Supporting Information

Metal-Free Visible-Light-Promoted C(sp^3)–H Functionalization of Aliphatic Cyclic Ethers Using Trace O_2

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General Considerations

All reagents and solvents were purchased and used without further purification, unless otherwise noted. All reactions were performed under an inert atmosphere unless otherwise stated. Room temperature refers to 25 °C, unless otherwise stated. Moisture-sensitive reactions were performed using flame-dried glassware under an atmosphere of dry argon (Ar). Air- and water sensitive reactions were setup in a Vacuum Atmosphere GENESIS glovebox held under an atmosphere of argon gas (working pressure 2−6 mbar).

Flame-dried equipment was stored in a 130 °C oven before use and either allowed to cool in a cabinet desiccator or assembled hot and allowed to cool under an inert atmosphere. Chromatographic purification of products was accomplished using flash column chromatography Silicycle Silica flash F60 (particle size 40−63 μm, 230−400 mesh). Thin-layer chromatography was performed on EMD Millipore silica gel 60 F254 glass-backed plates (layer thickness 250 μm, particle size 10−12 μm, impregnated with a fluorescent indicator). Visualization of the developed chromatogram was accomplished by fluorescence quenching under shortwave UV light and/or by staining with phosphomolybdic acid (PMA), *p*-anisaldehyde (PAA), or $KMnO_4$ stains.

Instrumentation. For NMR spectrometry, NMR spectra were obtained on Bruker spectrometers operating at 400 or 500 MHz for ^1H NMR; 101 or 126 MHz for $^{13}C\{^1H\}$ NMR; 377 MHz for ^{19}F NMR; and 162 MHz for ^{31}P NMR. The data were reported in the following order: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, q = quartet, m = multiplet), coupling constant, (Hz), relative integral made in reference to NMR solvent signals.

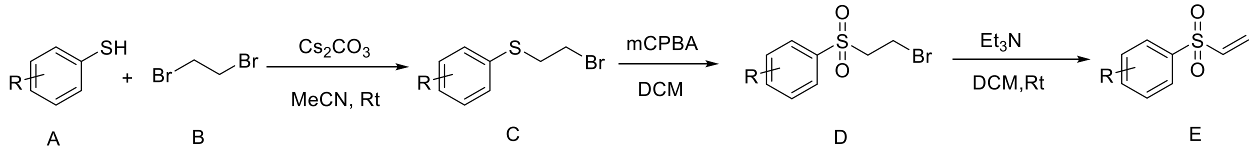
For mass spectrometry, gas chromatograph−mass spectrometry (GC-MS) was obtained using a Hewlett-Packard GC System HP 6890 Series coupled with a HP 5973 Mass Selective Detector. High-resolution mass spectra were obtained using an Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS with electrospray ionization (ESI)

Materials. Ethers and solvents were used as received from commercial suppliers without further purification. Commercially available regents were used without further purification. General procedure for the synthesis of vinylsulfones derivatives followed the reported procedures indicated in their respective references. Ethers and THF purity was 99.7%.

LED Lamps. Kessil broadband Blue LED (440 nm) lamp 40 W or Purple (390nm) LED lamp 40 W were used for this light-promoted reaction.

Procedure for Preparation of Starting Vinyl Sulfones[1–11]

Procedure A:

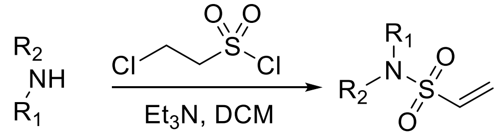


A suspension of thiophenol derivatives **A** (10 mmol) and Cs_2CO_3 (30 mmol) in MeCN (30 mL) was stirred and 1,2-dibromoethane (**B**) (30 mmol) was slowly added to the suspension. The resulting mixture was stirred overnight (12–14h) at room temperature. The reaction was then filtered, and the resulting filtrate was concentrated under vacuum to obtain crude product **C**. The crude product was dissolved in CH_2Cl_2, and the mixture was cooled to 0 °C and *m*CPBA (4 equiv) were added. The mixture was stirred for 30 minutes at 0 °C, the cold-bath was then removed and the solution was allowed to warm to room temperature and continuously stirred overnight. The resulting suspension was washed with saturated aqueous $NaHCO_3$. The organic layers were separated, and the aqueous solution extracted with CH_2Cl_2. The combined organic layers were washed with brine and dried with Na_2SO_4 and concentrated under reduced pressure to get crude product **D**. Crude product **D** was dissolved in CH_2Cl_2 (30 mL) and treated with Et_3N (3.0 equiv). After 30 min of stirring, the reaction was further diluted with CH_2Cl_2 (10 mL) and washed with brine. The organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The resulting crude was purified by column chromatography to afford products **E**.

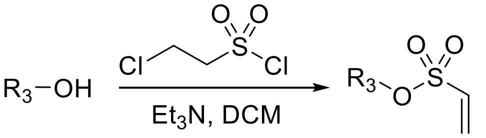
Procedure B:

General procedure for producing vinyl sulfonamides and vinyl sulfonates.

1)



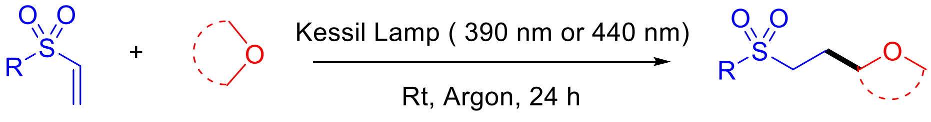
2)



2-Chloroethanesulfonyl chloride (1.0 equiv.) was added drop wise to a stirred solution of secondary amine or primary alcohol derivatives (1.0 equiv.) with Et_3N (3.5 equiv.) in CH_2Cl_2 at 0 ºC. After addition, stirring was continued at 0 ºC for 2 hrs. The mixture then was diluted with CH_2Cl_2, then washed with brine, dried over $MgSO_4$, and concentrated. The crude product was purified by flash column chromatography (Hexane/EtOAc = 8:1) to give vinyl sulfonamide or vinyl sulfonates as a colorless oil.

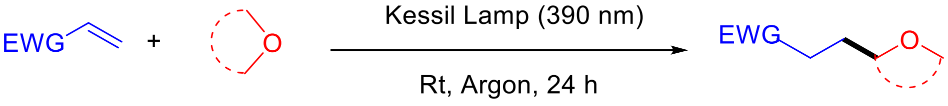
General Procedure for the Synthesis of 3 ,4 and 5.

Procedure A:



1 **2** **3 and 4**

On a bench top, a 10 mL microwave vial was charged with the appropriate (vinylsulfonyl)benzene (**1**) (0.2 mmol, 1 equiv), capped with 20 mm microwave crimp caps with septa, and then the vial was evacuated and filled with argon (3x) to obtain an inert argon atmosphere inside the vial. Then, 1 mL of the corresponding ether solvent (undistilled; commercial grade) was injected via syringe inside the capped vial. The vial containing the resulting mixture was then placed approximately 4 cm away from the Blue LED lamp (440 nm or purple light 390 nm) and then stirred at room temperature for 24 hours, unless otherwise stated. The resulting crude was then concentrated under reduced pressure to remove excess ether, and the concentrate was then purified by column chromatography using an ethyl acetate/hexanes mixture (1:10–1:2) as an eluent to give pure desired product.

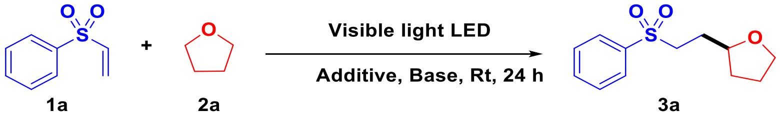


1 **2** **5**

Procedure B:

On a bench top, a 10 mL microwave vial was charged with the appropriate (**1**) (0.2 mmol, 1 equiv) electron deficient alkene, capped with 20 mm microwave crimp caps with septa, and then the vial was evacuated and filled with argon (3x) to obtain an inert argon atmosphere inside the vial. Then, 1 mL of the corresponding ether solvent (undistilled; commercial grade) was injected via syringe inside the capped vial. The vial containing the resulting mixture was then placed approximately 4 cm away from the kessil lamp 390 nm and then stirred at room temperature for 24 hours, unless otherwise stated. The resulting crude was then concentrated under reduced pressure to remove excess ether, and the concentrate was then purified by column chromatography using an ethyl acetate/hexanes mixture (1:10–1:2) as an eluent to give pure desired product.

Table S1 Full Table of Reaction Optimization



Entry[a]	Additive (mol %)	Base (equiv)	Solvent	Yield (%)[b]
1	Eosin Y (1)	K_2CO_3 (2)	CH_2Cl_2	76
2	-	K_2CO_3 (2)	CH_2Cl_2	40
3	Eosin Y (1)	-	CH_2Cl_2	50
4	-	-	CH_2Cl_2	72
5	-	-	CH_2Cl_2	40[c]
6	-	-	CH_2Cl_2	NR[d]
7			$PhCH_3$	trace
8	-	-	MeCN	trace
9	-	-	Acetone	trace
10	-	-	THF[e]	46%
11	-	-	THF[f]	87%
12	-	-	THF[g]	89%
13	-	-	Neat	95(92)[h]
14			Neat	NR[i]
15	EosinY (1)	-	Neat	92%
16	-	-	THF	35%[j]
17	-	-	THF	NR[k]
18	-	-	THF	80%[l]
19	-	-	THF	84%[m]

[a] Reaction conditions: **1a** (0,2 mmol), THF 10 equivalent, solvent 1 mL, base 2.0 equivalent, RT, under Argon atmosphere were irradiated with 40 W LED 440 nm for 24h. [b] Yields are based on **1a**, determined by ^{1}H-NMR using dibromomethane as the internal standard. [c] Air. [d] Dark. [e] Isolated yields, 0.3 mL THF. [f] Isolated yields, 0.5 mL THF. [g] Isolated yields, 0.7 mL THF. [h] Isolated yields, 1 mL THF. [i] Isolated yields, 1 mL THF, 60°C, dark. [j] NMR yield, dry THF, 24 h under 440 nm blue LED. [k] under O_2 balloon. [l] under N_2 balloon. [m] under Argon balloon.

Peroxide addition and Its Influence in Product Formation.

Different mol% of peroxides were added to freshly distilled THF (containing < 0.5ppm of peroxides, see S22) to prove that the THF peroxide/ethereal peroxide is responsible for the formation of the corresponding product.

Under standard reaction conditions:

-Freshly distilled THF (0–0.5ppm peroxide) gave 35% yield.

-Freshly distilled THF with added 5% DTBP (di-*tert*-butyl peroxide) gave 92% yield.

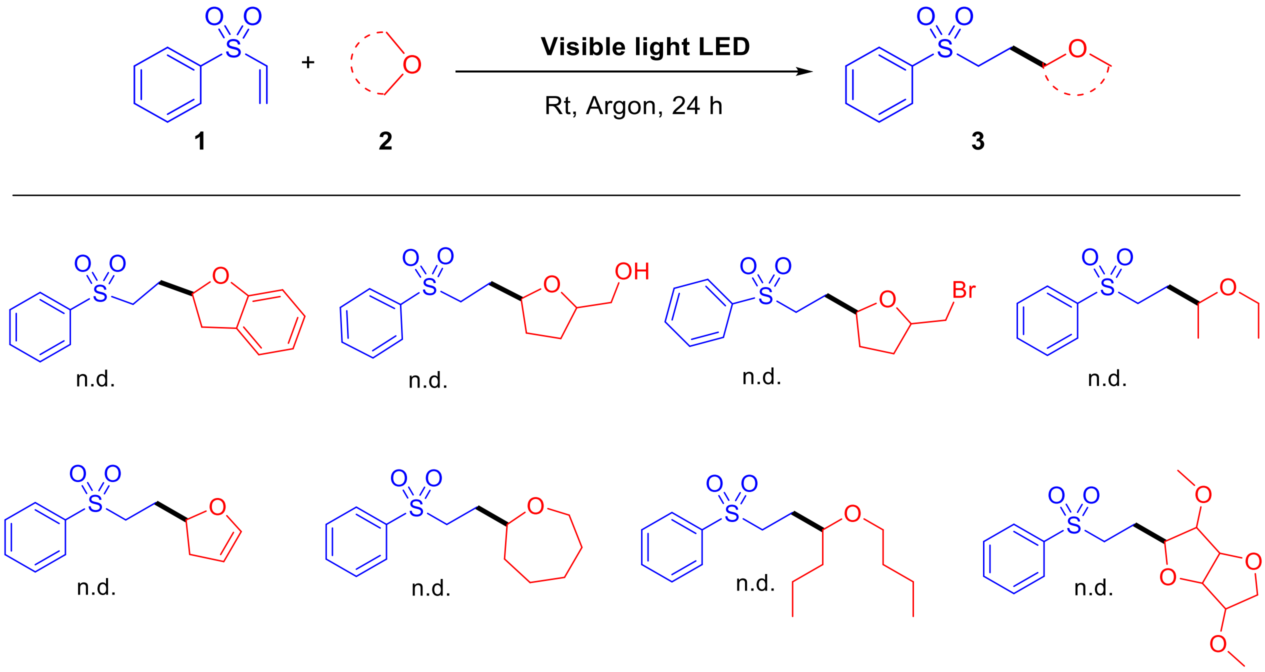
-Freshly distilled THF with added 10% DTBP (di-*tert*-butyl peroxide) gave 93% yield.

-Freshly distilled THF with added 20% DTBP (di-*tert*-butyl peroxide) gave 90% yield.

-Freshly distilled THF with added 1 equiv DTBP (di-*tert*-butyl peroxide) gave 70% yield.

These results show that catalytic amounts of peroxides are enough to initiate the reaction. However using excess peroxide has a deleterious effect on yield, presumable leading to side reactions and oxidations.

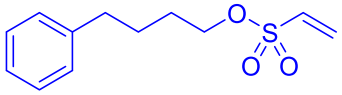
Figure S1: Additional Substrate Scope Explored for the Transformation



Reaction conditions: **1a** (0,2 mmol), ethers 1 mL, RT, under Argon atmosphere were irradiated with 40 W, LED 440 nm or 390 nm for 24h. N.D. (not detected).

Compound Characterization data

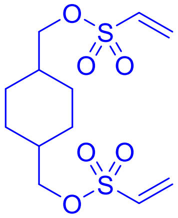
4-phenylbutyl ethenesulfonate, (1v)



1v

Colourless solid: ^{1}**H NMR** (400 MHz, $CDCl_3$) *δ* 7.34 – 7.25 (m, 2H), 7.24 – 7.19 (m, 3H), 6.57 – 6.40 (m, 2H), 6.13(d, *J* = 9.7 Hz, 1H), 4.17 – 4.14 (m, 2H), 2.68 (t, *J* = 6.9 Hz, 2H), 1.78 (dq, *J* = 6.9, 2.3, 1.5 Hz, 4H). ^{13}**C NMR** (101 MHz, $CDCl_3$) *δ* 141.54, 132.57, 130.01, 128.44, 128.41, 126.01, 70.75, 35.18, 28.50, 27.18. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{17}O_3SH$[M+H]+: 241.0898, found 241.0895.

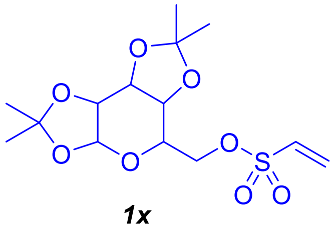
cyclohexane-1,4-diylbis(methylene) diethenesulfonate, (1w)



1w

Colourless solid: ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 6.59 – 6.31 (m, 4H), 6.13 (dd, *J* = 9.7, 5.2 Hz, 2H), 3.96 (dd, *J* = 34.4, 6.7 Hz, 4H), 2.03 – 1.78 (m, 4H), 1.78 – 1.51 (m, 3H), 1.45 (dt, *J* = 10.6, 5.3 Hz, 1H), 1.07 – 1.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 132.4, 130.3, 130.2, 75.1, 37.1, 28.1. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{21}O_6S$ [M+H]+: 325.0780, found 325.0790.

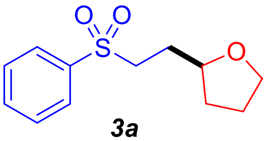
(2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl ethenesulfonate, (1x)



1x

Colourless solid: ^{1}**H NMR** (400 MHz, $CDCl_3$) *δ* 7.58 (dd, *J* = 6.7, 2.9 Hz, 2H), 7.30 (dd, *J* = 5.0, 1.9 Hz, 3H), 5.32 (d, *J* = 2.5 Hz, 1H), 4.54 (d, *J* = 5.4 Hz, 1H), 4.48 (d, *J* = 9.7 Hz, 1H), 4.24 (d, *J* = 2.4 Hz, 1H), 4.04 (dd, *J* = 9.6, 5.4 Hz, 1H), 1.50 (d, *J* = 17.6 Hz, 6H), 1.37 (d, *J* = 5.5 Hz, 6H). ^{13}**C NMR** (101 MHz, $CDCl_3$) *δ* 133.2, 132.3, 128.9, 128. 0, 111.3, 109.2, 97.2, 81.6, 75.6, 74.5, 71.6, 28.1, 27.8, 25.9, 25.5. **HRMS** (ESI, m/z): calcd. for $C_{14}H_{23}O_8SH$ [M+H]+: 351.1114, found 351.1110.

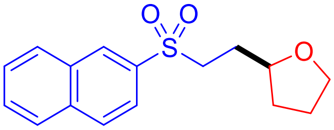
2-(2-(phenylsulfonyl)ethyl)tetrahydrofuran, (3a)



3a

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 92%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.84 -7.82 (m, 2H), 7.59-7.51 (m, 1H), 7.48 (dd, *J* = 8.4, 7.0 Hz, 2H), 3.76 (ddt, *J* = 26.8, 8.3, 6.8 Hz, 1H), 3.67 (dt, *J* = 8.3, 6.9 Hz, 1H), 3.59 (dt, *J* = 8.3, 6.9 Hz, 1H), 3.22 (ddd, *J* = 14.0, 11.4, 5.0 Hz, 1H), 3.06 (ddd, *J* = 14.0, 11.2, 4.9 Hz, 1H), 1.91 (dddt, *J* = 15.9, 11.4, 9.2, 5.4 Hz, 2H), 1.87-1.72 (m, 3H), 1.40-1.35 (m, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 139.2, 133.7, 129.3, 128.0, 67.8, 53.6, 31.2, 28.5, 25.6. **HRMS** (ESI, m/z): calcd. for C_{12}H16O_3SNa [M+Na]+: 263.0718, found: 263.0724.

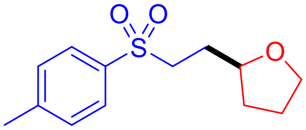
2-(2-(naphthalen-2-ylsulfonyl)ethyl)tetrahydrofuran, (3b)



3b

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 92%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 8.48 (s, 1H), 7.99 (dd, 2H), 7.87 (dd, J = 8.6, 1.8 Hz, 1H), 7.71-7.58 (m, 2H), 3.90-3.71 (m, 2H), 3.70- 3.60 (m, 1H), 3.37 (ddd, J = 13.9, 11.4, 4.9 Hz, 1H), 3.21 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 2.06-1.76 (m, 5H), 1.51-1.37 (m, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 136.1, 135.3, 132.2, 129.8, 129.6, 129.4, 129.3, 128.0, 127.7, 122.7, 67.9, 53.7, 31.2, 28.7, 25.6. **HRMS** (ESI, m/z): calcd. for $C_{16}H_{19}O_3S$ [M+H]+: 291.1055, found: 291.1058.

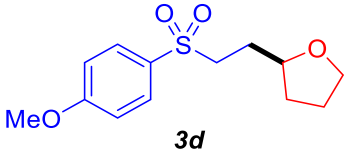
2-(2-tosylethyl)tetrahydrofuran, (3c)



3c

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 95%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 7.78- 7.76 (m, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 3.84-3.74 (m, 2H), 3.66 (dt, *J* = 8.3, 6.9 Hz, 1H), 3.26 (ddd, *J* = 14.0, 11.4, 5.0 Hz, 1H), 3.10 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 2.43 (s, 3H), 2.03-1.88 (m, 2H), 1.88-1.80 (m, 3H), 1.47-1.41 (m, 1H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 144.6, 136.3, 136.3, 129.9, 129.9, 128.1, 128.1, 67.8, 53.7, 31.2, 31.2, 28.6, 25.6, 25.6, 21.6. **HRMS** (ESI, m/z): calcd. for $C_{13}H_{19}O_3S$ [M+H]+: 255.1055, found: 255.1054.

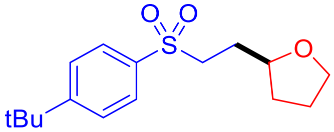
2-(2-((4-methoxyphenyl)sulfonyl)ethyl)tetrahydrofuran, (3d)



3d

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 67%. **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 7.82- 7.80 (m, 2H), 7.07- 6.99 (m, 2H), 3.87 (s, 3H), 3.84- 3.75 (m, 2H), 3.65 (dt, *J* = 8.3, 6.9 Hz, 1H), 3.25 (ddd, *J* = 13.9, 11.4, 5.0 Hz, 1H), 3.07 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 2.00-1.88 (m, 2H), 1.86-1.80 (m, 3H), 1.47-1.42 (m, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 163.7, 130.8, 130.2, 114.5, 67.8, 55.7, 53.9, 31.2, 28.7, 25.6. **HRMS** (ESI, m/z): calcd. for $C_{13}H_{19}O_4S$ [M+H]+: 271.1004, found: 271.1002.

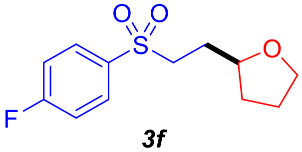
2-(2-((4-(tert-butyl)phenyl)sulfonyl)ethyl)tetrahydrofuran, (3e)



3e

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 82%. **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 7.87 – 7.80 (m, 2H), 7.56-7.54 (m, 2H), 3.85-3.81 (m, 1H), 3.79-3.75 (m, 1H), 3.67 (dt, *J* = 8.3, 6.9 Hz, 1H), 3.29 (ddd, *J* = 13.9, 11.4, 5.0 Hz, 1H), 3.14 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 1.98 (dddd, *J* = 15.8, 13.3, 7.7, 3.6 Hz, 2H), 1.97-1.82 (m, 3H), 1.48-1.43 (m, 1H), 1.34 (s, 9H). **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 157.6, 136.2, 127.9, 126.3, 67.8, 53.6, 35.3, 31.2, 31.1, 28.5, 25.6. **HRMS** (ESI, m/z): calcd. for $C_{16}H_{25}O_3S$ [M+H]+: 297.1524, found: 297.1523.

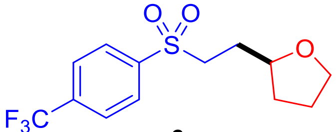
2-(2-((4-fluorophenyl)sulfonyl)ethyl)tetrahydrofuran, (3f)



3f

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 80%. **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 7.88– 7.84 (m, 2H), 7.21-7.17 (m, 2H), 3.79-3.71 (m, 2H), 3.69-3.58 (m, 1H), 3.22 (ddd, *J* = 13.9, 11.4, 4.9 Hz, 1H), 3.06 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 1.95-1.80 (m, 2H), 1.79-1.73 (m, 3H), 1.38 (dq, *J* = 12.1, 7.6 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 167.1, 164.5, 135.3 (d, *J* = 4.0 Hz), 130.9 (d, *J* = 9.0 Hz), 116.5 (d, *J* = 22.0 Hz), 67.9, 53.8, 31.2, 28.6, 25.6. **^{19}F NMR** (377 MHz, CDCl$_3$) δ -103.64 (tt, *J* = 8.9, 5.0 Hz, 1F) **HRMS** (ESI, m/z): calcd. for $C_{12}H_{16}FO_3S$ [M+H]+: 259.0804, found: 259.0808.

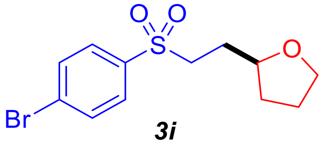
2-(2-((4-(trifluoromethyl)phenyl)sulfonyl)ethyl)tetrahydrofuran, (3g)



3g

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 68%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 8.03 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.2 Hz, 2H), 3.85-3.82 (m, 1H), 3.80-3.74 (m, 1H), 3.69-3.63 (m, 1H), 3.35 (ddd, *J* = 14.0, 11.4, 4.9 Hz, 1H), 3.16 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 2.02-1.93 (m, 2H), 1.89-1.80 (m, 3H), 1.46 (ddd, *J* = 11.6, 10.0, 5.9 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 142.8, 135.4 (q, *J* = 33 Hz), 128.7, 126.5 (q, *J* = 4 Hz) , 124.5, 121.8, 67.9, 53.5, 31.2, 28.4, 25.6. **^{19}F NMR** (377 MHz, CDCl$_3$) δ -63.2. **HRMS** (ESI, m/z): calcd. for $C_{13}H_{16}F_3O_3S$ [M+H]+: 309.0772, found: 309.0776.

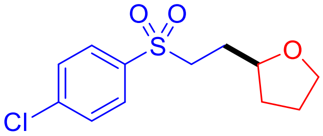
2-(2-((4-bromophenyl)sulfonyl)ethyl)tetrahydrofuran, (3i)



3i

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 78%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.76 (d, *J* = 8.6 Hz, 2H), 7.73-7.66 (m, 2H), 3.84-3.80 (m, 1H), 3.78 – 3.74 (m, 1H), 3.69-3.65 (m,1H), 3.27 (ddd, *J* = 14.1, 11.5, 4.9 Hz, 1H), 3.11 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 2.01-1.91 (m, 2H), 1.88-1.78 (m, 3H), 1.47-1.42 (m, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 138.2, 132.6, 129.6, 129.0, 67.9, 53.6, 31.2, 28.5, 25.6. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{16}BrO_3S$ [M+H]+: 319.0004, found: 319.0006.

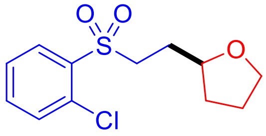
2-(2-((4-chlorophenyl)sulfonyl)ethyl)tetrahydrofuran, (3j)



3j

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 69%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.85- 7.83 (m, 2H), 7.54- 7.52 (m, 2H), 3.85-3.75 (m, 2H), 3.66 (dt, *J* = 8.4, 6.9 Hz, 1H), 3.27 (ddd, *J* = 14.0, 11.4, 4.9 Hz, 1H), 3.12 (ddd, *J* = 14.0, 11.3, 4.9 Hz, 1H), 2.01-1.92 (m, 2H), 1.89-1.79 (m, 3H), 1.46-1.31 (m, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 140.4, 137.7, 129.6, 129.6, 67.9, 53.7, 31.2, 28.6, 25.6. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{16}ClO_3S$ [M+H]+: 275.0509, found: 275.0504.

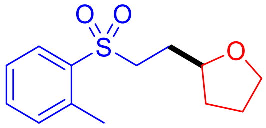
2-(2-((2-chlorophenyl)sulfonyl)ethyl)tetrahydrofuran, (3k)



3k

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 56%. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.13- 8.11 (m, 1H), 7.57-7.54 (m, 2H), 7.46 (ddd, J = 8.4, 6.1, 2.5 Hz, 1H), 3.89-3.81 (m, 1H), 3.79-3.71 (m, 1H) 3.69-3.60 (m, 1H), 3.60-3.56 (m, 1H), 3.49-3.45 (m, 1H), 2.01-1.90 (m,2H), 1.89- 1.82 (m, 3H), 1.49-1.44 (m, 1H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 136.7, 134.7, 132.8, 131.9, 131.7, 127.4, 67.9, 51.6, 31.2, 28.3, 25.6. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{15}ClNaO_3S$ [M+Na]+: 297.0328, found: 297.0323.

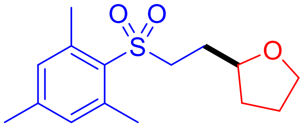
2-(2-(o-tolylsulfonyl) ethyl)tetrahydrofuran, (3l)



3l

Using 40 W 440 nm Blue LEDs, colorless oil: 75%. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 8.00 (dd, J = 7.9, 1.4 Hz, 1H), 7.52 (td, J = 7.5, 1.4 Hz, 1H), 7.38-7.28 (m, 2H), 3.87- 3.82 (m, 1H), 3.80-3.77 (m, 1H), 3.77-3.67 (m, 1H), 3.34 (dt, J = 8.4, 6.9 Hz, 1H), 3.18 (ddd, J = 13.9, 11.2, 5.0 Hz, 1H), 2.69 (s, 3H), 2.01-1.94 (m, 2H), 1.90-1.82 (m, 3H), 1.50-1.44 (m, 1H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 138.0, 137.3, 133.6, 132.7, 130.2, 126.8, 67.8, 52.7, 31.2, 28.3, 25.6, 20.4. **HRMS** (ESI, m/z): calcd. for $C_{13}H_{19}O_3S$ [M+H]+: 255.1055, found: 255.1057.

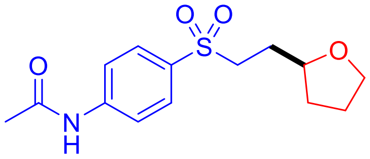
2-(2-(mesitylsulfonyl)ethyl)tetrahydrofuran, (3m)



3m

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 56%. ^{1}**H NMR** (400 MHz, CDCl$_3$) δ 6.96 (s, 2H), 3.88-3.81 (m, 1H), 3.79-3.71 (m, 1H), 3.69-3.65(m, 1H), 3.28 (ddd, J = 13.8, 11.3, 5.0 Hz, 1H), 3.10 (ddd, J = 13.8, 11.2, 4.9 Hz, 1H), 2.65 (s, 6H), 2.30 (s, 3H), 2.01 (dddd, J = 11.9, 8.8, 6.8, 4.5 Hz, 2H), 1.92 (dddd, J = 15.7, 10.2, 8.1, 4.5 Hz, 3H), 1.50-1.45 (m,1H). ^{13}**C NMR** (101 MHz, CDCl$_3$) δ 142.1, 139.0, 132.2, 131.2, 66.8, 52.5, 30.3, 26.9, 24.6, 21.9, 20.0. **HRMS** (ESI, m/z): calcd. for $C_{15}H_{23}O_3S$ [M+H]+: 283.1368, found: 283.1362.

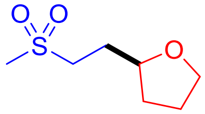
N-(4-((2-(tetrahydrofuran-2-yl)ethyl)sulfonyl)phenyl)acetamide, (3n)



3n

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 70%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 7.82 – 7.80 (m, 3H), 7.69 (d, J = 8.6 Hz, 2H), 3.85-3.81 (m, 1H), 3.79-3.70 (m, 1H), 3.68-3.65 (m, 1H), 3.28 (ddd, J = 14.0, 11.4, 4.9 Hz, 1H), 3.11 (ddd, J = 14.0, 11.3, 4.9 Hz, 1H), 2.21 (s, 3H), 2.01-1.79 (m, 5H), 1.47- 1.41 (m, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 168.8, 143.0, 133.6, 129.3, 119.5, 67.9, 53.8, 31.2, 28.7, 25.6, 24.7. **HRMS** (ESI, m/z): calcd. for $C_{14}H_{20}NO_4S$ [M+H]+: 298.1113, found: 298.1116.

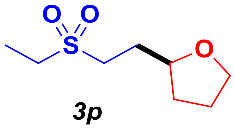
2-(2-(methylsulfonyl)ethyl)tetrahydrofuran, (3o)



3o

Using 40 W 390 nm LEDs, colorless oil, yield: 84%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 3.94-3.91 (m, 1H), 3.88-3.82 (m, 1H), 3.75-3.69 (m, 1H), 3.22-3.20 (m, 1H), 3.18-3.06 (m, 1H), 2.90 (s, 3H), 2.09-2.02 (m, 2H), 1.96-1.88 (m, 3H), 1.55-1.49 (m, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 68.0, 52.1, 40.7, 31.3, 28.3, 25.7. **HRMS** (ESI, m/z): calcd. for $C_7H_{15}O_3S$ [M+H]+: 179.0742, found: 179.0747.

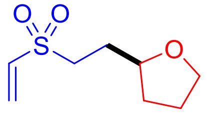
2-(2-(ethylsulfonyl)ethyl)tetrahydrofuran, (3p)



3p

Using 40 W 390 nm LEDs, colorless oil, yield: 89%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 3.93-3.90 (m, 1H), 3.85-3.81 (m, 1H), 3.75-3.69 (m, 1H), 3.14 (dt, J = 8.2, 6.8 Hz, 1H), 2.98 (dq, J = 9.6, 7.6, 6.7 Hz, 3H), 2.08-2.02 (m, 2H), 1.94-1.86 (m, 3H), 1.54-1.51 (m, 1H), 1.37 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 67.9, 49.1, 47.3, 31.3, 27.7, 25.7, 6.7. **HRMS** (ESI, m/z): calcd. for $C_8H_{17}O_3S$ [M+H]+: 193.0898, found: 193.0892.

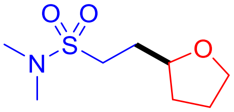
2-(2-(vinylsulfonyl)ethyl)tetrahydrofuran, (3q)



3q

Using 40 W 390 nm LEDs, colorless oil, yield: 68%. **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 6.65 (dd, *J* = 16.6, 9.9 Hz, 1H), 6.42 (d, *J* = 16.6 Hz, 1H), 6.16 (d, *J* = 9.9 Hz, 1H), 3.87 (ddt, *J* = 26.9, 8.4, 6.8 Hz, 2H), 3.81-3.69 (m, 1H), 3.18 (ddd, *J* = 14.1, 11.2, 5.0 Hz, 1H), 3.04 (ddd, *J* = 14.1, 11.1, 5.1 Hz, 1H), 2.06-1.98 (m, 2H), 1.93-1.86 (m, 3H), 1.53-1.48 (m, 1H), 1.20 (d, *J* = 14.6 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 136.2, 130.4, 67.9, 51.5, 31.3, 29.70, 28.3, 25.7. **HRMS** (ESI, m/z): calcd. for $C_8H_{14}NaO_3S$ [M+Na]+: 213.0561, found: 213.0568.

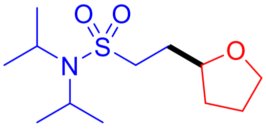
N,N-dimethyl-2-(tetrahydrofuran-2-yl)ethane-1-sulfonamide, (3r)



3r

Using 40 W 390 nm LEDs, colorless oil, yield: 65%. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 3.92-3.82 (m, 2H), 3.75-3.71 (m, 1H), 3.12 (ddd, *J* = 13.6, 11.1, 5.0 Hz, 1H), 2.94 (ddd, *J* = 13.7, 11.0, 5.0 Hz, 1H), 2.87 (s, 6H), 2.03 (dddd, *J* = 13.6, 7.4, 6.0, 4.0 Hz, 2H), 1.99-1.85 (m, 3H), 1.51 (ddt, *J* = 12.0, 8.5, 7.3 Hz, 1H). **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 67.9, 45.4, 37.5, 31.3, 29.1, 25.7. **HRMS** (ESI, m/z): calcd. for $C_8H_{18}NO_3S$ [M+H]+: 208.1007, found: 208.1002.

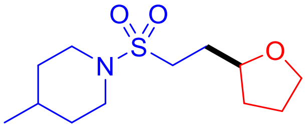
N,N-diisopropyl-2-(tetrahydrofuran-2-yl)ethane-1-sulfonamide, (3s)



3s

Using 40 W 390 nm LEDs, colorless oil, yield: 45%. **^{1}H NMR** (400 MHz, CDCl$_3$) *δ* 3.92-3.82 (m, 2H), 3.76-3.69 (m, 3H), 3.14-3.10 (m, 1H), 3.09-2.91(m, 1H), 2.06-1.86 (m, 4H), 1.32-1.31(m, 12H). **^{13}C NMR** (101 MHz, CDCl$_3$) *δ* 67.9, 52.3, 48.4, 31.4, 29.8, 25.6, 22.5, 22.4. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{26}NO_3S$ [M+H]+: 264.1633, found: 264.1637.

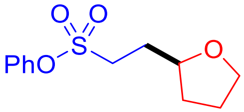
4-methyl-1-((2-(tetrahydrofuran-2-yl)ethyl)sulfonyl)piperidine, (3t)



3t

Using 40 W 390 nm LEDs, colorless oil, yield: 55%. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 3.9-3.83 (m, 1H), 3.78-72 (m, 2H), 3.10-3.06 (m, 1H), 2.96-2.92 (m, 1H), 2.77-2.71 (m, 2H), 2.06-2.00 (m, 2H), 1.94-1.90 (m, 2H), 1.89-1.72 (m, 2H), 0.97 (d, *J* = 4 Hz, 3H), 0.88-0.83 (m, 6H), 0.74-0.72 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 66.9, 45.5, 45.1, 45.1, 32.9, 30.3, 29.5, 28.7, 28.2, 24.7, 20.6. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{24}NO_3S$ [M+H]+: 262.1477, found: 262.1472.

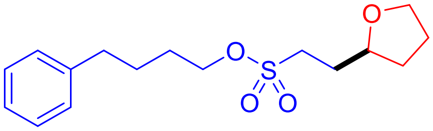
Phenyl-2-(tetrahydrofuran-2-yl)ethane-1-sulfonate, (3u)



3u

Using 40 W 390 nm LEDs, colorless oil, yield: 78%. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.35 – 7.32 (m, 2H), 7.26- 7.19 (m, 3H), 3.90- 3.80 (m, 1H), 3.78- 3.70 (m, 1H), 3.68-3.66 (m, 1H), 3.40- 3.36 (m, 1H), 3.28- 3.22 (m, 1H), 2.14-2.0 (m, 1H), 1.99-1.95 (m, 2H), 1.86-1.82 (m, 2H), 1.49-1.44(m, 1H).**^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 149.3, 130.0, 127.2, 122.1, 68.0, 47.8, 31.3, 29.6, 25.7. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{17}O_4S$ [M+H]+: 257.0848, found: 257.0844.

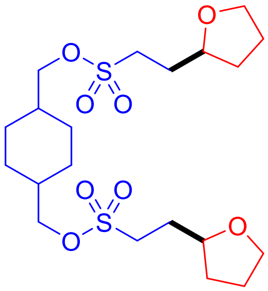
4-phenylbutyl-2-(tetrahydrofuran-2-yl)ethane-1-sulfonate, (3v)



3v

Using 40 W 390 nm LEDs, colorless oil, yield: 82%. **^{1}H NMR** (400 MHz, $CDCl_3$) *δ* 7.23-7.18 (m, 2H), 7.13-7.09 (m, 3H), 4.15 (t, *J* = 5.8 Hz, 2H), 3.82 (ddd, *J* = 10.7, 8.8, 5.4 Hz, 1H), 3.77 (dt, *J* = 8.3, 6.7 Hz, 1H), 3.76- 3.63 (m, 1H), 3.20 (ddd, *J* = 14.2, 10.8, 5.0 Hz, 1H), 3.10 (ddd, *J* = 14.2, 10.6, 5.4 Hz, 1H), 2.60 (t, *J* = 6.9 Hz, 2H), 1.97 (dddd, *J* = 20.1, 18.4, 8.9, 5.0 Hz, 2H), 1.96-1.82 (m, 2H), 1.80-1.65 (m, 4H), 1.45-1.40 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) *δ* 141.6, 128.4, 128.4, 126.0, 69.7, 67.9, 47.6, 35.2, 31.3, 29.6, 28.7, 27.2, 25.7. **HRMS** (ESI, m/z): calcd. for $C_{16}H_{26}O_4S$ [M+H]+: 313.1474, found: 313.1470.

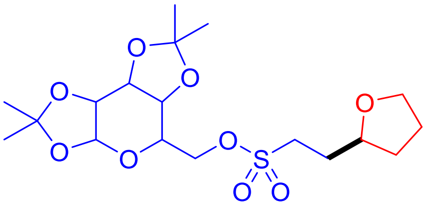
Cyclohexane-1,4-diylbis(methylene)bis(2-(tetrahydrofuran-2-yl)ethane-1-sulfonate), (3w)



3w

Using 40 W 390 nm LEDs, colorless oil, yield: 65%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.10 (d, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 6.3 Hz, 4H), 3.91-3.81 (m, 6H), 3.71 (dt, *J* = 8.2, 6.8 Hz, 3H), 3.27 (dddd, *J* = 14.2, 10.7, 5.0, 2.1 Hz, 3H), 3.15 (dddd, *J* = 14.2, 10.6, 5.4, 3.2 Hz, 3H), 2.08-1.97 (m, 7H), 1.91 (dddd, *J* = 17.8, 15.2, 9.3, 5.5 Hz, 14H), 1.53-1.48 (m, 8H), 1.05 (td, *J* = 9.1, 3.3 Hz, 4H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 74.1, 72.1, 67.9, 47.5, 47.5, 37.3, 34.8, 31.3, 29.6, 28.2, 25.7, 24.7. **HRMS** (ESI, m/z): calcd. for $C_{20}H_{38}O_8S_2$ [M+H]+: 469.1930, found: 469.1933.

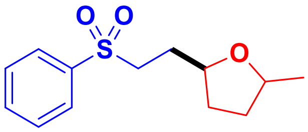
(2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl-2 (tetrahydrofuran-2-yl)ethane-1-sulfonate, (3x)



3x

Using 40 W 390 nm LEDs, colorless oil, yield: 71%[a]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.50 (dd, *J* = 5.0, 2.0 Hz, 1H), 4.61 (dd, *J* = 7.9, 2.5 Hz, 1H), 4.41 – 4.25 (m, 3H), 4.22 (dt, *J* = 8.0, 1.6 Hz, 1H), 4.08 (ddt, *J* = 8.0, 5.9, 2.5 Hz, 1H), 3.91 (dtt, *J* = 8.7, 6.9, 4.3 Hz, 1H), 3.83 (dt, *J* = 8.2, 6.7 Hz, 1H), 3.71 (dt, *J* = 8.3, 6.8 Hz, 1H), 3.35 (dtd, *J* = 14.2, 11.1, 5.2 Hz, 1H), 3.22 (tdd, *J* = 14.3, 10.7, 5.3 Hz, 1H), 2.17 – 1.91 (m, 3H), 1.91 – 1.77 (m, 2H), 1.51 (d, *J* = 2.1 Hz, 4H), 1.43 (s, 3H), 1.31 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 108.8, 108.0, 108.0, 95.2, 95.2, 70.0, 69.6, 69.6, 69.3, 67.7, 67.6, 66.8, 66.8, 65.4, 65.2, 46.9, 46.8, 30.2, 30.2, 28.5, 28.4, 25.0, 24.9, 24.6, 24.6, 23.9, 23.4, 23.4. **HRMS** (ESI, m/z): calcd. for $C_{18}H_{31}O_9S$ [M+H]+: 423.1689, found: 423.1687.

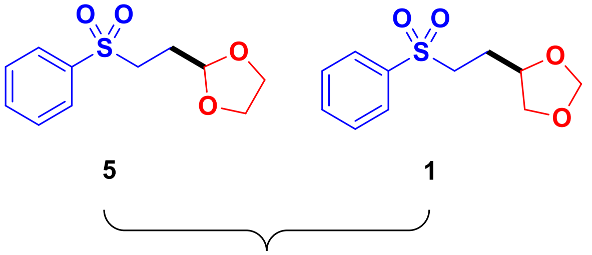
2-methyl-5-(2-(phenylsulfonyl)ethyl)tetrahydrofuran, (4a)



4a

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 95% dr = 4:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.91- 7.88 (m, 2H), 7.63 (td, *J* = 7.1, 1.5 Hz, 1H), 7.60-7.53 (m, 2H), 3.77- 3.73 (m, 1H), 3.66 -3.65 (m,1H), 3.20 – 3.02 (m, 2H), 1.92-1.81 (m, 4H), 1.69-1.65 (m, 2H), 1.13 (d, *J* = 9.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 133.6, 129.3, 129.3, 128.0, 128.0, 128.0, 80.8, 74.8, 67.4, 53.7, 53.5, 52.4, 37.2, 33.6, 32.9, 29.1, 28.8, 25.9, 25.7, 21.1. **HRMS** (ESI, m/z): calcd. for $C_{13}H_{19}O_3S$ [M+H]+: 255.1055, found: 255.1055.

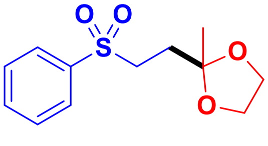
2-(2-(phenylsulfonyl)ethyl)-1,3-dioxolane/4-(2-(phenylsulfonyl)ethyl)-1,3-dioxolane, (4b)



4b

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 88%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.88(dd, *J* = 8.5, 7.1 Hz, 2H), 7.66-7.54 (m, 3H), 4.95- 4.93 (m, 1H), 3.91-3.88 (m, 3H), 3.49-3.21 (m, 2H), 2.06- 1.92 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.0, 133.9, 133.8, 129.8, 129.4, 129.3, 128.1, 128.0, 101.8, 95.1, 73.7, 69.2, 68.4, 65.2, 52.8, 50.7, 49.5, 27.1, 26.5. **HRMS** (ESI, m/z): calcd. for $C_{11}H_{15}O_4S$ [M+H]+: 243.0691, found: 243.0697.

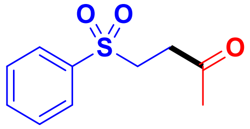
2-methyl-2-(2-(phenylsulfonyl)ethyl)-1,3-dioxolane, (4c)



4c

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 44%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H), 7.67- 7.63 (m, 1H),7.59-5.55 (m, 2H), 3.92- 3.84 (m, 2H), 3.22- 3.17 (m, 2H), 2.07-2.03 (m, 2H), 1.27 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.1, 133.7, 129.3, 128.1, 108.2, 64.8, 51.6, 31.9, 24.1. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{17}O_4S$ [M+H]+: 257.0848, found: 257.0851.

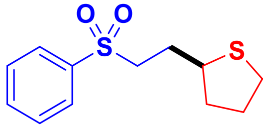
4-(phenylsulfonyl)butan-2-one (4c')



4c'

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 22%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.93 – 7.90 (m, 2H), 7.69- 7.60 (m, 1H), 7.59-7.56 (m, 2H), 3.37 (dd, *J* = 8.3, 6.8 Hz, 2H), 2.95-2.91 (m, 2H), 2.18 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 203.6, 139.0, 133.9, 129.4, 128.0, 50.6, 35.9, 29.9. **HRMS** (ESI, m/z): calcd. for $C_{10}H_{13}O_3S$ [M+H]+: 213.0585, found: 257.0588.

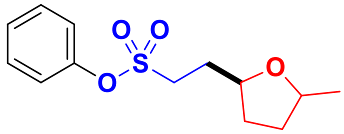
2-(2-(phenylsulfonyl)ethyl)tetrahydrothiophene, (4d)



4d

Using 40 W 440 nm Blue LEDs, colorless oil, yield: 75%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.89 (m, 2H),7.68-7.63 (m, 1H), 7.59-7.55 (m, 2H), 3.38-3.34 (m,1H), 3.22-3.16 (m, 1H),3.14-3.12(m, 1H), 2.85-2.81 (m, 2H), 2.11-1.84 (m, 5H), 1.60-1.56 (m, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 139.2, 133.7, 129, 128.0, 55.4, 47.2, 37.0, 32.4, 30.2, 30.1. HRMS (ESI, m/z): calcd. for $C_{12}H_{16}NaO_2S_2$ [M+Na]+: 279.0489, found: 279.0481.

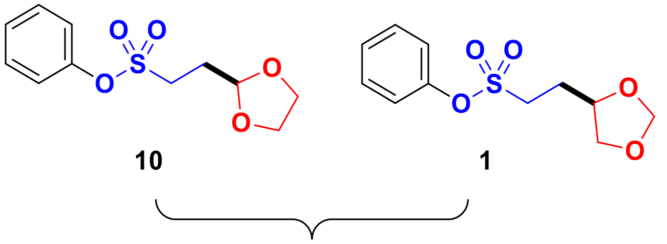
Phenyl-2-(2-methyltetrahydrofuran-2-yl)ethane-1-sulfonate, (4e)



4e

Using 40 W 390 nm Blue LEDs, colorless oil, yield: 72% dr=2:1. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35-7.31(m,2H), 7.25-7.19 (m, 3H), 3.79-3.71(m, 2H), 3.32-3.24 (m,2H),2.10-1.85 (m,4H),1.72-1.70(m,1H), 1.69-1.67 (m, 1H), 1.15 (m, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.3, 130.0, 130.0, 130.0, 127.2, 127.2, 122.1, 122.1, 122.1, 122.1, 122.0, 109.4, 81.5,80.7, 76.2, 75.9, 75.0, 67.6, 47.9, 47.6, 47.6, 46.6, 46.5, 37.6, 37.4, 34.1, 34.1, 33.6, 32.8, 32.1, 31.4, 31.2, 30.2, 30.0, 26.7, 26.0, 25.7, 25.6, 21.3,21.1 **HRMS** (ESI, m/z): calcd. for $C_{13}H_{19}O_4S$ [M+H]+: 271.1004, found: 271.1008.

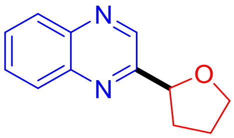
Phenyl-2-(1,3-dioxolan-2-yl)ethane-1-sulfonate/Phenyl-2-(1,3-dioxolan-4-yl)ethane-1-sulfonate, (4f)



4f

Using 40 W 390 nm Blue LEDs, colorless oil, yield: 70% [10:1]. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.40-7.35 (m, 2H), 7.30-7.23 (m,3H), 5.04-5.01 (m,1H), 3.98-3.84 (m, 4H), 3.37-3.33 (m, 2H)， 2.35-2.30 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.2, 130.0, 130.0, 127.4, 127,3, 122.1, 122.0, 101.4, 95.2, 73.2, 69.2, 65.3, 47.0, 44.8, 27.8, 27.7. **HRMS** (ESI, m/z): calcd. for $C_{11}H_{15}O_5S$ [M+H]+: 259.0640, found: 259.0640.

