Supplementary Information

Visible-Light-Driven Photocatalyst-Free Deoxygenative Homologation of Alcohols to Access Tertiary Alcohols

Xiaochuang Wang,[‡ab] Jun Zhang,[‡a] Lu Zhao[a] and Xuesong Wu*[a]

[a] Hubei Key Laboratory of Bioinorganic Chemistry & Materia Medica, School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, Wuhan, Hubei 430074, China

[b] Guangdong Provincial Key Laboratory of Advanced Green Lubricating Materials, SINOPEC Maoming Petrochemical Company Ltd., Guangdong 525000, P. R. China

‡These authors contributed equally to this work.

*Email: xswu@hust.edu.cn

Table of Contents

1. General Information

Commercially Reagents: Commercially reagents were purchased from Sigma Aldrich, Energy Chemical, TCI or Alfa Aesar and used without further purification. All experiments were performed in oven-dried or flame-dried glassware under an atmosphere of N_2. 1,2-Dimethoxyethane, dimethylsulfoxide was ultra-dry solvents with molecular sieve (MS) purchased from Energy Chemical and stored within a N_2 filled glove box.

NMR Spectra: ^{1}H NMR spectra were recorded on Bruker Ascend 400 or 600 MHz spectrometer. Chemical shifts are reported in parts per million (ppm) and the spectra are calibrated to the resonance resulting from incomplete deuteration of the solvent ($CDCl_3$: 7.26 ppm). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling. Chemical shifts are reported in ppm with the solvent resonance as the internal standard ($CDCl_3$: 77.16 ppm, t). Data are reported as follows: chemical shift δ/ppm, integration (^{1}H only), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or combinations thereof; ^{13}C signals are singlets unless otherwise stated), coupling constants *J* in Hz, assignment. ^{19}F NMR spectra was recorded on the same spectrometer.

Infra-Red Spectrometer (IR): IR spectra were recorded on the Thermo Scientific Nicolet iS50R spectrometer.

High Resolution Mass Spectrometry (HRMS): HRMS was measured on the BrukerDaltonics SolariX 7.0T mass spectrometer equipped with an ESI source.

Gas Chromatograph-Mass Spectrometer (GC-MS): All GC-MS were recorded on Agilent 5977B-7890B. Measured values are reported to 3 decimal places of the calculated value. The calculated values are based on the most abundant isotope.

Gas Chromatograph (GC): All GC were recorded on Fuli GC9790II.

UV/Vis: Measurements were made on Shanghai JiaPeng technology co. ZF-7 Spectro Fluorophotometer.

Photoreactor: The photoreactors used in this research were purchased from Taobao (Figure S1: 30W blue LEDs)

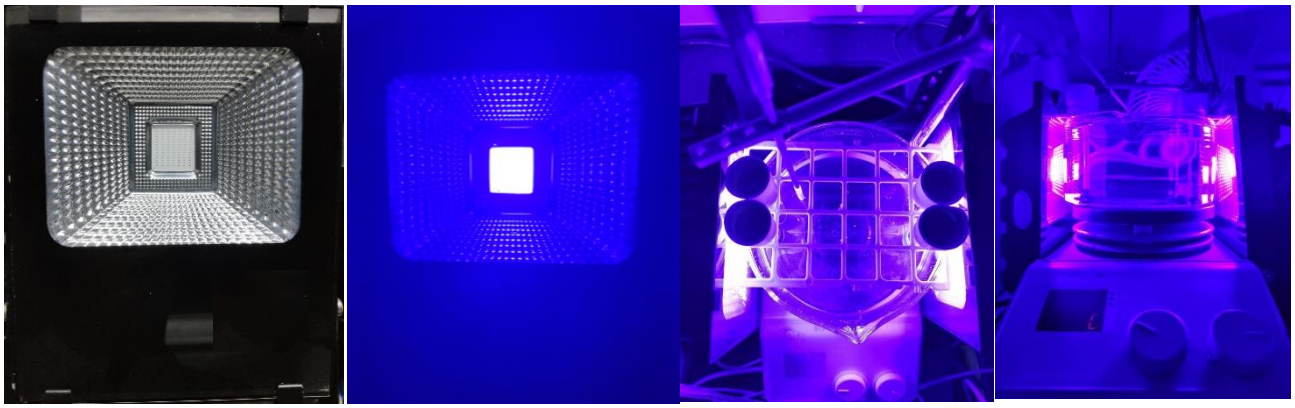
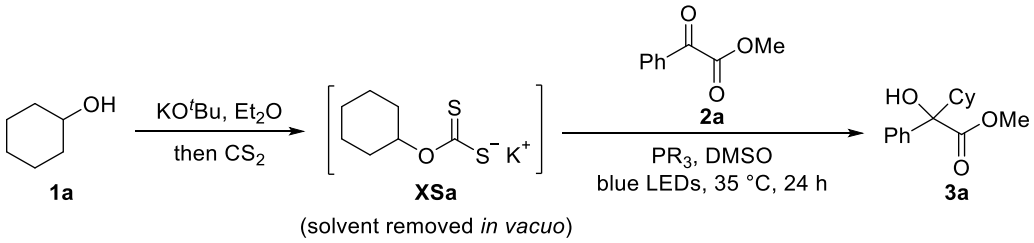


Figure S1. Photoreactor used in this research (30 W blue LEDs)

2. Detailed Optimization of Reaction Conditions

2.1 Optimization of Reaction Conditions

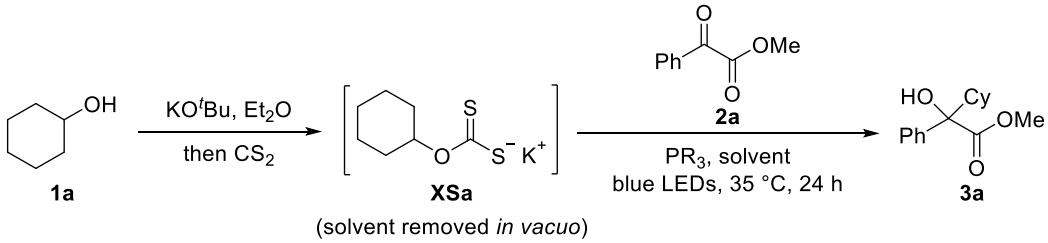
Table S1. Screening of Phosphine[a]



Entry	PR_3	Yield (%)[b]
1	PPh_3	trace
2	$P(4\text{-}MeC_6H_4)_3$	trace
3	$P(PMP)_3$	13
4	$P(Ph)_2Cy$	7
5	$P(OEt)_3$	0
6	P^tBu_3	45
7	P^iPr_3	54
8	PCy_3	74

[a]Standard procedure: **1a** (0.30 mmol), KO^{t}Bu (1.05 equiv.), Et_2O (3.0 mL), CS_2 (3.0 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (1.0 equiv.), PR_3 (1.1 equiv.), DMSO (10.0 mL), 24 h blue LED irradiation. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

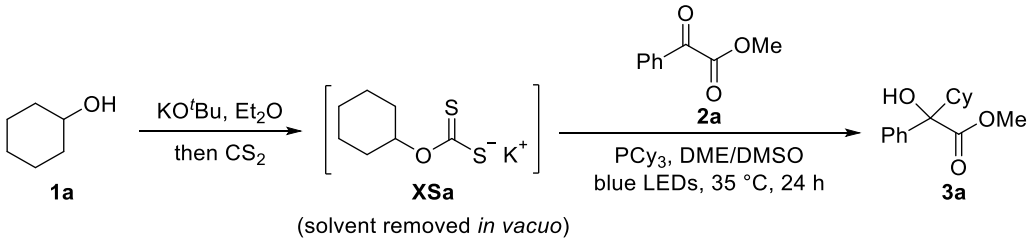
Table S2. Screening of Solvent[a]



Entry	Solvent	Yield (%)[b]
1	DCE	0
2	THF	8
3	$PhCF_3$	15
4	MeCN	30
5	DMF	40
6	1,4-Dioxane	19
7	DME	60
8	DMSO	74

[a]Standard procedure: **1a** (0.30 mmol), KO^{t}Bu (1.05 equiv.), Et_2O (3.0 mL), CS_2 (3.0 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (1.0 equiv.), PCy_3 (1.1 equiv.), solvent, 24 h blue LED irradiation. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

Table S3. Screening of Mixed Solvents[a]

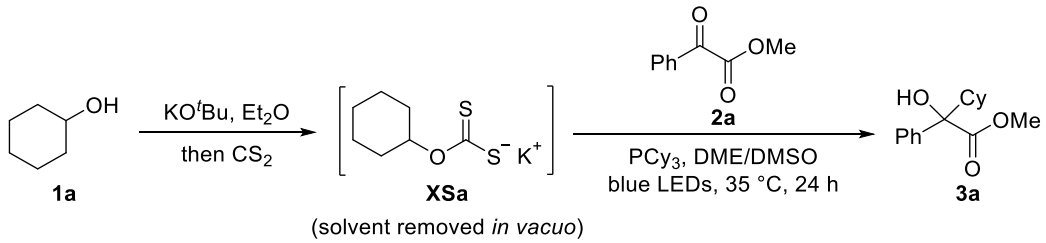


Entry	DME : DMSO	Yield (%)[b]
1	0 : 10	74
2	1 : 9	76
3	3 : 7	83
4	5 : 5	83
5	7 : 3	86
6	9 : 1	90
7	10 : 0	60

[a]Standard procedure: **1a** (0.30 mmol), KO^{t}Bu (1.05 equiv.), Et_2O (3.0 mL), CS_2 (3.0 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (1.0 equiv.), PCy_3 (1.1 equiv.), solvent (10.0 mL), 24 h blue LED irradiation. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

2.2 Control Experiments

Table S4. Control Experiments[a]

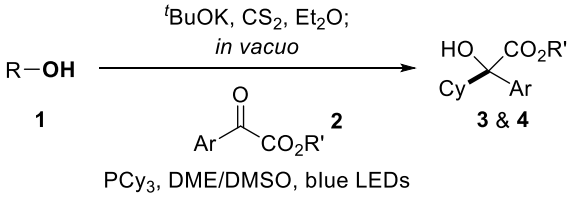


Entry	KO^{t}Bu	CS_2	light	PCy_3	Yield (%)[b]
1	×	√	√	√	N.D.
2	√	×	√	√	N.D.
3	√	√	×	√	N.D.
4	√	√	√	×	N.D.

[a]Standard procedure: **1a** (0.30 mmol), KO^{t}Bu (1.05 equiv.), Et_2O (3.0 mL), CS_2 (3.0 equiv.), 3 h. After removing solvent *in vacuo*, then **2a** (1.0 equiv.), PCy_3 (1.1 equiv.), DME/DMSO (9 : 1), 24 h blue LED irradiation. [b]Determined by GC analysis using 1,2,4,5-tetramethylbenzene as an internal standard.

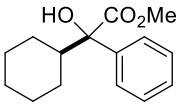
3. General Procedure and Characterization Data of Products

3.1 General Procedure for Deoxygenative Homologation of Alcohols



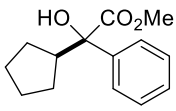
In a nitrogen-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with alcohol **1** (0.30 mmol, 1.0 equiv.), KO^{t}Bu (35.3 mg, 0.32 mmol, 1.05 equiv.), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (68.5 mg, 54.4 μL, 0.90 mmol) via microsyringe at 0 ºC and continued stirring at 0 ºC for 3 hours. After removing the solvent *in vacuo*, the system was transferred into the glovebox, then *α*-carbonyl ester **2** (0.30 mmol, 1.0 equiv.), PCy_3 (92.5 mg, 0.33 mmol, 1.1 equiv.) and the mixed solvents of DME/DMSO (9.0 mL/1.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at 35 ºC. After 24 hours, the reaction mixture was treated with saturated NH_4Cl aqueous solution (10 mL), then extracted with ethyl acetate (3 × 10 mL) and dried over sodium sulfate. After filtration and concentration *in vacuo*, the residue was purified by column chromatography to afford the desired product.

3.2 Characterization Data of Products



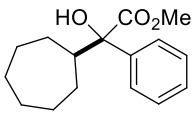
3a

Methyl 2-cyclohexyl-2-hydroxy-2-phenylacetate (**3a**): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a pale yellow oil (64.7 mg, 87% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.65 (m, 2H), 7.39 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 3.80 (s, 3H), 3.70 (brs, 1H), 2.29 – 2.21 (m, 1H), 1.84 – 1.81 (m, 1H), 1.68 – 1.66(m, 2H), 1.49 – 1.43 (m, 2H), 1.38 – 1.31 (m, 1H), 1.24 – 1.08 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 140.9, 128.2, 127.5, 126.1, 81.2, 53.4, 45.9, 27.5, 26.5 (2C), 26.3, 25.6. IR (ATR): ν = 3512, 1714 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{20}NaO_3$: 271.1305, found: 271.1304.



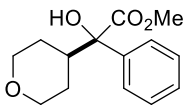
3b

Methyl 2-cyclopentyl-2-hydroxy-2-phenylacetate (3b): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a pale yellow oil (57.6 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.6 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.29 – 7.25 (m, 1H), 3.77 (s, 3H), 3.72 (brs, 1H), 2.94 – 2.85 (m, 1H), 1.69 – 1.65 (m, 1H), 1.62 – 1.53 (m, 4H), 1.49 – 1.44 (m, 1H), 1.36 – 1.31 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.3, 141.9, 128.2, 127.6, 126.1, 79.4, 53.4, 47.4, 27.1, 26.5, 26.4, 26.1. IR (ATR): ν = 3514, 1726 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{18}NaO_3$: 257.1148, found: 257.1148.



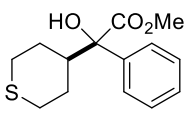
3c

Methyl 2-cycloheptyl-2-hydroxy-2-phenylacetate (3c): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a pale yellow oil (59.7 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.24 (m, 2H), 7.22 – 7.18 (m, 1H), 3.70 (s, 3H), 3.62 (brs, 1H), 2.41 – 2.36 (m, 1H), 1.68 – 1.64 (m, 1H), 1.52 – 1.40 (m, 8H), 1.24 – 1.15 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.5, 141.4, 128.3, 127.6, 126.2, 82.6, 53.4, 46.6, 29.7, 28.4, 28.2, 27.5, 27.4, 27.3. IR (ATR): ν = 3513, 1726 cm^{-1}. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{16}H_{23}O_3$: 263.1642, found: 263.1642.



3d

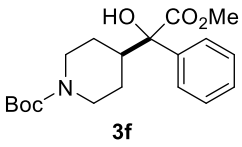
Methyl 2-hydroxy-2-phenyl-2-(tetrahydro-2H-pyran-4-yl)acetate (3d): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (59.8 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.37 – 7.32 (m, 2H), 7.31 – 7.26 (m, 1H), 4.04 – 4.01 (m, 1H), 3.91 – 3.88 (m, 1H), 3.80 (s, 3H), 3.70 (brs, 1H), 3.45 – 3.40 (m, 1H), 3.30 – 3.26 (m, 1H), 2.47 – 2.42 (m, 1H), 1.87 – 1.80 (m, 1H), 1.54 – 1.47 (m, 1H), 1.32 – 1.28 (m, 1H), 1.04 – 1.00 (m, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.4, 140.0, 128.3, 127.8, 126.0, 80.3, 68.2, 67.7, 53.5, 43.4, 27.4, 25.7. IR (ATR): ν = 3507, 1735, 1093 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{14}H_{18}NaO_4$: 273.1097, found: 273.1099.



3e

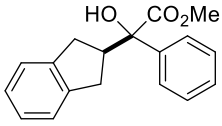
Methyl 2-hydroxy-2-phenyl-2-(tetrahydro-2*H*-thiopyran-4-yl)acetate (3e): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 40:1) as a colorless oil (63.0 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.24 (m, 1H), 7.21 – 7.19 (m, 1H), 3.72 (s, 3H), 3.63 (brs, 1H), 2.74 – 2.66 (m, 1H), 2.60 – 2.54 (m, 1H), 2.55 – 2.47 (m, 2H), 2.20 – 2.12 (m, 1H), 1.84 – 1.74

(m, 1H), 1.69 – 1.64 (m, 1H), 1.46 – 1.40 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 140.1, 128.4, 127.8, 126.0, 81.4, 53.6, 45.6, 29.2, 29.1, 28.9, 27.2. IR (ATR): ν = 3514, 1715, 1108 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{19}O_3S$: 267.1049, found: 267.1049.



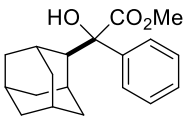
3f

***tert*-Butyl 4-(1-hydroxy-2-methoxy-2-oxo-1-phenylethyl)piperidine-1-carboxylate (3f)**: The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (69.1 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.6 Hz, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.36 (m, 1H), 4.28 – 4.05 (m, 2H), 3.80 (s, 3H), 3.68 (brs, 1H), 2.71 – 2.54 (m, 2H), 2.38 – 2.32 (m, 1H), 1.69 – 1.58 (m, 1H), 1.42 (s, 9H), 1.32 – 1.25 (m, 2H), 1.11 – 1.07 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 154.8, 140.2, 128.4, 127.8, 125.9, 80.4, 79.4, 53.6, 44.4, 28.5, 26.6, 24.9. IR (ATR): ν = 3409, 1682, 1669 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{28}NO_5$: 350.1962, found: 350.1962.



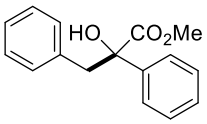
3g

Methyl 2-(2,3-dihydro-1H-inden-2-yl)-2-hydroxy-2-phenylacetate (3g): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (54.2 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.6 Hz, 2H), 7.43 – 7.38 (m, 2H), 7.36 – 7.31 (m, 1H), 7.21 – 7.18 (m, 1H), 7.16 – 7.07 (m, 3H), 3.85 (s, 3H), 3.83 (brs, 1H), 3.61 – 3.51 (m, 1H), 3.12 – 3.05 (m, 1H), 2.96 – 2.85 (m, 2H), 2.64 – 2.58 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 142.8, 142.5, 141.2, 128.4, 127.9, 126.4, 126.3, 126.0, 124.4 (2C), 79.0, 53.6, 47.5, 33.8, 33.4. IR (ATR): ν = 3507, 1719 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{19}O_3$: 283.1329, found: 283.1330.



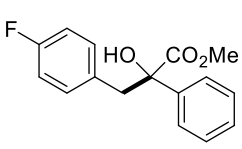
3h

Methyl 2-(adamantan-2-yl)-2-hydroxy-2-phenylacetate (3h): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (65.7 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.17 (m, 1H), 3.71 (s, 3H), 2.53 (brs, 1H), 2.48 – 2.44 (m, 1H), 2.30 – 2.25 (m, 1H), 1.82 – 1.72 (m, 5H), 1.68 – 1.40 (m, 7H), 1.27 – 1.23 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.8, 142.0, 128.2, 127.4, 126.0, 83.6, 53.6, 50.4, 41.1, 40.9, 38.5, 33.2, 32.3, 31.6, 28.8, 28.4, 27.6. IR (ATR): ν = 3509, 1715 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{19}H_{25}O_3$: 301.1798, found: 301.1803.



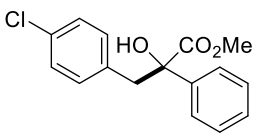
3i

Methyl 2-hydroxy-2,3-diphenylpropanoate (3i): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 40:1) as a white solid (53.8 mg, 70% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.61 – 7.58 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.21 (m, 1H), 7.20 – 7.12 (m, 5H), 3.64 (s, 3H), 3.53 – 3.49 (m, 2H), 3.13 (d, *J* = 13.8 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 141.6, 135.8, 130.6, 128.4, 128.2, 128.0, 127.1, 125.8, 78.9, 53.2, 46.0. IR (ATR): ν = 3508, 1716 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{16}NaO_3$: 279.0992, found: 279.0994.



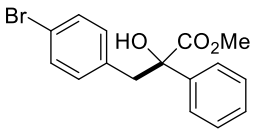
3j

Methyl 3-(4-fluorophenyl)-2-hydroxy-2-phenylpropanoate (3j): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (41.9 mg, 51% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.65 (m, 2H), 7.41 – 7.37 (m, 2H), 7.34 – 7.31 (m, 1H), 7.21 – 7.17 (m, 2H), 6.98 – 6.93 (m, 2H), 3.75 (s, 3H), 3.65 (brs, 1H), 3.55 (d, *J* = 14.0 Hz, 1H), 3.20 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 162.1 (d, *J* = 245 Hz), 141.4, 132.1 (d, *J* = 7.9 Hz), 131.5 (d, *J* = 3.2 Hz), 128.5, 128.1, 125.8, 115.0 (d, *J* = 21.2 Hz), 78.9, 53.3, 45.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ -116.0. IR (ATR): ν = 3513, 1723 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{16}H_{16}FO_3$: 275.1078, found: 275.1078.



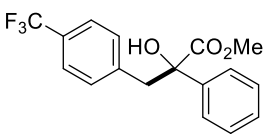
3k

Methyl 3-(4-chlorophenyl)-2-hydroxy-2-phenylpropanoate (3k): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (56.6 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.2 Hz, 2H), 7.41 – 7.36 (m, 2H), 7.35 – 7.31 (m, 1H), 7.23 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 3.75 (s, 3H), 3.66 (brs, 1H), 3.53 (d, *J* = 13.6 Hz, 1H), 3.20 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.7, 141.3, 134.3, 133.0, 132.0, 128.5, 128.3, 128.1, 125.7, 78.8, 53.3, 45.2. IR (ATR): ν = 3525, 1720 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{15}ClNaO_3$: 313.0602, found: 313.0602.



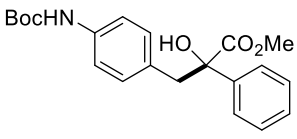
3l

Methyl 3-(4-bromophenyl)-2-hydroxy-2-phenylpropanoate (3l): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (62.2 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.41 – 7.36 (m, 4H), 7.35 – 7.31 (m, 1H), 7.10 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H), 3.66 (s, 1H), 3.52 (d, *J* = 13.6 Hz, 1H), 3.18 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 141.3, 134.8, 132.3, 131.2, 128.5, 128.2, 125.7, 121.2, 78.8, 53.3, 45.3. IR (ATR): ν = 3510, 1721 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{16}H_{15}BrNaO_3$: 357.0097, found: 357.0097.



3m

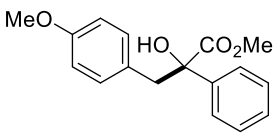
Methyl 2-hydroxy-2-phenyl-3-(4-(trifluoromethyl)phenyl) propanoate (3m): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 50:1) as a colorless oil (47.8 mg, 49% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.64 (m, 2H), 7.51 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 3H), 3.77 (s, 3H), 3.69 (brs, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 3.29 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 141.2, 140.0, 131.0, 129.3 (q, *J* = 32.4 Hz), 128.6, 128.3, 125.7, 125.0 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 273 Hz), 78.8, 53.4, 45.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.4. IR (ATR): ν = 3498, 1728 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{17}H_{15}F_3NaO_3$: 347.0865, found: 347.0865.



3n

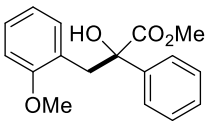
Methyl 3-(4-((*tert*-butoxycarbonyl)amino)phenyl)-2-hydroxy-2-phenyl-propanoate (3n): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a white solid (70.2 mg, 63% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.66 (m, 2H), 7.40 – 7.35 (m, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.25 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 2H), 6.51 (s, 1H), 3.72 (s, 3H), 3.62 (brs, 1H), 3.55 (d, *J* = 13.6 Hz, 1H), 3.15 (d, *J* = 13.6 Hz, 1H), 1.51 (s, 9H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ 174.8, 152.8, 141.5, 137.4, 131.1, 130.3, 128.4, 128.0, 125.8, 118.3, 80.6, 79.0, 53.2, 45.4, 28.4. IR (ATR): ν = 3521, 1725, 1706 cm^{-1}. HRMS (ESI): m/z $[M + NH_4]^+$ calcd for $C_{21}H_{29}N_2O_5$: 389.2071, found: 389.2071.



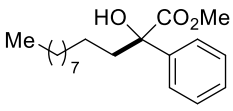
3o

Methyl 2-hydroxy-3-(4-methoxyphenyl)-2-phenylpropanoate (3o): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 30:1) as a colorless oil (61.8 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.0 Hz, 2H), 7.41 – 7.37 (m, 2H), 7.35 – 7.31 (m, 1H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 3H), 3.61 (brs, 1H), 3.56 (d, *J* = 14.0 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 158.7, 141.6, 131.5, 128.4, 128.0, 127.7, 125.8, 113.7, 79.0, 55.3, 53.2, 45.2. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}O_4$: 287.1278, found: 287.1279. This compound is known.[1]



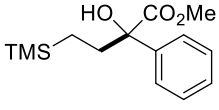
3p

Methyl 2-hydroxy-3-(2-methoxyphenyl)-2-phenylpropanoate (3p): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 30:1) as a white solid (69.5 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 – 7.65 (m, 2H), 7.38 – 7.34 (m, 2H), 7.32 – 7.28 (m, 1H), 7.25 – 7.20 (m, 1H), 7.12 – 7.09 (m, 1H), 6.88 –6.84 (m, 2H), 4.16 (brs, 1H), 3.82 (s, 3H), 3.76 (d, *J* = 14.0 Hz, 1H), 3.71 (s, 3H), 3.36 (d, *J* = 14.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.8, 157.7, 142.0, 132.6, 128.5, 128.2, 127.8, 125.9, 124.1, 120.8, 110.6, 79.1, 55.6, 52.9, 40.4. IR (ATR): ν = 3548, 1723, 1124 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{19}O_4$: 287.1278, found: 287.1278.



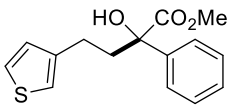
3q

Methyl 2-hydroxy-2-phenylhexanoate (3q): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (47.8 mg, 52% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.57 (m, 2H), 7.37 – 7.33 (m, 2H), 7.30 – 7.28 (m, 1H), 3.78 (s, 3H), 3.76 (brs, 1H), 2.20 – 2.14 (m, 1H), 2.03 – 1.95 (m, 1H), 1.31 – 1.18 (m, 16H), 0.87 (t, *J* = 6.4 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 176.1, 142.1, 128.4, 127.8, 125.6, 78.6, 53.4, 39.9, 32.0, 29.8, 29.73, 29.70, 29.6, 29.5, 23.8, 22.8, 14.3. IR (ATR): ν = 3518, 1730 cm^{-1}. HRMS (ESI): m/z $[M + NH_4]^+$ calcd for $C_{19}H_{34}NO_3$: 324.2533, found: 324.2533.



3r

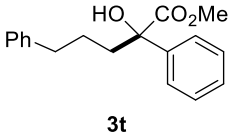
Methyl 2-hydroxy-2-phenyl-4-(trimethylsilyl)butanoate (3r): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (49.5 mg, 62% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.59 (m, 2H), 7.38 – 7.33 (m, 2H), 7.31 – 7.27 (m, 1H), 3.79 (s, 3H), 3.75 (brs, 1H), 2.21 – 2.13 (m, 1H), 1.98 – 1.90 (m, 1H), 0.68 – 0.61 (m, 1H), 0.39 – 0.31 (m, 1H), -0.01 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 176.0, 141.8, 128.4, 127.8, 125.8, 79.6, 53.3, 34.6, 10.1, -1.8. IR (ATR): ν = 3518, 1730, 837 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{14}H_{22}NaO_3Si$: 289.1230, found: 289.1230.



3s

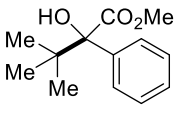
Methyl 2-hydroxy-2-phenyl-4-(thiophen-3-yl)butanoate (3s): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (60.5 mg, 73% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.65 – 7.61 (m, 2H), 7.40 – 7.36 (m, 2H), 7.33 – 7.29 (m, 1H), 7.26 – 7.23 (m,

1H), 6.97 – 6.92 (m, 2H), 3.88 (brs, 1H), 3.76 (s, 3H), 2.79 – 2.62 (m, 2H), 2.57 – 2.49 (m, 1H), 2.41 – 2.33 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 141.9, 141.6, 128.5, 128.3, 128.0, 125.6, 125.5, 120.4, 78.1, 53.5, 40.5, 24.7. IR (ATR): ν = 3507, 1730 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{15}H_{16}NaO_3S$: 299.0712, found: 299.0712.



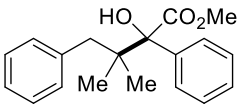
3t

Methyl 2-hydroxy-2,5-diphenylpentanoate (3t): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 40:1) as a white solid (34.1 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.47 (m, 2H), 7.28 – 7.25 (m, 2H), 7.22 – 7.17 (m, 3H), 7.12 – 7.07 (m, 3H), 3.75 – 3.55 (m, 4H), 2.55 (t, *J* = 7.6 Hz, 2H), 2.17 – 2.09 (m, 1H), 2.02 – 1.95 (m, 1H), 1.74 – 1.63 (m, 1H), 1.56 – 1.45 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 142.1, 141.8, 128.5, 128.42, 128.39, 127.8, 125.9, 125.6, 78.5, 53.4, 39.3, 35.9, 25.5. IR (ATR): ν = 3511, 1729 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{18}H_{20}NaO_3$: 307.1305, found: 307.1305.



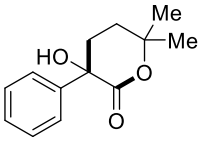
3u

Methyl 2-hydroxy-3,3-dimethyl-2-phenylbutanoate (3u): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (34.0 mg, 51% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.8 Hz, 2H), 7.34 – 7.31 (m, 2H), 7.30 – 7.27 (m, 1H), 3.87 (s, 3H), 3.69 (brs, 1H), 1.02 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 139.3, 127.6, 127.5, 127.4, 83.4, 52.9, 39.2, 25.9. IR (ATR): ν = 3510, 1722 cm^{-1}. HRMS (APCI): m/z [M – H]$^-$ calcd for $C_{13}H_{17}O_3$: 221.1183, found: 221.1181.



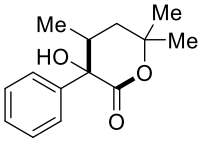
3v

Methyl 2-hydroxy-3,3-dimethyl-2,4-diphenylbutanoate (3v): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a white solid (52.7 mg, 59% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.7 Hz, 2H), 7.37 – 7.30 (m, 3H), 7.25 – 7.21 (m, 2H), 7.20 – 7.16 (m, 1H), 7.09 (d, *J* = 7.3 Hz, 2H), 3.88 (s, 3H), 3.81 (brs, 1H), 2.83 (d, *J* = 12.7 Hz, 1H), 2.67 (d, *J* = 12.7 Hz, 1H), 0.97 (s, 3H), 0.86 (s, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 139.0, 138.8, 131.4, 127.82, 127.78, 127.7, 127.6, 126.0, 83.8, 53.1, 42.9, 42.5, 22.20, 21.99. IR (ATR): ν = 3497, 1712 cm^{-1}. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{19}H_{23}O_3$: 299.1642, found: 299.1647.



3w

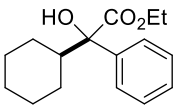
3-Hydroxy-6,6-dimethyl-3-phenyltetrahydro-2H-pyran-2-one (3w): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a white solid (35.6 mg, 54% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.20 (m, 5H), 3.34 (brs, 1H), 2.36 – 2.28 (m, 1H), 2.18 – 2.10 (m, 1H), 1.72 – 1.57 (m, 2H), 1.42 (m, 3H), 1.39 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.1, 143.3, 128.6, 128.4, 125.7, 85.2, 75.5, 32.5, 32.0, 30.0, 28.1. IR (ATR): ν = 3324, 1727, 1110 cm^{-1}. HRMS (APCI): m/z [M - H]$^+$ calcd for $C_{13}H_{15}O_3$: 219.1016, found: 219.1021.



3x

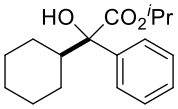
3-Hydroxy-4,6,6-trimethyl-3-phenyltetrahydro-2H-pyran-2-one (3x): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a white solid (56.9 mg, 81% yield, 1.3:1 dr). Data of one isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 1H), 7.36 – 7.30 (m, 4H), 3.67 (brs, 1H), 2.61 – 2.55 (m, 1H), 1.77 – 1.71 (m, 1H), 1.61 – 1.58 (m, 1H), 1.57 (s, 3H), 1.52 (s, 3H),

0.83 (d, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.8, 139.1, 128.3, 128.0, 127.0, 84.1, 78.1, 39.9, 34.4, 30.4, 28.5, 15.2. Data of the other isomer: ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.42 – 7.40 (m, 1H), 7.36 – 7.30 (m, 4H), 3.02 (brs, 1H), 2.43 – 2.36 (m, 1H), 2.09 – 2.03 (m, 1H), 1.70 – 1.65 (m, 1H), 1.60 (s, 3H), 1.52 (s, 3H), 0.96 (d, J = 6.7 Hz, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.1, 142.9, 128.4, 127.9, 125.2, 83.5, 77.6, 38.8, 36.3, 31.2, 28.0, 13.6. IR (ATR): ν = 3441, 1690, 1121 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{14}H_{19}O_3$: 235.1329, found: 235.1330.



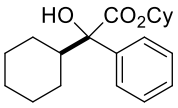
4b

Ethyl 2-cyclohexyl-2-hydroxy-2-phenylacetate (4b): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (66.8 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 7.6 Hz, 2H), 7.36 – 7.32 (m, 2H), 7.28 – 7.24 (m, 1H), 4.30 – 4.16 (m, 2H), 3.71 (s, 1H), 2.25 – 2.20 (m, 1H), 1.80 (d, J = 12.8 Hz, 1H), 1.65 – 1.63 (m, 2H), 1.47 – 1.41 (m, 2H), 1.30 – 1.26 (m, 4H), 1.20 – 1.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 141.0, 128.1, 127.4, 126.1, 81.0, 62.6, 45.9, 27.4, 26.5 (2C), 26.3, 25.6, 14.2. This compound is known.[2]



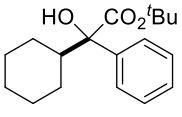
4c

Isopropyl 2-cyclohexyl-2-hydroxy-2-phenylacetate (4c): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (73.7 mg, 89% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, J = 7.2 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.19 – 7.16 (m, 1H), 4.99 – 4.93 (m, 1H), 3.66 (brs, 1H), 2.16 – 2.11 (m, 1H), 1.74 – 1.70 (m, 1H), 1.58 – 1.54 (m, 2H), 1.40 – 1.33 (m, 2H), 1.25 – 1.19 (m, 4H), 1.12 – 0.98 (m, 7H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.2, 141.2, 128.0, 127.3, 126.1, 80.8, 70.5, 45.8, 27.4, 26.51, 26.49, 26.4, 25.7, 21.8, 21.6. IR (ATR): ν = 3496, 1712 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{17}H_{25}O_3$: 277.1798, found: 277.1798.



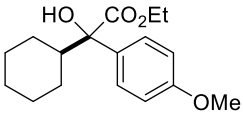
4d

Cyclohexyl 2-cyclohexyl-2-hydroxy-2-phenylacetate (4d): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (81.4 mg, 86% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.65 (d, J = 7.8 Hz, 2H), 7.34 – 7.30 (m, 2H), 7.26 – 7.24 (m, 1H), 4.85 – 4.81 (m, 1H), 3.75 (brs, 1H), 2.24 – 2.20 (m, 1H), 1.91 – 1.84 (m, 1H), 1.81 – 1.79 (m, 1H), 1.76 – 1.71 (m, 1H), 1.70 – 1.65 (m, 4H), 1.58 – 1.53 (m, 1H), 1.52 – 1.47 (m, 2H), 1.46 – 1.39 (m, 3H), 1.36 – 1.26 (m, 3H), 1.21 – 1.17 (m, 1H), 1.15 – 1.04 (m, 3H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 175.2, 141.2, 128.0, 127.4, 126.2, 80.8, 75.0, 45.9, 31.5, 31.1, 27.4, 26.5 (2C), 26.4, 25.7, 25.4, 23.5, 23.4. IR (ATR): ν = 3507, 1701 cm^{-1}. HRMS (APCI): m/z $[M - H]^-$ calcd for $C_{20}H_{27}O_3$: 315.1966, found: 315.1965.



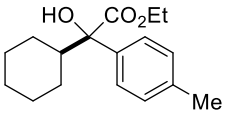
4e

***tert*-Butyl 2-cyclohexyl-2-hydroxy-2-phenylacetate (4e)**: The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (78.3 mg, 90% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 7.6 Hz, 2H), 7.27 – 7.23 (m, 2H), 7.19 – 7.15 (m, 1H), 3.70 (brs, 1H), 2.13 – 2.07 (m, 1H), 1.75 – 1.72 (m, 1H), 1.57 – 1.53 (m, 2H), 1.47 – 1.44 (m, 1H), 1.40 – 1.33 (m, 10H), 1.27 – 1.18 (m, 1H), 1.12 – 0.96 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 141.5, 128.0, 127.2, 126.2, 83.2, 80.9, 45.8, 28.0, 27.3, 26.59, 26.56, 26.4, 25.8. IR (ATR): ν = 3498, 1714 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{18}H_{27}O_3$: 291.1955, found: 291.1955.



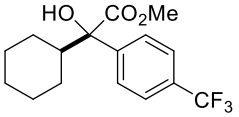
4f

Ethyl 2-cyclohexyl-2-hydroxy-2-(4-methoxyphenyl)acetate (4f): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 40:1) as a colorless oil (68.4 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.53 (m, 2H), 6.89 – 6.84 (m, 2H), 4.29 – 4.14 (m, 2H), 3.80 (s, 3H), 3.69 (brs, 1H), 2.22 – 2.15 (m, 1H), 1.81 – 1.77 (m, 1H), 1.68 – 1.63 (m, 2H), 1.47 – 1.38 (m, 2H), 1.34 – 1.22 (m, 5H), 1.16 – 1.01 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 158.9, 133.0, 127.3, 113.4, 80.6, 62.4, 55.3, 45.8, 27.4, 26.50, 26.48, 26.4, 25.6, 14.2. IR (ATR): ν = 3509, 1722, 1251 cm^{-1}. HRMS (APCI): m/z $[M - H]^-$ calcd for $C_{17}H_{23}O_4$: 291.1602, found: 291.1603.



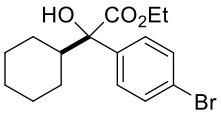
4g

Ethyl 2-cyclohexyl-2-hydroxy-2-(p-tolyl)acetate (4g): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (54.5 mg, 66% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.4 Hz, 2H), 7.15 (d, *J* = 8.0 Hz, 2H), 4.32 – 4.11 (m, 2H), 3.68 (brs, 1H), 2.34 (s, 3H), 2.26 – 2.15 (m, 1H), 1.81 – 1.77 (m, 1H), 1.66 – 1.62 (m, 2H), 1.46 – 1.42 (m, 2H), 1.30 – 1.25 (m, 4H), 1.23 – 1.20 (m, 1H), 1.16 – 1.05 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 138.1, 137.0, 128.8, 126.0, 80.8, 62.5, 45.8, 27.4, 26.5 (2C), 26.3, 25.6, 21.1, 14.2. IR (ATR): ν = 3511, 1724 cm^{-1}. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{17}H_{24}NaO_3$: 299.1618, found: 299.1618.



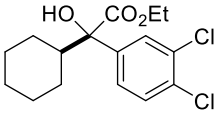
4h

Ethyl 2-cyclohexyl-2-hydroxy-2-(4-(trifluoromethyl)phenyl)acetate (4h): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (38.9 mg, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 3H), 3.76 (brs, 1H), 2.25 – 2.19 (m, 1H), 1.82 – 1.78 (m, 1H), 1.66 – 1.64 (m, 2H), 1.45 – 1.40 (m, 2H), 1.36 – 1.27 (m, 1H), 1.15 – 1.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 144.9, 129.8 (q, *J* = 32.4 Hz), 126.7, 125.1 (q, *J* = 3.7 Hz), 124.3 (d, *J* = 272.0 Hz), 81.1, 53.7, 46.2, 27.4, 26.4(2C), 26.2, 25.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5. IR (ATR): ν = 3512, 1724 cm^{-1}. HRMS (ESI): m/z $[M - OH]^+$ calcd for $C_{16}H_{18}F_3O_2$: 299.1253, found: 299.1252.



4i

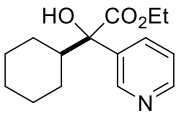
Ethyl 2-(4-bromophenyl)-2-cyclohexyl-2-hydroxyacetate (4i): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (89.8 mg, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.8 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 4.30 – 4.16 (m, 2H), 3.71 (brs, 1H), 2.16 – 2.12 (m, 1H), 1.81 – 1.77 (m, 1H), 1.65 – 1.63 (m, 2H), 1.44 – 1.38 (m, 2H), 1.30 – 1.26 (m, 4H), 1.18 – 1.04 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.3, 140.2, 131.2, 128.1, 121.7, 80.7, 62.8, 46.0, 27.4, 26.4 (2C), 26.2, 25.6, 14.2. IR (ATR): ν = 3506, 1724 cm^{-1}. HRMS (ESI): m/z $[M - OH]^+$ calcd for $C_{16}H_{20}BrO_2$: 323.0641, found: 323.0639.



4j

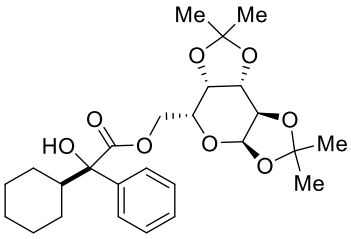
Ethyl 2-cyclohexyl-2-(3,4-dichlorophenyl)-2-hydroxyacetate (4j): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (72.3 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.50 – 7.47 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 4.32 – 4.19 (m, 2H), 3.74 (brs, 1H), 2.16 – 2.09 (m, 1H), 1.81 – 1.77 (m, 1H), 1.67 – 1.63 (m, 2H), 1.43 – 1.36 (m,

2H), 1.31 – 1.25 (m, 4H), 1.18 – 1.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.9, 141.5, 132.4, 131.6, 130.0, 128.5, 125.8, 80.4, 63.0, 46.1, 27.3, 26.3 (2C), 26.2, 25.5, 14.2. IR (ATR): ν = 3501, 1726 cm^{-1}. HRMS (ESI): m/z [M + Na]$^+$ calcd for $C_{16}H_{20}Cl_2NaO_3$: 353.0681, found: 353.0681.



