEMPO (3.0 equiv)	65%

Scheme S1. Radical Trapping Experiment

2.4 Cobalt-Copper Cocatalyzed Self-coupling and Cross-coupling Control Experiments



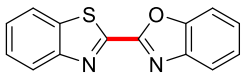
Scheme S2. Cobalt-Copper Cocatalyzed Self-coupling and Cross-coupling Control Experiments

[a] Reaction Conditions: **1a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (8 mg, 0.04 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), air, 130 °C, 18 h. [b]Reaction Conditions: **2a** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (8 mg, 0.04 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), air, 130 °C, 18 h. [c]Reaction conditions: **1a** (0.2 mmol), **2a** (0.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (8 mg, 0.04 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), air, 130 °C, 18 h. [d]Crude ^1H NMR yields determined by using dibromomethane as an internal standard. [e] Reaction Conditions: **2b** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (8 mg, 0.04 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), air, 130 °C, 18 h. [f]Reaction Conditions: **2l** (0.4 mmol), $Cu(OAc)_2 \cdot H_2O$ (8 mg, 0.04 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), air, 130 °C, 18 h. [g]Reaction conditions: **2b** (0.2 mmol), **2l** (0.2 mmol), $Cu(OAc)_2 \cdot H_2O$ (8 mg, 0.04 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (11.7 mg, 0.04 mmol), CH_3COONa (16.4 mg, 0.2 mmol), 1-fluoro-2-(trifluoromethyl)benzene (0.8 mL), air, 130 °C, 18 h.

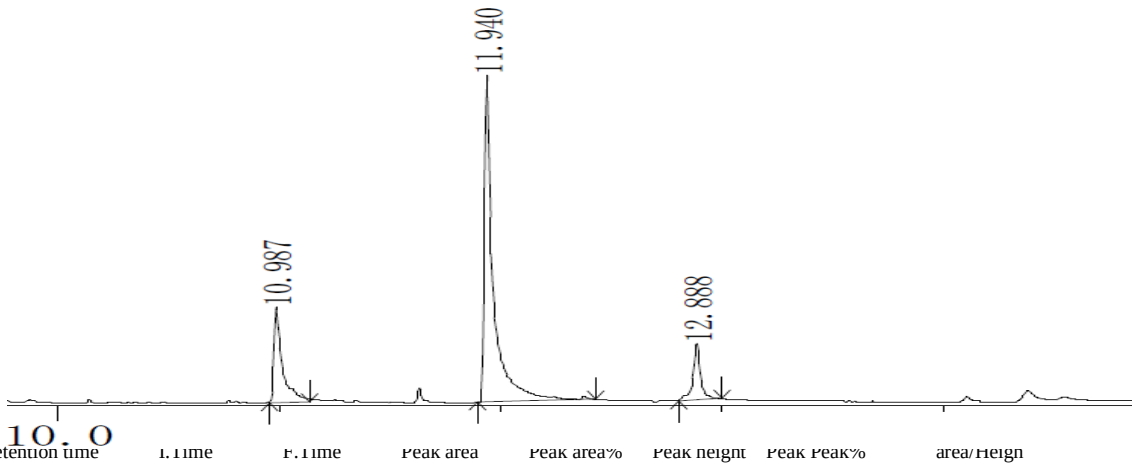
When the two reactants **1a** and **2a** were added in a ratio of 1/1, the cross-coupling product **3a**

was achieved with the yield of 54%, and the yields of the self-coupling product were 8% and 16%, respectively (GC-MS data can also initially show that the cross-coupling product **3a** is the major product). When only one of the reactants **1a** or **2a** was added, self-coupling product was obtained with yields of 10% and 38%, respectively. It is shown that this reaction tends to inhibit the self-coupling reaction and preferentially generates a cross-coupling product under these Co-Cu co-catalyzed conditions. However, when **2b** 5-Me benzoxazole and **2l** 5-t-Bu benzoxazole were added in a ratio of 1/1, there were no cross-coupling reaction selectivity, suggesting that the cross-coupling selectivity of the reaction involved the difference in the substrates.

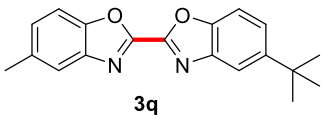
	Retention time	I.Time	F.Time	Peak area	Peak area%	Peak height	Peak Peak%	area/Heigh
1	10.987	10.955	11.140	24203985	18.97	9176772	19.90	2.64
2	11.940	11.895	12.430	90082909	70.59	31511773	68.35	2.86
3	12.888	12.805	13.000	13325183	10.44	5416247	11.75	2.46
				127612077	100.00	46104792	100.00	



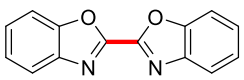
3a



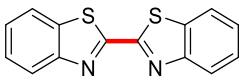
	Retention time	I.Time	F.Time	Peak area	Peak area%	Peak height	Peak Peak%	area/Heigh	
1	12.133	12.110	12.280	56304644	26.88	25882989	28.38	2.18	MI
2	13.217	13.165	13.405	99348177	47.44	41458108	45.46	2.40	MI
3	14.592	14.550	14.690	53782223	25.68	23851578	26.16	2.25	MI
				209435044	100.00	91192675	100.00		



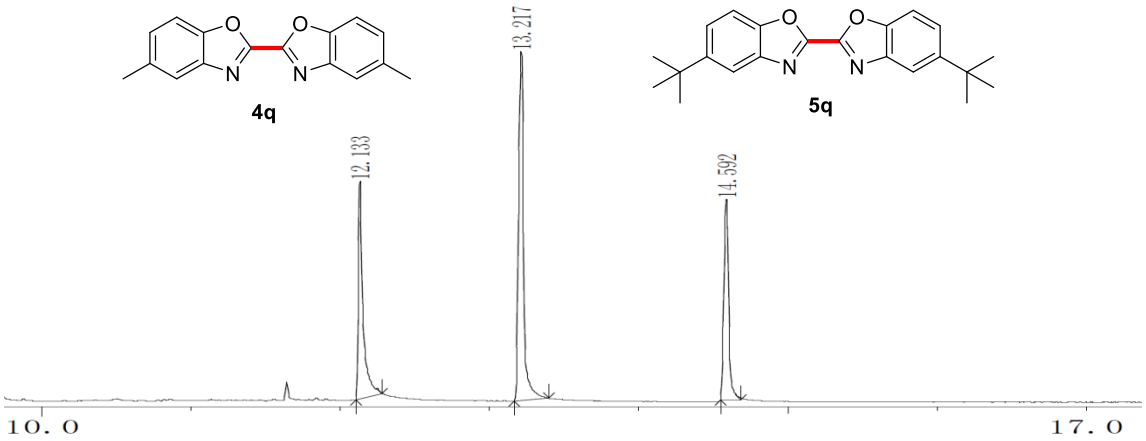
3q



5a



4a



3. References and Notes

(1) Derridj, F.; Roger, J.; Geneste, F.; Djebbar, S.; Doucet, H. *J. Organomet. Chem.* **2009**, 455.

(2) Li, Y.; Qian, F.; Wang, M.; Lu, H.; Li, G. *Org. Lett*., **2017**, *19*, 5589.

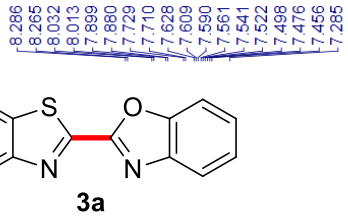
(3) Dong, J.; Huang, Y.; Qin, X.; Cheng, Y.; Hao, J.; Wan, D.; Li, W.; Liu, X.; You, J. *Chem. Eur. J*. **2012**, *18*, 6158.

(4) Han, W.; Mayer, Peter.; Ofial, A. R. *Angew. Chem., Int. Ed.* **2011**, *50*, 2178 .

(5) Fan, S.; Chen, Z.; Zhang, X. *Org. Lett.* **2012**, *14*, 4950.

4. ^{1}H and ^{13}C NMR Spectra

3a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8.032
8.013
7.899
7.880
7.729
7.710
7.628
7.609
7.590
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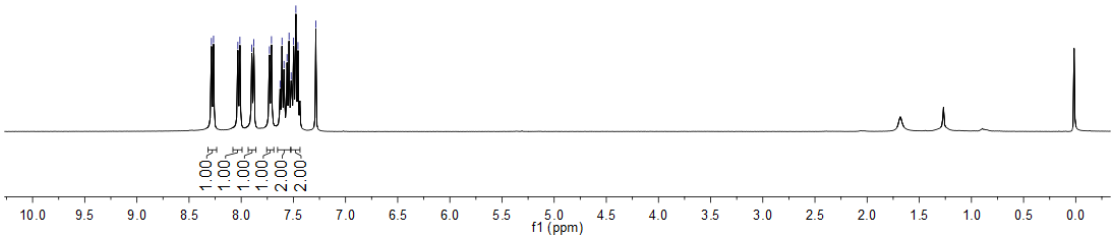
7.541
7.522
7.498
7.476
7.456
7.285
S
O
N
N

3a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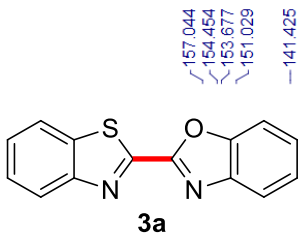
1.00
1.00
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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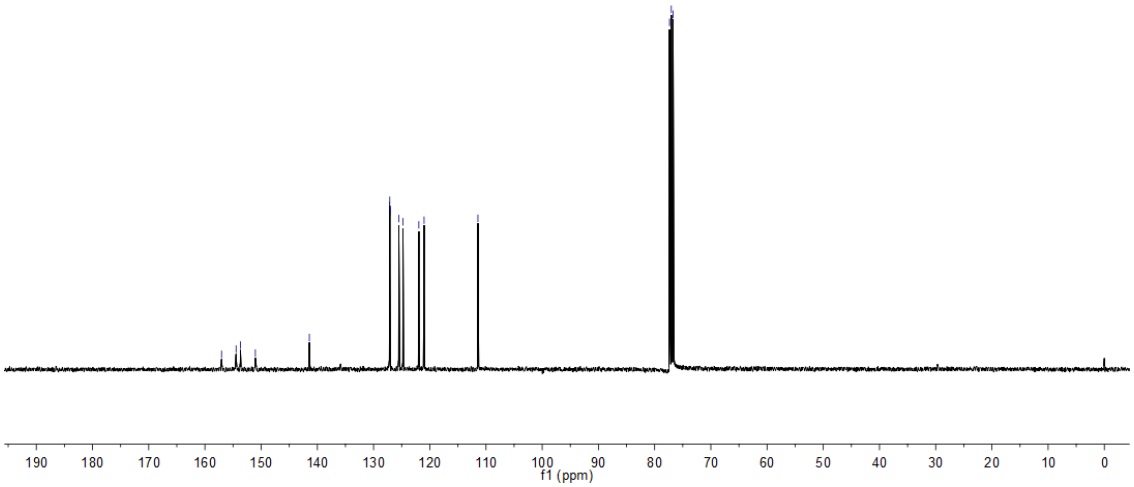
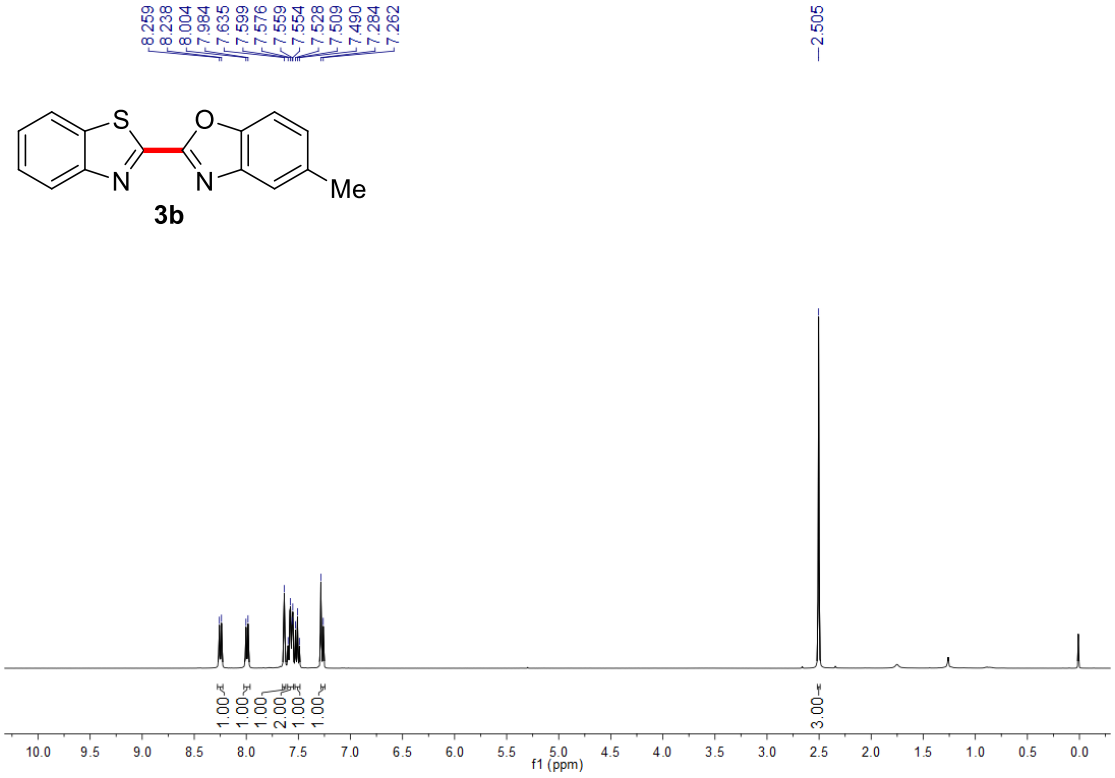
154.454
153.677
151.029
141.425
127.144
127.116
127.071
125.504
124.760
121.944
121.010
111.434
77.352
77.034
76.717
S
O
N
N

3a


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3b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8.238
8.004
7.984
7.635
7.599
7.576
7.559
7.554
7.528
7.509
7.490
7.284
7.262
2.505
S
O
N
N
Me
3b
1.00
1.00
1.00
2.00
1.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
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1.0
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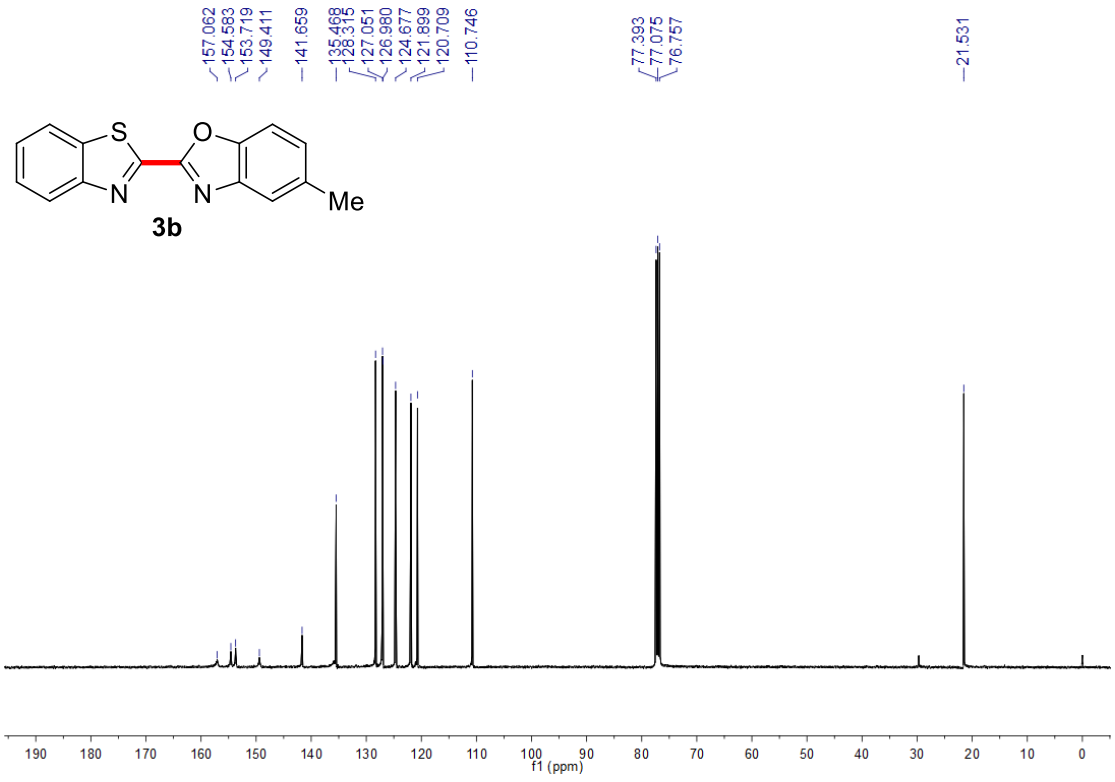
0.0
f1 (ppm)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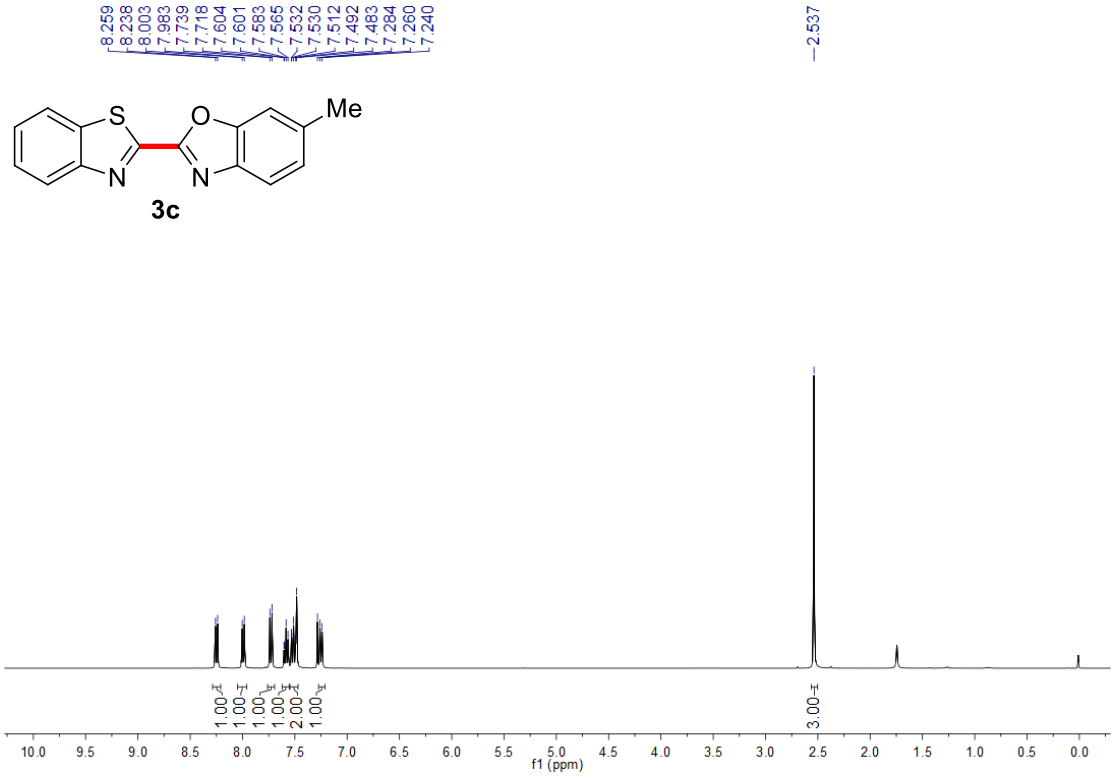
120.709
110.746
77.393
77.075
76.757
21.531
S
O
N
N
Me
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3c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7.565
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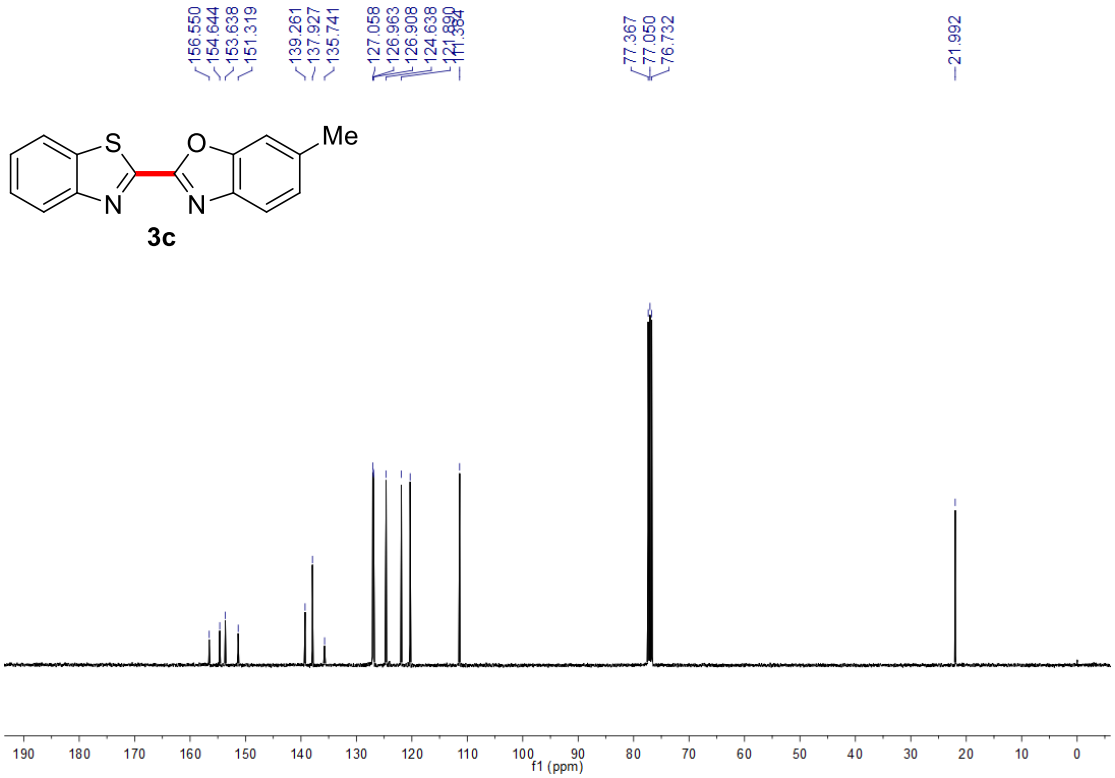
7.530
7.512
7.492
7.483
7.284
7.260
7.240
2.537
S
O
N
N
Me
3c
1.00
1.00
1.00
1.00
2.00
1.00
3.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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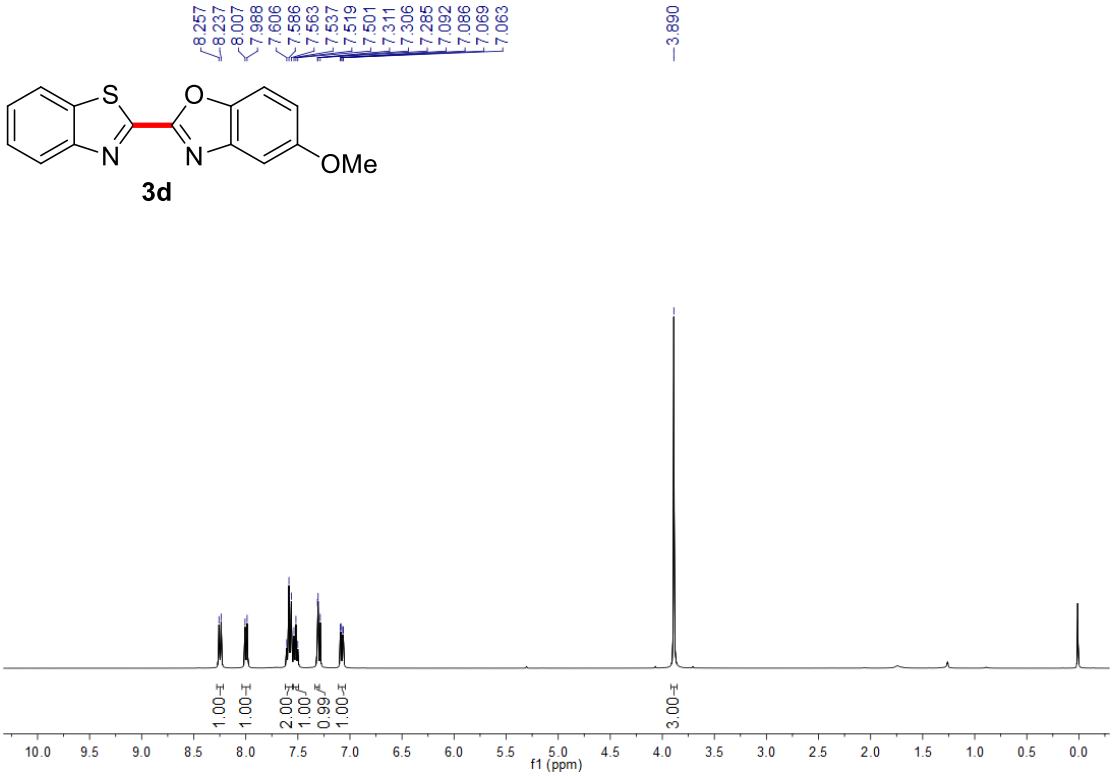
121.880
111.384
77.367
77.050
76.732
21.992
S
O
N
N
Me
3c
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

