Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Utilizing a Needle as a Source of Iron in Synergistic Dual Photoredox Catalytic Generation of Alkoxy Radicals

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Table of Contents

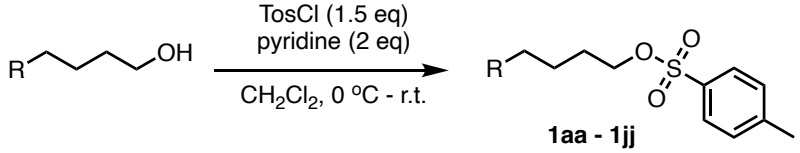
1. General Methods

All chemicals were obtained from commercial sources and used without further purification unless otherwise stated. Needles were obtained from Terumo®, Agani™ needle (VWR). All air sensitive reactions were performed under the nitrogen atmosphere using Schlenk technique. Solvents were dried using solvent purification system (PS-MD-5/7 Inert technology). Reactions were followed by thin-layer chromatography (TLC) using silica gel coated aluminum plates (silica gel 60 F250, Sigma-Aldrich and VWR). TLC plates were visualized by UV light (254 nm) or by staining with $KMnO_4$ or *p*-Anisaldehyde solution. Flash column chromatography was performed on silica gel (40 – 63 μm, VWR) or with Büchi Reveleris® X2 system using Büchi FlashPure EcoFlex silica gel 50 μm cartridges. GC-MS was performed on Agilent 19091S-433 gas chromatograph coupled to Agilent 5977E MSD detector. Separations were performed on HP-5MS Phenyl Methyl Silox of 30 m x 250 μm x 0.25 μm column. HR-MS was performed on Water XEVO-G2 QTOF mass spectrometer using ESI or APCI ionization source. NMR spectra were recorded on Varian NMR 400 spectrometer (or Bruker Avance III HD 700 MHz and 800 MHz spectrometer – NMR center). Chemical shifts (δ) are reported in ppm relative to the residual solvent peak. Splitting patterns are indicated as (s) singlet, (d) doublet, (dd) doublet of doublets, (ddd) doublet of doublet of doublets, (dddd) doublet of doublet of doublet of doublets, (t) triplet, (tt) triplet of triplets, (dt) doublet of triplets), (td) triplet of doublets, (ddt) doublet of doublet of triplets, (q) quartet, (dq) doublet of quartets, (p) pentet, (m) multiplet. Coupling constants (*J*) are reported in Hertz (Hz). Photoredox reactions were performed in EvoluChem™ PhotoRedOx Box by HepatoChem using EvoluChem LED 18 W (P201-18-2, 450 – 455 nm). Enantiomeric excess was determined by chiral HPLC using Chiralpak® AD-H column with hexane/*i*-PrOH as the eluent. ICP-MS was performed using Thermo Scientific ICAP-Q ICP-MS equipped with ESI FAST sample introduction system, operated in KED mode with helium as collision gas.

2. Preparation and characterization of *N*-alkoxythiazolethione precursors

Corresponding tosylates **1aa – 1jj** were prepared according to general method A. Tosylates **1gg, 1kk, 1mm** were used as a crude material without the purification. Corresponding mesylates **1ll, 1nn – 1rr** were prepared following the literature procedure[1] and used as a crude material without the purification.

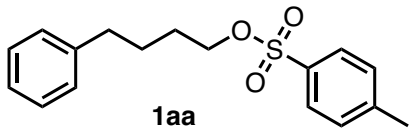
2.1 General method A for the synthesis of tosylates 1aa – 1jj



1aa - 1jj

Corresponding alcohol (1 eq) was dissolved in CH_2Cl_2 (1 ml/mmol) and the solution was cooled to 0 °C. Pyridine (2 eq) was added dropwise and the solution was let to stir for 10 min. TosCl (1.5 eq) was added portionwise into the solution. After the addition, the reaction mixture was let to warm up and stir at room temperature. After the full conversion of alcohol, the reaction mixture was diluted with Et_2O and organic solution was washed with water. *N,N*-dimethylethylenediamine (DMEN, 1 eq in respect to TosCl) was added into the organic solution and the solution was thoroughly washed with water, Brine, dried over Na_2SO_4 and concentrated under the reduced pressure. Final product was purified by flash column chromatography unless otherwise stated.

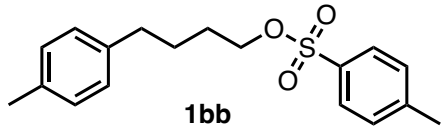
4-phenylbutyl 4-methylbenzenesulfonate (1aa)[2]



1aa

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/CH_2Cl_2, 60/40), isolated as colorless oil in 98% yield (9.8 mmol, 3.0 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.3 – 7.2 (m, 2H), 7.2 – 7.2 (m, 1H), 7.11 (d, *J* = 7.5 Hz, 2H), 4.04 (t, *J* = 6.0 Hz, 2H), 2.56 (t, *J* = 7.2 Hz, 2H), 2.44 (s, 3H), 1.69 – 1.62 (m, 4H).**^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.8, 141.7, 129.9, 128.5, 128.0, 126.0, 70.5, 35.2, 28.5, 27.2, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{18}NOS_2^+$ [(M+H)$^+$] 280.0824, found 280.0825.

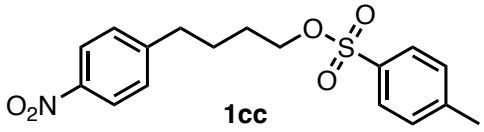
4-(*p*-tolyl)butyl 4-methylbenzenesulfonate (1bb)



1bb

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/EtOAc, 95/5), isolated as colorless oil in 38% yield (1.9 mmol, 0.6 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.8 Hz, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 2H), 4.03 (t, *J* = 6.3 Hz, 2H), 2.52 (t, *J* = 7.5 Hz, 2H), 2.44 (s, 3H), 2.31 (s, 3H), 1.68 – 1.65 (m, 2H), 1.63 – 1.60 (m, 2H).**^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.8, 138.6, 135.5, 133.3, 129.9, 129.2, 128.4, 128.0, 70.6, 34.8, 28.5, 27.3, 21.8, 21.1. **HRMS-ESI (m/z):** exact mass calculated for $C_{18}H_{23}O_3S^+$ [(M+H)$^+$] 319.1368, not detected using either ESI or APCI. **GC-MS(EI) (m/z)**: exact mass calculated for $C_{18}H_{22}O_3S^+$ [M$^+$] 318.1290, found 318.1.

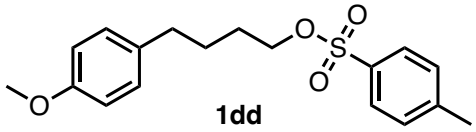
4-(4-nitrophenyl)butyl 4-methylbenzenesulfonate (1cc)



1cc

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 60/40), isolated as yellow oil in 98% yield (2.4 mmol, 0.8 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.15 – 8.11 (m, 2H), 7.78 (dd, *J* = 8.3, 1.8 Hz, 2H), 7.34 (d, *J* = 7.9 Hz, 2H), 7.29 – 7.25 (m, 2H), 4.07 – 4.03 (m, 2H), 2.69 (t, *J* = 6.9 Hz, 2H), 2.45 (s, 3H), 1.71 – 1.67 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 149.5, 146.6, 145.0, 133.2, 130.0, 129.3, 128.0, 123.8, 70.1, 35.1, 28.5, 26.9, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{17}H_{20}NO_5S^+$ [(M+H)$^+$] 350.1062, found 350.1061.

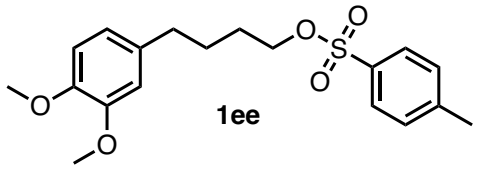
4-(4-methoxyphenyl)butyl 4-methylbenzenesulfonate (1dd)[2]



1dd

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 50/50), isolated as colorless oil in 99% yield (10.4 mmol, 3.5 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.78 (d, *J* = 7.9 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 7.02 (d, *J* = 8.1 Hz, 2H), 6.80 (d, *J* = 8.2 Hz, 2H), 4.04 – 4.02 (m, 2H), 3.78 (t, *J* = 1.2 Hz, 3H), 2.50 (t, *J* = 7.5 Hz, 2H), 2.4 (s, 3H), 1.69 – 1.64 (m, 2H), 1.62 – 1.58 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 157.9, 144.8, 133.8, 133.3, 129.9, 129.4, 128.0, 113.9, 70.6, 55.4, 34.3, 28.4, 27.4, 21.8.

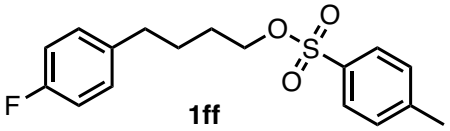
4-(3,4-dimethoxyphenyl)butyl 4-methylbenzenesulfonate (1ee)



1ee

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 40/60), isolated as colorless oil in 71% yield (4.5 mmol, 1.7 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 8.6 Hz, 1H), 6.65 – 6.64 (m, 2H), 4.03 (t, *J* = 6.2 Hz, 2H), 3.85 (d, *J* = 6.3 Hz, 6H), 2.52 (t, *J* = 7.4 Hz, 2H), 2.44 (s, 3H), 1.69 – 1.61 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 148.9, 147.4, 144.8, 134.4, 133.3, 129.9, 128.0, 120.3, 111.8, 111.3, 70.6, 56.1, 55.9, 34.8, 28.5, 27.4, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{19}H_{25}O_5S^+$ [$(M+H)^+$] 365.1423, found 365.1425.

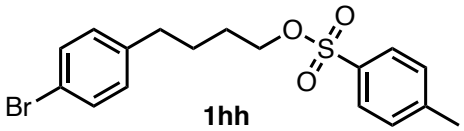
4-(4-fluorophenyl)butyl 4-methylbenzenesulfonate (1ff)



1ff

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 50/50), isolated as colorless oil in 30% yield (3.2 mmol, 1.0 g).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.73 (m, 2H), 7.35 – 7.31 (m, 2H), 7.08 – 7.03 (m, 2H), 6.97 – 6.91 (m, 2H), 4.04 – 4.01 (m, 2H), 2.58 – 2.49 (m, 2H), 2.44 (d, *J* = 0.8 Hz, 3H), 1.70 – 1.57 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 162.0, 160.8, 144.9, 137.3, 133.3, 129.9, 129.8, 129.8, 128.0, 115.3, 115.2, 70.4, 34.4, 28.4, 27.4, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{17}H_{20}FO_3S^+$ [$(M+H)^+$] 323.1117, not detected using either ESI or APCI. **GC-MS(EI) (m/z)**: exact mass calculated for $C_{17}H_{19}FO_3S^+$ [M^+] 322.1039, found 322.1.

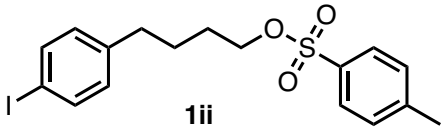
4-(4-bromophenyl)butyl 4-methylbenzenesulfonate (1hh)



1hh

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 60/40), isolated as colorless oil in 31% yield (1.0 mmol, 0.4 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.98 (d, *J* = 8.3 Hz, 2H), 4.03 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.67 – 1.60 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.9, 140.6, 133.3, 131.6, 130.3, 129.9, 128.0, 119.8, 70.4, 34.6, 28.4, 27.1, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{17}H_{20}BrO_3S^+$ [$(M+H)^+$] 383.0317, not detected using either ESI or APCI.

4-(4-iodophenyl)butyl 4-methylbenzenesulfonate (1ii)

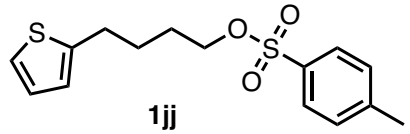


1ii

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 50/50), isolated as colorless oil in 69% yield (0.9 mmol, 0.5 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 7.9 Hz, 2H), 4.03 (t, *J* = 6.0 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H), 2.45 (s, 3H), 1.67 – 1.59 (m, 4H).

^{13}C NMR (201 MHz, $CDCl_3$) δ 144.9, 141.3, 137.6, 133.3, 130.6, 129.9, 128.0, 91.1, 70.4, 34.7, 28.4, 27.1, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{17}H_{20}IO_3S^+$ [(M+H)$^+$] 431.0178, not detected using either ESI or APCI.

4-(thiophen-2-yl)butyl 4-methylbenzenesulfonate (1jj)

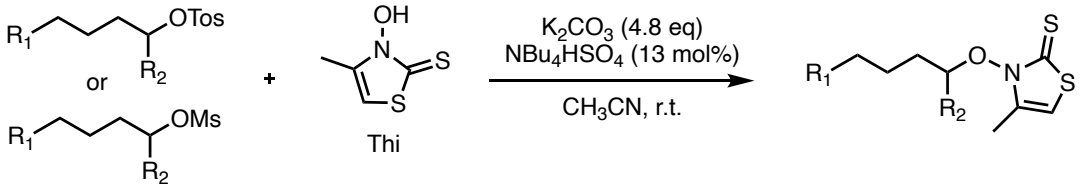


1jj

Prepared according to general method A, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 70/30), isolated as colorless oil in 72% yield (4.2 mmol, 1.3 g).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.77 (m, 2H), 7.36 – 7.2 (m, 2H), 7.10 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.90 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.73 (dq, *J* = 3.3, 1.0 Hz, 1H), 4.06 – 4.03 (m, 2H), 2.80 – 2.76 (m, 3H), 2.45 (s, 3H), 1.72 – 1.68 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.9, 144.4, 133.3, 130.0, 128.0, 126.9, 124.5, 123.3, 70.3, 29.2, 28.3, 27.6, 21.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{15}H_{19}O_3S_2^+$ [(M+H)$^+$] 311.0776, found 311.0781.

3. Preparation and characterization of *N*-alkoxythiazolethiones

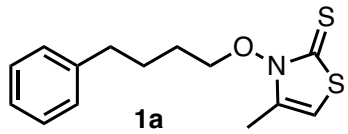
3.1 General method B for the synthesis of *N*-alkoxythiazolethiones 1a – 1r



1aa - 1rr **1a - 1r**

Cyclic thiohydroxamic acid (Thi)[3] (1.3 eq) was dissolved in CH_3CN (0.4 ml/mmol). K_2CO_3 (4.8 eq) and NBu_4HSO_4 (13 mol %) were added to the solution and resulting slurry was let to stir for 30 min. The corresponding sulfone (1 eq) was added, and the reaction was let to stir at room temperature for 24 – 48 h. Resulting viscous reaction mixture was diluted with water (30 ml) and extracted with CH_2Cl_2 (4 x 25 ml). Combined organic extracts were washed with 2 M NaOH, Brine, dried over Na_2SO_4 and concentrated under the reduced pressure. Final *N*-alkoxythiazolethione was purified by flash column chromatography.

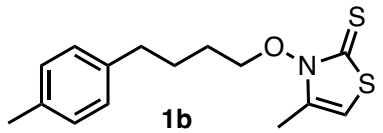
***N*-alkoxythiazolethione (1a)**



1a

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 80/20), isolated as yellow oil in 67% yield (4.3 mmol, 1.2 g).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 2H), 7.22 – 7.17 (m, 3H), 6.15 (q, *J* = 1.2 Hz, 1H), 4.43 – 4.40 (m, 2H), 2.73 – 2.69 (m, 2H), 2.25 (d, *J* = 1.2 Hz, 3H), 1.87 – 1.84 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 141.9, 137.8, 128.6, 128.5, 126.0, 102.9, 76.1, 35.7, 27.7, 27.6, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{18}NOS_2^+$ [(M+H)$^+$] 280.0830, found 280.0831.

***N*-alkoxythiazolethione (1b)**

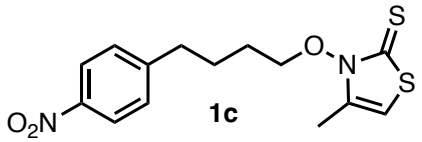


1b

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 85/15), isolated as orange oil in 58% yield (1.0 mmol, 0.3 g).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.09 (dd, *J* = 7.9, 5.8 Hz, 4H), 6.14 (q, *J* = 1.4 Hz, 1H), 4.41 (t, *J* = 6.1 Hz, 2H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.32 (s, 3H), 2.25 (t, *J* = 1.5 Hz, 3H), 1.87 – 1.80 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 138.9, 137.84, 135.5, 129.2, 128.5, 102.8, 76.2, 35.2, 27.8, 27.6, 21.1, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{15}H_{20}NOS_2^+$ [(M+H)$^+$] 294.0986, found 294.0987,

***N*-alkoxythiazolethione (1c)**

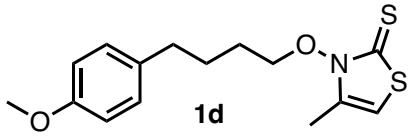


1c

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 30/70), isolated as orange solid in 56% yield (0.7 mmol, 0.3 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 – 8.13 (m, 2H), 7.38 – 7.35 (m, 2H), 6.17 (q, *J* = 1.3 Hz, 1H), 4.43 (t, *J* = 5.9 Hz, 2H), 2.85 (t, *J* = 7.3 Hz, 2H), 2.26 (d, *J* = 1.3 Hz, 3H), 1.97 – 1.83 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.6, 149.9, 146.6, 137.7, 129.4, 123.9, 103.0, 75.6, 35.5, 27.5, 27.4, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{17}N_2O_3S_2^+$ [(M+H)$^+$] 325.0681, found 325.0683. **Mp:** 114 – 115 °C.

***N*-alkoxythiazolethione (1d)**

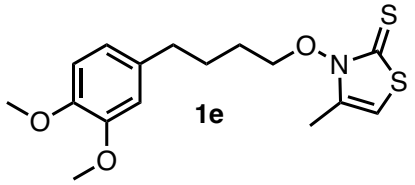


1d

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 40/60), isolated as brown oil in 63% yield (1.0 mmol, 0.3 g).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.2 Hz, 2H), 6.83 (d, *J* = 8.3 Hz, 2H), 6.14 (s, 1H), 4.41 (t, *J* = 6.2 Hz, 2H), 3.79 (s, 3H), 2.65 (t, *J* = 7.3 Hz, 2H), 2.25 (d, *J* = 1.5 Hz, 3H), 1.86 – 1.79 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 158.0, 137.8, 134.0, 129.5, 113.9, 102.8, 76.1, 55.4, 34.8, 27.9, 27.5, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{15}H_{20}NO_2S_2^+$ [(M+H)$^+$] 310.0935, found 310.0947.

***N*-alkoxythiazolethione (1e)**

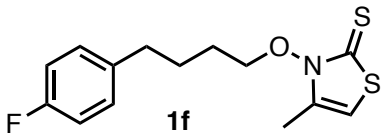


1e

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 30/70), isolated as brown oil in 64% yield (0.9 mmol, 0.3 g).

^{1}H NMR (800 MHz, $CDCl_3$) δ 6.80 (d, *J* = 8.1 Hz, 1H), 6.73 (d, *J* = 7.1 Hz, 2H), 6.15 (s, 1H), 4.42 (t, *J* = 6.0 Hz, 2H), 3.87 (d, *J* = 15.4 Hz, 6H), 2.66 (t, *J* = 7.1 Hz, 2H), 2.26 (s, 3H), 1.88 – 1.82 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.6, 149.0, 147.4, 137.8, 134.6, 120.4, 111.9, 111.4, 102.9, 76.1, 56.1, 56.0, 35.3, 27.9, 27.6, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{16}H_{22}NO_3S_2^+$ [(M+H)$^+$] 340.1041, found 340.1048.

***N*-alkoxythiazolethione (1f)**

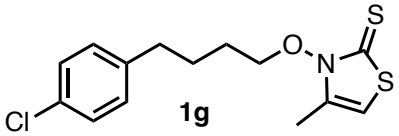


1f

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 80/20), isolated as brown oil in 78% yield (1.4 mmol, 0.3 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 – 7.12 (m, 2H), 6.99 – 6.94 (m, 2H), 6.16 – 6.15 (m, 1H), 4.42 – 4.40 (m, 2H), 2.70 – 2.66 (m, 2H), 2.26 (d, *J* = 1.3 Hz, 3H), 1.86 – 1.79 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 160.1, 161.8, 137.8, 137.5, 129.9, 129.9, 115.3, 115.2, 102.9, 76.0, 34.8, 27.8, 27.5, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{17}FNOS_2^+$ [(M+H)$^+$] 298.0736, found 298.0732.

***N*-alkoxythiazolethione (1g)**

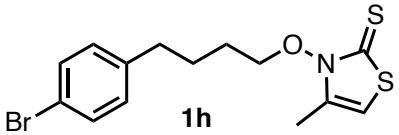


1g

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 50/50), isolated as brown oil in 18% yield (0.3 mmol, 85 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.23 (m, 2H), 7.14 – 7.11 (m, 2H), 6.2 (q, *J* = 1.2 Hz, 1H), 4.42 – 4.39 (m, 2H), 2.70 – 2.67 (m, 2H), 2.26 (d, *J* = 1.3 Hz, 3H), 1.87 – 1.80 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 140.4, 137.8, 131.7, 129.9, 128.6, 102.9, 75.9, 34.9, 27.6, 27.5, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{17}ClNOS_2^+$ [(M+H)$^+$] 314.0440, found 314.0444.

***N*-alkoxythiazolethione (1h)**

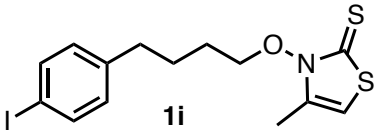


1h

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 80/20), isolated as brown oil in 64% yield (0.6 mmol, 0.2 g).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 2H), 7.09 – 7.06 (m, 2H), 6.15 (q, *J* = 1.3 Hz, 1H), 4.42 – 4.39 (m, 2H), 2.71 – 2.63 (m, 2H), 2.25 (d, *J* = 1.2 Hz, 3H), 1.85 – 1.82 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.6, 140.9, 137.8, 131.6, 130.4, 119.8, 102.9, 75.9, 35.0, 27.5, 27.5, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{17}BrNOS_2^+$ [(M+H)$^+$] 357.9935, found 357.9949.

***N*-alkoxythiazolethione (1i)**

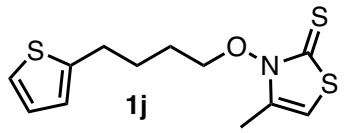


1i

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 80/20), isolated as brown oil in 67% yield (0.7 mmol, 0.3 g).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.61 – 7.59 (m, 2H), 6.96 – 6.94 (m, 2H), 6.15 (q, *J* = 1.3 Hz, 1H), 4.4 1 (s, 2H), 2.67 – 2.65 (m, 2H), 2.25 (d, *J* = 1.3 Hz, 3H), 1.86 – 1.81 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 141.6, 137.8, 137.6, 130.7, 102.9, 91.1, 75.9, 35.1, 27.5, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{17}INOS_2^+$ [(M+H)$^+$] 405.9796, found 405.9789.

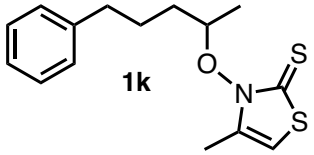
***N*-alkoxythiazolethione (1j)**



1j

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 50/50), isolated as yellow oil in 65% yield (1.1 mmol, 0.3 g).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (dd, *J* = 5.1, 1.2 Hz, 1H), 6.85 (dd, *J* = 5.1, 3.4 Hz, 1H), 6.75 (dq, *J* = 3.3, 1.0 Hz, 1H), 6.14 (q, *J* = 1.2 Hz, 1H), 4.34 (t, *J* = 5.9 Hz, 2H), 2.91 – 2.82 (m, 2H), 2.20 (d, *J* = 1.2 Hz, 3H), 1.90 – 1.75 (m, 4H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 179.7, 144.2, 137.5, 126.5, 124.1, 122.9, 122.9, 102.9, 102.6, 75.4, 29.2, 27.6, 26.9, 13.3, 13.1. **HRMS-ESI (m/z):** exact mass calculated for $C_{12}H_{16}NOS_3^+$ [(M+H)$^+$] 286.0394, not detected using either ESI or APCI.

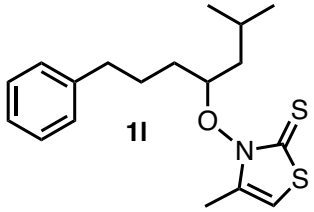
***N*-alkoxythiazolethione (1k)**



1k

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 95/5), isolated as brown oil in 32% yield (0.7 mmol, 0.2 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (d, *J* = 7.4 Hz, 3H), 6.15 (s, 1H), 5.47 (h, *J* = 6.5 Hz, 1H), 2.69 (t, *J* = 7.2 Hz, 2H), 2.20 (d, *J* = 1.5 Hz, 3H), 1.84 – 1.78 (m, 3H), 1.67 – 1.62 (m, 1H), 1.24 (d, *J* = 6.4 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 181.0, 142.1, 139.2, 128.6, 128.5, 126.0, 102.9, 81.3, 35.9, 34.4, 27.1, 18.4, 14.2. **HRMS-ESI (m/z):** exact mass calculated for $C_{15}H_{20}NOS_2^+$ [(M+H)$^+$] 294.0986, found 294.0982.

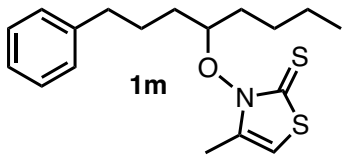
***N*-alkoxythiazolethione (1l)**



1l

Prepared according to general method B, purified by flash column chromatography (silica gel, cyclohexane/ Et_2O, 97/3), isolated as yellow oil in 62% yield (1.2 mmol, 0.4 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.28 – 7.26 (m, 2H), 7.19 – 7.17 (m, 3H), 6.14 (s, 1H), 5.53 (p, *J* = 6.2 Hz, 1H), 2.68 – 2.61 (m, 2H), 2.17 (s, 3H), 1.82 – 1.77 (m, 2H), 1.75 – 1.70 (m, 2H), 1.66 – 1.59 (m, 1H), 1.46 (t, *J* = 6.8 Hz, 2H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 181.6, 142.0, 139.4, 128.6, 128.5, 126.0, 102.9, 83.0, 41.9, 35.9, 32.3, 26.9, 24.0, 23.4, 22.9, 14.3. **HRMS-ESI (m/z):** exact mass calculated for $C_{18}H_{26}NOS_2^+$ [(M+H)$^+$] 336.1456, found 336.1462.

***N*-alkoxythiazolethione (1m)**

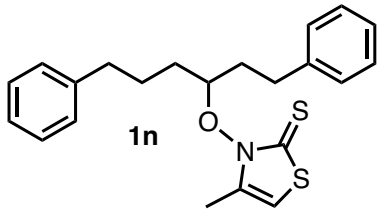


1m

Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 95/5), isolated as yellow oil in 21% yield (0.3 mmol, 0.1 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.27 (t, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.4 Hz, 3H), 6.14 (s, 1H), 5.39 (p, *J* = 6.1 Hz, 1H), 2.70 – 2.61 (m, 2H), 2.18 (s, 3H), 1.84 – 1.74 (m, 2H), 1.73 – 1.69 (m, 1H), 1.65 – 1.57 (m, 3H),

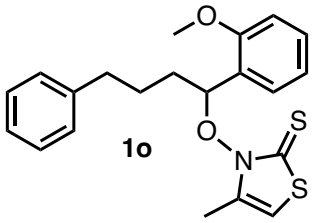
1.38 – 1.29 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.9, 142.1, 139.4, 128.6, 128.5, 126.0, 102.9, 84.6, 35.9, 31.9, 31.8, 27.2, 26.8, 23.0, 14.2, 14.1. **HRMS-ESI (m/z):** exact mass calculated for $C_{18}H_{26}NOS_2^+$ [(M+H)$^+$] 336.1456, found 336.1471.

***N*-alkoxythiazolethione (1n)**



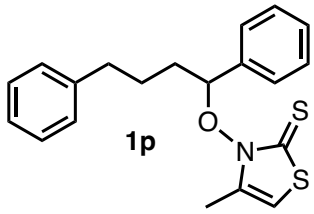
Prepared according to general method B, purified by flash column chromatography (silica gel, cyclohexane/ Et_2O, 97/3), isolated as yellow oil in 38% yield (0.5 mmol, 0.2 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.28 (td, *J* = 7.6, 1.8 Hz, 4H), 7.20 – 7.18 (m, 2H), 7.16 (dt, *J* = 7.6, 1.7 Hz, 4H), 6.14 (q, *J* = 1.2 Hz, 1H), 5.45 (p, *J* = 6.0 Hz, 1H), 2.77 – 2.73 (m, 2H), 2.67 – 2.63 (m, 2H), 2.17 (d, *J* = 1.3 Hz, 3H), 2.01 – 1.87 (m, 2H), 1.83 – 1.71 (m, 3H), 1.70 – 1.66 (m, 1H) **^{13}C NMR (201 MHz, $CDCl_3$)** δ 181.0, 141.9, 141.5, 139.2, 128.6, 128.6, 128.5, 128.4, 126.2, 126.1, 103.0, 84.3, 35.9, 34.2, 31.7, 31.5, 26.8, 14.3. **HRMS-ESI (m/z):** exact mass calculated for $C_{22}H_{26}NOS_2^+$ [(M+H)$^+$] 384.1456, found 384.1455.

***N*-alkoxythiazolethione (1o):**



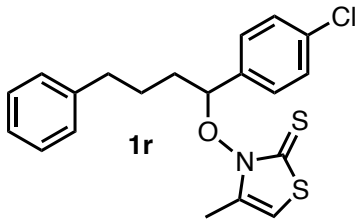
Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 95/5), isolated as yellow oil in 24% yield (0.4 mmol, 0.1 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.1 Hz, 1H), 7.32 (t, *J* = 7.8 Hz, 1H), 7.26 – 7.23 (m, 2H), 7.16 (d, *J* = 7.6 Hz, 3H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.59 (s, 1H), 5.87 (s, 1H), 3.65 (s, 1H), 2.75 – 2.72 (m, 1H), 2.69 – 2.66 (m, 1H), 2.49 – 2.44 (m, 1H), 2.13 – 2.06 (m, 1H), 1.86 – 1.81 (m, 1H), 1.73 – 1.68 (m, 1H), 1.49 (s, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 181.0, 158.8, 142.3, 139.5, 130.8, 128.7, 128.4, 125.8, 120.9, 110.9, 101.5, 55.6, 35.8, 31.4, 27.6, 13.3. **HRMS-ESI (m/z):** exact mass calculated for $C_{21}H_{24}NO_2S_2^+$ [(M+H)$^+$] 386.1248, found 386.1255.

***N*-alkoxythiazolethione (1p)**



Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 90/10), isolated as brown oil in 33% yield (0.5 mmol, 0.2 g).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 1H), 7.29 – 7.24 (m, 4H), 7.20 (t, *J* = 7.5 Hz, 2H), 7.11 (dd, *J* = 7.7, 5.9 Hz, 3H), 6.20 (t, *J* = 7.4 Hz, 1H), 5.82 (s, 1H), 2.71 – 2.61 (m, 2H), 2.40 – 2.33 (m, 1H), 2.06 – 1.99 (m, 1H), 1.81 – 1.74 (m, 1H), 1.68 – 1.61 (m, 1H), 1.46 (s, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 142.0, 139.4, 136.9, 129.8, 129.2, 128.8, 128.6, 128.4, 125.9, 102.0, 85.8, 35.7, 31.5, 27.4, 13.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{20}H_{22}NOS_2^+$ [(M+H)$^+$] 356.1142, found 356.1143.

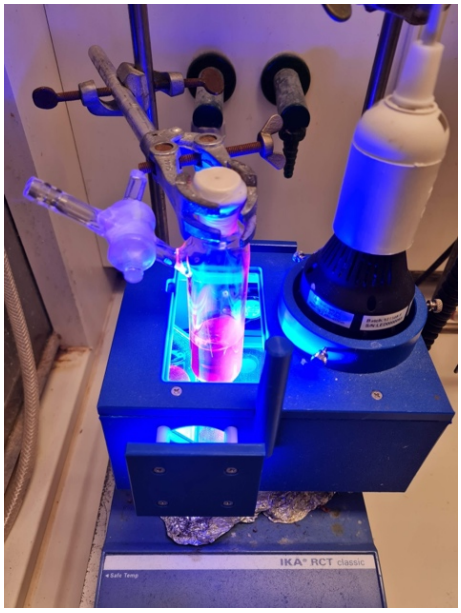
***N*-alkoxythiazolethione (1r)**

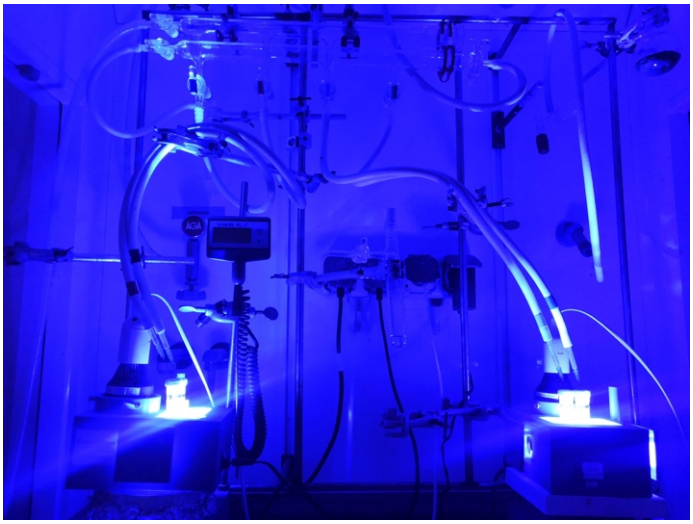


Prepared according to general method B, purified by flash column chromatography (silica gel, hexane/ EtOAc, 90/10), isolated as yellow oil in 60% yield (0.8 mmol, 0.3 g).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.24 (m, 6H), 7.19 – 7.13 (m, 3H), 6.27 (dd, *J* = 8.2, 6.5 Hz, 1H), 5.91 (q, *J* = 1.3 Hz, 1H), 2.75 – 2.63 (m, 2H), 2.42 – 2.33 (m, 1H), 2.05 – 1.96 (m, 1H), 1.83 – 1.75 (m, 1H), 1.70 – 1.59 (m, 1H), 1.59 (d, *J* = 1.3 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 180.5, 141.8, 139.1, 135.8, 135.5, 130.5, 129.1, 128.6, 128.5, 126.0, 102.4, 84.7, 35.6, 31.6, 27.3, 13.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{20}H_{21}ClNOS_2^+$ [(M+H)$^+$] 390.0753, found 390.0760.

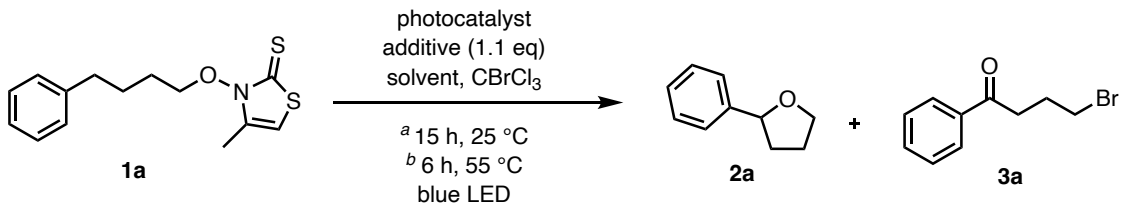
4. Photoredox catalytic studies

Photoredox reactions were performed in EvoluChem™ PhotoRedOx Box by HepatoChem using EvoluChem LED 18 W (P201-18-2, 450 – 455 nm). Fans were removed from the set-up, and the reaction temperature 55°C was reached with the heat produced by the lamp (see below).
Reactions that followed General photoredox method D were performed under the continuous positive pressure of N_2 delivered into the capped vial via a metallic needle, where the needle (4.5 cm) was fully inserted into the headspace of the vial (vial: 8 cm, headspace: 6.5 cm).





4.1 Photoredox optimization studies

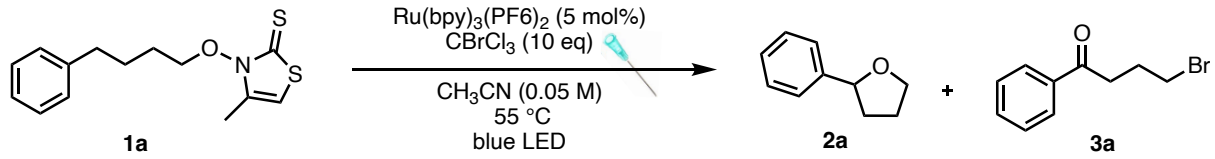


Entry	Photocatalyst	Solvent	Additive	$CBrCl_3$ (eq)	Yield (%)[e]	
					2a	3a
1 [a]	$Ir(ppy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	10	0	17
2 [a]	$Ir(ppy)_2(dtbpy)$ (5 mol %)	CH_3CN (0.05 M)	-	10	21	2
3 [a]	$Ru(dtbbpy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	10	23	4
4 [a]	Fukuzumi (5 mol %)	CH_3CN (0.05 M)	-	10	18	0
5 [a]	4CzIPN (5 mol %)	CH_3CN (0.05 M)	-	10	18	0
6 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	10	24	64
7 [a]	$Ru(bpy)_3$ (5 mol %)	DMF (0.05 M)	-	10	0	0
8 [a]	$Ru(bpy)_3$ (5 mol %)	DCE (0.05 M)	-	10	12	4
9 [a]	$Ru(bpy)_3$ (5 mol %)	$PhCF_3$ (0.05 M)	-	10	5	5
10 [a]	$Ru(bpy)_3$ (5 mol %)	C_6H_6 (0.05 M)	-	10	8	16
11 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	1.5	62	43
12 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	5	50	6
13 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	20	-	69
14 [a]	$Ru(bpy)_3$ (2 mol %)	CH_3CN (0.05 M)	-	10	65	5
15 [a]	$Ru(bpy)_3$ (1 mol %)	CH_3CN (0.05 M)	-	10	52	-
16 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.025 M)	-	10	44	4
17 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.01 M)	-	10	21	29
18 [a]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.1 M)	-	10	63	-
19 [b, c]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	-	10	-	66
20 [b, c]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	LiBr	10	49	15
21 [b, c]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	NBS	10	28	9
22 [b, c]	**$Ru(bpy)_3$** (5 mol %)	**CH_3CN (0.05 M)**	**TBAB**	**10**	**-**	**95**
23 [b, c]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	TBAB	1.5	54	24
24 [b]	**$Ru(bpy)_3$** (5 mol %)	**CH_3CN (0.05 M)**	**TBAB**	**10**	**72**	**19**
25 [b, d]	$Ru(bpy)_3$ (5 mol %)	CH_3CN (0.05 M)	TBAB	10	trace	trace[c]
26 [b]	No catalyst	CH_3CN (0.05 M)	TBAB	10	0	0 [c]

Table S1. [a] reaction time 15 h, reaction temperature 25 °C, [b] reaction time 6 h, reaction temperature 55 °C, [c] reaction performed with a metallic needle inserted into the system, [d] reaction performed in the dark, [e] yields were determined by ^1H NMR using ethylene carbonate as an internal standard

4.2 NMR study of *N*-alkoxythiazolethione 1a transformation

The transformation of **1a** was followed in time. The reaction was prepared and performed according to General photoredox method D. Results are summarized below.



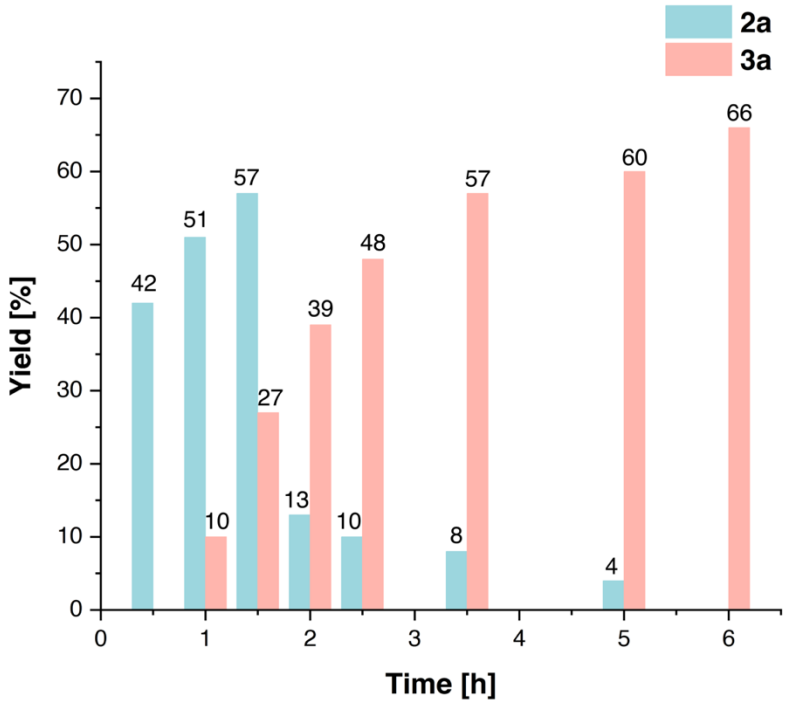


Figure S1 Reaction conditions: **1a** (0.1 mmol), $Ru(bpy)_3(PF_6)_2$ (5 mol%), $CBrCl_3$ (10 eq), in CH_3CN (0.05 M), blue LED irradiation at 55 °C, needle inserted into the vial. Yields of **2a** (blue) and **3a** (orange) were determined by ^1H NMR using ethylene carbonate as an internal standard.

As shown in Figure S1, tetrahydrofuran **2a** is formed prior to ketone **3a**, and the concentration of **2a** starts decreasing simultaneously with increasing concentration of **3a**.

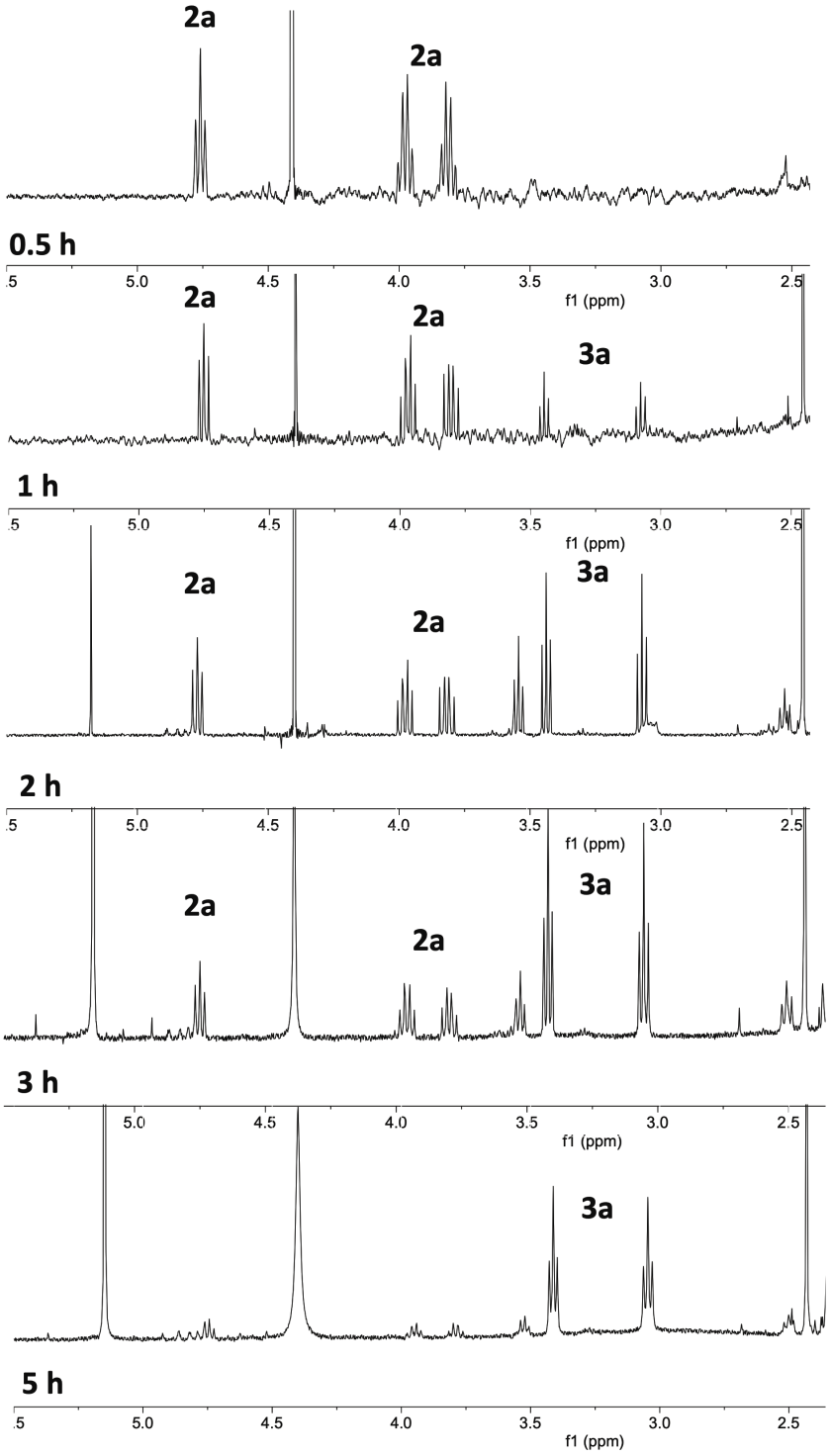


Figure S2 Reaction conditions: **1a** (0.1 mmol), $Ru(bpy)_3(PF_6)_2$ (5 mol%), $CBrCl_3$ (10 eq), in CH_3CN (0.05 M), blue LED irradiation at 55 °C, needle inserted into the vial. **2a** (4.75 ppm, 4.01 – 3.90, ppm, 3.85 – 3.75 ppm), **3a** (3.46 ppm, 3.05 ppm).

4.3 Screening of different metal sources

Since it was observed that the presence of a metallic needle in the system significantly improves the formation of bromoketone **3a**, the exact metal composition of the needle was identified. Elemental analysis has shown iron, chromium, and nickel (633 218 μg/g, 152 918 μg/g, 73 844 μg/g respectively) to be major metals present in the needle used in our experiments.

ICP-MS analysis of crude reaction mixture proved the presence of the above-mentioned metals (0.4896 mg/l, 0.1945 mg/l, 0.0887 mg/l respectively, reaction prepared and performed according to General photoredox method D).

Additionally, in replacement for the needle, different sources of iron, chromium, and nickel were tested under our optimized conditions. Reactions were prepared according to General photoredox method C. Reactions were performed with *N*-alkoxythiazolethione **1a**, and a corresponding metal source (0.02 mmol, 0.2 eq) was added. Results are summarized below.

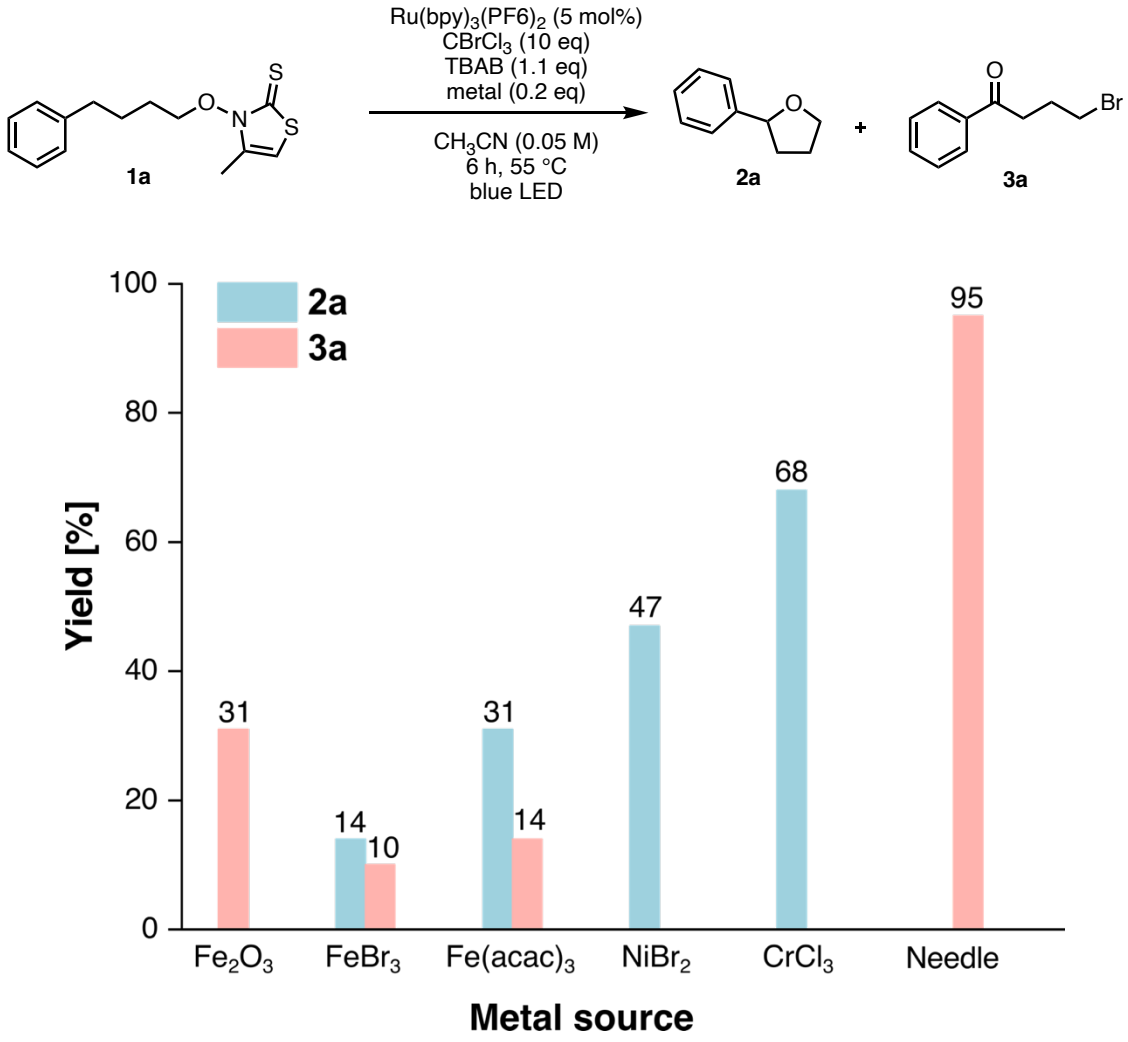
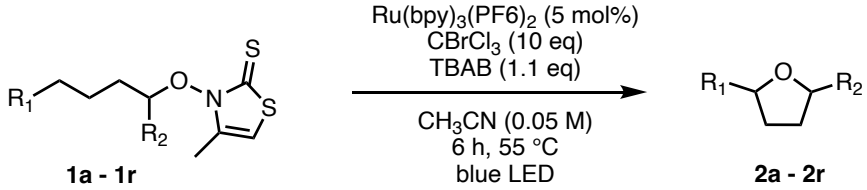


Figure S3 Reaction conditions: **1a** (0.1 mmol), $Ru(bpy)_3(PF_6)_2$ (5 mol%), $CBrCl_3$ (10 eq), TBAB (1.1 eq), metal source (0.2 eq) in CH_3CN (0.05 M), blue LED irradiation at 55 °C, 6h. Yields of **2a** (blue) and **3a** (orange) were determined by ^{1}H NMR using ethylene carbonate as an internal standard.

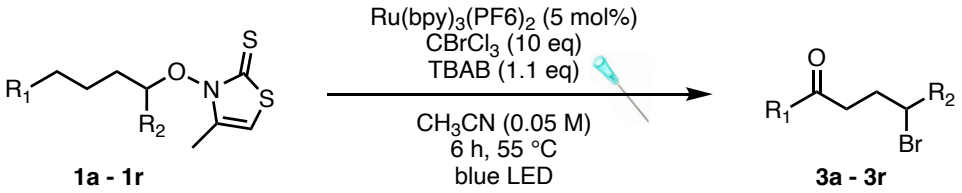
5. Preparation and characterization of photoredox products

5.1 General photoredox method C for the synthesis of cyclic ethers 2a – 2r



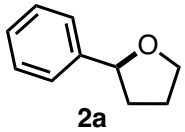
An oven-dried Biotage MW vial was charged with corresponding *N*-alkoxythiazolethione **1** (0.1 mmol), $Ru(bpy)_3(PF_6)_2$ (4.3 mg, 5 mol%) and TBAB (35.5 mg, 1.1 eq). The vial was capped, and the headspace of the vial was exchanged for the nitrogen by three vacuum/N_2 cycles. $CBrCl_3$ (98.7 μl, 10 eq) and anhydrous CH_3CN (2 ml, 0.05 M) were added. Both $CBrCl_3$ and CH_3CN were deoxygenated by sparging with argon for 20 min prior to the addition. The resulting reaction mixture was placed into the photoreactor and irradiated with blue light for 6 h at 55 °C. Crude reaction mixture was absorbed on Celite and purified by flush column chromatography.

5.2 General photoredox method D for the synthesis of bromoketones 3a – 3r



An oven-dried Biotage MW vial was charged with corresponding *N*-alkoxythiazolethione **1** (0.1 mmol), $Ru(bpy)_3(PF_6)_2$ (4.3 mg, 5 mol%) and TBAB (35.5 mg, 1.1 eq). The vial was capped, and the headspace of the vial was exchanged for the nitrogen by three vacuum/N_2 cycles. $CBrCl_3$ (98.7 μl, 10 eq) and anhydrous CH_3CN (2 ml, 0.05 M) were added. Both $CBrCl_3$ and CH_3CN were deoxygenated by sparging with argon for 20 min prior to the addition. The resulting reaction mixture was placed into the photoreactor and irradiated with blue light for 6 h at 55 °C. Reaction was performed under the continuous positive pressure of N_2 delivered into the vial via a metallic needle. Crude reaction mixture was absorbed on Celite and purified by flush column chromatography.

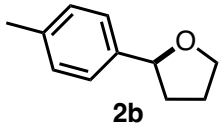
2-phenyltetrahydrofuran (2a)[4]



2a

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as yellow oil in 62% yield (0.062 mmol, 9.2 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 4H), 7.24 – 7.22 (m, 1H), 4.88 (t, *J* = 7.2 Hz, 1H), 4.12 – 4.06 (m, 1H), 3.96 – 3.90 (m, 1H), 2.36 – 2.27 (m, 1H), 2.04 – 1.96 (m, 2H), 1.84 – 1.75 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 143.6, 128.4, 127.3, 125.8, 80.8, 68.8, 34.8, 26.2.

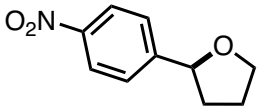
2-(*p*-tolyl)tetrahydrofuran (2b)[5]



2b

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 95% yield (0.095 mmol, 15.4 mg).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (d, *J* = 8.0 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 4.86 (t, *J* = 7.2 Hz, 1H), 4.11 – 4.06 (m, 1H), 3.95 – 3.89 (m, 1H), 2.33 (s, 3H), 2.33 – 2.26 (m, 1H), 2.04 – 1.96 (m, 2H), 1.84 – 1.75 (m, 1H). **^{13}C NMR (176 MHz, $CDCl_3$)** δ 140.5, 136.9, 129.1, 125.8, 80.7, 68.7, 34.7, 26.2, 21.2.

