

Electronic Supporting Information

Palladium-Catalyzed Desulfitative Arylation of Azoles with Arylsulfonyl Hydrazides

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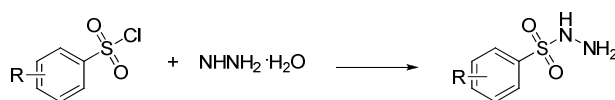
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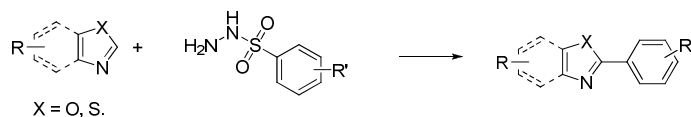
General.

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 CDCl₃ on 400 MHz Bruker DRX-400 or 500 MHz Bruker DRX-500 NMR spectrometers. The chemical shifts for ¹H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.26 ppm for CDCl₃). The chemical shifts for ¹³C NMR were recorded in ppm downfield using the central peak of CDCl₃ (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.



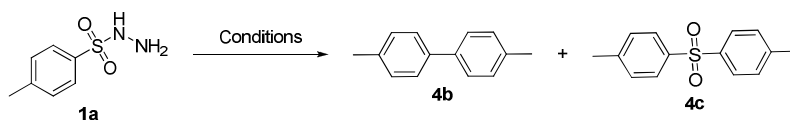
Preparation of Arylsulfonyl Hydrazides. Arylsulfonyl hydrazides were prepared according to a literature procedure.^[1] Hydrazine monohydrate (80%) (275 mg, 4.4 mmol) was added water (260 mg) and was cooled to 0 °C. To this solution was added dropwise a solution of arylsulfonyl chloride (2.0 mmol) in 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(CH₃CN)₂Cl₂ (6.5 mg, 0.025 mmol), phenanthroline hydrate (6 mg, 0.03 mmol), Na₂CO₃ (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 N₂. The reaction mixture was stirred for 5 min. at room temperature, and then stirred at 100 °C 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 TsNHNH₂^a



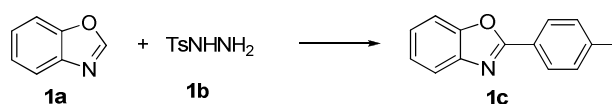
Entry	Catalyst	Oxidant	Yield ^b	
			4b	4c
1	---	Cu(OAc) ₂ (4 equiv.)	13%	25%
2	Pd(CH ₃ CN) ₂ Cl ₂ (10 mol%), Phen.·H ₂ O (12 mol%).	---	trace	---- ^b
3	Pd(CH ₃ CN) ₂ Cl ₂ (10 mol%), Phen.·H ₂ O (12 mol%).	Cu(OAc) ₂ (4 equiv.).	65%	trace

^a Condition: **1a** (0.5 mmol), catalyst, oxidant, Dioxane/DMSO (9:1) (6mL), 100 °C, N₂, 4h.

^b Isolated yield.

^c Not detected.

2. Effects of Radical Inhibitors.^a

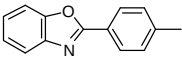


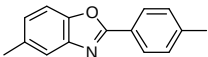
Entry	Additive (20 mol%)	Yield ^b
1	--	90%
2	TEMPO	90%
3	BHT	91%

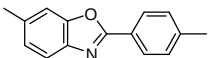
^a Condition: **1a** (0.5 mmol), **2a** (1.5 equiv.), Pd(CH₃CN)₂Cl₂ (5 mol%), Phen.H₂O (6 mol%), Na₂CO₃ (1.5 equiv.), TBAB (0.2 equiv.), Cu(OAc)₂ (6 equiv.), additive (20 mol%).

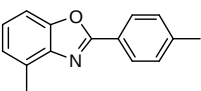
^b HPLC yield.

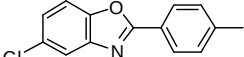
Analytical Data

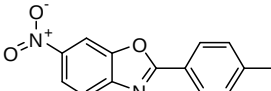
 **2-p-Tolylbenzo[d]oxazole (3a)**,^[2] white solid, yield:90%; ¹H NMR (400 MHz, CDCl₃) δ 8.15 (d, *J* = 8.2 Hz, 2H), 7.80 – 7.73 (m, 1H), 7.61 – 7.54 (m, 1H), 7.38 – 7.28 (m, 4H), 2.44 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 150.8, 142.3, 142.1, 129.7, 127.7, 124.9, 124.5, 124.5, 119.9, 110.6, 21.7.

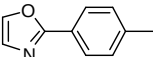
 **5-Methyl-2-p-tolylbenzo[d]oxazole (3b)**,^[2] white solid, yield: 92%; ¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 7.6 Hz, 2H), 7.54 (s, 1H), 7.43 (d, *J* = 8.3 Hz, 1H), 7.32 (d, *J* = 7.5 Hz, 2H), 7.14 (d, *J* = 8.1 Hz, 1H), 2.48 (s, 3H), 2.43 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 163.5, 149.1, 142.6, 1420, 134.4, 129.7, 127.7, 126.1, 124.7, 119.9, 109.96, 21.7, 21.7.

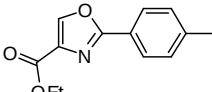
 **6-Methyl-2-p-tolylbenzo[d]oxazole (3c)**,^[2] white solid, yield: 89%; ¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.08 (m, 2H), 7.62 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.36 (s, 1H), 7.32 (d, *J* = 6.8 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 1H), 2.50 (d, *J* = 1.8 Hz, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.0, 151.1, 141.9, 140.1, 135.4, 129.7, 127.6, 125.8, 124.75, 119.3, 110.8, 21.9, 21.8.

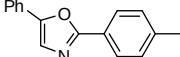
 **4-Methyl-2-p-tolylbenzo[d]oxazole (3d)**, pink solid, yield: 88%; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 2.68 (s, 3H), 2.44 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 162.65, 150.60, 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 C₁₅H₁₄NO⁺ (M+H): 224.1075, found 224.1079.

 **5-Chloro-2-p-tolylbenzo[d]oxazole (3e)**,^[2] white solid, yield: 85%; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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.

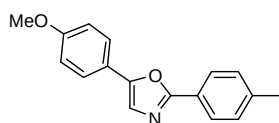
 **6-Nitro-2-p-tolylbenzo[d]oxazole (3f)**,^[5] white solid, yield: 40%; ¹H NMR (400 MHz, CDCl₃) δ 8.44 (d, *J* = 2.1 Hz, 1H), 8.29 (dd, *J* = 8.8, 2.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 2H), 7.79 (d, *J* = 8.8 Hz, 1H), 7.35 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 167.90, 150.02, 147.77, 145.16, 144.00, 130.13, 128.43, 123.37, 120.99, 119.73, 107.28, 21.98.

 **2-p-Tolylloxazole (3g)**,^[6] colorless oil, yield: 88%; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 162.2, 140.6, 138.3, 129.5, 128.3, 126.3, 124.9, 21.5.

 **Ethyl 2-p-tolylloxazole-4-carboxylate (3h)**,^[2] white solid, yield: 91%; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (101 MHz, CDCl₃) δ 162.7, 161.5, 143.4, 141.6, 134.6, 129.5, 126.9, 123.8, 61.3, 21.6 14.4.

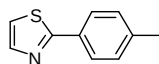
 **5-Phenyl-2-p-tolylloxazole (3i)**,^[8] white solid, yield:84%; ¹H NMR (400 MHz, CDCl₃) δ

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.



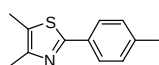
5-(4-Methoxyphenyl)-2-p-tolylloxazole (3j),^[6] white solid, yield: 78%; ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, J = 7.3 Hz, 2H), 7.64 (d, J = 7.4 Hz, 2H), 7.34 – 7.21 (m, 3H), 6.96 (d, J = 7.5 Hz, 2H), 3.85 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.8, 159.8, 151.0, 140.4, 129.5, 126.1,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

114.4, 55.3, 21.5.

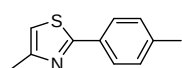


2-p-Tolylthiazole (3k),^[2] yellow oil, yield: 87%; ^1H NMR (500 MHz, CDCl_3) δ 7.88 – 7.85 (m, 2H), 7.84 (d, J = 3.3 Hz, 1H), 7.27 (d, J = 3.3 Hz, 1H), 7.24 (d, J = 7.9 Hz, 2H), 2.39 (s, 3H);

^{13}C NMR (126 MHz, CDCl_3) δ 168.7, 143.6, 140.3, 131.1, 129.7, 126.6, 118.4, 21.5.

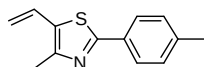


4, 5-Dimethyl-2-p-tolylthiazole (3l),^[2] white solid, yield: 71%; ^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.2 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 2.37 (d, J = 2.5 Hz, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 149.1, 139.5, 131.5, 129.6, 126.1, 126.0, 21.4, 14.9, 11.5.



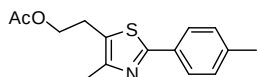
4-Methyl-2-p-tolylthiazole (3m),^[2] colorless oil, yield 86%; ^1H NMR (400 MHz, CDCl_3) δ 7.87 – 7.80 (m, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.81 (d, J = 0.9 Hz, 1H), 2.50 (d, J = 1.0 Hz,

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.

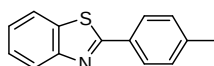


4-Methyl-2-p-tolyl-5-vinylthiazole (3n), yellow solid, m.p. 66-68 °C, yield: 43%; ^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, J = 8.2 Hz, 2H), 7.22 (d, J = 7.9 Hz, 2H), 6.84 – 6.72 (m, 1H),

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 $\text{C}_{13}\text{H}_{14}\text{NS}^+$ (M+H): 216.0847, found 216.0842.

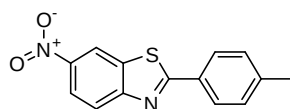


2-(4-Methyl-2-p-tolylthiazol-5-yl)ethyl acetate (3o), yellow oil, yield: 78%; ^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.1 Hz, 2H), 7.16 (d, J = 8.1 Hz, 2H), 4.21 (t, J = 6.7 Hz, 2H), 3.03 (t, J = 6.7 Hz, 2H), 2.37 (s, 3H), 2.32 (s, 3H), 2.03 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 170.8, 165.0, 150.2, 139.9, 131.3, 129.6, 126.7, 126.2, 64.2, 26.1, 21.5, 21.0, 15.2; HRMS (ESI) calculated for $\text{C}_{15}\text{H}_{18}\text{NO}_2\text{S}^+$ (M+H): 276.1058, found 276.1054 (M+H).



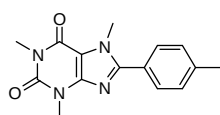
2-p-Tolylbenzo[d]thiazole (3p),^[2] white solid, yield: 71%; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, J = 7.7 Hz, 1H), 8.00 (d, J = 7.4 Hz, 2H), 7.90 (d, J = 8.1 Hz, 1H), 7.49 (t, J = 7.5

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.

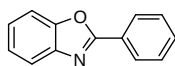


6-Nitro-2-p-tolylbenzo[d]thiazole (3q),^[2] yellow solid, yield: 54%; ^1H NMR (400 MHz, CD_2Cl_2) δ 8.81 (d, J = 2.2 Hz, 1H), 8.33 (dd, J = 9.0, 2.3 Hz, 1H), 8.09 (d, J = 9.0 Hz, 1H), 8.01 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 2.44 (s, 3H);

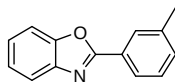
^{13}C NMR (126 MHz, CDCl_3) δ 174.05, 158.07, 144.90, 143.16, 135.35, 130.23, 130.10, 128.00, 123.18, 121.96, 118.25, 21.75.



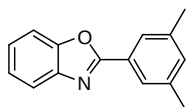
1,3,7-Trimethyl-8-*p*-tolyl-1H-purine-2,6-(3H,7H)-dione (3r),^[3] white solid, yield: 93%; ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 4.03 (s, 3H), 3.61 (s, 3H), 3.42 (s, 3H), 2.43 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 155.7, 152.5, 151.9, 148.4, 140.8, 129.7, 129.2, 125.7, 108.6, 34.0, 29.9, 28.1, 21.6.



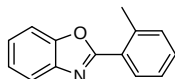
2-Phenylbenzo[d]oxazole (3s),^[2] white solid, yield: 92%; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (d, *J* = 3.1 Hz, 2H), 7.79 (d, *J* = 4.4 Hz, 1H), 7.57 (s, 1H), 7.53 (s, 3H), 7.41 – 7.30 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.1, 150.9, 142.2, 131.6, 129.0, 127.7, 127.3, 125.2, 124.7, 120.1, 110.7, 104.0, 77.5, 77.2, 76.8.



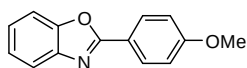
2-m-Tolylbenzo[d]oxazole (3t),^[2] white solid, yield: 86%; ¹H NMR (400 MHz, CDCl₃) δ 8.10 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 7.81 – 7.74 (m, 1H), 7.62 – 7.54 (m, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.31 (m, 3H), 2.46 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 150.9, 142.3, 138.9, 132.5, 129.0, 128.3, 127.2, 125.2, 124.9, 124.7, 120.1, 110.7, 21.5.