4k

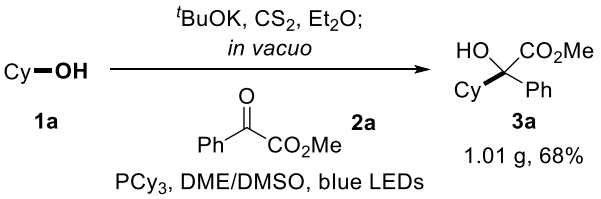
Ethyl 2-cyclohexyl-2-hydroxy-2-(pyridin-3-yl)acetate (4k): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (43.4 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 2.5 Hz, 1H), 8.52 (d, *J* = 3.4 Hz, 1H), 8.03 – 7.98 (m, 1H), 7.32 – 7.27 (m, 1H), 4.32 – 4.19 (m, 2H), 3.80 (brs, 1H), 2.38 – 2.31 (m, 1H), 2.22 – 2.14 (m, 1H), 1.82 – 1.78 (m, 1H), 1.68 – 1.64 (m, 2H), 1.46 – 1.38 (m, 2H), 1.32 – 1.28 (m, 4H), 1.15 – 1.09 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.0, 148.3, 147.8, 136.9, 134.6, 123.2, 79.8, 63.1, 46.1, 27.2, 26.3 (2C), 26.2, 25.6, 14.2. IR (ATR): ν = 3504, 1730 cm^{-1}. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{15}H_{22}NO_3$: 264.1594, found: 264.1598.



4l

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-Tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 2-cyclohexyl-2-hydroxy-2-phenylacetate (4l): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a white solid (74.3 mg, 52%, *dr* = 1:1). Data of one isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 5.54 – 5.52 (m, 1H), 4.60 – 4.57 (m, 1H), 4.46 – 4.42 (m, 1H), 4.33 – 4.31 (m, 1H), 4.30 – 4.27 (m, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 4.06 – 4.04 (m, 1H), 3.69 (brs, 1H), 2.26 – 2.23 (m, 1H), 1.80 – 1.76 (m, 1H), 1.63 – 1.58 (m, 2H), 1.50 – 1.39 (m, 8H), 1.32 – 1.25 (m, 7H), 1.18 – 1.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 140.8, 128.2, 127.5, 126.2, 109.7, 108.9, 96.4, 81.1, 71.1, 70.8, 70.5, 66.3, 65.2, 45.9, 27.3, 26.5, 26.4, 26.3, 26.0 (2C), 25.6, 25.1, 24.5. Data of the other isomer: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.6 Hz, 2H), 7.35 – 7.31 (m, 2H), 7.28 – 7.24 (m, 1H), 5.54 – 5.52 (m, 1H), 4.60 – 4.57 (m, 1H), 4.41 – 4.37 (m, 1H), 4.33 – 4.31 (m, 1H), 4.20 – 4.16 (m, 1H), 4.13 (d, *J* = 8.0 Hz, 1H), 3.96 – 3.94 (m, 1H), 3.69 (brs, 1H), 2.26 – 2.23 (m, 1H), 1.80 – 1.76 (m, 1H), 1.63 – 1.58 (m, 2H), 1.50 – 1.39 (m, 8H), 1.32 – 1.25 (m, 7H), 1.18 – 1.05 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 140.8, 128.2, 127.4, 126.2, 109.8, 108.8, 96.3, 81.2, 70.9, 70.8, 70.5, 65.7, 65.4, 45.8, 27.4, 26.6, 26.5, 26.3, 26.1, 26.0, 25.6, 25.1, 24.4. IR (ATR): ν = 3513, 1723, 1067 cm^{-1}. HRMS (ESI): m/z [M + H]$^+$ calcd for $C_{26}H_{37}O_8$: 477.2483, found: 477.2486.

4. Gram-Scale Reaction

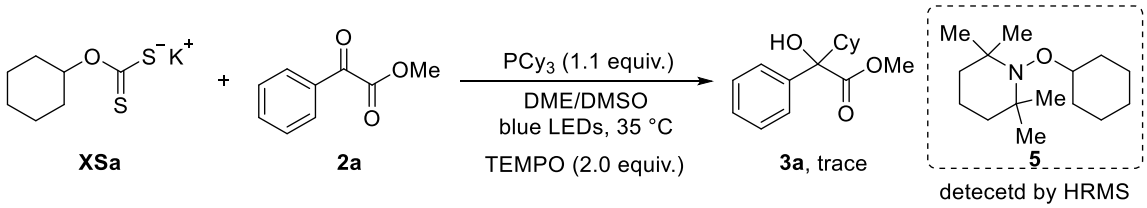


An oven-dried 250 mL Schlenk tube equipped with a magnetic stir bar was charged sequentially with cyclohexanol **1a** (0.64 g, 6.0 mmol), KO^{t}Bu (0.73 g, 6.3 mmol). The reaction vessel was evacuated and backfilled with nitrogen (three cycles) and dry Et_2O (70 mL) was added under nitrogen atmosphere, a balloon was attached. Then the reaction mixture was stirred at room temperature for 30

minutes, followed by the addition of CS_2 (1.37 g, 1.1 mL, 18 mmol) via syringe at 0 ℃ and continued stirring at 0 ℃ for 3 hours. After removing the solvent *in vacuo*, α-carbonyl ester **2a** (0.99 g, 6.0 mmol), PCy_3 (1.89 g, 6.6 mmol) were added. The Schlenk tube was sealed with a rubber plug, evacuated and backfilled with nitrogen (three cycles), and a nitrogen balloon was attached, followed by the addition of DME/DMSO (54.0 mL/6.0 mL) via syringe. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at 35 ℃. After 24 hours, the reaction mixture was treated with saturated NH_4Cl aqueous solution (100 mL), then extracted with ethyl acetate (3 × 100 mL) and dried over sodium sulfate. After filtration and concentration *in vacuo*, the residue was purified by column chromatography to afford the product **3a** as a pale yellow oil (1.01 g, 68% yield).

5. Mechanism Studies

5.1 Radical Trapping Experiment



In nitrogen-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **XSa** (64.2 mg, 0.30 mmol, 1.0 equiv.), α-carbonyl ester **2a** (49.3 mg, 0.30 mmol, 1.0 equiv.), PCy_3 (92.5 mg, 0.33 mmol, 1.1 equiv.), TEMPO (93.8 mg, 0.60 mmol, 2.0 equiv.), and the mixed solvents of DME/DMSO (9.0 mL/1.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at 35 ℃. After 24 hours, the reaction mixture was treated with saturated NH_4Cl aqueous solution (10.0 mL), then extracted with ethyl acetate (3 × 10 mL) and dried over sodium sulfate. After filtration, the solvent was removed *in vacuo* and the residue was directly put into an NMR tube for analysis by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard.

The formation of **3a** was significantly suppressed by radical quenchers, which suggested the reaction proceeded through a radical-involved pathway. When TEMPO was used as the radical quencher, product **5** was detected by HRMS (Figure S2), which could be the evidence for the cyclohexyl radical formation. HRMS (ESI, m/z). Calcd for $C_{15}H_{30}NO$ $[M + H^+]$: 240.2322, found: 240.2320.

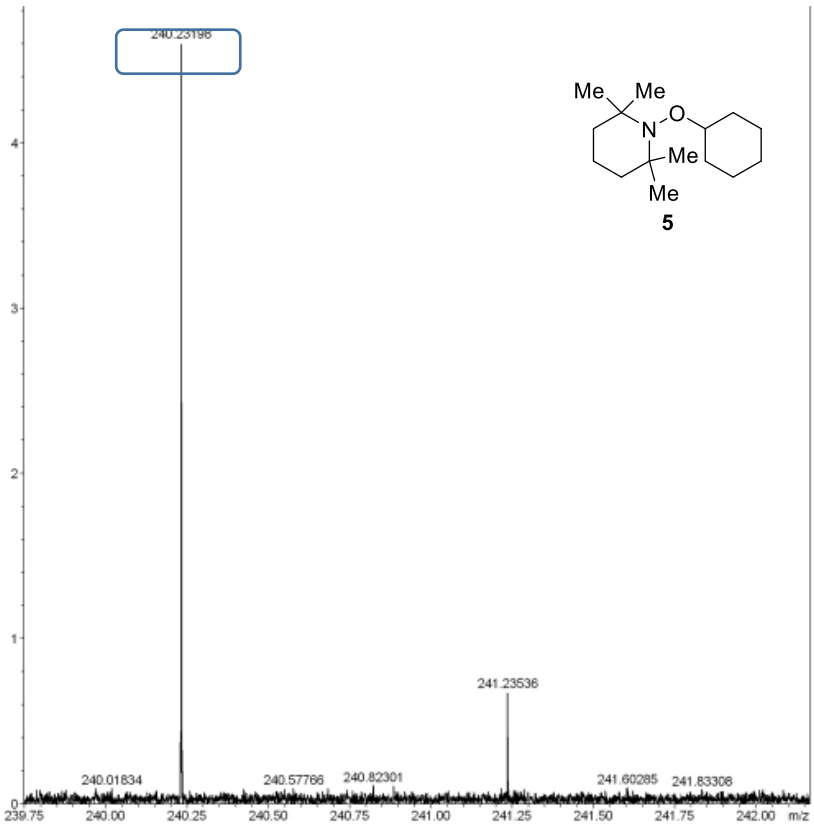
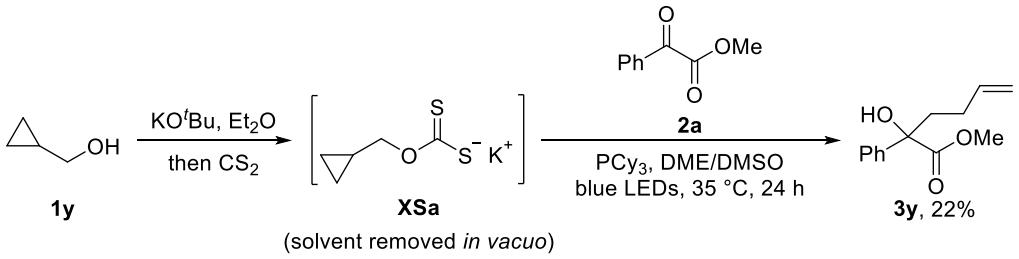


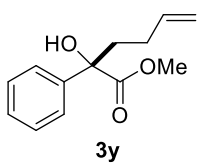
Figure S2. Radical Trapping Experiment

5.2 Radical Clock Experiment



In nitrogen-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with cyclopropyl carbinol **1y** (21.6 mg, 0.30 mmol, 1.0 equiv.), KO^{t}Bu (35.3 mg, 0.32 mmol, 1.05 equiv.), and dry Et_2O (3.0 mL). After being sealed with a septum cap and transferred out of the glovebox, the reaction mixture was stirred at room temperature for 30 minutes, followed by the addition of CS_2 (68.5 mg, 54.4 µL, 0.90 mmol) via microsyringe at 0 ºC and continued to be stirred for 3 hours at 0 ºC before removing the solvent *in vacuo*. The system was transferred into the glovebox, then α-carbonyl ester **2a** (49.3 mg, 0.30 mmol, 1.0 equiv.), PCy_3 (92.5 mg, 0.33 mmol, 1.1 equiv.) and the mixed solvents of DME/DMSO (9.0 mL/1.0 mL) were added. The vial was sealed with a septum cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W blue LEDs lamp, maintained at 35 ºC. After 24 hours, the reaction mixture was treated with saturated NH_4Cl

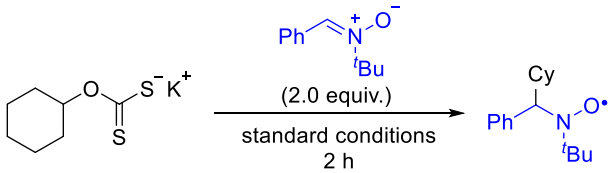
aqueous solution (10.0 mL), then extracted with ethyl acetate (3 × 10 mL) and dried over sodium sulfate. After filtration, the solvent was removed *in vacuo* and the residue was purified by column chromatography to afford the desired product.



3y

Methyl 2-hydroxy-2-phenylhex-5-enoate (3y): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 100:1) as a colorless oil (14.5 mg, 22% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.2 Hz, 2H), 7.38 – 7.34 (m, 2H), 7.31 – 7.27 (m, 1H), 5.86 – 5.76 (m, 1H), 5.05 – 4.94 (m, 2H), 3.79 (s, 3H), 3.76 (brs, 1H), 2.33 – 2.25 (m, 1H), 2.21 – 2.01 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 141.8, 138.0, 128.4, 127.9, 125.6, 115.0, 78.2, 53.4, 38.9, 28.2. IR (ATR): ν = 3508, 1715, 955 cm^{-1}. HRMS (APCI): m/z $[M + H]^+$ calcd for $C_{13}H_{17}O_3$: 221.1172, found: 221.1170.

5.3 EPR Experiment



XSa **6**

The electron paramagnetic resonance (EPR) spectroscopy was recorded on a Bruker EMXmicro-6/1. With the addition of *tert*-butyl-α-phenylnitrone (PBN) as a free radical spin trap, we detected signals that are clearly identified as EPR signals of the CyPBN adduct according to the literature data. EPR spectra obtained in DME/DMSO at 298 K in the presence of PBN. Line P: A solution of PBN (70.9 mg, 0.4 mmol) in DME/DMSO (10.0 mL). Line T: A solution of **XSa** (64.2 mg, 0.30 mmol, 1.0 equiv.), *α*-carbonyl ester **2a** (49.3 mg, 0.30 mmol, 1.0 equiv.), PCy_3 (92.5 mg, 0.33 mmol, 1.1 equiv.), PBN (106.4 mg, 0.6 mmol, 2.0 equiv.) in DME/DMSO (9:1, 10.0 mL). Line M: Analog signal of **6**.

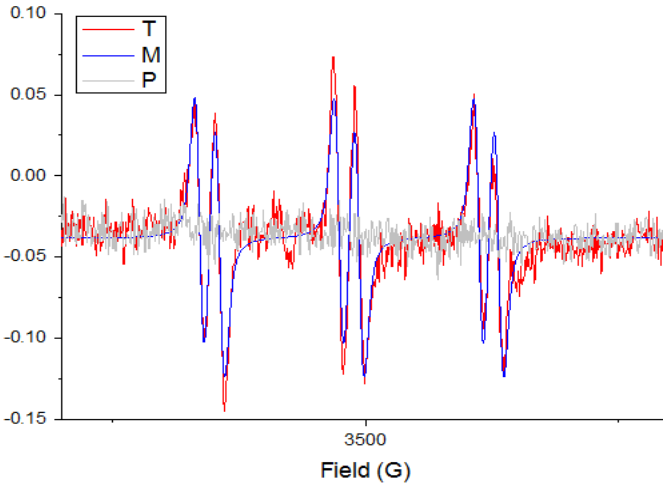


Figure S3. EPR spectra

The X-band EPR spectrum of trapped cyclohexyl radical (Cy = cyclohexyl) and corresponding simulated spectrum based on hyperfine coupling constants of A_N = 13.7911 G, A_H = 1.99185 G (g-factor = 2.00664).

Experiment parameters:

Center-Field: 3508.95 G

Width: 200.0 G

Modulation Frequency: 9.815572 GHz

Microwave Power: 2.0 mW

Time constant: 1.28 ms

5.4 UV/Vis Absorption Spectra

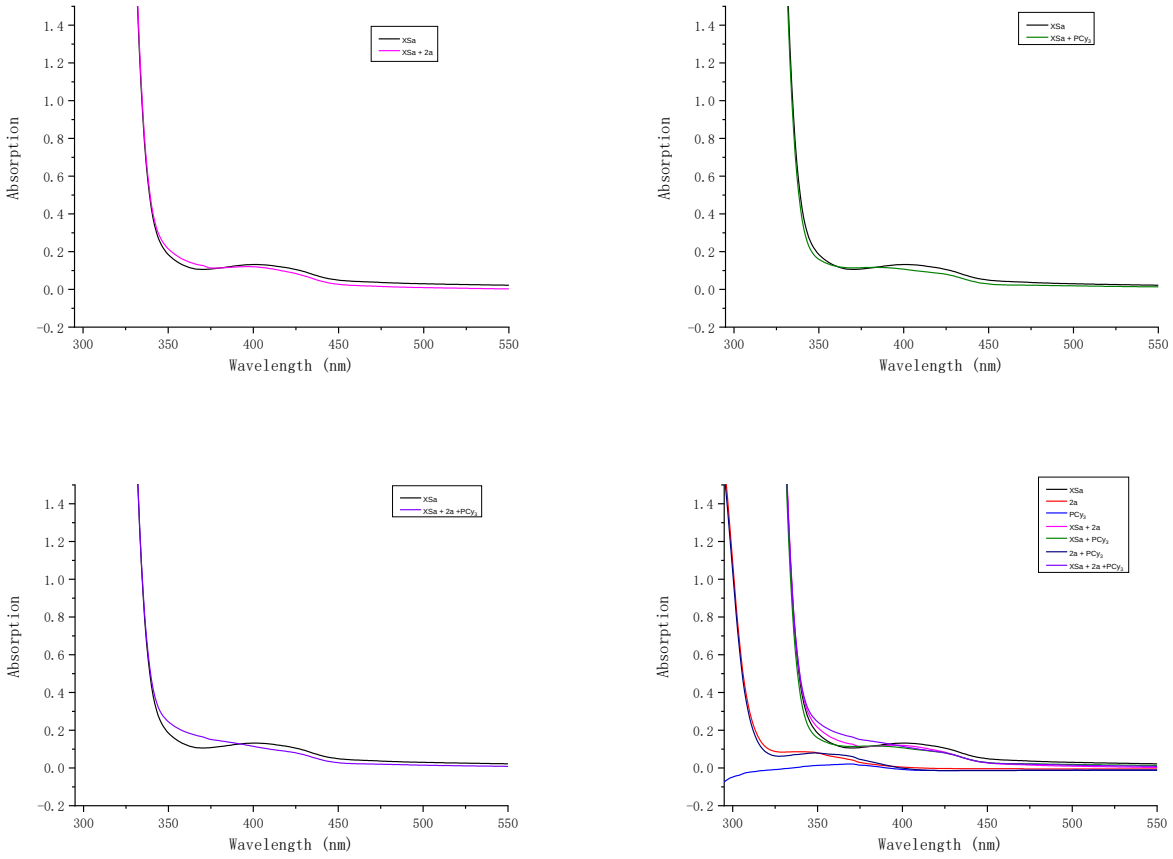


Figure S4. UV/Vis absorption spectra of the combined reaction components

The UV-Vis Absorption Spectra of all solution was introduced to a 1 cm path length quartz cuvette and analyzed using a Shimadzu UV/Vis spectrophotometer UV-2600. **XSa**: 1.0 x 10^{-3} M in DME/DMSO. Methyl 2-oxo-2-phenylacetate (**2a**): 1.0 x 10^{-3} M in DME/DMSO. PCy_3: 1.0 x 10^{-3} M in DME/DMSO.

5.5 Luminescence Quenching Experiments

Stern-Volmer experiments tracking the quenching of the phosphorescence of **XSa** were conducted on an Shimadzu Fluorescence Spectrophotometer RF-5301PC for all experiments. Fresh stock solutions of methyl 2-oxo-2-phenylacetate (**2a**) were prepared in DME/DMSO (9/1) and mixed together at varying concentrations in volumetric flasks. The solutions were loaded into quartz cuvettes and shielded from light exposure before collection. All the solutions were excited at 390 nm and the emission intensity was collected at 442 nm.

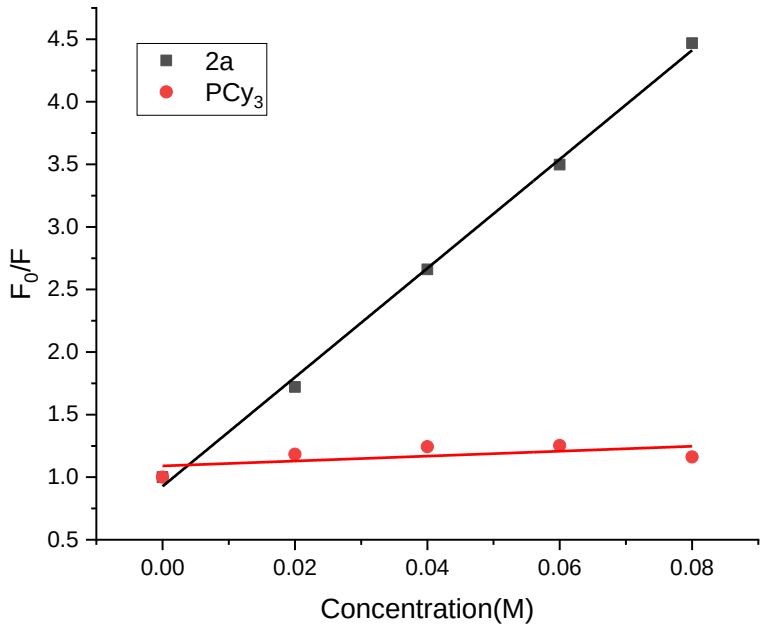
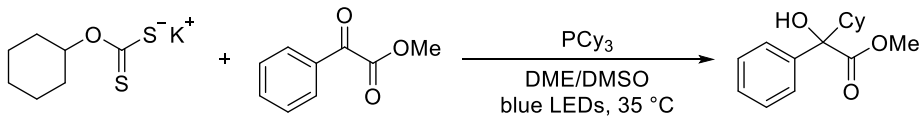


Figure S5. Stern-Volmer plots of **XSa** and quenchers. I_0 and I are luminescence intensities in the absence and presence of the indicated concentrations (10^{-3} M) of the corresponding quencher.

5.6 Light On-Off Experiments



XSa **2a** **3a**

In nitrogen-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **XSa** (64.2 mg, 0.30 mmol, 1.0 equiv.), α-carbonyl ester **2a** (49.3 mg, 0.30 mmol, 1.0 equiv.), PCy_3 (92.5 mg, 0.33 mmol, 1.1 equiv.), 1,2,4,5-tetramethylbenzene (20.1 mg, 0.15 mmol), and the mixed solvents of DME/DMSO (9.0 mL/1.0 mL) were added. The vial was sealed with a headspace cap and transferred out of the glovebox. The reaction mixture was irradiated with a 30 W

blue LEDs lamp, maintained at 35 ºC, and stirred for 2 hours. The vial was wrapped in tin foil and a 50 µL sample of the reaction mixture was taken with a syringe and measured by GC. After being stirred for 2 hours at 35 ºC in dark, a 50 µL sample of the reaction mixture was taken with a syringe and measured by GC.The reaction mixture was then irradiated with a 30 W blue LEDs lamp, maintained at 35 ºC, and stirred for 2 hours. Repeating this process three times.

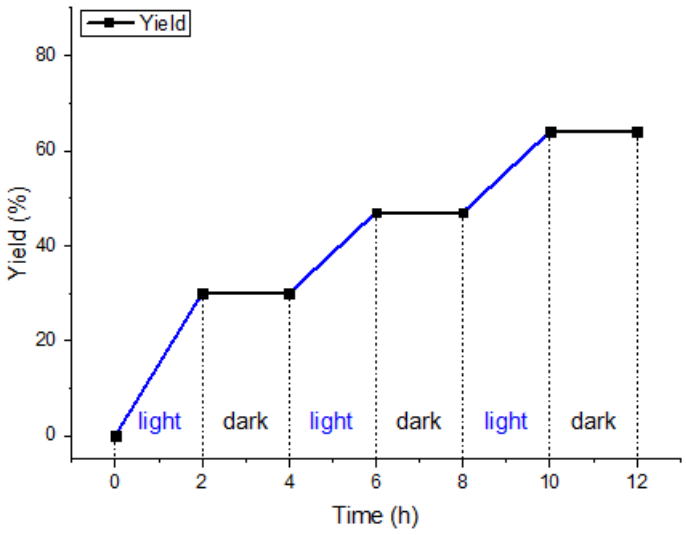


Figure S6. Light On-Off Experiments

5.7 Quantum Yield Measurement

The photon flux of blue LED was determined by standard ferrioxalate actinometry. 0.15 M solution of ferrioxalate was prepared by dissolving potassium ferrioxalate hydrate (328 mg, 0.75 mmol) in 5.0 mL of 0.20 M aqueous sulfuric acid. 0.15 M buffered solution of 1,10-phenanthroline was prepared by dissolving 1,10-phenanthroline (54.1 mg, 0.3 mmol) and sodium acetate (1.23 g, 15 mmol) in 20 mL of 0.20 M aqueous sulfuric acid.

The actinometry measurements were done as follows:

To a 4-mL borosilicate vial equipped with a stir bar was added 0.50 mL of the ferrioxalate solution. The vial was sealed and placed 2 cm away from a 25 W blue LEDs. After irradiation for 10 seconds, 1.5 mL of the aqueous sulfuric acid and 2.0 mL of the buffered solution was added to the vial. The solution was then allowed to rest for 1 hour to allow the resultant ferrous ions to react completely with 1,10-phenanthroline. 50 µL of the resulting solution was taken as an aliquot and diluted with 3.0 mL of 0.20 M aqueous sulfuric acid. The absorbance of the resulting solution in a cuvette (l = 1.0 cm) at 510 nm was measured by UV-Vis spectrometer. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured.

The amount of ferrous ion formed was calculated as follows:

$$\text{mol } Fe^{2+} = \frac{v \times \Delta A}{l \times \varepsilon}$$

where V is the total volume (0.24 L) of the solution that was analyzed, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated samples, l is the path length (1.00 cm), and ε is the molar absorptivity at 510 nm (11,100 L/mol•cm).

The photon flux was calculated as follows:

$$\text{photo flux} = \frac{\text{mol } Fe^{2+}}{\Phi \times t \times f}$$

where Φ is the quantum yield for the ferrioxalate actinometer (approximated as 0.845, which was reported for a 0.15 M solution at λ = 457.9 nm) , t is the irradiation time, and f is the fraction of light absorbed at 450 nm (0.9870).

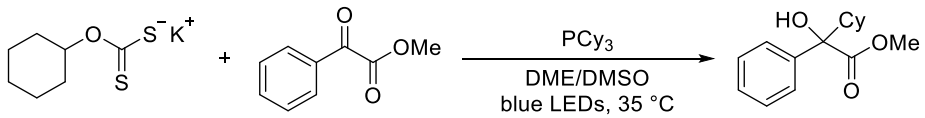
The fraction of light absorbed was determined by the following equation:

$$f = 1.0000 - 10^{-A}$$

where A is the measured absorbance (1.887) of the 0.15 M solution of potassium ferrioxalate at 450 nm.

The photo flux is 5. 62 × 10^{-7} Einstein/s.

Determination of quantum yield:



XSa **2a** **3a**

In nitrogen-filled glovebox, an oven-dried 12 mL glass vial equipped with a magnetic stir bar was charged sequentially with **XSa** (64.2 mg, 0.30 mmol, 1.0 equiv.), α-carbonyl ester **2a** (49.3 mg, 0.30 mmol, 1.0 equiv.), PCy_3 (92.5 mg, 0.33 mmol, 1.1 equiv.), 1,2,4,5-tetramethylbenzene (20.1 mg, 0.15 mmol), and the mixed solvents of DME/DMSO (9.0 mL/1.0 mL) were added. The vial was sealed with a headspace cap and transferred out of the glovebox. The vial was capped, transferred out of the glovebox. The vial was placed 2 cm away from a 25 W blue LEDs lamp. After irradiation for 1 hour, the reaction mixture was treated with saturated NH_4Cl aqueous solution (10.0 mL), then extracted with EA (3 times) and dried over sodium sulfate. After filtration, the solvent was removed *in vacuo* and the yield of product was determined by ^1H NMR using 1,3,5-trimethoxybenzene as internal standard, to be 27% (8.1×10^{-5} mol).

The quantum yield was calculated as follows:

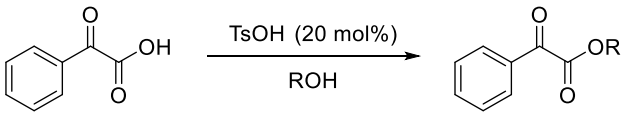
$$\Phi = \frac{\text{mol product}}{\text{flux} \times t \times f}$$

where flux is the photon flux determined by ferrioxalate actinometry (5.62×10^{-7} Einstein/s), t is the time (3600 s), and f is the fraction of light absorbed by the irradiated reaction system at 450 nm. and the absorbance of the irradiated reaction system at 450 nm was 1.778. The fraction of light absorbed at 450 nm was calculated: $f = 1.0000 - 10^{-A} = 1.0000 - 10^{-1.778} = 0.98333$.

The quantum yield was calculated: **Φ = 0.041**

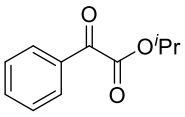
6. Preparation and Characterization Data of Substrates

6.1 General Procedure for Synthesis of α-Keto Esters



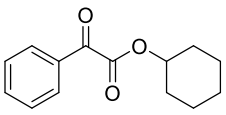
A solution of 2-oxo-2-phenylacetic acid (750 mg, 5.0 mmol) and TsOH (170 mg, 1.0 mmol) in ROH (60 mmol) was refluxed overnight. After cooling to room temperature, the reaction mixture was quenched with saturated Na_2CO_3 aq. and extracted with Et_2O/hexane (15/15 mL × 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The crude residue was purified by column chromatography on silica gel to afford the desired product.

6.2 Characterization Data of α-Keto Esters



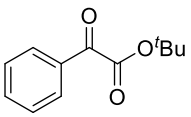
2c

Isopropyl 2-oxo-2-phenylacetate (**2c**): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (0.86 g, 90% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 – 7.95 (m, 2H), 7.63 – 7.57 (m, 1H), 7.49 – 7.44 (m, 2H), 5.33 – 5.27 (m, 1H), 1.37 (d, *J* = 6.3 Hz, 6H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 186.8, 163.7, 134.9, 132.5, 129.9, 128.9, 70.7, 21.8 (2C). This compound is known.[3]



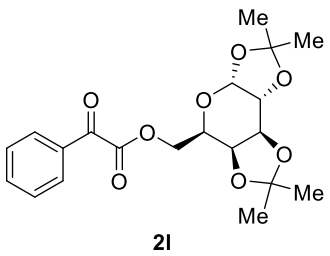
2d

Cyclohexyl 2-oxo-2-phenylacetate (**2d**): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (0.56 g, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.67 – 7.60 (m, 1H), 7.53 – 7.47 (m, 2H), 5.12-5.05 (m, 1H), 2.03 – 1.95 (m, 2H), 1.80 – 1.73 (m, 2H), 1.63 – 1.53 (m, 3H), 1.46 – 1.36 (m, 2H), 1.33 – 1.24 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 163.7, 134.9, 132.6, 130.0, 128.9, 75.5, 31.5 (2C), 25.2, 23.7 (2C). This compound is known.[4]



2e

tert-Butyl 2-oxo-2-phenylacetate (**2e**): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 10:1) as a colorless oil (0.77 g, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 – 7.93 (m, 2H), 7.67 – 7.61 (m, 1H), 7.53 – 7.48 (m, 2H), 1.63 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.9, 163.8, 134.7, 132.6, 123.0, 129.0, 84.9, 28.2 (3C). This compound is known.[5]



2l

((3aR,5R,5aS,8aS,8bR)-2,2,7,7-tetramethyltetrahydro-5H-bis([1,3]dioxolo)[4,5-b:4',5'-d]pyran-5-yl)methyl 2-oxo-2-phenylacetate (**2l**): The title compound was isolated by eluting with petroleum ether and ethyl acetate (PE/EA = 5:1) as a colorless oil (0.81 g, 41% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 8.04 (m, 2H), 7.67 – 7.63 (m, 1H), 7.53 – 7.48 (m, 2H), 5.58 (d, *J* = 4.8 Hz, 1H), 4.65 (dd, *J* = 7.6, 2.4 Hz, 1H), 4.58 – 4.54 (m, 2H), 4.36 (dd, *J* = 5.2, 2.8 Hz, 1H), 4.29 (dd, *J* = 7.6, 2.0 Hz, 1H), 4.24 – 4.20 (m, 1H), 1.50 (s, 3H), 1.48 (s, 3H), 1.35 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 186.6, 164.1, 135.1, 132.5, 130.4, 129.0, 110.0, 109.1, 96.5, 71.0, 70.8, 70.5, 65.9, 64.9, 26.2, 26.1, 25.1, 24.6. IR (ATR): ν =2932, 1691, 1064 cm^{-1}. HRMS (ESI): m/z $[M + H]^+$ calcd for $C_{20}H_{25}O_8$: 393.1544, found: 393.1539.

7. References

[1] H.-L. Jiang, Y.-H. Yang, Y.-H. He and Z. Guan, *Org. Lett*., 2022, **24**, 4258–4263.

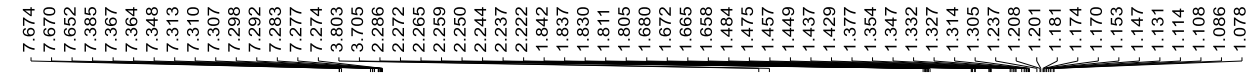
[2] O. Tokuda, T. Kano, W.-G. Gao, T. Ikemoto and K. Maruoka, *Org. Lett*., 2005, **7**, 5103–5105.

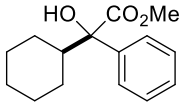
[3] Y. Su, L. Zhang, N. Jiao, *Org. Lett*., 2011, **13**, 2168–2171.

[4] F. Cai, X. Pu, X. Qi, V. Lynch, A. Radha and J. M. Ready, *J. Am. Chem. Soc*., 2011, **133**, 18066–18069.

[5] S. K. Alamsetti and G. Sekar, *Chem. Commun*., 2010, **46**, 7235–7237.

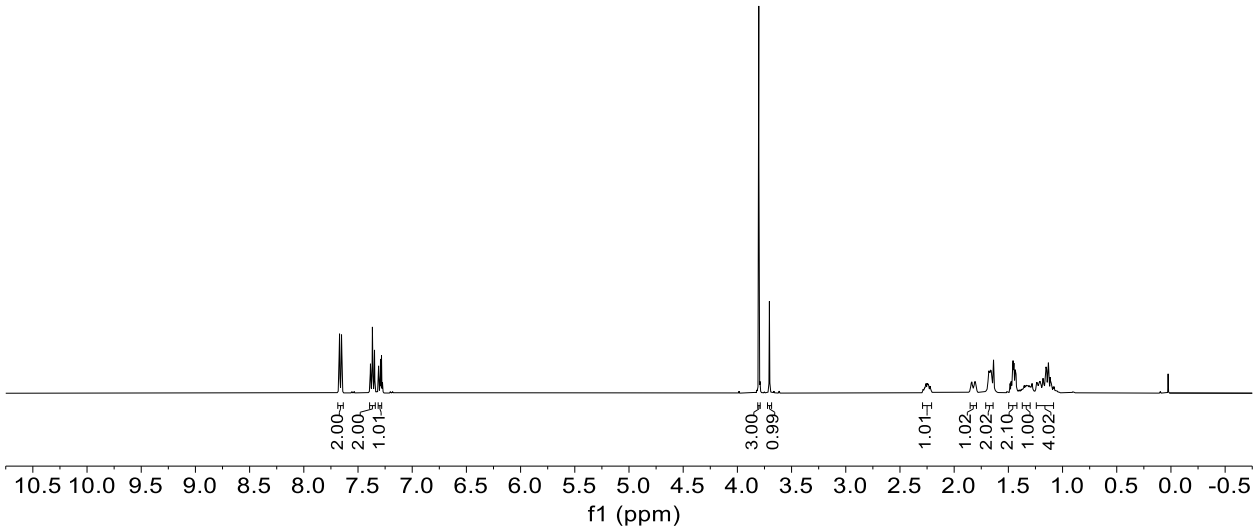
8. NMR Spectra

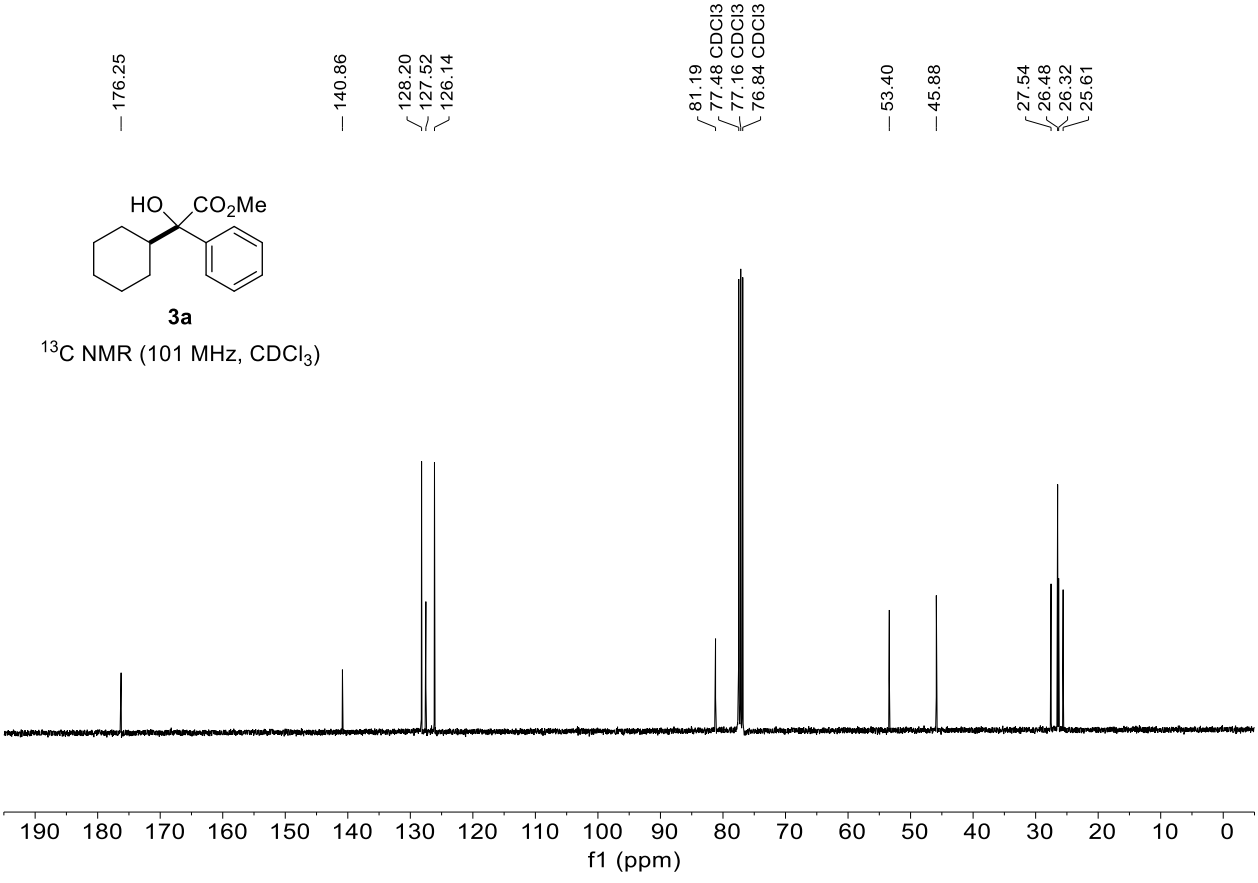




3a

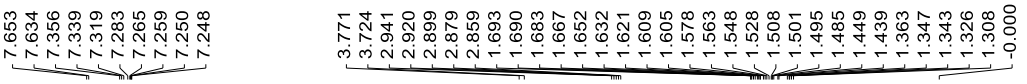
^{1}H NMR (400 MHz, $CDCl_3$)

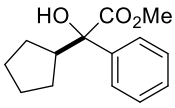




3a

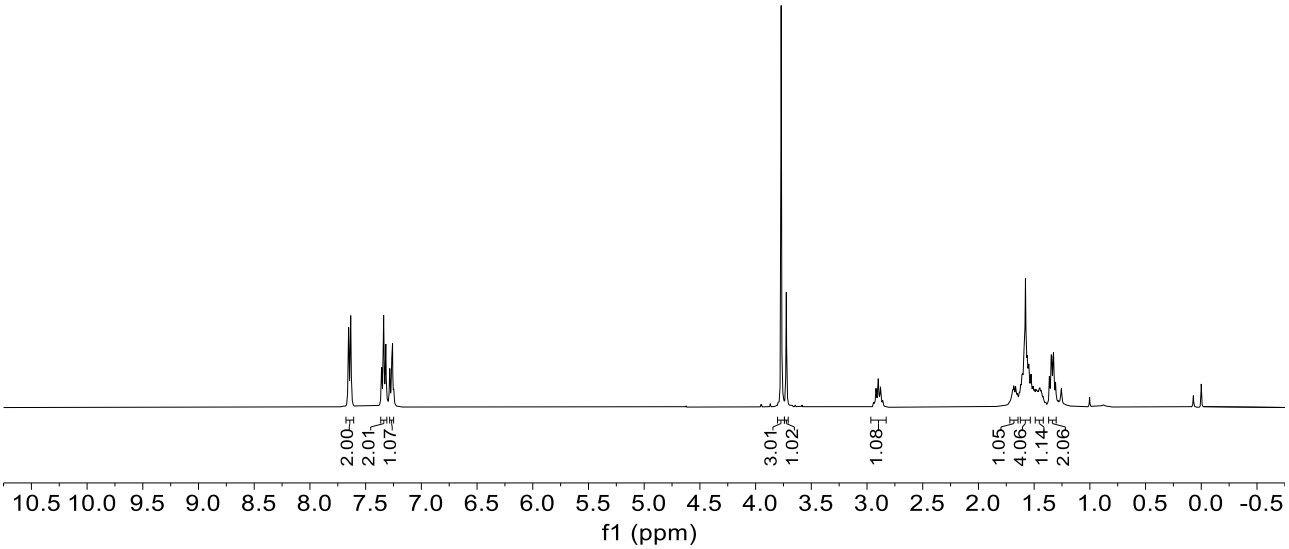
^{13}C NMR (101 MHz, $CDCl_3$)

