Supporting Information

Metal-free Photocatalytic Oxidative Coupling of Cyclic Ether and Alcohol

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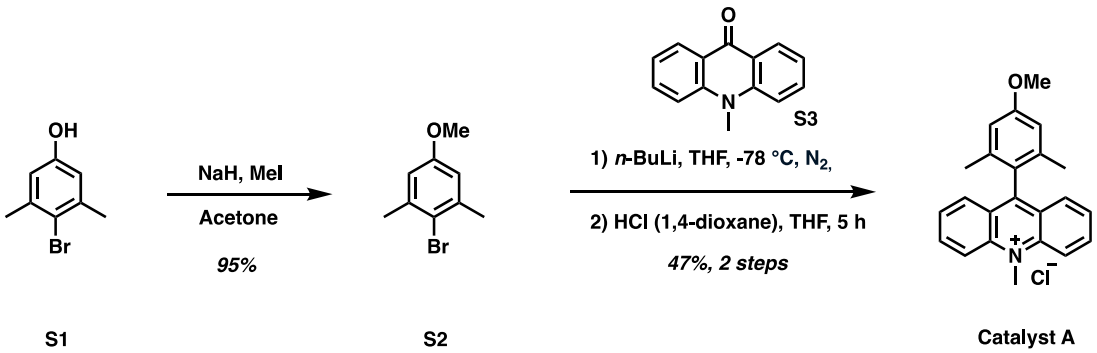
1. General Information

All commercially available chemicals were used without further purification unless otherwise noted. Reactions were monitored by thin layer chromatography using TLC silica gel 60-F_{254} plates. TLC plates were visualized by UV fluorescence (254 nm) or stained by Cerium Molybdate followed by heating. Purification of the reaction products was carried out by column chromatography using Siliaflash-P60 (40-63 µm) silica gel available from Silicycle. ^{1}H-NMR spectra were recorded on a BRUKER AV-500 (500 MHz) and ^{13}C-NMR spectra were recorded on a BRUKER AV-500 (125 MHz). Data for ^{1}H-NMR are recorded as follows: chemical shift (δ, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, q = quartet), coupling constant(s) in Hz and integration. Data for ^{13}C-NMR are reported in terms of chemical shift (δ, ppm). High-resolution mass spectral analysis (HRMS) data were obtained using Agilent Technologies 6530 Accurate Mass Q-TOF LC/MS. Irradiation of photochemical reactions was carried out using two 12W PAR38 Blue LED flood lamps from ABi LED lighting. Yields refer to chromatographically and spectroscopically purified compounds.

2. Experimental Procedures and Characterization Data

Preparation of Acridinium Catalysts



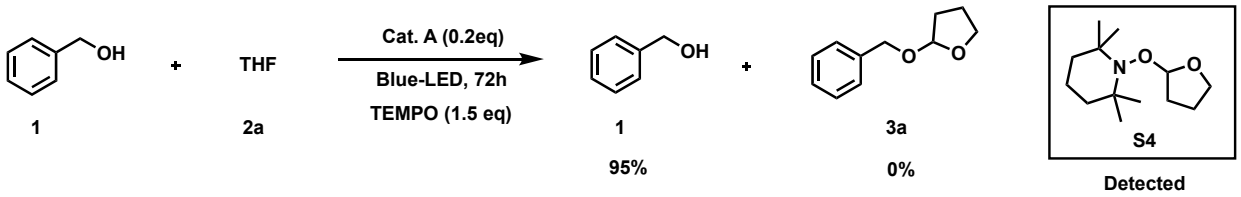
S1 S2 Catalyst A

2-Bromo-5-methoxy-1,3-dimethylbenzene (S2) was prepared according to literature procedure.[1]
To a solution of 2-Bromo-5-methoxy-1,3-dimethylbenzene (5.83 g, 1.0 eq) in anhydrous THF (50 mL) was added *n*-BuLi (11.88 mL, 2.5 M in hexanes, 1.1 eq) dropwise at -78 °C under N_2 atmosphere. The reaction mixture was stirred at -78 °C for 1 hour. Subsequently, 10-methylacridin-9(10H)-one (4.81 g, 0.85 eq) was added, and the reaction was monitored by thin-layer chromatography (TLC) plate. After completion, the reaction was quenched with saturated aqueous $NaHCO_3$, and the mixture was extracted with Ethyl Acetate (3 × 50 mL). The combined organic layers were dried over anhydrous sodium sulfate and concentrated in vacuo. The crude product was purified by flash column chromatograph to afford hydroxy substituted intermediate. Then, the purified intermediate was dissolved in 50 mL anhydrous THF, and HCl (8.6 mL, 4M in 1,4-dioxane, 1.5 eq) was added dropwise. The mixture was stirred at room temperature for 5 hours. The resulting yellow solid was collected by filtration and dried under vacuum to yield the final acridinium catalyst as a yellow powder. [2]

General Procedure:

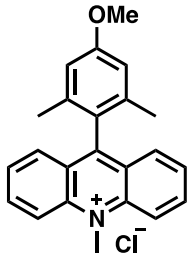
To a 5 mL oven-dried glass vial equipped with a magnetic stir bar, 0.2 mmol of the alcohol and 0.04 mmol of the photocatalyst were added, followed by 2 mL of anhydrous tetrahydrofuran (THF). The vial was capped with a rubber septum, and a needle was inserted to allow air flow. The mixture was stirred continuously under Blue-LED irradiation for three days. Progress of the reaction was monitored periodically by thin-layer chromatography (TLC), using a hexane:ethyl acetate (10:1) solvent system and visualized with cerium ammonium molybdate (CAM) stain. Upon completion, the reaction mixture was concentrated under reduced pressure. The crude product was then purified by flash column chromatography to yield the desired product.

TEMPO Trap Experiment:



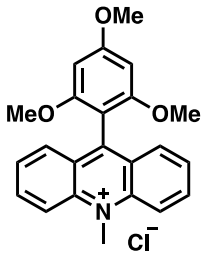
To a 5 mL oven-dried glass vial equipped with a magnetic stir bar, 0.2 mmol of the benzyl alcohol, 0.04 mmol of the photocatalyst A, and 0.3 mmol TEMPO were added, followed by 2 mL of anhydrous tetrahydrofuran (THF). The vial was capped with a rubber septum, and a needle was inserted to allow air flow. The mixture was stirred continuously under Blue-LED irradiation for three days. Progress of the reaction was monitored periodically by thin-layer chromatography (TLC), using a hexane:ethyl acetate (10:1) solvent system and visualized with cerium ammonium molybdate (CAM) stain. A new spot of TEMPO trapped product (S4) was isolated by flash column chromatography and confirmed by ^{1}H-NMR.
TEMPO trapped product (S4)
^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (d, *J* = 5.4 Hz, 1H), 3.93 – 3.78 (m, 2H), 2.04 – 1.91 (m, 3H), 1.78 (dd, *J* = 9.1, 5.1 Hz, 1H), 1.64 – 1.40 (m, 6H), 1.22 (s, 3H), 1.10 (s, 3H), 1.07 (s, 3H), 1.04 (s, 3H).

Catalyst A



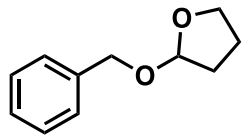
^{1}H NMR (500 MHz, DMSO) δ 8.89 (d, *J* = 9.2 Hz, 2H), 8.49 – 8.42 (m, 2H), 7.93 (dd, *J* = 8.9, 6.4 Hz, 2H), 7.80 (dd, *J* = 8.5, 1.7 Hz, 2H), 7.03 (s, 2H), 4.93 (s, 3H), 3.90 (s, 3H), 1.69 (s, 6H).
^{13}C NMR (126 MHz, DMSO) δ 161.06, 160.68, 141.80, 139.07, 137.79, 128.98, 128.73, 126.23, 125.02, 120.23, 114.03, 55.76, 20.25.
ESI-HRMS calcd for $C_{23}H_{22}NO^{+}$ $[M]^{+}$ 328.1696, found 328.1702.

Catalyst D



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.88 (d, *J* = 9.2 Hz, 2H), 8.37 (t, *J* = 7.1 Hz, 2H), 7.98 (d, *J* = 8.7 Hz, 2H), 7.74 (dd, *J* = 8.8, 6.6 Hz, 2H), 6.38 (s, 2H), 5.22 (s, 3H), 3.98 (s, 3H), 3.57 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 164.14, 158.47, 141.37, 138.95, 129.96, 127.51, 127.12, 119.19, 102.23, 90.99, 67.98, 55.89, 40.13, 25.61.
ESI-HRMS calcd for $C_{23}H_{22}NO_3^{+}$ $[M]^{+}$ 360.1594, found 360.1615.

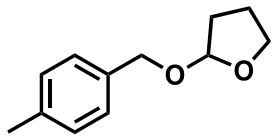
Compound 3a: 2-(benzyloxy)tetrahydrofuran



3a

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 (d, *J* = 4.5 Hz, 4H), 7.29 (t, *J* = 4.4 Hz, 1H), 5.24 – 5.23 (m, 1H), 4.73 (d, *J* = 12.0 Hz, 1H), 4.49 (d, *J* = 11.9 Hz, 1H), 3.99 – 3.89 (m, 2H), 2.08 – 1.86 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 138.39, 128.39, 127.89, 127.52, 103.13, 68.80, 67.05, 32.38, 23.50.

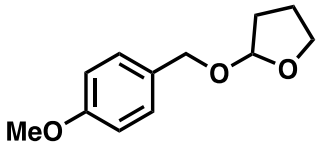
Compound 3b: 2-((4-methylbenzyl)oxy)tetrahydrofuran



3b

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 (d, *J* = 6.1 Hz, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 5.21 (s, 1H), 4.67 (d, *J* = 11.7 Hz, 1H), 4.44 (d, *J* = 11.7 Hz, 1H), 3.99 – 3.85 (m, 2H), 2.34 (s, 3H), 2.05 – 1.82 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.20, 135.28, 129.05, 128.01, 102.96, 68.65, 66.98, 32.34, 23.48, 21.16.

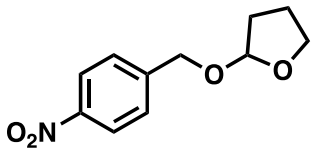
Compound 3c: 2-((4-methoxybenzyl)oxy)tetrahydrofuran



3c

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 6.4 Hz, 2H), 6.87 (d, *J* = 6.6 Hz, 2H), 5.21 (s, 1H), 4.64 (d, *J* = 12.1 Hz, 1H), 4.41 (d, *J* = 11.4 Hz, 1H), 3.92 (dt, *J* = 15.3, 7.8 Hz, 2H), 3.80 (s, 3H), 2.10 – 1.81 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 129.53, 129.44, 113.81, 102.86, 71.48, 68.47, 66.99, 55.30, 32.35, 23.51.

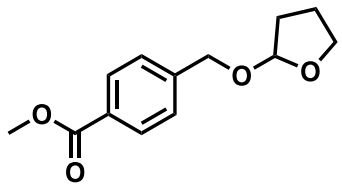
Compound 3d: 2-((4-nitrobenzyl)oxy)tetrahydrofuran



3d

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 6.6 Hz, 2H), 7.49 (d, *J* = 6.7 Hz, 2H), 5.23 (s, 1H), 4.80 (d, *J* = 13.4 Hz, 1H), 4.58 (d, *J* = 15.6 Hz, 1H), 3.94 – 3.90 (m, 2H), 2.07 – 1.88 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 147.27, 146.27, 127.81, 123.58, 103.69, 67.59, 67.33, 32.43, 23.44.

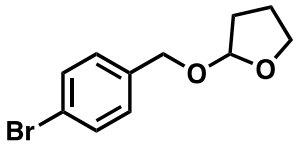
Compound 3e: methyl 4-(((tetrahydrofuran-2-yl)oxy)methyl)benzoate



3e

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 6.3 Hz, 2H), 7.40 (d, *J* = 6.6 Hz, 2H), 5.22 (s, 1H), 4.76 (d, *J* = 12.8 Hz, 1H), 4.53 (d, *J* = 12.7 Hz, 1H), 3.95 – 3.90 (m, 2H), 3.91 (s, 3H), 2.06 – 1.86 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.02, 143.83, 129.68, 129.21, 127.30, 103.45, 77.28, 77.23, 77.03, 76.77, 68.18, 67.17, 52.08, 32.40, 23.46.

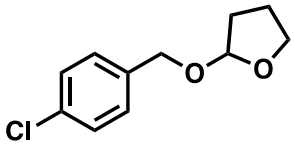
Compound 3f: 2-((4-bromobenzyl)oxy)tetrahydrofuran



3f

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.4 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.20 (s, 1H), 4.65 (d, *J* = 9.6 Hz, 1H), 4.43 (d, *J* = 12.1 Hz, 1H), 3.91 (q, *J* = 8.7 Hz, 2H), 2.04 – 1.82 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 137.47, 131.45, 129.46, 121.34, 103.21, 68.02, 67.12, 32.37, 23.46.

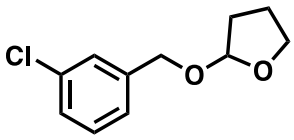
Compound 3g: 2-((4-chlorobenzyl)oxy)tetrahydrofuran



3g

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 6.3 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 2H), 5.19 (s, 1H), 4.67 (d, *J* = 14.5 Hz, 1H), 4.44 (d, *J* = 12.1 Hz, 1H), 3.94 – 3.89 (m, 2H), 2.06 – 1.84 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.94, 133.22, 129.13, 128.50, 103.20, 68.00, 67.11, 32.37, 23.46.

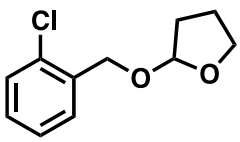
Compound 3h: 2-((3-chlorobenzyl)oxy)tetrahydrofuran



3h

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.20 (d, *J* = 7.9 Hz, 2H), 5.20 (s, 1H), 4.68 (d, *J* = 12.2 Hz, 1H), 4.45 (d, *J* = 12.4 Hz, 1H), 3.96 – 3.88 (m, 2H), 2.07 – 1.83 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 140.58, 134.27, 129.60, 127.75, 127.57, 125.70, 103.30, 67.98, 67.15, 32.38, 23.45.

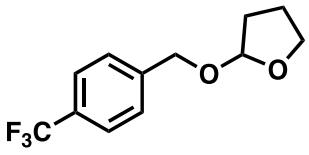
Compound 3i: 2-((2-chlorobenzyl)oxy)tetrahydrofuran



3i

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 7.6 Hz, 1H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.29 – 7.18 (m, 2H), 5.27 (s, 1H), 4.81 (d, *J* = 13.0 Hz, 1H), 4.58 (d, *J* = 13.0 Hz, 1H), 3.98 – 3.91 (m, 2H), 2.10 – 1.87 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.21, 133.08, 129.28, 129.18, 128.56, 126.69, 103.64, 67.19, 66.08, 32.41, 23.45.

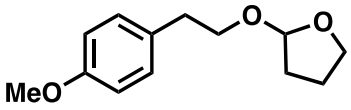
Compound 3j: 2-((4-(trifluoromethyl)benzyl)oxy)tetrahydrofuran



3j

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.9 Hz, 2H), 7.45 (d, *J* = 7.7 Hz, 2H), 5.22 (s, 1H), 4.76 (d, *J* = 12.5 Hz, 1H), 4.53 (d, *J* = 12.5 Hz, 1H), 3.92 (q, *J* = 6.9 Hz, 2H), 2.07 – 1.86 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 142.62, 129.76, 129.51, 127.69, 125.32, 125.29, 125.26, 125.23, 123.13, 103.43, 67.98, 67.19, 32.39, 23.44.
^{19}F NMR (471 MHz, $CDCl_3$) δ -62.50.

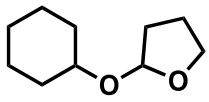
Compound 3k: 2-(4-methoxyphenethoxy)tetrahydrofuran



3k

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, *J* = 6.7 Hz, 2H), 6.83 (d, *J* = 8.7 Hz, 2H), 5.11 (s, 1H), 3.83 (t, *J* = 7.9 Hz, 3H), 3.79 (s, 3H), 3.57 (q, *J* = 8.4 Hz, 1H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.00 – 1.78 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 158.01, 131.19, 129.84, 113.71, 103.81, 68.20, 66.88, 55.26, 35.47, 32.37, 23.49.

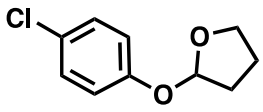
Compound 3l: 2-(cyclohexyloxy)tetrahydrofuran



3l

^{1}H NMR (500 MHz, $CDCl_3$) δ 5.28 (d, *J* = 5.0 Hz, 1H), 3.89 (q, *J* = 7.1 Hz, 1H), 3.86 – 3.81 (m, 1H), 3.52 (hept, *J* = 4.1 Hz, 1H), 2.06 – 1.85 (m, 4H), 1.84 – 1.70 (m, 4H), 1.34 – 1.12 (m, 6H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 101.71, 74.63, 66.55, 33.99, 32.61, 32.07, 25.75, 24.51, 24.37, 23.59.

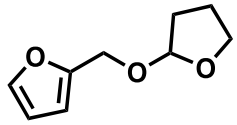
Compound 3m: 2-(4-chlorophenoxy)tetrahydrofuran



3m

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 4.9 Hz, 2H), 6.96 (d, *J* = 6.6 Hz, 2H), 5.74 (s, 1H), δ 3.99 (dq, *J* = 43.8, 8.4 Hz, 2H), 2.19 – 1.91 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 155.81, 129.26, 126.46, 117.90, 102.60, 68.14, 32.70, 23.38.

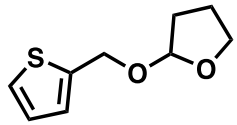
Compound 3n: 2-(((tetrahydrofuran-2-yl)oxy)methyl)furan



3n

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 1.9, 0.9 Hz, 1H), 6.38 – 6.25 (m, 2H), 5.21 (t, *J* = 3.1 Hz, 1H), 4.60 (d, *J* = 12.8 Hz, 1H), 4.45 (d, *J* = 12.8 Hz, 1H), 3.91 (dtd, *J* = 22.1, 8.0, 6.0 Hz, 2H), 2.03 – 1.81 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 151.77, 142.78, 110.25, 109.16, 102.72, 67.10, 60.57, 32.28, 23.39.

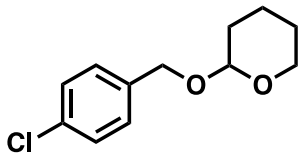
Compound 3o: 2-(thiophen-2-ylmethoxy)tetrahydrofuran



3o

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (d, *J* = 5.0 Hz, 1H), 7.01 (d, *J* = 3.6 Hz, 1H), 6.96 (dd, *J* = 5.1, 3.4 Hz, 1H), 5.24 (t, *J* = 3.2 Hz, 1H), 4.83 (d, *J* = 12.4 Hz, 1H), 4.68 (d, *J* = 12.5 Hz, 1H), 3.93 (dtd, *J* = 27.4, 8.0, 5.9 Hz, 2H), 2.06 – 1.83 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 141.10, 126.67, 126.41, 125.74, 102.60, 67.15, 63.13, 32.33, 23.43.

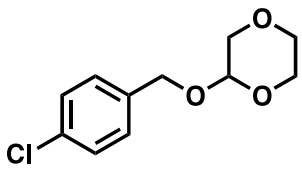
Compound 3p: 2-((4-chlorobenzyl)oxy)tetrahydro-2*H*-pyran



3p

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 1.7 Hz, 4H), 4.75 (d, *J* = 12.2 Hz, 1H), 4.69 (t, *J* = 3.6 Hz, 1H), 4.47 (d, *J* = 12.2 Hz, 1H), 3.90 (ddd, *J* = 11.3, 8.3, 2.8 Hz, 1H), 3.54 (dq, *J* = 10.6, 3.5 Hz, 1H), 1.86 (qt, *J* = 8.1, 3.9 Hz, 1H), 1.74 (tt, *J* = 9.6, 3.5 Hz, 1H), 1.68 – 1.53 (m, 4H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.84, 133.25, 129.11, 128.51, 97.83, 68.06, 62.19, 30.54, 25.45, 19.34.