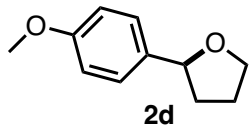
2-(4-nitrophenyl)tetrahydrofuran (2c)[6]



2c

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 95/5), isolated as yellow oil in 54% yield (0.054 mmol, 10.4 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 8.21 – 8.17 (m, 2H), 7.51 – 7.47 (m, 2H), 4.99 (t, *J* = 7.3 Hz, 1H), 4.12 (dt, *J* = 8.3, 6.7 Hz, 1H), 3.98 (td, *J* = 8.0, 6.4 Hz, 1H), 2.44 – 2.38 (m, 1H), 2.07 – 1.98 (m, 2H), 1.79 – 1.73 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 151.5, 147.2, 126.3, 123.8, 79.8, 69.2, 34.9, 26.1.

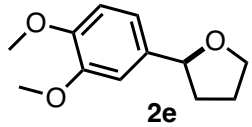
2-(4-methoxyphenyl)tetrahydrofuran (2d)[7]



2d

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as yellow oil in 59% yield (0.059 mmol, 10.5 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.26 – 7.24 (m, 2H), 6.87 – 6.88 (m, 2H), 4.83 (t, *J* = 7.3 Hz, 1H), 4.09 – 4.06 (m, 1H), 3.92 – 3.89 (m, 1H), 3.80 (d, *J* = 1.5 Hz, 3H), 2.29 – 2.25 (m, 1H), 2.05 – 1.96 (m, 2H), 1.81 – 1.77 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 158.9, 135.5, 127.1, 113.8, 80.6, 68.6, 55.4, 34.6, 26.2.

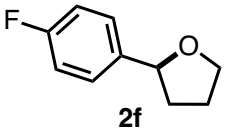
2-(3,4-dimethoxyphenyl)tetrahydrofuran (2e)[5]



2e

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 90/10), isolated as yellow oil in 72% yield (0.072 mmol, 15.0 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 6.83 (d, *J* = 1.9 Hz, 1H), 6.80 (dd, *J* = 8.3, 1.9 Hz, 1H), 6.76 (d, *J* = 8.2 Hz, 1H), 4.76 (t, *J* = 7.2 Hz, 1H), 4.02 (td, *J* = 7.9, 6.3 Hz, 1H), 3.84 (td, *J* = 8.1, 6.2 Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 2.24 – 2.20 (m, 1H), 1.99 – 1.90 (m, 2H), 1.76 – 1.71 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 149.1, 148.3, 135.8, 118.1, 111.1, 109.1, 80.7, 68.7, 56.2, 55.9, 34.6, 26.2.

2-(4-fluorophenyl)tetrahydrofuran (2f)[7]

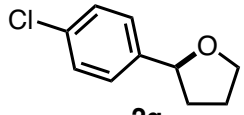


2f

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 94% yield (0.094 mmol, 15.6 mg). Compound is highly volatile.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.28 (m, 2H), 7.03 – 6.99 (m, 2H), 4.85 (t, *J* = 7.2 Hz, 1H), 4.11 – 4.06 (m, 1H), 3.95 – 3.90 (m, 1H), 2.35 – 2.27 (m, 1H), 2.05 – 1.97 (m, 2H), 1.81 – 1.72 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 162.8, 139.2, 127.4, 127.4, 115.3, 115.2, 80.3, 68.8, 34.8, 26.2.

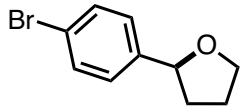
2-(4-chlorophenyl)tetrahydrofuran (2g)[7]



2g

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 97/3), isolated as yellow oil in 55% yield (0.055 mmol, 10.0 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.29 – 7.28 (m, 2H), 7.26 – 7.25 (m, 2H), 4.85 (t, *J* = 7.2 Hz, 1H), 4.09 – 4.06 (m, 1H), 3.93 (q, *J* = 8.0, 7.4 Hz, 1H), 2.33 – 2.29 (m, 1H), 2.01 – 1.97 (m, 2H), 1.76 – 1.72 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 142.4, 133.1, 128.7, 127.3, 80.3, 69.1, 35.0, 26.3.

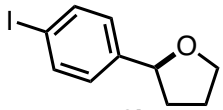
2-(4-bromophenyl)tetrahydrofuran (2h)[8]



2h

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 84% yield (0.084 mmol, 19.0 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.45 – 7.44 (m, 2H), 7.21 – 7.20 (m, 2H), 4.84 (t, *J* = 7.2 Hz, 1H), 4.08 (dt, *J* = 8.3, 6.8 Hz, 1H), 3.92 (dt, *J* = 8.2, 6.9 Hz, 1H), 2.34 – 2.30 (m, 1H), 2.02 – 1.98 (m, 2H), 1.77 – 1.71 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 142.7, 131.5, 127.5, 120.9, 80.2, 68.9, 34.8, 26.1.

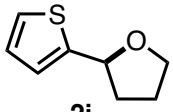
2-(4-iodophenyl)tetrahydrofuran (2i)



2i

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as colorless oil in 79% yield (0.079 mmol, 21.7 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.66 – 7.64 (m, 2H), 7.09 – 7.08 (m, 2H), 4.83 (t, *J* = 7.2 Hz, 1H), 4.08 (dt, *J* = 8.3, 6.8 Hz, 1H), 3.93 (dt, *J* = 8.3, 7.0 Hz, 1H), 2.32 – 2.29 (m, 1H), 2.01 – 1.97 (m, 2H), 1.76 – 1.72 (m, 1H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 143.5, 137.5, 127.8, 92.4, 80.2, 68.9, 34.8, 26.1. **HRMS-ESI (m/z):** exact mass calculated for $C_{10}H_{12}IO^+$ [(M+H)$^+$] 274.9933, not detected using either ESI or APCI. **GC-MS(EI) (m/z)**: exact mass calculated for $C_{10}H_{11}IO^+$ [M$^+$] 273.9855, found 274.0.

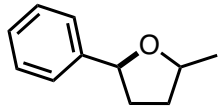
2-(thiophen-2-yl)tetrahydrofuran (2j)[9]



2j

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 85/15), isolated as colorless oil in 58% yield (0.058 mmol, 8.9 mg). Compound is highly volatile.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.21 (m, 1H), 6.96 – 6.95 (m, 2H), 5.15 (t, *J* = 6.5 Hz, 1H), 4.09 – 4.03 (m, 1H), 3.92 – 3.87 (m, 1H), 2.38 – 2.30 (m, 1H), 2.08 – 1.96 (m, 3H). **^{13}C NMR (176 MHz, $CDCl_3$)** δ 131.3, 129.2, 127.0, 124.7, 124.0, 68.7, 34.9, 30.1, 26.3.

2-methyl-5-phenyltetrahydrofuran (2k)[10]

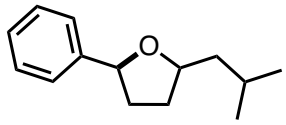


2k

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 68% yield (0.068 mmol, 11.0 mg). Mixture of cis/trans isomers in 1:1 ratio. Compound is highly volatile.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.30 (m, 8H), 7.27 – 7.22 (m, 2H), 5.06 – 5.02 (m, 1H), 4.98 (t, *J* = 7.3 Hz, 1H), 4.36 (dddd, *J* = 12.2, 8.1, 6.4, 5.9 Hz, 1H), 4.17 (dp, *J* = 7.4, 6.2 Hz, 1H), 2.43 – 2.25 (m, 2H), 2.20 – 2.07 (m, 2H), 1.93 – 1.78 (m, 2H), 1.67 – 1.60 (m, 2H), 1.37 (d, *J* = 6.1 Hz, 3H), 1.32 (d, *J* = 6.1 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 143.7, 128.4, 128.4, 127.3, 127.2, 126.0, 125.7, 81.2, 80.4, 76.1, 76.1, 35.8, 34.8, 34.4, 33.3, 21.7, 21.5.

2-isobutyl-5-phenyltetrahydrofuran (2l)

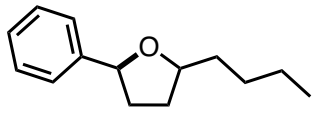


2l

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as colorless oil in 70% yield (0.070 mmol, 14.3 mg). Mixture of cis/trans isomers in 1:1 ratio.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.33 (q, *J* = 9.0, 8.3 Hz, 8H), 7.25 – 7.23 (m, 2H), 5.00 (t, *J* = 7.4 Hz, 1H), 4.87 (t, *J* = 7.3 Hz, 1H), 4.3 – 4.2 (m, 1H), 4.1 (p, *J* = 6.9 Hz, 1H), 2.39 – 2.35 (m, 1H), 2.31 – 2.27 (m, 1H), 2.15 – 2.12 (m, 1H), 2.09 – 2.05 (m, 1H), 1.87 – 1.77 (m, 4H), 1.69 (dt, *J* = 13.8, 7.0 Hz, 1H), 1.65 – 1.58 (m, 3H), 1.41 (ddd, *J* = 13.4, 7.5, 5.7 Hz, 1H), 1.35 (ddd, *J* = 13.6, 7.6, 5.8 Hz, 1H), 0.97 – 0.95 (m, 12H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.3, 143.9, 128.4, 128.4, 127.2, 127.1, 126.0, 125.7, 80.8, 80.0, 78.5, 78.5, 45.5, 35.5, 34.6, 33.1, 31.9, 25.8, 25.7, 23.4, 23.3, 22.9, 22.8. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{21}O^+$ [$(M+H)^+$] 205.1592, found 205.1590.

2-butyl-5-phenyltetrahydrofuran (2m)[11]

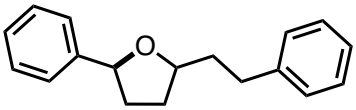


2m

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as yellow oil in 58% yield (0.058 mmol, 11.8 mg). Mixture of cis/trans isomers in 1:1 ratio.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.36 – 7.31 (m, 8H), 7.25 – 7.21 (m, 2H), 4.99 (dd, *J* = 8.3, 6.4 Hz, 1H), 4.87 (t, *J* = 7.3 Hz, 1H), 4.18 (dq, *J* = 8.2, 6.3 Hz, 1H), 4.01 (p, *J* = 6.7 Hz, 1H), 2.38 – 2.34 (m, 1H), 2.30 – 2.26 (m, 1H), 2.14 – 2.11 (m, 1H), 2.08 – 2.04 (m, 1H), 1.87 – 1.83 (m, 1H), 1.82 – 1.74 (m, 1H), 1.72 – 1.68 (m, 1H), 1.67 – 1.62 (m, 2H), 1.61 – 1.56 (m, 2H), 1.54 – 1.51 (m, 1H), 1.50 – 1.41 (m, 2H), 1.41 – 1.33 (m, 6H), 0.94 – 0.91 (m, 6H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.2, 143.8, 128.4, 128.4, 127.2, 127.1, 126.0, 125.8, 80.9, 80.3, 36.0, 35.9, 35.6, 34.6, 32.6, 31.5, 28.6, 28.5, 23.0, 14.2.

2-phenethyl-5-phenyltetrahydrofuran (2n)

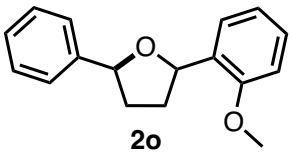


2n

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as yellow oil in 75% yield (0.075 mmol, 18.9 mg). Mixture of cis/trans isomers in 1:1 ratio.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.38 – 7.32 (m, 8H), 7.30 (td, *J* = 7.6, 2.6 Hz, 4H), 7.27 – 7.22 (m, 6H), 7.20 (td, *J* = 7.3, 2.2 Hz, 2H), 5.03 (dd, *J* = 8.3, 6.4 Hz, 1H), 4.90 (t, *J* = 7.3 Hz, 1H), 4.22 (ddd, *J* = 13.5, 7.7, 5.8 Hz, 1H), 4.06 (p, *J* = 6.8 Hz, 1H), 2.88 – 2.80 (m, 2H), 2.79 – 2.70 (m, 2H), 2.41 – 2.35 (m, 1H), 2.34 – 2.27 (m, 1H), 2.18 – 2.12 (m, 1H), 2.12 – 2.04 (m, 2H), 2.04 – 1.98 (m, 1H), 1.95 – 1.89 (m, 1H), 1.89 – 1.80 (m, 3H), 1.73 – 1.65 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 144.1, 143.6, 142.4, 128.6, 128.5, 128.5, 128.4, 127.3, 127.2, 125.9, 125.9, 125.8, 81.0, 80.4, 79.4, 79.4, 38.0, 37.9, 35.6, 34.7, 32.7, 32.7, 32.6, 31.5. **HRMS-ESI (m/z):** exact mass calculated for $C_{18}H_{21}O^+$ [(M+H)$^+$] 253.1592, found 253.1580.

(2-methoxyphenyl)-5-phenyltetrahydrofuran (2o)

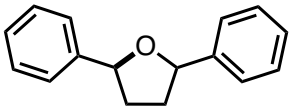


2o

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as colorless oil in 69% yield (0.069 mmol, 17.5 mg). Mixture of cis/trans isomers in 1:1 ratio.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.64 – 7.62 (m, 1H), 7.54 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.49 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.42 (dd, *J* = 7.9, 1.4 Hz, 2H), 7.39 – 7.32 (m, 4H), 7.30 – 7.27 (m, 1H), 7.26 – 7.22 (m, 3H), 6.98 (tdd, *J* = 7.4, 2.0, 1.0 Hz, 2H), 6.87 (ddd, *J* = 8.2, 6.0, 1.0 Hz,2H), 5.53 (t, *J* = 7.1 Hz, 1H), 5.32 (t, *J* = 7.3 Hz, 1H), 5.28 (t, *J* = 7.1 Hz, 1H), 5.02 (t, *J* = 7.5 Hz, 1H), 3.85 (d, *J* = 7.2 Hz, 6H), 2.57 – 2.49 (m, 2H), 2.44 – 2.37 (m, 2H), 2.00 – 1.94 (m, 1H), 1.94 – 1.89 (m, 1H), 1.89 – 1.83 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 156.3, 144.1, 143.2, 132.5, 131.9, 128.5, 128.0, 127.9, 127.4, 127.2, 125.8, 120.7, 110.3, 110.2, 81.2, 81.1, 76.4, 55.5, 55.4, 35.6, 34.4, 34.0, 33.3. **HRMS-ESI (m/z):** exact mass calculated for $C_{17}H_{19}O_2^+$ [(M+H)$^+$] 255.1385, found 255.1381.

2,5-diphenyltetrahydrofuran (2p)[12]

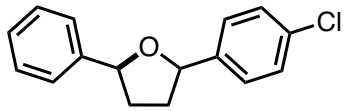


2p

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as colorless oil in 59% yield (0.059 mmol, 13.2 mg). Mixture of cis/trans isomers in 1:1 ratio.

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 4H), 7.42 (d, *J* = 7.6 Hz, 4H), 7.36 (td, *J* = 7.6, 4.5 Hz, 8H), 7.28 (dd, *J* = 9.4, 7.4 Hz, 4H), 5.27 (t, *J* = 6.7 Hz, 2H), 5.06 (t, *J* = 5.8 Hz, 2H), 2.50 – 2.47 (m, 2H), 2.45 – 2.41 (m, 2H), 2.04 – 1.96 (m, 4H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 143.8, 143.1, 128.5, 127.4, 127.3, 126.1, 125.7, 81.5, 81.4, 35.7, 34.5.

2-(4-chlorophenyl)-5-phenyltetrahydrofuran (2r)

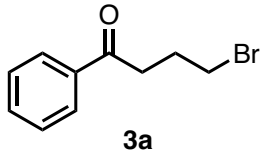


2r

Prepared according to general method C, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as colorless oil in 63% yield (0.063 mmol, 16.3 mg). Formed as a mixture of cis/trans isomers in 1:1 ratio, isolated as a mixture of cis/trans isomers in 0.6:1 ratio.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.27 (m, 15H), 5.29 – 5.20 (m, 2H), 5.09 – 4.99 (m, 1H), 2.53 – 2.40 (m, 3H), 2.07 – 1.88 (m, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 143.5, 142.4, 132.9, 131.5, 128.6, 128.6, 127.5, 127.1, 125.7, 81.6, 80.8, 35.8, 35.6. **HRMS-APCI (m/z):** exact mass calculated for $C_{16}H_{16}ClO^+$ [$(M+H)^+$] 259.0889, found 259.0879.

4-bromo-1-phenylbutan-1-one (3a)[13]

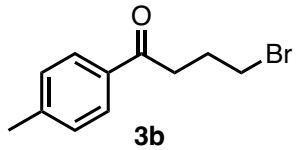


3a

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as yellow oil in 90% yield (0.090 mmol, 20.4 mg).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.99 – 7.98 (m, 2H), 7.59 – 7.57 (m, 1H), 7.49 – 7.47 (m, 2H), 3.56 (td, J = 6.3, 1.5 Hz, 2H), 3.19 (td, J = 7.0, 1.5 Hz, 2H), 2.32 (p, J = 7.3, 6.6 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 198.9, 136.9, 133.4, 128.8, 128.2, 36.7, 33.8, 27.0.

4-bromo-1-(*p*-tolyl)butan-1-one (3b)[13]

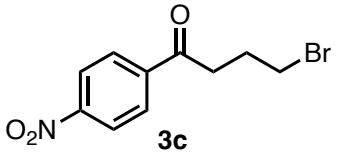


3b

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 85% yield (0.085 mmol, 20.5 mg).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.99 (d, J = 7.9 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 3.55 (t, J = 6.3 Hz, 2H), 3.16 (t, J = 6.9 Hz, 3H), 2.42 (s, 3H), 2.31 (p, J = 6.6 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 198.6, 144.2, 134.4, 129.5, 128.3, 36.6, 33.9, 27.1, 21.8.

4-bromo-1-(4-nitrophenyl)butan-1-one (3c)

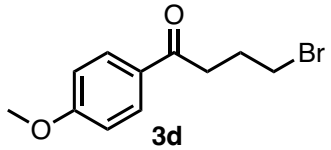


3c

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 95/5), isolated as yellow oil in 78% yield (0.078 mmol, 21.1 mg).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 – 8.32 (m, 2H), 8.16 – 8.12 (m, 2H), 3.57 (dd, J = 6.5, 5.9 Hz, 2H), 3.25 (t, J = 6.9 Hz, 2H), 2.34 (tt, J = 6.8, 6.1 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 197.4, 150.6, 141.2, 129.2, 124.1, 37.3, 33.3, 29.9, 26.6. **HRMS-ESI (m/z):** exact mass calculated for $C_{10}H_{11}BrNO_3^+$ [$(M+H)^+$] 271.9922, not detected using either ESI or APCI. **GC-MS(EI) (m/z)**: exact mass calculated for $C_{10}H_{10}BrNO_3^+$ [M^+] 270. 9844, found 271.0.

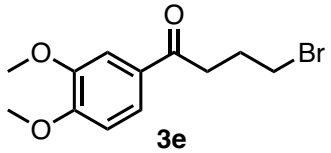
4-bromo-1-(4-methoxyphenyl)butan-1-one (3d)[13]



3d

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 50% yield (0.050 mmol, 12.8 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.97 – 7.96 (m, 2H), 6.94 (dd, *J* = 8.7, 1.5 Hz, 2H), 3.88 (d, *J* = 1.4 Hz, 3H), 3.55 (td, *J* = 6.3, 1.4 Hz, 2H), 3.13 (td, *J* = 6.9, 1.4 Hz, 2H), 2.32 – 2.29 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 197.5, 163.7, 130.5, 130.0, 113.9, 55.6, 36.3, 33.9, 27.2.

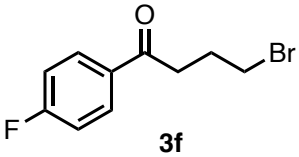
4-bromo-1-(3,4-dimethoxyphenyl)butan-1-one (3e)[14]



3e

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 90/10), isolated as yellow oil in 68% yield (0.068 mmol, 19.5 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.54 (d, *J* = 2.0 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 3.96 (s, 3H), 3.95 (s, 3H), 3.56 (t, *J* = 6.3 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.31 (p, *J* = 6.7 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 197.6, 153.6, 149.2, 130.2, 122.9, 110.2, 110.2, 56.3, 56.2, 36.2, 33.9, 27.4.

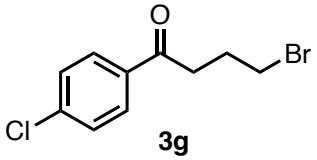
4-bromo-1-(4-fluorophenyl)butan-1-one (3f)[13]



3f

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as colorless oil in 65% yield (0.065 mmol, 15.9 mg). Compound is highly volatile.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 8.00 (m, 2H), 7.17 – 7.12 (m, 2H), 3.55 (t, *J* = 6.3 Hz, 2H), 3.16 (t, *J* = 6.9 Hz, 2H), 2.34 – 2.28 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 197.5, 131.0, 130.9, 116.1, 116.0, 36.8, 33.9, 30.0, 27.1.

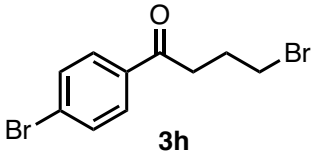
4-bromo-1-(4-chlorophenyl)butan-1-one (3g)[13]



3g

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 68% yield (0.068 mmol, 17.8 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.93 – 7.91 (m, 2H), 7.46 – 7.44 (m, 2H), 3.55 (td, *J* = 6.3, 1.8 Hz, 2H), 3.16 (td, *J* = 6.9, 2.0 Hz, 2H), 2.31 (pd, *J* = 6.7, 1.8 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 197.73, 139.87, 135.19, 129.59, 129.14, 36.68, 33.63, 26.88.

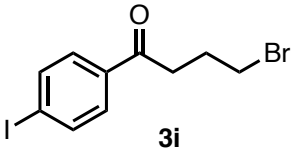
4-bromo-1-(4-bromophenyl)butan-1-one (3h)[13]



3h

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as colorless oil in 84% yield (0.084 mmol, 25.7 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.85 – 7.84 (m, 2H), 7.63 – 7.61 (m, 2H), 3.55 (t, *J* = 6.3 Hz, 2H), 3.15 (t, *J* = 6.9 Hz, 2H), 2.31 (p, *J* = 6.6 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 197.9, 135.6, 132.1, 129.7, 128.6, 36.7, 33.6, 26.9.

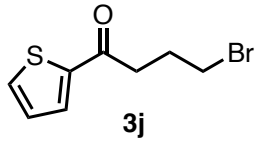
4-bromo-1-(4-iodophenyl)butan-1-one (3i)



3i

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as yellow oil in 86% yield (0.086 mmol, 30.4 mg).
^{1}H NMR (800 MHz, $CDCl_3$) δ 7.85 – 7.84 (m, 2H), 7.69 – 7.68 (m, 2H), 3.55 (t, *J* = 6.3 Hz, 2H), 3.14 (t, *J* = 6.9 Hz, 2H), 2.30 (p, *J* = 6.6 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 198.3, 138.2, 136.1, 129.6, 101.4, 36.6, 33.6, 26.9. **HRMS-APCI (m/z):** exact mass calculated for $C_{10}H_{12}BrIO^+$ [(M+H)$^+$] 352.9038, found 352.9028.

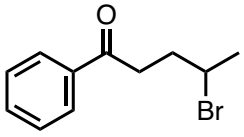
4-bromo-1-(thiophen-2-yl)butan-1-one (3j)



3j

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 97/3), isolated as yellow oil in 50% yield (0.050 mmol, 11.7 mg).
^{1}H NMR (700 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 3.8, 1.1 Hz, 1H), 7.65 (dt, *J* = 4.9, 1.4 Hz, 1H), 7.14 (ddd, *J* = 5.1, 3.8, 1.3 Hz, 1H), 3.54 (t, *J* = 6.3 Hz, 2H), 3.13 (t, *J* = 7.0 Hz, 2H), 2.31 (p, *J* = 6.7 Hz, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 191.9, 144.2, 133.9, 132.2, 128.3, 37.3, 33.6, 27.2. **HRMS-ESI (m/z):** exact mass calculated for $C_8H_{10}BrOS^+$ [(M+H)$^+$] 232.9635, found 232.9633.

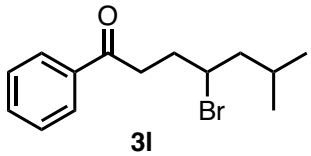
4-bromo-1-phenylpentan-1-one (3k)



3k

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 97/3), isolated as yellow oil in 64% yield (0.064 mmol, 15.4 mg).
^{1}H NMR (700 MHz, $CDCl_3$) δ 8.01 – 7.97 (m, 2H), 7.60 – 7.56 (m, 1H), 7.49 – 7.46 (m, 2H), 4.27 (dqd, *J* = 10.1, 6.6, 3.5 Hz, 1H), 3.28 – 3.18 (m, 2H), 2.35 – 2.29 (m, 1H), 2.19 – 2.10 (m, 1H), 1.79 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 199.2, 136.9, 133.4, 128.8, 128.2, 51.6, 36.9, 35.2, 26.9.
HRMS-ESI (m/z): exact mass calculated for $C_{11}H_{14}BrO^+$ [(M+H)$^+$] 241.0228, not detected using either ESI or APCI, fragmentation of the compound observed.

4-bromo-6-methyl-1-phenylheptan-1-one (3l)

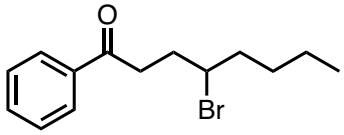


3l

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ CH_2Cl_2, 90/10), isolated as yellow oil in 65% yield (0.065 mmol, 18.4 mg).

^{1}H NMR (700 MHz, $CDCl_3$) δ 8.01 – 7.98 (m, 2H), 7.59 – 7.56 (m, 1H), 7.49 – 7.46 (m, 2H), 4.24 – 4.17 (m, 1H), 3.32 – 3.23 (m, 2H), 2.42 – 2.33 (m, 1H), 2.15 – 2.08 (m, 1H), 1.96 – 1.88 (m, 2H), 1.65 – 1.60 (m, 1H), 0.96 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.4 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 199.4, 136.9, 133.3, 128.8, 128.2, 56.6, 48.7, 36.8, 33.6, 26.6, 22.9, 21.5. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{20}BrO^+$ [$(M+H)^+$] 283.0698, not detected using either ESI or APCI, fragmentation of the compound observed.

4-bromo-1-phenyloctan-1-one (3m)

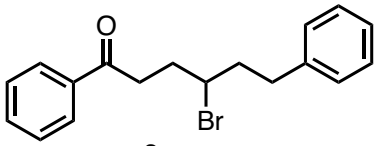


3m

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as yellow oil in 48% yield (0.048 mmol, 13.6 mg).

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.03 – 7.99 (m, 2H), 7.64 – 7.61 (m, 1H), 7.53 – 7.50 (m, 2H), 4.02 – 3.97 (m, 1H), 3.24 – 3.16 (m, 2H), 1.91 – 1.85 (m, 1H), 1.85 – 1.79 (m, 1H), 1.40 – 1.25 (m, 6H), 0.89 (td, J = 7.3, 1.4 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 193.8, 134.4, 130.0, 129.1, 113.2, 52.9, 43.3, 38.6, 29.7, 22.1, 16.0, 14.0. **HRMS-ESI (m/z):** exact mass calculated for $C_{14}H_{20}BrO^+$ [$(M+H)^+$] 283.0698, not detected using either ESI or APCI, fragmentation of the compound observed.

4-bromo-1,6-diphenylhexan-1-one (3n)

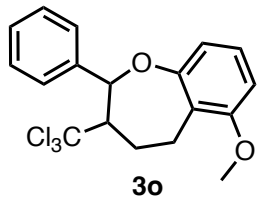


3n

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 99/1), isolated as yellow oil in 65% yield (0.065 mmol, 21.5 mg).

^{1}H NMR (800 MHz, $CDCl_3$) δ 8.00 – 7.95 (m, 2H), 7.65 – 7.61 (m, 1H), 7.54 – 7.48 (m, 2H), 7.28 – 7.24 (m, 2H), 7.20 – 7.16 (m, 1H), 7.16 – 7.14 (m, 2H), 4.02 – 3.96 (m, 1H), 3.28 – 3.19 (m, 2H), 2.91 – 2.85 (m, 1H), 2.72 – 2.66 (m, 1H), 2.22 – 2.16 (m, 1H), 2.15 – 2.09 (m, 1H), 1.28 – 1.21 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 193.6, 140.5, 136.3, 135.1, 134.4, 129.9, 129.1, 128.7, 128.6, 126.3, 124.7, 52.0, 43.2, 40.4, 33.8, 29.9. **HRMS-ESI (m/z):** exact mass calculated for $C_{18}H_{20}BrO^+$ [$(M+H)^+$] 331.0698, not detected using either ESI or APCI, fragmentation of the compound observed.

6-methoxy-2-phenyl-3-(trichloromethyl)-2,3,4,5-tetrahydrobenzoxepine (3o)

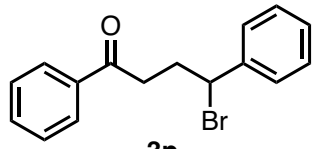


3o

Prepared according to general method D, purified by flash column chromatography (silica gel, hexane/ EtOAc, 98/2), isolated as yellow oil in 54% yield (0.054 mmol, 20.0 mg). Mixture of cis/trans isomers in > 20:1 ratio.

^{1}H NMR (700 MHz, $CDCl_3$) δ 7.18 – 7.15 (m, 1H), 7.12 – 7.09 (m, 1H), 7.08 – 7.05 (m, 1H), 7.04 – 7.00 (m, 1H), 6.99 – 6.96 (m, 2H), 6.86 – 6.81 (m, 2H), 4.89 (d, *J* = 5.8 Hz, 1H), 3.78 (s, 3H), 3.38 – 3.33 (m, 1H), 3.05 – 2.94 (m, 2H), 2.59 – 2.53 (m, 1H), 2.13 – 2.06 (m, 1H). **^{13}C NMR (176 MHz, $CDCl_3$)** δ 156.6, 139.0, 136.8, 135.8, 131.0, 129.9, 128.0, 127.7, 126.4, 125.7, 120.7, 111.3, 105.4, 59.9, 55.5, 42.5, 27.9, 26.2. **HRMS-ESI (m/z):** exact mass calculated for $C_{18}H_{16}Cl_3O_2^-$ [(M-H)$^-$] 369.0215, found 369.0211.

4-bromo-1,4-diphenylbutan-1-one (3p)

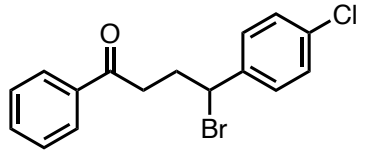


3p

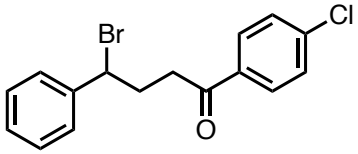
Prepared according to general method D, reaction time 3 h, purified by flash column chromatography (silica gel, hexane/ EtOAc, 85/15), isolated as yellow oil in 70% yield (0.070 mmol, 21.2 mg).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.90 – 7.86 (m, 2H), 7.50 – 7.48 (m, 1H), 7.40 – 7.37 (m, 2H), 7.33 – 7.31 (m, 2H), 7.31 – 7.28 (m, 2H), 7.23 – 7.20 (m, 1H), 4.78 (dd, *J* = 7.8, 4.9 Hz, 1H), 3.06 (t, *J* = 6.9 Hz, 2H), 2.20 – 2.10 (m, 2H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 200.7, 144.5, 137.0, 133.3, 128.7, 128.7, 128.3, 128.2, 127.8, 127.1, 125.9, 73.8, 34.9, 33.2. **HRMS-ESI (m/z):** exact mass calculated for $C_{16}H_{16}BrO^+$ [(M+H)$^+$] 303.0385, not detected using either ESI or APCI, fragmentation of the compound observed.

4-bromo-4-(4-chlorophenyl)-1-phenylbutan-1-one (3r)
4-bromo-1-(4-chlorophenyl)-4-phenylbutan-1-one (3r')



3r



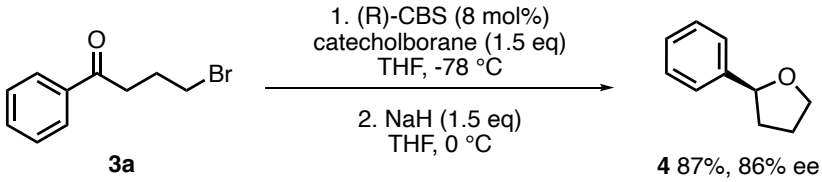
3r'

Prepared according to general method D, reaction time 3 h, purified by flash column chromatography (silica gel, hexane/ EtOAc, 85/15), isolated as an inseparable mixture of two regioisomers, yellow oil in 62% yield (0.062 mmol, 20.9 mg).

^{1}H NMR (800 MHz, $CDCl_3$) δ 7.97 – 7.94 (m, 2H), 7.90 – 7.88 (m, 2H), 7.58 – 7.55 (m, 1H), 7.48 – 7.34 (m, 12H), 7.31 – 7.28 (m, 1H), 4.84 (dd, *J* = 8.2, 4.8 Hz, 2H), 3.17 – 3.07 (m, 4H), 2.23 – 2.13 (m, 4H). (aliphatic signals for the regioisomers overlap) **^{13}C NMR (201 MHz, $CDCl_3$)** δ 200.7, 199.3, 144.4, 143.0, 139.7, 136.9, 135. 3, 133.4, 129.7, 129.1, 128.8, 128.7, 128.3, 127.9, 127.3, 125.9, 73.7, 73.1, 34.9, 34.8, 33.2, 33.1. **HRMS-ESI (m/z):** exact mass calculated for $C_{16}H_{15}BrClO^+$ [(M+H)$^+$] 334.9838, not detected using either ESI or APCI, fragmentation of the compound observed.

6. Synthetic applications of γ-bromoketone 3a

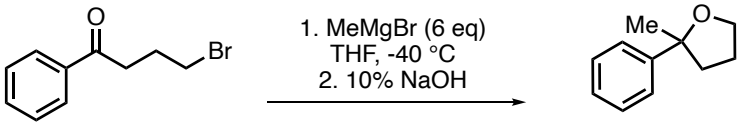
(S)-2-phenyltetrahydrofuran (4)[15]



3a **4** 87%, 86% ee

(R)-CBS (8 mol%, 11.1 mg) was dissolved in anhydrous THF (0.2 ml) and catecholborane (0.75 mmol, 0.75 ml, 1.5 eq) was added. Solution was cooled to - 78 °C, solution of bromoketone **3a** (0.5 mmol, 114 mg) in anhydrous THF (0.2 ml) was added dropwise and resulting mixture was let to stir for 12 h. Solution was diluted with DCM (15 ml), washed with 1M HCl (2x15 ml), dried over Na_2SO_4 and concentrated under reduced pressure. Crude material was dissolved in anhydrous THF (5 ml) and NaH (60% in mineral oil, 0.75 mmol, 30 mg, 1.5 eq) was added in portions. Reaction was heated to 70 °C for 12 h. Reaction was diluted with sat. NH_4Cl (15 ml) and extracted with Et_2O (3x25 ml), dried over Na_2SO_4 and concentrated under reduced pressure. Crude material was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 97/3) and the final product **4** was isolated as yellow oil in 87% yield, 86% ee (0.43 mmol, 98 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.26 – 7.21 (m, 4H), 7.19 – 7.12 (m, 1H), 4.80 (t, *J* = 7.2 Hz, 1H), 4.04 – 3.96 (m, 1H), 3.88 – 3.80 (m, 1H), 2.29 – 2 .17 (m, 1H), 1.97 – 1.86 (m, 2H), 1.77 – 1.66 (m, 1H).**^{13}C NMR (101 MHz, $CDCl_3$)** δ 142.6, 127.4, 126.2, 124.8, 79.8, 67.8, 33.8, 25.2. Enantiomeric ratio of **4** was determined by HPLC analysis using Chiralpac AD-4 column: hexane 100%, flow rate 1 ml/min: t_1 (major) = 13.3 min, t_2 (minor) = 16.3 min.

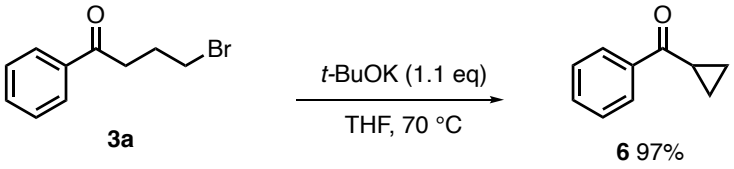
2-methyl-2-phenyltetrahydrofuran (5)[16]



3a **5** 85%

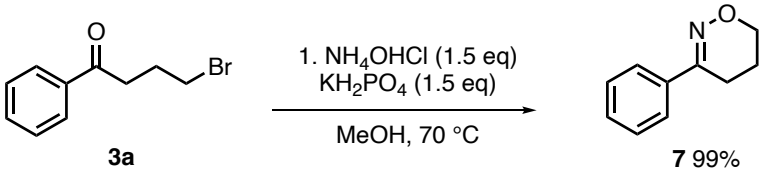
Bromoketone **3a** (0.5 mmol, 114 mg) was dissolved in anhydrous THF (0.5 M). Solution was cooled to - 40 °C, MeMgBr (3 mmol, 1 ml, 6 eq) was added dropwise and resulting mixture was let to stir at room temperature for 12 h. Solution was cooled to 0 °C, 10% aq NaOH was slowly added to the solution and let to stir for 4 h. Resulting solution was extracted with Et_2O (3x25 ml), washed with Brine, dried over Na_2SO_4 and concentrated under reduced pressure. Crude material was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 90/10) and the final product **5** was isolated as colorless oil in 85% yield (0.43 mmol, 69 mg).**^{1}H NMR (800 MHz, $CDCl_3$)** δ 7.42 – 7.38 (m, 2H), 7.34 – 7.30 (m, 2H), 7.23 – 7.20 (m, 1H), 4.02 (q, *J* = 7.3 Hz, 1H), 3.91 (td, *J* = 8.2, 7.7, 5.8 Hz, 1H), 2.23 – 2.19 (m, 1H), 2.05 – 1.94 (m, 2H), 1.84 – 1.78 (m, 1H), 1.53 (d, *J* = 1.6 Hz, 3H). **^{13}C NMR (201 MHz, $CDCl_3$)** δ 148.3, 128.2, 126.5, 124.8, 84.4, 67.7, 39.6, 29.9, 25.9.

cyclopropyl-(phenyl)-methanone (6)[17]



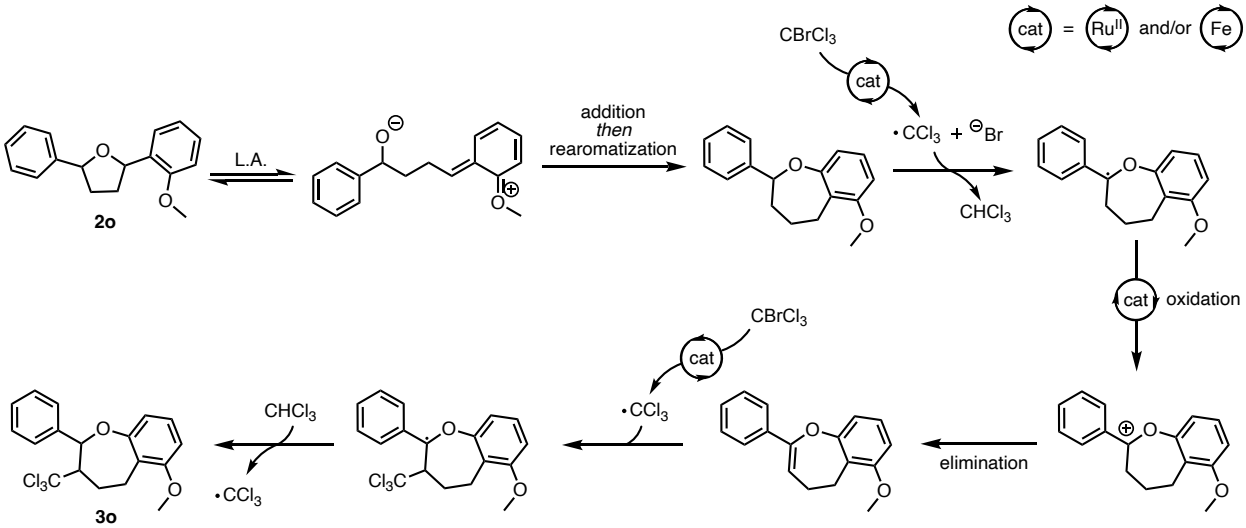
Bromoketone **3a** (0.2 mmol, 45 mg) was dissolved in anhydrous THF (0.2 M), *t*-BuOK (0.22 mmol, 24.7 mg, 1.1 eq) was added and resulting mixture was heated to 70 °C for 12 h. Reaction was diluted with sat. NH_4Cl (10 ml) and extracted with Et_2O (3x15 ml), dried over Na_2SO_4 and concentrated under reduced pressure. Crude material was purified by flash column chromatography (silica gel, petroleum ether/EtOAc, 95/5) and the final product **6** was isolated as yellow oil in 97% yield (0.19 mmol, 28 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04 – 7.99 (m, 2H), 7.59 – 7.53 (m, 1H), 7.51 – 7.45 (m, 2H), 2.68 (tt, *J* = 7.8, 4.6 Hz, 1H), 1.28 – 1.22 (m, 2H), 1.08 – 1.01 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 200.8, 138.1, 132.9, 128.6, 128.1, 17.3, 11.8.

3-phenyl-*4H*-5,6-dihydro-1,2-oxazine (7)[18]



Bromoketone **3a** (0.2 mmol, 45 mg) was dissolved in MeOH (0.2 M). NH_4OHCl (0.3 mmol, 21.15 mg, 1.5 eq) and KH_2PO_4 (0.3 mmol, 40.8 mg, 1.5 eq) was added and resulting mixture was heated to 70 °C for 2 h. Reaction mixture was diluted with Na_2CO_3 (10 ml) and extracted with EtOAc (3x10 ml), dried over Na_2SO_4, and concentrated under reduced pressure. Final product **7** was recrystallized from diisopropyl ether and isolated as white solids in 99% yield (0.19 mmol, 31 mg). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.36 – 8.28 (m, 2H), 7.47 – 7.37 (m, 3H), 4.22 (tt, *J* = 7.9, 1.9 Hz, 2H), 3.17 (ddt, *J* = 8.3, 6.6, 1.9 Hz, 2H), 2.26 – 2.13 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 140.5, 130.3, 129.3, 128.5, 127.3, 65.1, 31.0, 16.7. **GC-MS(EI) (m/z)**: exact mass calculated for $C_{10}H_{11}NO^+$ [M^+] 161.0841, found 161.1.

7. Mechanistic details for the formation of tetrahydrobenzoxepine 3o



Scheme S1. Proposed mechanism for the formation of 6-methoxy-2-phenyl-3-(trichloromethyl)-2,3,4,5-tetrahydrobenzoxepine **(3o)**.

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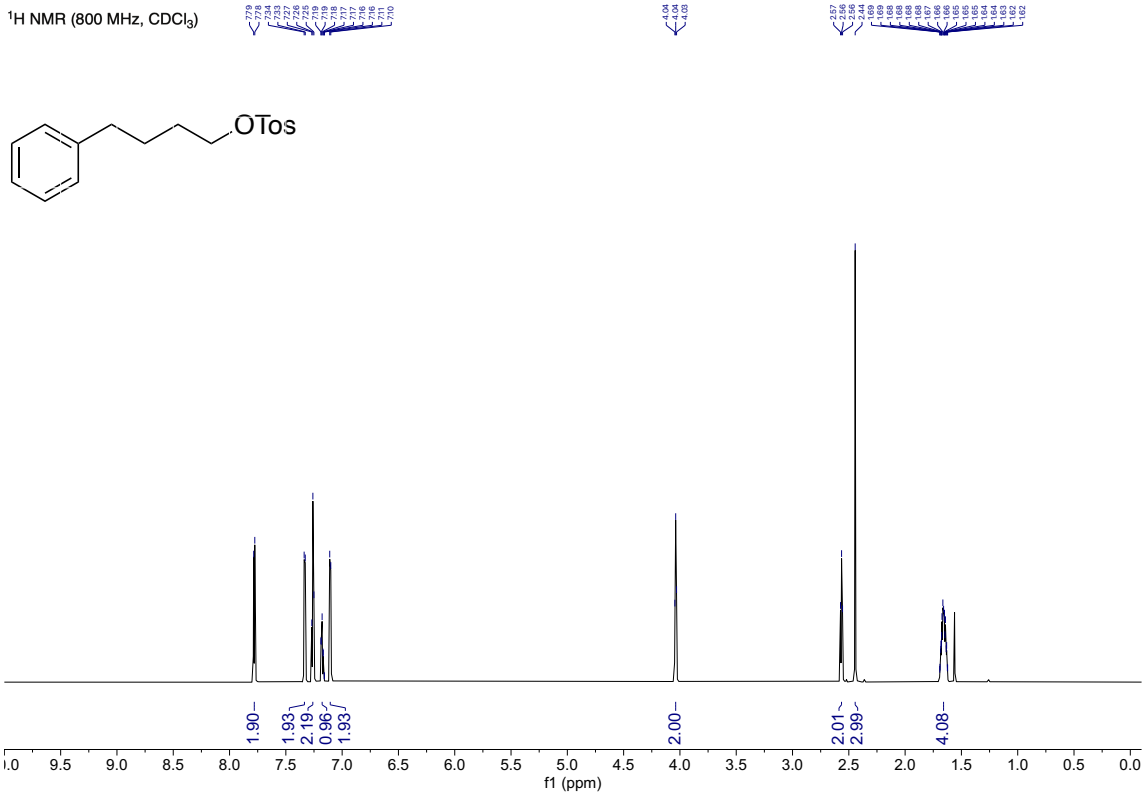
9. Appendix

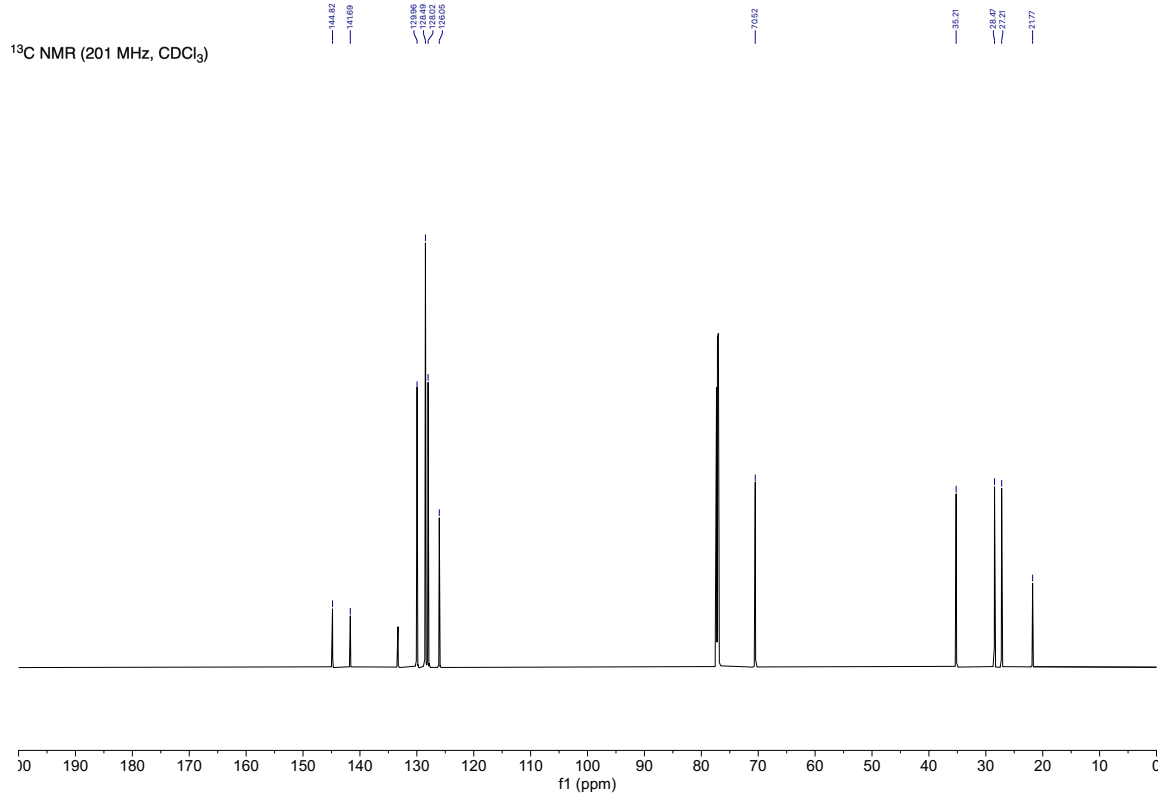
9.1 NMR spectra

4-phenylbutyl 4-methylbenzenesulfonate (1aa)

^{1}H NMR (800 MHz, $CDCl_3$)

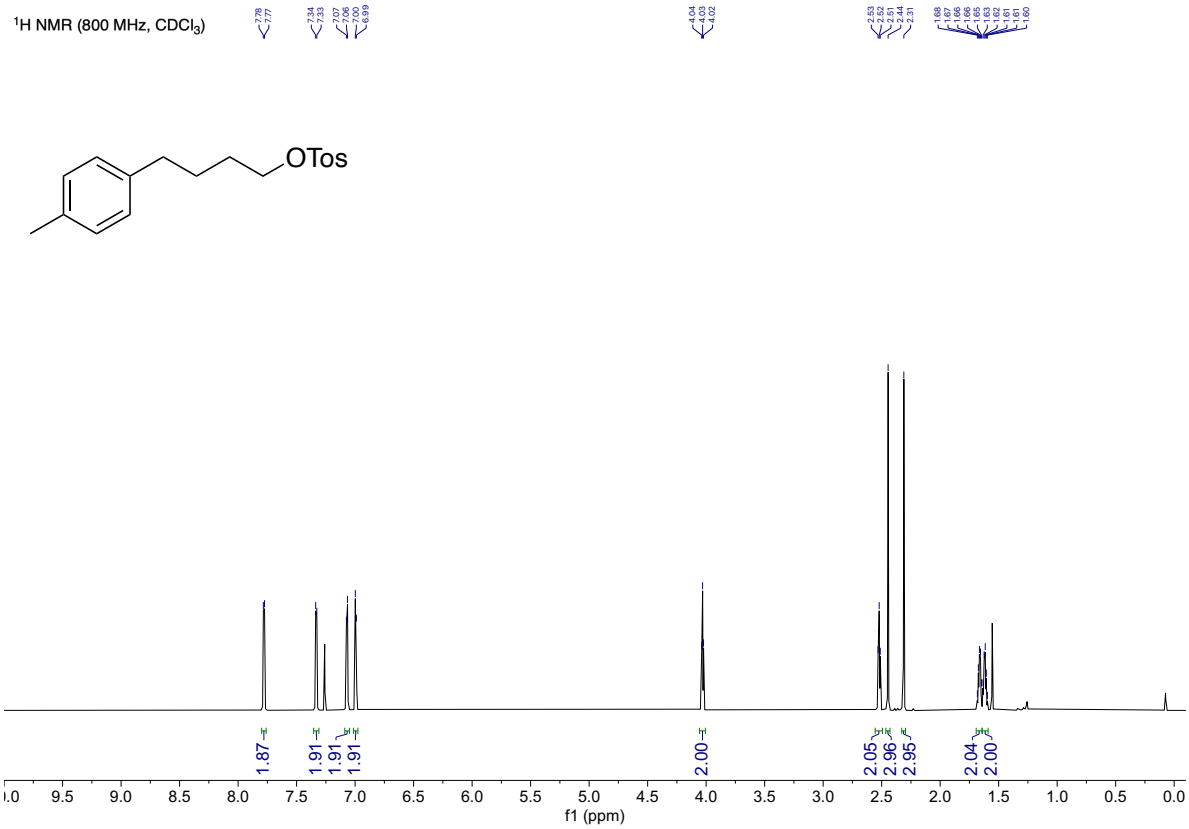


^{13}C NMR (201 MHz, $CDCl_3$)

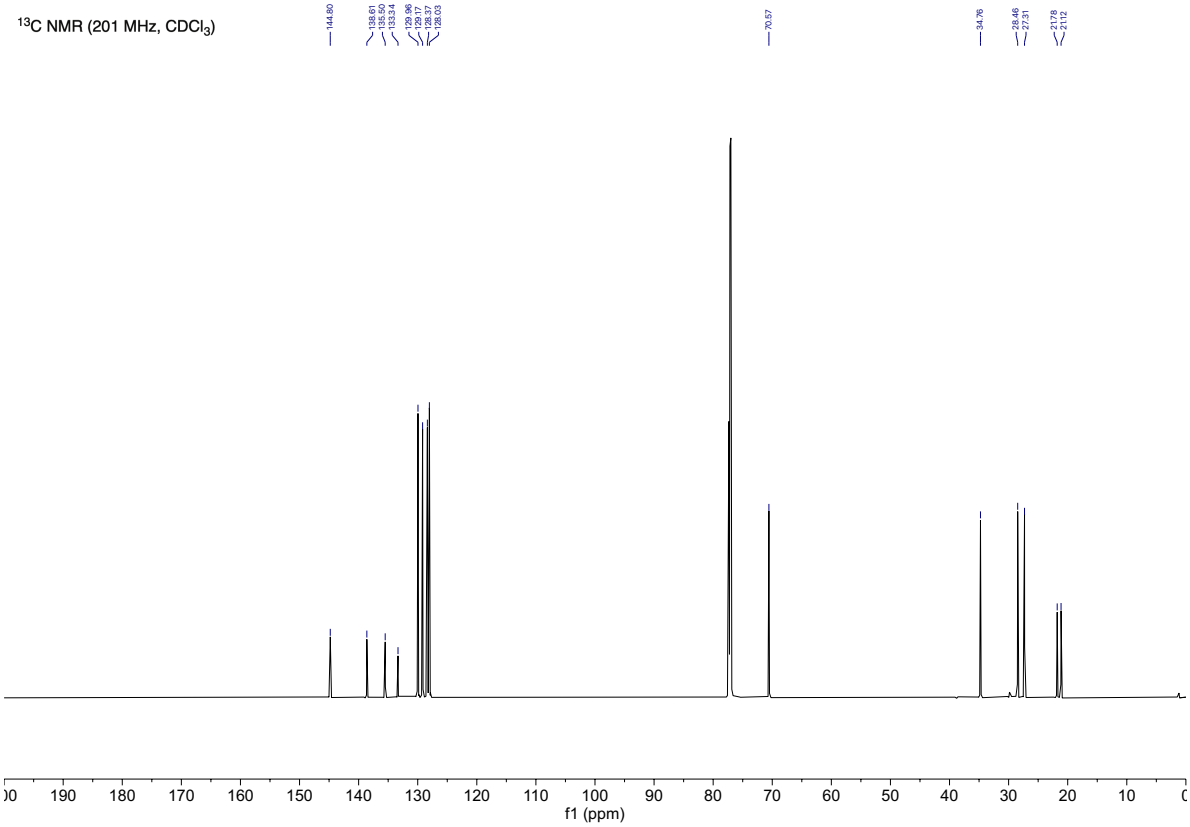


4-(*p*-tolyl)butyl 4-methylbenzenesulfonate (1bb)