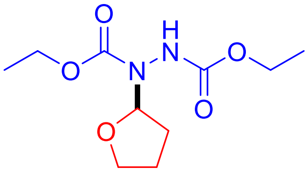
2-(tetrahydrofuran-2-yl)quinoxaline, (5a)



5a

Using 40 W 390 nm LEDs, colorless oil, yield: 35%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.15-8.04 (m, 2H), 7.74- 7.71 (m, 2H), 5.15 (t, J = 7.0 Hz, 1H), 4.18 (dt, J = 8.3, 6.7 Hz, 1H), 4.05 (dt, J = 8.3, 6.8 Hz, 2H), 2.55-2.50 (m, 1H), 2.51- 2.48 (m, 1H), 2.19-2.03 (m, 2H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 157.6, 143.6, 142.00, 141.6, 132.0, 130.2, 129.4, 129.3, 129.2, 129.1, 80.5, 69.4, 32.9, 26.0. **HRMS** (ESI, m/z): calcd. for $C_{12}H_{13}N_2O$ [M+H]+: 201.1028, found: 201.1021.

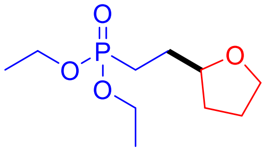
Diethyl 1-(tetrahydrofuran-2-yl)hydrazine-1,2-dicarboxylate, (5b)



5b

Using 40 W 390 nm LEDs, colorless oil, yield: 58%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 6.48 (s, 1H), 5.98 (s, 1H), 4.23- 4.15 (m, 4H), 3.98 (dt, J = 7.8, 6.2 Hz, 1H), 3.74 (q, J = 7.2 Hz, 1H), 2.07-1.84 (m, 4H), 1.21 (td, J = 7.2, 2.7 Hz, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 156.7, 155.6, 87.6, 68.7, 62.8, 62.1, 28.3, 25.3, 14.4, 14.4. **HRMS** (ESI, m/z): calcd. for $C_{10}H_{19}N_2O_5$ [M+H]+: 247.1294, found: 247.1292.

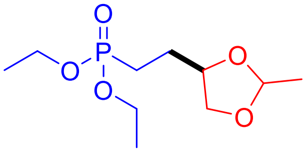
Diethyl-(2-(tetrahydrofuran-2-yl)ethyl)phosphonate, (5c)



5c

Using 40 W 390 nm LEDs, colorless oil, yield: 62%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.10-4.02 (m, 4H), 3.78 (tdd, *J* = 8.9, 6.4, 2.0 Hz, 2H), 3.70-3.68 (m, 1H), 1.97- 1.76 (m, 4H), 1.74-1.71 (m, 3H),1.47-1.42 (m,1H), 1.25 (t, *J* = 7.0 Hz, 6H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 78.9, 78.7, 67.8, 61.5, 61.5, 61.5, 61.4, 31.0, 28.4, 28.4, 25.7, 23.1, 21.7, 16.5, 16.4. ^{31}**P NMR** (162 MHz, $CDCl_3$) δ 32.31. HRMS (ESI, m/z): calcd. for $C_{12}H_{22}O_4P$ [M+H]+: 237.1256, found: 237.1252.

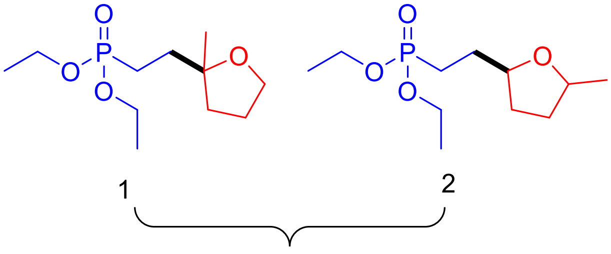
Diethyl (2-(2-methyl-1,3-dioxolan-4-yl)ethyl)phosphonate, (5d)



5d

Using 40 W 390 nm LEDs, colorless oil, yield: 62%. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.11-4.01 (m, 4H), 3.98- 3.86 (m,4H), 1.90- 1.75 (m, 4H), 1.33- 1.23 (m, 9H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 109.2, 64.8, 61.6, 31.8, 23.8, 20.9, 19.5, 16.4. ^{31}**P NMR** (162 MHz, $CDCl_3$) δ 32.55. **HRMS** (ESI, m/z): calcd. for $C_{10}H_{22}O_5P$ [M+H]+: 253.1205, found: 253.1209.

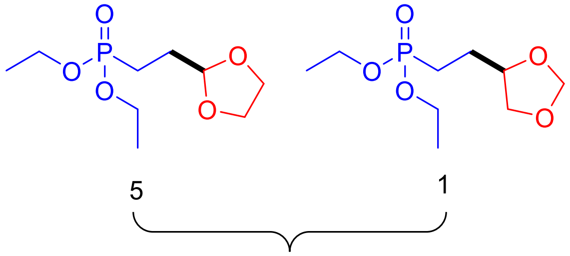
Diethyl-(2-(2-methyltetrahydrofuran-2-yl)ethyl)phosphonate/diethyl-(2-(5-methyltetrahydrofuran-2-yl)ethyl)phosphonate, (5e)



5e

Using 40 W 390 nm LEDs, colorless oil, yield: 61% [1:2]. ^{1}**H NMR** (400 MHz, $CDCl_3$) δ 4.11- 4.03 (m, 4H), 3.83- 3.75 (m, 2H), 2.02-1.66 (m, 8H), 1.54-1.32(m, 1H), 1.32-1.24 (m, 6H), 1.21-1.16 (m, 3H). ^{13}**C NMR** (101 MHz, $CDCl_3$) δ 81.8, 81.6, 79.0, 79.8, 78.5, 75.5, 74.6, 67.4, 61.6, 61.5, 61.5, 61.5, 61.5, 61.5, 36.7, 33.8, 33.1, 33.0, 32.9, 31.8, 30.9, 28.9, 28.9, 28.8, 28.7, 26.1, 25.4, 23.1, 23.0, 21.7, 21.5, 21.4, 21.2, 20.1, 16.5, 16.4. **^{31}P NMR** (162 MHz, CDCl$_3$) δ 33.11, 32.56. **HRMS** (ESI, m/z): calcd. for $C_{11}H_{24}O_4P$ [M+H]+: 251.1412, found: 251.1419.

Diethyl-(2-(1,3-dioxolan-2-yl)ethyl)phosphonate/diethyl-(2-(1,3-dioxolan-4-yl)ethyl)phosphonate, (5f)



5f

Using 40 W 390 nm LEDs, colorless oil, yield: 68% [5:1]. **^{1}H NMR** (400 MHz, CDCl$_3$) δ 4.98 (t, *J* = 4.0 Hz, 1H), 4.10- 3.94 (m, 4H), 3.93- 3.81 (m, 4H), 1.93 -1.77(m, 4H), 1.26 (td, *J* = 7.0, 2.7 Hz, 6H). **^{13}C NMR** (101 MHz, CDCl$_3$) δ 103.4, 103.2, 95.0, 75.6, 75.4, 69.2, 65.1, 61.6, 61.6, 61.5, 26.9, 26.9, 26.3, 26.2, 22.6, 21.2, 20.3, 18.8, 16.4, 16.4. **^{31}P NMR** (162 MHz, CDCl$_3$) δ 31.99 (d, *J* = 26.1 Hz), 31.94, 31.35. **HRMS** (ESI, m/z): calcd. for $C_9H_{20}O_5P$ [M+H]+: 239.1048, found: 239.1055.

Mechanistic Studies

UV-Vis spectra

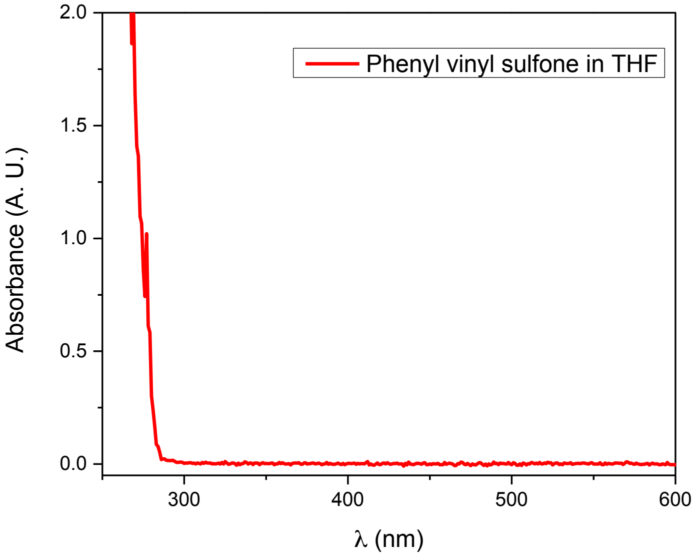


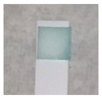
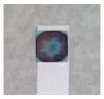
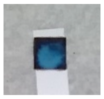
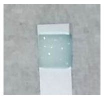
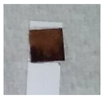
Figure S2: UV-Vis spectra
UV-vis spectroscopic measurements on combination of phenyl vinyl sulfone in THF.
Spectra taken with 0.2 mmol of substrate in 1mL THF, concentration 0.2 mmol/mL.

To further investigate the role played by phenyl vinyl sulfone, we performed UV-vis spectroscopic measurements. Phenyl vinyl sulfone in THF does not show significant light absorption throughout the wavelength in this test, which indicates that phenyl vinyl sulfone does not act as triplet-state photocatalyst.

Peroxide Test Under light Irradiation

1 mL of THF under argon/air was irradiated for 24 hours with a 440 and 427 nm lamp and immediately after we performed a peroxide strip test. These results show that under light irradiation, the amounts of peroxides increase. A higher increase is observed when THF is open to air during irradiation.

Figure S3. Peroxide test of THF with and without light irradiation. Scale of peroxides concentration: white (0 mg/L) to dark blue (25 mg/L).

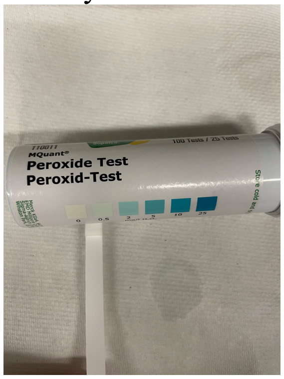
Dark, Ar	427 nm, Ar	440 nm, Ar	Dark, Air	440 nm, Air
				

Measuring Peroxide in THF Prior to Reaction

THF directly from the bottle used in the reactions:

The amount of peroxides measured were around 2–5ppm.

Freshly distilled THF used in Table 1 entry 15 of the manuscript (product yield 35%):



The amount of peroxides measured were around 0–0.5ppm.

These results confirm that trace amounts of peroxides are required to initiate the reaction.

Oxygen Leaching Experiments.

While the reaction is performed under argon, the septa used allow for oxygen leaching over the course of the reaction. This additional oxygen is presumed to help sustain the reaction over time. To measure the rate of oxygen leaching, we performed a series of time dependent experiments using Ph_3P as indicator for presence of O_2 in the system over time.

Under standard reaction conditions (**Argon**, THF, light, and 0.2 mmol Ph_3P):
- after 12h we obtained 6% triphenylphosphine oxide (Ph_3PO)
- after 24h we obtained 8% triphenylphosphine oxide (Ph_3PO)
- after 48h we obtained 13% triphenylphosphine oxide (Ph_3PO)

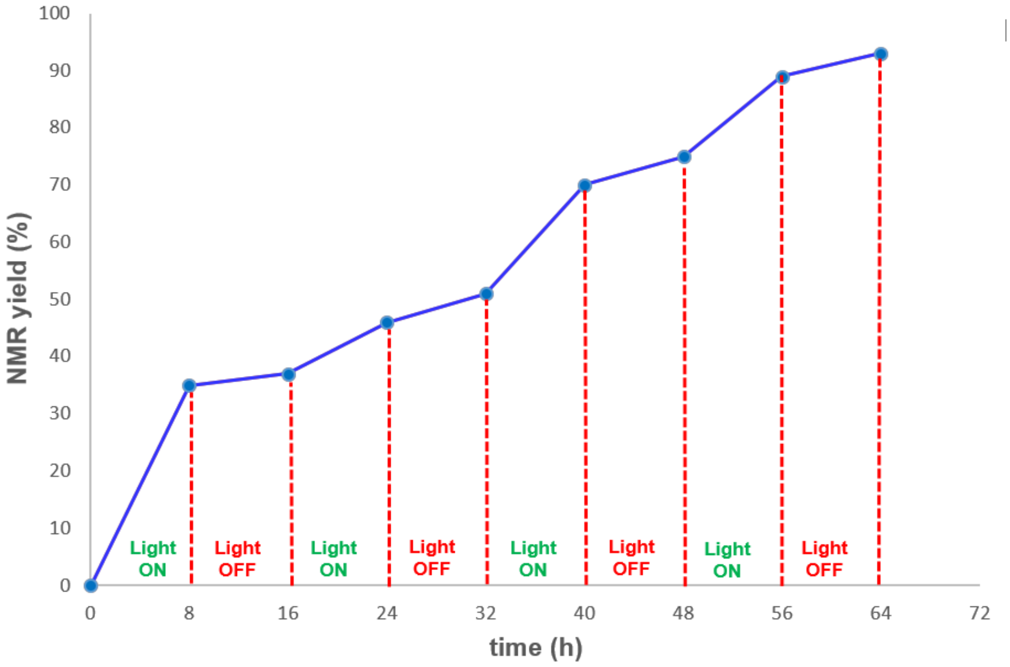
For comparison, when the same reaction is perfomed open to air (**Air**, THF, light, and 0.2 mmol Ph_3P):
- after 12h we obtain 58% triphenylphosphine oxide (Ph_3PO)
- after 24h we obtain 90% triphenylphosphine oxide (Ph_3PO).

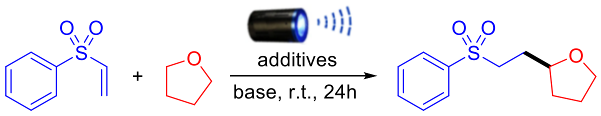
These results confirm that Ph_3PO formation is due to presence of oxygen in the system, and that oxygen can leach in the reaction over time at a rate approaching 2% every 12h, which corresponds to 0.004 mmol of O_2 every 12h.

Light ON-OFF Experiments

To evaluate the radical chain process and its influence in product formation, we performed light on/off experiments under standard reaction conditions and measured product formation over time.
We observe an increase in yield of around 4-5% during dark cycles, which suggests a short-lived radical chain process occurring during the transformation. See the Figure S4 below.

Figure S4. Light On-Off experiment. Product formation on vertical axis; time on horizontal axis.



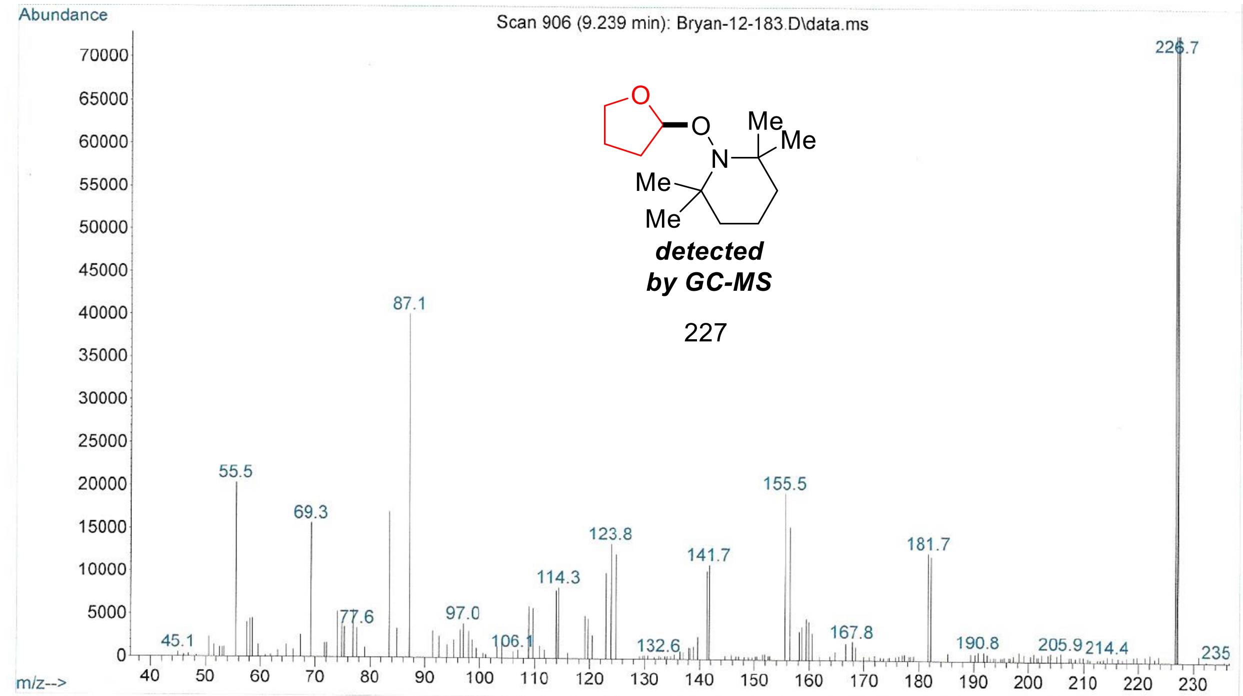


1a *2a* *3a*

Condition	Time (h)	Product yield (%)
Light	8	35
Dark	16	37
Light	24	46
Dark	32	51
Light	40	70
Dark	48	75
Light	56	89
Dark	64	93

Reaction conditions: **1a** (0.2 mmol), ethers 1 mL, RT, under argon atmosphere were irradiated with 40 W LED 440 nm, yields are all NMR yield using 1,2-dibromoethane dibromomethane as the internal standard.

THF Radical Trapping with TEMPO.



detected by GC-MS

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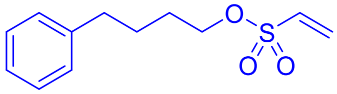
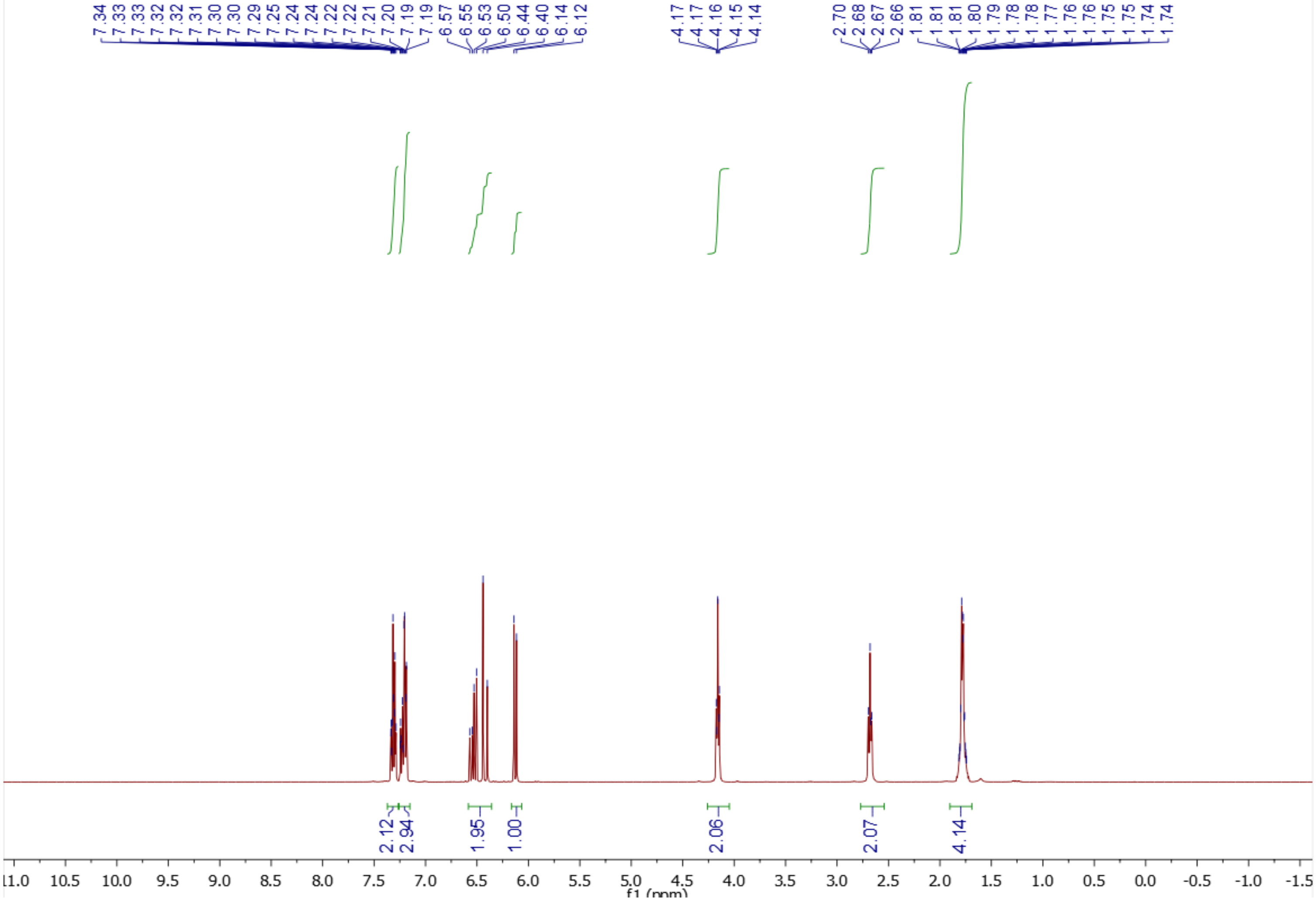
NMR Spectra

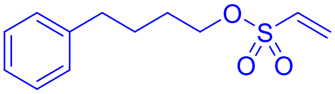
^{1}H-NMR (400 MHz, $CDCl_3$) of **1v**



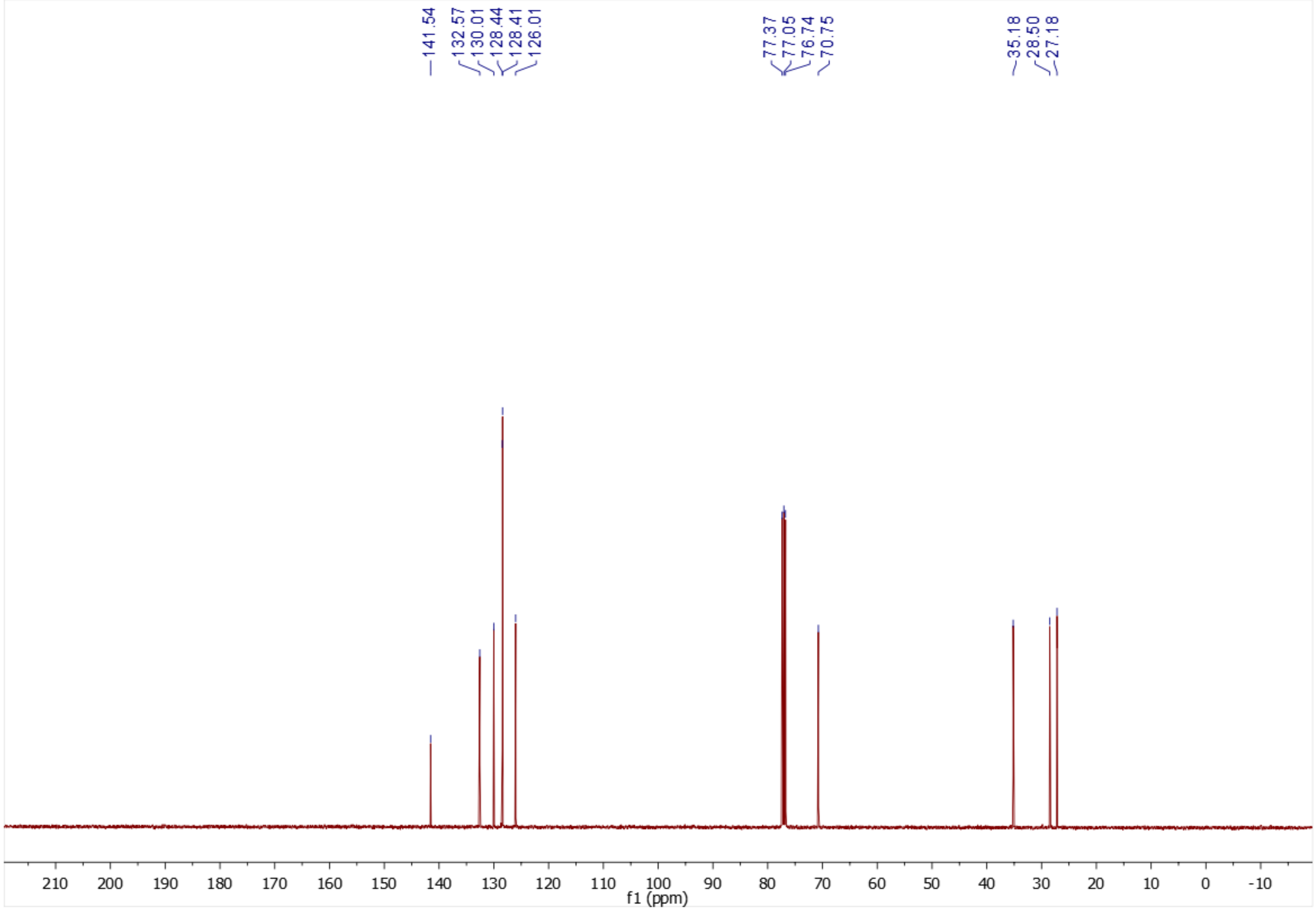
1v



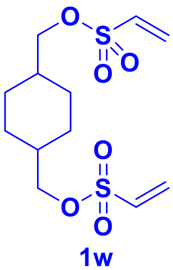
^{13}C-NMR (101 MHz, CDCl$_3$) of **1v**



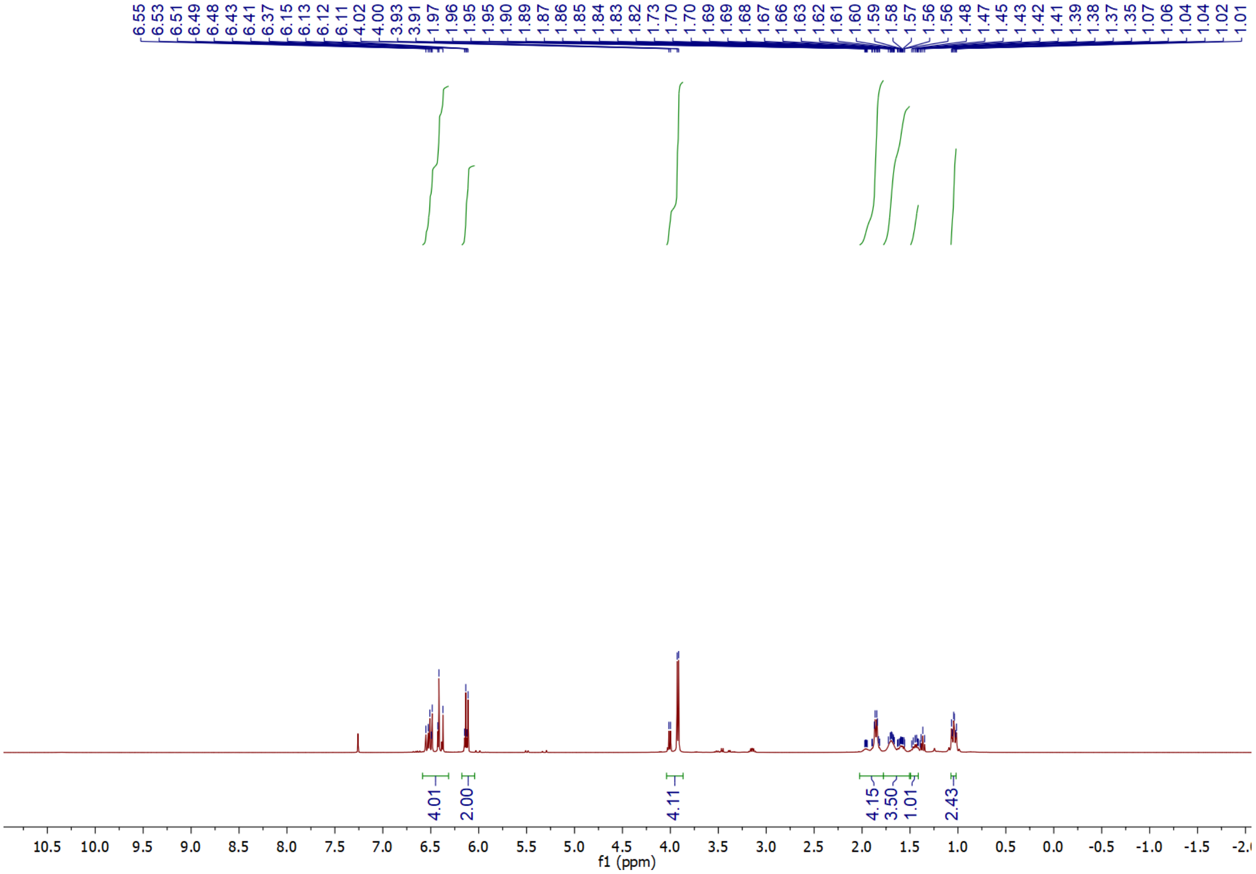
1v



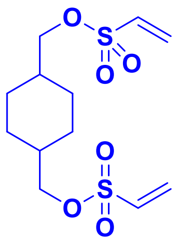
^{1}H-NMR (400 MHz, CDCl$_3$) of **1w**



1w



^{13}C-NMR (101 MHz, CDCl$_3$) of **1w**



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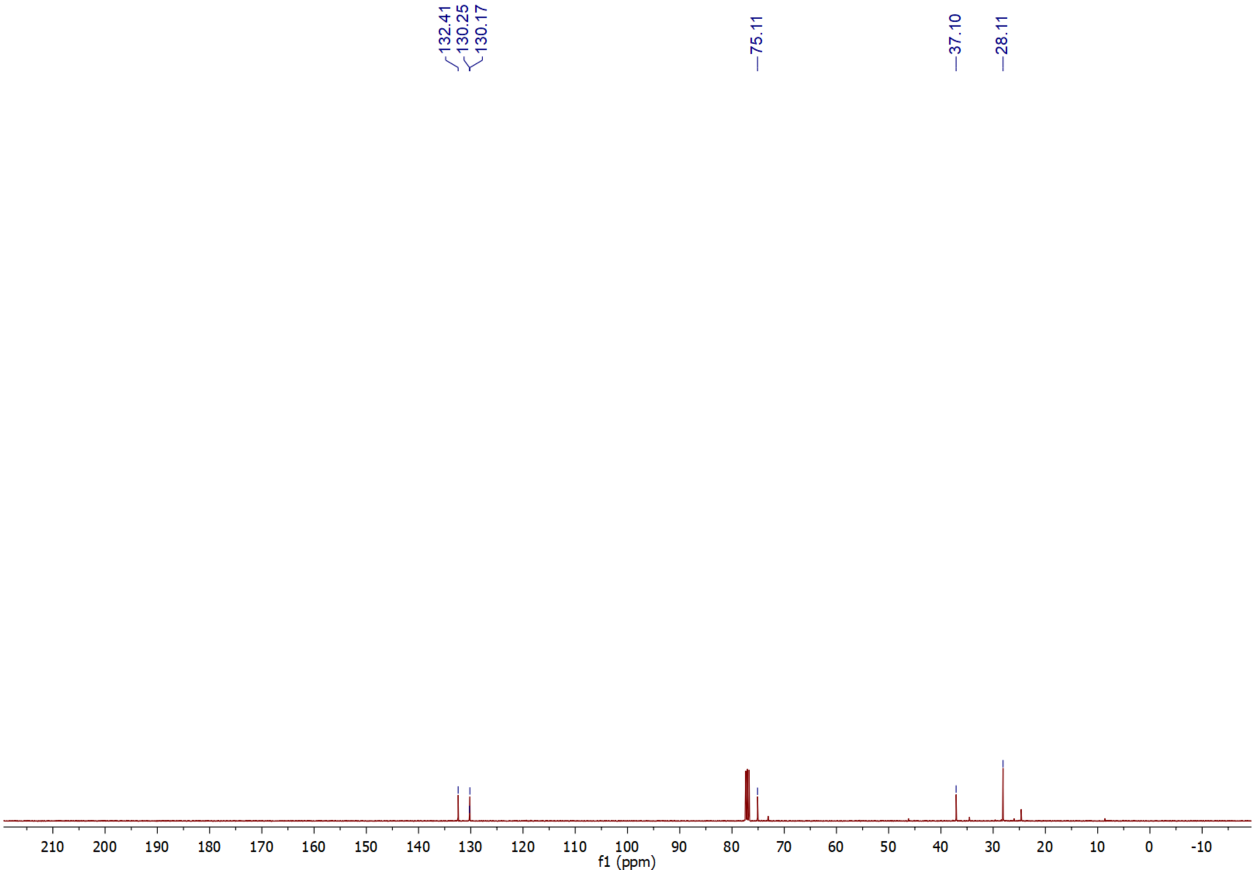
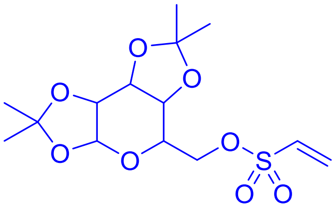


^{1}H-NMR (400 MHz, CDCl$_3$) of **1x**



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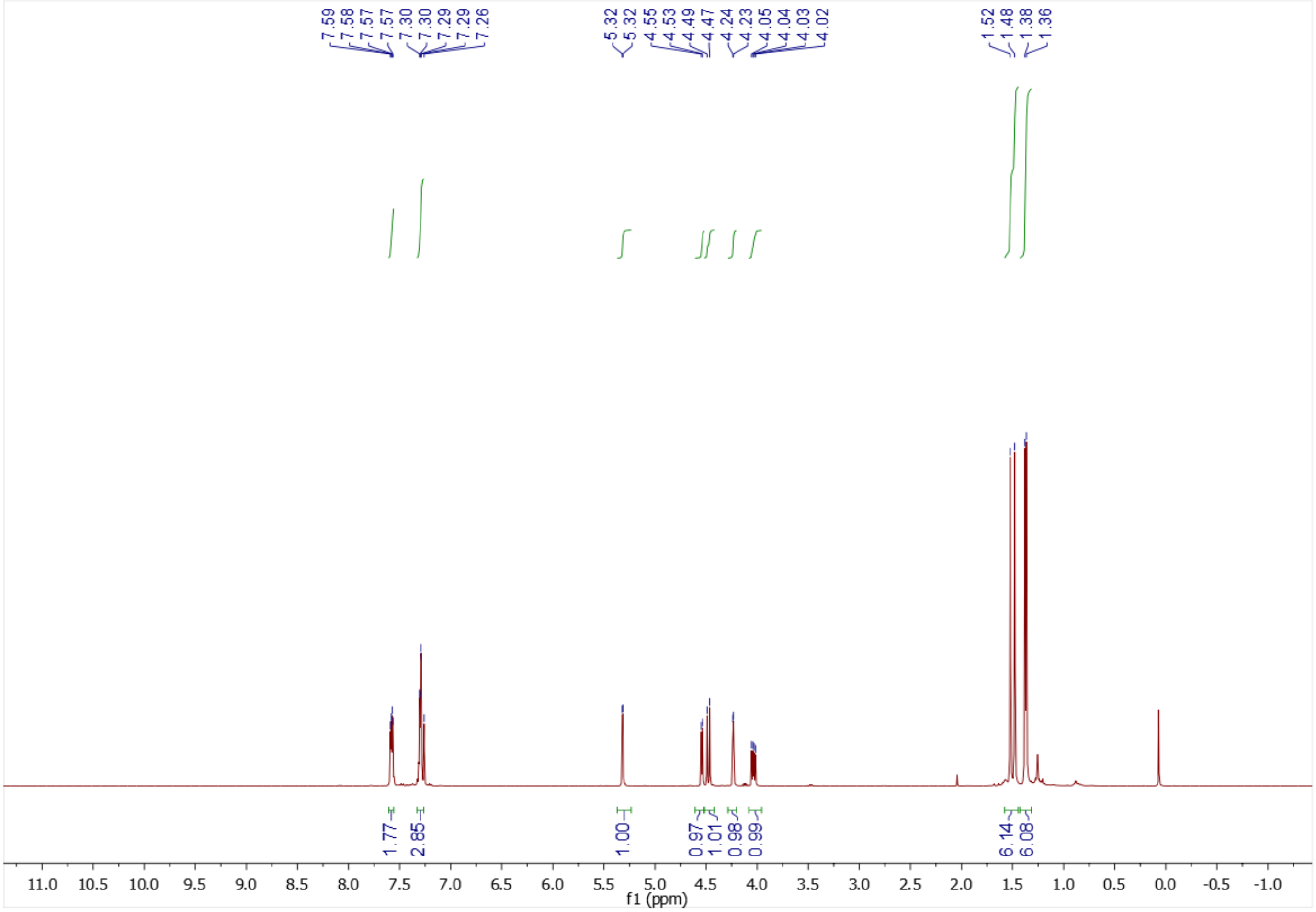
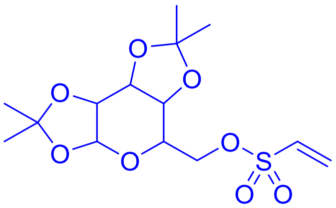


^{13}C-NMR (101 MHz, $CDCl_3$) of **1x**



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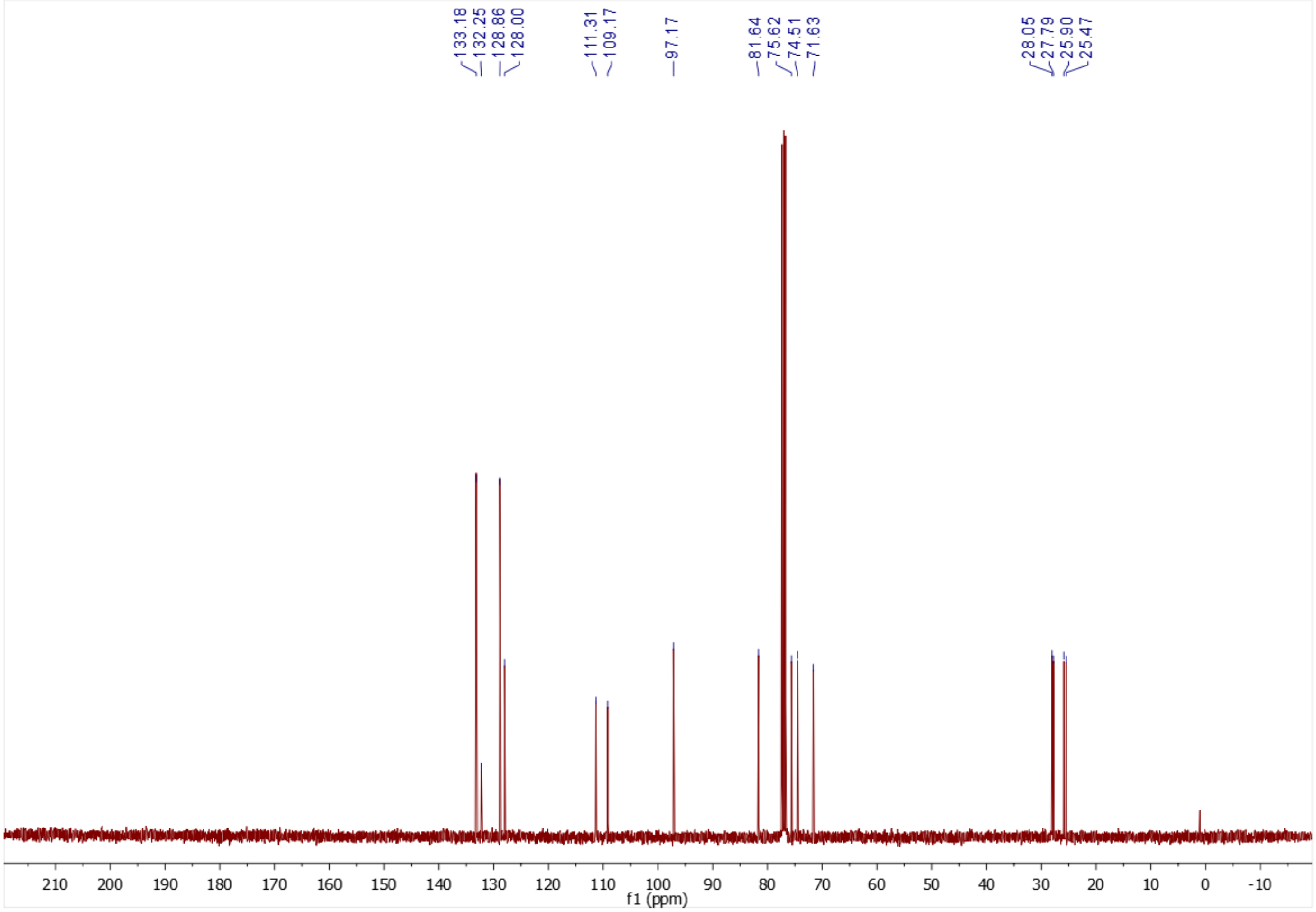
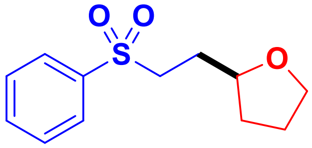


^{1}H-NMR (400 MHz, CDCl$_3$) of **3a**



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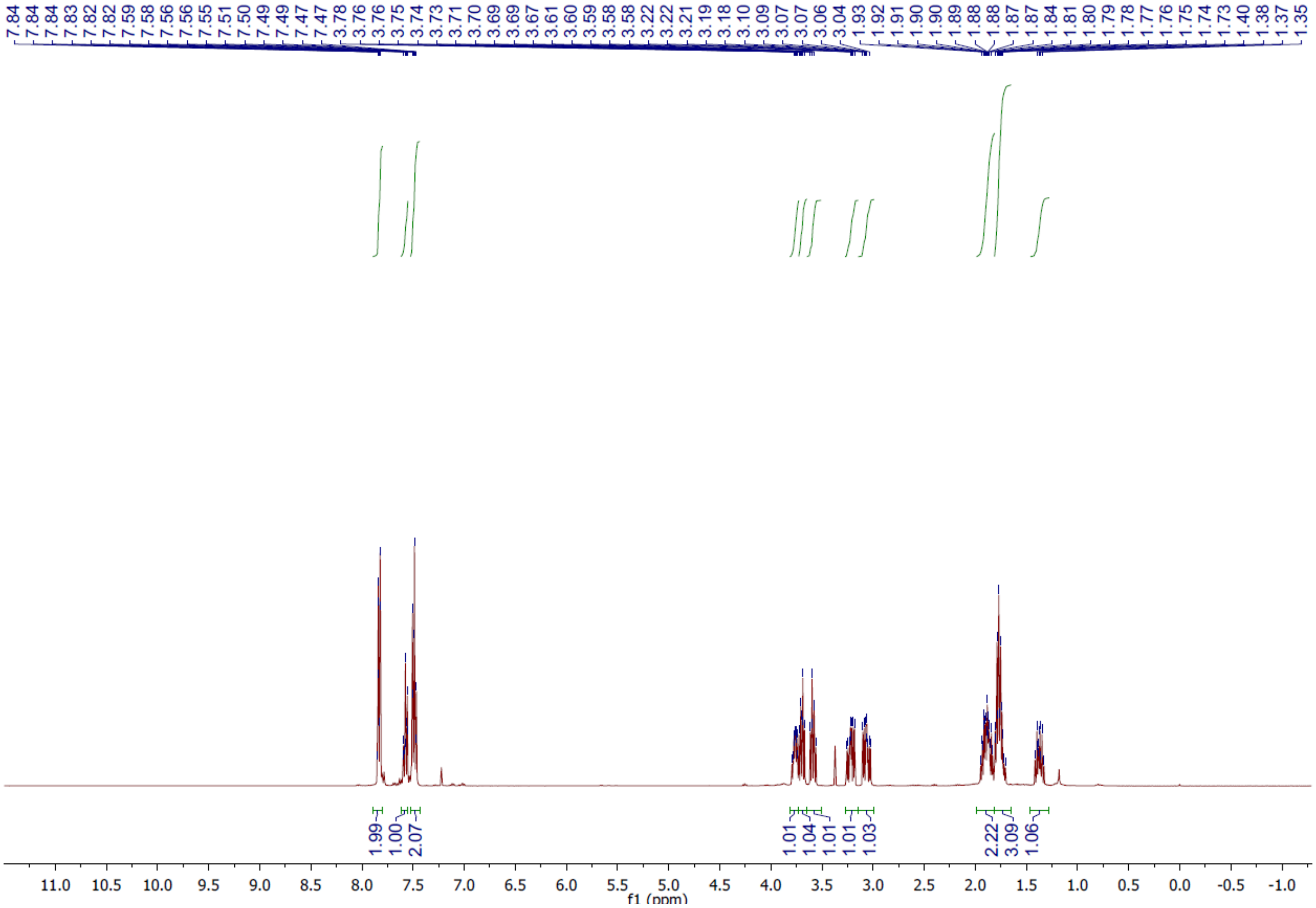
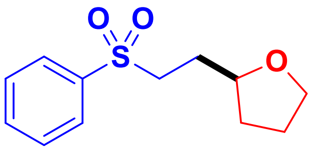


^{13}C-NMR (101 MHz, CDCl$_3$) of **3a**



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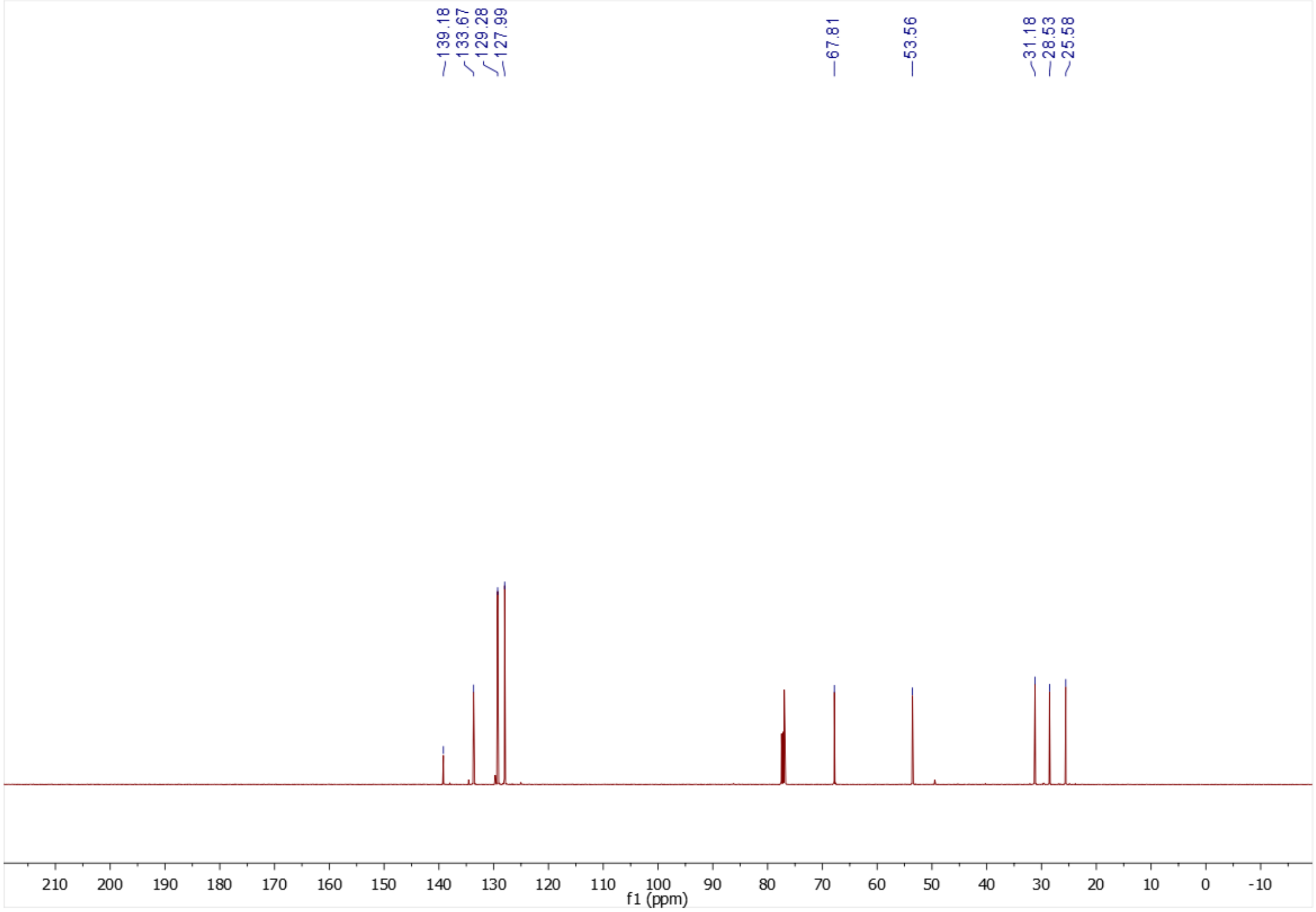
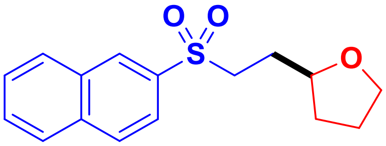