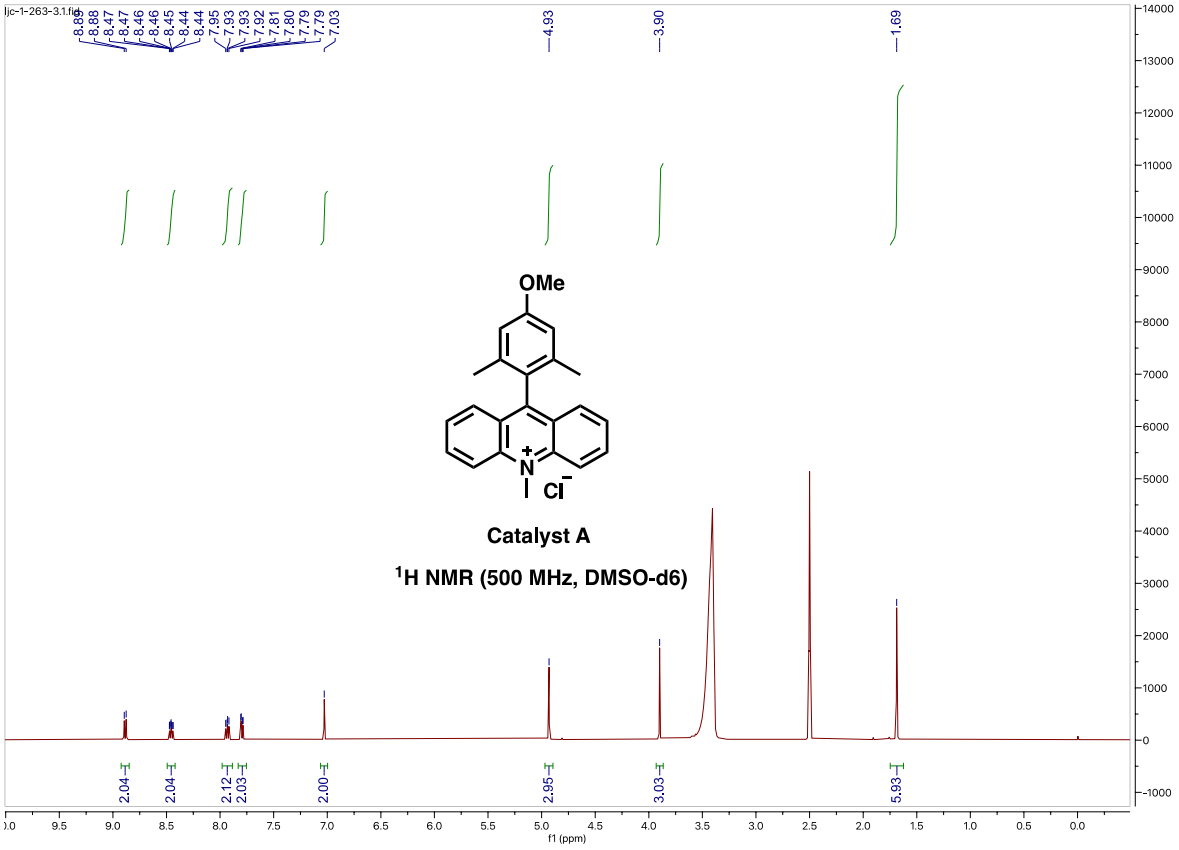
Compound 3q: 2-((4-chlorobenzyl)oxy)-1,4-dioxane

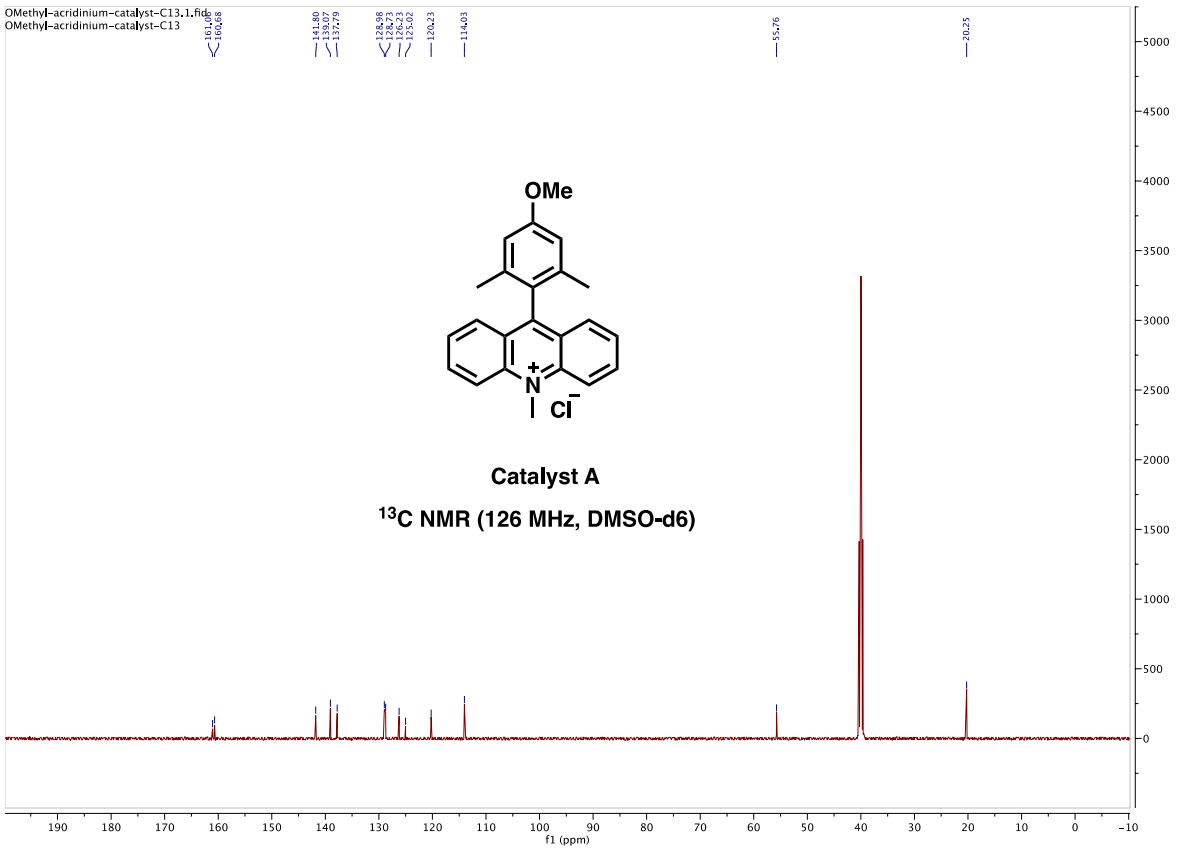


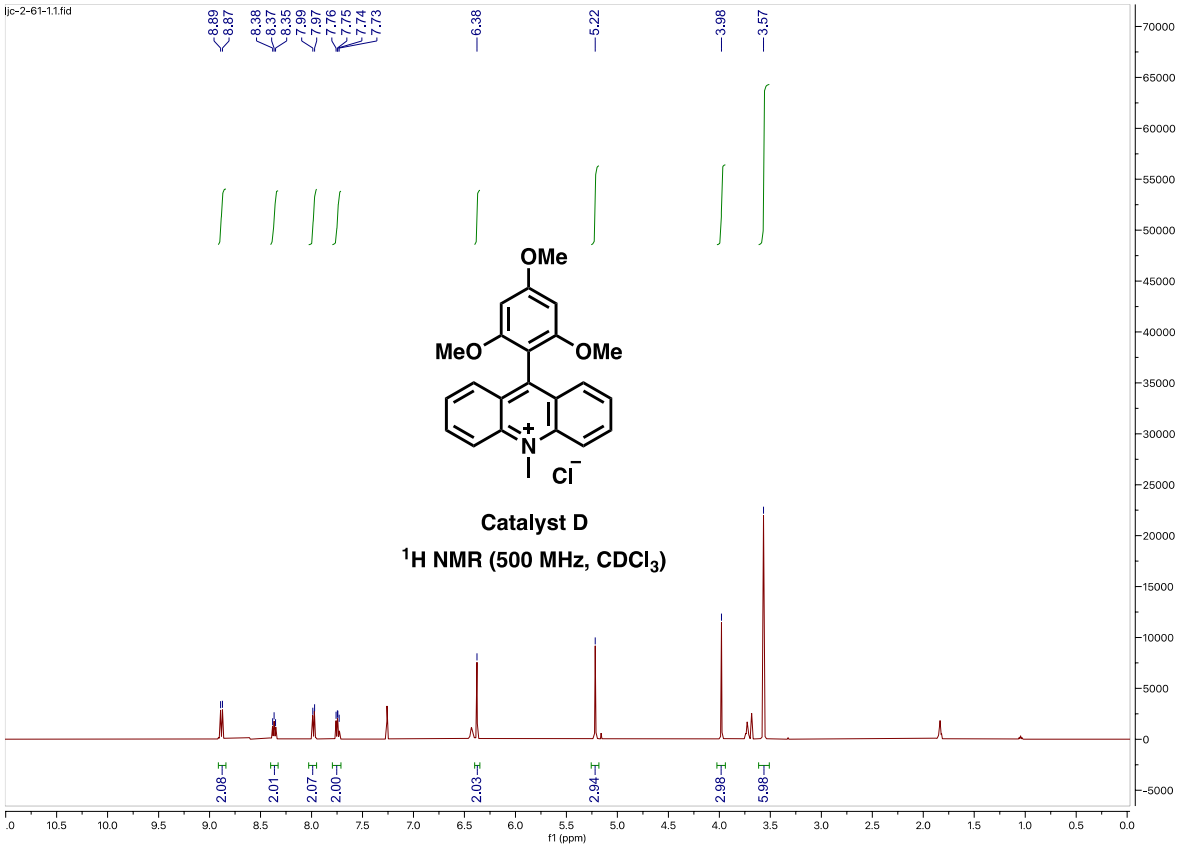
3q

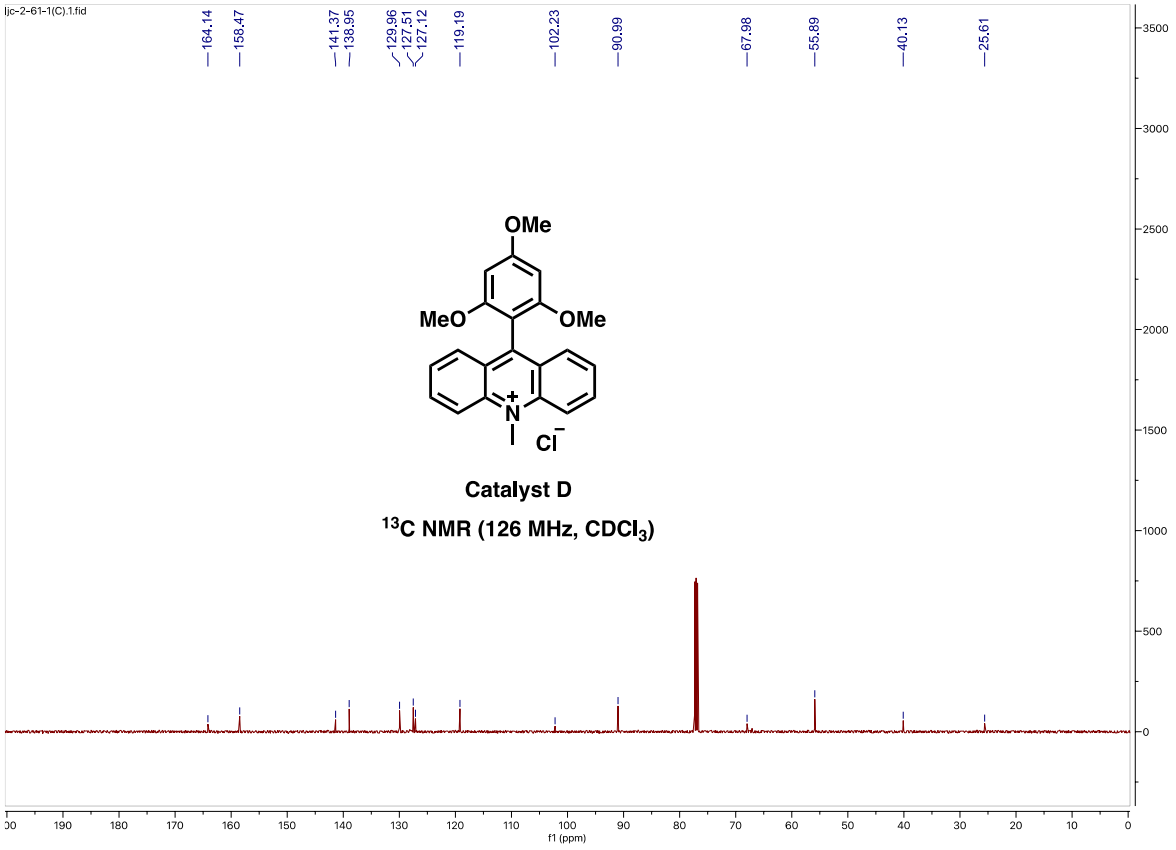
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31 (d, *J* = 3.2 Hz, 4H), 4.80 (d, *J* = 12.1 Hz, 1H), 4.61 (t, *J* = 2.9 Hz, 1H), 4.54 (d, *J* = 12.2 Hz, 1H), 4.07 (ddd, *J* = 11.2, 6.9, 3.6 Hz, 1H), 3.75 – 3.66 (m, 3H), 3.64 – 3.55 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 136.01, 133.60, 129.32, 128.61, 94.72, 68.85, 68.53, 66.21, 61.52.

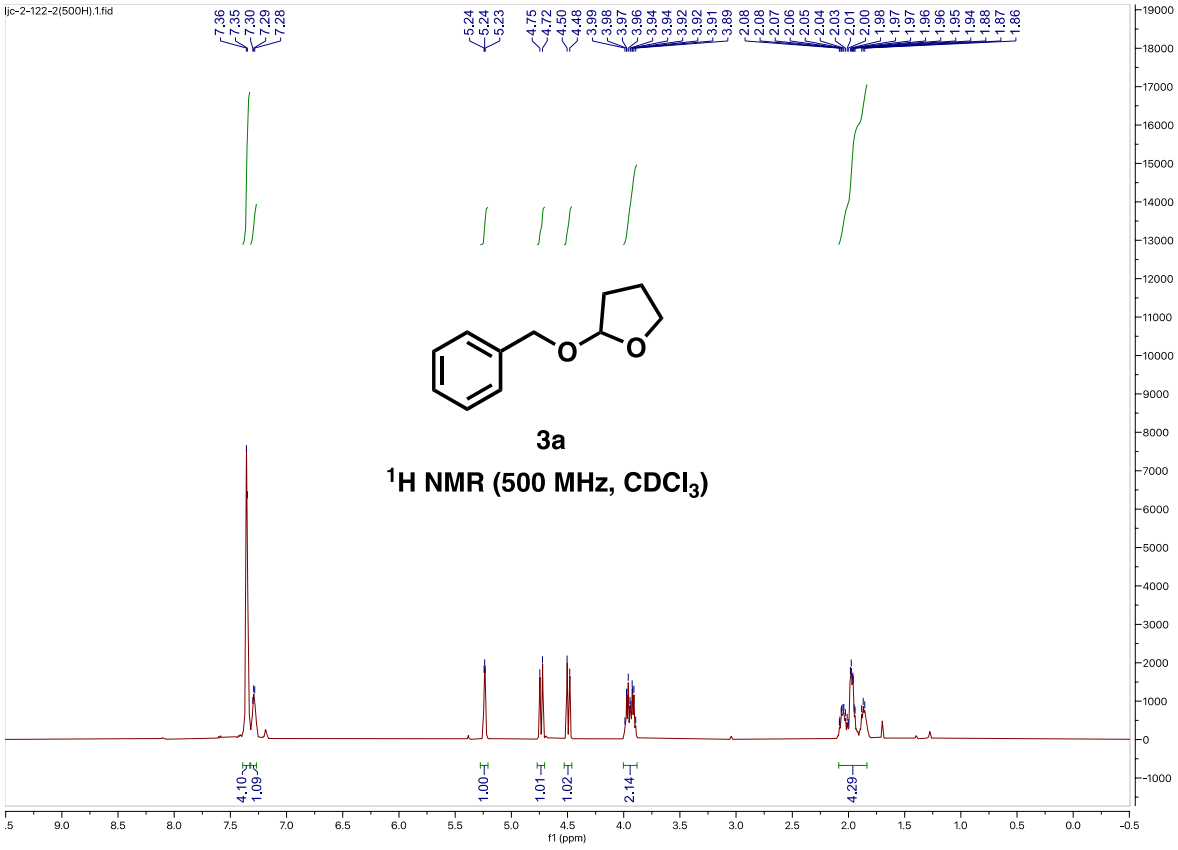
3. Copies of Related NMR Spectra

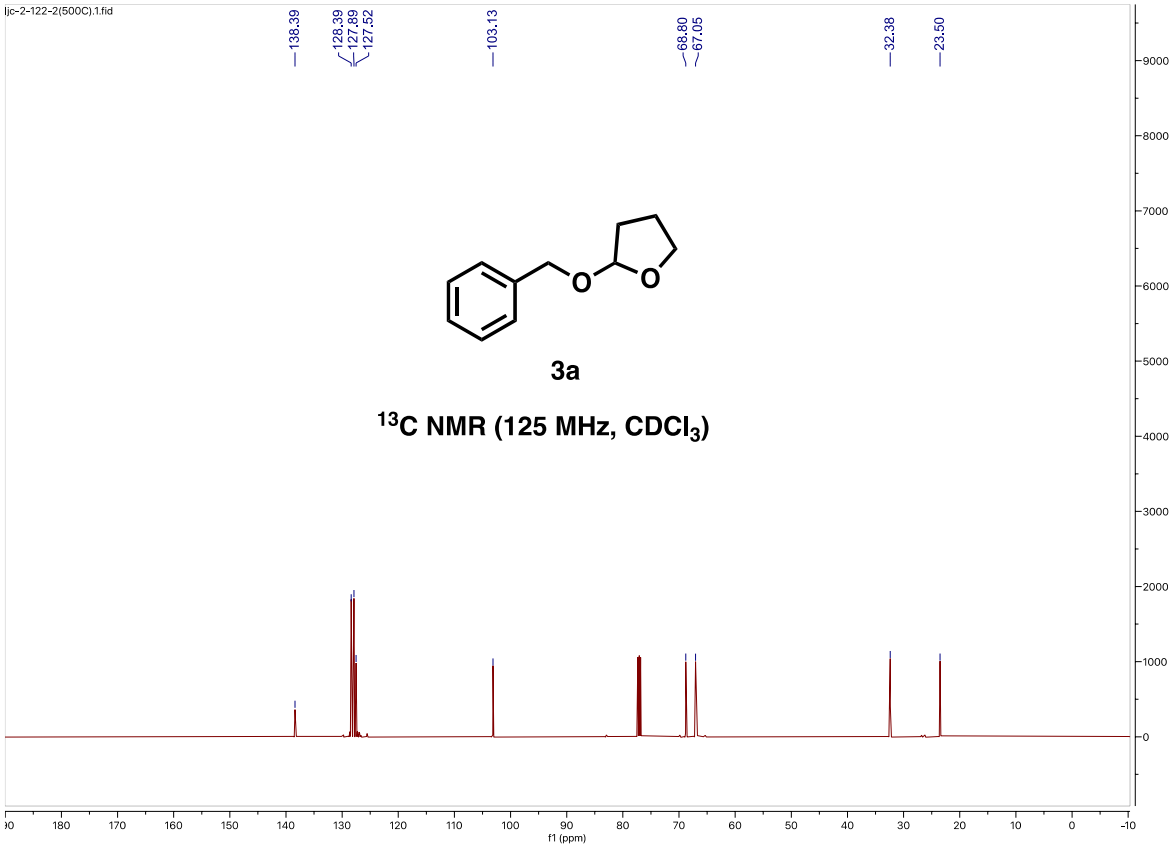



OMethyl-acridinium-catalyst-C13.1.fid
OMethyl-acridinium-catalyst-C13
161.08
160.68
141.80
139.07
137.79
128.98
128.73
126.23
125.02
120.23
114.03
55.76
20.25
OMe
N
Cl
Catalyst A
13C NMR (126 MHz, DMSO-d6)
f1 (ppm)


ljc-2-61-1.1.fid
8.89
8.87
8.38
8.37
8.35
7.99
7.97
7.76
7.75
7.74
7.73
6.38
5.22
3.98
3.57
OMe
MeO
OMe
N
Cl⁻
Catalyst D
¹H NMR (500 MHz, CDCl₃)
2.08
2.01
2.07
2.00
2.03
2.94
2.98
5.98
f1 (ppm)

