Supporting Information

Decarboxylative halogenation of aliphatic carboxylic acids catalyzed by iron salts under visible light

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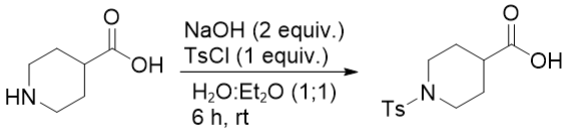
Content

1. General information

All manipulations were carried out with standard Schlenk techniques unless otherwise noted. Commercially available reagents were used without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded using Bruker advance III (400 MHz or 600 MHz) spectrometer. Measurements were done at ambient temperature. ^{1}H NMR chemical shifts are referenced to the residual hydrogen signals of the deuterated solvent (7.26 ppm for $CDCl_3$). The ^{13}C NMR chemical shifts are referenced to the ^{13}C signals of the deuterated solvent (77.2 ppm for $CDCl_3$). The NMR data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). The data of HRMS were measured on a high-resolution mass spectrometer (LCMS-IT-TOF) or Q Exactive GC. GC-MS analyses were carried out on Agilent 5977B and Agilent GC/MSD 8890 GC system. UV-Vis spectra were measured on a Lambda 950. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254). Flash column chromatography was conducted using silica gel (200–300 mesh) with solvent as indicated. The photoreactors[1] utilized were purchased from Wuhan GeAo Chem Company (Purple LEDs: 400 nm, (4 positions, 6×1W); Blue LEDs: 458 nm, (4 positions, 6×1W); Green LEDs: 525 nm, (4 positions, 6×1W)) or assembled using the 400 nm chips (20 W, λ_{max} = 402 nm) purchased from MinGuang Chips. The distance from the light source to the reaction vessel is 1 cm.

2. Synthesis and characterizations of substrates

1-tosylpiperidine-4-carboxylic acid[2].

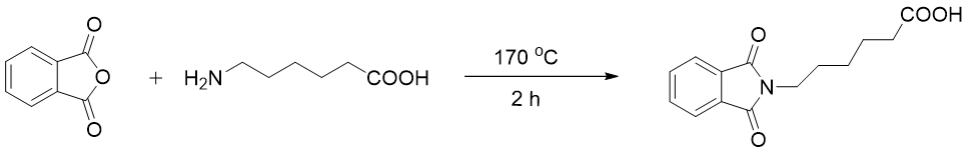


Piperidine-4-carboxylic acid (3.2 g, 25 mmol) was dissolved in 25 mL of Et_2O and 25 mL of 2 M aqueous solution of NaOH were carefully added at 0 °C. Then TsCl (4.75 g, 25 mmol) was carefully added and the mixture was stirred at room temperature for 6 h. A precipitate was formed over the reaction time. After this time the reaction mixture was further diluted with water until the precipitate was completely dissolved and the layers were separated. The aqueous layer was acidified to pH=3 by addition of 4 M HCl aqueous solution and extracted with EtOAc three times. The organic layer was dried over Na_2SO_4, filtered and concentrated to give the compound (4.98 g, 70%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 7.8 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 3.67 – 3.61 (m, 2H), 2.45 – 2.39 (m, 5H), 2.31 – 2.22 (m, 1H), 2.00 – 1.95 (m, 2H), 1.83 – 1.77 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 179.02, 143.84, 133.25, 129.88, 127.86, 45.52, 39.85, 27.40, 21.73.

6-(1,3-dioxoisoindolin-2-yl)hexanoic acid[3].

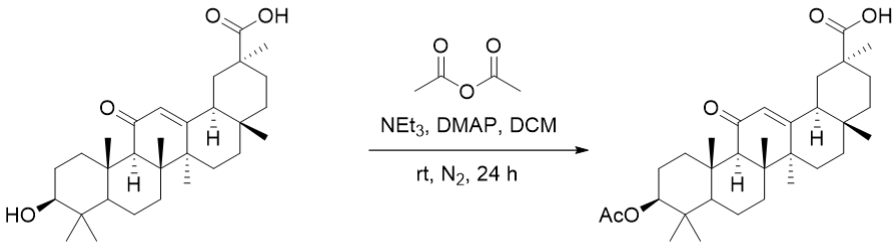


A mixture of phthalic anhydride (20 mmol, 1 equiv.) and the amino acid (20 mmol, 1 equiv.) was melted in a round bottom flask at 170 °C with an oil bath for 2 h (open to air in order to evaporate water). After cooling the reaction to room temperature, the crude mixture was dissolved in DCM and filtrated through a pad of silica gel. The filtrate was then concentrated in vacuo to yield the desired compound (4.70 g, 90%) as white solid which was used without further purification.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.82 (m, 2H), 7.72 – 7.69 (m, 2H), 3.69 (t, *J* = 7.2 Hz, 2H), 2.35 (t, *J* = 7.4 Hz, 2H), 1.72 – 1.66 (m, 4H), 1.45 – 1.35 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 178.87, 168.63, 134.08, 132.30, 123.39, 37.92, 33.85, 28.43, 26.45, 24.37.

(2R,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylic acid[4].

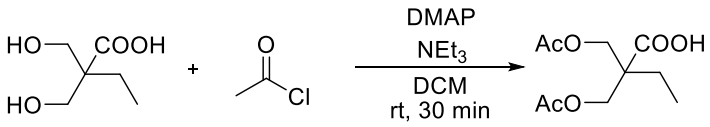


Glycyrrhetinic acid (473.5 mg, 1 mmol) and 12.2 mg (10 mol%) of DMAP were dissolved in 100 mL of dry CH_2Cl_2 (20 mL). Acetic anhydride (0.28 ml, 3 mmol) and NEt_3 (0.6 ml, 3 mmol) were added to the reaction mixture. After 24 hours of stirring, the reaction mixture was extracted with five portions (10 mL) of HCl (1 M). The combined aqueous phase was extracted with two portions (20 mL) of Saturated NaCl solution. The residue was purified by chromatography on silica gel (DCM: MeOH= 50:1) to obtain the final product (1.2 g, 78%) as a white solid.

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.71 (s, 1H), 4.52 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.83 – 2.77 (m, 1H), 2.37 (s, 1H), 2.22 – 2.17 (m, 1H), 2.09 – 1.94 (m, 6H), 1.90 – 1.56 (m, 7H), 1.51 – 1.31 (m, 9H), 1.23 (s, 4H), 1.17 (s, 3H), 1.13 (s, 3H), 1.08 – 0.99 (m, 2H), 0.88 (s, 6H), 0.84 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.44, 181.39, 171.18, 169.51, 128.69, 80.86, 61.94, 55.27, 48.48, 45.68, 43.99, 43.44, 41.12, 39.02, 38.28, 37.94, 37.19, 32.96, 32.08, 31.16, 28.74, 28.62, 28.27, 26.71, 26.65, 23.80, 23.55, 21.47, 18.92, 17.61, 16.88, 16.60.

2,2-bis(acetoxymethyl)butanoic acid[5].

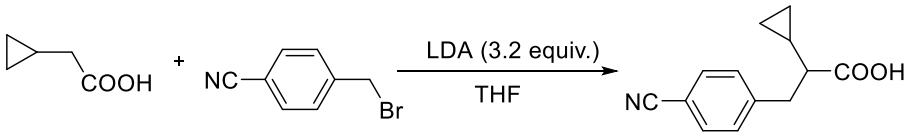


2,2-Bis(hydroxymethyl)butyric acid (2.00 g, 13.49 mmol), 3.412 g (33.72 mmol) of TEA and 0.083 g (0.67 mmol) of DMAP were dissolved in 100 mL of dry CH_2Cl_2 (36 mL). Acetylchloride (2.24 g, 28.61 mmol) was added drop by drop to the reaction mixture. After 30 min of stirring, the reaction mixture was extracted with three portions (40 mL) of Na2CO3 (10%). The combined aqueous phase was acidified with HCl (concentrated) and extracted with three portions (40 mL) of CH_2Cl_2.The residue was purified by column chromatography (silica gel) using petroleum ether/ethyl acetate mixture as eluent (4:1-1:1) to get white solid product (1.425 g, 50%).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.27 – 4.20 (m, 4H), 2.02 (s, 6H), 1.66 – 1.60 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.34, 171.00, 63.08, 49.93, 24.03, 20.84, 8.20.

3-(4-cyanophenyl)-2-cyclopropylpropanoic acid[6]



2-cyclopropanoic acid (10 mmol, 0.93 ml, 1.0 equiv.) was dissolved in dry THF (20 ml) and slowly added to the LDA solution (2 M in THF, 16 ml, 3.2 equiv.) cooled in an ice water bath under N_2 atmosphere. After that, the reaction mixture was heated to 45 °C using an oil bath. After 3 hours, the reaction liquid was cooled to -78 °C and 4-(bromoethyl) benzonitrile (6.27 g, 3.2 equiv.) was added dropwise. Later, the reaction mixture was left to room temperature and stirred overnight. The reaction mixture was then quenched by slowly adding water (60 mL) and the pH was adjusted to 14 by adding 2.0 M NaOH (aq.). The resulting mixture was extracted with ether (30 mL×2) and DCM (30 mL×2). Then, 3 M HCl aqueous solution was added to the aqueous phase, the pH was adjusted to 1-2, and the extraction was performed with ethyl acetate (200 mL). The organic layer was then dried over Na_2SO_4 and concentrated to give the target product (1.91 g, 89%) as a light yellow solid without further purification.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.56 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 3.15 – 3.10 (m, 1H), 3.03 – 2.98 (m, 1H), 1.87 – 1.93 (m, 1H), 1.01 – 0.93 (m, 1H), 0.64 – 0.50 (m, 2H), 0.44 – 0.33 (m, 1H), 0.11 –0.01 (m, 1H).

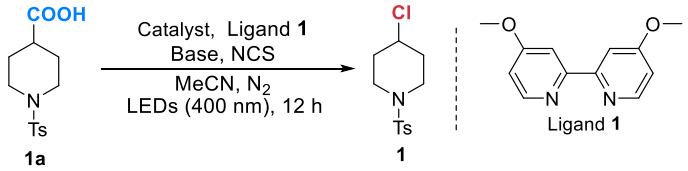
^{13}C NMR (101 MHz, Chloroform-d) δ 179.51, 144.88, 132.36, 130.01, 119.04, 110.63, 52.01, 38.50, 13.87, 5.18, 4.04.

3 Study of reaction conditions

General procedure for the optimization of the reaction

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with 1-tosylpiperidine-4-carboxylic acid (0.1 mmol), Ligand, NCS. Then the Schlenk-tube was transferred to nitrogen-filled glovebox to added iron pre-catalyst and anhydride MeCN. After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added 2,4,6-Trimethylpyridine via syringe or microsyringe, respectively. Finally, the reaction mixture was stirred and irradiated for different time under different LEDs, cooling with a fan. The reaction solution was washed with water and extracted with DCM (3×10 mL), the organic layer was filtered and washed through a short plug of silica with DCM to remove the iron species and concentrated by rotary evaporation. The crude yield of product 1.1 was then detected by ^{1}H NMR using 1,3,5-Trimethylbenzene (0.1 mmol) as an internal standard.

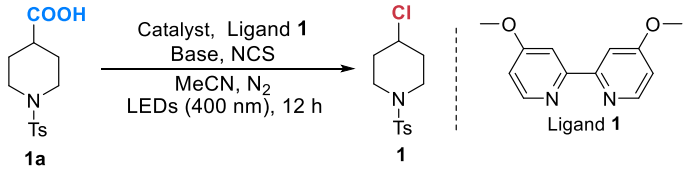
Table S1 Selected Optimization Studies



Entry [a]	Catalyst	Base	Solvent	Yield (%)[b]
1	$Fe(OAc)_2$	2,6-lutidine	MeCN	62
2[c]	$Fe(OAc)_2$	2,6-lutidine	MeCN	55
3	$Fe(OTf)_3$	2,6-lutidine	MeCN	52
4	$Fe_2(SO_4)_3$	2,6-lutidine	MeCN	44
5	$Fe(OH)(OAc)_2$	2,6-lutidine	MeCN	56
6	$FeBr_2$	2,6-lutidine	MeCN	52
7	$Fe(OH)_3$	2,6-lutidine	MeCN	52
8	$Fe(OAc)_2$	2,6-lutidine	MeCN: H2O= 1:1	48
9	$Fe(OAc)_2$	2,6-lutidine	DCM	48
10	$Fe(OAc)_2$	2,6-lutidine	acetone	trace
11	$Fe(OAc)_2$	DBU	MeCN	27
12	$Fe(OAc)_2$	$NaHCO_3$	MeCN	10
13	$Fe(OAc)_2$	2-methylpyridine	MeCN	33
14	**$Fe(OAc)_2$**	**2,4,6-Collidine**	**MeCN**	**86 (80)[d]**

[a]Reaction conditions: **1a** (0.1 mmol), Base (1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand **1** (10 mol%), NCS (2.1 equiv.), Solvent (1 ml), LEDs (400 nm, 6 W), 12 h. [b]Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard. [c]LEDs (455nm) was applied. [d]Isolated yield.

Table S2 Control experiments

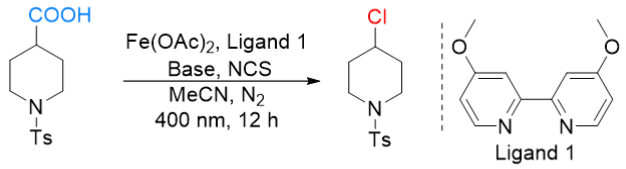


Entry [a]	Base	Fe	Ligand	Yield (%)[b]
1	2,6-lutidine	$Fe(OAc)_2$	-	trace
2	-	$Fe(OAc)_2$	Ligand **1**	n.d.

3[c]	2,6-lutidine	$Fe(OAc)_2$	Ligand **1**	55
4[d]	2,6-lutidine	$Fe(OAc)_2$	Ligand **1**	n.d.
5	2,6-lutidine	-	Ligand **1**	trace

[a]Reaction conditions: **1a** (0.1 mmol), Solvent (1 ml), Base (1.8 equiv.), $Fe(OAc)_2$ (10 mol%), ligand (10 mol%), NCS (2.1 equiv.), Solvent (MeCN, 1 ml). [b]Determined by ^1H NMR using 1,3,5-Trimethylbenzene as an internal standard. [c]Under air atmosphere. [d]Without light

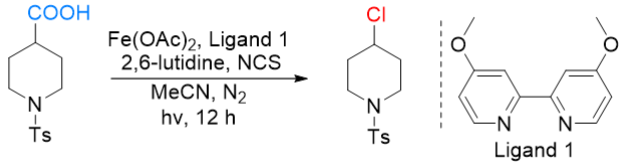
Table S3 Base optimization



Entry [a]	Base	Yield (%)[b]
1	2,6-lutidine	60
2	DBU	27
3	N,N-dimethyl-aniline	60
4	quinoline	trace
5	K_3PO_4	trace
6	Na_3PO_4	trace
7	Li_3PO_4	trace
8	PhCOOK	trace
9	HCOONa	trace
10	DMAP	10
11	NaOH	11
12	$NaHCO_3$	10
13	2-methylpyridine	33
14	2,6-Di-tert-butylpyridine	trace
15	2-Dimethylaminopyridine	27
16	2,4,6-Collidine	86

[a]Reaction conditions: **Acid** (0.1 mmol), Base (1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), NCS (2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 6 W). [b] Determined by ^1H NMR using 1,3,5-Trimethylbenzene as an internal standard.

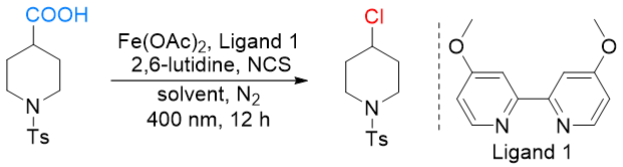
Table S4 Wavelength optimization



Entry [a]	Wavelength	Yield (%)[b]
1	400 nm（6 W）	64
2	365 nm（6 W）	trace
3	White LED	36
5	455 nm（6 W）	55

[a]Reaction conditions: **Acid** (0.1 mmol), NCS (2.1 equiv.), Base (2,6-lutidine, 1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), Solvent (MeCN, 1 ml) [b] Determined by ^1H NMR using 1,3,5-Trimethylbenzene as an internal standard.

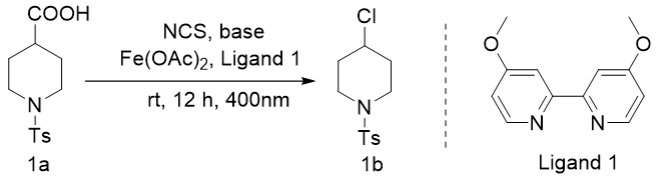
Table S5 Solvent optimization



Entry [a]	solvent	Atmosphere	Yield (%)[b]
1	acetone	N_2	trace
2	Acetone: H_2O	N_2	n.d.
3	MeCN: H_2O	N_2	48
4	THF	N_2	n.d.
5	DMSO	N_2	n.d.
6	DCM	N_2	48
7	MeCN (0.5 ml)	N_2	56
8	MeCN (1.5 ml)	N_2	43
9	MeCN (2 ml)	N_2	56

[a]Reaction conditions: **Acid** (0.1 mmol), Base (2,6-lutidine, 1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), NCS (2.1 equiv.), Solvent (1 ml), LEDs (400 nm, 6 W) [b] Determined by ^1H NMR using 1,3,5-Trimethylbenzene as an internal standard.

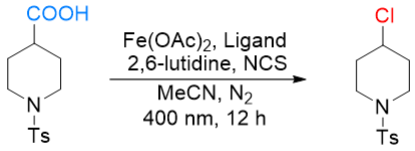
Table S6 Time optimization



Entry [a]	Base	Time (h)	Atmosphere	Yield (%)[b]
1	2,6-lutidine	2	N_2	20
2	2,6-lutidine	4	N_2	50
3	2,6-lutidine	8	N_2	52
4	**2,6-lutidine**	**12**	**N_2**	**62**
5	2,6-lutidine	16	N_2	49
6	2,6-lutidine	20	N_2	52
7	2,6-lutidine	24	N_2	49

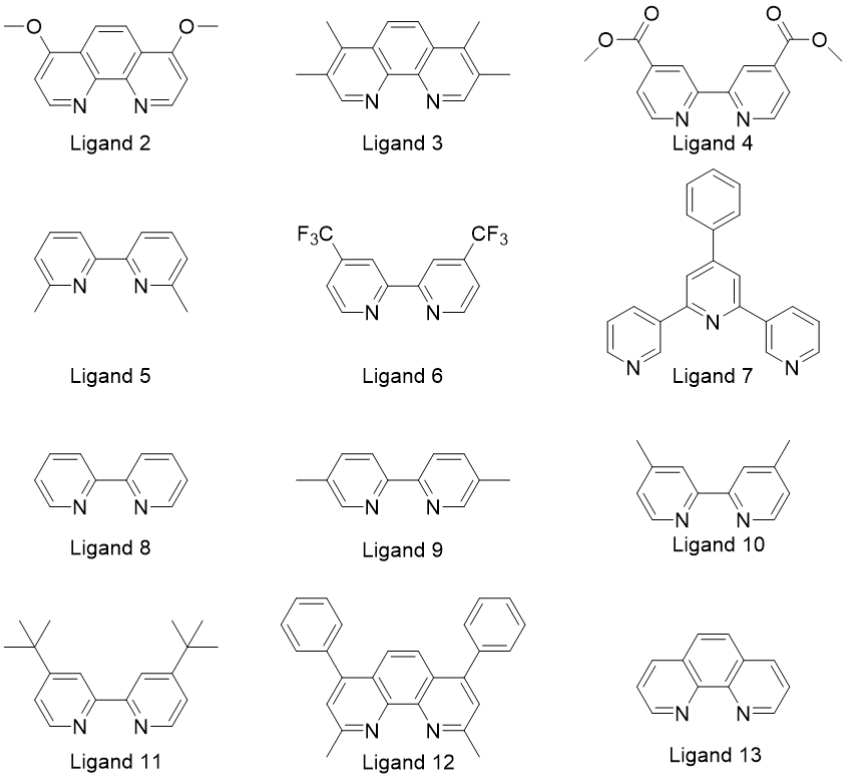
[a]Reaction conditions: **1a** (0.1 mmol), Base (1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), NCS (2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 6 W) [b]Determined by ^1H NMR using 1,3,5-Trimethylbenzene as an internal standard.

Table S7 Ligand optimization



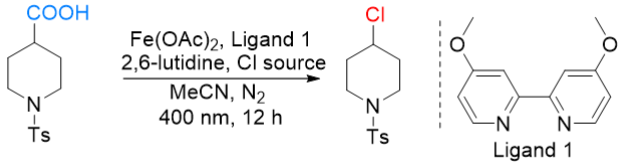
Entry [a]	Ligand	Atmosphere	Yield (%)[b]
1	Ligand 2	N_2	trace
2	Ligand 3	N_2	38
3	Ligand 4	N_2	32
4	Ligand 5	N_2	36
5	Ligand 6	N_2	19
6	Ligand 7	N_2	trace
7	Ligand 8	N_2	30
8	Ligand 9	N_2	32
9	Ligand 10	N_2	40
10	Ligand 11	N_2	36
11	Ligand 12	N_2	48

12	Ligand 13	N_2	44



[a]Reaction conditions: **Acid** (0.1 mmol), Base (2,6-lutidine, 1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), NCS (2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 6 W) [b] Determined by ^1H NMR using 1,3,5-Trimethylbenzene as an internal standard.

Table S8 Cl source optimization

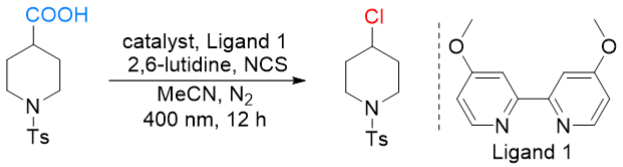


Entry [a]	Cl	Atmosphere	Yield (%)[b]
1	t-BuOCl	N_2	trace
2	NCP	N_2	35
3	1,3-dichloro-5,5-dimethylhydantoin	N_2	64
4	$ZnCl_2$	N_2	n.d.
5	Trichloroisocyanuric acid	N_2	trace
6	N-Chlorosaccharin	N_2	trace

[a]Reaction conditions: **Acid** (0.1 mmol), Base (2,6-lutidine, 1.8 equiv.), $Fe(OAc)_2$ (10 mol%),

Ligand (10 mol%), Cl source (2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 6 W) [b] Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

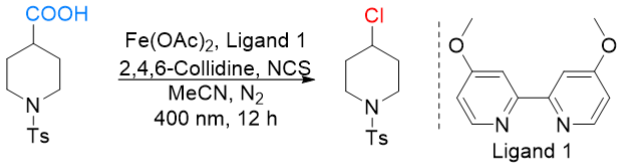
Table S9 Catalyst optimization



Entry [a]	catalyst	Yield (%)[b]
1	$FeCl_2$	trace
2	$Fe(OTf)_2$	trace
3	$Fe(OTf)_3$	52
4	$FeCl_3$	67
5	$Fe(SO_4)_3$	44
6	$Fe(OH)(OAc)_2$	56
7	$FeBr_2$	52
8	$FeBr_3$	49
9	$Fe(OH)_3$	52
10	Iron(III) i-propoxide	44
11	$Fe(acac)_2$	48

[a]Reaction conditions: **Acid** (0.1 mmol), Base (2,6-lutidine, 1.8 equiv.), [Fe] (10 mol%), Ligand (10 mol%), NCS (2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 6 W) [b] Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

Table S10 Quantity optimization

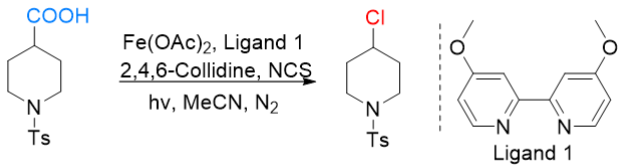


Entry [a]	NCS	Base	$Fe(OAc)_2$	Ligand	Yield (%)[b]
1	1.8 equiv.	1.8 equiv.	10 mol%	10 mol%	54
2	2.4 equiv.	1.8 equiv.	10 mol%	10 mol%	60
3	2.1 equiv.	1.5 equiv.	10 mol%	10 mol%	76
4	2.1 equiv.	2.1 equiv.	10 mol%	10 mol%	69
5	2.1 equiv.	1.8 equiv.	2 mol%	10 mol%	66
6	2.1 equiv.	1.8 equiv.	5 mol%	10 mol%	71
7	2.1 equiv.	1.8 equiv.	10 mol%	2 mol%	20

8	2.1 equiv.	1.8 equiv.	10 mol%	5 mol%	58

[a]Reaction conditions: **Acid** (0.1 mmol), Solvent (MeCN, 1 ml), LEDs (400 nm, 6 W) [b]Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

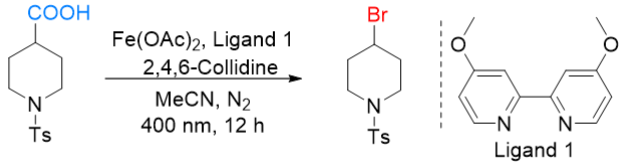
Table S11 0.4 mmol scale reaction optimization

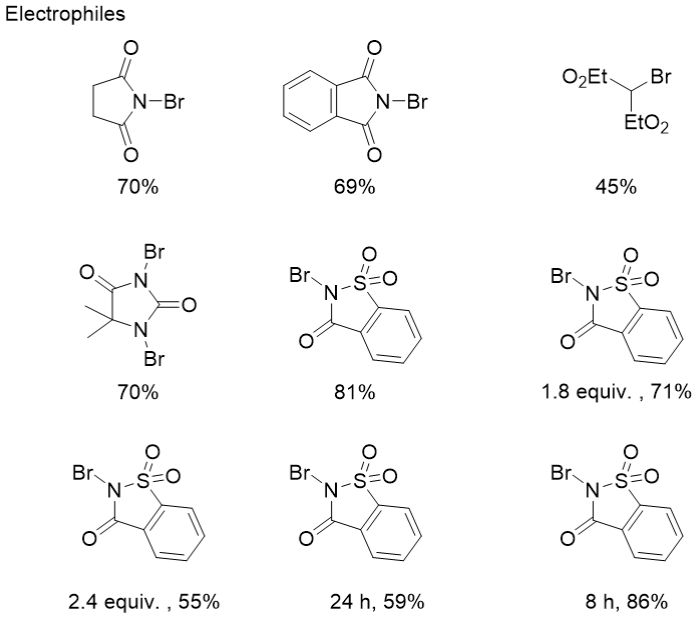


Entry [a]	Acid	Wavelength	MeCN	Time	Yield (%)[b]
1	0.2 mmol	400 nm（6W）	2 ml	12 h	43
2	0.3 mmol	400 nm（6W）	3 ml	12 h	38
3	0.4 mmol	400 nm（6W）	4 ml	12 h	49
4	0.5 mmol	400 nm（6W）	5 ml	12 h	41
5	0.2 mmol	400 nm（20W）	2 ml	12 h	39
6	0.4 mmol	400 nm（20W）	4 ml	12 h	58
7	0.2 mmol	400 nm（20W）	2 ml	10 h	52
8	0.4 mmol	400 nm（20W）	4 ml	10 h	54
9	0.2 mmol	400 nm（20W）	2 ml	8 h	61
10	0.4 mmol	400 nm（20W）	4 ml	8 h	60
11	0.4 mmol	400 nm（20W）	4 ml	6 h	67
12	0.4 mmol	400 nm（20W）	2.5 ml	6 h	71
13	**0.4 mmol**	**400 nm（20W）**	**3 ml**	**6 h**	**80**
14	0.4 mmol	400 nm（20W）	3.5 ml	6 h	74
15	0.4 mmol	400 nm（20W）	4.5 ml	6 h	69
16	0.4 mmol	400 nm（20W）	5 ml	6 h	73
17	0.4 mmol	400 nm（20W）	3 ml	5 h	60
18	0.4 mmol	400 nm（20W）	3 ml	7 h	63

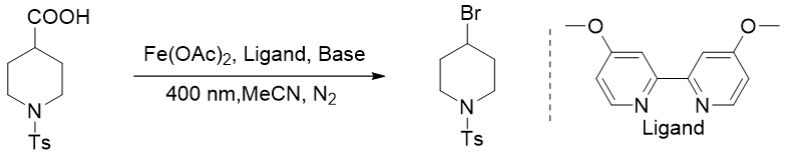
[a]Reaction conditions: Base (2,4,6-Collidine, 1.8 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), Solvent (MeCN) [b]Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

Optimization of bromination:





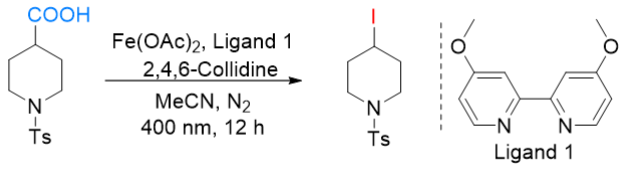
[a] Reaction conditions: **Acid** (0.1 mmol), Base (2,4,6-Collidine, 1.8 equiv.), Fe (10 mol%), Ligand (10 mol%), [Br] (N-Bromosaccharin, 2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 20 W) [b] Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

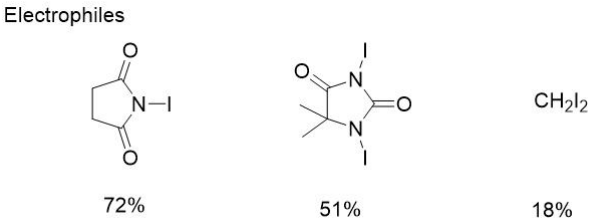


Entry [a]	Time	Wavelength	Yield (%)[b]
1	12 h	400 nm（20W）	76
2	14 h	400 nm（20W）	79
3	**16 h**	**400 nm（20W）**	**86**
4	18 h	400 nm（20W）	78

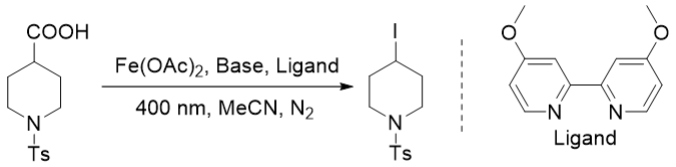
[a] Reaction conditions: **Acid** (0.4 mmol), Base (2,4,6-Collidine, 1.8 equiv.), Fe (10 mol%), Ligand (10 mol%), [Br] (N-Bromosaccharin, 2.1 equiv.), Solvent (MeCN, 4 ml) [b] Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

Optimization of iodination:



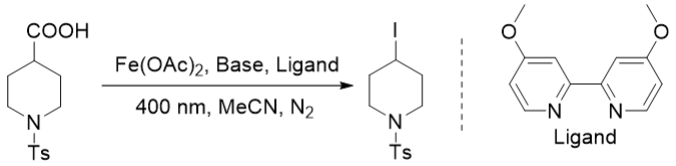


[a]Reaction conditions: **Acid** (0.1 mmol), Base (2,4,6-Collidine, 1.8 equiv.), Fe (10 mol%), Ligand (10 mol%), [I] (2.1 equiv.), Solvent (MeCN, 1 ml), LEDs (400 nm, 20 W) [b]Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.



Entry [a]	Base	NIS	Time	Yield (%)[b]
1	1.8 equiv.	1.8 equiv.	12 h	66
2	1.8 equiv.	2.4 equiv.	12 h	74
3	1.5 equiv.	2.1 equiv.	12 h	74
4	2.1 equiv.	2.1 equiv.	12 h	67

[a]Reaction conditions: **Acid** (0.1 mmol), Base (2,4,6-Collidine), $Fe(OAc)_2$ (10 mol%), Catalyst (10 mol%), Solvent (MeCN, 1 ml), LEDs (400 nm, 20 W) [b]Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

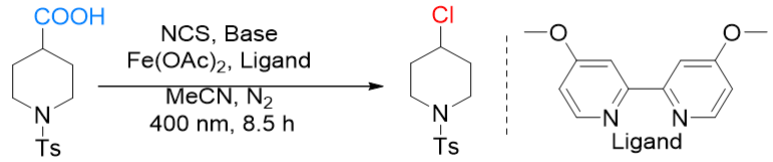


Entry [a]	Time	Wavelength	Yield (%)[b]
1	12 h	400 nm（20 W）	72
2	**14 h**	**400 nm（20 W）**	**91**
3	16 h	400 nm（20 W）	83

[a]Reaction conditions: **Acid** (0.4 mmol), NIS (2.1 equiv.), Base (2,4,6-Collidine, 1.5 equiv.), $Fe(OAc)_2$ (10 mol%), Ligand (10 mol%), Solvent (MeCN, 1 ml) [b]Determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard.

4. Experimental section

Gram scale synthesis of product 1



An oven-dried 100 mL Schlenk-tube equipped with a magnetic stir bar was charged with 1-tosylpiperidine-4-carboxylic acid (5 mmol, 1.415 g), Ligand (10 mol%, 108 mg), NCS (1.402 g, 2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to added $Fe(OAc)_2$ (10 mol%, 87 mg) and anhydride MeCN (37.5 ml). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added 2,4,6-Trimethylpyridine (1.2 ml, 1.8 equiv.) via syringe or microsyringe, respectively. Finally, the reaction mixture was stirred and irradiated for 8.5 h under LEDs (40 W, 400 nm), cooling with a fan. The reaction solution was concentrated by rotary evaporation. The residue was purified by chromatography on silica gel (DCM) to obtain the final product **1** (0.737 g, 54%) as a white solid.

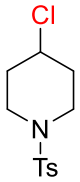
Figure S1 Photoreactor for gram scale

General procedure for chlorination

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with alkyl carboxylic acid (0.4 mmol, 1 equiv.), ligand **1** (10 mol%, 8.6 mg), *N*-chlorosuccinimide (2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to add $Fe(OAc)_2$ (10 mol%, 6.9 mg) and anhydride MeCN (3 ml). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added 2,4,6-Trimethylpyridine (96 µl, 1.8 equiv.) via syringe or microsyringe, respectively. Finally, the reaction mixture was stirred and irradiated for 6 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was then extracted with DCM, filtered, and concentrated by rotary evaporation. The

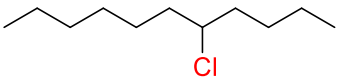
crude reaction mixture was purified by flash column chromatography through silica gel to afford the pure alkyl chloride product.

4-chloro-1-tosylpiperidine (1)



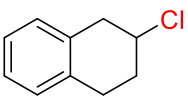
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 87% yield (66 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 2H), 7.31 – 7.26 (m, 2H), 4.10– 4.07 (m, 1H), 3.19 – 3.13 (m, 2H), 3.07 – 3.01 (m, 2H), 2.40 (s, 3H), 2.14 – 2.06 (m, 2H), 1.93 – 1.87 (m, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 133.2, 129.8, 127.6, 77.5, 77.2, 76.9, 55.4, 43.0, 34.1, 21.6.
HRMS (ESI): calcd for $C_{12}H_{16}ClNO_2SNa^+$ [M+Na] $^+$: 296.0479; found 296.0482.

5-chloroundecane (4)



The title compound was obtained after purification by column chromatography on silica gel (PE) in 80% yield (87 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.92 – 3.87 (m, 1H), 1.77 – 1.65 (m, 4H), 1.55 – 1.46 (m, 2H), 1.41 – 1.24 (m, 10H), 0.93 – 0.87 (m, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 64.5, 38.7, 38.4, 31.9, 29.1, 28.9, 26.7, 22.8, 22.5, 14.2, 14.2.
HRMS (APCI): calcd for $C_{11}H_{23}Cl$ [M+H] $^+$: 191.1561; found 191.1534.

2-chloro-1,2,3,4-tetrahydronaphthalene (5)



The title compound was obtained after purification by column chromatography on silica gel (PE: DCM= 3:1) in 58% yield (39 mg).

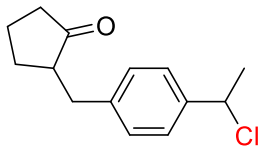
Physical state: colorless oil

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.17 – 7.07 (m, 4H), 4.48 – 4.41 (m, 1H), 3.36 – 3.30 (m, 1H), 3.15 – 3.04 (m, 2H), 2.93 – 2.85 (m, 1H), 2.34 – 2.27 (m, 1H), 2.18 – 2.09 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 134.9, 133.8, 129.2, 128.9, 126.5, 126.2, 56.7, 39.5, 32.7, 27.5.

HRMS (APCI): calcd for $C_{10}H_{11}Cl$ $(M+H)^+$: 167.0622; found 167.0670.

2-(4-(1-chloroethyl)benzyl)cyclopentan-1-one (8)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 59% yield (56 mg).

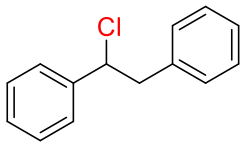
Physical state: white solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.31 (m, 2H), 7.17 – 7.14 (m, 2H), 5.10 – 5.05 (m, 1H), 3.16 – 3.10 (m, 1H), 2.57 – 2.50 (m, 1H), 2.40 – 2.26 (m, 2H), 2.14 – 2.04 (m, 2H), 2.01 – 1.89 (m, 1H), 1.88 – 1.66 (m, 4H), 1.58 – 1.47(m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.85, 140.34, 129.28, 129.15, 126.75, 58.81, 53.60, 51.07, 38.30, 35.37, 29.33, 26.58, 20.68.

HRMS (APCI): calcd for $C_{14}H_{17}O$ $(M-Cl)^+$: 202.1352; found 202.1307.

(1-chloroethane-1,2-diyl)dibenzene[7] (9)



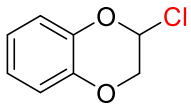
The title compound was obtained after purification by column chromatography on silica gel (PE: DCM= 1:1) in 50% yield (43 mg).

Physical state: yellow solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.21 (m, 10H), 5.06 – 5.02 (m, 1H), 3.43 – 3.31 (m, 2H).

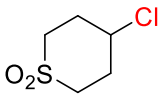
^{13}C NMR (101 MHz, Chloroform-*d*) δ 129.60, 128.72, 128.51, 127.32, 127.01, 64.32, 46.68.

1-chloro-2,3-dihydrobenzo[b][1,4]dioxine (10)

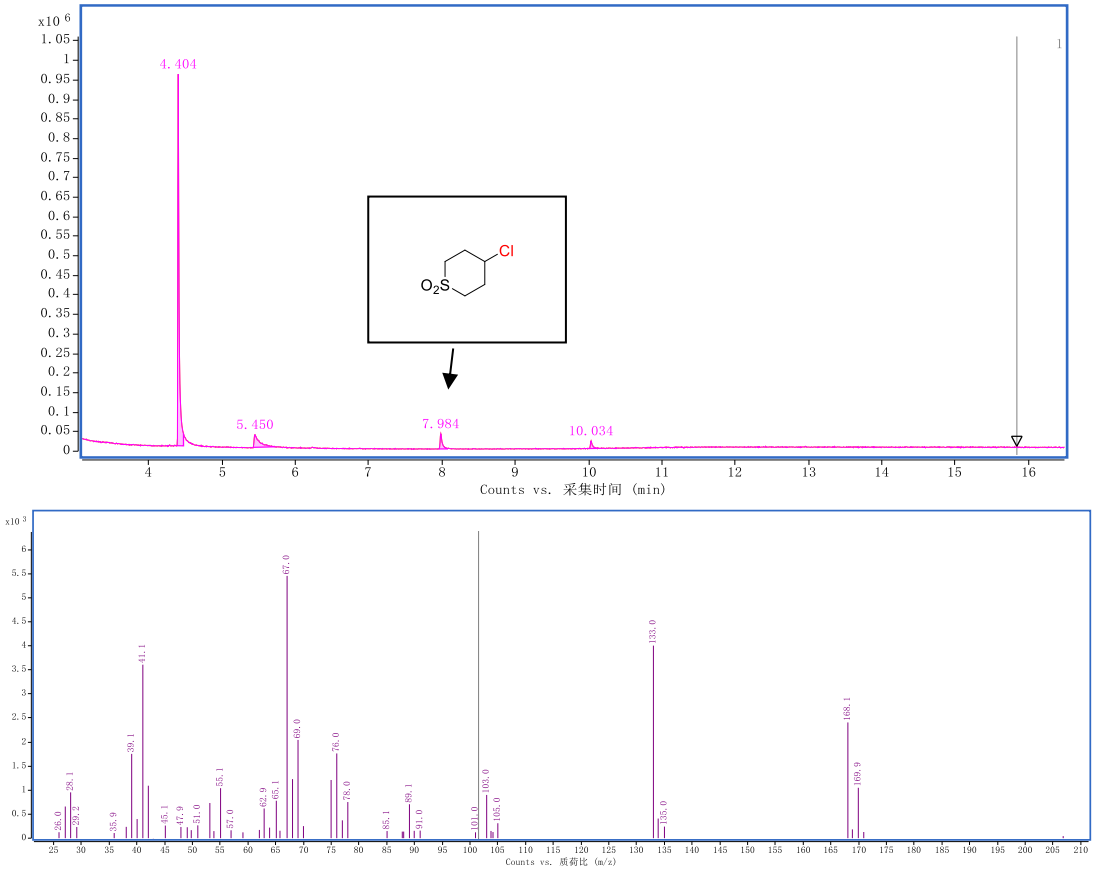


The title compound was obtained after purification by column chromatography on silica gel (DCM) in 49% yield (33 mg).
Physical state: yellow solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.97 – 6.85 (m, 4H), 5.57 – 5.55 (m, 1H), 4.15 – 4.06 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.94, 141.16, 122.58, 122.11, 117.92, 117.38, 89.18, 66.85.
HRMS (APCI): calcd for $C_8H_7O_2$ (M-Cl) $^+$: 135.0441; found 135.0444.