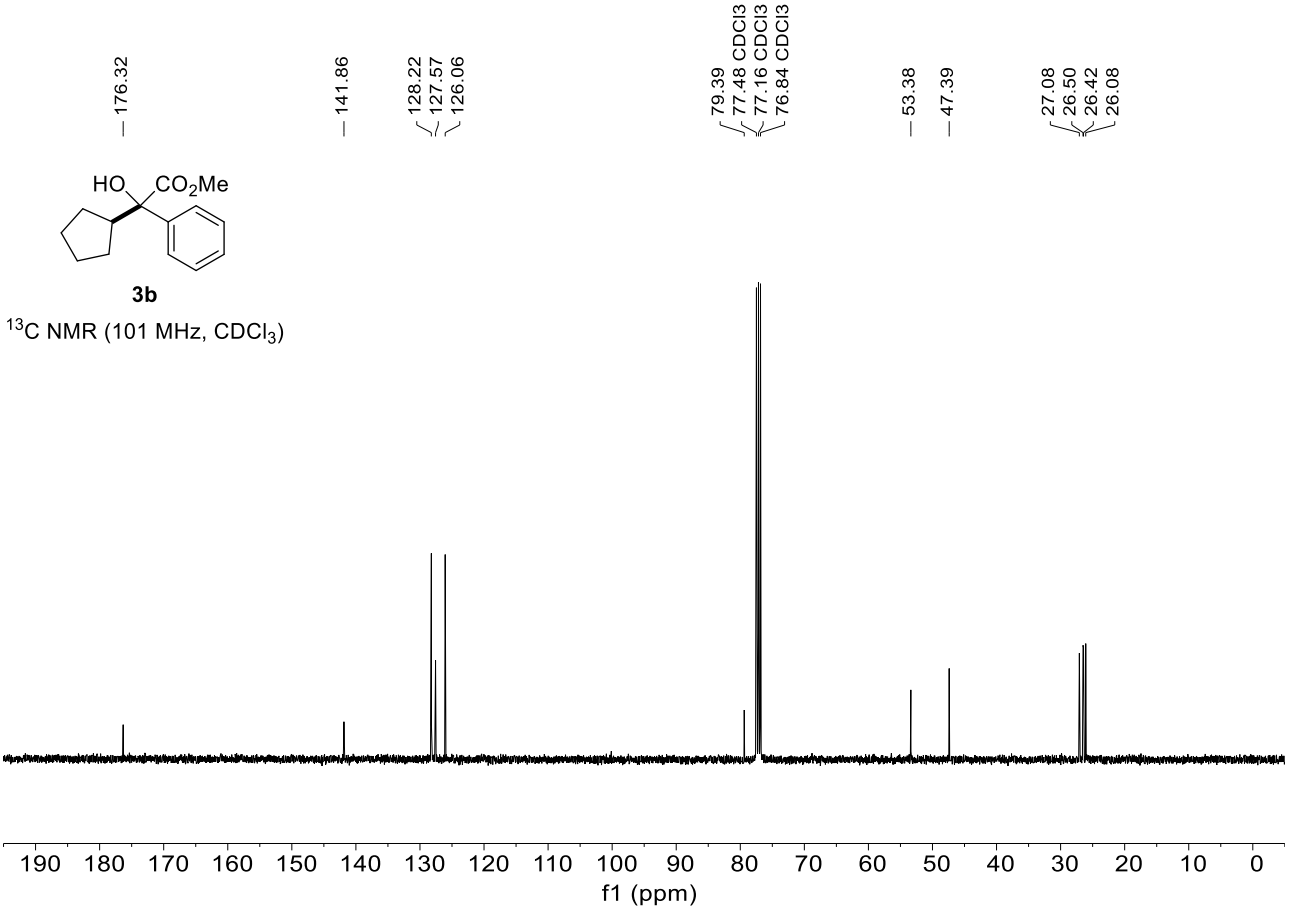




3b

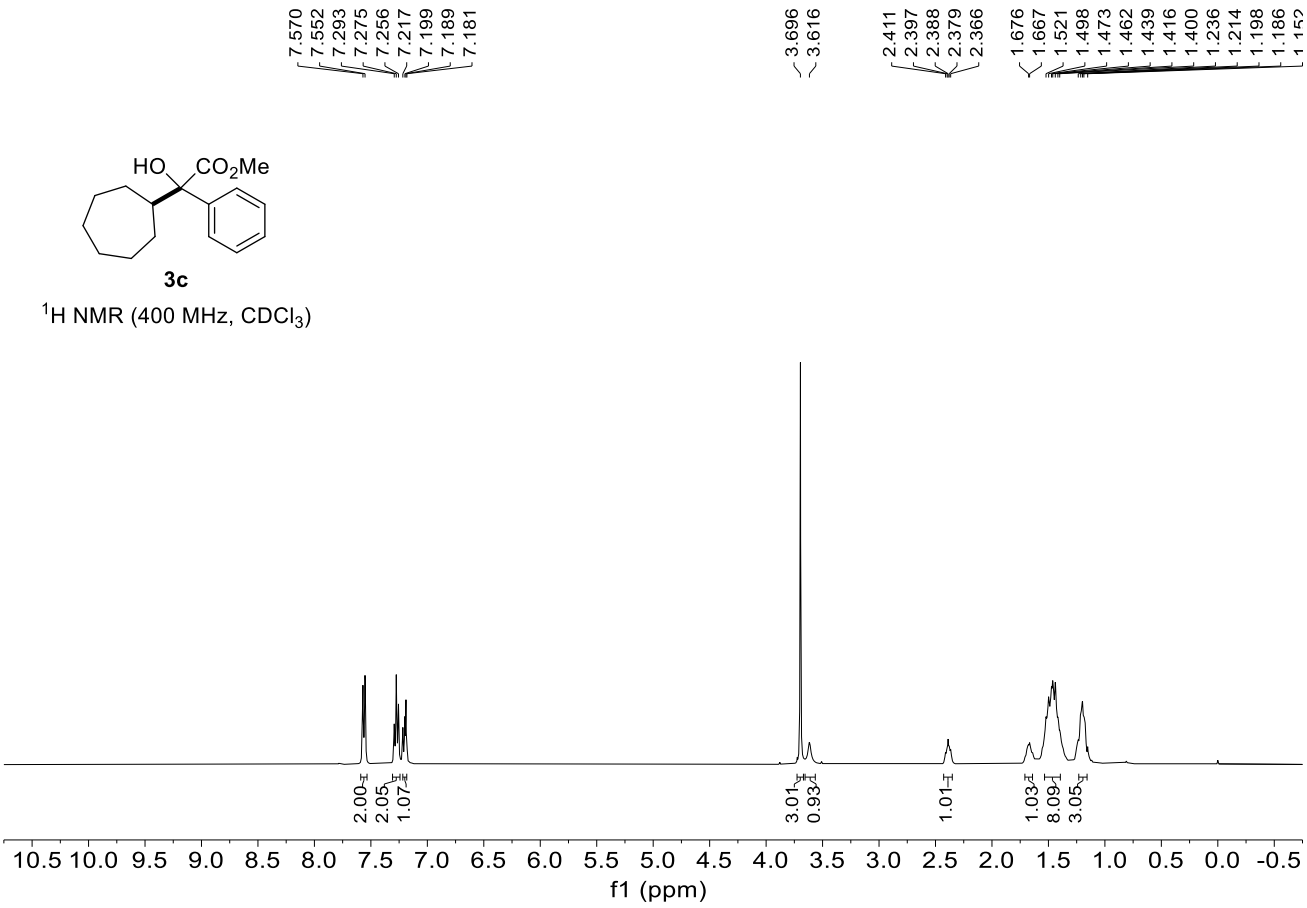
^{1}H NMR (400 MHz, $CDCl_3$)





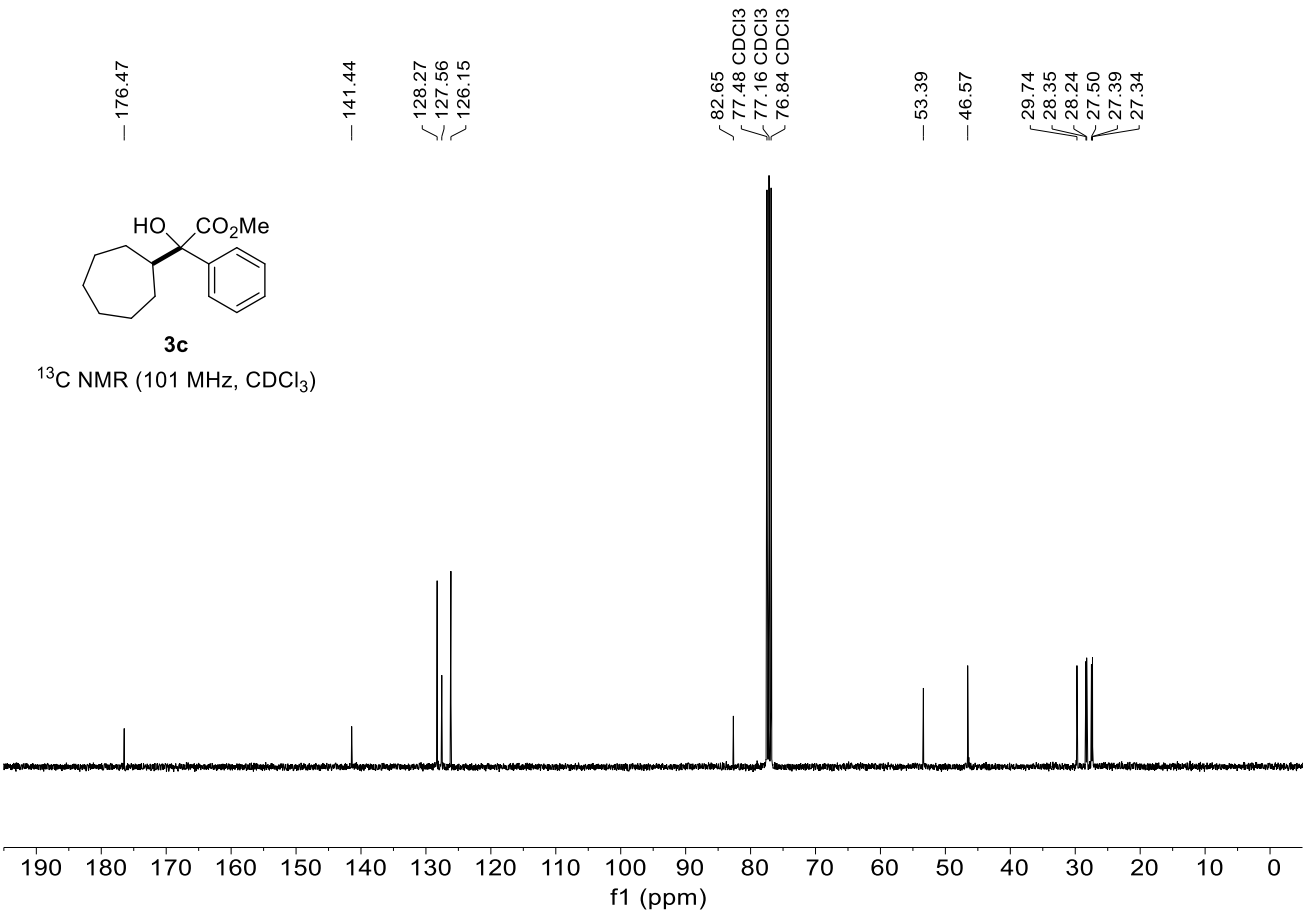
3b

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



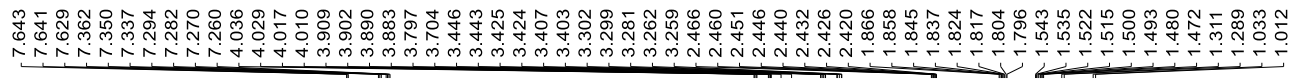
3c

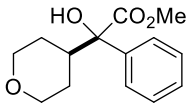
^{1}H NMR (400 MHz, $CDCl_3$)



3c

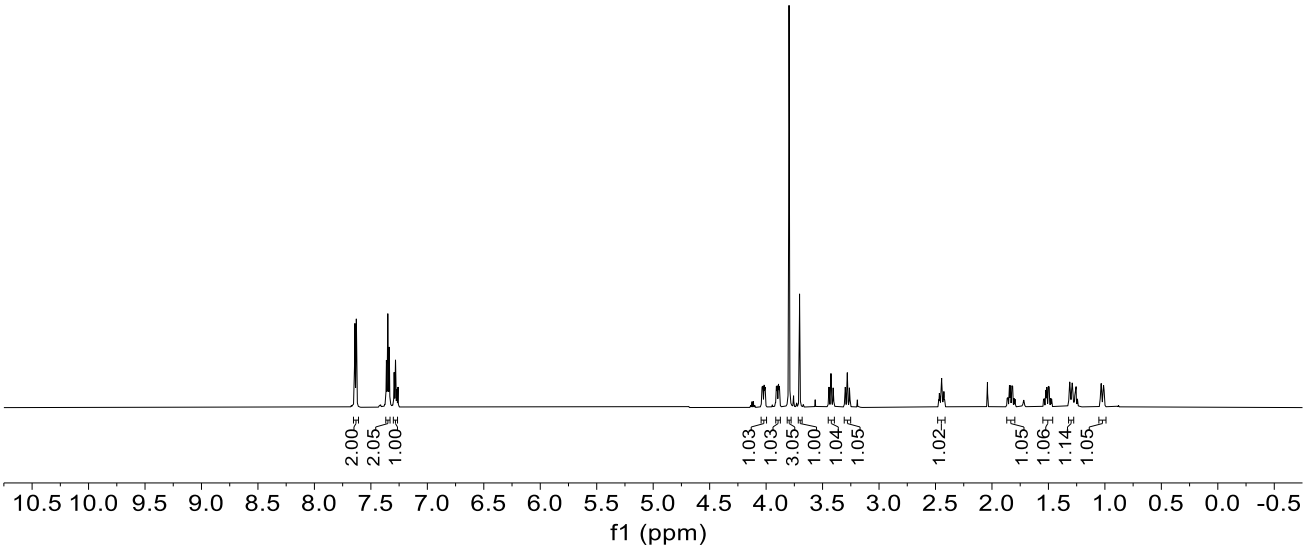
^{13}C NMR (101 MHz, $CDCl_3$)

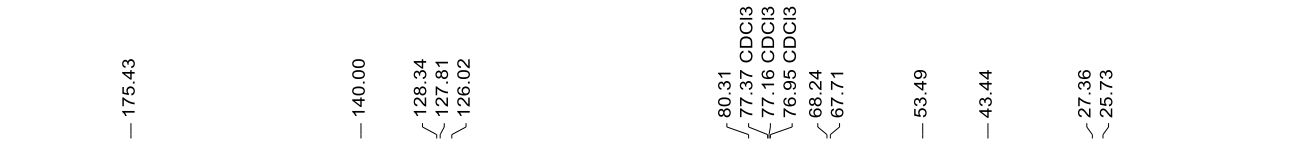


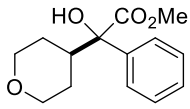


3d

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

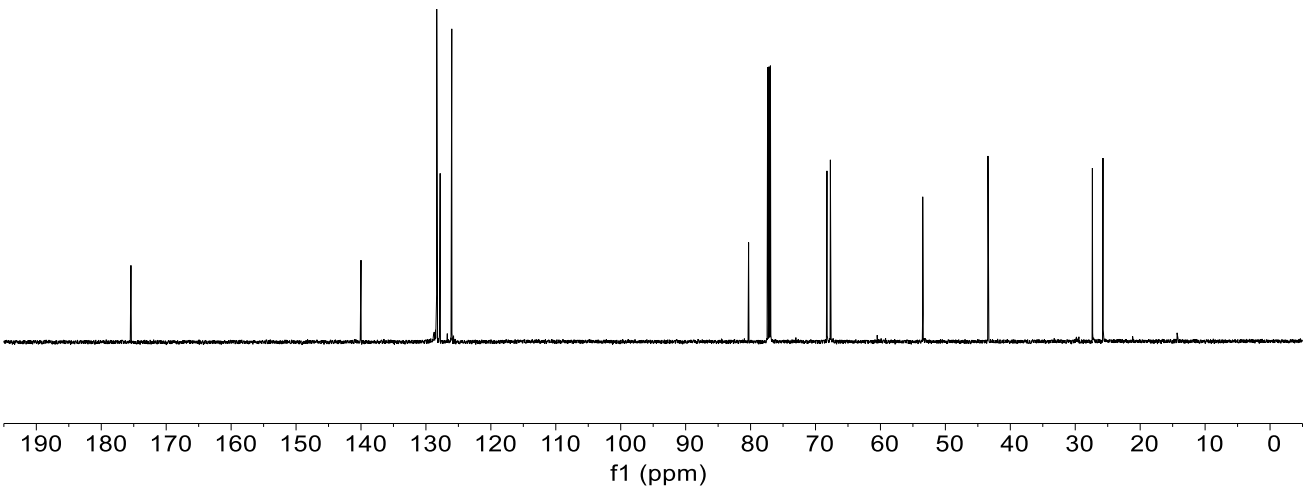


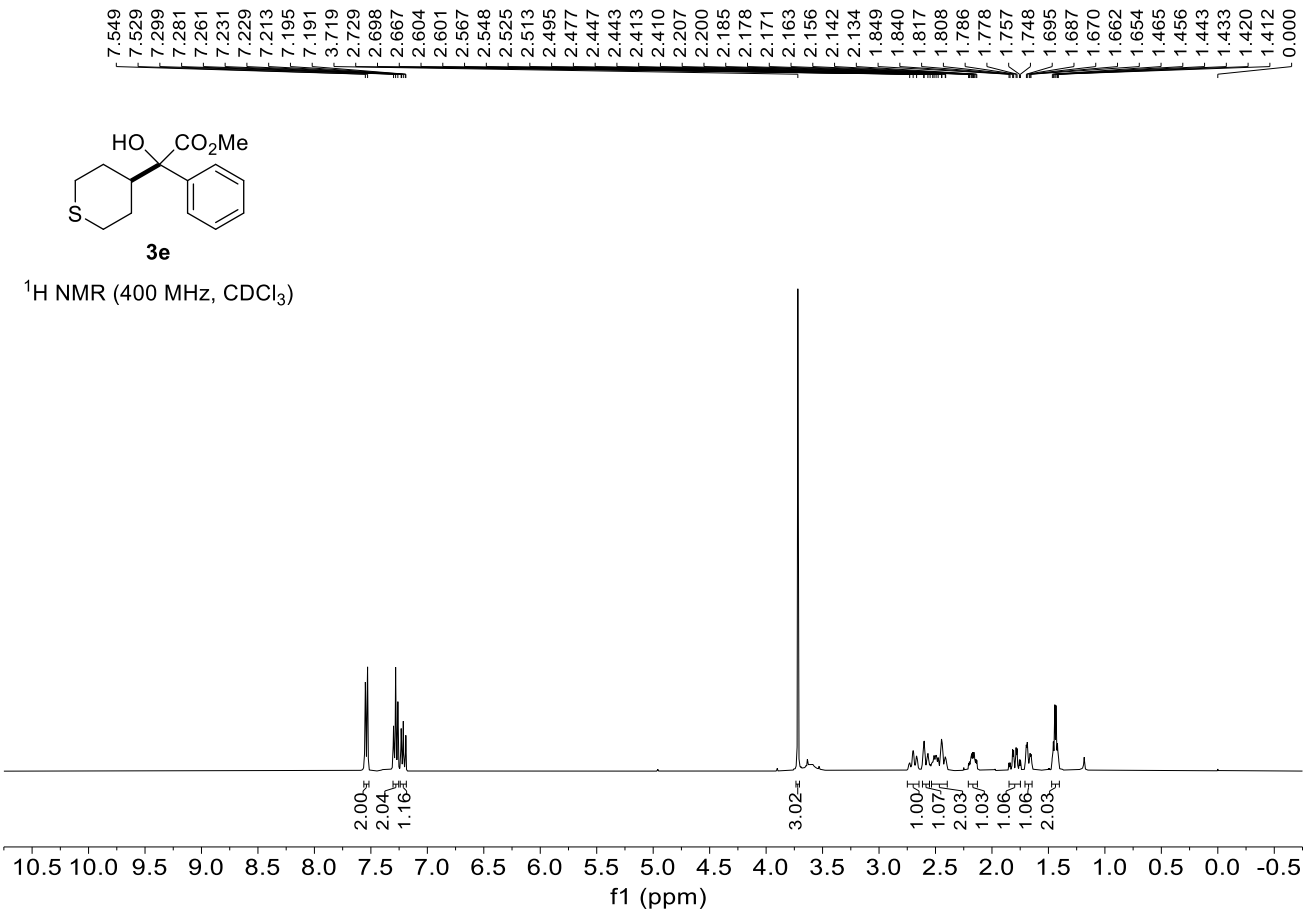


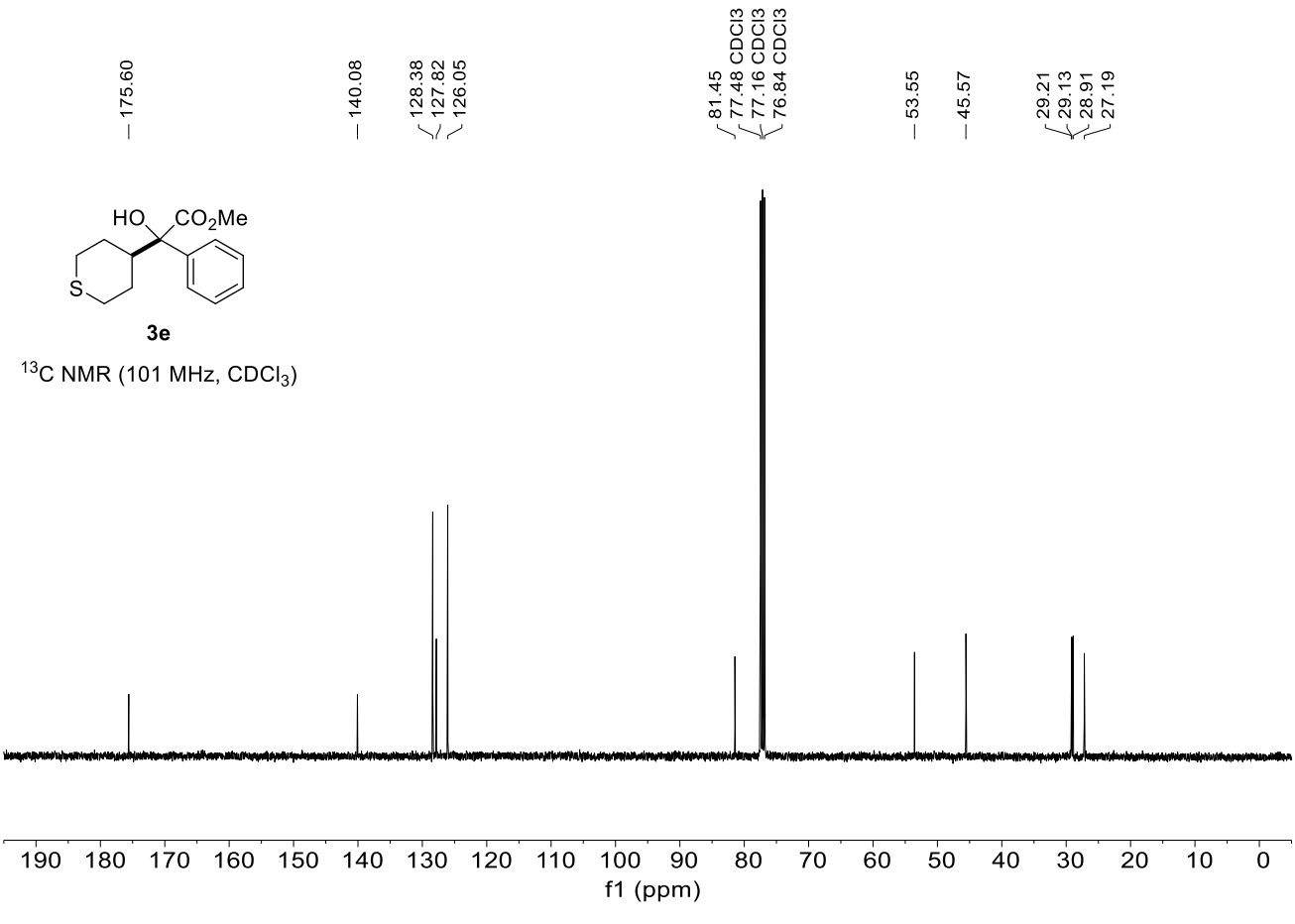


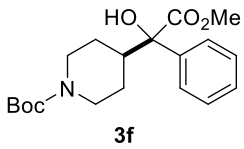
3d

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



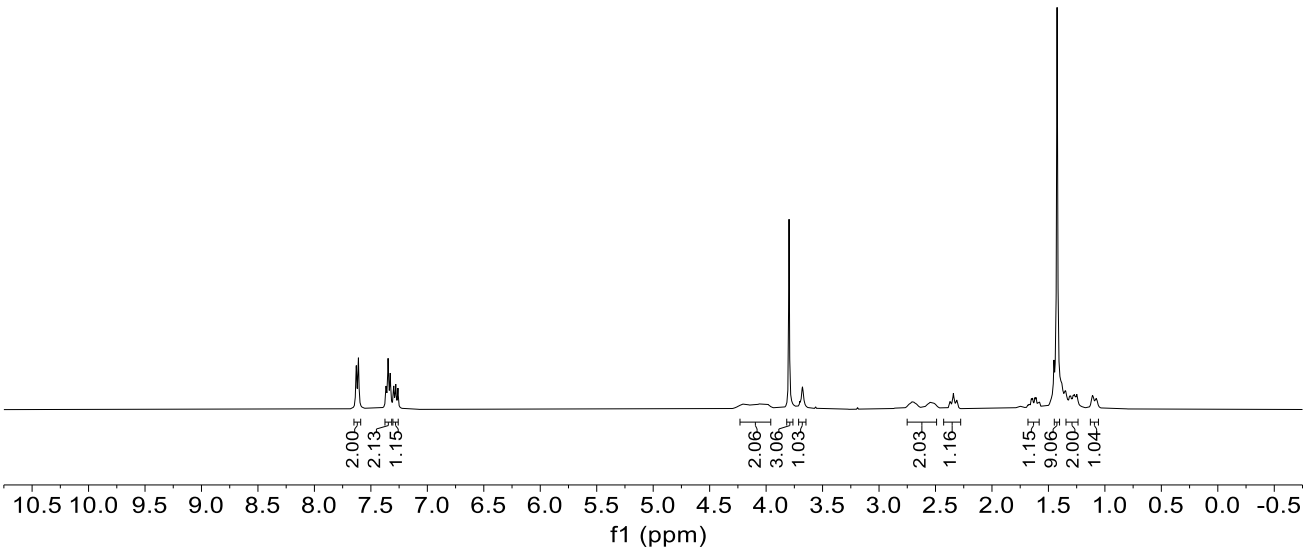

7.549
7.529
7.299
7.281
7.261
7.231
7.229
7.213
7.195
7.191
3.719
2.729
2.698
2.667
2.604
2.601
2.567
2.548
2.525
2.513
2.495
2.477
2.447
2.443
2.413
2.410
2.207
2.200
2.185
2.178
2.171
2.163
2.156
2.142
2.134
1.849
1.840
1.817
1.808
1.786
1.778
1.757
1.748
1.695
1.687
1.670
1.662
1.654
1.465
1.456
1.443
1.433
1.420
1.412
0.000
HO
CO2Me
S
3e
1H NMR (400 MHz, CDCl3)
2.00
2.04
1.16
3.02
1.00
1.07
2.03
1.03
1.06
1.06
2.03
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)

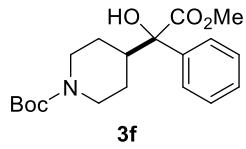

175.60
140.08
128.38
127.82
126.05
81.45
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.55
45.57
29.21
29.13
28.91
27.19
HO
CO2Me
S
3e
13C NMR (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



3f

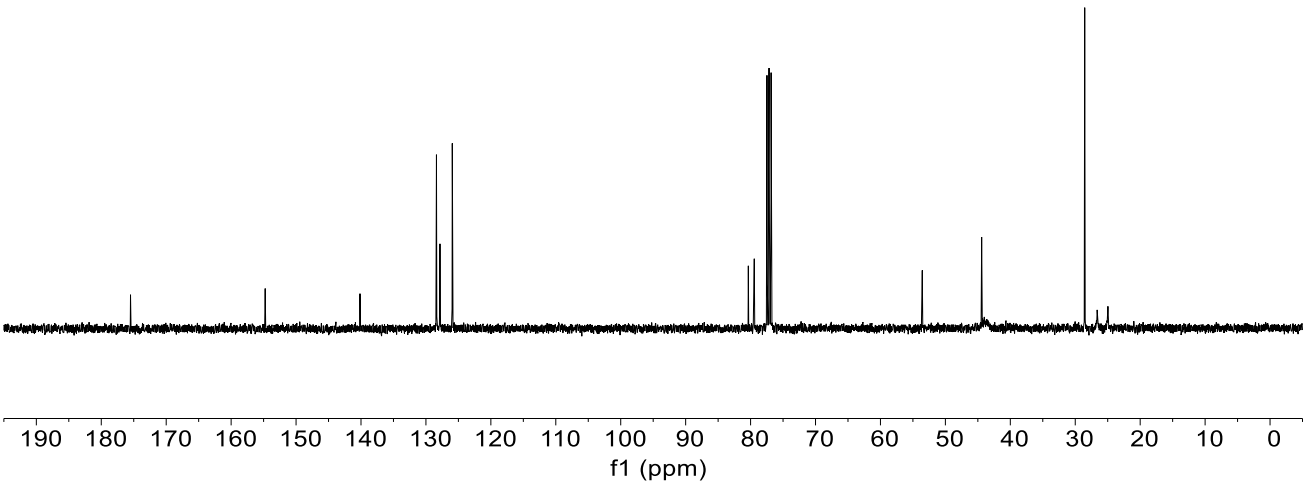
^{1}H NMR (400 MHz, $CDCl_3$)

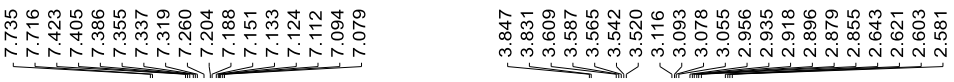


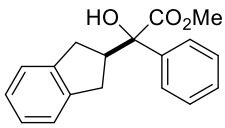


3f

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

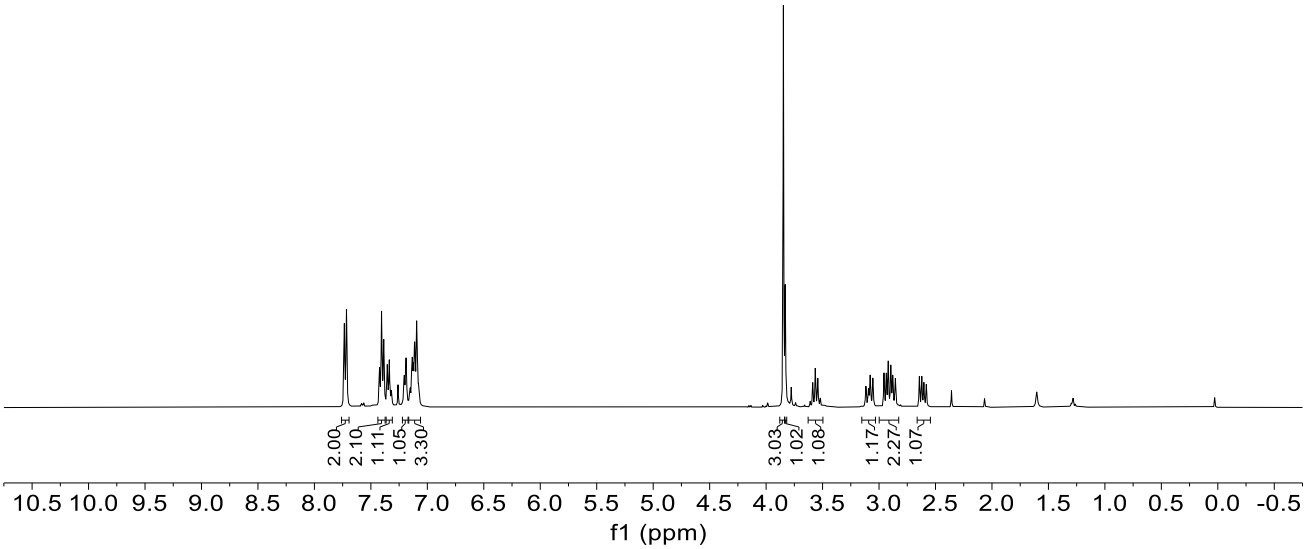


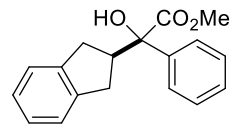




3g

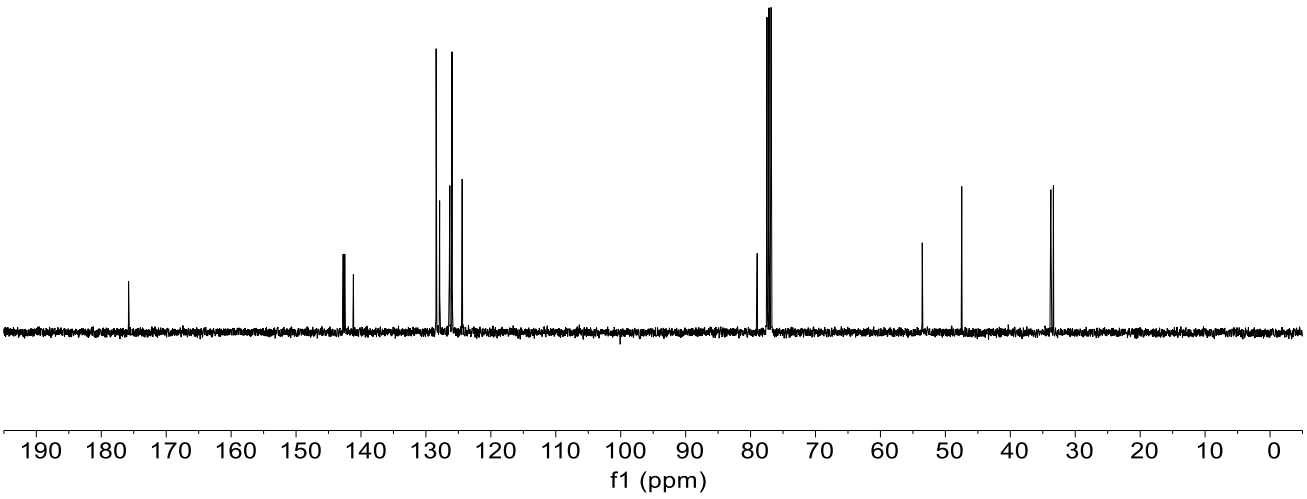
^{1}H NMR (400 MHz, $CDCl_3$)

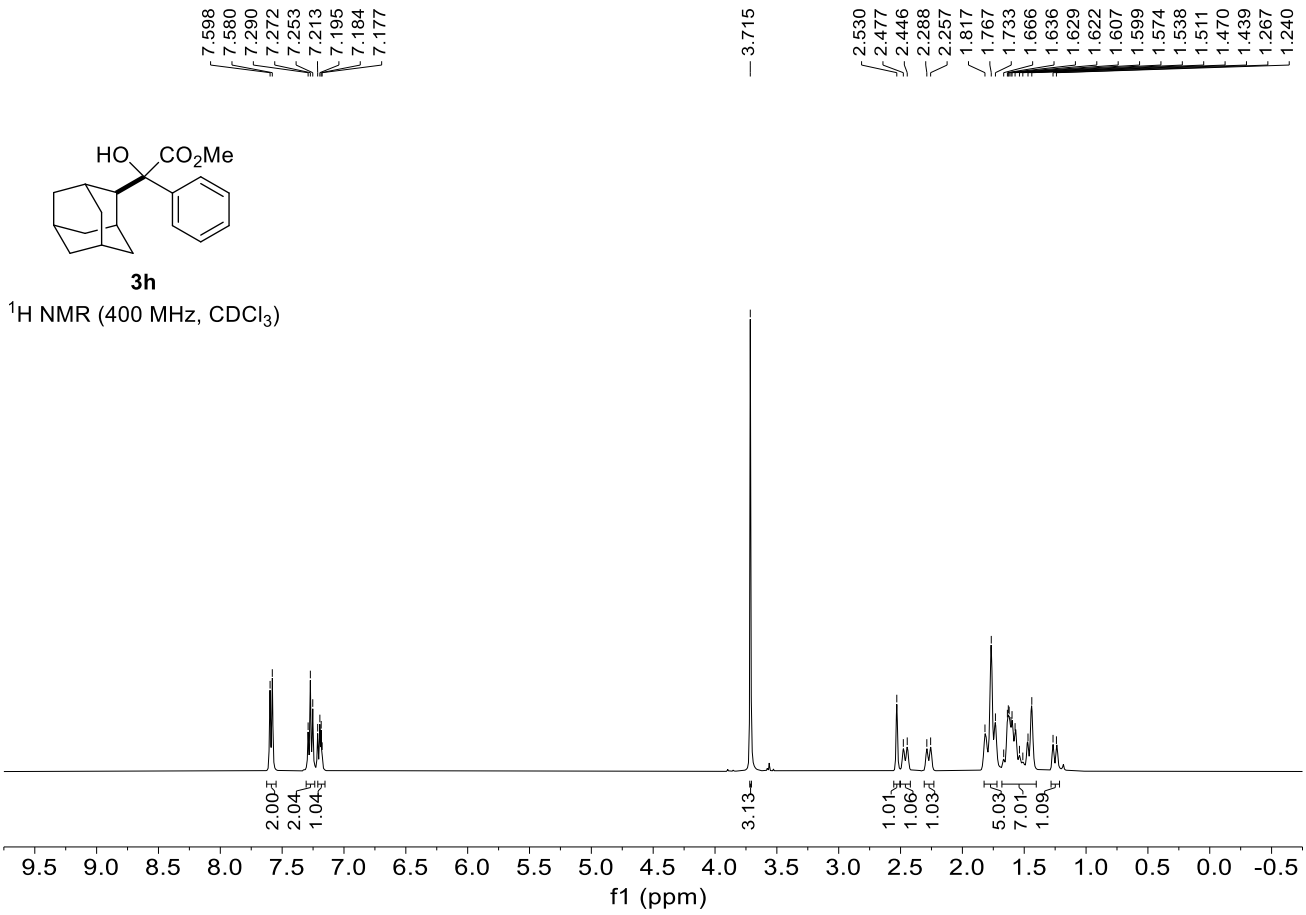




3g

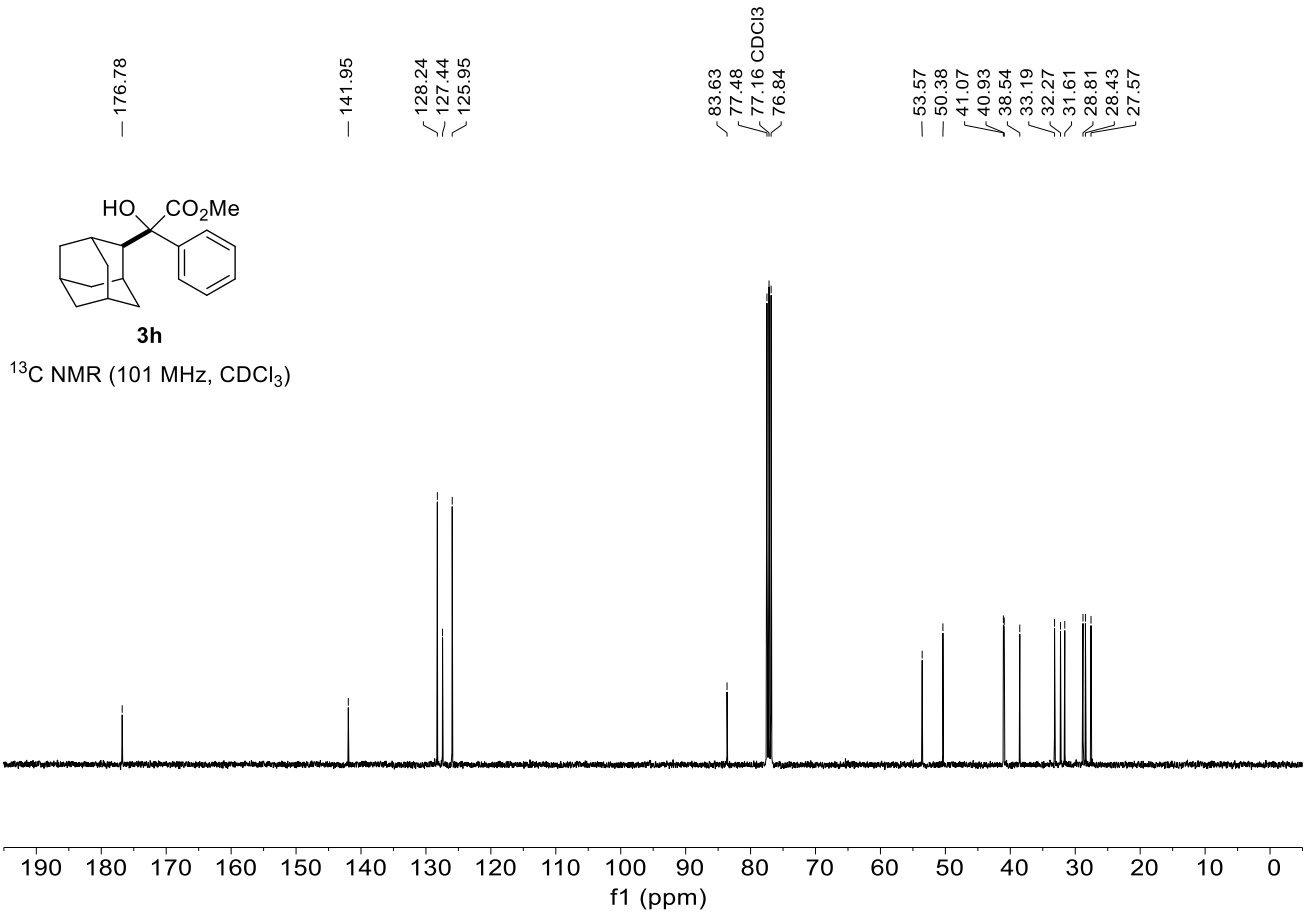
^{13}C NMR (101 MHz, $CDCl_3$)