^{1}H NMR (800 MHz, $CDCl_3$)

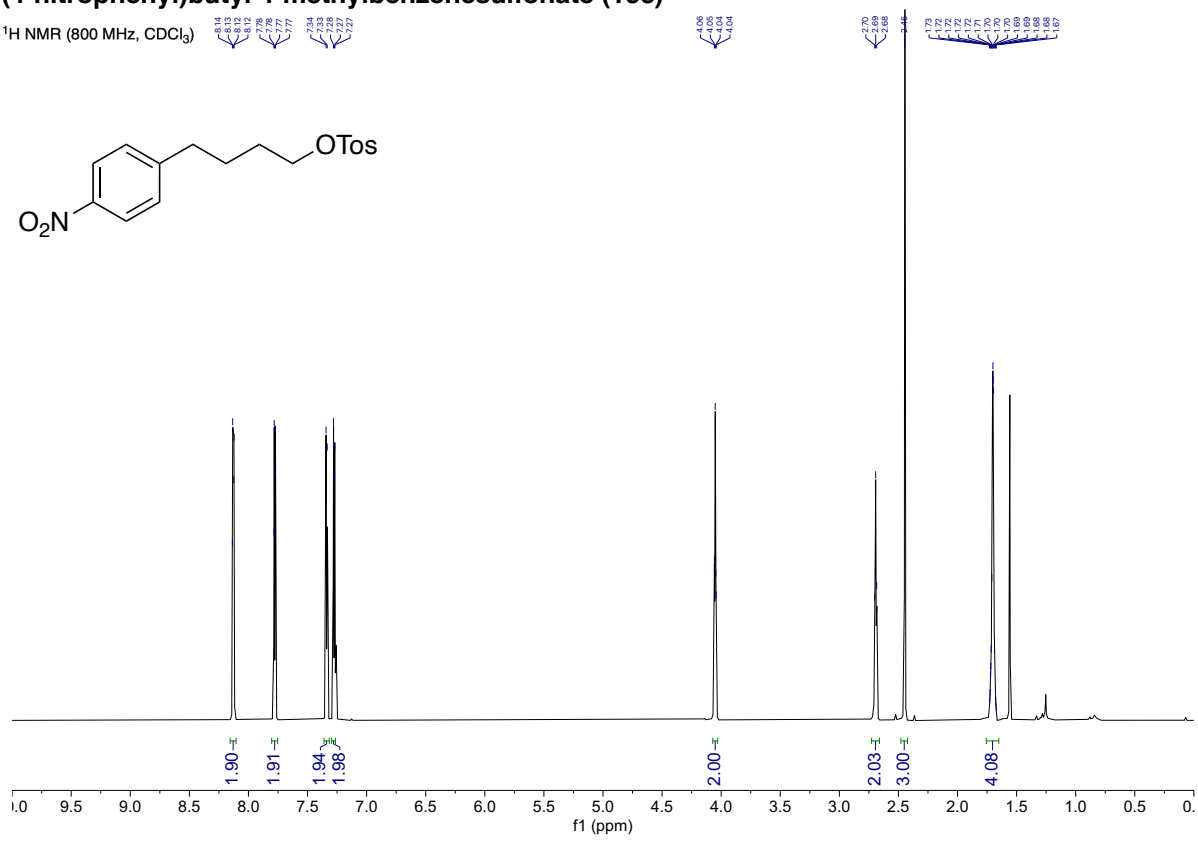


^{13}C NMR (201 MHz, $CDCl_3$)

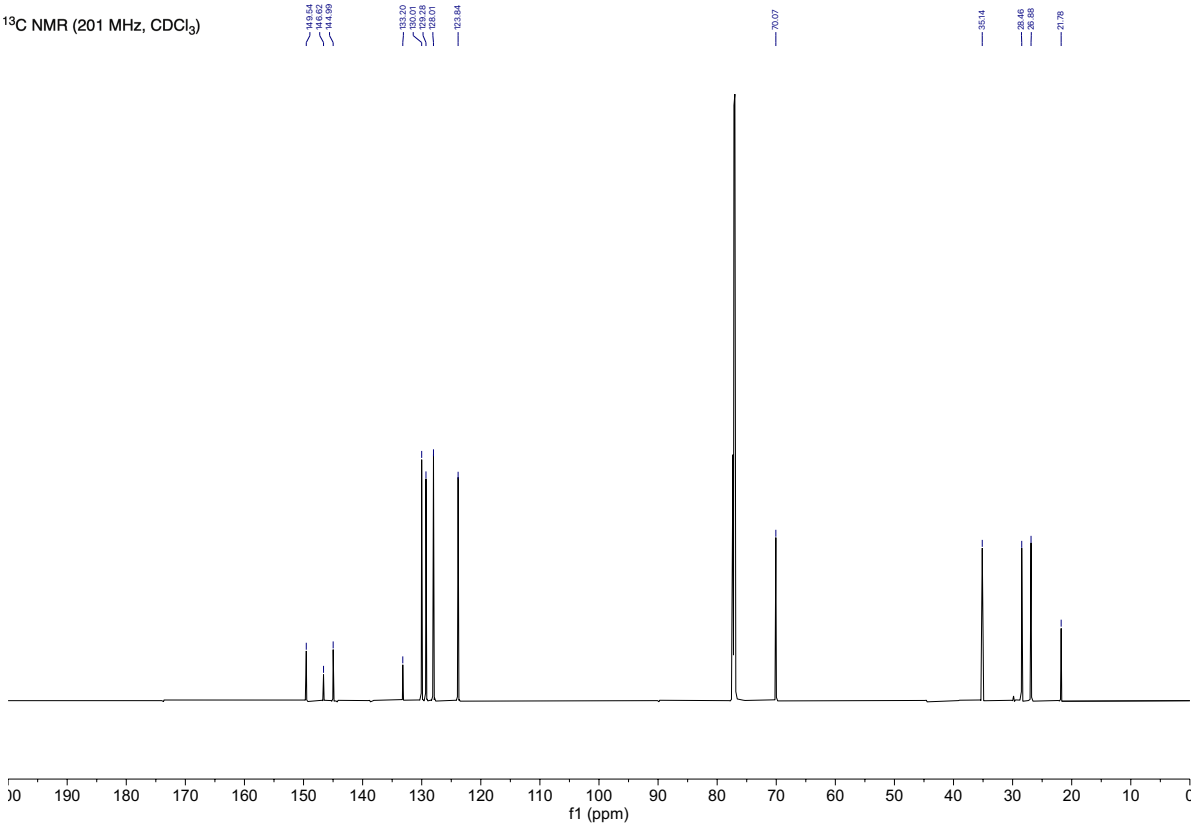


4-(4-nitrophenyl)butyl 4-methylbenzenesulfonate (1cc)

^{1}H NMR (800 MHz, $CDCl_3$)

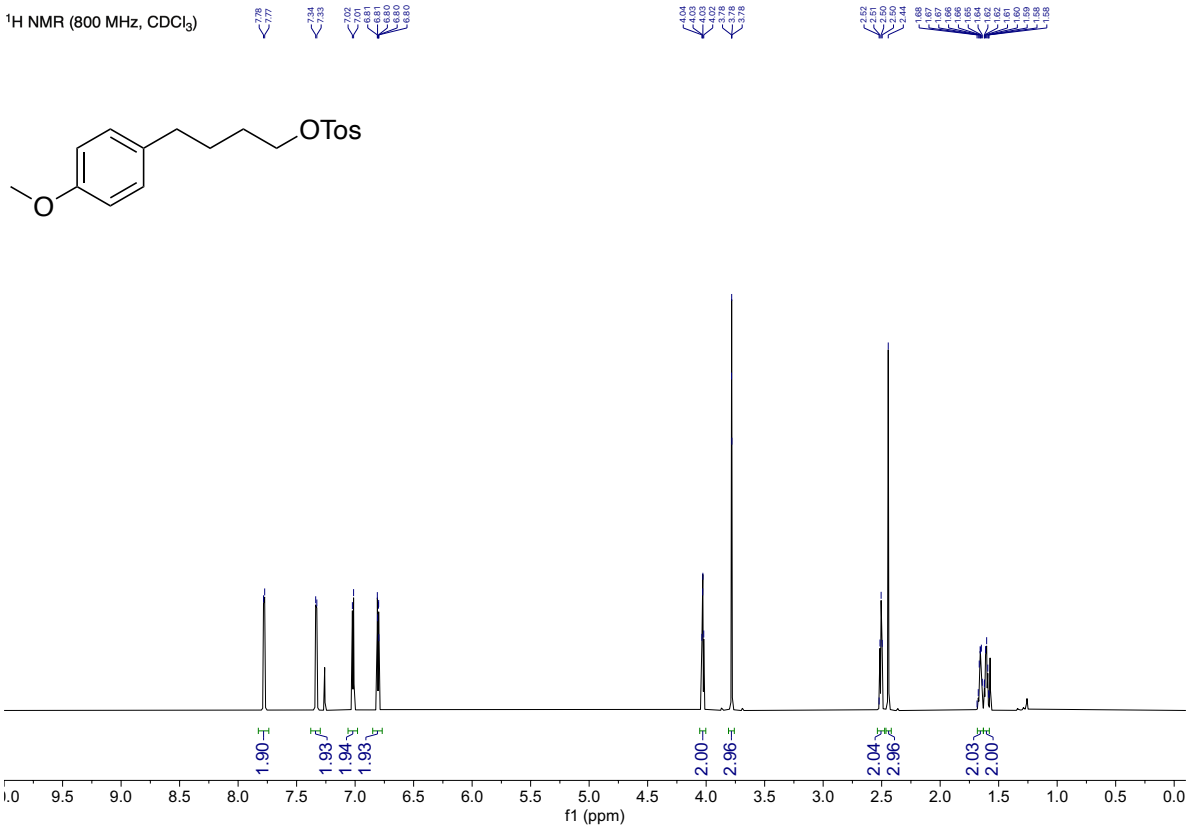


^{13}C NMR (201 MHz, $CDCl_3$)

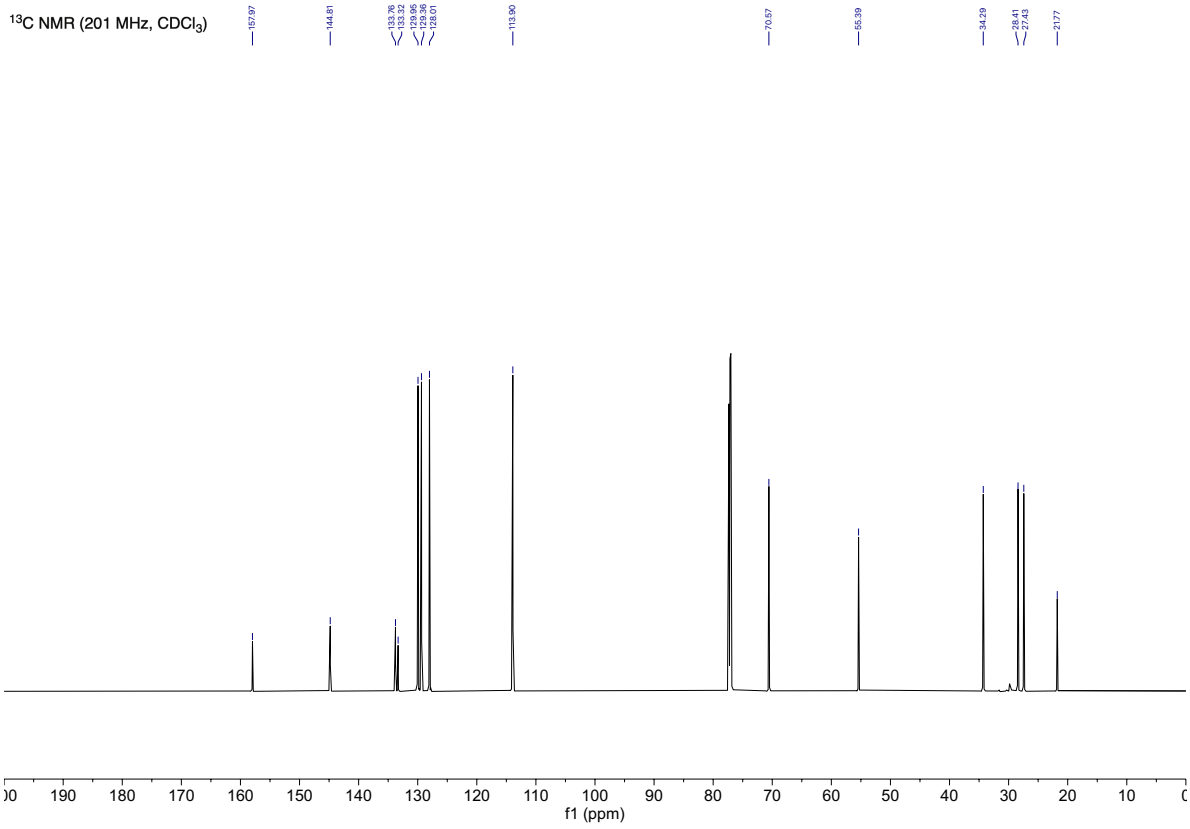


4-(4-methoxyphenyl)butyl-4-methylbenzenesulfonate (1dd)

^{1}H NMR (800 MHz, $CDCl_3$)

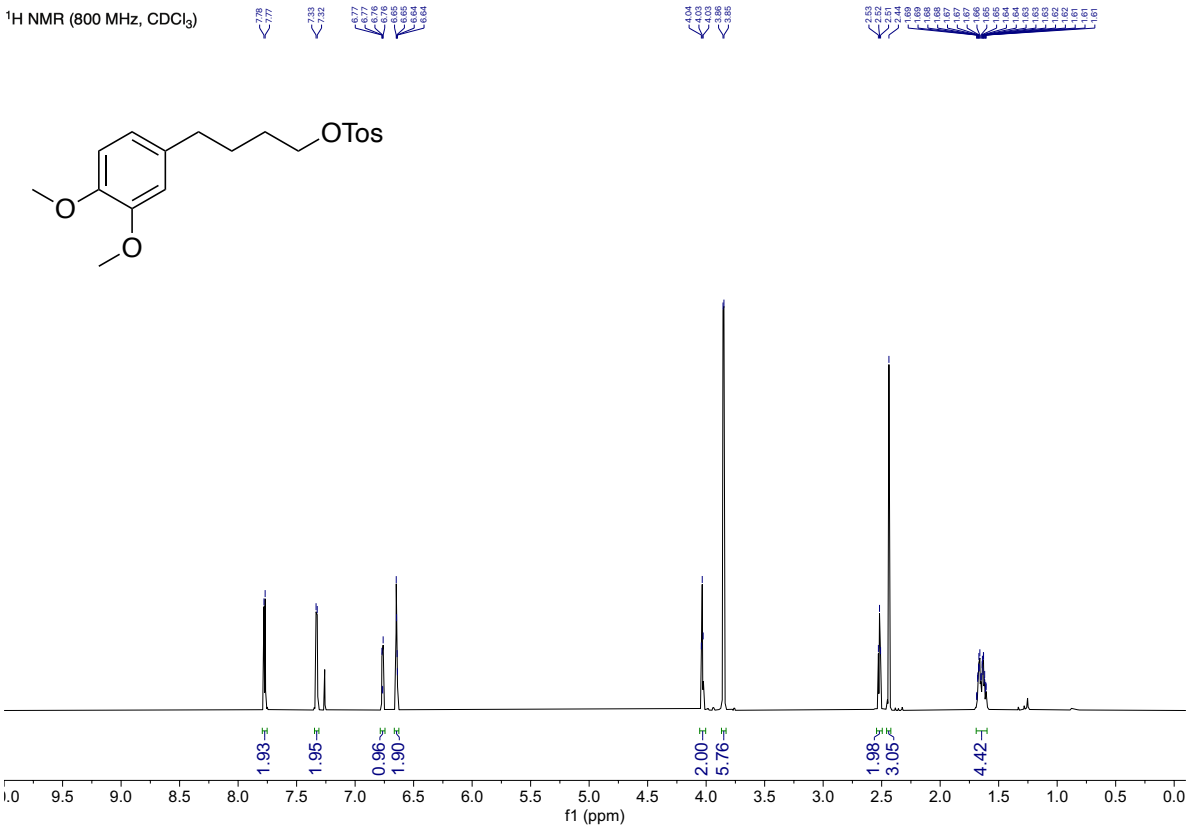


^{13}C NMR (201 MHz, $CDCl_3$)

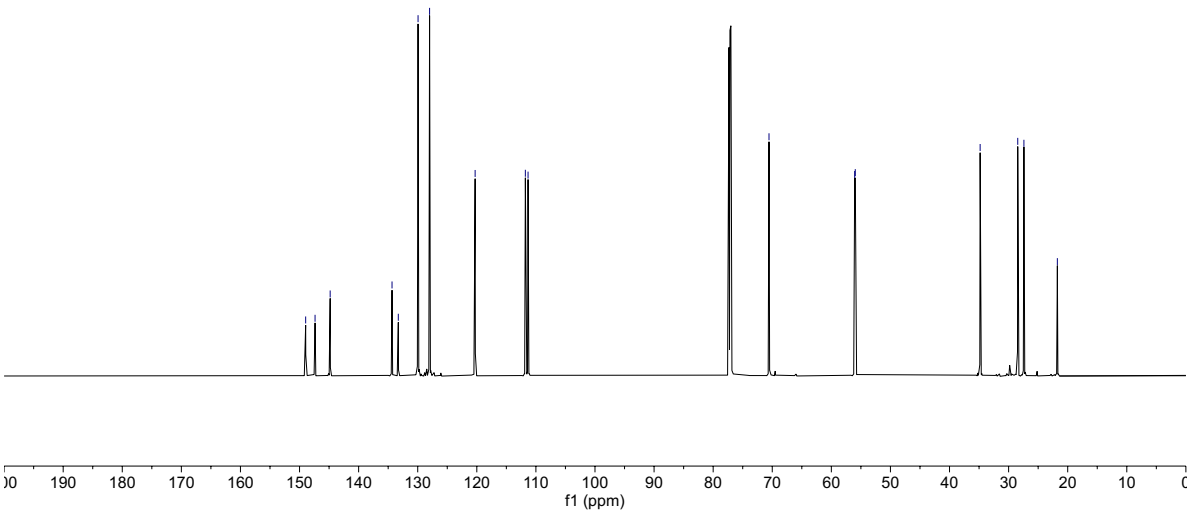


4-(3,4-dimethoxyphenyl)butyl 4-methylbenzenesulfonate (1ee)

^{1}H NMR (800 MHz, $CDCl_3$)

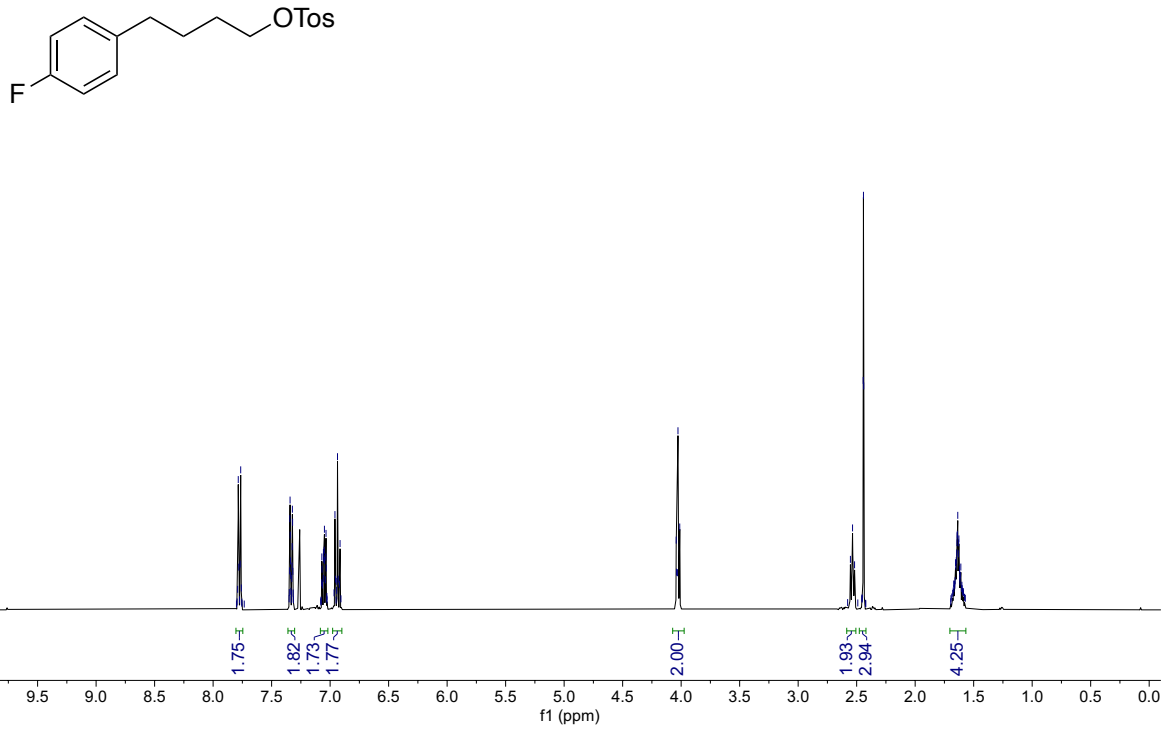


^{13}C NMR (201 MHz, $CDCl_3$)

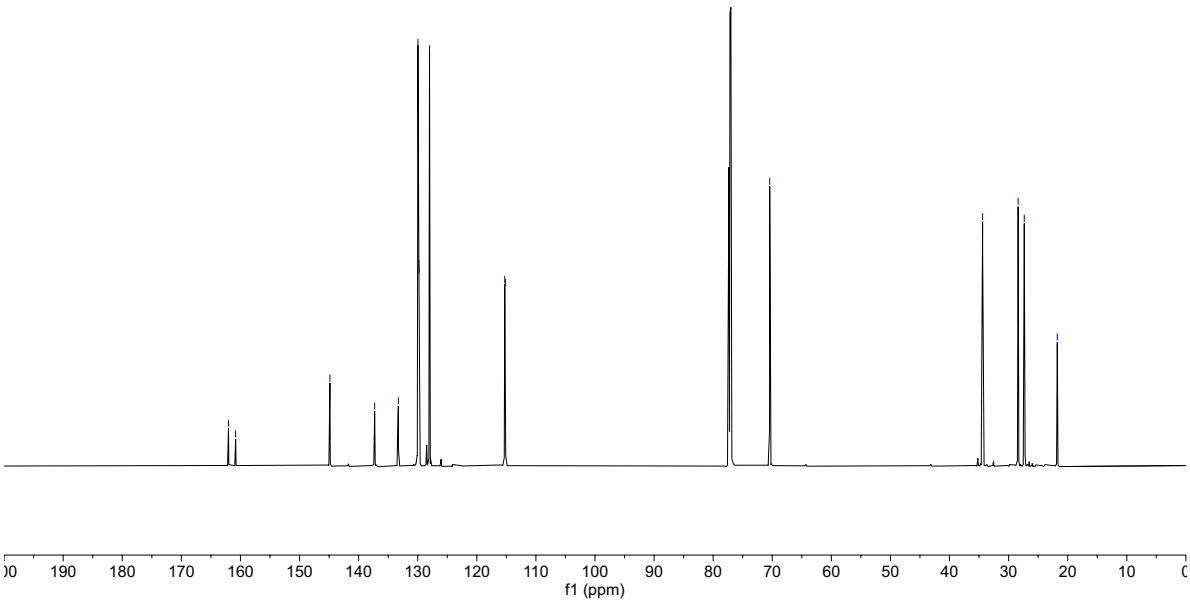


4-(4-fluorophenyl)butyl 4-methylbenzenesulfonate (1ff)

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

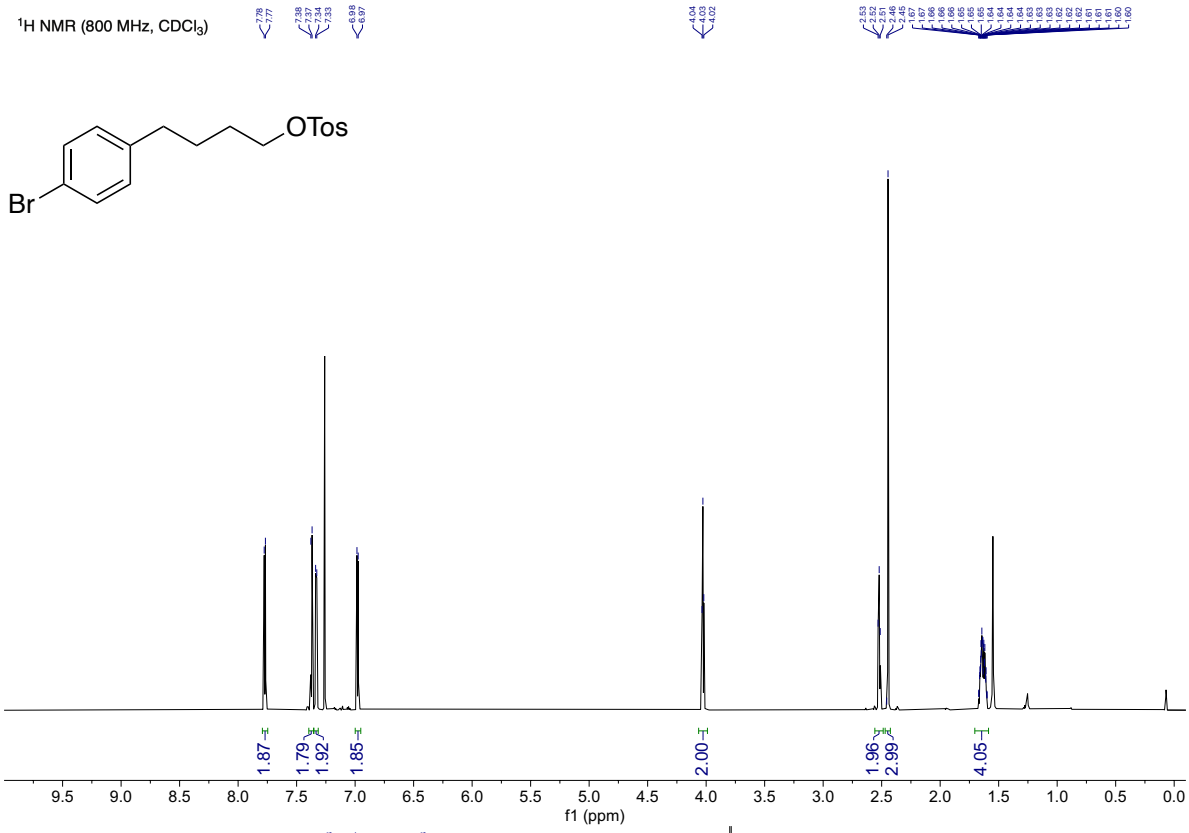


^{13}C NMR (201 MHz, $CDCl_3$)

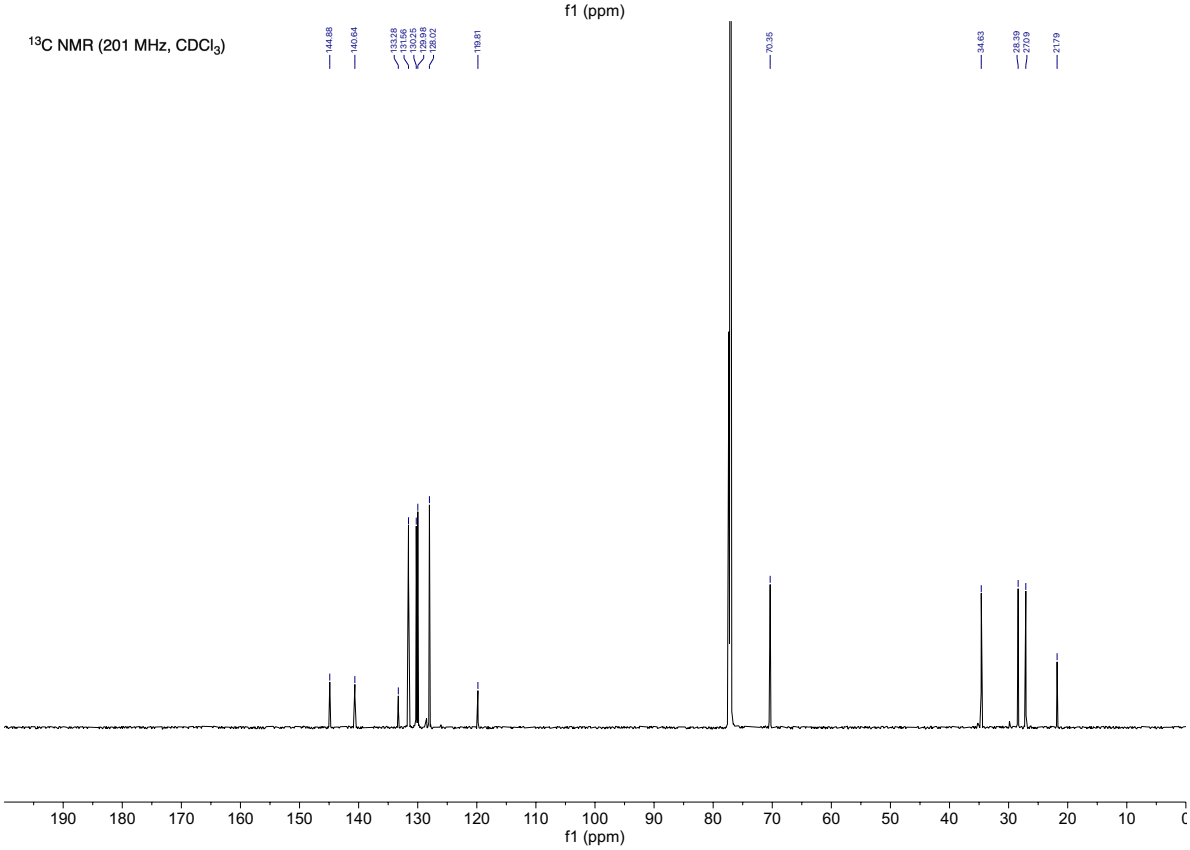


4-(4-bromophenyl)butyl 4-methylbenzenesulfonate (1hh)

^{1}H NMR (800 MHz, $CDCl_3$)

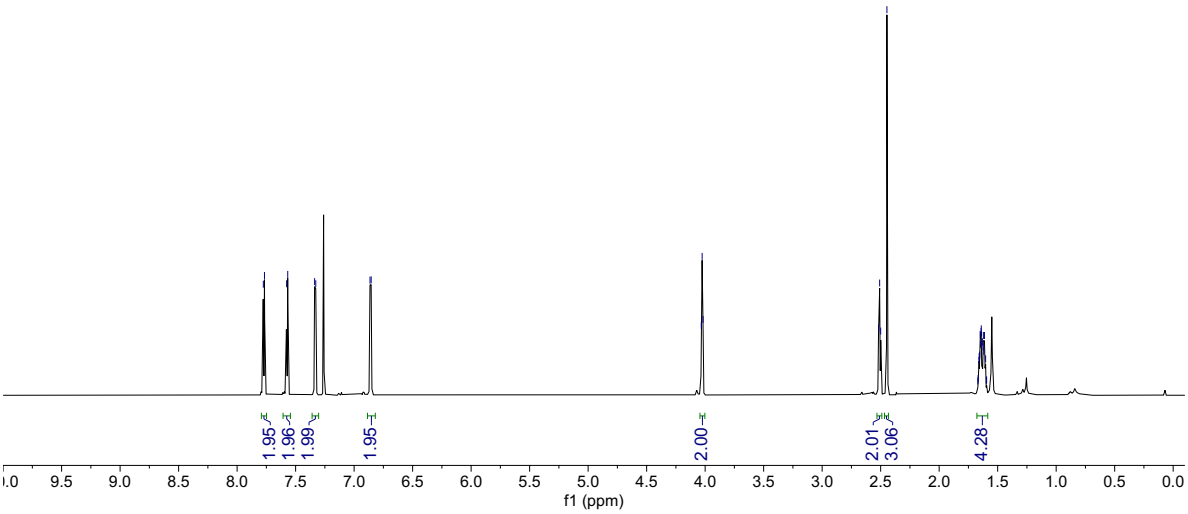


^{13}C NMR (201 MHz, $CDCl_3$)

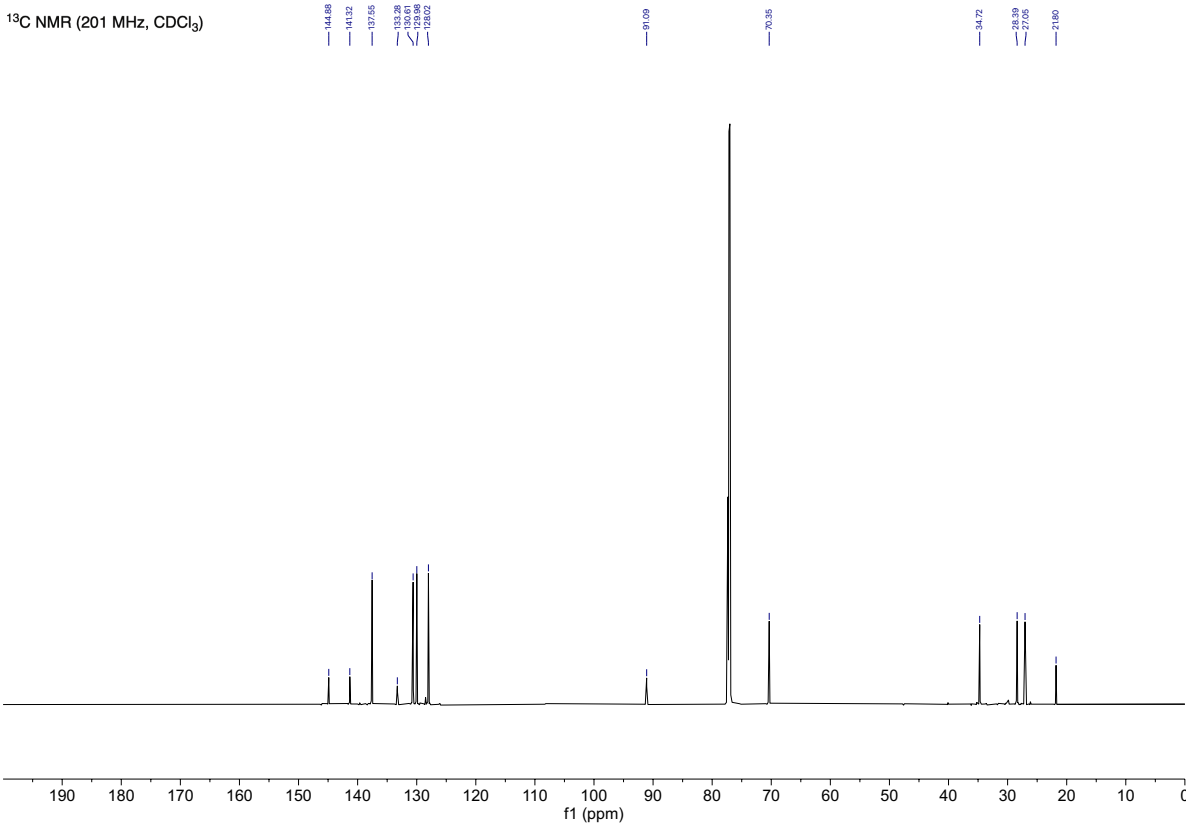


4-(4-iodophenyl)butyl 4-methylbenzenesulfonate (1ii)

^{1}H NMR (800 MHz, $CDCl_3$)

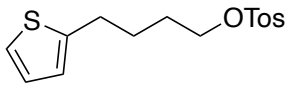


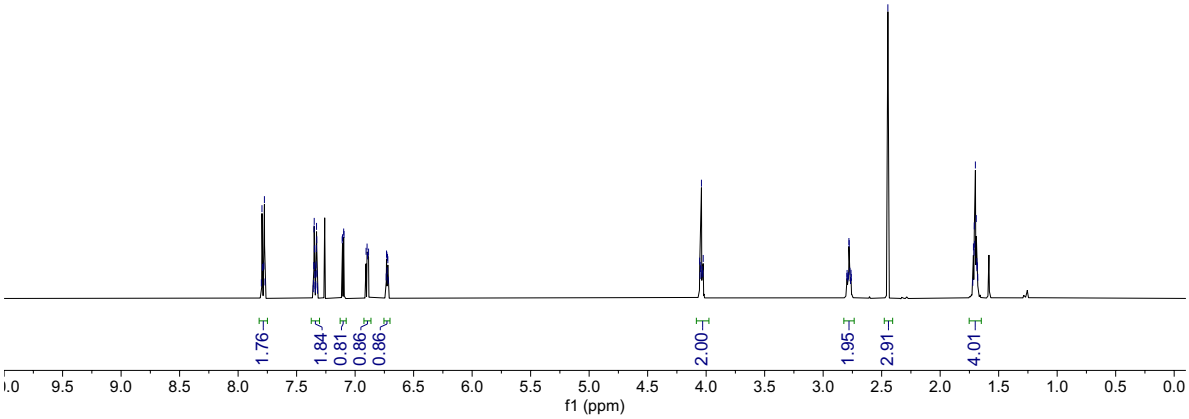
^{13}C NMR (201 MHz, $CDCl_3$)



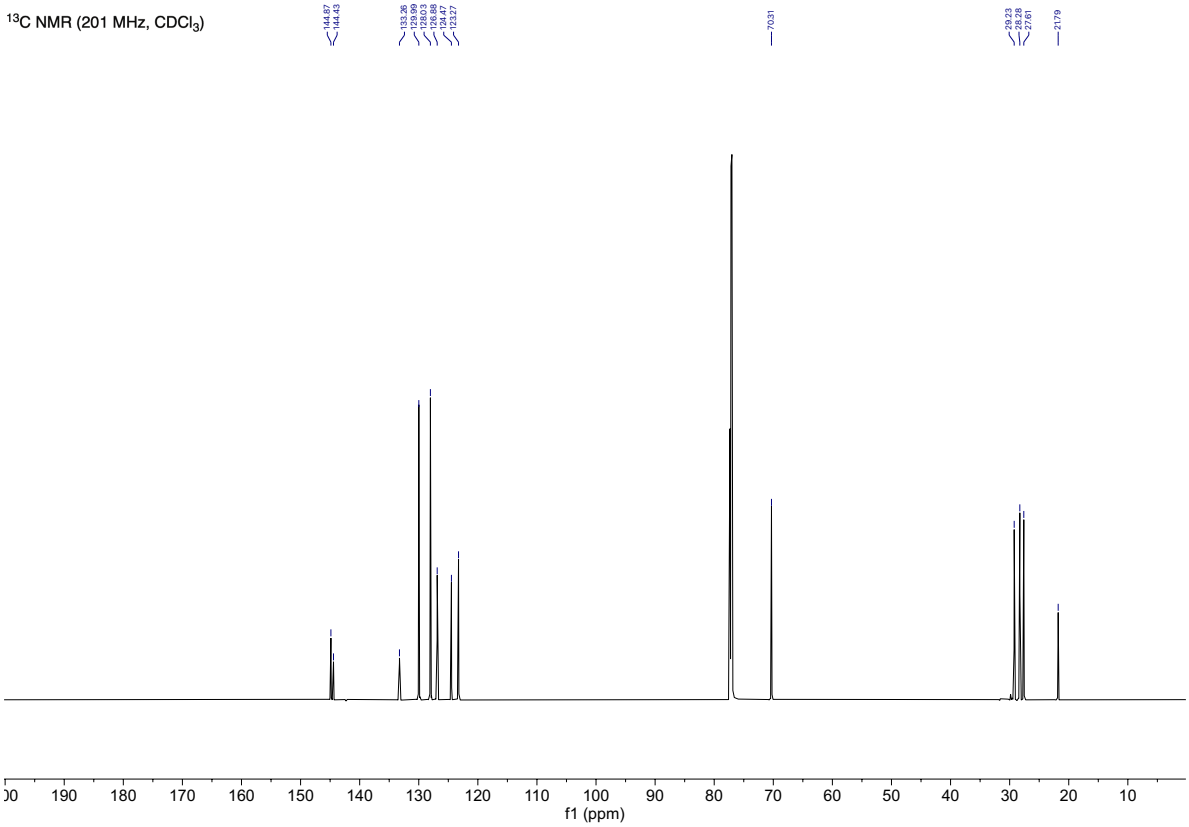
4-(thiophen-2-yl)butyl 4-methylbenzenesulfonate (1jj)

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



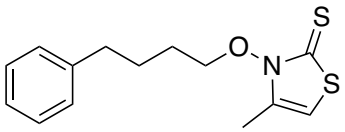


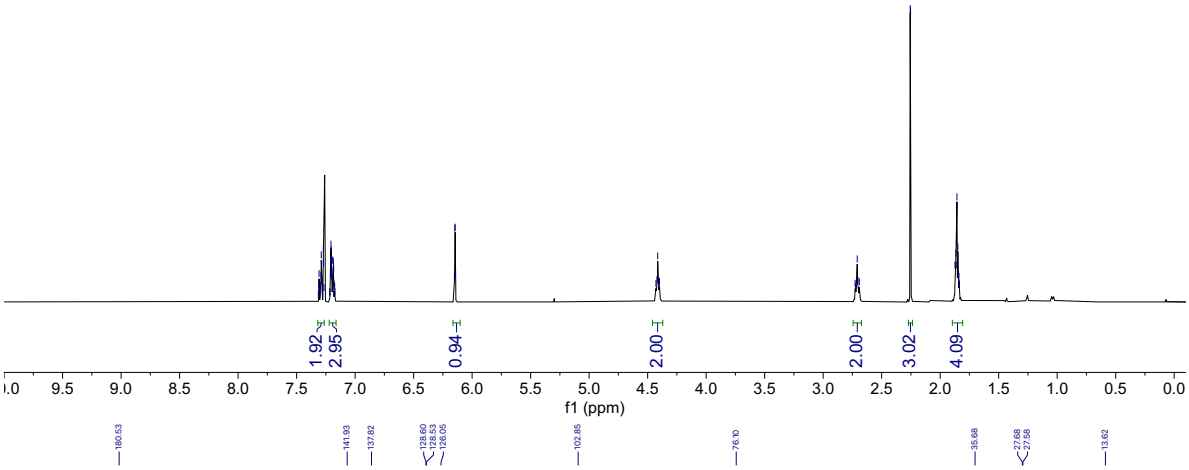
^{13}C NMR (201 MHz, $CDCl_3$)



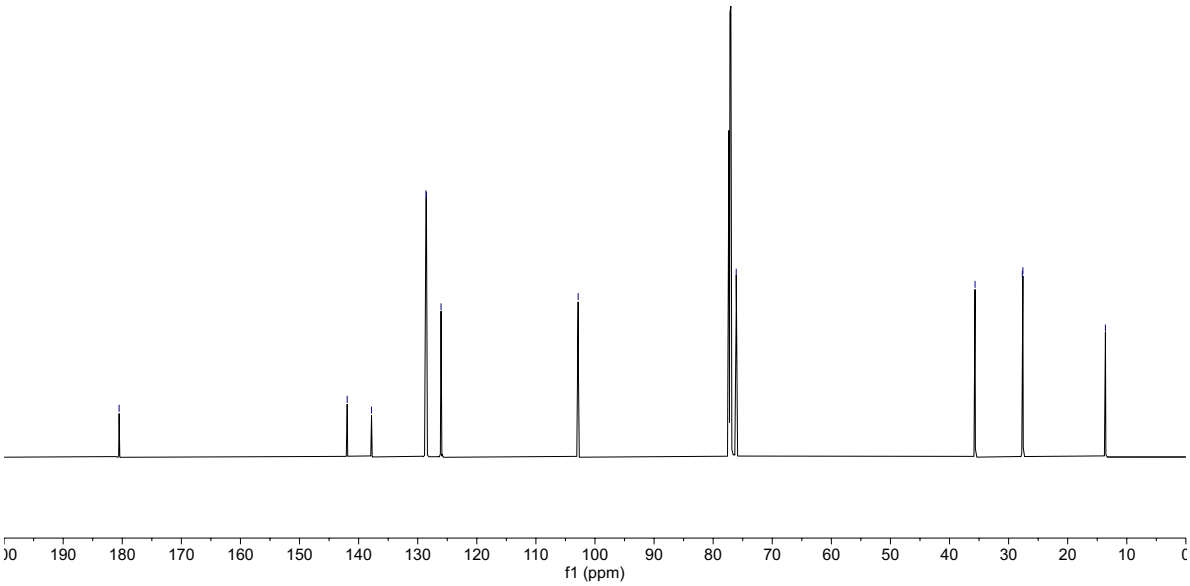
N-alkoxythiazolethione (1a)

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



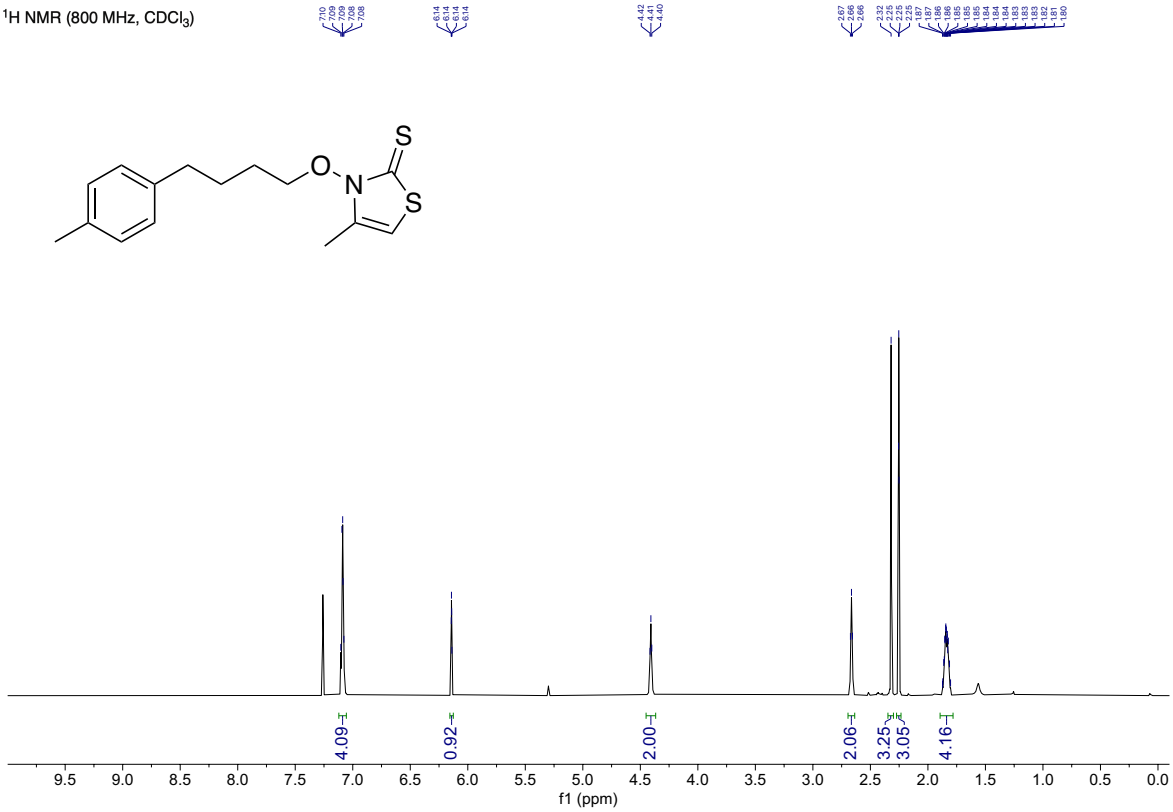


^{13}C NMR (201 MHz, $CDCl_3$)

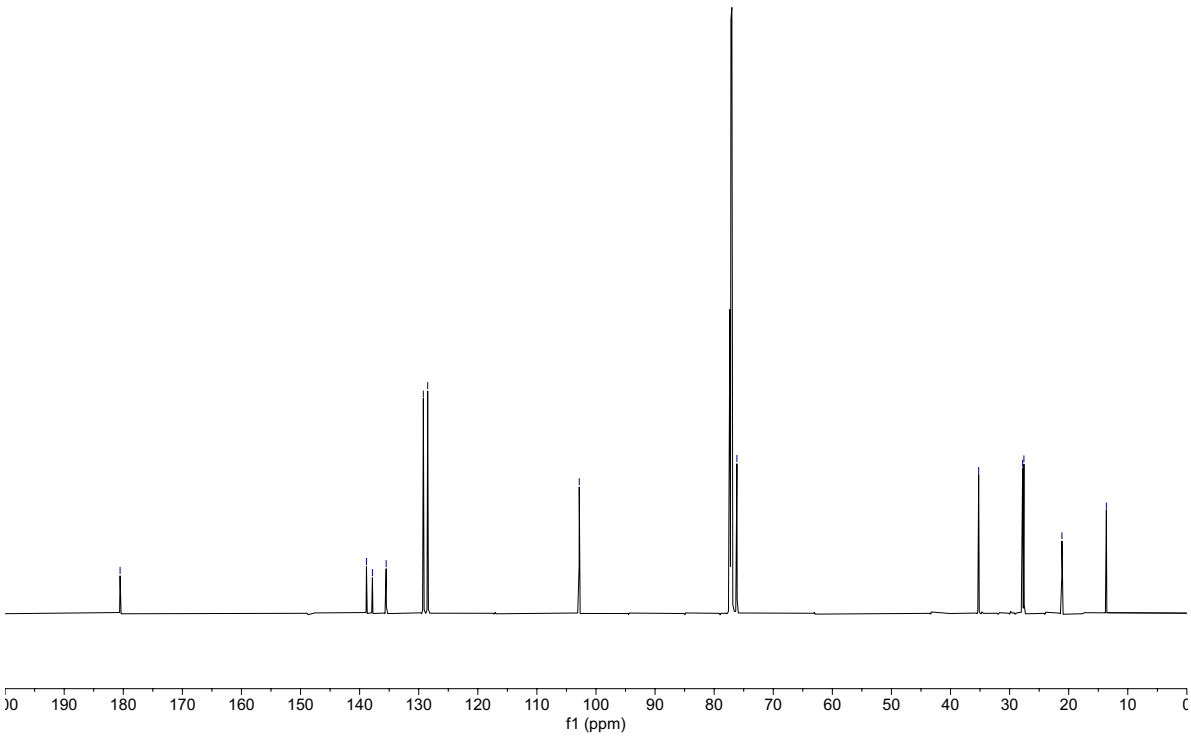


N-alkoxythiazolethione (1b)

^{1}H NMR (800 MHz, $CDCl_3$)

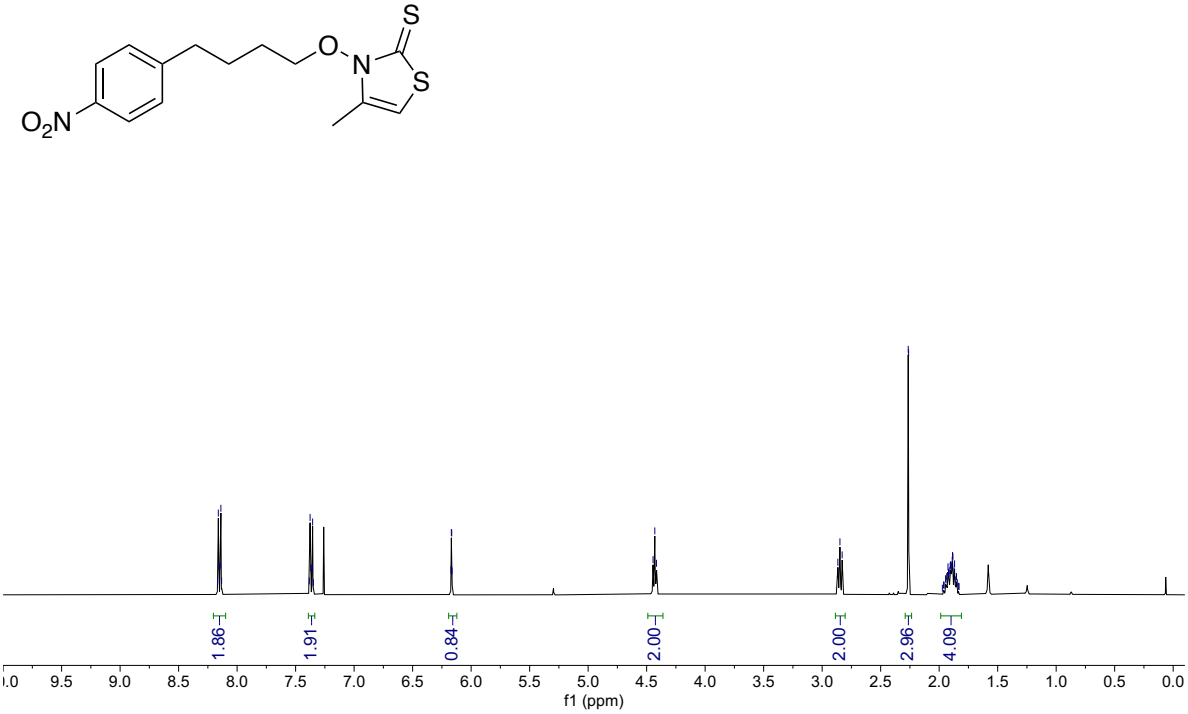


^{13}C NMR (201 MHz, $CDCl_3$)

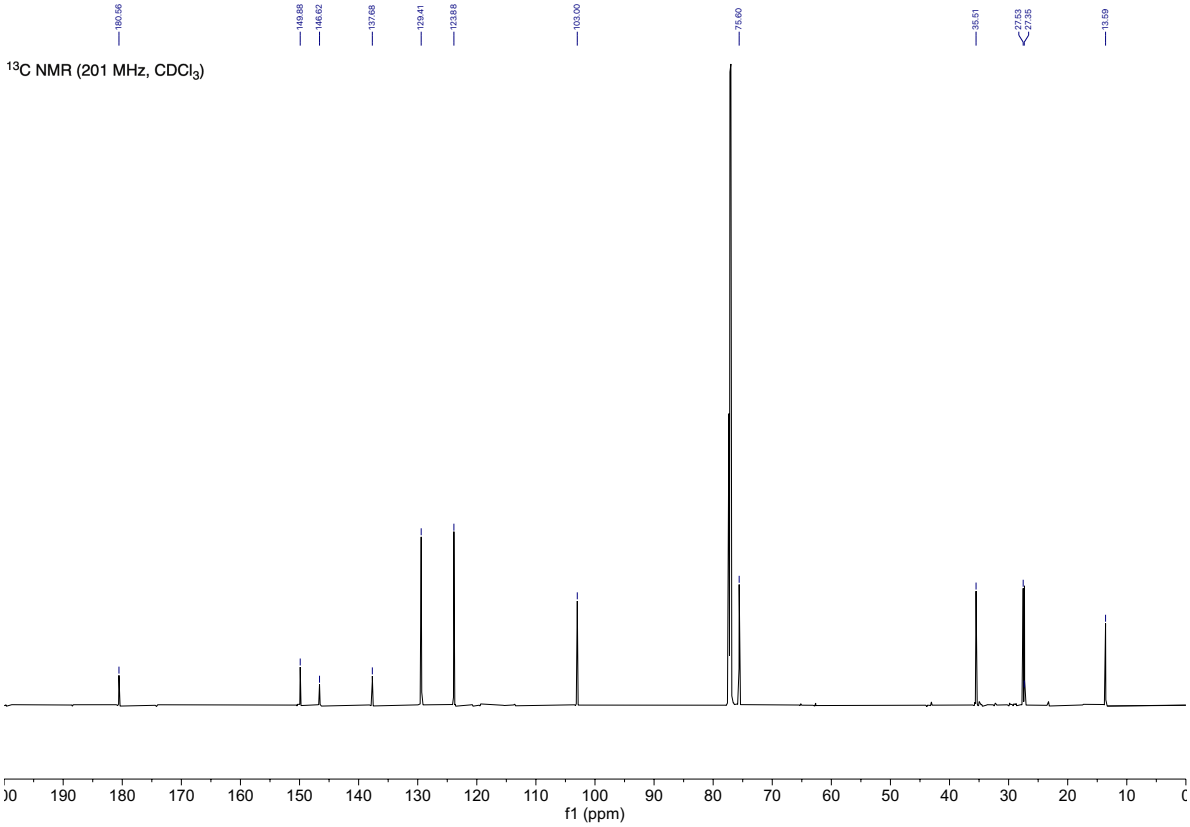


N-alkoxythiazolethione (1c)