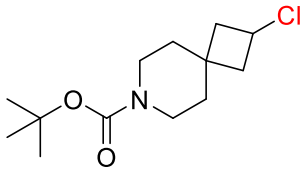
4-chlorotetrahydro-2H-thiopyran 1,1-dioxide[8] (12)



The title compound was determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard in 63% yield. And this compound also detected by GC-Ms.

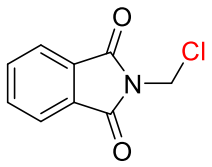


tert-butyl 2-chloro-7-azaspiro[3.5]nonane-7-carboxylate (13)



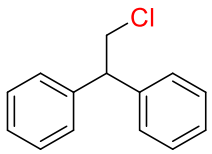
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 65% yield (33 mg).
Physical state:
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.39 – 4.35 (m, 1H), 3.33 – 3.22 (m, 4H), 2.50 – 2.42 (m, 2H), 2.09 – 2.01 (m, 2H), 1.59 – 1.54 (m, 2H), 1.50 – 1.46 (m, 2H), 1.40 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.92, 79.51, 48.63, 44.13, 40.83, 40.69, 39.37, 35.75, 34.20, 28.52.
HRMS (APCI): calcd for $C_8H_{14}ClN$ $(M+H)^+$: 160.0887; found 160.0888.

2-(chloromethyl)isoindoline-1,3-dione[9] (15)



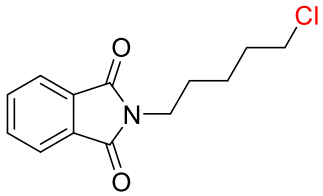
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 45% yield (35 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.91 (m, 2H), 7.81 – 7.78 (m, 2H), 5.50 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 166.10, 134.95, 131.95, 124.20, 44.84.

(2-chloroethane-1,1-diyl)dibenzene[3] (16)



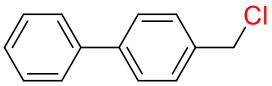
The title compound was obtained after purification by column chromatography on silica gel (PE) in 60% yield (52 mg).
Physical state: light yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.33 (m, 5H), 7.30 – 7.26 (m, 6H), 4.36 (t, *J* = 7.6 Hz, 1H), 4.14 – 4.06 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 128.85, 128.21, 127.22, 53.80, 47.38.

3-(5-chloropentyl)isoindoline-1,3-dione (18)



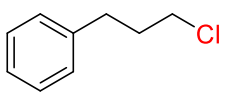
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 70% yield (70 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.80 (m, 2H), 7.74 – 7.66 (m, 2H), 3.67 (td, *J* = 7.2, 3.6 Hz, 2H), 3.50 (td, *J* = 6.8, 3.6 Hz, 2H), 1.87 – 1.62 (m, 5H), 1.54 – 1.41 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.49, 134.17, 134.03, 132.20, 123.43, 123.31, 44.83, 37.79, 32.15, 27.97, 24.23.
HRMS (APCI): calcd for $C_{13}H_{14}ClNO_2$ $(M+H)^+$: 252.0785; found 252.0787.

4-(chloromethyl)-1,1'-biphenyl[9] (21)



The title compound was obtained after purification by column chromatography on silica gel (PE) in 47% yield (38 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 – 7.59 (m, 4H), 7.51 – 7.45 (m, 4H), 7.41 – 7.37 (m, 1H), 4.66 (s, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.53, 140.63, 136.59, 129.22, 128.98, 127.70, 127.65, 127.28, 46.22.

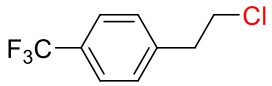
(3-chloropropyl)benzene[4] (22)



The title compound was obtained after purification by column chromatography on silica gel (PE) in 46% yield (28 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.31 (m, 2H), 7.25 – 7.21 (m, 3H), 3.57 (t, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 7.2 Hz, 2H), 2.15 – 2.07 (m, 2H).

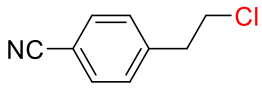
^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.85, 128.71, 128.65, 126.29, 44.41, 34.20, 32.93.

1-(2-chloroethyl)-4-(trifluoromethyl)benzene[9] (23)



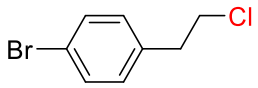
The title compound was obtained after purification by column chromatography on silica gel (PE: DCM= 1:1) in 48% yield (48 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 3.75 (t, *J* = 7.2 Hz, 2H), 3.13 (t, *J* = 7.2 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.25, 129.56, 129.38, 129.24, 125.68, 125.64, 123.01, 44.56, 38.87.

4-(2-chloroethyl)benzonitrile[9] (25)



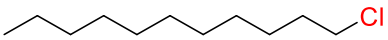
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 65% yield (43 mg).
Physical state: light yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 3.74 (t, *J* = 6.8 Hz, 2H), 3.12 (t, *J* = 6.8 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.62, 132.45, 129.82, 118.90, 110.95, 44.21, 38.91.

1-bromo-4-(2-chloroethyl)benzene[9] (27)



The title compound was obtained after purification by column chromatography on silica gel (PE) in 50% yield (44 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.51 – 7.41 (m, 2H), 7.16 – 7.07 (m, 2H), 3.70 (td, *J* = 7.2, 2.2 Hz, 2H), 3.02 (td, *J* = 7.2, 2.1 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 137.18, 131.88, 131.84, 130.75, 130.58, 120.98, 44.81, 38.60.

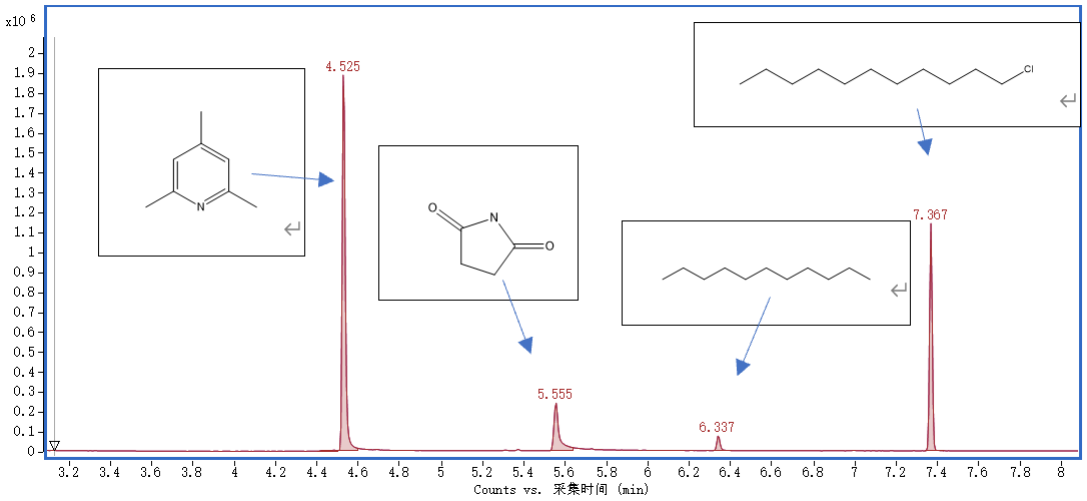
1-chloroundecane[10] (29)

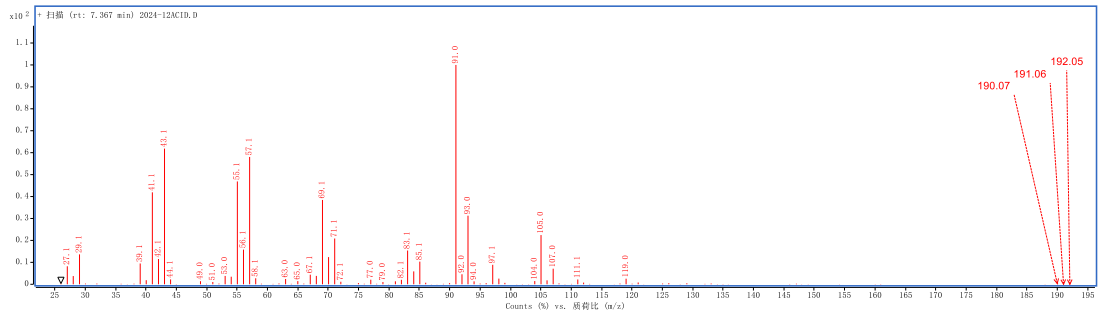


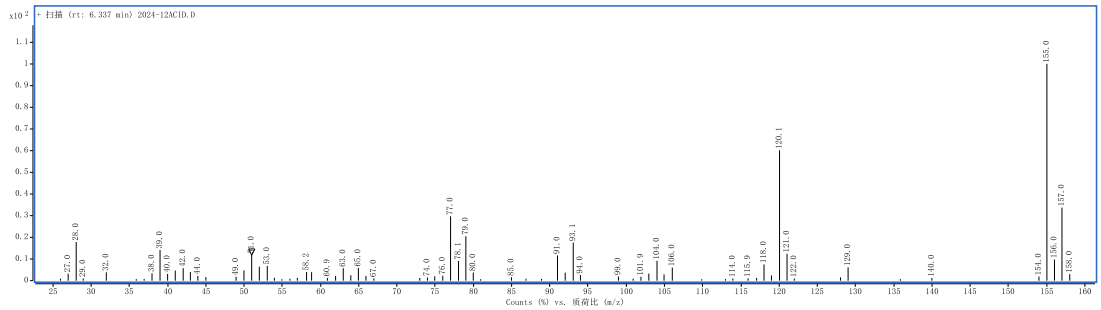
The title compound was determined by ^{1}H NMR using 1,3,5-Trimethylbenzene as an internal standard in 60% yield. And this compound also detected by GC-Ms.

^{1}H NMR (400 MHz, Chloroform-d) δ 3.53 (t, J = 6.8 Hz, 2H), 1.80 – 1.73 (m, 2H), 1.42 (t, J = 7.4 Hz, 2H), 1.33 – 1.20 (m, 14H), 0.88 (t, J = 6.6 Hz, 3H).

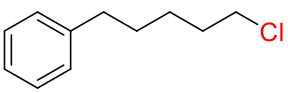
^{13}C NMR (101 MHz, Chloroform-d) δ 45.40, 32.86, 32.10, 29.78, 29.75, 29.66, 29.52, 29.09, 27.09, 22.88, 14.31.





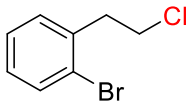


(4-chlorobutyl)benzene[7,9] (32)



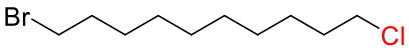
The title compound was obtained after purification by column chromatography on silica gel (PE) in 50% yield (34 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 3.59 – 3.51 (m, 2H), 2.70 – 2.58 (m, 2H), 1.85 – 1.73 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.01, 128.54, 126.05, 77.52, 77.20, 76.88, 45.06, 35.26, 32.25, 28.73.

1-bromo-2-(2-chloroethyl)benzene[11] (33)



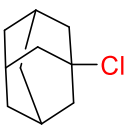
The title compound was obtained after purification by column chromatography on silica gel (PE) in 54% yield (47 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-d) δ 7.57 (d, J = 7.5 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.16 – 7.11 (m, 1H), 3.76 (t, J = 7.4 Hz, 2H), 3.22 (t, J = 7.4 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-d) δ 137.41, 133.12, 131.49, 128.83, 127.67, 124.56, 43.32, 39.50.

2-bromo-10-chlorodecane (36)



The title compound was obtained after purification by column chromatography on silica gel (PE) in 20% yield (47 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.52 (t, *J* = 6.8 Hz, 2H), 3.40 (t, *J* = 6.8 Hz, 2H), 1.87 – 1.72 (m, 4H), 1.44 – 1.40 (m, 4H), 1.30 (s, 8H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 45.31, 34.14, 32.99, 32.81, 29.51, 29.48, 29.01, 28.88, 28.32, 27.03.
HRMS (APCI): calcd for $C_{10}H_{20}Br$ (M-Cl) $^{+}$: 219.0742; found 219.0691.

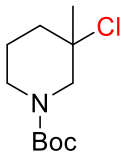
1-chloroadamantane[6] (37)



The title compound was obtained after purification by column chromatography on silica gel

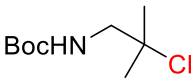
(PE) in 44% yield (30 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.14 (s, 9H), 1.68 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 69.11, 47.93, 35.77, 31.90.

tert-butyl 3-chloro-3-methylpiperidine-1-carboxylate (39)



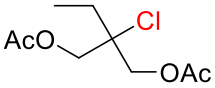
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 38% yield (35 mg).
Physical state: light yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.96 – 3.61 (m, 2H), 3.27 – 2.96 (m, 2H), 2.01 – 1.96 (m, 1H), 1.91 – 1.66 (m, 3H), 1.55 (s, 3H), 1.45 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.83, 79.93, 67.67, 40.40, 29.20, 28.55, 28.55.
HRMS (APCI): calcd for $C_6H_{12}ClN$ (M-Boc) $^{+}$: 133.0652; found 133.0612.

tert-butyl (2-chloro-2-methylpropyl)carbamate (40)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 63% yield (52 mg).
Physical state: yellow solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.00 (s, 1H), 3.34 (d, *J* = 6.4 Hz, 2H), 1.54 (s, 6H), 1.44 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.18, 79.72, 71.14, 52.89, 29.90, 28.50.
HRMS (APCI): calcd for $C_9H_{18}NO_2$ (M-Cl) $^{+}$: 172.1332; found 172.1326.

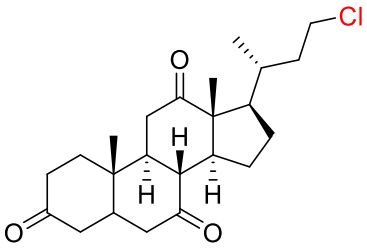
2-chloro-2-ethylpropane-1,3-diyl diacetate (41)



The title compound was obtained after purification by column chromatography on silica gel (PE: EA= 5:1) in 71% yield (63 mg).
Physical state: colorless oil

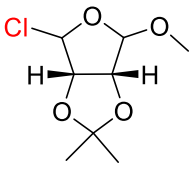
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.27 – 4.13 (m, 4H), 2.03 (s, 6H), 1.80 (q, *J* = 7.6 Hz, 2H), 0.99 (t, *J* = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.16, 70.08, 66.05, 29.02, 20.71, 7.87.
HRMS (APCI): calcd for $C_9H_{15}ClO_4$ $(M+H)^+$: 223.0731; found 223.0724.

(8R,9S,10S,13R,14S,17R)-17-((R)-4-chlorobutan-2-yl)-10,13-dimethyldodecahydro-3H-cyclopenta[a]phenanthrene-3,7,12(2H,4H)-trione (44)



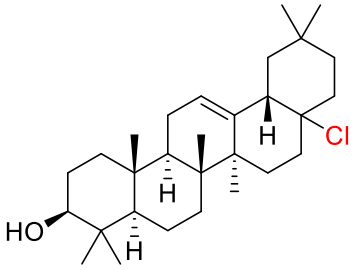
The title compound was obtained after purification by column chromatography on silica gel (PE: EA= 3:1) in 55% yield (86 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.65 – 3.59 (m, 1H), 3.56 – 3.45 (m, 1H), 3.00 – 2.79 (m, 4H), 2.73 (s, 1H), 2.39 – 2.07 (m, 7H), 2.05 – 1.77 (m, 5H), 1.64 – 1.42 (m, 3H), 1.41 – 1.16 (m, 5H), 1.07 (s, 3H), 0.85 – 0.83 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 212.08, 209.19, 208.80, 57.10, 51.91, 49.10, 46.94, 45.10, 45.10, 43.39, 42.90, 38.76, 38.52, 36.59, 36.14, 35.39, 33.80, 29.72, 27.82, 25.25, 22.02, 18.54, 11.95.
HRMS (APCI): calcd for $C_{23}H_{33}O_3$ $[M-Cl]^+$: 357.2414; found 357.2424

(3aS,6aR)-4-chloro-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-d][1,3]dioxole (45)



The title compound was obtained after purification by column chromatography on silica gel (PE: EA= 10:1 then PE: EA= 3: 1) in 31% yield (26 mg).
Physical state: light yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.05 (s, 1H), 5.17 (s, 1H), 5.02 (d, *J* = 5.6 Hz, 1H), 4.75 (d, *J* = 5.6 Hz, 1H), 3.41 (s, 3H), 1.43 (s, 3H), 1.31 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 113.45, 112.61, 97.07, 88.65, 83.99, 55.47, 26.44, 25.23.
HRMS (APCI): calcd for $C_8H_{13}O_4$ $[M-Cl]^+$: 173.0808; found 173.0810

(3S,4aR,6aR,6bS,12aS,14aR,14bR)-8a-chloro-4,4,6a,6b,11,11,14b-heptamethyl-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-ol (46)



The title compound was obtained after purification by column chromatography on silica gel (PE then PE: EA= 5:1) in 45% yield (80 mg).

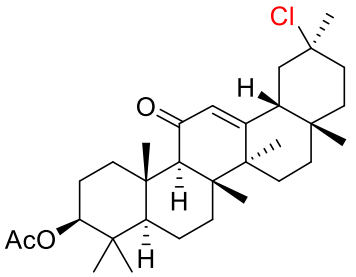
Physical state: white solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.53 – 5.50 (m, 1H), 3.22 (dd, *J* = 10.8, 5.6 Hz, 1H), 2.10 – 1.84 (m, 7H), 1.76 – 1.47 (m, 10H), 1.38 – 1.23 (m, 5H), 1.00 (s, 4H), 0.96 (d, *J* = 4.8 Hz, 6H), 0.90 (s, 3H), 0.87 (s, 6H), 0.79 – 0.75 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 140.43, 129.23, 125.44, 116.72, 79.15, 55.64, 47.53, 41.28, 39.73, 38.96, 38.76, 37.17, 35.43, 33.98, 29.61, 29.45, 29.08, 28.54, 28.42, 28.27, 27.45, 27.43, 23.66, 21.24, 18.55, 17.02, 16.14, 15.84.

HRMS (APCI): calcd for $C_{29}H_{47}O$ [M-Cl] $^{+}$: 411.3621; found 411.3609.

(3S,6aR,6bS,8aS,12aS,14aR,14bS)-11-chloro-4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-yl acetate (47)



The title compound was obtained after purification by column chromatography on silica gel (PE then PE: EA= 5:1) in 84% yield (169 mg).

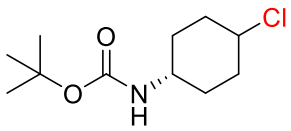
Physical state: white solid

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.63 (s, 1H), 4.48 (dd, *J* = 11.6, 4.8 Hz, 1H), 2.80 – 2.72 (m, 1H), 2.50 – 2.29 (m, 2H), 2.02 (s, 3H), 1.96 – 1.71 (m, 5H), 1.70 – 1.53 (m, 8H), 1.48 – 1.28 (m, 6H), 1.19 – 1.08 (m, 7H), 1.07 – 0.95 (m, 2H), 0.91 – 0.82 (m, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 199.96, 199.93, 171.07, 171.02, 168.55, 167.65, 128.79, 80.66, 71.73, 70.33, 61.83, 61.80, 55.09, 55.03, 49.32, 47.42, 47.12, 46.21, 45.53, 45.50, 43.35,

43.32, 38.89, 38.84, 38.14, 38.01, 37.03, 36.43, 36.35, 34.19, 32.78, 32.74, 32.22, 31.92, 28.23, 28.15, 27.19, 26.55, 26.43, 26.35, 23.65, 23.48, 21.43, 18.79, 17.47, 16.80, 16.52.
HRMS (APCI): calcd for $C_{31}H_{47}O_3$ [M-Cl] $^+$: 468.3542; found 468.3553.

tert-butyl (4-chlorocyclohexyl)carbamate (50)

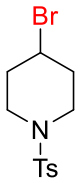


The title compound was obtained after purification by column chromatography on silica gel (DCM) in 27% yield (25 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.58 – 4.26 (m, 2H), 3.47 (s, 1H), 2.18 – 2.14 (m, 1H), 2.08 – 1.91 (m, 2H), 1.90 – 1.63 (m, 5H), 1.42 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.34, 79.43, 58.39, 35.42, 32.96, 32.43, 28.58, 28.56, 27.89, 24.89.
HRMS (APCI): calcd for $C_6H_{12}ClN$ [M-Boc] $^+$: 133.0652; found 133.0610.

General procedure for bromination

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with alkyl carboxylic acid (0.4 mmol, 1 equiv.), ligand (10 mol%, 8.6 mg), N-Bromosaccharin (2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to add $Fe(OAc)_2$ (10 mol%, 6.9 mg) and anhydride MeCN (4 ml). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added 2,4,6-Trimethylpyridine (96 μl, 1.8 equiv.) via syringe or microsyringe, respectively. Finally, the reaction mixture was stirred and irradiated for 16 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was then extracted with DCM, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash column chromatography through silica gel to afford the pure alkyl chloride products.

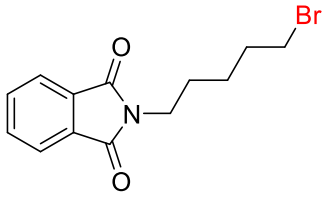
1-bromo-1-tosylpiperidine (2)



The title compound was obtained after purification by column chromatography on silica gel (PE: DCM= 1:1) in 81% yield (103 mg).
Physical state: white solid

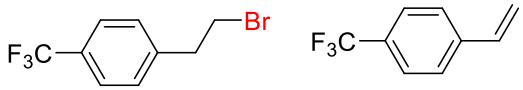
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.63 (m, 2H), 7.34 – 7.32 (m, 2H), 4.26 – 4.22 (m, 1H), 3.22 – 3.16 (m, 2H), 3.12 – 3.06 (m, 2H), 2.44 (s, 3H), 2.22 – 2.14 (m, 2H), 2.08 – 2.00 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.88, 133.43, 129.93, 127.75, 47.98, 43.96, 34.88, 21.72.
HRMS (ESI): calcd for $C_{12}H_{16}BrNO_2S$ $[M+Na]^+$: 339.9977; found 339.9976.

N-(5-bromopentyl)phthalimide[12] (19)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 65% yield (77 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.83 – 7.78 (m, 2H), 7.70 – 7.66 (m, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 3.36 (t, *J* = 6.8 Hz, 2H), 1.91 – 1.83 (m, 2H), 1.72 – 1.64 (m, 2H), 1.50 – 1.42 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.44, 134.01, 132.18, 123.28, 37.73, 33.49, 32.28, 27.81, 25.48.

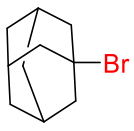
2-[4-(trifluoromethyl)phenyl]ethyl bromide[13] (24)



24'

The title compound was obtained after purification by column chromatography on silica gel (PE) in 42% yield with an unseparated byproduct **24'**.
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-d) δ 7.65 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.4 Hz, 2H), 5.15 (dd, J = 11.0, 5.0 Hz, 1H), 4.10 – 4.06 (m, 1H), 4.02 – 3.90 (m, 1H).

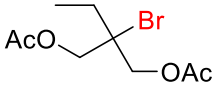
1-Bromoadamantane[14] (38)



The title compound was obtained after purification by column chromatography on silica gel

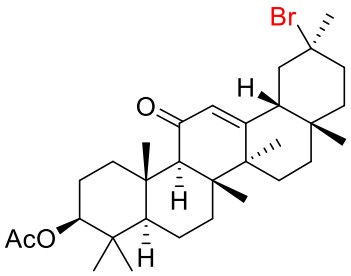
(PE) in 73% yield (62 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.36 (s, 6H), 2.10 (s, 3H), 1.73 (s, 6H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 66.98, 49.50, 35.71, 32.78.

1-bromo-2-ethylpropane-1,3-diyl diacetate (42)



The title compound was obtained after purification by column chromatography on silica gel (PE:EA=10:1) in 94% yield (100 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.47 – 4.40 (m, 2H), 4.36 – 4.28 (m, 2H), 2.15 – 2.12 (m, 6H), 2.01 – 1.91 (m, 2H), 1.15 – 1.10 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 170.29, 66.72, 66.55, 29.88, 20.88, 9.28.
HRMS (APCI): Calcd for $C_6H_{12}ClN$ [M-Boc] $^{+}$: 133.0652; found 133.0610.

(3S,6aR,6bS,8aS,11S,12aS,14aR,14bS)-11-bromo-4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-yl acetate (48)

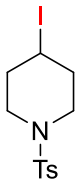


The title compound was obtained after purification by column chromatography on silica gel (PE then DCM) in 27% yield (59 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.67 (s, 1H), 4.55 – 4.48 (m, 1H), 2.83 – 2.73 (m, 1H), 2.61 – 2.50 (m, 1H), 2.41 – 2.29 (m, 1H), 2.04 (s, 3H), 1.91 – 1.79 (m, 5H), 1.75 – 1.53 (m, 8H), 1.52 – 1.37 (m, 6H), 1.34 – 1.25 (m, 5H), 1.20 – 1.10 (m, 5H), 1.09 – 0.99 (m, 2H), 0.95 – 0.91 (m, 2H), 0.88 – 0.77 (m, 7H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 200.00, 171.18, 168.46, 129.02, 80.79, 70.53, 61.95, 55.23, 48.29, 47.74, 45.61, 43.46, 39.01, 38.25, 37.98, 37.61, 37.16, 35.91, 32.92, 32.11, 31.81, 31.63, 29.87, 28.28, 28.24, 27.11, 26.53, 23.76, 23.50, 21.48, 18.90, 17.58, 16.87, 16.82, 16.59.
HRMS (APCI): calcd for $C_6H_{12}ClN$ [M-Boc] $^{+}$: 133.0652; found 133.0610.

General procedure for iodination

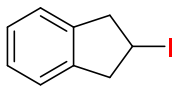
An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with alkyl carboxylic acid (0.4 mmol, 1 equiv.), ligand (10 mol%, 8.6 mg), N-Iodosuccinimide (2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to added $Fe(OAc)_2$ (10 mol%, 6.9 mg) and anhydride MeCN (4 ml). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added 2,4,6-Trimethylpyridine (80 μl, 1.5 equiv.) via syringe or microsyringe, respectively. Finally, the reaction mixture was stirred and irradiated for 14 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was then extracted with DCM, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash column chromatography through silica gel to afford the pure alkyl chloride products.

3-iodo-1-tosylpiperidine (3)



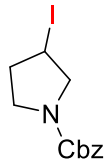
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 79% yield (115 mg).
Physical state: white solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 6.4 Hz, 2H), 7.33 (d, *J* = 6.6 Hz, 2H), 4.32 – 4.25 (m, 1H), 3.21 – 3.12 (m, 2H), 3.00 – 2.93 (m, 2H), 2.43 (s, 3H), 2.15 – 2.06 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.90, 133.43, 129.94, 127.77, 45.83, 36.65, 25.72, 21.74.
HRMS (ESI): calcd for $C_{12}H_{16}INO_2SNa^+$ $[M+Na]^+$: 387.9833; found 387.9838.

2-iodo-2,3-dihydro-1H-indene[15] (6)



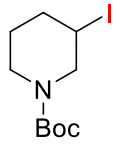
The title compound was obtained after purification by column chromatography on silica gel (PE: DCM= 1:1) in 83% yield (81 mg).
Physical state: yellow solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.30 – 7.19 (m, 4H), 4.76 – 4.68 (m, 1H), 3.53 – 3.36 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-d) δ 140.37, 127.17, 124.80, 59.33, 44.07.

benzyl 3-iodopyrrolidine-1-carboxylate (7)



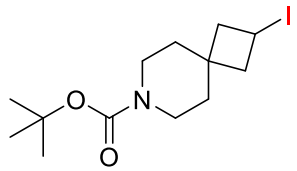
The title compound was obtained after purification by column chromatography on silica gel (PE: DCM= 1:1) in 83% yield (81 mg).
Physical state: purple oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.30 (m, 5H), 5.17 – 5.14 (m, 2H), 4.40 – 4.34 (m, 1H), 3.94 – 3.75 (m, 2H), 3.70 – 3.62 (m, 1H), 3.56 – 3.47 (m, 1H), 2.28 – 2.27 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.76, 136.81, 128.62, 128.15, 127.99, 67.14, 57.35, 45.46, 37.63, 19.62.
HRMS (APCI): calcd for $C_{12}H_{14}INO_2$ $[M+H]^+$: 332.0142; found 332.0144.

tert-butyl 3-iodopiperidine-1-carboxylate[16] (11)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 78% yield (97 mg).
Physical state: yellow liquid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.19 – 4.12 (m, 1H), 4.04 – 3.85 (m, 1H), 3.78 – 3.65 (m, 1H), 3.12 (s, 1H), 2.31 – 2.07 (m, 2H), 2.06 – 1.85 (m, 2H), 1.77 – 1.67 (m, 1H), 1.45 (s, 9H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.41, 80.33, 53.36, 45.62, 28.57, 28.22.

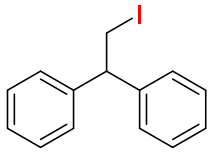
tert-butyl 2-iodo-7-azaspiro[3.5]nonane-7-carboxylate[15] (14)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 60% yield (84 mg).
Physical state: brown solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.54 – 4.41 (m, 1H), 3.36 – 3.21 (m, 4H), 2.71 – 2.59 (m, 2H), 2.47 – 2.35 (m, 2H), 1.68 – 1.62 (m, 2H), 1.54 – 1.51 (m, 2H), 1.41 (s, 9H).

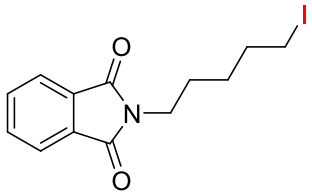
^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.94, 79.58, 46.39, 39.88, 35.22, 28.55, 9.67.

(2-iodoethane-1,1-diyl)dibenzene[17] (17)



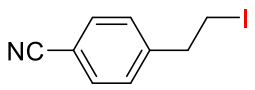
The title compound was obtained after purification by column chromatography on silica gel (DCM) in 83% yield (102 mg).
Physical state: yellow solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.33 (m, 4H), 7.32 – 7.25 (m, 6H), 4.39 (t, *J* = 8.0 Hz, 1H), 3.79 (d, *J* = 8.0 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.63, 128.81, 127.83, 127.16, 54.43, 9.68.

3-(5-iodopentyl)isoindoline-1,3-dione (20)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 83% yield (114 mg).
Physical state: yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.80 (m, 2H), 7.70 – 7.67 (m, 2H), 3.66 (t, *J* = 7.2 Hz, 2H), 3.14 (t, *J* = 7.0 Hz, 2H), 1.89 – 1.79 (m, 2H), 1.72 – 1.63 (m, 2H), 1.46 – 1.38 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.45, 134.02, 132.17, 123.29, 37.73, 32.98, 27.79, 27.58, 6.54.
HRMS (APCI): calcd for $C_{13}H_{14}INO_2$ $[M+H]^+$: 344.0142; found 344.0143.

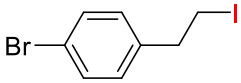
4-(2-iodoethyl)benzonitrile[18] (26)



The title compound was obtained after purification by column chromatography on silica gel (DCM) in 88% yield (90 mg).

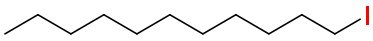
Physical state: yellow solid
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 (d, *J* = 8.4 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 3.37 – 3.32 (m, 2H), 3.24 – 3.20 (m, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 145.74, 132.49, 129.29, 110.76, 76.88, 39.76, 4.29.

1-bromo-4-(2-iodoethyl)benzene[19] (28)



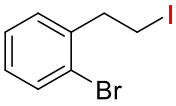
The title compound was obtained after purification by column chromatography on silica gel (PE) in 44% yield (55 mg).
Physical state: yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 3.32 (t, *J* = 7.6 Hz, 2H), 3.13 (t, *J* = 7.6 Hz, 2H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.58, 131.90, 130.23, 120.92, 39.67, 5.13.

2-Iodoundecane[20] (31)



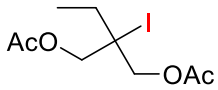
The title compound was obtained after purification by column chromatography on silica gel (PE) in 65% yield (73 mg).
Physical state: colorless oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.18 (t, *J* = 7.0 Hz, 2H), 1.87 – 1.78 (m, 2H), 1.40 – 1.35 (m, 2H), 1.32 – 1.26 (m, 14H), 0.90 – 0.86 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 33.74, 32.07, 30.68, 29.75, 29.73, 29.60, 29.50, 28.73, 22.85, 14.30, 7.46.

2-bromo-2-(2-iodoethyl)benzene[21] (34)



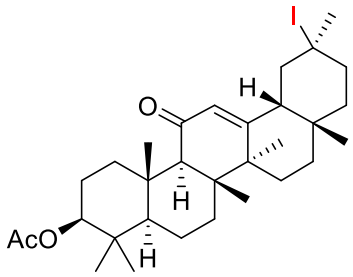
The title compound was obtained after purification by column chromatography on silica gel (PE) in 56% yield (69 mg).
Physical state: yellow oil
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.48 (m, 1H), 7.35 – 7.07 (m, 3H), 3.43 – 3.24 (m, 4H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.92, 133.17, 130.84, 128.77, 127.74, 124.20, 40.67, 3.49.

3-ethyl-2-iodopropane-1,3-diyl diacetate (43)



The title compound was obtained after purification by column chromatography on silica gel (PE: EA= 3:1) in 45% yield (57 mg).
Physical state: purple oil
^{1}H NMR (400 MHz, Chloroform-d) δ 4.31 – 4.16 (m, 4H), 2.08 (s, 6H), 1.84 (d, J = 7.4 Hz, 2H), 1.03 (t, J = 7.4 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.19, 68.69, 52.48, 31.56, 20.90, 11.67.
HRMS (APCI): calcd for $C_9H_{15}IO_4$ $[M+H]^+$: 315.0088; found 315.0028.

(3S,6aR,6bS,8aS,11S,12aS,14aR,14bS)-11-iodo-4,4,6a,6b,8a,11,14b-heptamethyl-14-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,14,14a,14b-icosahydropicen-3-yl acetate (49)



The title compound was obtained after purification by column chromatography on silica gel (PE then DCM) in 42% yield (100 mg).
Physical state: white solid
1H NMR (400 MHz, Chloroform-d) δ 5.67 (s, 1H), 4.99 (s, 1H), 4.51 (dd, J = 11.6, 4.9 Hz, 1H), 2.80 – 2.71 (m, 1H), 2.62 – 2.55 (m, 1H), 2.39 – 2.32 (m, 1H), 2.04 (s, 3H), 1.95 – 1.77 (m, 3H), 1.77 – 1.68 (m, 1H), 1.66 – 1.53 (m, 6H), 1.50 – 1.37 (m, 4H), 1.34 – 1.26 (m, 1H), 1.20 (d, J = 10.2 Hz, 5H), 1.14 (d, J = 10.2 Hz, 4H), 1.08 – 0.96 (m, 3H), 0.87 (d, J = 3.0 Hz, 9H).
13C NMR (101 MHz, Chloroform-d) δ 200.58, 171.23, 132.59, 128.49, 128.44, 126.37, 126.34, 80.88, 61.53, 55.36, 51.13, 44.55, 38.99, 38.22, 37.17, 36.68, 33.43, 31.54, 28.26, 28.23, 27.73, 27.14, 26.10, 23.76, 23.43, 21.49, 20.67, 18.75, 17.59, 16.94, 16.86, 16.83.
HRMS (APCI): calcd for $C_{13}H_{14}INO_2$ $[M+H]^+$: 344.0142; found 344.0143.

5. Mechanistic studies

Carbon radical trapping experiments

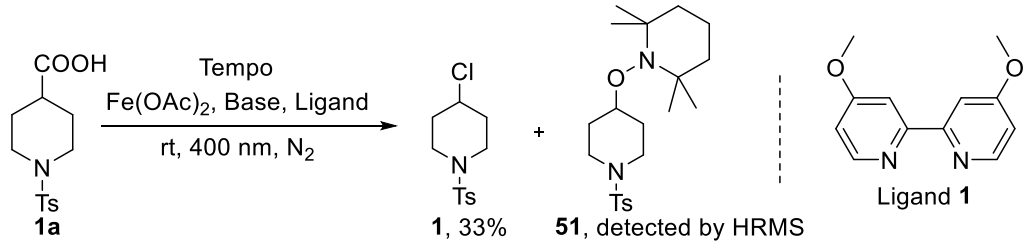
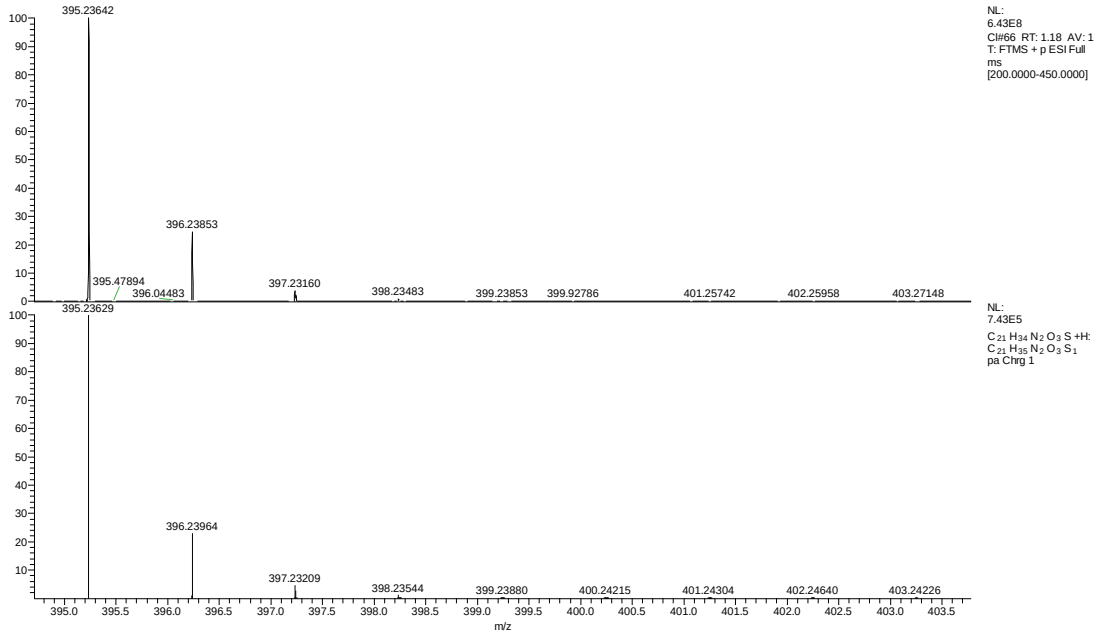
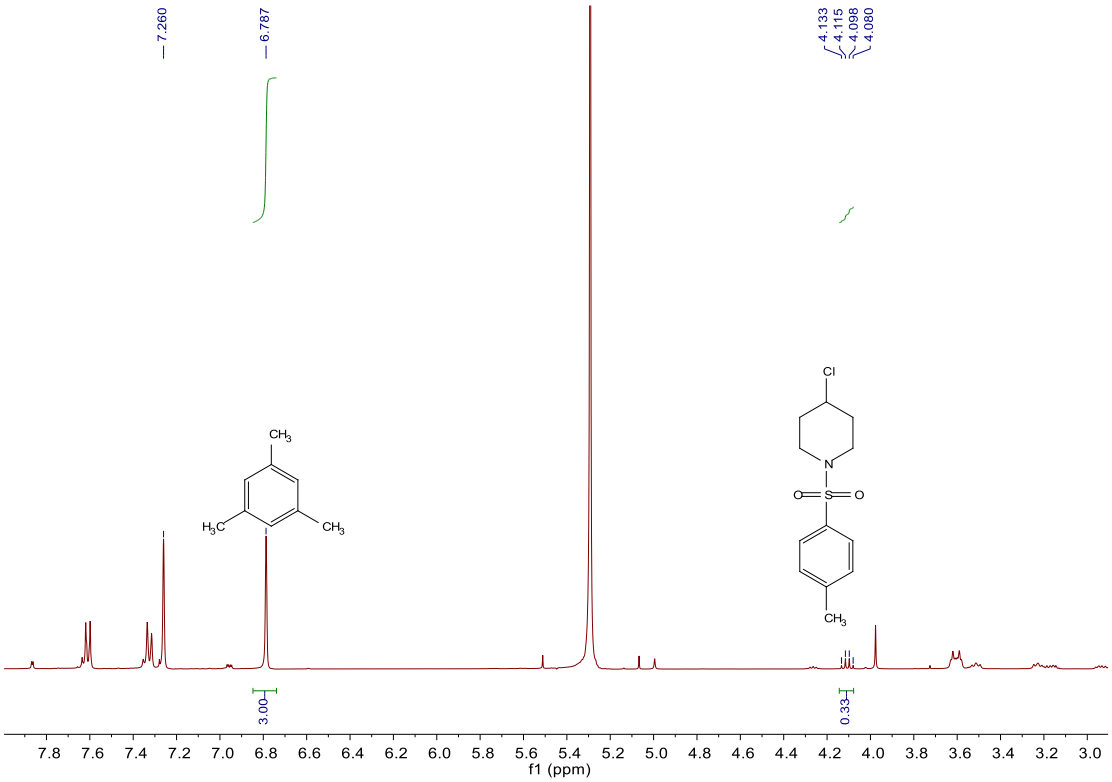


Figure S2 Carbon radical trapping experiment with NCS

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with 1-tosylpiperidine-4-carboxylic acid (0.1 mmol, 28.3 mg), ligand **1** (10 mol%, 2.16 mg), TEMPO (31.2 mg, 2 equiv.), NCS (20 mg, 2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to add $Fe(OAc)_2$ (10 mol%, 1.74 mg). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added degassed MeCN (1 mL) and 2,4,6-Collidine (24 μL, 1.8 equiv.) via syringe or micro-syringe, respectively. Finally, the reaction mixture was stirred and irradiated for 6 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was washed with water and extracted with DCM (3×10 mL), the organic layer was dried over Na_2SO_4, filtered, and washed through a short plug of silica with DCM to remove the iron species and concentrated by rotary evaporation. The reaction mixture was then detected by ^1H NMR using 1,3,5-Trimethylbenzene (0.1 mmol) as an internal standard and found that 33% of the product was formed. Compound **51** was detected by HRMS.