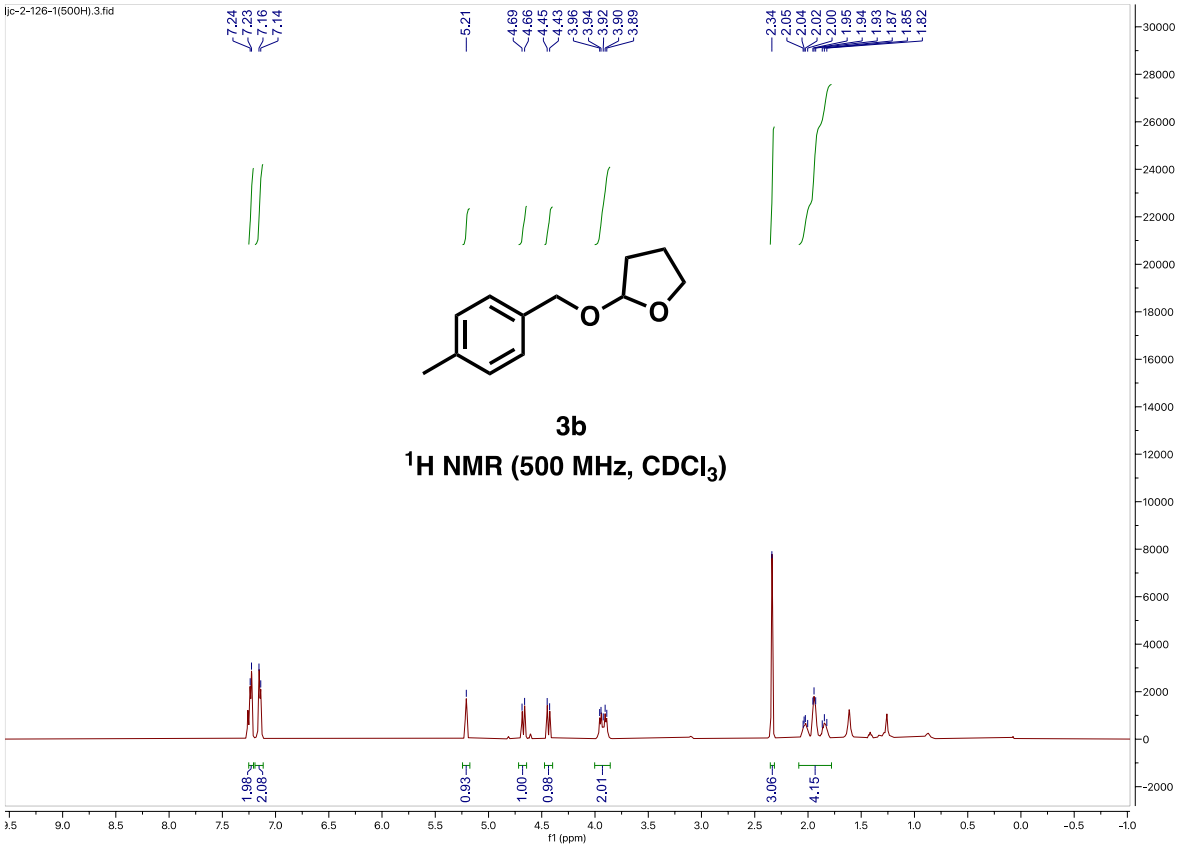

ljc-2-61-1(C).1.fid
164.14
158.47
141.37
138.95
129.96
127.51
127.12
119.19
102.23
90.99
67.98
55.89
40.13
25.61
OMe
MeO
OMe
N
Cl
Catalyst D
13C NMR (126 MHz, CDCl3)
f1 (ppm)


ljc-2-122-2(500H).1.fid
7.36
7.35
7.30
7.29
7.28
5.24
5.24
5.23
4.75
4.72
4.50
4.48
3.99
3.98
3.97
3.96
3.94
3.94
3.92
3.92
3.91
3.89
2.08
2.08
2.07
2.06
2.05
2.04
2.03
2.01
2.00
1.98
1.97
1.97
1.96
1.96
1.95
1.94
1.88
1.87
1.86
O
O
3a
1H NMR (500 MHz, CDCl3)
4.10
1.09
1.00
1.01
1.02
2.14
4.29
f1 (ppm)



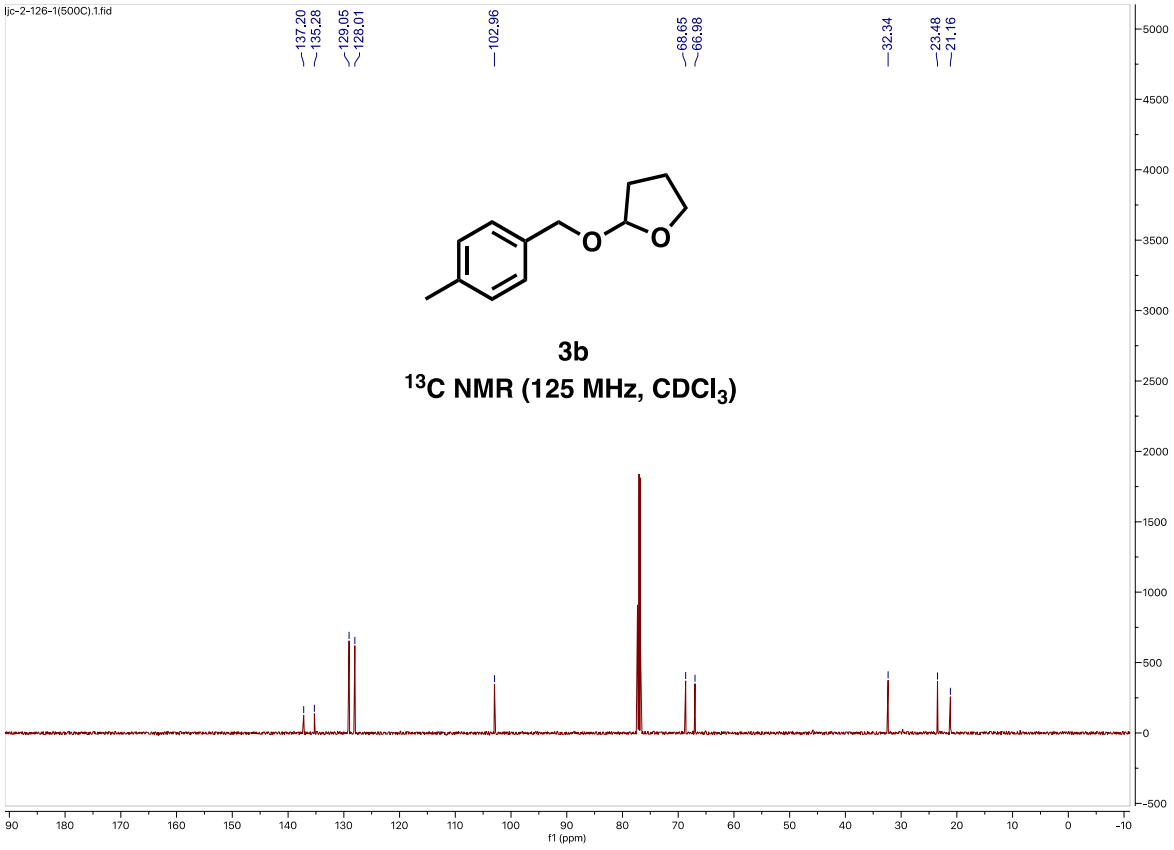
3a

^{13}C NMR (125 MHz, $CDCl_3$)



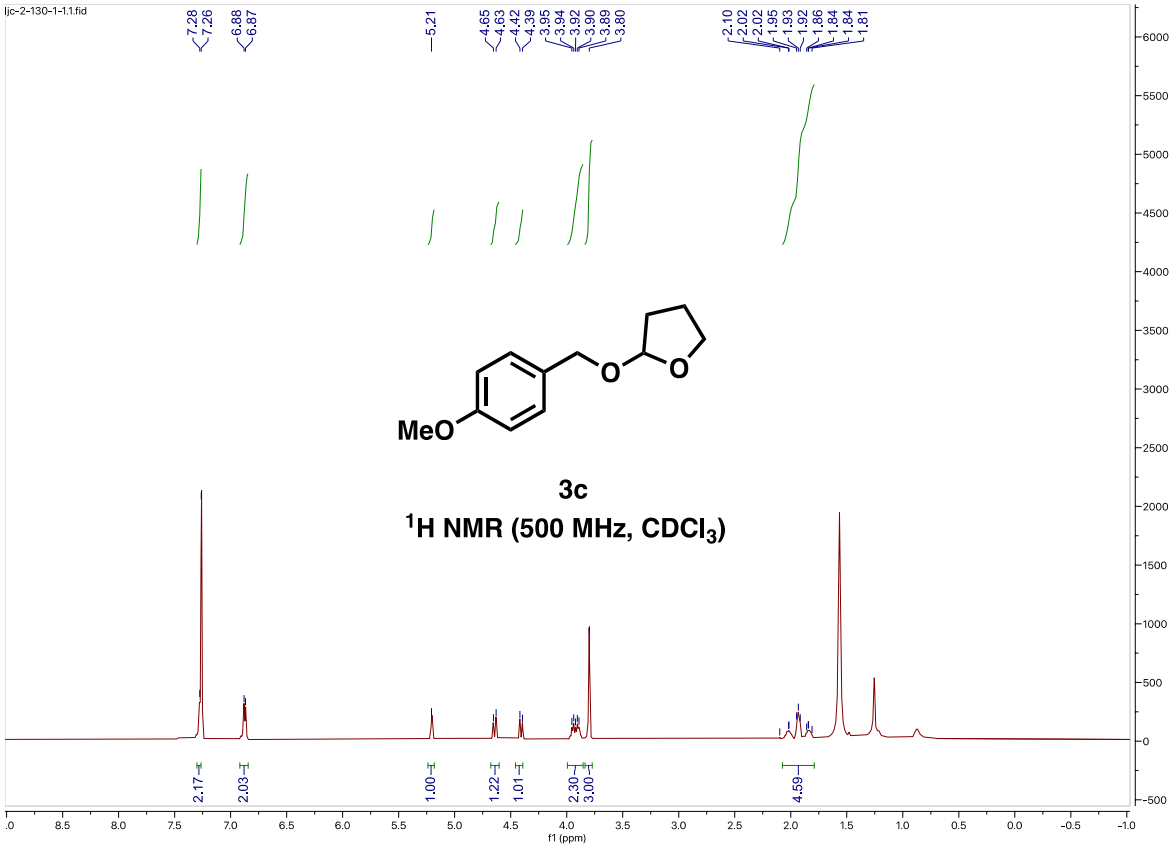
3b

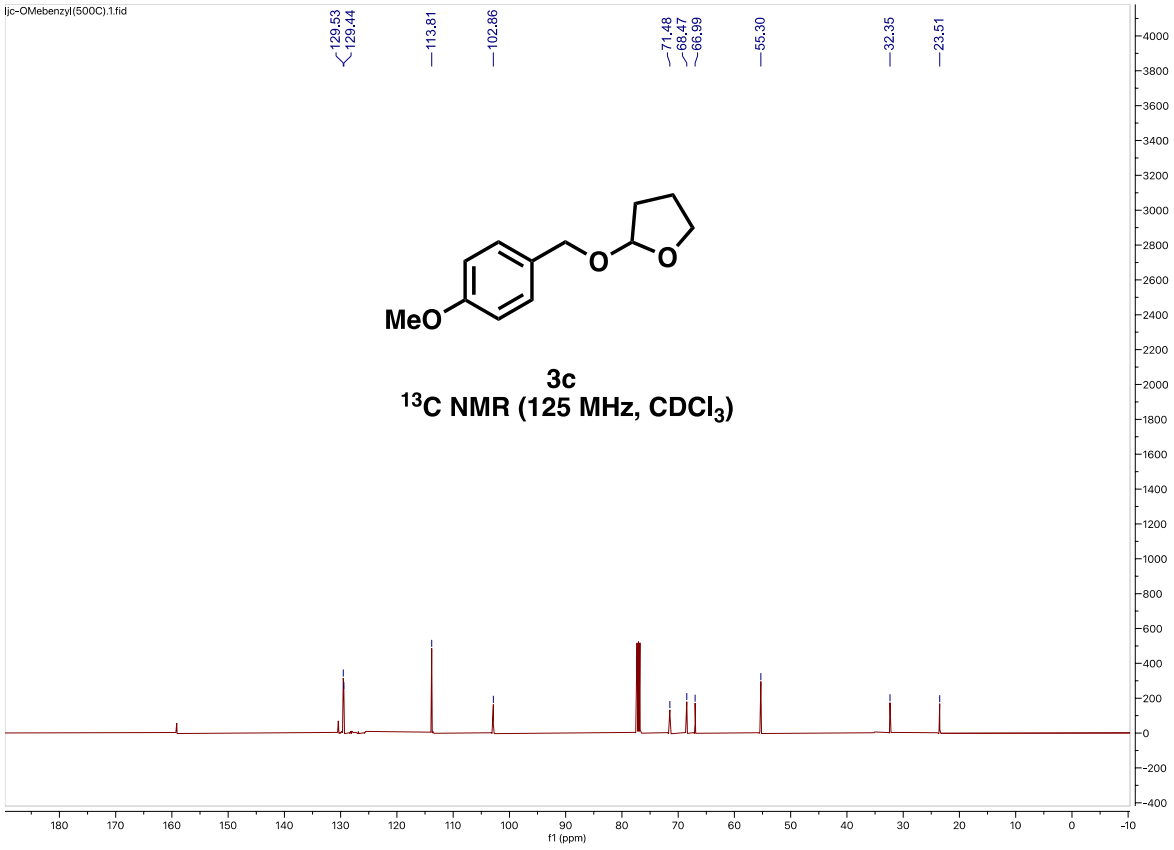
^{1}H NMR (500 MHz, $CDCl_3$)



3b

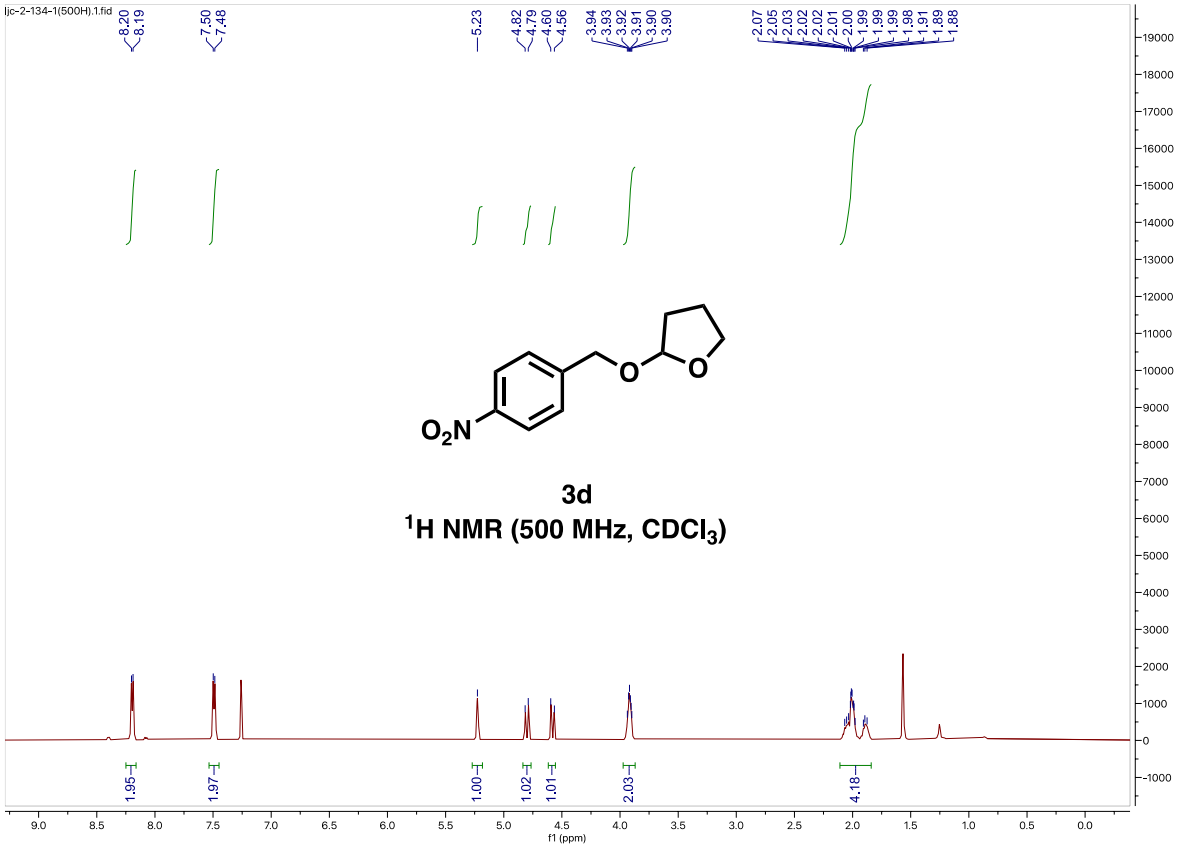
^{13}C NMR (125 MHz, $CDCl_3$)


ljc-2-130-1-1.1.fid
7.28
7.26
6.88
6.87
5.21
4.65
4.63
4.42
4.39
3.95
3.94
3.92
3.90
3.89
3.80
2.10
2.02
2.02
1.95
1.93
1.92
1.86
1.84
1.84
1.81
MeO
O
O
3c
1H NMR (500 MHz, CDCl3)
2.17
2.03
1.00
1.22
1.01
2.30
3.00
4.59
f1 (ppm)