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

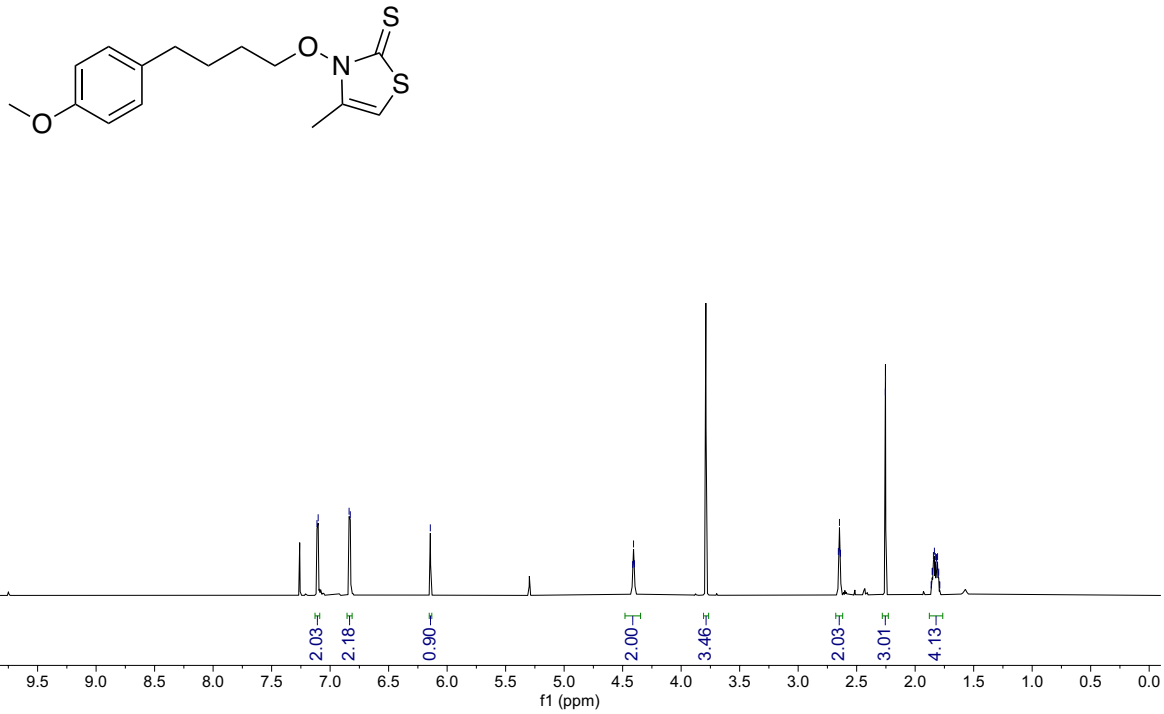


^{13}C NMR (201 MHz, $CDCl_3$)

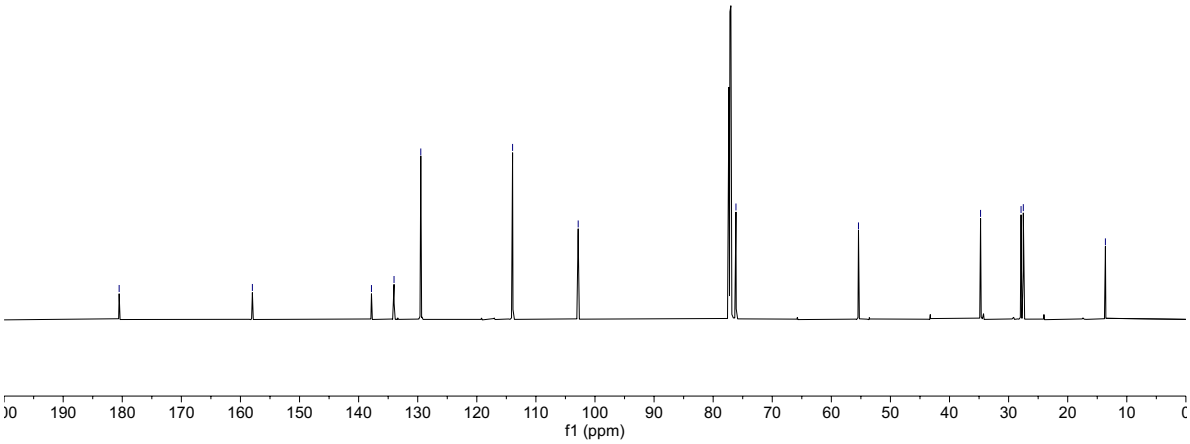


N-alkoxythiazolethione (1d)

^{1}H NMR (800 MHz, $CDCl_3$)

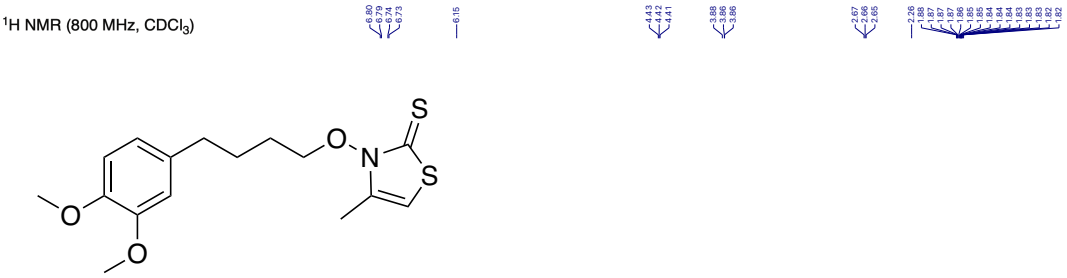


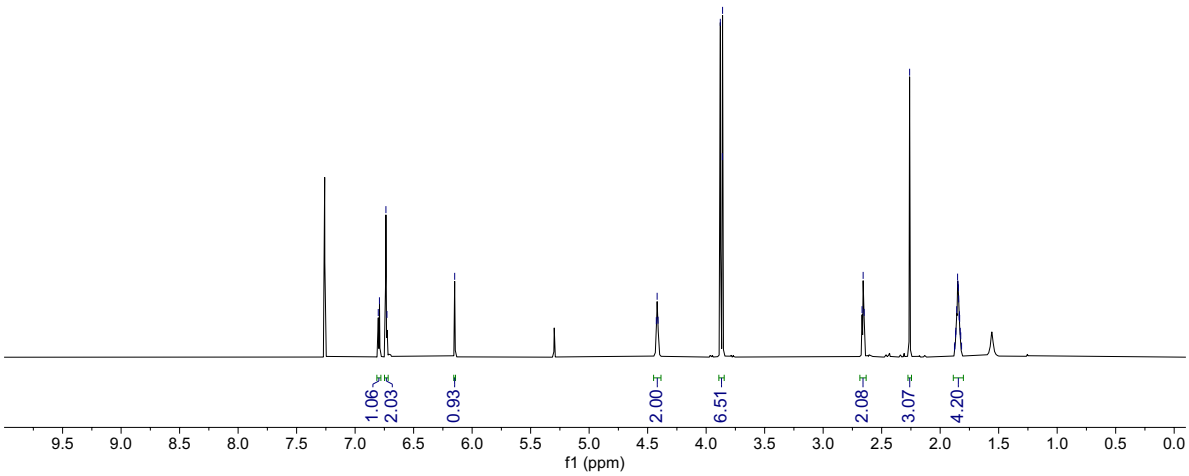
^{13}C NMR (201 MHz, $CDCl_3$)



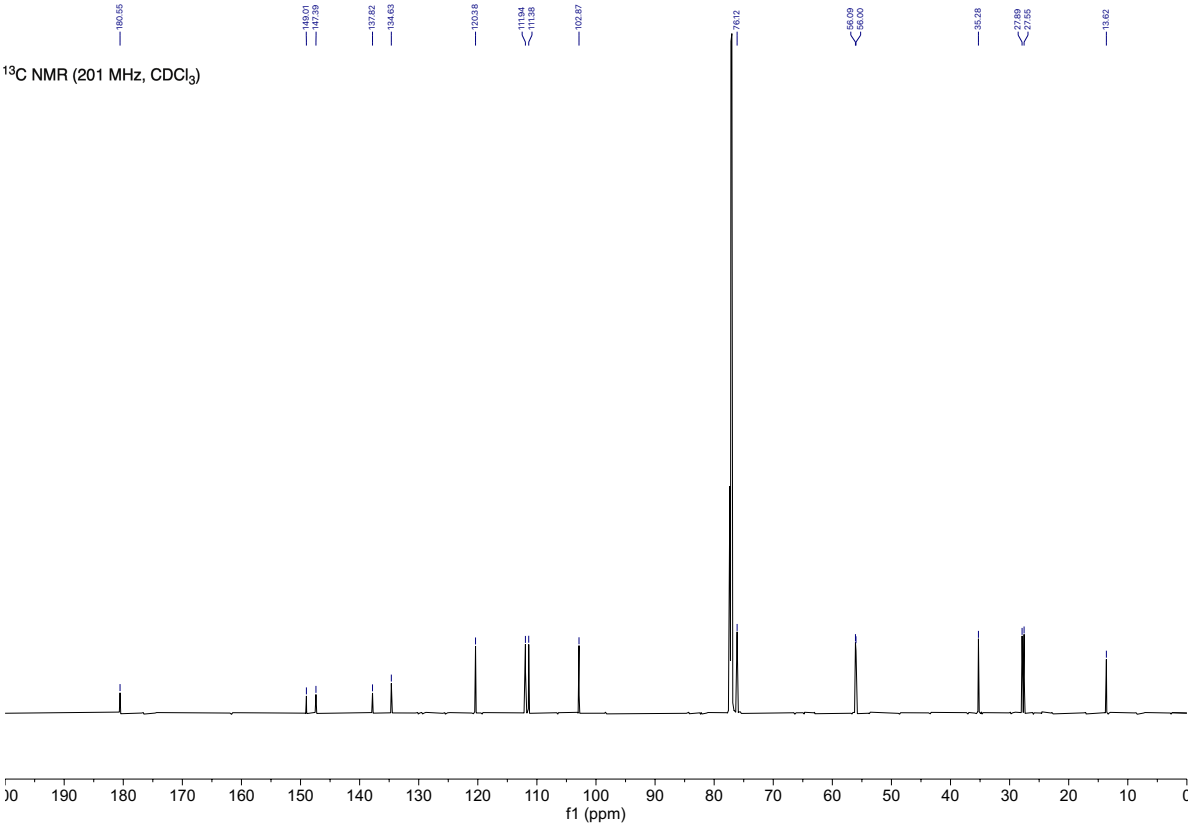
N-alkoxythiazolethione (1e)

^{1}H NMR (800 MHz, $CDCl_3$)



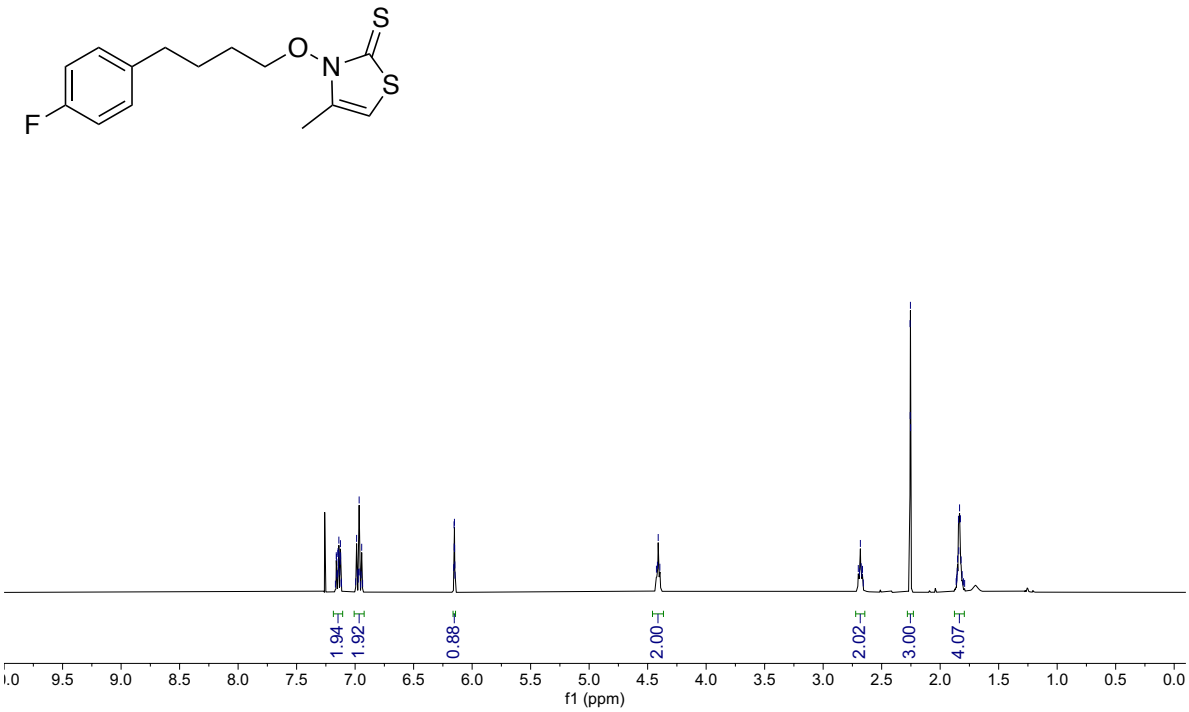


^{13}C NMR (201 MHz, $CDCl_3$)

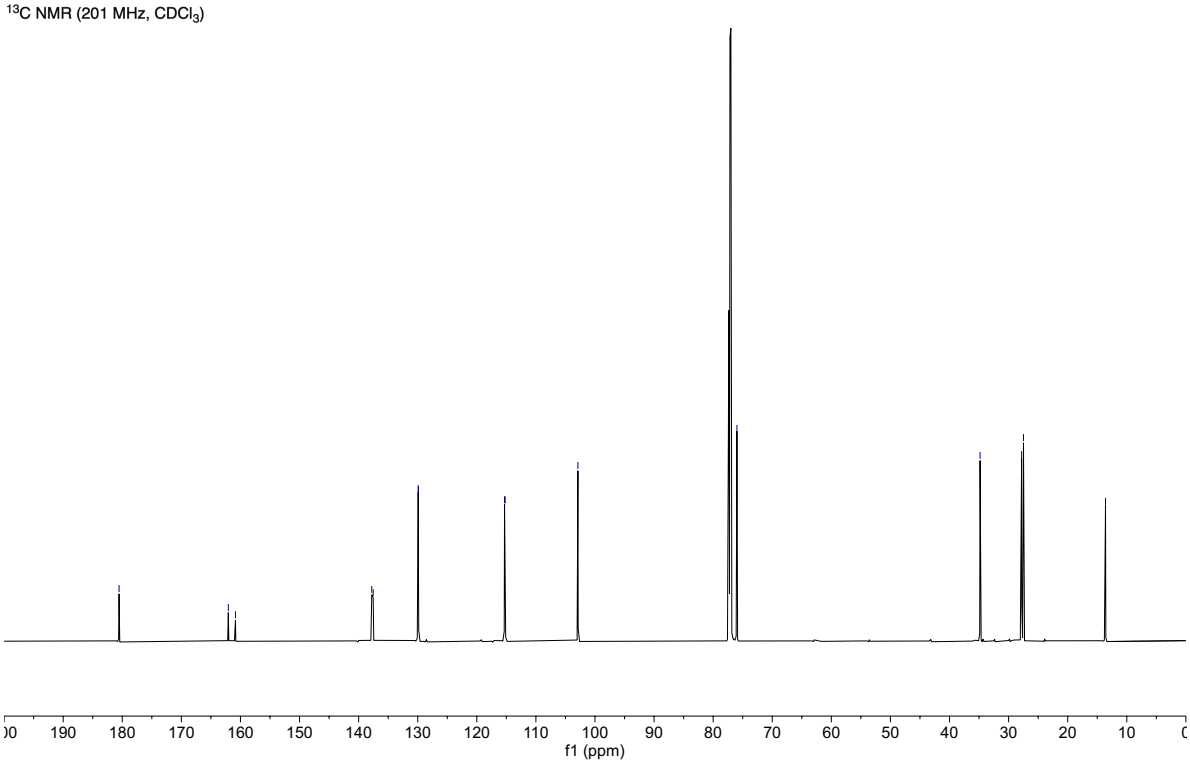


N-alkoxythiazolethione (1f)

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

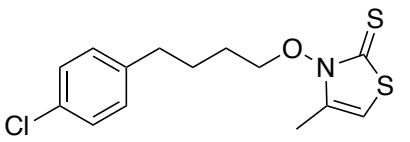


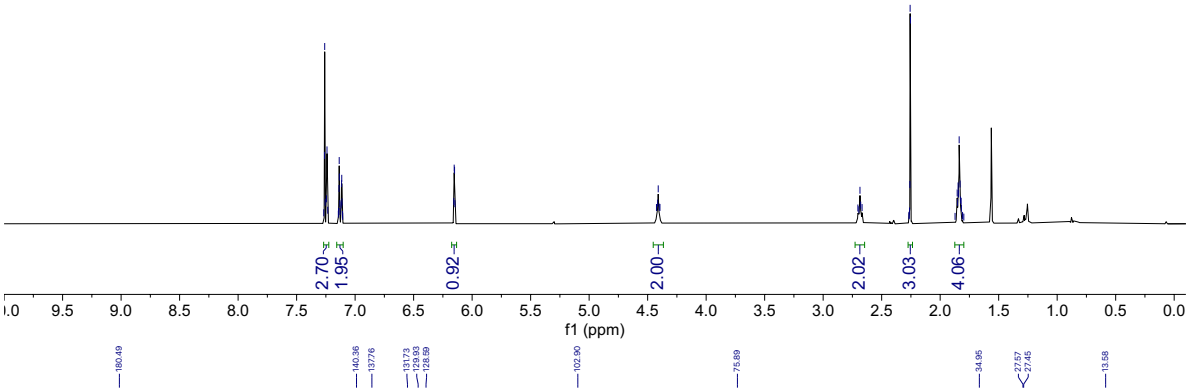
^{13}C NMR (201 MHz, $CDCl_3$)



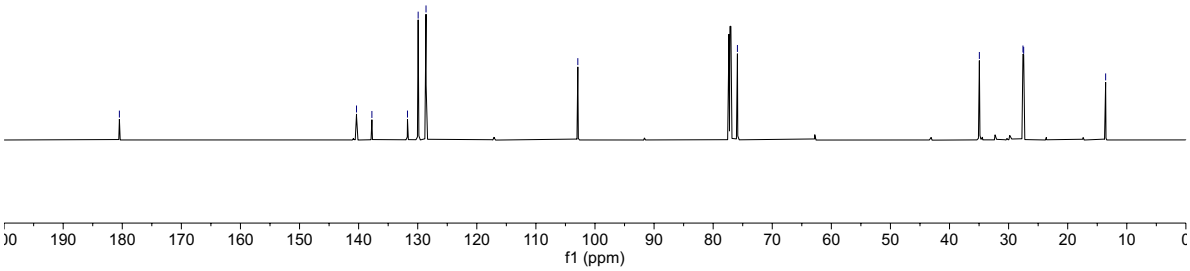
N-alkoxythiazolethione (1g)

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



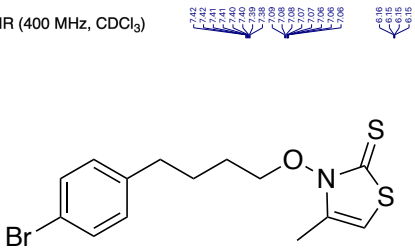


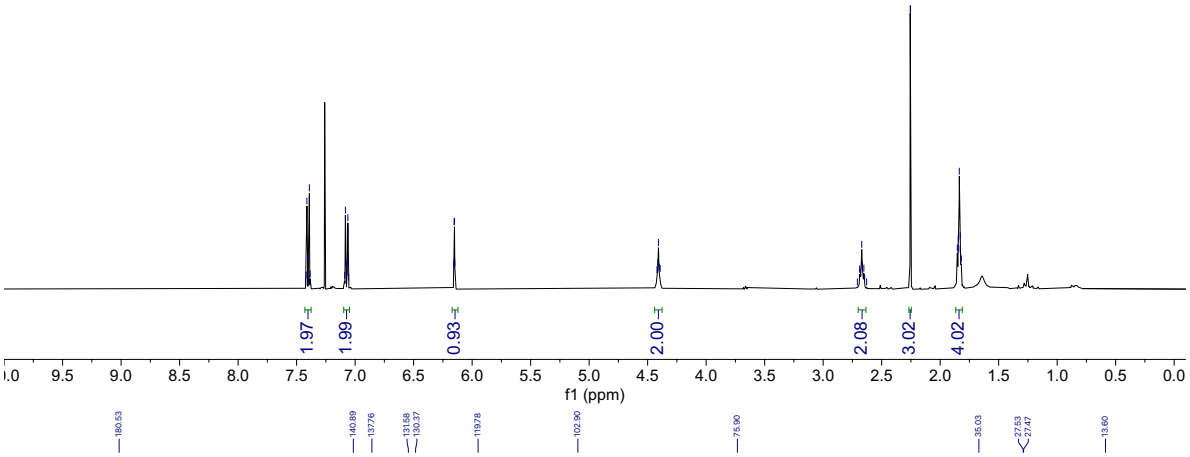
^{13}C NMR (201 MHz, $CDCl_3$)



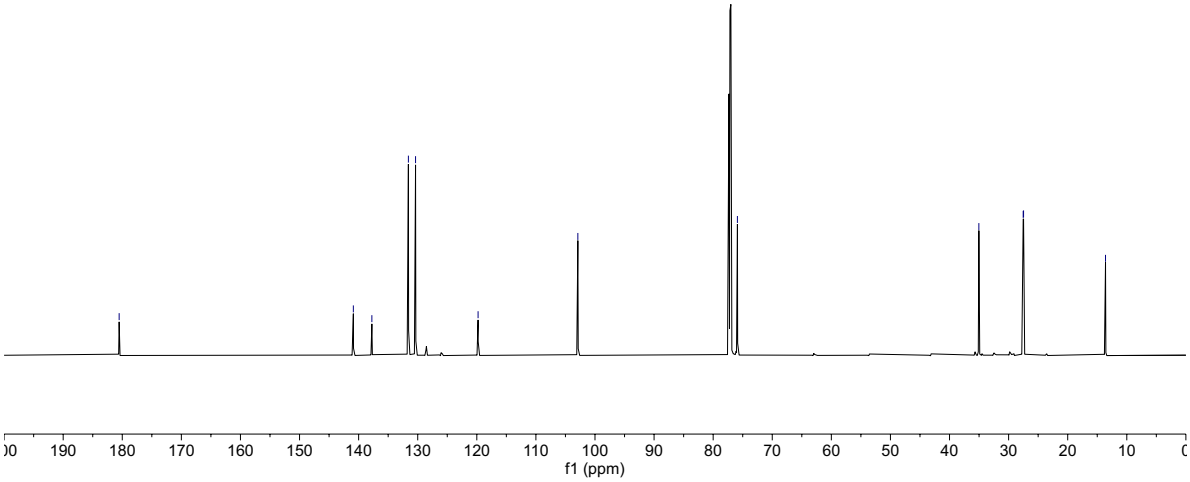
N-alkoxythiazolethione (1h)

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



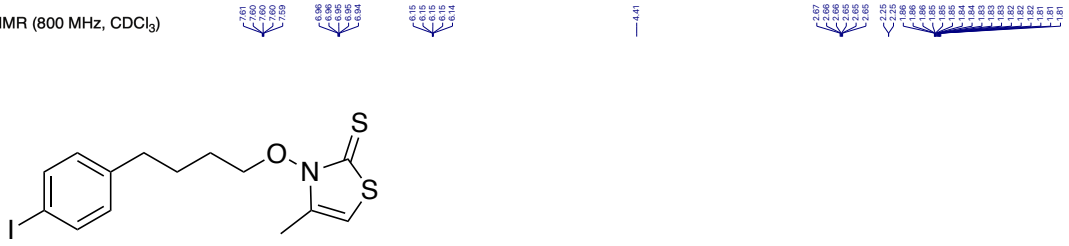


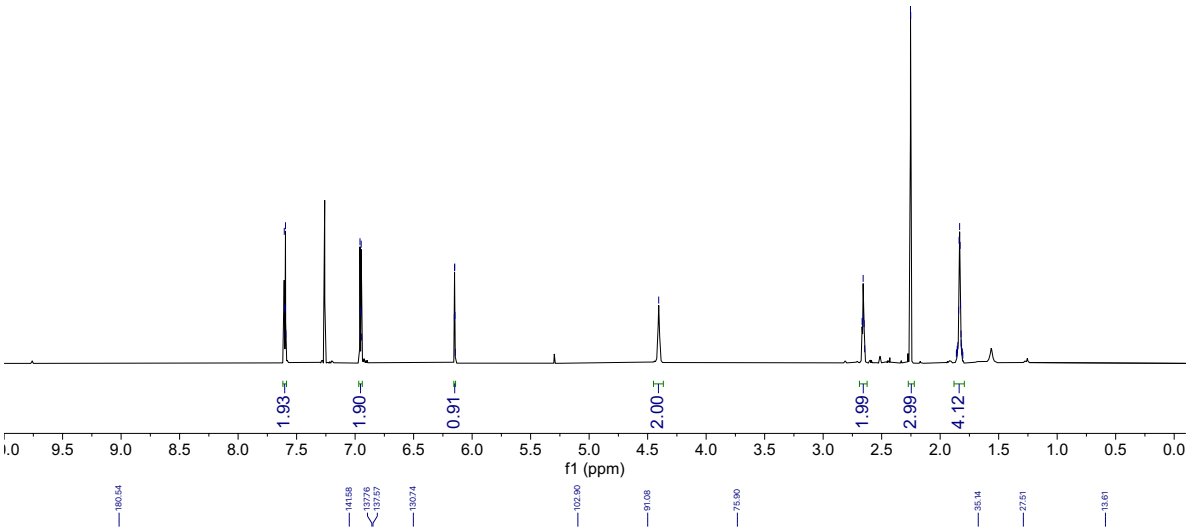
^{13}C NMR (201 MHz, $CDCl_3$)



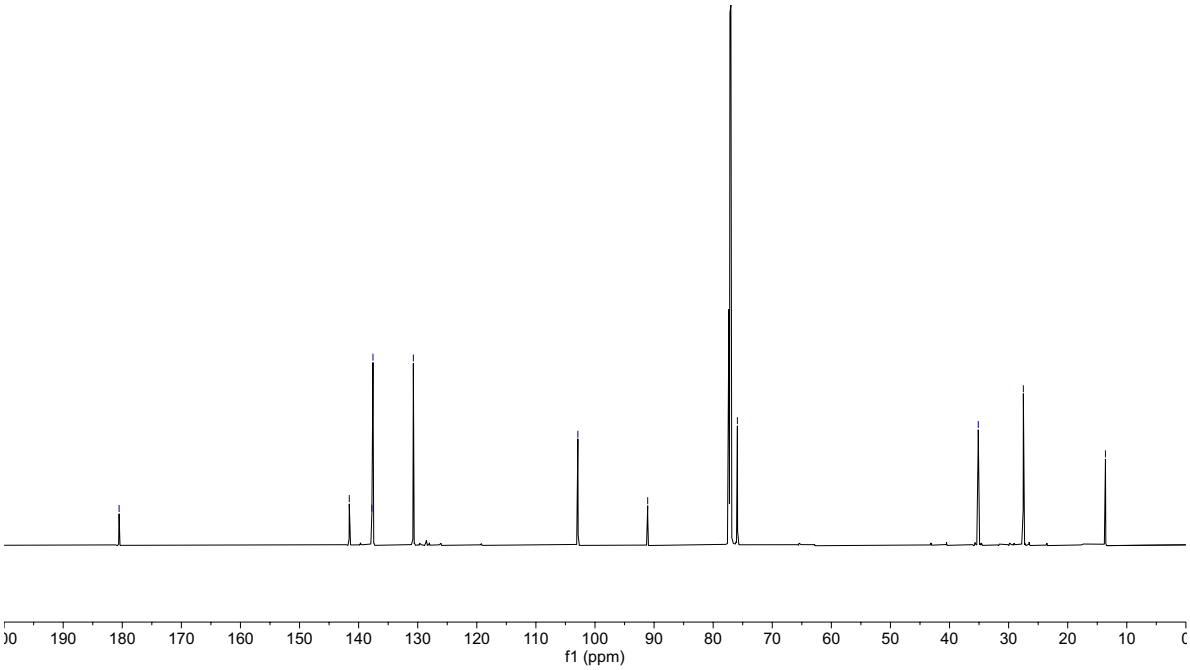
N-alkoxythiazolethione (1i)

^{1}H NMR (800 MHz, $CDCl_3$)



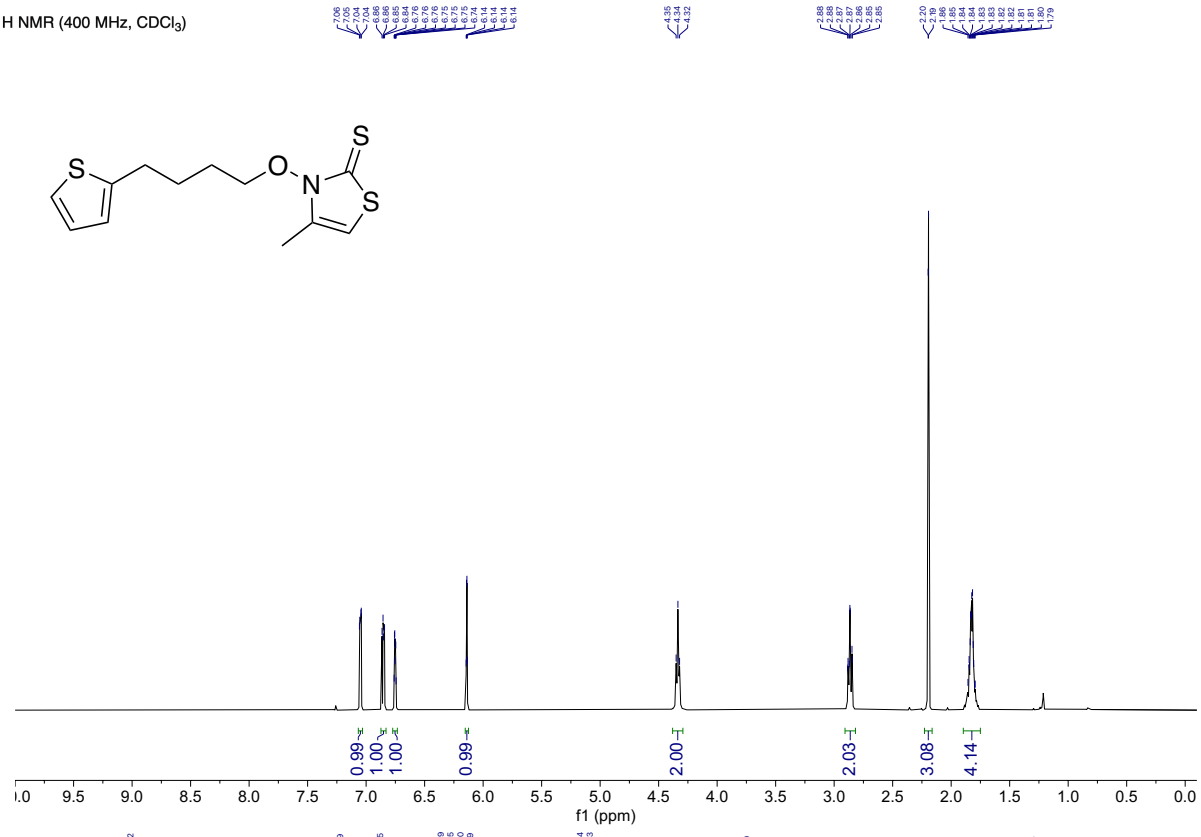


^{13}C NMR (201 MHz, $CDCl_3$)

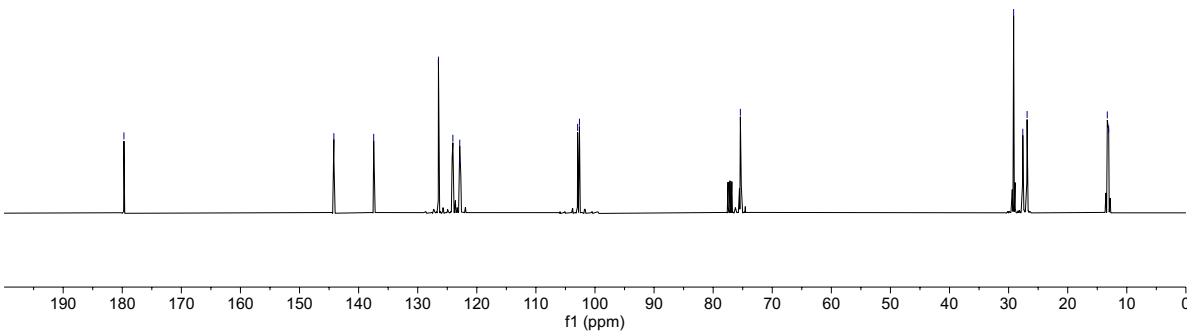


N-alkoxythiazolethione (1j)

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

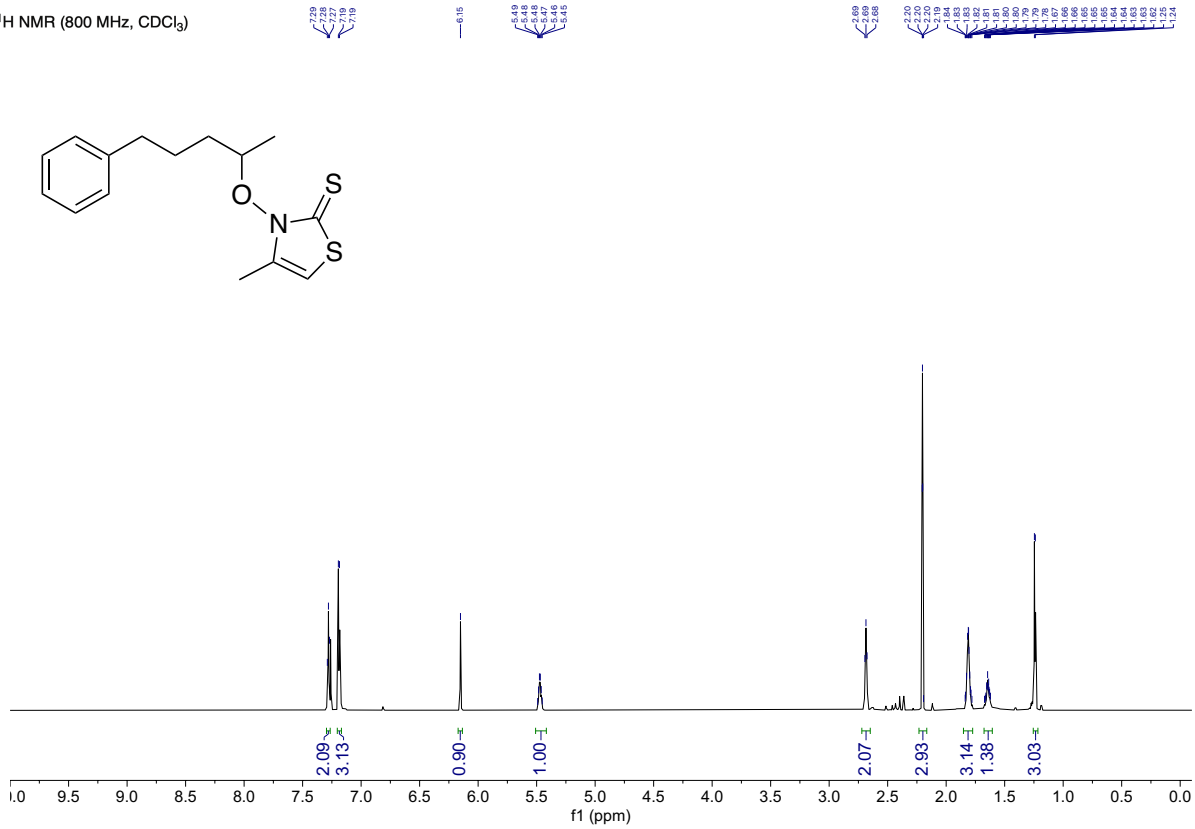


^{13}C NMR (101 MHz, $CDCl_3$)

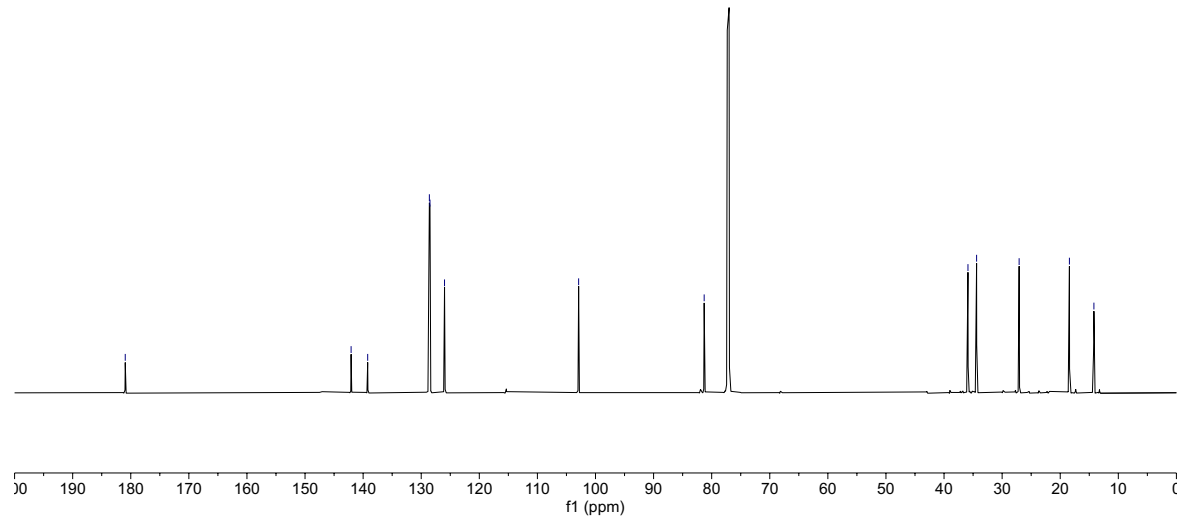


N-alkoxythiazolethione (1k)

^{1}H NMR (800 MHz, $CDCl_3$)

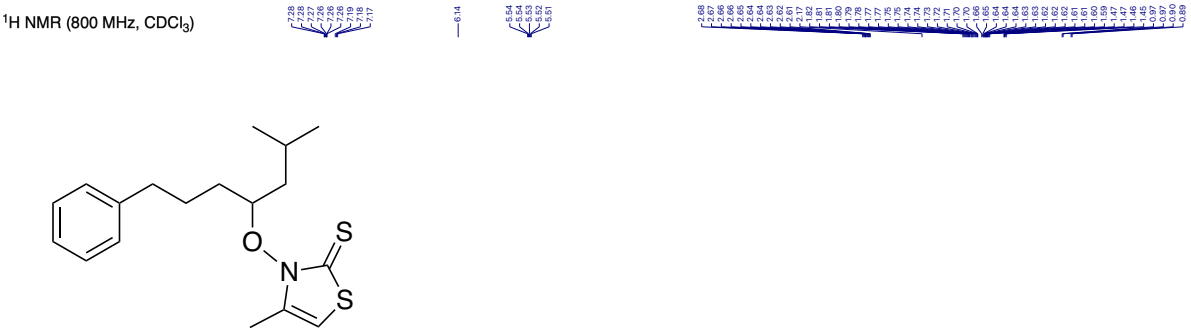


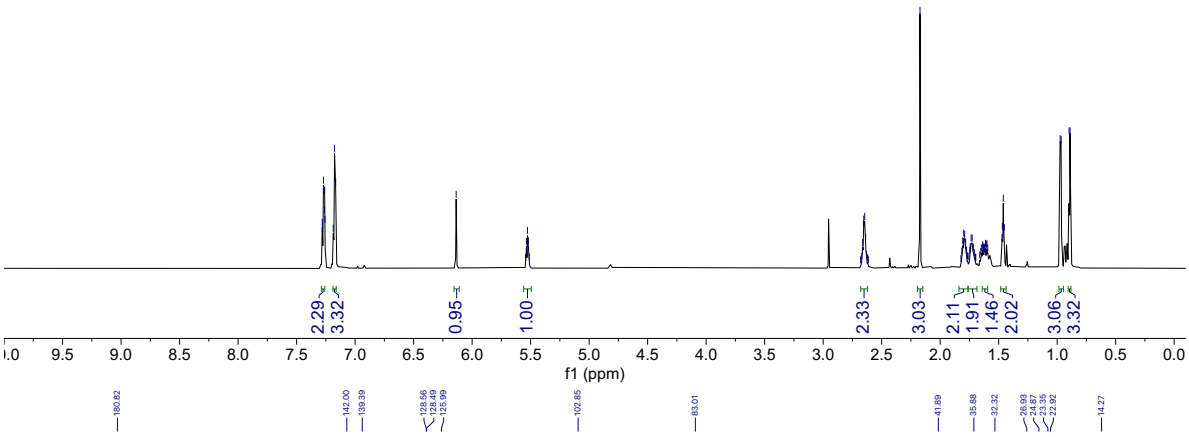
^{13}C NMR (201 MHz, $CDCl_3$)



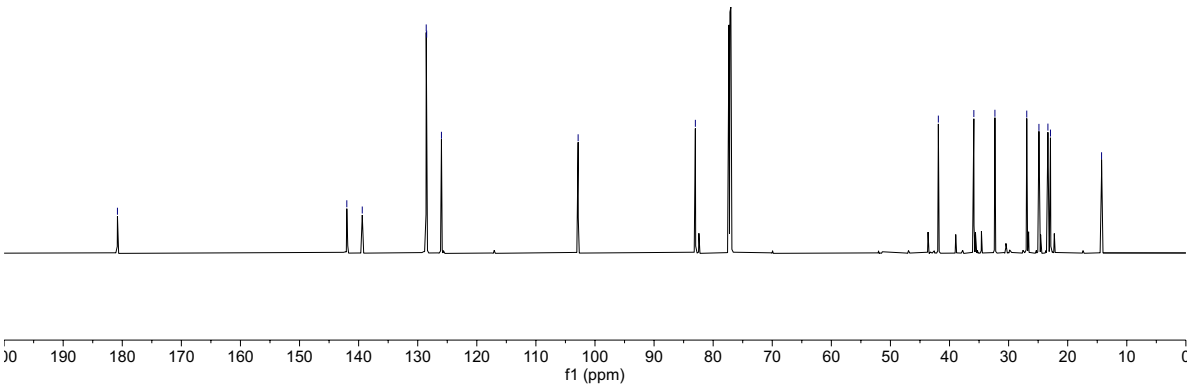
N-alkoxythiazolethione (1l)

^{1}H NMR (800 MHz, $CDCl_3$)



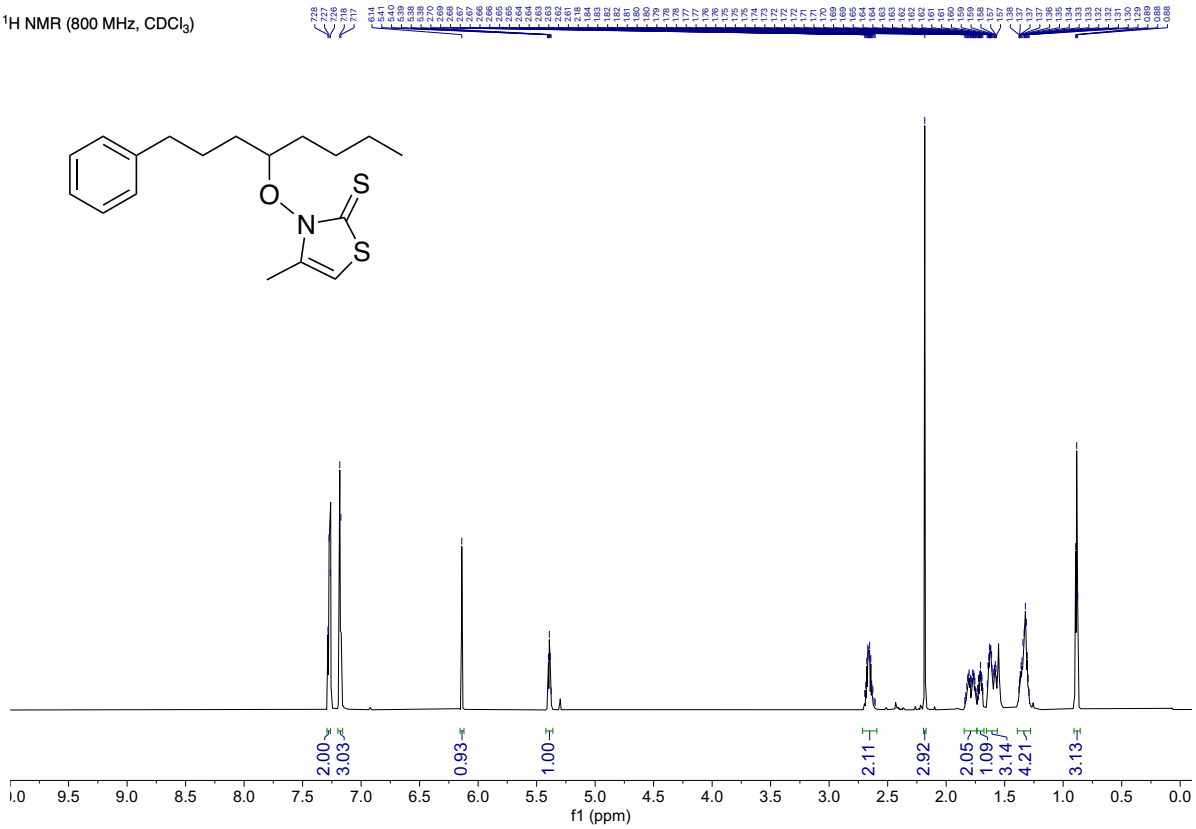


^{13}C NMR (201 MHz, $CDCl_3$)

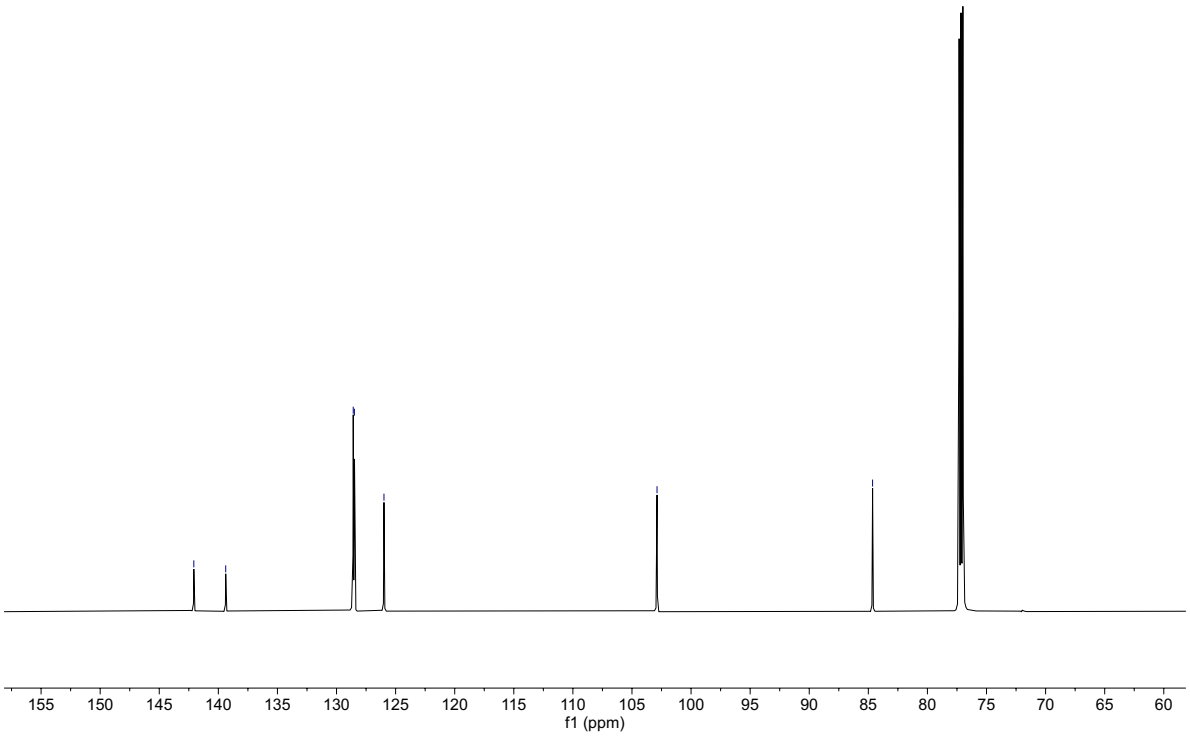


N-alkoxythiazolethione (1m)

^{1}H NMR (800 MHz, $CDCl_3$)

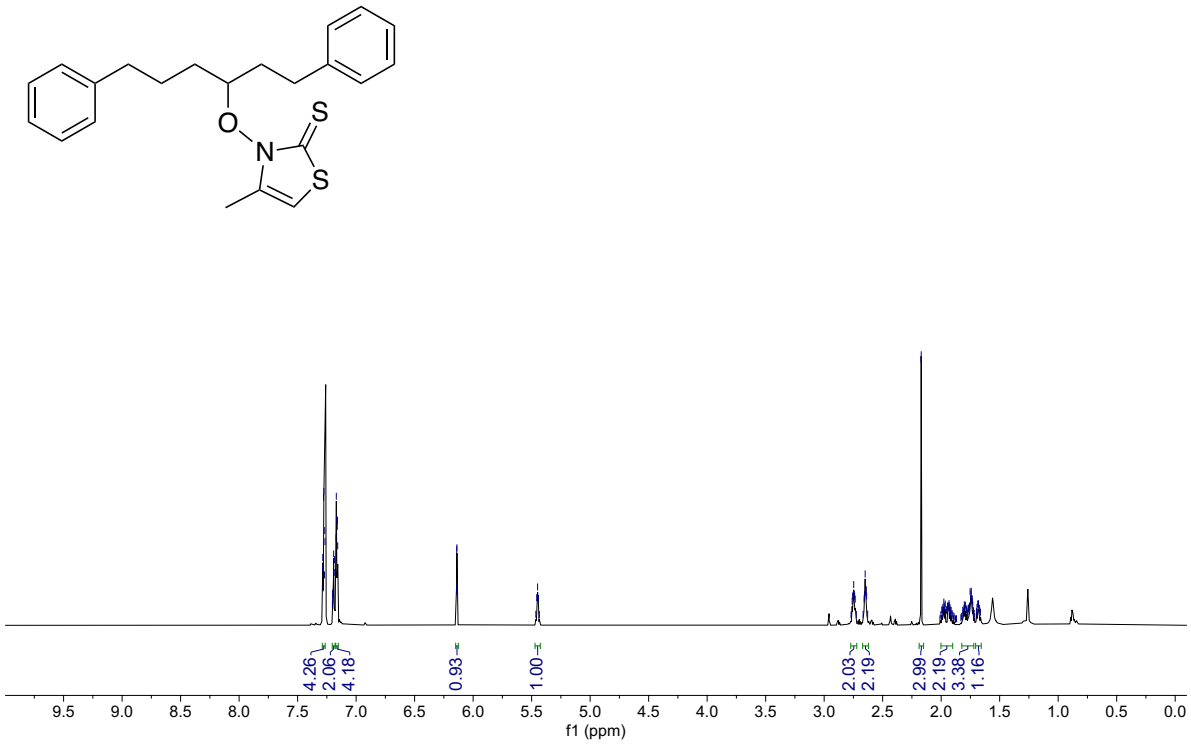


^{13}C NMR (201 MHz, $CDCl_3$)

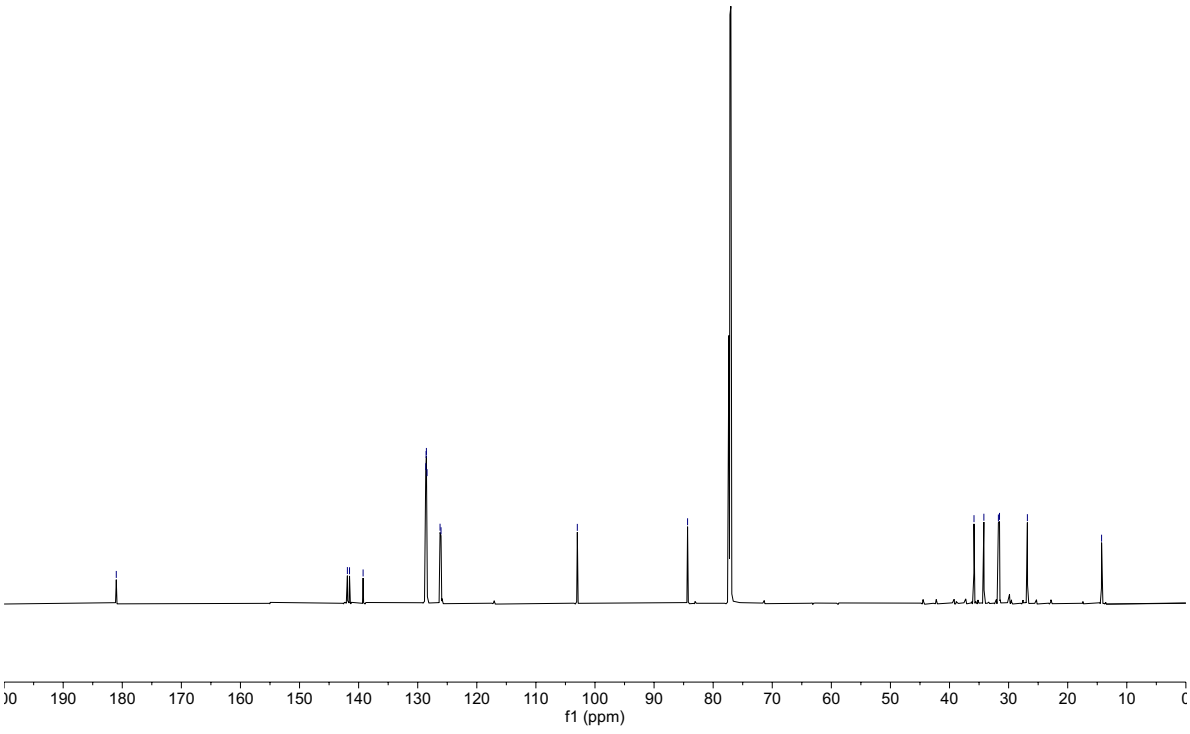


N-alkoxythiazolethione (1n)

