

Supporting Information

Ruthenium Pincer Complex-Catalyzed Heterocyclic Compatible Alkoxy carbonylation of Alkyl Iodides: Substrate Keep the Catalyst Active

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1. General Remarks

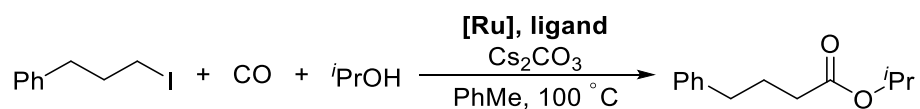
Reagents and solvents: Unless otherwise noted, the chemicals were commercially available from *Sigma-Aldrich*, *Strem*, *TCI* or *Alfa Aesar* and were used without further purification. Solvents (anhydrous and under inert atmosphere) were collected from the solvent purification system by MBRAUN and used under standard Schlenk technique.

Purification: The products were isolated from the reaction mixture by column chromatography on silica gel 60, 0.063-0.2 mm, 70-230 mesh (Merck). Gradient flash chromatography was conducted eluting with PE/EA, PE refers to pentane and EA refers to ethyl acetate, they were listed as volume/volume ratios.

Data collection: GC-yields were calculated using hexadecane as internal standard. GC analysis was performed on an Agilent HP-7890A instrument with FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 μm film thickness) using argon as carrier gas. Electron impact (EI) mass spectra were recorded on AMD 402 mass spectrometer (70 eV). The data are given as mass units per charge (m/z). NMR spectra were recorded on Bruker Avance 300 and Bruker ARX 400 spectrometers. Multiplets were assigned as s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet) and br. s (broad singlet). Chemical shifts (ppm) are given relative to solvent: references for CDCl_3 were 7.26 ppm (^1H NMR) and 77.00 ppm (^{13}C NMR). All measurements were carried out at room temperature unless otherwise stated.

NOTE: Carbon monoxide should only be handled in a well-ventilated fume hood. The laboratory should be well-equipped with a CO detector and alarm system.

2. Additional Optimization Information

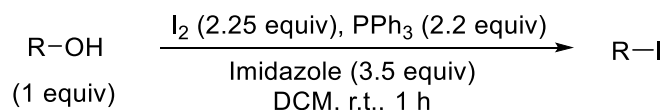


Entry ^a	[Ru]	Ligand	Yield [%] ^b
1	[RuCl ₂ (cymene)] ₂	-	5
2	[RuCl ₂ (cymene)] ₂	Xantphos	16
3	[RuCl ₂ (cymene)] ₂	DPEphos	19
4	[RuCl ₂ (cymene)] ₂	PPh ₃	11
5	[RuCl ₂ (cymene)] ₂	DPPE	20
6	[RuCl ₂ (cymene)] ₂	DPPD	17
7	[RuCl ₂ (cymene)] ₂	DPPP	20

[a] Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), [Ru] (2,5 mol%), ligand (5 mol%), Cs₂CO₃ (0.6 mmol), toluene (0.5 mL), CO (10 bar), 100 °C, 12 h. [b] Determined by GC with hexadecane as internal standard.

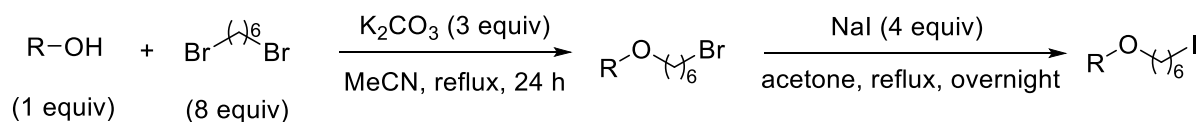
3. Preparation of Substrates

General Procedure A:



A round-bottom flask containing a stirring bar was charged with PPh₃ (2.2 equiv) and DCM (0.2 M). Iodine (2.25 equiv) was slowly added under N₂. The mixture was stirred for 10 min at room temperature. Imidazole (3.5 equiv) was then added to the solution and the mixture was allowed to stir for another 10 min. Then, the alcohol (1 equiv) was added to the suspension drop wise and the reaction was stirred at room temperature. The reaction could be tracked by TLC. After the reaction was completed (about 1 hour), the reaction mixture was quenched with the saturated aqueous solution of Na₂SO₃ (0.2 M). The aqueous and organic layers were separated, and the aqueous layer was extracted with DCM three times. The combined organic layer was dried over Na₂SO₄, filtered, and concentrated in vacuum. The resulting crude product was purified by flash column chromatography on silica gel to give the desired product.

General Procedure B:



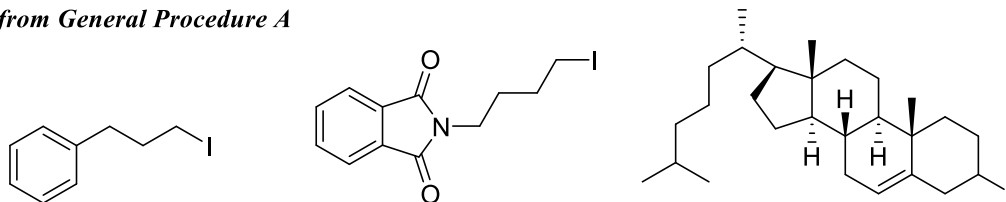
A round-bottom flask containing a stirring bar was charged with the alcohol (1 equiv), 1,6-dibromopropane (8.0 equiv), and CH₃CN (0.3 M). Then K₂CO₃ (9.0 mmol, 3.0 equiv) was added. The reaction mixture was stirred and refluxed for 24 h. After the reaction was completed, the reaction mixture was filtered under reduced pressure and concentrated by rotary evaporator. The crude product was purified by flash column chromatography on silica gel to give the desired intermediate (the alkyl bromide).

The alkyl bromide (1 equiv) and NaI (4.0 equiv) were dissolved in acetone (0.25 M) and then refluxed overnight. After the reaction was completed, the reaction mixture was quenched with saturated aqueous solution of Na₂SO₃ (0.2 M). The aqueous and organic layers were separated, and the aqueous layer was extracted with DCM three times. The combined organic layers were washed with brine and dried over Na₂SO₄, filtered, and concentrated in vacuum.

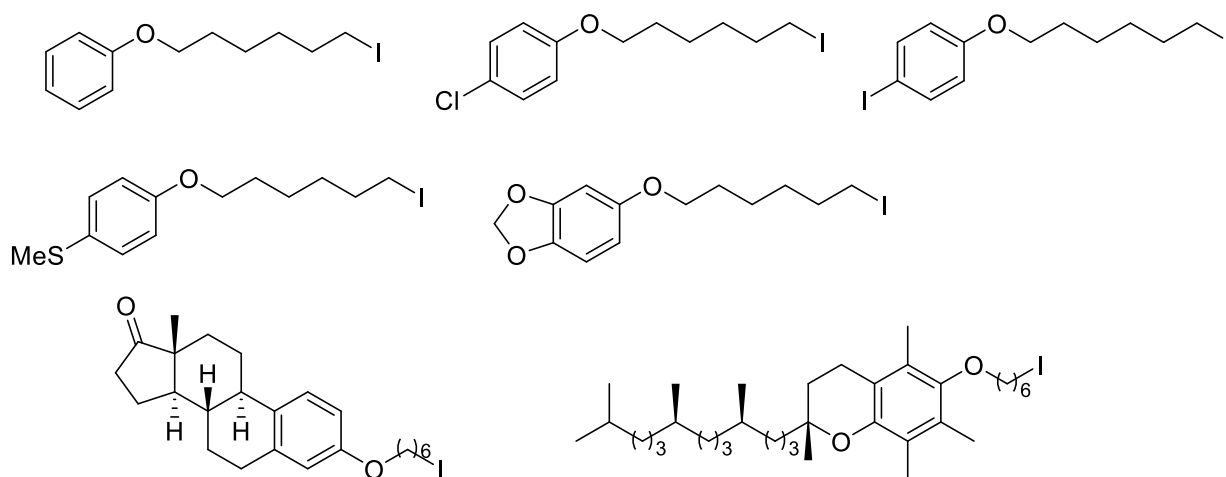
The crude residue was purified by flash column chromatography on silica gel to give the desired product.

The following substrates could be simply synthesized and purified by *General Procedure A* and *B*.

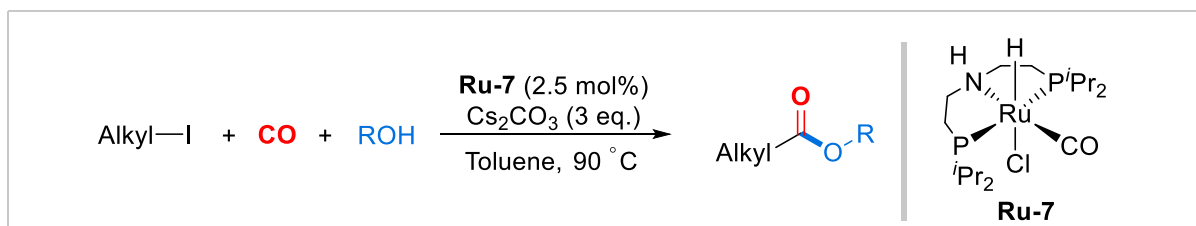
from General Procedure A



from General Procedure B



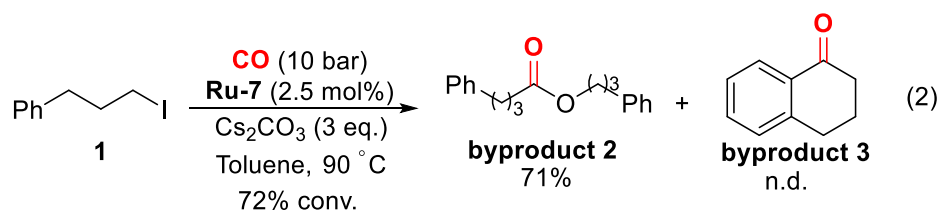
4. General Procedure of the Alkoxycarbonylation



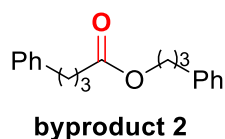
In a glovebox, an oven-dried vial (4 mL) containing a stirring bar was charged with **Ru-7** (0.005 mmol, 2.4 mg), Cs₂CO₃ (0.6 mmol, 195.5 mg), alkyl iodide (0.2 mmol, if it is solid), and alcohol (0.6 mmol, if it is solid). The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and removed from the glovebox. Then, alkyl iodide (0.2 mmol, if it is liquid), and alcohol (0.6 mmol, if it is liquid), and toluene (0.5 mL) were added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 12 h at 90 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. The product was purified by column chromatography on silica gel (pentane/EA), with KMnO₄ solution or ethanol solution of 12MoO₃·H₃PO₄ as the color rendering agent for TLC, to deliver the desired product.

5. Mechanism Studies

5.1 Control experiments



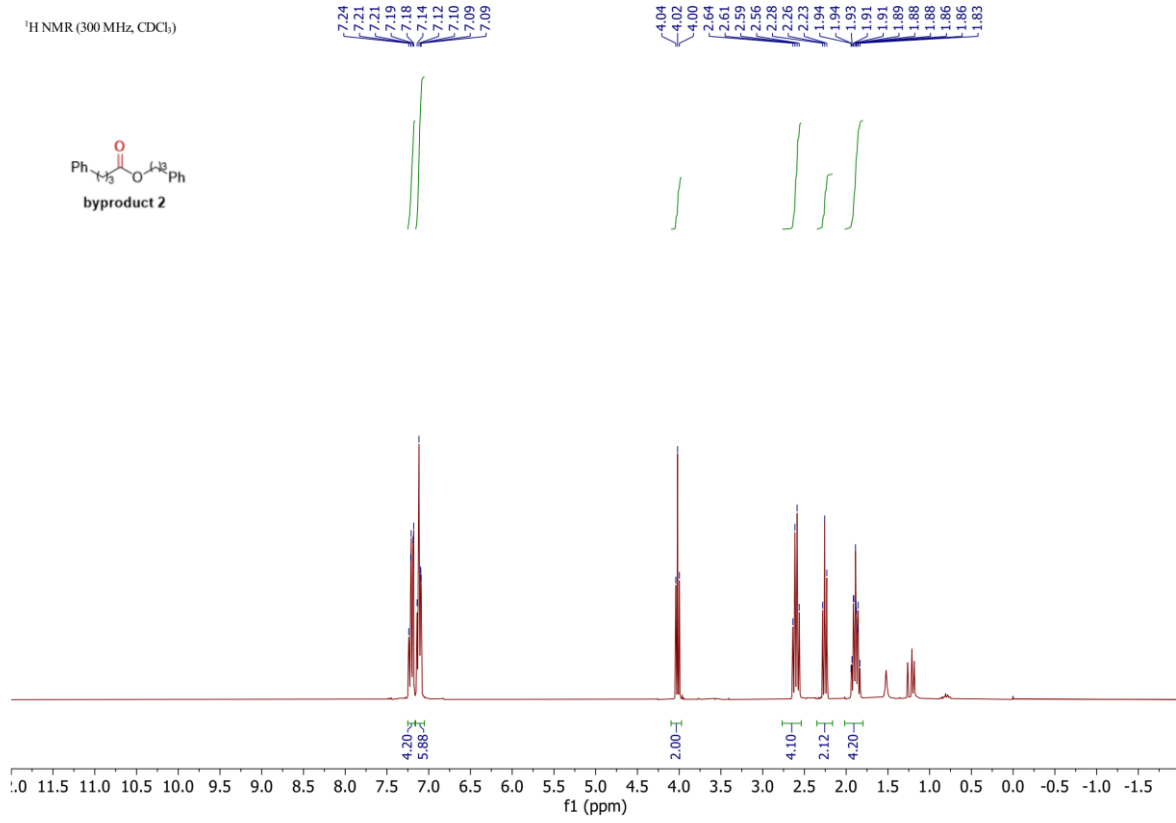
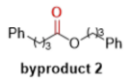
In a glovebox, an oven-dried vial (4 mL) containing a stirring bar was charged with **Ru-7** (0.005 mmol, 2.4 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), **1** (0.2 mmol, 49 mg). The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and removed from the glovebox. Then, toluene (0.5 mL) was added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 12 h at 90 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. A proper amount of solution was taken for GC and GC-MS analysis. The product was purified by column chromatography on silica gel (pentane/EA), with KMnO_4 solution or ethanol solution of $12\text{MoO}_3 \cdot \text{H}_3\text{PO}_4$ as the color rendering agent for TLC, to deliver the desired product. The result is shown above. The characterization and NMR spectrum of **byproduct 2** are given:



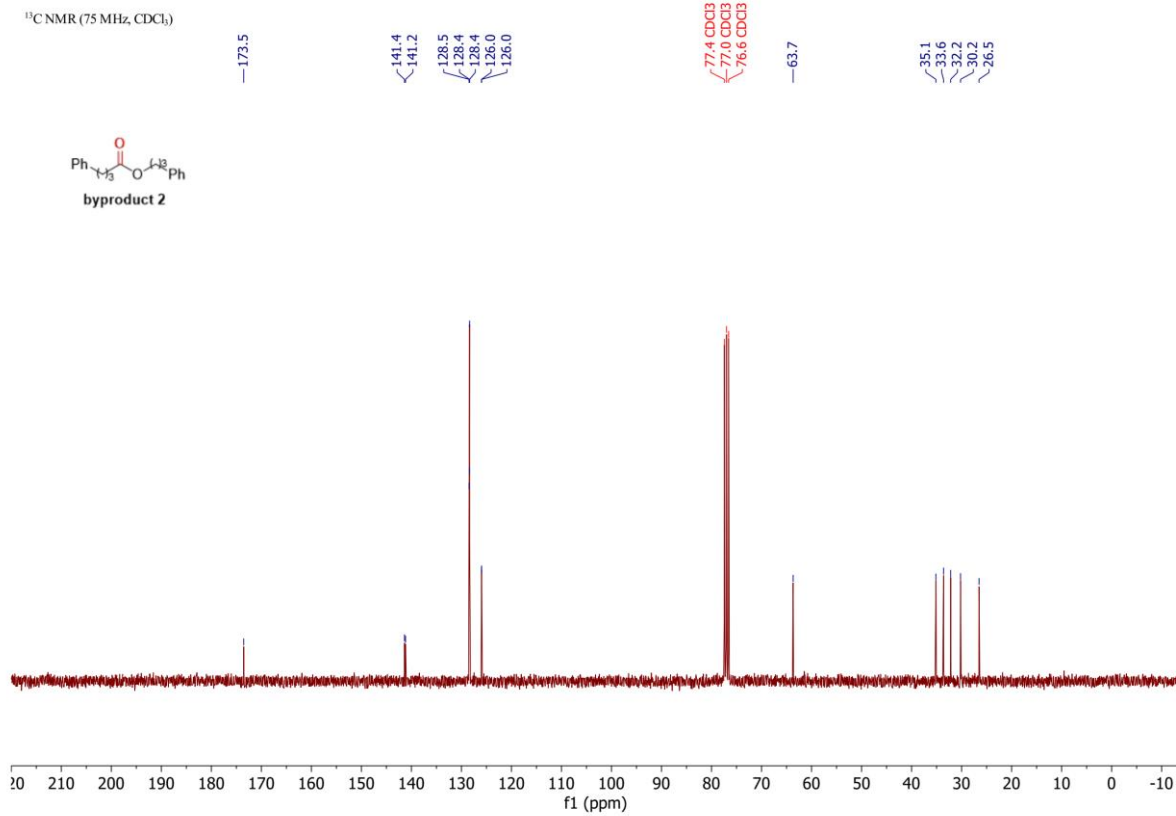
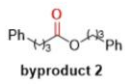
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.27 – 7.15 (m, 4H), 7.17 – 7.06 (m, 6H), 4.02 (t, $J = 6.5$ Hz, 2H), 2.60 (q, $J = 7.5$ Hz, 4H), 2.26 (t, $J = 7.5$ Hz, 2H), 1.97 – 1.79 (m, 4H).

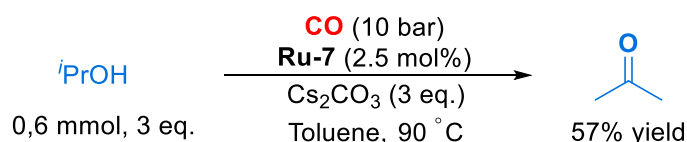
$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.5, 141.4, 141.2, 128.5, 128.4, 128.4, 126.0, 126.0, 63.7, 35.1, 33.6, 32.2, 30.2, 26.5.

¹H NMR (300 MHz, CDCl₃)



¹³C NMR (75 MHz, CDCl₃)

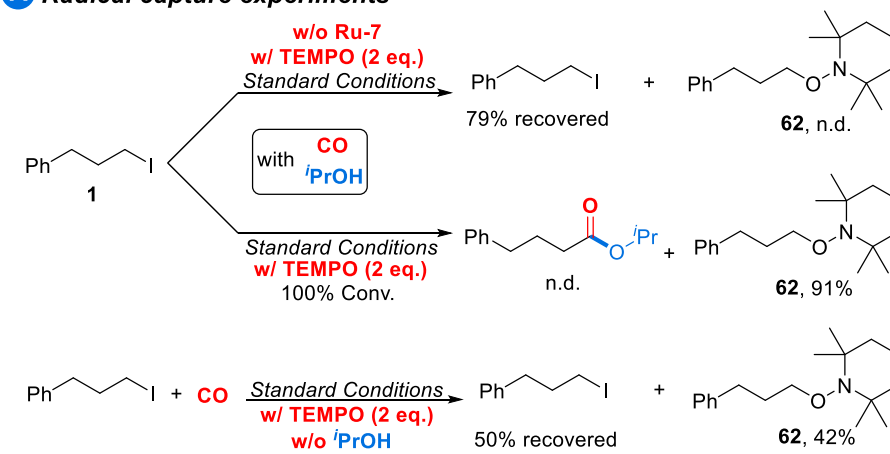




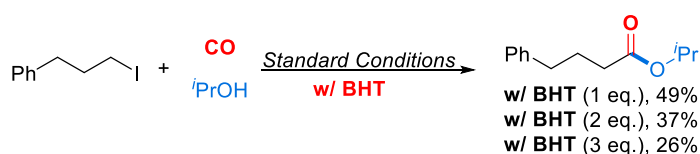
In a glovebox, an oven-dried vial (4 mL) containing a stirring bar was charged with **Ru-7** (0.005 mmol, 2.4 mg), Cs_2CO_3 (0.6 mmol, 195.5 mg), **1** (0.2 mmol, 49 mg). The vial was then sealed with a PTFE/white rubber septum (Wheaton 13 mm Septa) and phenolic cap and removed from the glovebox. Then, toluene (0.5 mL) was added by syringe. The vial was placed in an alloy plate, which was transferred into a 300 mL autoclave of the 4560 series from Parr Instruments. After flushing the autoclave three times with CO, a pressure of 10 bar of CO was adjusted at ambient temperature. Then, the mixture was stirred for 12 h at 90 °C. After the reaction was complete, the autoclave was cooled down to room temperature and the pressure was released carefully. Then 10 μL of hexadecane was added as internal standard and a proper amount of solution was taken after it was well mixed for GC analysis. The result is shown above.

5.2 Radical capture, inhibition, and clock experiments

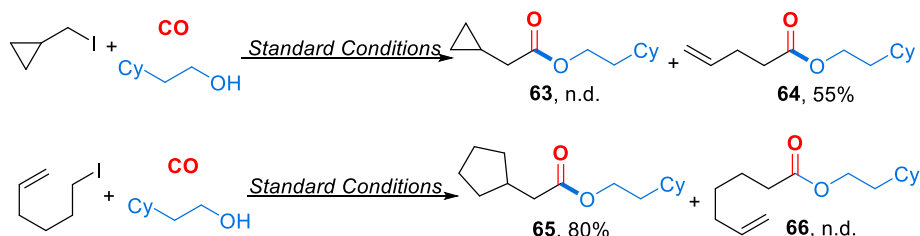
A Radical capture experiments



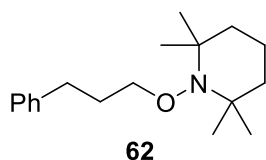
B Radical inhibition experiments



C Radical clock experiments

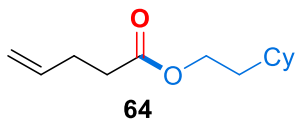


The above reactions were conducted according to the *General Procedure of the Alkoxyacylation*, the result was shown above. The characterization and NMR spectrum of **62**, **64**, **65** are given:



¹H NMR (300 MHz, CDCl₃) δ 7.35–7.24 (m, 2H), 7.27–7.13 (m, 3H), 3.80 (t, J = 6.5 Hz, 2H), 2.78–2.67 (m, 2H), 1.96–1.80 (m, 2H), 1.54–1.29 (m, 6H), 1.16 (s, 6H), 1.14 (s, 6H).

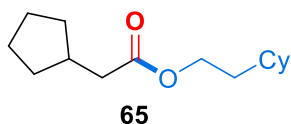
¹³C NMR (75 MHz, CDCl₃) 13C NMR (75 MHz, CDCl₃) δ 142.4, 128.3, 128.2, 125.6, 76.1, 59.6, 39.6, 33.0, 32.7, 30.5, 20.1, 17.1.



$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 5.93–5.73 (m, 1H), 5.15–4.89 (m, 2H), 4.11 (t, $J = 6.9$ Hz, 2H), 2.46–2.32 (m, 4H), 1.75–1.62 (m, 5H), 1.51 (q, $J = 6.8$ Hz, 2H), 1.42–1.13 (m, 4H), 1.01–0.84 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.2, 136.8, 115.4, 62.7, 36.0, 34.5, 33.6, 33.1, 28.9, 26.5, 26.2.

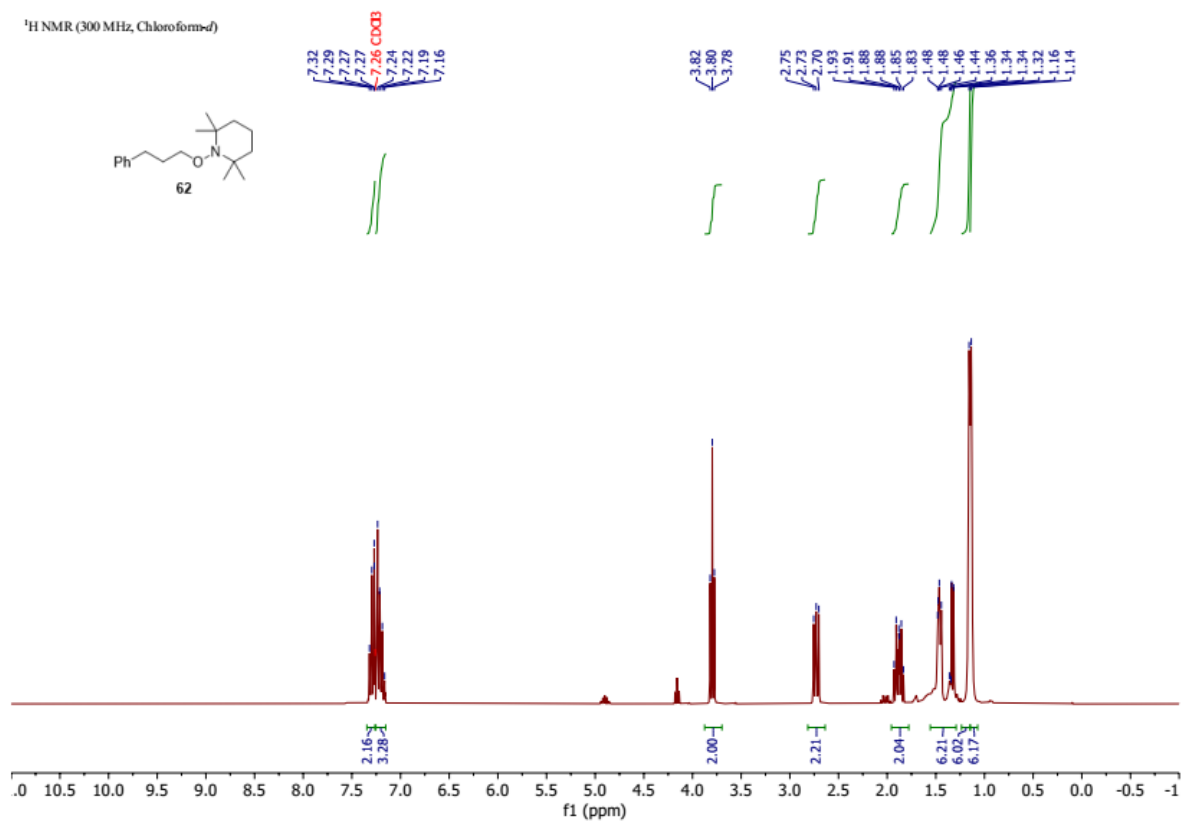
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{13}\text{H}_{22}\text{O}_2\text{H}^+$ ($[\text{M}+\text{H}^+]$) 211.1698, found 211.1697.



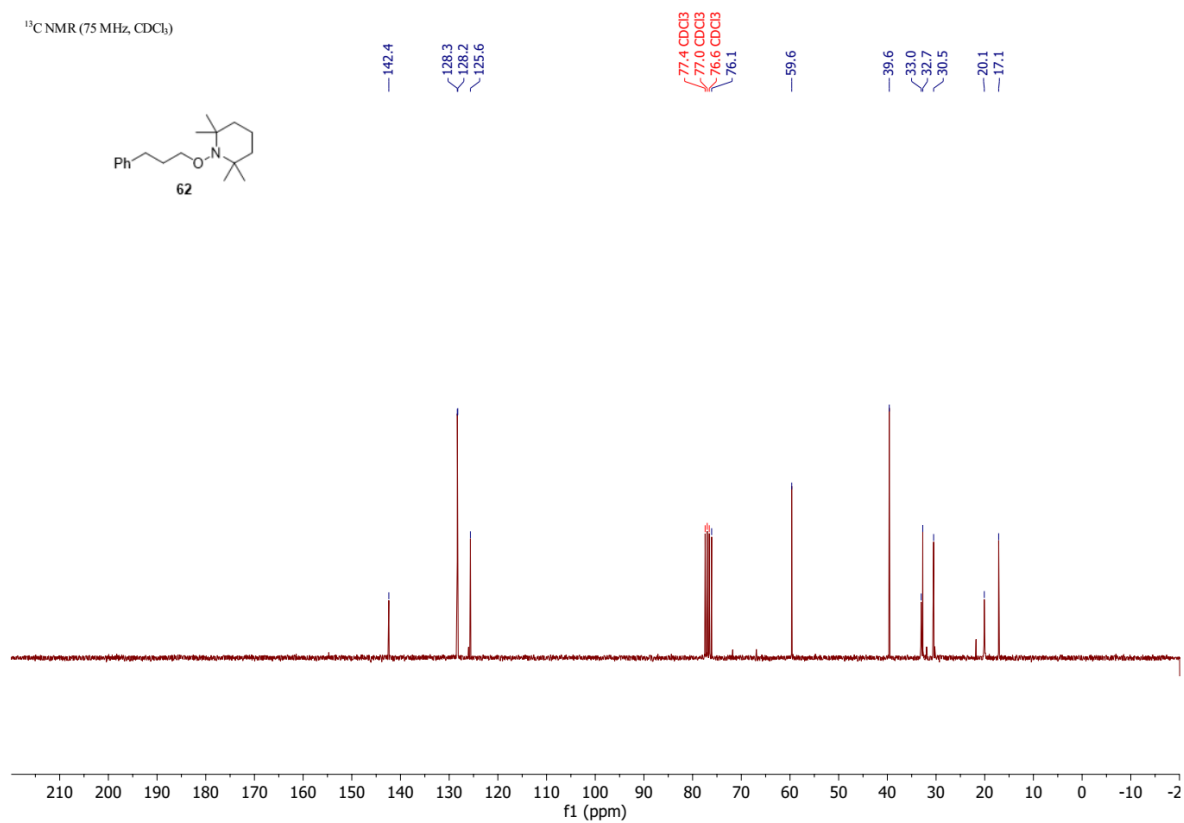
$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.09 (t, $J = 6.9$ Hz, 2H), 2.33–2.13 (m, 3H), 1.86–1.44 (m, 13H), 1.40–1.08 (m, 6H), 1.00–0.81 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.5, 62.4, 40.5, 36.5, 36.0, 34.5, 33.1, 32.4, 26.5, 26.2, 25.0.

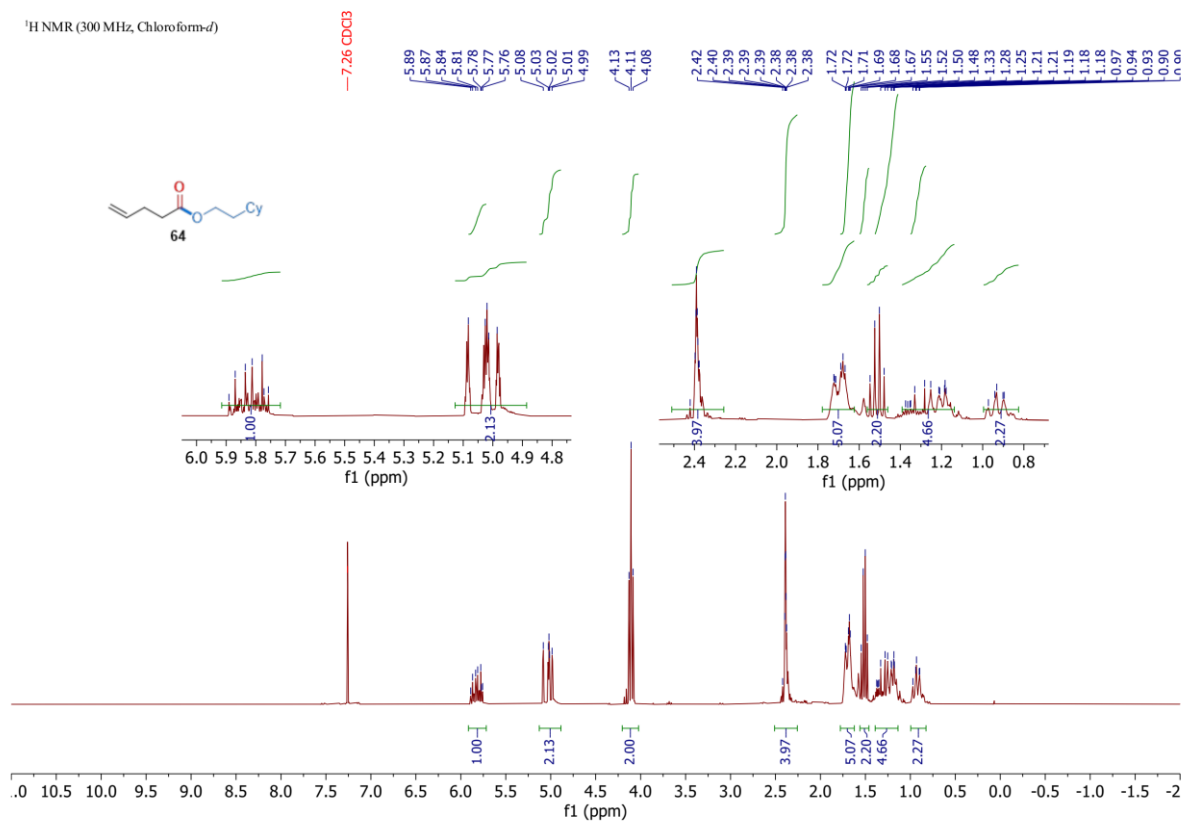
¹H NMR (300 MHz, Chloroform-*d*)



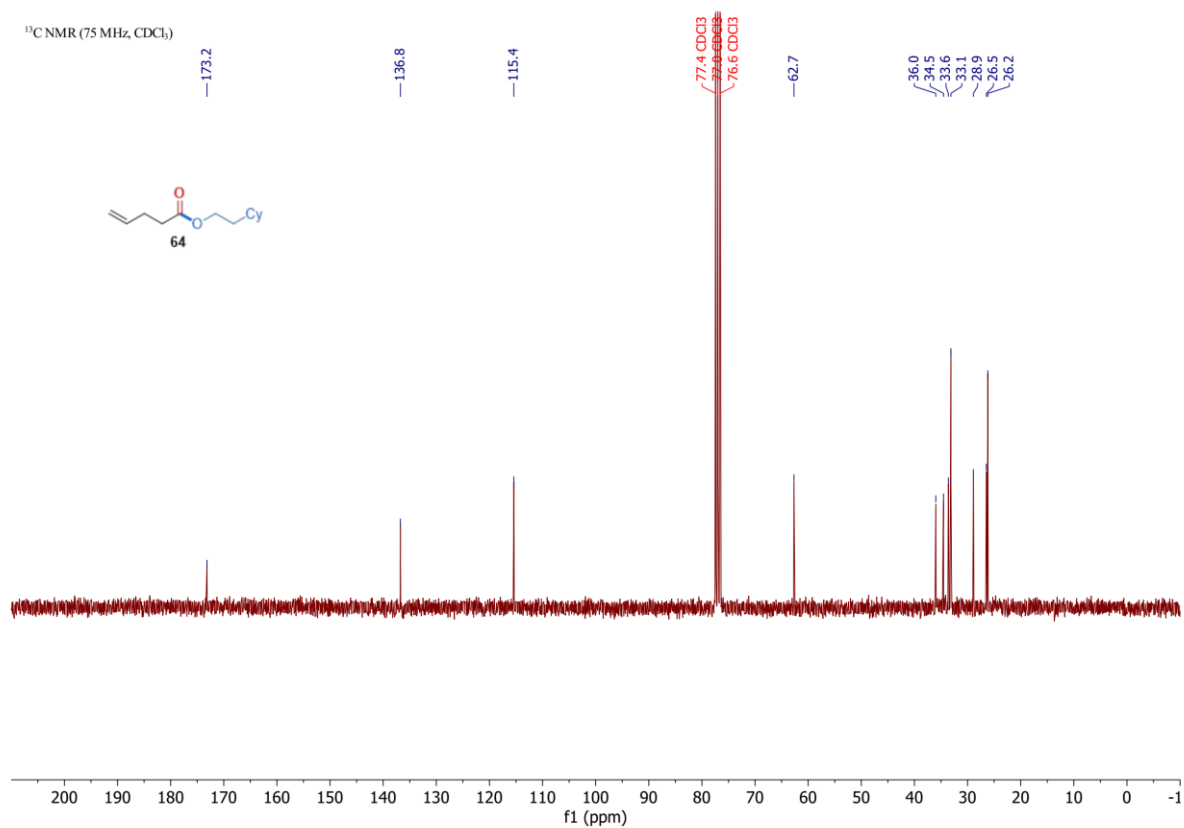
¹³C NMR (75 MHz, CDCl₃)



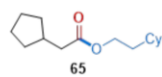
¹H NMR (300 MHz, Chloroform-*d*)



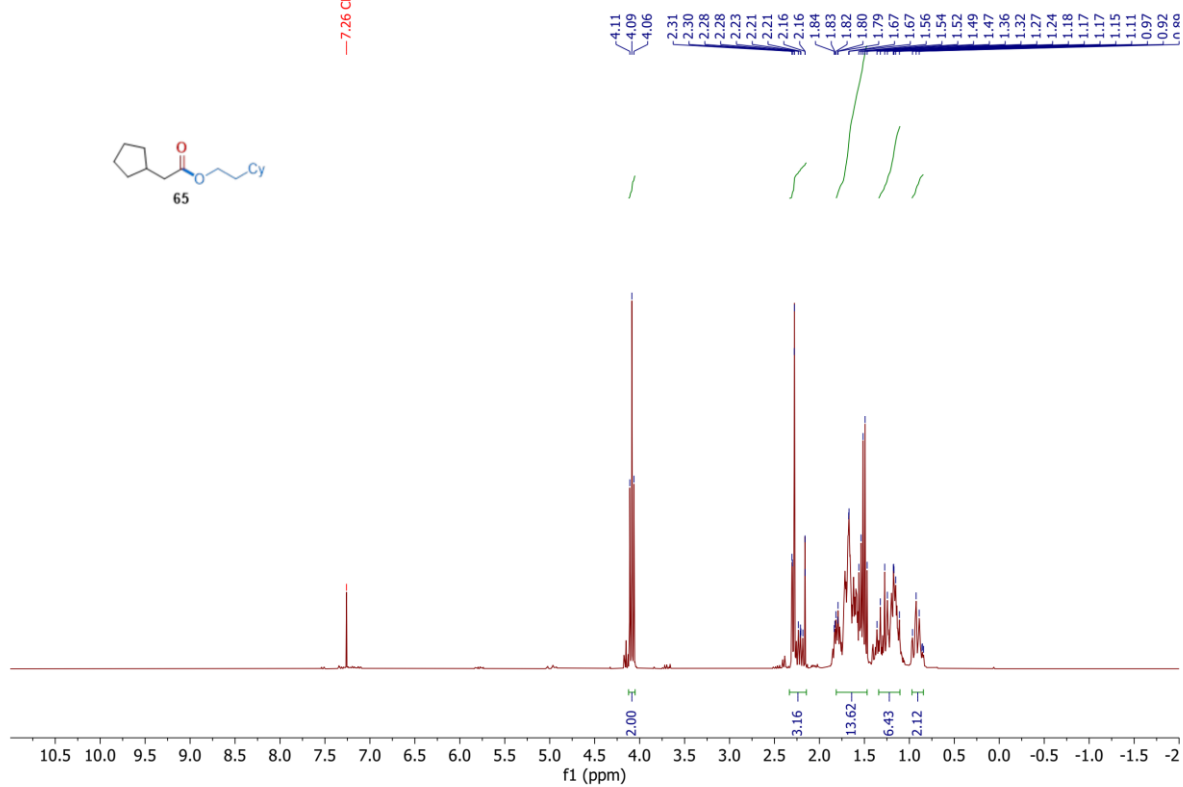
¹³C NMR (75 MHz, CDCl₃)



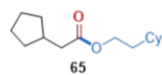
¹H NMR (300 MHz, Chloroform-*d*)



-7.26 CDCl₃



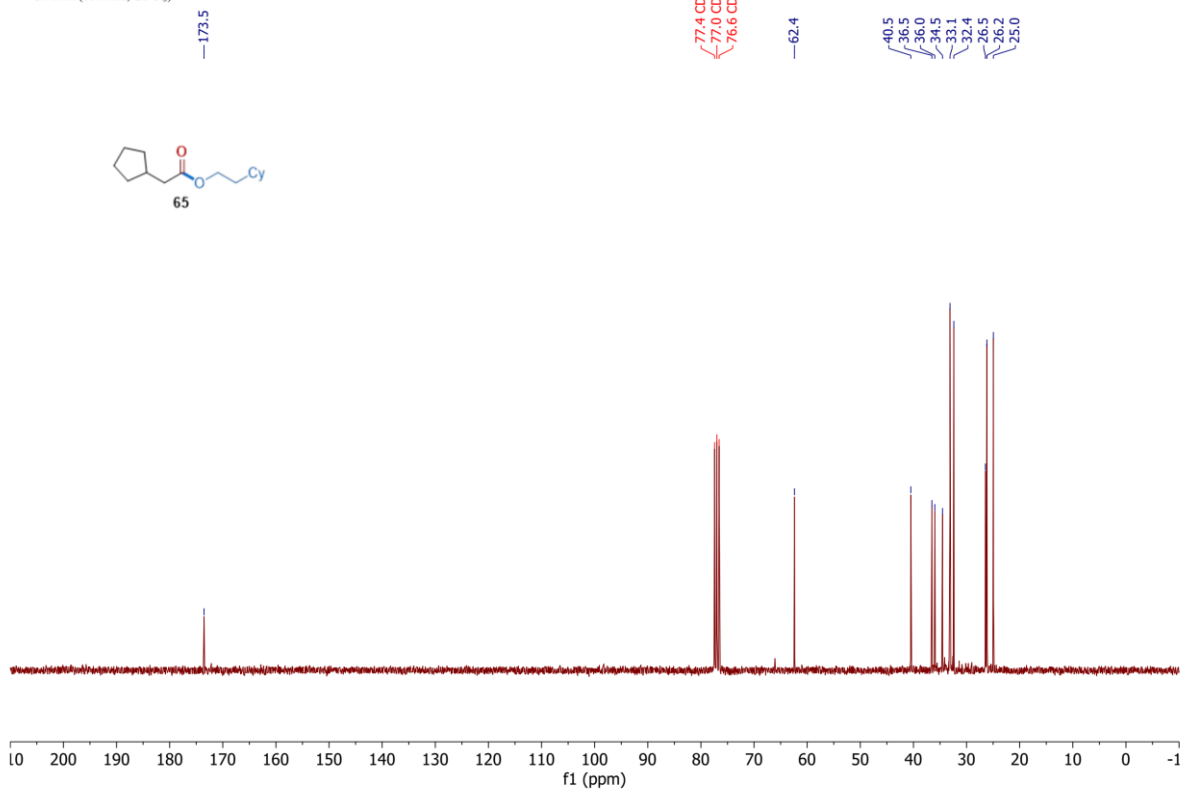
¹³C NMR (75 MHz, CDCl₃)



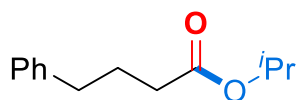
77.4 CDCl₃
77.0 CDCl₃
76.6 CDCl₃

62.4

40.5
36.5
36.0
34.5
33.1
32.4
26.5
26.2
25.0



6. Characterization of the Products



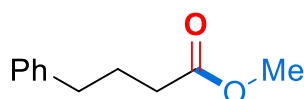
3

Isopropyl 4-phenylbutanoate (3) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (33.8 mg, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.33 - 7.25 (m, 2H), 7.24 - 7.15 (m, 3H), 5.02 (hept, *J* = 6.3 Hz, 1H), 2.69 - 2.61 (m, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.01 - 1.88 (m, 2H), 1.24 (s, 3H), 1.23 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.1, 141.5, 128.5, 128.4, 126.0, 67.5, 35.2, 34.1, 26.7, 21.9.

HRMS (ESI-TOF): *m/z* calcd. for C₁₃H₁₈O₂Na⁺ ([M+Na⁺]) 229.1204, found 229.1207.



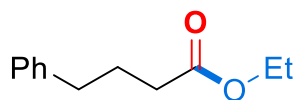
4

Methyl 4-phenylbutanoate (4) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (29.9 mg, 84% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (m, 2H), 7.24 - 7.15 (m, 3H), 3.67 (s, 3H), 2.66 (t, 2H), 2.34 (t, *J* = 7.5 Hz, 2H), 1.97 (p, *J* = 7.6 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 173.9, 141.3, 128.5, 128.4, 126.0, 51.5, 35.1, 33.4, 26.4.

HRMS (ESI-TOF): *m/z* calcd. for C₁₁H₁₄O₂Na⁺ ([M+Na⁺]) 201.0891, found 201.0896.



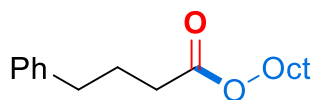
5

Ethyl 4-phenylbutanoate (5) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (31.1 mg, 81% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, *J* = 8.0, 6.6 Hz, 2H), 7.24 - 7.16 (m, 3H), 4.13 (q, *J* = 7.2 Hz, 2H), 2.66 (t, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.03 - 1.91 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.5, 141.4, 128.5, 128.3, 125.9, 60.2, 35.1, 33.6, 26.5, 14.2.

HRMS (EI): *m/z* calcd. for C₁₂H₁₆O₂• ([M+•]) 192.11448, found 192.11380.



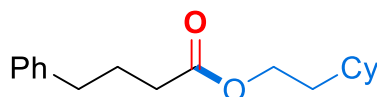
6

Octyl 4-phenylbutanoate (6) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (50 mg, 91% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (dd, *J* = 8.1, 6.5 Hz, 2H), 7.24 - 7.16 (m, 3H), 4.07 (t, *J* = 6.7 Hz, 2H), 2.72 - 2.62 (m, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 1.97 (p, *J* = 7.5 Hz, 2H), 1.71 - 1.57 (m, 2H), 1.42 - 1.24 (m, 10H), 0.89 (t, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 173.6, 141.4, 128.4, 128.3, 125.9, 64.5, 35.1, 33.6, 31.7, 29.2, 29.1, 28.6, 26.5, 25.9, 22.6, 14.0.

HRMS (ESI-TOF): *m/z* calcd. for C₁₈H₂₈O₂Na⁺ ([M+Na⁺]) 299.1986, found 299.1993.



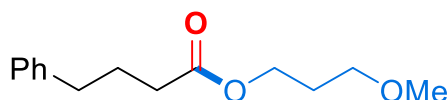
7

2-Cyclohexylethyl 4-phenylbutanoate (7) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (45 mg, 82% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.33 - 7.22 (m, 2H), 7.24 - 7.13 (m, 3H), 4.09 (t, *J* = 6.9 Hz, 2H), 2.70 - 2.59 (t, 2H), 2.31 (t, *J* = 7.4 Hz, 2H), 2.06 - 1.86 (m, 2H), 1.75 - 1.60 (m, 5H), 1.51 (q, *J* = 6.9 Hz, 2H), 1.41 - 1.08 (m, 4H), 1.01 - 0.82 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.6, 141.4, 128.5, 128.3, 125.9, 62.6, 36.0, 35.1, 34.5, 33.7, 33.1, 26.5, 26.5, 26.2.

HRMS (ESI-TOF): *m/z* calcd. for C₁₈H₂₆O₂Na⁺ ([M+Na⁺]) 297.1830, found 297.1835.



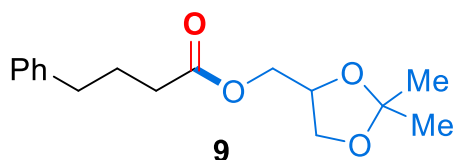
8

3-Methoxypropyl 4-phenylbutanoate (8) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (38.5 mg, 82% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.33 - 7.24 (m, 2H), 7.23 - 7.15 (m, 3H), 4.16 (t, *J* = 6.5 Hz, 2H), 3.44 (t, *J* = 6.3 Hz, 2H), 3.33 (s, 3H), 2.66 (t, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.02 - 1.86 (m, 4H).

¹³C NMR (101 MHz, CDCl₃) δ 173.4, 141.4, 128.4, 128.3, 125.9, 69.1, 61.5, 58.6, 35.1, 33.6, 28.9, 26.5.

HRMS (ESI-TOF): *m/z* calcd. for C₁₄H₂₀O₃Na⁺ ([M+Na⁺]) 259.1310, found 259.1312.

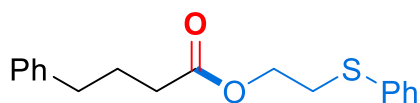


(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-phenylbutanoate (9) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a colorless oil (46 mg, 83% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.37 - 7.25 (m, 2H), 7.31 - 7.14 (m, 3H), 4.40 - 4.26 (m, 1H), 4.26 - 4.04 (m, 3H), 3.75 (dd, *J* = 8.5, 6.1 Hz, 1H), 2.68 (t, 2H), 2.40 (t, *J* = 7.6 Hz, 2H), 2.07 - 1.91 (m, 2H), 1.45 (s, 3H), 1.39 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 173.2, 141.2, 128.4, 128.3, 126.0, 109.8, 73.6, 66.3, 64.6, 35.0, 33.3, 26.6, 26.4, 25.3.

HRMS (ESI-TOF): *m/z* calcd. for C₁₆H₂₂O₄Na⁺ ([M+Na⁺]) 301.1415, found 301.1416.

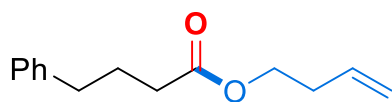


(2,2-Dimethyl-1,3-dioxolan-4-yl)methyl 4-phenylbutanoate (10) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (47 mg, 78% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.47 - 7.38 (m, 2H), 7.38 - 7.27 (m, 4H), 7.29 - 7.17 (m, 4H), 4.27 (t, *J* = 6.9 Hz, 2H), 3.17 (t, *J* = 6.9 Hz, 2H), 2.68 (t, 2H), 2.33 (t, *J* = 7.5 Hz, 2H), 2.08 - 1.89 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.2, 141.3, 135.1, 129.8, 129.0, 128.5, 128.3, 126.5, 126.0, 62.9, 62.8, 35.0, 33.4, 32.4, 26.3.

HRMS (ESI-TOF): *m/z* calcd. for C₁₈H₂₀O₂SNa⁺ ([M+Na⁺]) 323.1081, found 323.1086.

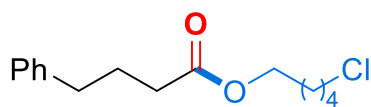


But-3-en-1-yl 4-phenylbutanoate (11) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (21.8 mg, 50% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.33 - 7.25 (m, 2H), 7.24 - 7.15 (m, 3H), 5.79 (ddt, *J* = 17.0, 10.2, 6.7 Hz, 1H), 5.18 - 5.03 (m, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 2.70 - 2.61 (m, 2H), 2.39 (qt, *J* = 6.8, 1.4 Hz, 2H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.96 (p, *J* = 7.5 Hz, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 173.5, 141.4, 134.1, 128.5, 128.4, 126.0, 117.2, 63.4, 35.1, 33.6, 33.1, 26.5.

HRMS (ESI-TOF): *m/z* calcd. for C₁₄H₁₈O₂H⁺ ([M+H⁺]) 219.1385, found 219.1389.



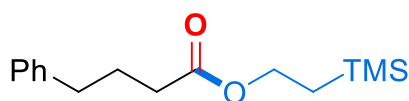
12

5-Chloropentyl 4-phenylbutanoate (12) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (48 mg, 90% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.27 - 7.15 (m, 2H), 7.17 - 7.06 (m, 2H), 4.00 (t, *J* = 6.5 Hz, 2H), 3.46 (t, *J* = 6.6 Hz, 2H), 2.58 (t, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.97 - 1.81 (m, 2H), 1.81 - 1.66 (m, 2H), 1.66 - 1.51 (m, 2H), 1.51 - 1.32 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.5, 141.4, 128.5, 128.4, 126.0, 64.0, 44.7, 35.1, 33.6, 32.1, 27.9, 26.5, 23.3.

HRMS (ESI-TOF): *m/z* calcd. for C₁₅H₂₁O₂ClNa⁺ ([M+Na⁺]) 291.1127, found 291.1135.



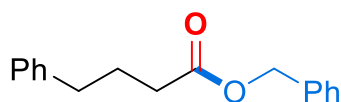
13

2-(Trimethylsilyl)ethyl 4-phenylbutanoate (13) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (43 mg, 81% yield).

¹H NMR (400 MHz, CDCl₃) δ 7.33 - 7.25 (m, 2H), 7.24 - 7.15 (m, 3H), 4.21 - 4.10 (m, 2H), 2.70 - 2.62 (m, 2H), 2.32 (t, *J* = 7.5 Hz, 2H), 2.03 - 1.90 (m, 2H), 1.06 - 0.94 (m, 2H), 0.05 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 173.6, 141.4, 128.5, 128.3, 125.9, 62.4, 35.1, 33.8, 26.5, 17.3, -1.5.

HRMS (ESI-TOF): *m/z* calcd. for C₁₅H₂₄SiO₂Na⁺ ([M+Na⁺]) 287.1443, found 287.1437.



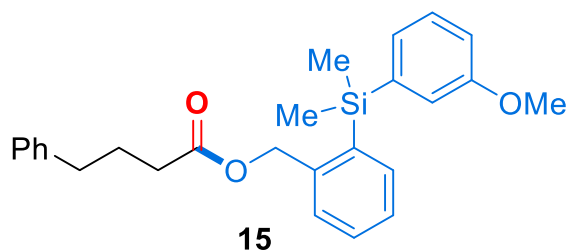
14

Benzyl 4-phenylbutanoate (14) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (44 mg, 87% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.31 - 7.25 (m, 4H), 7.23 - 7.15 (m, 2H), 7.16 - 7.04 (m, 4H), 5.04 (s, 2H), 2.63 - 2.52 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 1.92 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.3, 141.3, 136.0, 128.5, 128.5, 128.4, 128.2, 126.0, 66.1, 35.1, 33.6, 26.5.

HRMS (ESI-TOF): *m/z* calcd. for C₁₇H₁₈O₂Na⁺ ([M+Na⁺]) 277.1204, found 277.1207.

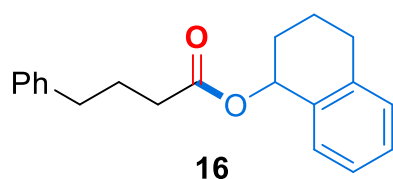


2-((3-Methoxyphenyl)dimethylsilyl)benzyl 4-phenylbutanoate (15) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a colorless oil (66.9 mg, 80% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.63 (d, *J* = 6.5 Hz, 1H), 7.52 - 7.39 (m, 3H), 7.36 - 7.28 (m, 3H), 7.27 - 7.16 (m, 3H), 7.12 - 7.04 (m, 2H), 7.01 - 6.88 (m, 1H), 5.07 (s, 2H), 3.82 (s, 3H), 2.65 (t, 2H), 2.27 (t, 2H), 1.95 (t, 2H), 0.66 (d, *J* = 0.6 Hz, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 173.0, 159.0, 141.4, 141.3, 140.1, 137.0, 135.7, 129.8, 129.4, 129.1, 128.4, 128.3, 127.6, 126.2, 125.9, 119.6, 114.2, 66.4, 55.0, 35.1, 33.4, 26.3, -1.1.