3d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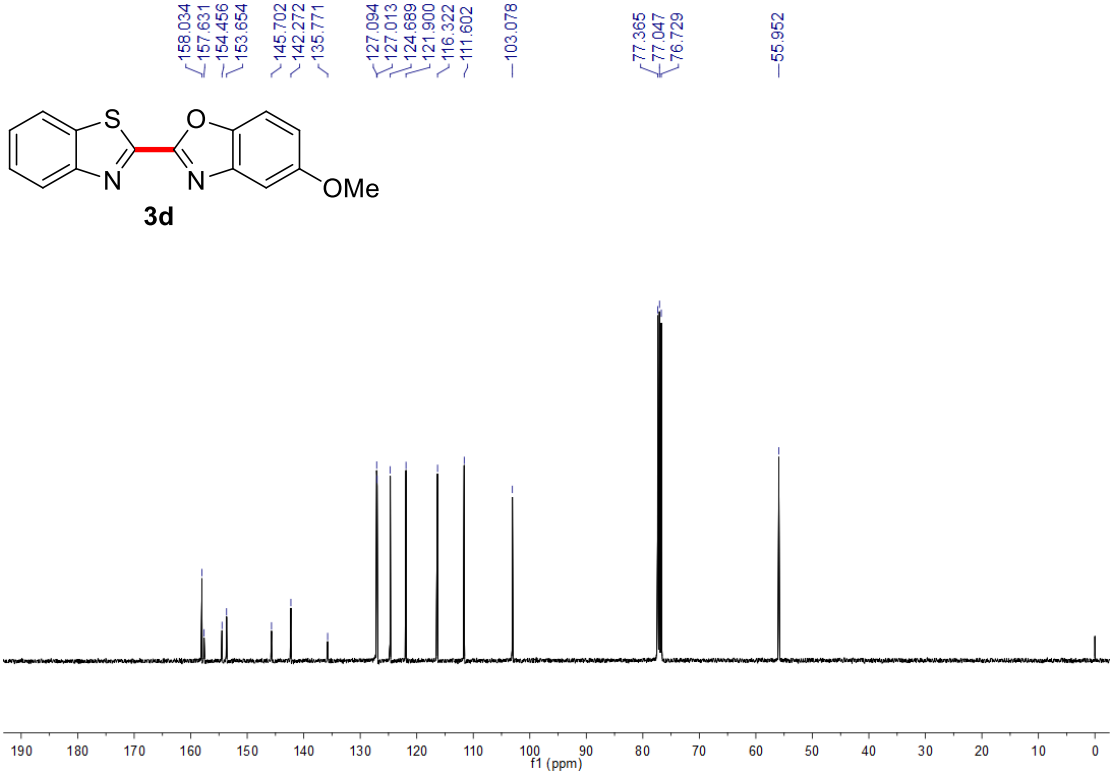
7.537
7.519
7.501
7.311
7.306
7.285
7.092
7.086
7.069
7.063
3.890
S
O
N
N
OMe
3d
1.00
1.00
2.00
1.00
0.99
1.00
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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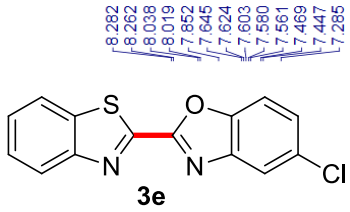
127.013
124.689
121.900
116.322
111.602
103.078
77.365
77.047
76.729
55.952
S
O
N
N
OMe
3d
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3e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7.852
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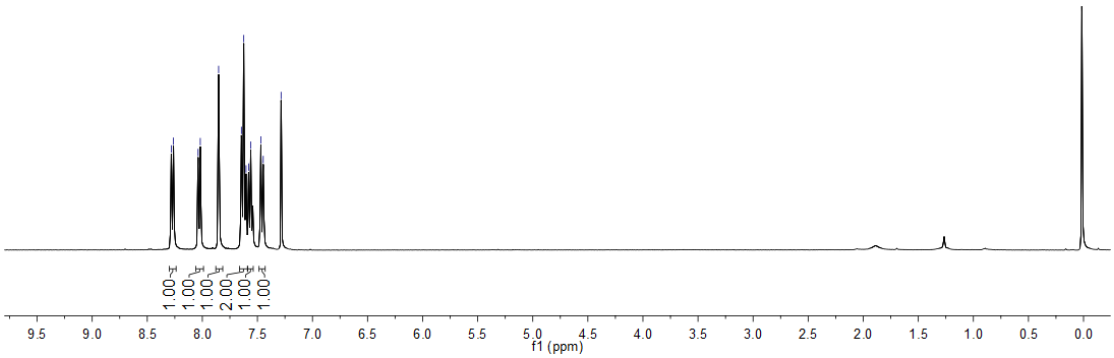
7.603
7.580
7.561
7.469
7.447
7.285
S
O
N
N
Cl

3e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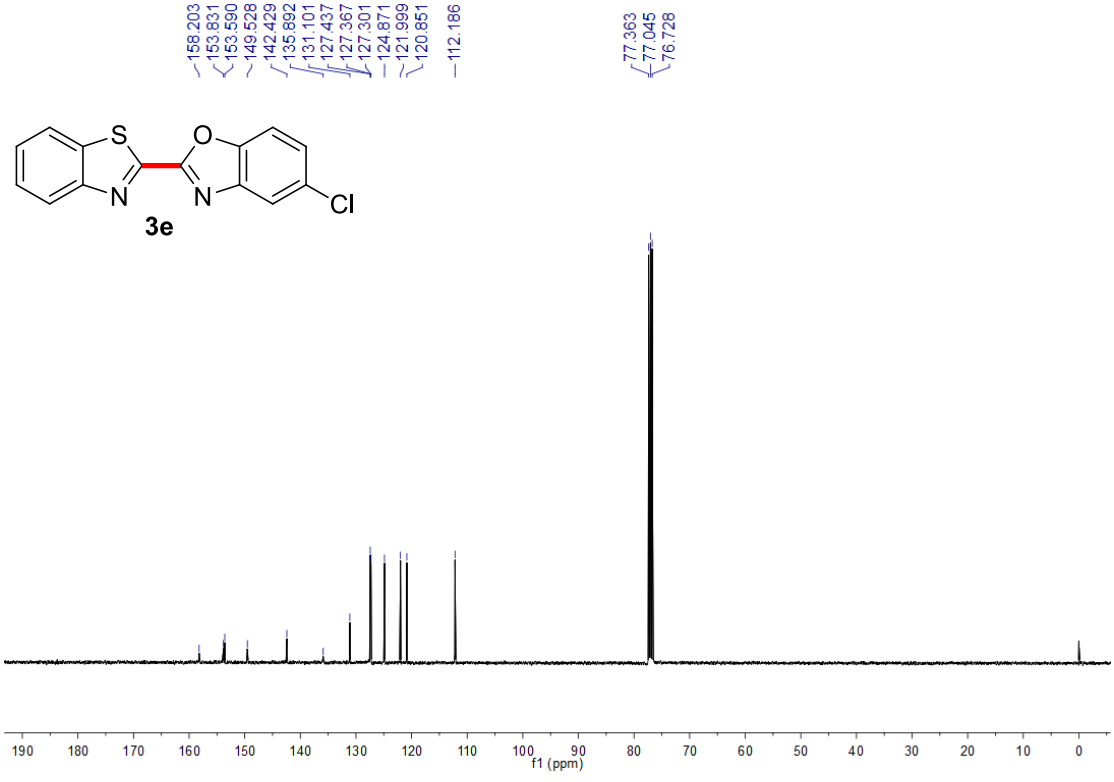
1.00
1.00
2.00
1.00
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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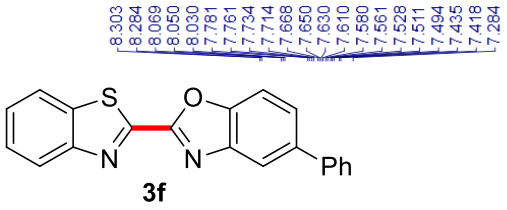
124.871
121.999
120.851
112.186
77.363
77.045
76.728
S
O
N
N
Cl
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3e

3f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7.668
7.650
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7.610
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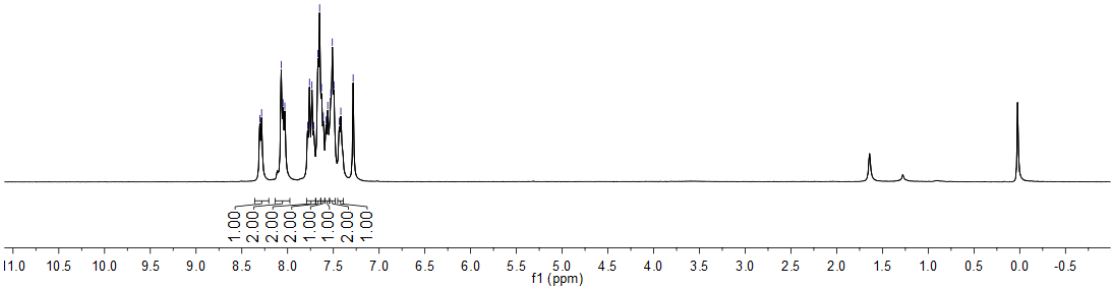
7.511
7.494
7.435
7.418
7.284
S
O
N
N
Ph

3f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2.00
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1.00
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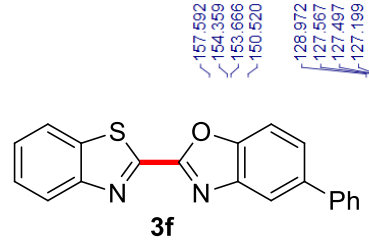
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128.972
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127.497
127.199
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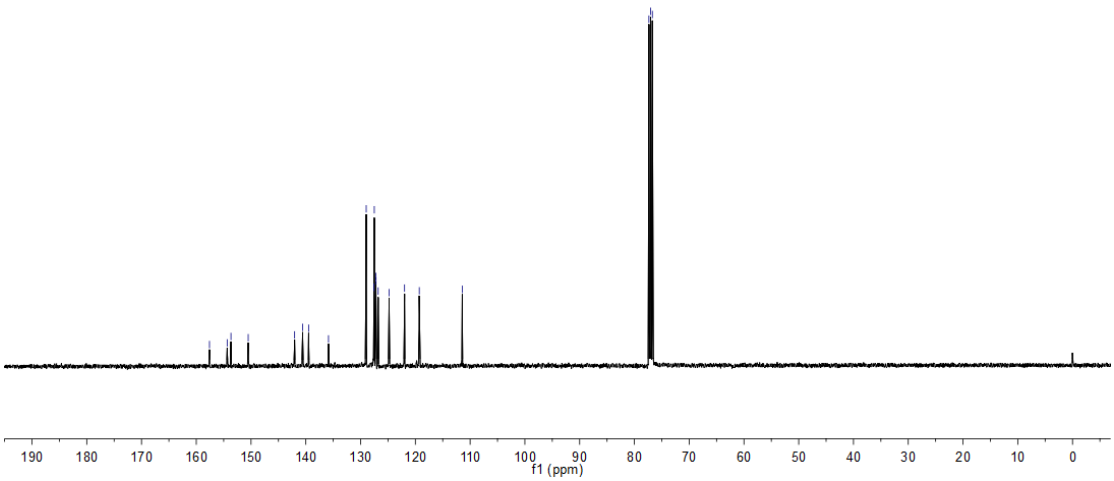
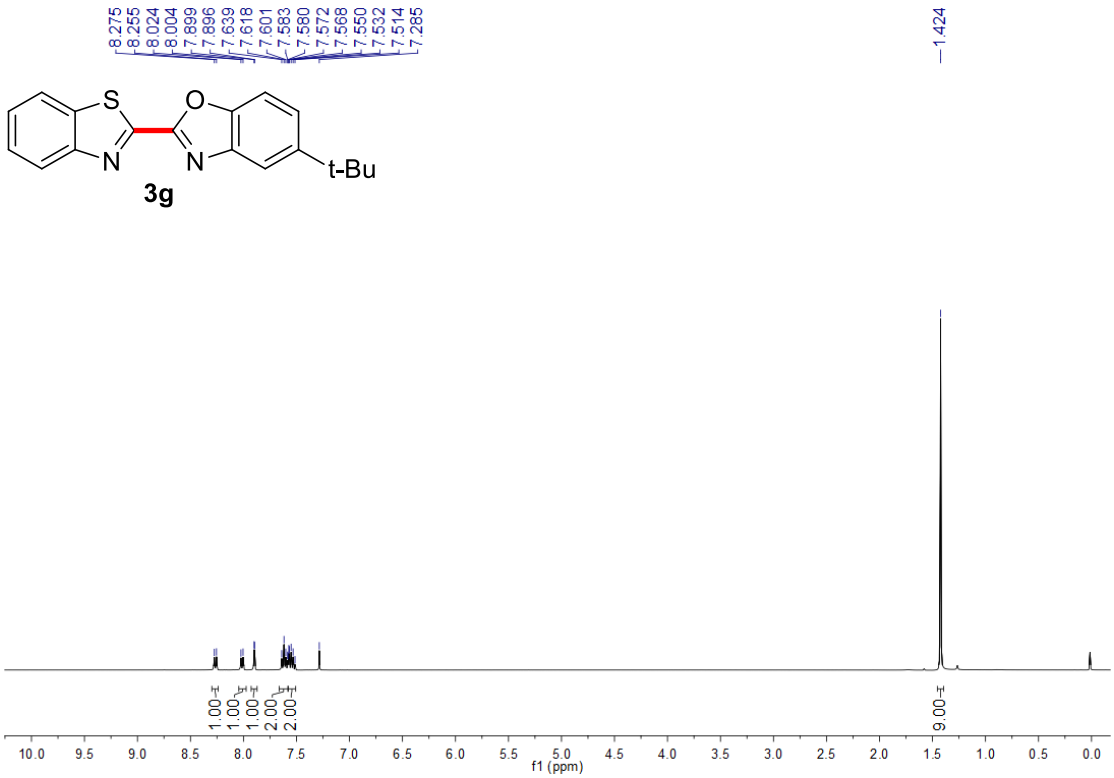
76.719
S
O
N
N
Ph

3f


f1 (ppm)

3g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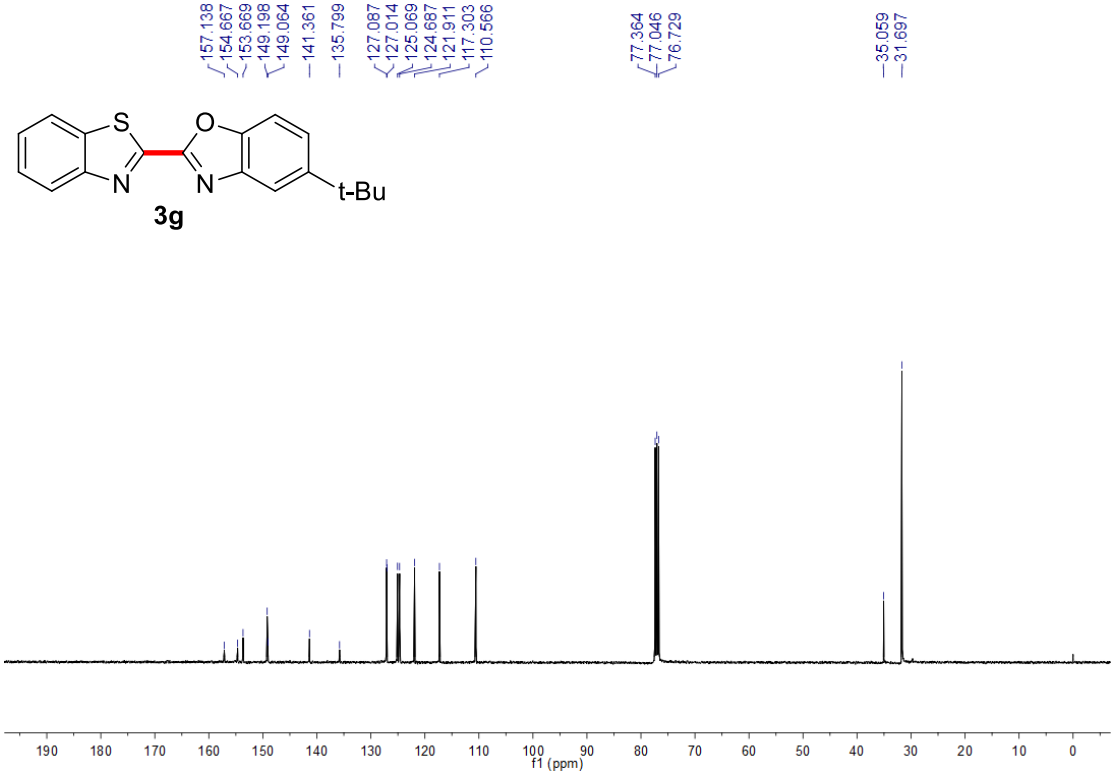
7.899
7.896
7.639
7.618
7.601
7.583
7.580
7.572
7.568
7.550
7.532
7.514
7.285
1.424
S
O
N
N
t-Bu
3g
1.00
1.00
1.00
2.00
2.00
9.00
f1 (ppm)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135.799
127.087
127.014
125.069
124.687
121.911
117.303
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77.364
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76.729
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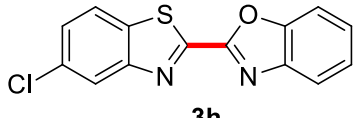
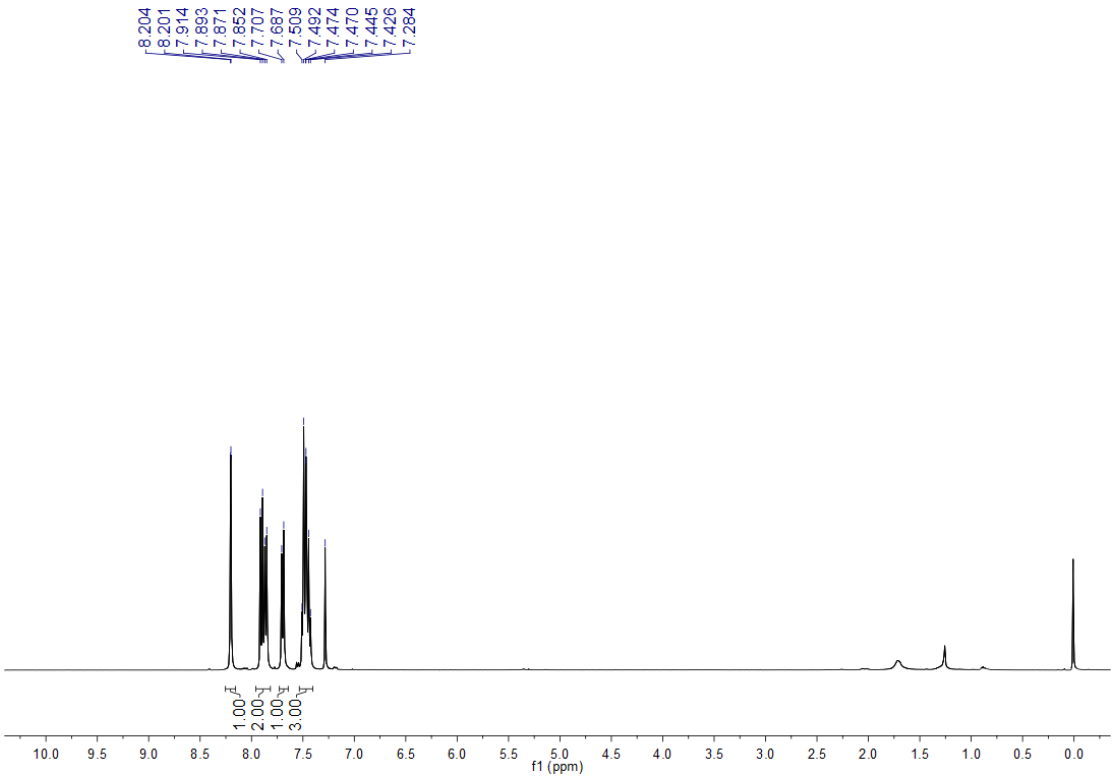
31.697
S
O
N
N
t-Bu
3g
f1 (ppm)

