Supplementary Information

Synthesis of Alcohols: Streamlined C1 to Cn Hydroxyalkylation through Photoredox Catalysis

Authors: Francesco Pasca,[a,Ŧ] Yuri Gelato,[a,Ŧ] Michael Andresini,[a] Giuseppe Romanazzi,[b] Leonardo Degennaro,[a] Marco Colella,[a,*] and Renzo Luisi[a,*]

[a]*Flow Chemistry and Microreactor Technology FLAME-Lab, Department of Pharmacy – Drug Sciences, University of Bari "A. Moro", Bari 70125, Italy*

[b]*DICATECh, Politecnico di Bari, Via E. Orabona 4, Bari 70125, Italy*

[Ŧ]*These authors contributed equally.*

**Correspondence to:* renzo.luisi@uniba.it*

Table of contents

1 General information

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AscendTM 400 spectrometer (400 MHz for ^{1}H, 101 MHz for ^{13}C, 377 MHz for ^{19}F), ^{31}P NMR spectra were recorded on Agilent 500 spectrometer (202 MHz for ^{13}P). Chemical shifts (δ) are reported in parts per million (ppm) relatives to residual $CHCl_3$ (^{1}H: δ = 7.26 ppm) and relative to $CDCl_3$ (^{13}C: δ = 77.16 ppm). Spin-spin coupling constants (J) are given in Hz. The multiplicity of the signals is reported as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), br (broad signal), m (multiplet). Spin-spin coupling constants (J) are given in Hz. As far as possible, complete and unambiguous assignment of all resonances was performed by combined application of 2D NMR techniques, i.e. HSQC and COSY experiments. NOESY experiments were performed for structural evaluations of the products. ^{1}H NMR on the reaction crude was used to establish the diastereomeric ratio. Thermoscientific Nicolet Summit PRO FTIR Spectrometer was employed to obtain the infrared spectra. Agilent 6530 accurate mass Q-TOF instrument and Excalibur data system were used to record the high resolution mass spectrometry (HRMS) spectra. Flash column chromatography was performed using 40-63 µm mesh silica for chromatography under the reported conditions for each compound and using standard techniques. Solutions were concentrated under reduced pressure with a rotary evaporator. Aluminium sheets precoated with silica gel 60 F254 (Merck) were used for the thin layer chromatography (TLC). The spots were visualized under UV light (λ = 254 nm) or by oxidation with $KMnO_4$ (aq.). GC analyses were performed using a gas chromatograph (dimethylsilicon capillary column, 30 m, 0.25 mm i.d.) equipped with a mass selective detector operating at 70 eV (EI). Photochemical transformations were performed employing a ThalesNanoTM photocube device. The employed flow apparatus consisted of Harvard PHD 2000 syringe pumps, equipped with gastight syringes purchased from SGE. All the chemicals were purchased from Alfa Aesar, Sigma-Aldrich, Fluorochem, Fluka, BLDpharm and TCI Europe, and used without further purification unless otherwise specified.

2 α-hydroxy carboxylic acids and SOMOphiles collection

2.1 α-hydroxy carboxylic acids collection

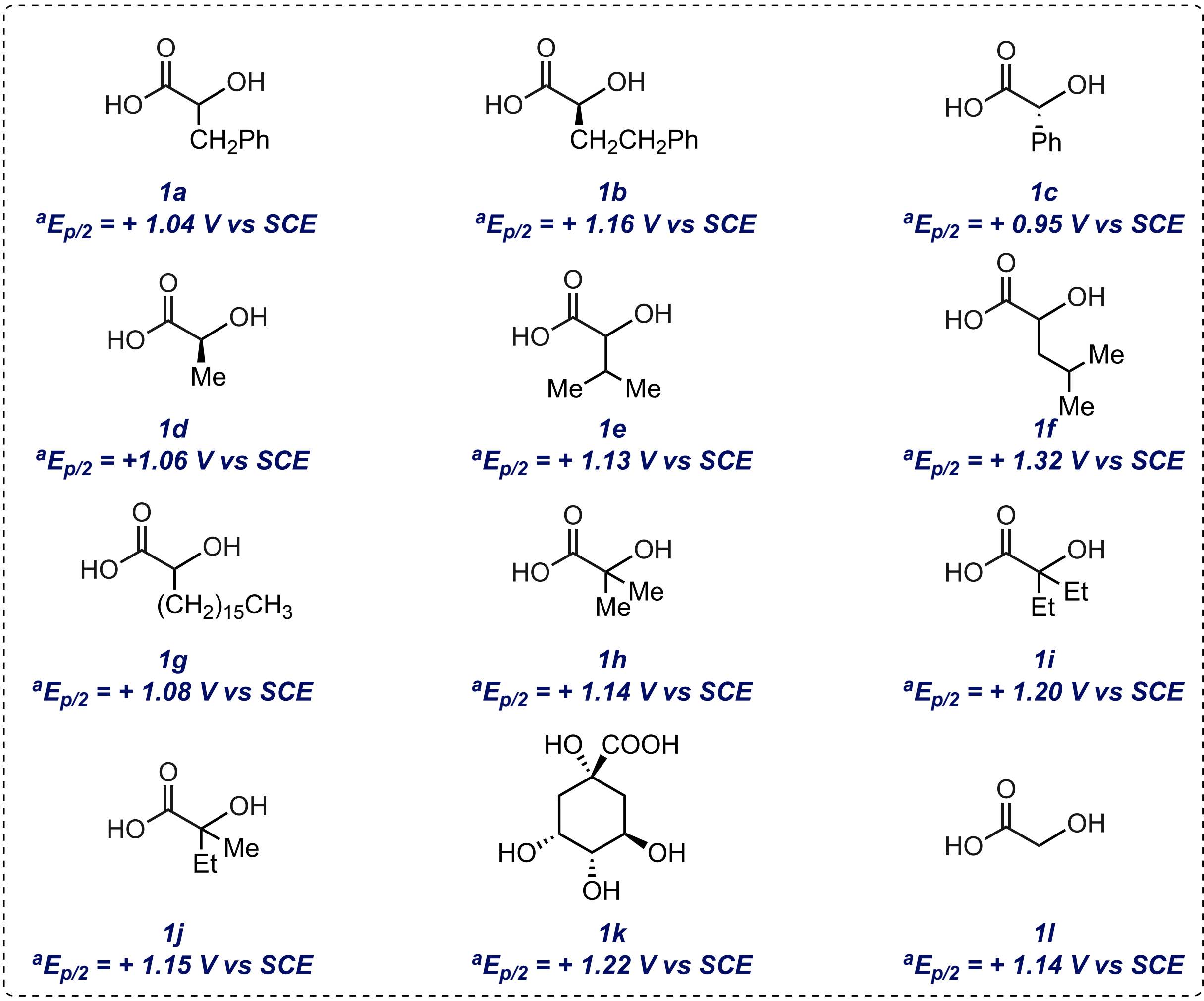


Figure 1. Collection of employed α-hydroxy carboxylic acids.

[a] $E_{p/2}$ potentials listed are related to the carboxylate form of the corresponding acid.

2.2 SOMOphile collection

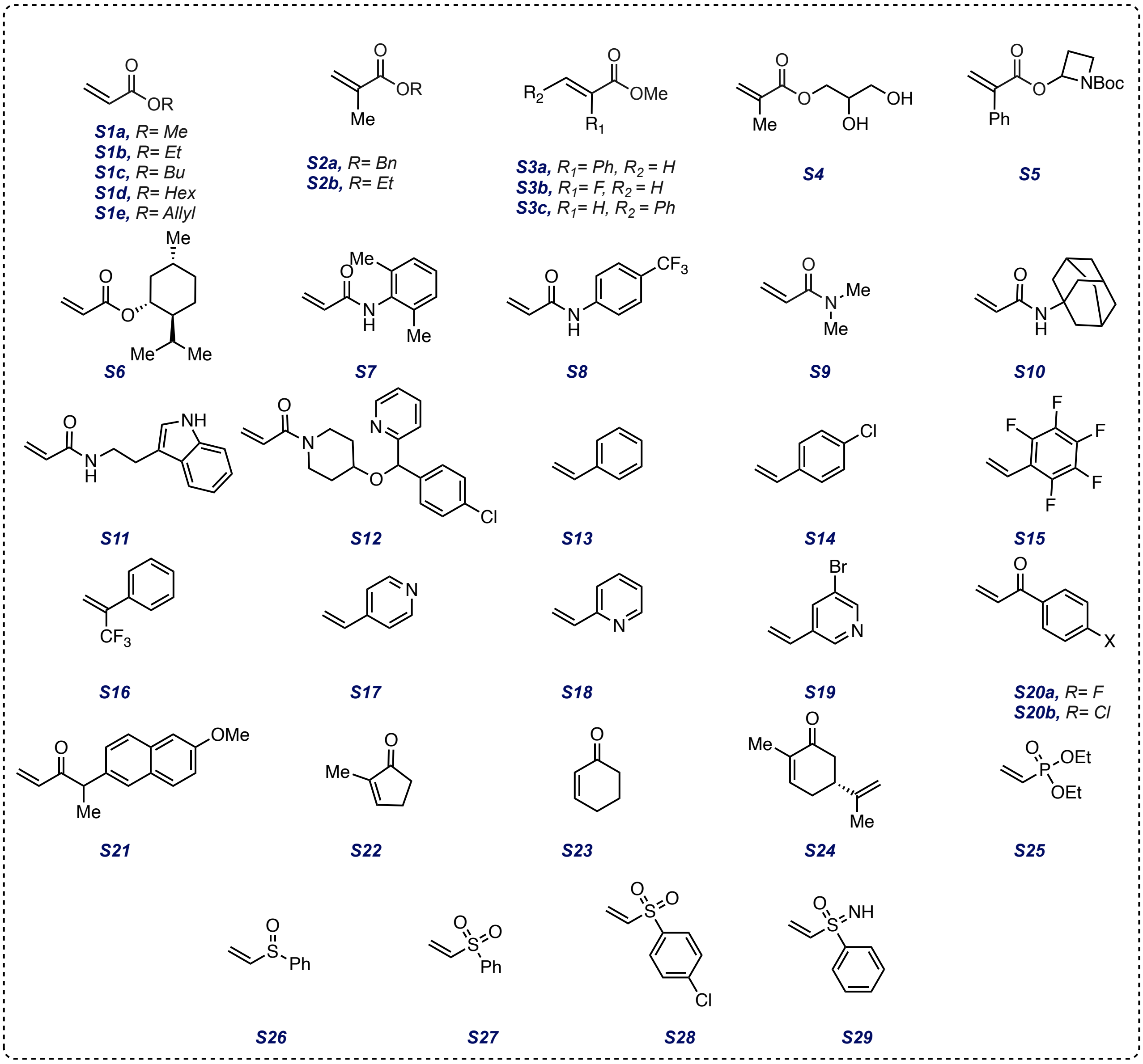


Figure 2. Collection of employed SOMOphiles.

The SOMOphiles **S3a, S6-S8, S10-S12, S20a-S20b** were prepared according to reported procedure.[1,2,3,4,5,6,7] The SOMOphiles employed in this work are shown below.

2.3 Ineffective SOMOphiles

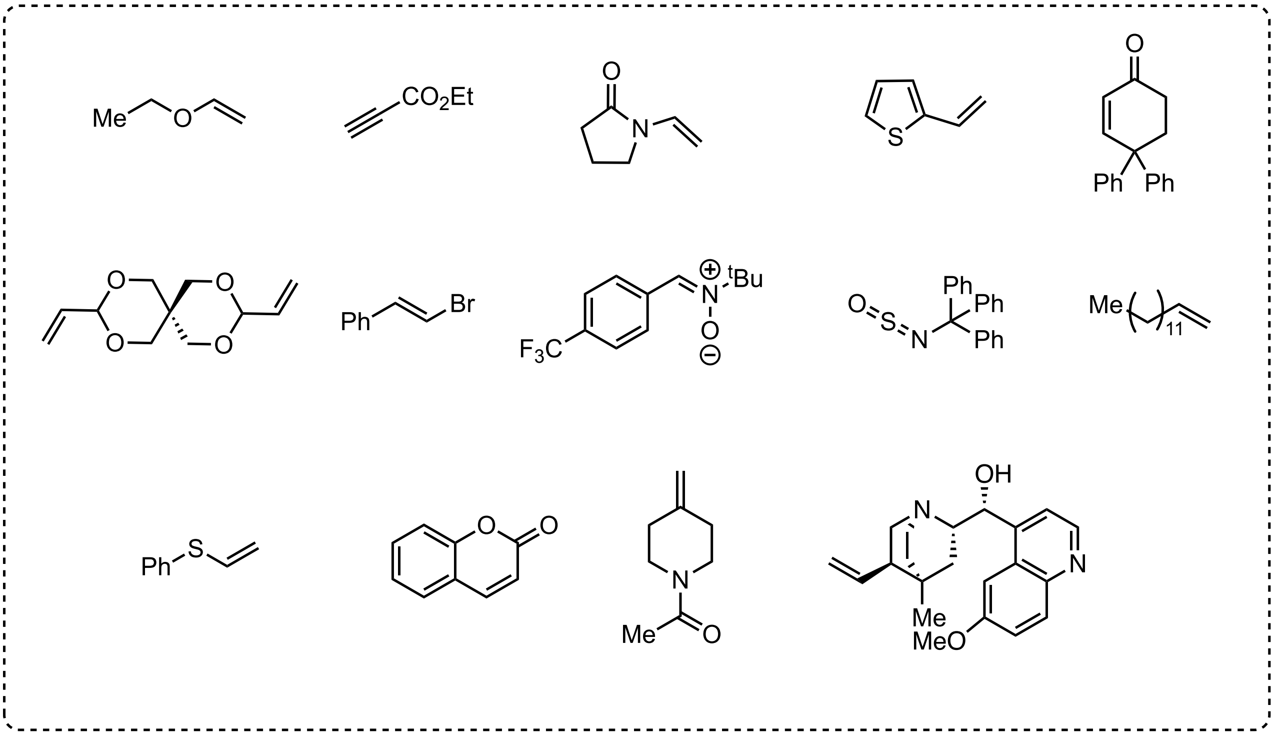
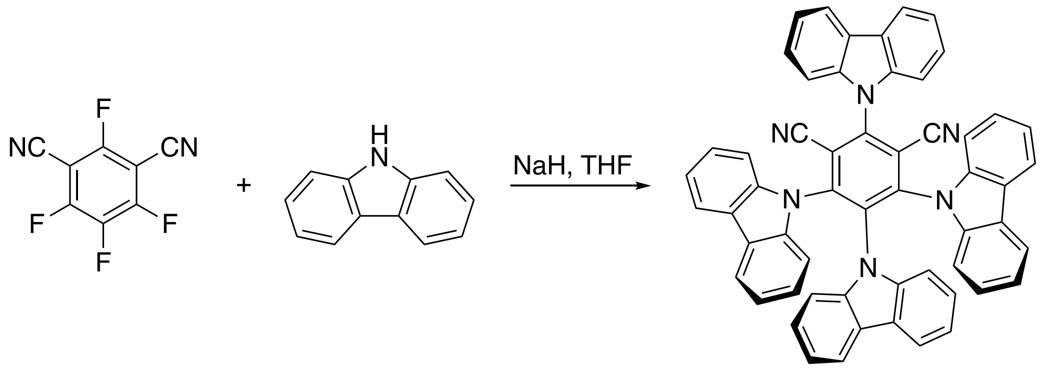


Figure 3. List of ineffective SOMOphiles.

3 Synthesis of photocatalyst and substrates

3.1 Synthesis of 2,4,5,6-tetrakis(carbazol-9-yl)-4,6-dicyanobenzene (4CzIPN)



To a flamed-dried round bottom flask charged with a stir bar, were added carbazole (5.0 equiv., 12 mmol, 2.0 g) and dry THF (24 mL). The solution was cooled down to 0 °C and NaH (60% in mineral oil, 7.5 equiv., 18 mmol, 0.72 g) was slowly added under vigorous stirring. After 2 hours, tetrafluoroisophthalonitrile (1.0 equiv., 2.4 mmol, 0.48 g) was added and the mixture was stirred at room temperature overnight. A yellow precipitate progressively appeared. When TLC analysis showed a full conversion of the starting material, water (1 mL) was added dropwise under vigorous stirring to neutralize the excess of NaH, and the mixture was evaporated to give a yellow solid. The solid was successively washed with water and ethanol to afford 1.35 g (1.38 mmol, 71.3% yield) of spectroscopically pure 4CzIPN. Spectroscopic data are in agreement with those reported in literature.[8]

3.2 Synthesis and characterization of the substrates

3.2.1 Synthesis of tert-butyl 2-((2-phenylacryloyl)oxy)azetidine-1-carboxylate (S5)

To a 25 mL round-bottom-flask charged with a stir bar, were added a solution of 2-aryl acetic acid (1eq, 6.75 mmol, 1.00 g) in DCM (7 mL) and tert-butyl azete-1(2H)-carboxylate (1.1 eq, 7.40 mmol, 1.15 g). After stirring at room temperature for 2h, the mixture was concentrated in vacuo and the product **S5** was isolated as a pale-yellow oil and used without any further purification with a 97% yield (1.98 g, 6.55mmol).

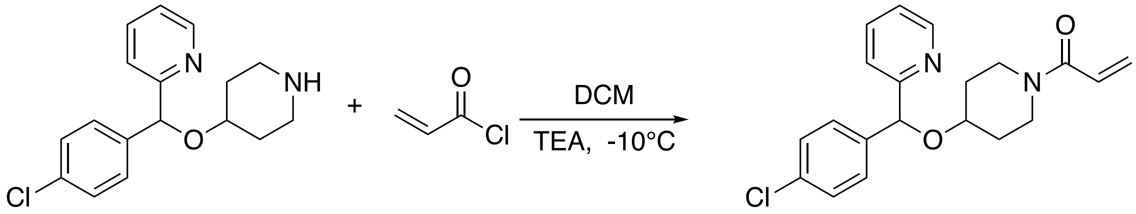
^{1}H NMR δ 7.50 – 7.45 (m, 2H), 7.43 – 7.34 (m, 3H), 6.57 – 6.43 (m, 2H), 6.01 (dd, *J* = 21.2, 1.1 Hz, 1H), 3.98 – 3.74 (m, 2H), 2.78 – 2.58 (m, 1H), 2.33 – 2.16 (m, 1H), 1.47 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 154.7, 141.0, 136.3, 129.1, 128.4, 128.3, 128.1, 127.5, 84.5, 80.6, 44.4, 28.3, 25.1.

IR (film)/cm^{-1} 2976, 1708, 1394, 1366, 1169, 1084, 1026, 949, 775, 700.

HRMS calcd for $C_{17}H_{21}NNaO_4$ $[M+Na]^+$ 326.1368; found 326.1375.

3.2.2 Synthesis of 1-(4-((4-chlorophenyl)(pyridin-2-yl)methoxy)piperidin-1-yl)prop-2-en-1-one (S12)



Compound **S12** was synthetized adapting the procedure reported by Nomura and co–workers.[4] A solution of 2-((4-chlorophenyl)(piperidin-4-yloxy)methyl)pyridine (1.00 g, 3.31 mmol) and triethylamine (0.41 g, 3.97 mmol) in DCM (0.8 M) was cooled in an ice bath with NaCl to below -10°C. Acryloyl chloride (0.33 g, 3.64 mmol) was added dropwise over ~10 min. The residue was diluted with Et_2O and washed 3 times with NH_4Cl (0.1 M x 10 mL). The organic phase was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. Compound **S12** was isolated as a pale-yellow oil in 98% yield (1.16 g, 3.24 mmol).

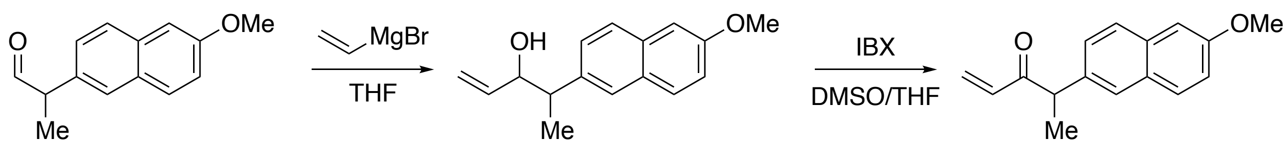
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 4.7, 0.7 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.54 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.33 – 7.28 (m, 2H), 7.20 (ddd, *J* = 7.5, 4.9, 1.2 Hz, 1H), 6.59 (dd, *J* = 16.8, 10.6 Hz, 1H), 6.27 (dd, *J* = 16.8, 1.9 Hz, 1H), 5.69 (dd, *J* = 10.6, 1.9 Hz, 1H), 5.64 (s, 1H), 3.99 – 3.90 (m, 1H), 3.83 – 3.77 (m, 2H), 3.54 – 3.35 (m, 2H), 1.94 – 1.68 (m, 4H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 165.4, 161.7, 149.0, 140.0, 137.0, 133.5, 128.6, 128.1, 127.7, 127.5, 122.6, 120.6, 81.2, 72.2, 43.0, 39.1, 31.7, 30.9.

IR (film)/cm^{-1} 2950, 1643, 1589, 1434, 1263, 1218, 1085, 1014, 730, 700.

HRMS calcd for $C_{20}H_{21}ClN_2NaO_2$ $[M+Na]^+$ 379.1189; found 379.1160.

3.2.3 Synthesis of (S)-4-(6-methoxynaphthalen-2-yl)pent-1-en-3-one (S21)



Under argon atmosphere, a flamed-dried 50 mL round bottom flask charged with a stir bar, was charged a solution of (S)-2-(6-methoxynaphthalen-2-yl)propanal (0.35 g, 1.63 mmol) in THF (0.1 M) was a dded. Vinylmagnesium bromide (1 M in THF, 0.045 g, 0.34 mmol) was added dropwise over ~10 min at room temperature. Vinylmagnesium bromide was added until complete substrate conversion. When TLC analysis showed a full conversion of the starting material, the crude was quenched with 20 mL of HCl (0.1 M) and extracted 3 times with 30 mL of Et_2O. The mixture was concentrated in vacuo and (4S)-4-(6-methoxynaphthalen-2-yl)pent-1-en-3-ol was used in the next step without any further purification with a 78% yield (0.31 g, 1.27 mmol).

Compound **S21** was synthetized adapting the procedure reported by Santagostino and co–workers.[9] O-iodoxybenzoic acid (IBX) (0.43 g, 1.55 mmol) was dissolved in DMSO (0.2 M) and (4S)-4-(6-methoxynaphthalen-2-yl)pent-1-en-3-ol (0.31 g, 1.27 mmol) dissolved in 0.2 mL of THF was added. After stirring 2 h at room temperature, when the TLC showed a complete consumption of the starting material, the mixture was diluted with 20 mL of AcOEt and washed 3 times with 20 mL of $NaHCO_3$ (0.1 M). The crude residue was purified by silica gel chromatography (Hex : AcOEt 9:1). Compound **S11** was isolated as a pale-yellow oil in 95% yield (0.23 g, 1.21 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 8.6, 4.9 Hz, 2H), 7.64 – 7.61 (m, 1H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.23 – 7.07 (m, 2H), 6.50 – 6.21 (m, 2H), 5.64 (dd, *J* = 10.1, 1.8 Hz, 1H), 3.95 (s, 1H), 3.94 (s, 3H), 1.53 (d, *J* = 6.8 Hz, 3H).

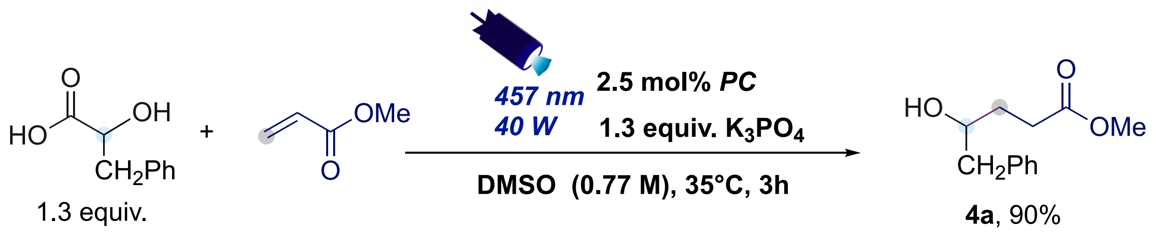
^{13}C NMR (101 MHz, $CDCl_3$) δ 199.8, 157.7, 135.5, 134.7, 129.2, 128.3, 127.6, 126.7, 126.6, 119.2, 105.6, 55.3, 51.0, 17.7.

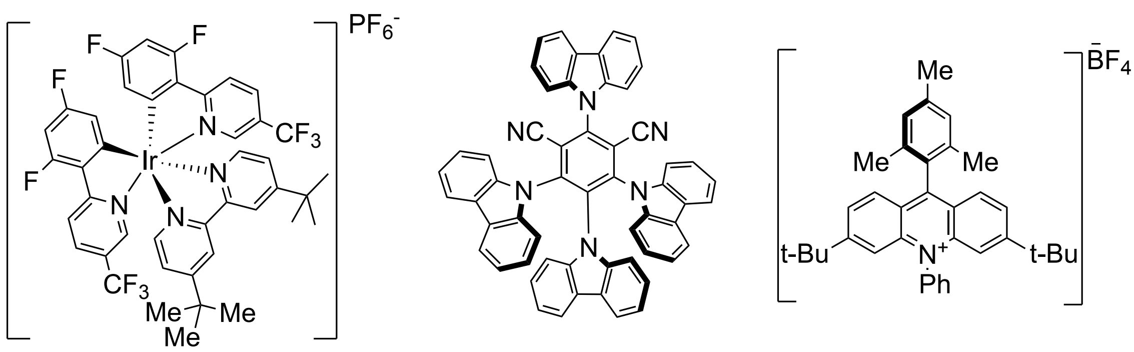
IR (film)/cm^{-1} 2972, 2935, 1697, 1605, 1504, 1481, 1391, 1266, 1031, 853.

HRMS calcd for $C_{16}H_{16}NaO_2$ $[M+Na]^+$ 263.1048; found 263.1039.

4 Optimization

4.1 Photocatalyst optimization



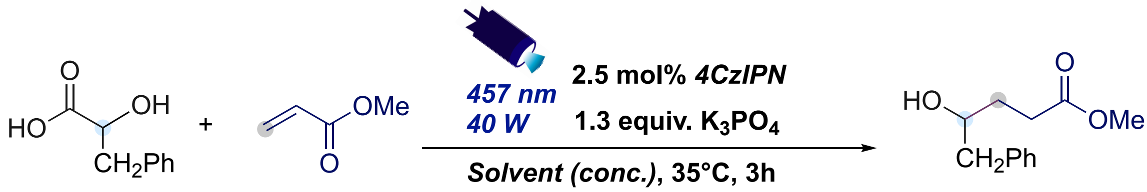


PC1 *PC2* *PC3*

Entry [a]	*Photocatalyst*	*Yield (%)*[b]
1	***(PC2)*** 4CzIPN	90
2	***(PC3)*** Mes-Acr$^+$BF$_4^-$	10
3	***(PC1)*** (Ir[dF(CF$_3$)ppy]$_2$(dtbpy))PF$_6$	22
4	No photocatalyst	0

Table 1. [a] Reactions performed on 0.3 mmol scale. [b] Determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

4.2 Solvent optimization



4a, 90%

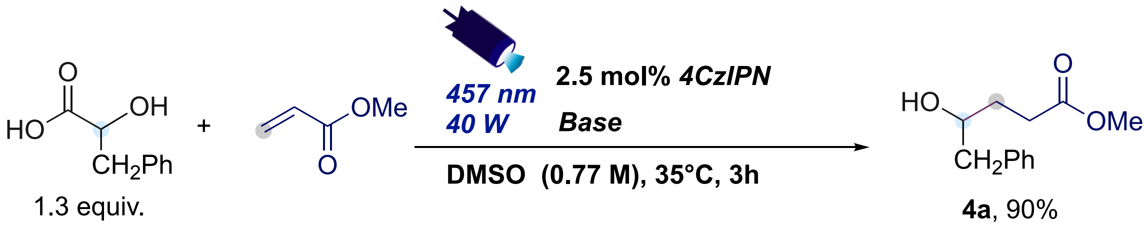
Entry [a]	*Solvent (0.31 M)*	*Yield (%)*[b]
1	DMSO	90
2	DMF	90
3	MeCN	22
4	2-MeTHF	15
5	DCM	5

Table 2. [a] *Reactions performed on 0.3 mmol scale. [b] Determined by* ^{1}*H NMR analysis using* CH_2Br_2 *as internal standard.*

Entry [a]	*Concentration DMSO (M)*	*Yield (%)*[b]
1	0.77	90
2	0.46	90
3	0.31	90

Table 3. [a] *Reactions performed on 0.3 mmol scale.* [b] *Determined by* ^{1}*H NMR analysis using* CH_2Br_2 *as internal standard.*

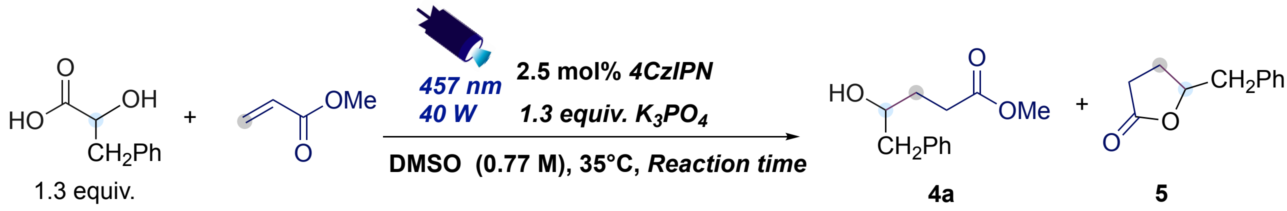
4.3 Base optimization



Entry [a]	***Base***	***Yield (%)***[b]
1	K_3PO_4	90
2	KO*t*Bu	88
3	K_3PO_4 (20% mol)	50
4	NaH_2PO_4	23
5	2,6-Lutidine	<5
6	DABCO	<5
7	No Base	0

Table 4. [a] *Reactions performed on 0.3 mmol scale.* [b] *Determined by* ^{1}H *NMR analysis using* CH_2Br_2 *as internal standard.*

4.4 Reaction time optimization



Entry [a]	Reaction time	Yield (%)	4a:5
1	3h	90[b]	100:0
2	2h	70[b]	100:0
3	16h	90[c]	0:100

Table 5. [a] Reactions performed on 0.3 mmol scale. [b] Determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard. [c] Determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene (TMB) as internal standard.

Reaction crude after 3h[a][c]

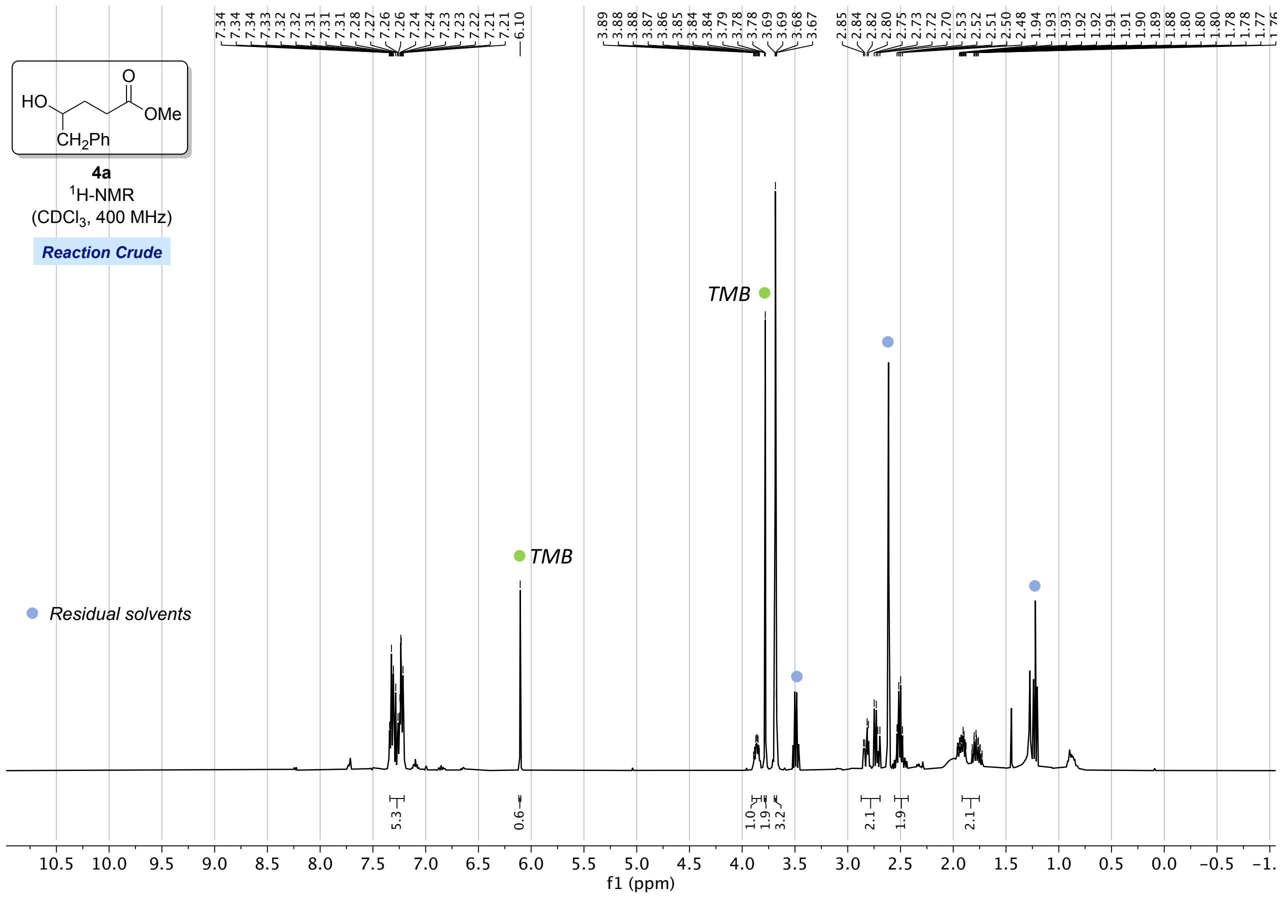


Figure 4. Reaction crude after 3 h with internal standard (TMB).

Reaction crude after 16h[a][b]

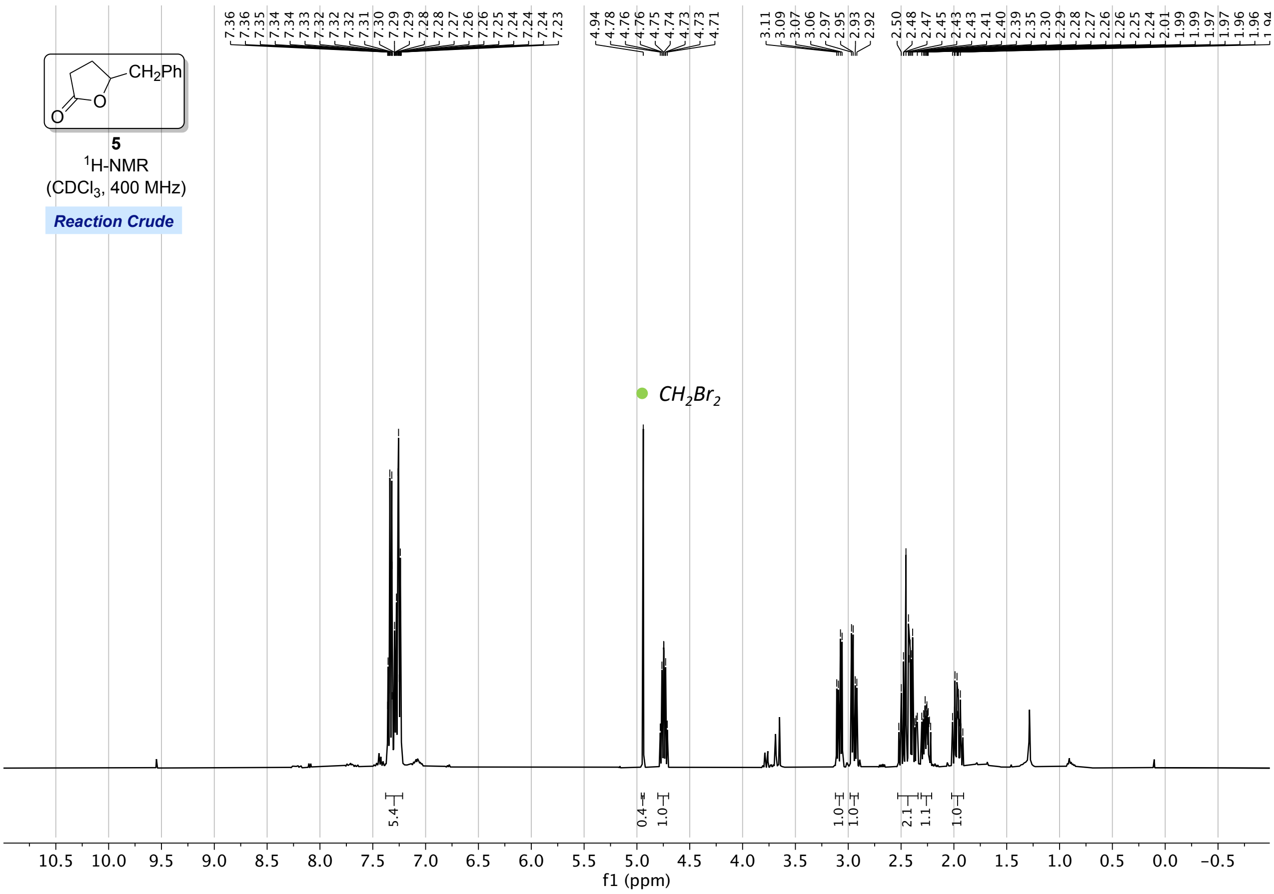
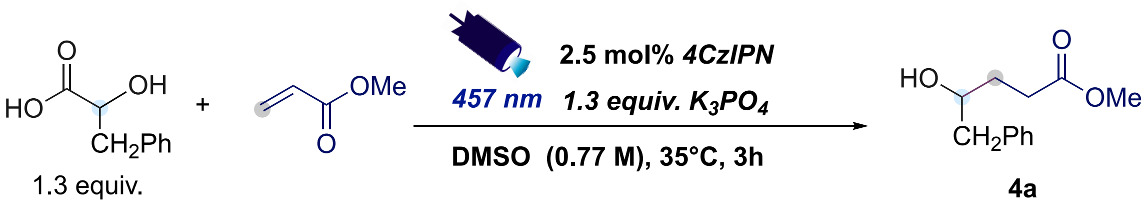


Figure 5. Reaction crude after 16 h with internal standard (CH_2Br_2).

4.5 Irradiation power optimization

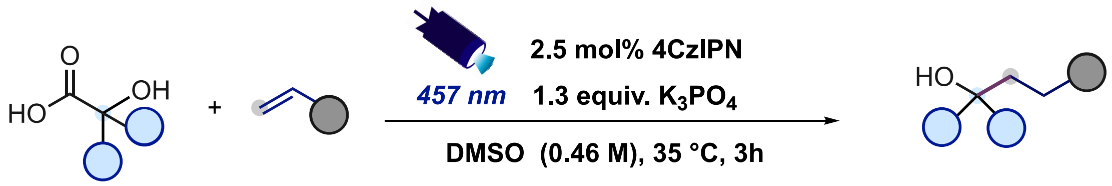


Entry [a]	*Irradiation power*	*Yield (%)*[b]
1	40 W	90
2	128 W	90
3	0	0

Table 6. [a] Reactions performed on 0.3 mmol scale. [b] Determined by ^{1}H NMR analysis using CH_2Br_2 as internal standard.

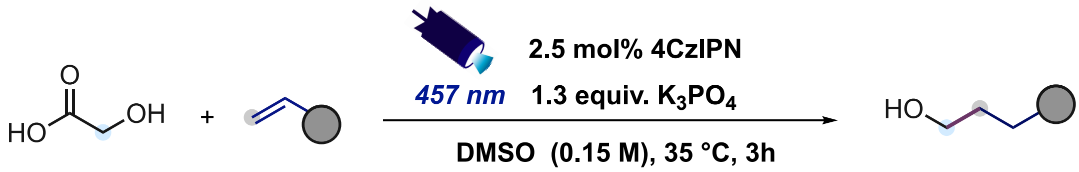
5 Batch experiment

5.1 General procedure 1: radical hydroxyalkylation from (AHA)s in batch



To an oven-dried 4 mL vial equipped with a stirring bar were added the α-hydroxy acid (0.3 mmol, 1.3 equiv.), potassium phosphate tribasic (0.3 mmol, 1.3 equiv.), 4CzIPN (5.9 mg, 2.5 mol%), the SOMOphile (0.23 mmol, 1 equiv.) and dry DMSO (0.5 mL). Subsequently, the vial was sealed with a rubber septum and the solution was sparged with N_2 (1 min). The solution was stirred and irradiated in a PhotoCube™ photochemical reactor equipped with a blue lamp (λ = 457 nm, 38.4 W) for 3 h or 16 h. Then the vial was removed from the photochemical reactor. The solution was diluted with 20 mL of AcOEt and transferred to a separatory funnel where it was washed three times with 30 mL of brine. The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* using a rotatory evaporator. The crude reaction mixture was analyzed by ^{1}H-NMR and, when necessary, purified by flash column chromatography on silica gel.

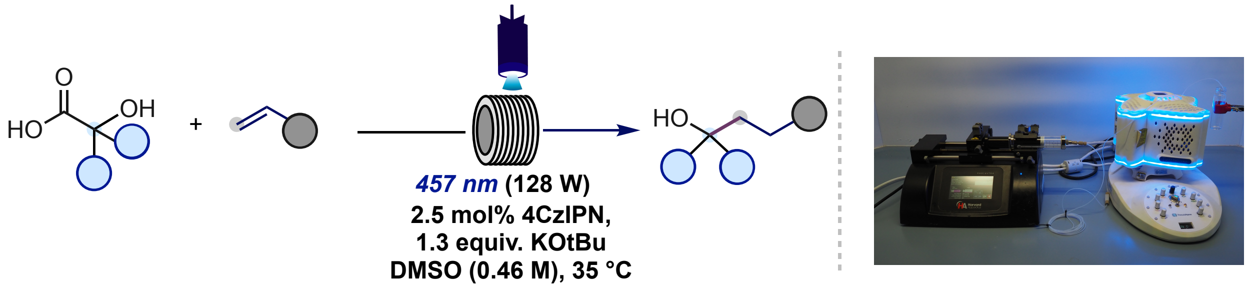
5.2 General procedure 2 (GP2): radical hydroxyalkylation from glycolic acid in batch



To an oven-dried 4 mL vial equipped with a stirring bar were added the glycolic acid (0.3 mmol, 1.3 equiv.), potassium phosphate tribasic (0.3 mmol, 1.3 equiv.), 4CzIPN (5.9 mg, 2.5 mol%), the SOMOphile (0.23 mmol, 1 equiv.) and dry DMSO (1.5 mL). Subsequently, the vial was sealed with a rubber septum and the solution was sparged with N_2 (1 min). The solution was stirred and irradiated in a PhotoCube™ photochemical reactor equipped with a blue lamp (λ = 457 nm, 38.4 W or 128 W) for 3 h or 16 h. Then the vial was removed from the photochemical reactor. The solution was diluted with 20 mL of AcOEt and transferred to a separatory funnel where it was washed three times with 30 mL of brine. The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* using a rotatory evaporator. The crude reaction mixture was analyzed by ^{1}H-NMR and, when necessary, purified by flash column chromatography on silica gel.

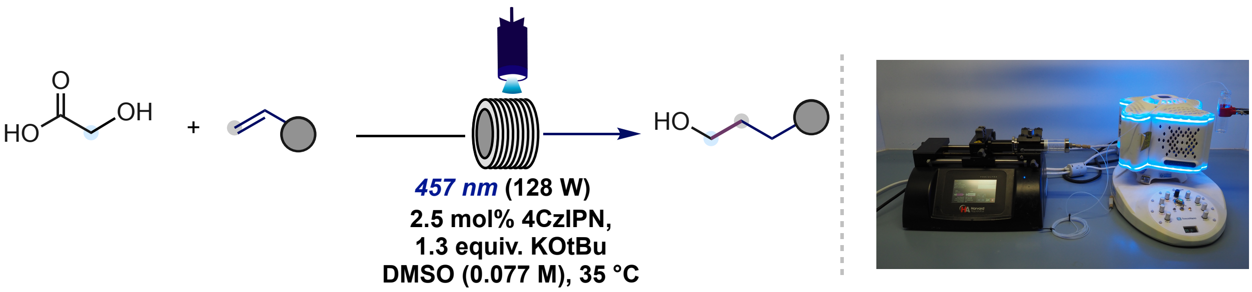
6 Flow experiment

6.1 General procedure 3 (GP3): radical hydroxyalkylation from (AHA)s in continuous flow



To an oven-dried 4 mL vial equipped with a stirring bar were added the α-hydroxy acid (0.3 mmol, 1.3 equiv.), potassium tert-butoxide (0.3 mmol, 1.3 equiv.), 4CzIPN (5.9 mg, 2.5 mol%), the SOMOphile (0.23 mmol, 1 equiv.) and dry DMSO (0.5 mL). Subsequently, the vial was sealed with a rubber septum and the solution was sparged with N_2 (1 min). The solution was loaded in a 0.5 mL PTFE loop connected with coil reactor (8 mL) contained in a PhotoCube™ photo-flow reactor equipped with a blue lamp (λ = 457 nm, 38.4 W or 128 W). The solution was pumped (0.27 mL/min or 0.04 mL/min) through the coil employing a syringe pump equipped with a gastight syringe containing dry DMSO (10 mL). The reaction mixture was collected after 30 minutes (or 180 minutes) from the start for 2 minutes (or 12 minutes). The solution was diluted with 20 mL of AcOEt and transferred to a separatory funnel where it was washed three times with 30 mL of brine. The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* using a rotatory evaporator. The crude reaction mixture was analyzed by ^{1}H-NMR and, when necessary, purified by flash column chromatography on silica gel.

6.2 General procedure 4 (GP4): radical hydroxyalkylation from glycolic acid in continuous flow



To an oven-dried 4 mL vial equipped with a stirring bar were added the glycolic acid (0.3 mmol, 1.3 equiv.) and potassium tert-butoxide (0.3 mmol, 1.3 equiv.). Upon complete solubilization, 4CzIPN (5.9 mg, 2.5 mol%), the SOMOphile (0.23 mmol, 1 equiv.) and dry DMSO (3 mL) were added. Subsequently, the vial was sealed with a rubber septum and the solution was sparged with N_2 (1 min). The solution was loaded in a 3 mL PTFE loop connected with coil reactor (8 mL) contained in a PhotoCube™ photo-flow reactor equipped with a blue lamp (λ = 457 nm, 38.4 W or 128 W). The solution was pumped (0.27 mL/min or 0.04 mL/min) through the coil employing a syringe pump equipped with a gastight syringe containing dry DMSO (10 mL). The reaction mixture was collected after 30 minutes (or 180 minutes) from the start for 12 minutes (or 70 minutes). The solution was diluted with 20 mL of AcOEt and transferred to a separatory funnel where it was washed three times with 30 mL of brine. The organic extracts were combined, dried over Na_2SO_4, filtered and concentrated *in vacuo* using a rotatory evaporator. The crude reaction mixture was analyzed by ^{1}H-NMR and, when necessary, purified by flash column chromatography on silica gel.

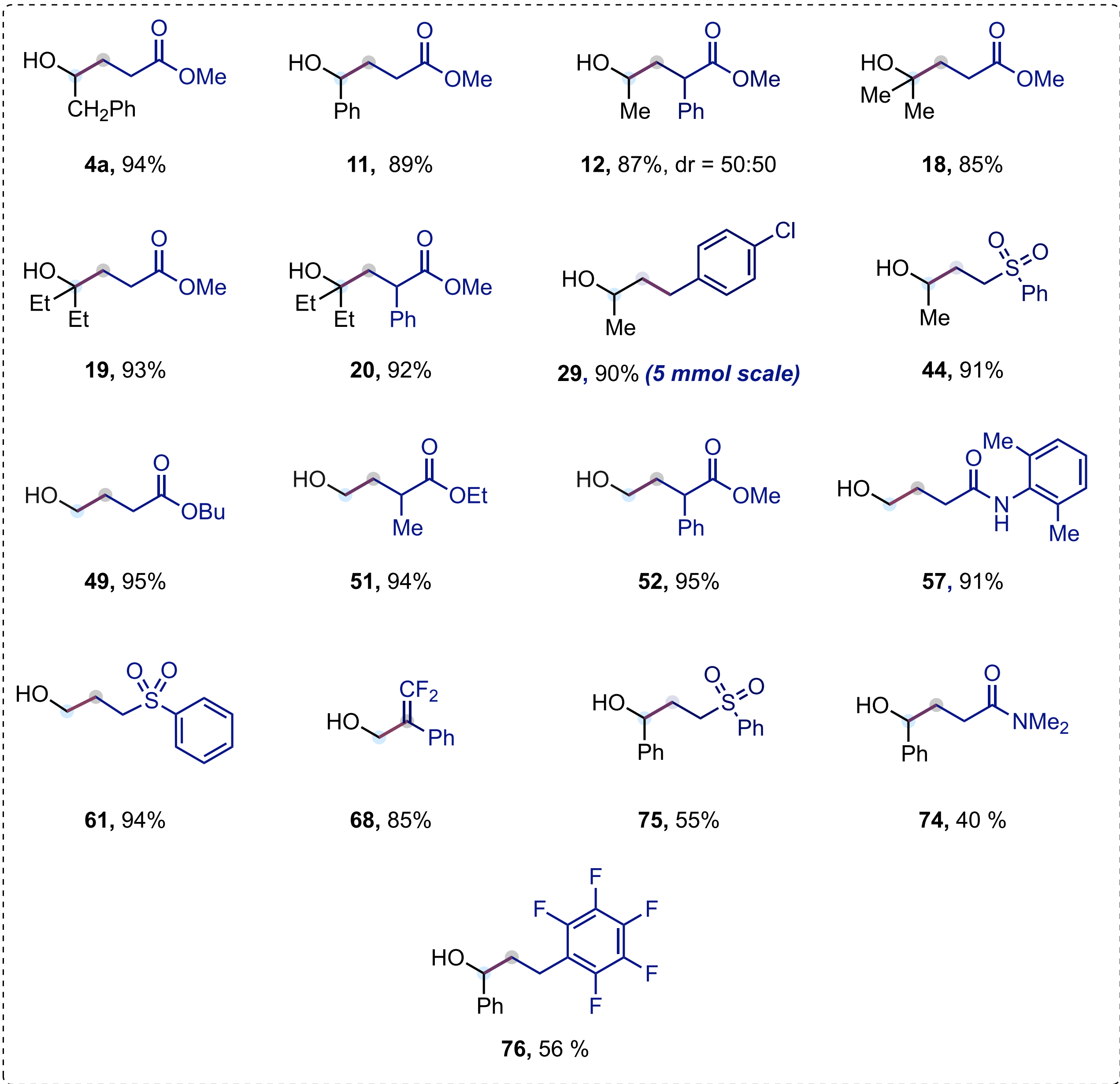
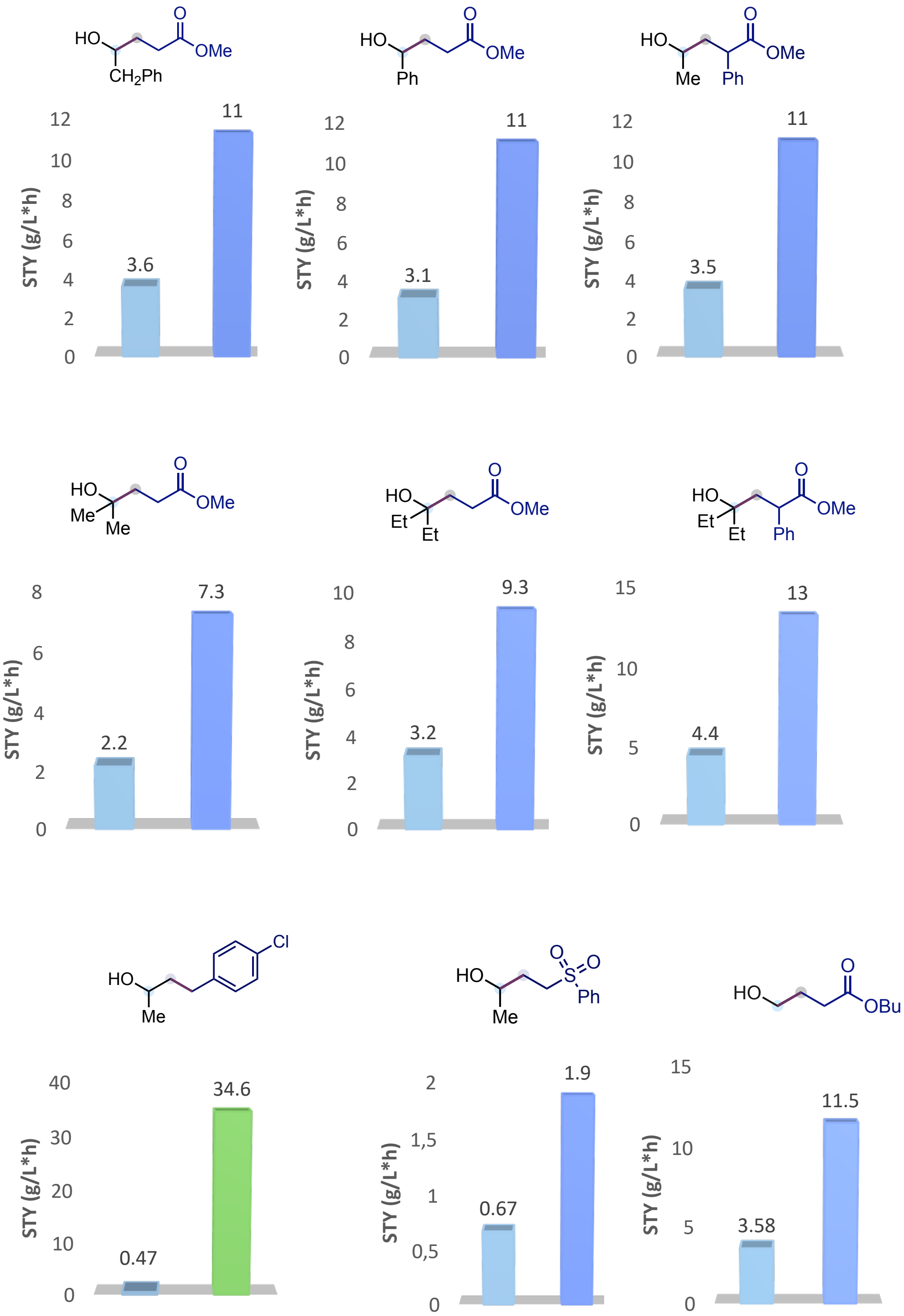


Figure 6. Products with flow protocol.

6.3 Space Time Yields Calculation

Batch
Flow
Gram scale

$$STY = \frac{Mass\ of\ product}{Reaction\ Time \cdot Reactor\ volume}$$



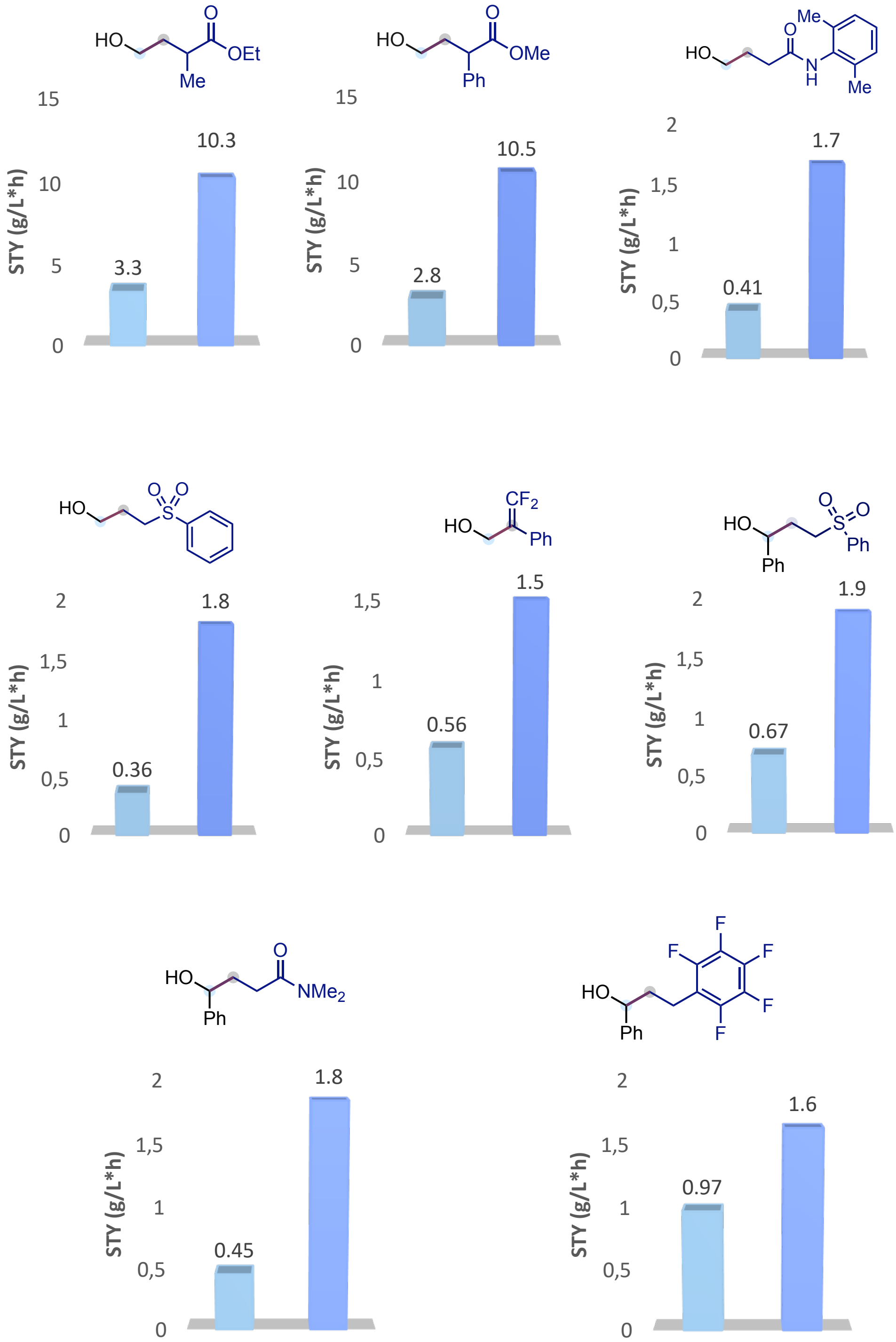
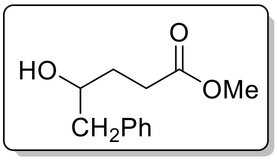


Figure 7. Space time yield comparisons.

7 Substrate scope

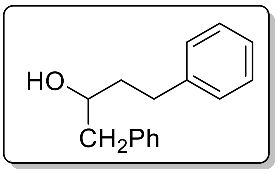
methyl 4-hydroxy-5-phenylpentanoate (4a)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and methyl acrylate **S1a** as starting materials. Compound **4a** was isolated as a colorless oil (43 mg, 90%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.22 (m, 5H), 3.90 – 3.85 (m, 1H), 3.70 (s, 3H), 2.85 (dd, *J* = 13.5, 4.6 Hz, 1H), 2.73 (dd, *J* = 13.5, 8.2 Hz, 1H), 2.57 – 2.47 (m, 2H), 1.99–1.89 (m, 1H), 1.86 (d, *J* = 3.9 Hz, 1H), 1.84–1.73 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.5, 138.1, 129.4, 128.6, 126.6, 72.0, 51.7, 44.2, 31.6, 30.6.
IR (film)/cm^{-1} 3421, 2950, 2921 2849, 1733, 1437, 1173, 1082, 745, 700.
HRMS calcd for $C_{12}H_{16}NaO_3$ $[M+Na]^+$ 231.0997; found 231.0985.

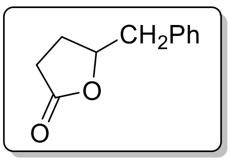
1,4-diphenylbutan-2-ol (4b)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and styrene **S13** as starting materials. Compound **4b** was isolated as a colorless oil (44 mg, 85%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.19 (m, 10H), 3.95 – 3.79 (m, 1H), 2.95 – 2.84 (m, 2H), 2.81 – 2.68 (m, 2H), 1.97 – 1.82 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 138.4, 129.5, 128.6, 128.5, 128.4, 126.6, 125.9, 72.0, 44.2, 38.5, 32.2.
Spectroscopic data matched those previously reported in the literature.[10,11]

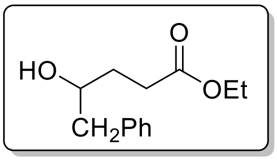
5-benzyldihydrofuran-2(3H)-one (5)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and methyl acrylate **S1a** as starting materials. Compound **5** was isolated as a colorless oil (37 mg, 92%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 5H), 4.80 – 4.71 (m, 1H), 3.10 (dd, *J* = 14.0, 6.1 Hz, 1H), 2.95 (dd, *J* = 14.0, 6.3 Hz, 1H), 2.55 – 2.34 (m, 2H), 2.33 – 2.22 (m, 1H), 2.04 – 1.91 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 177.0, 135.9, 129.5, 128.7, 127.0, 80.8, 41.4, 28.6, 27.1.
IR (film)/cm^{-1} 3027, 2921, 2850, 1767, 1454, 1172, 1020, 988, 747, 700.
HRMS calcd for $C_{11}H_{12}NaO_2$ $[M+Na]^+$ 199.0735 ; found 199.0727.

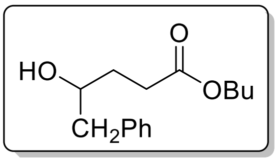
ethyl 4-hydroxy-5-phenylpentanoate (6)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and ethyl acrylate **S1b** as starting materials. Compound **6** was isolated as a colorless oil (46 mg, 90%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 5H), 4.15 (q, *J* = 7.1 Hz, 2H), 3.93 – 3.82 (m, 1H), 2.84 (dd, *J* = 13.5, 4.7 Hz, 1H), 2.73 (dd, *J* = 13.5, 8.1 Hz, 1H), 2.57 – 2.42 (m, 2H), 1.99 – 1.88 (m, 2H), 1.85 – 1.73 (m, 1H), 1.27 (t, *J* = 7.1 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.1, 138.2, 129.4, 128.6, 126.6, 72.0, 60.5, 44.2, 31.6, 30.8, 14.2.
IR (film)/cm^{-1} 3422, 3027, 2980, 2930, 1731, 1259, 1183, 1083, 746, 701.
HRMS calcd for $C_{13}H_{18}NaO_3$ $[M+Na]^+$ 245.1154; found 245.1148.

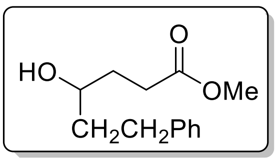
butyl 4-hydroxy-5-phenylpentanoate (7)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and butyl acrylate **S1c** as starting materials. Compound **7** was isolated as a colorless oil (52 mg, 90%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 5H), 4.10 (t, *J* = 6.7 Hz, 2H), 3.93 – 3.82 (m, 1H), 2.84 (dd, *J* = 13.5, 4.7 Hz, 1H), 2.73 (dd, *J* = 13.5, 8.1 Hz, 1H), 2.54 – 2.47 (m, 2H), 1.98 – 1.87 (m, 2H), 1.85 – 1.72 (m, 1H), 1.68 – 1.57 (m, 2H), 1.46 – 1.33 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.1, 138.2, 129.4, 128.6, 126.6, 72.0, 64.4, 44.2, 31.6, 30.8, 30.7, 19.1, 13.7.
IR (film)/cm^{-1} 3447, 2958, 2933, 1730, 1177, 1082, 746, 700.
HRMS calcd for $C_{15}H_{22}NaO_3$ $[M+Na]^+$ 273.1467; found 273.1464.

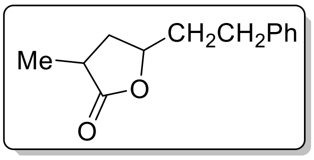
methyl 4-hydroxy-6-phenylhexanoate (8)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with *(S)*-2-hydroxy-4-phenylbutanoic acid **1b** and methyl acrylate **S1a** as starting materials. Compound **8** was isolated as a colorless oil (46 mg, 91%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.17 (m, 5H), 3.75 – 3.60 (m, 4H), 2.87 – 2.66 (m, 2H), 2.49 (t, *J* = 7.2 Hz, 2H), 1.94 – 1.76 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.6, 141.9, 128.5, 128.4, 125.9, 70.7, 51.7, 39.2, 32.2, 32.0, 30.5.
IR (film)/cm^{-1} 3418, 2921, 2850, 1769, 1454, 1175, 1030, 918, 750, 700.
HRMS calcd for $C_{13}H_{18}NaO_3$ $[M+Na]^+$ 245.1154; found 245.1138.

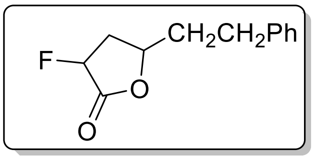
3-methyl-5-phenethyldihydrofuran-2(3H)-one (9)



Prepared following **GP1** with (reaction time = 16 h, irradiation power = 38.4 W) *(S)*-2-hydroxy-4-phenylbutanoic acid **1b** and 2,3-dihydroxypropyl methacrylate **S4c** as starting materials, compound **9** was obtained as a yellow oil (mixture of diastereoisomers, dr = 55:45). Compound **9** was isolated as a colorless oil (mixture of diastereomers, dr = 63:37, 37 mg, 79%) after flash column chromatography (SiO_2). (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.29 (m, 2.9H)$^{M+m}$, 7.27 – 7.19 (m, 4.5H) $^{M+m}$, 4.58 – 4.47 (m, 0.6H)^{m}, 4.40 – 4.27 (m, 1H) ^{M}, 2.92 – 2.62 (m, 4.5H) $^{M+m}$, 2.54 – 2.44 (m, 1H) ^{M}, 2.21 – 1.83 (m, 4.4H) $^{M+m}$, 1.61 – 1.50 (m, 0.6H)^{m}, 1.34 – 1.26 (m, 4.8H) $^{M+m}$.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.0 , 179.5 , 140.82 , 140.76 , 128.55, 128.46, 126.2, 77.6 , 77.2 , 37.3, 35.9, 35.5, 34.0, 31.74 , 31.71 , 15.9 , 15.1 .
IR (film)/cm^{-1} 2916, 2848, 1625, 1601, 1491, 1450, 1335, 928, 747, 728.
HRMS calcd for $C_{13}H_{16}NaO_2$ $[M+Na]^+$ 227.1048; found 227.1043.

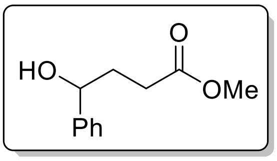
3-fluoro-5-phenethyldihydrofuran-2(3H)-one (10)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxy-4-phenylbutanoic acid **1b** and methyl 2-fluoroacrylate **S3b** as starting materials, compound **10** was obtained as a yellow oil (mixture of diastereoisomers, dr = 64:36). Compound **10-major** was isolated as a colorless oil (28 mg, 59%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.12 (m, 5H), 5.23 (ddd, *J* = 51.2, 9.4, 8.4 Hz, 1H), 4.45 – 4.32 (m, 1H), 2.95 – 2.69 (m, 3H), 2.25 – 1.94 (m, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.3 (d, *J* = 21.2 Hz), 140.1, 128.7, 128.5, 126.4, 85.9 (d, *J* = 193.2 Hz), 75.5 (d, *J* = 6.7 Hz), 37.3, 35.3 (d, *J* = 18.7 Hz), 31.2.
^{19}F NMR (377 MHz, $CDCl_3$) δ -193.86 (ddd, *J* = 51.2, 22.8, 6.1 Hz, 1F).
IR (film)/cm^{-1} 2958, 1787, 1454, 1264, 1099, 1013, 950, 800, 733, 700.
HRMS calcd for $C_{12}H_{13}FNaO_2$ $[M+Na]^+$ 231.0798; found 231.0800.

Compound **10-minor** was isolated as a colorless oil (16 mg, 33%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.15 (m, 5H), 5.16 (ddd, *J* = 51.3, 6.9, 4.1 Hz, 1H), 4.77 – 4.64 (m, 1H), 2.92 – 2.71 (m, 2H), 2.66 – 2.51 (m, 1H), 2.30 – 2.13 (m, 1H), 2.11 – 1.90 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.0 (d, *J* = 20.4 Hz), 140.1, 128.7, 128.4, 126.4, 86.4 (d, *J* = 185.0 Hz), 78.0 (d, *J* = 2.2 Hz), 37.5, 35.3 (d, *J* = 20.3 Hz), 31.5.
^{19}F NMR (377 MHz, $CDCl_3$) δ -192.36 (ddd, *J* = 51.4, 27.1, 24.4 Hz, 1H).
IR (film)/cm^{-1} 2958, 1787, 1454, 1264, 1099, 1013, 950, 800, 733, 700.
HRMS calcd for $C_{12}H_{13}FNaO_2$ $[M+Na]^+$ 231.0798; found 231.0800.

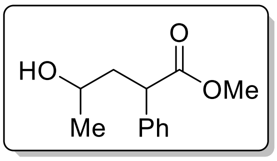
methyl 4-hydroxy-4-phenylbutanoate (11)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with *(R)*-2-hydroxy-2-phenylacetic acid **1c** and methyl acrylate **S1a** as starting materials. Compound **11** was isolated as a colorless oil (34 mg, 77%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.29 (m, 5H), 4.83 – 4.72 (m, 1H), 3.69 (s, 3H), 2.47 (t, *J* = 7.2 Hz, 2H), 2.10 (dd, *J* = 14.0, 7.0 Hz, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.3, 144.0, 128.5, 127.7, 125.8, 73.6, 51.7, 33.8, 30.4.
IR (film)/cm^{-1} 3417, 2918, 2849, 1735, 1702, 1479, 1393, 1156, 760, 700.
HRMS calcd for $C_{11}H_{14}NaO_3$ 217.0841 $[M+Na]^+$; found 217.0846.

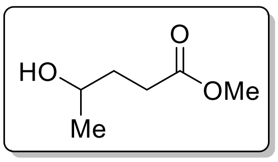
methyl 4-hydroxy-2-phenylpentanoate (12)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with *(S)*-2-hydroxypropanoic acid **1d** and methyl 2-phenylacrylate **S3a** as starting materials, compound **12** was obtained as a yellow oil (mixture of diastereomers, dr = 50:50). Compound **12** was isolated as a colorless oil (mixture of diastereomers, dr = 50:50, 42 mg, 87%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 – 7.27 (m, 10H), 3.94 – 3.89 (m, 1H) , 3.87 – 3.83 (m, 1H) , 3.69 (s, 3H), 3.68 (s, 3H), 2.37 – 2.28 (m, 1H), 2.26 – 2.17 (m, 1H), 2.00 – 1.91 (m, 1H), 1.88 – 1.77 (m, 1H), 1.25 (d, *J* = 6.2 Hz, 3H), 1.22 (d, *J* = 6.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.0, 174.5, 139.2, 138.9, 128.8, 128.7, 128.1, 127.8, 127.3, 66.1, 66.0, 52.2, 52.1, 48.6, 48.0, 42.8, 42.5, 24.3, 23.8.
IR (film)/cm^{-1} 3435, 3030, 2964, 1968, 1732, 1496, 1435, 1164, 734, 697.
HRMS calcd for $C_{12}H_{16}NaO_3$ $[M+Na]^+$ 231.0997; found 231.0991.

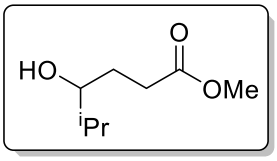
methyl 4-hydroxypentanoate (13)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with *(S)*-2-hydroxypropanoic acid **1d** and methyl acrylate **S1a** as starting materials. Compound **13** was isolated as a colorless oil (28 mg, 87%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.92 – 3.82 (m, 1H), 3.71 (s, 3H), 2.48 (t, *J* = 7.3 Hz, 2H), 1.90 – 1.70 (m, 2H), 1.24 (d, *J* = 6.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.6, 67.4, 51.7, 33.8, 30.5, 23.6.
IR (film)/cm^{-1} 3415, 2961, 2917, 2849, 1734, 1687, 1447, 1259, 1085, 1015, 795.
HRMS calcd for $C_6H_{12}NaO_3$ $[M+Na]^+$ 155.0684; found 155.0684.

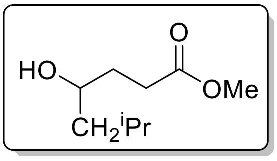
methyl 4-hydroxy-5-methylhexanoate (14)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-hydroxy-3-methylbutanoic acid **1e** and methyl acrylate **S1a** as starting materials. Compound **14** was isolated as a colorless oil (31 mg, 85%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.71 (s, 3H), 3.44 – 3.33 (m, 1H), 2.59 – 2.40 (m, 2H), 1.91 – 1.80 (m, 1H), 1.75 – 1.64 (m, 2H), 0.96 (d, *J* = 2.0 Hz, 3H), 0.94 (d, *J* = 2.0 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.8, 76.2, 51.7, 33.9, 31.0, 29.1, 18.6, 17.4.
IR (film)/cm^{-1} 3460, 2958, 2876, 1737, 1438, 1260, 1169, 1058, 810, 750.
HRMS calcd for $C_8H_{16}NaO_3$ $[M+Na]^+$ 183.0997; found 183.0987.

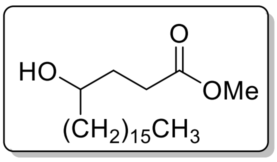
methyl 4-hydroxy-6-methylheptanoate (15)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-hydroxy-4-methylpentanoic acid **1f** and methyl acrylate **S1a** as starting materials. Compound **15** was isolated as a colorless oil (38 mg, 95%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.77 – 3.71 (m, 1H), 3.70 (s, 3H), 2.52 – 2.46 (m, 2H), 1.90 – 1.69 (m, 3H), 1.48 – 1.38 (m, 1H), 1.30 – 1.21 (m, 1H), 0.96 – 0.91 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 69.3, 51.7, 46.8, 32.6, 30.5, 24.6, 23.3, 22.1.
IR (film)/cm^{-1} 3430, 2954, 2870, 1738, 1467, 1438, 1367, 1168, 1055, 922.
HRMS calcd for $C_9H_{18}NaO_3$ $[M+Na]^+$ 197.1154; found 197.1151.

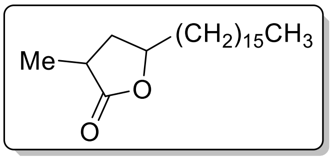
methyl 4-hydroxyicosanoate (16)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-hydroxyoctadecanoic acid **1g** and methyl acrylate **S1a** as starting materials. Compound **16** was isolated as a colorless oil (69 mg, 87%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 3.67 – 3.55 (m, 1H), 2.53 – 2.43 (m, 2H), 1.94 – 1.80 (m, 1H), 1.77 – 1.67 (m, 1H), 1.51 – 1.41 (m, 2H), 1.34 – 1.25 (m, 28H), 0.90 (t, *J* = 6.7 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 71.3, 51.7, 37.6, 32.1, 31.9, 30.5, 29.7, 29.68, 29.66, 29.63, 29.61, 29.4, 25.6, 22.7, 14.1.
IR (film)/cm^{-1} 3351, 2952, 2915, 2848, 1739, 1464, 1437, 1182, 913, 720.
HRMS calcd for $C_{21}H_{42}NaO_3$ $[M+Na]^+$ 365.3032; found 365.3008.

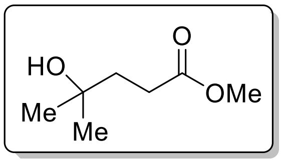
5-hexadecyl-3-methyldihydrofuran-2(3H)-one (17)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W, concentration = 0.15 M) with 2-hydroxyoctadecanoic acid **1g** and 2,3-dihydroxypropyl methacrylate **S4c** as starting materials. Compound **17** was obtained as a yellow oil (mixture of diastereomers, dr = 63:37). Compound **17** was isolated as a colorless oil (mixture of diastereomers, 63:37, 52 mg, 70%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.56 – 4.46 (m, 0.6H)^m, 4.40 – 4.28 (m, 1H)^M, 2.79 – 2.60 (m, 1H)^M, 2.57 – 2.41 (m, 1H)^M, 2.18 – 2.06 (m, 0.6H)^m, 2.06 – 1.93 (m, 0.6H)^m, 1.77 – 1.24 (m, 54.4H)$^{M+m}$, 0.94 – 0.85 (m, 4.8H)$^{M+m}$.
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 180.1, 179.6, 78.7, 78.5, 37.4, 35.9, 35.6, 35.48, 35.46, 34.0, 31.9, 29.70, 29.68, 29.66, 29.6, 29.53, 29.47, 29.4, 29.3, 25.4, 25.3, 22.7, 15.9, 15.1, 14.1.
IR (film)/cm^{-1} 2924, 2852, 1716, 1637, 1298, 1171, 1048, 944, 814, 750.
HRMS calcd for $C_{21}H_{40}NaO_2$ 347.2926 $[M+Na]^+$; found 347.2912.

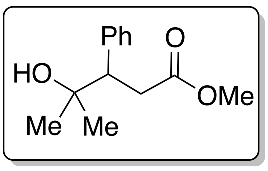
methyl 4-hydroxy-4-methylpentanoate (18a)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-hydroxy-2-methylpropanoic acid **1h** and methyl acrylate **S1a** as starting materials. Compound **18a** was isolated as a colorless oil (26 mg, 77%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.66 (s, 3H), 2.45 – 2.40 (m,2H), 1.83 – 1.77 (m, 2H), 1.21 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.9, 70.1, 51.7, 38.0, 29.21, 29.18, 27.7.
IR (film)/cm^{-1} 3461, 2966, 2879, 1737, 1437, 1172, 1017, 901, 795, 678.
HRMS calcd for $C_7H_{14}NaO_3$ $[M+Na]^+$ 169.0841; found 169.0830.

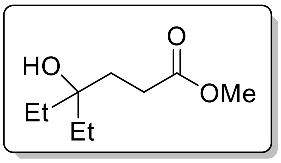
methyl 4-hydroxy-4-methyl-3-phenylpentanoate (18b)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 128 W) with 2-hydroxy-2-methylpropanoic acid 1h and methyl cinnamate **S3c** as starting materials. Compound **18b** was isolated as a colorless oil (38 mg, 75%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.15 (m, 5H), 3.51 (s, 3H), 3.02 (d, *J* = 7.9 Hz, 2H), 2.87 (br, 1H), 2.74 (t, *J* = 7.9 Hz, 1H), 1.35 (s, 3H), 1.32 (s, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.7, 139.4, 128.7, 128.4, 126.4, 71.1, 58.1, 51.4, 33.9, 29.1, 26.9.
IR (film)/cm^{-1} 3453, 2973, 2921, 2852, 1729, 1454, 1359, 1208, 1154, 699.
HRMS calcd for $C_{13}H_{18}NaO_3$ $[M+Na]^+$ 245.1154; found 245.1147.

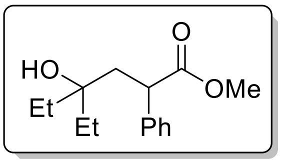
methyl 4-ethyl-4-hydroxyhexanoate (19)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and methyl acrylate **S1a** as starting materials. Compound **19** was isolated as a colorless oil (38 mg, 95%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 (s, 3H), 2.44 – 2.35 (m, 2H), 1.82 – 1.71 (m, 2H), 1.51 – 1.42 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.0, 73.9, 51.7, 33.0, 30.7, 28.5, 7.8.
IR (film)/cm^{-1} 3468, 2967, 2882, 1738, 1438, 1197, 1173, 931, 891, 801.
HRMS calcd for $C_9H_{18}NaO_3$ $[M+Na]^+$ 197.1154; found 197.1150.

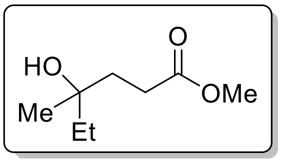
methyl 4-ethyl-4-hydroxy-2-phenylhexanoate (20)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and methyl 2-phenylacrylate **S3a** as starting materials. Compound **20** was isolated as a colorless oil (52 mg, 91%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.23 (m, 5H), 3.83 (dd, *J* = 10.2, 3.2 Hz, 1H), 3.67 (s, 3H), 2.51 (dd, *J* = 14.5, 10.3 Hz, 1H), 1.78 (dd, *J* = 14.5, 3.2 Hz, 1H), 1.61 – 1.47 (m, 4H), 0.90 (t, *J* = 7.5 Hz, 3H), 0.85 (t, *J* = 7.5 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.7, 140.4, 128.8, 127.8, 127.2, 74.5, 52.2, 46.6, 42.5, 31.9, 29.6, 8.2, 7.6.
IR (film)/cm^{-1} 3497, 2666, 2881, 1732, 1454, 1198, 1161, 978, 923, 698.
HRMS calcd for $C_{15}H_{22}NaO_3$ $[M+Na]^+$ 273.1467; found 273.1463.

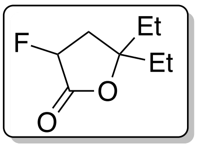
methyl 4-hydroxy-4-methylhexanoate (21)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 2-hydroxy-2-methylbutanoic acid **1j** and methyl acrylate **S1a** as starting materials. Compound **21** was isolated as a colorless oil (29 mg, 80%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.70 (s, 3H), 2.46 (dd, *J* = 11.5, 4.4 Hz, 2H), 1.91 – 1.72 (m, 2H), 1.52 (q, *J* = 7.5 Hz, 2H), 1.17 (s, 3H), 0.93 (t, *J* = 7.5 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 175.0, 72.2, 51.7, 35.7, 34.6, 28.8, 25.9, 8.2.
IR (film)/cm^{-1} 3460, 2968, 2882, 1737, 1437, 1375, 1261, 1121, 901, 797.
HRMS calcd for $C_8H_{16}NaO_3$ $[M+Na]^+$ 183.0997; found 183.0982.

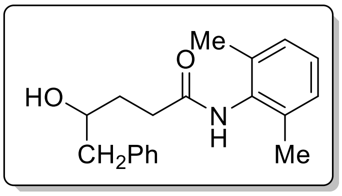
5,5-diethyl-3-fluorodihydrofuran-2(3H)-one (22)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and methyl 2-fluoroacrylate **S3b** as starting materials. Compound **22** was isolated as a colorless oil (34 mg, 93%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.25 (ddd, *J* = 51.6, 8.8, 7.2 Hz, 1H), 2.51 (ddd, *J* = 14.0, 12.6, 8.8 Hz, 1H), 2.24 (ddd, *J* = 27.6, 14.1, 7.2 Hz, 1H), 1.85 – 1.75 (m, 2H), 1.74 – 1.64 (m, 2H), 1.00 – 0.89 (m, 6H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 171.4 (d, *J* = 20.7 Hz), 87.9 (d, *J* = 4.2 Hz), 86.7 (d, *J* = 188.6 Hz), 37.1 (d, *J* = 18.8 Hz), 31.7, 31.1, 7.8, 7.5.
^{19}F NMR (377 MHz, $CDCl_3$) δ -189.40 (ddd, *J* = 51.6, 27.6, 12.5 Hz, 1F).
IR (film)/cm^{-1} 2974, 2944, 2886, 1778, 1462, 1217, 1151, 1097, 941, 826.
HRMS calcd for $C_8H_{13}FNaO_2$ $[M+Na]^+$ 183.0798; found 183.0785.

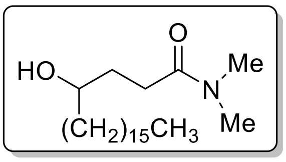
N-(2,6-dimethylphenyl)-4-hydroxy-5-phenylpentanamide (23)



Prepared following **GP1** (reaction time = 3 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and N-(2,6-dimethylphenyl)acrylamide **S7** as starting materials. Compound **23** was isolated as a white waxy solid (48 mg, 70%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, CD_3OD) δ 7.35 – 7.06 (m, 8H), 3.96 – 3.86 (m, 1H), 2.87 – 2.81 (m, 2H), 2.72 – 2.49 (m, 2H), 2.21 (s, 6H), 2.06 – 1.94 (m, 1H), 1.88 – 1.74 (m, 1H).
$^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD) δ 173.6, 138.8, 135.5, 134.2, 129.1, 127.9, 127.6, 126.9, 125.8, 71.8, 43.7, 32.5, 32.1, 17.0.
IR (film)/cm^{-1} 3254, 2922, 2855, 1647, 1523, 1453, 1082, 1031, 768, 700.
HRMS calcd for $C_{19}H_{22}NO_2$ $[M-H]^-$ 296.1651; found 296.1647.

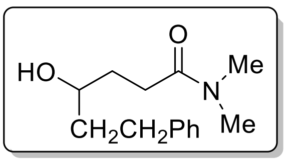
4-hydroxy-N,N-dimethylicosanamide (24)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W, concentration = 0.15 M) with 2-hydroxyoctadecanoic acid **1g** and N,N-dimethylacrylamide **S9** as starting materials. Compound **24** was isolated as a white waxy solid (65 mg, 80%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 3.67 – 3.56 (m, 1H), 3.04 (s, 3H), 2.97 (s, 3H), 2.60 – 2.42 (m, 2H), 1.93 – 1.82 (m, 1H), 1.79 – 1.67 (m, 1H), 1.55 – 1.19 (m, 30H), 0.95 – 0.85 (m, 3H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.9, 71.7, 37.9, 37.4, 35.6, 31.9, 31.8, 30.2, 29.73, 29.7, 29.65, 29.63, 29.4, 25.7, 22.7, 14.1.
IR (film)/cm^{-1} 3394, 2916, 2849, 1626, 1467, 1401, 1262, 1083, 910, 750.
HRMS calcd for $C_{22}H_{45}NNaO_2$ $[M+Na]^+$ 378.3348; found 378.3342.

4-hydroxy-N,N-dimethyl-6-phenylhexanamide (25)

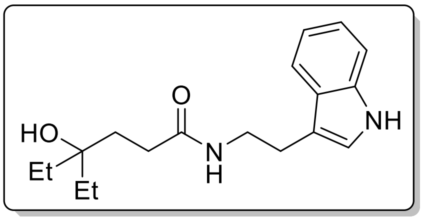


Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W, concentration = 0.15 M) with (S)-2-hydroxy-4-phenylbutanoic acid **1b** and N,N-dimethylacrylamide **S9** as starting materials. Compound **25** was isolated as a white waxy solid (51 mg, 95%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.16 (m, 5H), 3.72 – 3.62 (m, 1H), 3.56 – 3.49 (m, 1H), 3.04 (s, 3H), 2.98 (s, 3H), 2.89 – 2.78 (m, 1H), 2.77 – 2.66 (m, 1H), 2.63 – 2.42 (m, 2H), 1.95 – 1.73 (m, 4H).
$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ 173.9, 142.4, 128.5, 128.4, 125.7, 71.0, 39.6, 37.4, 35.7, 32.1, 31.8, 30.3.

IR (film)/cm^{-1} 3384, 3025, 2925, 1621, 1495, 1453, 1261, 1056, 748, 699.
HRMS calcd for $C_{14}H_{21}NNaO_2$ $[M+Na]^+$ 258.1470; found 258.1462.

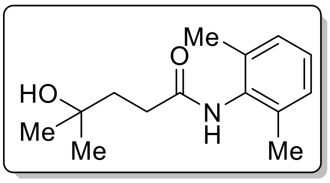
N-(2-(1H-indol-3-yl)ethyl)-4-ethyl-4-hydroxyhexanamide (26)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and N-(2-(1H-indol-3-yl)ethyl)acrylamide **S11** as starting materials. Compound **26** was isolated as a pale yellow oil (63 mg, 91%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (br, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.40 (d, *J* = 8.1 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.19 – 7.11 (m, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 5.73 (br, 1H), 3.68 – 3.52 (m, 2H), 2.99 (t, *J* = 6.7 Hz, 2H), 2.45 (br, 1H), 2.23 (t, *J* = 7.3 Hz, 2H), 1.75 (t, *J* = 7.3 Hz, 2H), 1.54 – 1.40 (m, 4H), 0.86 (t, *J* = 7.5 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.0, 136.4, 127.4, 122.2, 122.1, 119.5, 118.7, 113.0, 111.3, 73.8, 39.9, 33.4, 30.8, 30.7, 25.2, 7.9.
IR (film)/cm^{-1} 3401, 3285, 2966, 2933, 2879, 1632, 1533, 1456, 1339, 740.
HRMS calcd for $C_{18}H_{25}N_2O_2$ 301.1916 $[M-H]^-$; found 301.1912.

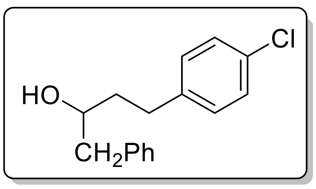
N-(2,6-dimethylphenyl)-4-hydroxy-4-methylpentanamide (27)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-hydroxy-2-methylpropanoic acid **1h** and N-(2,6-dimethylphenyl)acrylamide **S7** as starting materials. Compound **27** was isolated as a white waxy solid (49 mg, 91%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (br, 1H), 7.05 – 6.91 (m, 3H), 3.19 (br, 1H), 2.46 (t, *J* = 7.4 Hz, 2H), 2.11 (s, 6H), 1.81 (t, *J* = 7.4 Hz, 2H), 1.18 (s, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.1, 135.4, 134.0, 128.0, 127.1, 69.9, 38.7, 31.3, 29.3, 18.3.
IR (film)/cm^{-1} 3244, 2969, 1650, 1522, 1470, 1376, 1122, 935, 765, 702.
HRMS calcd for $C_{14}H_{20}NO_2$ $[M-H]^-$ 234.1494; found 234.1497.

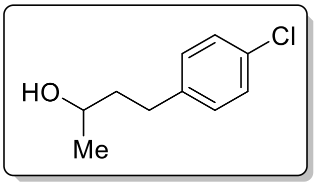
4-(4-chlorophenyl)-1-phenylbutan-2-ol (28)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and 1-chloro-4-vinylbenzene **S14** as starting materials. Compound **28** was isolated as a colorless oil (47 mg, 78%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.20 (m, 7H), 7.18 – 7.12 (m, 2H), 3.92 – 3.78 (m, 1H), 2.91 – 2.78 (m, 2H), 2.77 – 2.65 (m, 2H), 1.90 – 1.77 (m, 2H), 1.57 (d, *J* = 3.7 Hz, 1H).
^{13}C{1H} NMR (101 MHz, $CDCl_3$) δ 140.5, 138.2, 131.6, 129.8, 129.4, 128.7, 128.5, 126.6, 71.7, 44.2, 38.3, 31.4.
IR (film)/cm^{-1} 3401, 2922, 2856, 1492, 1406, 1091,1015, 927, 744, 700.
HRMS calcd for $C_{16}H_{17}ClNaO$ $[M+Na]^+$ 283.0866; found 283.0849.

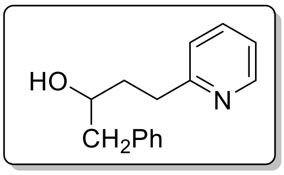
4-(4-chlorophenyl)butan-2-ol (29)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxypropanoic acid **1d** and 1-chloro-4-vinylbenzene **S14** as starting materials. Compound **29** was isolated as a colorless oil (30 mg, 70%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.00 (m, 4H), 3.89 – 3.77 (m, 1H), 2.84 – 2.61 (m, 2H), 1.82 – 1.69 (m, 2H), 1.25 (d, *J* = 6.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.5, 131.5, 129.8, 128.5, 67.3, 40.7, 31.5, 23.7.
IR (film)/cm^{-1} 3351, 2964, 2926, 1491, 1454, 1259, 1090, 1014, 954, 801.
HRMS calcd for $C_{10}H_{13}ClNaO$ 207.0553 [M+Na]$^+$; found 207.0522.

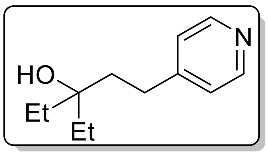
1-phenyl-4-(pyridin-2-yl)butan-2-ol (30)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and 2-vinylpyridine **S18** as starting materials. Compound **30** was isolated as a white waxy solid (27 mg, 51%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 – 8.48 (m, 1H), 7.61 (td, *J* = 7.6, 1.8 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.27 – 7.09 (m, 5H), 3.96 – 3.88 (m, 1H), 3.08 – 2.95 (m, 2H), 2.90 – 2.77 (m, 2H), 2.07 – 1.97 (m, 1H), 1.94 – 1.82 (m, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.6, 148.7, 139.0, 136.8, 129.4, 128.4, 126.2, 123.1, 121.1, 72.3, 44.3, 35.5, 34.8.
IR (film)/cm^{-1} 3367, 2961, 2923, 2852, 1630, 1379, 1260, 1085, 1031, 799.
HRMS calcd for $C_{15}H_{17}NNaO$ 250.1208 [M+Na]$^+$; found 250.1201.

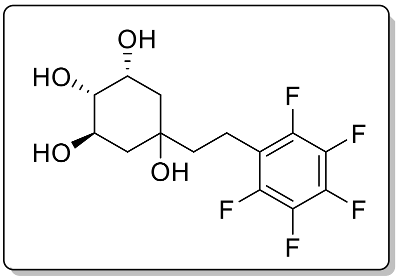
3-ethyl-1-(pyridin-4-yl)pentan-3-ol (31)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and 4-vinylpyridine **S17** as starting materials. Compound **31** was isolated as a dark orange oil (40 mg, 90%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.5, 1.6 Hz, 2H), 7.12 (dd, *J* = 4.5, 1.5 Hz, 2H), 2.68 – 2.60 (m, 2H), 1.75 – 1.67 (m, 2H), 1.54 (q, *J* = 7.5 Hz, 4H), 0.89 (t, *J* = 7.5 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 152.1, 149.5, 123.9, 74.3, 39.2, 30.9, 29.3, 7.8.
IR (film)/cm^{-1} 3364, 2926, 2854, 1601, 1454, 1416, 1335, 1229, 808, 749.
HRMS calcd for $C_{12}H_{20}NO$ [M+H]$^+$ 194.1540; found 194.1539.

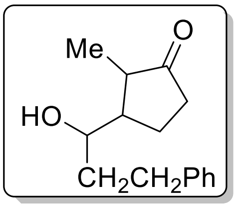
(1R,3R)-5-(2-(perfluorophenyl)ethyl)cyclohexane-1,2,3,5-tetraol (32)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(1S,3R,4S,5R)*-1,3,4,5-tetrahydroxycyclohexane-1-carboxylic acid **1k** and 1,2,3,4,5-pentafluoro-6-vinylbenzene **S15** as starting materials, compound **32** was obtained as a yellow oil (mixture of diastereomers, dr = 50:50). Compound **32** was isolated as a white waxy solid (mixture of diastereomers, dr = 50:50, 70 mg, 89%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, CD_3OD) δ 4.19 – 4.13 (m, 1H), 4.12 – 4.07 (m, 1H), 4.07 – 3.95 (m, 2H), 3.83 – 3.77 (m, 1H), 3.39 – 3.35 (m, 1H), 2.96 – 2.79 (m, 4H), 2.14 – 2.01 (m, 2H), 1.88 – 1.61 (m, 8H), 1.50 – 1.41 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ 146.56 – 143.45 (m), 141.00 – 137.87 (m), 138.92 – 135.71 (m), 116.19 – 115.52 (m), 76.2, 73.4, 73.2, 72.5, 71.0, 70.8, 67.0, 65.3, 43.5, 41.7, 41.6, 39.2, 38.4, 16.0.
^{19}F NMR (377 MHz, CD_3OD) δ -146.74 – -146.89 (m, 4F), -161.63 – -161.85 (m, 2F), -166.12 – -166.33 (m, 4F).
IR (film)/cm^{-1} 3359, 2925, 1656, 1520, 1501, 1453, 1260, 1122, 1058, 962.
HRMS calcd for $C_{14}H_{15}F_5NaO_4$ $[M+Na]^+$365.0788 ; found 365.0777.

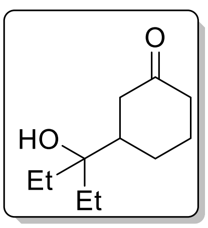
3-(1-hydroxy-3-phenylpropyl)-2-methylcyclopentan-1-one (33)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxy-4-phenylbutanoic acid **1b** and 2-methylcyclopent-2-en-1-one **S22** as starting materials, compound **33** was obtained as a yellow oil (mixture of diastereomers, dr = 50:50). Compound **33** was isolated as a colorless oil (mixture of diastereomers, dr = 50:50, 49 mg, 91%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.17 (m, 10H), 3.88 – 3.77 (m, 1H), 3.74 – 3.65 (m, 1H), 2.96 – 2.82 (m, 2H), 2.80 – 2.67 (m, 2H), 2.48 – 2.33 (m, 2H), 2.25 – 2.13 (m, 2H), 2.11 – 2.00 (m, 2H), 1.99 – 1.74 (m, 8H), 1.66 – 1.51 (m, 2H), 1.22 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 221.1, 220.9, 141.7, 141.6, 128.6, 128.42, 128.38, 126.09, 126.08, 74.9, 70.0, 50.3, 49.8, 47.0, 45.7, 37.24, 37.23, 36.99, 36.95, 32.7, 32.2, 23.8, 19.8, 15.5, 12.7.
IR (film)/cm^{-1} 3438, 2929, 2873, 1729, 1454, 1284, 1155, 1092, 951, 700.
HRMS calcd for $C_{15}H_{20}NaO_2$ $[M+Na]^+$ 255.1360; found 255.1343.

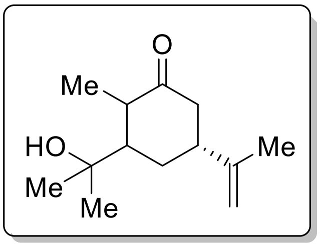
3-(3-hydroxypentan-3-yl)cyclohexan-1-one (34)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and cyclohex-2-en-1-one **S23** as starting materials. Compound **34** was isolated as a colorless oil (38 mg, 89%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.48 – 2.35 (m, 2H), 2.33 – 2.22 (m, 2H), 2.21 – 2.09 (m, 1H), 1.99 – 1.83 (m, 2H), 1.68 – 1.40 (m, 6H), 0.92 – 0.82 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.8, 75.4, 44.7, 42.4, 41.3, 28.2, 27.8, 25.3, 24.9, 7.64, 7.61.
IR (film)/cm^{-1} 3470, 2965, 2940, 2881, 1701, 1455, 1229, 1139, 953, 750.
HRMS calcd for $C_{11}H_{20}NaO_2$ $[M+Na]^+$ 207.1361; found 207.1363.

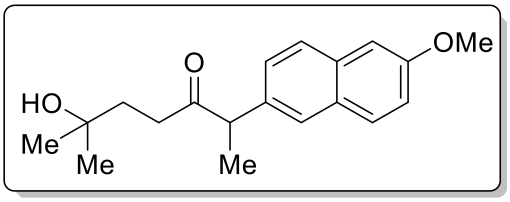
(5R)-3-(2-hydroxypropan-2-yl)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one (35)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 128 W) with 2-hydroxy-2-methylpropanoic acid **1h** and *(R)*-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one **S24** as starting materials, compound **35** was obtained as a yellow oil (mixture of diastereomers, dr = 1:1:1:1). Compound **35** was isolated as a colorless oil (mixture of diastereomers, dr = 1:1:1:1, 41 mg, 85%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.90 – 4.86 (m, 1H), 4.82 – 4.77 (m, 4H), 4.77 – 4.75 (m, 2H), 4.74 – 4.71 (m, 1H), 3.02 – 2.88 (m, 1H), 2.86 – 2.17 (m, 16H), 2.11 – 1.82 (m, 8H), 1.80 – 1.74 (m, 12H), 1.72 – 1.59 (m, 4H), 1.33 – 1.20 (m, 36H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 216.1, 215.0, 214.8, 213.9, 148.1, 147.62, 147.56, 146.5, 112.3, 110.0, 109.9, 109.6, 73.6, 73.5, 72.73, 72.70, 53.9, 50.7, 49.6, 47.2, 46.9, 46.7, 45.4, 45.1, 44.8, 44.6, 43.2, 42.4, 42.1, 41.4, 40.5, 40.0, 33.0, 30.7, 29.9, 29.84, 29.80, 28.3, 28.0, 27.9, 27.0, 25.60, 25.57, 23.7, 21.9, 20.7, 20.4, 20.3, 18.7, 16.6, 13.5, 12.9.
IR (film)/cm^{-1} 3440, 2968, 2877, 1698, 1645, 1452, 1375, 1260, 1025, 890.
HRMS calcd for $C_{13}H_{22}NaO_2$ $[M+Na]^+$ 233.1517; found 233.1507.

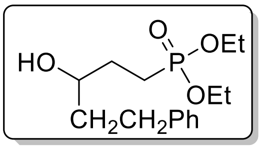
6-hydroxy-2-(6-methoxynaphthalen-2-yl)-6-methylheptan-3-one (36)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 128 W) with 2-hydroxy-2-methylpropanoic acid **1h** and 4-(6-methoxynaphthalen-2-yl)pent-1-en-3-one **S21** as starting materials. Compound **36** was isolated as a colorless oil (61 mg, 88%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 – 7.71 (m, 2H), 7.65 – 7.62 (m, 1H), 7.31 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.20 – 7.12 (m, 2H), 3.99 – 3.91 (m, 4H), 2.56 (t, *J* = 7.2 Hz, 2H), 1.83 – 1.73 (m, 1H), 1.72 – 1.62 (m, 1H), 1.49 (d, *J* = 6.9 Hz, 3H), 1.14 (d, *J* = 5.6 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 212.0, 157.7, 135.8, 133.7, 129.2, 129.1, 127.6, 126.5, 126.4, 119.2, 105.6, 70.1, 55.3, 53.1, 37.0, 36.2, 29.7, 29.5, 17.6.
IR (film)/cm^{-1} 3438, 2966, 2927, 2853, 1707, 1605, 1264, 1031, 809, 750.
HRMS calcd for $C_{19}H_{24}NaO_3$ $[M+Na]^+$ 323.1623; found 323.1615.

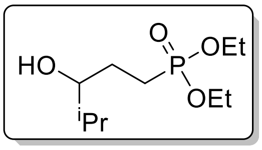
diethyl (3-hydroxy-5-phenylpentyl)phosphonate (37)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with (S)-2-hydroxy-4-phenylbutanoic acid **1b** and diethyl vinylphosphonate **S25** as starting materials. Compound **37** was isolated as a pale yellow oil (64 mg, 93%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.16 (m, 5H), 4.19 – 4.01 (m, 4H), 3.72 – 3.60 (m, 1H), 2.88 – 2.77 (m, 1H), 2.75 – 2.65 (m, 1H), 2.06 – 1.64 (m, 6H), 1.39 – 1.28 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.0, 128.44, 128.39, 125.8, 70.6 (d, *J* = 13.1 Hz) 61.8 – 61.6 (m), 38.9, 32.1, 30.2 (d, *J* = 4.8 Hz), 22.0 (d, *J* = 141.6 Hz), 16.5, 16.4.
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 33.35 (s, 1P).
IR (film)/cm^{-1} 3387, 2981, 2928, 1453, 1368, 1226, 1021, 959, 747, 699.
HRMS calcd for $C_{15}H_{25}NaO_4P$ $[M+Na]^+$ 323.1388; found 323.1365.

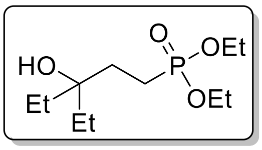
diethyl (3-hydroxy-4-methylpentyl)phosphonate (38)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-hydroxy-3-methylbutanoic acid **1e** and diethyl vinylphosphonate **S25** as starting materials. Compound **38** was isolated as a pale yellow oil (50 mg, 91%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.19 – 4.04 (m, 4H), 3.46 – 3.36 (m, 1H), 2.08 – 1.93 (m, 1H), 1.91 – 1.76 (m, 2H), 1.75 – 1.62 (m, 2H), 1.38 – 1.30 (m, 6H), 0.95 (t, *J* = 6.4 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 76.5 (d, *J* = 12.8 Hz), 61.7 (dd, *J* = 6.5, 3.6 Hz), 33.7, 27.0 (d, *J* = 4.7 Hz), 23.1, 21.7, 18.7, 17.5, 16.5 (d, *J* = 6.0 Hz).
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 33.46 (s, 1P).
IR (film)/cm^{-1} 3390, 2962, 2585, 2234, 2157, 2021, 1715, 1057, 1028, 964.
HRMS calcd for $C_{10}H_{23}NaO_4P$ $[M+Na]^+$ 261.1232; found 261.1221.

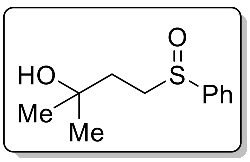
diethyl (3-ethyl-3-hydroxypentyl)phosphonate (39)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and diethyl vinylphosphonate **S25** as starting materials. Compound **39** was isolated as a pale yellow oil (50 mg, 92%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.18 – 3.97 (m, 4H), 2.07 (br, 1H), 1.84 – 1.63 (m, 4H), 1.45 (qd, *J* = 7.4, 1.4 Hz, 4H), 1.31 (t, *J* = 7.1 Hz, 6H), 0.84 (t, *J* = 7.5 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 73.7 (d, *J* = 15.0 Hz), 61.6, 61.5, 30.7 (d, *J* = 4.7 Hz), 30.4, 19.7 (d, *J* = 141.9 Hz), 16.4 (d, *J* = 6.0 Hz), 7.8.
^{31}P{^{1}H} NMR (202 MHz, $CDCl_3$) δ 32.97 (s, 1P).
IR (film)/cm^{-1} 3410, 2967, 2936, 1460, 1392, 1238, 1026, 947, 791, 750.
HRMS calcd for $C_{11}H_{25}NaO_4P$ $[M+Na]^+$ 275.1388; found 275.1377.

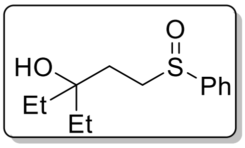
2-methyl-4-(phenylsulfinyl)butan-2-ol (40)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-hydroxy-2-methylpropanoic acid **1h** and (vinylsulfinyl)benzene **S26** as starting materials. Compound **40** was isolated as a colorless oil (44 mg, 91%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 – 7.46 (m, 5H), 3.10 – 2.83 (m, 2H), 1.95 – 1.69 (m, 2H), 1.22 (d, *J* = 10.2 Hz, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.3, 131.0, 129.2, 124.1, 69.4, 52.0, 35.3, 29.6, 29.2.
IR (film)/cm^{-1} 3384, 2969, 2928, 1476, 1443, 1202, 1028, 996, 745, 691.
HRMS calcd for $C_{11}H_{16}NaO_2S$ 235.0769 $[M+Na]^+$; found 235.0762.

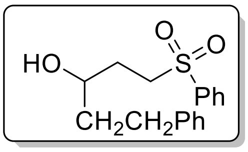
3-ethyl-1-(phenylsulfinyl)pentan-3-ol (41)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-ethyl-2-hydroxybutanoic acid **1i** and (vinylsulfinyl)benzene **S26** as starting materials. Compound **41** was isolated as a colorless oil (44 mg, 79%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.57 (m, 2H), 7.54 – 7.45 (m, 3H), 2.98 (ddd, *J* = 13.3, 10.4, 5.4 Hz, 1H), 2.82 (ddd, *J* = 13.3, 10.3, 5.5 Hz, 1H), 2.48 (br, 1H), 1.82 (ddd, *J* = 15.7, 10.3, 5.4 Hz, 1H), 1.70 (ddd, *J* = 14.3, 10.4, 5.5 Hz, 1H), 1.52 – 1.34 (m, 4H), 0.86 – 0.73 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.4, 131.0, 129.2, 124.1, 73.5, 51.5, 31.0, 30.6, 30.5, 7.80, 7.77.
IR (film)/cm^{-1} 3395, 2964, 2937, 2879, 1443, 1019, 986, 915, 745, 691.
HRMS calcd for $C_{13}H_{20}NaO_2S$ $[M+Na]^+$ 263.1082; found 263.1083.

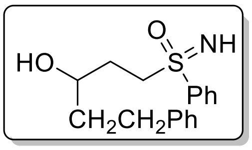
1-phenyl-5-(phenylsulfonyl)pentan-3-ol (42)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxy-4-phenylbutanoic acid **1b** and (vinylsulfonyl)benzene **S27** as starting materials. Compound **42** was isolated as a white waxy solid (60 mg, 85%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.71 – 7.64 (m, 1H), 7.62 – 7.55 (m, 2H), 7.32 – 7.15 (m, 5H), 3.77 – 3.67 (m, 1H), 3.38 – 3.16 (m, 2H), 2.82 – 2.61 (m, 2H), 2.02 – 1.93 (m, 1H), 1.88 – 1.73 (m, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.4, 139.1, 133.8, 129.4, 128.5, 128.4, 128.0, 126.1, 69.3, 53.1, 39.1, 31.9, 30.1.
IR (film)/cm^{-1} 3384, 3025, 2922, 2856, 1443, 1086, 1018, 997, 747, 698.
HRMS calcd for $C_{17}H_{20}NaO_3S$ $[M+Na]^+$ 327.1031; found 327.1038.

(3-hydroxy-5-phenylpentyl)(imino)(phenyl)-λ^6-sulfanone (43)

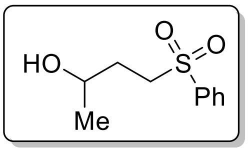


Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxy-4-phenylbutanoic acid **1b** and imino(phenyl)(vinyl)-λ^6-sulfanone **S29** as starting materials. Compound **43** was isolated as a dark yellow oil (mixture of diastereomers, dr = 50:50, 63 mg, 90%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.95 (m, 4H), 7.68 – 7.62 (m, 2H), 7.61 – 7.54 (m, 4H), 7.33 – 7.26 (m, 5H), 7.25 – 7.17 (m, 5H), 3.90 – 3.80 (m, 1H), 3.79 – 3.70 (m, 1H), 3.39 – 3.25 (m, 4H), 2.87 – 2.77 (m, 2H), 2.75 – 2.65 (m, 2H), 2.13 – 2.02 (m, 2H), 2.02 – 1.93 (m, 2H), 1.86 – 1.73 (m, 4H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.11, 142.10, 141.76, 141.73, 133.2, 129.3, 128.5, 128.43, 128.41, 128.35,

128.3, 125.9, 69.2, 69.1, 54.9, 54.7, 39.17, 39.12, 32.04, 31.97, 30.8, 30.6.
IR (film)/cm^{-1} 3507, 2927, 2859, 1447, 1304, 1147, 1085, 744, 688, 539.
HRMS calcd for $C_{17}H_{21}NaNO_2S$ 326.1191; found 326.1183.

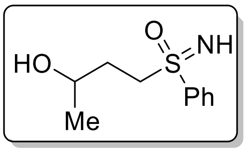
4-(phenylsulfonyl)butan-2-ol (44)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxypropanoic acid **1d** and (vinylsulfonyl)benzene **S27** as starting materials. Compound **44** was isolated as a pale yellow waxy solid (43 mg, 88%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.58 (m, 5H), 4.00 – 3.86 (m, 1H), 3.36 –3.19 (m, 2H), 2.01 – 1.75 (m, 2H), 1.22 (d, *J* = 6.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.2, 133.7, 129.3, 128.0, 66.2, 53.1, 31.6, 23.7.
IR (film)/cm^{-1} 3495, 2969, 2928, 1447, 1301, 1142, 1085, 935, 745, 689.
HRMS calcd for $C_{10}H_{14}NaO_3S$ $[M+Na]^+$ 237.0562; found 237.0554.

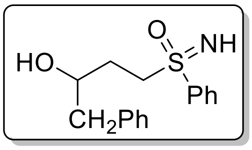
(3-hydroxybutyl)(imino)(phenyl)-λ^6-sulfanone (45)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(S)*-2-hydroxypropanoic acid **1d** and imino(phenyl)(vinyl)-λ^6-sulfanone **S29** as starting materials. Compound **45** was isolated as a dark yellow oil (mixture of diastereomers, dr = 50:50, 44 mg, 89%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.98 (m, 4H), 7.69 – 7.63 (m, 2H), 7.62 – 7.55 (m, 4H), 4.07 – 3.99 (m, 1H), 3.98 – 3.91 (m, 1H), 3.41 – 3.24 (m, 4H), 2.10 – 2.00 (m, 1H), 1.99 – 1.92 (m, 2H), 1.83 – 1.72 (m, 1H), 1.26 – 1.21 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.2, 133.2, 129.3, 128.4, 128.3, 66.3, 66.1, 54.9, 54.7, 32.3, 32.1, 23.6, 23.5.
IR (film)/cm^{-1} 3265, 2965, 2924, 2854, 1667, 1445, 1216, 1092, 991, 689.
HRMS calcd for $C_{10}H_{15}NNaO_2S$ $[M+Na]^+$ 236.0721; found 236.0712.

(3-hydroxy-4-phenylbutyl)(imino)(phenyl)-λ^6-sulfanone (46)

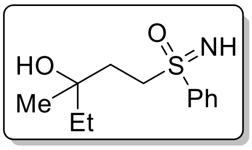


Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 3-phenyl-2-hydroxypropanoic acid **1a** and imino(phenyl)(vinyl)-λ^6-sulfanone **S29** as starting materials. Compound **46** was isolated as a dark yellow oil (mixture of diastereomers, dr = 50:50, 60 mg, 90%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.9 Hz, 4H), 7.68 – 7.62 (m, 2H), 7.61 – 7.53 (m, 4H), 7.36 – 7.24 (m, 6H), 7.22 – 7.17 (m, 4H), 4.08 – 3.99 (m, 1H), 3.99 – 3.90 (m, 1H), 3.44 – 3.27 (m, 4H), 2.82 – 2.77 (m, 2H), 2.14 – 1.97 (m, 4H), 1.86 – 1.75 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 137.8, 133.2, 129.4, 129.3, 128.7, 128.4, 128.3, 126.7, 71.0, 70.8, 54.9, 54.7, 44.1, 44.0, 30.0, 29.8.
IR (film)/cm^{-1} 3293, 2922, 2852, 1961, 1918, 1445, 1215, 1082, 991, 741.