HRMS (ESI-TOF): *m/z* calcd. for C₂₆H₃₀O₃SiNa⁺ ([M+Na⁺]) 441.1861, found 441.1866.

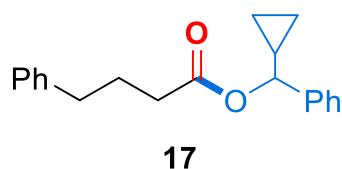


1,2,3,4-Tetrahydronaphthalen-1-yl 4-phenylbutanoate (16) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (41.2 mg, 70% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.29 - 7.03 (m, 9H), 5.98 (t, *J* = 4.3 Hz, 1H), 2.90 - 2.67 (m, 2H), 2.65 - 2.54 (m, 2H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.00 - 1.70 (m, 6H).

¹³C NMR (75 MHz, CDCl₃) δ 173.1, 160.7, 141.4, 137.9, 134.6, 129.4, 129.1, 128.5, 128.3, 128.0, 126.0, 125.9, 69.8, 35.1, 34.1, 29.1, 28.9, 26.7, 18.8.

HRMS (ESI-TOF): *m/z* calcd. for C₂₀H₂₂O₂Na⁺ ([M+Na⁺]) 317.1517, found 317.1525.

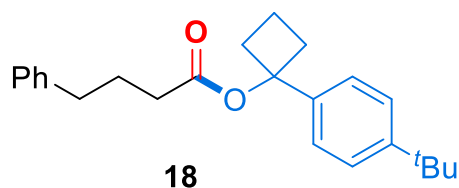


Cyclopropyl(phenyl)methyl 4-phenylbutanoate (17) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (51.2 mg, 87% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.33 - 7.16 (m, 7H), 7.14 - 7.04 (m, 3H), 5.17 (d, *J* = 8.7 Hz, 2H), 2.61 - 2.50 (m, 2H), 2.30 (td, *J* = 7.4, 2.5 Hz, 2H), 1.96 - 1.80 (m, 2H), 1.34 - 1.15 (m, 1H), 0.61 - 0.39 (m, 3H), 0.38 - 0.25 (m, 1H).

^{13}C NMR (75 MHz, CDCl_3) δ 172.8, 141.5, 140.5, 128.5, 128.4, 127.9, 126.6, 126.0, 79.6, 35.1, 34.0, 26.7, 16.6, 4.1, 3.1.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{20}\text{H}_{22}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 317.1517, found 317.1513.

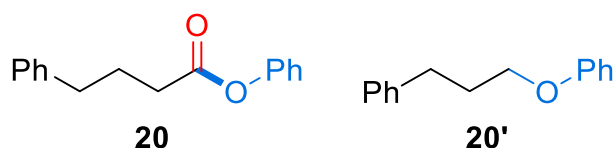


1-(4-(*tert*-Butyl)phenyl)cyclobutyl 4-phenylbutanoate (18) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (22 mg, 31% yield).

^1H NMR (300 MHz, CDCl_3) δ 7.37 - 7.23 (m, 4H), 7.24 - 7.14 (m, 2H), 7.15 - 7.00 (m, 3H), 2.68 - 2.42 (m, 6H), 2.18 (t, 2H), 1.94 - 1.58 (m, 4H), 1.23 (s, 9H).

^{13}C NMR (75 MHz, CDCl_3) δ 172.0, 150.0, 141.5, 139.5, 128.5, 128.4, 125.9, 125.4, 125.1, 82.1, 35.0, 34.9, 34.5, 34.2, 31.4, 26.5, 14.3.

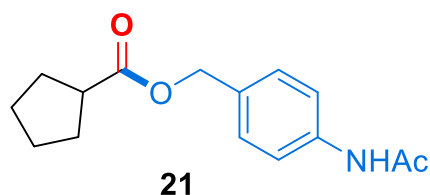
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{24}\text{H}_{30}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 373.2143, found 373.2142.



Phenyl 4-phenylbutanoate (20) and **(3-phenoxypropyl)benzene (20')** Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compounds as colorless oil (43 mg, 29% and 68% yield respectively).

^1H NMR (300 MHz, CDCl_3) mixture of **20** and **20'**, see the NMR Spectrum.

^{13}C NMR (75 MHz, CDCl_3) mixture of **20** and **20'**, see the NMR Spectrum.

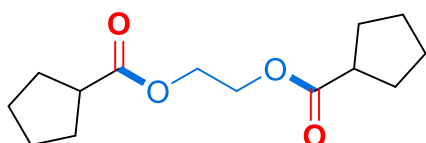


4-Acetamidobenzyl cyclopentanecarboxylate (21) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 3:1) to afford the title compound as a colorless oil (25 mg, 48% yield).

^1H NMR (300 MHz, CDCl_3) δ 7.49 (d, J = 8.5 Hz, 2H), 7.38 (s, 1H), 7.30 (d, J = 8.4 Hz, 2H), 5.06 (s, 2H), 2.85 - 2.68 (m, 1H), 2.17 (s, 3H), 2.00 - 1.47 (m, 8H).

^{13}C NMR (75 MHz, CDCl_3) δ 176.6, 168.4, 137.7, 132.2, 128.9, 119.8, 65.6, 43.8, 30.0, 25.8, 24.6.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{15}\text{H}_{19}\text{NO}_3\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 284.1262, found 284.1257.



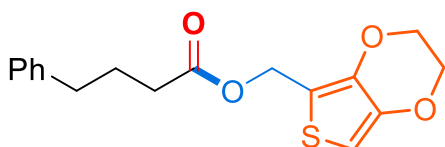
22

Ethane-1,2-diyl dicyclopentanecarboxylate (22) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (21 mg, 83% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.27 (s, 4H), 2.82 - 2.66 (m, 2H), 1.97 - 1.51 (m, 16H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.5, 62.0, 43.7, 29.9, 25.8.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{14}\text{H}_{22}\text{O}_4\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 277.1415, found 277.1414.



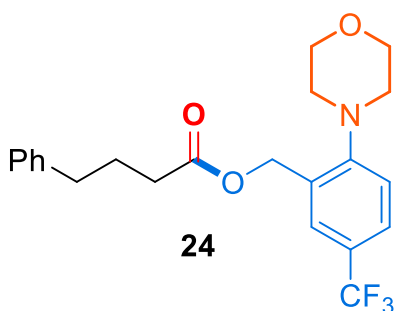
23

(2,3-Dihydrothieno[3,4-*b*][1,4]dioxin-5-yl)methyl 4-phenylbutanoate (23) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a light-yellow oil (28 mg, 44% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.33 - 7.22 (m, 2H), 7.23 - 7.12 (m, 3H), 6.34 (s, 1H), 5.12 (s, 2H), 4.27 - 4.14 (m, 4H), 2.64 (t, 2H), 2.35 (t, $J = 7.4$ Hz, 2H), 2.04 - 1.88 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.4, 141.4, 141.2, 140.6, 128.5, 128.4, 126.0, 110.9, 100.1, 64.8, 64.5, 56.7, 35.1, 33.6, 26.5.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{17}\text{H}_{18}\text{O}_4\text{SNa}^+$ ($[\text{M}+\text{Na}^+]$) 341.0823, found 341.0831.



24

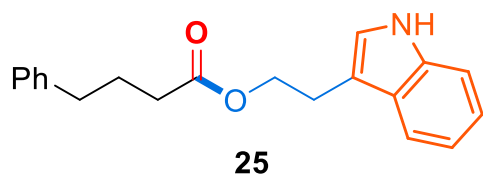
2-Morpholino-5-(trifluoromethyl)benzyl 4-phenylbutanoate (24) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a light-yellow oil (67 mg, 82% yield).

δ 7.68 (s, 1H), 7.60 (dd, $J = 8.5, 1.6$ Hz, 1H), 7.37 - 7.25 (m, 2H), 7.26 - 7.17 (m, 4H), 5.27 (s, 2H), 3.94 - 3.81 (m, 4H), 3.03 - 2.93 (m, 4H), 2.70 (t, 2H), 2.45 (t, $J = 7.4$ Hz, 2H), 2.05 (q, $J = 7.7$ Hz, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.2, 154.2, 141.1, 131.4, 128.4, 128.4, 126.6 (q, $J = 3.8$ Hz), 126.1, 125.7, 124.1 (q, $J = 269.3$ Hz), 120.1, 119.8, 77.4, 77.0, 76.6, 67.1, 61.5, 52.9, 35.0, 33.5, 26.4.

$^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -62.0.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{22}\text{H}_{24}\text{F}_3\text{NO}_3\text{H}^+$ ($[\text{M}+\text{H}^+]$) 408.1786, found 408.1780.

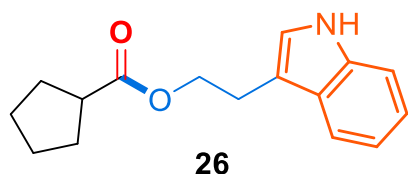


2-(1H-Indol-3-yl)ethyl 4-phenylbutanoate (25) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a light-yellow oil (25.2 mg, 41% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.92 (s, 1H), 7.60 - 7.51 (m, 1H), 7.32 - 7.22 (m, 1H), 7.25 - 7.10 (m, 2H), 7.15 - 6.99 (m, 5H), 6.94 (d, *J* = 2.4 Hz, 1H), 4.28 (t, *J* = 7.2 Hz, 2H), 3.02 (td, *J* = 7.2, 0.9 Hz, 2H), 2.67 - 2.44 (m, 2H), 2.25 (t, *J* = 7.5 Hz, 2H), 1.95 - 1.76 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.5, 141.4, 136.2, 128.5, 128.3, 127.4, 125.9, 122.1, 122.0, 119.4, 118.8, 112.1, 111.1, 64.4, 35.1, 33.7, 26.5, 24.8.

HRMS (ESI-TOF): *m/z* calcd. for C₂₀H₂₁NO₂Na⁺ ([M+Na⁺]) 330.1469, found 330.1467.

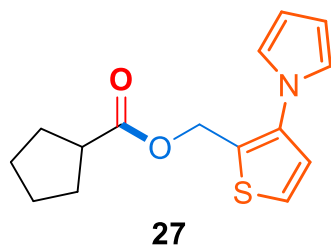


2-(1H-Indol-3-yl)ethyl cyclopentanecarboxylate (26) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a yellow oil (24 mg, 47% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.08 (s, 1H), 7.66 (dd, *J* = 7.9, 0.7 Hz, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.25 - 7.17 (m, 1H), 7.19 - 7.10 (m, 1H), 7.04 (d, *J* = 2.4 Hz, 1H), 4.37 (t, *J* = 7.2 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 2.83 - 2.69 (m, 1H), 1.96 - 1.67 (m, 6H), 1.64 - 1.54 (m, 2H).

¹³C NMR (101 MHz, CDCl₃) δ 176.9, 136.1, 127.4, 122.0, 122.0, 119.3, 118.8, 112.1, 111.1, 64.4, 43.9, 30.0, 25.8, 24.8.

HRMS (ESI-TOF): *m/z* calcd. for C₁₆H₁₉NO₂Na⁺ ([M+Na⁺]) 280.1313, found 280.1319.

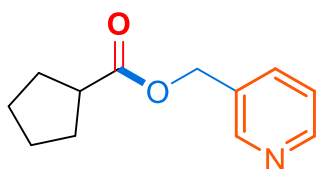


(3-(1H-Pyrrol-1-yl)thiophen-2-yl)methyl cyclopentanecarboxylate (27) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a light-yellow oil (49 mg, 89% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.34 (d, *J* = 5.3 Hz, 1H), 7.03 (d, *J* = 5.3 Hz, 1H), 6.93 (t, *J* = 2.0 Hz, 2H), 6.33 (t, *J* = 2.0 Hz, 2H), 5.18 (s, 2H), 2.87 - 2.71 (m, 1H), 2.02 - 1.49 (m, 8H).

¹³C NMR (75 MHz, CDCl₃) δ 176.3, 139.1, 126.3, 125.8, 124.4, 121.8, 109.6, 57.6, 43.6, 29.9, 25.8.

HRMS (ESI-TOF): *m/z* calcd. for C₁₅H₁₇NO₂SNa⁺ ([M+Na⁺]) 298.0877, found 298.0873.



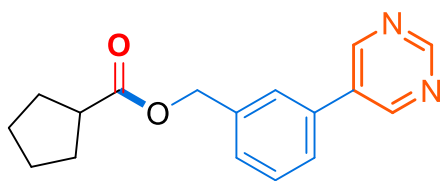
28

Pyridin-3-ylmethyl cyclopentanecarboxylate (28) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 3:1) to afford the title compound as a light-yellow oil (37 mg, 90% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.60 - 8.43 (m, 2H), 7.62 (dt, $J = 7.8, 1.9$ Hz, 1H), 7.31 - 7.15 (m, 1H), 5.06 (s, 2H), 2.71 (m, 1H), 1.93 - 1.39 (m, 8H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.3, 149.3, 135.8, 131.9, 123.4, 63.4, 43.6, 29.9, 25.7.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{12}\text{H}_{15}\text{NO}_2\text{H}^+$ ($[\text{M}+\text{H}^+]$) 206.1181, found 206.1183.



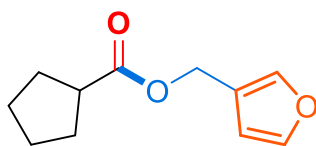
29

3-(Pyrimidin-5-yl)benzyl cyclopentanecarboxylate (29) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 2:1) to afford the title compound as a light-yellow oil (46 mg, 82% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 9.20 (s, 1H), 8.94 (s, 2H), 7.58 - 7.39 (m, 4H), 5.19 (s, 2H), 2.80 (p, $J = 7.9$ Hz, 1H), 2.00 - 1.48 (m, 8H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.4, 157.5, 154.9, 137.8, 134.6, 134.0, 129.6, 128.4, 126.6, 126.4, 65.5, 43.7, 30.0, 25.7.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2\text{H}^+$ ($[\text{M}+\text{H}^+]$) 283.1447, found 283.1443.



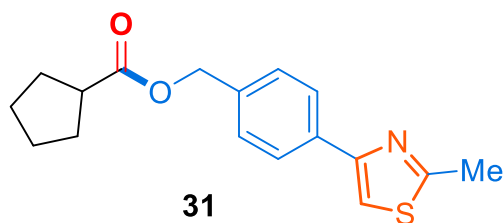
30

Furan-3-ylmethyl cyclopentanecarboxylate (30) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a colorless oil (31 mg, 80% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.49 - 7.42 (m, 1H), 7.42 - 7.35 (m, 1H), 6.41 (dd, $J = 1.8, 0.9$ Hz, 1H), 4.98 (s, 2H), 2.82 - 2.63 (m, 1H), 1.95 - 1.51 (m, 8H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.6, 143.3, 141.3, 120.7, 110.4, 57.5, 43.7, 29.9, 25.8.

HRMS (EI): m/z calcd. for $\text{C}_{11}\text{H}_{14}\text{O}_3\cdot$ ($[\text{M}+\cdot]$) 194.09375, found 194.09389.

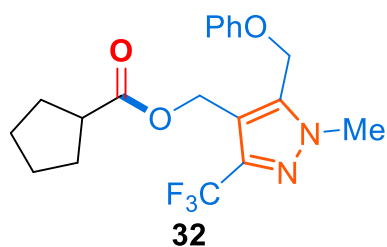


4-(2-Methylthiazol-4-yl)benzyl cyclopentanecarboxylate (31) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 10:1) to afford the title compound as a colorless oil (42 mg, 70% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.91 - 7.81 (m, 2H), 7.44 - 7.34 (m, 2H), 7.31 (s, 1H), 5.13 (s, 2H), 2.87 - 2.70 (m, 4H), 1.99 - 1.48 (m, 8H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.5, 165.9, 154.6, 136.0, 134.3, 128.4, 126.4, 112.5, 77.4, 77.0, 76.6, 65.7, 43.8, 30.0, 25.8, 19.3.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{17}\text{H}_{19}\text{NO}_2\text{SH}^+$ ($[\text{M}+\text{H}^+]$) 302.1215, found 302.1205.

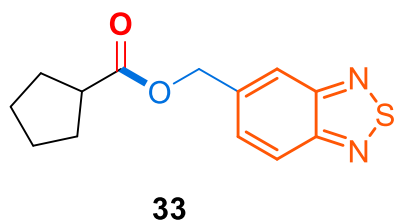


(1-Methyl-5-(phoxymethyl)-3-(trifluoromethyl)-1H-pyrazol-4-yl)methyl cyclopentanecarboxylate (32) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a colorless oil (70 mg, 92% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.39 - 7.27 (m, 2H), 7.19 - 7.08 (m, 1H), 6.98 - 6.87 (m, 2H), 4.82 (s, 2H), 3.70 (s, 3H), 2.65 - 2.49 (m, 1H), 1.85 - 1.41 (m, 8H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.1, 156.4, 148.4, 139.67 (q, $J=38.25$ Hz), 130.1, 124.2, 120.95 (q, $J=268.5$), 115.4, 102.2, 102.2, 53.9, 43.5, 35.2, 29.7, 25.7.

$^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -62.1.

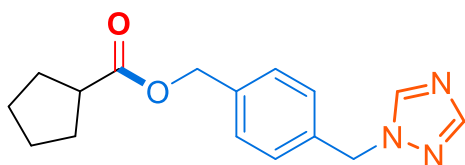


Benzo[c][1,2,5]thiadiazol-5-ylmethyl cyclopentanecarboxylate (33) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a light-yellow oil (37 mg, 71% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.04 - 7.94 (m, 2H), 7.55 (dd, $J=9.0, 1.7$ Hz, 1H), 5.28 (s, 2H), 2.93 - 2.76 (m, 1H), 2.02 - 1.53 (m, 8H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 176.4, 154.8, 154.4, 138.2, 129.3, 121.6, 119.7, 65.2, 43.8, 30.0, 25.8.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{13}\text{H}_{14}\text{N}_2\text{O}_2\text{SH}^+$ ($[\text{M}+\text{H}^+]$) 263.0854, found 263.0850.



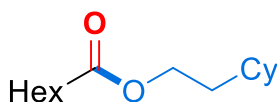
34

4-((1H-1,2,4-triazol-1-yl)methyl)benzyl cyclopentanecarboxylate (34) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (DCM/MeOH = 10:1) to afford the title compound as a light-yellow oil (50.2 mg, 88% yield).

¹H NMR (300 MHz, CDCl₃) δ 8.12 (s, 1H), 7.99 (s, 1H), 7.37 (d, *J* = 8.2 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 5.36 (s, 2H), 5.11 (s, 2H), 2.87 - 2.70 (m, 1H), 2.00 - 1.48 (m, 8H).

¹³C NMR (75 MHz, CDCl₃) δ 176.4, 152.0, 143.0, 137.0, 134.3, 128.5, 128.2, 65.3, 53.2, 43.7, 29.9, 25.7.

HRMS (ESI-TOF): *m/z* calcd. for C₁₆H₁₉N₃O₂H⁺ ([M+H⁺]) 286.1555, found 286.1558.



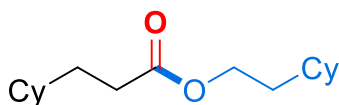
35

2-Cyclohexylethyl 2-oxoheptanoate (35) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (44 mg, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.08 (t, *J* = 6.9 Hz, 2H), 2.27 (t, *J* = 7.5 Hz, 2H), 1.76 - 1.55 (m, 7H), 1.50 (q, *J* = 6.8 Hz, 2H), 1.40 - 1.12 (m, 10H), 1.02 - 0.81 (m, 5H).

¹³C NMR (75 MHz, CDCl₃) δ 174.0, 62.5, 36.0, 34.5, 34.4, 33.1, 31.4, 28.8, 26.4, 26.2, 24.9, 22.5, 14.0.

HRMS (ESI-TOF): *m/z* calcd. for C₁₅H₂₈O₂Na⁺ ([M+Na⁺]) 263.1982, found 263.1988.

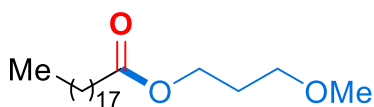


36

2-Cyclohexylethyl 3-cyclohexylpropanoate (36) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (48 mg, 90% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.08 (t, *J* = 6.8 Hz, 2H), 2.29 (t, 2H), 1.69 (m, 10H), 1.57 - 1.44 (m, 4H), 1.38 - 1.12 (m, 8H), 1.02 - 0.78 (m, 4H).

¹³C NMR (75 MHz, CDCl₃) δ 174.3, 62.5, 37.2, 36.0, 34.5, 33.1, 32.9, 32.4, 32.0, 26.5, 26.5, 26.2, 26.2.



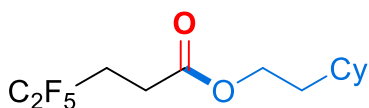
37

3-Methoxypropyl nonadecanoate (37) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (56 mg, 76% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.14 (t, $J = 6.5$ Hz, 2H), 3.43 (t, $J = 6.3$ Hz, 2H), 3.32 (s, 3H), 2.28 (t, $J = 7.5$ Hz, 2H), 1.88 (p, $J = 6.4$ Hz, 2H), 1.59 (dt, $J = 14.5, 7.2$ Hz, 2H), 1.31 - 1.19 (m, 30H), 0.92 - 0.81 (t, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.8, 69.1, 61.3, 58.6, 34.3, 31.9, 29.7, 29.6, 29.6, 29.4, 29.3, 29.2, 29.1, 29.0, 25.0, 22.7, 14.1.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{23}\text{H}_{46}\text{O}_3\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 393.3339, found 393.3339.



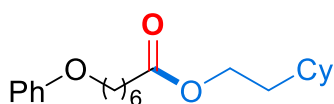
38

2-Cyclohexylethyl 4,4,5,5,5-pentafluoropentanoate (38) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (28 mg, 46% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.15 (t, $J = 6.9$ Hz, 2H), 2.61 (t, 2H), 2.52 - 2.30 (m, 2H), 1.78 - 1.57 (m, 5H), 1.53 (q, $J = 6.9$ Hz, 2H), 1.38 - 1.14 (m, 4H), 1.02 - 0.80 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 171.1, 77.4, 77.0, 76.6, 63.5, 35.8, 34.5, 33.1, 26.4, 26.2 (t, $J = 22.5$ Hz), 26.1, 25.6 (t, $J = 3.75$ Hz)

$^{19}\text{F NMR}$ (282 MHz, CDCl_3) δ -85.5, -118.8.



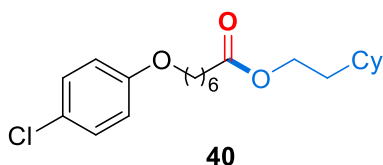
39

2-Cyclohexylethyl 7-phenoxyheptanoate (39) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (50 mg, 75% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.30 (dd, $J = 8.7, 7.3$ Hz, 2H), 7.01 - 6.87 (m, 3H), 4.13 (t, $J = 6.9$ Hz, 2H), 3.98 (t, $J = 6.5$ Hz, 2H), 2.34 (t, $J = 7.4$ Hz, 2H), 1.90 - 1.63 (m, 9H), 1.61 - 1.14 (m, 11H), 1.05 - 0.86 (m, 2H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.8, 159.0, 129.3, 120.4, 114.4, 67.6, 62.5, 36.0, 34.5, 34.3, 33.1, 29.1, 28.8, 26.4, 26.2, 25.7, 24.9.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_3\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 355.2249, found 355.2245.

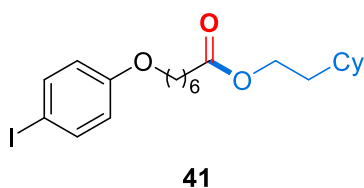


2-Cyclohexylethyl 7-(4-chlorophenoxy)heptanoate (40) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (52 mg, 71% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.26 - 7.15 (m, 2H), 6.85 - 6.74 (m, 2H), 4.09 (t, *J* = 6.9 Hz, 2H), 3.90 (t, *J* = 6.4 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.84 - 1.57 (m, 9H), 1.56 - 1.15 (m, 10H), 1.02 - 0.82 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.7, 157.6, 129.2, 125.3, 115.7, 68.0, 62.5, 35.9, 34.5, 34.2, 33.1, 28.9, 28.8, 26.4, 26.2, 25.6, 24.8.

HRMS (ESI-TOF): *m/z* calcd. for C₂₁H₃₁O₃ClNa⁺ ([M+Na⁺]) 389.1854, found 389.1859.

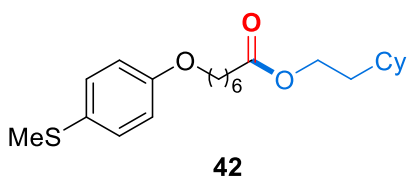


2-Cyclohexylethyl 7-(4-iodophenoxy)heptanoate (41) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (62.3 mg, 68% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.59 - 7.48 (m, 2H), 6.72 - 6.61 (m, 2H), 4.10 (t, *J* = 6.9 Hz, 2H), 3.90 (t, *J* = 6.5 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.84 - 1.13 (m, 19H), 1.01 - 0.82 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.8, 158.9, 138.1, 116.9, 82.4, 67.9, 62.6, 36.0, 34.6, 34.3, 33.1, 31.4, 30.2, 28.9, 28.8, 26.5, 26.2, 25.7, 24.9.

HRMS (ESI-TOF): *m/z* calcd. for C₂₁H₃₁O₃IH⁺ ([M+H⁺]) 459.1396, found 459.1405.

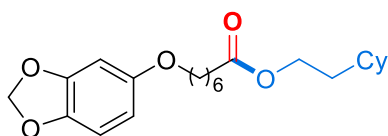


2-Cyclohexylethyl 7-(4-(methylthio)phenoxy)heptanoate (42) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (45 mg, 60% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.35 - 7.22 (m, 2H), 6.91 - 6.80 (m, 2H), 4.12 (t, *J* = 6.9 Hz, 2H), 3.94 (t, *J* = 6.5 Hz, 2H), 2.46 (s, 3H), 2.33 (t, *J* = 7.4 Hz, 2H), 1.87 - 1.60 (m, 9H), 1.63 - 1.10 (m, 10H), 1.04 - 0.82 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.8, 157.7, 130.2, 128.5, 115.2, 67.9, 62.5, 36.0, 34.5, 34.3, 33.1, 29.0, 28.8, 26.4, 26.2, 25.7, 24.9, 18.1.

HRMS (ESI-TOF): *m/z* calcd. for C₂₂H₃₄O₃SNa⁺ ([M+Na⁺]) 401.2121, found 401.2122.



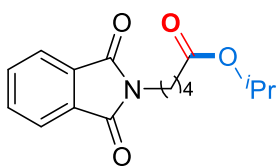
43

2-Cyclohexylethyl 7-(benzo[d][1,3]dioxol-5-yloxy)heptanoate (43) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a light-yellow oil (69 mg, 92% yield).

¹H NMR (300 MHz, CDCl₃) δ 6.68 (d, *J* = 8.4 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 6.30 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.89 (s, 2H), 4.09 (t, *J* = 6.9 Hz, 2H), 3.86 (t, *J* = 6.4 Hz, 2H), 2.30 (t, *J* = 7.4 Hz, 2H), 1.81 - 1.57 (m, 9H), 1.55 - 1.12 (m, 10H), 1.01 - 0.80 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 173.8, 154.6, 148.1, 141.4, 107.8, 105.6, 101.0, 98.0, 68.7, 62.5, 35.9, 34.5, 34.2, 33.1, 29.1, 28.8, 26.4, 26.1, 25.7, 24.8.

HRMS (ESI-TOF): *m/z* calcd. for C₂₂H₃₂O₅Na⁺ ([M+Na⁺]) 399.2142, found 399.2144.



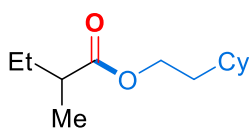
44

Isopropyl 5-(1,3-dioxoisindolin-2-yl)pentanoate (44) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a light-yellow oil (26 mg, 45% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.87 - 7.79 (m, 2H), 7.76 - 7.64 (m, 2H), 4.98 (hept, *J* = 6.3 Hz, 1H), 3.69 (t, *J* = 6.9 Hz, 2H), 2.38 - 2.26 (m, 2H), 1.80 - 1.57 (m, 4H), 1.22 (s, 3H), 1.20 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 172.7, 168.3, 133.9, 132.1, 123.2, 67.6, 37.5, 34.0, 28.0, 22.2, 21.8.

HRMS (ESI-TOF): *m/z* calcd. for C₁₆H₁₉NO₄Na⁺ ([M+Na⁺]) 312.1211, found 312.1213.

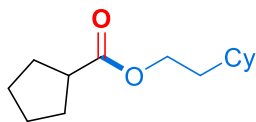


45

2-Cyclohexylethyl 2-methylbutanoate (45) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (40 mg, 94% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.09 (td, *J* = 6.9, 1.0 Hz, 2H), 2.34 (h, *J* = 7.0 Hz, 1H), 1.79 - 1.58 (m, 6H), 1.57 - 1.17 (m, 7H), 1.12 (d, *J* = 7.0 Hz, 3H), 1.01 - 0.78 (m, 5H).

¹³C NMR (75 MHz, CDCl₃) δ 176.8, 62.4, 41.1, 36.0, 34.6, 33.1, 26.8, 26.5, 26.2, 16.6, 11.6.



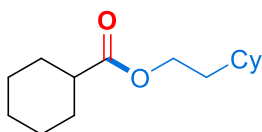
46

2-Cyclohexylethyl cyclopentanecarboxylate (46) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (42.6 mg, 95% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.09 (t, *J* = 6.9 Hz, 2H), 2.79 - 2.62 (m, 1H), 2.00 - 1.57 (m, 11H), 1.55 - 1.43 (m, 2H), 1.43 - 1.13 (m, 4H), 1.01 - 0.82 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 176.9, 62.5, 43.9, 36.0, 34.6, 33.1, 30.0, 26.5, 26.2, 25.8.

HRMS (ESI-TOF): *m/z* calcd. for C₁₄H₂₄O₂Na⁺ ([M+Na⁺]) 247.1673, found 247.1677.



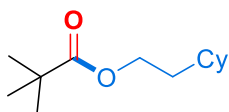
47

2-Cyclohexylethyl cyclohexanecarboxylate (47) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (46 mg, 97% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.07 (t, *J* = 6.8 Hz, 2H), 2.26 (tt, *J* = 11.2, 3.6 Hz, 1H), 1.94 - 1.82 (m, 2H), 1.79 - 1.58 (m, 8H), 1.54 - 1.12 (m, 11H), 1.02 - 0.80 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 176.2, 62.3, 43.2, 36.0, 34.6, 33.1, 29.0, 26.4, 26.2, 25.7, 25.4.

HRMS (ESI-TOF): *m/z* calcd. for C₁₅H₂₆O₂Na⁺ ([M+Na⁺]) 261.1830, found 261.1829.



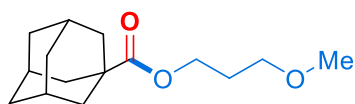
48

2-Cyclohexylethyl pivalate (48) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (32 mg, 76% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.08 (t, *J* = 6.8 Hz, 2H), 1.76 - 1.61 (m, 6H), 1.52 (q, *J* = 6.8 Hz, 2H), 1.43 - 1.21 (m, 3H), 1.19 (s, 9H), 1.00 - 0.83 (m, 2H).

¹³C NMR (75 MHz, CDCl₃) δ 178.7, 62.7, 38.7, 35.9, 34.7, 33.2, 27.2, 26.5, 26.2.

HRMS (ESI-TOF): *m/z* calcd. for C₁₃H₂₄O₂Na⁺ ([M+Na⁺]) 235.1673, found 235.1674.



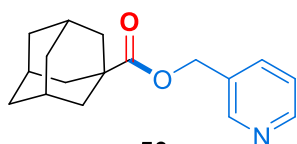
49

3-Methoxypropyl (1-adamantane) carboxylate (49) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a colorless oil (20 mg, 40% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 4.13 (t, $J = 6.4$ Hz, 2H), 3.44 (t, $J = 6.4$ Hz, 2H), 3.33 (s, 3H), 2.06 - 1.83 (m, 11H), 1.79 - 1.59 (m, 6H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 177.6, 69.2, 61.1, 58.7, 40.7, 38.8, 36.5, 29.0, 27.9.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{15}\text{H}_{24}\text{O}_3\text{H}^+$ ($[\text{M}+\text{H}^+]$) 253.1803, found 253.1804.



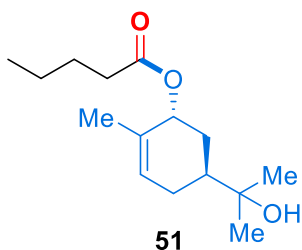
50

Pyridin-3-ylmethyl (1-adamantane) carboxylate (50) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 3:1) to afford the title compound as a light-yellow oil (25 mg, 46% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 8.64 - 8.52 (m, 2H), 7.72 - 7.62 (m, 1H), 7.35 - 7.25 (m, 1H), 5.11 (s, 2H), 2.05 - 1.96 (m, 3H), 1.90 (d, $J = 3.0$ Hz, 6H), 1.78 - 1.61 (m, 6H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 177.3, 149.2, 149.1, 135.7, 132.3, 123.5, 63.2, 40.8, 38.8, 36.4, 27.9.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{17}\text{H}_{21}\text{NO}_2\text{H}^+$ ($[\text{M}+\text{H}^+]$) 272.1650, found 272.1657.



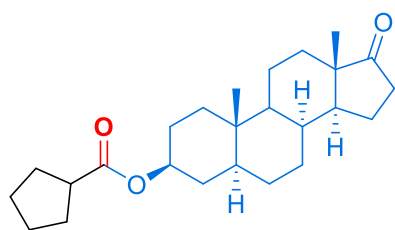
51

(1R,5S)-5-(2-Hydroxypropan-2-yl)-2-methylcyclohex-2-en-1-yl pentanoate (51) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 5:1) to afford the title compound as a colorless oil (20 mg, 40% yield).

$^1\text{H NMR}$ (300 MHz, CDCl_3) δ 5.72 (dt, $J = 5.6, 1.7$ Hz, 1H), 5.31 - 5.23 (m, 1H), 2.37 - 2.26 (t, 2H), 2.26 - 2.10 (m, 1H), 1.99 (dq, $J = 13.9, 2.2$ Hz, 1H), 1.92 - 1.52 (m, 7H), 1.53 - 1.26 (m, 4H), 1.18 (s, 3H), 1.17 (s, 3H), 0.91 (t, $J = 7.3$ Hz, 3H).

$^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 173.7, 131.0, 127.8, 72.0, 70.5, 39.5, 34.5, 30.0, 27.3, 27.3, 26.8, 26.8, 22.2, 20.6, 13.7.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_3\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 277.1779, found 277.1775.

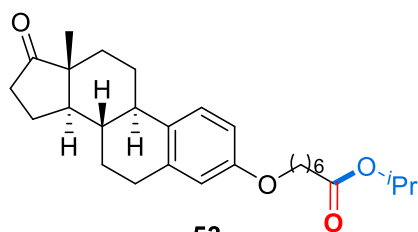


52

(3*S*,5*S*,8*S*,10*S*,13*S*,14*S*)-10,13-Dimethyl-17-oxohexadecahydro-1*H* cyclopenta[*a*]phenanthren-3-yl cyclopentanecarboxylate (52) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a white solid (72 mg, 93% yield).

¹H NMR (300 MHz, CDCl₃) δ 4.75 - 4.58 (m, 1H), 2.74 - 2.58 (m, 1H), 2.42 (dd, *J* = 19.0, 8.8 Hz, 1H), 2.14 - 1.96 (m, 1H), 1.92 - 0.90 (m, 27H), 0.84 (s, 6H), 0.77 - 0.60 (m, 1H).

¹³C NMR (75 MHz, CDCl₃) δ 221.2, 176.3, 73.0, 54.2, 51.3, 47.7, 44.6, 44.0, 36.7, 35.8, 35.6, 35.0, 33.9, 31.5, 30.8, 30.0, 29.9, 28.2, 27.4, 25.8, 21.7, 20.4, 13.8, 12.2.



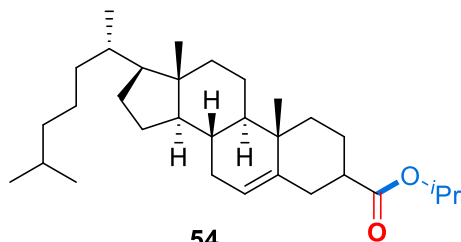
53

Isopropyl 7-(((8*S*,9*R*,13*R*,14*R*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)heptanoate (53) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a light-yellow solid (50 mg, 57% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.18 (d, *J* = 8.1 Hz, 1H), 6.70 (dd, *J* = 8.6, 2.8 Hz, 1H), 6.63 (d, *J* = 2.7 Hz, 1H), 5.00 (hept, *J* = 6.3 Hz, 1H), 3.92 (t, *J* = 6.5 Hz, 2H), 2.88 (dd, *J* = 7.8, 3.2 Hz, 2H), 2.60 - 2.34 (m, 2H), 2.33 - 1.90 (m, 7H), 1.84 - 1.35 (m, 14H), 1.24 (s, 3H), 1.22 (s, 3H), 0.90 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 173.2, 157.1, 137.6, 131.8, 126.2, 114.5, 112.1, 67.7, 67.3, 50.4, 48.0, 43.9, 38.4, 35.8, 34.6, 31.6, 29.6, 29.1, 28.8, 26.5, 25.9, 25.7, 24.9, 21.8, 21.5, 13.8.

HRMS (ESI-TOF): *m/z* calcd. for C₂₈H₄₀O₄H⁺ ([M+H⁺]) 441.3005, found 441.3004.



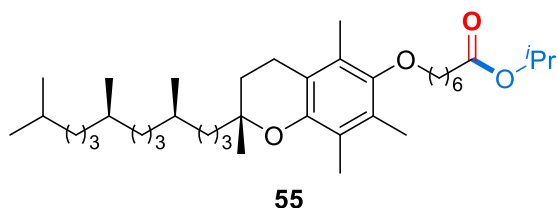
54

Isopropyl (8*R*,9*R*,10*S*,13*S*,14*R*,17*S*)-10,13-dimethyl-17-((*S*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthrene-3-carboxylate (54)

Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 100:1) to afford the title compound as a light-yellow oil (70 mg, 77% yield).

¹H NMR (300 MHz, CDCl₃) δ 5.39 - 5.30 (m, 1H), 4.99 (p, *J* = 6.3 Hz, 1H), 2.50 - 2.30 (m, 1H), 2.28 - 2.11 (m, 1H), 2.07 - 0.97 (m, 36H), 0.95 - 0.82 (m, 9H), 0.67 (s, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 175.3, 141.1, 120.9, 67.2, 56.8, 56.2, 50.3, 44.9, 42.3, 39.8, 39.5, 38.8, 36.9, 36.2, 35.8, 34.9, 31.9, 31.8, 28.2, 28.0, 25.2, 24.3, 23.8, 22.8, 22.5, 21.8, 20.9, 19.3, 18.7, 11.8.

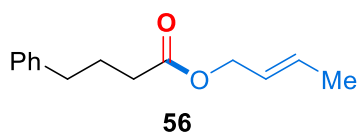


Iopropyl 7-(((*R*)-2,5,7,8-tetramethyl-2-(((4*R*,8*R*)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)heptanoate (55)

Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 50:1) to afford the title compound as a light-yellow oil (68 mg, 57% yield).

¹H NMR (300 MHz, CDCl₃) δ 5.02 (hept, *J* = 6.3 Hz, 1H), 3.63 (t, *J* = 6.5 Hz, 2H), 2.58 (t, *J* = 6.8 Hz, 2H), 2.30 (t, *J* = 7.5 Hz, 2H), 2.17 (s, 3H), 2.12 (s, 3H), 2.09 (s, 3H), 1.87 - 1.05 (m, 40H), 0.92 - 0.81 (m, 12H).

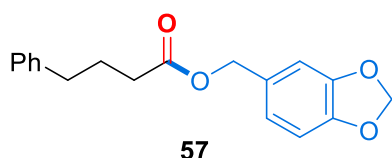
¹³C NMR (75 MHz, CDCl₃) δ 173.3, 148.3, 147.6, 127.8, 125.7, 122.7, 117.4, 74.7, 72.9, 67.3, 40.1, 39.4, 37.4, 37.4, 37.3, 34.7, 32.8, 32.7, 31.3, 31.3, 30.2, 29.1, 28.0, 25.9, 25.0, 24.8, 24.8, 24.4, 23.9, 22.7, 22.6, 21.8, 21.0, 20.6, 19.7, 19.7, 12.7, 11.8, 11.8.



(*E*)-But-2-en-1-yl 4-phenylbutanoate (56) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (22 mg, 50% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.26 - 7.15 (m, 2H), 7.17 - 7.06 (m, 3H), 5.83 - 5.57 (m, 1H), 5.62 - 5.40 (m, 1H), 4.47 - 4.38 (m, 2H), 2.63 - 2.52 (t, 2H), 2.26 (t, *J* = 7.5 Hz, 1H), 1.98 - 1.78 (m, 2H), 1.72 - 1.58 (m, 3H).

¹³C NMR (75 MHz, CDCl₃) δ 173.3, 141.4, 131.4, 128.5, 128.4, 125.9, 125.1, 65.1, 35.1, 33.6, 26.5, 17.8.

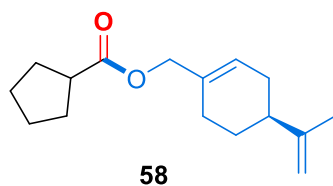


Benzo[*d*][1,3]dioxol-5-ylmethyl 4-phenylbutanoate (57) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 20:1) to afford the title compound as a light-yellow oil (40 mg, 67% yield).

¹H NMR (300 MHz, CDCl₃) δ 7.36 - 7.25 (m, 2H), 7.27 - 7.14 (m, 3H), 6.93 - 6.74 (m, 3H), 5.98 (s, 2H), 5.03 (s, 2H), 2.67 (t, 2H), 2.39 (t, *J* = 7.5 Hz, 2H), 2.08 - 1.91 (m, 2H).

^{13}C NMR (75 MHz, CDCl_3) δ 173.3, 147.8, 147.6, 141.3, 129.7, 128.5, 128.3, 125.9, 122.2, 109.0, 108.2, 101.1, 66.3, 66.1, 35.1, 33.6, 26.4.

HRMS (ESI-TOF): m/z calcd. for $\text{C}_{18}\text{H}_{18}\text{O}_4\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 321.1102, found 321.1107.

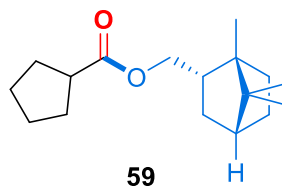


(S)-4-(Prop-1-en-2-yl)cyclohex-1-en-1-yl methyl cyclopentanecarboxylate (58) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (45 mg, 91% yield).

^1H NMR (300 MHz, CDCl_3) δ 5.78 - 5.70 (m, 1H), 4.72 (m, 2H), 4.46 (s, 2H), 2.83 - 2.66 (m, 1H), 2.26 - 1.19 (m, 18H).

^{13}C NMR (75 MHz, CDCl_3) δ 176.7, 149.7, 132.9, 125.3, 108.8, 68.2, 43.9, 40.9, 30.5, 30.1, 27.3, 27.2, 26.3, 25.8, 20.8.

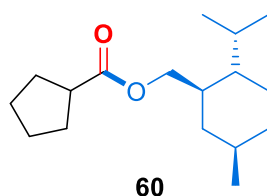
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{16}\text{H}_{24}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 271.1673, found 271.1675.



((1S,2S,4R)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-yl) methyl cyclopentanecarboxylate (59) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (35 mg, 66% yield).

^1H NMR (300 MHz, CDCl_3) δ 4.93 - 4.82 (m, 1H), 2.83 - 2.64 (m, 1H), 2.45 - 2.26 (m, 1H), 2.04 - 1.51 (m, 12H), 1.39 - 1.14 (m, 3H), 0.90 (s, 3H), 0.86 (s, 3H), 0.82 (s, 3H).

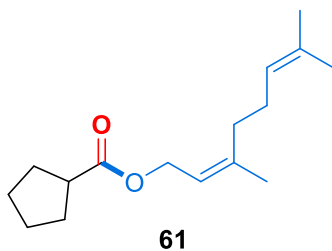
^{13}C NMR (75 MHz, CDCl_3) δ 177.0, 79.3, 48.8, 47.8, 44.9, 44.2, 36.8, 30.1, 29.9, 28.0, 27.1, 25.8, 25.7, 19.7, 18.8, 13.5.



((1R,2R,5R)-2-Isopropyl-5-methylcyclohexyl) methyl cyclopentanecarboxylate (60) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (32 mg, 60% yield).

^1H NMR (300 MHz, CDCl_3) δ 4.65 (td, J = 10.9, 4.4 Hz, 1H), 2.77 - 2.61 (m, 1H), 2.02 - 0.94 (m, 18H), 0.90 (d, J = 1.3 Hz, 3H), 0.88 (d, J = 1.9 Hz, 3H), 0.75 (d, J = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, CDCl_3) δ 176.3, 73.8, 47.1, 44.2, 40.9, 34.3, 31.4, 30.1, 29.9, 26.2, 25.8, 25.8, 23.4, 22.0, 20.8, 16.2.



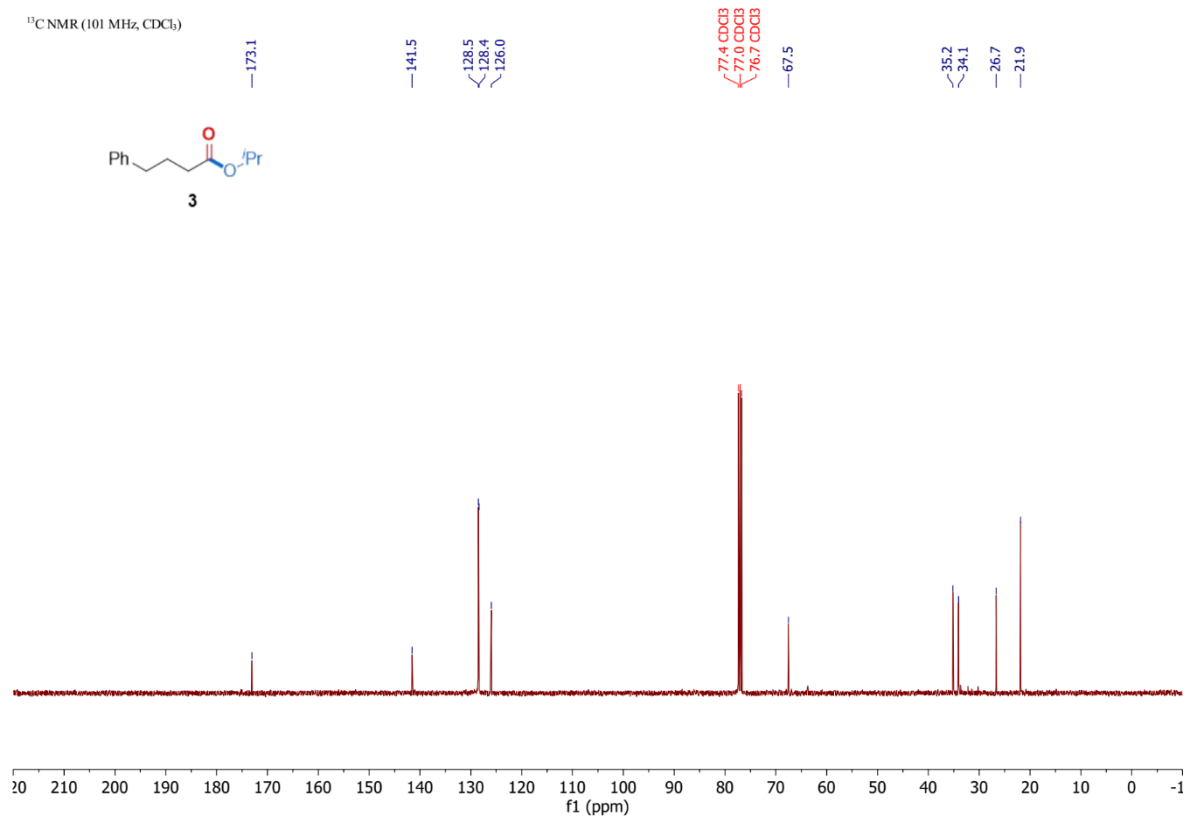
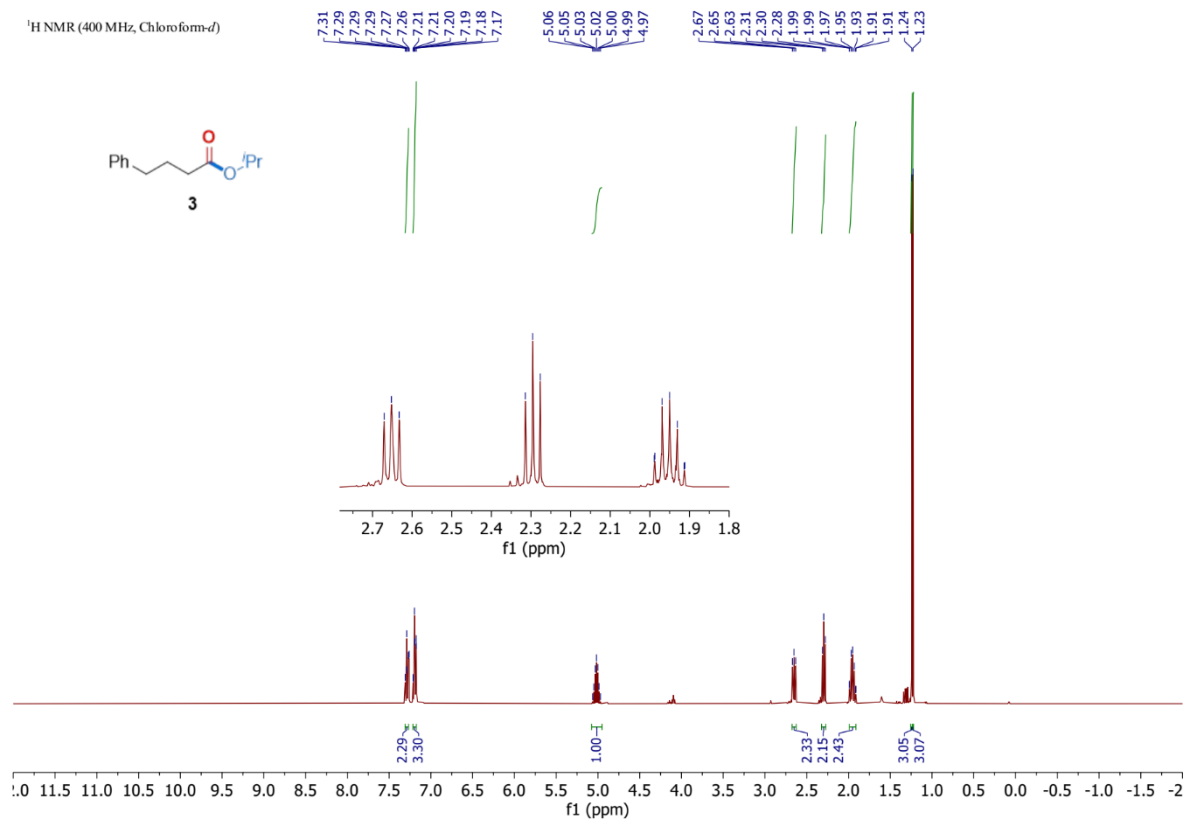
(Z)-3,7-Dimethylocta-2,6-dien-1-yl cyclopentanecarboxylate (61) Prepared according to the general procedure. The crude product was purified by silica gel chromatography (PE/EA = 200:1) to afford the title compound as a colorless oil (44 mg, 88% yield).