3h


S
O
N
N
Cl
3h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7.687
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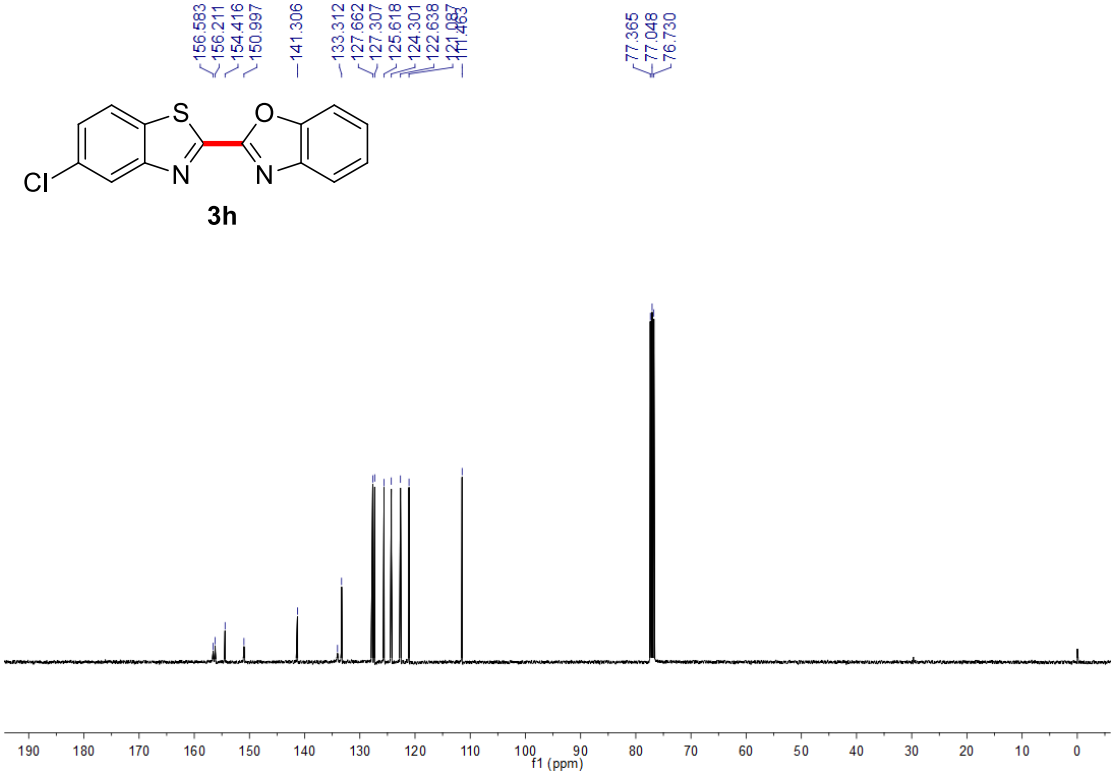
1.00
3.00
f1 (ppm)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127.307
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124.301
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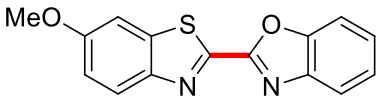
77.365
77.048
76.730
f1 (ppm)

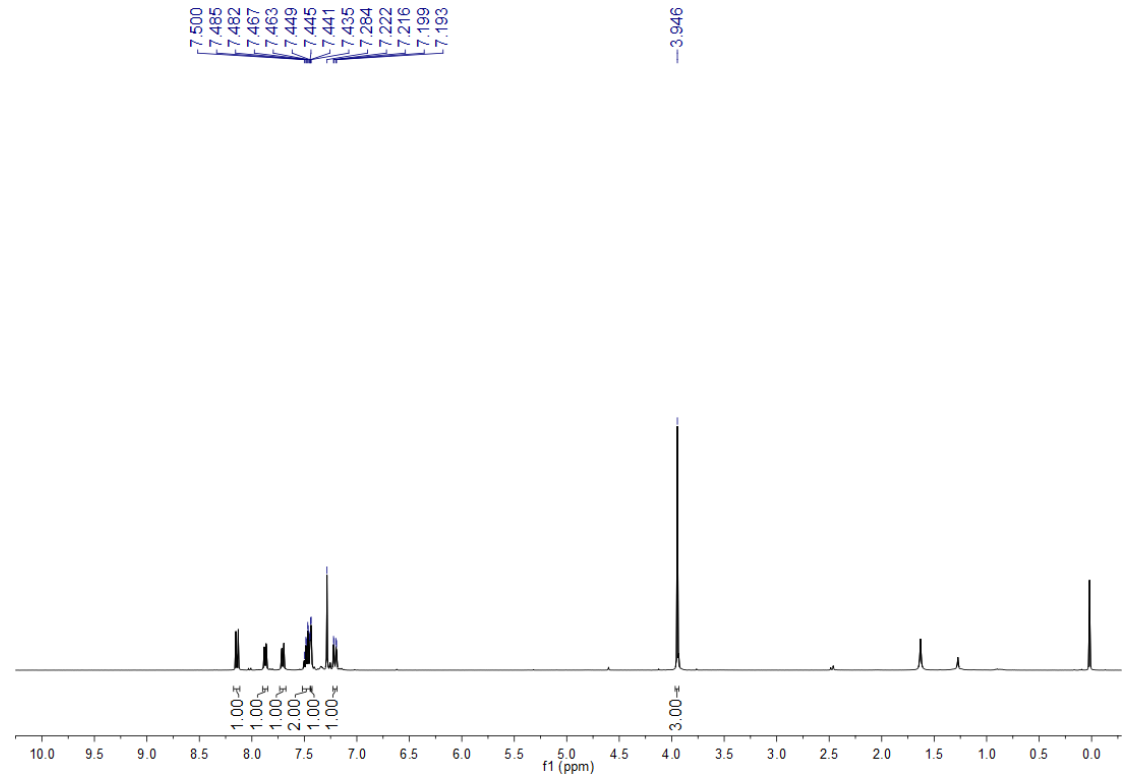
S
O
N
N
Cl

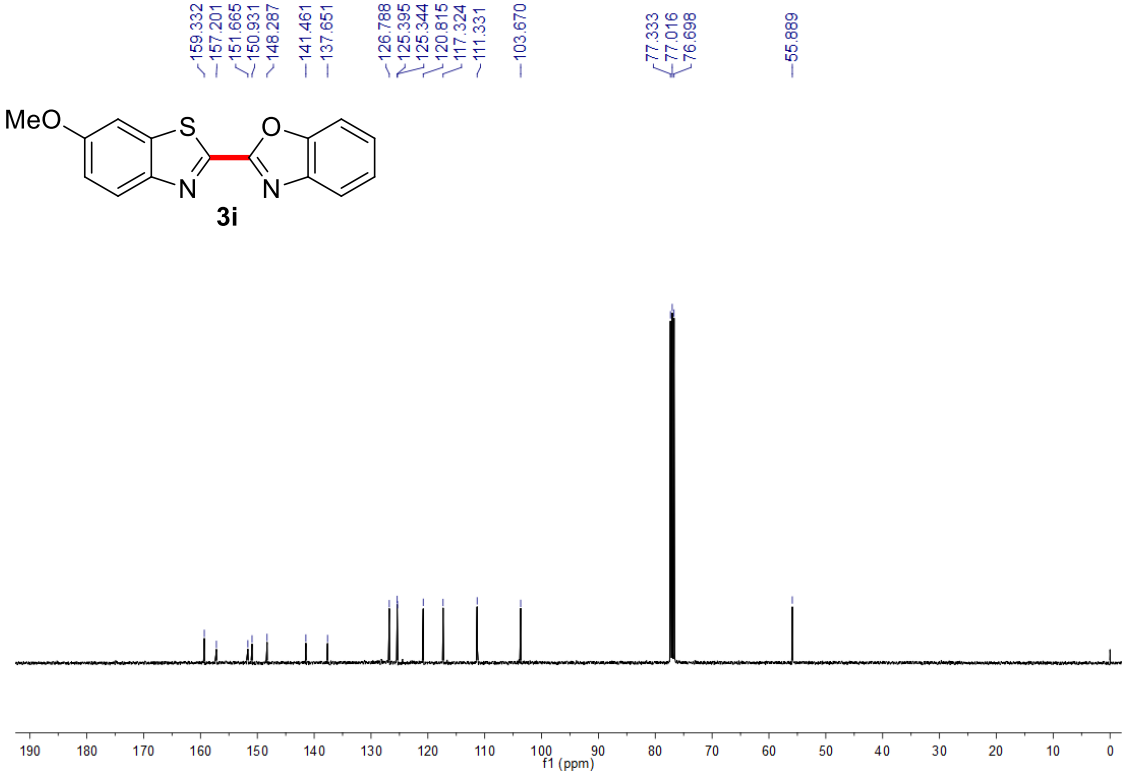
3h

3i


MeO
S
O
N
N

3i

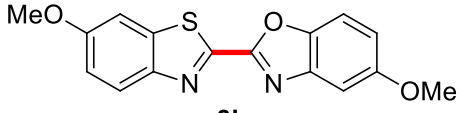

7.500
7.485
7.482
7.467
7.463
7.449
7.445
7.441
7.435
7.284
7.222
7.216
7.199
7.193
3.946
1.00
1.00
1.00
2.00
1.00
1.00
3.00
f1 (ppm)

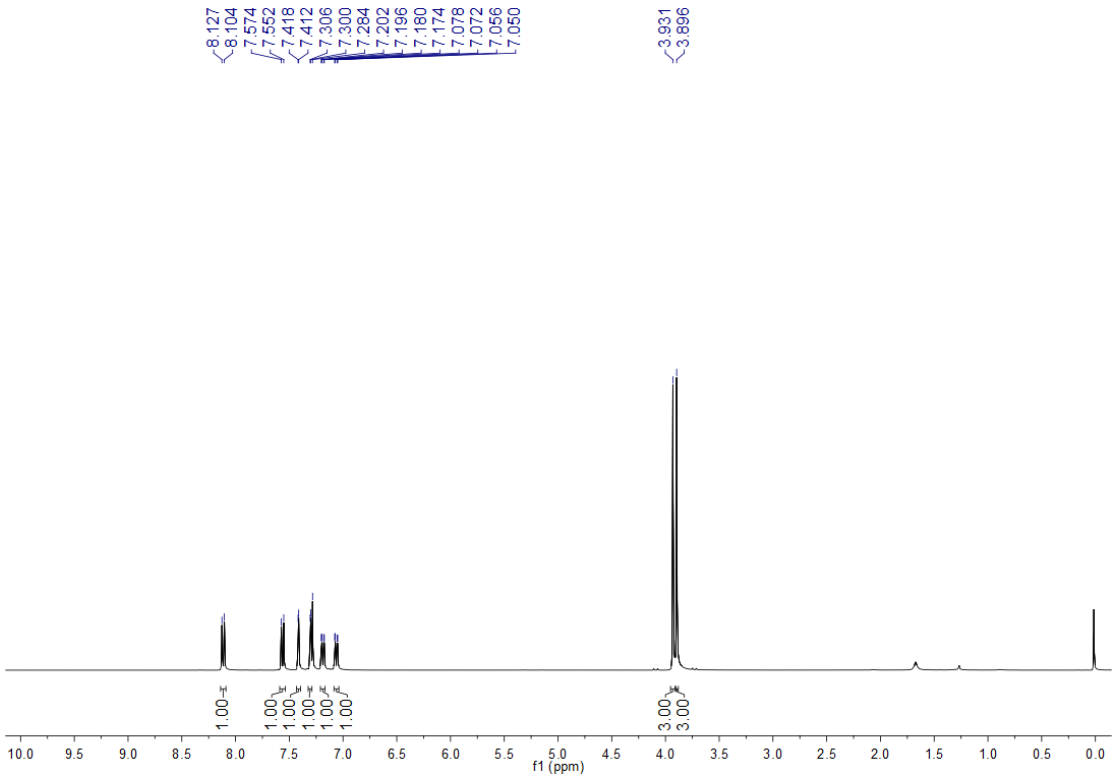

159.332
157.201
151.665
150.931
148.287
141.461
137.651
126.788
125.395
125.344
120.815
117.324
111.331
103.670
77.333
77.016
76.698
55.889
f1 (ppm)

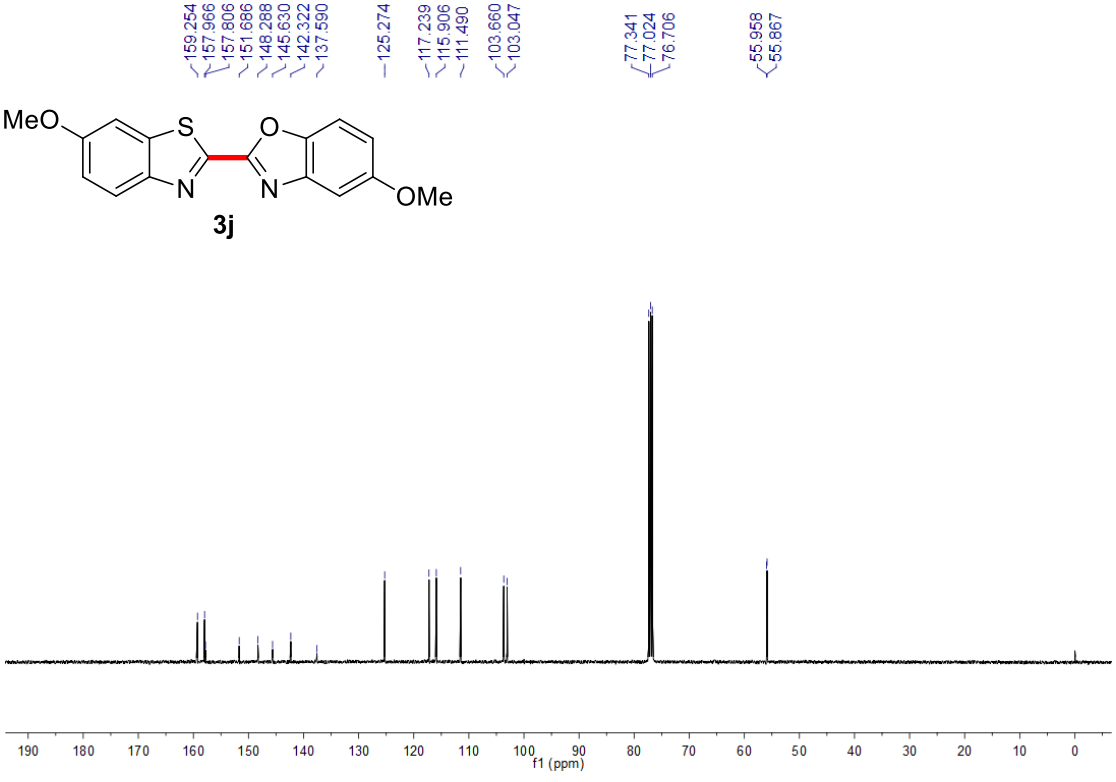
MeO
S
O
N
N

3i

3j


MeO
S
O
N
N
OMe

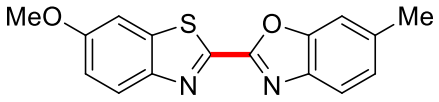

8.127
8.104
7.574
7.552
7.418
7.412
7.306
7.300
7.284
7.202
7.196
7.180
7.174
7.078
7.072
7.056
7.050
3.931
3.896
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


159.254
157.966
157.806
151.686
148.288
145.630
142.322
137.590
125.274
117.239
115.906
111.490
103.660
103.047
77.341
77.024
76.706
55.958
55.867
f1 (ppm)

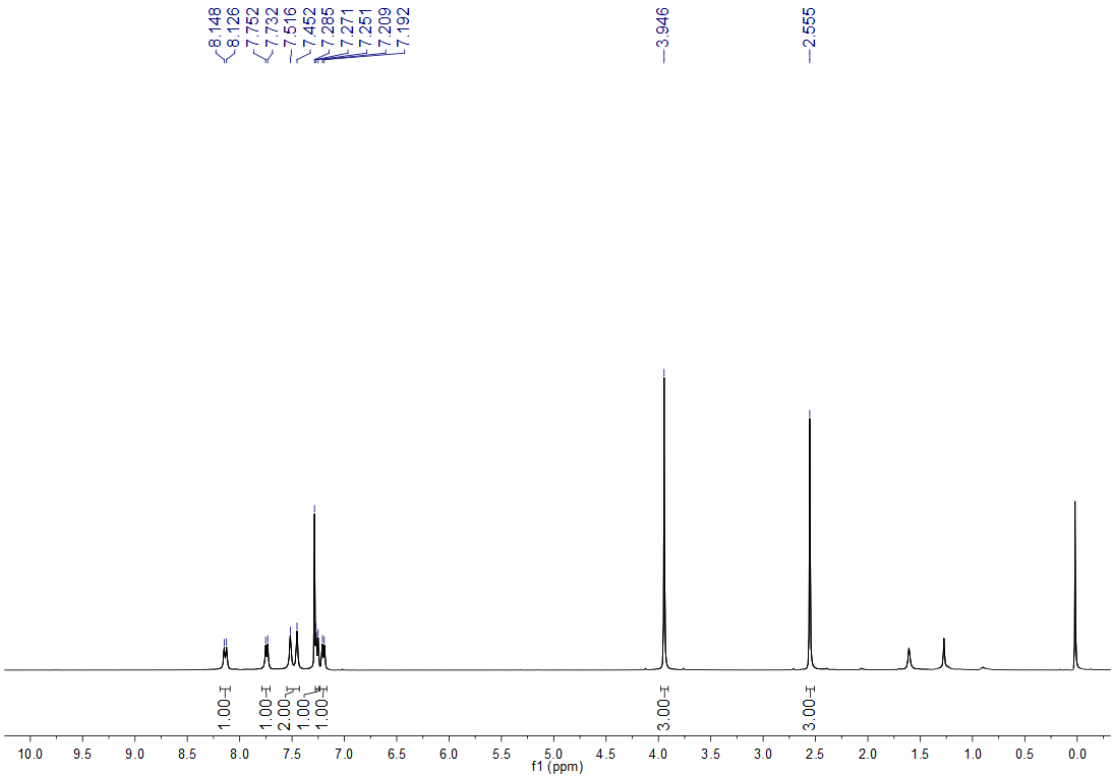
MeO
S
O
N
N
OMe

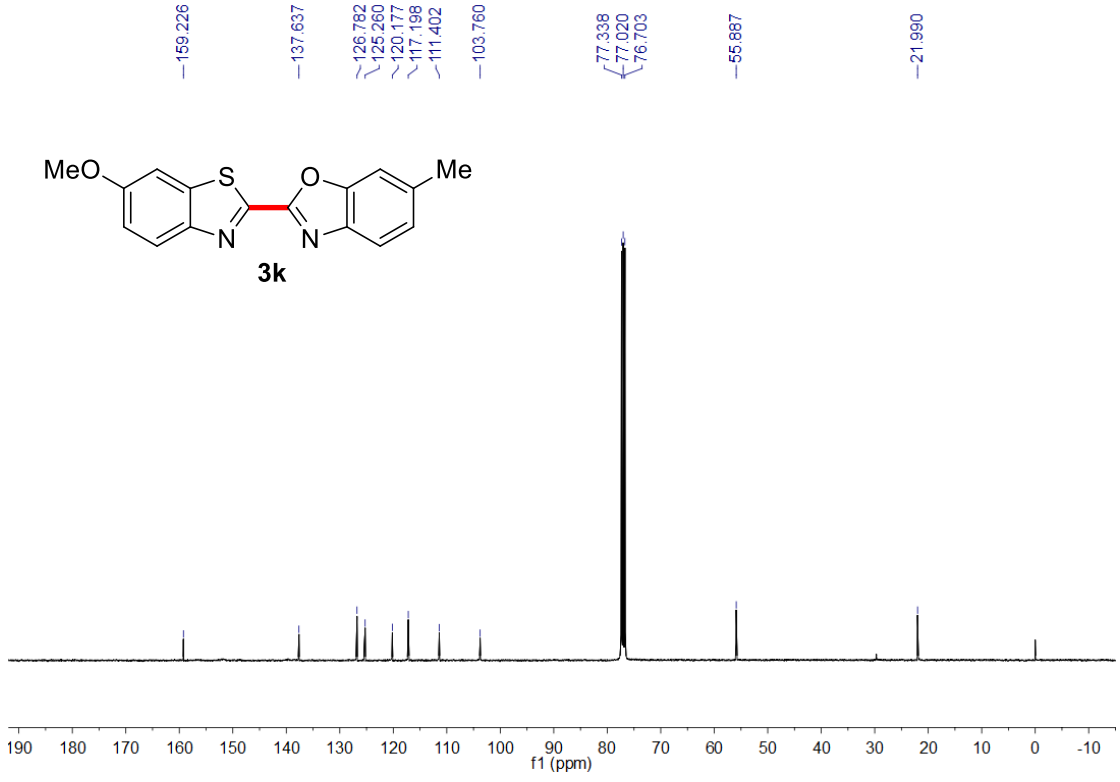
3j

3k


MeO
S
O
N
N
Me

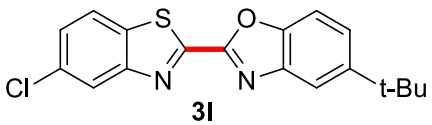
3k


8.148
8.126
7.752
7.732
7.516
7.452
7.285
7.271
7.251
7.209
7.192
3.946
2.555
1.00
1.00
2.00
1.00
1.00
3.00
3.00
f1 (ppm)