HRMS calcd for $C_{16}H_{19}NNaO_2S$ $[M+Na]^+$ 312.1034; found 312.1025.

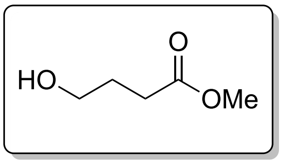
(3-hydroxy-3-methylpentyl)(imino)(phenyl)-λ⁶-sulfanone (47)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with 2-hydroxy-2-methylbutanoic acid **1j** and imino(phenyl)(vinyl)-λ^6-sulfanone **S29** as starting materials. Compound **47** was isolated as a dark yellow oil (mixture of diastereomers, dr = 50:50, 51 mg, 91%) after flash column chromatography (SiO_2) (ethyl acetate).

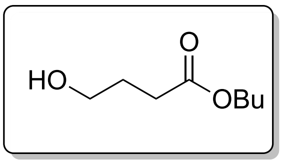
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 4H), 7.68 – 7.62 (m, 2H), 7.61 – 7.55 (m, 4H), 3.37 – 3.24 (m, 4H), 2.06 – 1.82 (m, 4H), 1.56 – 1.47 (m, 4H), 1.16 (d, *J* = 8.5 Hz, 6H), 0.93 – 0.86 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.2, 142.1, 133.1, 129.2, 128.4, 71.5, 71.4, 53.2, 34.9, 34.8, 33.74, 33.67, 26.1, 8.2.
IR (film)/cm^{-1} 3257, 2961, 2923, 2852, 1445, 1211, 1096, 990, 745, 689.
HRMS calcd for $C_{12}H_{19}NNaO_2S$ $[M+Na]^+$ 264.1034; found 264.1028.

methyl 4-hydroxybutanoate (48)



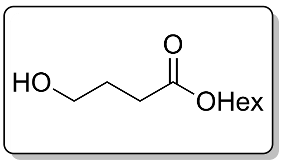
Prepared following **GP2** with (reaction time = 3 h, irradiation power = 38.4W) d_6-DMSO as solvent with glycolic acid **1l** and methyl acrylate **S1a** as starting materials. The reaction crude was analyzed directly by ^{1}H-NMR and ^{13}C-NMR without any purification.
Spectroscopic data matched those previously reported in the literature.[12]

butyl 4-hydroxybutanoate (49)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and butyl acrylate **S1c** as starting materials, compound **49** was isolated as a colorless oil (43 mg, 90%) after flash column chromatography (SiO_2) (9:1 hexane/ethyl acetate).
Spectroscopic data matched those previously reported in the literature.[13]

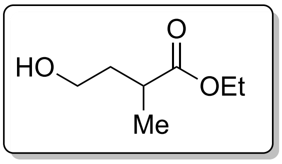
hexyl 4-hydroxybutanoate (50)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and hexyl acrylate **S1d** as starting materials, compound **50** was isolated as a colorless oil (51 mg, 90%) by washing the reaction crude with hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.08 (t, *J* = 6.8 Hz, 2H), 3.78 – 3.65 (m, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.89 (m, 2H), 1.71 – 1.54 (m, 2H), 1.46 – 1.18 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.1, 64.8, 62.1, 31.4, 31.1, 28.6, 27.7, 25.6, 22.5, 14.0.
IR (film)/cm^{-1} 3443, 2954, 2928, 2858, 1731, 1454, 1229, 1162, 1059, 749;
HRMS calcd for $C_{10}H_{20}NaO_3$ $[M+Na]^+$ 211.1310; found 211.1307.

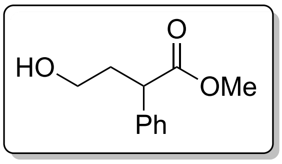
ethyl 4-hydroxy-2-methylbutanoate (51)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and ethyl methacrylate **S2b** as starting materials, compound **51** was isolated as a colorless oil (40 mg, 92%) after flash column chromatography (SiO_2) (9:1 hexane/ethyl acetate).

Spectroscopic data matched those previously reported in the literature.[13]

methyl 4-hydroxy-2-phenylbutanoate (52)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and methyl 2-phenylacrylate **S3a** as starting materials, compound **52** was isolated as a colorless oil (44 mg, 75%) after flash column chromatography (SiO_2) (9:1 hexane/ethyl acetate).

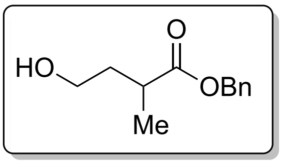
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.19 (m, 5H), 3.80 – 3.74 (m, 1H), 3.61 (s, 3H), 3.60 – 3.56 (m, 1H), 3.55 – 3.46 (m, 2H), 2.36 – 2.25 (m, 1H), 2.01 – 1.87 (m, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 174.7, 138.7, 128.8, 128.0, 127.4, 60.4, 52.2, 48.0, 36.1.

IR (film)/cm^{-1} 3405, 2925, 2852, 1731, 1434, 1218, 1159, 1043, 733, 698.

HRMS calcd for $C_{11}H_{14}NaO_3$ $[M+Na]^+$ 217.0841; found 217.0850.

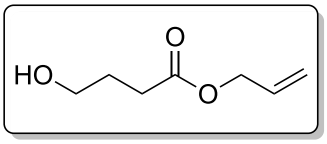
benzyl 4-hydroxy-2-methylbutanoate (53)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and benzyl methacrylate **S2a** as starting materials, compound **53** was isolated as a colorless oil (34 mg, 55%) after flash column chromatography (SiO_2) (9:1 hexane/ethyl acetate).

Spectroscopic data matched those previously reported in the literature.[14]

allyl 4-hydroxybutanoate (54)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and allyl acrylate **S1d** as starting materials, compound **54** was isolated as a colorless oil (37 mg, 85%) after flash column chromatography (SiO_2) (9:1 hexane/ethyl acetate).

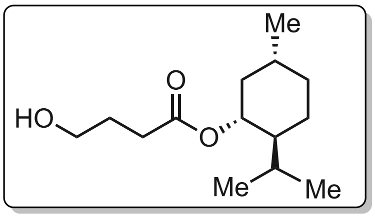
^{1}H NMR (400 MHz, $CDCl_3$) δ 5.98 – 5.89 (m, 1H), 5.37 – 5.24 (m, 2H), 4.62 – 4.59 (m, 2H), 3.72 (t, *J* = 6.1 Hz, 2H), 2.50 (t, *J* = 7.2 Hz, 2H), 1.96 – 1.89 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.6, 132.1, 118.3, 65.2, 62.1, 31.0, 27.7.

IR (film)/cm^{-1} 3415, 2935, 1731, 1648, 1447, 1381, 1158, 1057, 988, 933.

HRMS calcd for $C_7H_{12}NaO_3$ $[M+Na]^+$ 167.0684; found 167.0672.

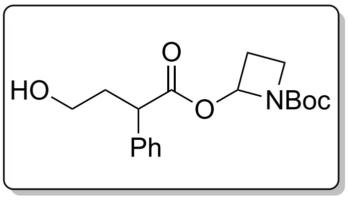
2-isopropyl-5-methylcyclohexyl 4-hydroxybutanoate (55)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and 2-isopropyl-5-methylcyclohexyl acrylate **S6** as starting materials, compound **55** was isolated as a colorless oil (70 mg, 95%) by washing the reaction crude with hexane.

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.71 (td, *J* = 10.9, 4.4 Hz, 1H), 3.70 (t, *J* = 6.1 Hz, 2H), 2.43 (t, *J* = 7.1 Hz, 2H), 2.06 – 1.96 (m, 1H), 1.95 – 1.82 (m, 4H), 1.70 (ddq, *J* = 12.9, 6.4, 3.1 Hz, 2H), 1.58 – 1.44 (m, 1H), 1.43 – 1.34 (m, 1H), 1.16 – 0.94 (m, 2H), 0.91 (dd, *J* = 6.8, 3.8 Hz, 6H), 0.78 (d, *J* = 7.0 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.5, 74.4, 62.2, 47.0, 40.9, 34.2, 31.5, 31.4, 27.9, 26.3, 23.5, 22.0, 20.7, 16.3.
IR (film)/cm^{-1} 3439, 2952, 2927, 2869, 1728, 1454, 1246, 1058, 843, 748.
HRMS calcd for $C_{14}H_{26}NaO_3$ [M+Na]$^+$ 265.1780; found 265.1760.

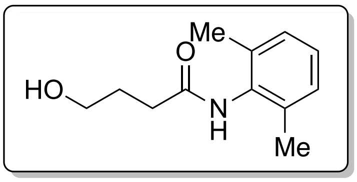
Tert-butyl 2-((4-hydroxy-2-phenylbutanoyl)oxy)azetidine-1-carboxylate (56)



Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4W) with glycolic acid **1l** and tert-butyl 2-((2-phenylacryloyl)oxy)azetidine-1-carboxylate **S5** as starting materials, compound **56** was obtained as a yellow oil (mixture of diastereoisomers, dr = 50:50). Compound **56** was isolated as a colorless oil (mixture of diastereoisomer, dr = 50: 50, 34 mg, 55%) after flash column chromatography (SiO_2) (1:1 hexane/ethyl acetate).

^{1}H NMR (400 MHz, CD_3OD) δ 7.43 – 7.11 (m, 10H)$^{M+m}$, 6.33 (dd, *J* = 6.4, 3.7 Hz, 1H)^{M}, 6.27 (dd, *J* = 6.4, 3.6 Hz, 1H)^{m}, 3.92 – 3.76 (m, 4H)$^{M+m}$, 3.74 – 3.66 (m, 4H)$^{M+m}$, 3.65 – 3.52 (m, 2H)$^{M+m}$, 2.68 – 2.25 (m, 8H)$^{M+m}$, 2.19 – 2.08 (m, 2H)$^{M+m}$, 2.07 – 1.88 (m, 4H)$^{M+m}$, 1.43 (s, 18H)$^{M+m}$.
^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ 172.7, 172.6, 154.9, 154.6, 138.4, 138.3, 128.7, 128.1, 128.0, 127.4, 84.3, 84.0, 80.8, 80.5, 60.1, 48.2, 44.5, 44.3, 36.5, 35.9, 28.4, 28.2, 28.1, 25.0, 24.9.
IR (film)/cm^{-1} 3387, 2974, 1770, 1707, 1497, 1454, 1366, 1257, 1160, 699.
HRMS calcd for $C_{18}H_{25}NNaO_5$ [M+Na]$^+$ 358.1630; found 358.1634.

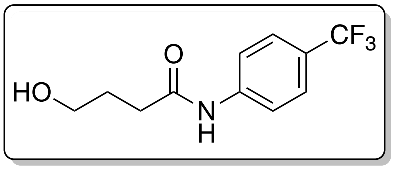
N-(2,6-dimethylphenyl)-4-hydroxybutanamide (57)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4W) with glycolic acid **1l** and *N*-(2,6-dimethylphenyl)acrylamide **S7** as starting materials, compound **57** was isolated as a colorless oil (34 mg, 55%) after flash column chromatography (SiO_2) (1:99 hexane/ethyl acetate).

^{1}H NMR (400 MHz, CD_3OD) δ 7.13 – 7.08 (m, 3H), 3.68 (t, *J* = 6.4 Hz, 2H), 2.53 (t, *J*= 7.28 Hz, 2H), 2.23 (s, 6H), 2.01 – 1.92 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ 173.4, 135.4, 134.2, 127.6, 126.9, 61.0, 32.1, 28.6, 17.0.
IR (film)/cm^{-1} 3254, 3023, 2923, 2391, 1647, 1522, 1476, 1194, 1057, 768.
HRMS calcd for $C_{12}H_{17}NNaO_2$ [M+Na]$^+$ 230.1157; found 230.1140.

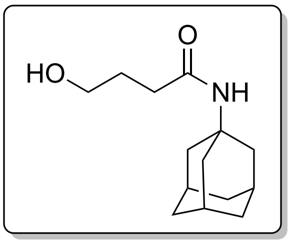
4-hydroxy-*N*-(4-(trifluoromethyl)phenyl)butanamide (58)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4W) with glycolic acid **1l** and *N*-(4-(trifluoromethyl)phenyl)acrylamide **S8** as starting materials, compound **58** was isolated as a colorless oil (52 mg, 70%) after flash column chromatography (SiO_2) (1:99 hexane/ethyl acetate).

^{1}H NMR (400 MHz, CD_3OD) δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 3.64 (t, *J* = 6.3 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 1.98 – 1.86 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, CD_3OD) δ 173.2, 142.1, 125.6 (q, *J* = 3.9 Hz), 125.0 (q, *J* = 30.1 Hz), 124.3 (q, *J* = 270.5 Hz), 119.3, 60.8, 33.1, 28.0.
^{19}F NMR (377 MHz, CD_3OD) δ -63.56 (s, 3F).
IR (film)/cm^{-1} 3301, 2954, 2888, 2469, 1650, 1532, 1405, 1323, 1127, 838.
HRMS calcd for $C_{11}H_{11}F_3NO_2$ [M-H]$^-$ 246.0747; found 246.0750.

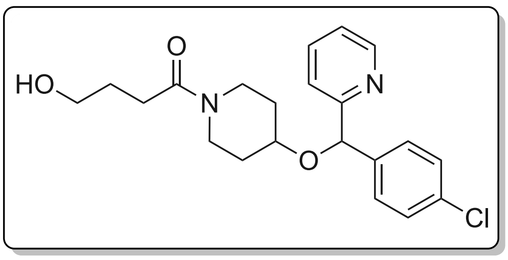
***N*-((3*s*,5*s*,7*s*)-adamantan-1-yl)-4-hydroxybutanamide (59)**



Prepared following **GP2** (reaction time = 16 h, irradiation power = 128 W) with glycolic acid **1l** and N-((3s,5s,7s)-adamantan-1-yl)acrylamide **S10** as starting materials, compound **59** was isolated as a colorless oil (66 mg, 93%) after flash column chromatography (SiO_2) (1:1 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.37 (s, 1H), 3.70 (t, *J* = 5.7 Hz, 2H), 2.39 – 2.21 (m, 2H), 2.20 – 2.04 (m, 3H), 2.04 – 1.97 (m, 6H), 1.86 (td, *J* = 11.7, 6.0 Hz, 2H), 1.75 – 1.54 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.8, 62.5, 52.1, 41.6, 36.3, 35.2, 29.4, 28.2.
IR (film)/cm^{-1} 3303, 2905, 2849, 1645, 1547, 1453, 1359, 1057, 730.
HRMS calcd for $C_{14}H_{22}NO_2$ [M-H]$^-$ 236.1656; found 236.1651.

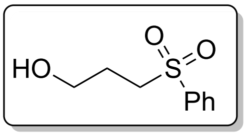
1-(4-((4-chlorophenyl)(pyridin-2-yl)methoxy)piperidin-1-yl)-4-hydroxybutan-1-one (60)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 128 W) with glycolic acid **1l** and 1-(4-((4-chlorophenyl)(pyridin-2-yl)methoxy)piperidin-1-yl)prop-2-en-1-one **S12** as starting materials, compound **60** was isolated as an dark-yellow oil (106 mg, 91%) after flash column chromatography (SiO_2) (1:1 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.9 Hz, 1H), 7.86 (td, *J* = 7.7, 1.7 Hz, 1H), 7.67 (d, *J* = 7.9 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.38 – 7.28 (m, 3H), 5.69 (s, 1H), 3.95 – 3.83 (m, 1H), 3.82 – 3.67 (m, 2H), 3.59 (t, *J* = 6.2 Hz, 2H), 3.42 – 3.35 (m, 2H), 2.48 (t, *J* = 7.3 Hz, 2H), 1.97 – 1.88 (m, 2H), 1.86 – 1.77 (m, 2H), 1.75 – 1.60 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 176.2, 165.4, 152.1, 144.1, 141.7, 137.1, 132.2, 132.1, 132.0, 130.6, 126.8, 125.2, 84.4, 76.4, 64.8, 46.6, 42.7, 35.3, 34.6, 33.1, 31.9.
IR (film)/cm^{-1} 3405, 2924, 2856, 1626, 1589, 1434, 1265, 1085, 769.
HRMS calcd for $C_{21}H_{25}ClN_2NaO_3$ [M+Na]$^+$ 411.1451; found 411.1438.

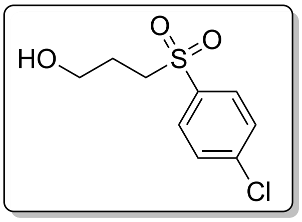
3-(phenylsulfonyl)propan-1-ol (61)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4W) with glycolic acid **1l** and (vinylsulfonyl)benzene **S27** as starting materials, compound **61** was isolated as a colorless oil (30 mg, 50%) after flash column chromatography (SiO_2) (1:1 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 – 7.88 (m, 2H), 7.79 – 7.52 (m, 3H), 3.83 – 3.64 (m, 2H), 3.45 – 3.12 (m, 2H), 2.19 – 1.92 (m, 2H), 1.76 (br, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.1, 133.8, 129.4, 128.0, 60.6, 53.3, 25.7;
IR (film)/cm^{-1} 3503, 2960, 1446, 1303, 1260, 1143, 1085, 1022, 794, 688.
HRMS calcd for $C_9H_{12}NaO_3S$ [M+Na]$^+$ 223.0405; found 223.0397.

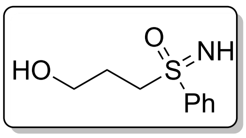
3-((4-chlorophenyl)sulfonyl)propan-1-ol (62)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 128 W) with glycolic acid **1l** and (vinylsulfonyl)benzene **S28** as starting materials, compound **62** was isolated as a colorless oil (65 mg, 93%) after flash column chromatography (SiO_2) (6:4 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.86 (m, 2H), 7.59 – 7.55 (m, 2H), 3.75 (t, *J* = 5.9 Hz, 2H), 3.28 – 3.24 (m, 2H), 2.02 – 1.96 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.6, 137.5, 129.7, 129.6, 60.4, 53.4, 25.7.
IR (film)/cm^{-1} 3504, 2922, 2852, 1721, 1582, 1476, 1308, 1276, 1147, 10862
HRMS calcd for $C_9H_{11}ClNaO_3S$ [M+Na]$^+$ 257.0015; found 257.0039.

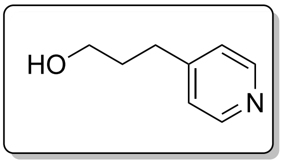
(3-hydroxypropyl)(imino)(phenyl)-λ^6-sulfanone (63)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 128 W) with glycolic acid **1l** and imino(phenyl)(vinyl)-l6-sulfanone **S29** as starting materials, compound **63** was isolated as a colorless oil (30 mg, 50%) after flash column chromatography (SiO_2) (Ethyl acetate).

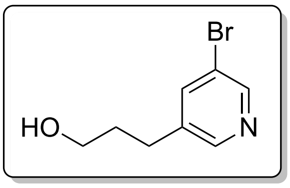
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 – 7.81 (m, 2H), 7.70 – 7.63 (m, 1H), 7.63 – 7.56 (m, 2H), 4.00 – 3.57 (m, 2H), 3.52 – 3.13 (m, 2H), 2.26 – 1.89 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.1, 133.3, 129.3, 128.4, 60.9, 55.6, 26.2.
IR (film)/cm^{-1} 3259, 2960, 2922, 2848, 1648, 1608, 1444, 1259, 1210, 1095.
HRMS calcd for $C_9H_{13}NNaO_2S$ [M+Na]$^+$ 222.0565; found 222.0563.

3-(pyridin-4-yl)propan-1-ol (64)



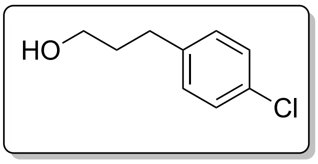
Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.6 W) with glycolic acid **1l** and 4-vinylpyridine **S17** as starting materials, compound **64** was isolated as a colorless oil (33 mg, 80%) after flash column chromatography (SiO_2) (1:9 hexane/ethyl acetate).
Spectroscopic data matched those previously reported in the literature.[15]

3-(4-bromopyridin-2-yl)propan-1-ol (65)



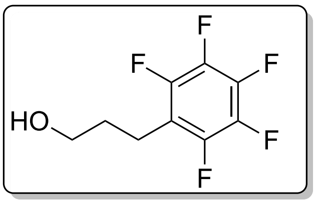
Prepared following **GP2** (reaction time = 3 h, irradiation power = 38.4 W) with glycolic acid **1l** and 3-bromo-5-vinylpyridine **S19** as starting materials, compound **65** was isolated as a colorless oil (55 mg, 85%) after flash column chromatography (SiO_2) (1:9 hexane/ethyl acetate).
Spectroscopic data matched those previously reported in the literature.[16]

3-(4-chlorophenyl)propan-1-ol (**66)**



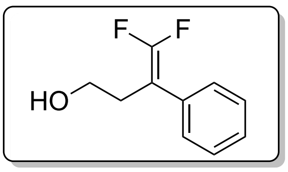
Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4 W) with glycolic acid **1l** and 1-chloro-4-vinylbenzene **S14** as starting materials, compound **66** was isolated as a colorless oil compound (44 mg, 87%) after flash column chromatography (SiO_2) (8:2 hexane/ethyl acetate). Spectroscopic data matched those previously reported in the literature.[17]

3-(perfluorophenyl)propan-1-ol (67)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4 W) with glycolic acid **1l** and 1,2,3,4,5-pentafluoro-6-vinylbenzene **S15** as starting materials, compound **67** was isolated as a colorless oil compound (54 mg, 80%) after flash column chromatography (SiO_2) (8:2 hexane/ethyl acetate). Spectroscopic data matched those previously reported in the literature.[18]

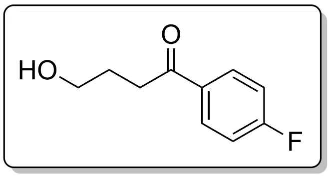
4,4-difluoro-3-phenylbut-3-en-1-ol (68)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4 W) with glycolic acid **1l** and (3,3,3-trifluoroprop-1-en-2-yl)benzene **S16** as starting materials, compound **68** was isolated as an colorless oil (47 mg, 85%) after flash column chromatography (SiO_2) (8:2 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.23 (m, 5H), 3.63 (t, *J* = 6.7 Hz, 2H), 2.69 – 2.61 (tt, J=6.8, 2.3 Hz, 2H), 1.59 (s, 1H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 154.3 (dd, *J* = 291.1, 287.7 Hz), 133.2 (dd, *J* = 4.4, 3.2 Hz), 128.6, 128.3 (t, *J* = 3.2 Hz), 127.5, 89.3 (dd, *J* = 21.6, 14.5 Hz), 60.5 – 60.4 (m), 31.2 (d, *J* = 1.5 Hz).
^{19}F NMR (377 MHz, $CDCl_3$) δ -89.68 (d, *J* = 41.1 Hz, 1H), -90.57 (d, *J* = 41.1 Hz, 1H).
IR (film)/cm^{-1} 3336, 2916, 1727, 1449, 1445, 1305, 1232, 1047, 762, 659.
HRMS calcd for $C_{10}H_{10}F_2NaO$ $[M+Na]^+$ 207.0597; found 207.058.

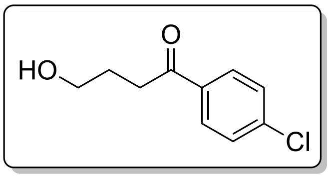
1-(4-fluorophenyl)-4-hydroxybutan-1-one (69)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4 W) with glycolic acid **1l** and 1-(4-fluorophenyl)prop-2-en-1-one **S20a** as starting materials, compound **69** was isolated as an colorless oil (44 mg, 80%) after flash column chromatography (SiO_2) (7:3 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 – 8.01 (m, 2H), 7.18 – 7.13 (m, 2H), 3.78 (dd, *J* = 11.2, 5.9 Hz, 2H), 3.13 (t, *J* = 6.9 Hz, 2H), 2.11 – 1.95 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.8, 165.8 (d, *J* = 254.7 Hz), 133.3 (d, *J* = 2.9 Hz), 130.7 (d, *J* = 9.3 Hz), 115.7 (d, *J* = 21.9 Hz), 62.3, 35.2, 26.9.
^{19}F NMR (377 MHz, $CDCl_3$) δ -105.26 (tt, *J* = 8.4, 5.4 Hz, 1H).
IR (film)/cm^{-1} 3341, 2918, 1680, 1596, 1506, 1409, 1231, 1156, 1091, 916, 834.
HRMS calcd for $C_{10}H_{11}FNaO_2$ $[M+Na]^+$ 205.0641; found 205.0629.

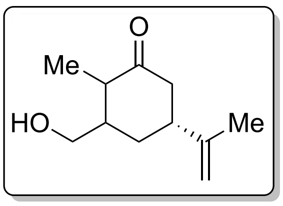
1-(4-chlorophenyl)-4-hydroxybutan-1-one (70)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 38.4 W) with glycolic acid **1l** and 1-(4-chlorophenyl)prop-2-en-1-one **S20b** as starting materials, compound **70** was isolated as an colorless oil (35 mg, 60%) after flash column chromatography (SiO_2) (7:3 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.89 (m, 2H), 7.46 – 7.40 (m, 2H), 3.74 (t, *J* = 6.0 Hz, 2H), 3.10 (t, *J* = 6.9 Hz, 2H), 2.09 – 1.96 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 199.2, 139.6, 135.2, 129.5, 128.9, 62.2, 35.2, 26.8.
IR (film)/cm^{-1} 3361, 2932, 2458, 1680, 1588, 1400, 1091, 1012, 812, 730;
HRMS calcd for $C_{10}H_{11}ClNaO_2$ $[M+Na]^+$ 221.0345; found 221.0332.

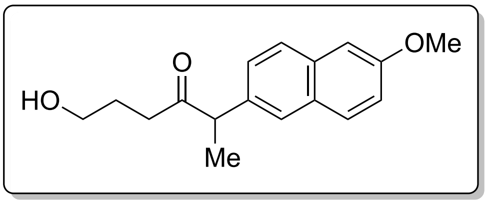
(5R)-3-(hydroxymethyl)-2-methyl-5-(prop-1-en-2-yl)cyclohexan-1-one (71)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 128 W) with glycolic acid **1l** and (R)-2-methyl-5-(prop-1-en-2-yl)cyclohex-2-en-1-one **S24** as starting materials, compound **71** was obtained as a yellow oil (mixture of 3 diastereoisomers, dr = 1:1:1). Compound **71** was isolated as an colorless oil (dr = 1:1:1, 52 mg, 95%) after flash column chromatography (SiO_2) (7:3 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 4.85 (s, 1H), 4.81 – 4.74 (m, 4H), 4.71 (s, 1H), 3.82 – 3.51 (m, 6H), 2.80 – 2.56 (m, 4H), 2.53 – 2.25 (m, 9H), 2.16 (m, 1H), 2.08 – 1.88 (m, 3H), 1.83 (m, 2H), 1.76 (s, 6H), 1.75 (s, 3H), 1.59 (m, 2H), 1.14 (d, *J* = 6.8 Hz, 3H), 1.11 – 1.04 (m, 6H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 213.8, 212.9, 212.7, 147.6, 147.5, 146.8, 111.7, 109.9, 109.8, 64.8, 64.6, 61.7, 46.5, 46.5, 46.3, 46.2, 45.8, 45.5, 44.9, 43.9, 43.0, 42.2, 41.4, 40.6, 34.2, 32.5, 29.6, 21.7, 20.7, 20.4, 13.3, 11.8, 11.3.
IR (film)/cm^{-1} 3414, 2968, 2929, 1702, 1644, 1449, 1376, 1225, 1045, 891.
HRMS calcd for $C_{11}H_{18}NaO_2$ $[M+Na]^+$ 205.1204; found 205.1193.

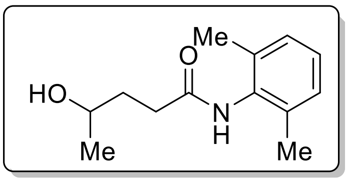
6-hydroxy-2-(6-methoxynaphthalen-2-yl)hexan-3-one (72)



Prepared following **GP2** (reaction time = 16 h, irradiation power = 128 W) with glycolic acid **1l** and (S)-4-(6-methoxynaphthalen-2-yl)pent-1-en-3-one **S21** as starting materials, compound **72** was isolated as an colorless oil (53 mg, 65%) after flash column chromatography (SiO_2) (1:1 hexane/ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (dd, *J* = 8.6, 3.0 Hz, 2H), 7.67 – 7.55 (m, 1H), 7.30 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.23 – 6.98 (m, 3H), 3.94 (s, 3H), 3.93 – 3.87 (m, 1H), 3.81 – 3.39 (m, 2H), 2.70 – 2.46 (m, 2H), 1.91 – 1.66 (m, 2H), 1.49 (d, *J* = 7.0 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 211.6, 157.8, 135.7, 133.7, 129.2, 129.1, 127.6, 126.5, 126.3, 119.2, 105.6, 62.2, 55.3, 53.1, 37.8, 26.7, 17.4.
IR (film)/cm^{-1} 3397, 2929, 1707, 1604, 1390, 1262, 1029, 908, 852, 729.
HRMS calcd for $C_{17}H_{20}NaO_3$ $[M+Na]^+$ 295.1310; found 295.1303.

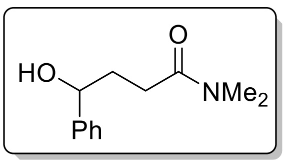
N-(2,6-dimethylphenyl)-4-hydroxypentanamide (73)



Prepared following **GP3** (reaction time = 3 h, irradiation power = 128 W) with *(S)*-2-hydroxypropanoic acid **1d** and N-(2,6-dimethylphenyl)acrylamide **S7** as starting materials. Compound **73** was isolated as a white waxy solid (47 mg, 92%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10 – 7.02 (m, 3H), 3.97 – 3.86 (m, 1H), 2.61 – 2.51 (m, 2H), 2.26 (s, 1H), 2.20 (s, 6H), 1.98 – 1.88 (m, 1H), 1.86 – 1.73 (m, 1H), 1.23 (d, *J* = 6.2 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 172.2, 135.4, 133.7, 128.2, 127.4, 67.7, 34.4, 33.2, 23.8, 18.4.
IR (film)/cm^{-1} 3244, 2964, 2923, 2856, 1652, 1524, 1476, 1375, 1074, 767.
HRMS calcd for $C_{13}H_{19}NNaO_2$ $[M+Na]^+$ 244.1313; found 244.1314.

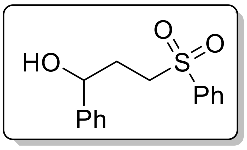
4-hydroxy-N,N-dimethyl-4-phenylbutanamide (74)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with (R)-2-hydroxy-2-phenylacetic acid **1c** and N,N-dimethylacrylamide **S9** as starting materials. Compound **74** was isolated as a colorless oil (19 mg, 40%) after flash column chromatography (SiO_2) (ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.33 (m, 4H), 7.30 – 7.24 (m, 1H), 4.87 – 4.79 (m, 1H), 4.24 (br, 1H), 3.01 (s, 3H), 3.00 (s, 3H), 2.50 (t, *J* = 6.3 Hz, 2H), 2.18 – 2.11 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 173.8, 145.0, 128.3, 127.2, 125.7, 73.8, 37.4, 35.7, 33.7, 30.0.
IR (film)/cm^{-1} 3235, 2960, 2918, 2856, 1652 , 1476, 1375, 1074, 767, 699.
HRMS calcd for $C_{12}H_{17}NNaO_2$ $[M+Na]^+$ 230.1157; found 230.1149.

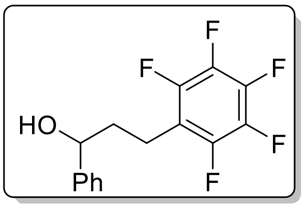
1-phenyl-3-(phenylsulfonyl)propan-1-ol (75)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(R)*-2-hydroxy-2-phenylacetic acid **1c** and (vinylsulfonyl)benzene **S27** as starting materials, compound **75** was isolated as a white waxy solid (33 mg, 52%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.90 (m, 2H), 7.71 – 7.65 (m, 1H), 7.64 – 7.56 (m, 2H), 7.40 – 7.29 (m, 5H), 4.90 – 4.80 (m, 1H), 3.34 – 3.16 (m, 2H), 2.24 – 2.12 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 143.0, 139.1, 133.7, 129.3, 128.8, 128.14, 128.05, 125.6, 72.3, 52.9, 31.8.
IR (film)/cm^{-1} 3496, 2919, 2849, 1447, 1304, 1148, 1084, 1024, 742, 688.
HRMS calcd for $C_{15}H_{16}NaO_3S$ $[M+Na]^+$ 299.0718; found 299.0708.

3-(perfluorophenyl)-1-phenylpropan-1-ol (76)



Prepared following **GP1** (reaction time = 16 h, irradiation power = 38.4 W) with *(R)*-2-hydroxy-2-phenylacetic acid **1c** and 1,2,3,4,5-pentafluoro-6-vinylbenzene **S15** as starting materials, compound **76** was isolated as a colorless oil (62 mg, 89%) after flash column chromatography (SiO_2) (8:2 hexane/ ethyl acetate).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 5H), 4.77 – 4.70 (m, 1H), 2.96 – 2.74 (m, 2H), 2.15 – 1.97 (m, 2H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.50 – 146.02 (m), 144.13 – 143.88 (m), 143.78, 141.17 – 140.49 (m), 139.01 – 138.10 (m), 136.54 – 135.86 (m), 128.65, 127.96, 125.78, 115.48 – 114.26 (m), 73.82, 37.95, 19.03.
^{19}F NMR (377 MHz, $CDCl_3$) δ -144.02 (dd, *J* = 22.5, 8.4 Hz, 2F), -157.88 (t, *J* = 20.8 Hz, 1F), -162.91 (dd, *J* = 20.8, 14.0 Hz, 2F).
IR (film)/cm^{-1} 3346, 2943, 2832, 1520, 1502, 1454, 1266, 1024, 964, 736.
HRMS calcd for $C_{15}H_{11}F_5NaO$ $[M+Na]^+$ 325.0628; found 325.0613.

8 Mechanistic experiments

8.1 Cyclic Voltammetry Studies

Cyclic voltammetry (CV) was performed on a Metrohm Autolab PGSTAT 302-N potentiostat using a three-electrode cell (a glassy carbon as working electrode, an Ag-wire as quasi-reference electrode, and a platinum counter electrode) and Nova 2.1.6 as software. CV measurements were carried out at 25°C in dry acetonitrile (MeCN) containing tetrabutylammonium hexafluorophosphate (0.10 M) as the supporting electrolyte, with a scan rate of 100 mV/s ranging from –2.2 and +2.8 V, starting at 0 V in the positive scan direction. Oxygen-free conditions were achieved by purging the electrochemical cell with nitrogen gas for 5 minutes before each measurement. Three scans were carried out per measurement, and numerical values were extracted from the third scan. The analyte (acid or its corresponding carboxylate) concentrations ranged between 1.0 and 10 mM. Carboxylates were generated in situ by addding of 1.0 equiv tetrabutylammonium hydroxide solution (1.0 M in methanol, Sigma-Aldrich) to the carboxylic acid. After each experiment, the potential of the Ag electrode was calibrated against the ferrocene/ferrocenium redox couple (for nonaqueous electrochemistry, IUPAC recommends the use of a redox couple such as ferrocene/ferrocenium ion (Fc/Fc^+) as an internal (or marker) standard.[19,20]) converted to *vs.* SCE by adding 380 mV.[21] Between each set of experiments (consisting of 3 CV scans of analyte and 3 CV scans of analyte with ferrocene) the glassy carbon electrode was mechanically polished in a figure-of-eight motion using an aqueous 0.05 µm alumina slurry on a nylon polishing pad. Then, it was rinsed with deionized water, and dried under a stream of nitrogen gas. All compounds evaluated showed chemically irreversible oxidation waves and, as suggested by Nicewicz and co-workers[22], the oxidation (anodic) potentials are reported as the potentials at half the peak ($E_{p/2}$) instead of anodic peak potentials (E_{pa}).

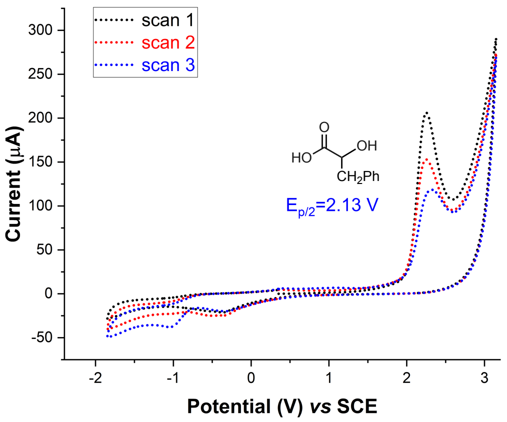


Figure 8. Cyclic Voltammetry of 1a.

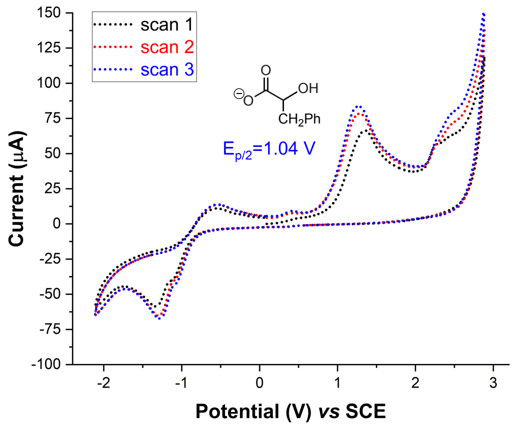


Figure 9. Cyclic Voltammetry of carboxylate 1a.

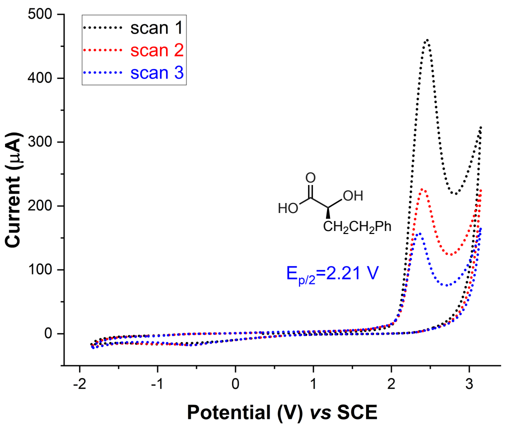


Figure 10. Cyclic Voltammetry of 1b.

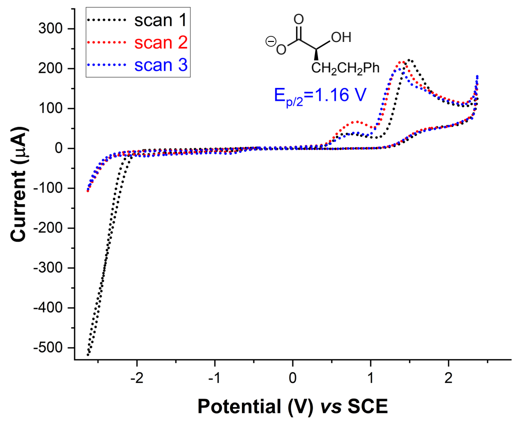


Figure 11. Cyclic Voltammetry of carboxylate 1b.

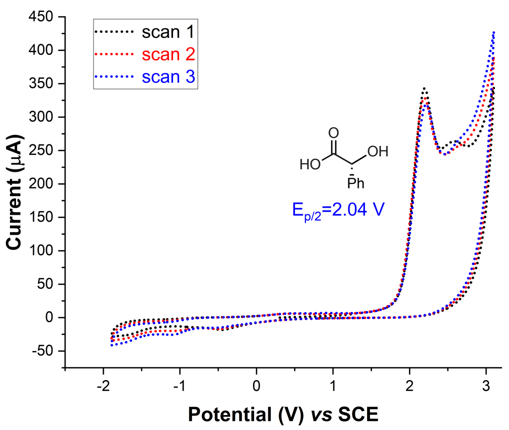


Figure 12. Cyclic Voltammetry of 1c.

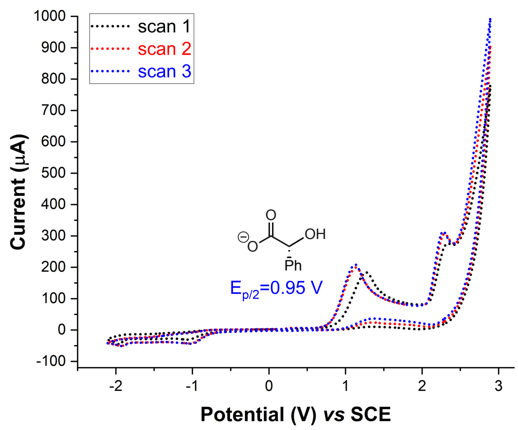


Figure 13. Cyclic Voltammetry of carboxylate 1c.

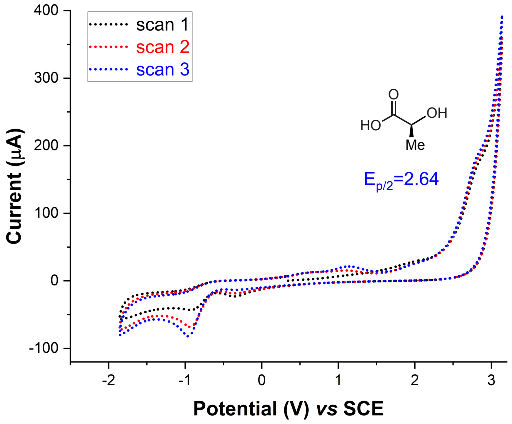


Figure 14. Cyclic Voltammetry of 1d.

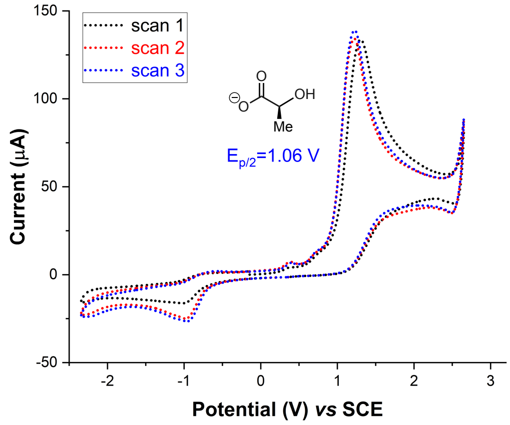


Figure 15. Cyclic Voltammetry of carboxylate 1d.

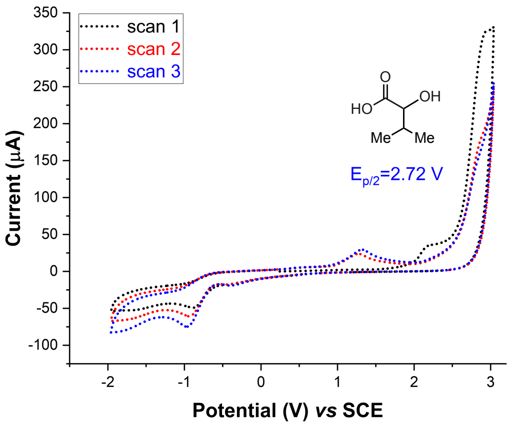


Figure 16. Cyclic Voltammetry of 1e.

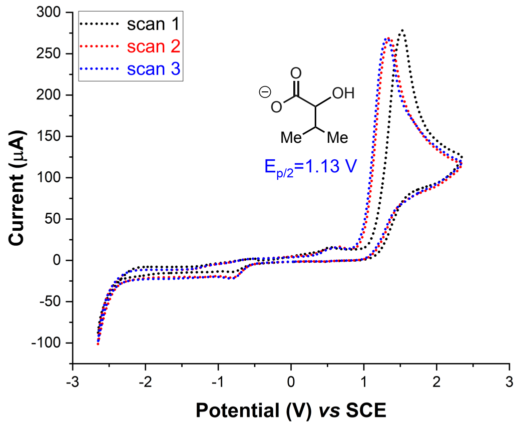


Figure 17. Cyclic Voltammetry of carboxylate 1e.

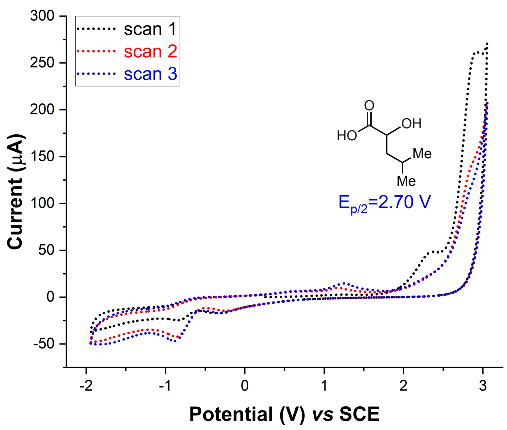


Figure 18. Cyclic Voltammetry of 1f.

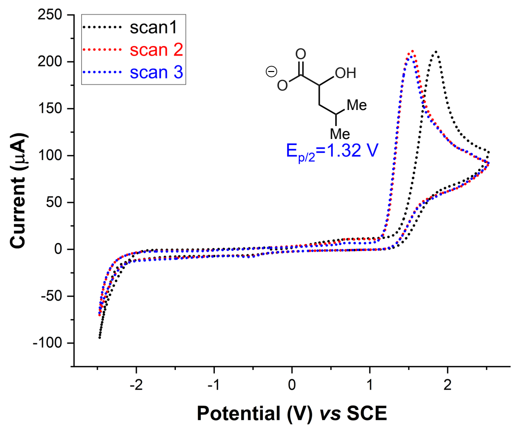


Figure 19. Cyclic Voltammetry of carboxylate 1f.

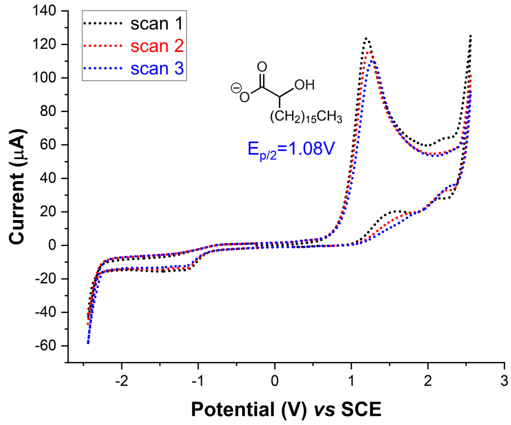


Figure 20. Cyclic Voltammetry of 1g [a].
[a]The potential for the corresponding hydroxyacid has not been recorded due to its insolubility in the analysis solvent.

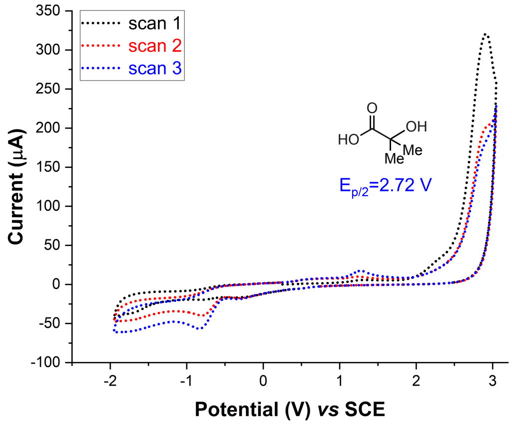


Figure 21 Cyclic Voltammetry of 1h.

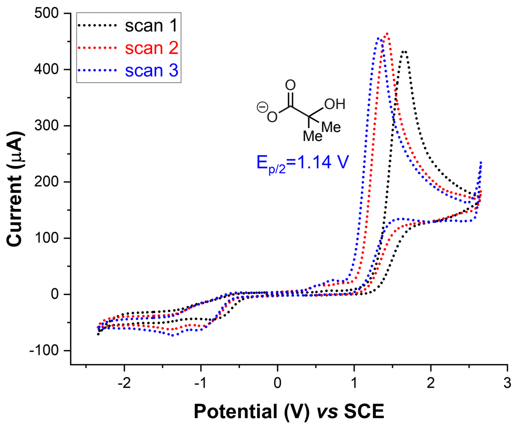


Figure 22. Cyclic Voltammetry of carboxylate 1h.

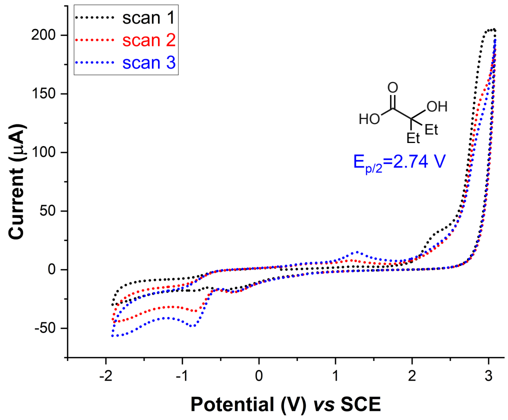


Figure 23. Cyclic Voltammetry of 1i.

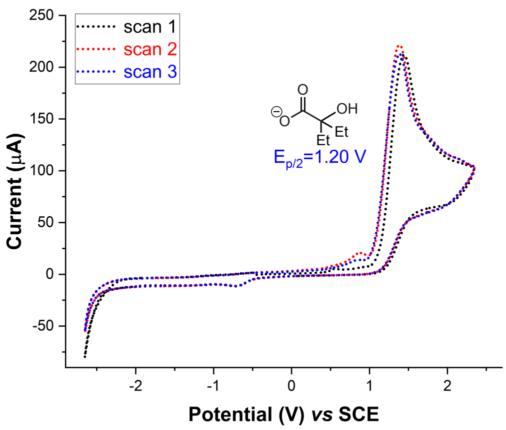


Figure 24. Cyclic Voltammetry of carboxylate 1i.

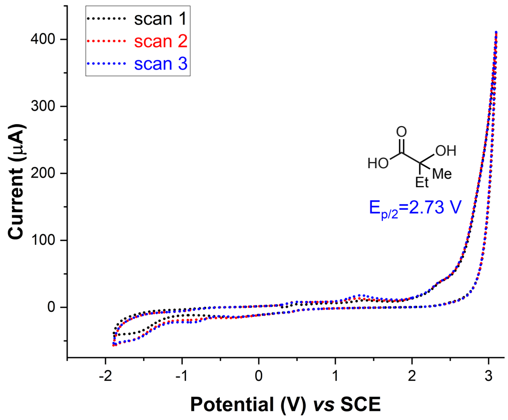


Figure 25 Cyclic Voltammetry of 1j.

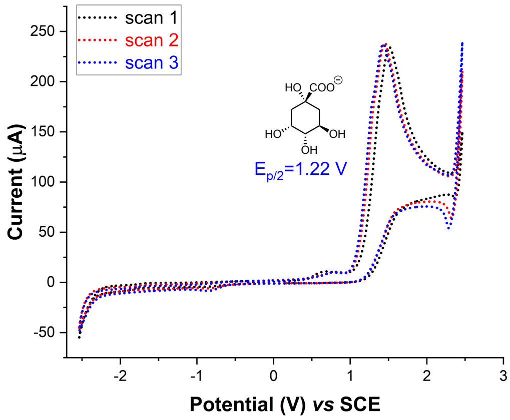


Figure 26. Cyclic Voltammetry of carboxylate 1k[a].
[a]The potential for the corresponding hydroxyacid has not been recorded due to its insolubility in the analysis solvent.

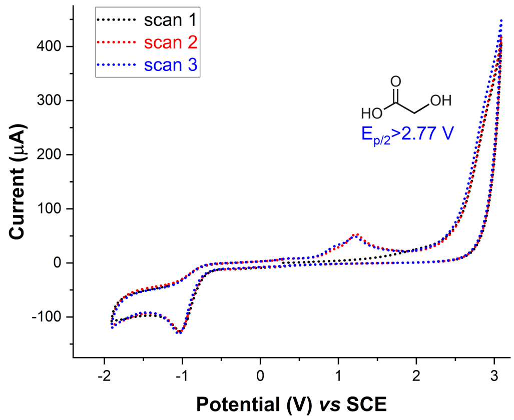


Figure 27. Cyclic Voltammetry of 1j.

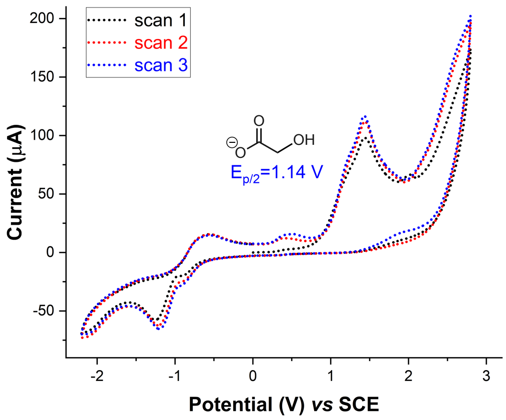


Figure 28. Cyclic Voltammetry of carboxylate 1j.

8.2 Stern–Volmer Quenching Studies

Steady-state photoluminescence (PL) spectra were acquired using a Varian Cary Eclipse instrument. In a typical experiment, fluorescence intensity was measured using a quartz cuvette (optical path length 10x10 mm, chamber volume 4500 μL). Stern-Volmer quenching experiments were run using freshly prepared solutions, in degassed DMSO, of 4CzIPN at 0.02 mM, potassium 2-hydroxy-3-phenylpropanoic carboxylate (K^+**1a**$^-$) at 4.0 mM, and methyl methacrylate at 4.0 mM. The cuvette was filled with a mixture prepared from 2.0 mL of 4CzIPN solution and the appropriate amount of solution of the chosen quencher and pure DMSO for affording 4.0 mL of final mixture with the desired quencher concentration (0, 0.125, 0.25, 0.50, 1.0 and 2.0 mM). The cuvette was then sealed using a septum and deoxygenated with a stream of nitrogen gas for 5 minutes before measurement. All samples were irradiated at 365 nm and emission was recorded from 415 to 750 nm.

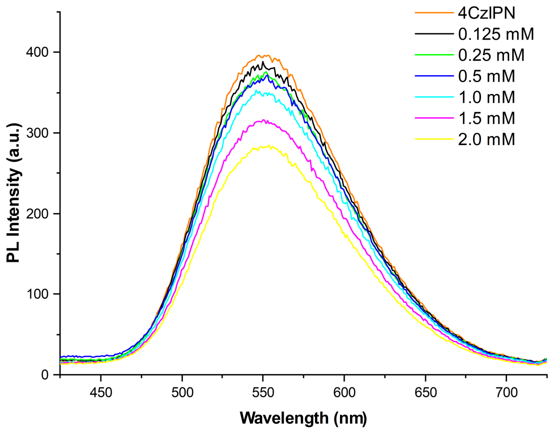


Figure 29. Photoluminescence spectra of 4CzIPN (0.01 mM) at different concentrations of potassium 2-hydroxy-3-phenylpropanoate.

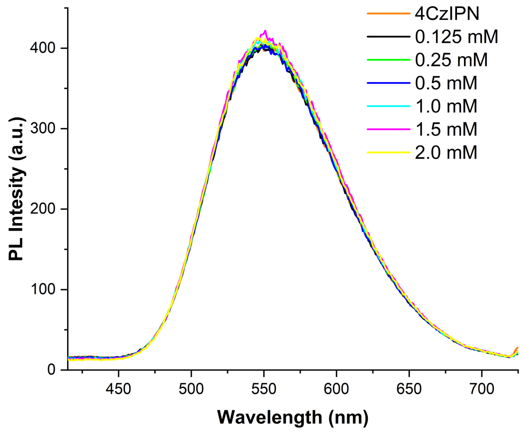


Figure 30. Photoluminescence spectra of 4CzIPN (0.01 mM) at different concentrations of methyl acrylate.

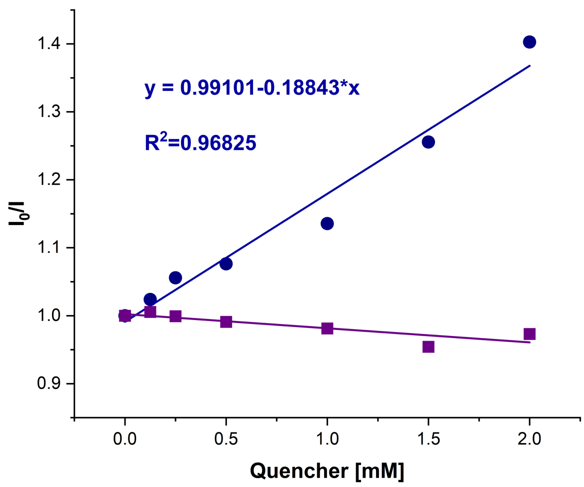
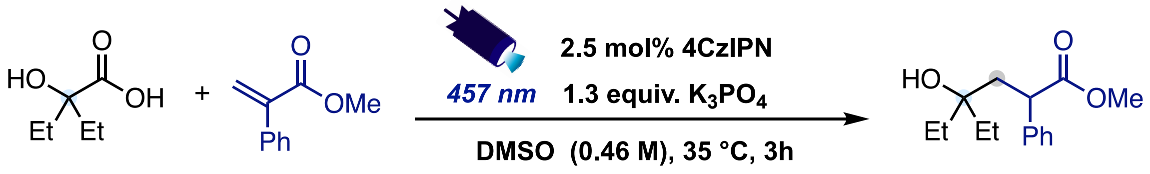


Figure 31. Summary of Stern-Volmer quenching experiments.

8.3 ON-OFF experiment



1i **S3a** **20**

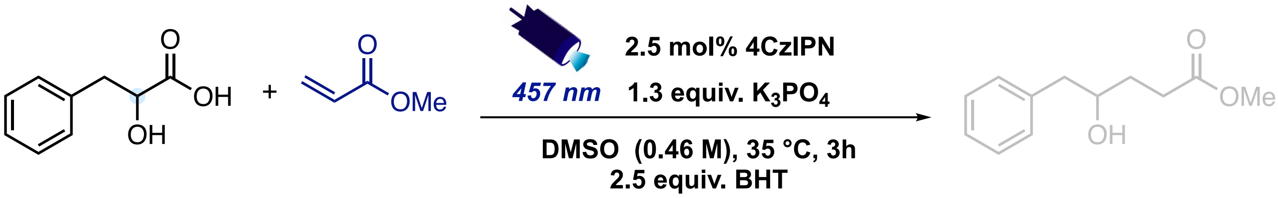
To an oven-dried 4 mL vial equipped with a stirring bar were added 2-ethyl-2-hydroxybutanoic acid (0.3 mmol, 1.3 equiv.), potassium phosphate tribasic (0.3 mmol, 1.3 equiv.), 4CzIPN (5.9 mg, 2.5 mol%), methyl 2-phenylacrylate (0.23 mmol, 1 equiv.), and dry DMSO (0.5 mL). Subsequently, the vial was sealed with a rubber septum and the solution was sparged with N_2 (1 min) and placed in a PhotoCube™ photochemical reactor equipped with a blue lamp (λ = 457 nm, 38.4 W). The solution was stirred and irradiated discontinuously and after each light-phase and each dark phase, an aliquot of 0.02 mL was withdrawn, diluted with AcOEt and analyzed by GC affording the following data.

Time (minutes)	Conversion of **S3a** (%)	Light
0-5	12	ON
5-10	14	OFF
10-15	37	ON
15-20	37	OFF
20-25	56	ON
25-30	57	OFF
30-60	98	ON
60-90	100	OFF
90-120	100	ON
120-150	100	OFF
150-180	100	ON

Table 7. Results of the ON/OFF experiment.

8.4 Radical Trapping Experiment

BHT trapping experiment



To an oven-dried 4 mL vial equipped with a stirring bar were added 2-hydroxy-3-phenylpropanoic acid (0.3 mmol, 1.3 equiv.), potassium phosphate tribasic (0.3 mmol, 1.3 equiv.), 4CzIPN (5.9 mg, 2.5 mol%), methyl acrylate (0.23 mmol, 1 equiv.), butylated hydroxytoluene (0.575 mmol, 2.5 eq.) and dry DMSO (0.5 mL). Subsequently, the vial was sealed with a rubber septum and the solution was sparged with N_2 (1 min). The solution was stirred and irradiated in a PhotoCube™ photochemical reactor equipped with a blue lamp (λ = 457 nm, 38.4 W) for 3 h. Then the vial was removed from the photochemical reactor. The solution was diluted with AcOEt and transferred to a separatory funnel where it was washed three times with brine. The organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude reaction mixture was analyzed by ^{1}H-NMR. The crude NMR showed no formation of product **4a**. No BHT adduct was detected via NMR or HRMS.

8.5 Computational studies

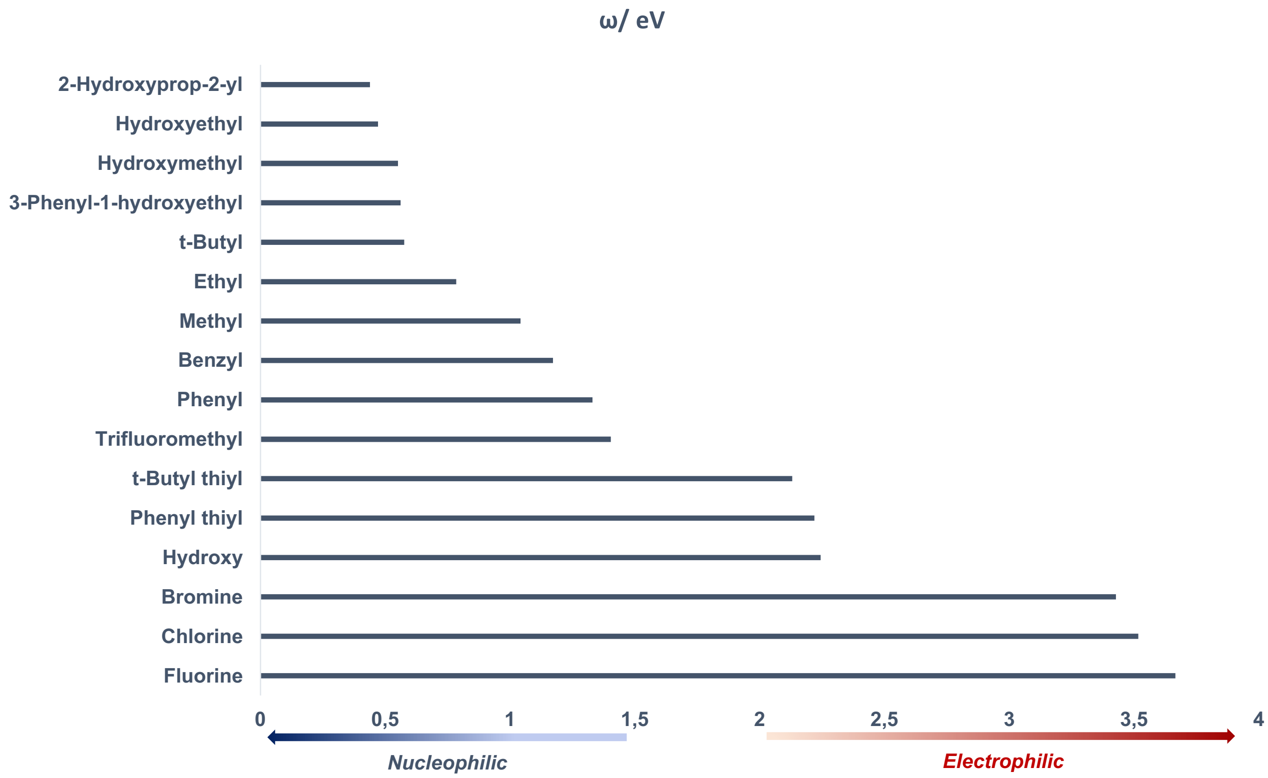
Computational methods

All calculations were performed using ORCA (v. 5.0.1).[24] The geometries employed in the philicity study were obtained at the ωB97X-D3/def2-TZVP level of theory and assessed as minima through vibrational analysis. Electronic affinity and ionization energy were computed at the ωB97X-D3/def2-TZVP level of theory using unrestricted formalism. ω (electrophilicity indexes) are defined as $\omega = \mu^2/2\eta$, where μ (electronic chemical potential) and η (chemical hardness) were computed as functions of vertical ionization potentials and electron affinities.[21] Geometry optimisations and frequency calculations for the reactivity study were obtained at the ωB97X-D3/def2-SVP level of theory.[25,26] Single point energies were refined at the SMD(DMSO)-ωB97X-D3/def2-TZVP level of theory on the optimised structures.[27] Stationary points for the redox potential calculations were refined at the SMD(DMSO)-M06-2X/ma-def2-TZVP//ωB97X-D3/def2-SVP level. The vibrational analysis was used to assign stationary points as either minima (no imaginary frequencies) or transition states (singular large imaginary frequency) and to calculate thermal corrections (298.15K, 1 atm). All open-shell systems were calculated using unrestricted formalism. Vibrational entropies were computed according to the QRRHO of S. Grimme.[28] The standard reduction potentials were calculated using the reported equation:

$$E^0 = \frac{-\Delta G^0}{nF}$$

where ΔG° are the standard free energy change associated with the reduction process (1 M), n is the number of electrons transferred (in all the cases studied equal to 1) and F is the Faraday constant (96485 C mol^{-1}). The free energy of the electron based on the ion convention formalism is -0.04 eV.[29] The reduction potentials were referenced to the standard calomel electrode (SCE, 0.244 V) itself referenced to the standard hydrogen electrode (further correction of 4.28 eV). ΔG for the reduction of Giese products by $4CzIPN^{\bullet-}$ was obtained from the aforementioned equation using the corresponding cell potentials.[30] Structures were visualized using Avogadro and Chemcraft software.

Table 8. Global electrophilicity indexes.



Radical	Electron Affinity (eV)	Ionization energy (eV)	μ	η	ω
Fluorine	2,85	18,73	-10,79	15,88	3,67
Chlorine	3,37	13,59	-8,48	10,22	3,52
Bromine	3,35	12,38	-7,86	9,02	3,43
Hydroxy	1,16	14,06	-7,61	12,90	2,24
Phenyl thiyl	2,10	8,80	-5,45	6,69	2,22
t-Butyl thiyl	1,77	10,25	-6,01	8,48	2,13
Trifluoromethyl	0,03	11,15	-5,59	11,12	1,40
Phenyl	0,46	9,17	-4,81	8,70	1,33
Benzyl	0,62	7,30	-3,96	6,68	1,17
Methyl	-0,52	9,80	-4,64	10,32	1,04
Ethyl	-0,86	8,53	-3,84	9,39	0,78
t-Butyl	-1,02	7,15	-3,07	8,17	0,58
3-Phenyl-1-hydroxyethyl	-1,12	7,24	-3,06	8,36	0,56
Hydroxymethyl	-1,58	8,12	-3,27	9,70	0,55
Hydroxyethyl	-1,61	7,45	-2,92	9,05	0,47
2-Hydroxyprop-2-yl	-1,51	6,96	-2,73	8,47	0,44

Cartesian coordinates (global electrophilicity indexes)

Hydroxy radical

8	-5.792926000	2.786682000	3.099074000
1	-6.077784000	3.318368000	2.333296000

Phenyl thiyl radical

1	-5.977290000	-1.857920000	2.217060000
6	-5.947140000	-0.798650000	1.987550000
1	-6.039390000	-1.099990000	-0.139570000
6	-5.981700000	-0.370900000	0.661320000
1	-5.846630000	-0.186840000	4.047150000
6	-5.874490000	0.127940000	3.010640000
6	-5.942490000	0.989390000	0.358840000
6	-5.834740000	1.509270000	2.725240000
1	-5.969150000	1.316330000	-0.674650000
6	-5.869770000	1.922030000	1.376370000
16	-5.744090000	2.658290000	3.987210000
1	-5.838350000	2.983160000	1.159010000

t-Butyl thiyl radical

6	-8.658270000	1.413950000	-0.056920000
6	-7.123070000	1.405240000	-0.100760000
6	-9.163400000	2.792970000	0.371430000
6	-9.164290000	0.332070000	0.898920000
16	-9.189760000	1.051450000	-1.749140000
1	-8.821030000	3.016590000	1.387140000
1	-10.255280000	2.828020000	0.365530000
1	-8.793420000	3.567560000	-0.302490000
1	-6.740830000	1.628650000	0.900070000
1	-6.742260000	2.162000000	-0.790000000
1	-6.741050000	0.428510000	-0.405180000
1	-8.820380000	0.543350000	1.916670000
1	-8.796650000	-0.651130000	0.600590000
1	-10.256240000	0.300160000	0.909190000

Trifluoromethyl radical

6	-10.422260000	4.516230000	-0.000360000
9	-10.820730000	5.488790000	0.797850000
9	-10.820780000	3.339410000	0.445100000
9	-10.820610000	4.719530000	-1.242590000

Phenyl radical

6	-7.745023000	2.240164000	1.950465000
6	-7.122913000	2.372021000	3.165289000
1	-7.674994000	2.472460000	4.093205000
6	-5.726175000	2.370443000	3.151588000
1	-5.180785000	2.471326000	4.084461000
6	-5.037446000	2.240146000	1.950362000
1	-3.953077000	2.240139000	1.950318000
6	-5.726267000	2.109857000	0.749184000
1	-5.180945000	2.008966000	-0.183728000
6	-7.123003000	2.108298000	0.735592000
1	-7.675181000	2.007870000	-0.192267000

Benzyl radical

1	-6.014846000	-1.808676000	2.268306000
6	-5.982930000	-0.755308000	2.010877000
1	-5.928467000	-1.118998000	-0.113031000
6	-5.934255000	-0.369332000	0.670069000
1	-6.027671000	-0.109791000	4.052375000
6	-5.990262000	0.194457000	3.011302000
6	-5.893069000	0.987352000	0.342762000
6	-5.949008000	1.580022000	2.705305000
1	-5.855571000	1.290347000	-0.698240000
6	-5.900115000	1.946018000	1.334563000
6	-5.956218000	2.550081000	3.718488000
1	-5.993639000	2.263784000	4.762466000
1	-5.868567000	2.999503000	1.075704000
1	-5.924972000	3.605832000	3.478573000

Methyl radical

6	-10.651770000	4.361680000	-0.320380000
1	-10.497820000	3.467610000	0.267360000
1	-10.910920000	4.283100000	-1.366850000
1	-10.542460000	5.334920000	0.137200000

Ethyl radical

6	-10.365847000	2.192683000	0.001825000
6	-8.901199000	1.938182000	0.034245000
1	-10.678797000	2.633290000	-0.948831000
1	-10.678890000	2.859279000	0.810165000
1	-10.940808000	1.261507000	0.121766000
1	-8.364817000	1.665437000	-0.866323000
1	-8.365462000	1.895632000	0.974552000

t-Butyl radical

6	-6.401180000	2.057450000	-0.001250000
6	-4.945510000	1.727770000	0.000880000
6	-7.039480000	2.483840000	1.278850000
6	-7.039540000	2.467550000	-1.286630000
1	-6.670900000	1.900570000	2.127620000
1	-8.128380000	2.386320000	1.238580000
1	-6.824050000	3.542390000	1.502940000
1	-4.661890000	1.160330000	0.892070000
1	-4.325710000	2.640360000	-0.004720000
1	-4.661800000	1.149270000	-0.883140000
1	-6.824360000	3.523240000	-1.524070000
1	-8.128430000	2.370350000	-1.245050000
1	-6.670910000	1.873710000	-2.128000000

3-Phenyl-1-hydroxyethyl radical (2a)

6	-7.727732000	1.800794000	-0.393517000
6	-6.346401000	1.778288000	-0.951266000
1	-2.577042000	-0.914637000	1.843505000
6	-3.337895000	-0.377066000	1.288364000

6	-4.682713000	-0.613554000	1.534761000
1	-4.978028000	-1.338733000	2.285608000
6	-5.659752000	0.077444000	0.825547000
1	-6.707236000	-0.113853000	1.028807000
6	-5.303812000	1.013444000	-0.140466000
6	-3.949846000	1.246314000	-0.378917000
1	-3.658515000	1.979741000	-1.125525000
6	-2.973192000	0.558787000	0.326776000
1	-1.924837000	0.756516000	0.129648000
1	-6.003306000	2.810568000	-1.069143000
1	-6.373725000	1.357789000	-1.967111000
8	-8.523620000	0.692308000	-0.513267000
1	-7.970721000	2.382898000	0.487389000
1	-8.218345000	0.163421000	-1.258031000

Hydroxymethyl radical

6	-6.464206000	0.540245000	-0.365383000
8	-5.283301000	0.790812000	0.267913000
1	-7.038601000	-0.332492000	-0.074072000
1	-6.943938000	1.426701000	-0.755760000
1	-4.945595000	-0.023216000	0.652290000

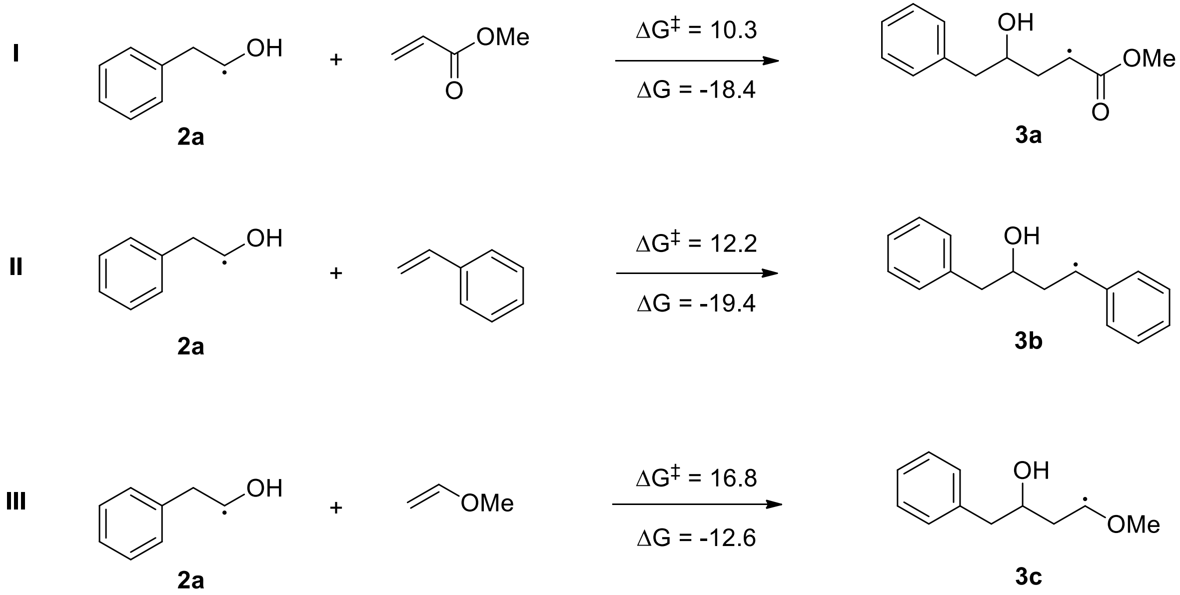
Hydroxyethyl radical

1	1.450854000	5.753000000	-1.294892000
8	2.148812000	5.176098000	0.529710000
6	1.441301000	4.910386000	-0.613624000
1	2.055119000	4.434885000	1.136934000
1	-0.533489000	4.389316000	0.090526000
6	0.276726000	3.985952000	-0.537062000
1	-0.131020000	3.805864000	-1.533533000
1	0.564618000	3.014689000	-0.115561000

2-Hydroxyprop-2-yl radical

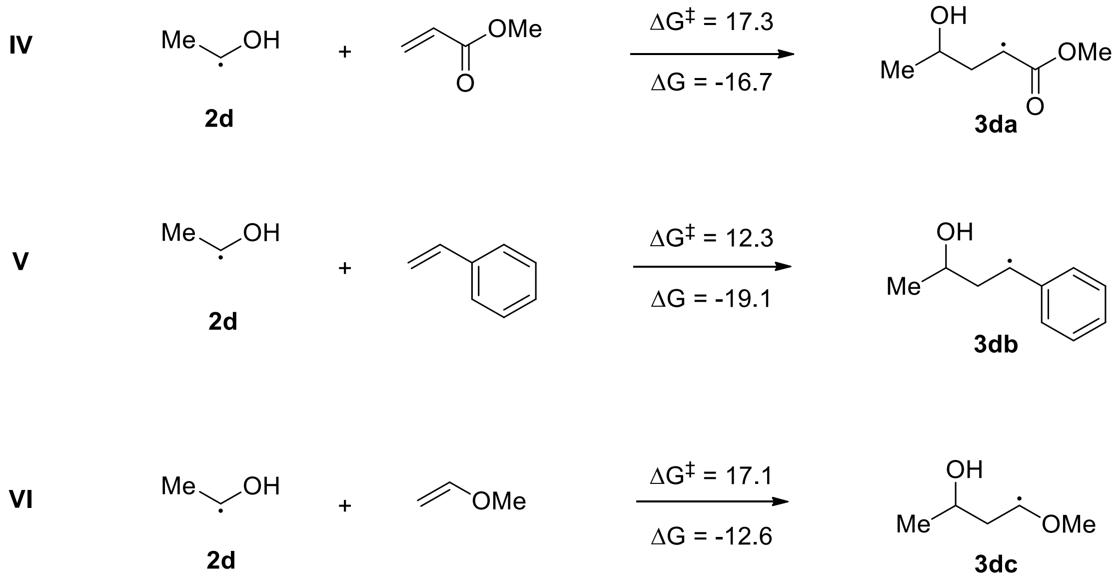
6	-10.445200000	2.279830000	0.044620000
6	-8.963720000	2.091380000	0.036530000
1	-10.793920000	2.632360000	-0.927860000
1	-10.753370000	3.015840000	0.795900000
1	-10.973030000	1.338140000	0.268480000
6	-8.287720000	1.389890000	-1.089300000
8	-8.369130000	1.823390000	1.251510000
1	-8.639870000	1.774960000	-2.048450000
1	-8.487390000	0.306560000	-1.067710000
1	-7.205140000	1.524820000	-1.032930000
1	-8.882250000	2.240130000	1.950430000

Table 9. Giese addition reaction of α-hydroxy phenylethyl radical with three different SOMOphiles (methyl acrylate, styrene and methyl vinyl ether). The table shows the differences in Gibbs free energy (ΔG), electronic energy (ΔE), zero-point energy (ΔZPE), enthalpy (ΔH) and entropy (TΔS) computed at the optimization level of theory (ωB97X-D3/def2-SVP). ΔE, ΔH and ΔG at the single-point level of theory (SMD(DMSO)-ωB97X-D3/def2-TZVP) were obtained using thermal corrections from the optimization level. Energies are reported in kcal mol^{-1}. Gibbs free energies were calculated at standard conditions (298.15 K and 1 M).



System		ωB97X-D3/def2-SVP					SMD(DMSO)-ωB97X-D3/def2-TZVP			
		ΔE	***ΔZPE***	***ΔH***	***TΔS***	***ΔG***	***ΔE***	***ΔH***	***ΔG (1atm)***	***ΔG (1M)***
I	TS	-10,0	1,3	-9,4	-14,9	5,5	-3,4	-2,7	12,2	10,3
	adduct	-41,7	3,8	-38,8	-15,5	-23,3	-34,9	-32,0	-16,5	-18,4
II	TS	-4,6	-23,3	-4,2	-13,8	10,2	-0,7	-0,2	14,1	12,2
	adduct	-40,8	3,4	-38,1	-14,5	-23,1	-35,3	-32,6	-17,5	-19,4
III	TS	-2,0	1,2	-1,5	-16,6	12,5	4,1	4,7	18,7	16,8
	adduct	-36,8	4,1	-33,6	-17,4	-18,8	-28,7	-25,6	-10,8	-12,6

Table 10. Giese addition reaction of the radical derived from decarboxylation of lactic acid with three different SOMOphiles (methyl acrylate, styrene and methyl vinyl ether). The table shows the differences in Gibbs free energy (ΔG), electronic energy (ΔE), zero-point energy (ΔZPE), enthalpy (ΔH) and entropy (TΔS) computed at the optimization level of theory (ωB97X-D3/def2-SVP). ΔE, ΔH and ΔG at the single-point level of theory (SMD(DMSO)-ωB97X-D3/def2-TZVP) were obtained using thermal corrections from the optimization level. Energies are reported in kcal mol^{-1}. Gibbs free energies were calculated at standard conditions (298.15 K and 1 M).



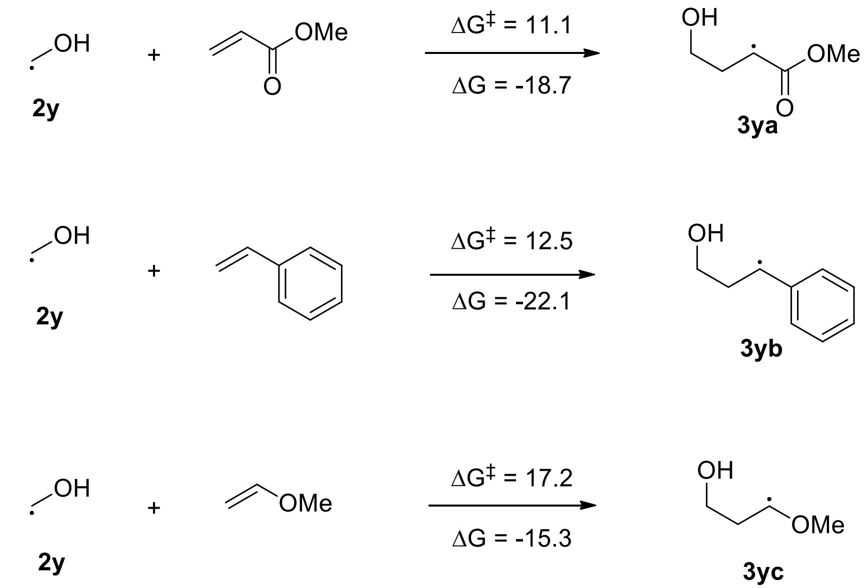
System		ωB97X-D3/def2-SVP					SMD(DMSO)-ωB97X-D3/def2-TZVP			
		ΔE	***ΔZPE***	***ΔH***	***TΔS***	***ΔG***	***ΔE***	***ΔH***	***ΔG (1atm)***	***ΔG (1M)***
IV	TS	-3,0	1,2	-2,7	-12,9	10,2	-1,5	-1,2	11,7	9,8
	adduct	-33,6	3,6	-30,8	-13,3	-17,4	-31,0	-28,1	-14,8	-16,7
V	TS	-2,7	1,3	-1,9	-12,4	11,0	0,6	1,4	14,2	12,3
	adduct	-38,8	3,7	-36,6	-14,0	-22,1	-34,0	-31,8	-17,3	-19,1
VI	TS	0,8	1,5	1,6	-15,4	14,4	5,4	6,2	19,0	17,1
	adduct	-32,9	4,2	-29,8	-16,0	-16,3	-27,3	-24,1	-10,7	-12,6

Table 11. Giese addition reaction of the radical derived from decarboxylation of glycolic acid with three different SOMOphiles (methyl acrylate, styrene and methyl vinyl ether). The table shows the differences in Gibbs free energy (ΔG), electronic energy (ΔE), zero-point energy (ΔZPE), enthalpy (ΔH) and entropy (TΔS) computed at the optimization level of theory (ωB97X-D3/def2-SVP). ΔE, ΔH and ΔG at the single-point level of theory (SMD(DMSO)-ωB97X-D3/def2-TZVP) were obtained using thermal corrections from the optimization level. Energies are reported in kcal mol^{-1}. Gibbs free energies were calculated at standard conditions (298.15 K and 1 M).

VII

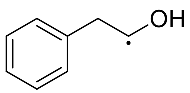
VIII

IX

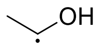


		ωB97X-D3/def2-SVP					SMD(DMSO)-ωB97X-D3/def2-TZVP			
System		*ΔE*	*ΔZPE*	*ΔH*	*TΔS*	*ΔG*	*ΔE*	*ΔH*	*ΔG (1atm)*	*ΔG (1M)*
VII	TS	-0,1	1,5	0,8	-11,6	12,4	0,5	1,4	13,0	11,1
	adduct	-33,7	4,0	-30,5	-12,4	-18,2	-32,3	-29,1	-16,8	-18,7
VIII	TS	-0,9	1,3	-0,1	-11,5	11,8	1,7	2,4	14,4	12,5
	adduct	-39,9	4,2	-36,7	-12,6	-23,7	-36,4	-33,2	-20,2	-22,1
IX	TS	2,3	1,8	3,1	-14,7	15,2	6,1	7,0	19,1	17,2
	adduct	-34,0	4,7	-30,5	-15,2	-17,8	-29,6	-26,1	-13,4	-15,3

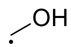
Table 12. Potential of radicals and Giese adducts obtained from α-hydroxy radicals with methyl acrylate, styrene, and vinyl methyl ether. The table shows the differences in Gibbs free energy (ΔG), electronic energy (ΔE), zero-point energy (ΔZPE), enthalpy (ΔH) and entropy (TΔS) computed at the optimization level of theory (ωB97X-D3/def2-SVP). ΔE, ΔH and ΔG at the single-point level of theory (SMD(DMSO)-M06-2X/ma-def2-TZVP) were obtained using thermal corrections from the optimization level. Energies are reported in kcal mol^{-1}. Gibbs free energies were calculated at standard conditions (298.15 K and 1 M). E^0 are expressed versus SCE.



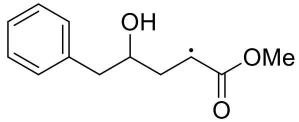
2a



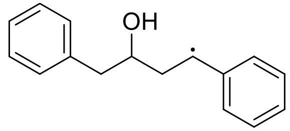
2d



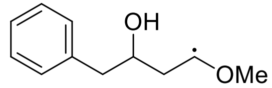
2y



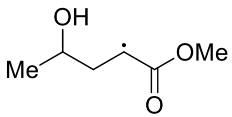
3a



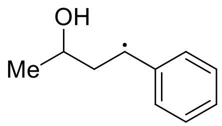
3b



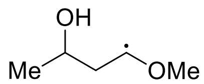
3c



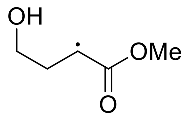
3da



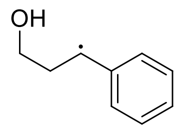
3db



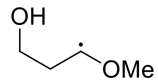
3dc



3ya



3yb



3yc

	ωB97X-D3/def2-SVP					SMD(DMSO)-M06-2X/ma-def2-TZVP				
Process	***ΔE***	***ΔZPE***	***ΔH***	***TΔS***	***ΔG***	***ΔE***	***ΔH***	***ΔG (1atm)***	***ΔG (1M)***	***E^{o} vs SCE***
2a$^{\cdot}$ + e^{-} → **2a**$^{-}$	0,52	-0,09	0,44	-0,01	0,49	-2,39	-2,48	-2,51	-2,59	-1,93
2d$^{\cdot}$ + e^{-} → **2d**$^{-}$	1,04	-0,08	0,96	-0,02	1,02	-2,25	-2,33	-2,35	-2,43	-2,09
2y$^{\cdot}$ + e^{-} → **2y**$^{-}$	1,05	-0,07	0,98	-0,01	1,03	-2,48	-2,54	-2,56	-2,64	-1,88
3a$^{\cdot}$ + e^{-} → **3a**$^{-}$	-1,57	-0,05	-1,62	-0,02	-1,57	-3,62	-3,68	-3,68	-3,76	-0,76
3b$^{\cdot}$ + e^{-} → **3b**$^{-}$	-0,86	-0,07	-0,93	-0,01	-0,88	-3,00	-3,07	-3,09	-3,17	-1,35
3da$^{\cdot}$ + e^{-} → **3da**$^{-}$	0,31	-0,08	0,22	-0,03	0,28	-2,27	-2,35	-2,38	-2,46	-2.06
3db$^{\cdot}$ + e^{-} → **3db**$^{-}$	-1,59	-0,03	-1,63	-0,04	-1,56	-3,64	-3,68	-3,65	-3,73	-0,79
3dc$^{\cdot}$ + e^{-} → **3dc**$^{-}$	-0,84	-0,06	-0,87	0,01	-0,84	-3,02	-3,05	-3,06	-3,14	-1,39
3ya$^{\cdot}$ + e^{-} → **3ya**$^{-}$	0,25	-0,07	0,17	-0,04	0,25	-2,37	-2,45	-2,45	-2,54	-1,99
3ya$^{\cdot}$ + e^{-} → **3ya**$^{-}$	-1,54	-0,03	-1,58	-0,04	-1,50	-3,68	-3,72	-3,68	-3,77	-0.76
3yb$^{\cdot}$ + e^{-} → **3yb**$^{-}$	-0,81	-0,06	-0,87	-0,02	-0,81	-3,02	-3,08	-3,09	-3,17	-1.35
3yc$^{\cdot}$ + e^{-} → **3yc**$^{-}$	0,29	-0,08	0,21	-0,03	0,28	-2,41	-2,49	-2,51	-2,59	-1.93
4CzIPN + e^{-} → **4CzIPN**$^{\cdot -}$										-1.21[(a)]

[(a)] Ref value from Uoyama, H., Goushi, K., Shizu, K. et al. Highly efficient organic light-emitting diodes from delayed fluorescence. Nature 492, 234–238 (2012).

Cartesian coordinates (mechanistic investiations)

Methyl acrylate

6	-1.301710000	-0.693140000	0.029850000
6	-0.036980000	0.094610000	-0.038090000
8	0.035250000	1.294820000	-0.138350000
8	1.037980000	-0.707600000	0.030960000
1	-1.205330000	-1.778760000	0.119110000
6	-2.482240000	-0.073910000	-0.017440000
1	-3.423580000	-0.628390000	0.031620000
1	-2.522490000	1.016450000	-0.106860000
6	2.300900000	-0.051940000	-0.022300000
1	2.406240000	0.658090000	0.812000000
1	2.411930000	0.502310000	-0.966720000
1	3.060330000	-0.840460000	0.049310000

Styrene

6	7.294507000	1.241613000	0.058468000
6	7.106888000	-0.141317000	0.058224000
6	5.817636000	-0.670578000	0.000493000
6	4.720506000	0.194041000	-0.057776000
6	4.911043000	1.573774000	-0.057174000
6	6.203467000	2.121636000	0.002549000
6	6.456965000	3.581564000	0.009171000
1	8.307951000	1.652325000	0.103848000
1	7.973047000	-0.807530000	0.103465000
1	5.665295000	-1.753483000	-0.000086000
1	3.706234000	-0.212563000	-0.105012000
1	4.040835000	2.233046000	-0.105765000
6	5.543982000	4.558115000	-0.002734000
1	7.517104000	3.861579000	0.028597000
1	4.468186000	4.359015000	-0.018445000
1	5.849266000	5.608113000	0.004488000

Methyl vinyl ether

6	4.684208000	-0.566391000	-0.067140000
1	5.732004000	-0.347477000	0.208189000
1	4.435652000	-1.581753000	0.270563000
1	4.588893000	-0.526054000	-1.168037000
8	3.784851000	0.315836000	0.564342000
6	3.884311000	1.617950000	0.204617000
6	3.251668000	2.597330000	0.852772000
1	4.512130000	1.817536000	-0.676357000
1	2.632425000	2.382354000	1.727589000
1	3.342817000	3.627360000	0.503961000

2a· (radical)

6	-7.694690000	1.870965000	-0.382346000
6	-6.351419000	1.708988000	-1.020945000
1	-2.568214000	-0.883553000	1.896734000
6	-3.332004000	-0.361759000	1.313191000
6	-4.681211000	-0.679622000	1.476047000
1	-4.978683000	-1.453493000	2.189761000
6	-5.657675000	-0.011659000	0.734292000
1	-6.713141000	-0.260848000	0.870781000
6	-5.299580000	0.985234000	-0.182305000
6	-3.942996000	1.299183000	-0.335432000
1	-3.648699000	2.081364000	-1.042990000
6	-2.965147000	0.631853000	0.403293000
1	-1.911074000	0.893274000	0.271382000
1	-5.962695000	2.704229000	-1.291432000
1	-6.470520000	1.167831000	-1.981360000
8	-8.551655000	0.806777000	-0.347392000
1	-7.825367000	2.531383000	0.480528000
1	-8.361949000	0.230321000	-1.098645000

2a⁻ (anion)

6	-7.526705000	2.104639000	-0.549105000
6	-6.345074000	1.438907000	-1.299641000
1	-2.687002000	-0.685118000	2.133437000
6	-3.413474000	-0.264863000	1.429415000
6	-4.647567000	-0.891330000	1.218113000
1	-4.891458000	-1.808020000	1.768337000
6	-5.572045000	-0.364231000	0.317437000
1	-6.550167000	-0.828977000	0.181431000
6	-5.301122000	0.819929000	-0.400567000
6	-4.059400000	1.438984000	-0.167205000
1	-3.826806000	2.364039000	-0.707849000
6	-3.127184000	0.909335000	0.727285000
1	-2.165746000	1.415726000	0.874709000
1	-5.857444000	2.205206000	-1.933065000
1	-6.736143000	0.656804000	-1.982300000
8	-8.156600000	1.029428000	0.269754000
1	-7.032799000	2.764182000	0.212591000
1	-9.019983000	0.955829000	-0.139614000

2d· (radical)

1	1.447826000	5.765521000	-1.294864000
8	2.150064000	5.179047000	0.532741000
6	1.444578000	4.914452000	-0.606286000
1	2.074135000	4.422933000	1.127728000
1	-0.553234000	4.393904000	0.080987000
6	0.275580000	3.988460000	-0.536370000
1	-0.124624000	3.793253000	-1.542651000
1	0.558575000	3.012629000	-0.098794000

2d⁻ (anion)

1	1.358922000	5.680173000	-1.138310000
8	1.827040000	5.127995000	0.807404000
6	1.589656000	4.706952000	-0.616339000
1	2.661700000	4.695452000	0.991254000
1	-0.598219000	4.499241000	-0.045580000
6	0.241529000	3.979887000	-0.592495000
1	-0.117926000	3.804446000	-1.629384000
1	0.310198000	2.976052000	-0.114059000

2y· (radical)

6	-6.452688000	0.537213000	-0.371629000
8	-5.286343000	0.794609000	0.276315000
1	-7.045244000	-0.334599000	-0.068403000
1	-6.948490000	1.430846000	-0.758704000

1	-4.942875000	-0.026019000	0.647410000

2y$^-$ (anion)

6	-6.395495000	0.328935000	-0.505369000
8	-5.477643000	0.635031000	0.656809000
1	-7.311351000	-0.117311000	-0.002375000
1	-6.815803000	1.348095000	-0.780213000
1	-4.675348000	0.207300000	0.356138000

I-TS

6	-8.572118000	0.228047000	0.526076000
6	-8.939786000	1.251254000	1.338668000
6	-8.371344000	1.354030000	2.690095000
8	-8.538759000	2.560908000	3.238832000
6	-9.459251000	-1.812026000	1.453177000
1	-11.342394000	-2.494727000	2.179240000
6	-11.008341000	0.813953000	5.627975000
6	-11.507499000	1.340310000	4.435681000
6	-10.463026000	-0.472050000	5.638031000
6	-11.457703000	0.584320000	3.263110000
6	-10.416578000	-1.223739000	4.464259000
6	-10.905532000	-0.701798000	3.258266000
6	-10.844092000	-1.522735000	1.989162000
8	-8.433736000	-2.069517000	2.293370000
1	-11.048423000	1.402979000	6.548988000
1	-11.936859000	2.346063000	4.415581000
1	-10.072798000	-0.894953000	6.568252000
1	-11.851651000	1.002124000	2.332220000
1	-9.986364000	-2.228881000	4.477229000
1	-8.256545000	-1.278718000	2.849599000
1	-11.427609000	-1.033660000	1.192604000
1	-9.426758000	-2.442675000	0.553801000
1	-7.691692000	-0.372314000	0.761279000
1	-8.977612000	0.150620000	-0.486718000
1	-9.689564000	1.991942000	1.051967000
6	-8.051175000	2.714659000	4.569268000
8	-7.812095000	0.442880000	3.281106000
1	-6.959501000	2.579592000	4.599968000
1	-8.520436000	1.977495000	5.236075000
1	-8.317150000	3.734426000	4.874658000

3a$^·$ (radical)

6	-8.930885000	-0.125078000	0.764829000
6	-9.051543000	1.063848000	1.658210000
6	-8.284025000	1.196182000	2.883213000
8	-8.503779000	2.358230000	3.511963000
6	-9.339819000	-1.504980000	1.344208000
1	-10.989833000	-2.567098000	2.191767000
6	-11.156037000	1.004767000	5.430568000
6	-11.783557000	1.362793000	4.237134000
6	-10.432634000	-0.188917000	5.497061000
6	-11.677153000	0.535345000	3.118177000
6	-10.327437000	-1.012827000	4.376591000
6	-10.937639000	-0.655002000	3.165217000
6	-10.764583000	-1.518912000	1.938337000
8	-8.392735000	-2.020636000	2.239776000
1	-11.236033000	1.650882000	6.309658000
1	-12.358692000	2.291020000	4.175525000
1	-9.944601000	-0.482148000	6.431365000
1	-12.172503000	0.821334000	2.184608000
1	-9.749587000	-1.938303000	4.425182000
1	-7.977757000	-1.282025000	2.722780000
1	-11.480864000	-1.211758000	1.158231000
1	-9.356636000	-2.191944000	0.478662000
1	-7.877010000	-0.234490000	0.446358000
1	-9.525526000	0.056277000	-0.143243000
1	-9.704194000	1.899163000	1.397075000
6	-7.827697000	2.528821000	4.753366000
8	-7.514934000	0.350527000	3.321140000
1	-6.736881000	2.501981000	4.609917000
1	-8.112454000	1.732768000	5.456755000
1	-8.139384000	3.507997000	5.137348000

3a$^-$ (anion)

6	-8.798595000	-0.221102000	0.654872000
6	-8.883276000	1.075038000	1.420434000
6	-8.307755000	1.218830000	2.661166000
8	-8.458556000	2.486795000	3.234224000
6	-9.289109000	-1.495686000	1.377323000
1	-11.102581000	-2.379474000	2.128278000
6	-11.182787000	0.827041000	5.663546000
6	-11.706356000	1.345762000	4.475524000
6	-10.501815000	-0.389850000	5.633932000
6	-11.551610000	0.646677000	3.280303000
6	-10.347022000	-1.084124000	4.432197000
6	-10.872648000	-0.578339000	3.235901000
6	-10.726652000	-1.356689000	1.947007000
8	-8.383650000	-1.948498000	2.347167000
1	-11.293942000	1.377794000	6.603517000
1	-12.224558000	2.310144000	4.477889000
1	-10.070039000	-0.798409000	6.553599000
1	-11.934698000	1.071114000	2.348174000
1	-9.786254000	-2.020239000	4.398765000
1	-8.030987000	-1.125479000	2.799383000
1	-11.371957000	-0.908662000	1.172214000
1	-9.355232000	-2.296213000	0.609030000
1	-7.763078000	-0.460070000	0.326852000
1	-9.390305000	-0.122488000	-0.274461000
1	-9.411786000	1.929990000	0.991240000
6	-8.043523000	2.585413000	4.568896000
8	-7.690094000	0.353158000	3.349598000
1	-6.967802000	2.366399000	4.692631000
1	-8.597676000	1.894557000	5.228009000
1	-8.242071000	3.624425000	4.884571000

II-TS

6	-7.041237000	-7.391612000	-3.827493000
6	-5.536637000	-7.392898000	-3.681840000
1	-3.010118000	-11.535515000	-6.110904000
6	-3.516756000	-10.699789000	-5.620103000
6	-4.309166000	-10.921748000	-4.493915000
1	-4.425163000	-11.933512000	-4.095313000

6	-4.948416000	-9.851784000	-3.863673000
1	-5.541745000	-10.031198000	-2.961476000
6	-4.826265000	-8.545577000	-4.360603000
6	-4.024620000	-8.337707000	-5.490011000
1	-3.911538000	-7.323621000	-5.885482000
6	-3.370983000	-9.401200000	-6.112764000
1	-2.745098000	-9.215356000	-6.990636000
1	-5.288354000	-7.418210000	-2.601324000
1	-5.151792000	-6.435119000	-4.065296000
8	-7.720425000	-8.549717000	-3.593721000
1	-7.564163000	-6.532491000	-3.389213000
1	-7.320840000	-9.259693000	-4.118950000
1	-5.754219000	-10.199517000	-7.730119000
1	-6.464087000	-12.576394000	-7.733018000
6	-6.732756000	-10.475506000	-7.328063000
1	-6.118308000	-7.920898000	-7.295563000
6	-7.130248000	-11.811010000	-7.324231000
6	-7.073619000	-8.080747000	-6.787208000
6	-7.560050000	-9.466336000	-6.800053000
6	-8.371404000	-12.172767000	-6.796353000
1	-8.685794000	-13.220207000	-6.790975000
1	-7.198912000	-6.040617000	-6.189276000
6	-7.627156000	-7.043389000	-6.102612000
6	-8.812509000	-9.847186000	-6.277058000
6	-9.209833000	-11.182317000	-6.275339000
1	-8.633781000	-7.103808000	-5.683326000
1	-9.479354000	-9.090825000	-5.857782000
1	-10.185835000	-11.454009000	-5.862627000

3b· (radical)

6	-7.084716000	-7.434914000	-4.165032000
6	-5.601217000	-7.281643000	-3.770595000
1	-2.483385000	-11.094792000	-6.030742000
6	-3.094723000	-10.320538000	-5.558442000
6	-3.966753000	-10.649289000	-4.518540000
1	-4.039026000	-11.683747000	-4.170452000
6	-4.743853000	-9.660077000	-3.914483000
1	-5.413036000	-9.919574000	-3.089214000
6	-4.682926000	-8.329529000	-4.354687000
6	-3.784326000	-8.008919000	-5.380516000
1	-3.714038000	-6.972561000	-5.726752000
6	-2.996505000	-8.992883000	-5.979591000
1	-2.303714000	-8.722262000	-6.781863000
1	-5.560223000	-7.320209000	-2.670076000
1	-5.259378000	-6.278863000	-4.073827000
8	-7.658907000	-8.594660000	-3.603950000
1	-7.621085000	-6.590887000	-3.699586000
1	-7.359201000	-9.354566000	-4.120461000
1	-5.994811000	-10.712842000	-7.731992000
1	-7.196884000	-12.853595000	-8.083276000
6	-7.010218000	-10.842543000	-7.345448000
1	-5.894851000	-8.512683000	-6.929528000
6	-7.682466000	-12.039597000	-7.536992000
6	-6.885743000	-8.549995000	-6.471578000
6	-7.611408000	-9.759029000	-6.637567000
6	-8.979891000	-12.213187000	-7.031620000
1	-9.508550000	-13.158308000	-7.182430000
1	-6.849854000	-6.449992000	-6.076040000
6	-7.345786000	-7.355962000	-5.690686000
6	-8.928344000	-9.962088000	-6.129599000
6	-9.590850000	-11.167119000	-6.328243000
1	-8.430128000	-7.208896000	-5.826370000
1	-9.414266000	-9.168457000	-5.559101000
1	-10.600107000	-11.298086000	-5.927030000

3b⁻ (anion)

6	-6.967115000	-7.714170000	-4.129080000
6	-5.557570000	-7.200030000	-3.751917000
1	-1.624586000	-10.412143000	-5.652685000
6	-2.406311000	-9.753525000	-5.261449000
6	-3.191060000	-10.156669000	-4.177219000
1	-3.028354000	-11.137291000	-3.718721000
6	-4.192388000	-9.322487000	-3.684457000
1	-4.831461000	-9.645917000	-2.859839000
6	-4.435242000	-8.068372000	-4.265096000
6	-3.640287000	-7.674846000	-5.347816000
1	-3.824908000	-6.704821000	-5.820844000
6	-2.634608000	-8.507266000	-5.845051000
1	-2.032412000	-8.182343000	-6.699566000
1	-5.504235000	-7.149526000	-2.650665000
1	-5.438150000	-6.172029000	-4.135853000
8	-7.219505000	-8.956600000	-3.533478000
1	-7.684006000	-6.975893000	-3.715742000
1	-7.102692000	-9.569595000	-4.311160000
1	-6.476314000	-11.492812000	-7.589335000
1	-8.153973000	-13.126448000	-8.316270000
6	-7.531184000	-11.325897000	-7.340709000
1	-5.847487000	-9.417394000	-6.525410000
6	-8.482412000	-12.244885000	-7.749453000
6	-6.873980000	-9.217045000	-6.196783000
6	-7.865443000	-10.132916000	-6.601188000
6	-9.849878000	-12.074968000	-7.465123000
1	-10.597077000	-12.805596000	-7.790068000
1	-6.553549000	-7.063252000	-6.168744000
6	-7.172799000	-7.836853000	-5.672749000
6	-9.271015000	-9.999455000	-6.310992000
6	-10.208466000	-10.933284000	-6.733995000
1	-8.220544000	-7.566536000	-5.893242000
1	-9.609183000	-9.151347000	-5.708022000
1	-11.262977000	-10.770080000	-6.473587000

III-TS

6	-8.794154000	0.388357000	0.616080000
6	-8.932689000	1.262747000	1.646967000
8	-8.074392000	1.186822000	2.711036000
6	-8.256319000	2.168834000	3.711621000
6	-9.288750000	-1.633124000	1.579134000
1	-10.942463000	-2.639983000	2.486032000
6	-11.534563000	1.114710000	5.376018000
6	-12.141204000	1.299277000	4.131982000
6	-10.648117000	0.050427000	5.555485000
6	-11.861008000	0.424926000	3.079672000

6	-10.373501000	-0.822667000	4.501452000
6	-10.976311000	-0.648021000	3.246469000
6	-10.702921000	-1.621406000	2.119417000
8	-8.253873000	-1.683023000	2.476079000
1	-11.755309000	1.794456000	6.203951000
1	-12.841532000	2.126027000	3.980394000
1	-10.172511000	-0.107232000	6.528031000
1	-12.342773000	0.573783000	2.108118000
1	-9.688764000	-1.661871000	4.650317000
1	-8.179731000	-0.815811000	2.909583000
1	-11.391521000	-1.426631000	1.281544000
1	-9.128607000	-2.327377000	0.742288000
1	-7.831430000	-0.099457000	0.449084000
1	-9.488260000	0.453207000	-0.224948000
1	-9.802257000	1.914660000	1.780898000
1	-7.573709000	1.923394000	4.536499000
1	-9.292579000	2.162642000	4.089141000
1	-8.009277000	3.173936000	3.326444000

3c· (radical)

6	-8.870465000	-0.034883000	0.776890000
6	-8.905217000	1.177895000	1.644012000
8	-8.121634000	1.102098000	2.759706000
6	-8.300574000	2.139230000	3.704731000
6	-9.199559000	-1.367408000	1.489381000
1	-10.782223000	-2.502829000	2.366575000
6	-11.578503000	1.092841000	5.427129000
6	-12.187533000	1.312172000	4.190231000
6	-10.660830000	0.048399000	5.563866000
6	-11.874962000	0.494097000	3.102121000
6	-10.354319000	-0.768645000	4.474660000
6	-10.953960000	-0.554590000	3.223991000
6	-10.633388000	-1.456898000	2.052180000
8	-8.231938000	-1.669801000	2.470208000
1	-11.822775000	1.728469000	6.283055000
1	-12.914234000	2.121318000	4.071573000
1	-10.185106000	-0.137402000	6.531464000
1	-12.360375000	0.669761000	2.136518000
1	-9.643343000	-1.590730000	4.585915000
1	-8.007534000	-0.836807000	2.911069000
1	-11.345555000	-1.266311000	1.232407000
1	-9.120673000	-2.161496000	0.725701000
1	-7.859353000	-0.154867000	0.345749000
1	-9.565636000	0.113755000	-0.064430000
1	-9.786139000	1.825083000	1.717373000
1	-7.641039000	1.924540000	4.556234000
1	-9.345978000	2.170540000	4.054353000
1	-8.025683000	3.114072000	3.266127000

3c⁻ (anion)

6	-8.857431000	0.052883000	0.812036000
6	-8.854054000	1.318516000	1.662318000
8	-8.117232000	0.919745000	2.910903000
6	-7.883455000	1.994587000	3.741172000
6	-9.206844000	-1.302754000	1.473528000
1	-10.789825000	-2.446752000	2.351499000
6	-11.816096000	1.095797000	5.383040000
6	-12.552422000	1.114742000	4.195859000
6	-10.698564000	0.263314000	5.476288000
6	-12.158261000	0.322202000	3.117985000
6	-10.314318000	-0.536393000	4.399582000
6	-11.028773000	-0.505941000	3.190919000
6	-10.646398000	-1.398718000	2.030014000
8	-8.250362000	-1.643514000	2.462432000
1	-12.111667000	1.725290000	6.228798000
1	-13.431221000	1.761734000	4.103582000
1	-10.112053000	0.239321000	6.400897000
1	-12.725267000	0.361202000	2.181848000
1	-9.440297000	-1.184445000	4.470145000
1	-7.988601000	-0.771499000	2.832968000
1	-11.349896000	-1.223785000	1.197494000
1	-9.151381000	-2.096823000	0.695857000
1	-7.865352000	-0.113326000	0.337231000
1	-9.567188000	0.219269000	-0.022533000
1	-9.904543000	1.462684000	2.018098000
1	-7.184791000	1.694713000	4.548714000
1	-8.815967000	2.363477000	4.228089000
1	-7.456270000	2.846076000	3.170026000

IV-TS

6	-1.066229000	1.207890000	-2.706500000
6	-1.166468000	0.338839000	-1.518769000
8	-1.904983000	0.515406000	-0.574003000
8	-0.332574000	-0.717867000	-1.601576000
1	-0.399171000	0.886278000	-3.510494000
6	-1.820718000	2.329097000	-2.785383000
1	-1.721501000	3.023660000	-3.622534000
1	-2.383628000	2.654720000	-1.906204000
6	-0.372078000	-1.618804000	-0.502701000
1	-1.377667000	-2.052492000	-0.387974000
1	-0.108982000	-1.105823000	0.435041000
1	0.358736000	-2.407234000	-0.723661000
1	-5.141972000	-0.062455000	-3.487574000
1	-3.282171000	0.979686000	-5.391236000
6	-4.187020000	0.385805000	-3.151680000
1	-4.197469000	0.462816000	-2.055132000
8	-3.728457000	1.790054000	-5.112678000
6	-3.953860000	1.722247000	-3.772654000
1	-3.373397000	-0.312787000	-3.419968000
1	-4.511052000	2.595474000	-3.416810000

3da· (radical)

6	-1.323125000	1.061398000	-2.777736000
6	-1.242077000	0.222973000	-1.588956000
8	-1.945036000	0.349277000	-0.604969000
8	-0.295939000	-0.732982000	-1.697522000
1	-0.656596000	0.829284000	-3.613431000
6	-2.317476000	2.161655000	-2.862022000
1	-1.858517000	3.036343000	-3.351775000
1	-2.631914000	2.441810000	-1.844673000
6	-0.165483000	-1.595869000	-0.574528000
1	-1.102968000	-2.143554000	-0.391174000

1	0.083483000	-1.024039000	0.332617000
1	0.643165000	-2.296761000	-0.817033000
1	-5.268451000	0.444091000	-3.670184000
1	-2.829019000	0.676495000	-5.090226000
6	-4.353786000	0.627745000	-3.086447000
1	-4.626173000	0.825815000	-2.039109000
8	-3.239395000	1.548135000	-5.041555000
6	-3.574449000	1.791560000	-3.689185000
1	-3.747953000	-0.294830000	-3.097751000
1	-4.218948000	2.685963000	-3.706831000

3da$^-$ (anion)

6	-1.279468000	1.098329000	-2.810950000
6	-1.282008000	0.156124000	-1.780372000
8	-2.155285000	-0.096181000	-0.933100000
8	-0.095716000	-0.614151000	-1.739392000
1	-0.339649000	1.245291000	-3.351480000
6	-2.362402000	2.146590000	-2.907885000
1	-1.949764000	3.047445000	-3.399239000
1	-2.721149000	2.458767000	-1.907587000
6	-0.092302000	-1.618944000	-0.768198000
1	-0.904340000	-2.355354000	-0.917127000
1	-0.214198000	-1.219582000	0.255602000
1	0.880833000	-2.135209000	-0.843099000
1	-5.345059000	0.414613000	-3.543295000
1	-2.307258000	0.493079000	-4.432096000
6	-4.576613000	0.871096000	-2.895632000
1	-5.075645000	1.522985000	-2.156324000
8	-3.117047000	0.893688000	-4.829179000
6	-3.583733000	1.668682000	-3.744761000
1	-4.040599000	0.089825000	-2.334773000
1	-4.109253000	2.547416000	-4.173603000

V-TS

6	-7.364673000	3.871170000	-0.711725000
6	-5.931254000	4.189027000	-0.767139000
6	-5.245870000	4.510721000	0.420166000
1	-5.794871000	4.502904000	1.367064000
6	-3.890308000	4.834488000	0.408759000
1	-3.383264000	5.080110000	1.346539000
6	-3.180442000	4.846571000	-0.794100000
1	-2.116654000	5.099342000	-0.806268000
6	-3.844403000	4.531000000	-1.982807000
1	-3.298827000	4.536396000	-2.931125000
6	-5.199601000	4.205699000	-1.972507000
1	-5.698679000	3.969538000	-2.915143000
6	-8.156716000	3.579898000	-1.777545000
1	-7.827357000	3.957463000	0.277970000
1	-7.740229000	3.348250000	-2.760231000
1	-9.206001000	3.314152000	-1.621852000
1	-8.076610000	6.535902000	-0.911738000
6	-8.904064000	6.579062000	-1.642941000
1	-9.821865000	6.259929000	-1.126918000
1	-6.775767000	6.183664000	-2.907634000
1	-9.029841000	7.634807000	-1.951216000
6	-8.619448000	5.691156000	-2.809739000
8	-7.474912000	5.913724000	-3.519294000
1	-9.441705000	5.395090000	-3.471136000

3db$^{\cdot}$ (radical)

6	-7.268308000	4.283622000	-0.752105000
6	-5.853381000	4.386049000	-0.804517000
6	-5.112477000	4.573418000	0.400555000
1	-5.658377000	4.638120000	1.346800000
6	-3.729551000	4.670254000	0.390259000
1	-3.188708000	4.813450000	1.330296000
6	-3.022070000	4.585161000	-0.818157000
1	-1.931413000	4.661315000	-0.825012000
6	-3.725310000	4.405285000	-2.016332000
1	-3.179966000	4.344046000	-2.962656000
6	-5.110998000	4.305918000	-2.020129000
1	-5.640819000	4.192584000	-2.967689000
6	-8.174016000	4.097805000	-1.930368000
1	-7.730690000	4.379229000	0.236308000
1	-7.700404000	3.455077000	-2.690122000
1	-9.095528000	3.587251000	-1.604661000
1	-8.650883000	6.677649000	-0.852184000
6	-9.306430000	6.379130000	-1.687626000
1	-10.210441000	5.915647000	-1.261126000
1	-6.849546000	6.300765000	-2.523705000
1	-9.600818000	7.288491000	-2.232431000
6	-8.576620000	5.420805000	-2.625221000
8	-7.461125000	6.047431000	-3.227538000
1	-9.245479000	5.161560000	-3.463200000

3db$^-$ (anion)

6	-7.165217000	4.629759000	-0.737938000
6	-5.765463000	4.532718000	-0.801298000
6	-4.940984000	4.665210000	0.379091000
1	-5.444674000	4.841957000	1.337374000
6	-3.561166000	4.564869000	0.345411000
1	-3.002892000	4.670929000	1.285679000
6	-2.860550000	4.325884000	-0.851484000
1	-1.769069000	4.248932000	-0.871257000
6	-3.628551000	4.206584000	-2.020192000
1	-3.122893000	4.037716000	-2.980736000
6	-5.012916000	4.309465000	-2.014649000
1	-5.549450000	4.261523000	-2.966477000
6	-8.094096000	4.278732000	-1.871143000
1	-7.607829000	4.756068000	0.258088000
1	-7.576096000	3.636230000	-2.607185000
1	-8.967331000	3.694143000	-1.516672000
1	-9.381317000	6.461618000	-0.830135000
6	-9.737679000	6.230252000	-1.847840000
1	-10.638902000	5.597058000	-1.767328000
1	-6.998509000	6.269378000	-2.047705000
1	-10.011245000	7.177155000	-2.342000000
6	-8.621489000	5.527785000	-2.625596000
8	-7.548861000	6.415361000	-2.848512000
1	-9.016182000	5.230736000	-3.618058000

VI-TS

6	3.545188000	1.387990000	1.461732000
1	4.473515000	0.902153000	1.113041000
1	3.648302000	1.634398000	2.527447000
1	2.704340000	0.680127000	1.336968000
8	3.309544000	2.593357000	0.769508000
6	3.067745000	2.468818000	-0.577084000
6	3.162884000	3.566560000	-1.373054000
1	2.611299000	1.521345000	-0.892001000
1	3.774429000	4.412954000	-1.053994000
1	2.940847000	3.464203000	-2.437914000
1	2.265579000	4.380688000	1.072847000
8	2.023261000	5.205877000	0.622334000
1	0.483993000	3.036996000	-0.048838000
6	1.463327000	4.878462000	-0.581930000
6	0.258893000	3.987634000	-0.563596000
1	-0.584669000	4.462324000	-0.027872000
1	-0.070163000	3.751031000	-1.587434000
1	1.445955000	5.741653000	-1.259992000

3dc$^{\cdot}$ (radical)

6	3.481427000	1.398110000	1.459452000
1	4.390932000	0.887378000	1.099725000
1	3.590093000	1.624034000	2.528819000
1	2.613271000	0.729197000	1.315917000
8	3.293919000	2.623087000	0.783163000
6	3.094835000	2.534579000	-0.565844000
6	2.849438000	3.839000000	-1.246450000
1	2.643747000	1.596736000	-0.919652000
1	3.753694000	4.471207000	-1.189581000
1	2.651422000	3.642071000	-2.312251000
1	2.399097000	4.407111000	1.131960000
8	2.036674000	5.155190000	0.637290000
1	0.466964000	3.008226000	0.069479000
6	1.688043000	4.662604000	-0.639554000
6	0.373435000	3.885002000	-0.592229000
1	-0.424712000	4.527175000	-0.190790000
1	0.073926000	3.532326000	-1.592804000
1	1.548066000	5.553536000	-1.276479000

3dc^{-} (anion)

6	3.888337000	1.719399000	1.471361000
1	4.703930000	2.412217000	1.161671000
1	3.870823000	1.705809000	2.582115000
1	4.167918000	0.715418000	1.092620000
8	2.643453000	2.099039000	0.999565000
6	2.565685000	1.966057000	-0.507731000
6	2.720702000	3.387689000	-1.065889000
1	1.497755000	1.671938000	-0.648379000
1	3.757523000	3.752249000	-0.898659000
1	2.603883000	3.331149000	-2.167543000
1	2.130139000	3.719339000	1.160875000
8	1.896052000	4.629710000	0.865897000
1	-0.008990000	3.297724000	-0.588243000
6	1.786537000	4.507297000	-0.541193000
6	0.322362000	4.289238000	-0.936550000
1	-0.315308000	5.057895000	-0.467944000

1	0.187685000	4.333564000	-2.032376000
1	2.105785000	5.480840000	-0.979427000

VII-TS

8	-7.833402000	-1.048874000	-0.194451000
6	-7.421295000	-0.048953000	0.346791000
6	-8.159371000	0.723161000	1.364495000
6	-7.682956000	1.859061000	1.934048000
1	-9.117137000	0.286071000	1.659301000
1	-6.790506000	2.346027000	1.535045000
1	-8.299251000	2.425897000	2.636701000
8	-6.196437000	0.465253000	0.085531000
6	-5.443452000	-0.222159000	-0.906042000
1	-5.261570000	-1.266161000	-0.607866000
1	-4.492701000	0.317955000	-1.000318000
1	-5.975981000	-0.226656000	-1.869295000
1	-6.179644000	1.851151000	4.428343000
6	-6.322937000	1.025397000	3.724627000
8	-7.071803000	0.020849000	4.224074000
1	-5.511369000	0.777468000	3.028788000
1	-7.215879000	-0.636696000	3.529558000

3ya$^{\cdot}$ (radical)

8	-7.844898000	-0.979993000	-0.291910000
6	-7.383366000	-0.071330000	0.368079000
6	-8.085292000	0.604683000	1.451225000
6	-7.468761000	1.670053000	2.290993000
1	-9.099907000	0.241257000	1.635211000
1	-6.901438000	2.362566000	1.646101000
1	-8.254302000	2.237475000	2.813183000
8	-6.137847000	0.420873000	0.167491000
6	-5.401433000	-0.188401000	-0.886453000
1	-5.263162000	-1.263816000	-0.696638000
1	-4.430296000	0.321364000	-0.918025000
1	-5.925652000	-0.071037000	-1.847208000
1	-6.061096000	1.939029000	3.914612000
6	-6.495775000	1.102667000	3.344940000
8	-7.135924000	0.268307000	4.279378000
1	-5.665711000	0.586139000	2.826685000
1	-7.420829000	-0.531046000	3.821666000

3ya^{-} (anion)

8	-7.872641000	-0.942333000	-0.351919000
6	-7.460924000	-0.092055000	0.447398000
6	-8.086506000	0.521354000	1.537858000
6	-7.470675000	1.660945000	2.318002000
1	-9.156434000	0.316232000	1.640556000
1	-6.994535000	2.424158000	1.669370000
1	-8.270401000	2.175460000	2.883859000
8	-6.122164000	0.365049000	0.276344000
6	-5.434295000	-0.243853000	-0.776328000
1	-5.346518000	-1.338475000	-0.645840000
1	-4.423717000	0.199967000	-0.801809000
1	-5.927923000	-0.082676000	-1.752539000
1	-6.192054000	1.941799000	4.088907000
6	-6.416703000	1.164335000	3.330722000

8	-6.891261000	0.017373000	3.994268000
1	-5.475893000	0.951190000	2.781899000
1	-7.433046000	-0.389680000	3.278581000

VIII-TS

1	-1.241261000	1.392503000	-4.235510000
6	-0.666096000	0.807804000	-4.961478000
8	-1.062891000	-0.488155000	-5.023690000
1	0.407229000	1.023180000	-5.052316000
1	-0.579898000	-0.935241000	-5.732227000
6	-1.299906000	1.612061000	-7.122619000
6	-0.866143000	-2.555462000	-9.777013000
6	-2.020879000	-3.124567000	-9.235391000
6	-0.447316000	-1.292784000	-9.362208000
6	-2.748657000	-2.415764000	-8.275313000
6	-1.171400000	-0.561537000	-8.400604000
6	-0.687874000	0.765610000	-7.993417000
6	-2.332122000	-1.152380000	-7.861112000
1	-2.326042000	1.445239000	-6.785481000
1	-0.286033000	-3.100387000	-10.527461000
1	-2.351093000	-4.116319000	-9.556715000
1	-0.886642000	2.608001000	-6.943090000
1	0.458116000	-0.852489000	-9.791763000
1	-3.650755000	-2.855261000	-7.839798000
1	-2.902529000	-0.627016000	-7.092323000
1	0.284150000	1.057572000	-8.407803000

3yb· (radical)

1	-1.191426000	1.664519000	-4.564271000
6	-0.738562000	1.000912000	-5.318477000
8	-1.129036000	-0.308750000	-4.984267000
1	0.360414000	1.128273000	-5.246445000
1	-0.712515000	-0.914521000	-5.609936000
6	-1.208921000	1.431299000	-6.720356000
6	-0.888619000	-2.515820000	-9.846172000
6	-2.050964000	-3.098545000	-9.319480000
6	-0.423973000	-1.307244000	-9.350568000
6	-2.738201000	-2.450351000	-8.284884000
6	-1.106223000	-0.623968000	-8.299888000
6	-0.603572000	0.614119000	-7.820436000
6	-2.284623000	-1.238016000	-7.780420000
1	-2.309931000	1.373607000	-6.747872000
1	-0.344806000	-3.016320000	-10.652624000
1	-2.416133000	-4.051549000	-9.711706000
1	-0.938105000	2.491357000	-6.859465000
1	0.482189000	-0.856854000	-9.767218000
1	-3.641576000	-2.902675000	-7.865387000
1	-2.819282000	-0.763969000	-6.955362000
1	0.325824000	0.979107000	-8.272094000

3yb⁻ (anion)

1	-1.418446000	1.603881000	-4.499034000
6	-0.731481000	1.142718000	-5.236392000
8	-0.643848000	-0.231263000	-4.962385000
1	0.257882000	1.641108000	-5.106935000
1	-0.387182000	-0.594407000	-5.837414000
6	-1.218838000	1.369913000	-6.683874000
6	-0.941921000	-2.549625000	-9.870311000
6	-2.163001000	-3.102678000	-9.440137000
6	-0.413541000	-1.404959000	-9.300293000
6	-2.818261000	-2.444462000	-8.387322000
6	-1.069088000	-0.689551000	-8.226281000
6	-0.518590000	0.474556000	-7.672610000
6	-2.308711000	-1.297810000	-7.794674000
1	-2.310221000	1.191710000	-6.711559000
1	-0.387737000	-3.034124000	-10.685967000
1	-2.574720000	-4.008443000	-9.896032000
1	-1.079003000	2.442399000	-6.931645000
1	0.537203000	-1.005733000	-9.674632000
1	-3.763448000	-2.852672000	-8.003782000
1	-2.842037000	-0.861871000	-6.944935000
1	0.416946000	0.845922000	-8.111115000

IX-TS

6	3.526851000	1.393752000	1.460938000
1	4.432485000	0.879651000	1.093917000
1	3.659629000	1.638815000	2.523597000
1	2.662315000	0.712006000	1.354983000
8	3.314140000	2.605218000	0.770956000
6	3.046124000	2.486779000	-0.570921000
6	3.135542000	3.585103000	-1.367280000
1	2.569294000	1.546907000	-0.878699000
1	3.758007000	4.427656000	-1.057706000
1	2.893532000	3.487612000	-2.428027000
8	1.976892000	5.175096000	0.672025000
6	1.445394000	4.888982000	-0.548850000
1	0.625860000	4.154727000	-0.589101000
1	1.325790000	5.781334000	-1.176083000
1	2.247596000	4.341050000	1.087943000

3yc· (radical)

6	3.493266000	1.404360000	1.467576000
1	4.371536000	0.856236000	1.086178000
1	3.641423000	1.633587000	2.531474000
1	2.596114000	0.768794000	1.354236000
8	3.334301000	2.631348000	0.786902000
6	3.089438000	2.540437000	-0.554505000
6	2.857455000	3.849490000	-1.231804000
1	2.574497000	1.625004000	-0.882479000
1	3.761584000	4.479861000	-1.153083000
1	2.675995000	3.661522000	-2.302422000
8	1.949014000	5.099035000	0.666405000
6	1.681159000	4.645157000	-0.635945000
1	0.764792000	4.017934000	-0.672969000
1	1.488193000	5.535250000	-1.258424000
1	2.340700000	4.356685000	1.146530000

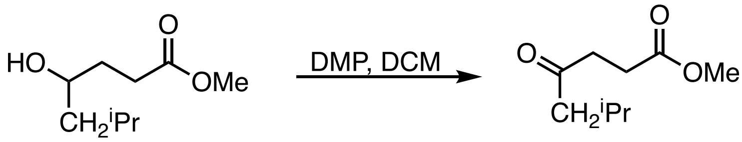
3yc⁻ (anion)

6	3.569457000	1.480159000	1.498716000
1	4.462738000	1.043285000	1.002671000
1	3.809719000	1.729475000	2.553847000

1	2.798435000	0.670652000	1.521743000
8	3.146685000	2.609954000	0.838524000
6	3.061198000	2.389312000	-0.654580000
6	2.897262000	3.803546000	-1.214659000
1	2.044063000	1.912483000	-0.777737000
1	3.824531000	4.392647000	-1.046994000
1	2.778857000	3.717954000	-2.314537000
8	1.812115000	4.886411000	0.704234000
6	1.723065000	4.645098000	-0.683855000
1	0.775450000	4.111328000	-0.936578000
1	1.669702000	5.633372000	-1.194937000
1	2.246189000	4.079024000	1.051813000

9 Derivatization of products

9.1 Synthesis of methyl 6-methyl-4-oxoheptanoate (77)



15 77

To a 5 mL round-bottom-flask charged with a stir bar, were added methyl 4-hydroxy-6-methylheptanoate **15** (1 eq, 0.49 mmol, 85 mg), DCM (3 mL), and 1,1,1-Tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3-(1H)-one (DMP) (1.2 eq, 0.59 mmol, 249 mg). The mixture was stirred at room temperature for 2 h. The crude was directly purified by silica gel chromatography (9:1 hexane/ ethyl acetate). Compound **77** was isolated as a pale-yellow oil in quantitative yield (84 mg, 0.49 mmol).