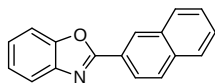
2-(3,5-Dimethylphenyl)benzo[d]oxazole (3u),^[7] white solid, yield: 84%; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (s, 2H), 7.81 – 7.74 (m, 1H), 7.62 – 7.54 (m, 1H), 7.35 (dd, *J* = 6.0, 3.3 Hz, 2H), 7.17 (s, 1H), 2.42 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 150.8, 142.2, 138.7, 133.4, 127.0, 125.5, 125.1, 124.6, 120.0, 110.6, 21.4.



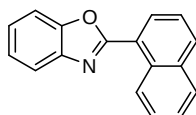
2-o-Tolylbenzo[d]oxazole (3v),^[2] white solid, yield: 67%; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.3 Hz, 1H), 7.83 (d, *J* = 3.1 Hz, 1H), 7.60 (d, *J* = 3.6 Hz, 1H), 7.46 – 7.30 (m, 5H), 2.84 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.5, 150.4, 142.3, 139.0, 131.9, 131.0, 130.0, 126.3, 126.2, 125.1, 124.5, 120.2, 110.6, 22.3.



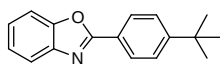
2-(4-Methoxyphenyl)benzo[d]oxazole (3w),^[2] white solid, yield: 86%; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.2 Hz, 2H), 7.73 (s, 1H), 7.55 (s, 1H), 7.33 (s, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 3.89 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 162.5, 150.8, 142.5, 129.5, 124.7, 124.5, 119.8, 119.7, 114.5, 110.5, 55.5.



2-(Naphthalen-2-yl)benzo[d]oxazole (3x),^[4] white solid, yield: 90%; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) 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.

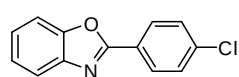


2-(Naphthalen-1-yl)benzo[d]oxazole (3y),^[7] white solid, yield: 47%; ¹H NMR (400 MHz, CDCl₃) δ 8.75 (s, 1H), 8.30 (d, *J* = 8.6 Hz, 1H), 7.95 (t, *J* = 8.1 Hz, 2H), 7.82 (ddd, *J* = 8.8, 8.1, 4.3 Hz, 2H), 7.64 – 7.49 (m, 3H), 7.41 – 7.31 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 163.2, 150.9, 142.3, 134.8, 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.

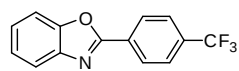


2-(4-*tert*-Butylphenyl)benzo[d]oxazole (3z),^[2] white solid, yield: 73%; ¹H NMR (400 MHz, CDCl₃) δ 8.25 – 8.14 (m, 2H), 7.81 – 7.73 (m, 1H), 7.63 – 7.51 (m, 3H), 7.40 – 7.29 (m, 2H), 1.38 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 155.1, 150.8, 142.3, 127.6, 126.0, 124.9, 124.5,

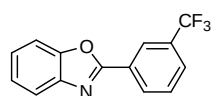
124.4, 119.9, 110.6, 35.1, 31.2.



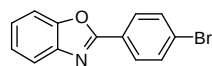
2-(4-Chlorophenyl)benzo[d]oxazole (3aa),^[2] white solid, yield: 83%; ¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 7.4 Hz, 2H), 7.77 (d, *J* = 3.4 Hz, 1H), 7.58 (d, *J* = 3.4 Hz, 1H), 7.51 (d, *J* = 7.6 Hz, 2H), 7.37 (d, *J* = 3.3 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 162.1, 150.8, 142.1, 137.8, 129.3, 128.9, 125.7, 125.4, 124.8, 120.2, 110.7.



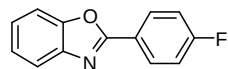
2-(4-(Trifluoromethyl)phenyl)benzo[d]oxazole (3ab),^[4] white solid, yield: 70%; ¹H NMR (400 MHz, CDCl₃) δ 8.37 (d, *J* = 8.1 Hz, 2H), 7.84 – 7.73 (m, 3H), 7.61 (dd, *J* = 5.1, 3.7 Hz, 1H), 7.40 (dd, *J* = 6.6, 2.7 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 161.5, 150.9, 142.0, 133.01 (dd, *J* = 63.6, 31.0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



2-(3-(Trifluoromethyl)phenyl)benzo[d]oxazole (3ac),^[8] white solid, yield: 87%; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (126 MHz, CDCl₃) 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; ¹⁹F NMR (471 MHz, CDCl₃) δ -63.95.



2-(4-Bromophenyl)benzo[d]oxazole (3ad):^[2] white solid, yield: 65%; ¹H NMR (400 MHz, CDCl₃) 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); ¹³C NMR (100 MHz, CDCl₃) δ 162.3, 150.9, 142.2, 132.4, 129.1, 126.4, 126.2, 125.5, 124.9, 120.3, 110.8.

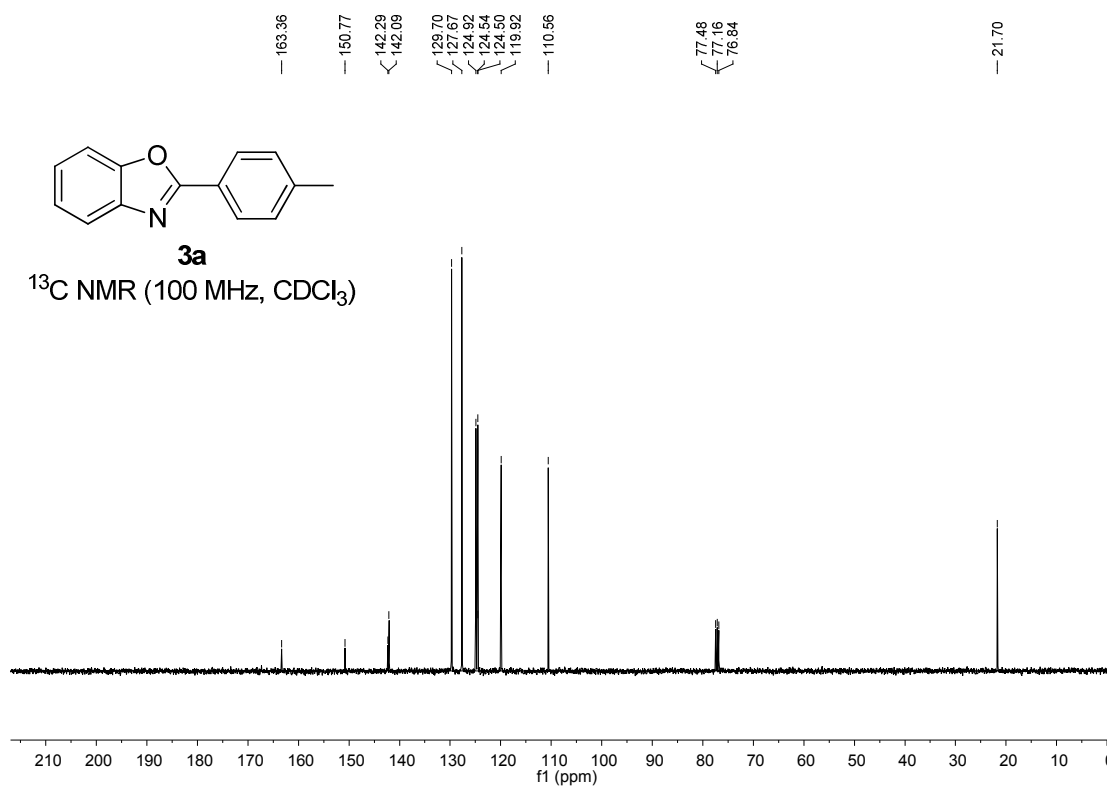
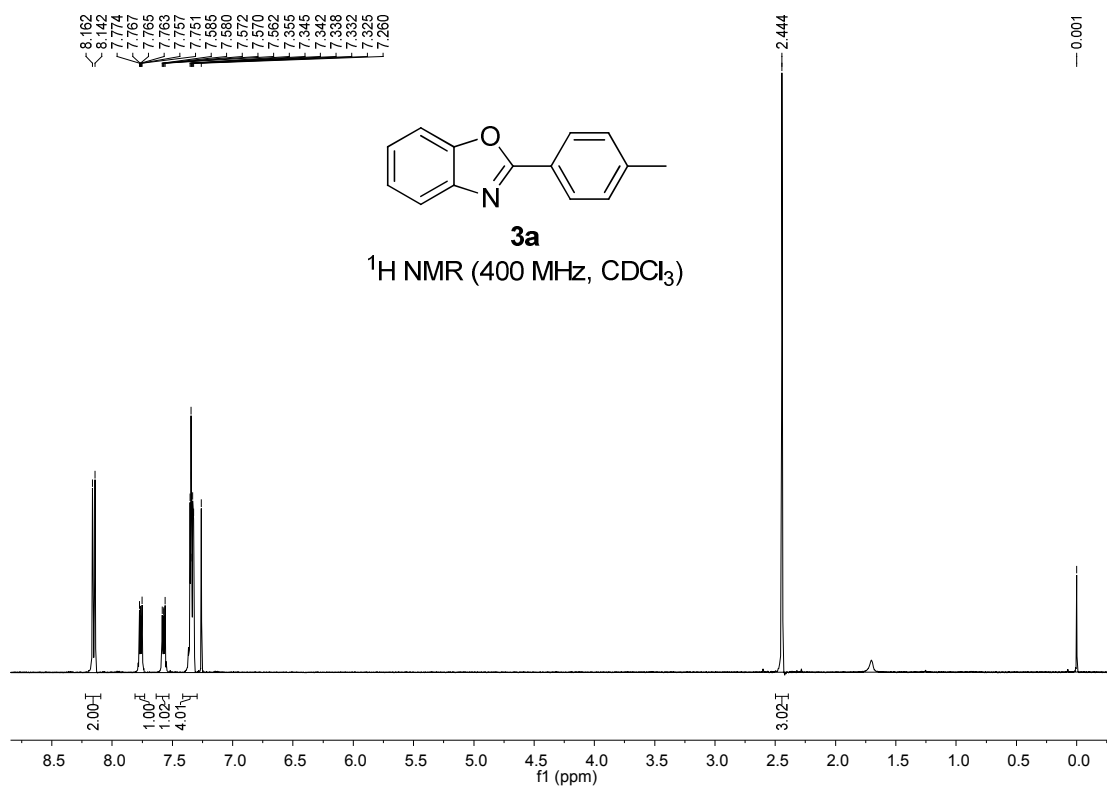


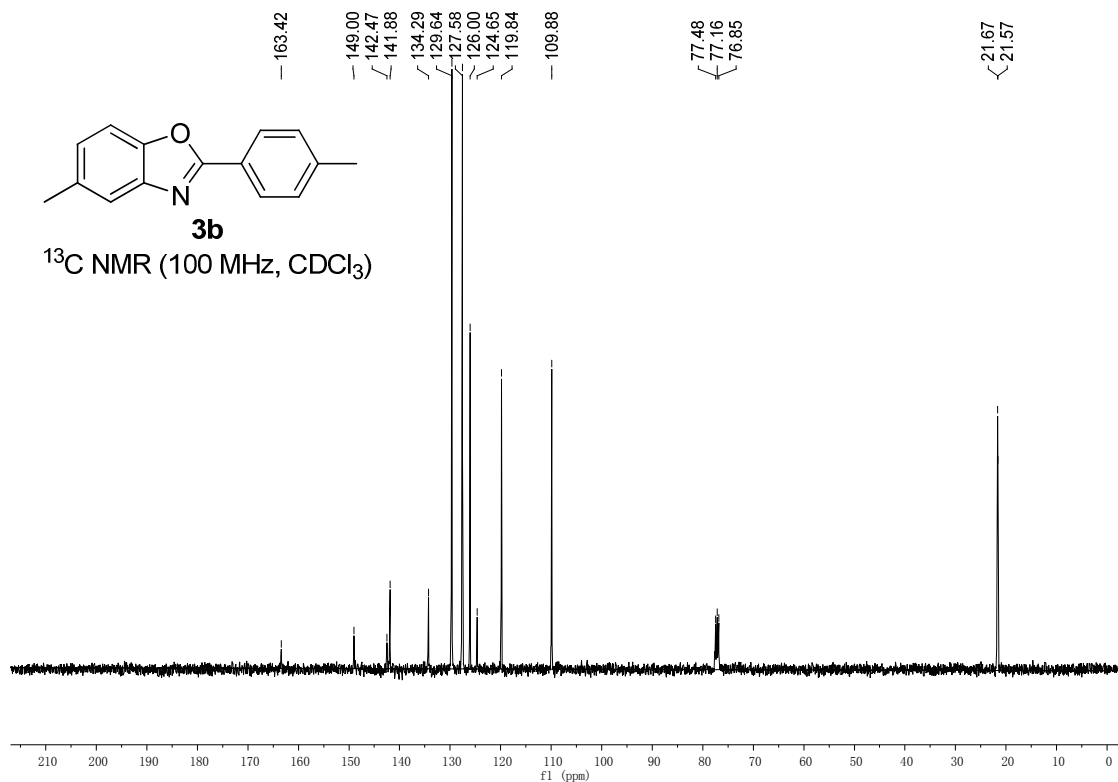
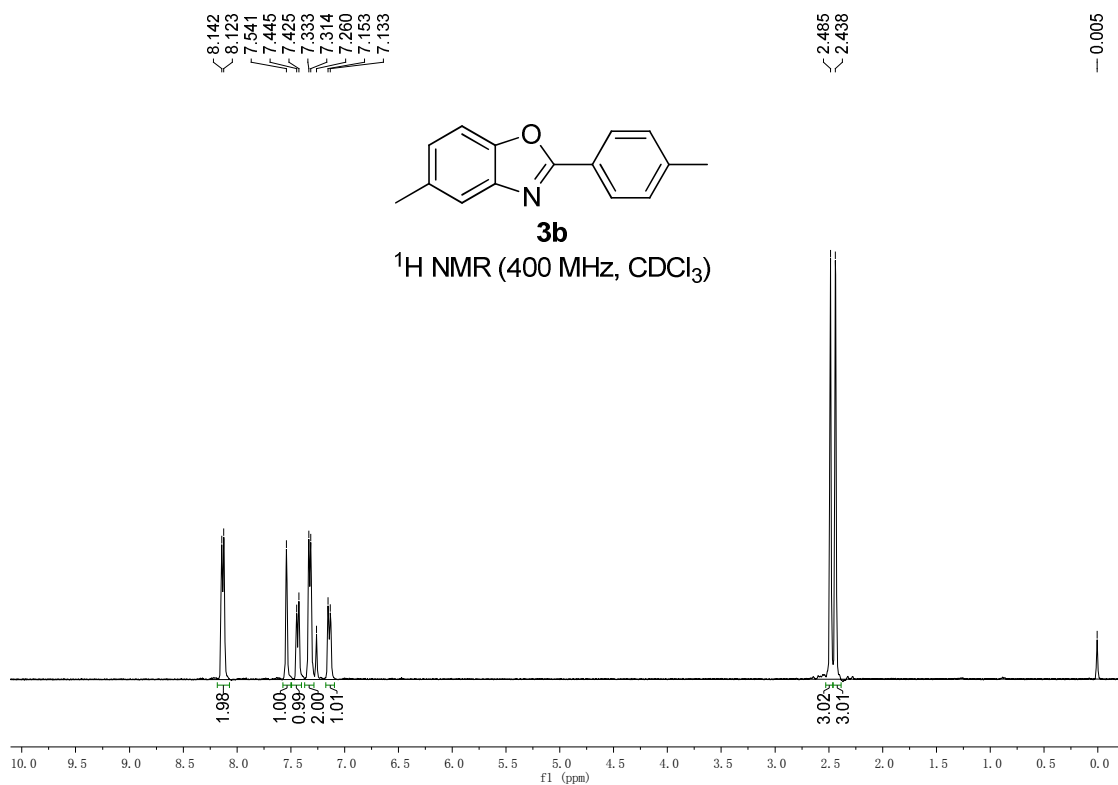
2-(4-Fluorophenyl)benzo[d]oxazole (3ae),^[2] white solid, yield: 92%; ¹H NMR (400 MHz, CDCl₃) δ 8.26 (dd, *J* = 8.7, 5.4 Hz, 2H), 7.83 – 7.72 (m, 1H), 7.57 (dt, *J* = 7.5, 3.9 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.21 (t, *J* = 8.6 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 164.86 (d, *J* = 252.9 Hz), 162.17, 150.83, 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; ¹⁹F NMR (377 MHz, CDCl₃) δ -108.06.