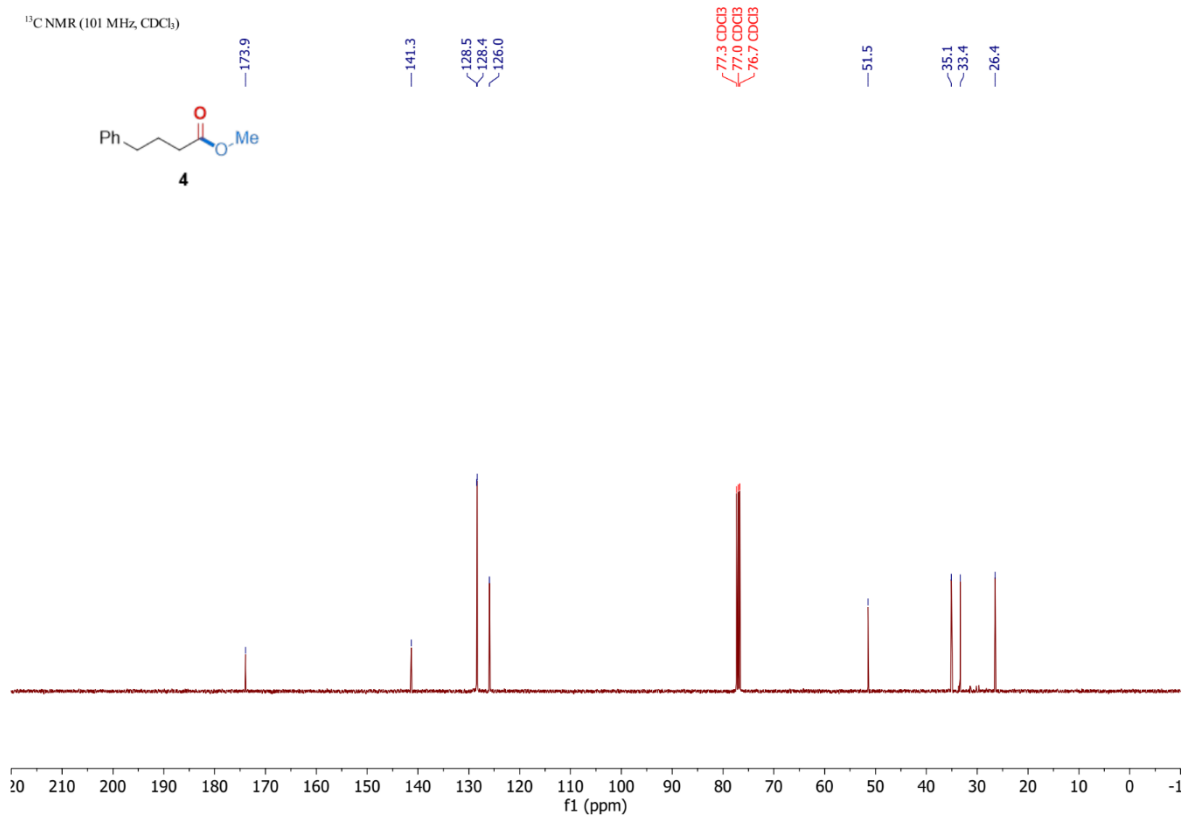
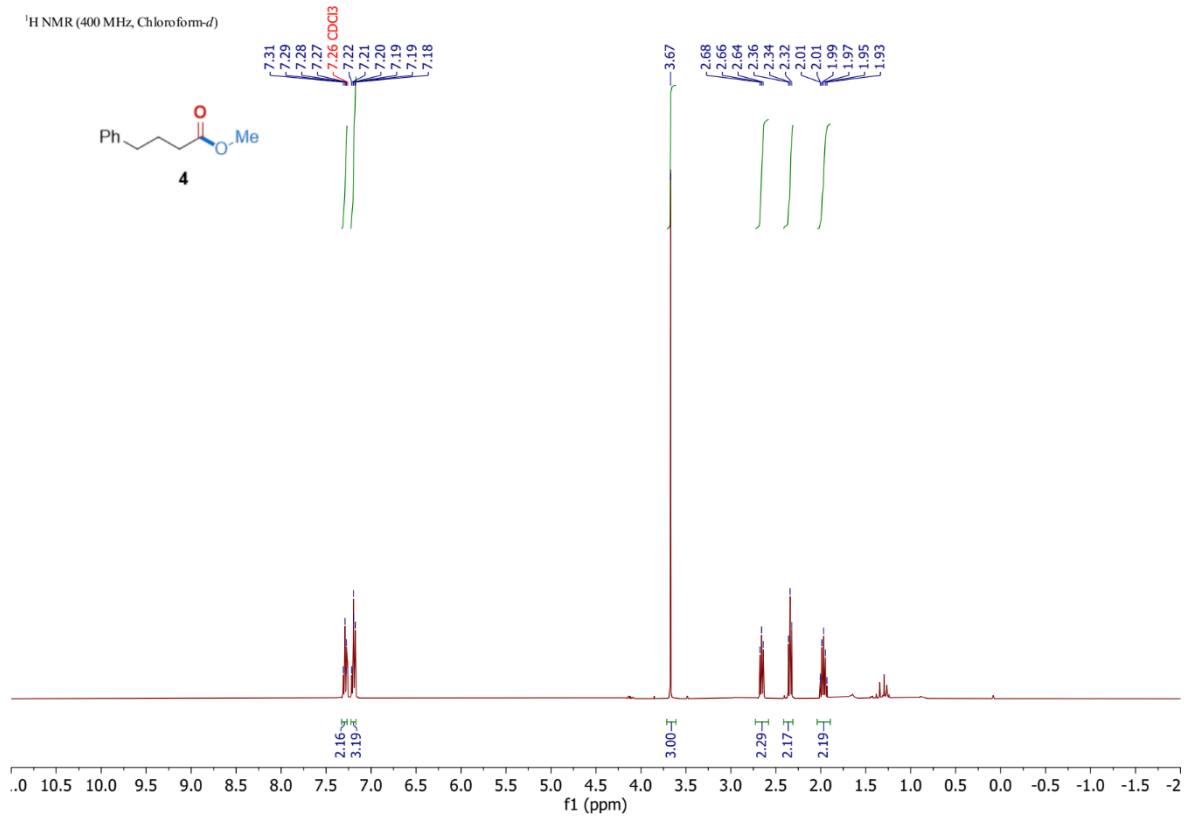
^1H NMR (300 MHz, CDCl_3) δ 5.42 - 5.28 (m, 1H), 5.08 (m, 1H), 4.58 (d, $J = 7.1$ Hz, 2H), 2.83 - 2.62 (m, 1H), 2.18 - 1.97 (m, 4H), 1.93 - 1.51 (m, 17H).

^{13}C NMR (75 MHz, CDCl_3) δ 176.9, 141.9, 131.8, 123.8, 118.6, 61.2, 43.9, 39.5, 30.1, 26.3, 25.8, 25.7, 17.7, 16.5.

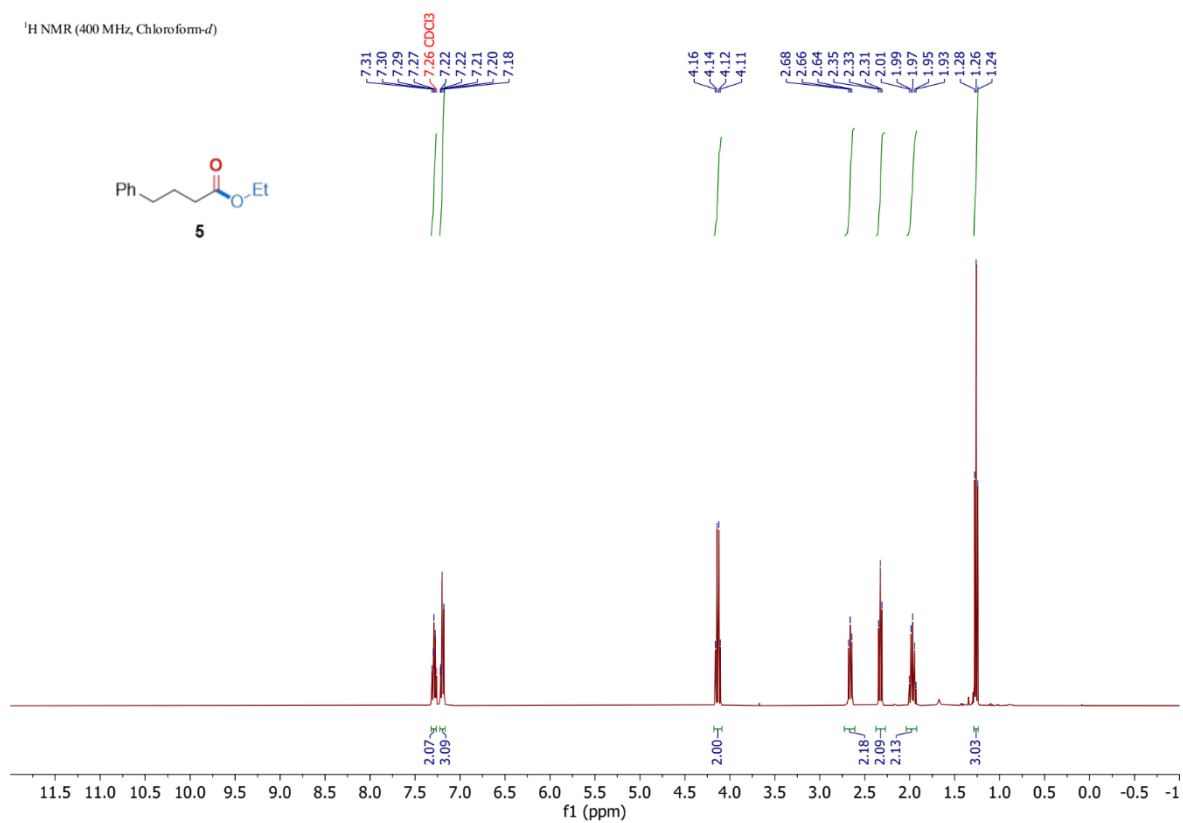
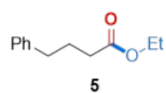
HRMS (ESI-TOF): m/z calcd. for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Na}^+$ ($[\text{M}+\text{Na}^+]$) 273.1825, found 273.1832.

7. NMR Spectrum

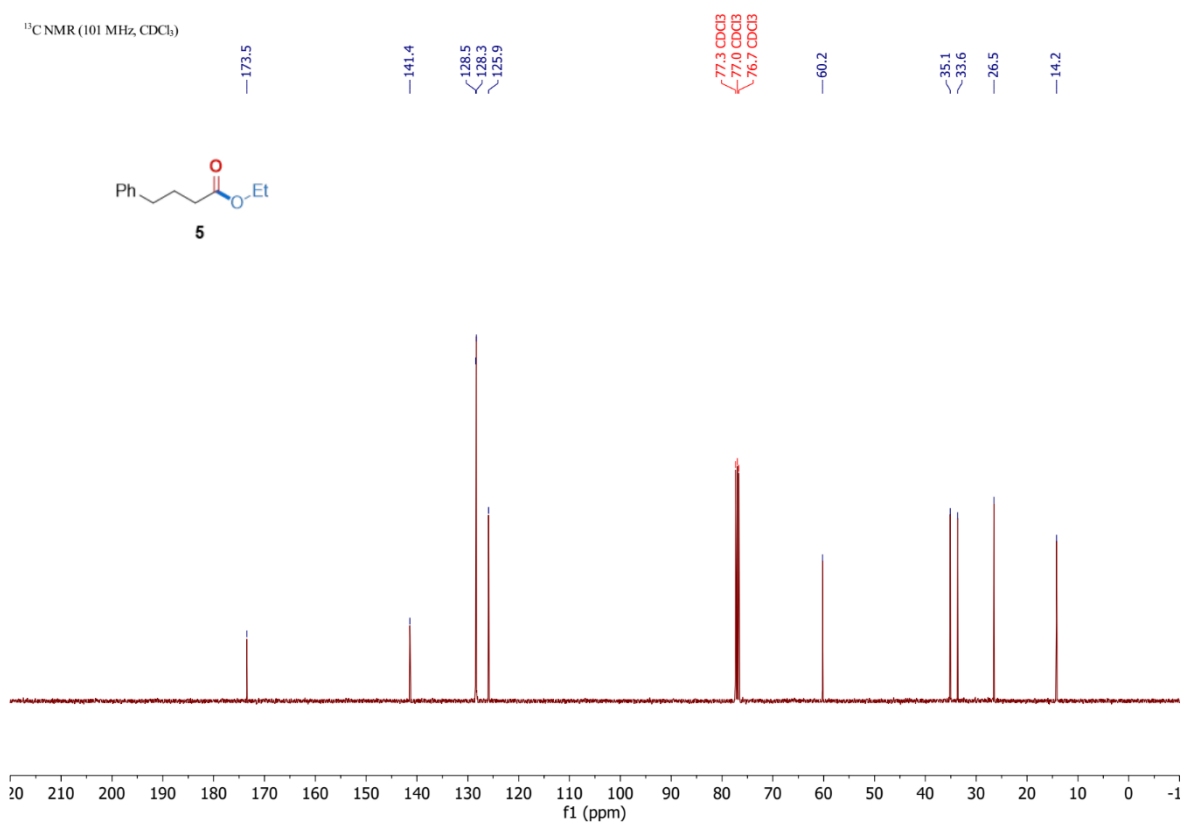
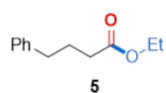




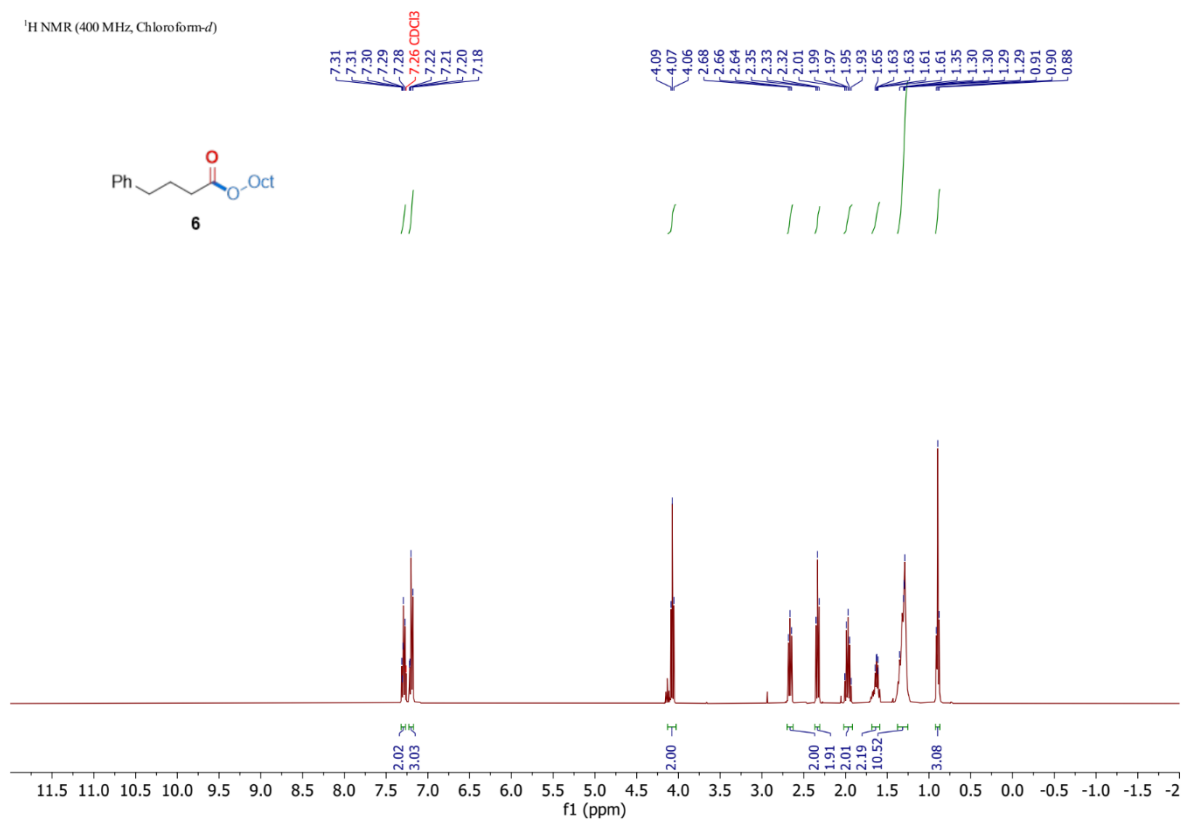
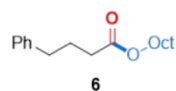
¹H NMR (400 MHz, Chloroform-*d*)



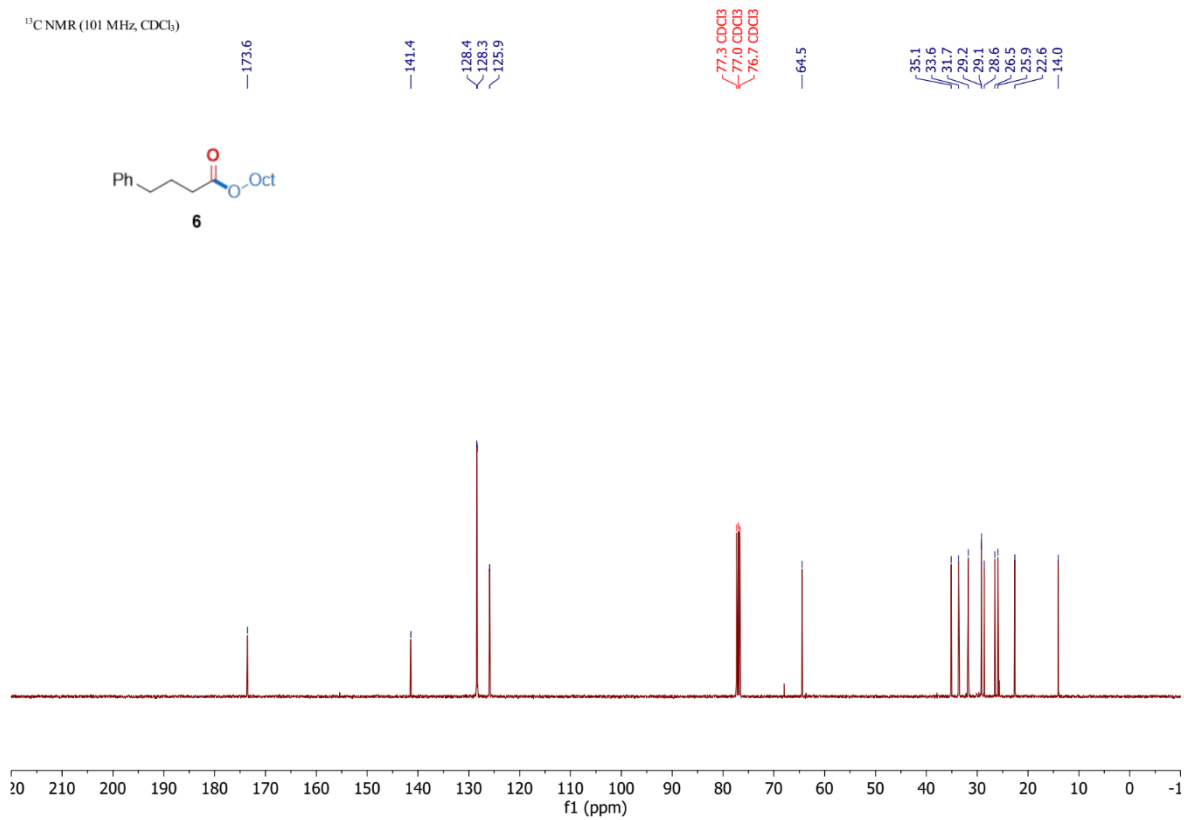
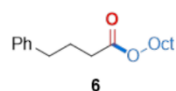
¹³C NMR (101 MHz, CDCl₃)

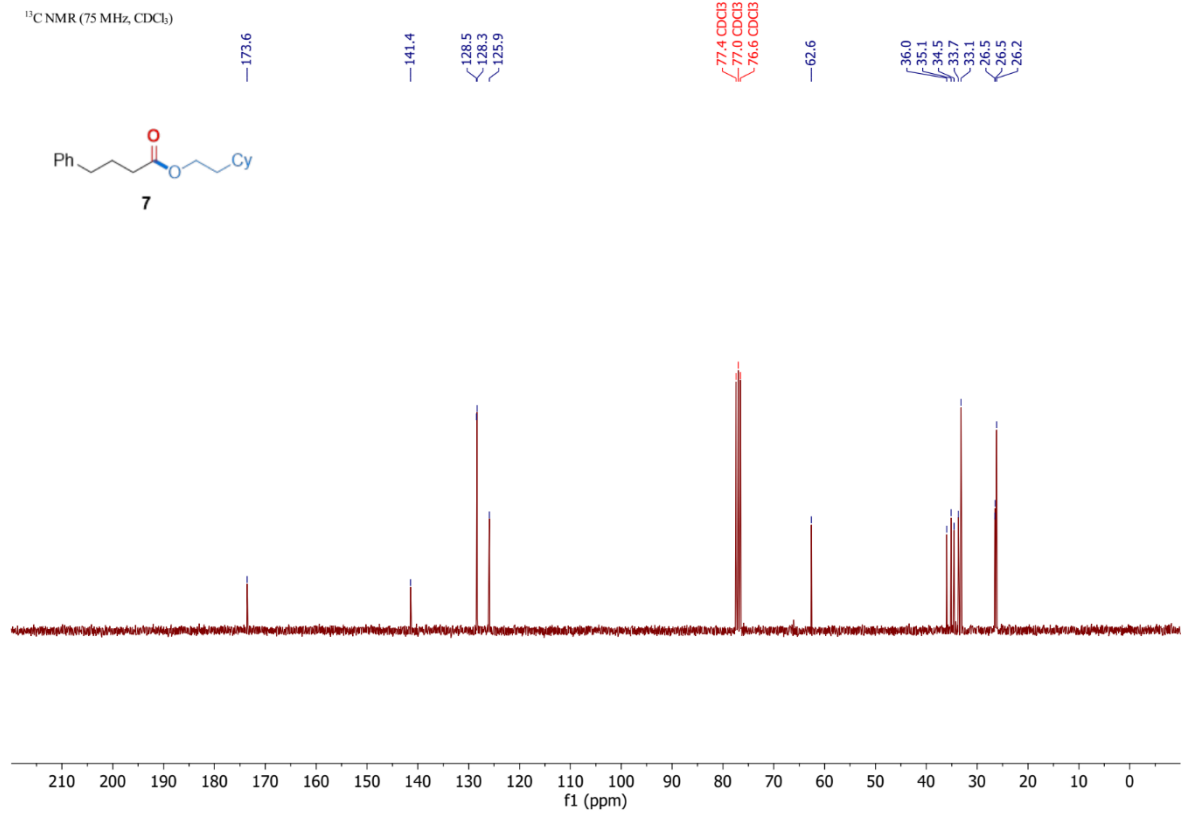
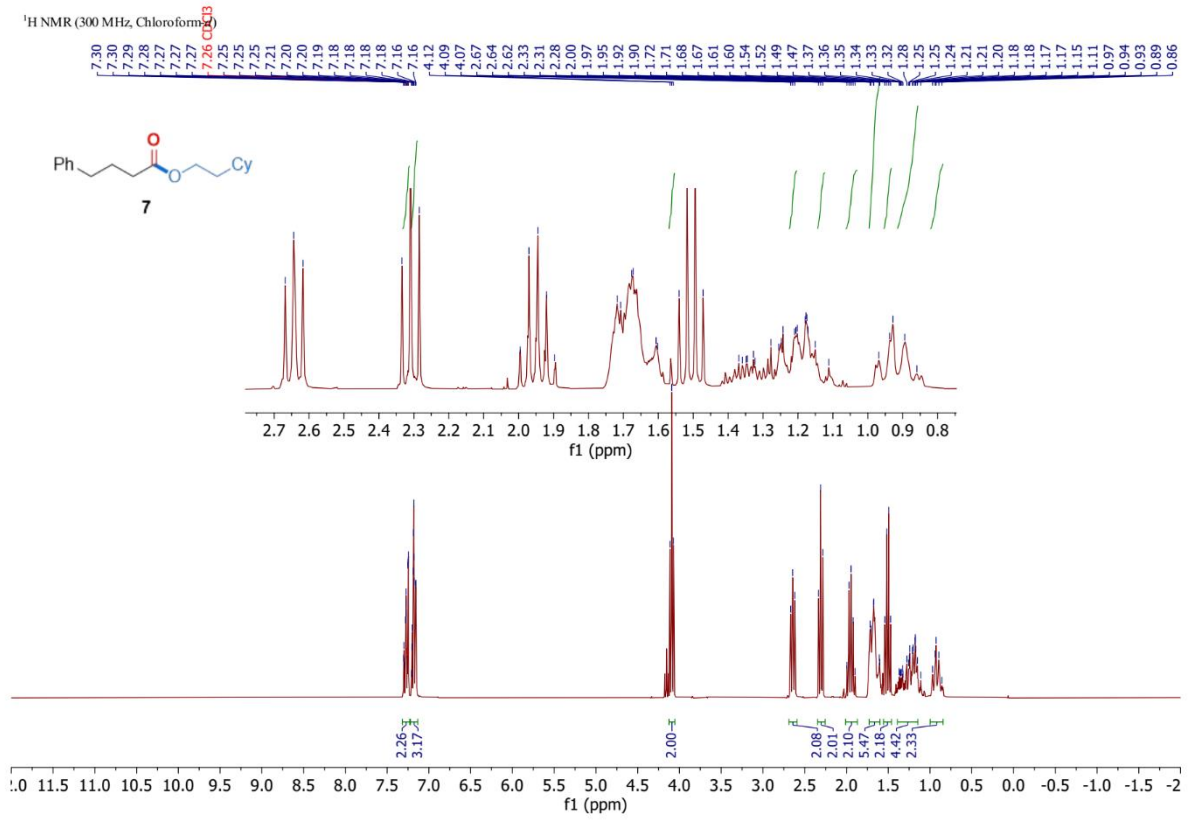


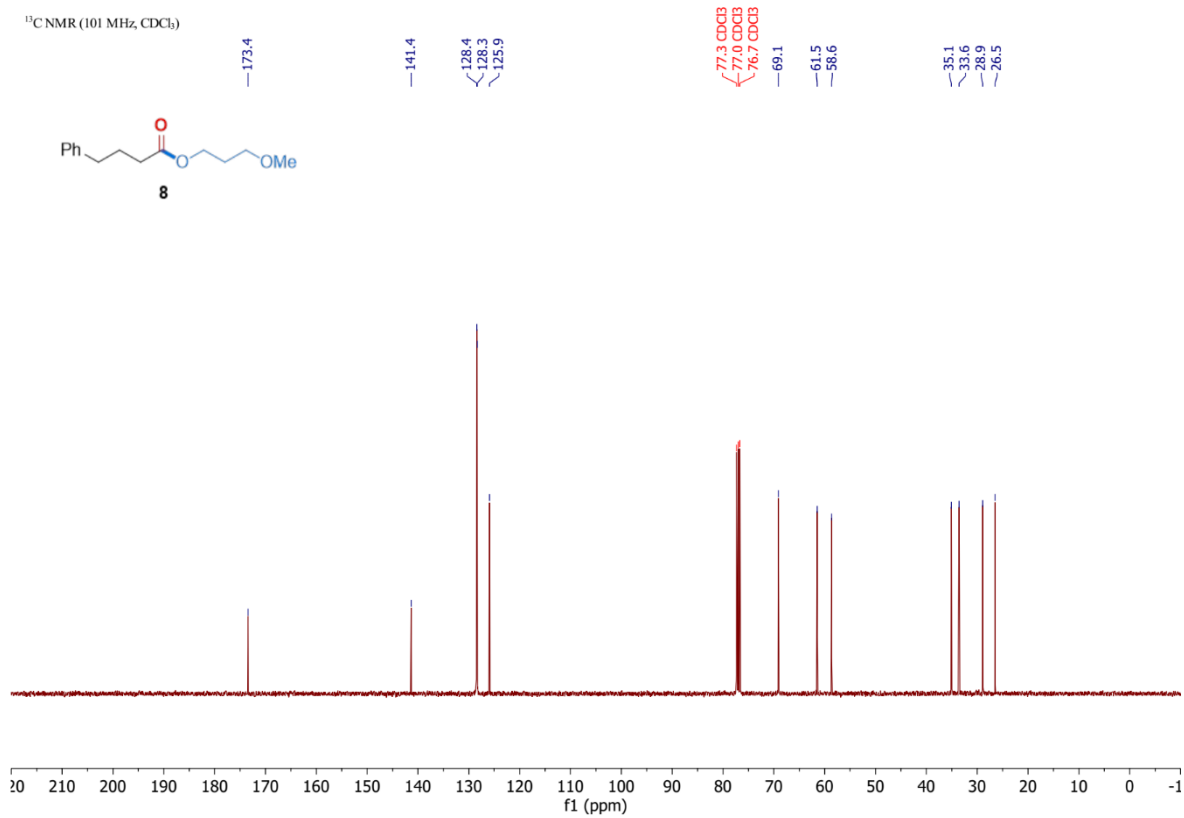
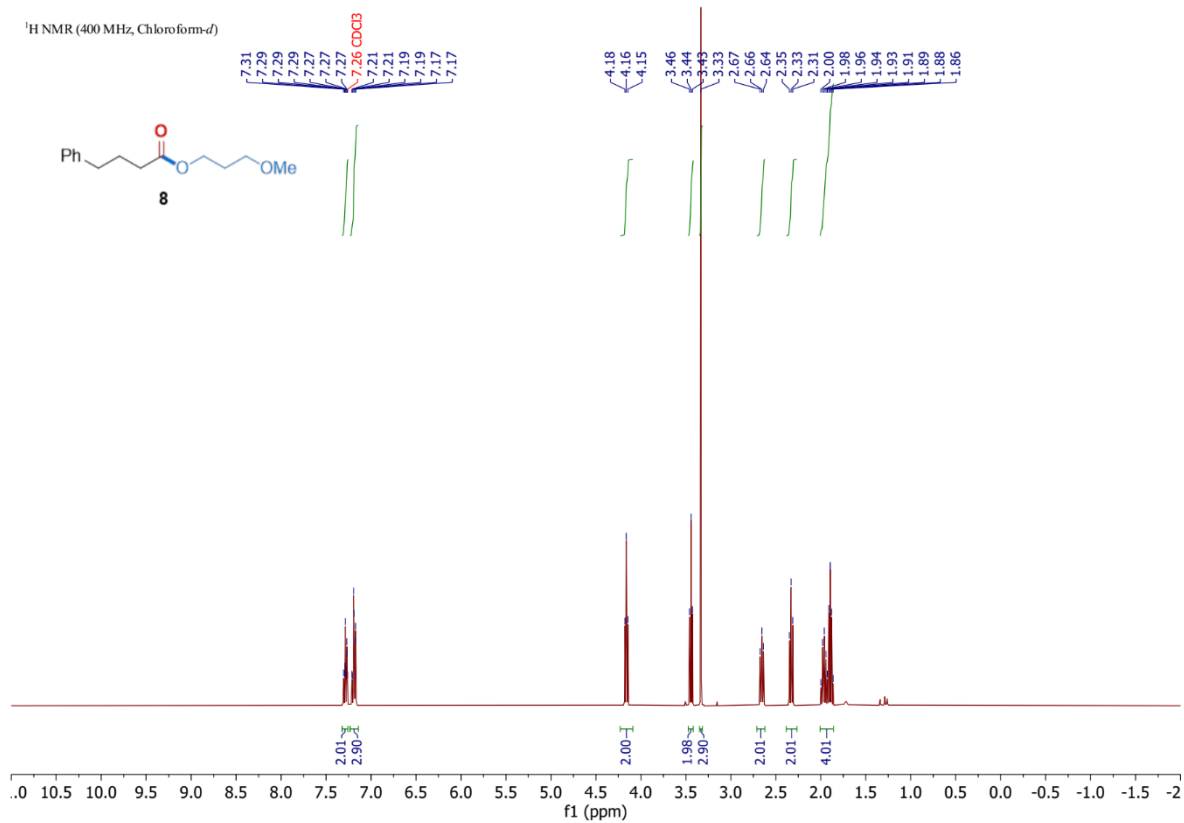
¹H NMR (400 MHz, Chloroform-*d*)

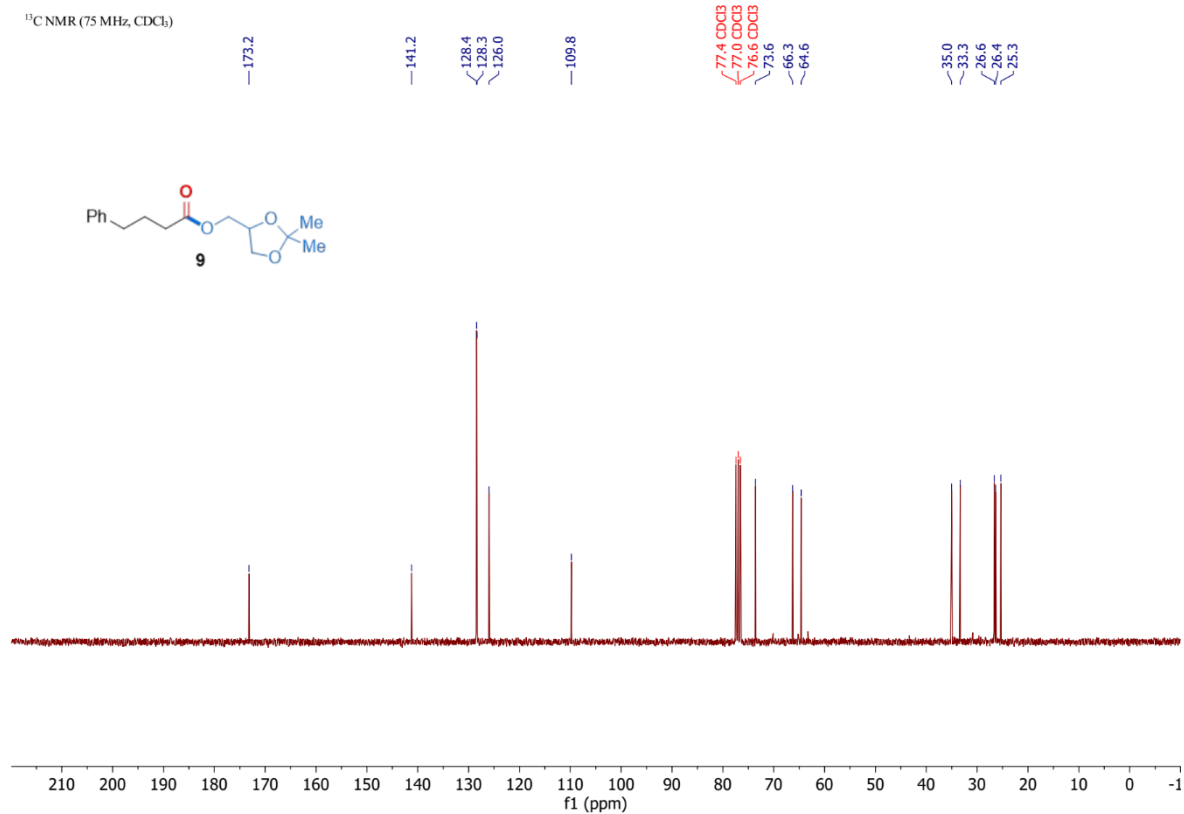
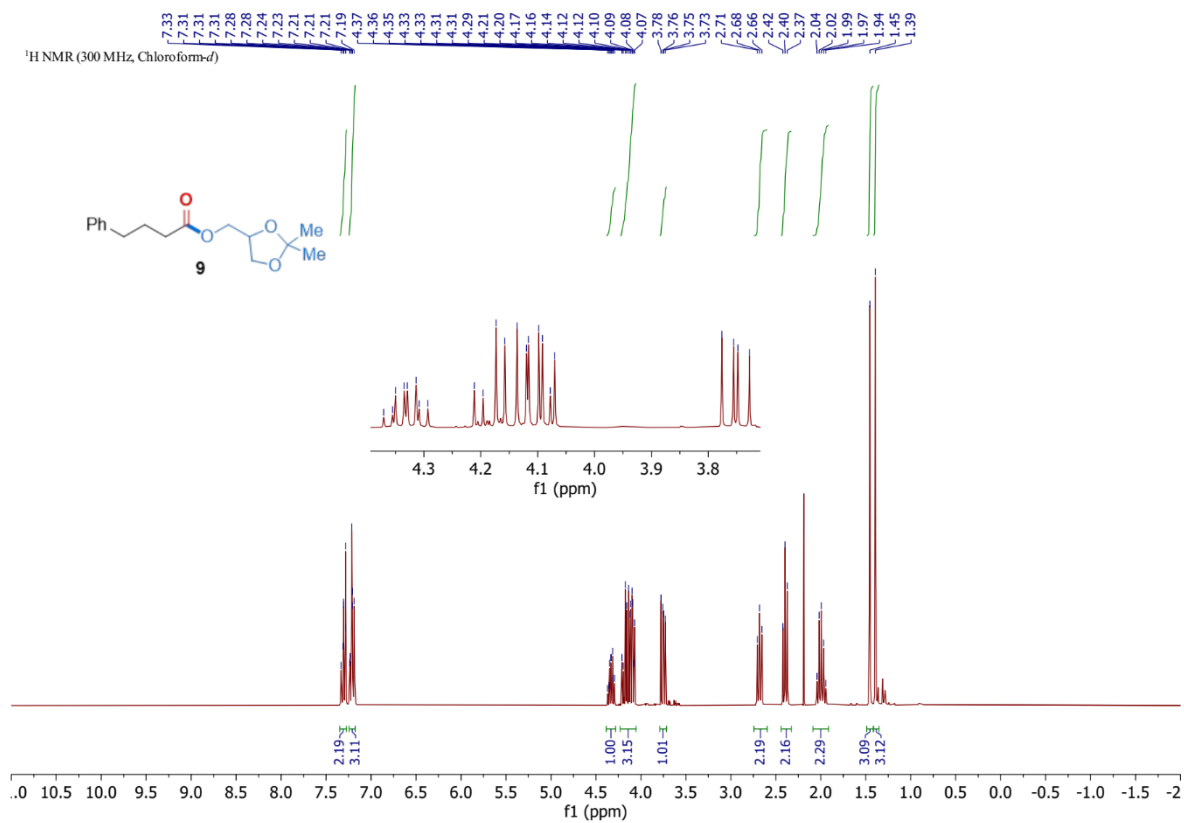


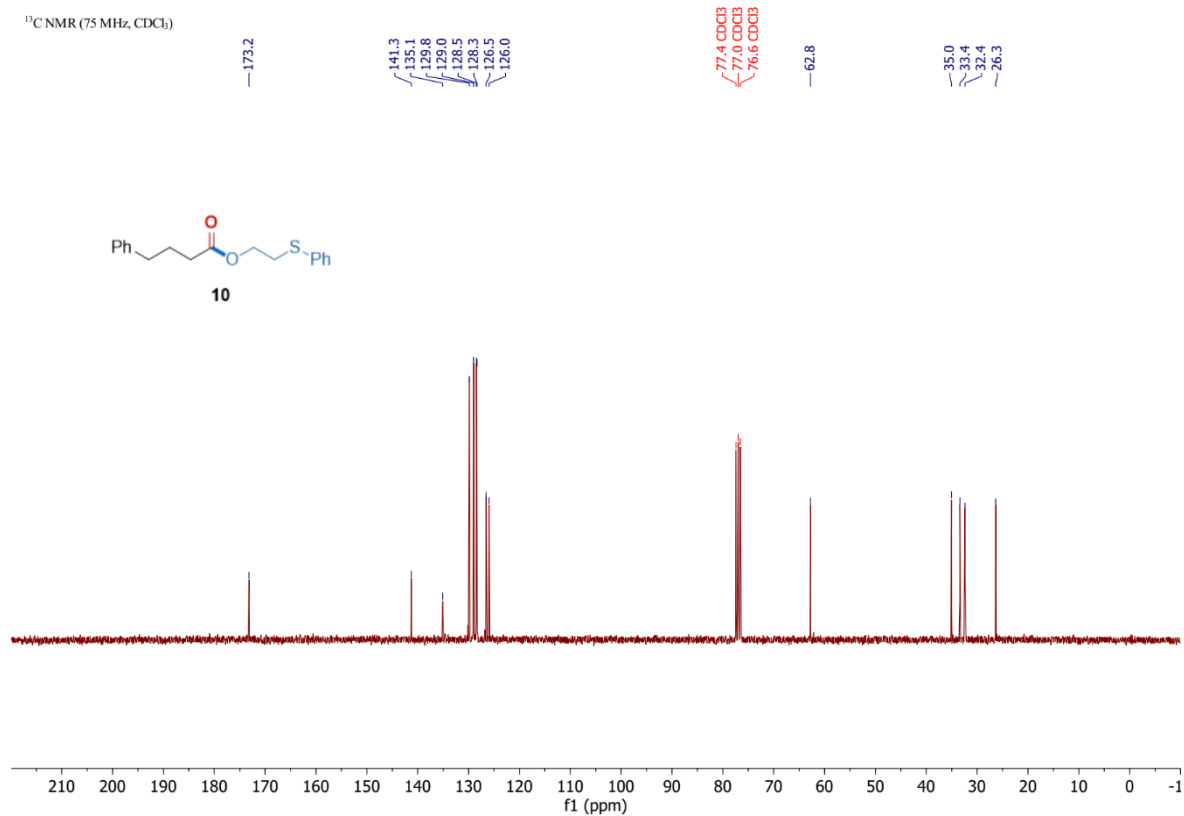
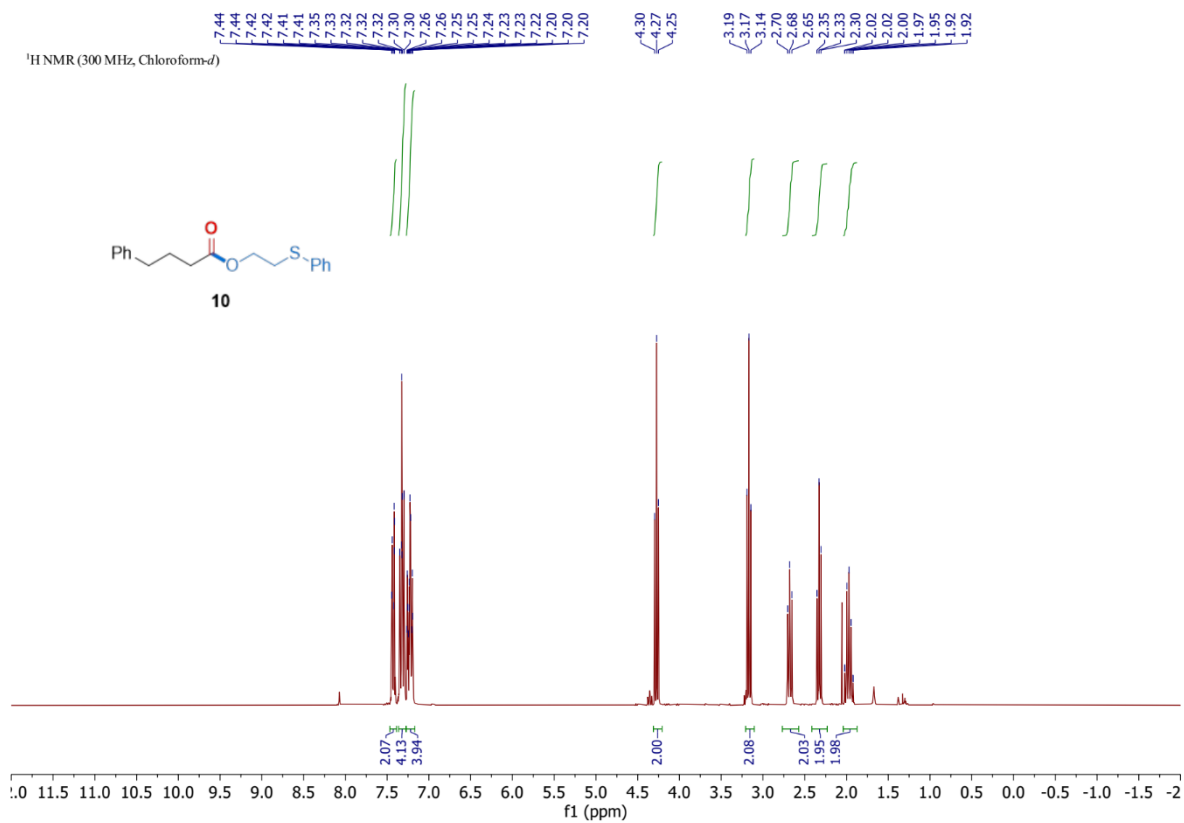
¹³C NMR (101 MHz, CDCl₃)

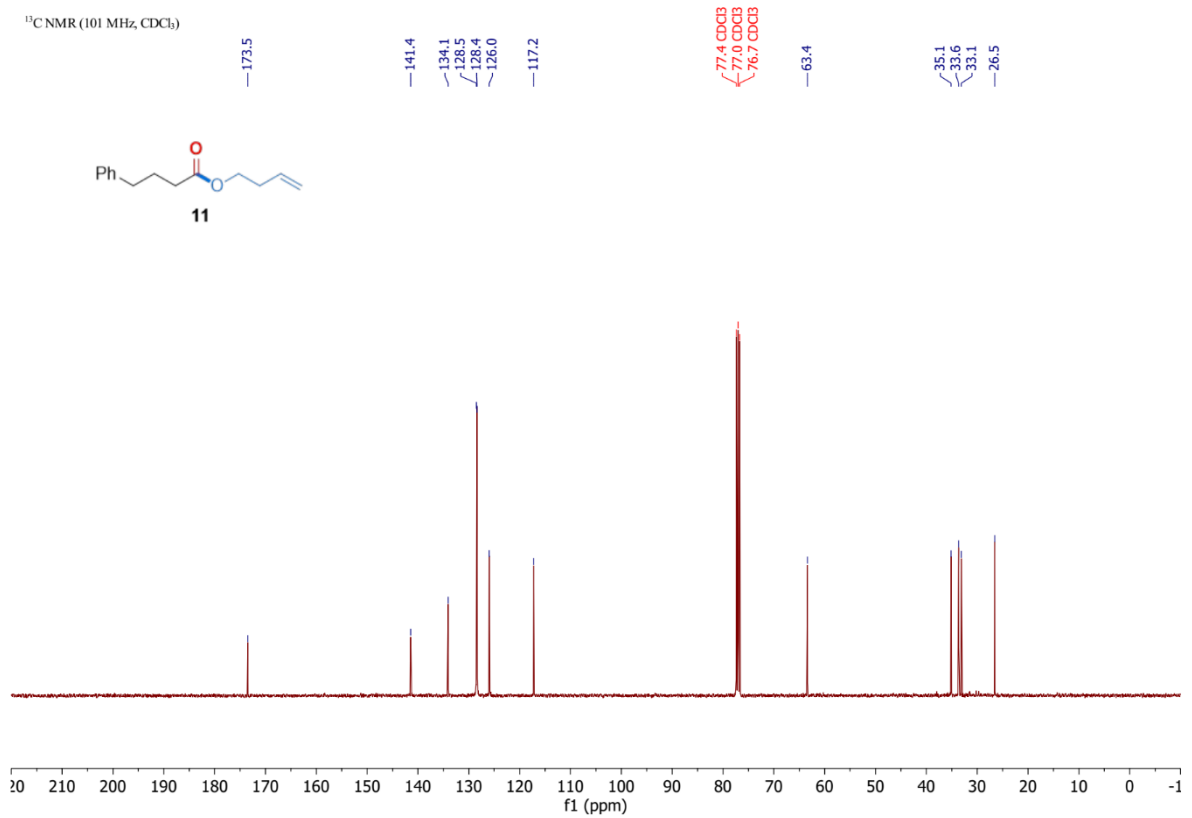
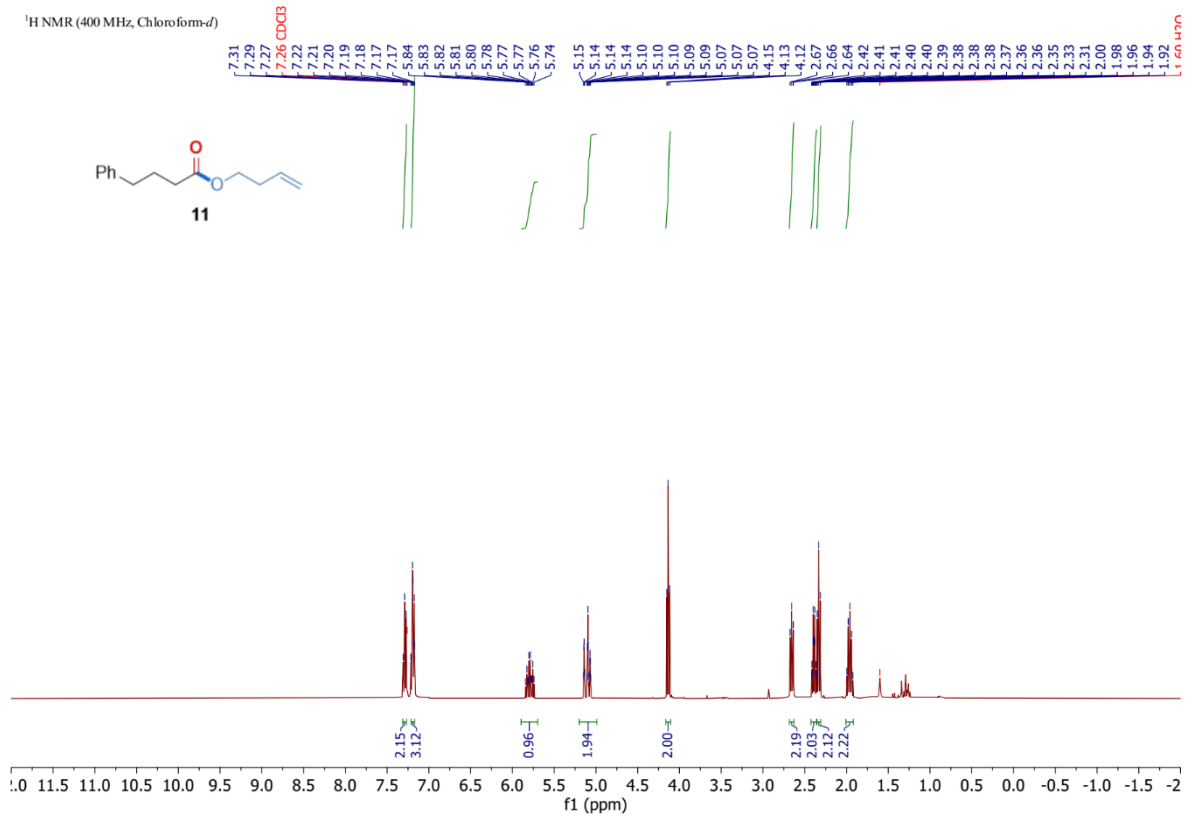




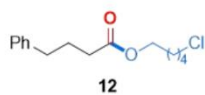






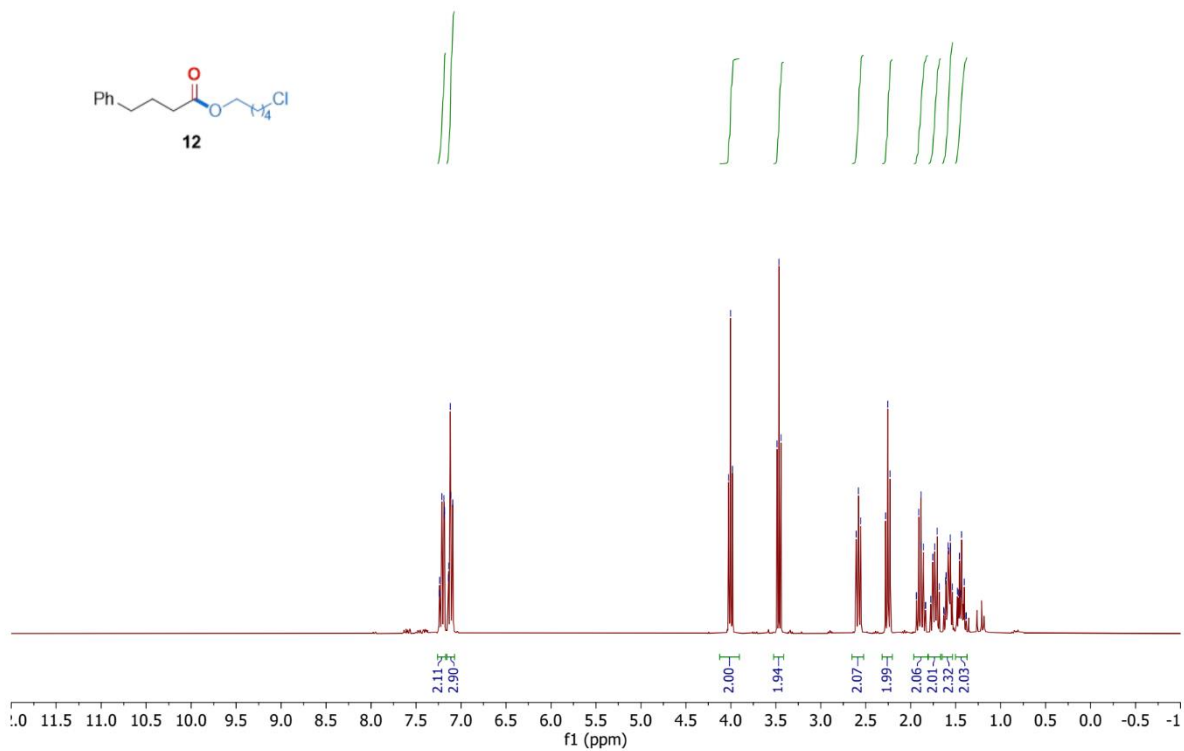


¹H NMR (300 MHz, Chloroform-*d*)

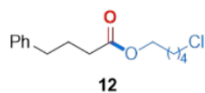


7.24
7.24
7.21
7.19
7.18
7.14
7.14
7.12
7.11
7.09

4.02
4.00
3.98
3.49
3.46
3.44
2.61
2.58
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1.71
1.68
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1.56
1.56
1.46
1.43
1.40



¹³C NMR (75 MHz, CDCl₃)