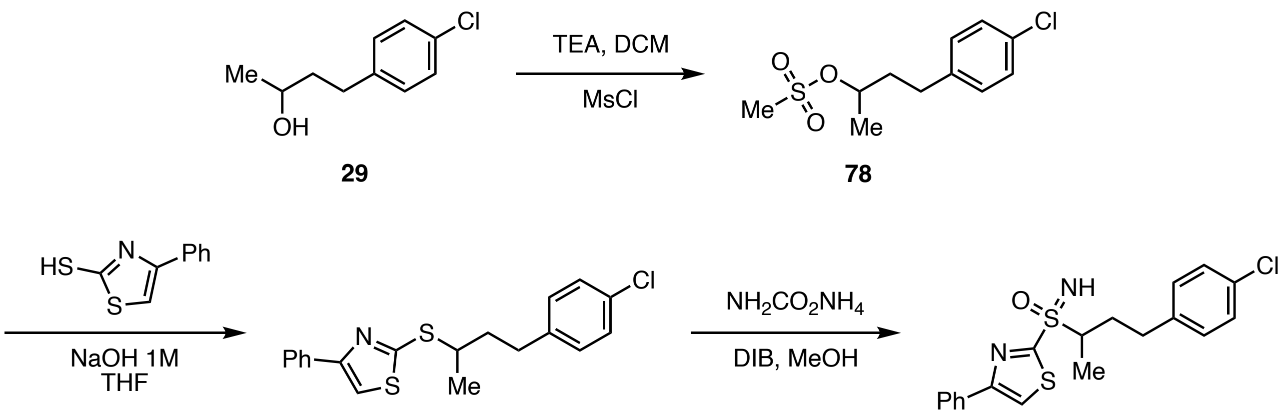
^{1}H NMR (400 MHz, $CDCl_3$) δ 3.69 (s, 3H), 2.76 – 2.68 (m, 2H), 2.63 – 2.55 (m, 2H), 2.34 (d, *J* = 6.9 Hz, 2H), 2.23 – 2.11 (m, 1H), 0.94 (m, 6H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 208.7, 173.3, 51.7, 37.6, 27.6, 24.7, 22.5.

IR (film)/cm^{-1} 2955, 2927, 1739, 1714, 1437, 1364, 1207, 1168, 1074, 988.

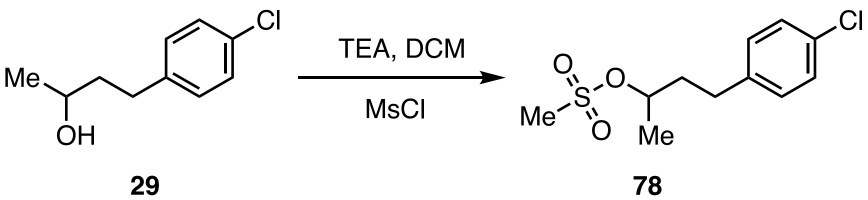
HRMS calcd for $C_9H_{16}NaO_3$ $[M+Na]^+$ 195.0997; found 195.1001.

9.2 Synthesis of (4-(4-chlorophenyl)butan-2-yl)(imino)(4-phenylthiazol-2-yl)-λ6-sulfanone (80)



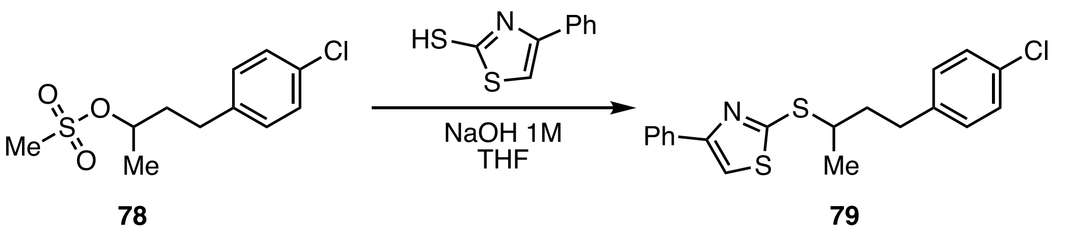
29 78 79 80

9.2.1 Synthesis of 4-(4-chlorophenyl)butan-2-yl methanesulfonate (78)



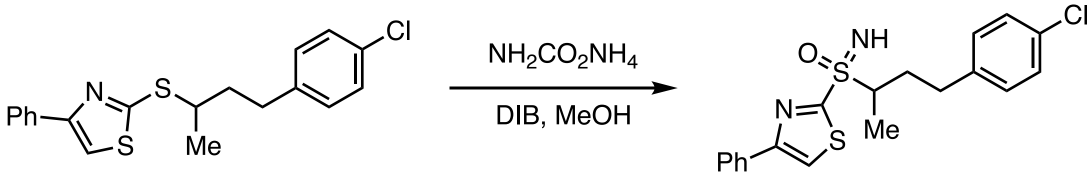
To a 5 mL round-bottom-flask charged with a stir bar, were added 4-(4-chlorophenyl)butan-2-ol **29** (1eq, 0.38 mmol, 70 mg), DCM (1 mL), and triethylamine (1.3 eq, 0.49 mmol, 50 mg) at 0°C. After stirring for 15 minutes, methanesulfonyl chloride (2 eq, 0.76 mmol, 87 mg) was added dropwise and the mixture was stirred at room temperature overnight. The residue was diluted with 10 mL of DCM and washed 3 times with NH_4Cl (0.1 M x 10 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (9:1 hexane/ ethyl acetate). Compound **78** was isolated as a pale-yellow oil in 95% yield (95 mg, 0.36 mmol).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.17 – 7.14 (m, 2H), 4.85 (m, 1H), 3.02 (s, 3H), 2.73 (m, 2H), 2.10 – 2.00 (m, 1H), 1.91 (m, 1H), 1.48 (d, *J* = 6.3 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 139.2, 132.0, 129.7, 128.7, 79.1, 38.8, 38.2, 30.8, 21.2.
IR (film)/cm^{-1} 2923, 2852, 1491, 1454, 1326, 1170, 1090, 970, 897, 809.
HRMS calcd for $C_{11}H_{15}ClNaO_3$ $[M+Na]^+$ 285.0328; found 285.0311.

9.2.2 Synthesis of 2-((4-(4-chlorophenyl)butan-2-yl)thio)-4-phenylthiazole (79)



To a 5 mL round-bottom-flask charged with a stir bar, were added 4-phenylthiazole-2-thiol (1eq, 0.32 mmol, 63 mg), THF (2 mL), and a solution of sodium hydroxide (1 M, 0.36 mmol, 360 μL) at 0°C. After stirring for 20 minutes, 4-(4-chlorophenyl)butan-2-yl methanesulfonate **78** (1.1 eq, 0.36 mmol, 95 mg) was added dropwise and the mixture was stirred at room temperature overnight. The residue was diluted with 10 mL of AcOEt and washed 3 times with 10 mL of distilled H_2O. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (hexane). Compound **79** was isolated as a colourless oil in 84% yield (97 mg, 0.27 mmol).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 – 7.88 (m, 2H), 7.48 – 7.34 (m, 4H), 7.30 – 7.24 (m, 2H), 7.18 – 7.13 (m, 2H), 3.79 (m, 1H), 2.84 (t, *J* = 7.8 Hz, 2H), 2.13 (m, 1H), 1.98 (m, 1H), 1.54 (d, *J* = 6.8 Hz, 3H).
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 163.1, 155.7, 139.8, 134.1, 131.7, 129.8, 128.7, 128.6, 128.2, 126.3, 113.1, 44.6, 38.3, 32.6, 21.4.
IR (film)/cm^{-1} 3109, 2923, 2852, 1497, 1443, 1091, 1023, 833, 723, 691.
HRMS calcd for $C_{19}H_{18}ClNNaS_2$ $[M+Na]^+$ 382.0467; found 382.0455.

9.2.3 Synthesis of (4-(4-chlorophenyl)butan-2-yl)(imino)(4-phenylthiazol-2-yl)-λ^6-sulfanone (80)



79 **80**

Compound **80** was synthetized adapting the procedure reported by Luisi and co–workers.[23] To a 5 mL round-bottom-flask charged with a stir bar, were added 2-((4-(4-chlorophenyl)butan-2-yl)thio)-4-phenylthiazole **79** (1 eq, 0.27 mmol, 97 mg), MeOH (1 mL), ammonium carbamate (4 eq, 1.08 mmol, 84.3 mg), and (Diacetoxyiodo)benzene (DIB) (3 eq, 0.81 mmol, 261 mg) and the mixture was stirred at room temperature for 3 hours. The organic solvent was evaporated under reduced pressure to give a yellow slurry, which is diluted with AcOEt (2 mL) and saturated aqueous $NaHCO_3$ (1 mL). The mixture is stirred for 5 min to neutralize the acetic acid formed during the reaction. The residue was diluted with distilled H_2O (10 mL) and extracted 3 times with 10 mL of AcOEt. The combined organic phases were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude residue was purified by silica gel chromatography (7:3 hexane/ ethyl acetate). Compound **80** was obtained as a pale yellow oil (mixture of diastereomers, dr = 50:50). Compound **80** was isolated as a colorless oil (mixture of diastereomers, dr = 50:50, 85 mg, 81%)

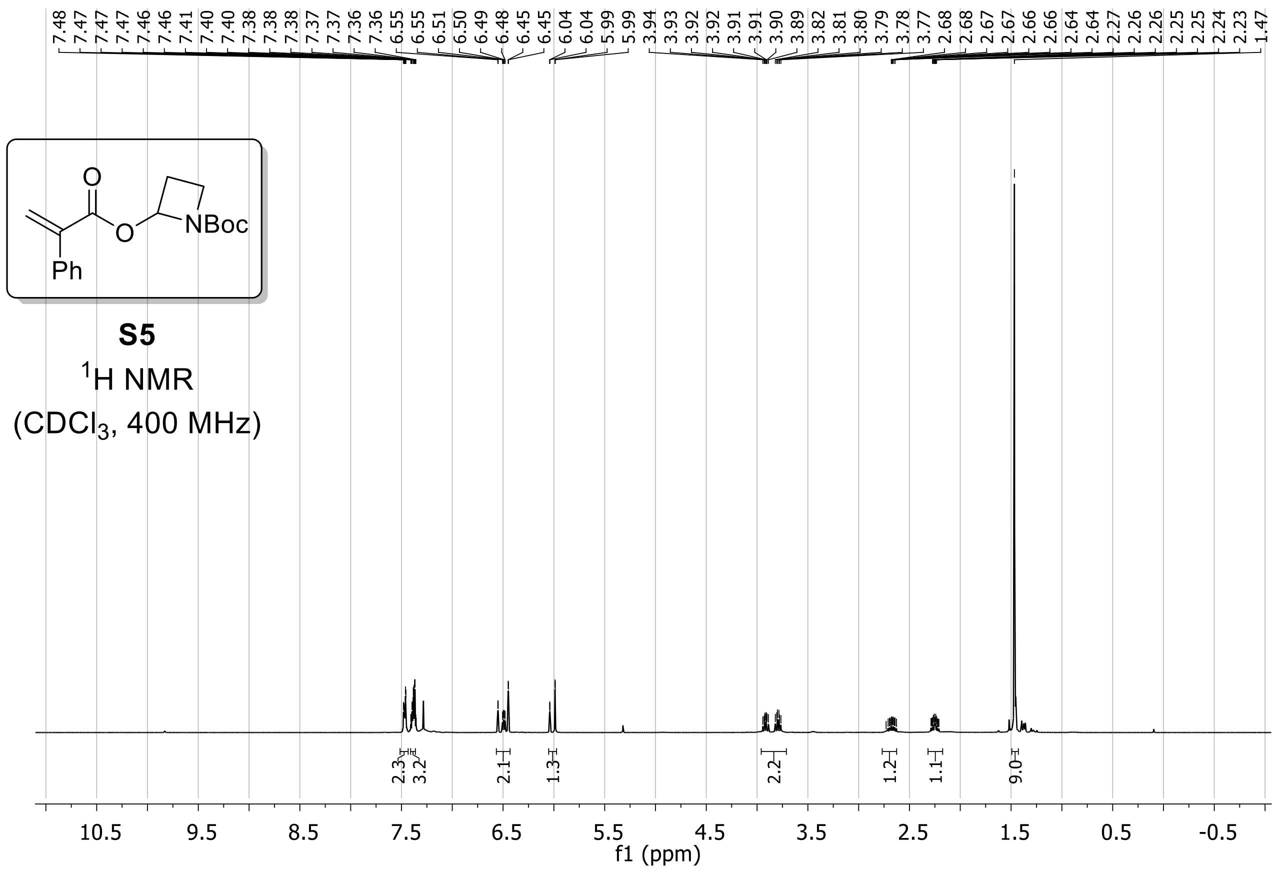
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 4H), 7.84 – 7.81 (m, 2H), 7.51 – 7.40 (m, 6H), 7.25 – 7.19 (m, 4H), 7.12 – 7.06 (m, 4H), 3.56 – 3.43 (m, 2H), 3.25 (br, 2H), 2.92 – 2.81 (m, 2H), 2.73 – 2.61 (m, 2H), 2.59 – 2.43 (m, 2H), 2.00 – 1.87 (m, 2H), 1.55 – 1.50 (m, 6H).

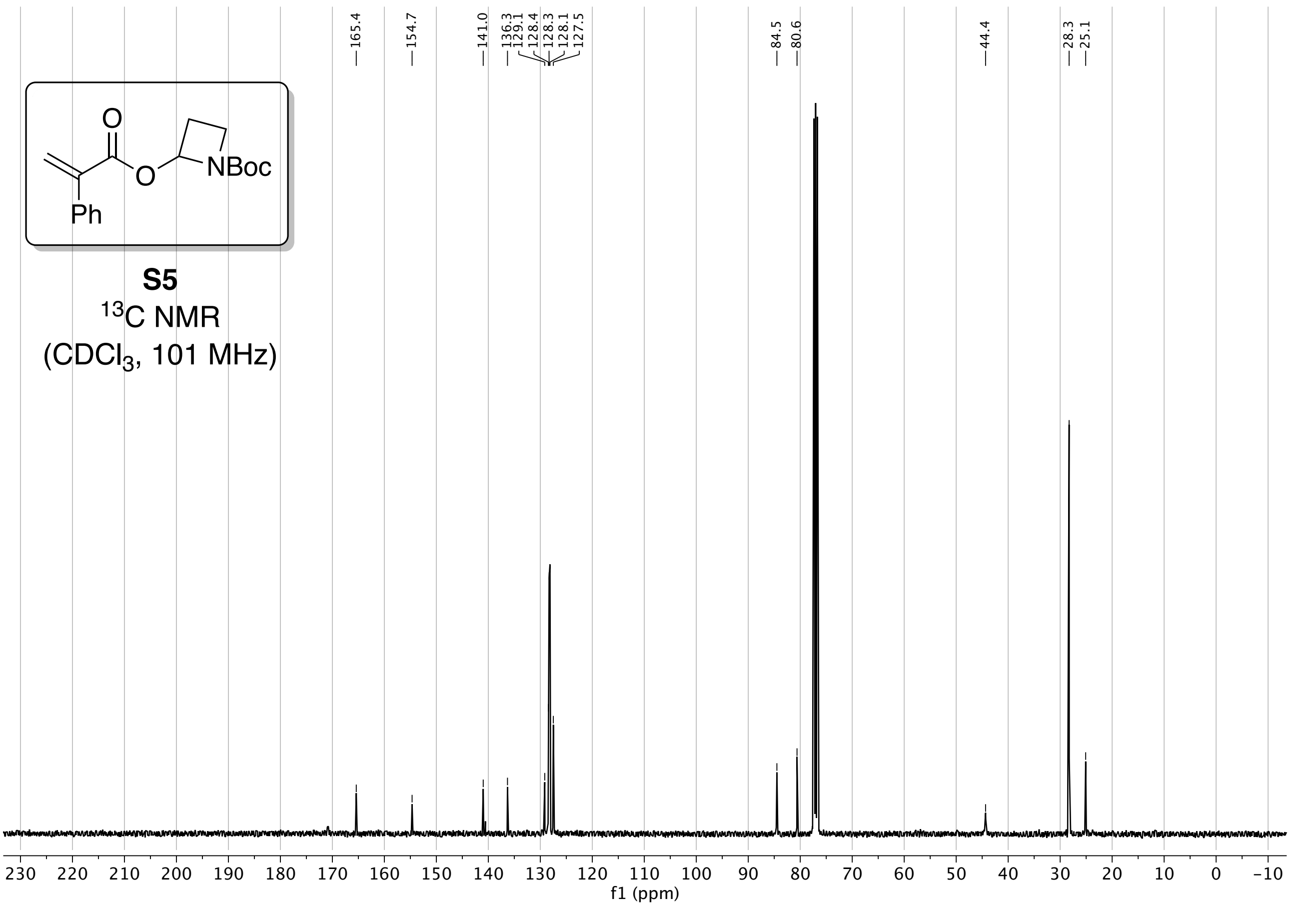
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 167.8, 158.1, 138.63, 138.58, 133.0, 132.13, 132.10, 129.7, 129.2, 129.0, 128.71, 128.69, 126.6, 119.5, 59.8, 59.6, 32.0, 31.9, 31.1, 30.9, 13.6, 13.2.

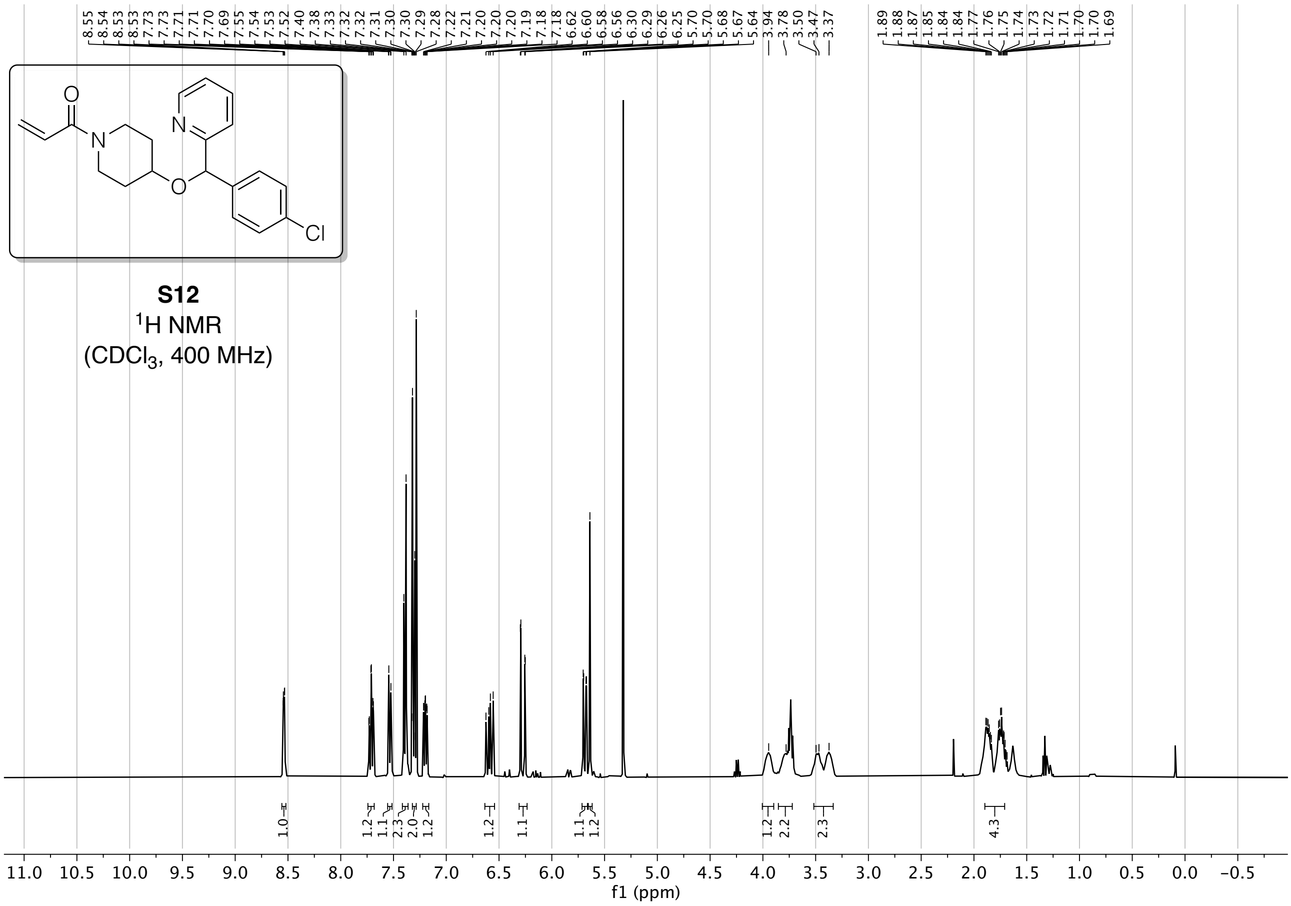
IR (film)/cm^{-1} 3277, 2924, 2853, 1724, 1492, 1230, 1092, 962, 752, 693.

HRMS calcd for $C_{19}H_{19}ClN_2NaOS_2$ $[M+Na]^+$ 413.0525; found 413.0518.

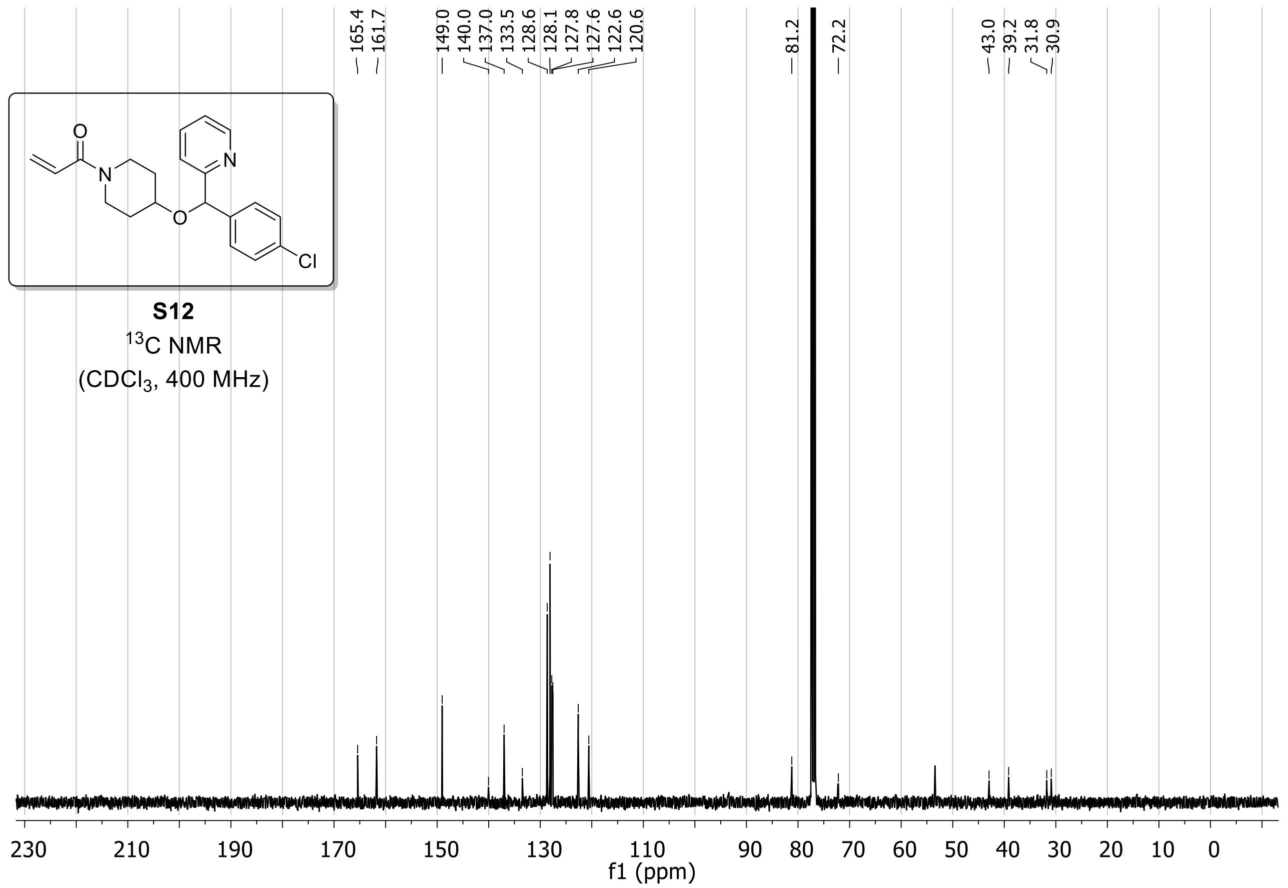
10 Copies of NMR spectra



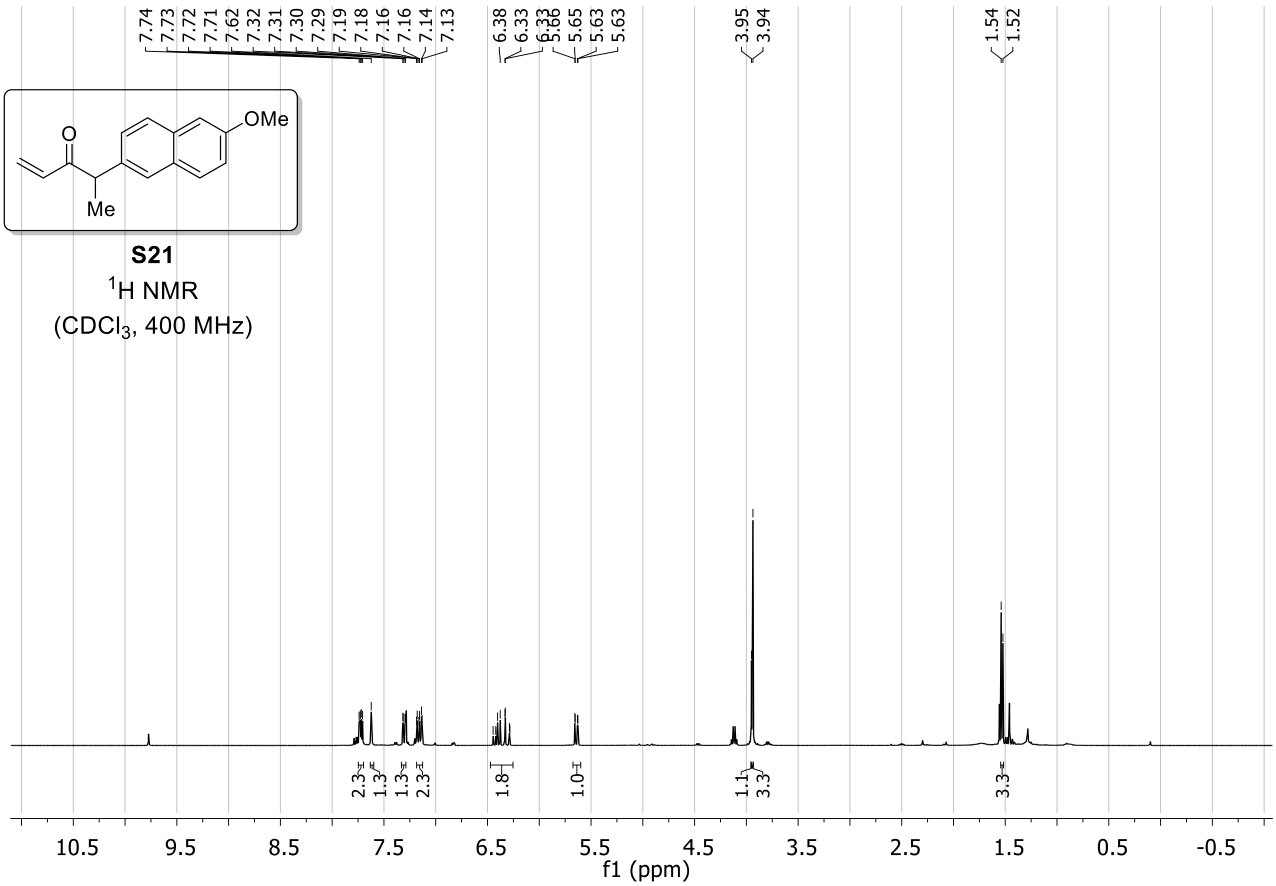




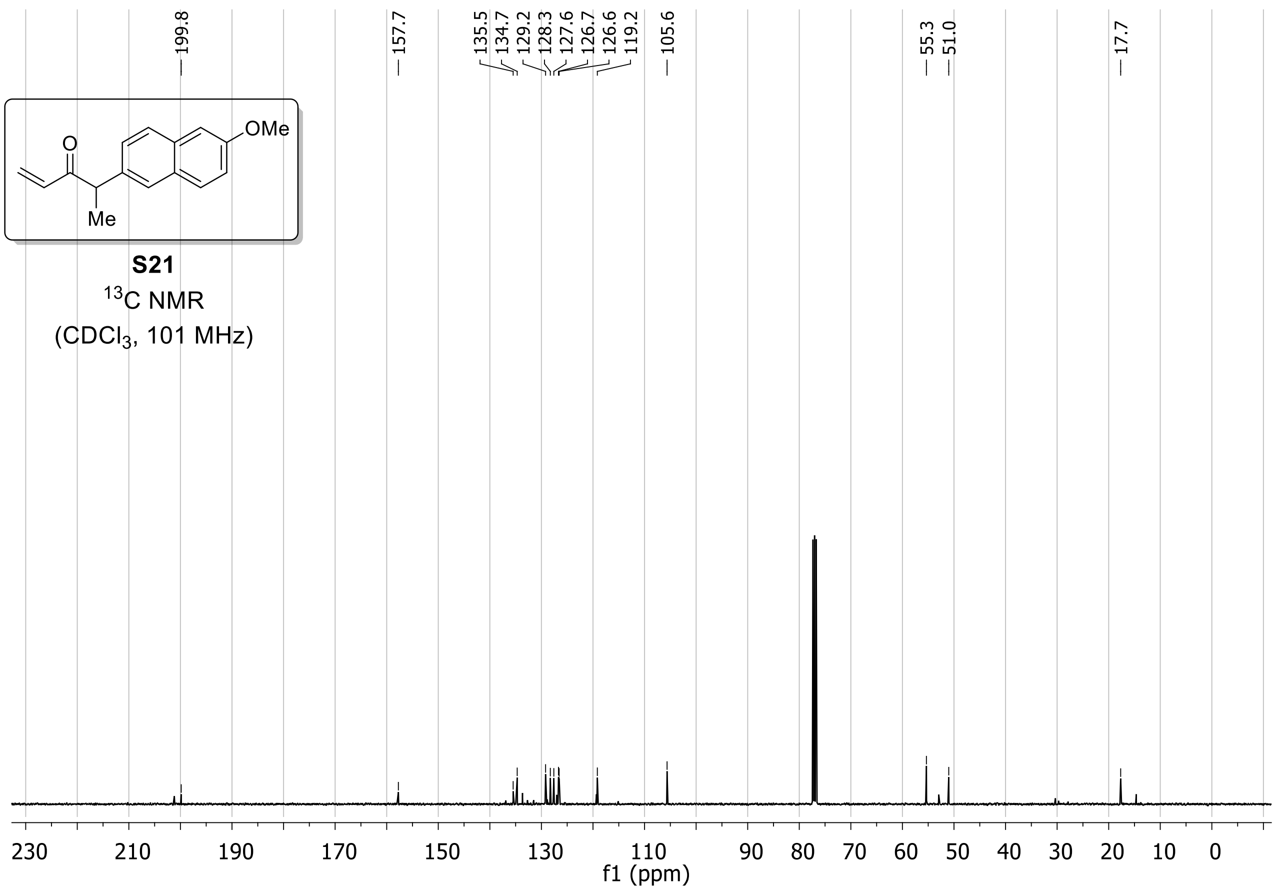
S12
^{1}H NMR
($CDCl_3$, 400 MHz)



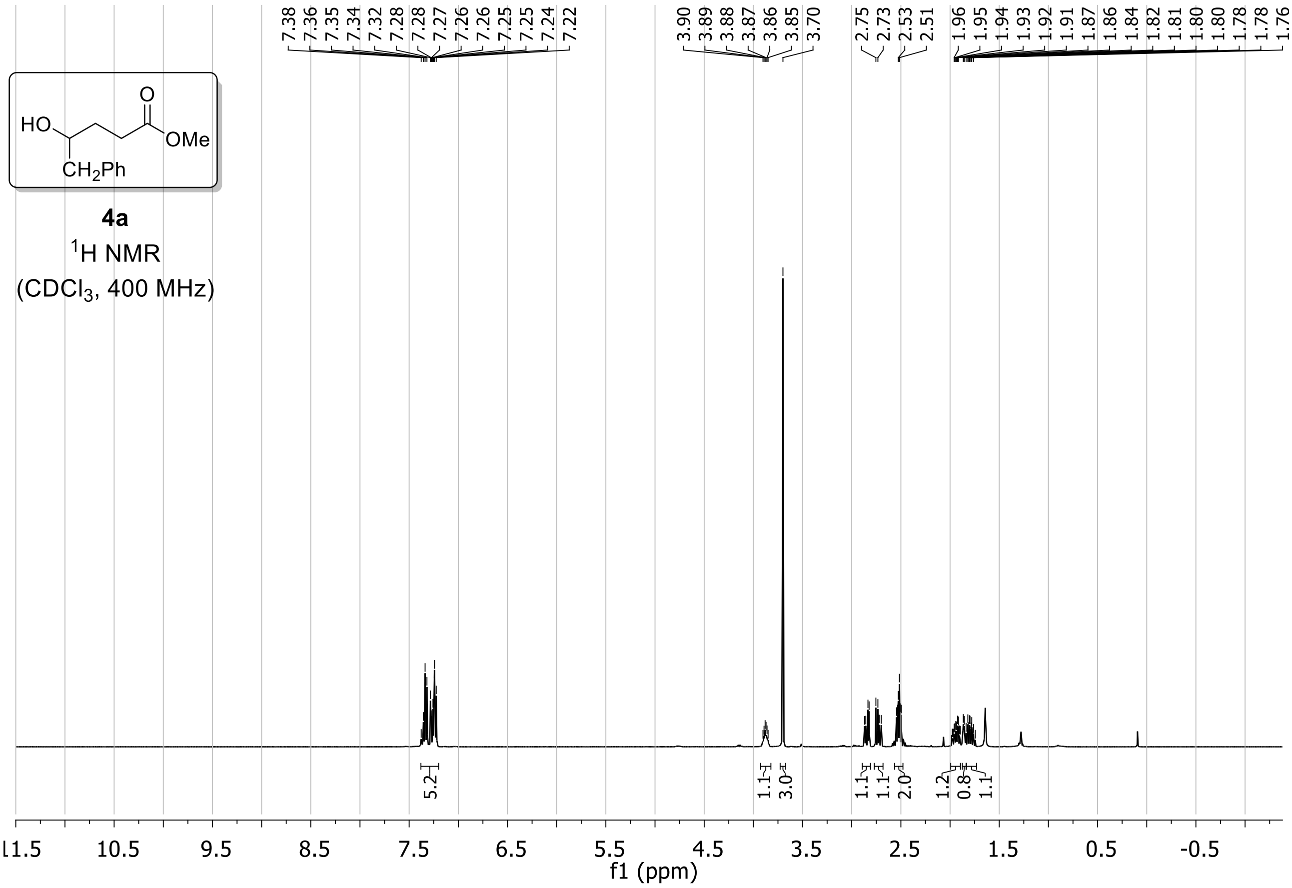
S12
^{13}C NMR
($CDCl_3$, 400 MHz)

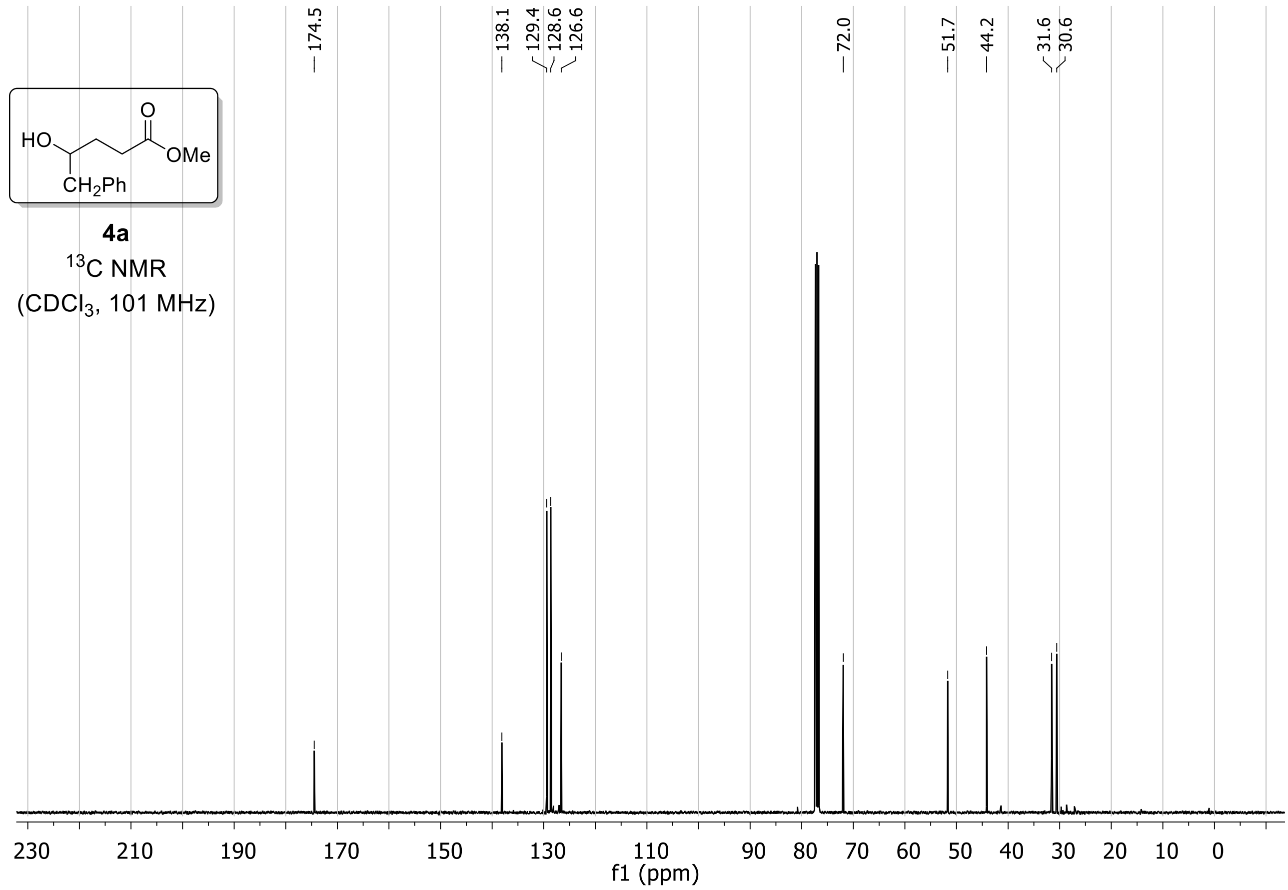


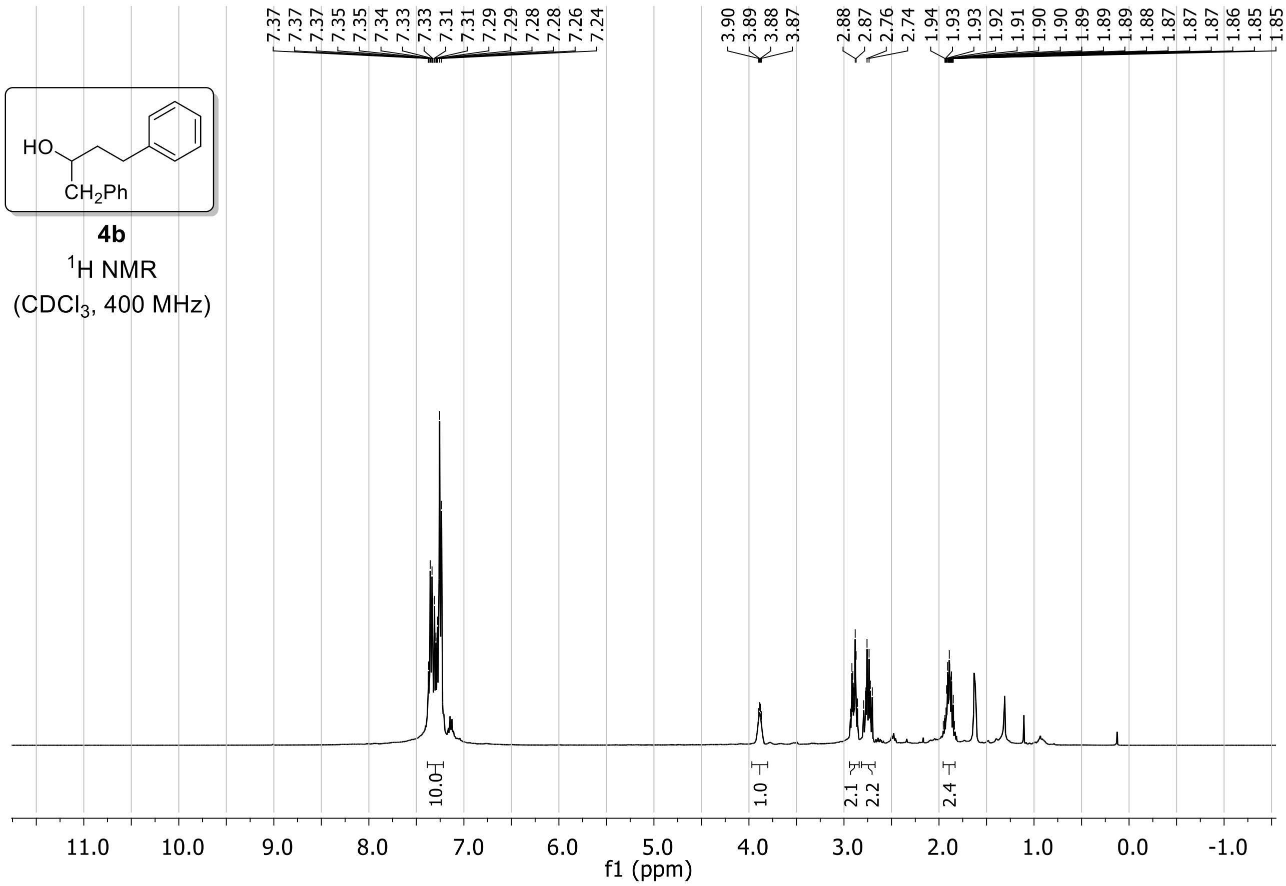
S21
^{1}H NMR
($CDCl_3$, 400 MHz)



S21
^{13}C NMR
($CDCl_3$, 101 MHz)


4a
^{1}H NMR
($CDCl_3$, 400 MHz)
f1 (ppm)

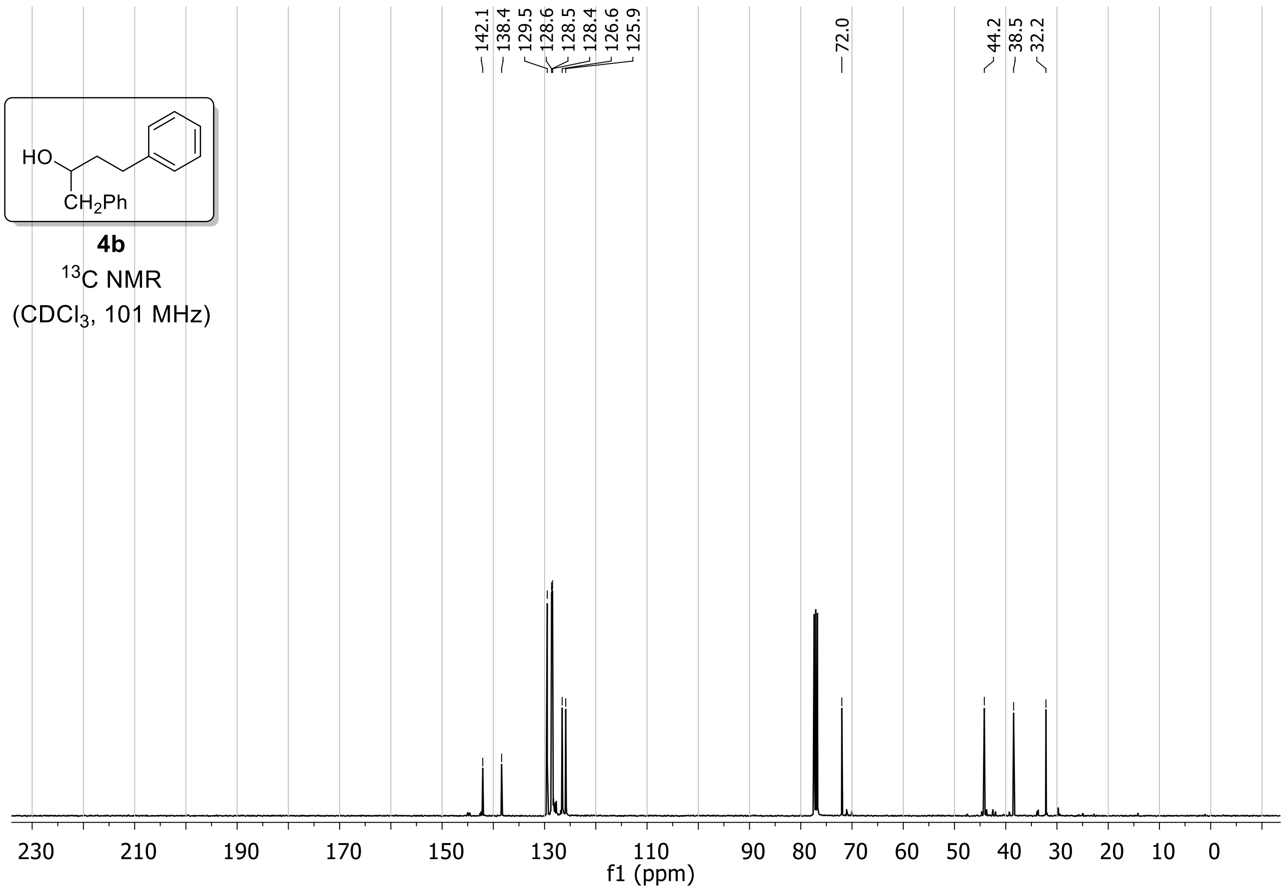

4a
^{13}C NMR
($CDCl_3$, 101 MHz)
f1 (ppm)



4b

^{1}H NMR

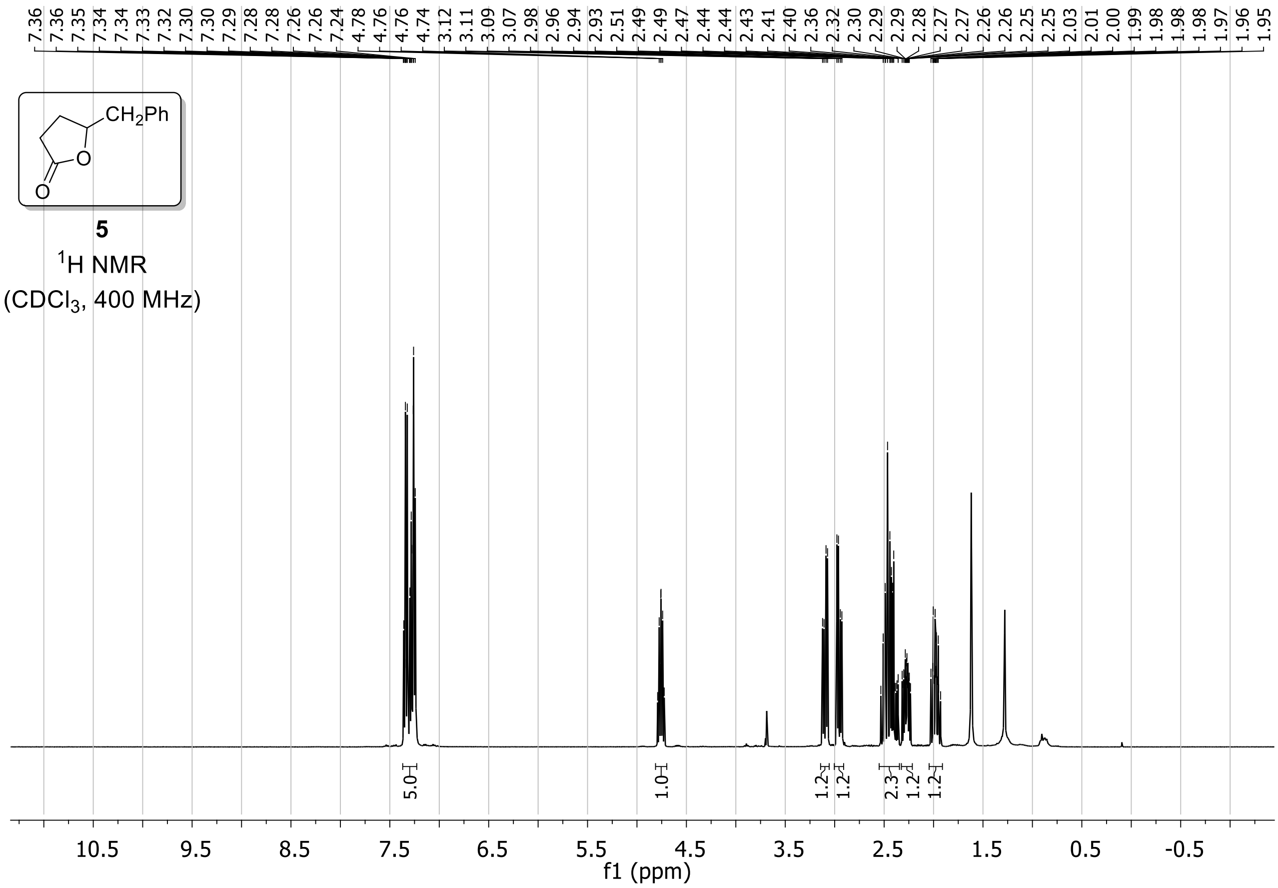
($CDCl_3$, 400 MHz)

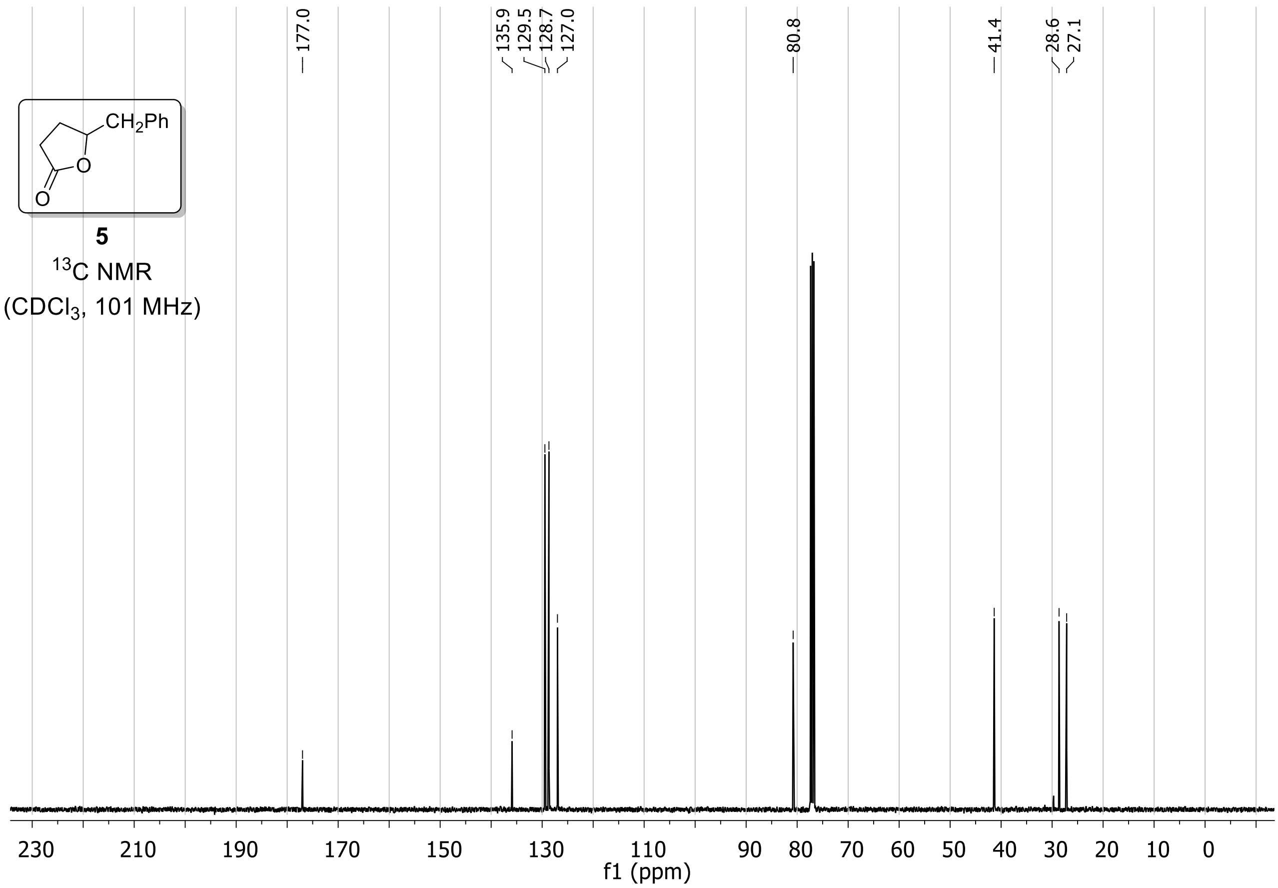


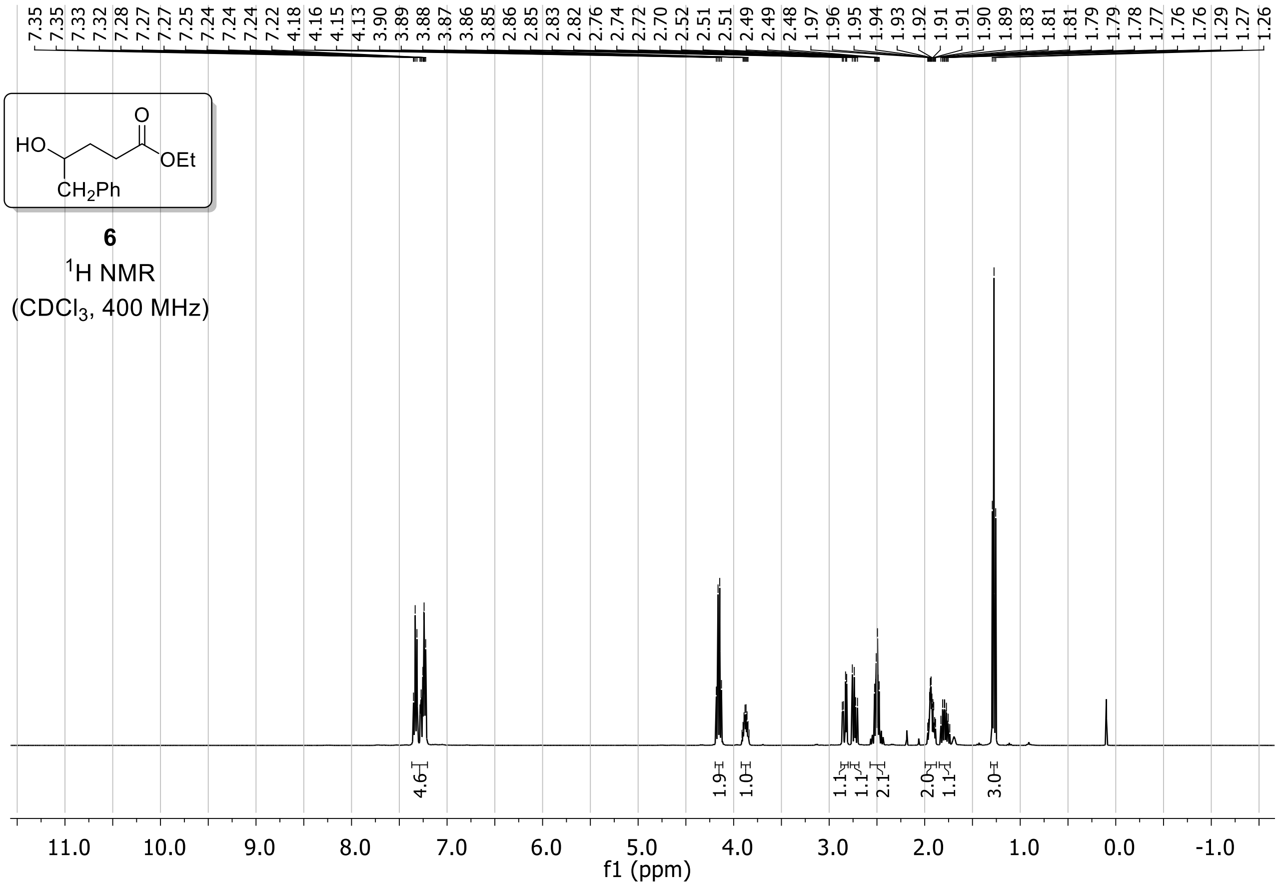
4b

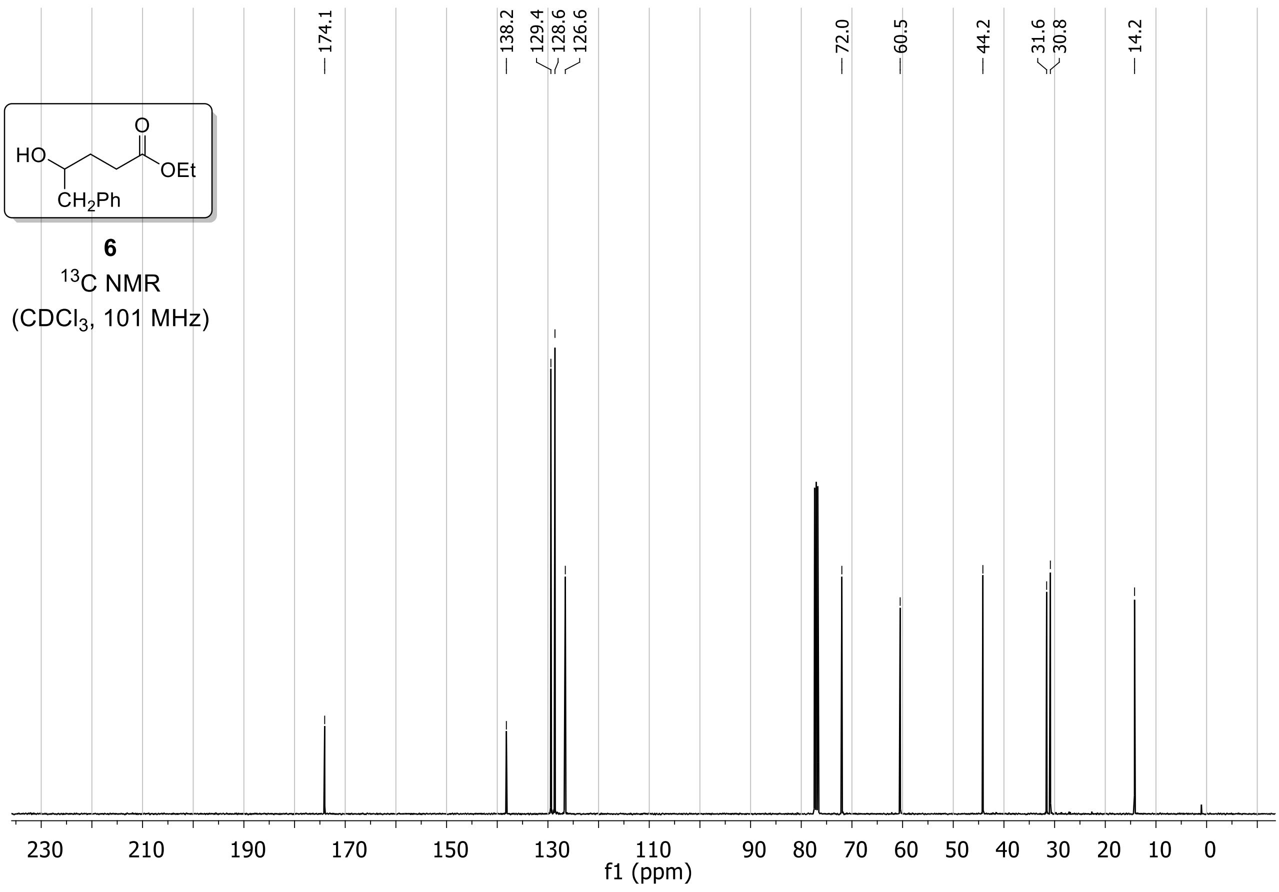
^{13}C NMR

($CDCl_3$, 101 MHz)

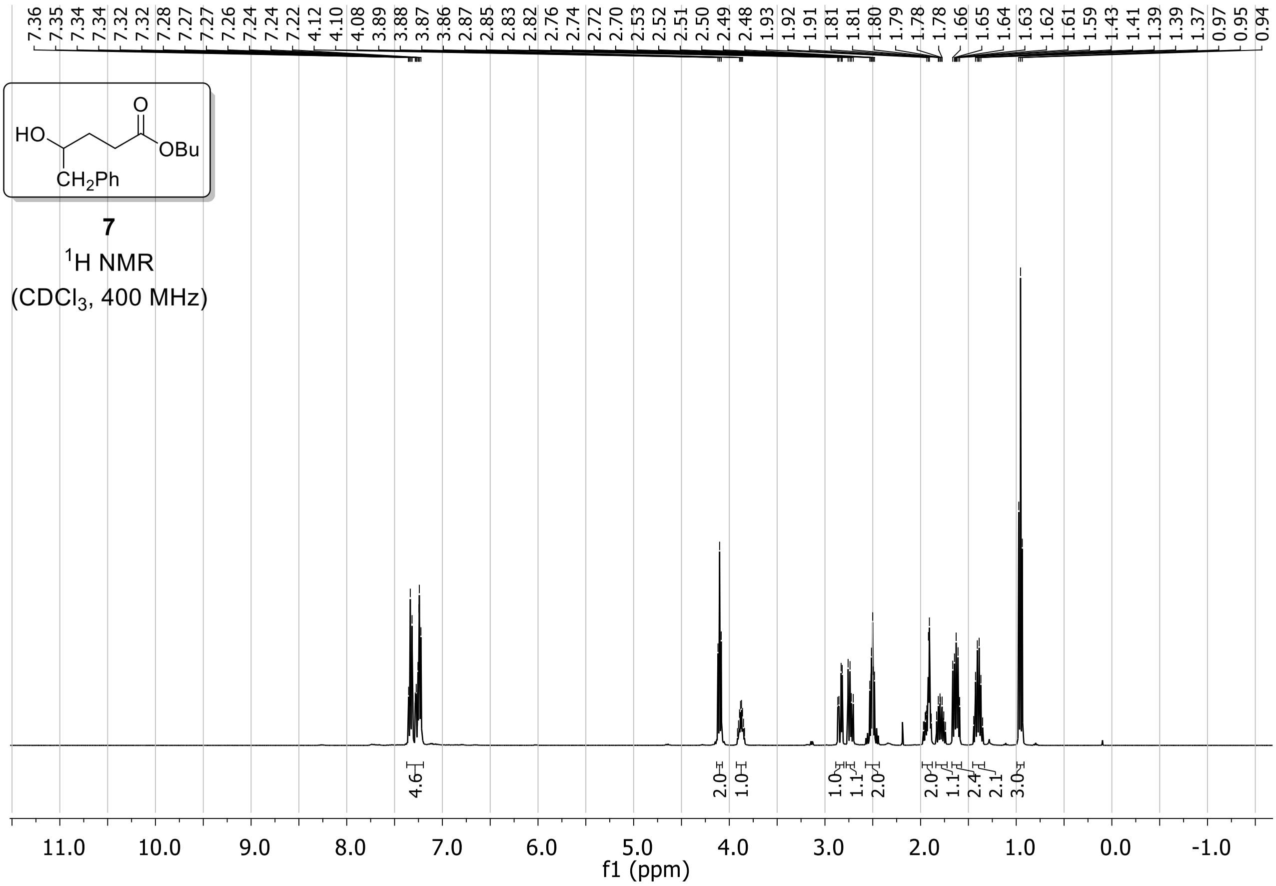

7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.30 7.30 7.29 7.28 7.28 7.26 7.26 7.24 4.78 4.76 4.76 4.74 3.12 3.11 3.09 3.07 2.98 2.96 2.94 2.93 2.51 2.49 2.49 2.47 2.44 2.44 2.43 2.41 2.40 2.36 2.32 2.30 2.29 2.29 2.28 2.27 2.26 2.26 2.25 2.25 2.03 2.01 2.00 1.99 1.98 1.98 1.98 1.97 1.96 1.95
CH2Ph
O
O
5
1H NMR
(CDCl3, 400 MHz)
5.0
1.0
1.2
1.2
2.3
1.2
1.2
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)


177.0
135.9 129.5 128.7 127.0
80.8
41.4
28.6 27.1
CH2Ph
O
O
5
13C NMR
(CDCl3, 101 MHz)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

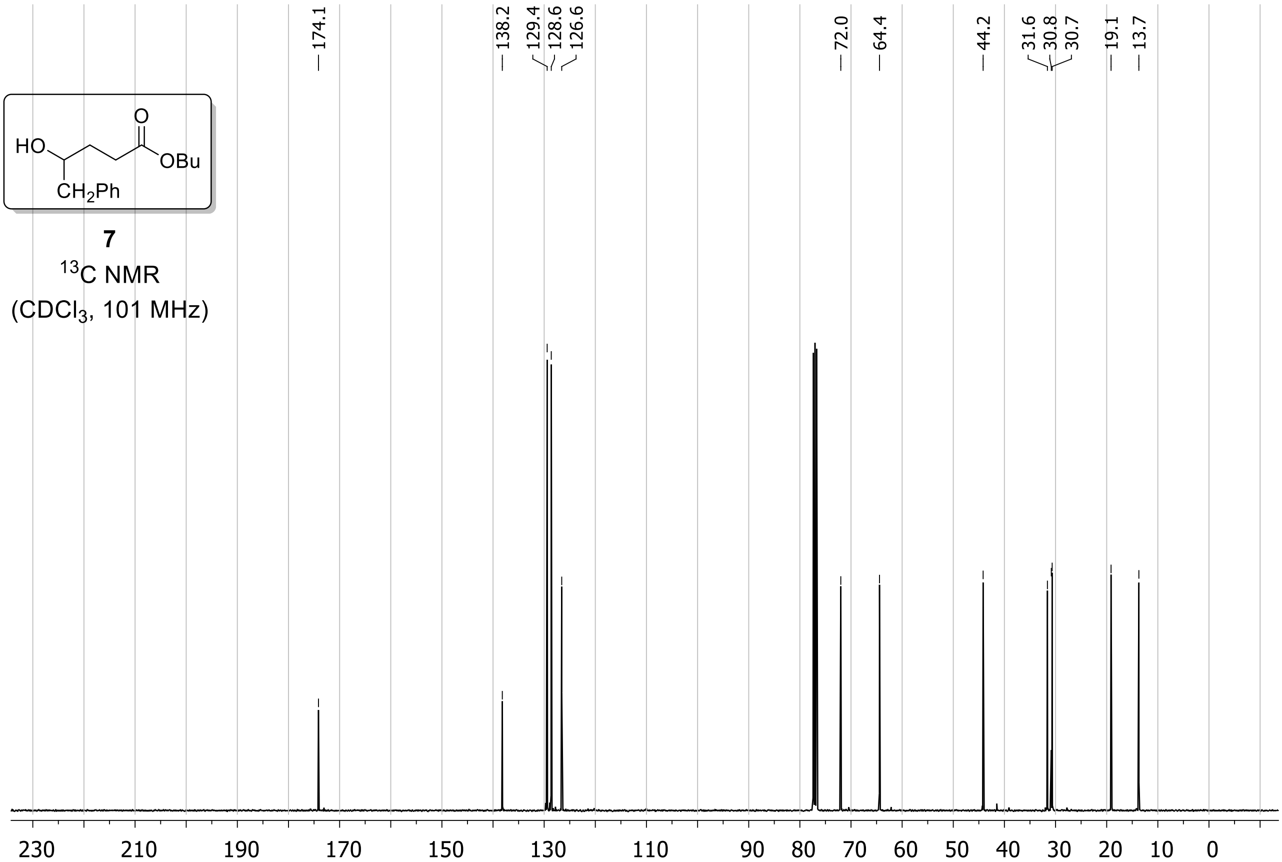

HO
O
OEt
CH2Ph
6
1H NMR
(CDCl3, 400 MHz)
7.35 7.35 7.33 7.32 7.28 7.27 7.27 7.25 7.24 7.24 7.24 7.22 4.18 4.16 4.15 4.13 3.90 3.89 3.88 3.87 3.86 3.85 2.86 2.85 2.83 2.82 2.76 2.74 2.72 2.70 2.52 2.51 2.51 2.49 2.49 2.48 1.97 1.96 1.95 1.94 1.93 1.92 1.91 1.91 1.90 1.89 1.83 1.81 1.81 1.79 1.79 1.78 1.77 1.76 1.29 1.27 1.26
4.6 1.9 1.0 1.1 1.1 2.1 2.0 1.1 3.0
f1 (ppm)

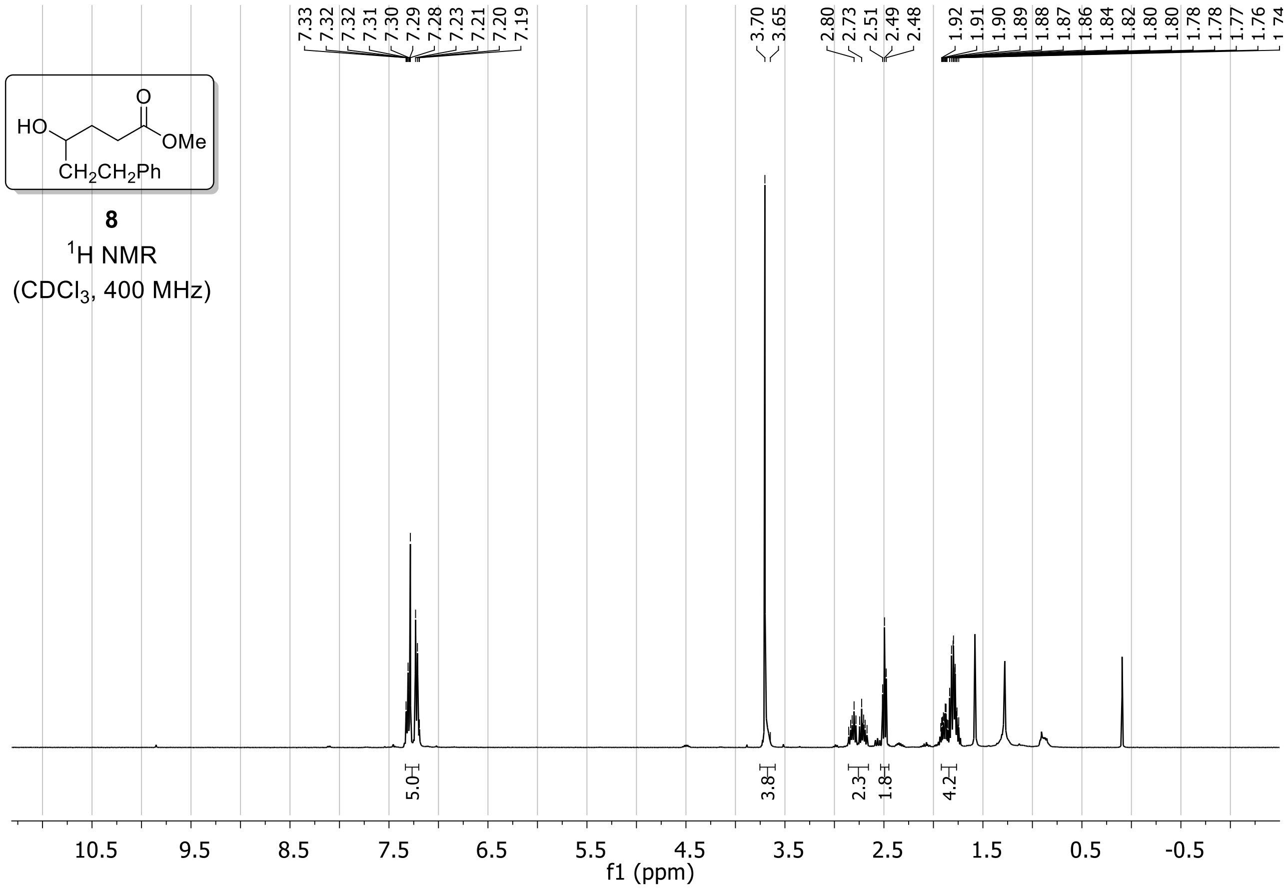

HO
O
OEt
CH2Ph
6
13C NMR
(CDCl3, 101 MHz)
174.1 138.2 129.4 128.6 126.6 72.0 60.5 44.2 31.6 30.8 14.2
f1 (ppm)

7
^{1}H NMR
($CDCl_3$, 400 MHz)

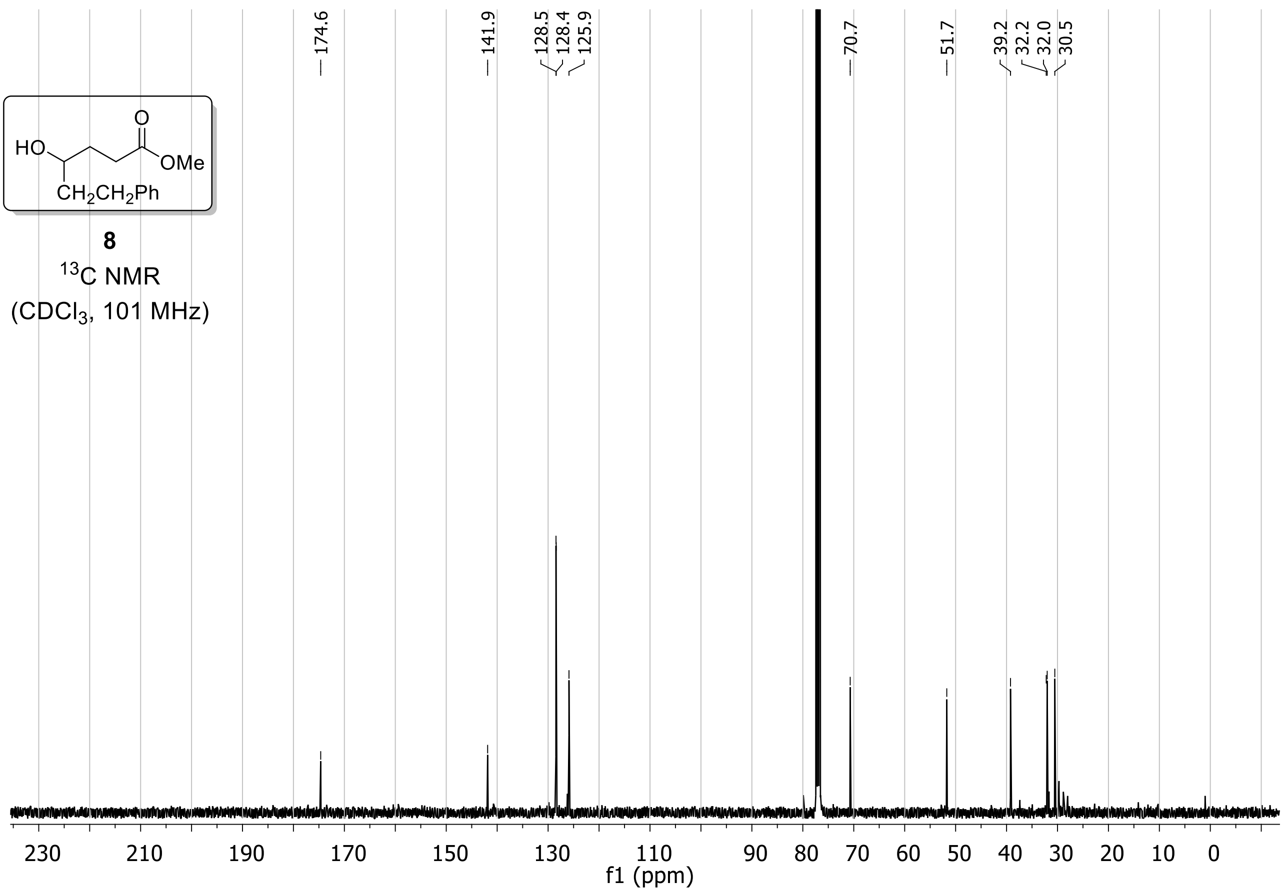


7
^{13}C NMR
($CDCl_3$, 101 MHz)

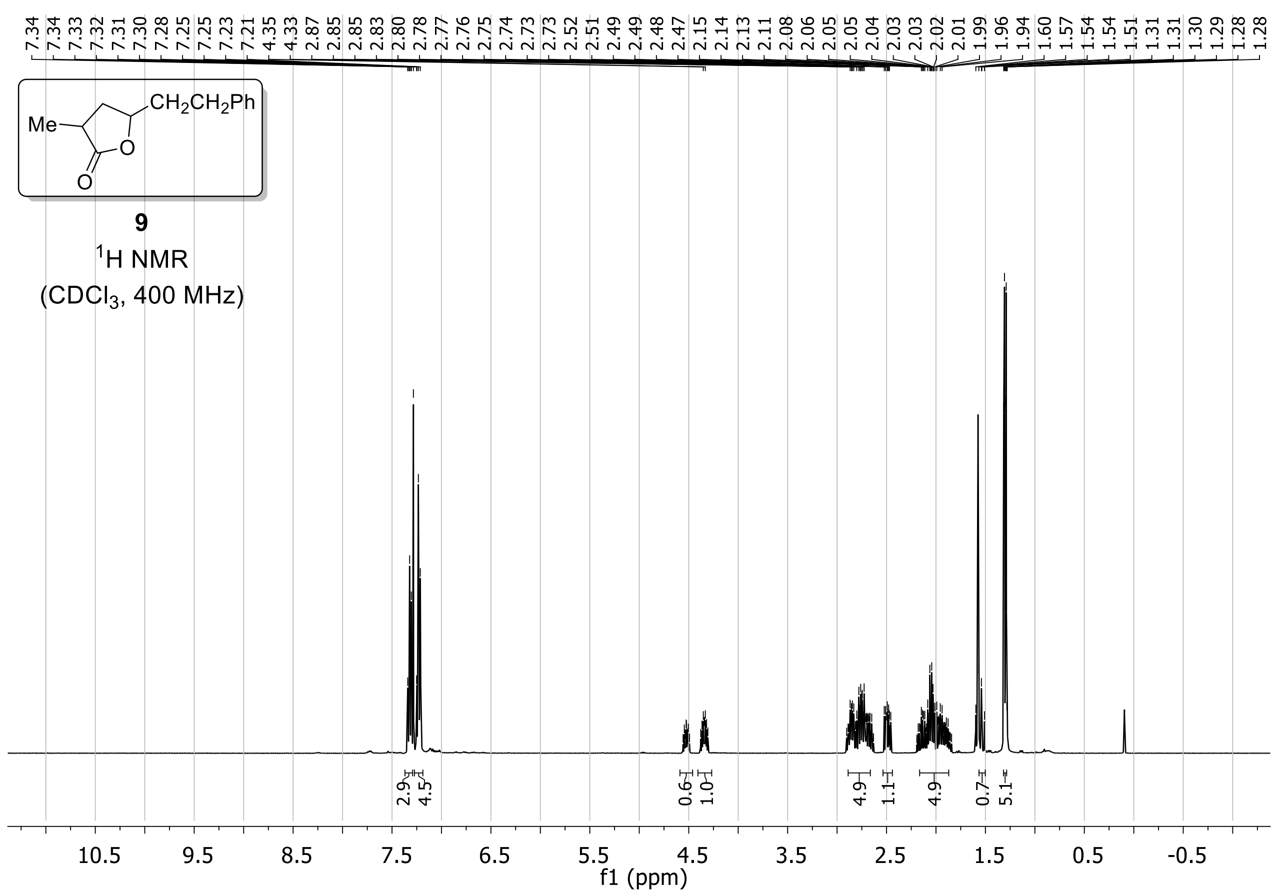




8
^{1}H NMR
($CDCl_3$, 400 MHz)



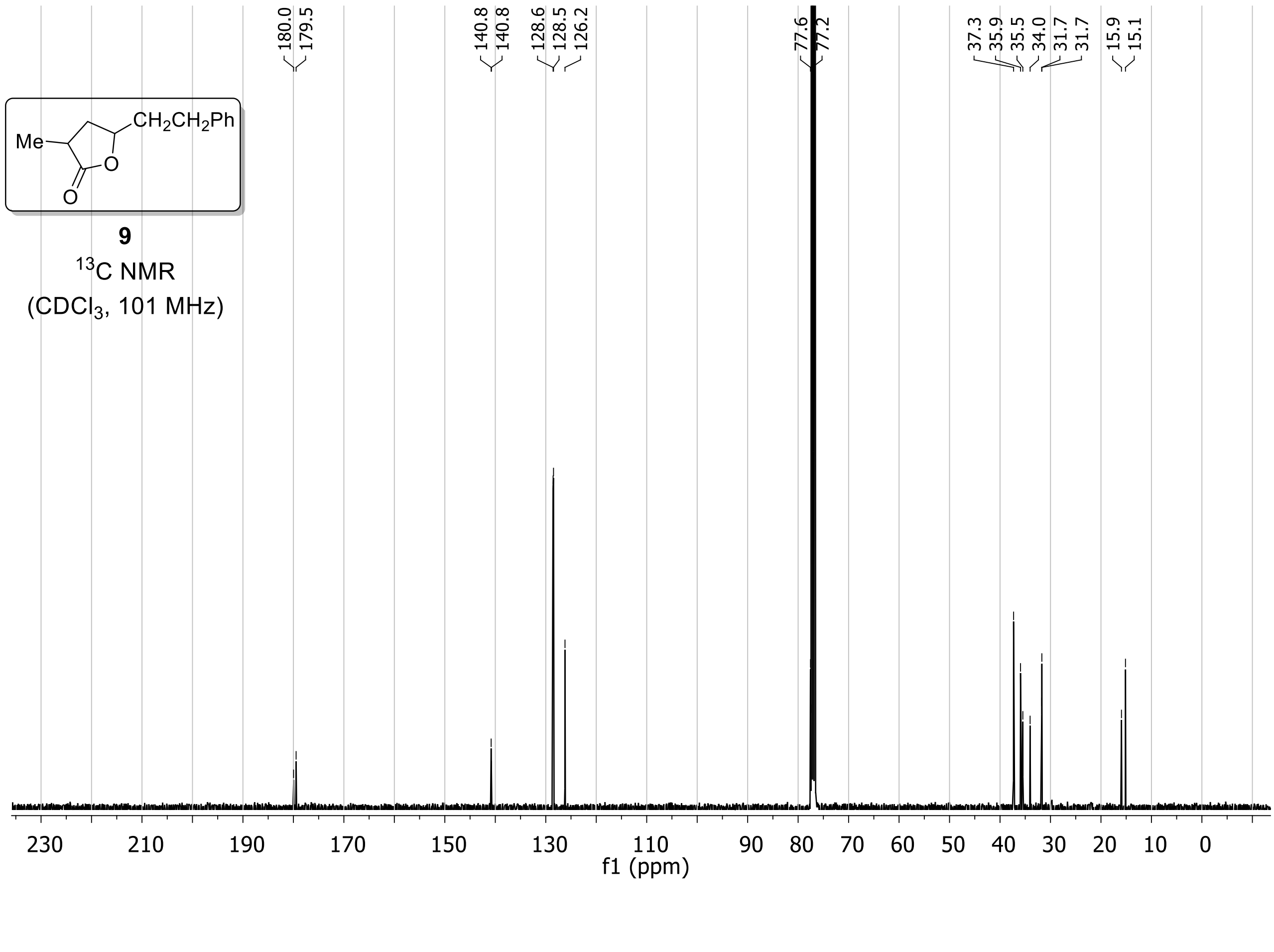
8
^{13}C NMR
($CDCl_3$, 101 MHz)



9

^{1}H NMR

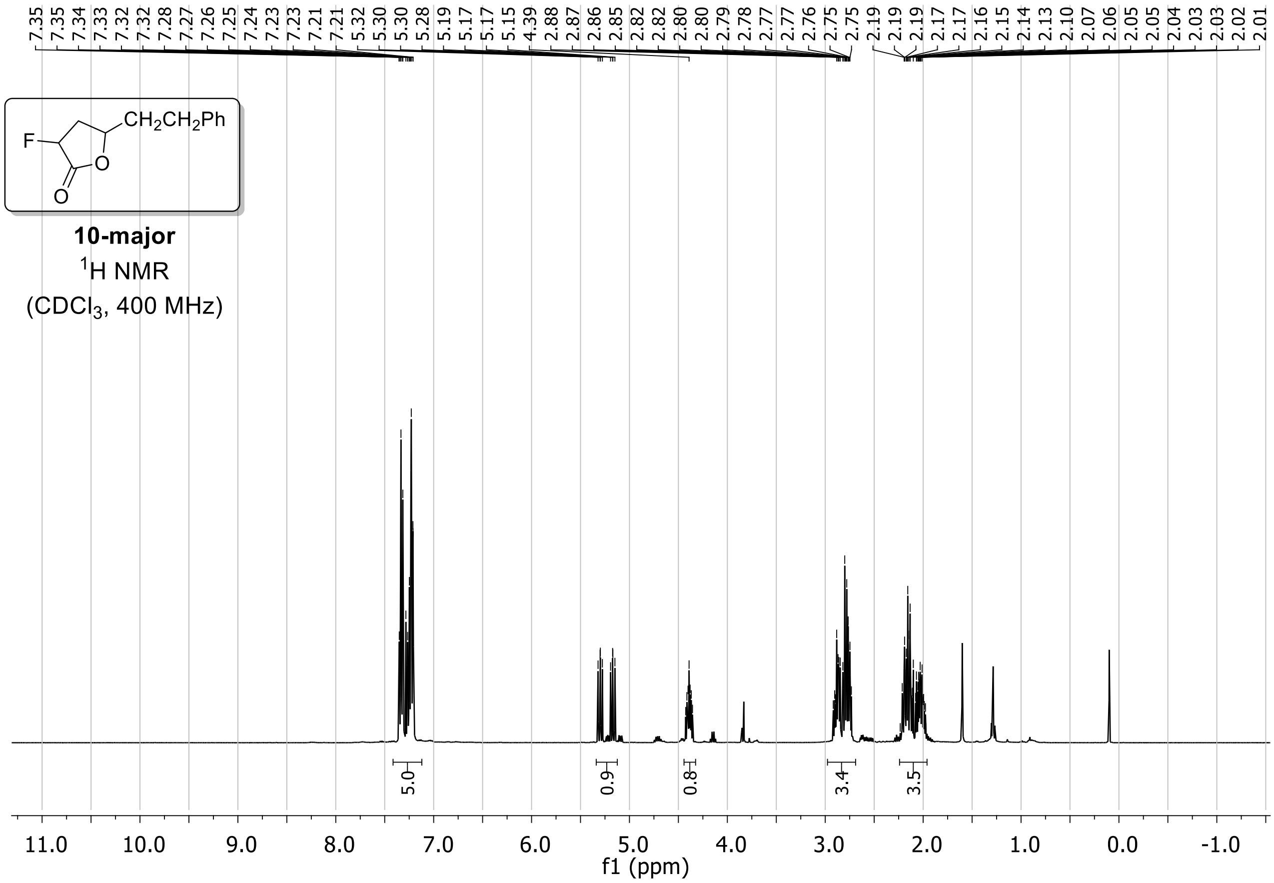
($CDCl_3$, 400 MHz)



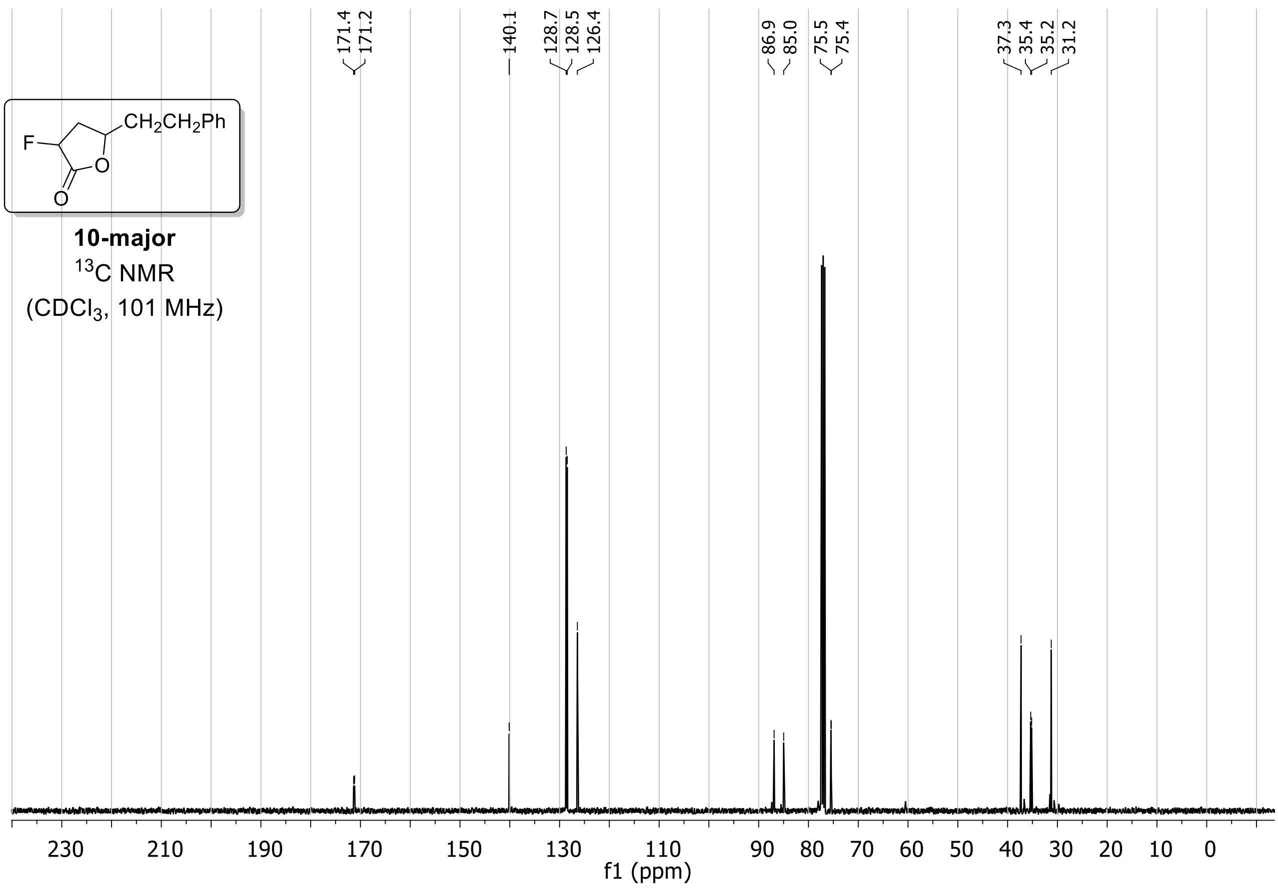
9

^{13}C NMR

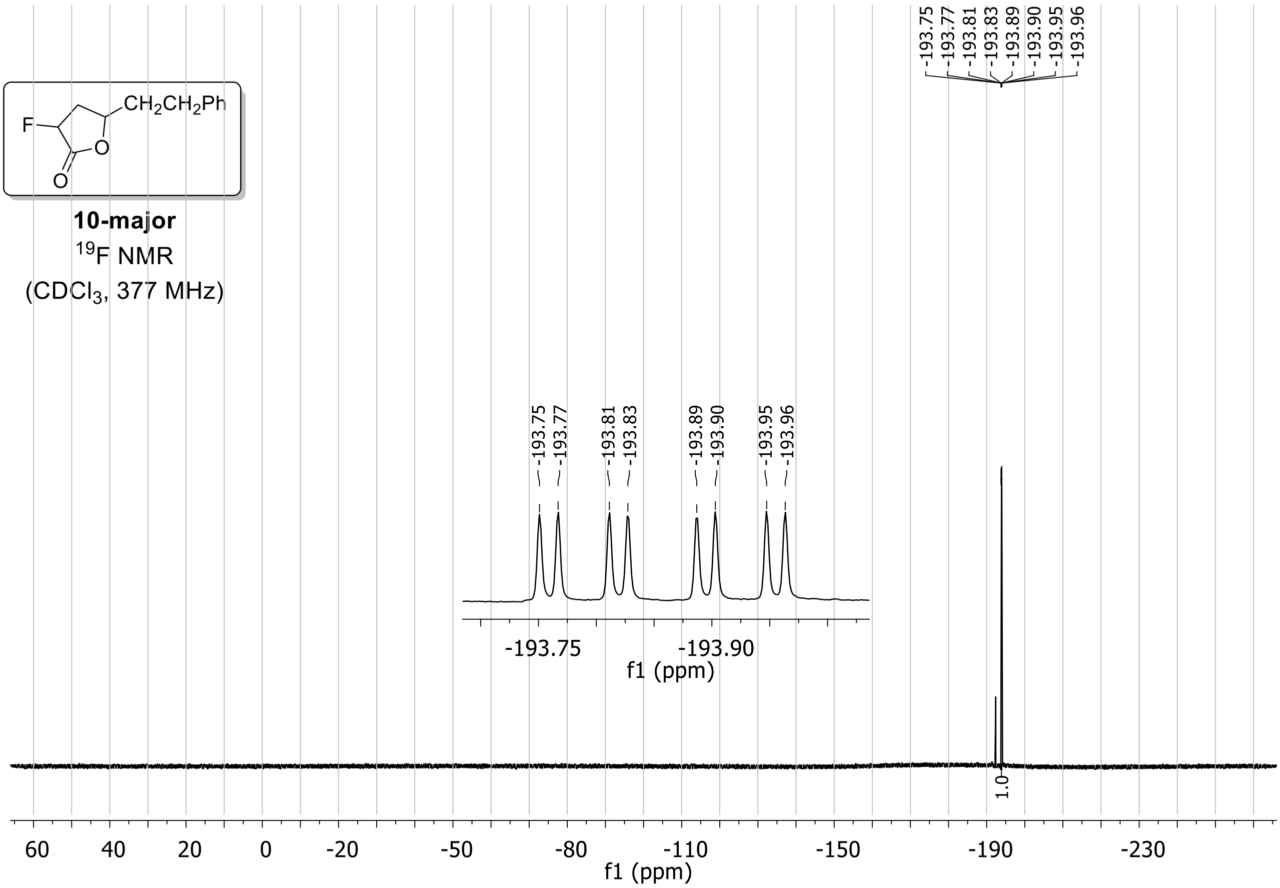
($CDCl_3$, 101 MHz)



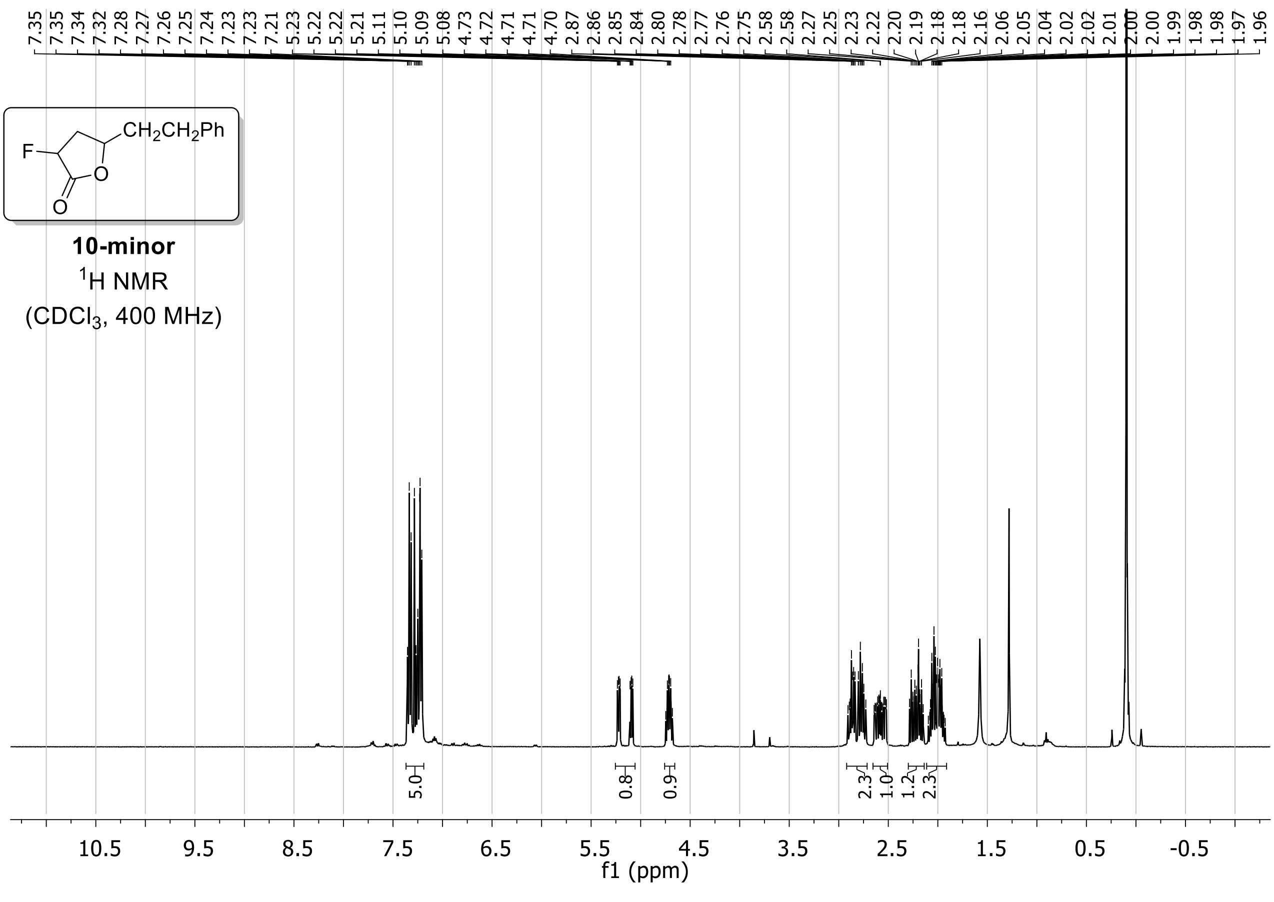
7.35 7.35 7.34 7.33 7.32 7.32 7.28 7.27 7.26 7.25 7.24 7.23 7.23 7.21 7.21 5.32 5.30 5.30 5.28 5.19 5.17 5.17 5.15 4.39 2.88 2.87 2.86 2.85 2.82 2.82 2.80 2.80 2.79 2.78 2.77 2.77 2.76 2.75 2.75 2.19 2.19 2.19 2.17 2.17 2.16 2.15 2.14 2.13 2.10 2.07 2.06 2.05 2.05 2.04 2.03 2.03 2.02 2.01
F
O
O
CH2CH2Ph
10-major
1H NMR
(CDCl3, 400 MHz)
5.0
0.9
0.8
3.4
3.5
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)