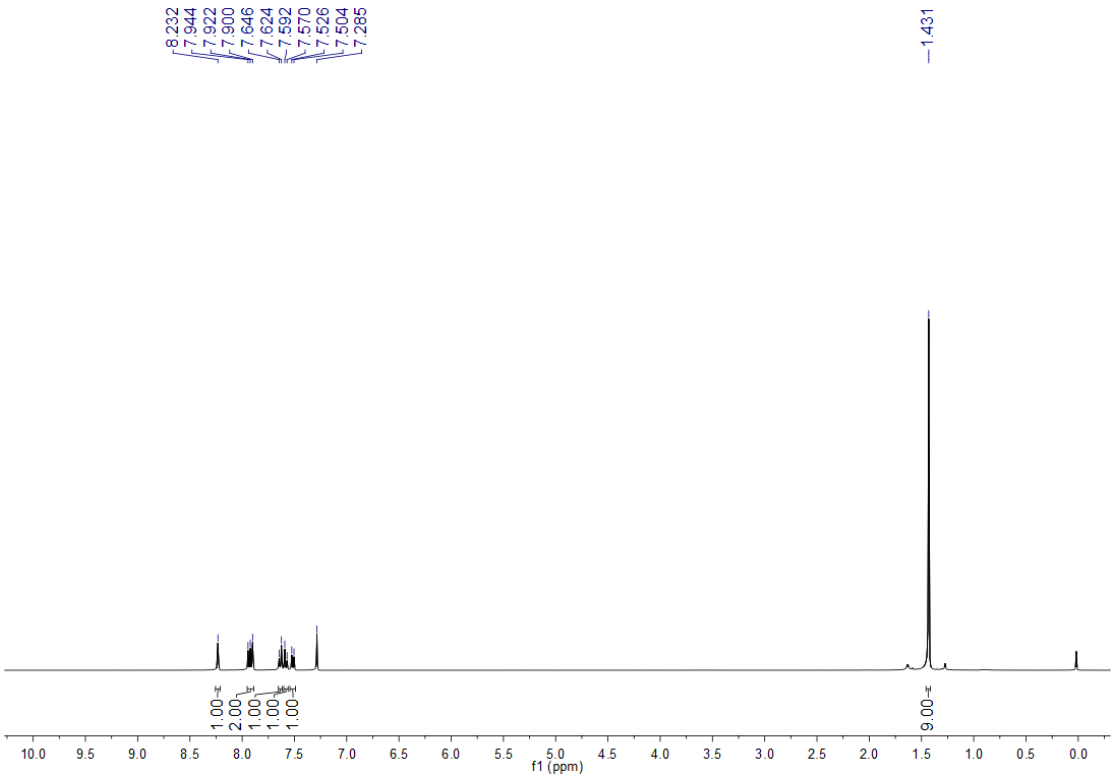

159.226
137.637
126.782
125.260
120.177
117.198
111.402
103.760
77.338
77.020
76.703
55.887
21.990
MeO
S
O
Me
N
N
f1 (ppm)

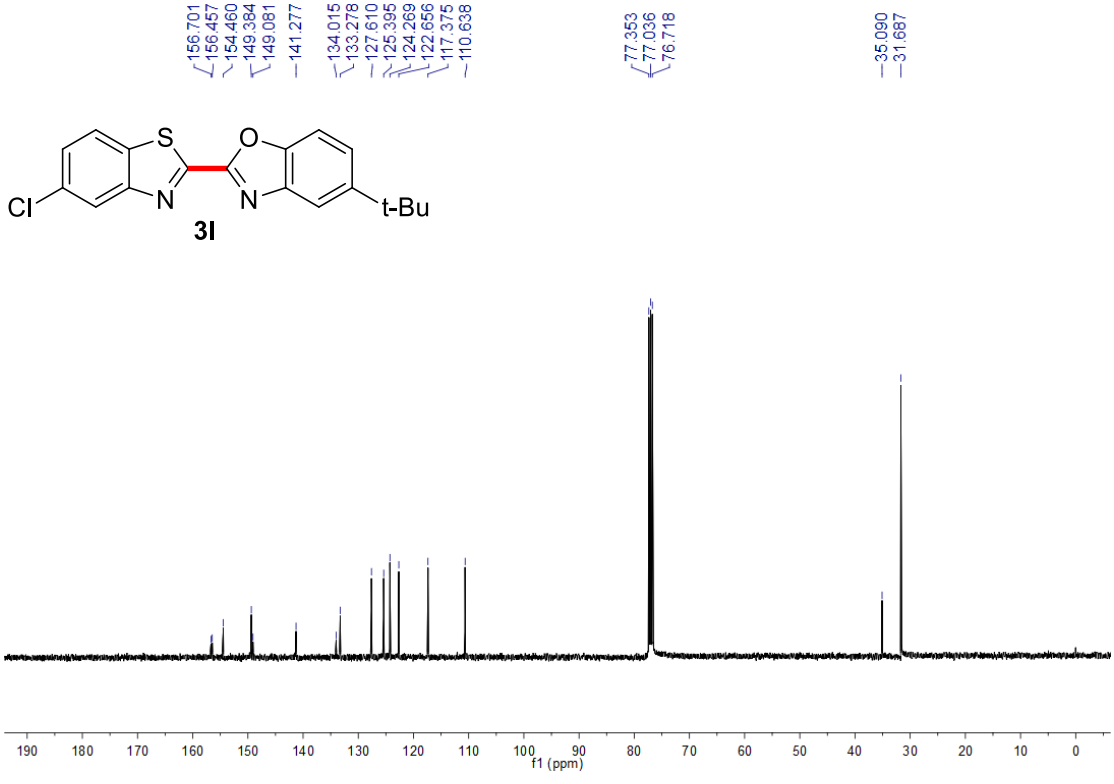
3k

3l


S
O
Cl
N
N
t-Bu

3l

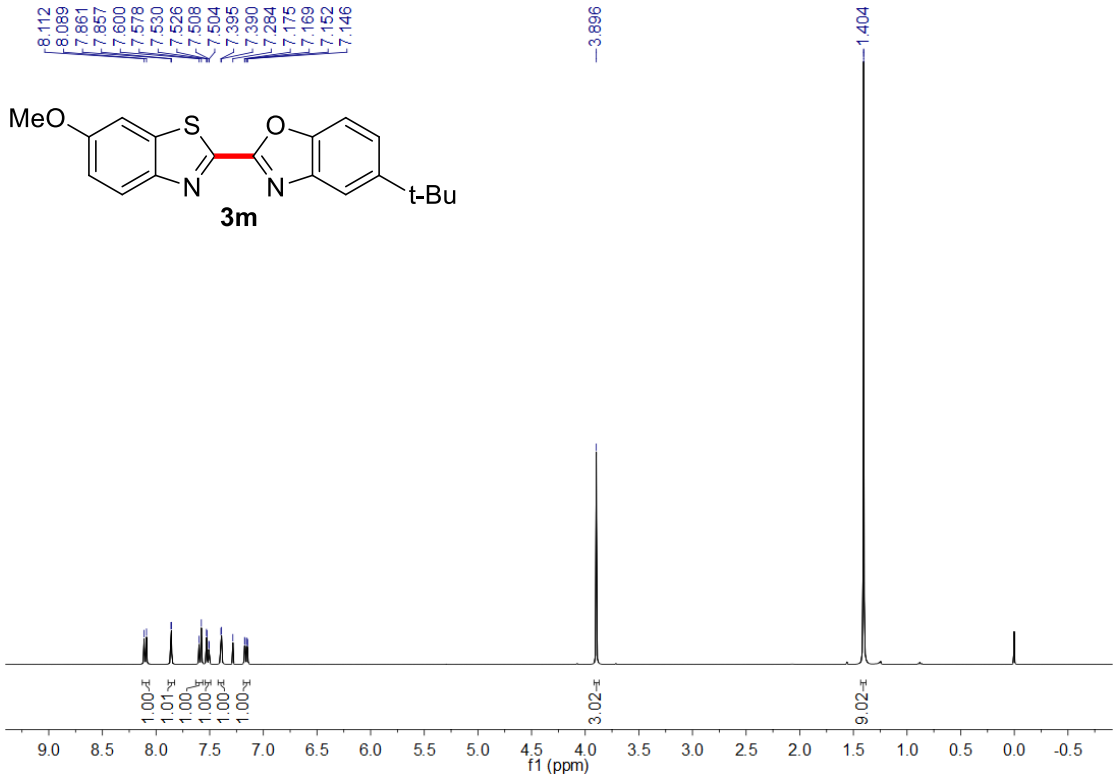

8.232
7.944
7.922
7.900
7.646
7.624
7.592
7.570
7.526
7.504
7.285
1.431
1.00
2.00
1.00
1.00
1.00
9.00
f1 (ppm)

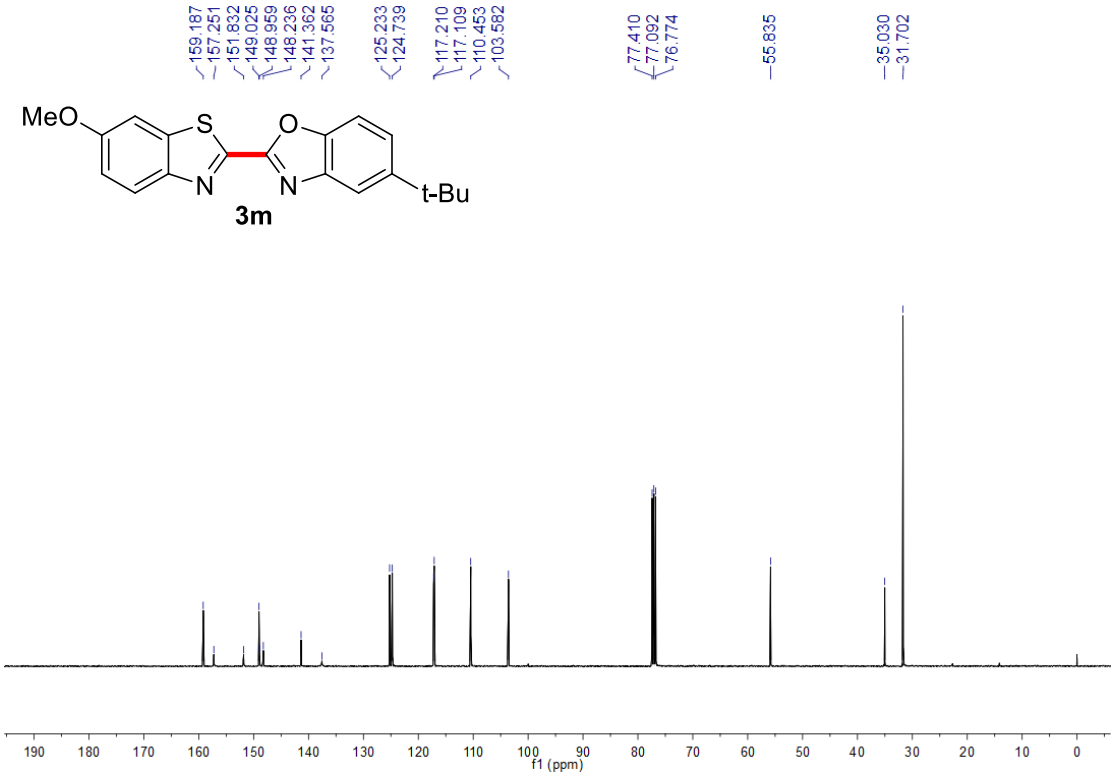

156.701
156.457
154.460
149.384
149.081
141.277
134.015
133.278
127.610
125.395
124.269
122.656
117.375
110.638
77.353
77.036
76.718
35.090
31.687
f1 (ppm)

S
O
N
N
Cl
t-Bu

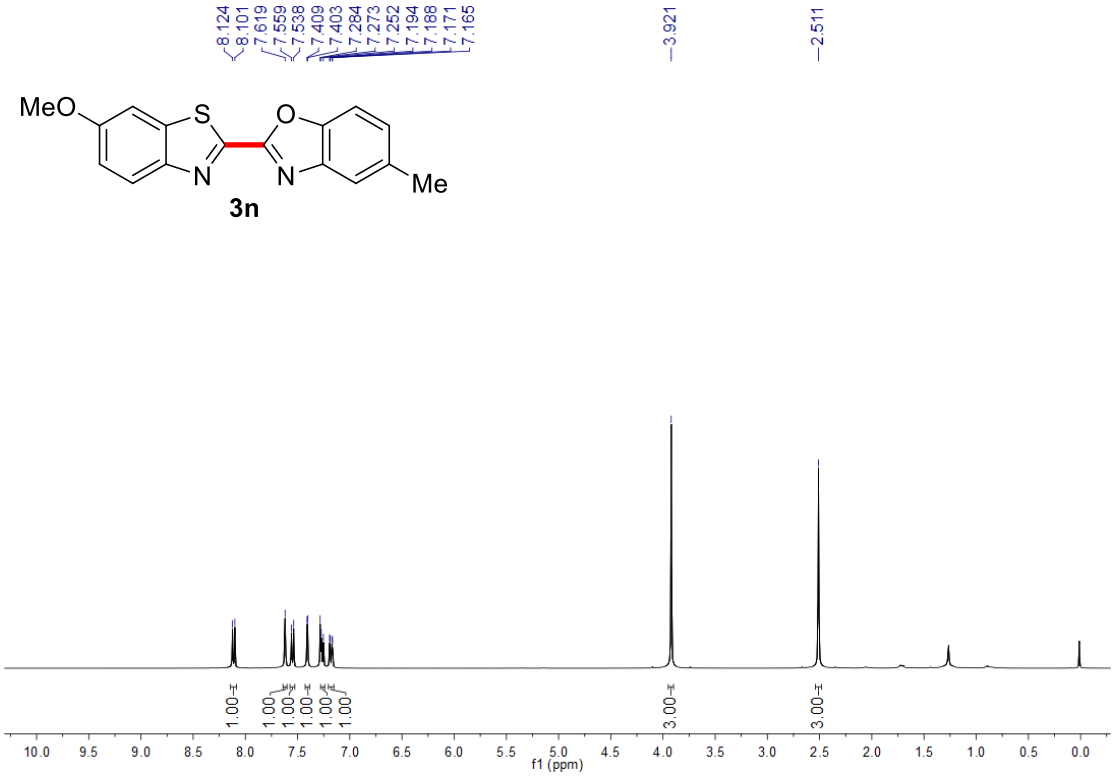
3l

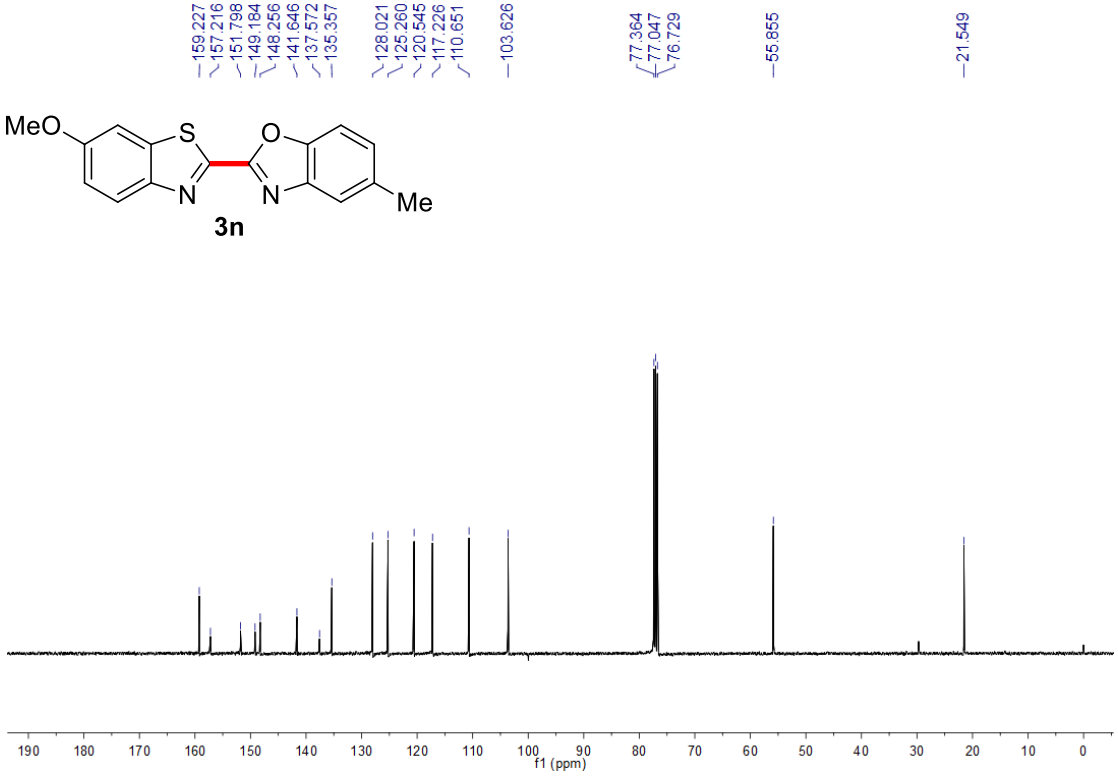
3m


8.112
8.089
7.861
7.857
7.600
7.578
7.530
7.526
7.508
7.504
7.395
7.390
7.284
7.175
7.169
7.152
7.146
3.896
1.404
MeO
S
O
N
N
t-Bu
3m
1.00
1.01
1.00
1.00
1.00
1.00
3.02
9.02
f1 (ppm)

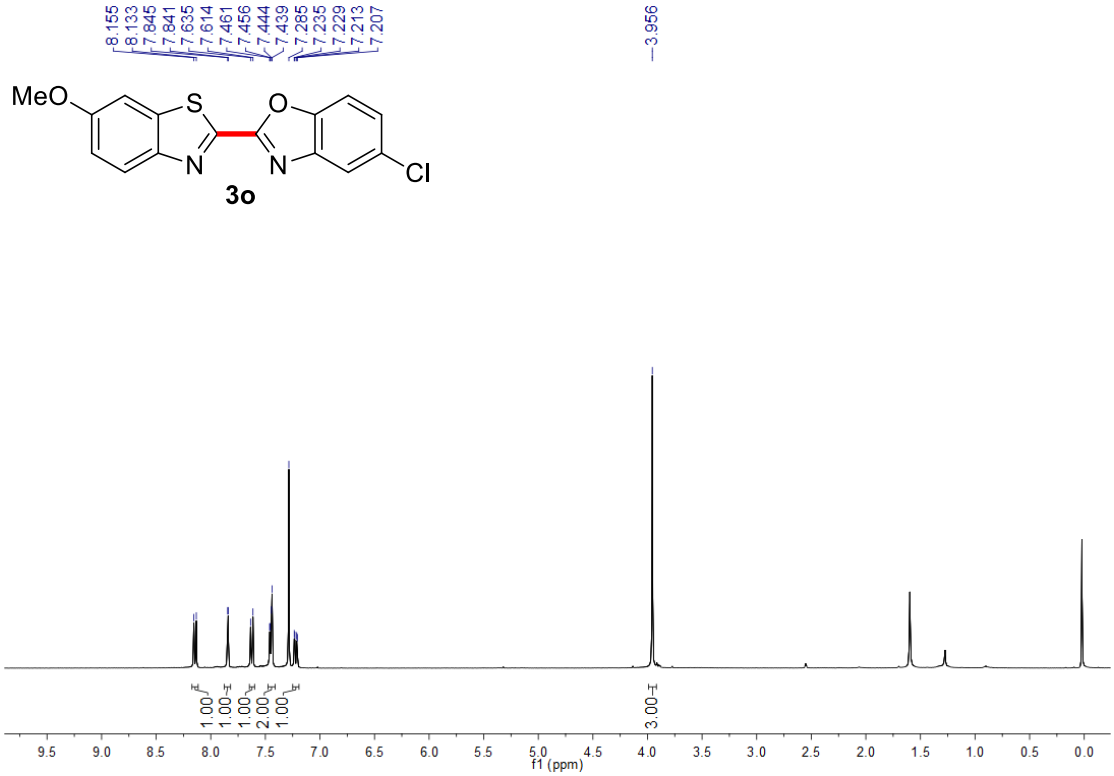

159.187
157.251
151.832
149.025
148.959
148.236
141.362
137.565
125.233
124.739
117.210
117.109
110.453
103.582
77.410
77.092
76.774
55.835
35.030
31.702
MeO
S
O
N
N
t-Bu
3m
f1 (ppm)