173.5

141.4

128.5

128.4

126.0

77.4 CDCl₃
77.0 CDCl₃
76.6 CDCl₃

64.0

44.7

35.1

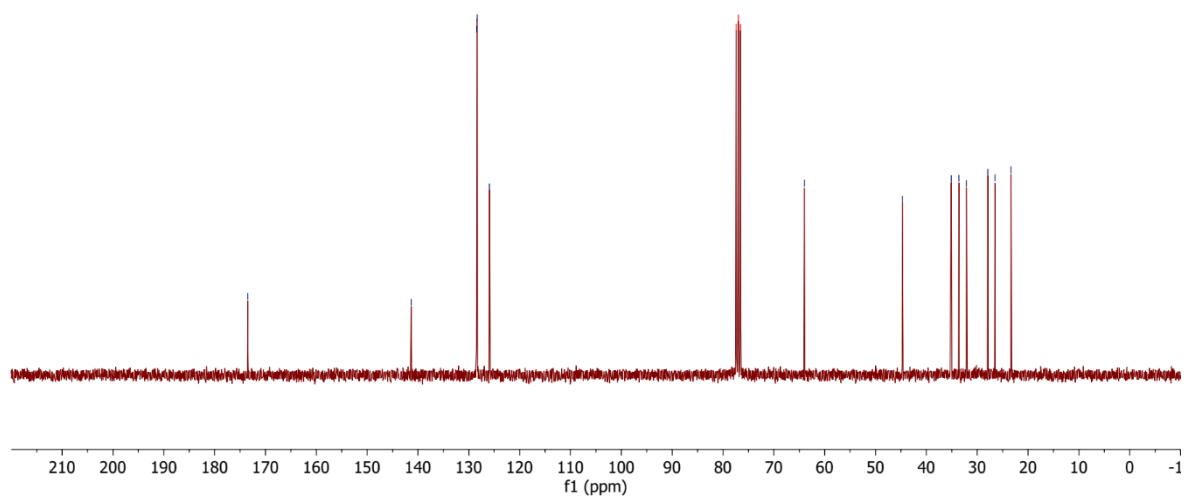
33.6

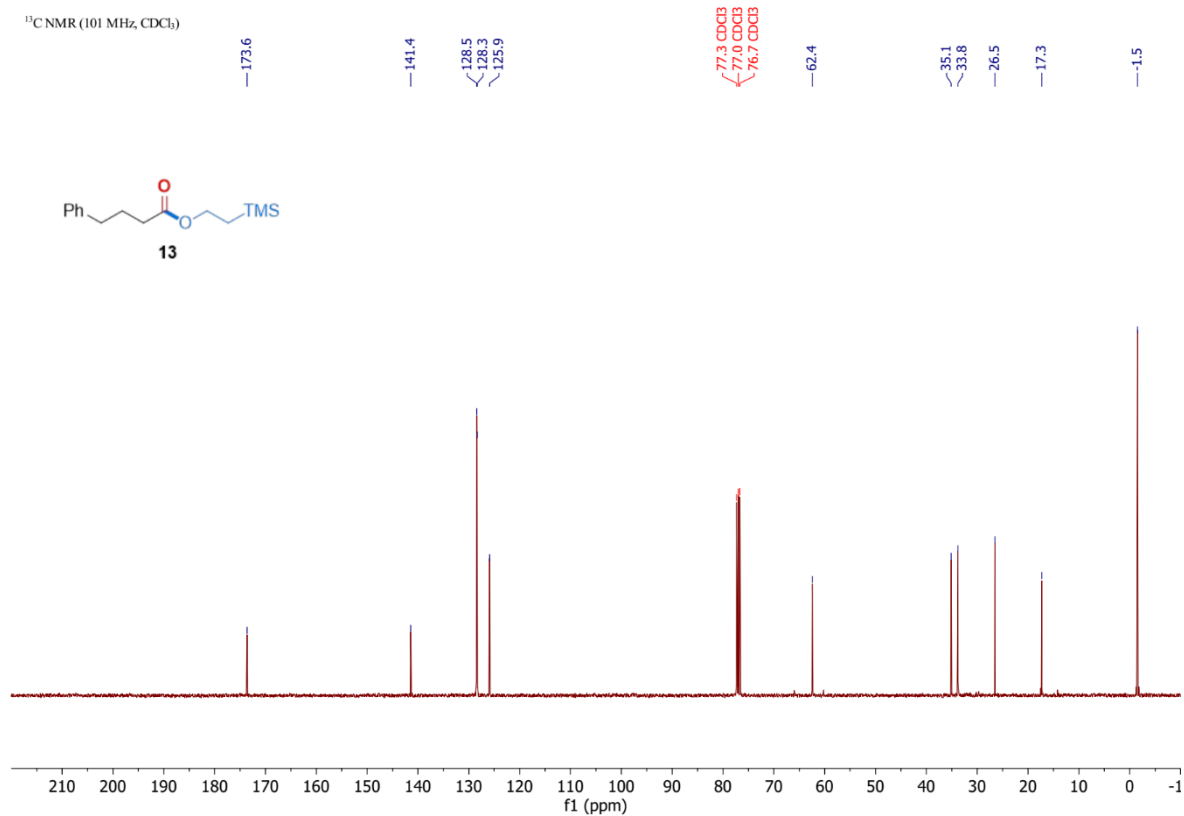
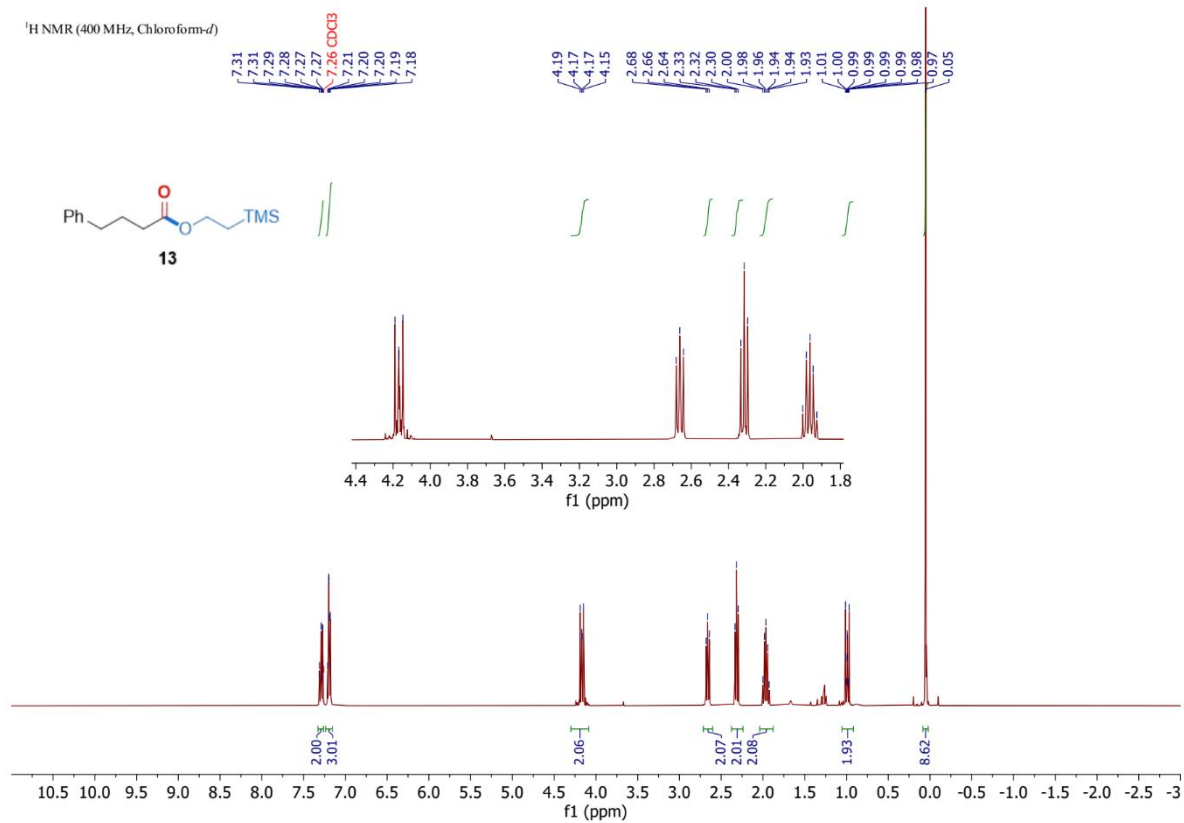
32.1

27.9

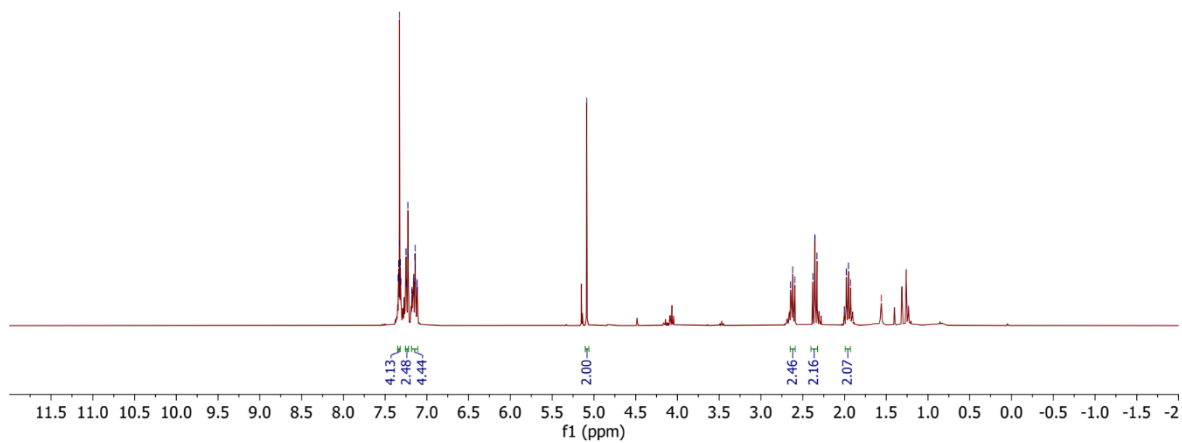
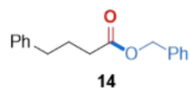
26.5

23.3

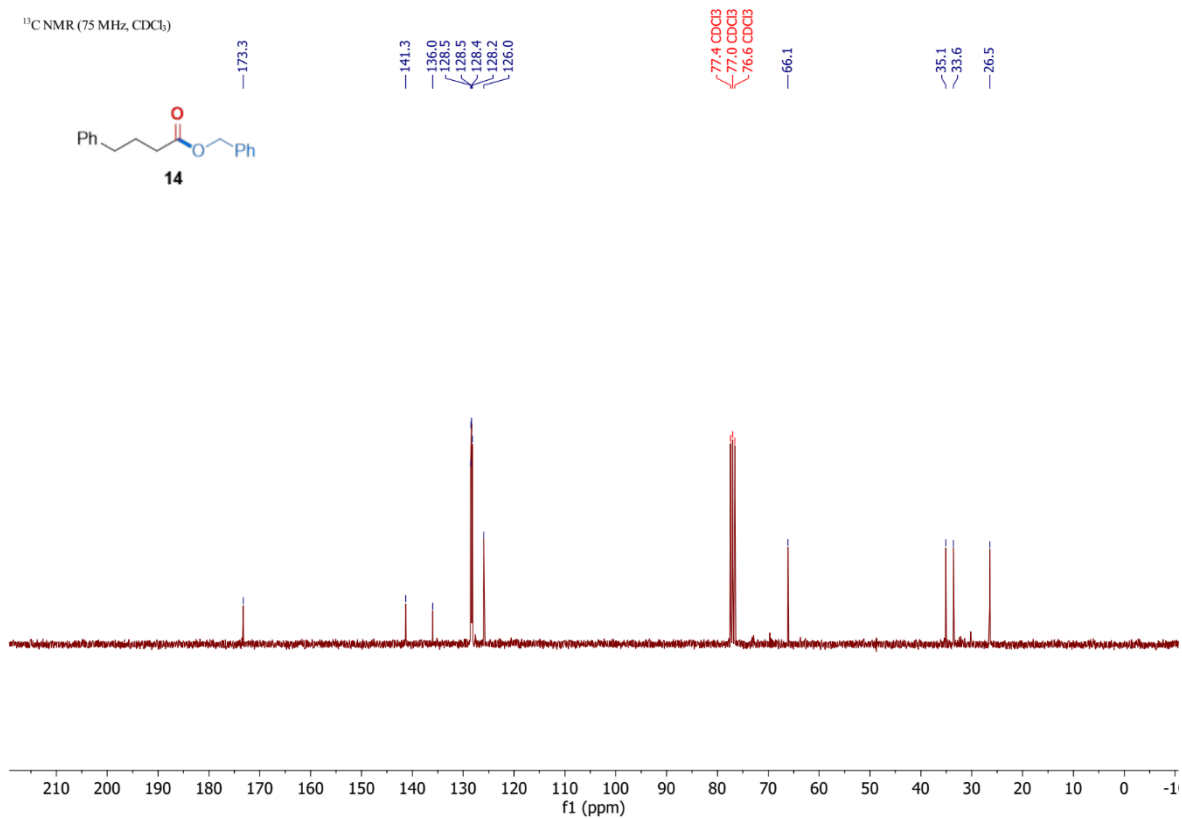
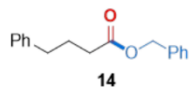


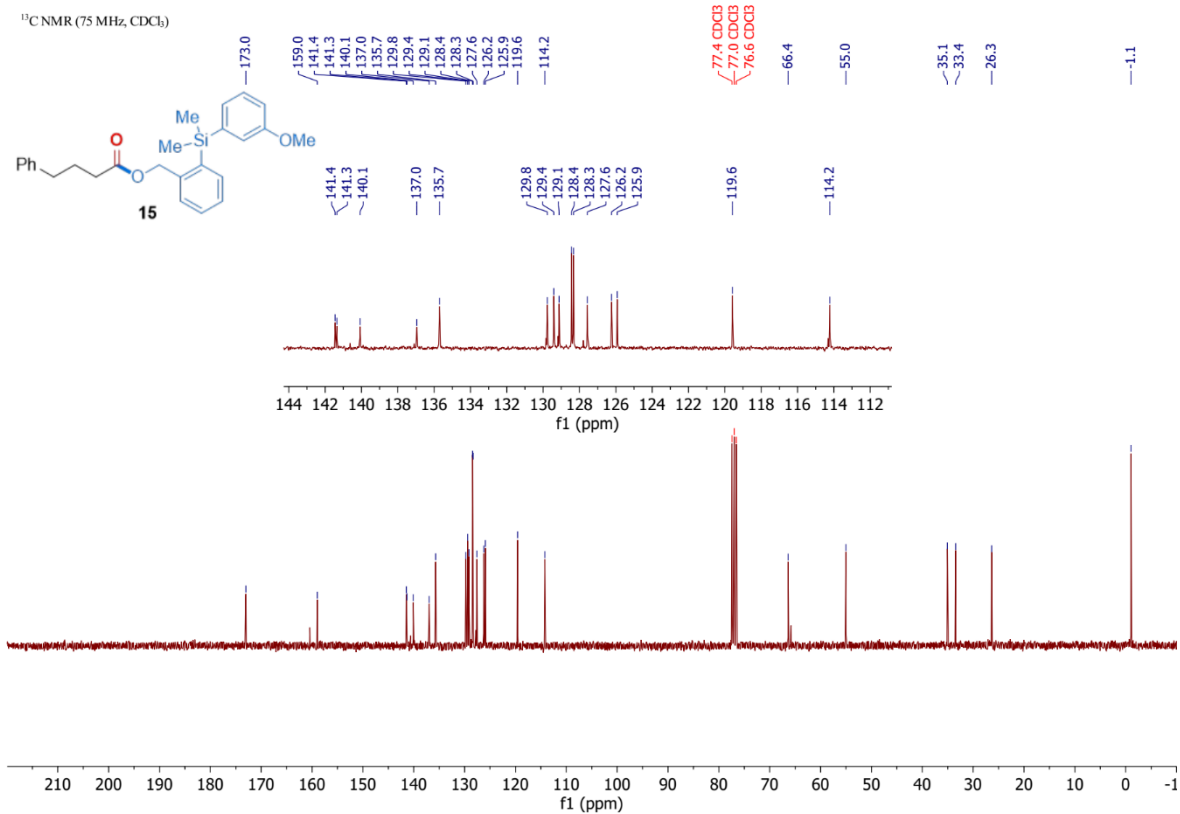
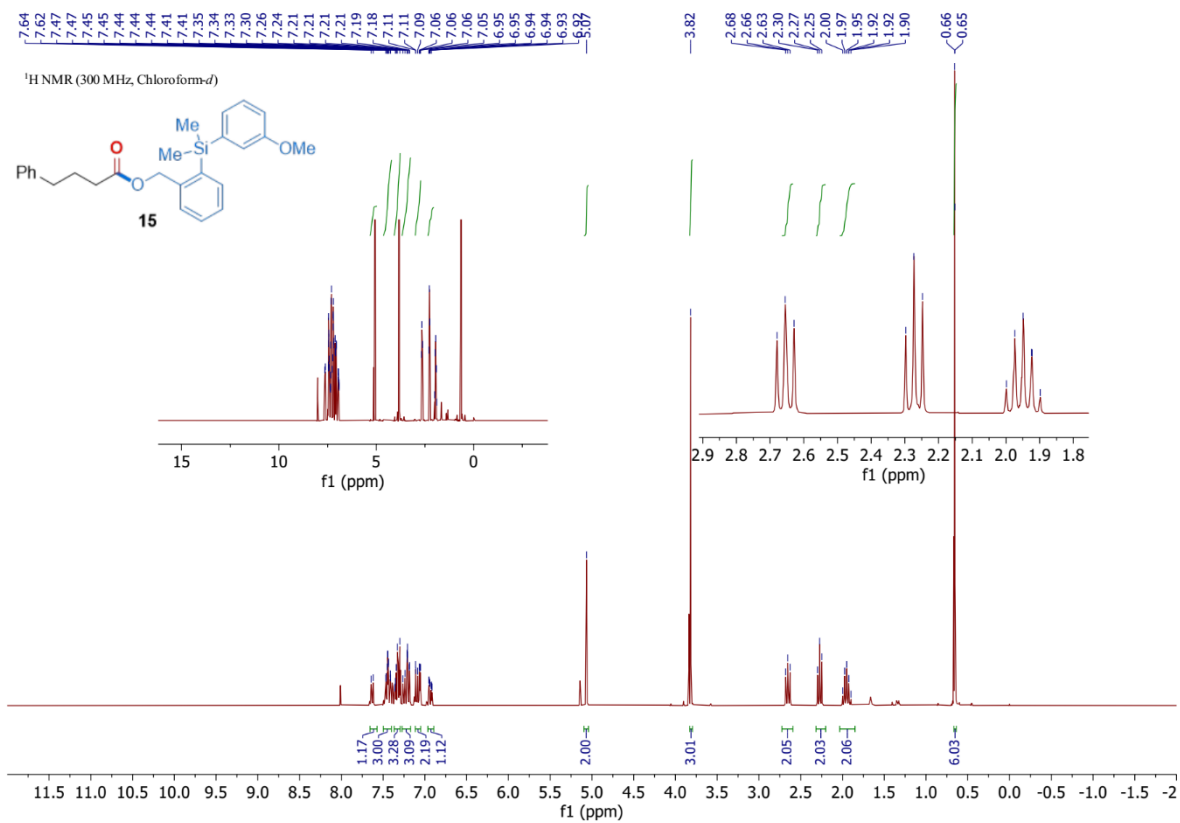


¹H NMR (300 MHz, Chloroform-d)

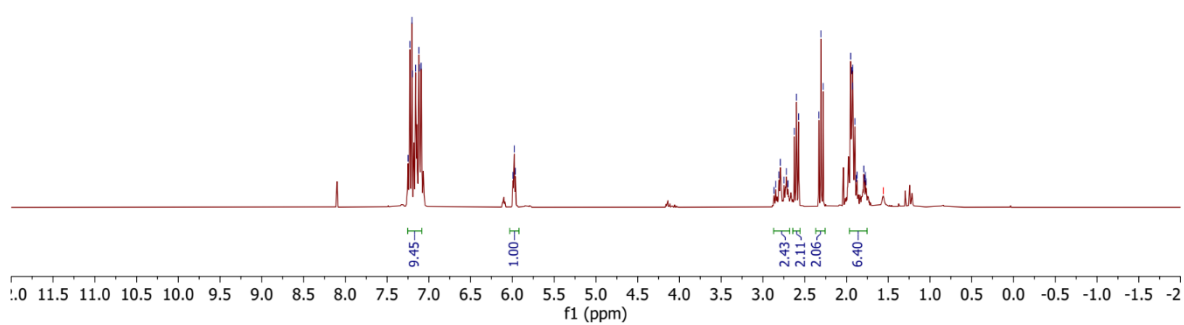
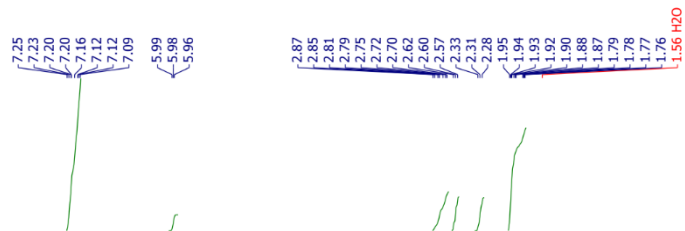
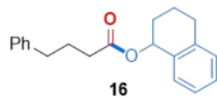


¹³C NMR (75 MHz, CDCl₃)

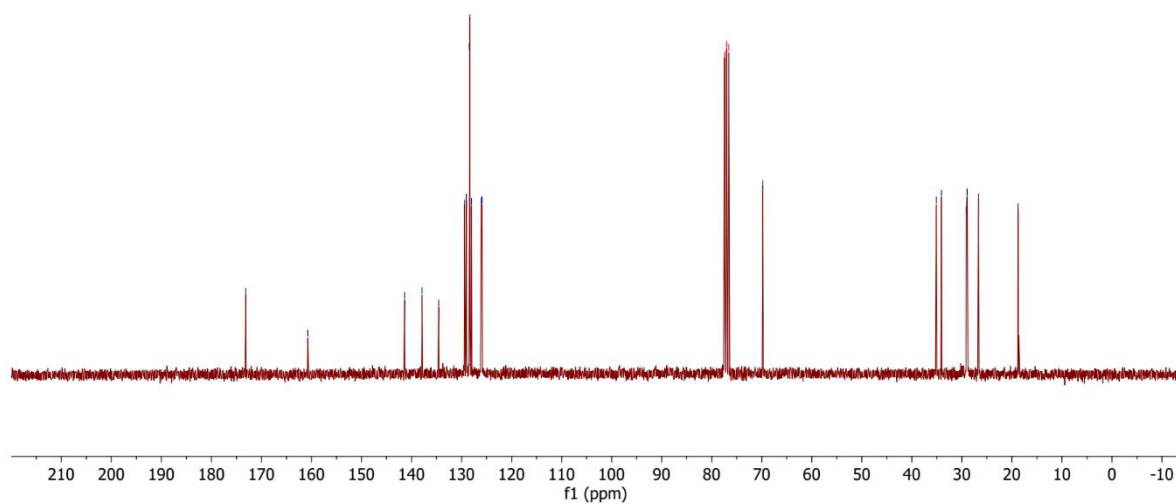
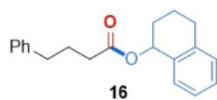


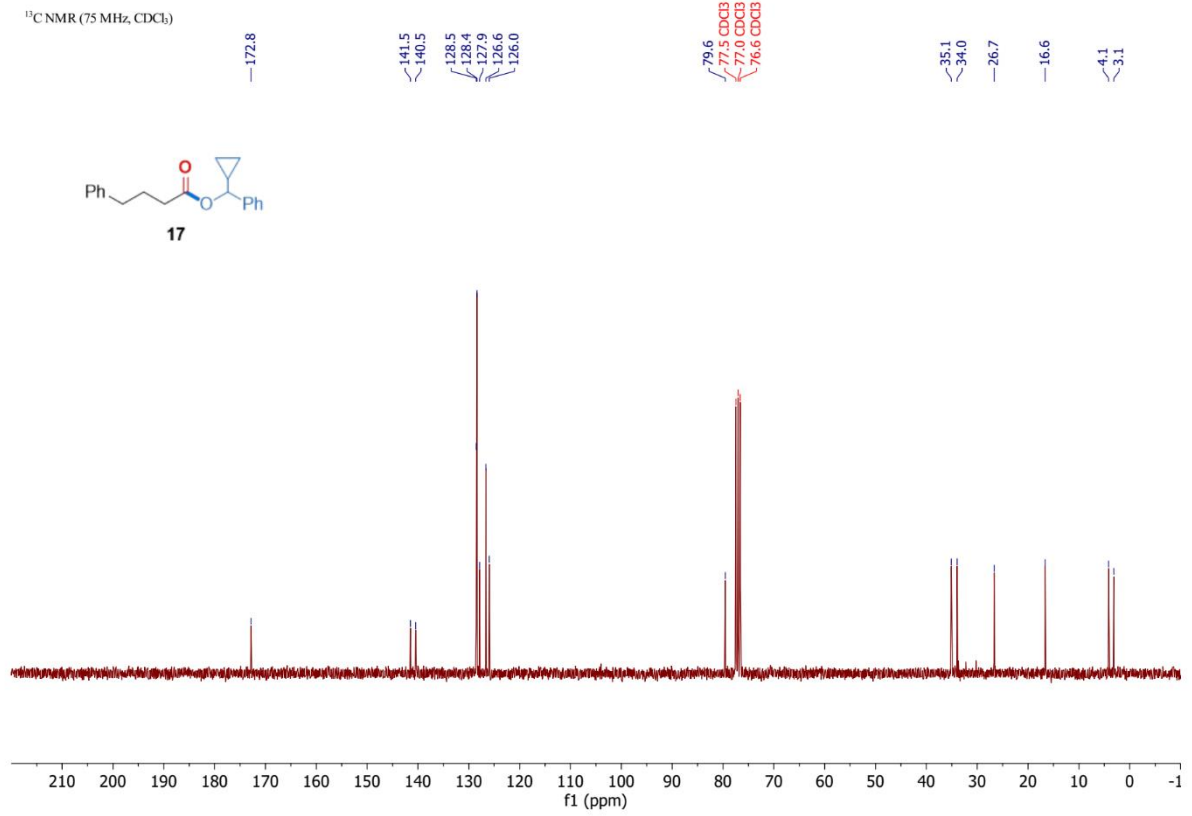
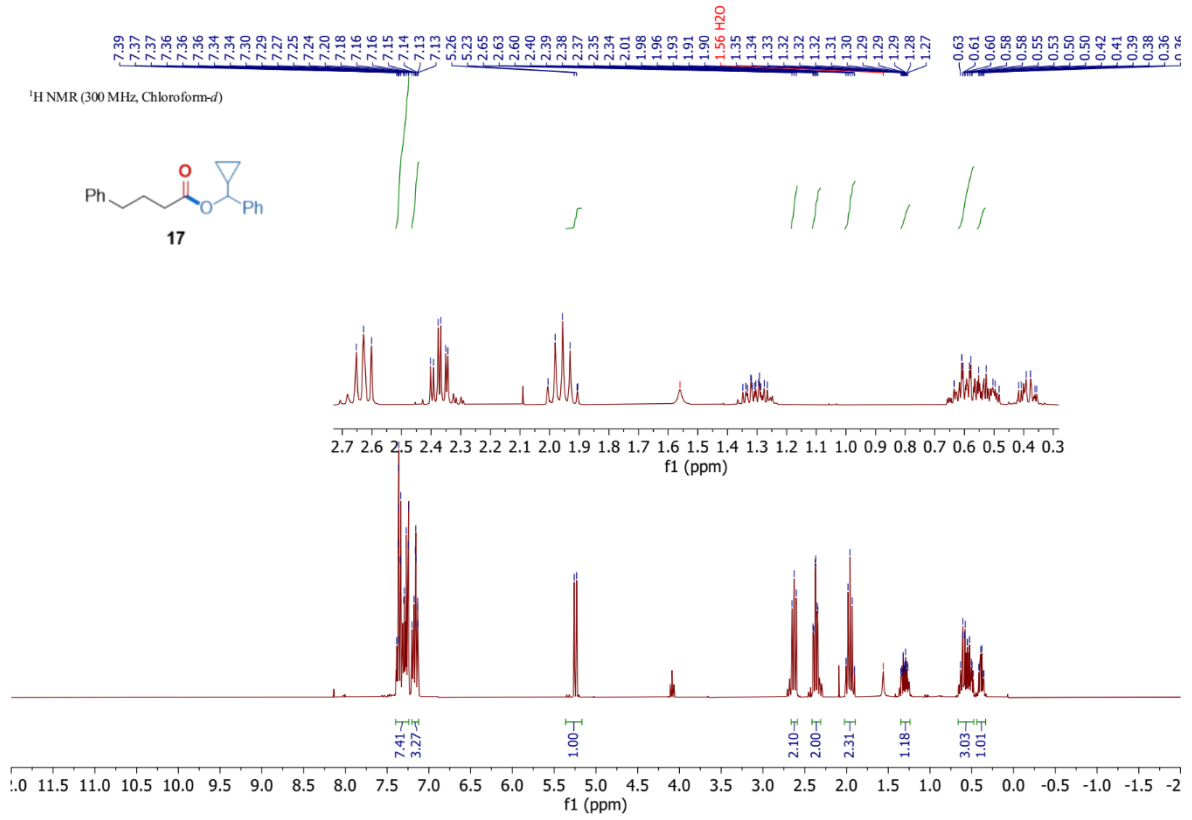


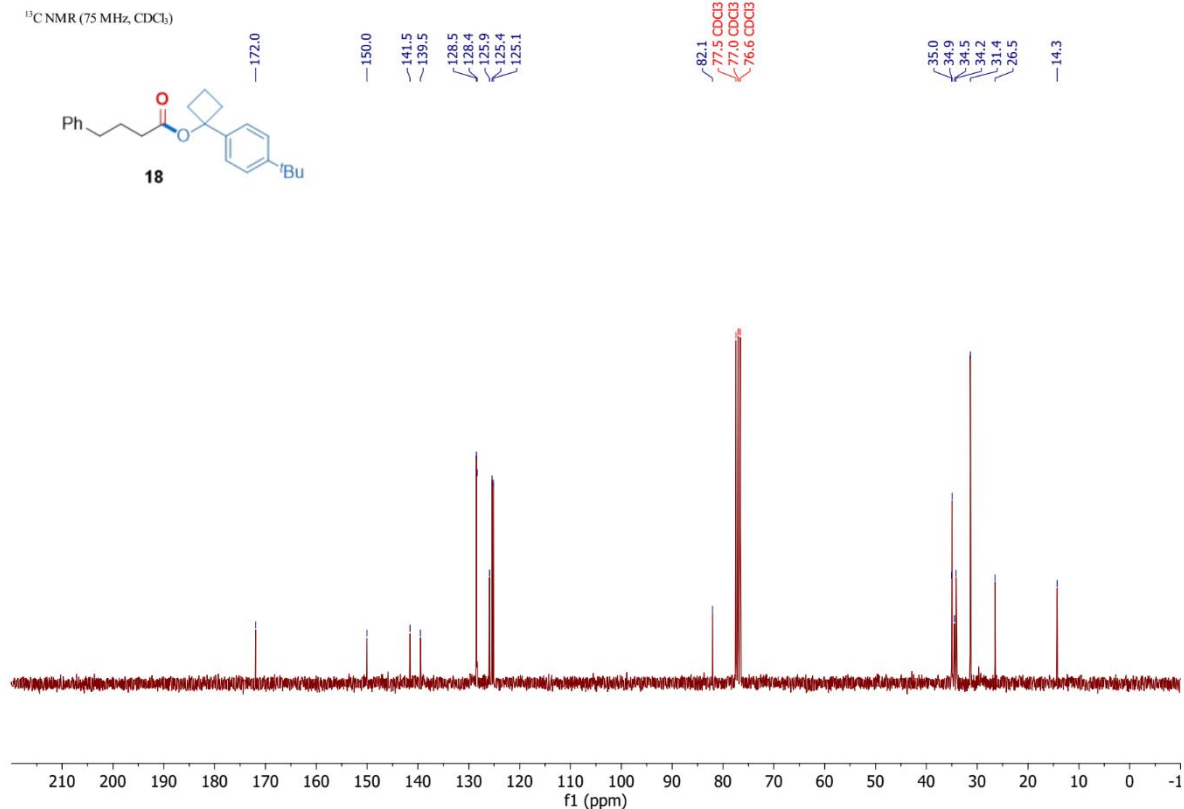
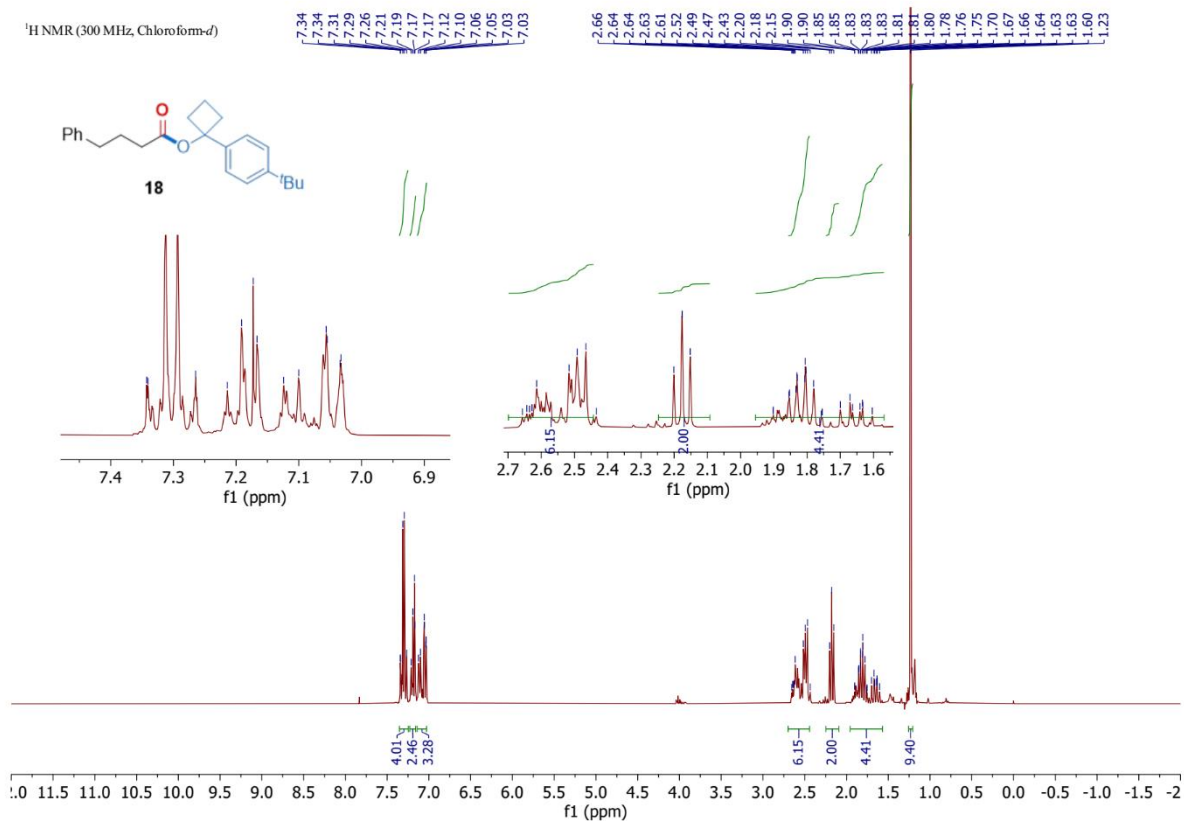
¹H NMR (300 MHz, Chloroform-*d*)

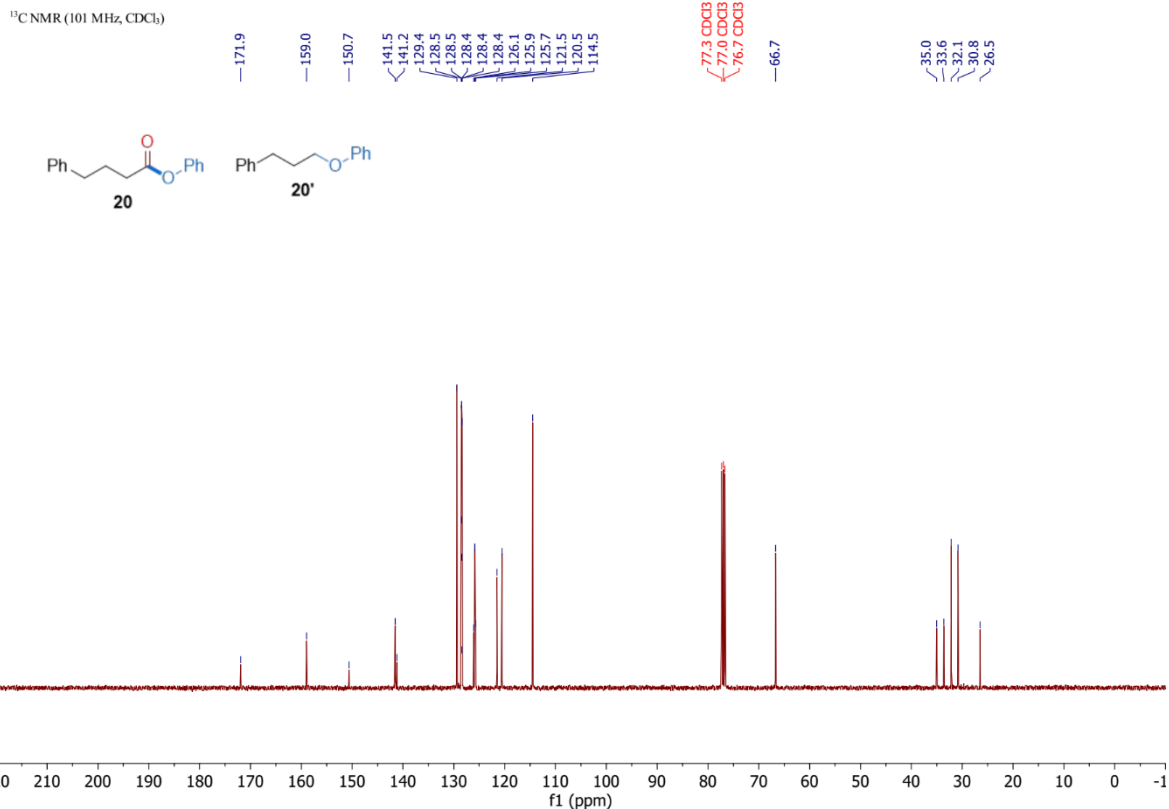
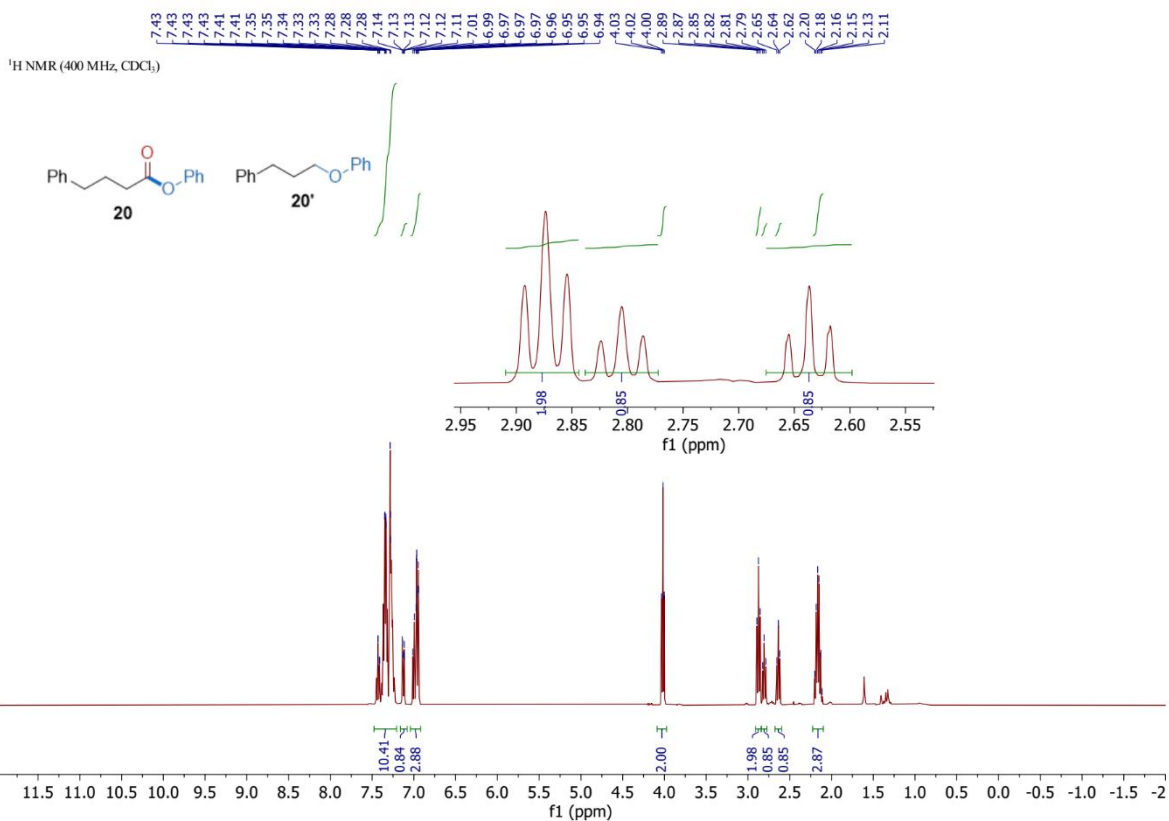


¹³C NMR (75 MHz, CDCl₃)

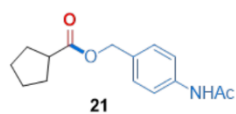








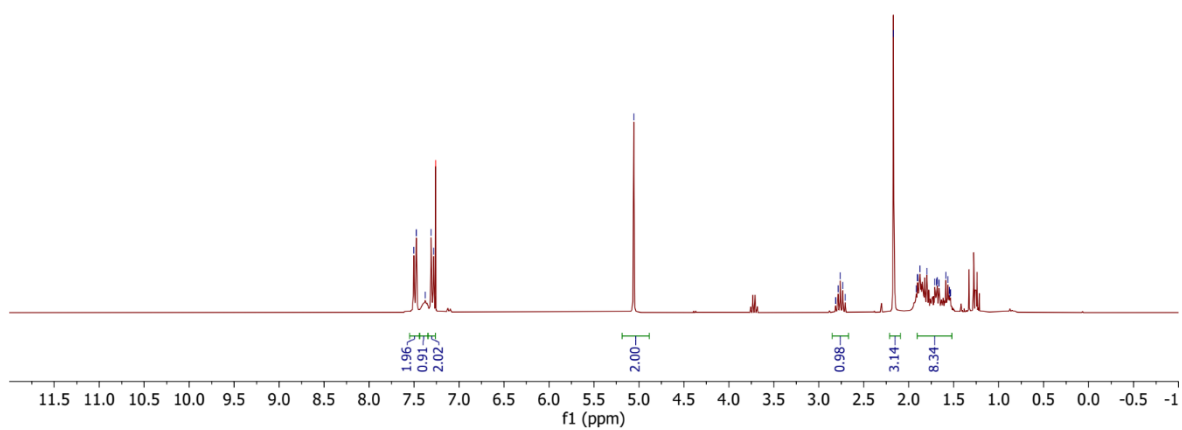
¹H NMR (300 MHz, Chloroform-*d*)



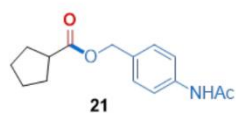
7.50
7.47
7.38
7.31
7.28
7.26 CDCl₃

5.06

2.81
2.78
2.75
2.73
2.71
2.17
1.92
1.90
1.87
1.80
1.71
1.69
1.68
1.66
1.59
1.57
1.55
1.54
1.53



¹³C NMR (75 MHz, CDCl₃)



176.6

168.4

137.7

132.2

128.9

119.8

77.4 CDCl₃

77.0 CDCl₃

76.6 CDCl₃

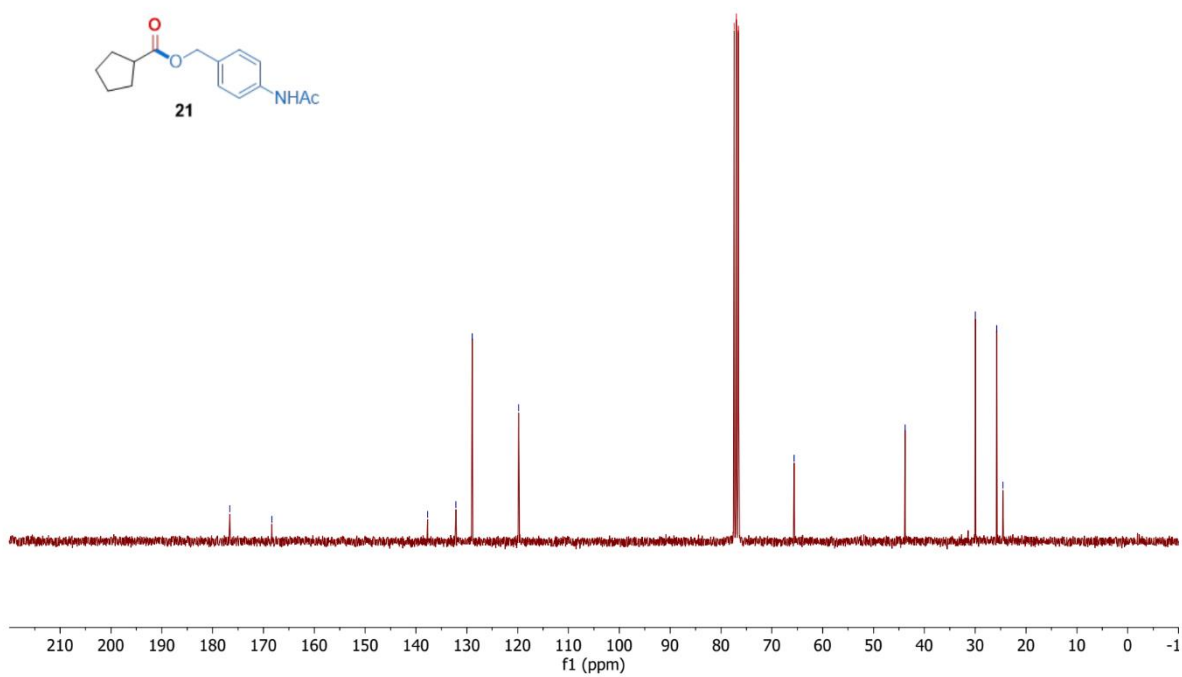
65.6

43.8

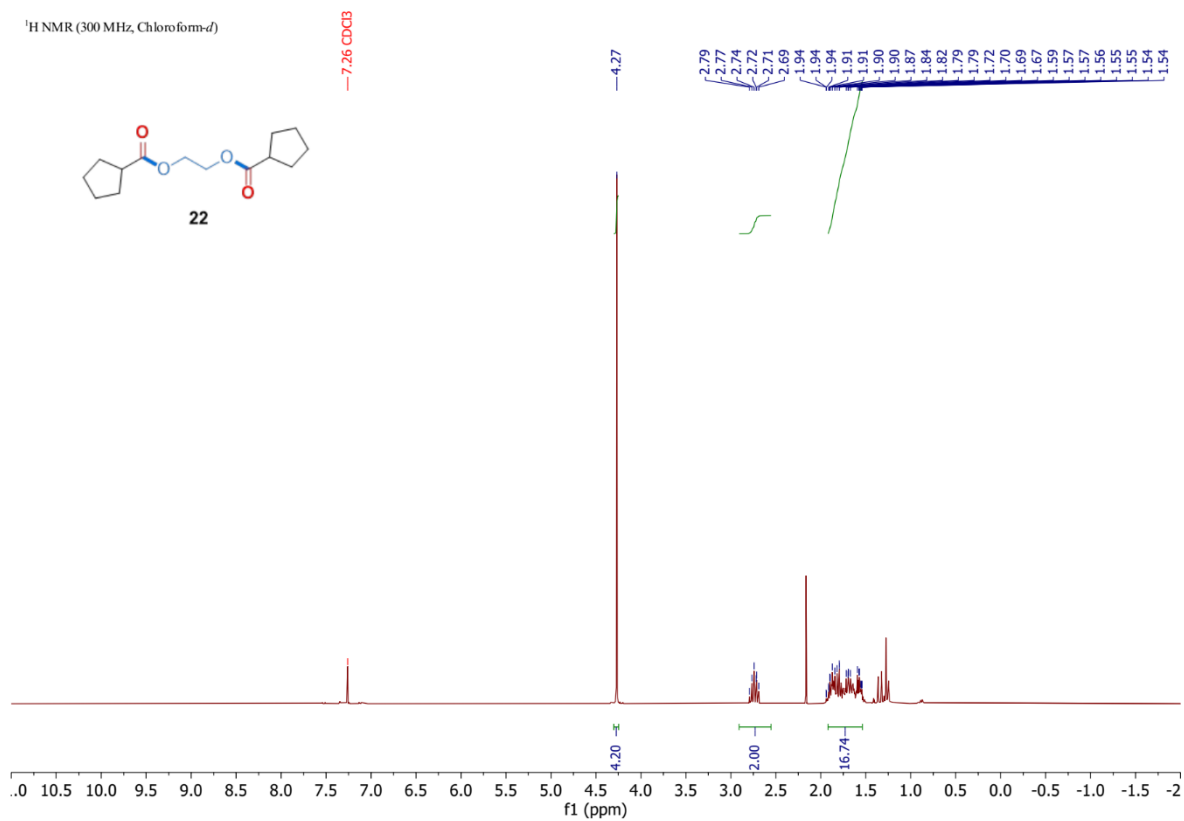
30.0

25.8

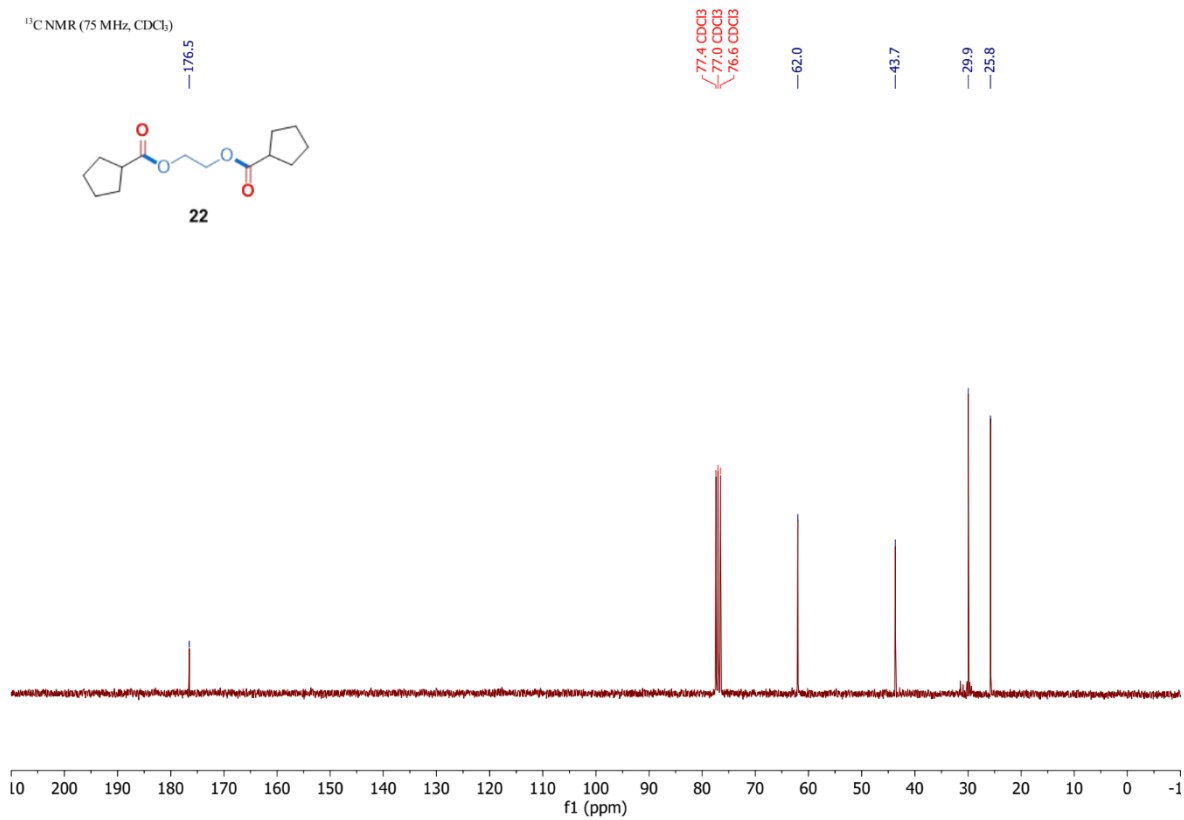
24.6



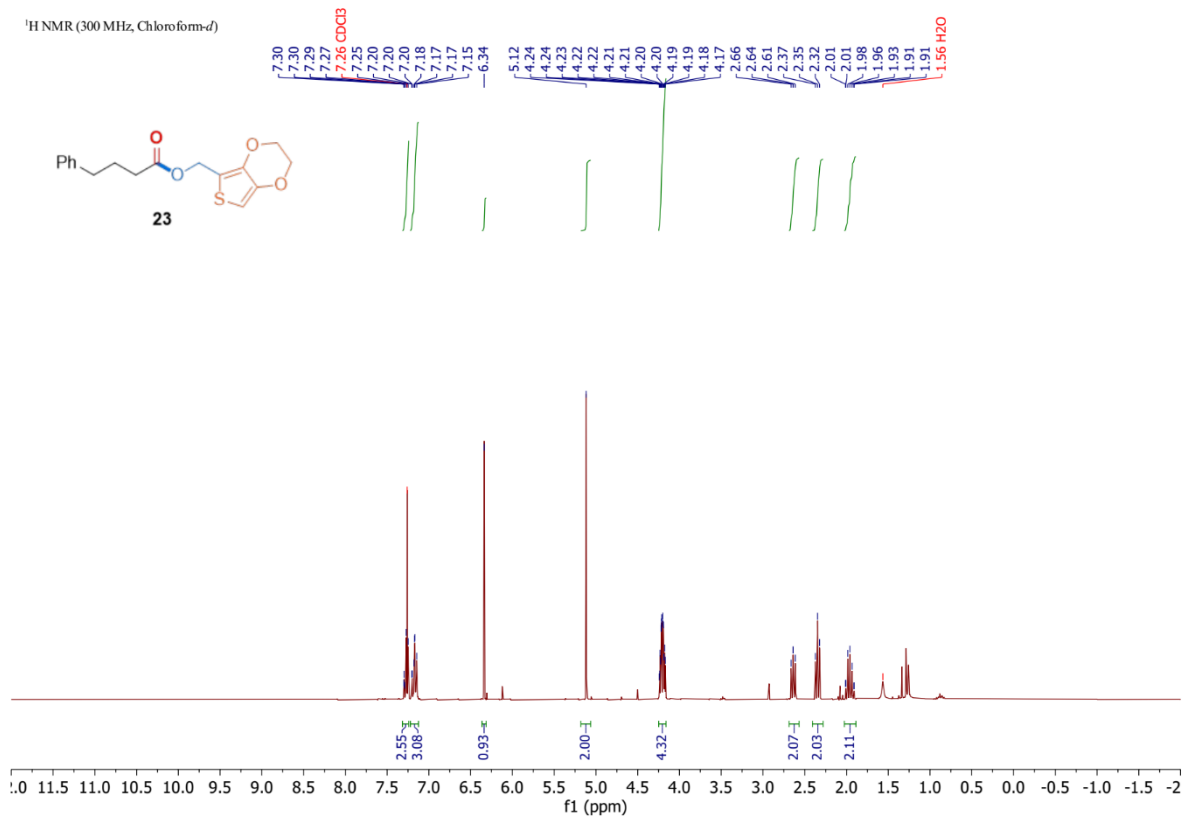
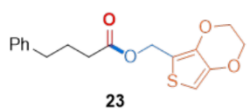
¹H NMR (300 MHz, Chloroform-*d*)



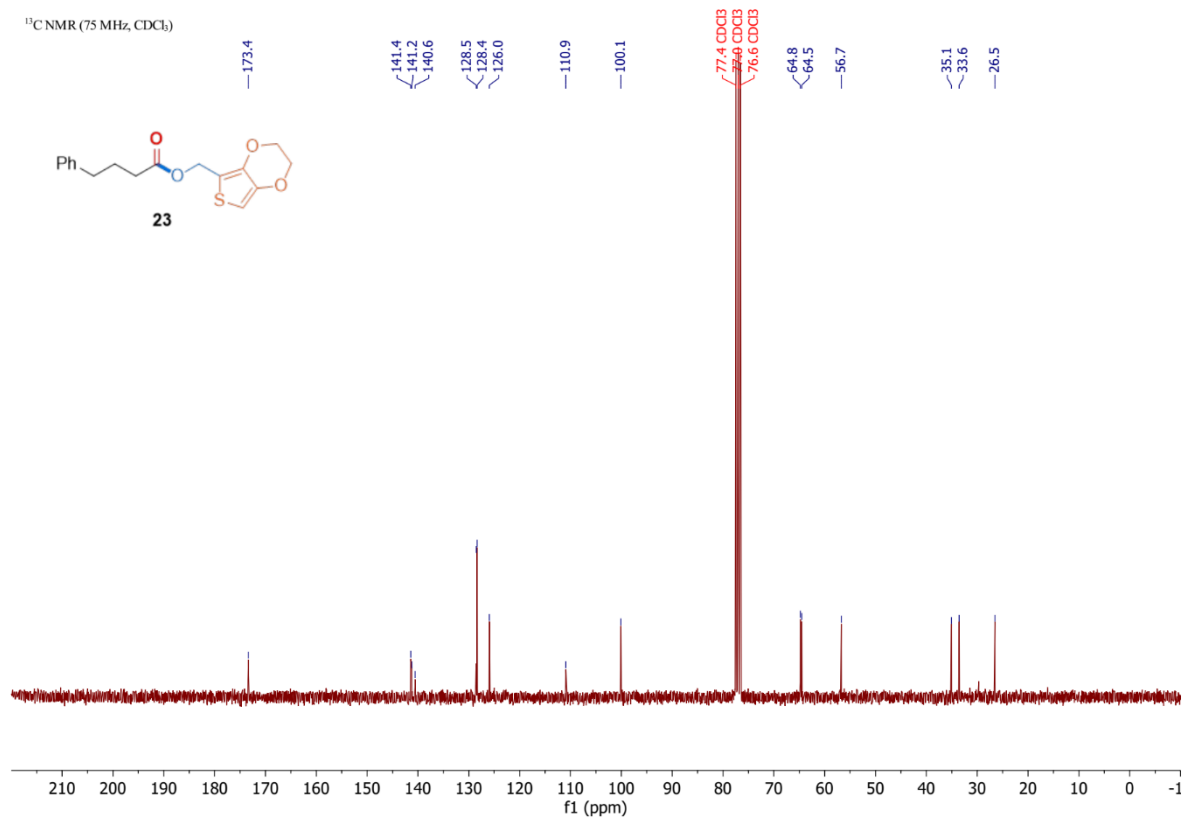
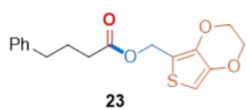
¹³C NMR (75 MHz, CDCl₃)