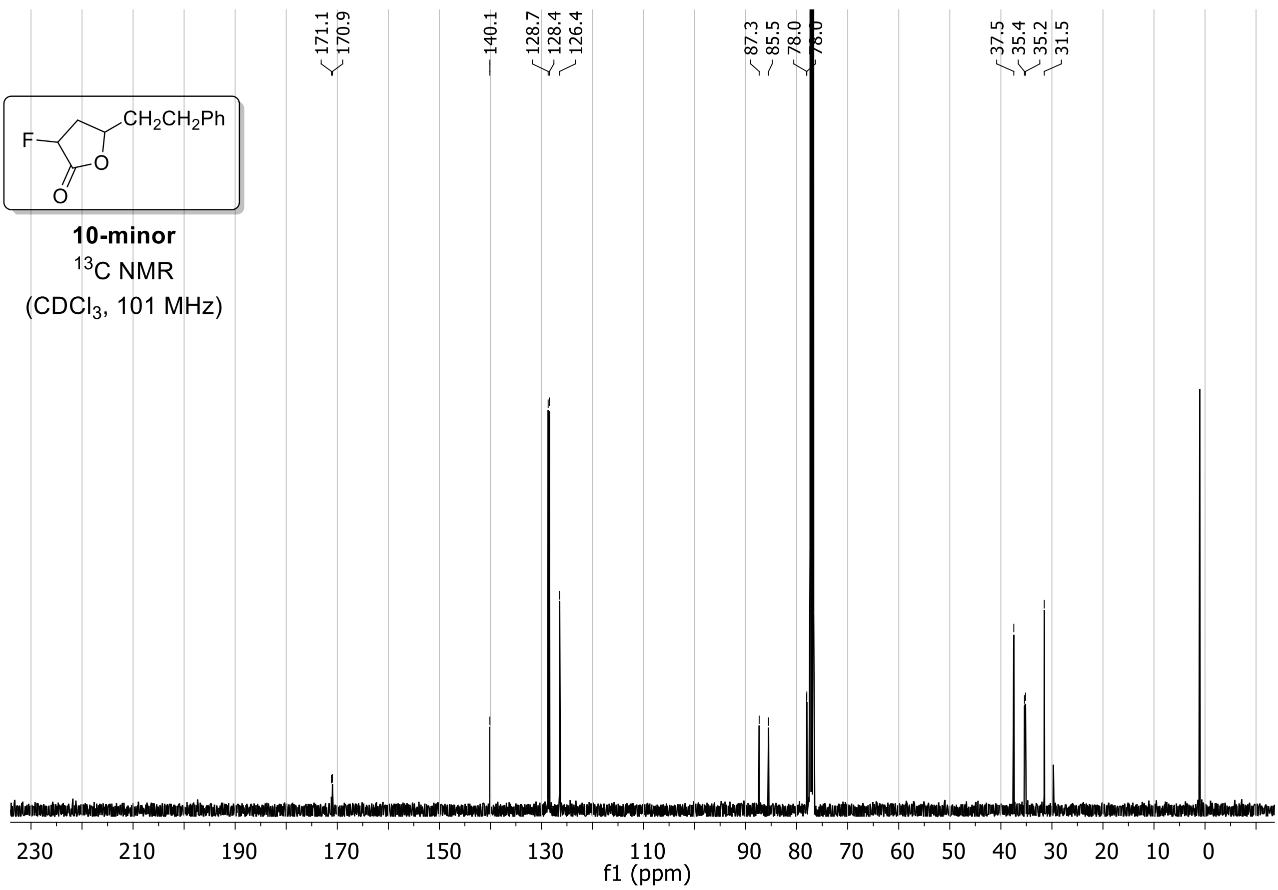
171.4 171.2 140.1 128.7 128.5 126.4 86.9 85.0 75.5 75.4 37.3 35.4 35.2 31.2
F
O
O
CH2CH2Ph
10-major
13C NMR
(CDCl3, 101 MHz)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

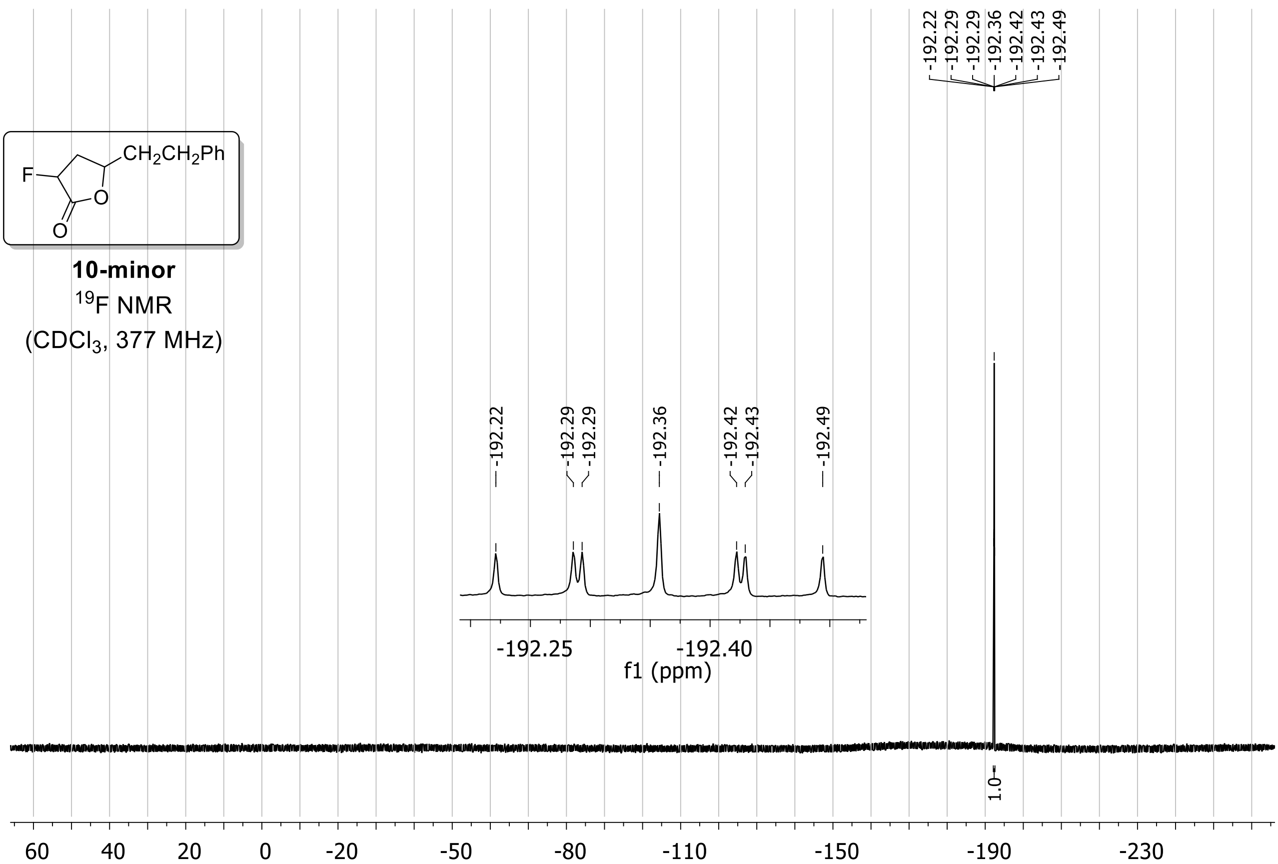


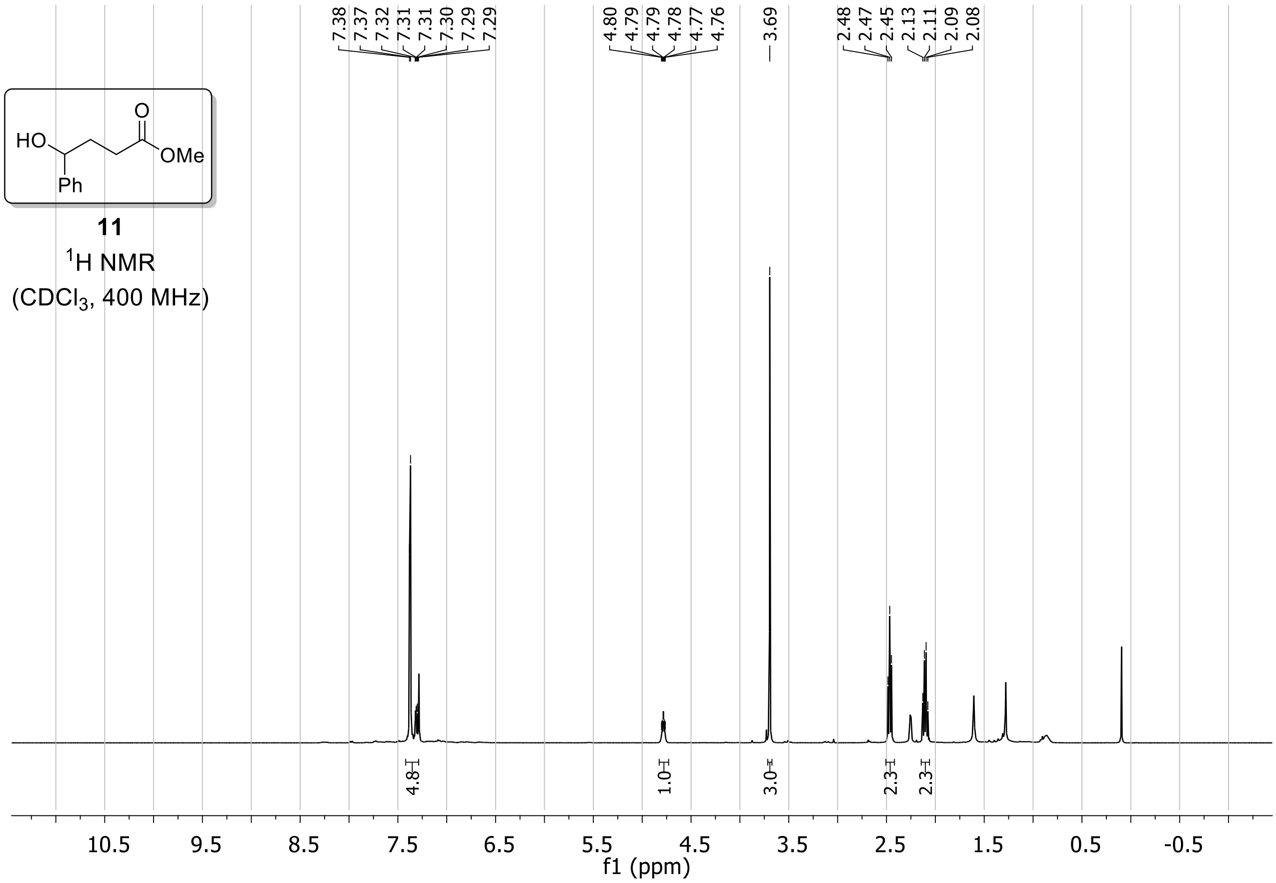
10-major
^{19}F NMR
($CDCl_3$, 377 MHz)

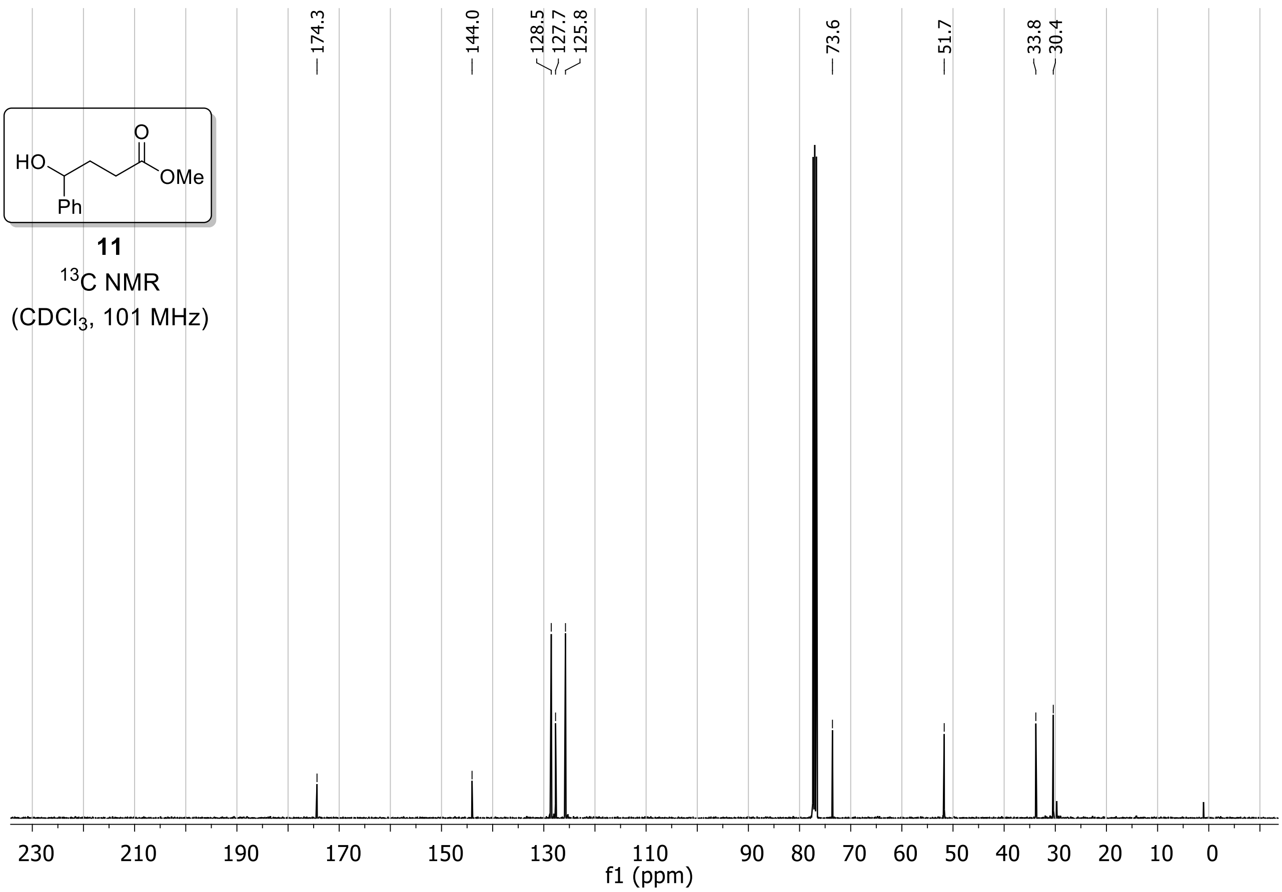


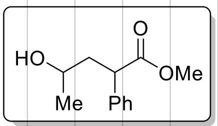
10-minor
^{1}H NMR
($CDCl_3$, 400 MHz)


171.1
170.9
140.1
128.7
128.4
126.4
87.3
85.5
78.0
76.0
37.5
35.4
35.2
31.5
CH2CH2Ph
F
O
O
10-minor
13C NMR
(CDCl3, 101 MHz)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

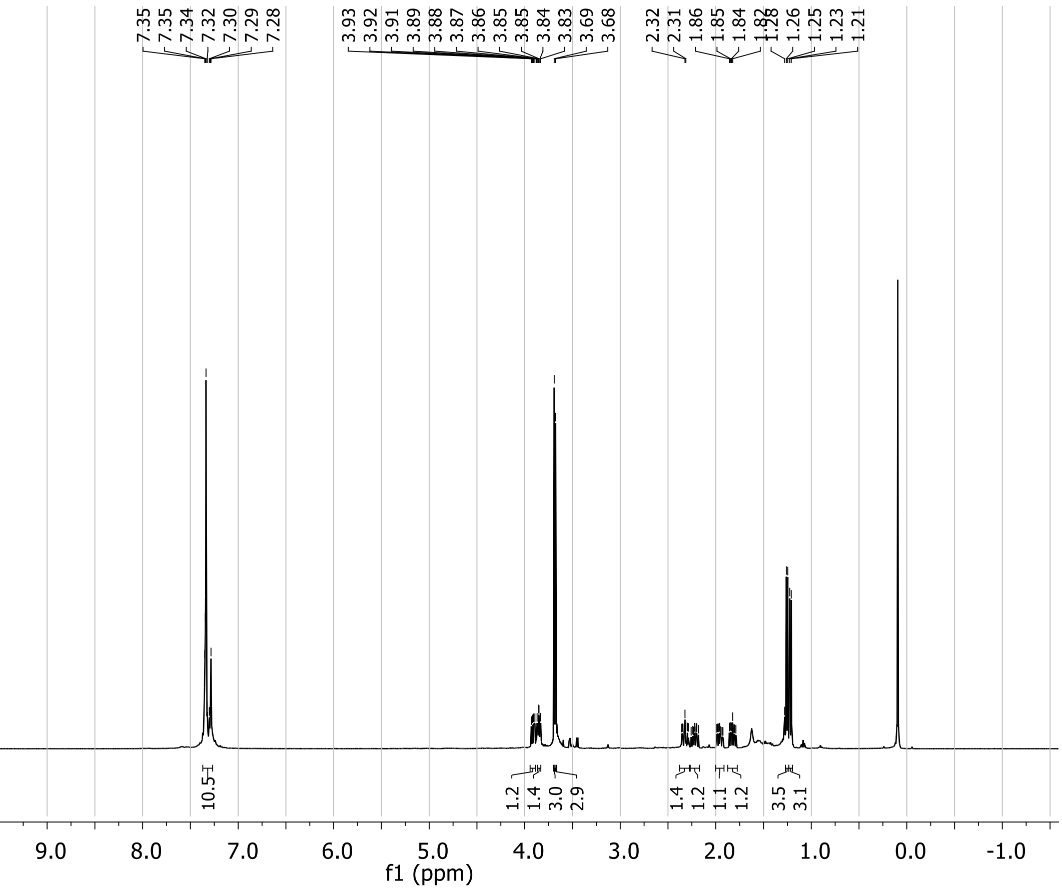

-192.22
-192.29
-192.29
-192.36
-192.42
-192.43
-192.49
CH2CH2Ph
F
O
O
10-minor
19F NMR
(CDCl3, 377 MHz)
-192.25
-192.40
f1 (ppm)
1.0
60 40 20 0 -20 -50 -80 -110 -150 -190 -230
f1 (ppm)

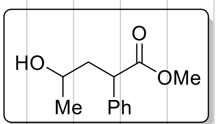

HO
O
OMe
Ph
11
^{1}H NMR
(CDCl$_3$, 400 MHz)
7.38 7.37 7.32 7.31 7.31 7.30 7.29 7.29
4.80 4.79 4.79 4.78 4.77 4.76
3.69
2.48 2.47 2.45 2.13 2.11 2.09 2.08
4.8
1.0
3.0
2.3
2.3
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)


HO
O
OMe
Ph
11
^{13}C NMR
(CDCl$_3$, 101 MHz)
174.3
144.0
128.5 127.7 125.8
73.6
51.7
33.8 30.4
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

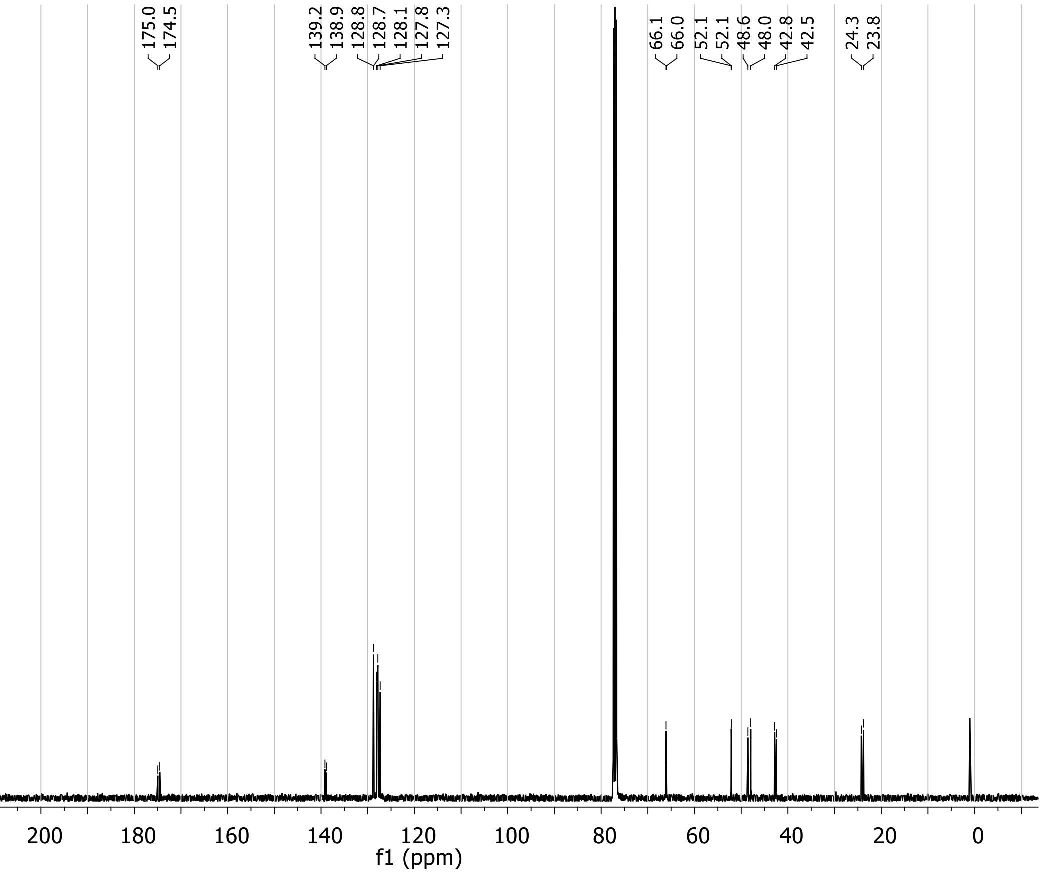


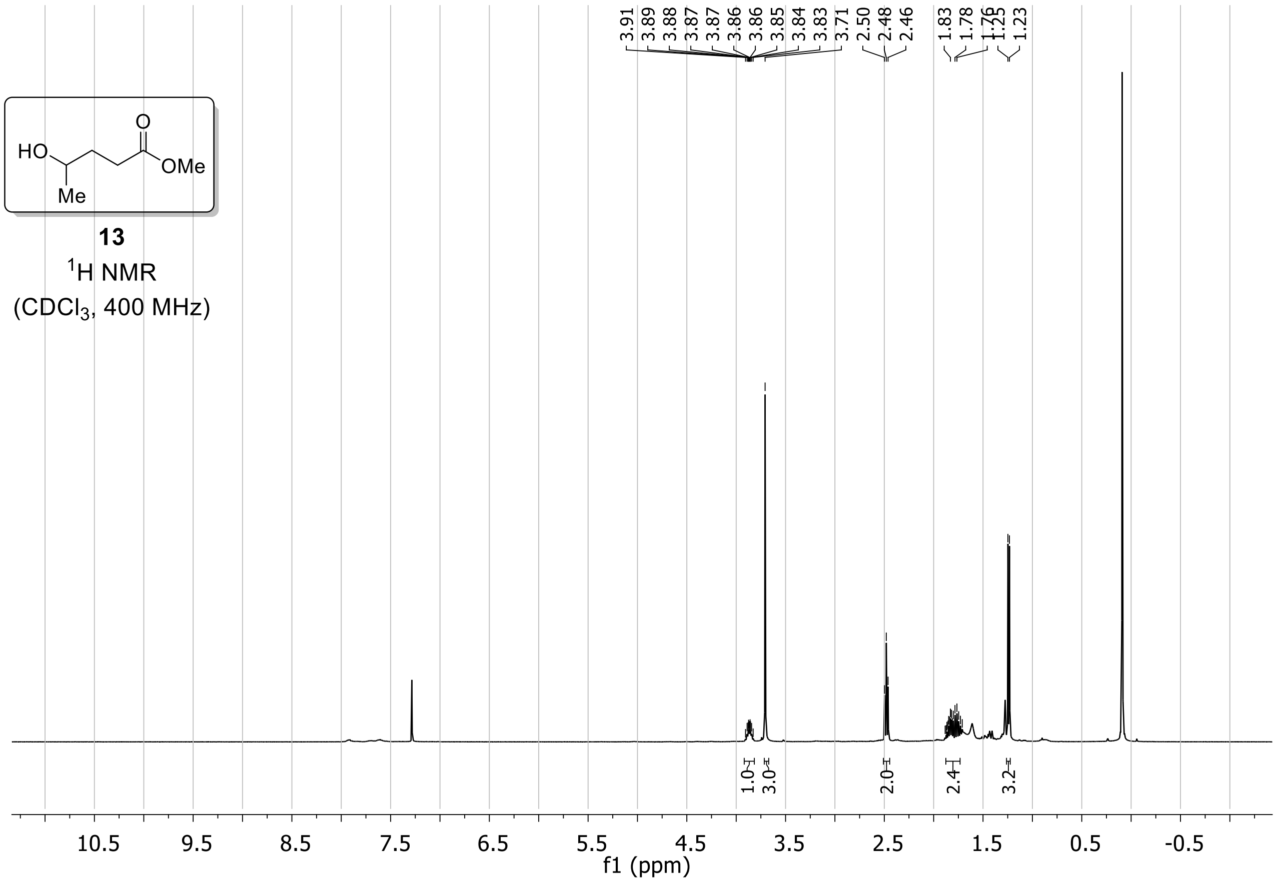
12
^{1}H NMR
($CDCl_3$, 400 MHz)



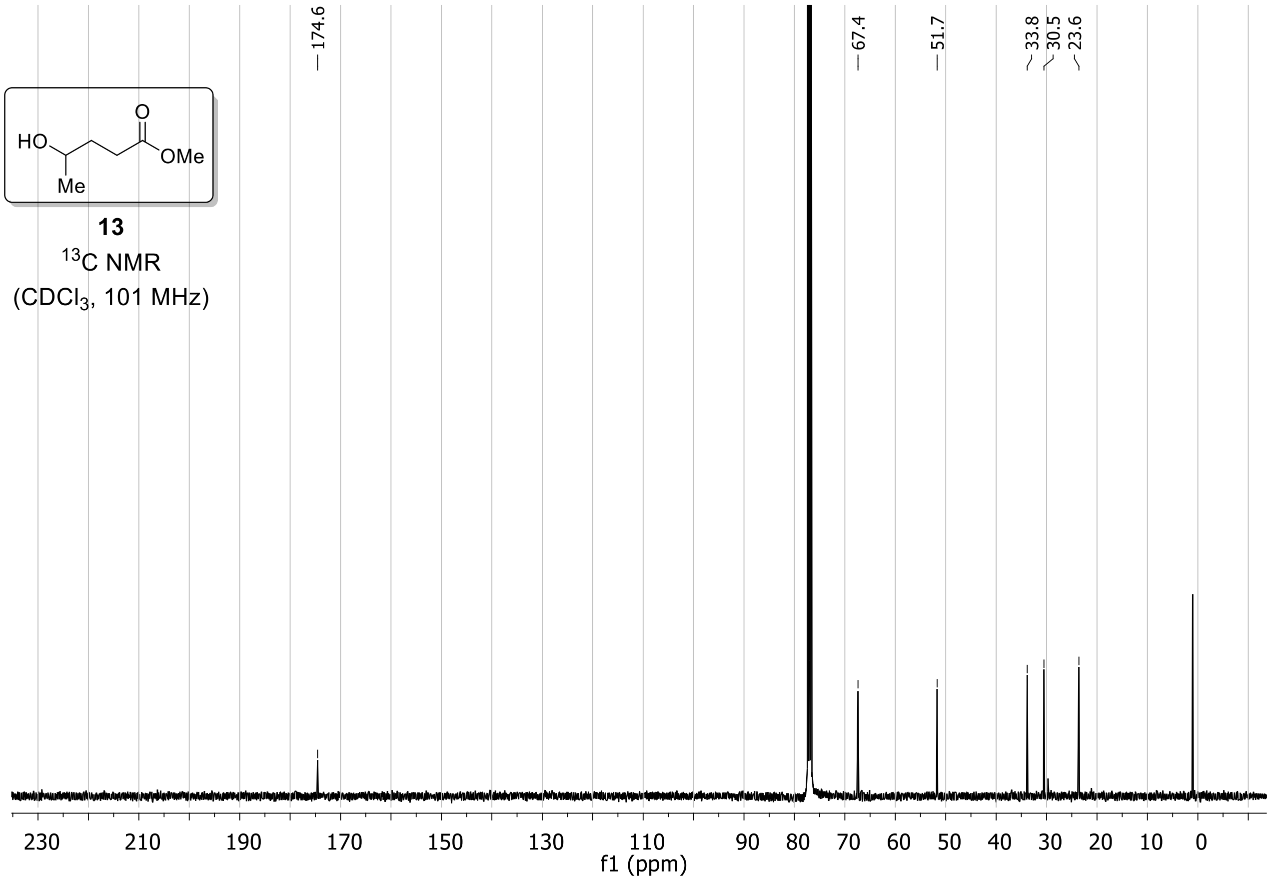


12
^{13}C NMR
($CDCl_3$, 101 MHz)

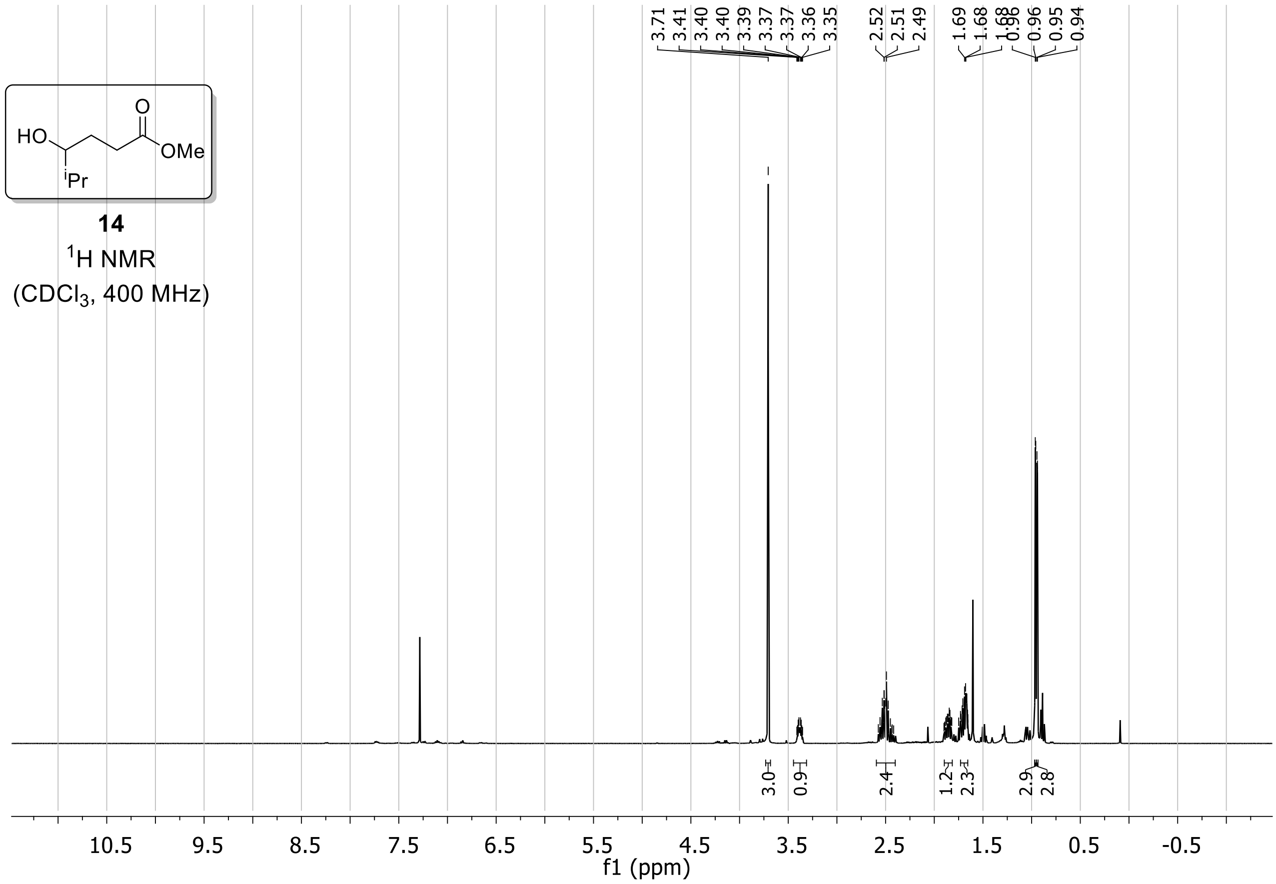




HO
O
OMe
Me
13
^{1}H NMR
(CDCl$_3$, 400 MHz)
3.91 3.89 3.88 3.87 3.87 3.86 3.86 3.85 3.84 3.83 3.71 2.50 2.48 2.46 1.83 1.78 1.76 1.25 1.23
1.0 3.0 2.0 2.4 3.2
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)



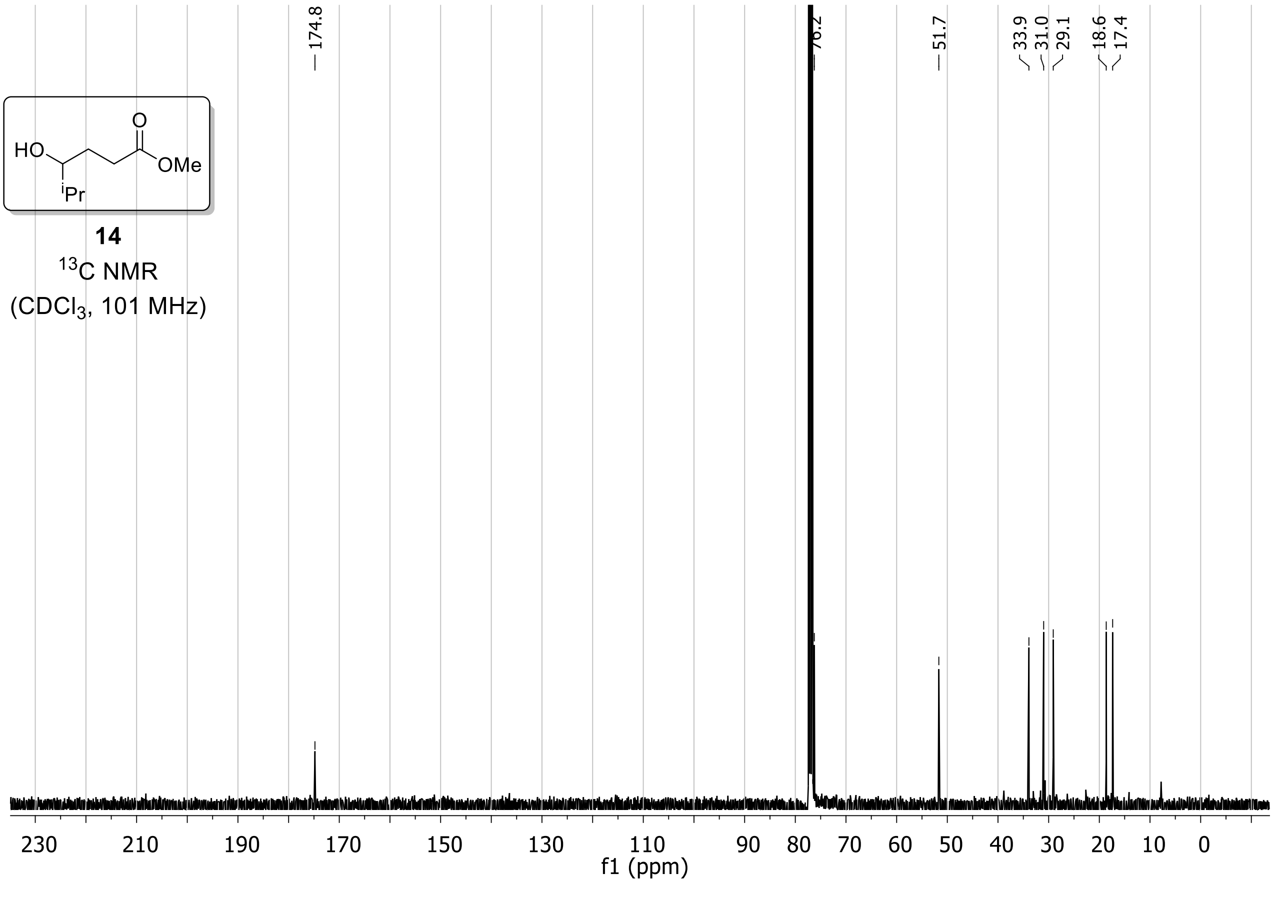
HO
O
OMe
Me
13
^{13}C NMR
(CDCl$_3$, 101 MHz)
174.6
67.4
51.7
33.8 30.5 23.6
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



14

^{1}H NMR

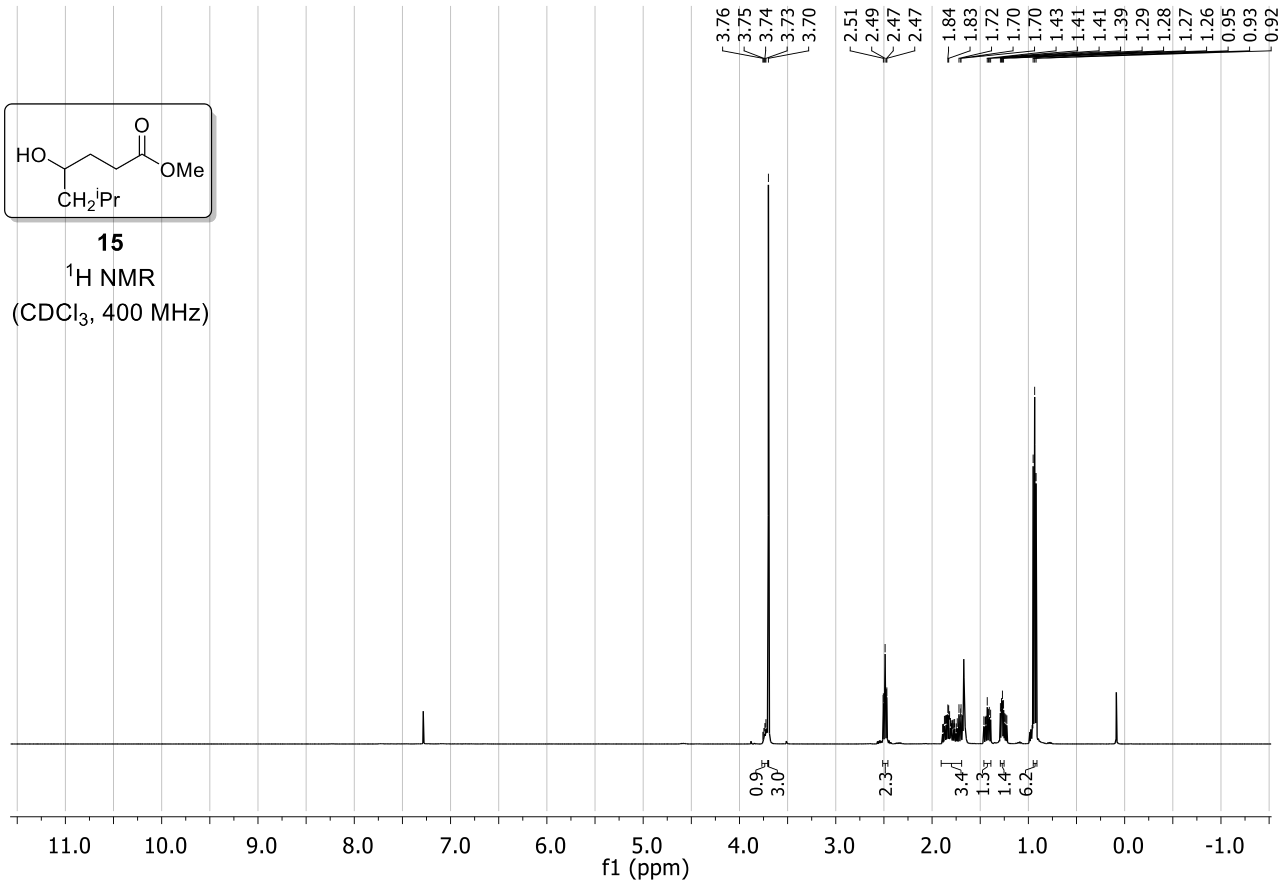
($CDCl_3$, 400 MHz)

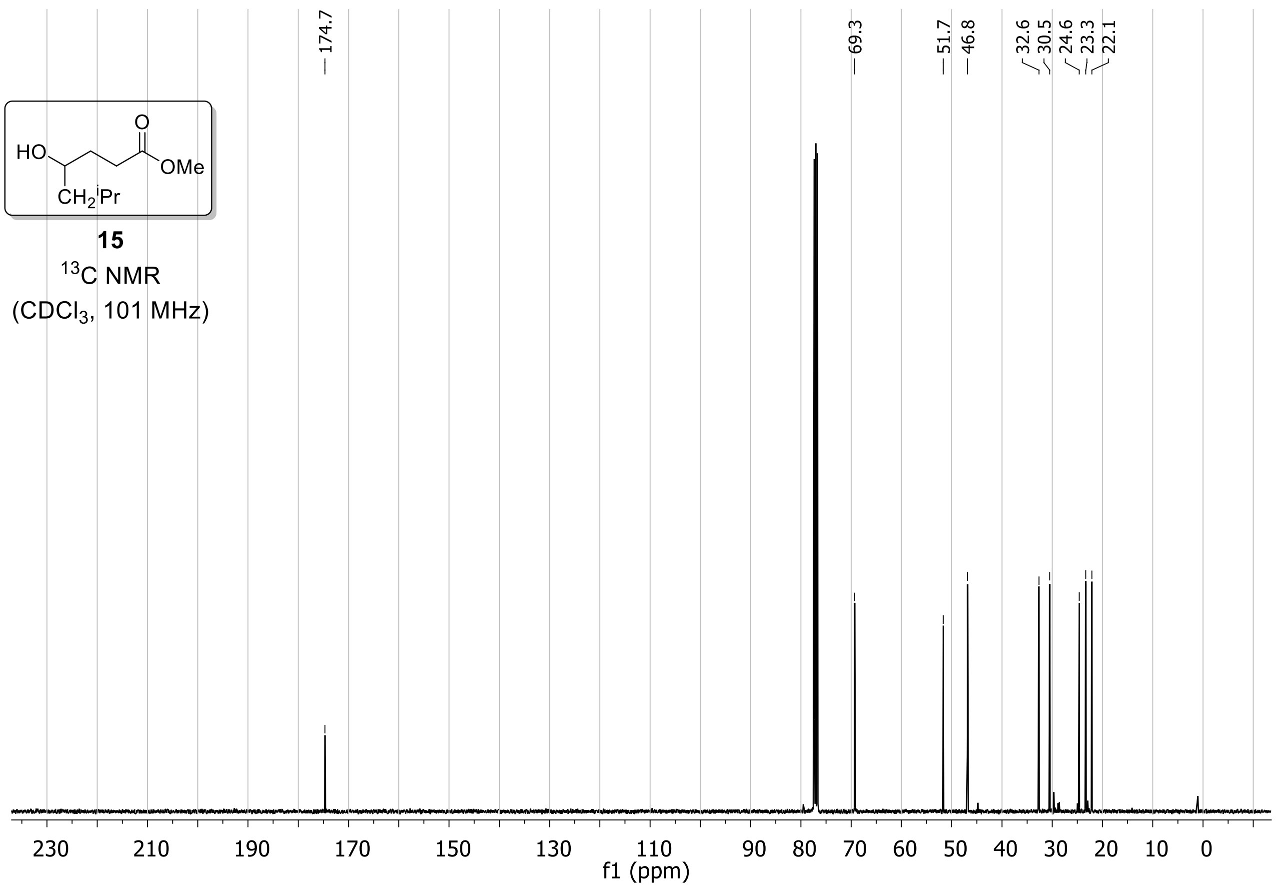


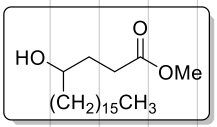
14

^{13}C NMR

($CDCl_3$, 101 MHz)



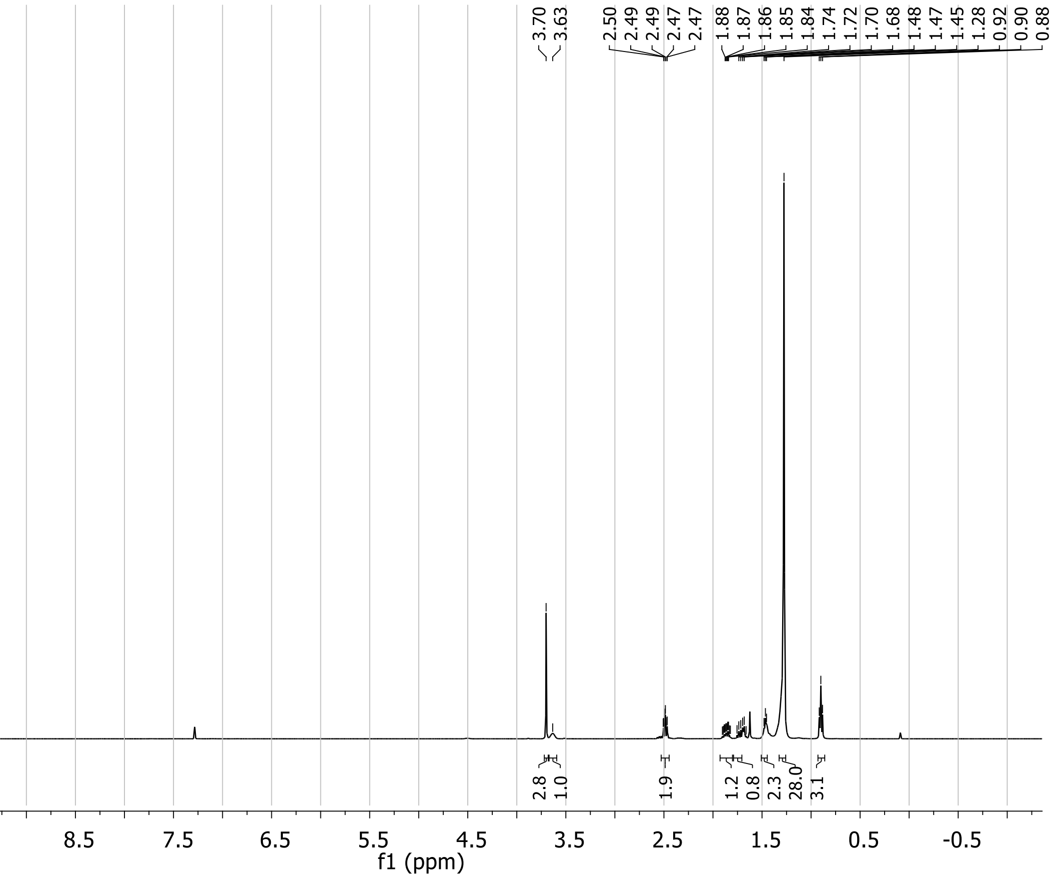


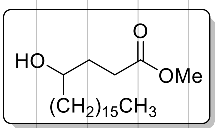


16

^{1}H NMR

($CDCl_3$, 400 MHz)

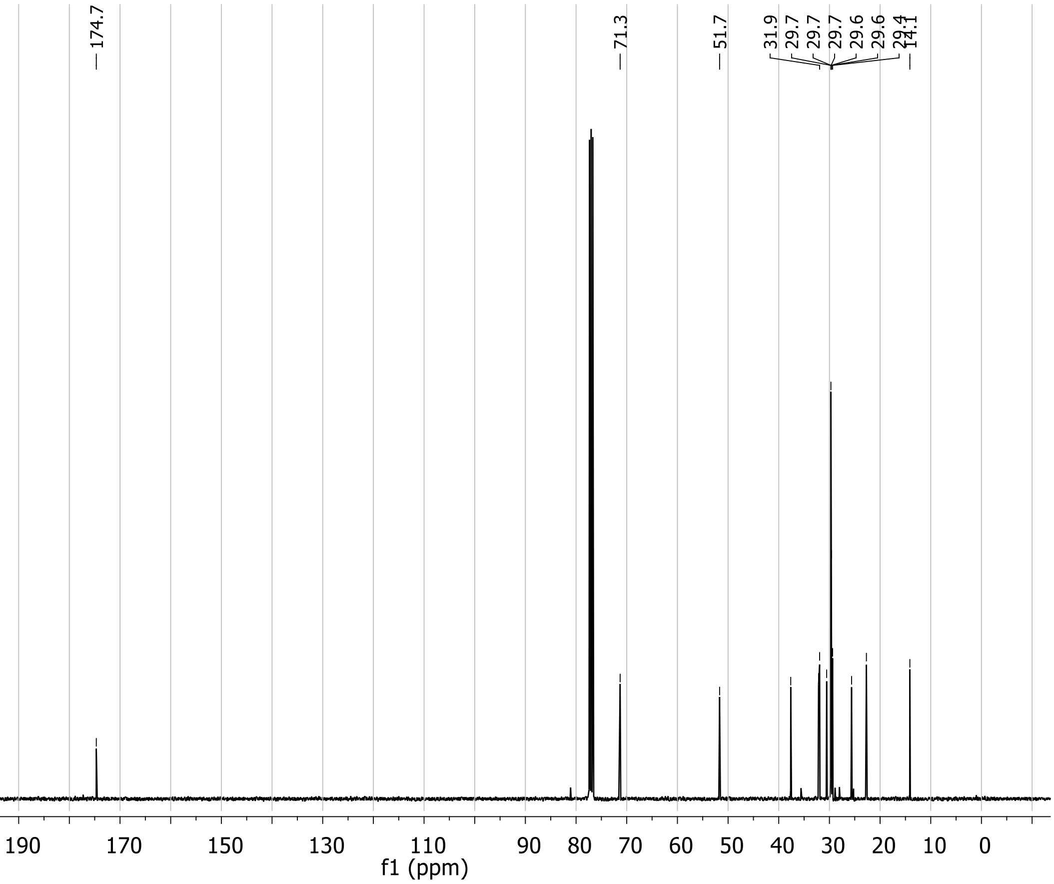


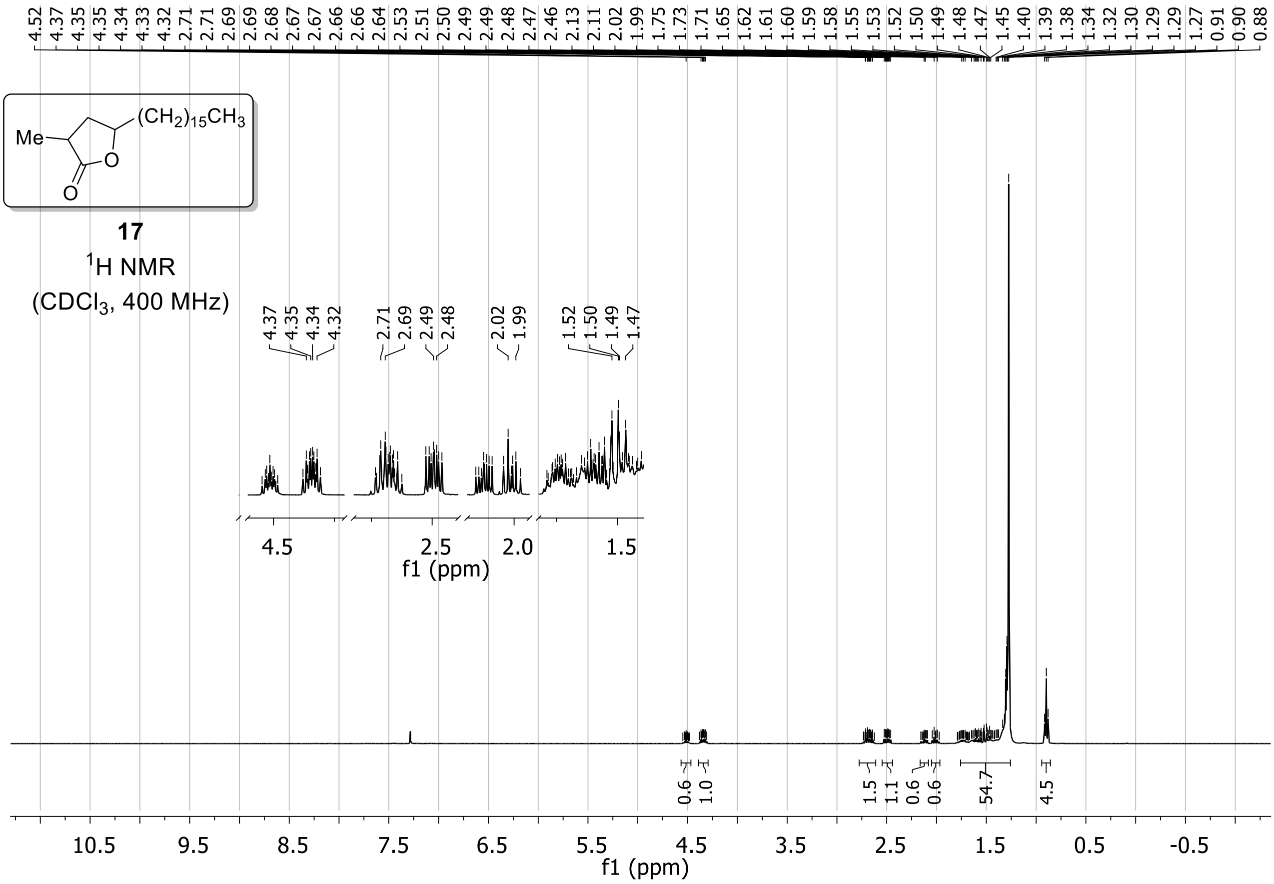


16

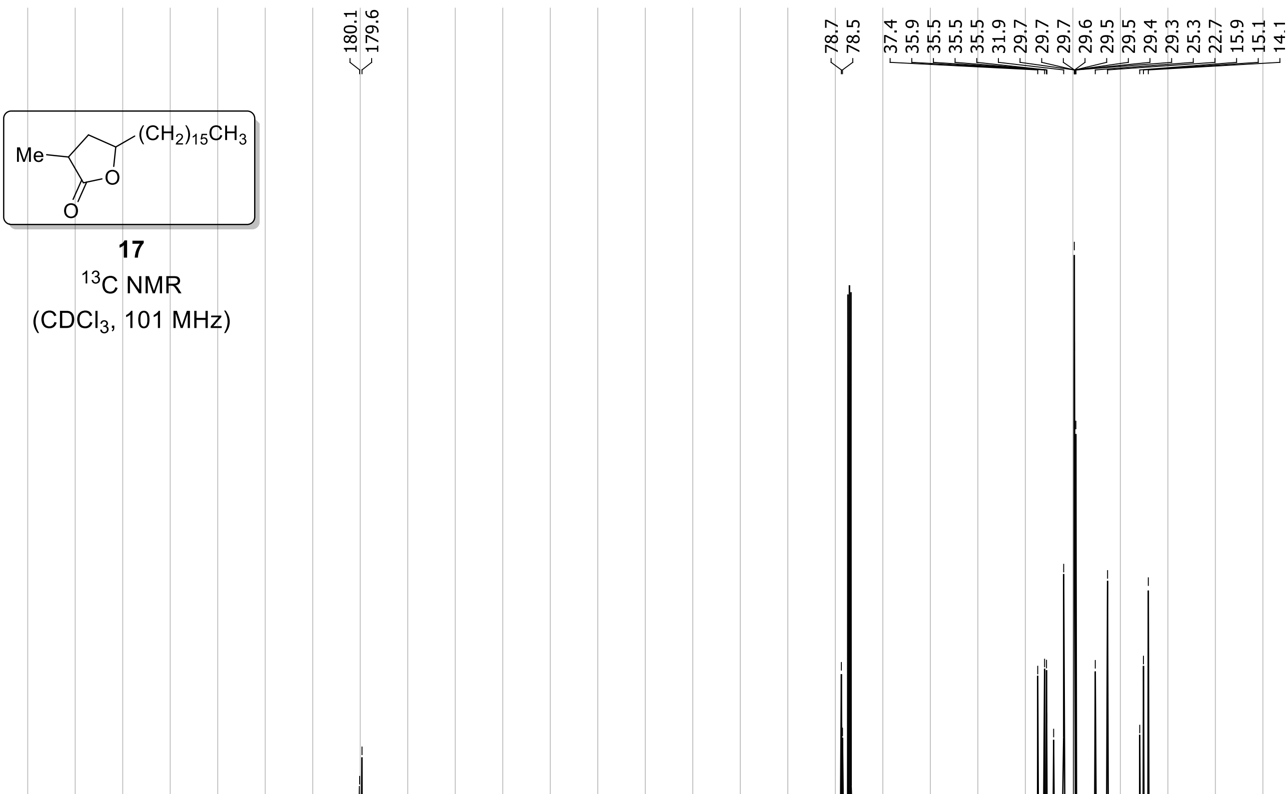
^{13}C NMR

($CDCl_3$, 101 MHz)

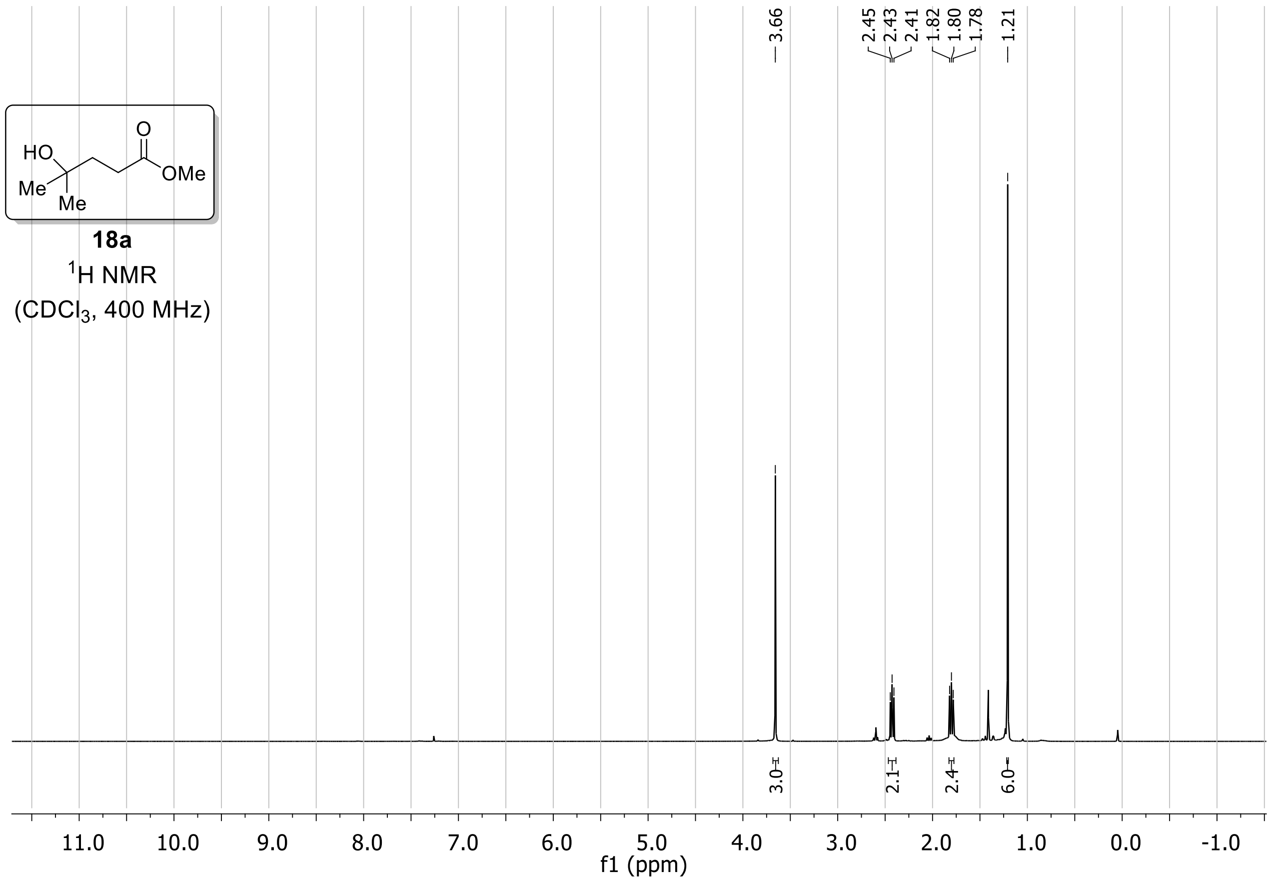


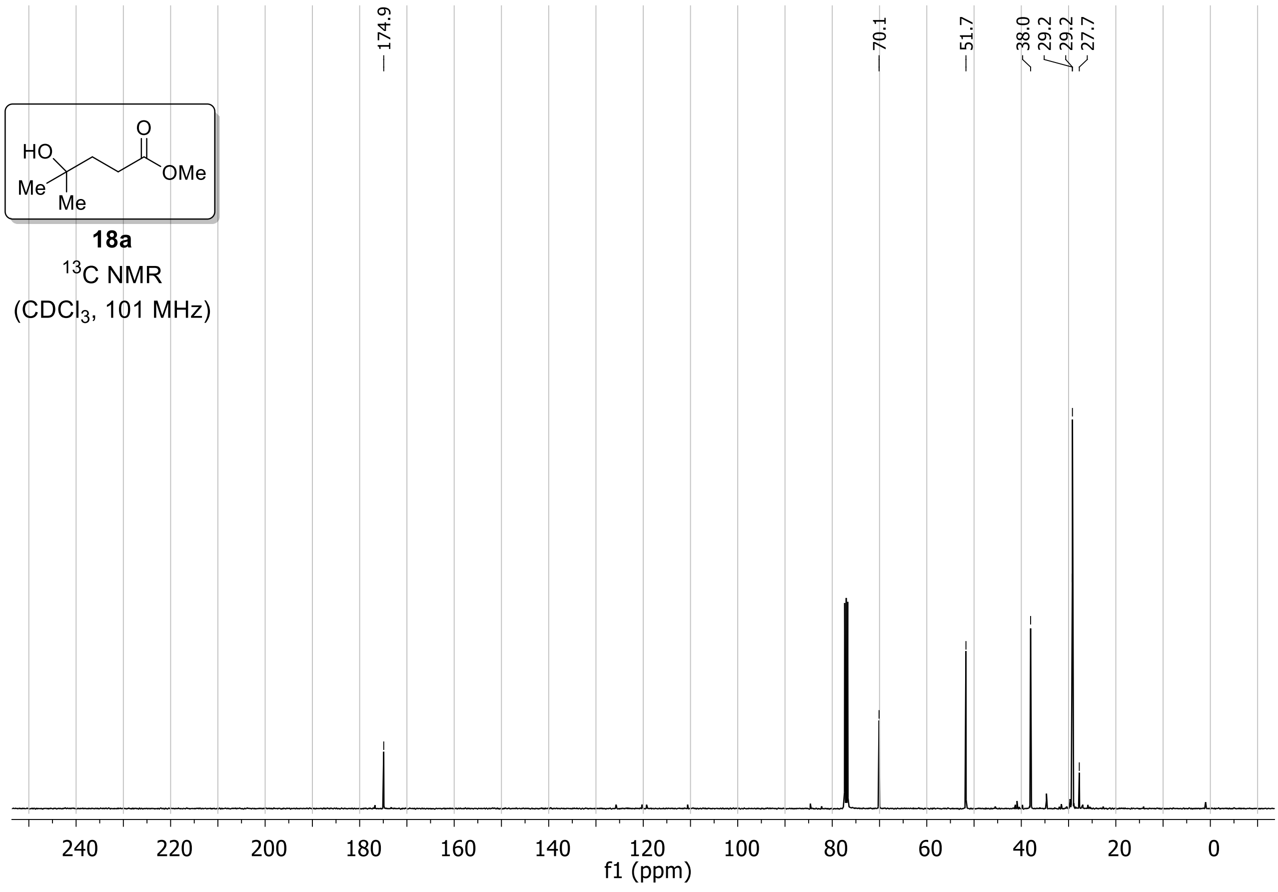


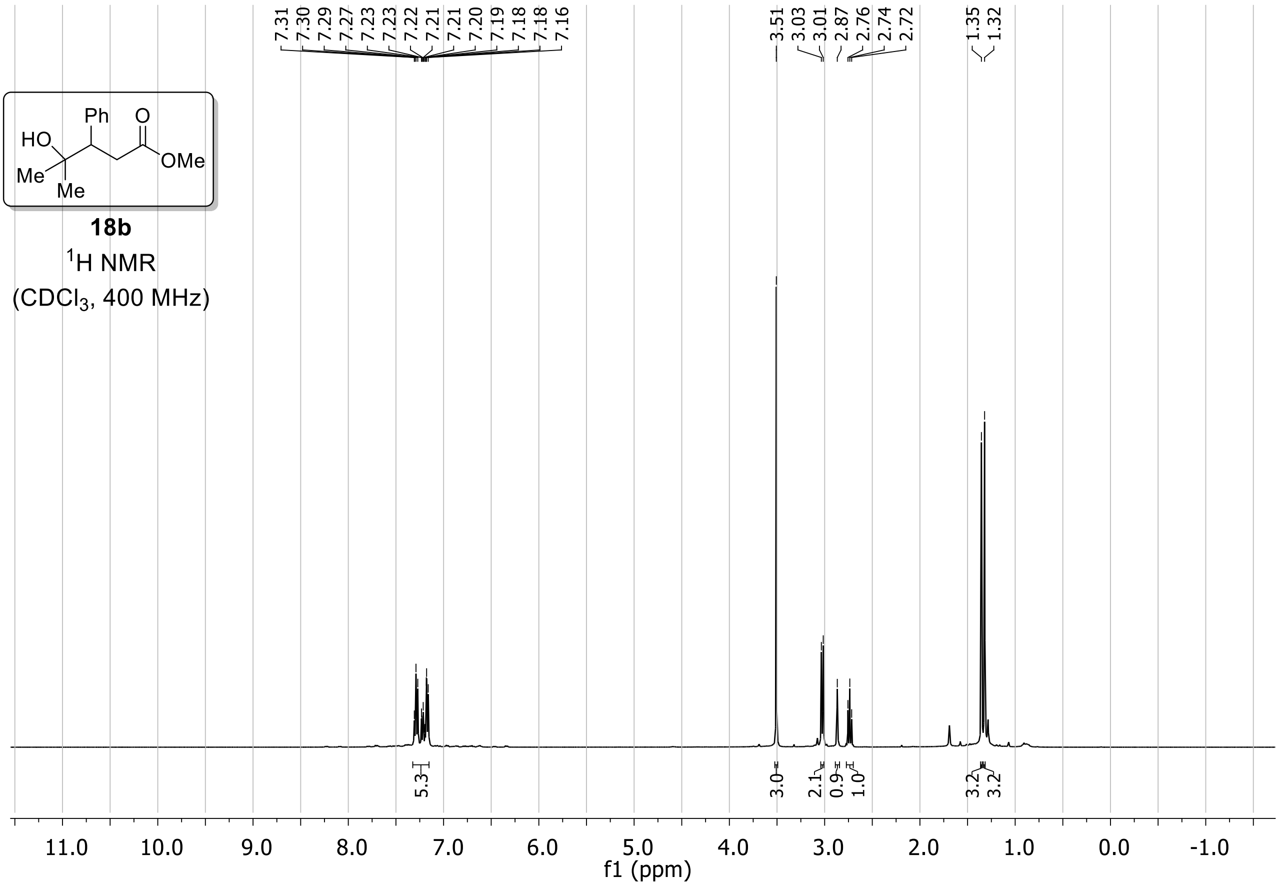
17
^{1}H NMR
($CDCl_3$, 400 MHz)



17
^{13}C NMR
($CDCl_3$, 101 MHz)


HO
O
OMe
Me
Me
18a
1H NMR
(CDCl3, 400 MHz)
3.66
2.45
2.43
2.41
1.82
1.80
1.78
1.21
3.0
2.1
2.4
6.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)

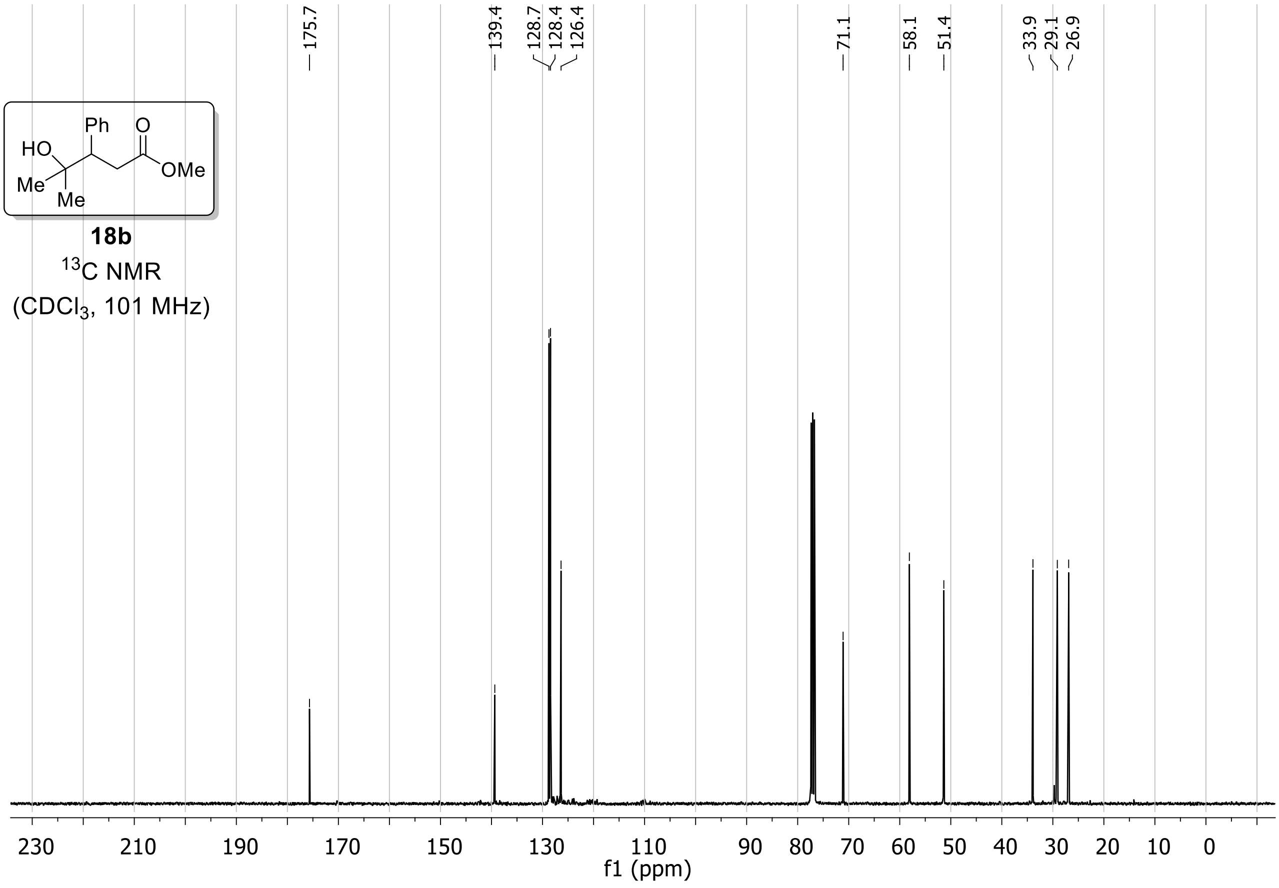

HO
O
OMe
Me
Me
18a
13C NMR
(CDCl3, 101 MHz)
174.9
70.1
51.7
38.0
29.2
29.2
27.7
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)



18b

^{1}H NMR

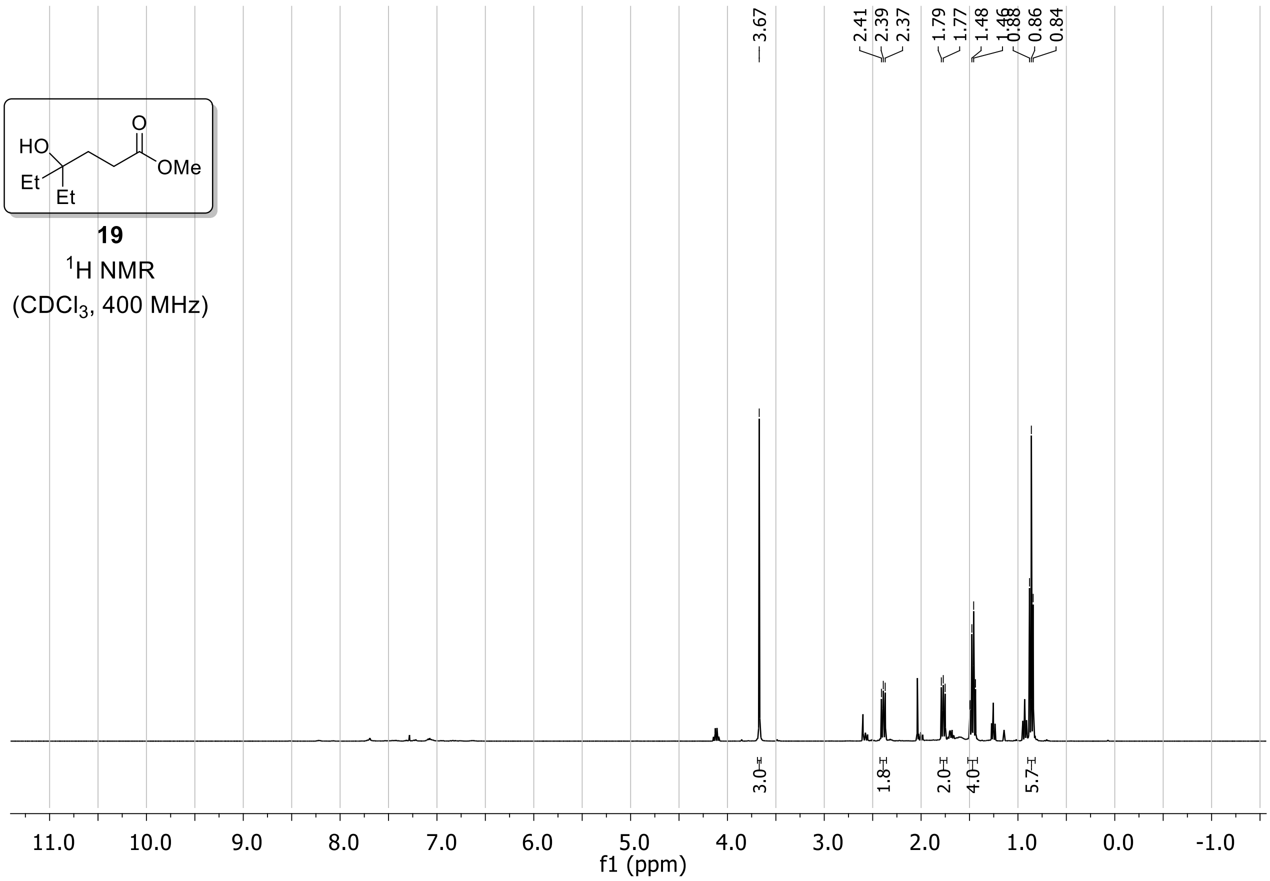
($CDCl_3$, 400 MHz)



18b

^{13}C NMR

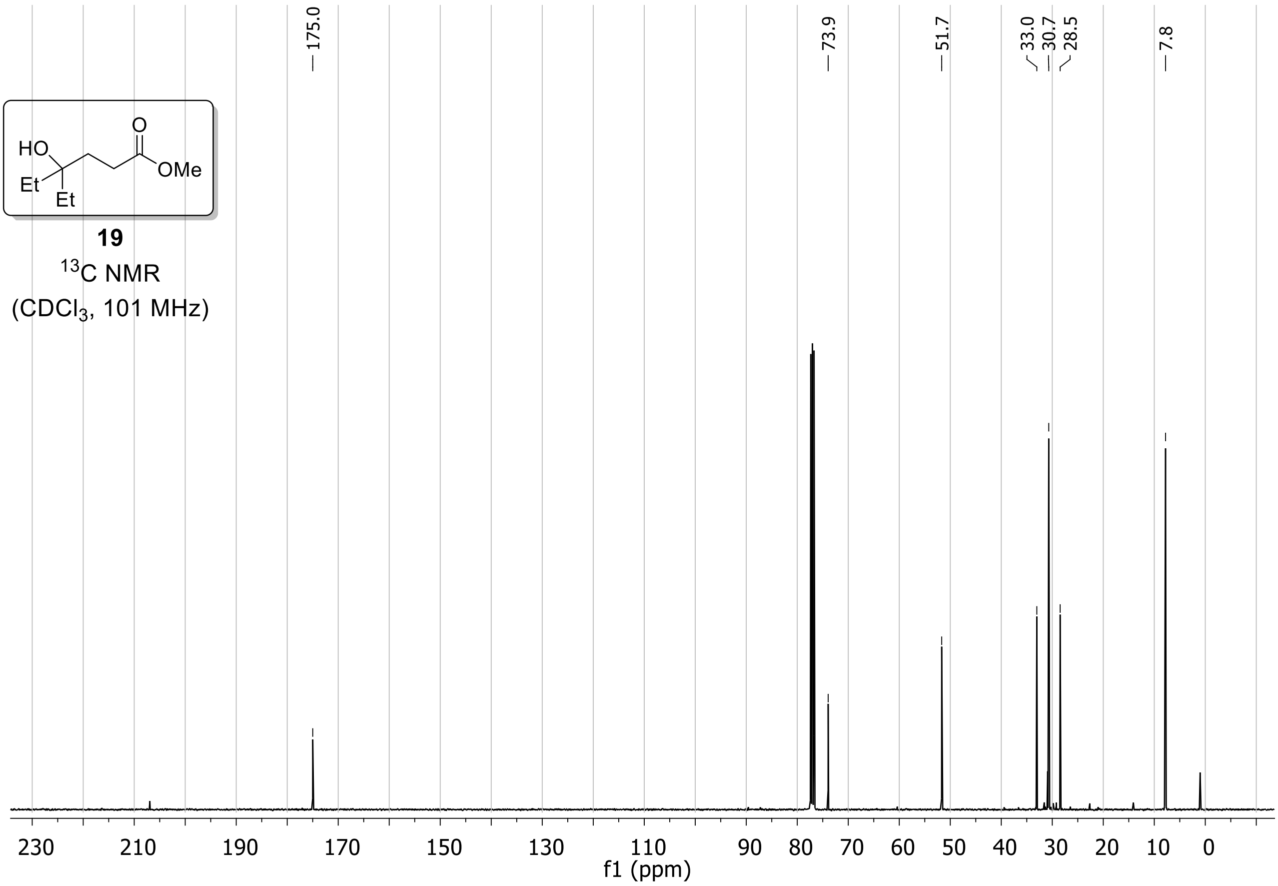
($CDCl_3$, 101 MHz)



19

^{1}H NMR

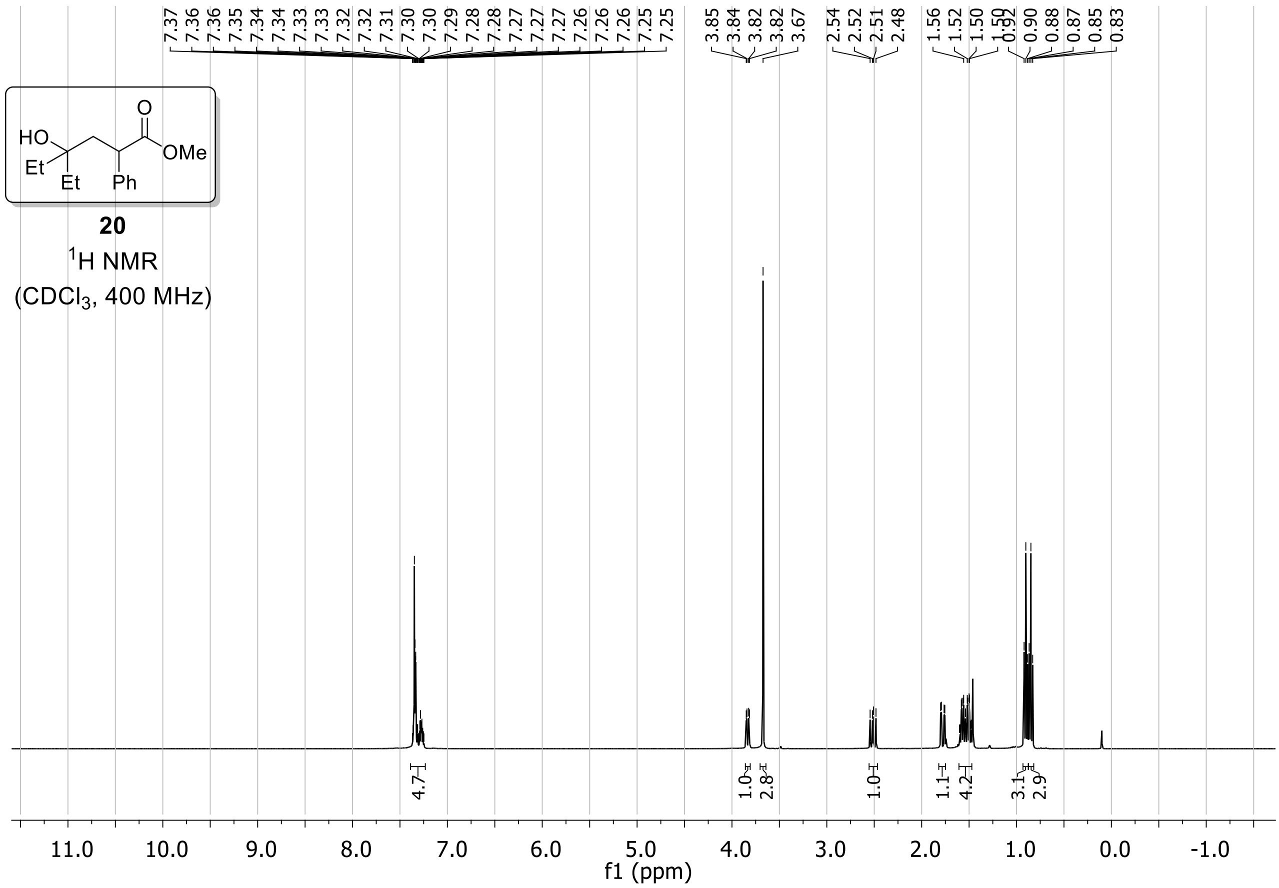
($CDCl_3$, 400 MHz)



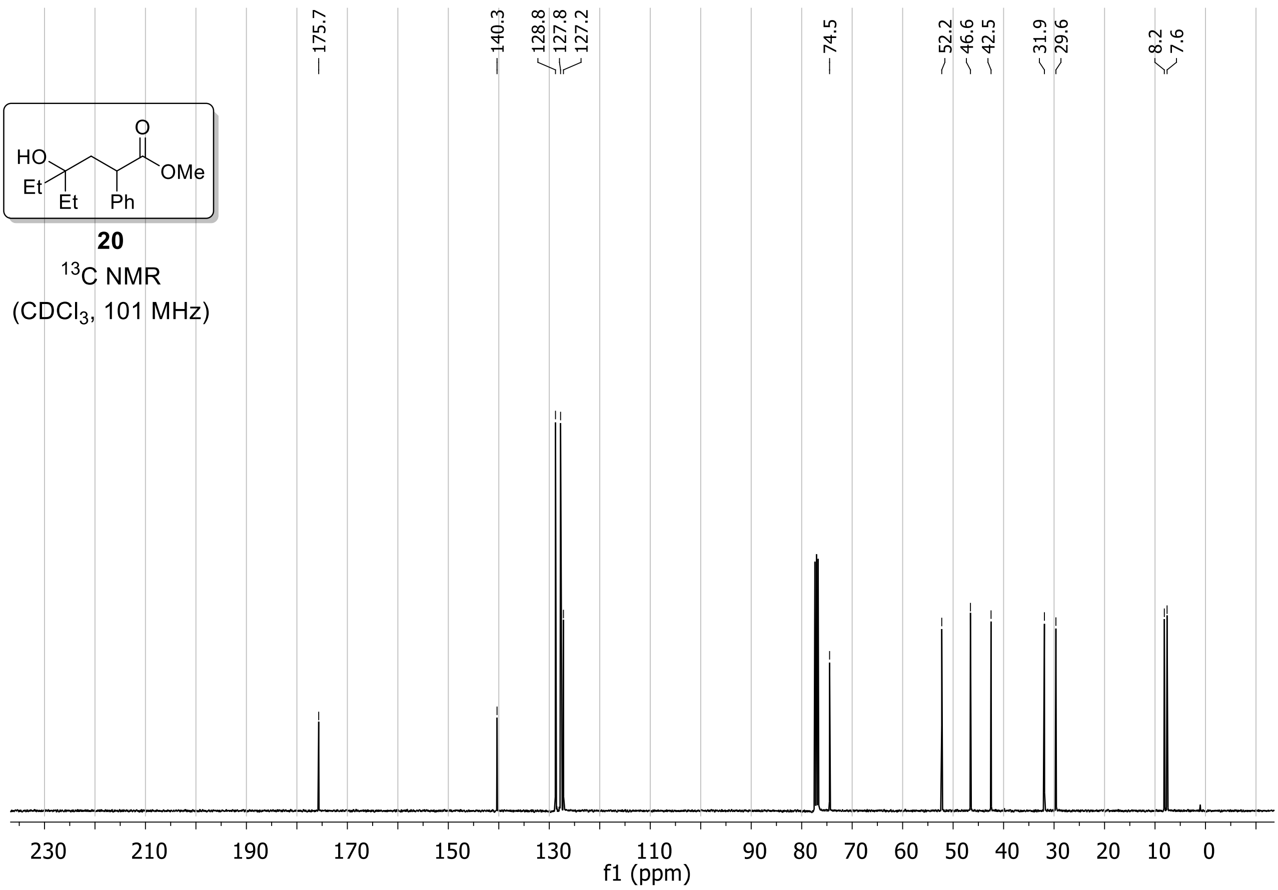
19

^{13}C NMR

($CDCl_3$, 101 MHz)



20
^{1}H NMR
($CDCl_3$, 400 MHz)

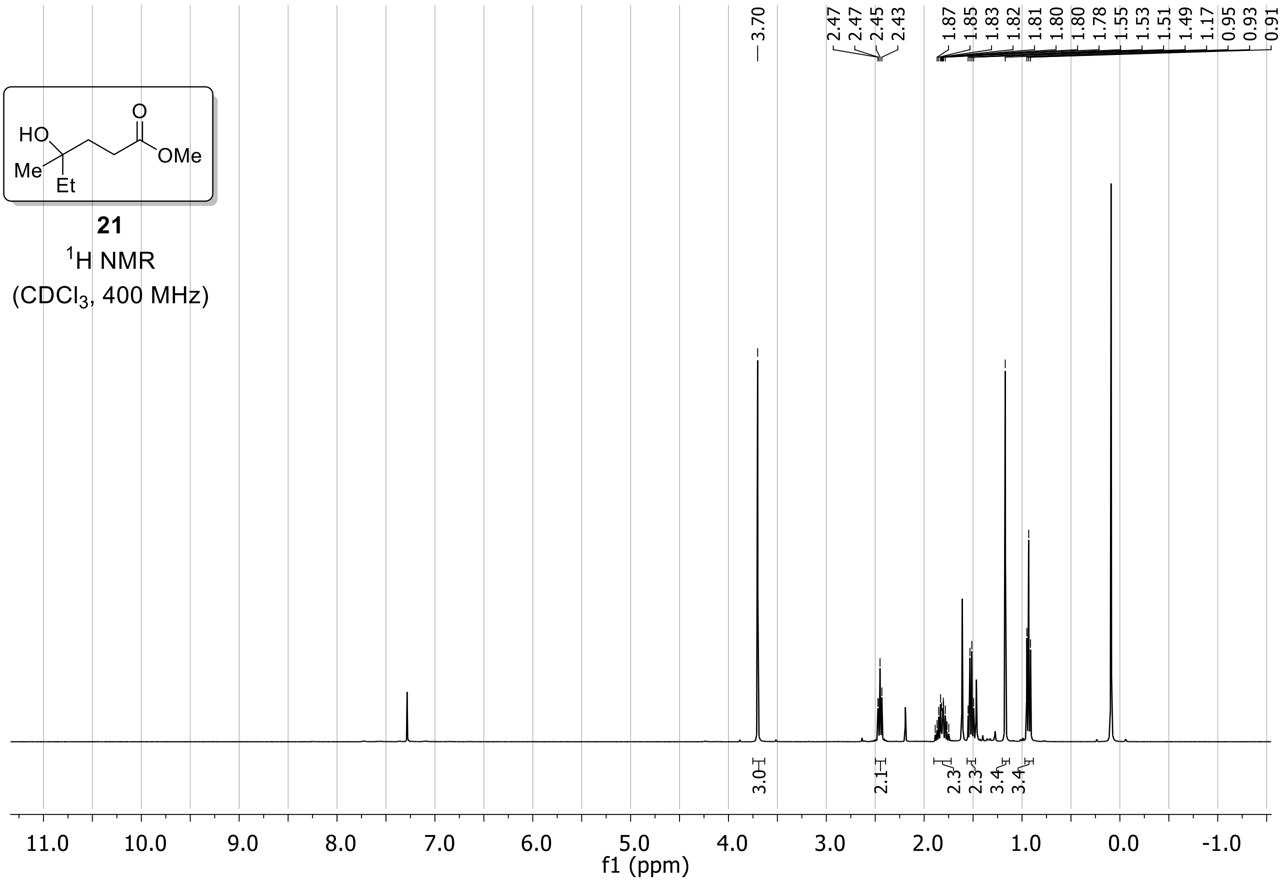


20
^{13}C NMR
($CDCl_3$, 101 MHz)

21

^{1}H NMR

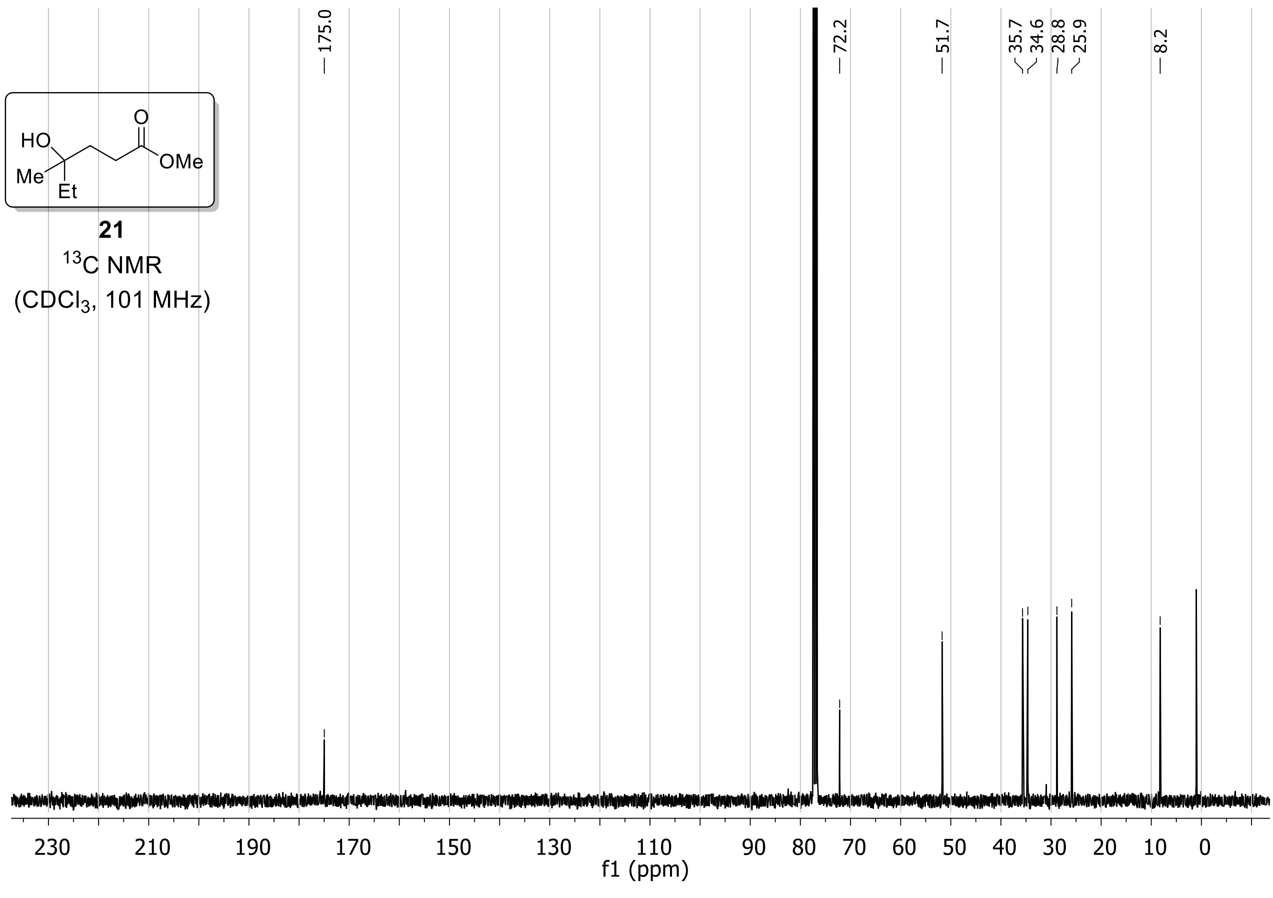
($CDCl_3$, 400 MHz)

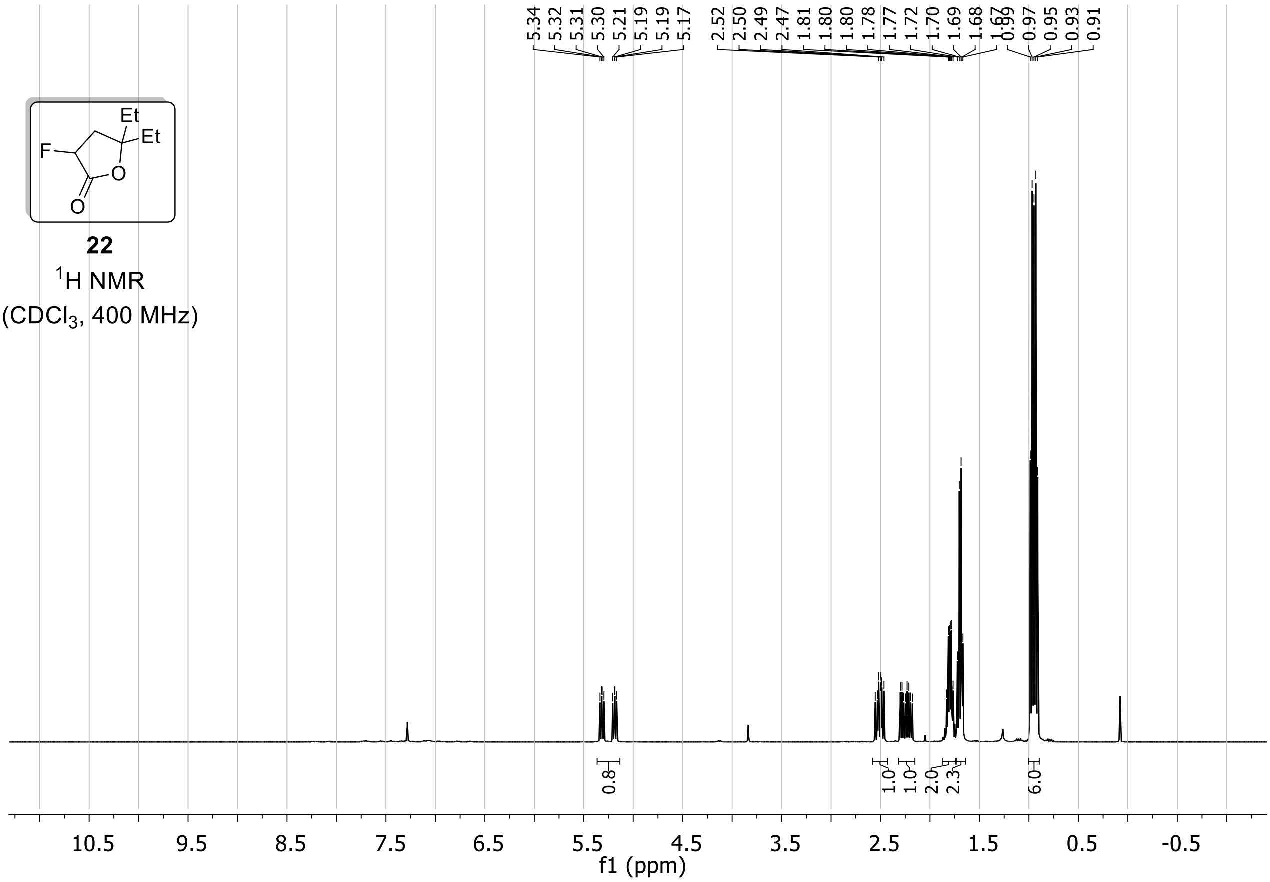


21

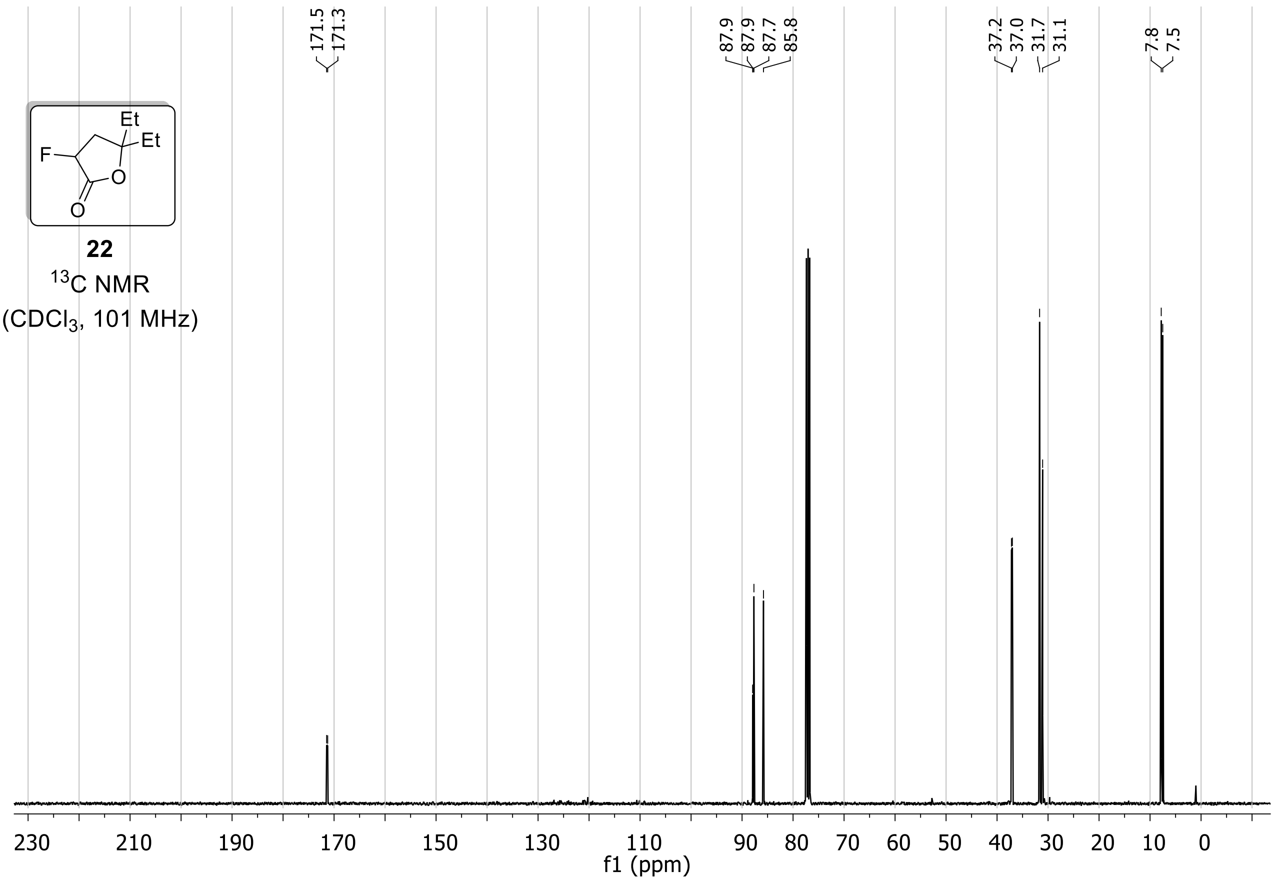
^{13}C NMR

($CDCl_3$, 101 MHz)

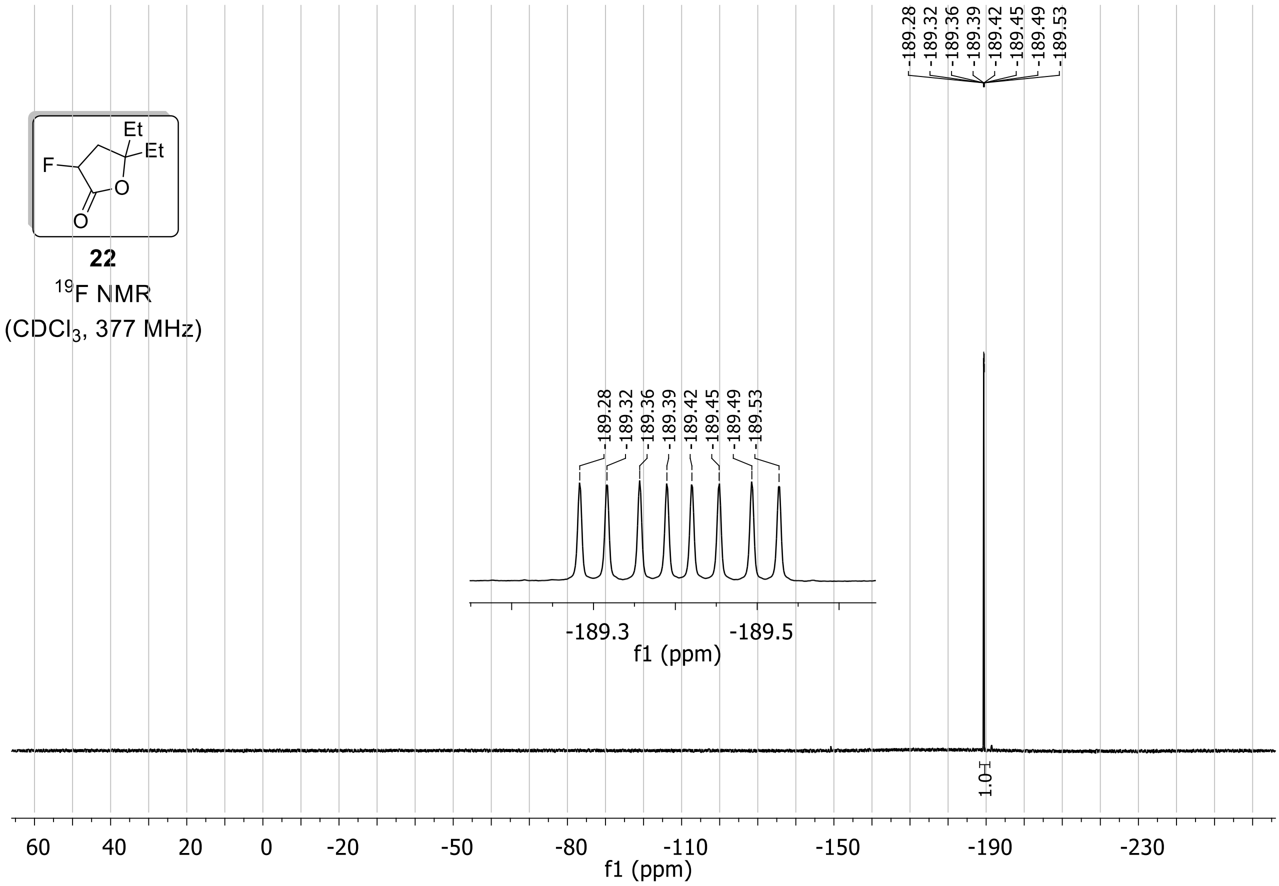


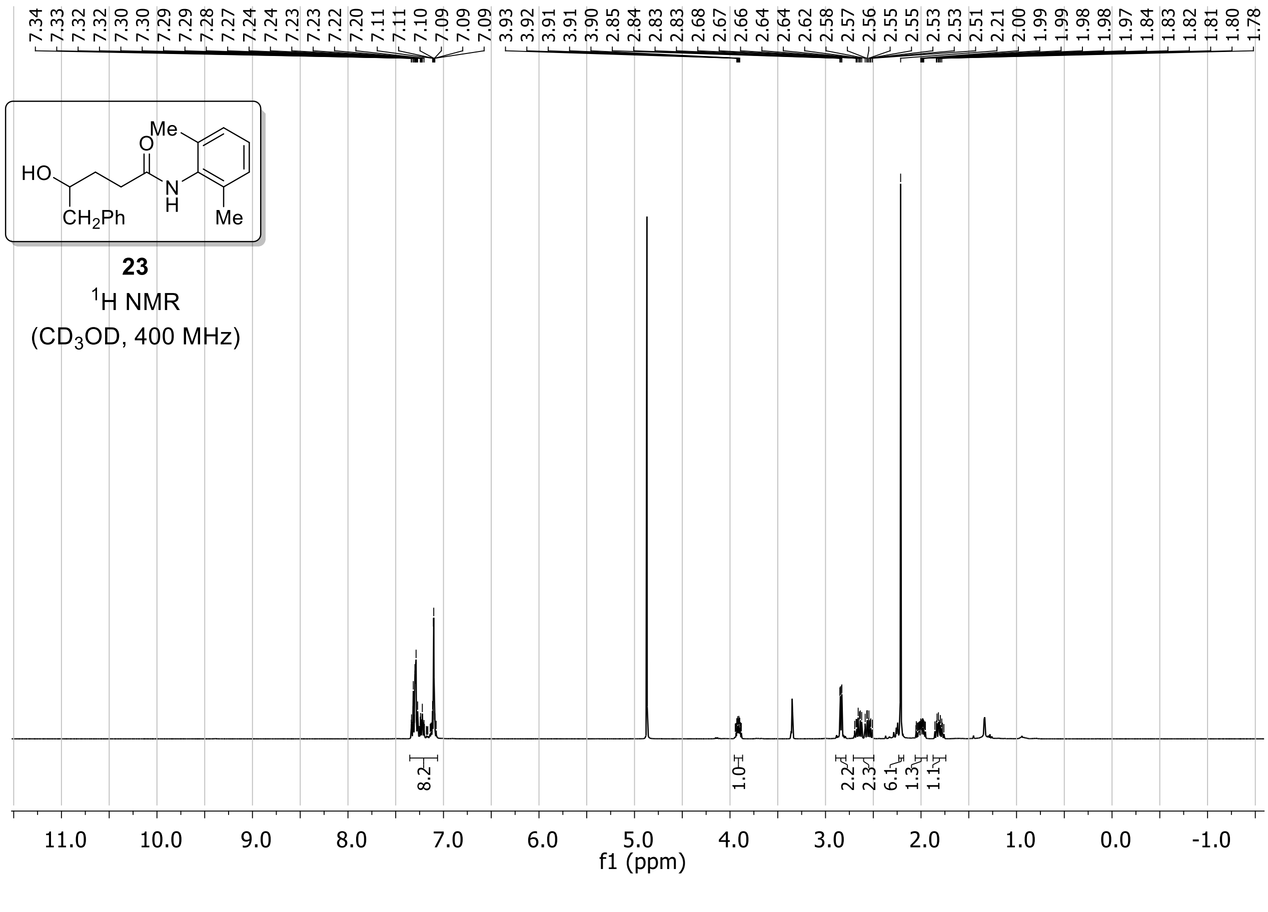


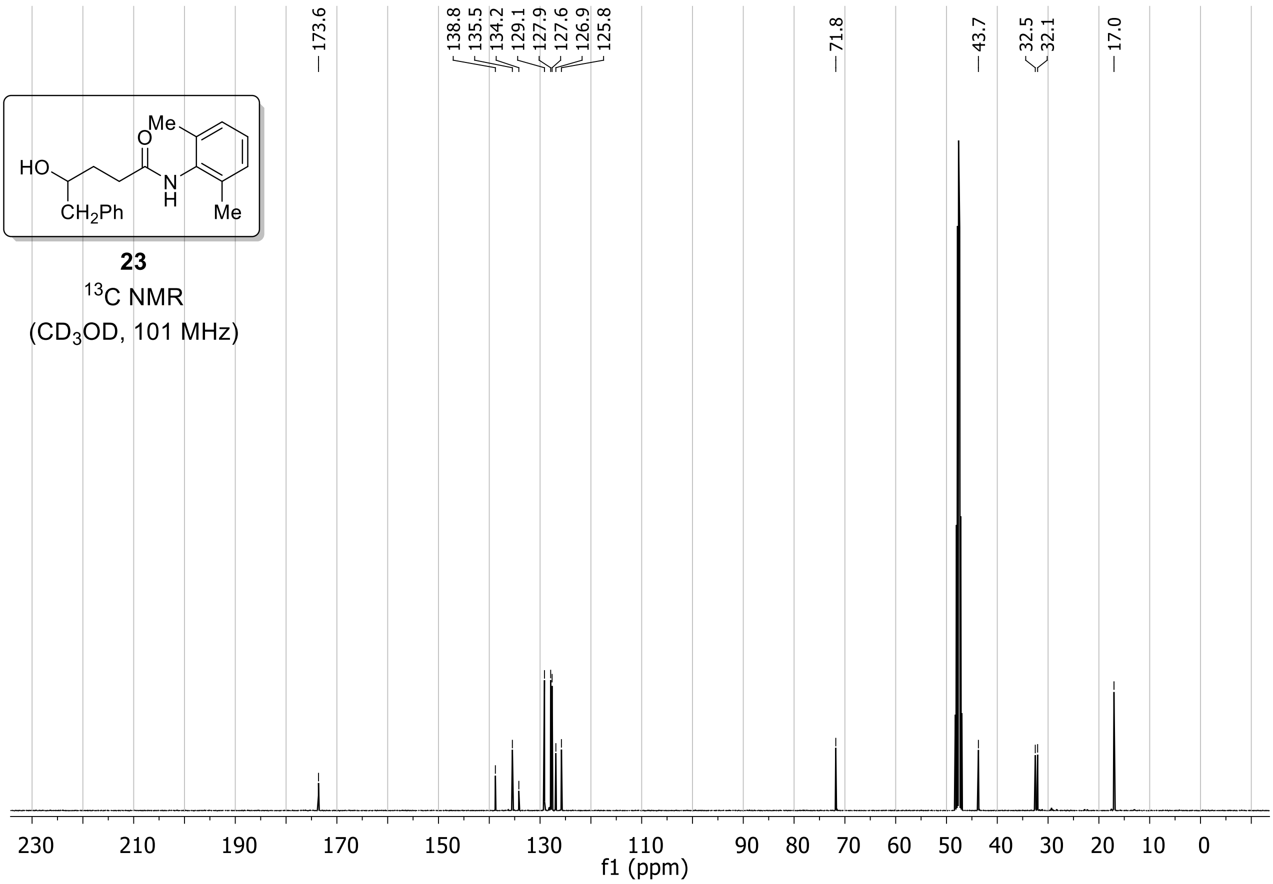
22
^{1}H NMR
($CDCl_3$, 400 MHz)



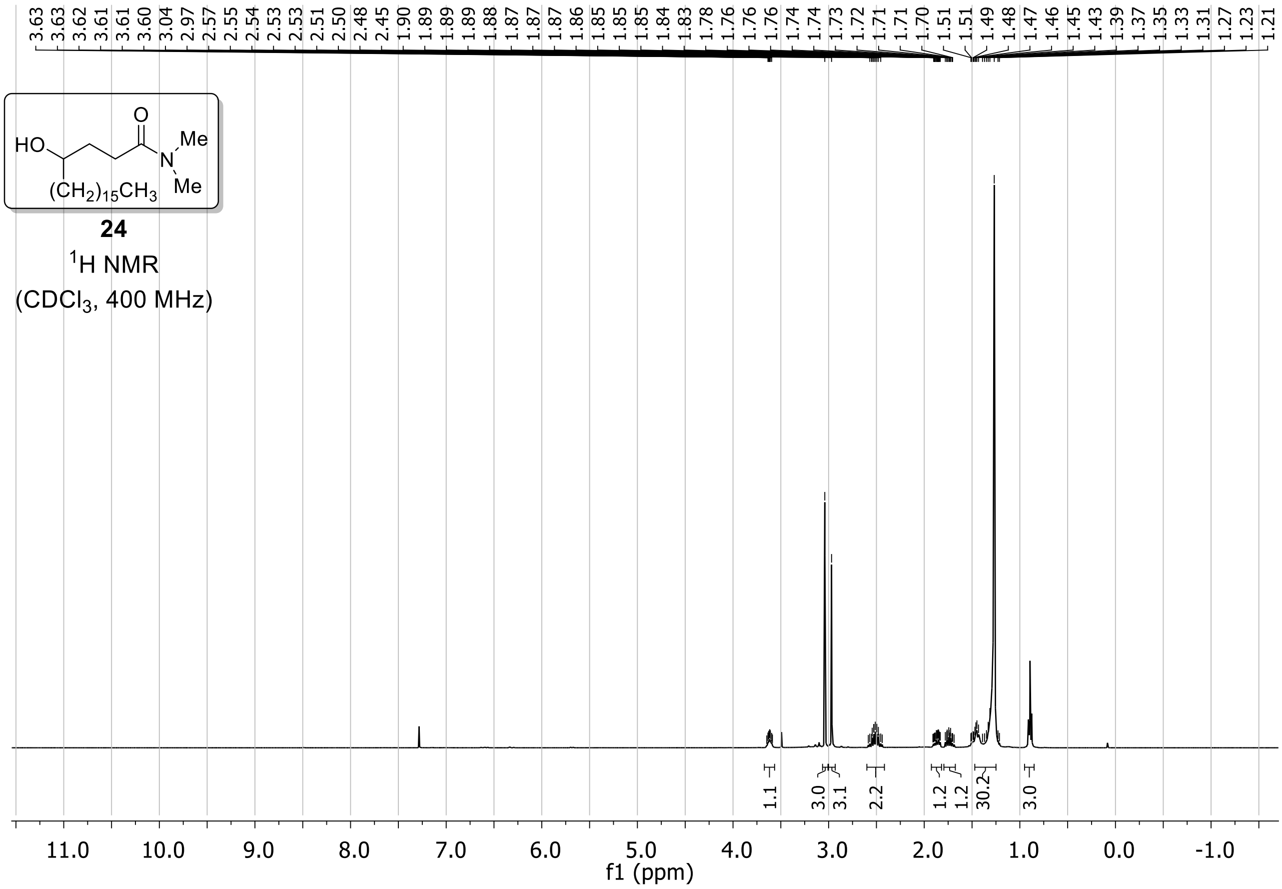
22
^{13}C NMR
($CDCl_3$, 101 MHz)