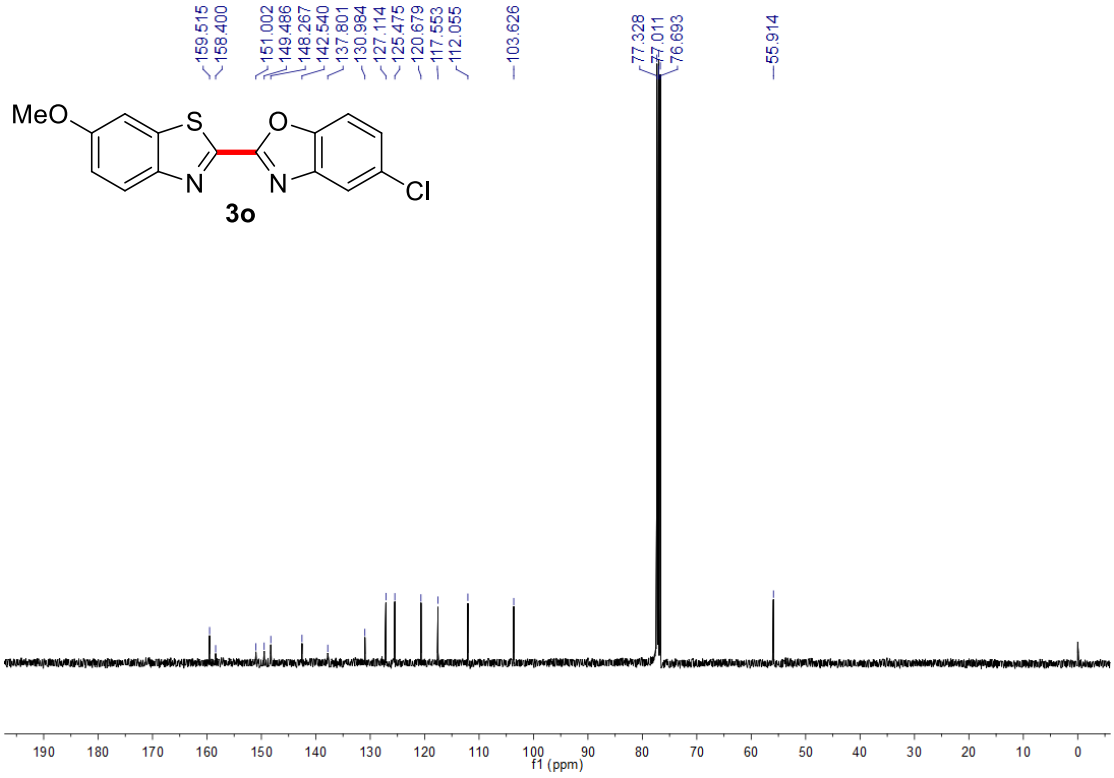
3n


8.124
8.101
7.619
7.559
7.538
7.409
7.403
7.284
7.273
7.252
7.194
7.188
7.171
7.165
3.921
2.511
MeO
S
O
N
N
Me
3n
1.00
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)

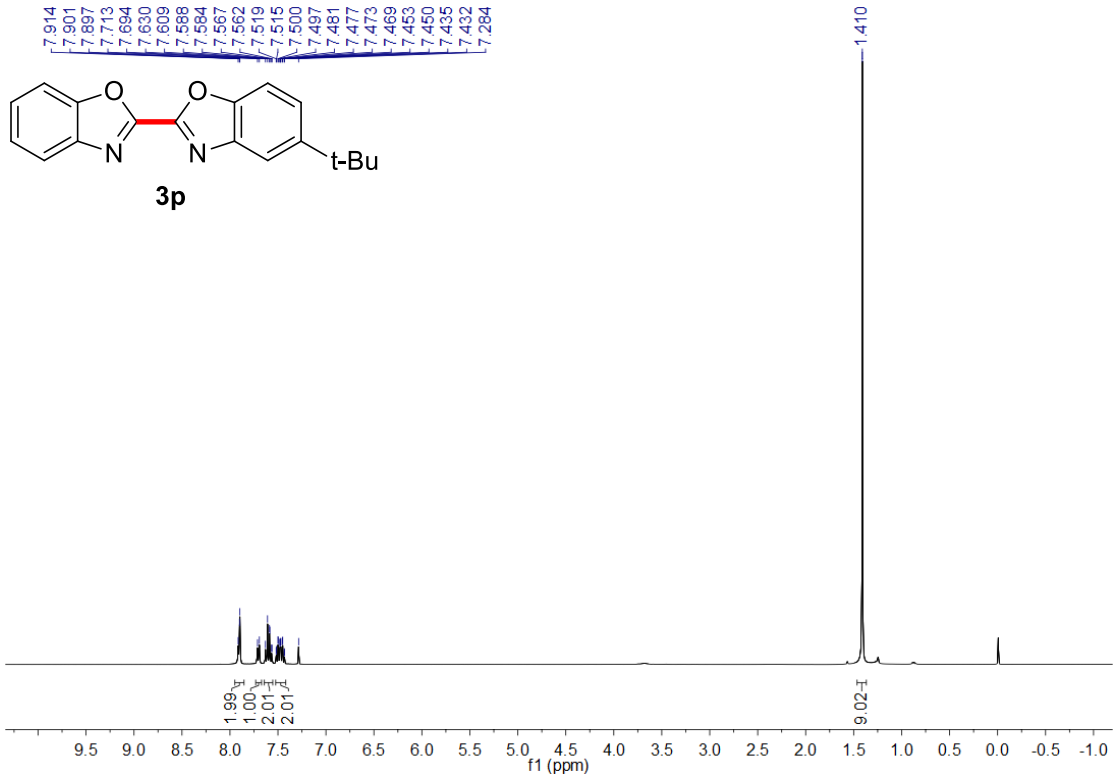

159.227
157.216
151.798
149.184
148.256
141.646
137.572
135.357
128.021
125.260
120.545
117.226
110.651
103.626
77.364
77.047
76.729
55.855
21.549
MeO
S
O
N
N
Me
3n
f1 (ppm)

3o

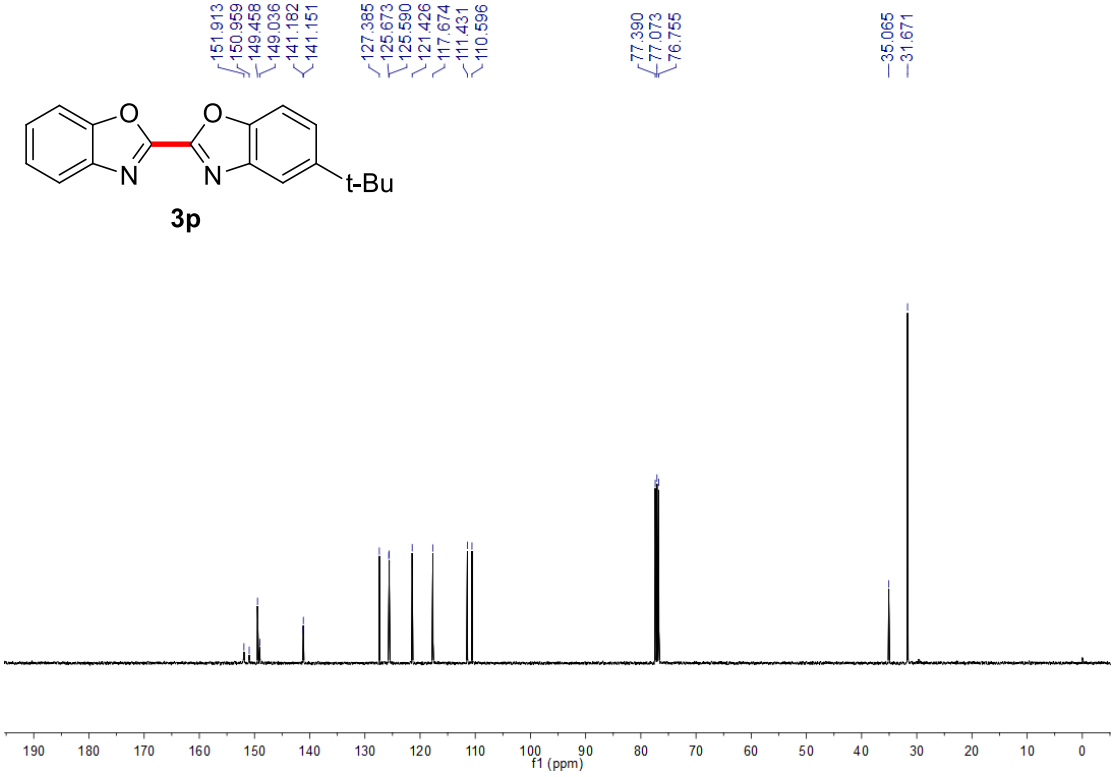

8.155
8.133
7.845
7.841
7.635
7.614
7.461
7.456
7.444
7.439
7.285
7.235
7.229
7.213
7.207
3.956
MeO
S
O
N
N
Cl
3o
1.00
1.00
1.00
2.00
1.00
3.00
f1 (ppm)


159.515
158.400
151.002
149.486
148.267
142.540
137.801
130.984
127.114
125.475
120.679
117.553
112.055
103.626
77.328
77.011
76.693
55.914
MeO
S
O
N
N
Cl
3o
f1 (ppm)

3p

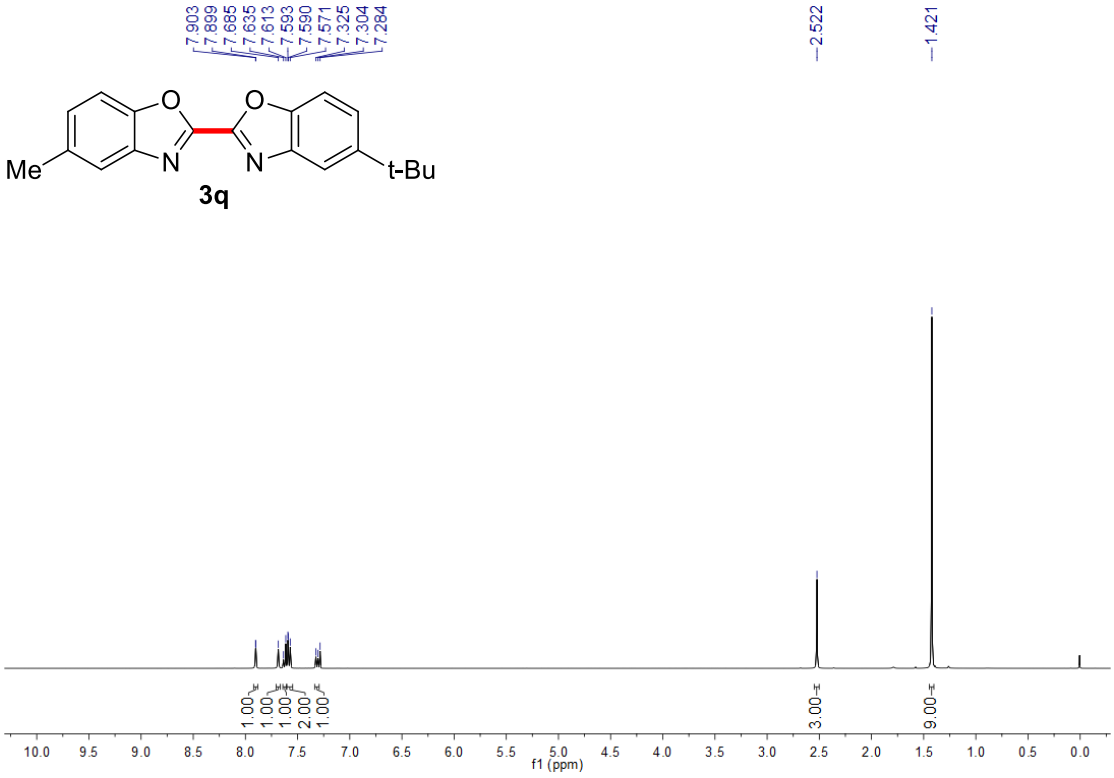

7.914
7.901
7.897
7.713
7.694
7.630
7.609
7.588
7.584
7.567
7.562
7.519
7.515
7.500
7.497
7.481
7.477
7.473
7.469
7.453
7.450
7.435
7.432
7.284
1.410
O
O
N
N
t-Bu
1.99
1.00
2.01
2.01
9.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)

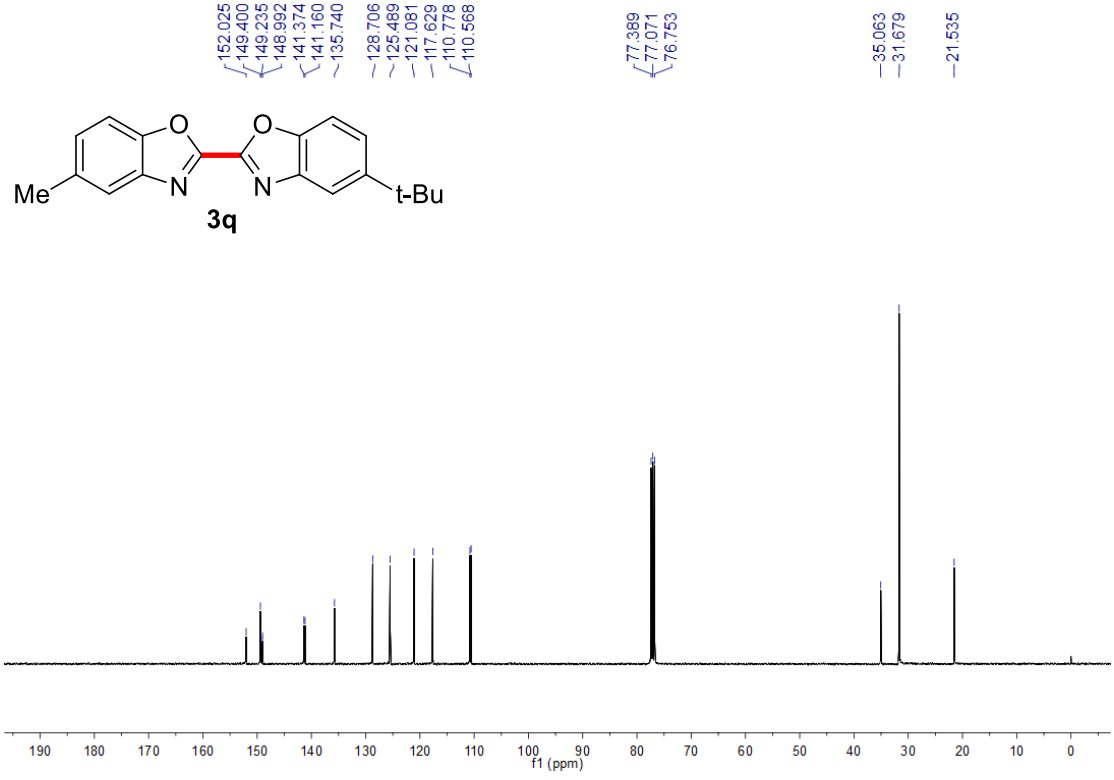
3p


151.913
150.959
149.458
149.036
141.182
141.151
127.385
125.673
125.590
121.426
117.674
111.431
110.596
77.390
77.073
76.755
35.065
31.671
O
O
N
N
t-Bu
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

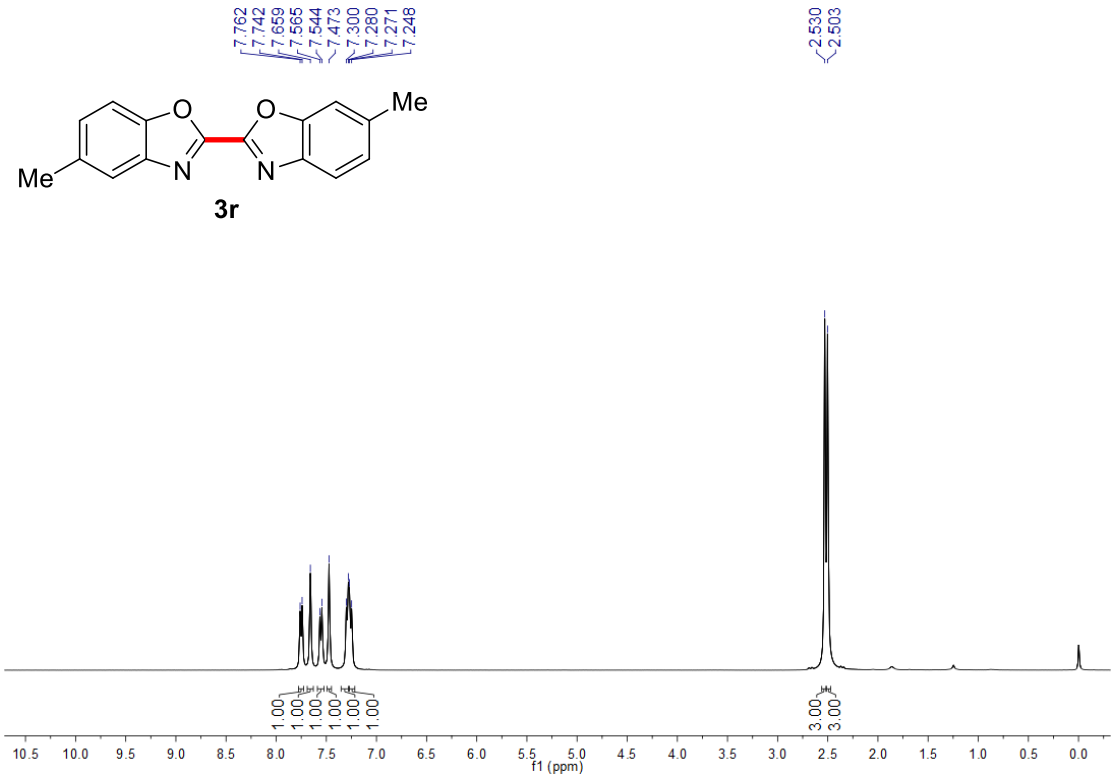
3p

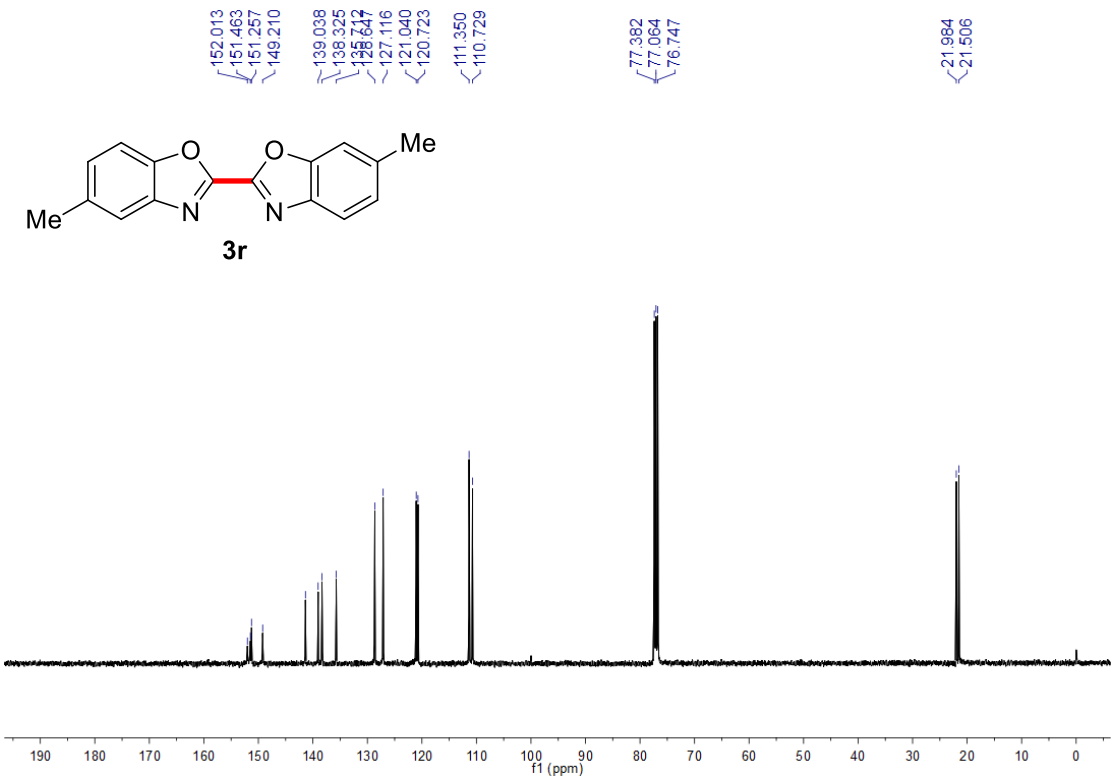
3q


7.903
7.899
7.685
7.635
7.613
7.593
7.590
7.571
7.325
7.304
7.284
2.522
1.421
Me
t-Bu
3q
1.00
1.00
1.00
2.00
1.00
3.00
9.00
f1 (ppm)

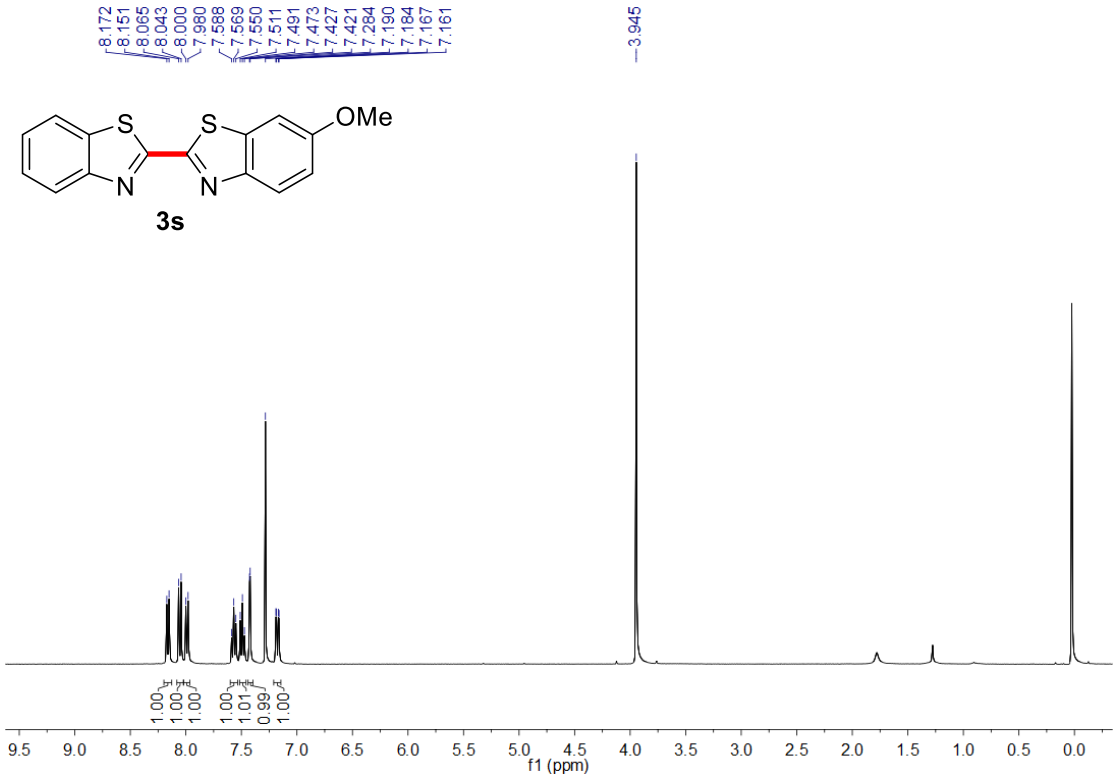

152.025
149.400
149.235
148.992
141.374
141.160
135.740
128.706
125.489
121.081
117.629
110.778
110.568
77.389
77.071
76.753
35.063
31.679
21.535
Me
t-Bu
3q
f1 (ppm)