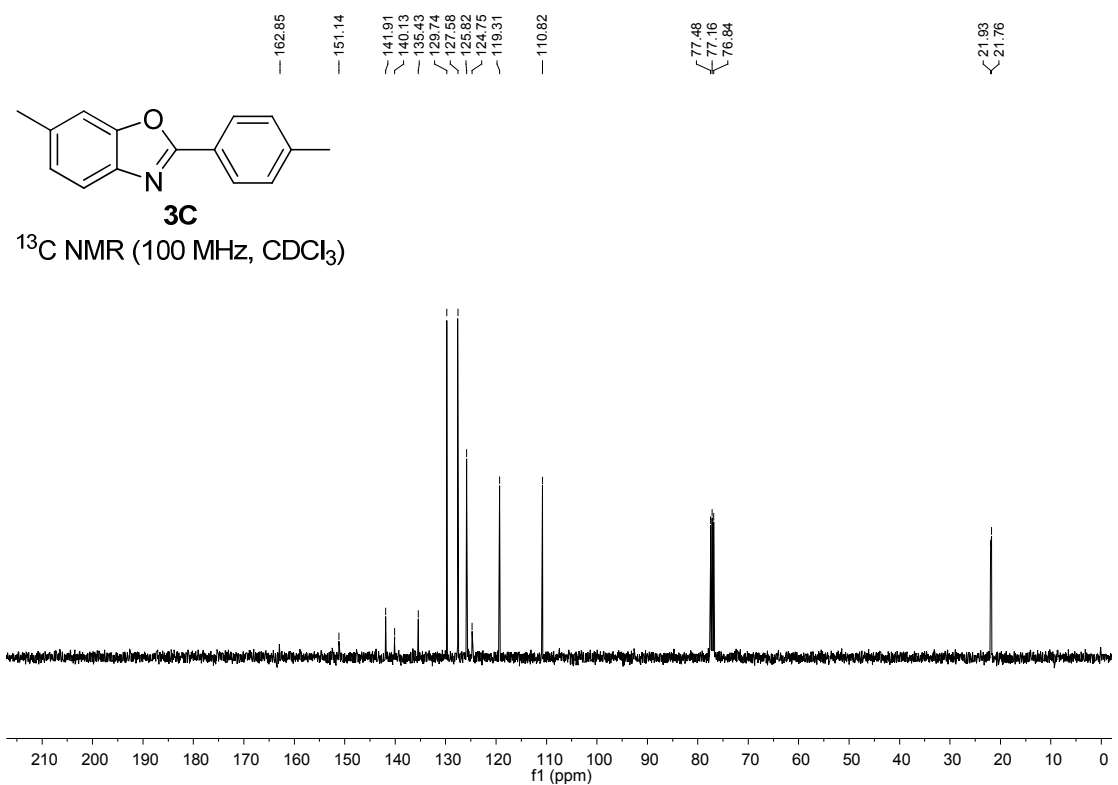
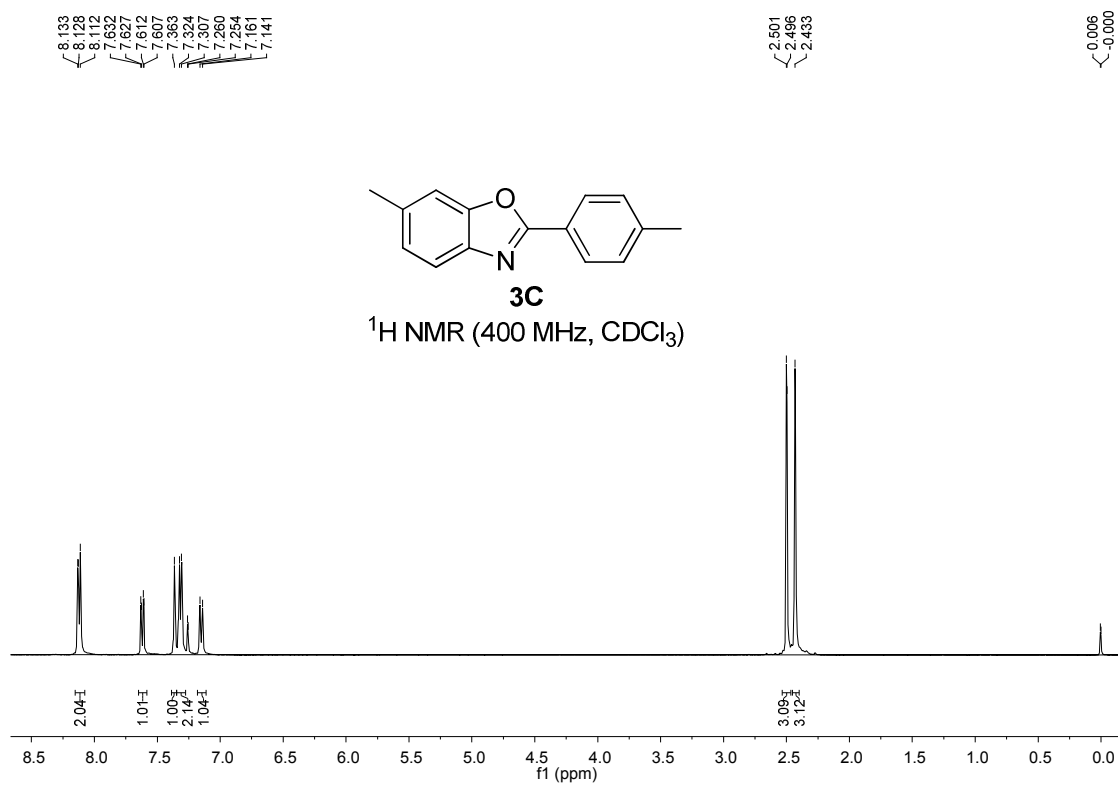
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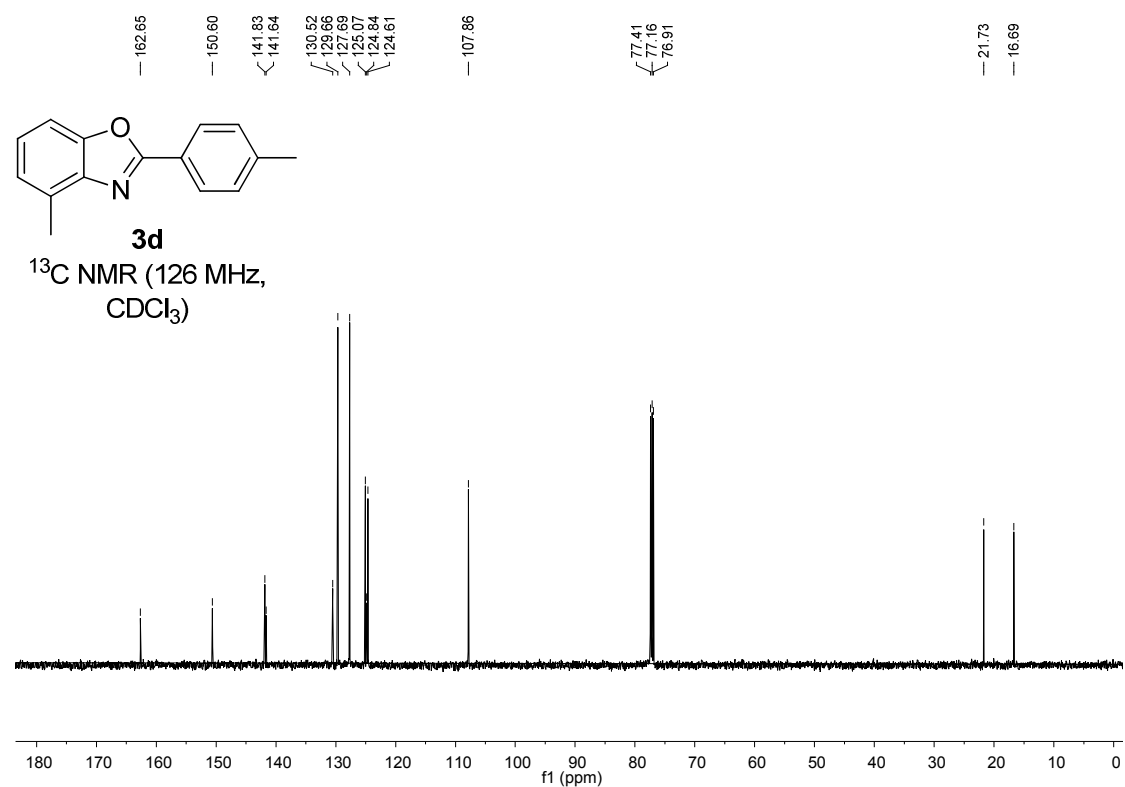
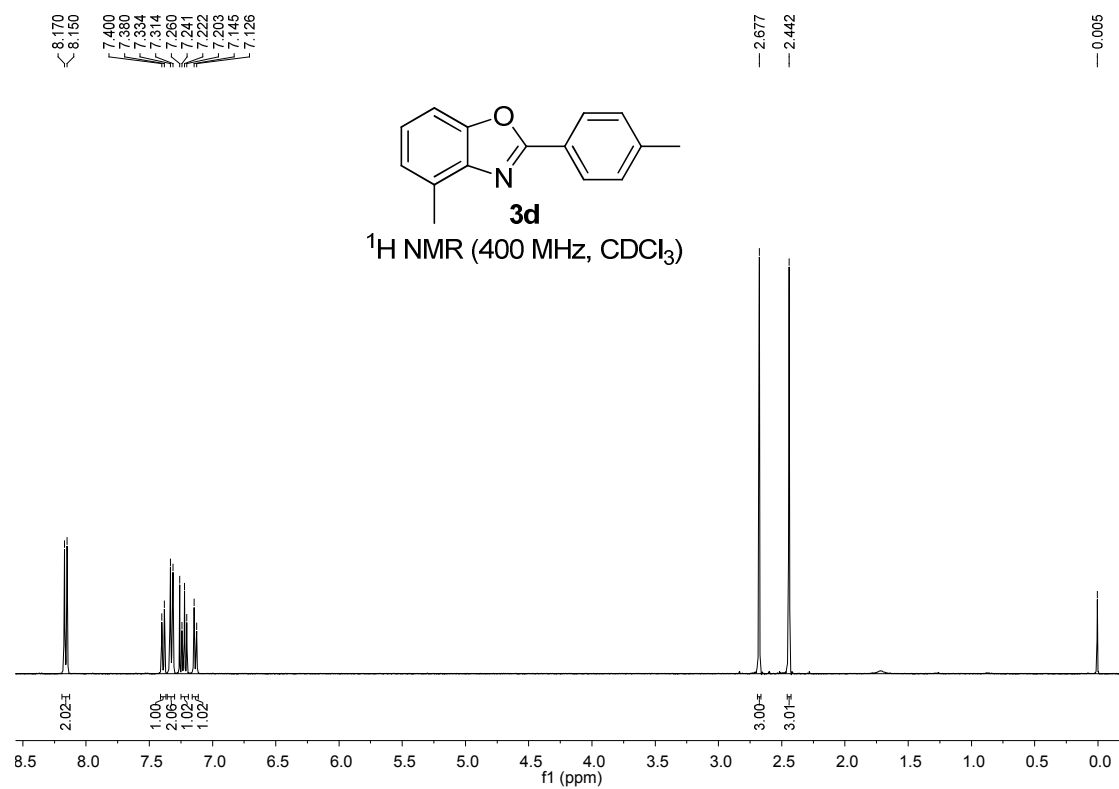
- [1] L. Friedman, R. L. Little and W. R. Reichle, *Organic synthesis*, 1973, **Coll. Vol. 5**, 1055.
- [2] M. Wang, D. Li, W. Zhou and L. Wang, *Tetrahedron*, 2012, **68**, 1926.
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- [5] C. O. Kangani, D. E. Kelley and B. W. Day, *Tetrahedron Lett.*, 2006, **47**, 6497.
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¹H and ¹³C spectra