^{1}H NMR (800 MHz, $CDCl_3$)

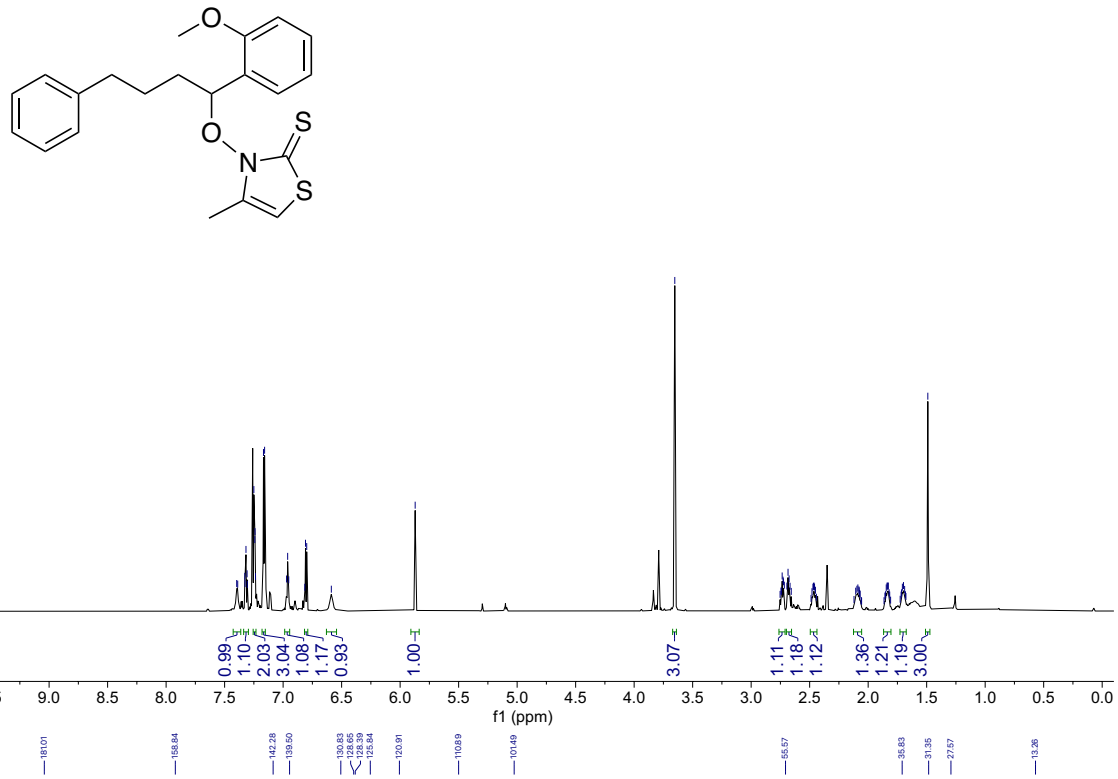


^{13}C NMR (201 MHz, $CDCl_3$)

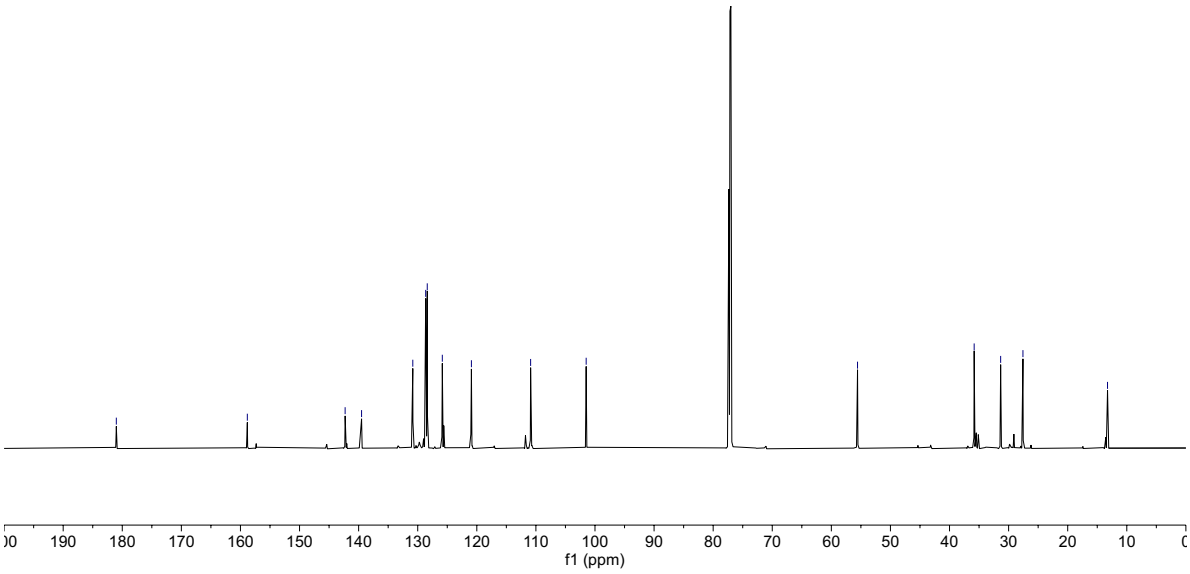


N-alkoxythiazolethione (1o)

^{1}H NMR (800 MHz, $CDCl_3$)

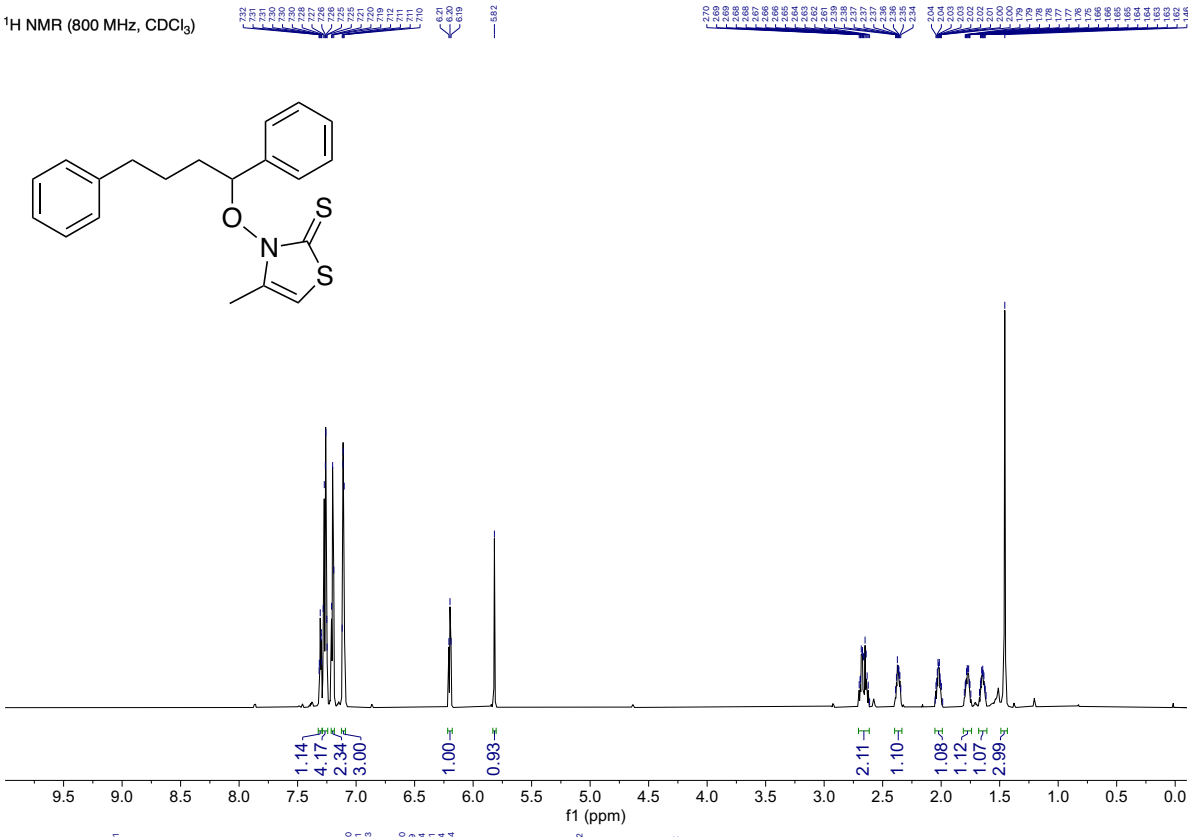


^{13}C NMR (201 MHz, $CDCl_3$)

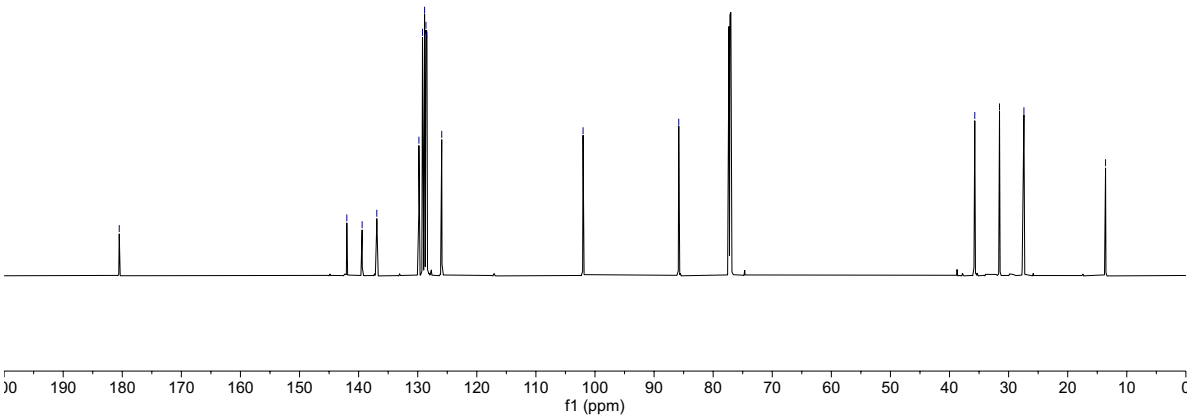


N-alkoxythiazolethione (1p)

^{1}H NMR (800 MHz, $CDCl_3$)

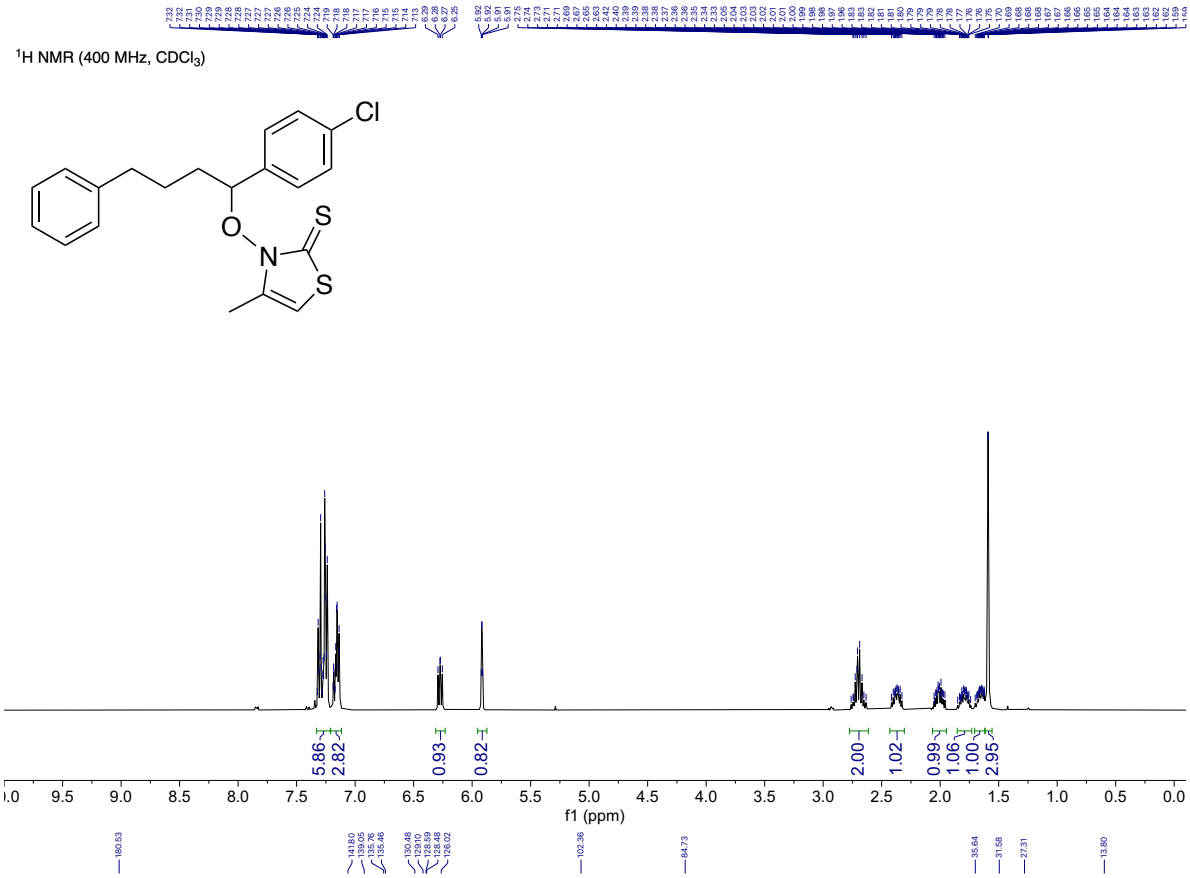


^{13}C NMR (201 MHz, $CDCl_3$)

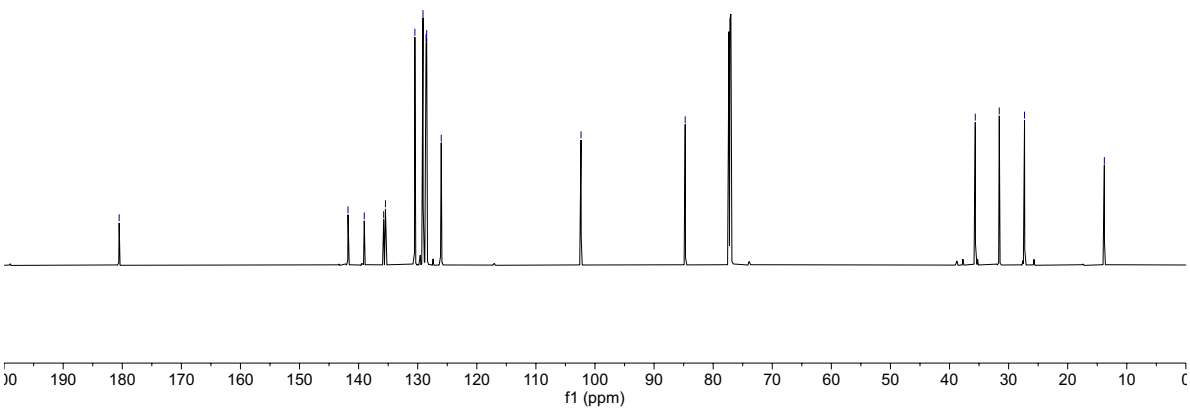


N-alkoxythiazolethione (1r)

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

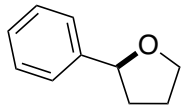


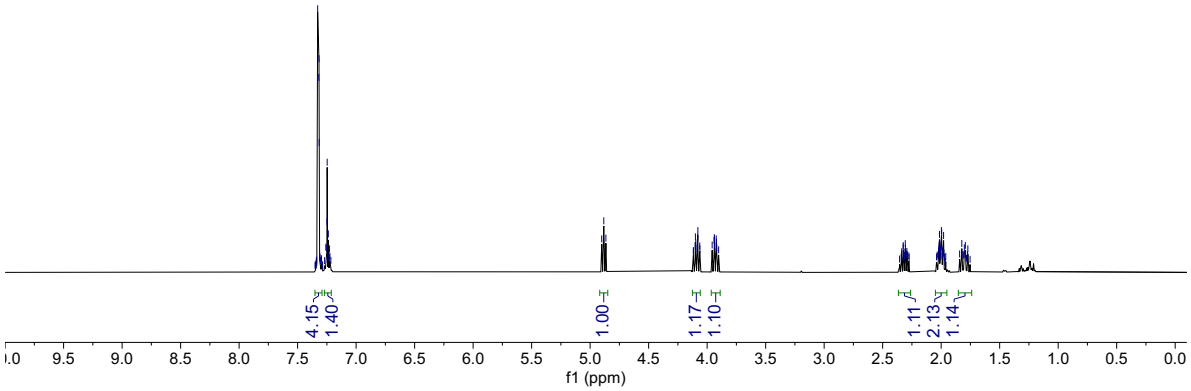
^{13}C NMR (201 MHz, $CDCl_3$)



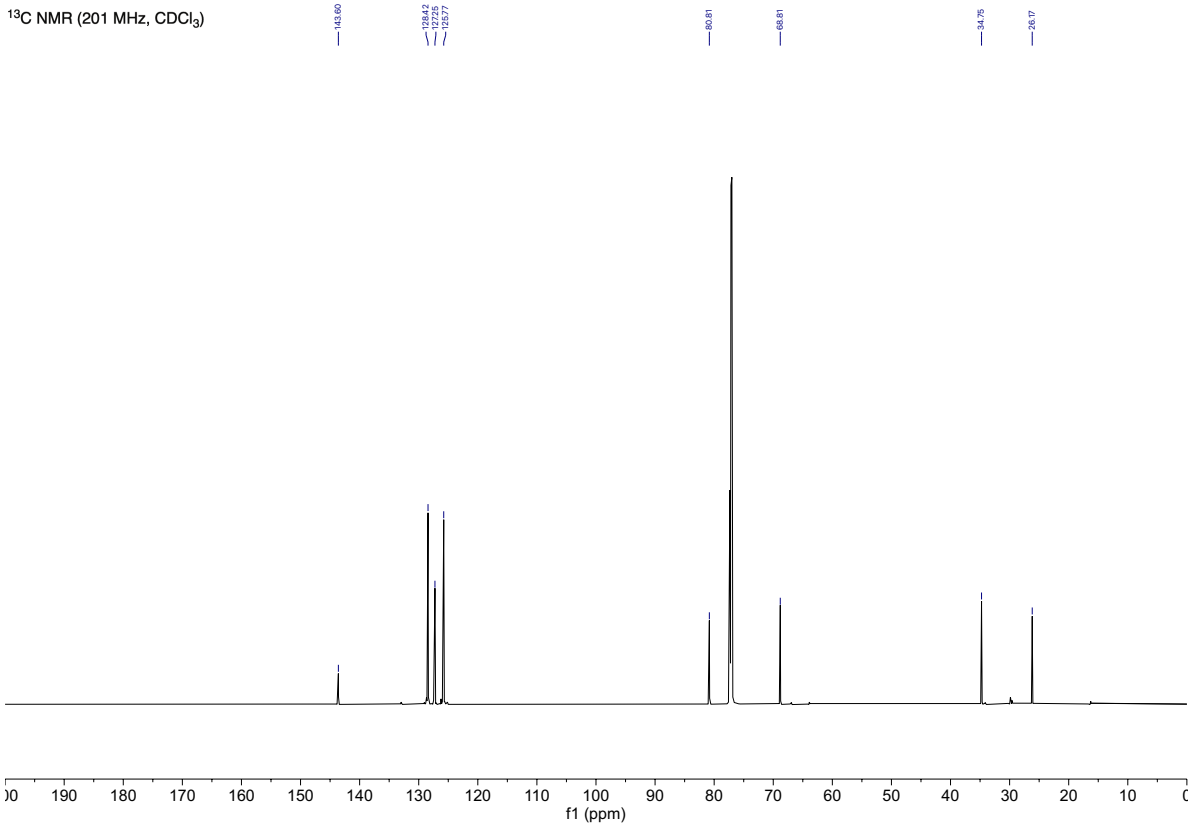
2-phenyltetrahydrofuran (2a)

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



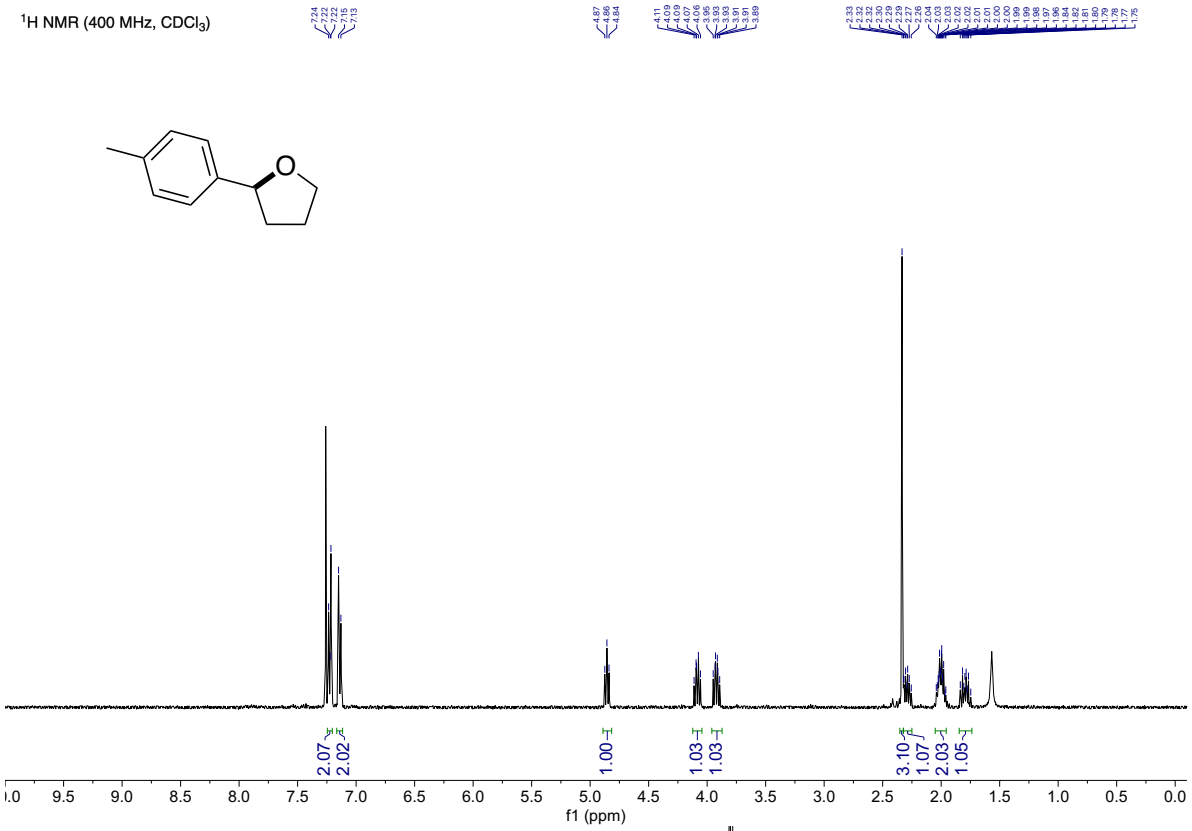


^{13}C NMR (201 MHz, $CDCl_3$)

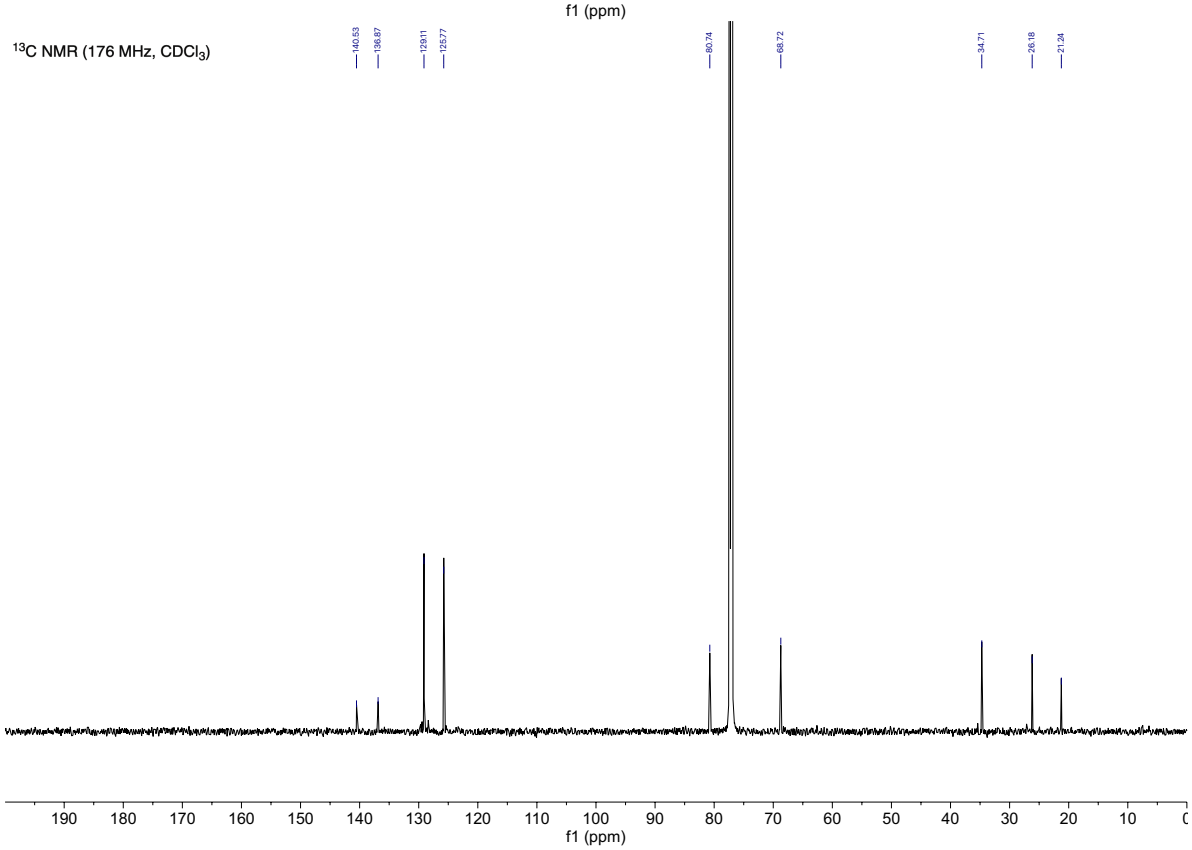


2-(*p*-tolyl)tetrahydrofuran (2b)

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

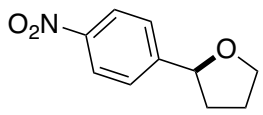


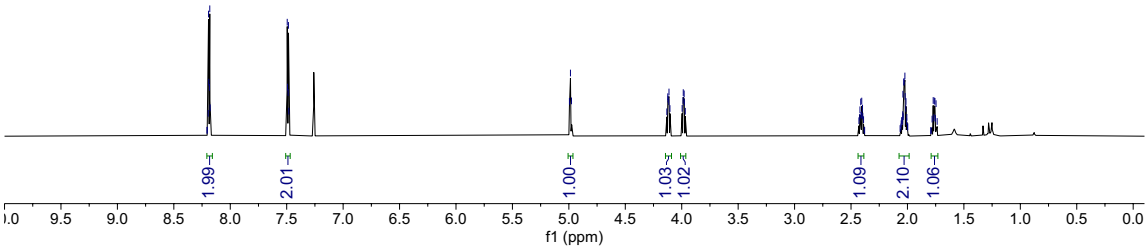
^{13}C NMR (176 MHz, $CDCl_3$)



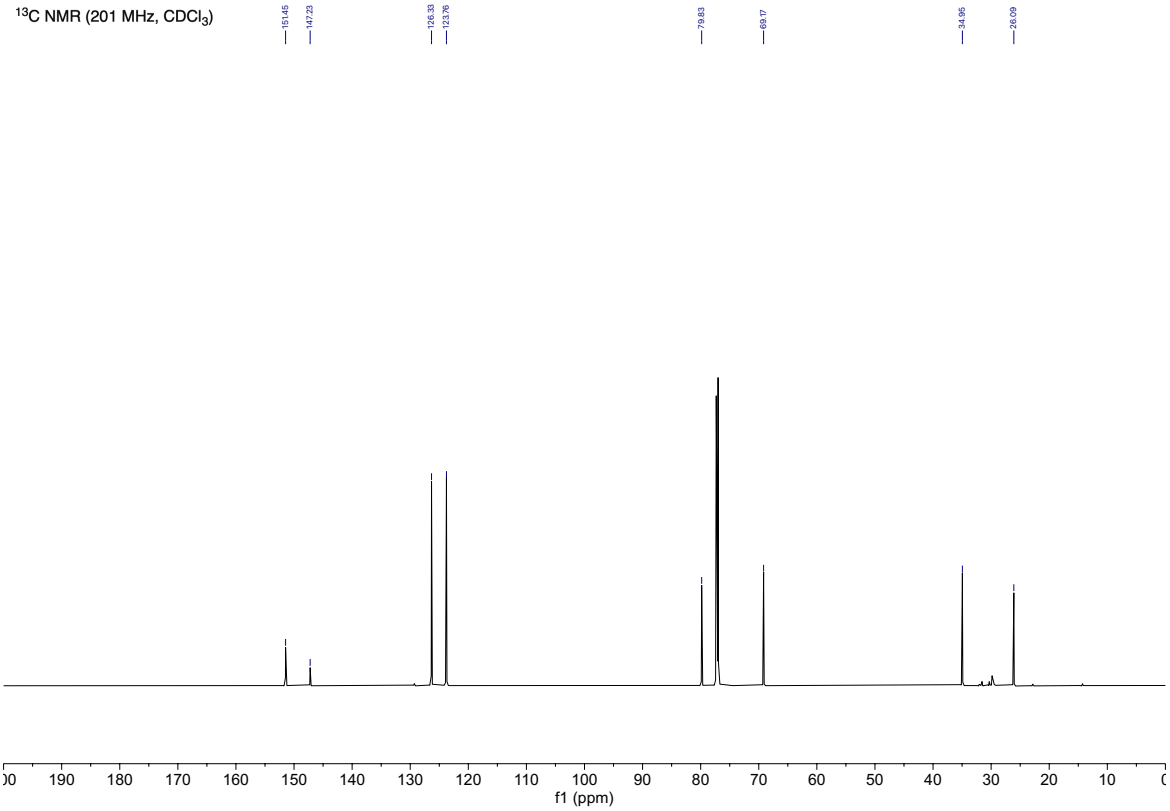
2-(4-nitrophenyl)tetrahydrofuran (2c)

^{1}H NMR (800 MHz, $CDCl_3$)



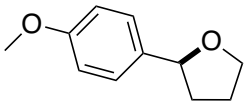


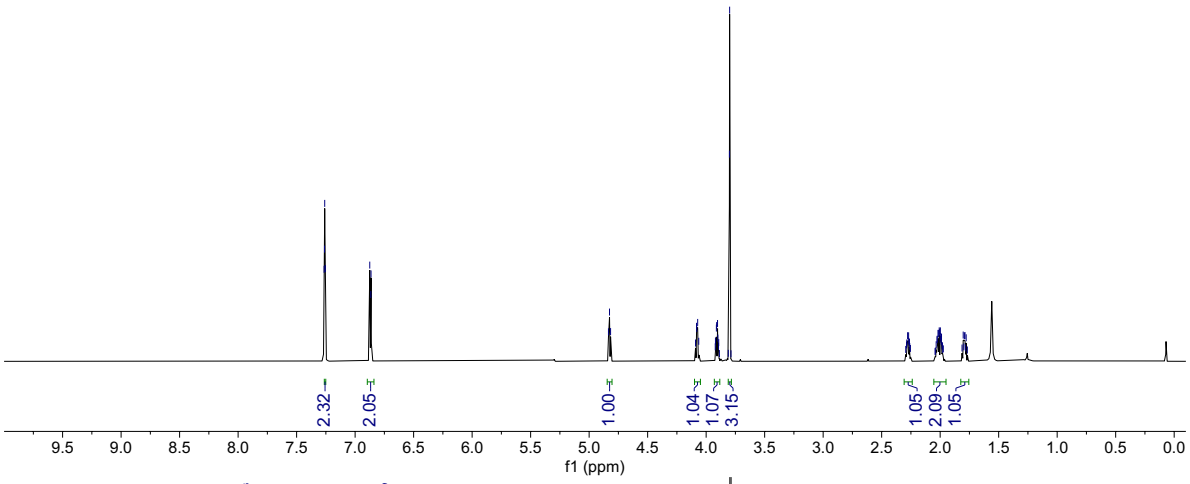
^{13}C NMR (201 MHz, $CDCl_3$)



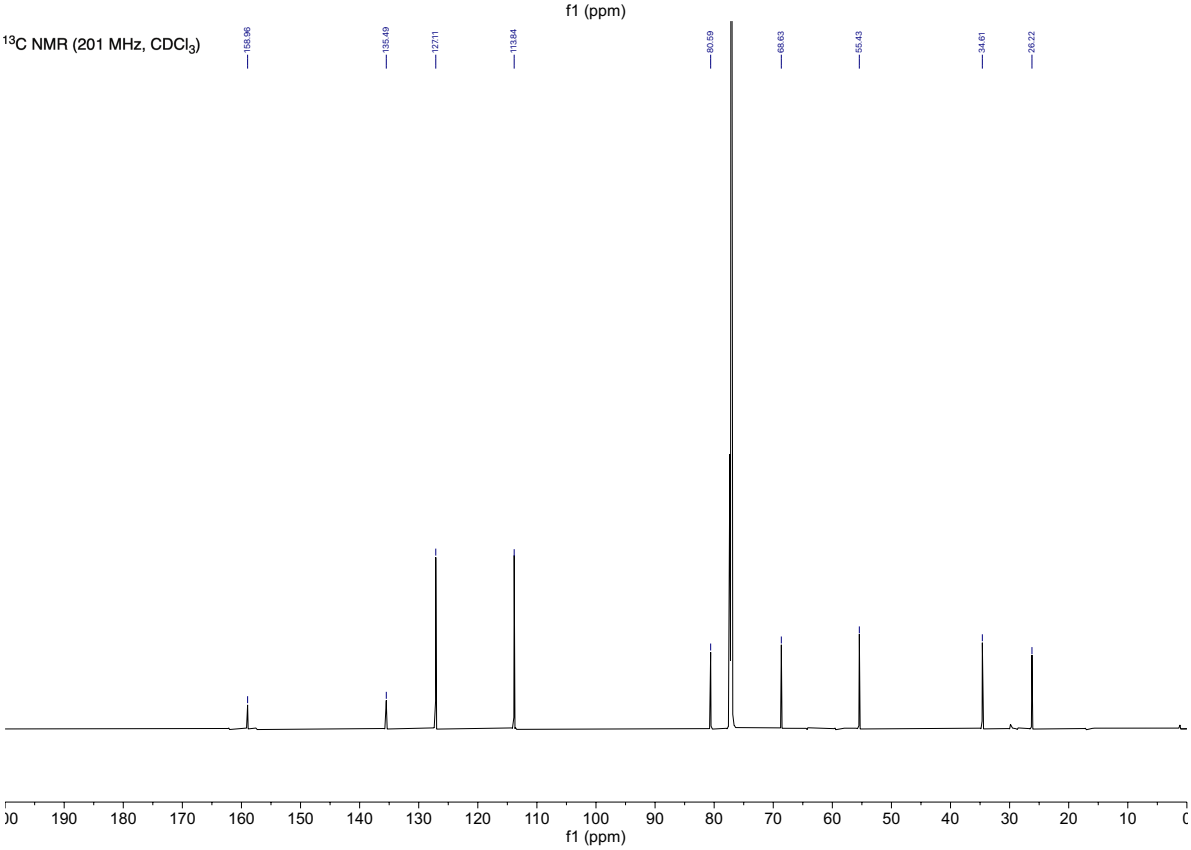
2-(4-methoxyphenyl)tetrahydrofuran (2d)

^{1}H NMR (800 MHz, $CDCl_3$)



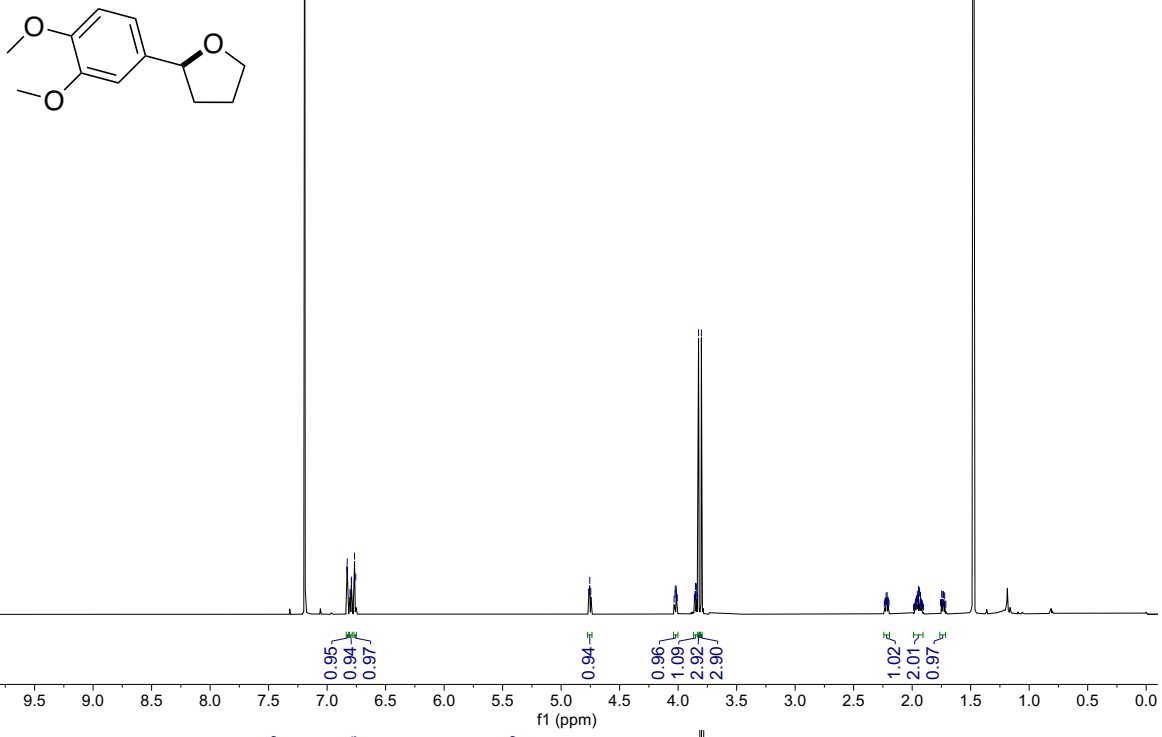


^{13}C NMR (201 MHz, $CDCl_3$)

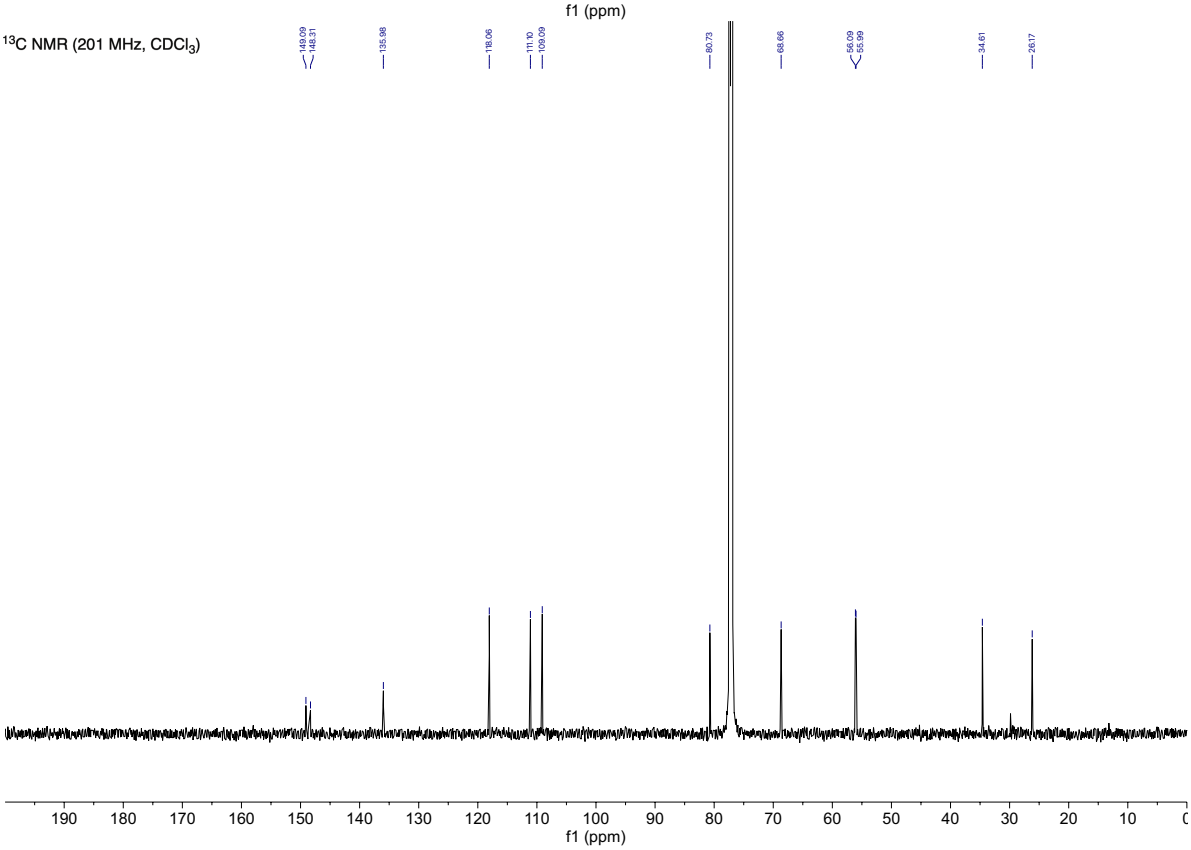


2-(3,4-dimethoxyphenyl)tetrahydrofuran (2e)

^{1}H NMR (800 MHz, $CDCl_3$)

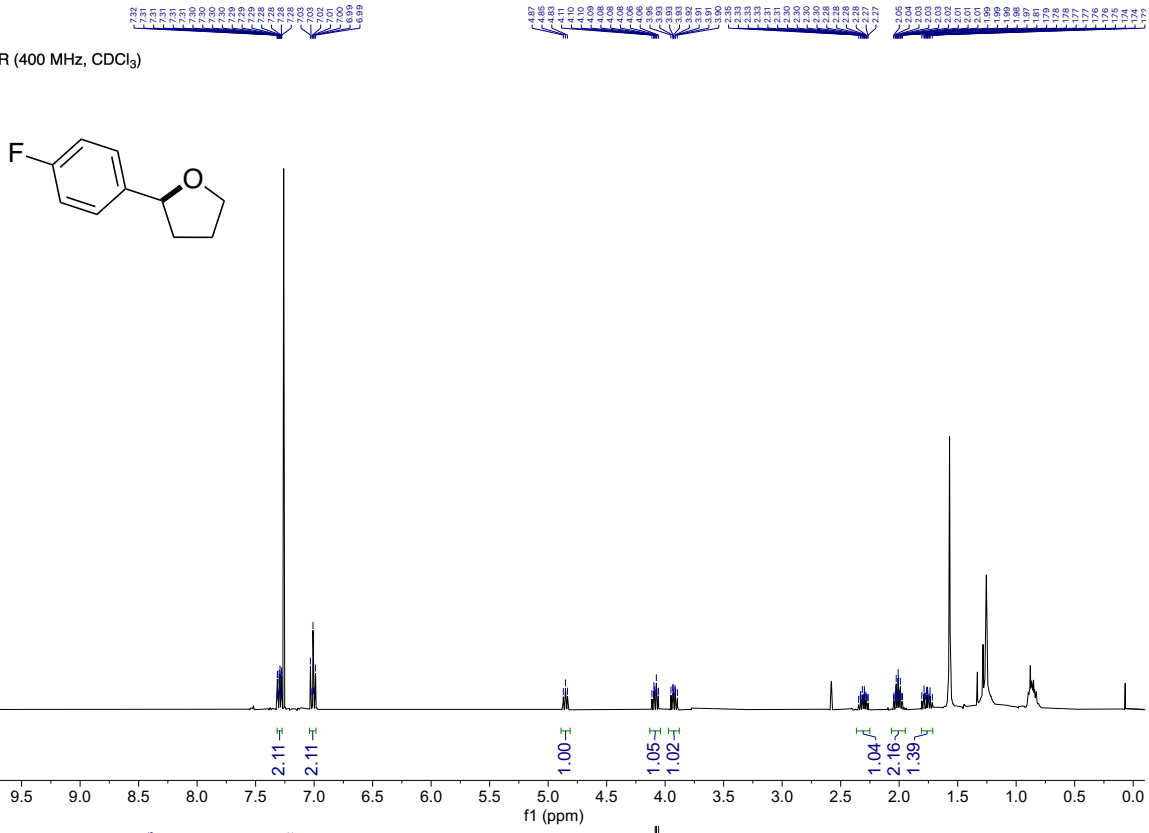


^{13}C NMR (201 MHz, $CDCl_3$)

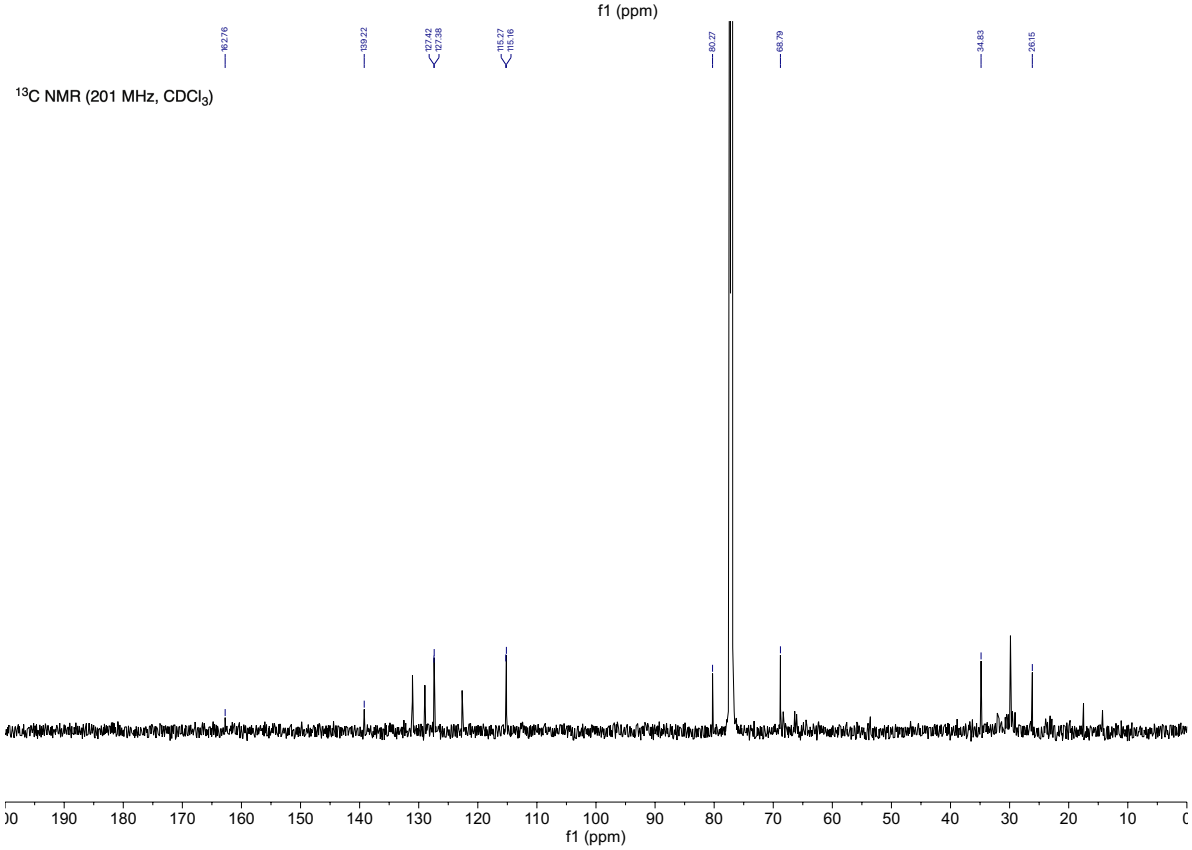


2-(4-fluorophenyl)tetrahydrofuran (2f)

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

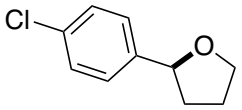


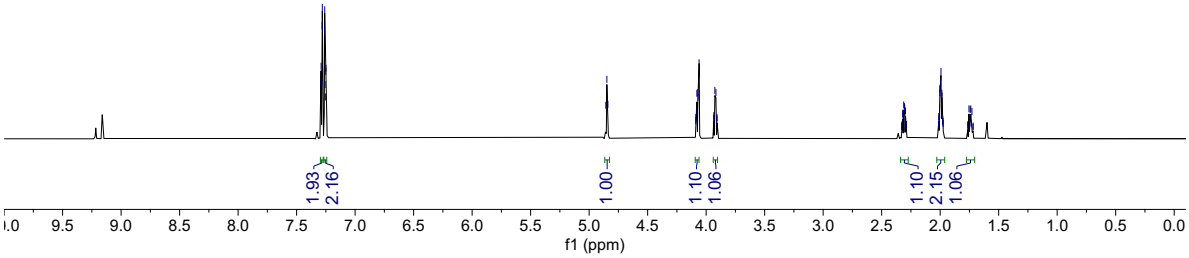
^{13}C NMR (201 MHz, $CDCl_3$)



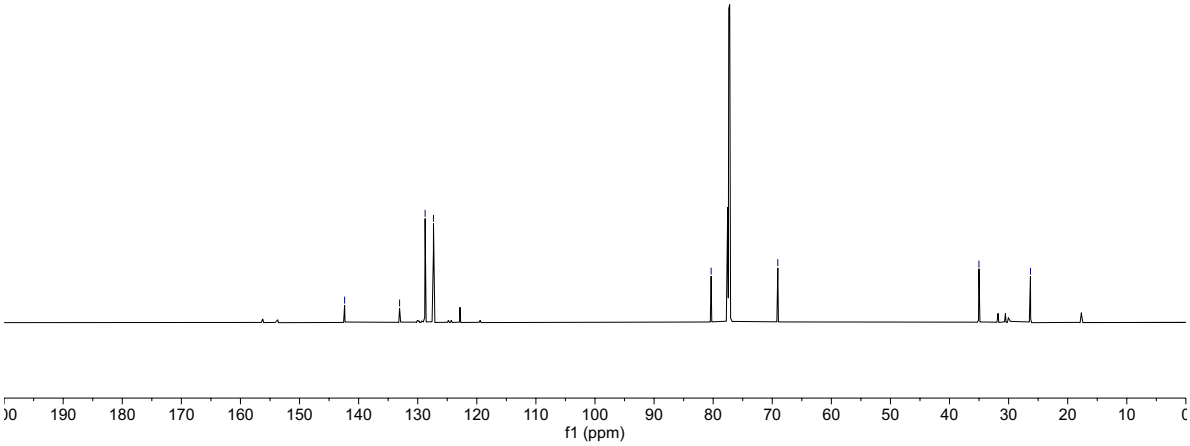
2-(4-chlorophenyl)tetrahydrofuran (2g)

^{1}H NMR (800 MHz, $CDCl_3$)



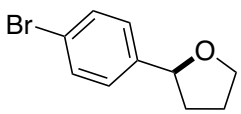


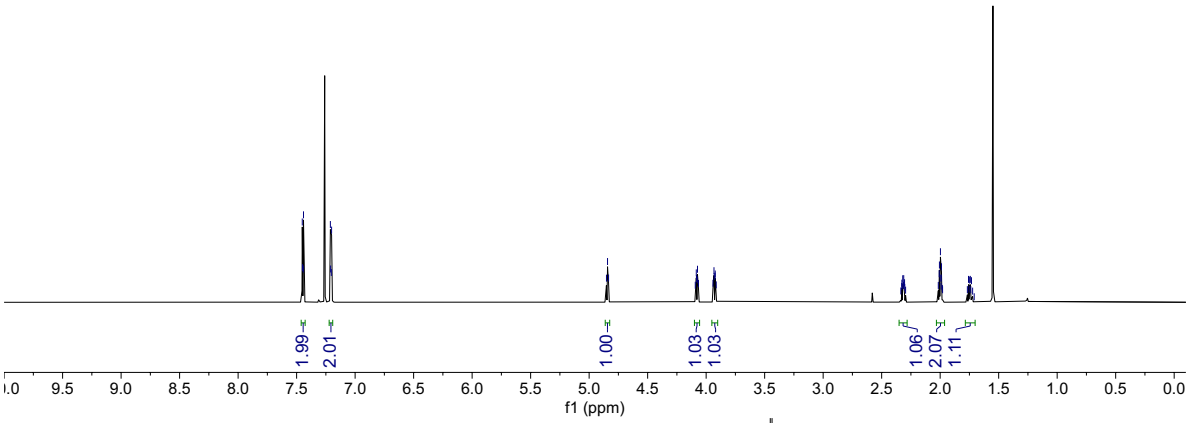
^{13}C NMR (201 MHz, $CDCl_3$)