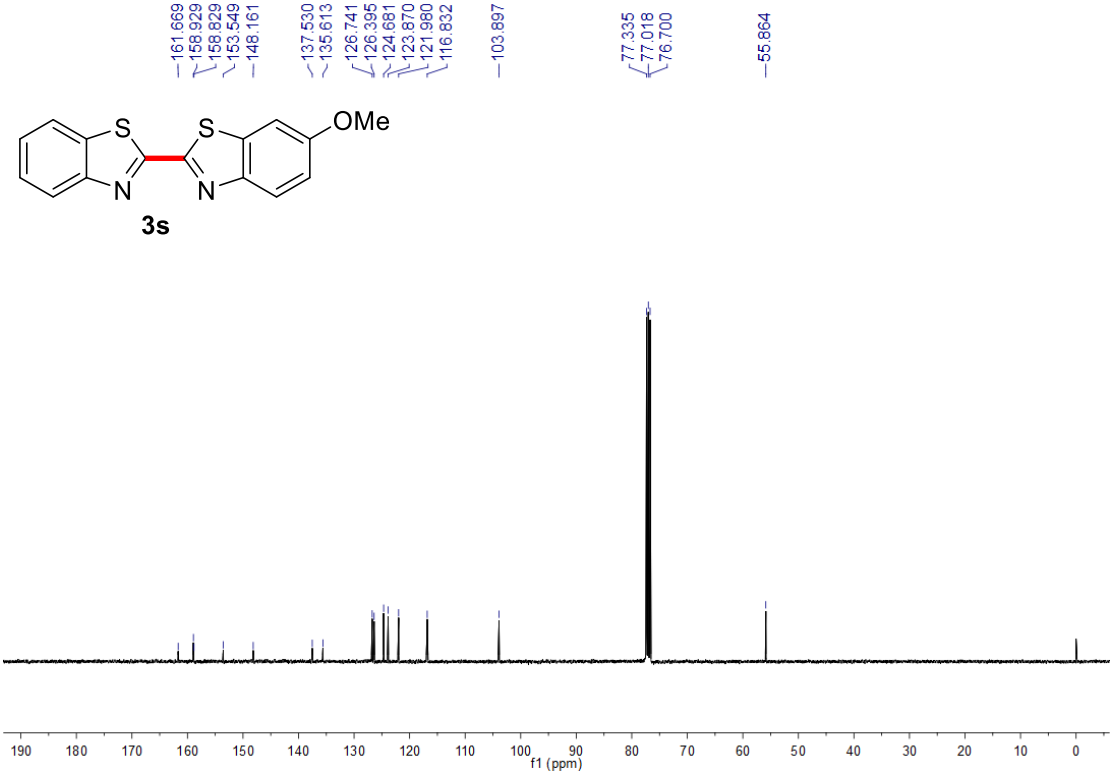
3r


7.762
7.742
7.659
7.565
7.544
7.473
7.300
7.280
7.271
7.248
2.530
2.503
Me
Me
O
O
N
N
3r
1.00
1.00
1.00
1.00
1.00
3.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


152.013
151.463
151.257
149.210
139.038
138.325
135.712
128.647
127.116
121.040
120.723
111.350
110.729
77.382
77.064
76.747
21.984
21.506
Me
Me
O
O
N
N
3r
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

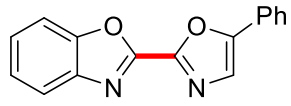
3s


8.172
8.151
8.065
8.043
8.000
7.980
7.588
7.569
7.550
7.511
7.491
7.473
7.427
7.421
7.284
7.190
7.184
7.167
7.161
3.945
OMe
S
S
N
N
3s
1.00
1.00
1.00
1.00
1.01
0.99
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

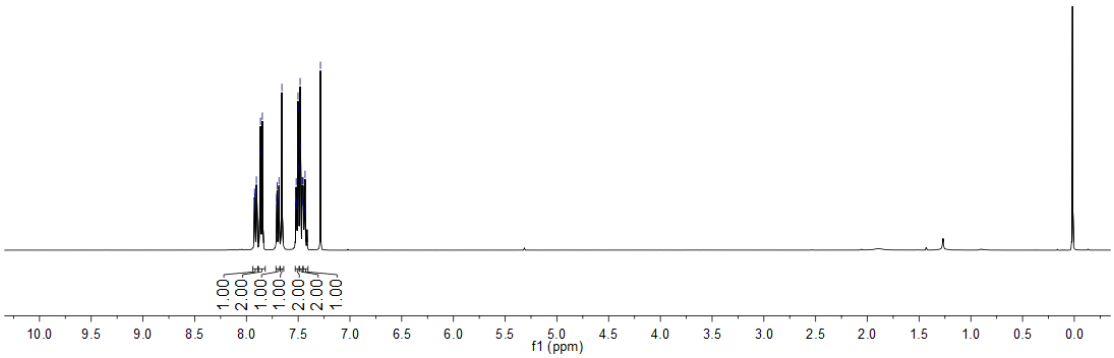

161.669
158.929
158.829
153.549
148.161
137.530
135.613
126.741
126.395
124.681
123.870
121.980
116.832
103.897
77.335
77.018
76.700
55.864
OMe
S
S
N
N
3s
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3t

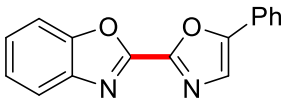

7.922
7.920
7.916
7.904
7.900
7.868
7.864
7.846
7.708
7.704
7.691
7.686
7.658
7.522
7.519
7.517
7.513
7.502
7.498
7.494
7.481
7.476
7.462
7.459
7.455
7.452
7.449
7.440
7.433
7.285


O
O
Ph
N
N

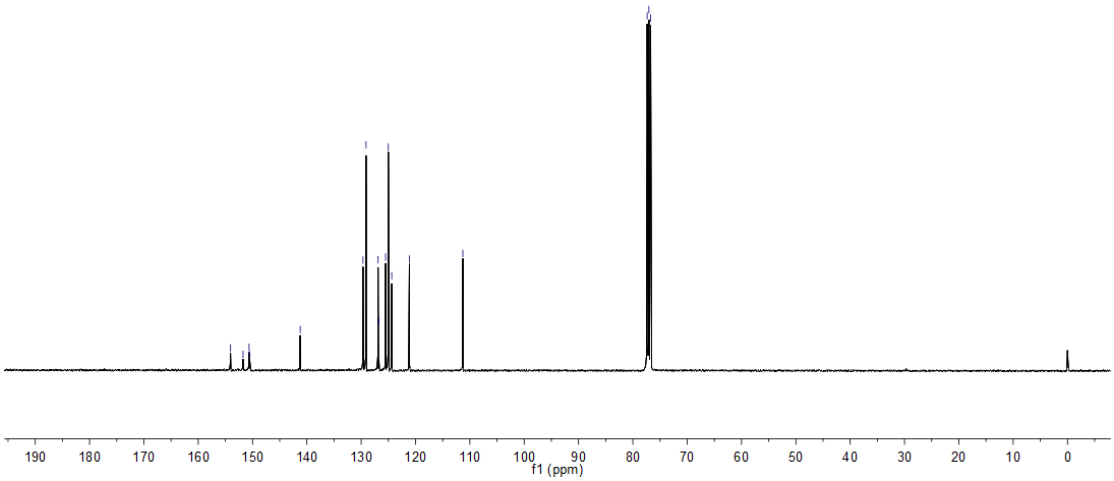
3t


1.00
2.00
1.00
1.00
2.00
2.00
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

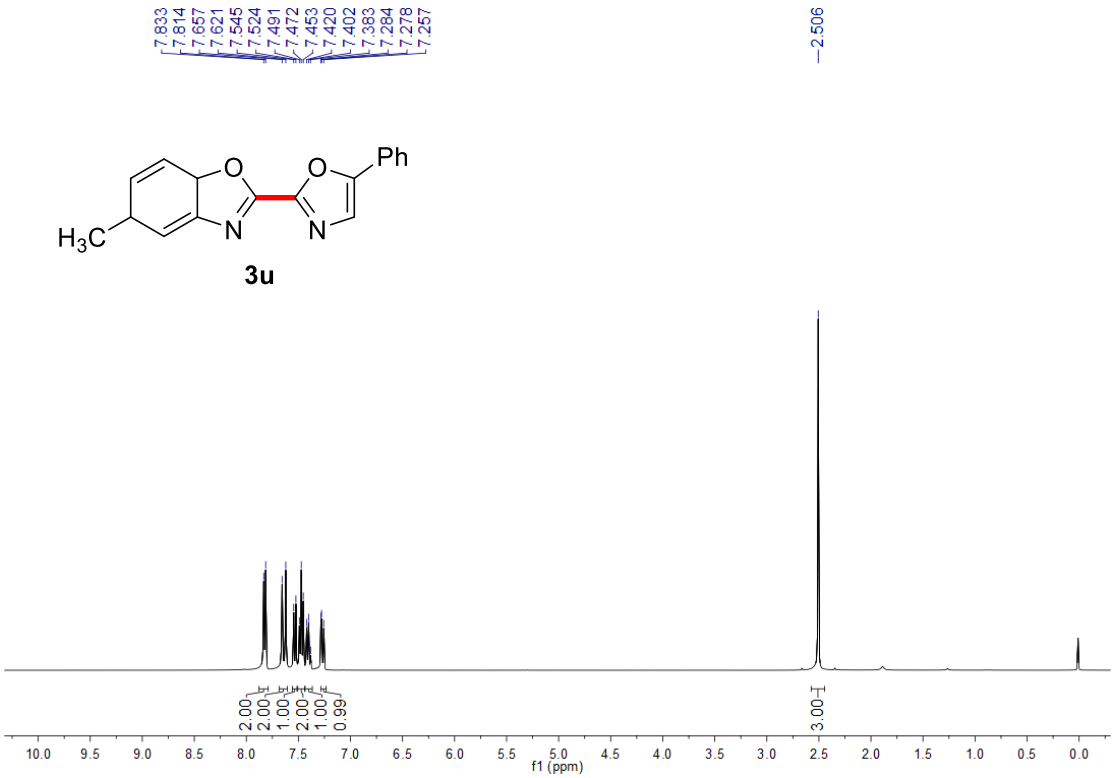

154.049
151.748
150.637
150.512
141.222
129.669
129.104
126.892
125.506
125.002
124.376
121.194
111.288
77.364
77.046
76.729

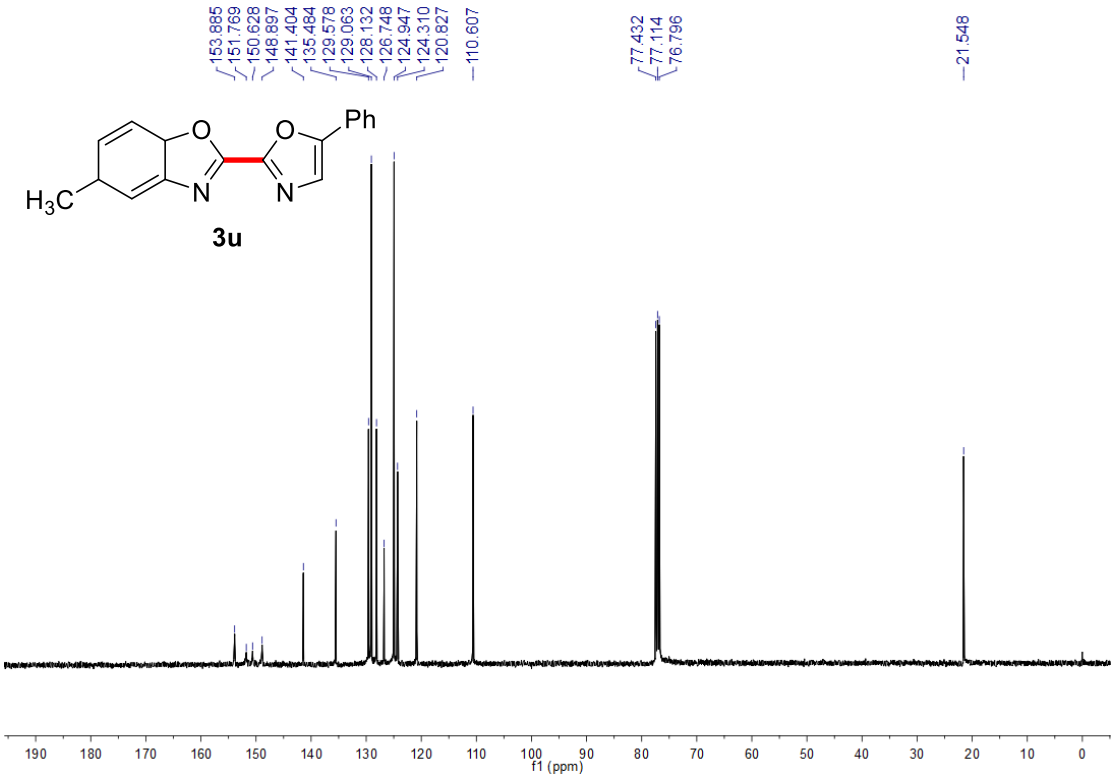

O
O
Ph
N
N

3t

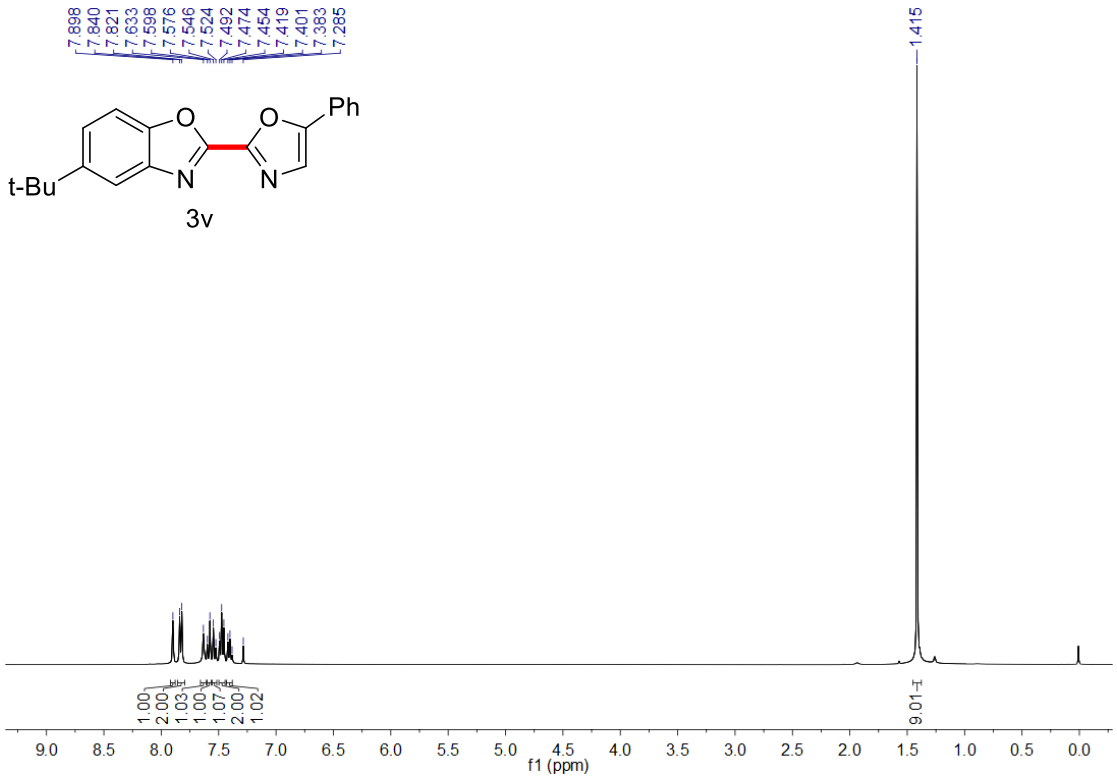

190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

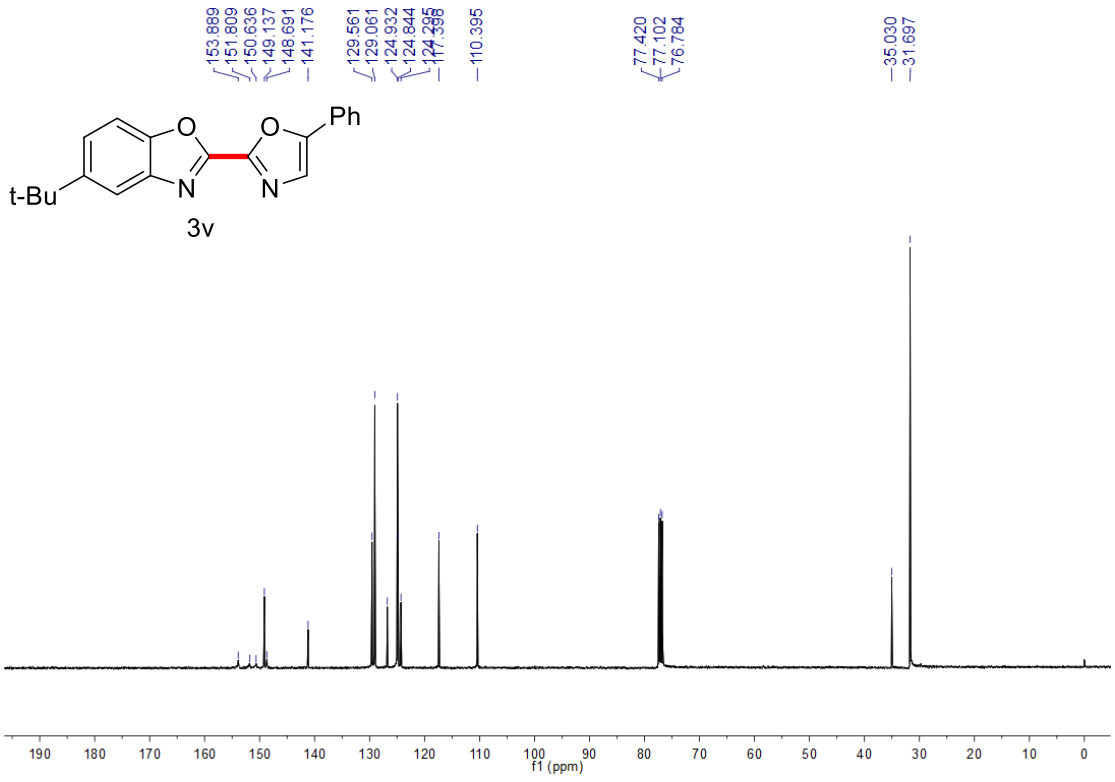
3u


7.833
7.814
7.657
7.621
7.545
7.524
7.491
7.472
7.453
7.420
7.402
7.383
7.284
7.278
7.257
2.506
Ph
O
O
N
N
H3C
3u
2.00
2.00
1.00
2.00
1.00
0.99
3.00
f1 (ppm)

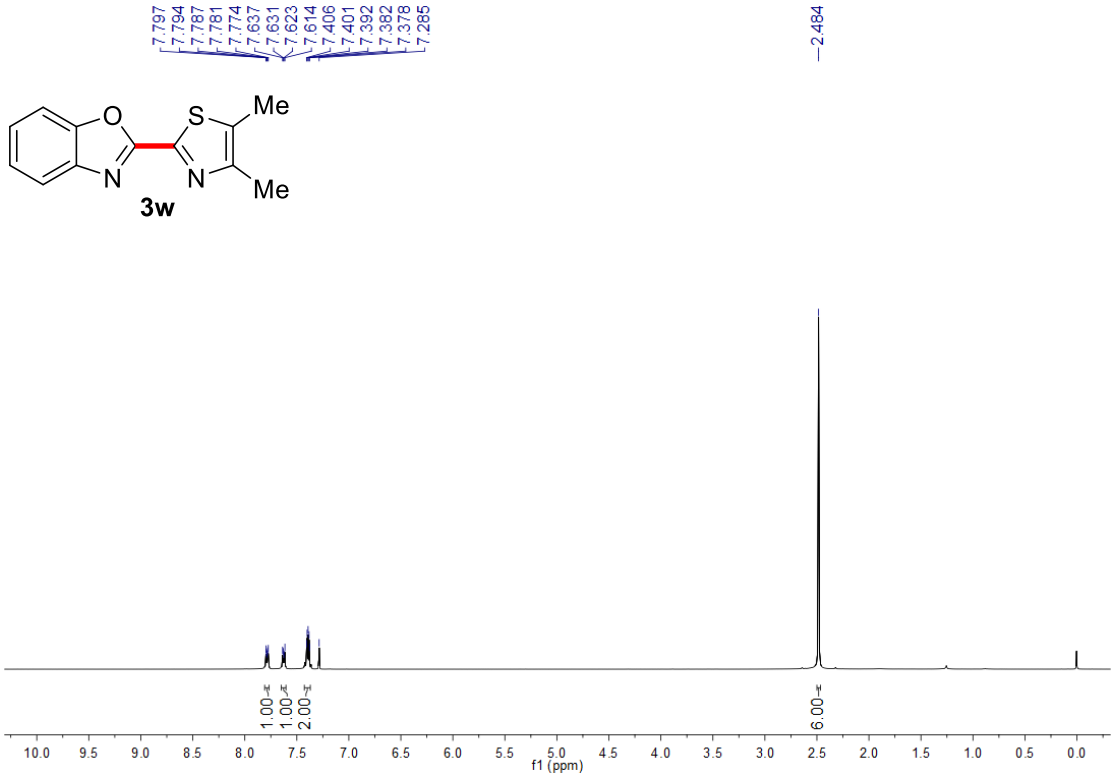

153.885
151.769
150.628
148.897
141.404
135.484
129.578
129.063
128.132
126.748
124.947
124.310
120.827
110.607
77.432
77.114
76.796
21.548
Ph
O
O
N
N
H3C
3u
f1 (ppm)