HRMS-ESI-TOF of compound **51**



Crude mixture of ^{1}H NMR of product **1**

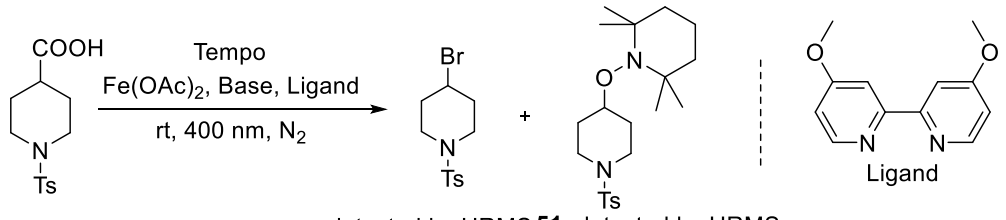
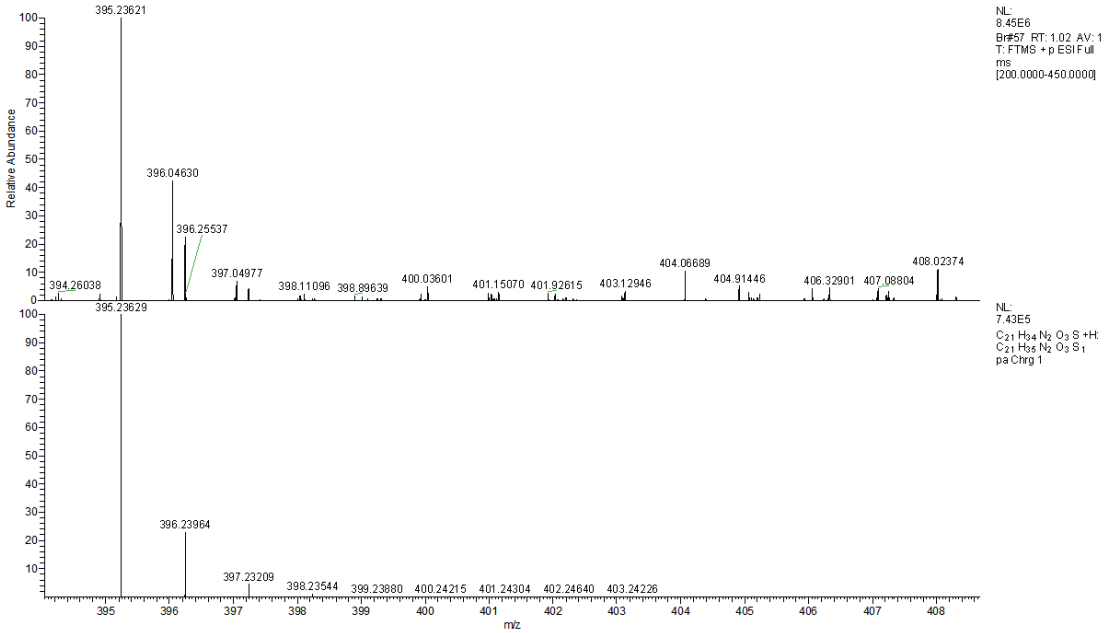
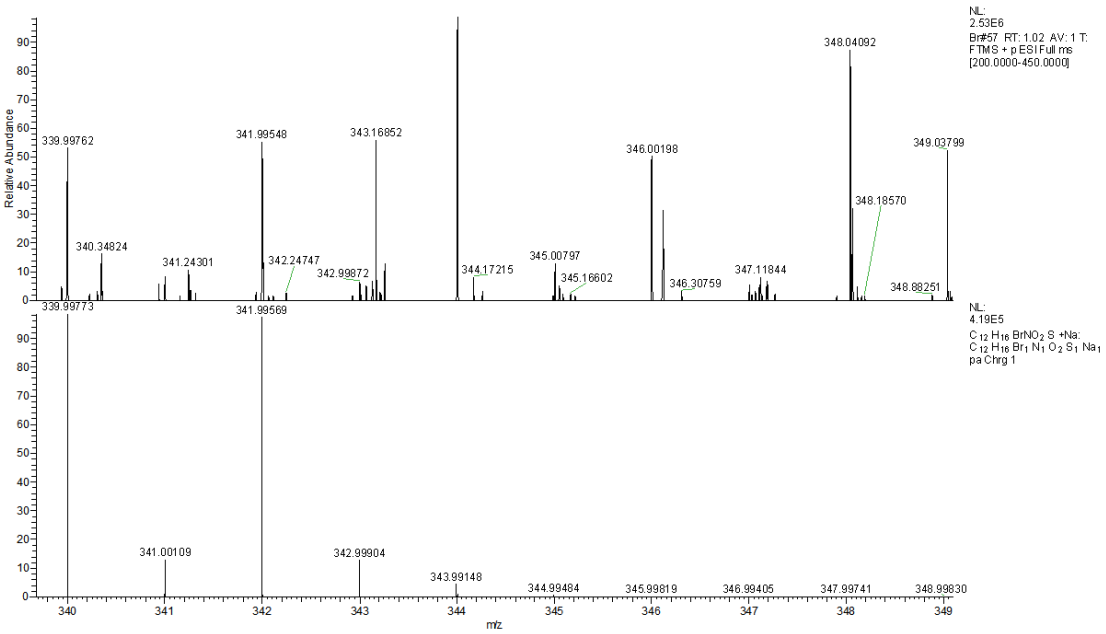


Figure S3 Carbon radical trapping experiment with N-Bromosaccharin

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with 1-tosylpiperidine-4-carboxylic acid (0.1 mmol, 28.3 mg), ligand (10 mol%, 2.16 mg), TEMPO (31.2 mg, 2 equiv.), N-Bromosaccharin (55 mg, 2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to add $Fe(OAc)_2$ (10 mol%, 1.74 mg). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added degassed MeCN (1 mL) and 2,4,6-Collidine (24 μL, 1.8 equiv.) via syringe or micro-syringe, respectively. Finally, the reaction mixture was stirred and irradiated for 16 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was washed with water and extracted with DCM (3×10 mL), the organic layer was dried over Na_2SO_4, filtered, and washed through a short plug of silica with DCM to remove the iron species and concentrated by rotary evaporation. The reaction mixture was then detected by HRMS and found that product **2** and TEMPO-adduct **51** were detected.



HRMS-ESI-TOF of compound **51**



HRMS-ESI-TOF of product **2**

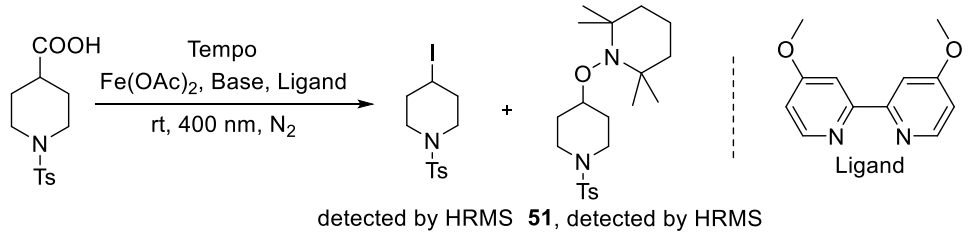
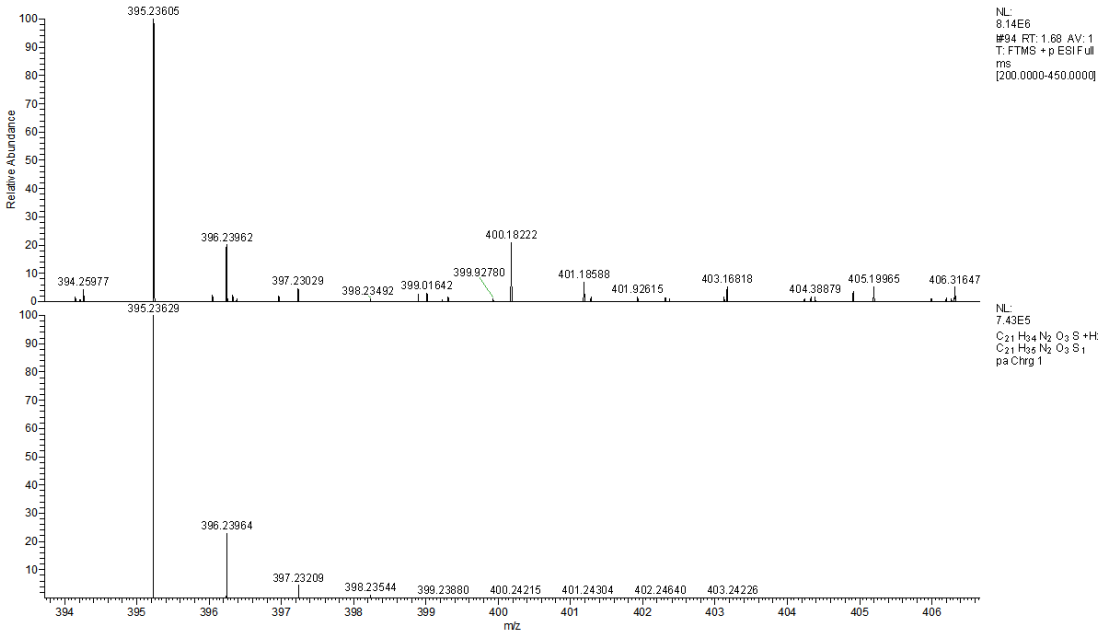
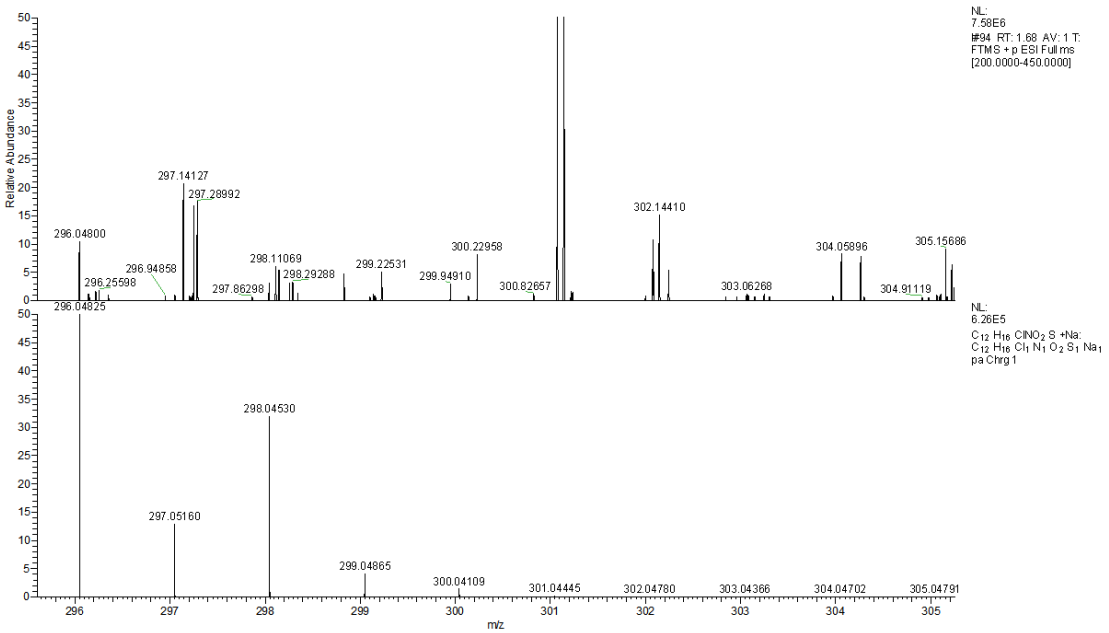


Figure S4 Carbon radical trapping experiment with NIS

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with 1-tosylpiperidine-4-carboxylic acid (0.1 mmol, 28.3 mg), ligand (10 mol%, 2.16 mg), TEMPO (31.2 mg, 2 equiv.), NIS (55 mg, 2.1 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox and added $Fe(OAc)_2$ (10 mol%, 1.74 mg). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added degassed MeCN (1 mL) and 2,4,6-Collidine (24 μL, 1.8 equiv.) via syringe or micro-syringe, respectively. Finally, the reaction mixture was stirred and irradiated for 16 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was washed with water and extracted with DCM (3×10 mL), the organic layer was dried over Na_2SO_4, filtered, and washed through a short plug of silica with DCM to remove the iron species and concentrated by rotary evaporation. The reaction mixture was then detected by HRMS and found that product **3** and TEMPO-adduct **51** were detected.



HRMS-ESI-TOF of compound **51**



HRMS-ESI-TOF of product **3**

Radical clock experiment

Figure S5 Radical clock experiment

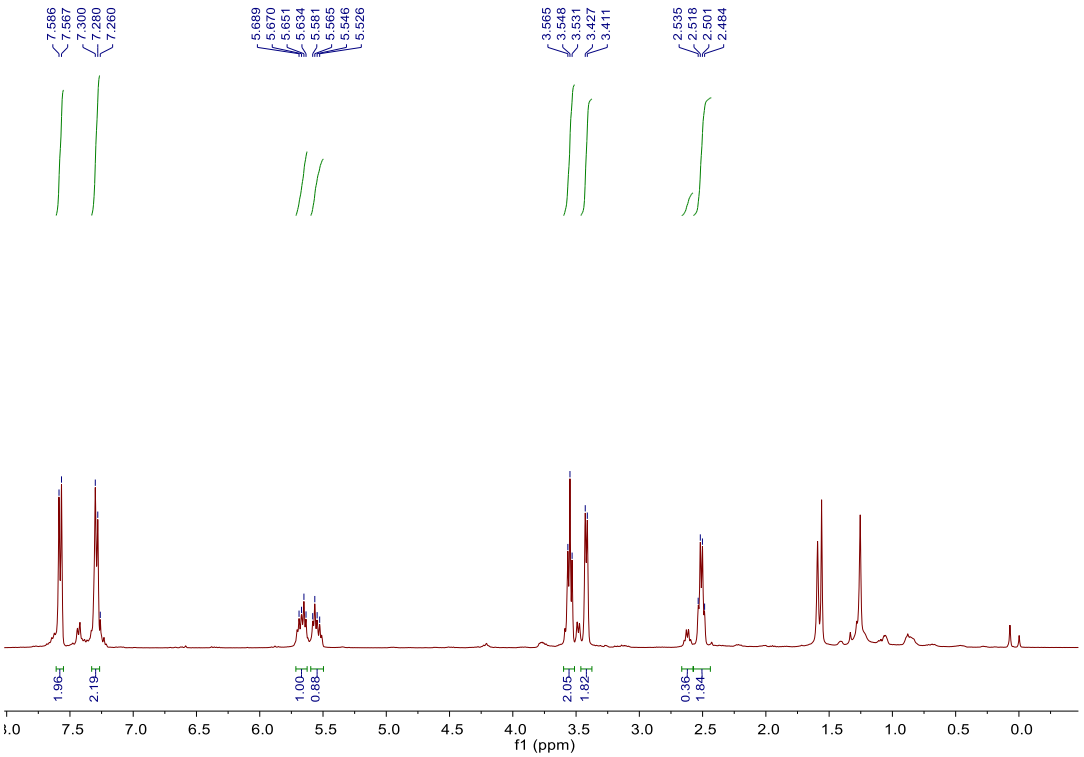
3-(4-cyanophenyl)-2-cyclopropylpropanoic acid (0.4 mmol, 86.0 mg), Ligand **1** (10 mol%) and NCS (2.1 equiv.) were added into the 25 mL Schlenk-tube fitted with a magnetic stir bar. The Schlenk-tube was then transferred to a nitrogenous glove box and $Fe(OAc)_2$ (10 mol%) was added. After that, the Schlenker-tube was sealed with a rubber plug and removed from the glove box. 2,4,6-Collidine (1.8 equiv.) was added by microsyringe. Finally, the reaction mixture was stirred, irradiated under LEDs (20 W, 400 nm) for 6 hours, and cooled by a fan. The reaction liquid was washed with water, extracted by DCM (3×20 mL), dried by Na_2SO_4 in the organic layer, filtered and concentrated under reduced pressure. The reaction mixture was purified directly on silica gel (PE: EA= 100:1) by flash chromatography, and the product **52** (35%, E/Z = 5 : 1) was obtained as colorless oil.

^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (d, J = 7.6 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 5.71 – 5.63 (m, 1H), 5.60 – 5.50 (m, 1H), 3.55 (t, J = 6.8 Hz, 2H), 3.42 (d, J = 6.6 Hz, 2H), 2.54 – 2.48 (m, 2H).

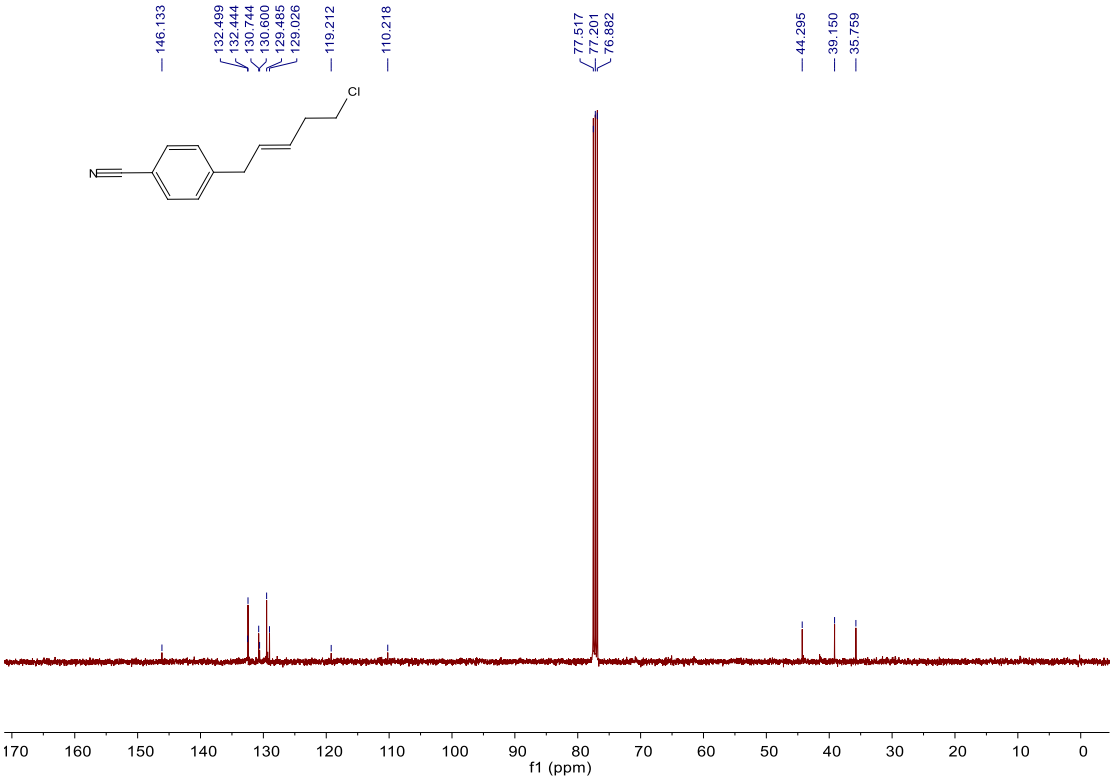
^{13}C NMR (101 MHz, Chloroform-d) δ 146.13, 132.50, 132.44, 130.74, 130.60, 129.48, 129.03, 119.21, 110.22, 44.30, 39.15, 35.76.

HRMS (APCI): calcd for $C_{12}H_{12}N$ $[M+Cl]^+$: 170.0964; found 170.0965.

^{1}H NMR (400 MHz, $CDCl_3$) of 52



^{13}C NMR (101 MHz, $CDCl_3$) of 52



Carboxyl radical trapping experiment

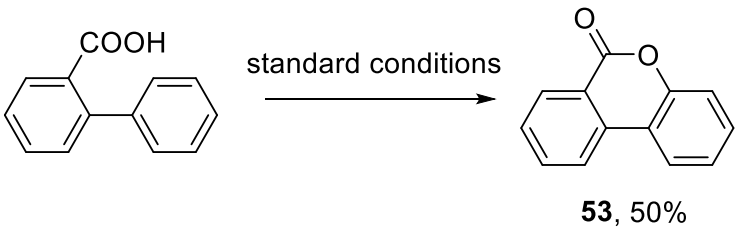


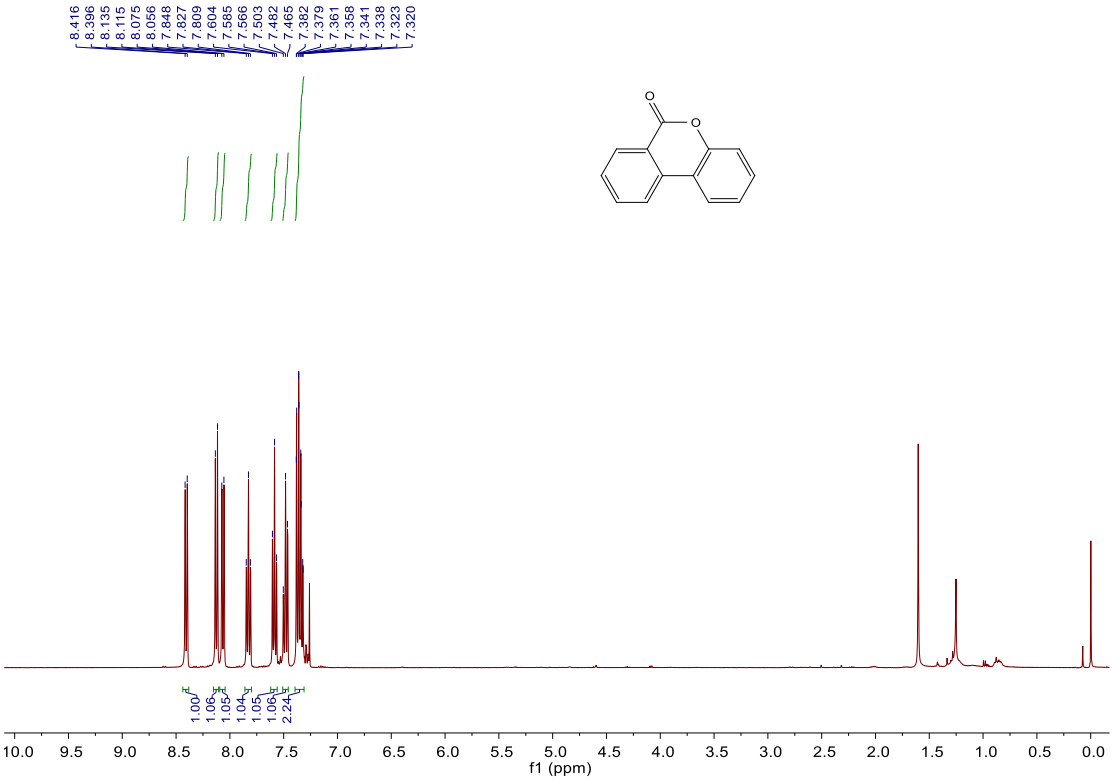
Figure S6 Carboxyl radical trapping experiment

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with [1,1'-biphenyl]-2-carboxylic acid (0.4 mmol, 79.2 mg), ligand **1** (10 mol%). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to add $Fe(OAc)_2$ (10 mol%). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added degassed MeCN (3 mL) and 2,4,6-Collidine (1.8 equiv.) via syringe or micro-syringe, respectively. Finally, the reaction mixture was stirred and irradiated for 6 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was then extracted with DCM, filtered, and concentrated by rotary evaporation. The crude reaction mixture was purified by flash column chromatography through silica gel (PE: EA= 10:1) to afford the white solid product in 55%.

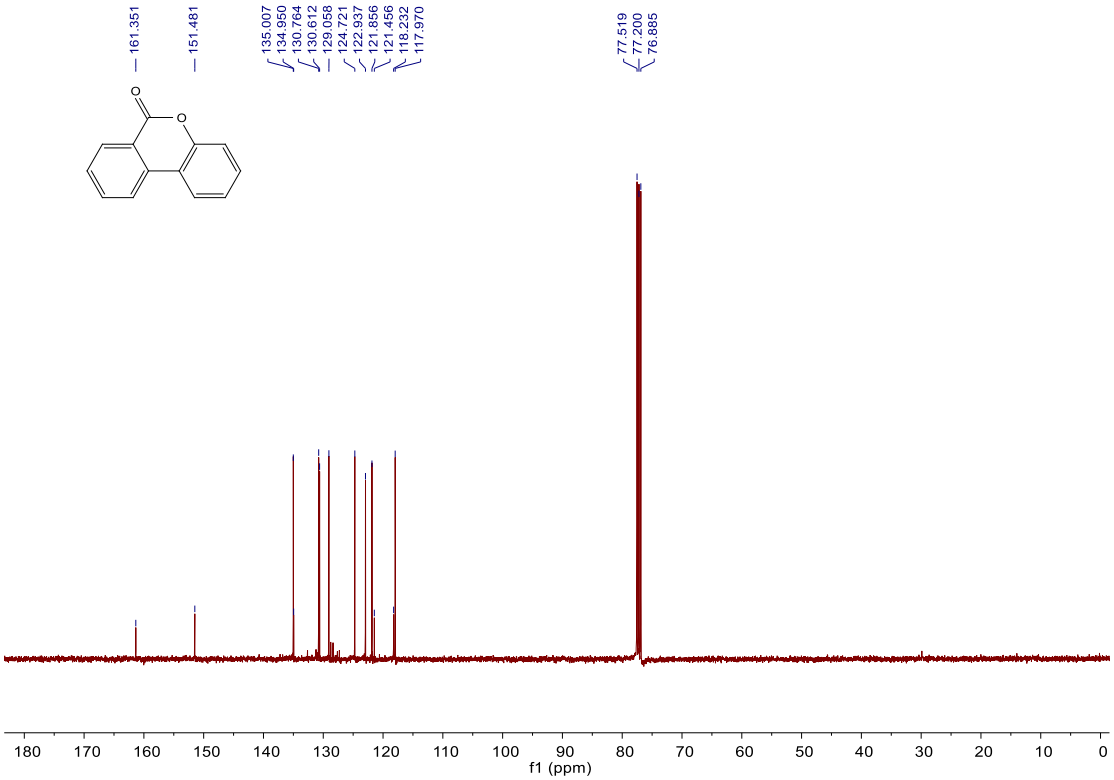
^{1}H NMR (400 MHz, Chloroform-d) δ 8.41 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 7.6 Hz, 1H), 7.83 (t, J = 7.2 Hz, 1H), 7.59 (t, J = 7.6 Hz, 1H), 7.48 (t, J = 8.4 Hz, 1H), 7.38 – 7.32 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-d) δ 161.35, 151.48, 135.01, 134.95, 130.76, 130.61, 129.06, 124.72, 122.94, 121.86, 121.46, 118.23, 117.97.

^{1}H NMR (400 MHz, $CDCl_3$) of 53



^{13}C NMR (101 MHz, $CDCl_3$) of 53



Evidence of Iron carboxylate intermediate

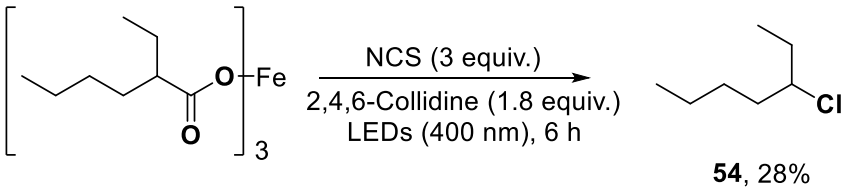
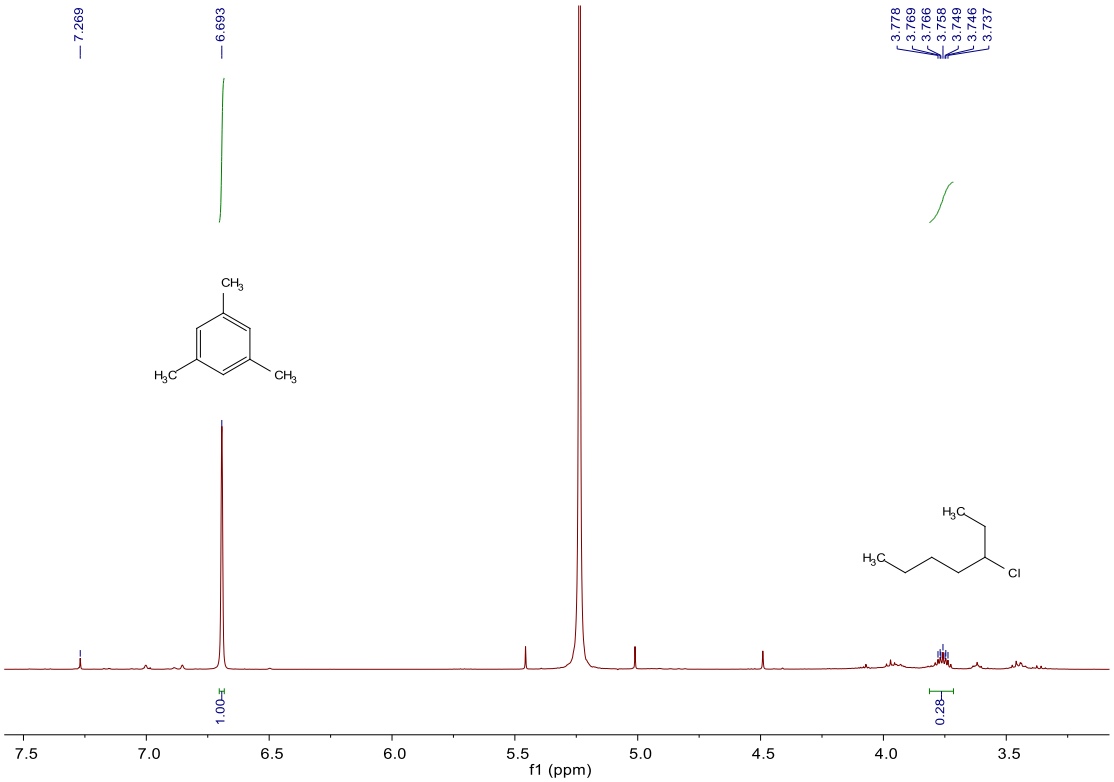


Figure S7 Evidence of Iron carboxylate intermediate

An oven-dried 25 mL Schlenk-tube equipped with a magnetic stir bar was charged with Iron(III) 2-ethylhexanoate (0.1 mmol, 28.3 mg), ligand **1** (10 mol%), NCS (3 equiv.). Then the Schlenk-tube was transferred to nitrogen-filled glovebox to add $Fe(OAc)_2$ (10 mol%). After that, the Schlenk-tube was sealed with rubber plug and taken out of the glovebox. The reaction mixture was added degassed MeCN (1 mL) and 2,4,6-Collidine (1.8 equiv.) via syringe or micro-syringe, respectively. Finally, the reaction mixture was stirred and irradiated for 6 h under LEDs (20 W, 400 nm), cooling with a fan. The reaction solution was washed with water and extracted with DCM (3×10 mL), the organic layer was dried over Na_2SO_4, filtered, and washed through a short plug of silica with DCM to remove the iron species and concentrated by rotary evaporation. The reaction mixture was then detected by ^{1}H NMR using 1,3,5-Trimethylbenzene (0.1 mmol) as an internal standard and found that 28% of product was formed.

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



6. Quantum Yield

Determination of the light intensity:

According to the procedure of Yoon[22], the photon flux of the LED (λmax = 394 nm) was determined by standard ferrioxalate actinometry.[21,22] A 0.15 M solution of ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the ferrioxalate solution was placed in a cuvette and irradiated for 90.0 seconds at λ= 394 nm with an emission slit width of 10.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate with the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm was measured. Conversion was calculated using eq 1.

$$\text{mol } Fe^{2+} = \frac{V \bullet \Delta A}{l \bullet \varepsilon} \qquad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, A is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, I is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L mol^{-1} cm^{-1}). The photon flux can be calculated using eq 2.

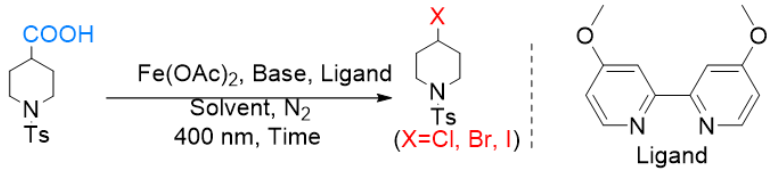
$$\text{Photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \bullet t \bullet f} \qquad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.01 for a 0.15 M solution at λ= 394 nm), t is the time (90.0 s), and f is the fraction of light absorbed at λ= 394 nm (eq 3). The absorbance of the above ferrioxalate solution at 415 nm was measured to be >3 indicating the fraction of light absorbed is >0.999. The fraction of light absorbed (f) by this solution was calculated using eq 3, where A is the measured absorbance at 394 nm.

$$f = 1 - 10^{-A} \qquad (3)$$

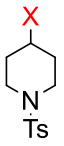
The photon flux was calculated to be 3.80×10^{-9} einstein s^{-1}.

Determination of quantum yield:



To a flask was added carboxylic acid (0.1 mmol, 1 equiv.), $Fe(OAc)_2$ (10 mol%), and electrophiles (2.1 equiv.) in a glove-box. The vial was removed from the glove-box and MeCN (1 mL). A needle was then inserted into the septum and the solution was purged with argon for 10 minutes. After this time, 1 mL of the reaction mixture was taken, and filtered through a syringetip filter (to remove any solids) into a quartz cuvette. The sample was stirred and irradiated (λmax = 394 nm) for 3600 s. After irradiation, the internal standard 1,3,5-Trimethylbenzene (1 equiv.) were added，the yield of product formed was determined by ^{1}H NMR analysis to be 6% based on the decane standard. The quantum yield was determined using eq 4. Essentially all incident light (f > 0.999) is absorbed by PC under the reaction conditions described.

$$\Phi = \frac{\text{mol prod}}{\text{flux} \bullet t \bullet f} \qquad (4)$$



X=Cl, 30% (3600 s)
X=I, 10% (3600 s)
X=Br, 11% (1800 s)

The quantum yield Φ for the chlorination was calculated to be 0.219.
The quantum yield Φ for the bromination was calculated to be 0.073.
The quantum yield Φ for the iodination was calculated to be 0.161.

7. UV-vis absorption spectroscopy

UV-vis Absorption Spectrum

All UV-vis measurements were recorded on a Lambda 950 using a screw-top quartz cuvette (Sevenlight fluorescence quartz cuvette, 10× 10 mm, 3.5 mL). All samples were dissolved at the specified concentration in the solvents of MeCN in a glovebox and then taken out of the glovebox to be tested.

UV-vis spectra of 1-tosylpiperidine-4-carboxylic acid (1×10^{-3} M), $Fe(OAc)_2$ (1×10^{-3} M), ligand (1×10^{-3} M), NCS (1×10^{-3} M), base (1×10^{-3} M) were recorded respectively after filtered by syringe filters (Figure S8).

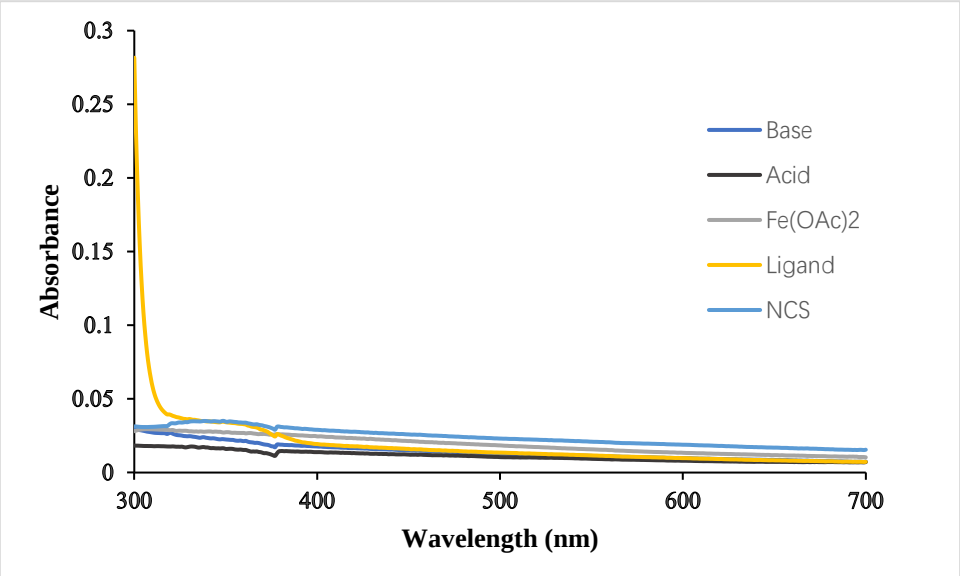


Figure S8 UV-vis spectra analysis of the reaction components

After that, the UV-vis spectra of the mixture of $Fe(OAc)_2$ (1×10^{-3} M)+ Ligand (1×10^{-3} M), $Fe(OAc)_2$ (1×10^{-3} M)+ Ligand (1×10^{-3} M)+ NCS (2.1×10^{-2} M), Fe(OAc)2 (1×10^{-3} M)+ Ligand (1×10^{-3} M)+ NCS (2.1×10^{-2} M)+ 2,4,6-Collidine (1.8×10^{-2} M)+ 1-tosylpiperidine-4-carboxylic acid (1×10^{-2} M) (after 0 h and 8 h, respectively) were measured after filtered by syringe filters. The red line is the spectrum of the sample standing for 8 h without light irradiation, which suggested that the Fe^{2+} in solution was oxidized to Fe^{3+} species (Figure S9).

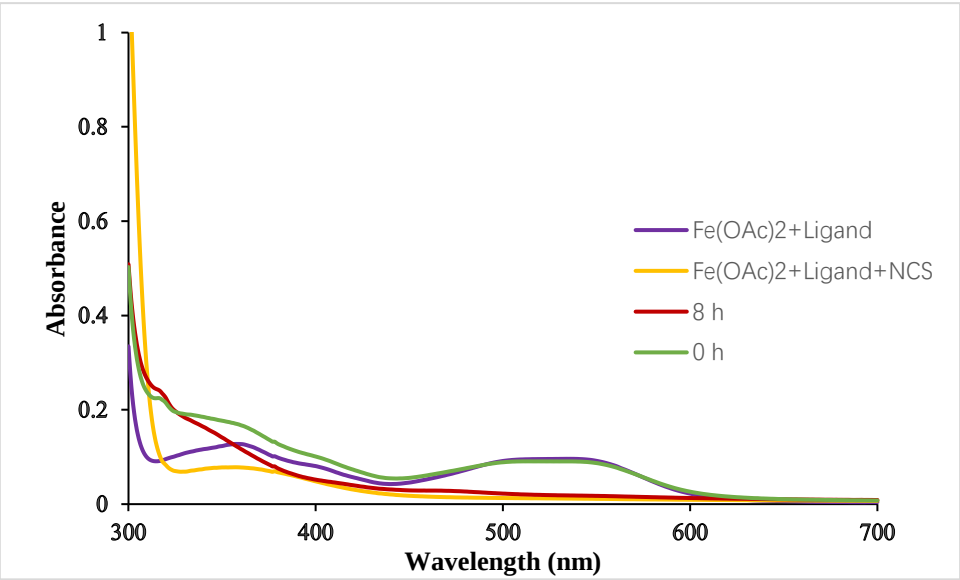


Figure S9 The UV-vis spectra of the mixture of $Fe(OAc)_2$ (1×10^{-3} M)+ ligand **1** (1×10^{-3} M)+ NCS

(2.1×10^{-2} M)+ 2,4,6-Collidine (1.8×10^{-2} M)+ 1-tosylpiperidine-4-carboxylic acid (1×10^{-2} M) in situ and after 8 h

After 8 h, the UV-vis spectra of the mixture of $Fe(OAc)_2$ (1×10^{-3} M)+ Ligand (1×10^{-3} M)+ NCS (2.1×10^{-2} M)+ 2,4,6-Collidine (1.8×10^{-2} M)+ 1-tosylpiperidine-4-carboxylic acid (1×10^{-2} M) were measured after different irradiation time (1 min- 40 min) with 400 nm LED (Figure S10).