^{1}H-NMR (400 MHz, CDCl$_3$) of **3b**



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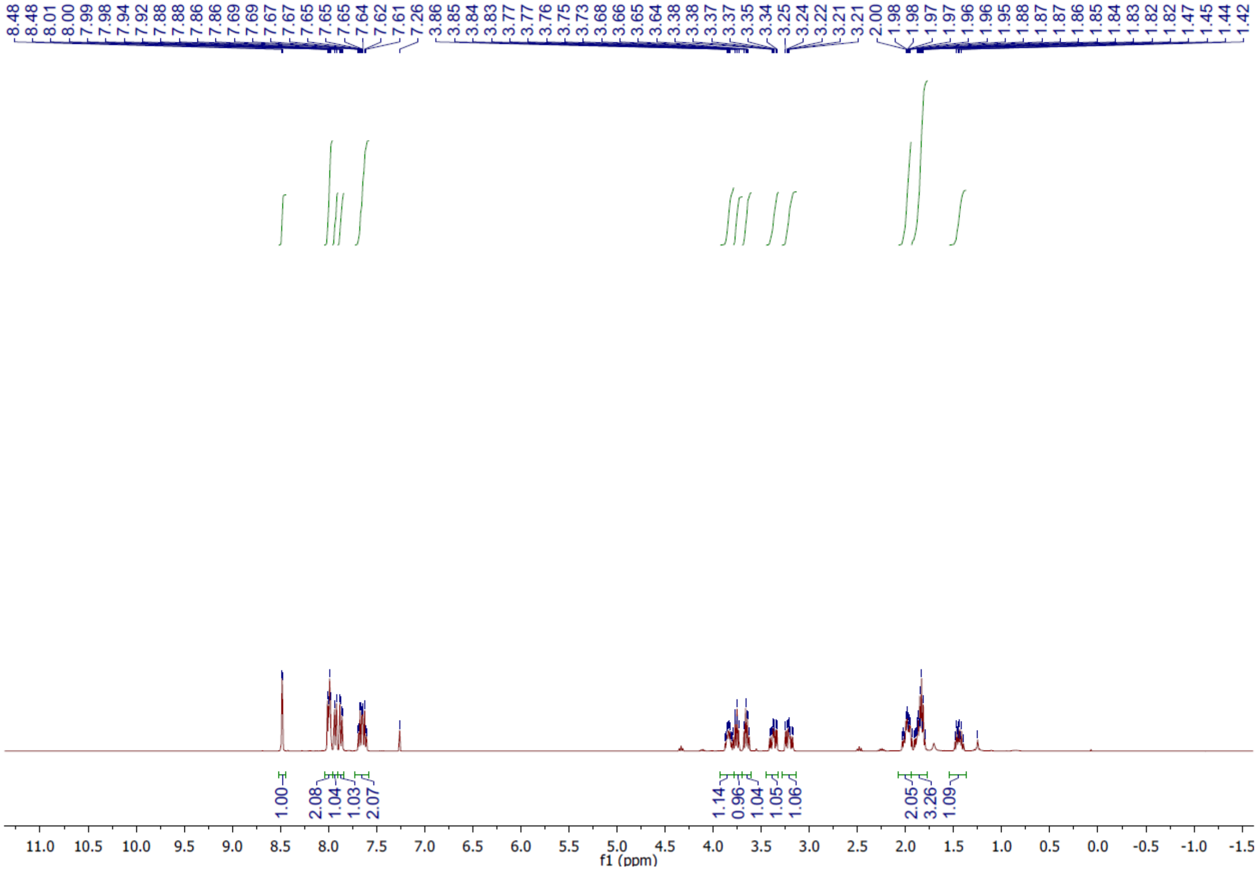
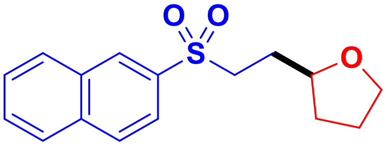


^{13}C-NMR (101MHz, CDCl$_3$) of **3b**



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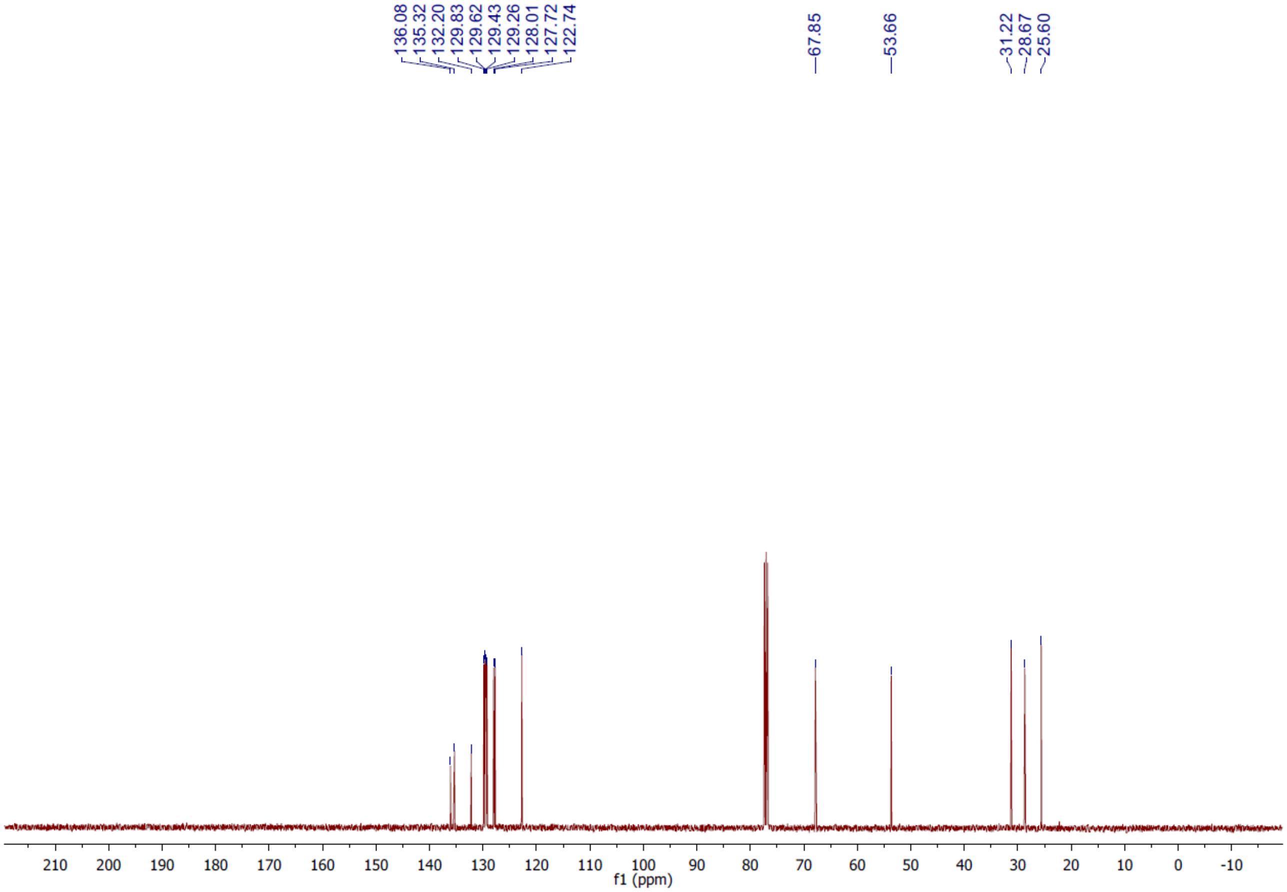
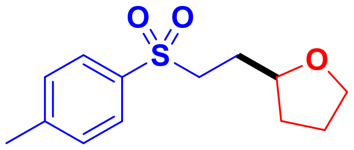


^{1}H-NMR (400 MHz, $CDCl_3$) of **3c**



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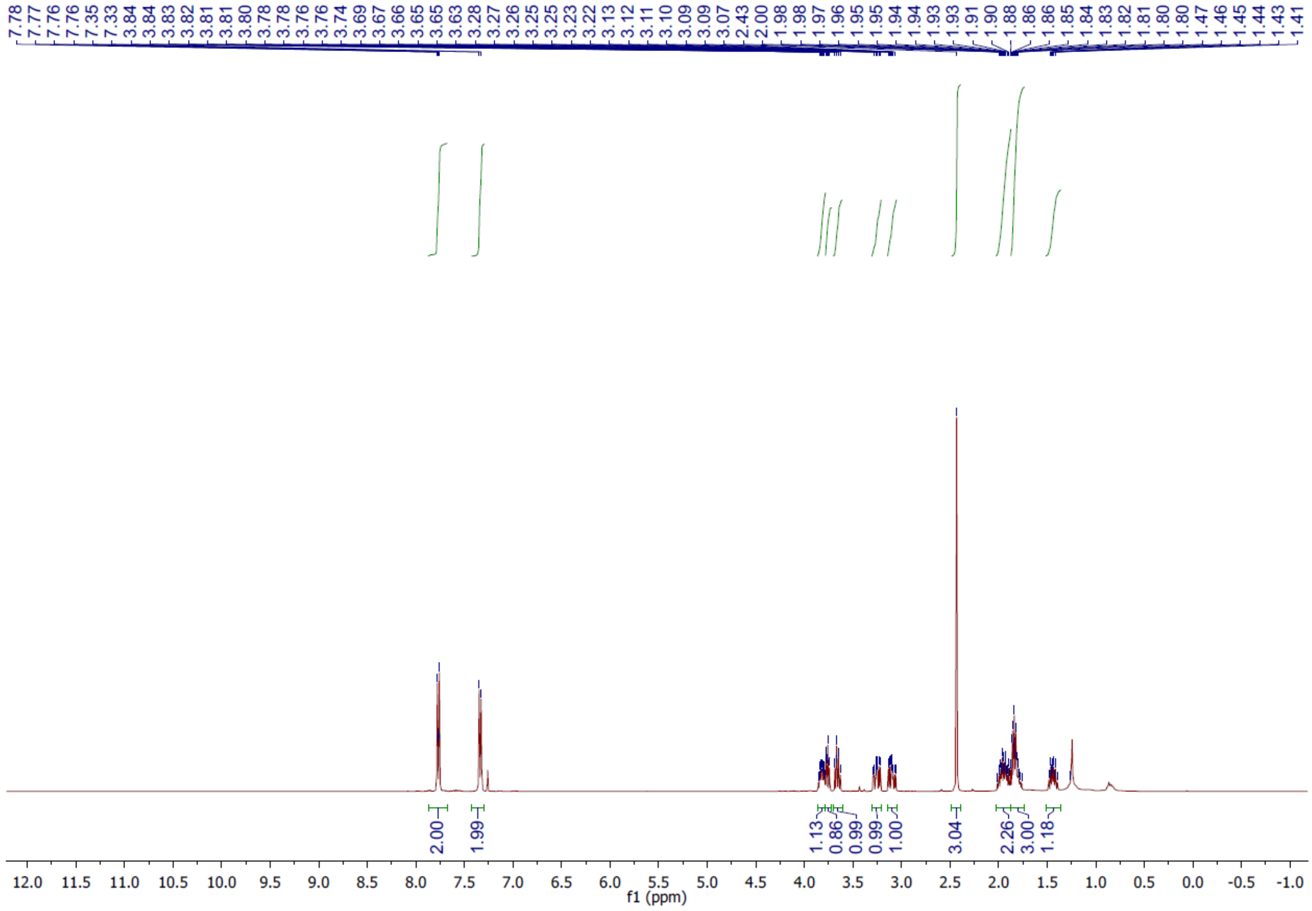
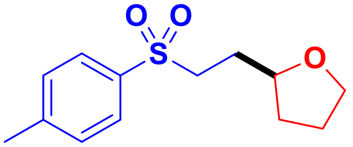


^{13}C-NMR (101 MHz, CDCl$_3$) of **3c**



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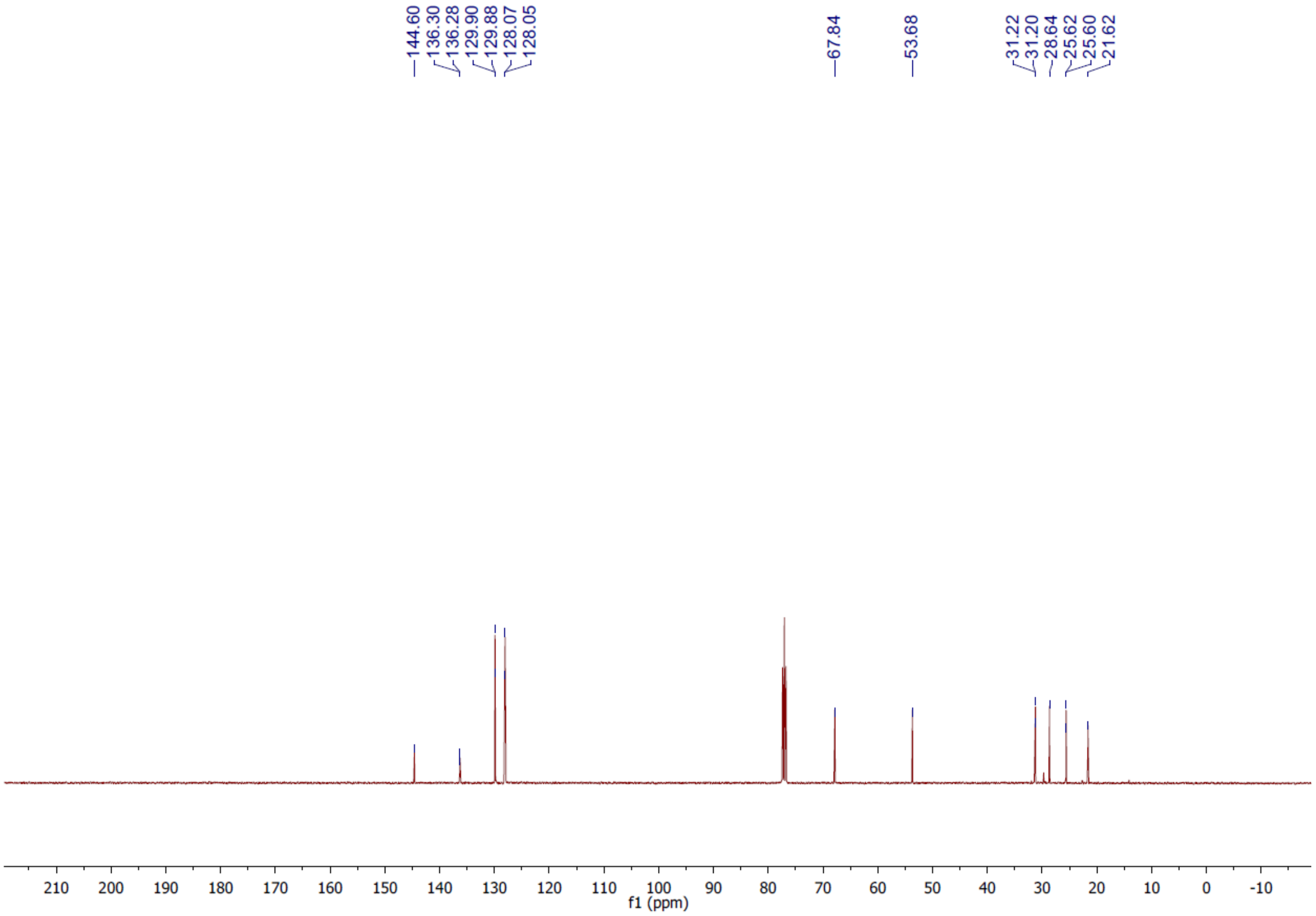
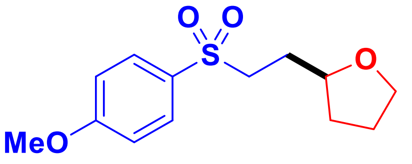


^{1}H-NMR (400 MHz, CDCl$_3$) of **3d**



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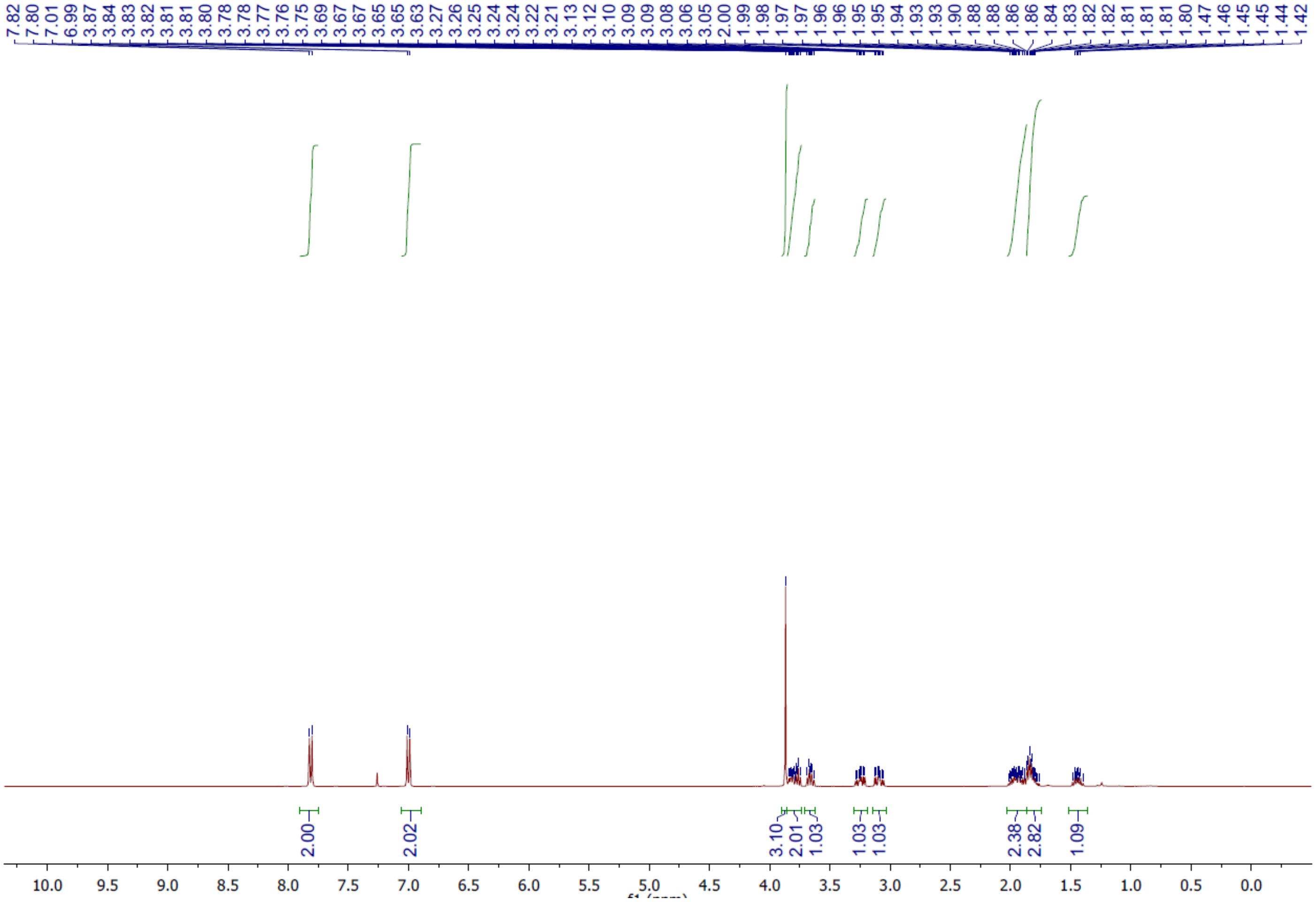
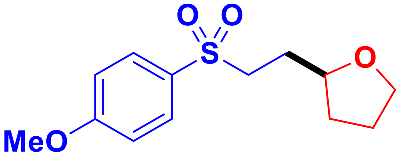


^{13}C-NMR (101 MHz, $CDCl_3$) of **3d**



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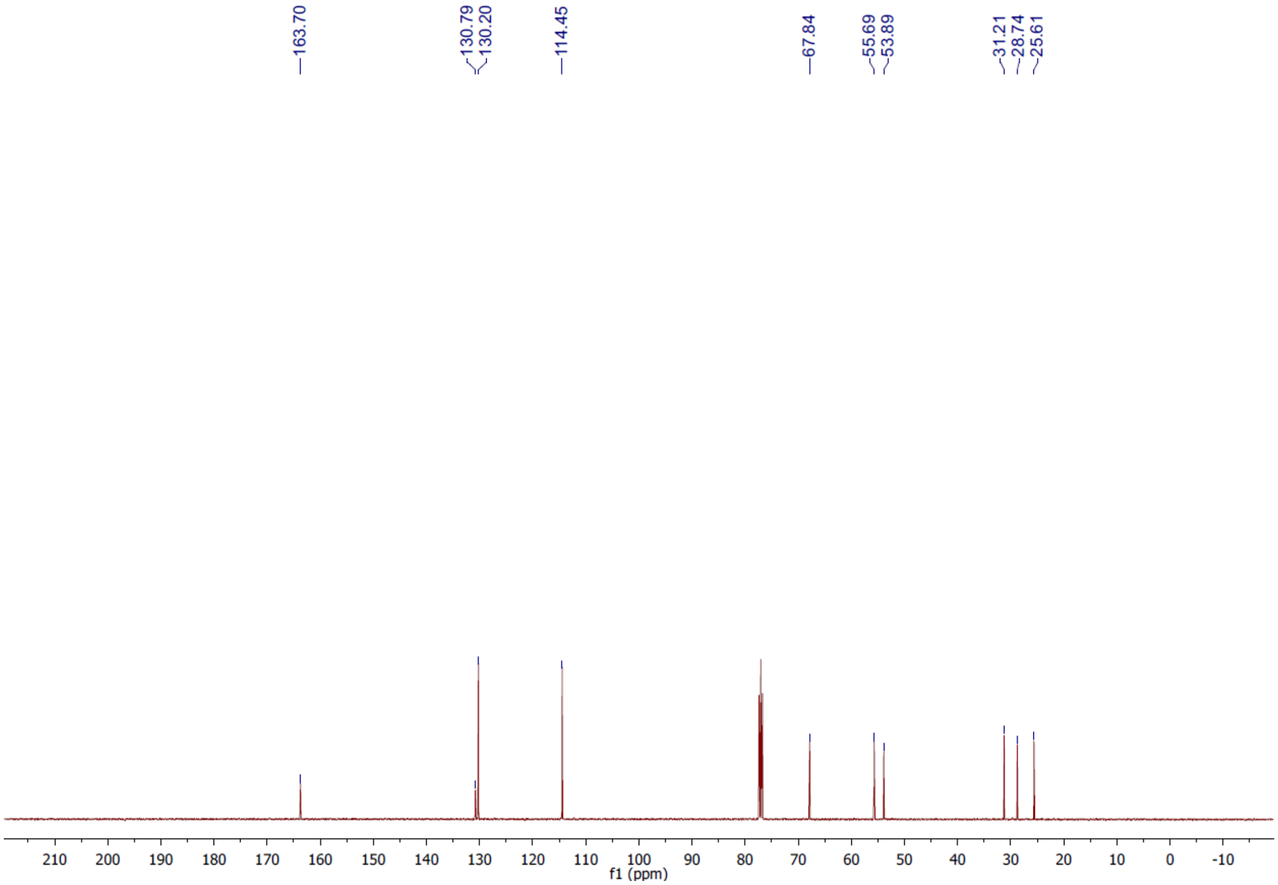
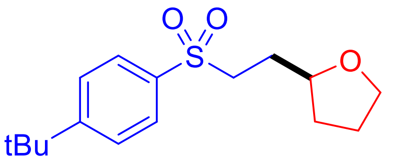


^{1}H-NMR (400 MHz, $CDCl_3$) of **3e**



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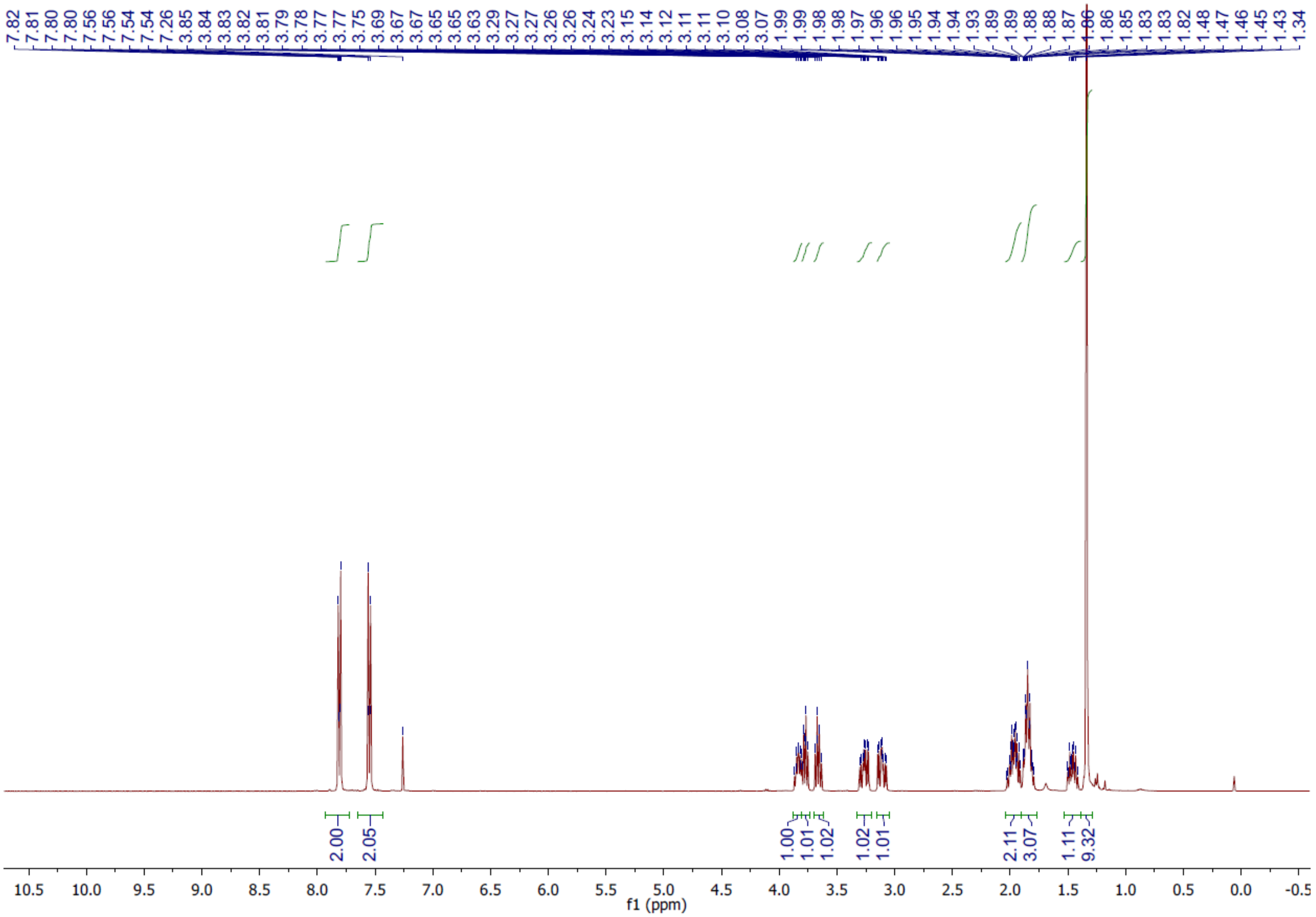
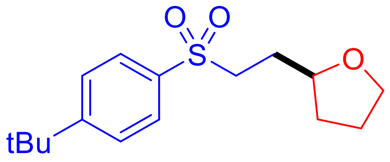


^{13}C-NMR (101 MHz, CDCl$_3$) of **3e**



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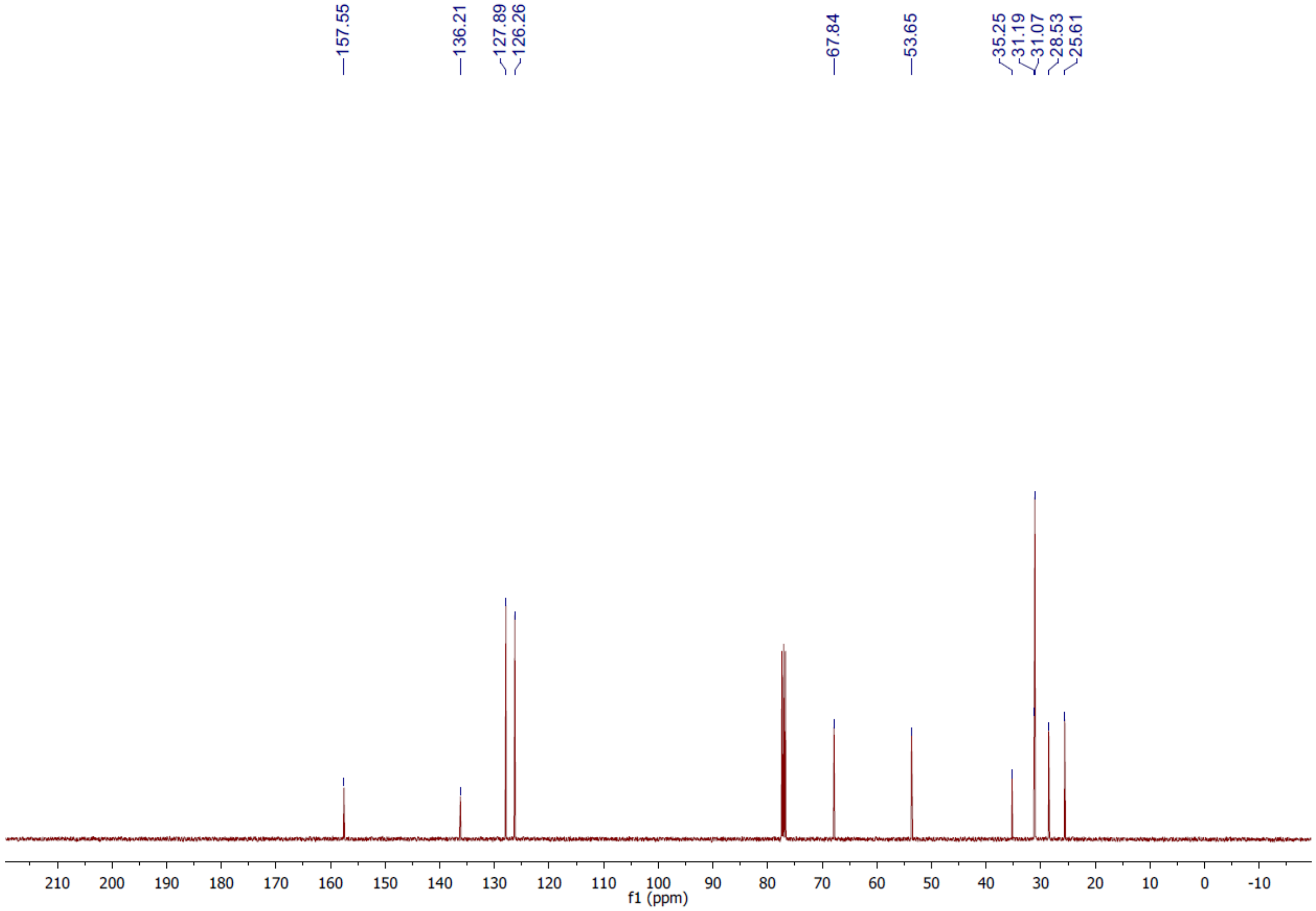
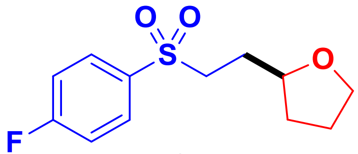


^{1}H-NMR (400 MHz, $CDCl_3$) of **3f**



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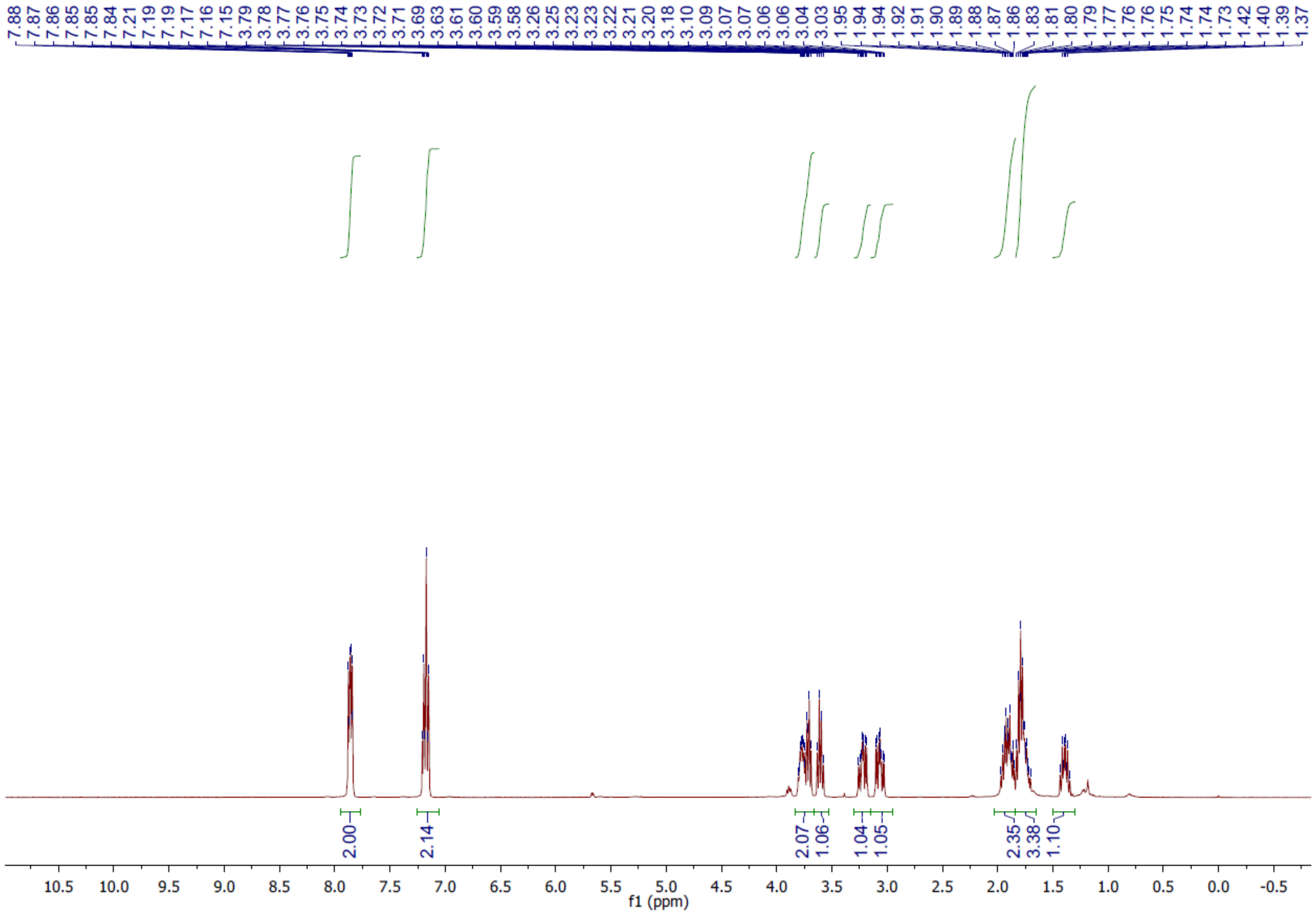
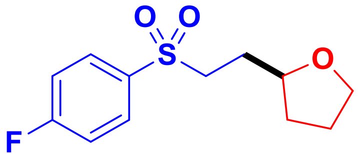


^{13}C-NMR (101 MHz, CDCl$_3$) of **3f**



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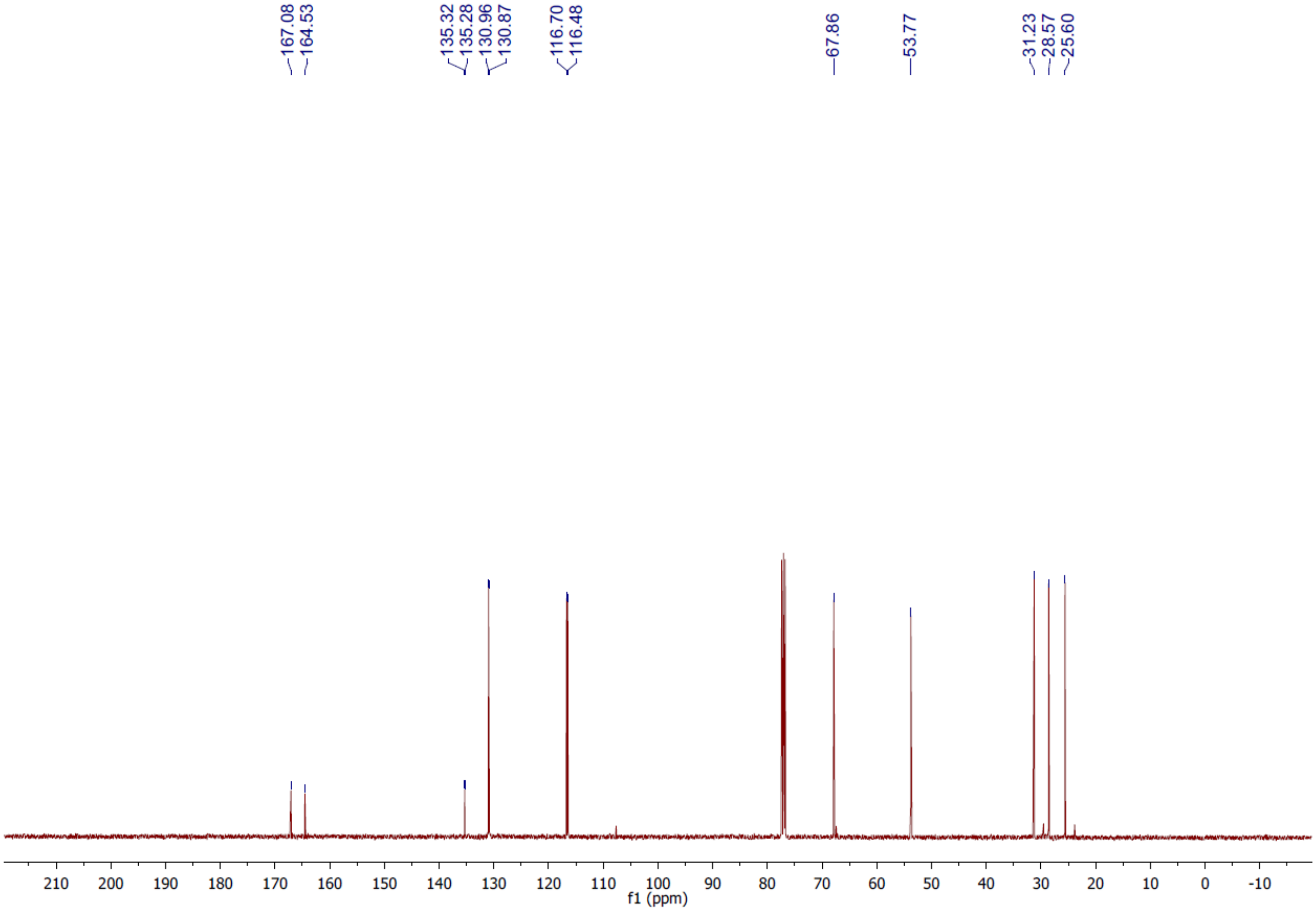
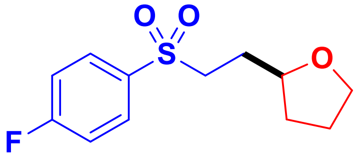


^{19}F-NMR (377 MHz, CDCl$_3$) of **3f**



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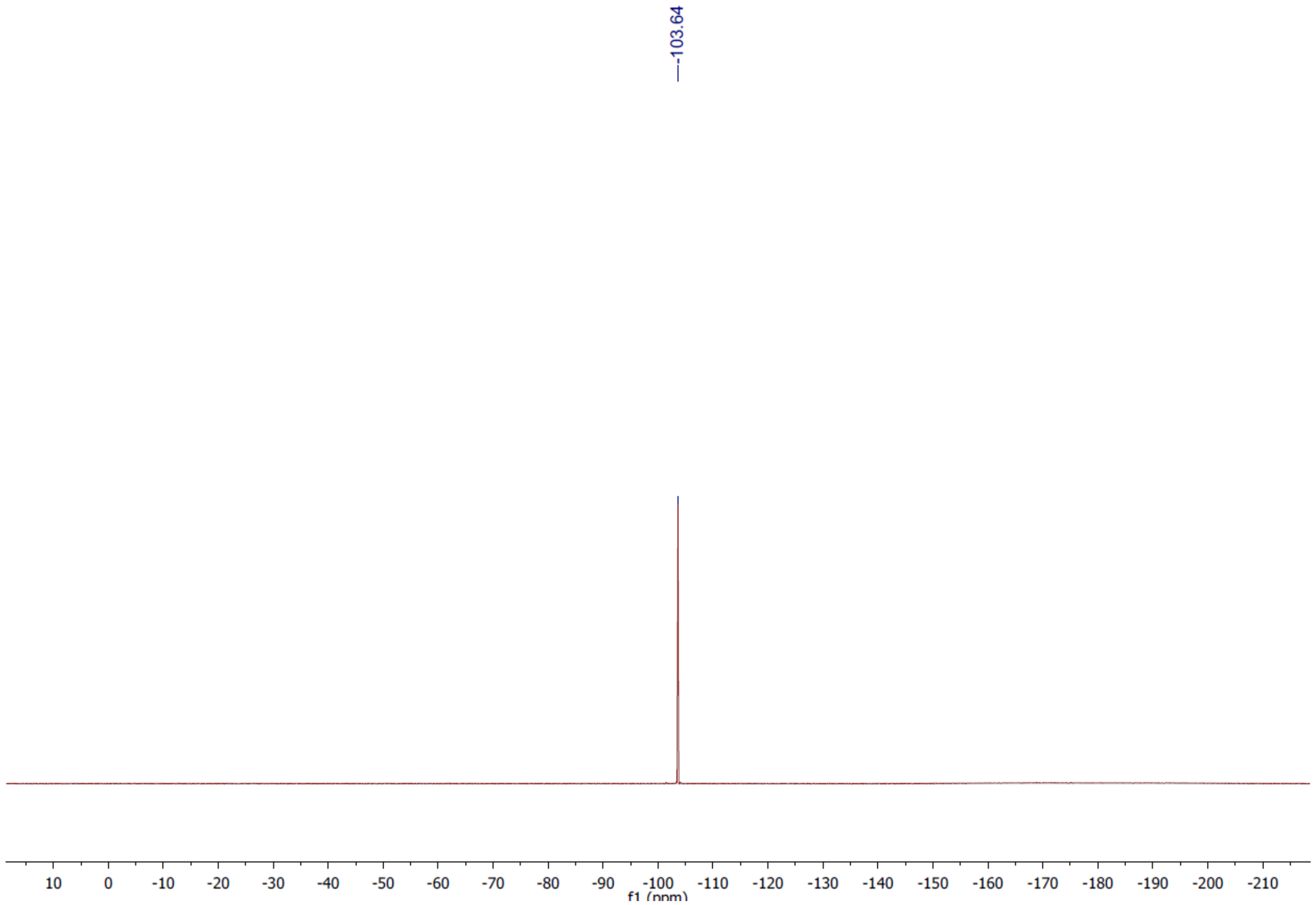
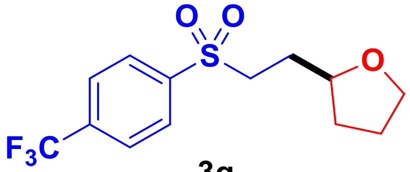


^{1}H-NMR (400 MHz, CDCl$_3$) of **3g**



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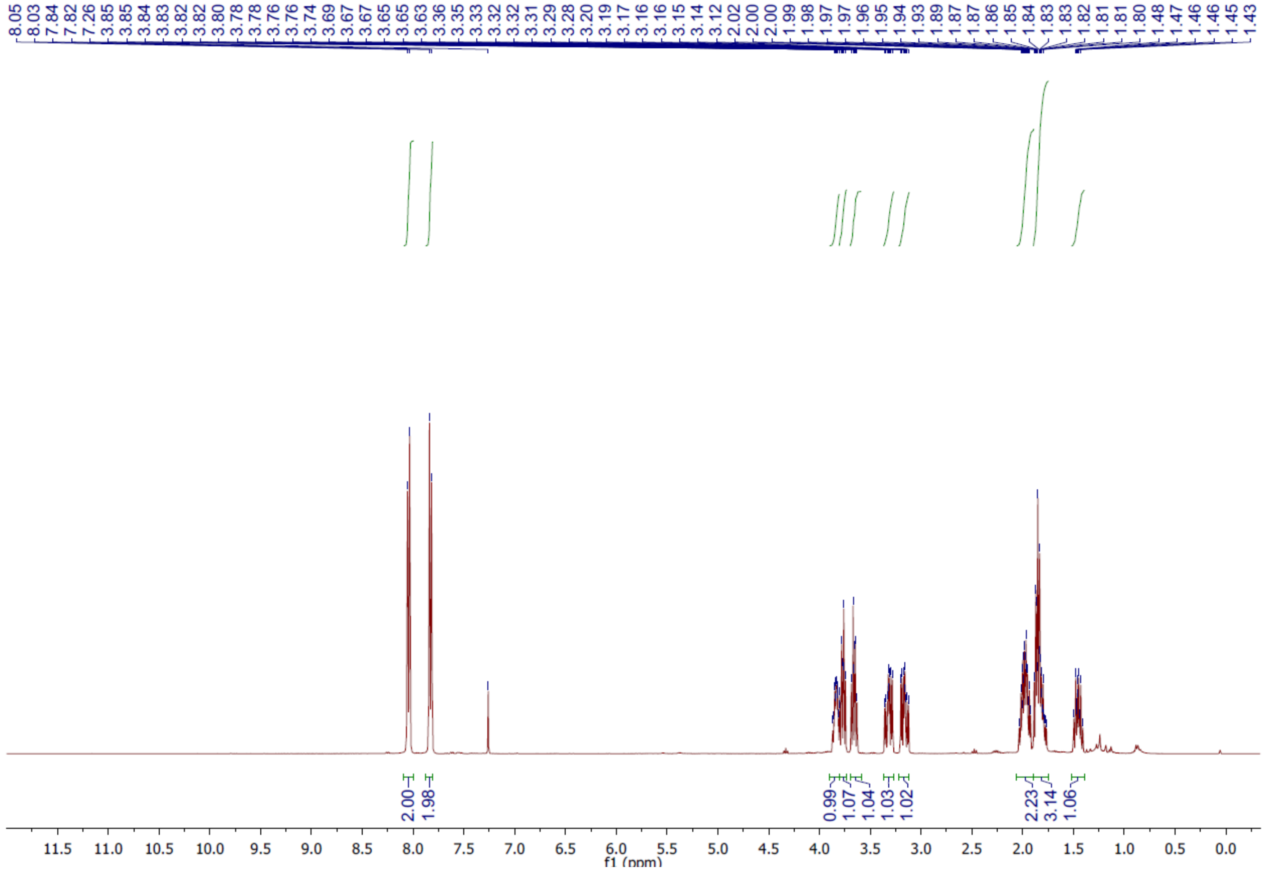
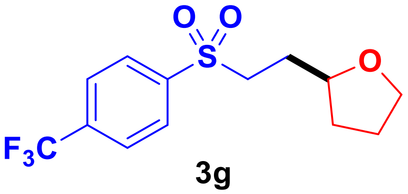