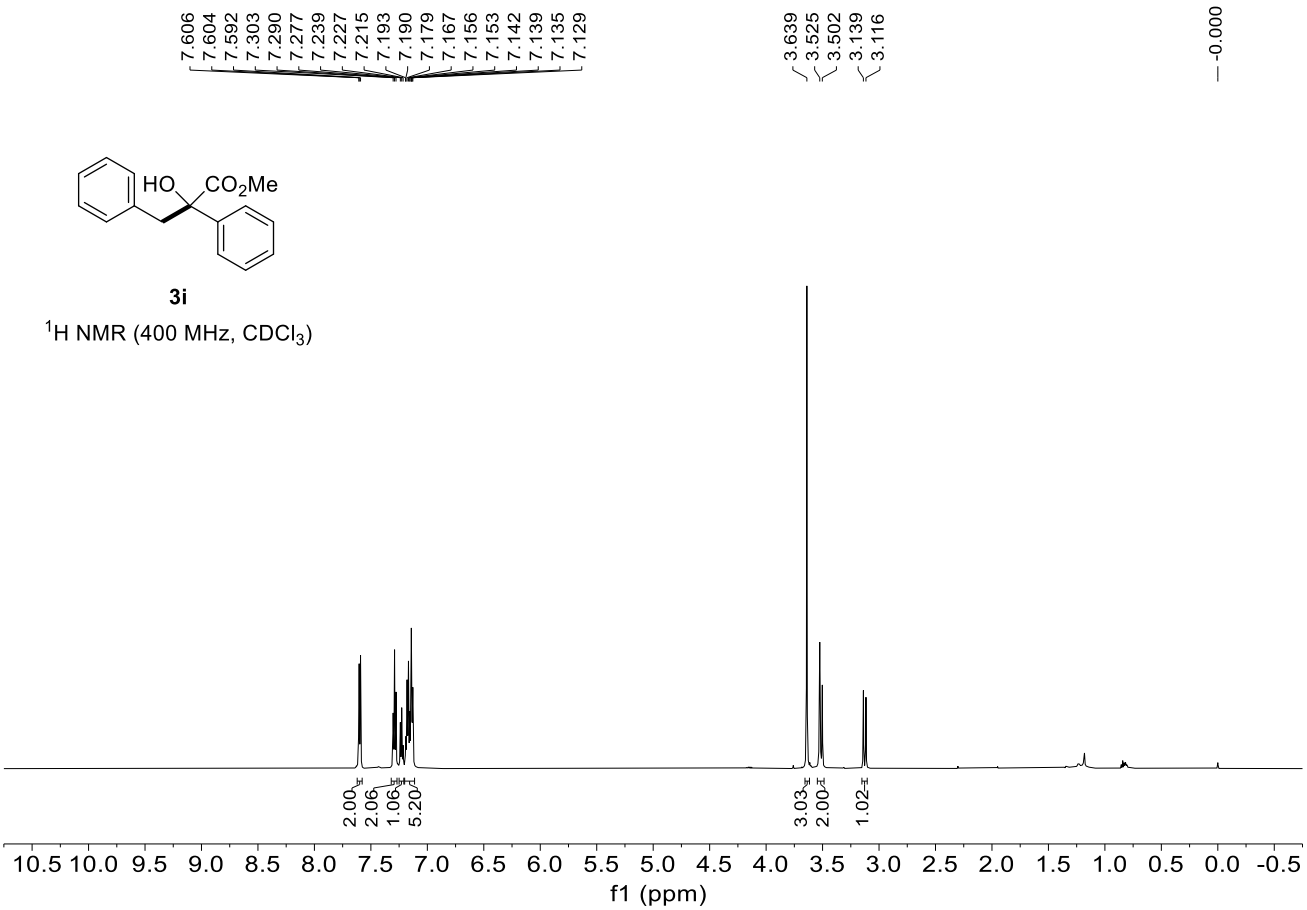
3h

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



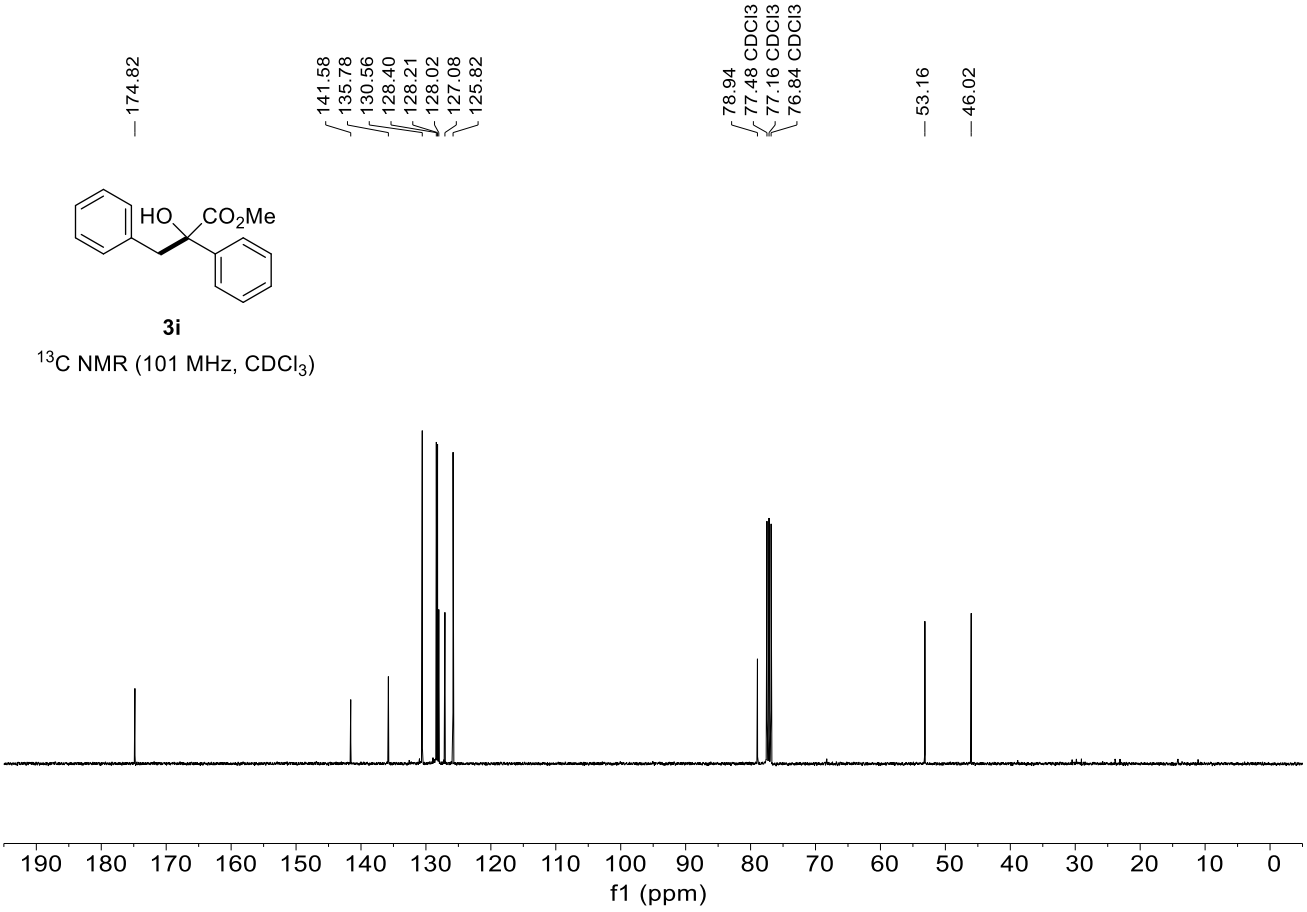
3h

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



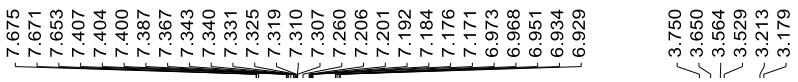
3i

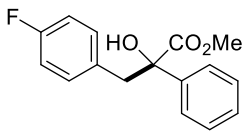
^{1}H NMR (400 MHz, $CDCl_3$)



3i

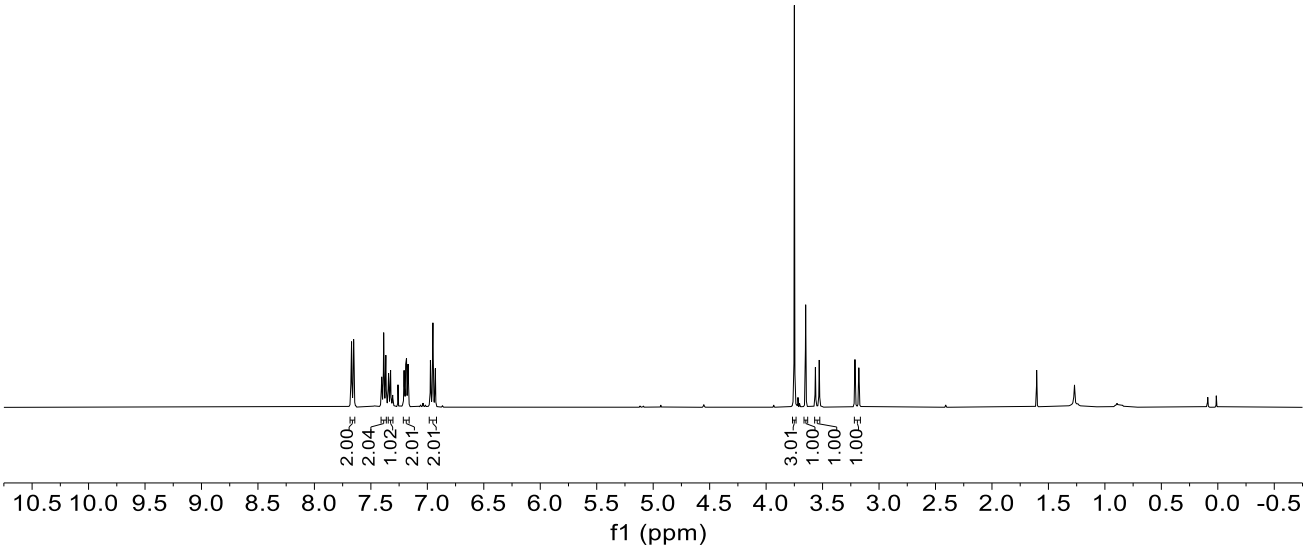
^{13}C NMR (101 MHz, $CDCl_3$)

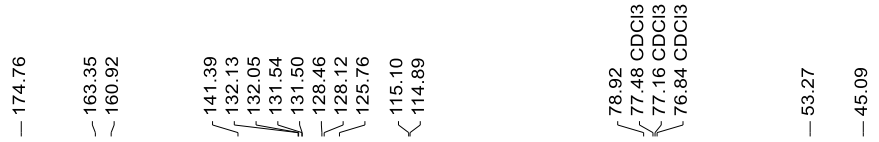


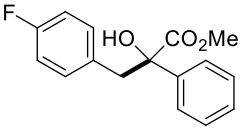


3j

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

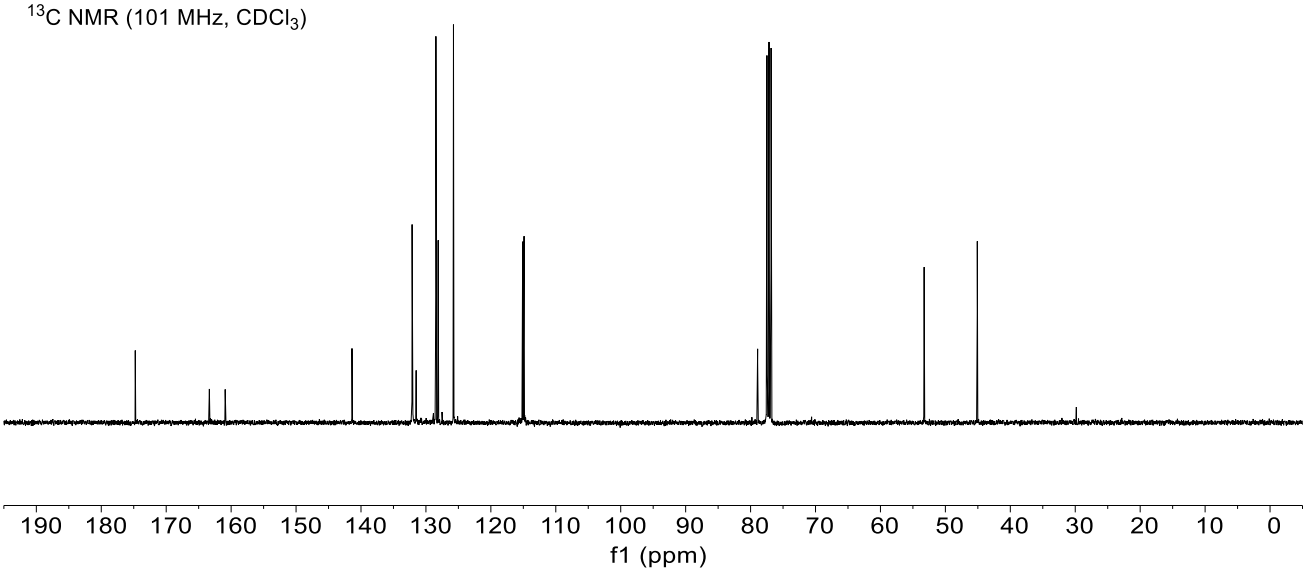


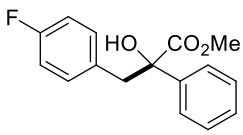




3j

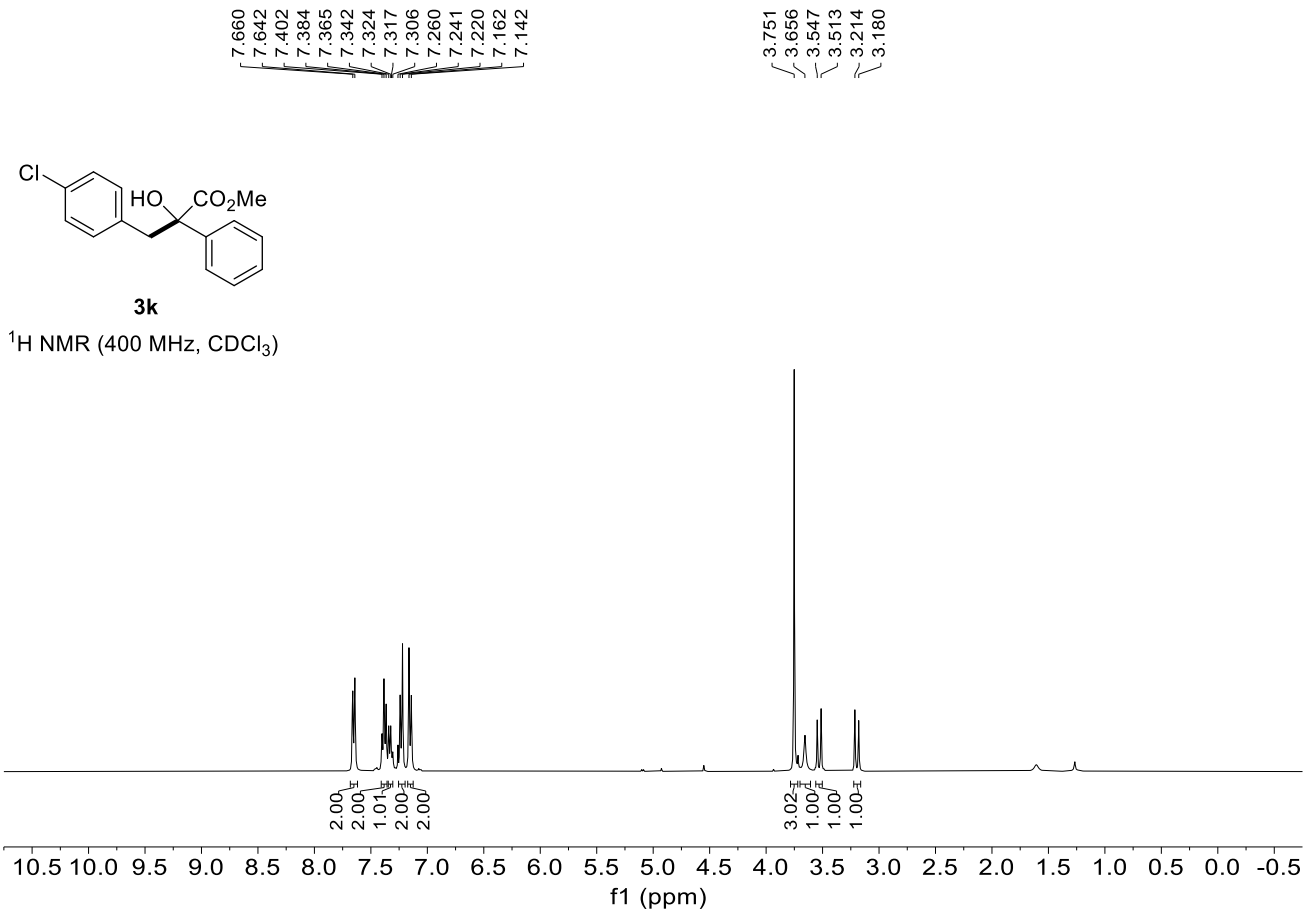
^{13}C NMR (101 MHz, $CDCl_3$)





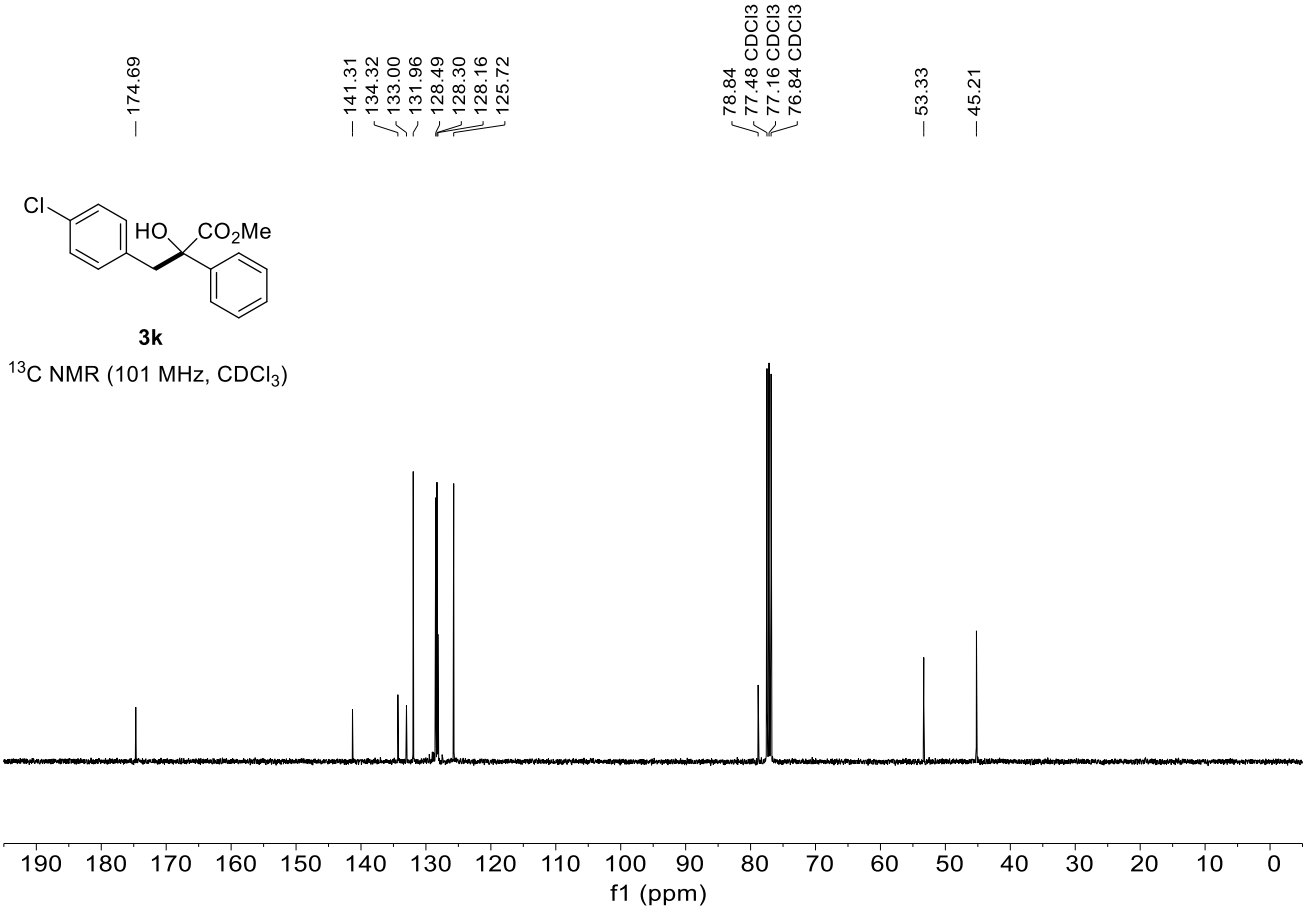
3j

^{19}F NMR (376 MHz, $CDCl_3$)



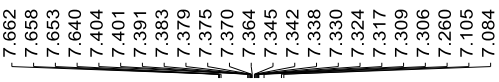
3k

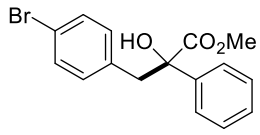
^{1}H NMR (400 MHz, $CDCl_3$)



3k

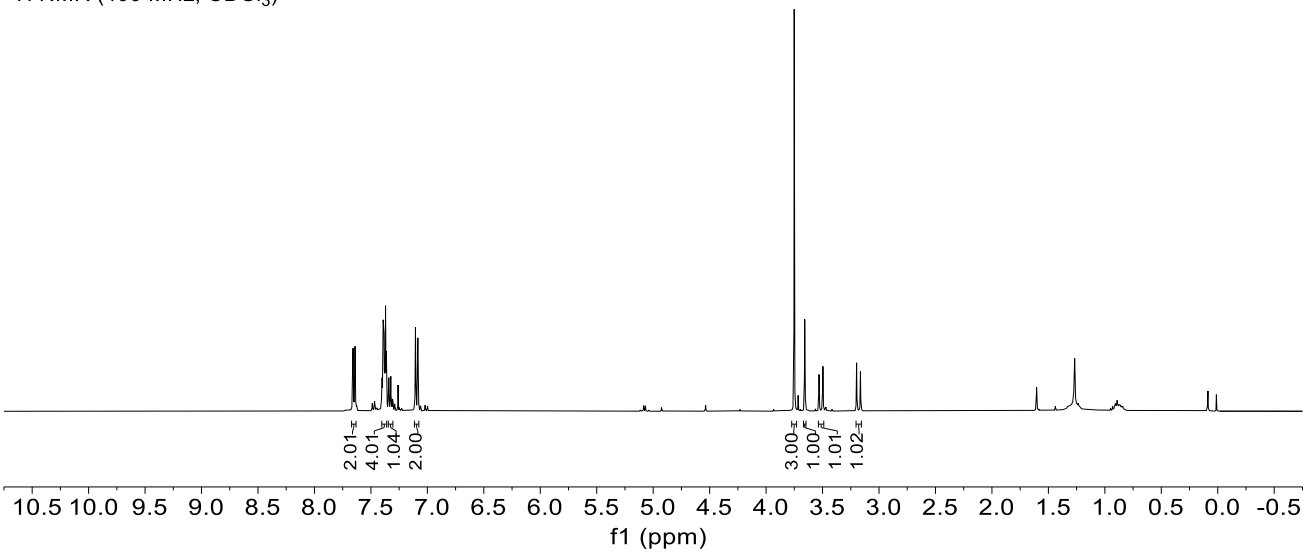
^{13}C NMR (101 MHz, $CDCl_3$)

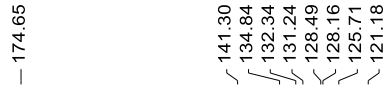


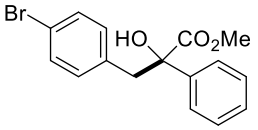


3l

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

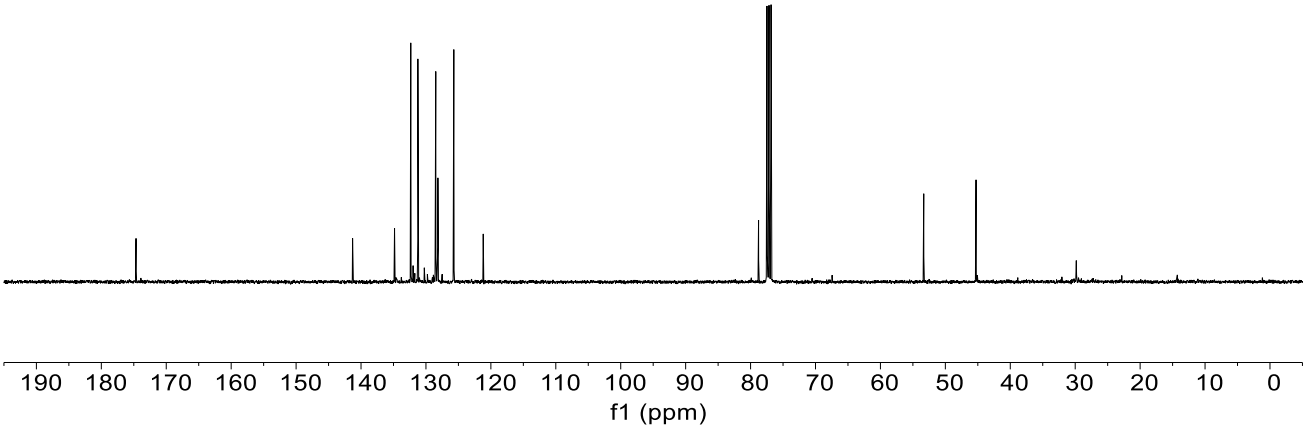


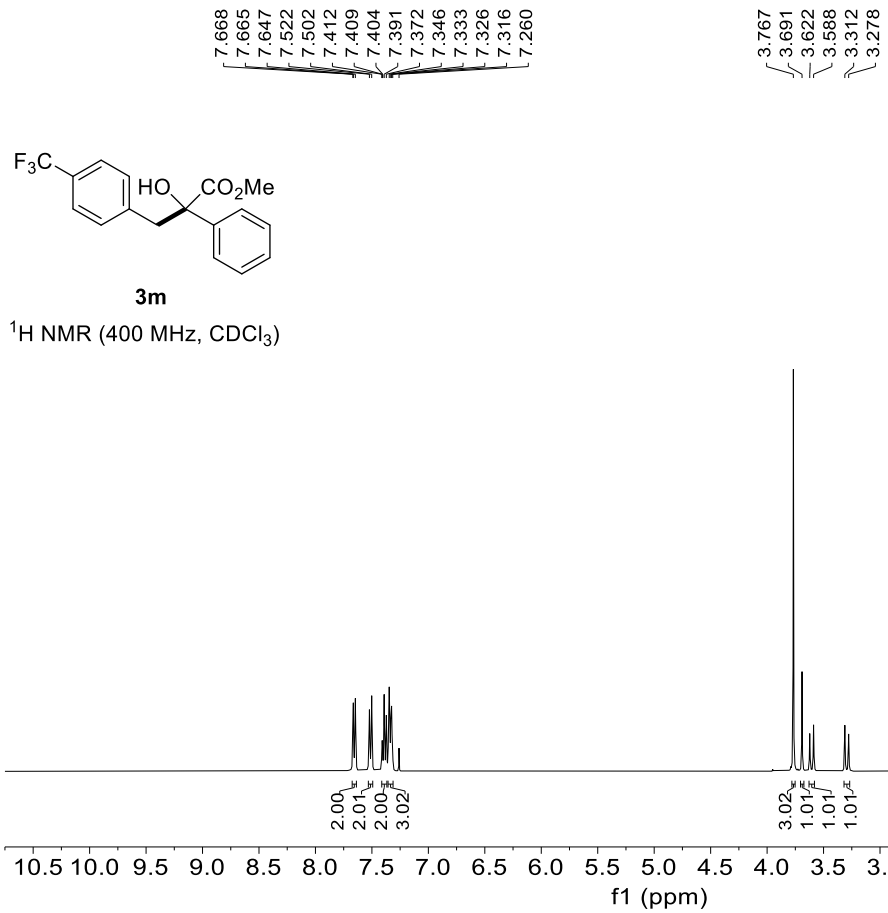


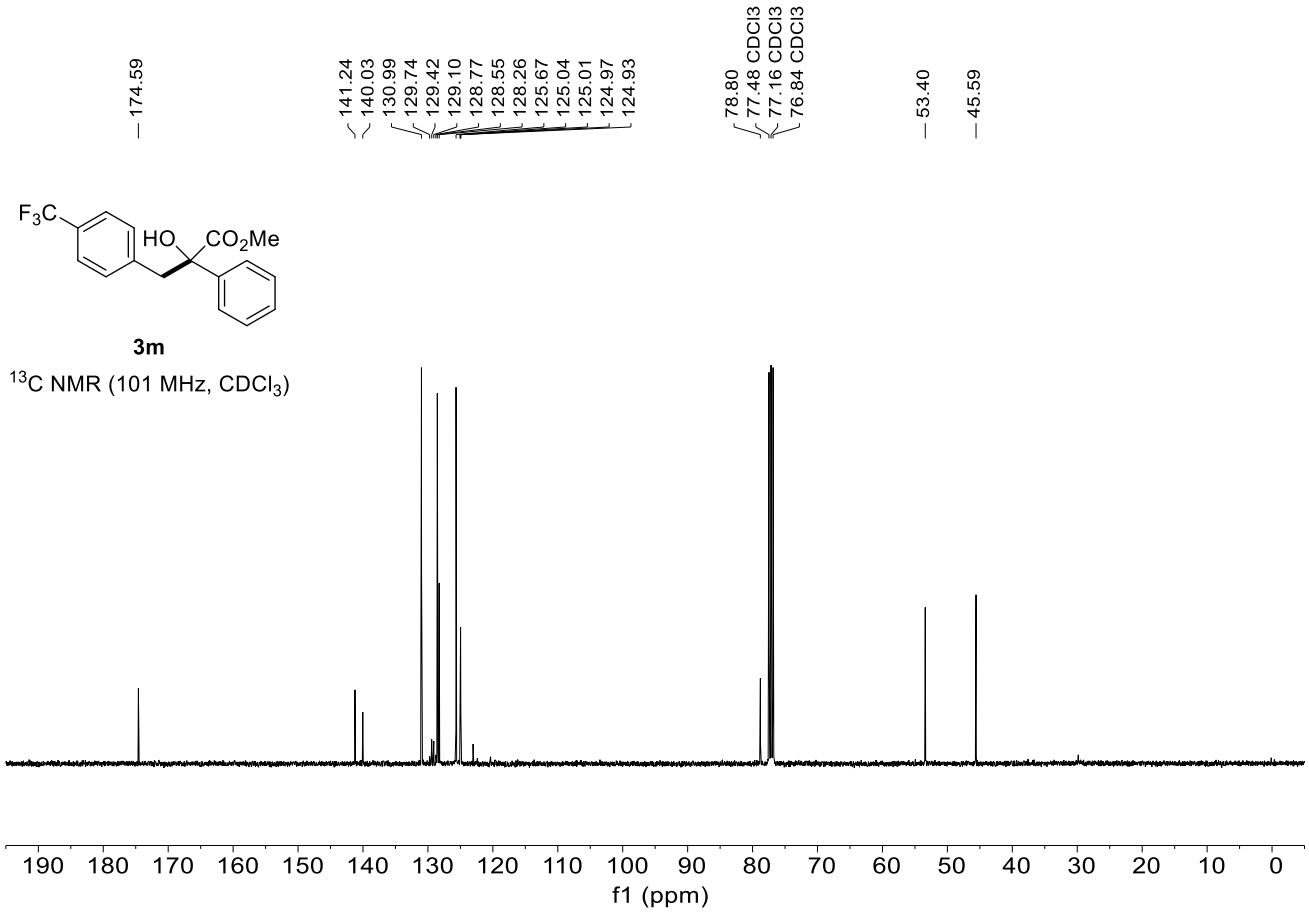


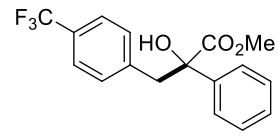
3l

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



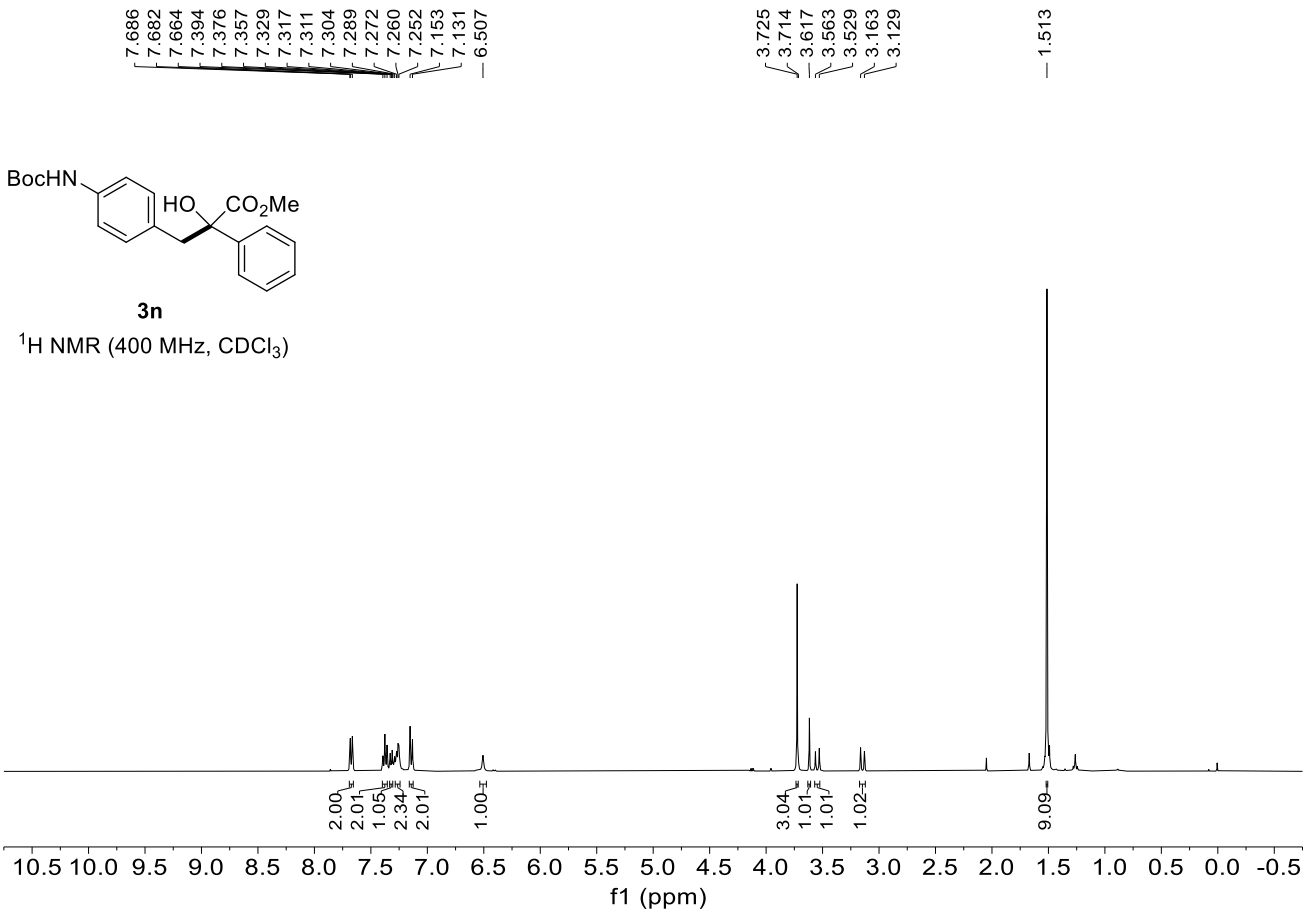

7.668
7.665
7.647
7.522
7.502
7.412
7.409
7.404
7.391
7.372
7.346
7.333
7.326
7.316
7.260
3.767
3.691
3.622
3.588
3.312
3.278
F3C
HO
CO2Me
3m
1H NMR (400 MHz, CDCl3)
2.00
2.01
2.00
3.02
3.02
1.01
1.01
1.01
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


174.59
141.24
140.03
130.99
129.74
129.42
129.10
128.77
128.55
128.26
125.67
125.04
125.01
124.97
124.93
78.80
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
53.40
45.59
F3C
HO
CO2Me
3m
13C NMR (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



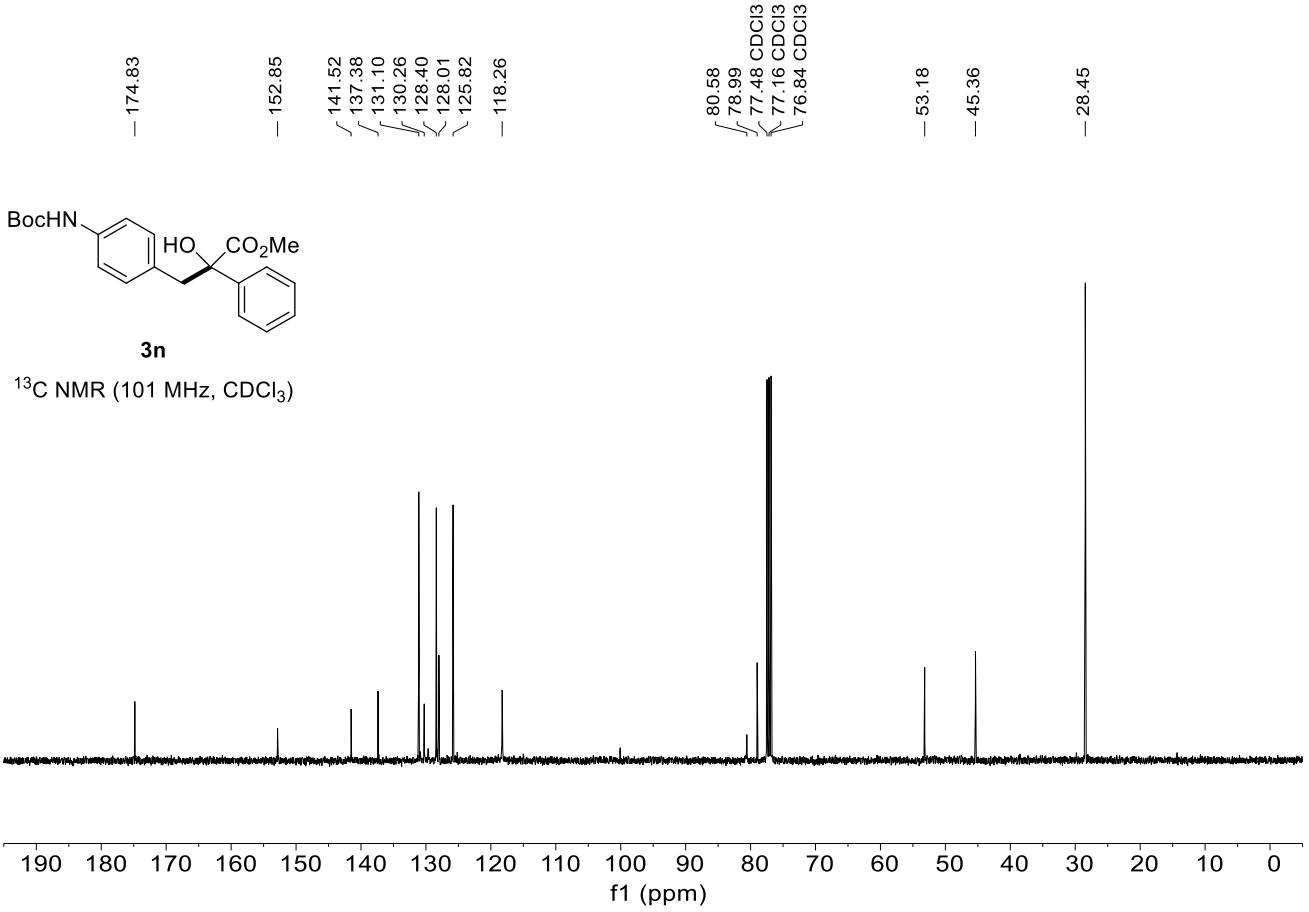
3m

^{19}F NMR (376 MHz, $CDCl_3$)



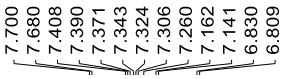
3n

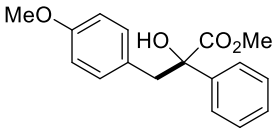
^{1}H NMR (400 MHz, $CDCl_3$)



3n

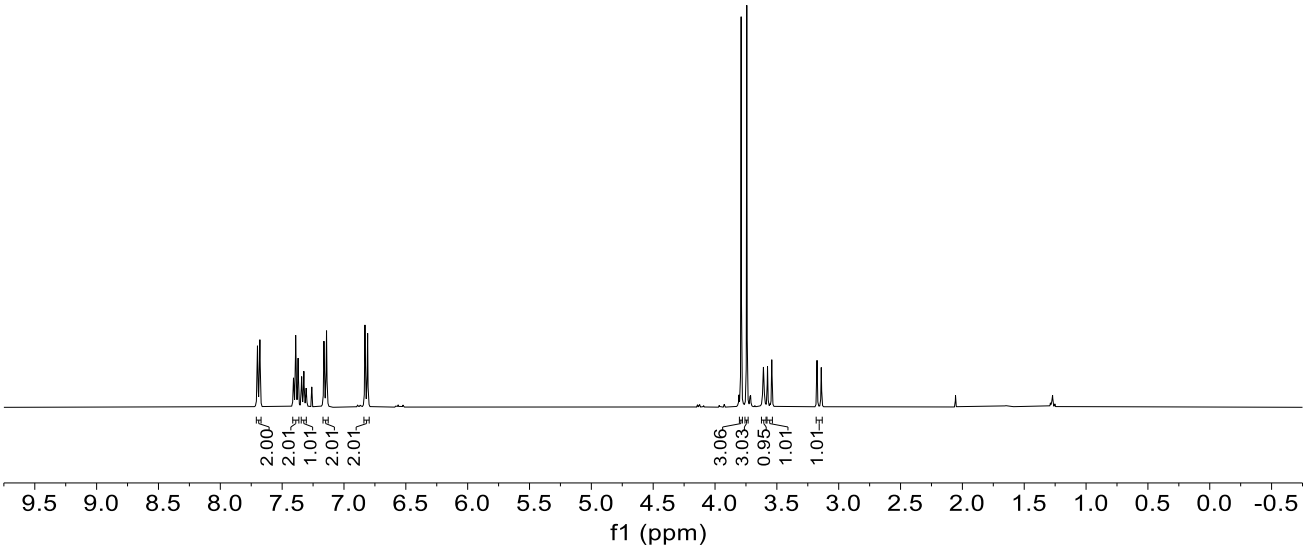
^{13}C NMR (101 MHz, $CDCl_3$)