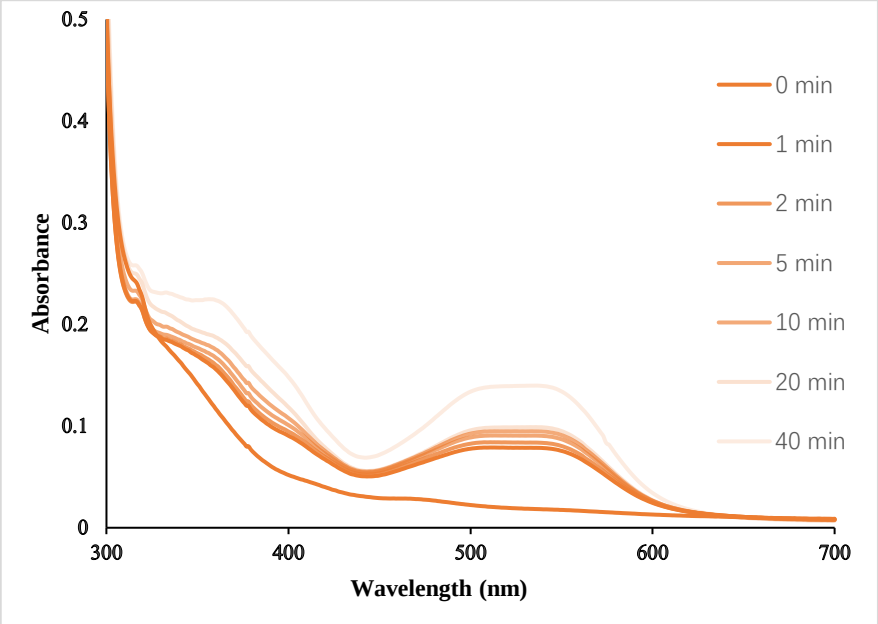


Figure S10 The UV-vis spectra of the mixture of $Fe(OAc)_2$ (1×10^{-3} M)+ ligand **1** (1×10^{-3} M)+ NCS (2.1×10^{-2} M)+ 2,4,6-Collidine (1.8×10^{-2} M)+ 1-tosylpiperidine-4-carboxylic acid (1×10^{-2} M) after 8 hours and the trace of the resulting mixture after irradiation (400 nm LEDs) for different time (0 min-40 min)

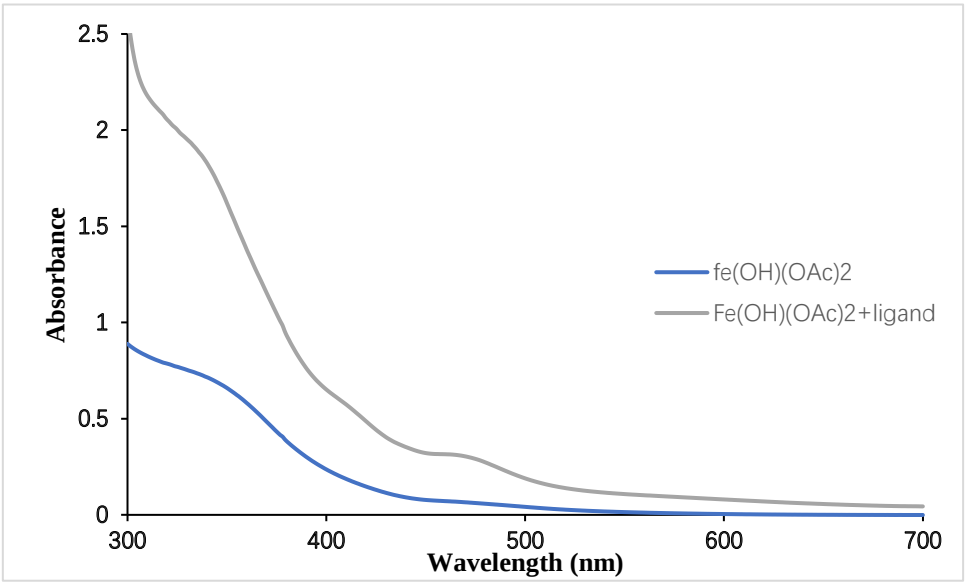


Figure S11 UV-vis spectra of $Fe(OH)(OAc)_2$ (1×10^{-3} M), and the mixture of $Fe(OH)(OAc)_2$ (1×10^{-3} M)+ ligand (1×10^{-3} M)

Furthermore, UV-vis spectra of the mixture of $Fe(OH)(OAc)_2$ (1×10^{-3} M)+ ligand (1×10^{-3} M)+ + 2,4,6-Collidine (1.8×10^{-2} M)+ 1-tosylpiperidine-4-carboxylic acid (1×10^{-2} M) were measured after different irradiation time (1 min- 40 min) with 400 nm LED (Figure S12).

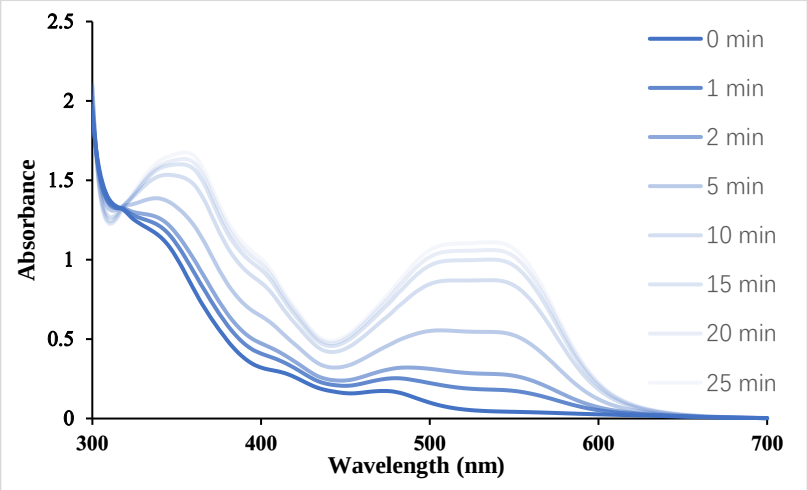
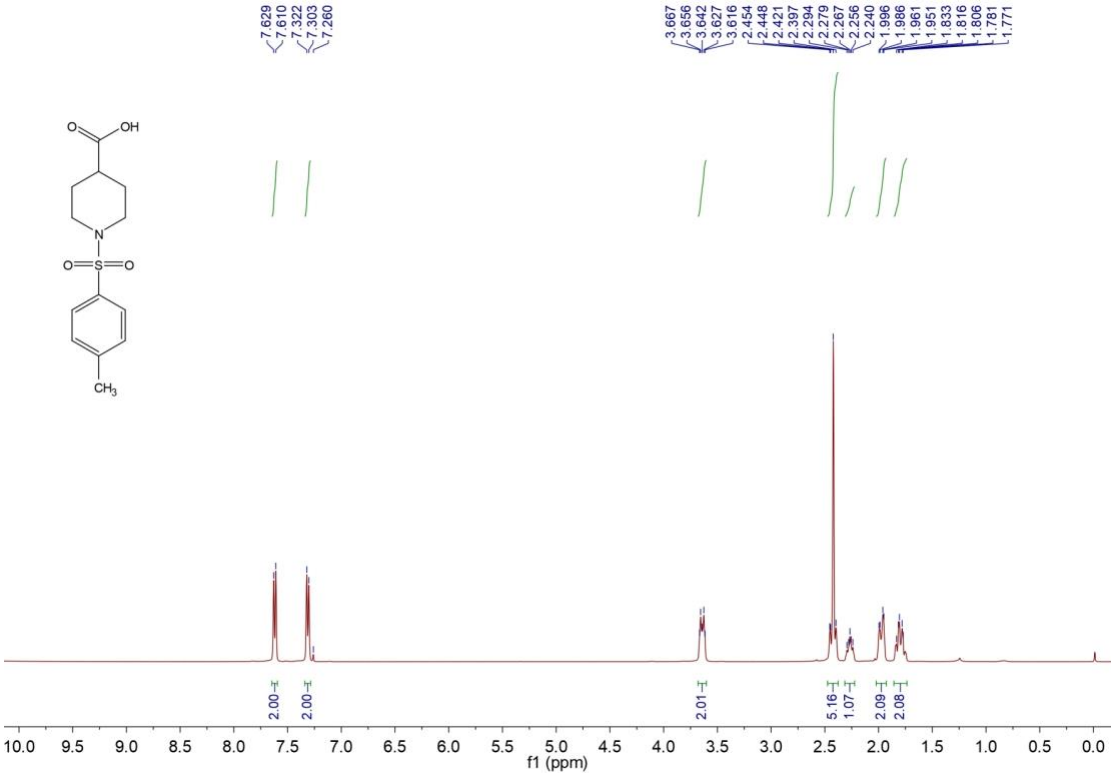


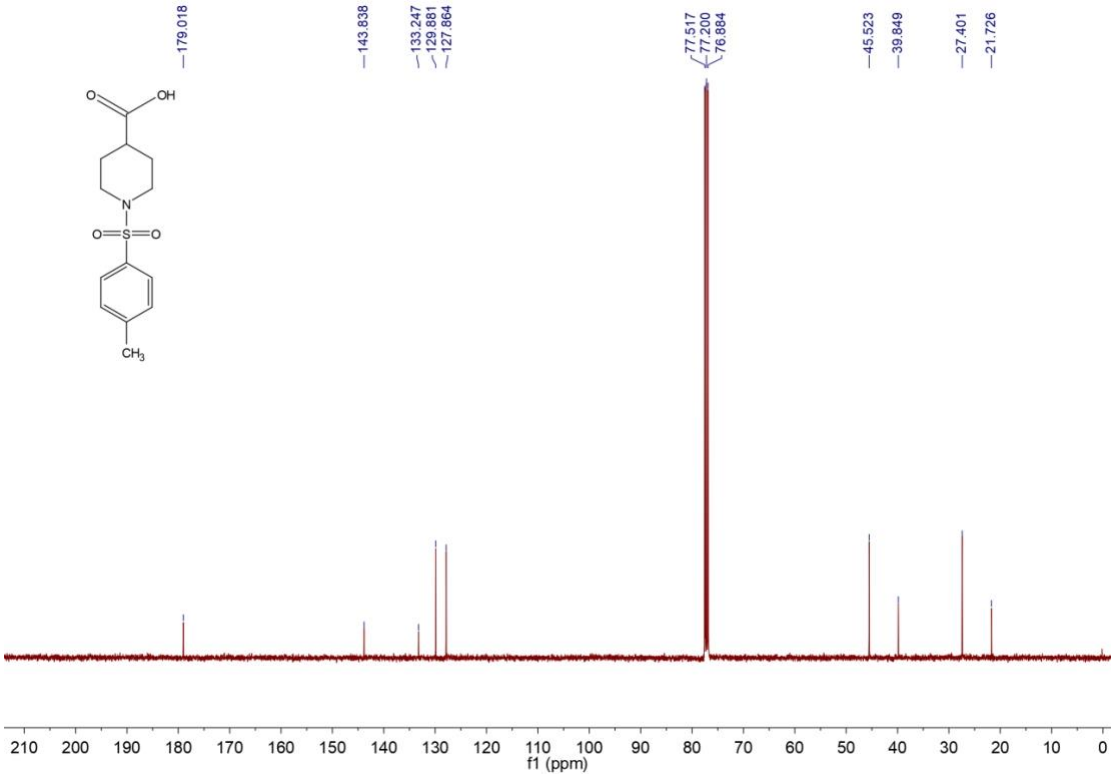
Figure S12 The UV-vis spectra trace of the mixture of $Fe(OH)(OAc)_2$ (1×10^{-3} M)+ ligand **1** (1×10^{-3} M)+ 2,4,6-Collidine (1.8×10^{-2} M)+ 1-tosylpiperidine-4-carboxylic acid (1×10^{-2} M) after irradiation (400 nm LEDs) for different time (0 min- 25 min)

8. NMR spectra

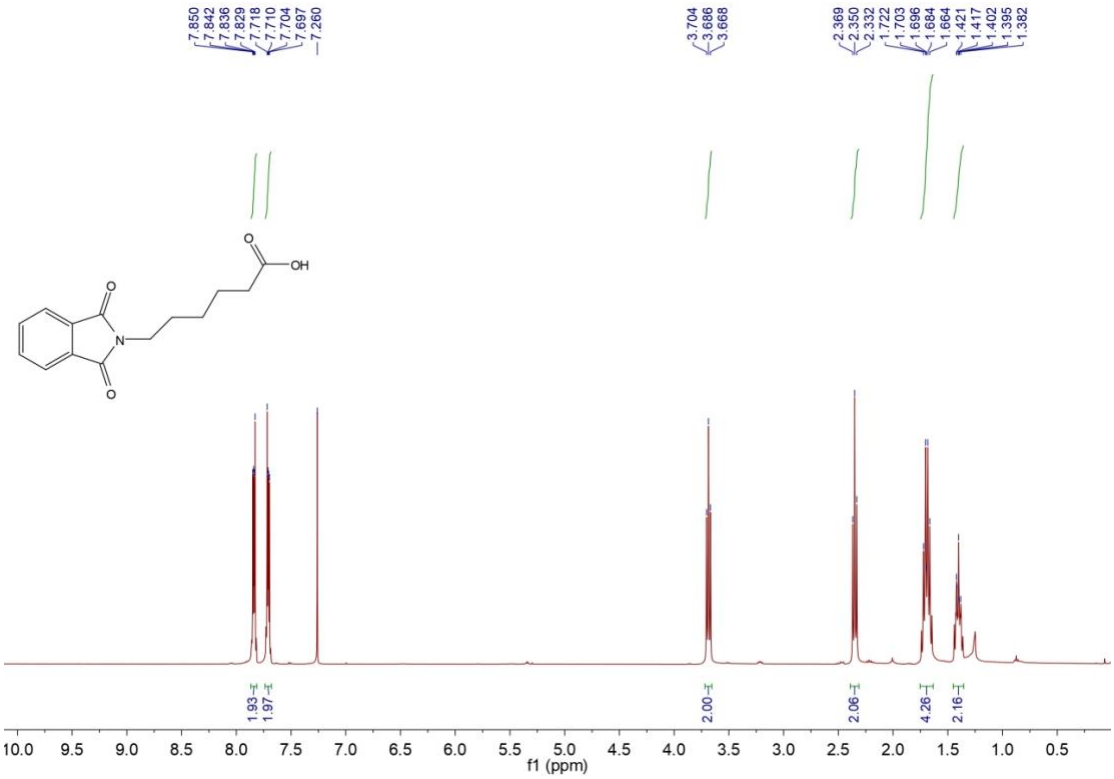
^{1}H NMR (400 MHz, $CDCl_3$) of 1-tosylpiperidine-4-carboxylic acid



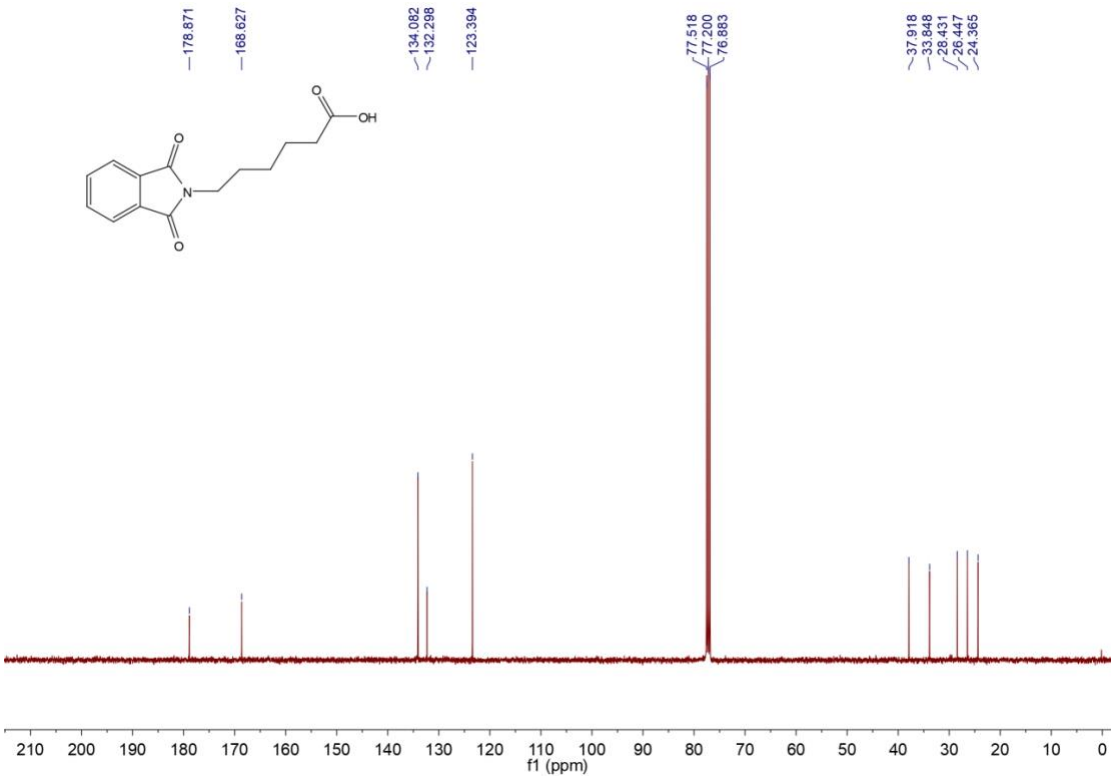
^{13}C NMR (101 MHz, $CDCl_3$) of 1-tosylpiperidine-4-carboxylic acid



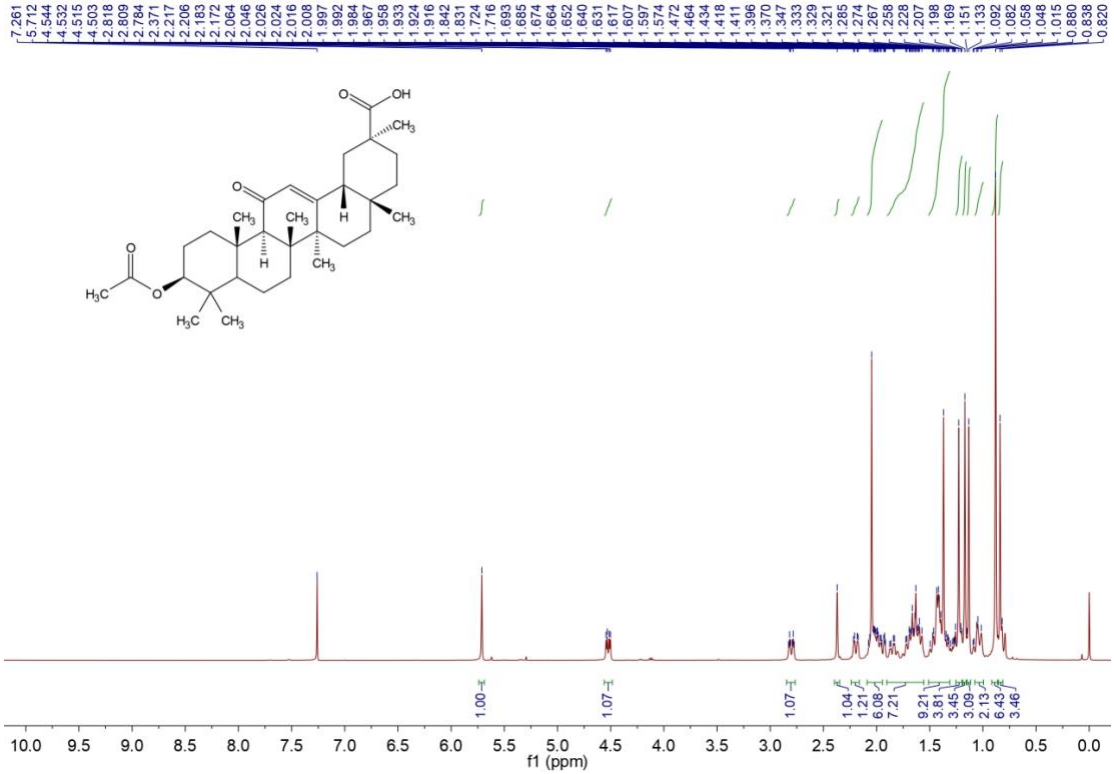
^{1}H NMR (400 MHz, $CDCl_3$) of 6-(1,3-dioxoisoindolin-2-yl)hexanoic acid



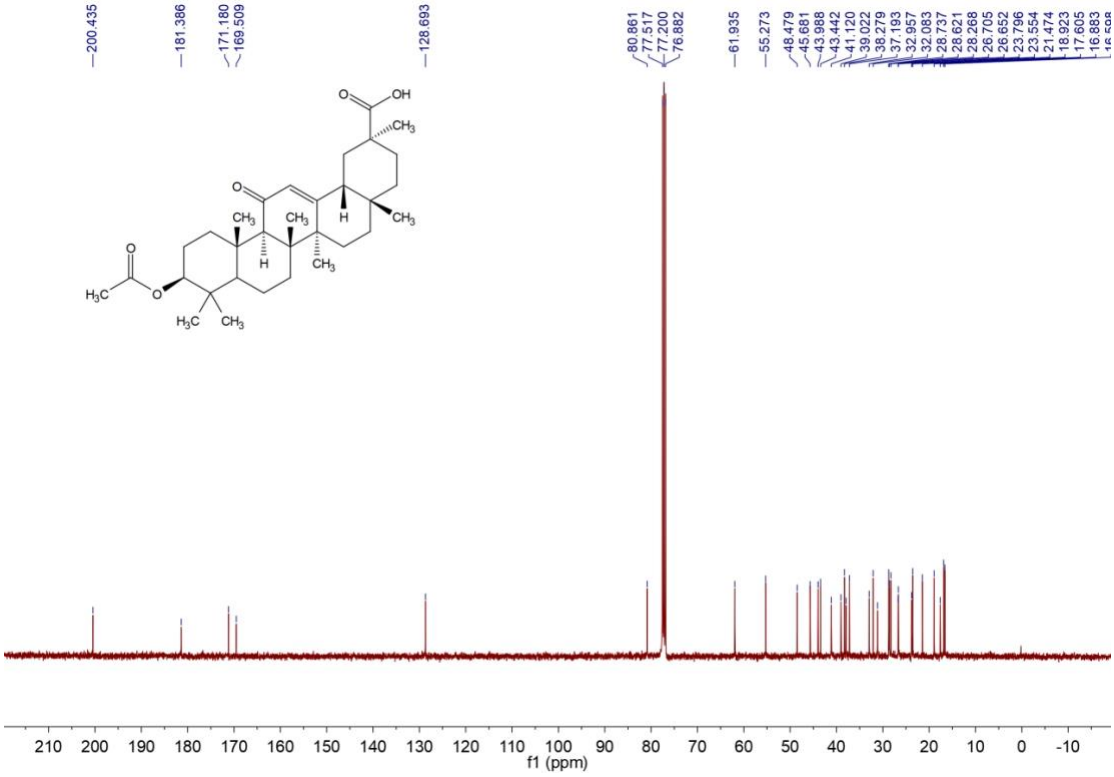
^{13}C NMR (101 MHz, $CDCl_3$) of 6-(1,3-dioxoisoindolin-2-yl)hexanoic acid



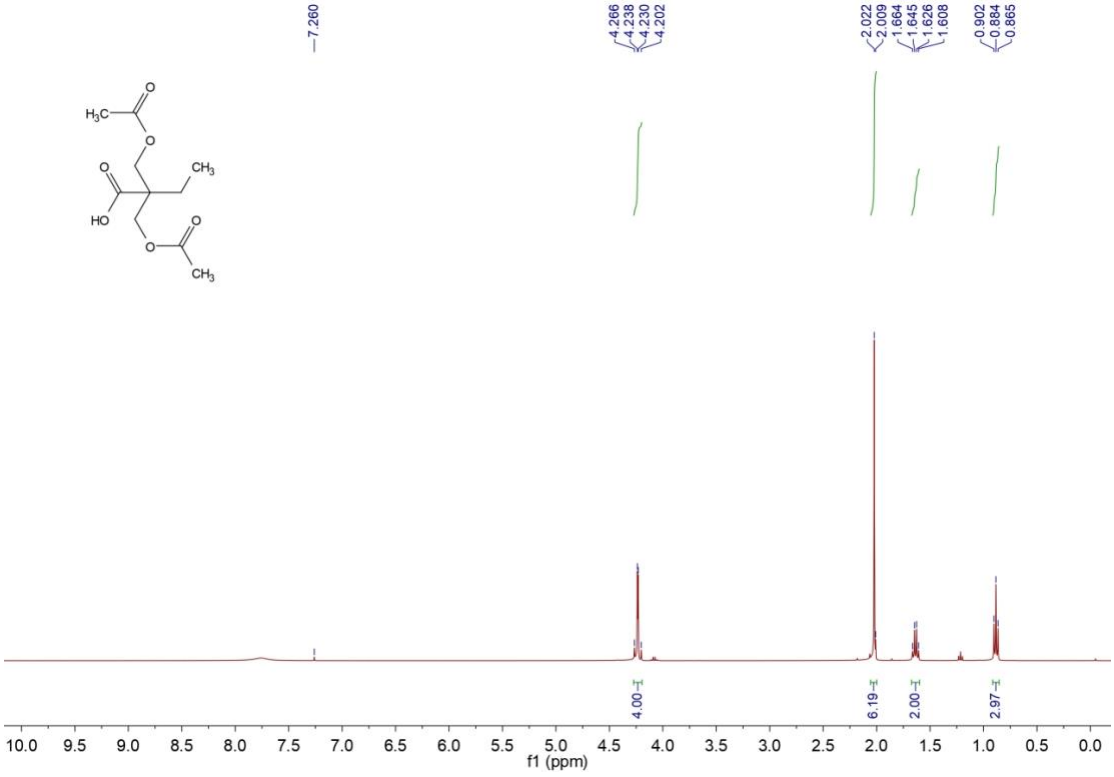
^{1}H NMR (400 MHz, $CDCl_3$) of (2R,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo 1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylic acid



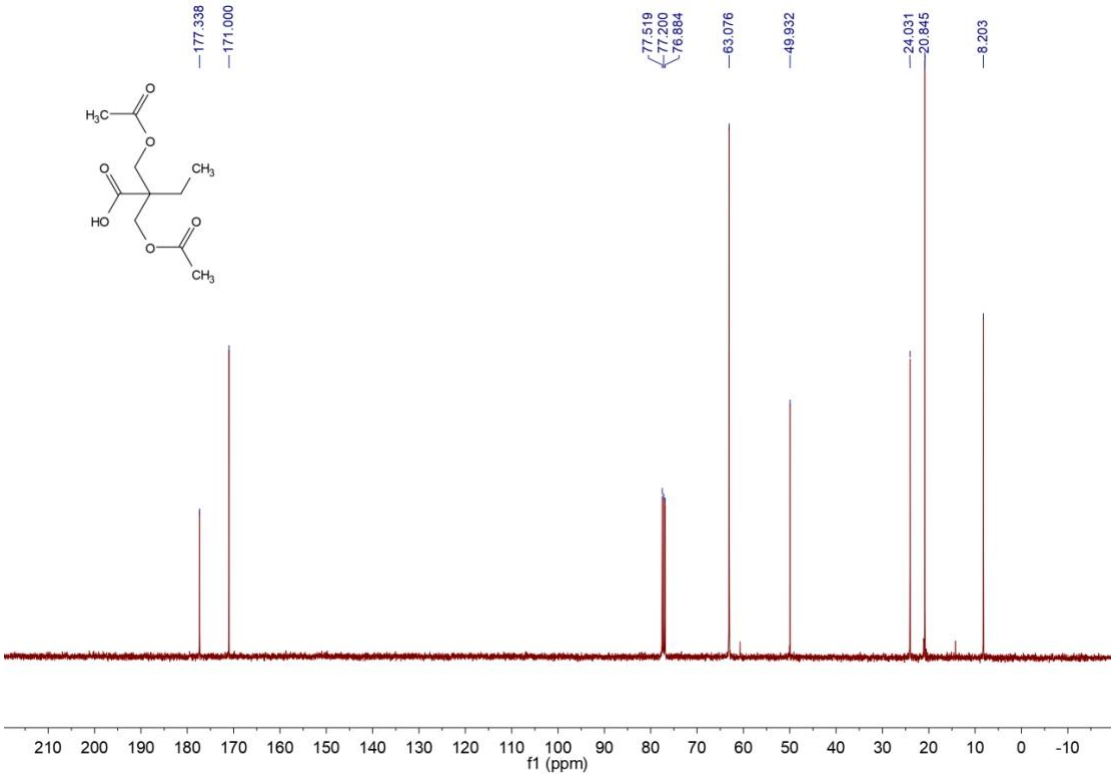
^{13}C NMR (101 MHz, $CDCl_3$) of (2R,4aS,6aS,6bR,8aR,10S,12aS,12bR,14bR)-10-acetoxy-2,4a,6a,6b,9,9,12a-heptamethyl-13-oxo-1,2,3,4,4a,5,6,6a,6b,7,8,8a,9,10,11,12,12a,12b,13,14b-icosahydropicene-2-carboxylic acid



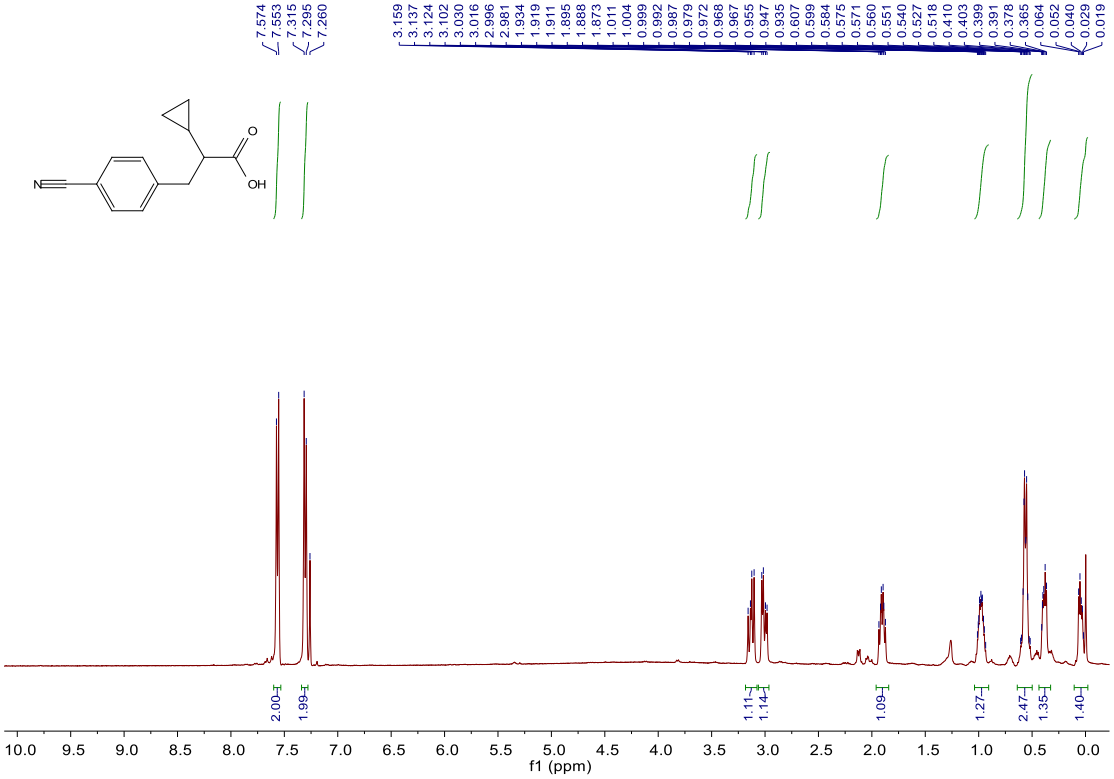
^{1}H NMR (400 MHz, $CDCl_3$) of 2,2-bis(acetoxymethyl)butanoic acid



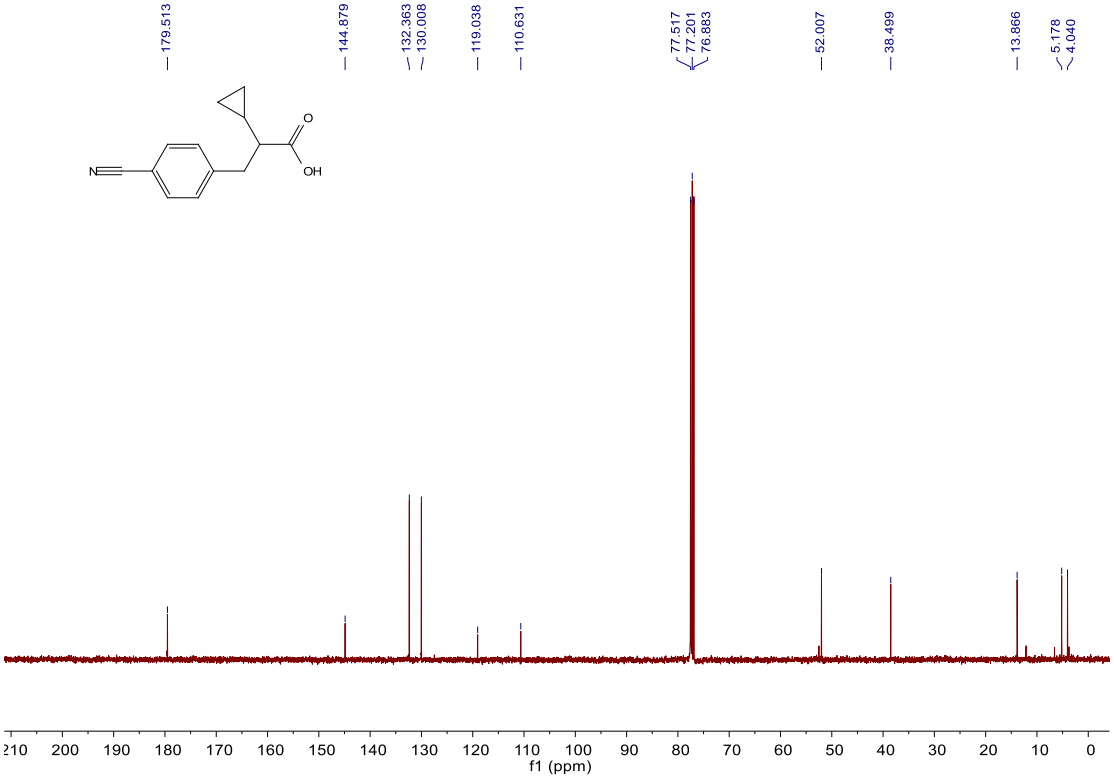
^{13}C NMR (101 MHz, $CDCl_3$) of 2,2-bis(acetoxymethyl)butanoic acid



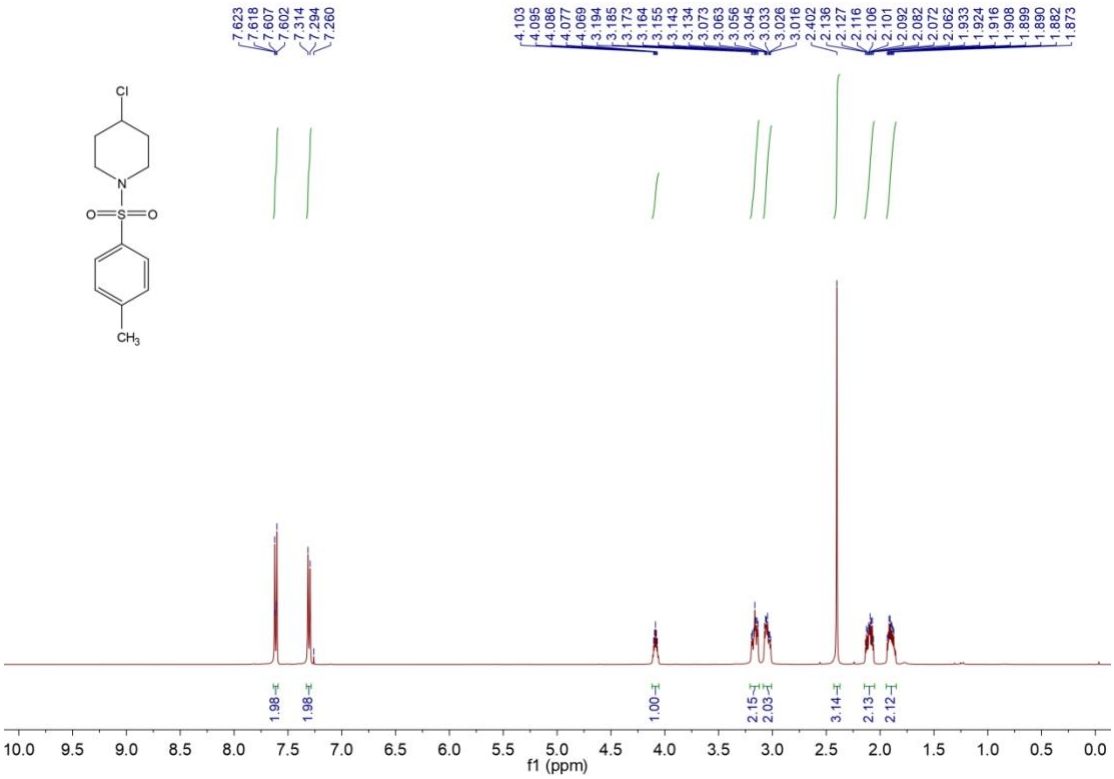
^{1}H NMR (400 MHz, $CDCl_3$) of 3-(4-cyanophenyl)-2-cyclopropylpropanoic acid



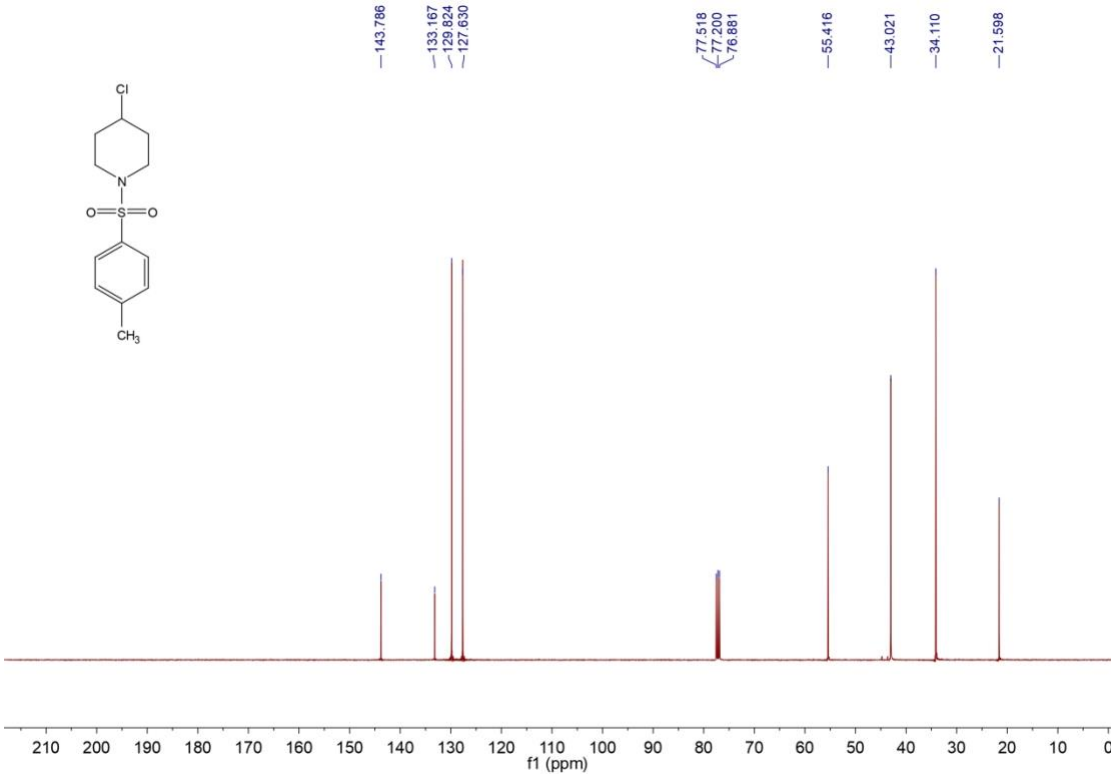
^{13}C NMR (101 MHz, $CDCl_3$) of 3-(4-cyanophenyl)-2-cyclopropylpropanoic acid



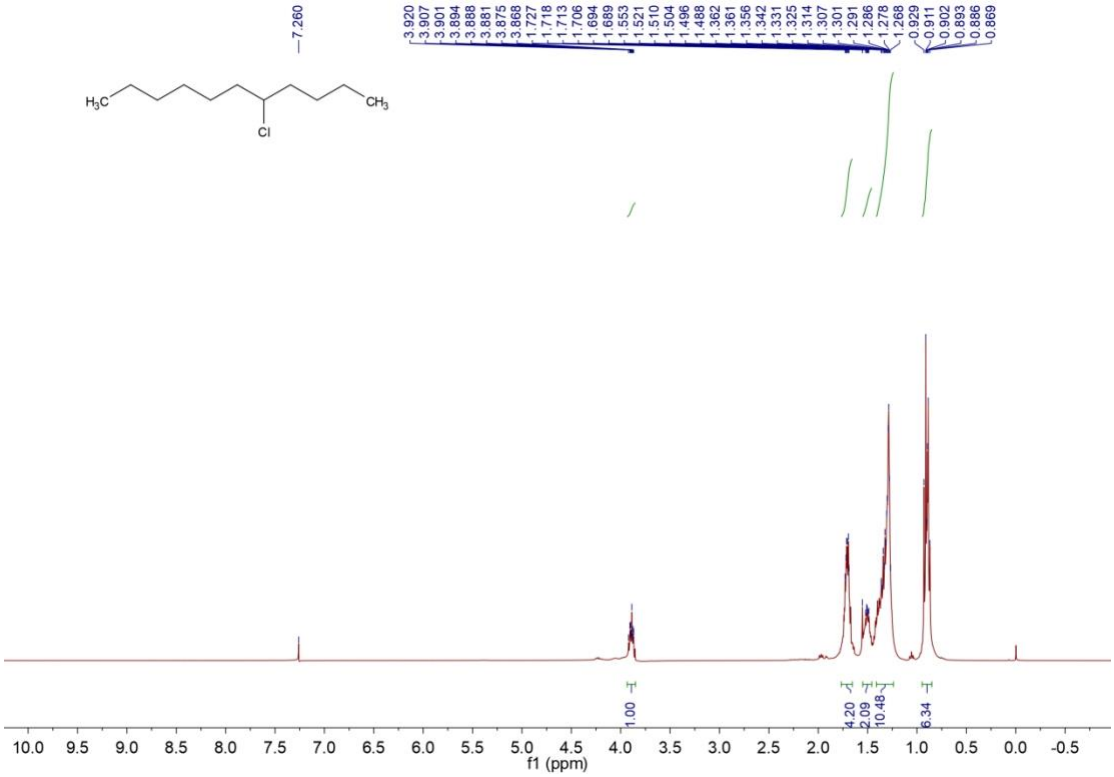
^{1}H NMR (400 MHz, $CDCl_3$) of product **1**



