Electronic Supporting Information

Palladium-Catalyzed Desulfitative Arylation of Azoles with Arylsulfonyl Hydrazides

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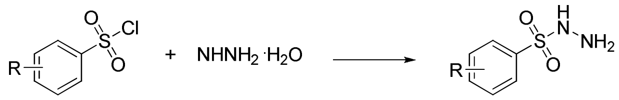
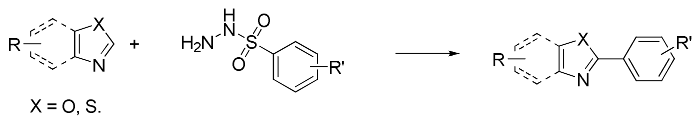
General.

Commercially available reagents were used without further purification. Solvents were purified prior to use according to the standard methods. All reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Column chromatography was carried out on silica gel (300–400 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. For TLC, silica gel GF-254 was used and visualized by fluorescence quenching under UV light. NMR spectra were recorded at room temperature in $CDCl_3$ on 400 MHz Bruker DRX-400 or 500 MHz Bruker DRX-500 NMR spectrometers. The chemical shifts for ^{1}H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for $CDCl_3$). The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.16 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. The abbreviations *s*, *d*, *t*, *q*, and *m* stand for singlet, doublet, triplet, quartet, and multiplet in that order. HRMS data were obtained with Micromass HPLC–Q–TOF mass spectrometer.

Experimental Section.



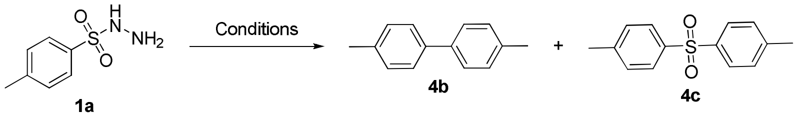
Preparation of Arylsulfonyl Hydrazides. Arylsulfonyl hydrazides were prepared according to a literature procedure.[1] Hydrazine monohydrate (80%) (275 mg, 4.4 mmol) was added water (260 mg) and was cooled to 0 °C. To this solution was added dropwise a solution of arylsulfonyl chloride (2.0 mmol) in THF (10 mL) at 0 °C. The mixture was further stirred at 0 °C for 30 min., flowed by addition of diethyl ether (10 mL). The mixture was extracted with saturated brine (3 × 10 mL). The organic layer was dried over sodium sulfate, filtered through Celite. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product. (Yield: 75-91 %)



General procedure for Arylation of Azoles with Arylsulfonyl Hydrazides. A flame-dried Schlenk tube with a magnetic stirring bar was charged with $Pd(CH_3CN)_2Cl_2$ (6.5 mg, 0.025 mmol), phenanthroline hydrate (6 mg, 0.03 mmol), Na_2CO_3 (80 mg, 0.75 mmol), azoles (0.5 mmol), arylsulfonyl hydrazide (0.75 mmol), $Cu(OAc)_2$ (545 mg, 3 mmol), DMSO (0.6 mL) and 1,4-dioxane (5 mL) in presence or absence of TBAB (32mg, 0.1 mmol) under N_2. The reaction mixture was stirred for 5 min. at room temperature, and then stirred at 100℃for 4.5 h. The reaction mixture was then cooled to ambient temperature, diluted with diethyl ether (20 mL), filtered through a Celite pad, and washed with 10-20 mL of diethyl ether. The combined organic extracts were concentrated and the resulting residue was purified by column chromatography on silica gel to provide the desired product.

Experimental data for mechanistic studies

1. Decomposition of $TsNHNH_2$ [a]



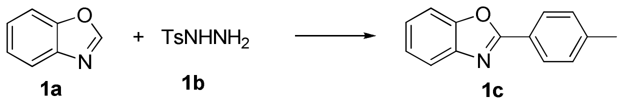
Entry	Catalyst	Oxidant	Yield [b]	
			4b	**4c**
1	---	$Cu(OAc)_2$ (4 equiv.)	13%	25%
2	$Pd(CH_3CN)_2Cl_2$ (10 mol%), Phen.·H_2O (12 mol%).	---	trace	----[b]
3	$Pd(CH_3CN)_2Cl_2$ (10 mol%), Phen.·H_2O (12 mol%).	$Cu(OAc)_2$ (4 equiv.).	65%	trace

[a] *Condition*:**1a (**0.5 mmol), catalyst, oxidant, Dioxane/DMSO (9:1) (6mL), 100 °C, N_2, 4h.

[b] Isolated yield.

[c] Not detected.

2. Effects of Radical Inhibitors. [a]



Entry	Additive (20 mol%)	Yield [b]
1	--	90%
2	TEMPO	90%
3	BHT	91%

[a] Condition: 1a (0.5 mmol), 2a (1.5 equiv.), $Pd(CH_3CN)_2Cl_2$ (5 mol%), Phen.H_2O (6 mol%), Na_2CO_3 (1.5 equiv.), TBAB (0.2 equiv.), $Cu(OAc)_2$ (6 equiv.), additive (20 mol%).

[b] HPLC yield.

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry
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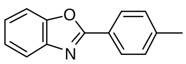
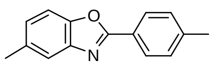
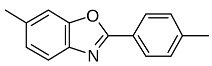
Analytical Data



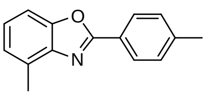
2-*p*-Tolylbenzo[*d*]oxazole (3a),[2] white solid, yield:90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.61 – 7.54 (m, 1H), 7.38 – 7.28 (m, 4H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 150.8, 142.3, 142.1, 129.7, 127.7, 124.9, 124.5, 124.5, 119.9, 110.6, 21.7.



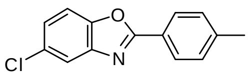
5-Methyl-2-*p*-tolylbenzo[*d*]oxazole (3b), [2] white solid, yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.54 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.5, 149.1, 142.6, 1420, 134.4, 129.7, 127.7, 126.1, 124.7, 119.9, 109.96, 21.7, 21.7.



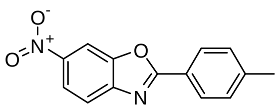
6-Methyl-2-*p*-tolylbenzo[*d*]oxazole (3c),[2] white solid, yield: 89%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 – 8.08 (m, 2H), 7.62 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.36 (s, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 2.50 (d, *J* = 1.8 Hz, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 151.1, 141.9, 140.1, 135.4, 129.7, 127.6, 125.8, 124.75, 119.3, 110.8, 21.9, 21.8.



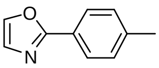
4-Methyl-2-p-tolylbenzo[*d*]oxazole (3d), pink solid, yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 162.65, 150.60, 141.83, 141.64, 130.52, 129.66, 127.69, 125.07, 124.84, 124.61, 107.86, 21.73, 16.69; RMS (ESI) calculated for $C_{15}H_{14}NO^{+}$ (M+H): 224.1075, found 224.1079.



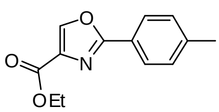
5-Chloro-2-p-tolylbenzo[d]oxazole (3e),[2] white solid, yield: 85%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 2H), 7.71 (d, *J* = 5.8 Hz, 1H), 7.47 (dd, *J* = 11.6, 4.8 Hz, 1H), 7.37 – 7.27 (m, 3H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 149.3, 143.4, 142.5, 129.9, 129.7, 127.7, 125.1, 123.9, 119.8, 111.2, 21.7.



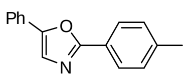
6-Nitro-2-p-tolylbenzo[*d*]oxazole(3f),[5] white solid, yield: 40%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 2.1 Hz, 1H), 8.29 (dd, *J* = 8.8, 2.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.90, 150.02, 147.77, 145.16, 144.00, 130.13, 128.43, 123.37, 120.99, 119.73, 107.28, 21.98.



2-*p*-Tolyloxazole (3g),[6] colorless oil, yield: 88%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.71 (s, 1H), 7.30 (d, *J* = 7.2 Hz, 2H), 7.26 (s, 1H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2, 140.6, 138.3, 129.5, 128.3, 126.3, 124.9, 21.5.

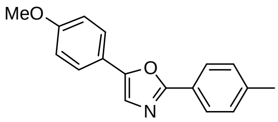


Ethyl 2-*p*-tolyloxazole-4-carboxylate (3h),[2] white solid, yield: 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (s, 1H), 7.99 (d, *J* = 8.2 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 4.42 (q, *J* = 7.1 Hz, 2H), 2.39 (s, 3H), 1.40 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.7, 161.5, 143.4, 141.6, 134.6, 129.5, 126.9, 123.8, 61.3, 21.6 14.4.

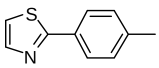


5-Phenyl-2-*p*-tolyloxazole (3i),[8] white solid, yield:84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ

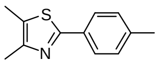
8.00 (d, *J* = 8.1 Hz, 2H), 7.72 (dd, *J* = 5.1, 3.3 Hz, 2H), 7.48 – 7.38 (m, 3H), 7.37 – 7.26 (m, 3H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.4, 150.9, 140.6, 129.5, 128.9, 128.3, 127.6, 126.3, 124.8, 124.1, 123.4, 21.5.



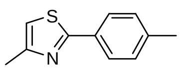
5-(4-Methoxyphenyl)-2-*p*-tolyloxazole (3j),[6] white solid, yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.64 (d, *J* = 7.4 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.96 (d, *J* = 7.5 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.8, 159.8, 151.0, 140.4, 129.5, 126.1, 125.7, 125.0, 121.9, 121.0, 114.4, 55.3, 21.5.



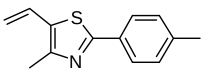
2-*p*-Tolylthiazole (3k),[2] yellow oil, yield: 87%; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.84 (d, *J* = 3.3 Hz, 1H), 7.27 (d, *J* = 3.3 Hz, 1H), 7.24 (d, *J* = 7.9 Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.7, 143.6, 140.3, 131.1, 129.7, 126.6, 118.4, 21.5.



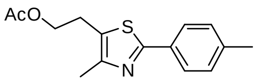
4, 5-Dimethyl-2-*p*-tolylthiazole (3l),[2] white solid, yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 2.37 (d, *J* = 2.5 Hz, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.7, 149.1, 139.5, 131.5, 129.6, 126.1, 126.0, 21.4, 14.9, 11.5.



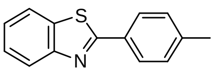
4-Methyl-2-*p*-tolylthiazole (3m),[2] colorless oil, yield 86%;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 – 7.80 (m, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.81 (d, *J* = 0.9 Hz, 1H), 2.50 (d, *J* = 1.0 Hz, 3H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 153.7, 140.0, 131.2, 129.6, 126.4, 113.0, 21.4, 17.3.



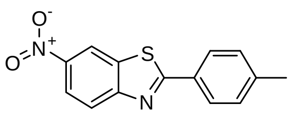
4-Methyl-2-*p*-tolyl-5-vinylthiazole (3n), yellow solid, m.p. 66-68 °C, yield: 43%;^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.84 – 6.72 (m, 1H), 5.45 (d, *J* = 17.1 Hz, 1H), 5.22 (d, *J* = 10.9 Hz, 1H), 2.46 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 150.8, 140.3, 131.0, 130.9, 129.6, 126.9, 126.4, 115.3, 21.5, 15.4; HRMS (ESI) calculated for $C_{13}H_{14}NS^+$ (M+H): 216.0847, found 216.0842.



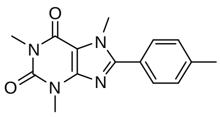
2-(4-Methyl-2-*p*-tolylthiazol-5-yl)ethyl acetate (3o), yellow oil, yield: 78%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.1 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 4.21 (t, *J* = 6.7 Hz, 2H), 3.03 (t, *J* = 6.7 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 165.0, 150.2, 139.9, 131.3, 129.6, 126.7, 126.2, 64.2, 26.1, 21.5, 21.0, 15.2; HRMS (ESI) calculated for $C_{15}H_{18}NO_2S^+$ (M+H): 276.1058, found 276.1054 (M+H).



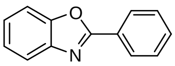
2-*p*-Tolylbenzo[*d*]thiazole (3p),[2] white solid, yield: 71%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 1H), 8.00 (d, *J* = 7.4 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.0 Hz, 1H), 7.31 (d, *J* = 7.2 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.2, 154.2, 141.3, 135.0, 131.0, 129.7, 127.5, 126.2, 125.0, 123.0, 121.5, 21.5.



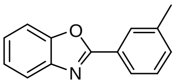
6-Nitro-2-p-tolylbenzo[*d*]thiazole (3q),[2] yellow solid, yield: 54%; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.81 (d, *J* = 2.2 Hz, 1H), 8.33 (dd, *J* = 9.0, 2.3 Hz, 1H), 8.09 (d, *J* = 9.0 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.05, 158.07, 144.90, 143.16, 135.35, 130.23, 130.10, 128.00, 123.18, 121.96, 118.25, 21.75.



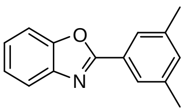
1,3,7-Trimethyl-8-*p*-tolyl-1H-purine-2,6-(3H,7H)-dione (3r),[3] white solid, yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.03 (s, 3H), 3.61 (s, 3H), 3.42 (s, 3H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.7, 152.5, 151.9, 148.4, 140.8, 129.7, 129.2, 125.7, 108.6, 34.0, 29.9, 28.1, 21.6.



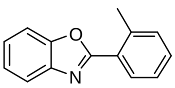
2-Phenylbenzo[*d*]oxazole (3s), [2] white solid, yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (d, *J* = 3.1 Hz, 2H), 7.79 (d, *J* = 4.4 Hz, 1H), 7.57 (s, 1H), 7.53 (s, 3H), 7.41 – 7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.1, 150.9, 142.2, 131.6, 129.0, 127.7, 127.3, 125.2, 124.7, 120.1, 110.7, 104.0, 77.5, 77.2, 76.8.



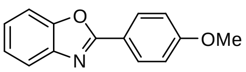
2-m-Tolylbenzo[*d*]oxazole (3t),[2] white solid, yield:86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.62 – 7.54 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.31 (m, 3H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.4, 150.9, 142.3, 138.9, 132.5, 129.0, 128.3, 127.2, 125.2, 124.9, 124.7, 120.1, 110.7, 21.5.



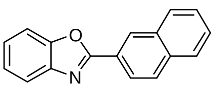
2-(3,5-Dimethylphenyl)benzo[*d*]oxazole (3u),[7] white solid, yield:84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (s, 2H), 7.81 – 7.74 (m, 1H), 7.62 – 7.54 (m, 1H), 7.35 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.17 (s, 1H), 2.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 150.8, 142.2, 138.7, 133.4, 127.0, 125.5, 125.1, 124.6, 120.0, 110.6, 21.4.



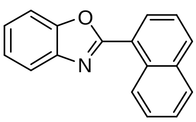
2-*o*-Tolylbenzo[*d*]oxazole (3v),[2] white solid, yield: 67%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 3.1 Hz, 1H), 7.60 (d, *J* = 3.6 Hz, 1H), 7.46 – 7.30 (m, 5H), 2.84 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.5, 150.4, 142.3, 139.0, 131.9, 131.0, 130.0, 126.3, 126.2, 125.1, 124.5, 120.2, 110.6, 22.3.



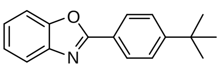
2-(4-Methoxyphenyl)benzo[*d*]oxazole (3w),[2] white solid, yield: 86%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.73 (s, 1H), 7.55 (s, 1H), 7.33 (s, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 162.5, 150.8, 142.5, 129.5, 124.7, 124.5, 119.8, 119.7, 114.5, 110.5, 55.5.



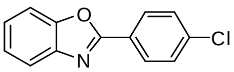
2-(Naphthalen-2-yl)benzo[*d*]oxazole (3x),[4] white solid, yield: 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 7.95 (t, *J* = 8.1 Hz, 2H), 7.82 (ddd, *J* = 8.8, 8.1, 4.3 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.41 – 7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.9, 142.3, 134.8, 133.0, 129.0, 128.8, 128.2, 128.0, 127.8, 126.9, 125.2, 124.7, 124.5, 124.0, 120.1, 110.7.



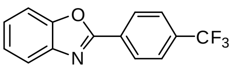
2-(Naphthalen-1-yl)benzo[*d*]oxazole (3y),[7] white solid, yield: 47%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 7.95 (t, *J* = 8.1 Hz, 2H), 7.82 (ddd, *J* = 8.8, 8.1, 4.3 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.41 – 7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.2, 150.9, 142.3, 134.8, 133.0, 129.0, 128.8, 128.2, 127.96, 127.8, 126.9, 125.2, 124.7, 124.5, 124.0, 120.1, 110.7.



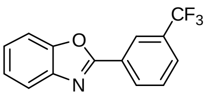
2-(4-*tert*-Butylphenyl)benzo[*d*]oxazole (3z),[2] white solid, yield: 73%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 – 8.14 (m, 2H), 7.81 – 7.73 (m, 1H), 7.63 – 7.51 (m, 3H), 7.40 – 7.29 (m, 2H), 1.38 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.1, 150.8, 142.3, 127.6, 126.0, 124.9, 124.5, 124.4, 119.9, 110.6, 35.1, 31.2.



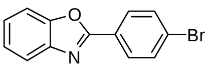
2-(4-Chlorophenyl)benzo[*d*]oxazole (3aa),[2] white solid, yield: 83%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 3.4 Hz, 1H), 7.58 (d, *J* = 3.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 3.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.1, 150.8, 142.1, 137.8, 129.3, 128.9, 125.7, 125.4, 124.8, 120.2, 110.7.



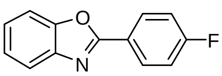
2-(4-(Trifluoromethyl)phenyl)benzo[*d*]oxazole (3ab),[4] white solid, yield: 70%; ^{1}H NMR (400 MHz, CDCl3) δ 8.37 (d, J = 8.1 Hz, 2H), 7.84 – 7.73 (m, 3H), 7.61 (dd, J = 5.1, 3.7 Hz, 1H), 7.40 (dd, J = 6.6, 2.7 Hz, 2H); ^{13}C NMR (100 MHz, CDCl3) δ 161.5, 150.9, 142.0, 133.01 (dd, J = 63.6, 31.0 Hz)., 130.5, 127.9, 125.9, 125.9, 125.0, 122.5, 120.5, 110.8; ^{19}F NMR (377 MHz, $CDCl_3$) δ -63.57.



2-(3-(Trifluoromethyl)phenyl)benzo[*d*]oxazole (3ac),[8] white solid, yield: 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.43 (d, *J* = 7.2 Hz, 1H), 7.78 (d, *J* = 5.9 Hz, 2H), 7.64 (dd, *J* = 18.5, 10.7 Hz, 2H), 7.39 (d, *J* = 3.0 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.60, 150.96, 142.02, 131.75 (q, *J* = 33.0 Hz), 130.72, 129.64, 128.20, 128.01 (dd, *J* = 7.1, 3.5 Hz), 125.83, 125.03, 124.61 (q, *J* = 3.7 Hz), 122.77, 120.45, 110.88; ^{19}F NMR (471 MHz, $CDCl_3$) δ -63.95.



2-(4-Bromophenyl)benzo[*d*]oxazole (3ad): [2] white solid, yield:65%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.6 Hz, 2H), 7.82 – 7.72 (m, 1H), 7.65 (d, *J* = 8.6 Hz, 2H), 7.61 – 7.53 (m, 1H), 7.41 – 7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.3, 150.9, 142.2, 132.4, 129.1, 126.4, 126.2, 125.5, 124.9, 120.3, 110.8.



2-(4-Fluorophenyl)benzo[*d*]oxazole (3ae),[2] white solid, yield: 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.83 – 7.72 (m, 1H), 7.57 (dt, *J* = 7.5, 3.9 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.21 (t, *J* = 8.6 Hz, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ164.86 (d, *J* = 252.9 Hz), 162.17, 150.83, 142.15, 129.87 (d, *J* = 8.8 Hz), 125.17, 124.70, 123.58, 120.06, 116.21 (d, *J* = 22.2 Hz), 110.61; ^{19}F NMR (377 MHz, $CDCl_3$) δ -108.06.

References:

[1] L. Friedman, R. L. Litle and W. R. Reichle, *Organic synthesis*, 1973, **Coll. Vol. 5**, 1055.

[2] M. Wang, D. Li, W. Zhou and L. Wang, *Tetrahedron*, 2012**, 68**, 1926.

[3] B. Liu, Q. Guo, Y. Cheng, J. Lan and J. You, *Chem. Eur. J*. 2011, **17**, 13415.

[4] M. Zhang, S. Zhang, M. Liu and J. Cheng, *Chem. Commun*. 2011, **47**, 11522.

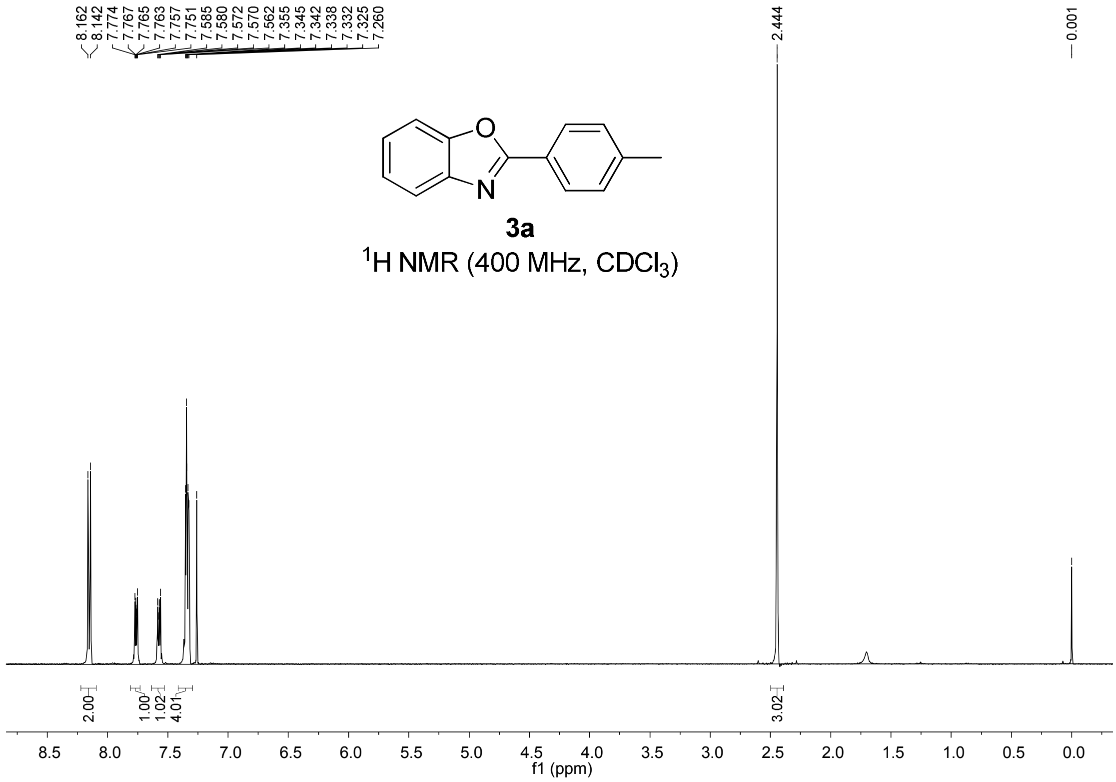
[5] C. O. Kangani, D. E. Kelley and B. W. Day, *Tetrahedron Lett.*, 2006, **47**, 6497.

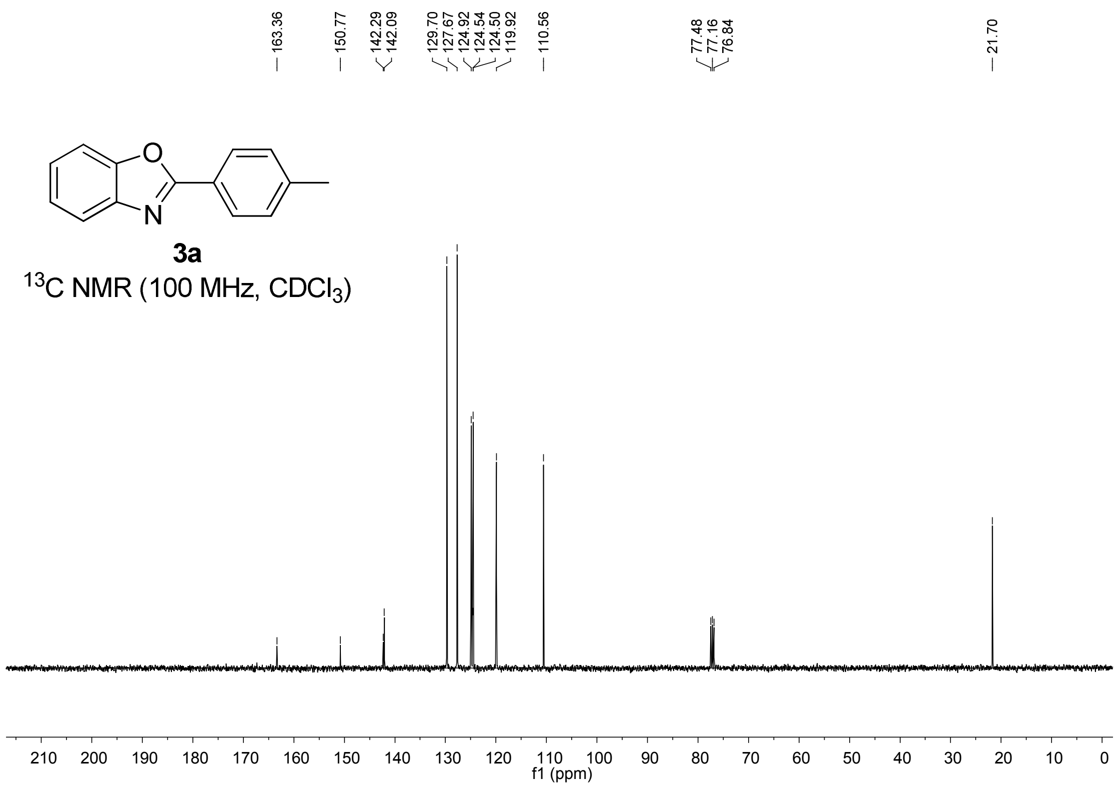
[6] S. A. Ohnmacht, P. Mamone, A. J. Culshaw and M. F. Greaney, *Chem. Commun*. 2008, 1241.