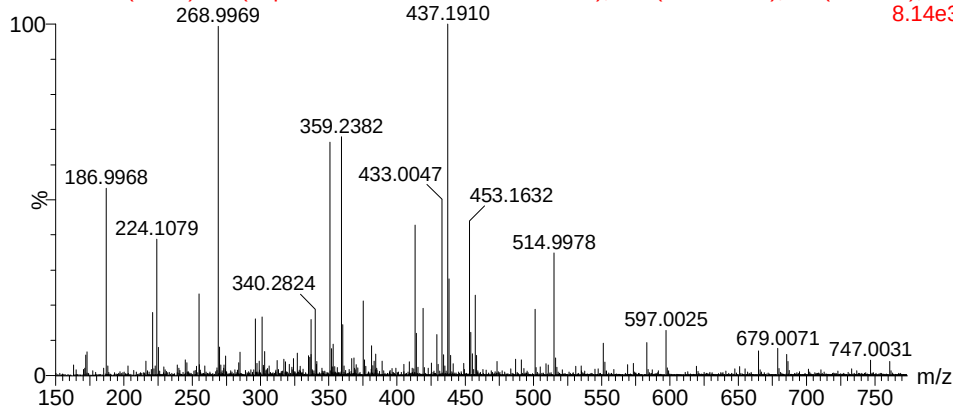




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Elemental Composition Report

Single Mass Analysis (displaying only valid results)

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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)