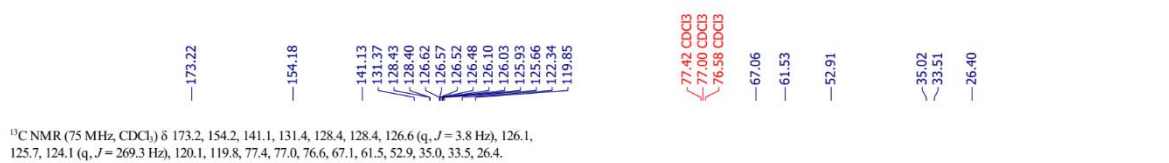
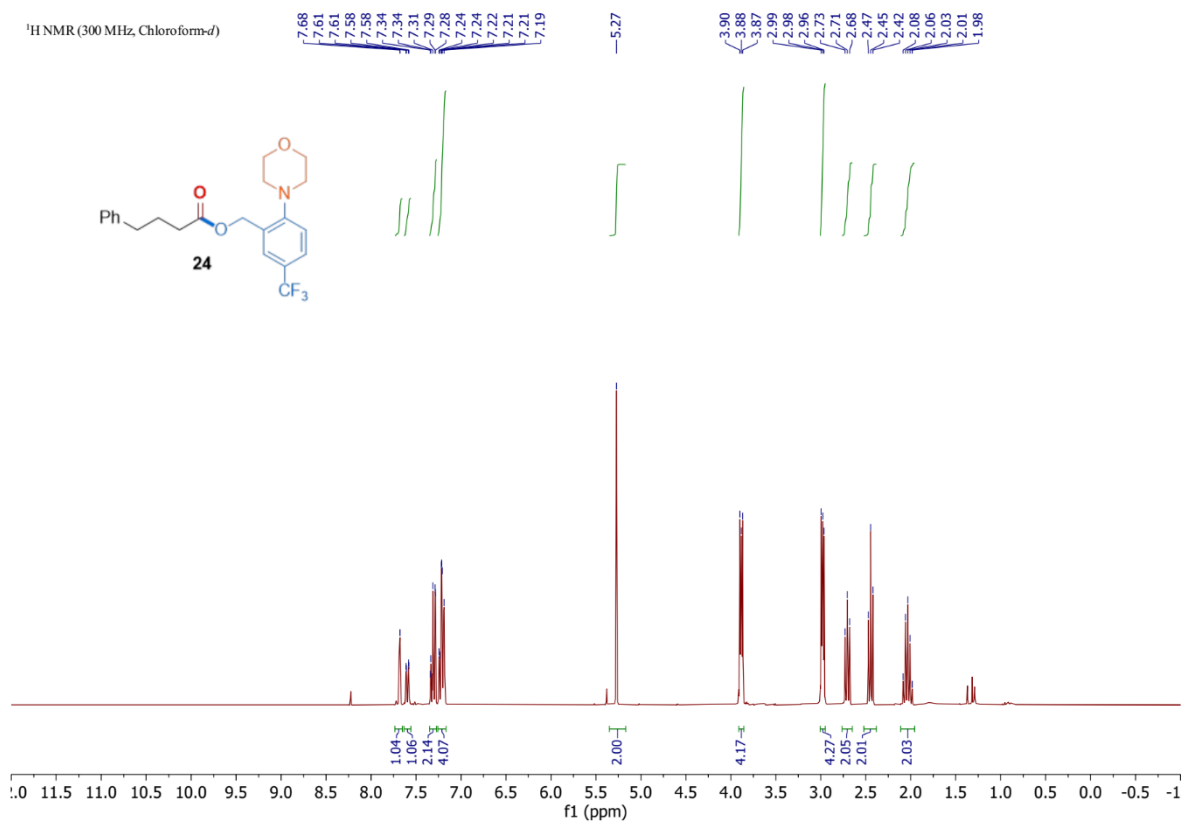


¹H NMR (300 MHz, Chloroform-*d*)

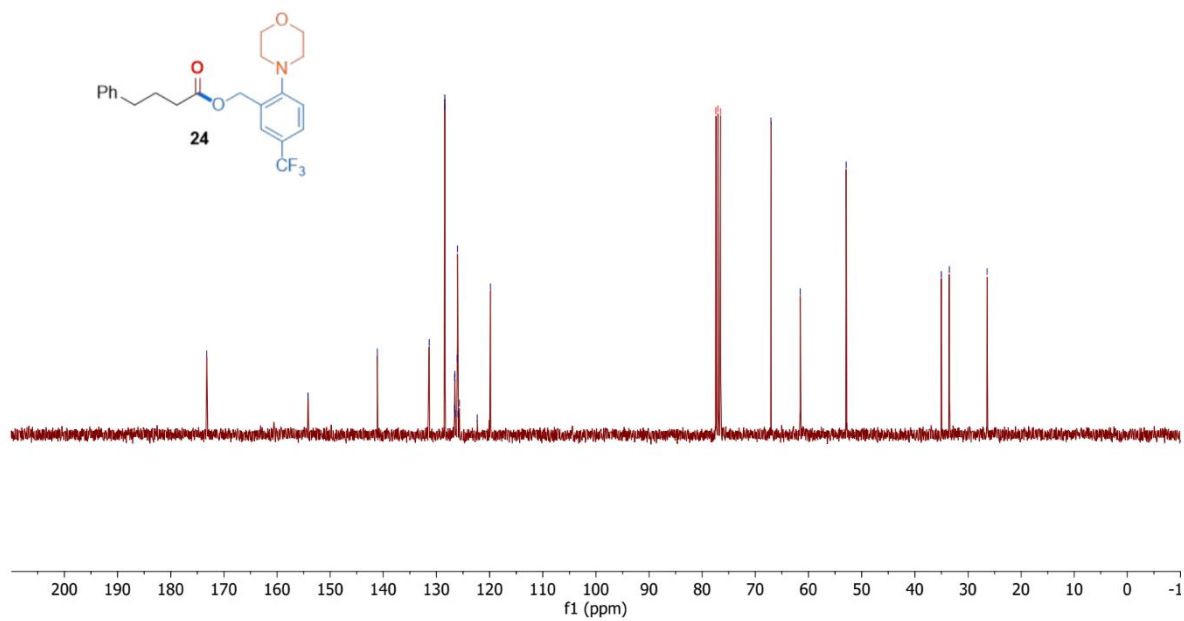


¹³C NMR (75 MHz, CDCl₃)



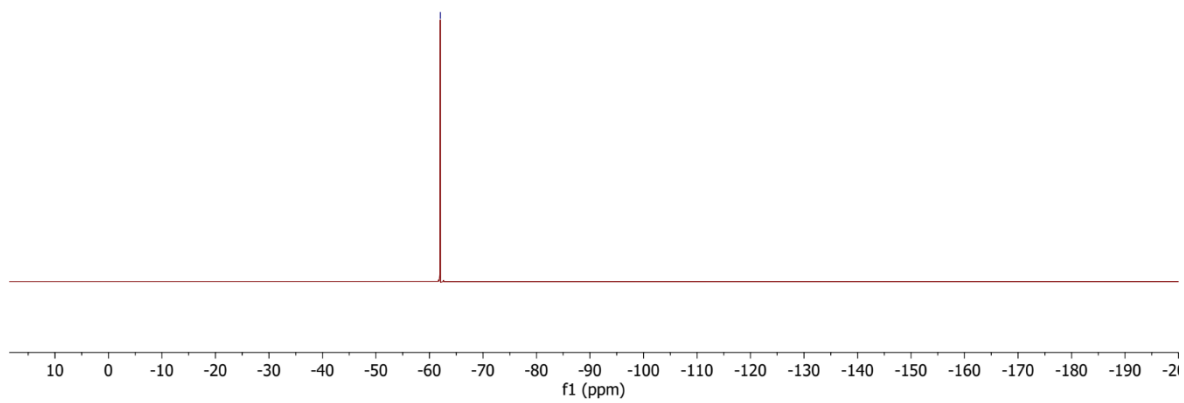
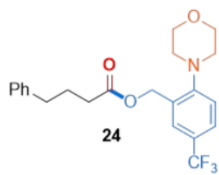


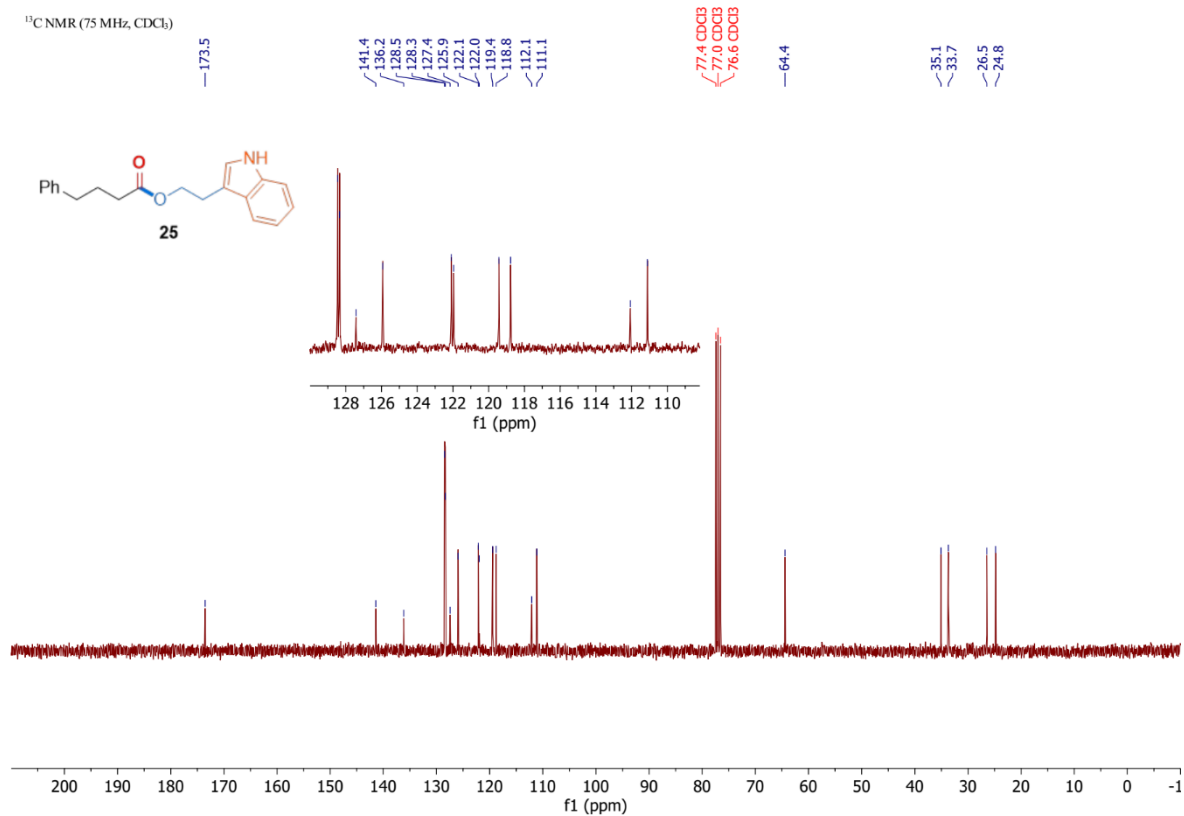
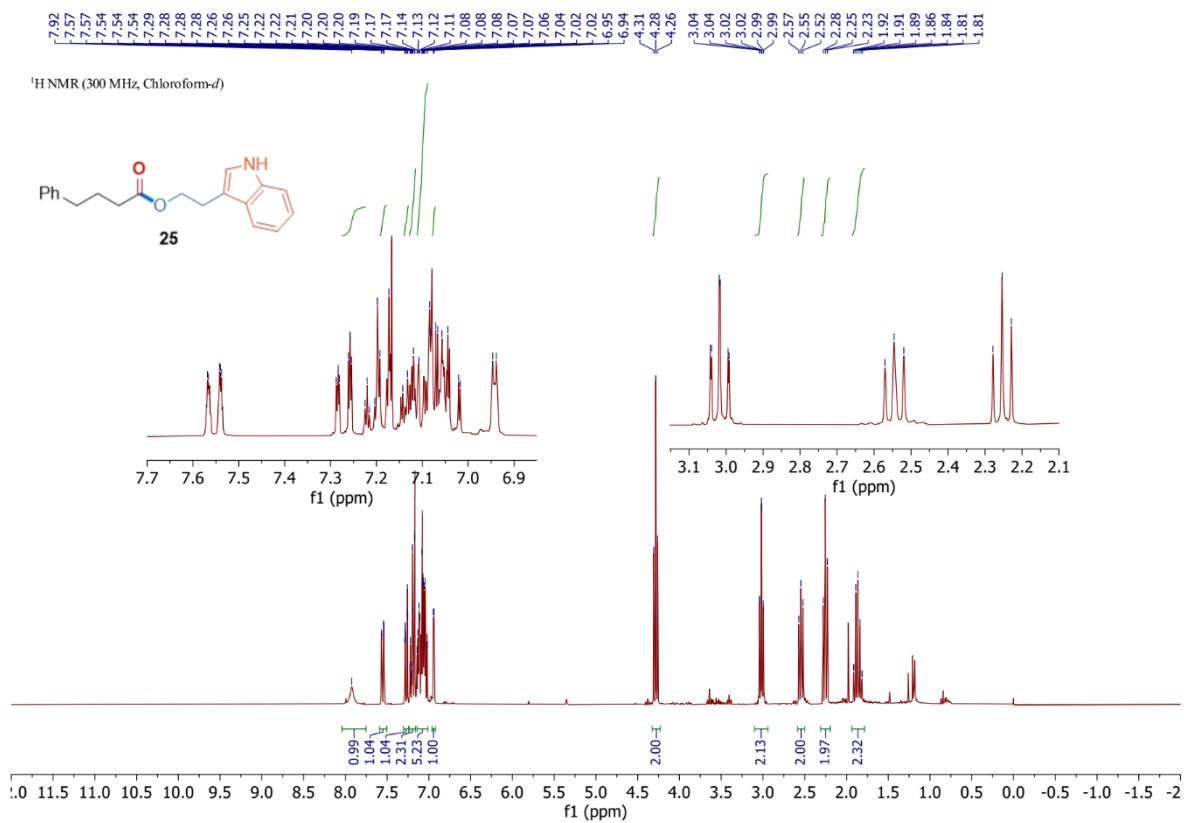
¹³C NMR (75 MHz, CDCl₃) δ 173.2, 154.2, 141.1, 131.4, 128.4, 128.4, 126.6 (q, *J* = 3.8 Hz), 126.1, 125.7, 124.1 (q, *J* = 269.3 Hz), 120.1, 119.8, 77.4, 77.0, 76.6, 67.1, 61.5, 52.9, 35.0, 33.5, 26.4.



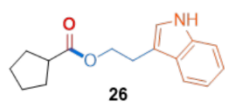
^{19}F NMR (282 MHz, CDCl_3)

— 62.0

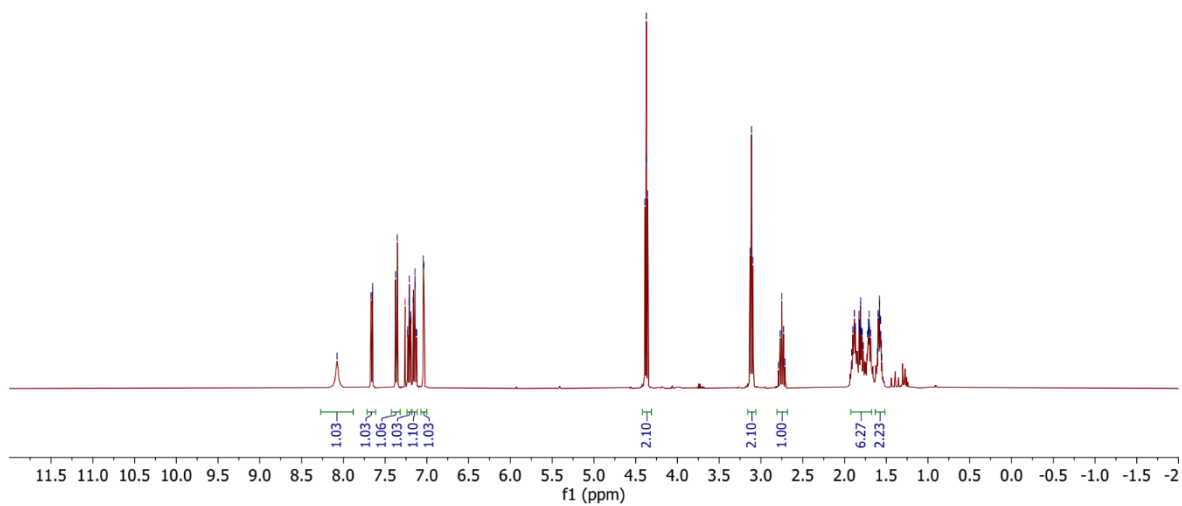




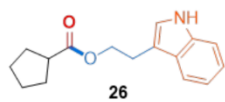
¹H NMR (400 MHz, CDCl₃)



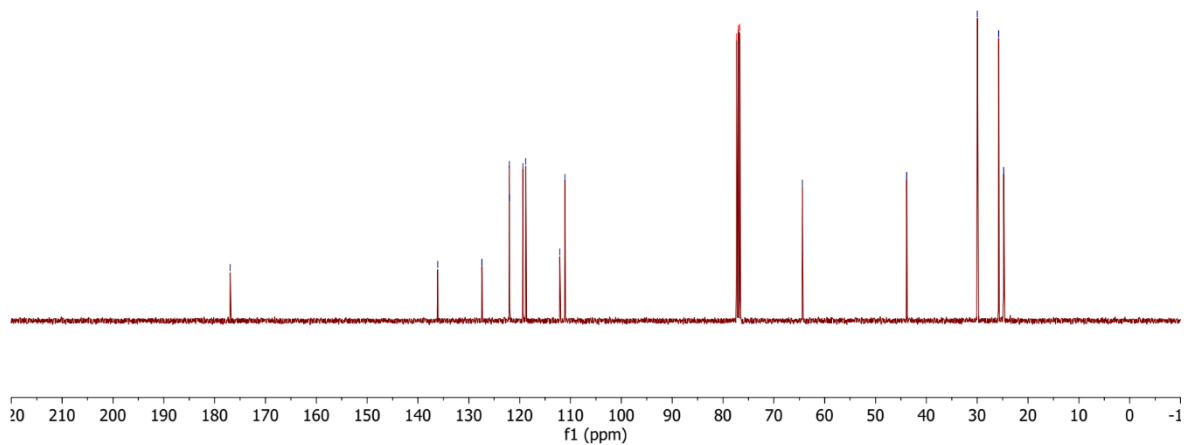
8.08
7.67
7.67
7.65
7.37
7.35
7.26 CDCl₃
7.23
7.21
7.21
7.19
7.19
7.16
7.16
7.14
7.14
7.13
7.12
7.04
7.04
4.39
4.37
4.37
4.35
3.13
3.11
3.09
2.79
2.77
2.75
2.73
2.71
1.90
1.88
1.87
1.83
1.82
1.82
1.81
1.81
1.81
1.80
1.80
1.71
1.71
1.70
1.70
1.60
1.59
1.58
1.57



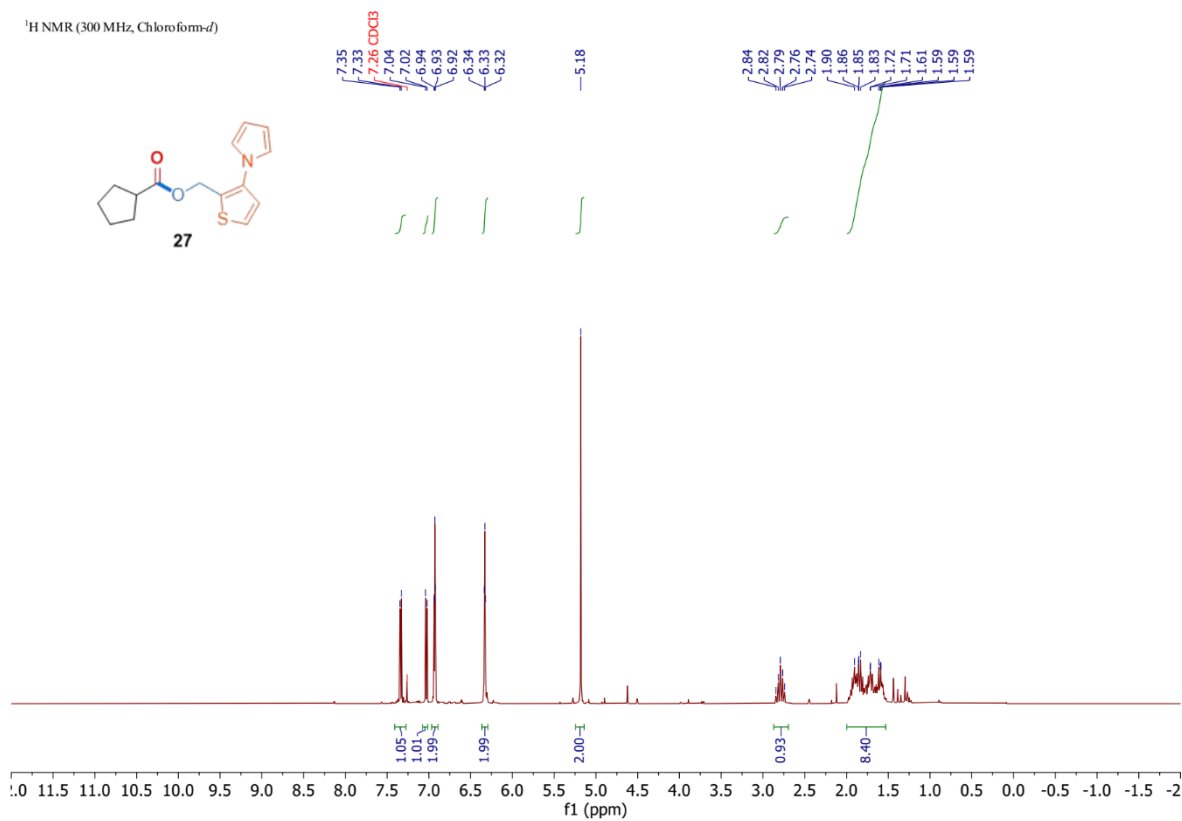
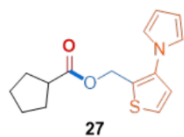
¹³C NMR (101 MHz, CDCl₃)



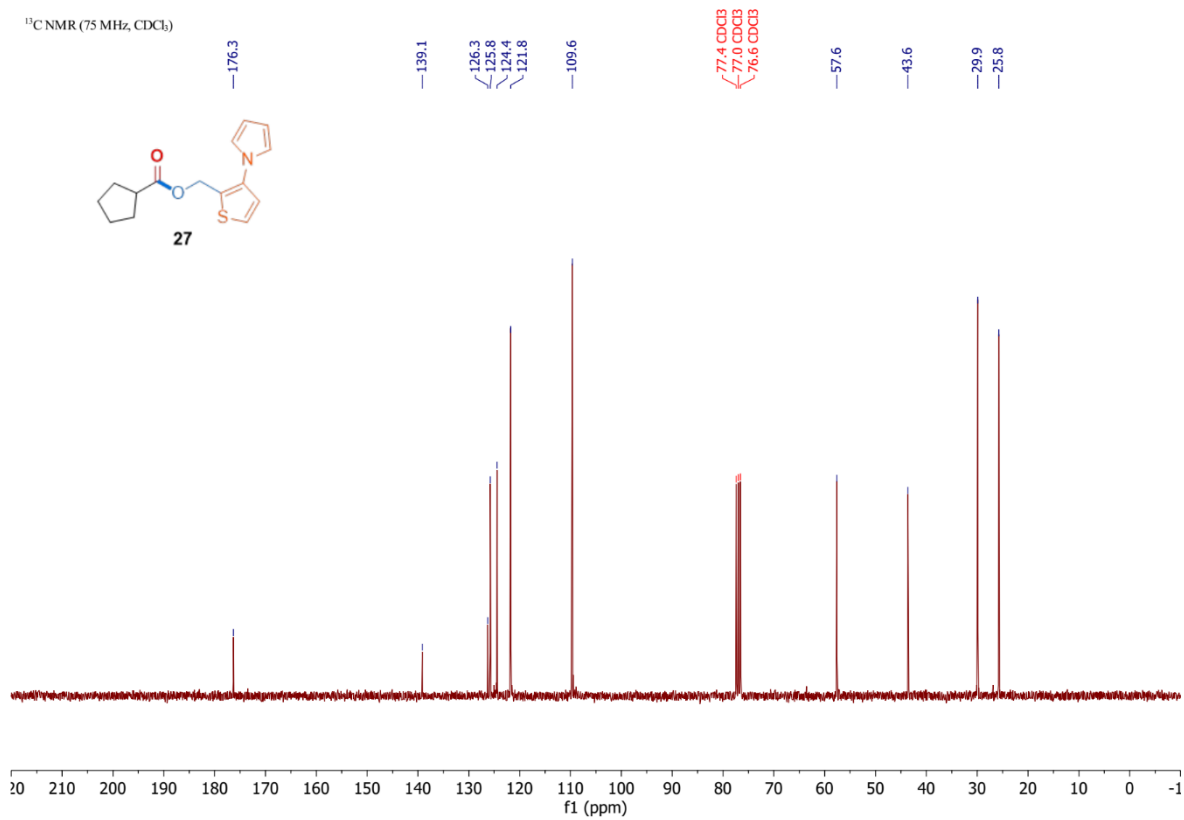
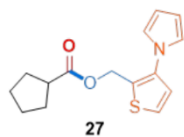
176.9
136.1
127.4
122.0
122.0
119.3
118.8
112.1
111.1
77.3 CDCl₃
77.0 CDCl₃
76.7 CDCl₃
64.4
43.9
30.0
25.8
24.8

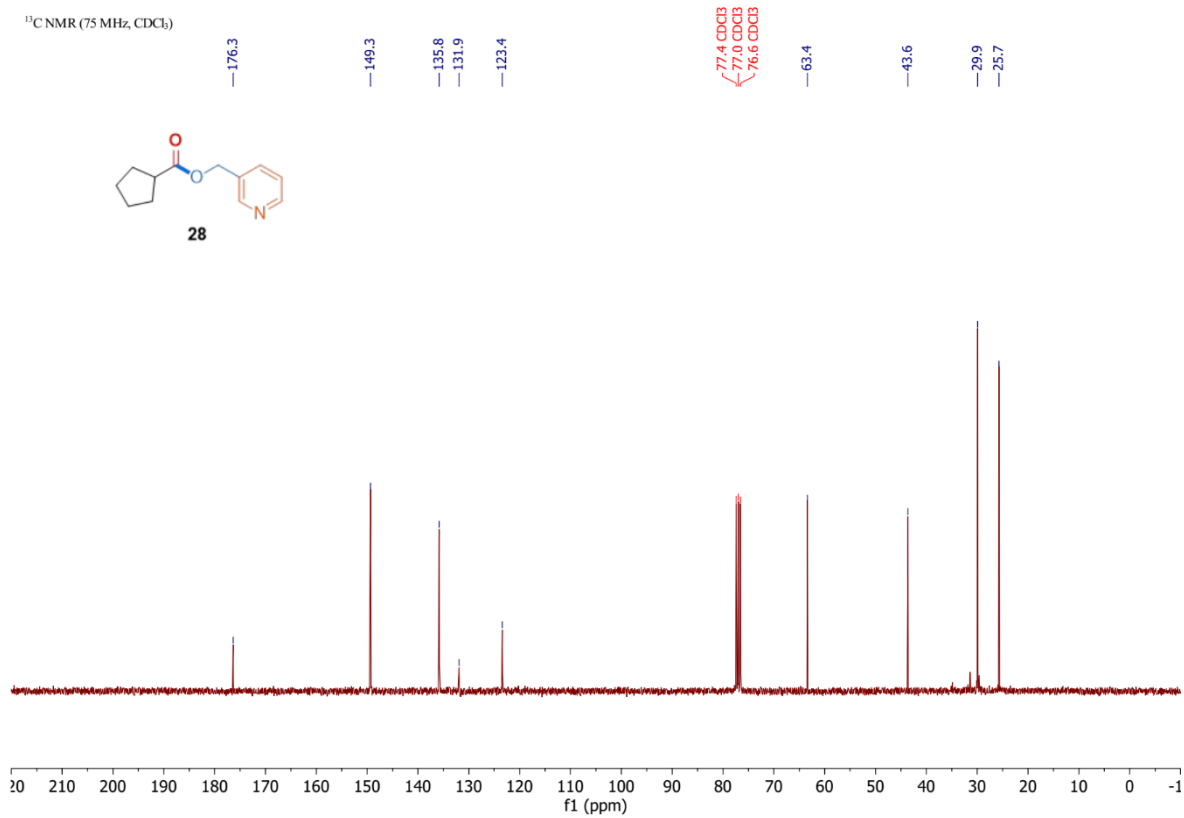
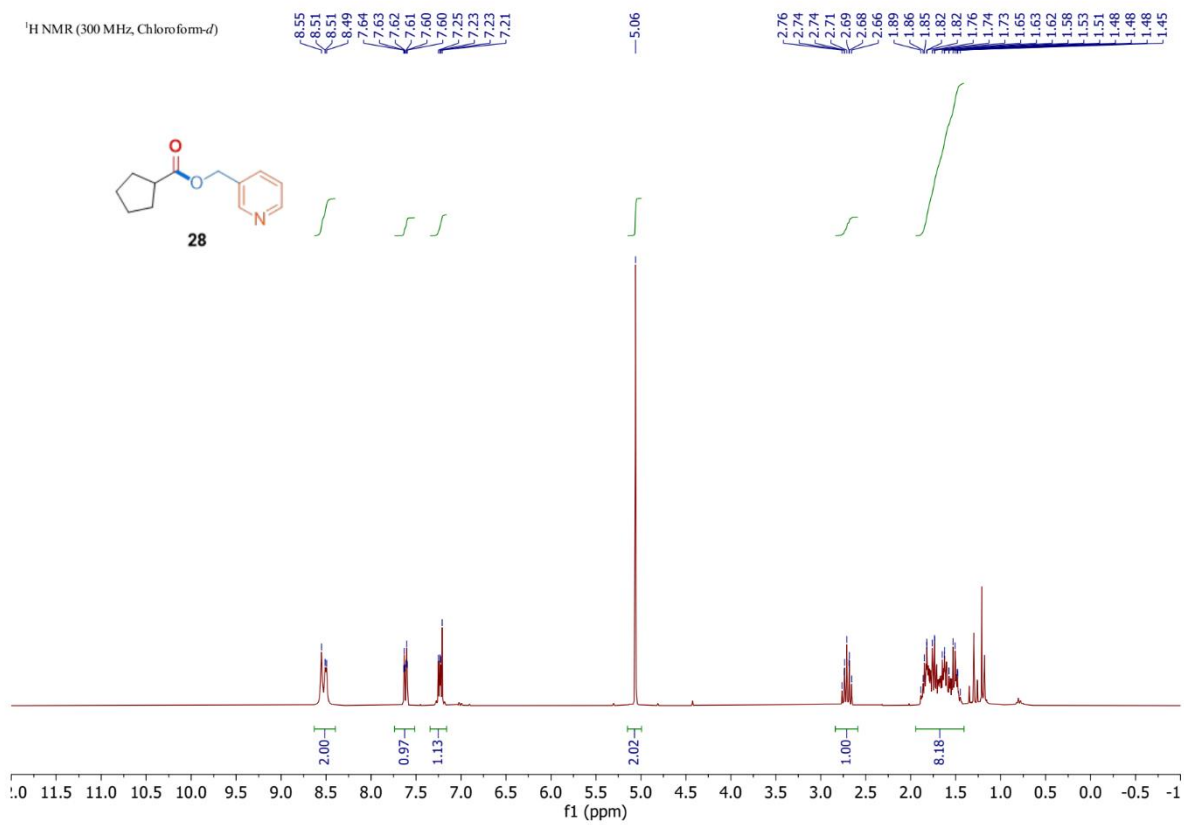


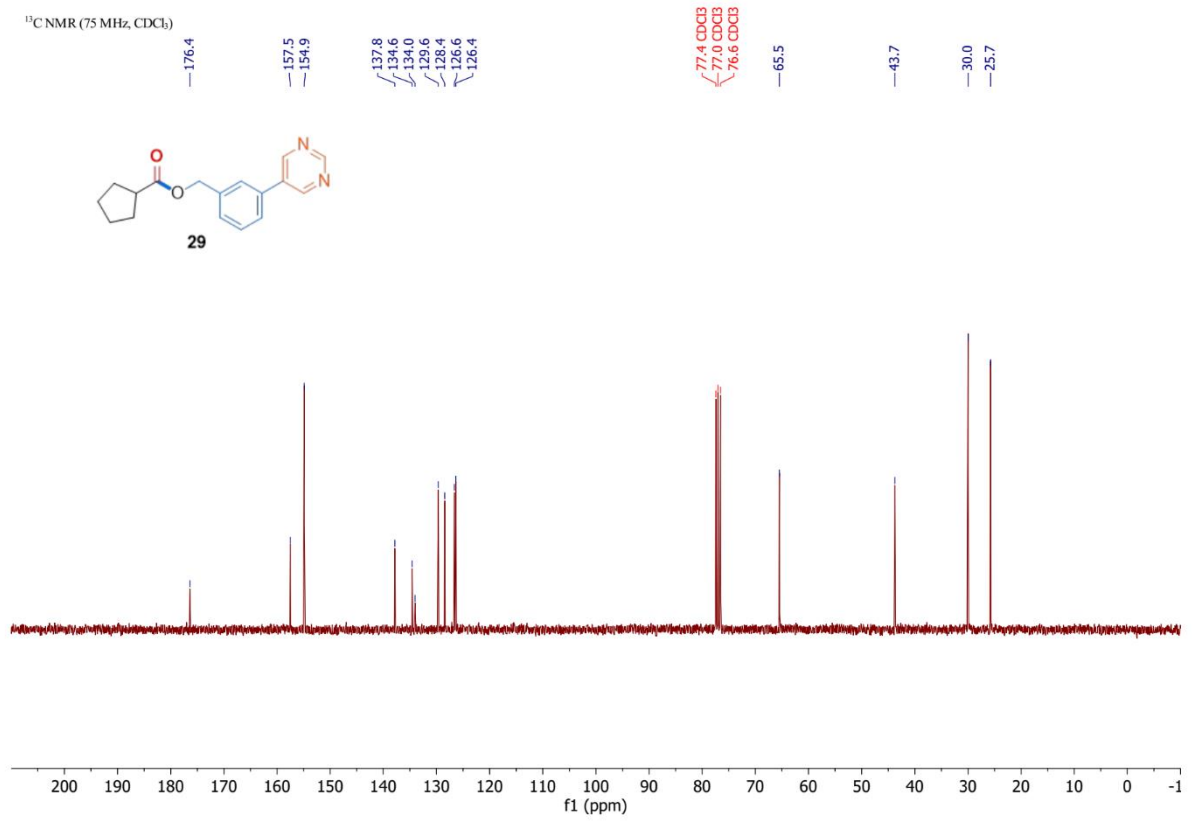
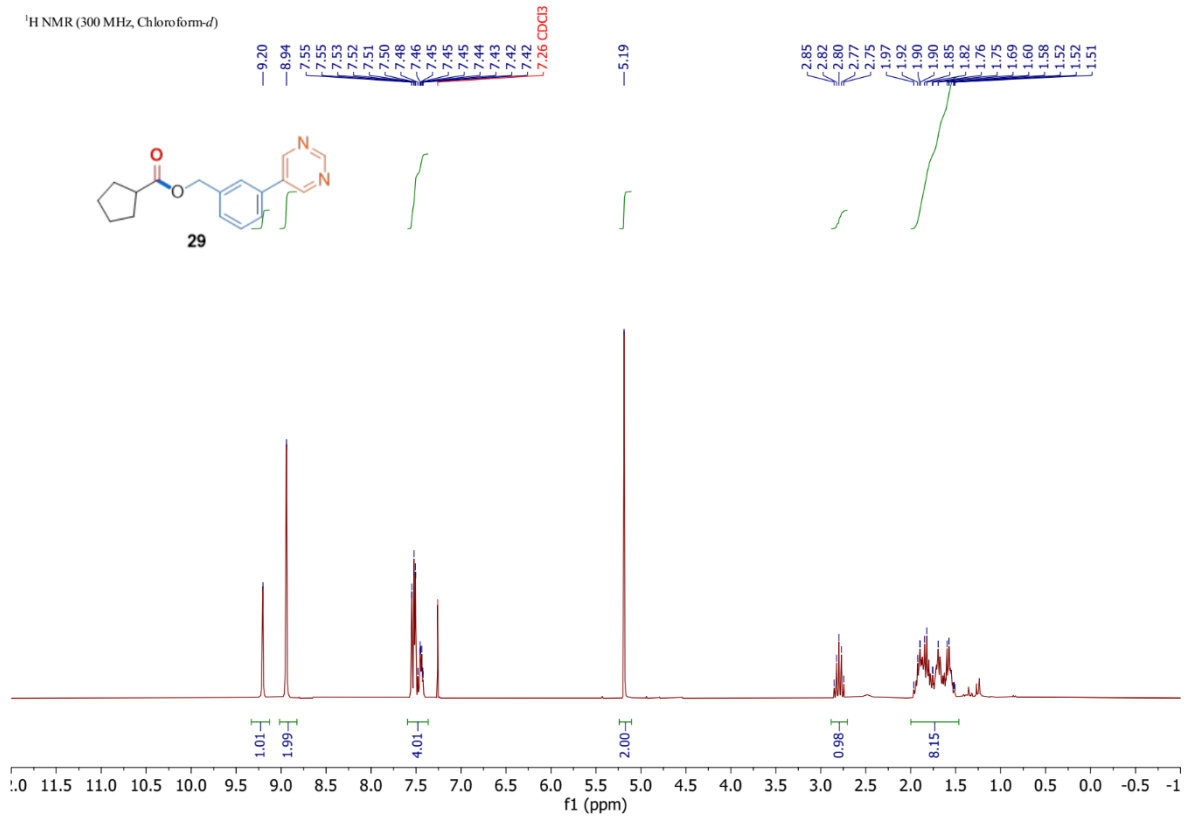
¹H NMR (300 MHz, Chloroform-*d*)



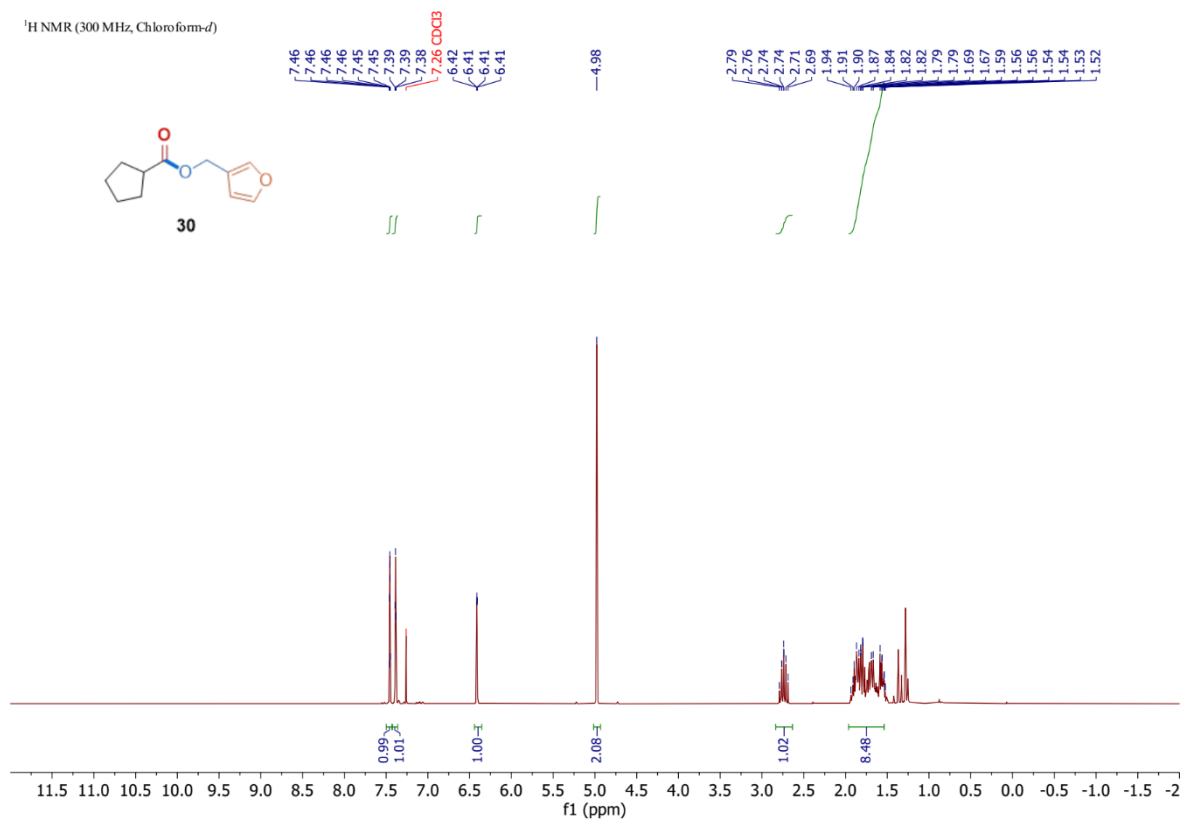
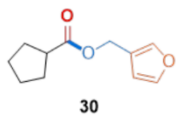
¹³C NMR (75 MHz, CDCl₃)



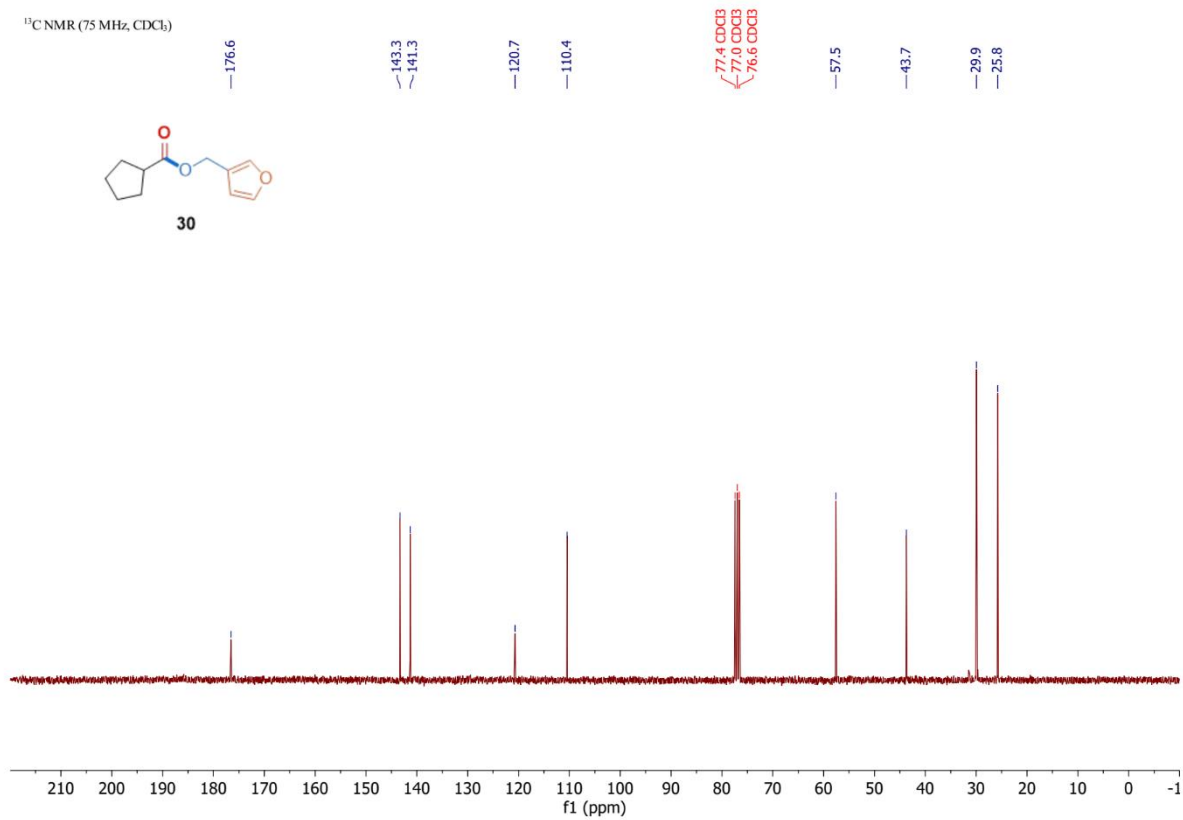




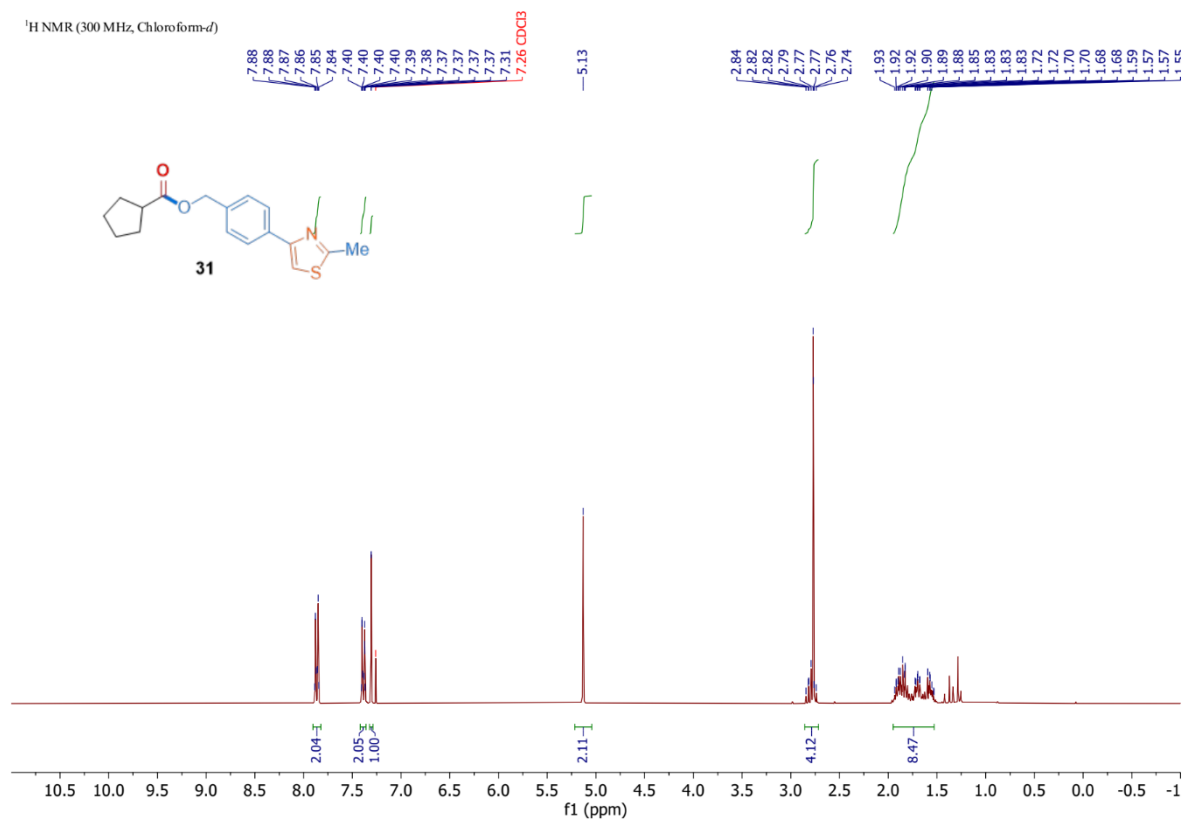
¹H NMR (300 MHz, Chloroform-*d*)



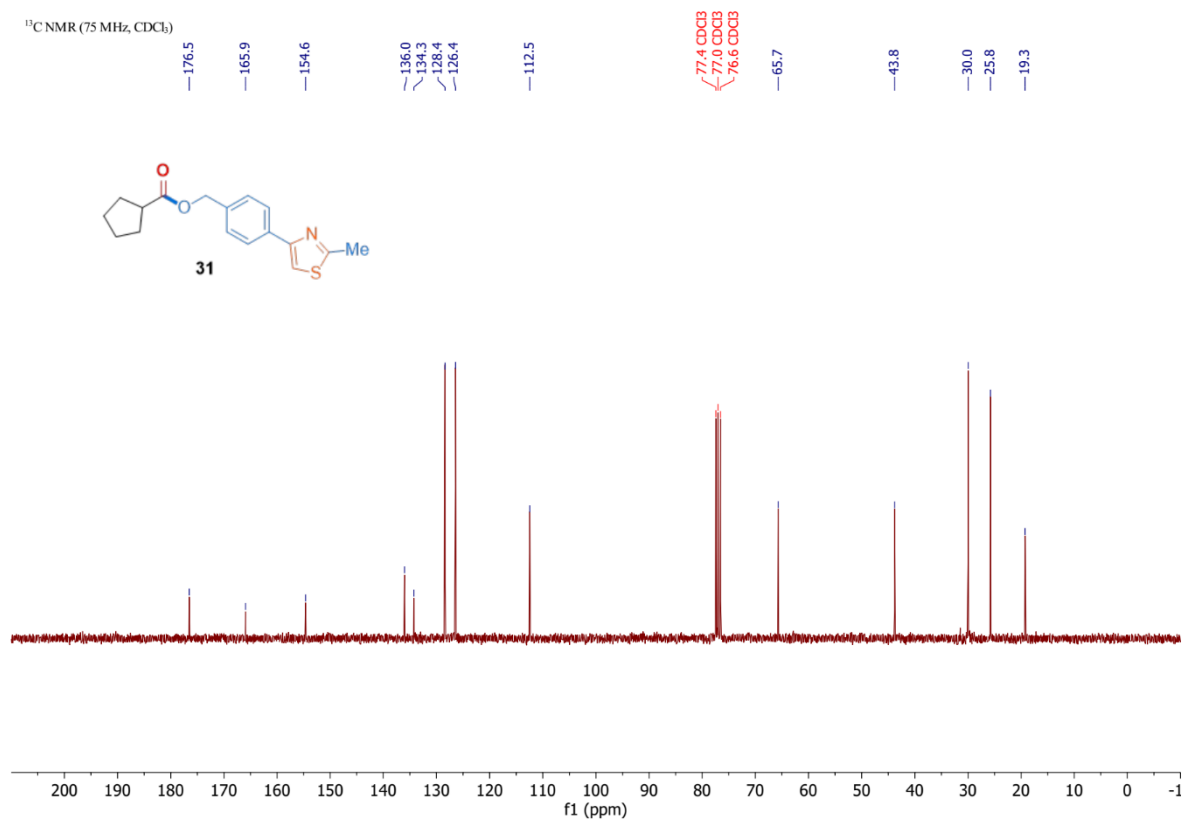
¹³C NMR (75 MHz, CDCl₃)

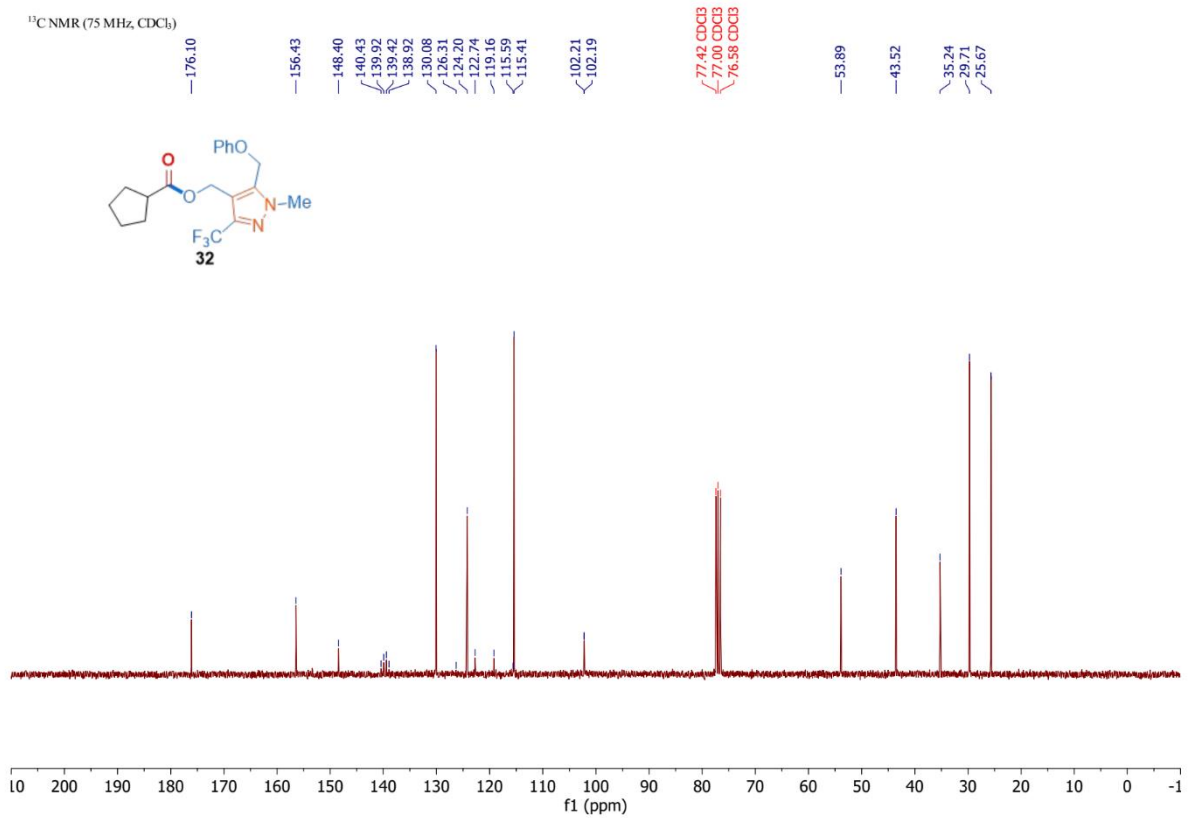
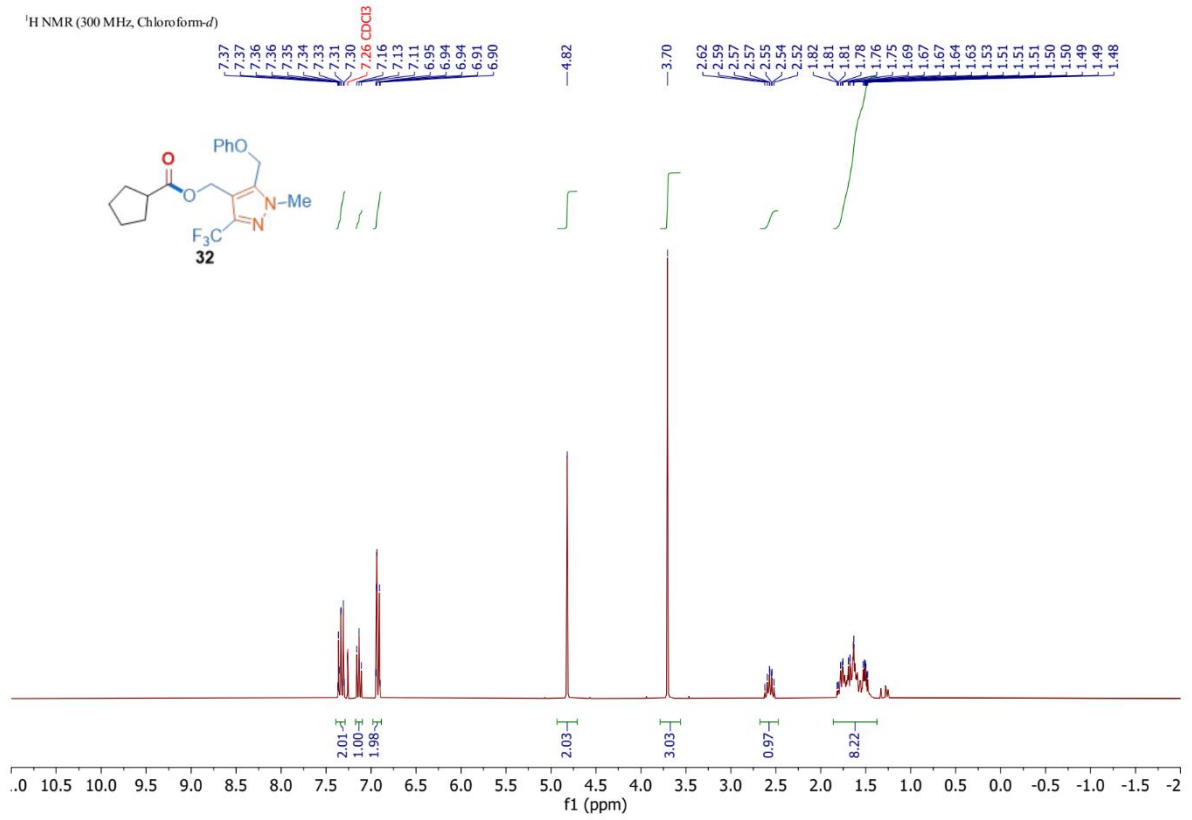