^{13}C-NMR (101 MHz, CDCl$_3$) of **3g**



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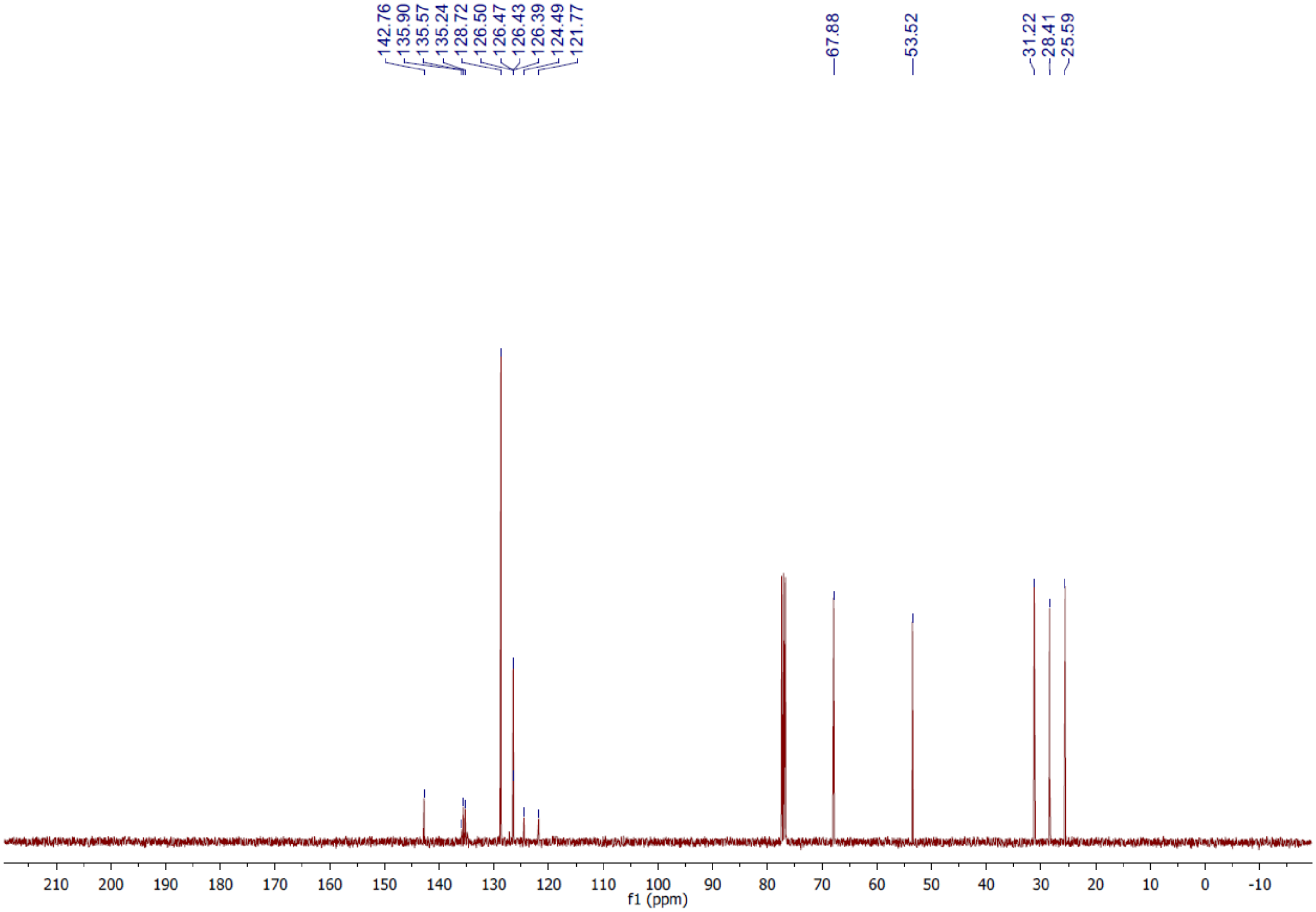
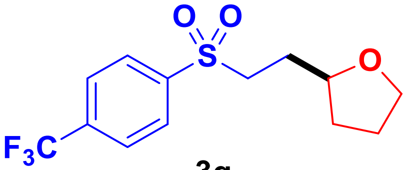


^{19}F-NMR (377 MHz, CDCl$_3$) of **3g**



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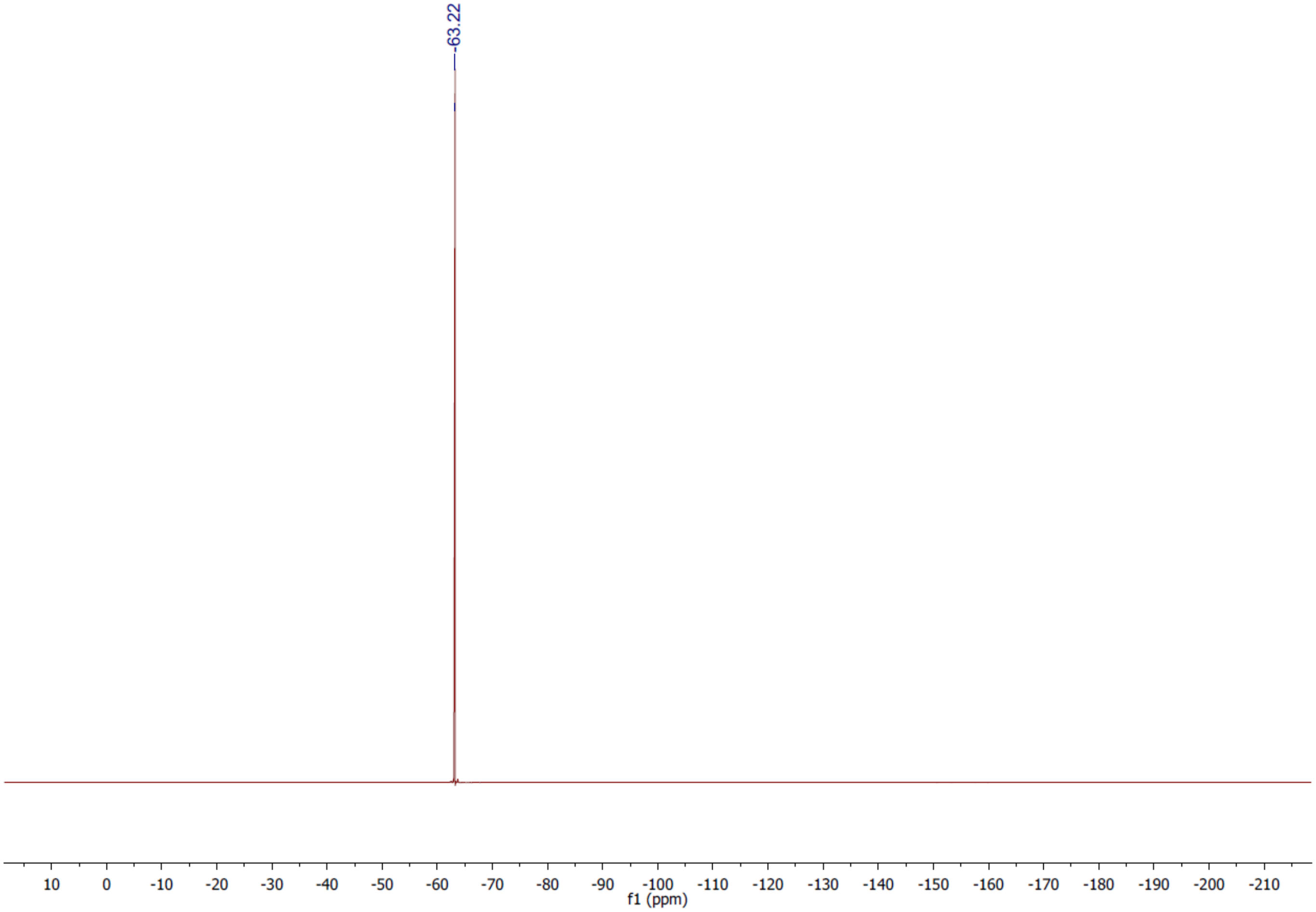
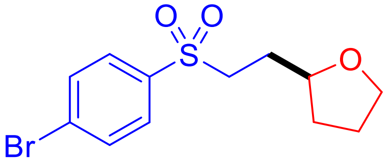


^{1}H-NMR (400 MHz, CDCl$_3$) of **3i**



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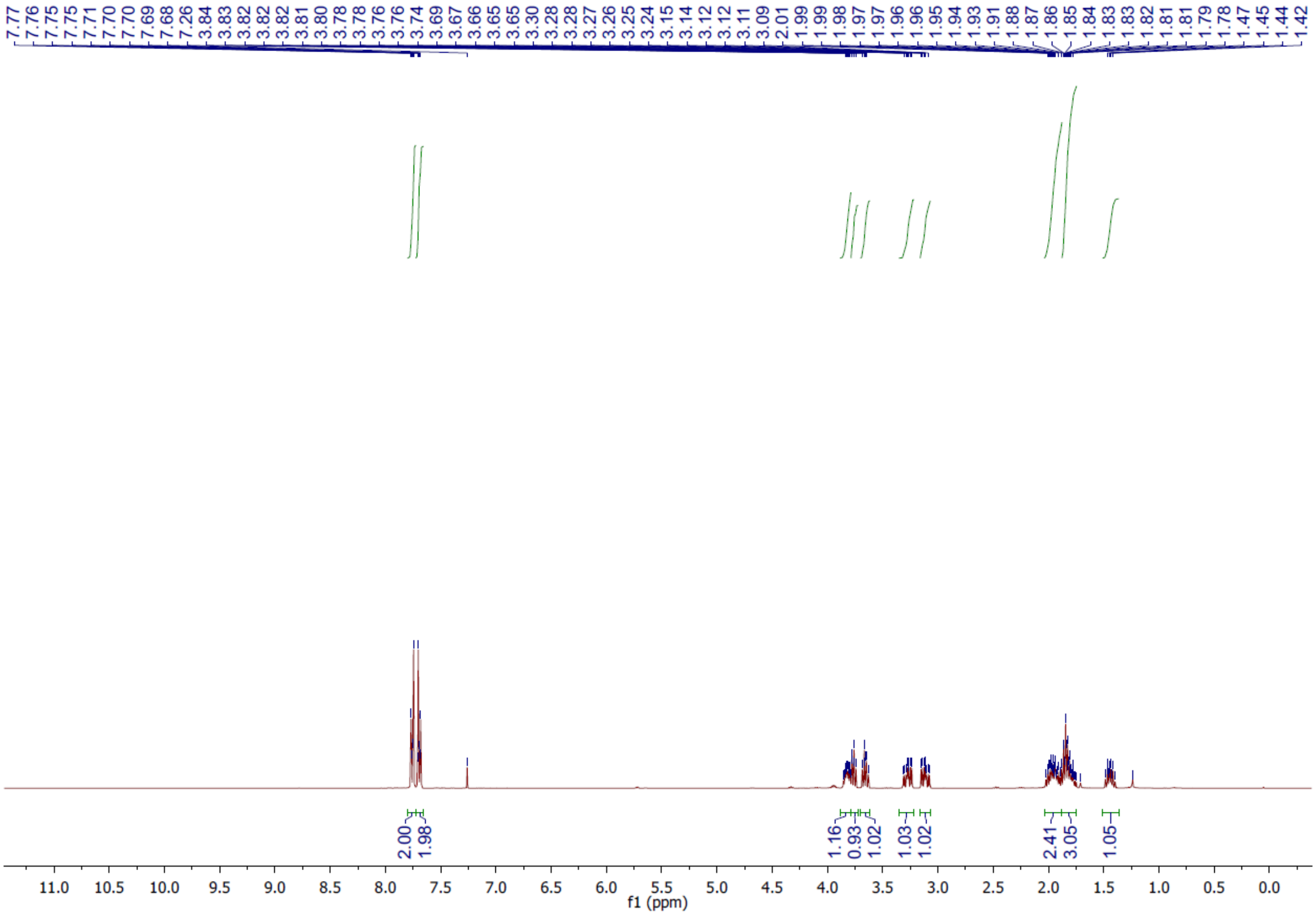
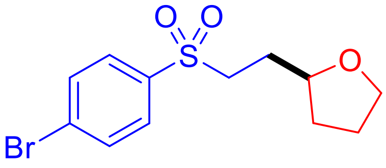


^{13}C-NMR (101 MHz, CDCl$_3$) of **3i**



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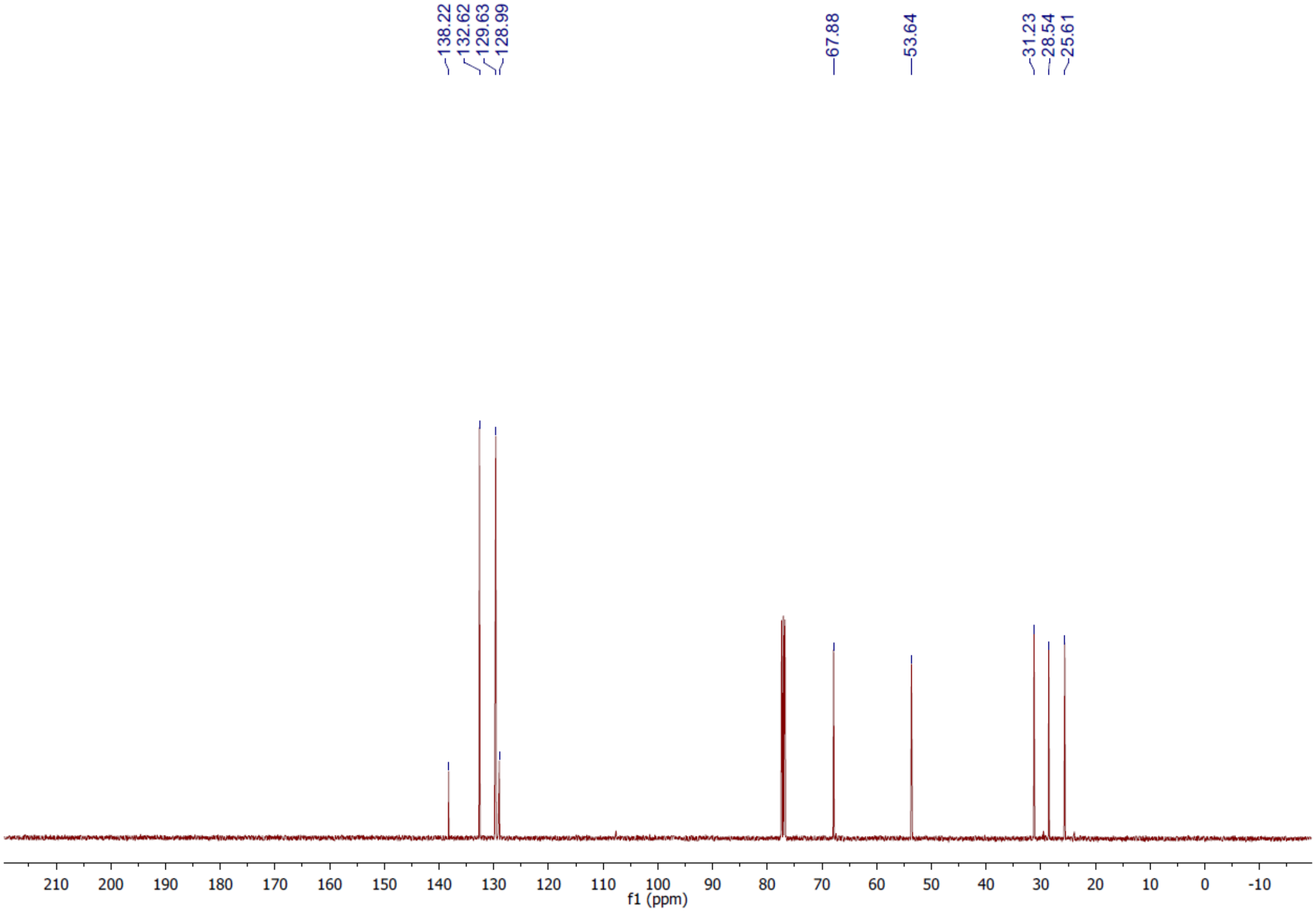
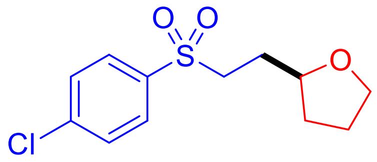


^{1}H-NMR (400 MHz, $CDCl_3$) of **3*J***



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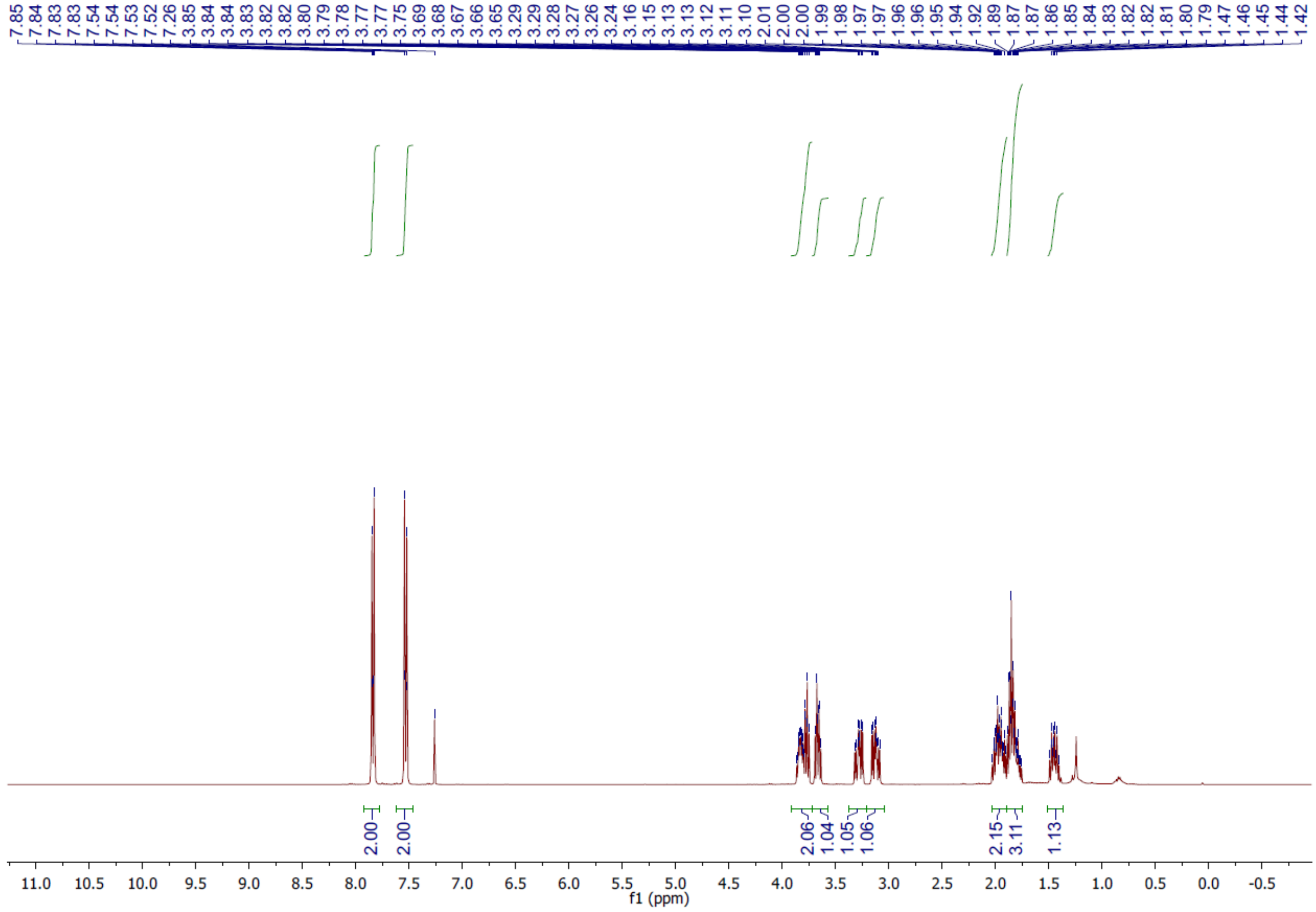
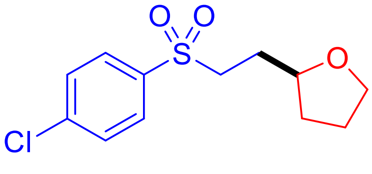


^{13}C-NMR (101 MHz, CDCl$_3$) of **3*J***



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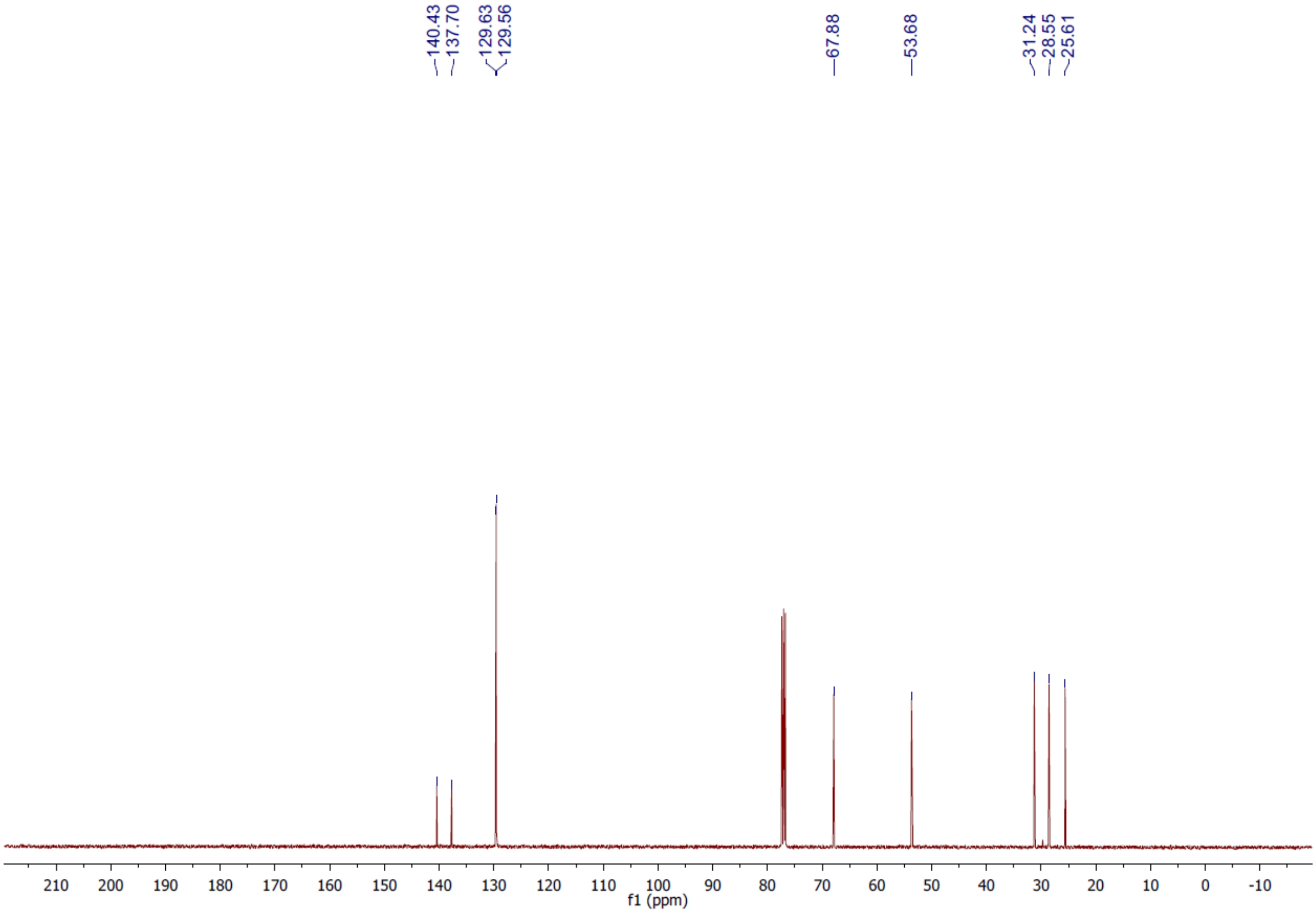

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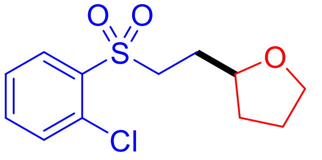
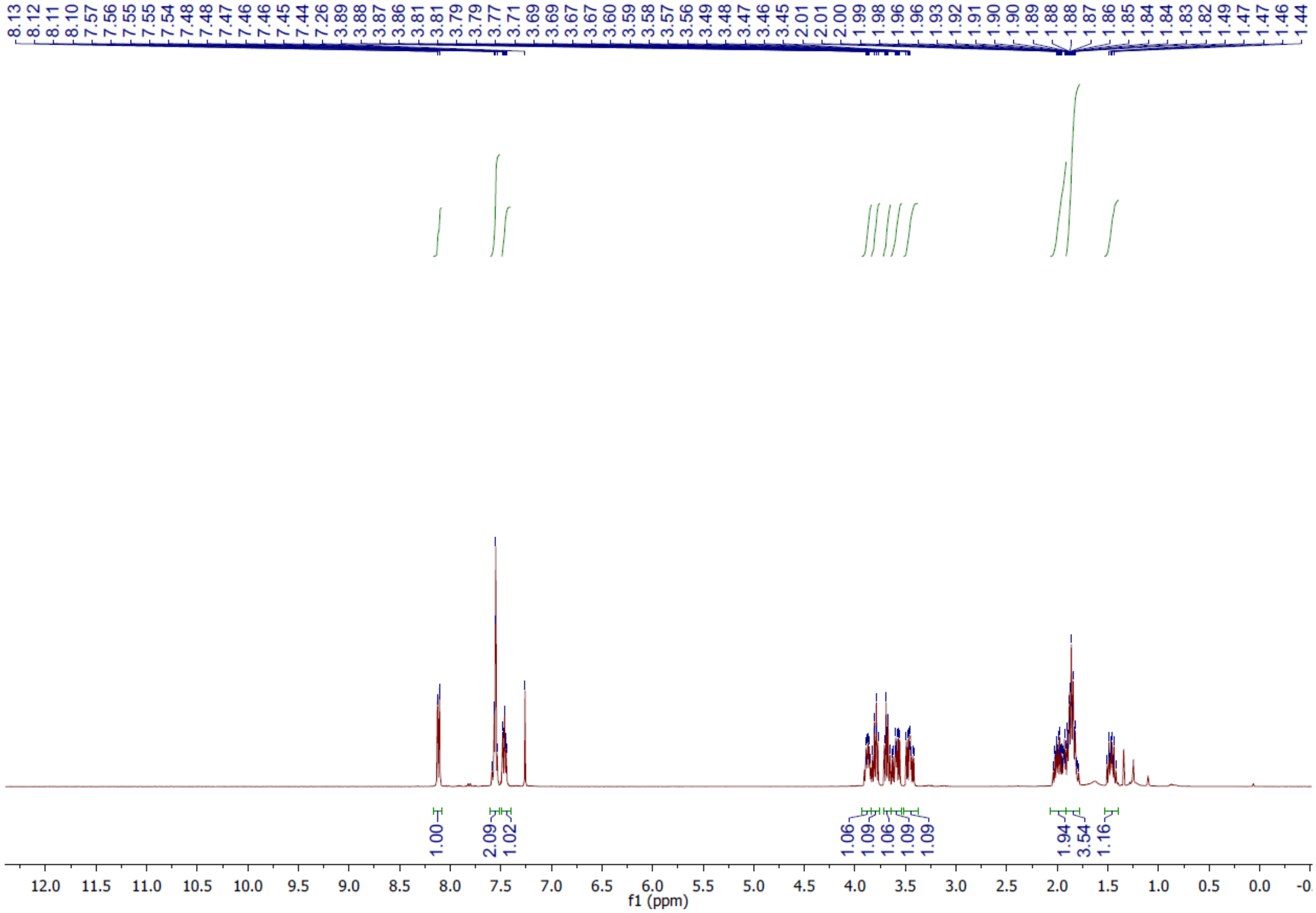
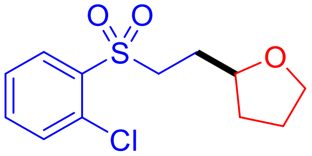
^{1}H-NMR (400 MHz, $CDCl_3$) of **3k**



3k



^{13}C-NMR (101 MHz, CDCl$_3$) of **3k**



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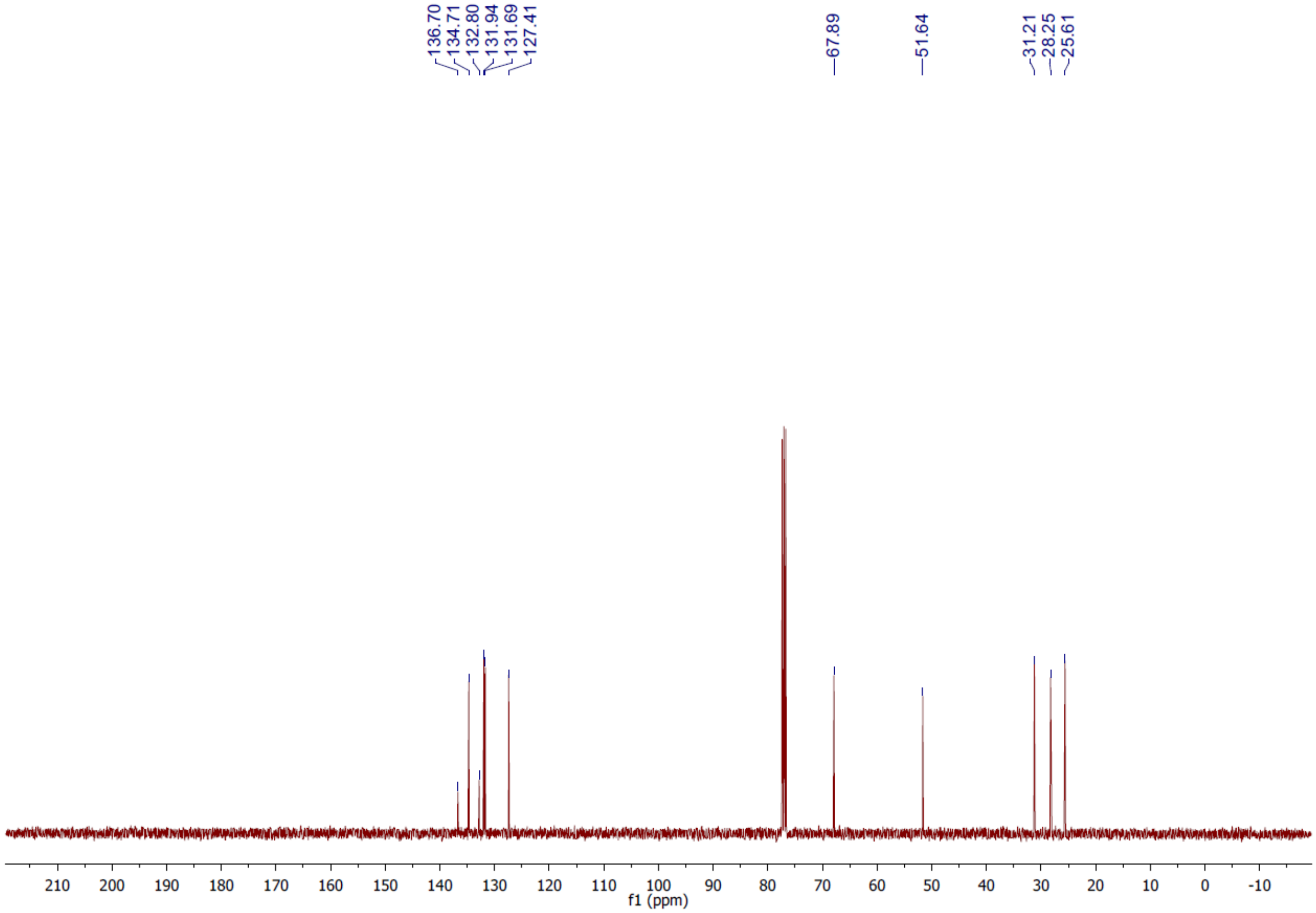
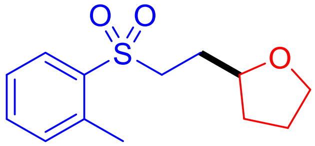


^{1}H-NMR (400 MHz, $CDCl_3$) of **3l**



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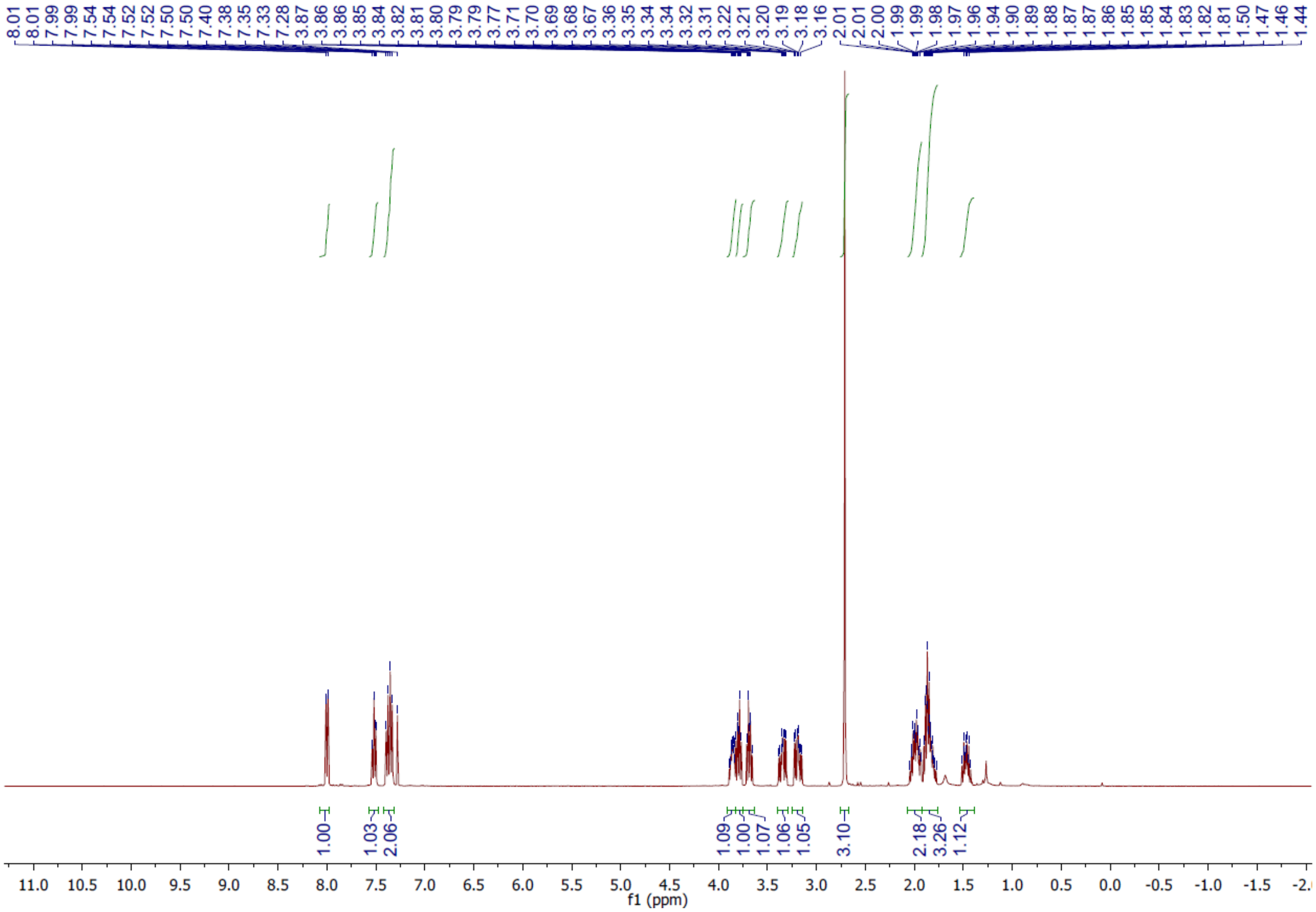
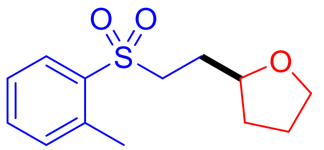


^{13}C-NMR (101 MHz, CDCl$_3$) of **3l**



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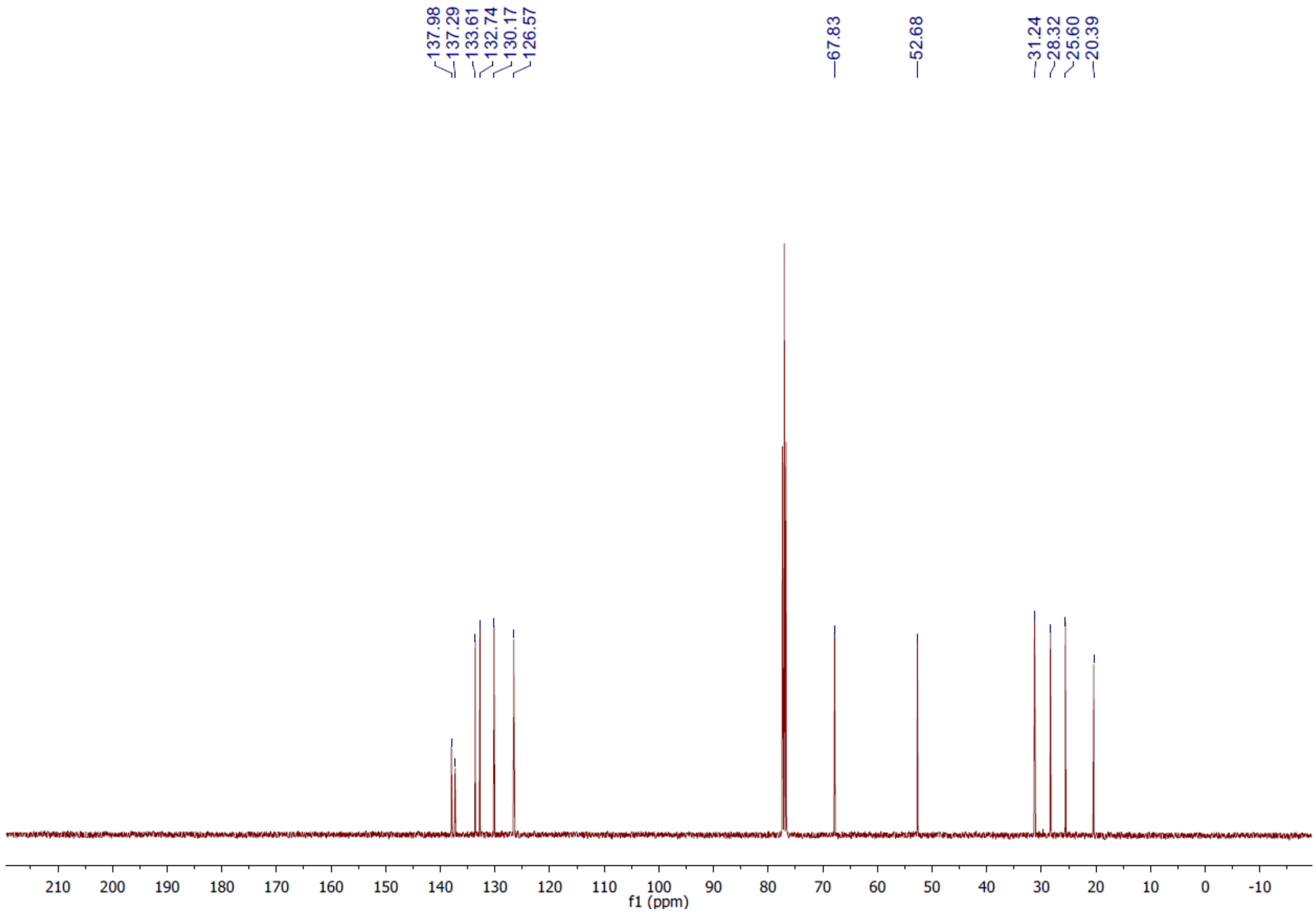
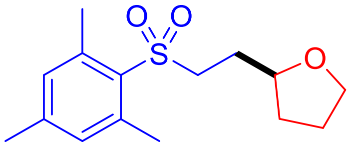


^{1}H-NMR (400 MHz, CDCl$_3$) of **3m**



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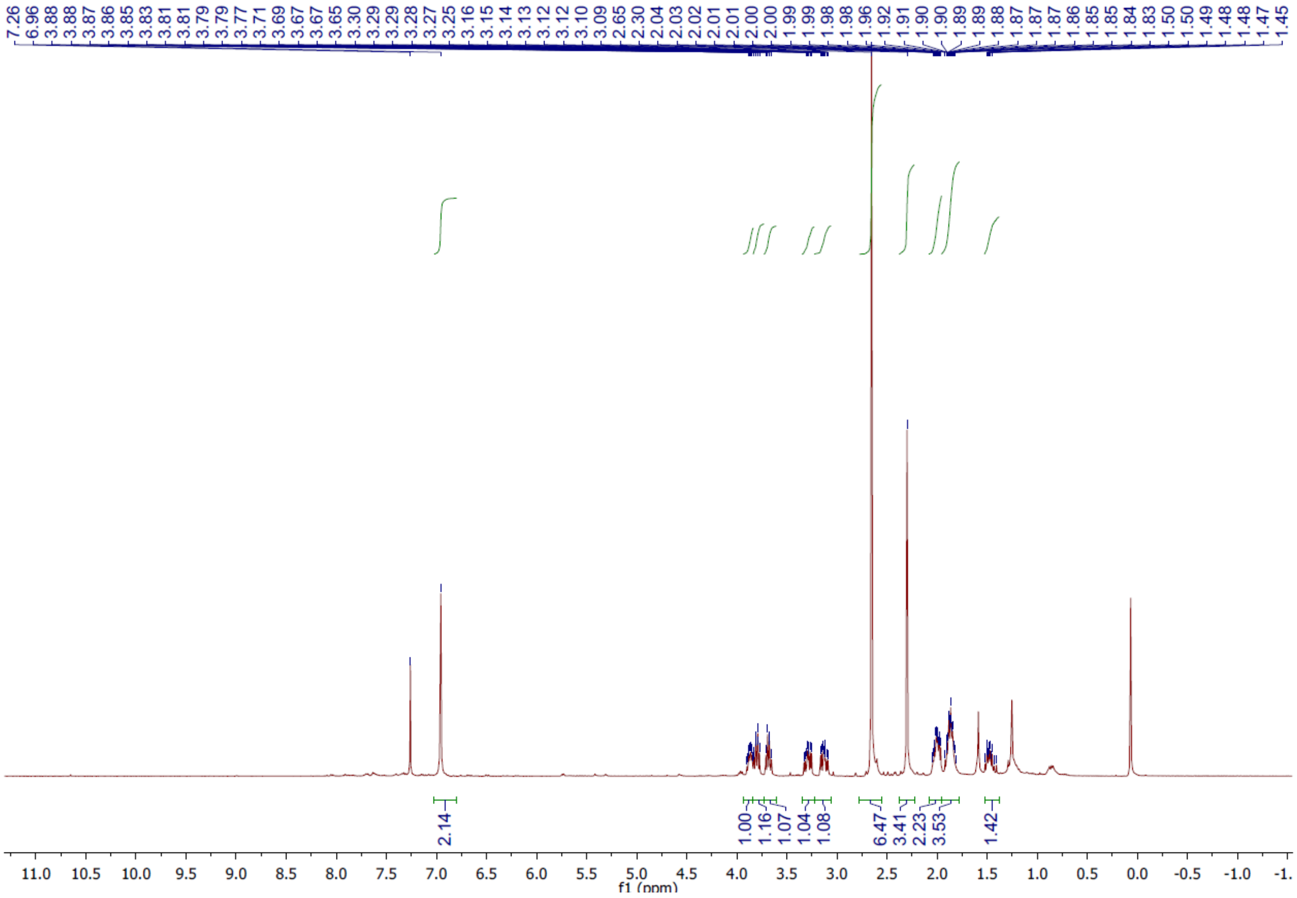
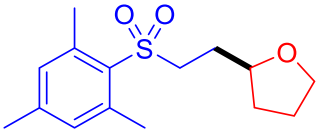


^{13}C-NMR (101 MHz, CDCl$_3$) of **3m**



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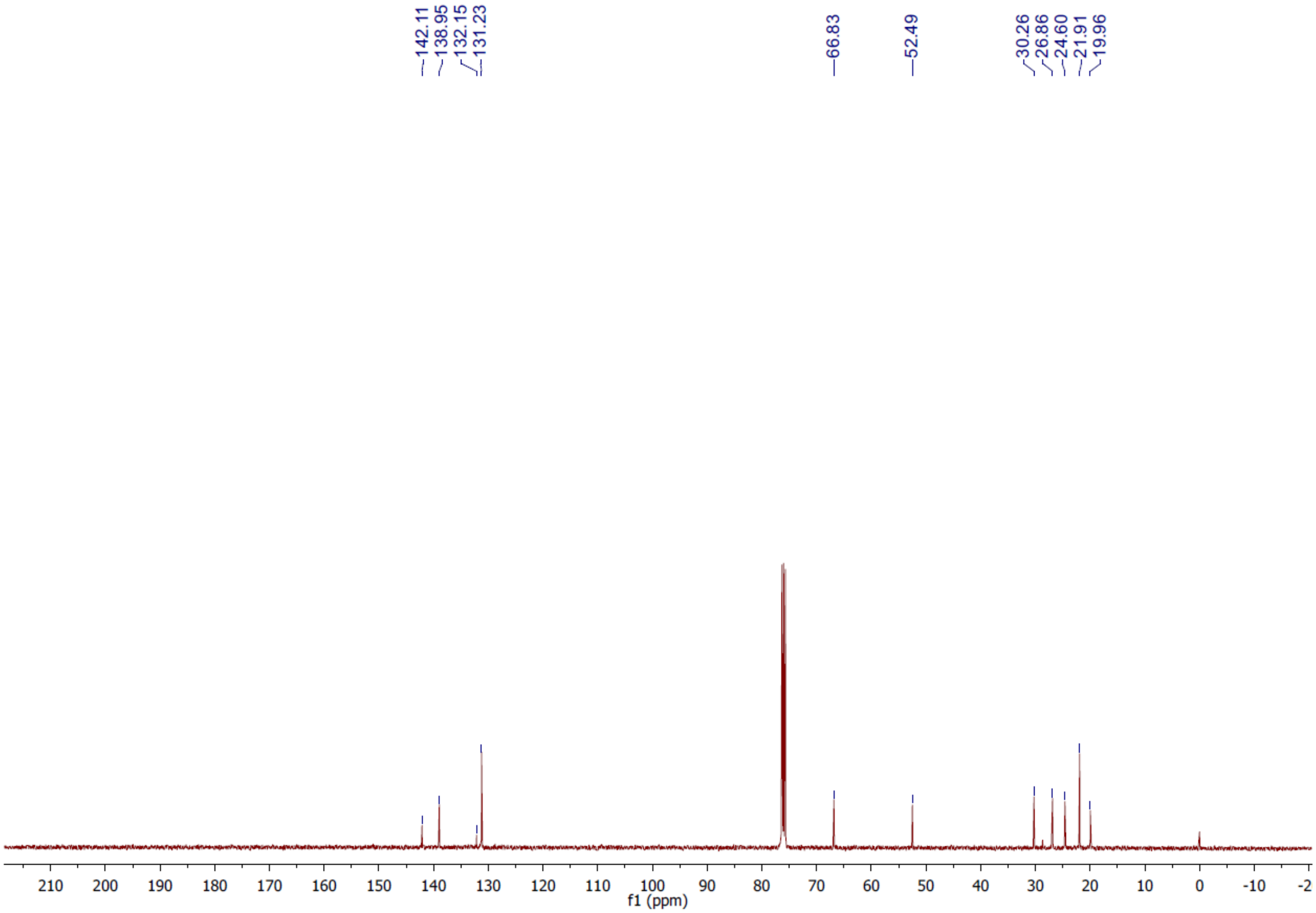
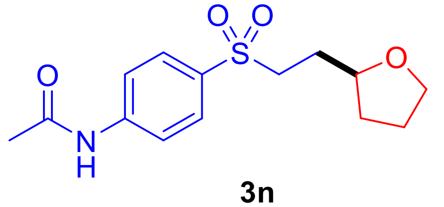


^{1}H-NMR (400 MHz, CDCl$_3$) of **3n**



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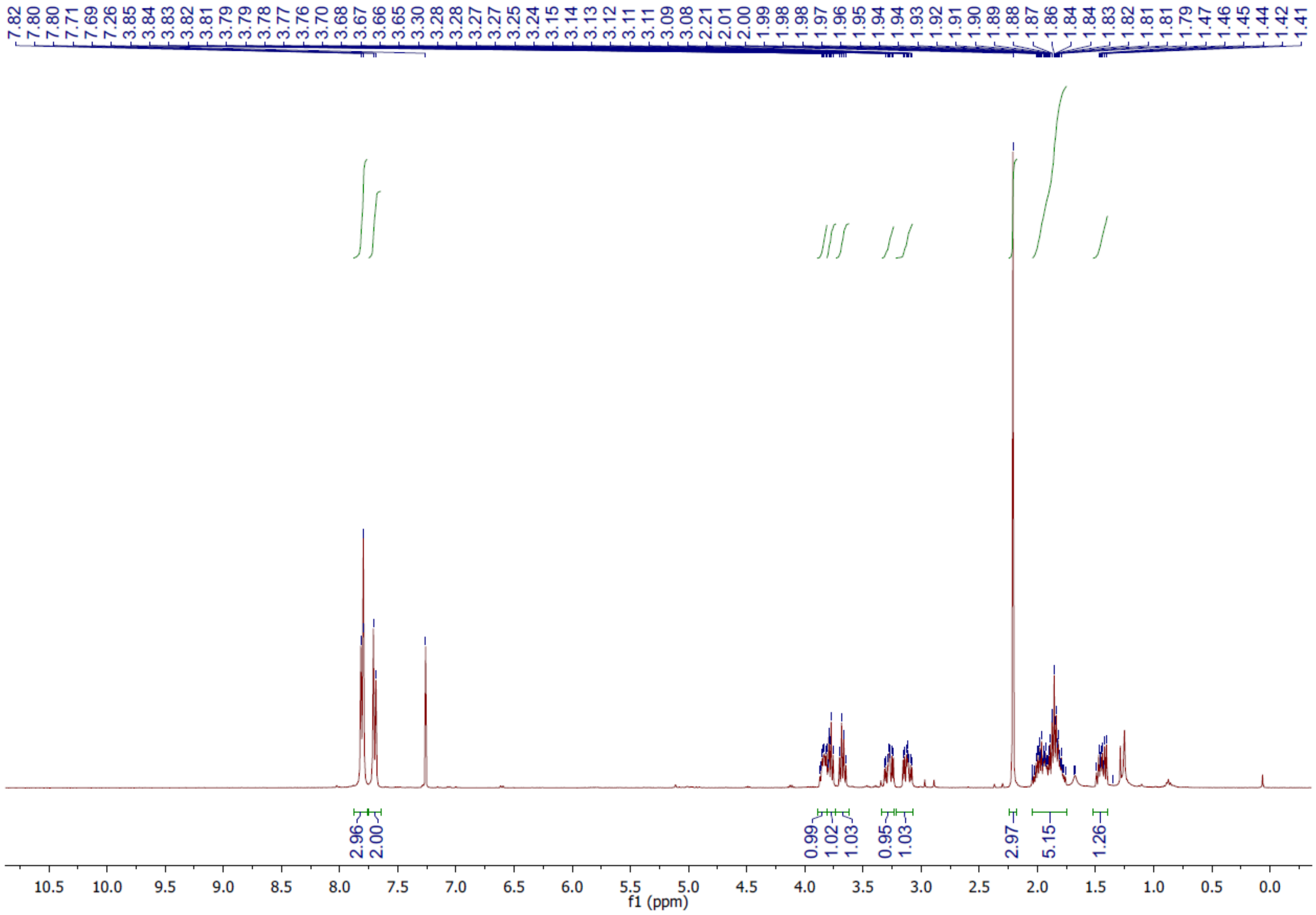
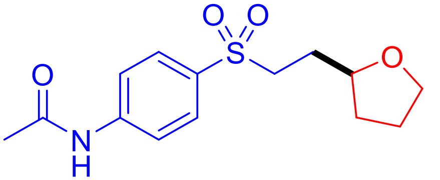