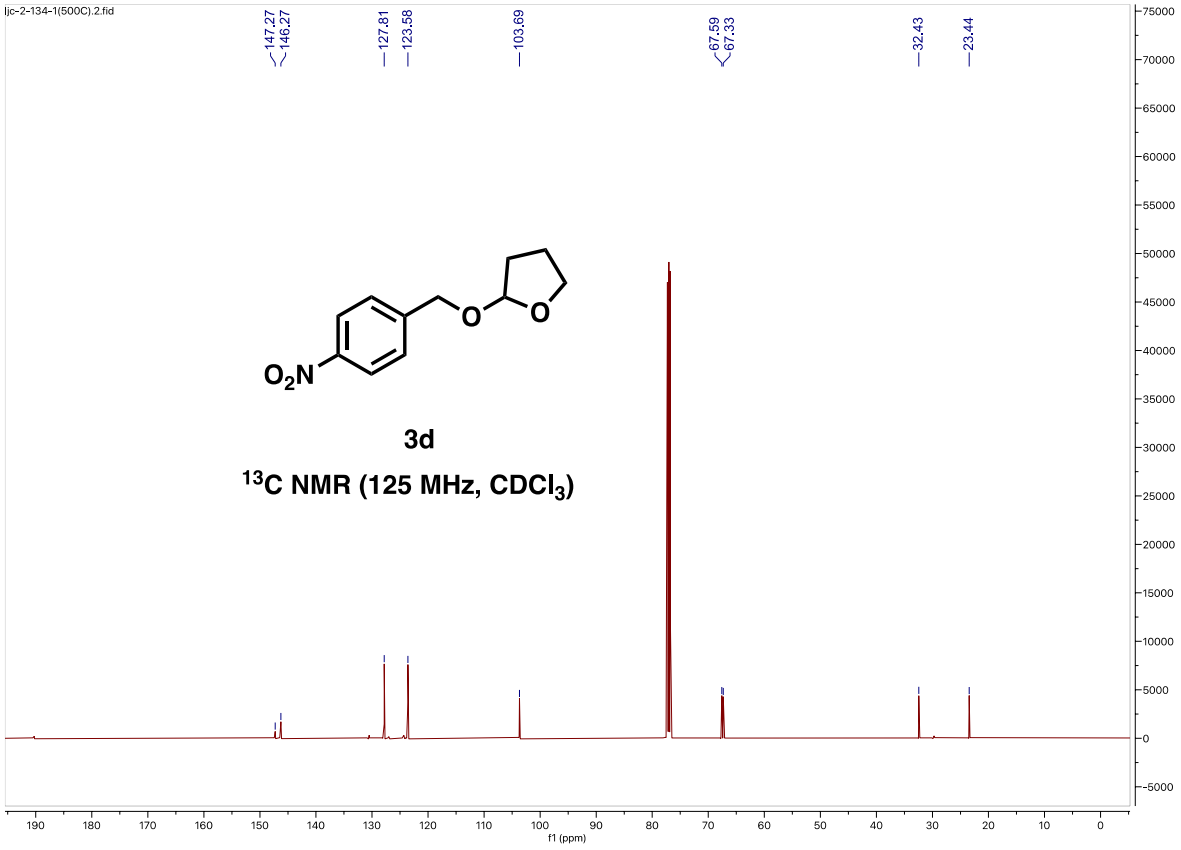
3c

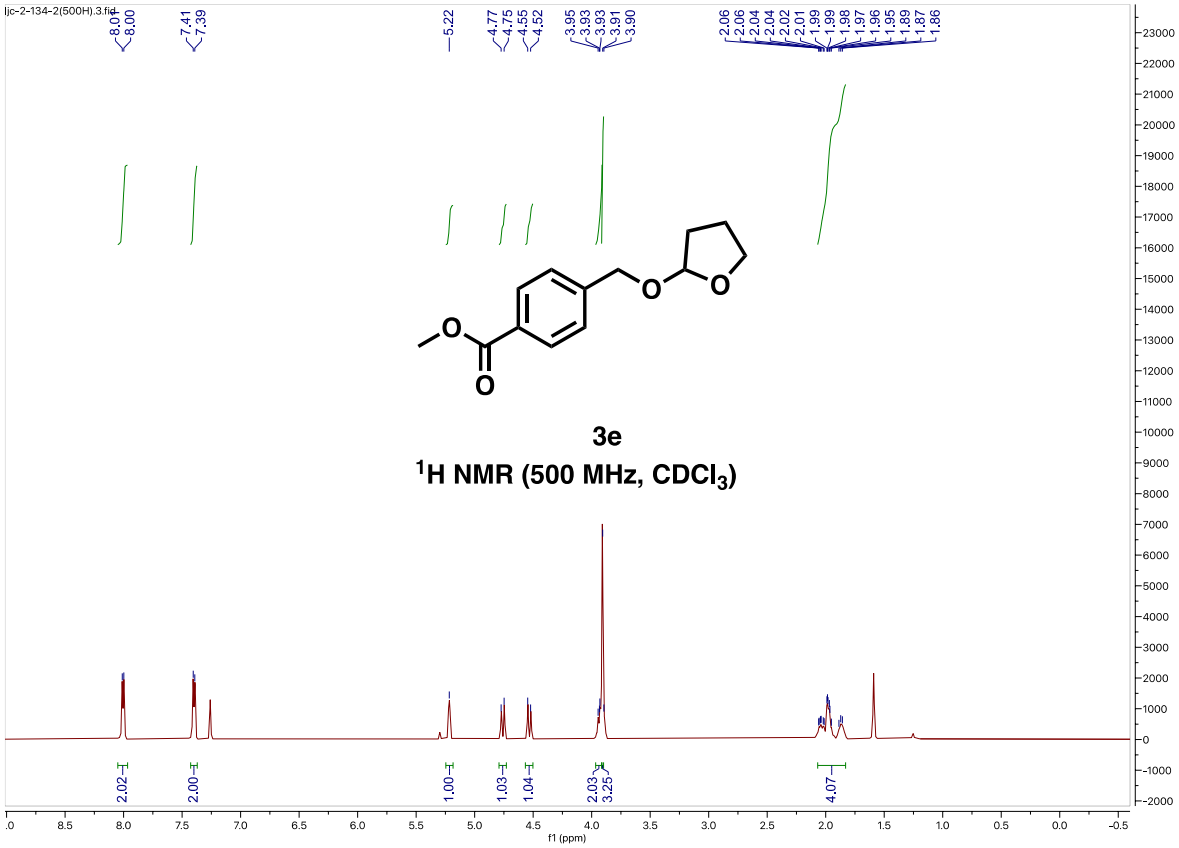
^{13}C NMR (125 MHz, $CDCl_3$)



3d

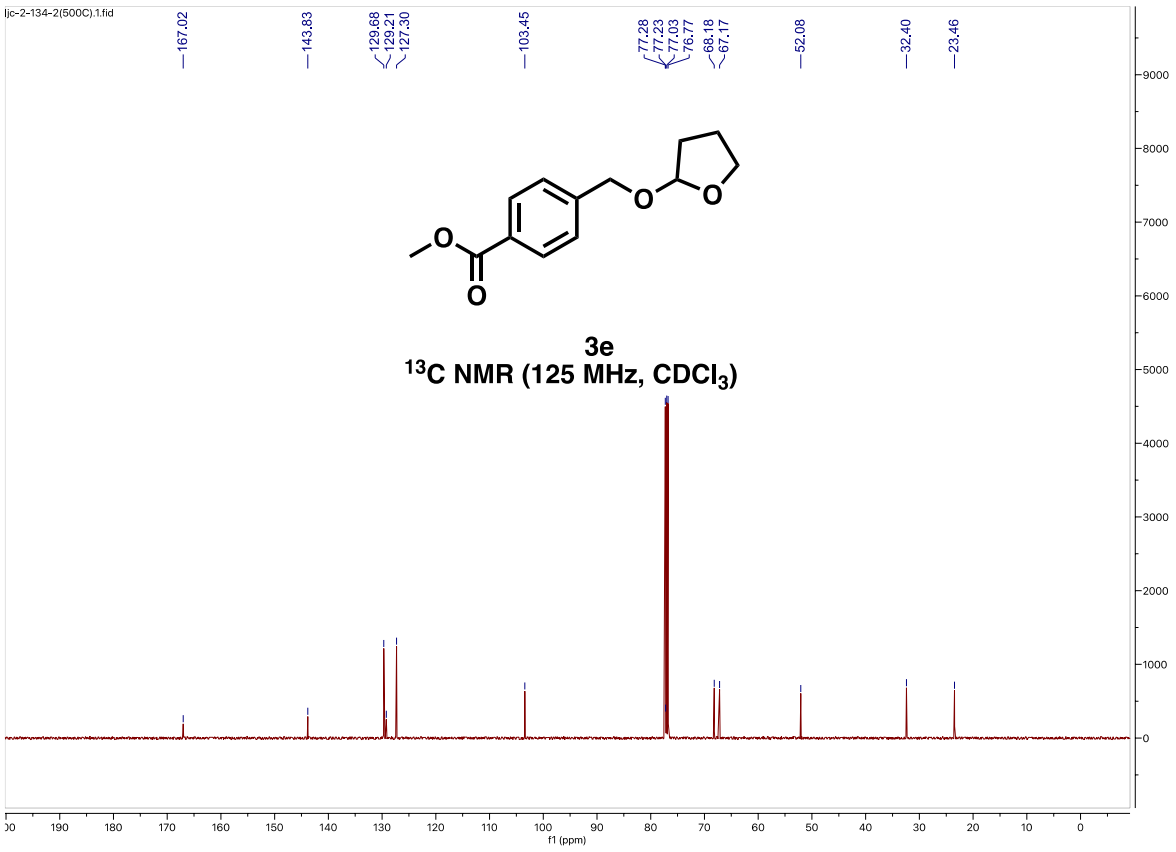
^{1}H NMR (500 MHz, $CDCl_3$)


ljc-2-134-1(500C).2.fid
147.27
146.27
127.81
123.58
103.69
67.59
67.33
32.43
23.44
O2N
O
O
3d
13C NMR (125 MHz, CDCl3)
f1 (ppm)



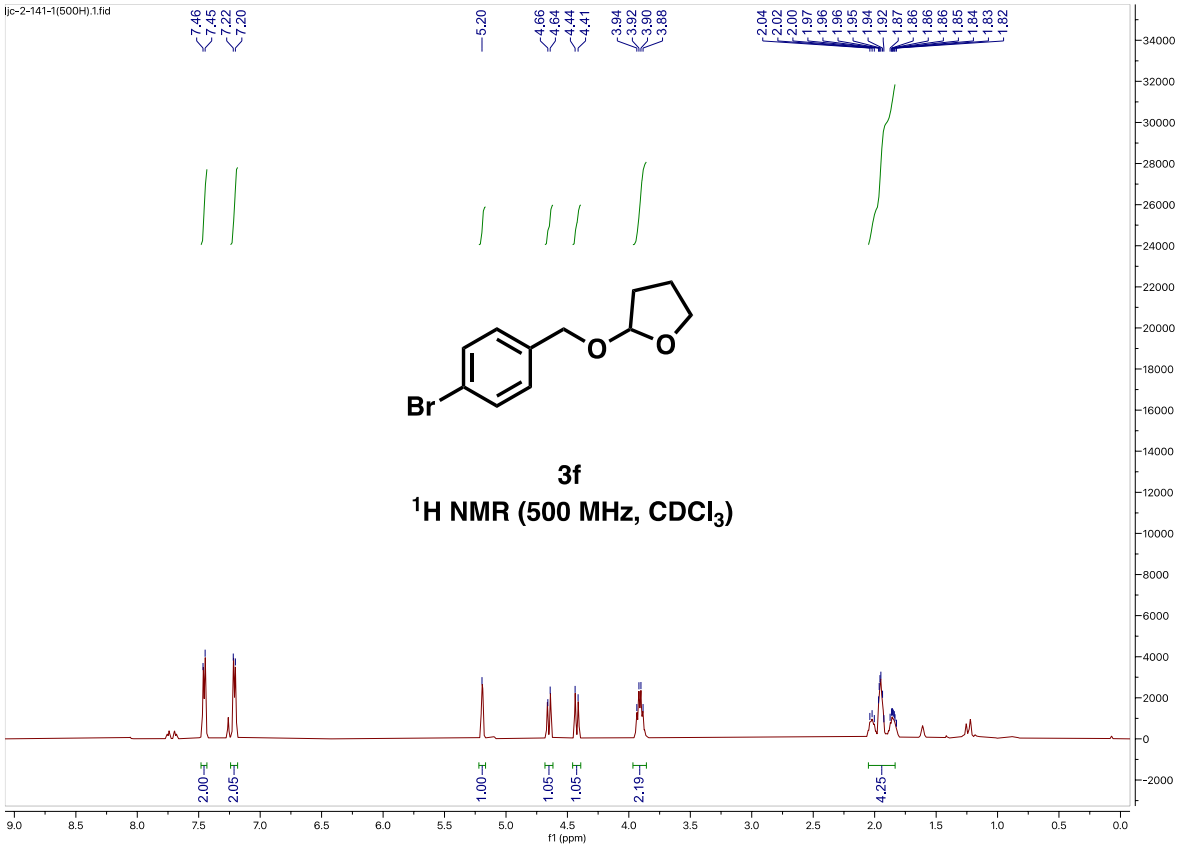
3e

^{1}H NMR (500 MHz, $CDCl_3$)



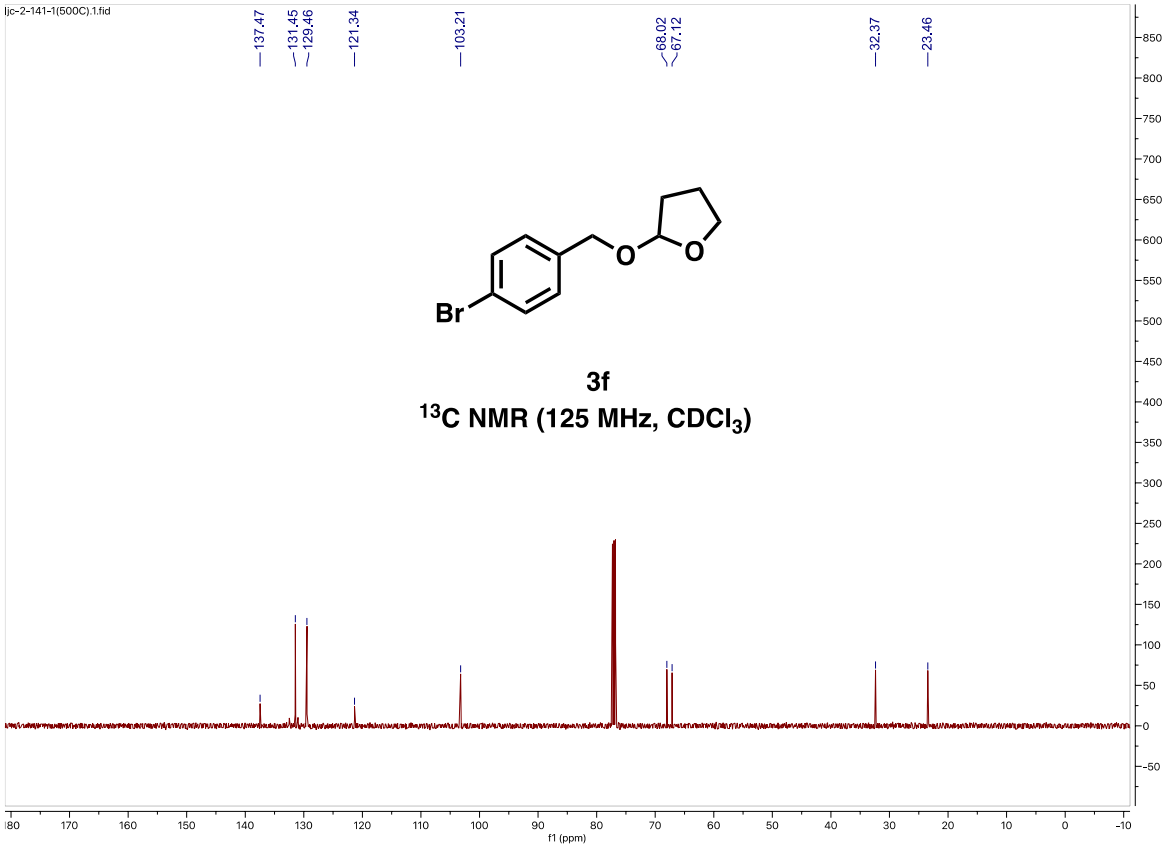
3e

^{13}C NMR (125 MHz, $CDCl_3$)



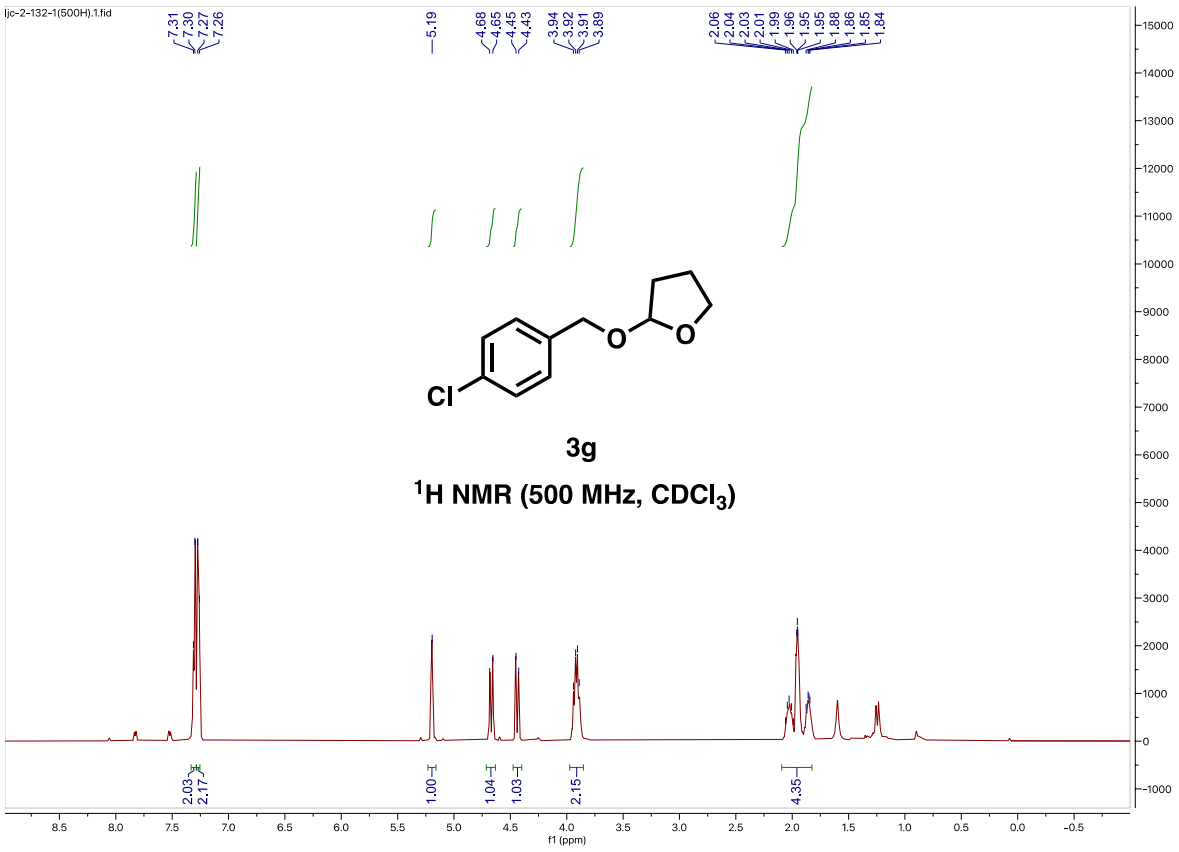
3f

^{1}H NMR (500 MHz, $CDCl_3$)