¹H NMR (300 MHz, Chloroform-*d*)



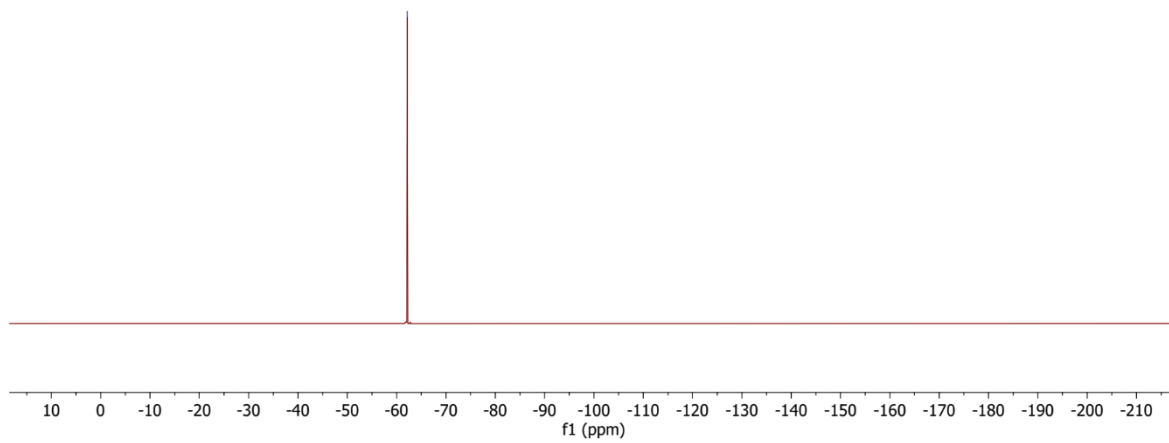
¹³C NMR (75 MHz, CDCl₃)



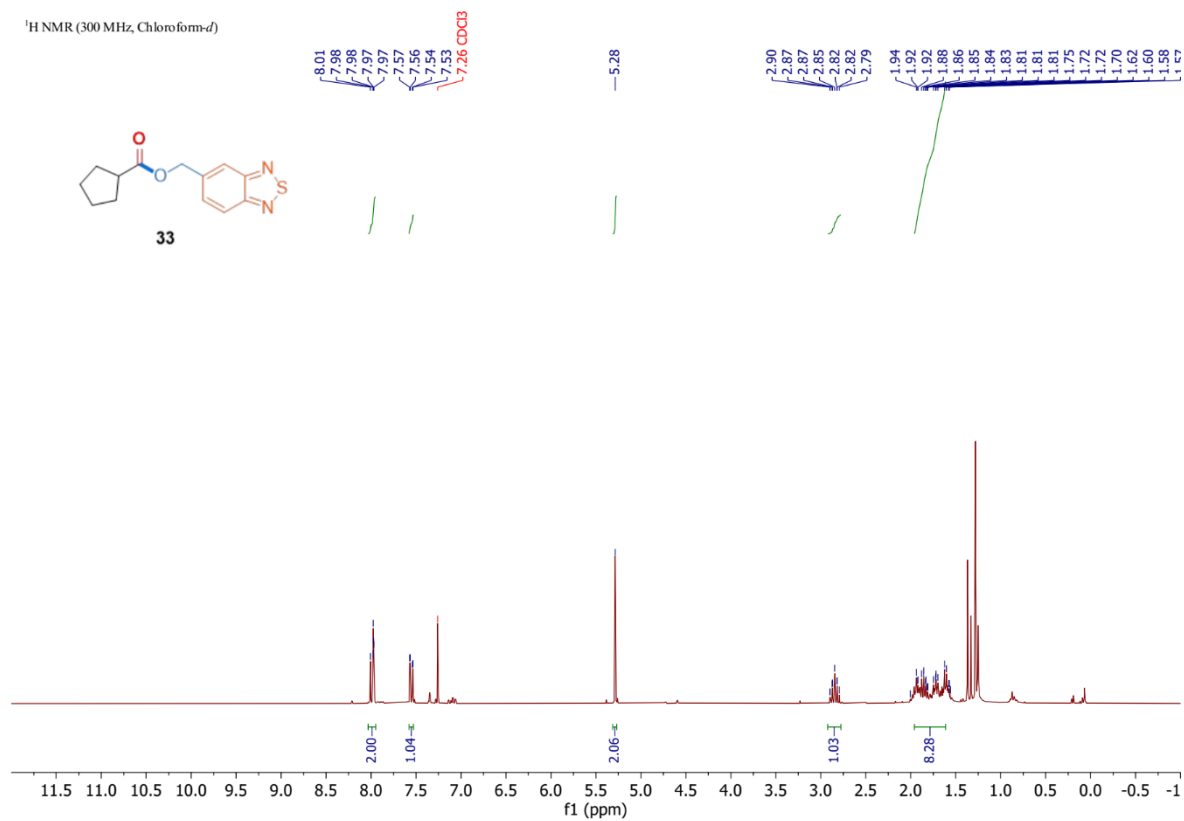


¹⁹F NMR (282 MHz, CDCl₃)

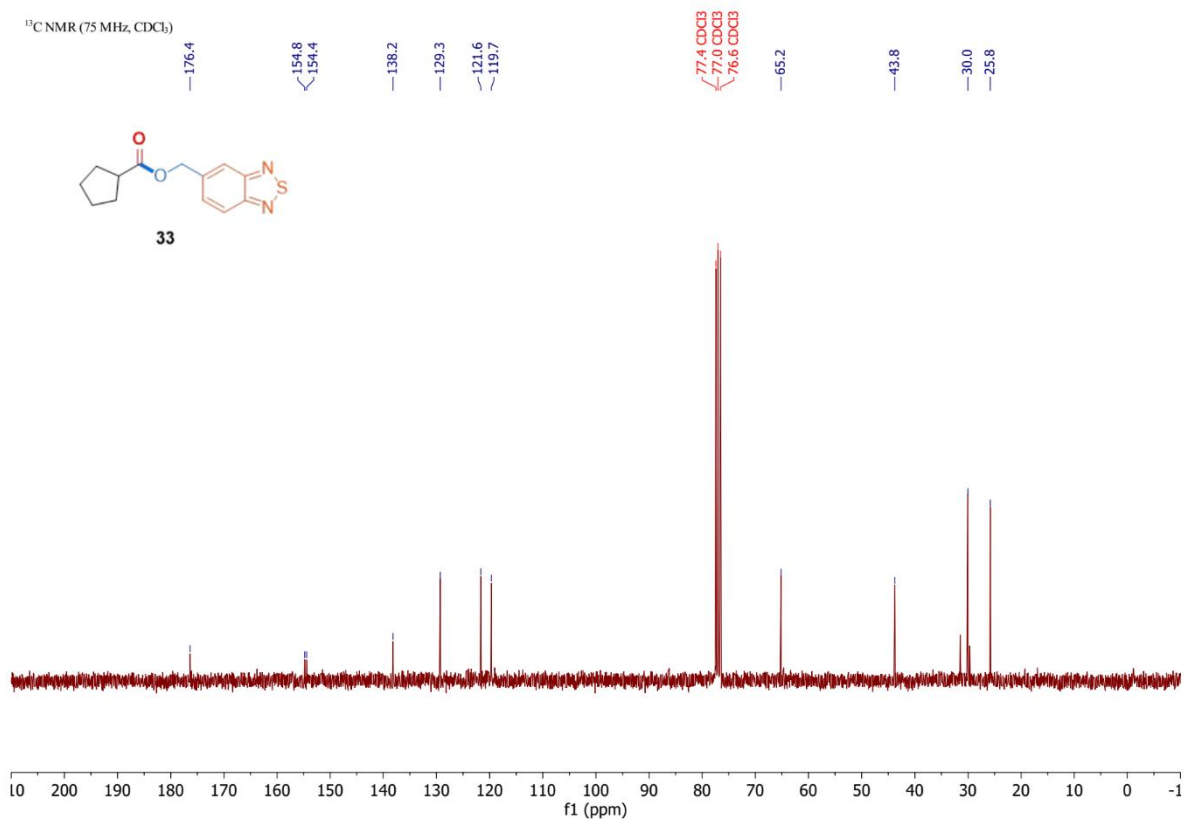
— 62.1



¹H NMR (300 MHz, Chloroform-*d*)



¹³C NMR (75 MHz, CDCl₃)

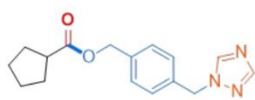


¹H NMR (300 MHz, Chloroform-*d*)

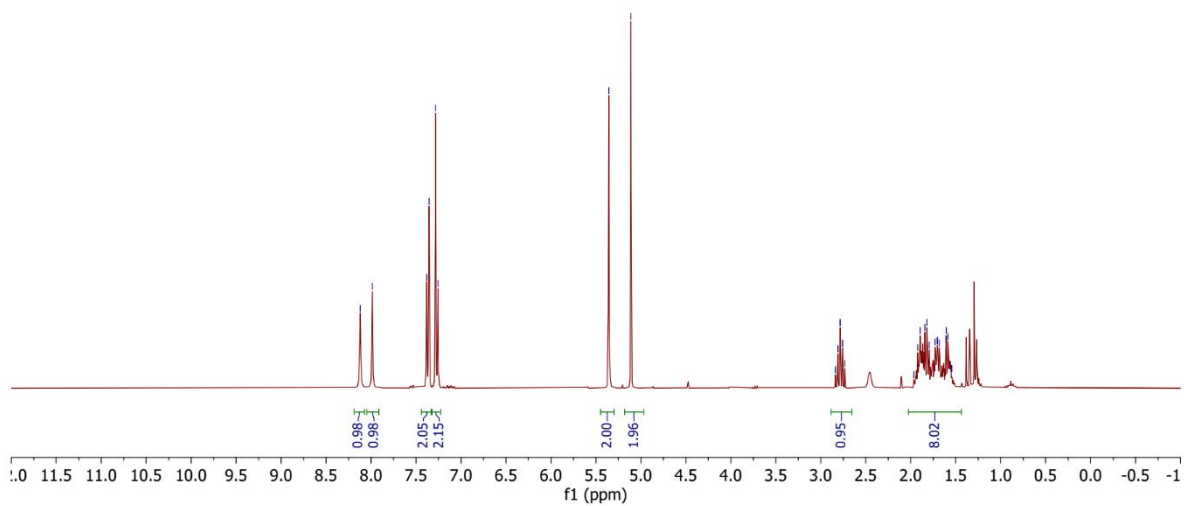
8.12
7.99
7.38
7.35
7.28
7.26

5.36
5.11

2.84
2.81
2.78
2.78
2.76
2.76
2.73
1.96
1.92
1.90
1.84
1.82
1.79
1.73
1.71
1.70
1.70
1.68
1.61
1.60
1.58
1.55
1.54



34



¹³C NMR (75 MHz, CDCl₃)

176.4

152.0

143.0

137.0

134.3

128.5

128.2

77.4 CDCl₃
77.0 CDCl₃
76.6 CDCl₃

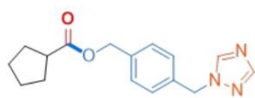
65.3

53.2

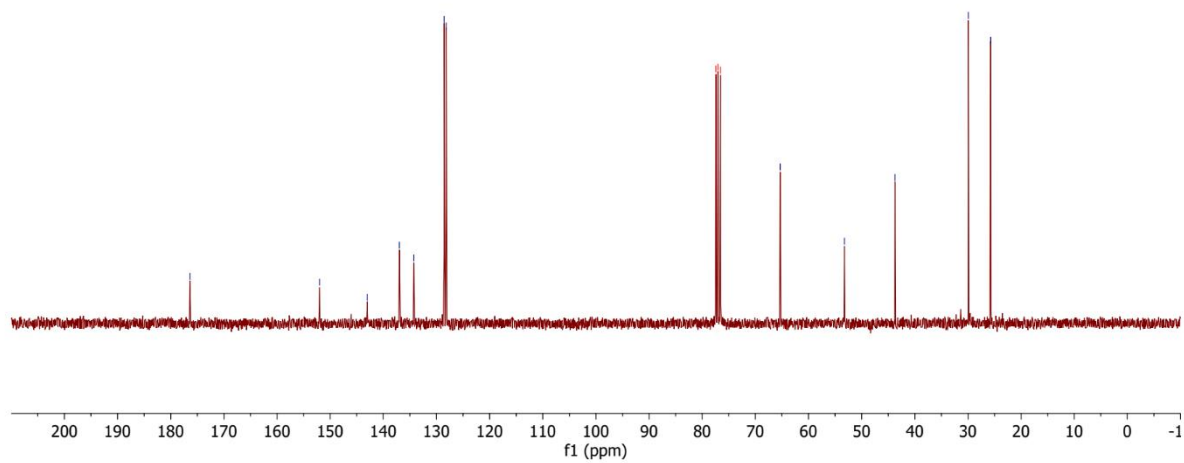
43.7

29.9

25.7

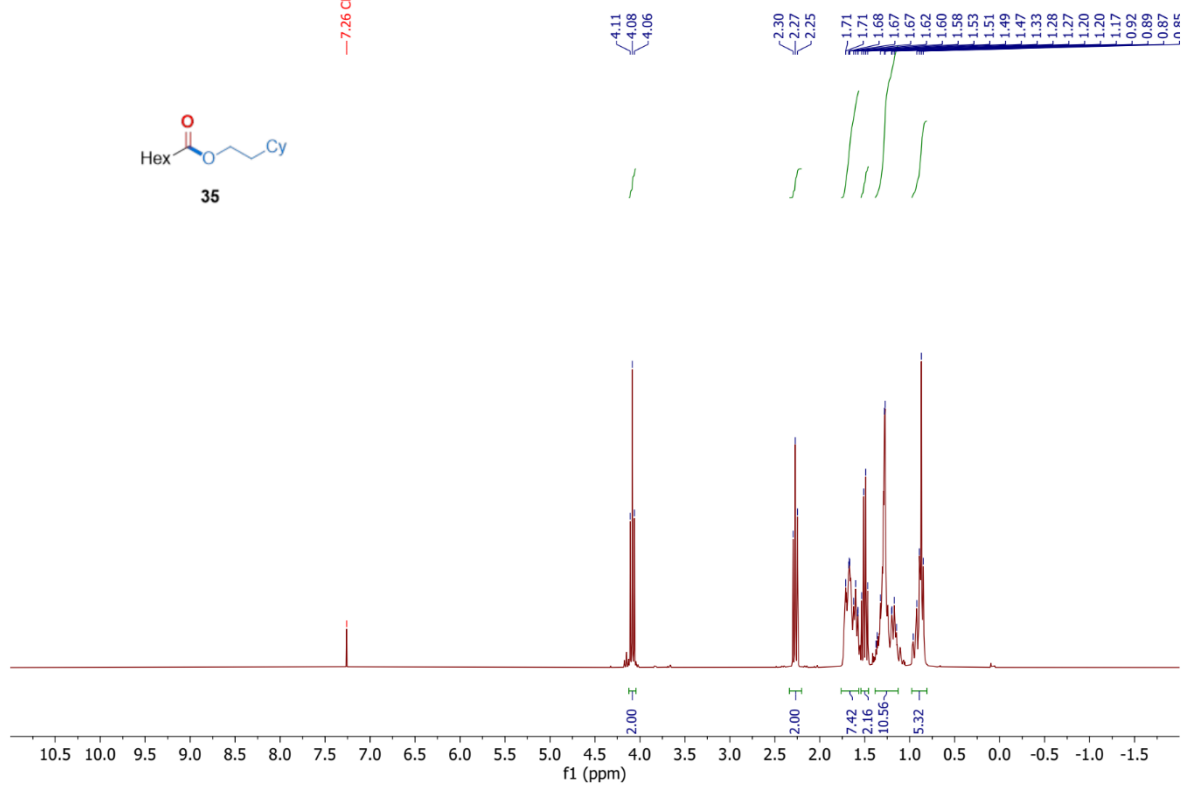
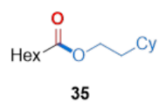


34



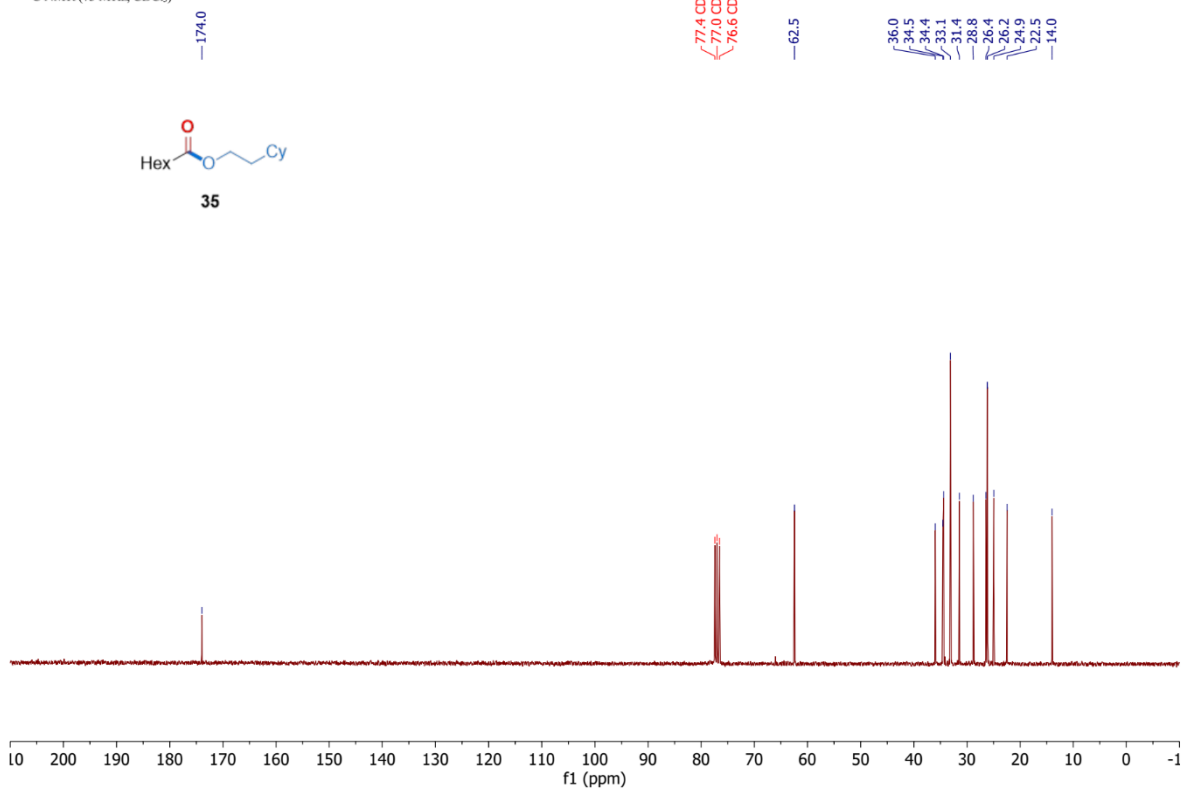
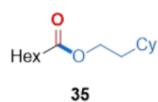
¹H NMR (300 MHz, Chloroform-*d*)

— 7.26 CDCl₃

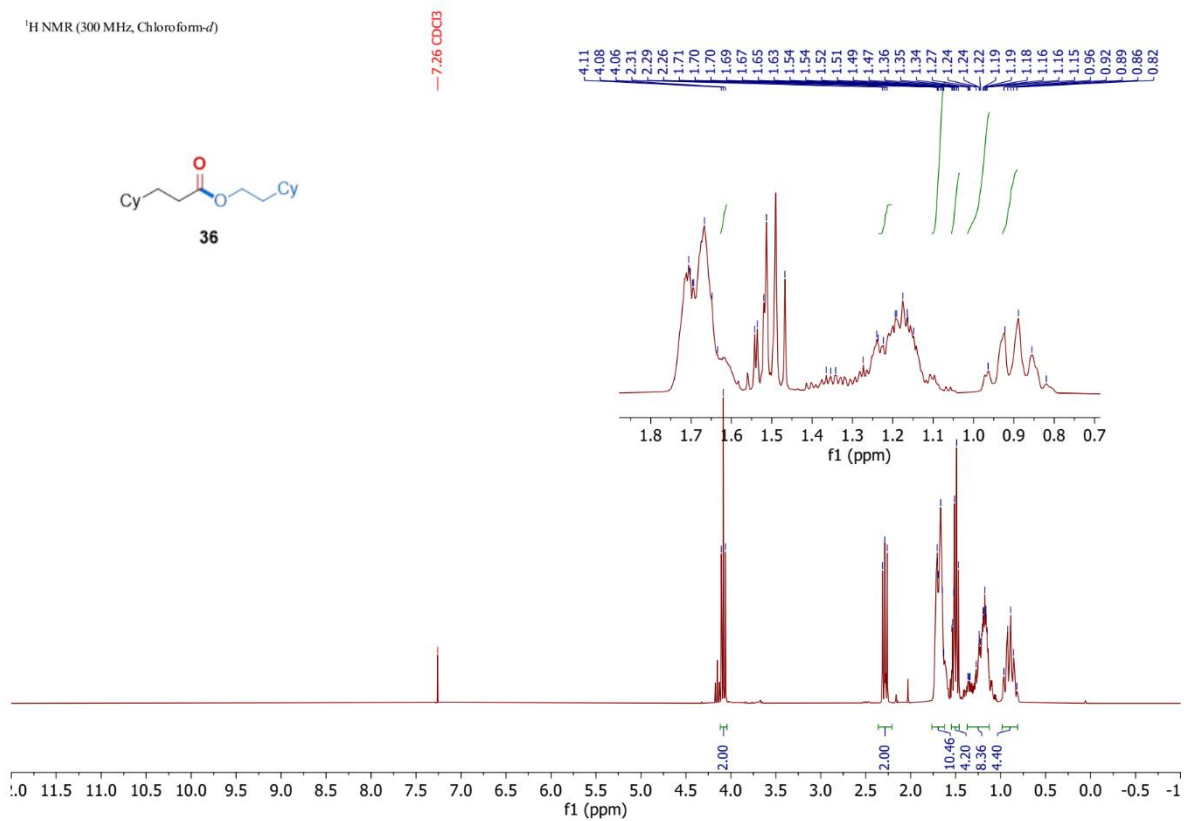
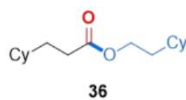


¹³C NMR (75 MHz, CDCl₃)

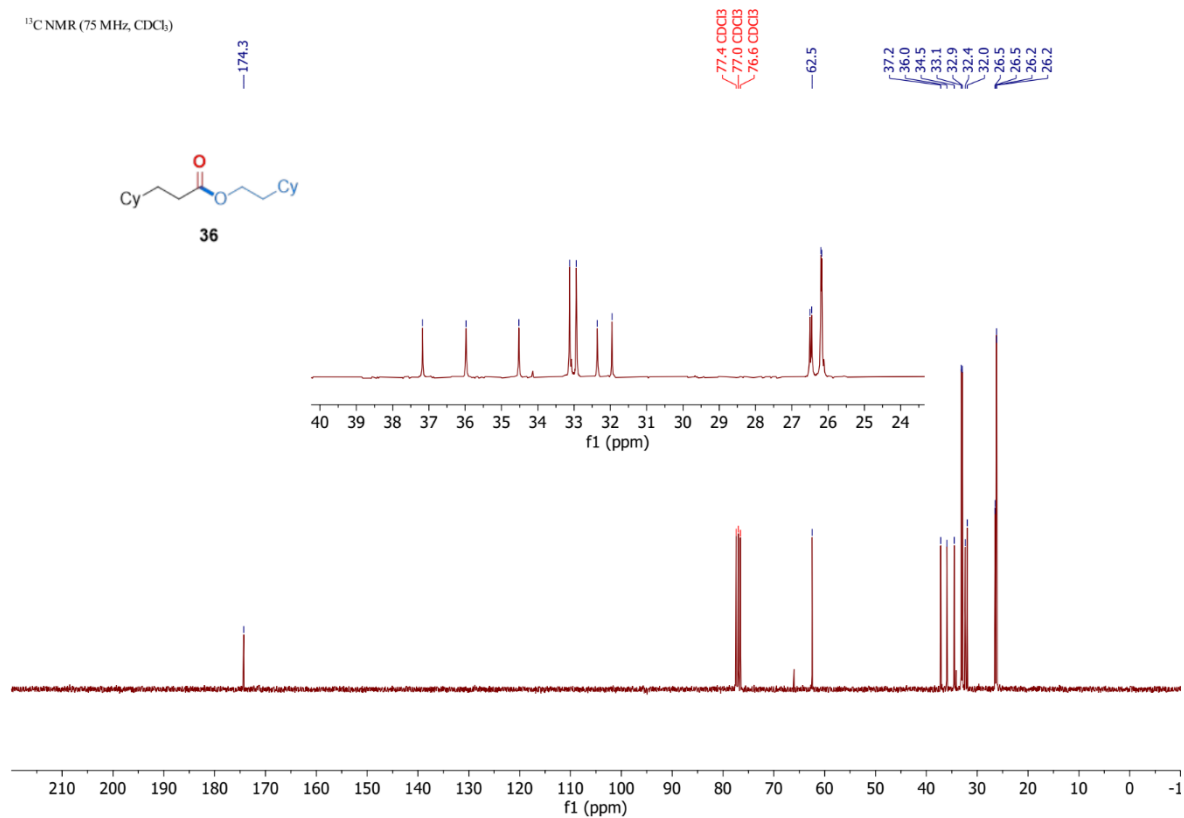
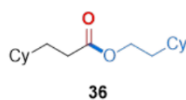
77.4 CDCl₃
77.0 CDCl₃
76.6 CDCl₃



¹H NMR (300 MHz, Chloroform-*d*)

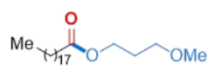


¹³C NMR (75 MHz, CDCl₃)

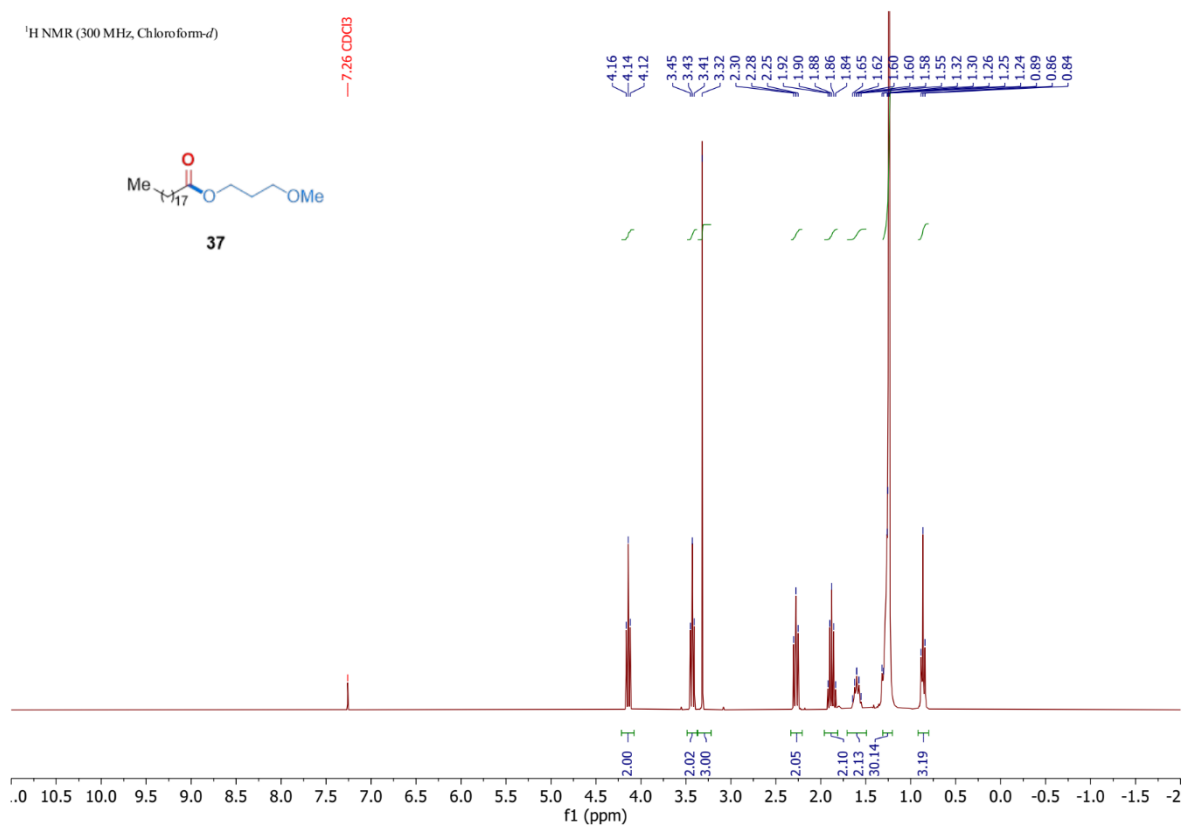


¹H NMR (300 MHz, Chloroform-*d*)

— 7.26 CDCl₃



37

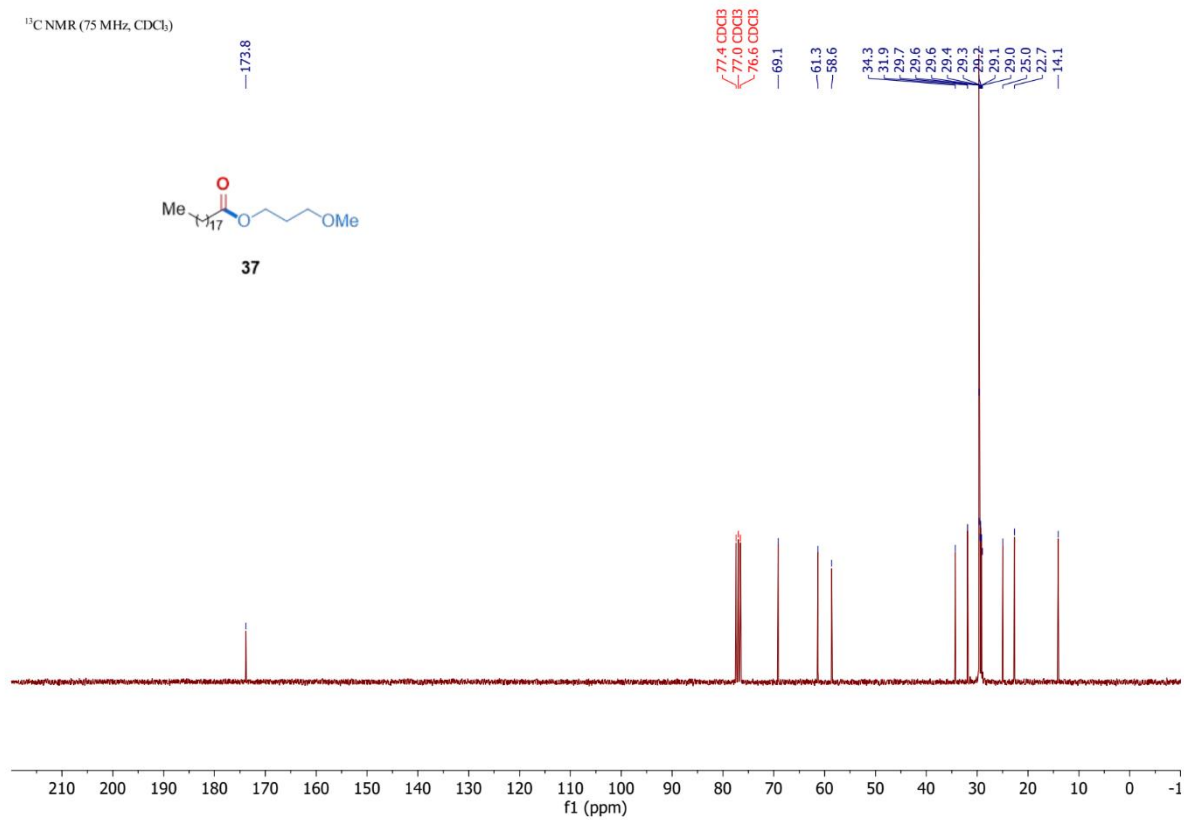


¹³C NMR (75 MHz, CDCl₃)

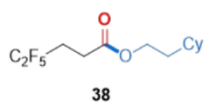
— 173.8



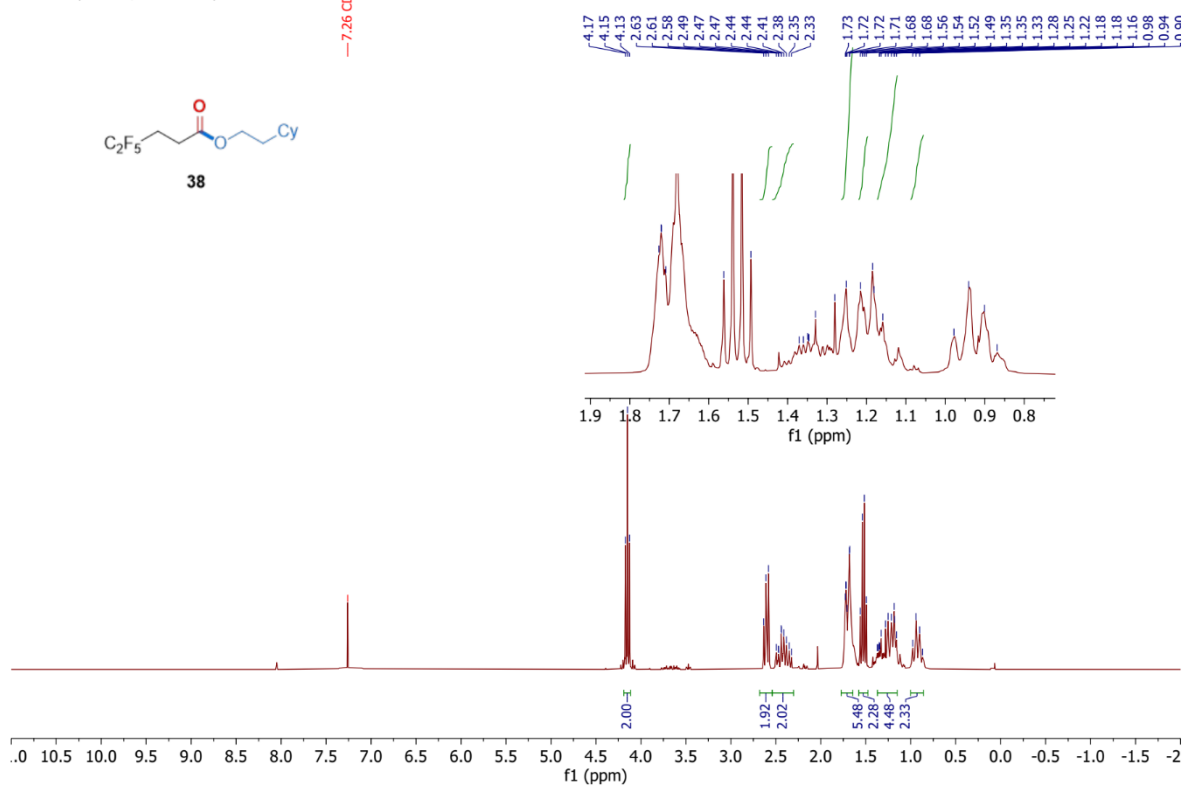
37



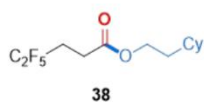
¹H NMR (300 MHz, Chloroform-*d*)



-7.26 CDCl₃



¹³C NMR (75 MHz, CDCl₃)

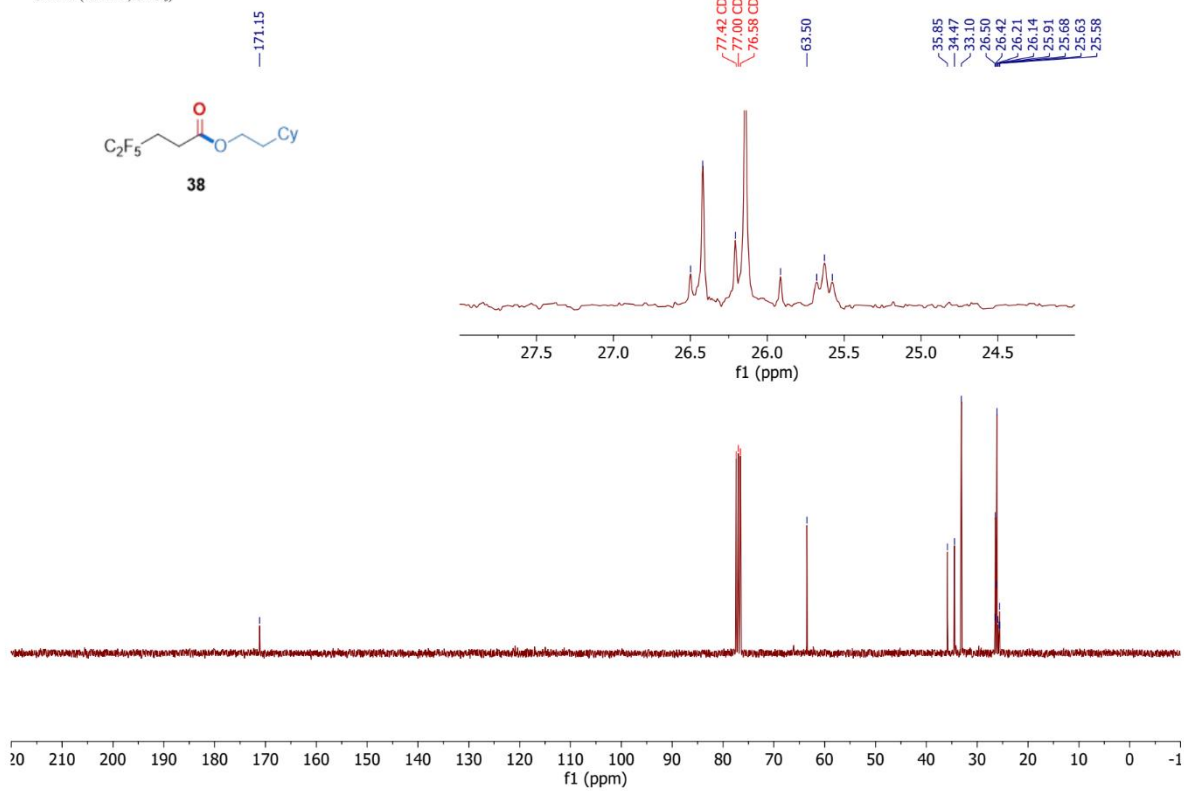


-171.15

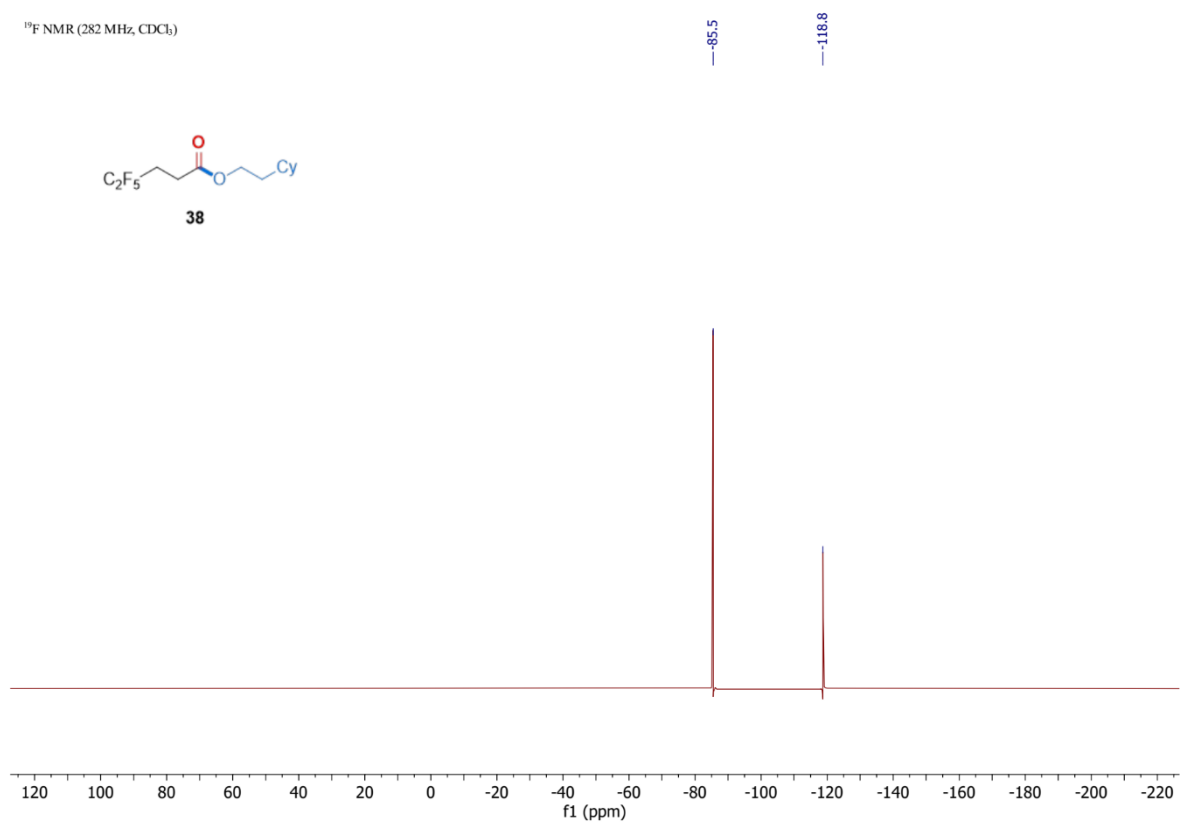
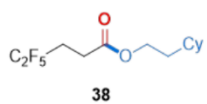
77.42 CDCl₃
77.00 CDCl₃
76.58 CDCl₃

-63.50

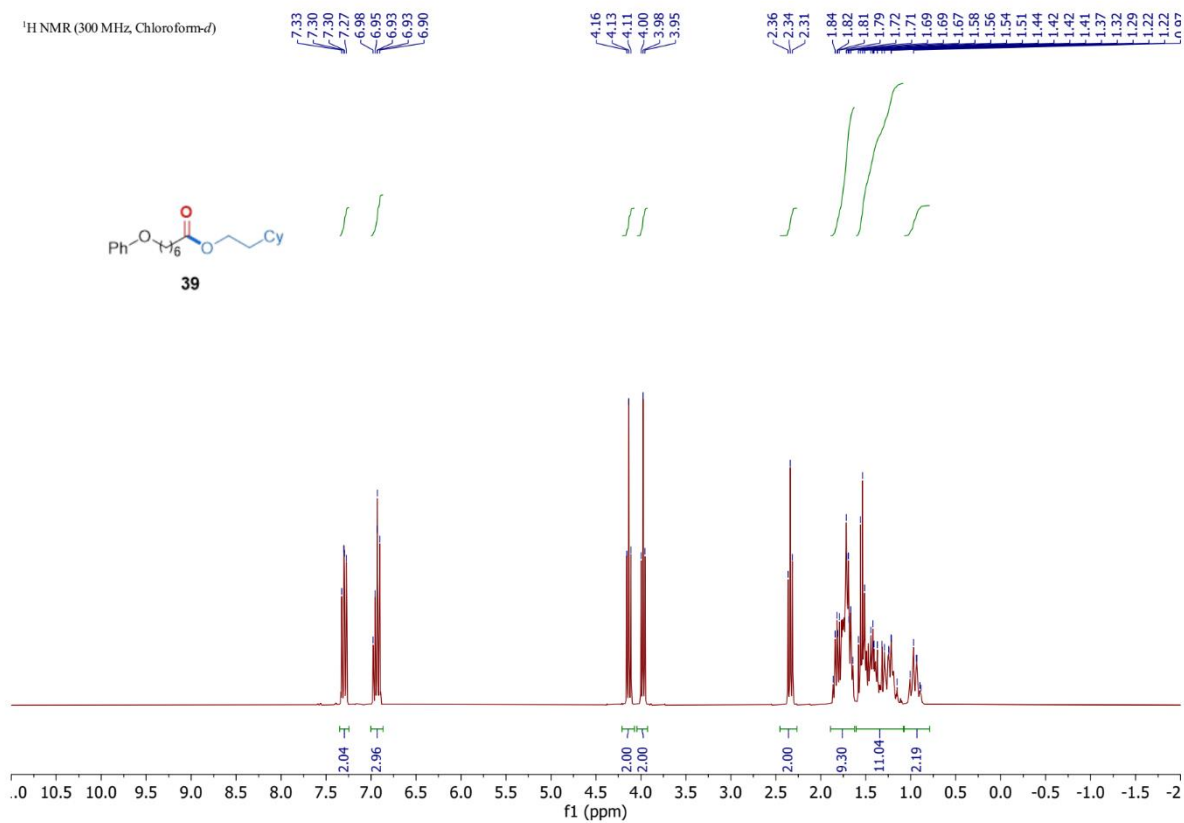
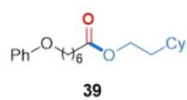
35.85
34.47
33.10
26.50
26.42
26.21
26.14
25.91
25.68
25.63
25.58



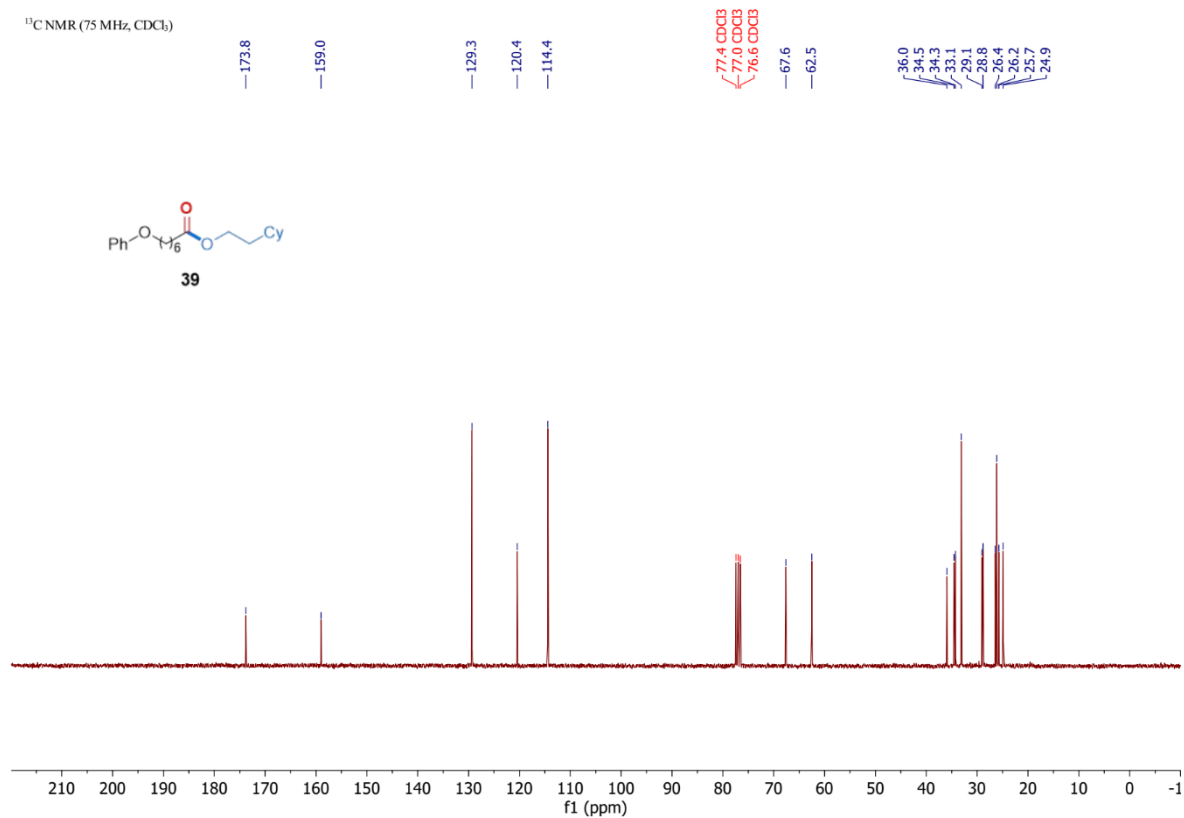
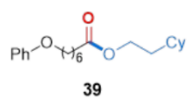
^{19}F NMR (282 MHz, CDCl_3)



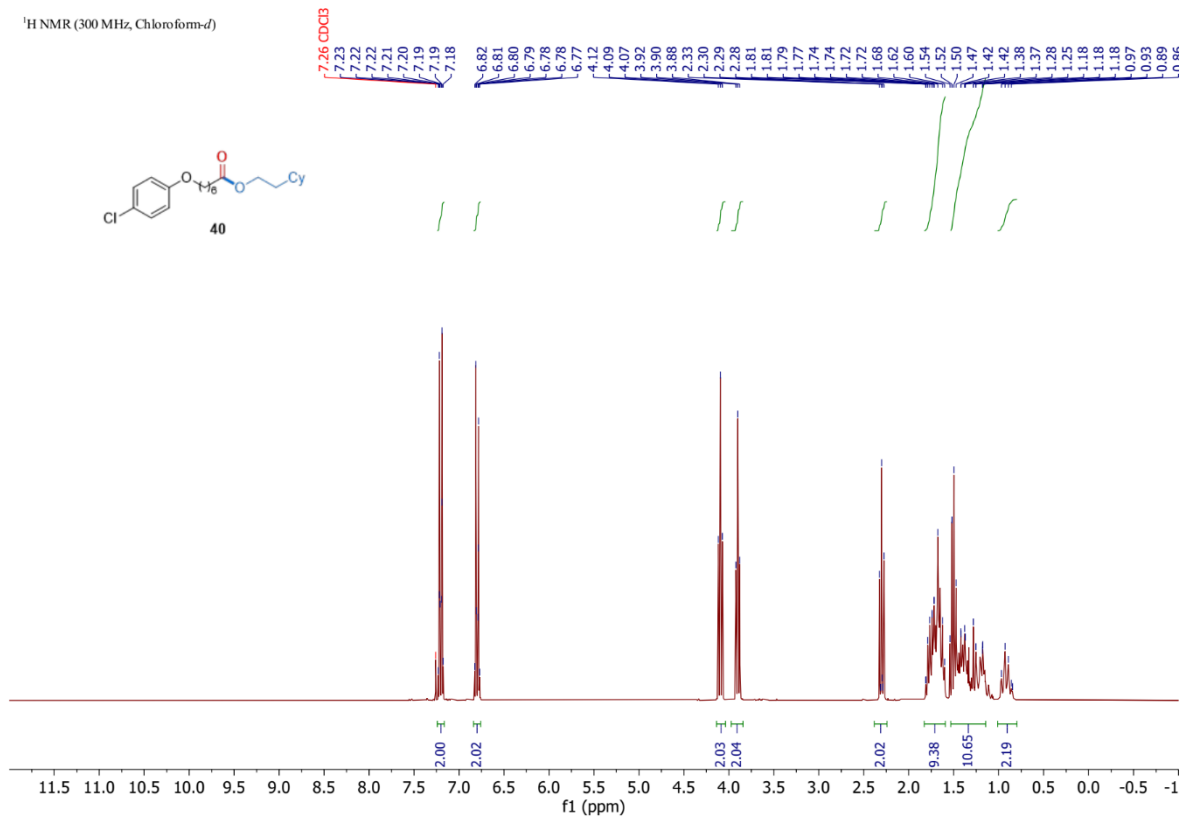
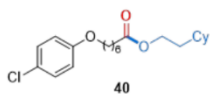
¹H NMR (300 MHz, Chloroform-*d*)