^{13}C-NMR (101 MHz, CDCl$_3$) of **3n**



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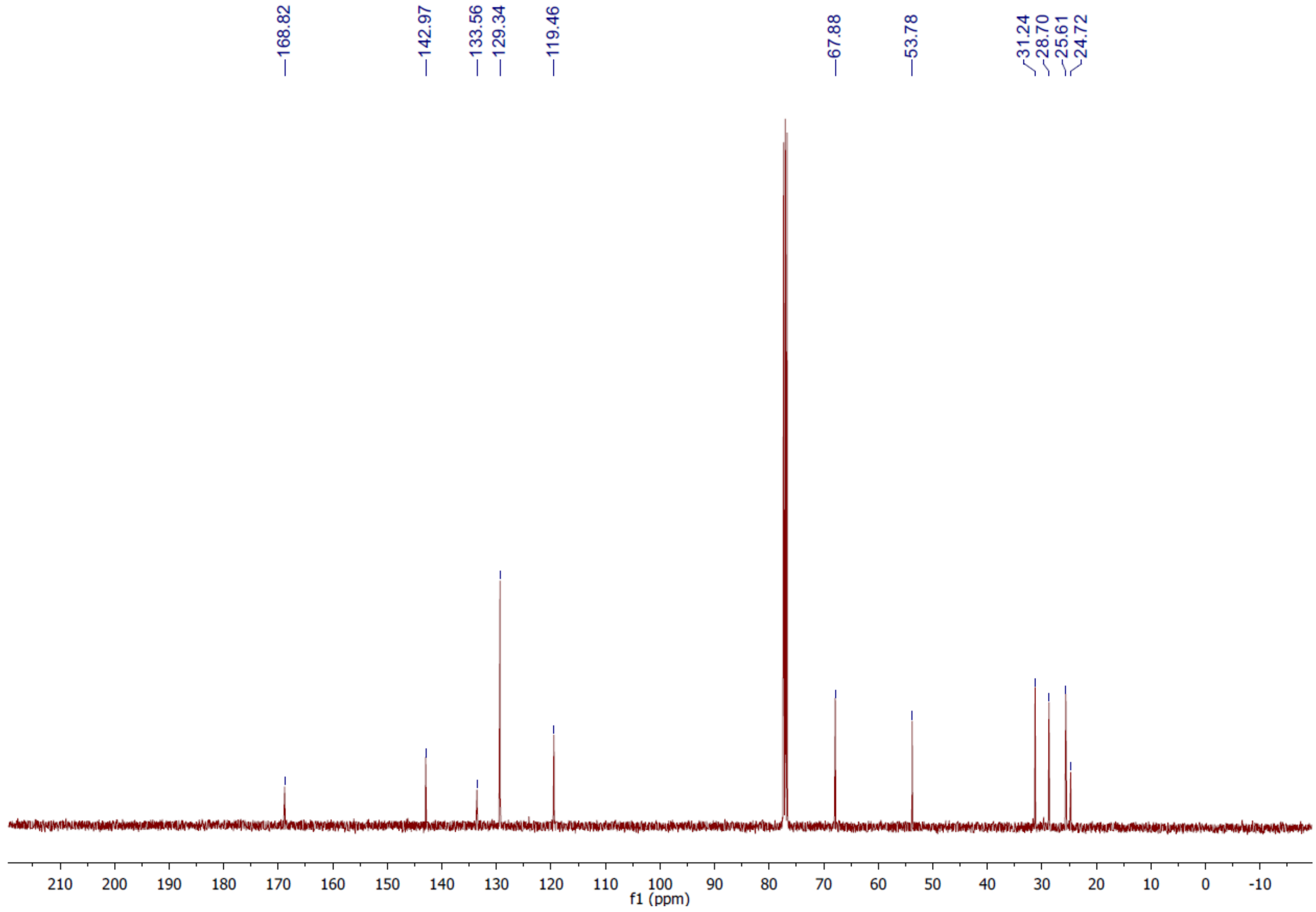
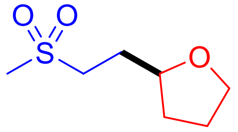


^{1}H-NMR (400 MHz, CDCl$_3$) of **3o**



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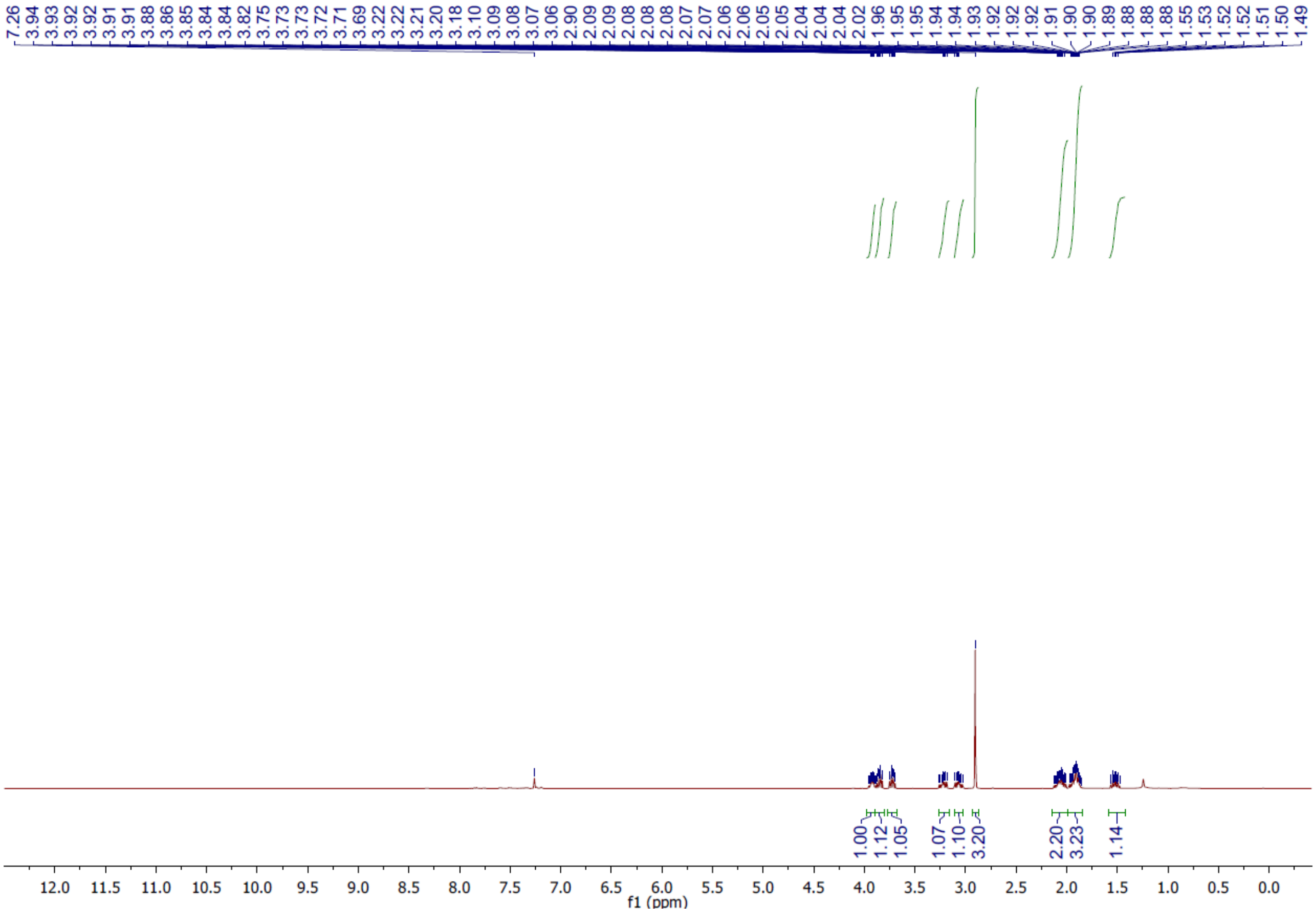
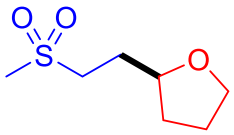


^{13}C-NMR (101 MHz, $CDCl_3$) of **3o**



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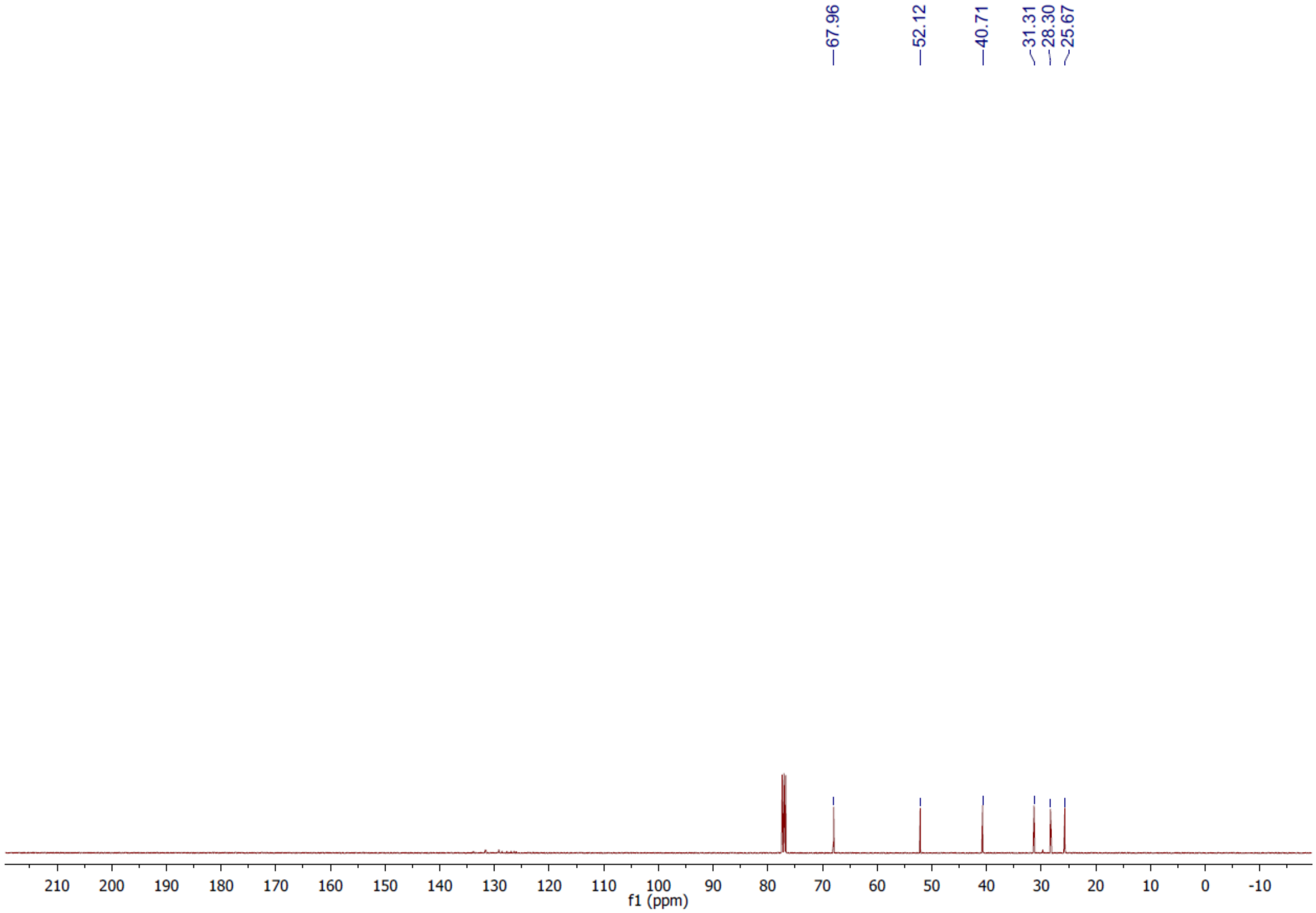
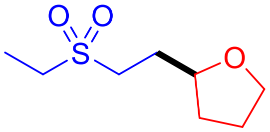
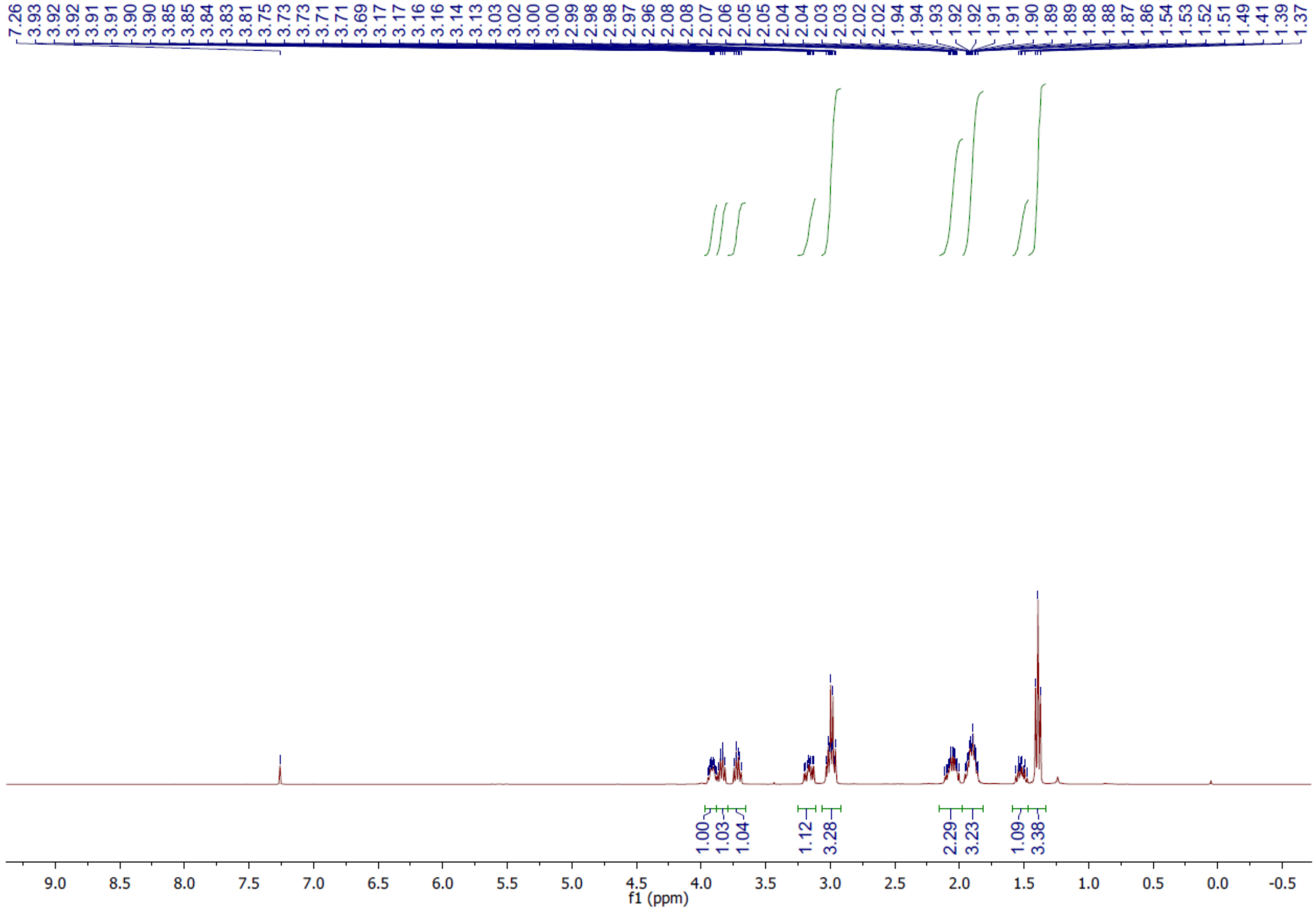


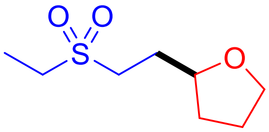
^{1}H-NMR (400 MHz, $CDCl_3$) of **3p**



3p



^{13}C-NMR (101 MHz, CDCl$_3$) of **3p**



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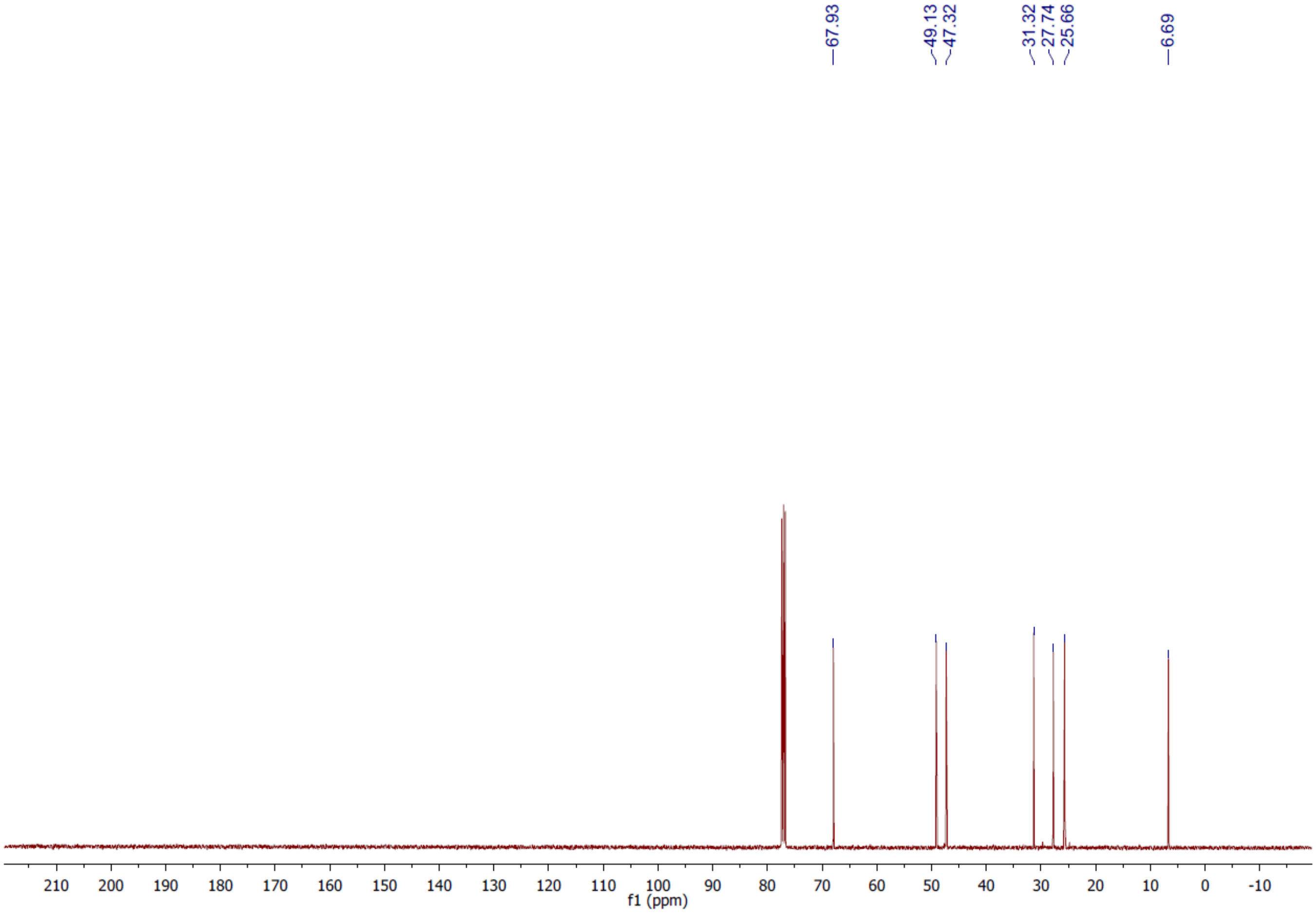
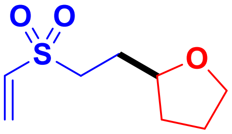


^{1}H-NMR (400 MHz, CDCl$_3$) of **3q**



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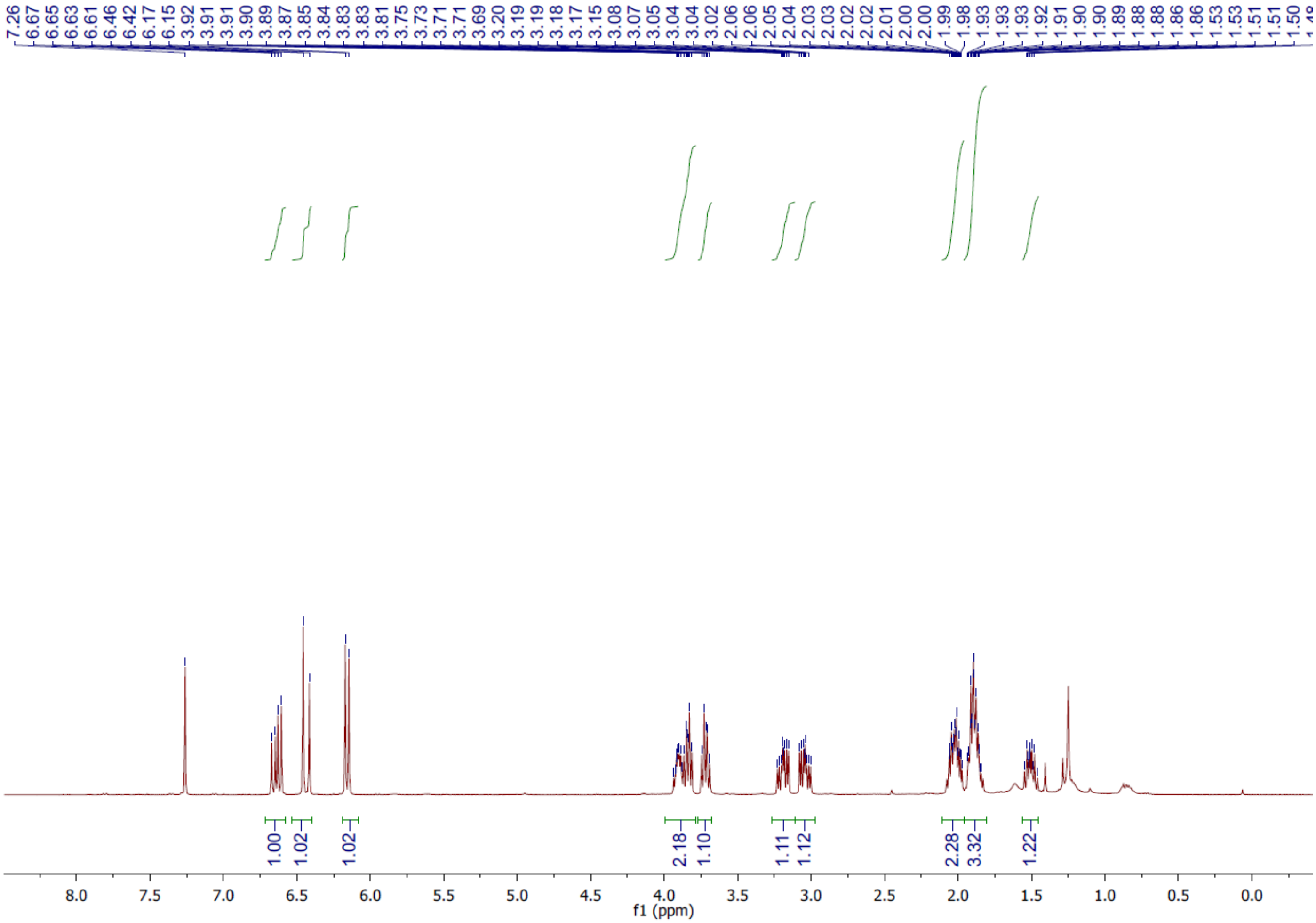
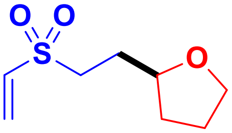


^{13}C-NMR (101 MHz, CDCl$_3$) of **3q**



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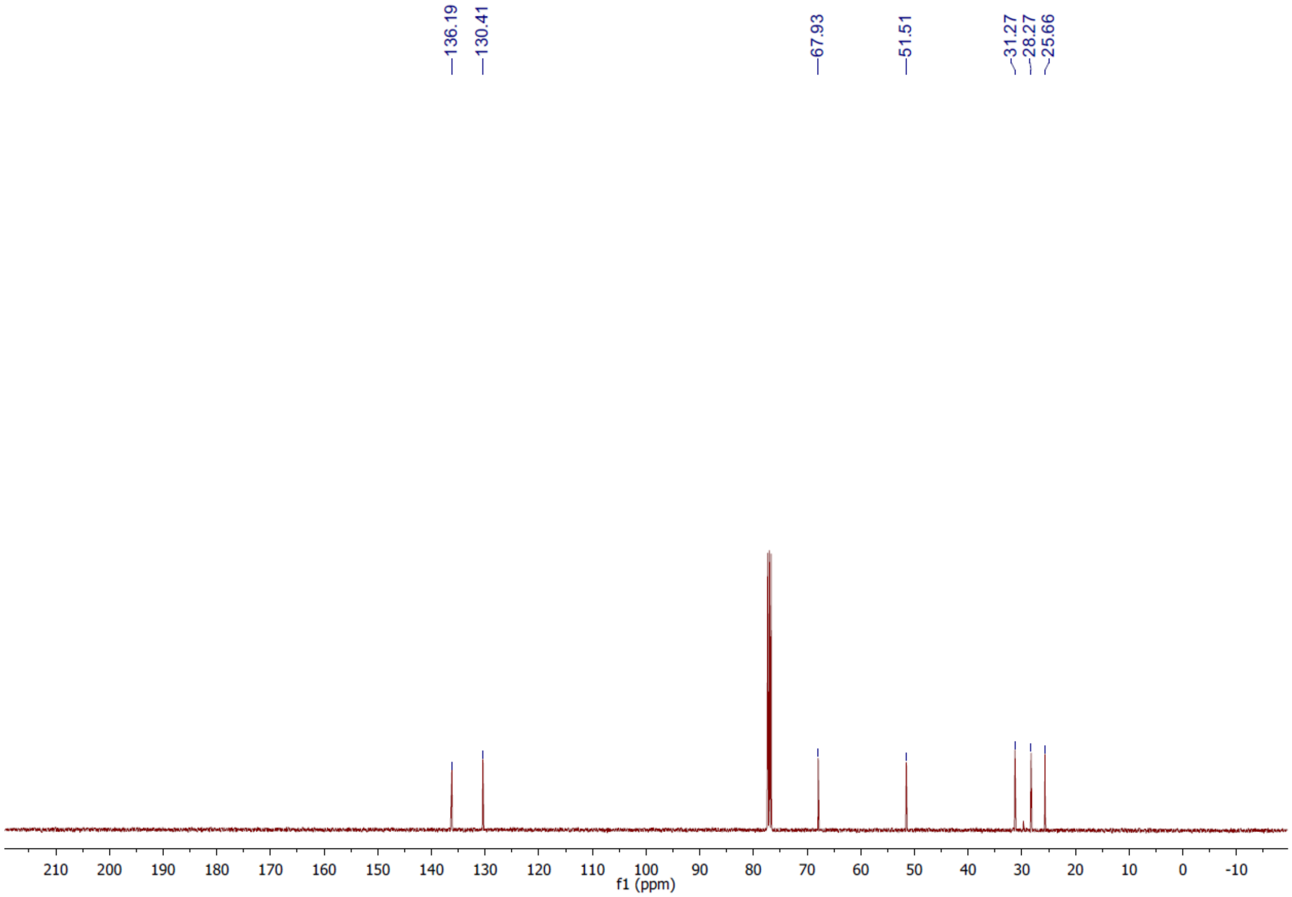
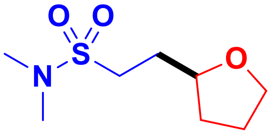


^{1}H-NMR (400 MHz, $CDCl_3$) of **3r**



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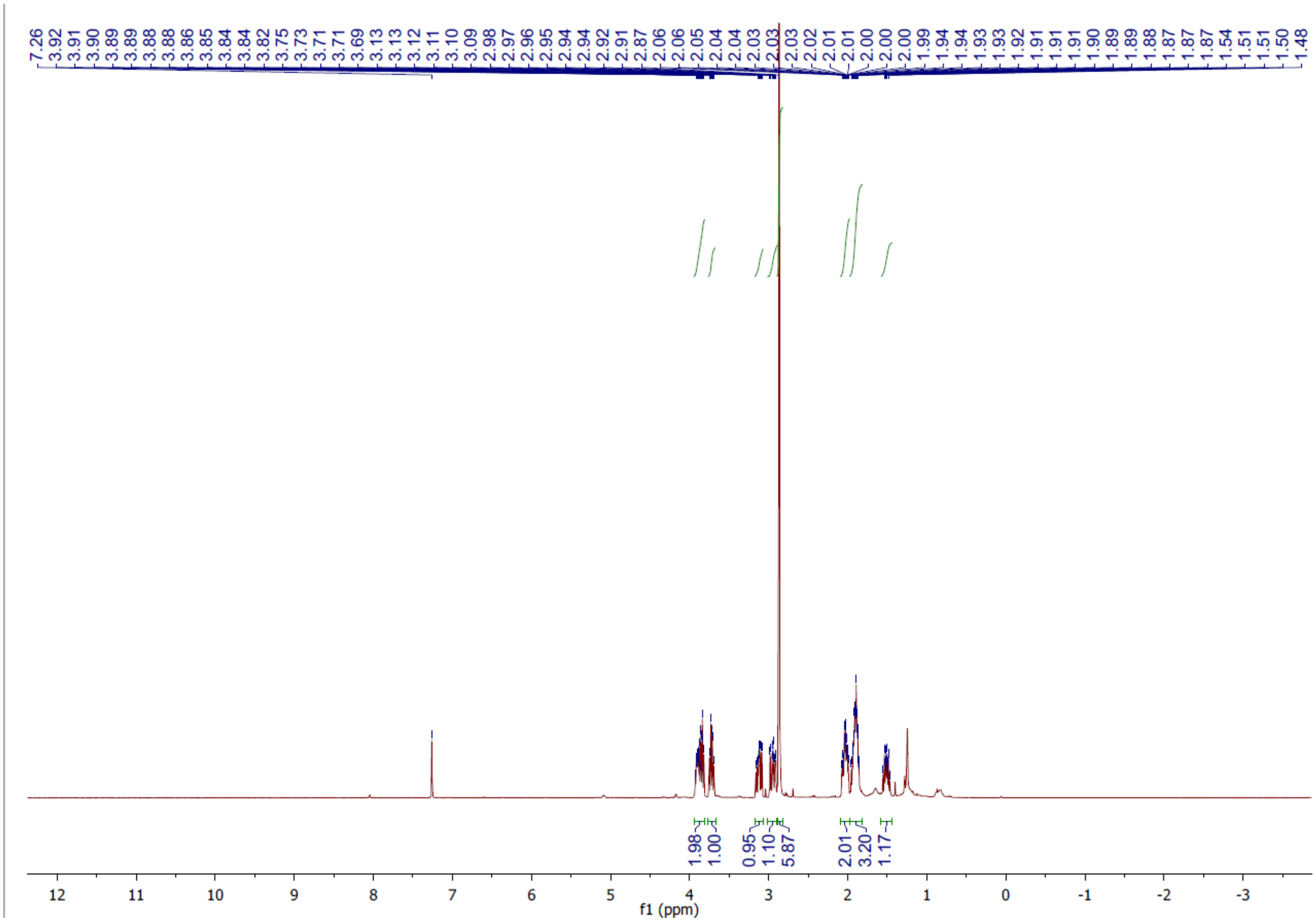
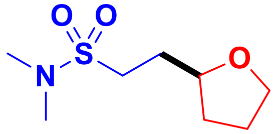


^{13}C-NMR (101MHz, CDCl$_3$) of **3r**



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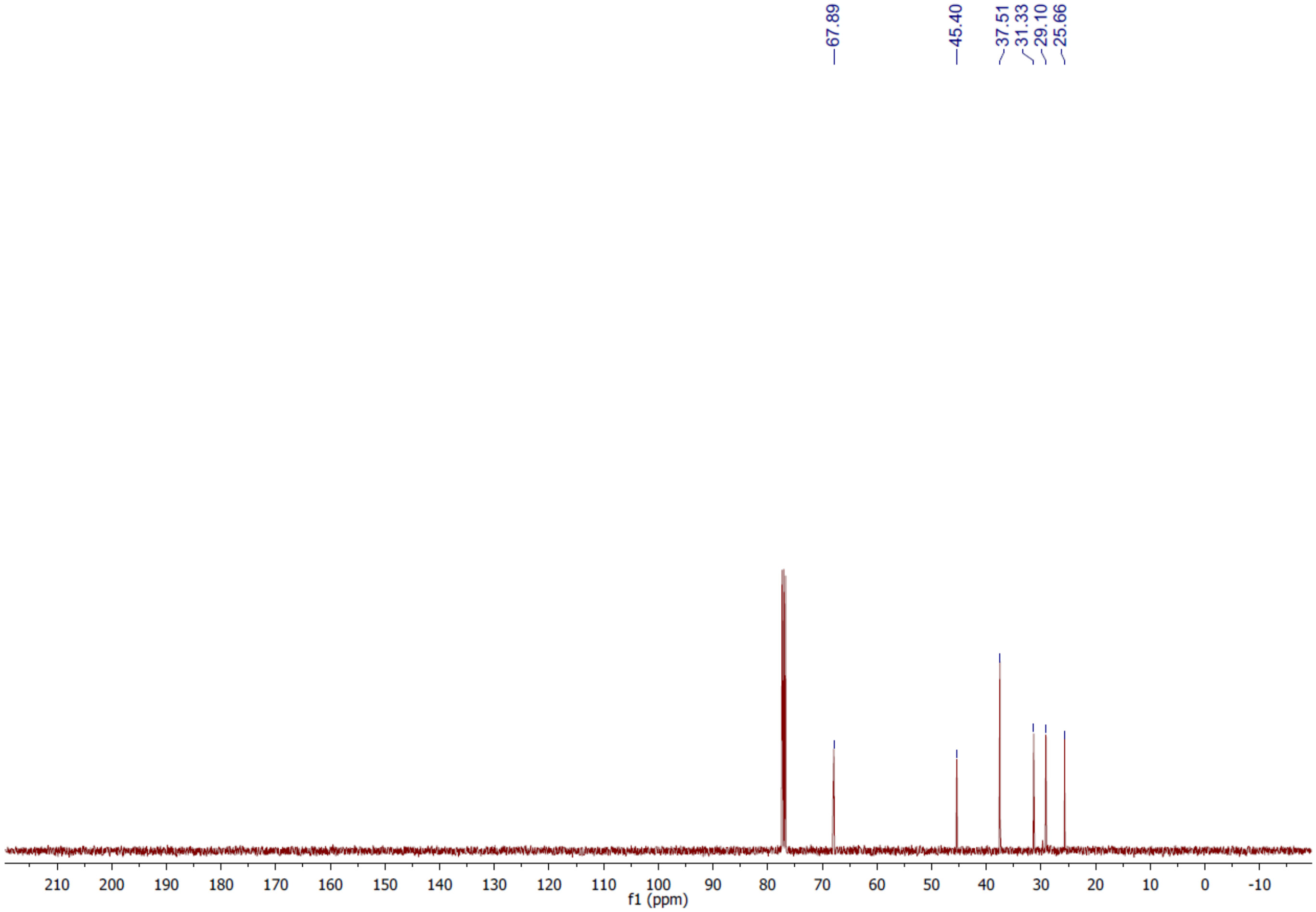
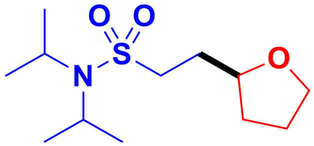


^{1}H-NMR (400 MHz, CDCl$_3$) of **3s**



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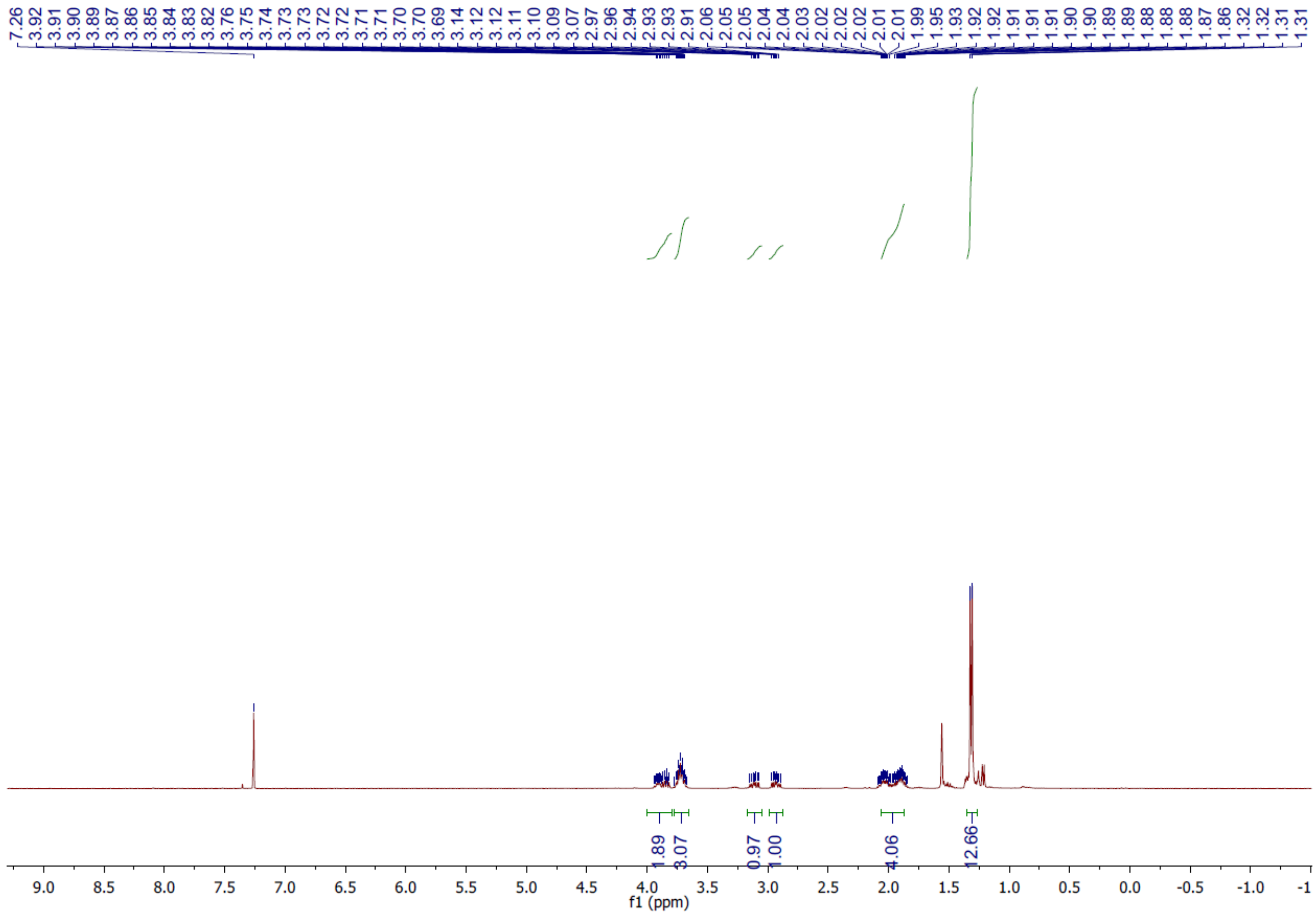
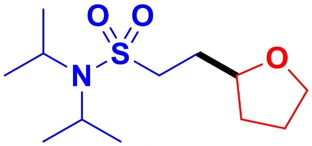


^{13}C-NMR (101MHz, CDCl$_3$) of **3s**



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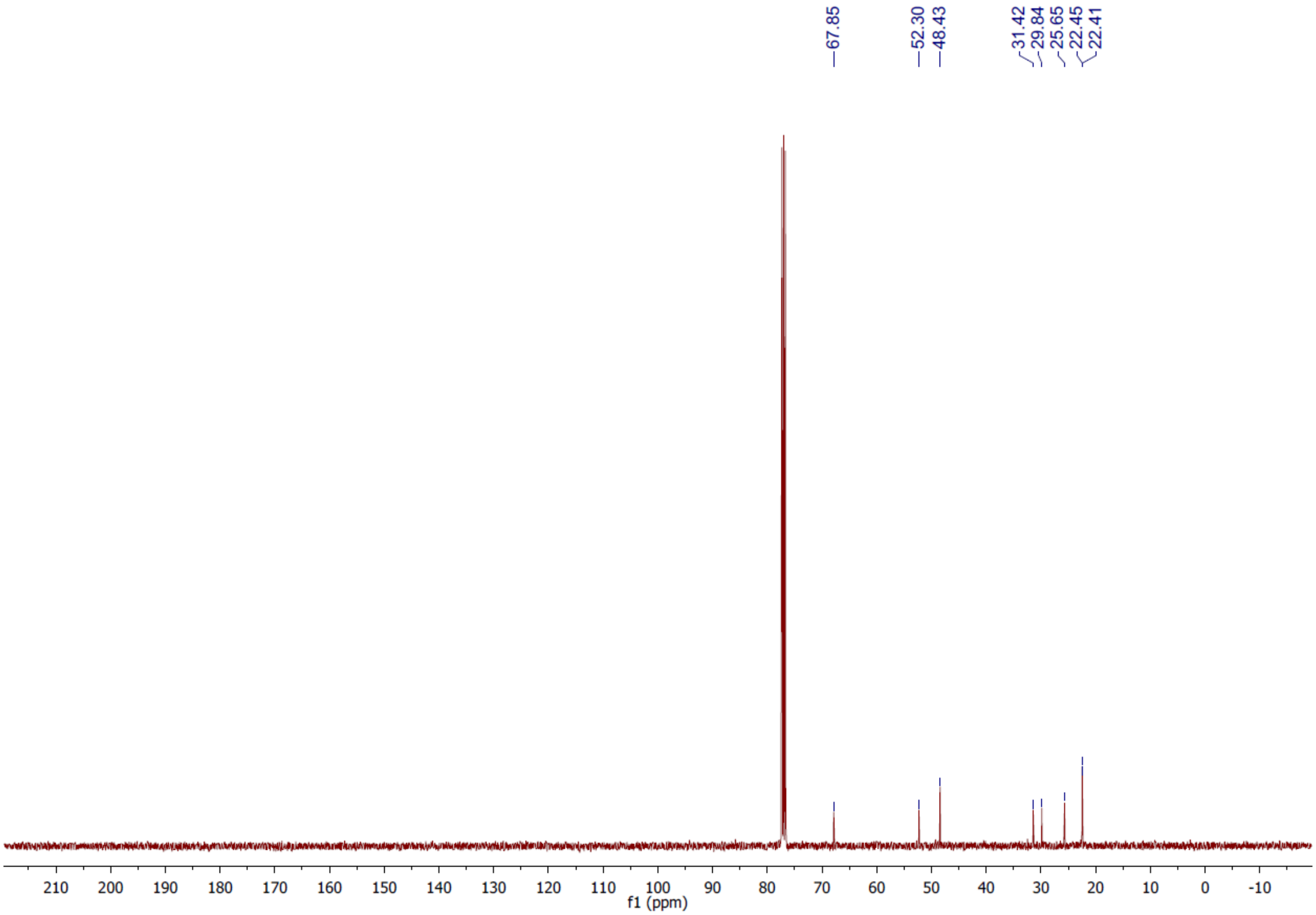
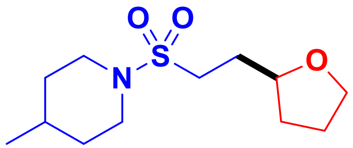


^{1}H-NMR (400 MHz, CDCl$_3$) of **3t**



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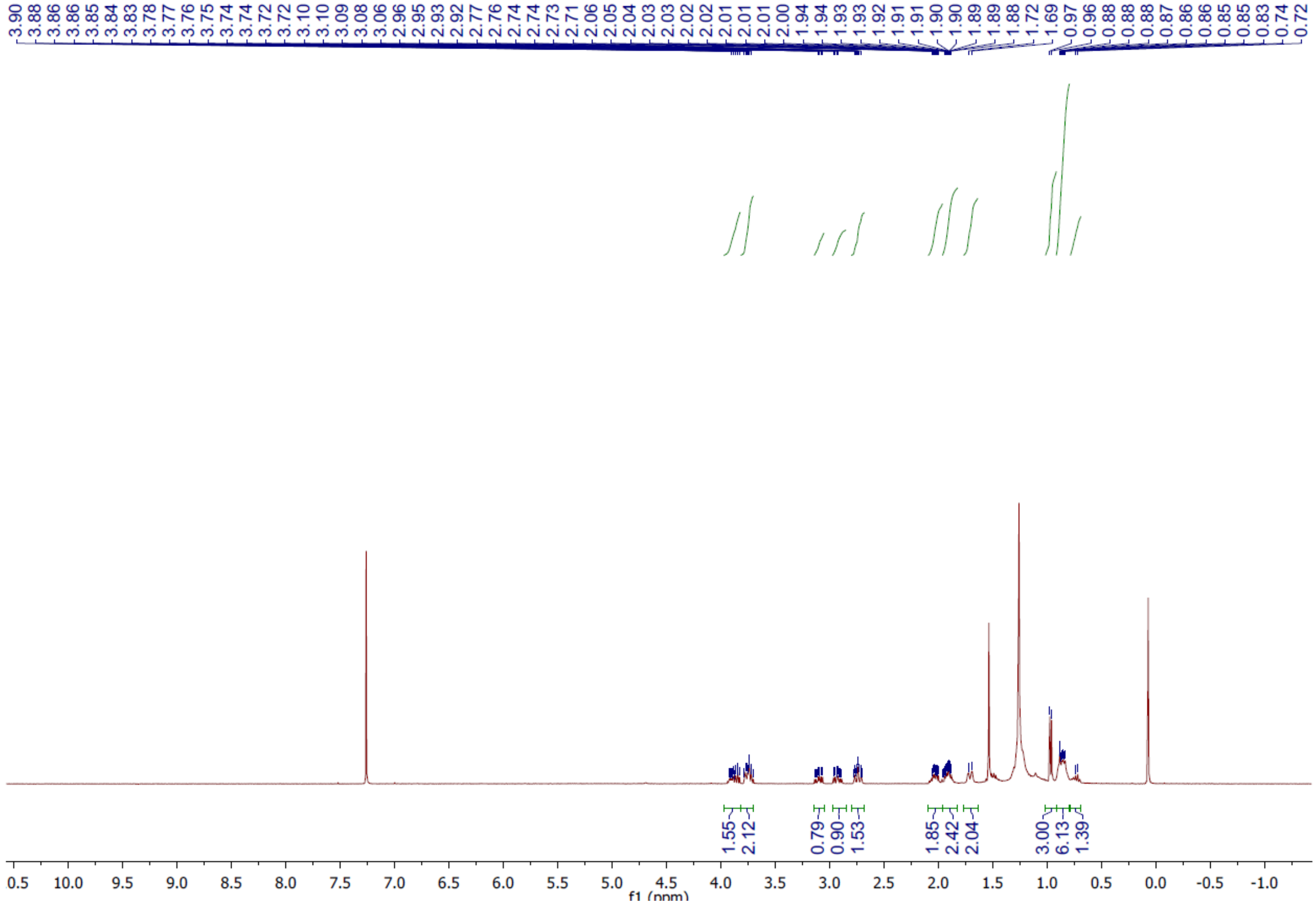
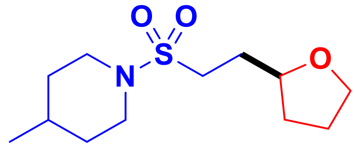