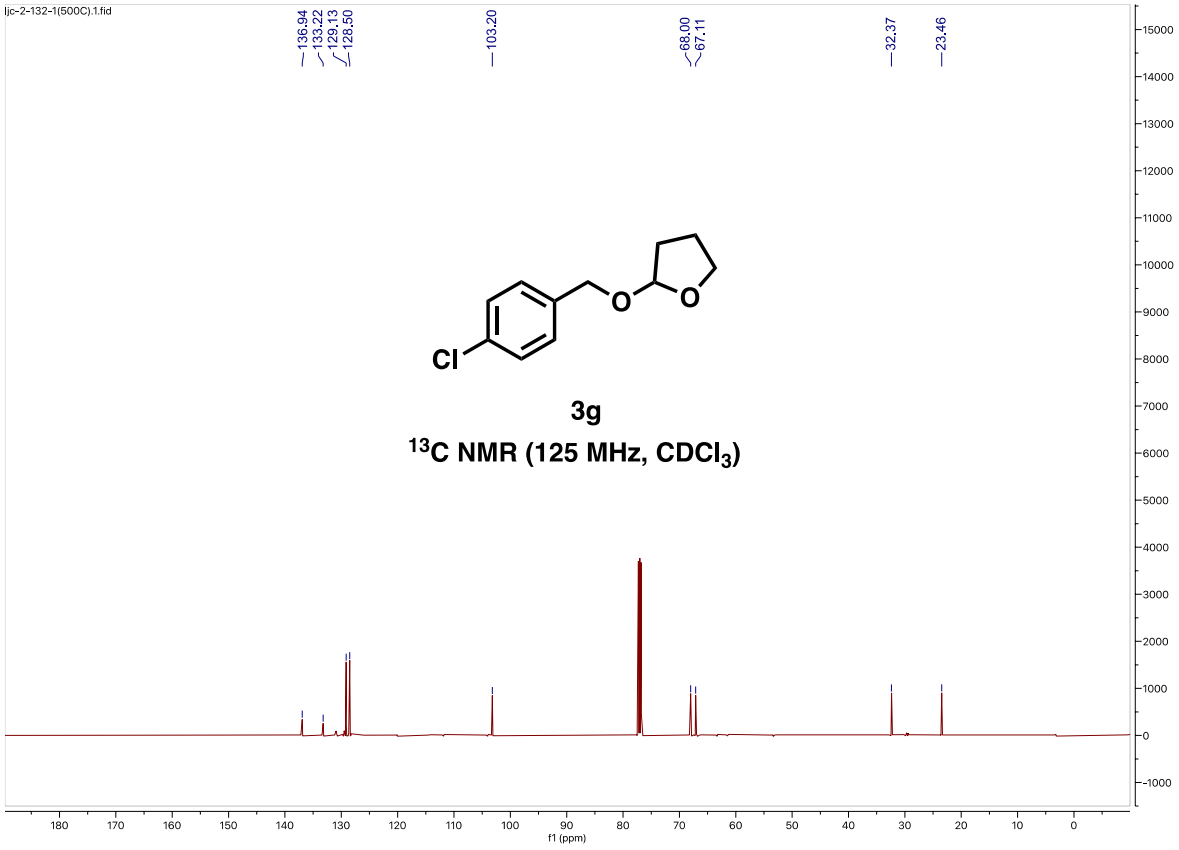
3f

^{13}C NMR (125 MHz, $CDCl_3$)



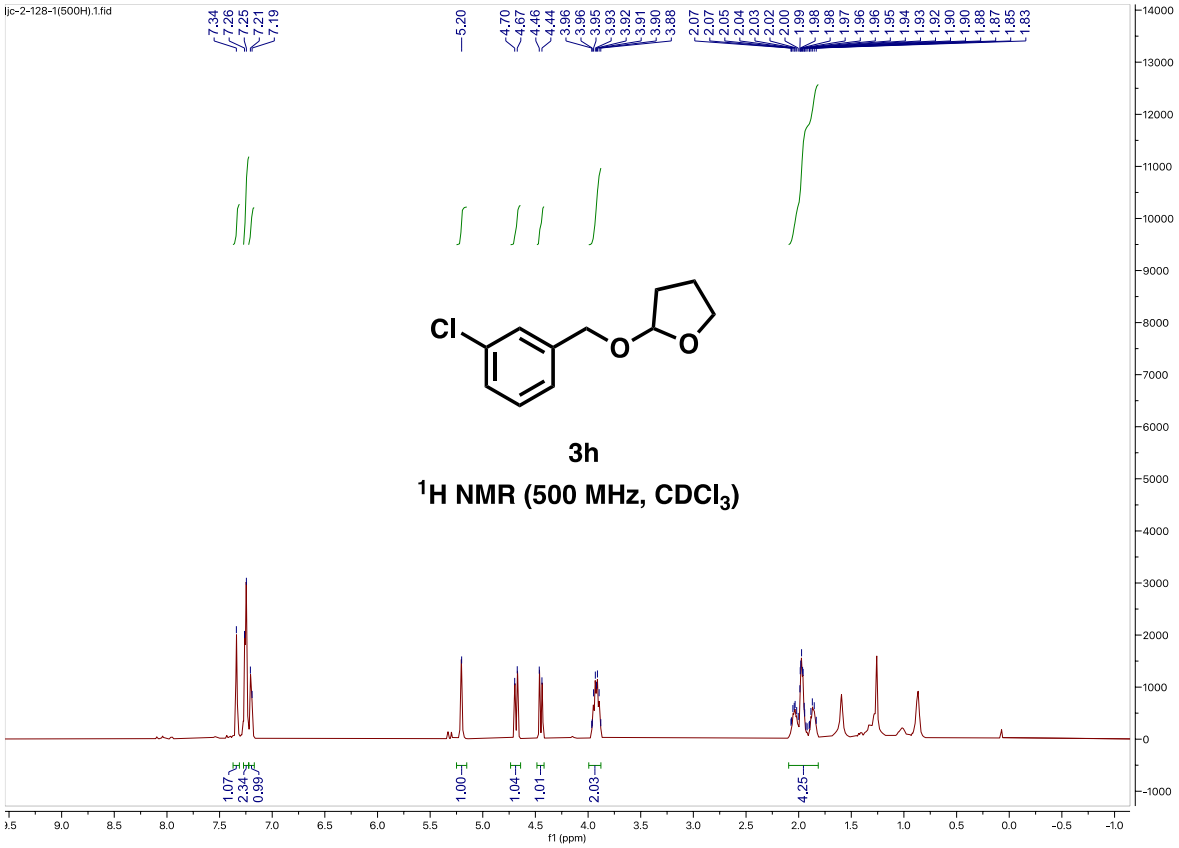
3g

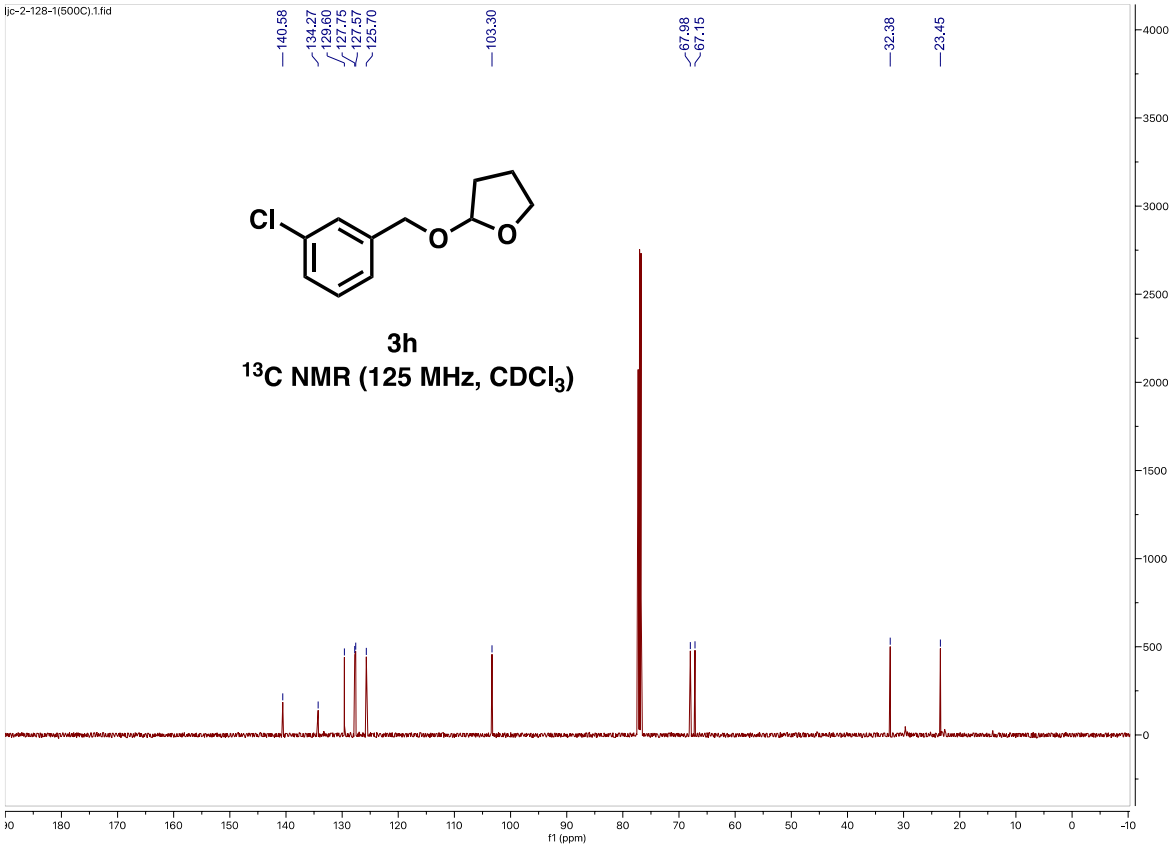
^{1}H NMR (500 MHz, $CDCl_3$)

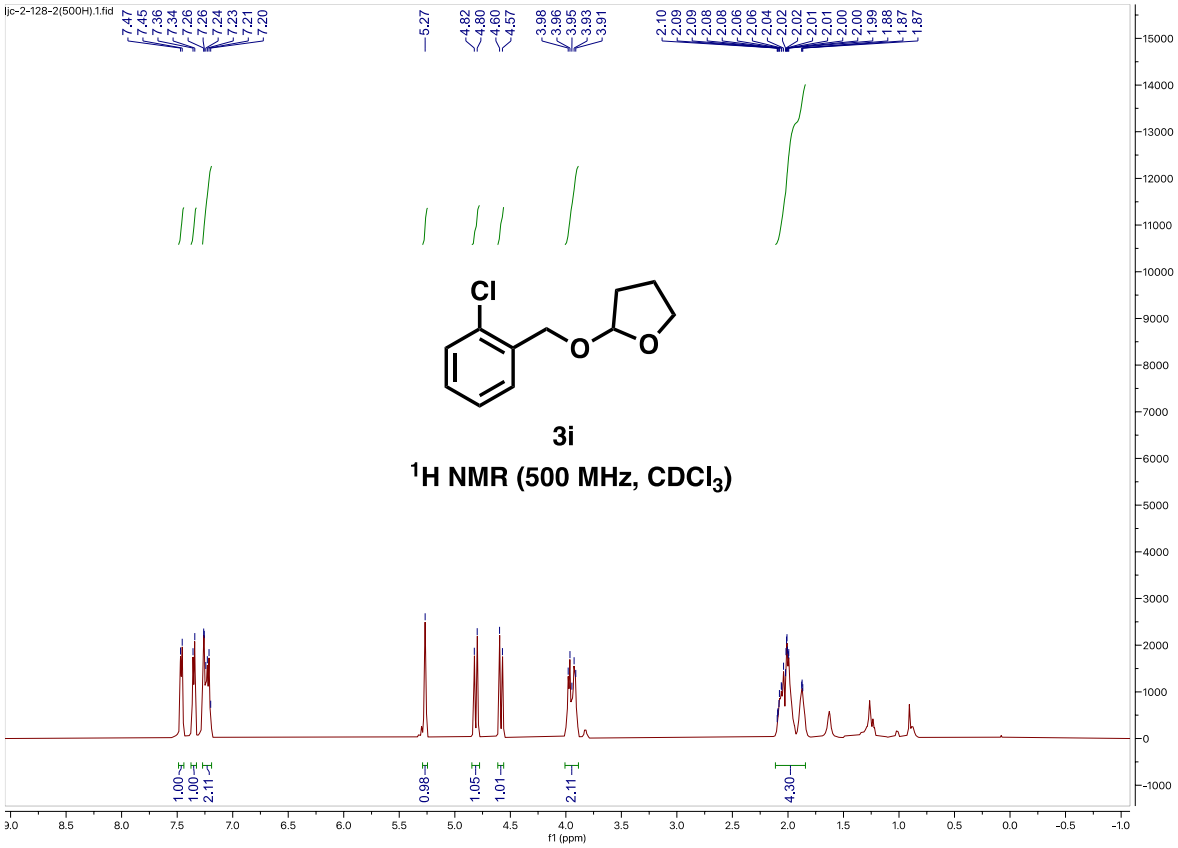


3g

^{13}C NMR (125 MHz, $CDCl_3$)

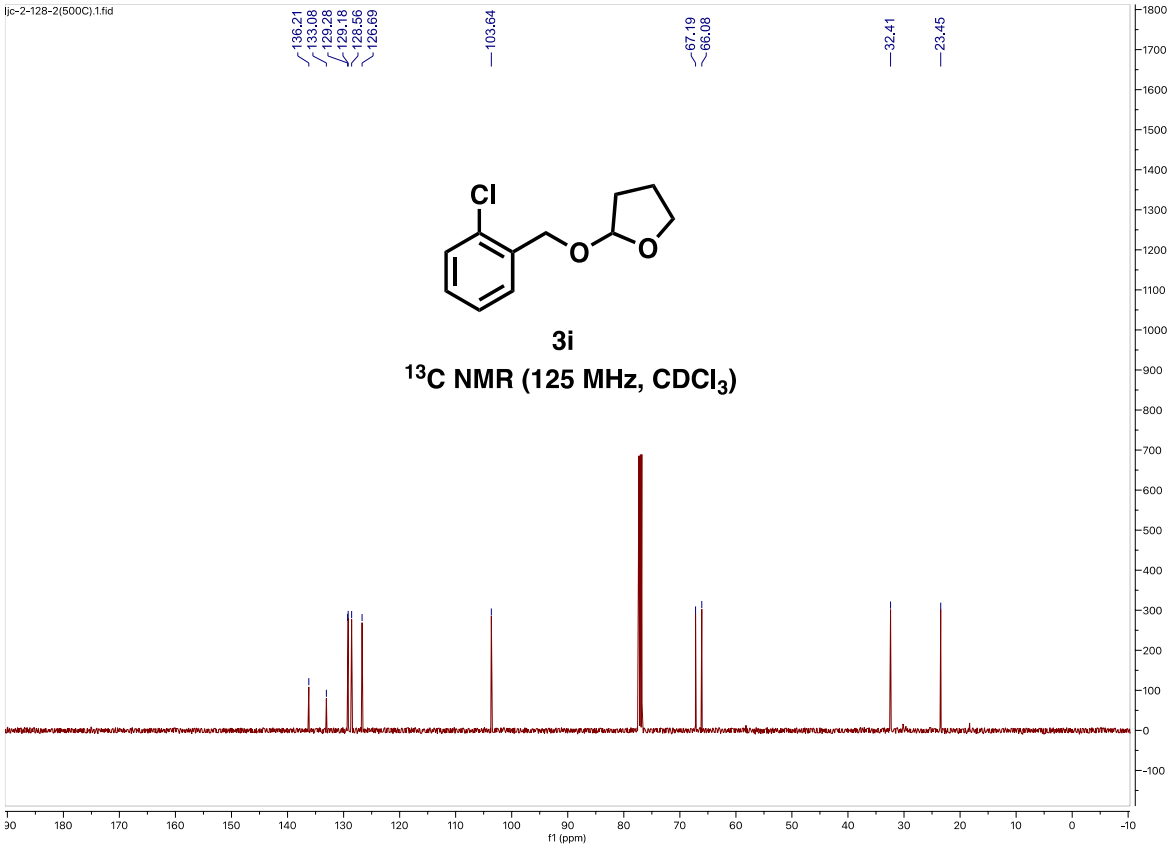

ljc-2-128-1(500H).1.fid
7.34
7.26
7.25
7.21
7.19
5.20
4.70
4.67
4.46
4.44
3.96
3.96
3.95
3.93
3.92
3.91
3.90
3.88
2.07
2.07
2.05
2.04
2.03
2.02
2.00
1.99
1.98
1.98
1.97
1.96
1.96
1.95
1.94
1.93
1.92
1.90
1.90
1.88
1.87
1.85
1.83
Cl
O
O
3h
1H NMR (500 MHz, CDCl3)
1.07
2.34
0.99
1.00
1.04
1.01
2.03
4.25
f1 (ppm)


ljc-2-128-1(500C).1.fid
140.58
134.27
129.60
127.75
127.57
125.70
103.30
67.98
67.15
32.38
23.45
Cl
O
O
3h
13C NMR (125 MHz, CDCl3)
f1 (ppm)



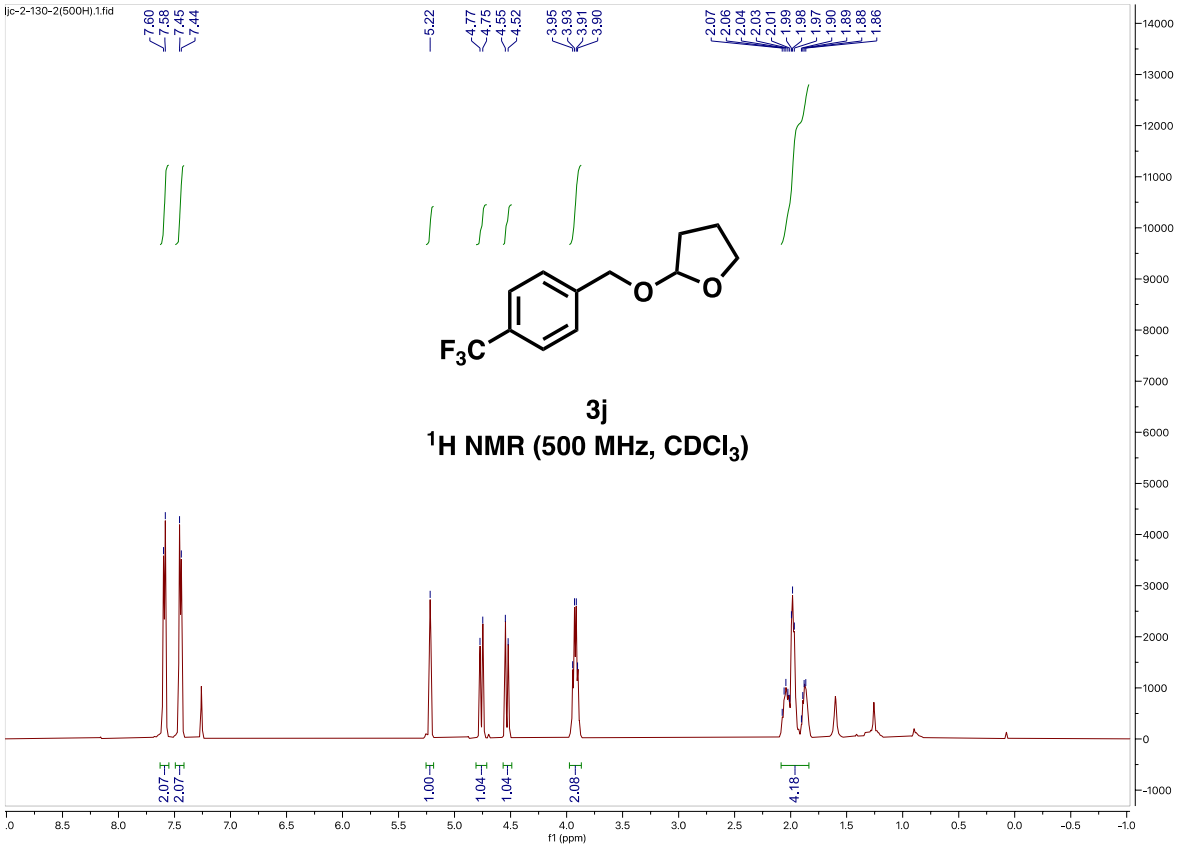
3i

^{1}H NMR (500 MHz, $CDCl_3$)