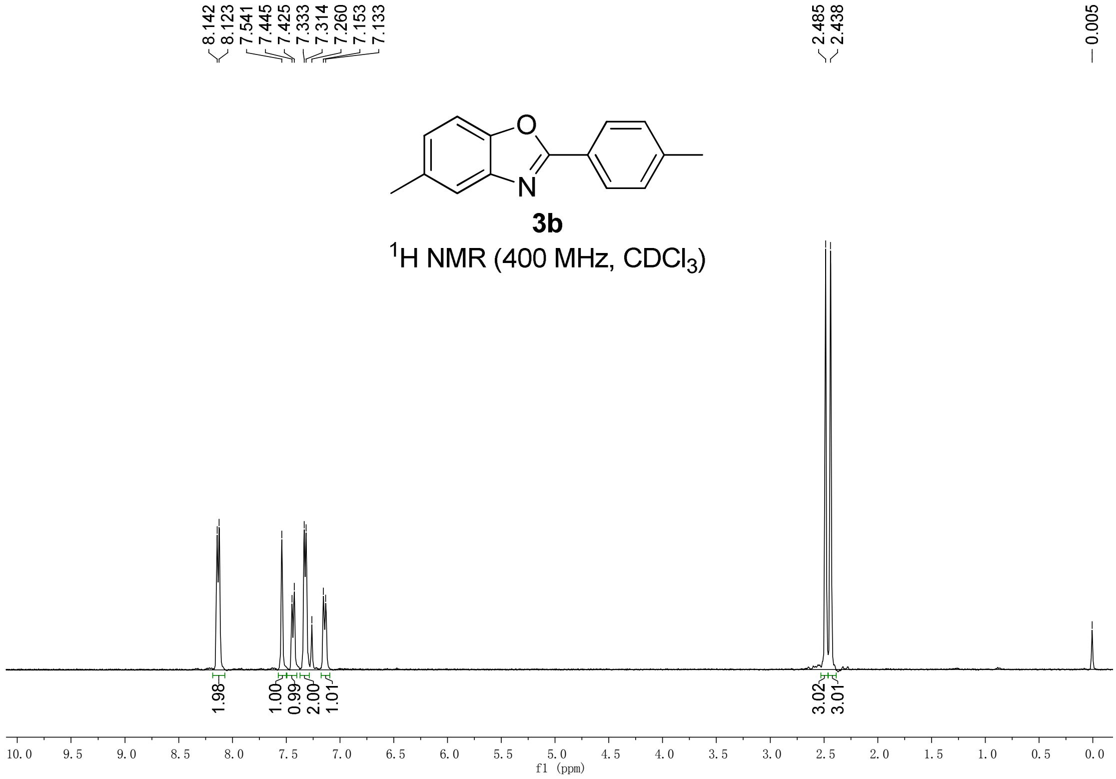
[7] H.-Q. Do and O. Daugulis, *J. Am. Chem. Soc*. 2007, **129**, 12404.

[8] L. Ackermann, A. Althammer and S. Fenner, *Angew. Chem. Int. Ed*. 2009, **48**, 201.

^{1}H and ^{13}C spectra



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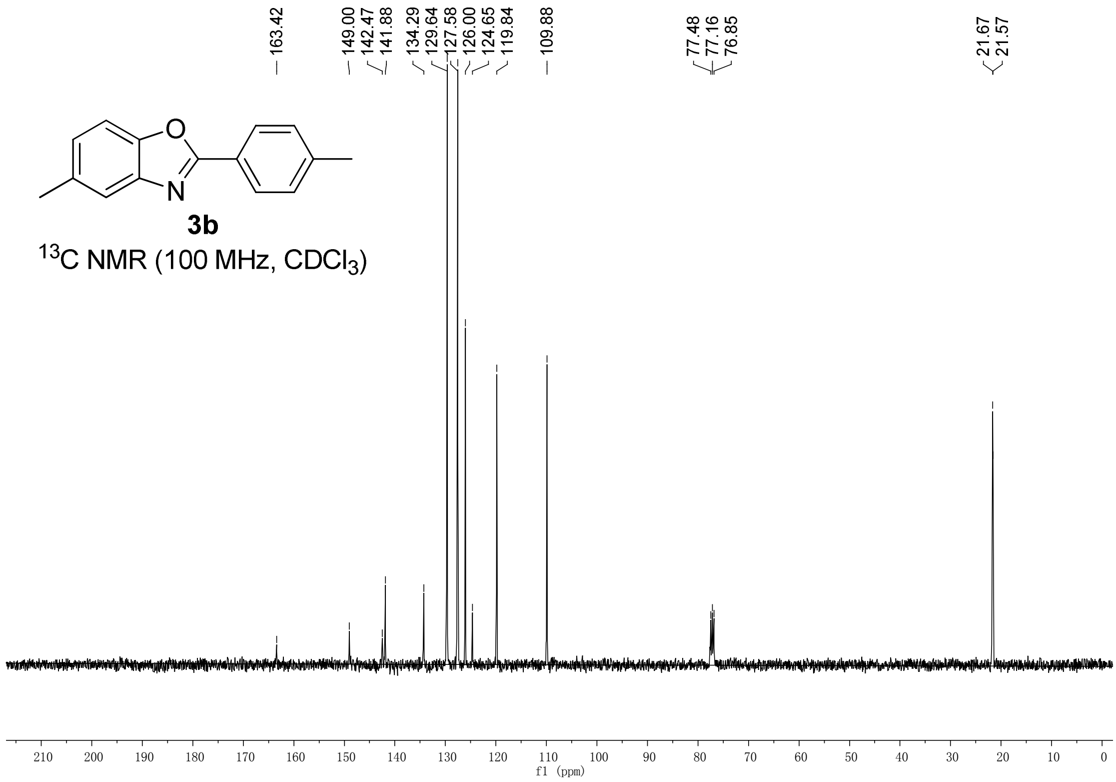
8.123
7.541
7.445
7.425
7.333
7.314
7.260
7.153
7.133
2.485
2.438
0.005
O
N
3b
^{1}H NMR (400 MHz, CDCl$_3$)
1.98
1.00
0.99
2.00
1.01
3.02
3.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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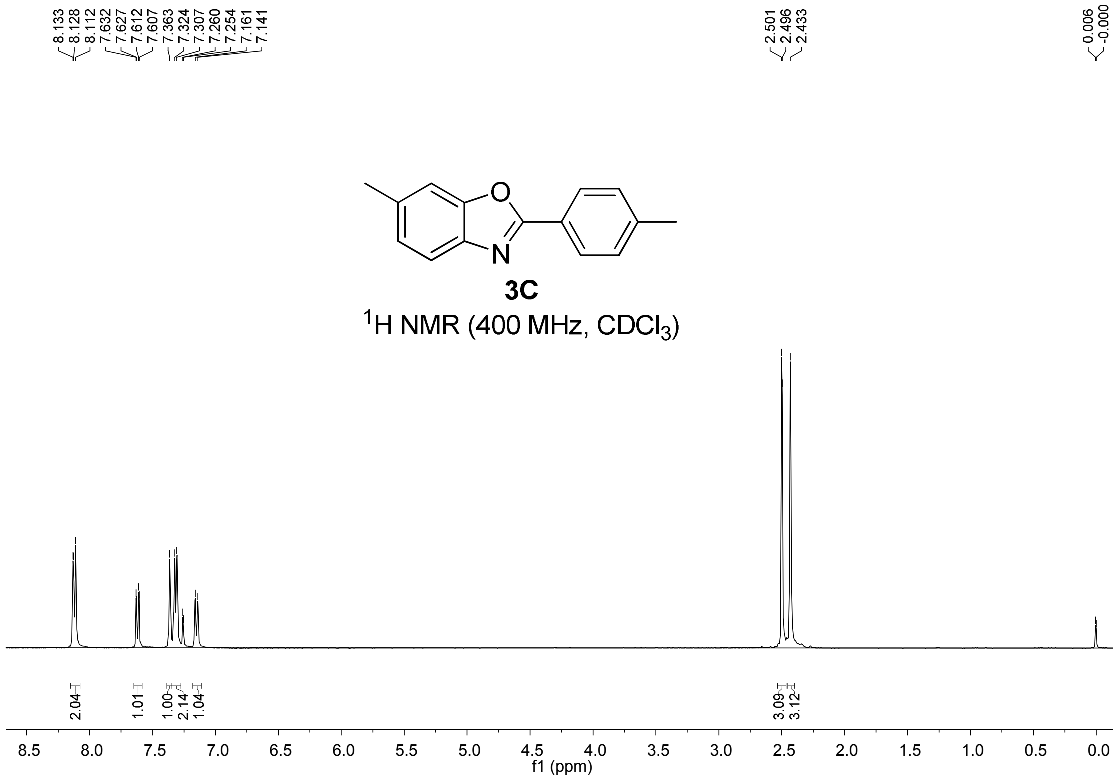
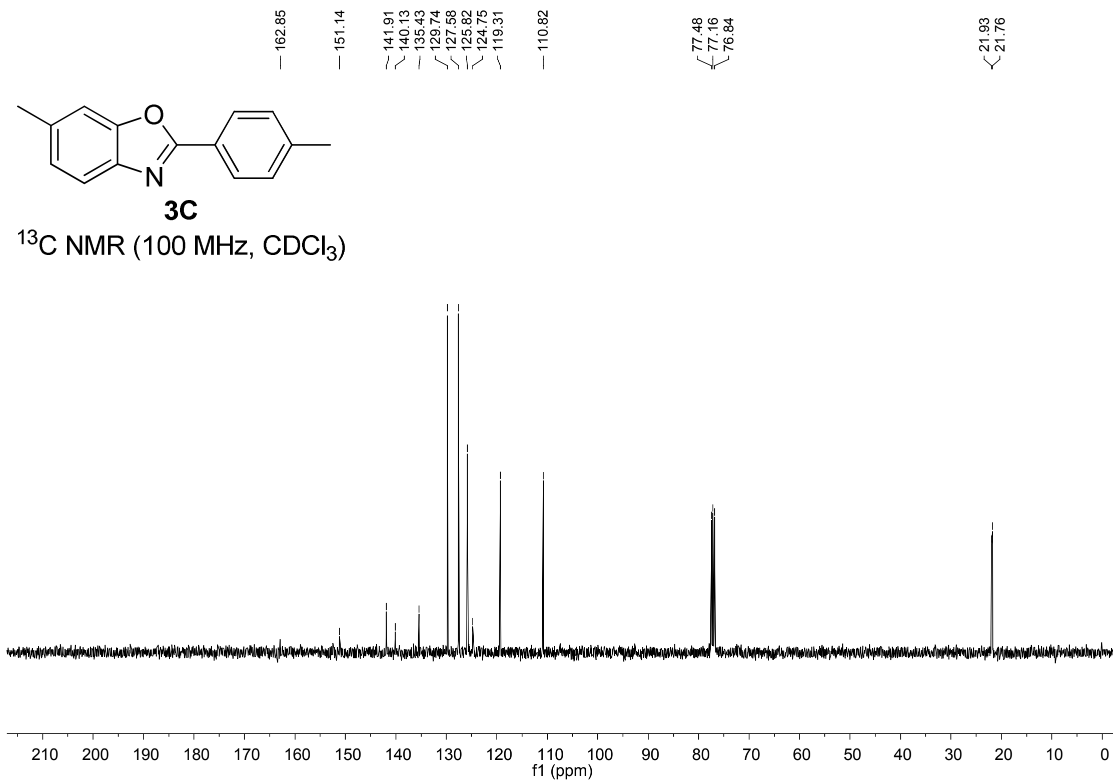
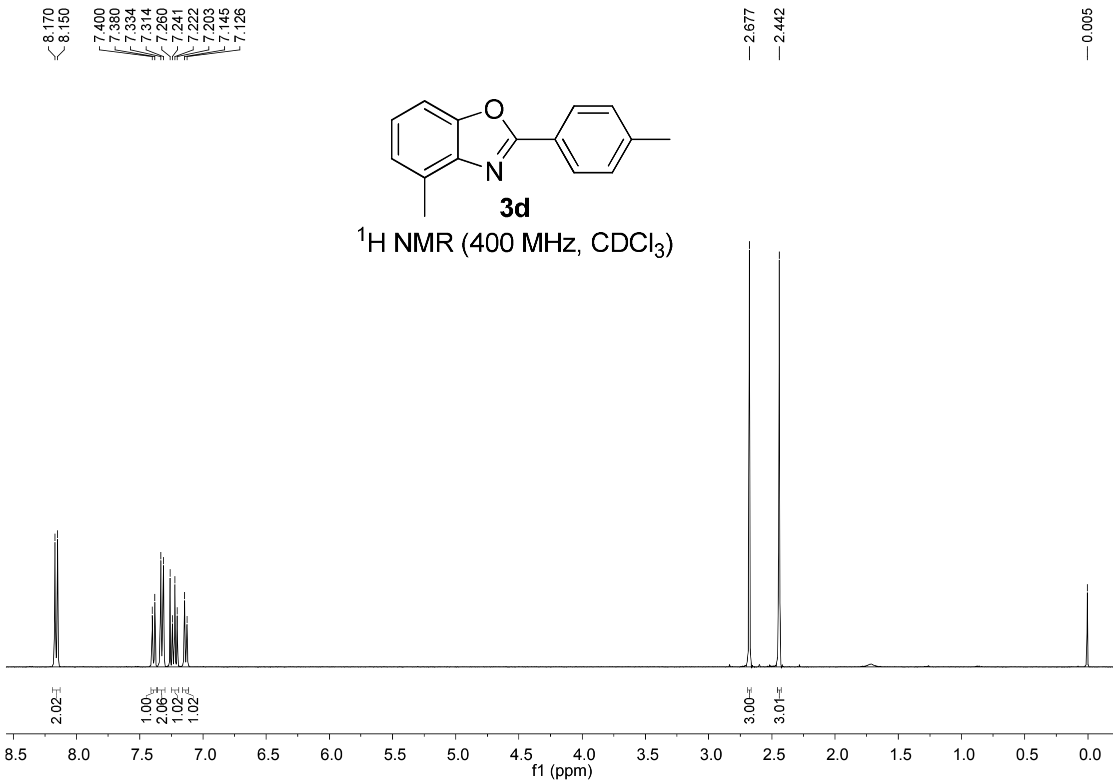
149.00
142.47
141.88
134.29
129.64
127.58
126.00
124.65
119.84
109.88
77.48
77.16
76.85
21.67
21.57
O
N
3b
^{13}C NMR (100 MHz, CDCl$_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry



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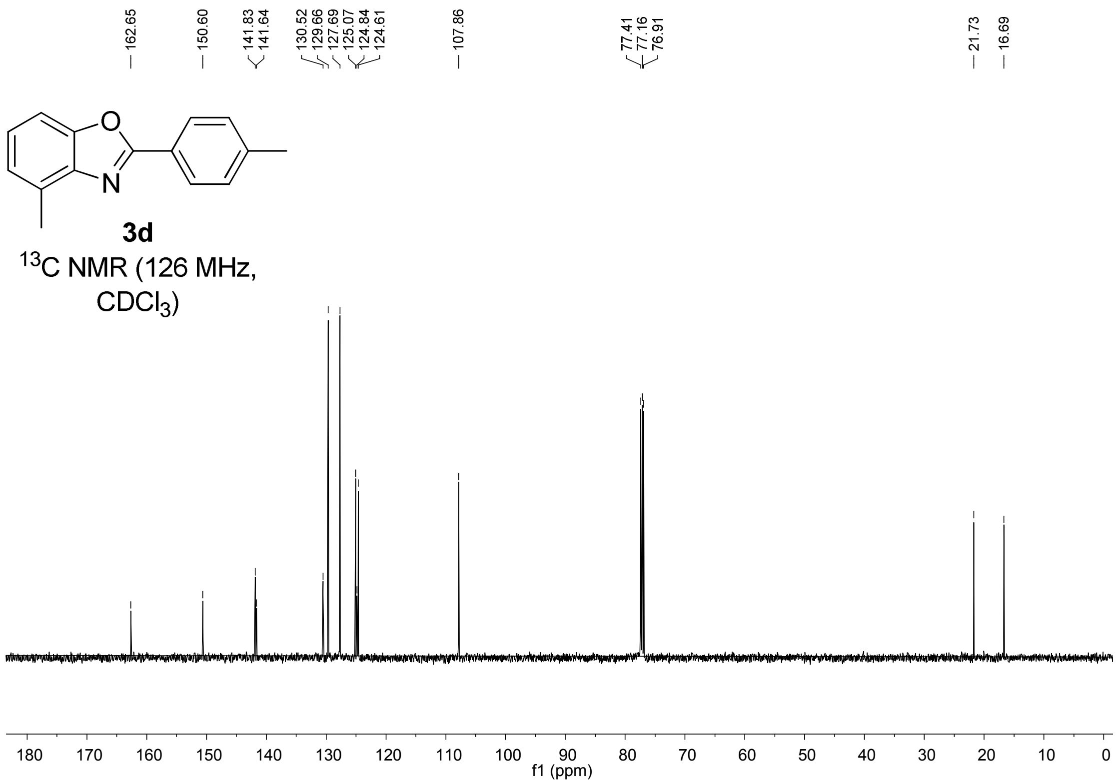
8.150
7.400
7.380
7.334
7.314
7.260
7.241
7.222
7.203
7.145
7.126
2.677
2.442
0.005
O
N
3d
1H NMR (400 MHz, CDCl3)
2.02
1.00
2.06
1.02
1.02
3.00
3.01
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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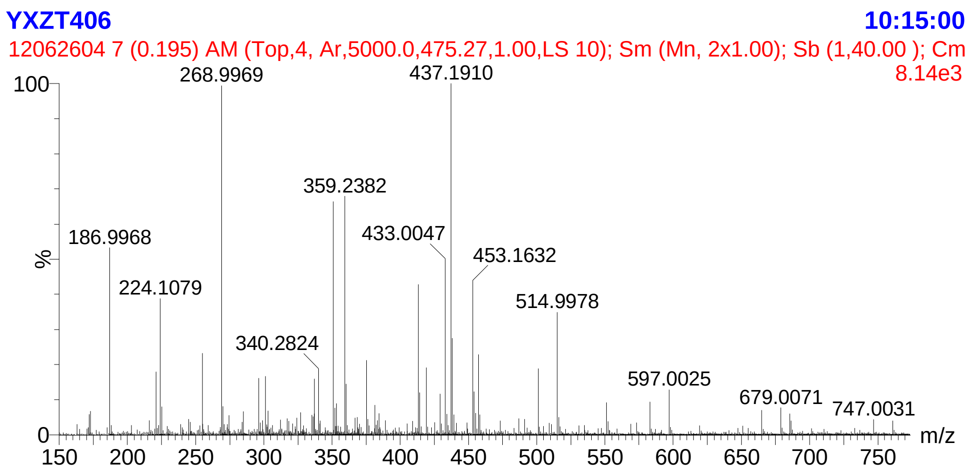
150.60
141.83
141.64
130.52
129.66
127.69
125.07
124.84
124.61
107.86
77.41
77.16
76.91
21.73
16.69
O
N
3d
13C NMR (126 MHz, CDCl3)
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



Elemental Composition Report

Single Mass Analysis (displaying only valid results)

Tolerance = 5.0 PPM / DBE: min = -200.0, max = 200.0

Selected filters: None

Monoisotopic Mass, Even Electron Ions

13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)

Elements Used:

C: 0-150 H: 0-150 N: 1-1 O: 1-1

Minimum:				-200.0		
Maximum:		5.0	5.0	200.0		
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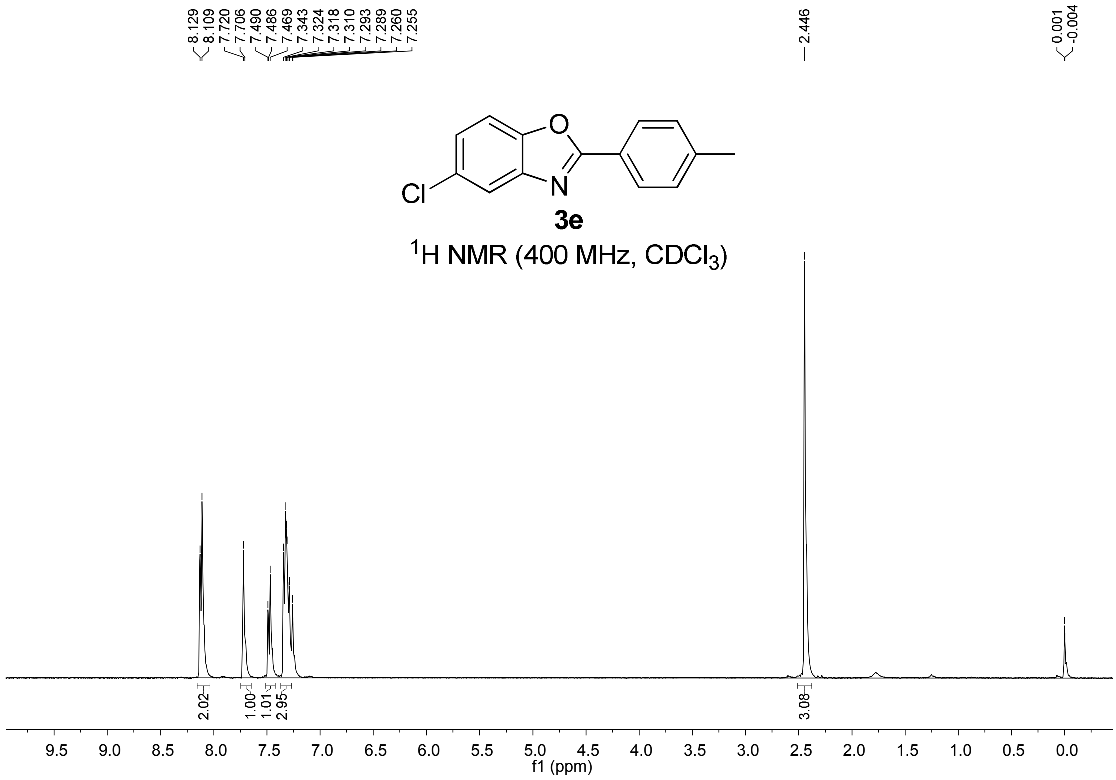
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7.343
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7.310
7.293
7.289
7.260
7.255
2.446
0.001
-0.004
Cl
O
N
3e
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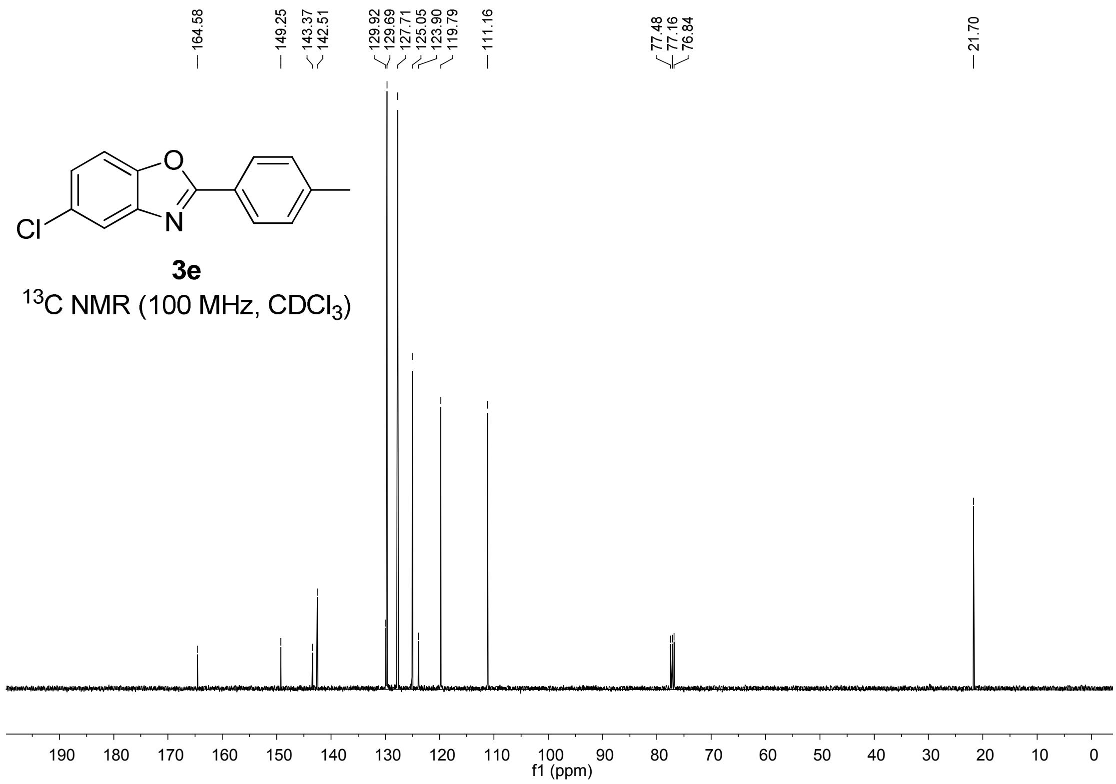
1.01
2.95
3.08
f1 (ppm)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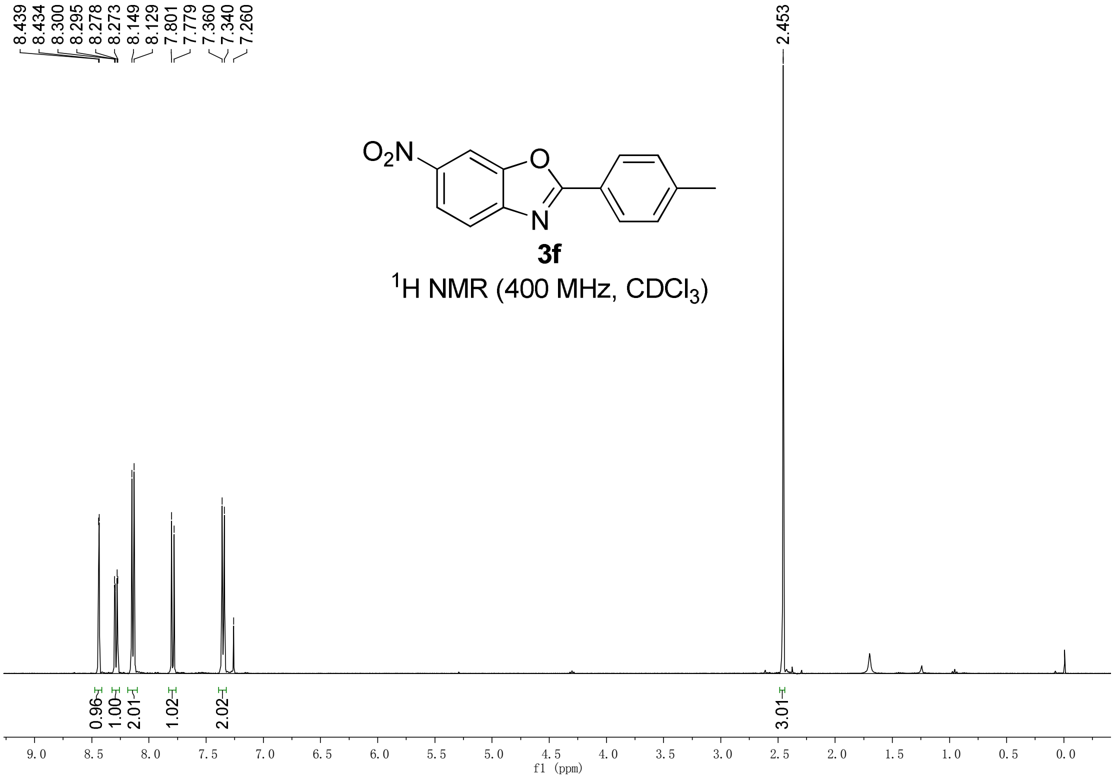
77.16
76.84
21.70
Cl
O
N
3e
13C NMR (100 MHz, CDCl3)
f1 (ppm)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8.129
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7.779
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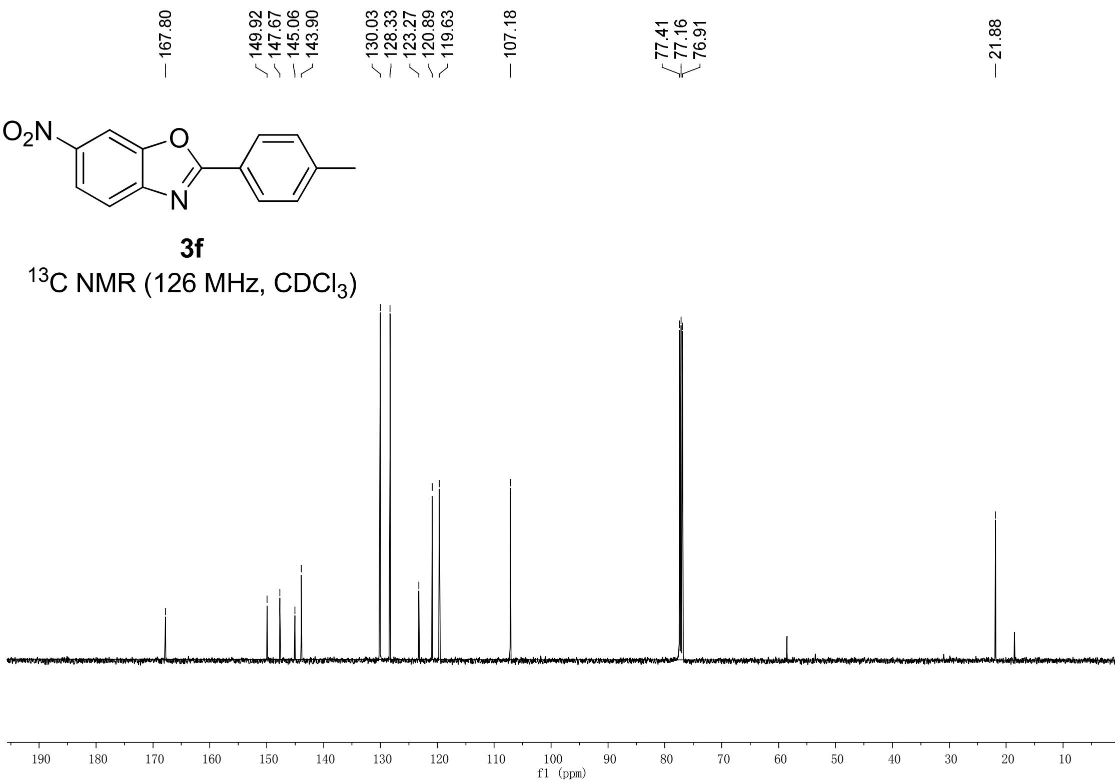
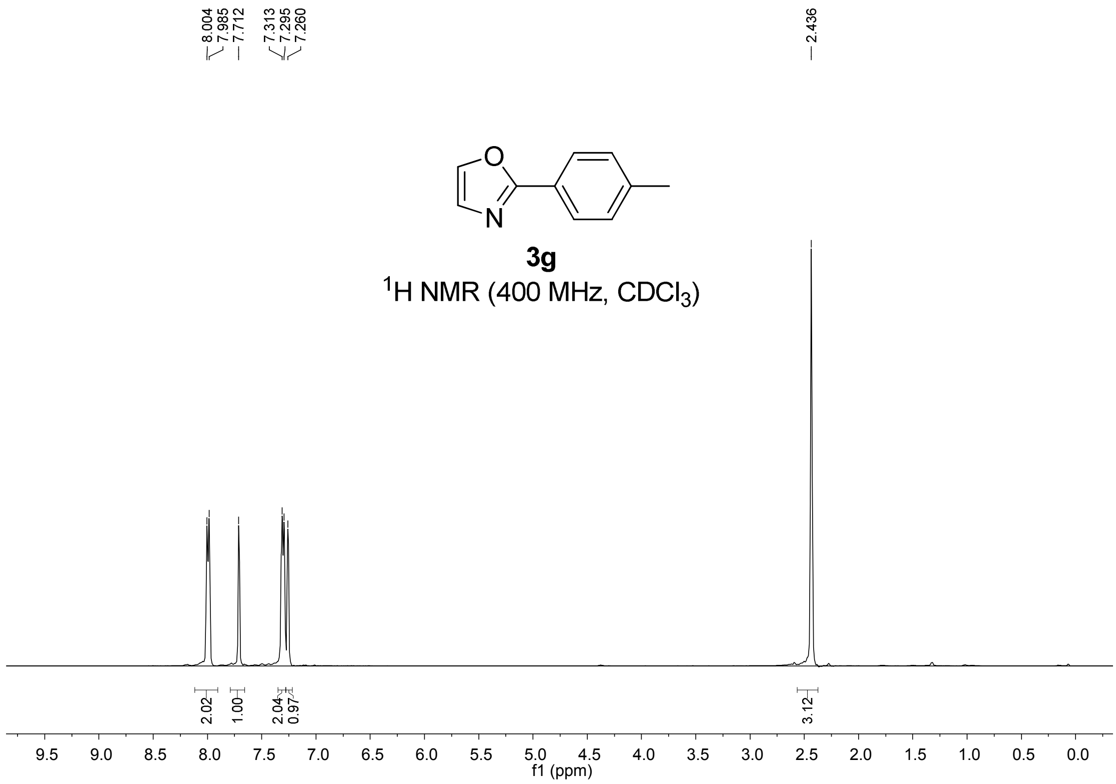
7.260
2.453
O2N
O
N
3f
1H NMR (400 MHz, CDCl3)
0.96
1.00
2.01
1.02
2.02
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


167.80
149.92
147.67
145.06
143.90
130.03
128.33
123.27
120.89
119.63
107.18
77.41
77.16
76.91
21.88
O2N
O
N
3f
13C NMR (126 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)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7.313
7.295
7.260
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N
3g
^{1}H NMR (400 MHz, $CDCl_3$)
2.02
1.00
2.04
0.97
3.12
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
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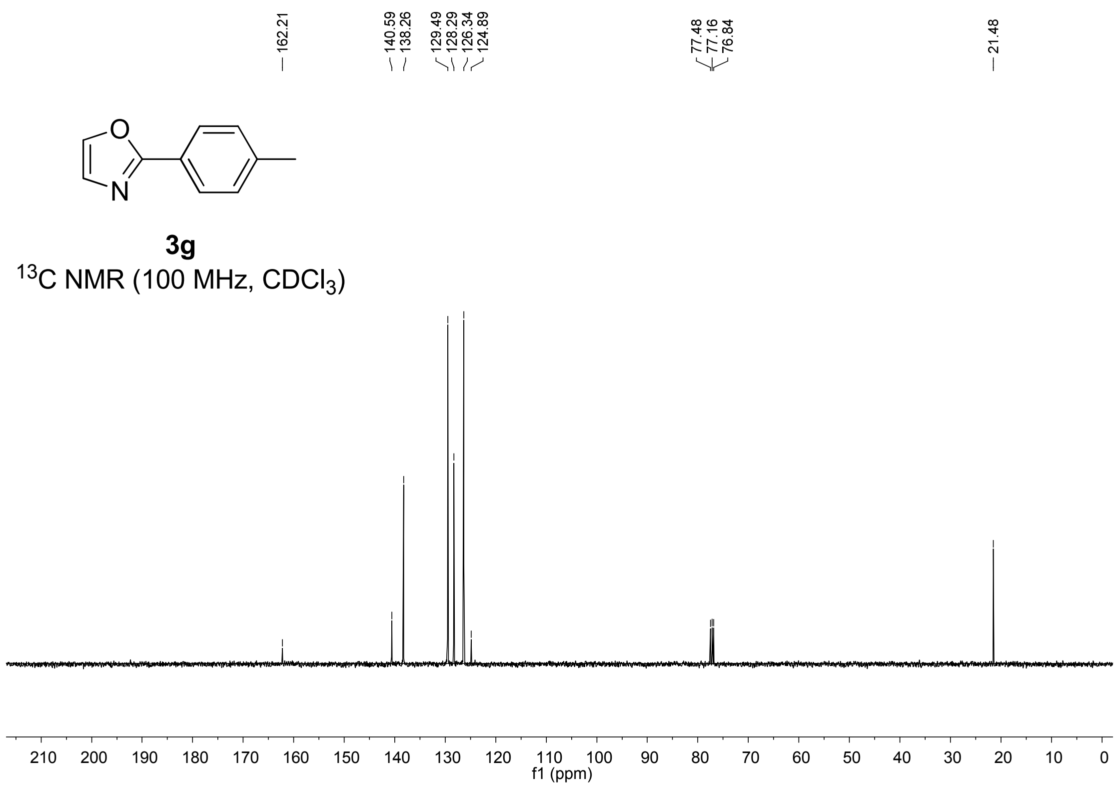
1.5
1.0
0.5
0.0
f1 (ppm)


162.21
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138.26
129.49
128.29
126.34
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77.48
77.16
76.84
21.48
O
N
3g
^{13}C NMR (100 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
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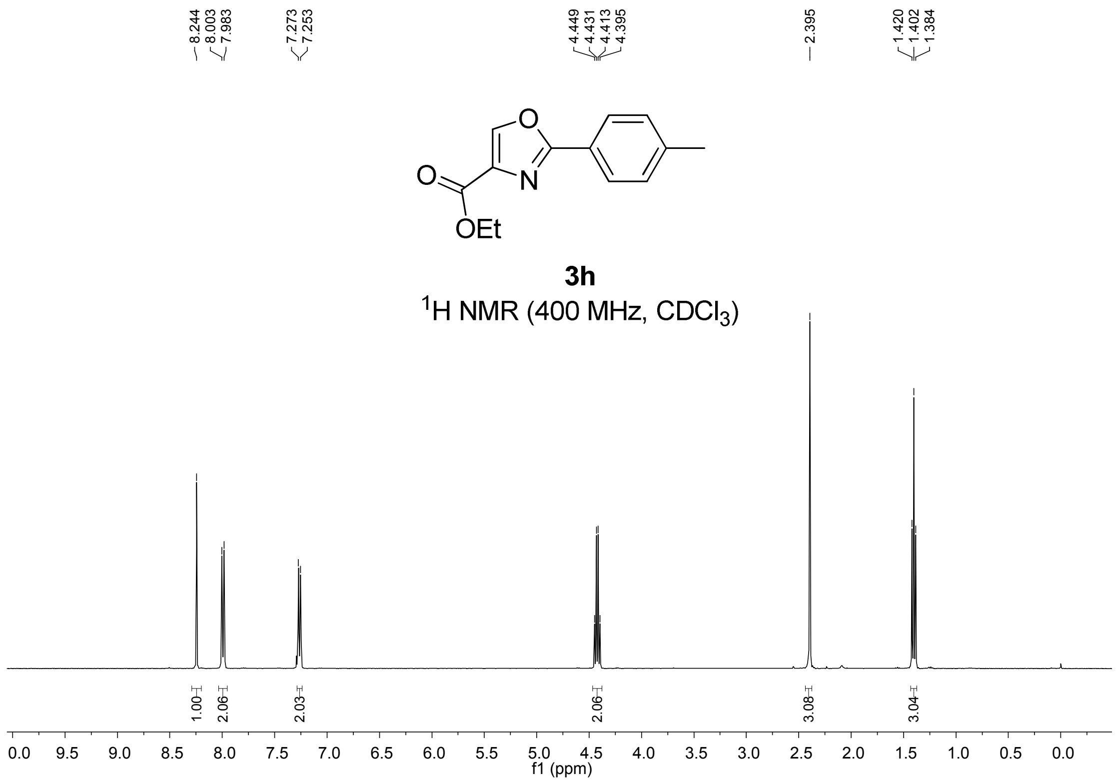
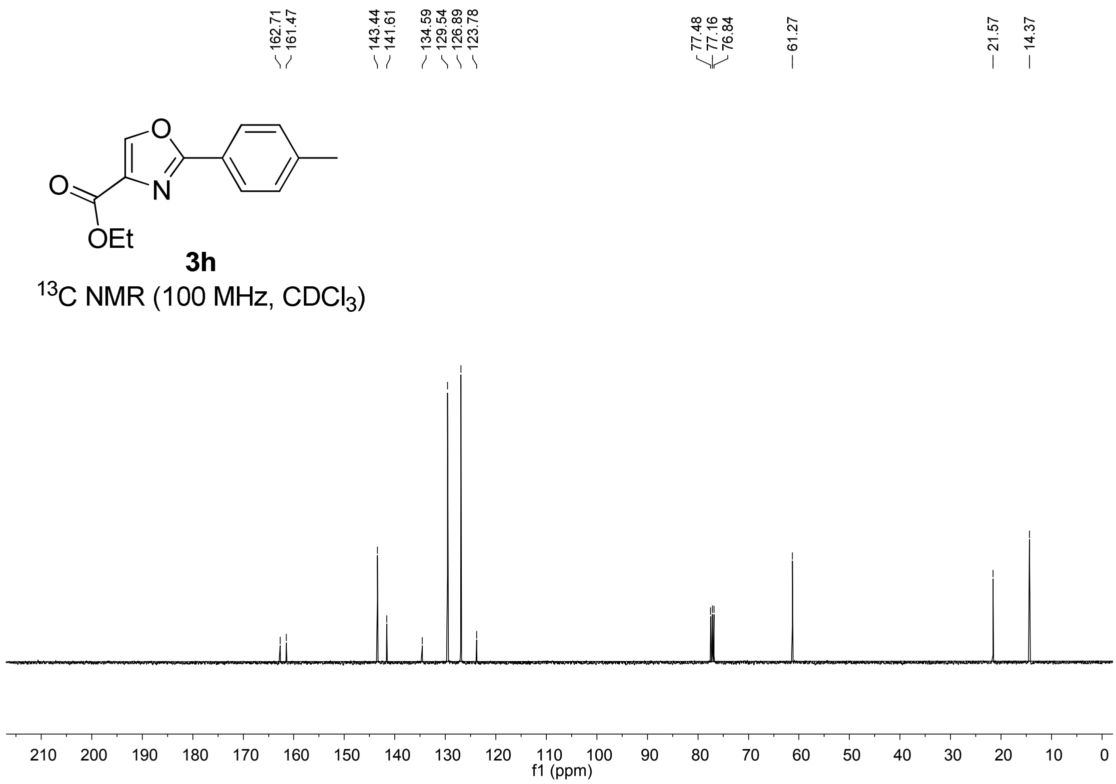
60
50
40
30
20
10
0
f1 (ppm)



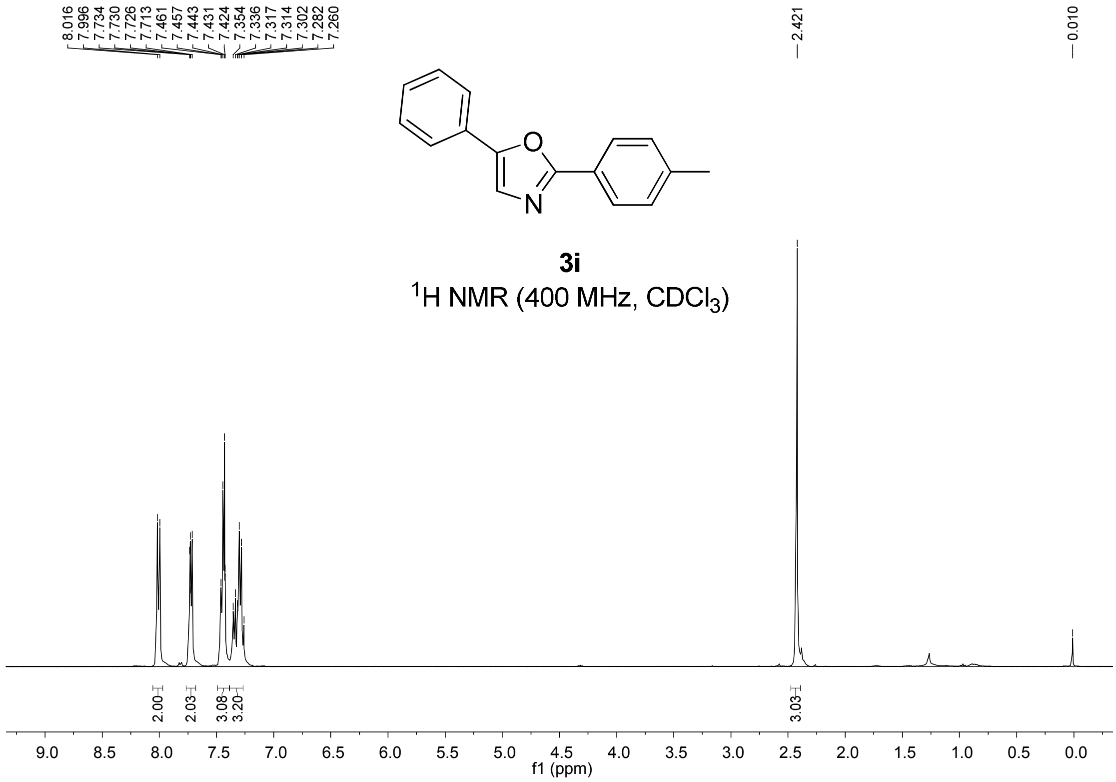
3h

^{1}H NMR (400 MHz, $CDCl_3$)



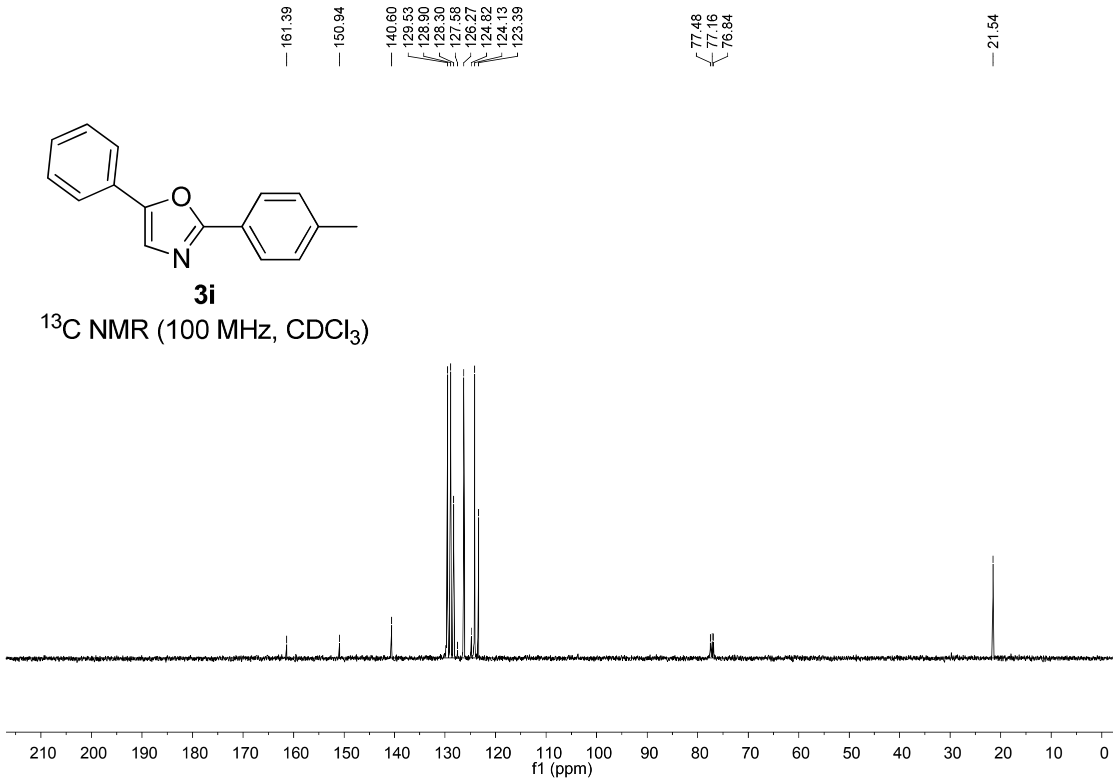
3h

^{13}C NMR (100 MHz, $CDCl_3$)



3i

^{1}H NMR (400 MHz, $CDCl_3$)