^{13}C-NMR (101 MHz, CDCl$_3$) of **3t**



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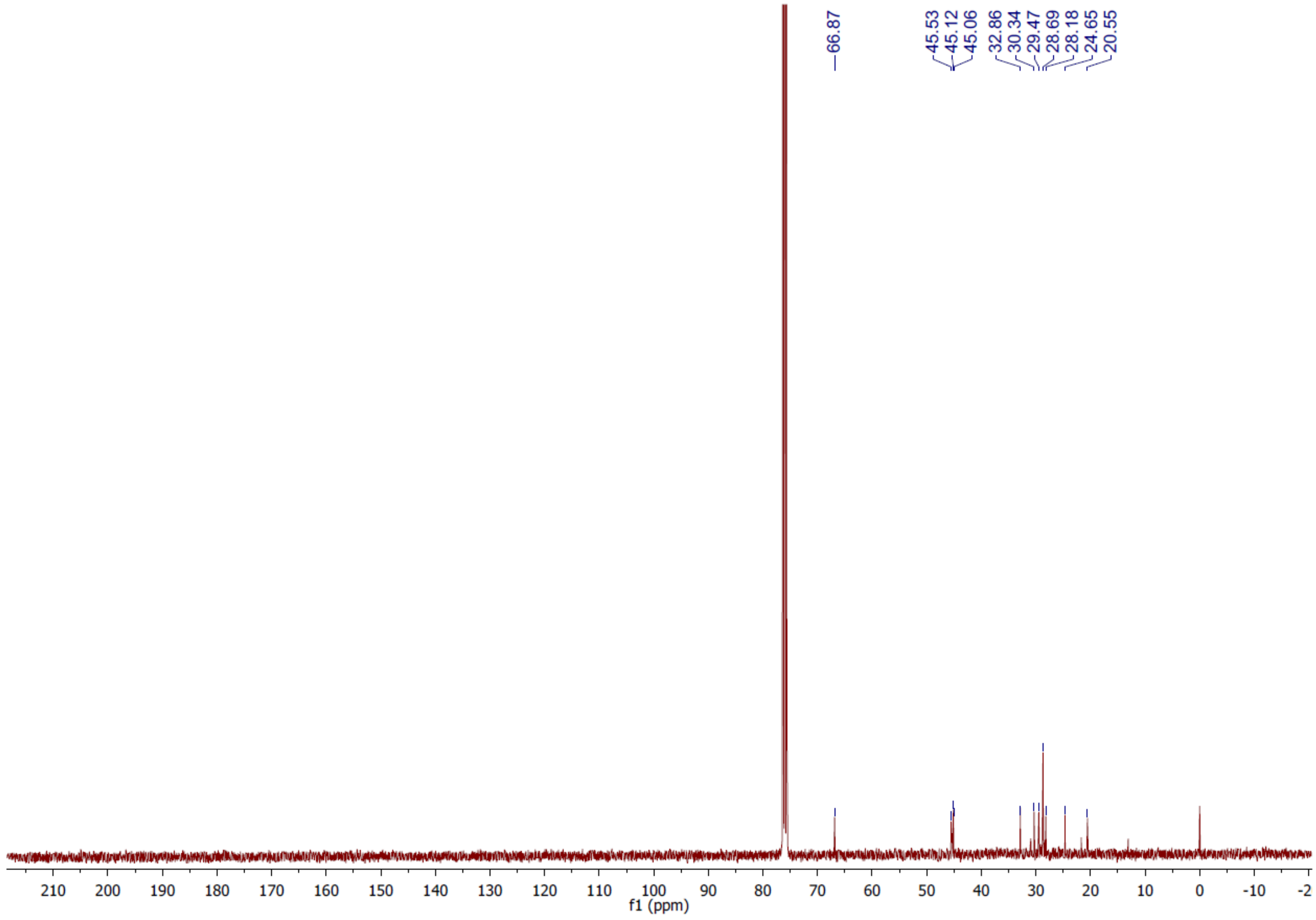
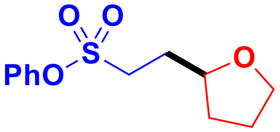


^{1}H-NMR (400 MHz, CDCl$_3$) of **3u**



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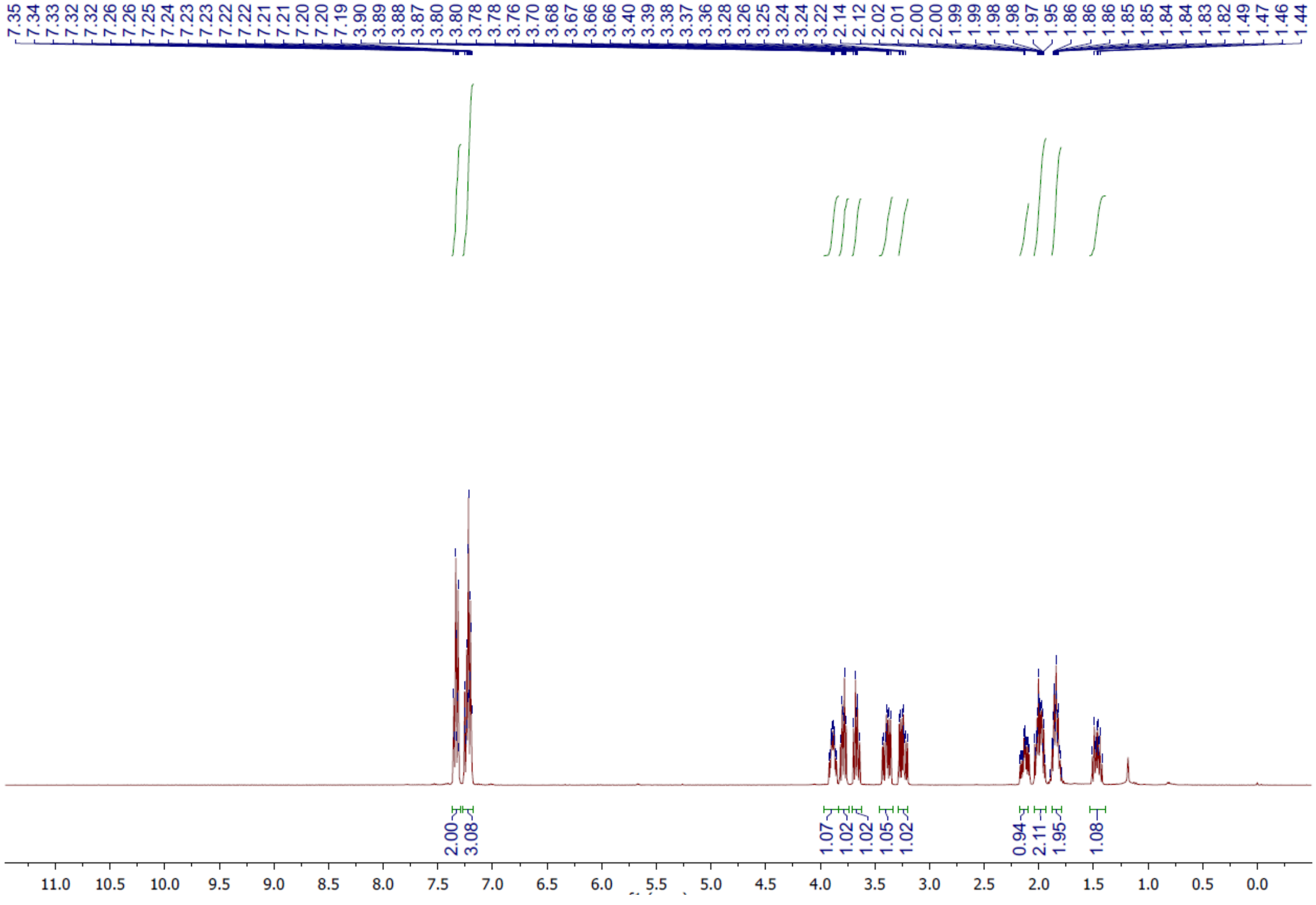
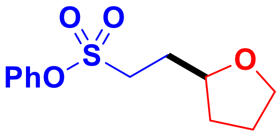


^{13}C-NMR (101 MHz, CDCl$_3$) of **3u**



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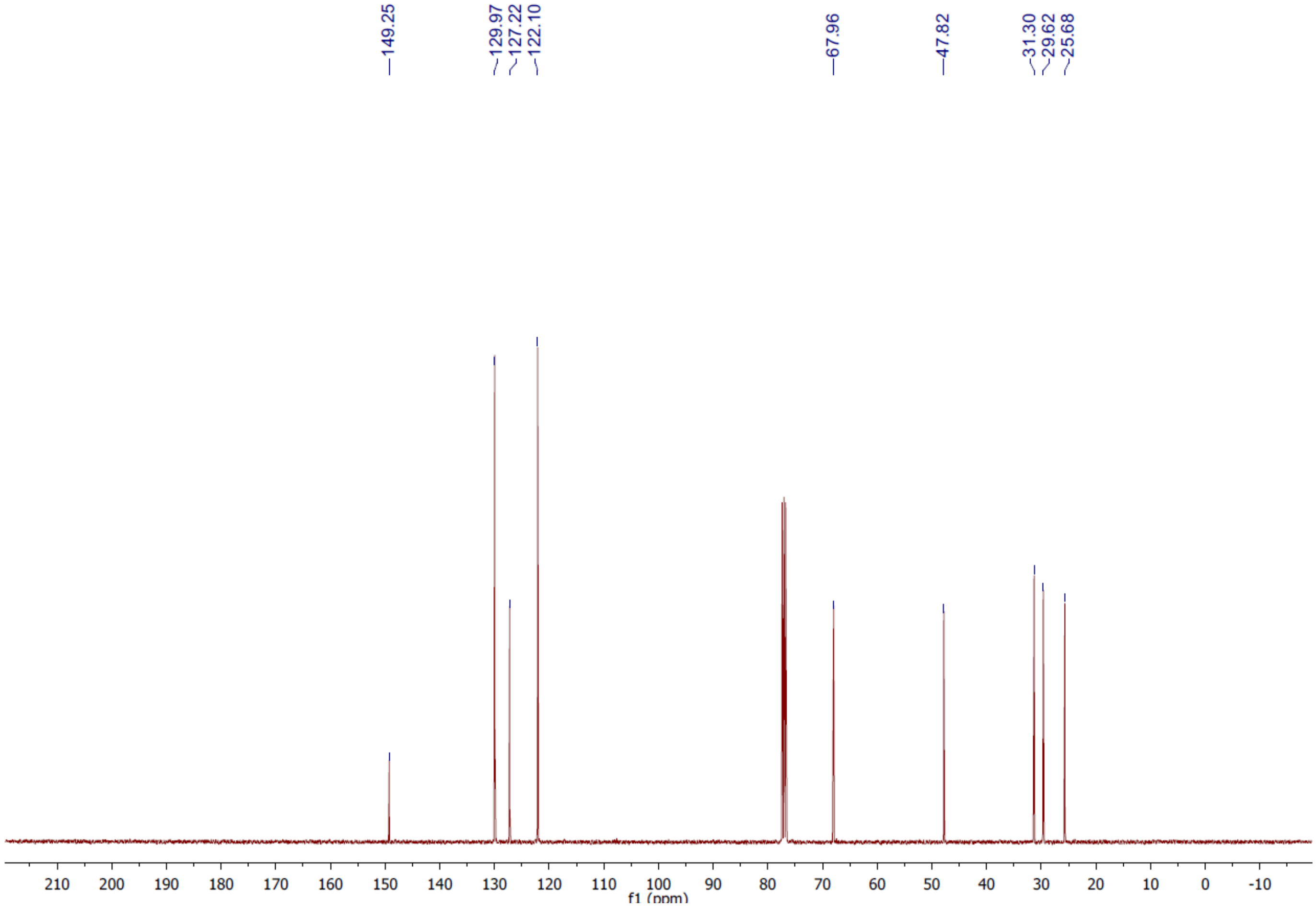
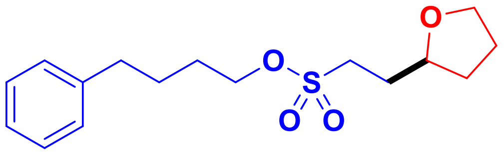


^{1}H-NMR (400 MHz, CDCl$_3$) of **3v**



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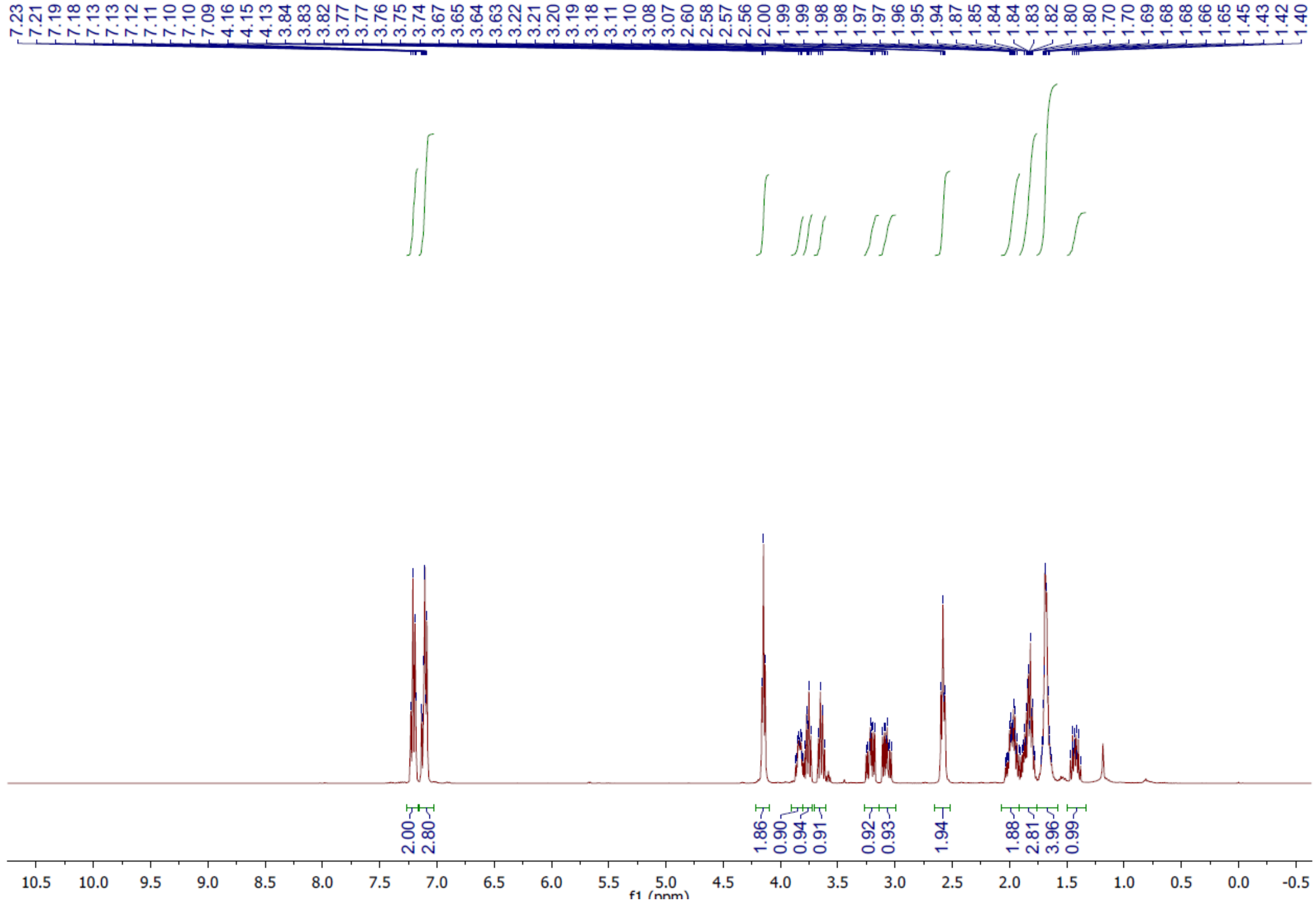
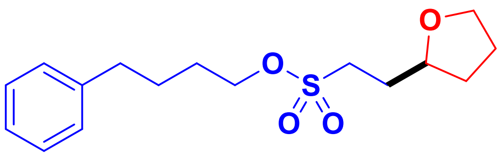


^{13}C-NMR (101 MHz, CDCl$_3$) of **3v**



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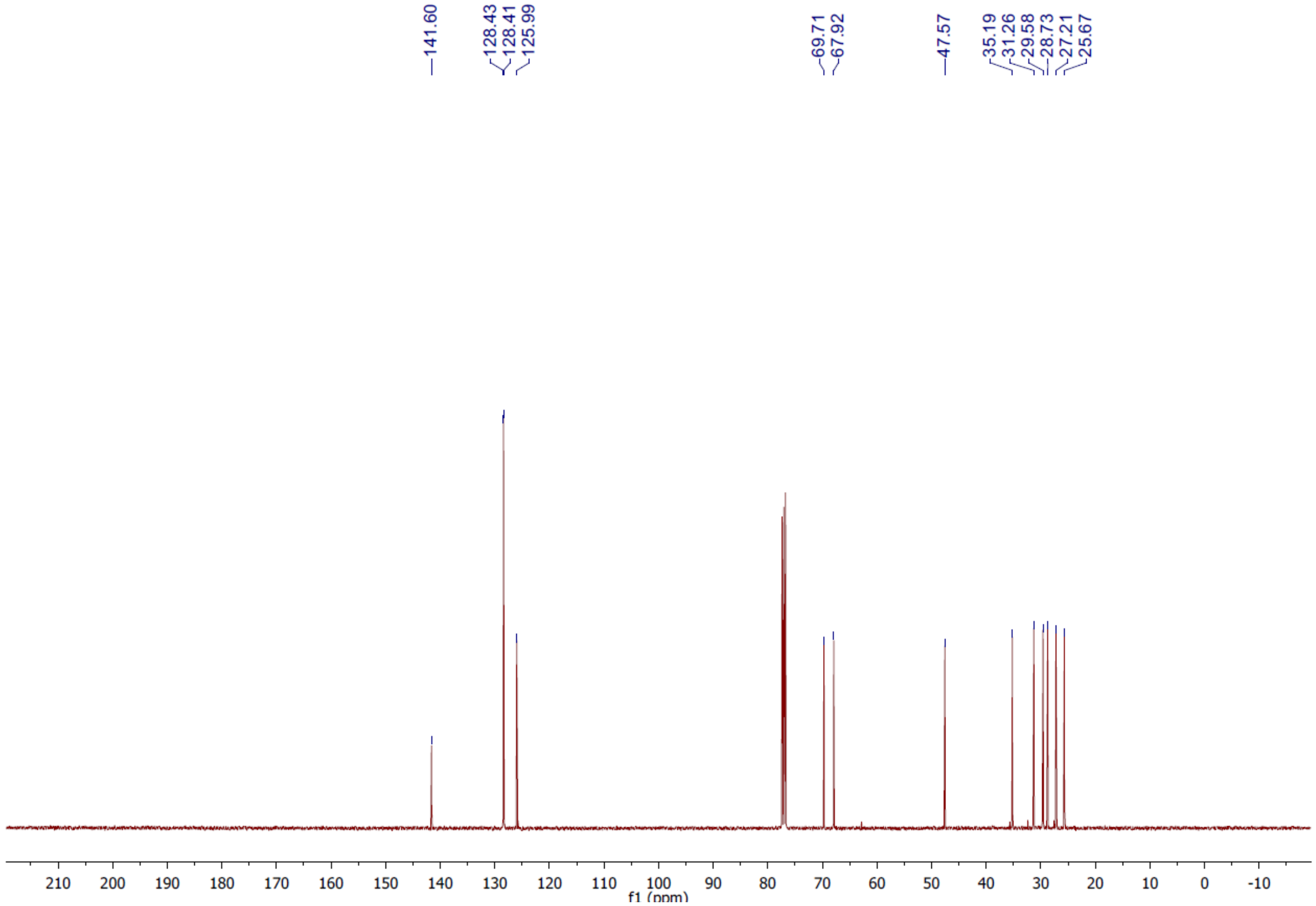
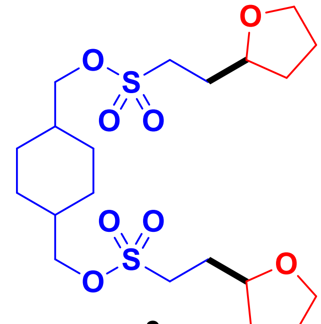


^{1}H-NMR (400 MHz, CDCl$_3$) of **3w**



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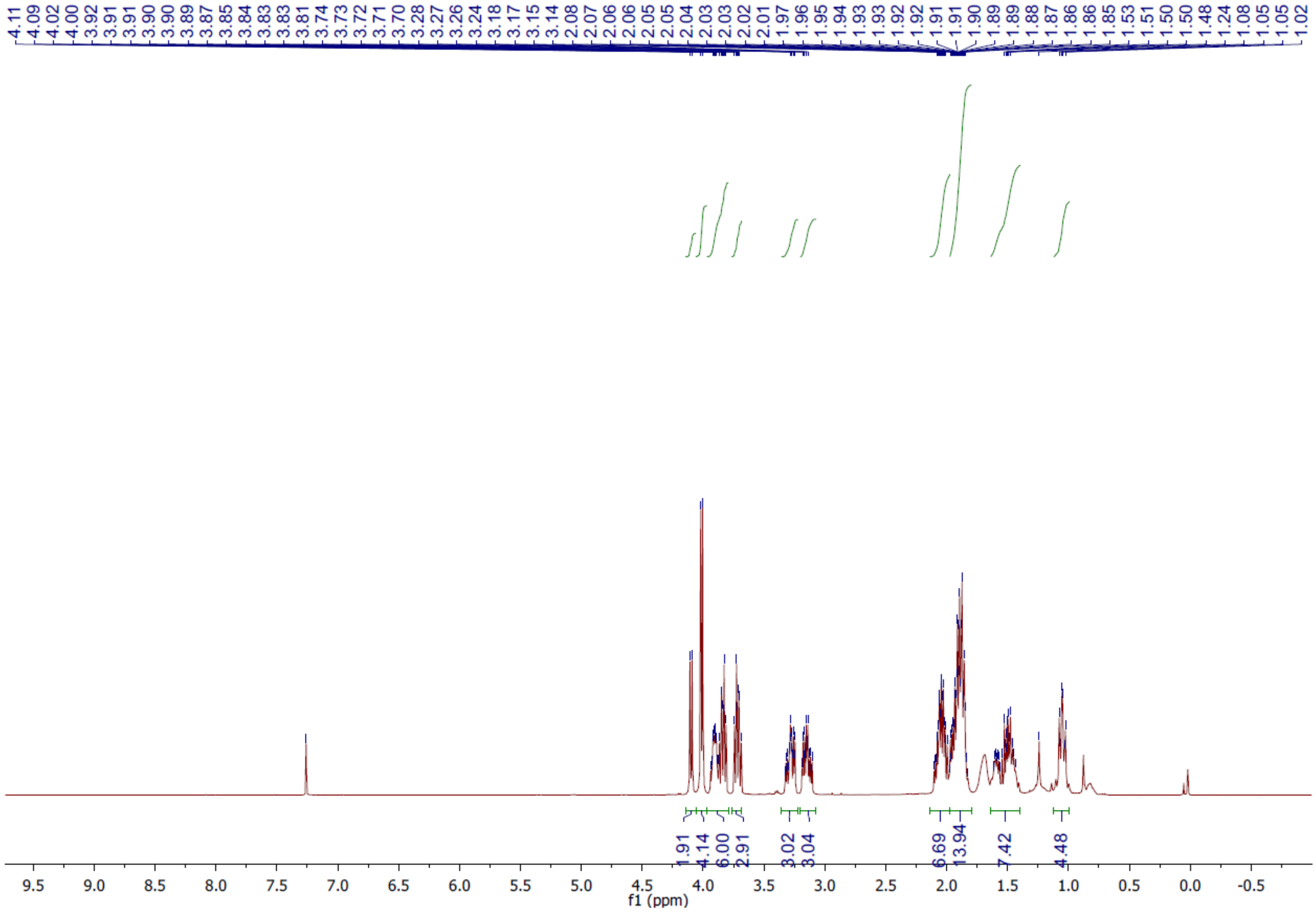
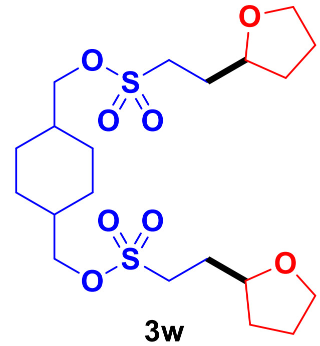


^{13}C-NMR (4101 MHz, CDCl$_3$) of **3w**



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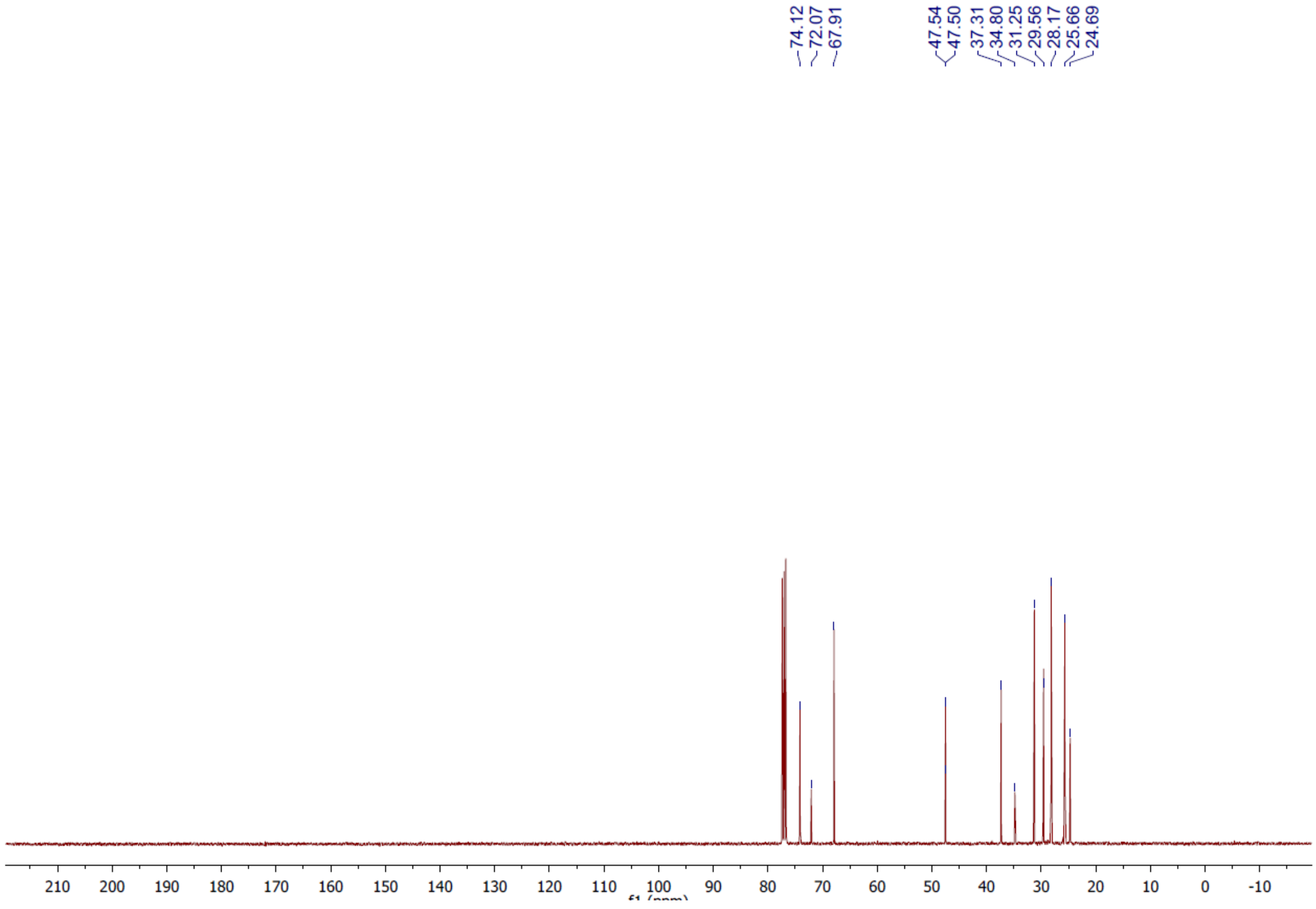
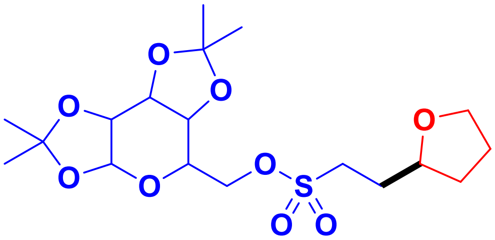


^{1}H-NMR (400 MHz, $CDCl_3$) of **3x**



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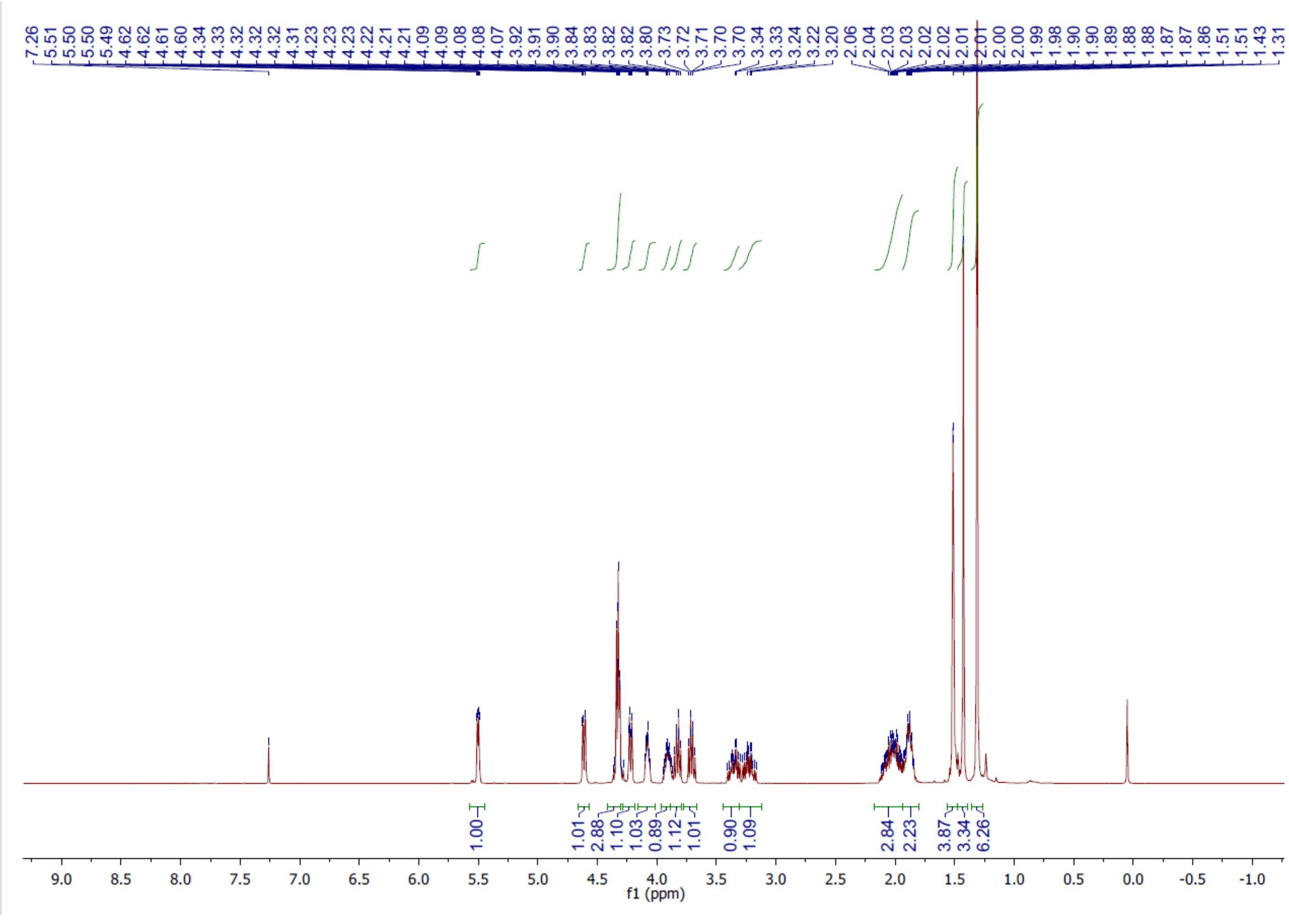
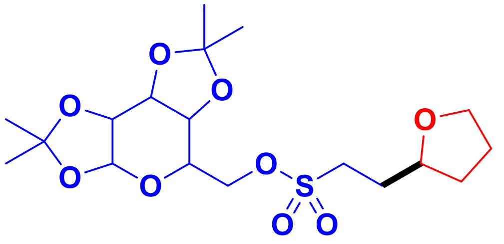
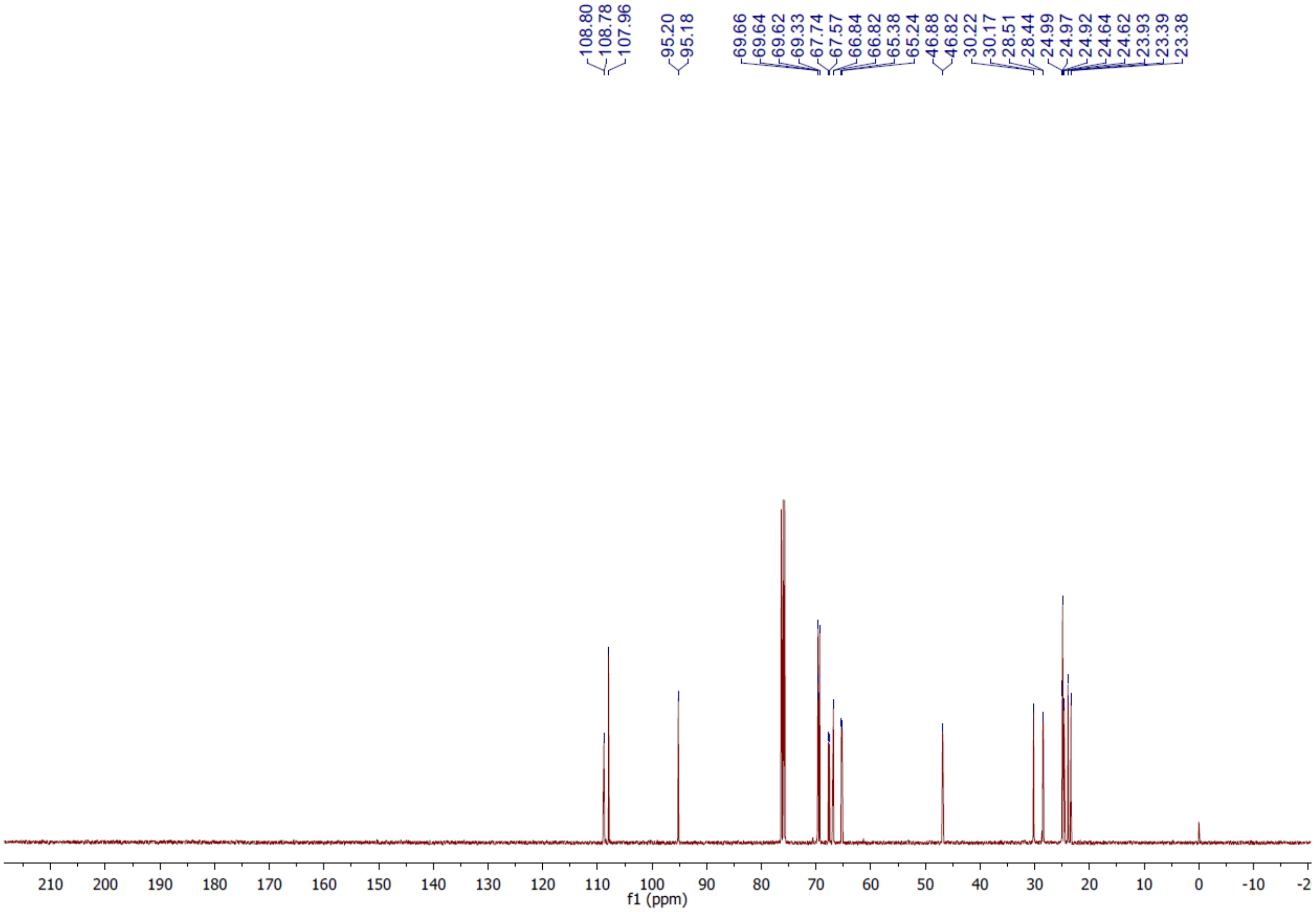


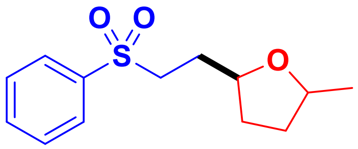
^{13}C-NMR (101 MHz, CDCl$_3$) of **3x**



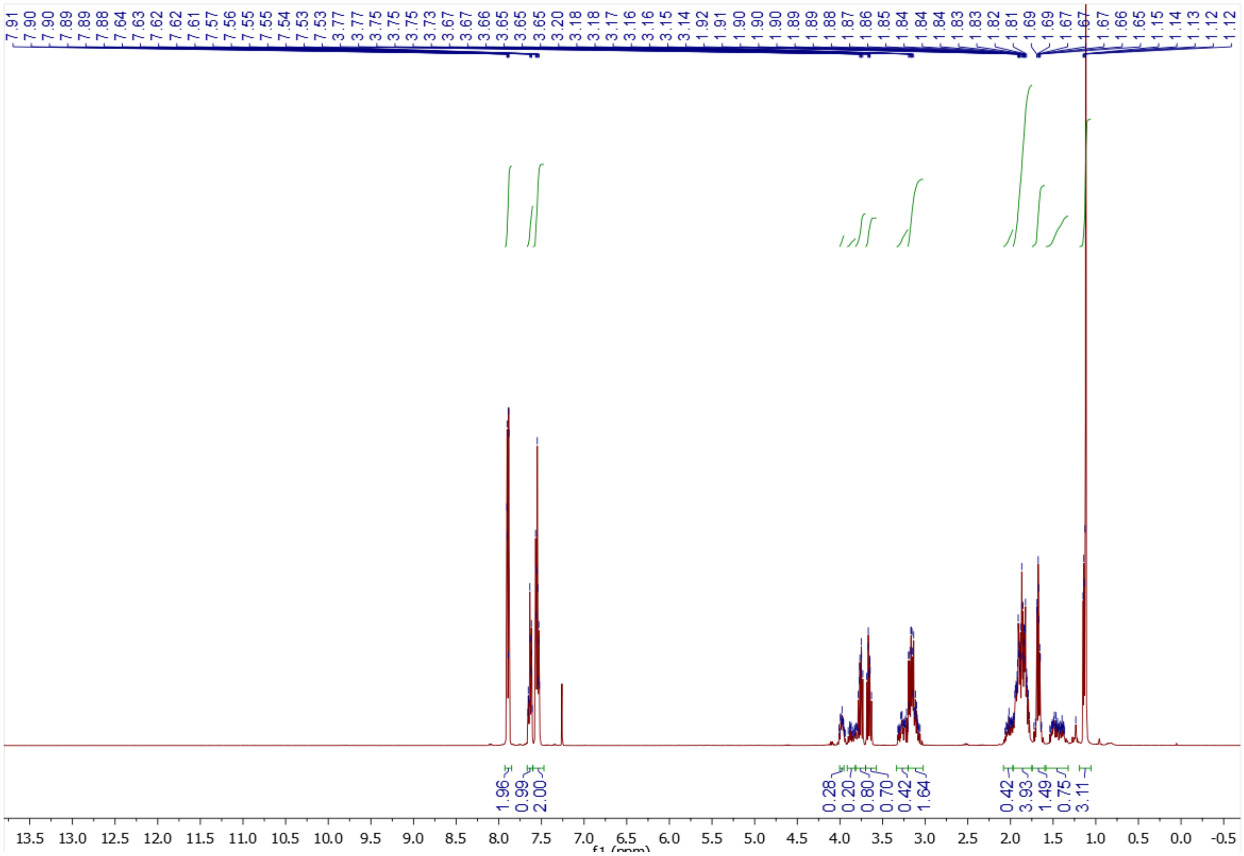
3x



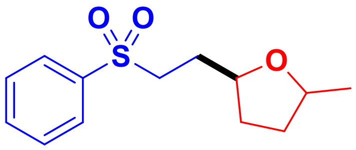
^{1}H-NMR (400 MHz, CDCl$_3$) of **4a**



4a



^{13}C-NMR (101 MHz, CDCl$_3$) of **4a**



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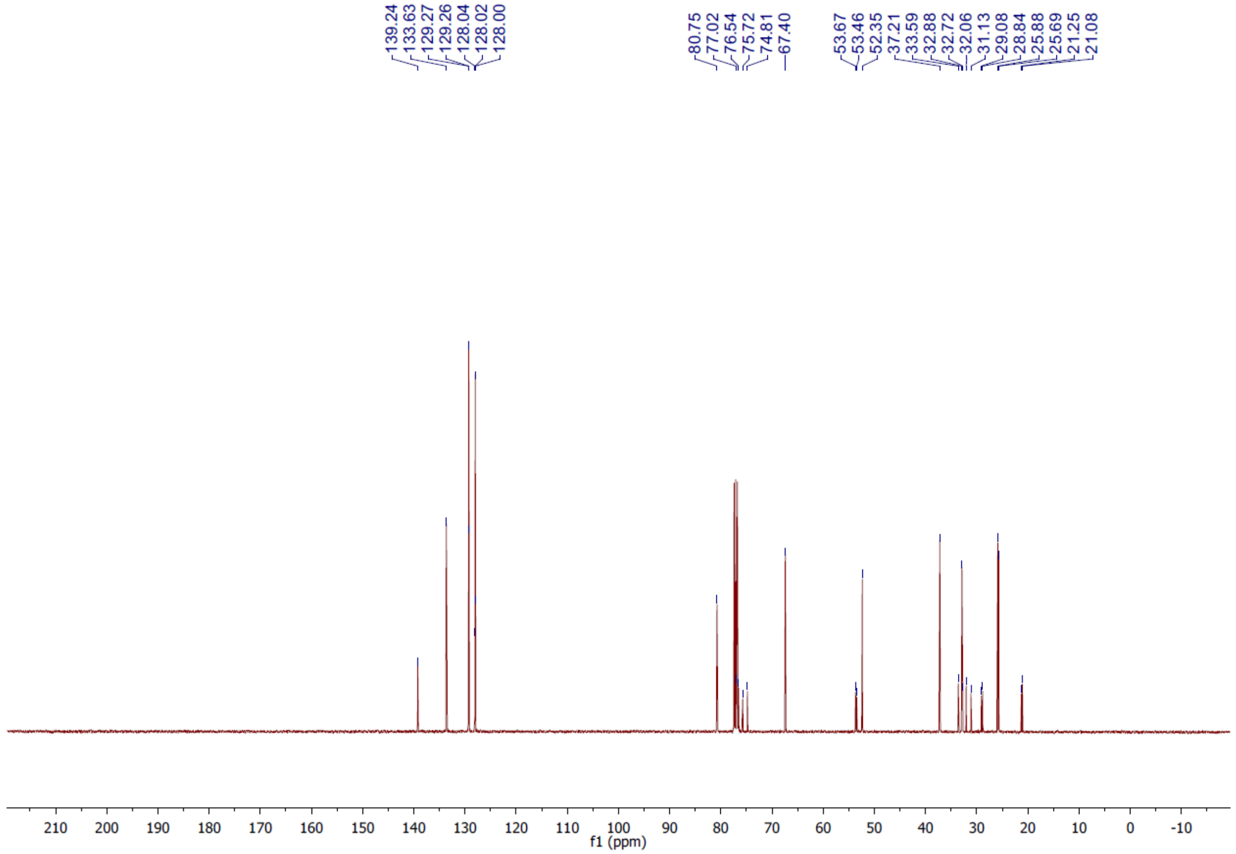
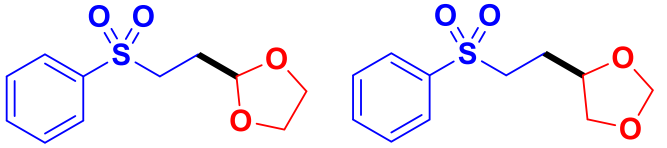


^{1}H-NMR (400 MHz, CDCl$_3$) of **4b**



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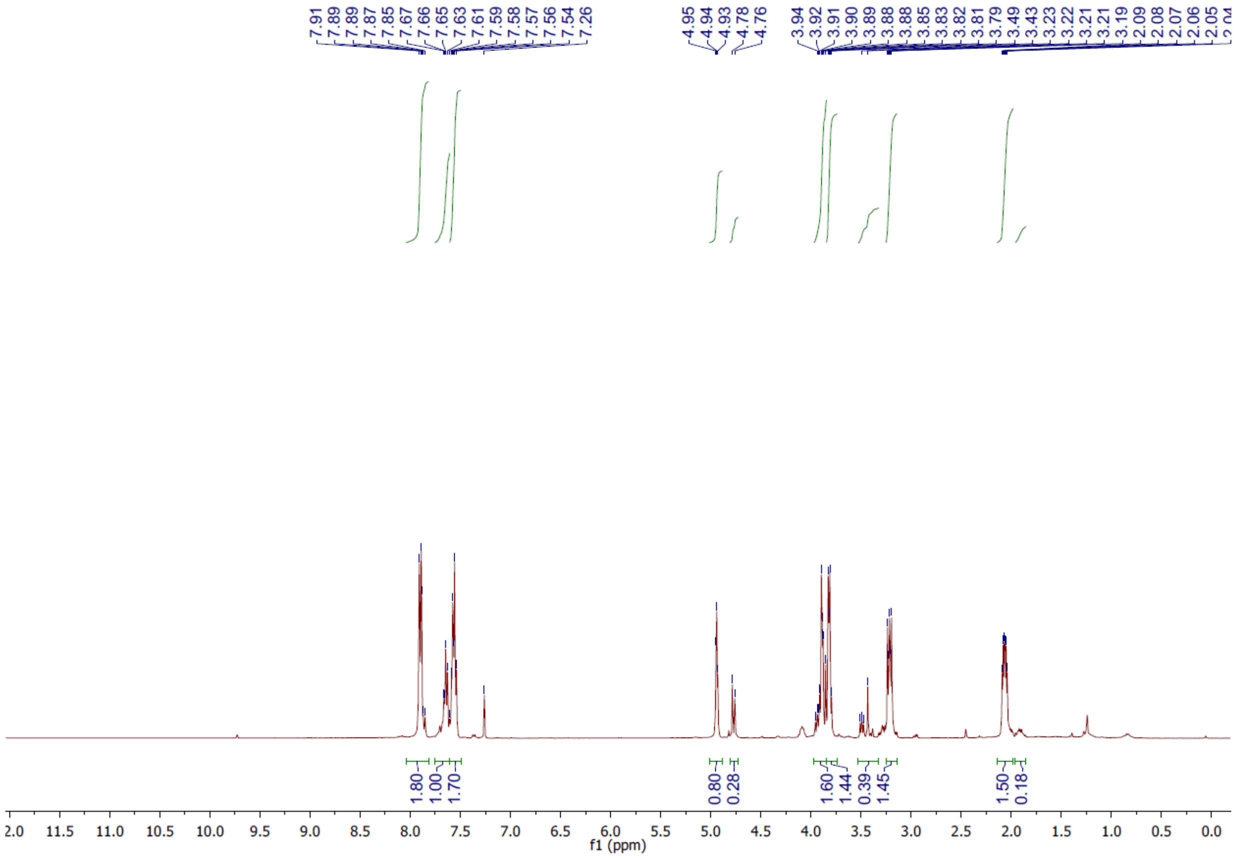
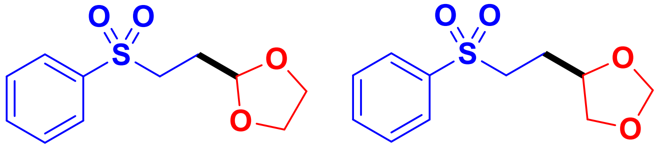