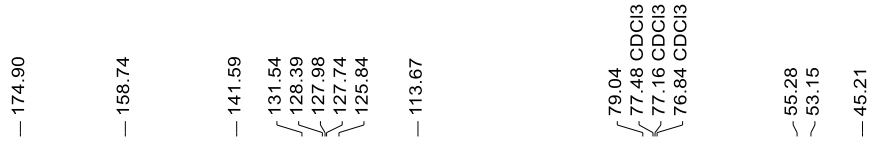


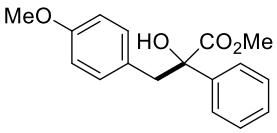


3o

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

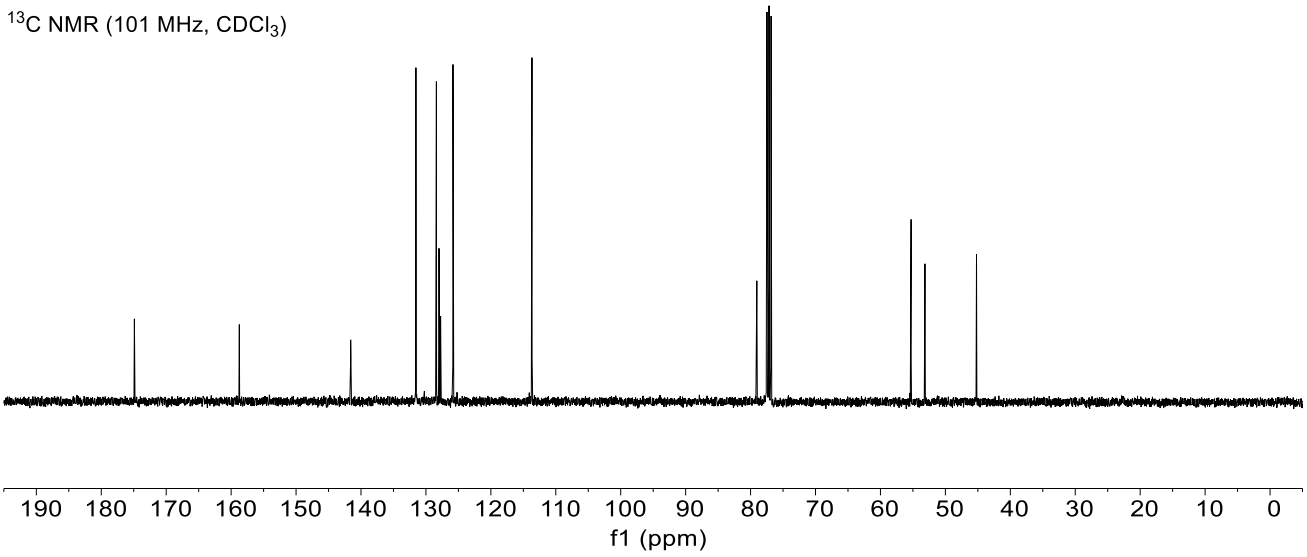


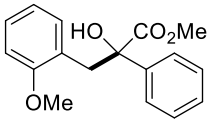




3o

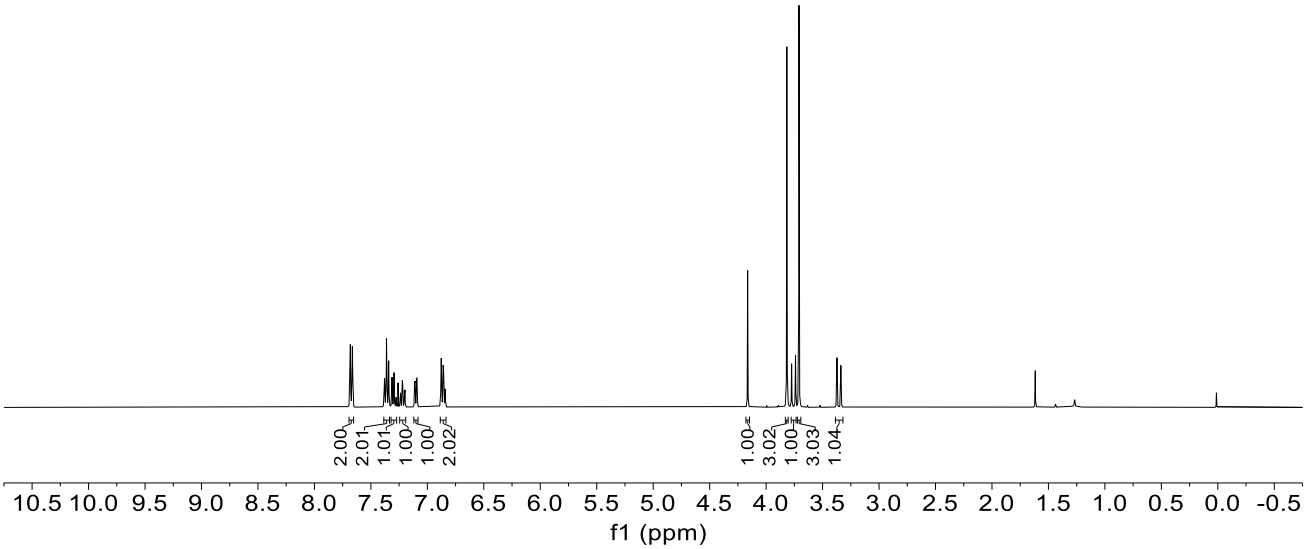
^{13}C NMR (101 MHz, $CDCl_3$)

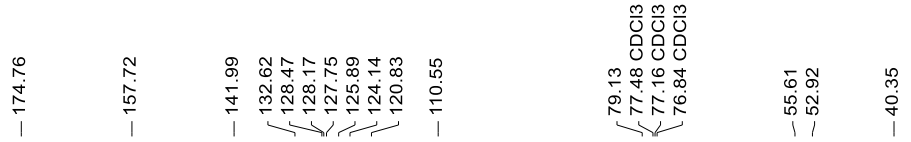


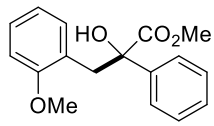


3p

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

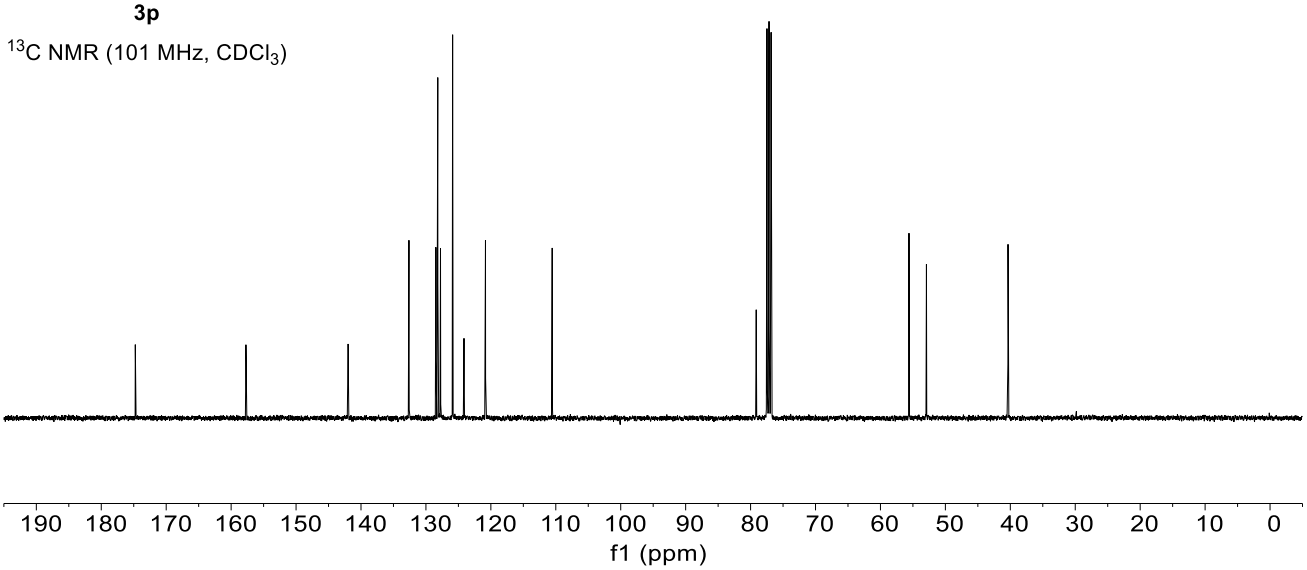


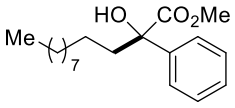




3p

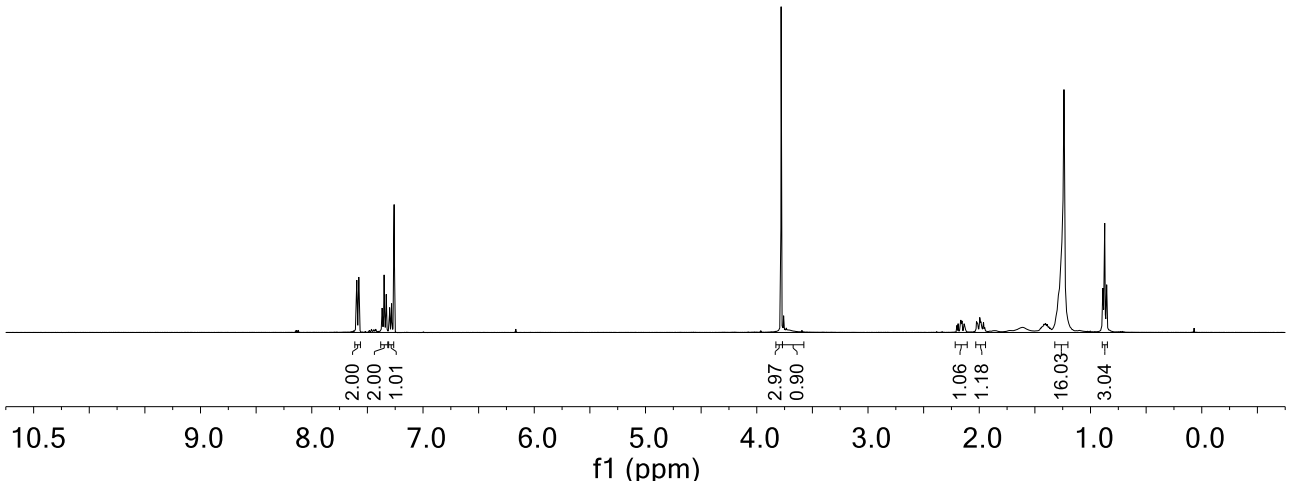
^{13}C NMR (101 MHz, $CDCl_3$)

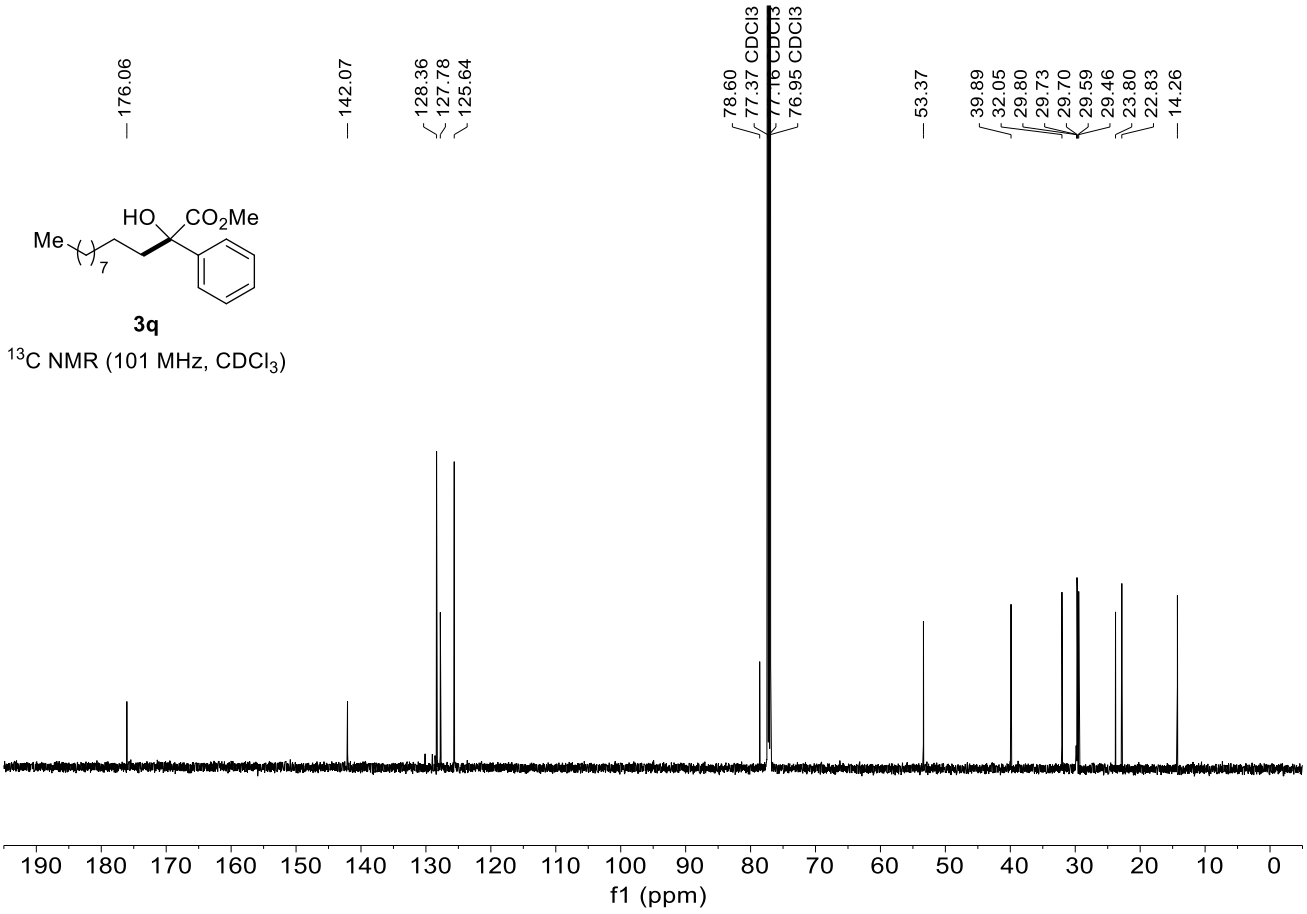




3q

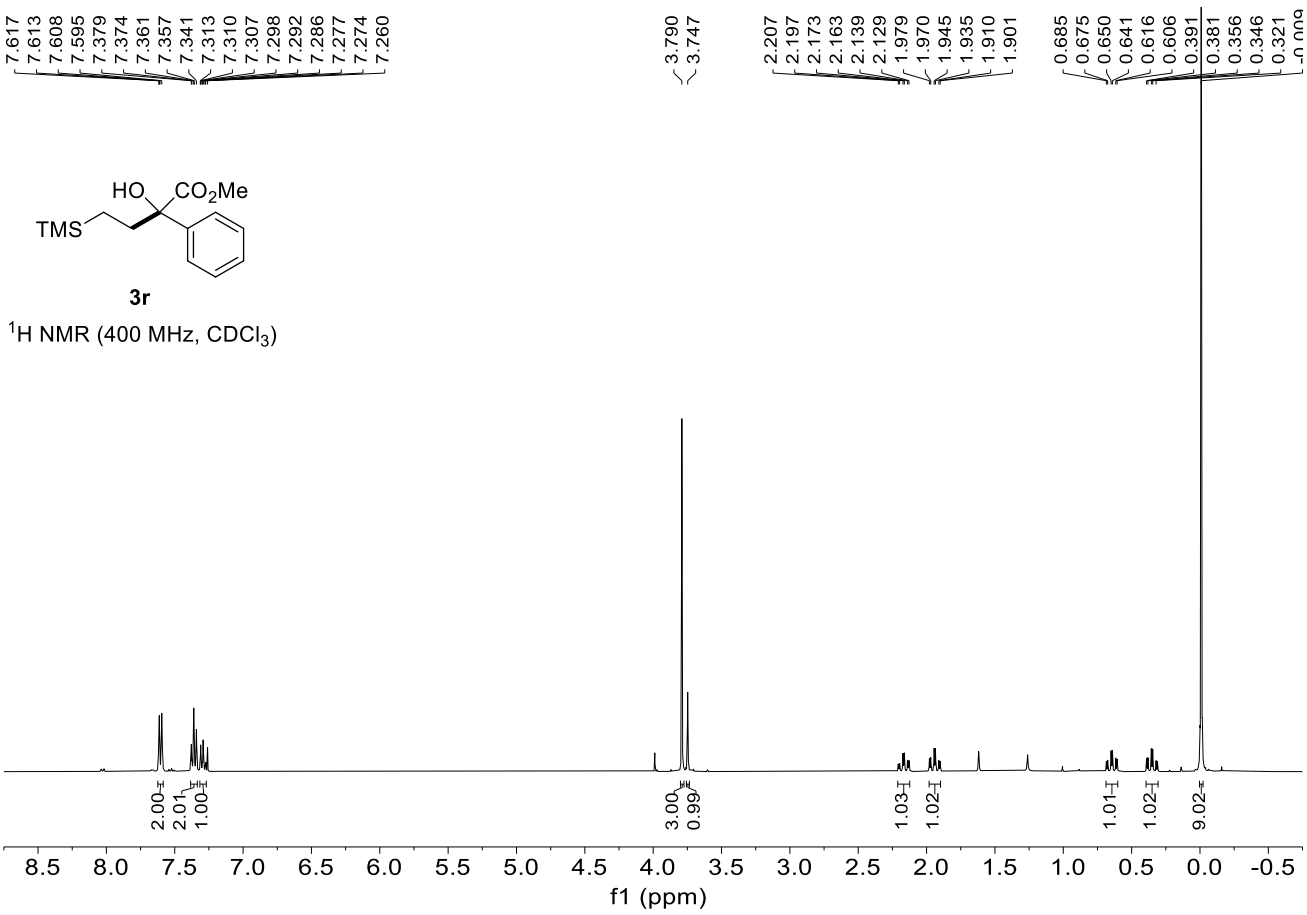
^{1}H NMR (400 MHz, $CDCl_3$)





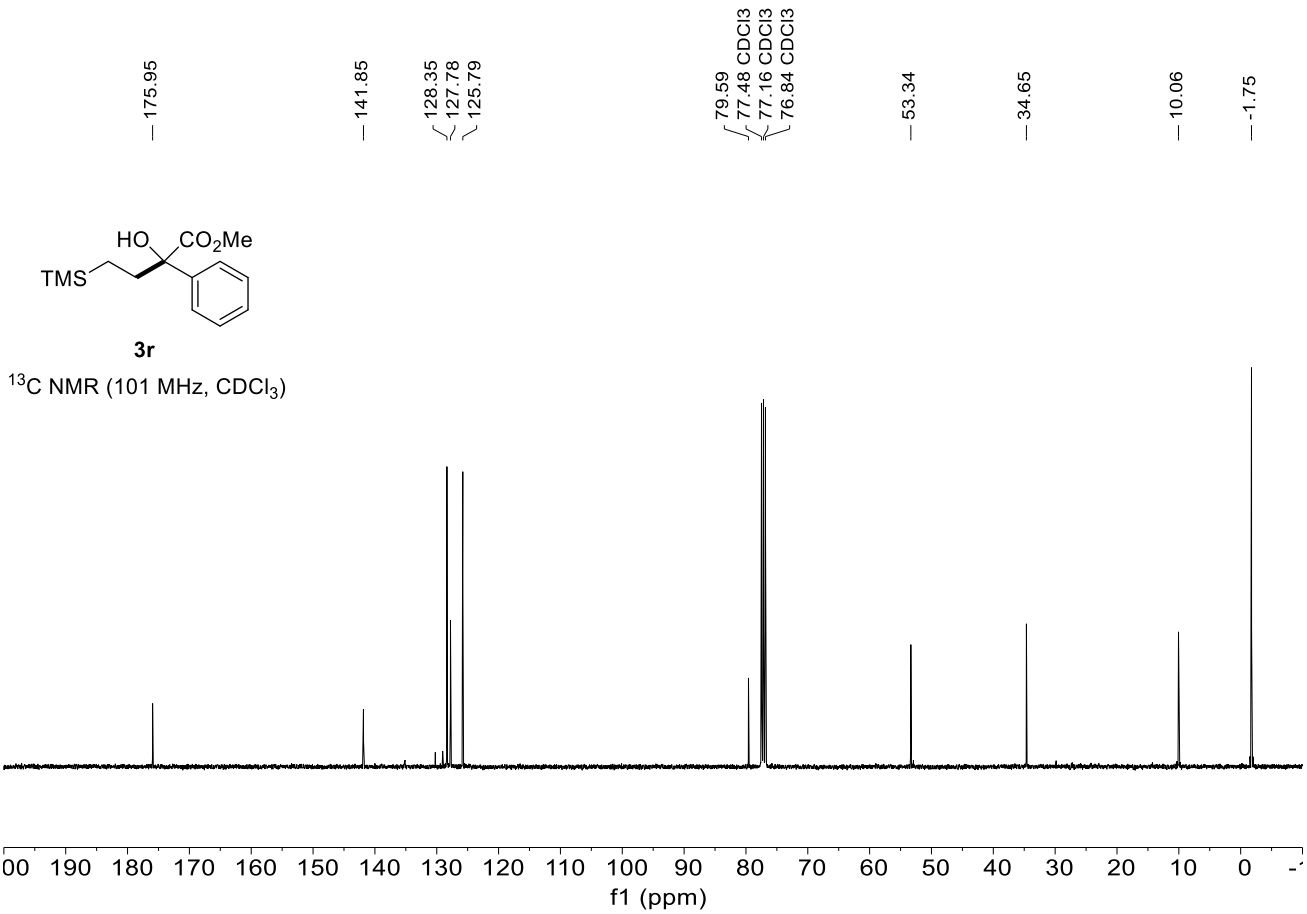
3q

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



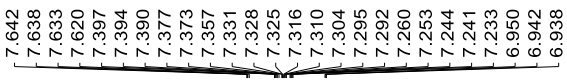
3r

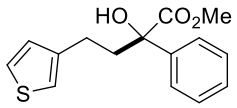
^{1}H NMR (400 MHz, $CDCl_3$)



3r

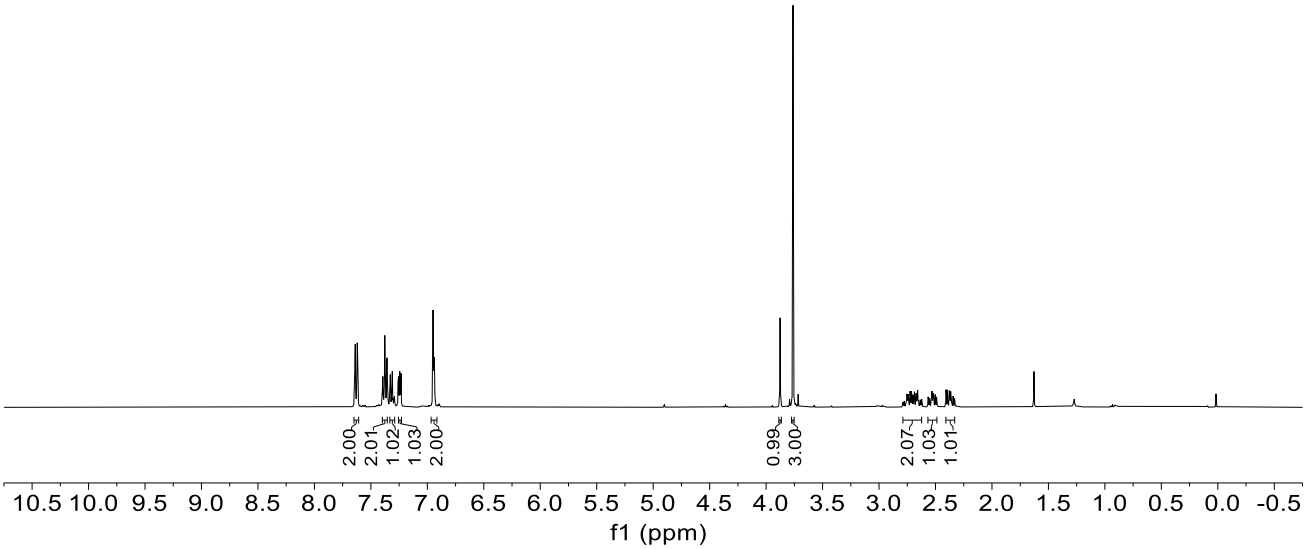
^{13}C NMR (101 MHz, $CDCl_3$)

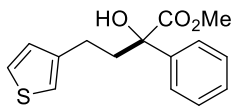




3s

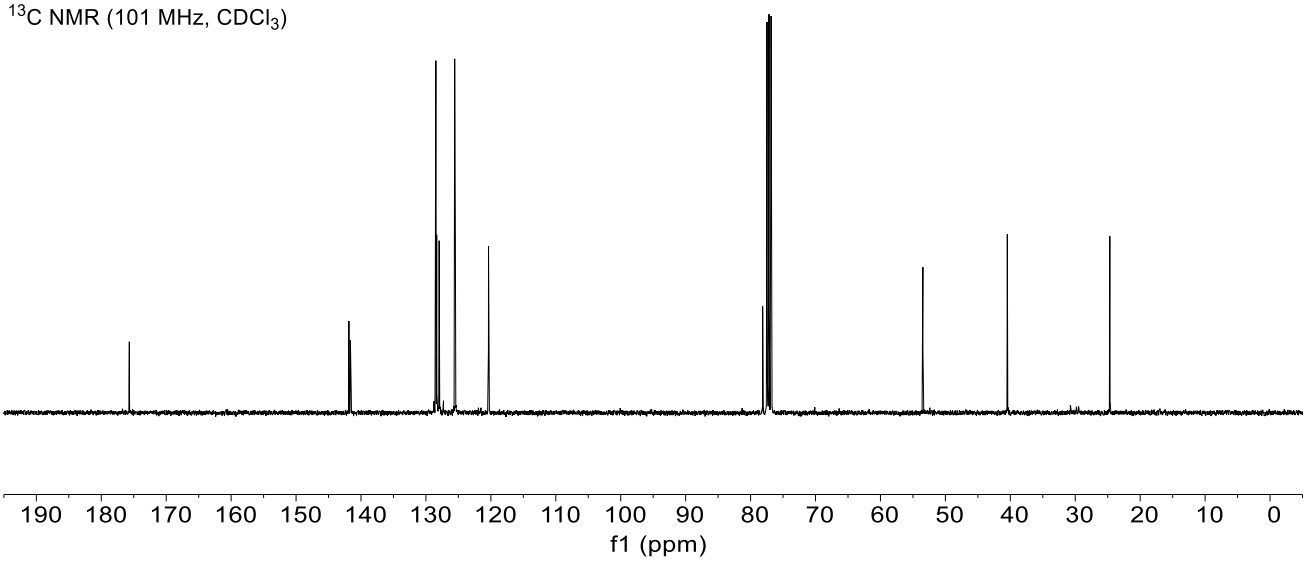
^{1}H NMR (400 MHz, $CDCl_3$)

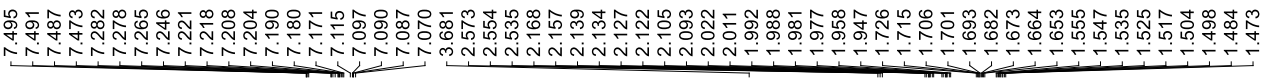


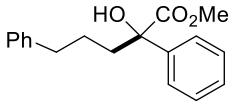


3s

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

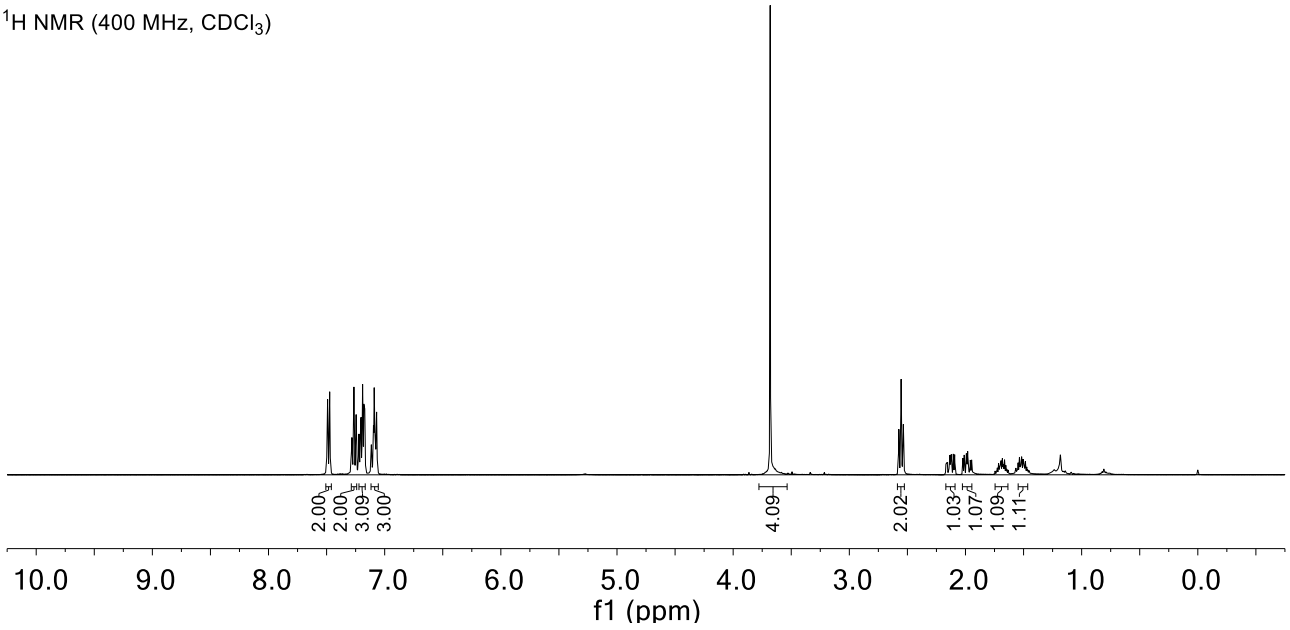


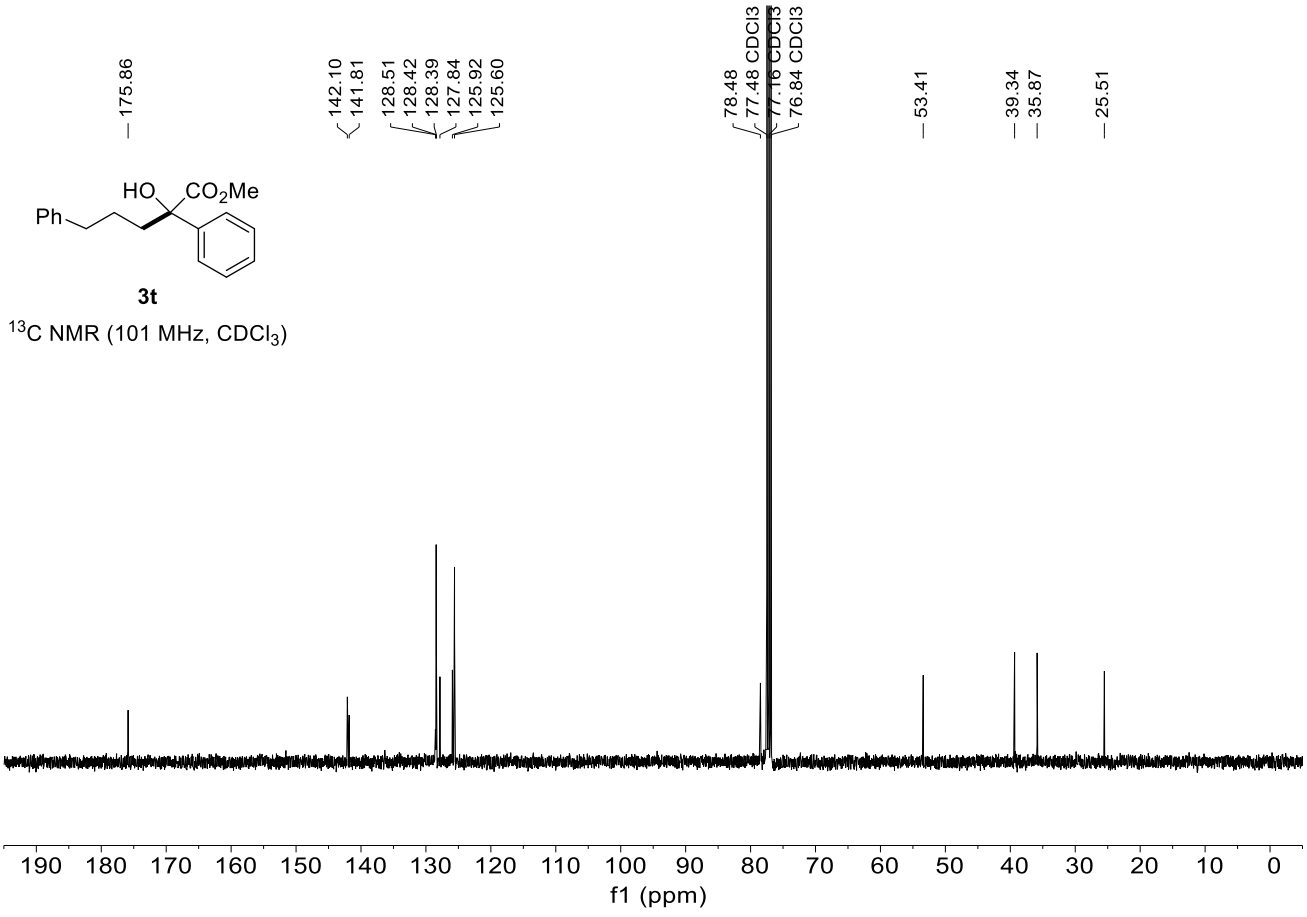




3t

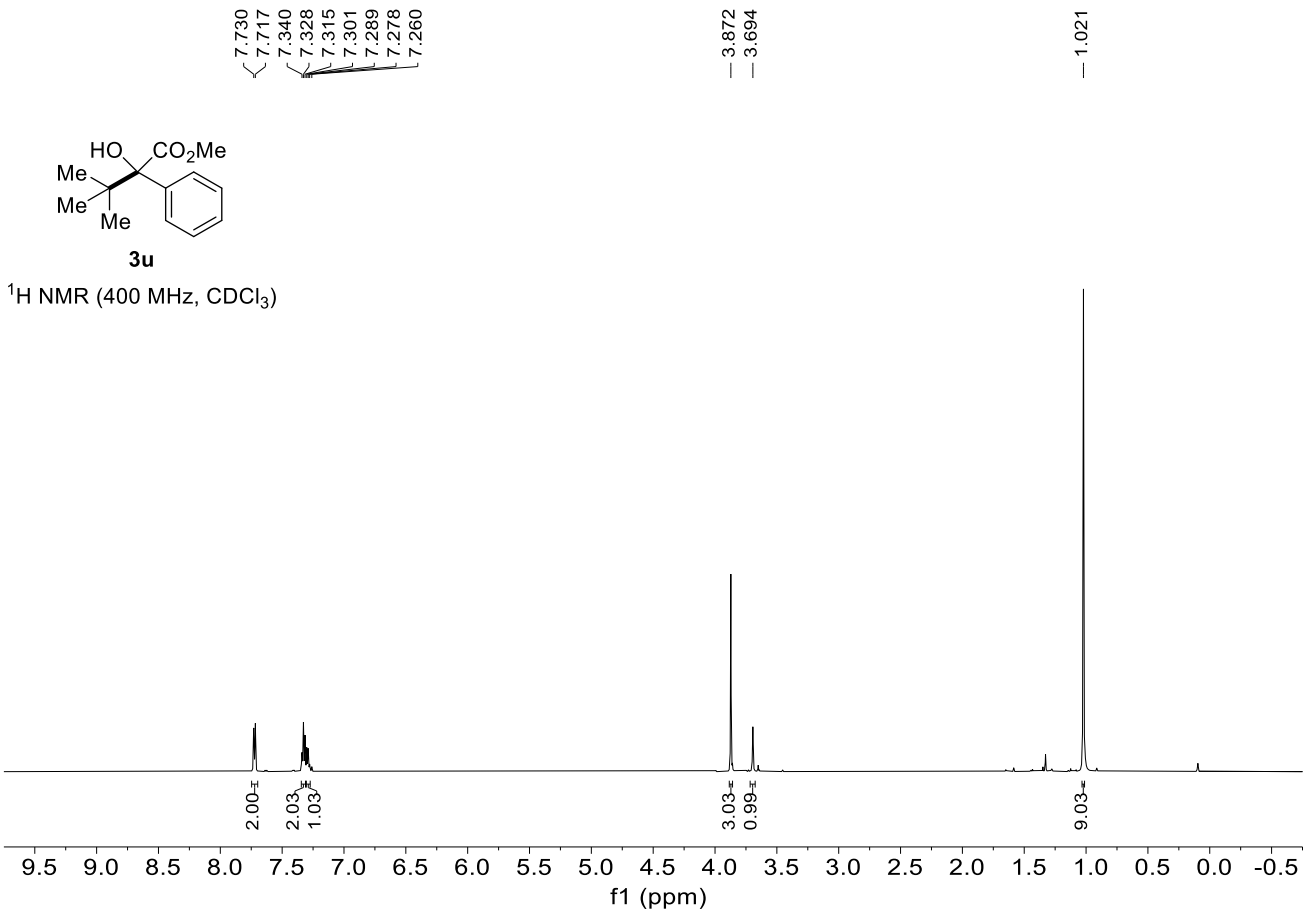
^{1}H NMR (400 MHz, $CDCl_3$)