3i

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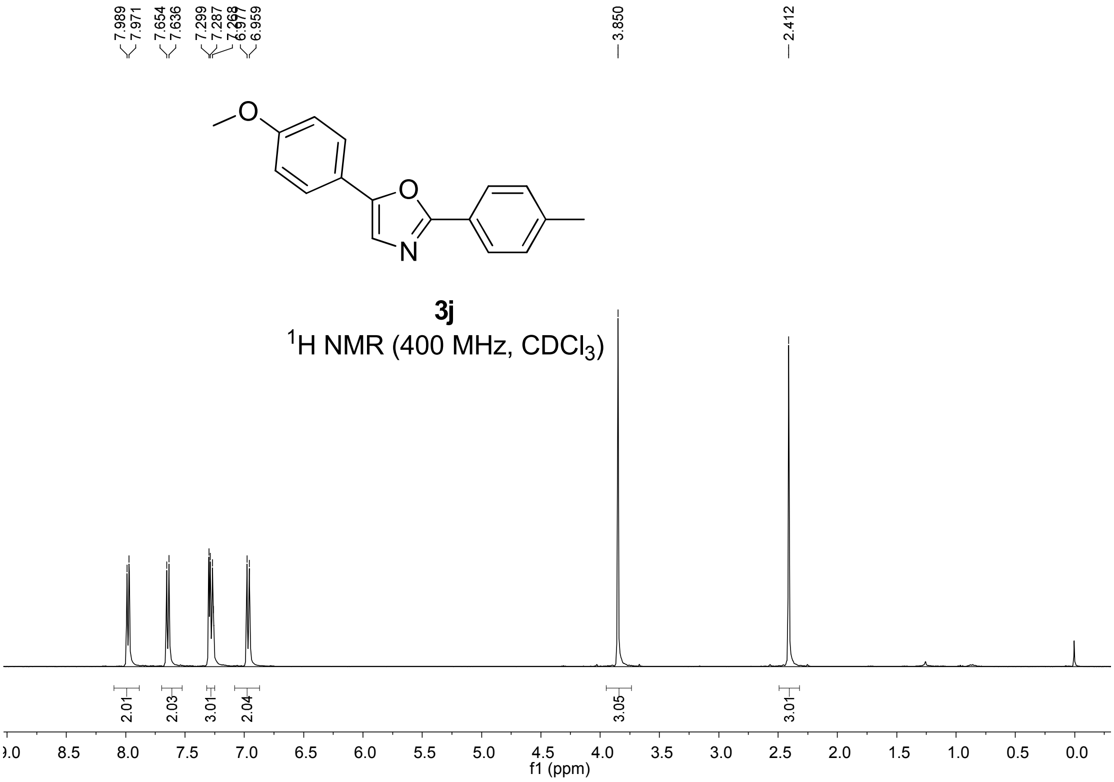
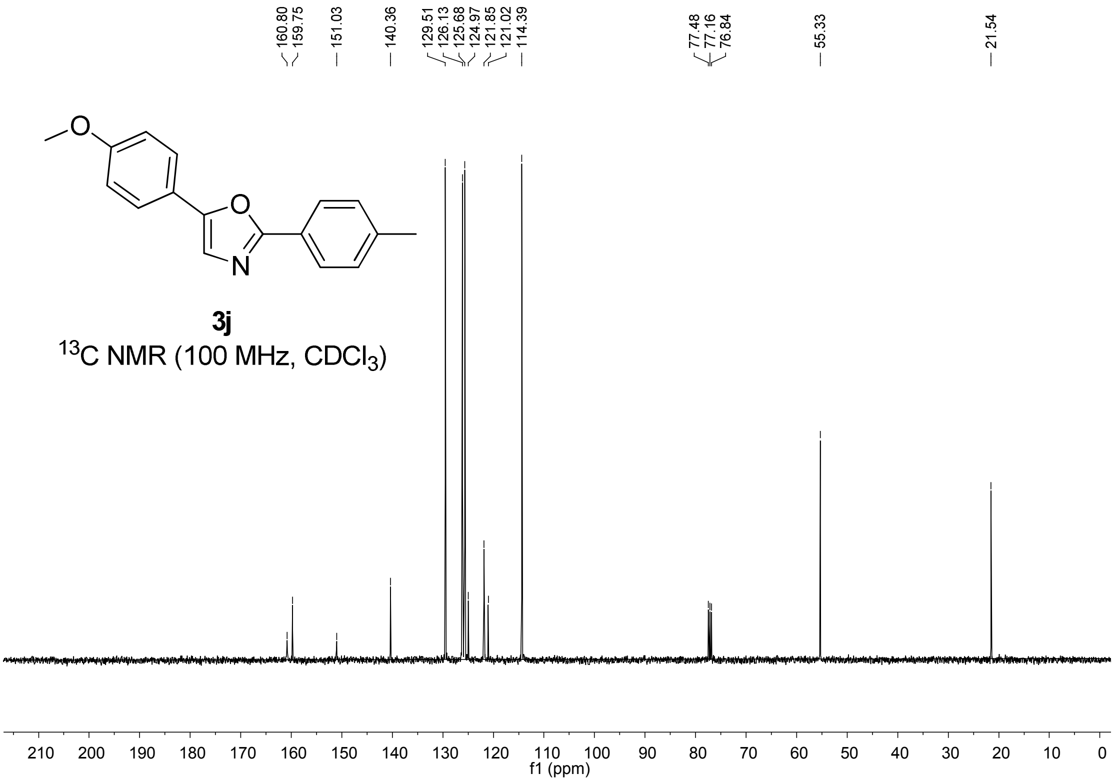
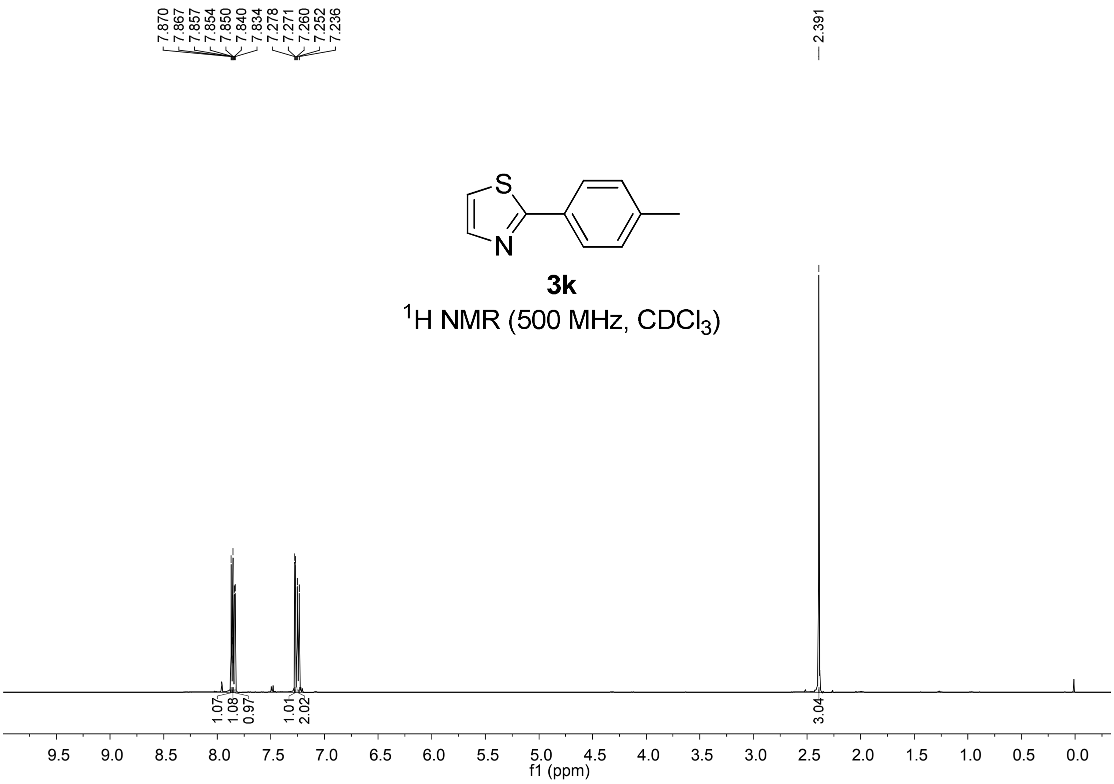


3j
^{1}H NMR (400 MHz, $CDCl_3$)



3j
^{13}C NMR (100 MHz, $CDCl_3$)


7.870
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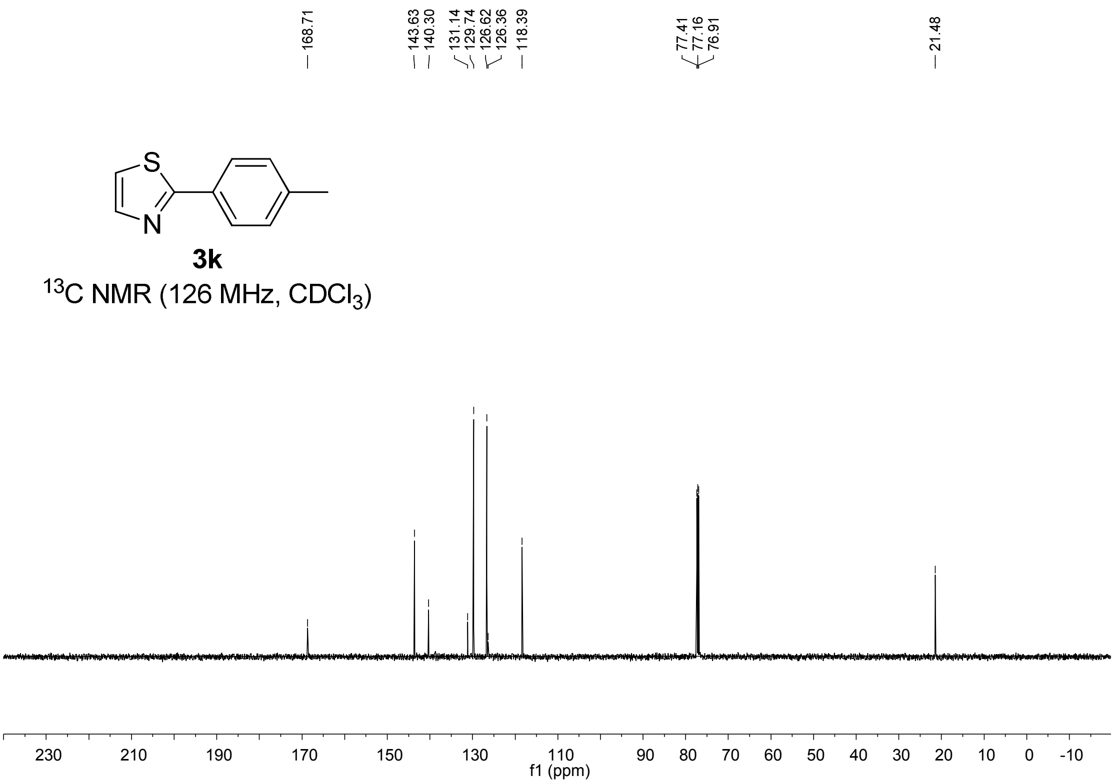
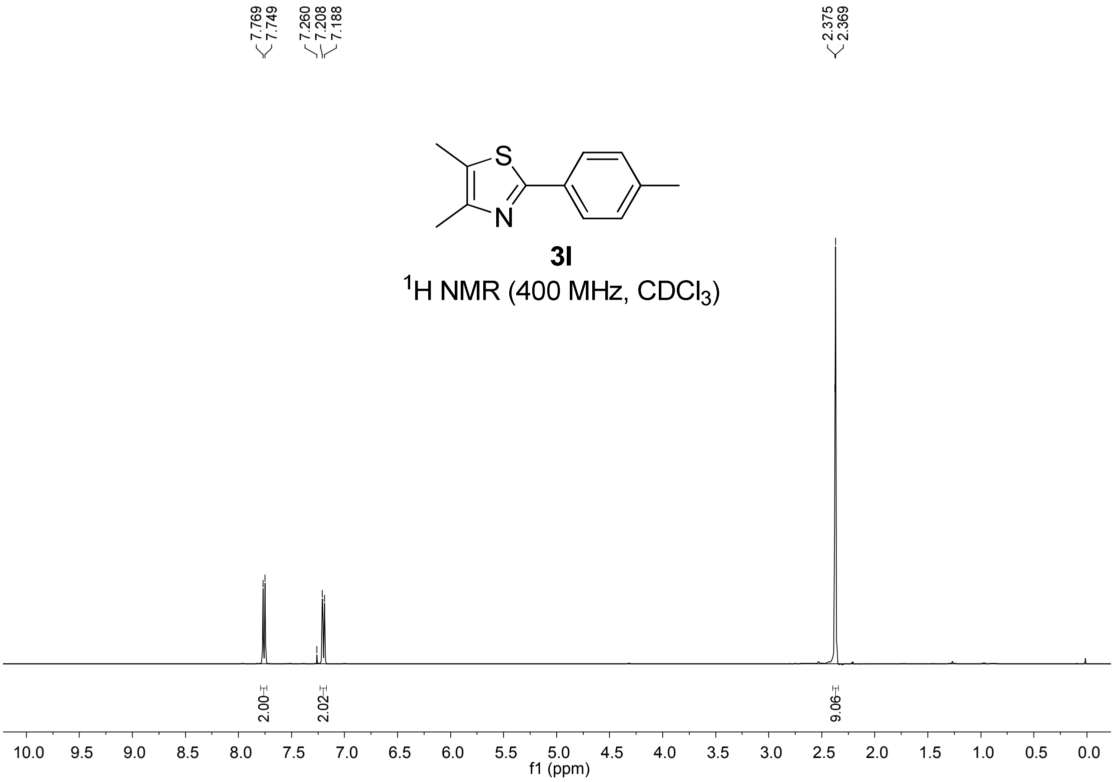
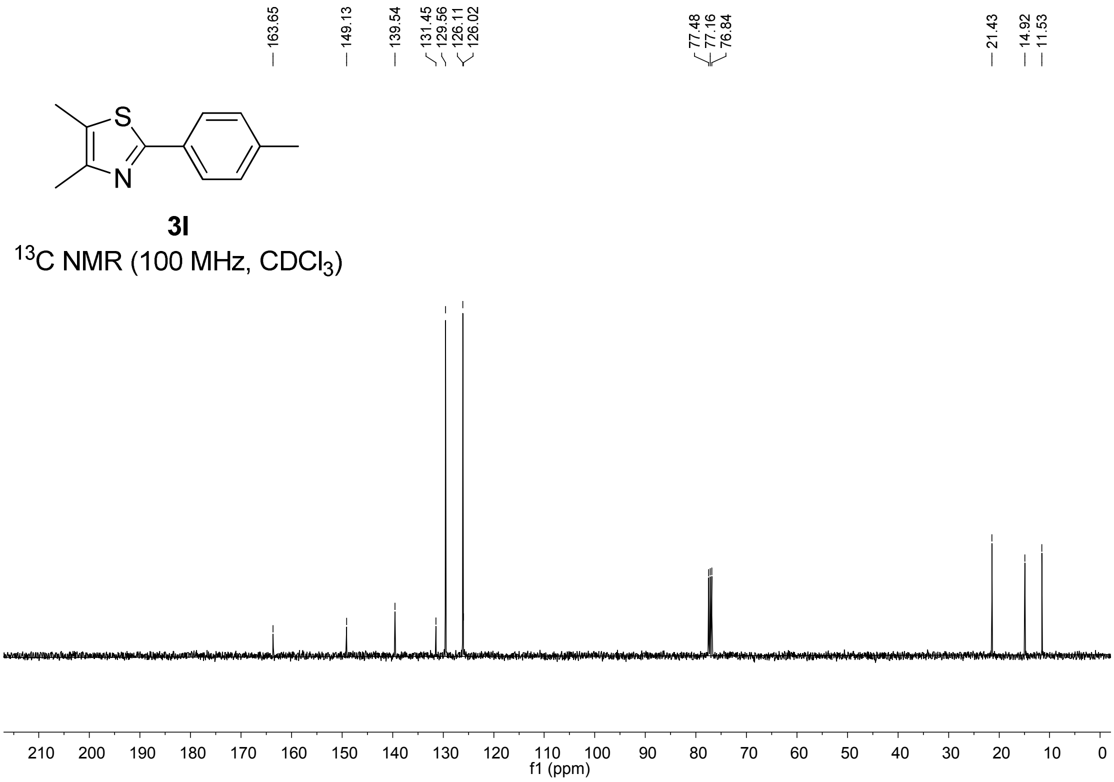
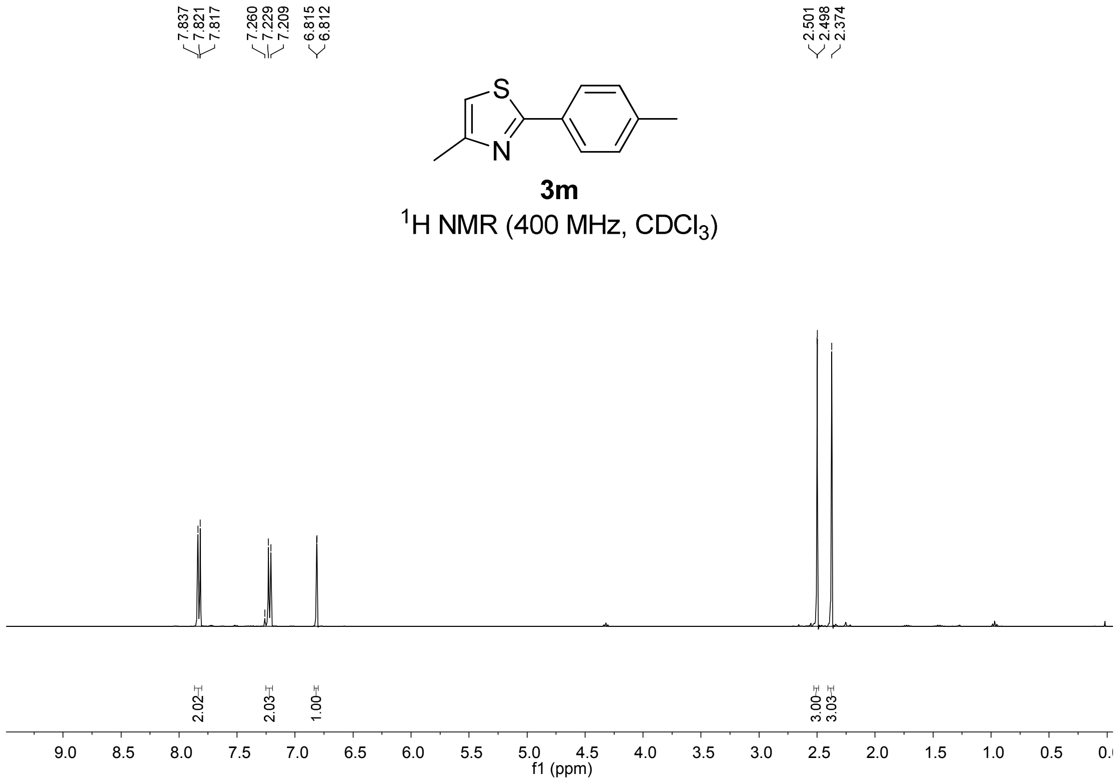
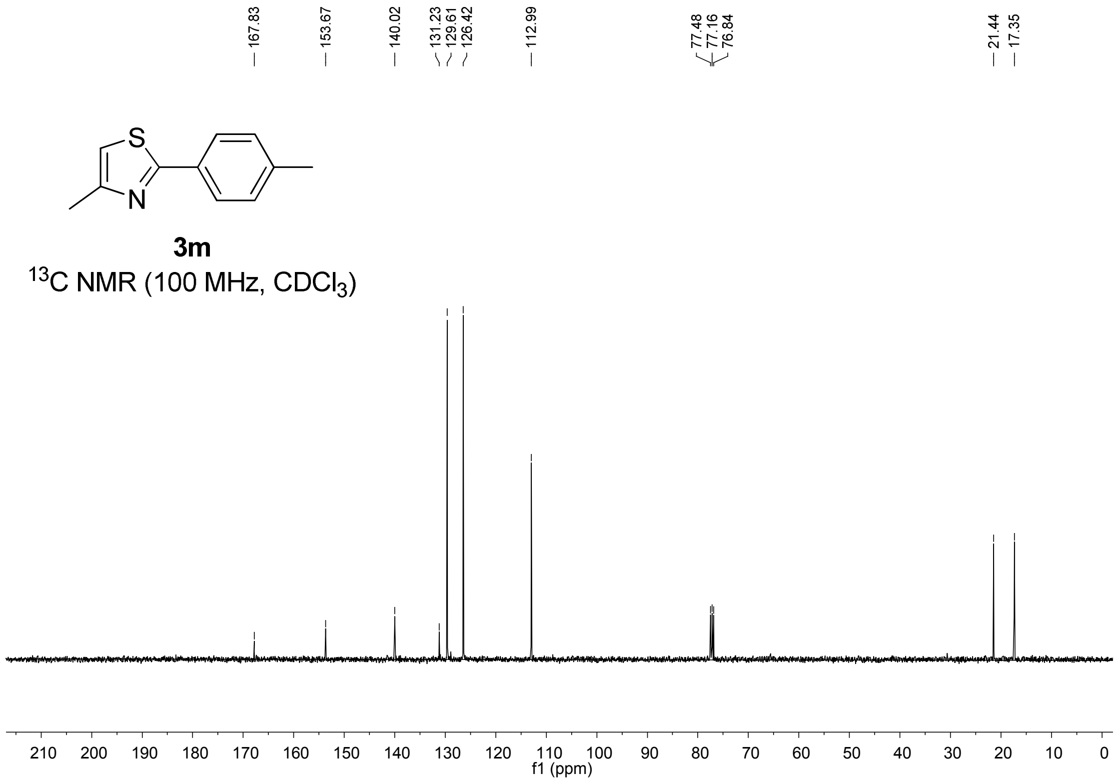
7.857
7.854
7.850
7.840
7.834
7.278
7.271
7.260
7.252
7.236
2.391
3k
1H NMR (500 MHz, CDCl3)
1.07
1.08
0.97
1.01
2.02
3.04
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

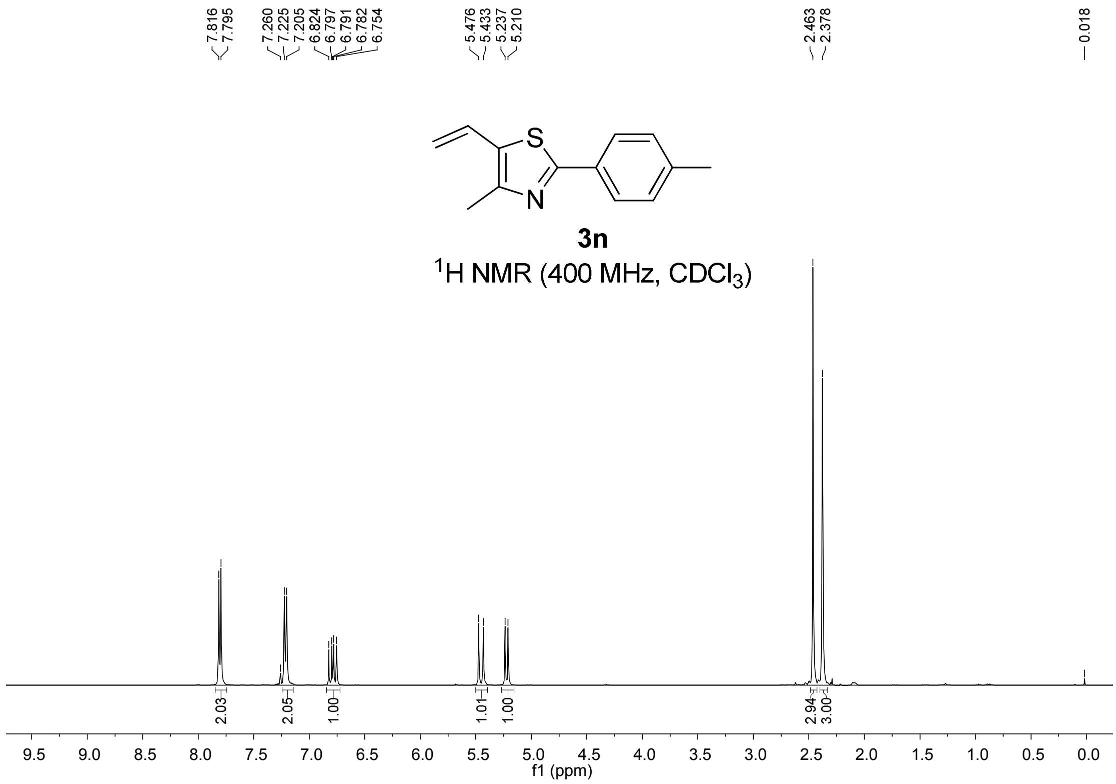

168.71
143.63
140.30
131.14
129.74
126.62
126.36
118.39
77.41
77.16
76.91
21.48
3k
13C NMR (126 MHz, CDCl3)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.769
7.749
7.260
7.208
7.188
2.375
2.369
S
N
3l
¹H NMR (400 MHz, CDCl₃)
2.00
2.02
9.06
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)


163.65
149.13
139.54
131.45
129.56
126.11
126.02
77.48
77.16
76.84
21.43
14.92
11.53
S
N
3l
¹³C NMR (100 MHz, CDCl₃)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

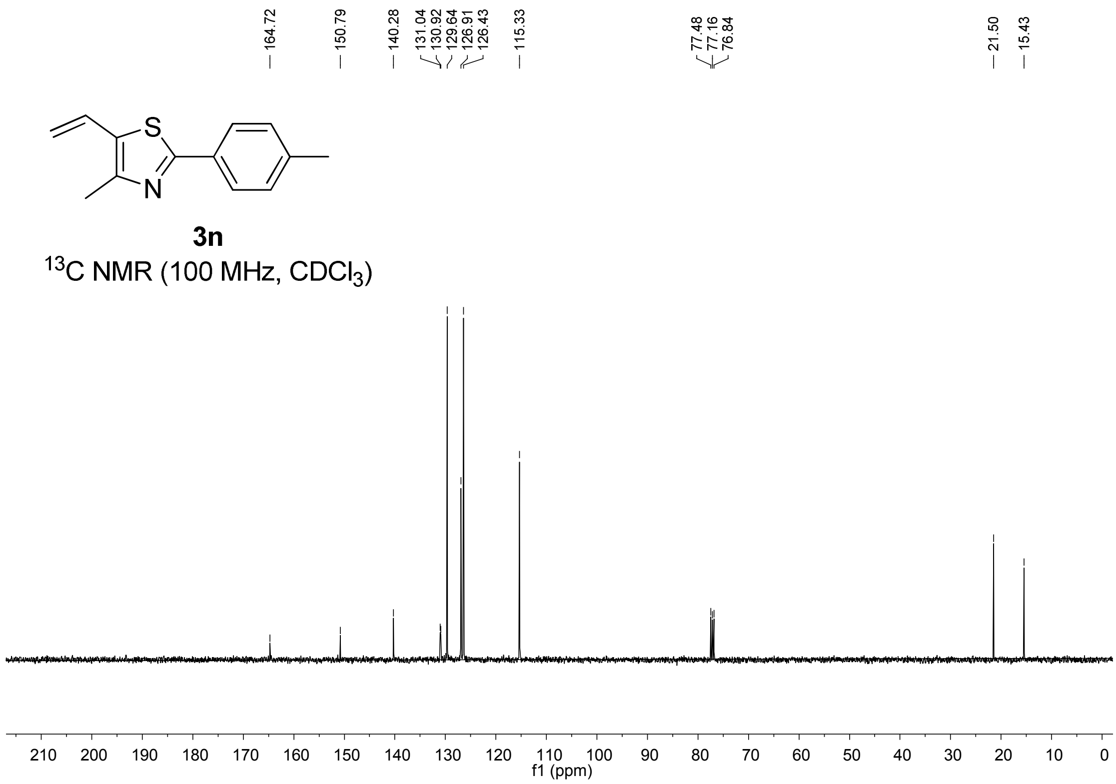

7.837
7.821
7.817
7.260
7.229
7.209
6.815
6.812
2.501
2.498
2.374
S
N
3m
¹H NMR (400 MHz, CDCl3)
2.02
2.03
1.00
3.00
3.03
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


167.83
153.67
140.02
131.23
129.61
126.42
112.99
77.48
77.16
76.84
21.44
17.35
S
N
3m
¹³C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3n

^{1}H NMR (400 MHz, $CDCl_3$)



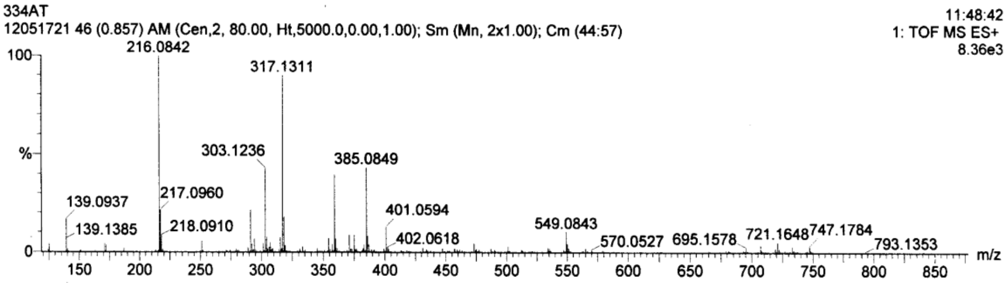
3n

^{13}C NMR (100 MHz, $CDCl_3$)