Et
Et
F
O
O
22
^{19}F NMR
($CDCl_3$, 377 MHz)
-189.28
-189.32
-189.36
-189.39
-189.42
-189.45
-189.49
-189.53
-189.3
-189.5
f1 (ppm)
1.0
60
40
20
0
-20
-50
-80
-110
-150
-190
-230
f1 (ppm)

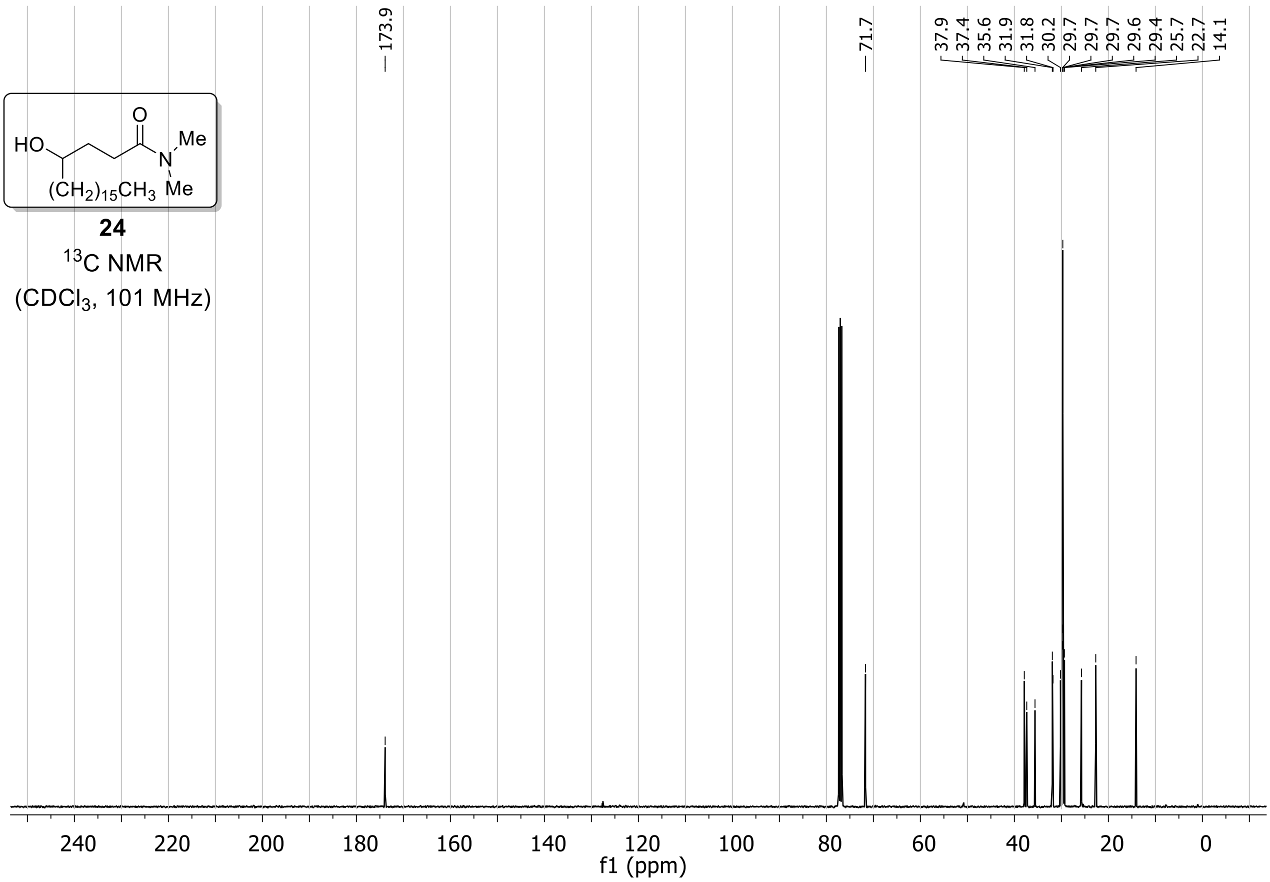

7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.29
7.28
7.27
7.24
7.24
7.23
7.23
7.22
7.22
7.20
7.11
7.11
7.10
7.09
7.09
7.09
3.93
3.92
3.91
3.91
3.90
2.85
2.84
2.83
2.83
2.68
2.67
2.66
2.64
2.64
2.62
2.58
2.57
2.56
2.55
2.55
2.53
2.53
2.51
2.21
2.00
1.99
1.99
1.98
1.98
1.97
1.84
1.83
1.82
1.81
1.80
1.78
Me
O
HO
N
H
CH2Ph
Me
23
^{1}H NMR
(CD_3OD, 400 MHz)
8.2
1.0
2.2
2.3
6.1
1.3
1.1
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)



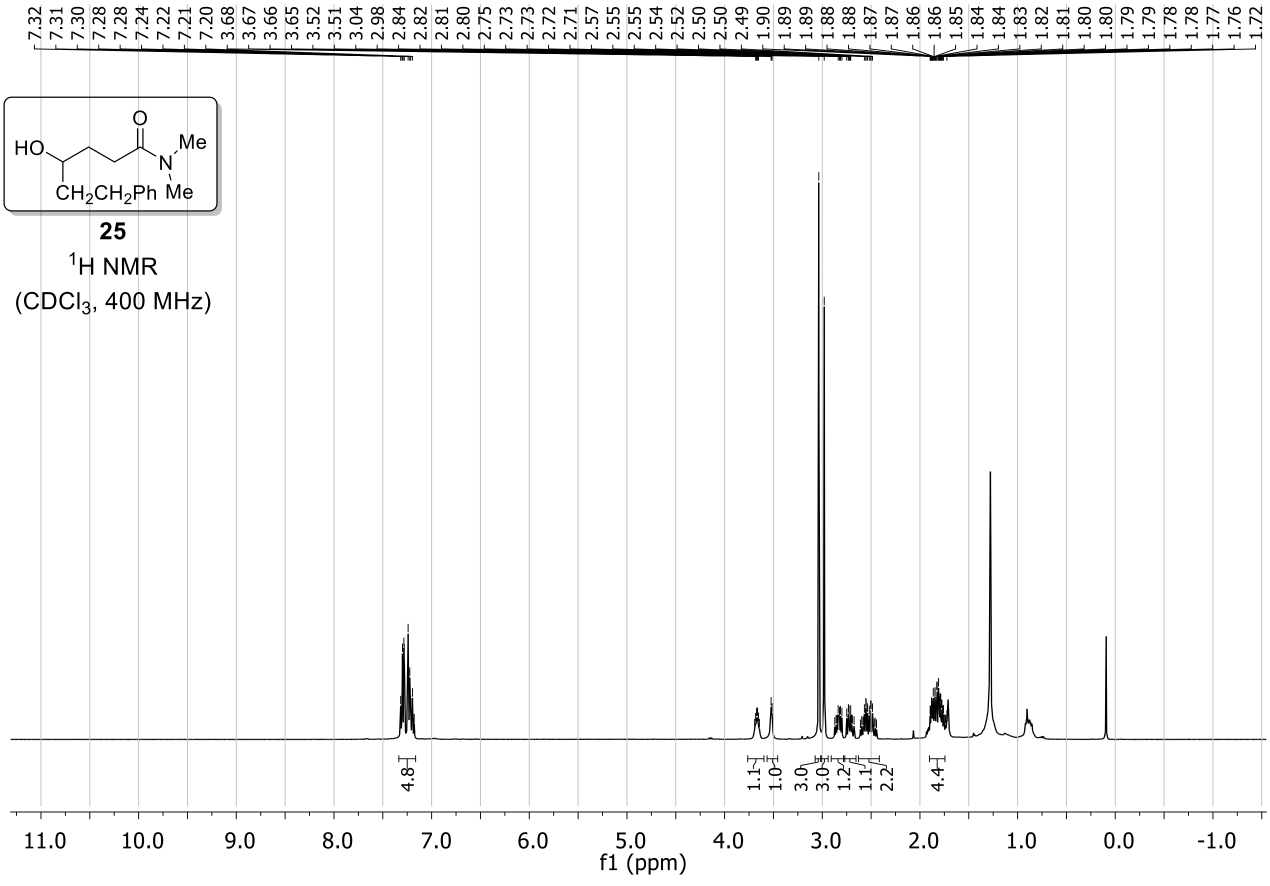
23
^{13}C NMR
(CD_3OD, 101 MHz)



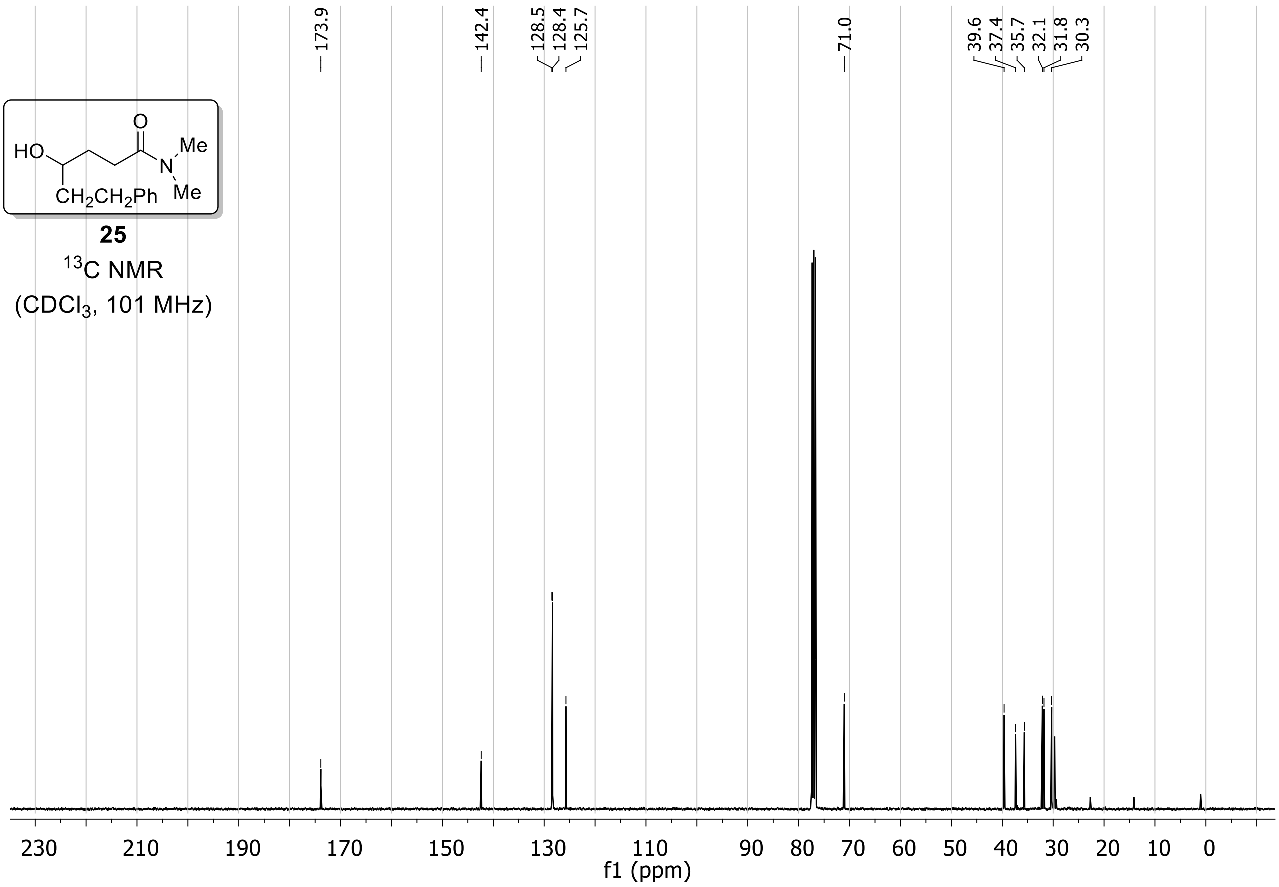
24
^{1}H NMR
($CDCl_3$, 400 MHz)



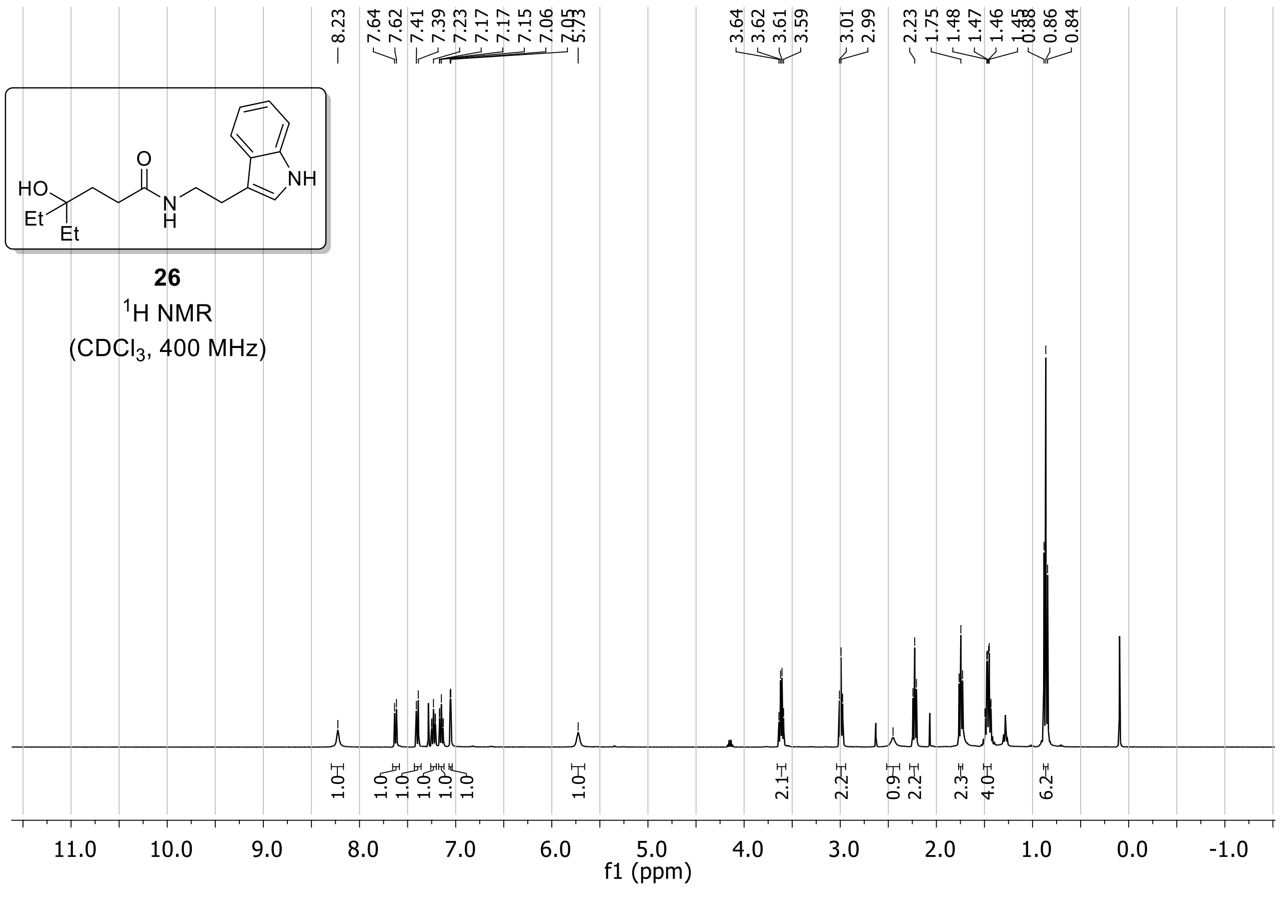
24
^{13}C NMR
($CDCl_3$, 101 MHz)



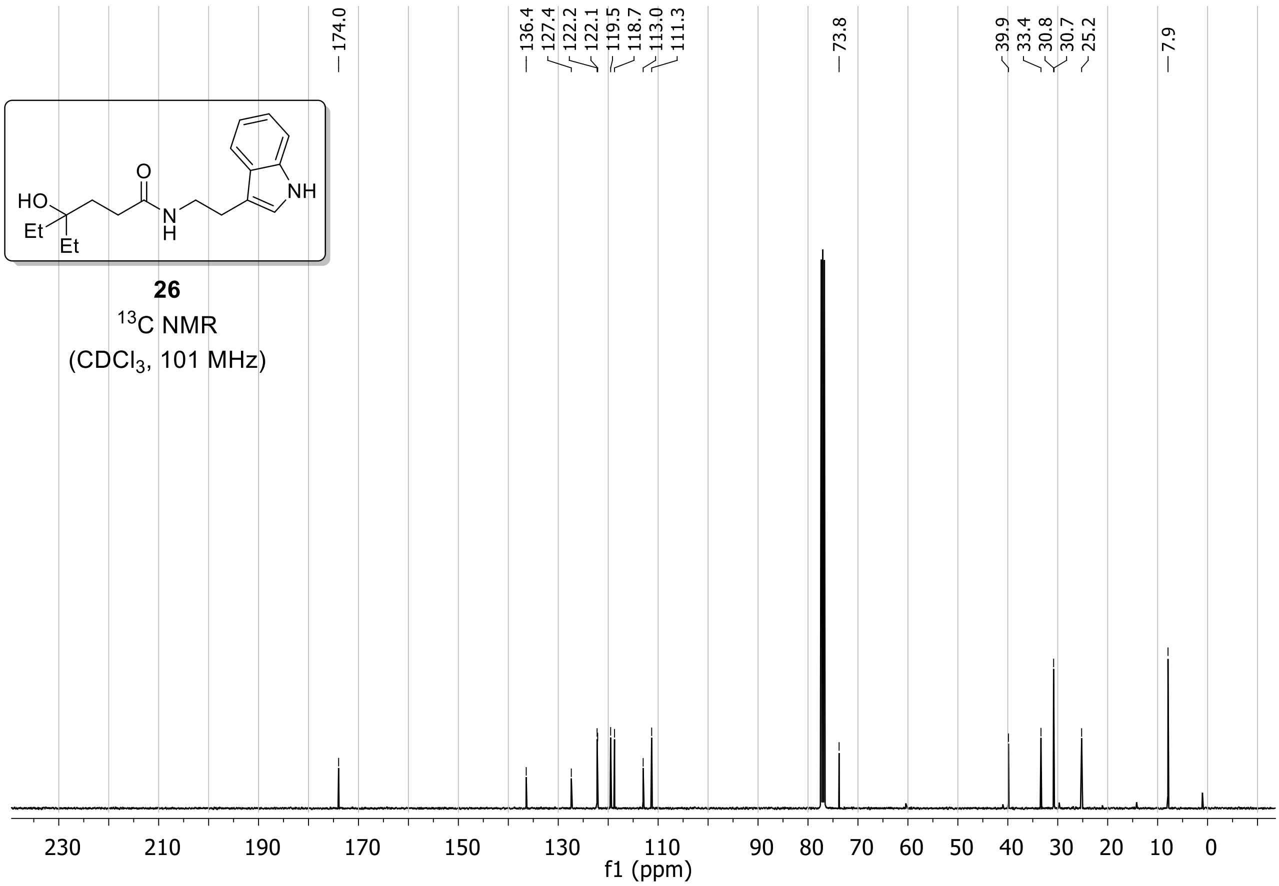
25
^{1}H NMR
($CDCl_3$, 400 MHz)



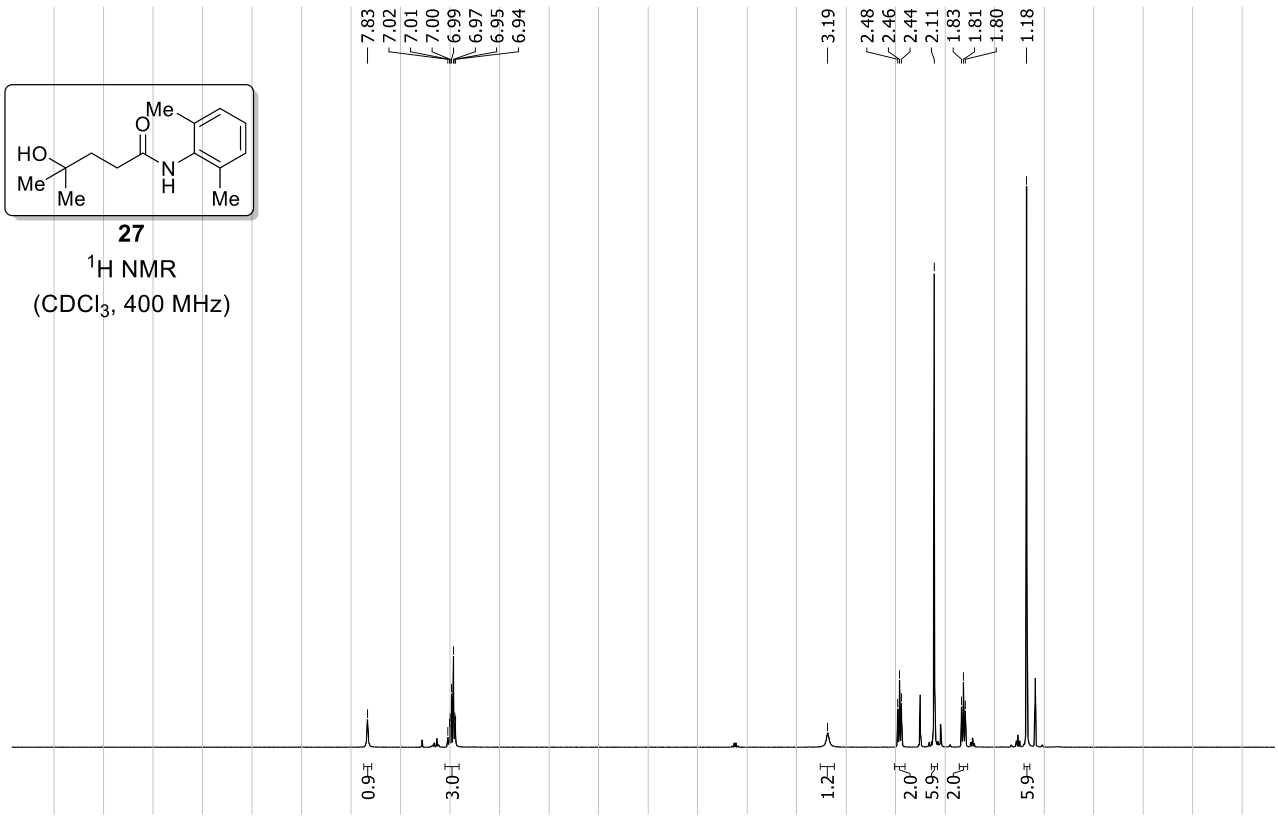
25
^{13}C NMR
($CDCl_3$, 101 MHz)



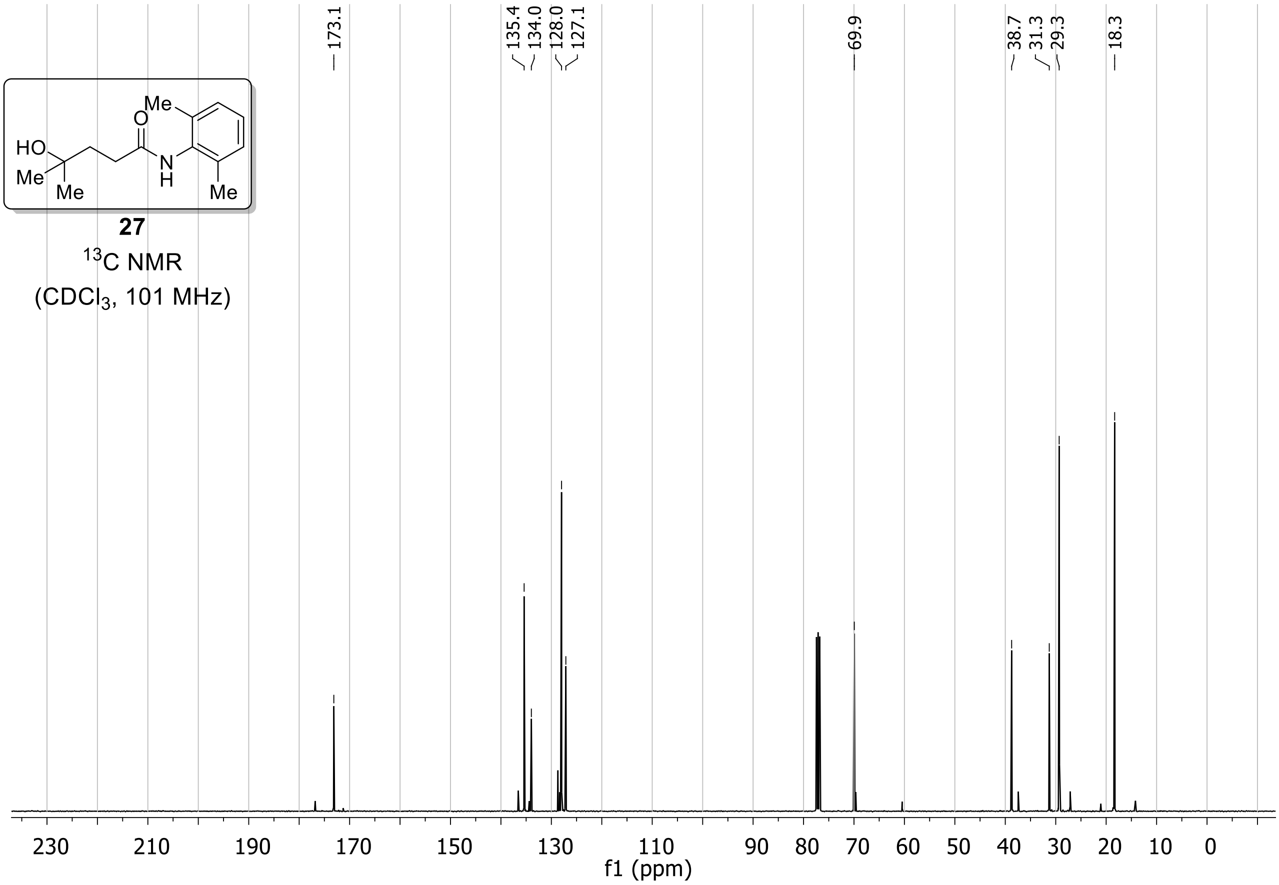
26
^{1}H NMR
($CDCl_3$, 400 MHz)



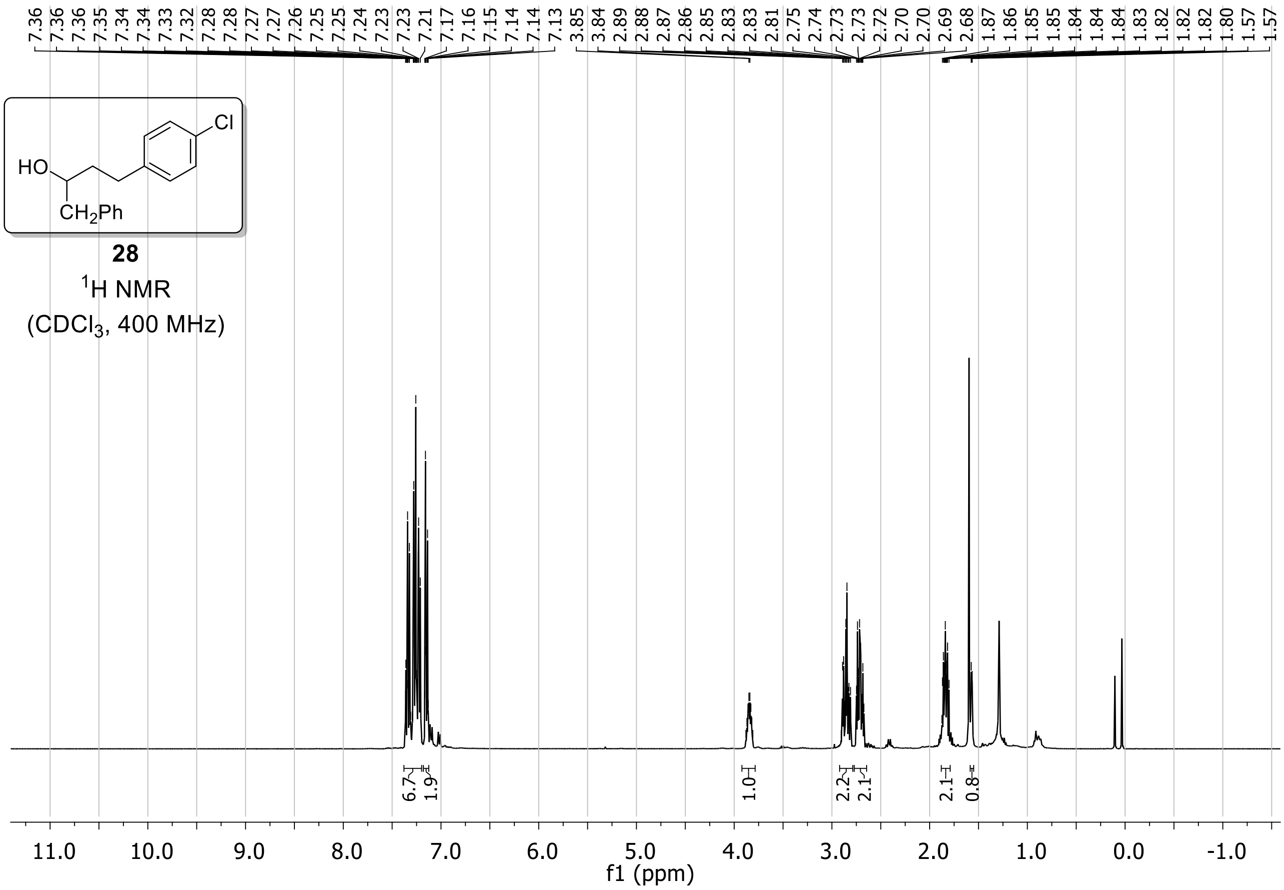
26
^{13}C NMR
($CDCl_3$, 101 MHz)



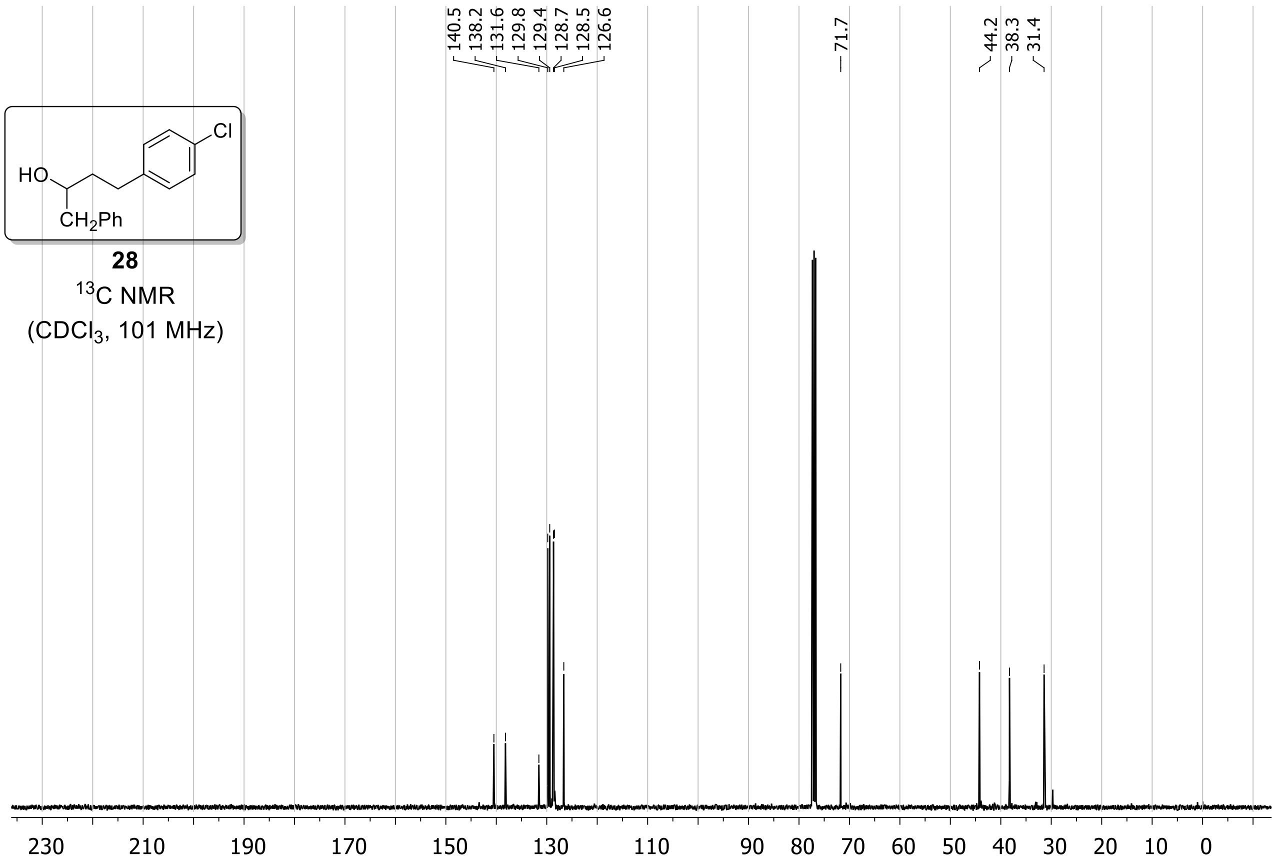
27
^{1}H NMR
($CDCl_3$, 400 MHz)



173.1
135.4
134.0
128.0
127.1
69.9
38.7
31.3
29.3
18.3
HO
Me
Me
O
Me
N
H
Me
27
^{13}C NMR
($CDCl_3$, 101 MHz)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



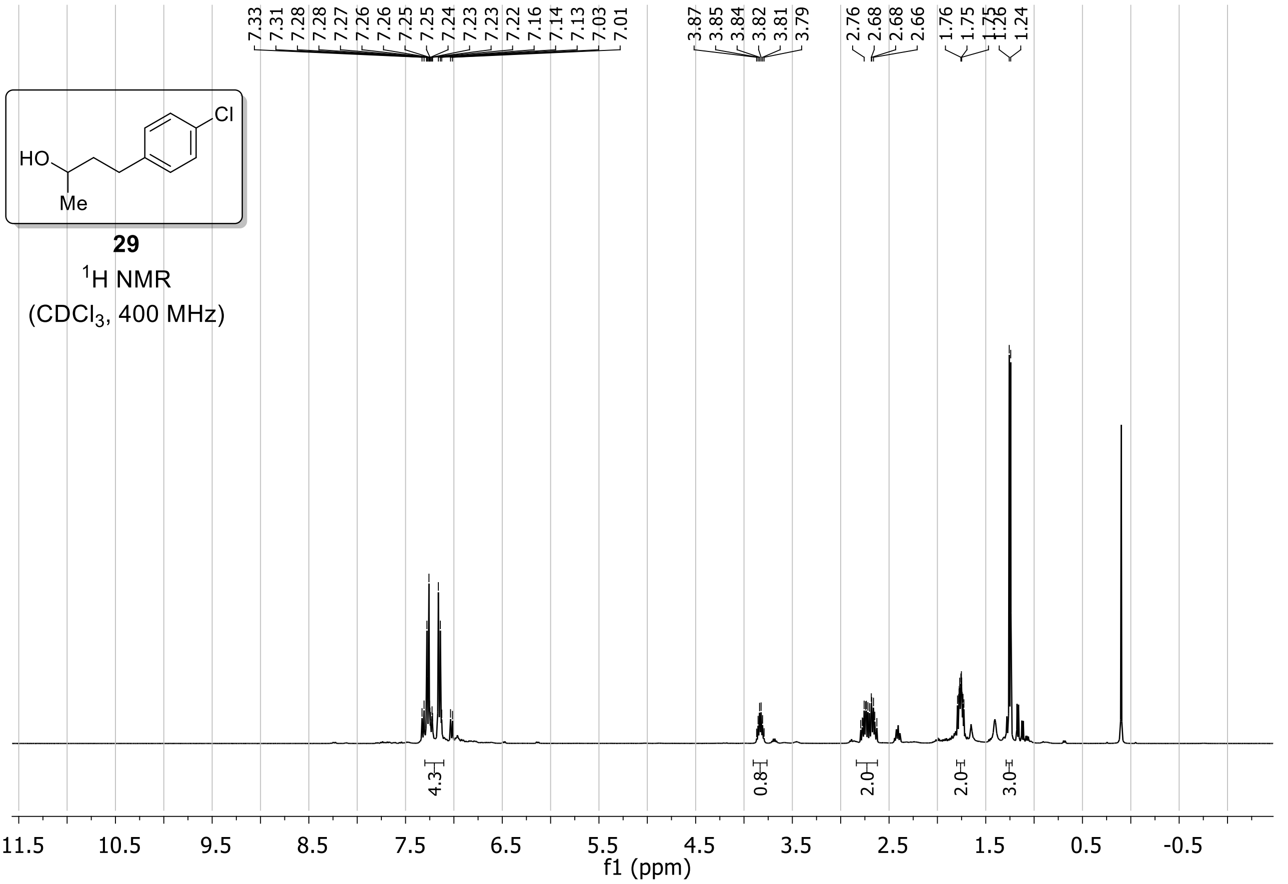
7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.28 7.28 7.27 7.26 7.25 7.25 7.24 7.23 7.23 7.21 7.17 7.16 7.15 7.14 7.14 7.13 3.85 3.84 2.89 2.88 2.87 2.86 2.85 2.83 2.83 2.81 2.75 2.74 2.73 2.73 2.72 2.70 2.70 2.69 2.68 1.87 1.86 1.85 1.85 1.84 1.84 1.84 1.83 1.82 1.82 1.82 1.80 1.57 1.57
Cl
HO
CH_2Ph
28
^{1}H NMR
($CDCl_3$, 400 MHz)
6.7
1.9
1.0
2.2
2.1
2.1
0.8
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
-1.0
f1 (ppm)



28

^{13}C NMR

($CDCl_3$, 101 MHz)



29

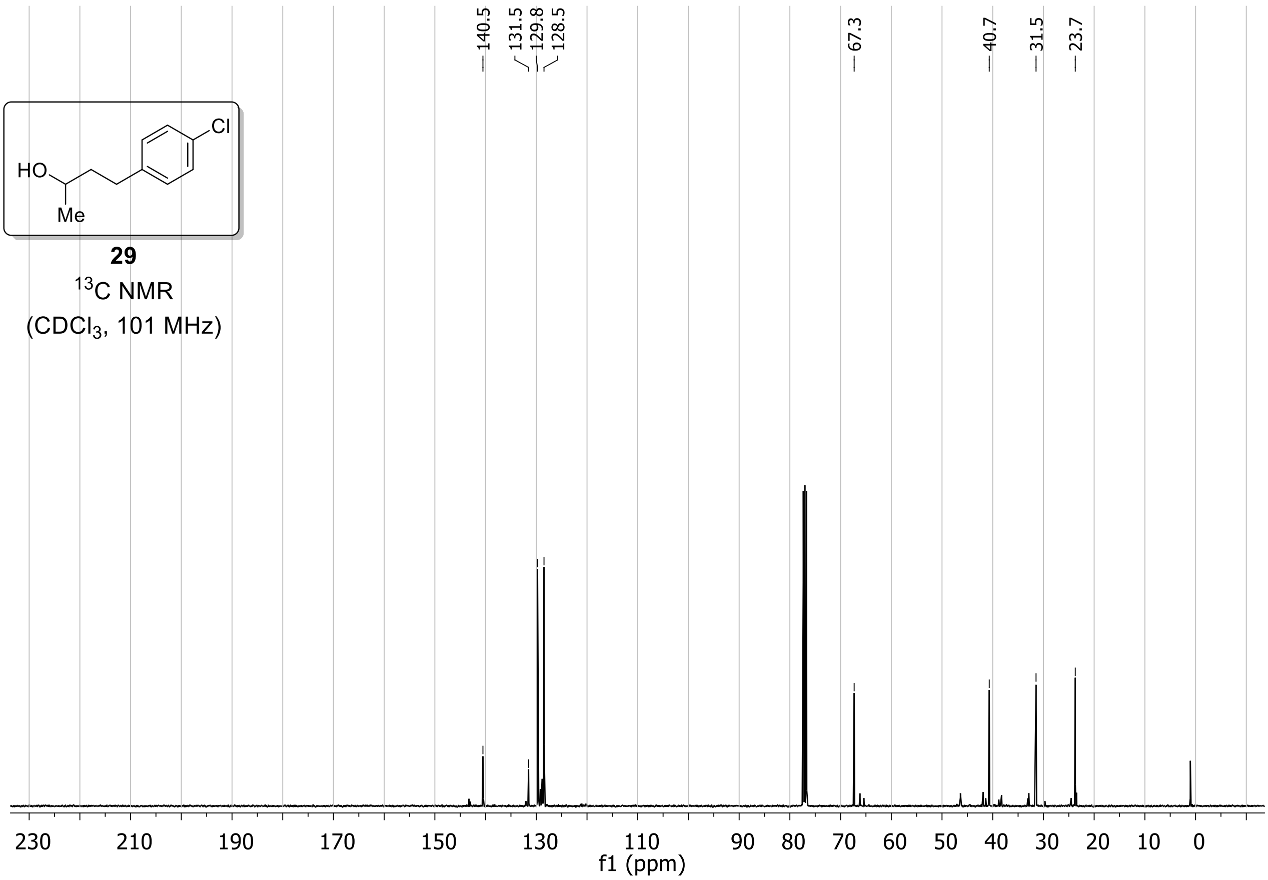
^{1}H NMR

($CDCl_3$, 400 MHz)

29

^{13}C NMR

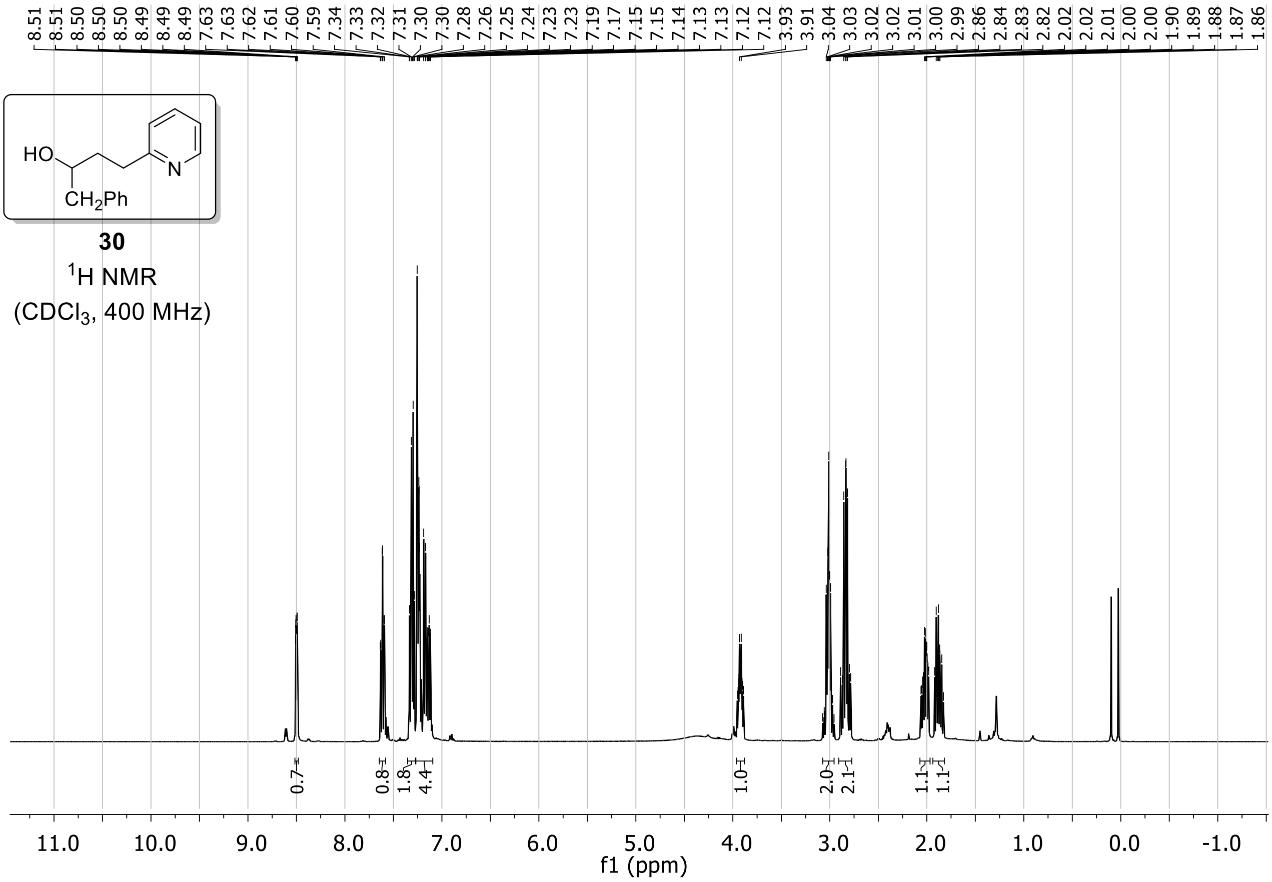
($CDCl_3$, 101 MHz)

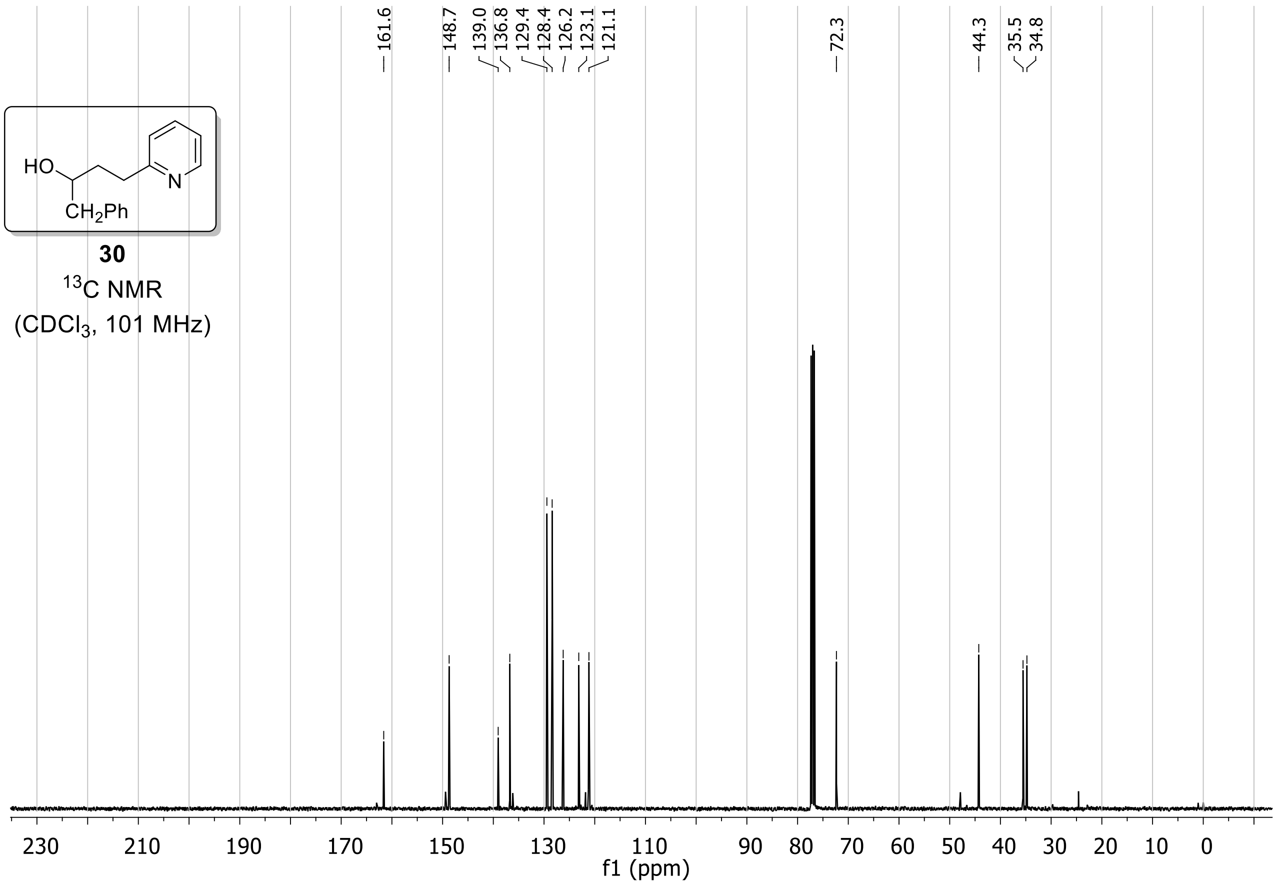


30

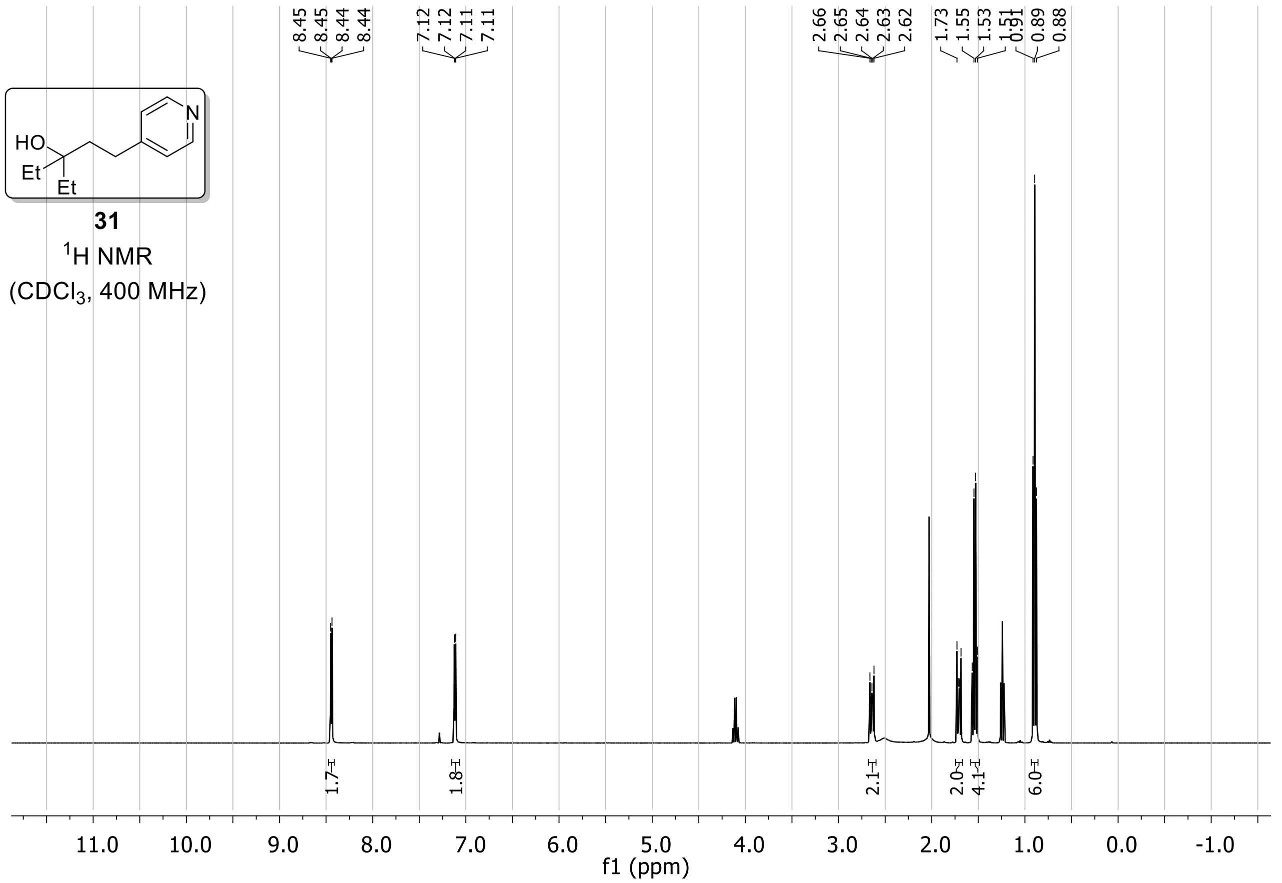
^{1}H NMR

($CDCl_3$, 400 MHz)

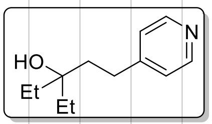




30
^{13}C NMR
($CDCl_3$, 101 MHz)



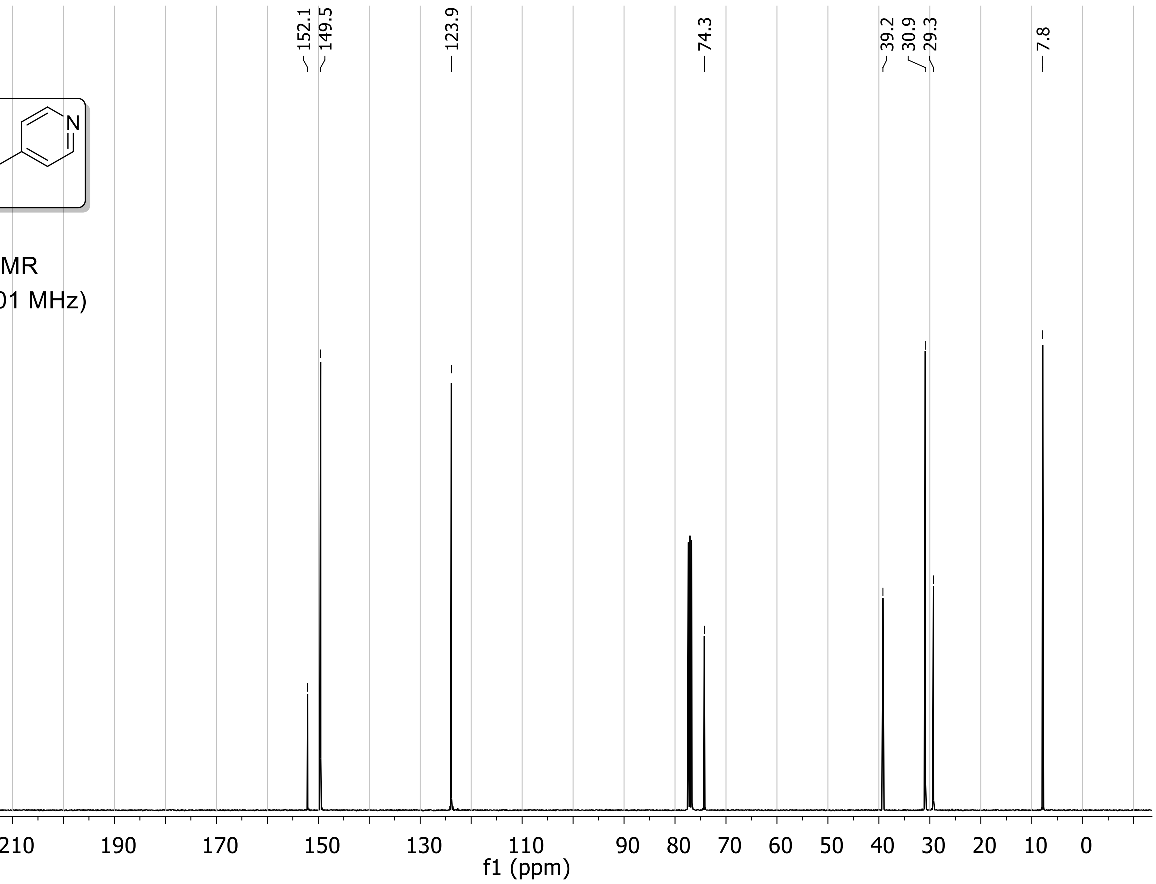
31
^{1}H NMR
($CDCl_3$, 400 MHz)

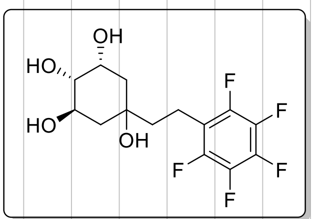


31

^{13}C NMR

($CDCl_3$, 101 MHz)

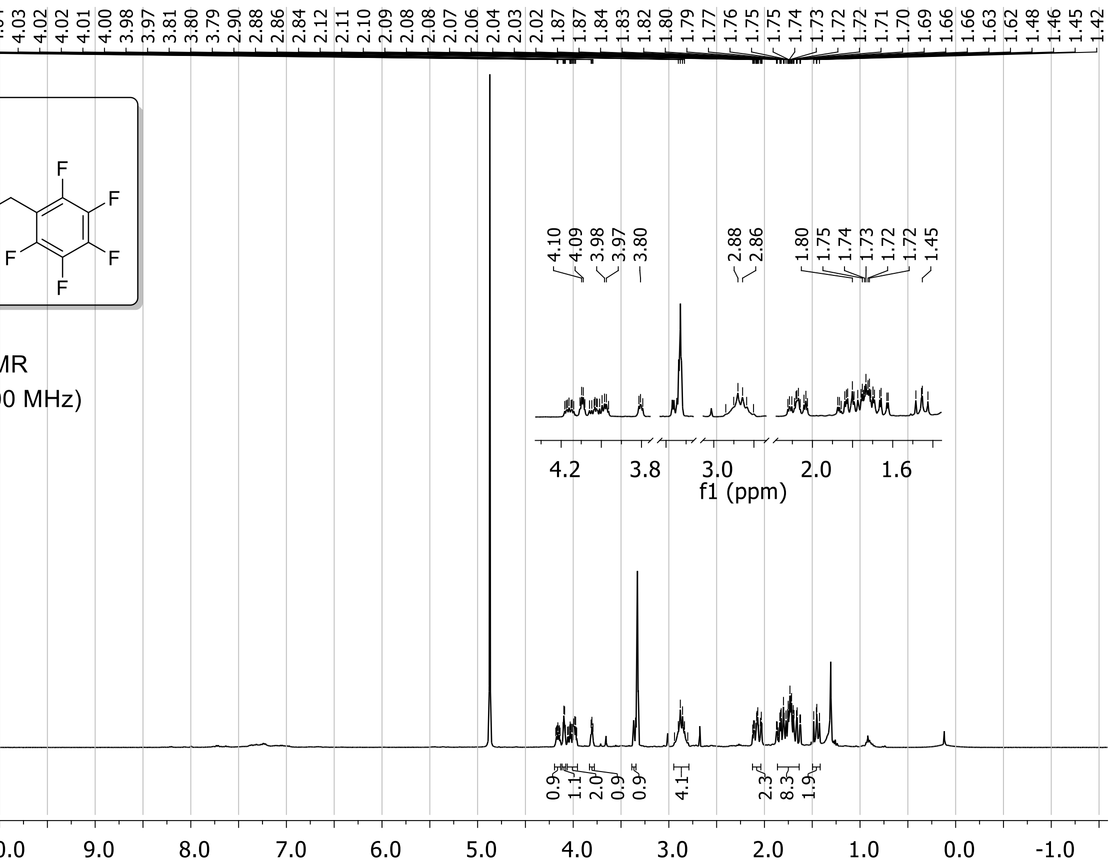


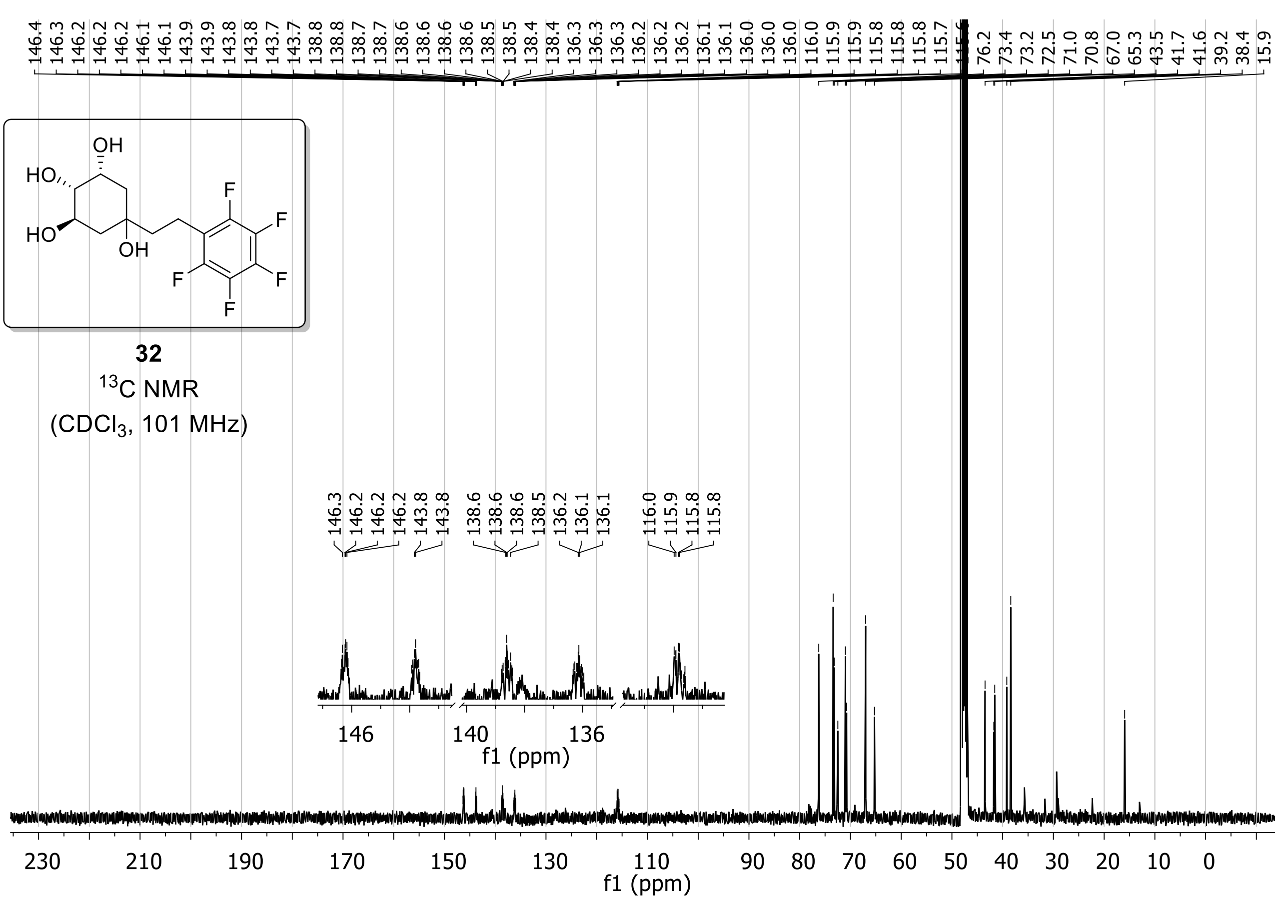


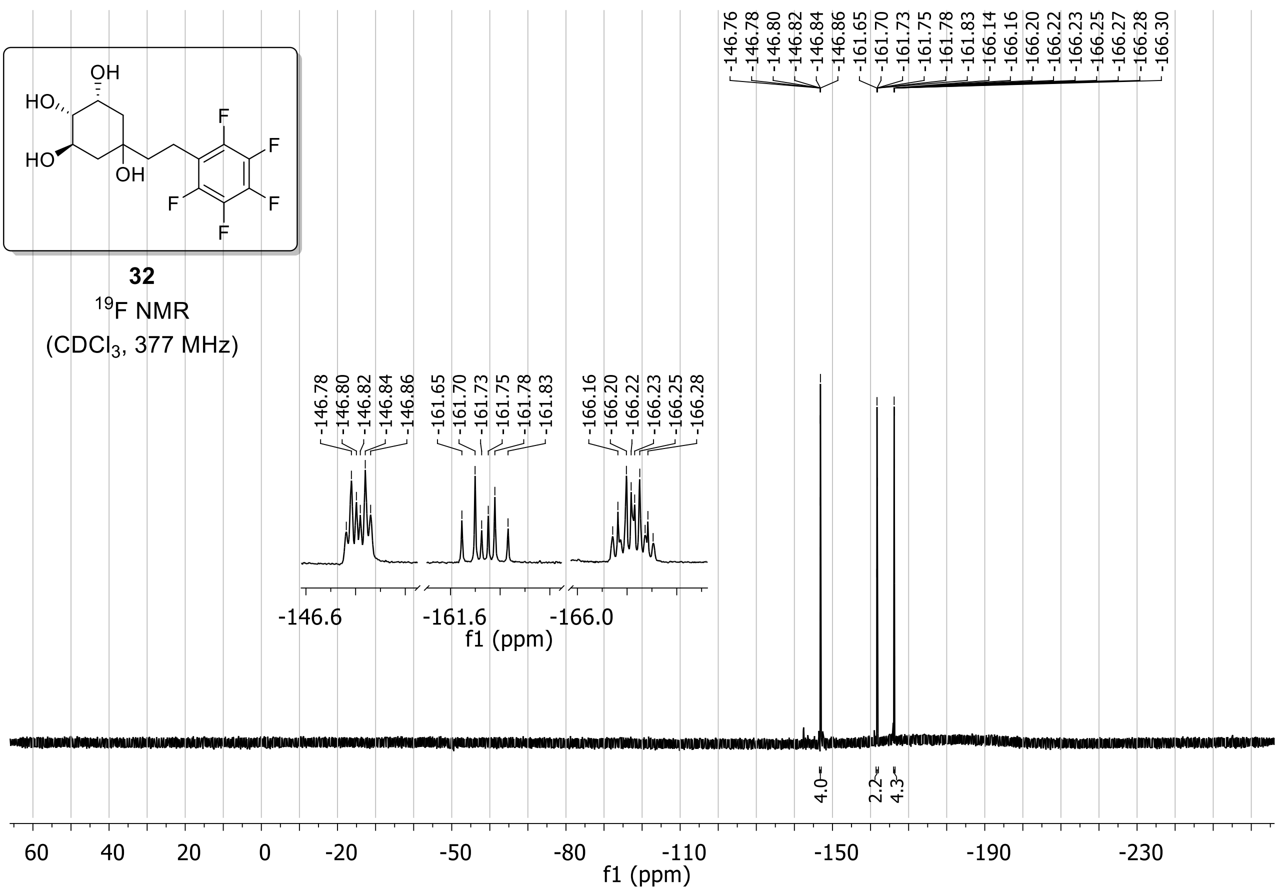
32

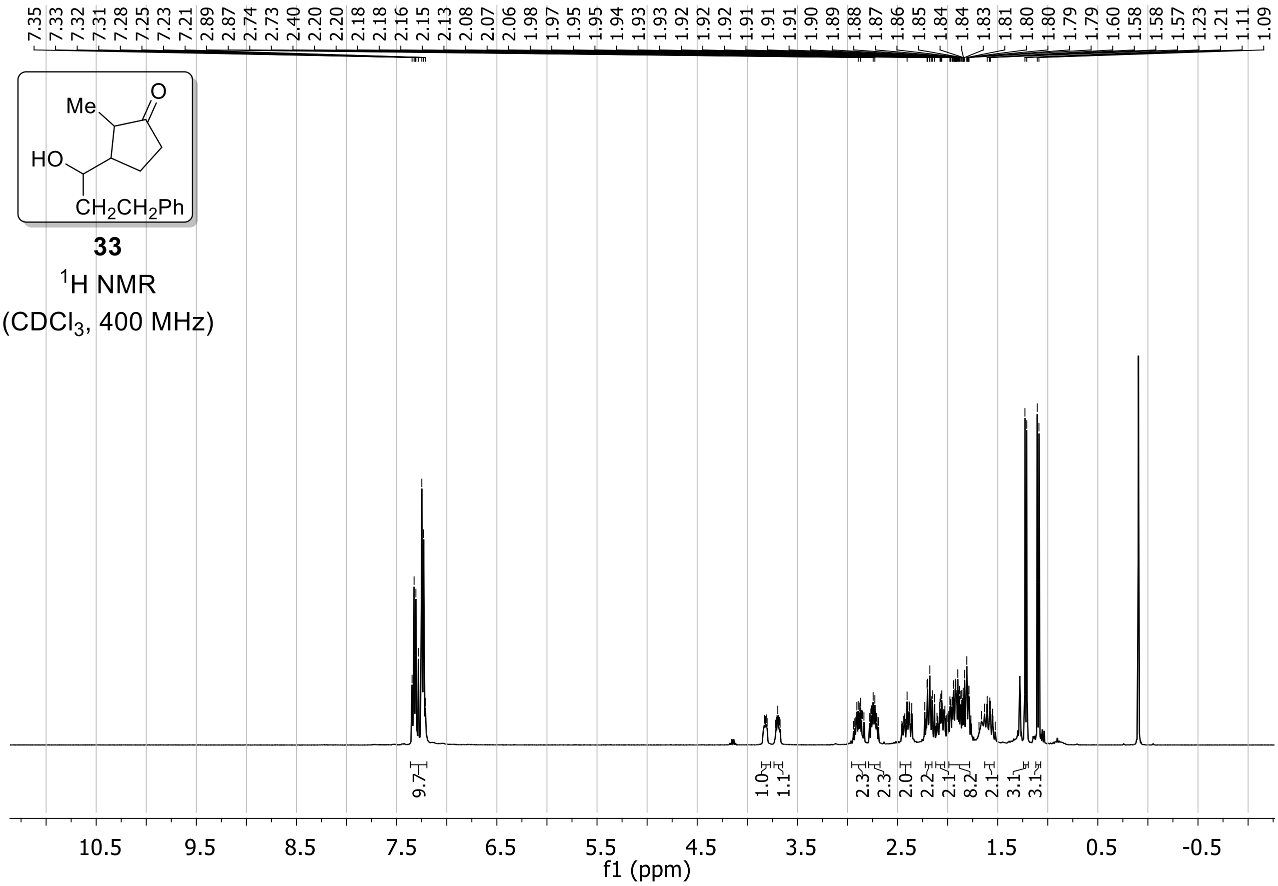
^{1}H NMR

($CDCl_3$, 400 MHz)




32
13C NMR
(CDCl3, 101 MHz)
f1 (ppm)

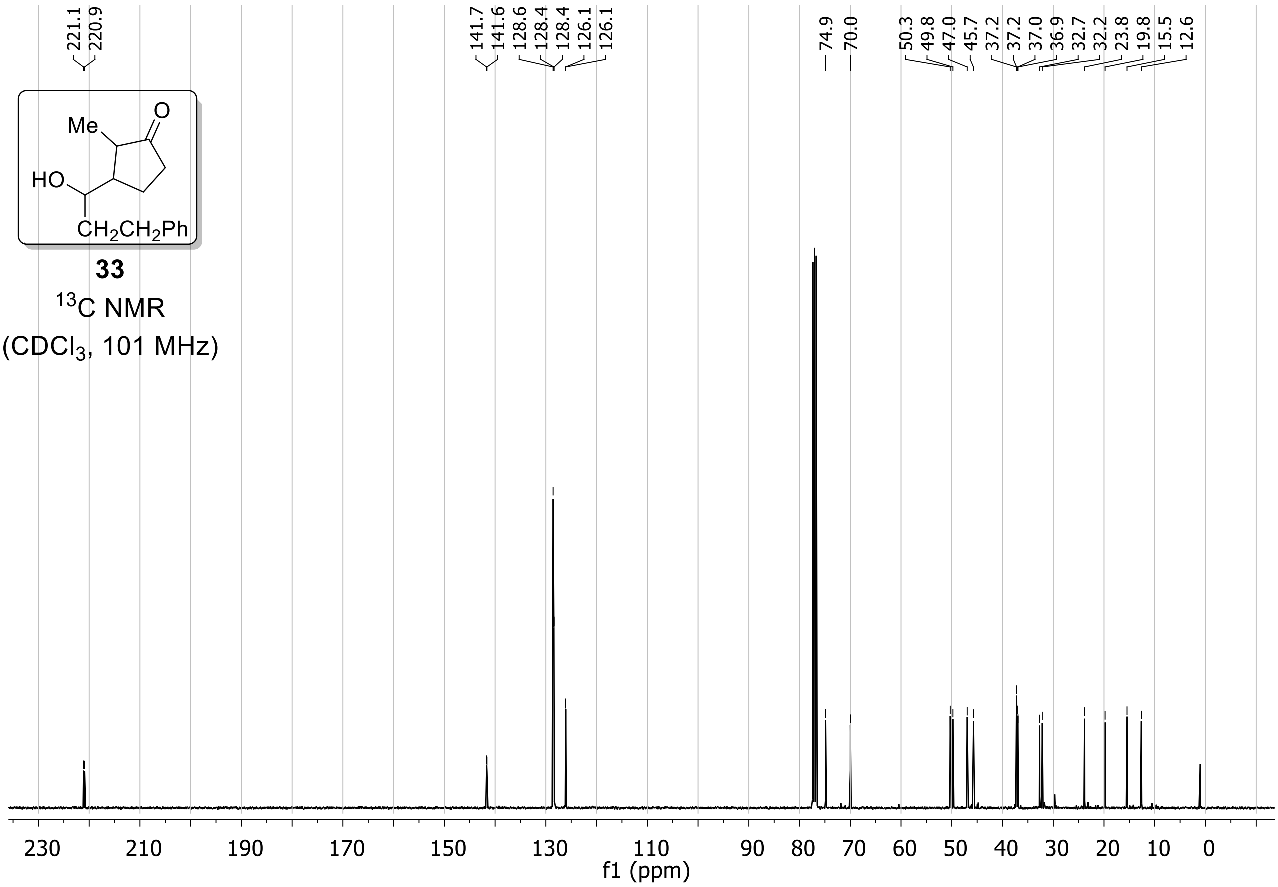

32
19F NMR
(CDCl3, 377 MHz)
f1 (ppm)



33

^{1}H NMR

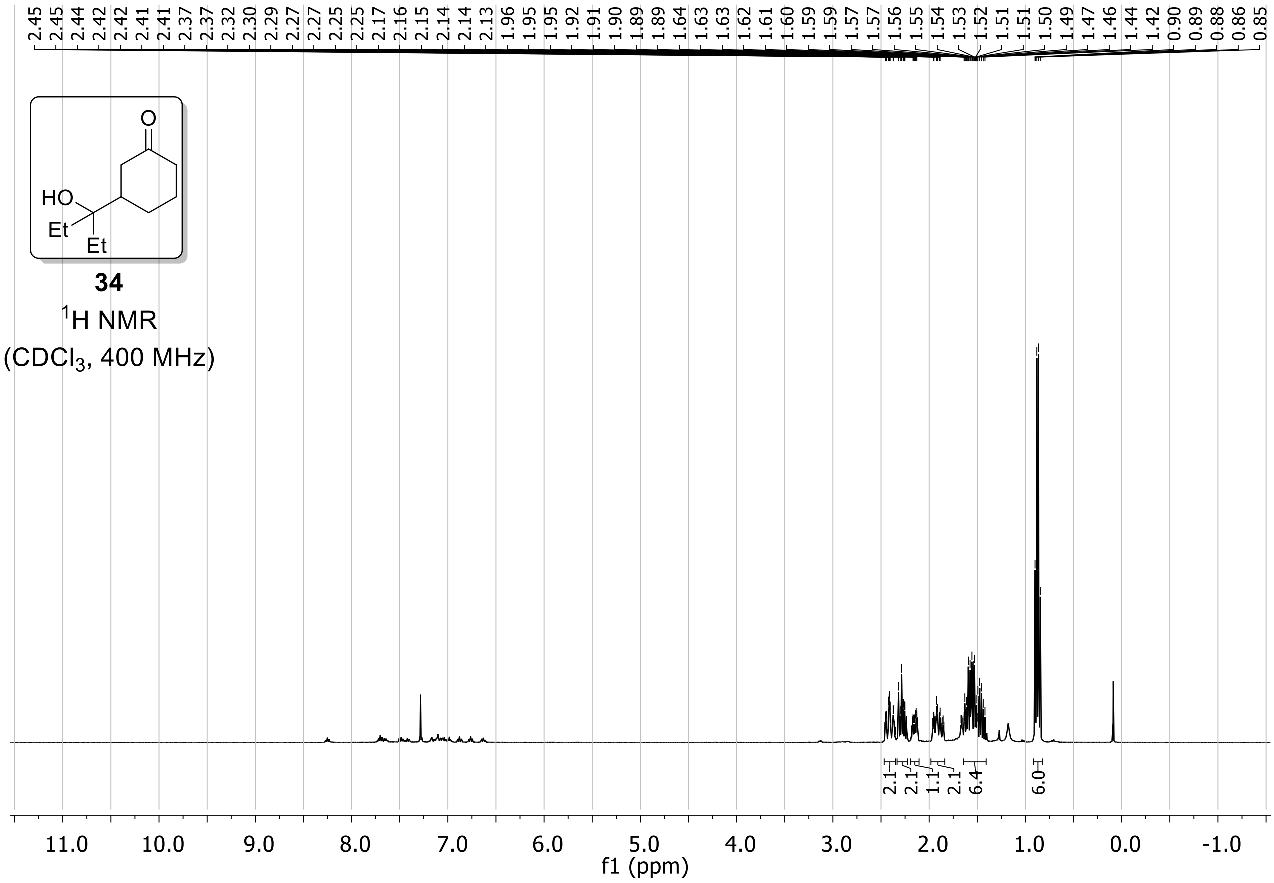
($CDCl_3$, 400 MHz)

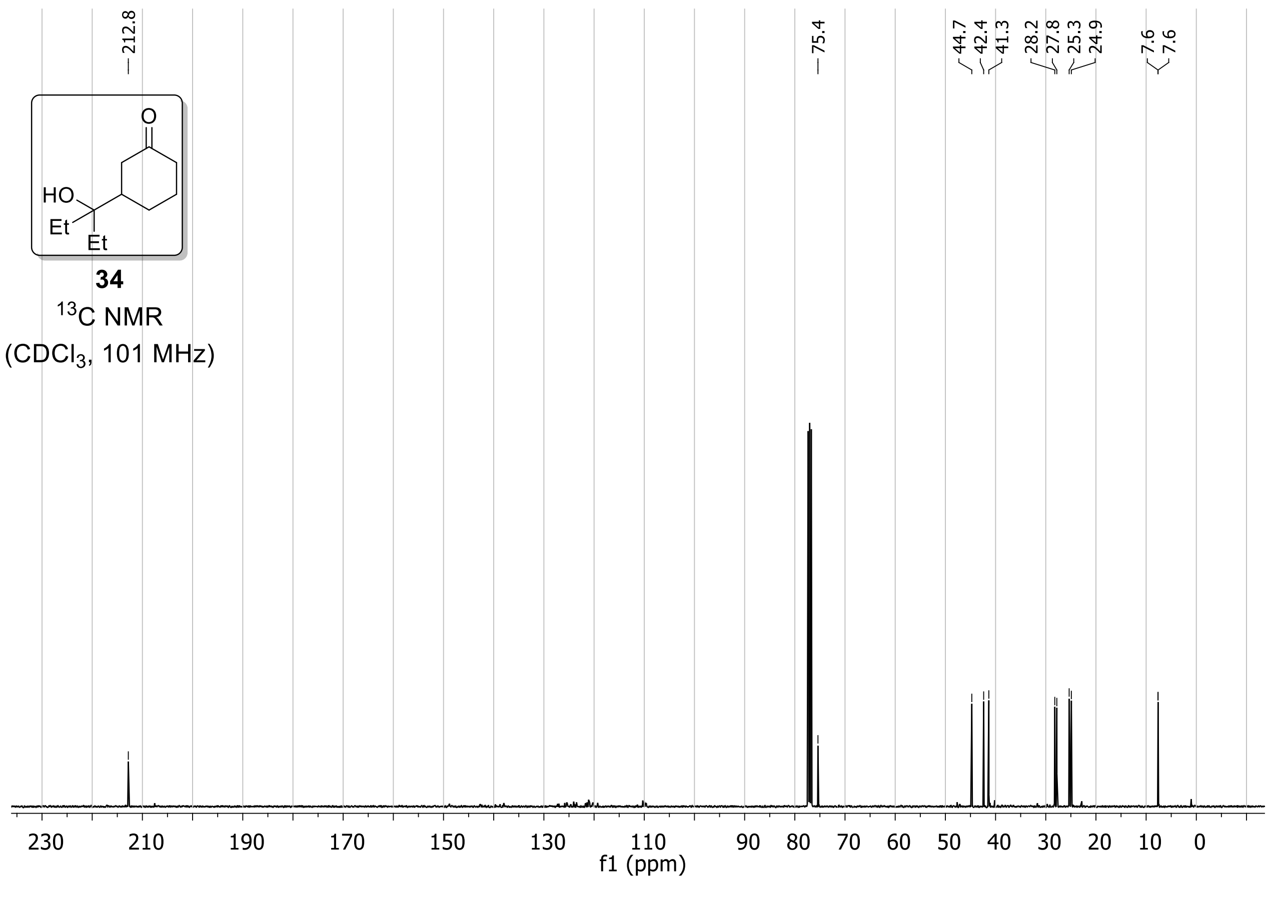


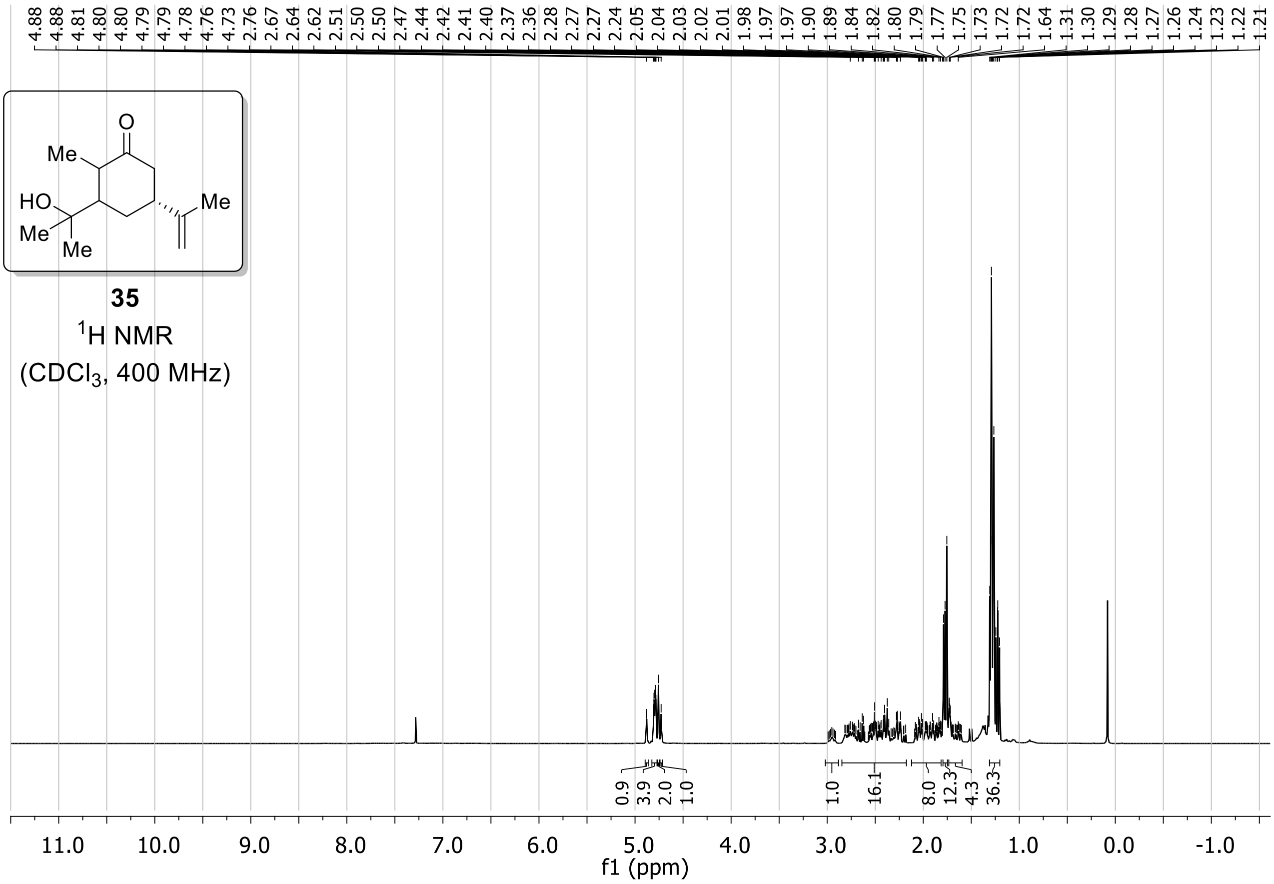
33

^{13}C NMR

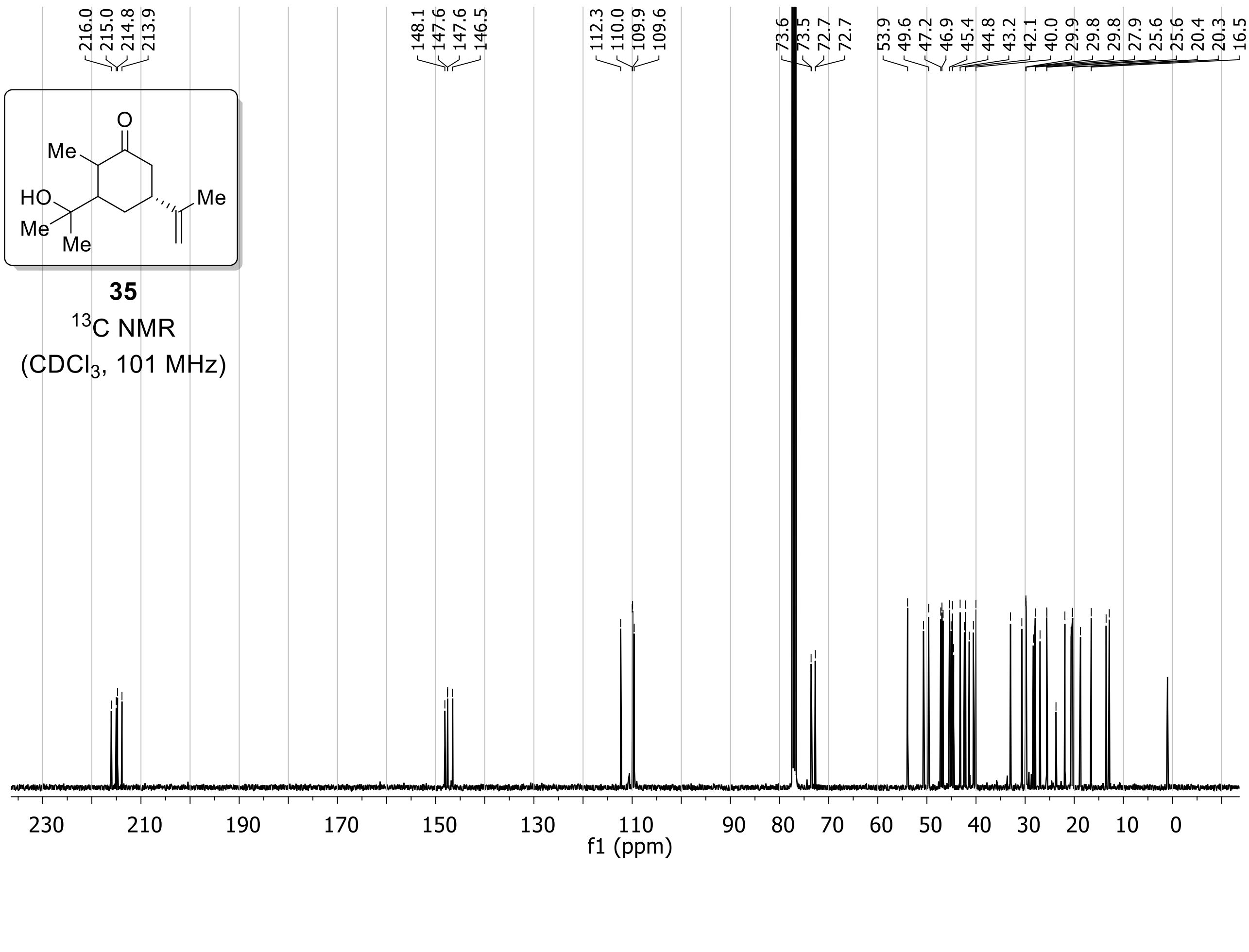
($CDCl_3$, 101 MHz)


2.45 2.45 2.44 2.42 2.42 2.41 2.41 2.37 2.37 2.32 2.30 2.29 2.27 2.27 2.25 2.25 2.17 2.16 2.15 2.14 2.14 2.13 1.96 1.95 1.95 1.92 1.91 1.90 1.89 1.89 1.64 1.63 1.63 1.62 1.61 1.60 1.59 1.59 1.57 1.57 1.56 1.55 1.54 1.53 1.52 1.51 1.51 1.50 1.49 1.47 1.46 1.44 1.42 0.90 0.89 0.88 0.86 0.85
O
HO
Et
Et
34
^{1}H NMR
($CDCl_3$, 400 MHz)
2.1 2.1 2.1 1.1 2.1 6.4 6.0
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)

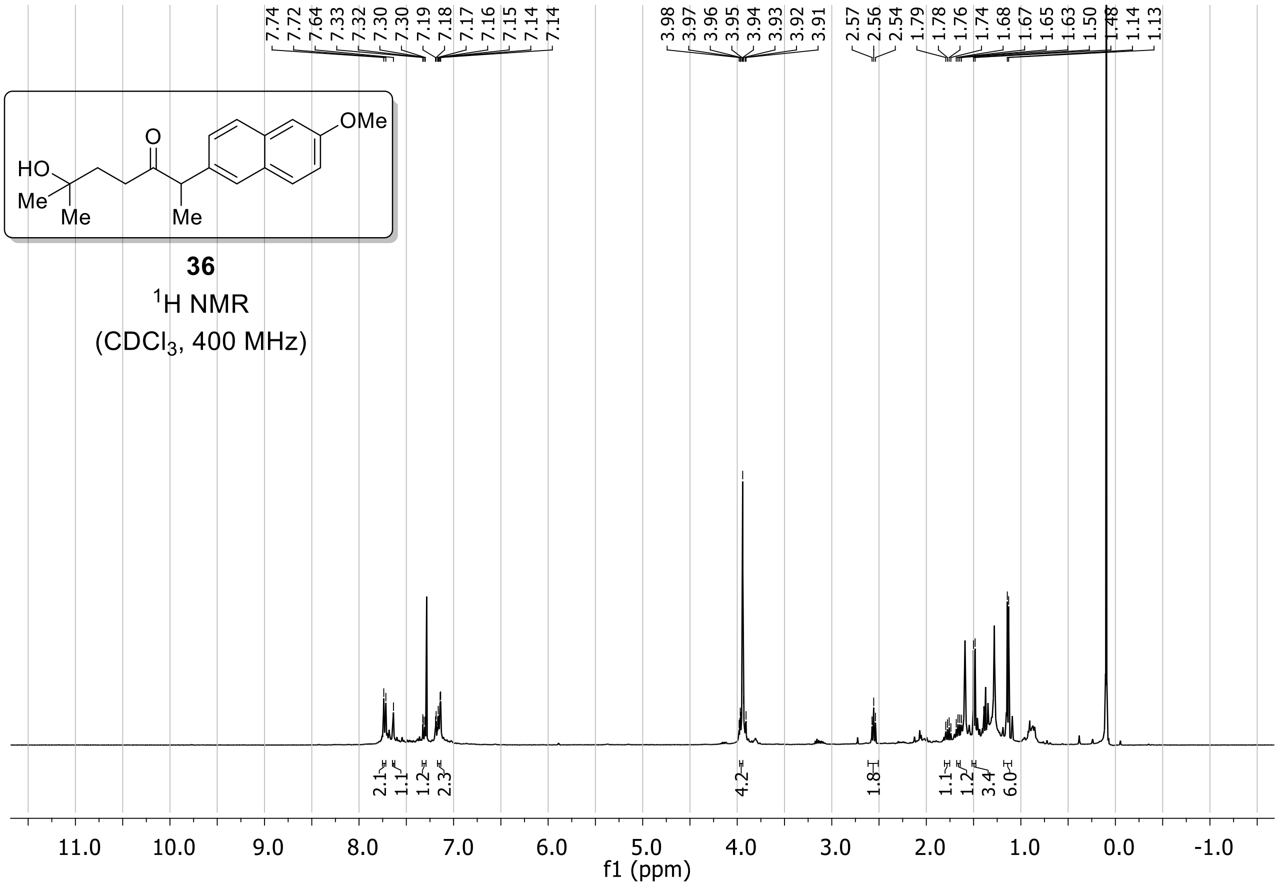

212.8
75.4
44.7 42.4 41.3 28.2 27.8 25.3 24.9 7.6 7.6
O
HO
Et
Et
34
^{13}C NMR
($CDCl_3$, 101 MHz)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



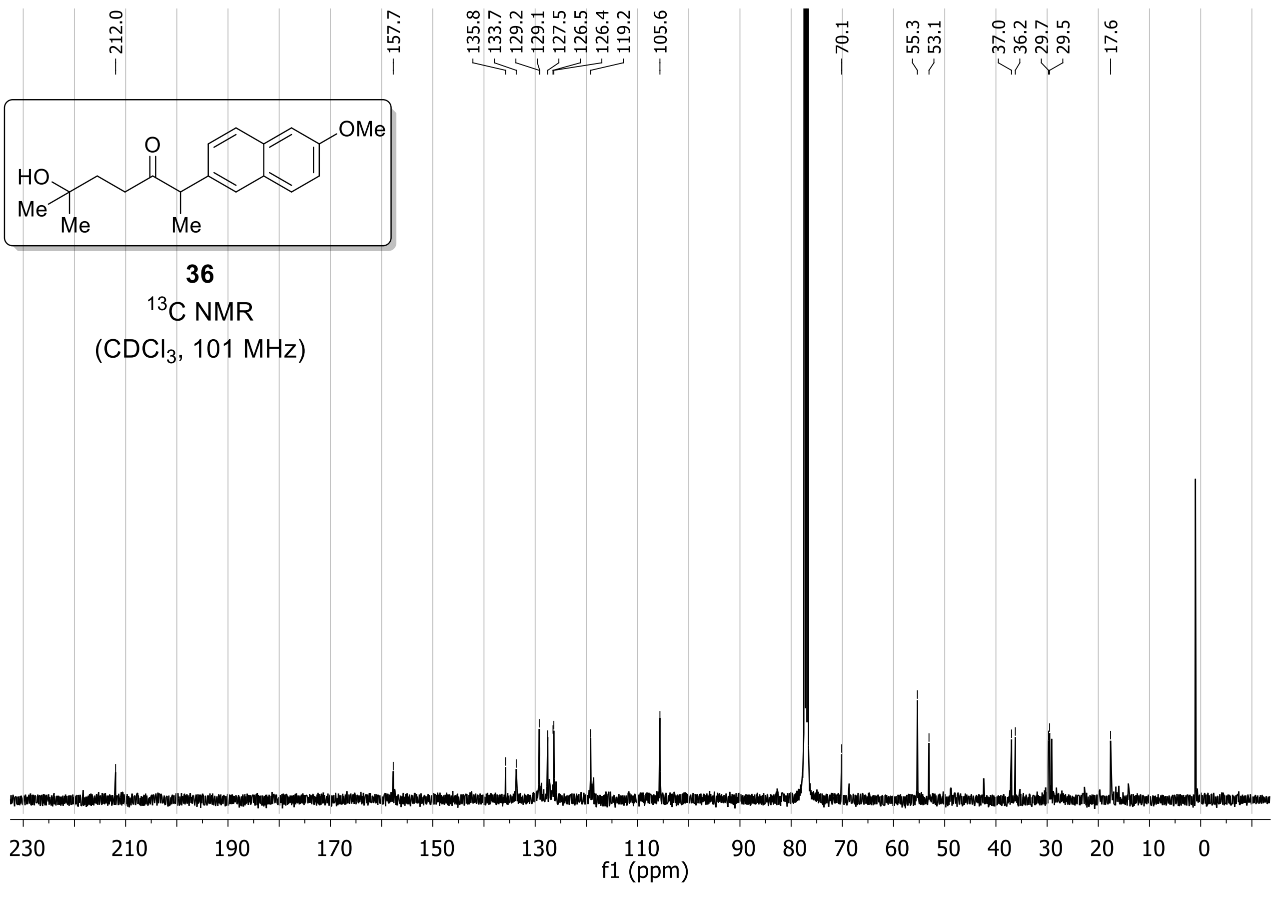
35
^{1}H NMR
(CDCl$_3$, 400 MHz)
f1 (ppm)



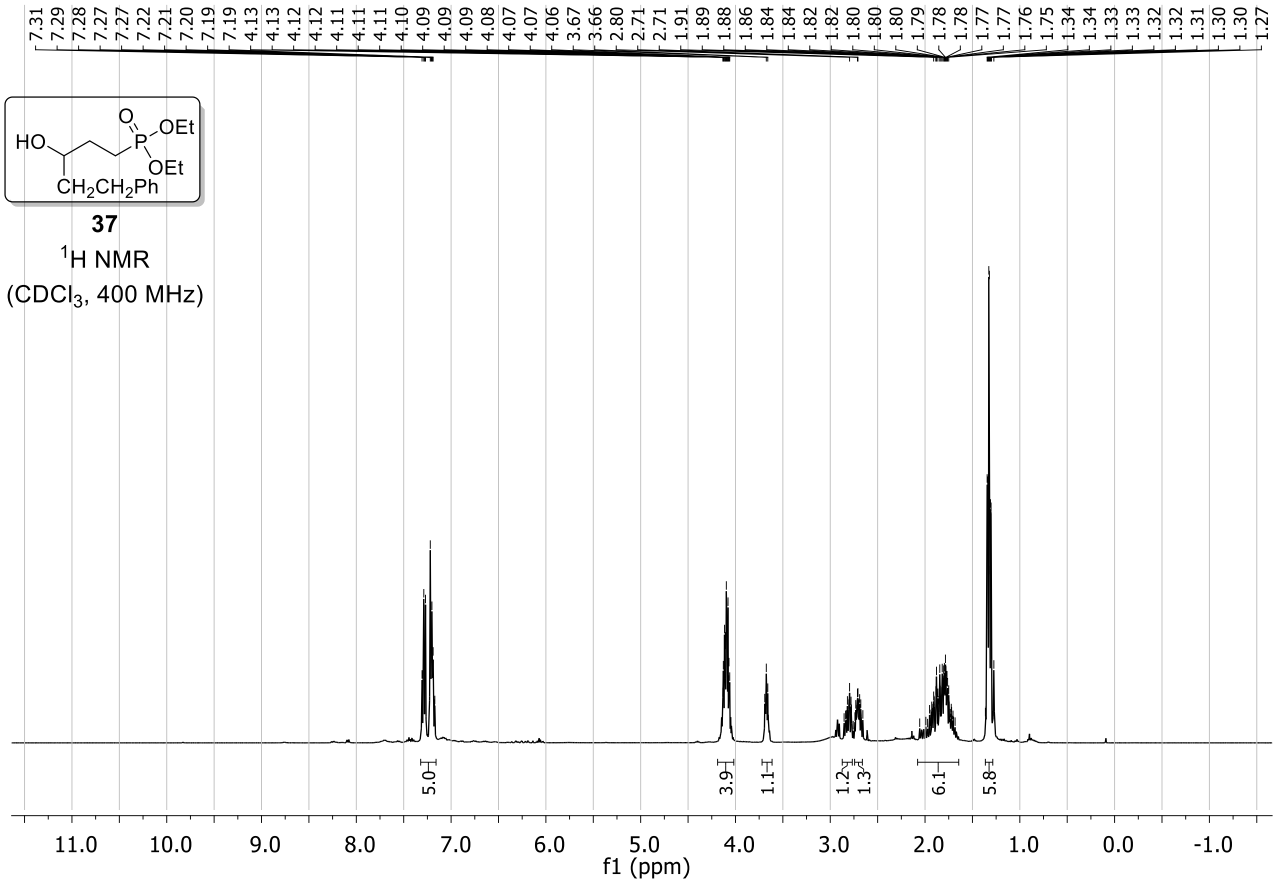
35
^{13}C NMR
(CDCl$_3$, 101 MHz)
f1 (ppm)



36
^{1}H NMR
($CDCl_3$, 400 MHz)



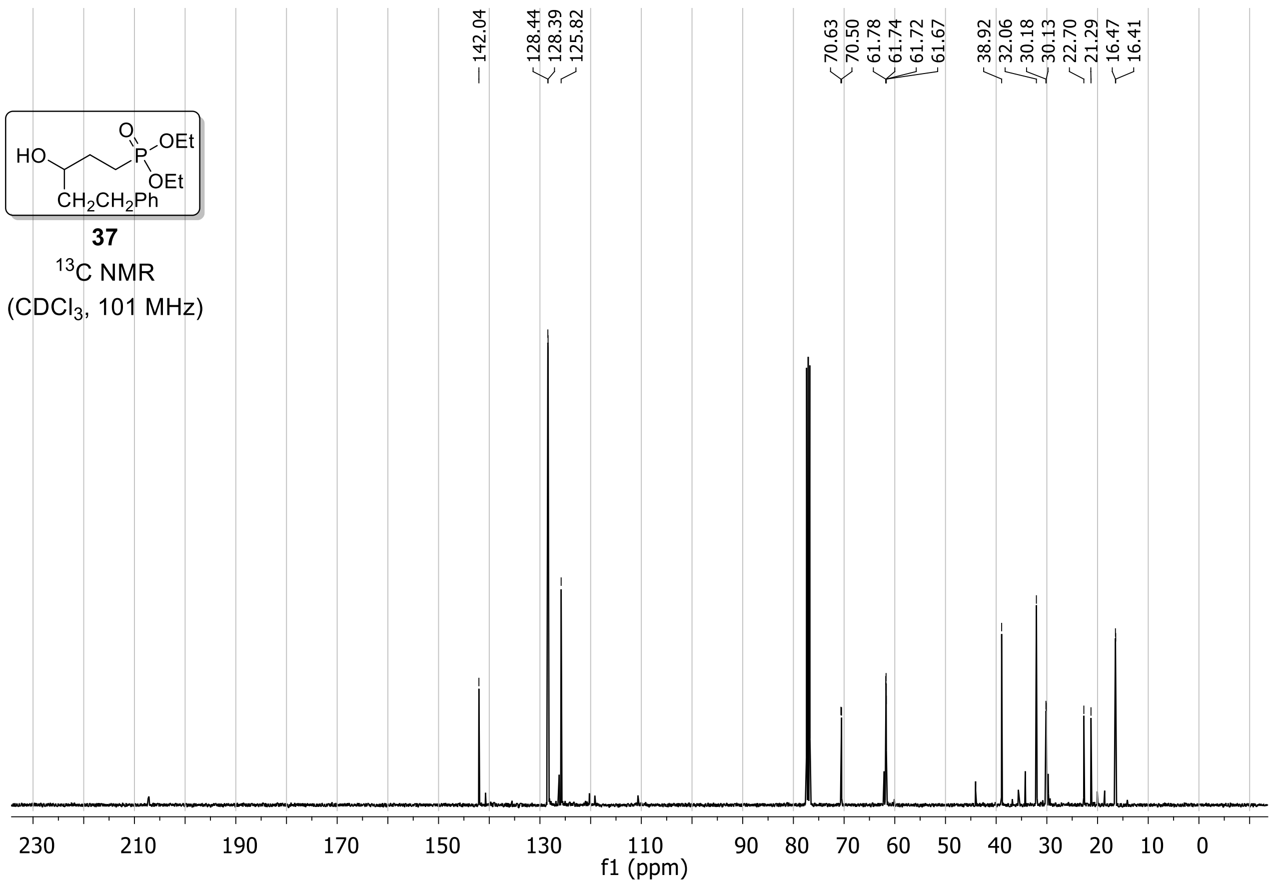
36
^{13}C NMR
($CDCl_3$, 101 MHz)



37

^1H NMR

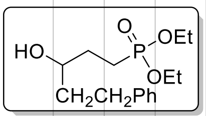
($CDCl_3$, 400 MHz)



37

^{13}C NMR

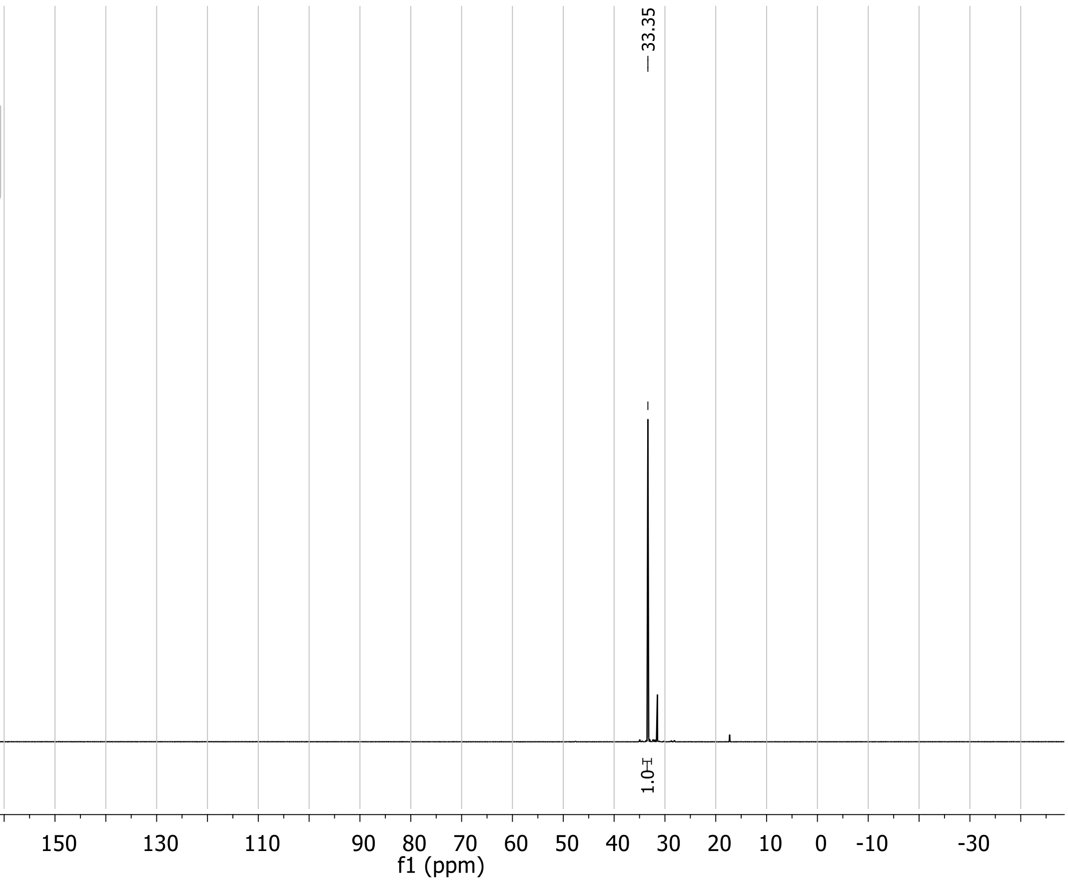
($CDCl_3$, 101 MHz)

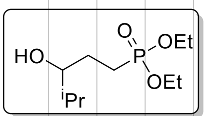


37

^{31}P NMR

($CDCl_3$, 202 MHz)

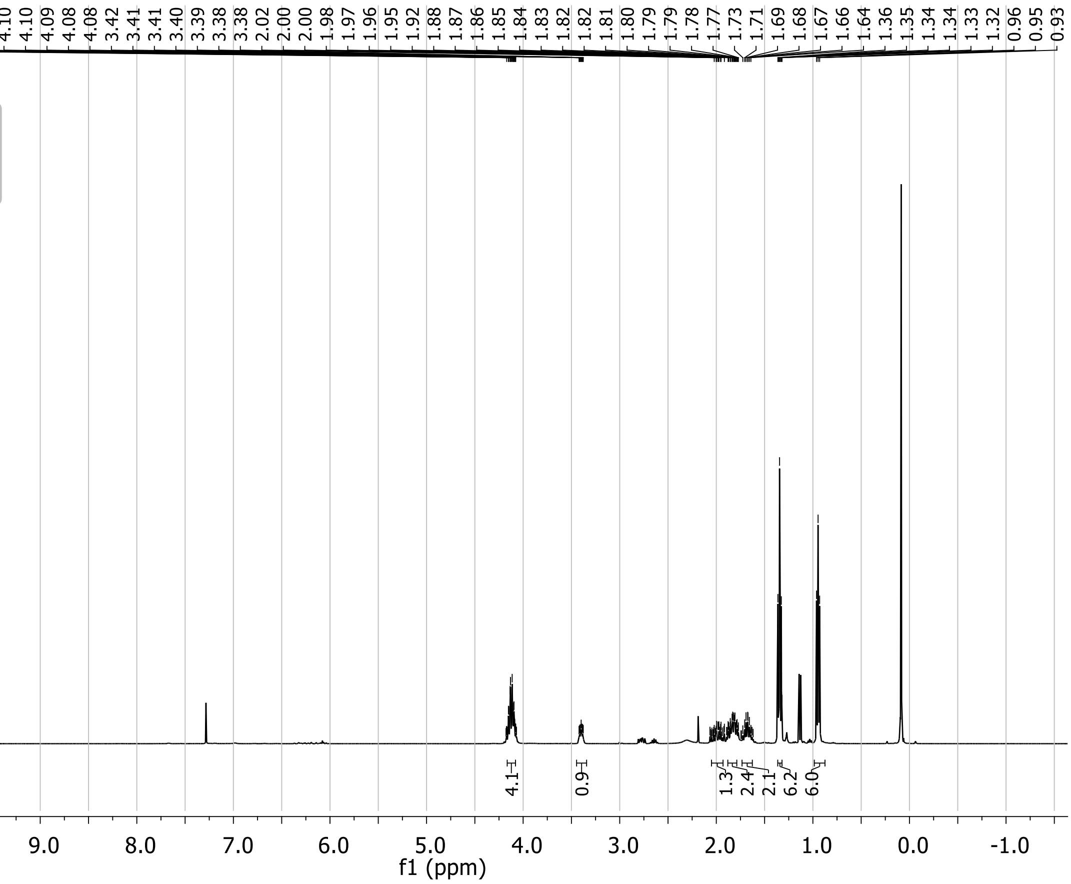


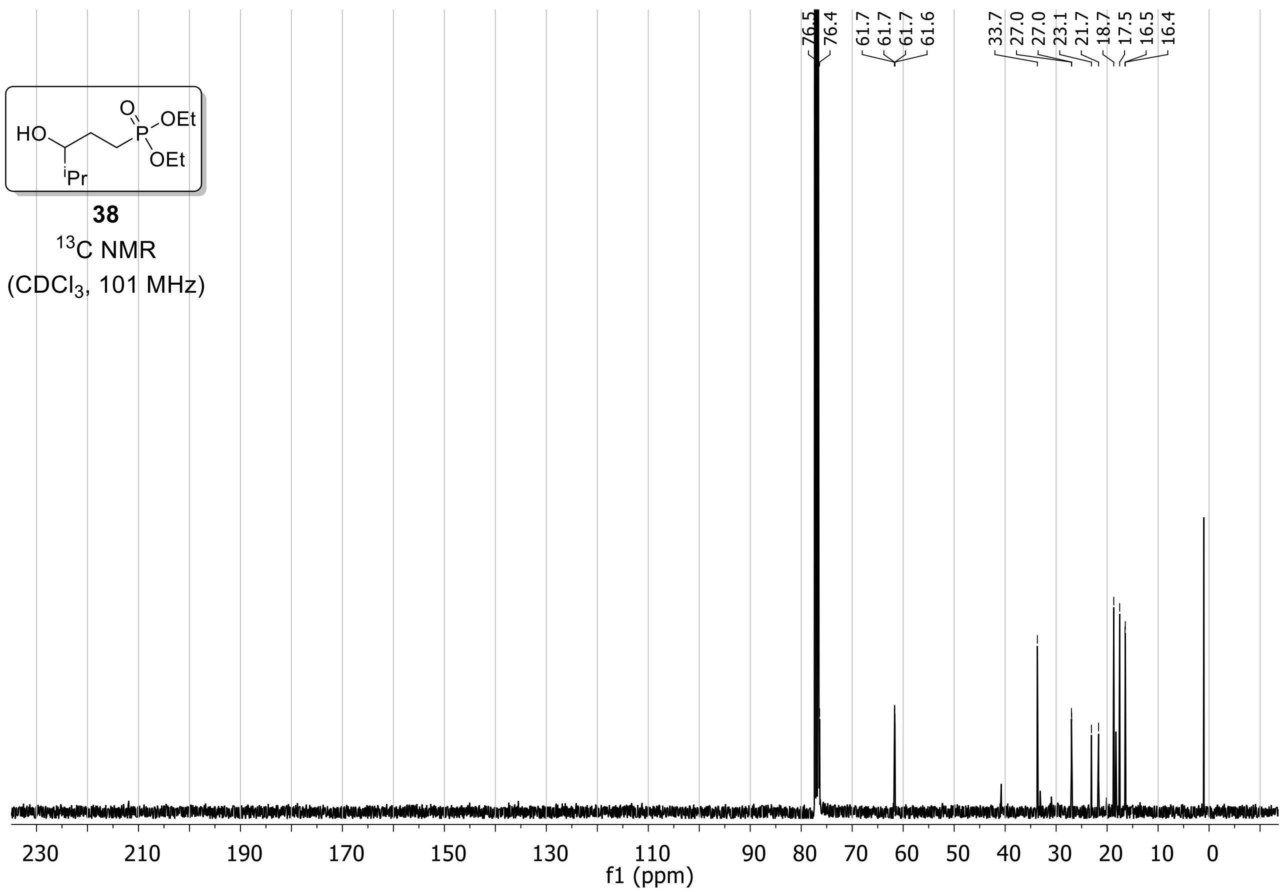


38

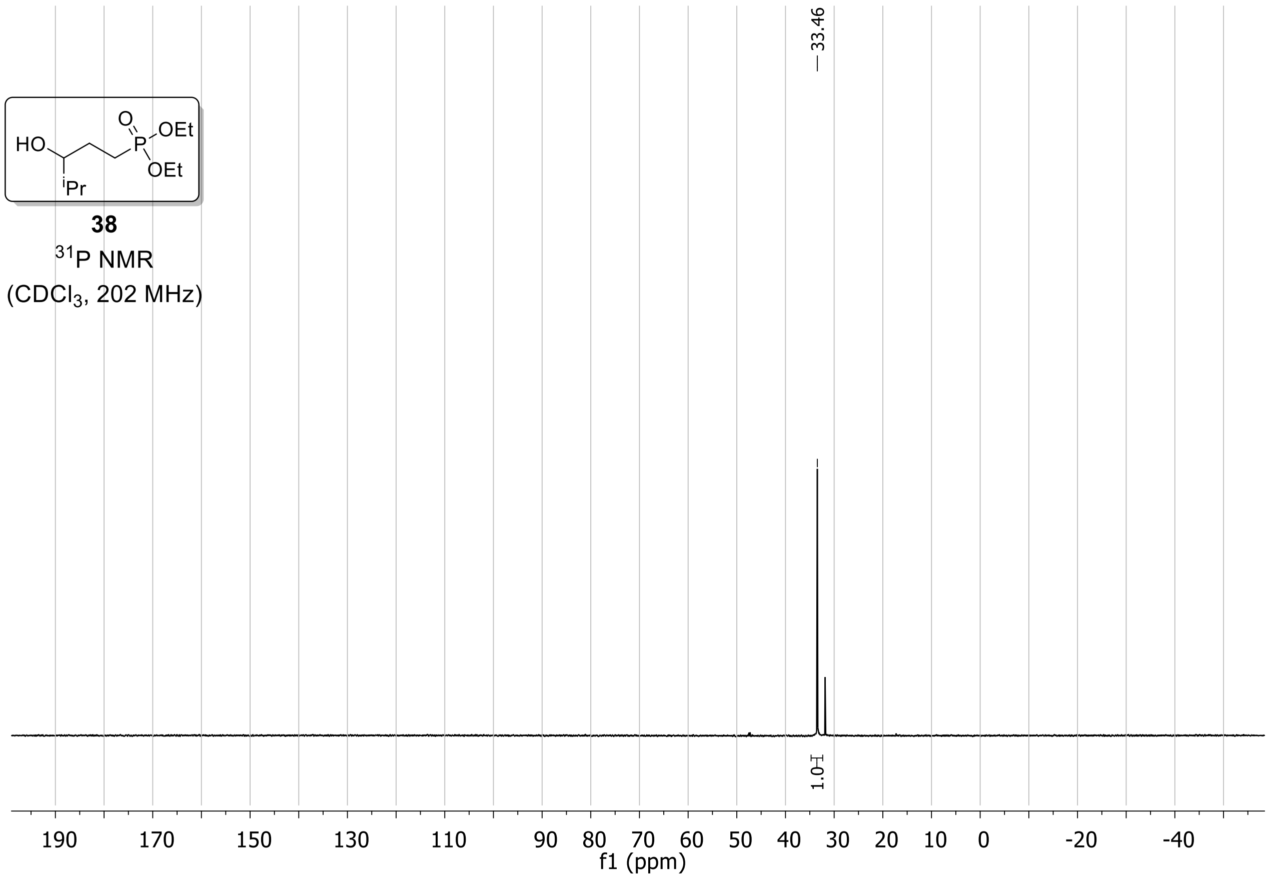
^{1}H NMR

($CDCl_3$, 400 MHz)