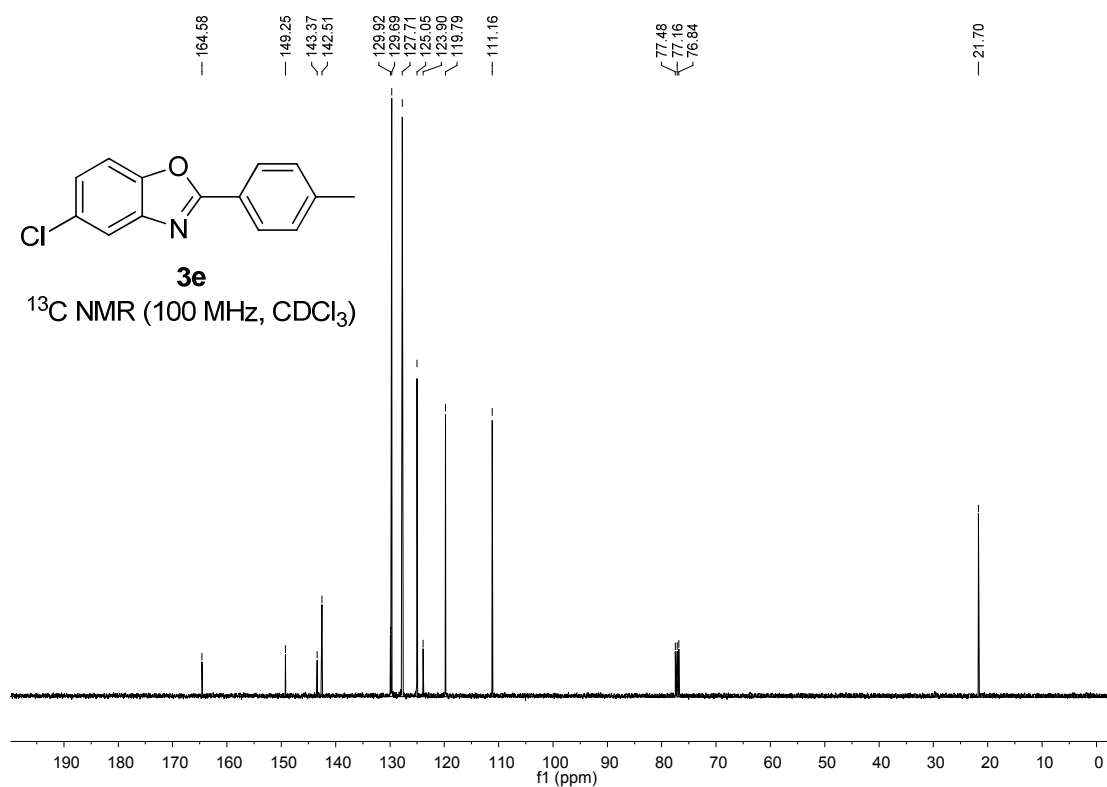
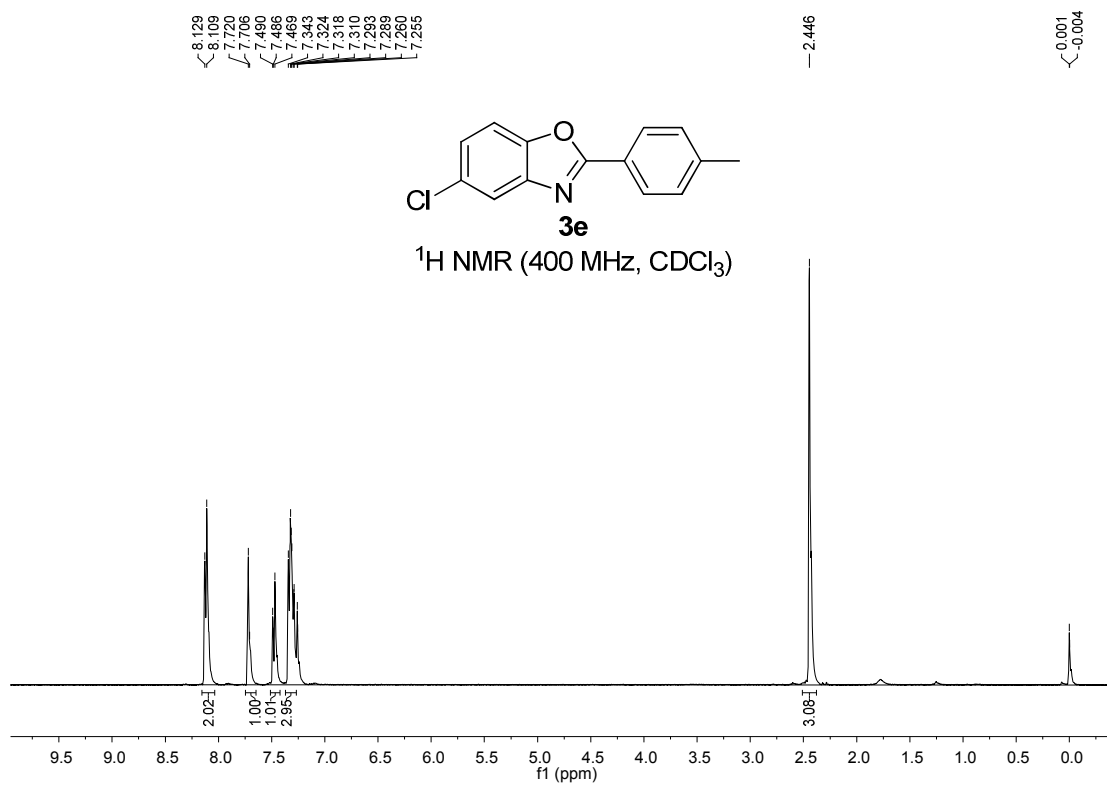
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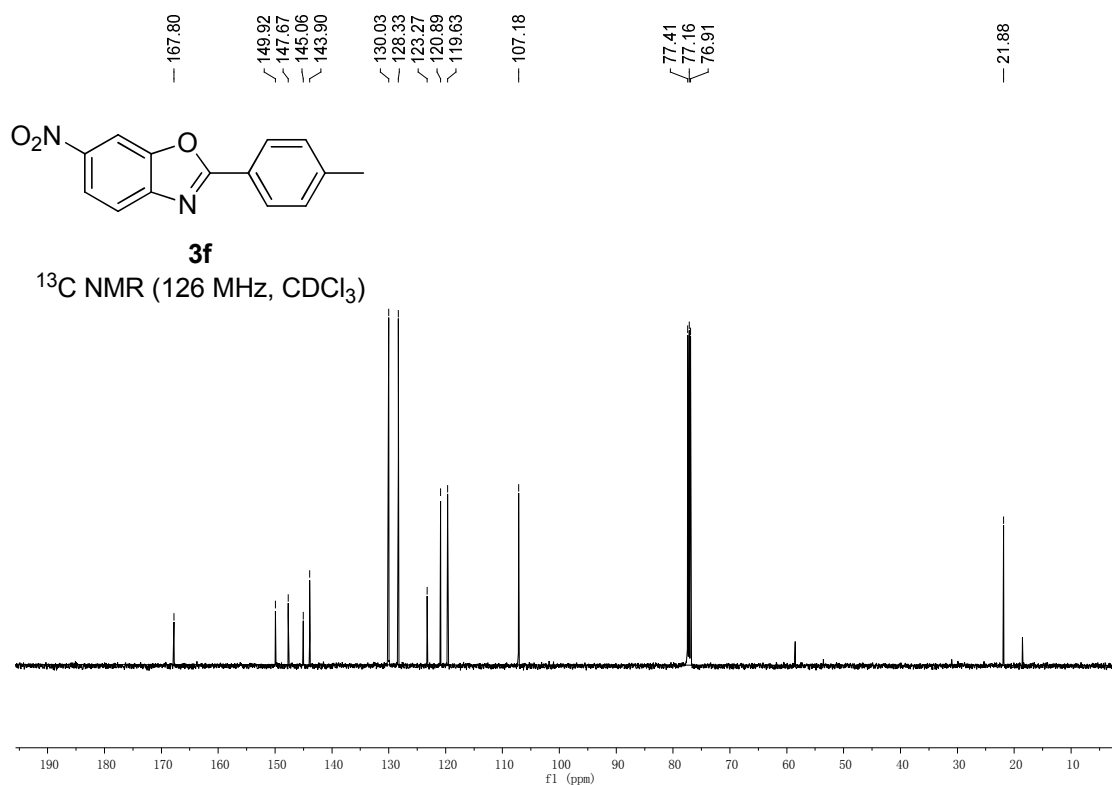
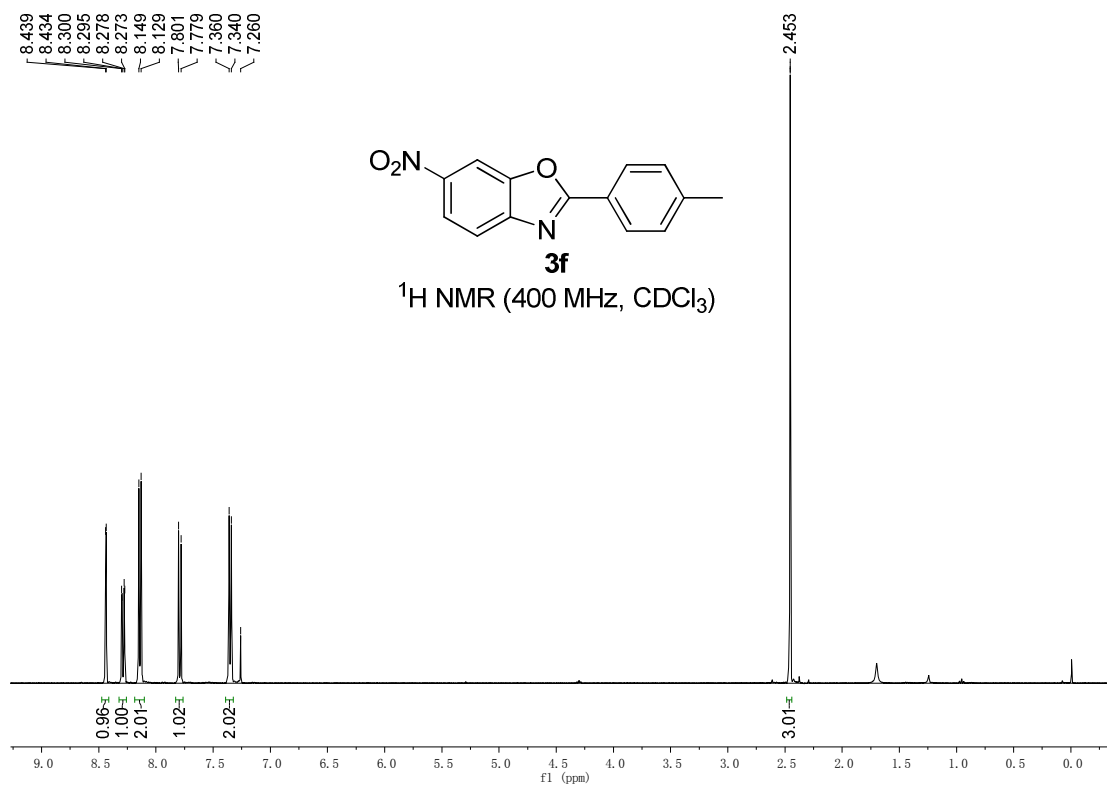
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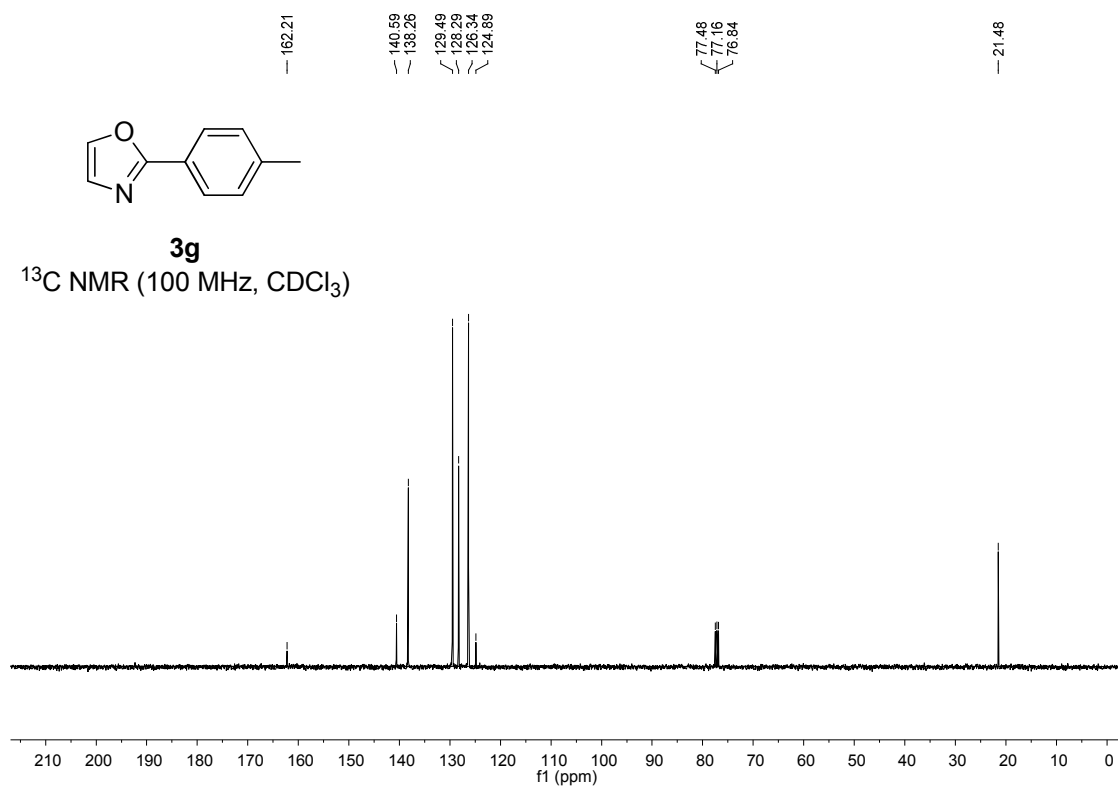
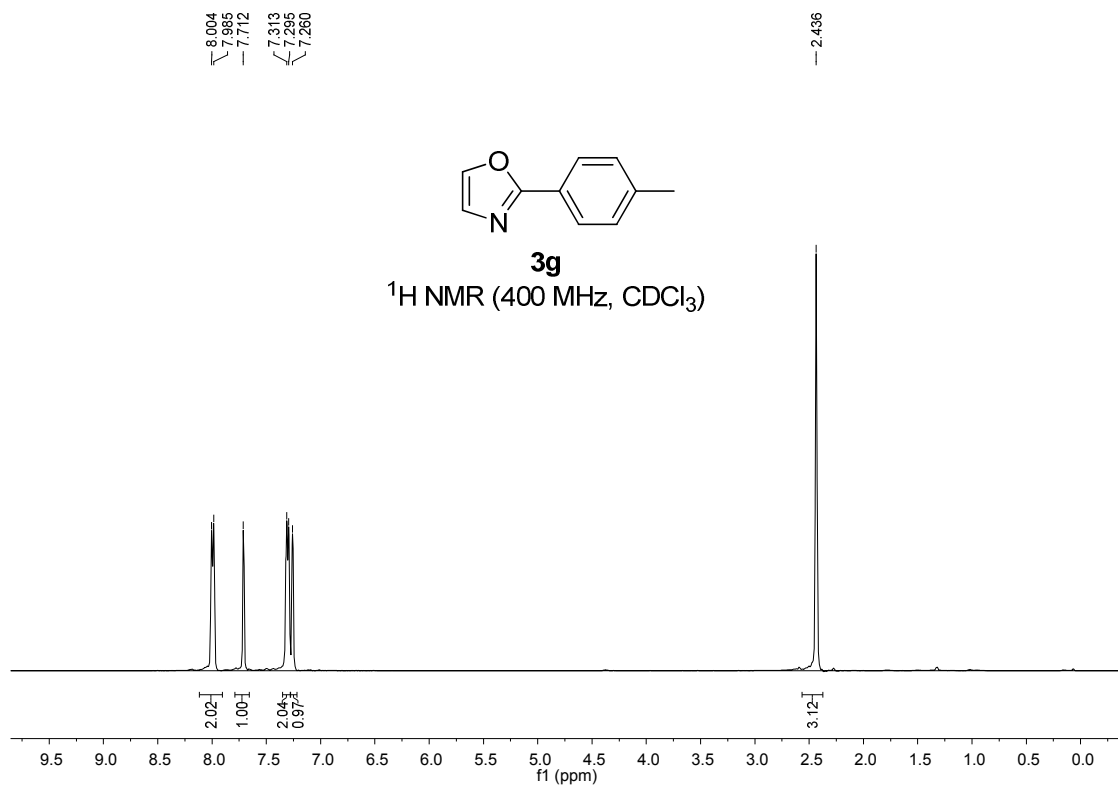
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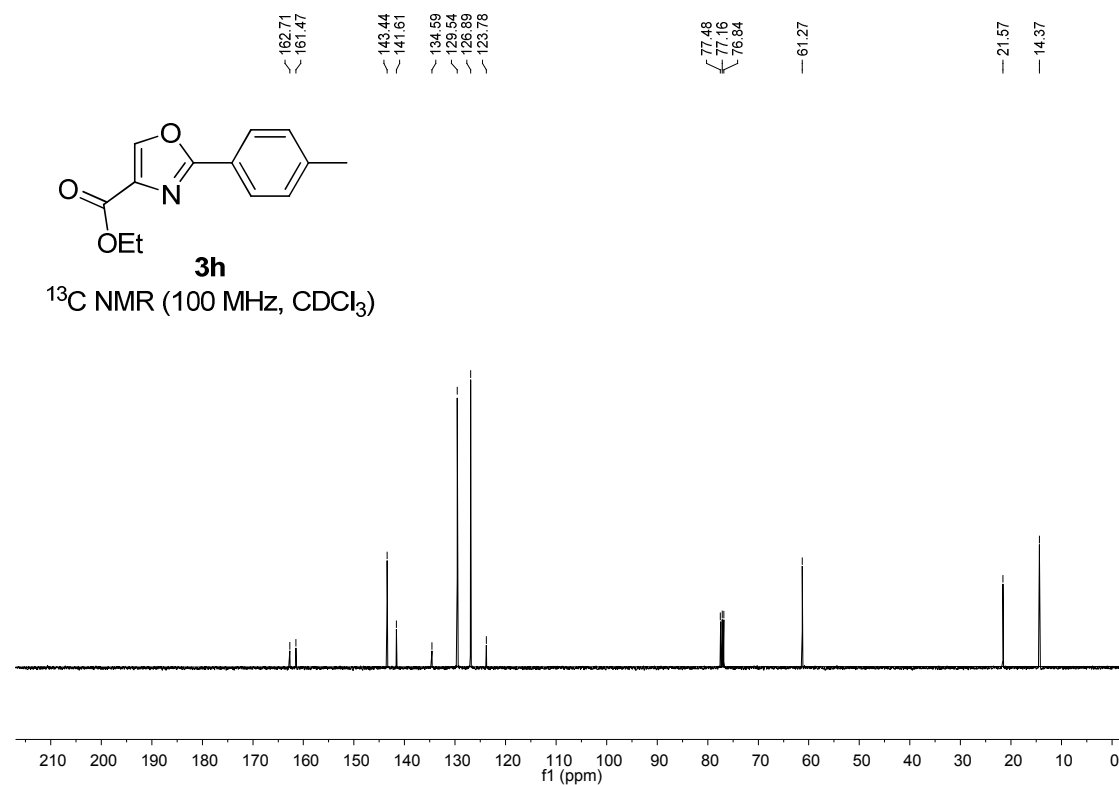
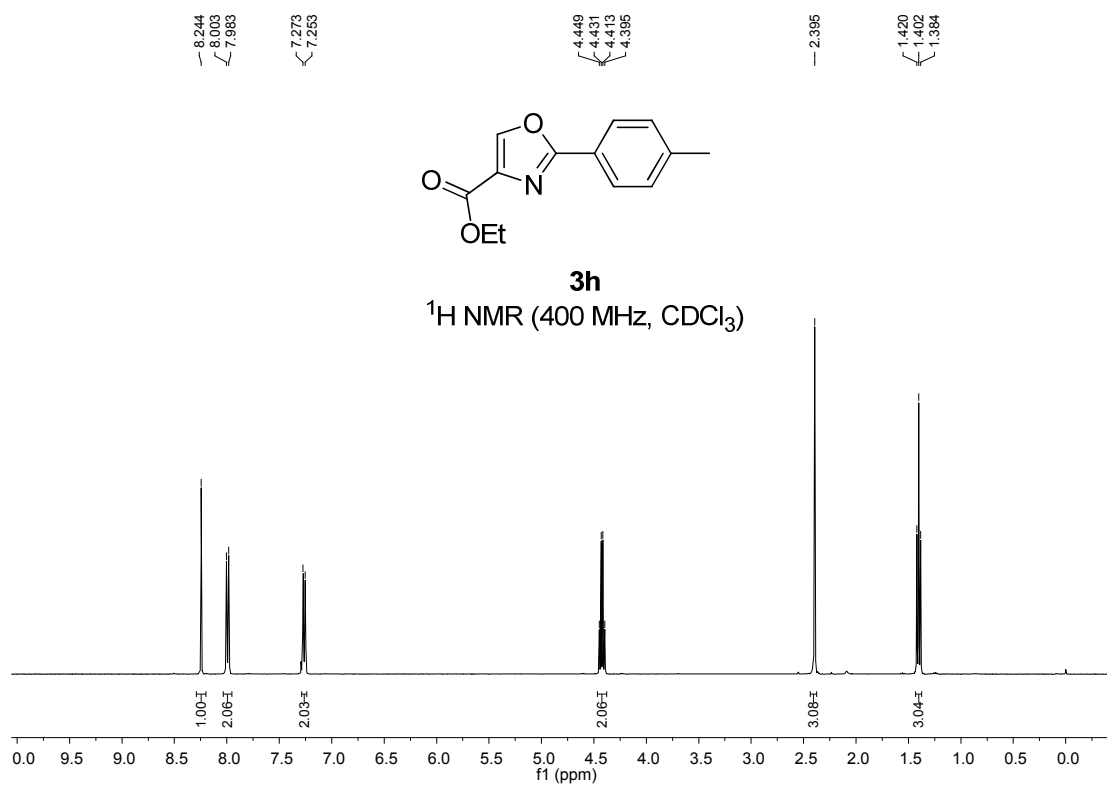
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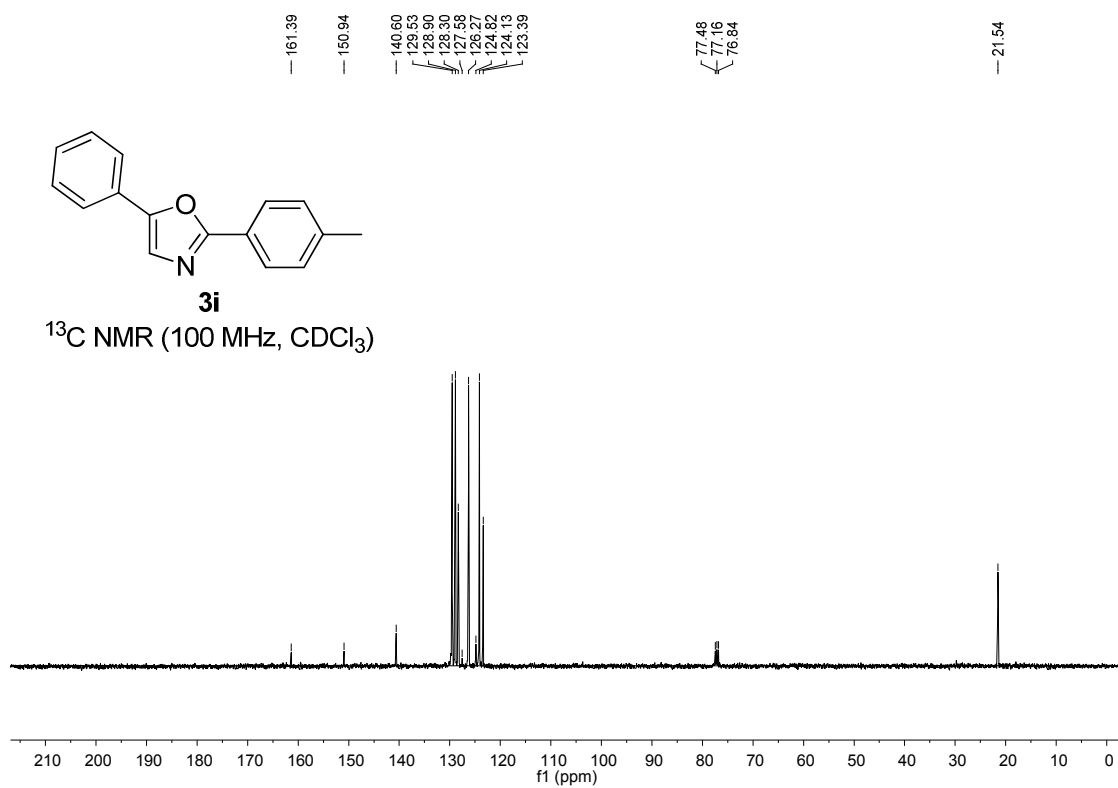
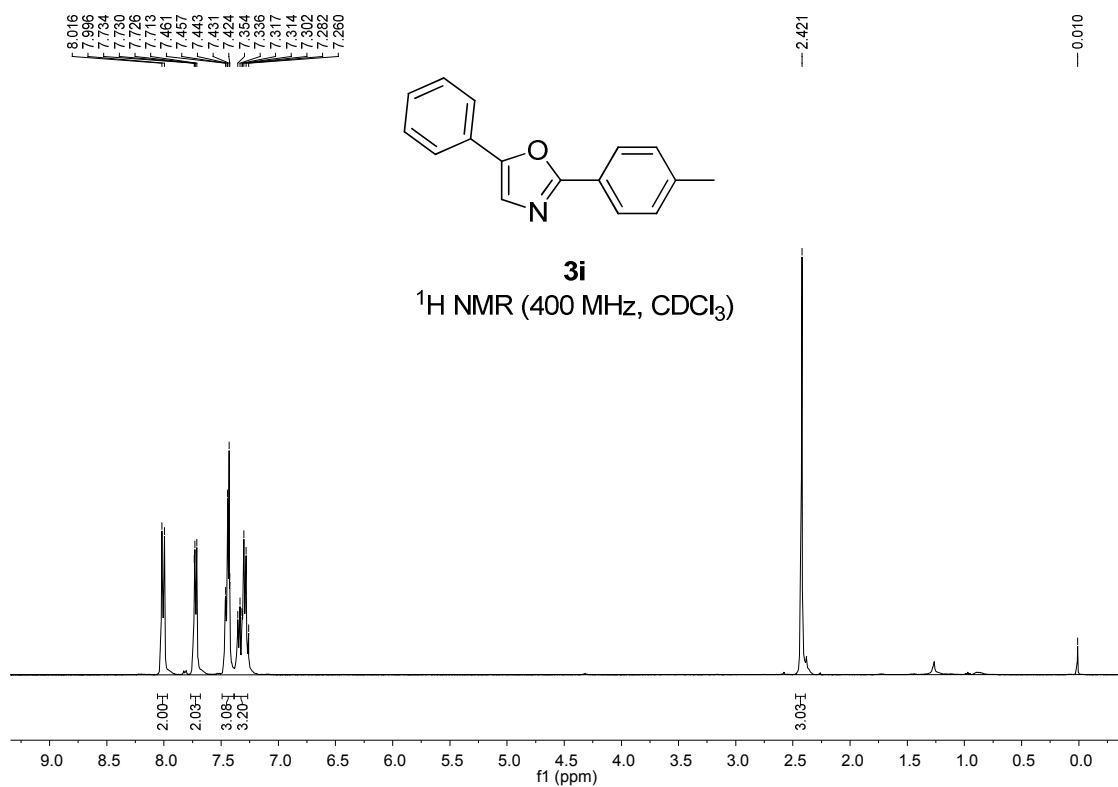
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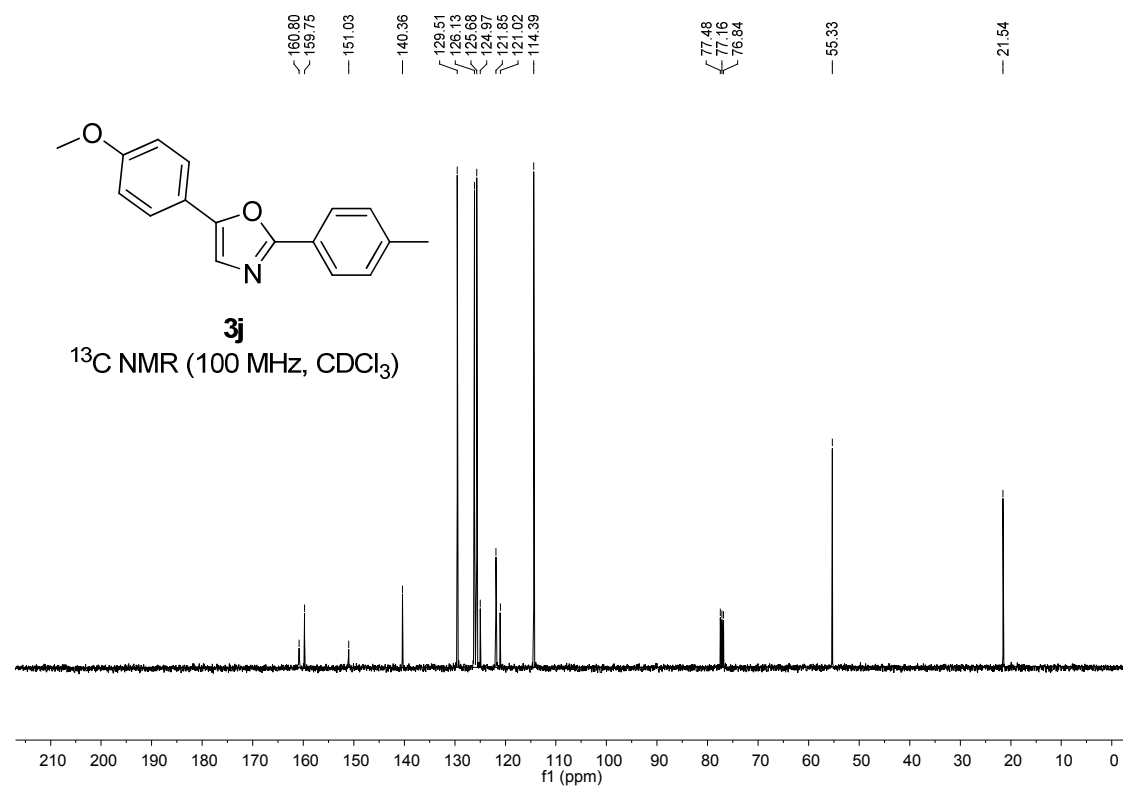
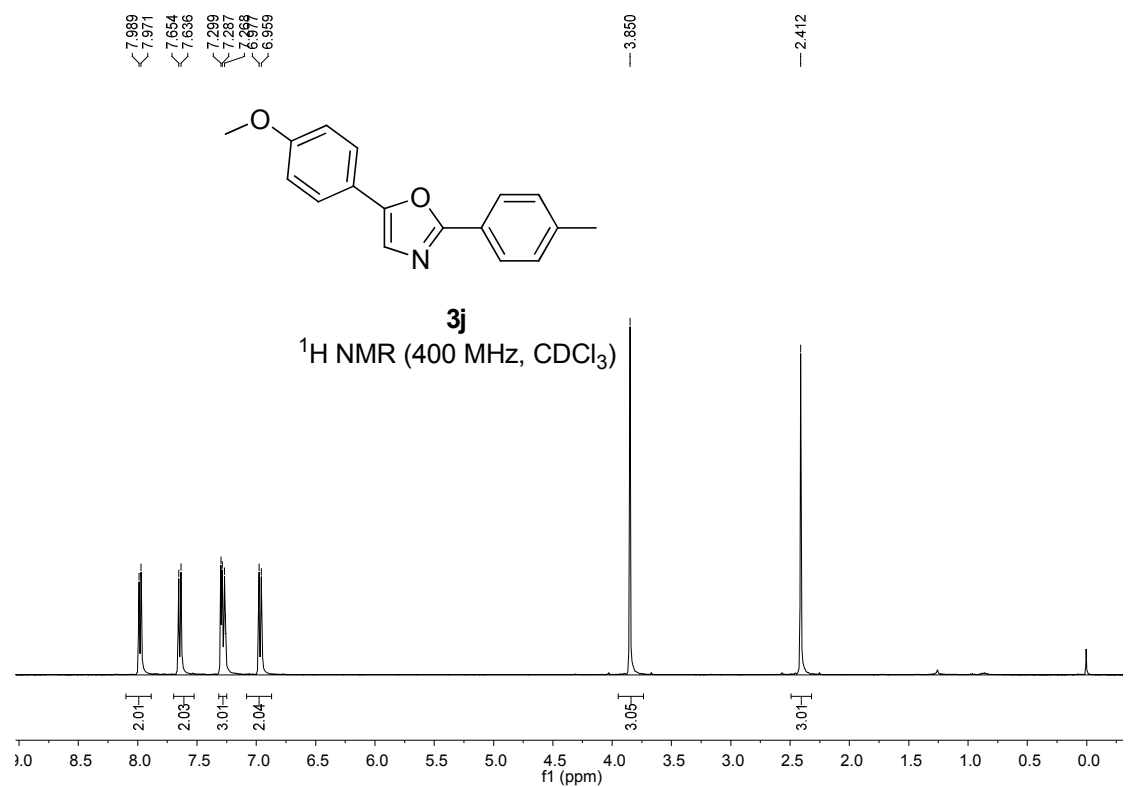