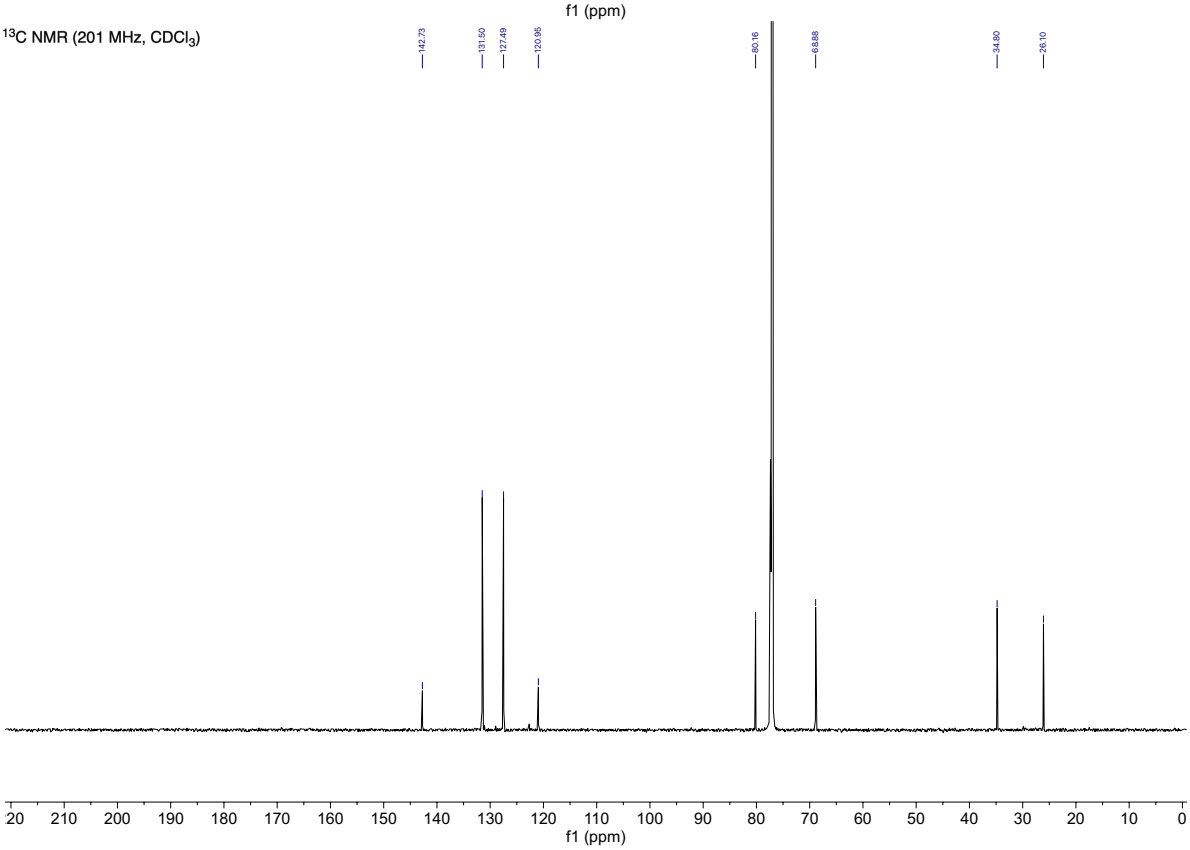
2-(4-bromophenyl)tetrahydrofuran (2h)

^{1}H NMR (800 MHz, $CDCl_3$)



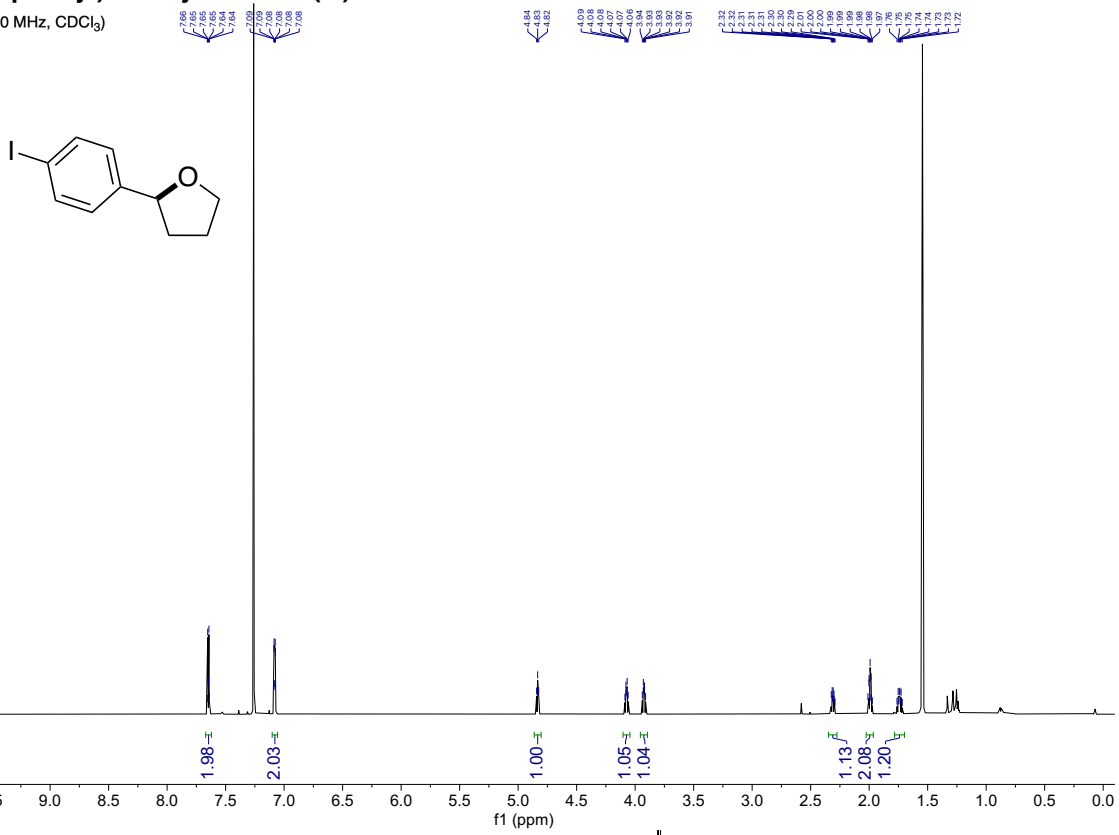


^{13}C NMR (201 MHz, $CDCl_3$)

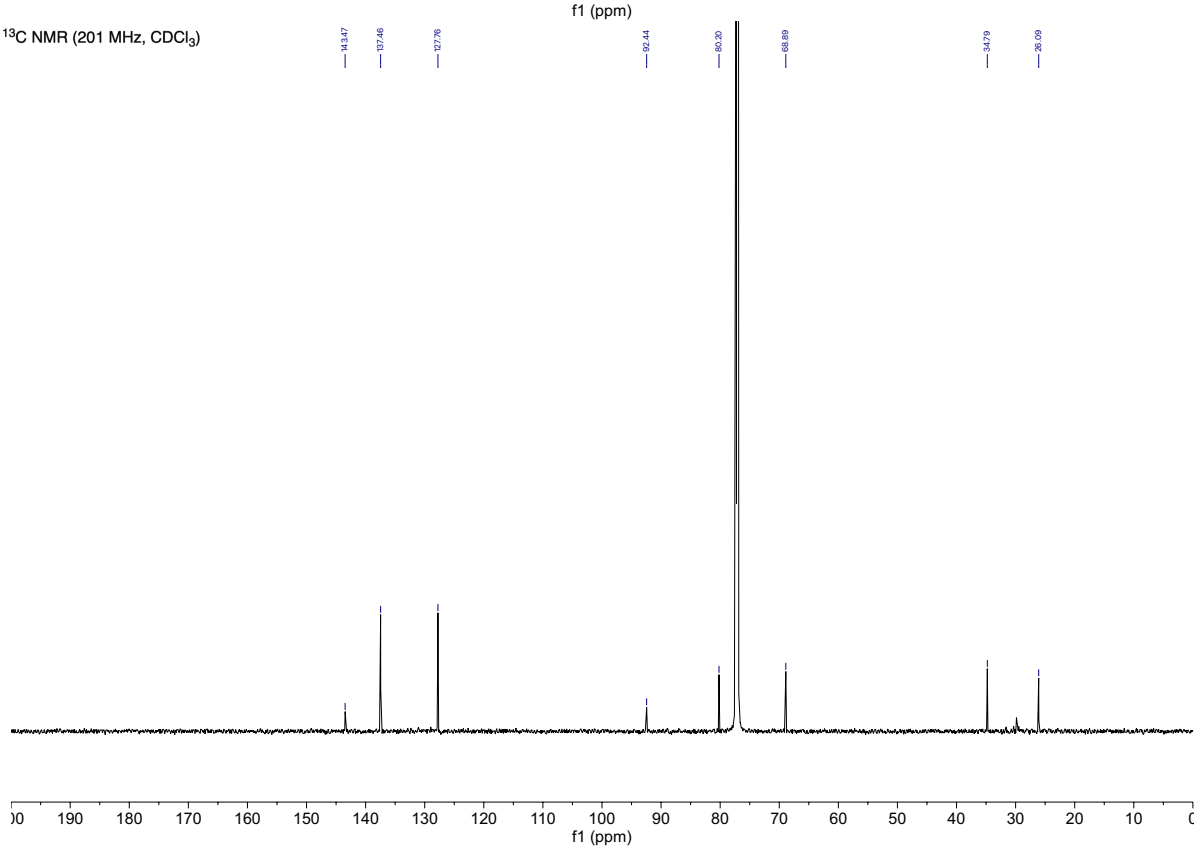


2-(4-iodophenyl)tetrahydrofuran (2i)

^{1}H NMR (800 MHz, $CDCl_3$)

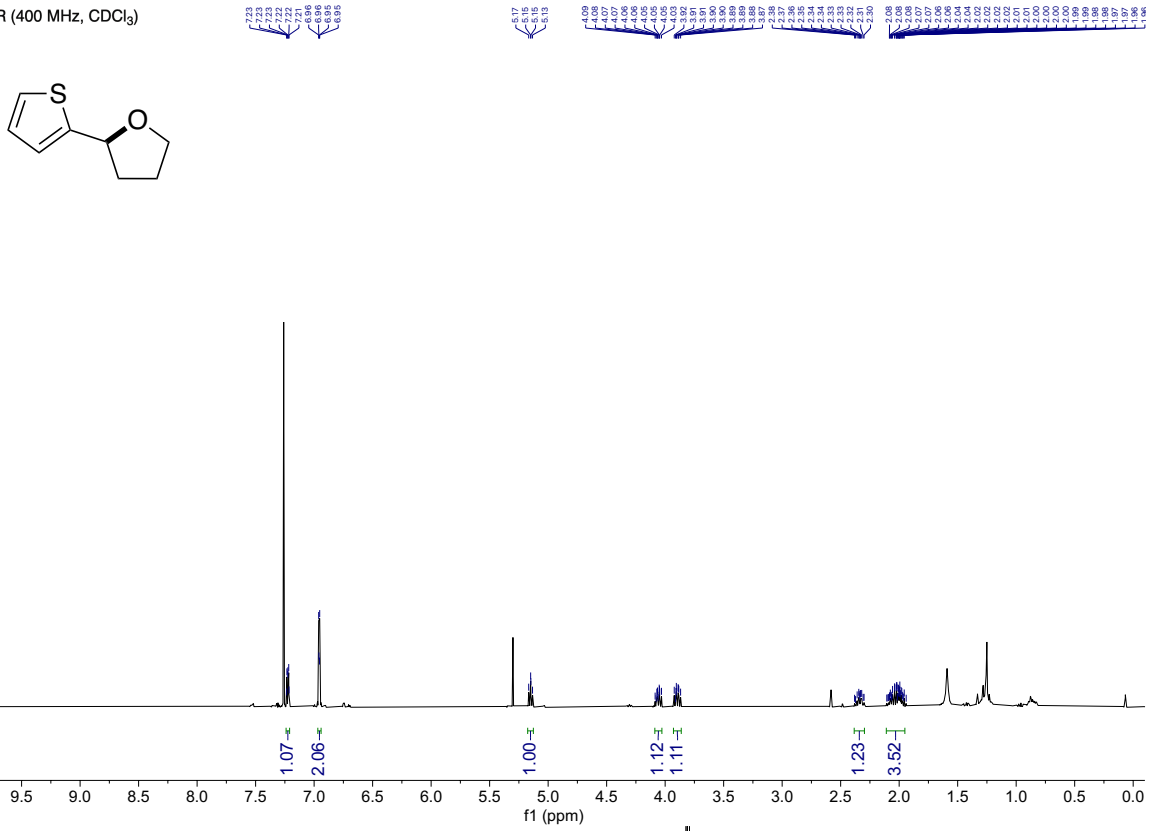


^{13}C NMR (201 MHz, $CDCl_3$)

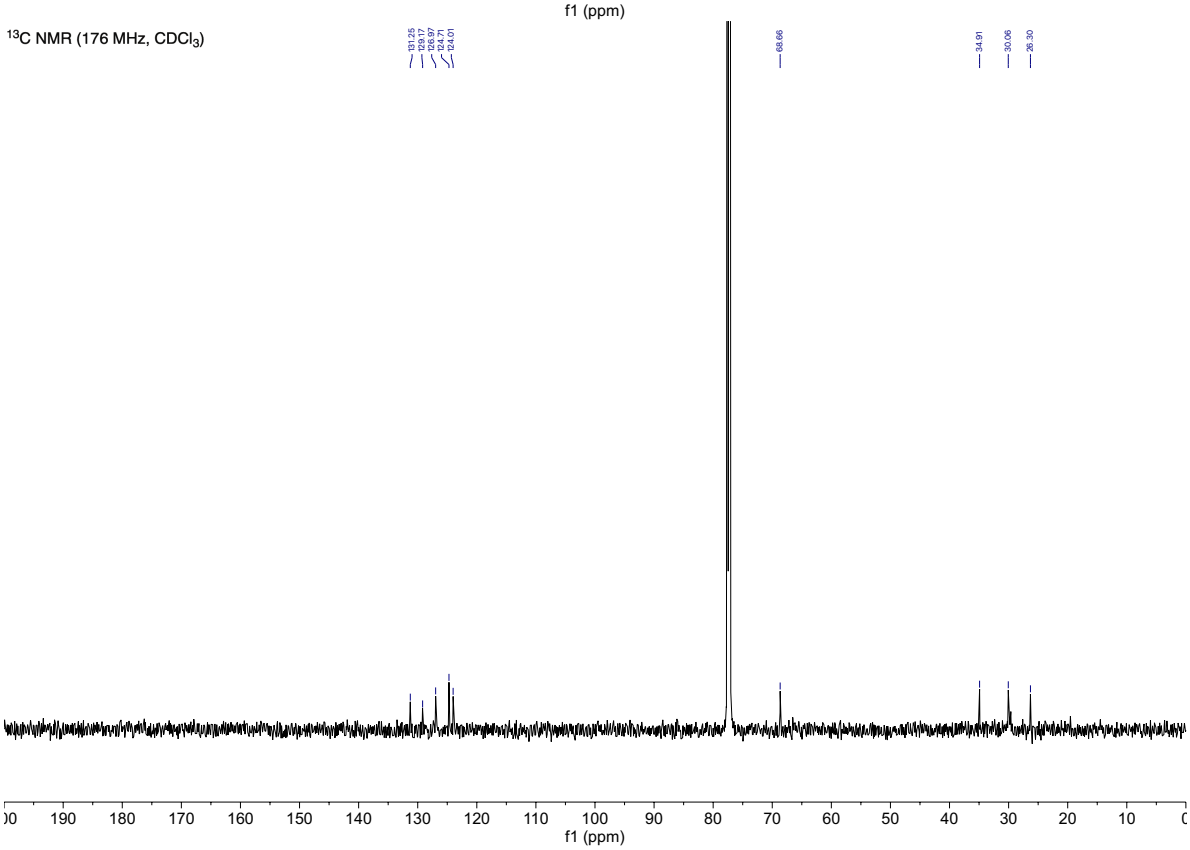


2-(thiophen-2-yl)tetrahydrofuran (2j)

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

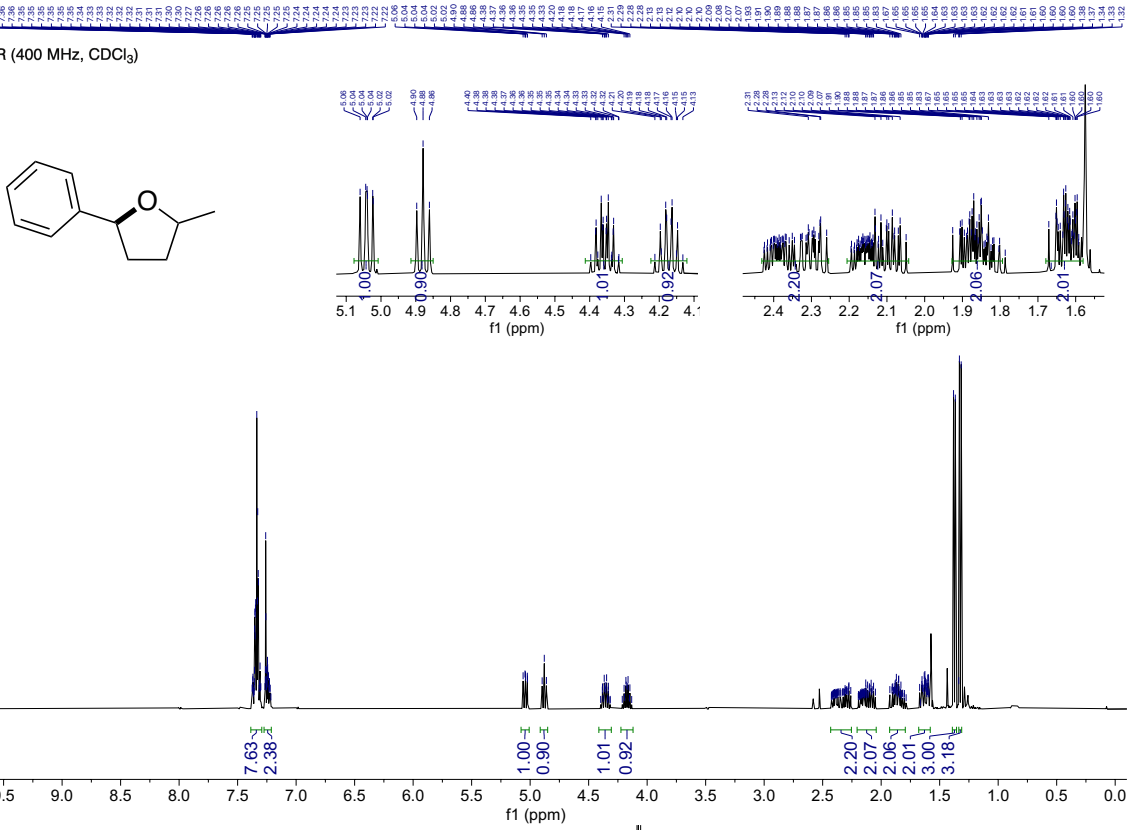


^{13}C NMR (176 MHz, $CDCl_3$)

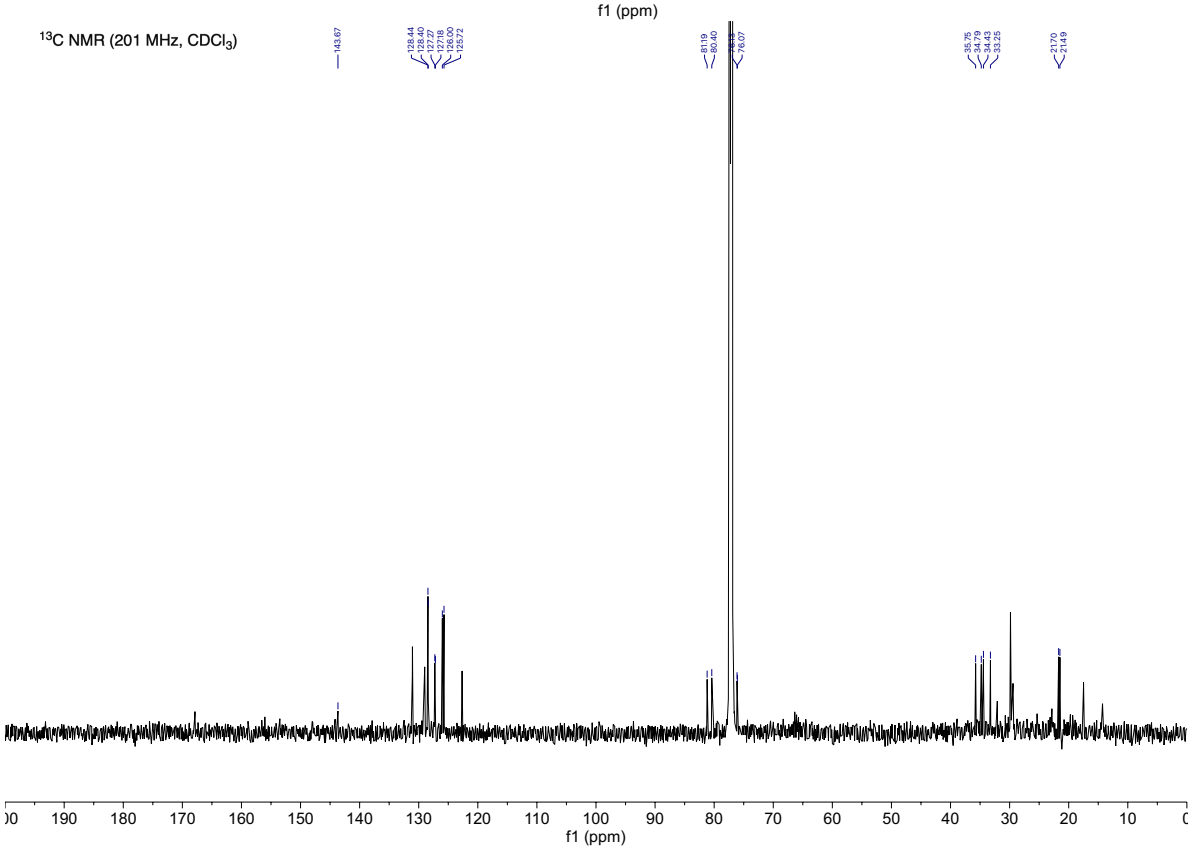


2-methyl-5-phenyltetrahydrofuran (2k)

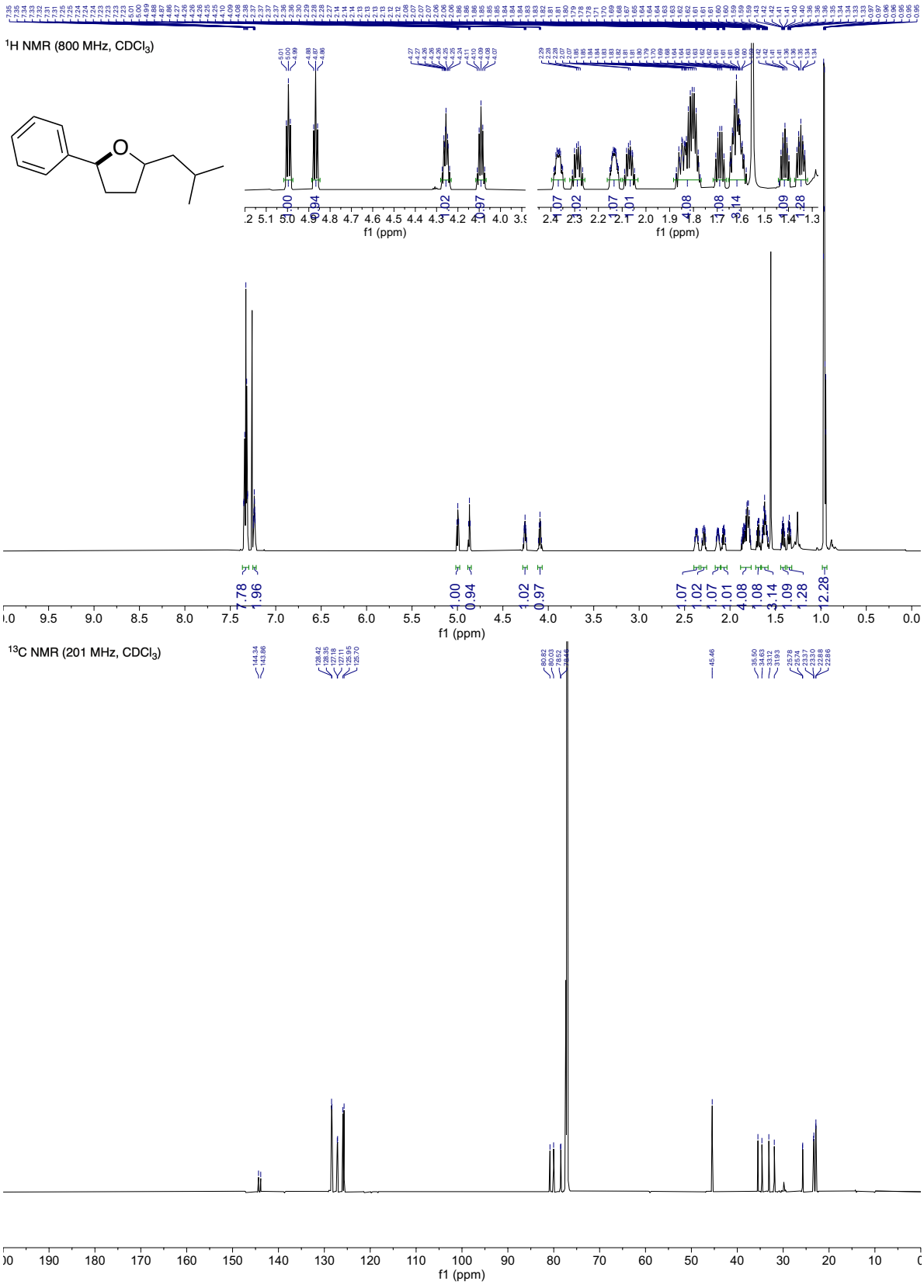
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (201 MHz, $CDCl_3$)

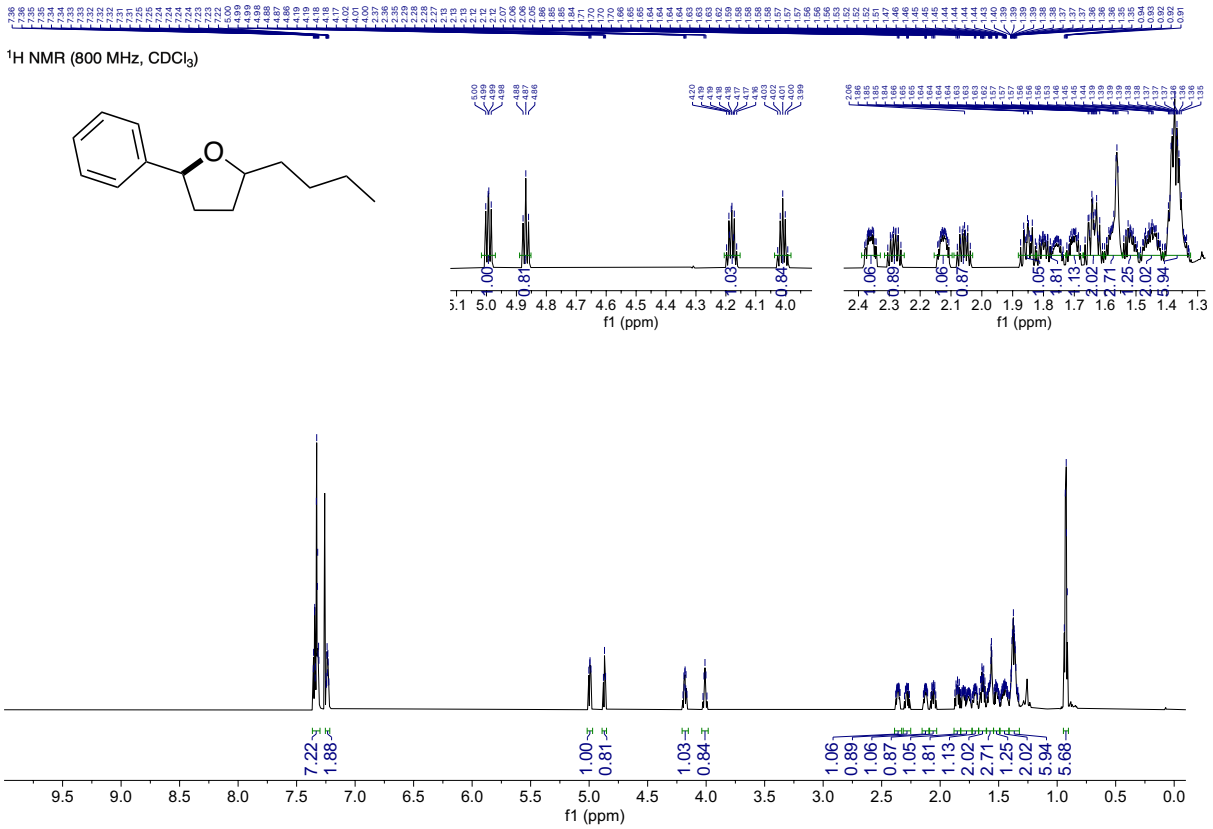


2-isobutyl-5-phenyltetrahydrofuran (2l)

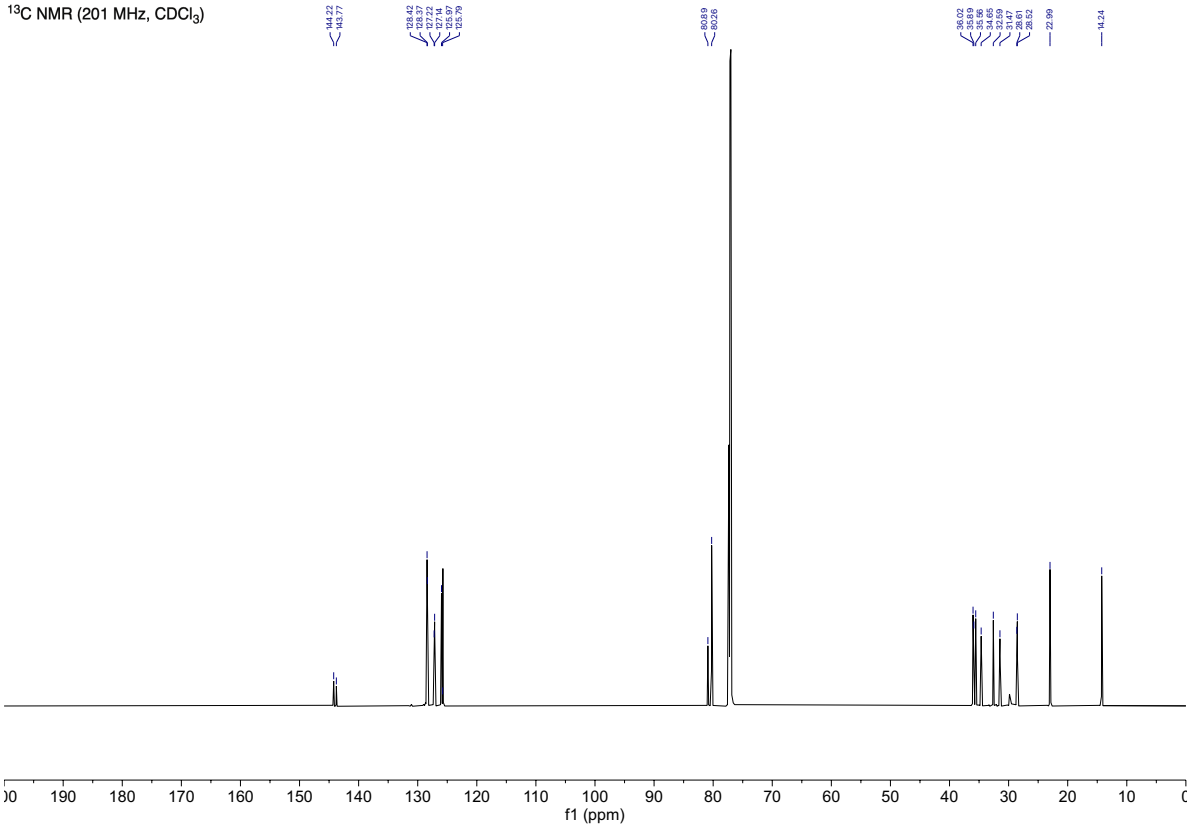


2-butyl-5-phenyltetrahydrofuran (2m)

^{1}H NMR (800 MHz, $CDCl_3$)

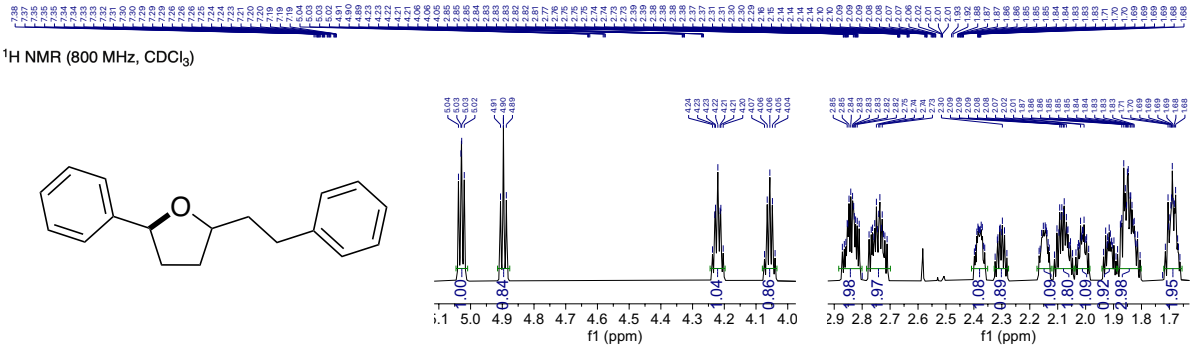


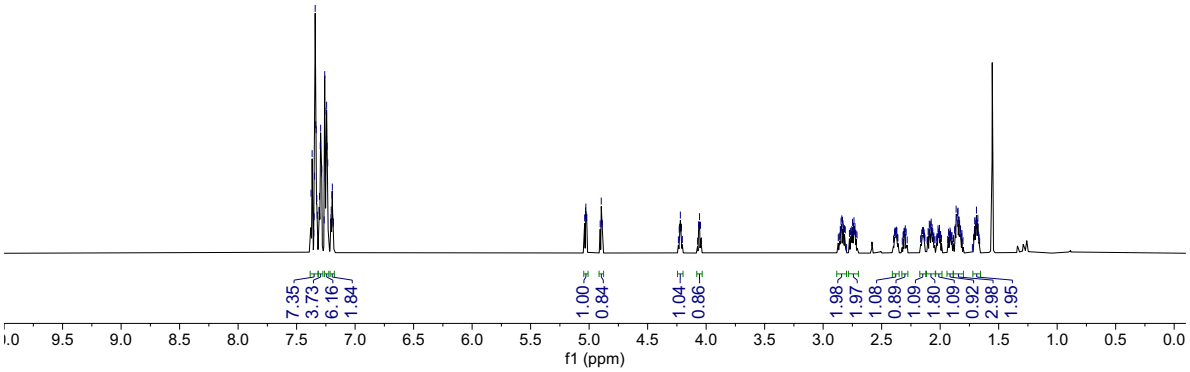
^{13}C NMR (201 MHz, $CDCl_3$)



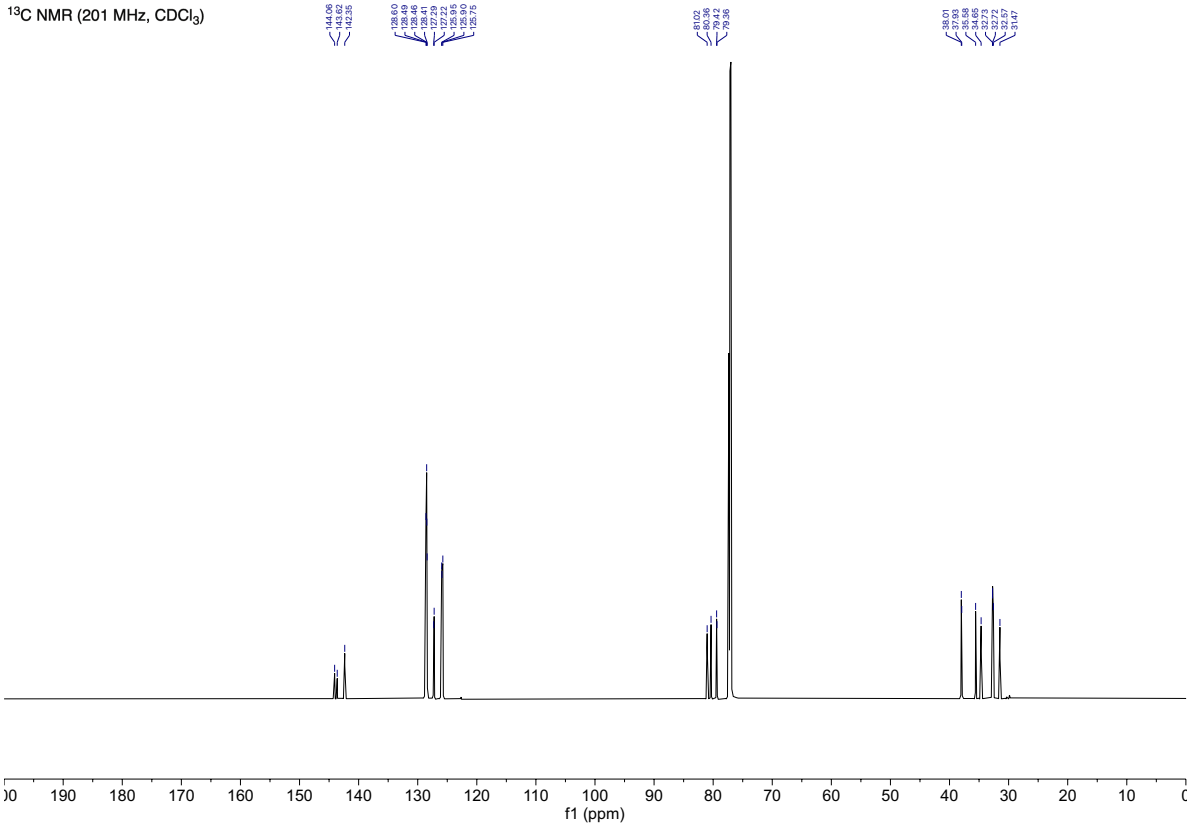
2-phenethyl-5-phenyltetrahydrofuran (2n)

^{1}H NMR (800 MHz, $CDCl_3$)

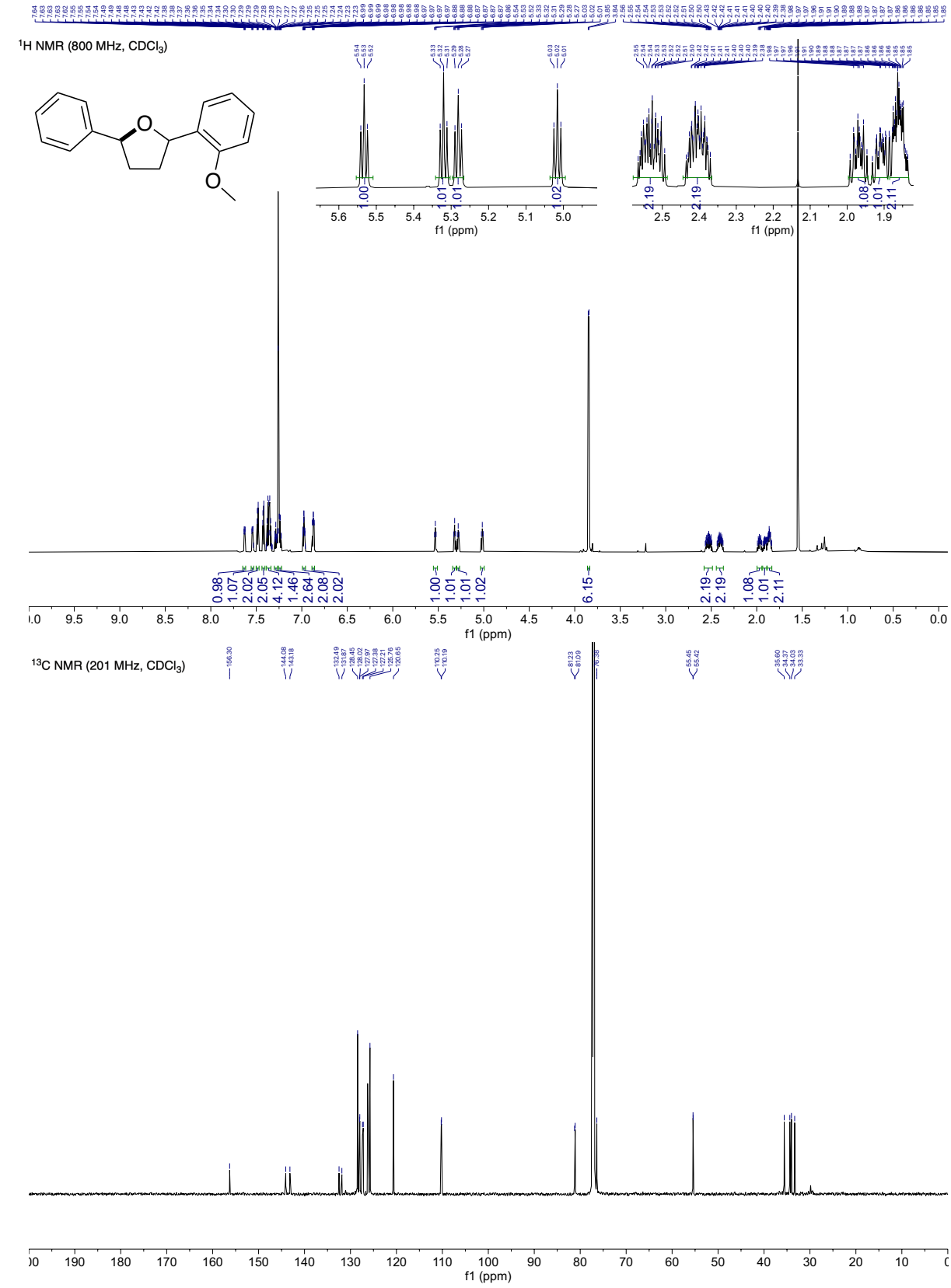




^{13}C NMR (201 MHz, $CDCl_3$)

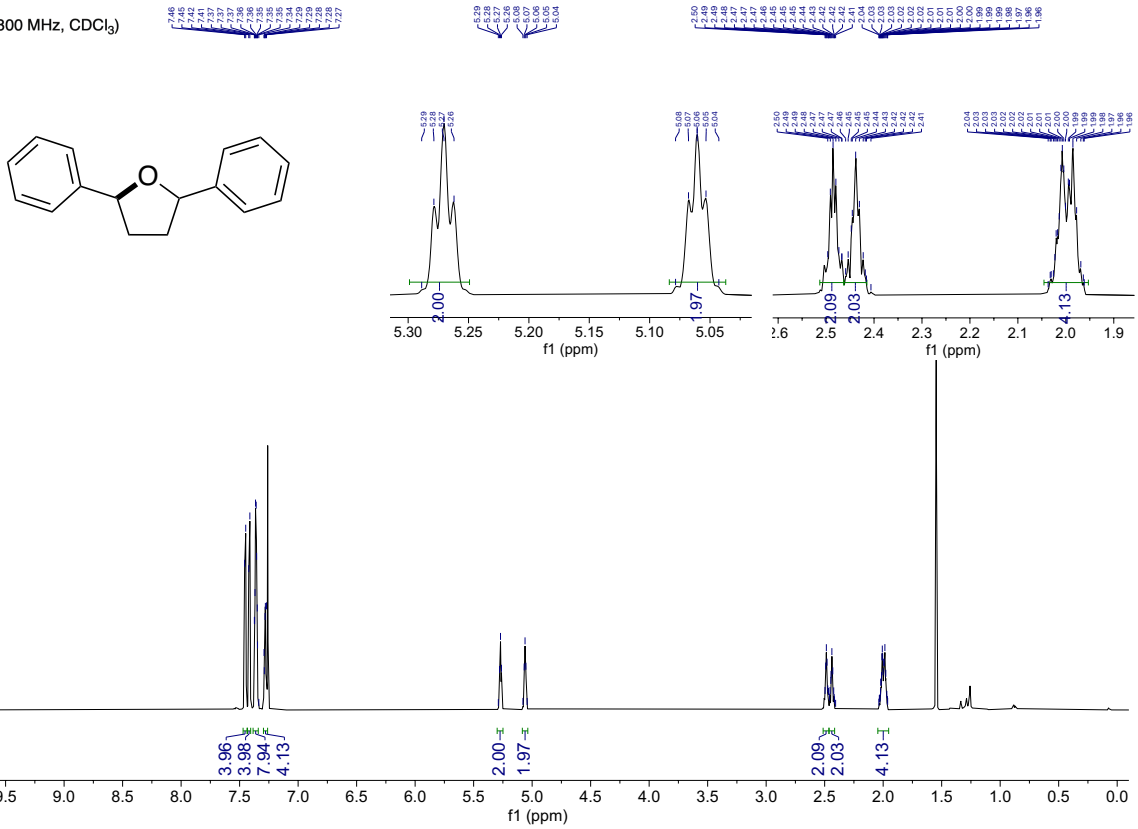


(2-methoxyphenyl)-5-phenyltetrahydrofuran (2o)

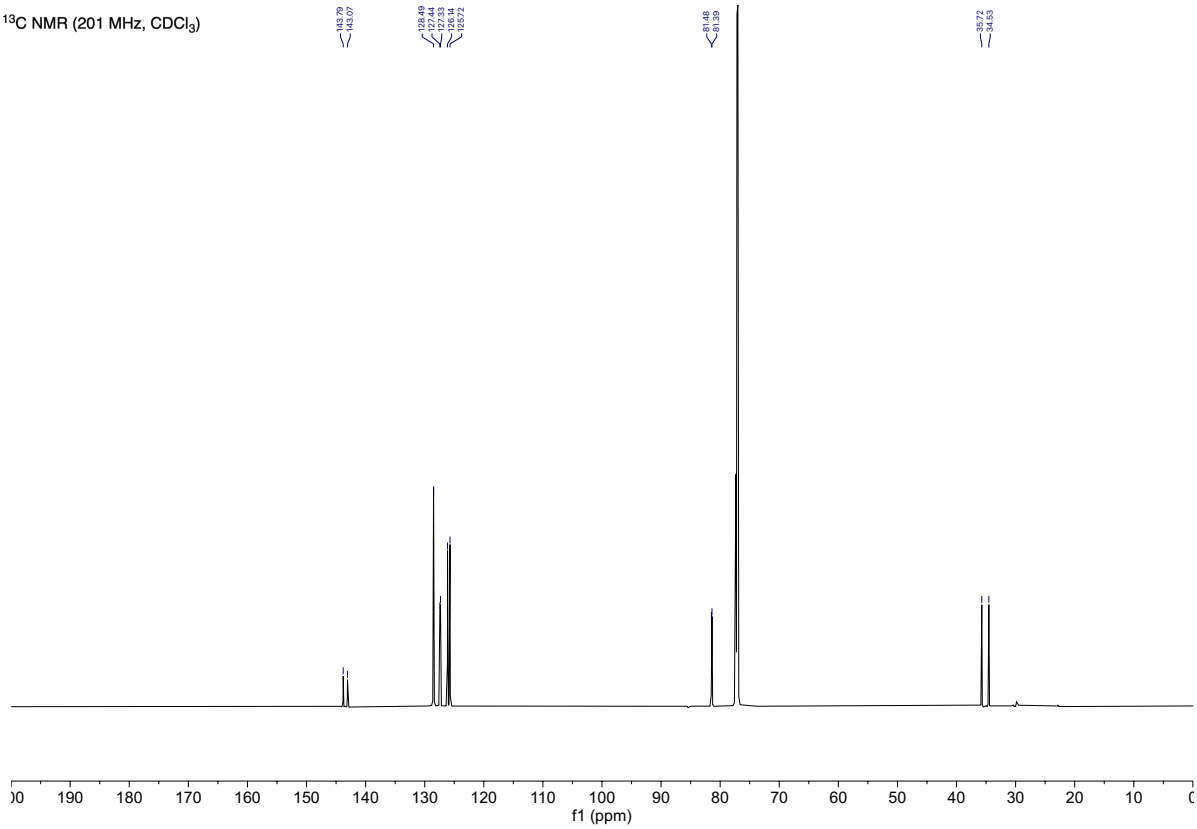


2,5-diphenyltetrahydrofuran (2p)

^{1}H NMR (800 MHz, $CDCl_3$)

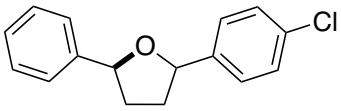


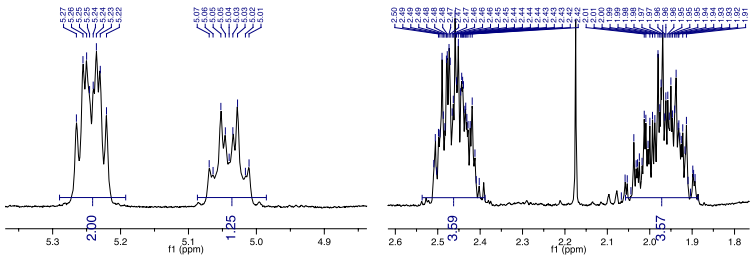
^{13}C NMR (201 MHz, $CDCl_3$)

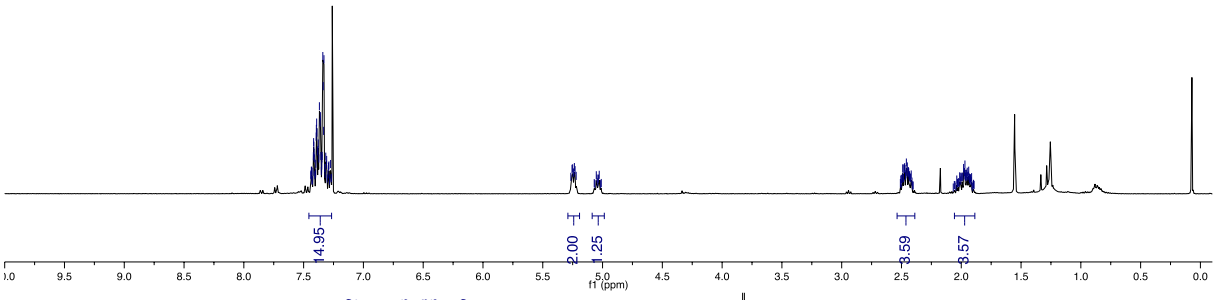


2-(4-chlorophenyl)-5-phenyltetrahydrofuran (2r)

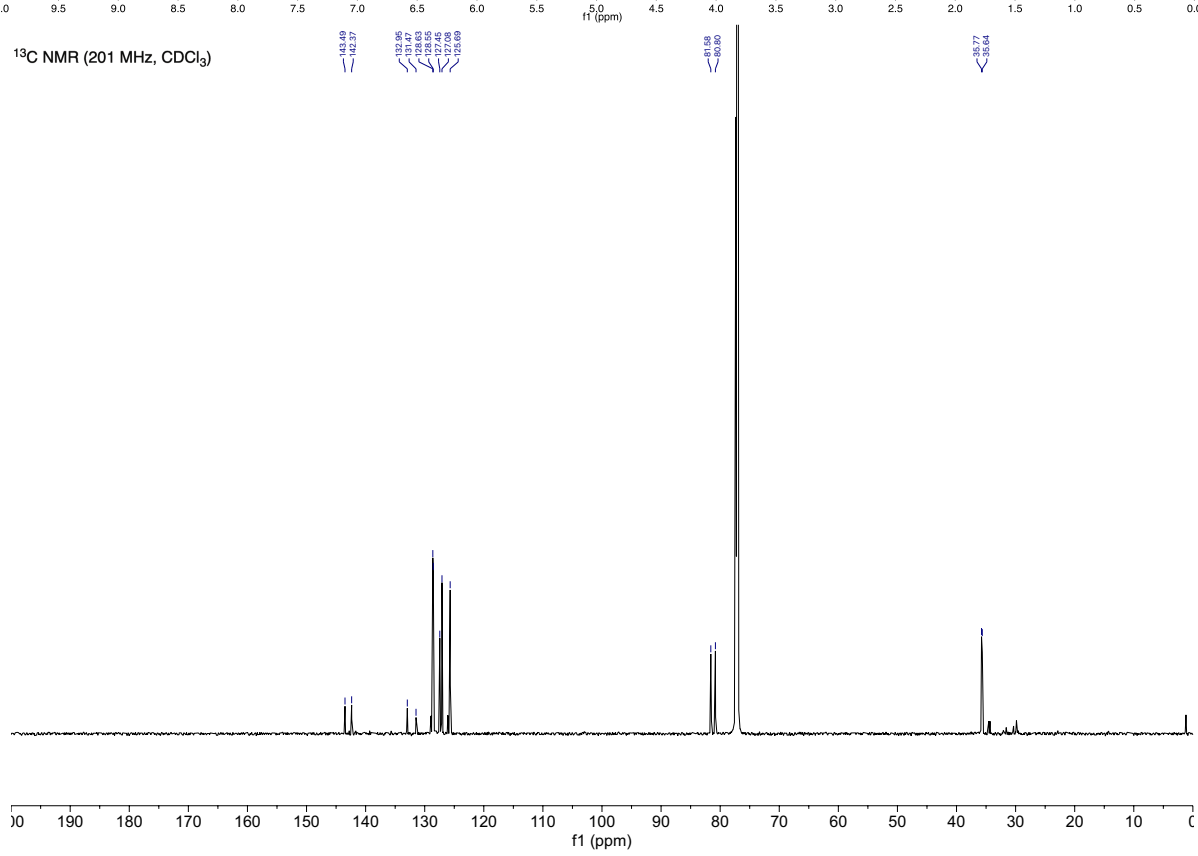
^{1}H NMR (400 MHz, $CDCl_3$)





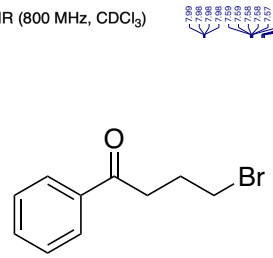


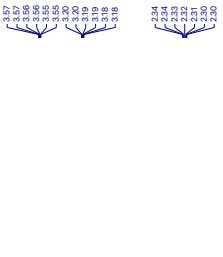
^{13}C NMR (201 MHz, $CDCl_3$)

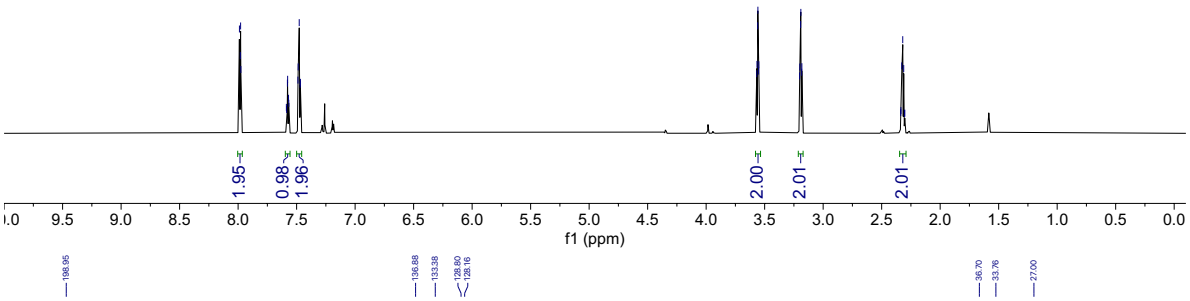


4-bromo-1-phenylbutan-1-one (3a)