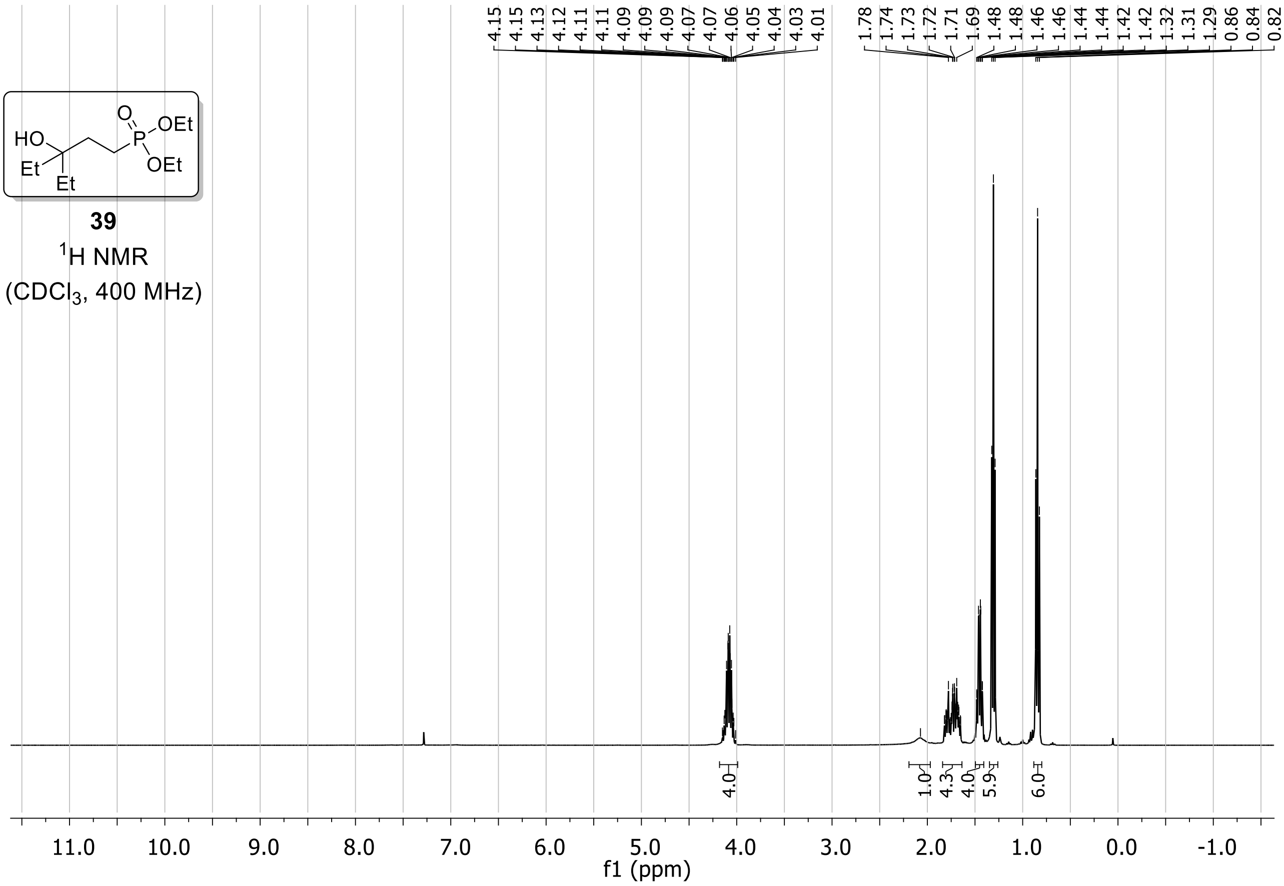




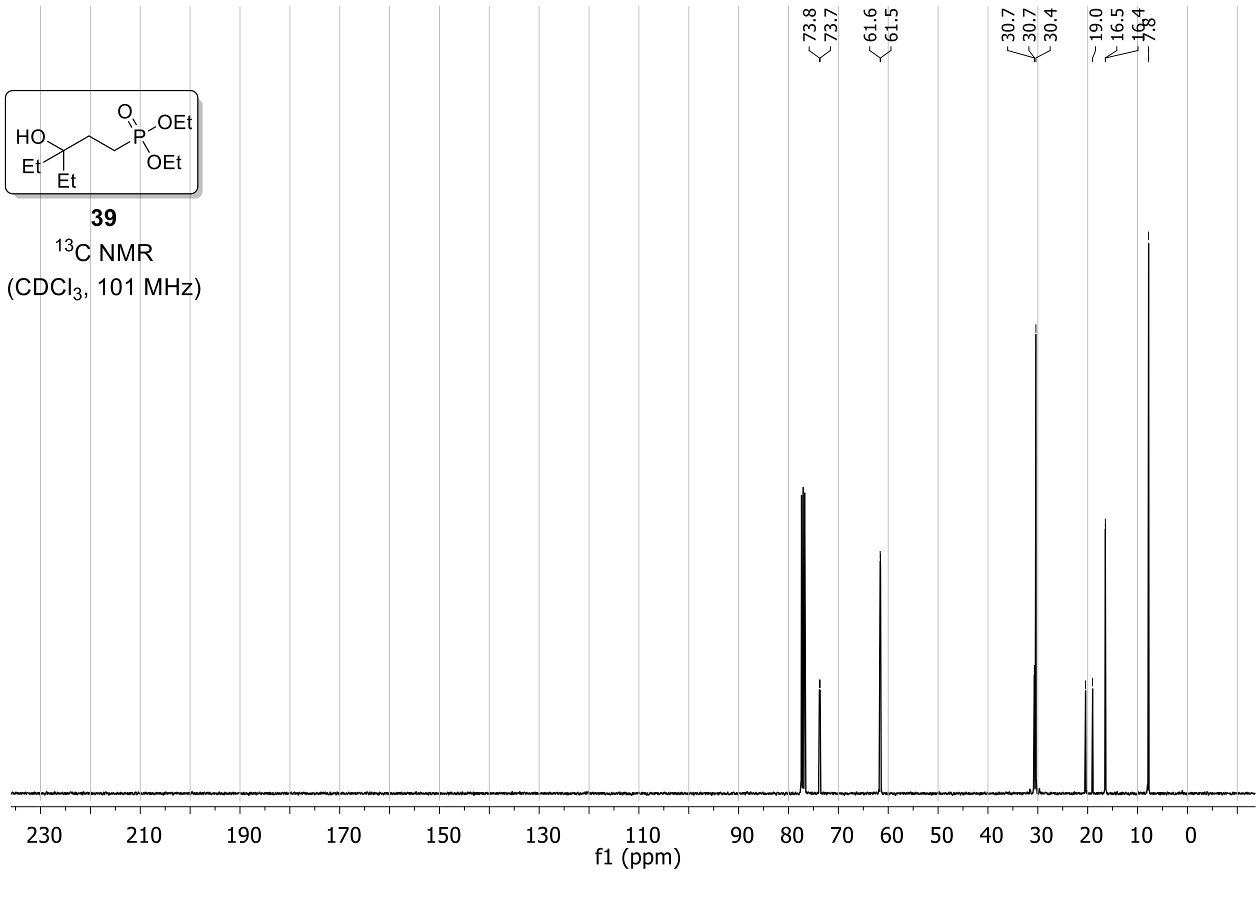
HO
OEt
OEt
ⁱPr
38
^{13}C NMR
(CDCl$_3$, 101 MHz)
76.5
76.4
61.7
61.7
61.7
61.6
33.7
27.0
27.0
23.1
21.7
18.7
17.5
16.5
16.4
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



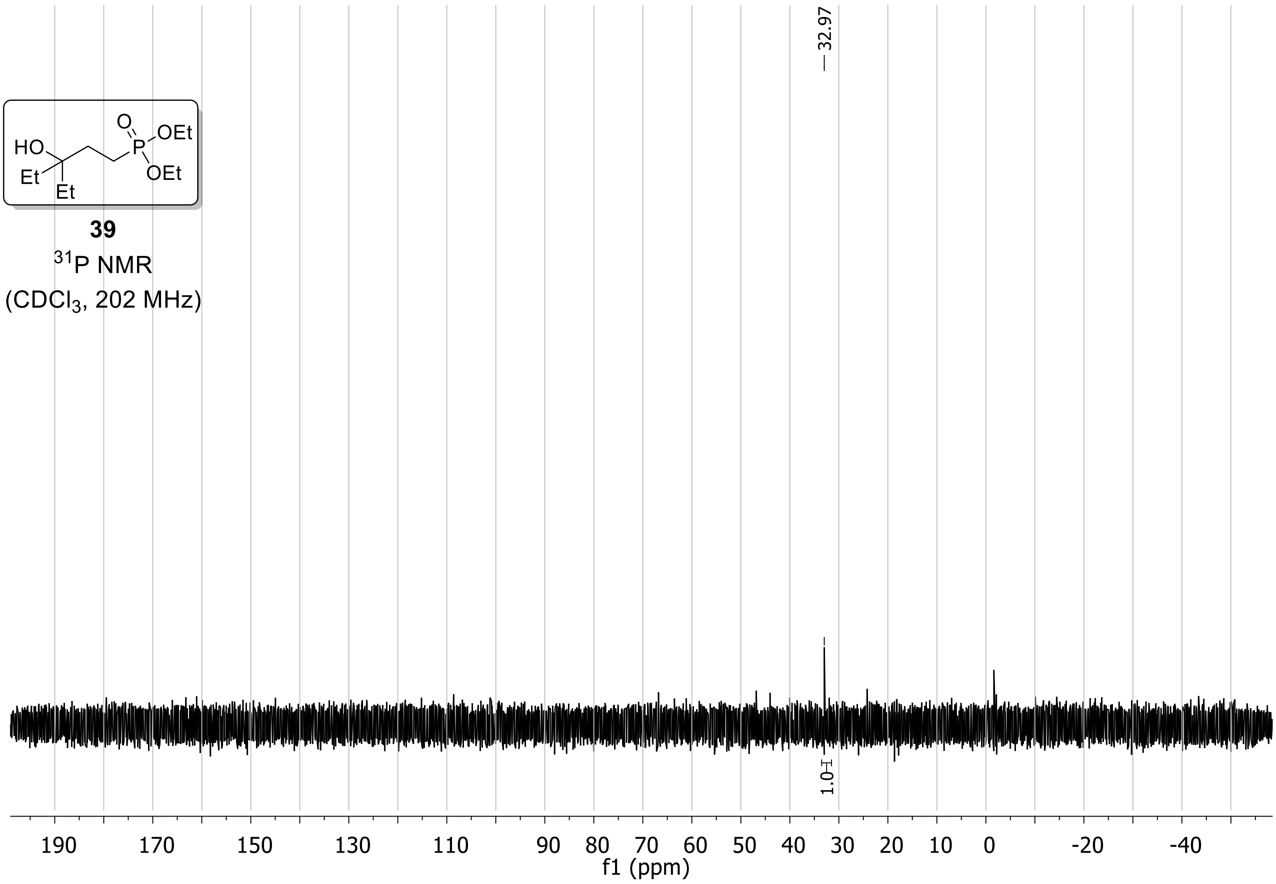
HO
OEt
OEt
ⁱPr
38
^{31}P NMR
(CDCl$_3$, 202 MHz)
33.46
1.0
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40
f1 (ppm)



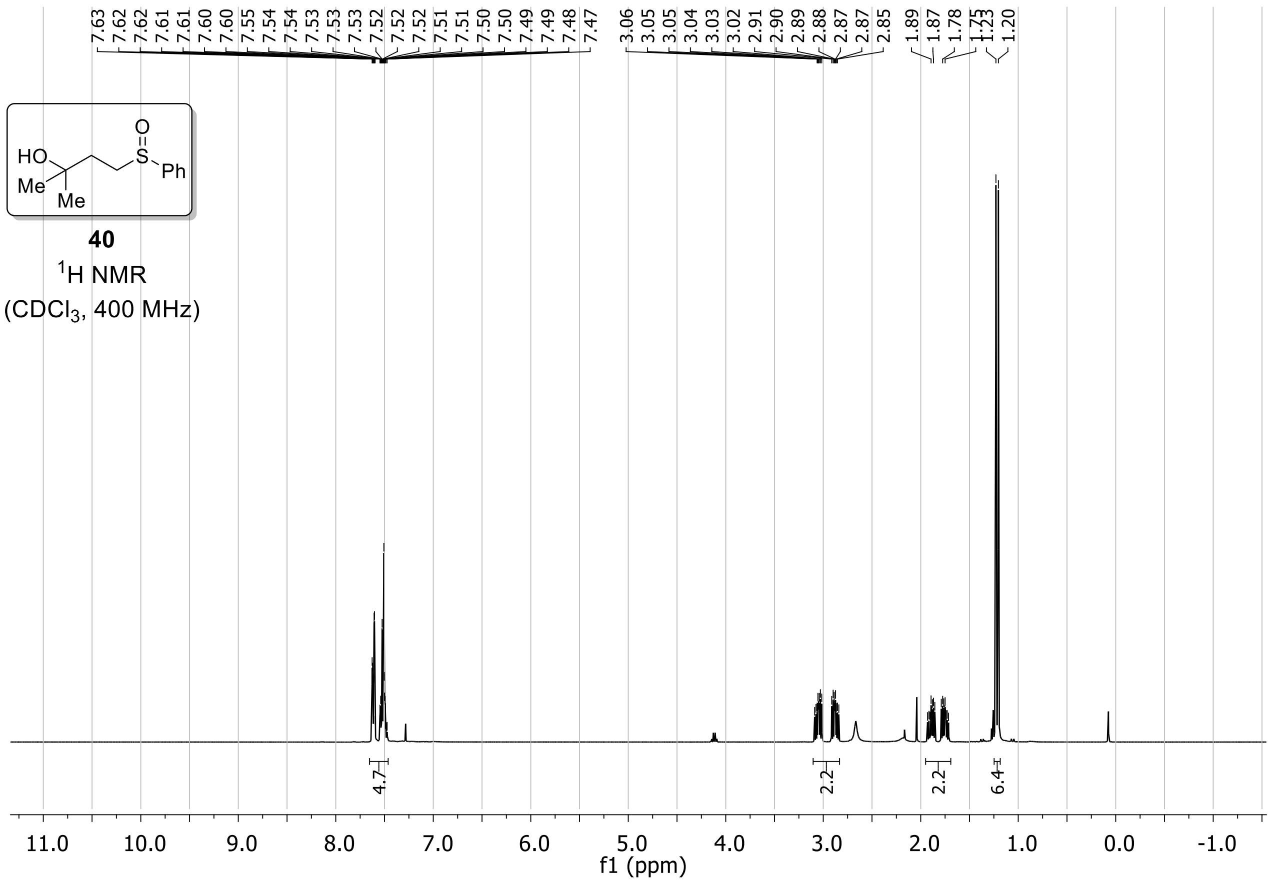
39
^{1}H NMR
($CDCl_3$, 400 MHz)
f1 (ppm)



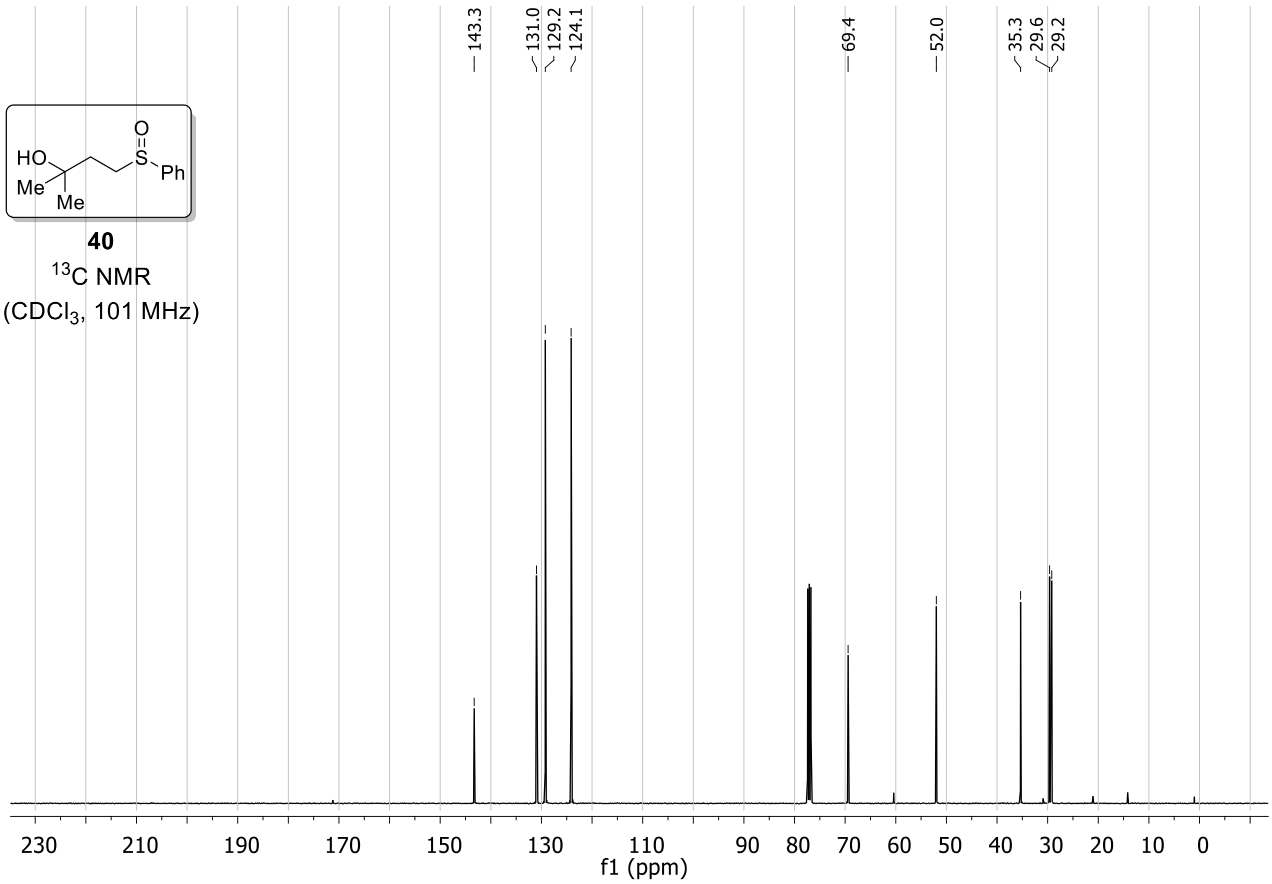
39
^{13}C NMR
($CDCl_3$, 101 MHz)
f1 (ppm)



O
HO
P
OEt
OEt
Et
Et
39
^{31}P NMR
(CDCl$_3$, 202 MHz)
32.97
1.0
190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -20 -40
f1 (ppm)



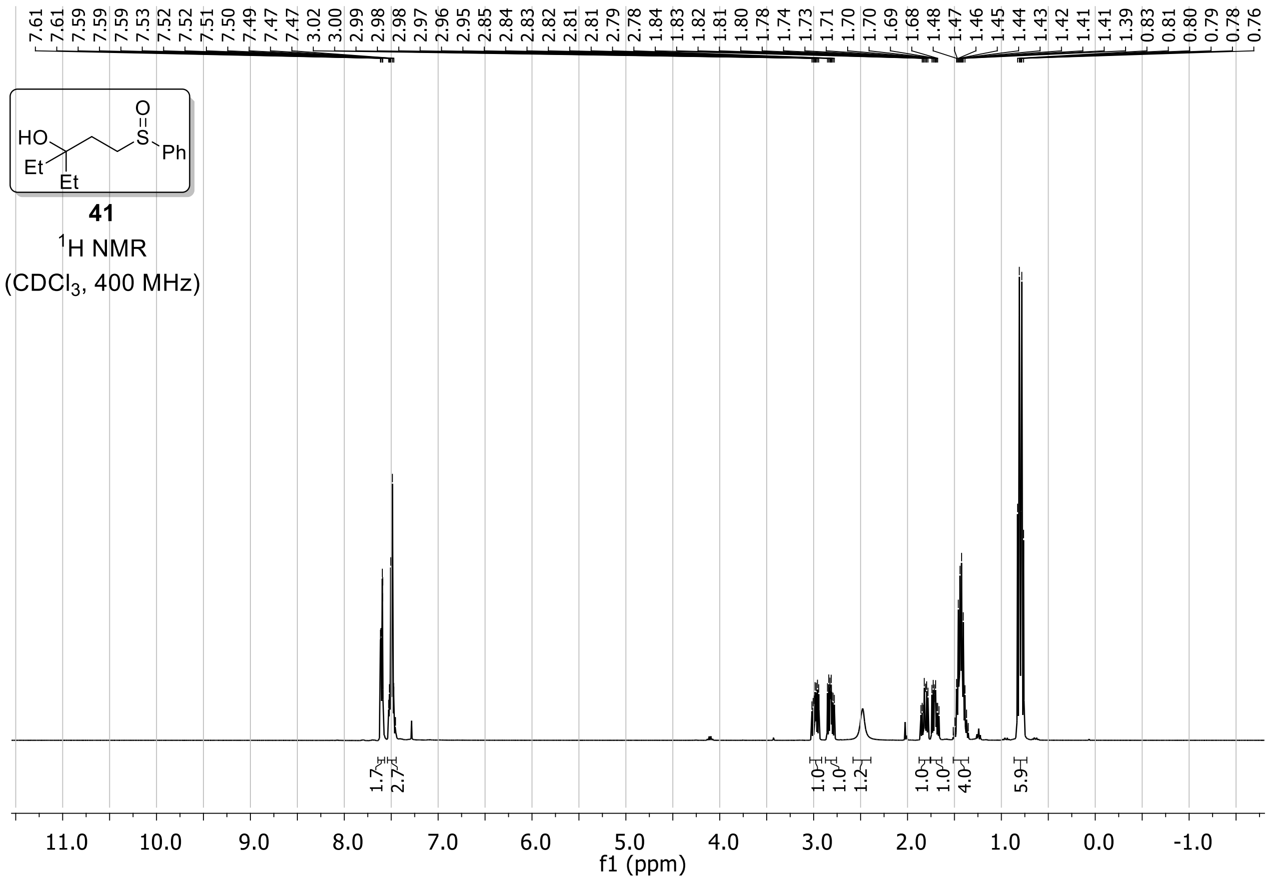
7.63 7.62 7.62 7.61 7.61 7.60 7.60 7.55 7.54 7.54 7.53 7.53 7.53 7.52 7.52 7.52 7.51 7.51 7.50 7.50 7.49 7.48 7.47
3.06 3.05 3.05 3.04 3.03 3.02 2.91 2.90 2.89 2.88 2.87 2.87 2.85
1.89 1.87 1.78 1.75 1.23 1.20
O
S
Ph
HO
Me
Me
40
^{1}H NMR
(CDCl$_3$, 400 MHz)
4.7
2.2
2.2
6.4
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0 -1.0
f1 (ppm)



40

^{13}C NMR

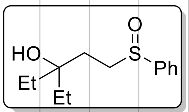
($CDCl_3$, 101 MHz)



41

^{1}H NMR

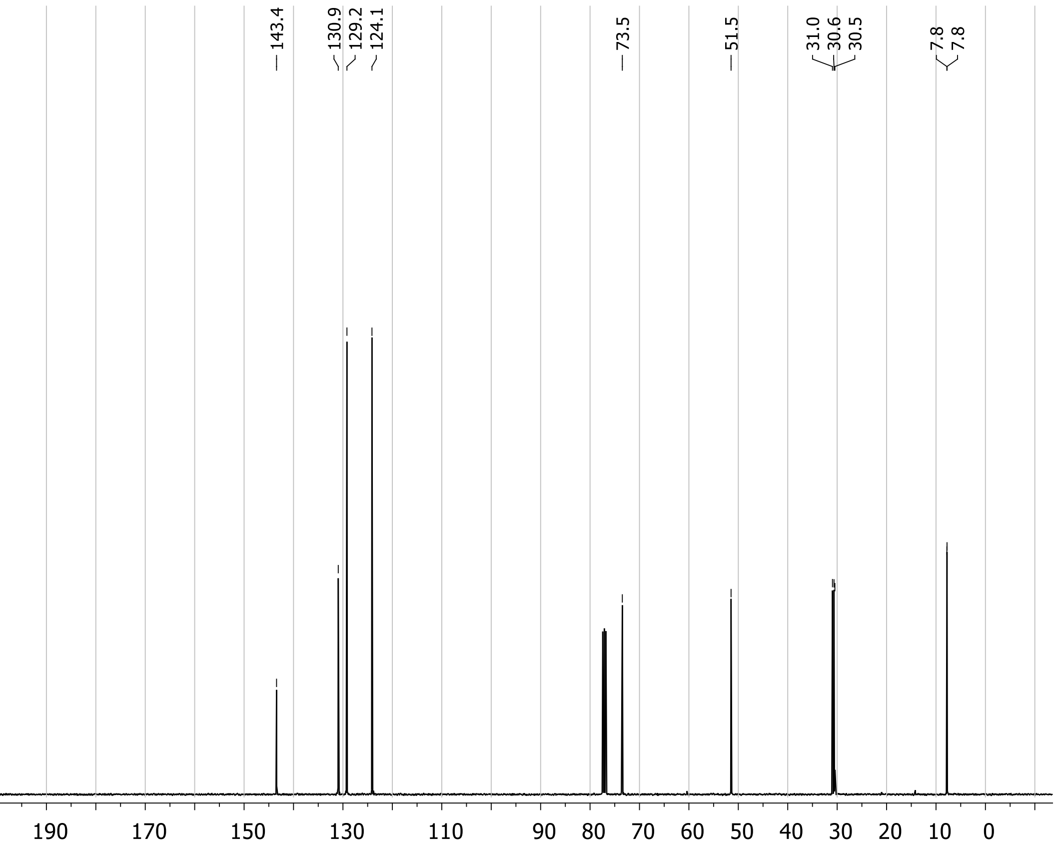
($CDCl_3$, 400 MHz)

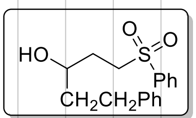


41

^{13}C NMR

($CDCl_3$, 101 MHz)

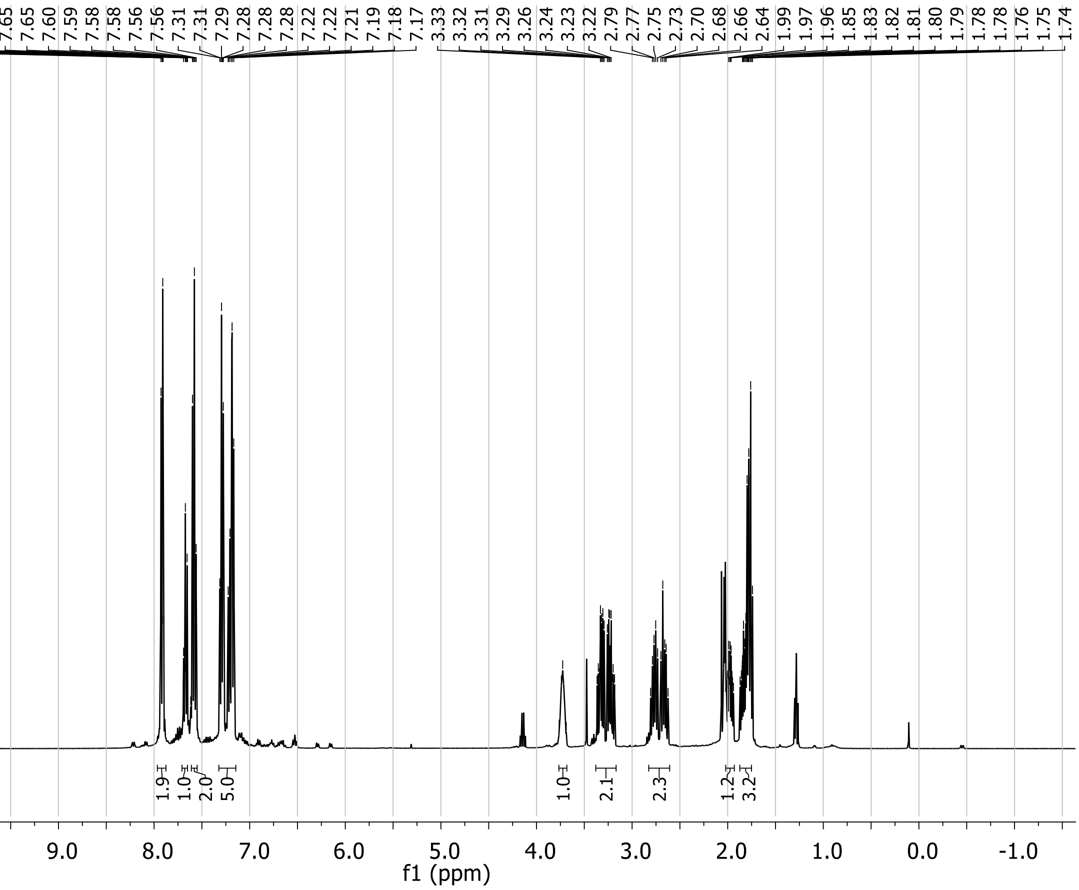


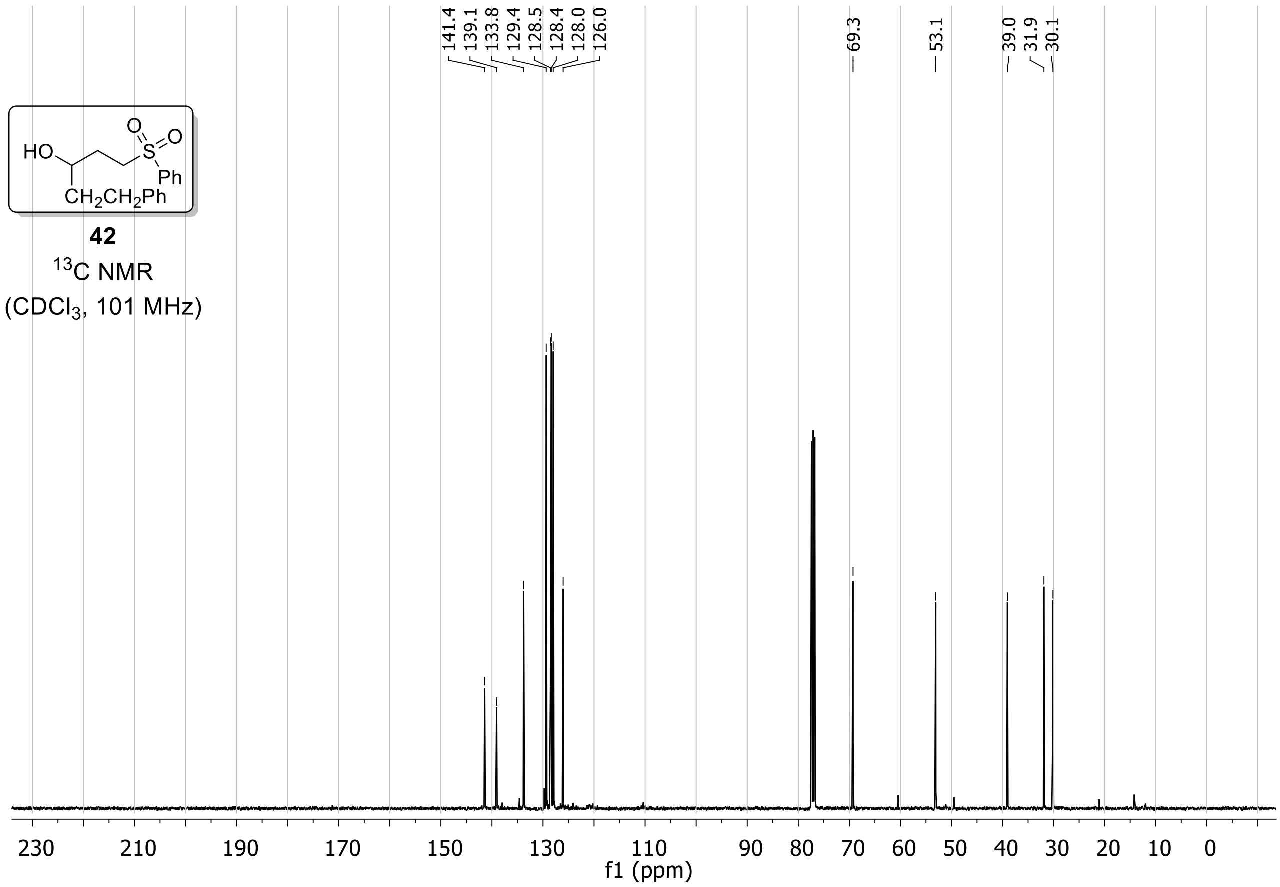


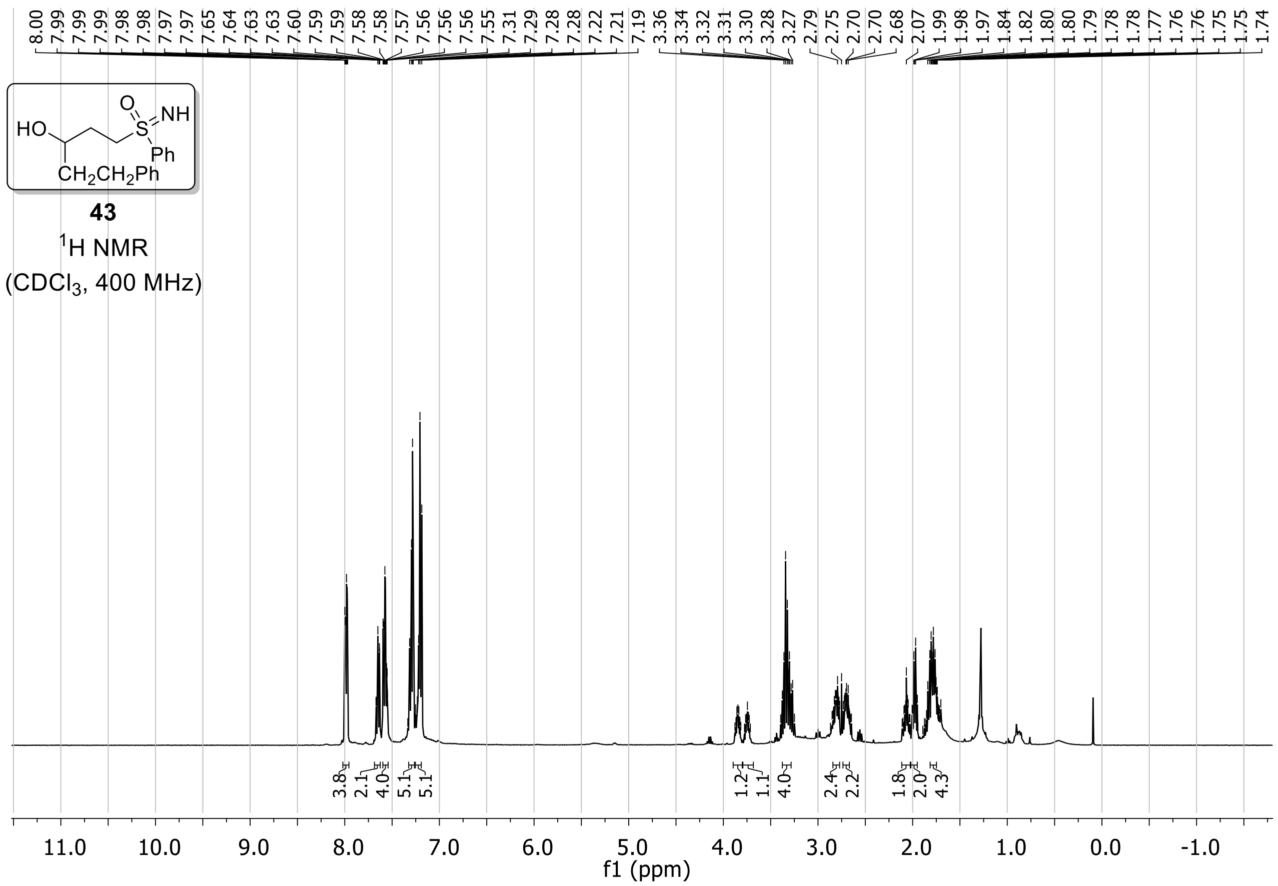
42

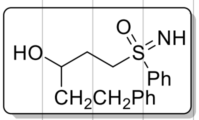
^{1}H NMR

($CDCl_3$, 400 MHz)




42
13C NMR
(CDCl3, 101 MHz)
141.4
139.1
133.8
129.4
128.5
128.4
128.0
126.0
69.3
53.1
39.0
31.9
30.1
f1 (ppm)

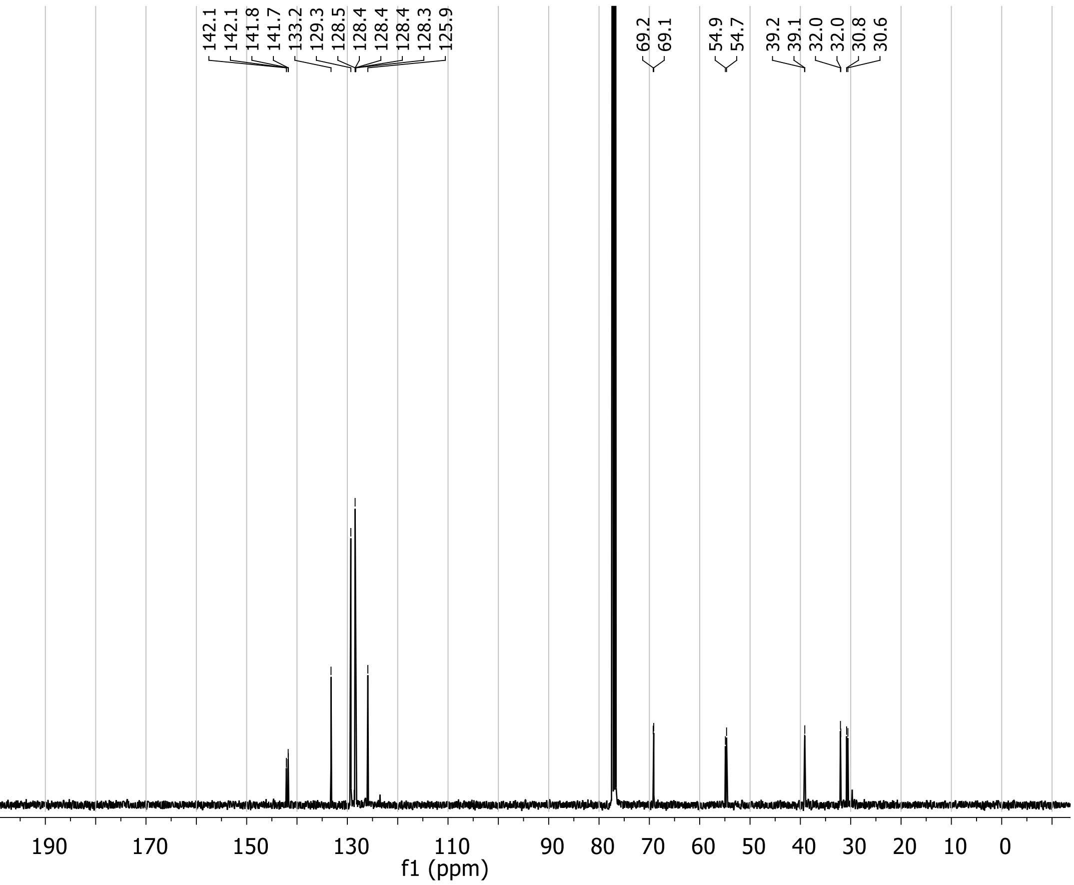

43
1H NMR
(CDCl3, 400 MHz)
f1 (ppm)

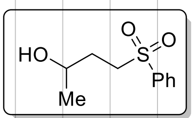


43

^{13}C NMR

($CDCl_3$, 101 MHz)

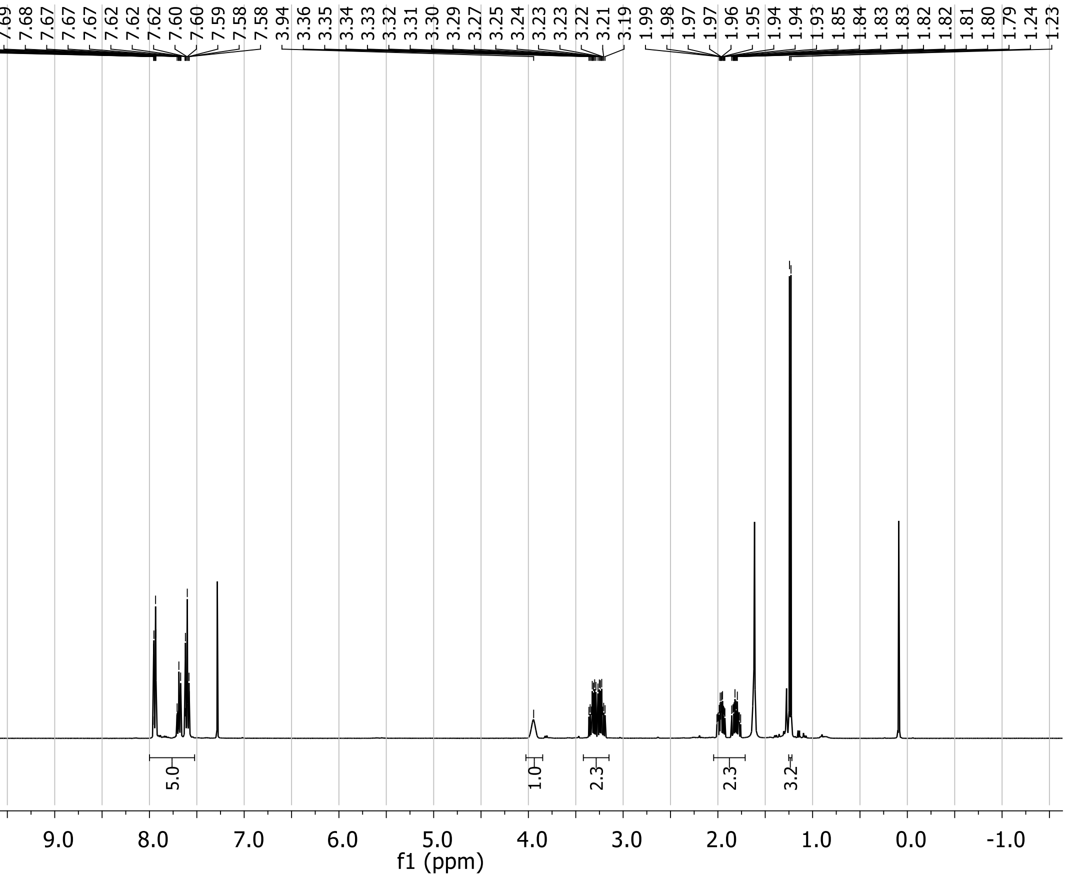




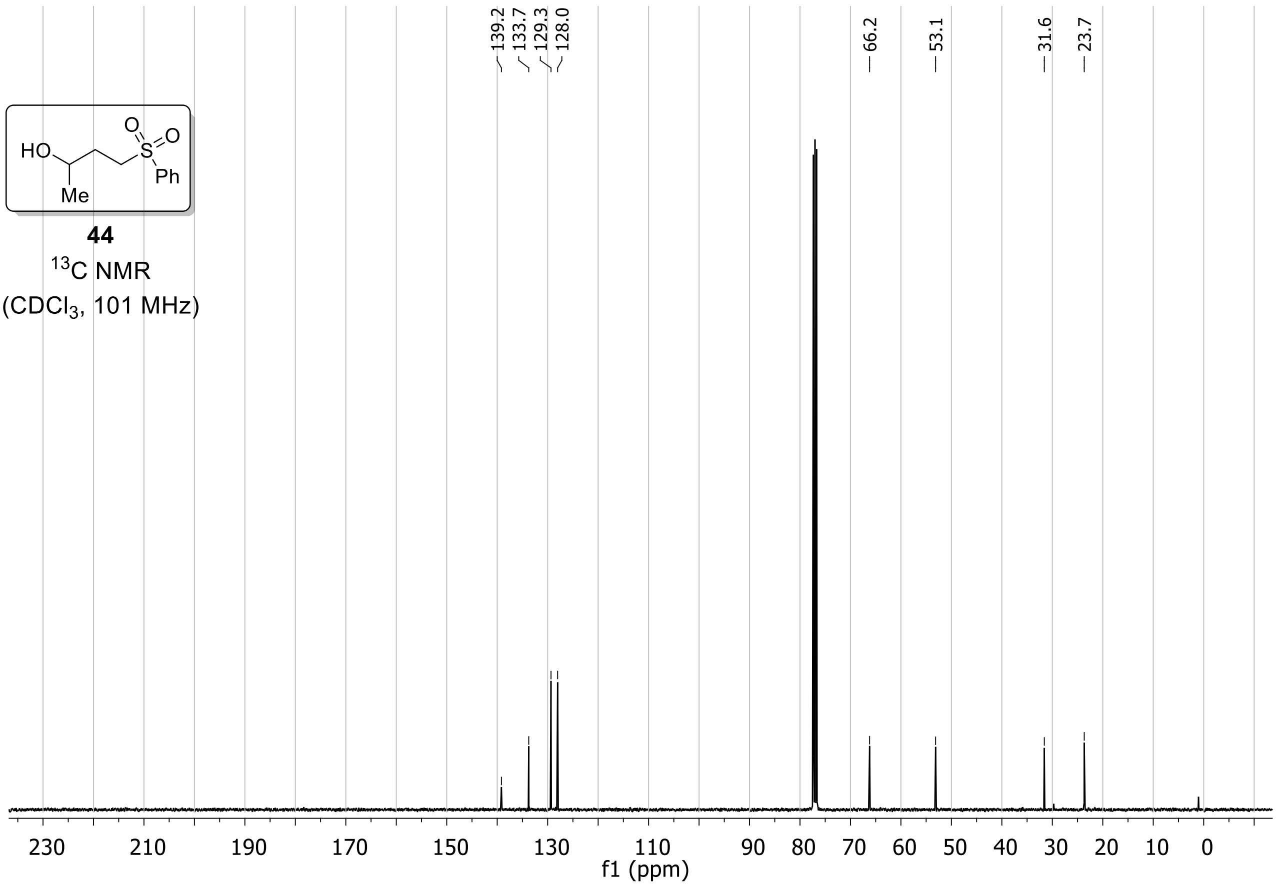
44

^{1}H NMR

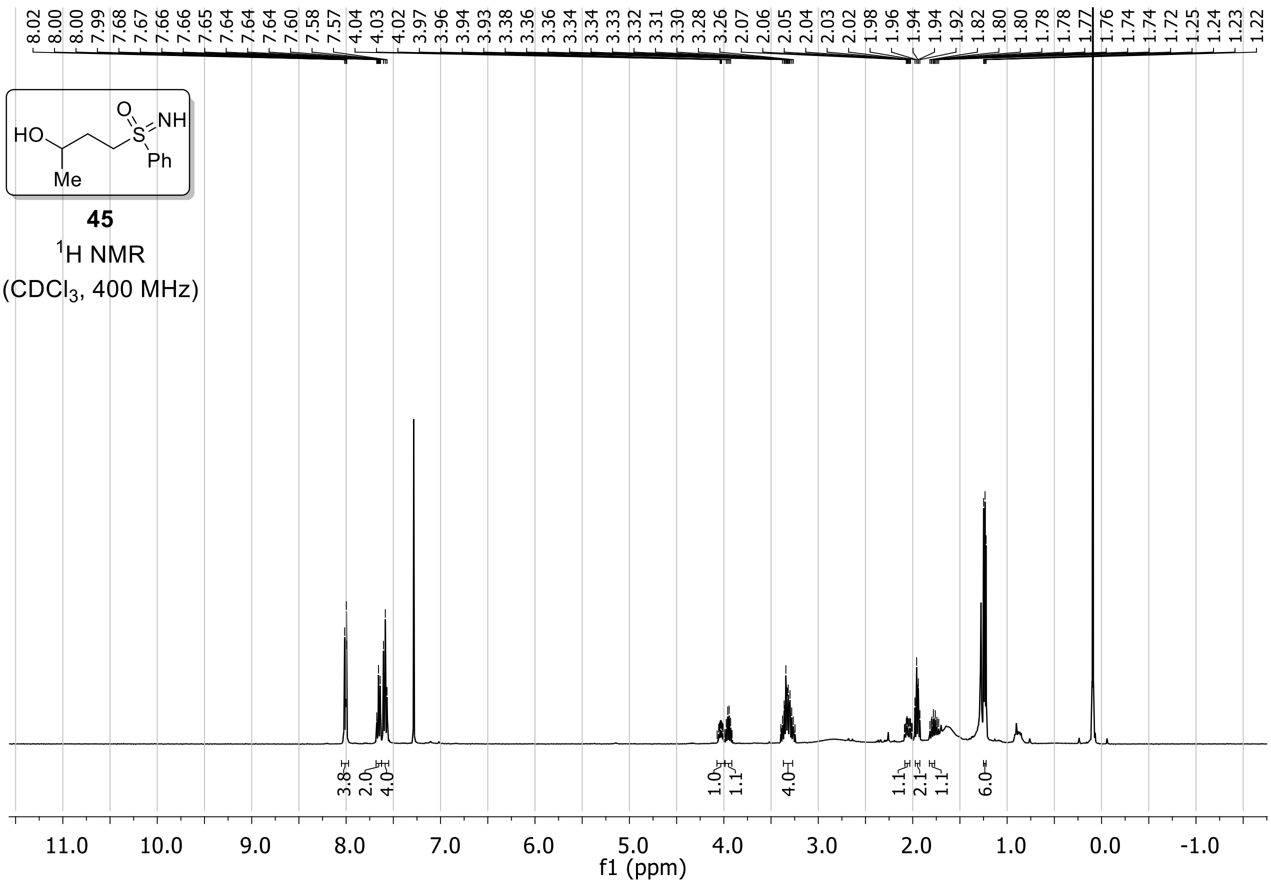
($CDCl_3$, 400 MHz)

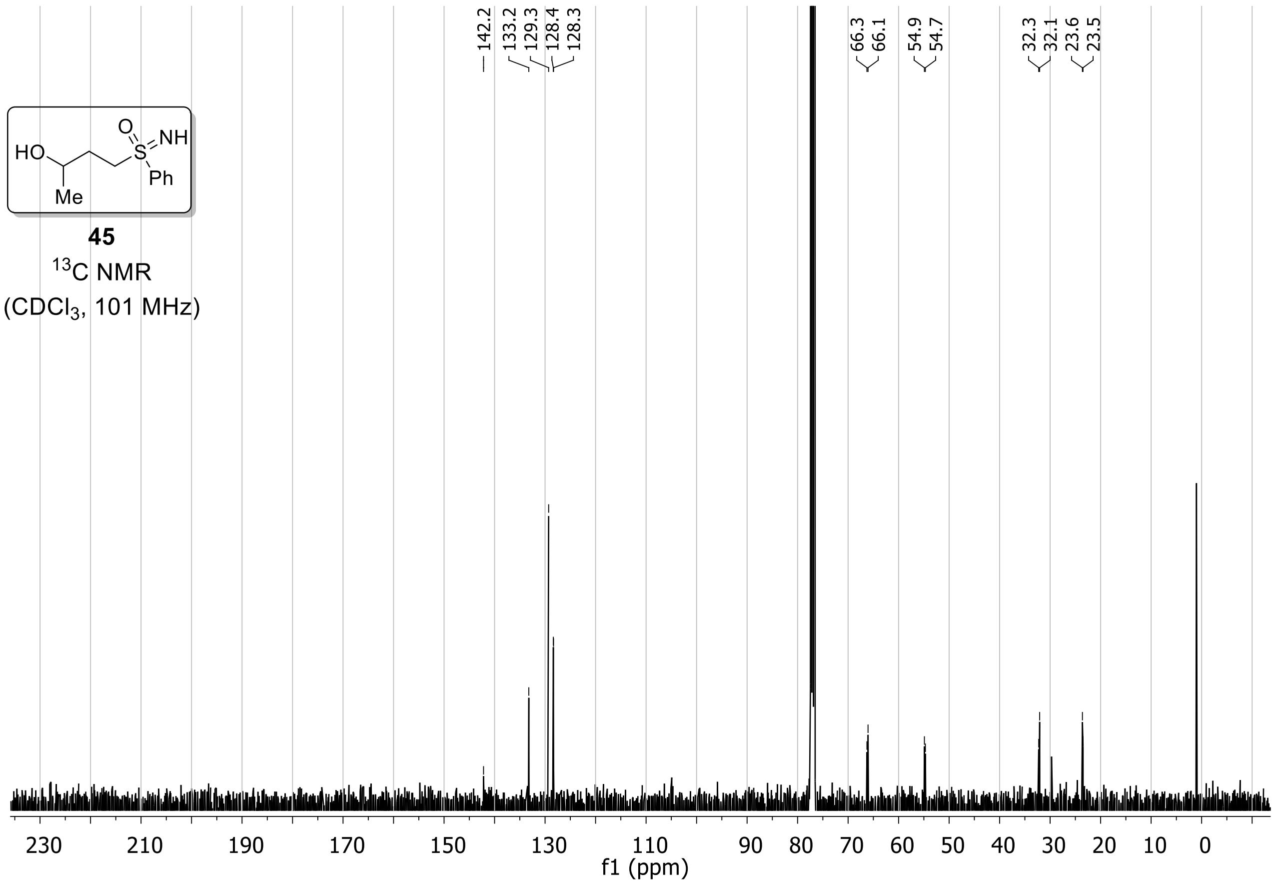


44
^{13}C NMR
($CDCl_3$, 101 MHz)

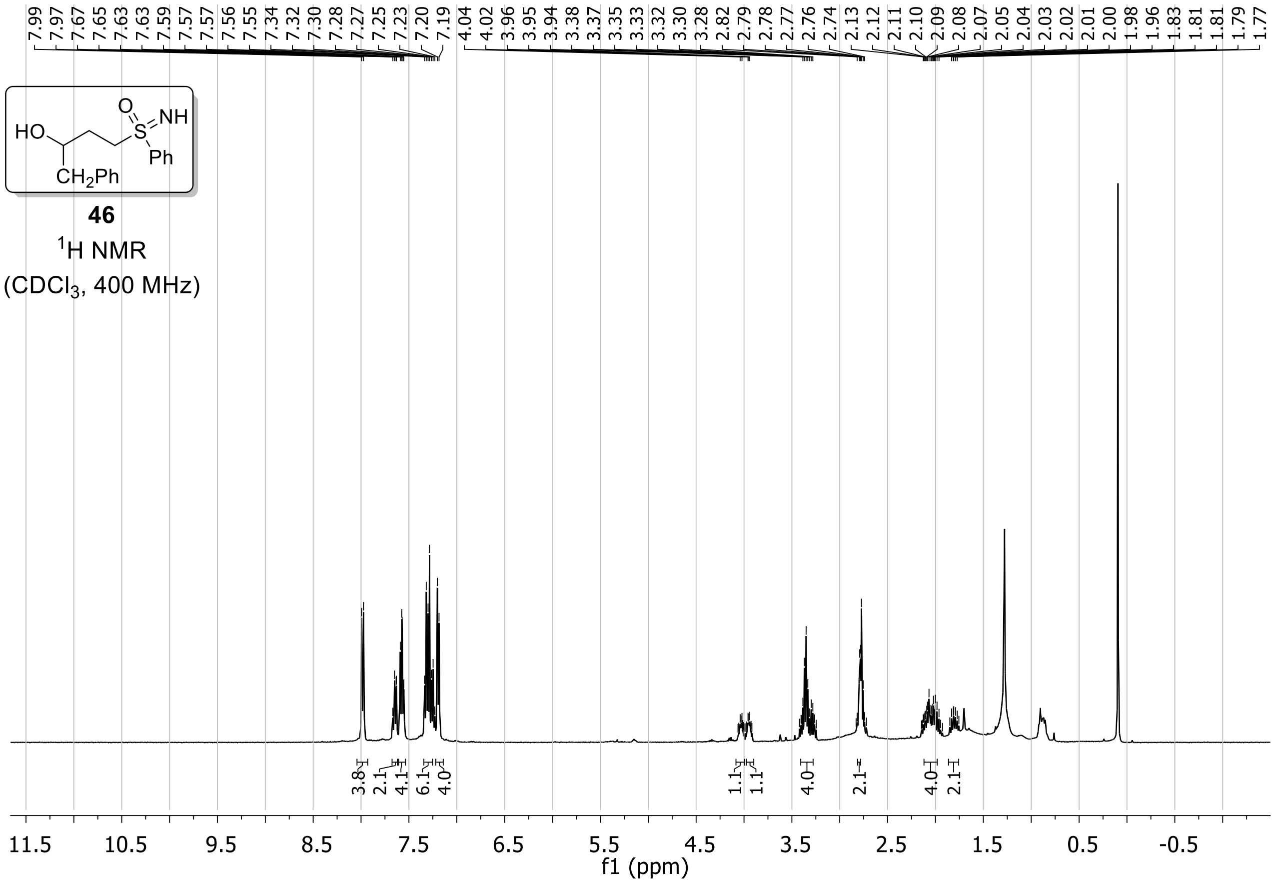


45
^1H NMR
($CDCl_3$, 400 MHz)

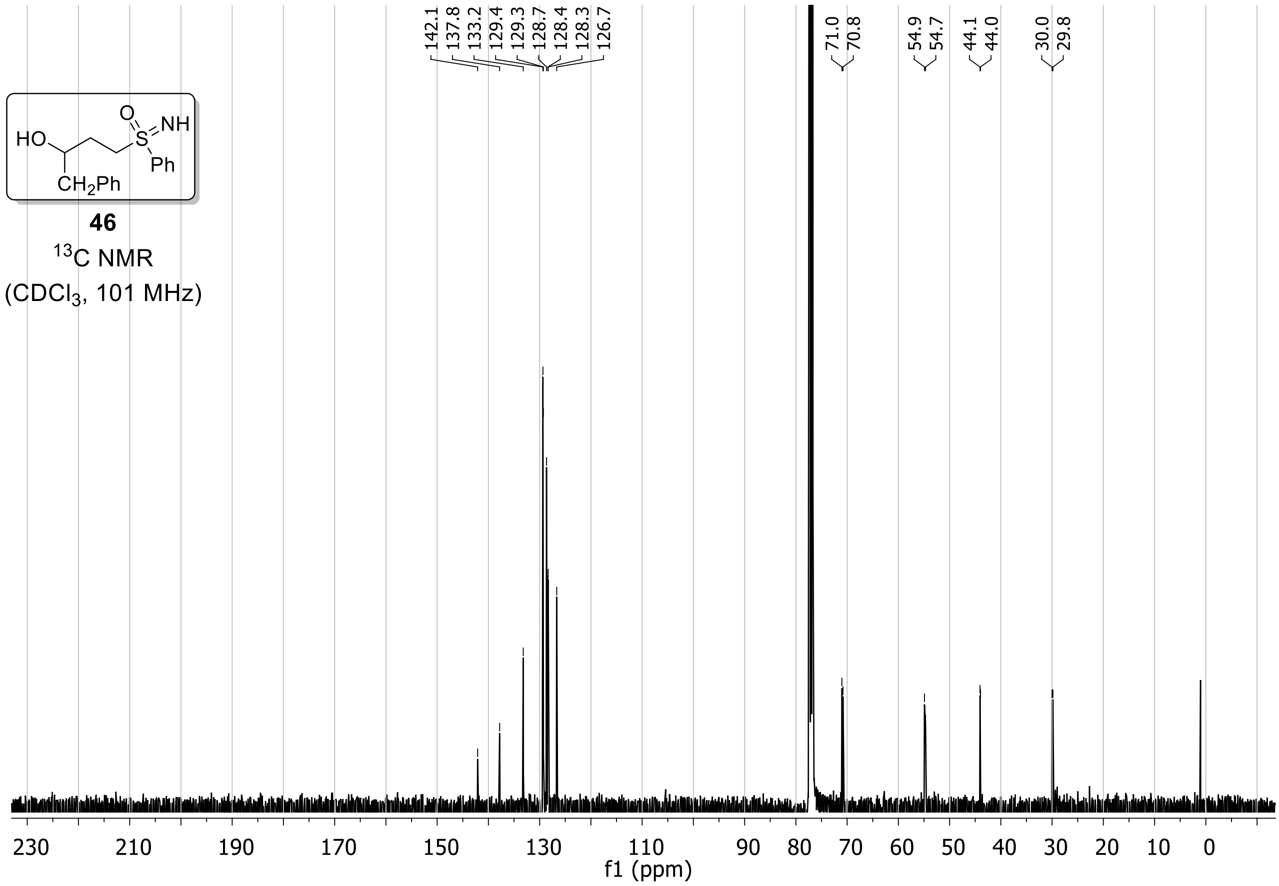




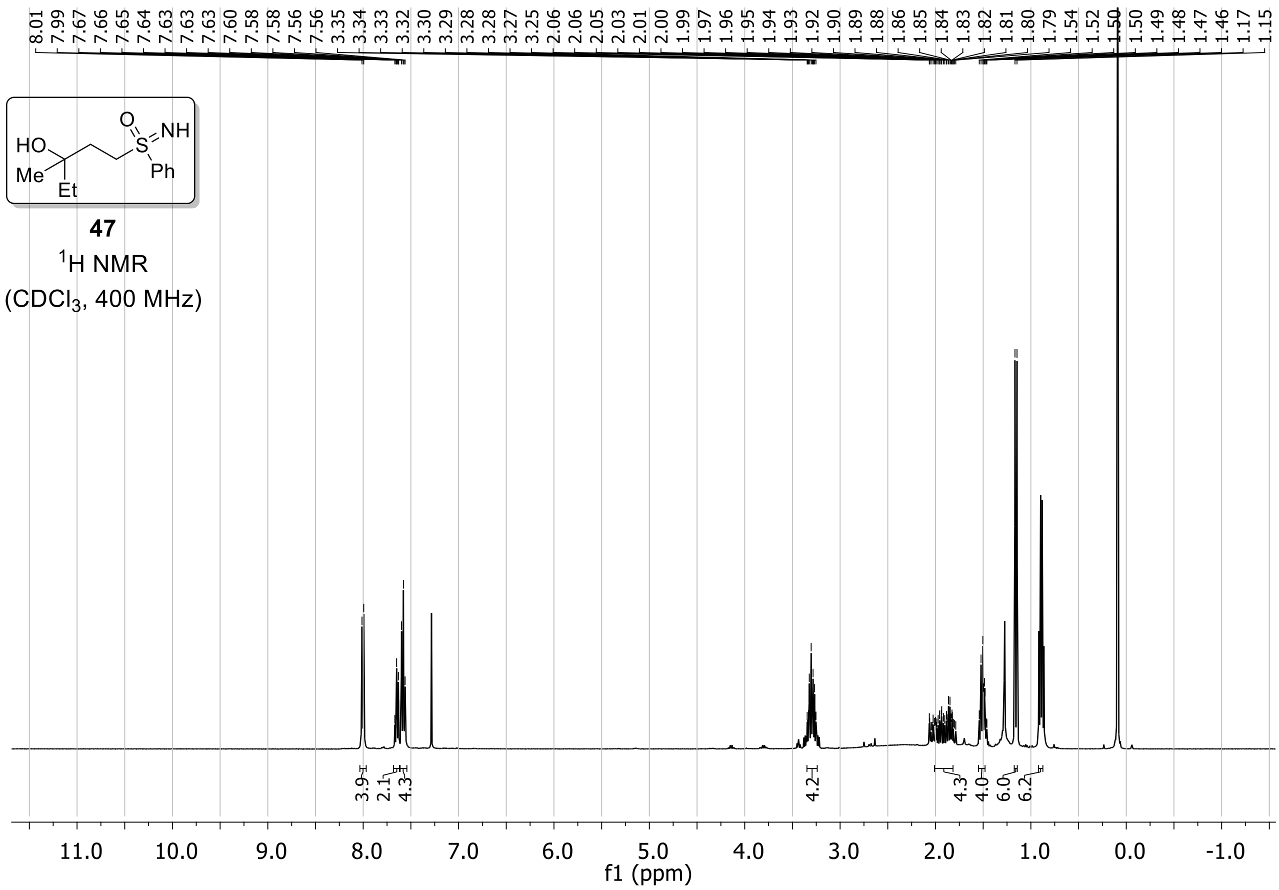
HO
O
S
NH
Ph
Me
45
^{13}C NMR
($CDCl_3$, 101 MHz)
142.2
133.2
129.3
128.4
128.3
66.3
66.1
54.9
54.7
32.3
32.1
23.6
23.5
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



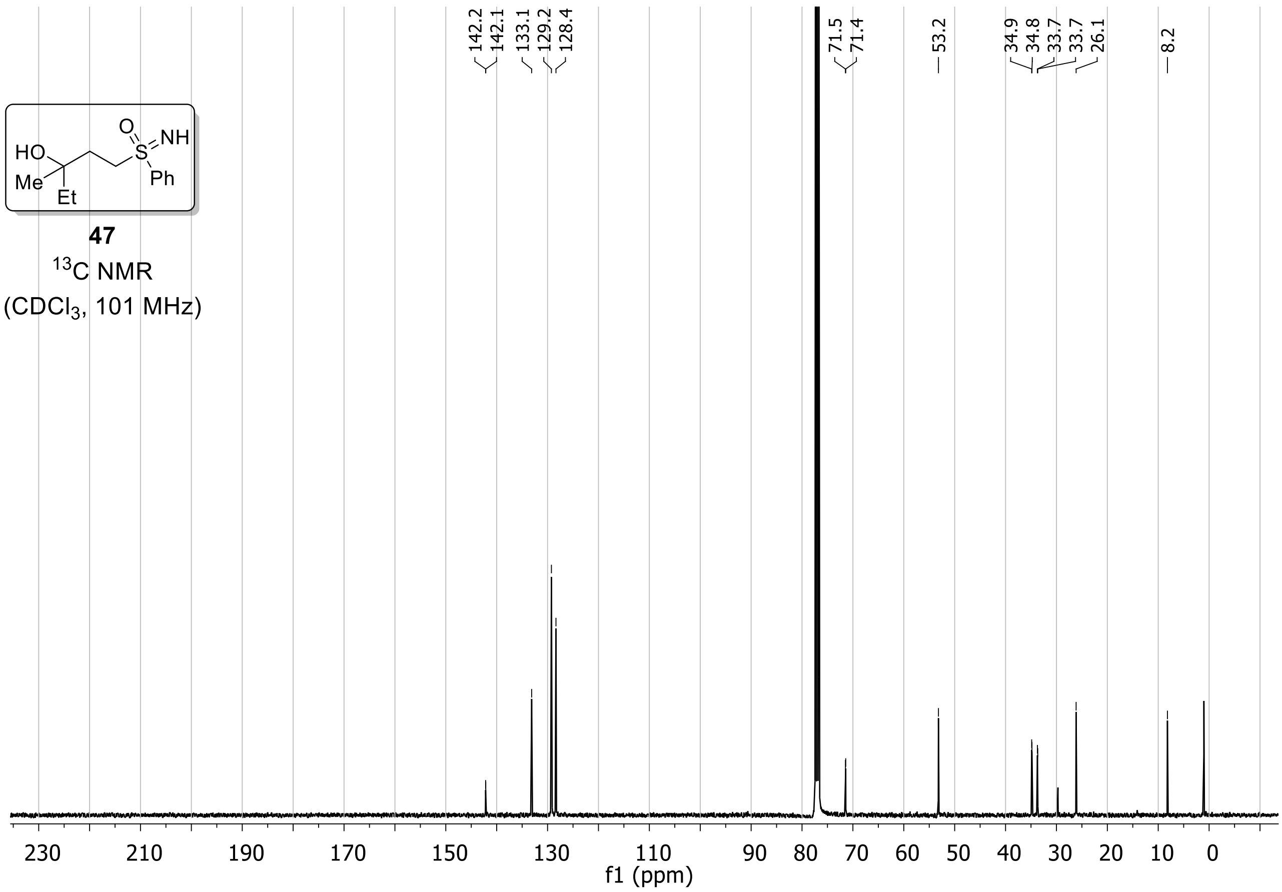
HO
O
S
NH
Ph
CH_2Ph
46
^{1}H NMR
($CDCl_3$, 400 MHz)
7.99 7.97 7.67 7.65 7.63 7.63 7.59 7.57 7.57 7.56 7.55 7.34 7.32 7.30 7.28 7.27 7.25 7.23 7.20 7.19
4.04 4.02 3.96 3.95 3.94 3.38 3.37 3.35 3.33 3.32 3.30 3.28 2.82 2.79 2.78 2.77 2.76 2.74 2.13 2.12 2.11 2.10 2.09 2.08 2.07 2.05 2.04 2.03 2.02 2.01 2.00 1.98 1.96 1.83 1.81 1.81 1.79 1.77
3.8 2.1 4.1 6.1 4.0
1.1 1.1 4.0 2.1 4.0 2.1
11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)



46
^{13}C NMR
($CDCl_3$, 101 MHz)



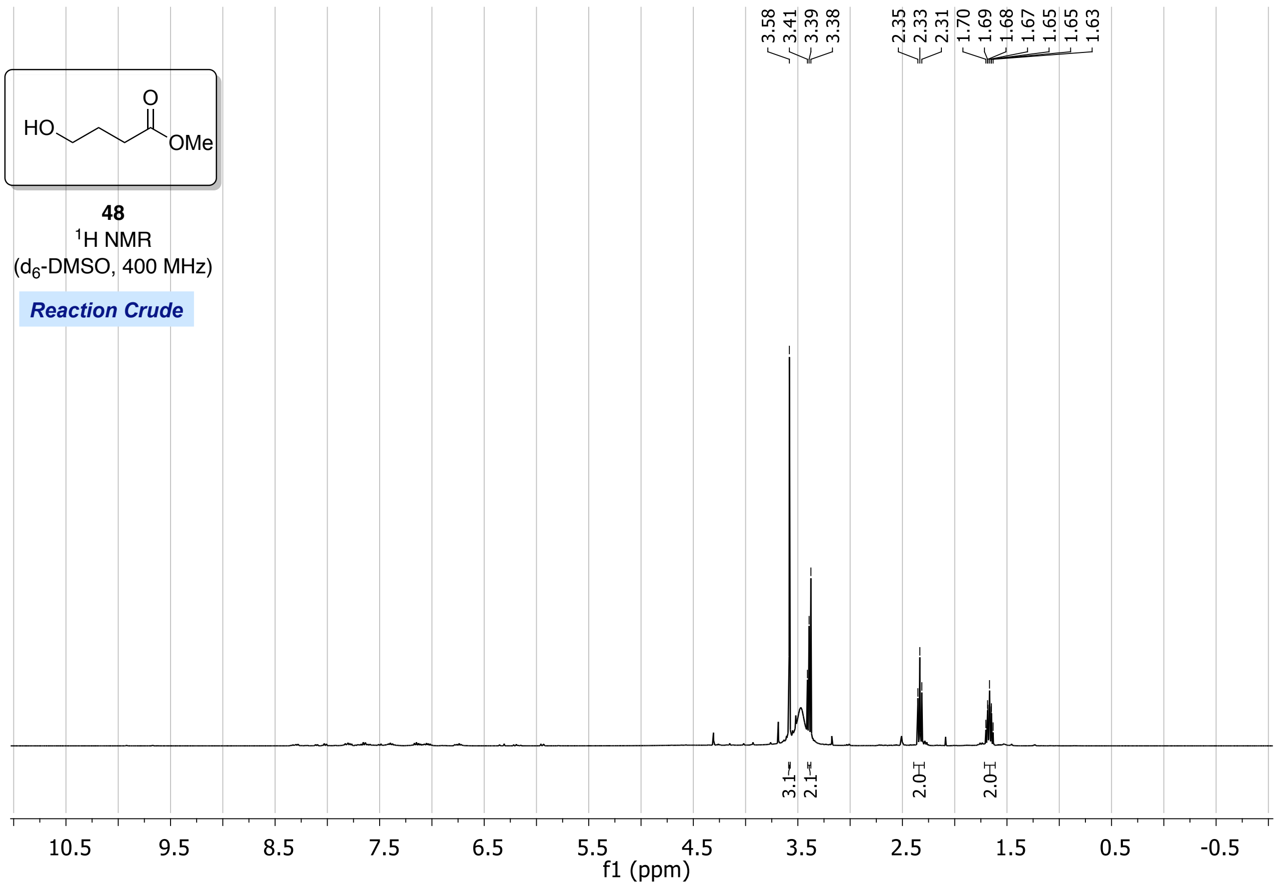
47
^{1}H NMR
($CDCl_3$, 400 MHz)



47

^{13}C NMR

($CDCl_3$, 101 MHz)

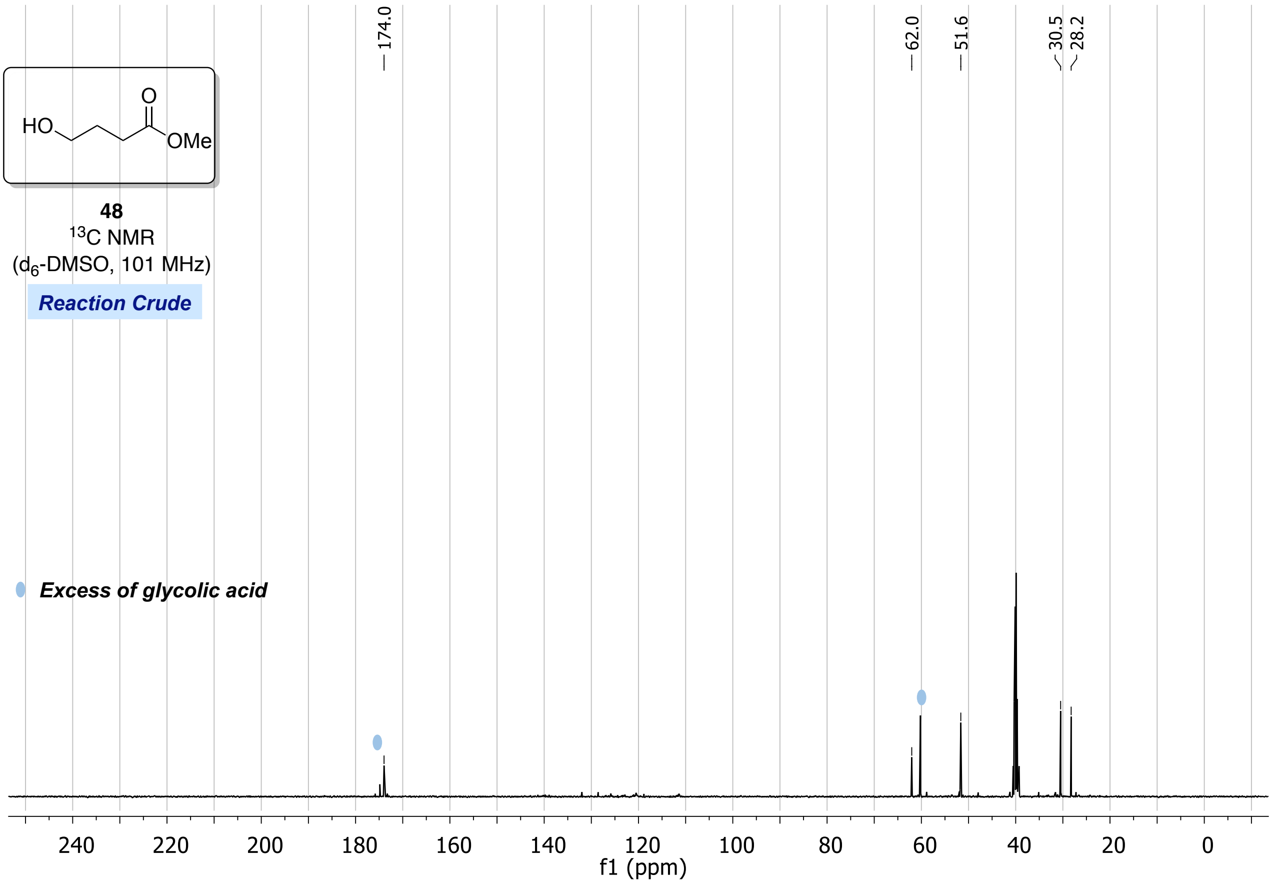


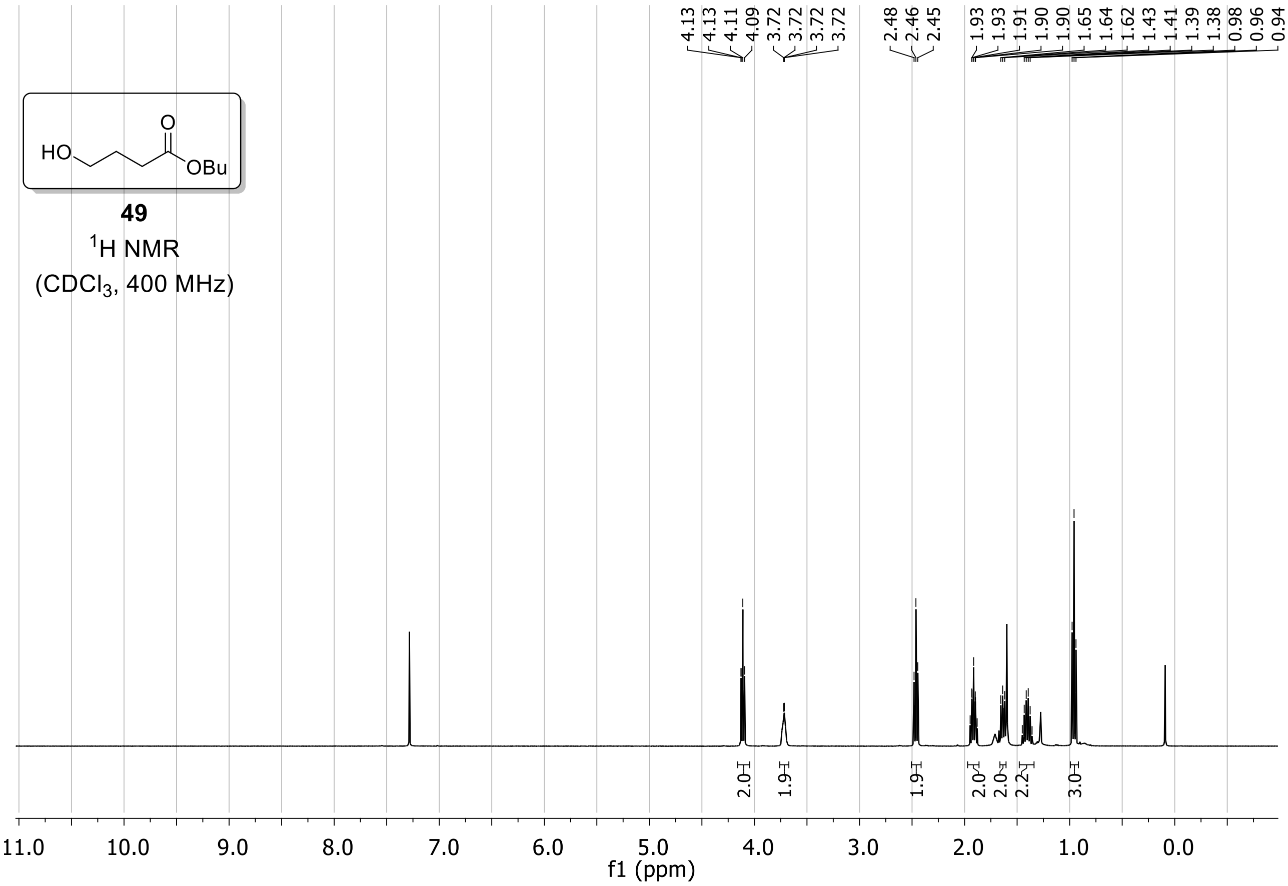
48

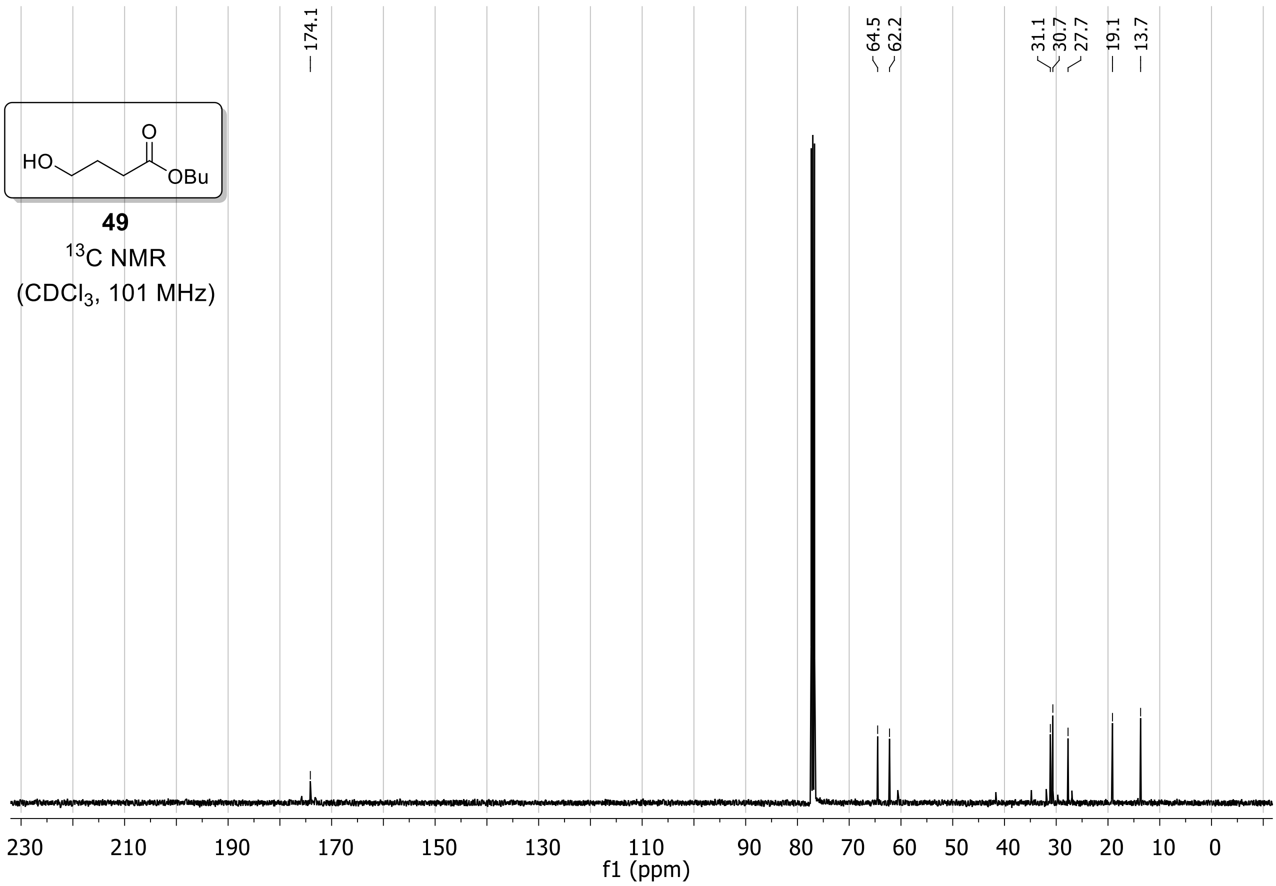
^{1}H NMR

(d_6-DMSO, 400 MHz)

Reaction Crude


HO
O
OMe
48
13C NMR
(d6-DMSO, 101 MHz)
Reaction Crude
Excess of glycolic acid
174.0
62.0
51.6
30.5
28.2
240
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

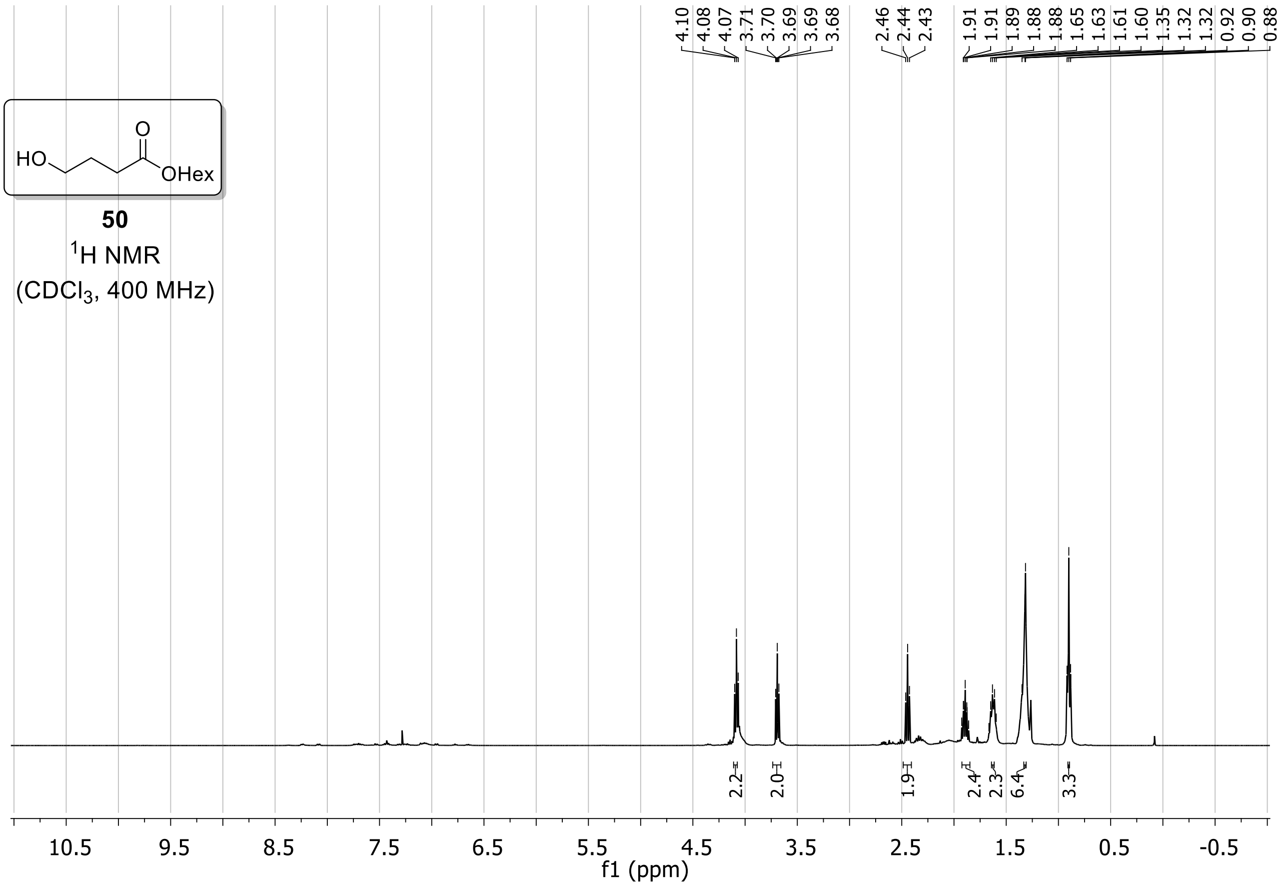

HO
O
OBu
49
1H NMR
(CDCl3, 400 MHz)
4.13
4.13
4.11
4.09
3.72
3.72
3.72
3.72
2.48
2.46
2.45
1.93
1.93
1.91
1.90
1.90
1.65
1.64
1.62
1.43
1.41
1.39
1.38
0.98
0.96
0.94
2.0
1.9
1.9
2.0
2.0
2.2
3.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)



49

^{13}C NMR

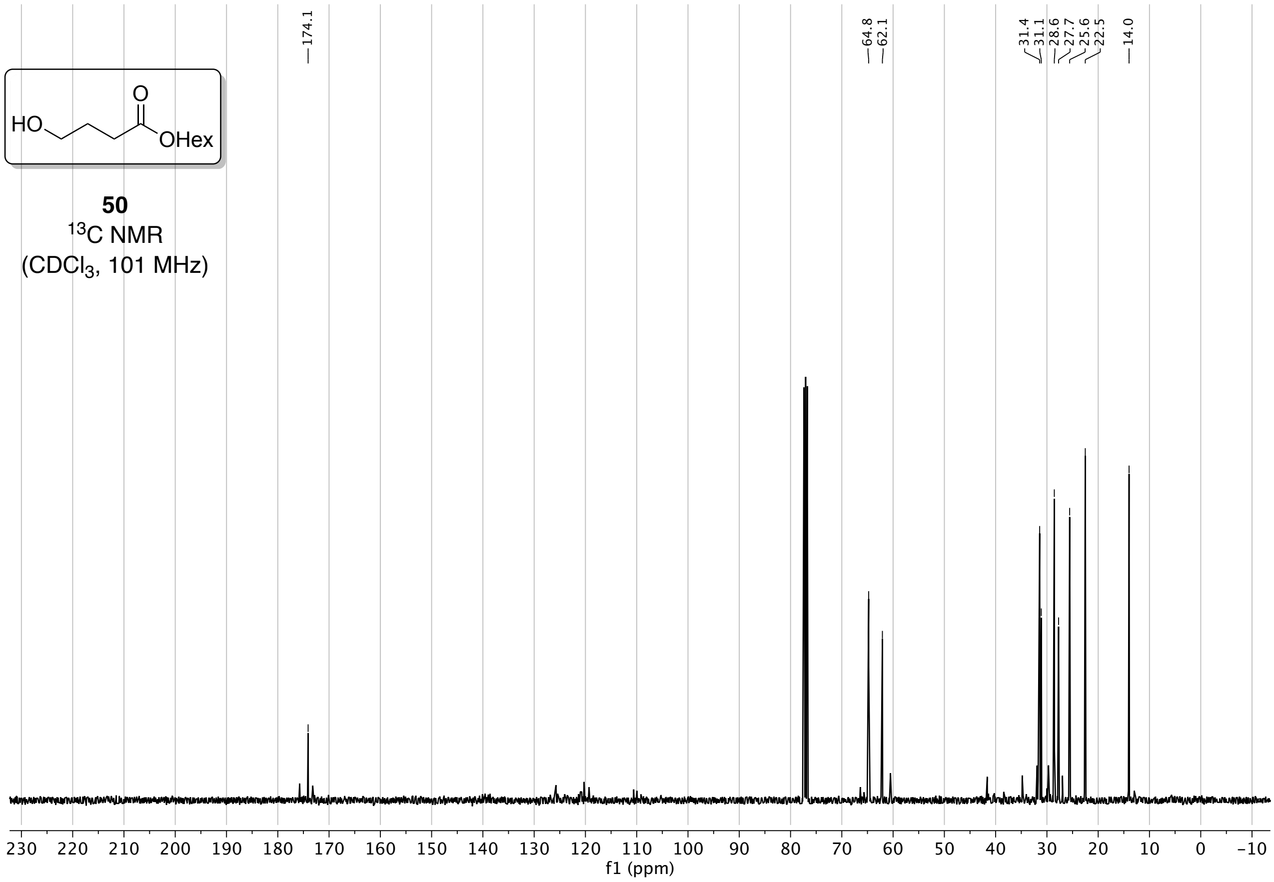
($CDCl_3$, 101 MHz)



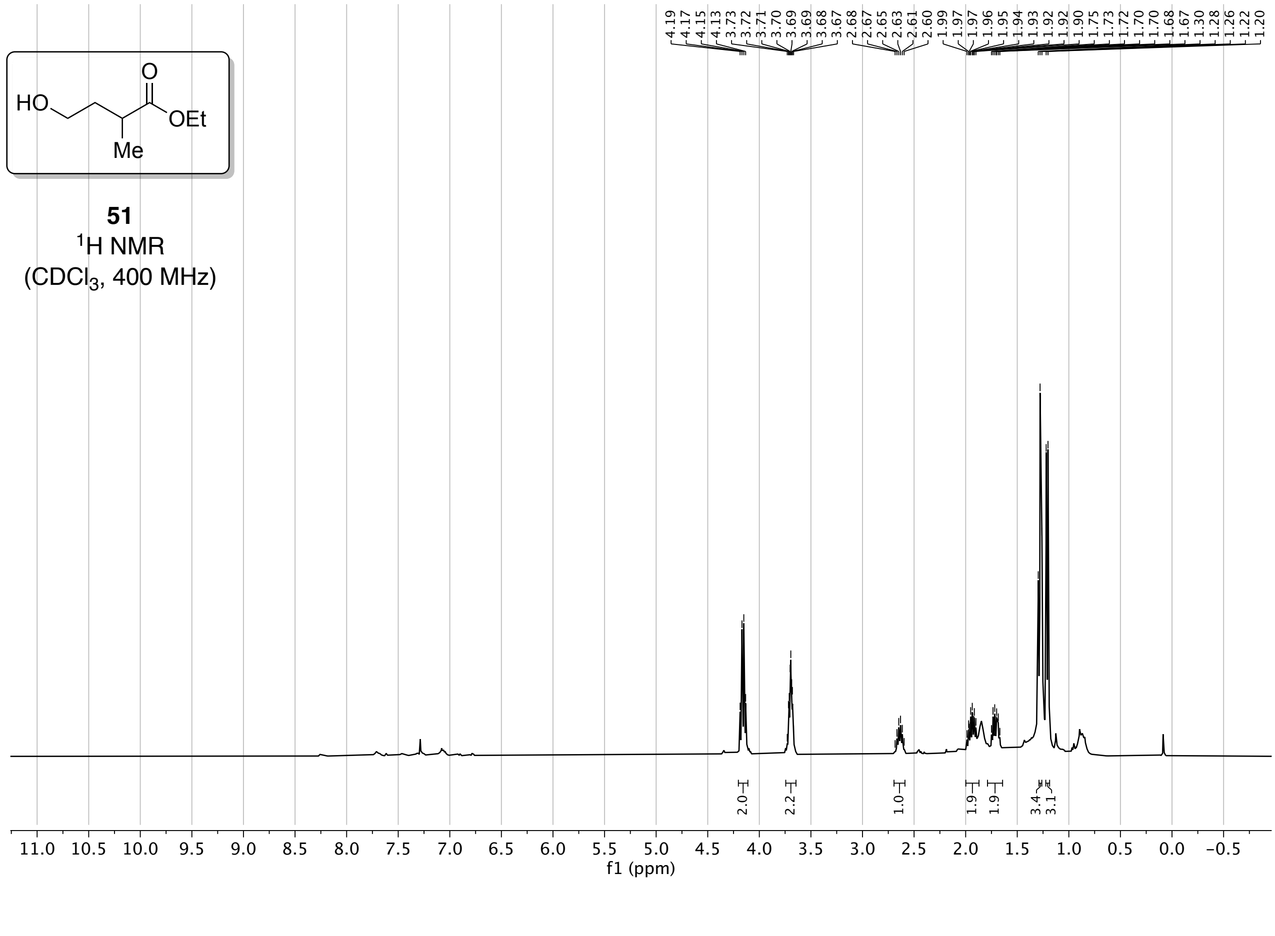
50

^{1}H NMR

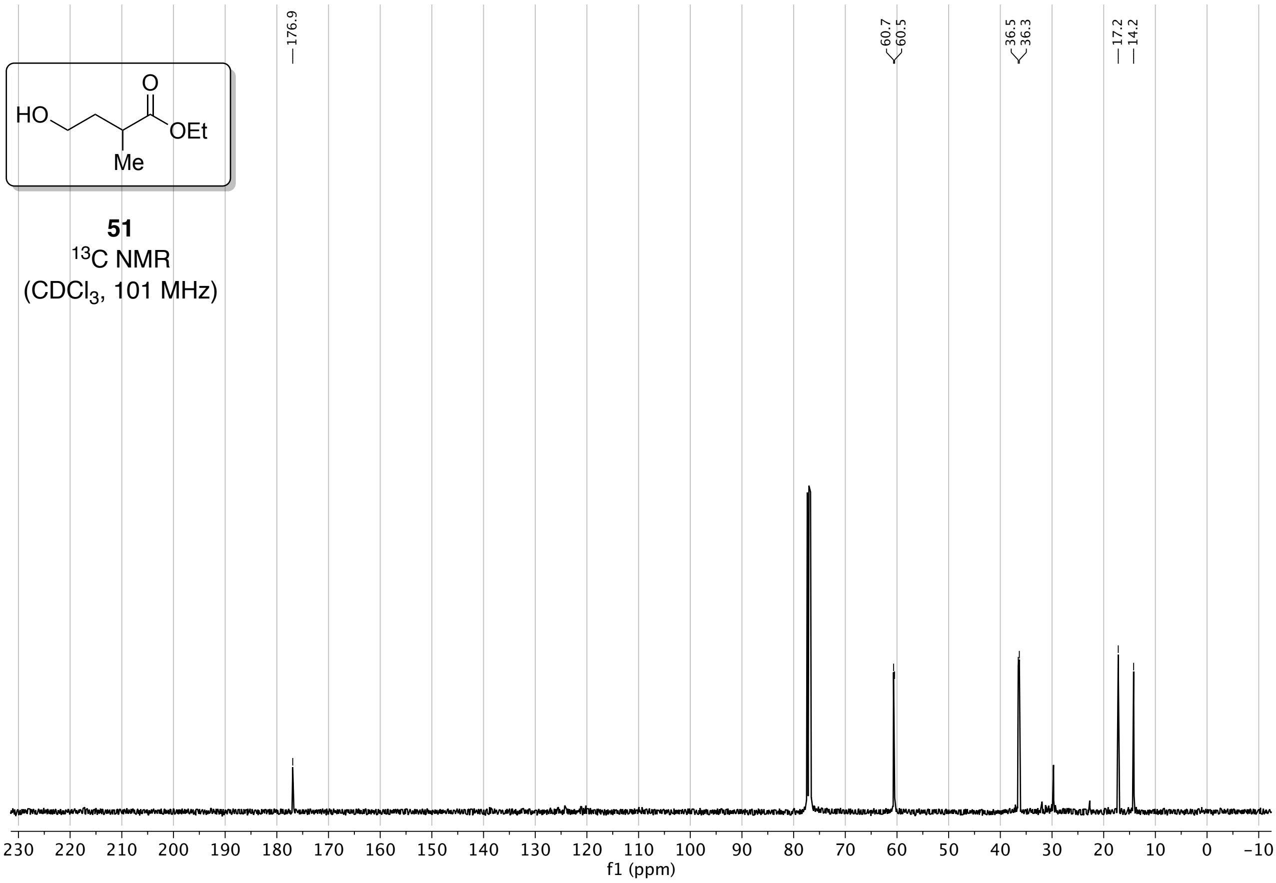
($CDCl_3$, 400 MHz)

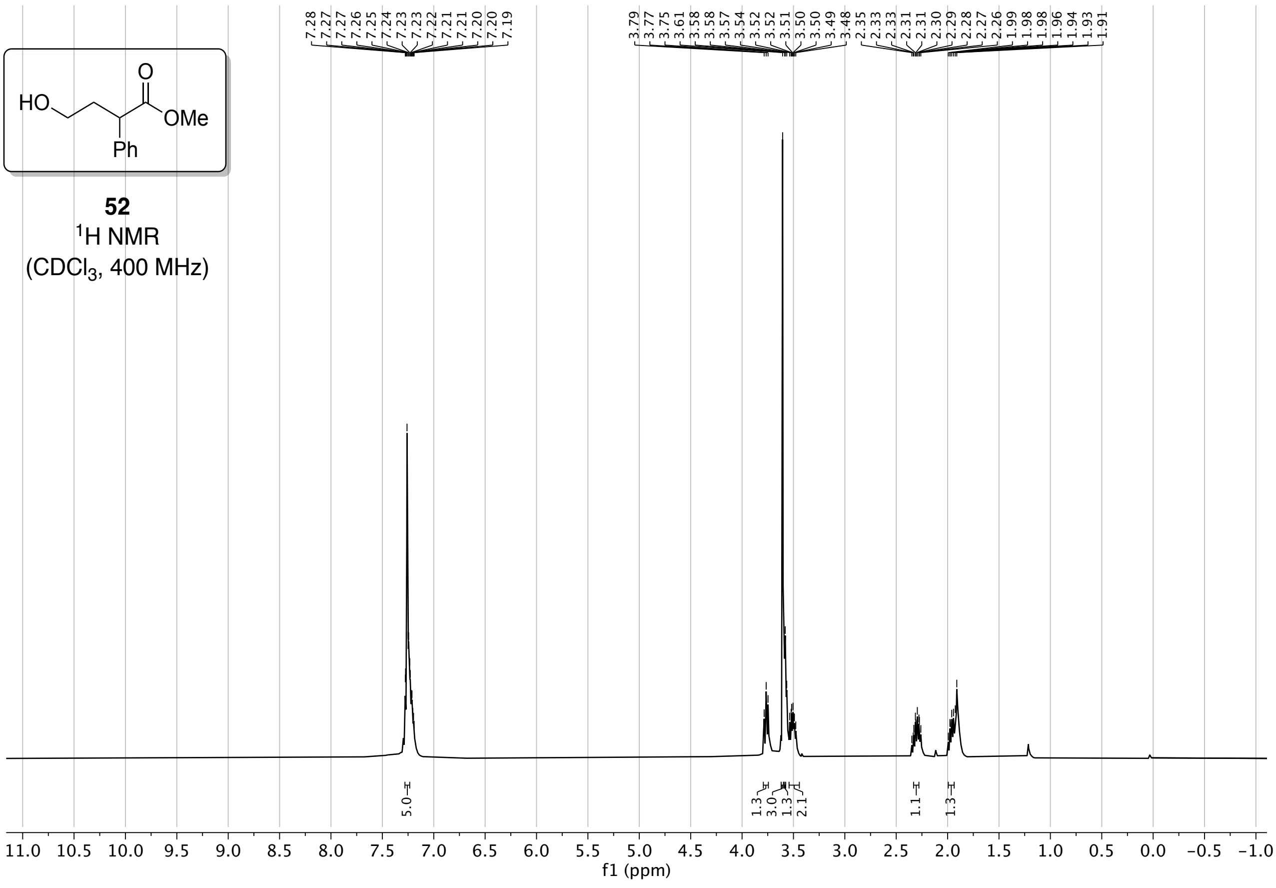


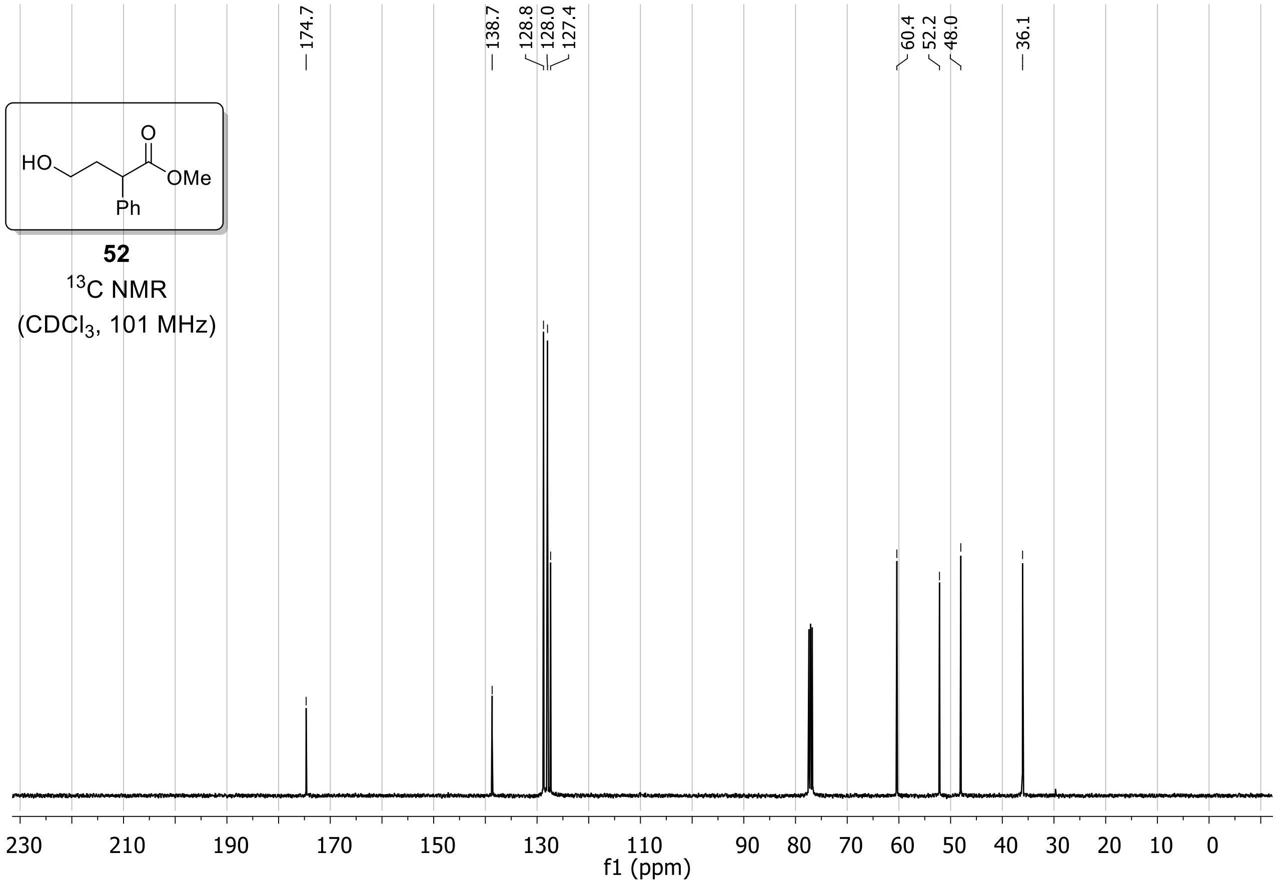
50
^{13}C NMR
($CDCl_3$, 101 MHz)

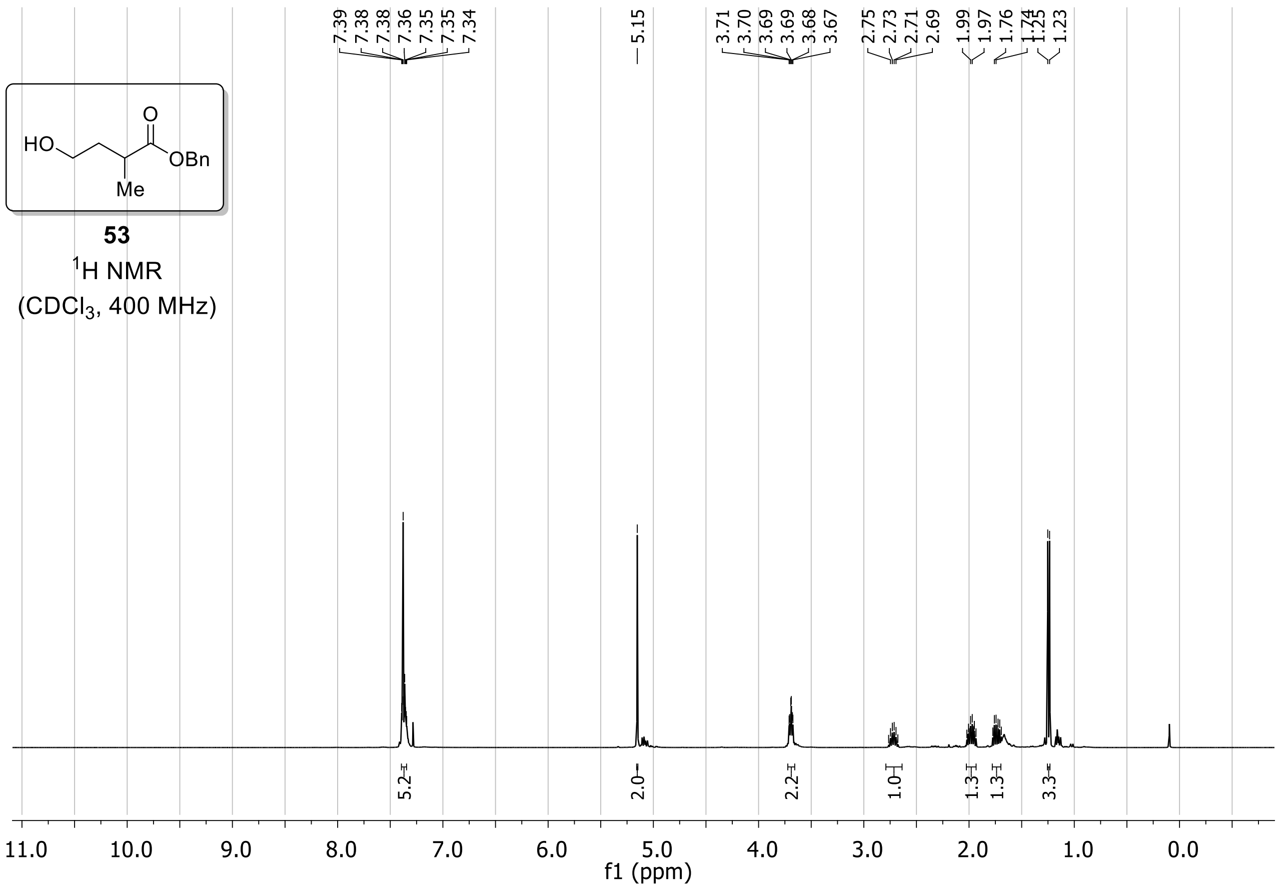


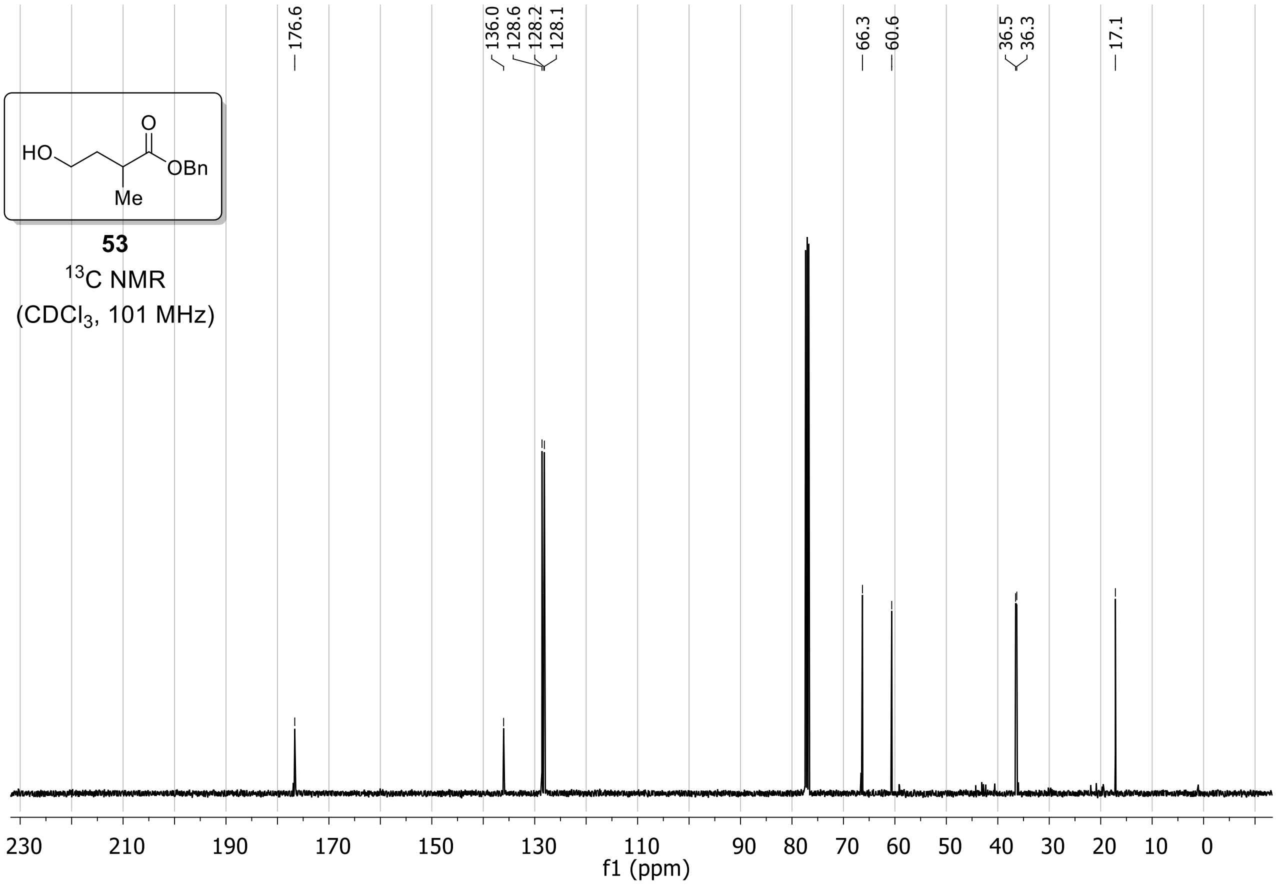
51
^{1}H NMR
($CDCl_3$, 400 MHz)