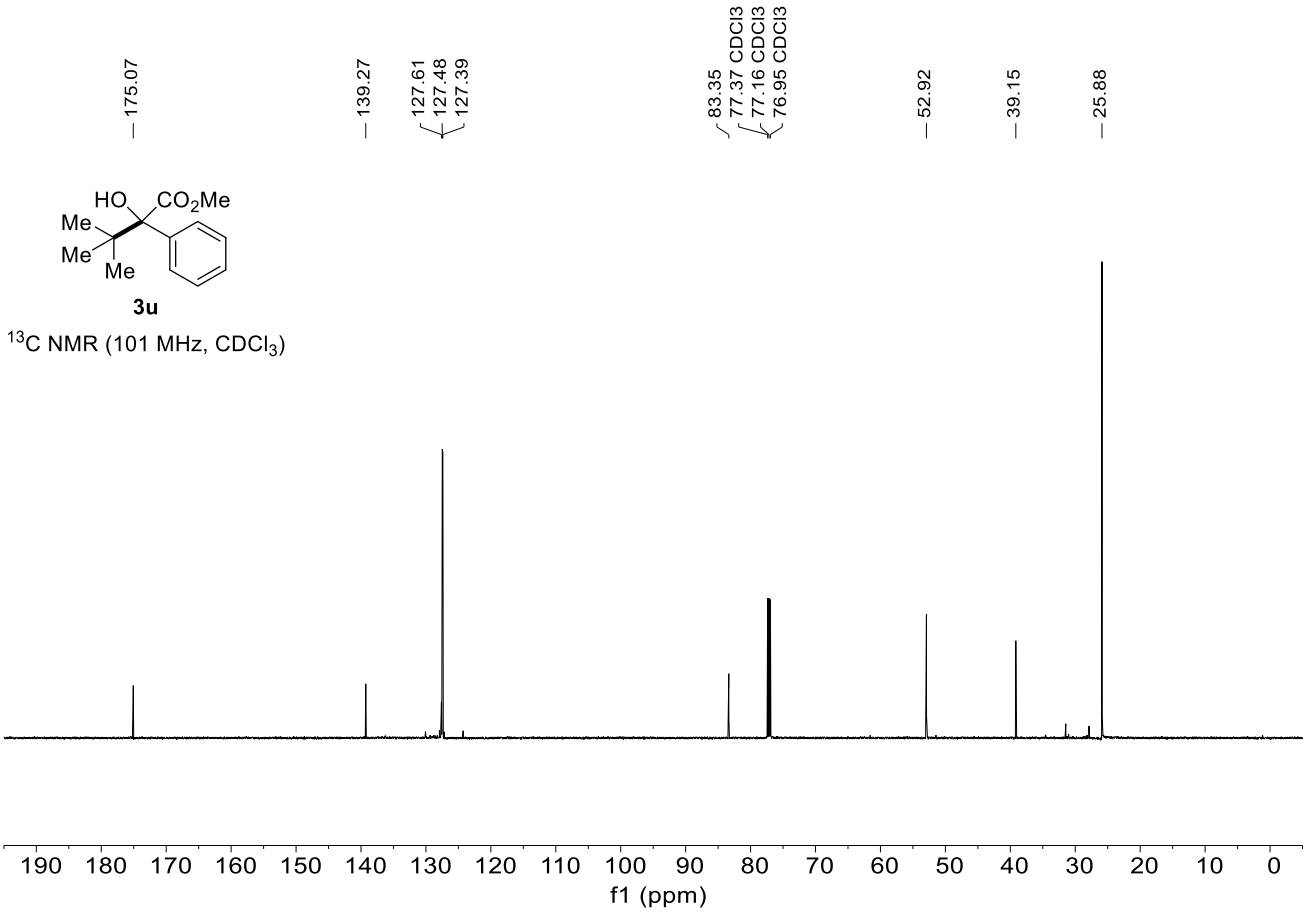
3t

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



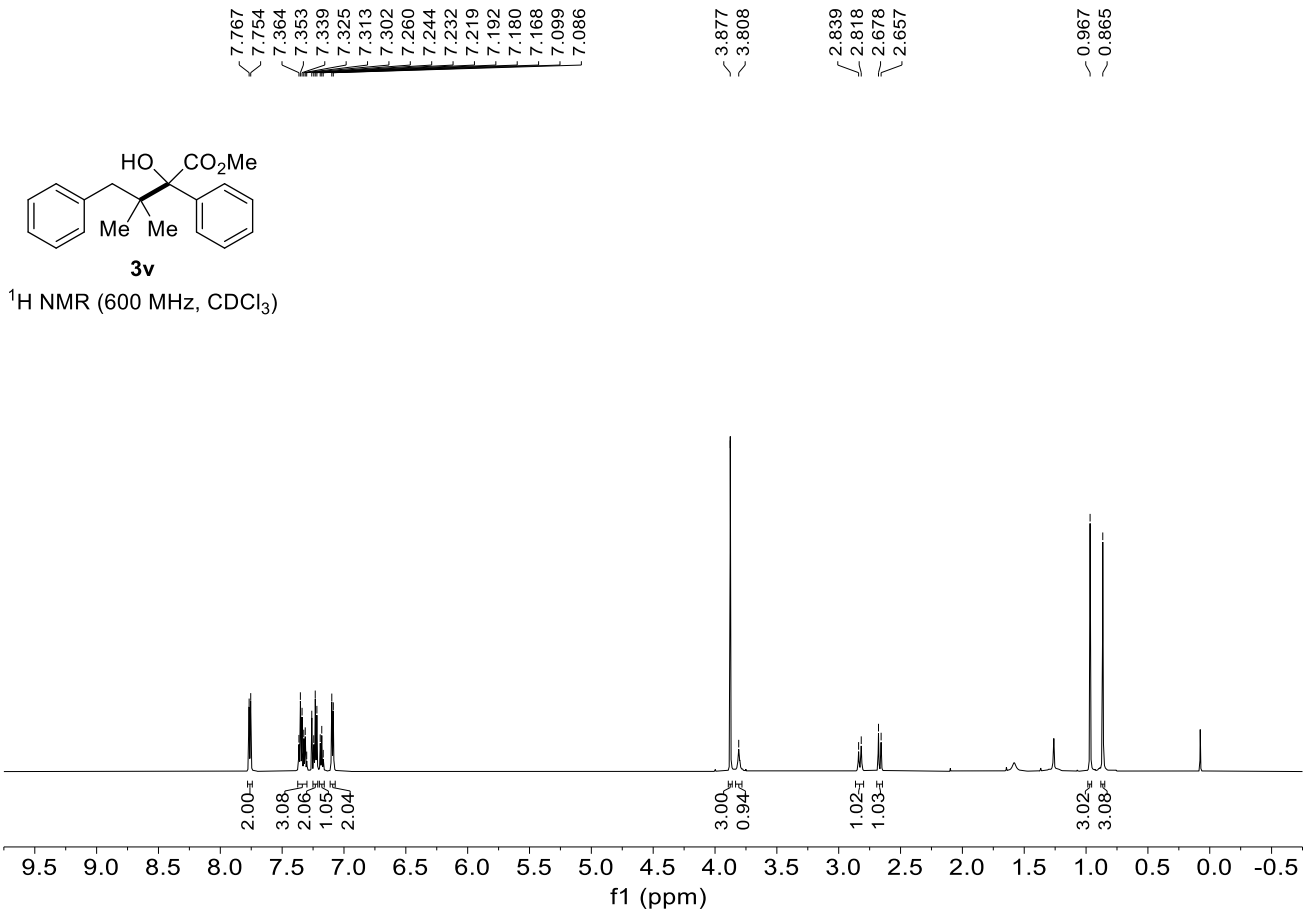
3u

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



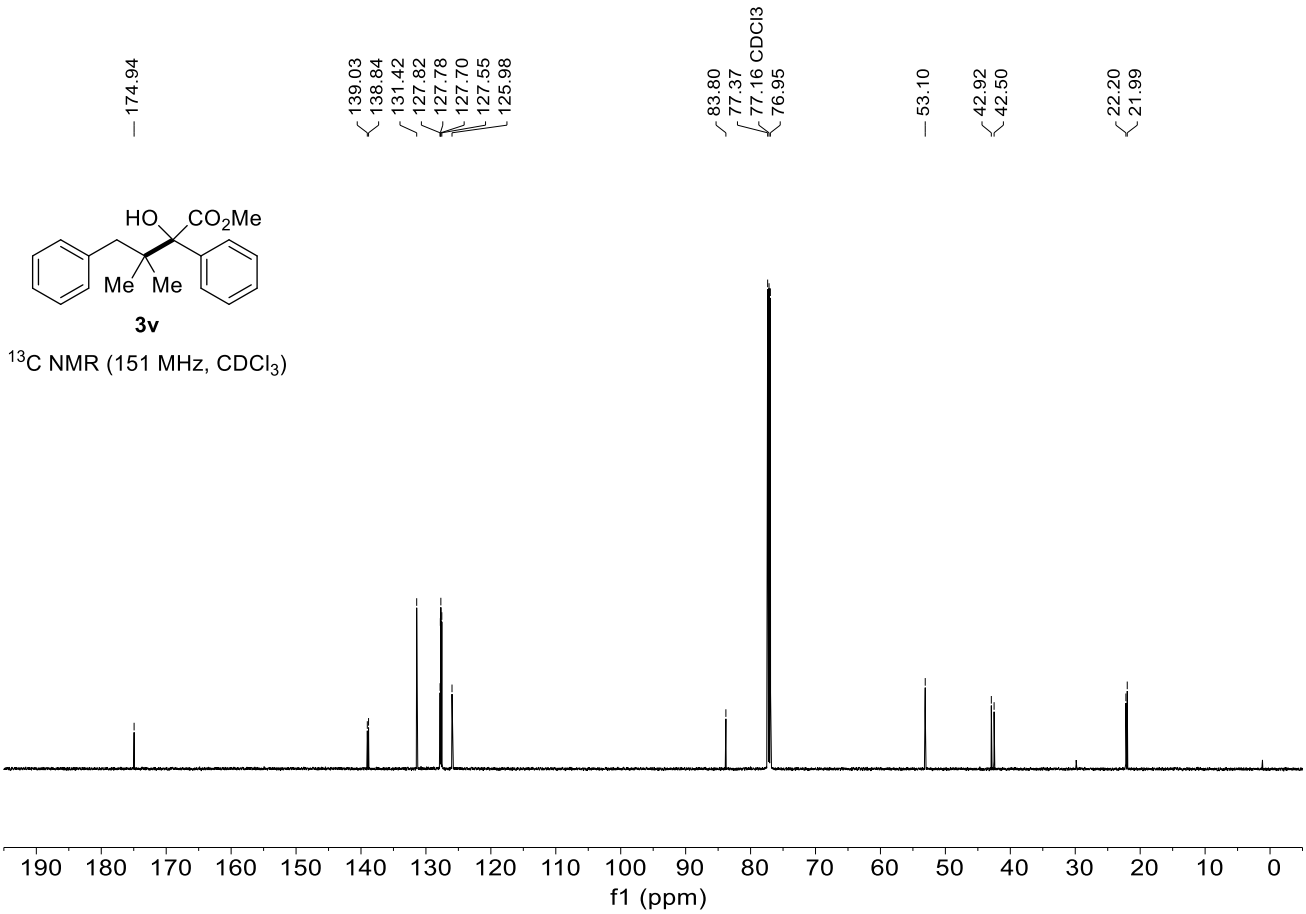
3u

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



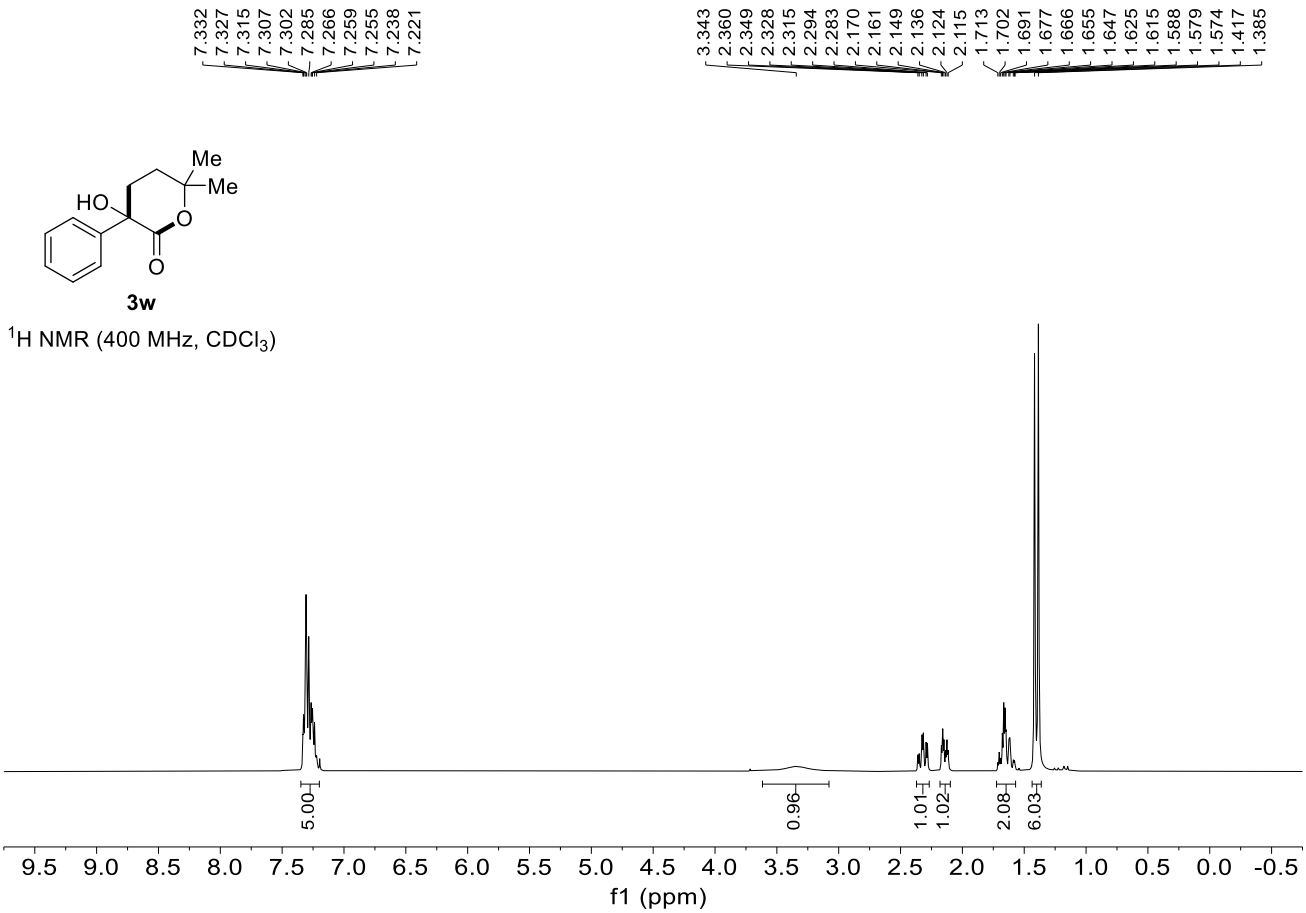
3v

^{1}H NMR (600 MHz, $CDCl_3$)



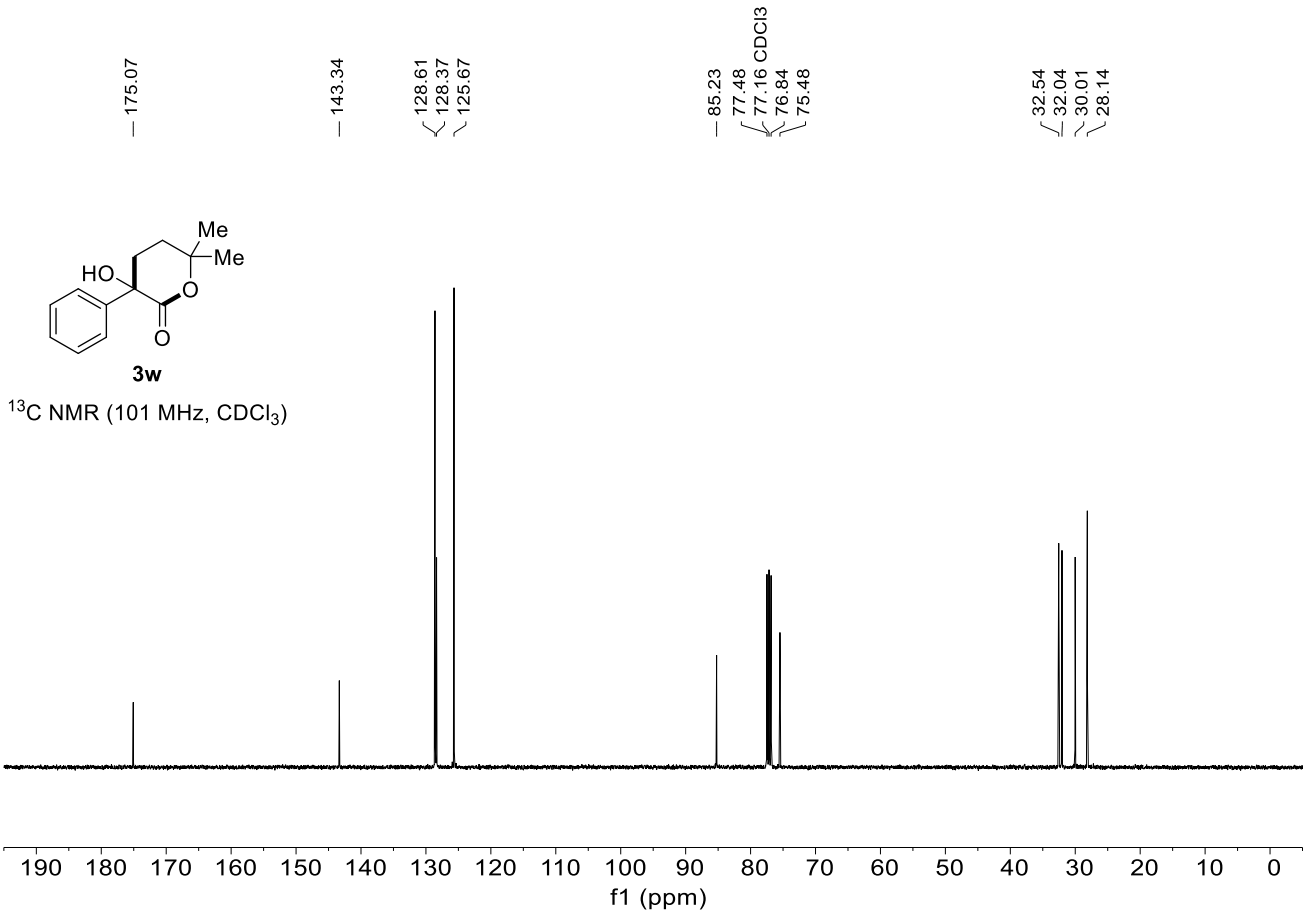
3v

^{13}C NMR (151 MHz, $CDCl_3$)



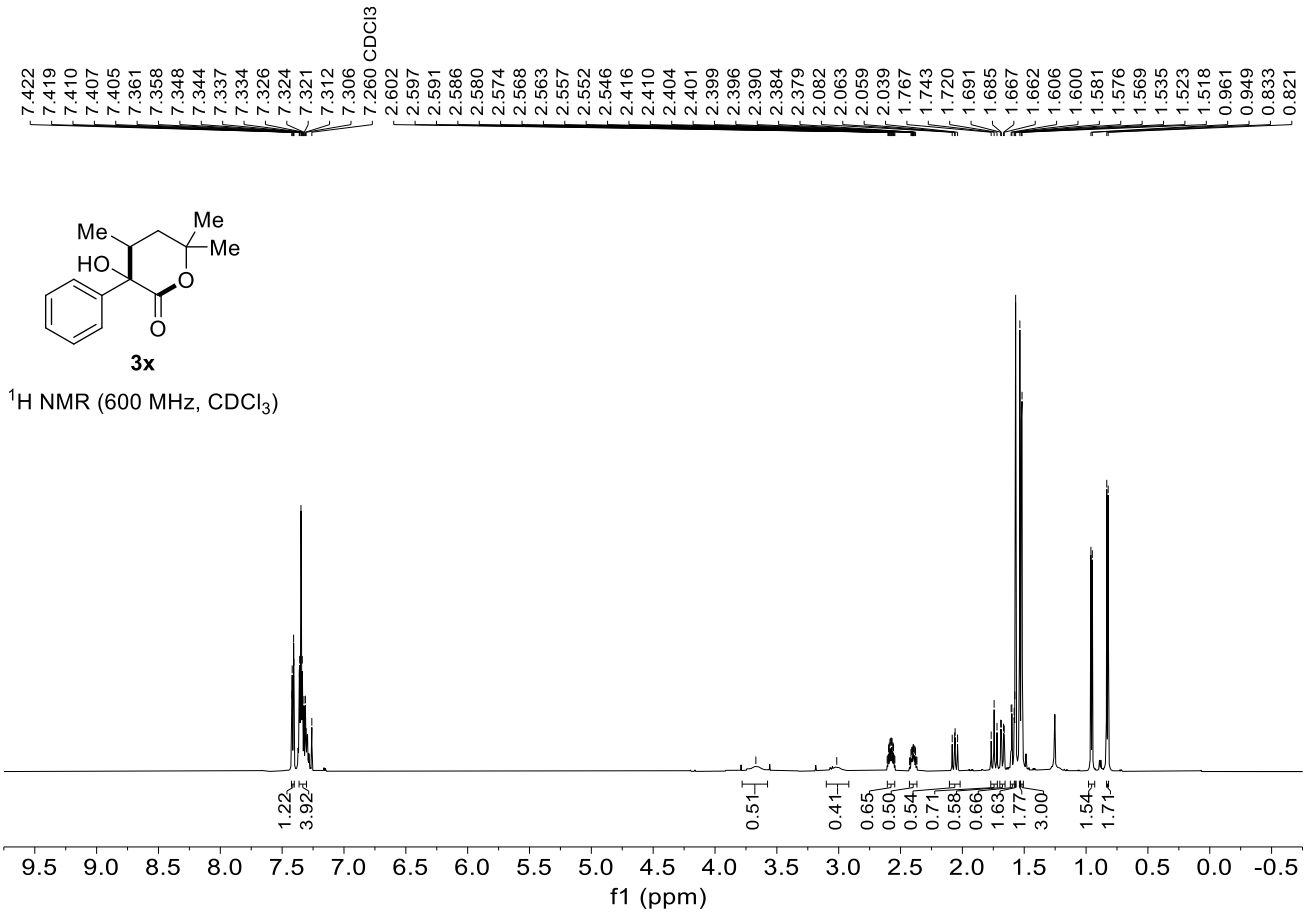
3w

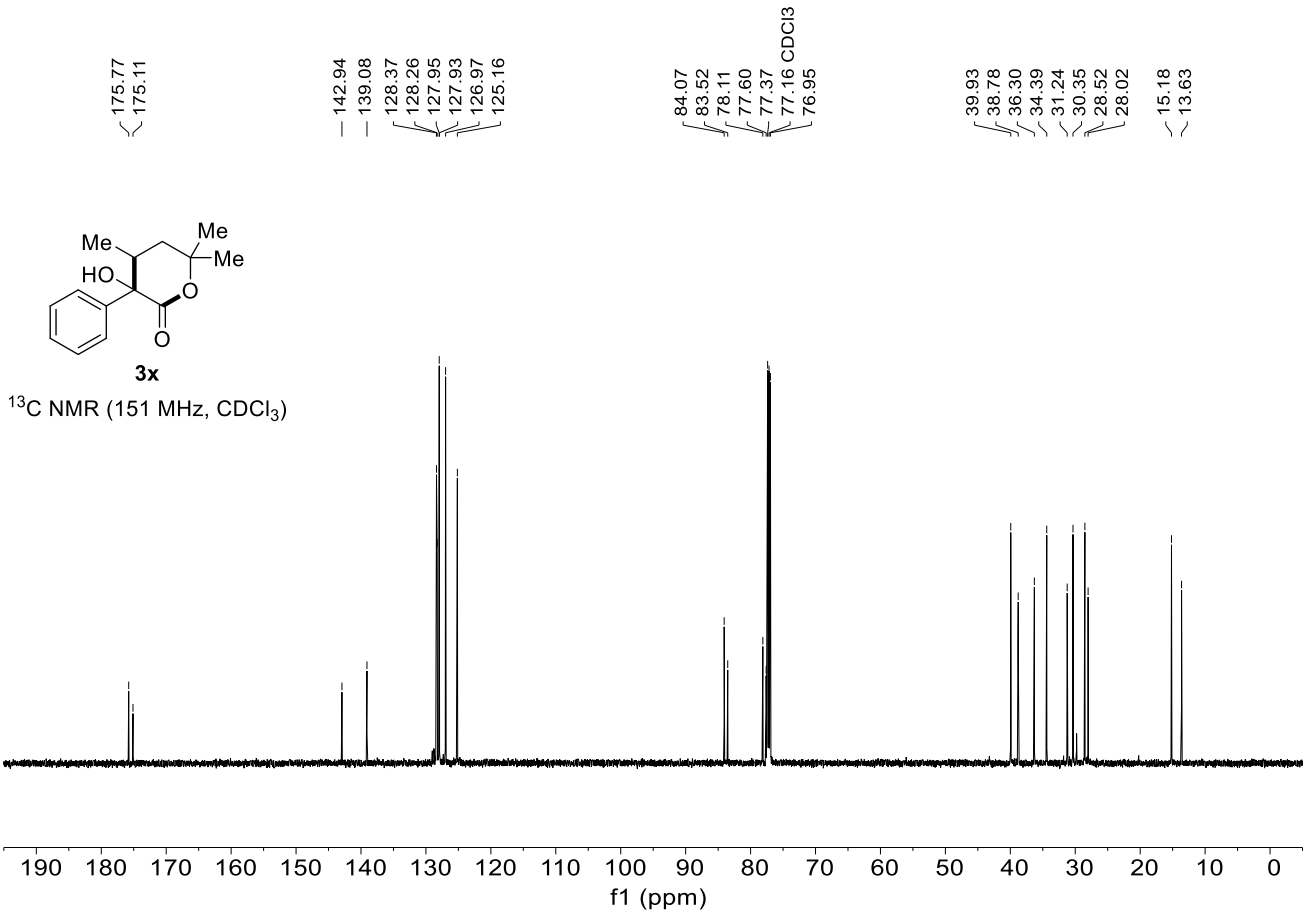
^{1}H NMR (400 MHz, $CDCl_3$)

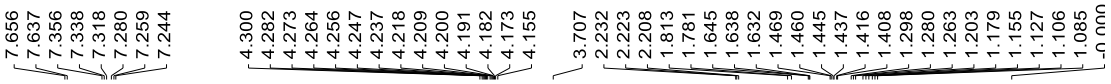


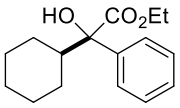
3w

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


7.422
7.419
7.410
7.407
7.405
7.361
7.358
7.348
7.344
7.337
7.334
7.326
7.324
7.321
7.312
7.306
CDCl3
7.260
2.602
2.597
2.591
2.586
2.580
2.574
2.568
2.563
2.557
2.552
2.546
2.416
2.410
2.404
2.401
2.399
2.396
2.390
2.384
2.379
2.082
2.063
2.059
2.039
1.767
1.743
1.720
1.691
1.685
1.667
1.662
1.606
1.600
1.581
1.576
1.569
1.535
1.523
1.518
0.961
0.949
0.833
0.821
Me
Me
Me
HO
O
O
3x
1H NMR (600 MHz, CDCl3)
1.22
3.92
0.51
0.41
0.65
0.50
0.54
0.71
0.58
0.66
1.63
1.77
3.00
1.54
1.71
f1 (ppm)

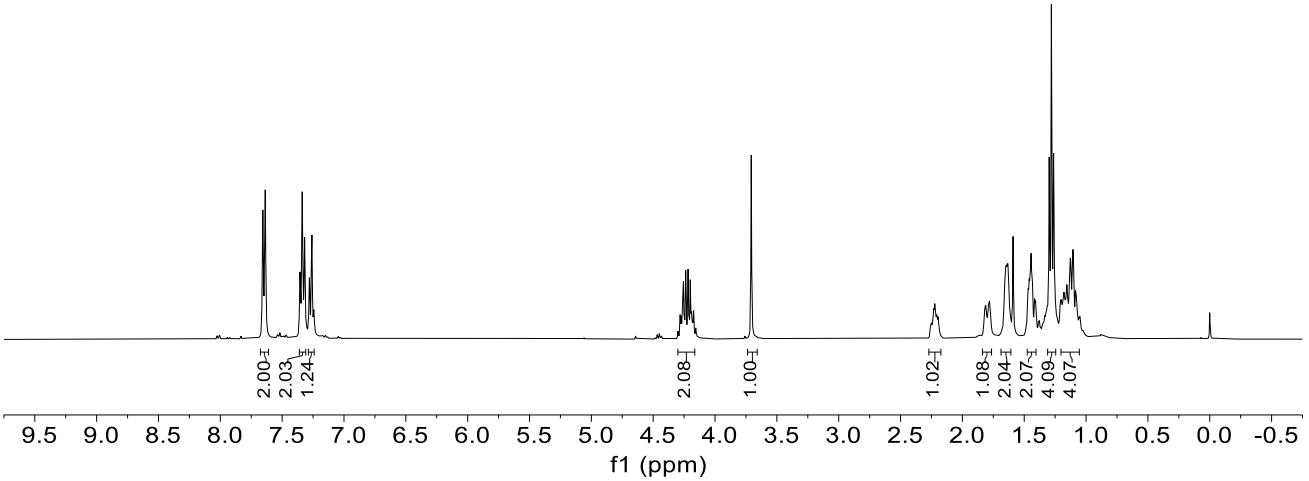

175.77
175.11
142.94
139.08
128.37
128.26
127.95
127.93
126.97
125.16
84.07
83.52
78.11
77.60
77.37
77.16
CDCl3
76.95
39.93
38.78
36.30
34.39
31.24
30.35
28.52
28.02
15.18
13.63
Me
Me
Me
HO
O
O
3x
13C NMR (151 MHz, CDCl3)
f1 (ppm)

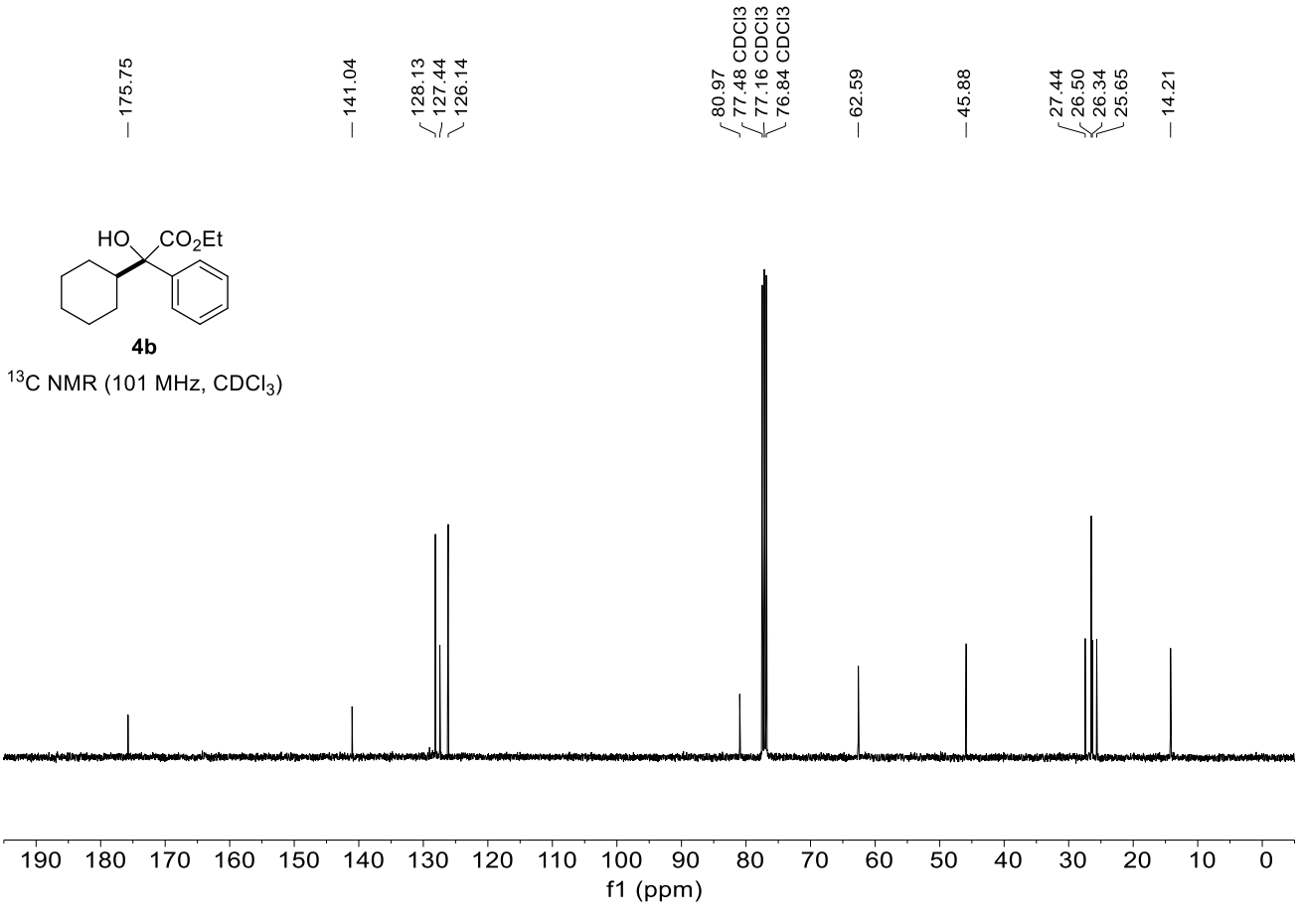




4b

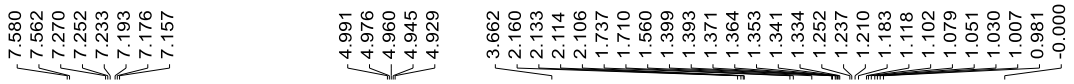
^{1}H NMR (400 MHz, $CDCl_3$)

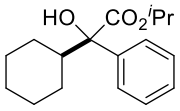




4b

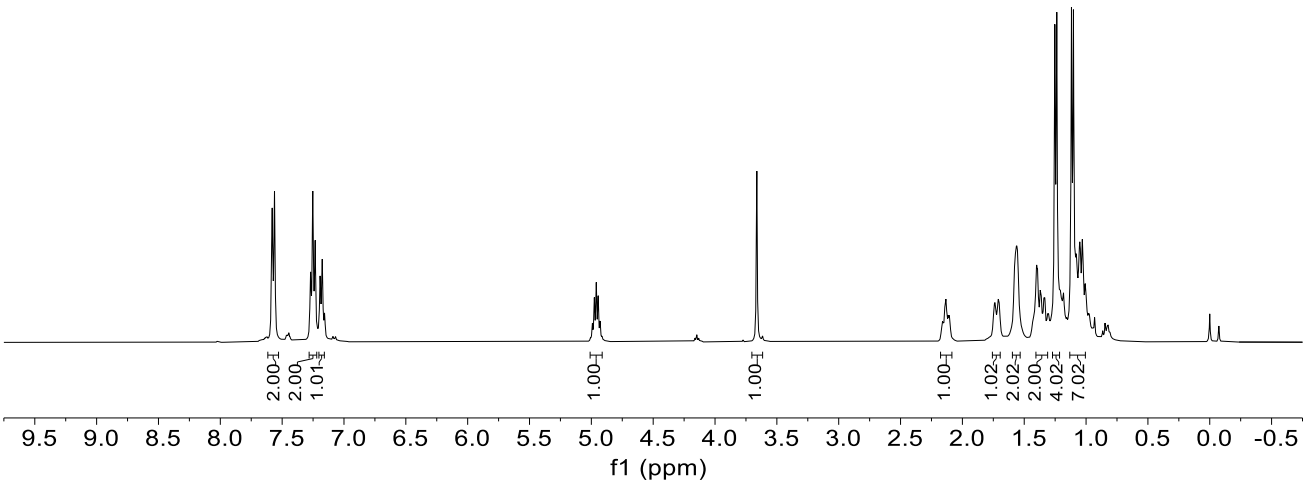
^{13}C NMR (101 MHz, $CDCl_3$)

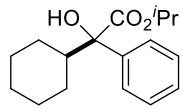




4c

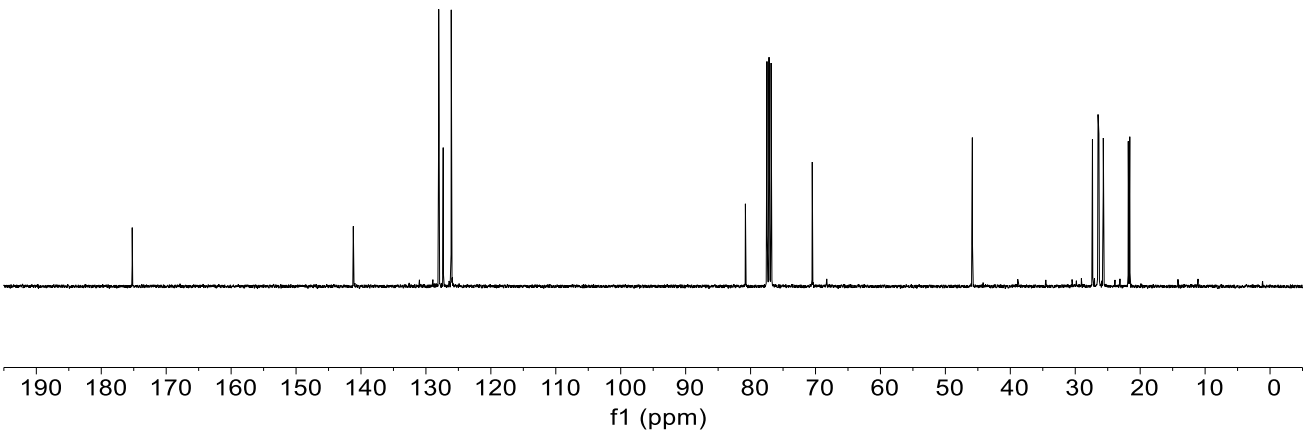
^{1}H NMR (400 MHz, $CDCl_3$)

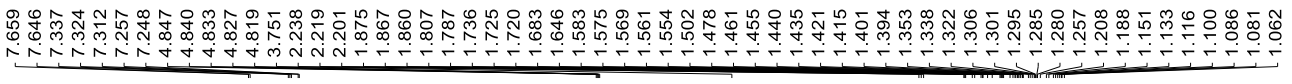


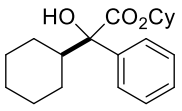


4c

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

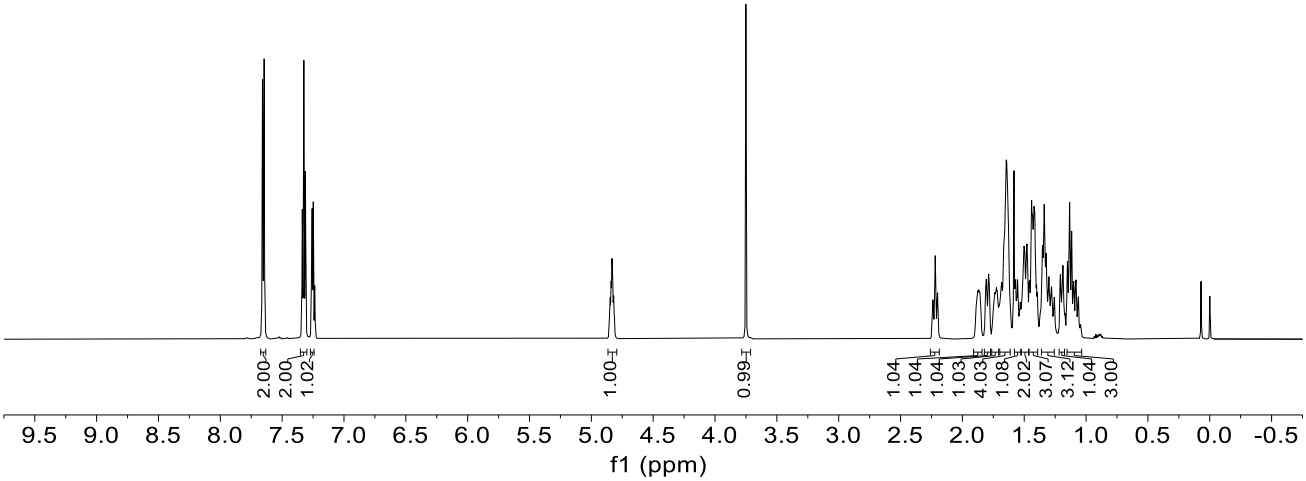


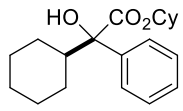




4d

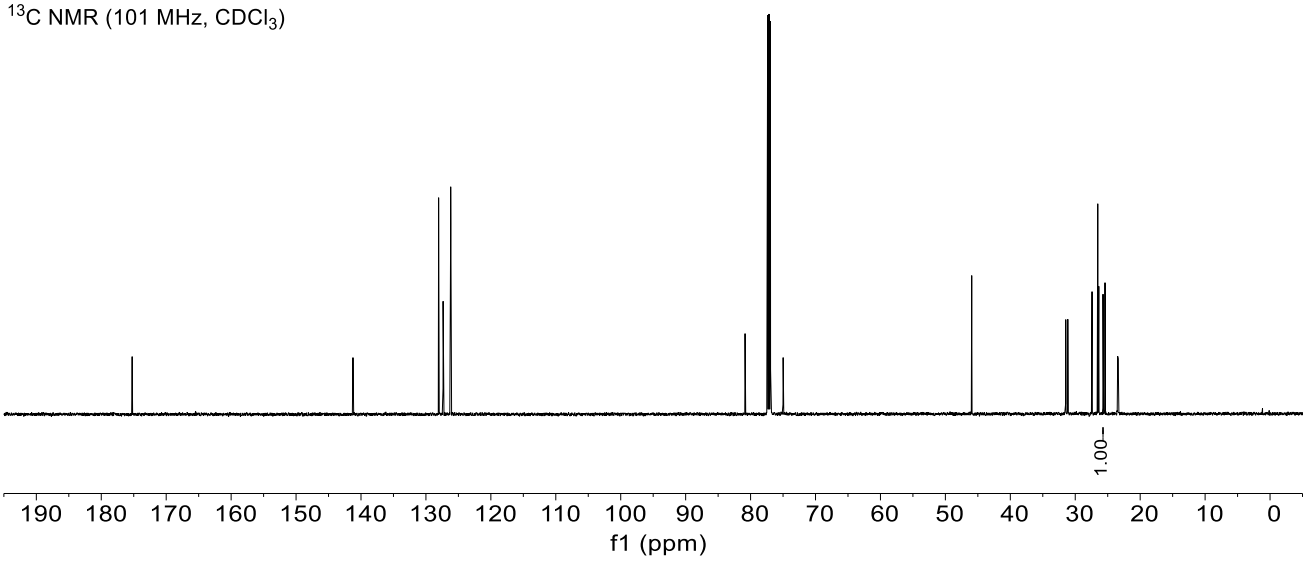
^{1}H NMR (400 MHz, $CDCl_3$)

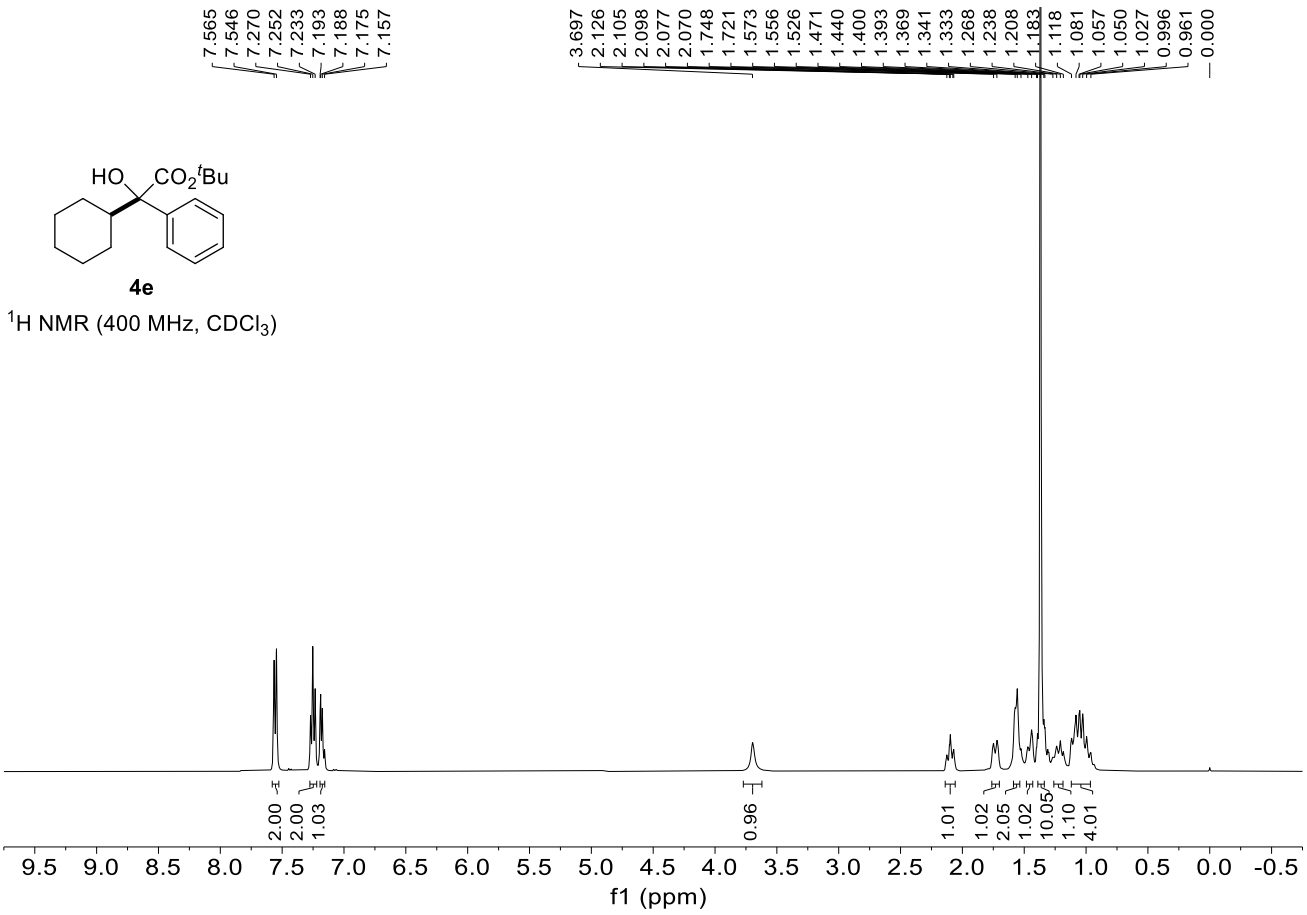




4d

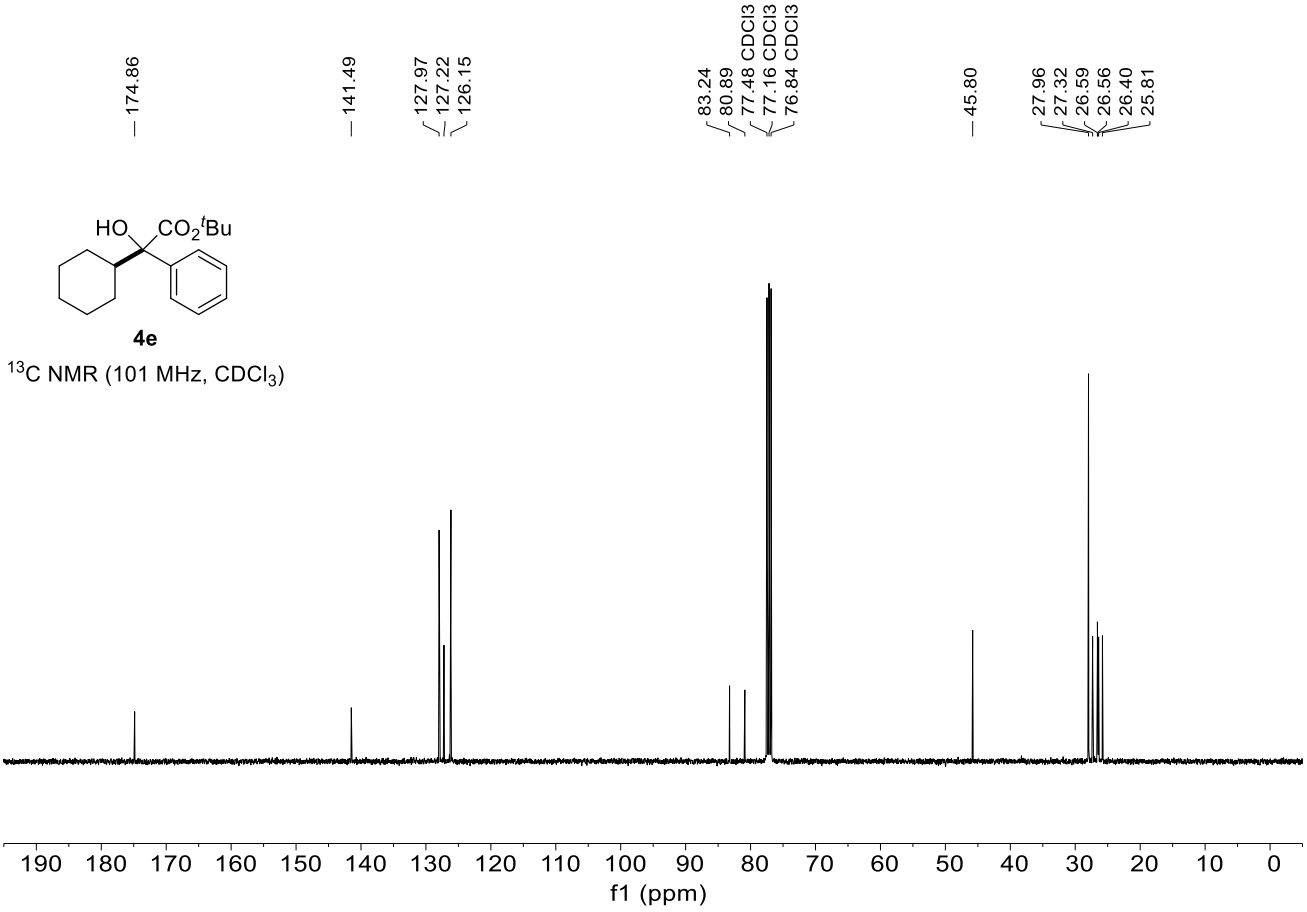
^{13}C NMR (101 MHz, $CDCl_3$)