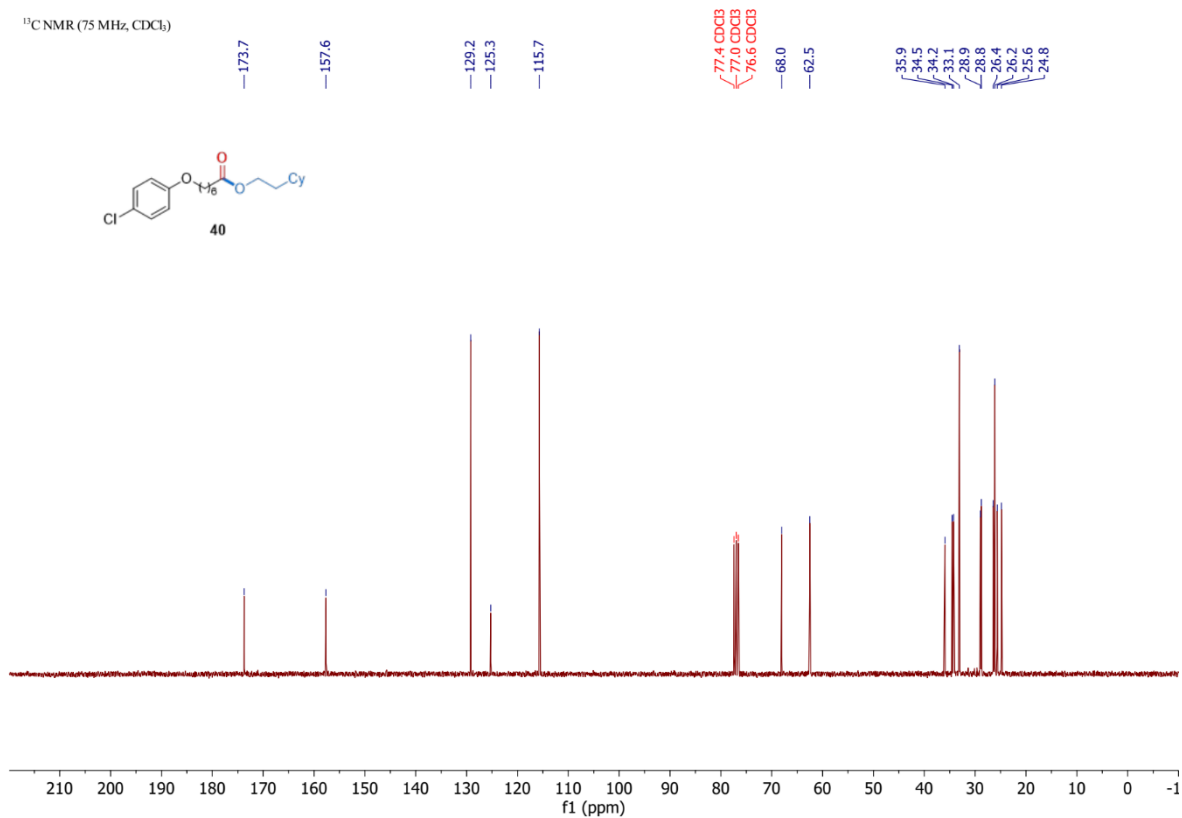
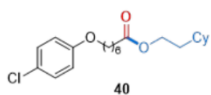
¹³C NMR (75 MHz, CDCl₃)



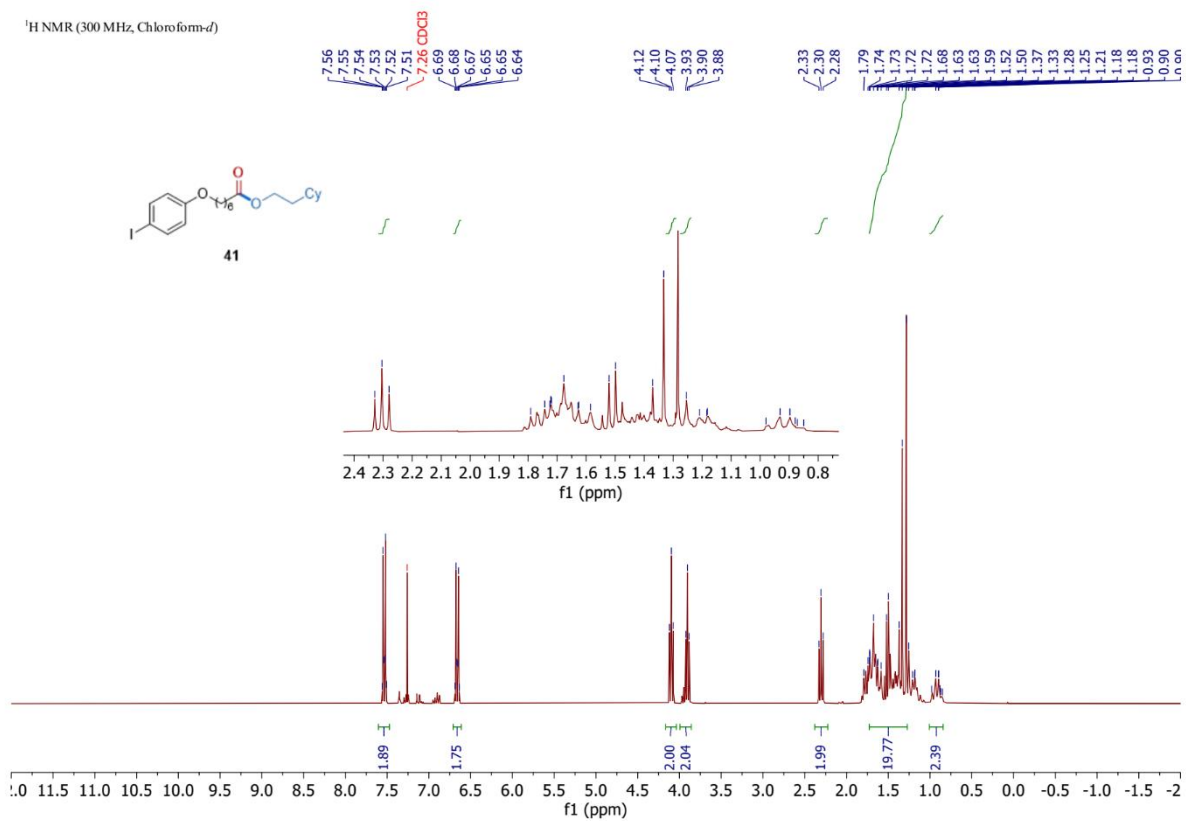
¹H NMR (300 MHz, Chloroform-*d*)



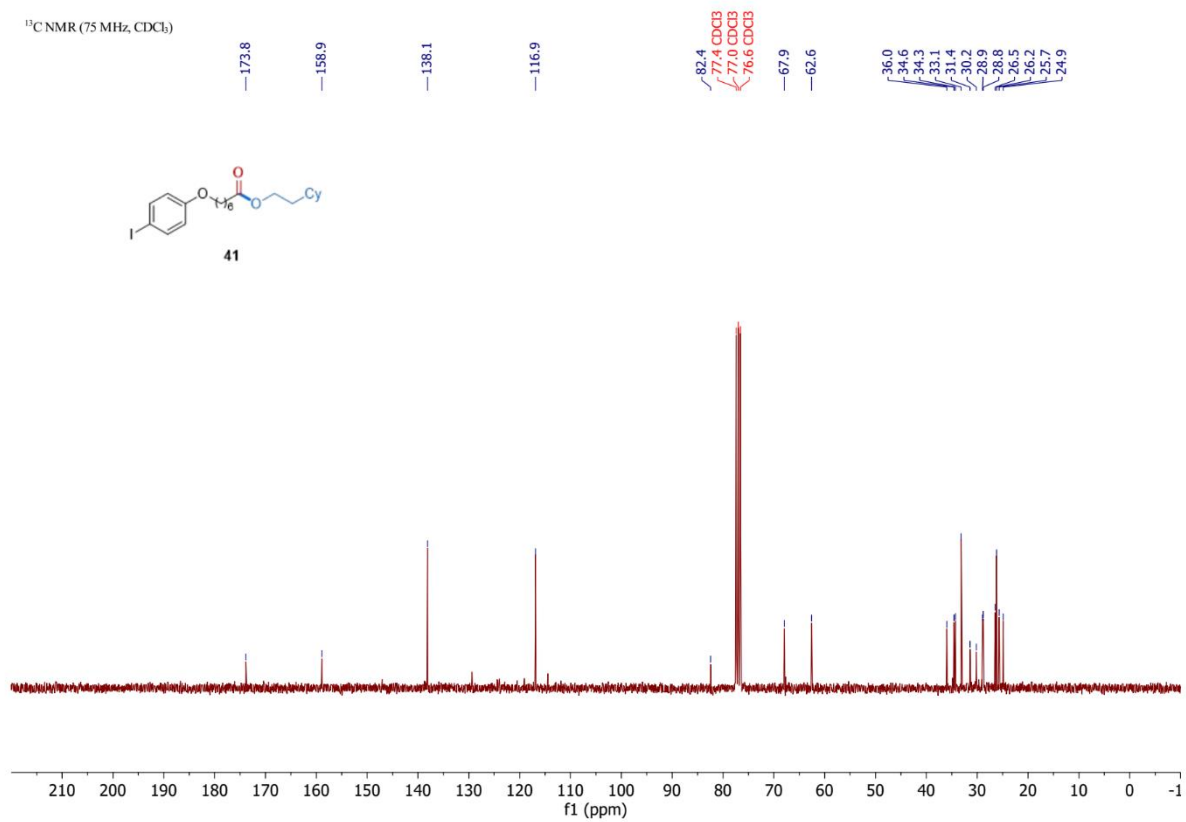
¹³C NMR (75 MHz, CDCl₃)



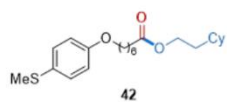
¹H NMR (300 MHz, Chloroform-*d*)



¹³C NMR (75 MHz, CDCl₃)



¹H NMR (300 MHz, Chloroform-*d*)

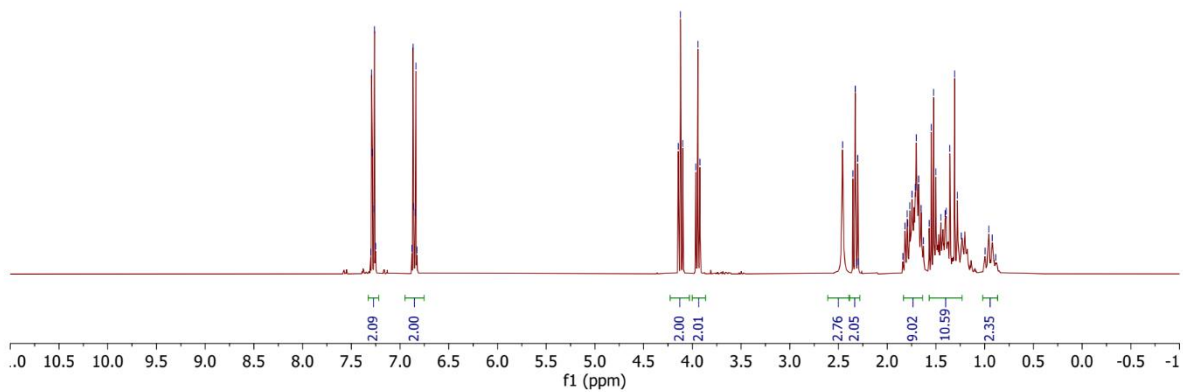


7.30
7.29
7.28
7.27
7.26
7.25
6.88
6.87
6.86
6.84
6.84
6.83

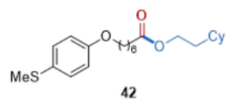
4.14
4.12
4.10
3.97
3.94
3.92

2.46
2.35
2.33
2.31
2.30
2.30

1.80
1.77
1.75
1.75
1.71
1.70
1.68
1.65
1.55
1.52
1.50
1.45
1.41
1.39
1.36
1.31
1.28



¹³C NMR (75 MHz, CDCl₃)



173.8

157.7

130.2

128.5

115.2

77.4 CDCl₃
77.0 CDCl₃
76.6 CDCl₃

67.9

62.5

36.0

34.5

34.3

33.1

29.0

28.8

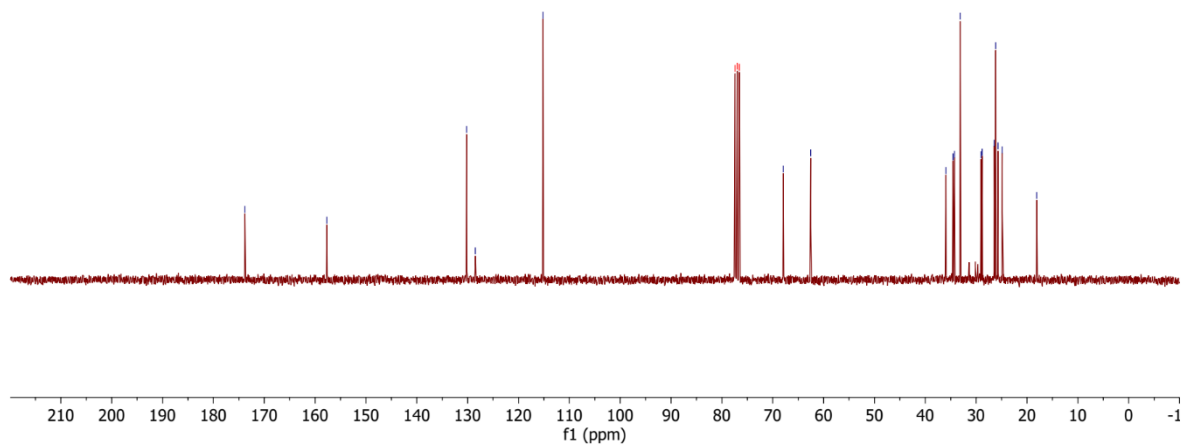
26.4

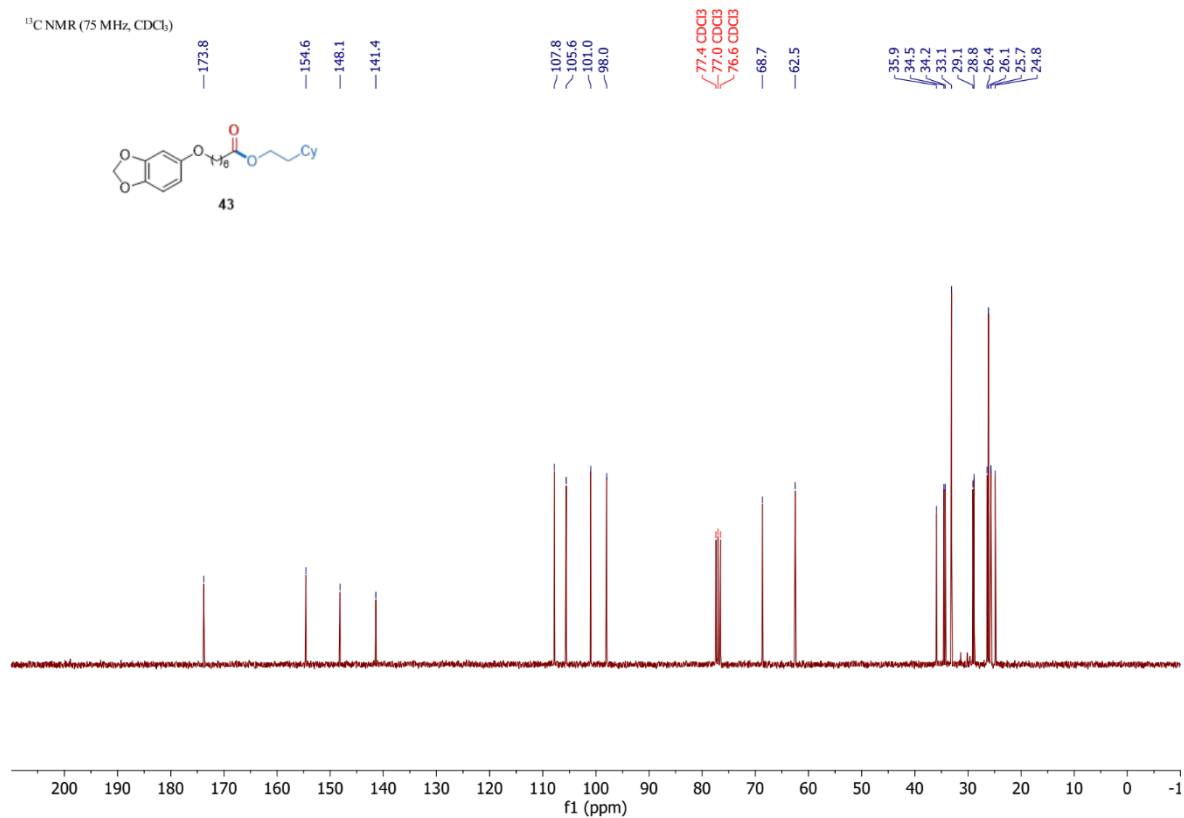
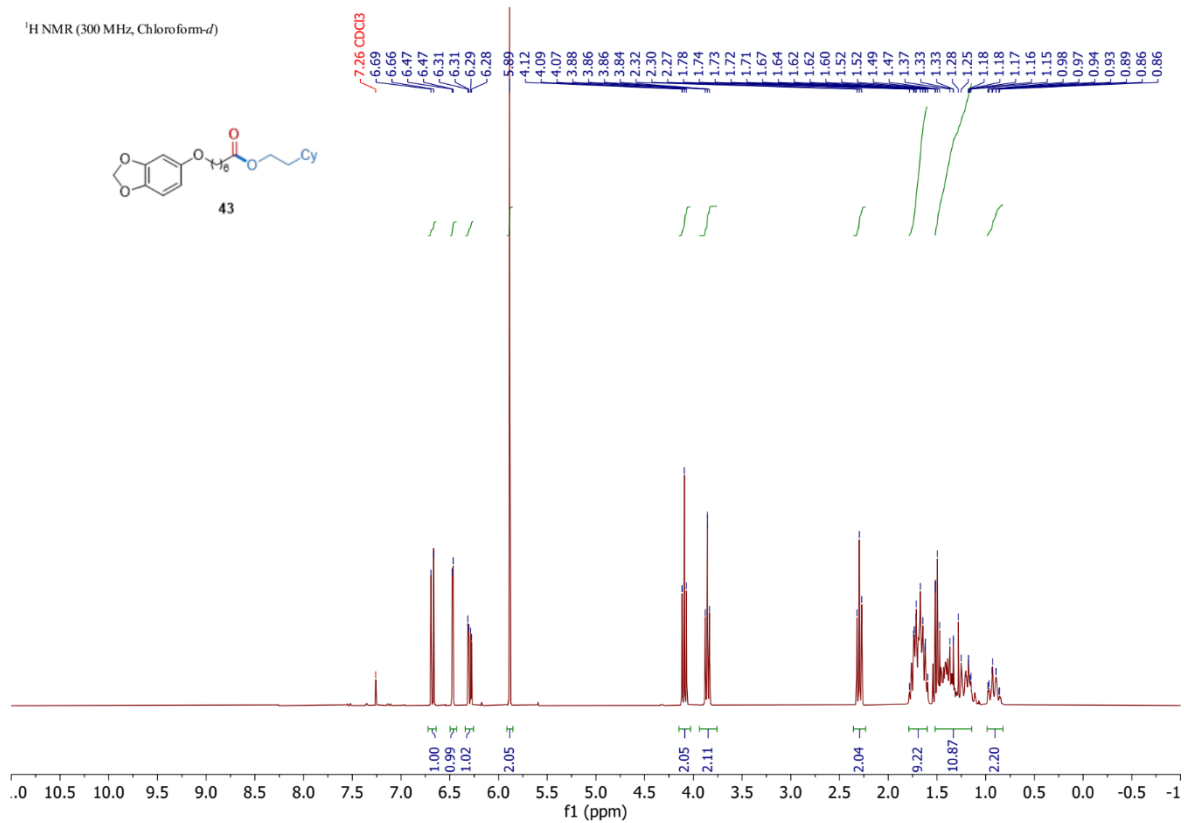
26.2

25.7

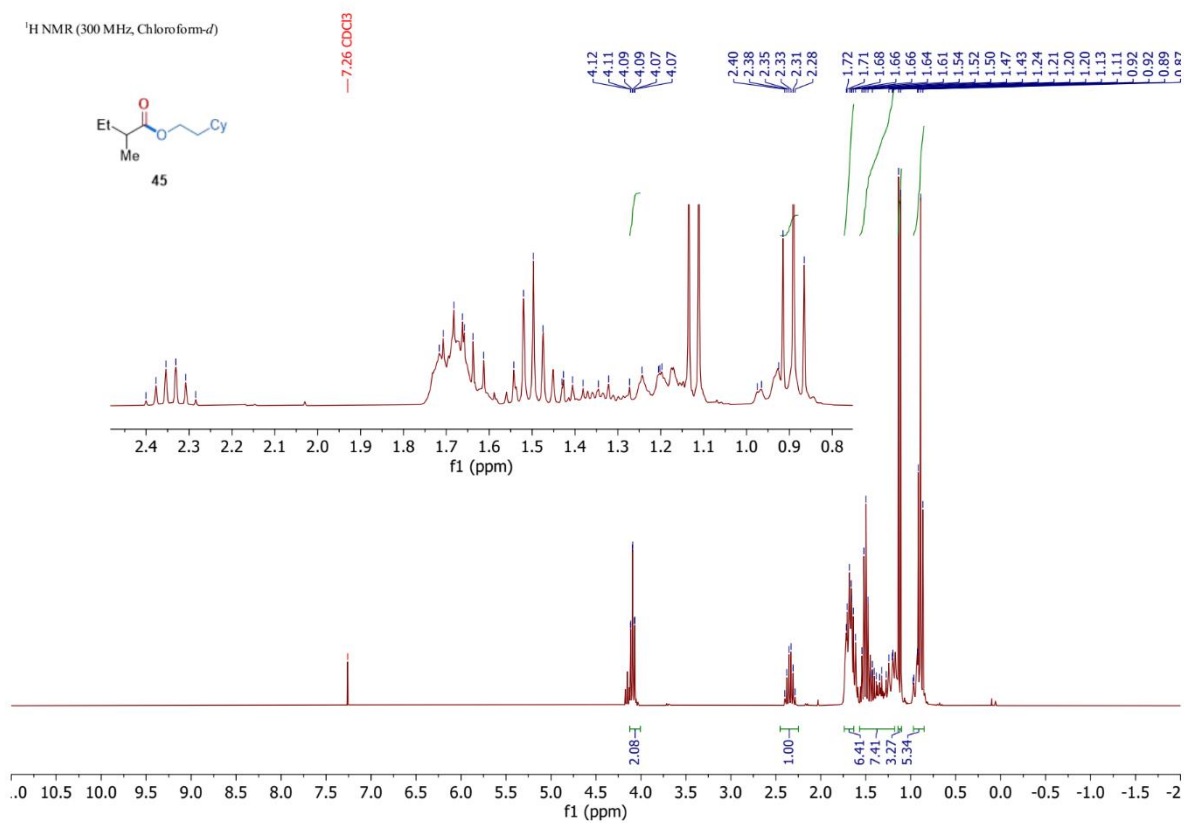
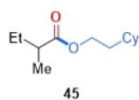
24.9

18.1

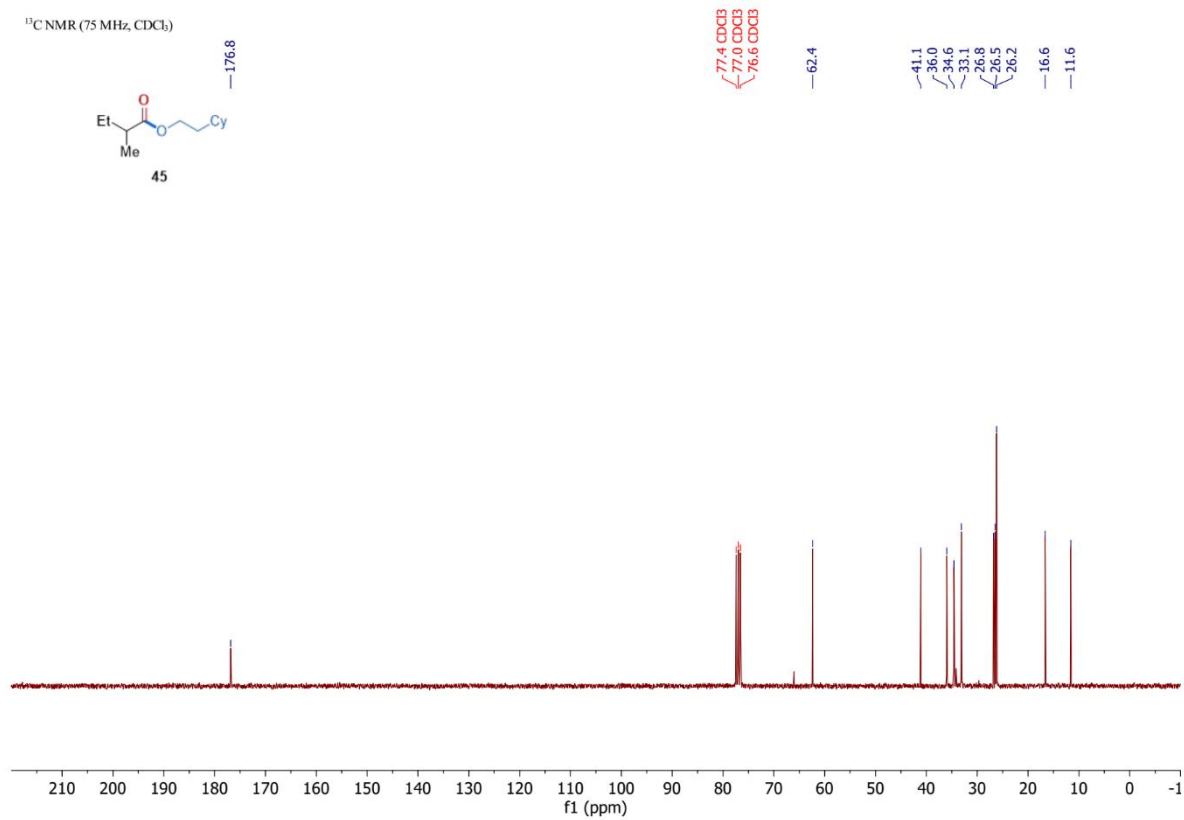
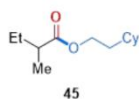




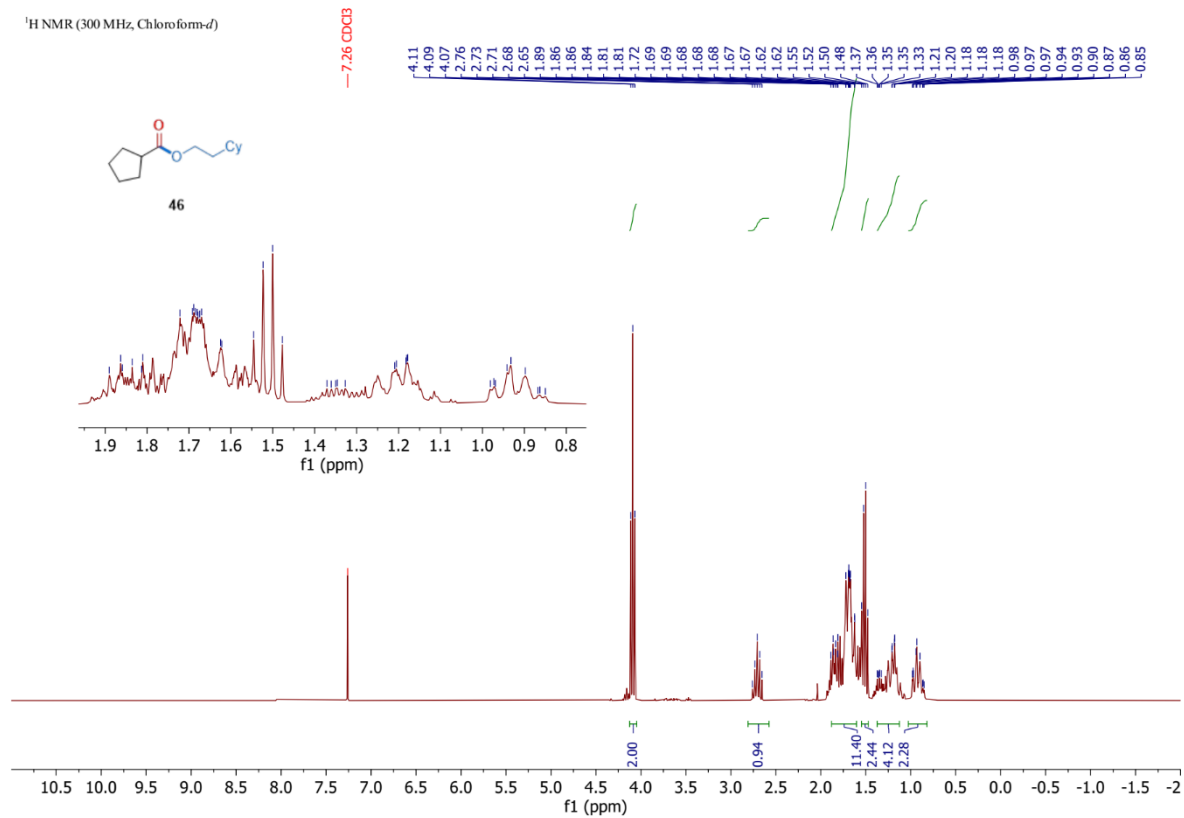
¹H NMR (300 MHz, Chloroform-*d*)



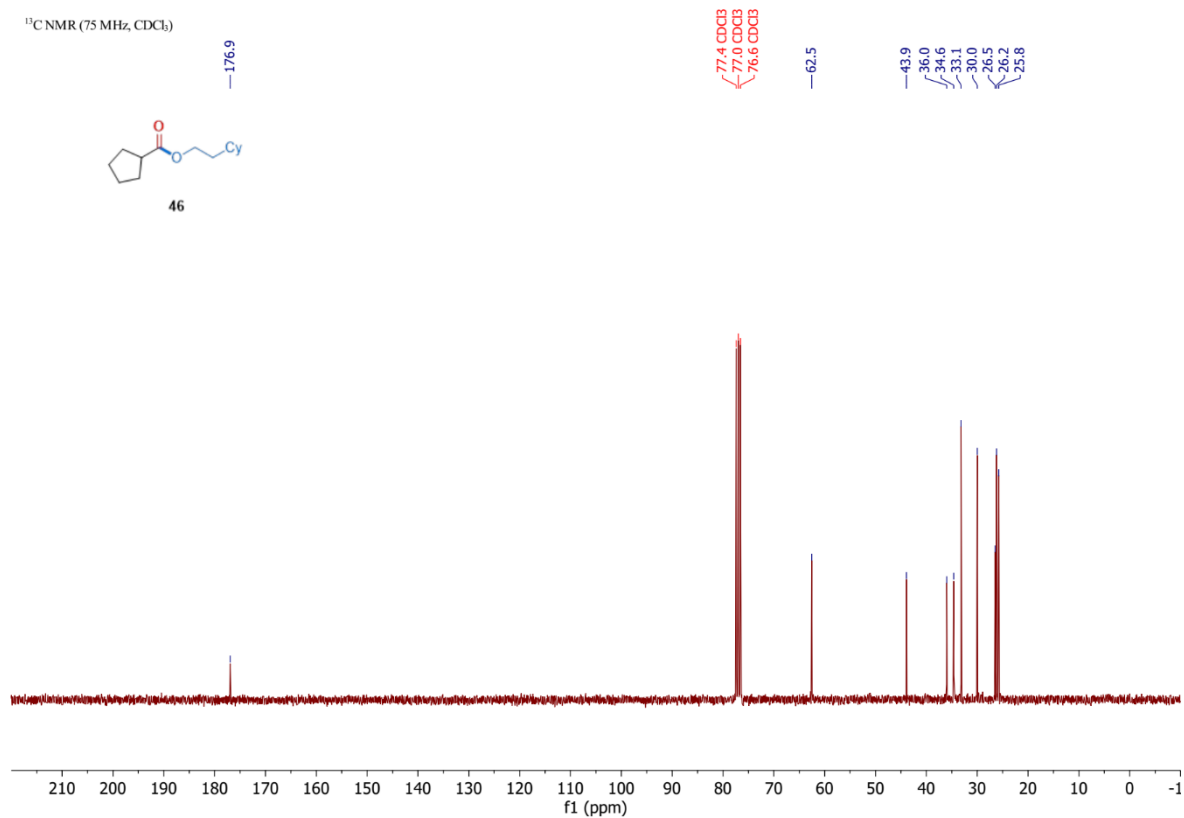
¹³C NMR (75 MHz, CDCl₃)



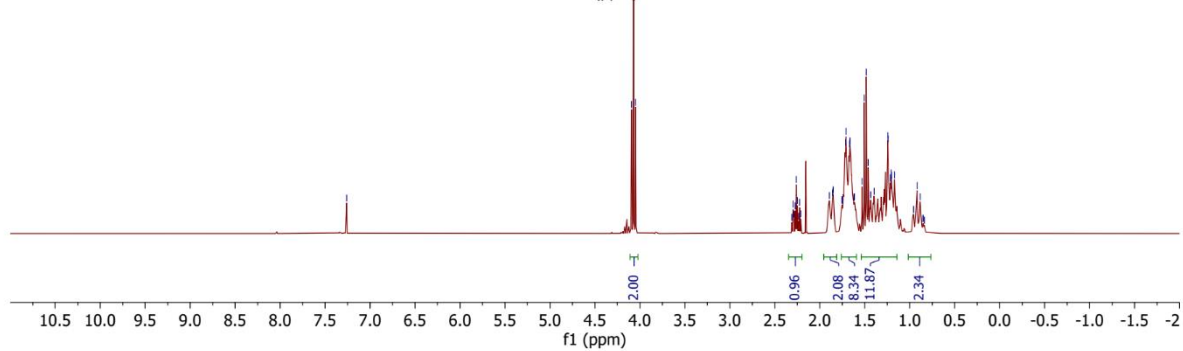
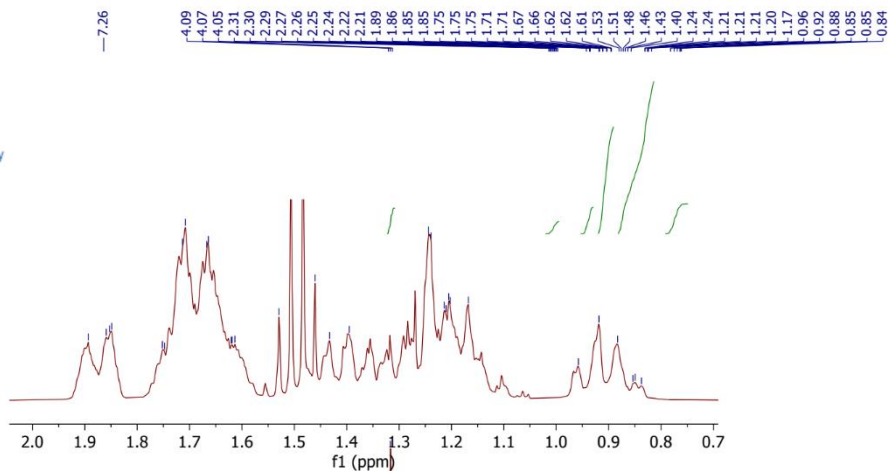
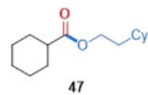
¹H NMR (300 MHz, Chloroform-*d*)



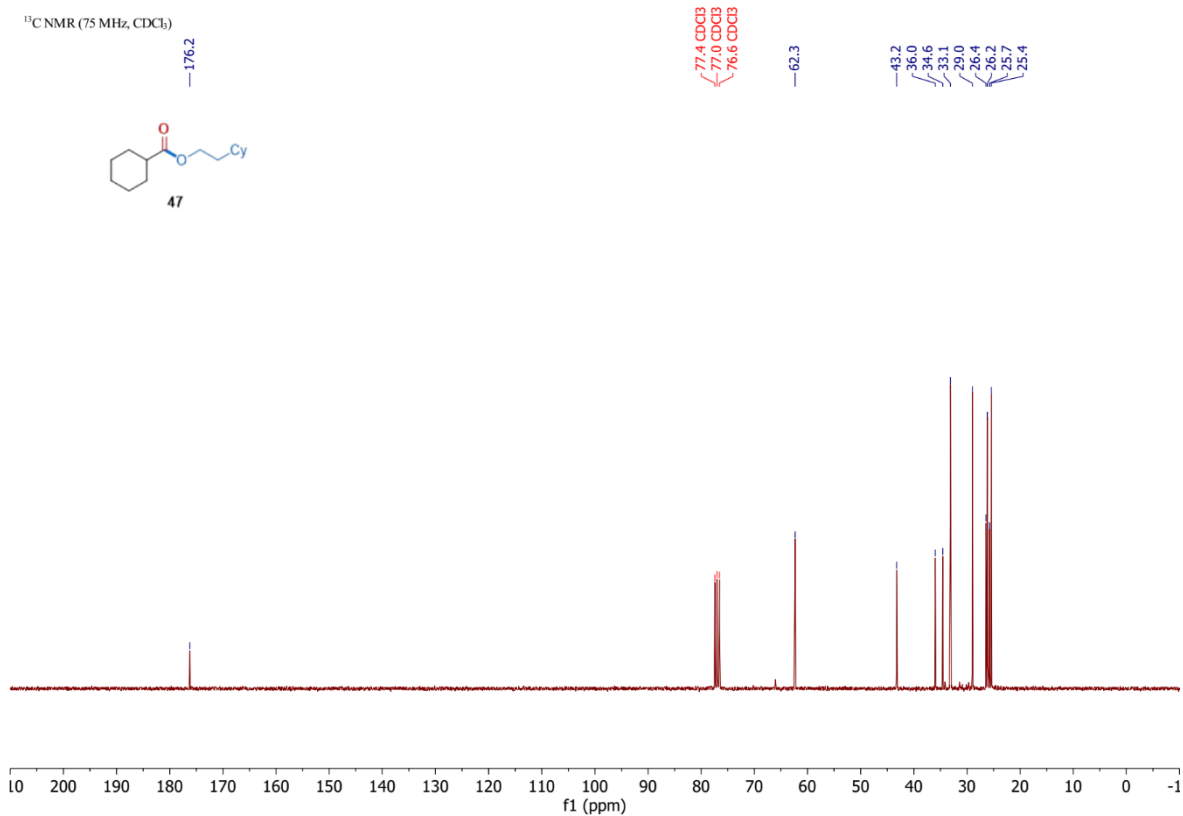
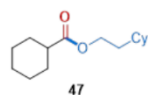
¹³C NMR (75 MHz, CDCl₃)



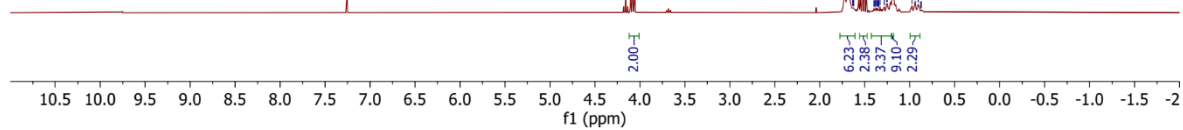
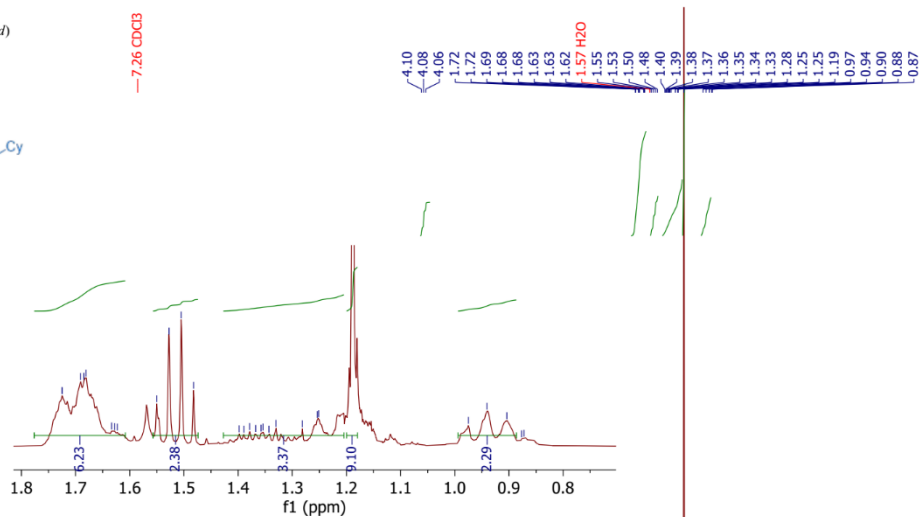
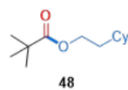
¹H NMR (300 MHz, Chloroform-*d*)



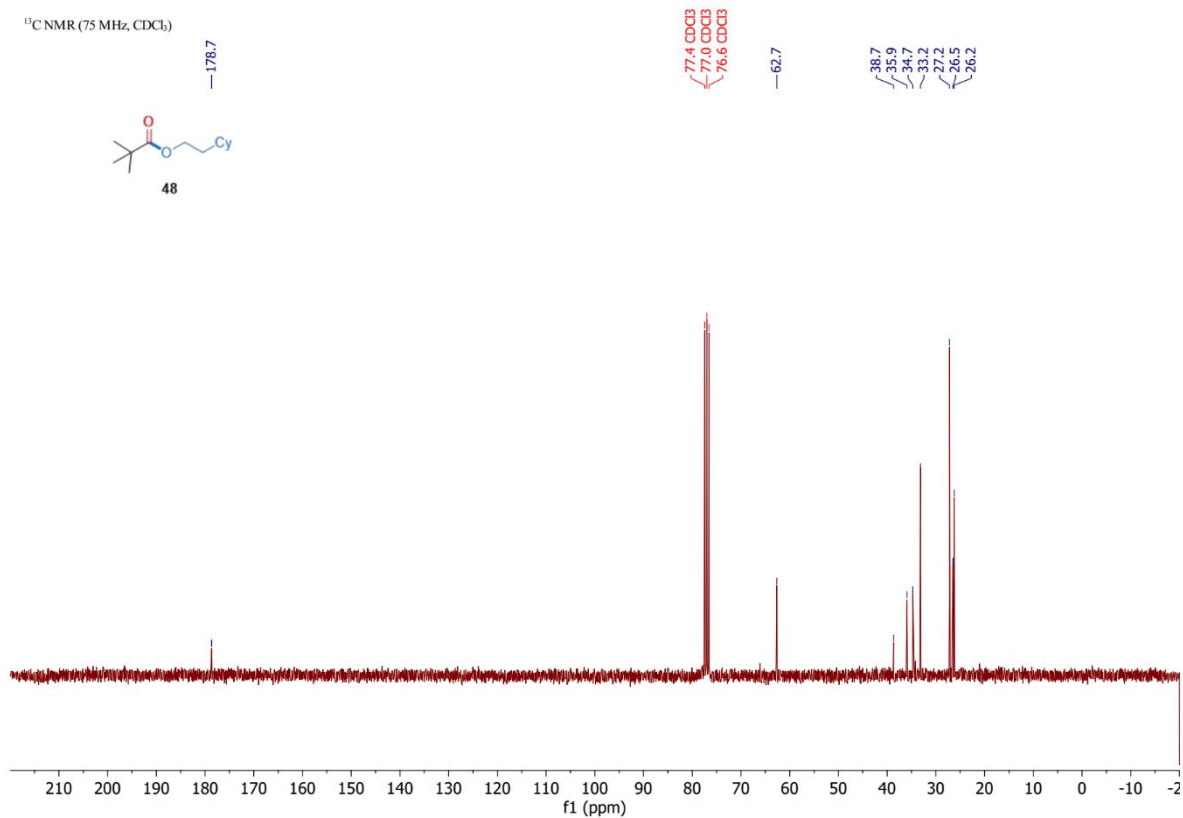
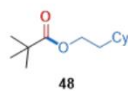
¹³C NMR (75 MHz, CDCl₃)



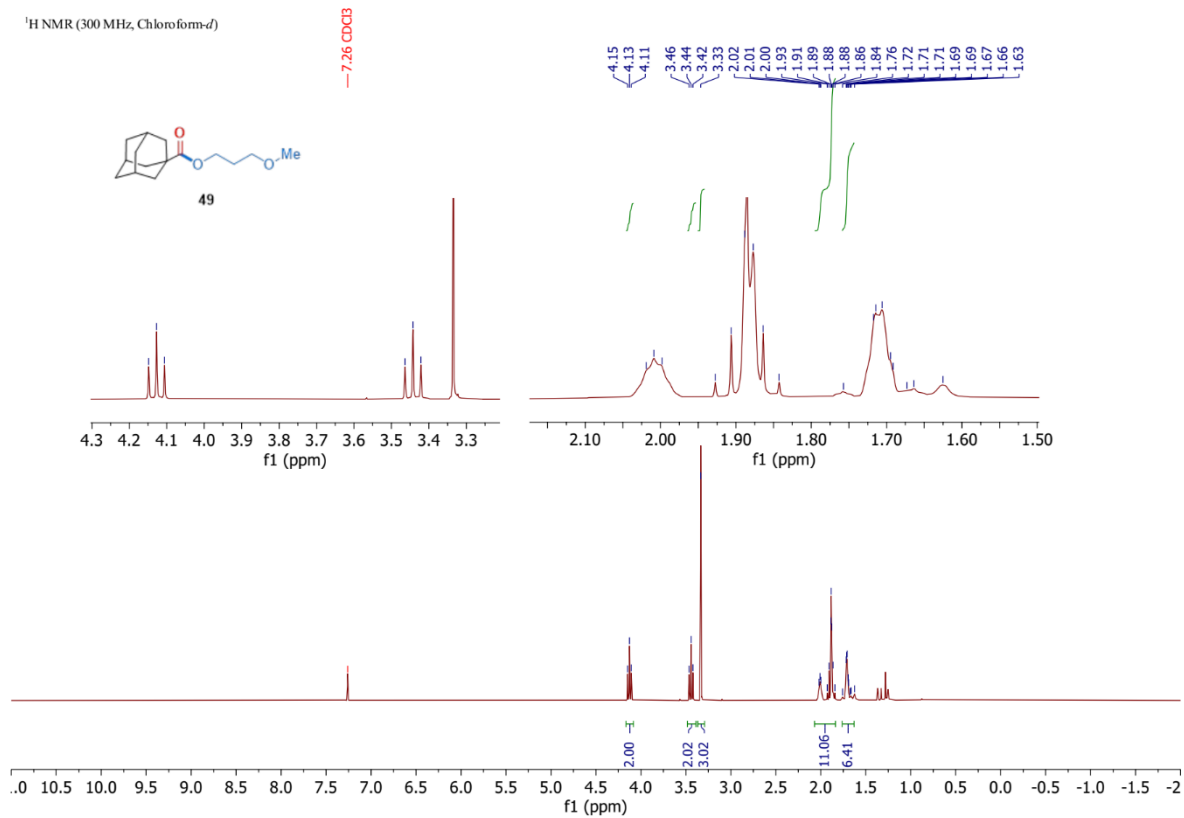
¹H NMR (300 MHz, Chloroform-d)



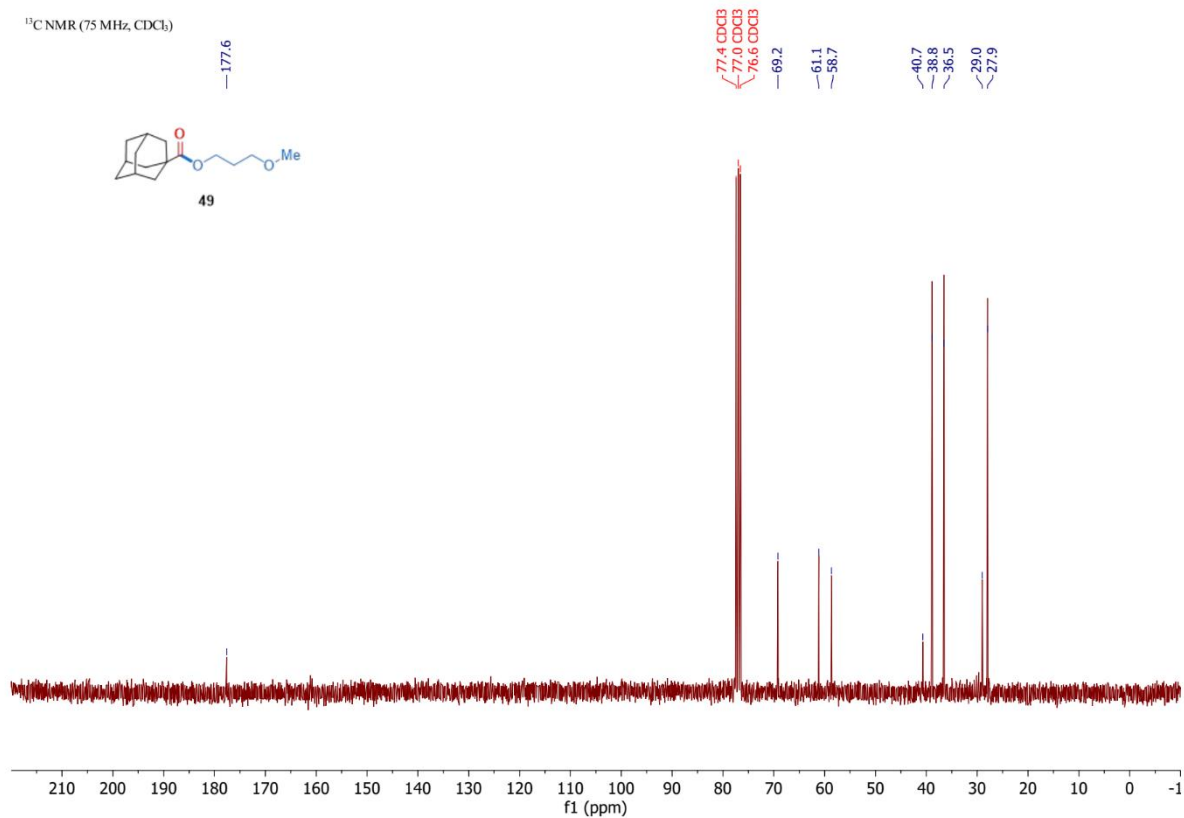
¹³C NMR (75 MHz, CDCl₃)



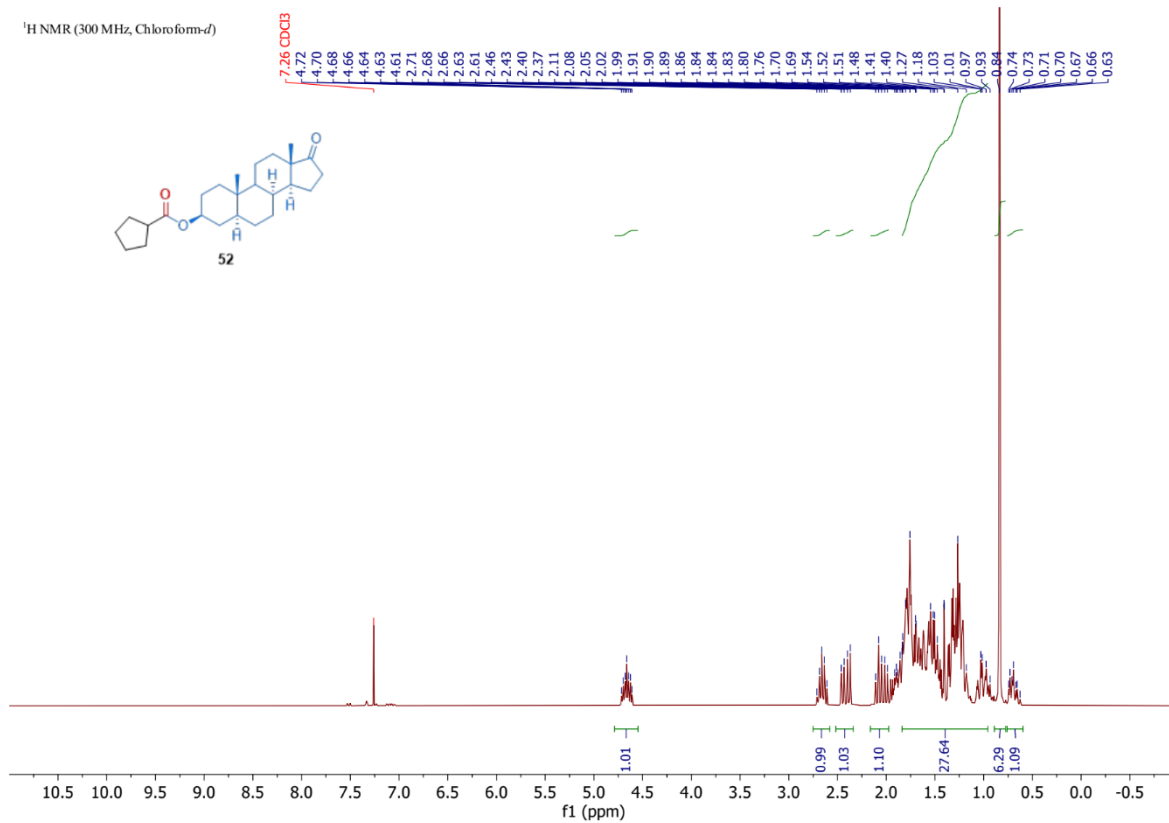
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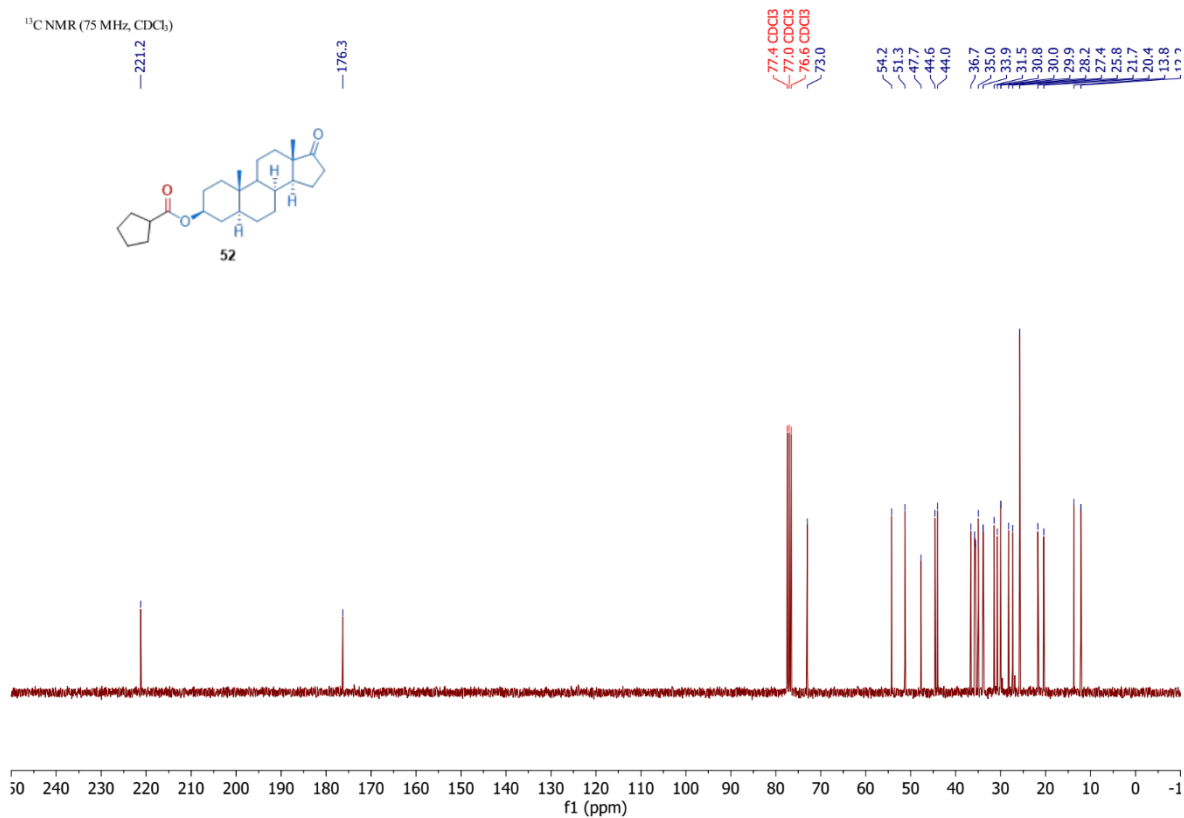
¹³C NMR (75 MHz, CDCl₃)