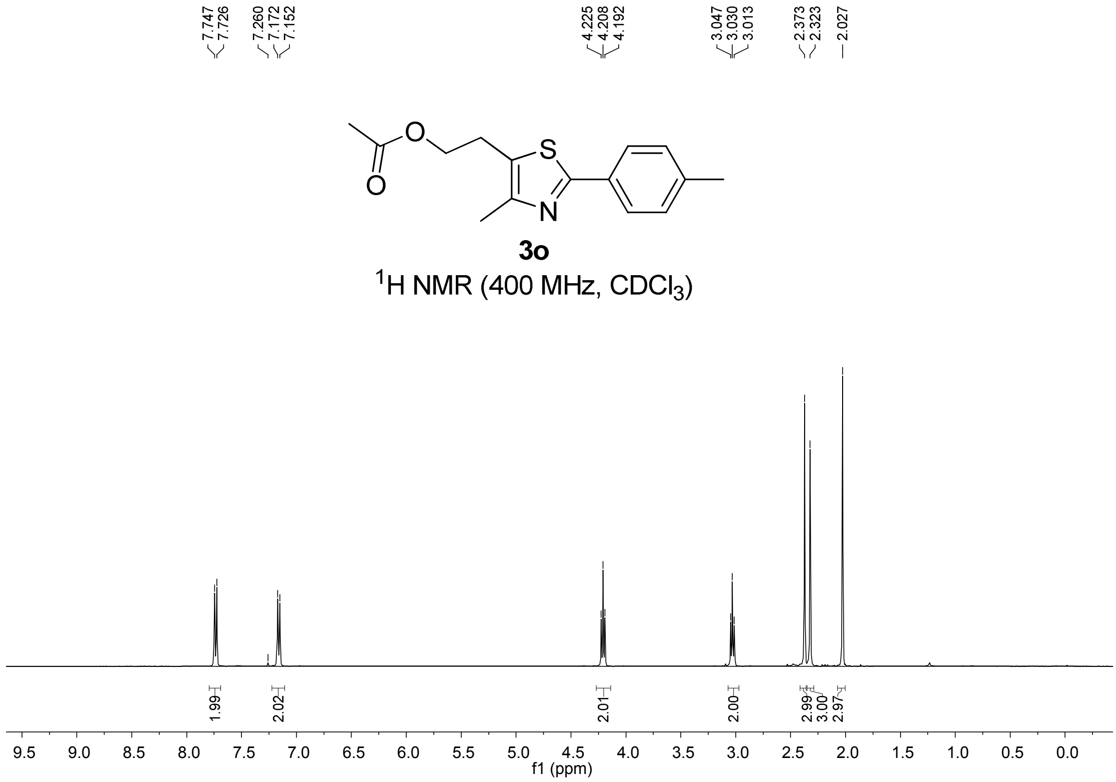
Elemental Composition Report **Page 1**

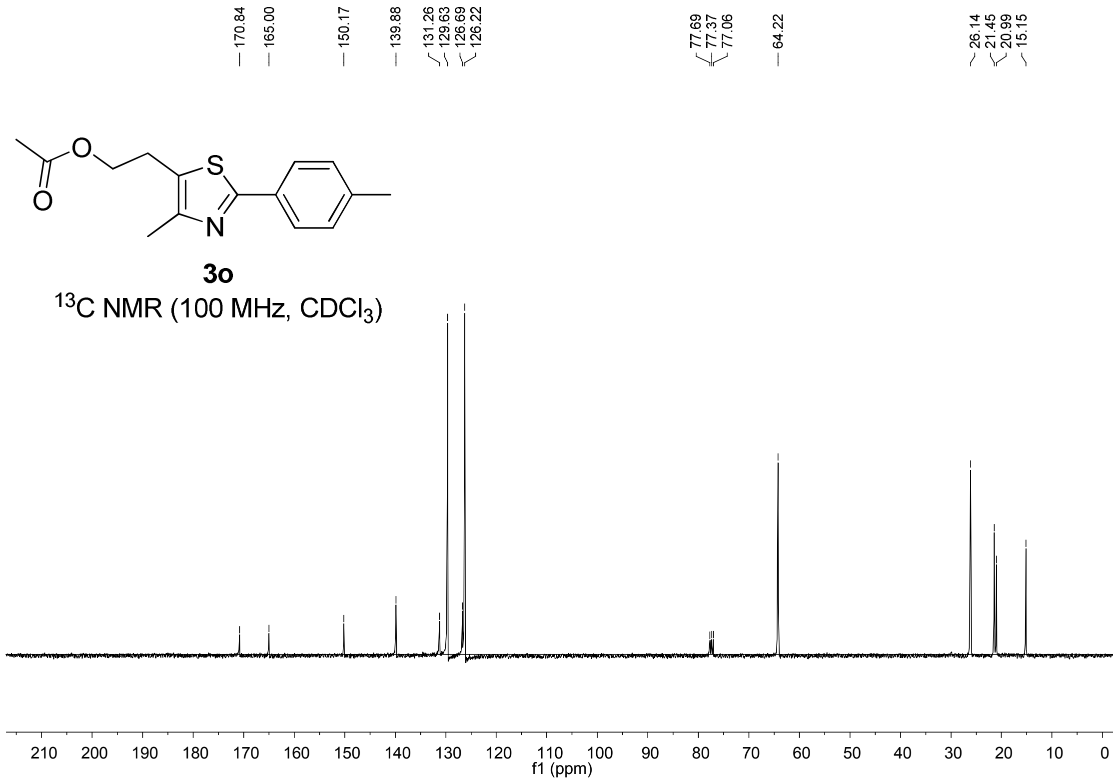
Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -200.0, max = 200.0
Selected filters: None

Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-150 H: 0-150 N: 1-1 S: 1-1



Minimum:				-200.0		
Maximum:		5.0	5.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
216.0842	216.0847	-0.5	-2.3	7.5	100.2	C13 H14 N S

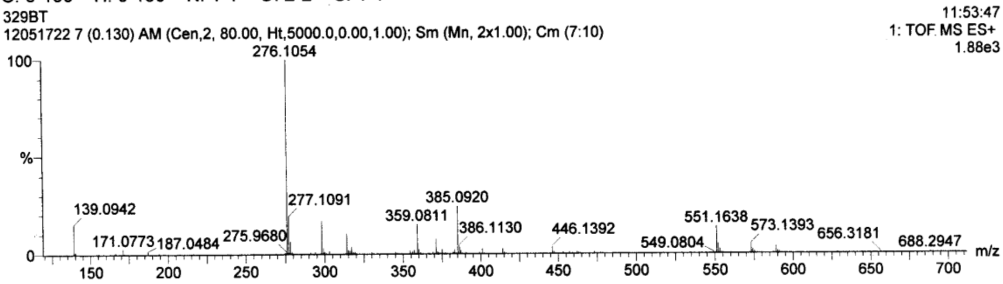

7.747
7.726
7.260
7.172
7.152
4.225
4.208
4.192
3.047
3.030
3.013
2.373
2.323
2.027
3o
1H NMR (400 MHz, CDCl3)
1.99
2.02
2.01
2.00
2.99
3.00
2.97
f1 (ppm)


170.84
165.00
150.17
139.88
131.26
129.63
126.69
126.22
77.69
77.37
77.06
64.22
26.14
21.45
20.99
15.15
3o
13C NMR (100 MHz, CDCl3)
f1 (ppm)

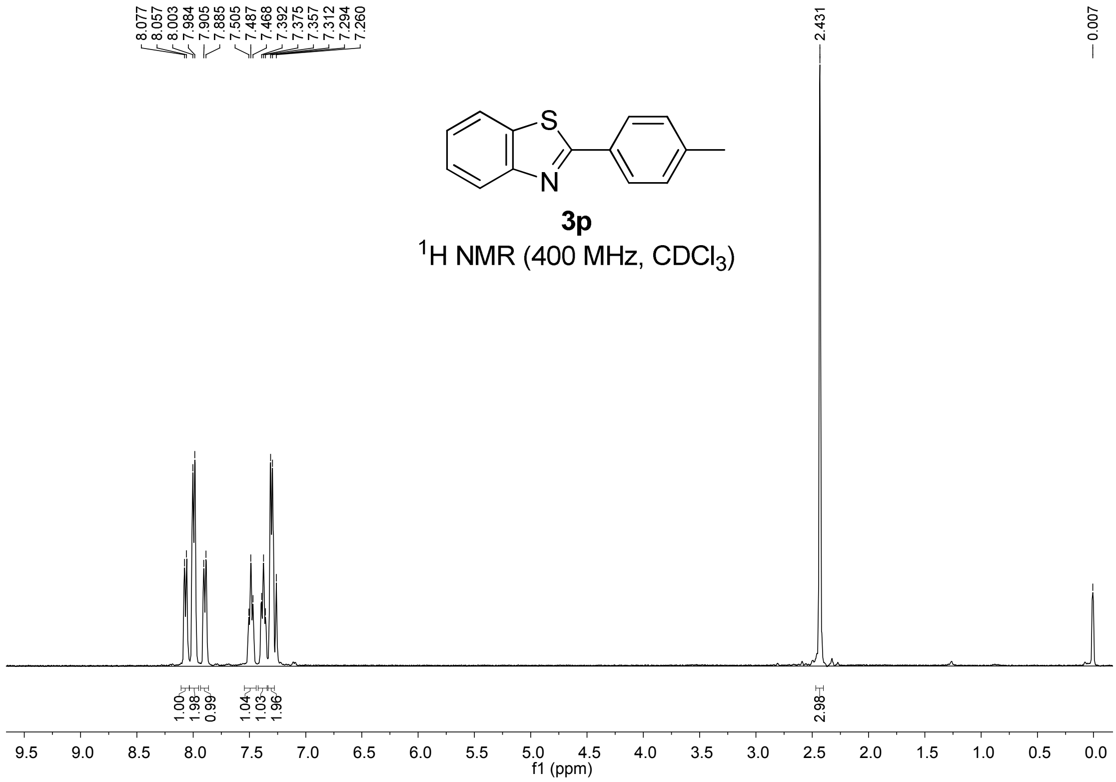
Elemental Composition Report **Page 1**

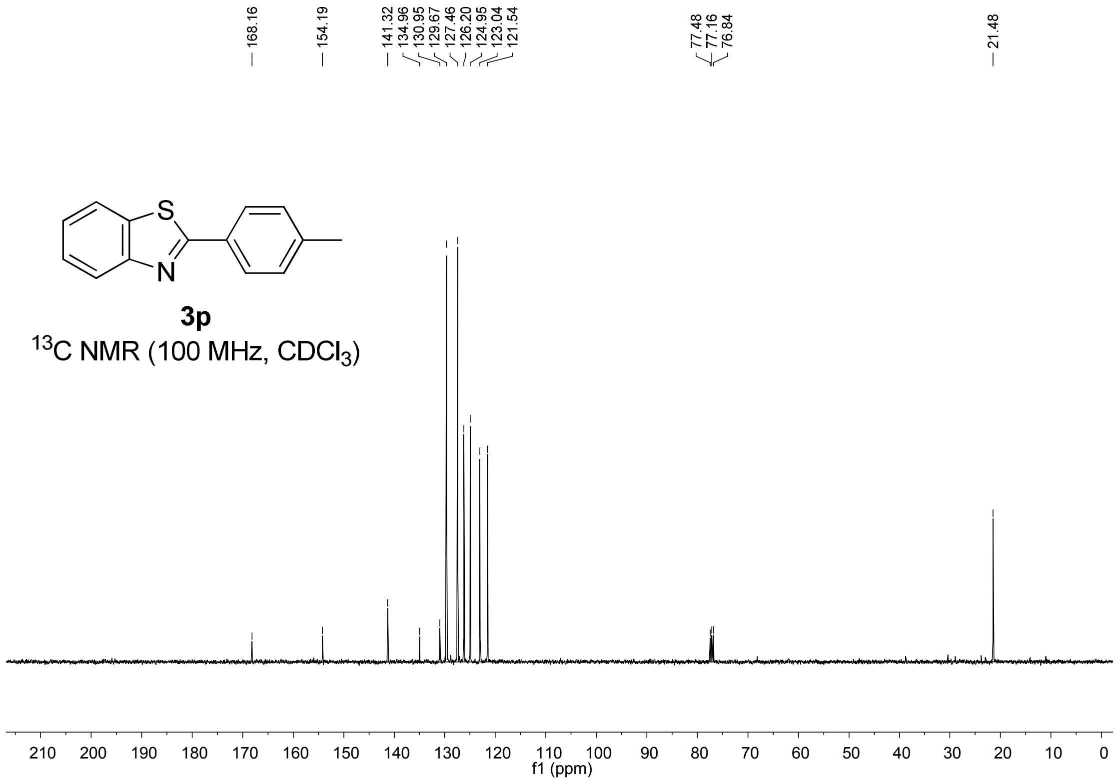
Single Mass Analysis (displaying only valid results)
Tolerance = 5.0 PPM / DBE: min = -200.0, max = 200.0
Selected filters: None

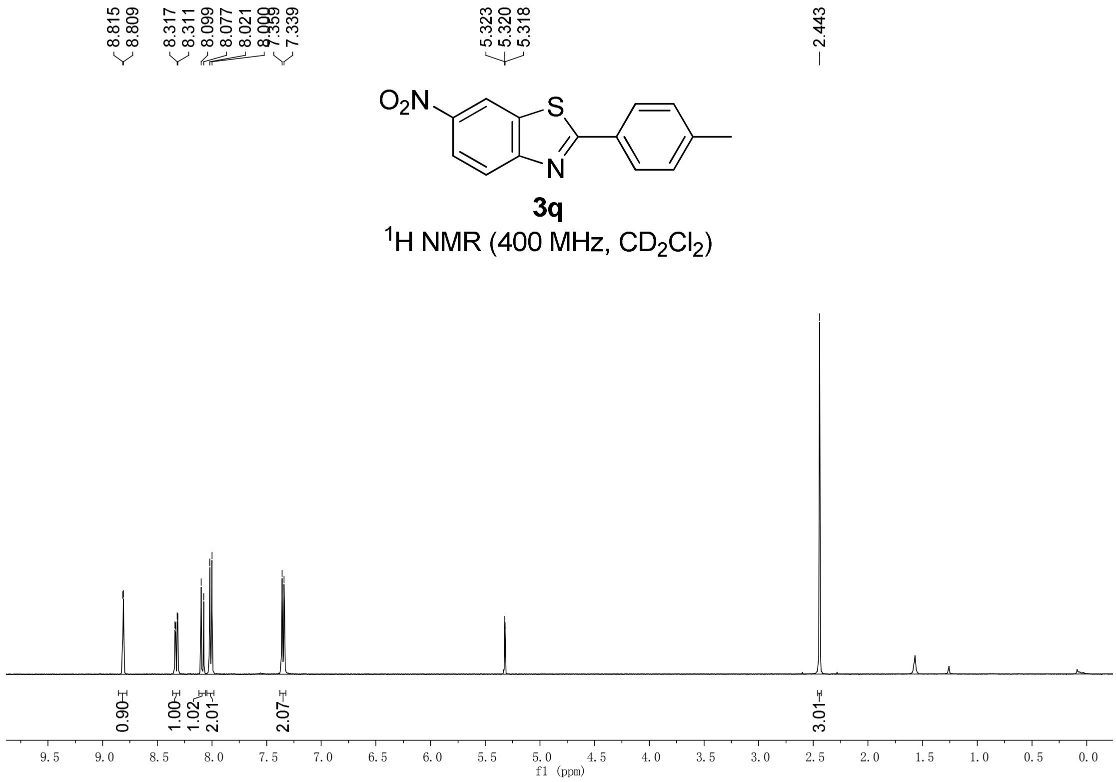
Monoisotopic Mass, Even Electron Ions
13 formula(e) evaluated with 1 results within limits (all results (up to 1000) for each mass)
Elements Used:
C: 0-150 H: 0-150 N: 1-1 O: 2-2 S: 1-1

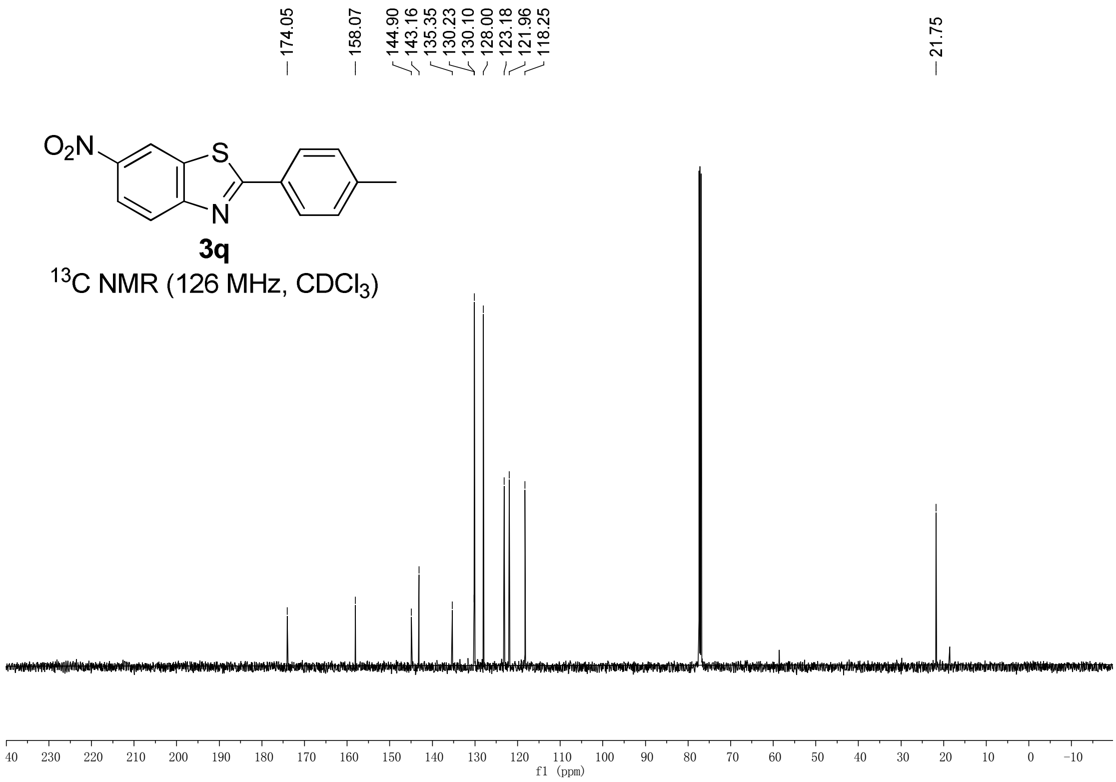


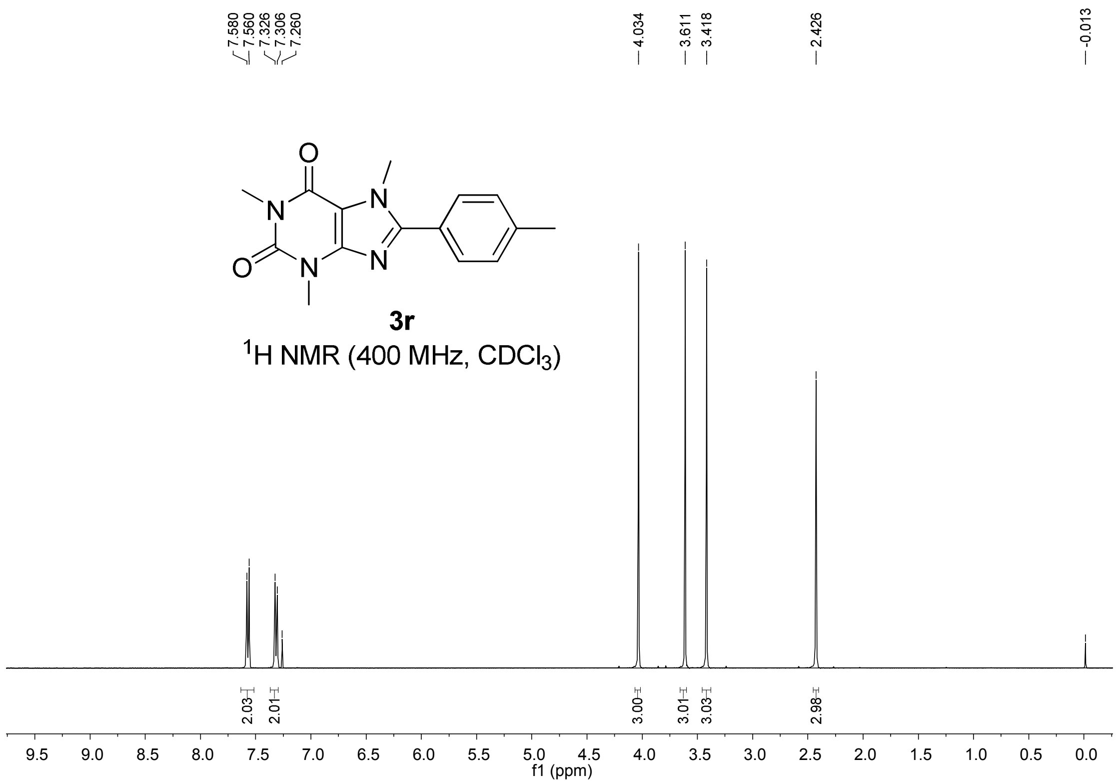
Minimum:				-200.0		
Maximum:		5.0	5.0	200.0		
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Formula
276.1054	276.1058	-0.4	-1.4	7.5	0.5	C15 H18 N O2 S

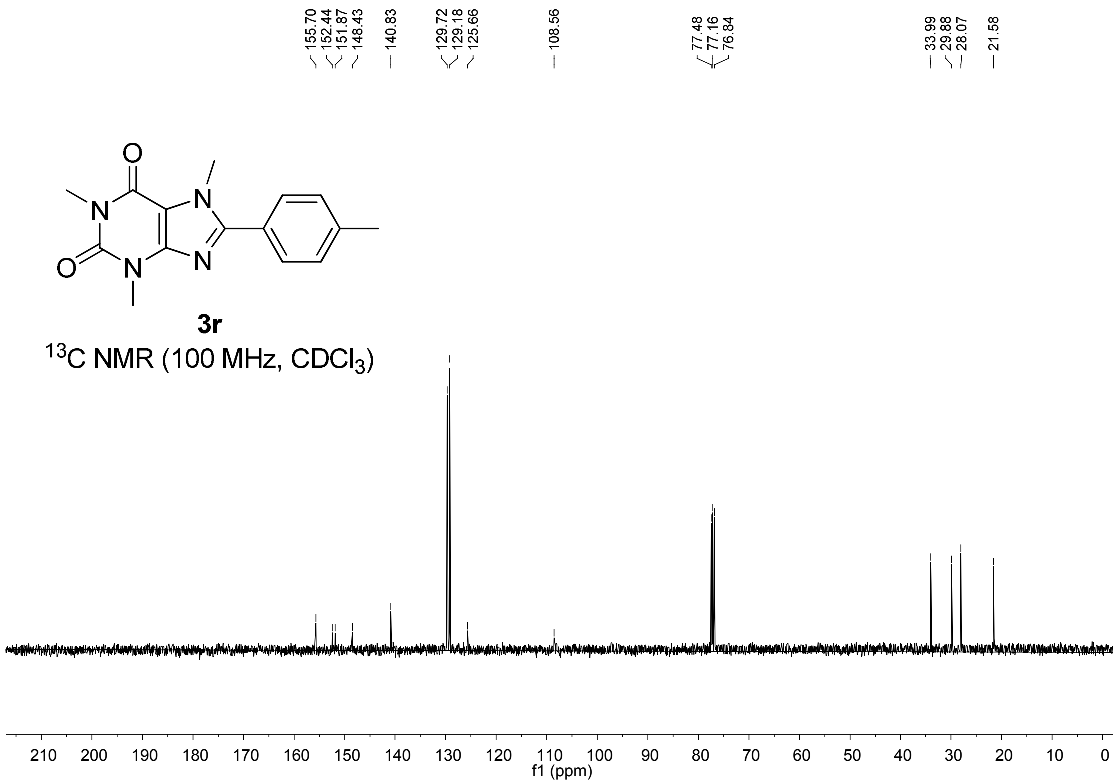

8.077
8.057
8.003
7.984
7.905
7.885
7.505
7.487
7.468
7.392
7.375
7.357
7.312
7.294
7.260
2.431
0.007
S
N
3p
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
1.98
0.99
1.04
1.03
1.96
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