^{13}C-NMR (101 MHz, CDCl$_3$) of **4b**



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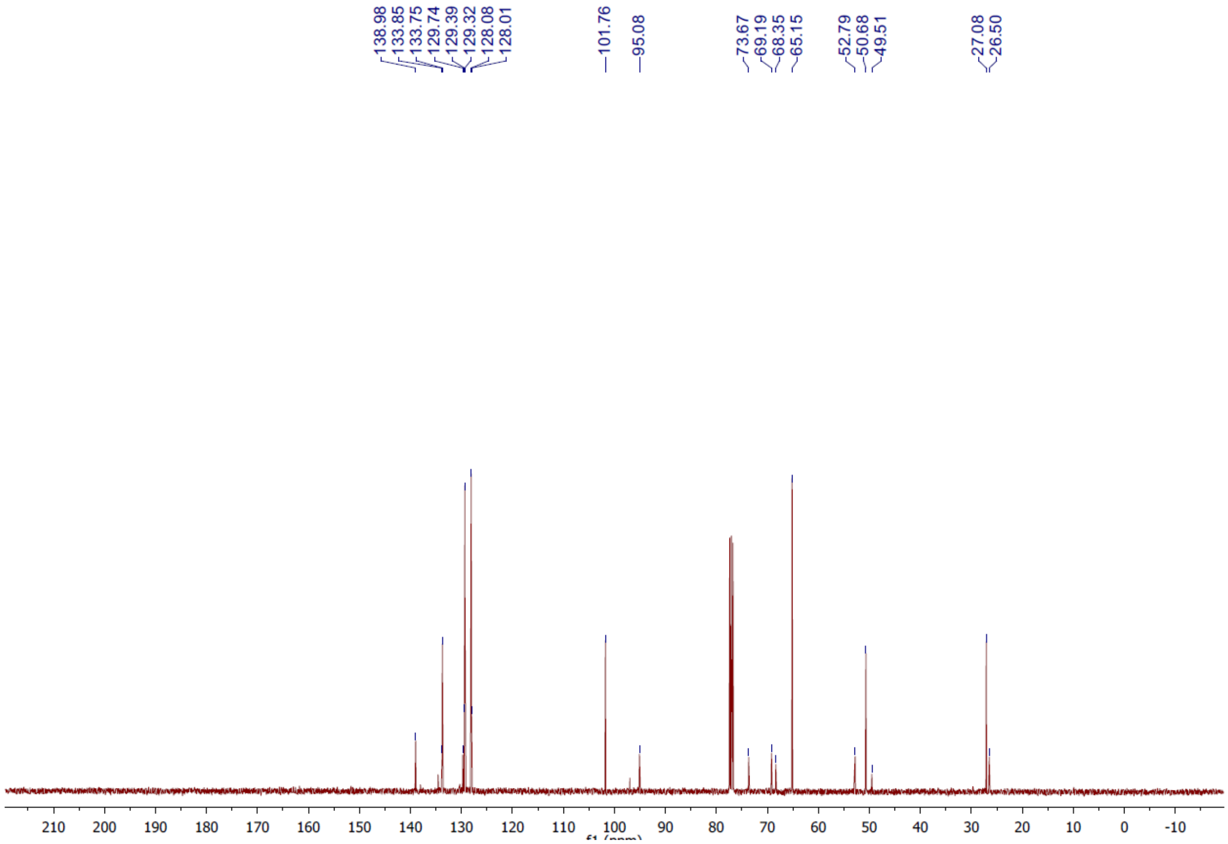
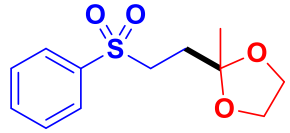


^{1}H-NMR (400 MHz, CDCl$_3$) of **4c**



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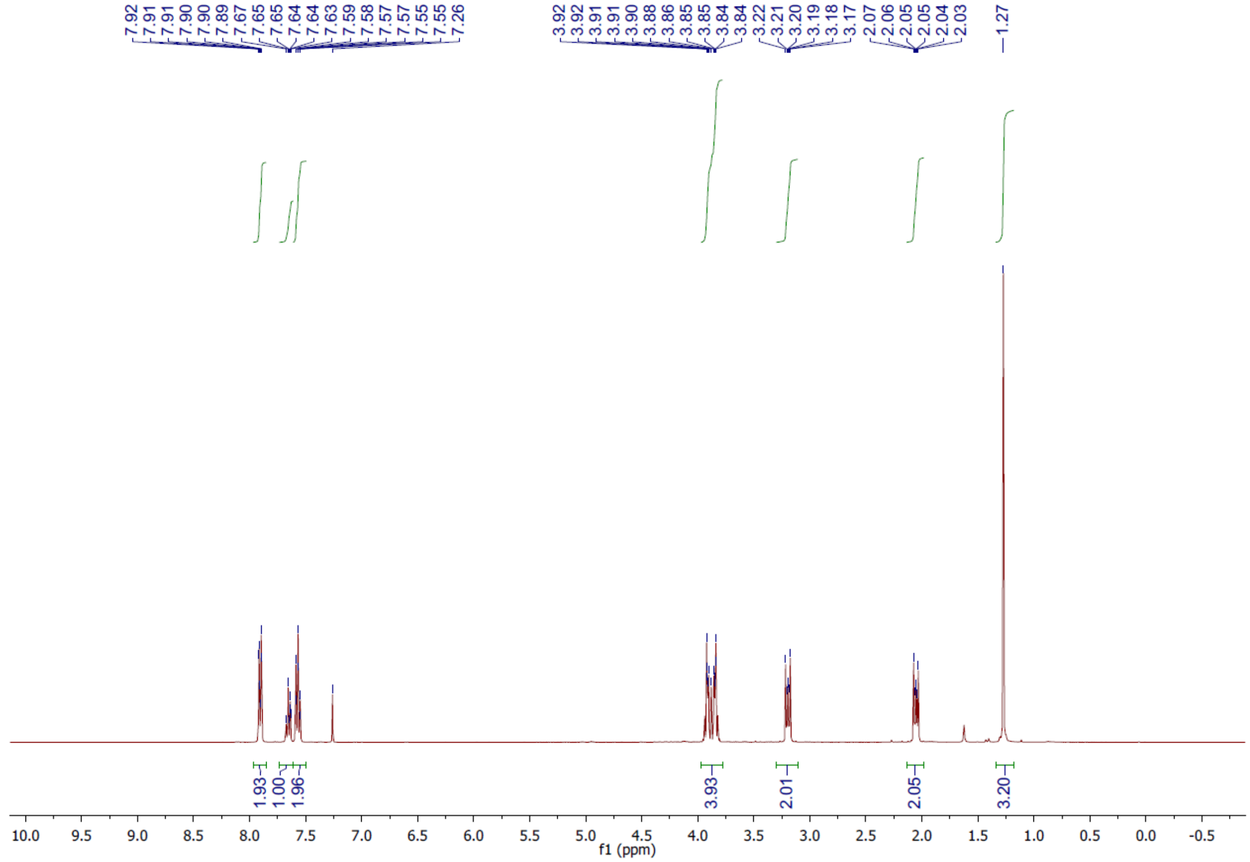
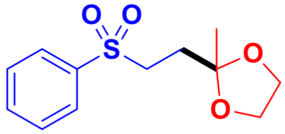


^{13}C-NMR (101 MHz, CDCl$_3$) of **4c**



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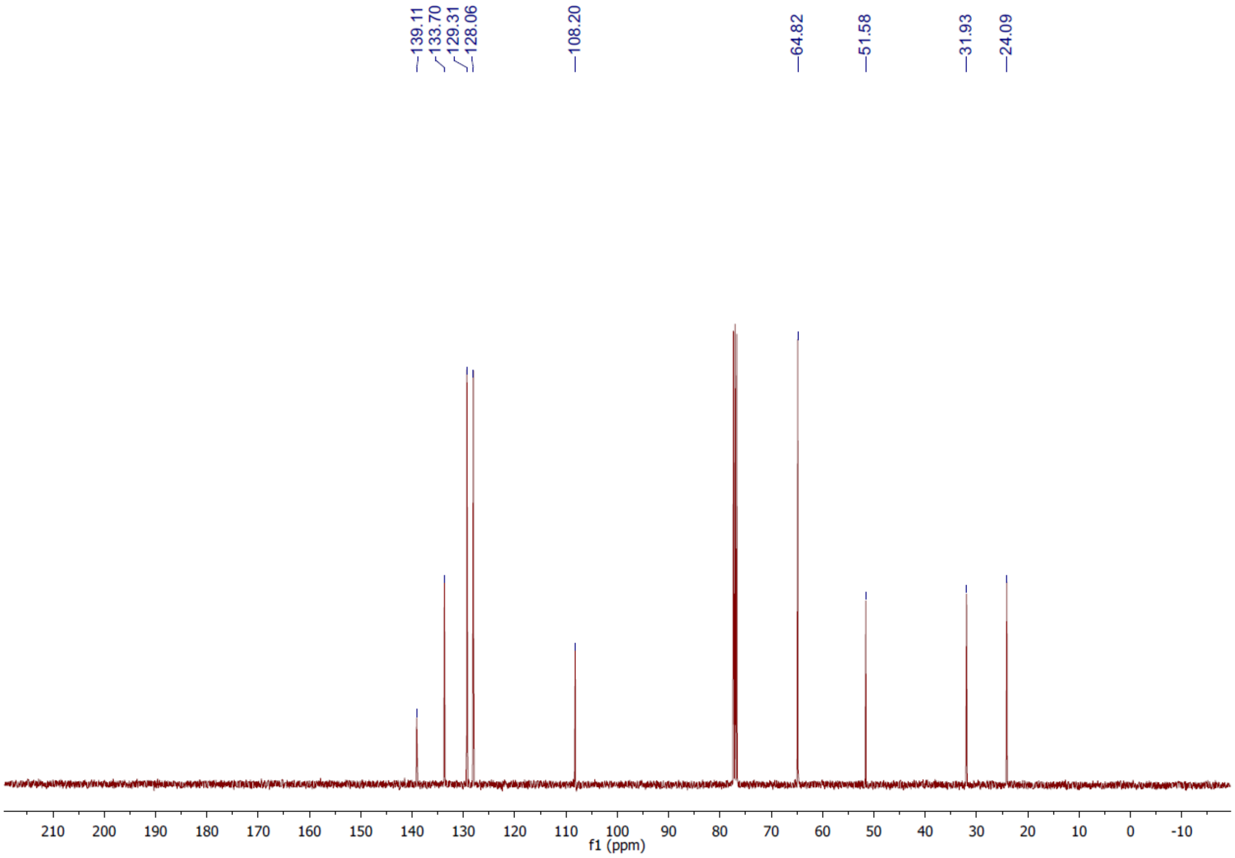
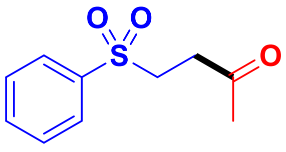
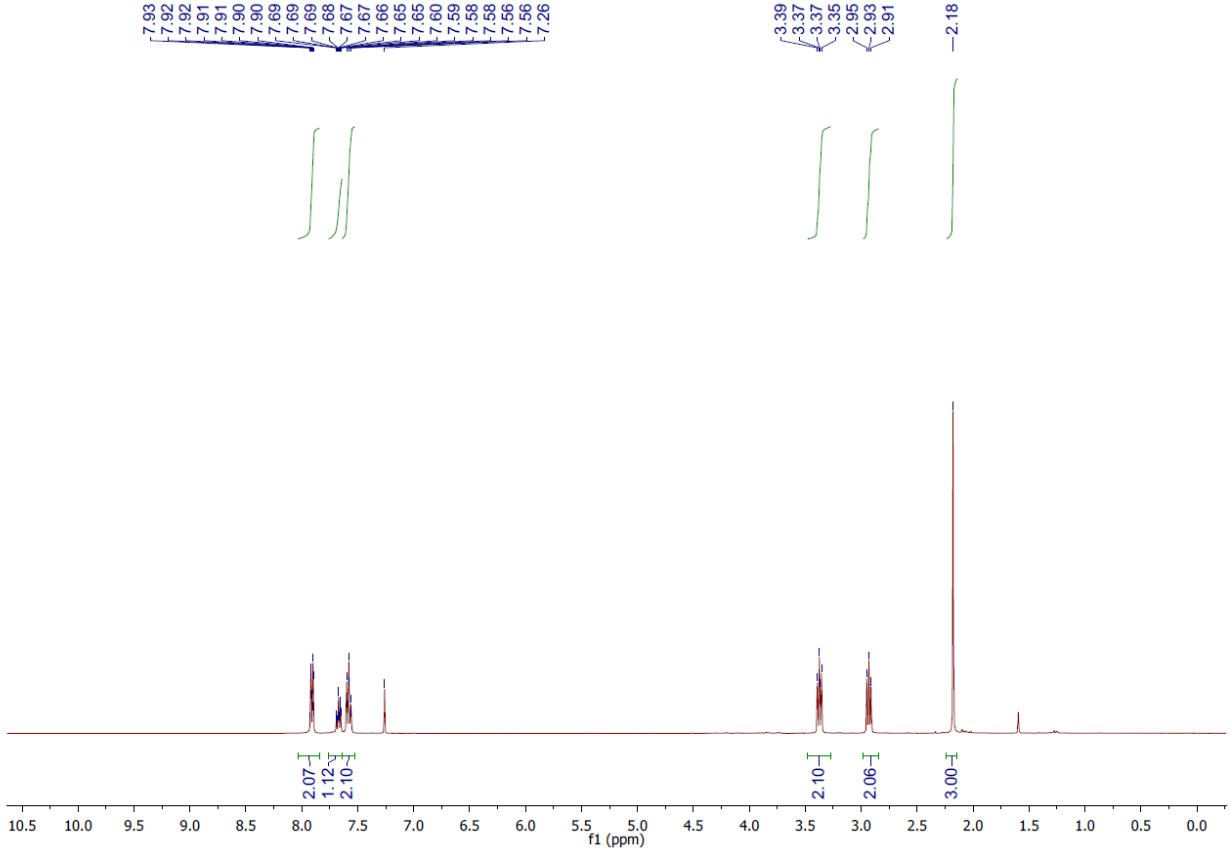


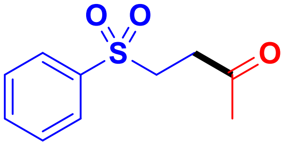
^{1}H-NMR (400 MHz, CDCl$_3$) of **4c'**



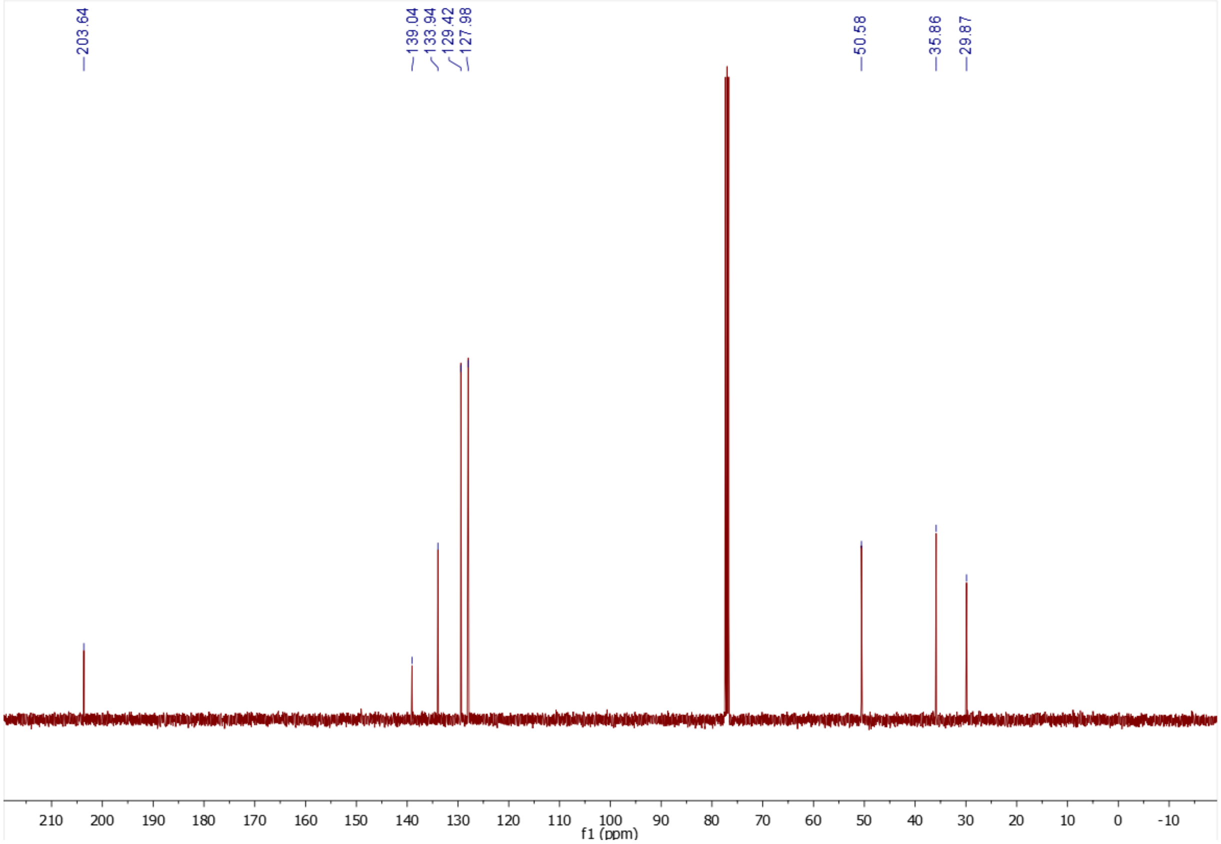
4c'



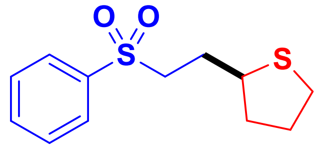
^{13}C-NMR (101 MHz, CDCl$_3$) of **4c'**



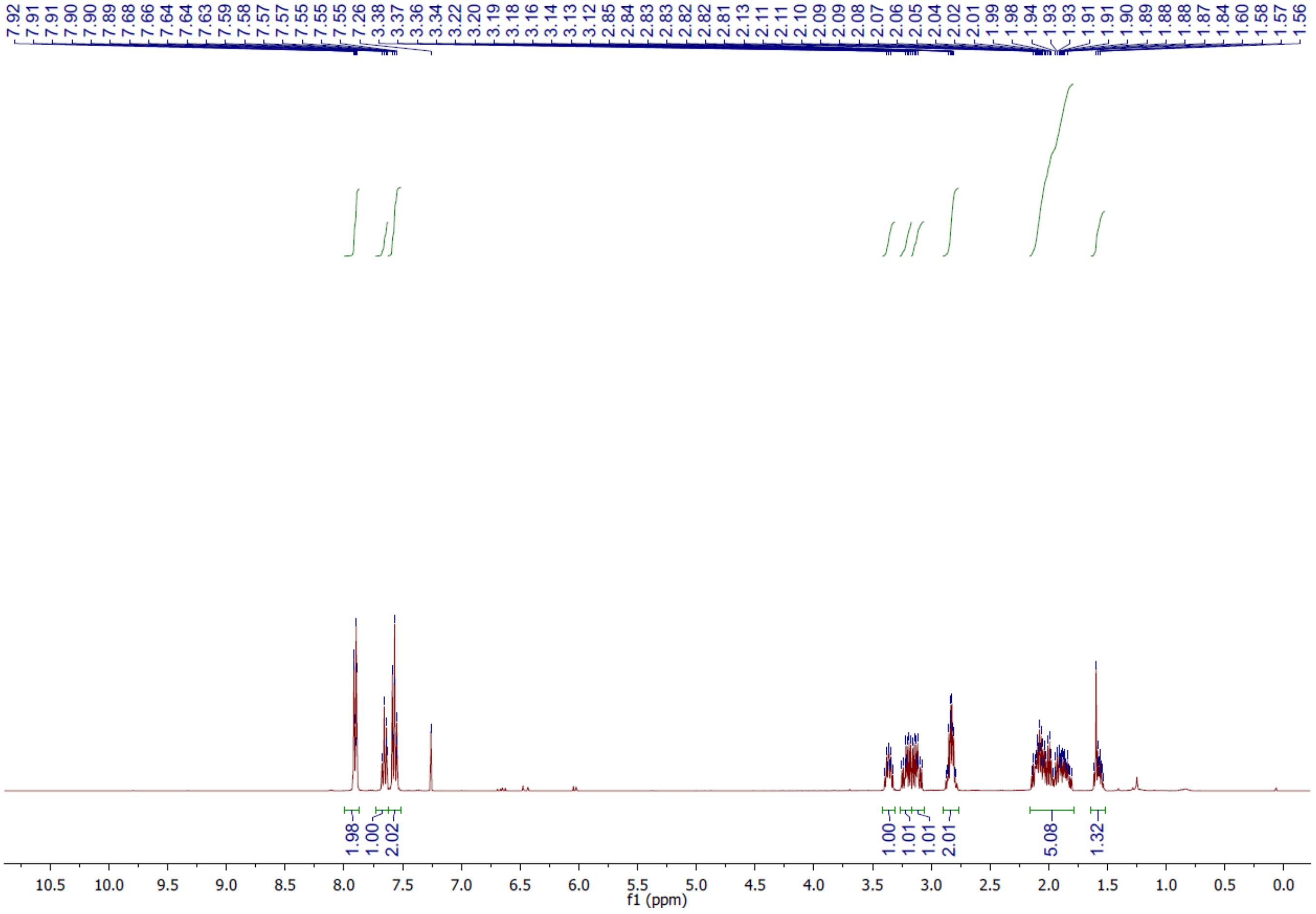
4c'



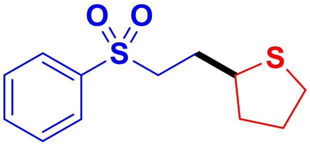
^{1}H-NMR (400 MHz, $CDCl_3$) of **4d**



4d



^{13}C-NMR (101 MHz, $CDCl_3$) of **4d**



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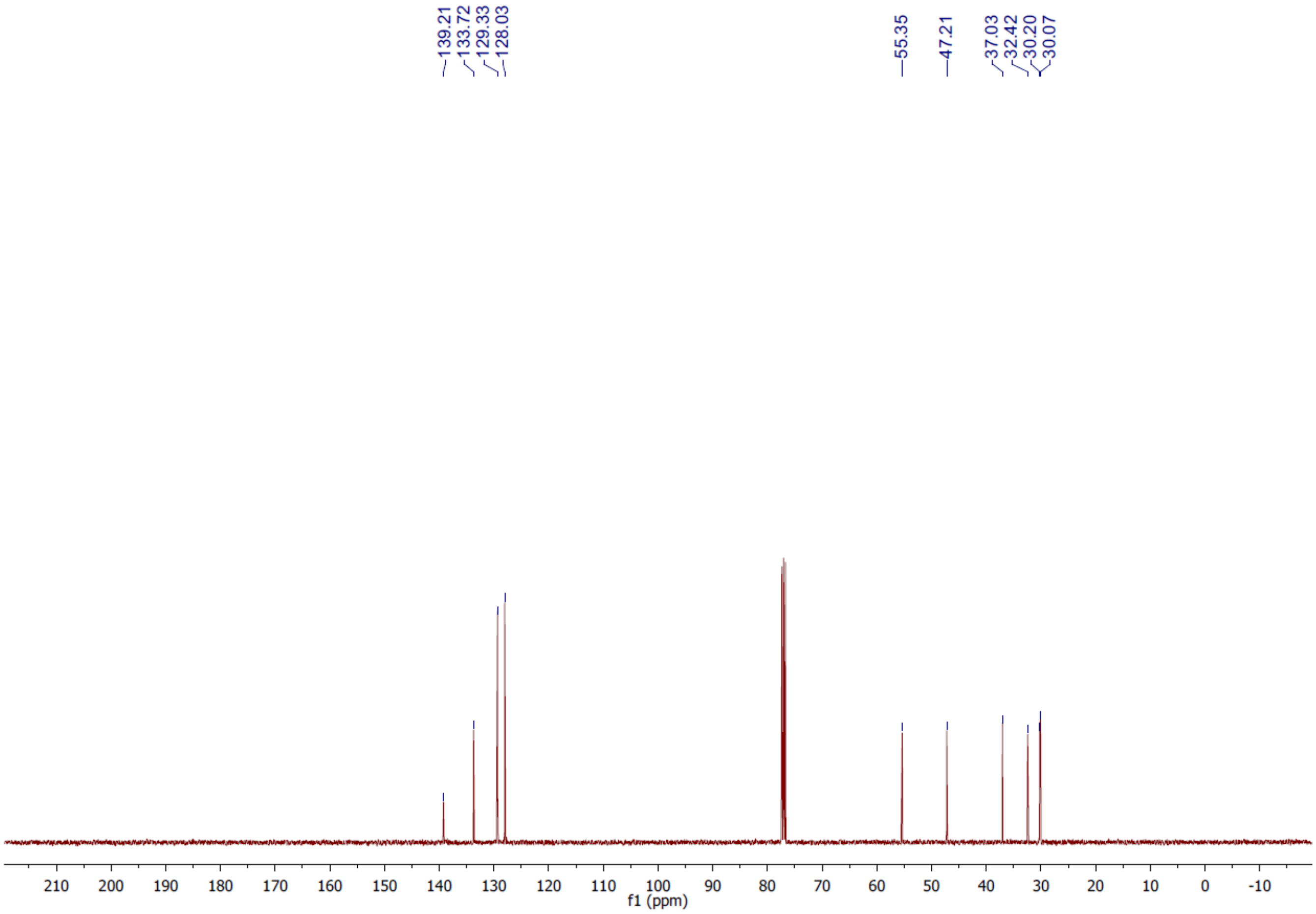

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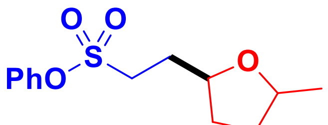

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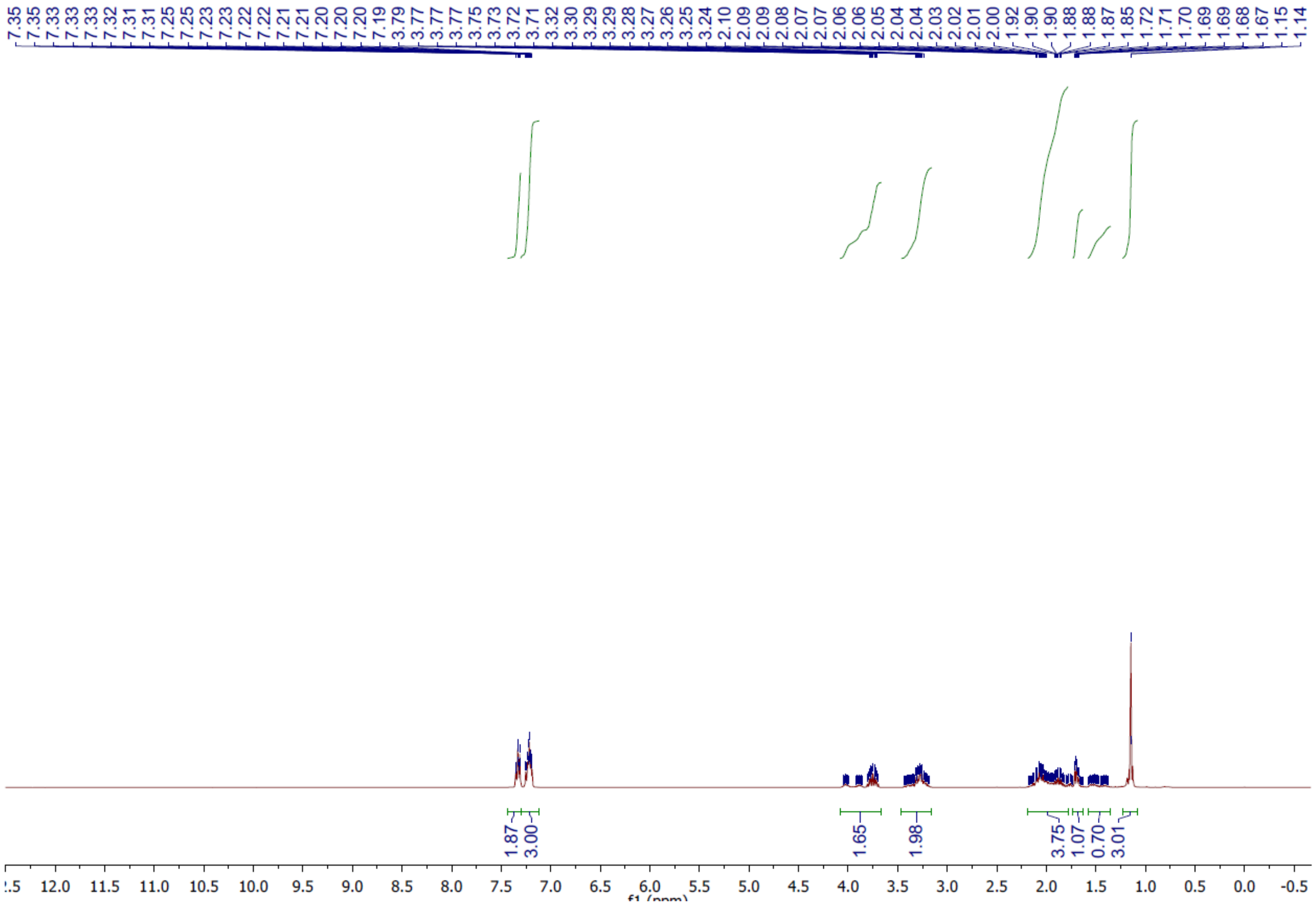
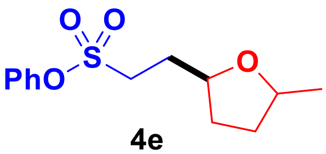


^{13}C-NMR (101 MHz, CDCl$_3$) of **4e**



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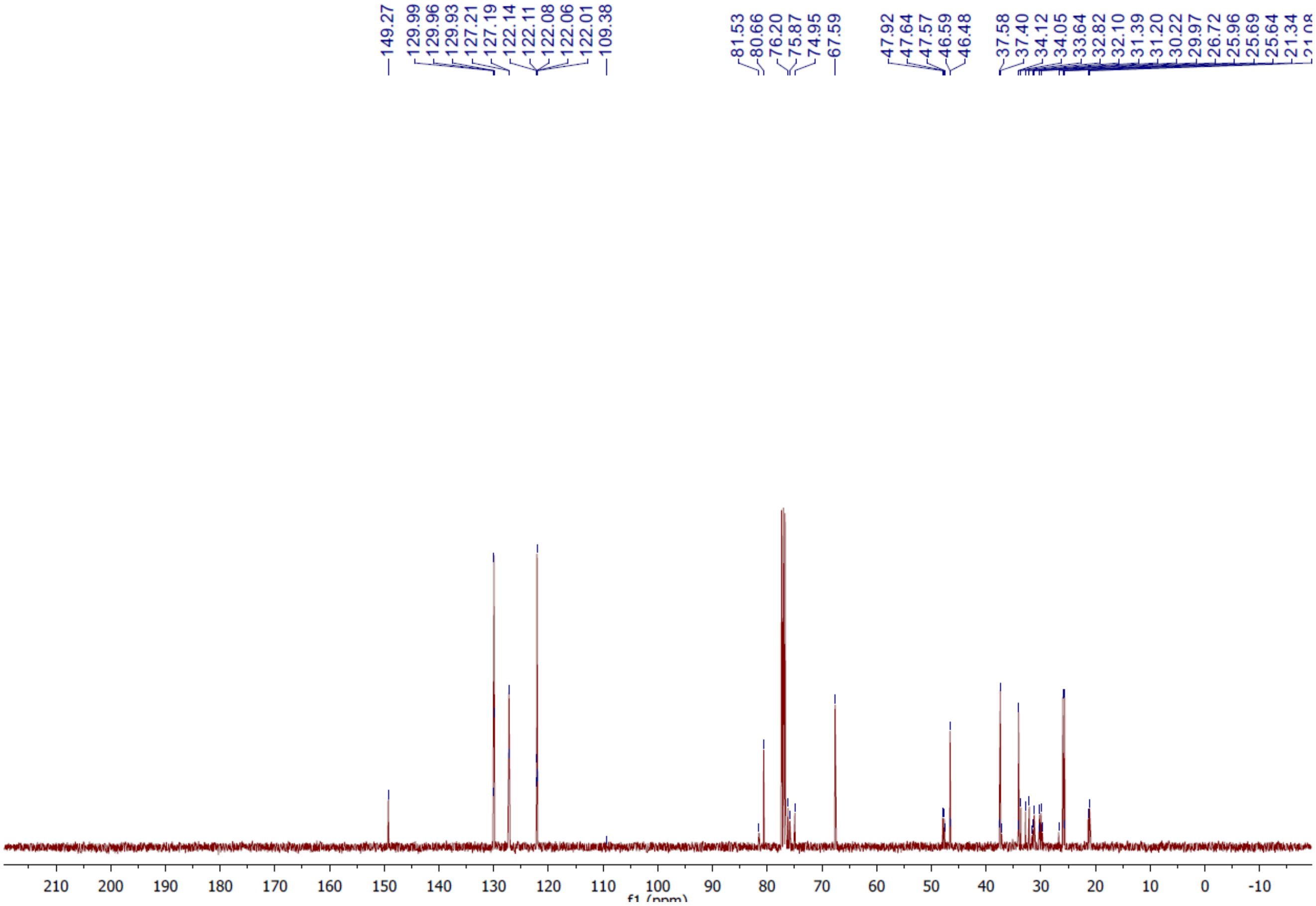
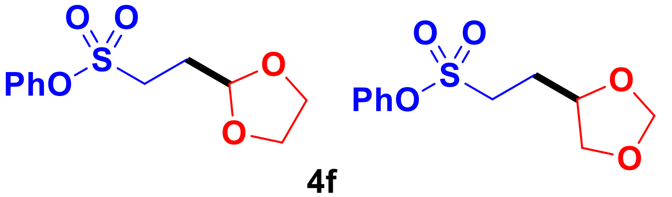


^{1}H-NMR (400 MHz, $CDCl_3$) of **4f**



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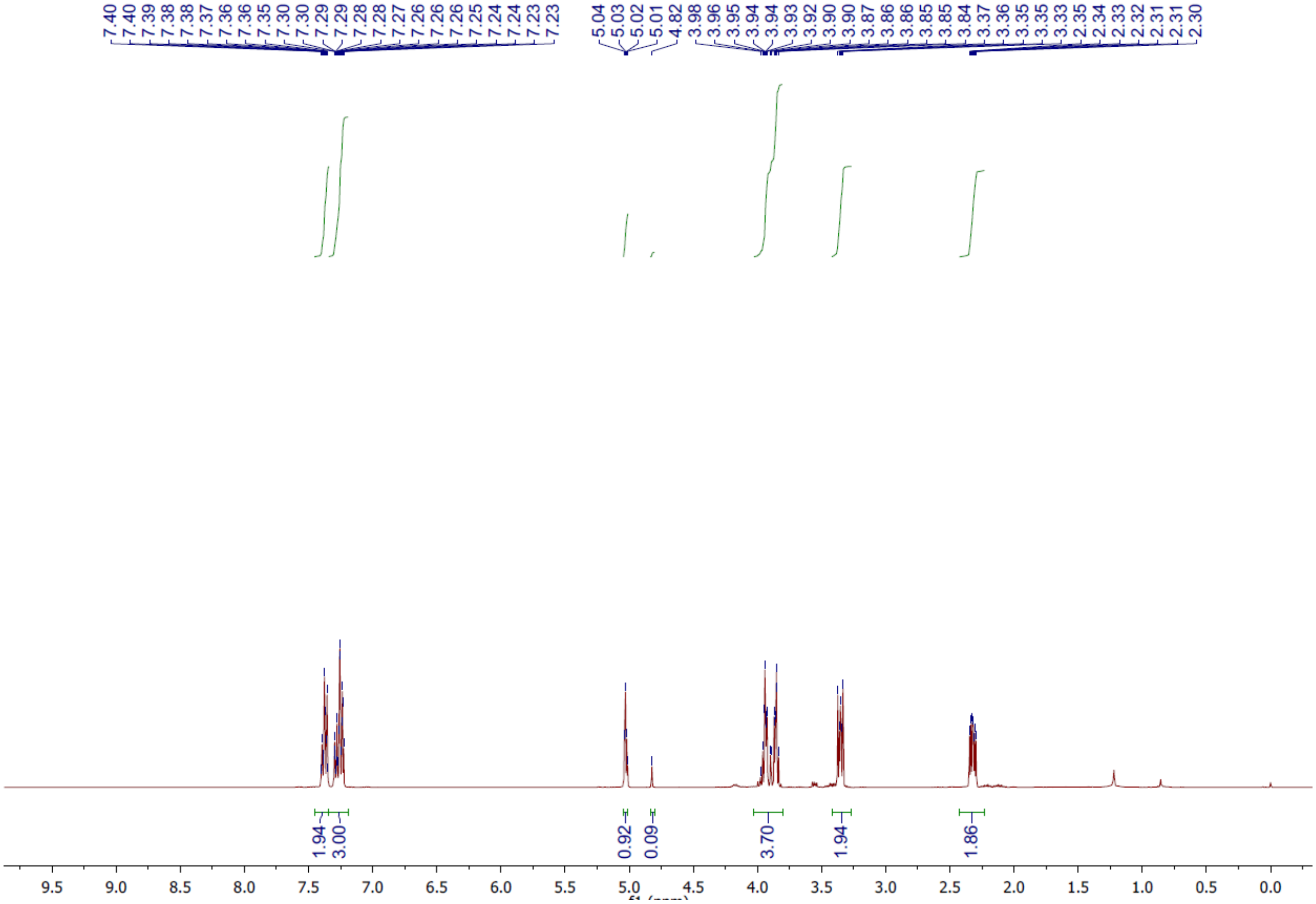

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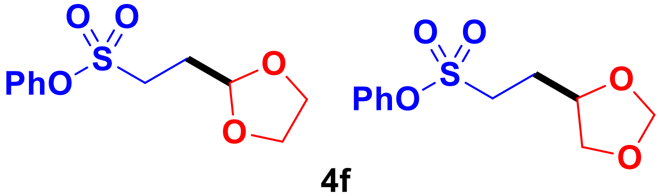

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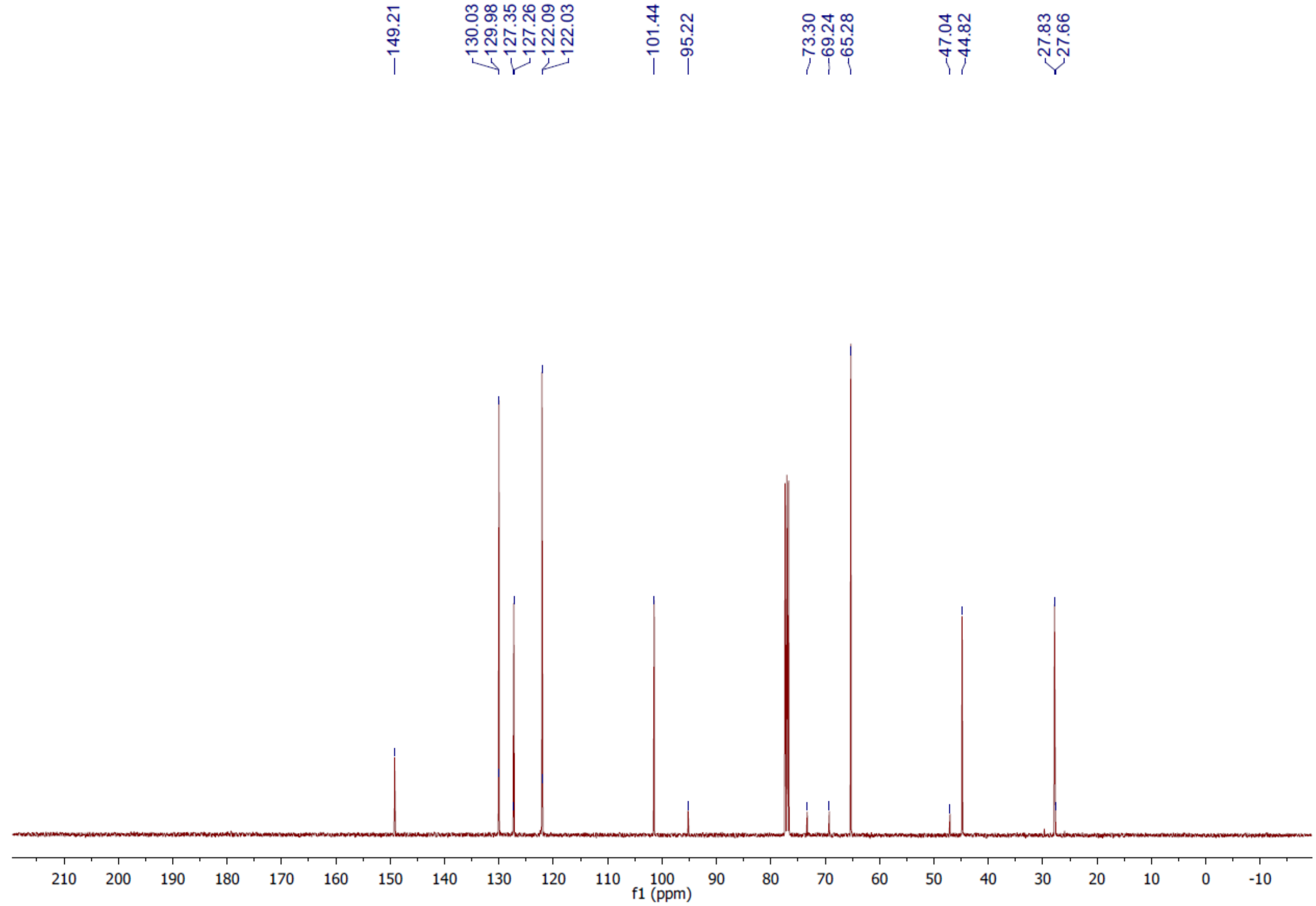
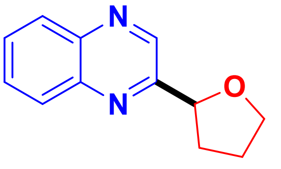
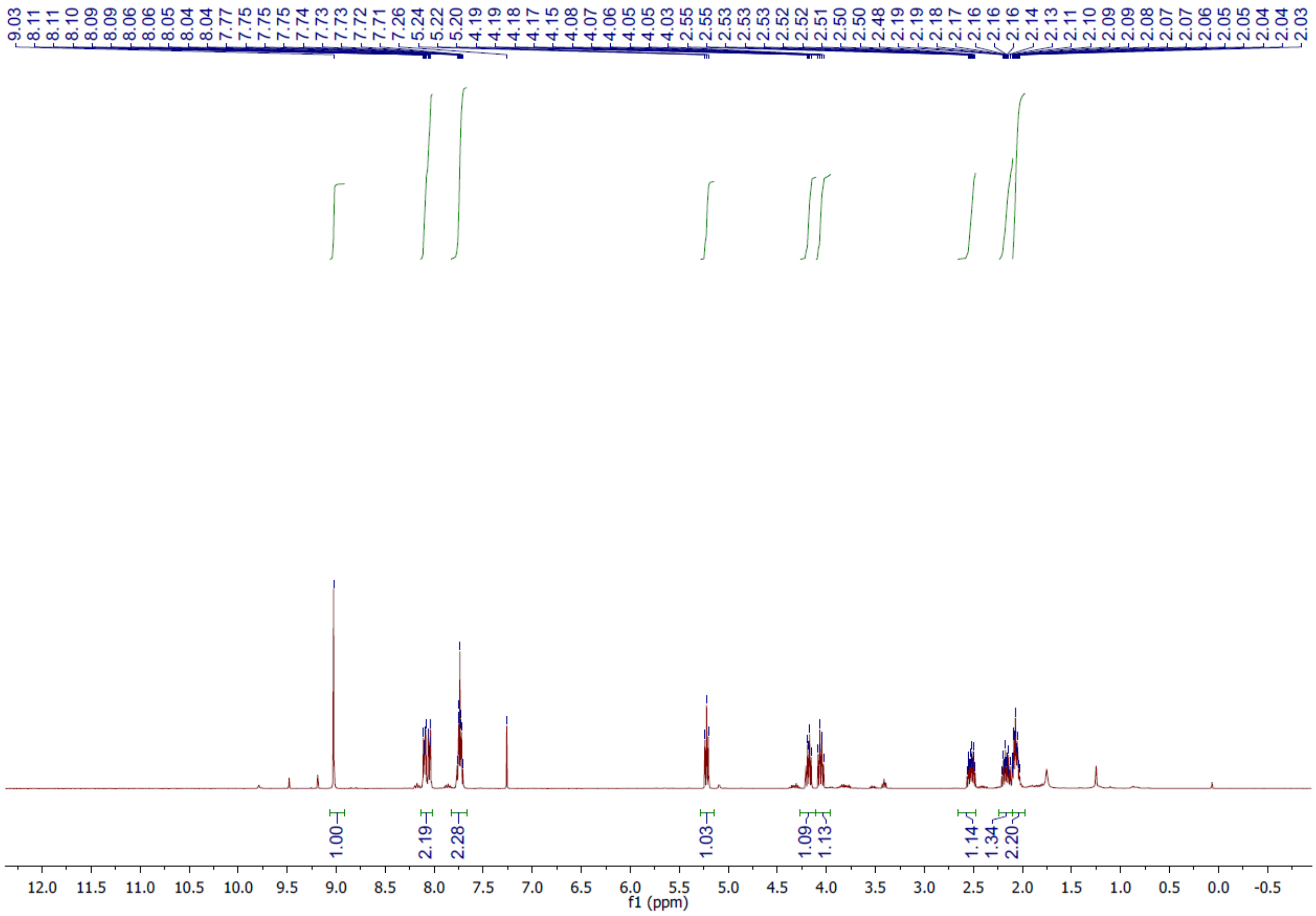


^{1}H-NMR (400 MHz, $CDCl_3$) of **5a**



5a



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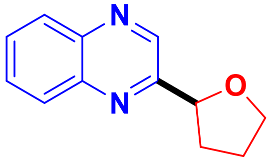

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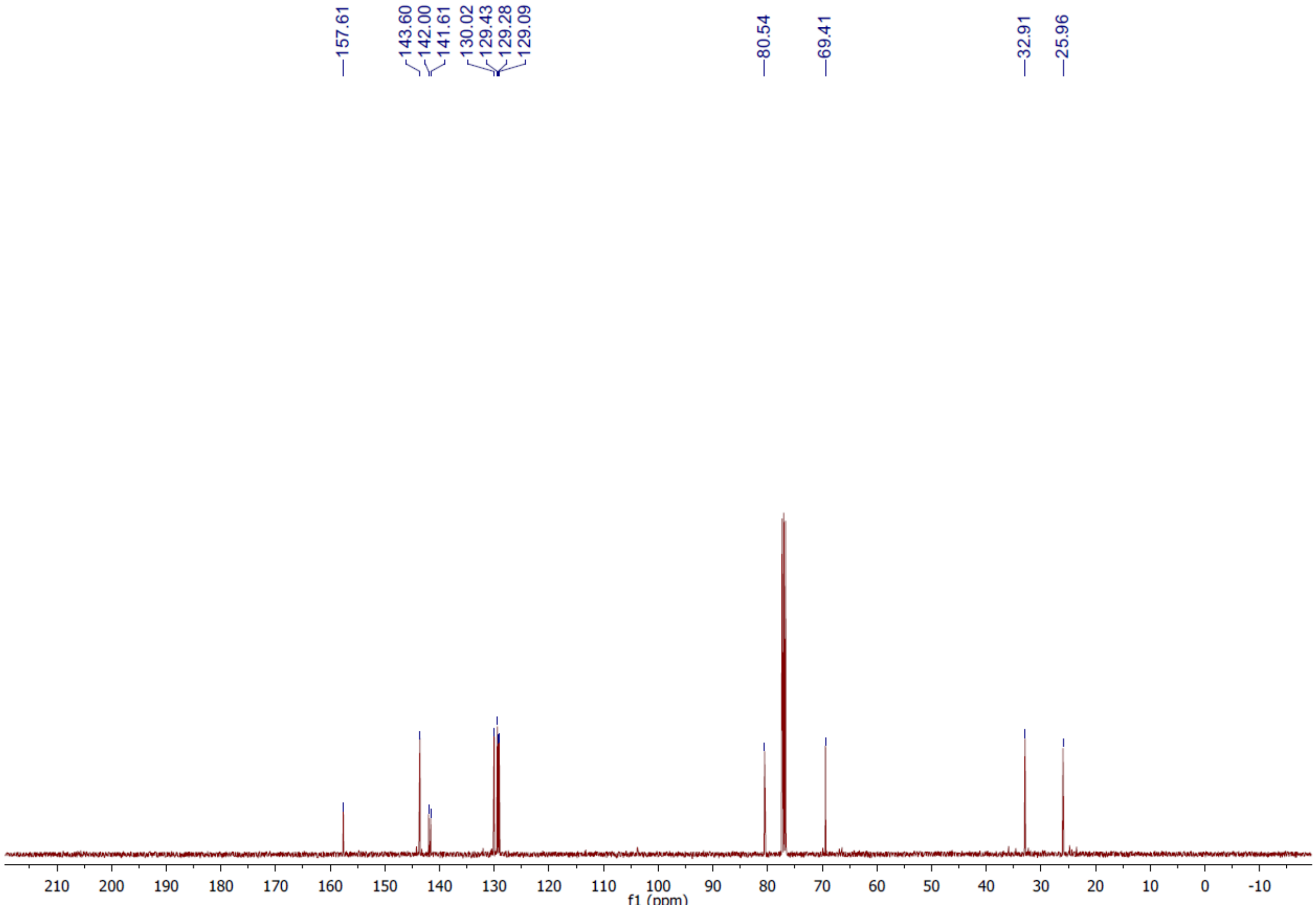
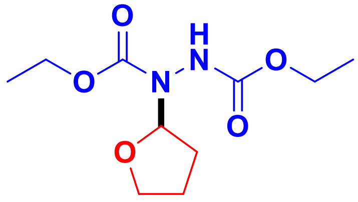
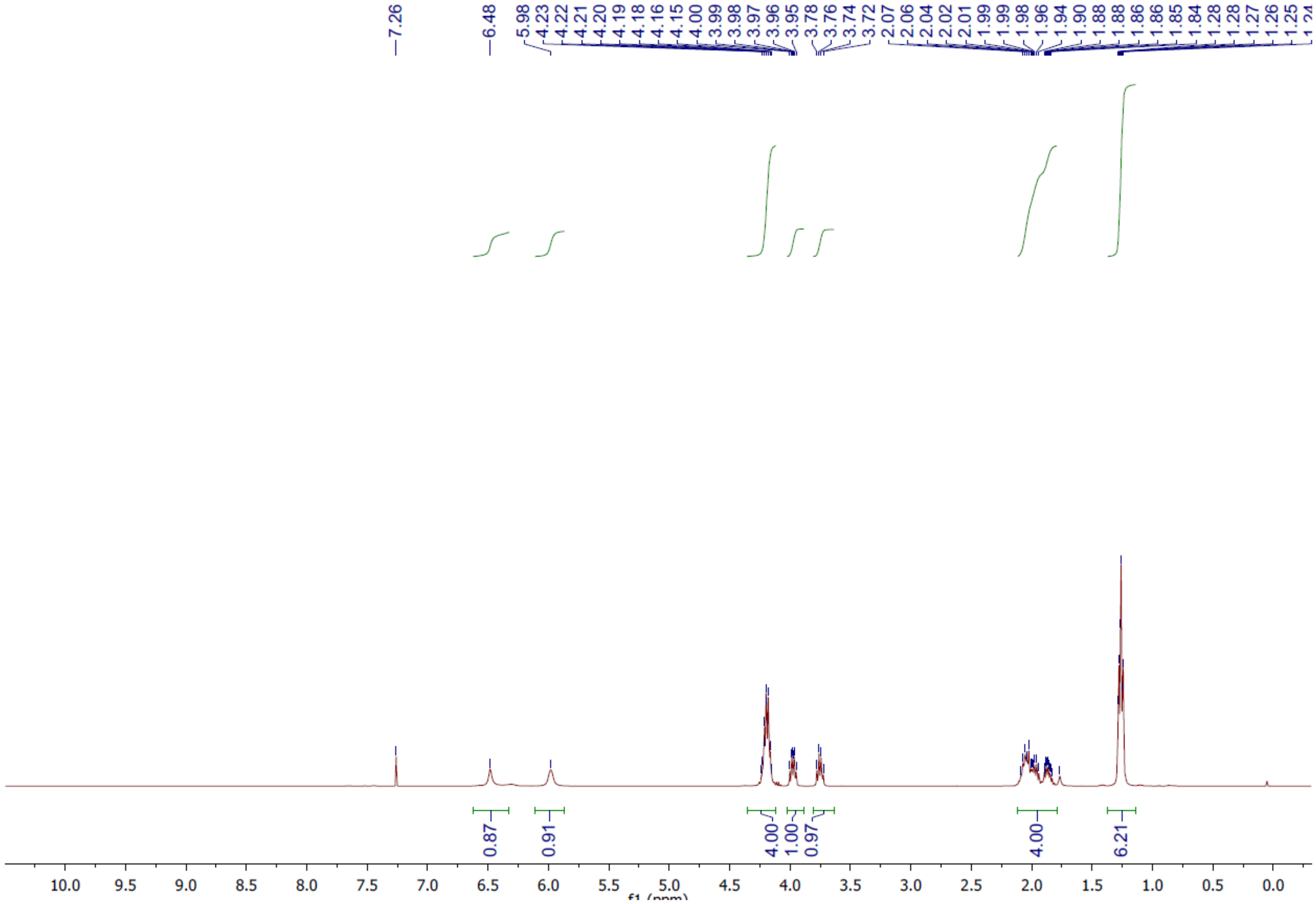