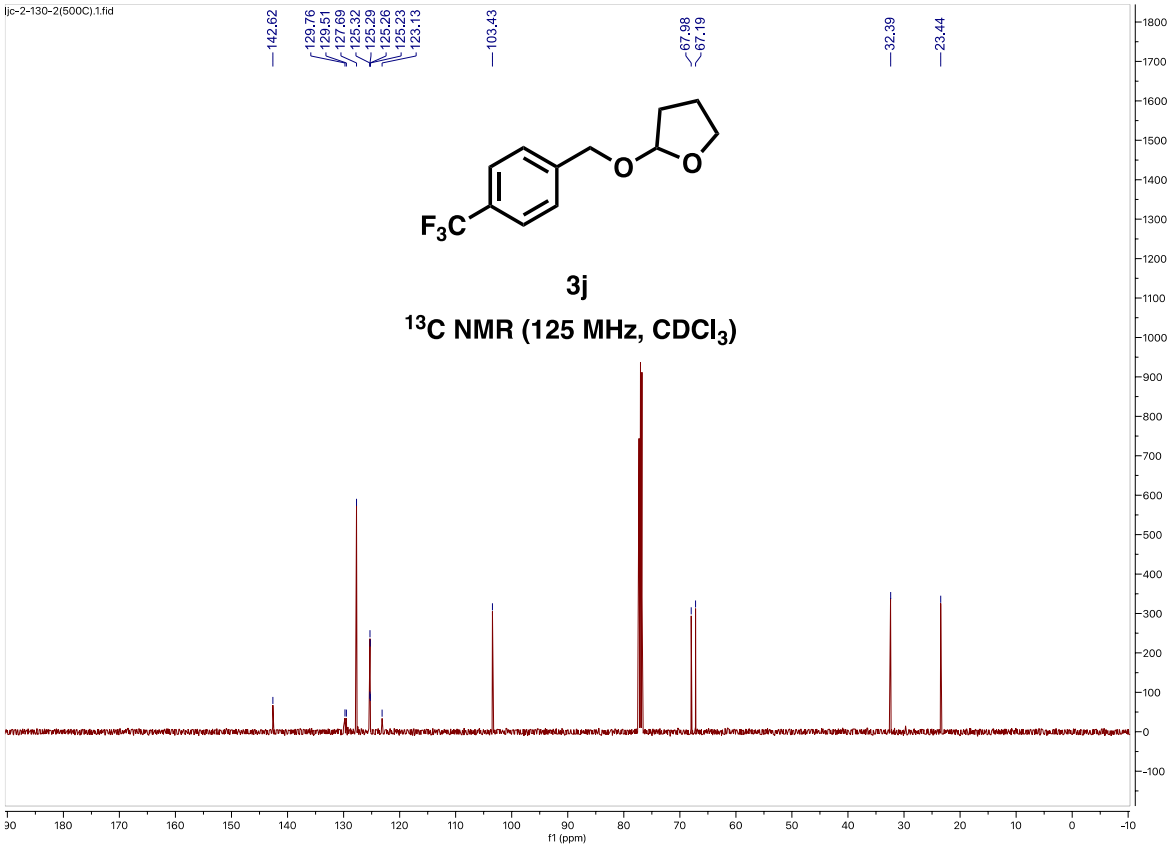
3i

^{13}C NMR (125 MHz, $CDCl_3$)



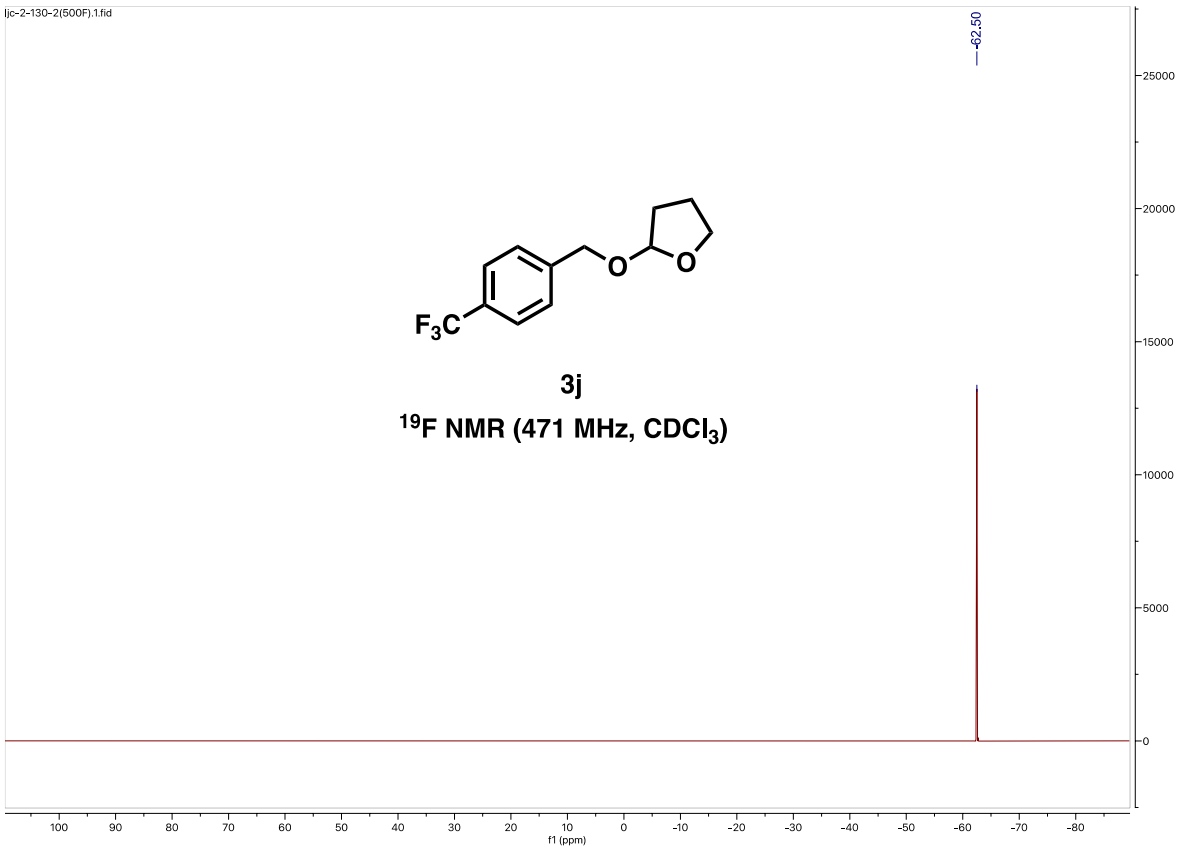
3j

^{1}H NMR (500 MHz, $CDCl_3$)



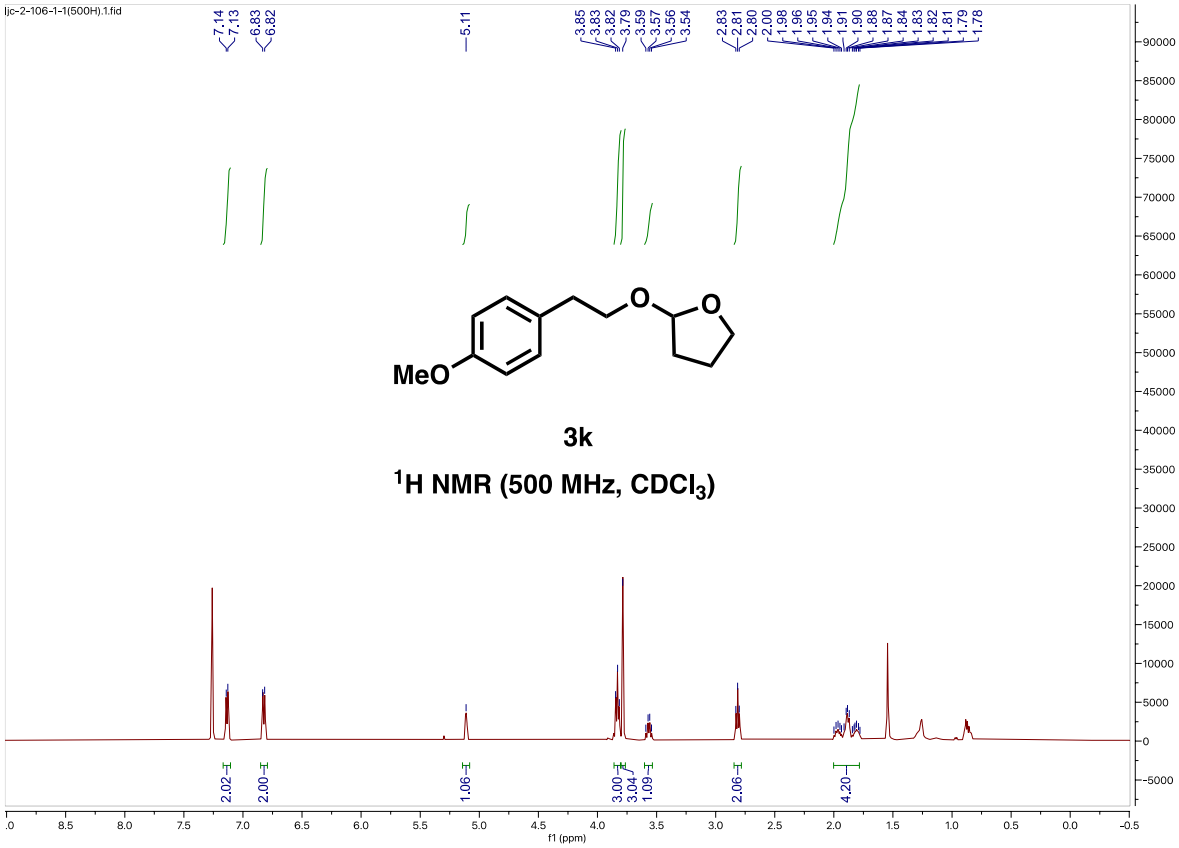
3j

^{13}C NMR (125 MHz, $CDCl_3$)



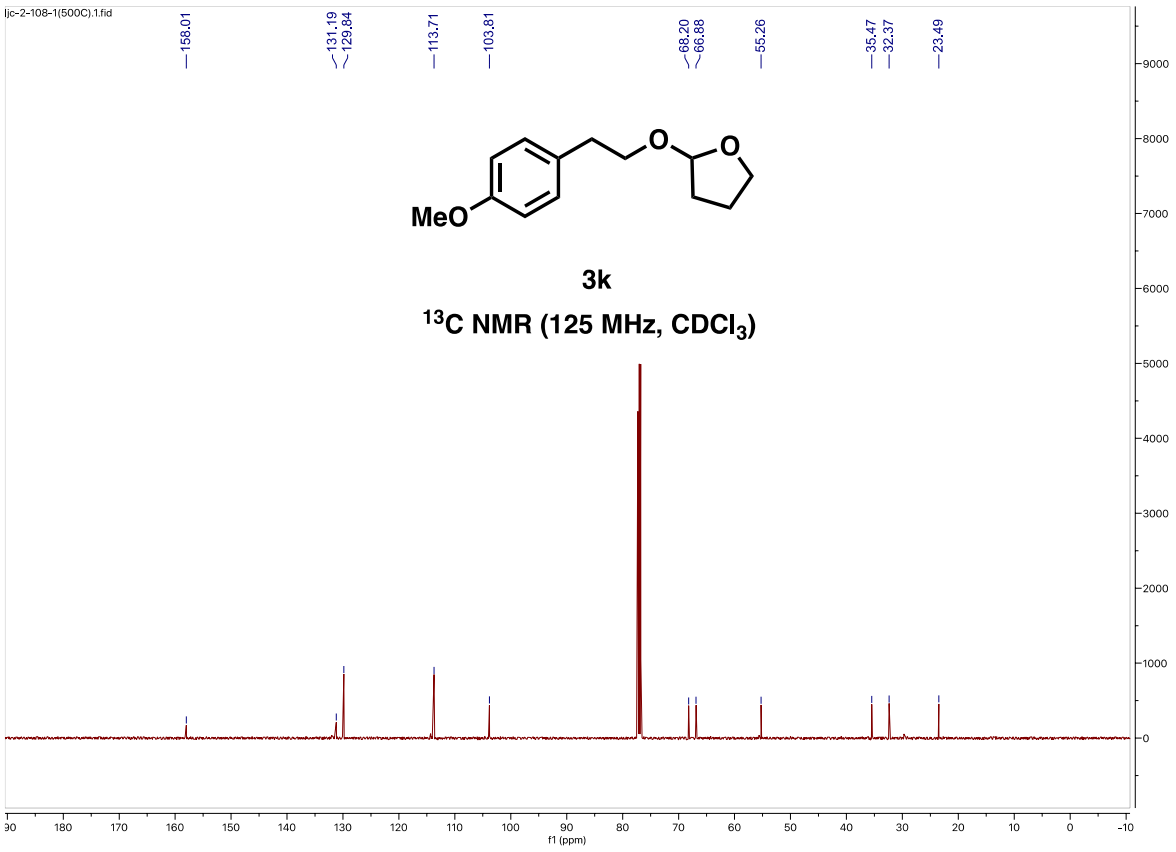
3j

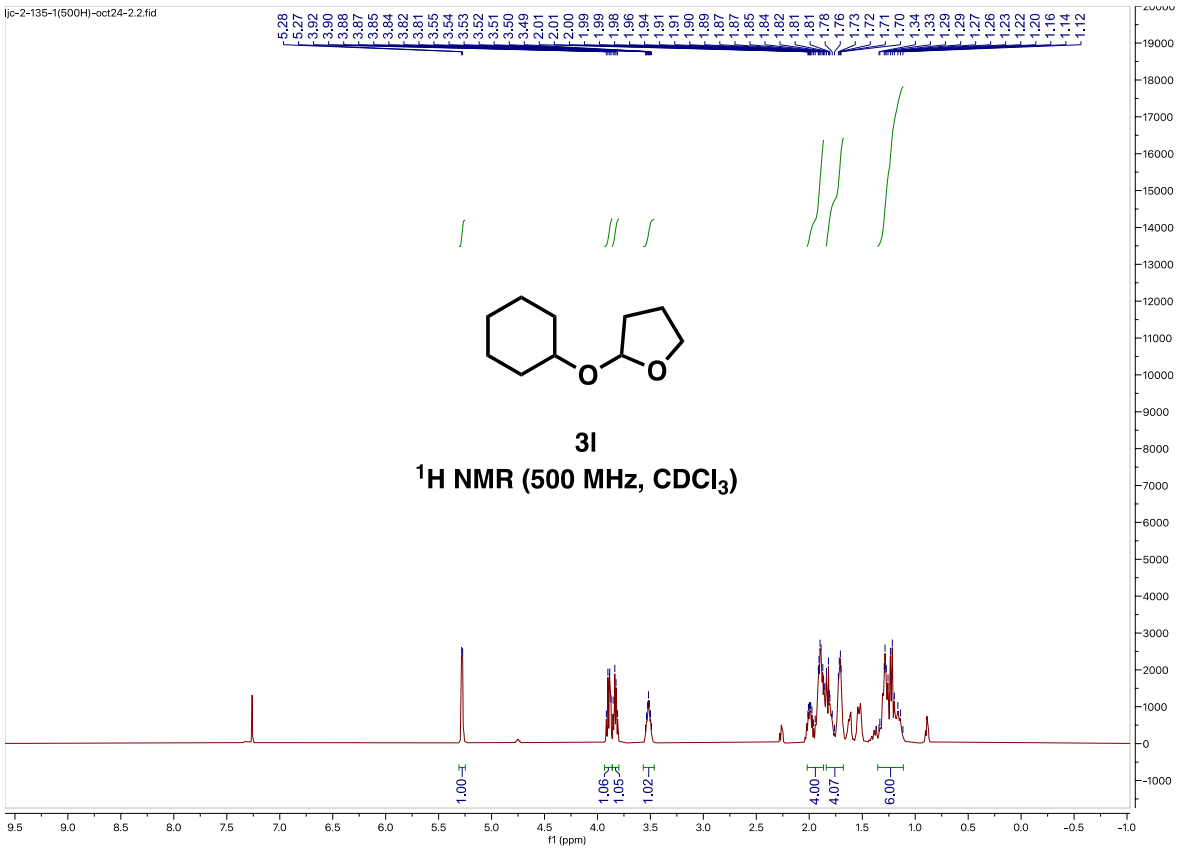
^{19}F NMR (471 MHz, $CDCl_3$)

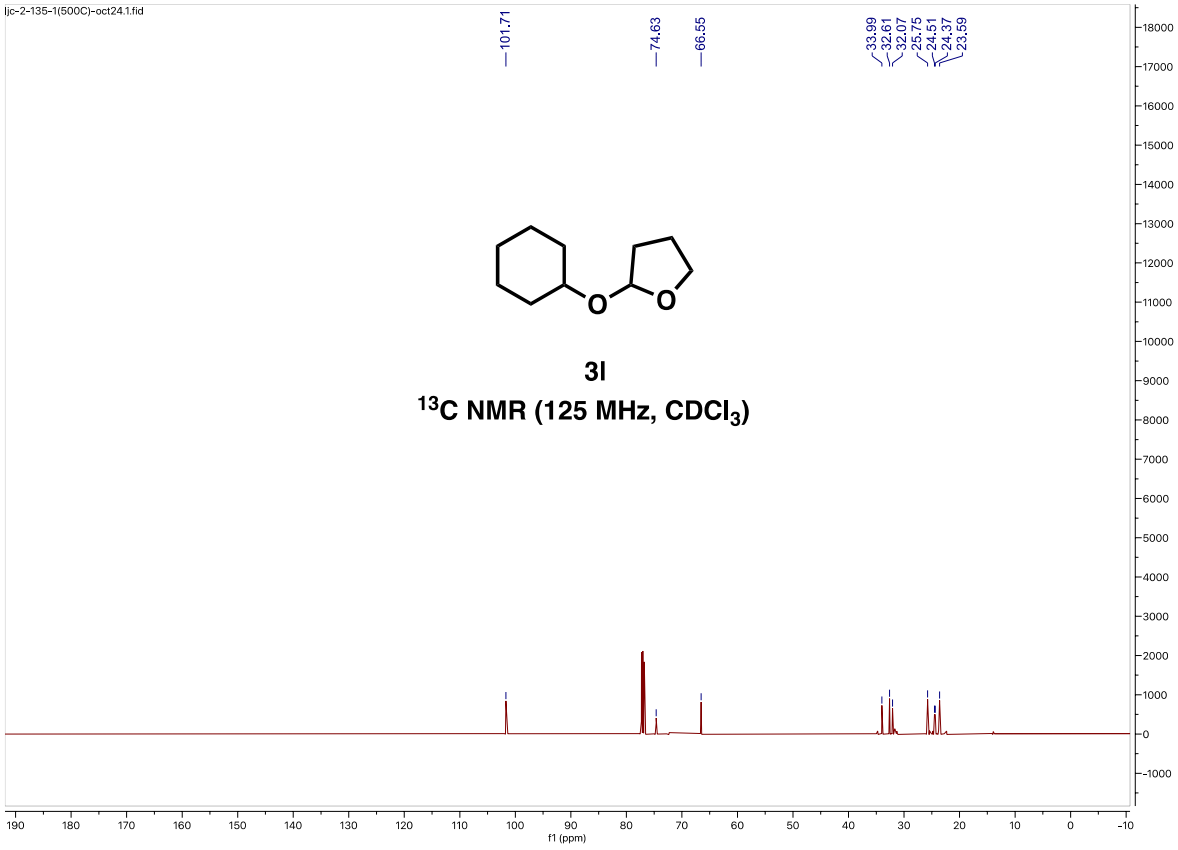


3k

^{1}H NMR (500 MHz, $CDCl_3$)