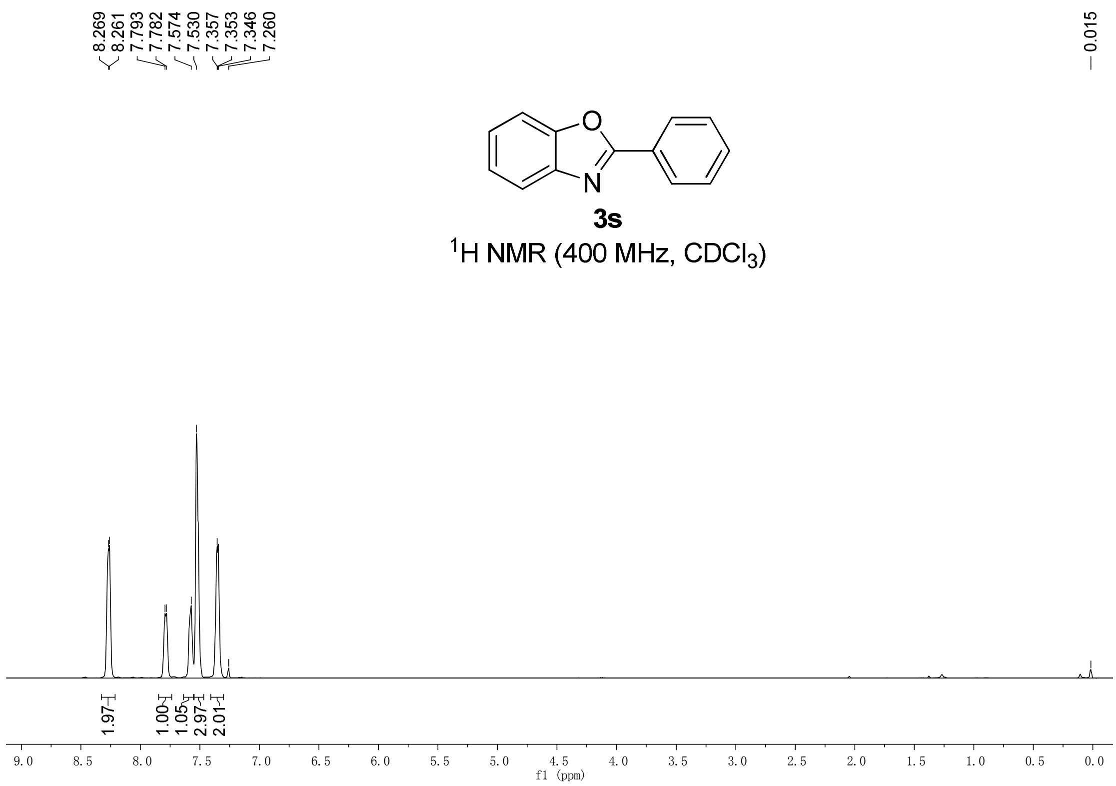

168.16
154.19
141.32
134.96
130.95
129.67
127.46
126.20
124.95
123.04
121.54
77.48
77.16
76.84
21.48
S
N
3p
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

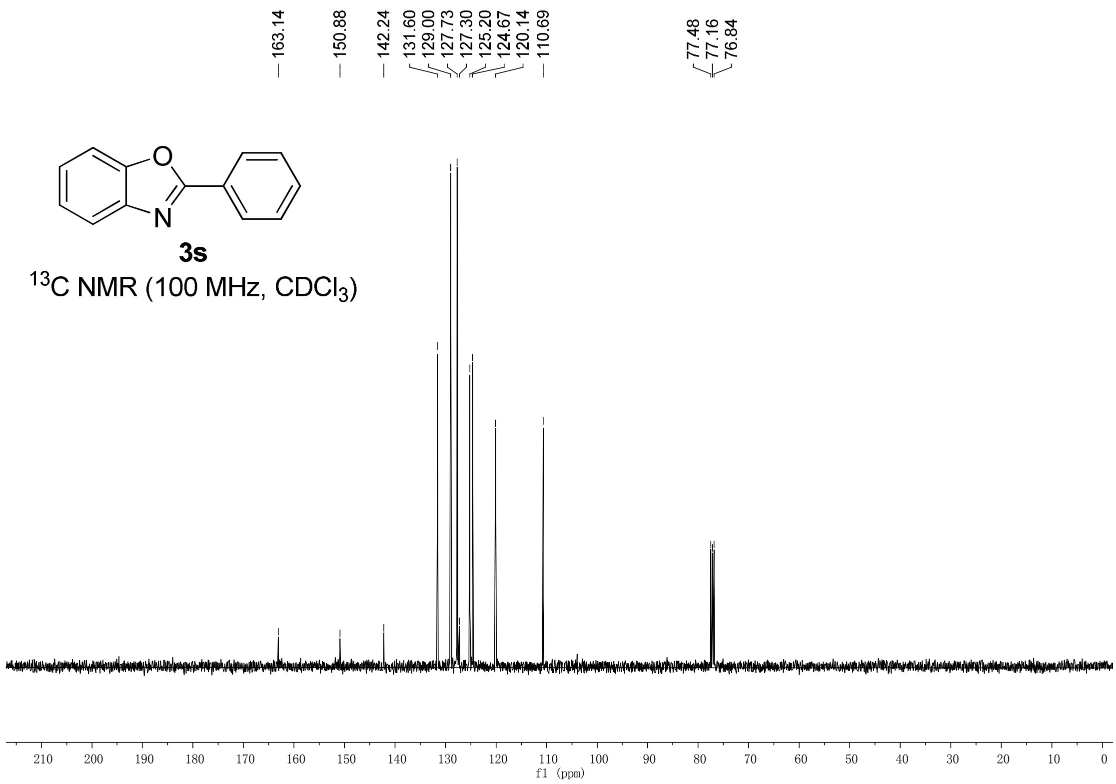

3q
^{1}H NMR (400 MHz, CD_2Cl_2)
f1 (ppm)

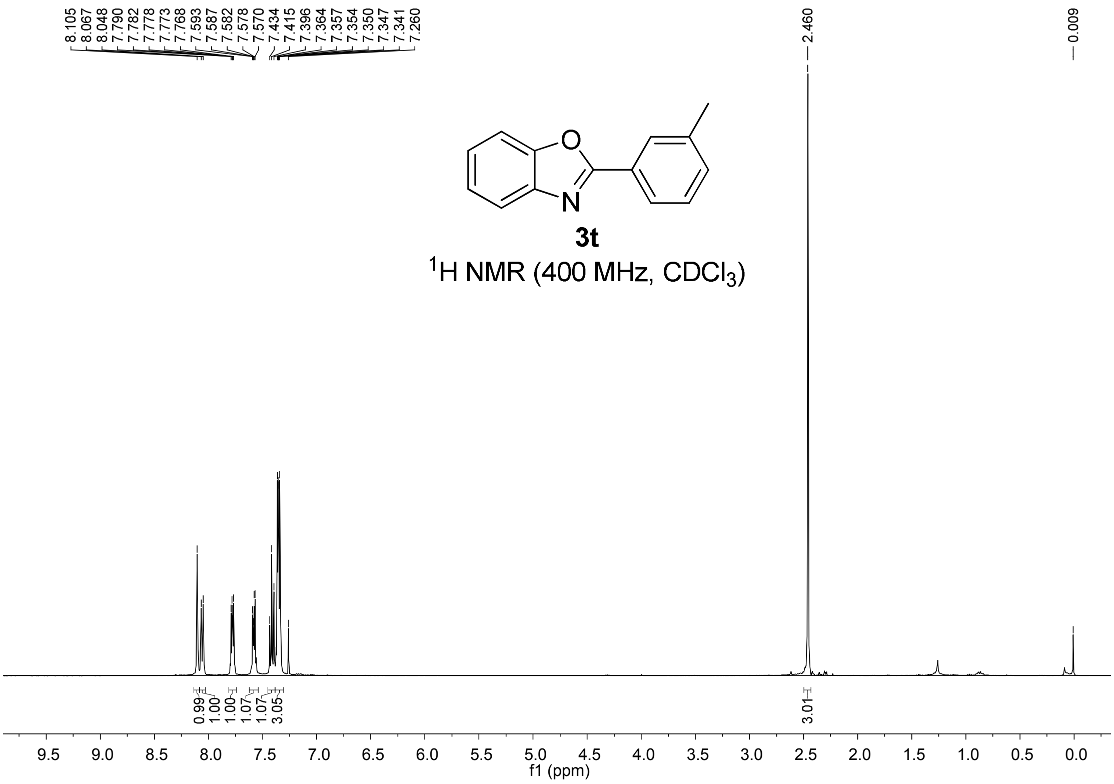

3q
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)

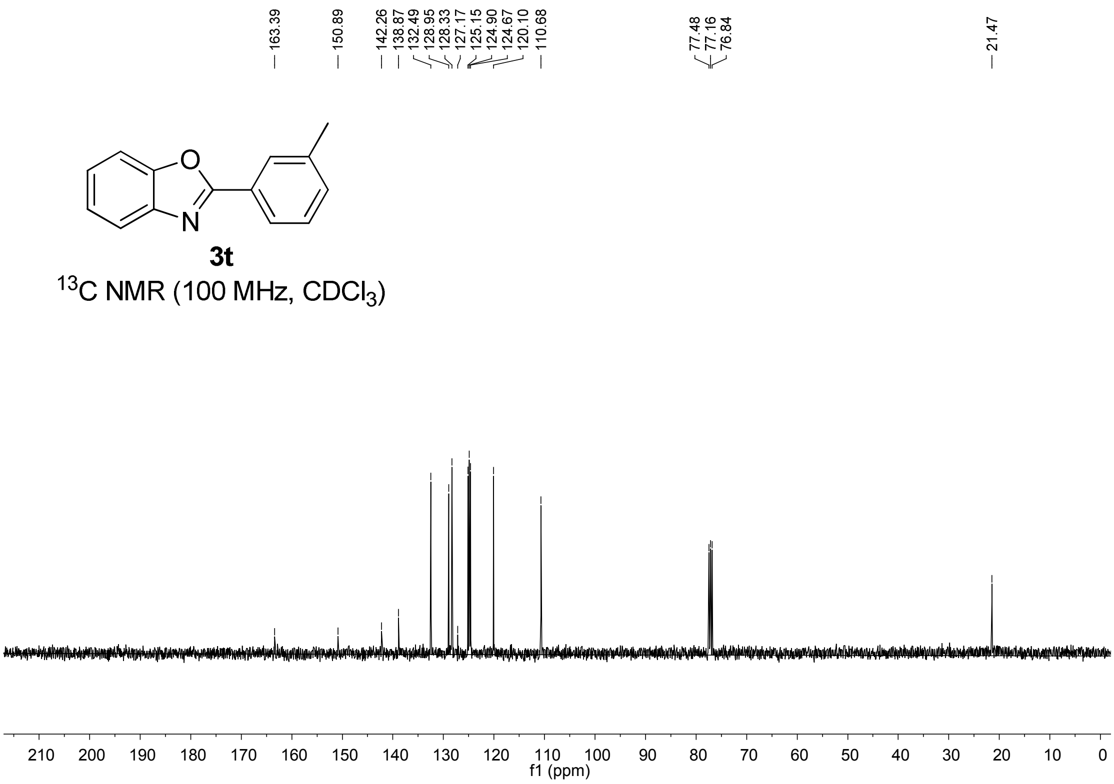

7.580
7.560
7.326
7.306
7.260
4.034
3.611
3.418
2.426
-0.013
3r
1H NMR (400 MHz, CDCl3)
2.03
2.01
3.00
3.01
3.03
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

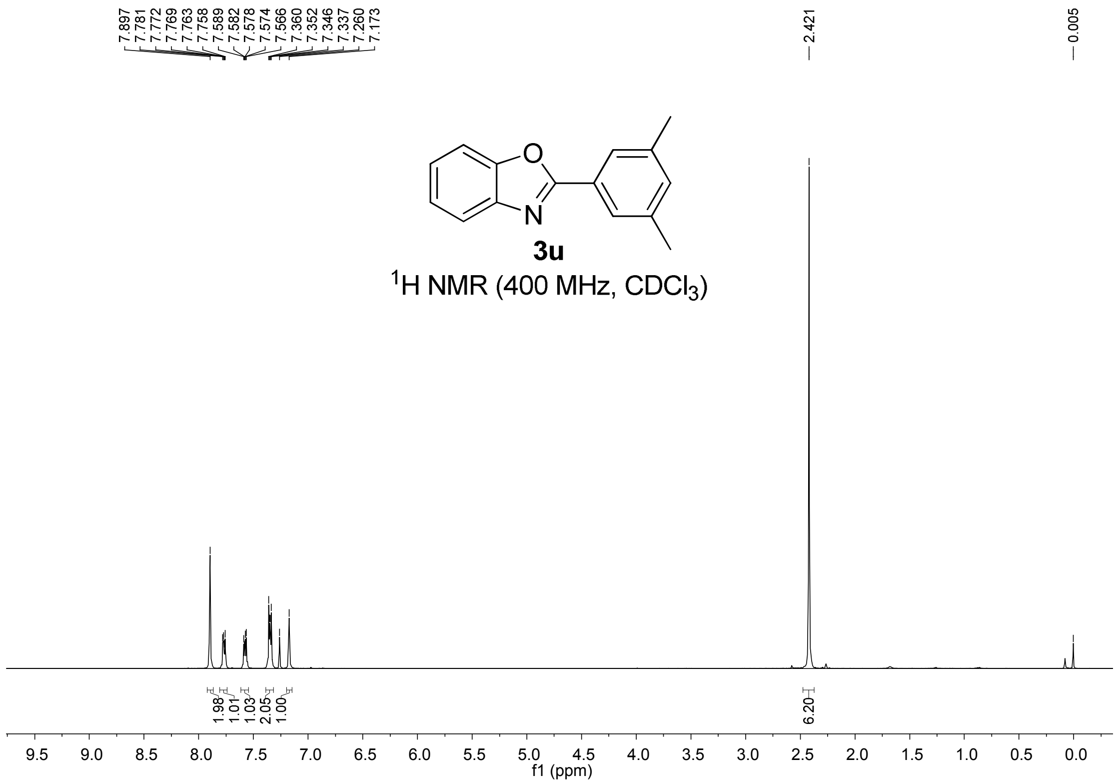

155.70
152.44
151.87
148.43
140.83
129.72
129.18
125.66
108.56
77.48
77.16
76.84
33.99
29.88
28.07
21.58
3r
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

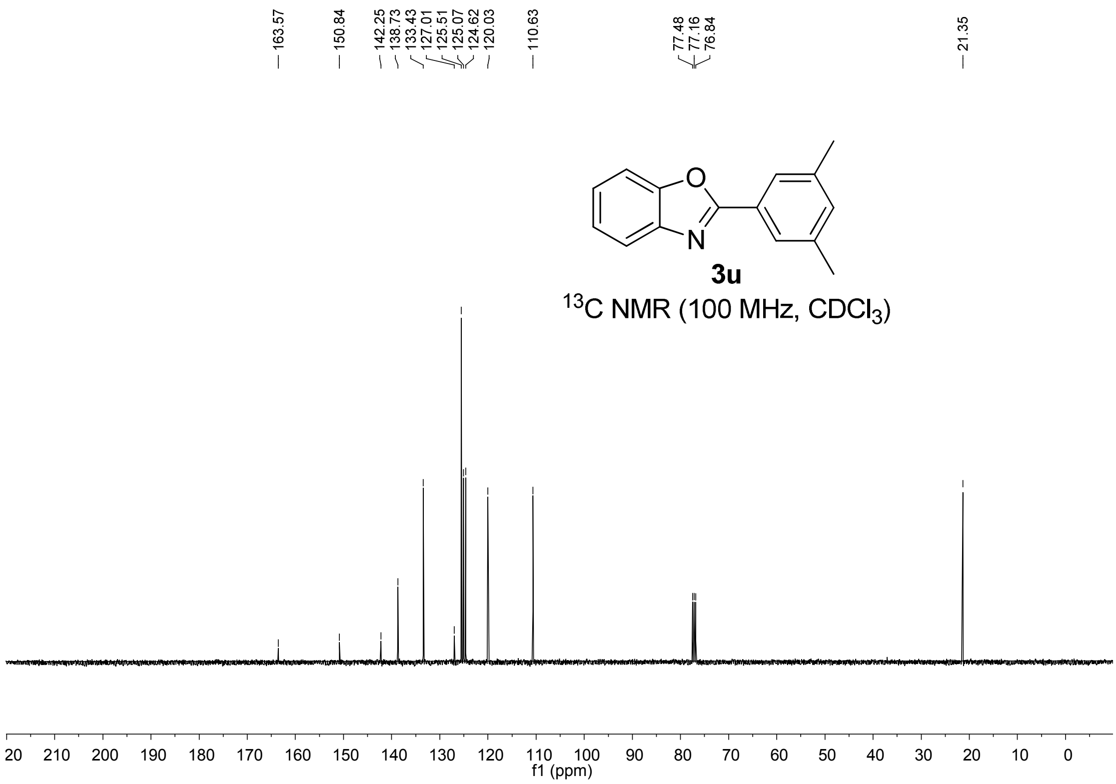

8.269
8.261
7.793
7.782
7.574
7.530
7.357
7.353
7.346
7.260
0.015
O
N
3s
^{1}H NMR (400 MHz, $CDCl_3$)
1.97
1.00
1.05
2.97
2.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


163.14
150.88
142.24
131.60
129.00
127.73
127.30
125.20
124.67
120.14
110.69
77.48
77.16
76.84
O
N
3s
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


8.105
8.067
8.048
7.790
7.782
7.778
7.773
7.768
7.593
7.587
7.582
7.578
7.570
7.434
7.415
7.396
7.364
7.357
7.354
7.350
7.347
7.341
7.260
2.460
0.009
O
N
3t
^{1}H NMR (400 MHz, $CDCl_3$)
0.99
1.00
1.00
1.07
1.07
3.05
3.01
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)


163.39
150.89
142.26
138.87
132.49
128.95
128.33
127.17
125.15
124.90
124.67
120.10
110.68
77.48
77.16
76.84
21.47
O
N
3t
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


7.897
7.781
7.772
7.769
7.763
7.758
7.589
7.582
7.578
7.574
7.566
7.360
7.352
7.346
7.337
7.260
7.173
2.421
0.005
O
N
3u
^{1}H NMR (400 MHz, CDCl$_3$)
1.98
1.01
1.03
2.05
1.00
6.20
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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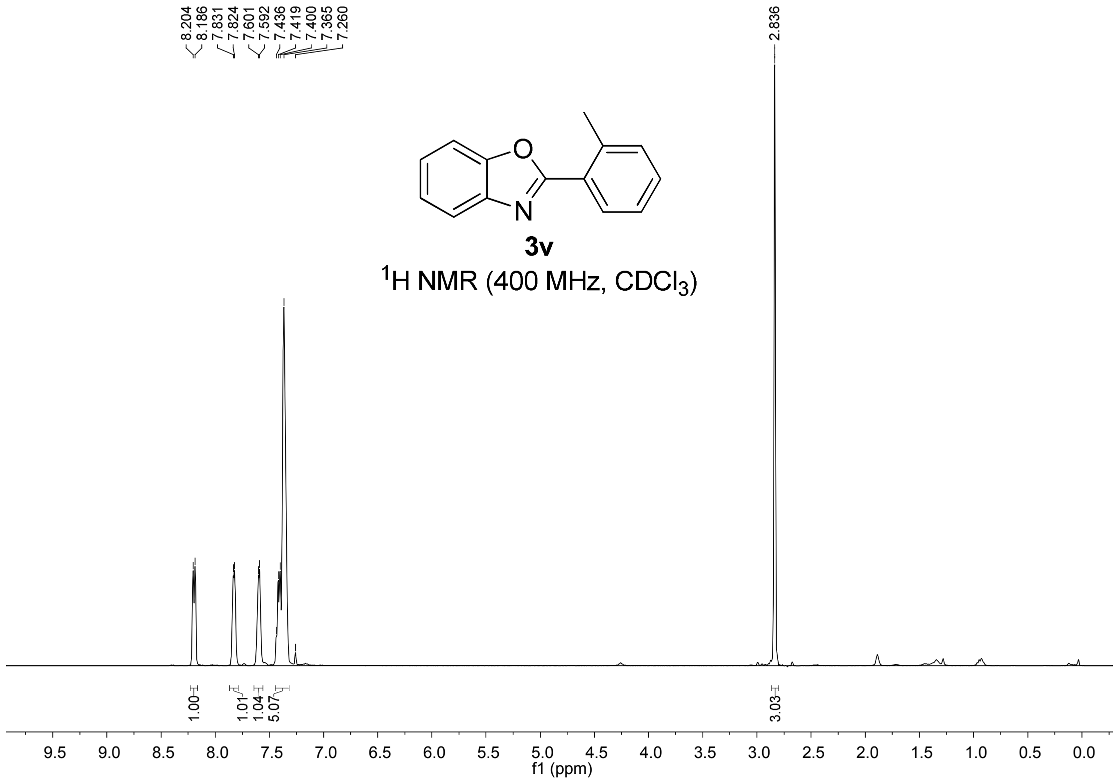
142.25
138.73
133.43
127.01
125.51
125.07
124.62
120.03
110.63
77.48
77.16
76.84
21.35
O
N
3u
^{13}C NMR (100 MHz, CDCl$_3$)
20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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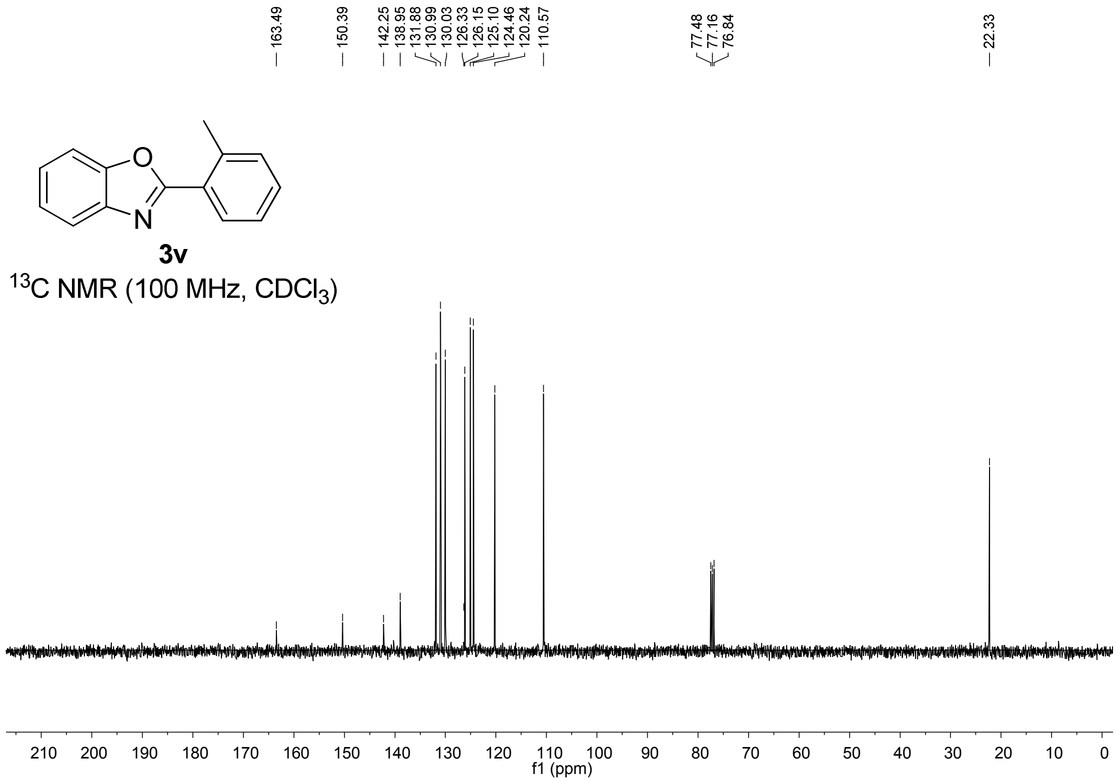
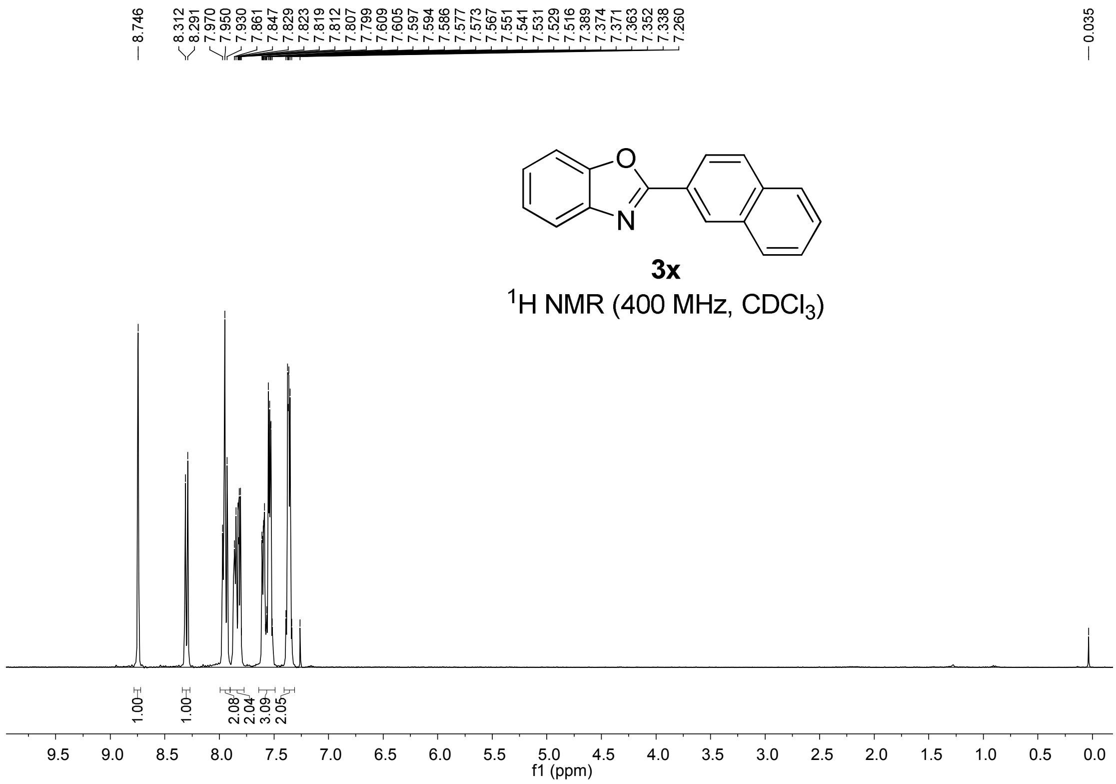
8.186
7.831
7.824
7.601
7.592
7.436
7.419
7.400
7.365
7.260
2.836
O
N
3v
1H NMR (400 MHz, CDCl3)
1.00
1.01
1.04
5.07
3.03
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