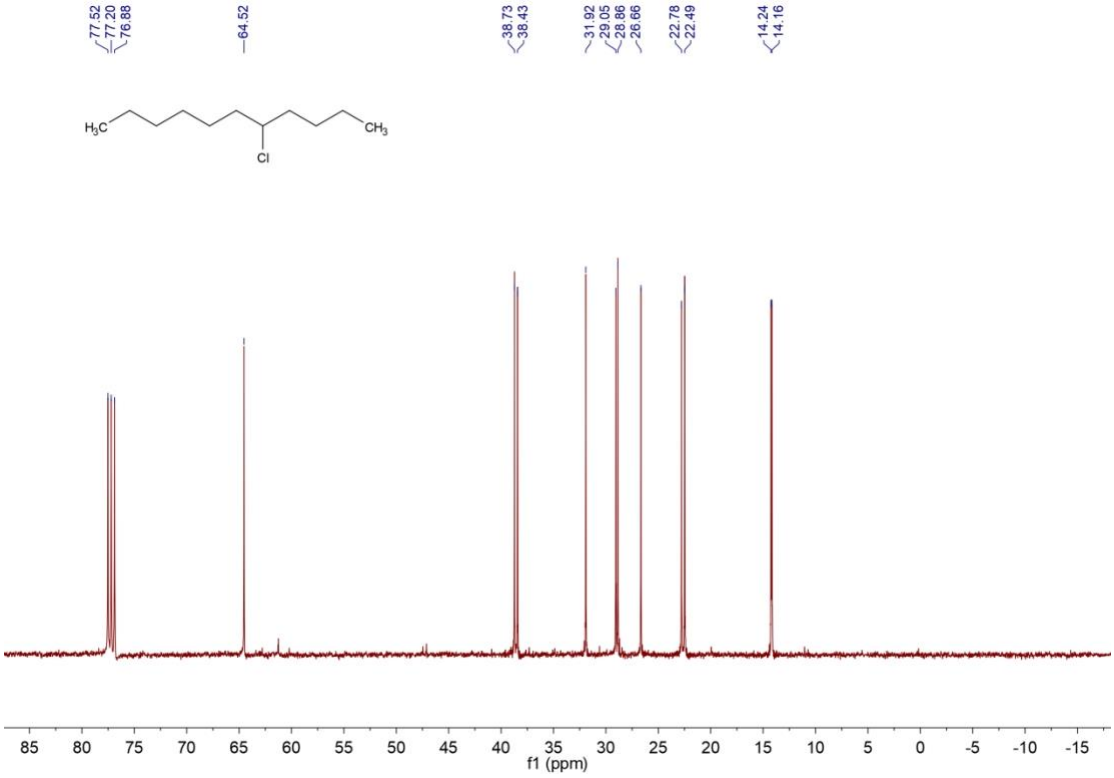
^{13}C NMR (101 MHz, $CDCl_3$) of product **1**



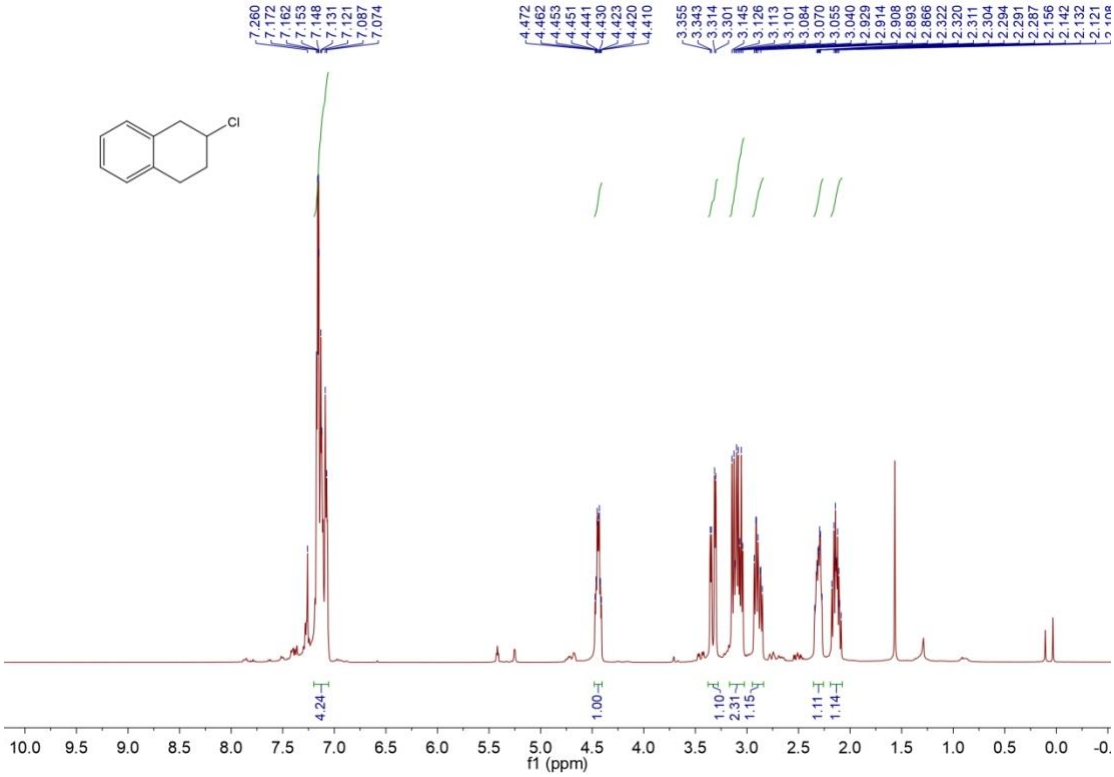
^{1}H NMR (400 MHz, $CDCl_3$) of product **4**



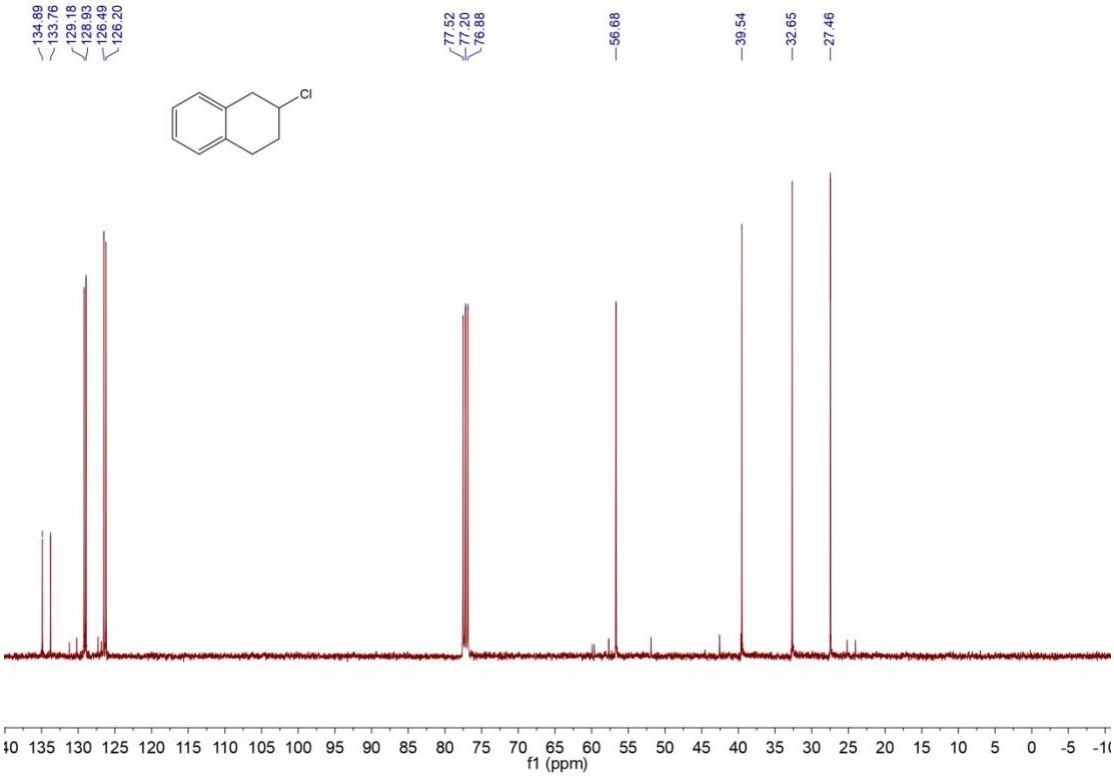
^{13}C NMR (101 MHz, $CDCl_3$) of product **4**



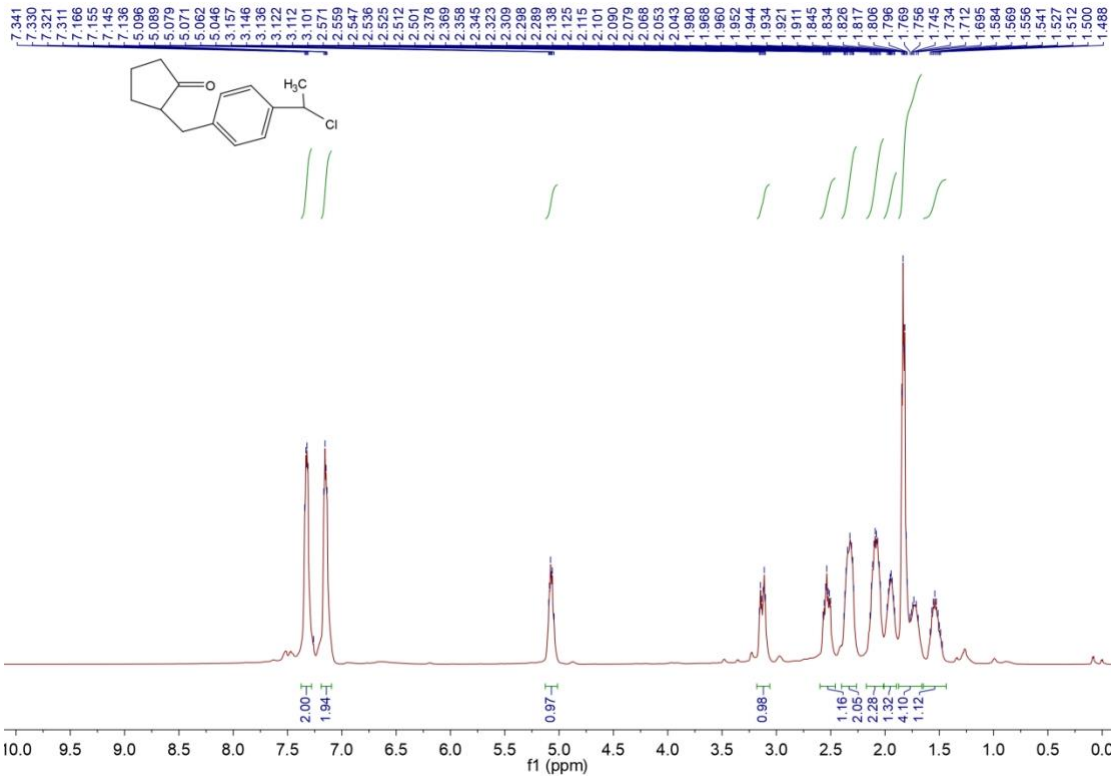
^{1}H NMR (400 MHz, $CDCl_3$) of product **5**



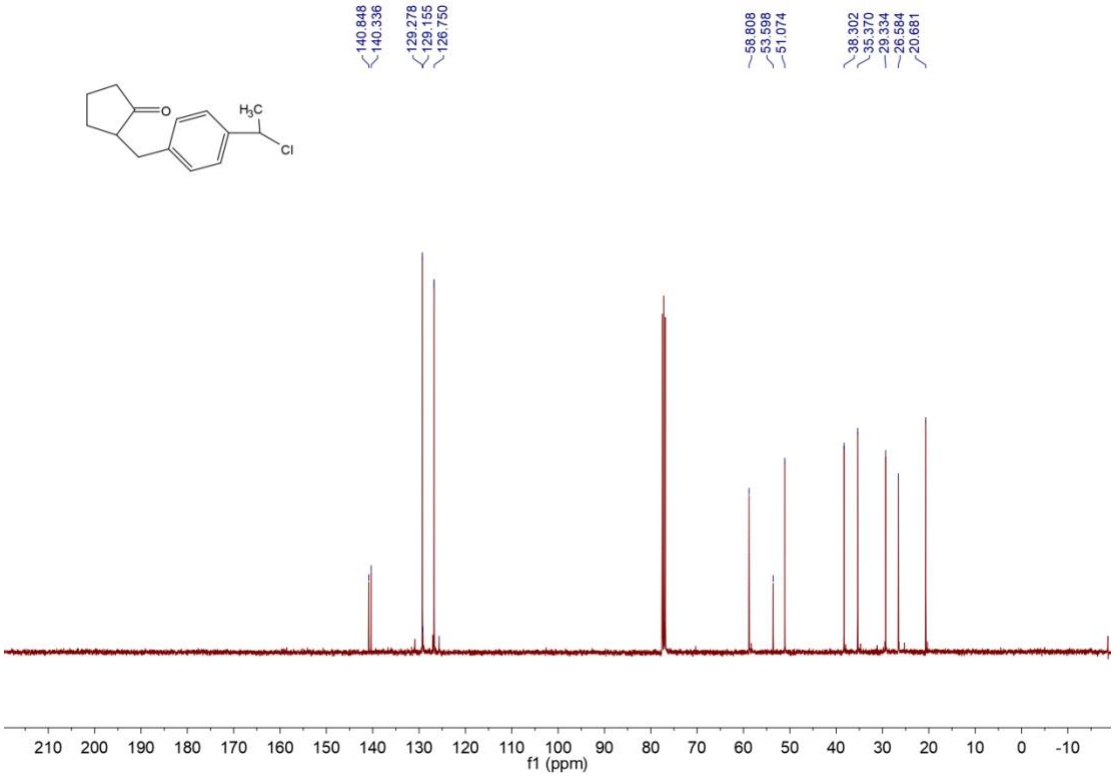
^{13}C NMR (101 MHz, $CDCl_3$) of product **5**



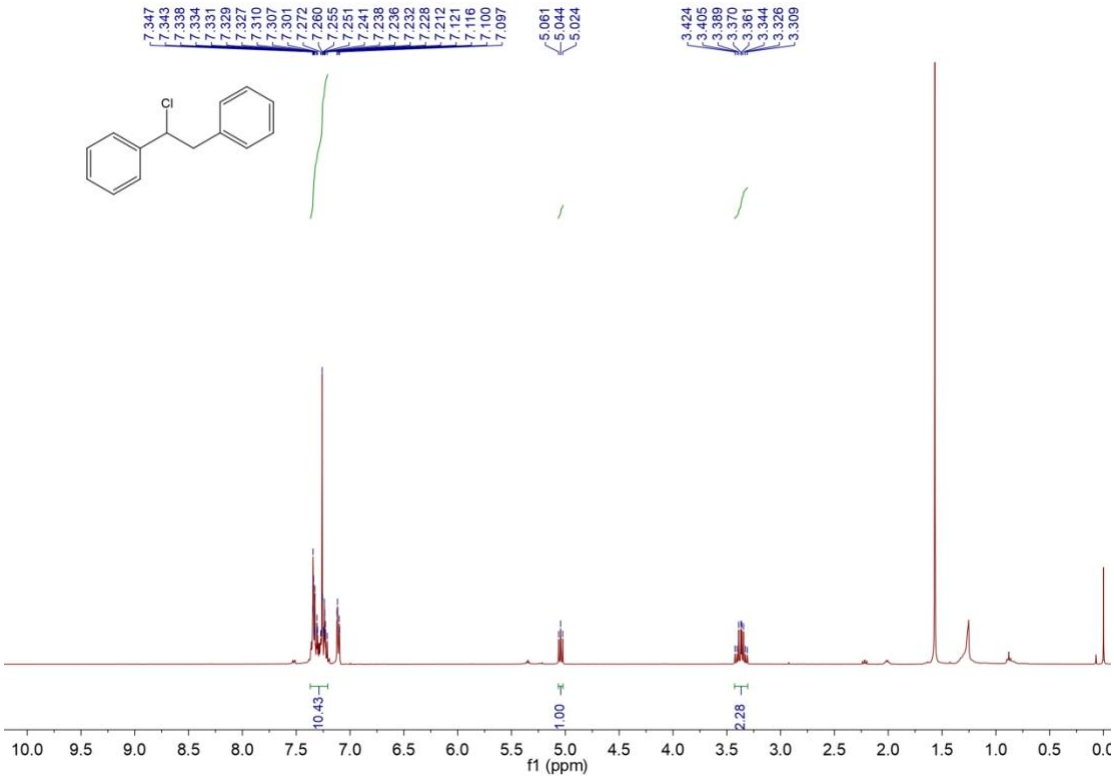
^{1}H NMR (400 MHz, $CDCl_3$) of product **8**



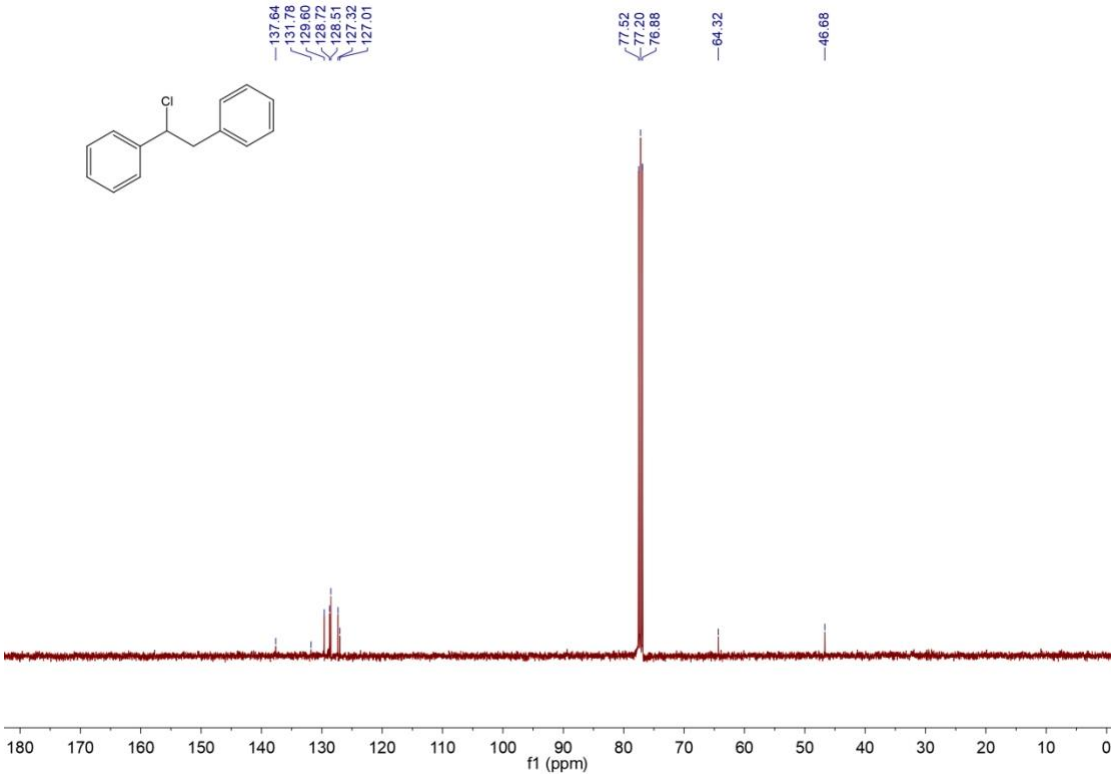
^{13}C NMR (101 MHz, $CDCl_3$) of product **8**



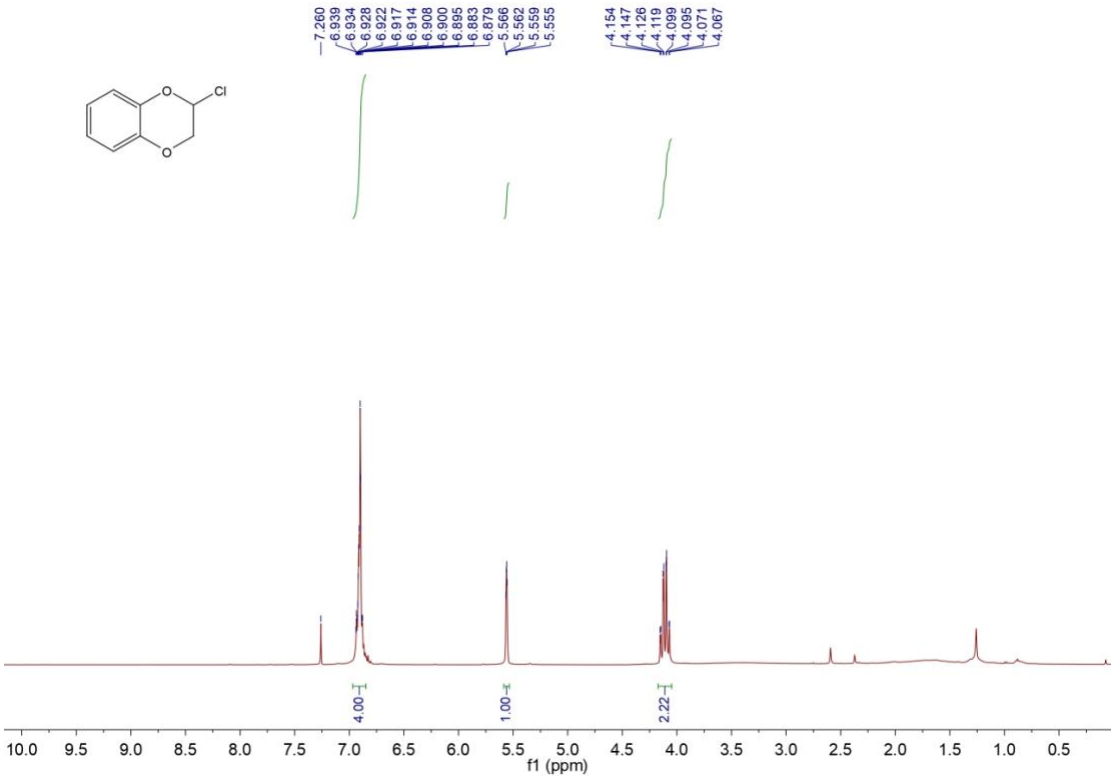
^{1}H NMR (400 MHz, $CDCl_3$) of product **9**



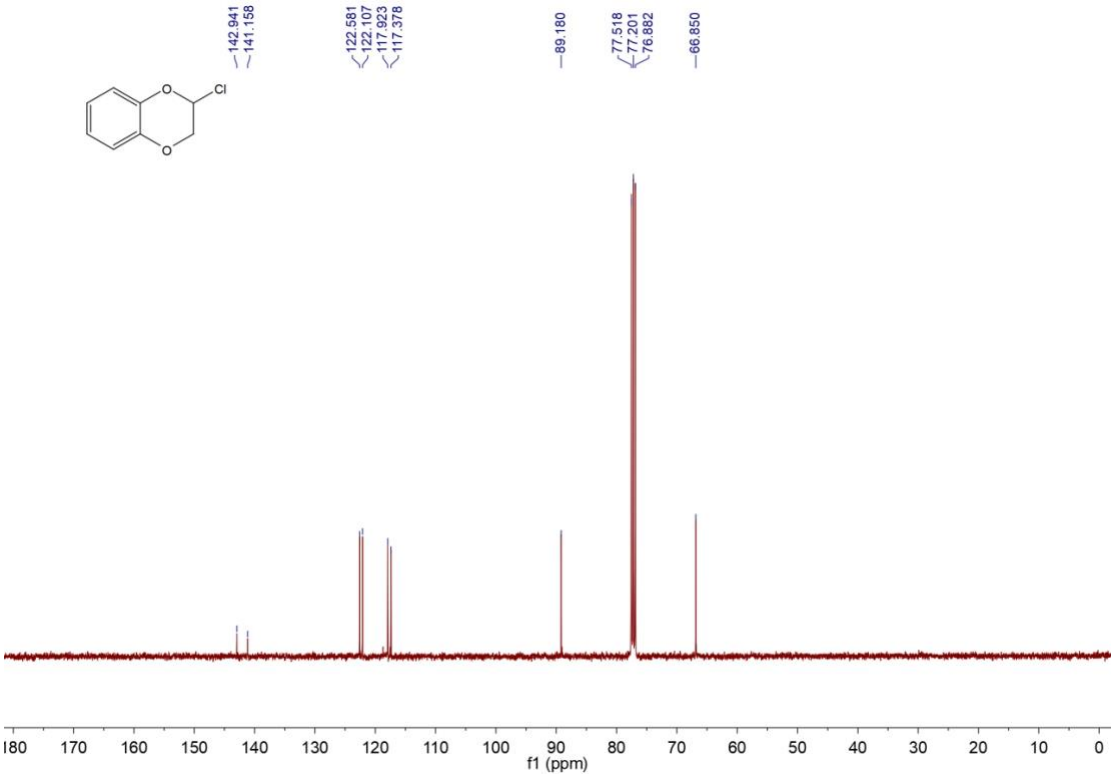
^{13}C NMR (101 MHz, $CDCl_3$) of product **9**



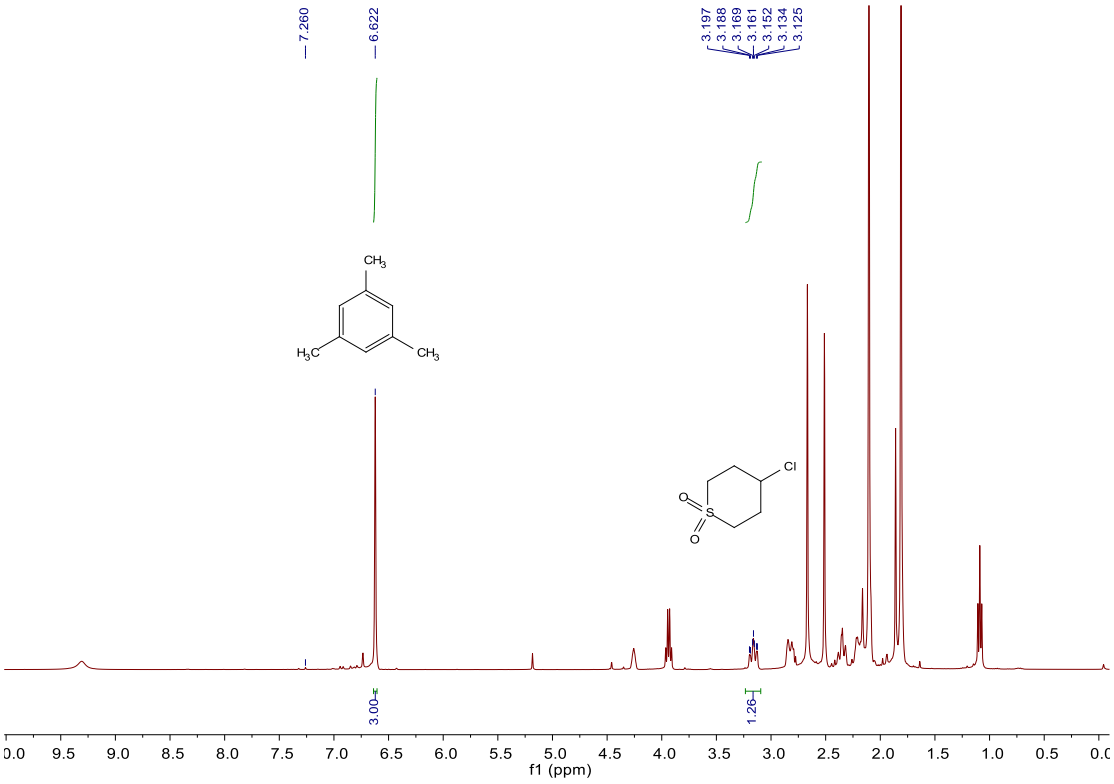
^{1}H NMR (400 MHz, $CDCl_3$) of product **10**



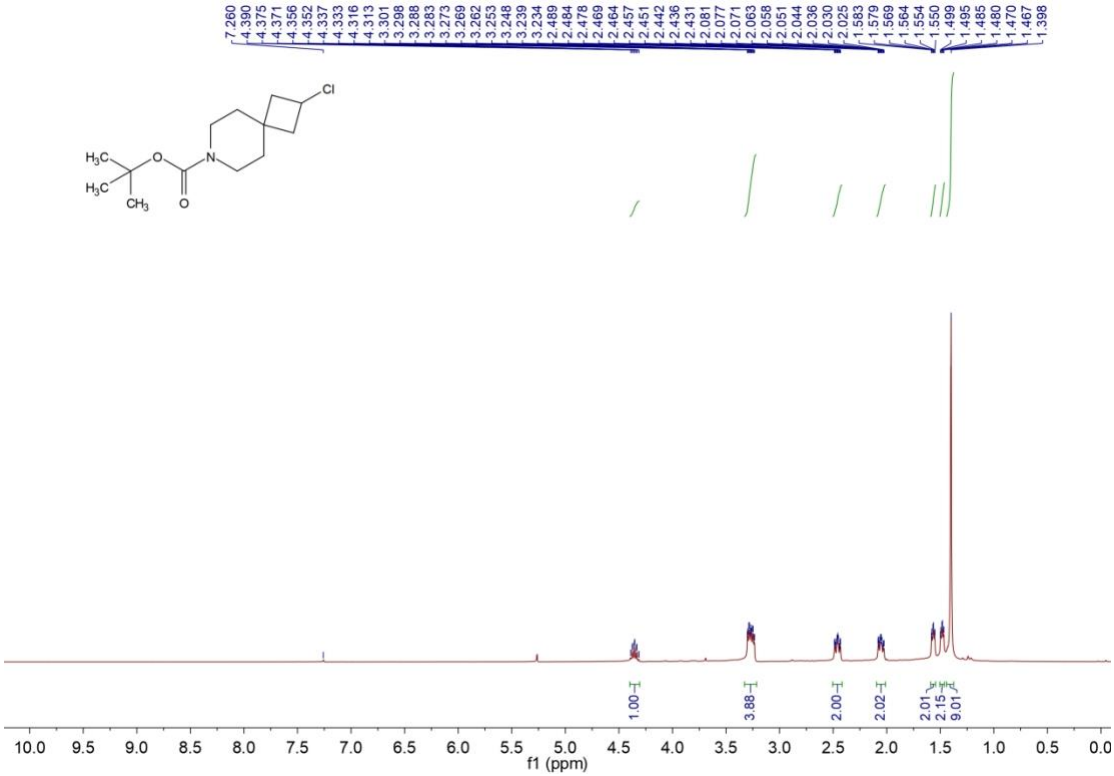
^{13}C NMR (101 MHz, $CDCl_3$) of product **10**



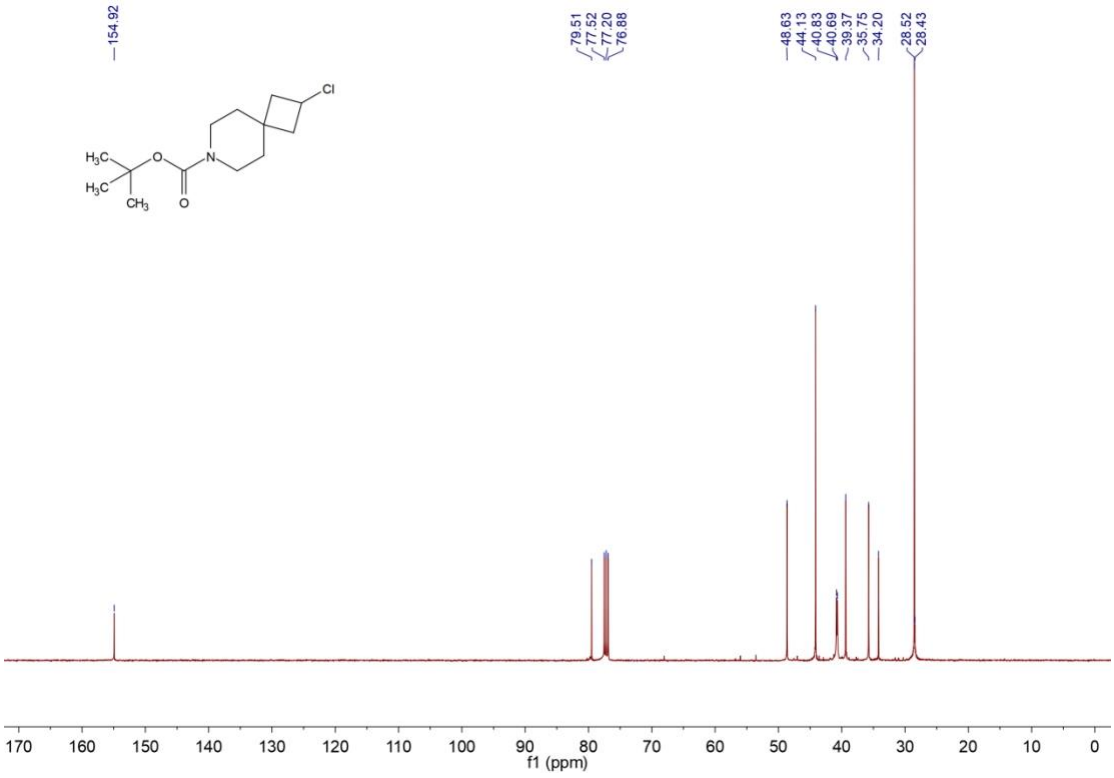
^{1}H NMR (400 MHz, $CDCl_3$) of product **12**



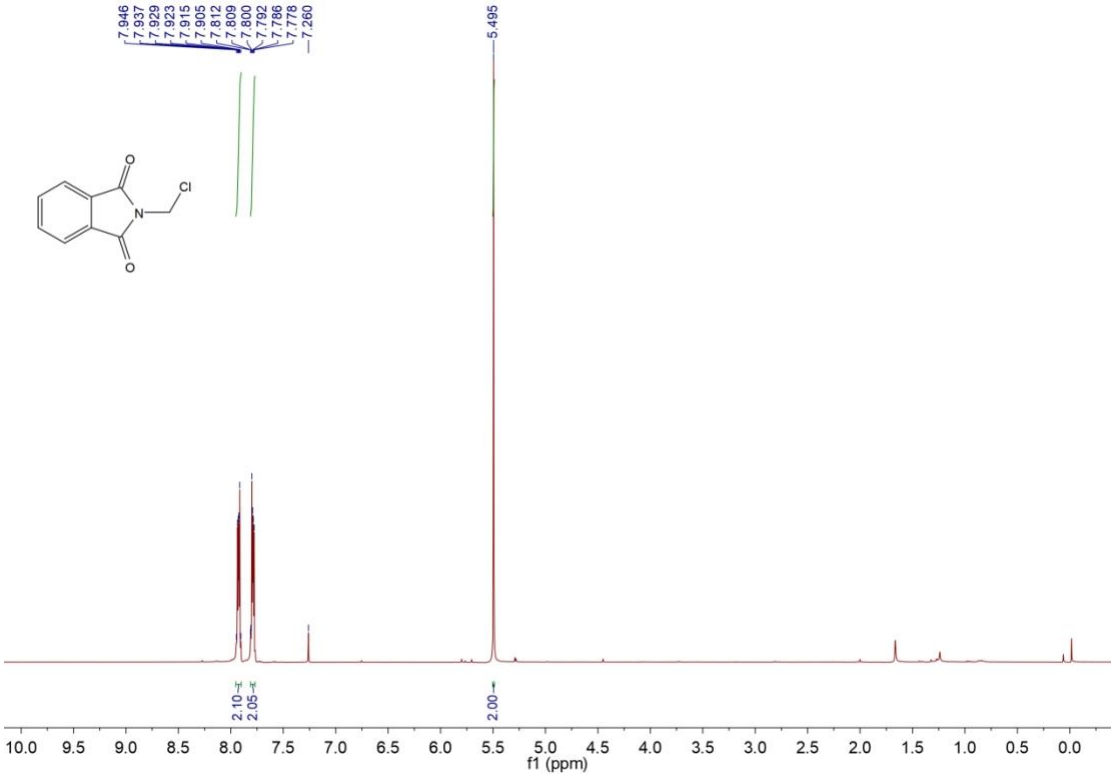
^{1}H NMR (400 MHz, $CDCl_3$) of product **13**



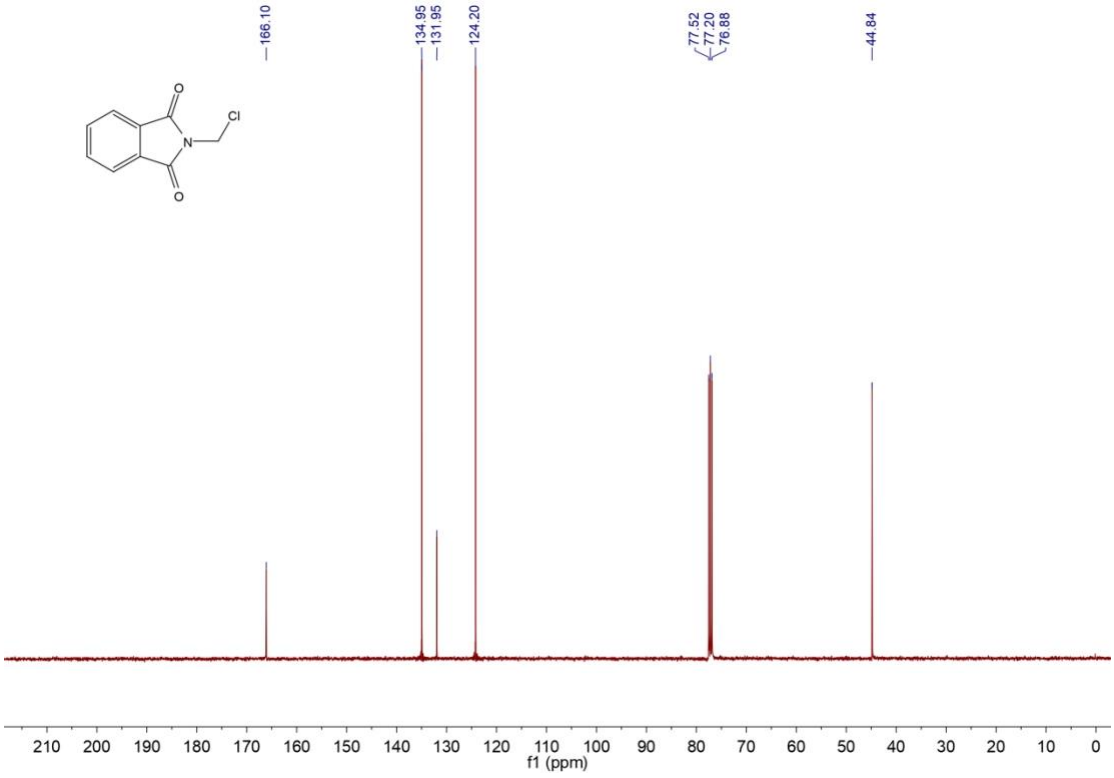
^{13}C NMR (101 MHz, $CDCl_3$) of product **13**



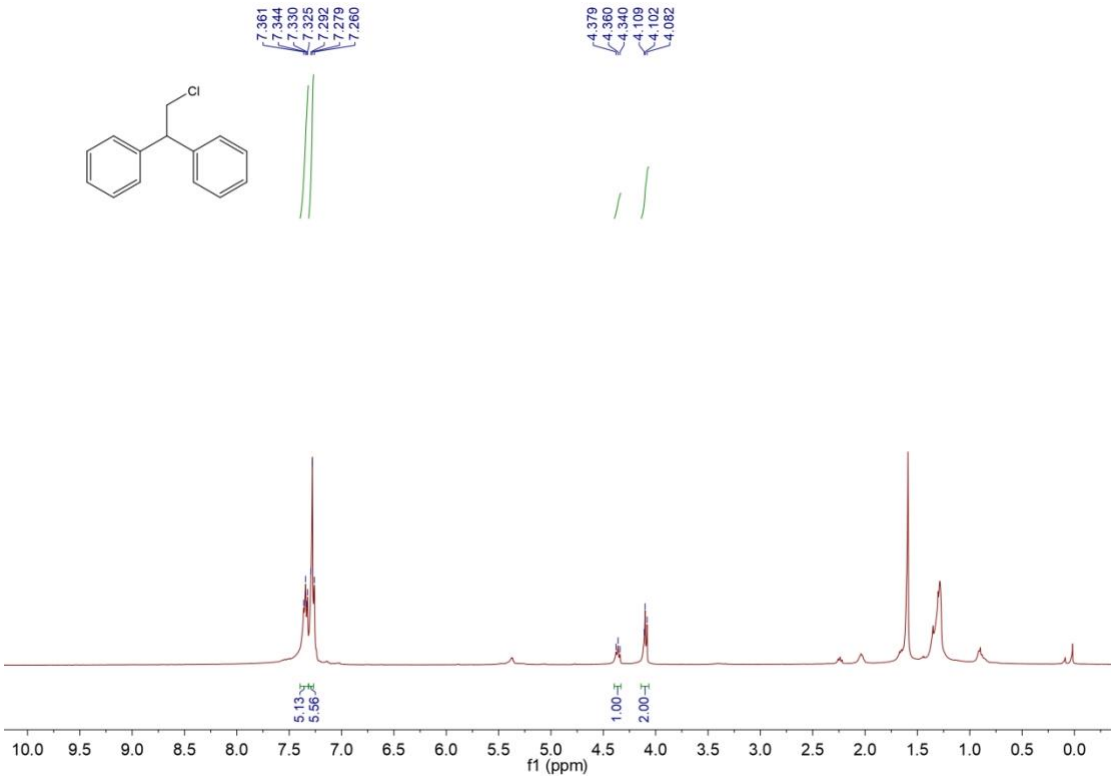
^{1}H NMR (400 MHz, $CDCl_3$) of product **15**