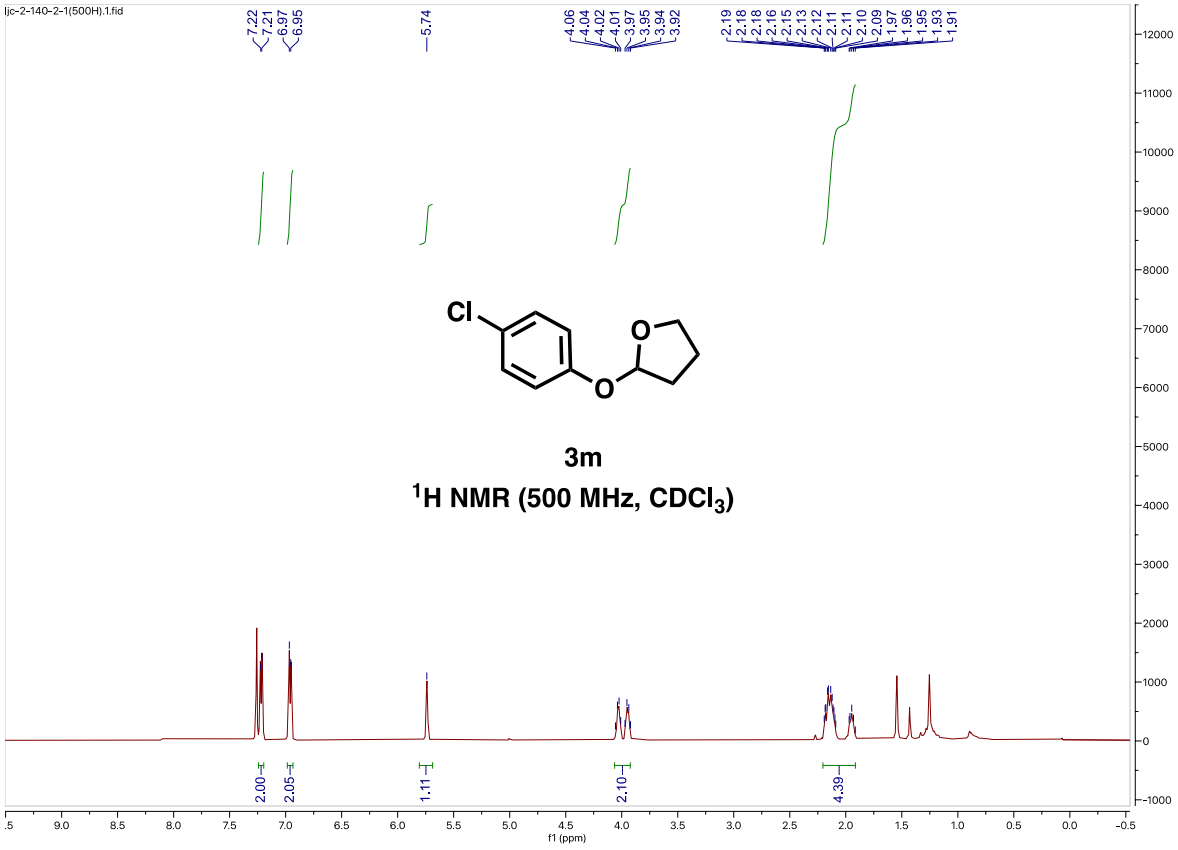

ljc-2-108-1(500C).1.fid
158.01
131.19
129.84
113.71
103.81
68.20
66.88
55.26
35.47
32.37
23.49
MeO
O
O
3k
13C NMR (125 MHz, CDCl3)
f1 (ppm)


ljc-2-135-1(500H)-oct24-2.2.fid
5.28 5.27 3.92 3.90 3.88 3.87 3.85 3.84 3.82 3.81 3.55 3.54 3.53 3.52 3.51 3.50 3.49 2.01 2.01 2.00 1.99 1.99 1.98 1.96 1.94 1.91 1.91 1.90 1.89 1.87 1.87 1.85 1.84 1.82 1.81 1.81 1.78 1.76 1.73 1.72 1.71 1.70 1.34 1.33 1.29 1.29 1.27 1.26 1.23 1.22 1.20 1.16 1.14 1.12
O
O
3l
^{1}H NMR (500 MHz, CDCl$_3$)
1.00 1.06 1.05 1.02 4.00 4.07 6.00
f1 (ppm)



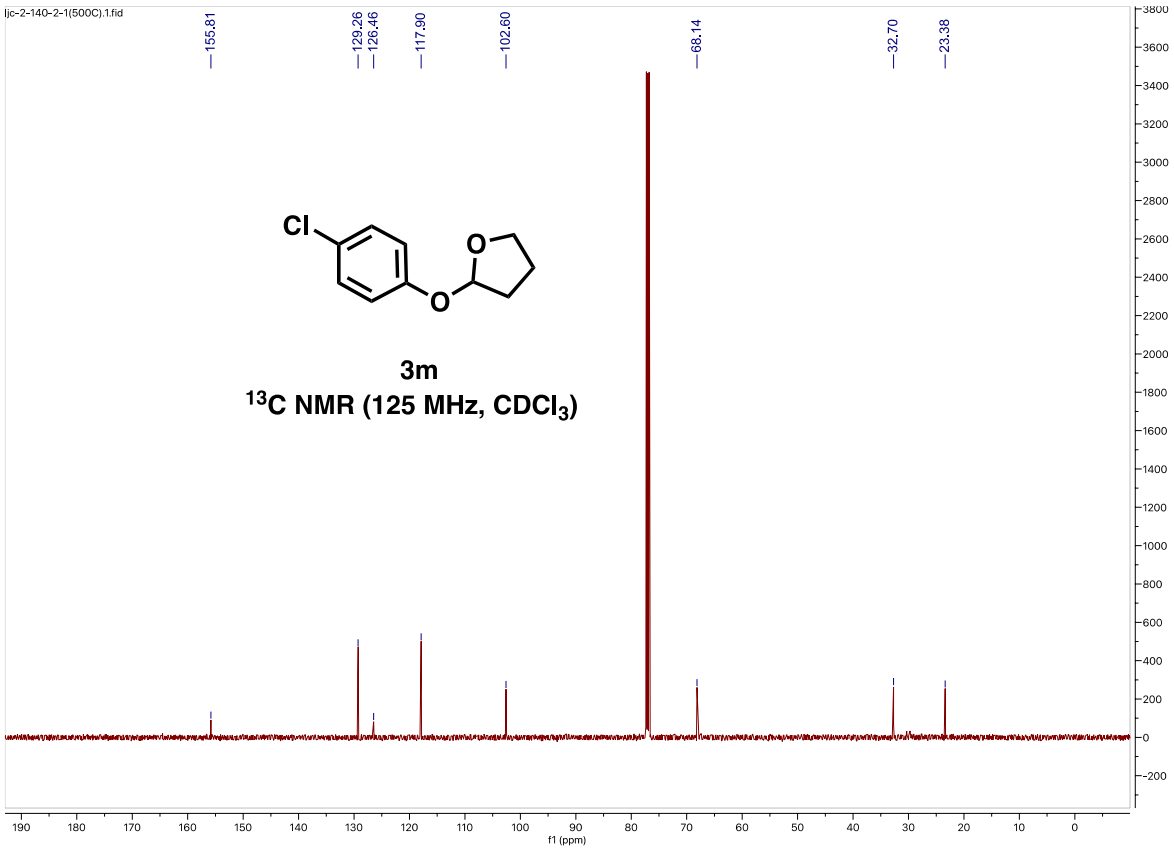
3l

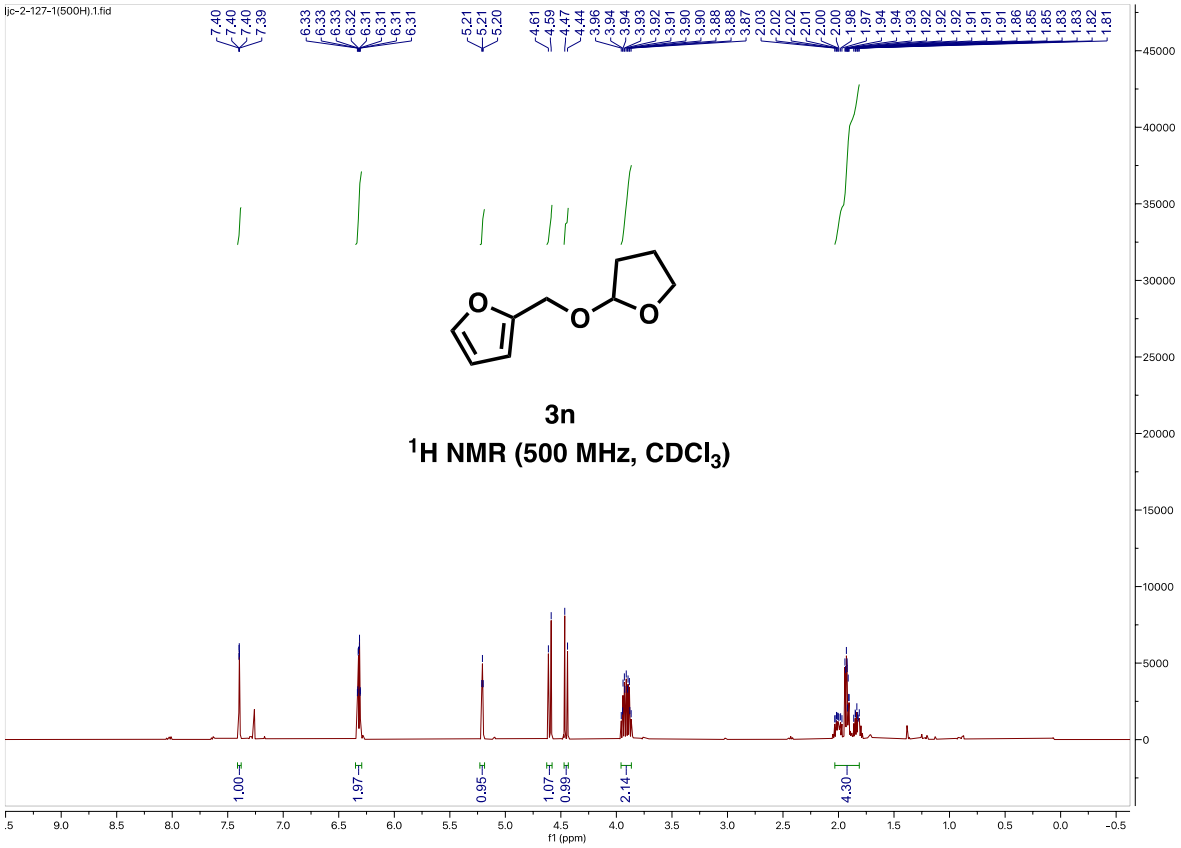
^{13}C NMR (125 MHz, $CDCl_3$)

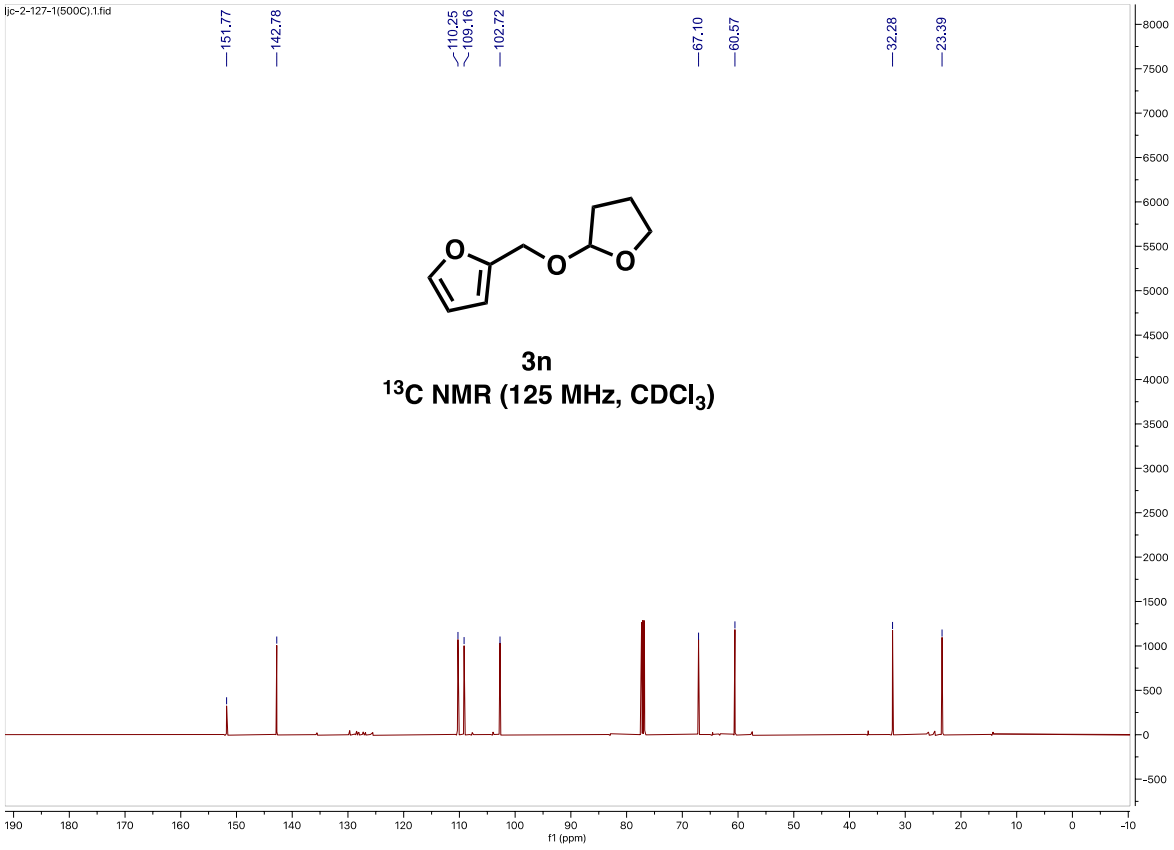


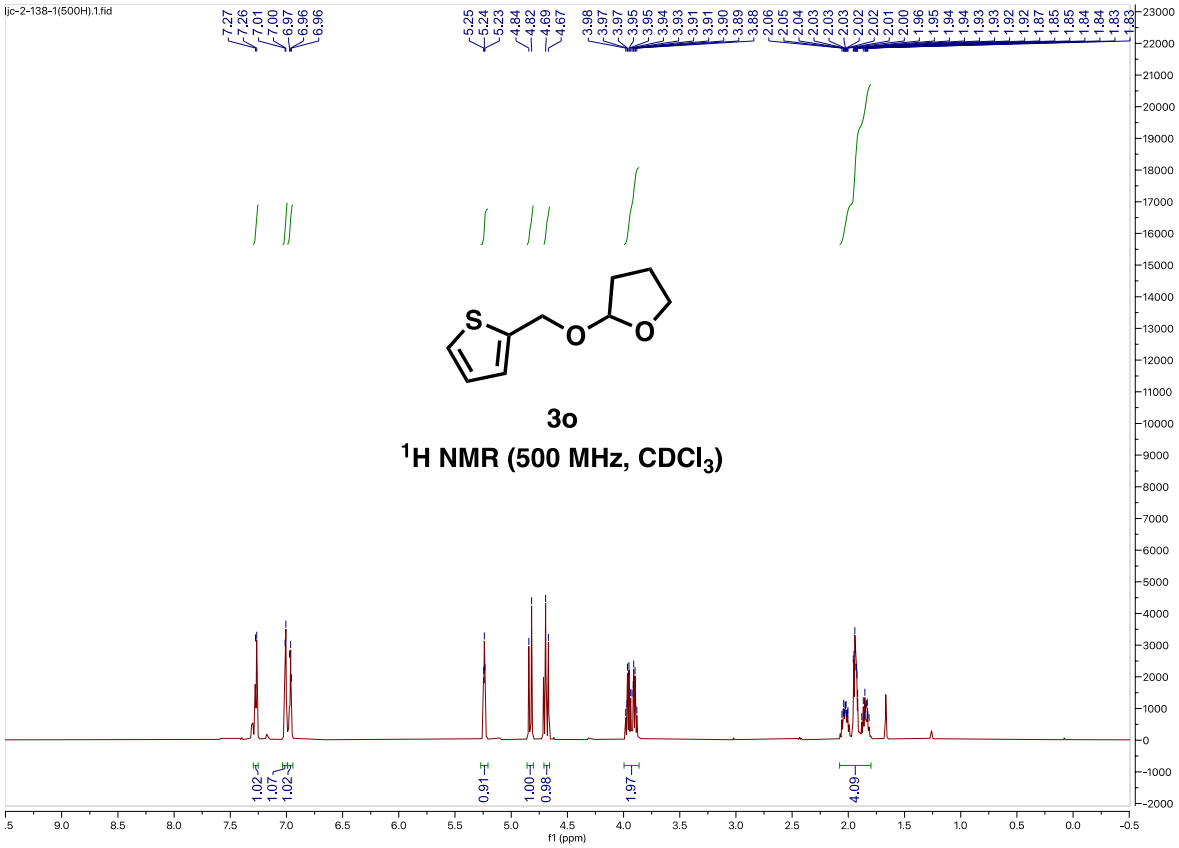
3m

^{1}H NMR (500 MHz, $CDCl_3$)


ljc-2-140-2-1(500C).1.fid
155.81
129.26
126.46
117.90
102.60
68.14
32.70
23.38
Cl
O
O
3m
13C NMR (125 MHz, CDCl3)
f1 (ppm)

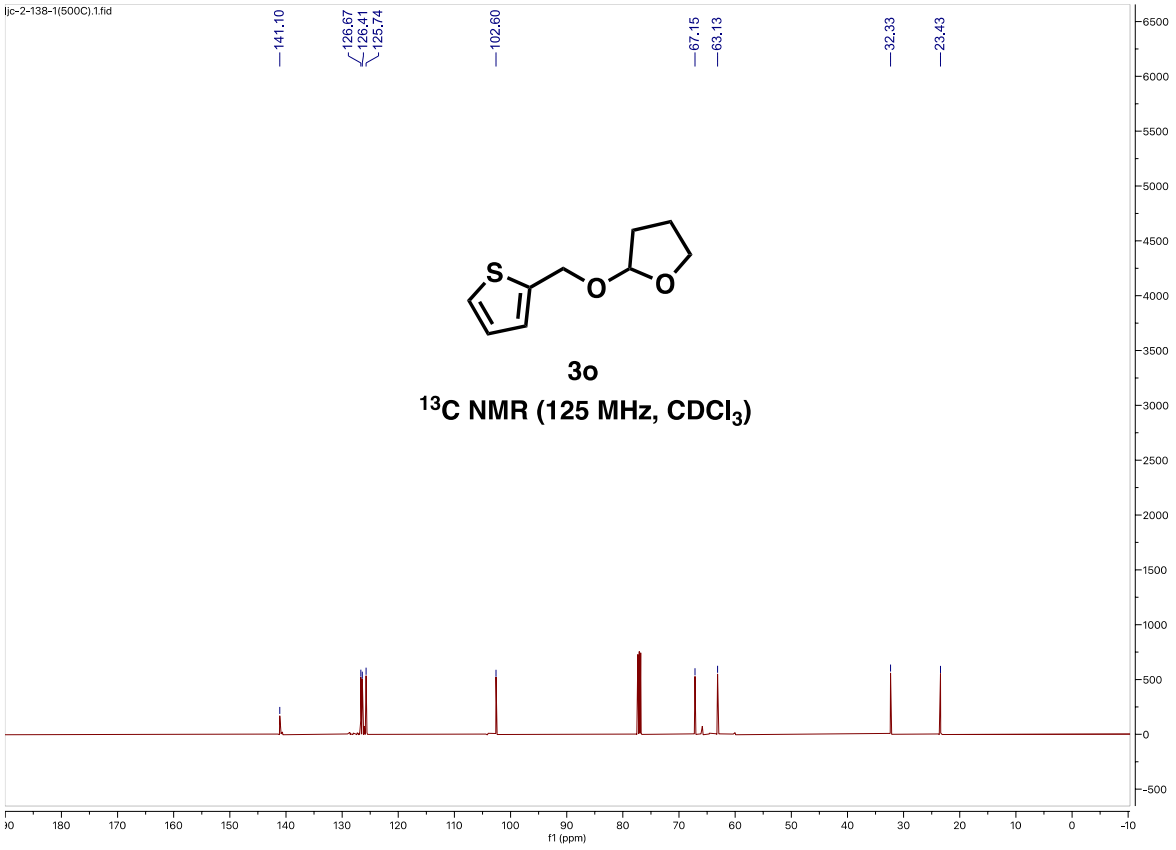

ljc-2-127-1(500H).1.fid
7.40
7.40
7.40
7.39
6.33
6.33
6.33
6.32
6.31
6.31
6.31
6.31
5.21
5.21
5.20
4.61
4.59
4.47
4.44
3.96
3.94
3.94
3.93
3.92
3.91
3.90
3.90
3.88
3.88
3.87
2.03
2.02
2.02
2.01
2.00
2.00
1.98
1.97
1.94
1.94
1.93
1.92
1.92
1.91
1.91
1.91
1.86
1.85
1.85
1.83
1.83
1.82
1.81
O
O
O
3n
1H NMR (500 MHz, CDCl3)
1.00
1.97
0.95
1.07
0.99
2.14
4.30
f1 (ppm)


ljc-2-127-1(500C).1.fid
151.77
142.78
110.25
109.16
102.72
67.10
60.57
32.28
23.39
O
O
O
3n
13C NMR (125 MHz, CDCl3)
f1 (ppm)