163.49
150.39
142.25
138.95
131.88
130.99
130.03
126.33
126.15
125.10
124.46
120.24
110.57
77.48
77.16
76.84
22.33
O
N
3v
13C NMR (100 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.970
7.950
7.930
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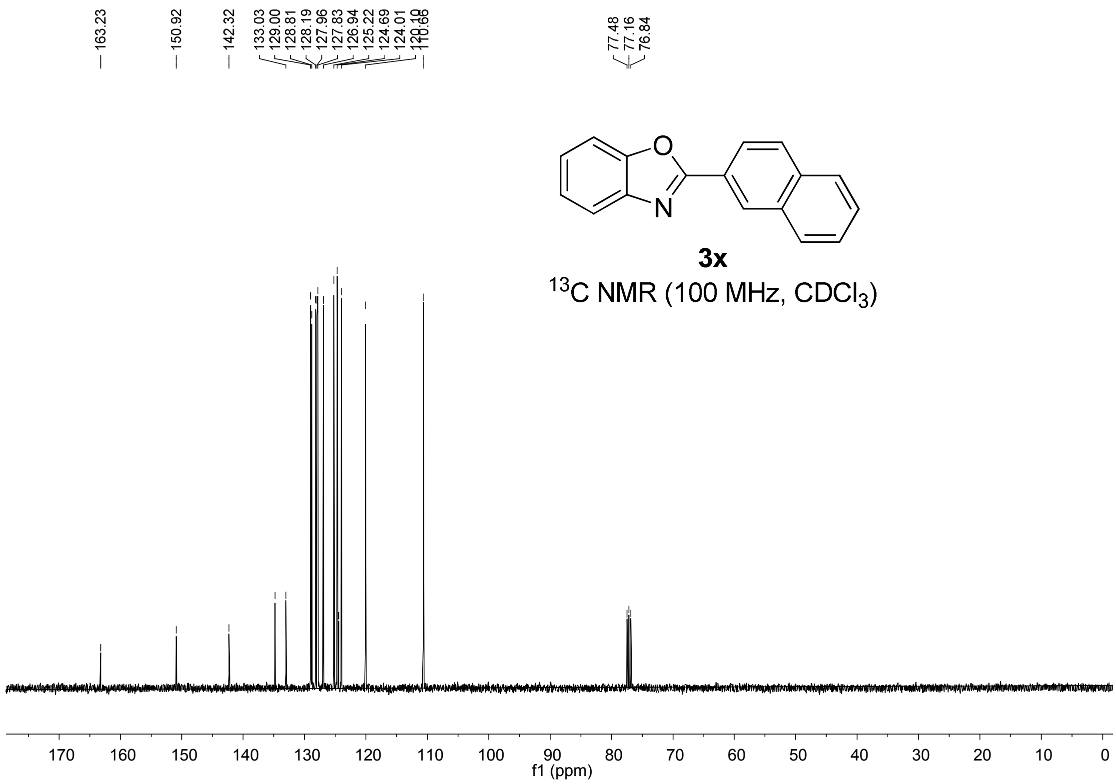
7.847
7.829
7.823
7.819
7.812
7.807
7.799
7.609
7.605
7.597
7.594
7.586
7.577
7.573
7.567
7.551
7.541
7.531
7.529
7.516
7.389
7.374
7.371
7.363
7.352
7.338
7.260
0.035
O
N
3x
1H NMR (400 MHz, CDCl3)
1.00
1.00
2.08
2.04
3.09
2.05
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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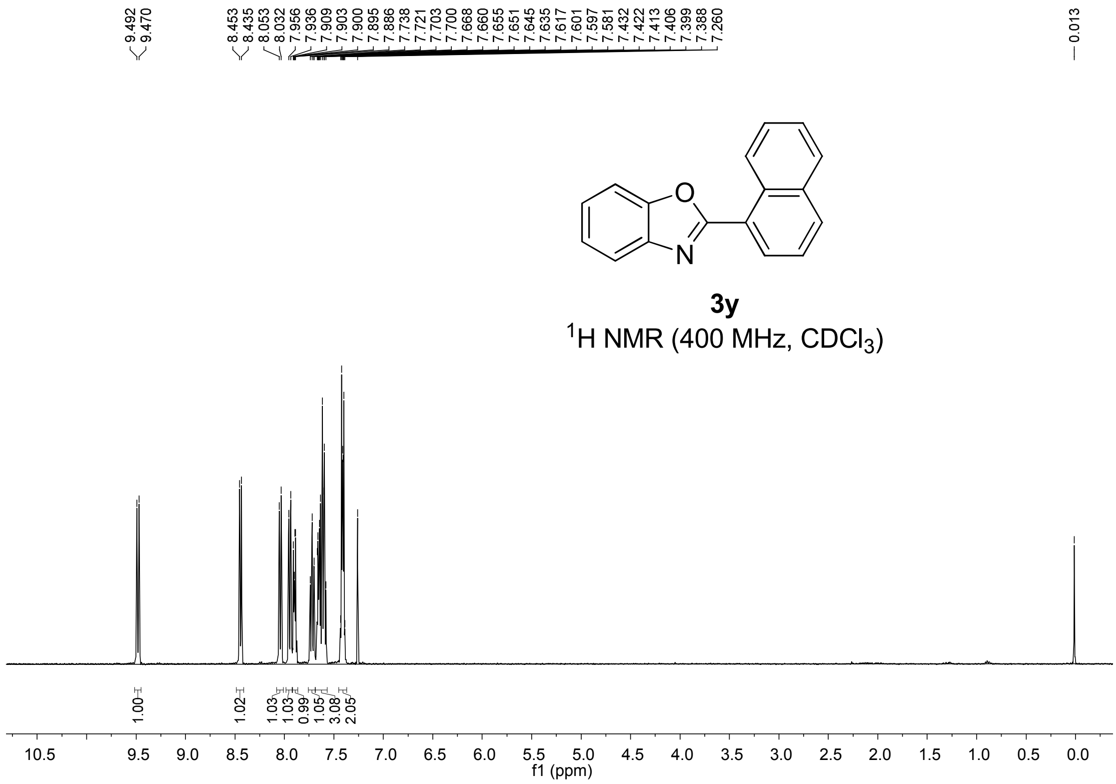
133.03
129.00
128.81
128.19
127.96
127.83
126.94
125.22
124.69
124.01
120.10
110.66
77.48
77.16
76.84
O
N
3x
13C NMR (100 MHz, CDCl3)
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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9.470
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8.435
8.053
8.032
7.956
7.936
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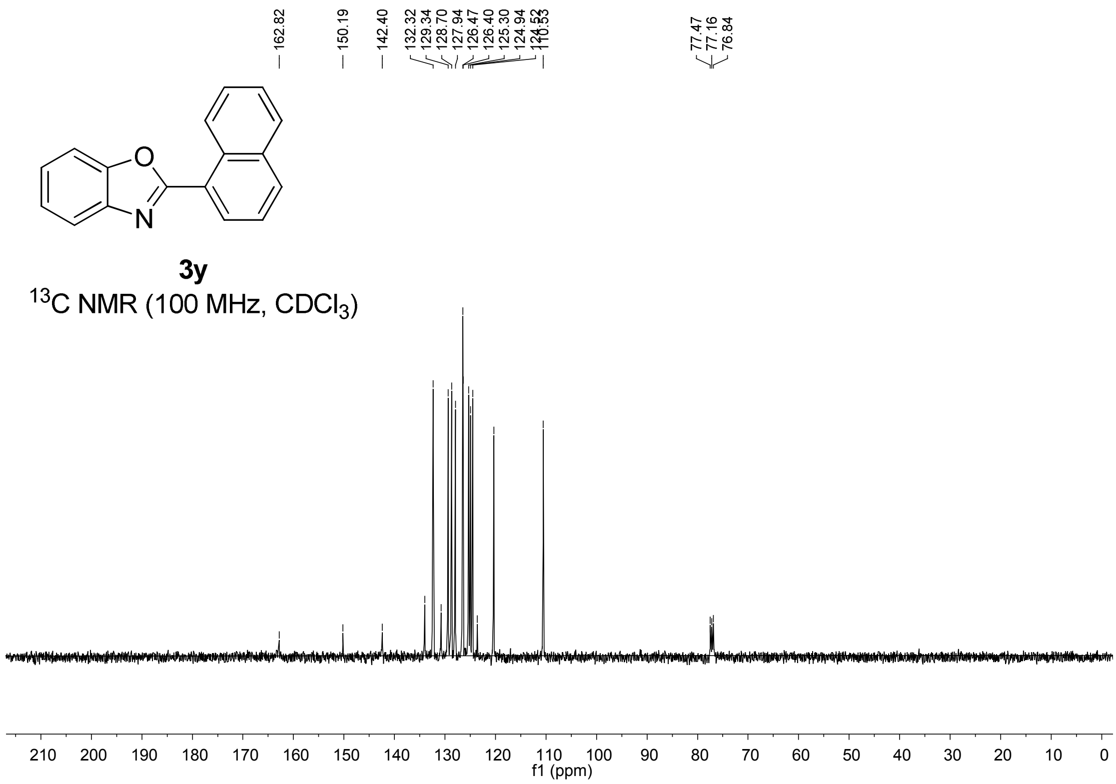
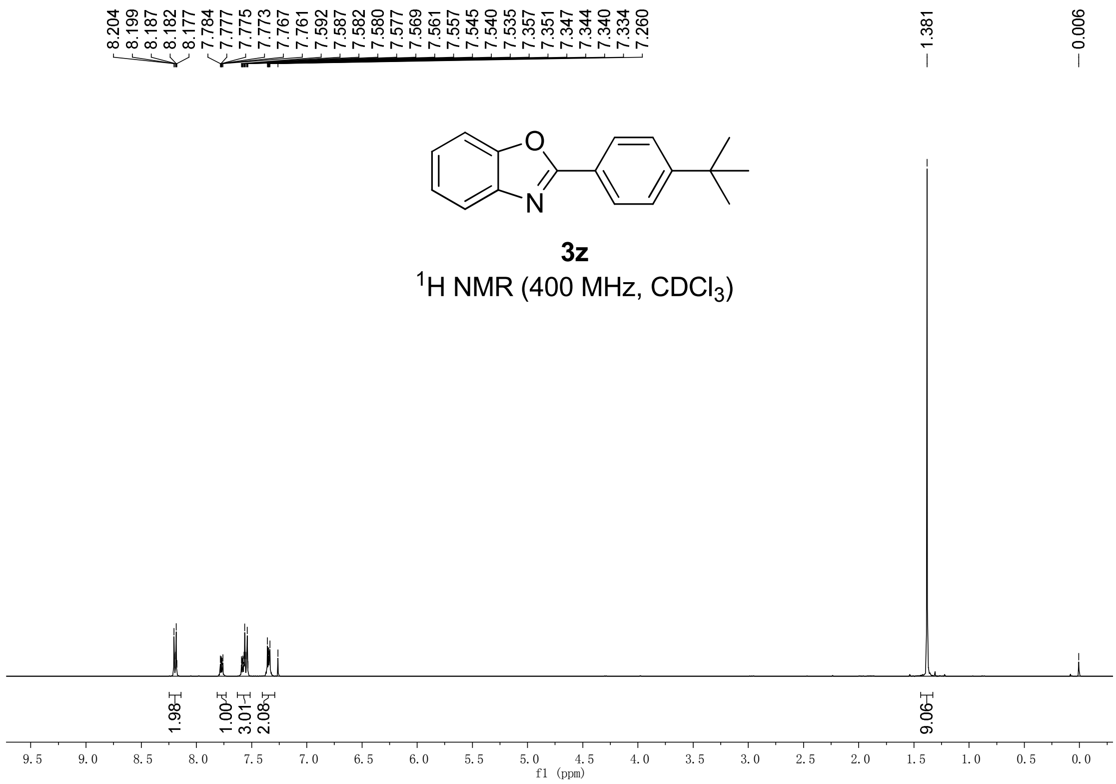
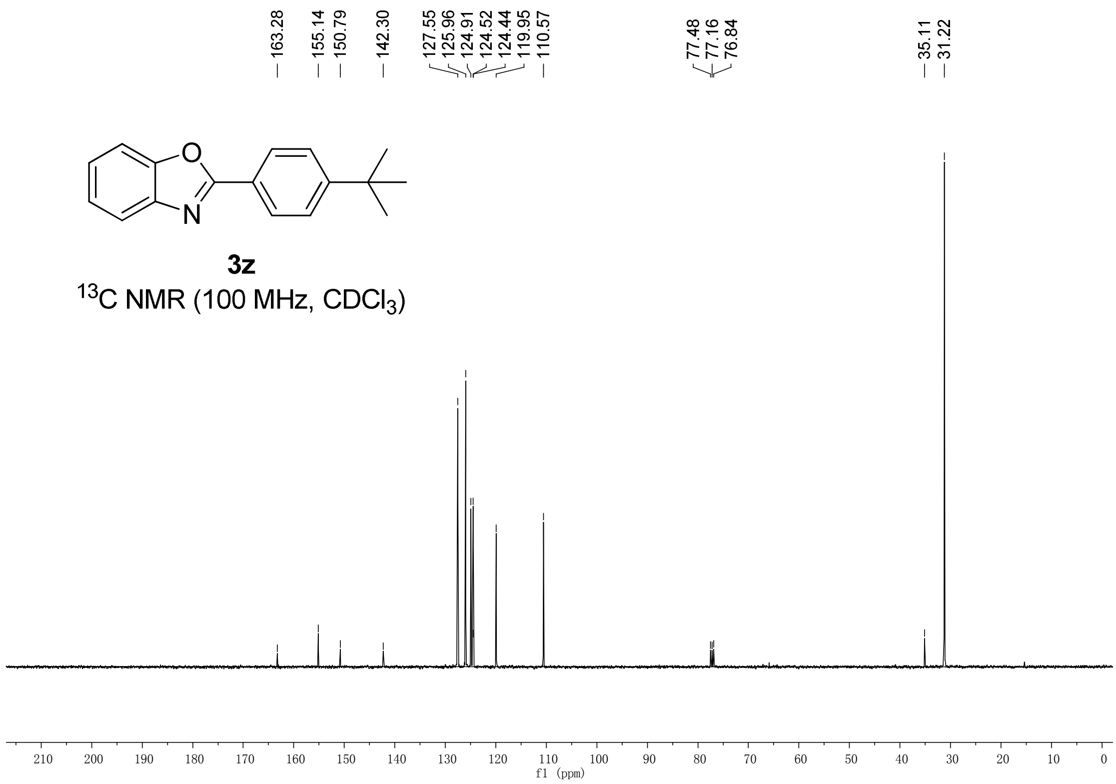
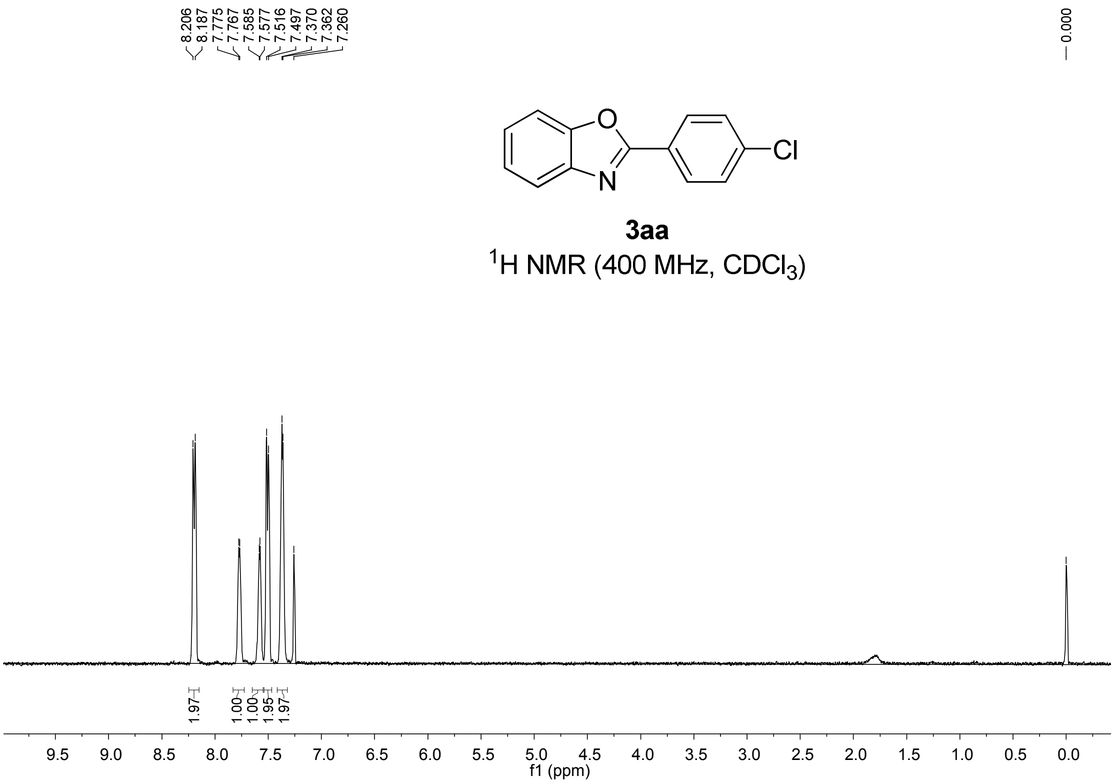
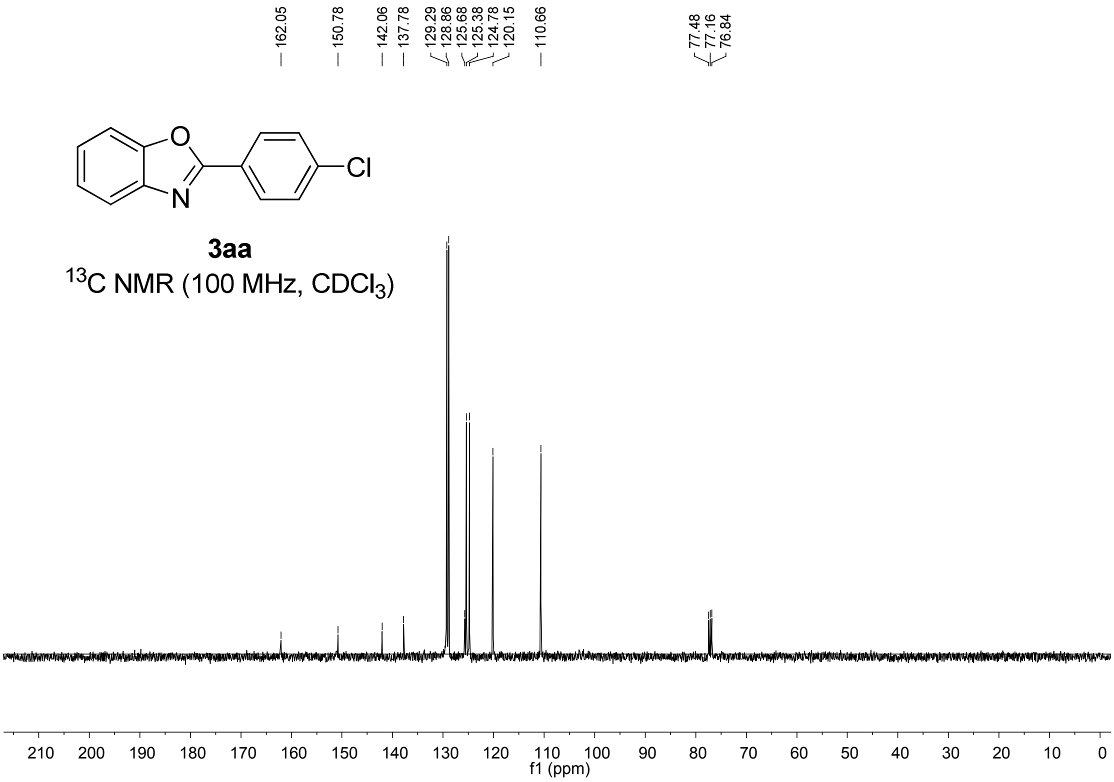
7.903
7.900
7.895
7.886
7.738
7.721
7.703
7.700
7.668
7.660
7.655
7.651
7.645
7.635
7.617
7.601
7.597
7.581
7.432
7.422
7.413
7.406
7.399
7.388
7.260
0.013
O
N
3y
1H NMR (400 MHz, CDCl3)
1.00
1.02
1.03
1.03
0.99
1.05
3.08
2.05
f1 (ppm)

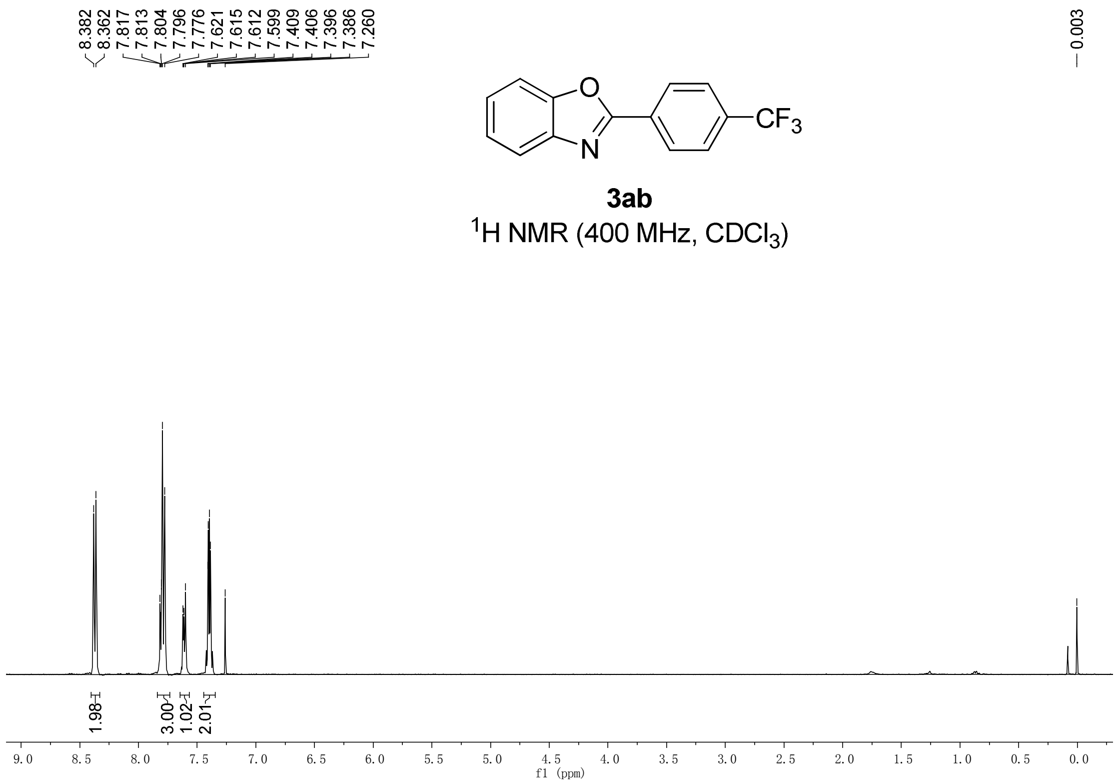

162.82
150.19
142.40
132.32
129.34
128.70
127.94
126.47
126.40
125.30
124.94
124.52
110.53
77.47
77.16
76.84
O
N
3y
13C NMR (100 MHz, CDCl3)
f1 (ppm)

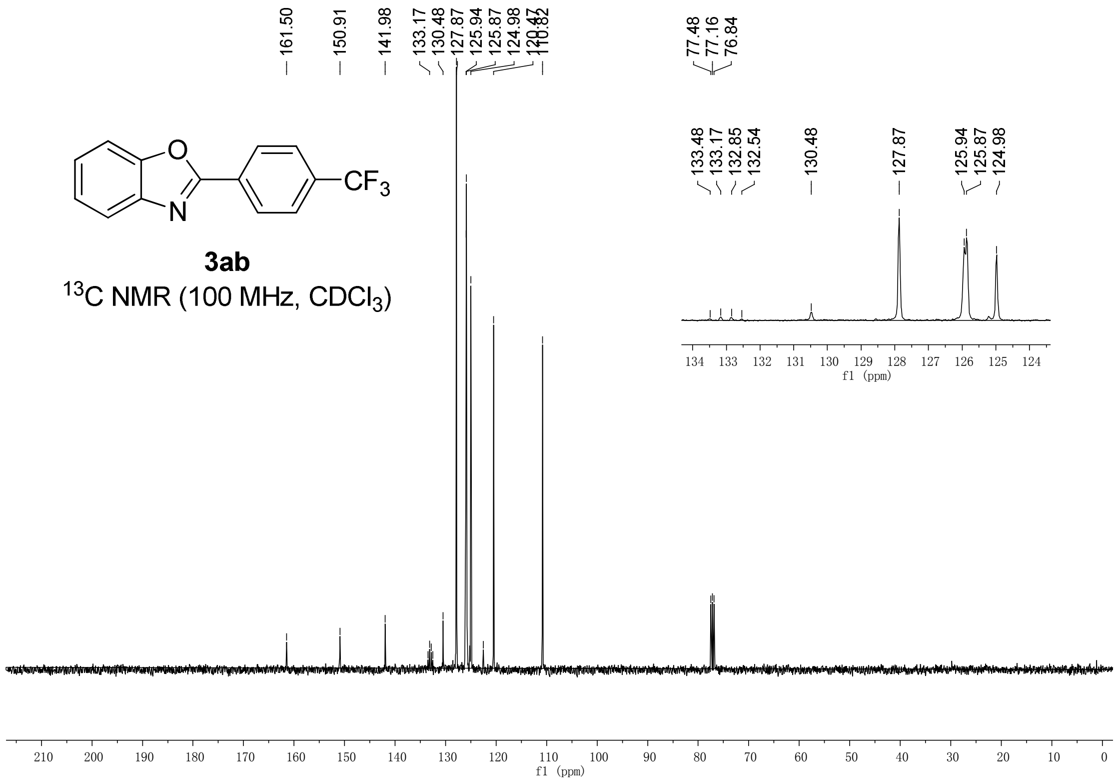

3z
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

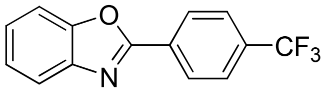

3z
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


8.206
8.187
7.775
7.767
7.585
7.577
7.516
7.497
7.370
7.362
7.260
0.000
O
N
Cl
3aa
^{1}H NMR (400 MHz, $CDCl_3$)
1.97
1.00
1.00
1.95
1.97
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)