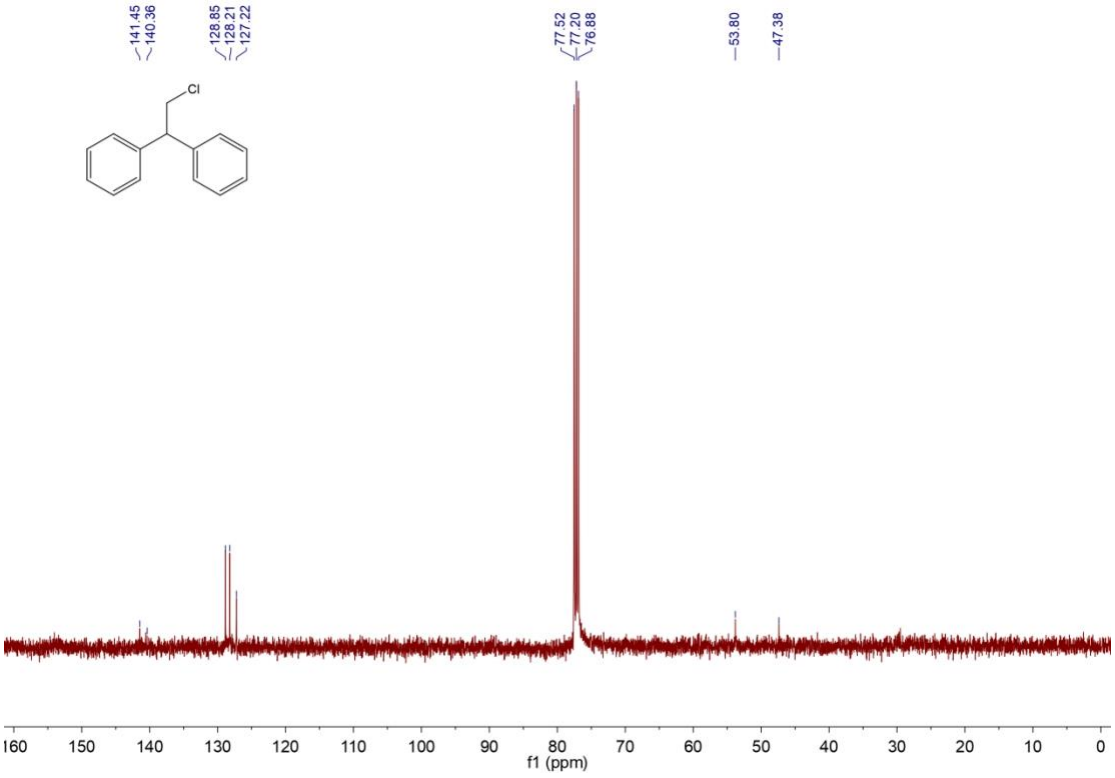
^{13}C NMR (101 MHz, $CDCl_3$) of product **15**



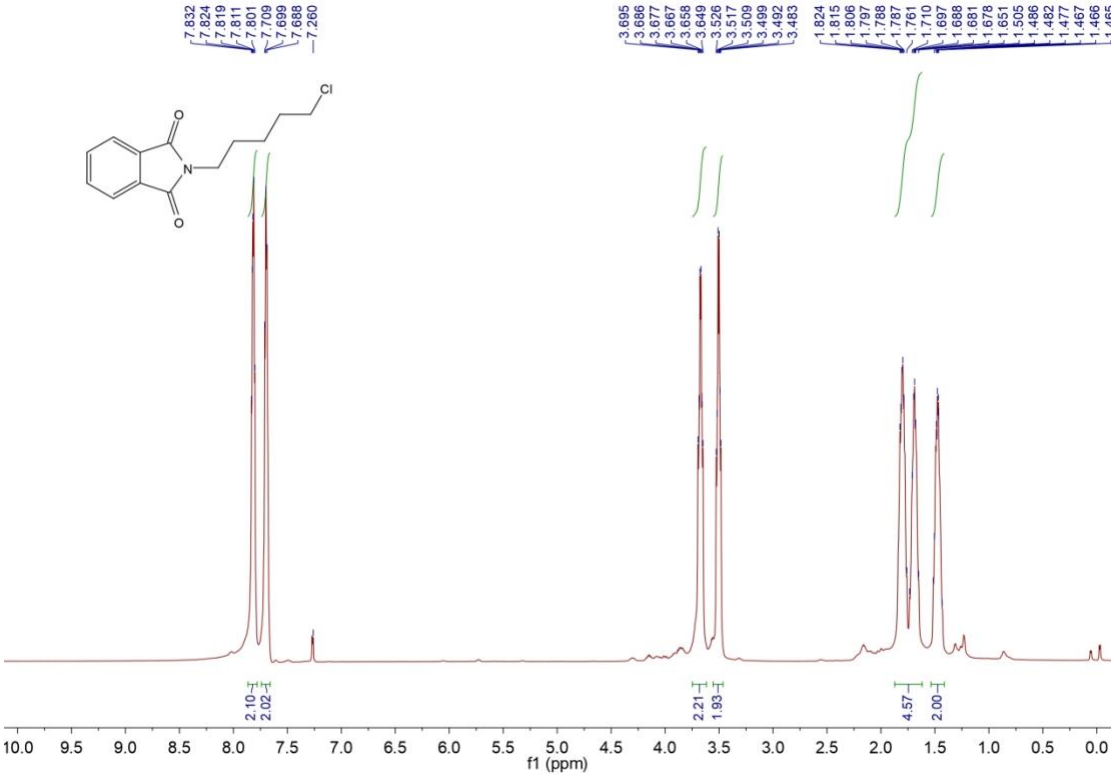
^{1}H NMR (400 MHz, $CDCl_3$) of product **16**



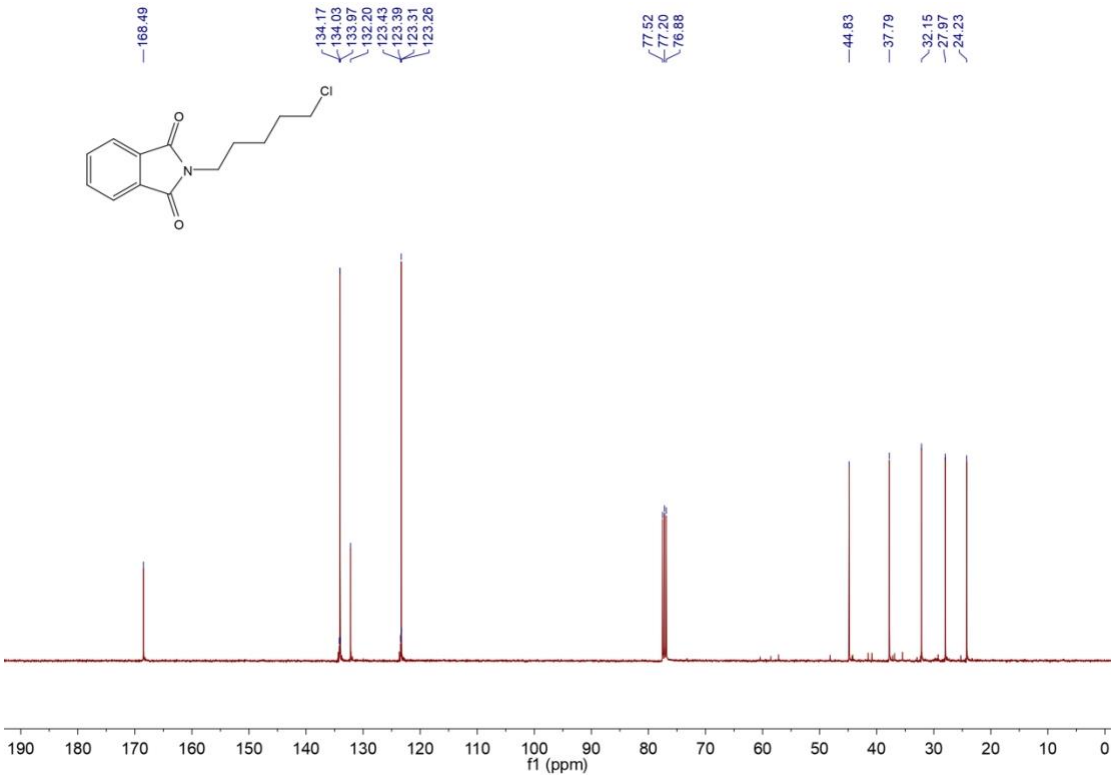
^{13}C NMR (101 MHz, $CDCl_3$) of product **16**



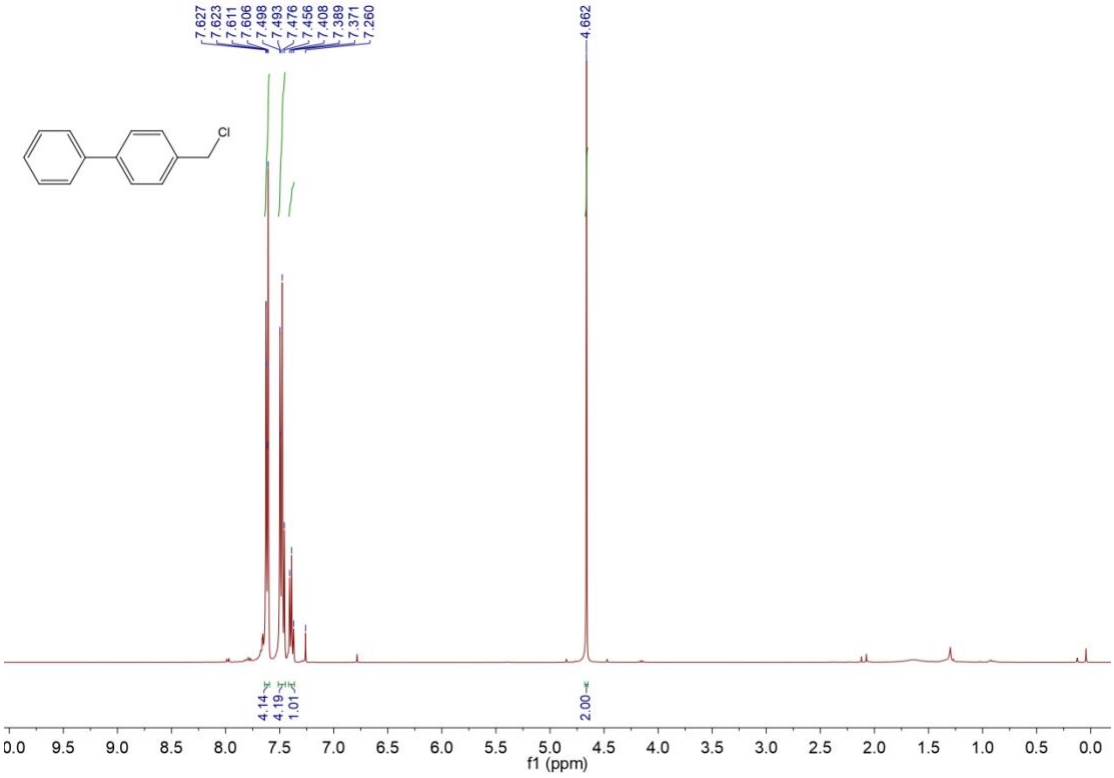
^{1}H NMR (400 MHz, $CDCl_3$) of product **18**



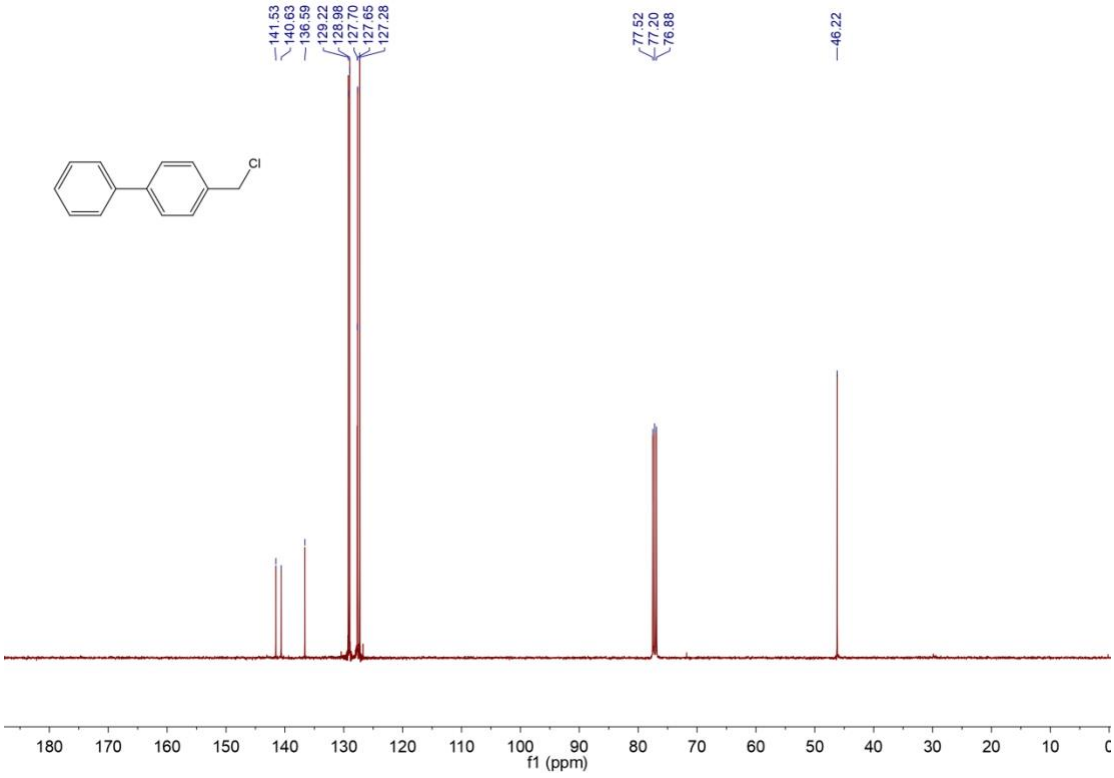
^{13}C NMR (101 MHz, $CDCl_3$) of product **18**



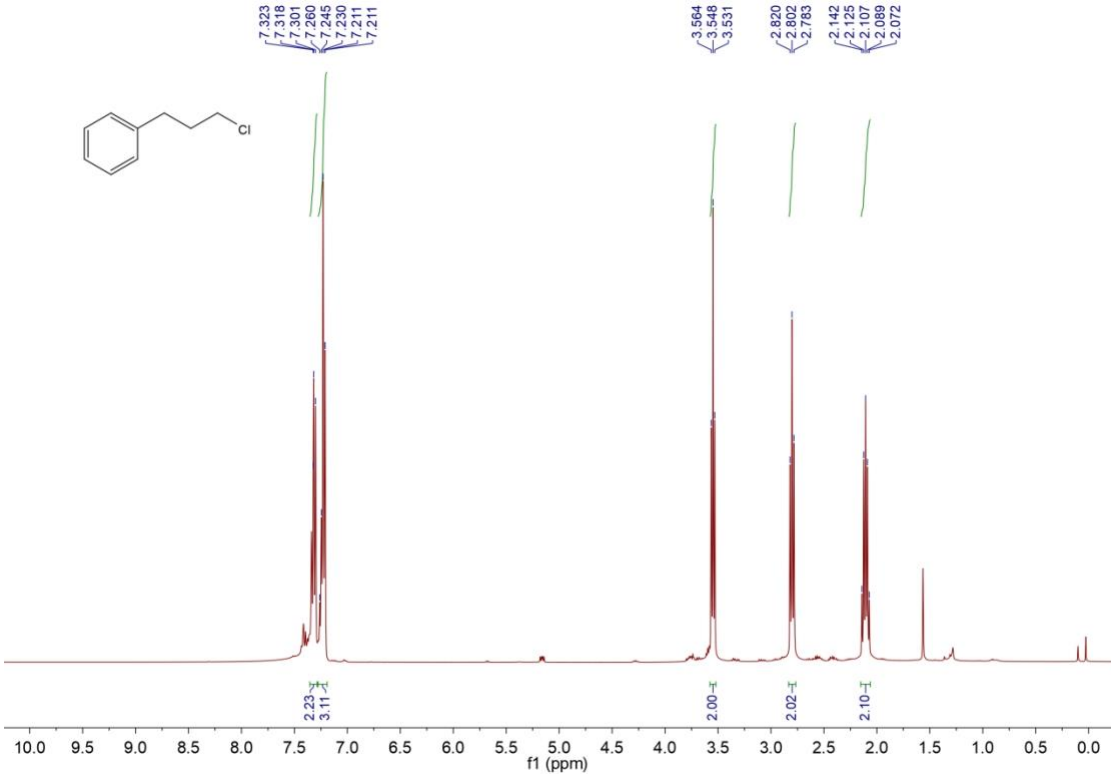
^{1}H NMR (400 MHz, $CDCl_3$) of product **21**



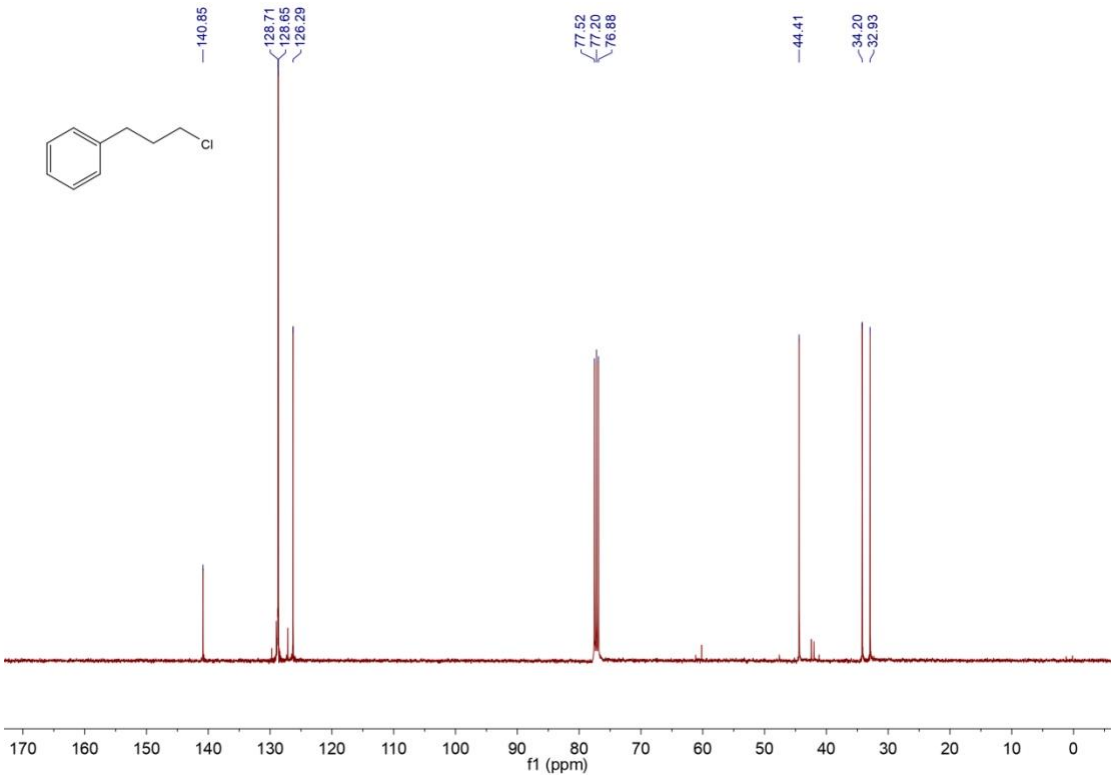
^{13}C NMR (101 MHz, $CDCl_3$) of product **21**



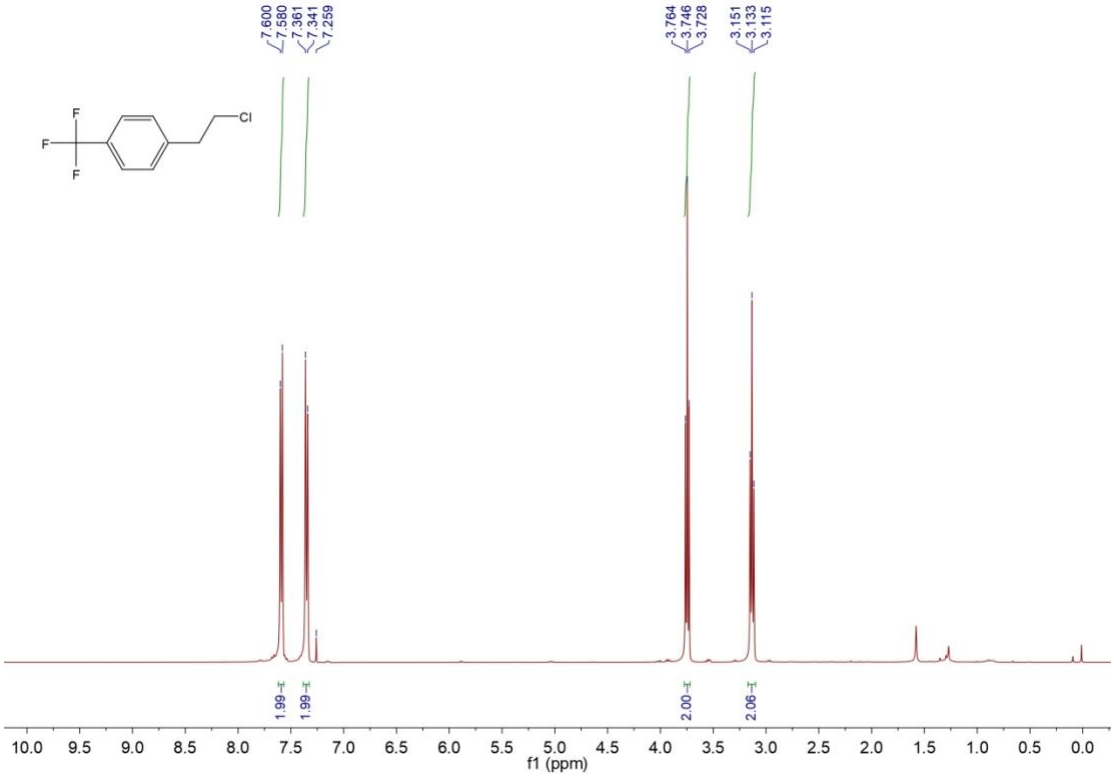
^{1}H NMR (400 MHz, $CDCl_3$) of product **22**



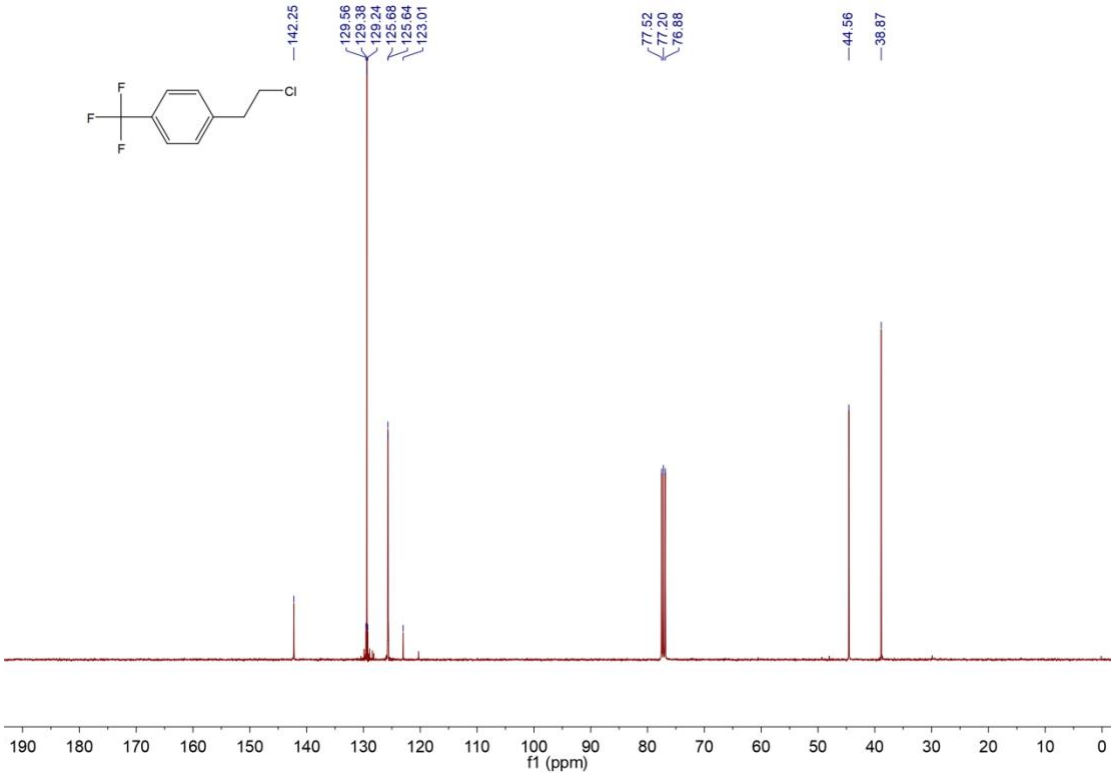
^{13}C NMR (101 MHz, $CDCl_3$) of product **22**



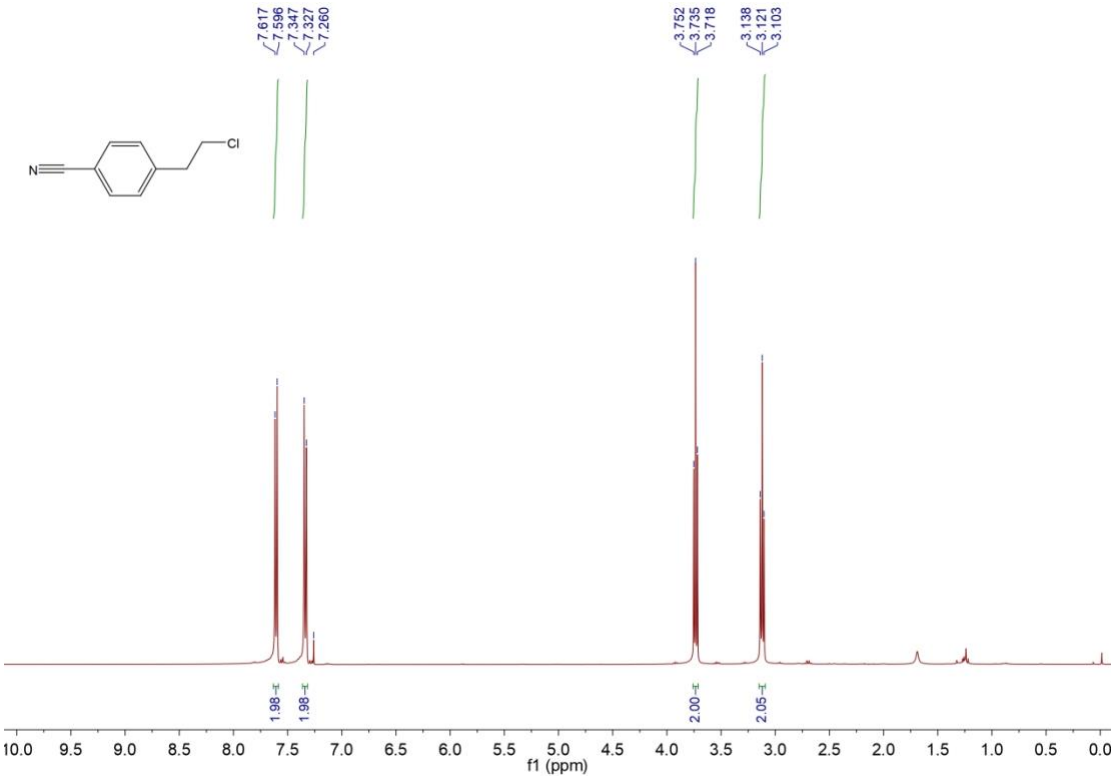
^{1}H NMR (400 MHz, $CDCl_3$) of product **23**



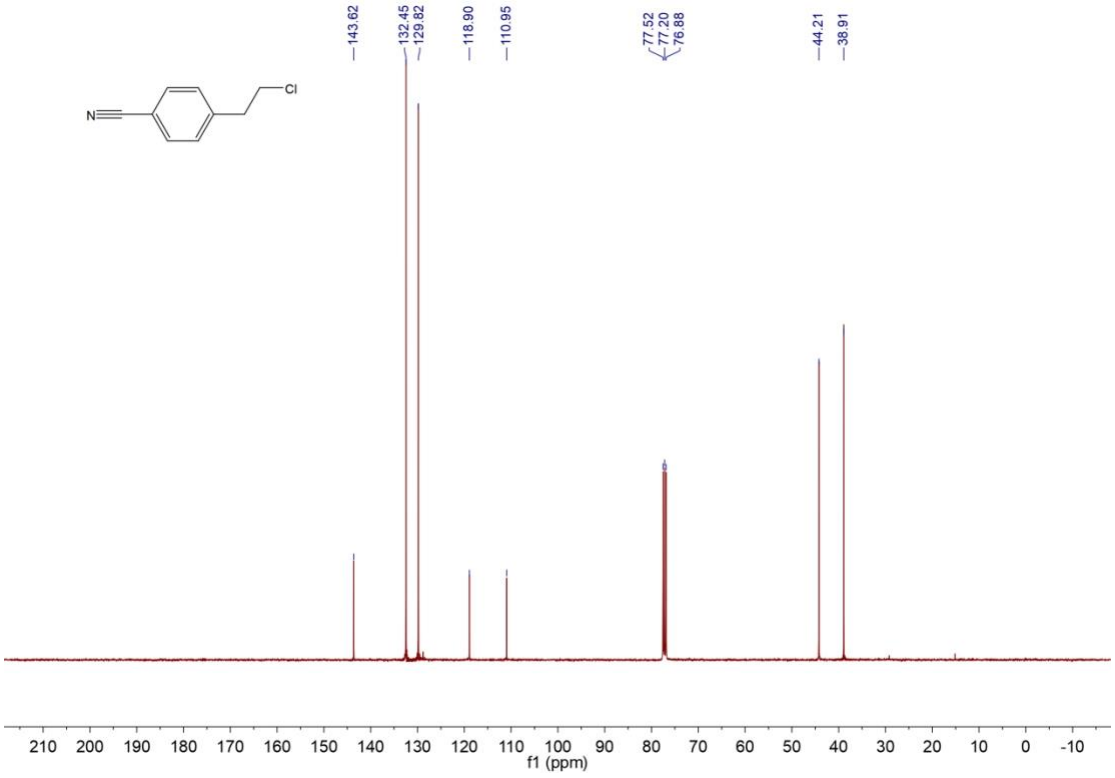
^{13}C NMR (101 MHz, $CDCl_3$) of product **23**



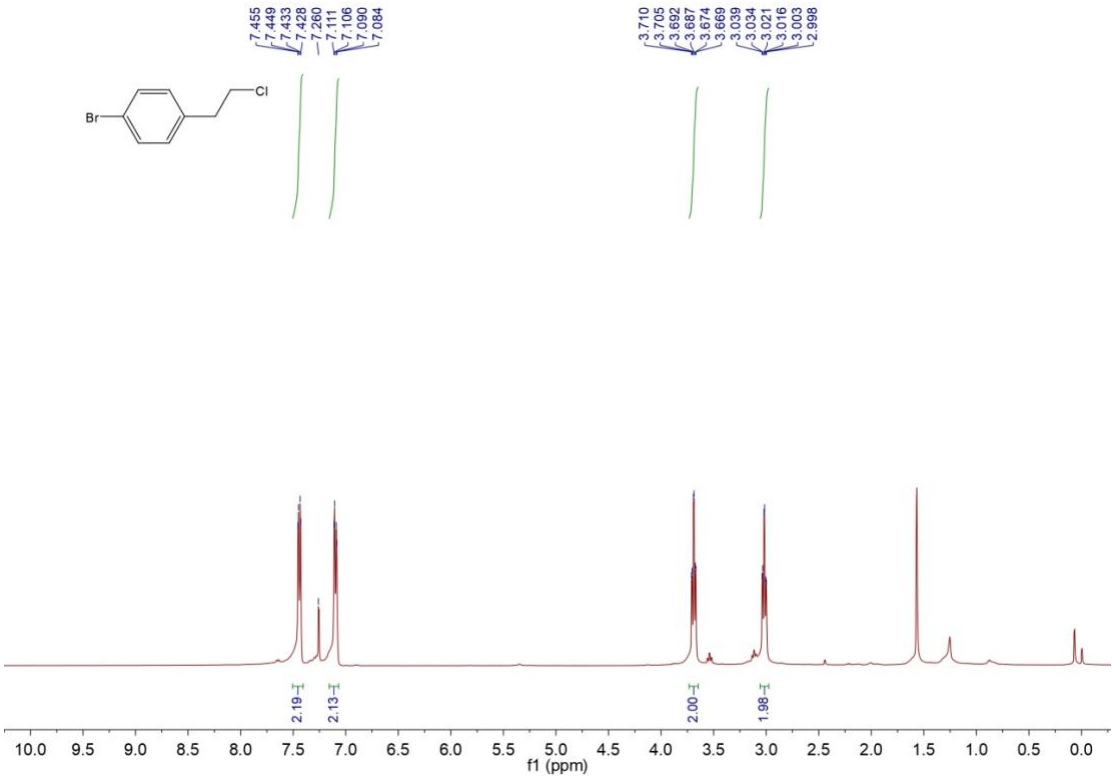
^{1}H NMR (400 MHz, $CDCl_3$) of product **25**



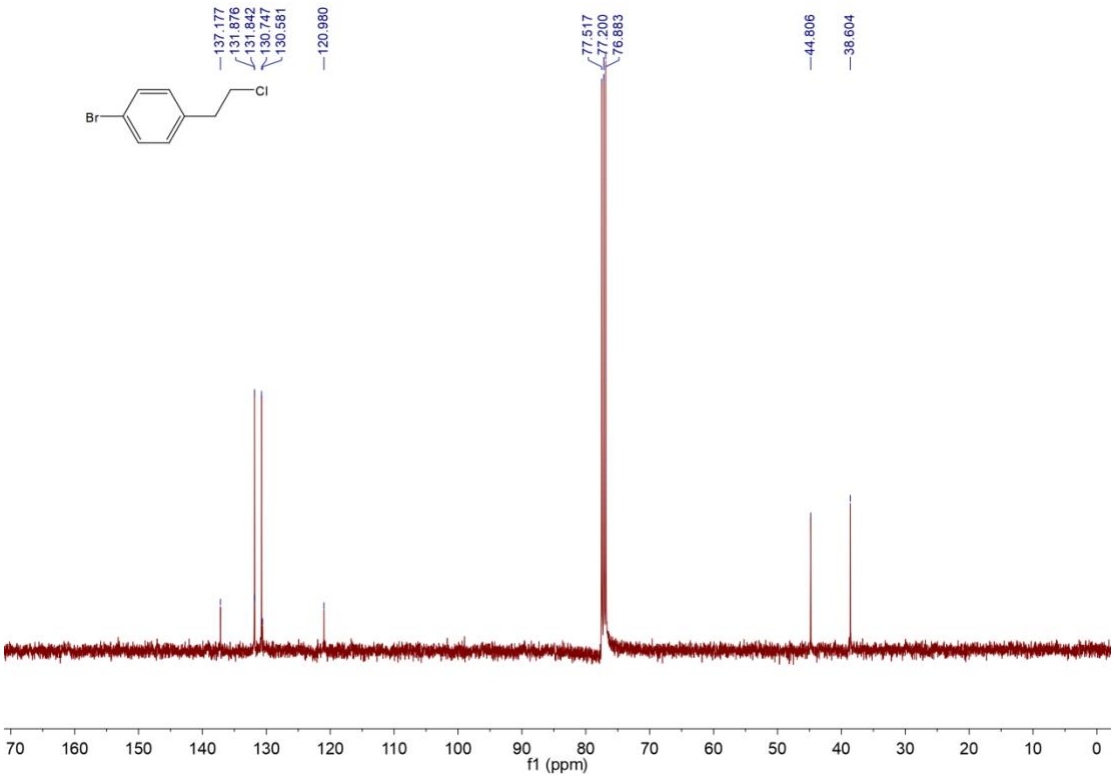
^{13}C NMR (101 MHz, $CDCl_3$) of product **25**



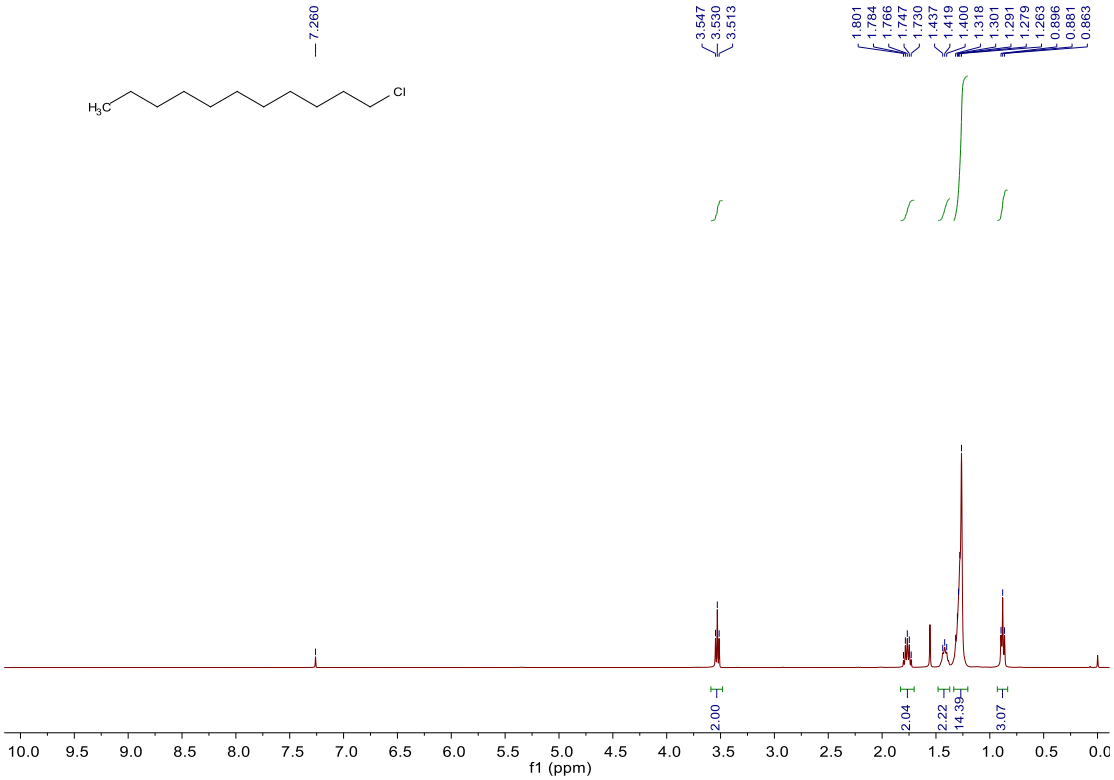
^{1}H NMR (400 MHz, $CDCl_3$) of product **27**



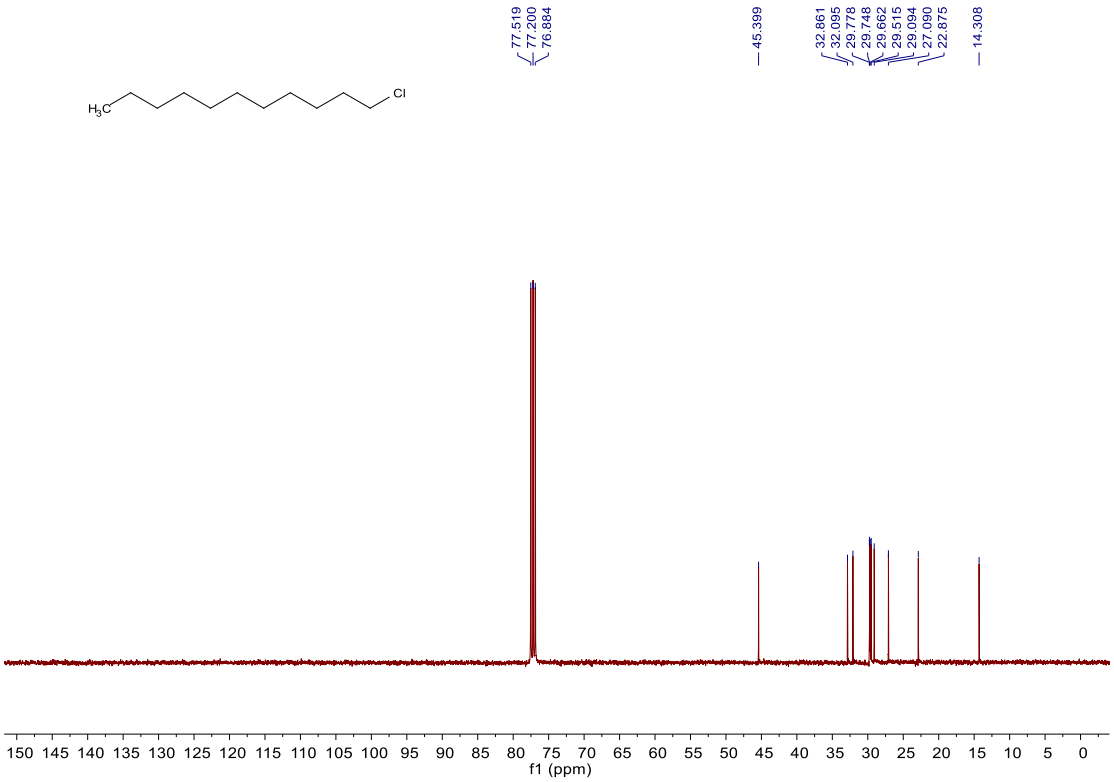
^{13}C NMR (101 MHz, $CDCl_3$) of product **27**