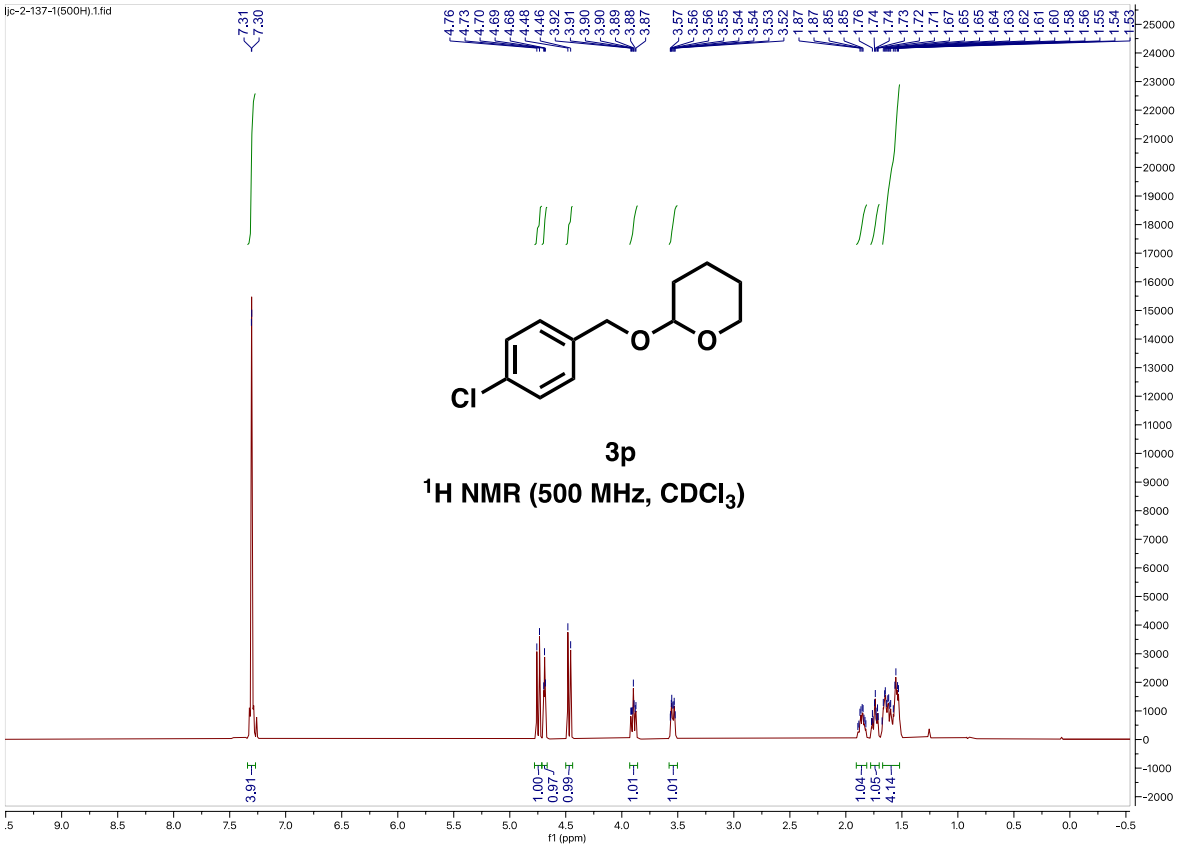
3o

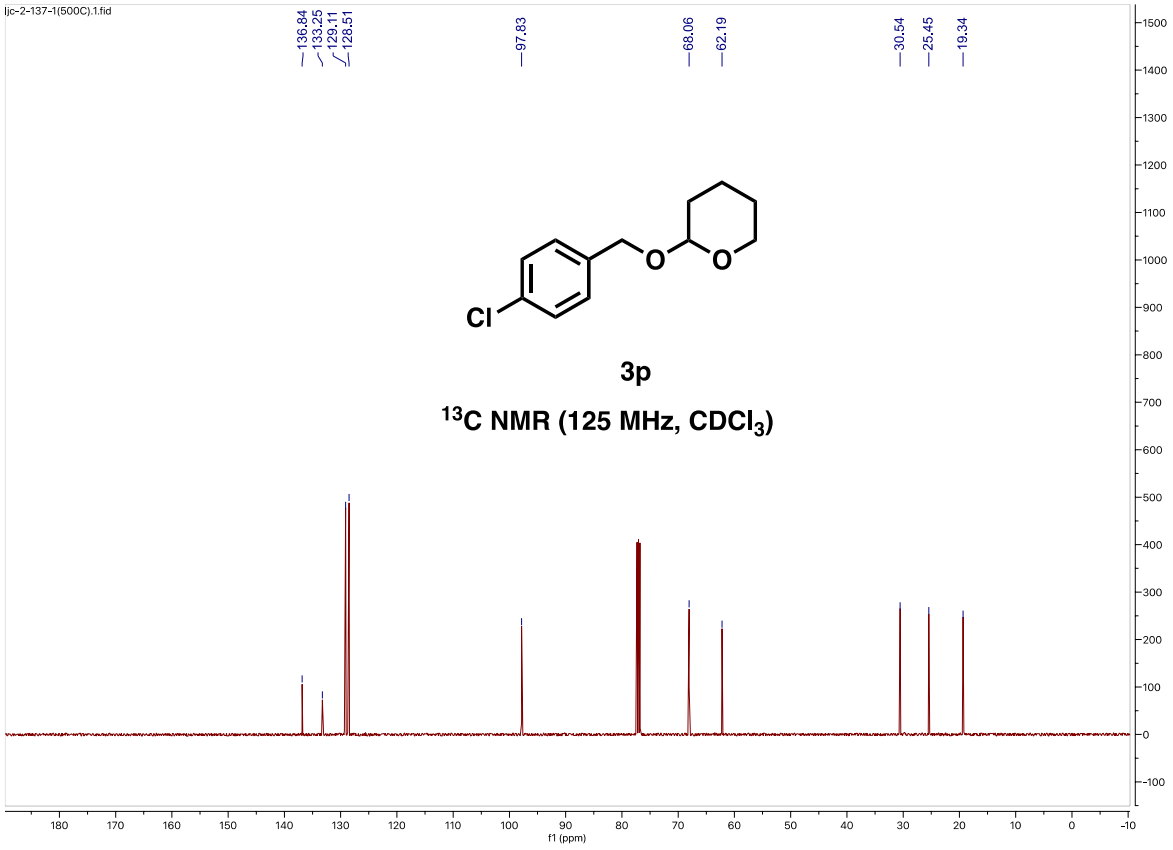
^{1}H NMR (500 MHz, $CDCl_3$)

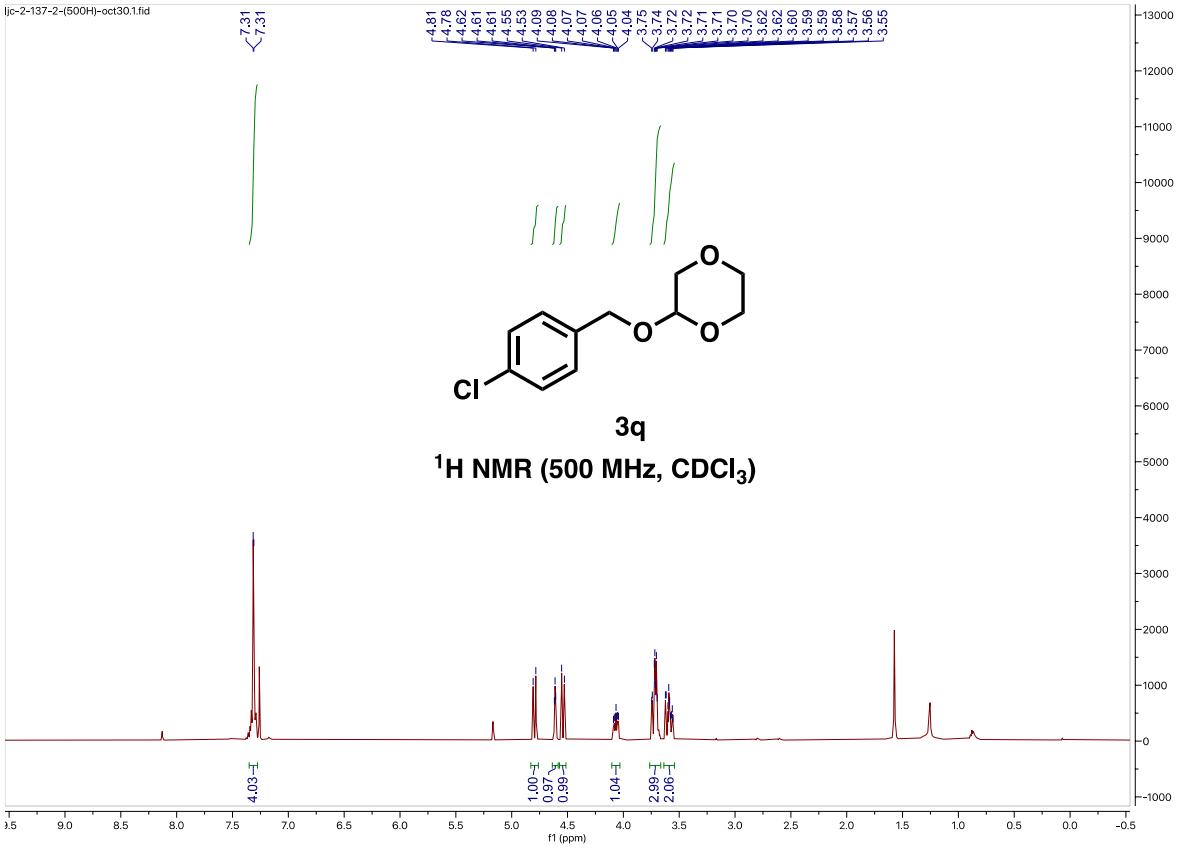


3o

^{13}C NMR (125 MHz, $CDCl_3$)

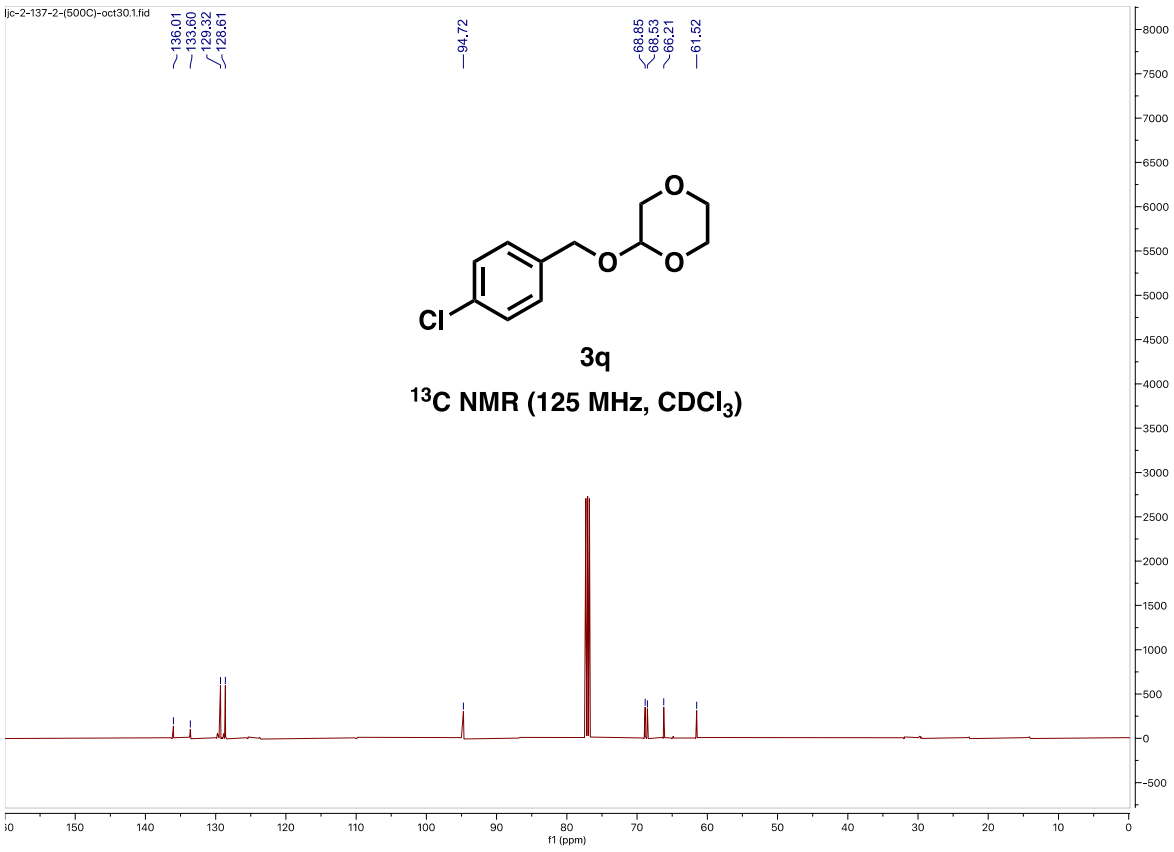

ljc-2-137-1(500H).1.fid
7.31
7.30
4.76
4.73
4.70
4.69
4.68
4.48
4.46
3.92
3.91
3.90
3.90
3.89
3.88
3.87
3.57
3.56
3.56
3.55
3.54
3.54
3.53
3.52
1.87
1.87
1.85
1.85
1.76
1.74
1.74
1.73
1.72
1.71
1.67
1.65
1.65
1.64
1.63
1.62
1.61
1.60
1.58
1.56
1.55
1.54
1.53
O
O
Cl
3p
1H NMR (500 MHz, CDCl3)
3.91
1.00
0.97
0.99
1.01
1.01
1.04
1.05
4.14
f1 (ppm)


ljc-2-137-1(500C).1.fid
136.84
133.25
129.11
128.51
97.83
68.06
62.19
30.54
25.45
19.34
Cl
O
O
3p
^{13}C NMR (125 MHz, CDCl$_3$)
f1 (ppm)



3q

^{1}H NMR (500 MHz, $CDCl_3$)



3. Crystal Structure Solution and Refinement

Data collection of **A-II** was performed on Bruker VENTURE system equipped with a PHOTON 100 CMOS detector, a Mo-target fine-focus X-ray source (λ = 0.71073 Å), and a graphite monochromator. The data was collected under 100(2) K (Oxford Cryosystems CRYOSTREAM 700) using 50 kV and 30 mA with an appropriate 0.5° ω scan strategy. Data reduction and integration were performed with SAINT (version 8.38A).[3] Data was corrected for absorption effects using the empirical methods as implemented in SADABS (version 2016/2).[4] The structure was solved by SHELXT (version 2018/2)[5] and refined by full-matrix least-squares procedures using the SHELXL program (version 2018/3)[6] through the OLEX2[7] graphical interface. All non-hydrogen atoms, including those in disordered parts, were refined anisotropically. All H-atoms were included at calculated positions and refined as riders, with U_{iso}(H) = 1.2 U_{eq}(C) and U_{iso}(H) = 1.5 U_{eq}(C) for methyl groups. Further crystal and data collection details are listed in Table S1.

Table S1. Crystal Data and Structure Refinement Parameters for **A-II**.

Chemical formula	$C_{23}H_{23}NO$
CCDC number	2440557
M_r	329.42
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	100(2)
a, b, c (Å)	8.6833 (10), 7.9494 (9), 25.996 (3)
β (°)	99.594 (2)
V (Å^3)	1769.3 (4)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.08
Crystal size (mm)	0.29 × 0.19 × 0.12
Diffractometer	Bruker D8 Venture PHOTON 100 CMOS
Absorption correction	Multi-scan *SADABS2016*/2 (Bruker, 2016/2) was used for absorption correction. wR2(int) was 0.0685 before and 0.0616 after correction. The Ratio of minimum to maximum transmission is 0.9411. The $\lambda/2$ correction factor is not present.
T_{min}, T_{max}	0.644, 0.684
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	68955, 6731, 5052
R_{int}	0.066
$(\sin \vartheta/\lambda)_{max}$ (Å^{-1})	0.770
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.060, 0.147, 1.06
No. of reflections	6731
No. of parameters	230
H-atom treatment	H-atom parameters constrained
$\Delta>_{max}$, $\Delta>_{min}$ (e Å^{-3})	0.42, -0.37

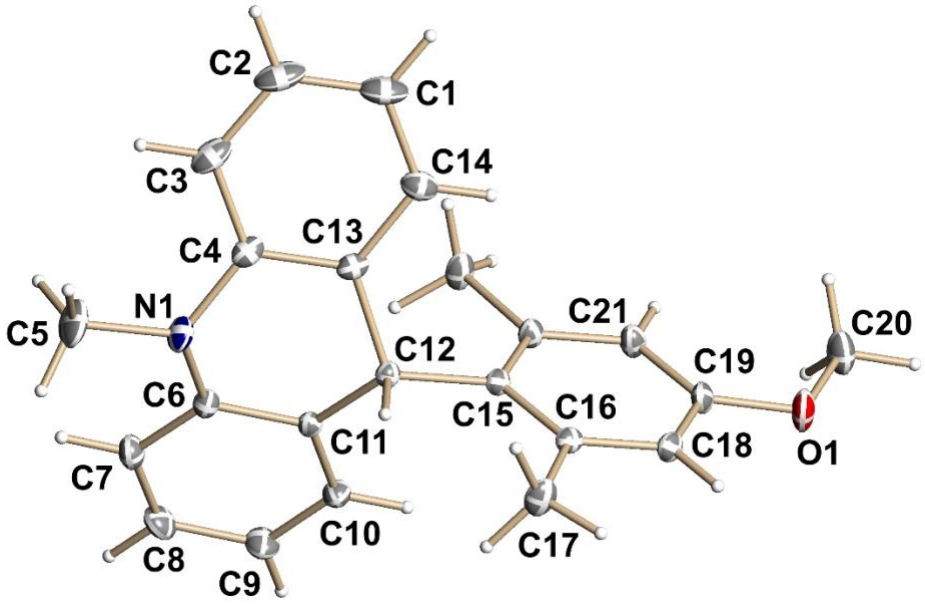


Figure S1. Solid-state structure of **A-II** drawn with thermal ellipsoids at the 50% probability level. Hydrogen atoms are represented by spheres of arbitrary radius. Only carbon, nitrogen, and oxygen atoms are labeled.

Crystallographic data for compound (A-II) has been deposited at the CCDC under 2440557. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

[1] L. González-Bulnes, I. Ibáñez, L. M. Bedoya, M. Beltrán, S. Catalán, J. Alcamí, S. Fustero and J. Gallego, *Angewandte Chemie International Edition* **2013**, *52*, 13405-13409.

[2] G. Zhao and T. Wang, *Angewandte Chemie International Edition* **2018**, *57*, 6120-6124.

[3] SAINT; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017.

[4] SADABS; part of Bruker APEX3 software package (version 2017.3-0): Bruker AXS, 2017.

[5] G. M. Sheldrick, *Acta Cryst.* **2015**, *A71*, 3-8.

[6] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.

[7] O.V. Dolomanov, L.J. Bourhis, R.J, Gildea, J.A.K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.