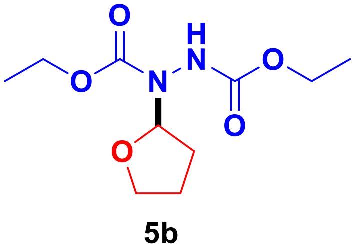
^{1}H-NMR (400 MHz, $CDCl_3$) of **5b**



5b



^{13}C-NMR (101 MHz, CDCl$_3$) of **5b**



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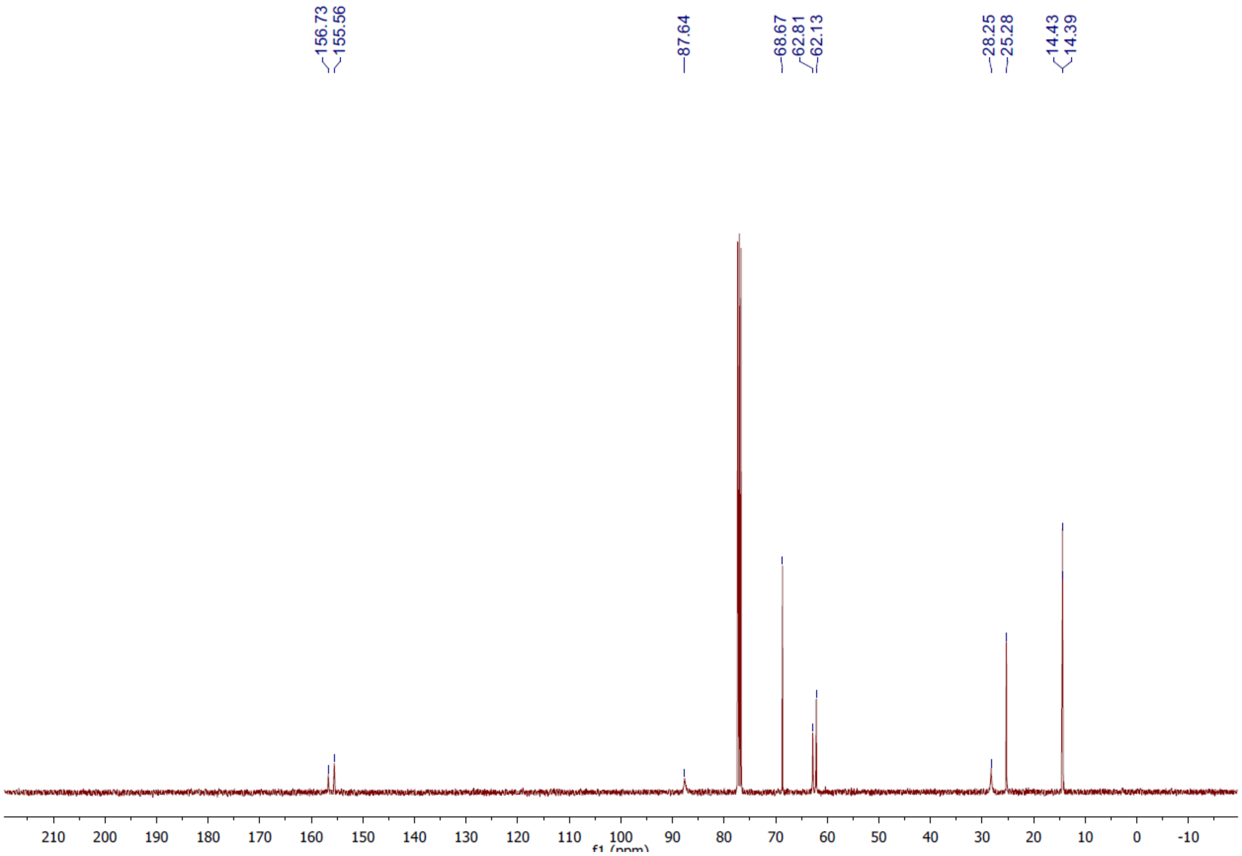
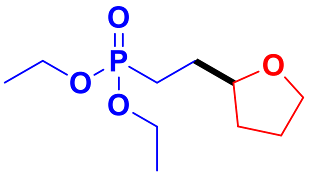


^{1}H-NMR (400 MHz, $CDCl_3$) of **5c**



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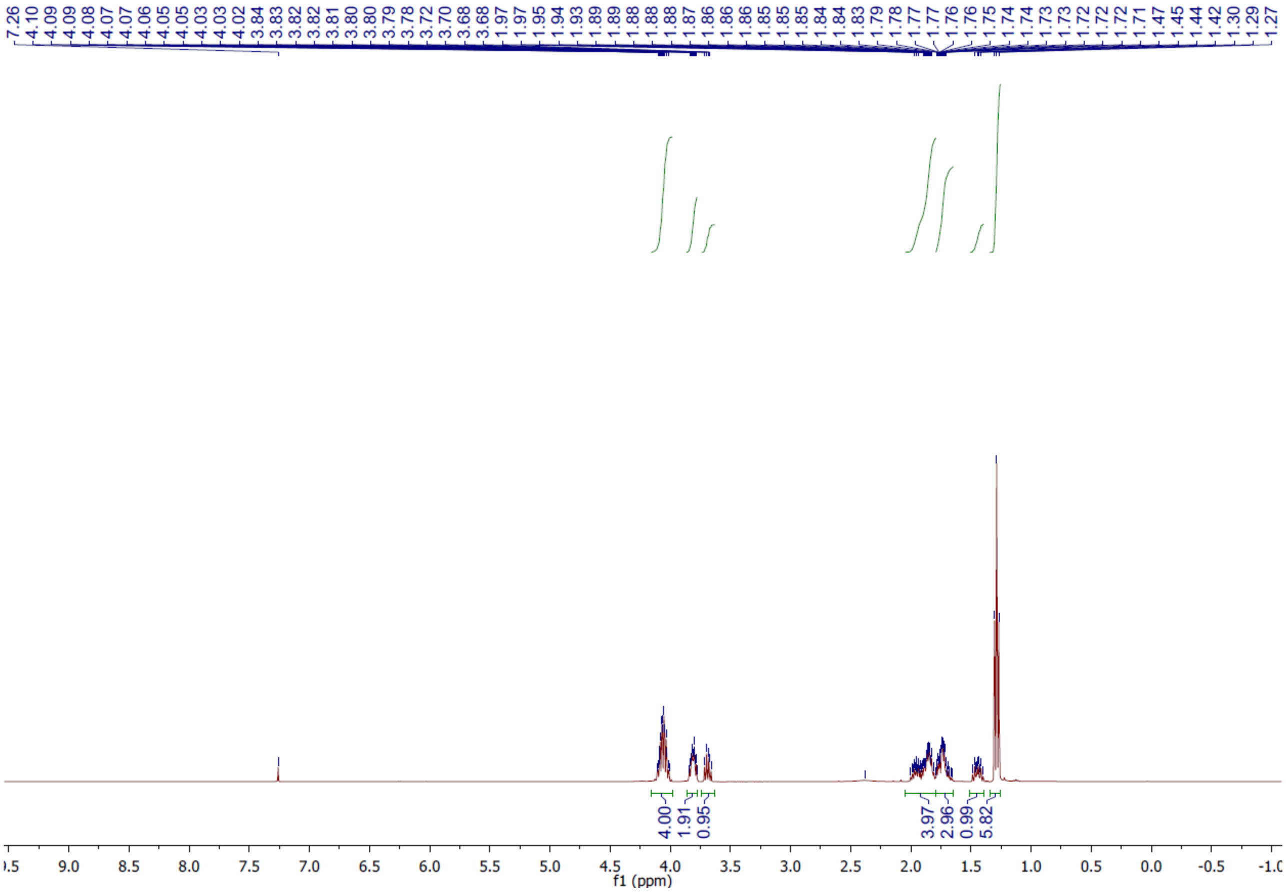
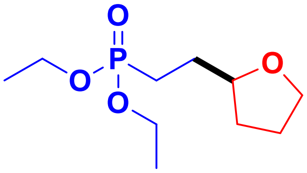


^{13}C-NMR (101 MHz, CDCl$_3$) of **5c**



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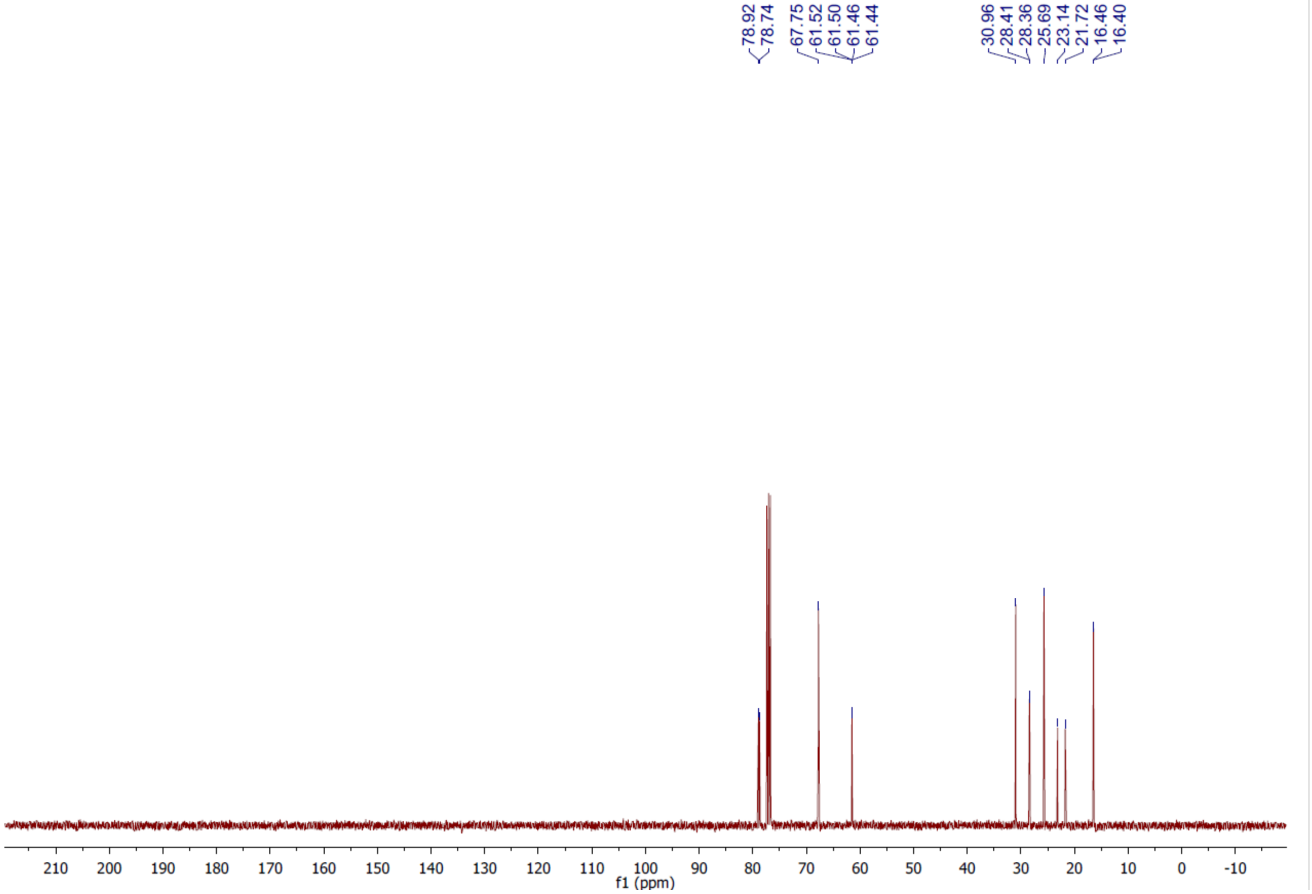
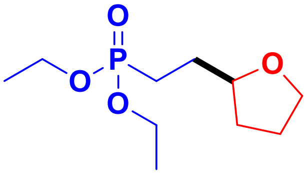


^{31}P-NMR (162 MHz, $CDCl_3$) of **5c**



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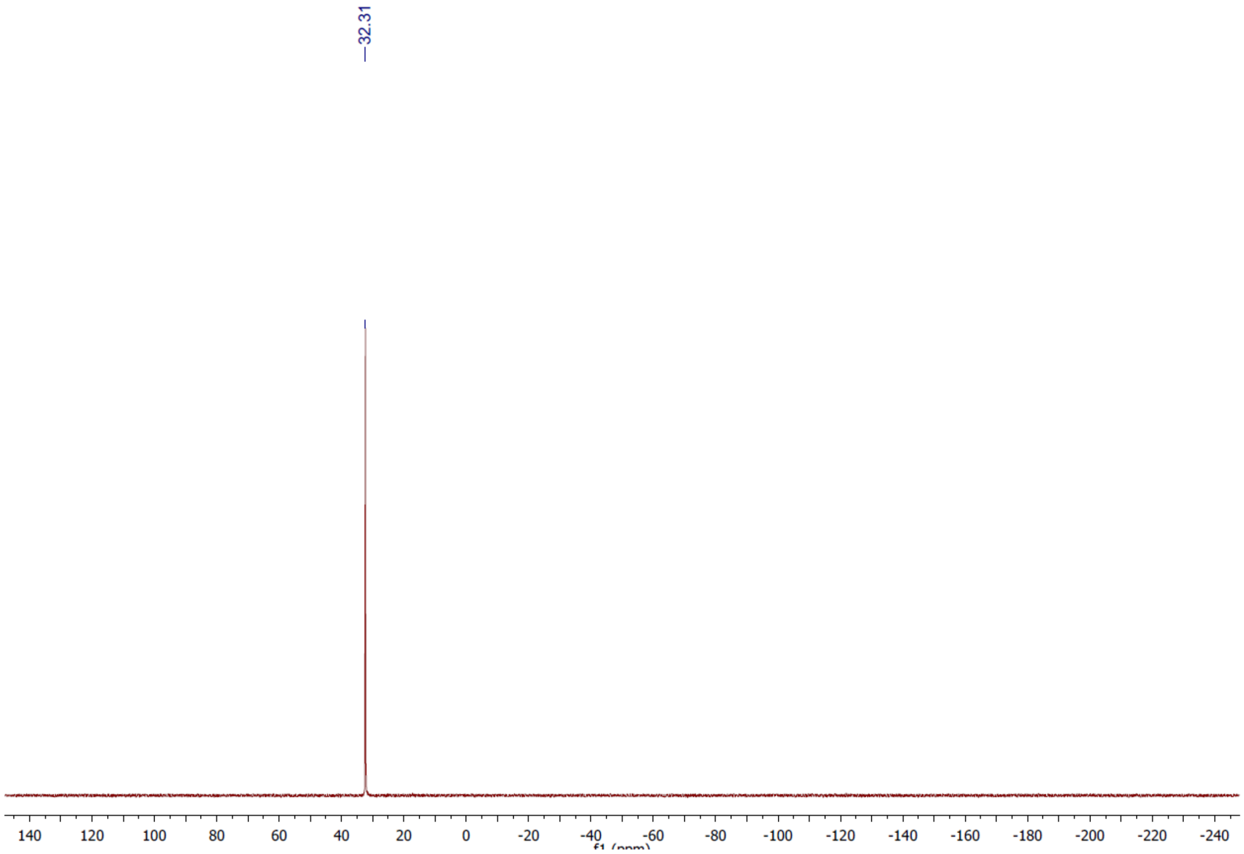
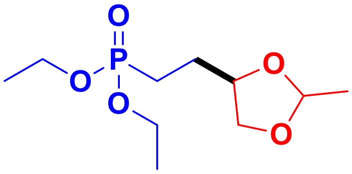
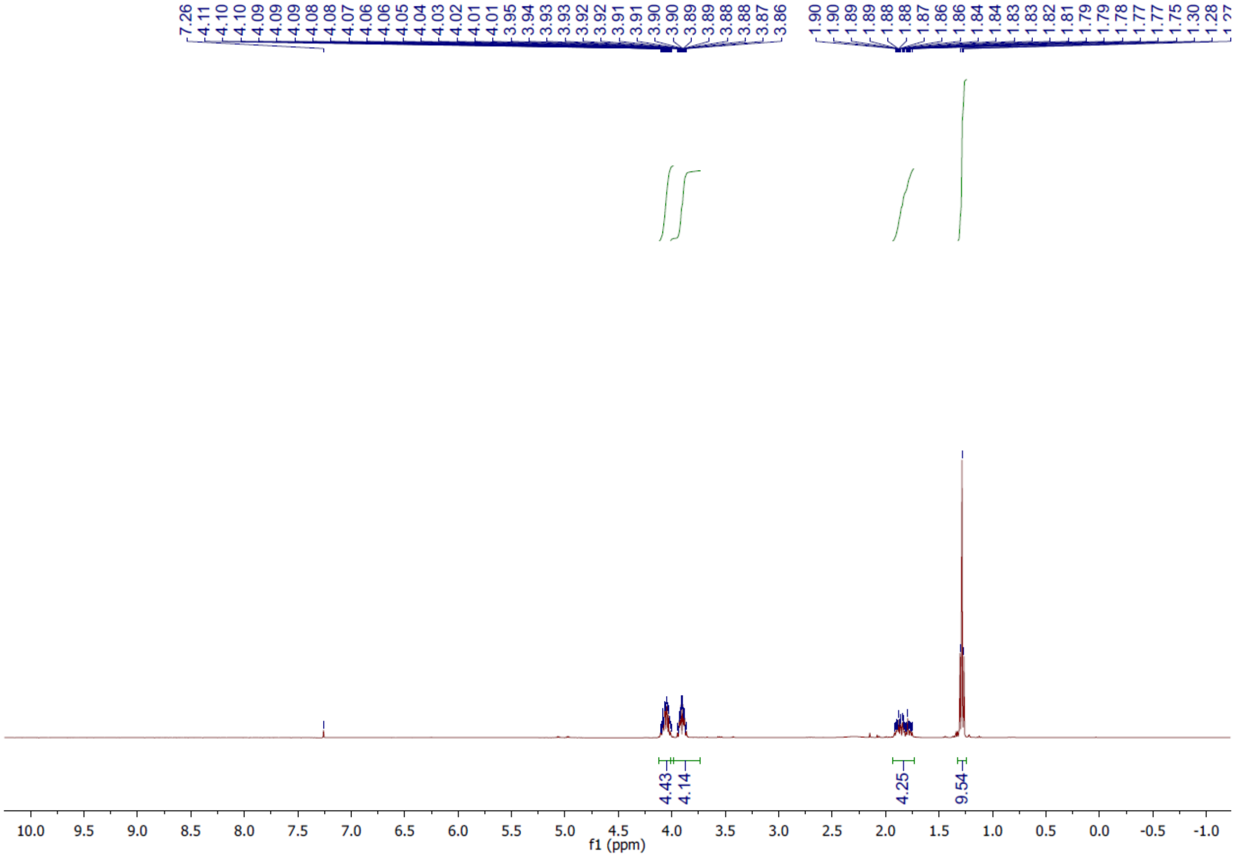


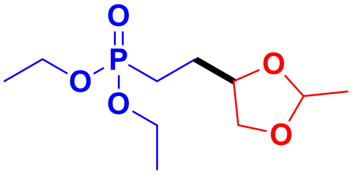
^{1}H-NMR (400 MHz, CDCl$_3$) of **5d**



5d



^{13}C-NMR (101 MHz, CDCl$_3$) of **5d**



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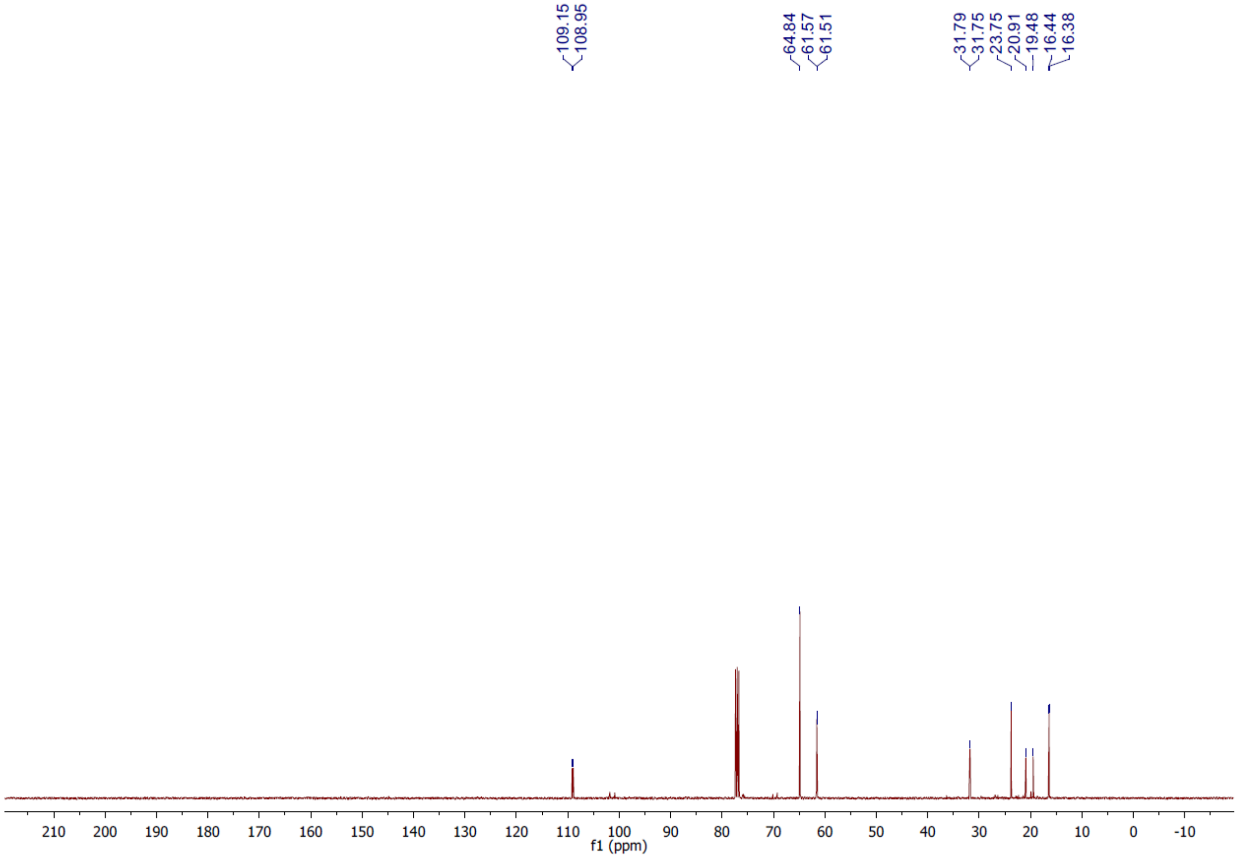
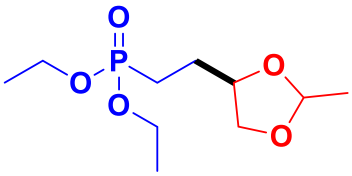


^{31}P-NMR (162 MHz, CDCl$_3$) of **5d**



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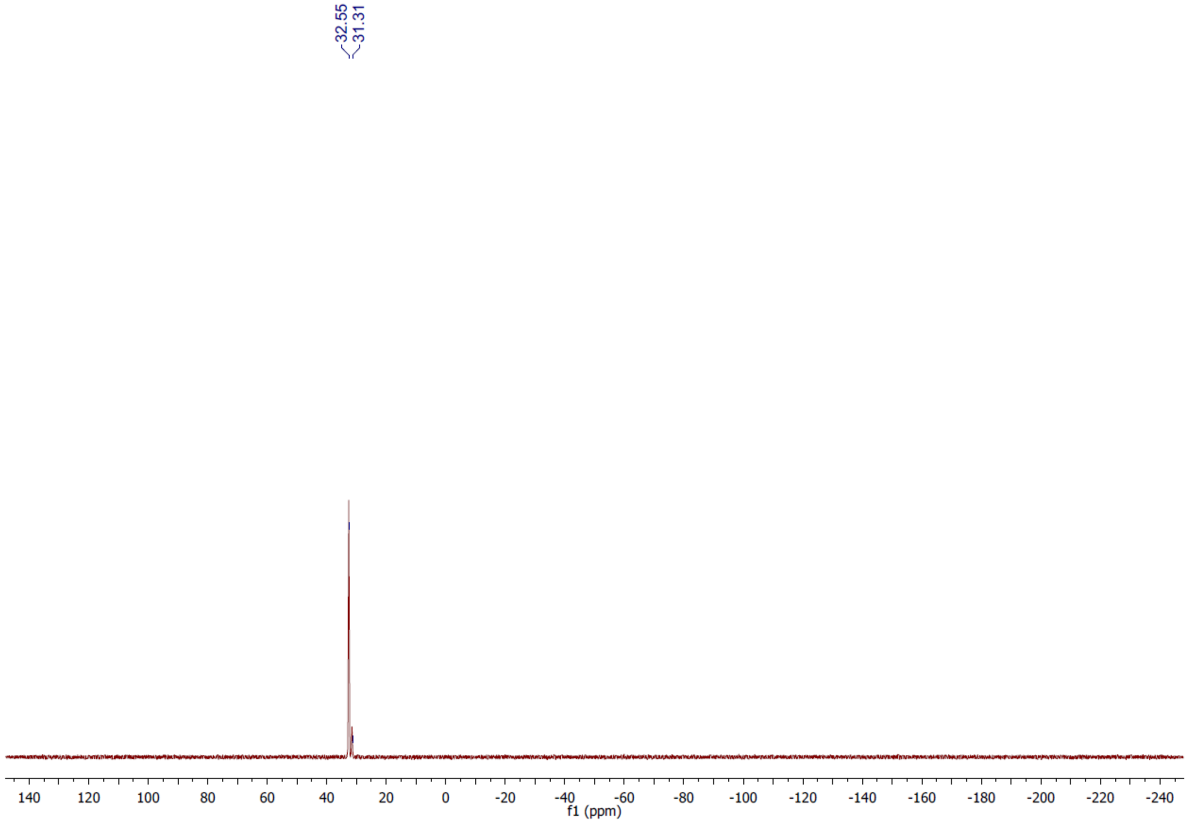
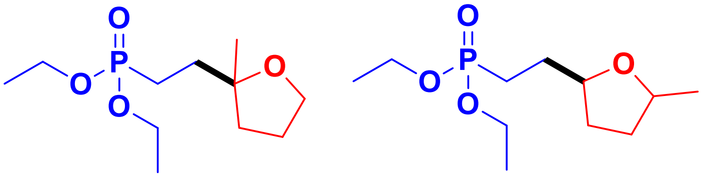
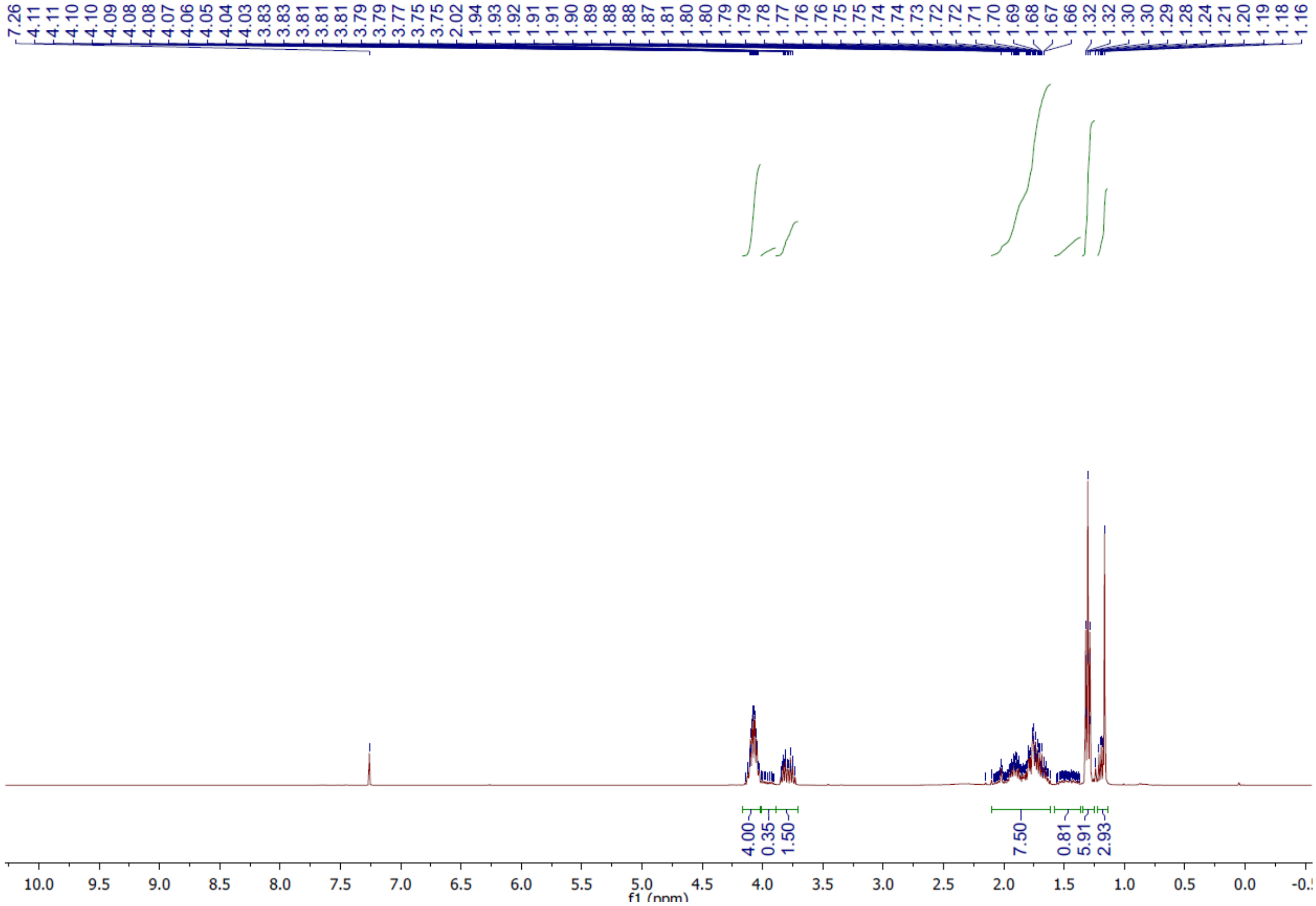


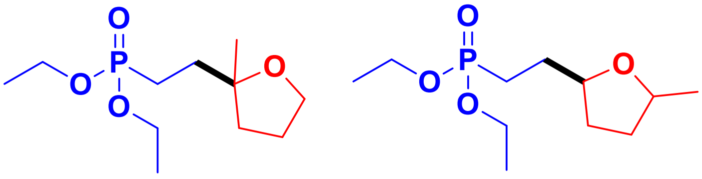
^{1}H-NMR (400 MHz, CDCl$_3$) of **5e**



5e



^{13}C-NMR (101 MHz, CDCl$_3$) of **5e**



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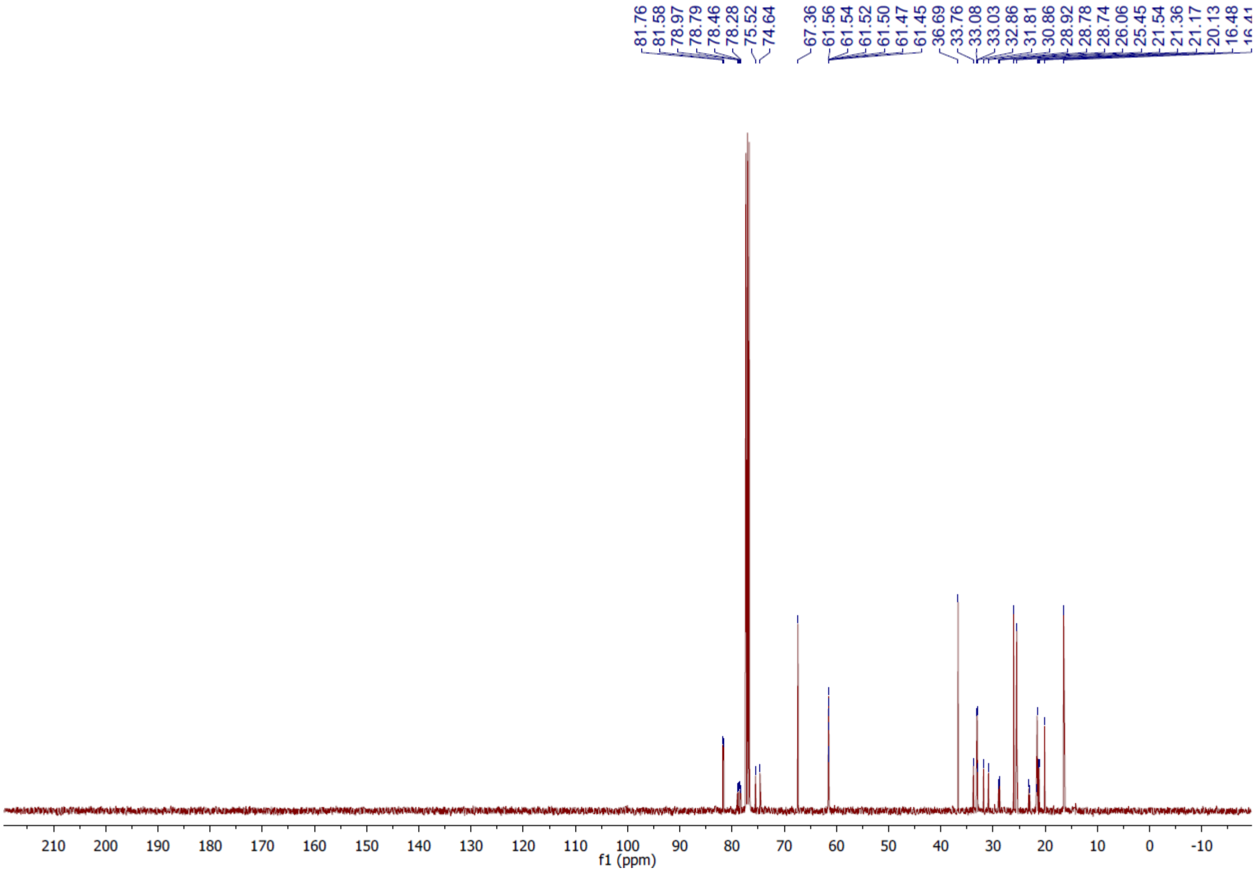
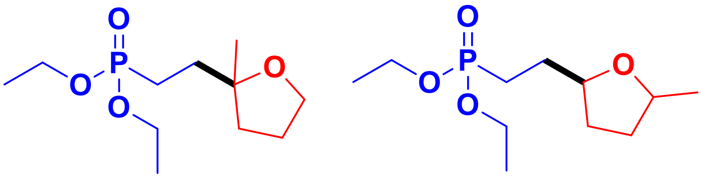


^{31}P-NMR (162 MHz, CDCl$_3$) of **5e**



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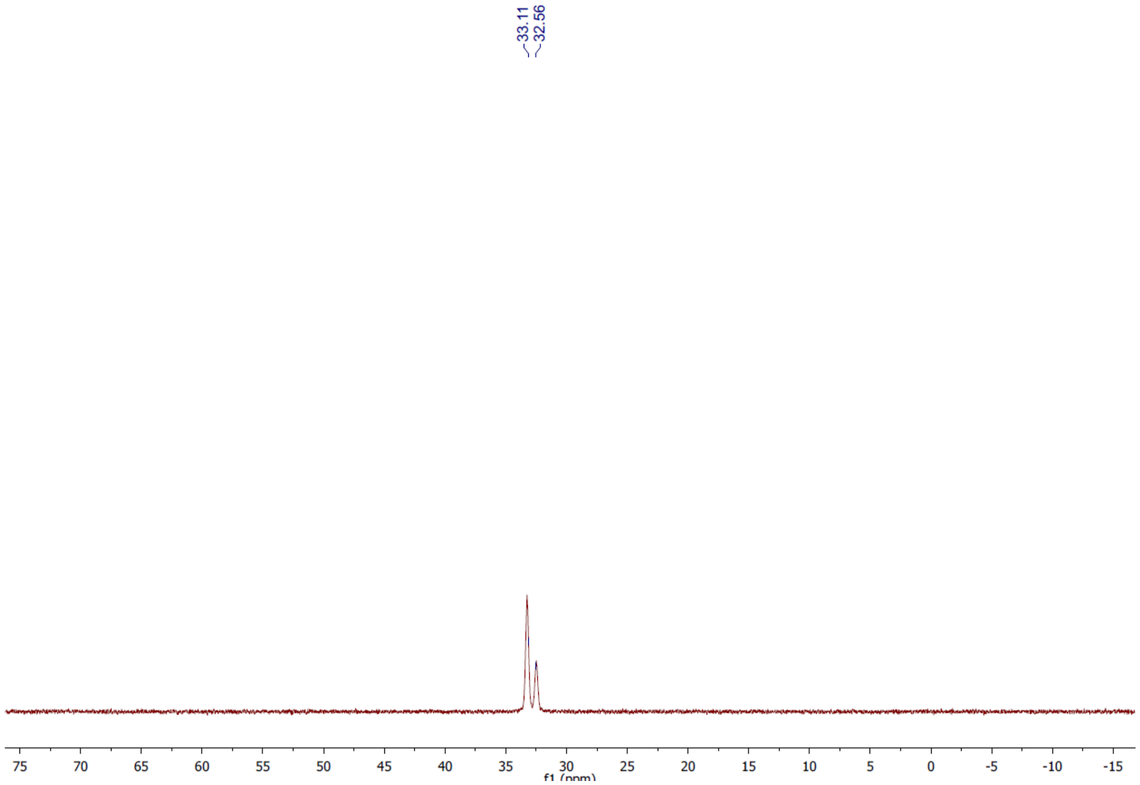
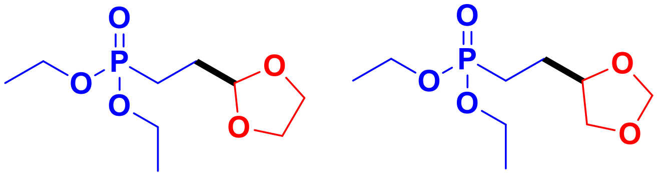


^{1}H-NMR (400 MHz, CDCl$_3$) of **5f**



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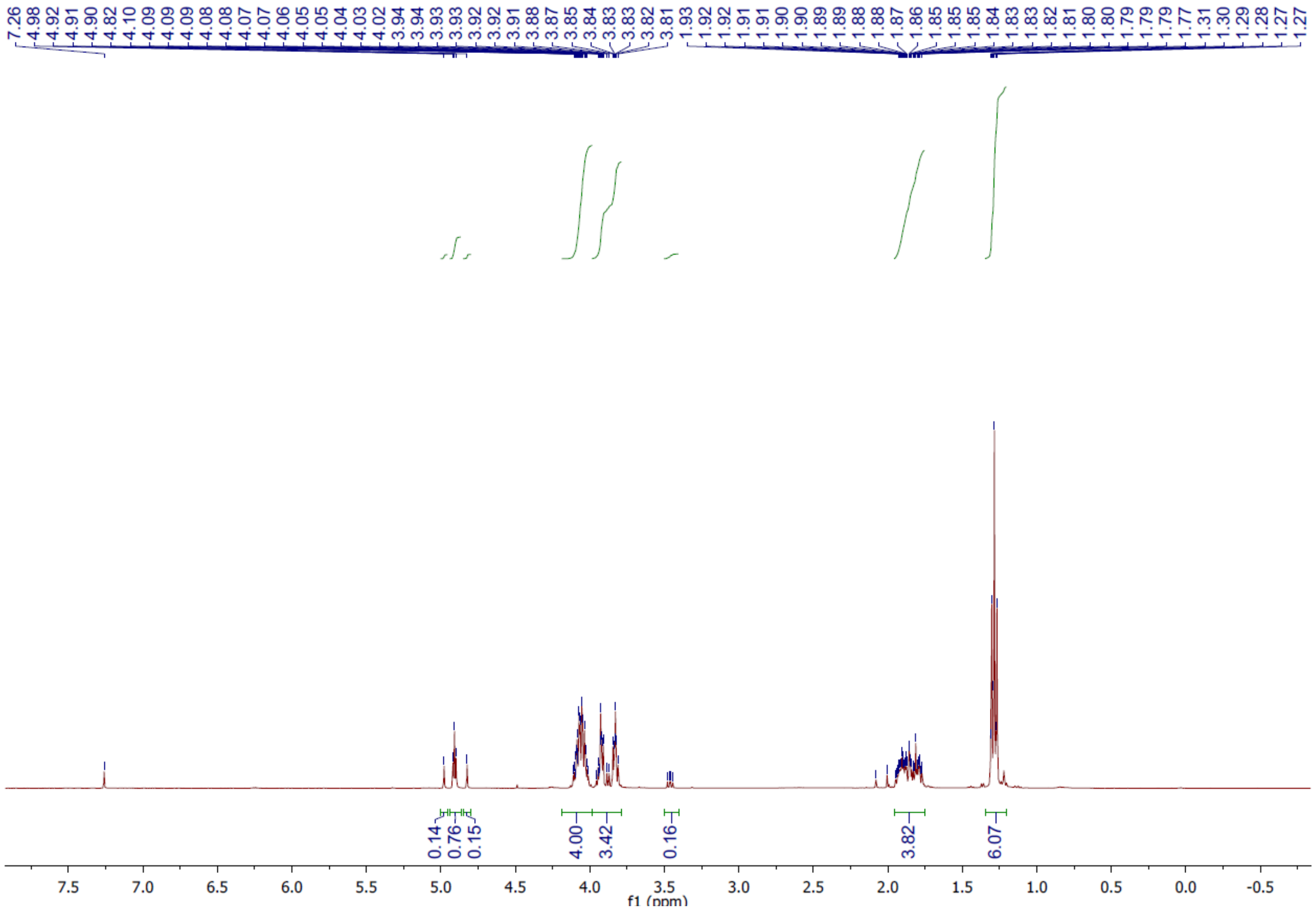
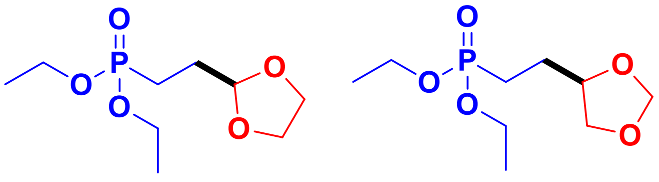


^{13}C-NMR (101 MHz, CDCl$_3$) of **5f**



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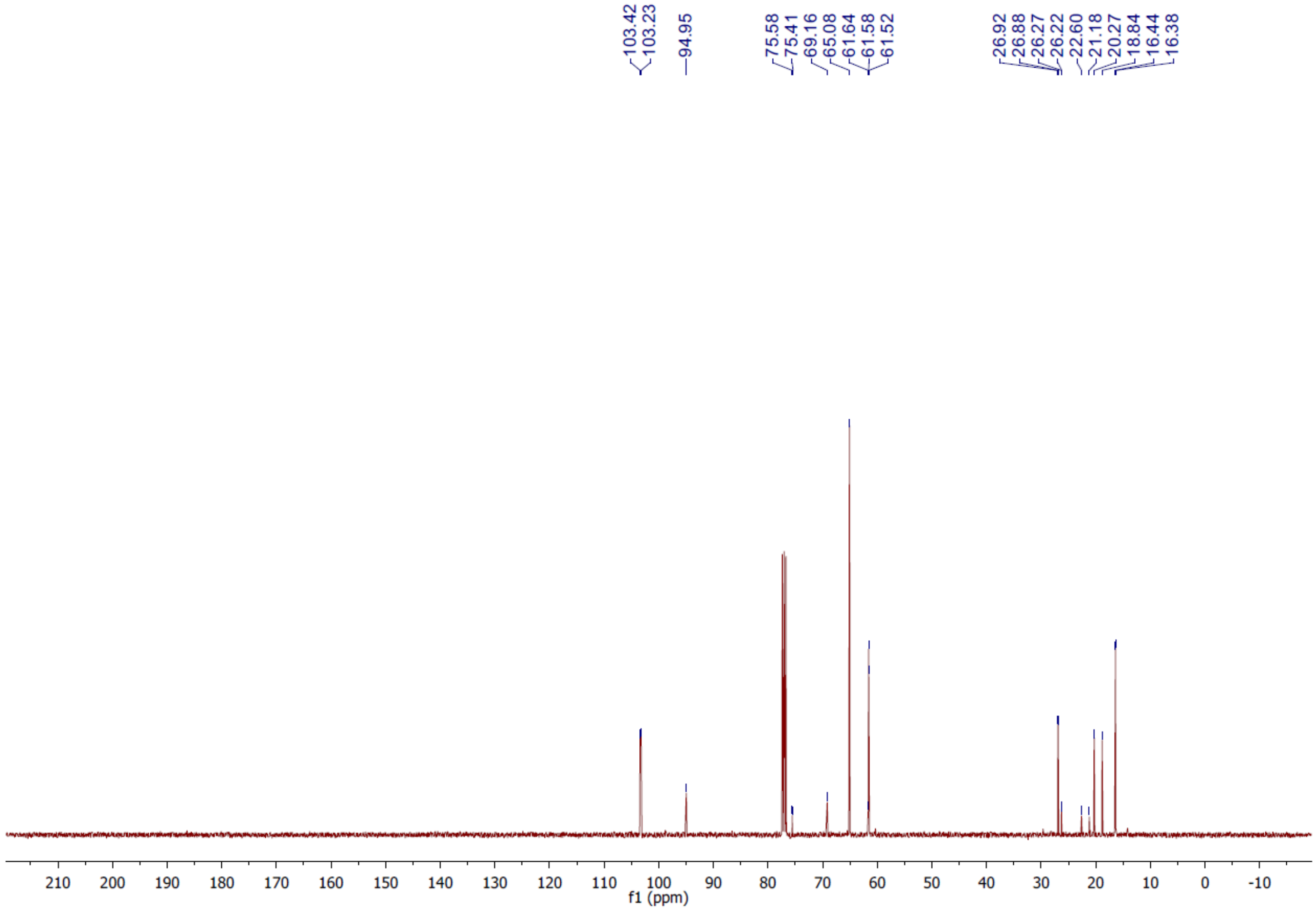
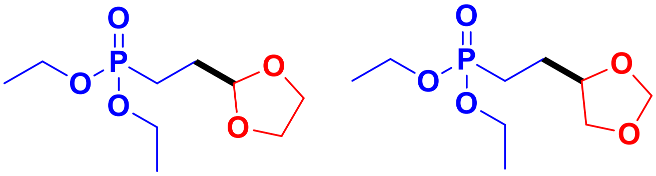


^{31}P-NMR (162 MHz, $CDCl_3$) of **5f**



5f