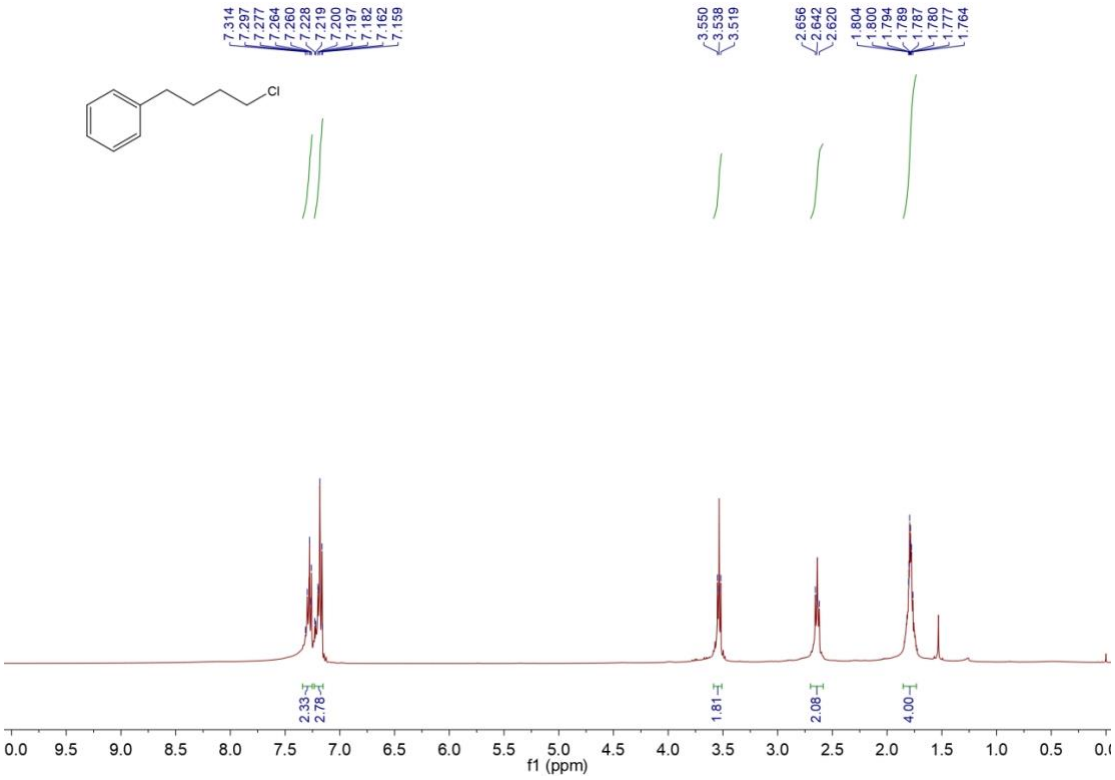
^{1}H NMR (400 MHz, $CDCl_3$) of product **29**



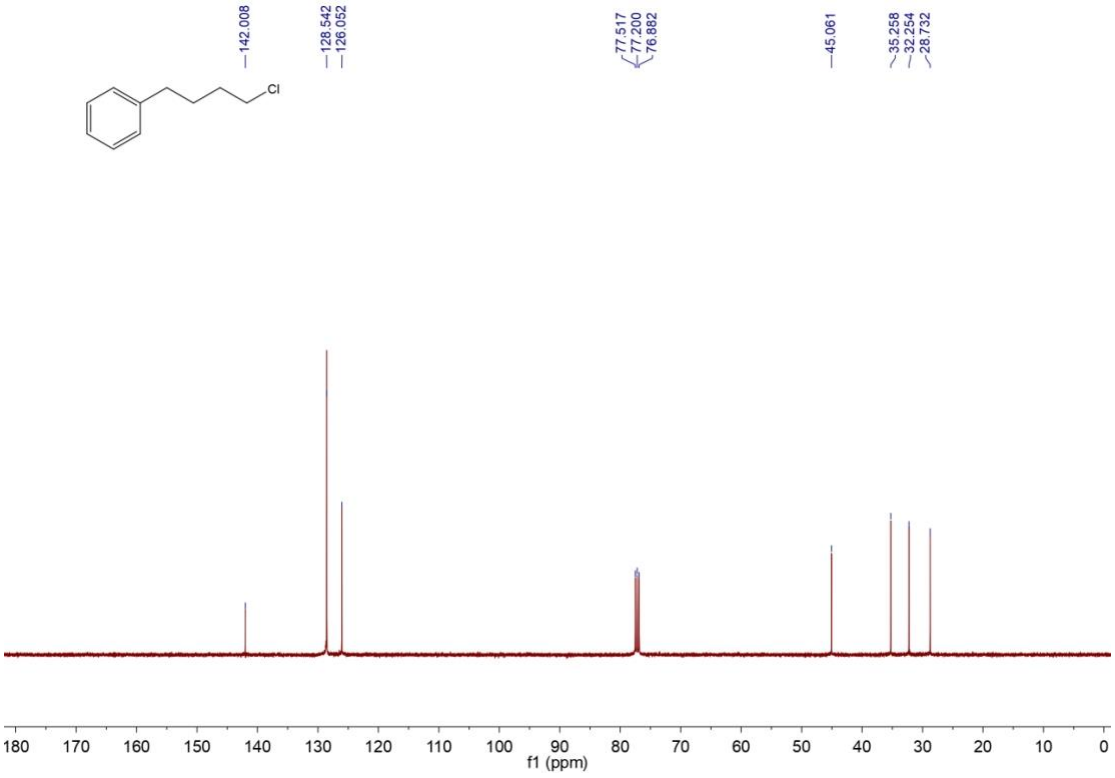
^{13}C NMR (101 MHz, $CDCl_3$) of product **29**



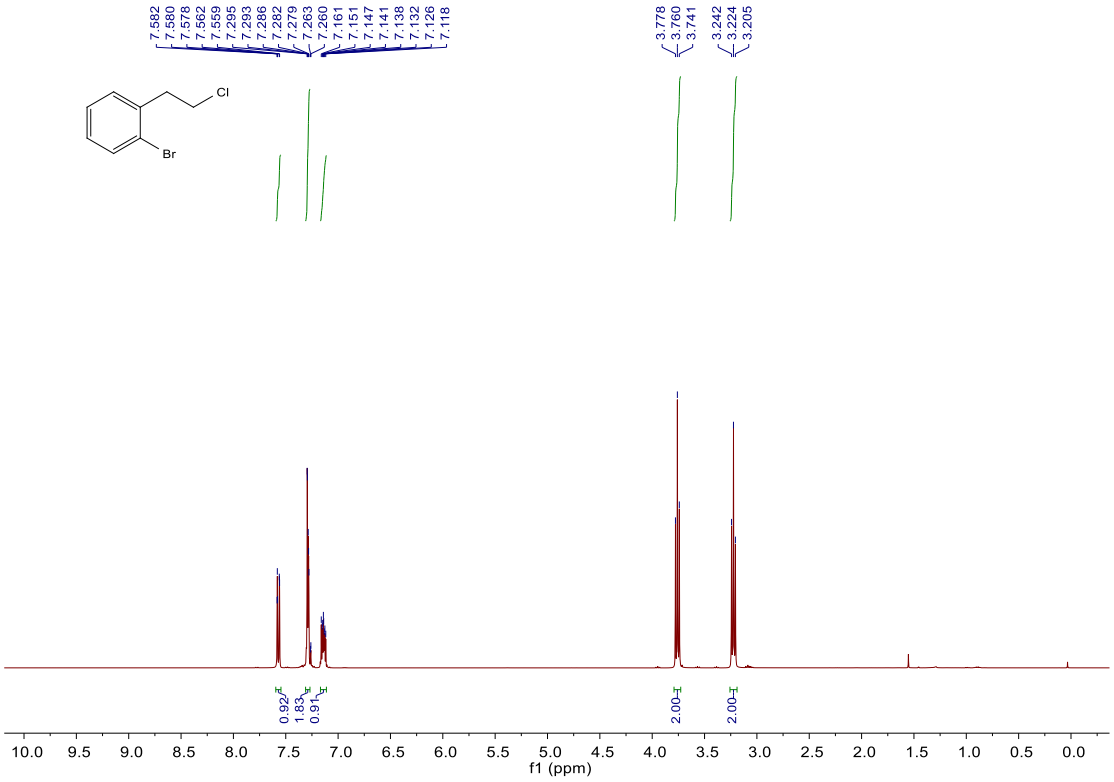
^{1}H NMR (400 MHz, $CDCl_3$) of product **32**



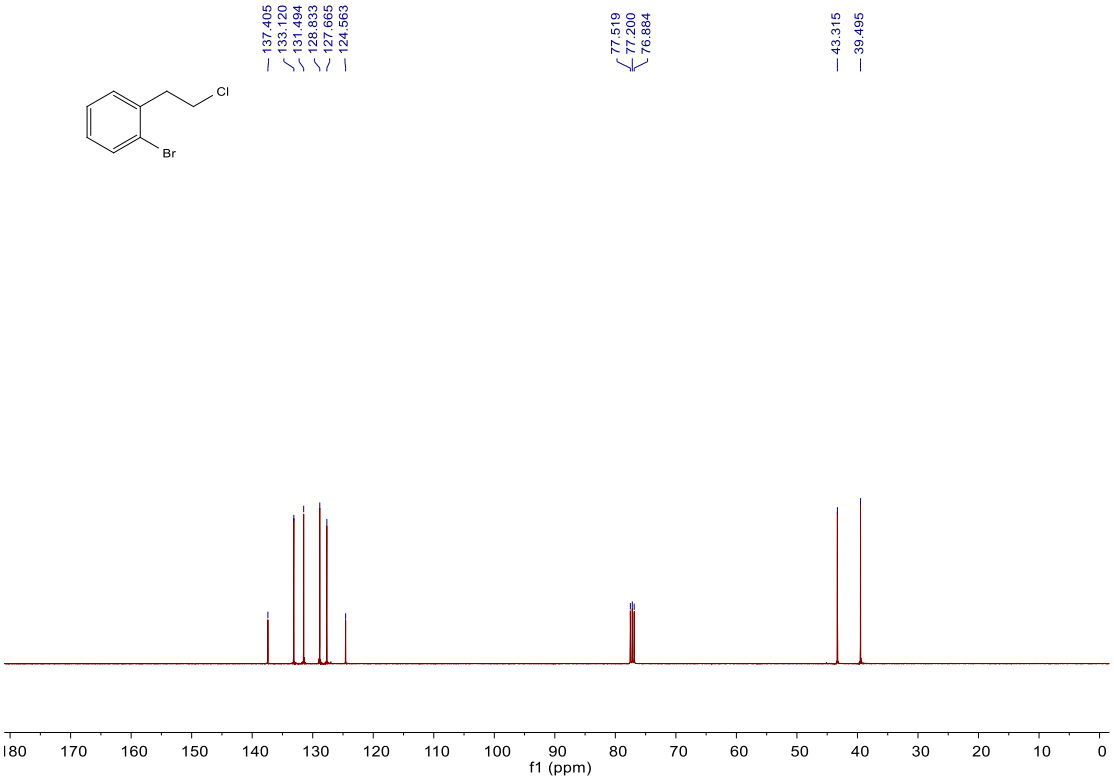
^{13}C NMR (101 MHz, $CDCl_3$) of product **32**



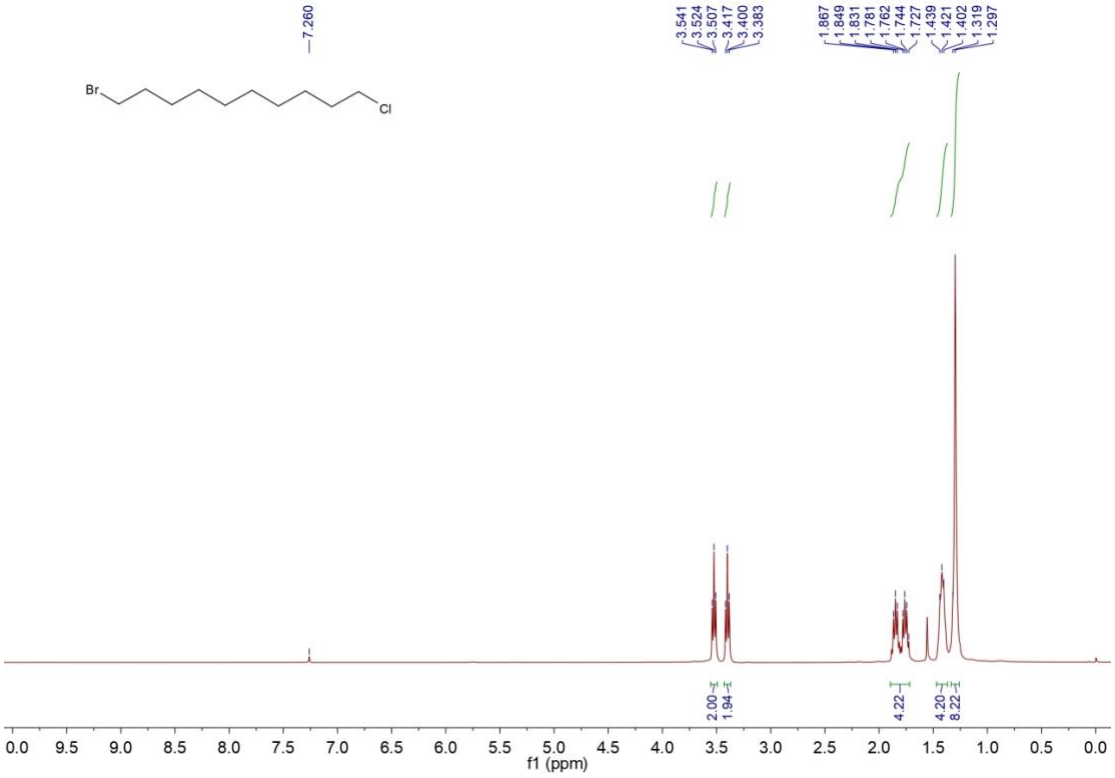
^{1}H NMR (400 MHz, $CDCl_3$) of product **33**



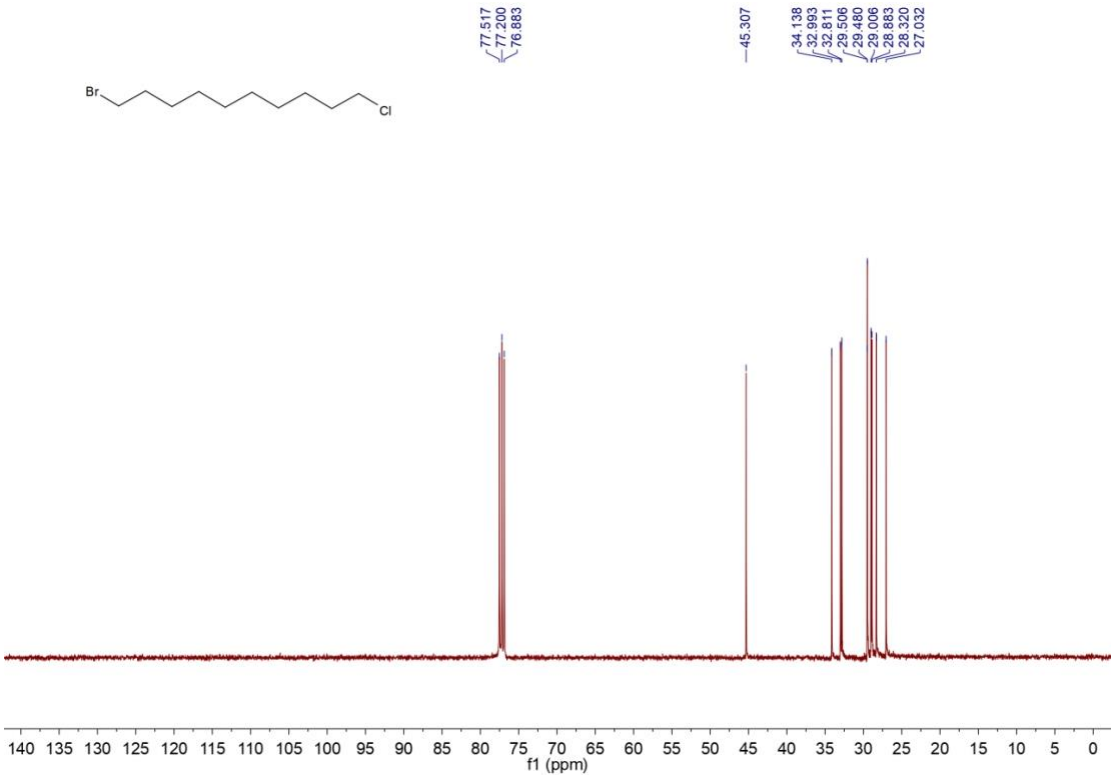
^{13}C NMR (101 MHz, $CDCl_3$) of product **33**



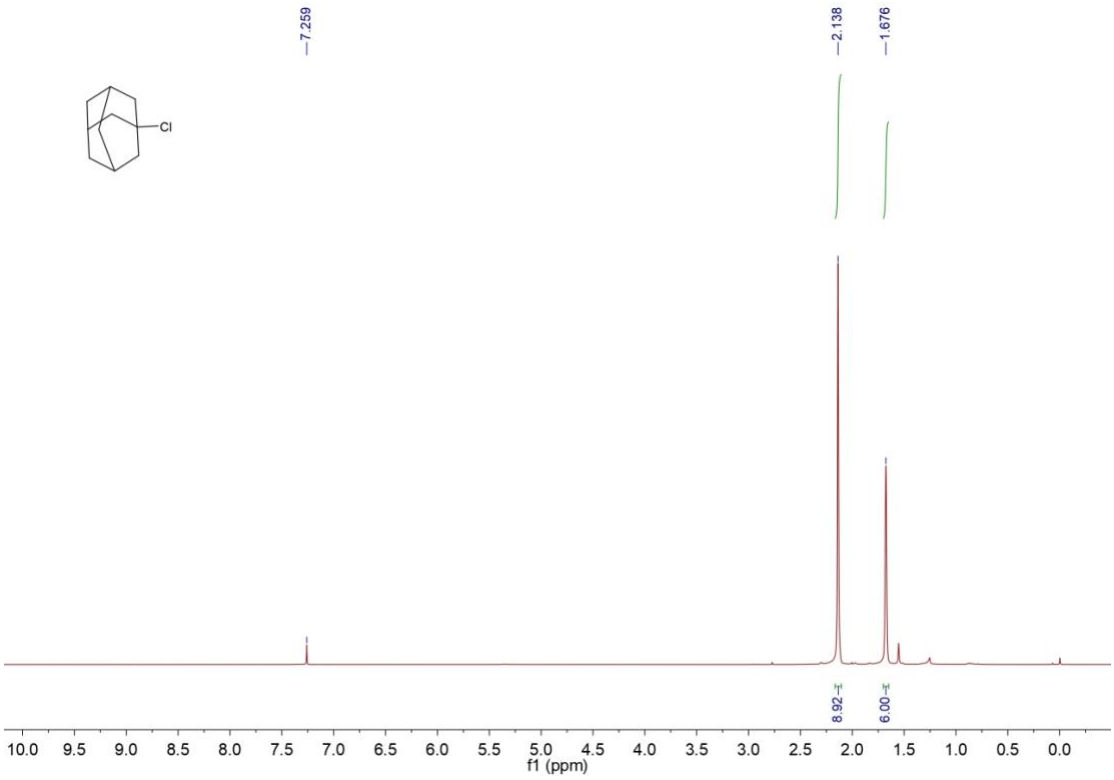
^{1}H NMR (400 MHz, $CDCl_3$) of product **36**



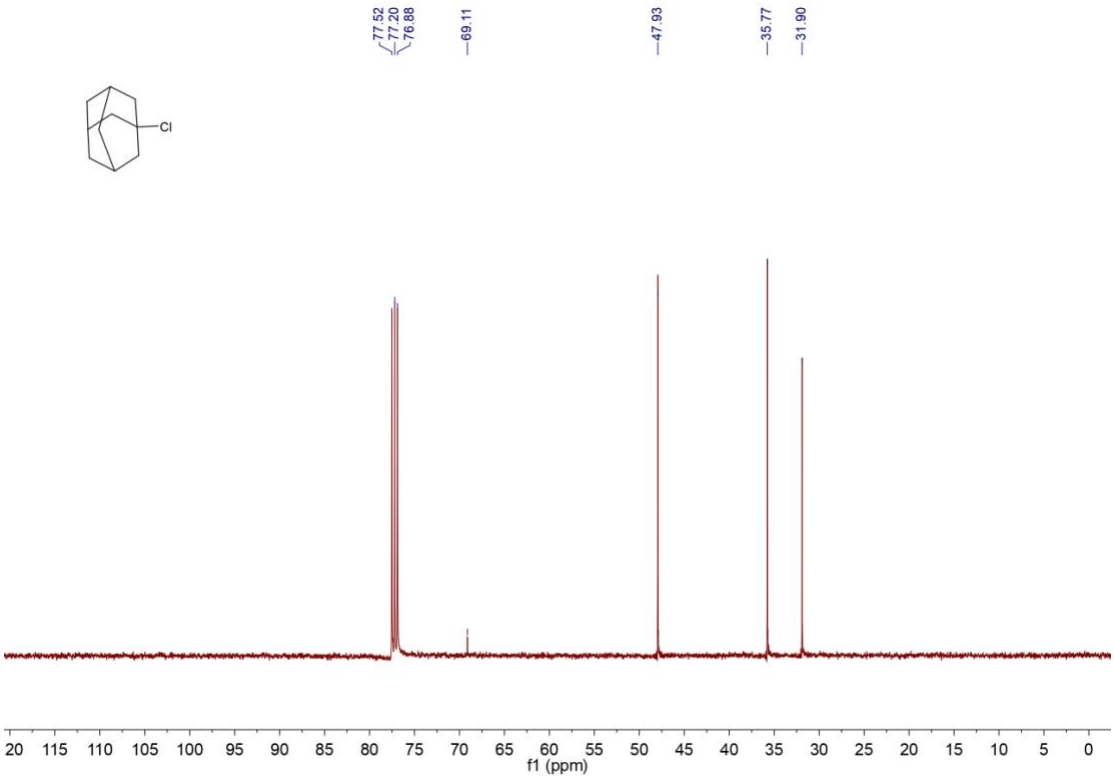
^{13}C NMR (101 MHz, $CDCl_3$) of product **36**



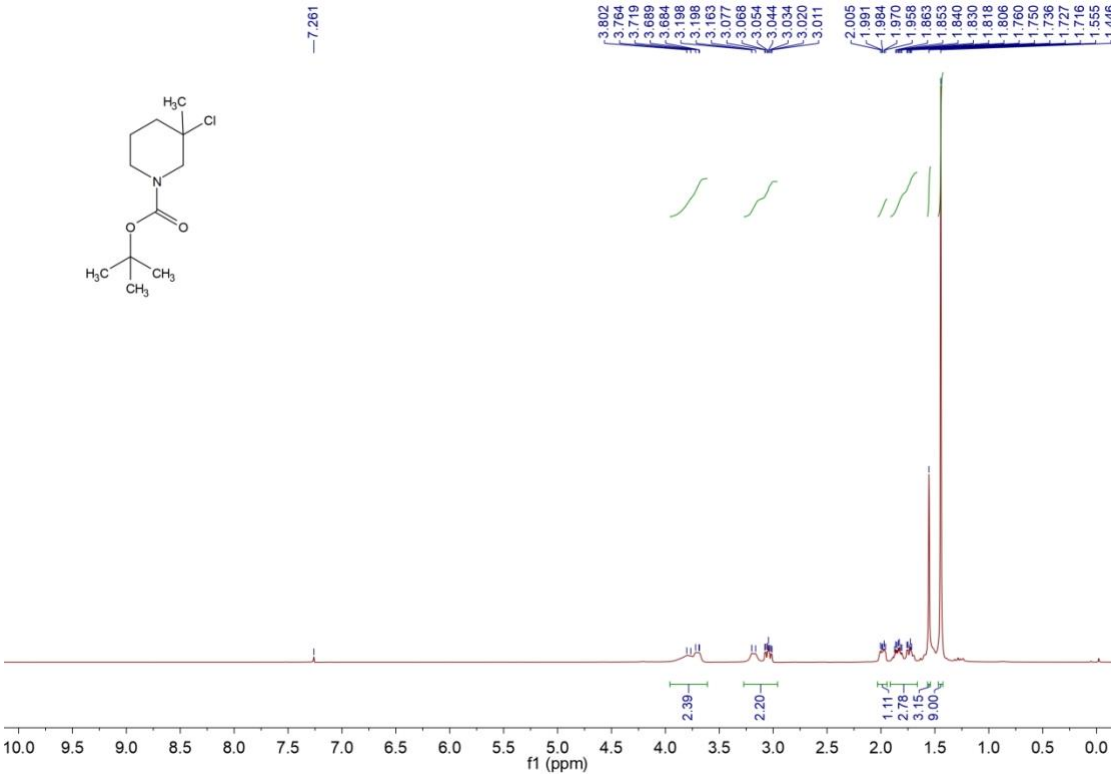
^{1}H NMR (400 MHz, $CDCl_3$) of product **37**



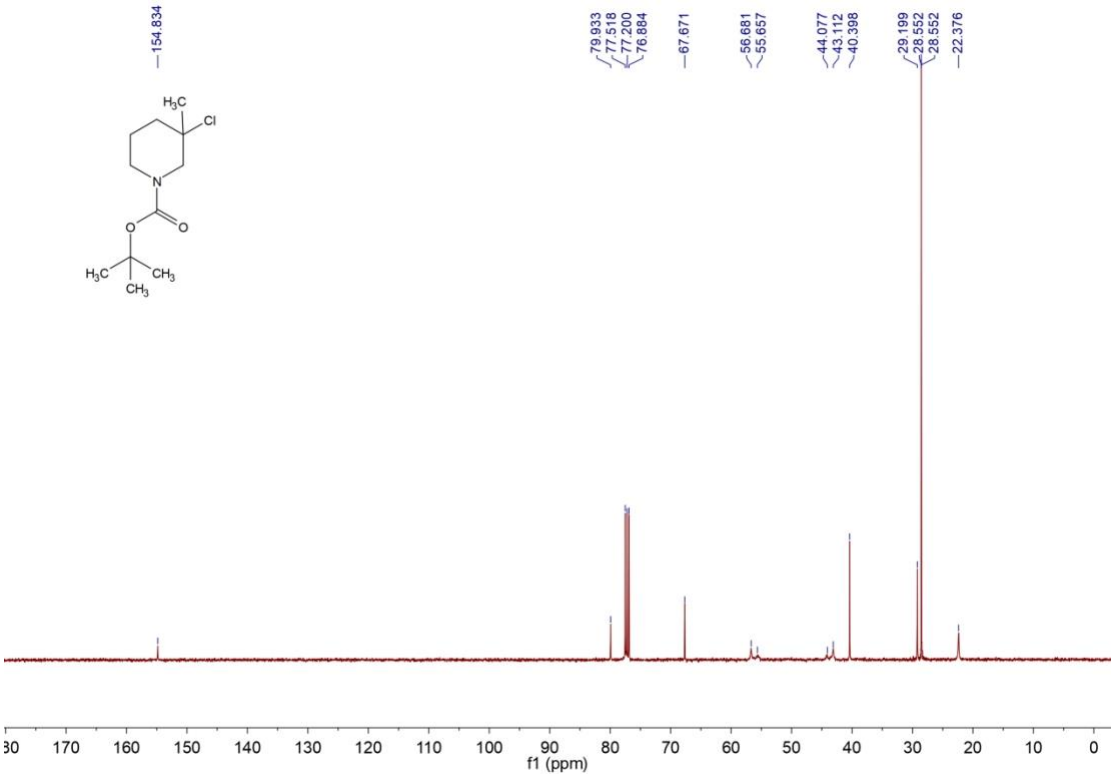
^{13}C NMR (101 MHz, $CDCl_3$) of product **37**



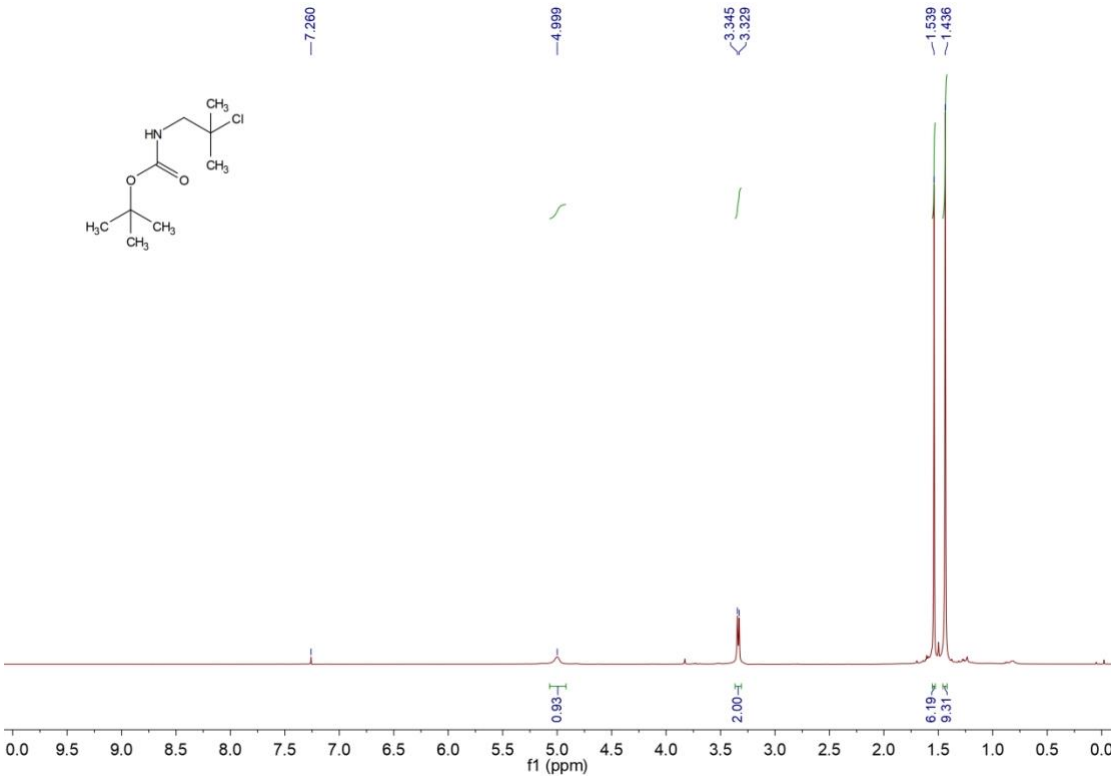
^{1}H NMR (400 MHz, $CDCl_3$) of product **39**



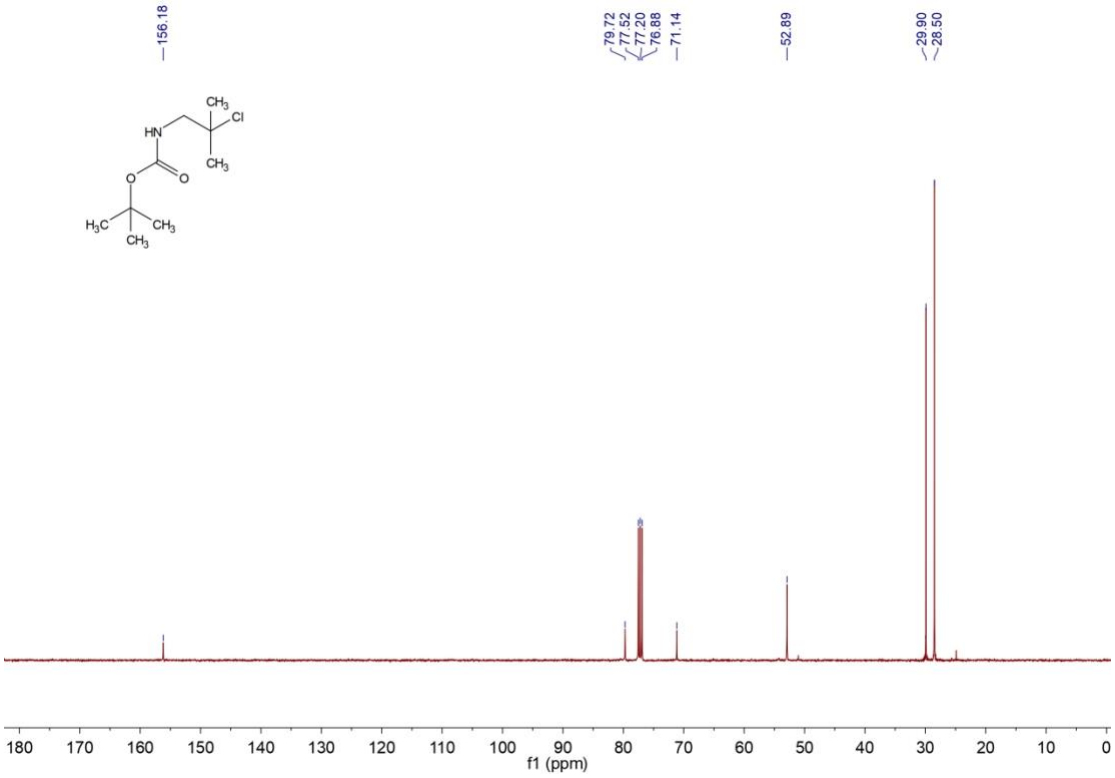
^{13}C NMR (101 MHz, $CDCl_3$) of product **39**



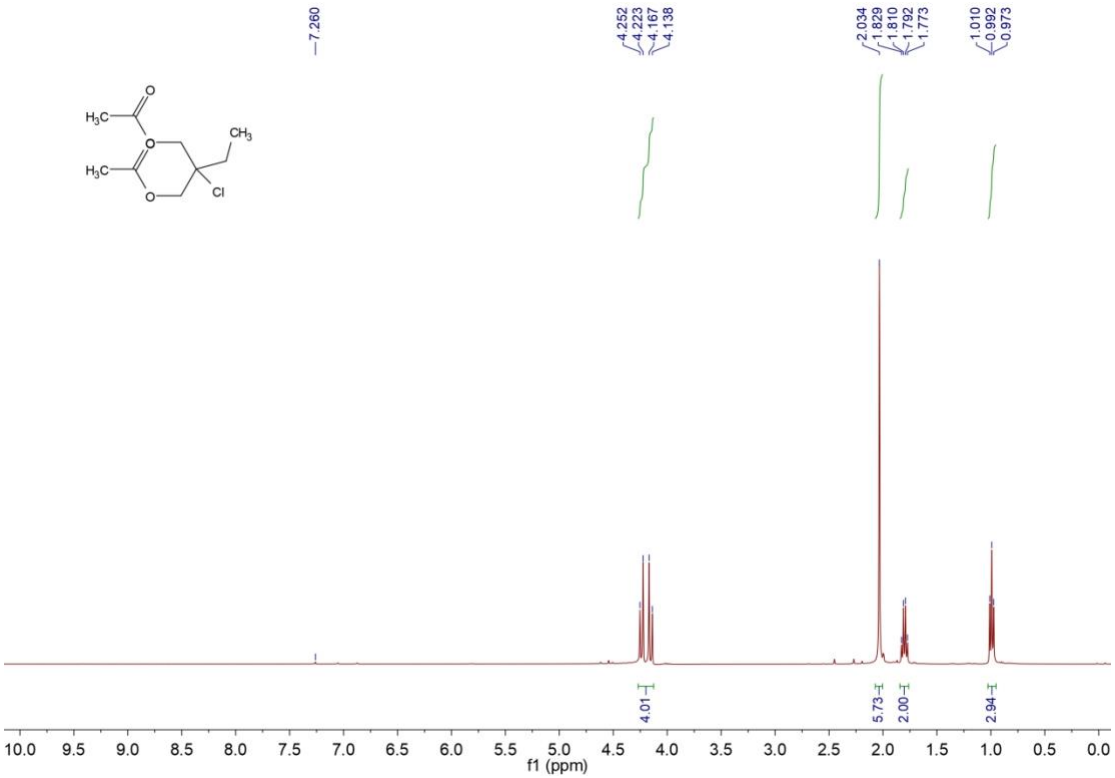
^{1}H NMR (400 MHz, $CDCl_3$) of product **40**



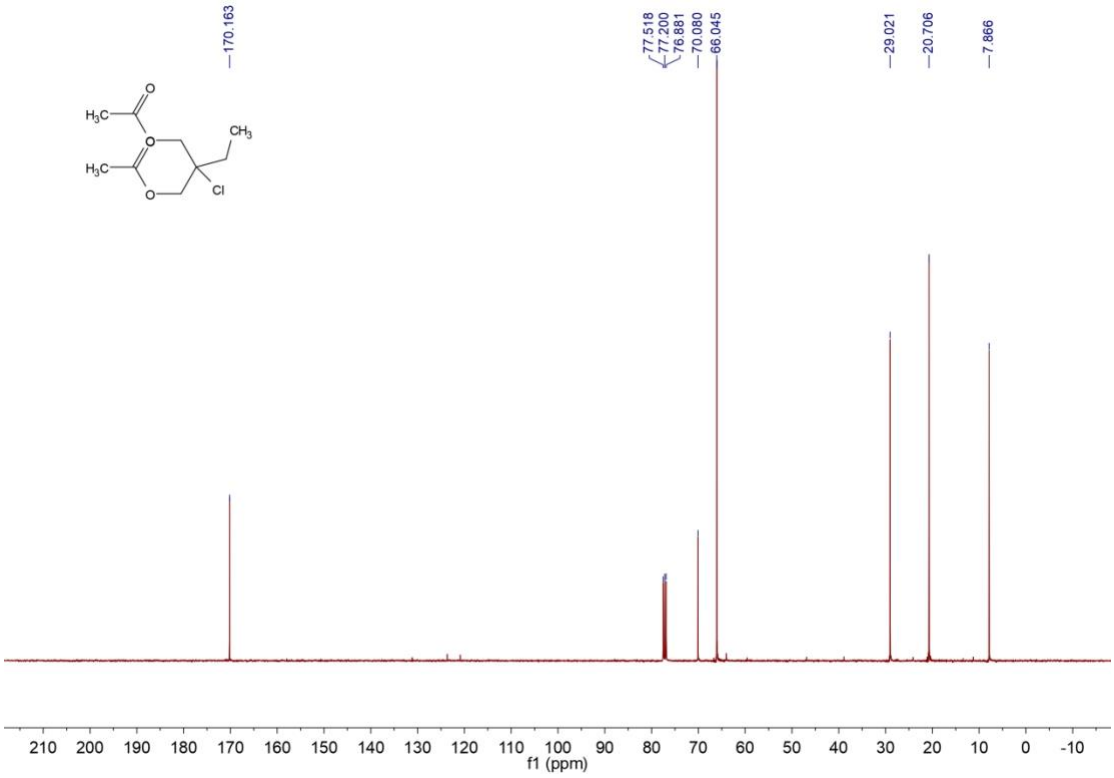
^{13}C NMR (101 MHz, $CDCl_3$) of product **40**



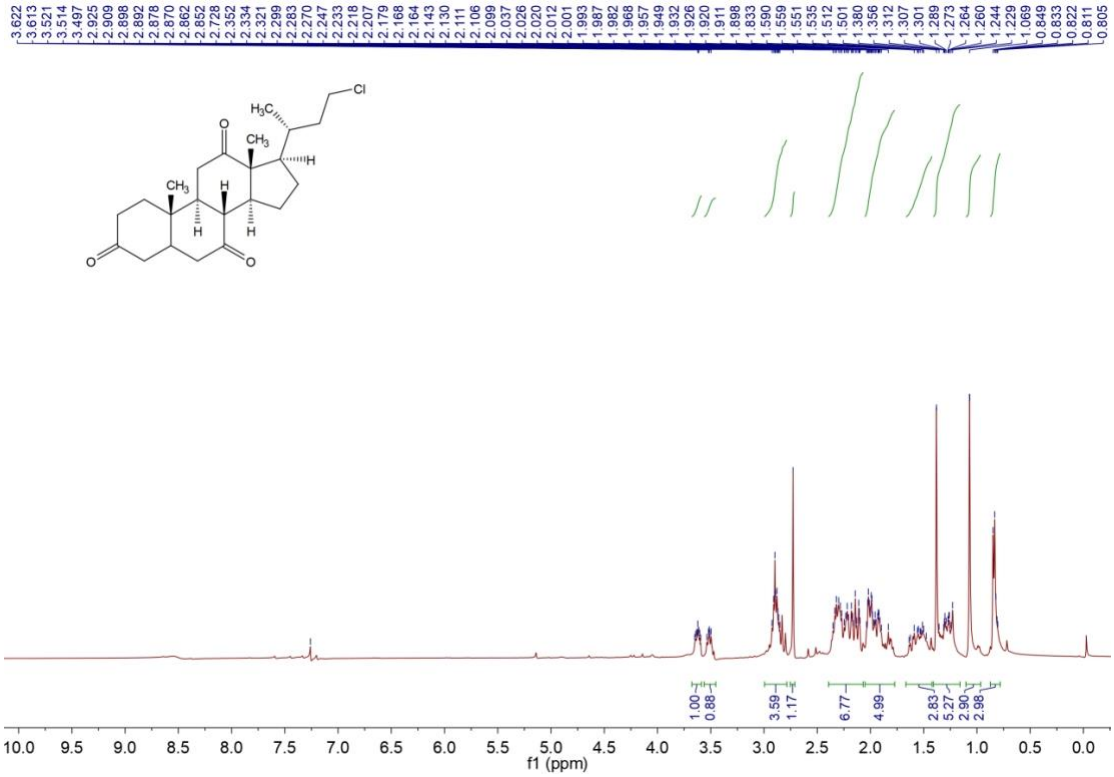
^{1}H NMR (400 MHz, $CDCl_3$) of product **41**