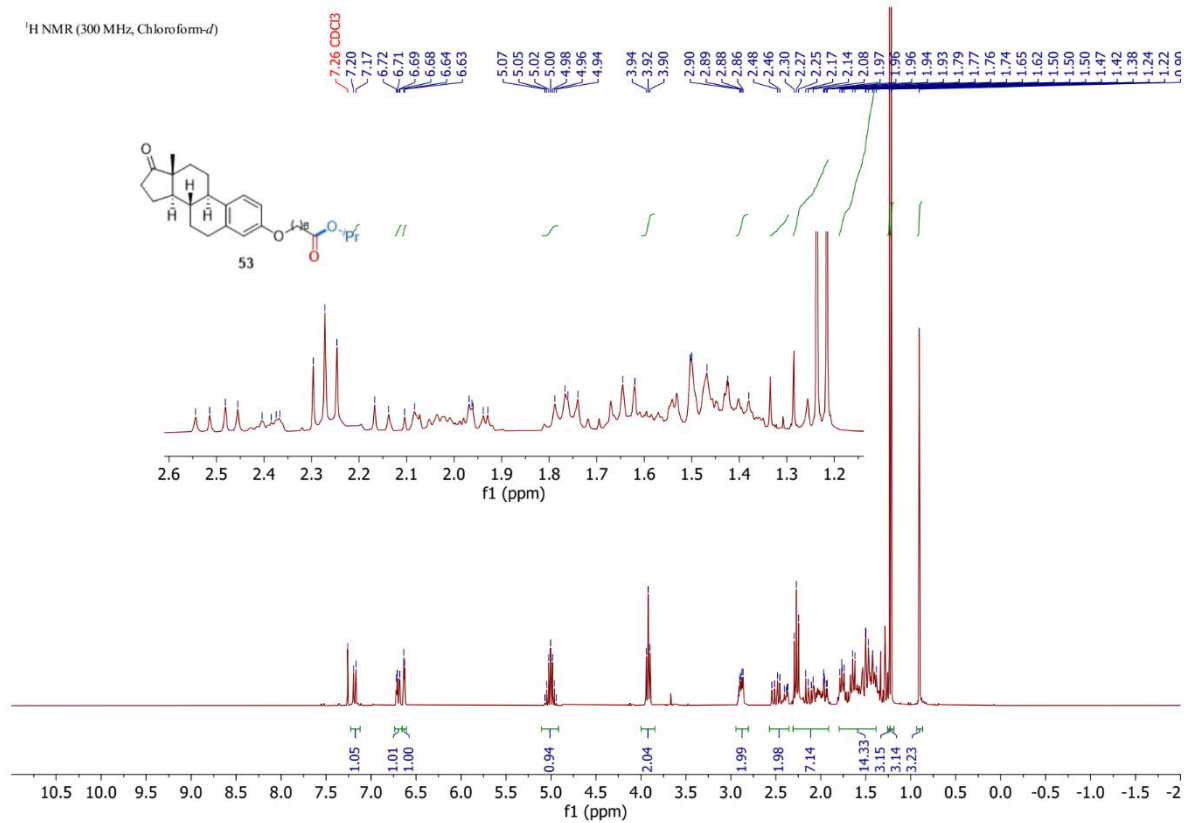
¹H NMR (300 MHz, Chloroform-*d*)



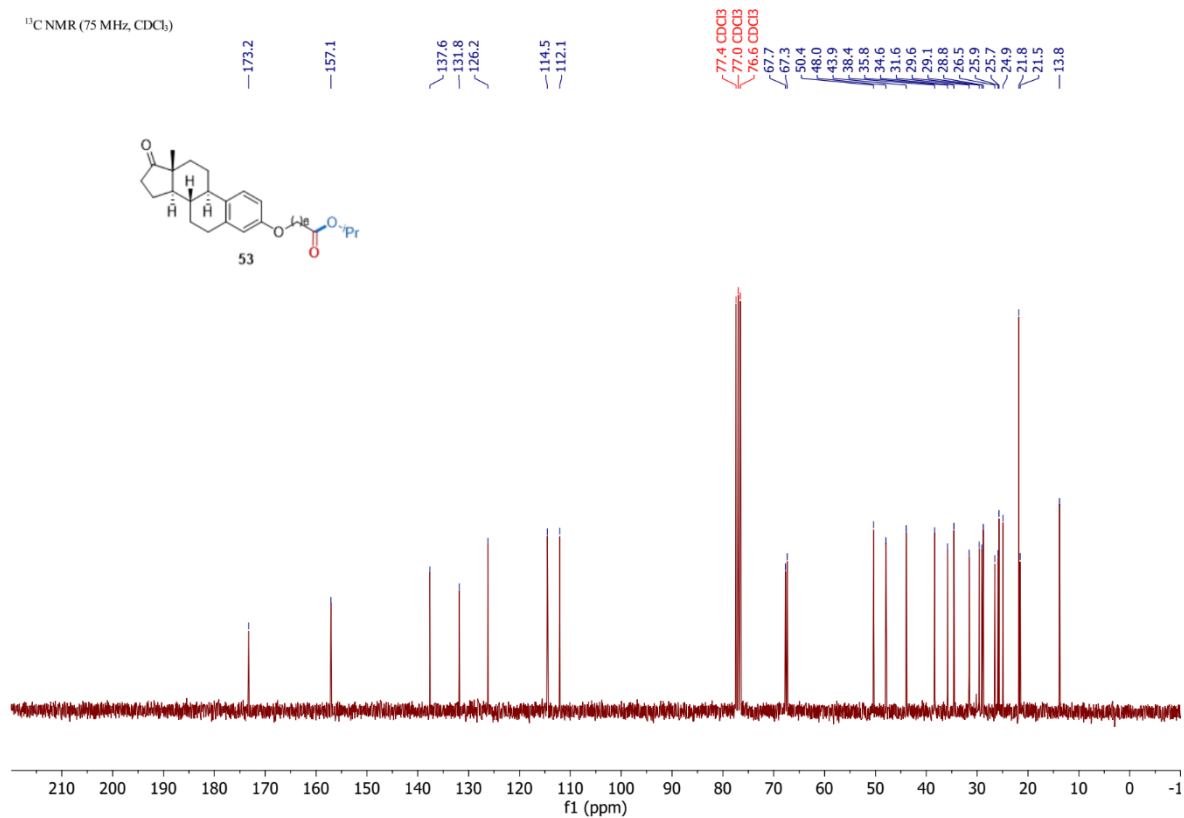
¹³C NMR (75 MHz, CDCl₃)



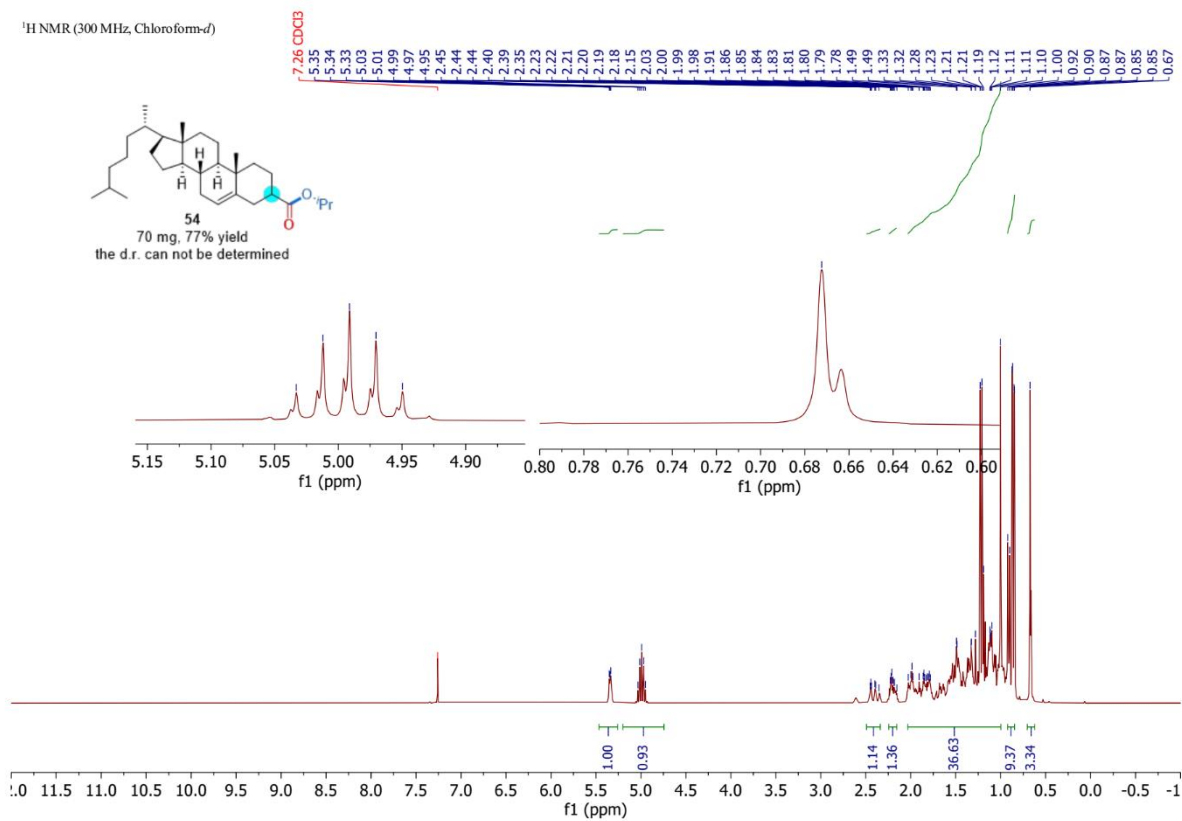
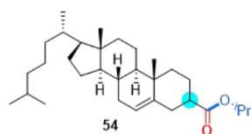
¹H NMR (300 MHz, Chloroform-*d*)



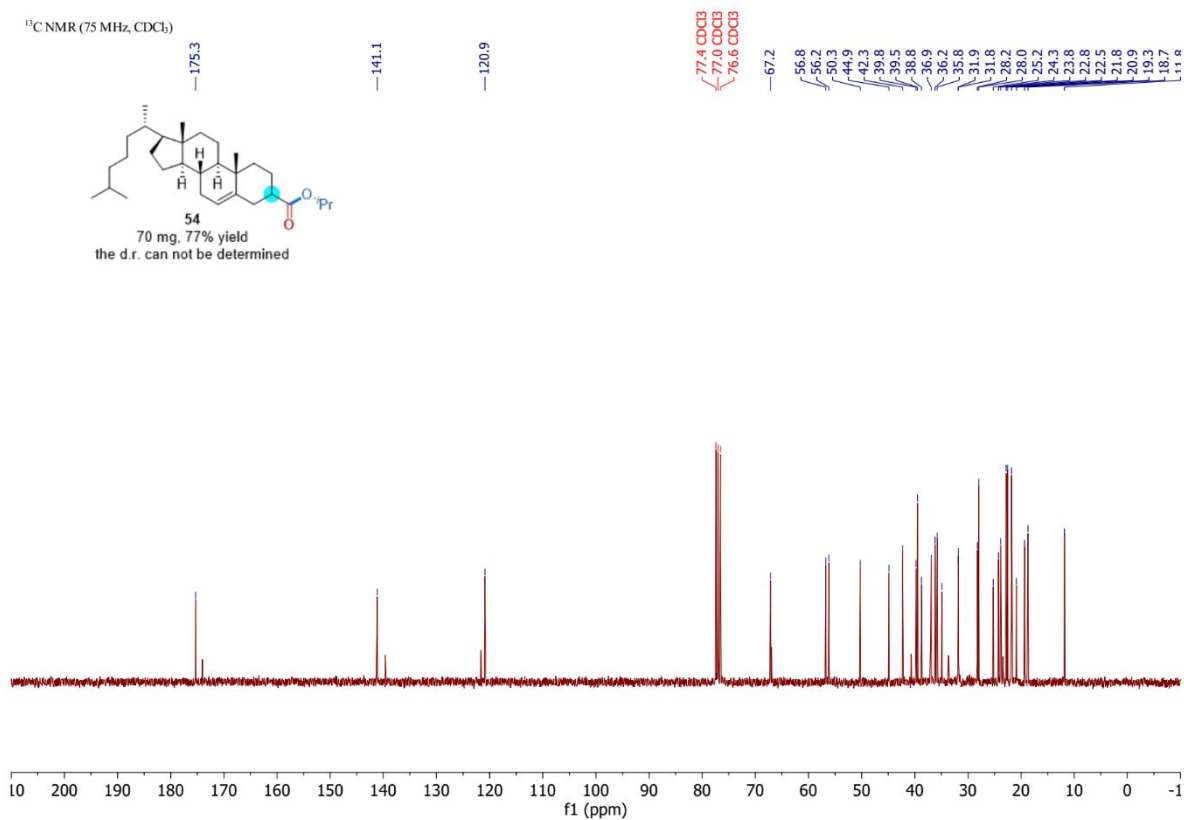
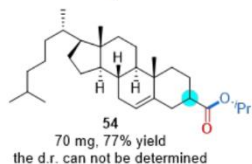
¹³C NMR (75 MHz, CDCl₃)



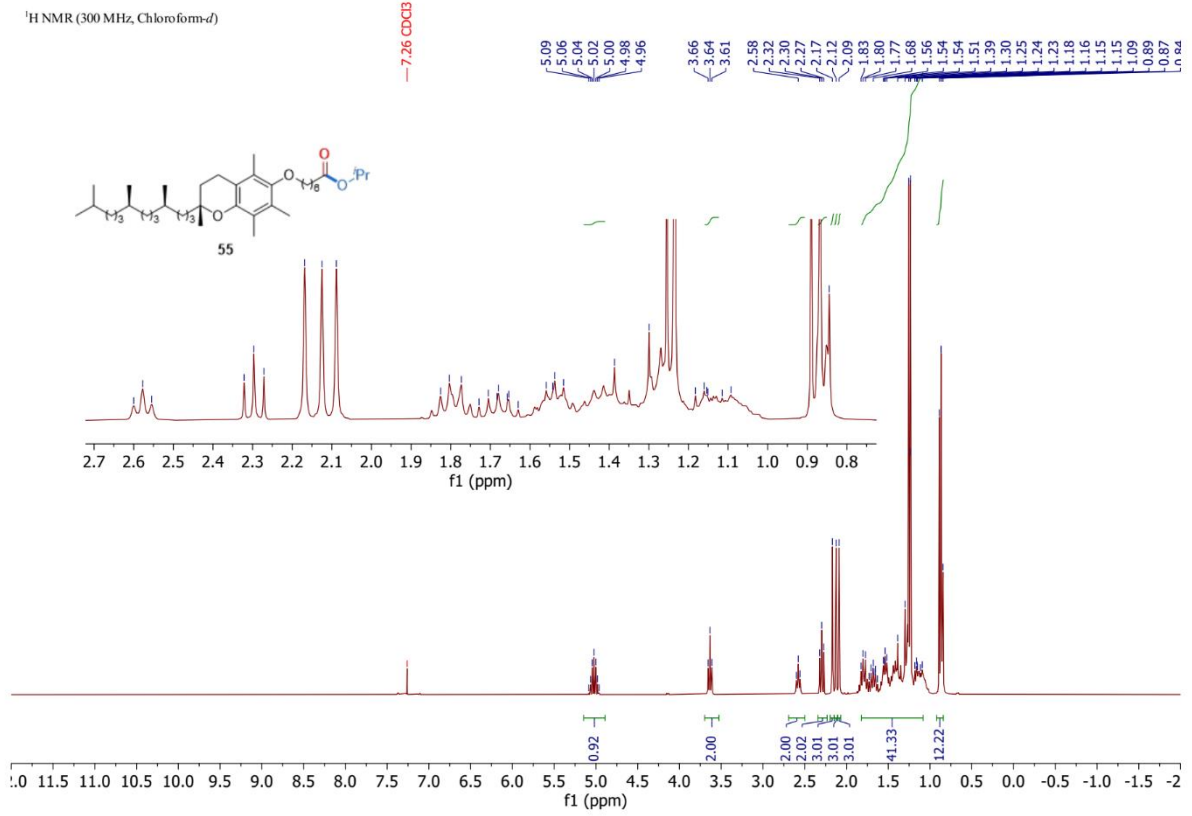
¹H NMR (300 MHz, Chloroform-d)



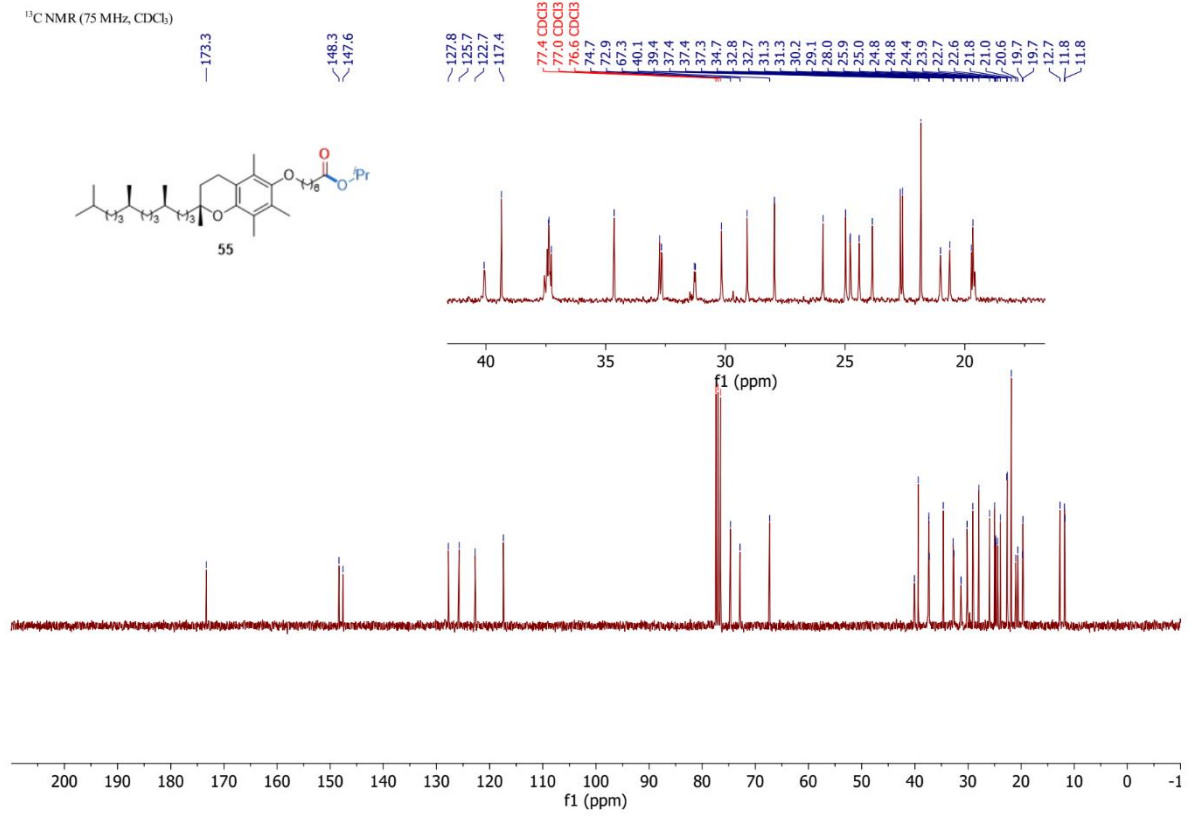
¹³C NMR (75 MHz, CDCl₃)

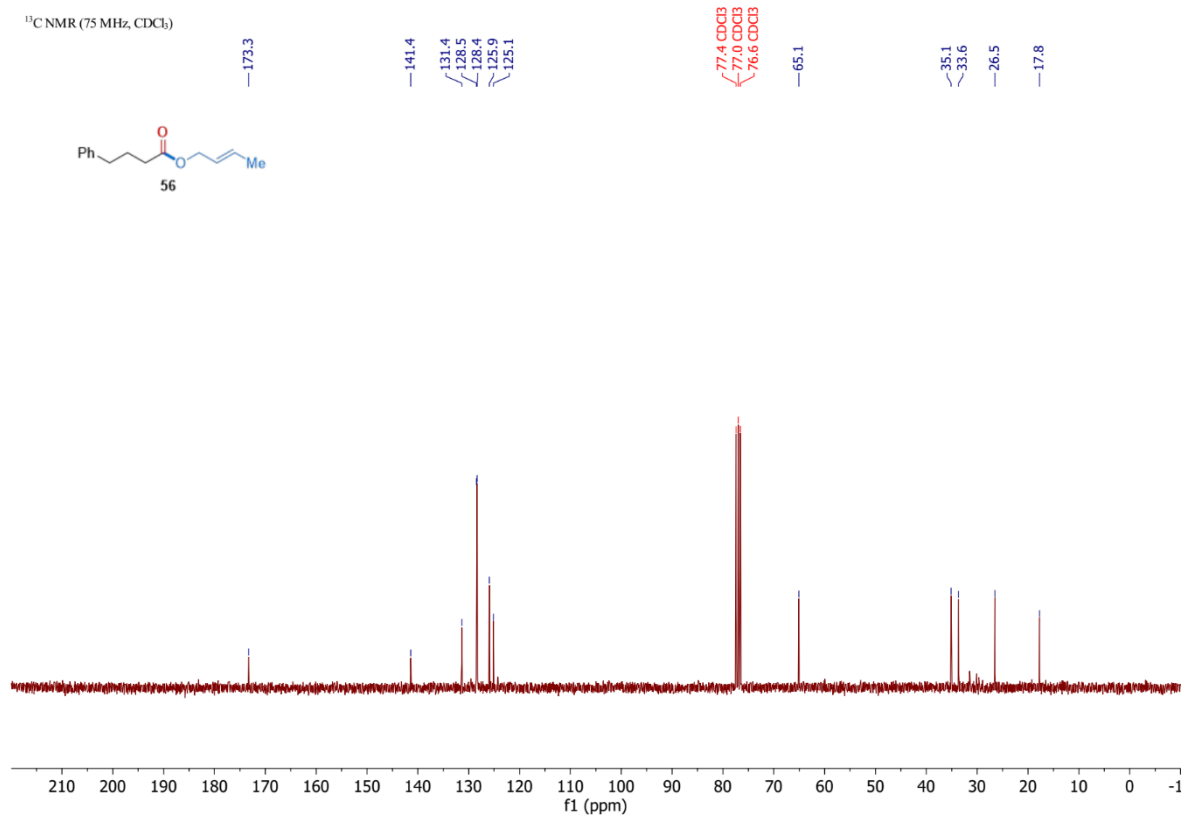
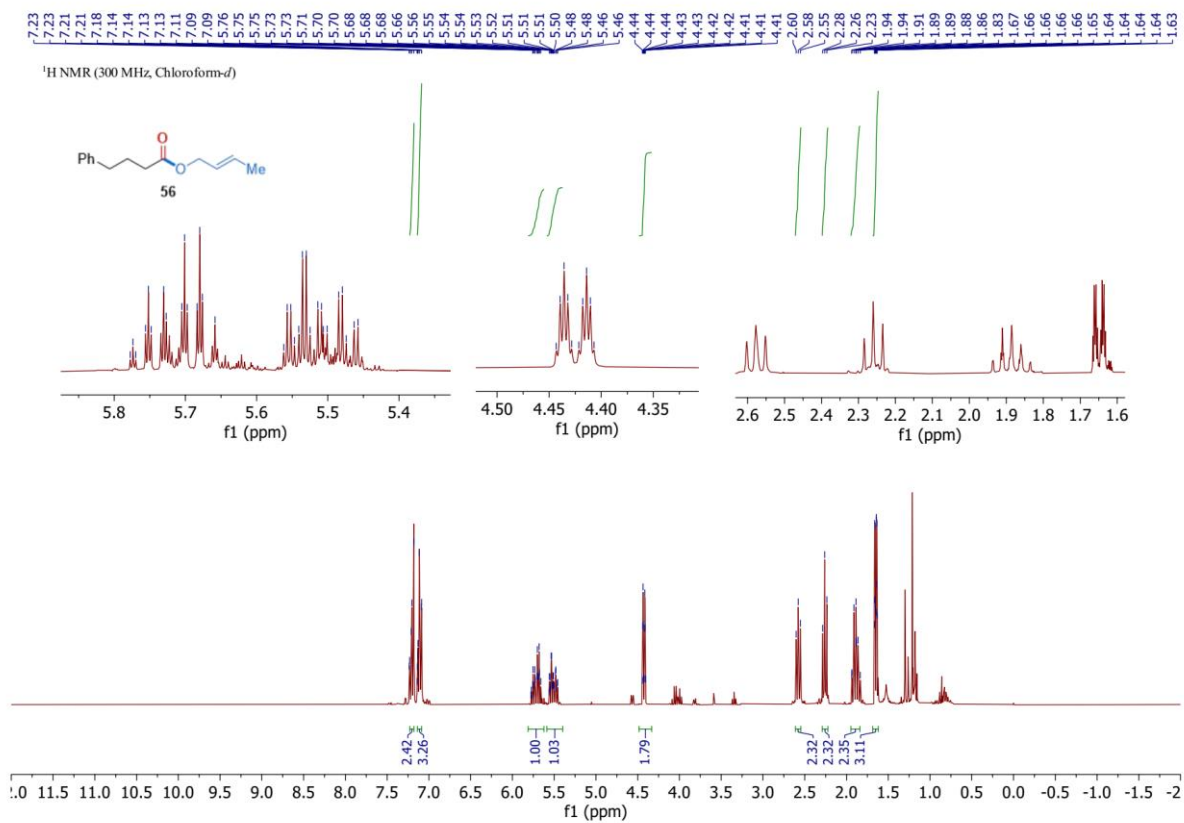


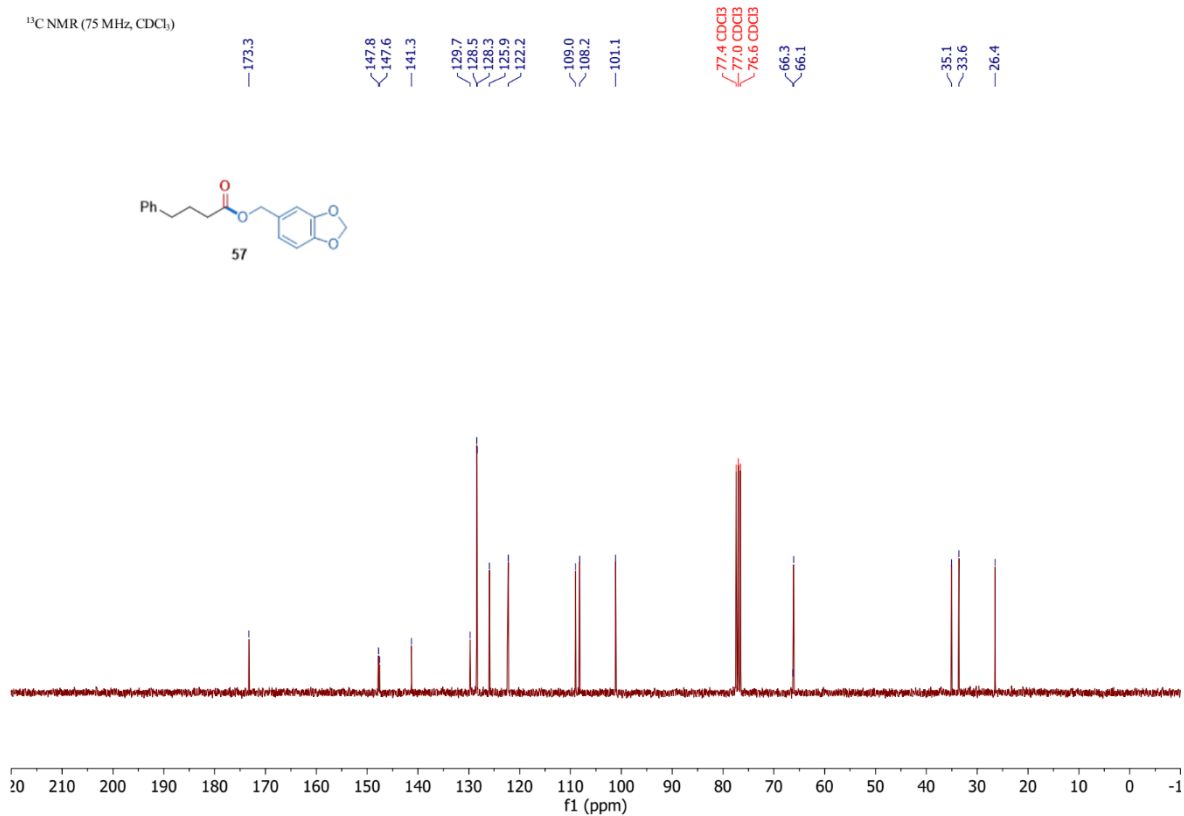
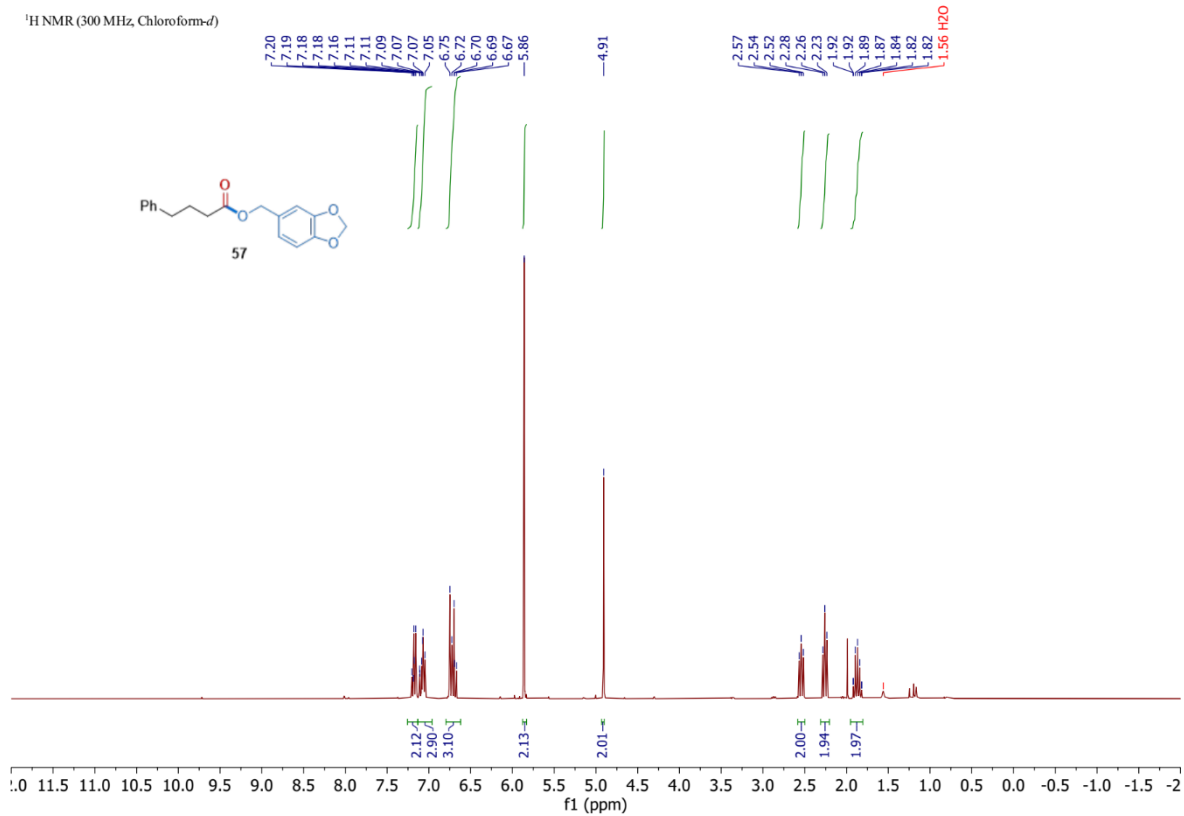
¹H NMR (300 MHz, Chloroform-*d*)



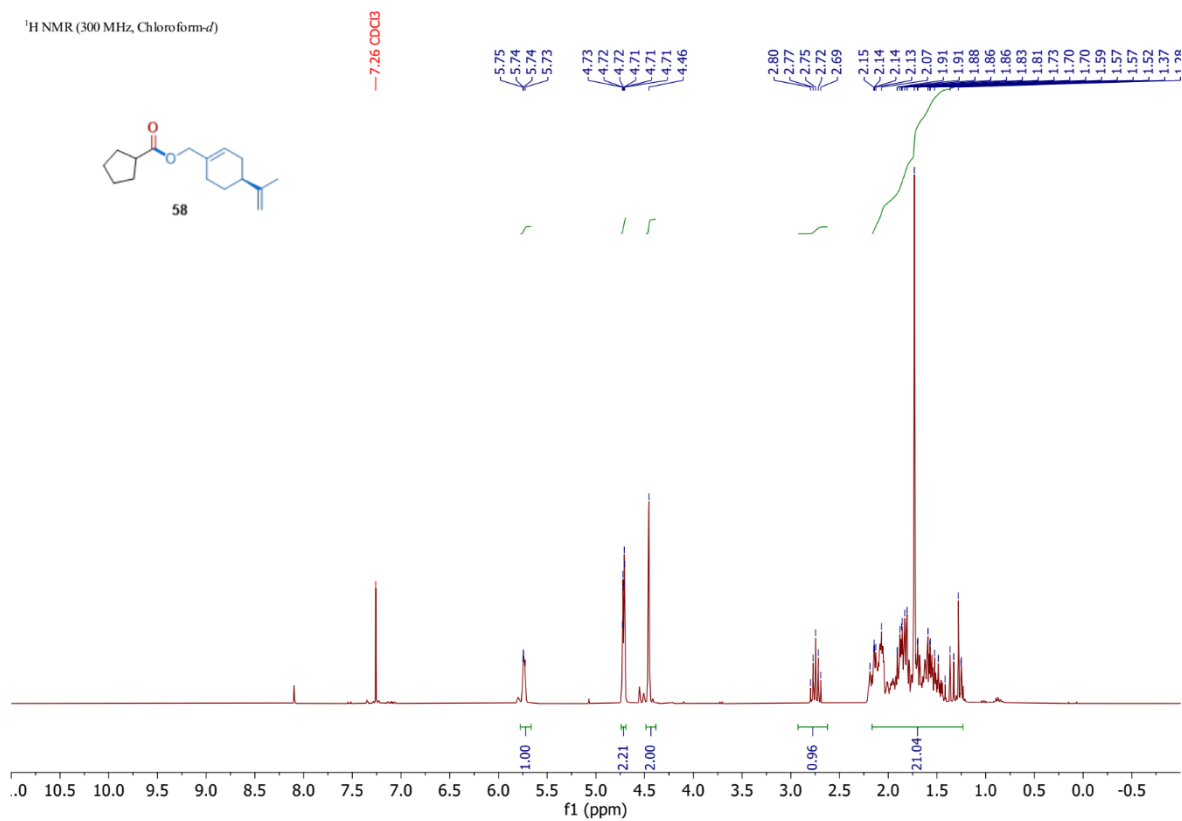
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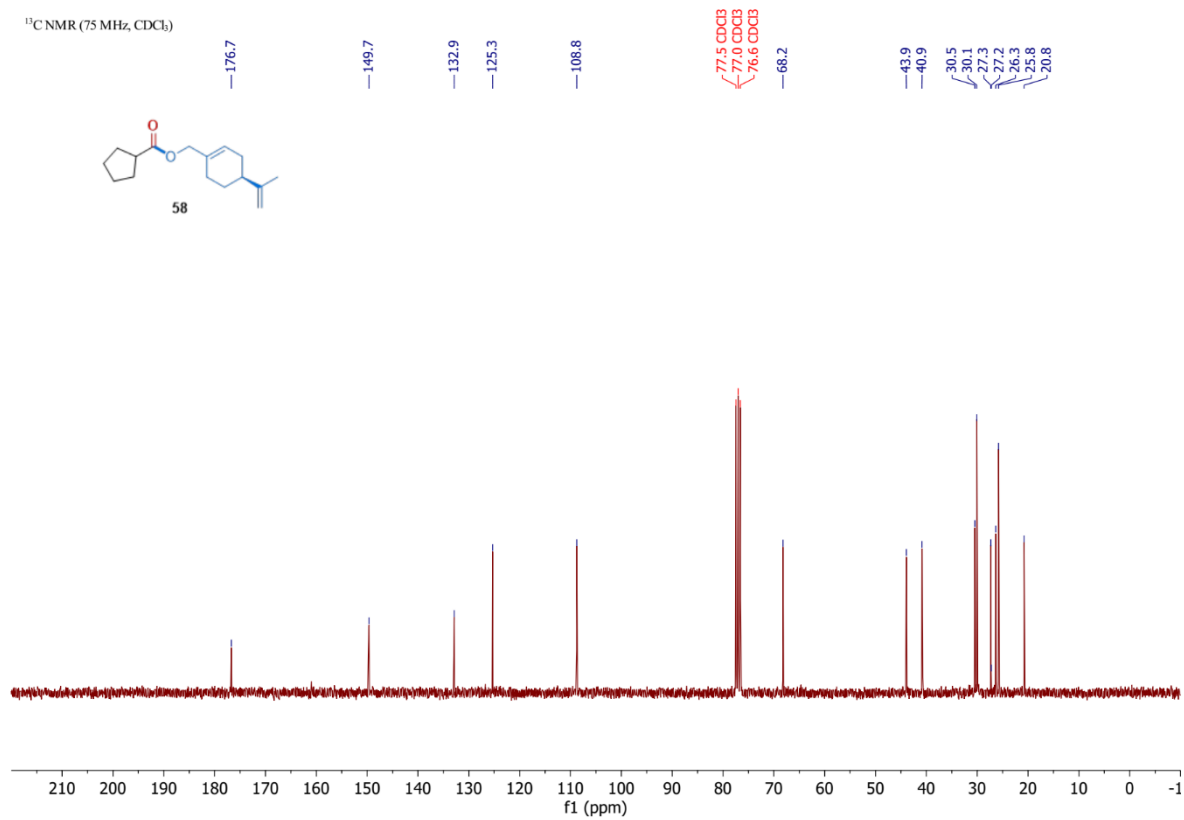


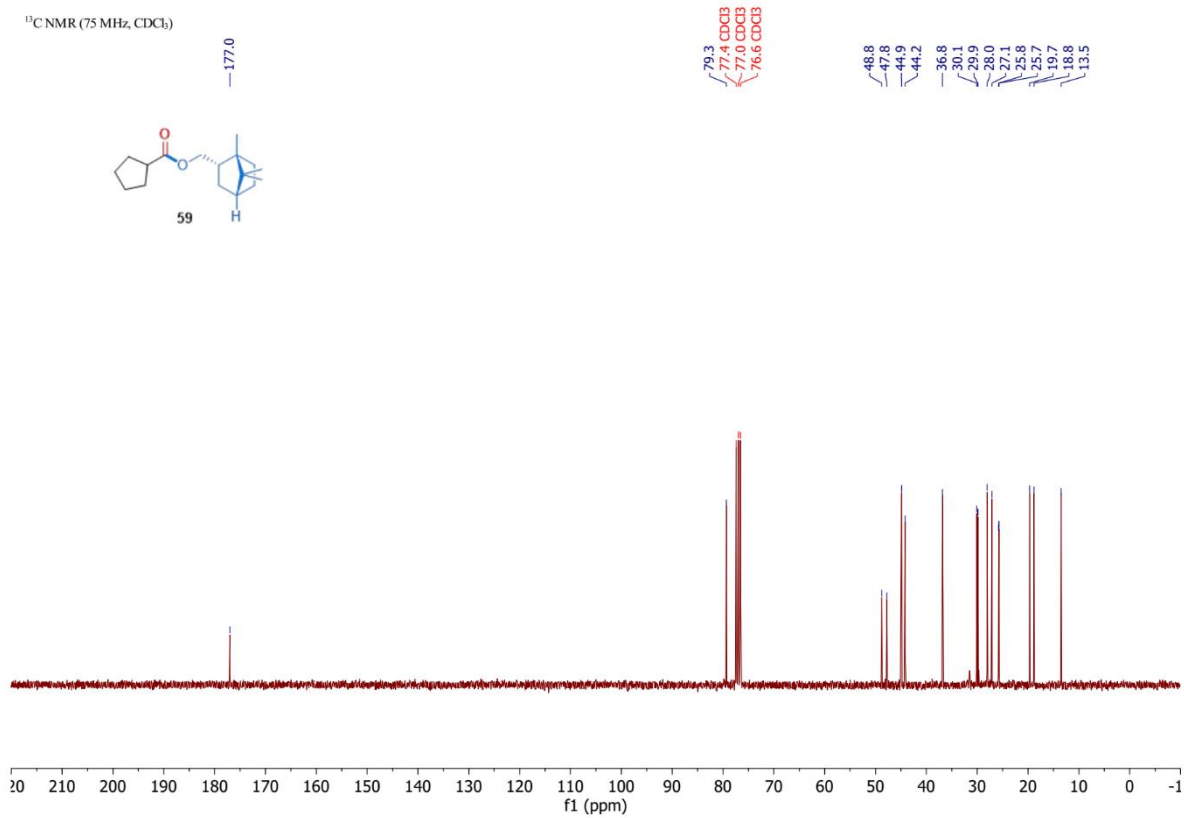
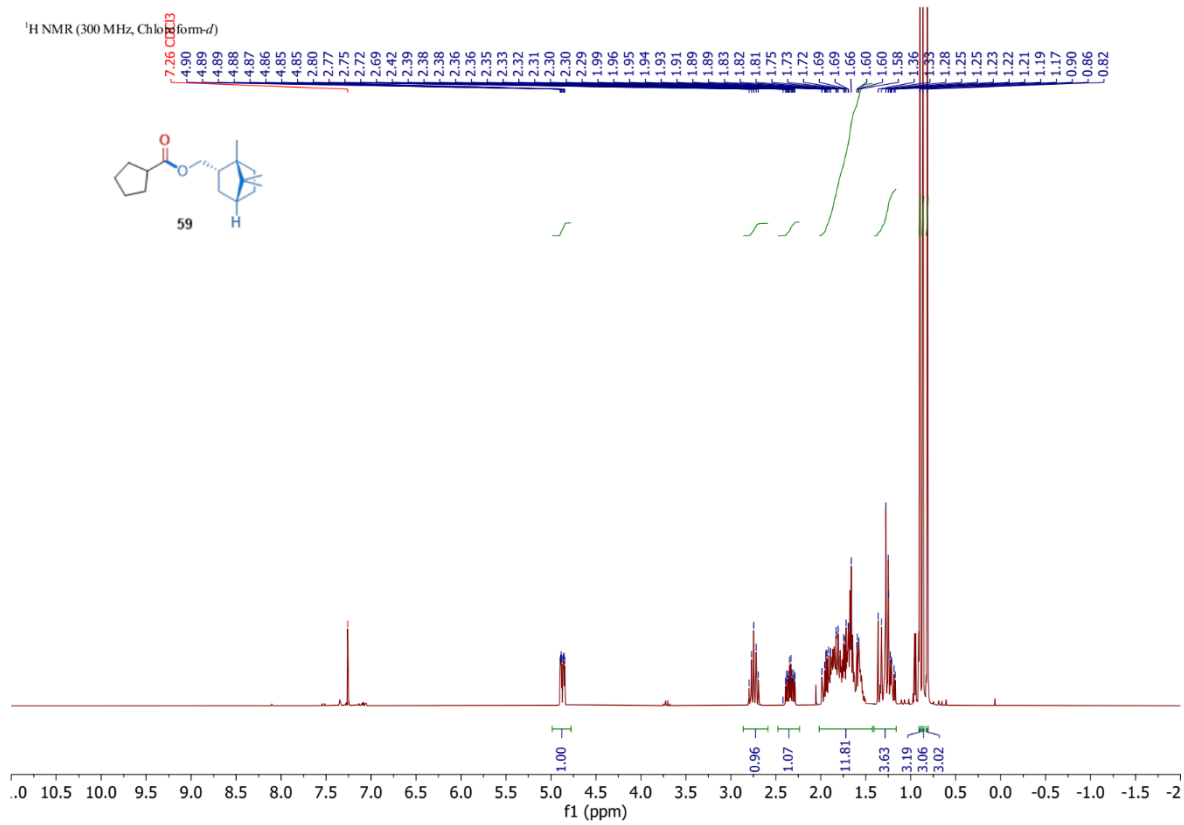


¹H NMR (300 MHz, Chloroform-*d*)

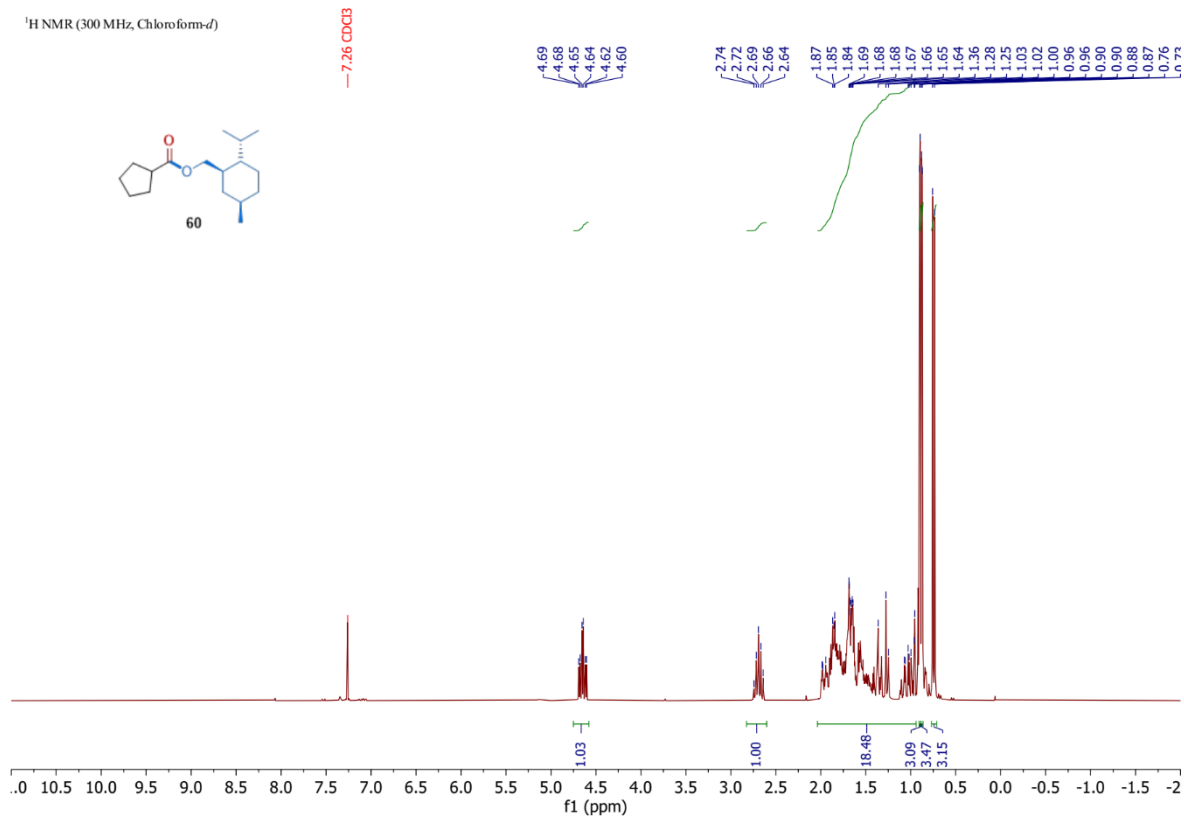


¹³C NMR (75 MHz, CDCl₃)

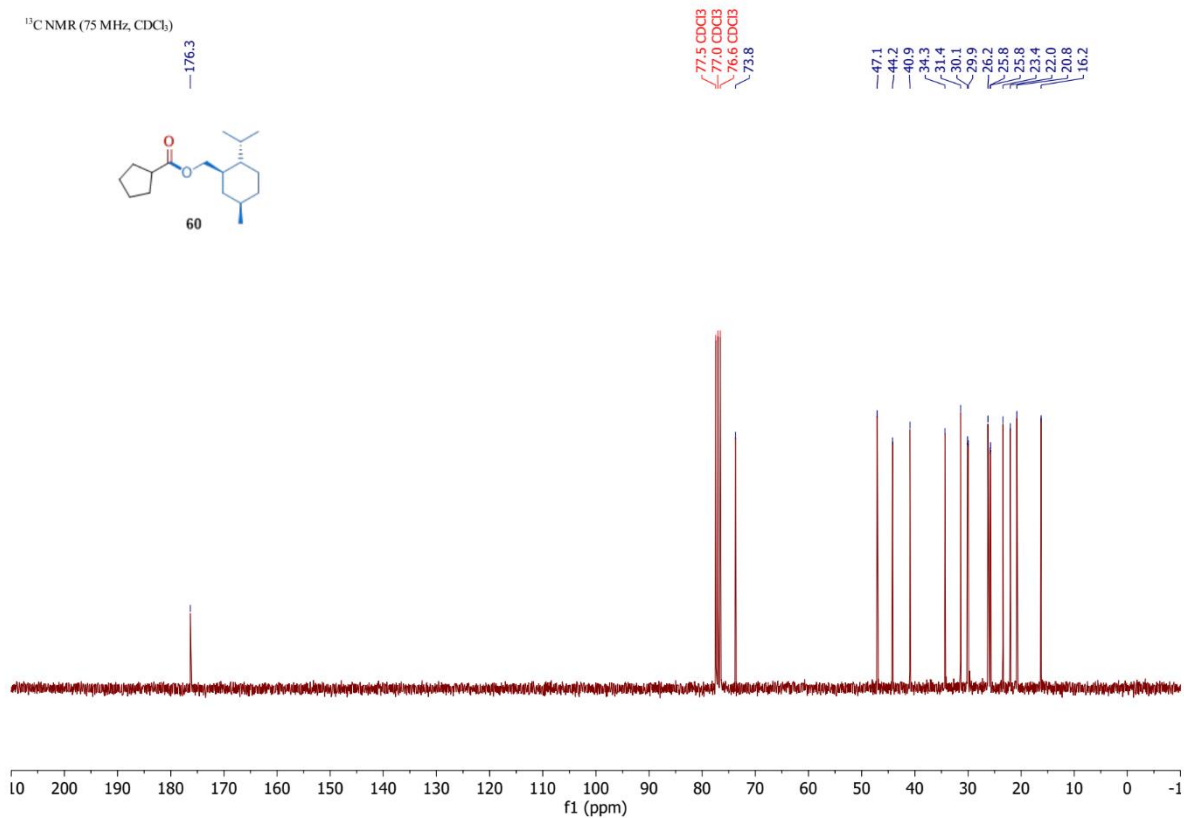




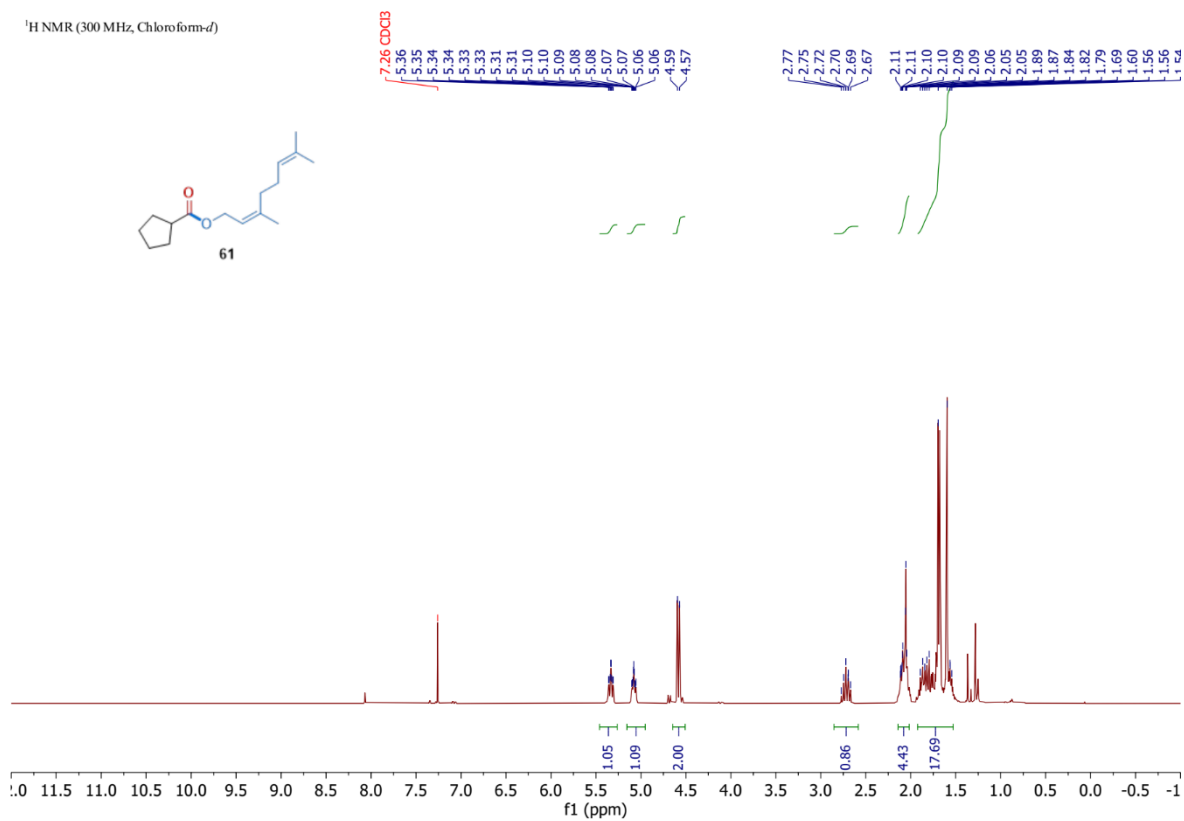
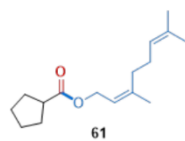
¹H NMR (300 MHz, Chloroform-*d*)



¹³C NMR (75 MHz, CDCl₃)



¹H NMR (300 MHz, Chloroform-*d*)



¹³C NMR (75 MHz, CDCl₃)