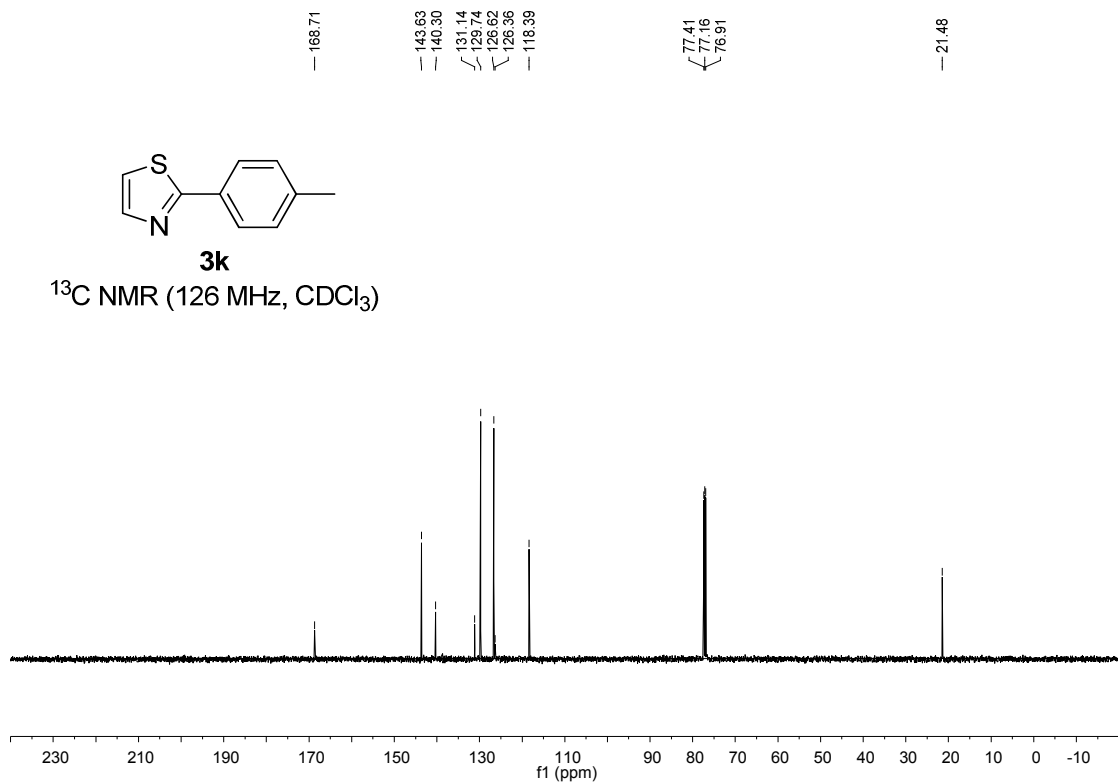
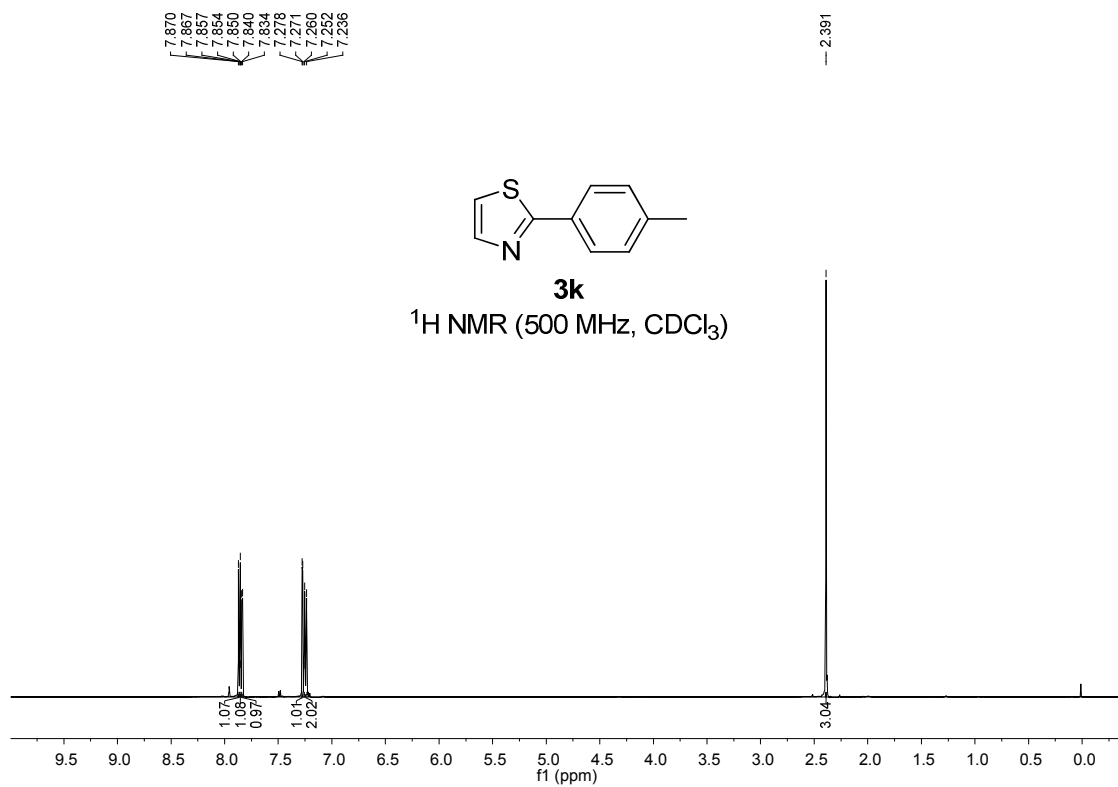