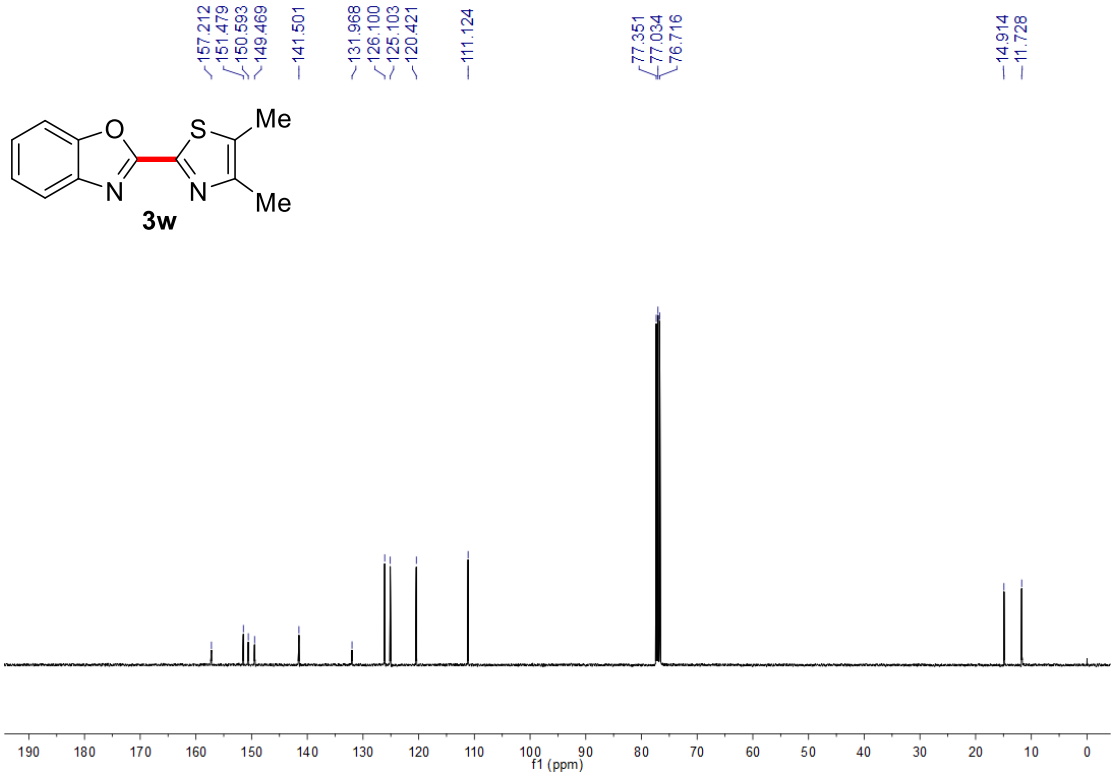
3v


7.898
7.840
7.821
7.633
7.598
7.576
7.546
7.524
7.492
7.474
7.454
7.419
7.401
7.383
7.285
1.415
Ph
O
O
N
N
t-Bu
3v
1.00
2.00
1.03
1.00
1.07
2.00
1.02
9.01
f1 (ppm)

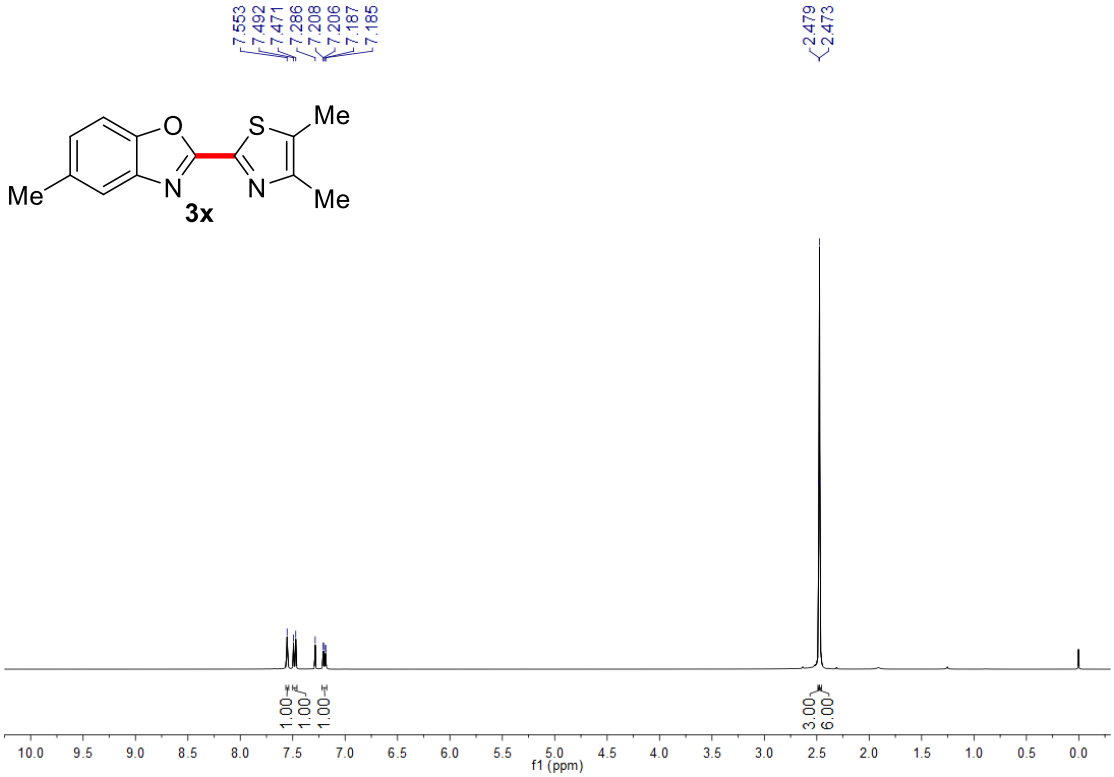

153.889
151.809
150.636
149.137
148.691
141.176
129.561
129.061
124.932
124.844
110.395
77.420
77.102
76.784
35.030
31.697
Ph
O
O
N
N
t-Bu
3v
f1 (ppm)

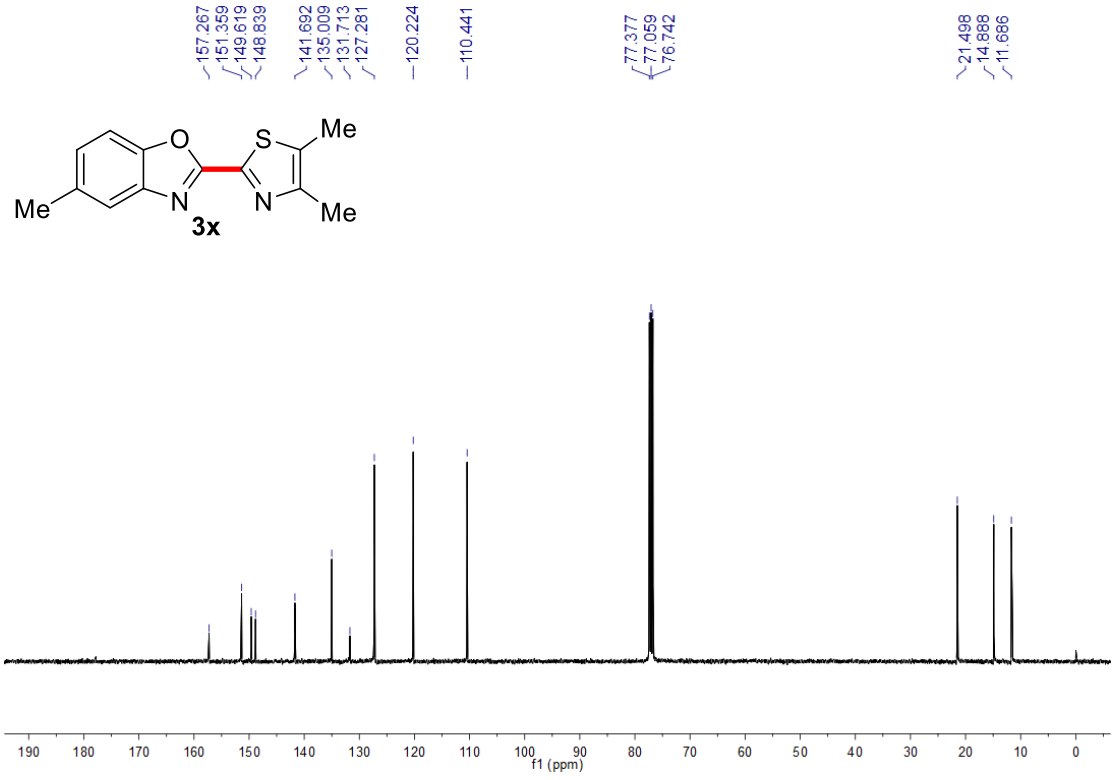
3w


7.797
7.794
7.787
7.781
7.774
7.637
7.631
7.623
7.614
7.406
7.401
7.392
7.382
7.378
7.285
2.484
O
S
Me
N
N
Me
3w
1.00
1.00
2.00
6.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

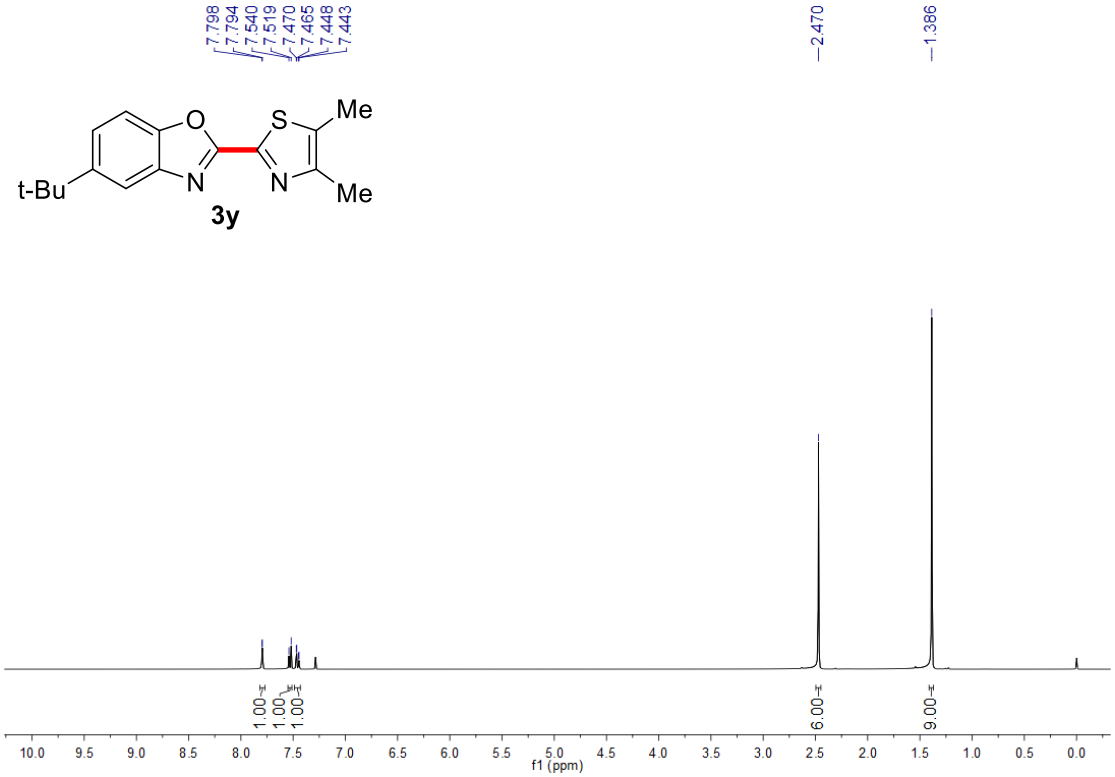

157.212
151.479
150.593
149.469
141.501
131.968
126.100
125.103
120.421
111.124
77.351
77.034
76.716
14.914
11.728
O
S
Me
N
N
Me
3w
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

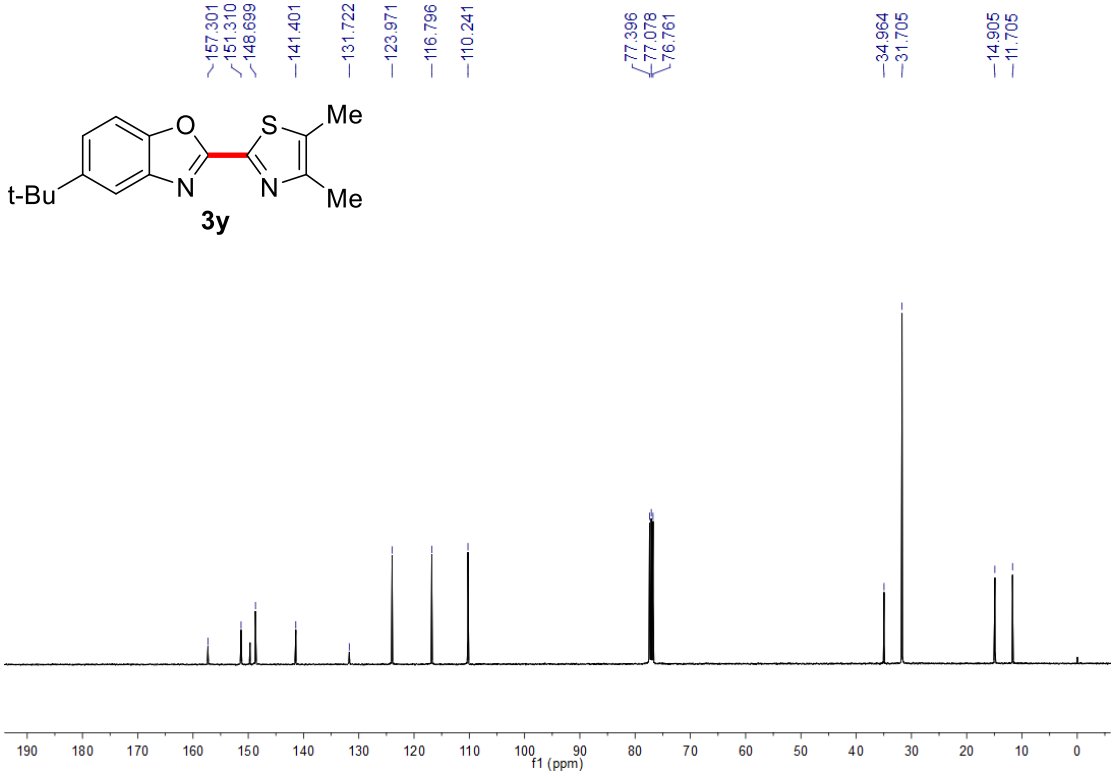
3x


7.553
7.492
7.471
7.286
7.208
7.206
7.187
7.185
2.479
2.473
O
S
Me
Me
N
N
Me
3x
1.00
1.00
1.00
3.00
6.00
f1 (ppm)

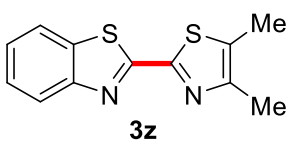

157.267
151.359
149.619
148.839
141.692
135.009
131.713
127.281
120.224
110.441
77.377
77.059
76.742
21.498
14.888
11.686
O
S
Me
Me
N
N
Me
3x
f1 (ppm)

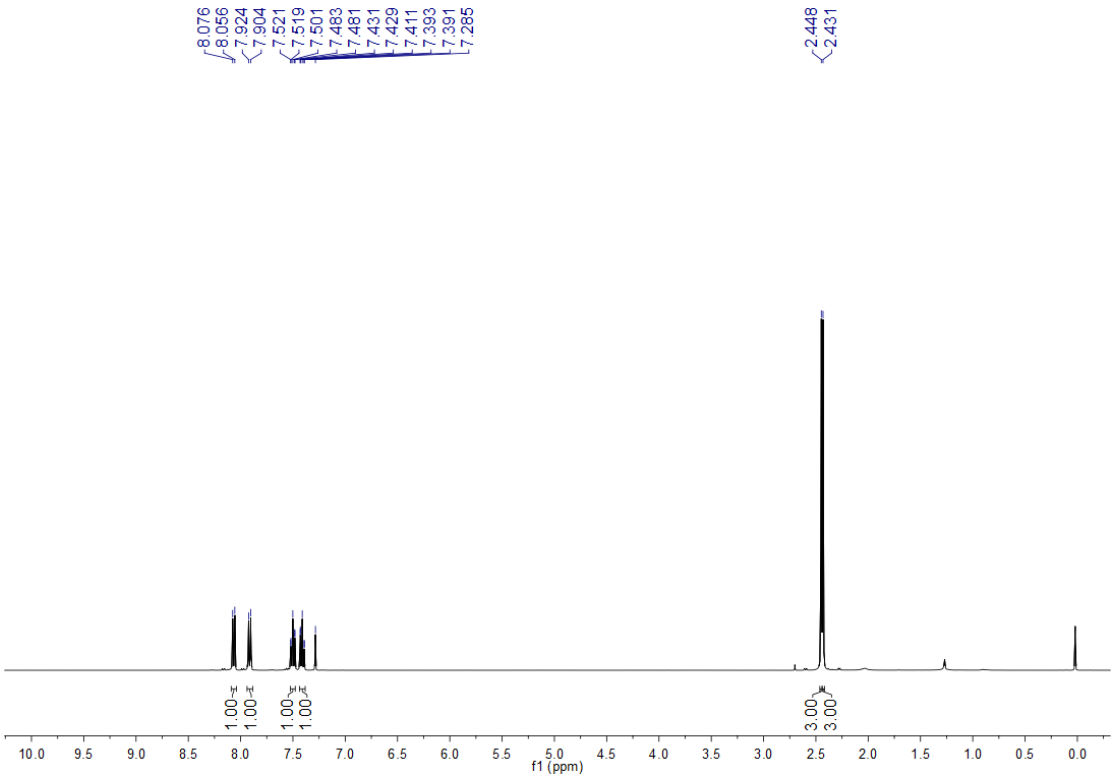
3y

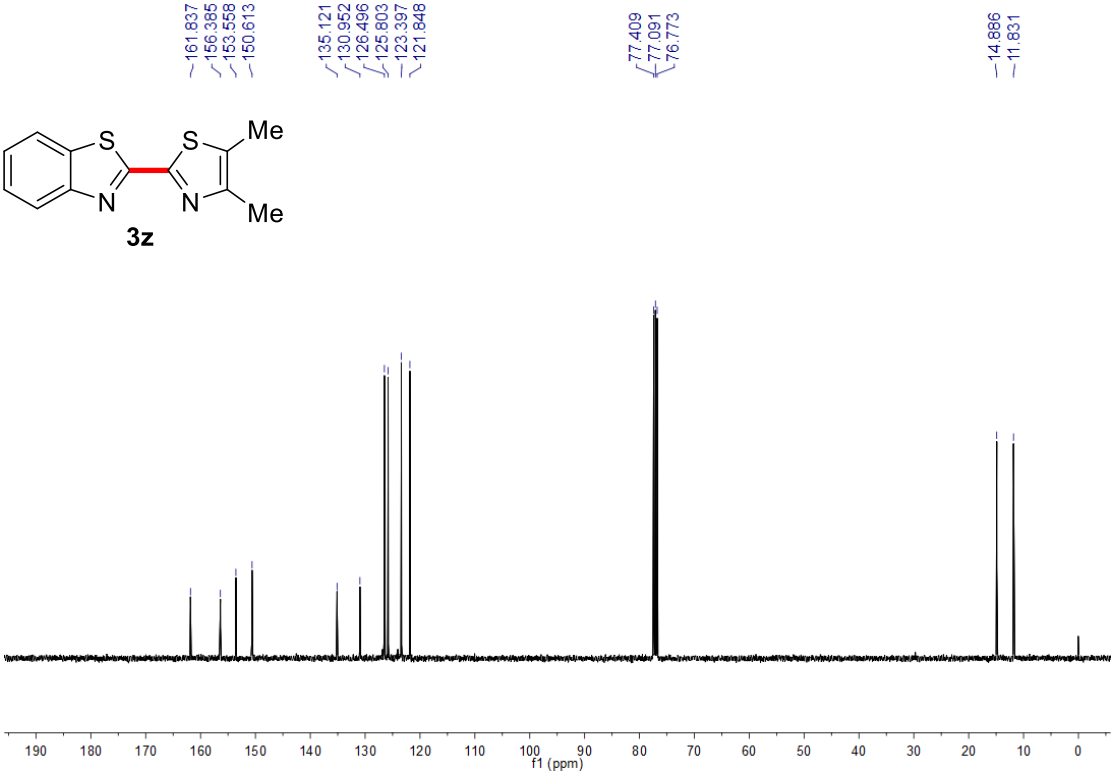

7.798
7.794
7.540
7.519
7.470
7.465
7.448
7.443
2.470
1.386
t-Bu
O
S
N
N
Me
Me
3y
1.00
1.00
1.00
6.00
9.00
f1 (ppm)


157.301
151.310
148.699
141.401
131.722
123.971
116.796
110.241
77.396
77.078
76.761
34.964
31.705
14.905
11.705
t-Bu
O
S
N
N
Me
Me
3y
f1 (ppm)