HO OEt O Me
51
^{13}C NMR
(CDCl$_3$, 101 MHz)
176.9
60.7
60.5
36.5
36.3
17.2
14.2
f1 (ppm)


HO OMe O Ph
52
^{1}H NMR
(CDCl$_3$, 400 MHz)
7.28 7.27 7.27 7.26 7.25 7.24 7.23 7.23 7.22 7.21 7.21 7.20 7.20 7.19
3.79 3.77 3.75 3.61 3.58 3.58 3.57 3.54 3.52 3.52 3.51 3.50 3.50 3.49 3.48
2.35 2.33 2.33 2.31 2.31 2.30 2.29 2.28 2.27 2.26 1.99 1.98 1.98 1.96 1.94 1.93 1.91
5.0
1.3 3.0 1.3 2.1
1.1
1.3
f1 (ppm)


HO
O
OMe
Ph
52
^{13}C NMR
($CDCl_3$, 101 MHz)
174.7
138.7
128.8
128.0
127.4
60.4
52.2
48.0
36.1
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

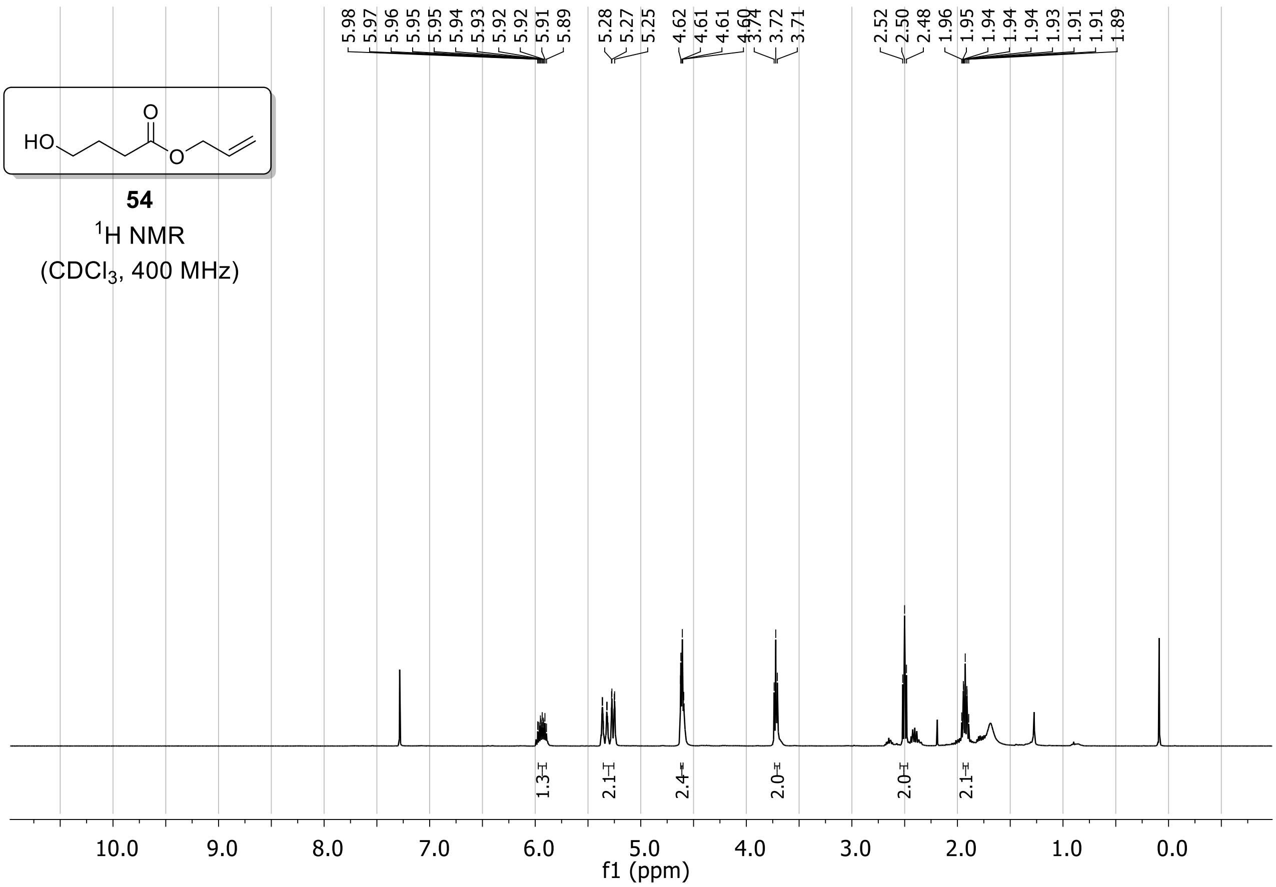

HO
O
OBn
Me
53
^{1}H NMR
($CDCl_3$, 400 MHz)
7.39
7.38
7.38
7.36
7.35
7.35
7.34
5.15
3.71
3.70
3.69
3.69
3.68
3.67
2.75
2.73
2.71
2.69
1.99
1.97
1.76
1.74
1.25
1.23
5.2
2.0
2.2
1.0
1.3
1.3
3.3
11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)



53

^{13}C NMR

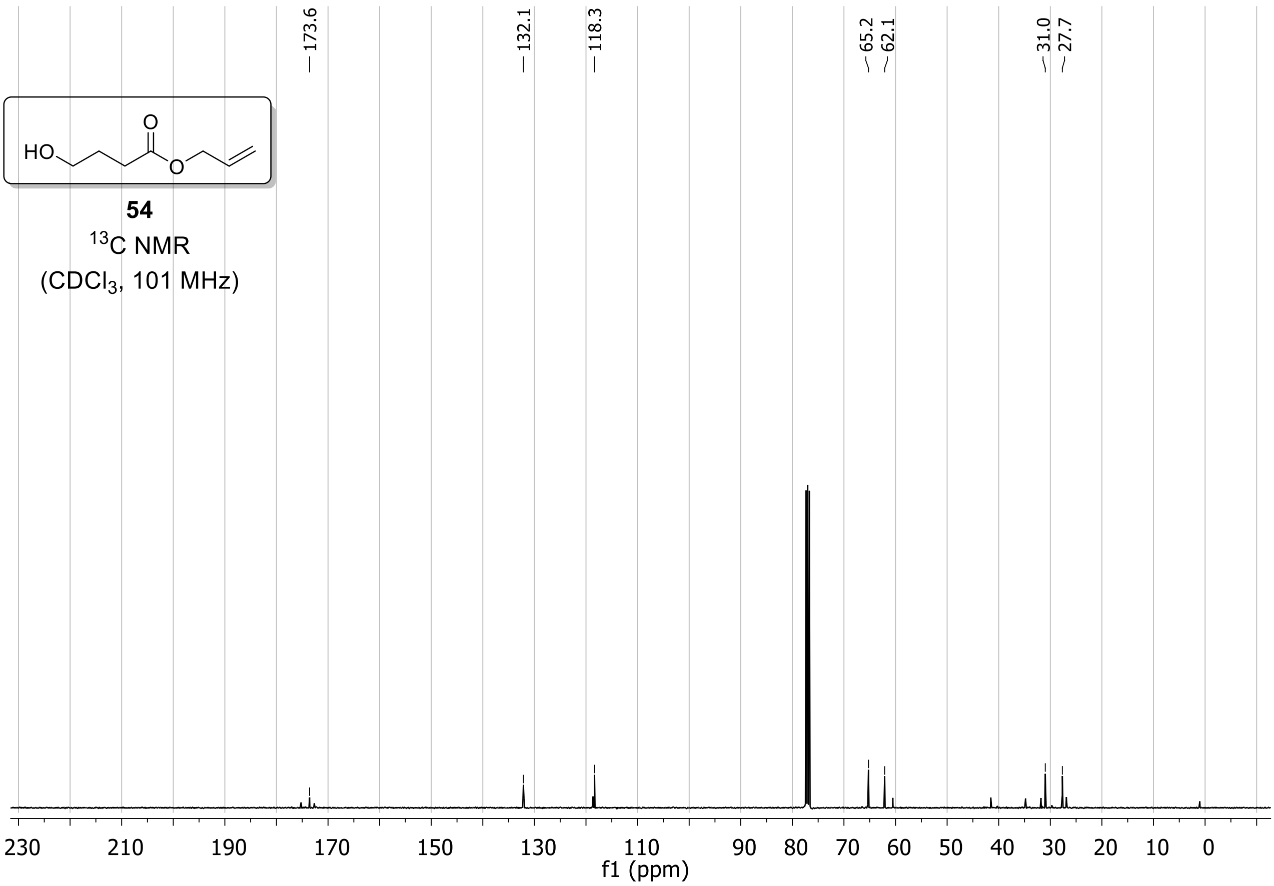
($CDCl_3$, 101 MHz)

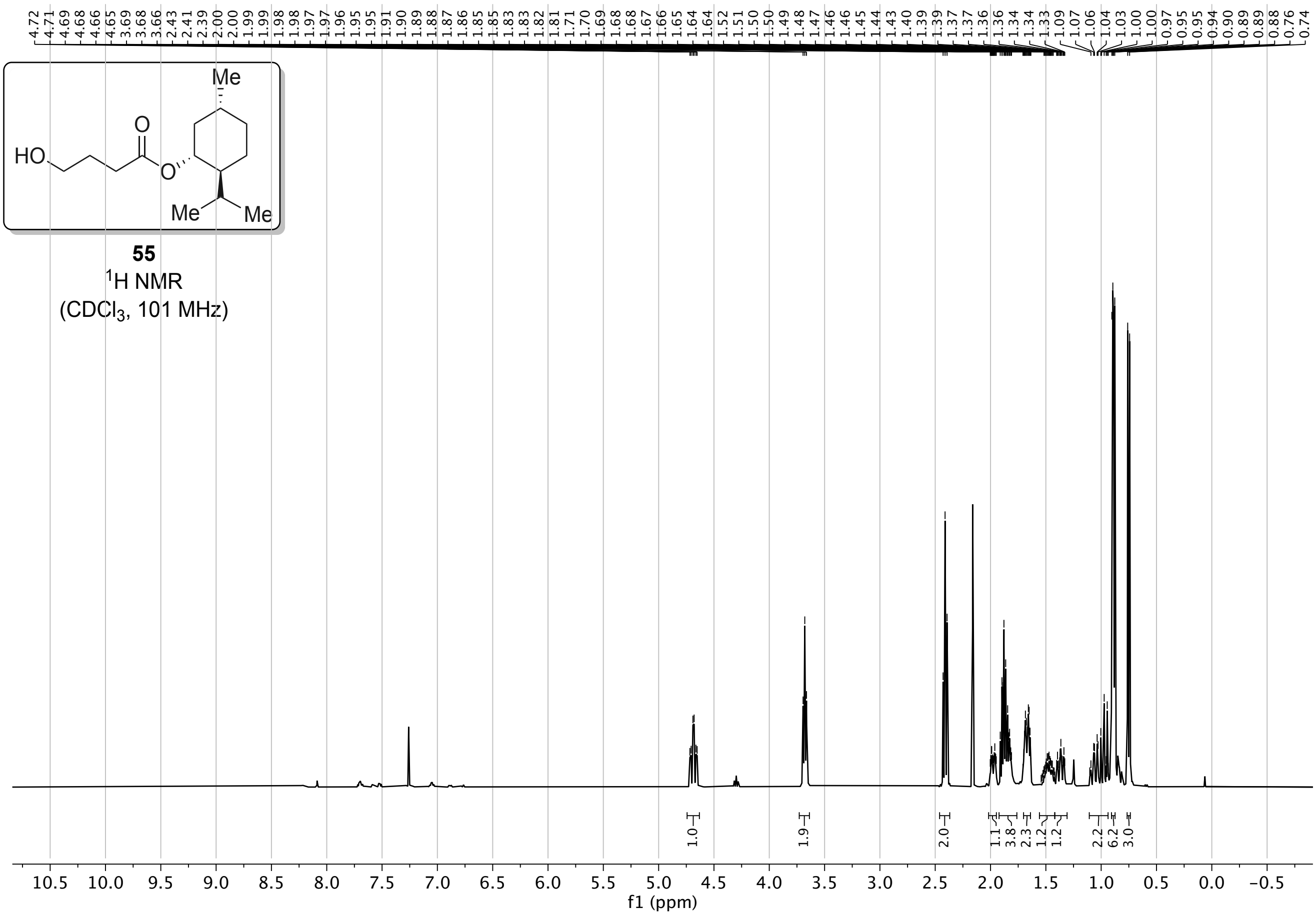


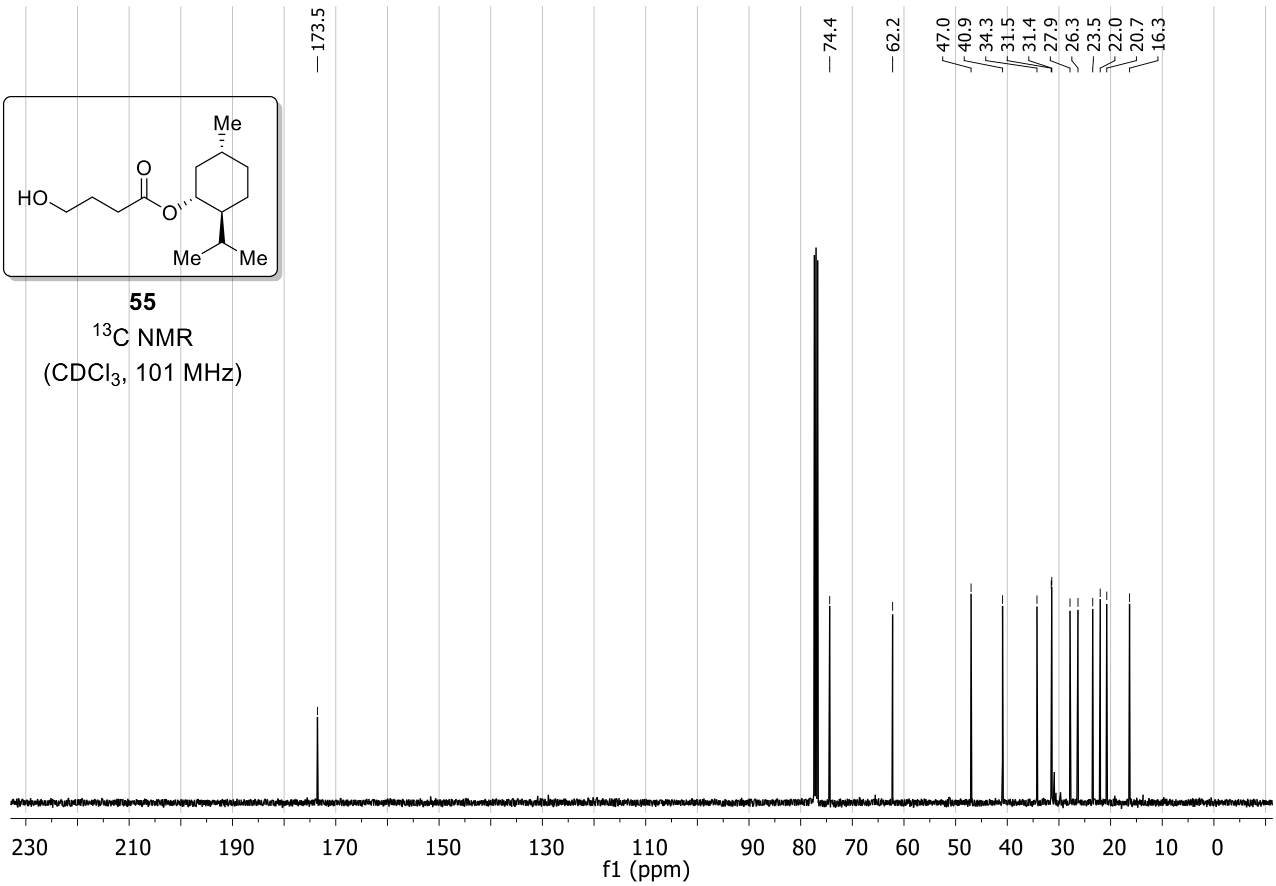
54

^{1}H NMR

($CDCl_3$, 400 MHz)


HO O O
54
^{13}C NMR
($CDCl_3$, 101 MHz)
173.6
132.1
118.3
65.2
62.1
31.0
27.7
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

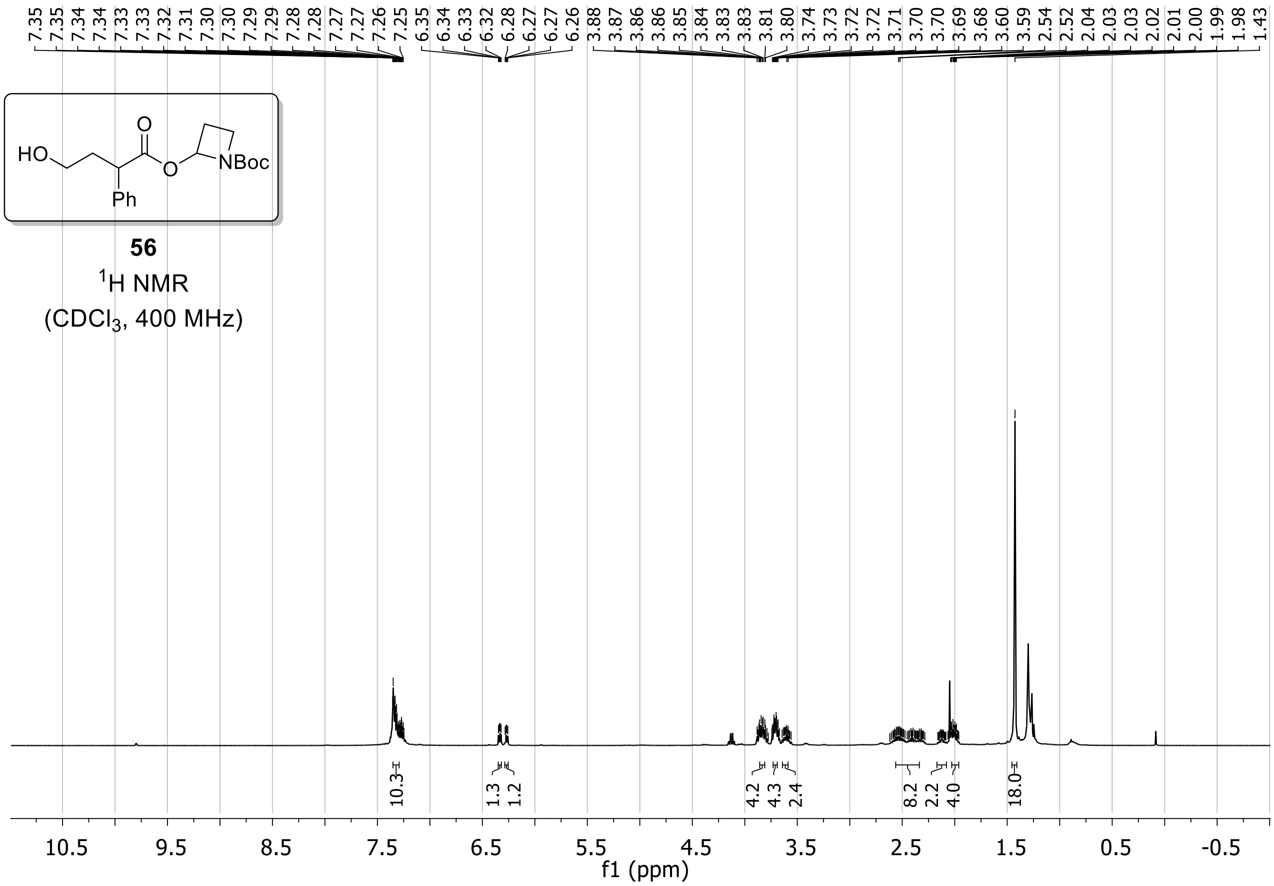

Me
HO O O
Me Me
55
^{1}H NMR
($CDCl_3$, 101 MHz)
4.72 4.71 4.69 4.68 4.66 4.65 3.69 3.68 3.66 2.43 2.41 2.39 2.00 2.00 1.99 1.99 1.98 1.98 1.97 1.97 1.96 1.95 1.95 1.91 1.90 1.89 1.88 1.87 1.86 1.85 1.85 1.83 1.83 1.82 1.81 1.71 1.70 1.69 1.68 1.67 1.66 1.65 1.64 1.64 1.52 1.51 1.50 1.49 1.48 1.47 1.46 1.46 1.45 1.44 1.43 1.40 1.39 1.39 1.37 1.37 1.36 1.36 1.34 1.34 1.33 1.09 1.07 1.06 1.04 1.03 1.00 1.00 0.97 0.95 0.95 0.94 0.90 0.89 0.88 0.76 0.74
1.0
1.9
2.0
1.1
3.8
2.3
1.2
1.2
2.2
6.2
3.0
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)



55

^{13}C NMR

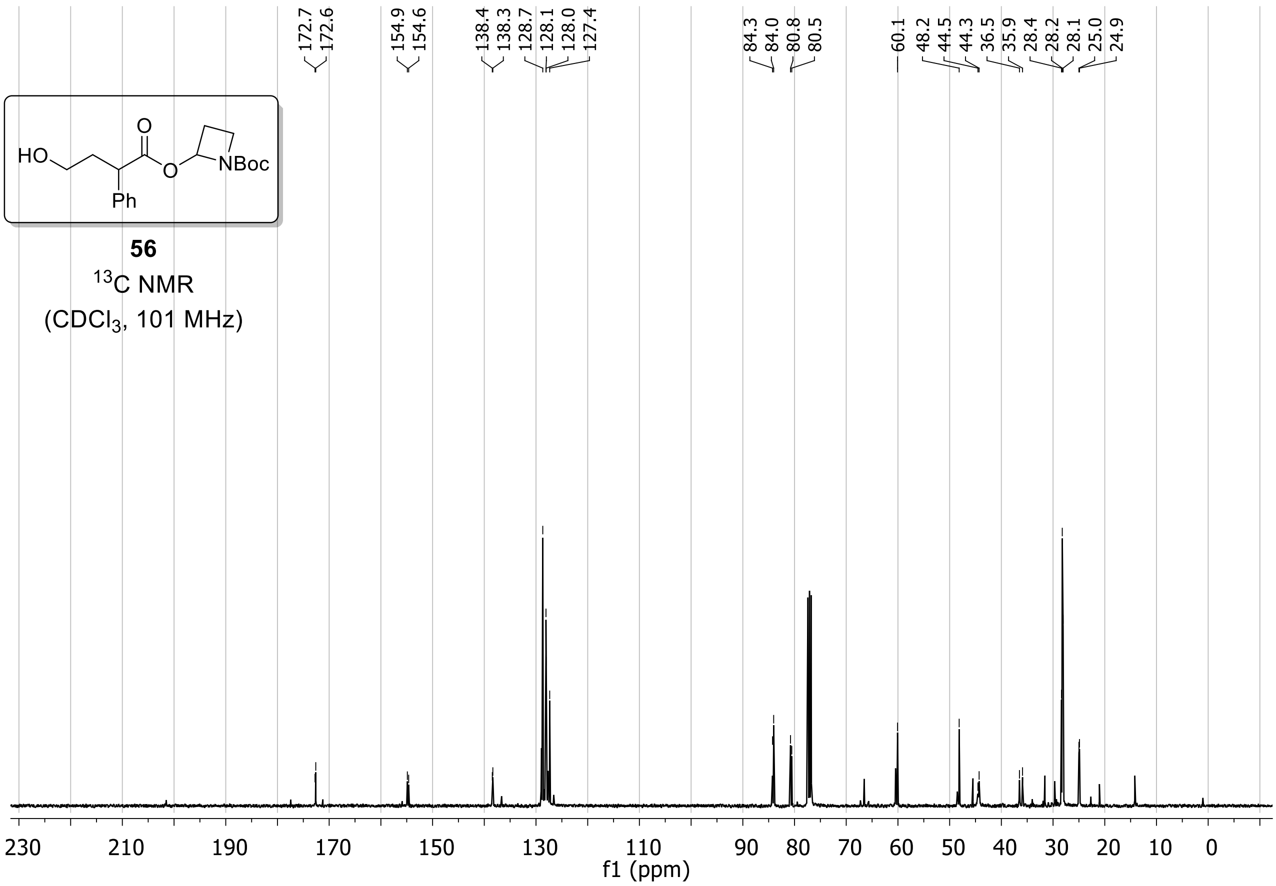
($CDCl_3$, 101 MHz)



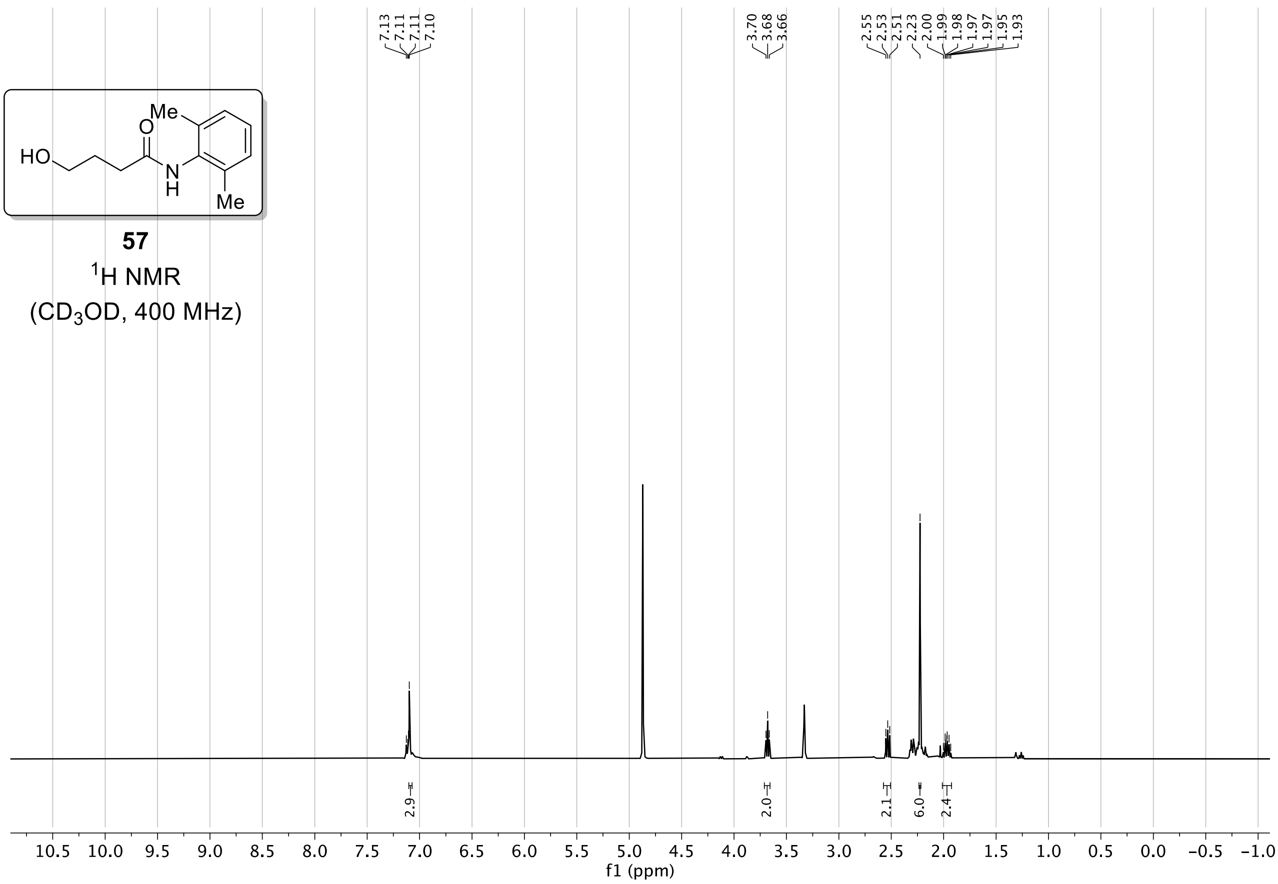
56

^{1}H NMR

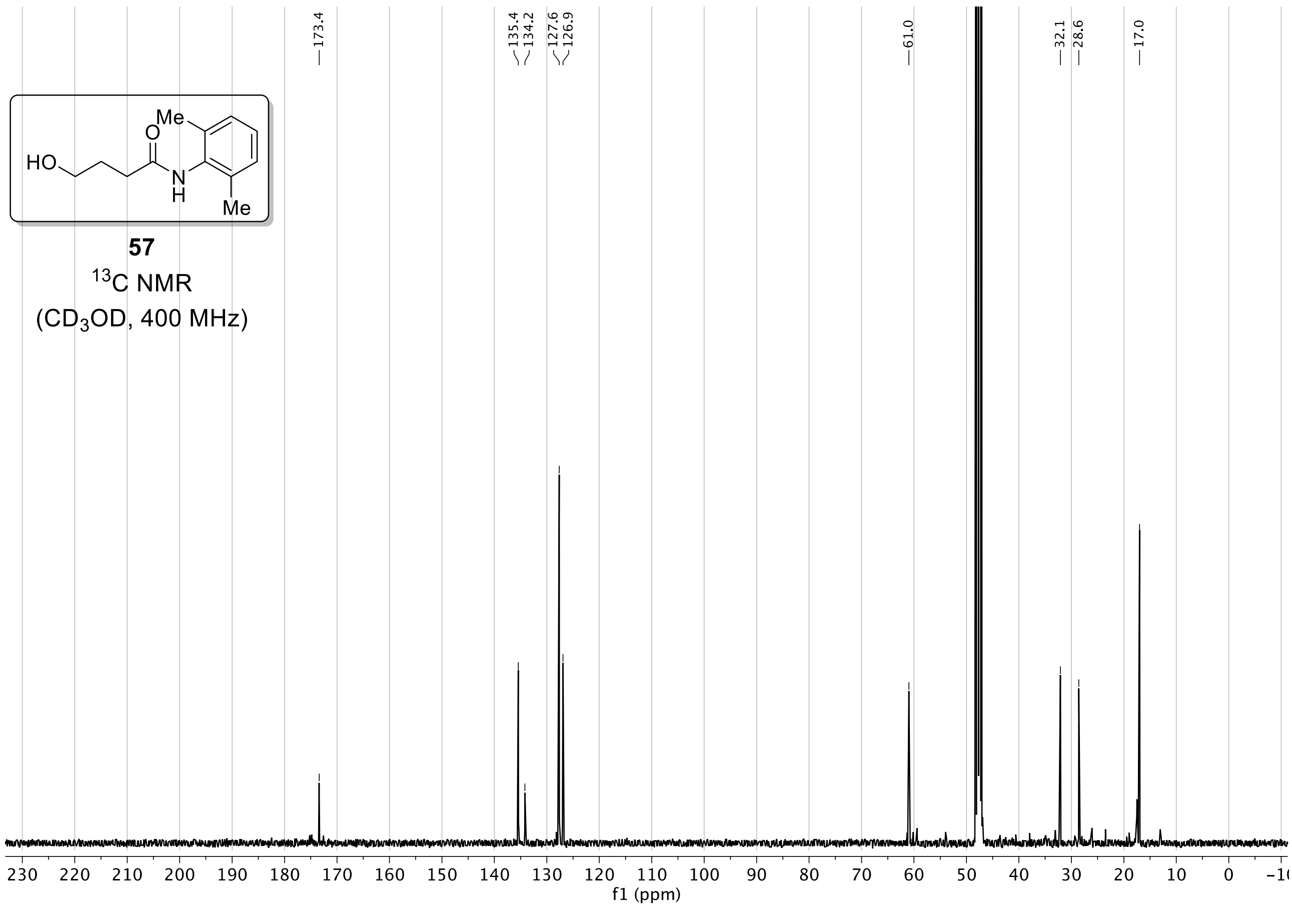
($CDCl_3$, 400 MHz)



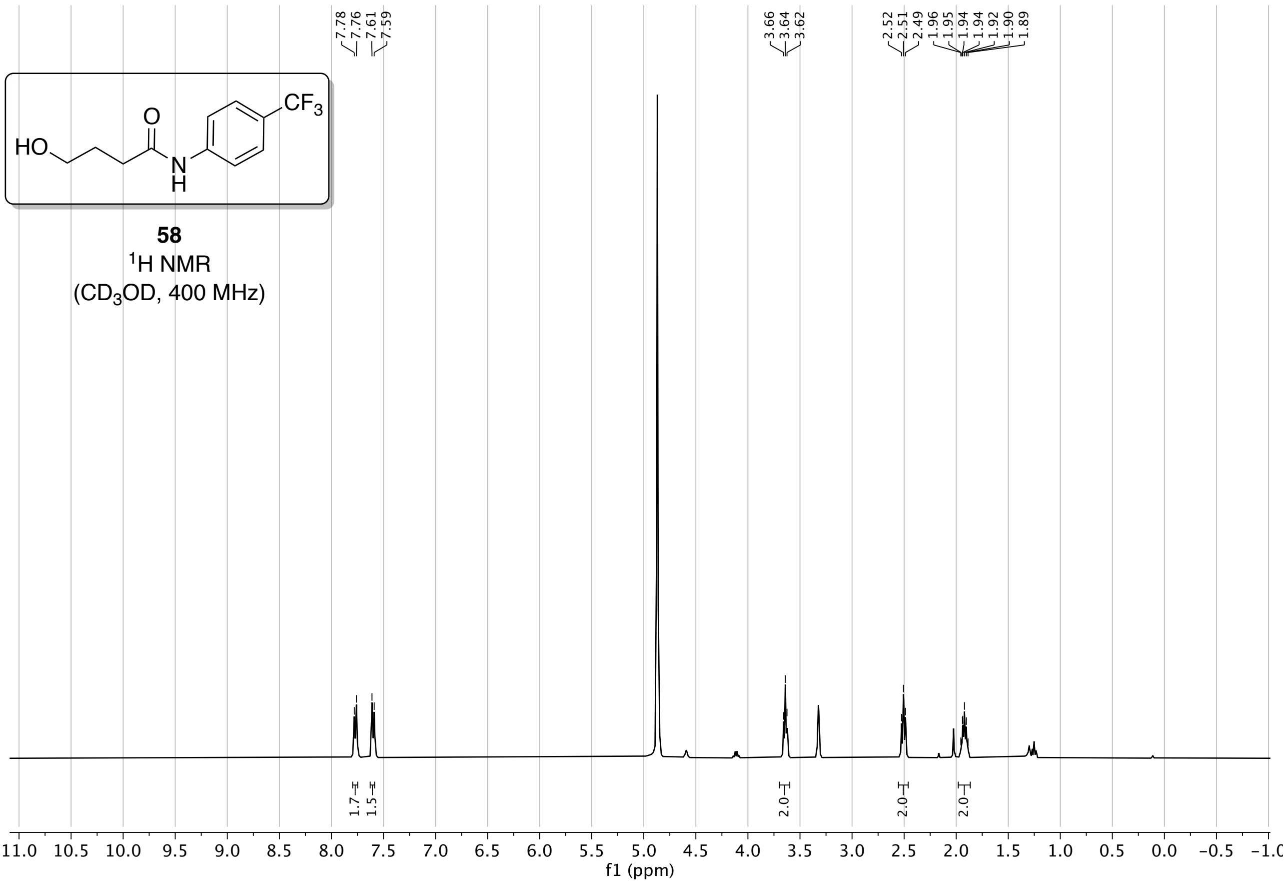
56
^{13}C NMR
($CDCl_3$, 101 MHz)



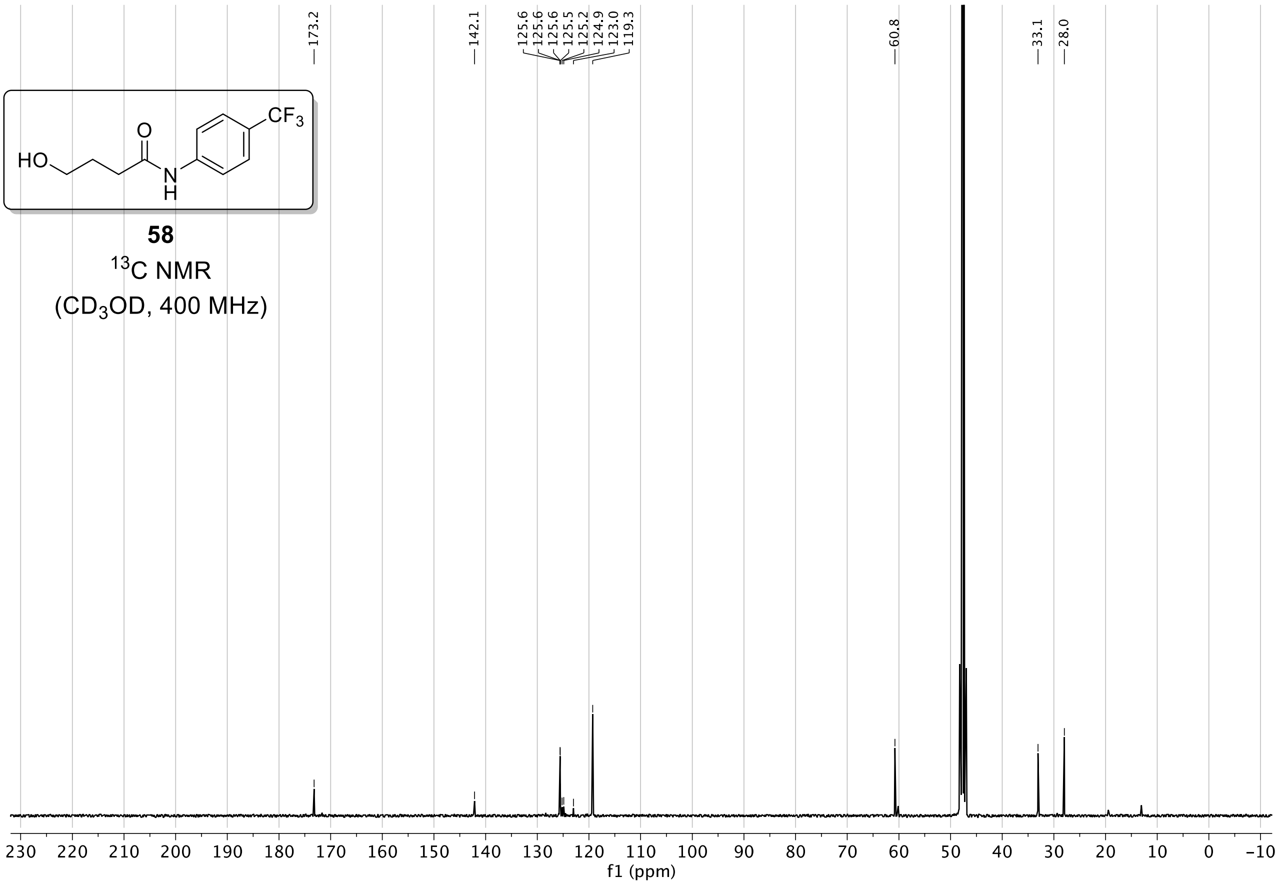
57
^{1}H NMR
(CD_3OD, 400 MHz)



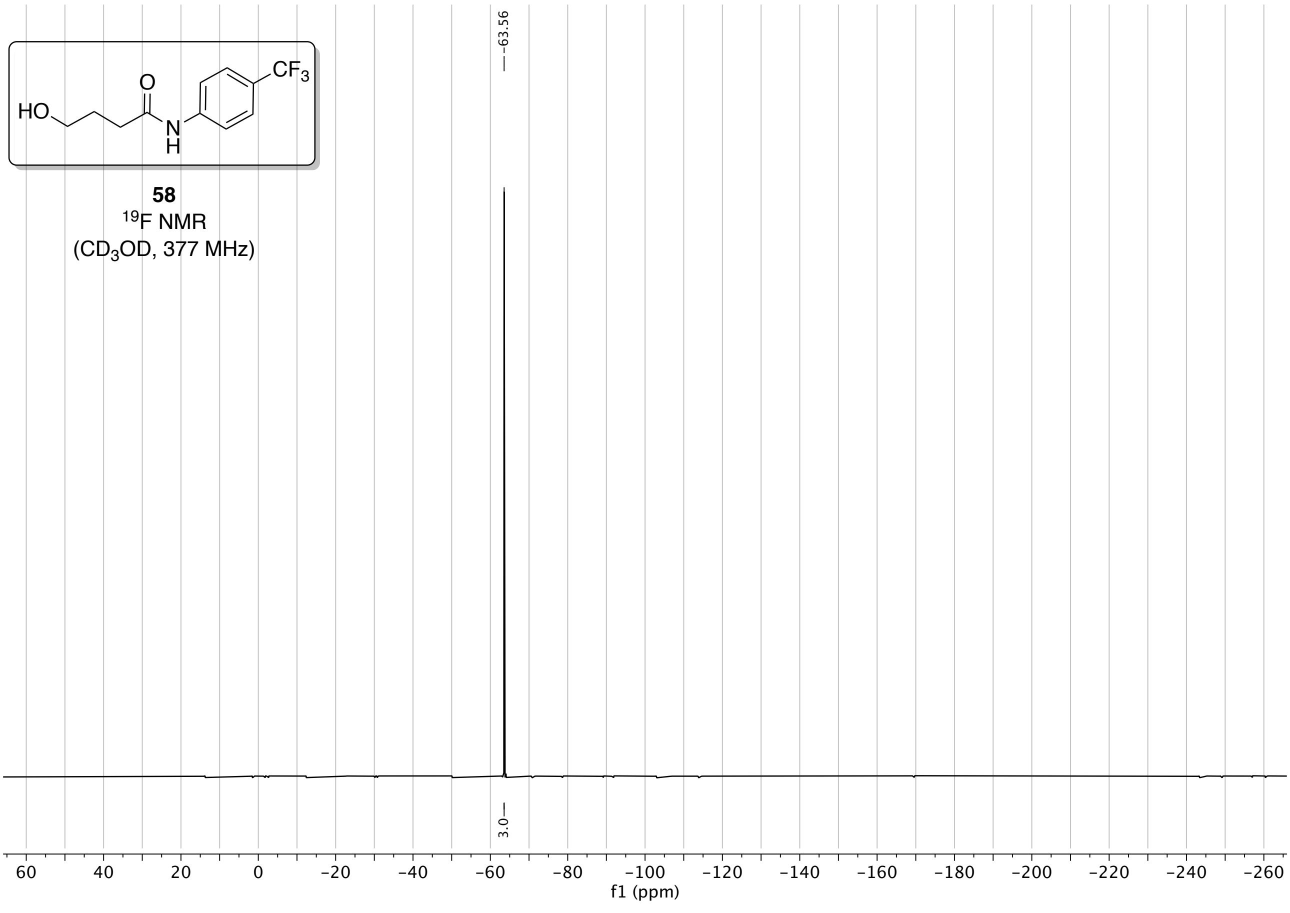
57
^{13}C NMR
(CD_3OD, 400 MHz)



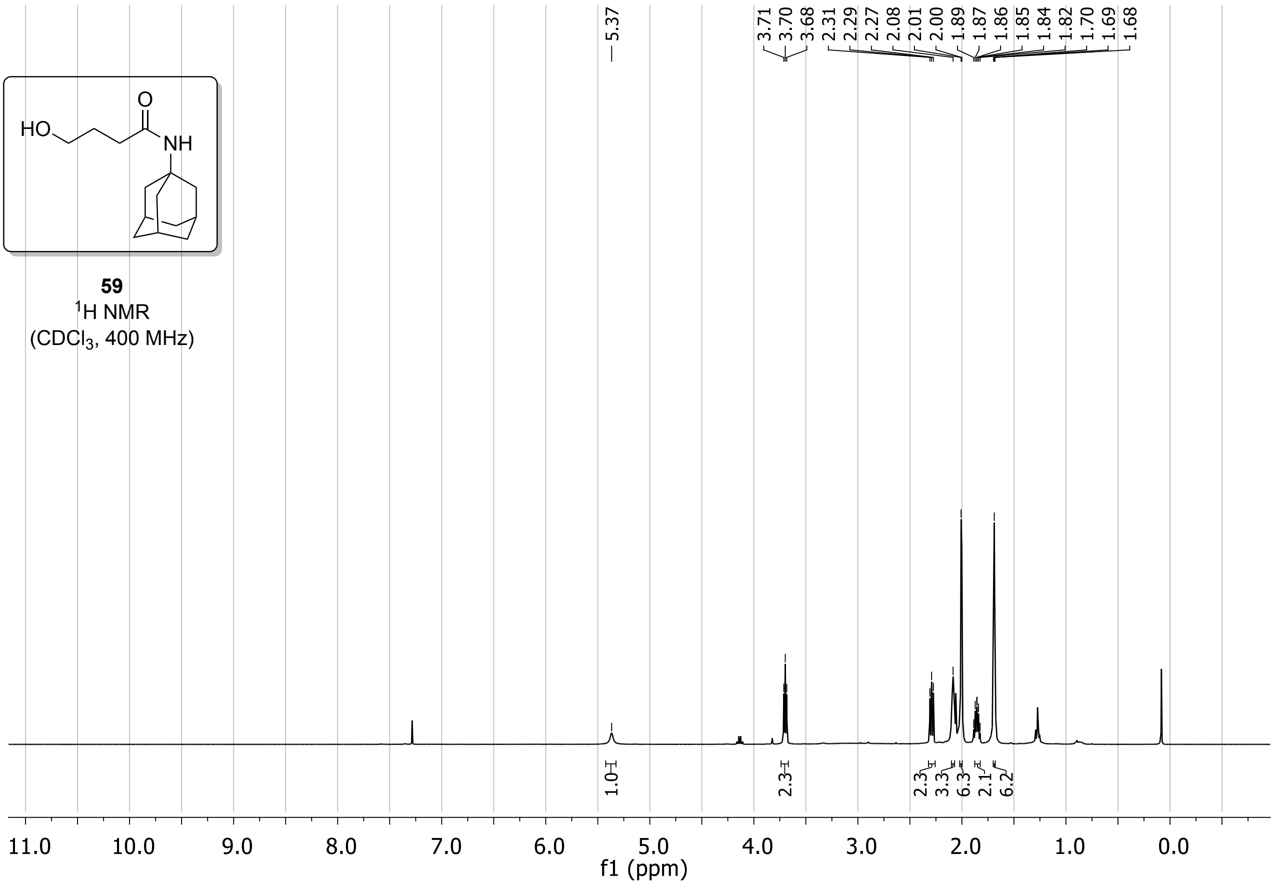
58
^{1}H NMR
(CD_3OD, 400 MHz)



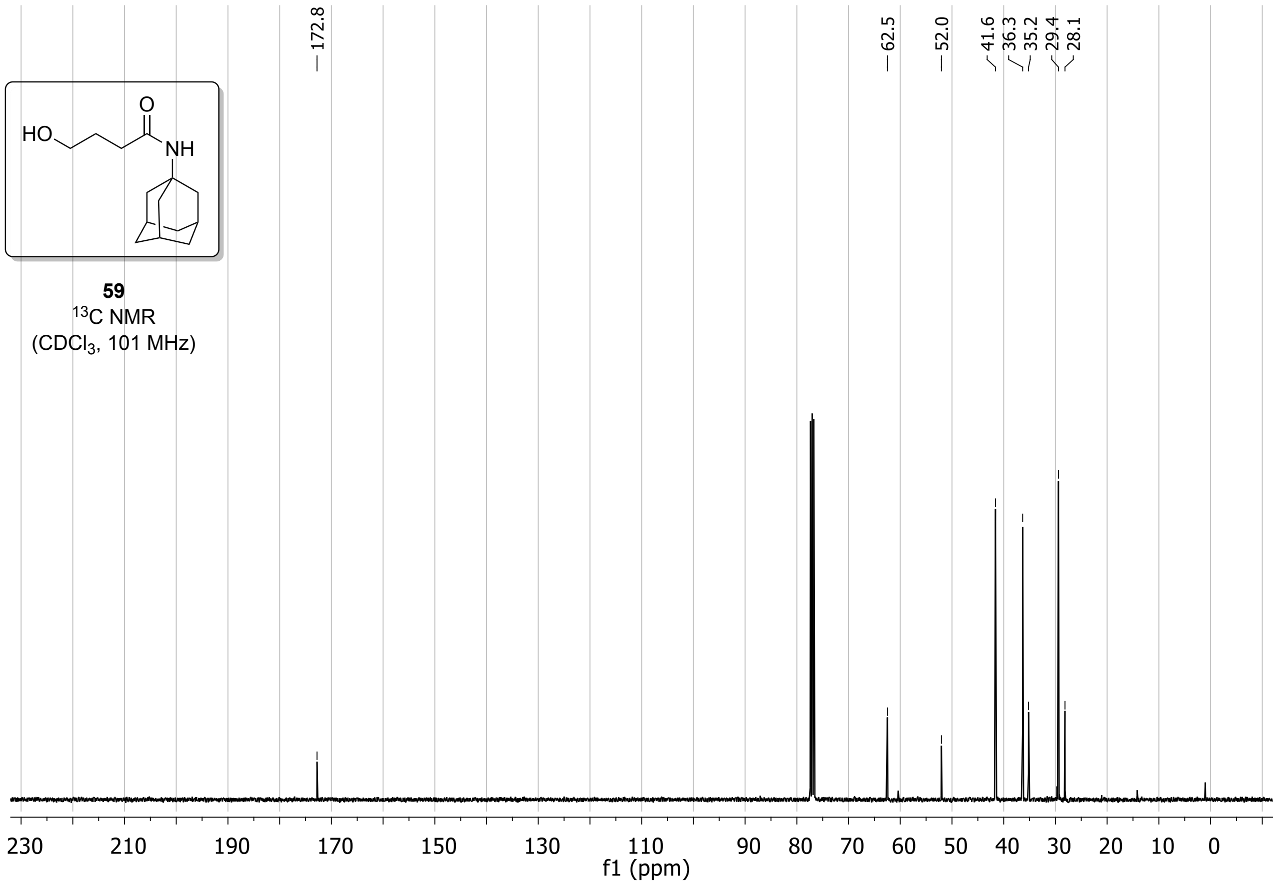
58
^{13}C NMR
(CD_3OD, 400 MHz)



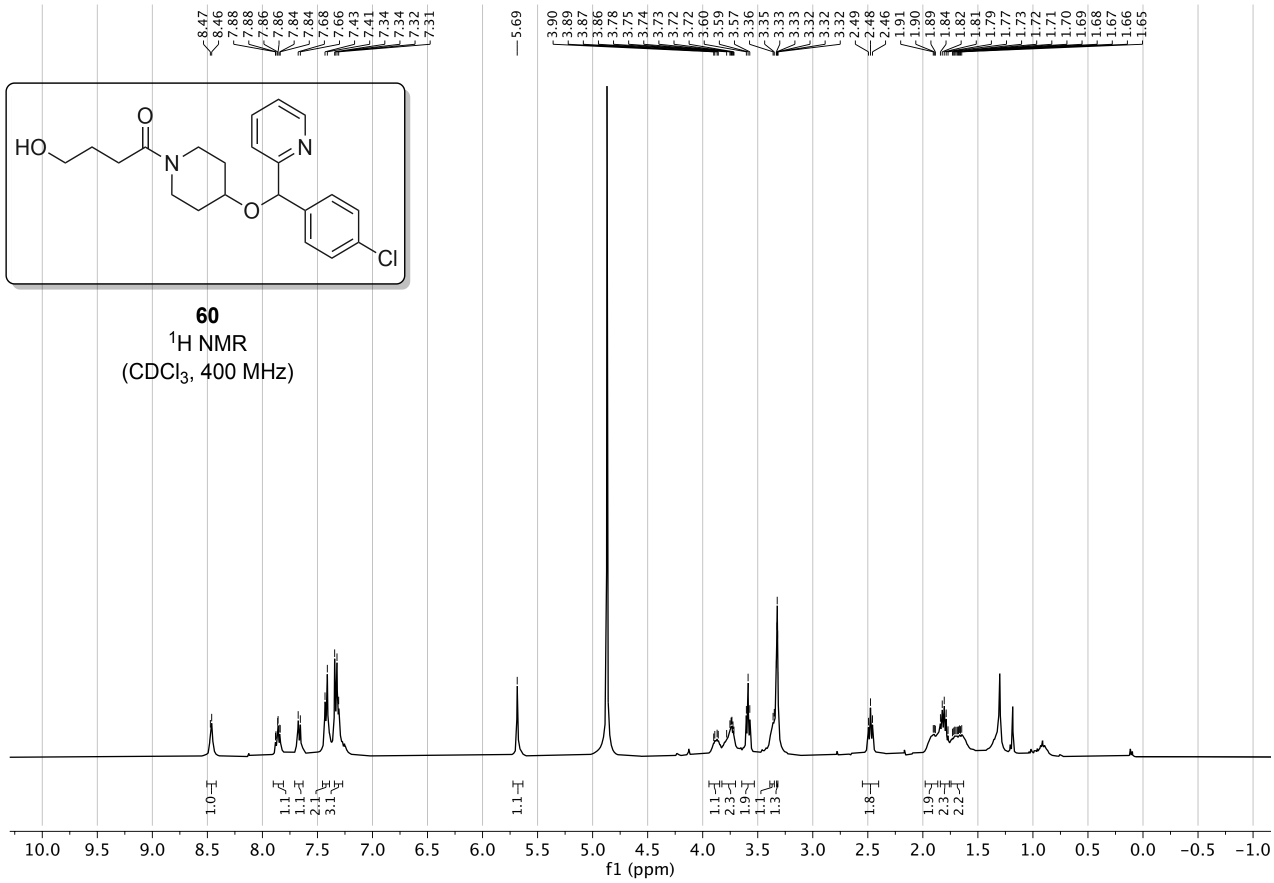
58
^{19}F NMR
(CD_3OD, 377 MHz)



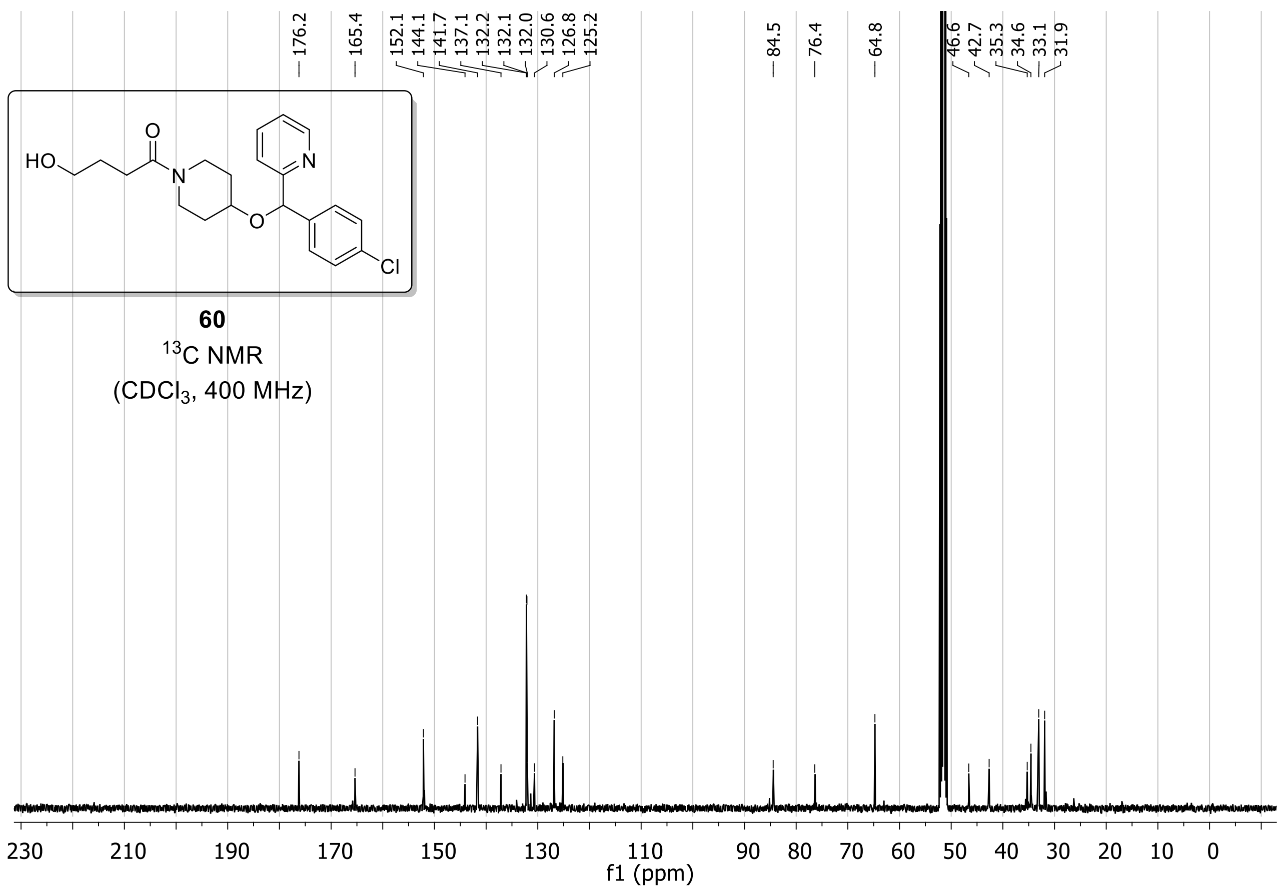
59
^{1}H NMR
($CDCl_3$, 400 MHz)



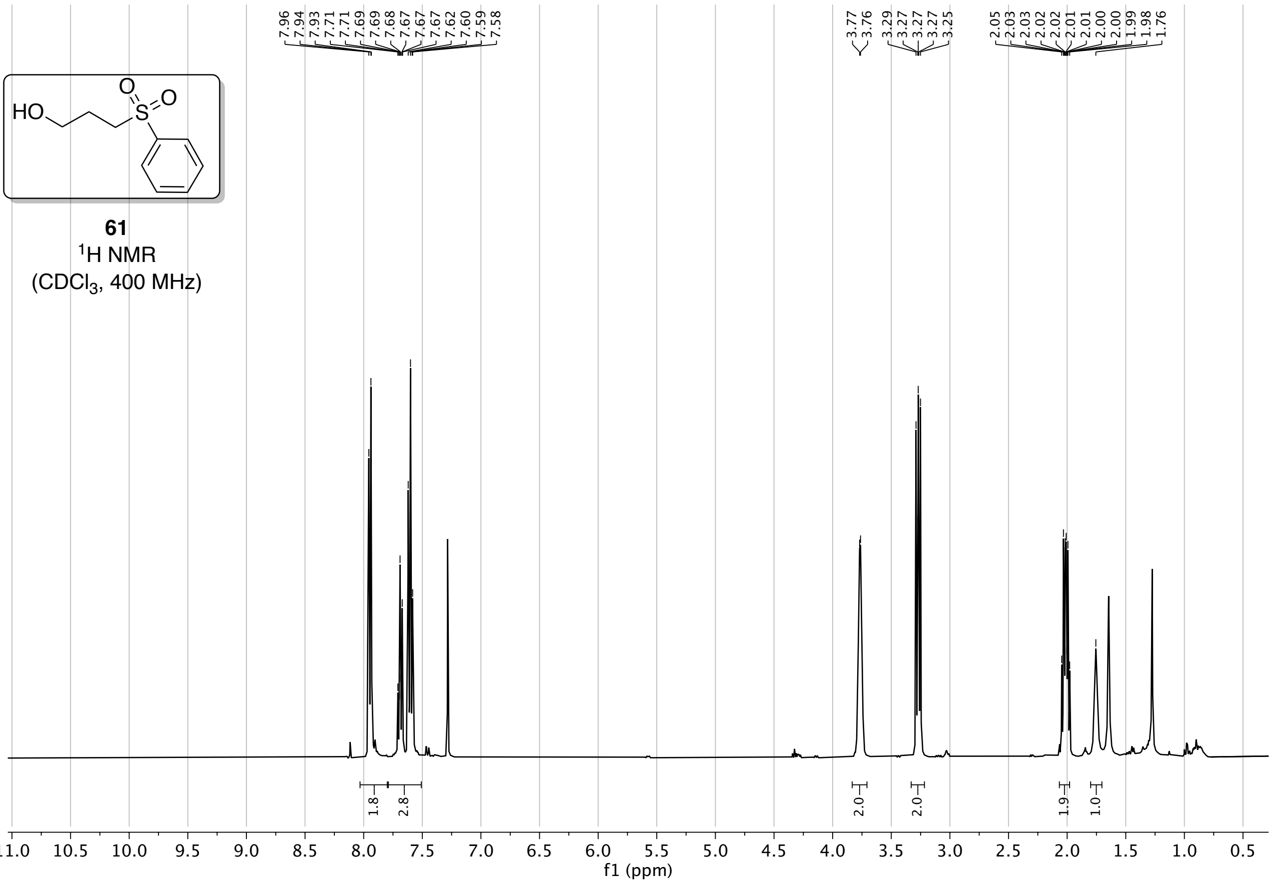
59
^{13}C NMR
($CDCl_3$, 101 MHz)



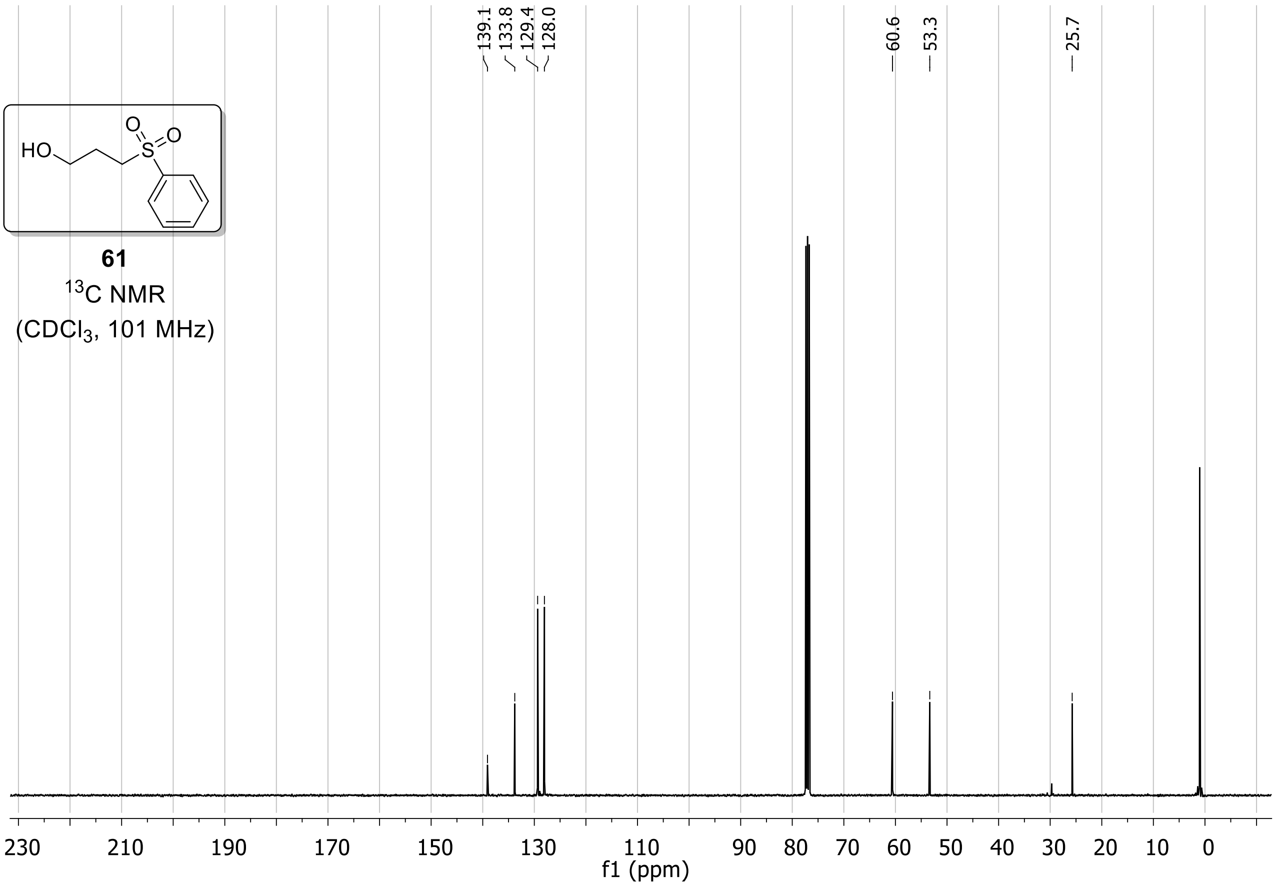
60
^{1}H NMR
($CDCl_3$, 400 MHz)



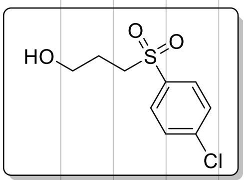
60
^{13}C NMR
($CDCl_3$, 400 MHz)



61
^{1}H NMR
($CDCl_3$, 400 MHz)



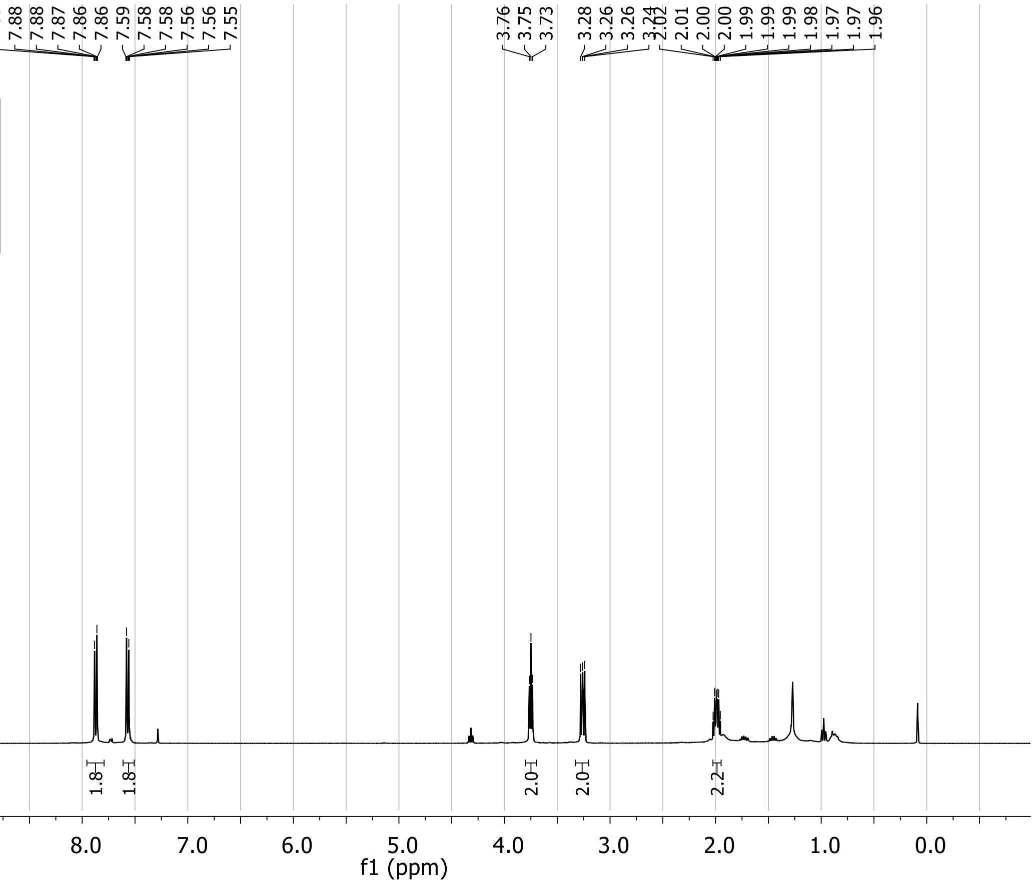
61
^{13}C NMR
($CDCl_3$, 101 MHz)

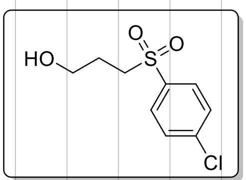


62

^{1}H NMR

($CDCl_3$, 400 MHz)

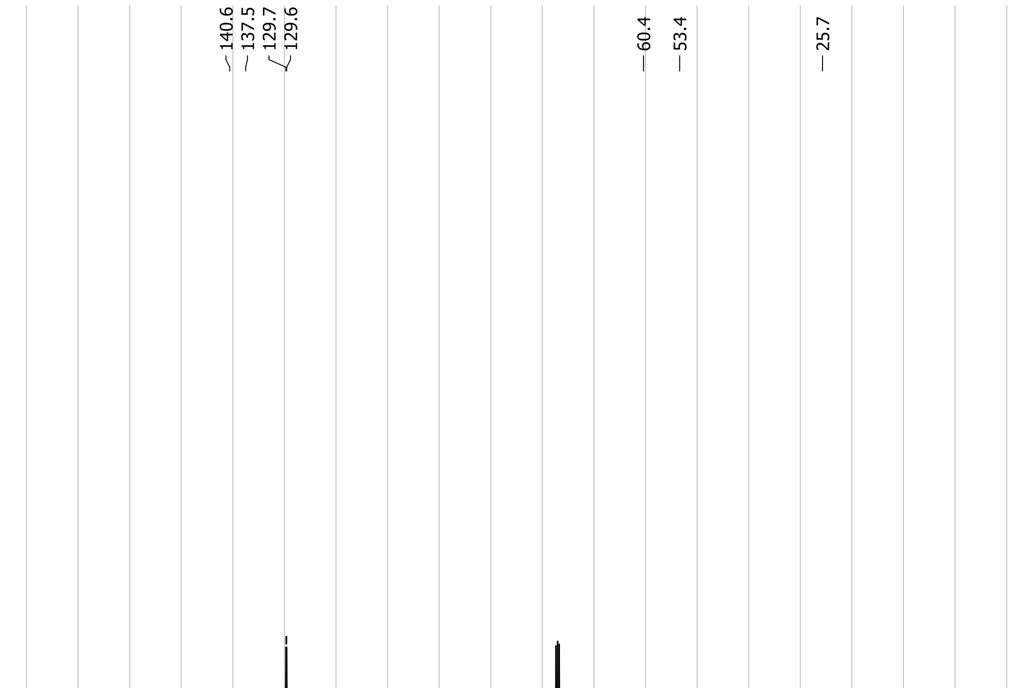


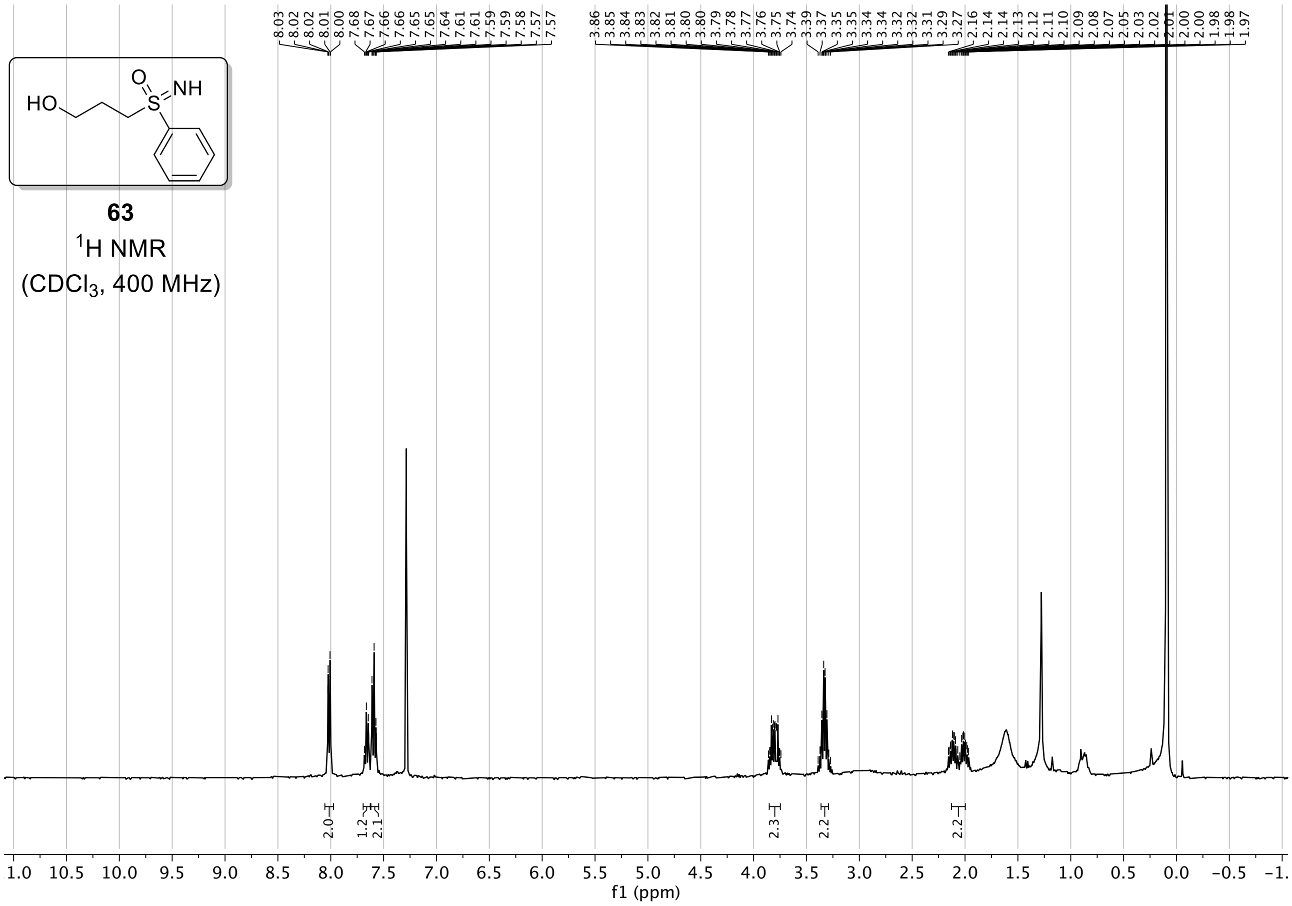


62

^{13}C NMR

($CDCl_3$, 101 MHz)

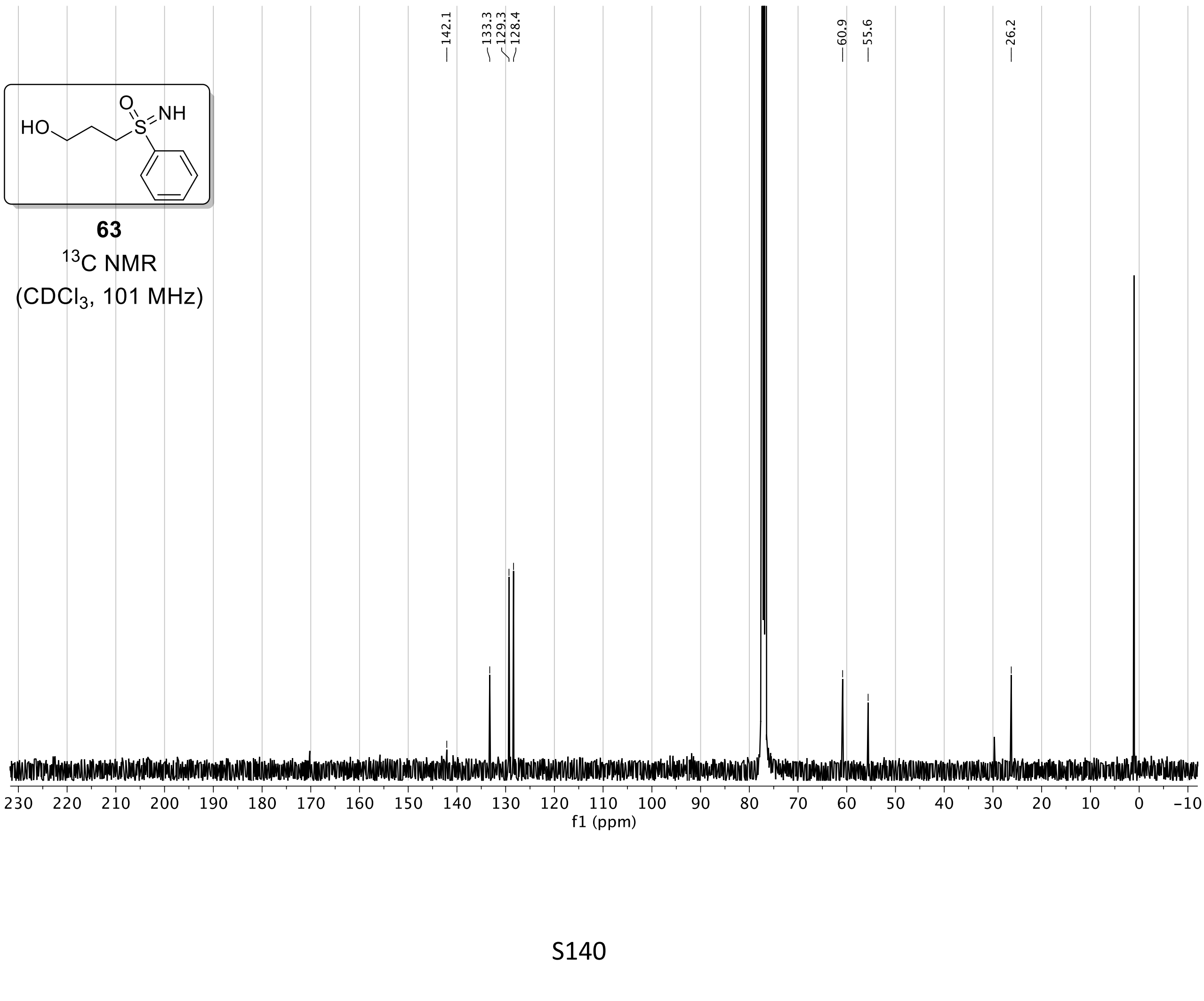




63

^{1}H NMR

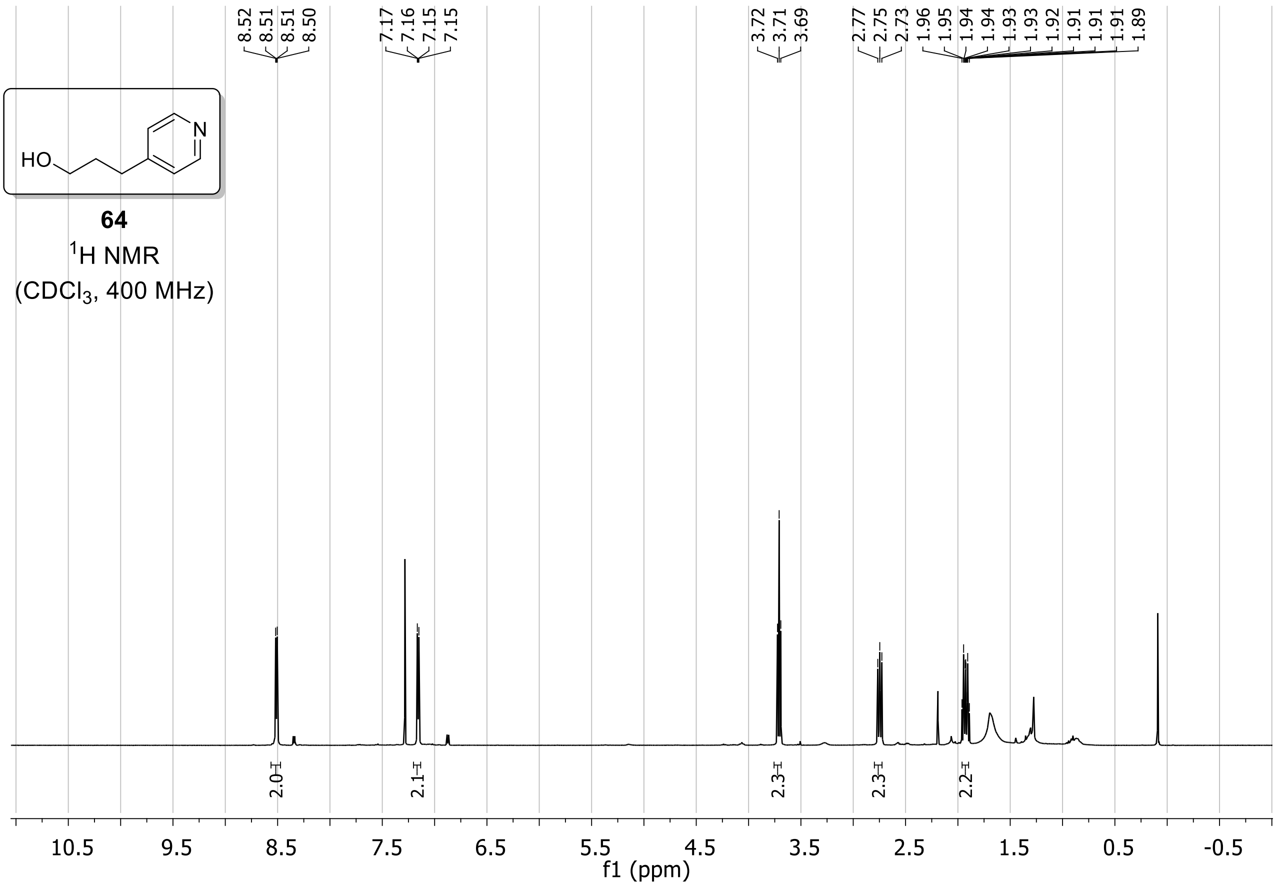
($CDCl_3$, 400 MHz)



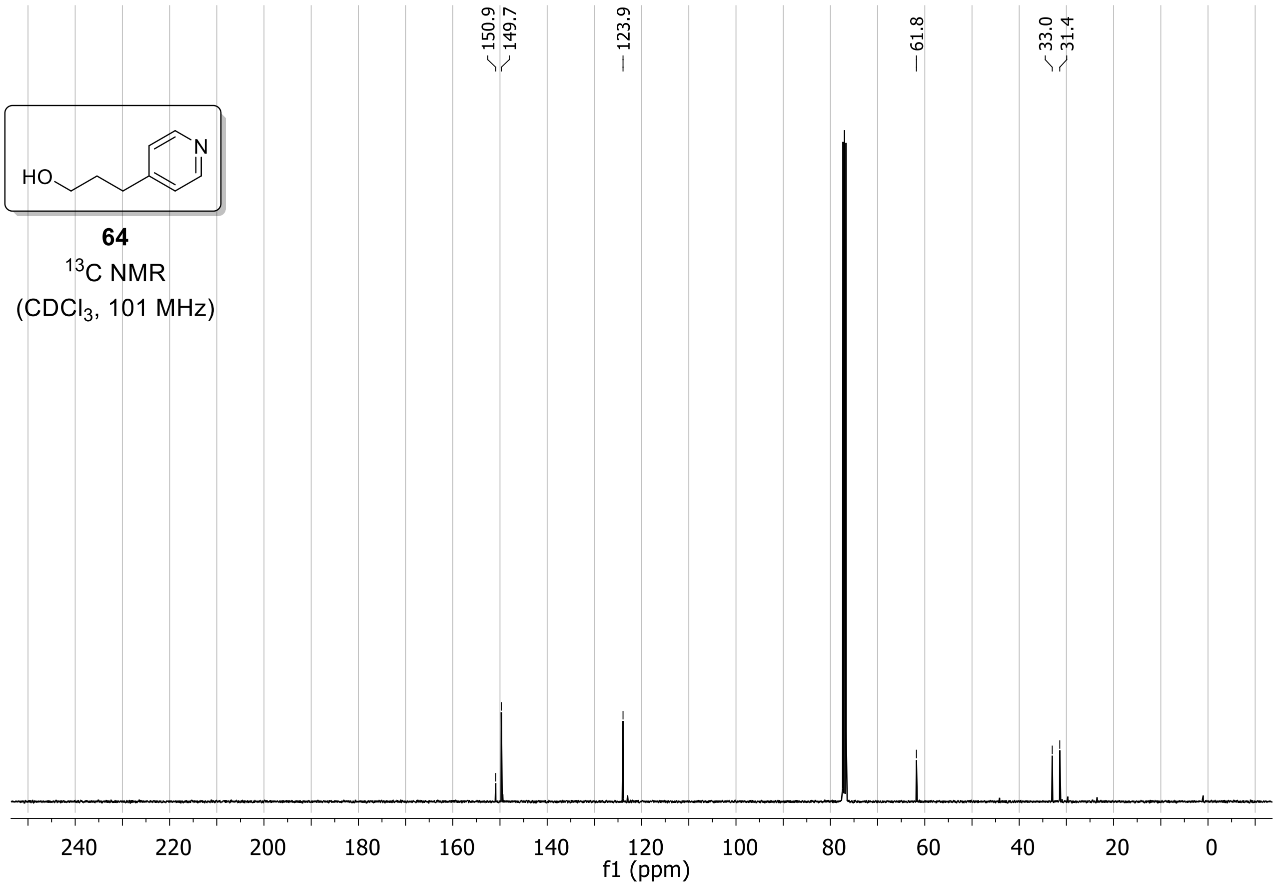
63

^{13}C NMR

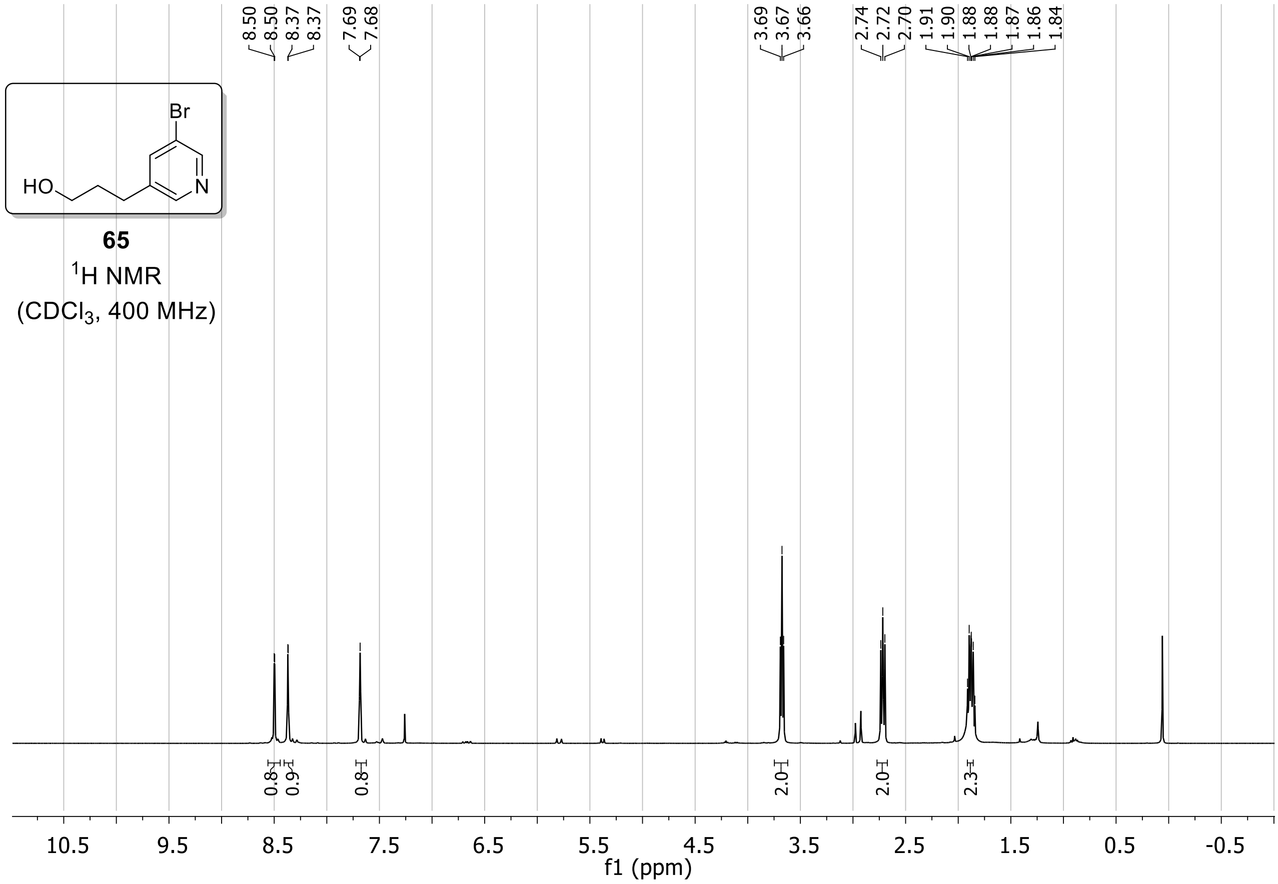
($CDCl_3$, 101 MHz)



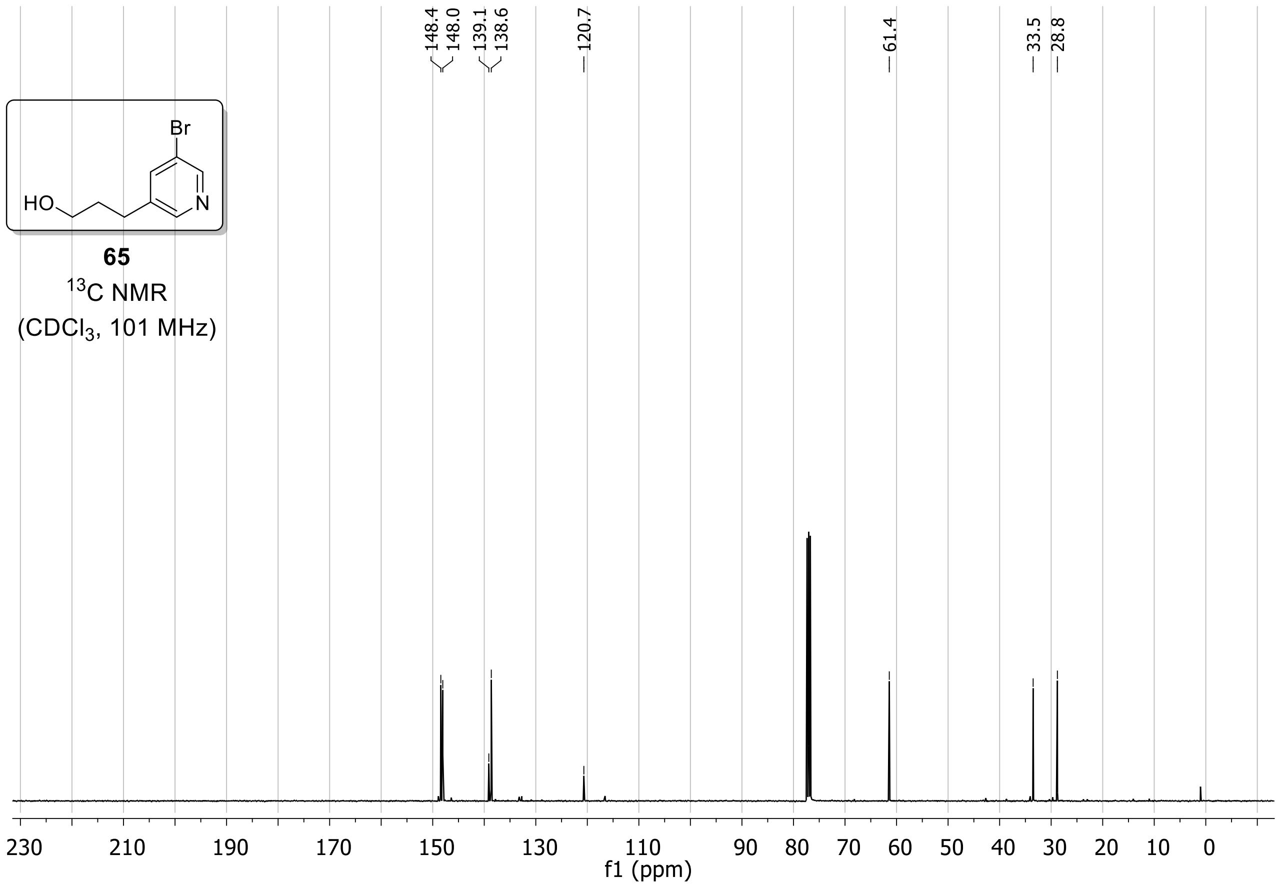
64
^{1}H NMR
($CDCl_3$, 400 MHz)



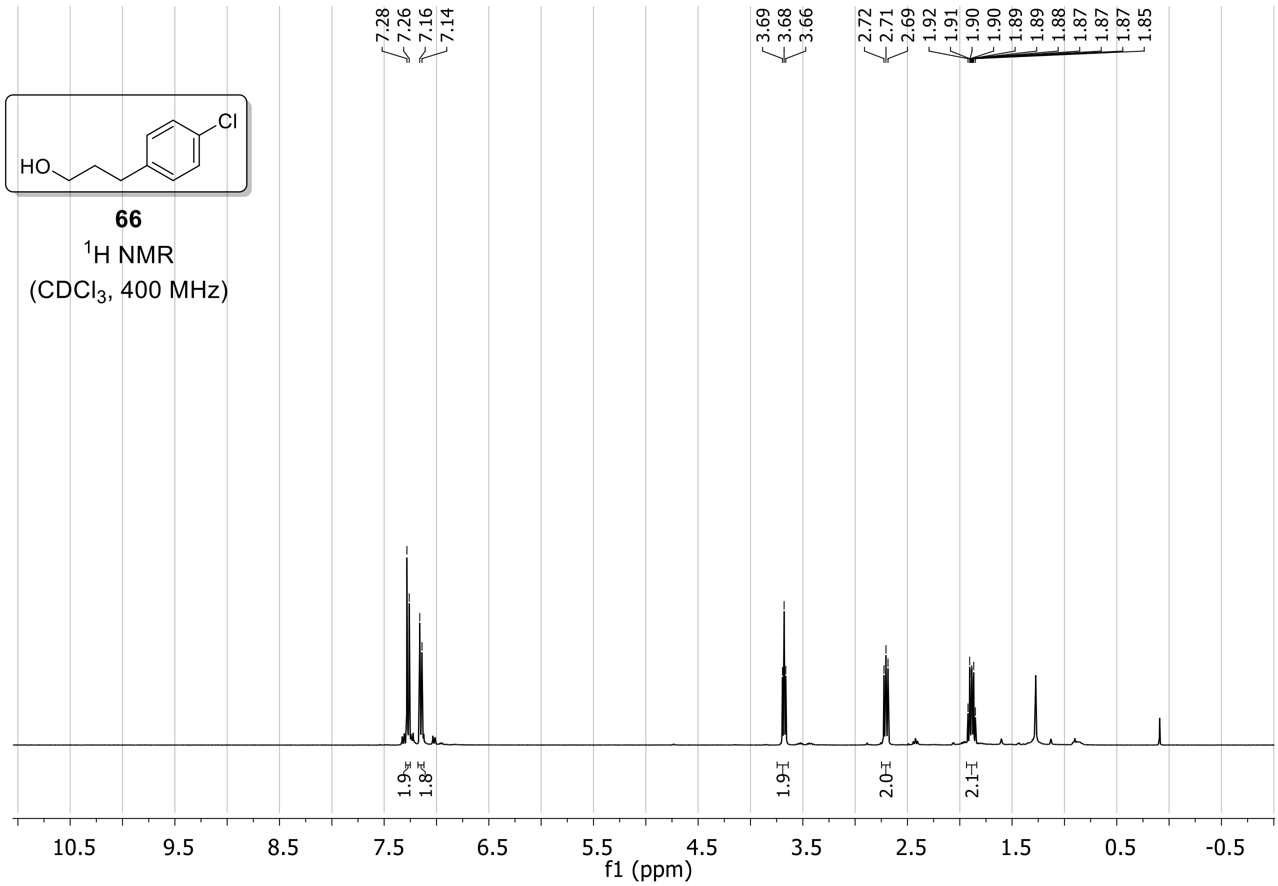
64
^{13}C NMR
($CDCl_3$, 101 MHz)

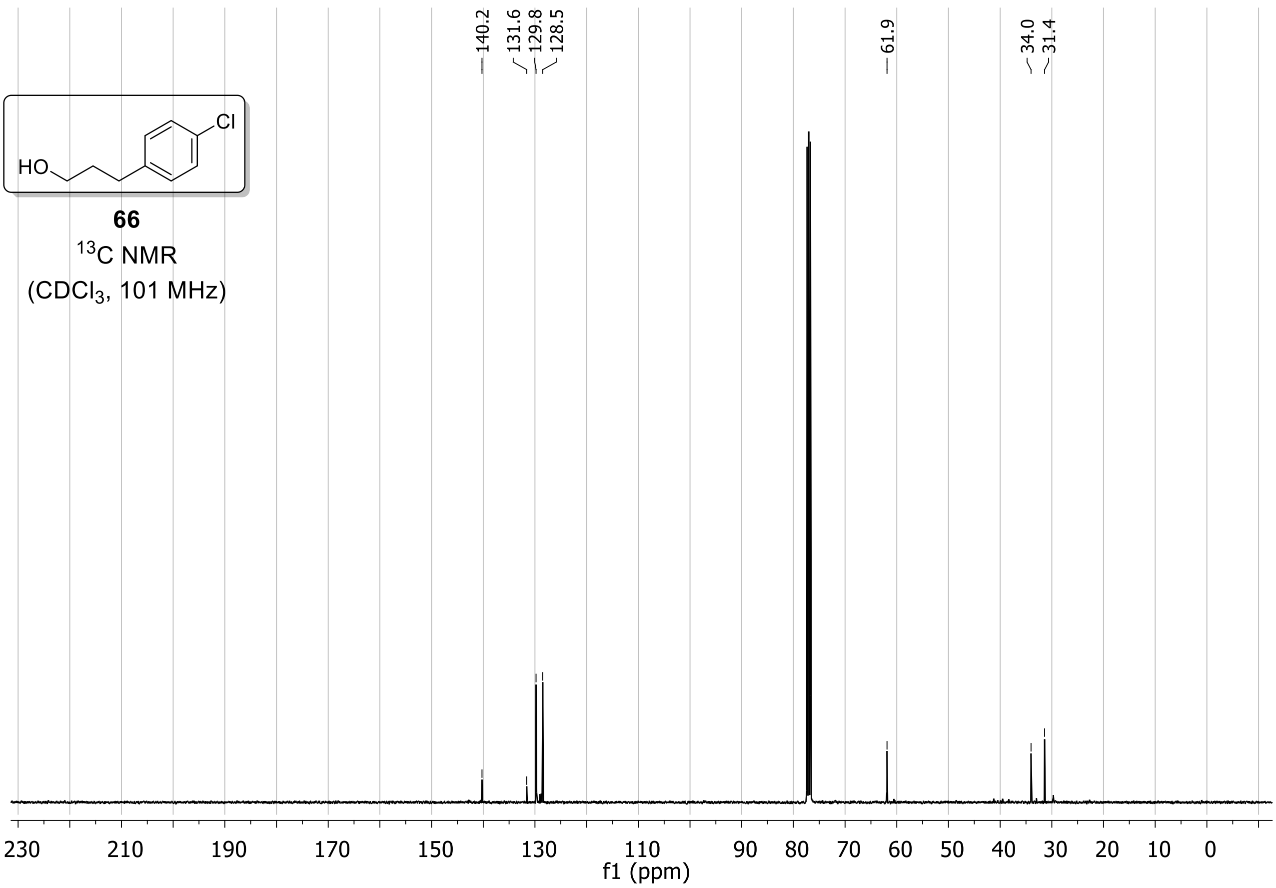


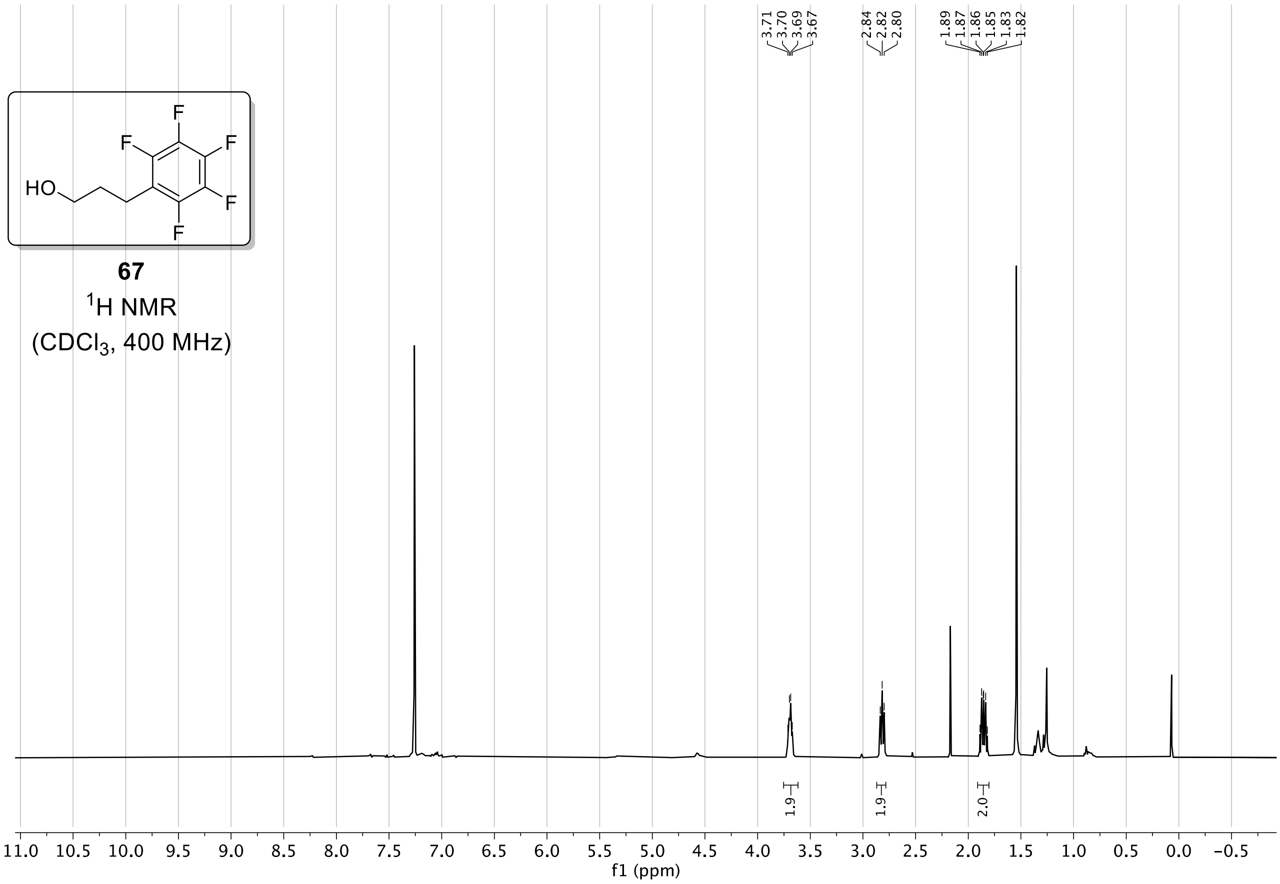
8.50
8.50
8.37
8.37
7.69
7.68
3.69
3.67
3.66
2.74
2.72
2.70
1.91
1.90
1.88
1.88
1.87
1.86
1.84
Br
HO
N
65
^{1}H NMR
(CDCl$_3$, 400 MHz)
0.8
0.9
0.8
2.0
2.0
2.3
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)



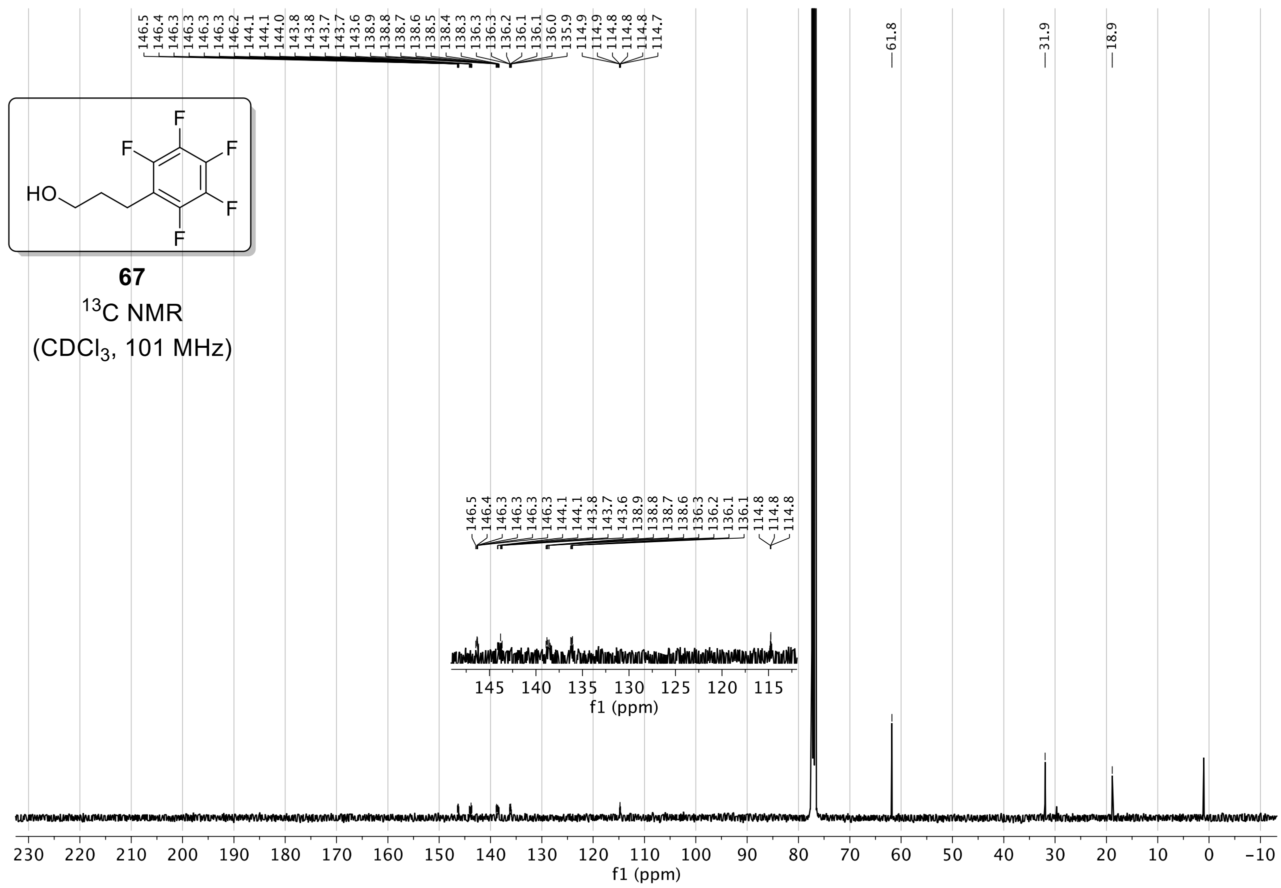
148.4
148.0
139.1
138.6
120.7
61.4
33.5
28.8
Br
HO
N
65
^{13}C NMR
(CDCl$_3$, 101 MHz)
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


HO
Cl
66
^{1}H NMR
($CDCl_3$, 400 MHz)
7.28
7.26
7.16
7.14
3.69
3.68
3.66
2.72
2.71
2.69
1.92
1.91
1.90
1.90
1.89
1.89
1.88
1.87
1.87
1.87
1.85
1.9
1.8
1.9
2.0
2.1
10.5
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
-0.5
f1 (ppm)

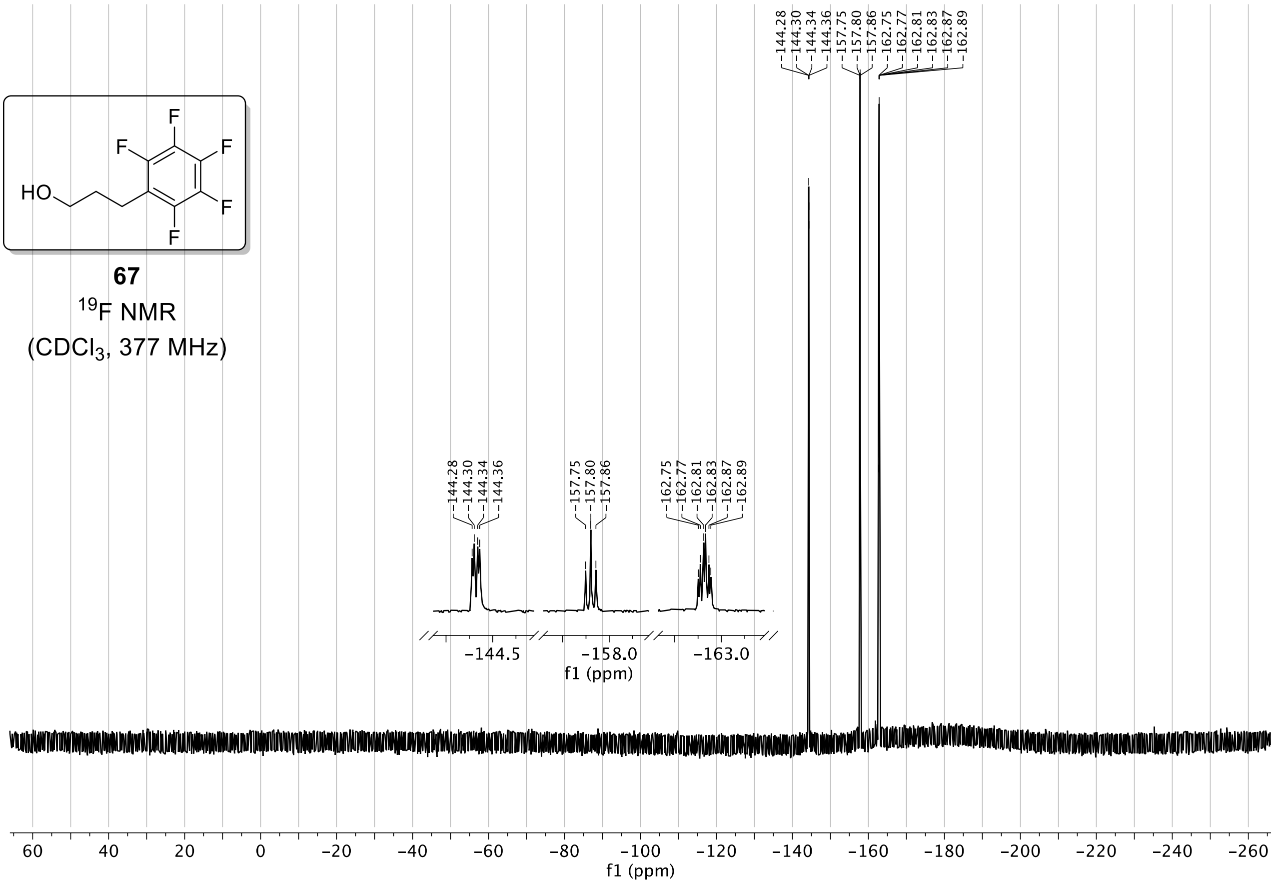

HO
Cl
66
^{13}C NMR
($CDCl_3$, 101 MHz)
140.2
131.6
129.8
128.5
61.9
34.0
31.4
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