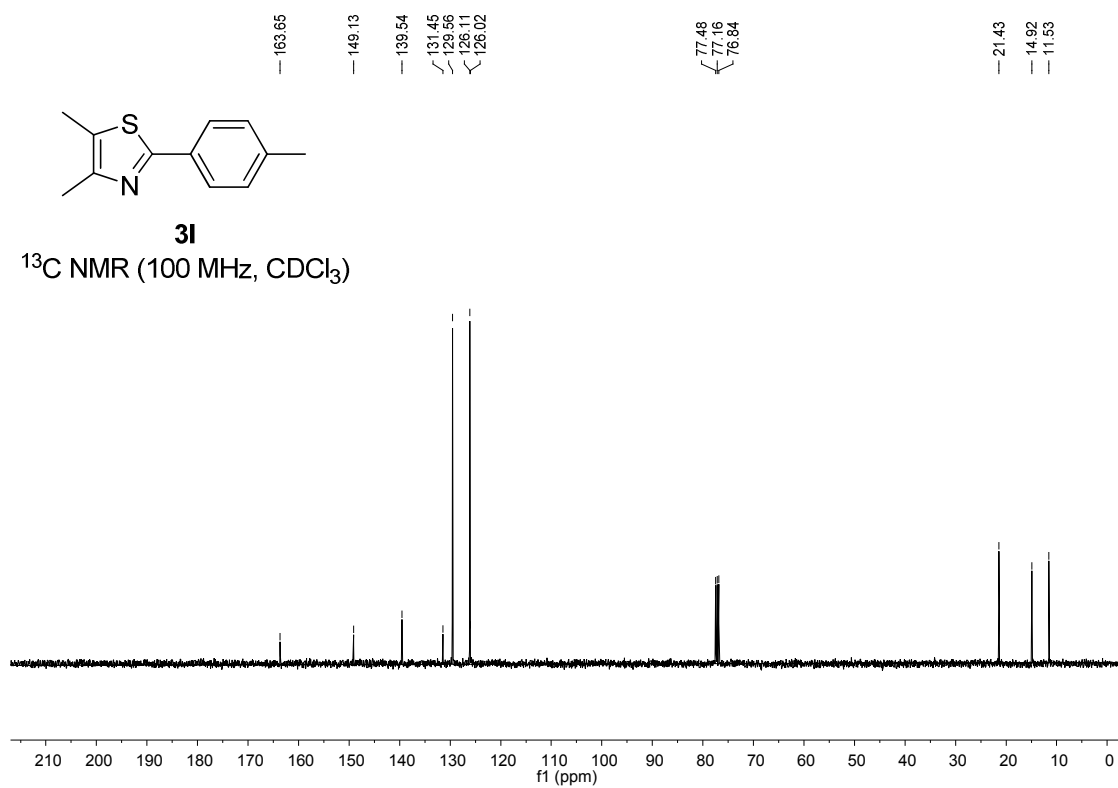
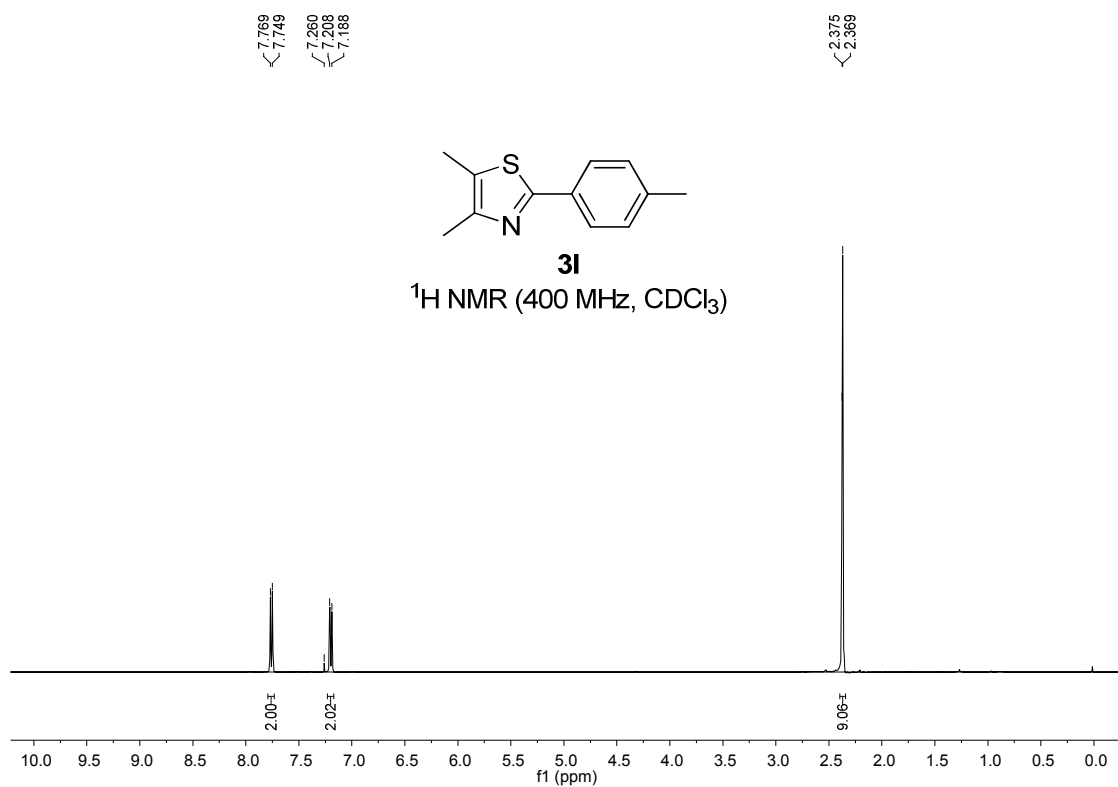


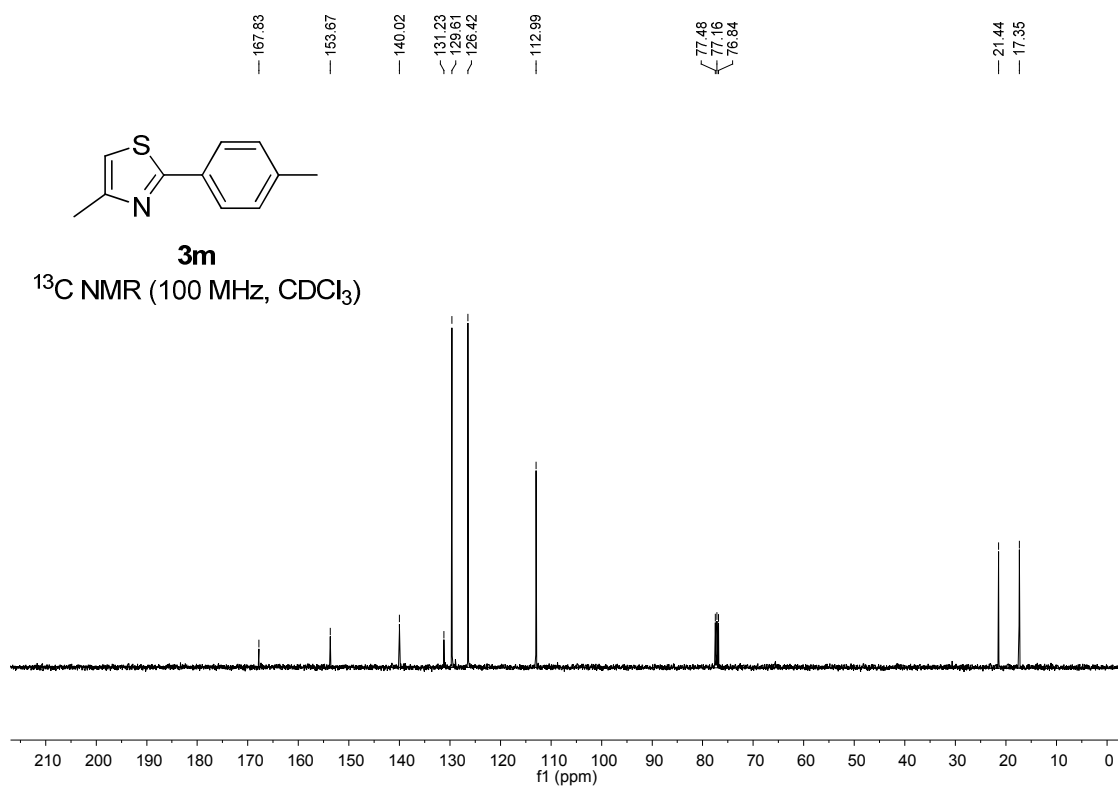
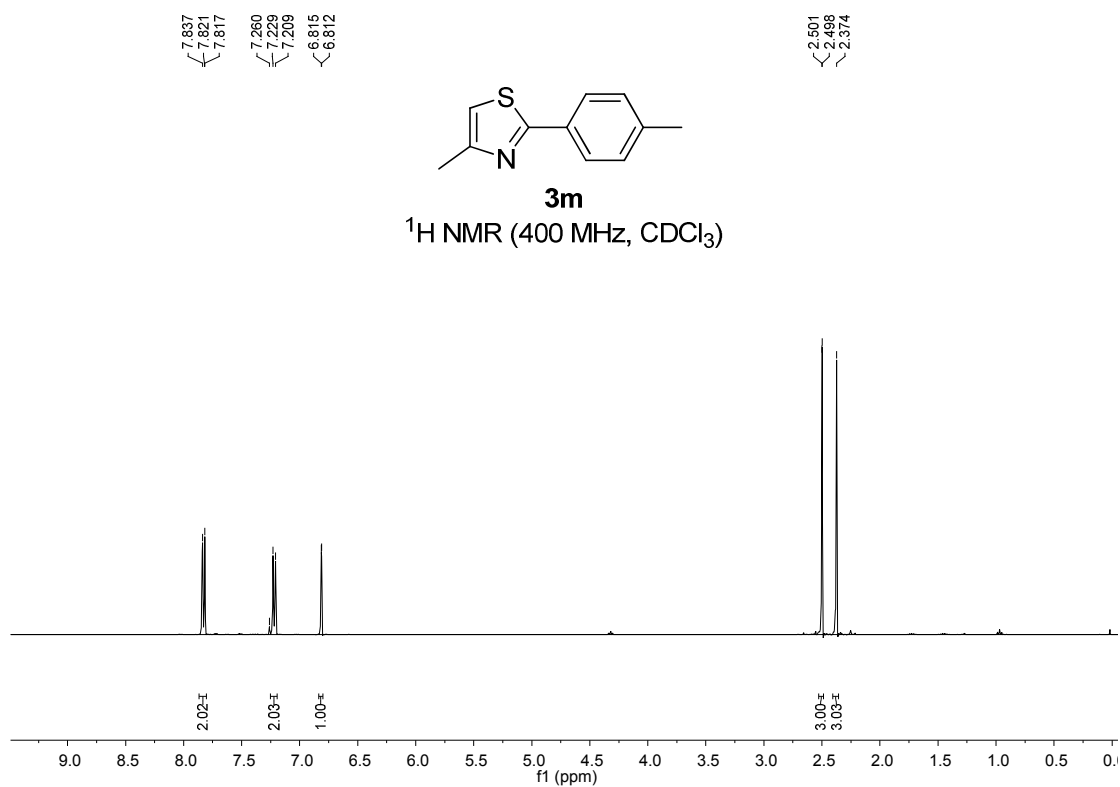