3z


S
S
N
N
Me
Me
3z

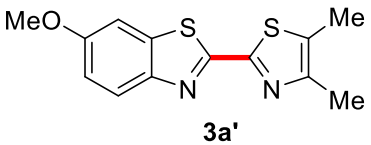

8.076
8.056
7.924
7.904
7.521
7.519
7.501
7.483
7.481
7.431
7.429
7.411
7.393
7.391
7.285
2.448
2.431
1.00
1.00
1.00
1.00
3.00
3.00
f1 (ppm)


161.837
156.385
153.558
150.613
135.121
130.952
126.496
125.803
123.397
121.848
77.409
77.091
76.773
14.886
11.831
f1 (ppm)

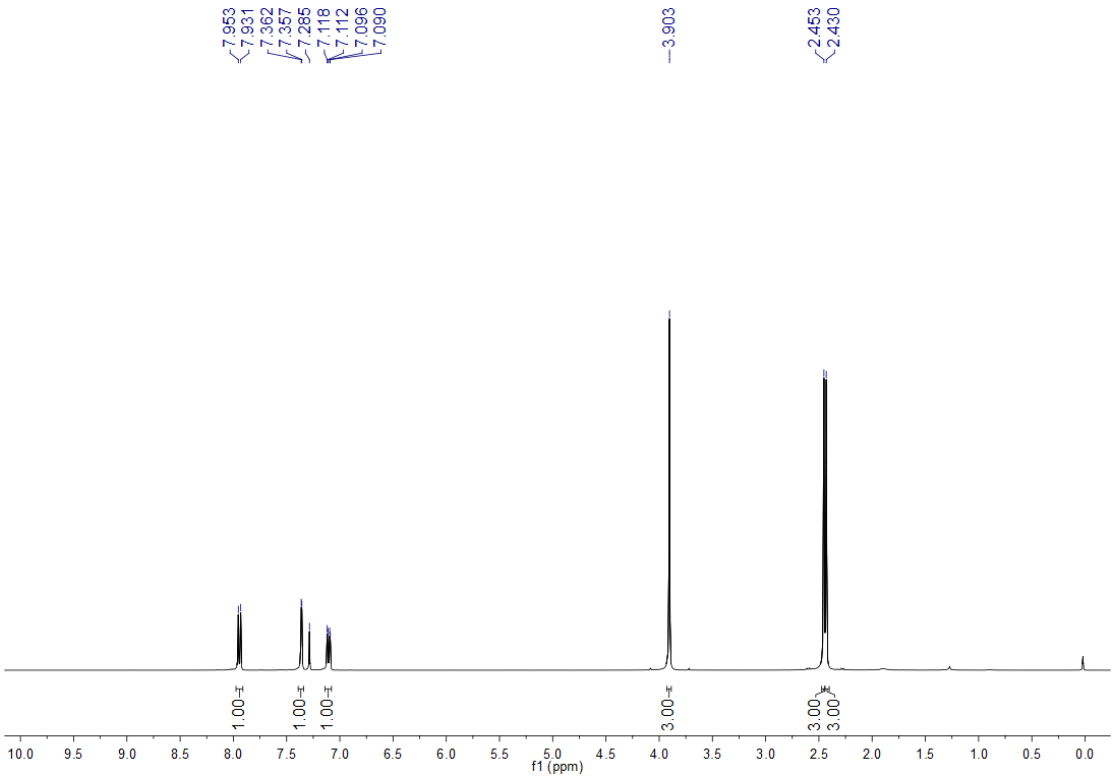
S
S
N
N
Me
Me

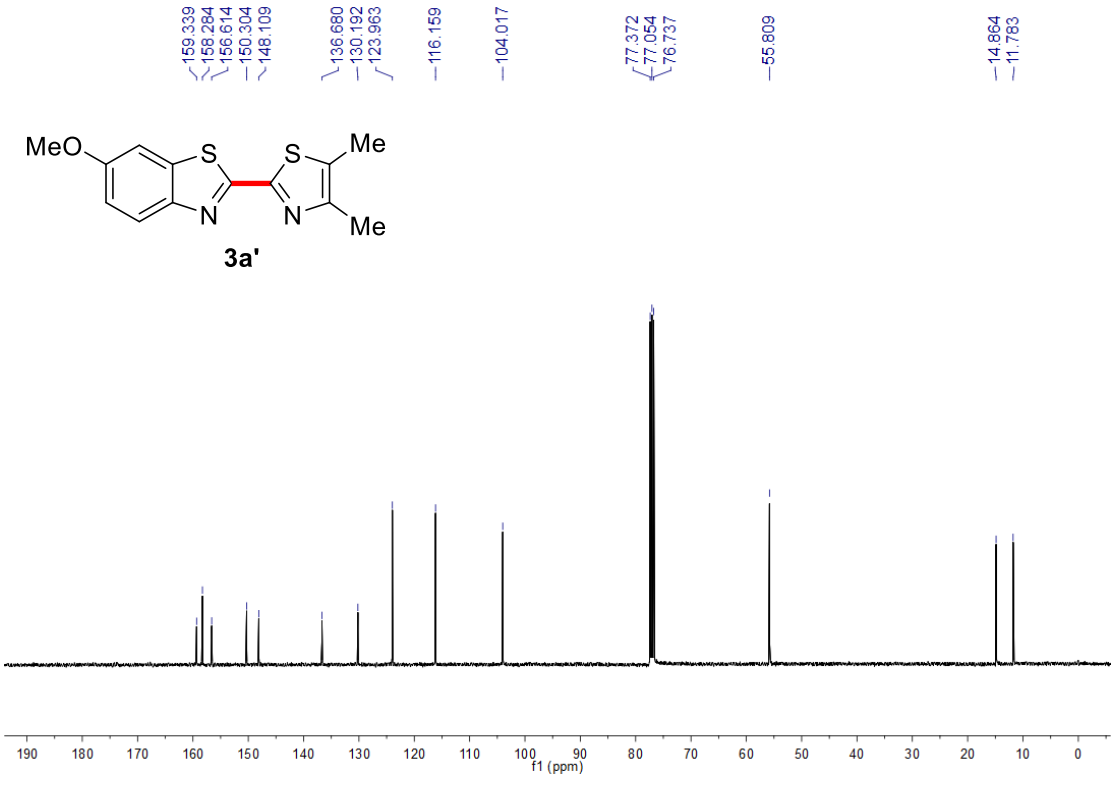
3z

3a’


MeO
S
S
N
N
Me
Me

3a'

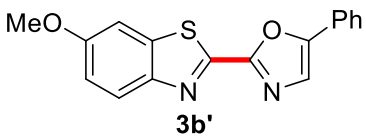

7.953
7.931
7.362
7.357
7.285
7.118
7.112
7.096
7.090
3.903
2.453
2.430
1.00
1.00
1.00
3.00
3.00
3.00
f1 (ppm)


159.339
158.284
156.614
150.304
148.109
136.680
130.192
123.963
116.159
104.017
77.372
77.054
76.737
55.809
14.864
11.783
f1 (ppm)

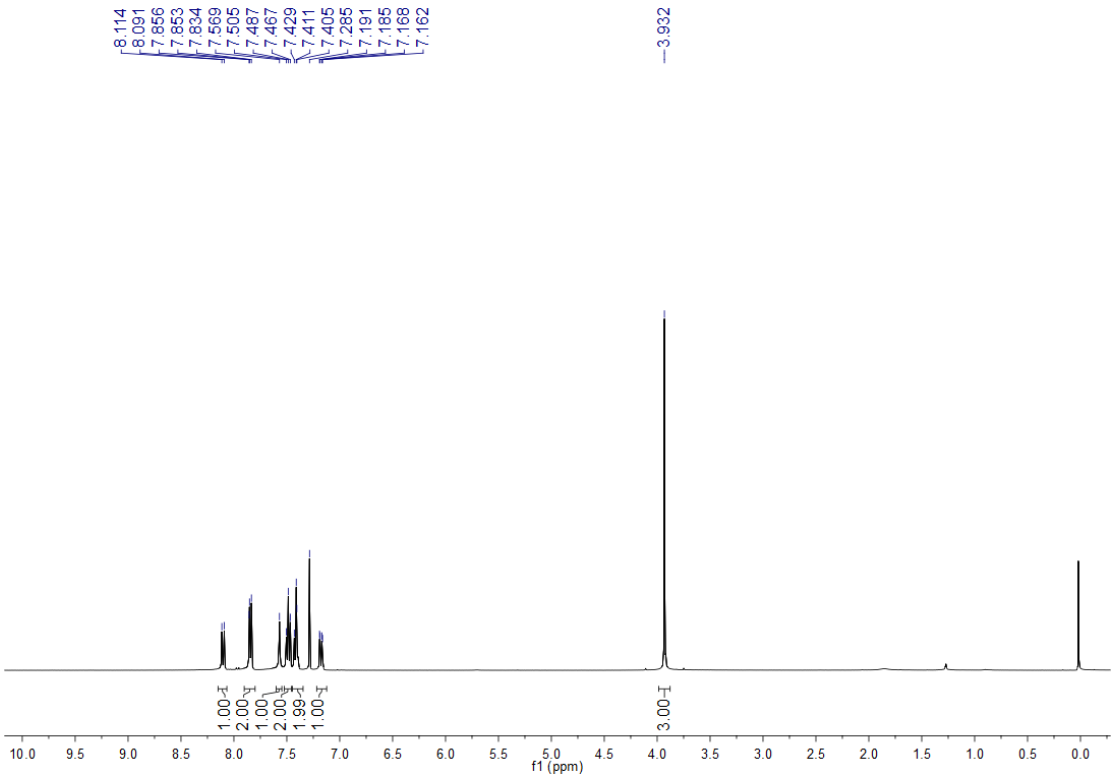
MeO
S
S
Me
N
N
Me

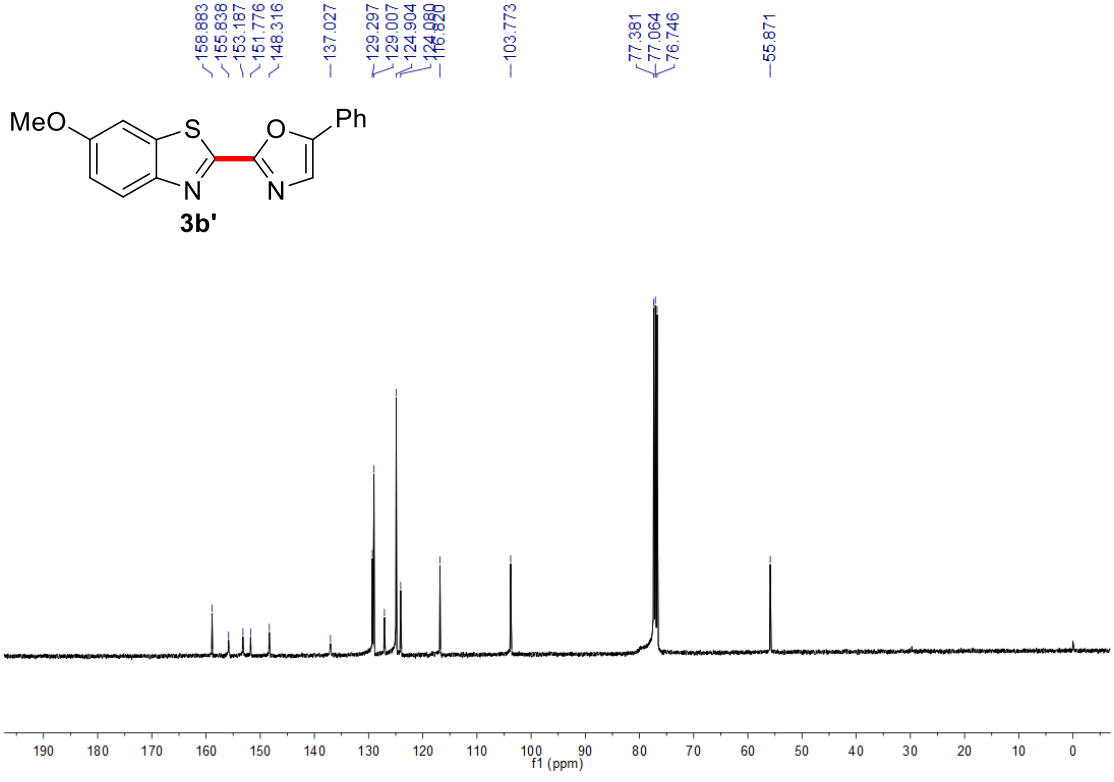
3a'

3b’


MeO
S
O
Ph
N
N

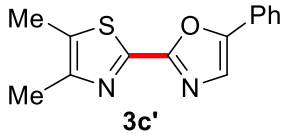
3b'


8.114
8.091
7.856
7.853
7.834
7.569
7.505
7.487
7.467
7.429
7.411
7.405
7.285
7.191
7.185
7.168
7.162
3.932
1.00
2.00
1.00
2.00
1.99
1.00
3.00
f1 (ppm)

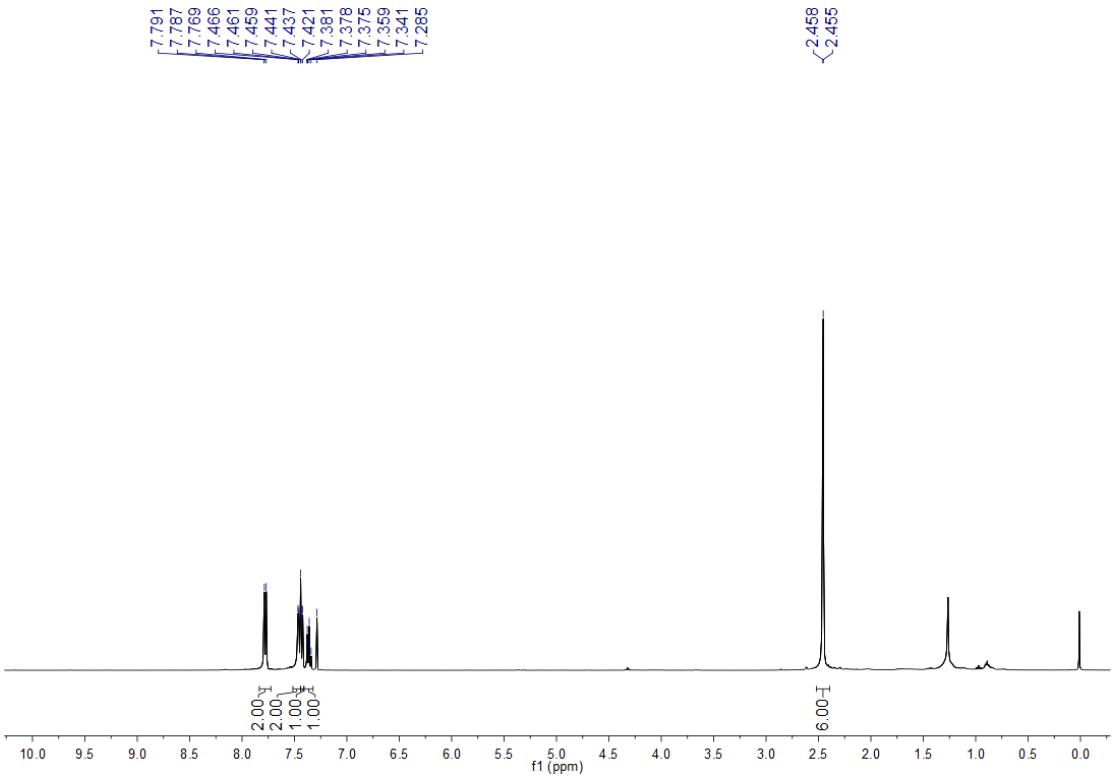

158.883
155.838
153.187
151.776
148.316
137.027
129.297
129.007
124.904
103.773
77.381
77.064
76.746
55.871
MeO
S
O
Ph
N
N
f1 (ppm)

3b'

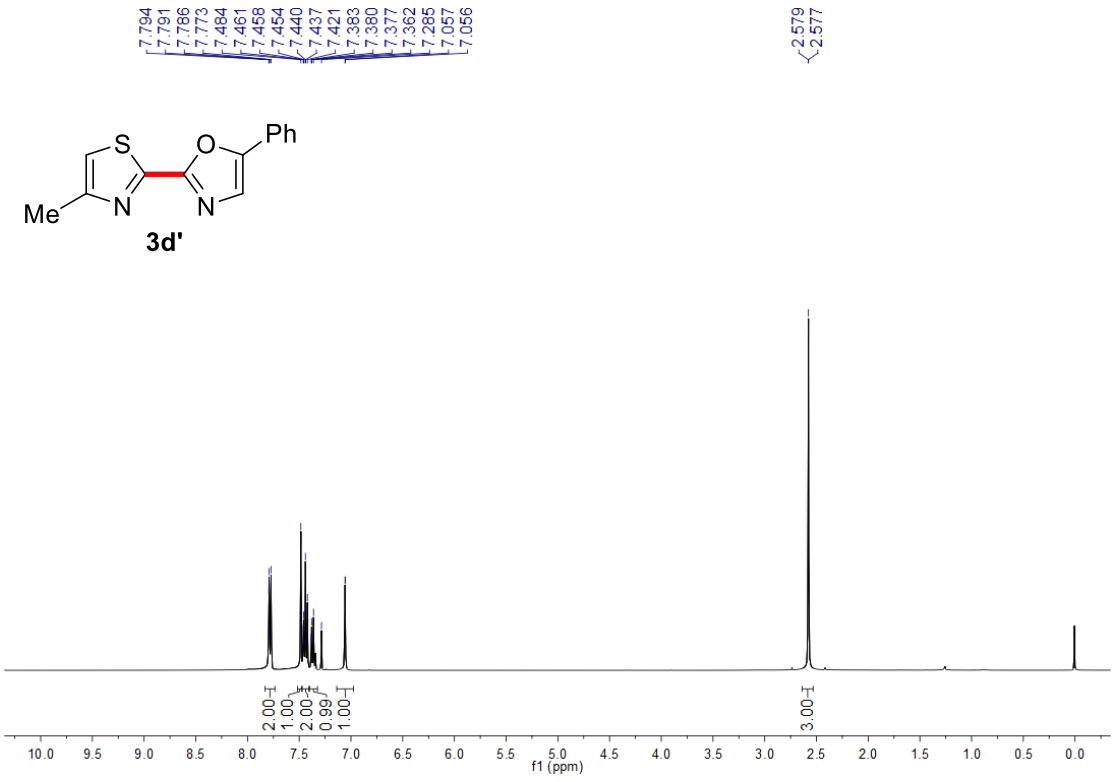
3c’


Me
S
O
Ph
Me
N
N

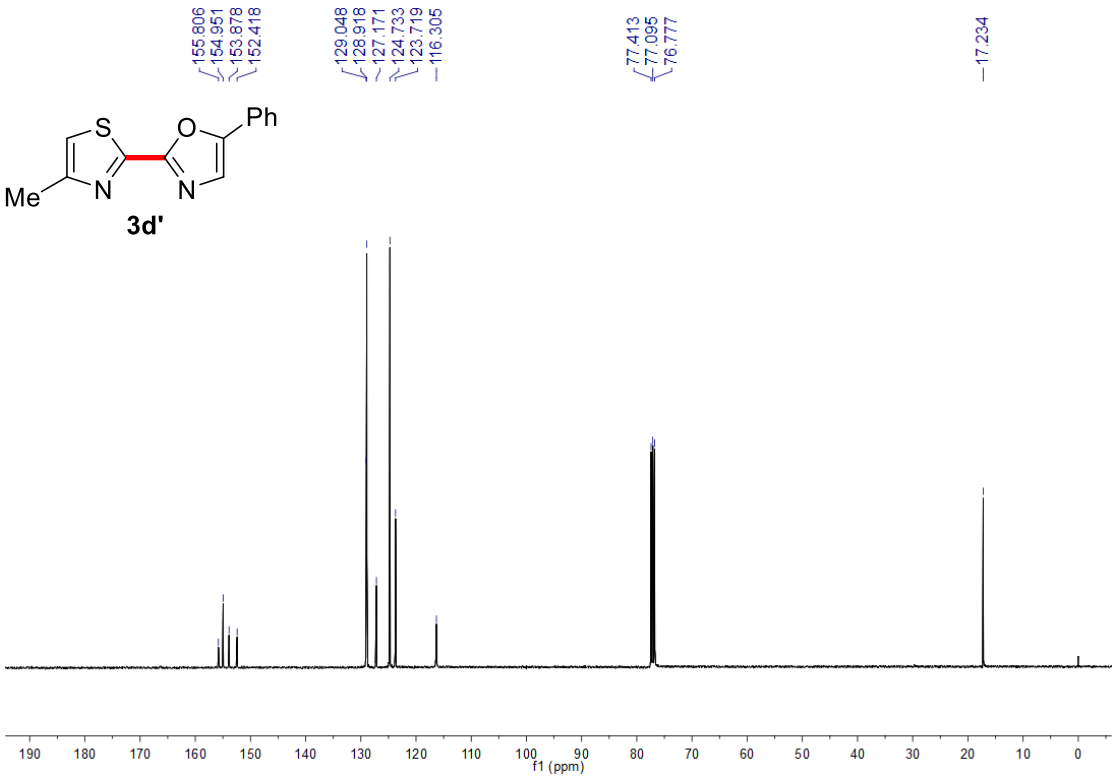
3c'


7.791
7.787
7.769
7.466
7.461
7.459
7.441
7.437
7.421
7.381
7.378
7.375
7.359
7.341
7.285
2.458
2.455
2.00
2.00
1.00
1.00
6.00
f1 (ppm)

3d’


7.794
7.791
7.786
7.773
7.484
7.461
7.458
7.454
7.440
7.437
7.421
7.383
7.380
7.377
7.362
7.285
7.057
7.056
2.579
2.577
S
O
Ph
Me
N
N
2.00
1.00
2.00
0.99
1.00
3.00
f1 (ppm)

3d'


155.806
154.951
153.878
152.418
129.048
128.918
127.171
124.733
123.719
116.305
77.413
77.095
76.777
17.234
S
O
Ph
Me
N
N
3d'
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)