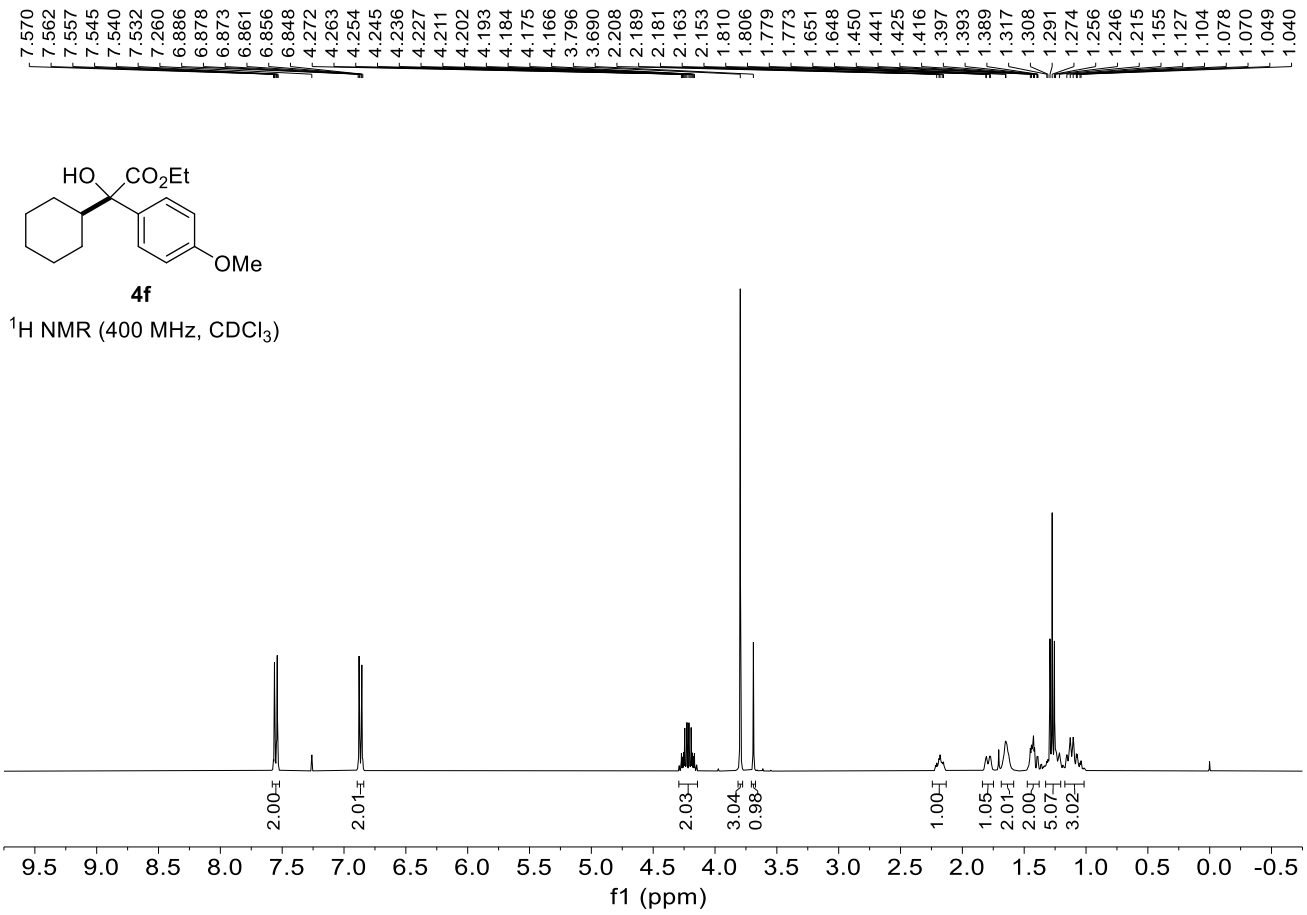
4e

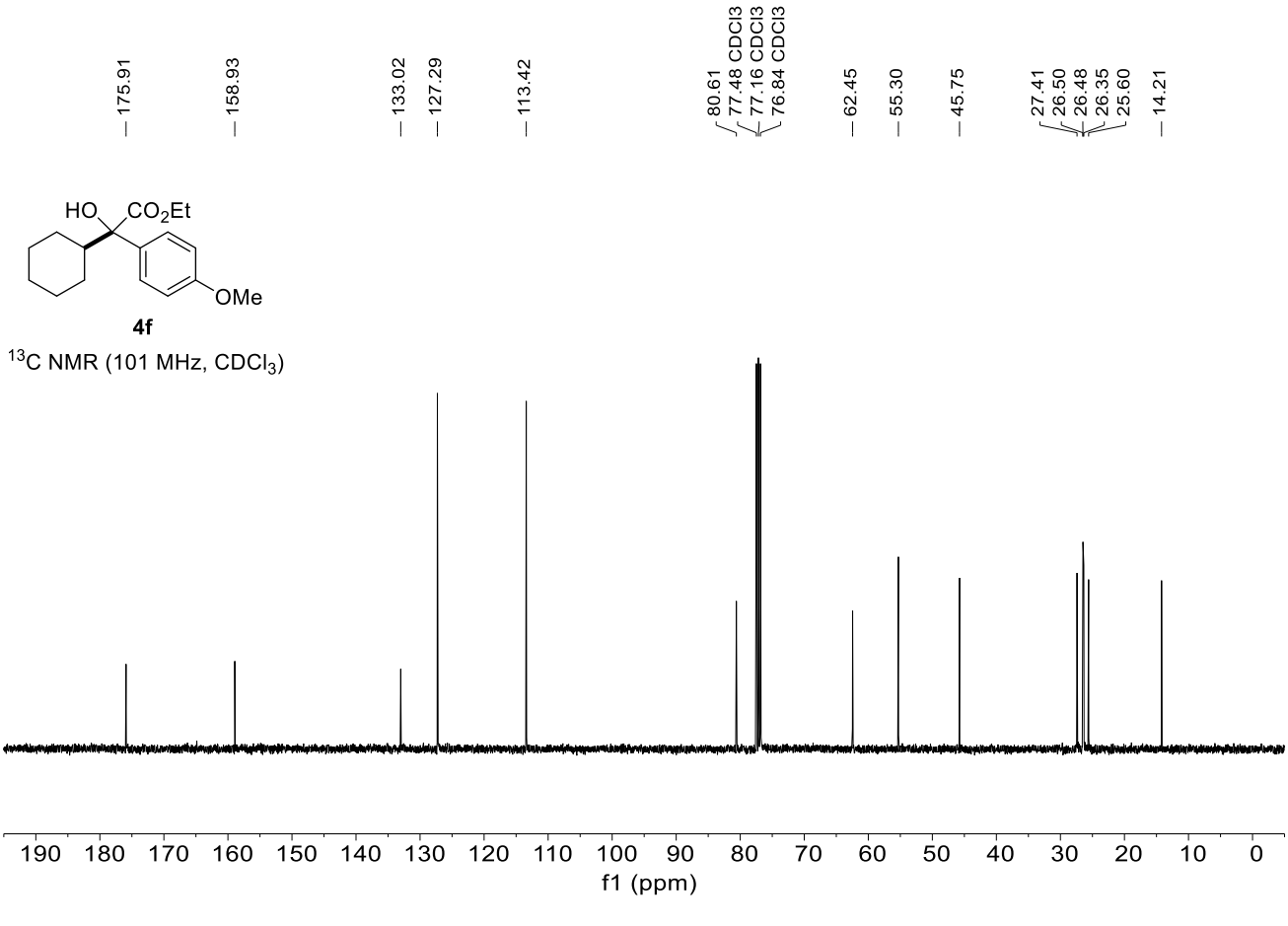
^{1}H NMR (400 MHz, $CDCl_3$)

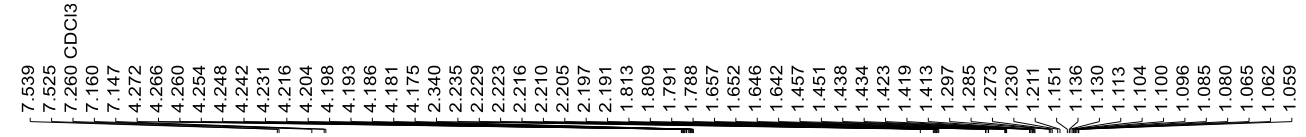


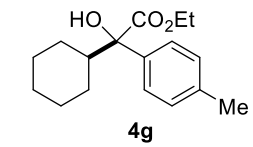
4e

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


7.570
7.562
7.557
7.545
7.540
7.532
7.260
6.886
6.878
6.873
6.861
6.856
6.848
4.272
4.263
4.254
4.245
4.236
4.227
4.211
4.202
4.193
4.184
4.175
4.166
3.796
3.690
2.208
2.189
2.181
2.163
2.153
1.810
1.806
1.779
1.773
1.651
1.648
1.450
1.441
1.425
1.416
1.397
1.393
1.389
1.317
1.308
1.291
1.274
1.256
1.246
1.215
1.155
1.127
1.104
1.078
1.070
1.049
1.040
HO
CO2Et
OMe
4f
1H NMR (400 MHz, CDCl3)
2.00
2.01
2.03
3.04
0.98
1.00
1.05
2.01
2.00
5.07
3.02
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)

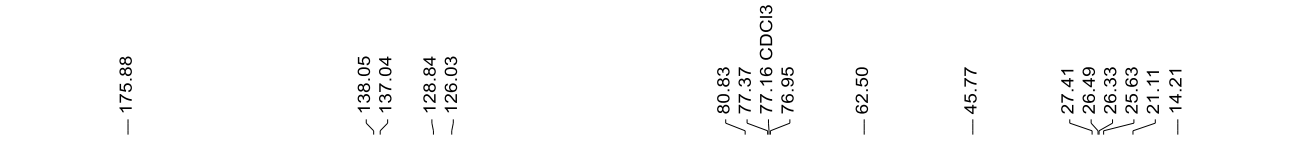

175.91
158.93
133.02
127.29
113.42
80.61
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
62.45
55.30
45.75
27.41
26.50
26.48
26.35
25.60
14.21
HO
CO2Et
OMe
4f
13C NMR (101 MHz, CDCl3)
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

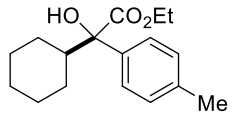




4g

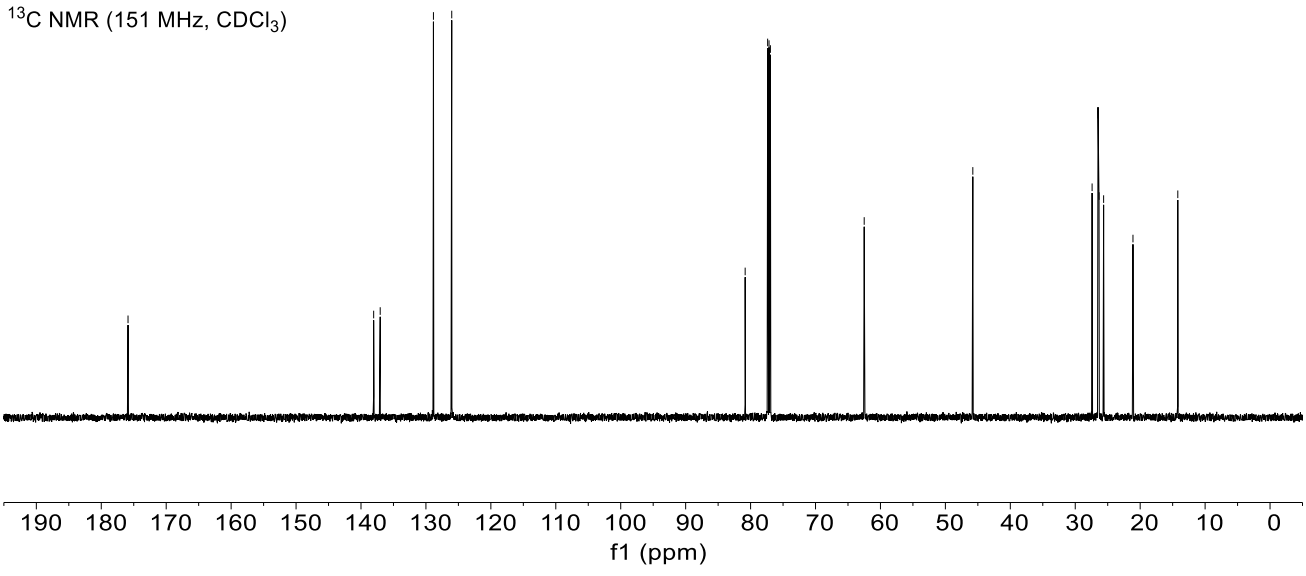
^{1}H NMR (600 MHz, $CDCl_3$)

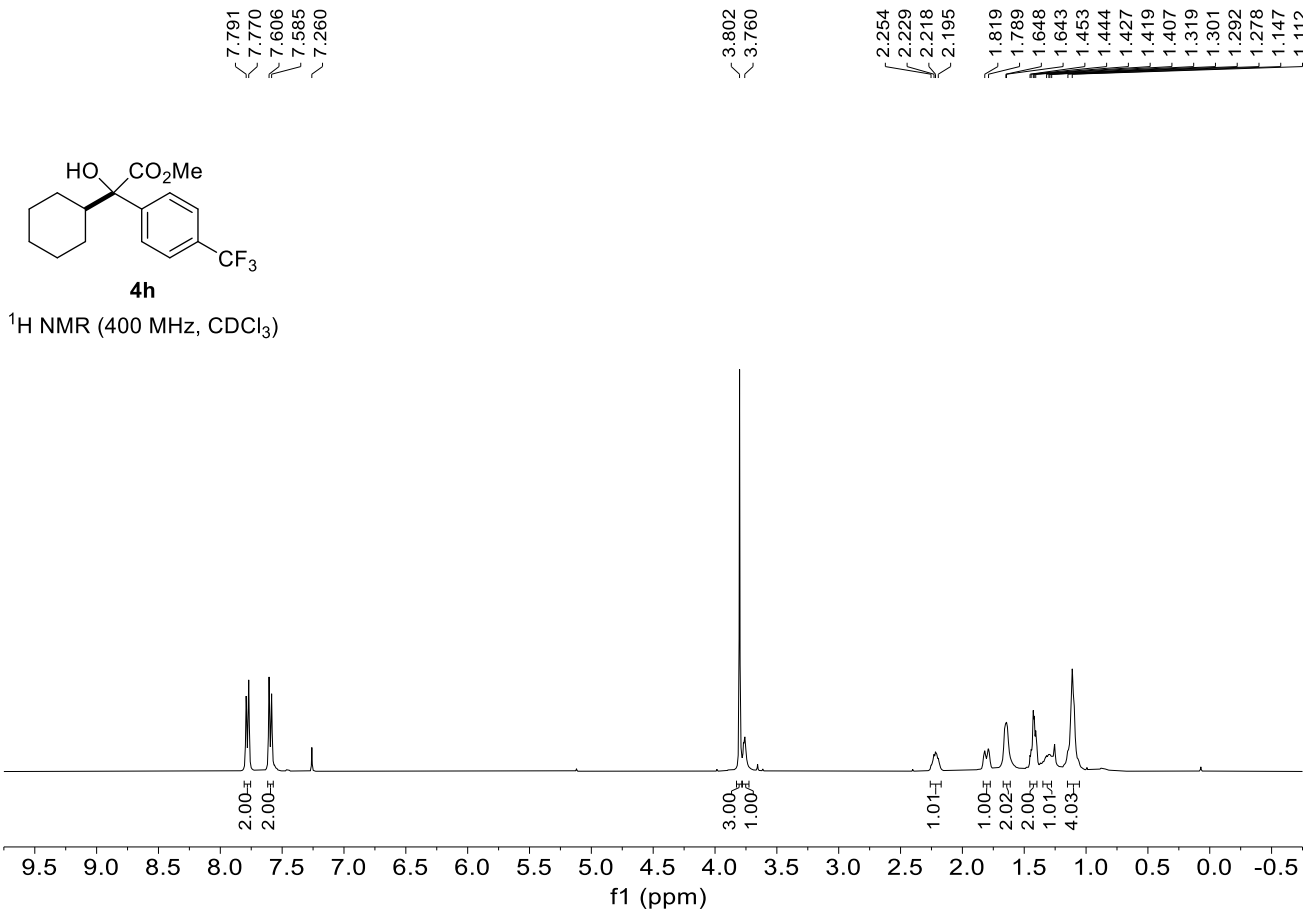




4g

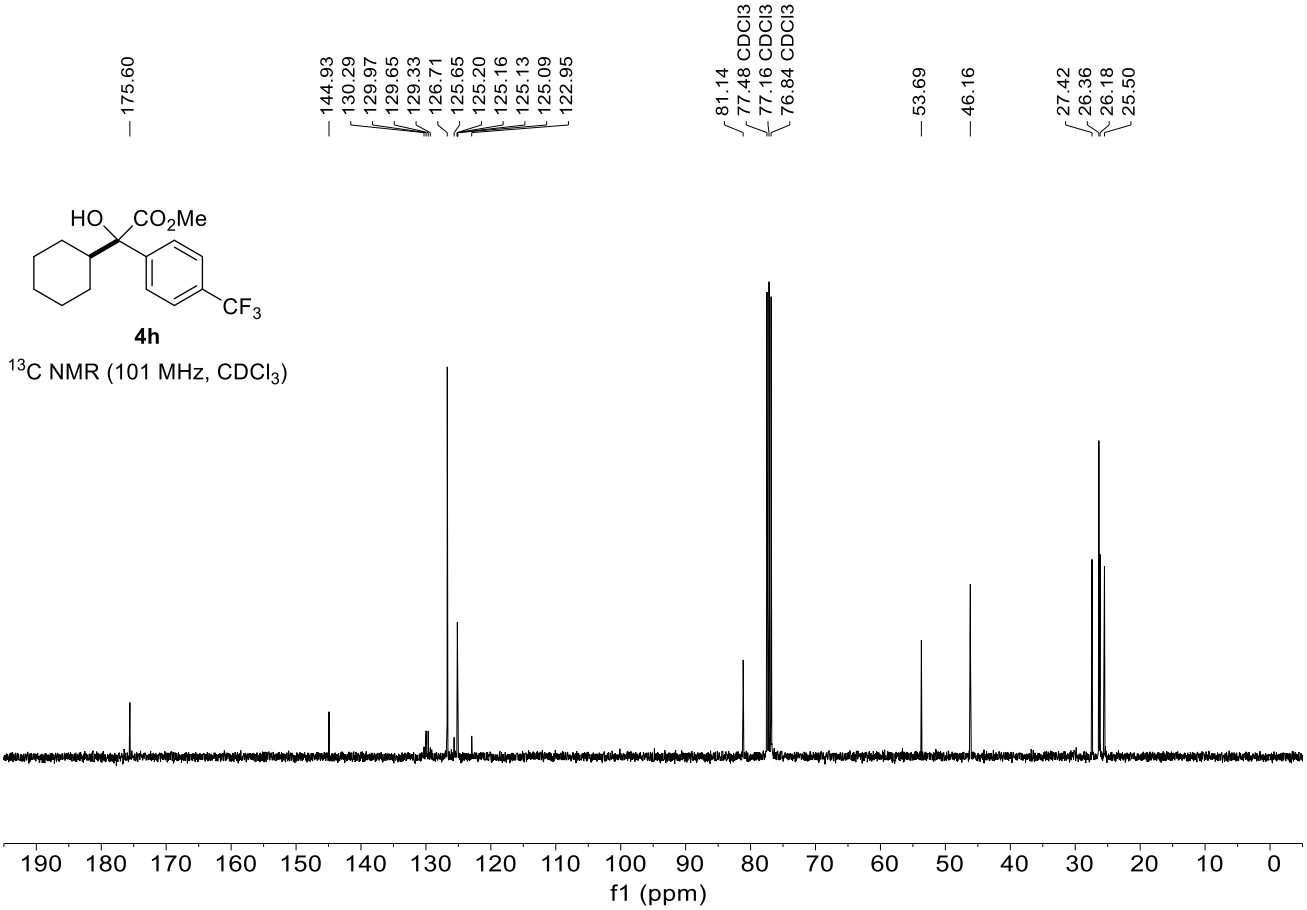
^{13}C NMR (151 MHz, $CDCl_3$)





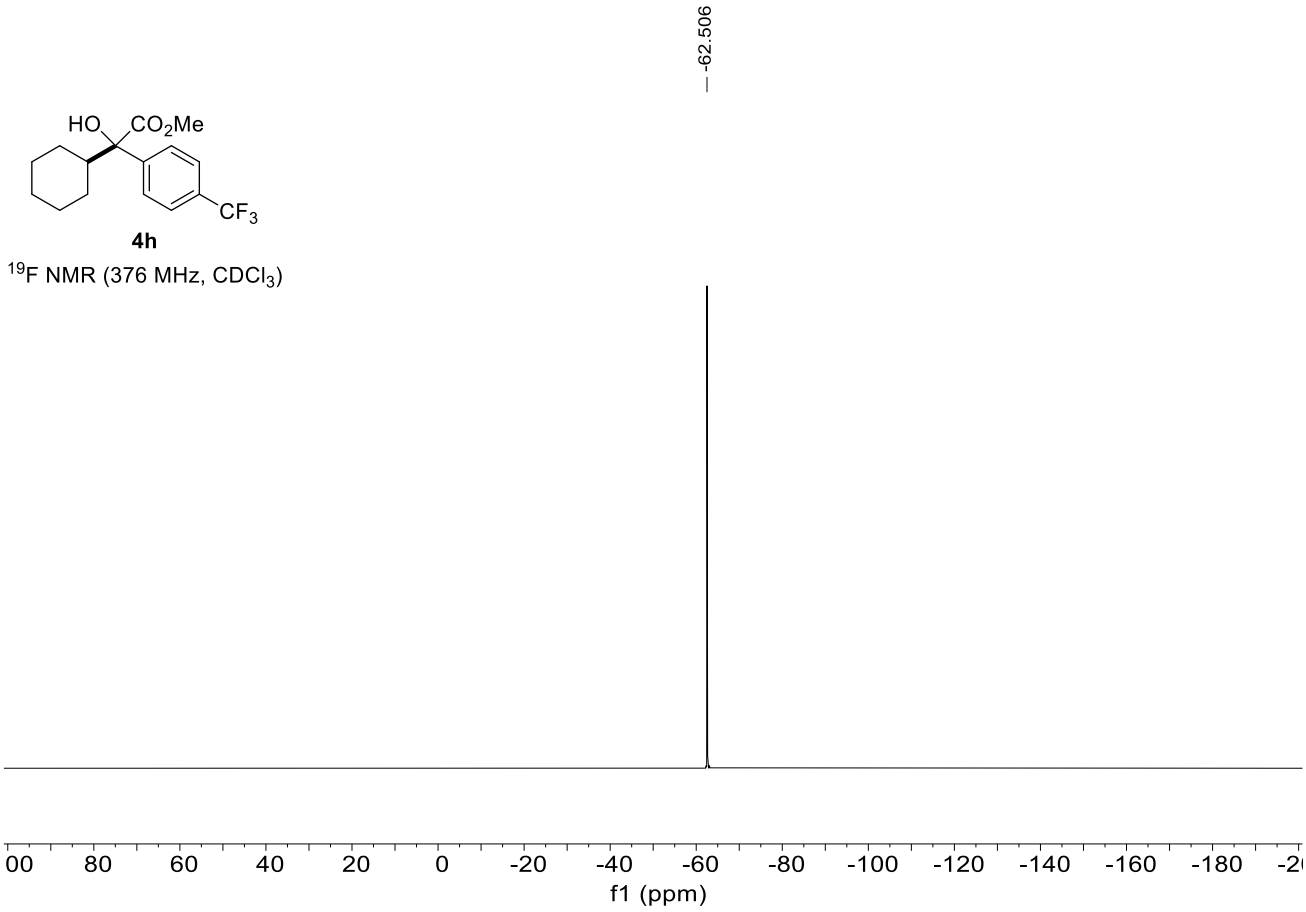
4h

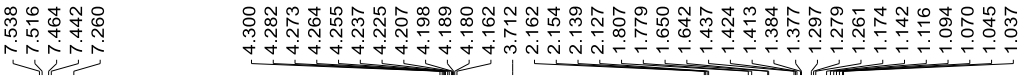
^{1}H NMR (400 MHz, $CDCl_3$)

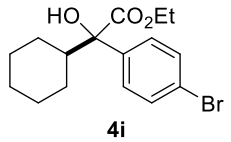


4h

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

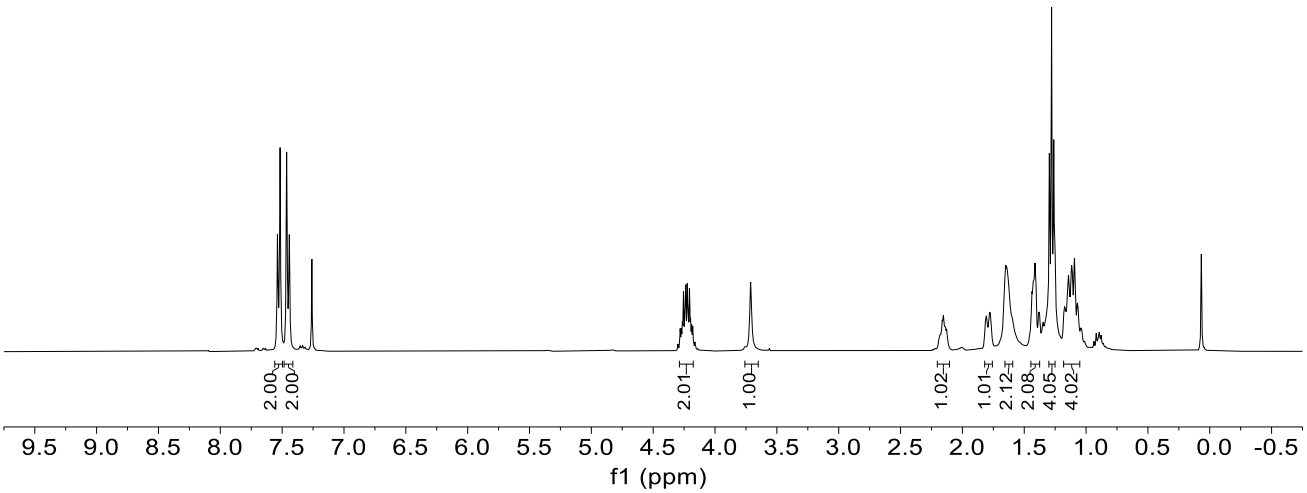

HO
CO2Me
CF3
4h
19F NMR (376 MHz, CDCl3)
-62.506
00
80
60
40
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
f1 (ppm)

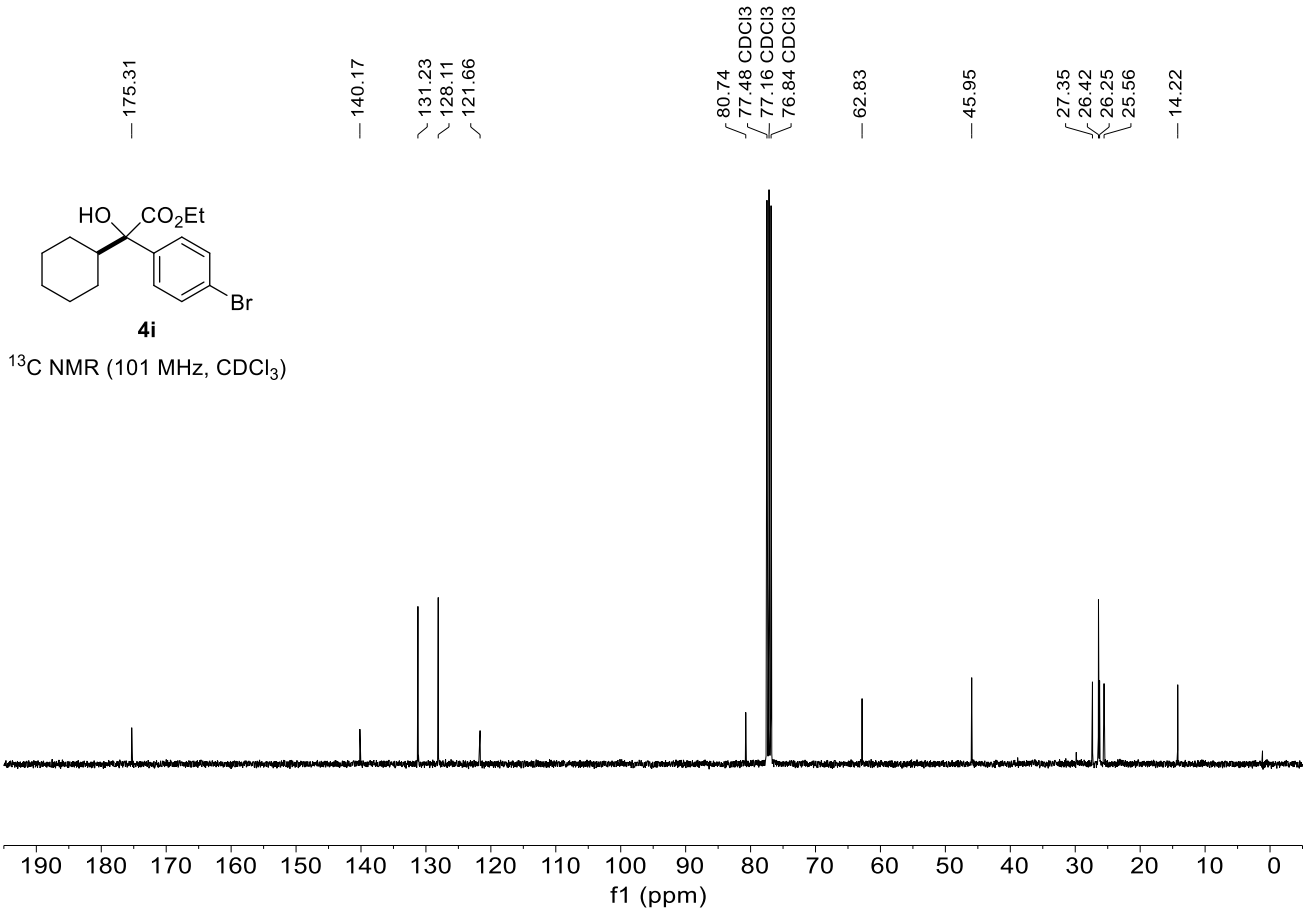




4i

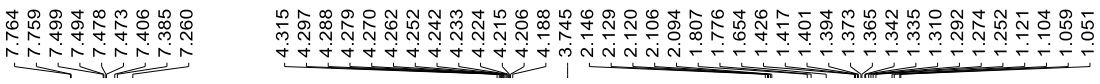
^{1}H NMR (400 MHz, $CDCl_3$)

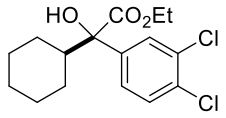




4i

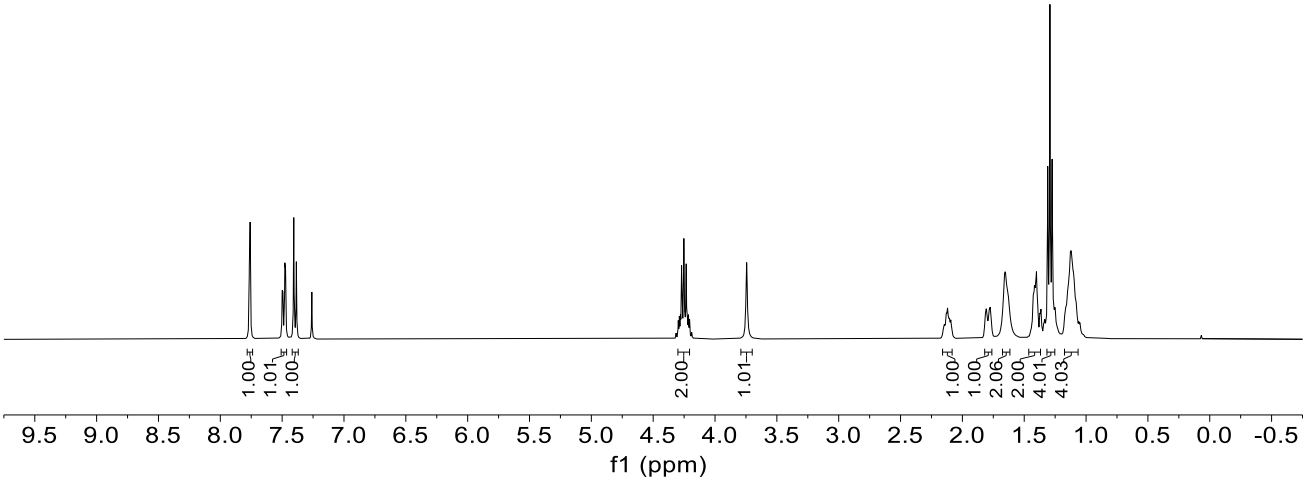
^{13}C NMR (101 MHz, $CDCl_3$)

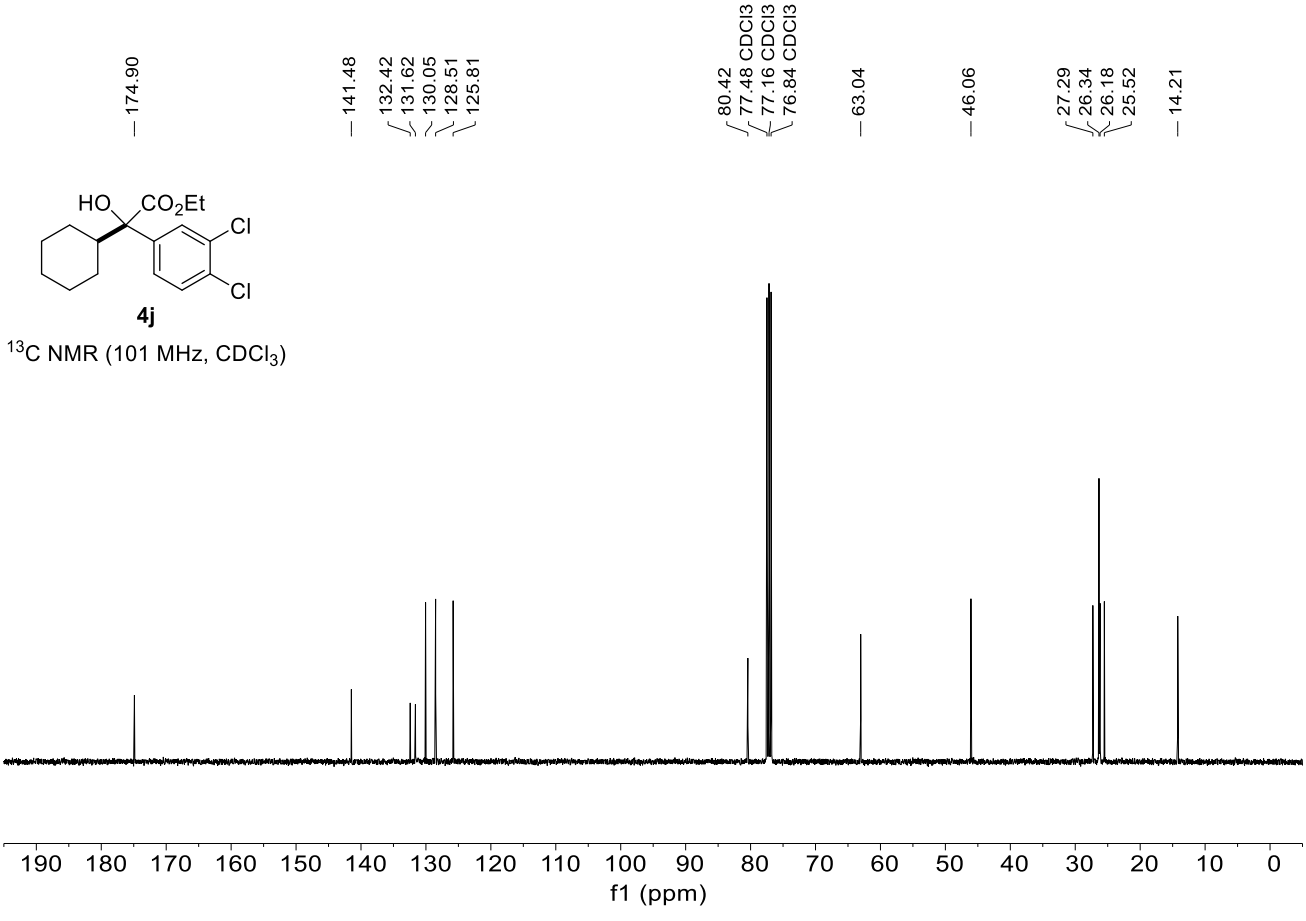




4j

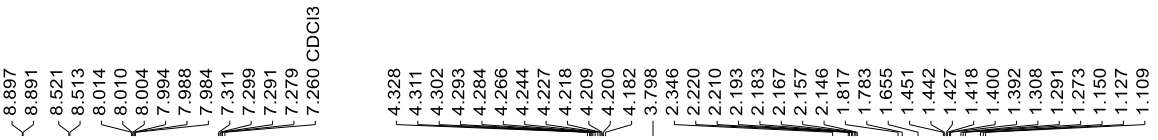
^{1}H NMR (400 MHz, $CDCl_3$)

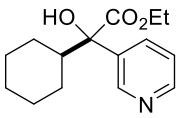




4j

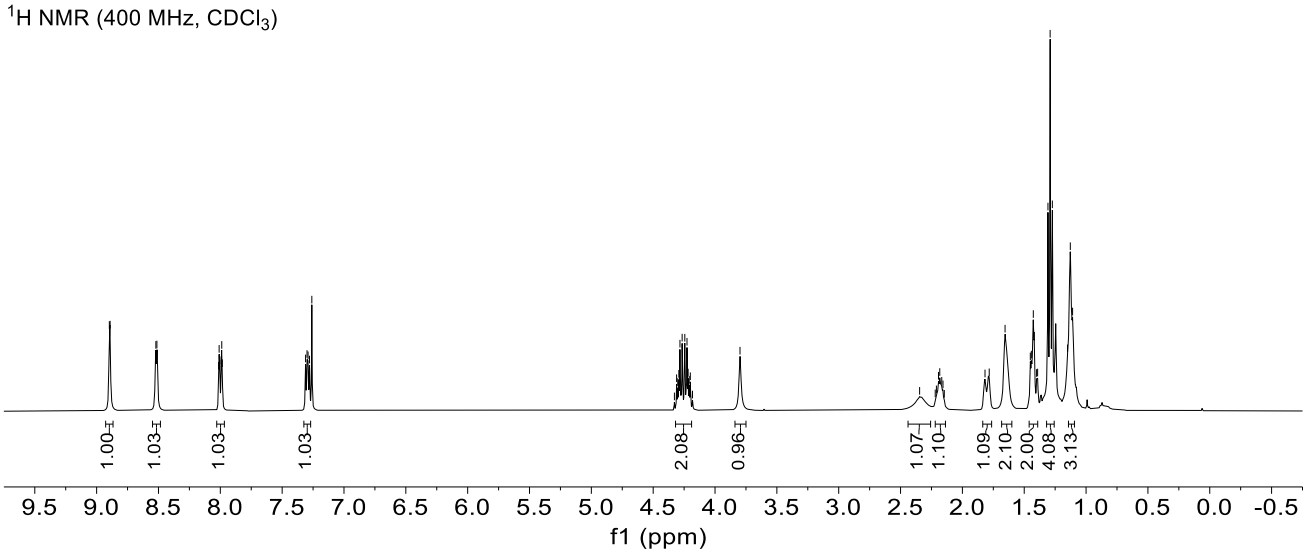
^{13}C NMR (101 MHz, $CDCl_3$)