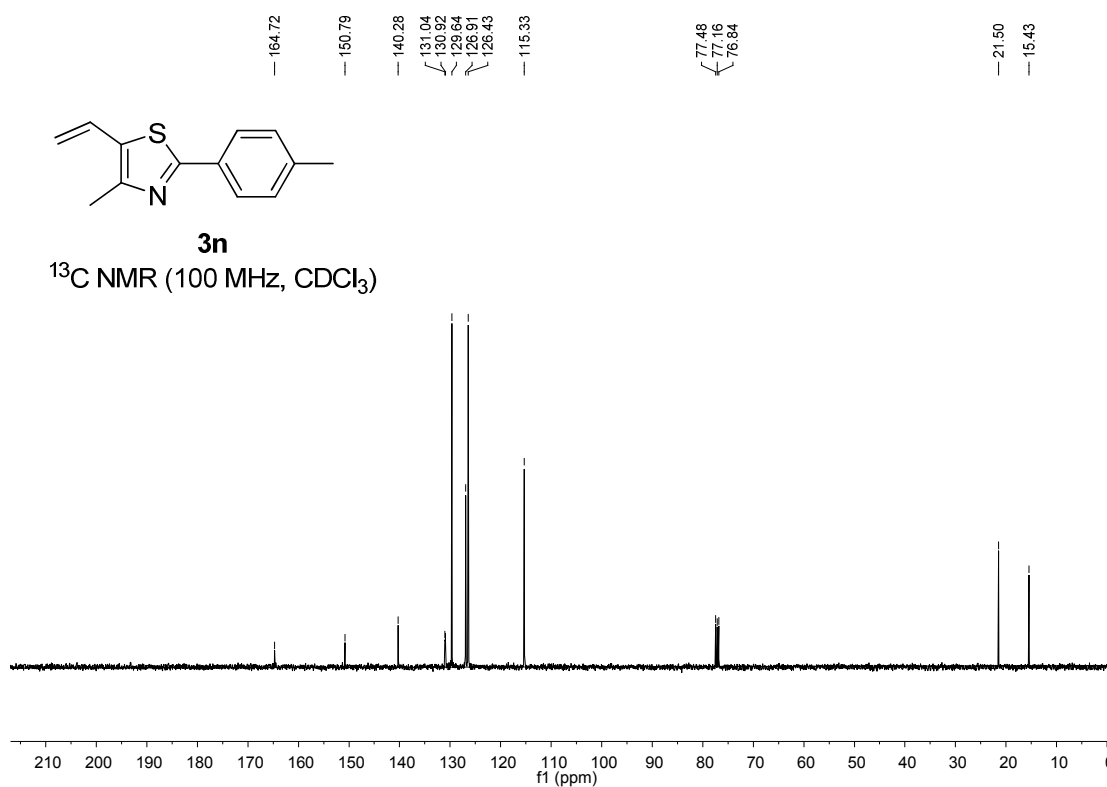
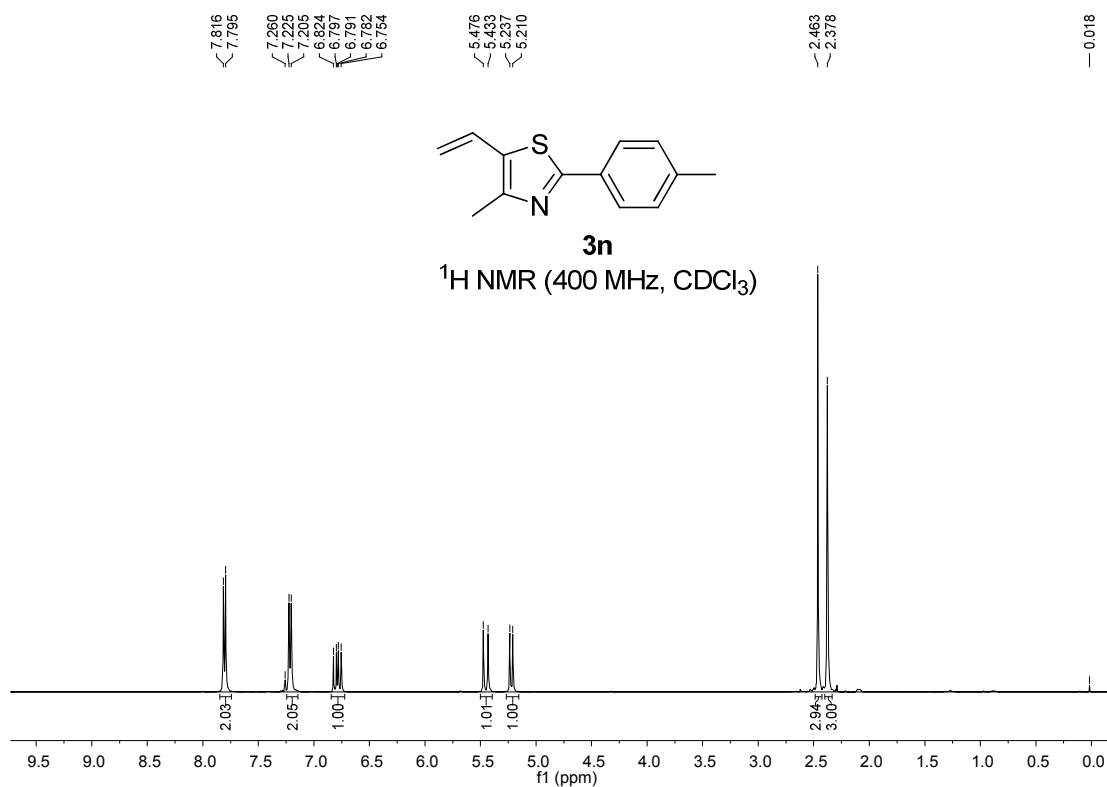












Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

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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)

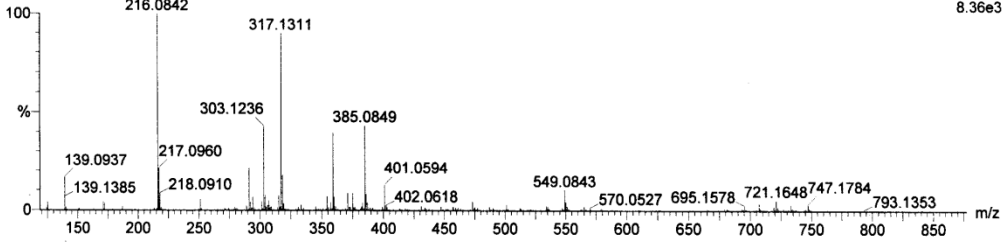
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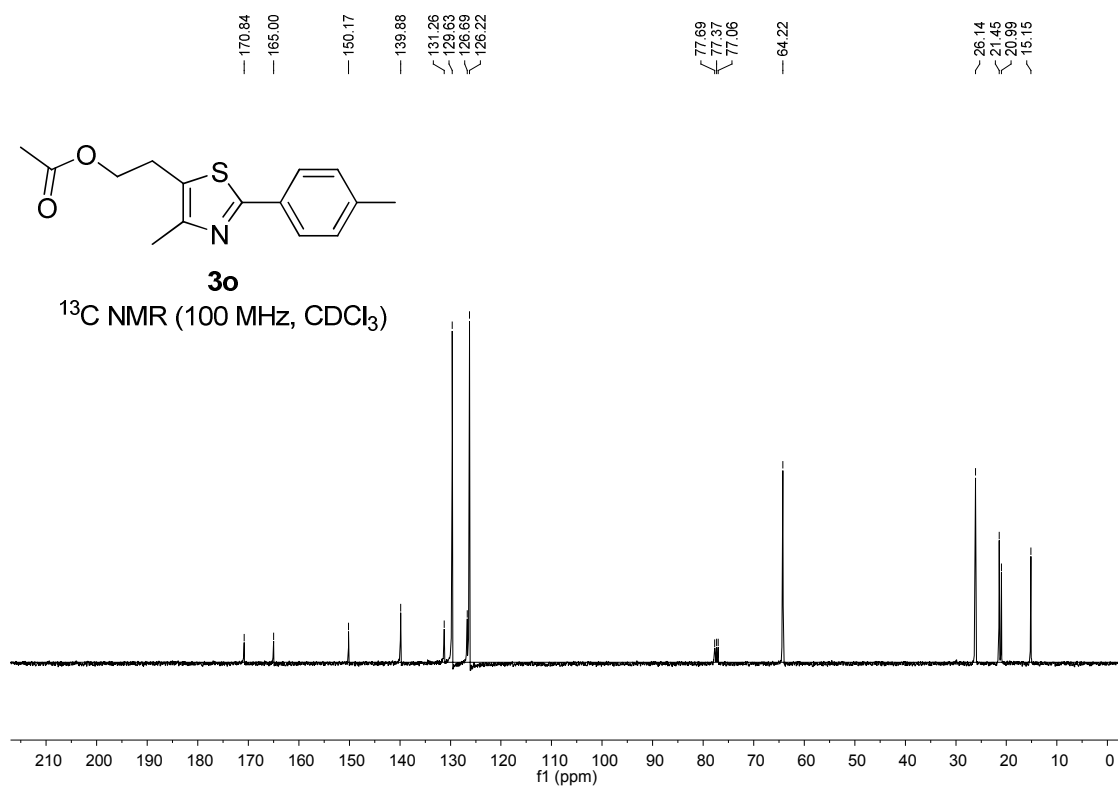
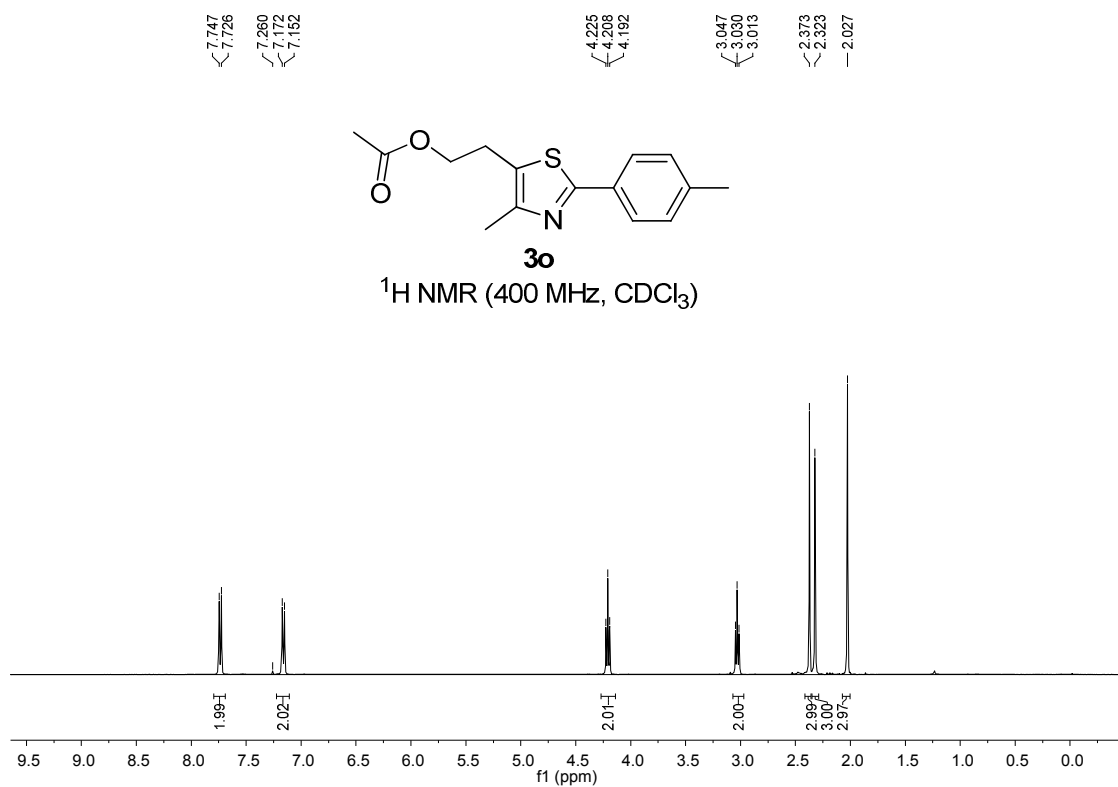
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Maximum: 200.0

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Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

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Monoisotopic Mass, Even Electron Ions

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

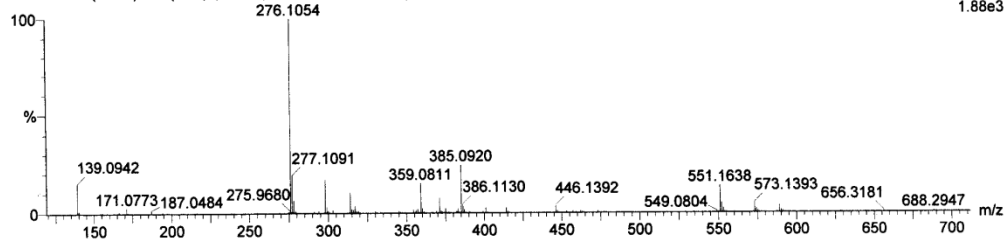
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329BT

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