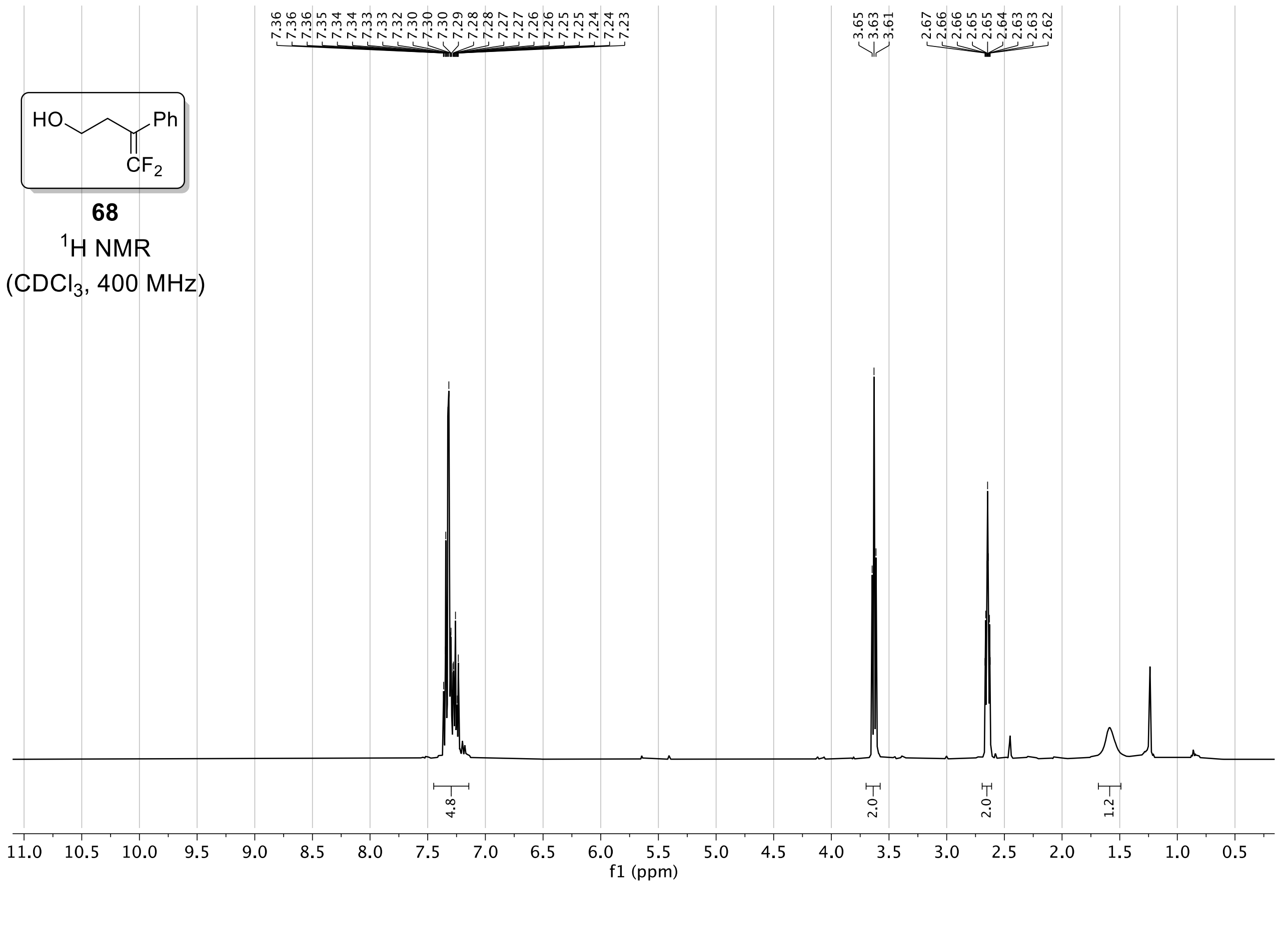


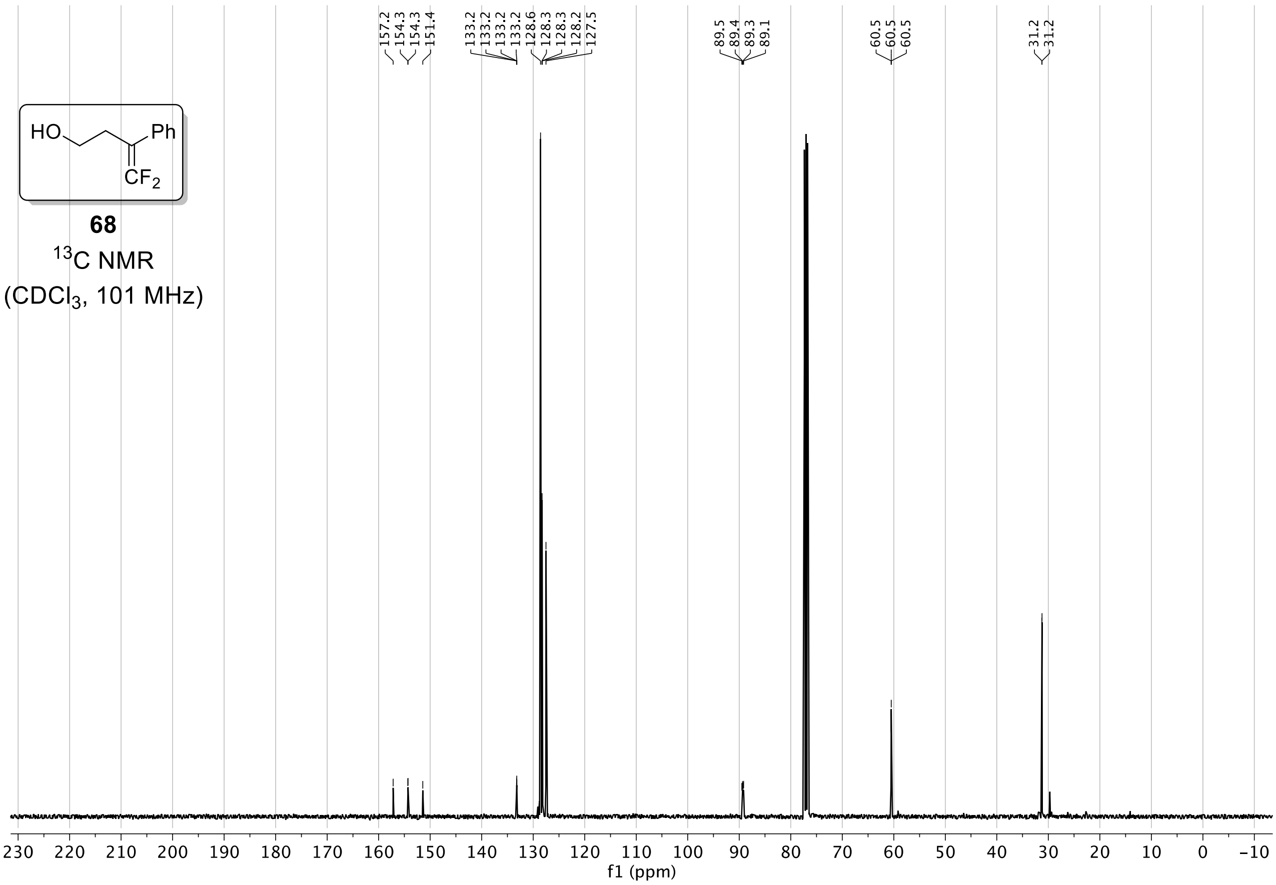
67
^{1}H NMR
($CDCl_3$, 400 MHz)

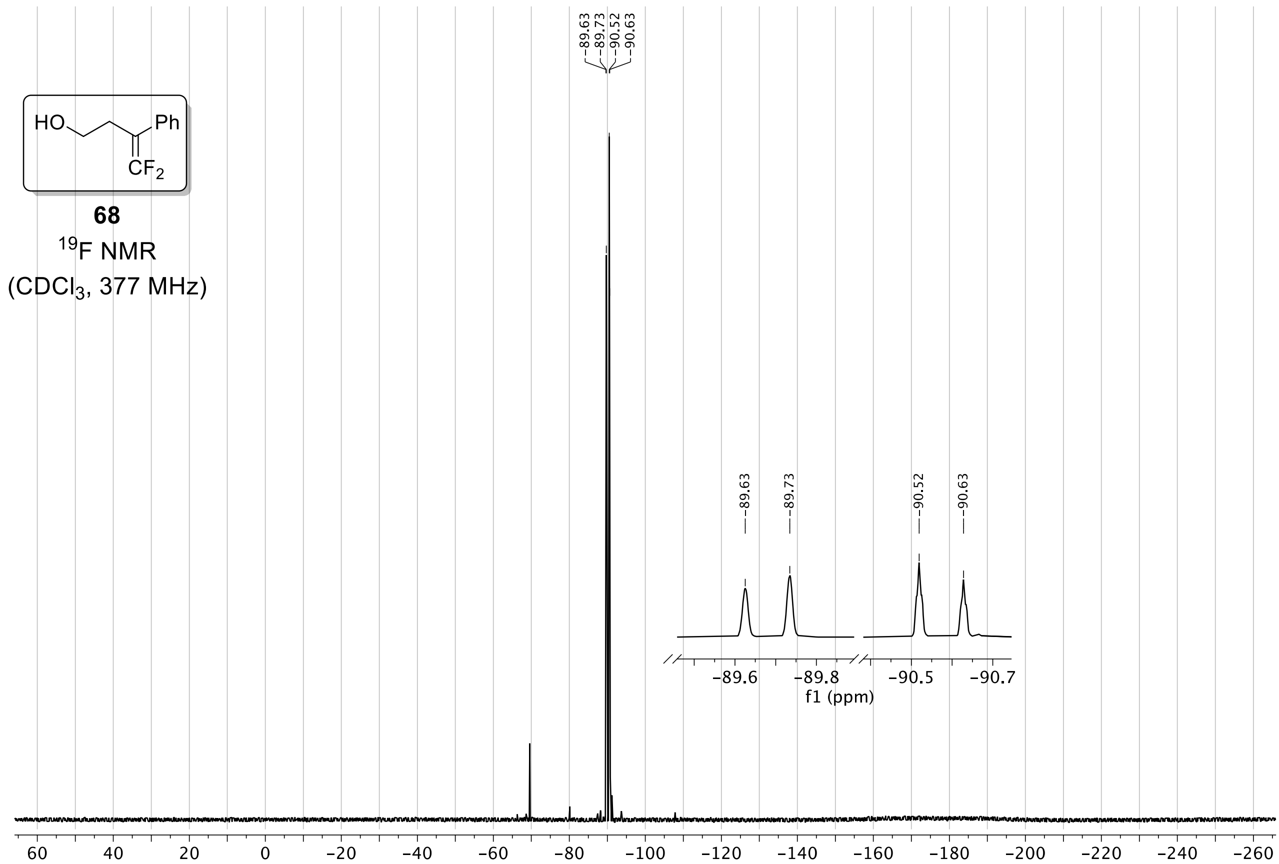


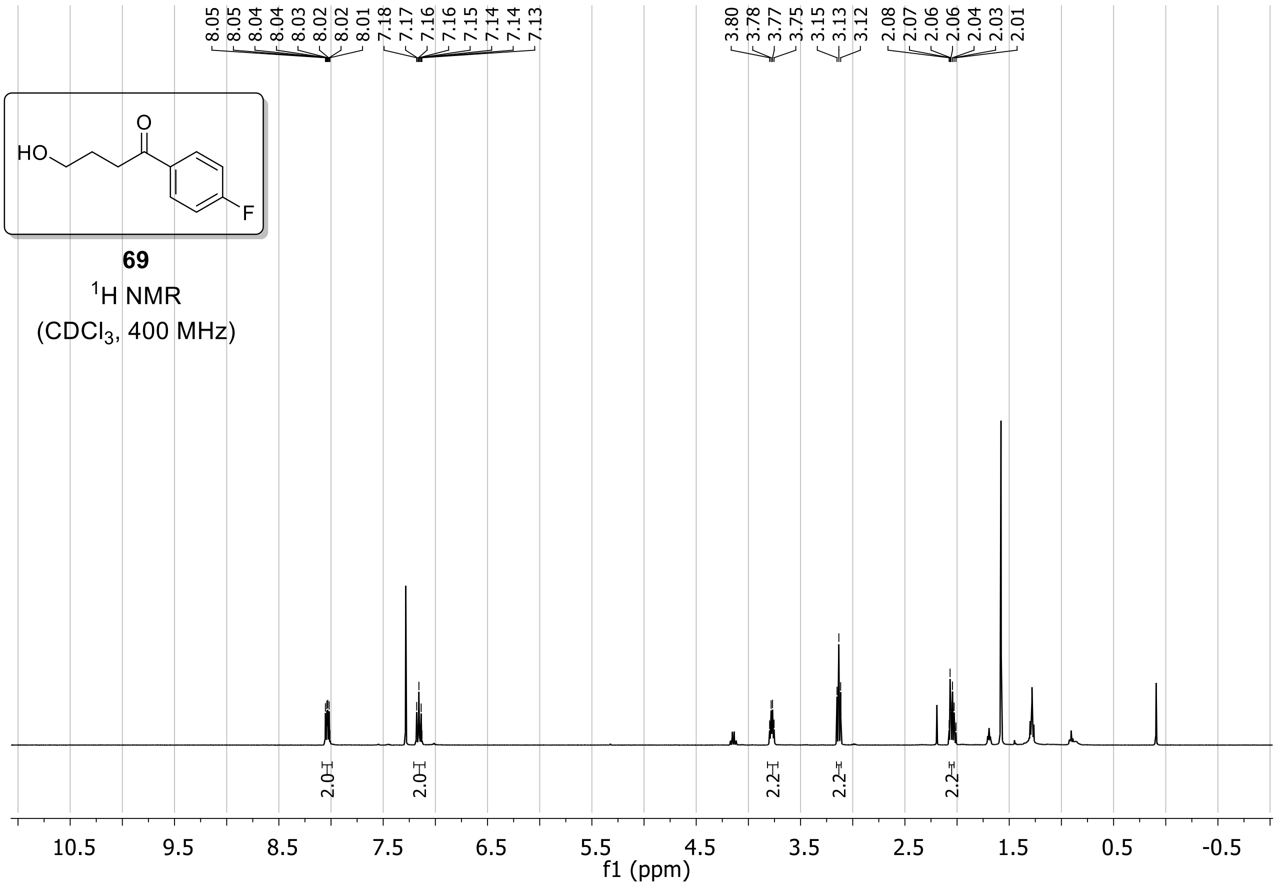
67
^{13}C NMR
($CDCl_3$, 101 MHz)

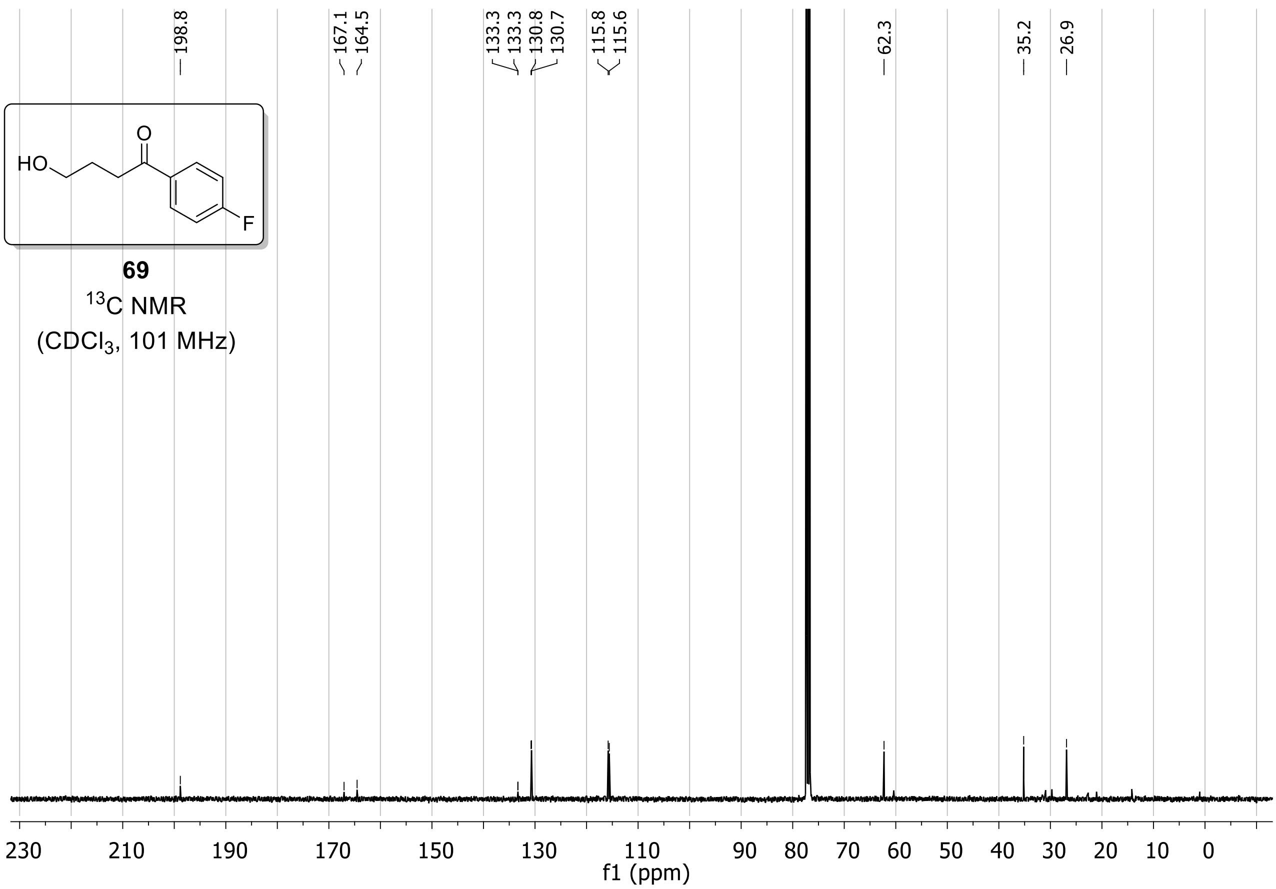

67
^{19}F NMR
($CDCl_3$, 377 MHz)
f1 (ppm)

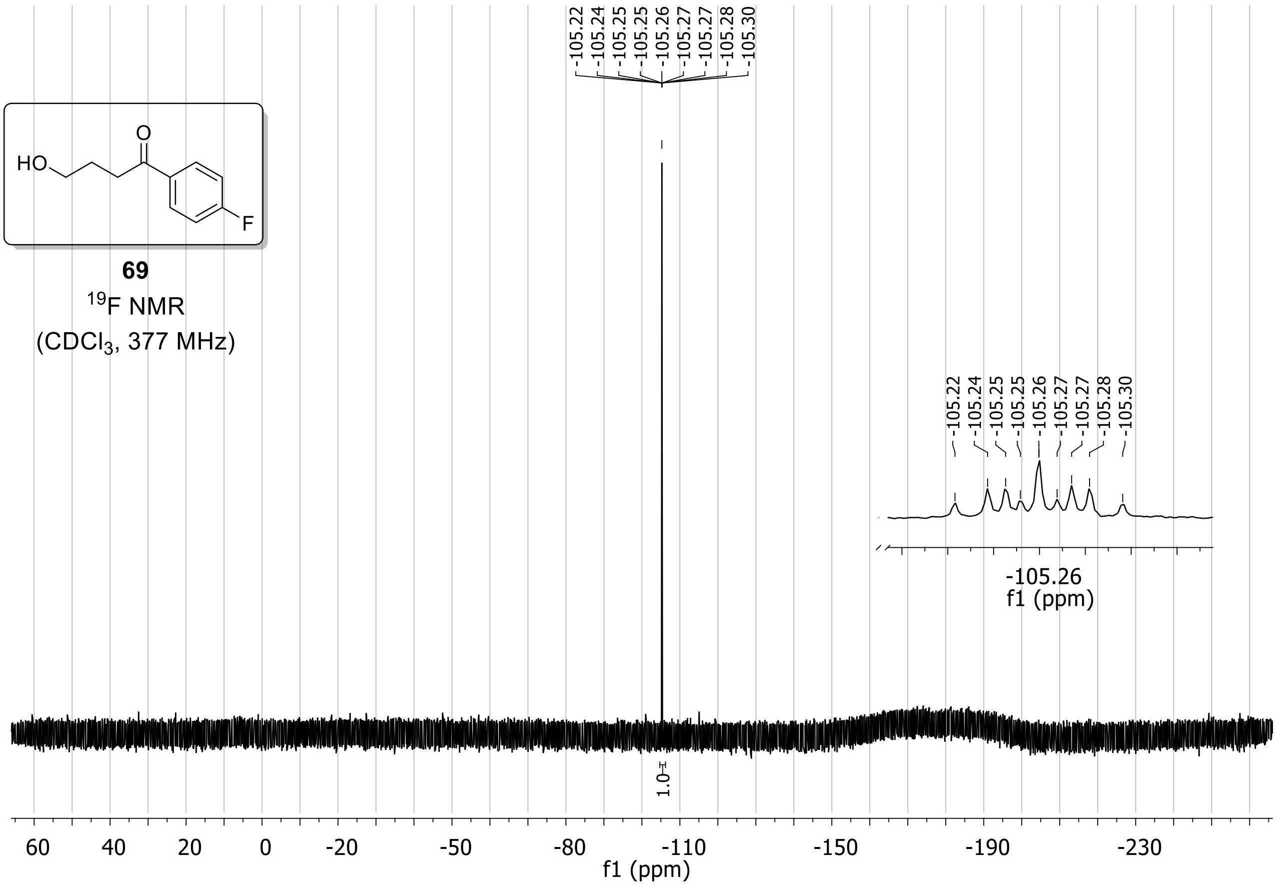

68
^{1}H NMR
($CDCl_3$, 400 MHz)
f1 (ppm)


HO Ph
CF2
68
13C NMR
(CDCl3, 101 MHz)
157.2
154.3
154.3
151.4
133.2
133.2
133.2
133.2
128.6
128.3
128.3
128.2
127.5
89.5
89.4
89.3
89.1
60.5
60.5
60.5
31.2
31.2
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


HO Ph
CF2
68
19F NMR
(CDCl3, 377 MHz)
−89.63
−89.73
−90.52
−90.63
−89.6 −89.8 −90.5 −90.7
f1 (ppm)
60 40 20 0 −20 −40 −60 −80 −100 −120 −140 −160 −180 −200 −220 −240 −260
f1 (ppm)


HO
O
F
69
^{1}H NMR
(CDCl$_3$, 400 MHz)
8.05 8.05 8.04 8.04 8.03 8.02 8.02 8.01 7.18 7.17 7.16 7.16 7.15 7.14 7.14 7.13
3.80 3.78 3.77 3.75 3.15 3.13 3.12 2.08 2.07 2.06 2.06 2.04 2.03 2.01
2.0 2.0 2.2 2.2 2.2
10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0.5
f1 (ppm)

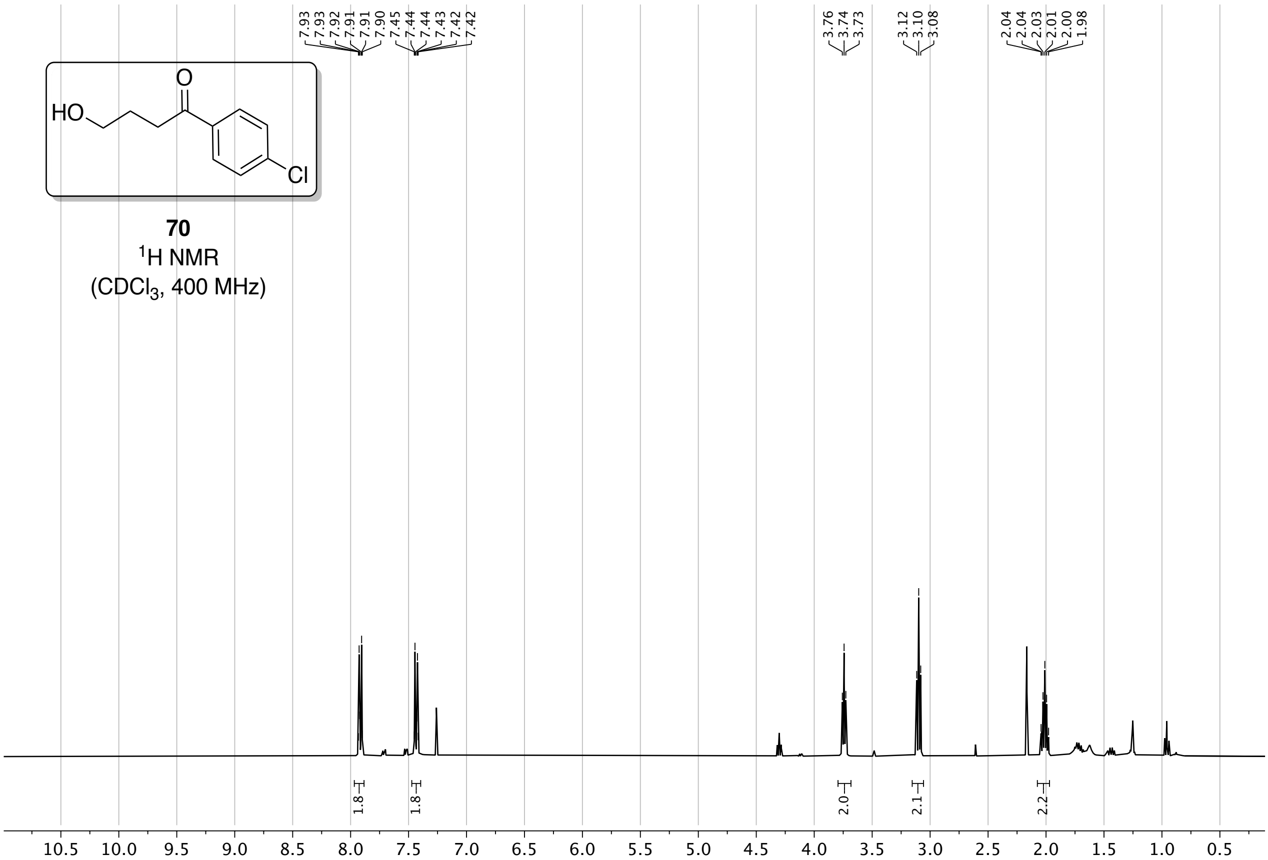

HO
O
F
69
^{13}C NMR
(CDCl$_3$, 101 MHz)
198.8
167.1 164.5
133.3 133.3 130.8 130.7
115.8 115.6
62.3
35.2
26.9
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



69

^{19}F NMR

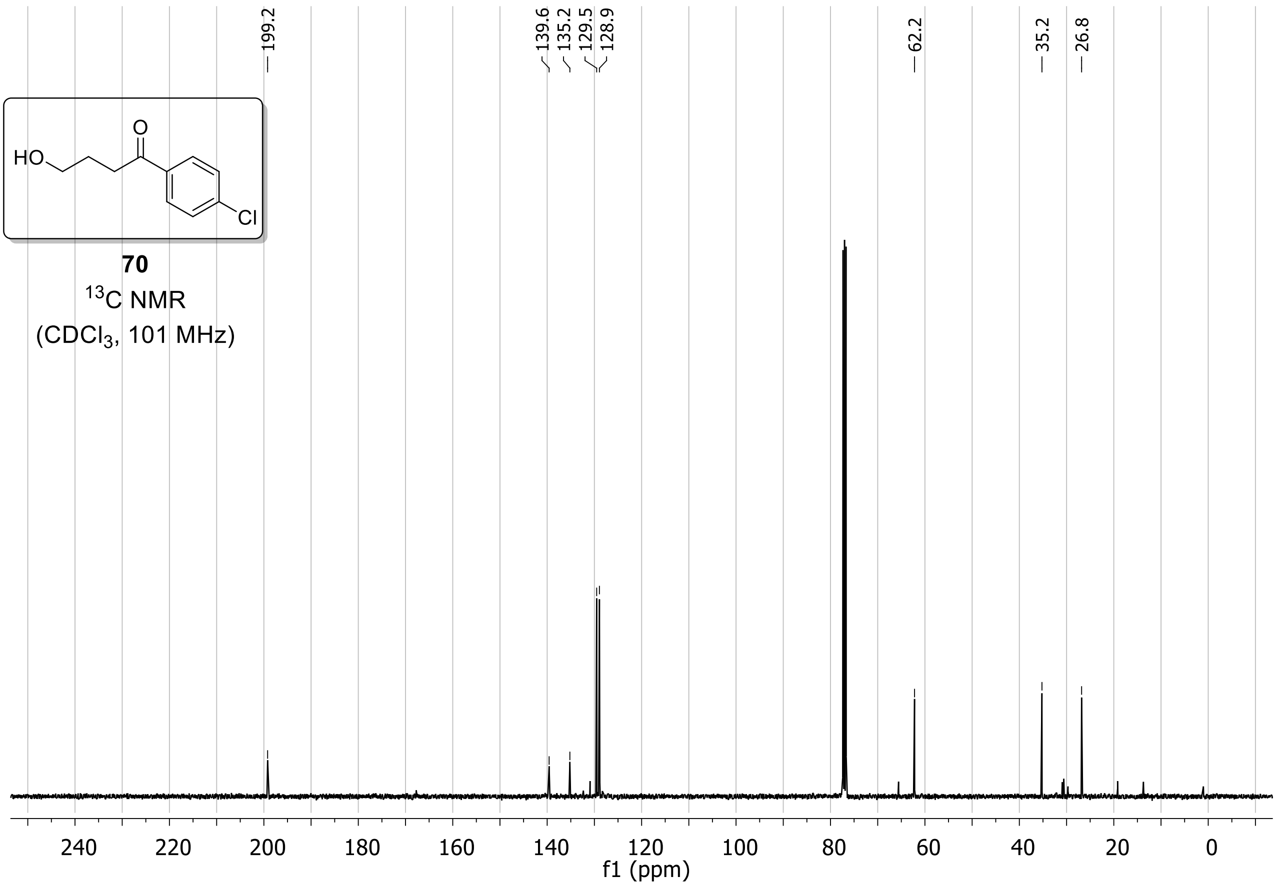
($CDCl_3$, 377 MHz)



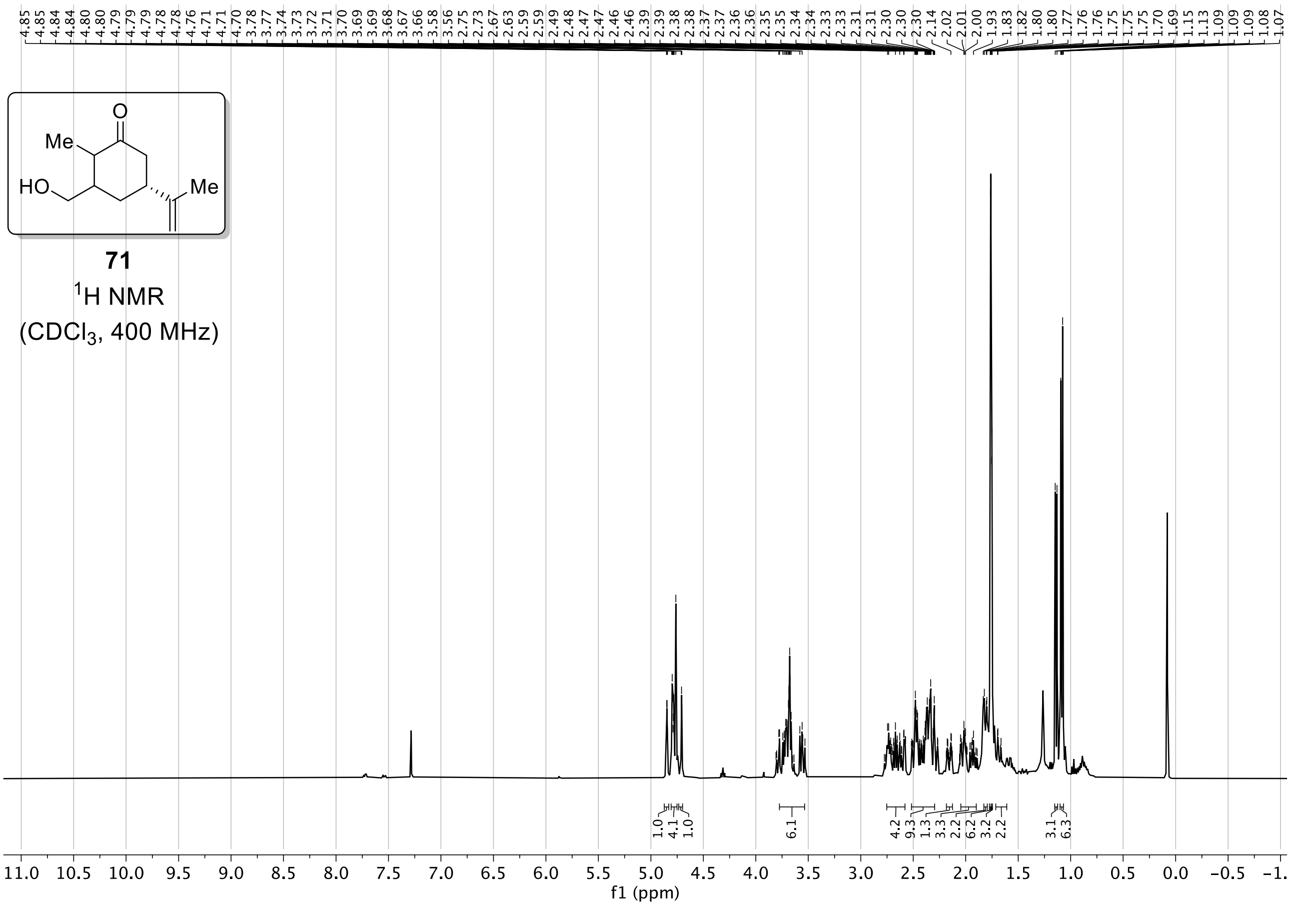
70

^{1}H NMR

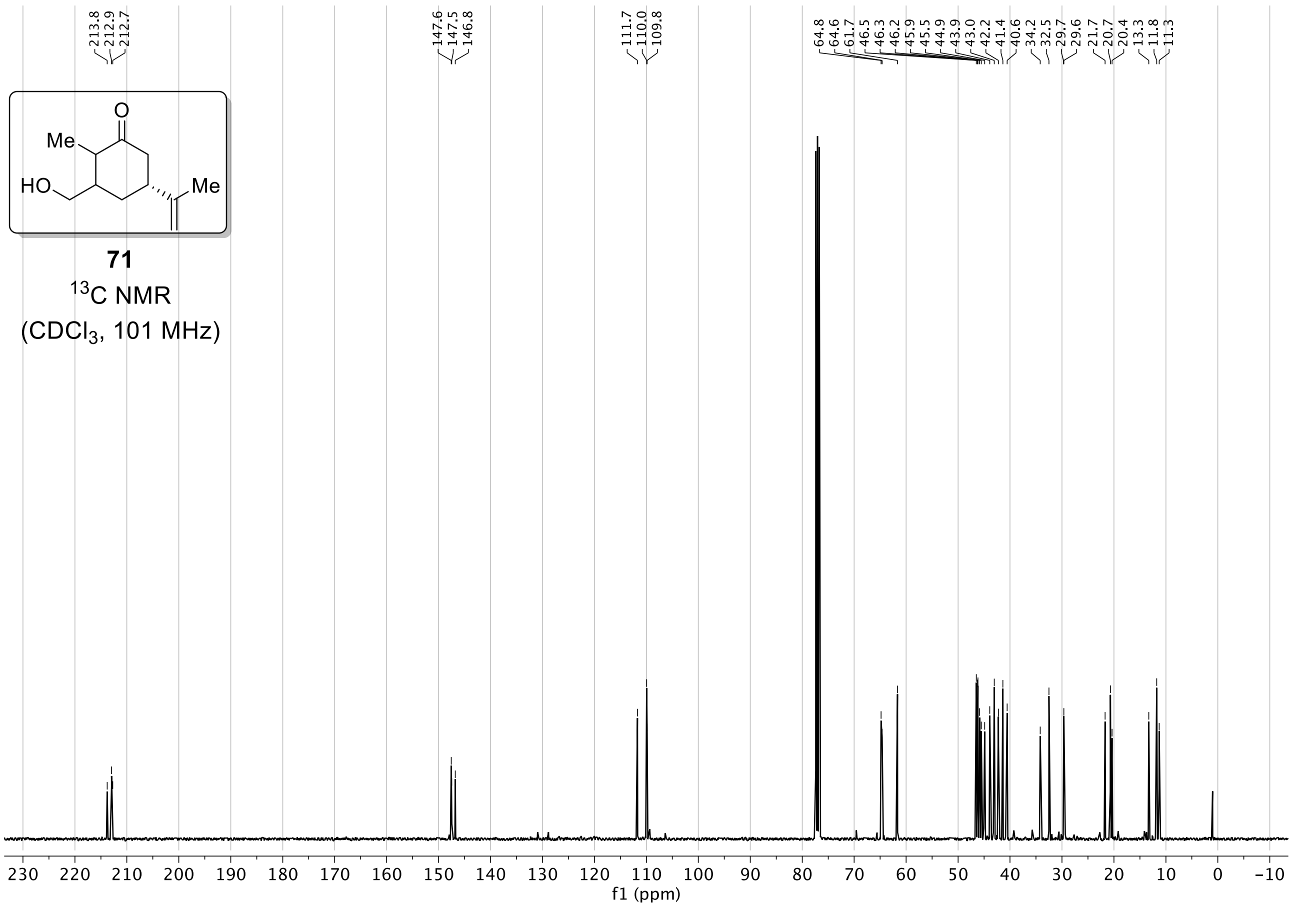
($CDCl_3$, 400 MHz)



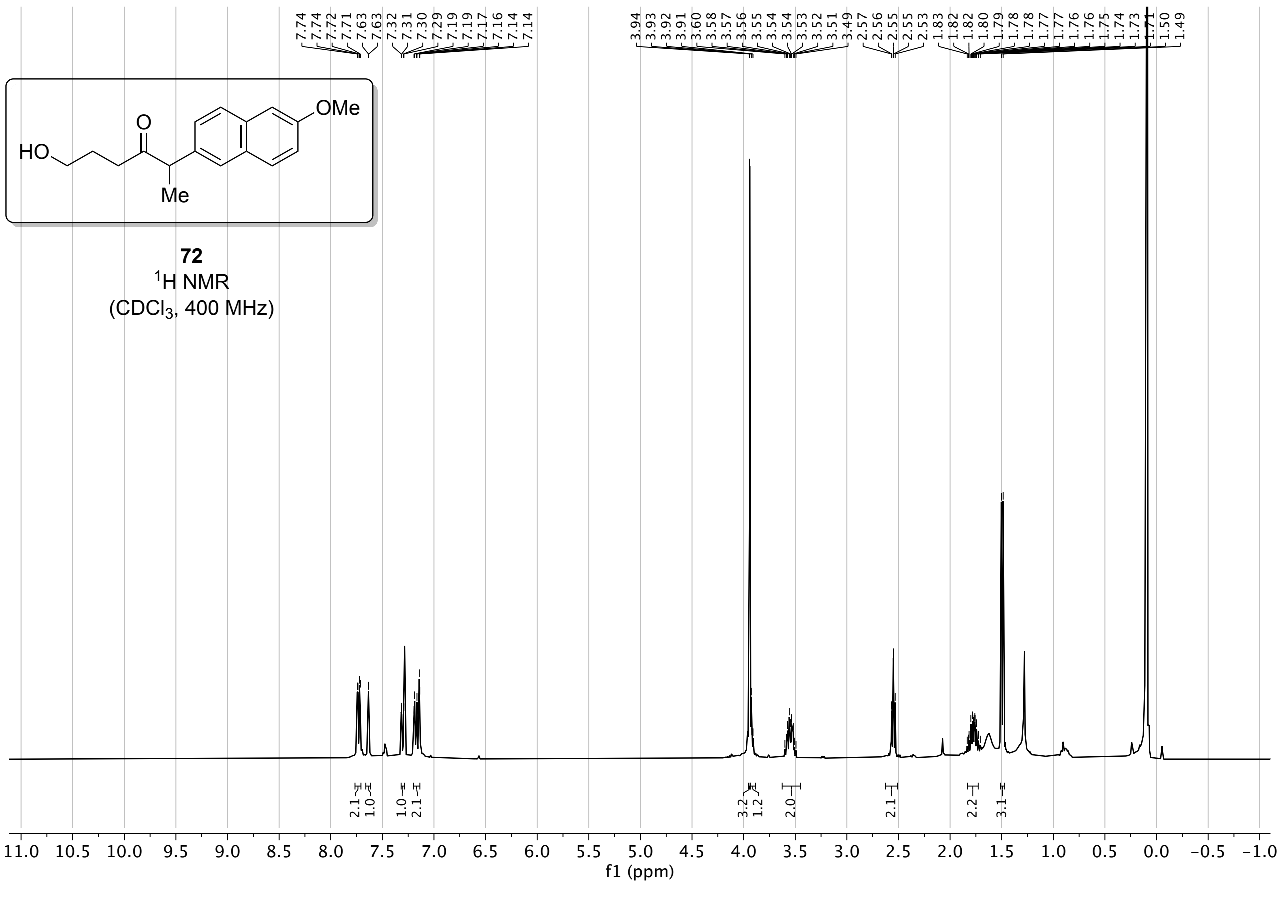
70
^{13}C NMR
($CDCl_3$, 101 MHz)



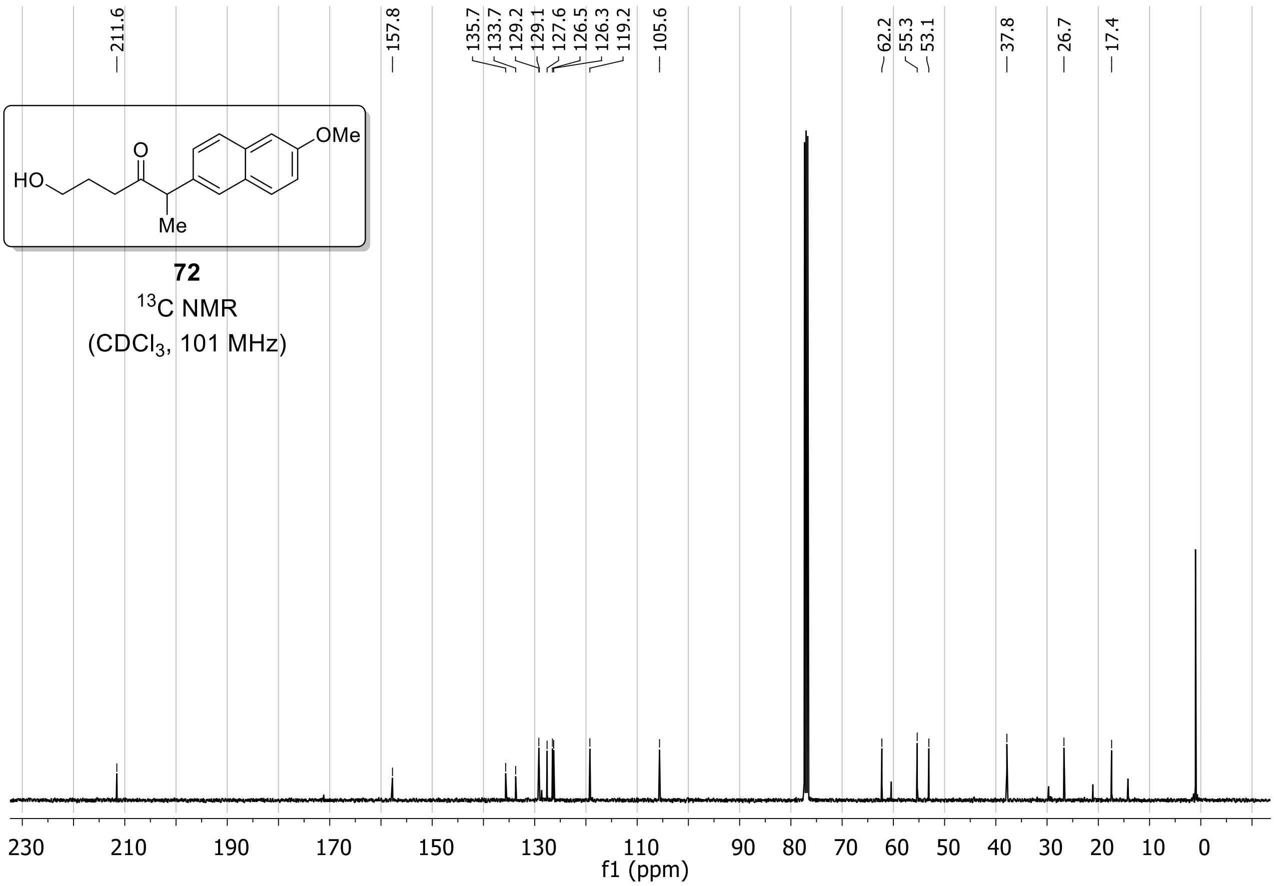
71
^{1}H NMR
($CDCl_3$, 400 MHz)



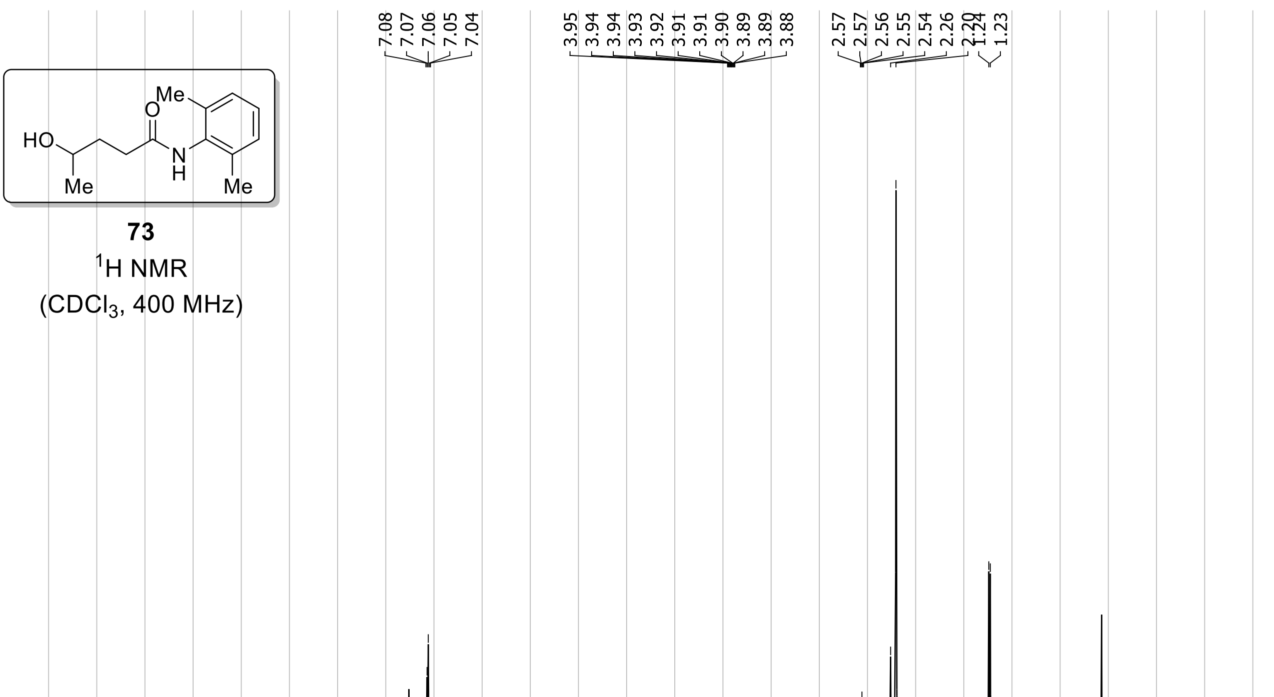
71
^{13}C NMR
($CDCl_3$, 101 MHz)



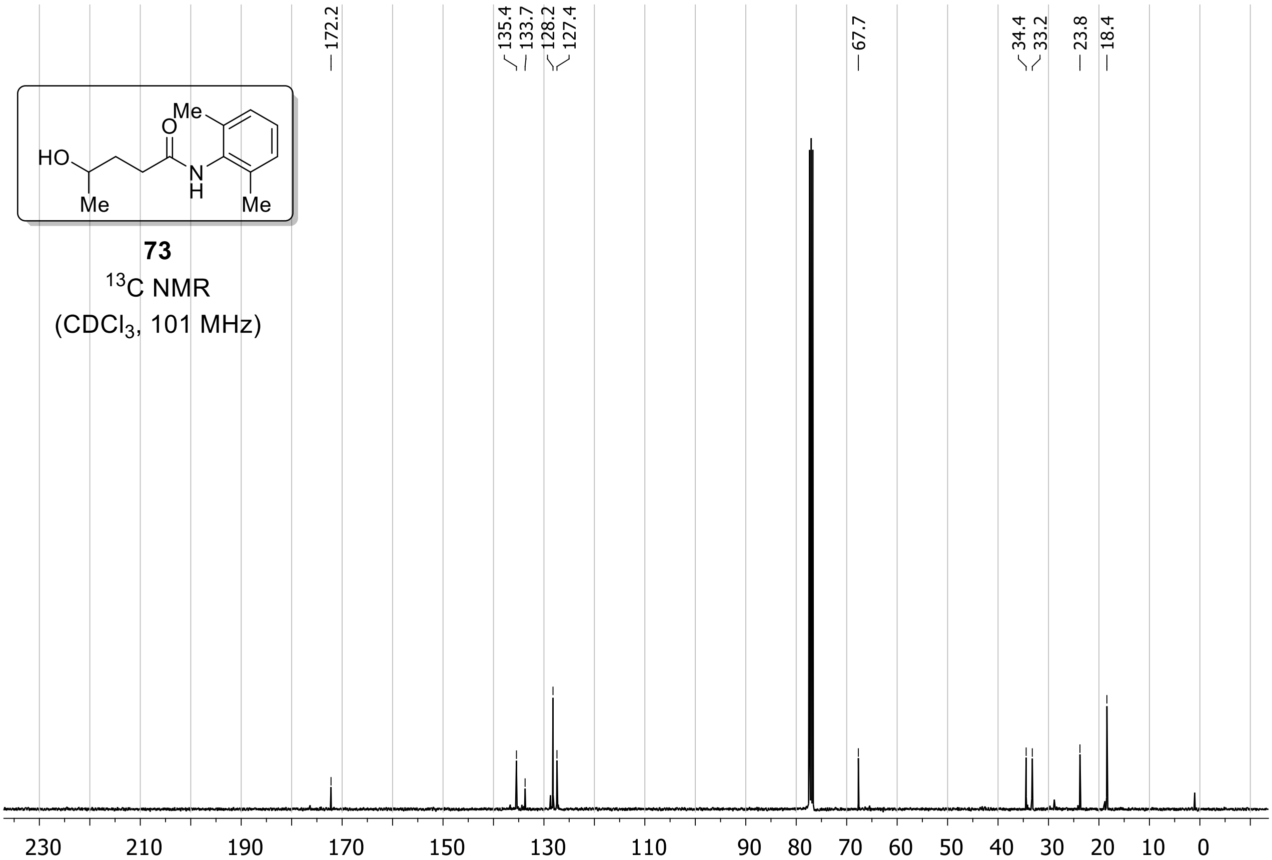
72
^{1}H NMR
($CDCl_3$, 400 MHz)



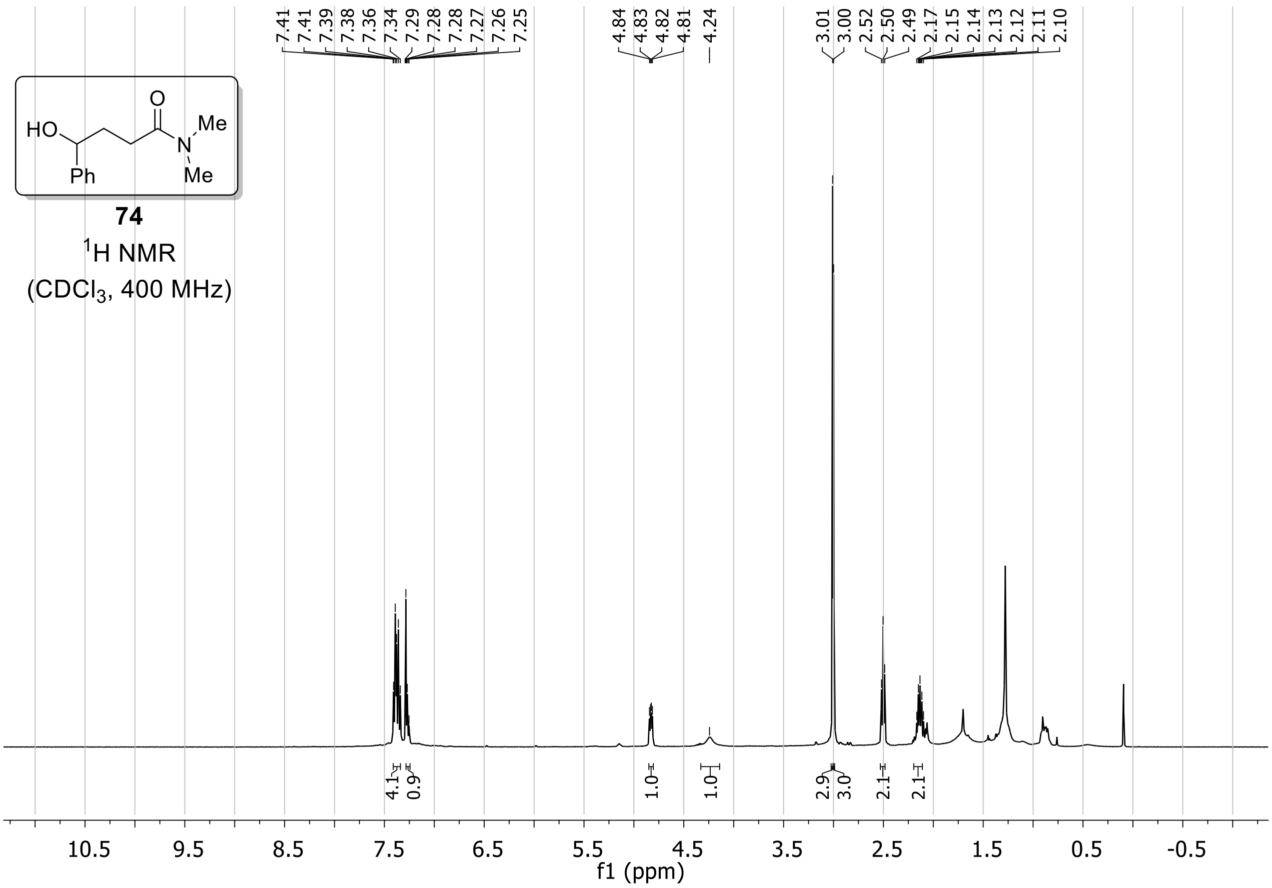
72
^{13}C NMR
($CDCl_3$, 101 MHz)



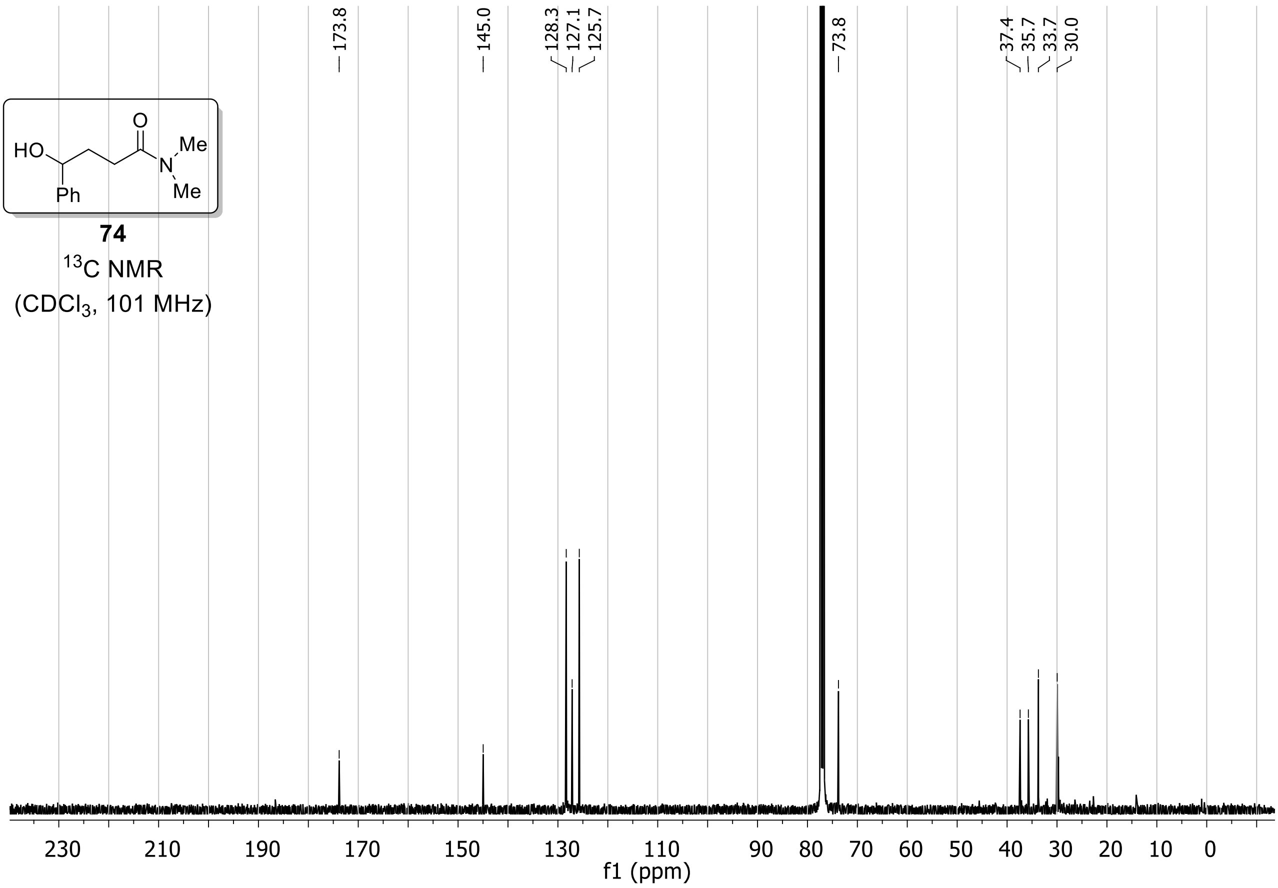
73
^{1}H NMR
($CDCl_3$, 400 MHz)



73
^{13}C NMR
($CDCl_3$, 101 MHz)



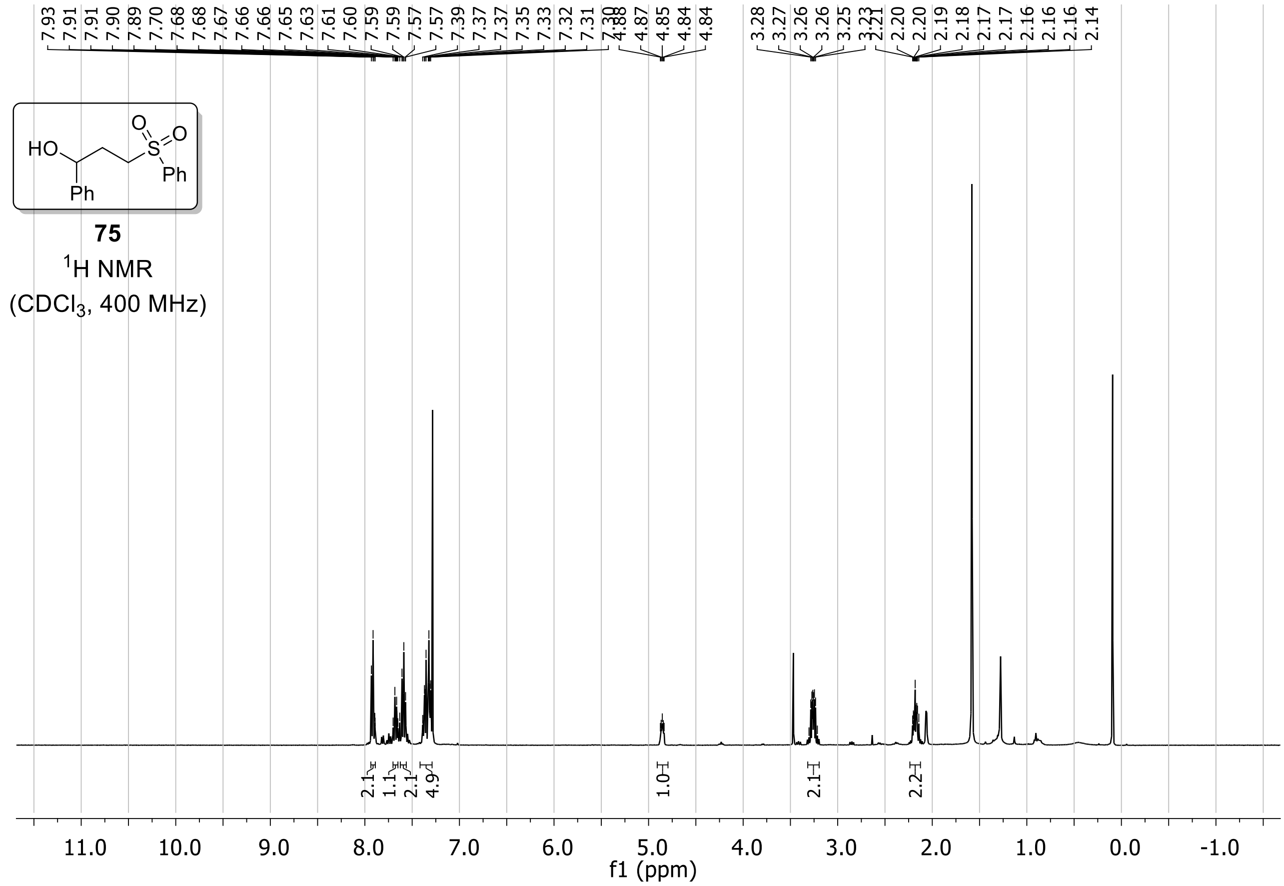
74
^{1}H NMR
($CDCl_3$, 400 MHz)



74

^{13}C NMR

($CDCl_3$, 101 MHz)



75

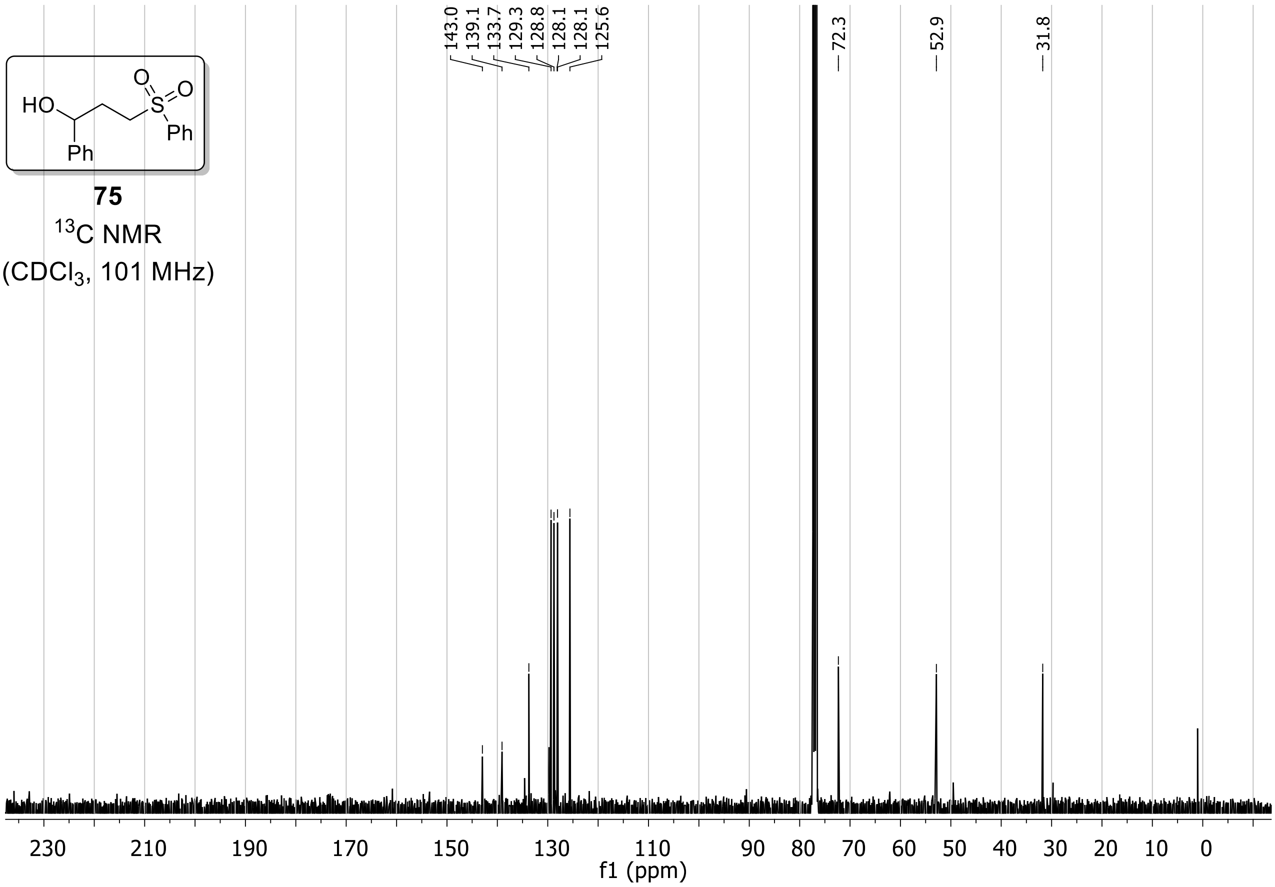
^{1}H NMR

($CDCl_3$, 400 MHz)

75

^{13}C NMR

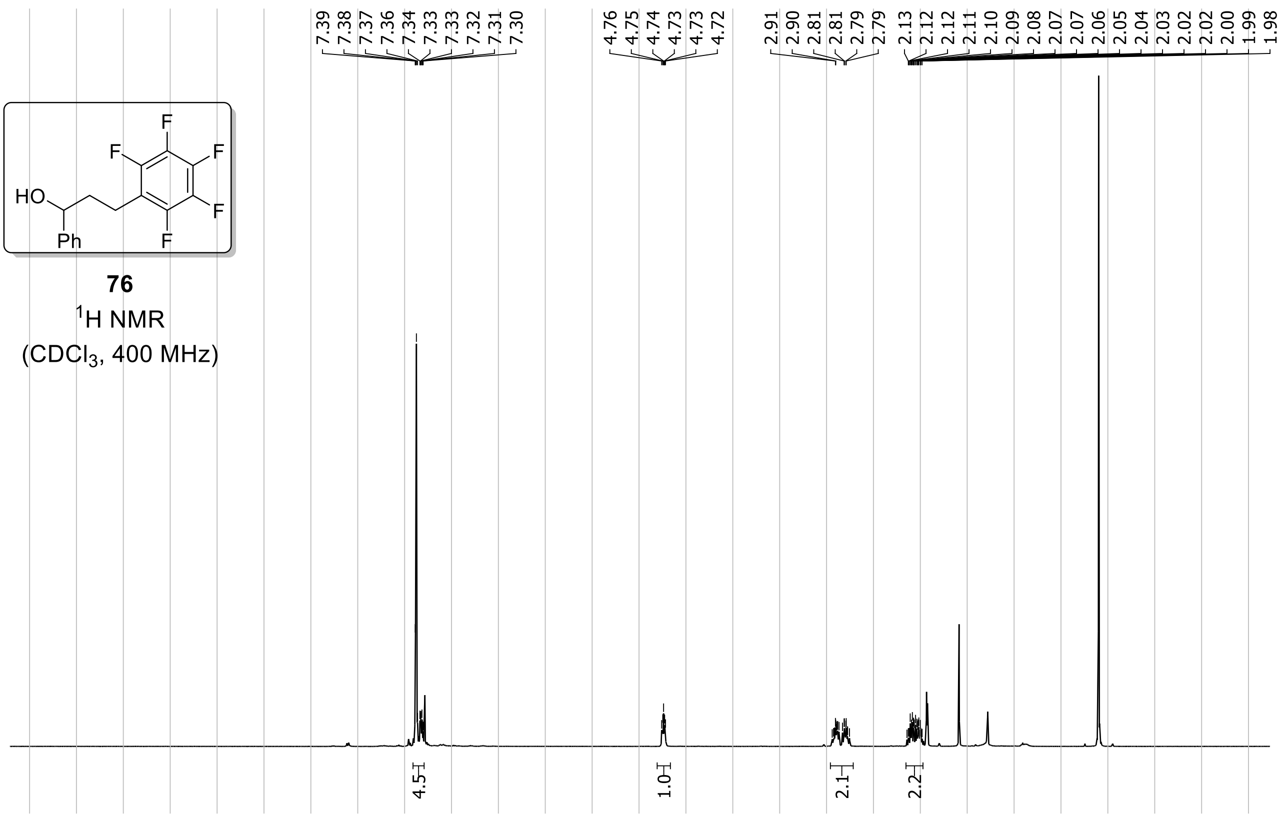
($CDCl_3$, 101 MHz)

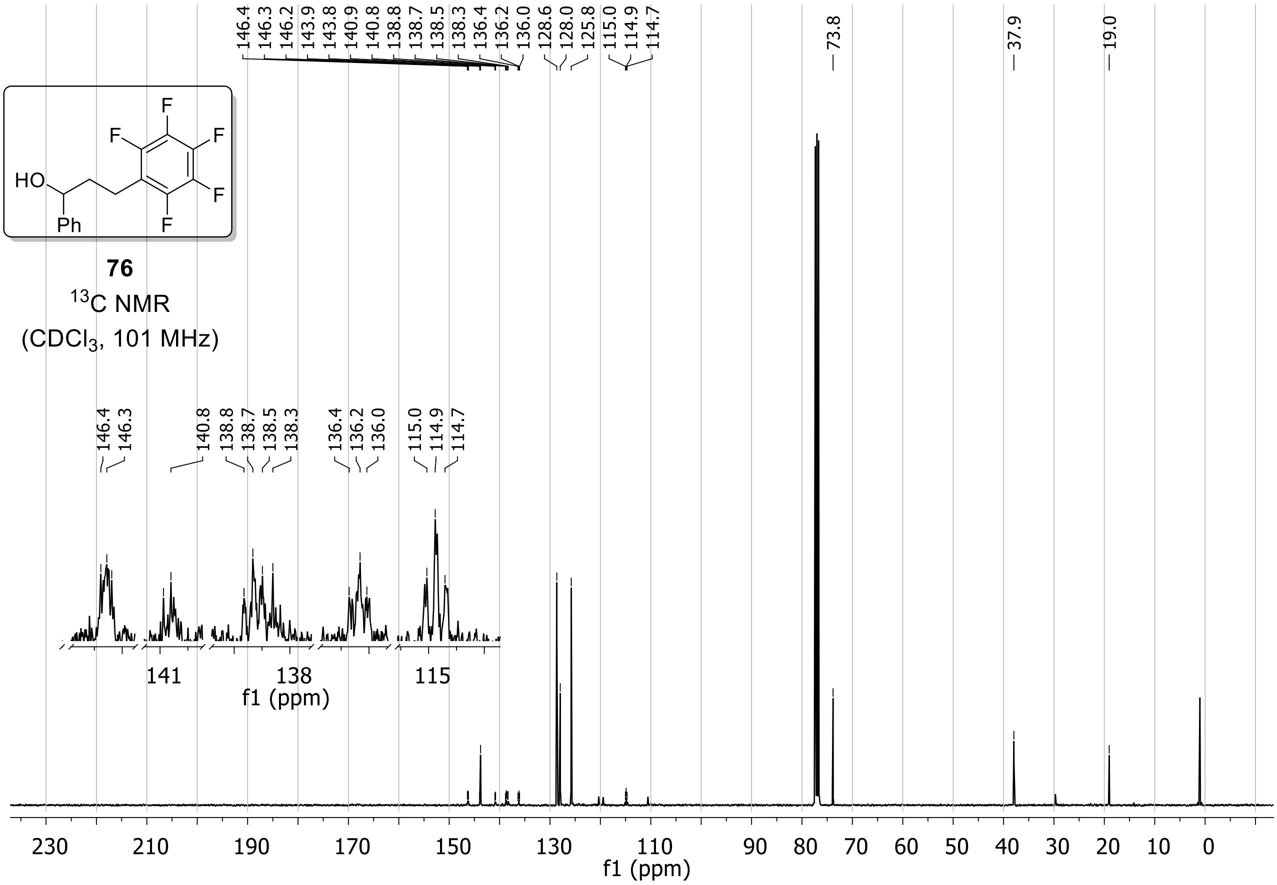


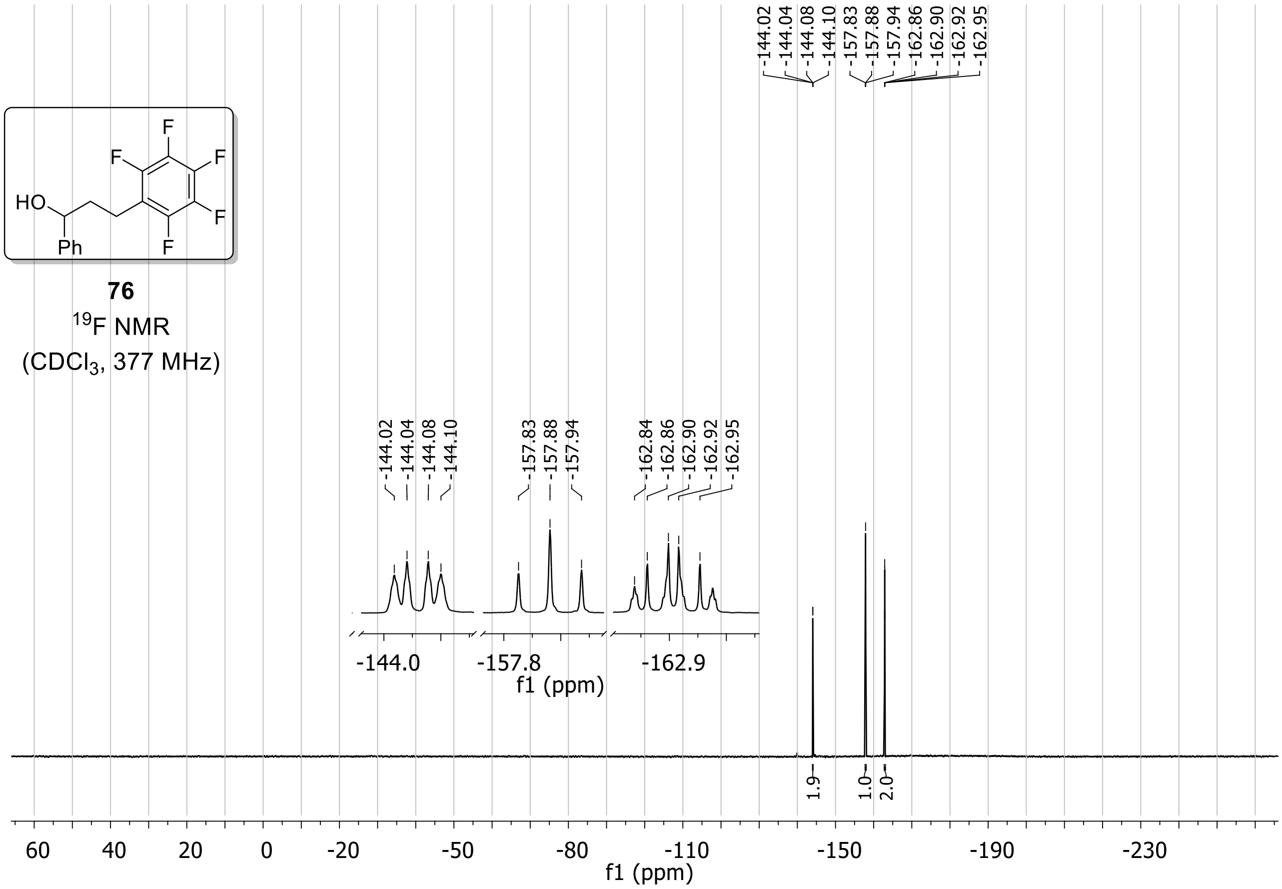
76

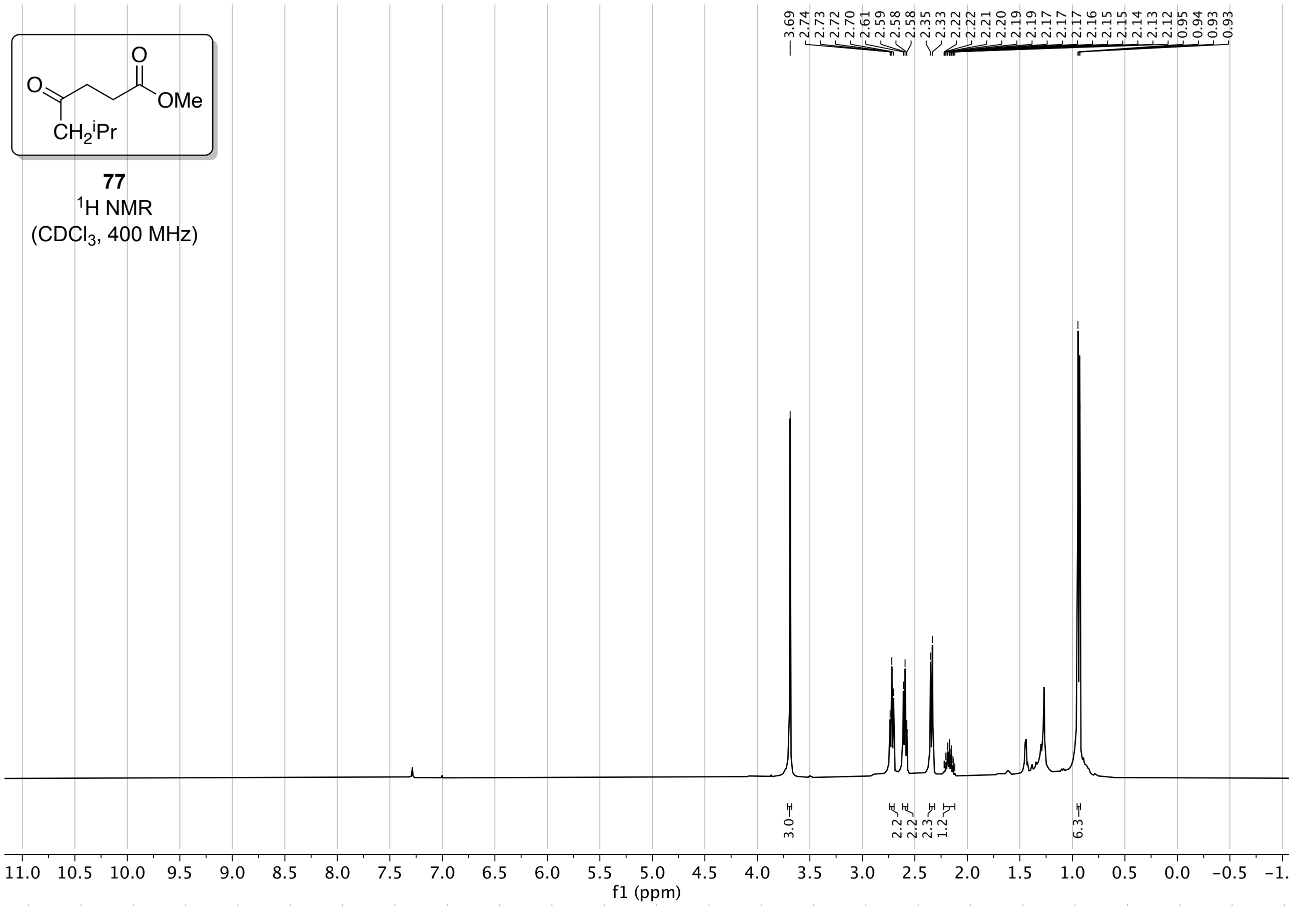
^{1}H NMR

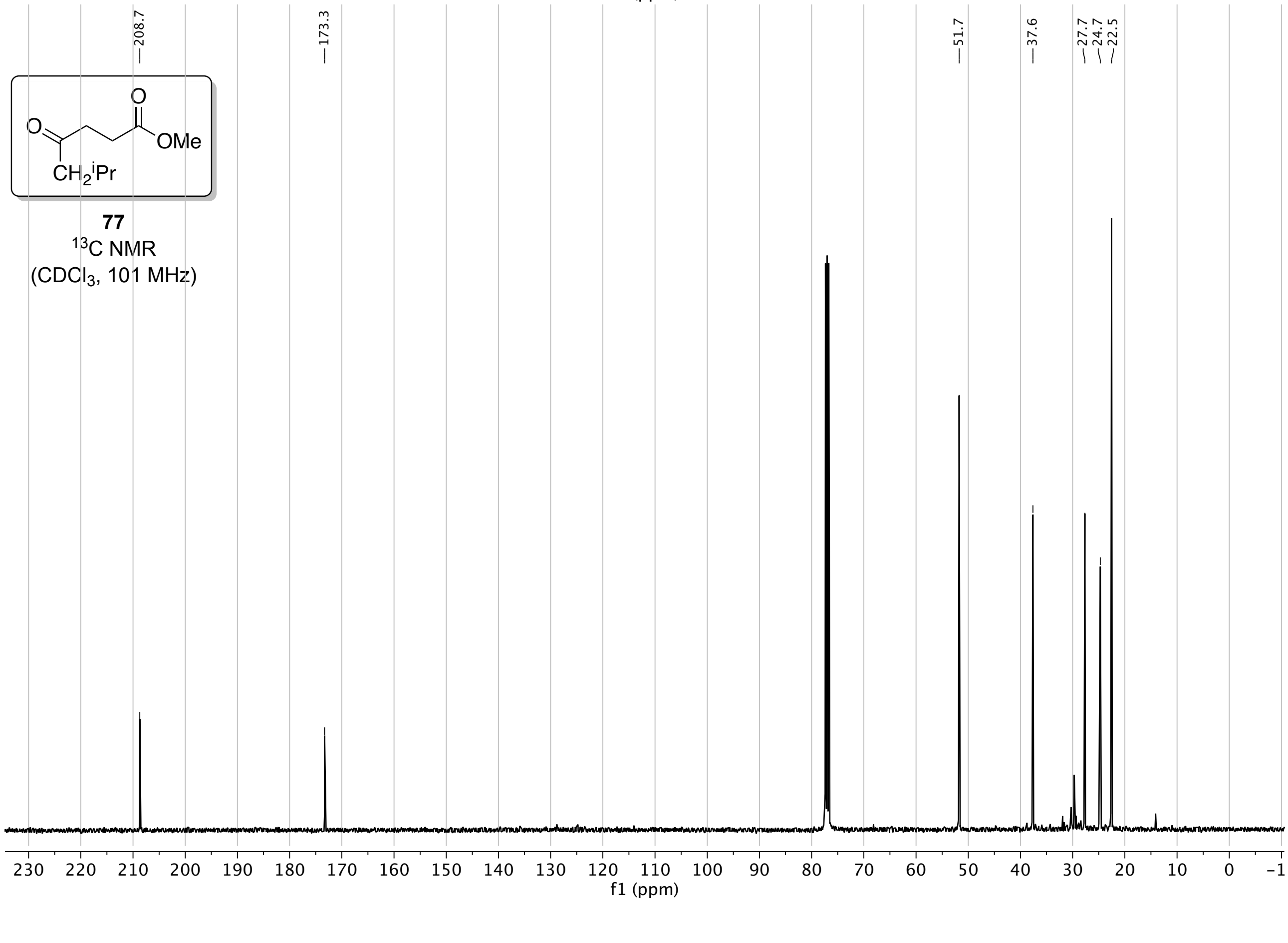
($CDCl_3$, 400 MHz)

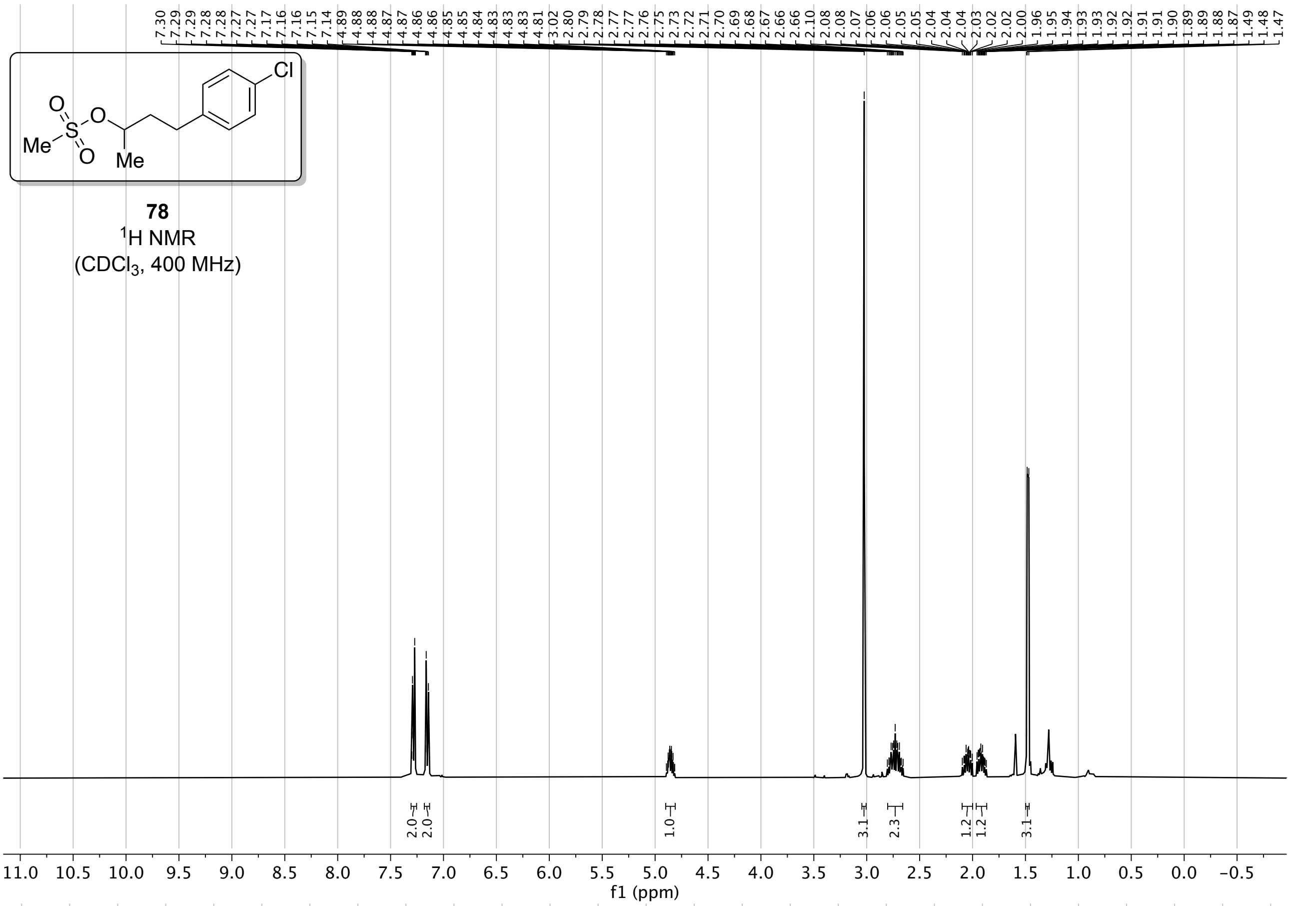



76
13C NMR
(CDCl3, 101 MHz)
HO
Ph
F
146.4 146.3 146.2 143.9 143.8 140.9 140.8 138.8 138.7 138.5 138.3 136.4 136.2 136.0 128.6 128.0 125.8 115.0 114.9 114.7
73.8
37.9
19.0
141
138
115
f1 (ppm)
230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

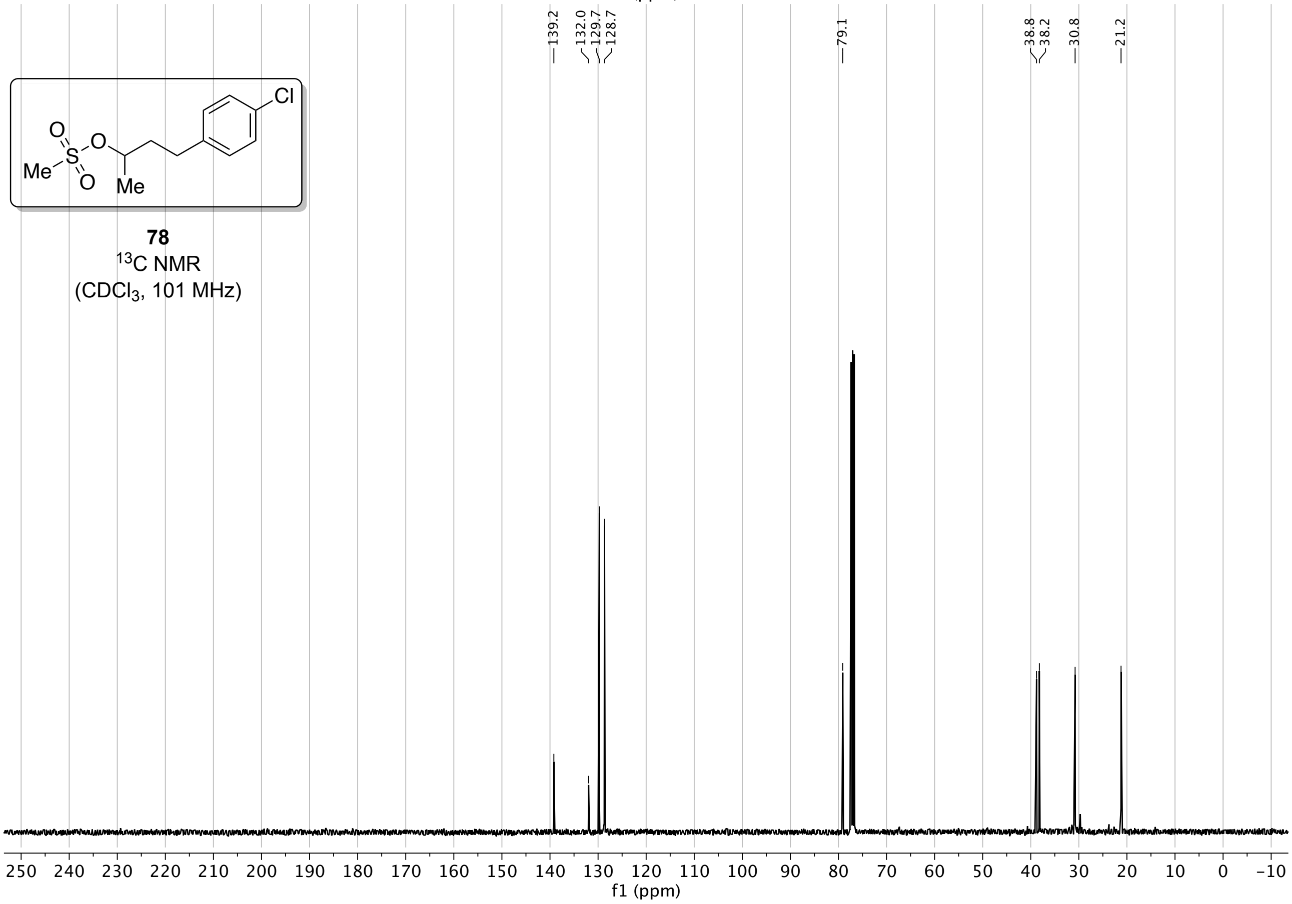

76
19F NMR
(CDCl3, 377 MHz)
HO
Ph
F
-144.02 -144.04 -144.08 -144.10 -157.83 -157.88 -157.94 -162.86 -162.90 -162.92 -162.95
-162.84
-144.0
-157.8
-162.9
f1 (ppm)
1.9
1.0
2.0
60 40 20 0 -20 -50 -80 -110 -150 -190 -230
f1 (ppm)


OMe
O
O
$CH_2{}^iPr$
77
^1H NMR
($CDCl_3$, 400 MHz)
f1 (ppm)

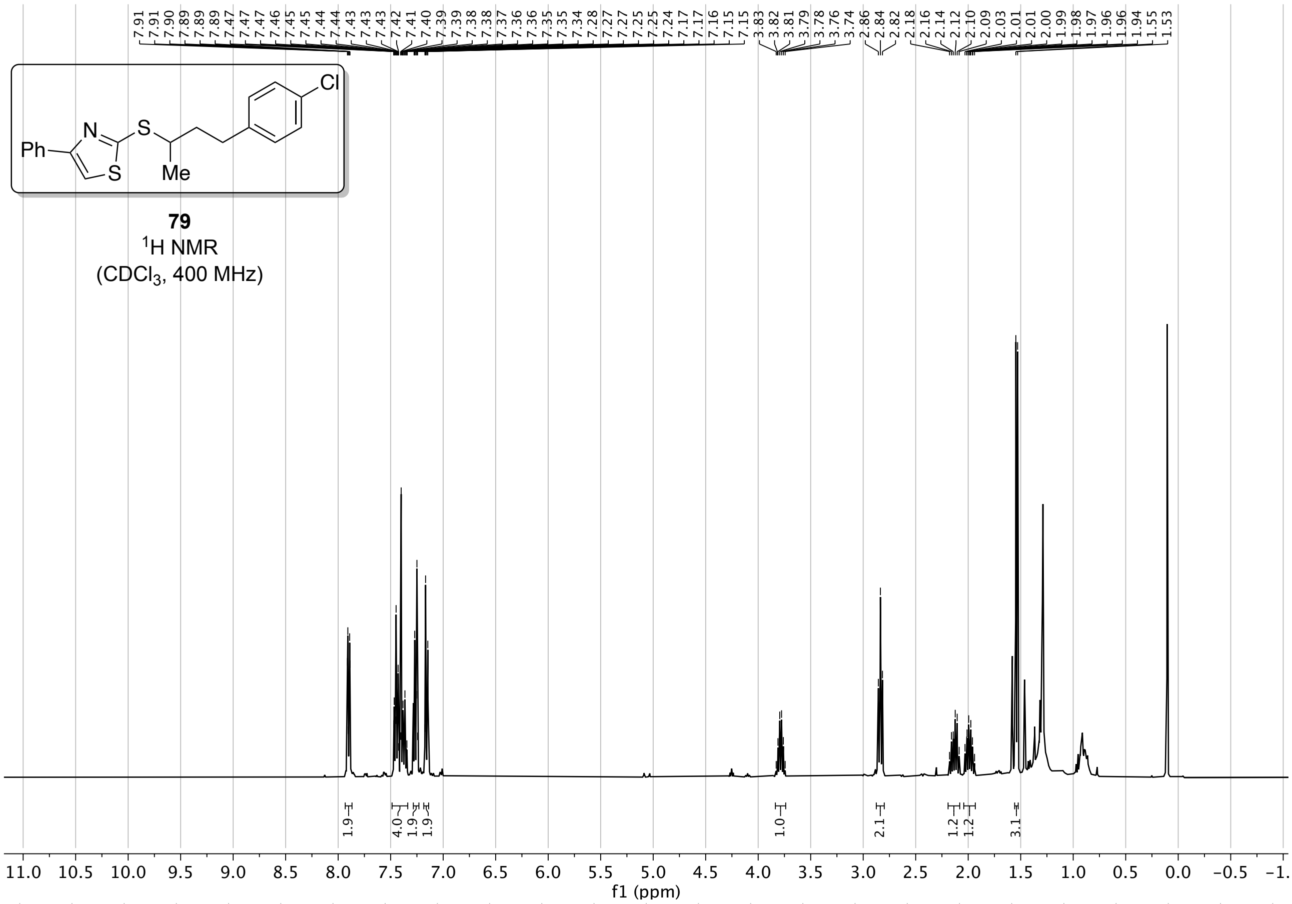

208.7
173.3
51.7
37.6
27.7
24.7
22.5
OMe
O
O
$CH_2{}^iPr$
77
^{13}C NMR
($CDCl_3$, 101 MHz)
f1 (ppm)



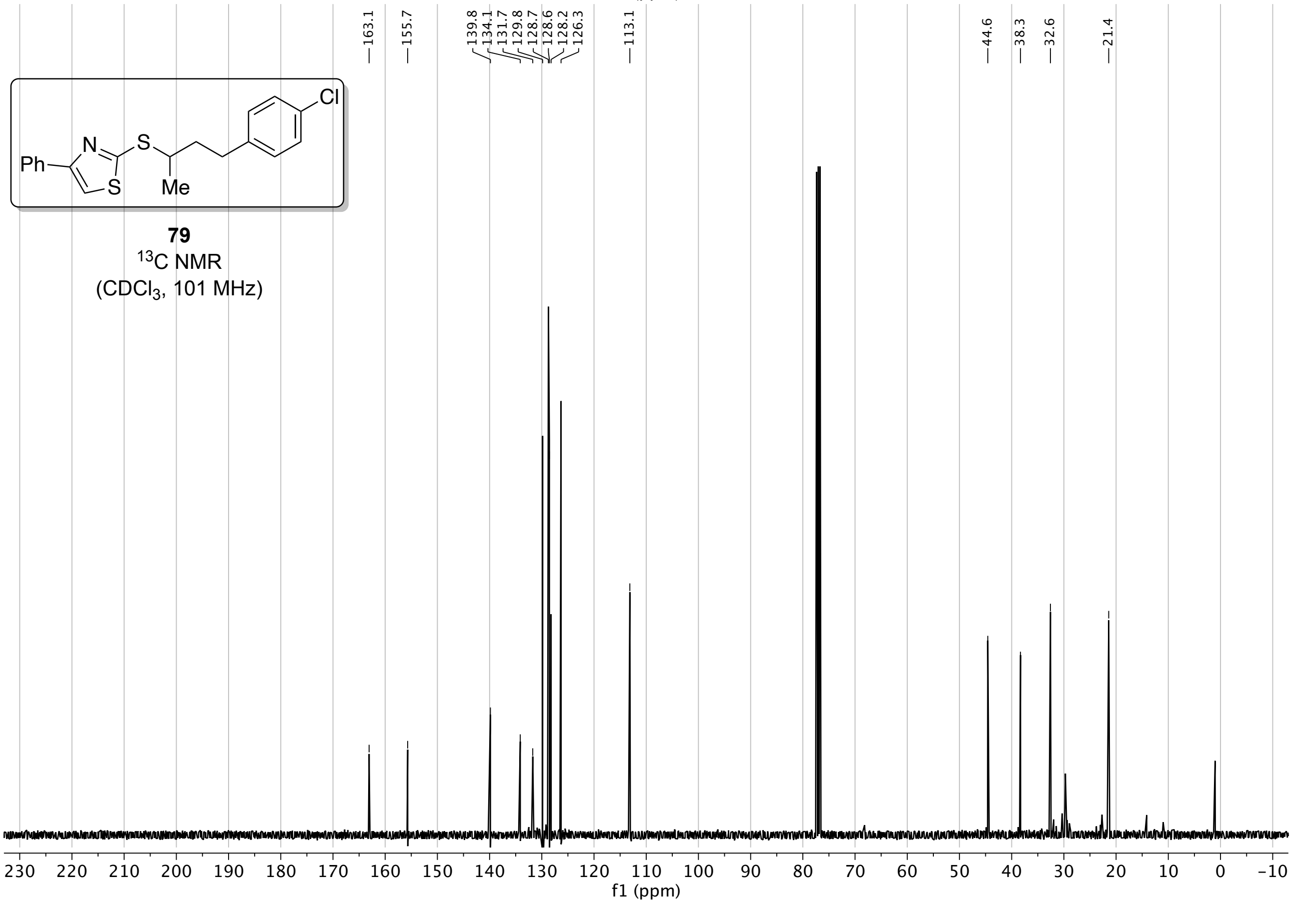
78
^{1}H NMR
($CDCl_3$, 400 MHz)



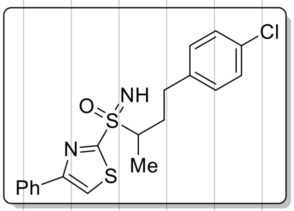
78
^{13}C NMR
($CDCl_3$, 101 MHz)



79
^{1}H NMR
($CDCl_3$, 400 MHz)



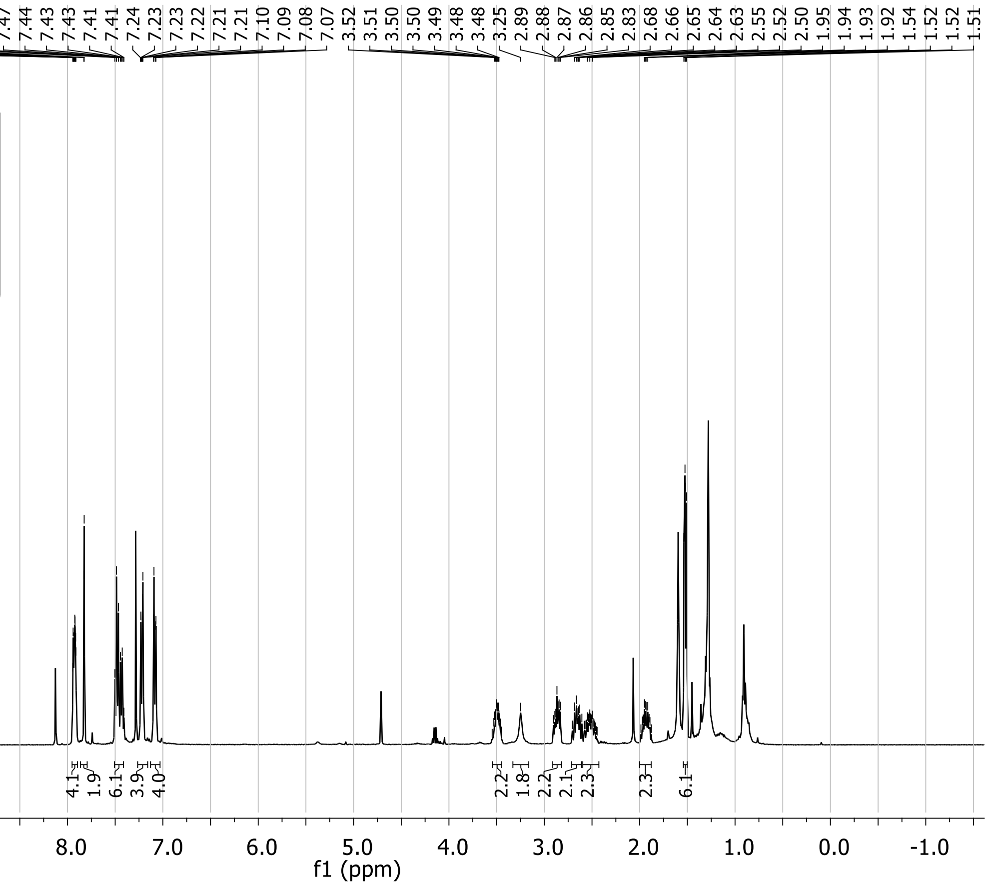
79
^{13}C NMR
($CDCl_3$, 101 MHz)

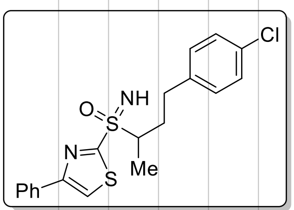


80

^{1}H NMR

($CDCl_3$, 400 MHz)

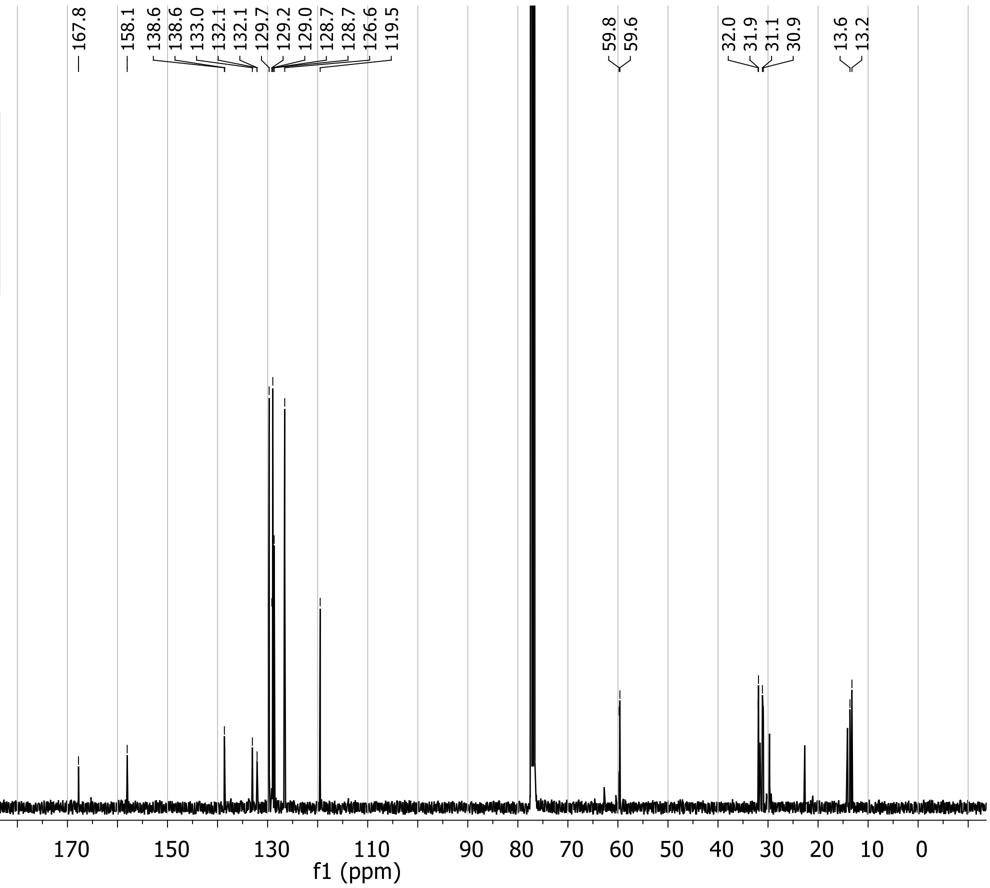




80

^{13}C NMR

($CDCl_3$, 400 MHz)



11 Author contribution

M.C. and R.L. conceived and designed the project. F.P. and Y.G. performed most of the experiments with input from L.D., M.C. and R.L. The computational investigations were carried out by M.A. The CV and Stern-Volmer experiments were carried out by G.R. All authors contributed to the writing and editing of the manuscript.

12 References

1. Harnedy, J., Deepak Hareram, M., J. Tizzard, G., J. Coles, S. & C. Morrill, L. Electrochemical oxidative Z -selective C(sp 2)–H chlorination of acrylamides. *Chem. Commun.* **57**, 12643–12646 (2021).
2. Sugeno, Y., Ishikawa, Y. & Oikawa, M. Asymmetric Organocatalytic Cyclopropanation on Chiral Menthyl Acrylate for the Synthesis of (–)-trans-2-Aminomethylcyclopropanecarboxylic Acid [(–)-TAMP]. *Synlett* **25**, 987–990 (2014).
3. Eriksson, J., Åberg, O. & Långström, B. Synthesis of [11C]/[13C]Acrylamides by Palladium-Mediated Carbonylation. *Eur. J. Org. Chem.* **2007**, 455–461 (2007).
4. Bateman, L. A. *et al.* Chemoproteomics-enabled covalent ligand screen reveals a cysteine hotspot in reticulon 4 that impairs ER morphology and cancer pathogenicity. *Chem. Commun.* **53**, 7234–7237 (2017).
5. Kretschmann, O. *et al.* Switchable Hydrogels Obtained by Supramolecular Cross-Linking of Adamantyl-Containing LCST Copolymers with Cyclodextrin Dimers. *Angew. Chem. Int. Ed.* **45**, 4361–4365 (2006).
6. Németh, A. G., Szabó, R., Németh, K., Keserű, G. M. & Ábrányi-Balogh, P. A stepwise one-pot synthesis of aliphatic thiols and their derivatives from acrylamides and sulfur. *Org. Biomol. Chem.* **20**, 4361–4368 (2022).
7. Yu, B., Mohamed, S., Ardisson, J., Lannou, M.-I. & Sorin, G. Silver oxide(I) promoted Conia-ene/radical cyclization for a straightforward access to furan derivatives. *Chem. Commun.* **58**, 1374–1377 (2022).
8. Huang, H. *et al.* Visible-Light-Promoted Nickel- and Organic-Dye-Cocatalyzed Formylation Reaction of Aryl Halides and Triflates and Vinyl Bromides with Diethoxyacetic Acid as a Formyl Equivalent. *Angew. Chem. Int. Ed.* **56**, 1500–1505 (2017).
9. Frigerio, M. & Santagostino, M. A mild oxidizing reagent for alcohols and 1,2-diols: o-iodoxybenzoic acid (IBX) in DMSO. *Tetrahedron Lett.* **35**, 8019–8022 (1994).
10. Li, C.-C. *et al.* Synergistic Relay Reactions To Achieve Redox-Neutral α-Alkylations of Olefinic Alcohols with Ruthenium(II) Catalysis. *Angew. Chem. Int. Ed.* **59**, 4544–4549 (2020).
11. Blakemore, P. R., Marsden, S. P. & Vater, H. D. Reagent-Controlled Asymmetric Homologation of Boronic Esters by Enantioenriched Main-Group Chiral Carbenoids. *Org. Lett.* **8**, 773–776 (2006).
12. Yimthachote, S. & Phomphrai, K. Rapid alcoholysis of cyclic esters using metal alkoxides: access to linear lactyllactate-grafted polyglycidol. *New J. Chem.* **47**, 2701–2705 (2023).
13. Drioli, S., Nitti, P., Pitacco, G., Tossut, L. & Valentin, E. Enantiomerically pure tetrahydro-5-oxo-2-furancarboxylic esters from dialkyl 2-oxoglutarates. *Tetrahedron Asymmetry* **10**, 2713–2728 (1999).
14. den Hartog, T., Maciá, B., Minnaard, A. J. & Feringa, B. L. Copper-Catalyzed Asymmetric Allylic Alkylation of Halocrotonates: Efficient Synthesis of Versatile Chiral Multifunctional Building Blocks. *Adv. Synth. Catal.* **352**, 999–1013 (2010).
15. Lu, Z. *et al.* A Visible-Light-Driven Approach to Free Alcohol from Esters of Quinone Propionic Acid. *Synthesis* **55**, 473–480 (2023).
16. Dalling, A. G., Späth, G. & Fürstner, A. Total Synthesis of the Tetracyclic Pyridinium Alkaloid epi-Tetradehydrohalicyclamine B. *Angew. Chem. Int. Ed.* **61**, e202209651 (2022).
17. Hendy, C. M., Smith, G. C., Xu, Z., Lian, T. & Jui, N. T. Radical Chain Reduction via Carbon Dioxide Radical Anion (CO2•–). *J. Am. Chem. Soc.* **143**, 8987–8992 (2021).
18. Pawłowska, A. *et al.* Perfluorophenyl phosphonate analogues of aromatic amino acids: Synthesis, X-ray and DFT studies. *Tetrahedron* **74**, 975–986 (2018).
19. Gritzner, G. & Kuta, J. Recommendations on reporting electrode potentials in nonaqueous solvents (Recommendations 1983). *Pure Appl. Chem.* **56**, 461–466 (1984).
20. Gritzner, G. Polarographic half-wave potentials of cations in nonaqueous solvents. *Pure Appl. Chem.* **62**, 1839–1858 (1990).
21. Pavlishchuk, V. V. & Addison, A. W. Conversion constants for redox potentials measured versus different reference electrodes in acetonitrile solutions at 25°C. *Inorganica Chim. Acta* **298**, 97–102 (2000).
22. Roth, H. G., Romero, N. A. & Nicewicz, D. A. Experimental and Calculated Electrochemical Potentials

of Common Organic Molecules for Applications to Single-Electron Redox Chemistry. *Synlett* **27**, 714–723 (2016).
23. Briggs, E. L. *et al.* Synthesis of Enantioenriched NH-Sulfoximines by NH Transfer to Sulfoxides Using Ammonium Carbamate and (Diacetoxyiodo)benzene. *Org Synth* (2023).
24. Neese, F., Wennmohs, F., Becker, U. & Riplinger, C. The ORCA quantum chemistry program package. *J. Chem. Phys.* **152**, 224108 (2020).
25. Long-Range Corrected Hybrid Density Functionals with Improved Dispersion Corrections | Journal of Chemical Theory and Computation. https://pubs.acs.org/doi/abs/10.1021/ct300715s.
26. Chai, J.-D. & Head-Gordon, M. Long-range corrected hybrid density functionals with damped atom–atom dispersion corrections. *Phys. Chem. Chem. Phys.* **10**, 6615–6620 (2008).
27. Marenich, A. V., Cramer, C. J. & Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **113**, 6378–6396 (2009).
28. Grimme, S. Supramolecular Binding Thermodynamics by Dispersion-Corrected Density Functional Theory. *Chem. – Eur. J.* **18**, 9955–9964 (2012).
29. *Organic Electrochemistry: Revised and Expanded*. (CRC Press, Boca Raton, 2015). doi:10.1201/b19122.
30. Dubois, M. A. J. *et al.* Visible Light Photoredox-Catalyzed Decarboxylative Alkylation of 3-Aryl-Oxetanes and Azetidines via Benzylic Tertiary Radicals and Implications of Benzylic Radical Stability. *J. Org. Chem.* **88**, 6476–6488 (2023).