162.05
150.78
142.06
137.78
129.29
128.86
125.68
125.38
124.78
120.15
110.66
77.48
77.16
76.84
O
N
Cl
3aa
^{13}C NMR (100 MHz, $CDCl_3$)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

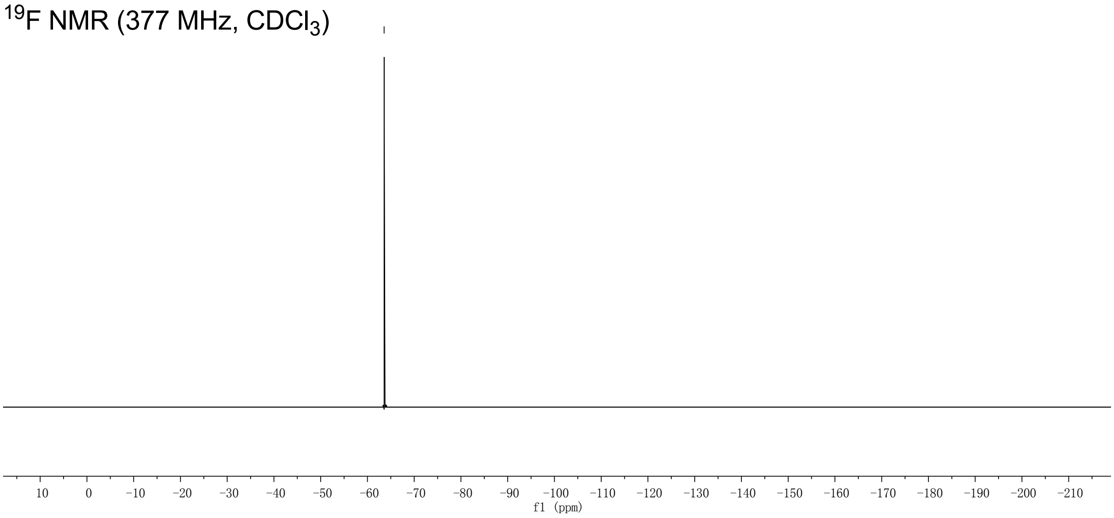

8.382
8.362
7.817
7.813
7.804
7.796
7.776
7.621
7.615
7.612
7.599
7.409
7.406
7.396
7.386
7.260
0.003
CF3
O
N
3ab
1H NMR (400 MHz, CDCl3)
1.98
3.00
1.02
2.01
f1 (ppm)

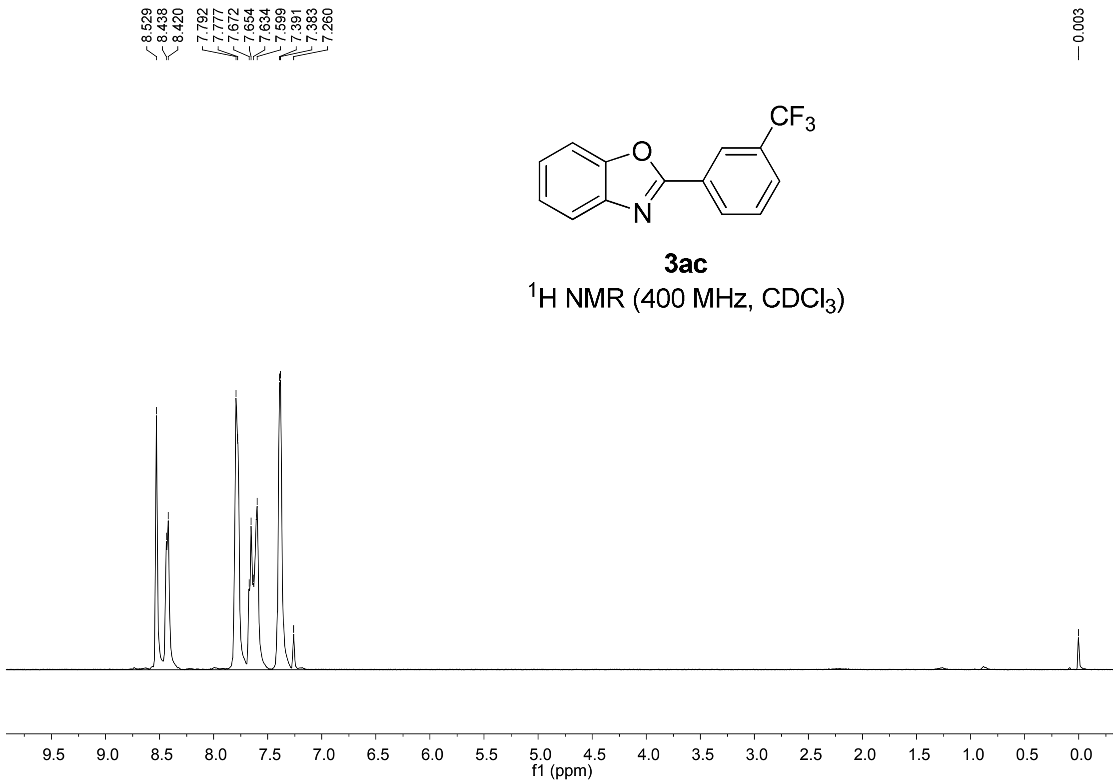

161.50
150.91
141.98
133.17
130.48
127.87
125.94
125.87
124.98
120.47
110.82
77.48
77.16
76.84
133.48
133.17
132.85
132.54
130.48
127.87
125.94
125.87
124.98
CF3
O
N
3ab
13C NMR (100 MHz, CDCl3)
f1 (ppm)

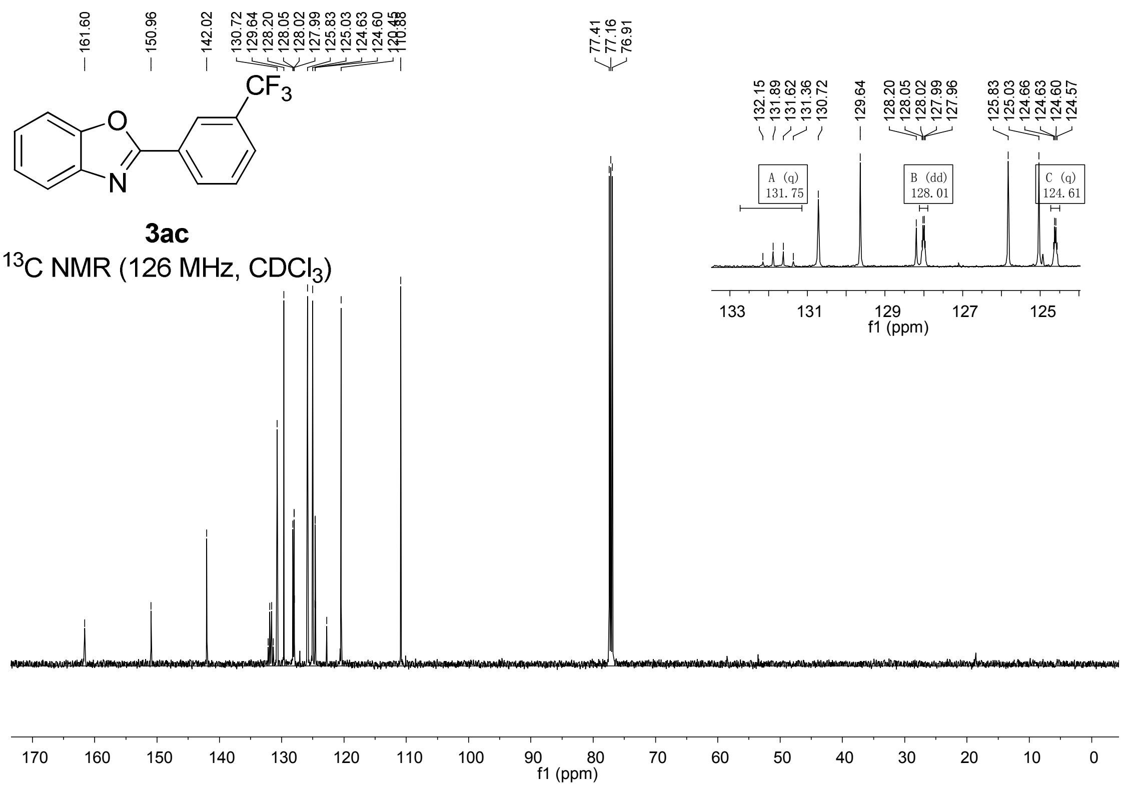


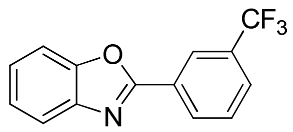
3ab

^{19}F NMR (377 MHz, $CDCl_3$)



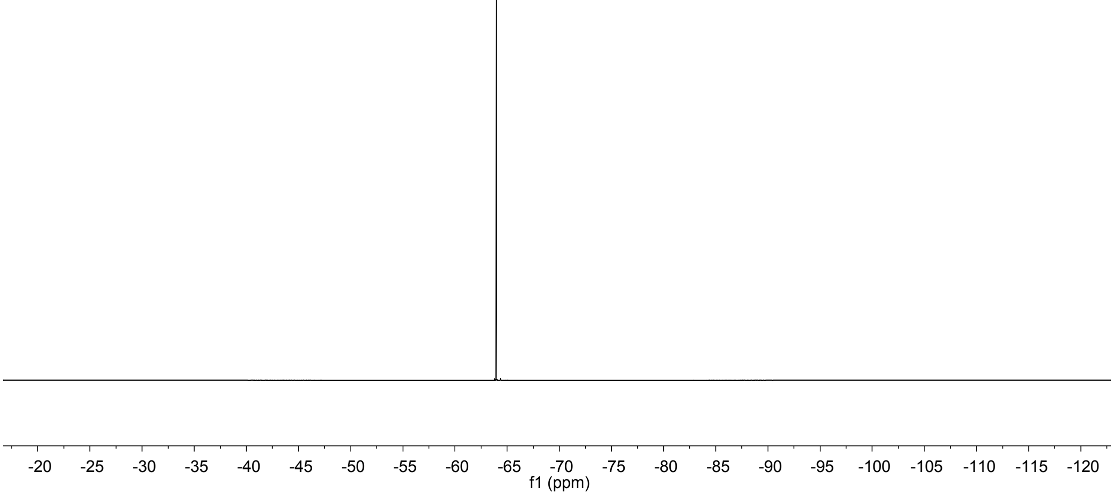

8.529
8.438
8.420
7.792
7.777
7.672
7.654
7.634
7.599
7.391
7.383
7.260
0.003
CF3
O
N
3ac
1H NMR (400 MHz, CDCl3)
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

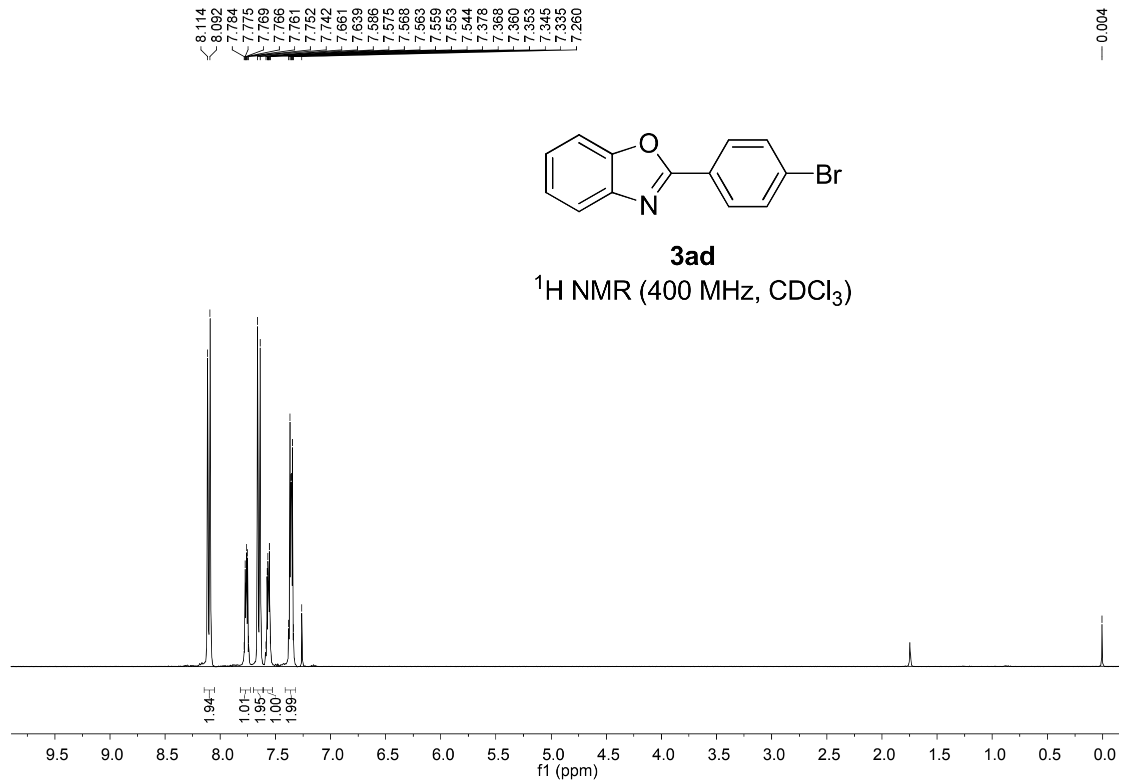

161.60
150.96
142.02
130.72
129.64
128.20
128.05
128.02
127.99
125.83
125.03
124.63
124.60
120.45
110.88
77.41
77.16
76.91
CF3
O
N
3ac
13C NMR (126 MHz, CDCl3)
132.15
131.89
131.62
131.36
130.72
129.64
128.20
128.05
128.02
127.99
127.96
125.83
125.03
124.66
124.63
124.60
124.57
A (q)
131.75
B (dd)
128.01
C (q)
124.61
133 131 129 127 125
f1 (ppm)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

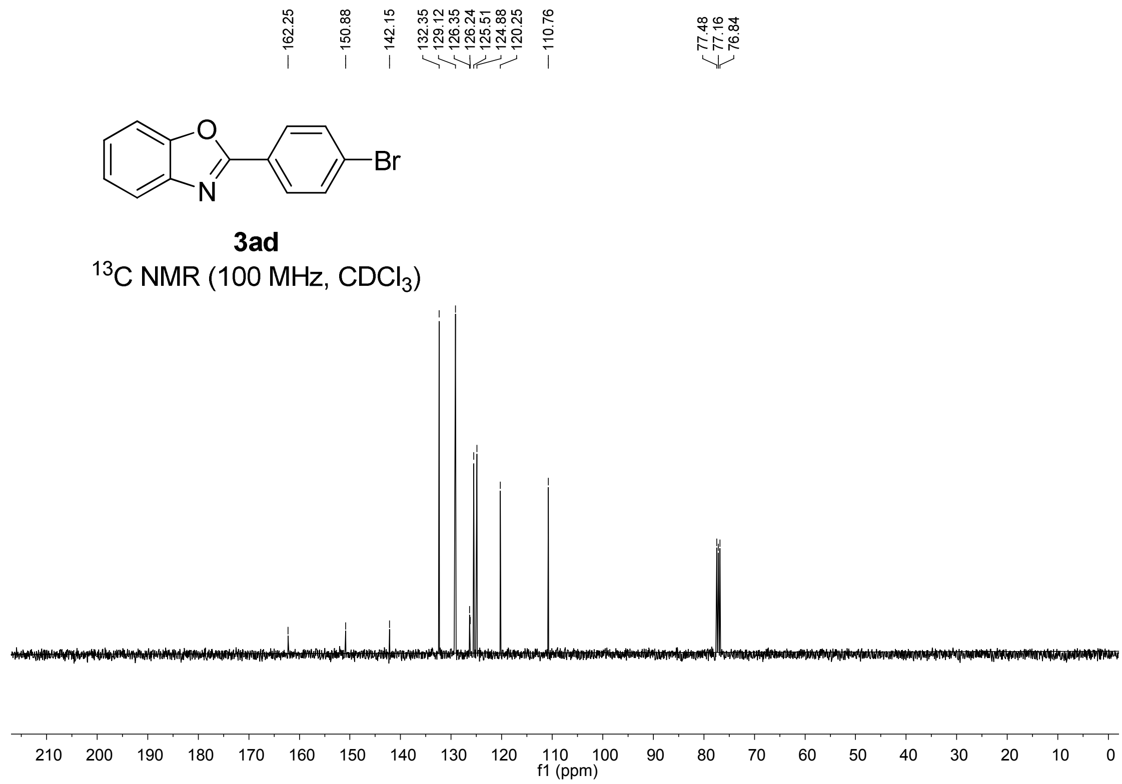


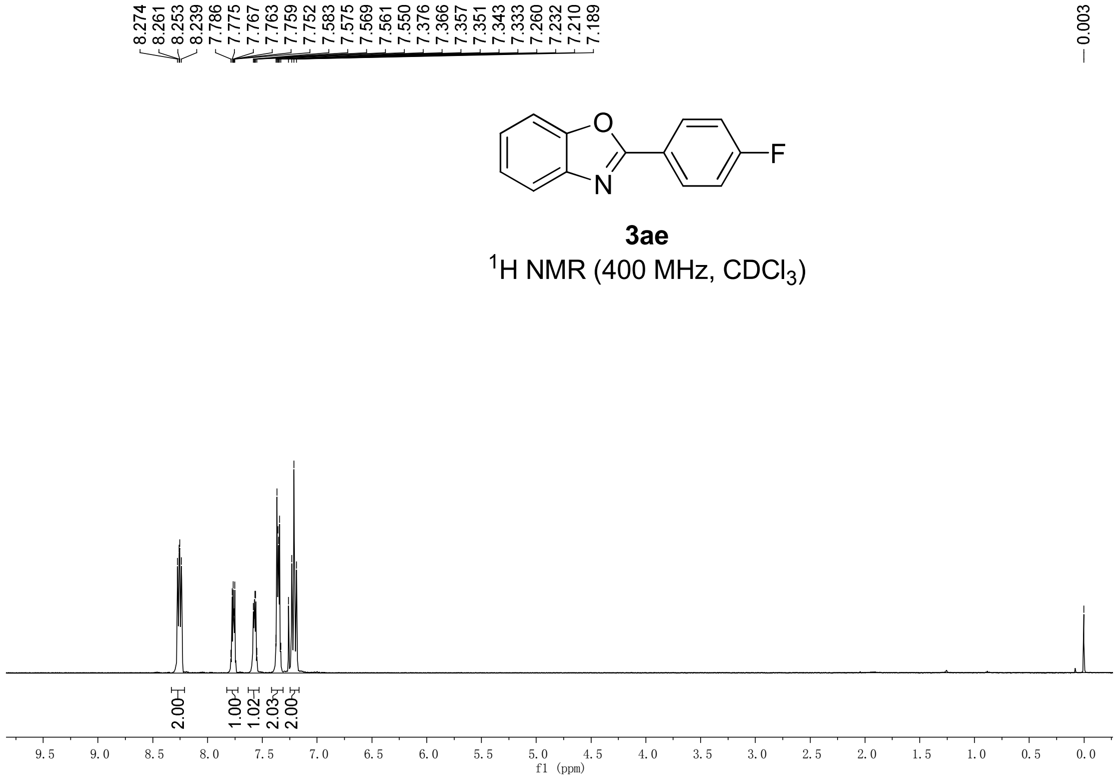
3ac

^{19}F NMR (471 MHz, $CDCl_3$)



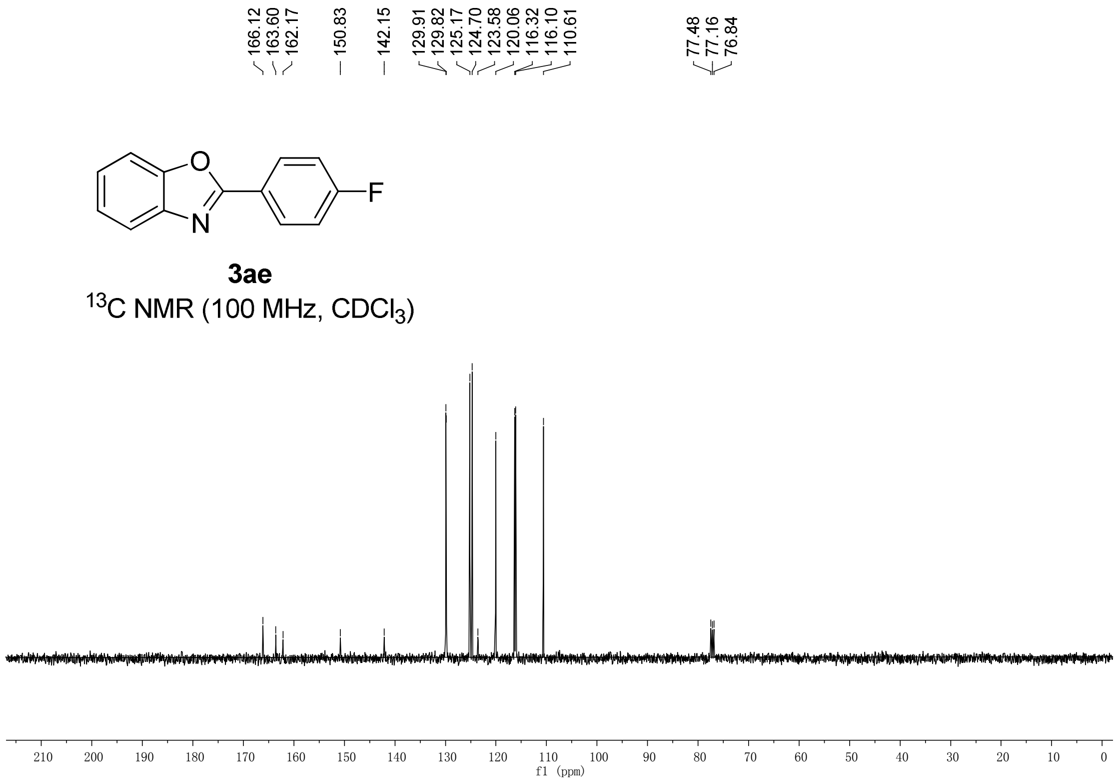

8.114
8.092
7.784
7.775
7.769
7.766
7.761
7.752
7.742
7.661
7.639
7.586
7.575
7.568
7.563
7.559
7.553
7.544
7.378
7.368
7.360
7.353
7.345
7.335
7.260
0.004
O
N
Br
3ad
^{1}H NMR (400 MHz, $CDCl_3$)
1.94
1.01
1.95
1.00
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


162.25
150.88
142.15
132.35
129.12
126.35
126.24
125.51
124.88
120.25
110.76
77.48
77.16
76.84
O
N
Br
3ad
^{13}C NMR (100 MHz, $CDCl_3$)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



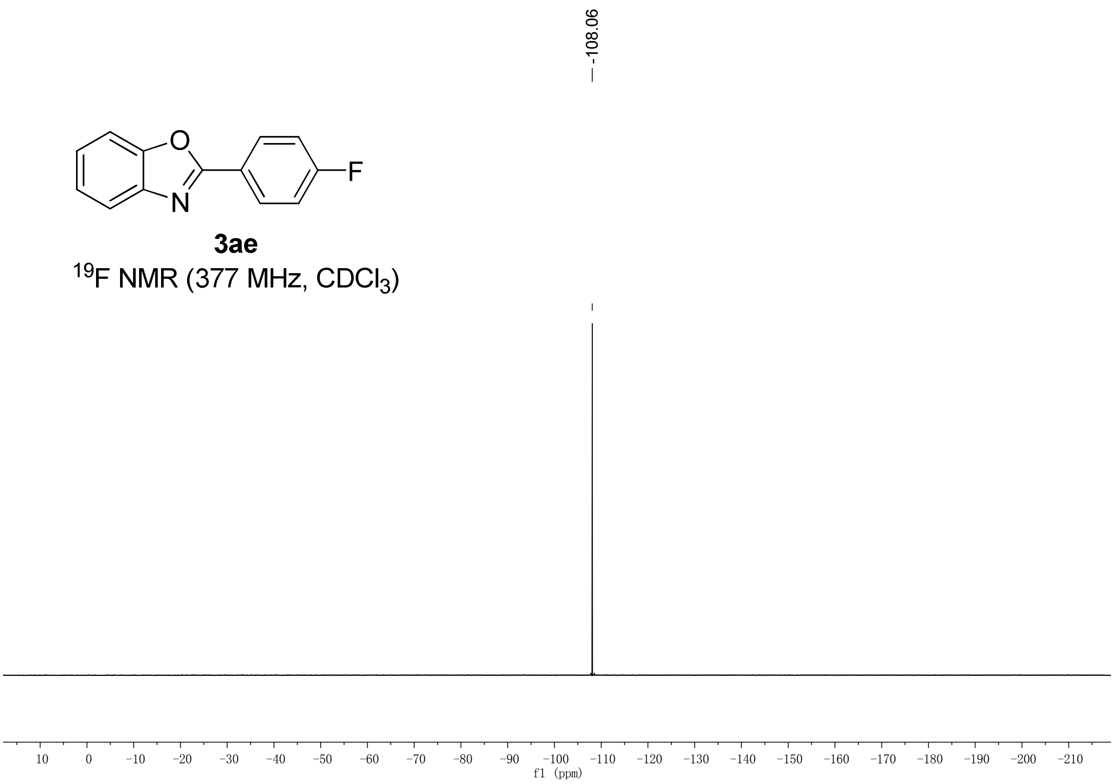
3ae

^{1}H NMR (400 MHz, $CDCl_3$)



3ae

^{13}C NMR (100 MHz, $CDCl_3$)


-108.06
O
N
F
3ae
19F NMR (377 MHz, CDCl3)
10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
f1 (ppm)