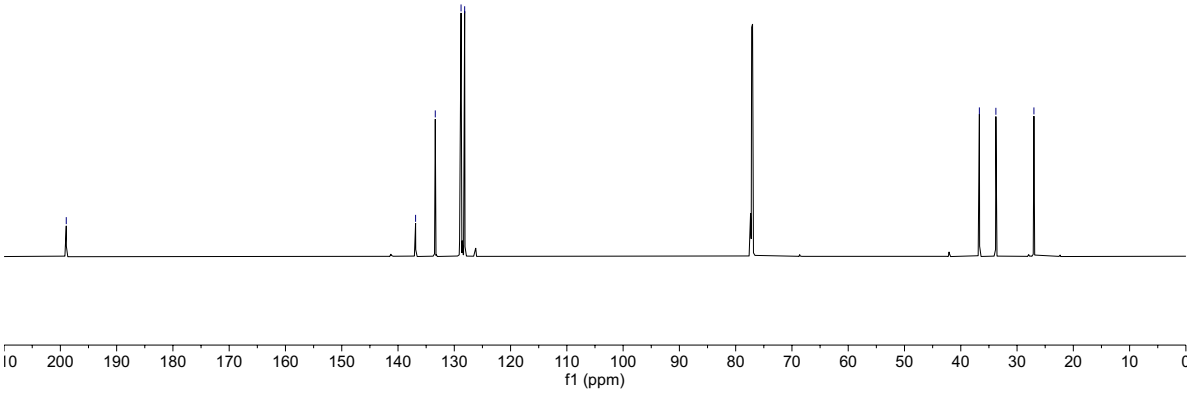
^{1}H NMR (800 MHz, $CDCl_3$)





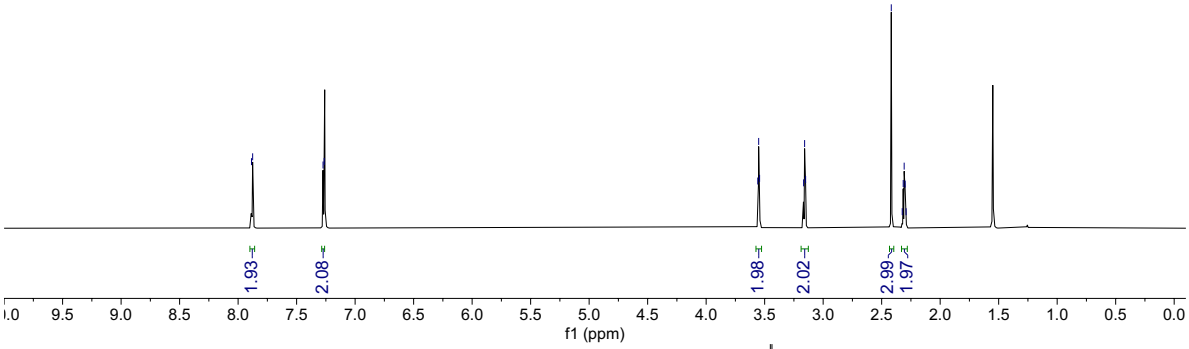


^{13}C NMR (201 MHz, $CDCl_3$)

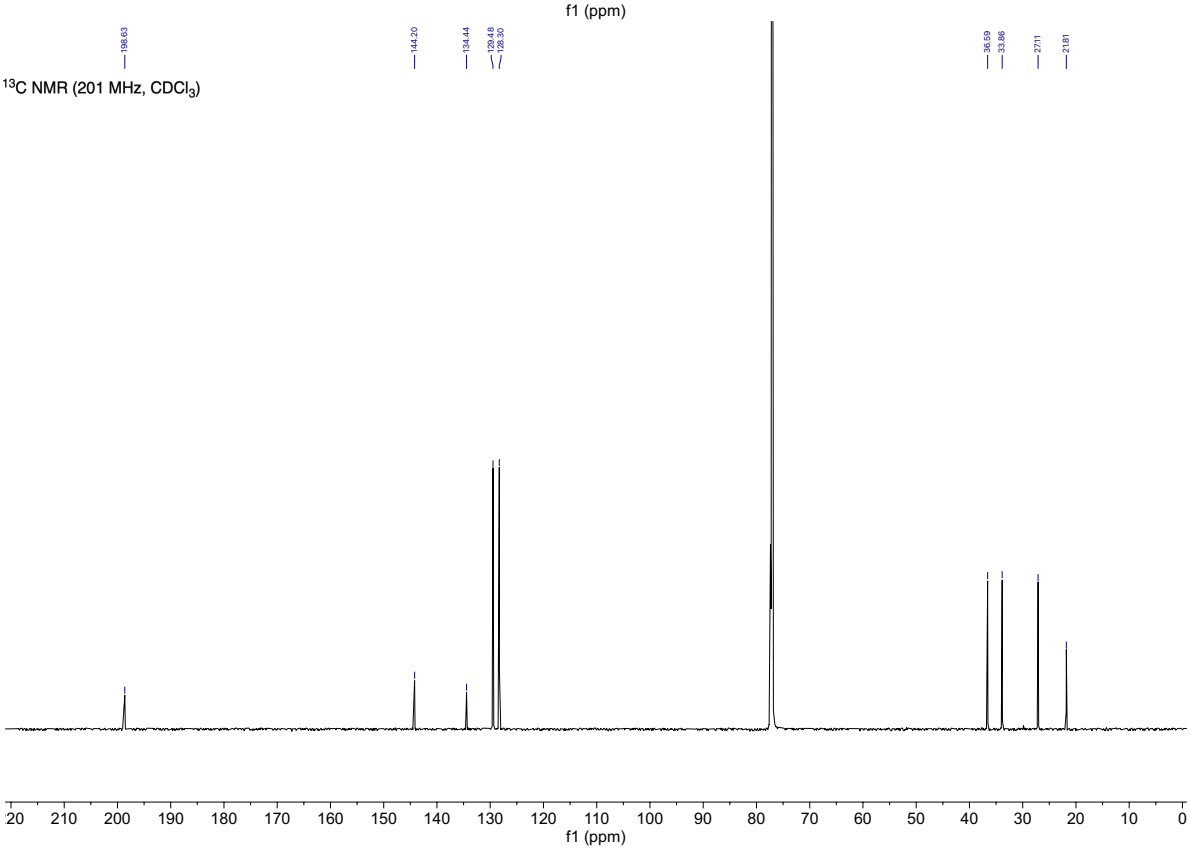


4-bromo-1-(*p*-tolyl)butan-1-one (3b)

^{1}H NMR (800 MHz, $CDCl_3$)

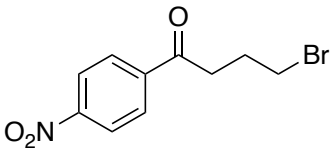


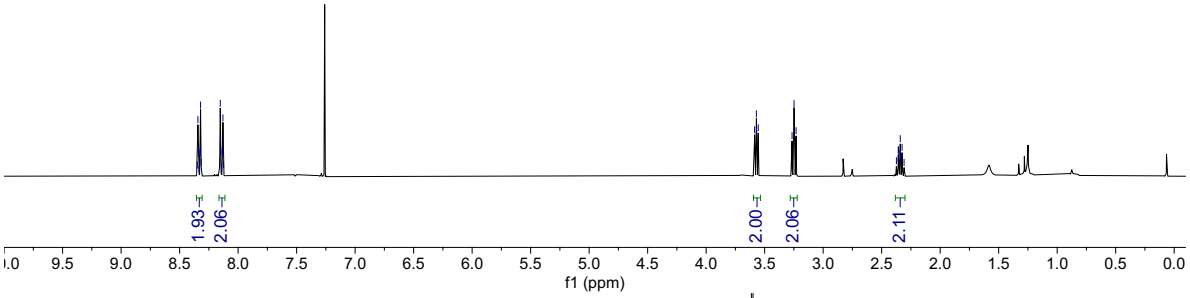
^{13}C NMR (201 MHz, $CDCl_3$)



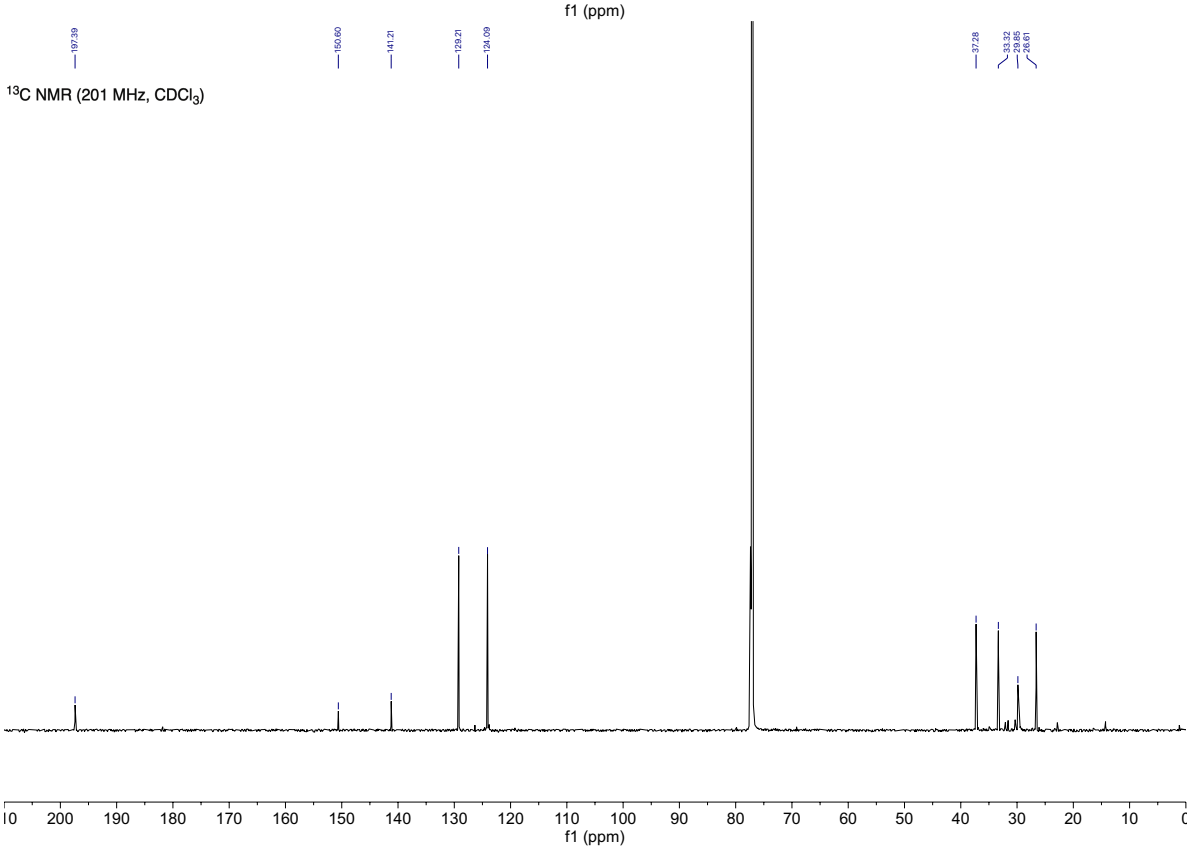
4-bromo-1-(4-nitrophenyl)butan-1-one (3c)

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



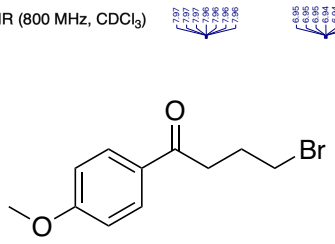


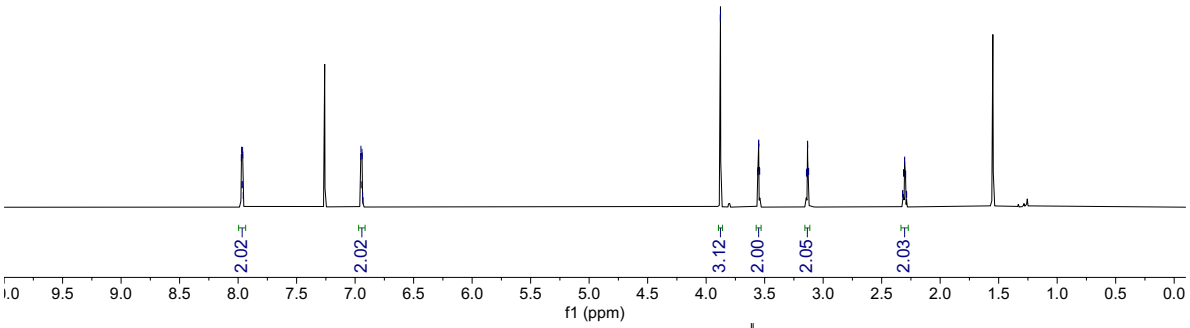
^{13}C NMR (201 MHz, $CDCl_3$)



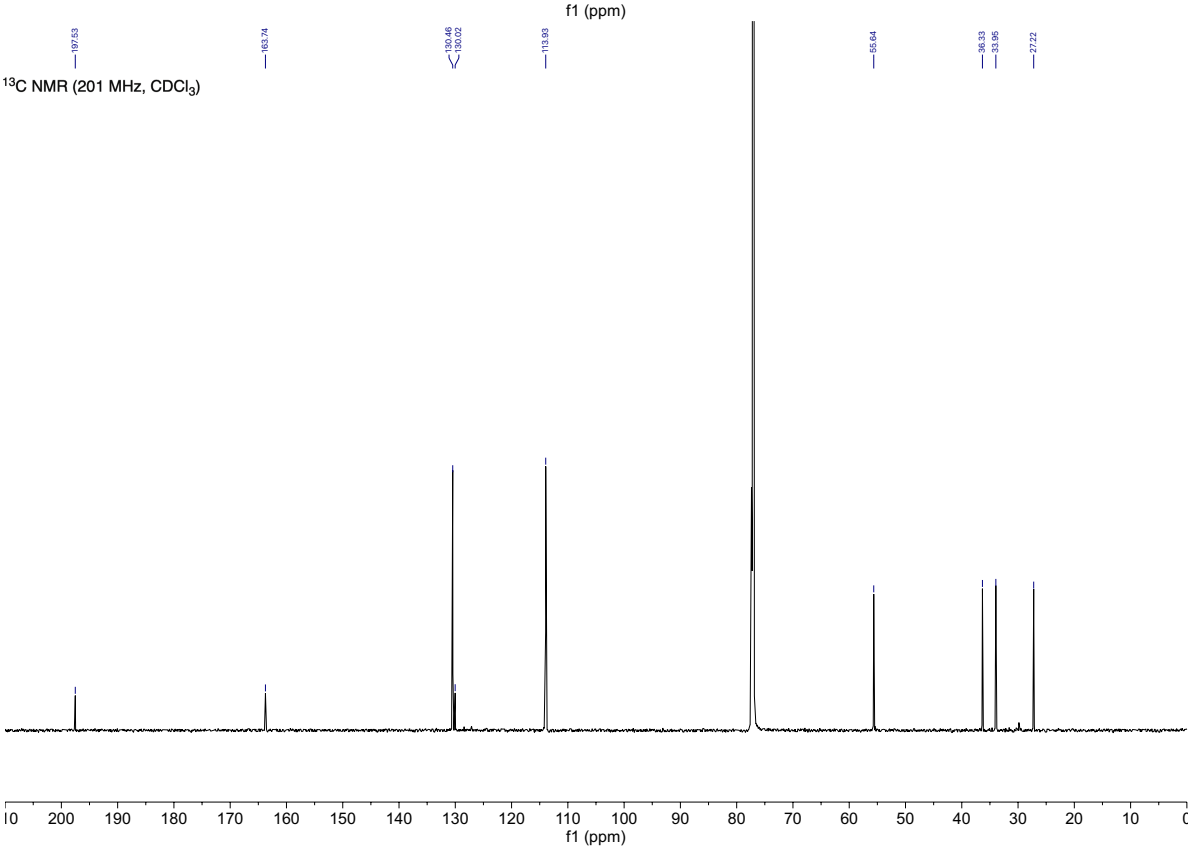
4-bromo-1-(4-methoxyphenyl)butan-1-one (3d)

^{1}H NMR (800 MHz, $CDCl_3$)



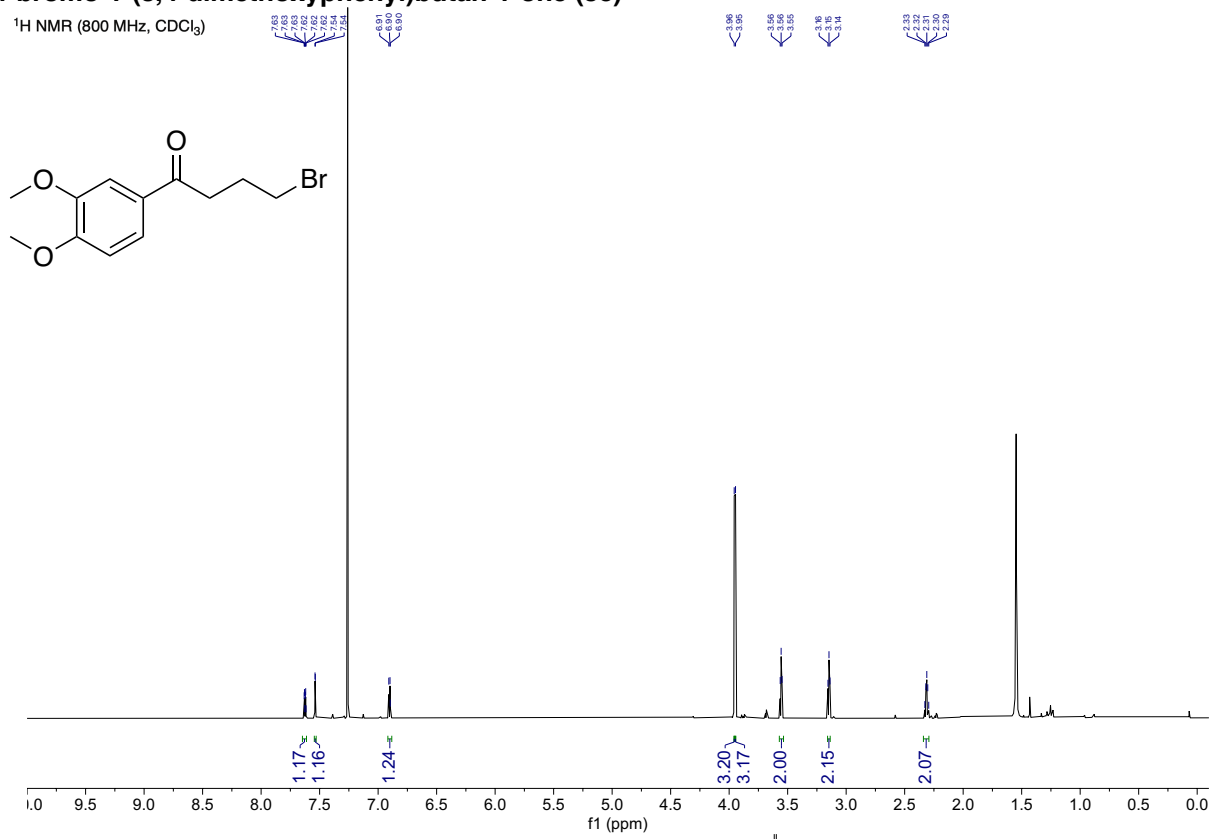


^{13}C NMR (201 MHz, $CDCl_3$)

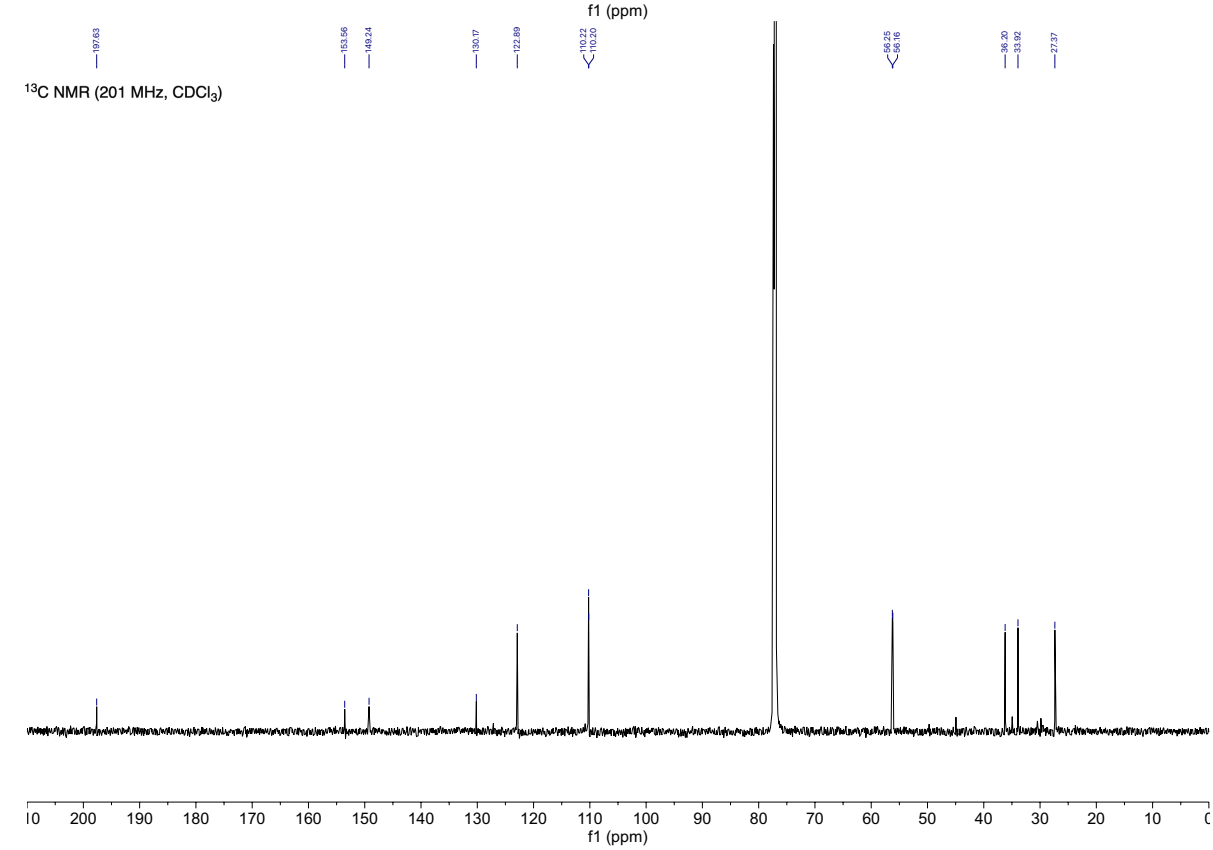


4-bromo-1-(3,4-dimethoxyphenyl)butan-1-one (3e)

^{1}H NMR (800 MHz, $CDCl_3$)

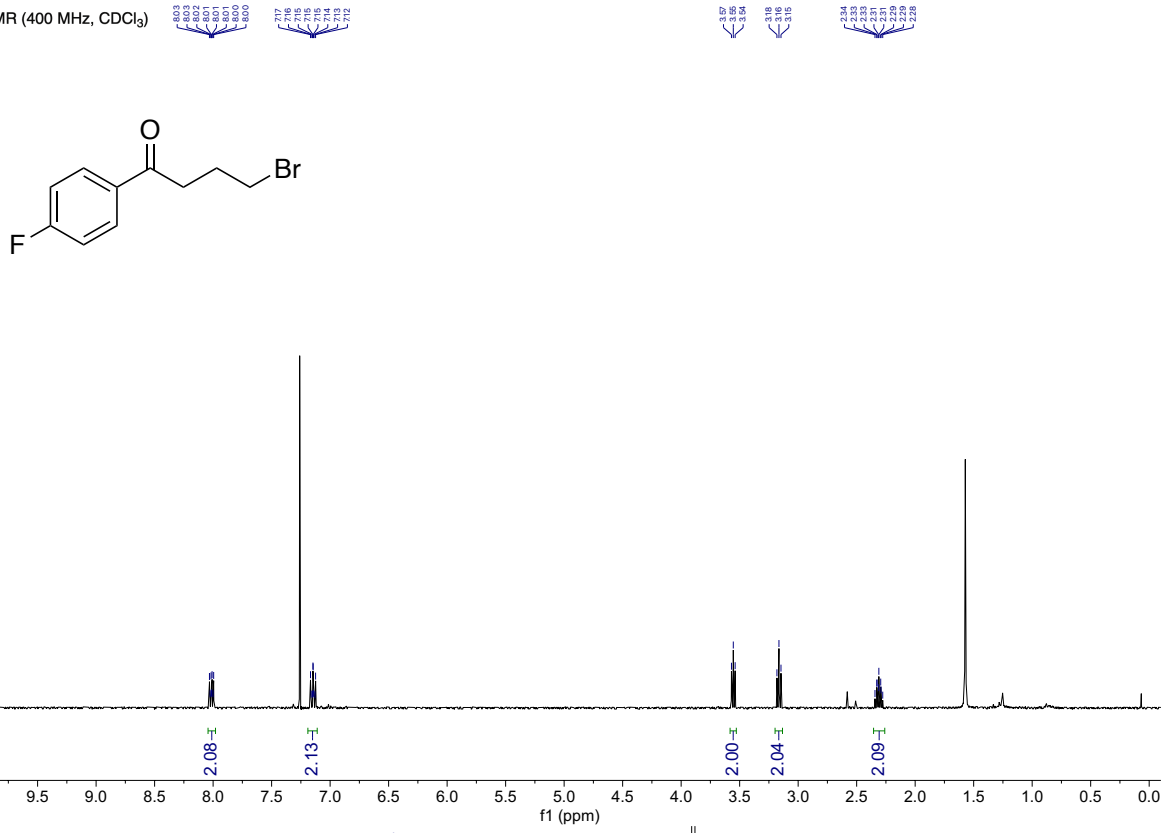


^{13}C NMR (201 MHz, $CDCl_3$)

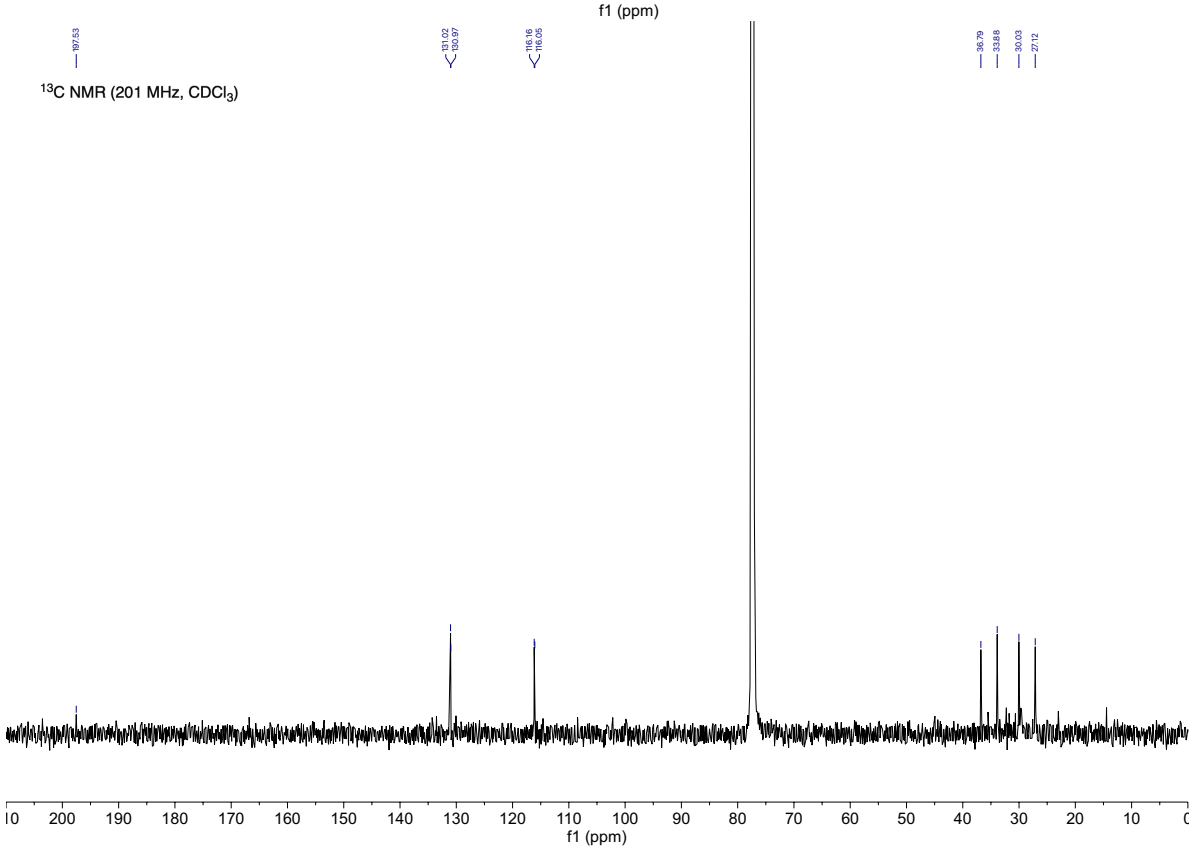


4-bromo-1-(4-fluorophenyl)butan-1-one (3f)

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

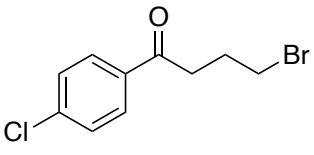


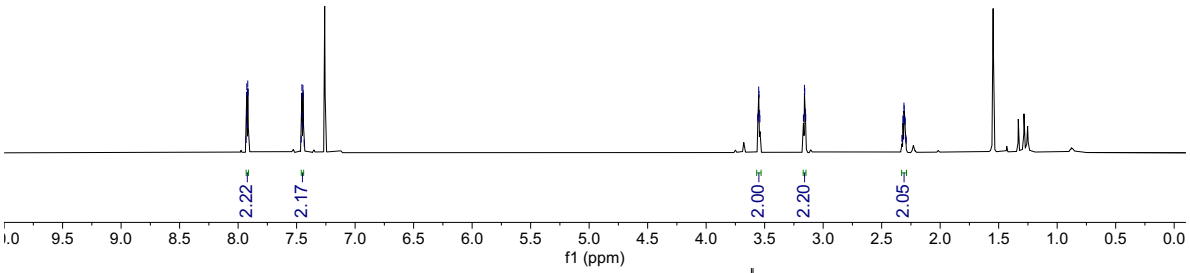
^{13}C NMR (201 MHz, $CDCl_3$)



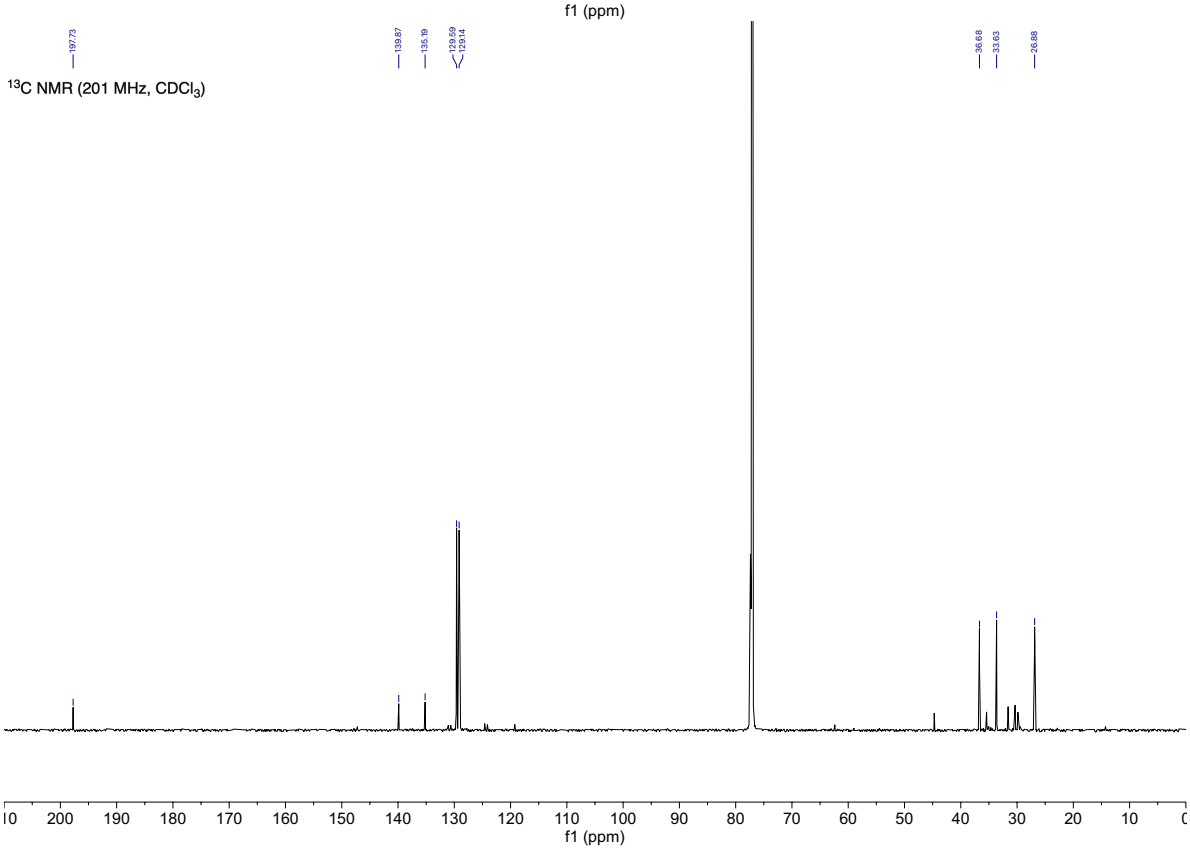
4-bromo-1-(4-chlorophenyl)butan-1-one (3g)

^{1}H NMR (800 MHz, $CDCl_3$)



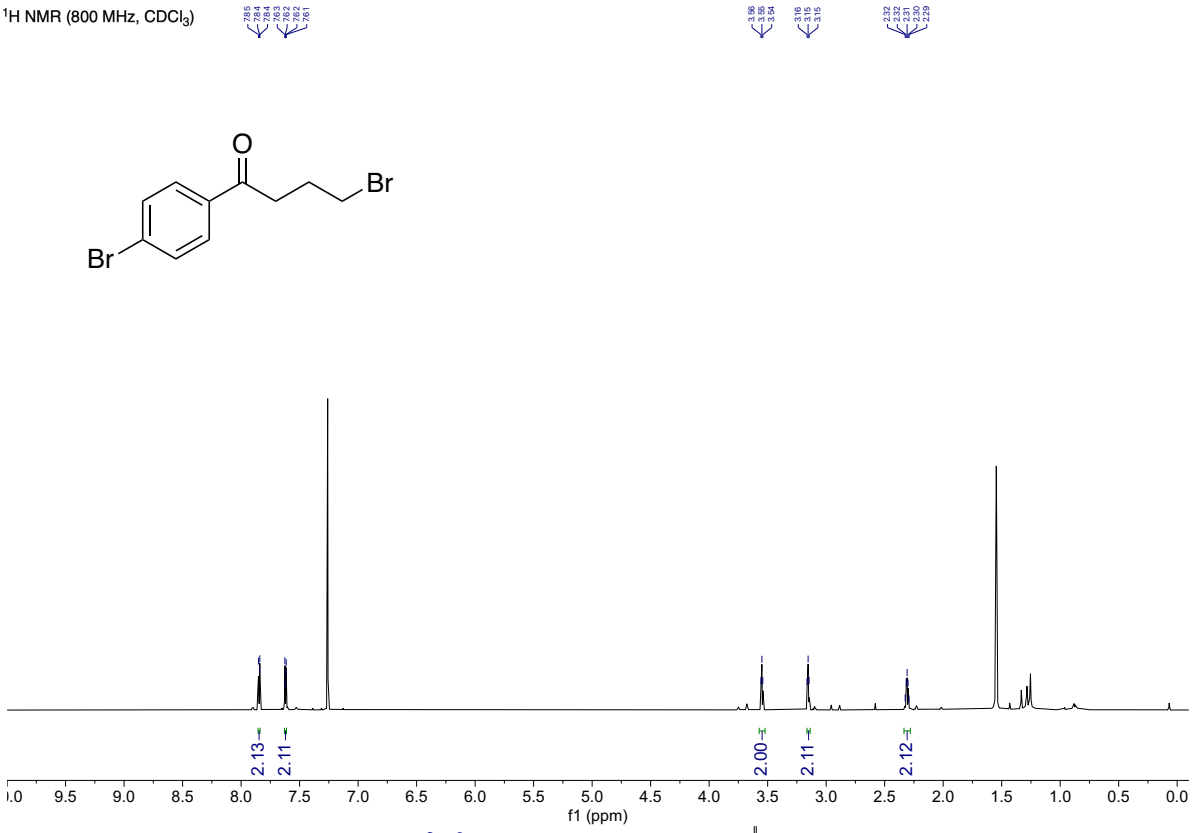


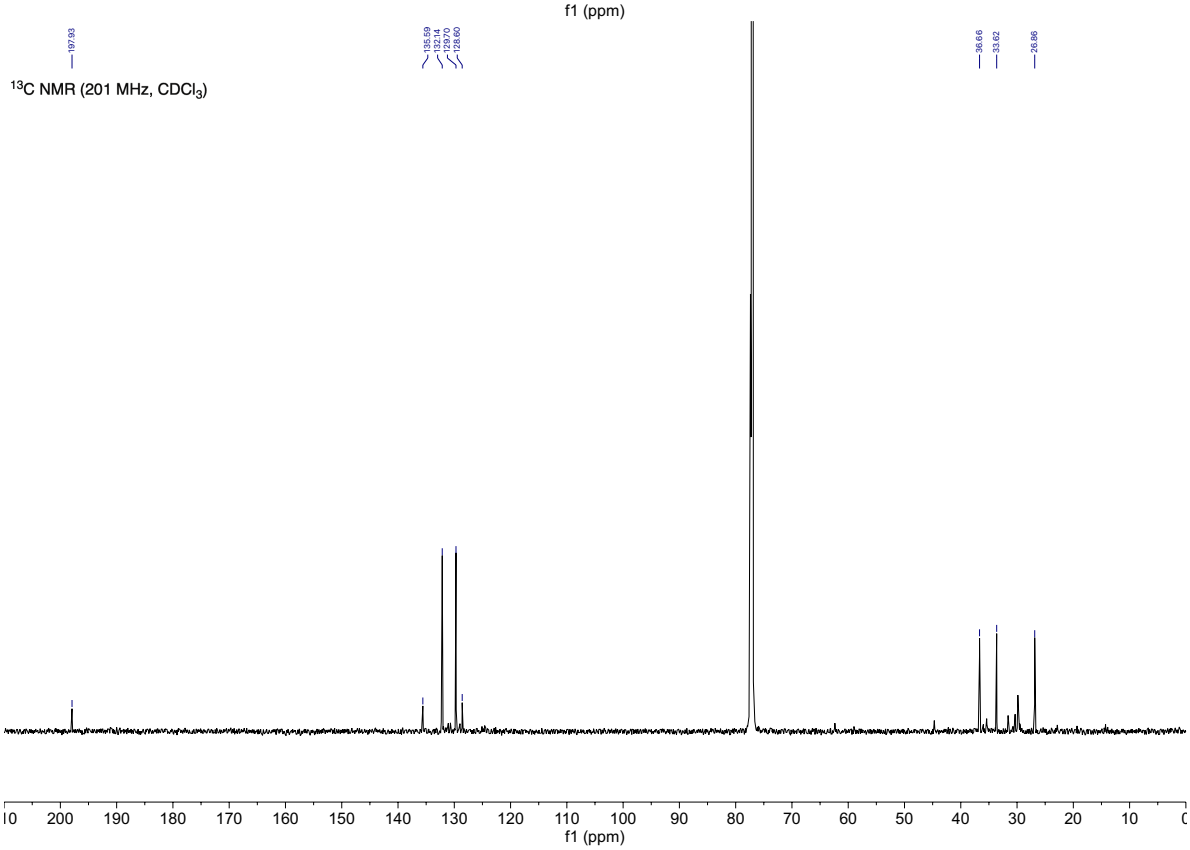
^{13}C NMR (201 MHz, $CDCl_3$)



4-bromo-1-(4-bromophenyl)butan-1-one (3h)

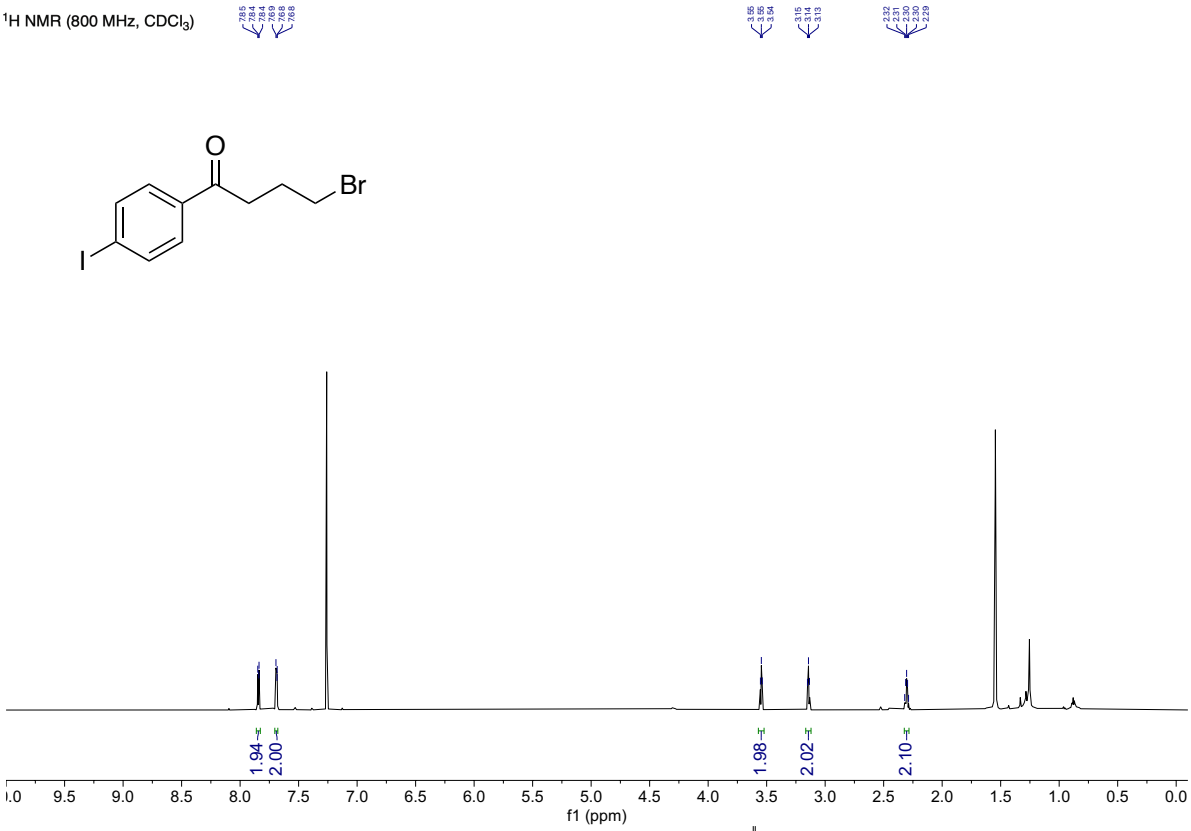
^{1}H NMR (800 MHz, $CDCl_3$)



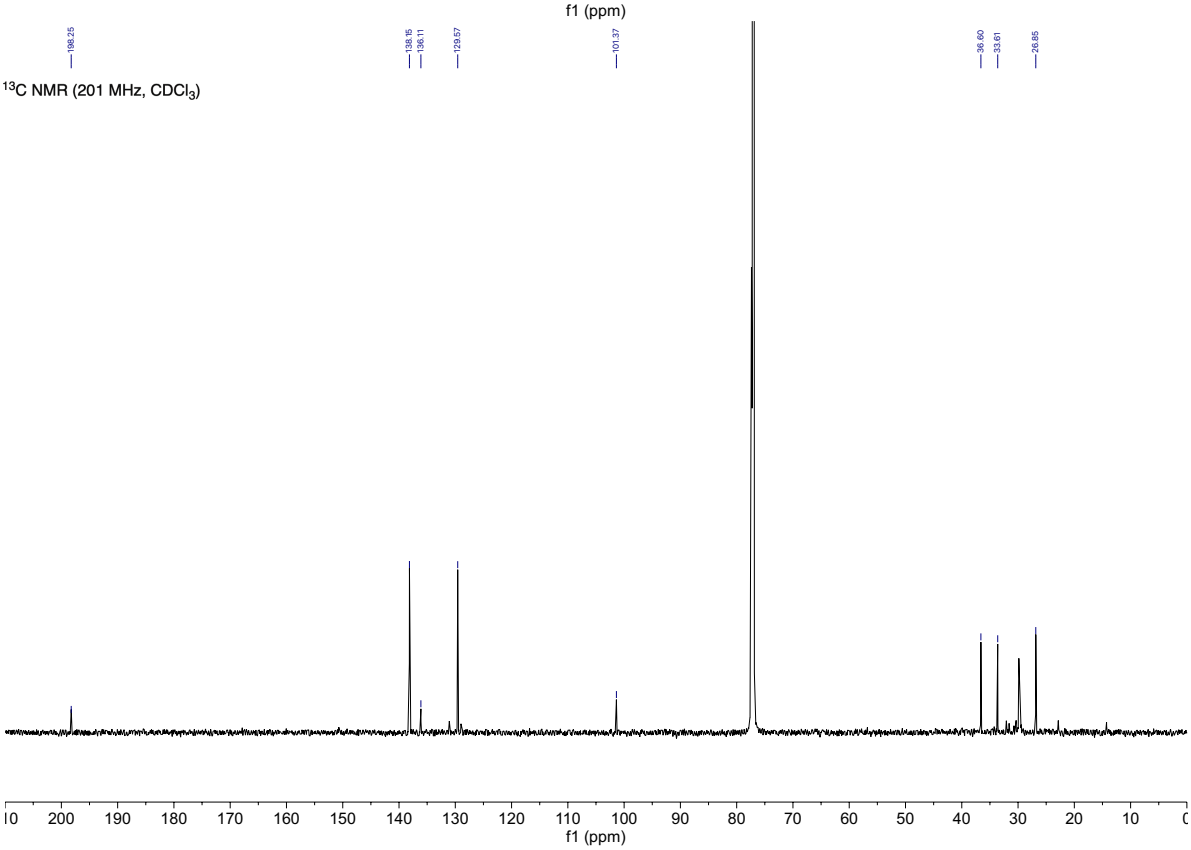


4-bromo-1-(4-iodophenyl)butan-1-one (3i)

^{1}H NMR (800 MHz, $CDCl_3$)

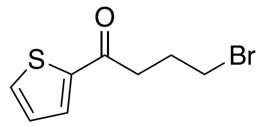


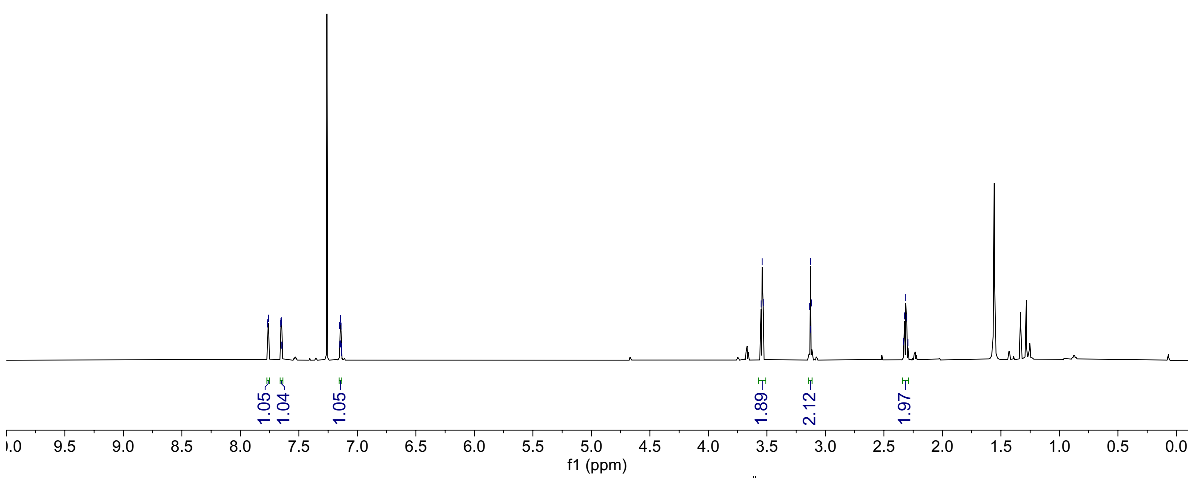
^{13}C NMR (201 MHz, $CDCl_3$)



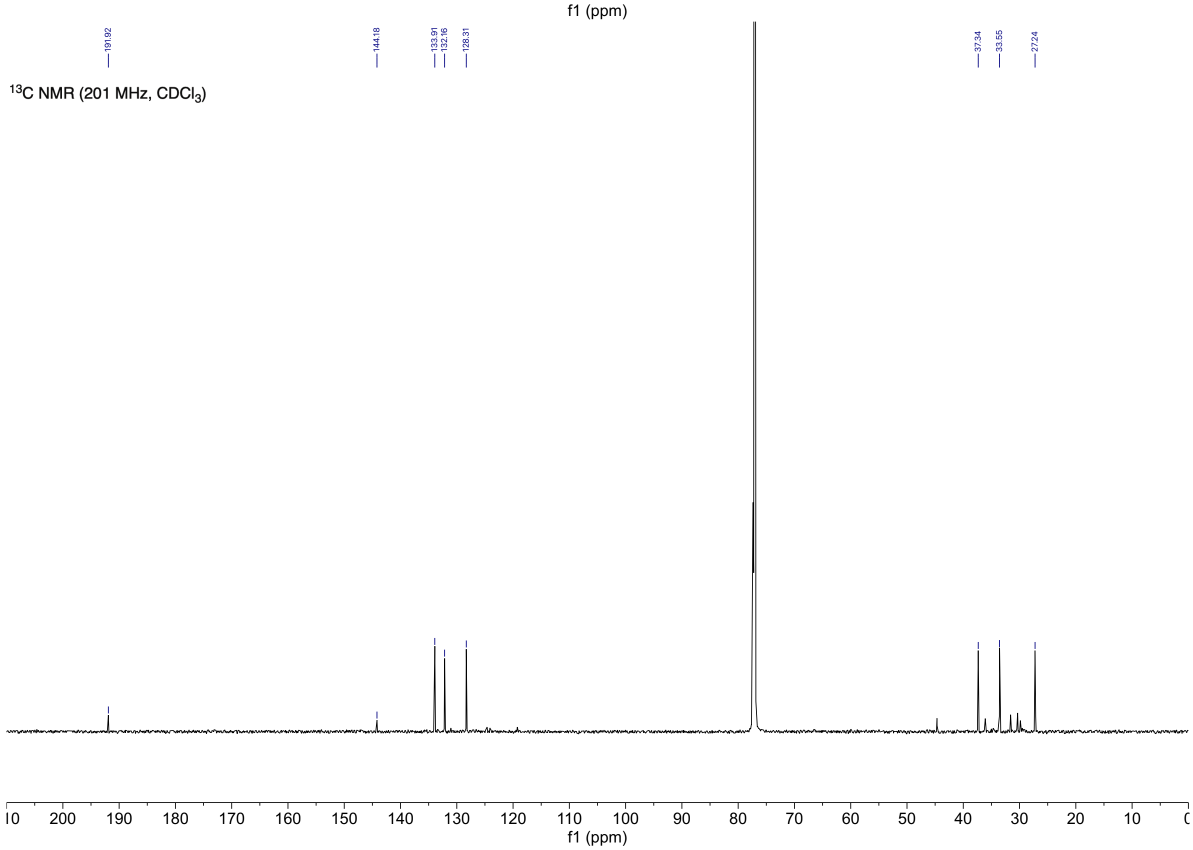
4-bromo-1-(thiophen-2-yl)butan-1-one (3j)

^{1}H NMR (700 MHz, $CDCl_3$)

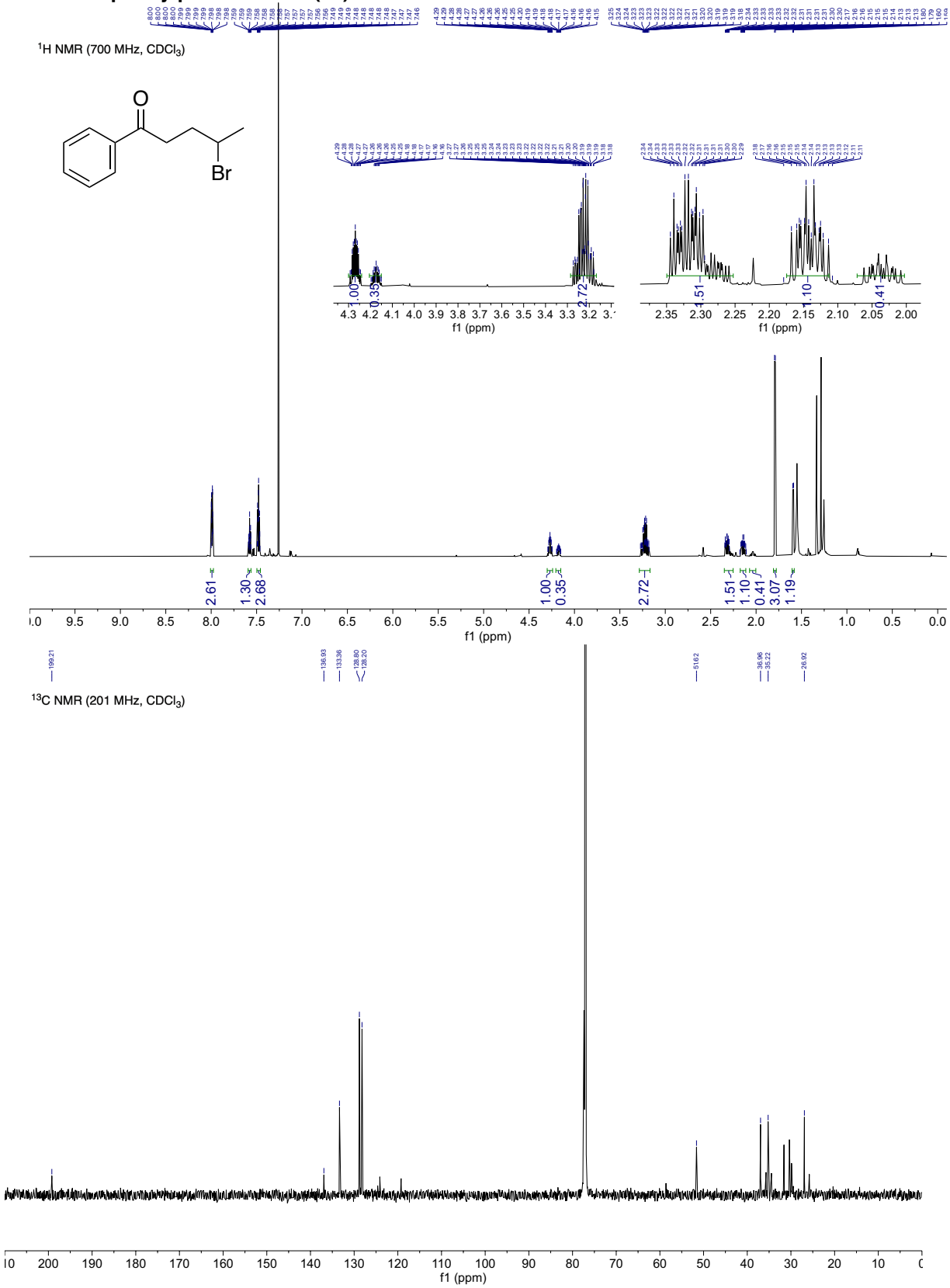




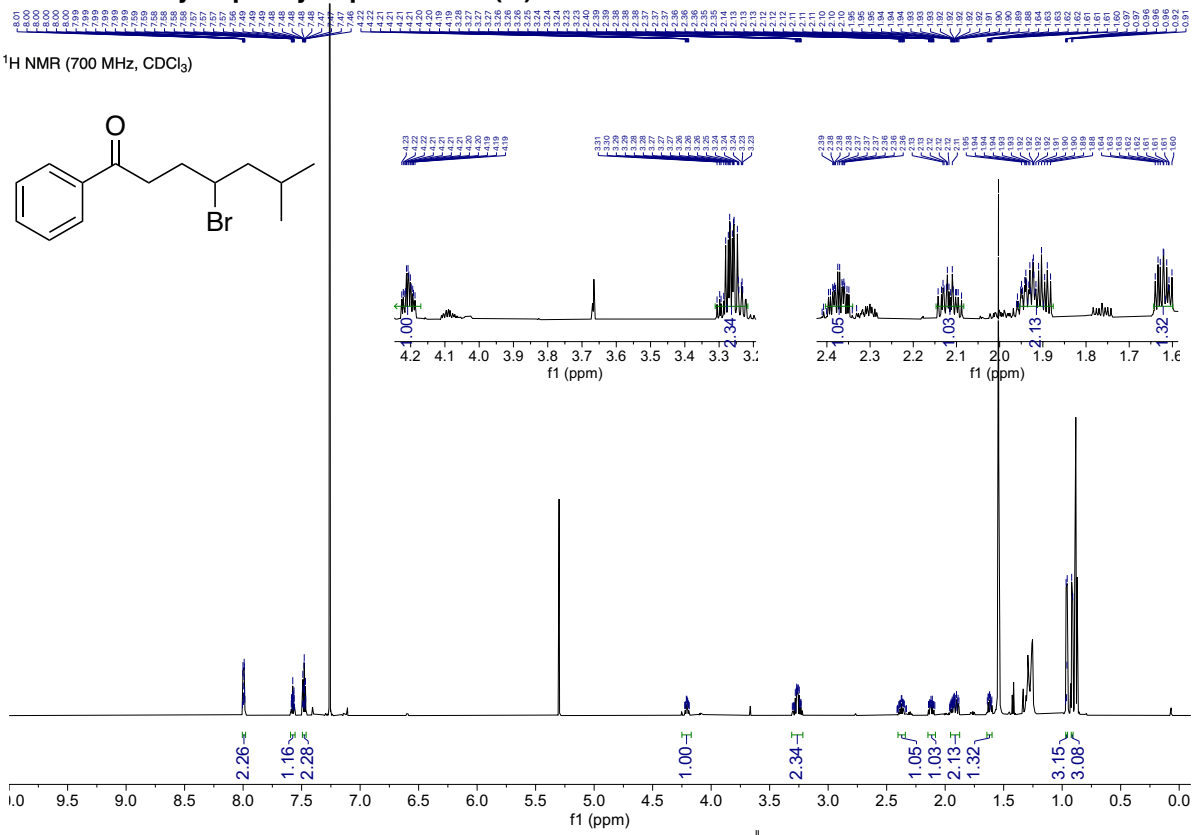
^{13}C NMR (201 MHz, $CDCl_3$)