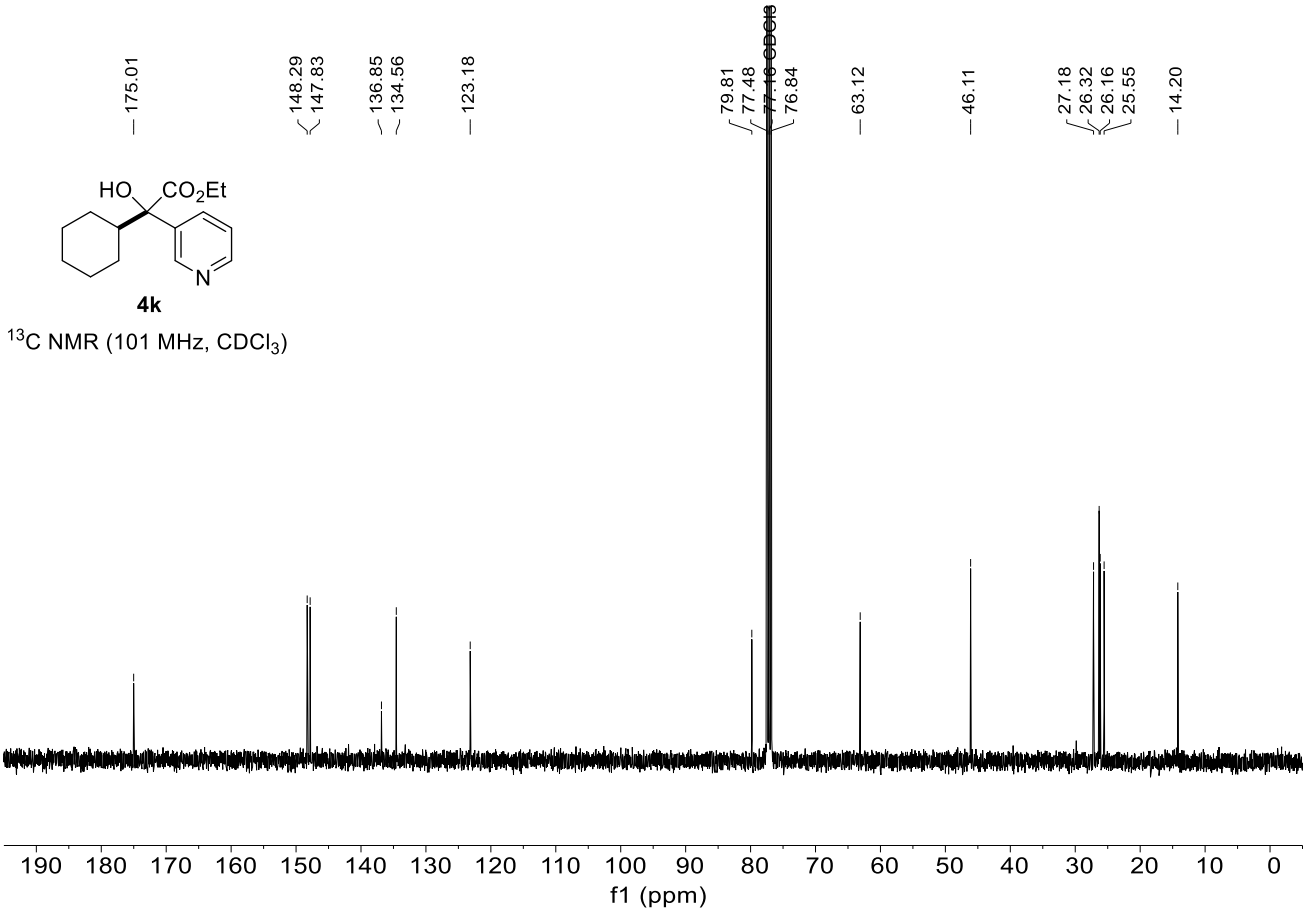




4k

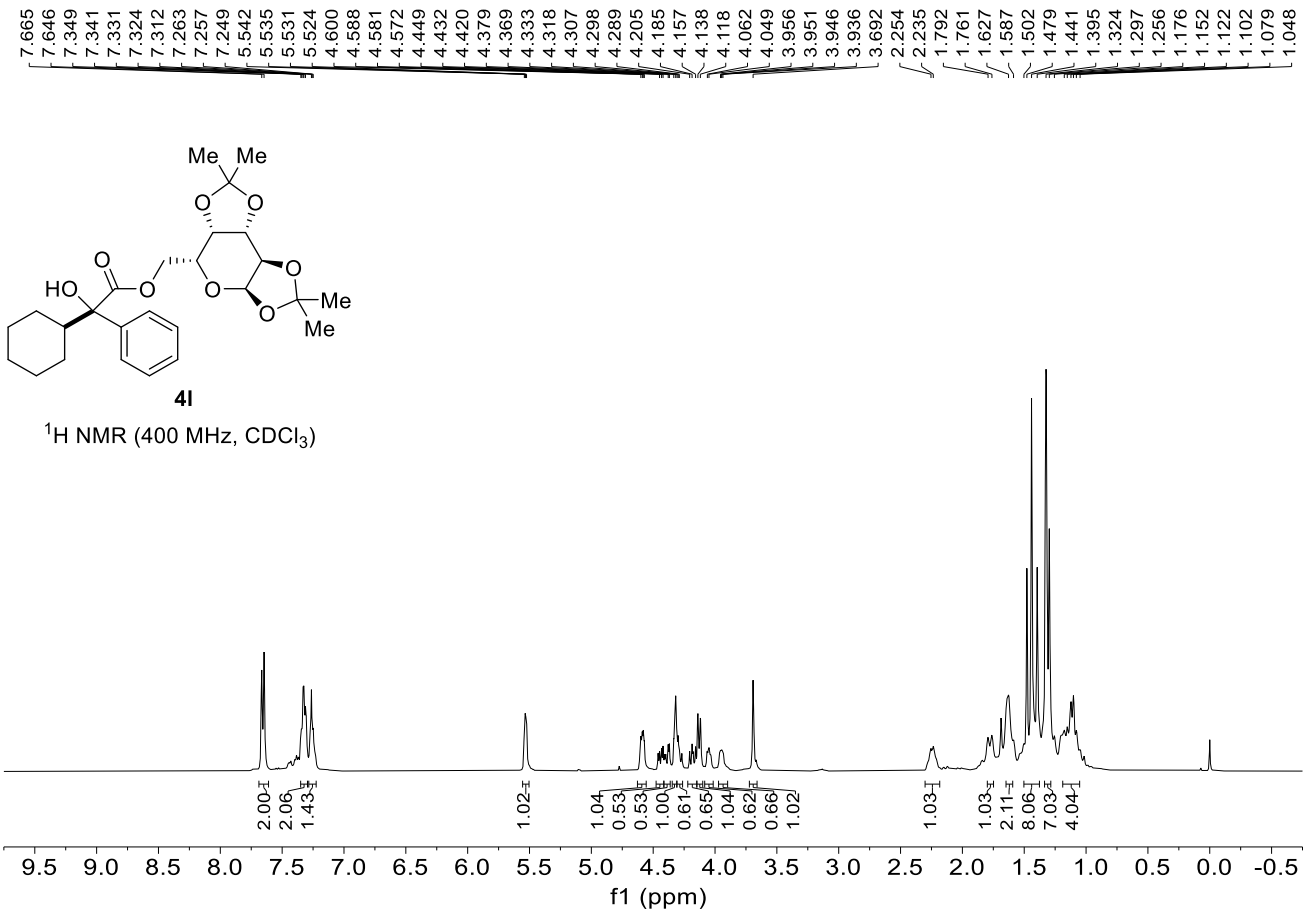
^{1}H NMR (400 MHz, $CDCl_3$)





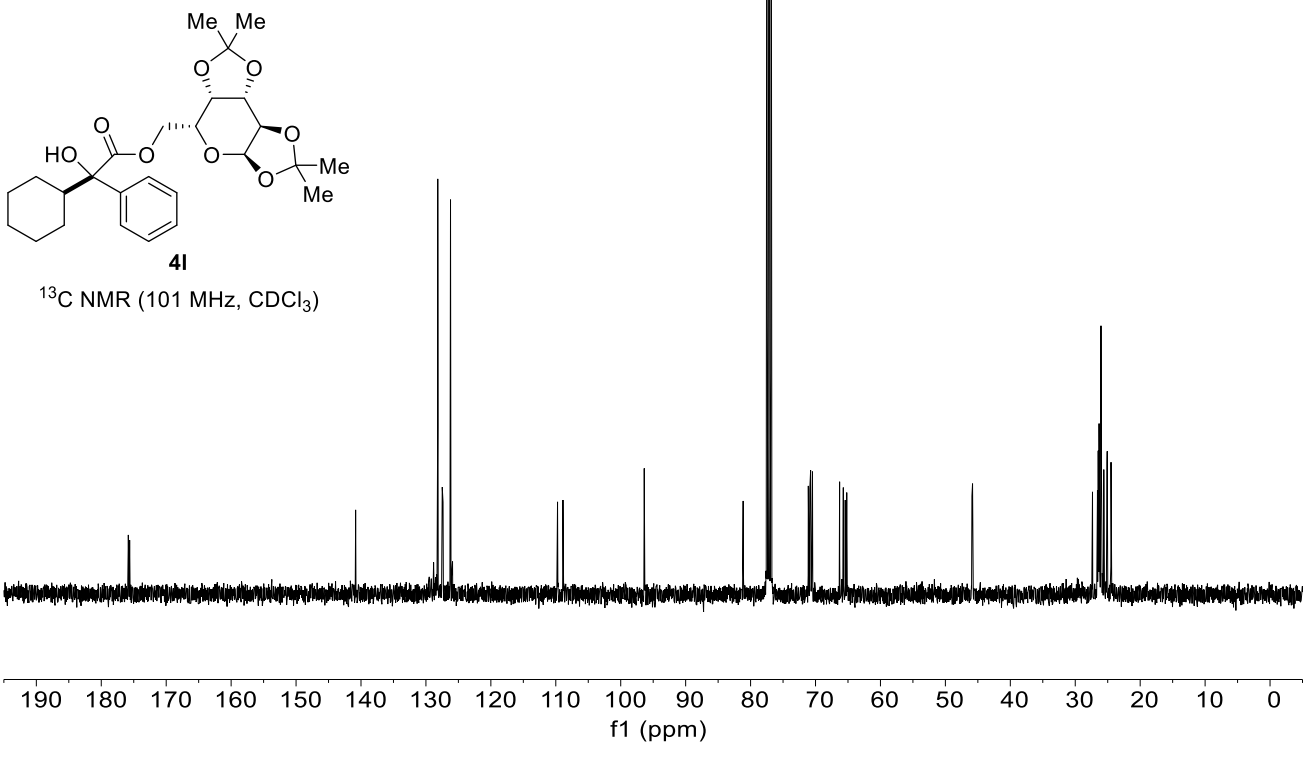
4k

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



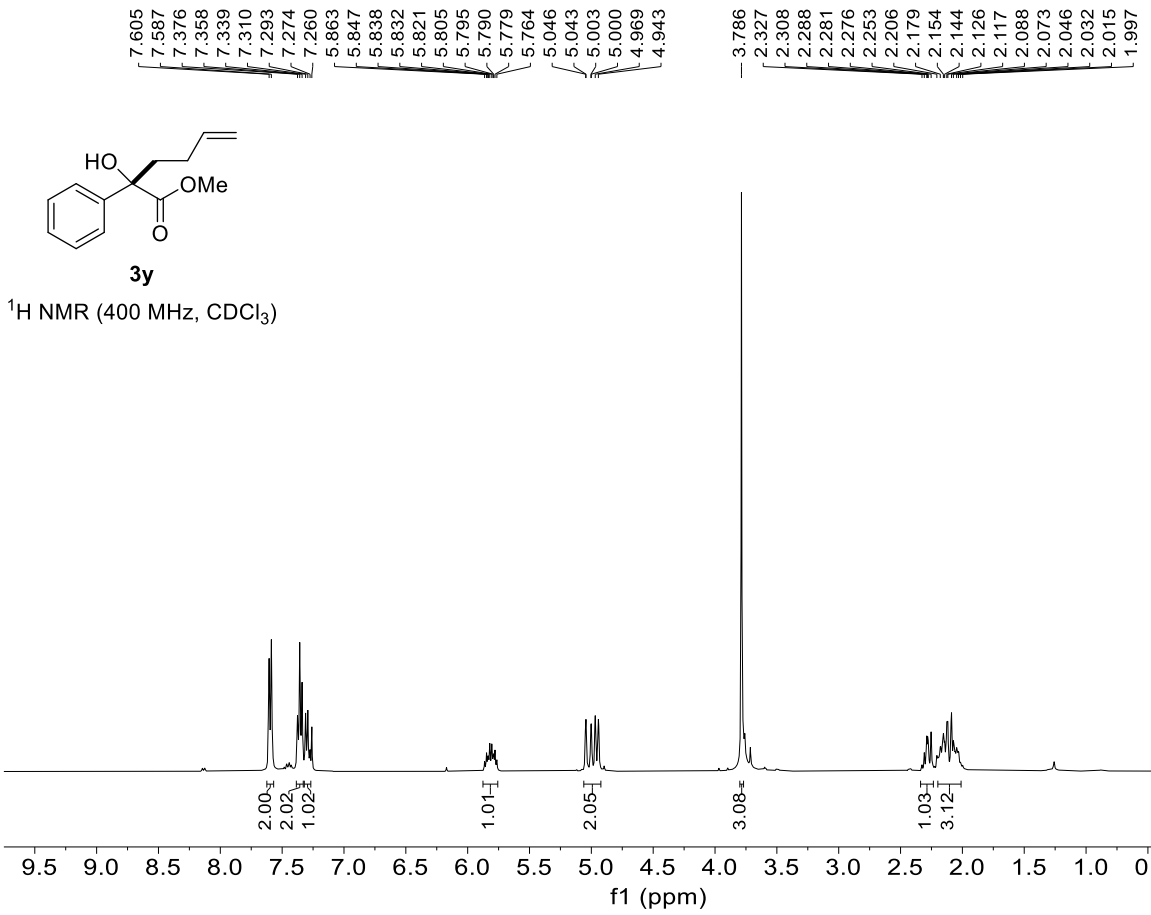
4l

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



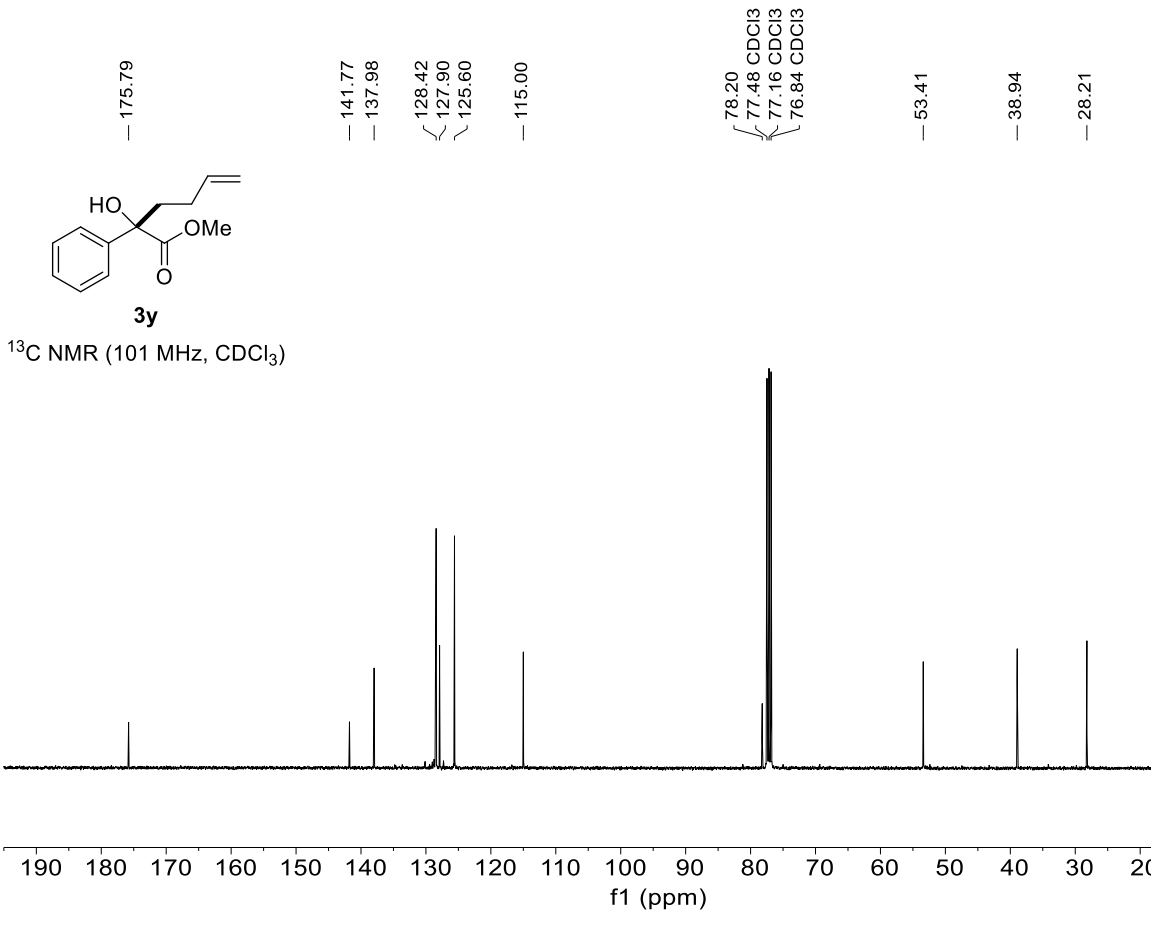
4l

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



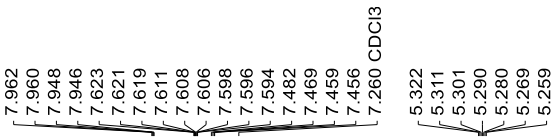
3y

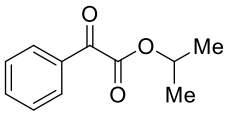
^{1}H NMR (400 MHz, $CDCl_3$)



3y

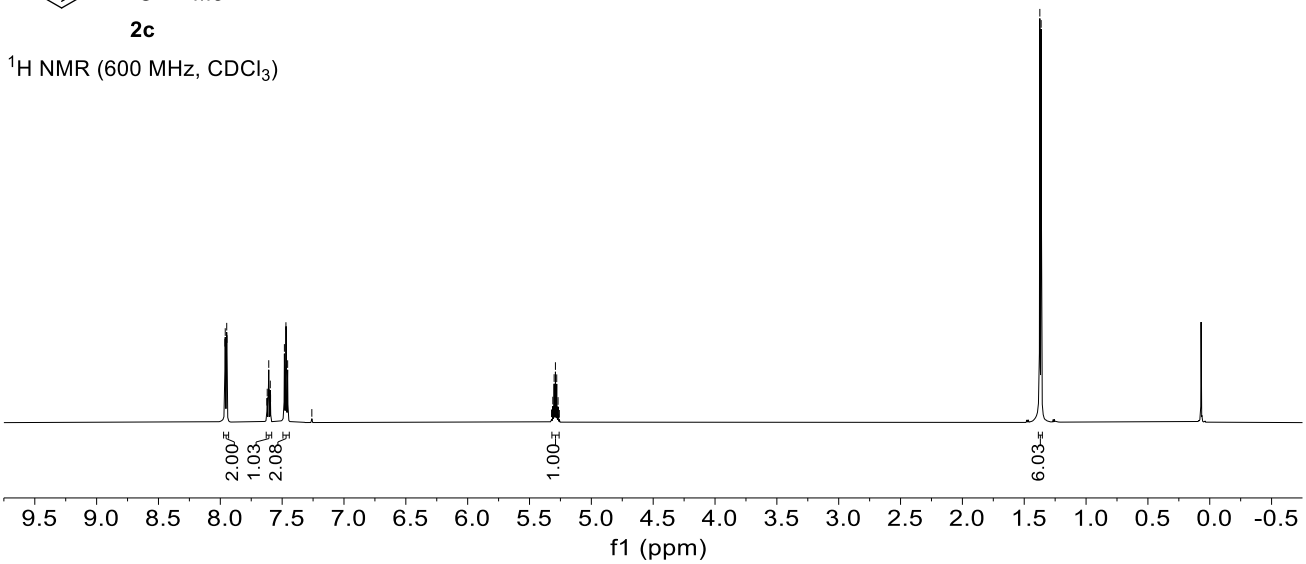
^{13}C NMR (101 MHz, $CDCl_3$)

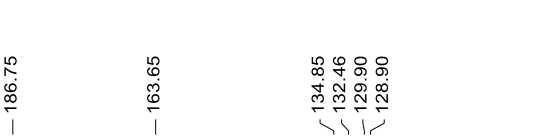


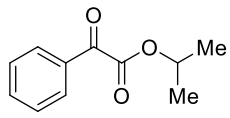


2c

^{1}H NMR (600 MHz, $CDCl_3$)

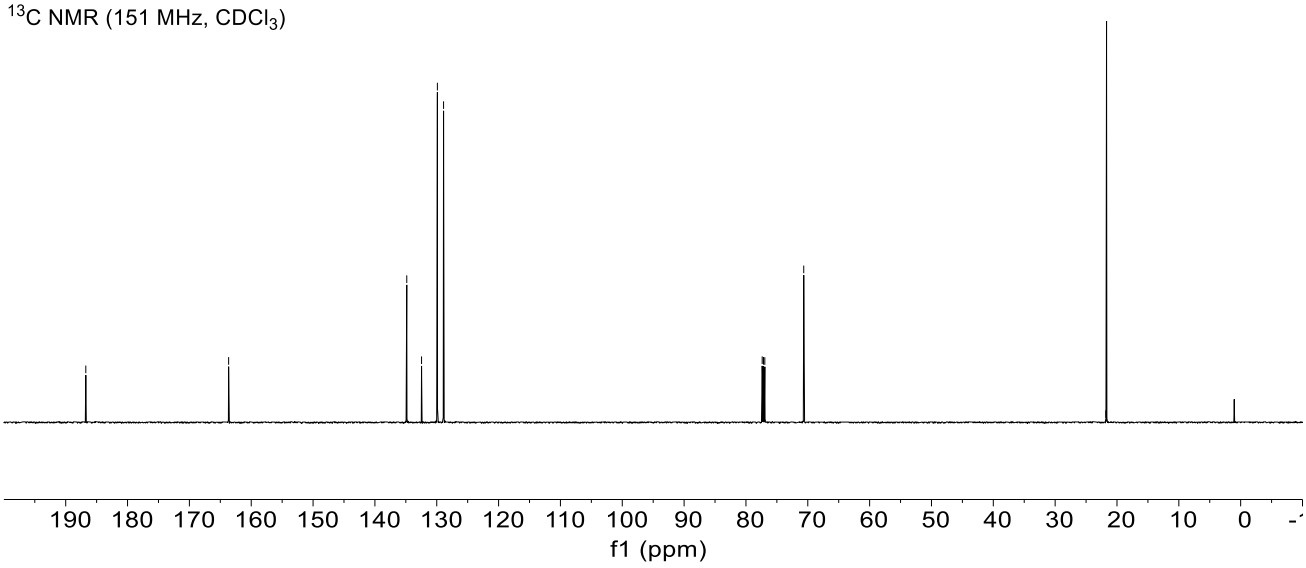


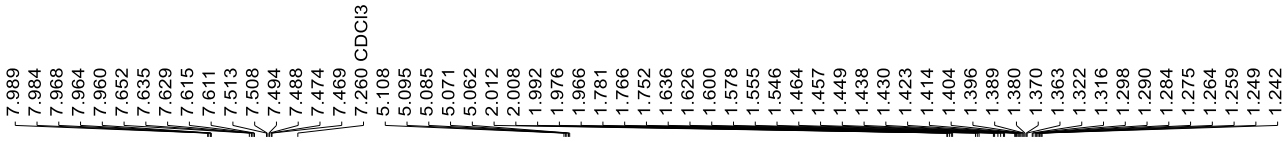


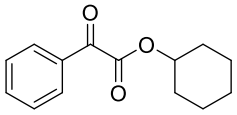


2c

^{13}C NMR (151 MHz, $CDCl_3$)

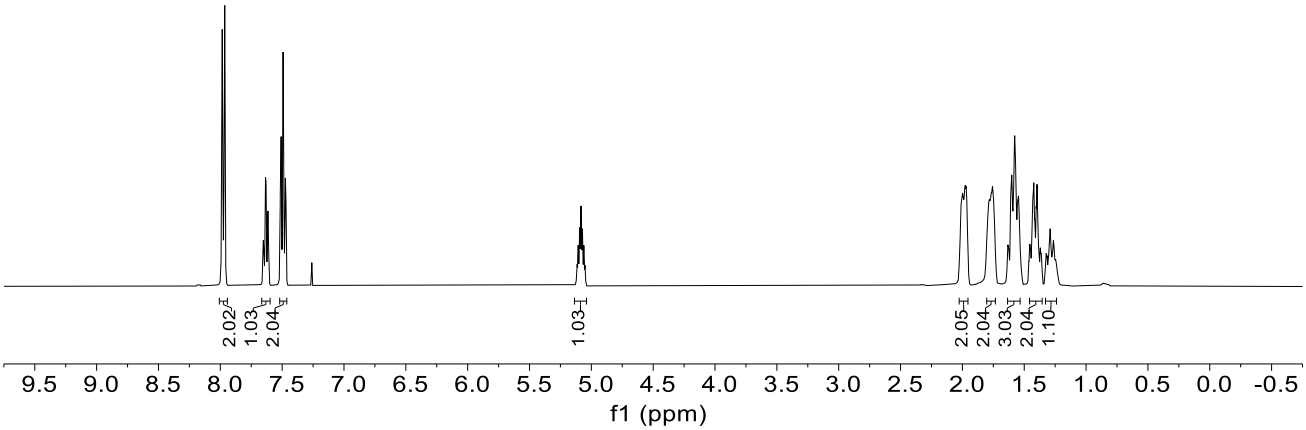


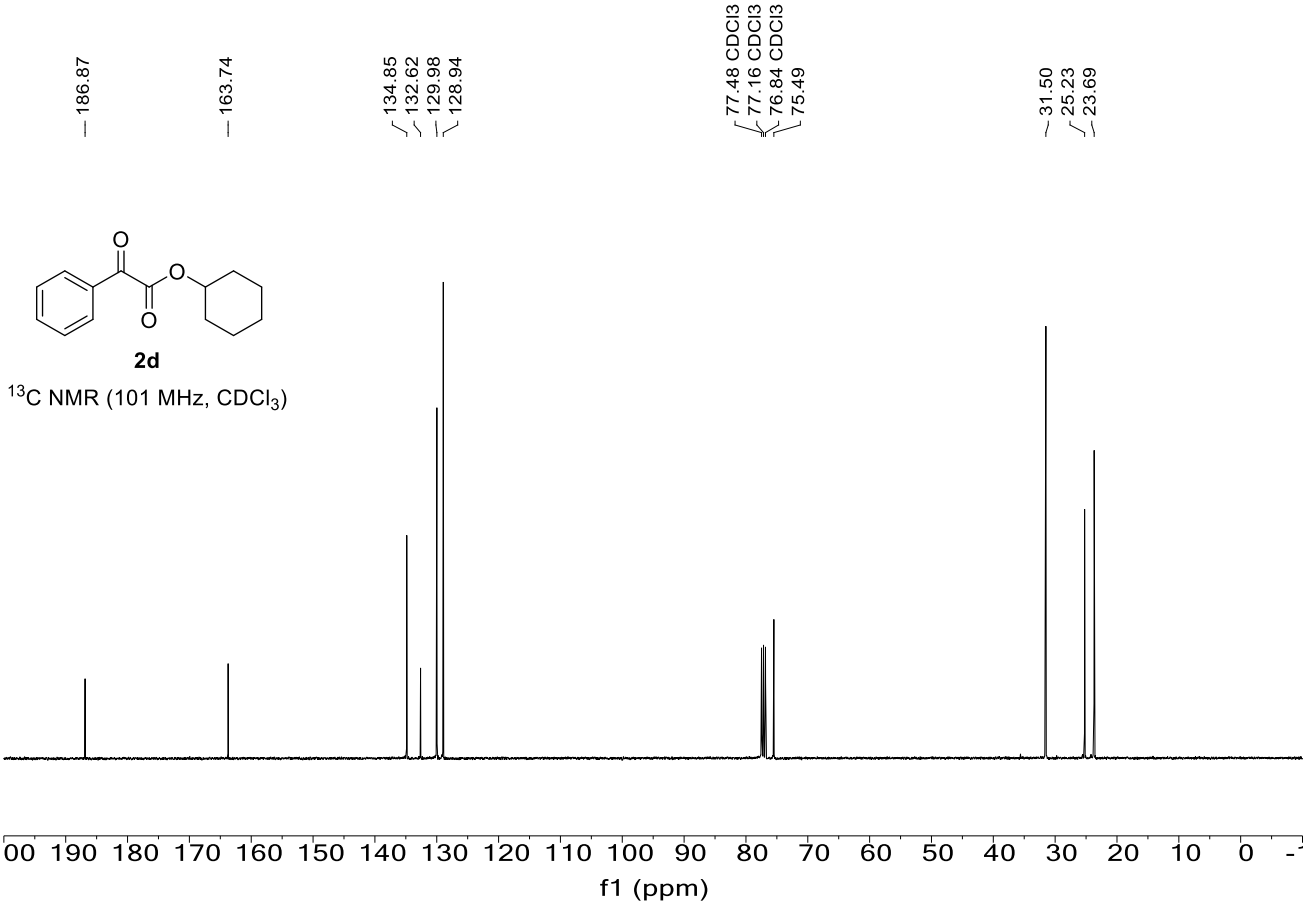




2d

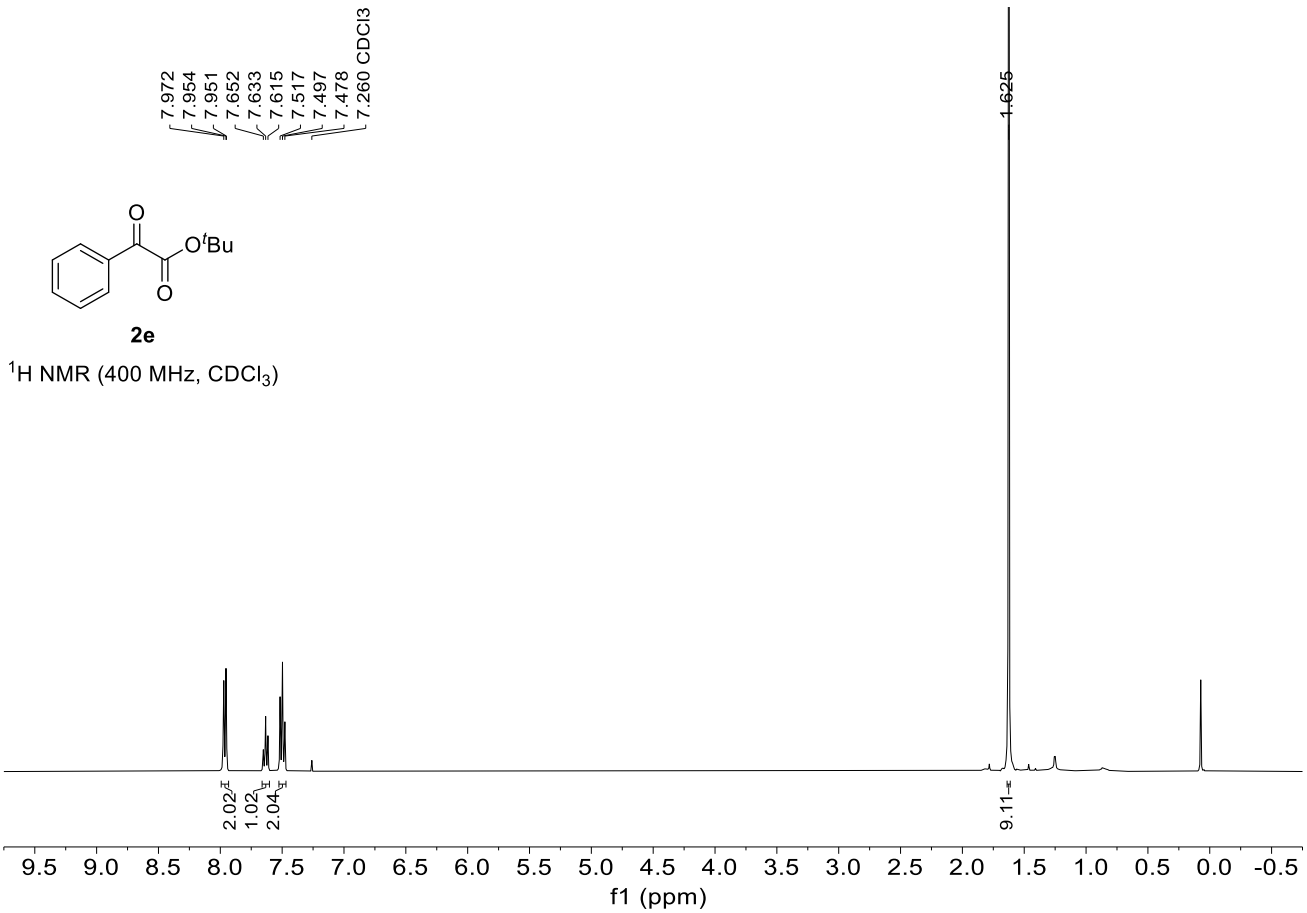
^{1}H NMR (400 MHz, $CDCl_3$)





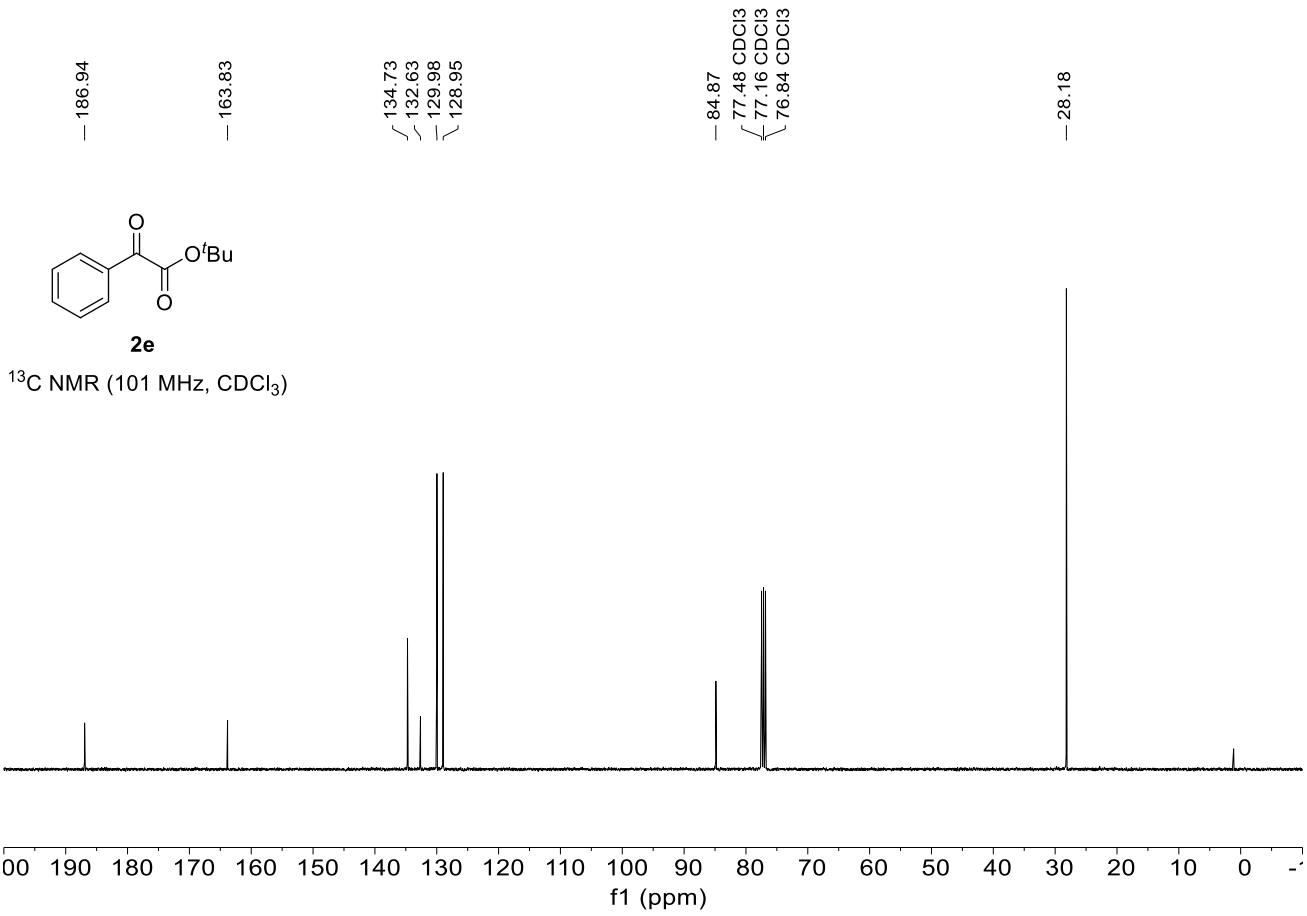
2d

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



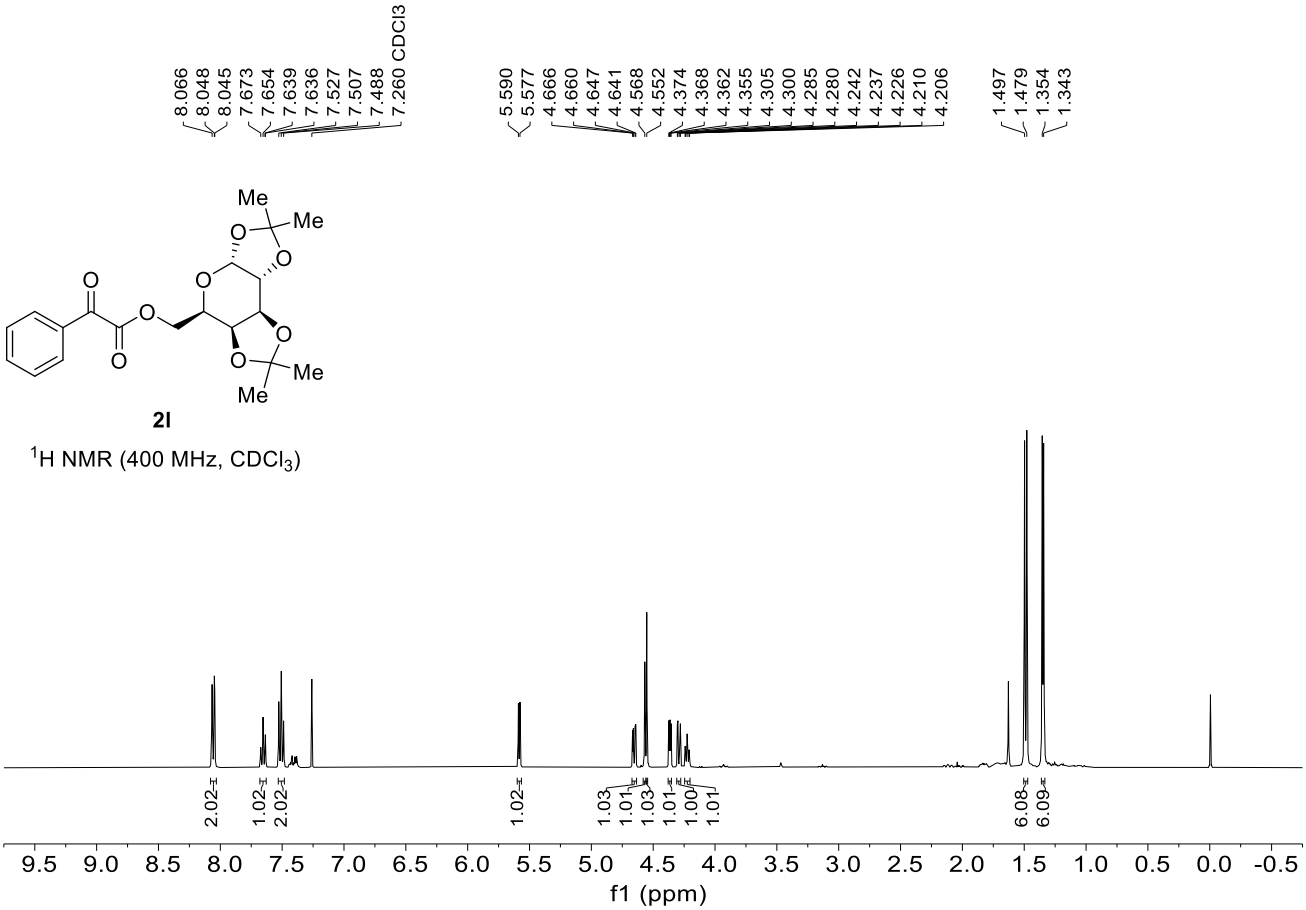
2e

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



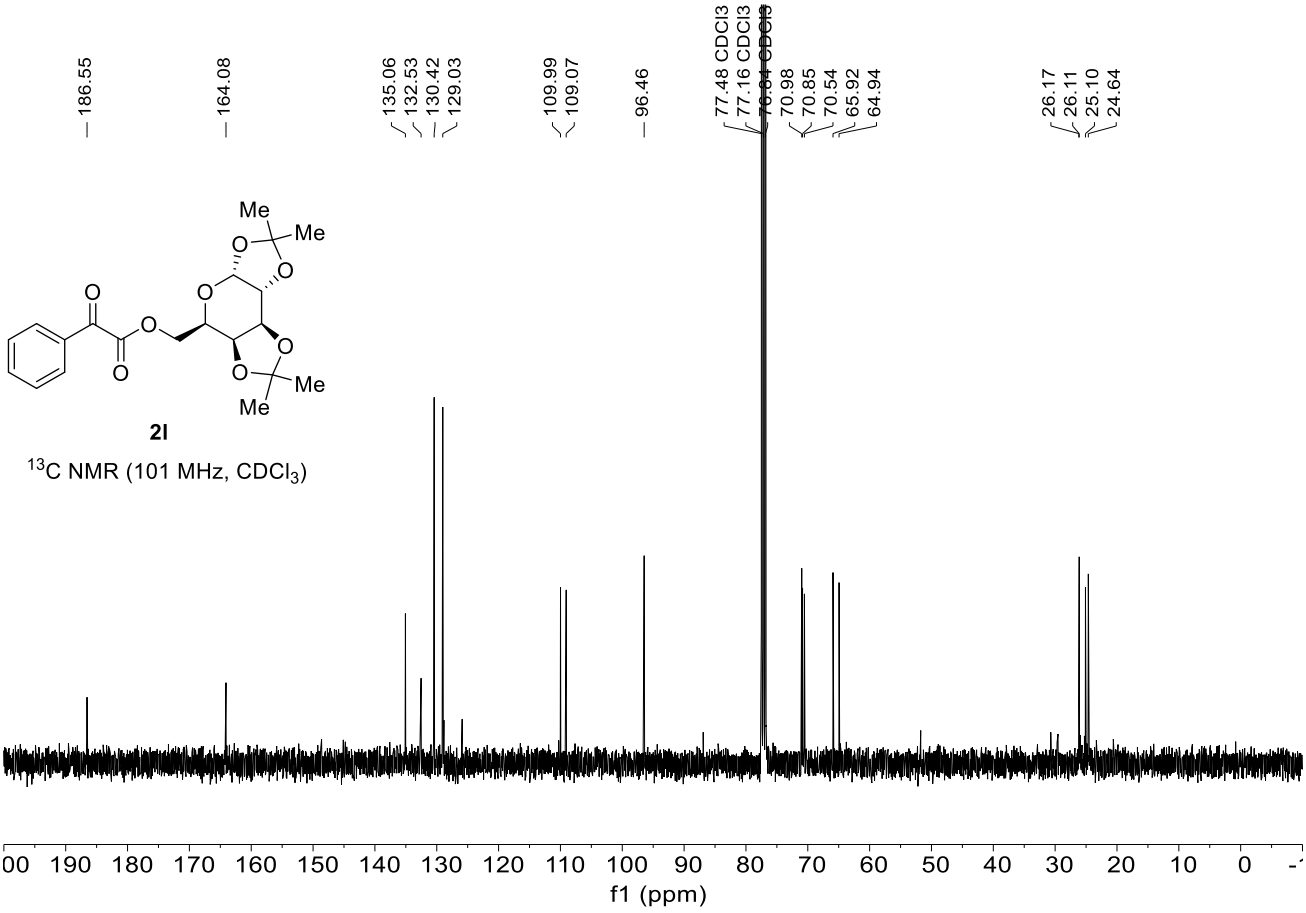
2e

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



2l

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



2l

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