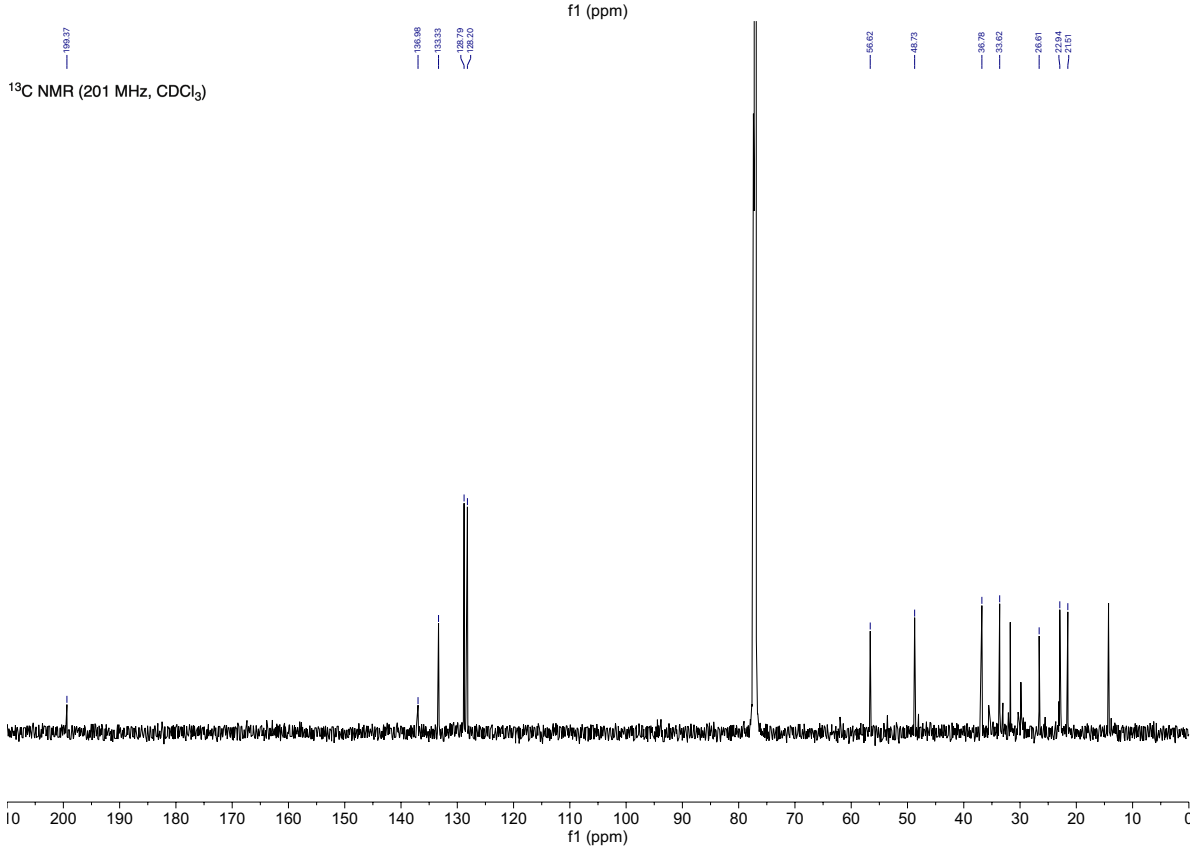


4-bromo-1-phenylpentan-1-one (3k)



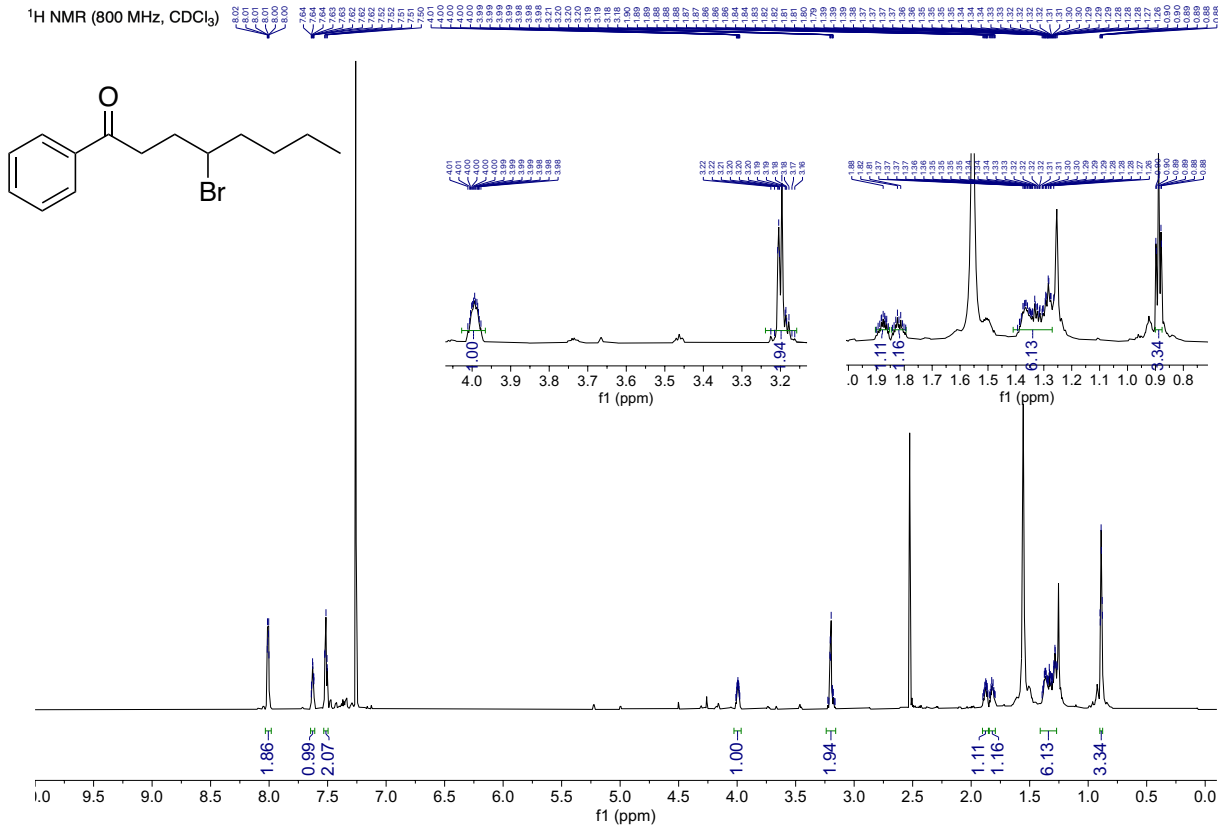
4-bromo-6-methyl-1-phenylheptan-1-one (3l)



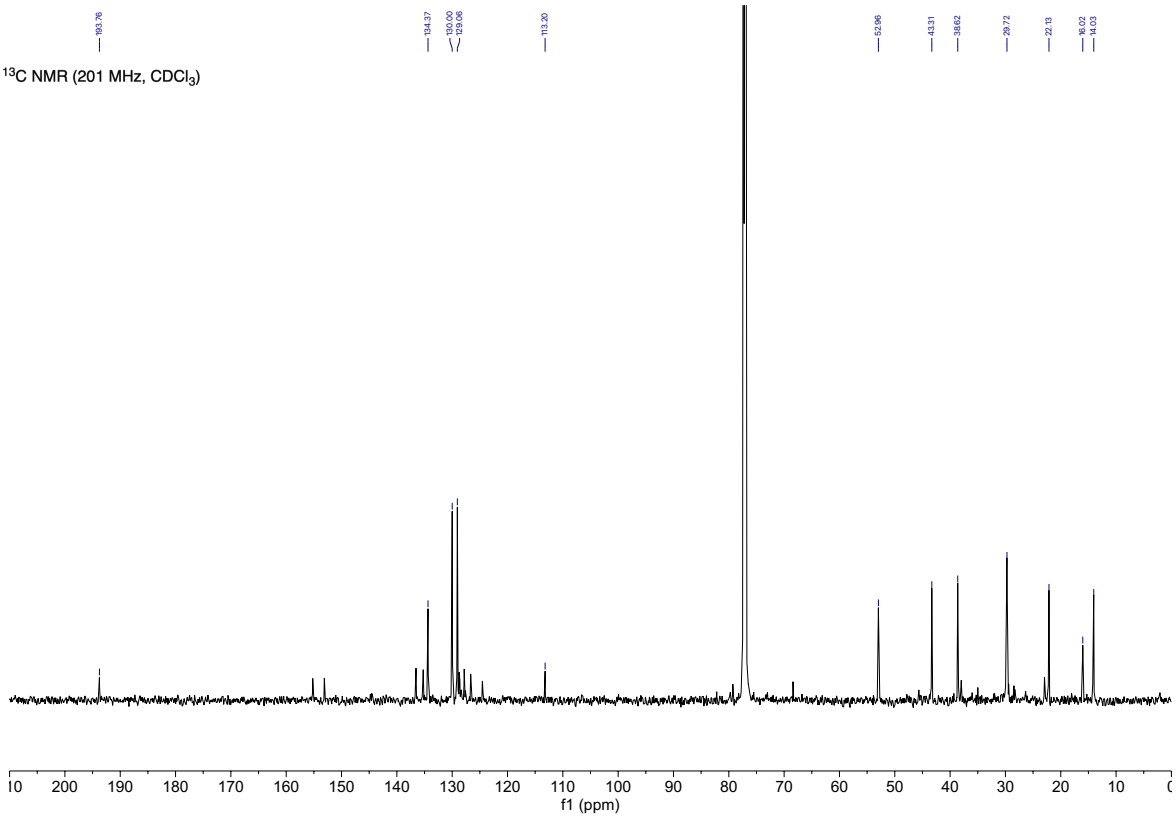


4-bromo-1-phenyloctan-1-one (3m)

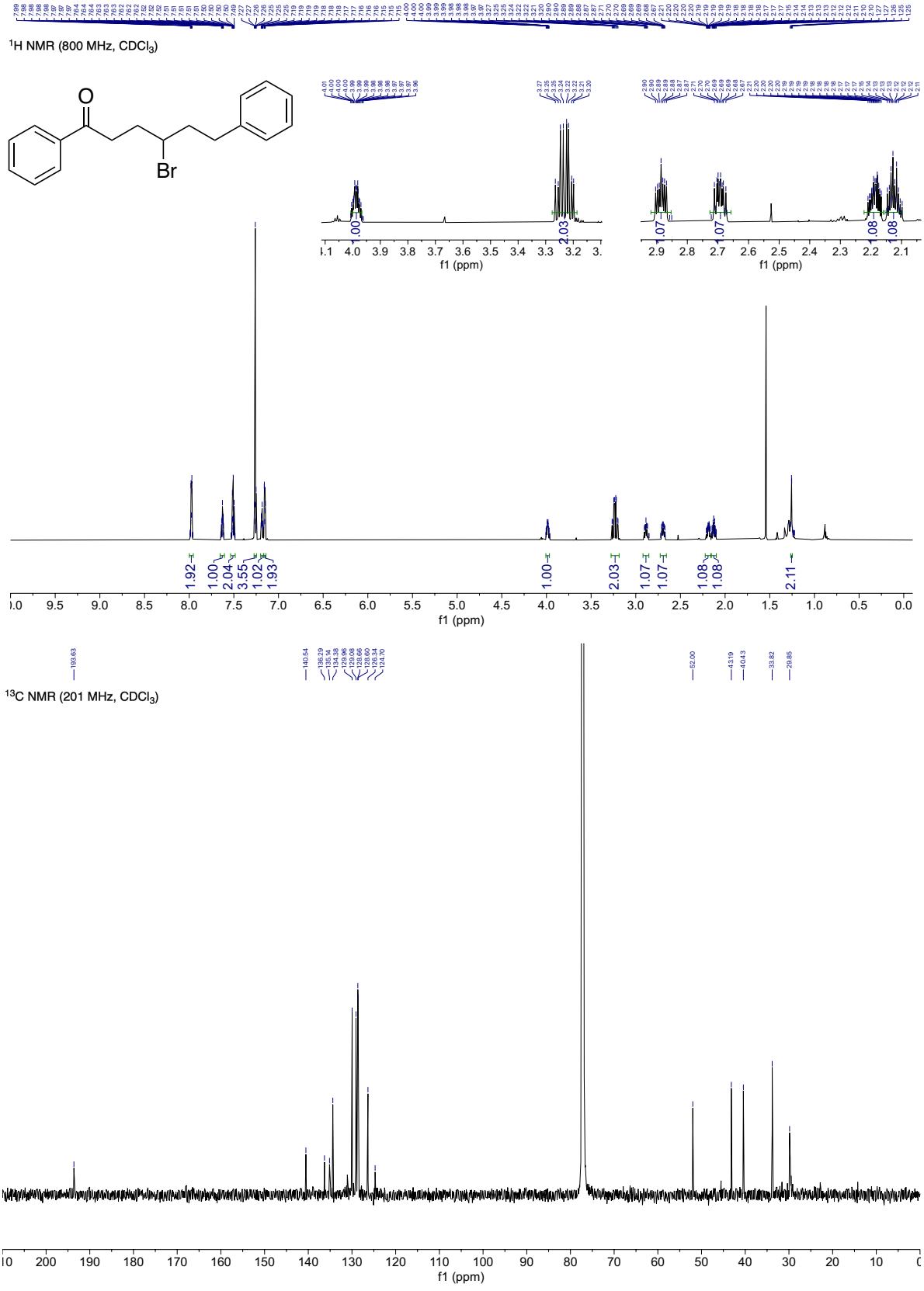
^{1}H NMR (800 MHz, $CDCl_3$)



^{13}C NMR (201 MHz, $CDCl_3$)

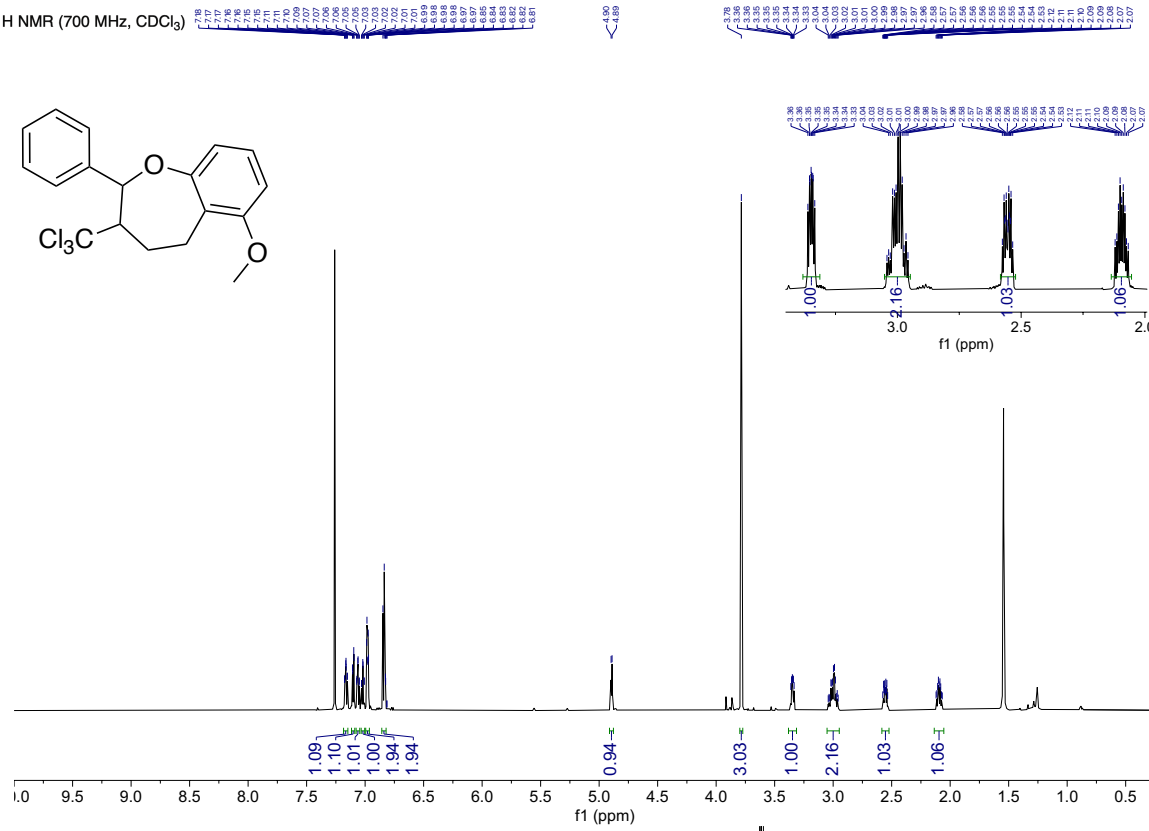


4-bromo-1,6-diphenylhexan-1-one (3n)

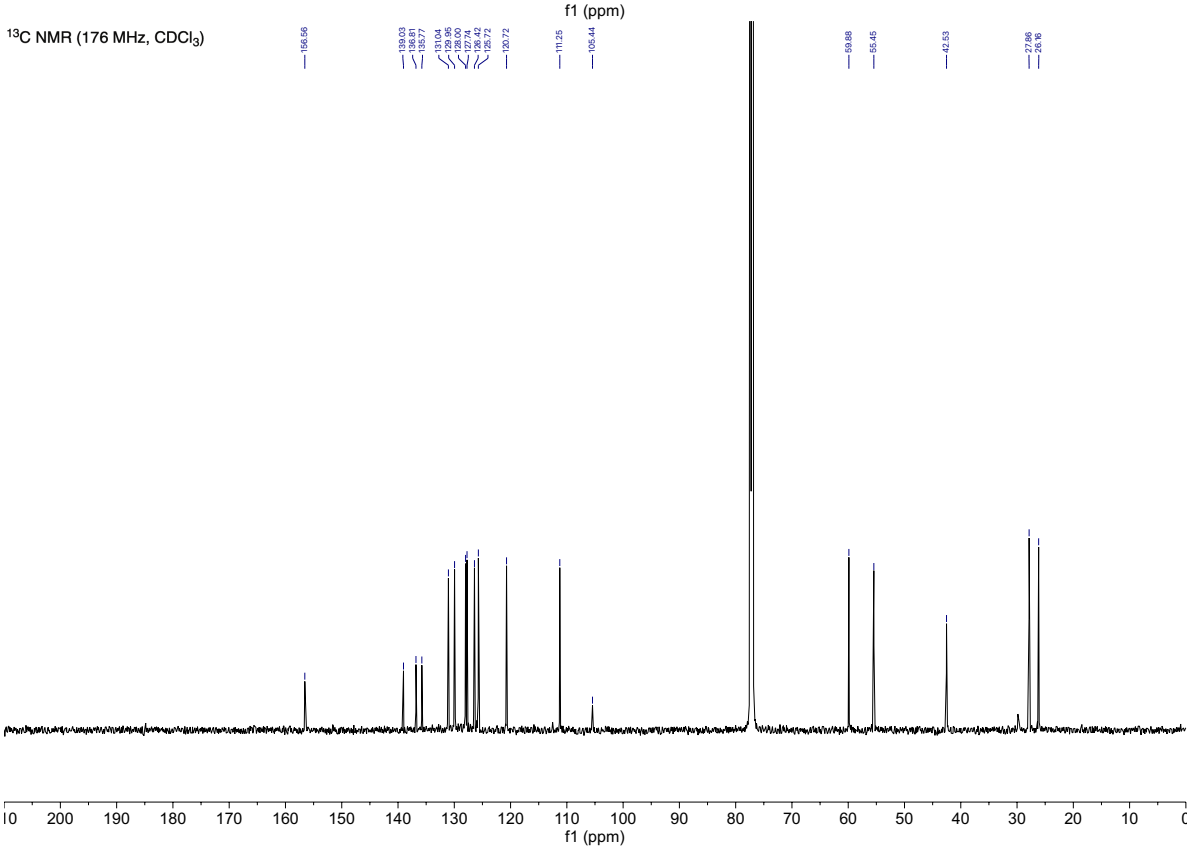


6-methoxy-2-phenyl-3-(trichloromethyl)-2,3,4,5-tetrahydrobenzoxepine (3o)

^{1}H NMR (700 MHz, $CDCl_3$)

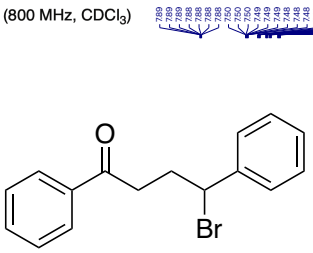


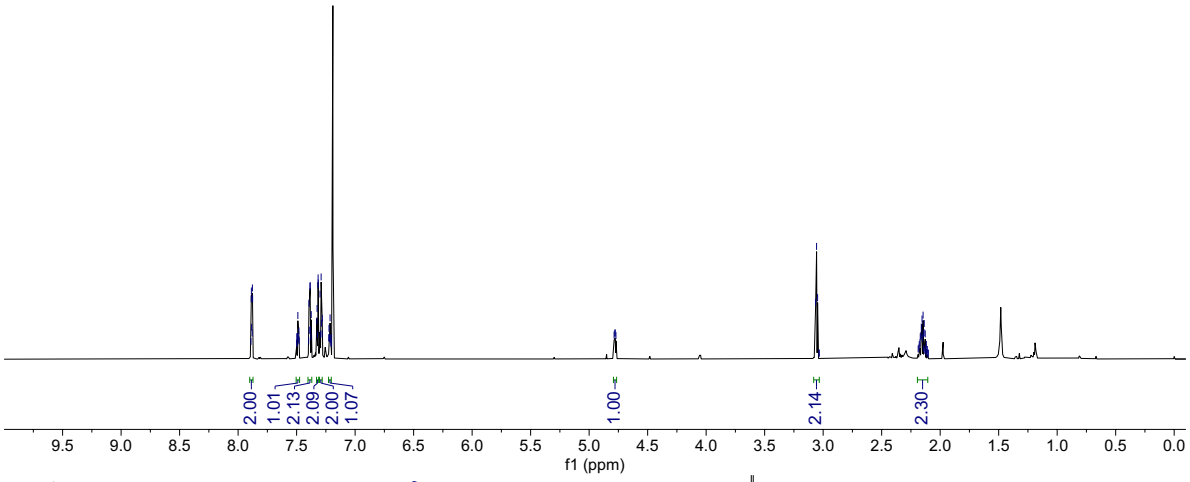
^{13}C NMR (176 MHz, $CDCl_3$)



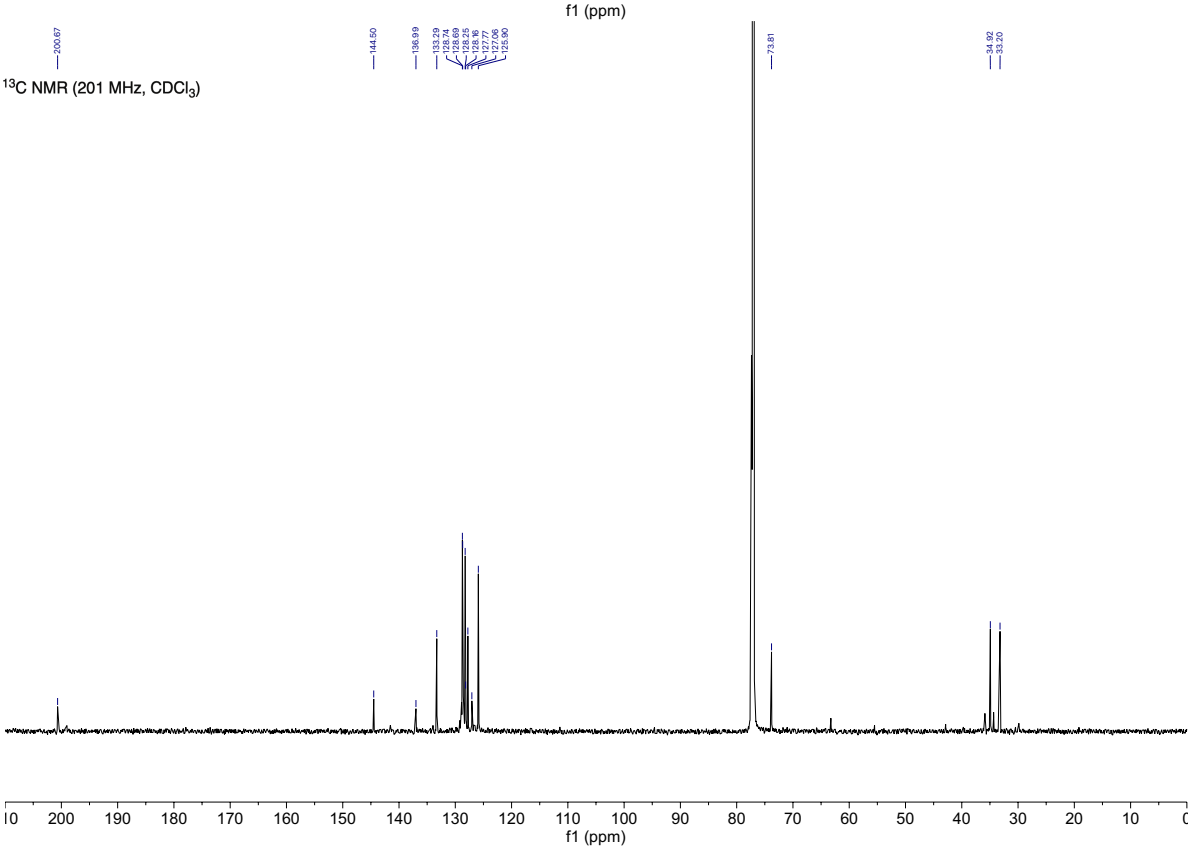
4-bromo-1,4-diphenylbutan-1-one (3p)

^{1}H NMR (800 MHz, $CDCl_3$)

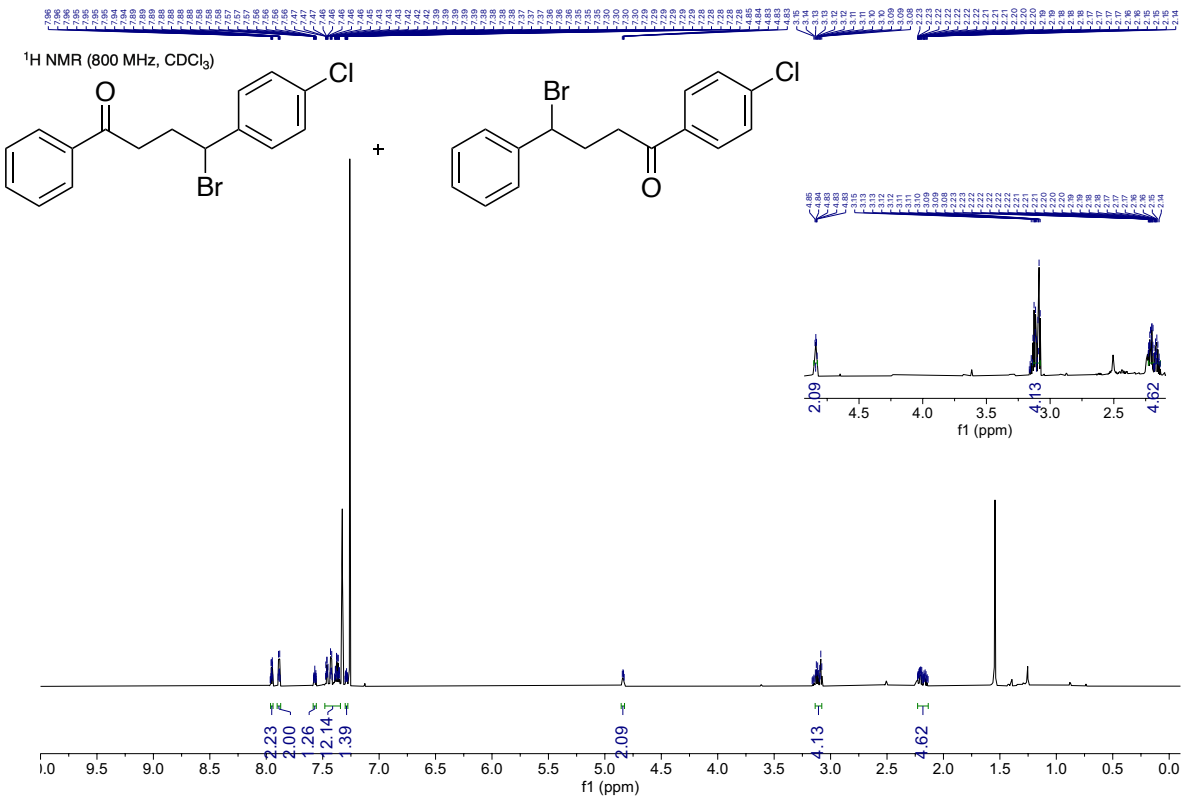


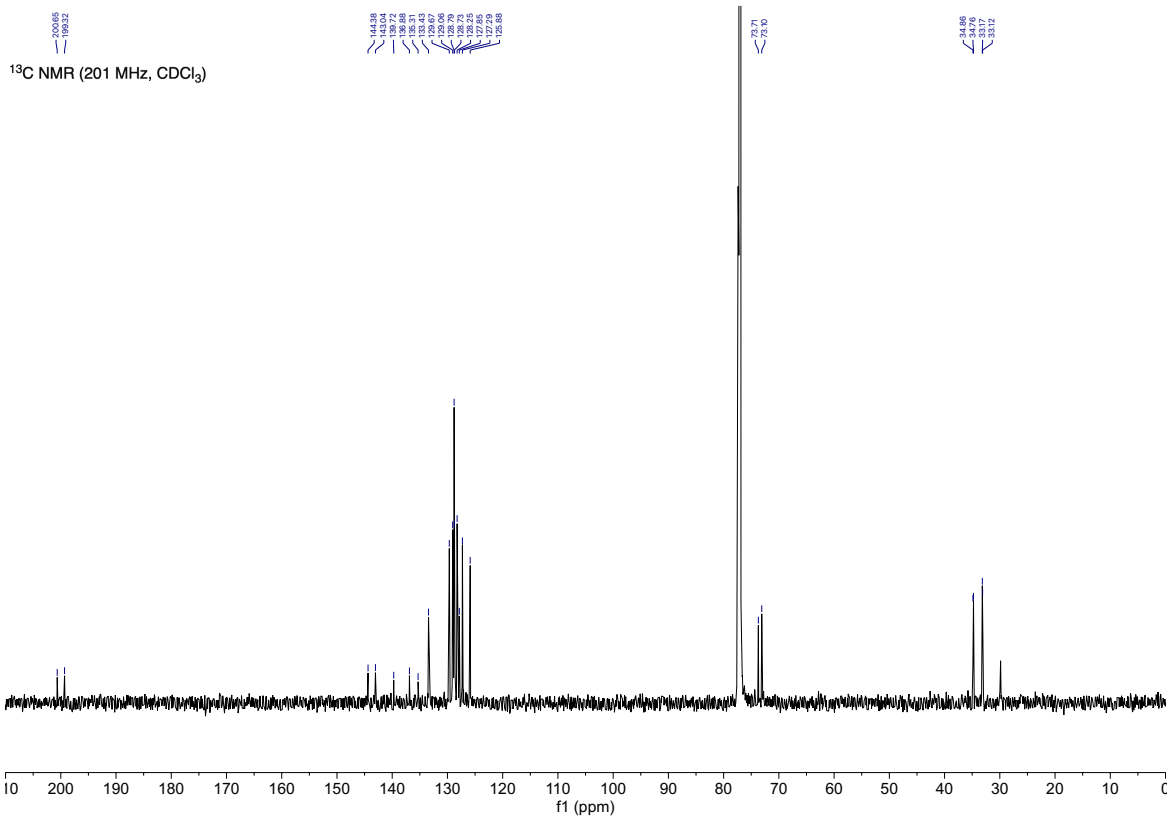


^{13}C NMR (201 MHz, $CDCl_3$)



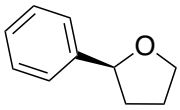
4-bromo-4-(4-chlorophenyl)-1-phenylbutan-1-one (3r)
4-bromo-1-(4-chlorophenyl)-4-phenylbutan-1-one (3r')

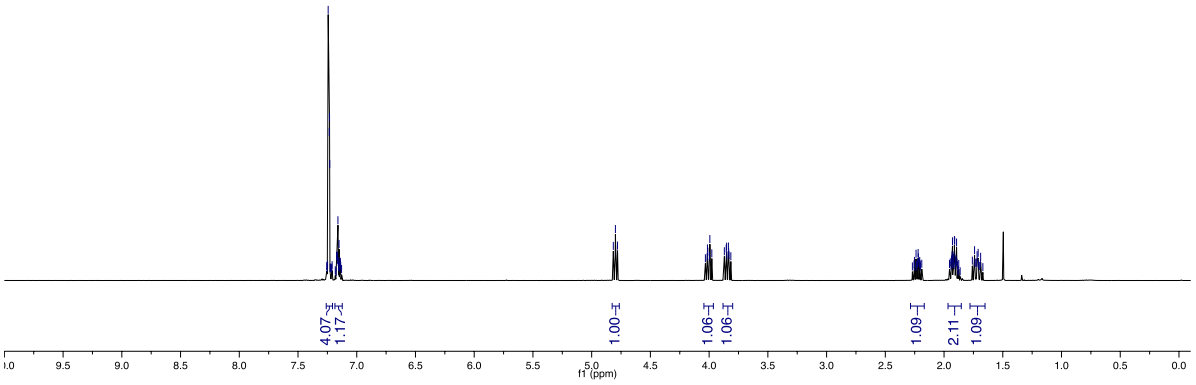




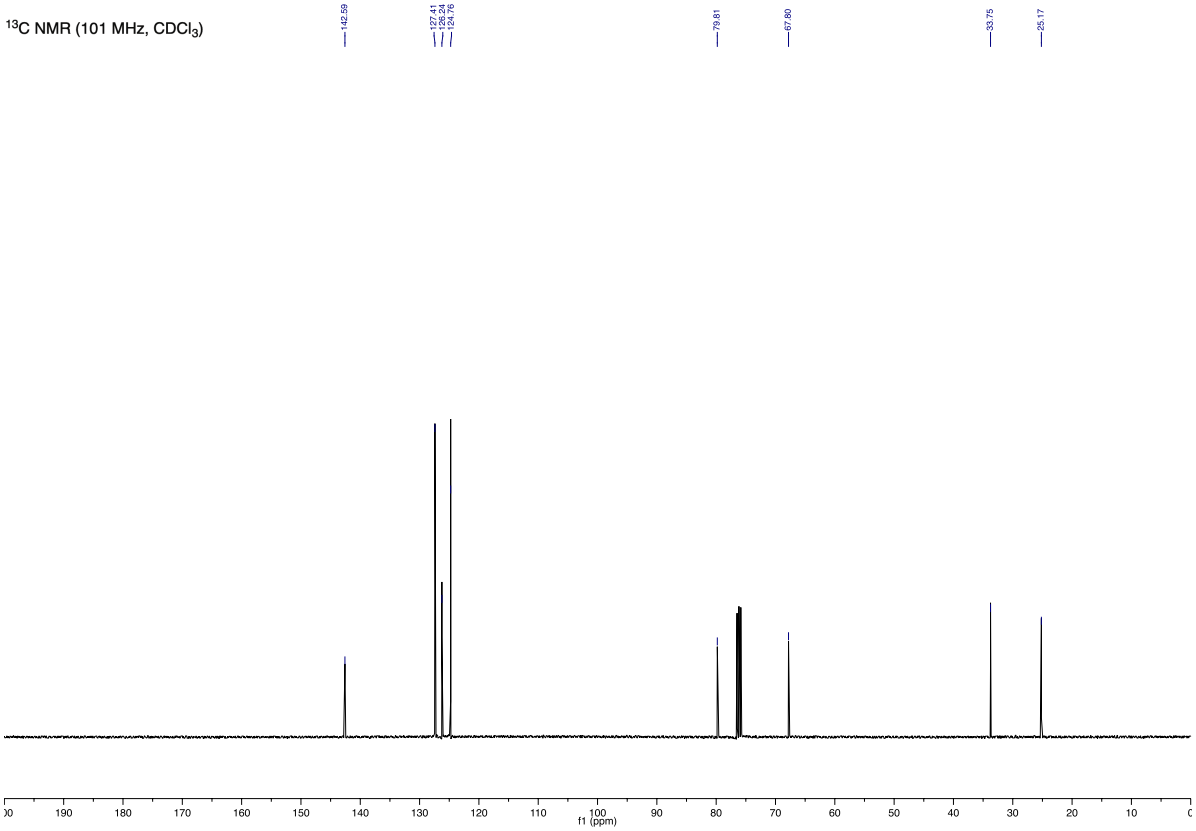
(S)-2-phenyltetrahydrofuran (4)

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



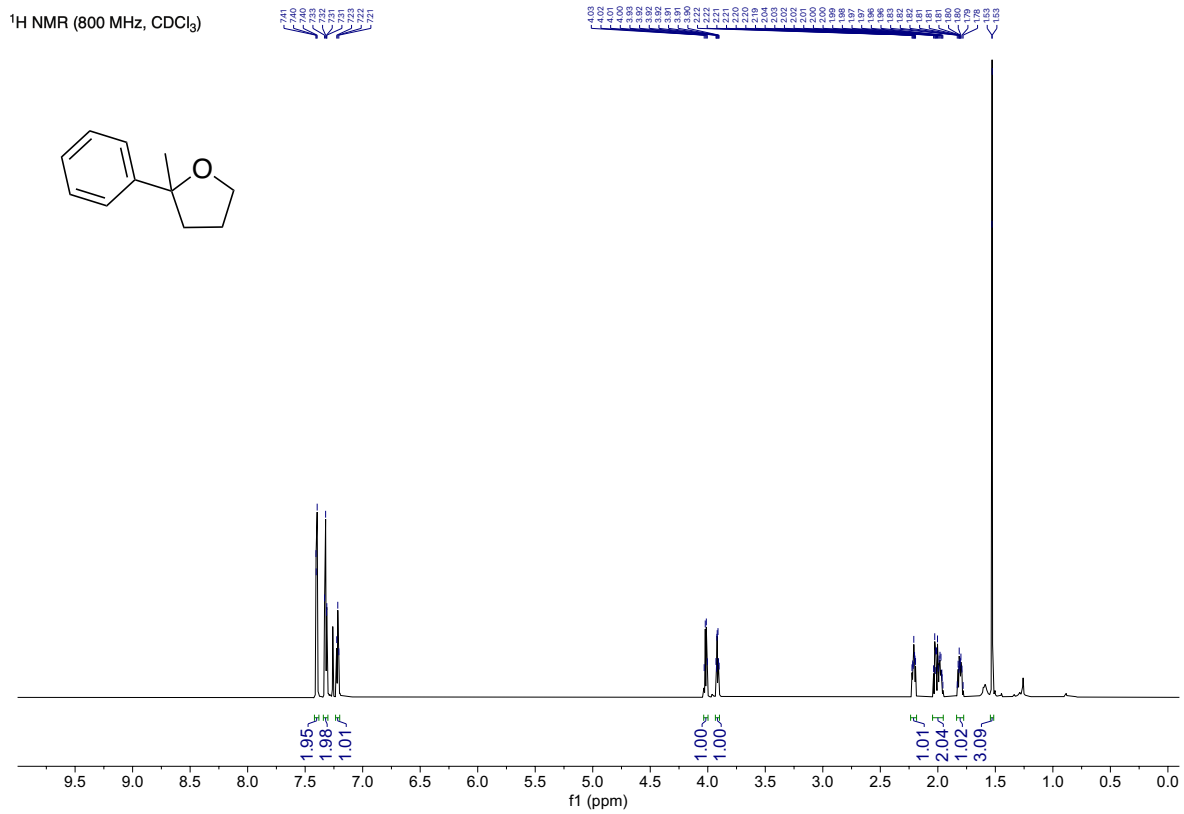


^{13}C NMR (101 MHz, $CDCl_3$)

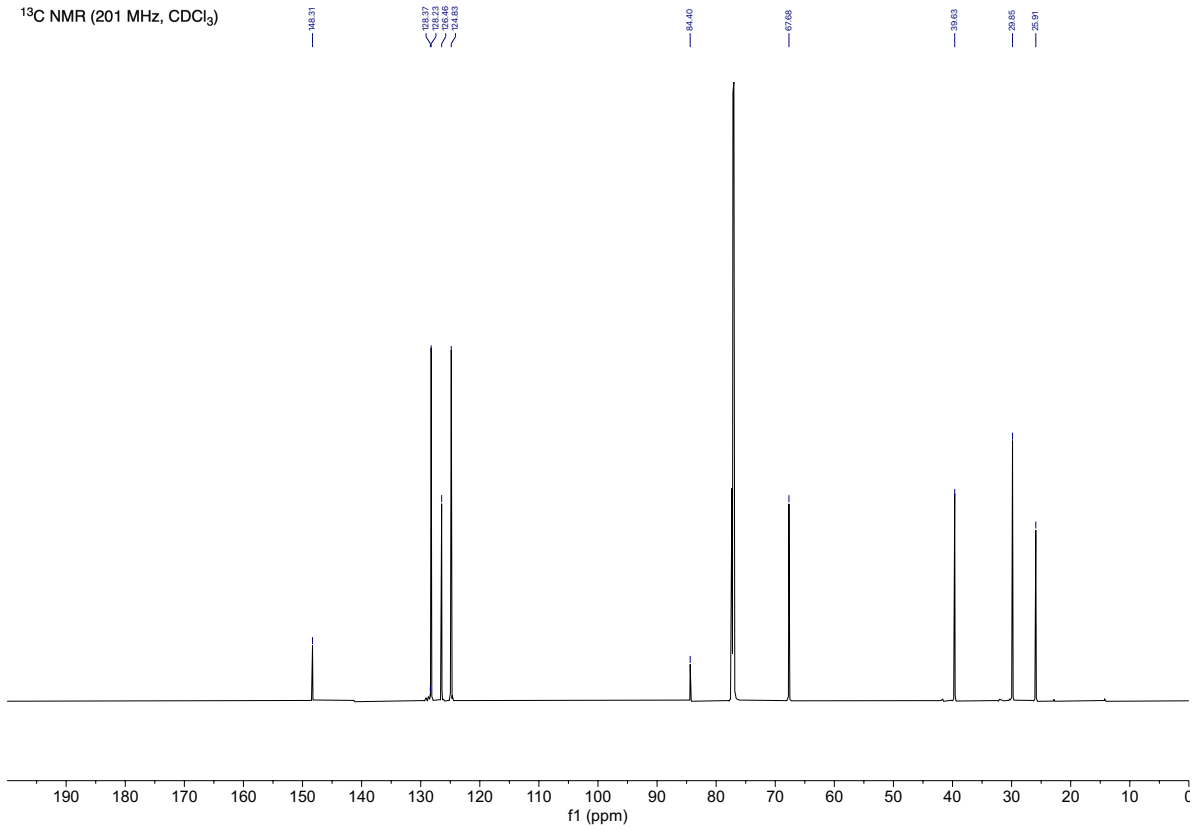


2-methyl-2-phenyltetrahydrofuran (5)

^{1}H NMR (800 MHz, $CDCl_3$)

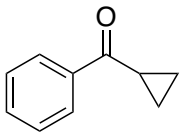


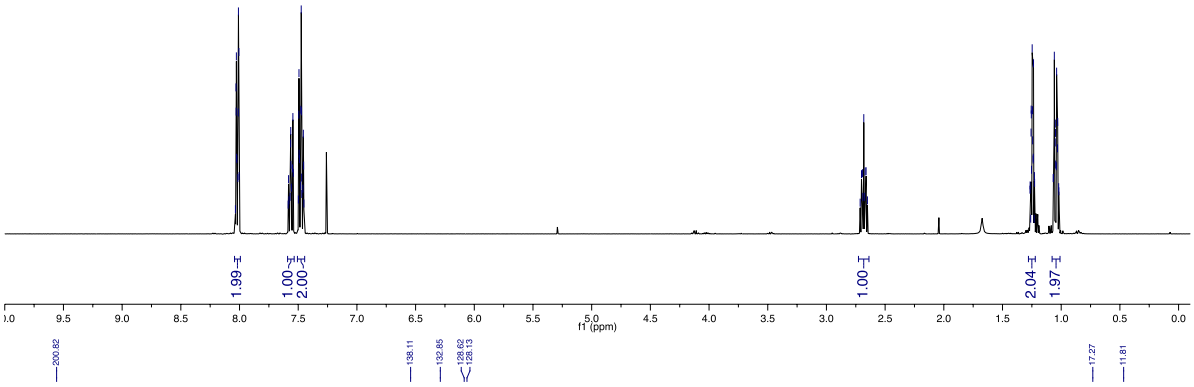
^{13}C NMR (201 MHz, $CDCl_3$)



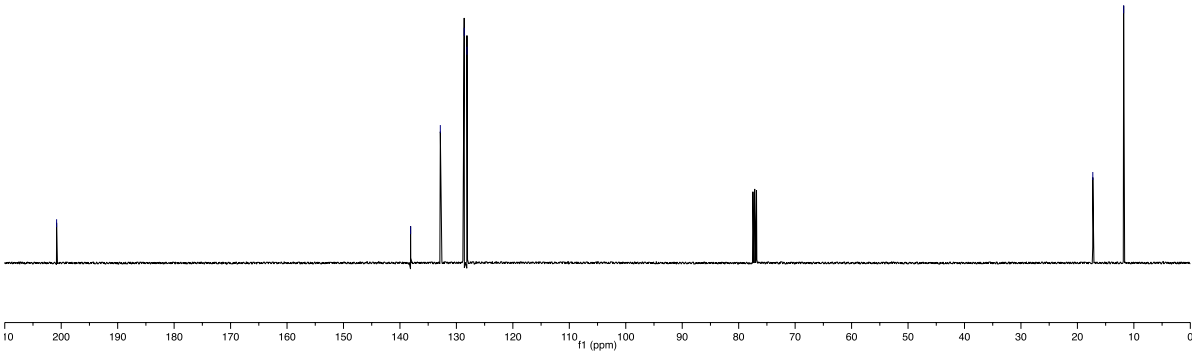
cyclopropyl-(phenyl)-methanone (6)

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



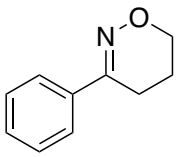


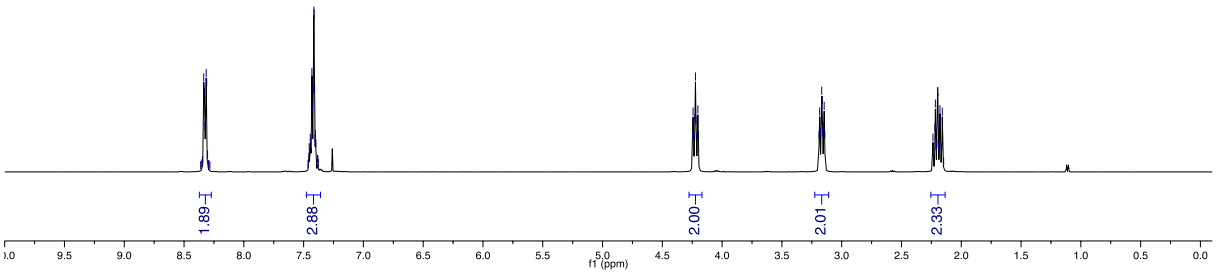
^{13}C NMR (101 MHz, $CDCl_3$)



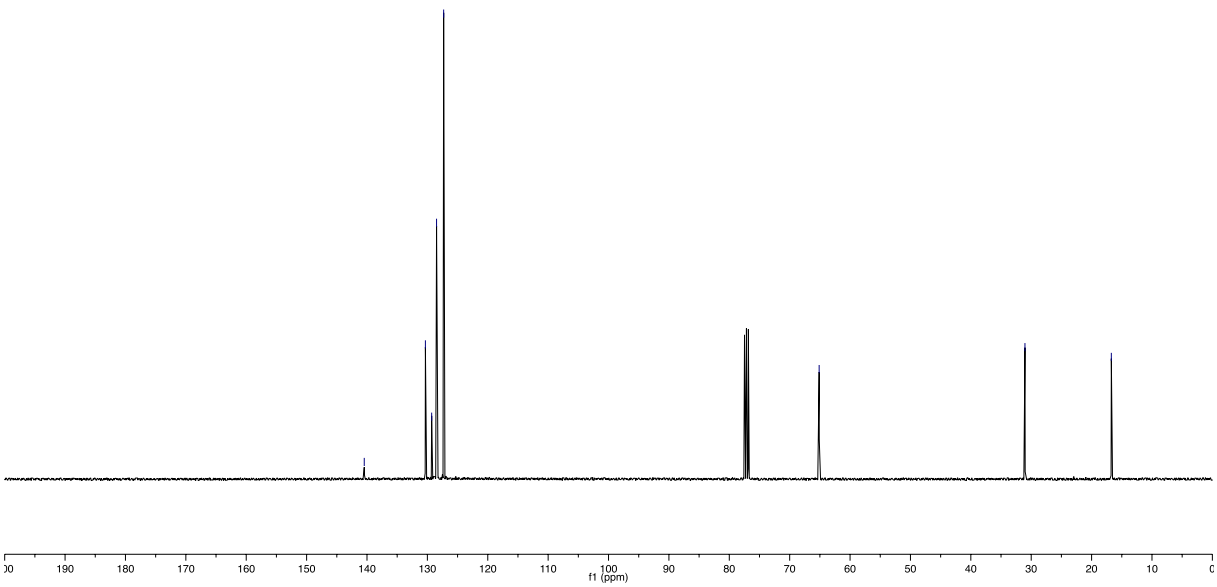
3-phenyl-4*H*-5,6-dihydro-1,2-oxazine (7)

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



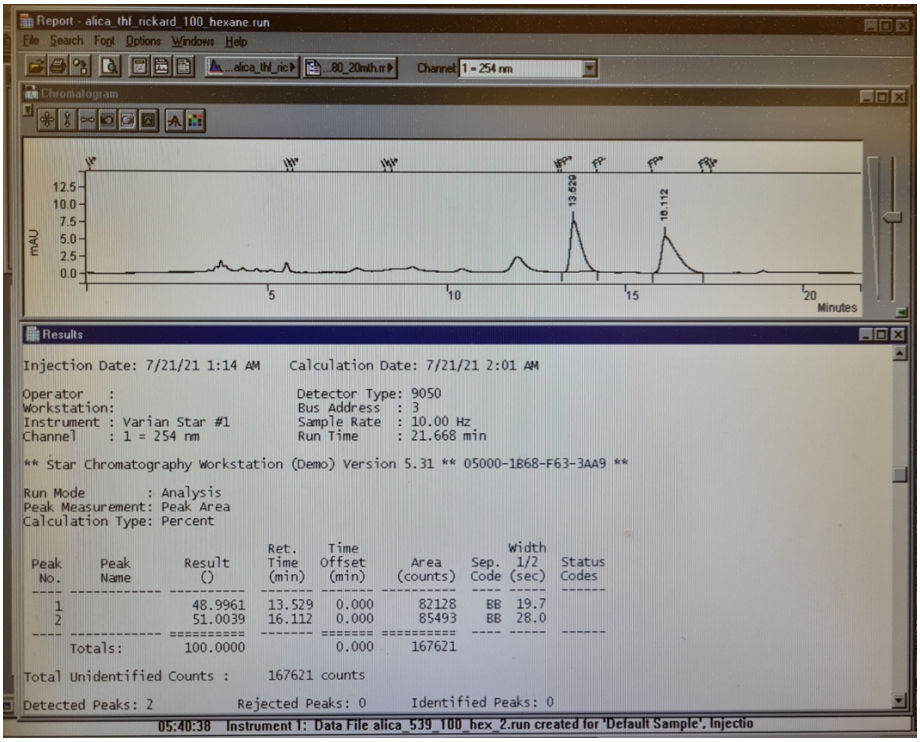


^{13}C NMR (101 MHz, $CDCl_3$)



9.2 HPLC chromatogram for (S)-2-phenyltetrahydrofuran (4)

2-phenyltetrahydrofuran racemate



(S)-2-phenyltetrahydrofuran (4)