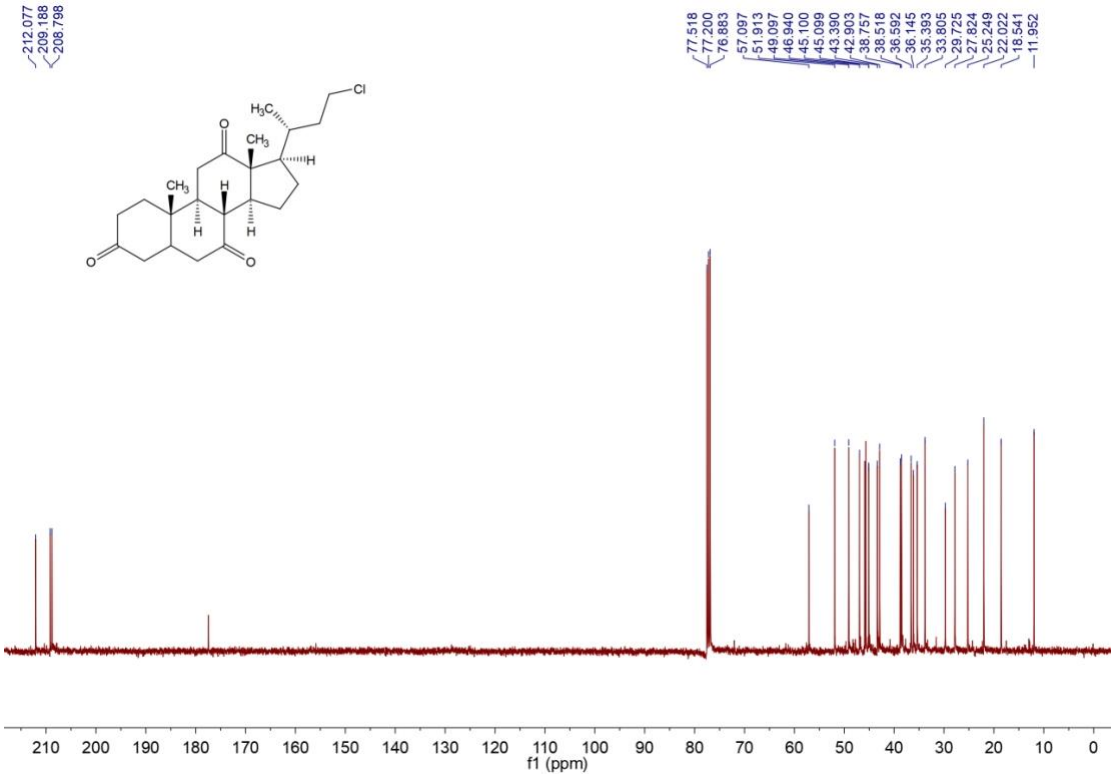
^{13}C NMR (101 MHz, $CDCl_3$) of product **41**



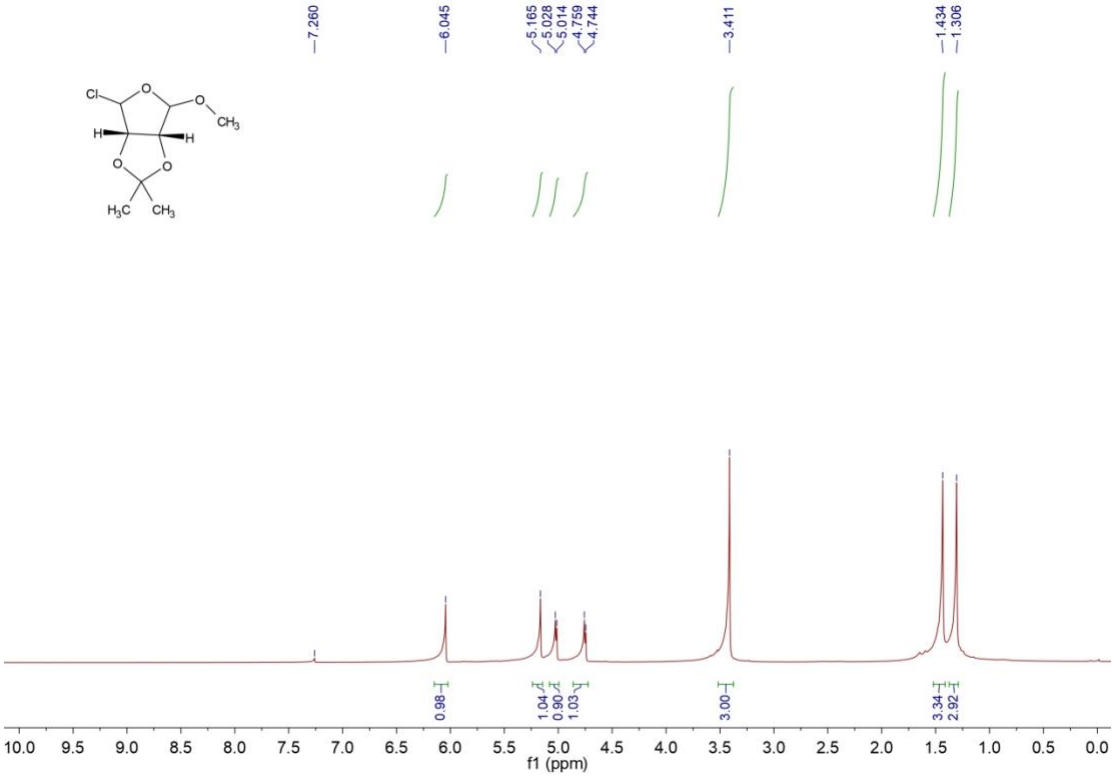
^{1}H NMR (400 MHz, $CDCl_3$) of product **44**



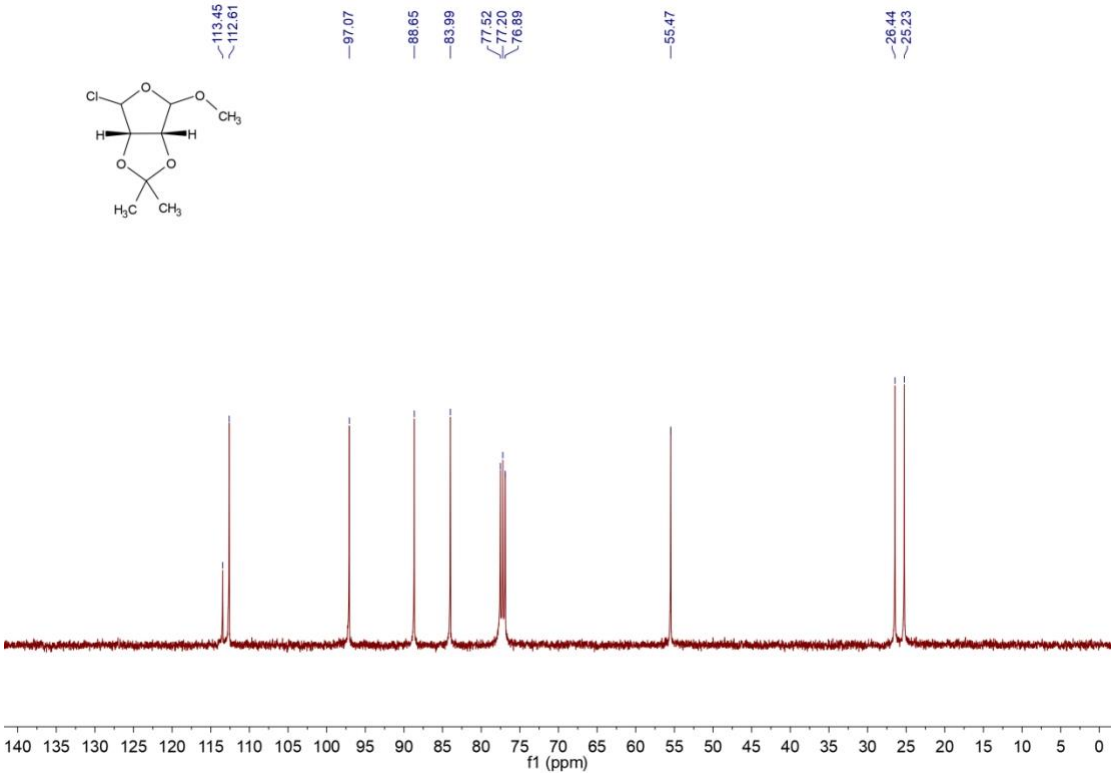
^{13}C NMR (101 MHz, $CDCl_3$) of product **44**



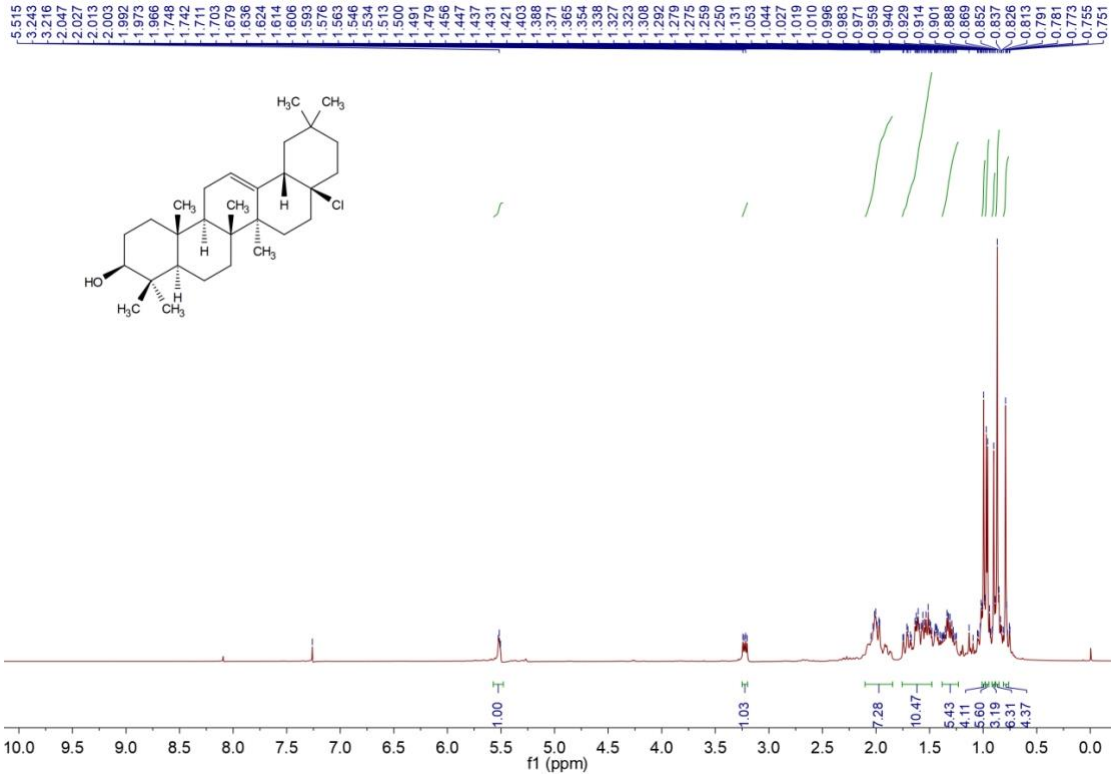
^{1}H NMR (400 MHz, $CDCl_3$) of product **45**



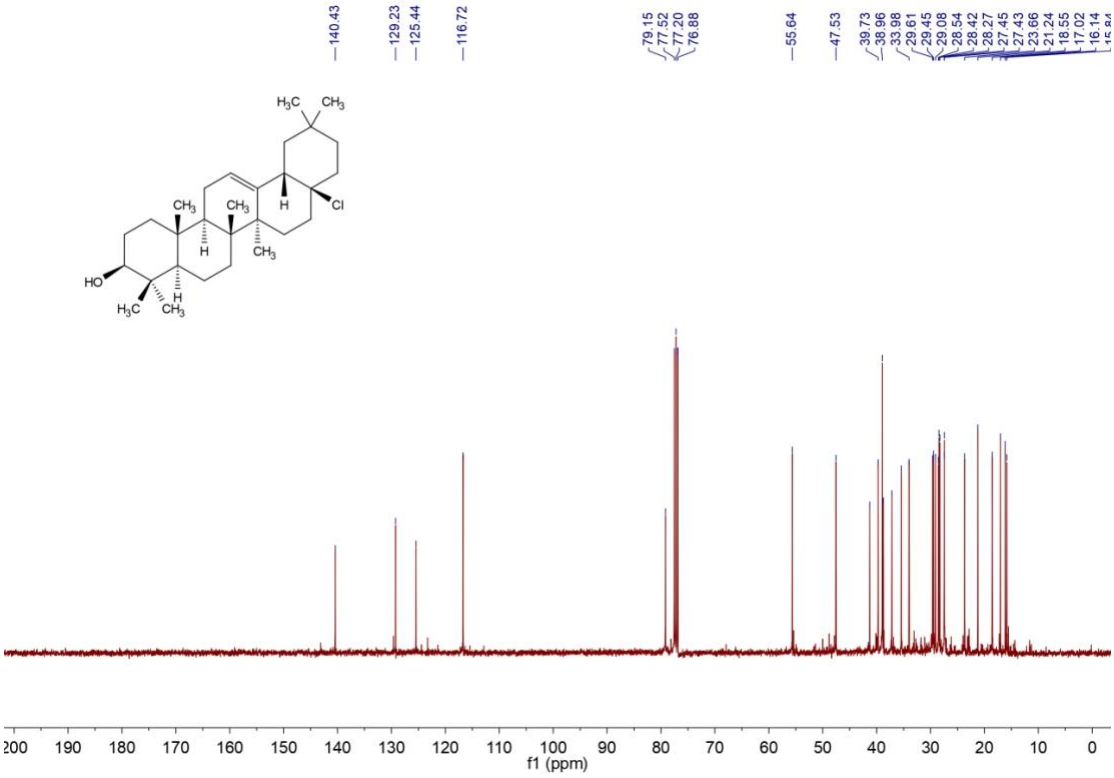
^{13}C NMR (101 MHz, $CDCl_3$) of product **45**



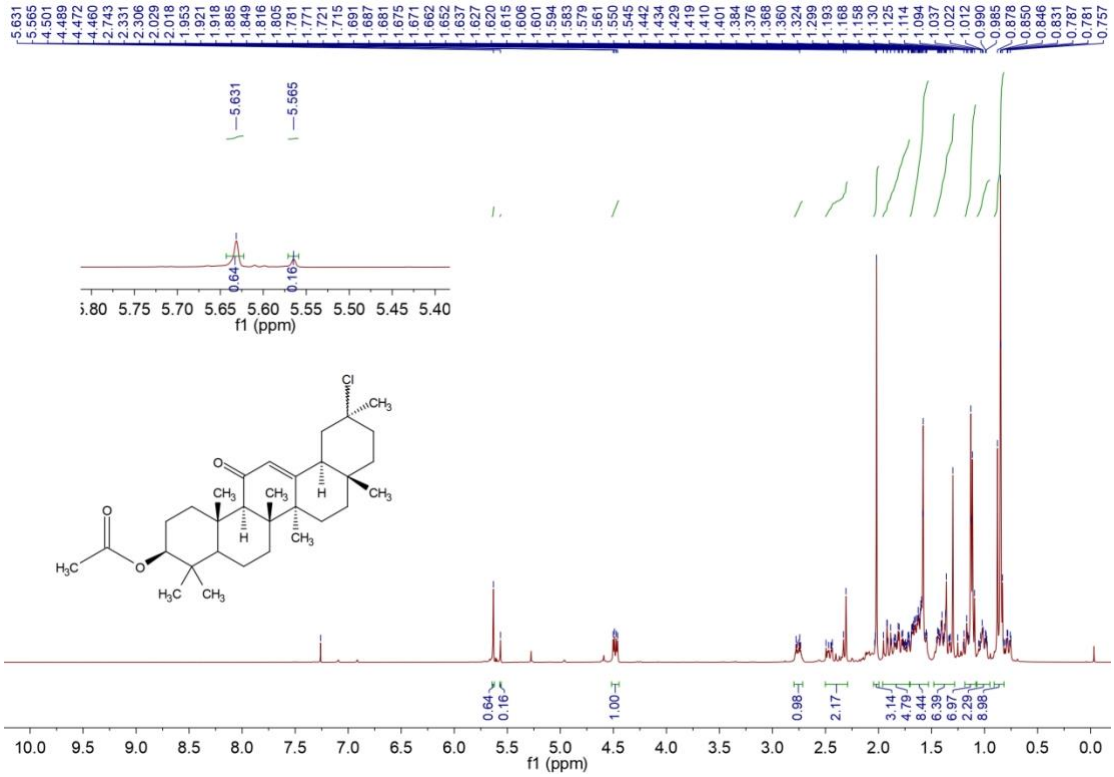
^{1}H NMR (400 MHz, $CDCl_3$) of product **46**



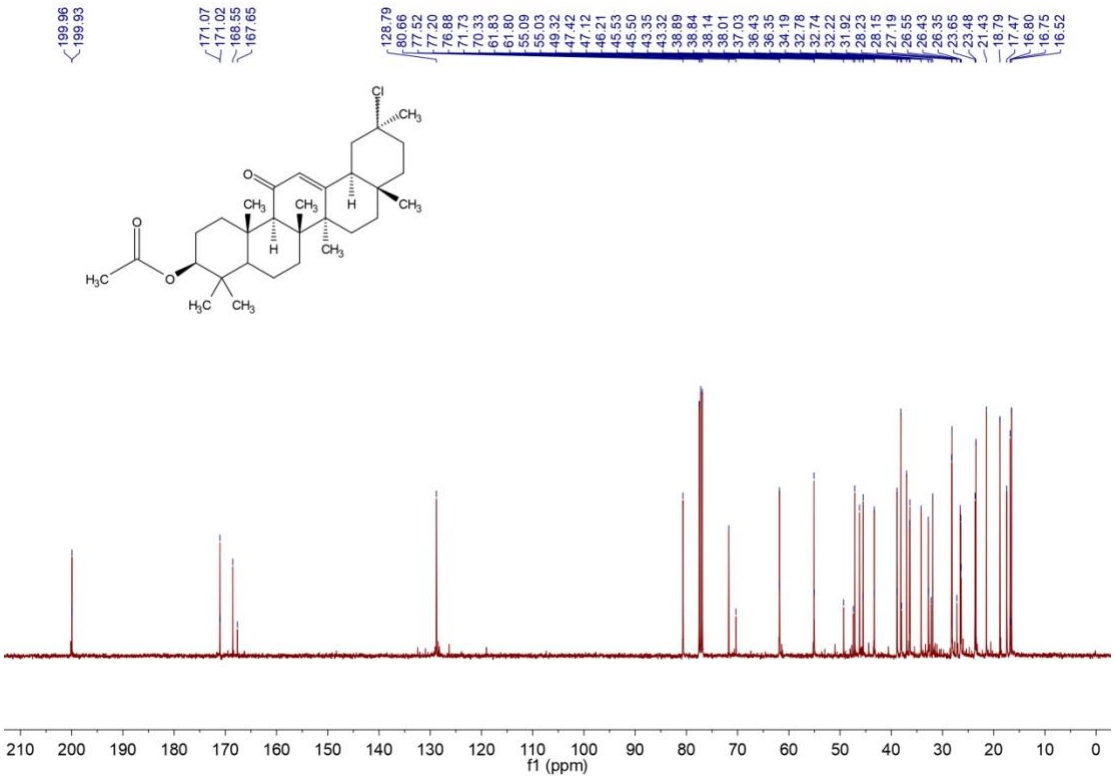
^{13}C NMR (101 MHz, $CDCl_3$) of product **46**



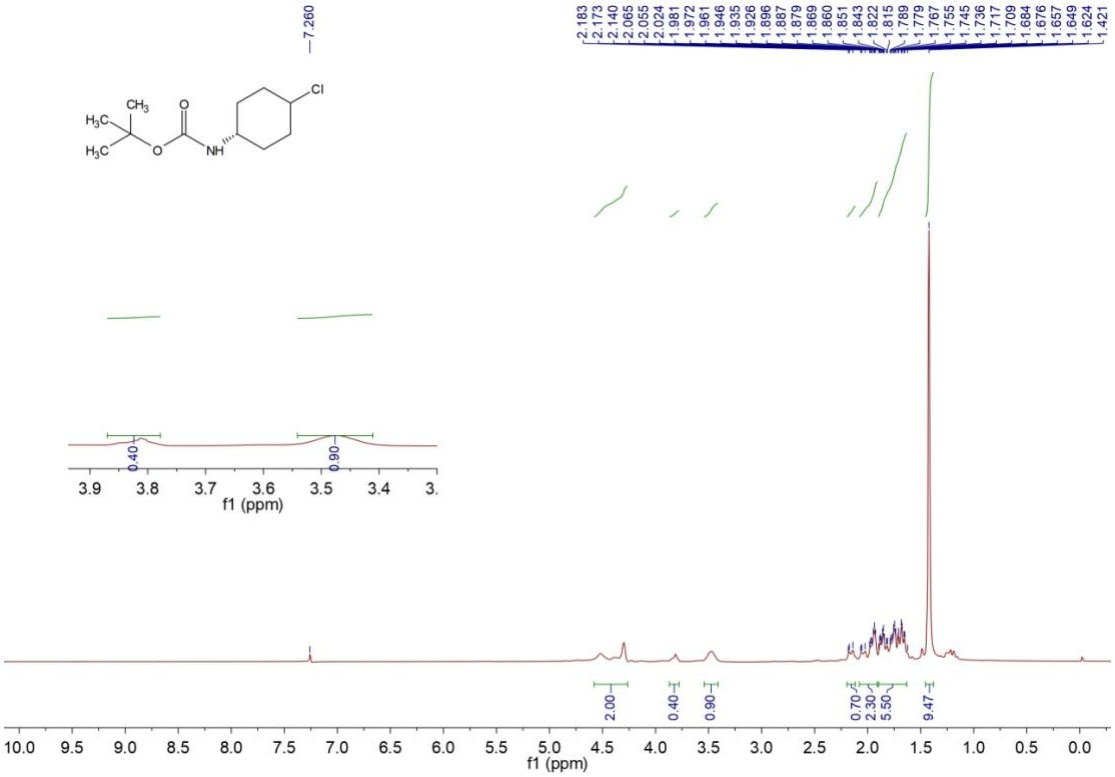
^{1}H NMR (400 MHz, $CDCl_3$) of product **47**



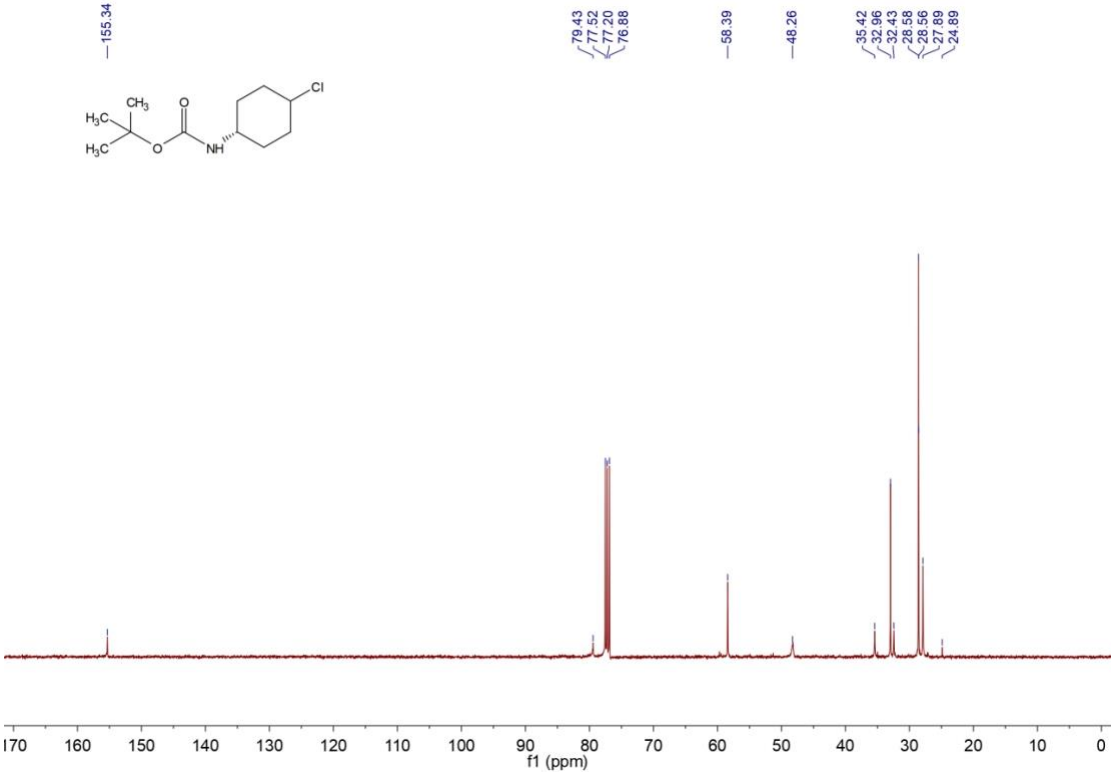
^{13}C NMR (101 MHz, $CDCl_3$) of product **47**



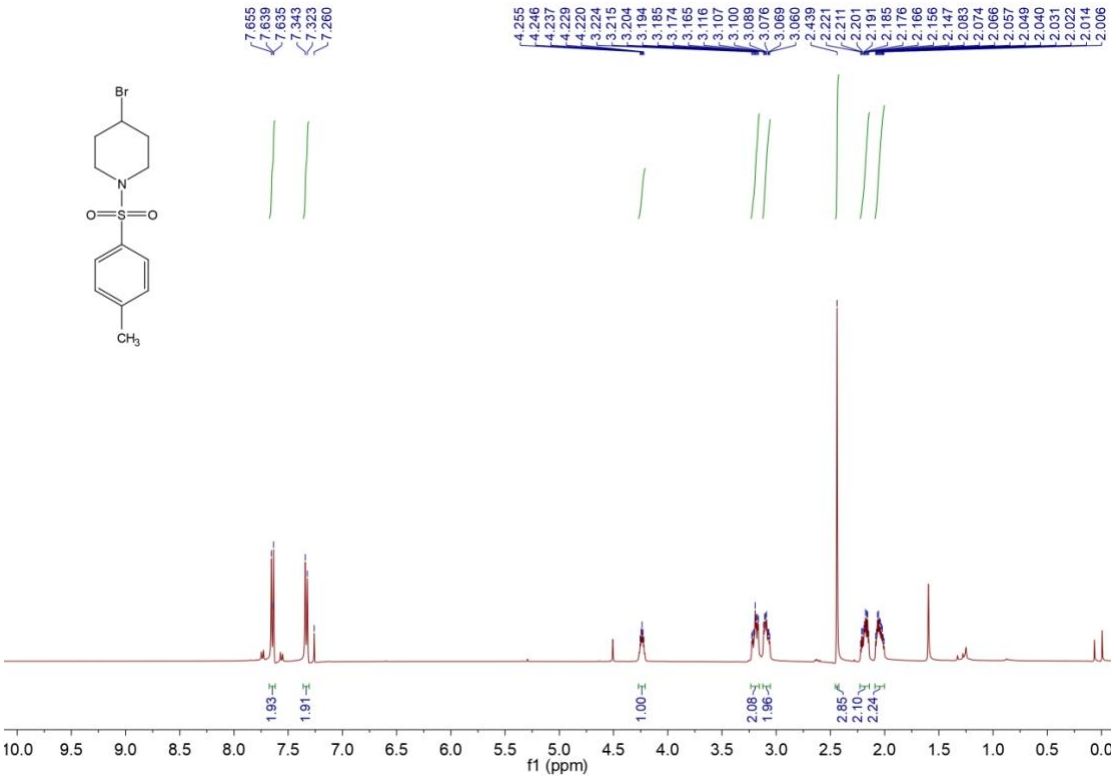
^{1}H NMR (400 MHz, $CDCl_3$) of product **50**



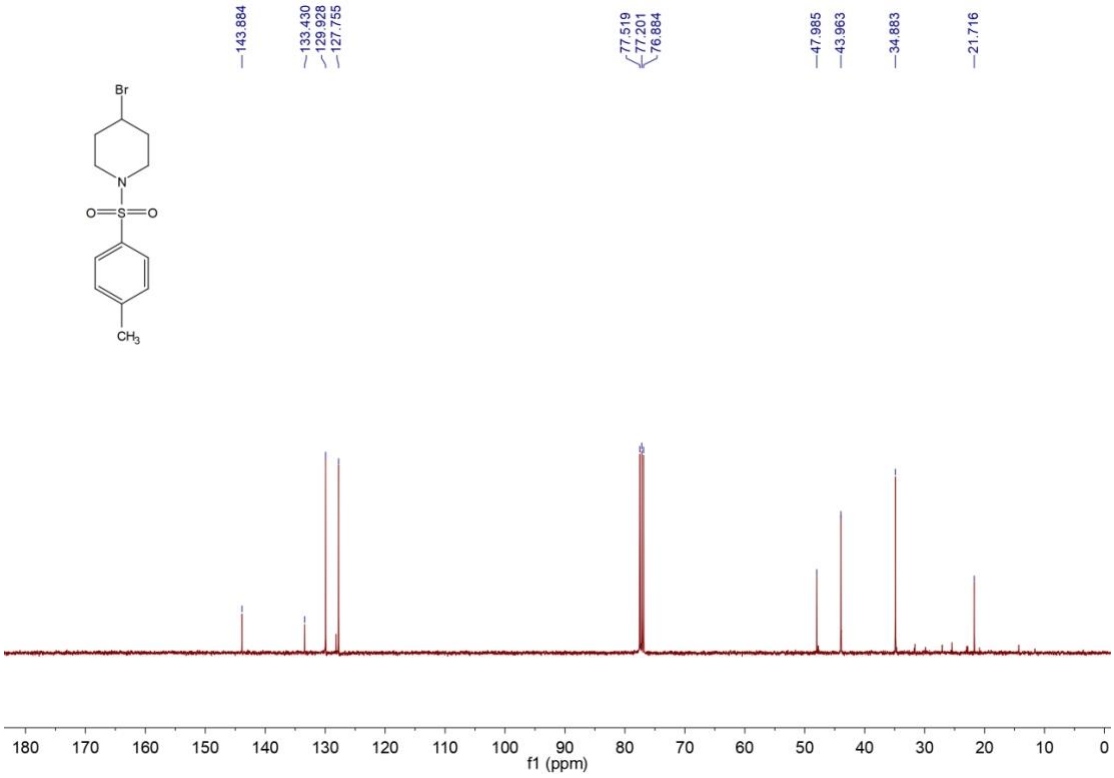
^{13}C NMR (101 MHz, $CDCl_3$) of product **50**



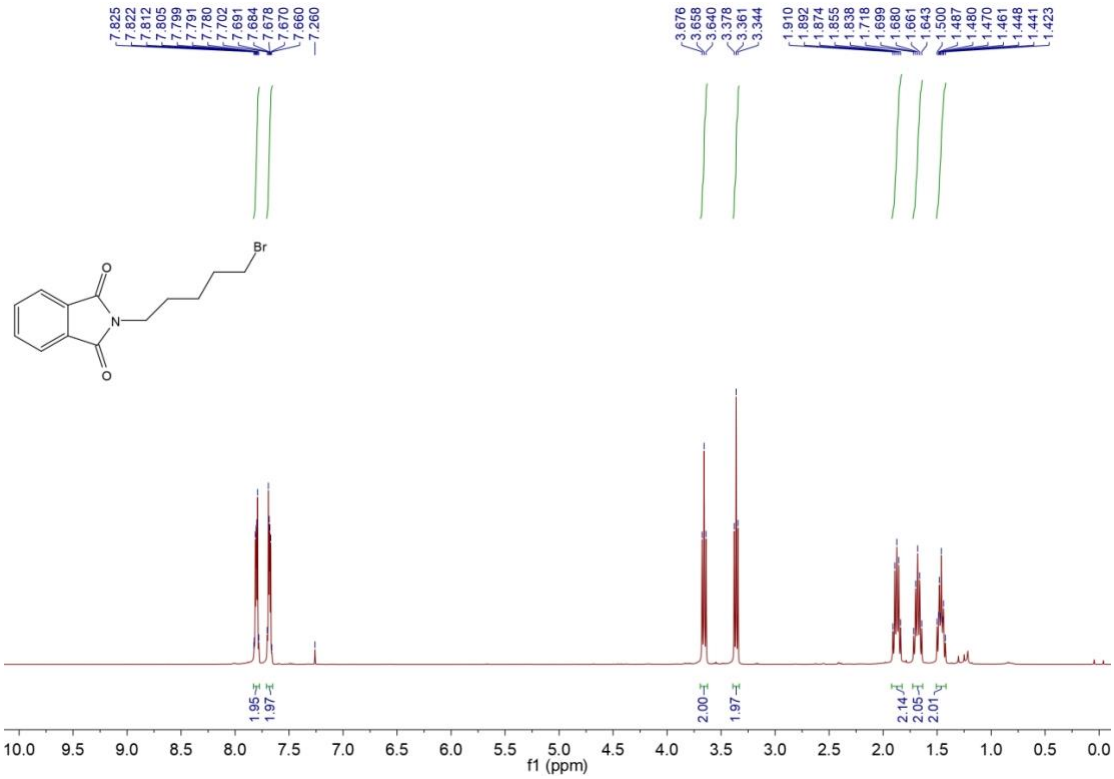
^{1}H NMR (400 MHz, $CDCl_3$) of product **2**



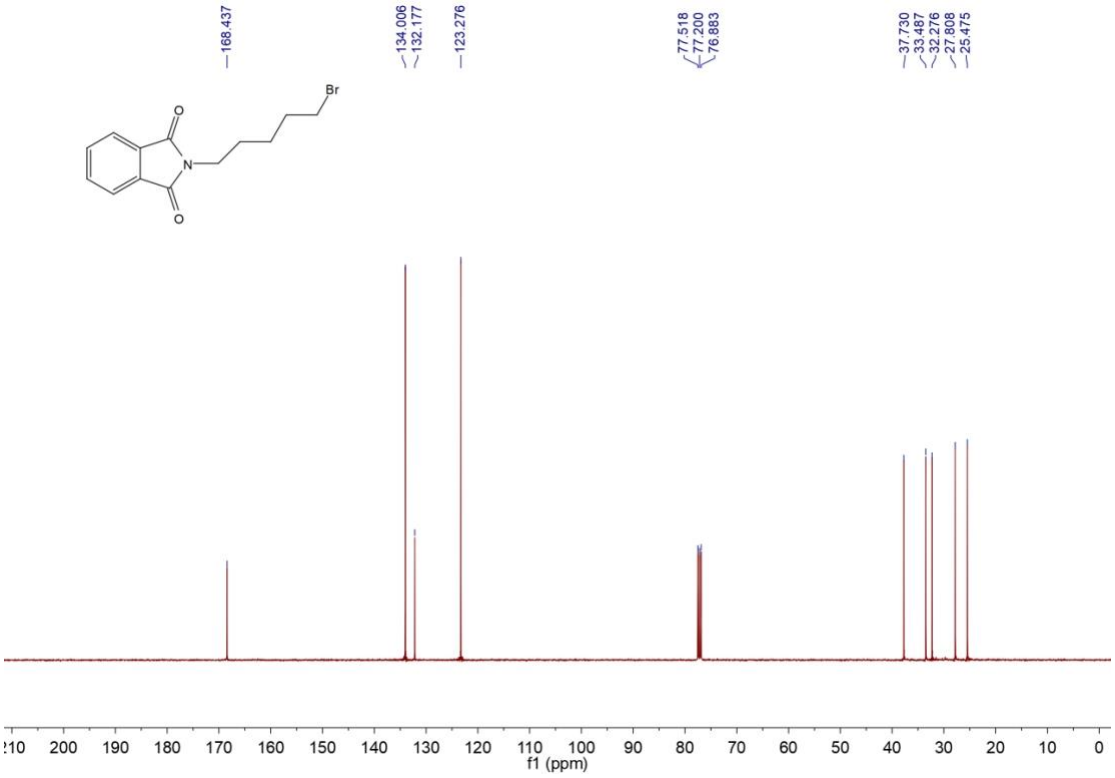
^{13}C NMR (101 MHz, $CDCl_3$) of product **2**



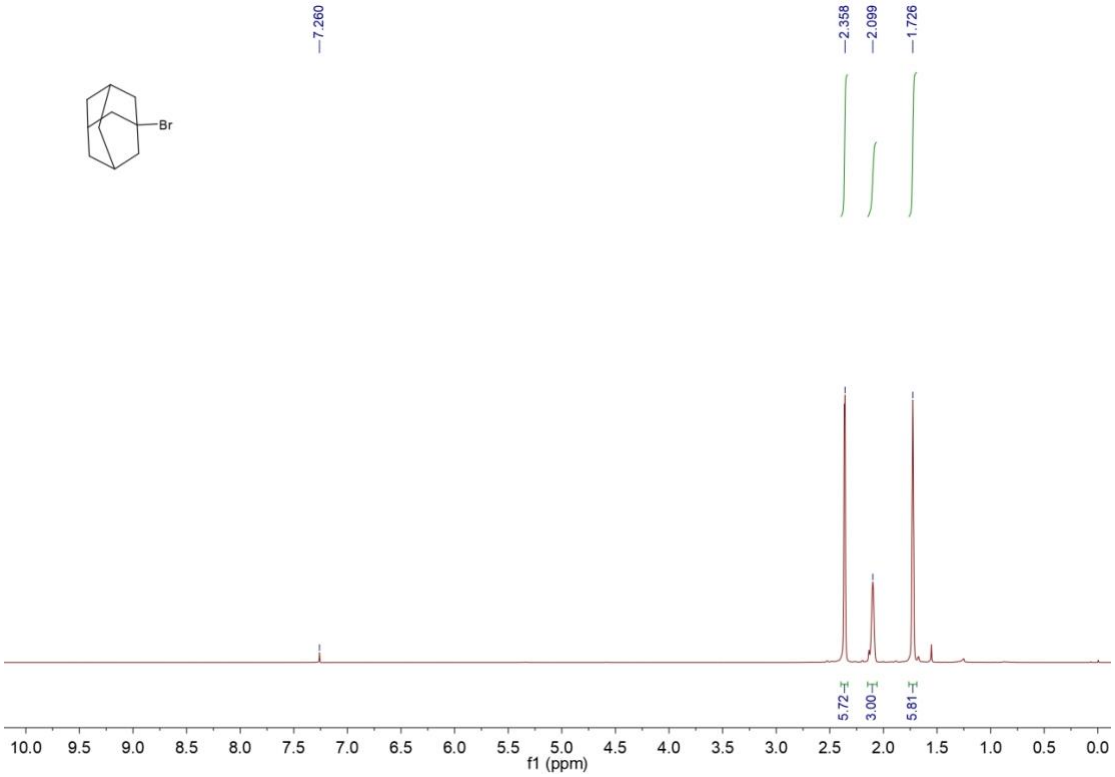
^{1}H NMR (400 MHz, $CDCl_3$) of product **19**



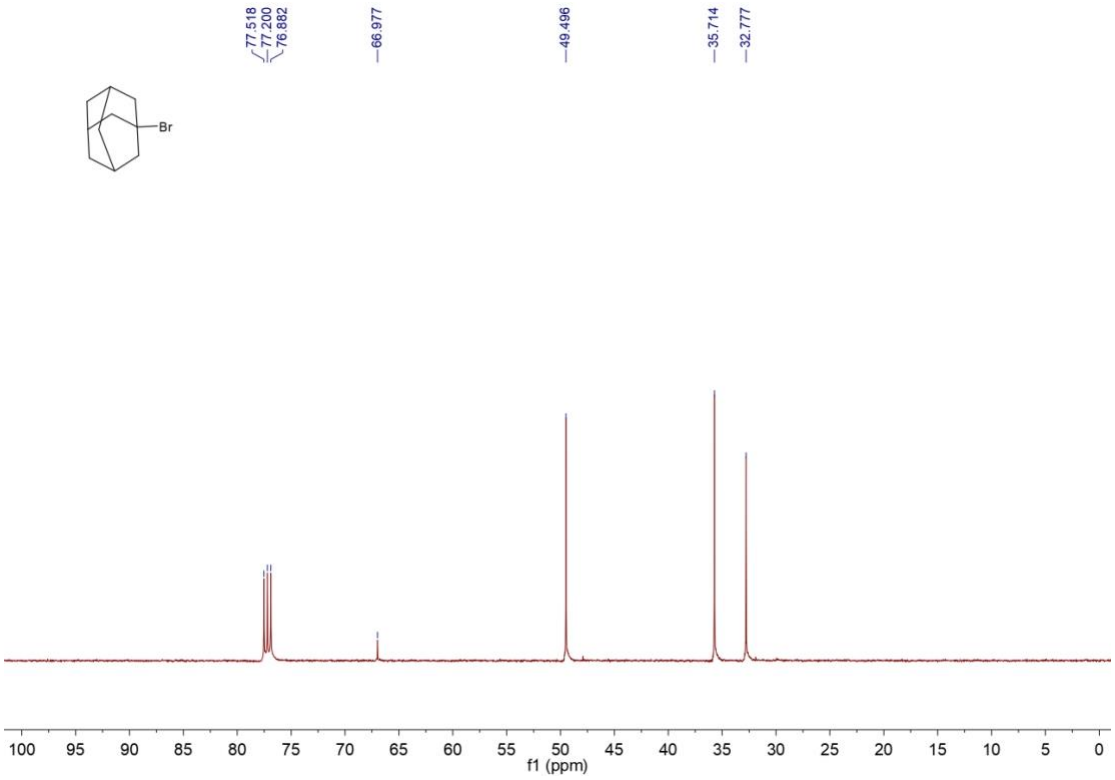
^{13}C NMR (101 MHz, $CDCl_3$) of product **19**



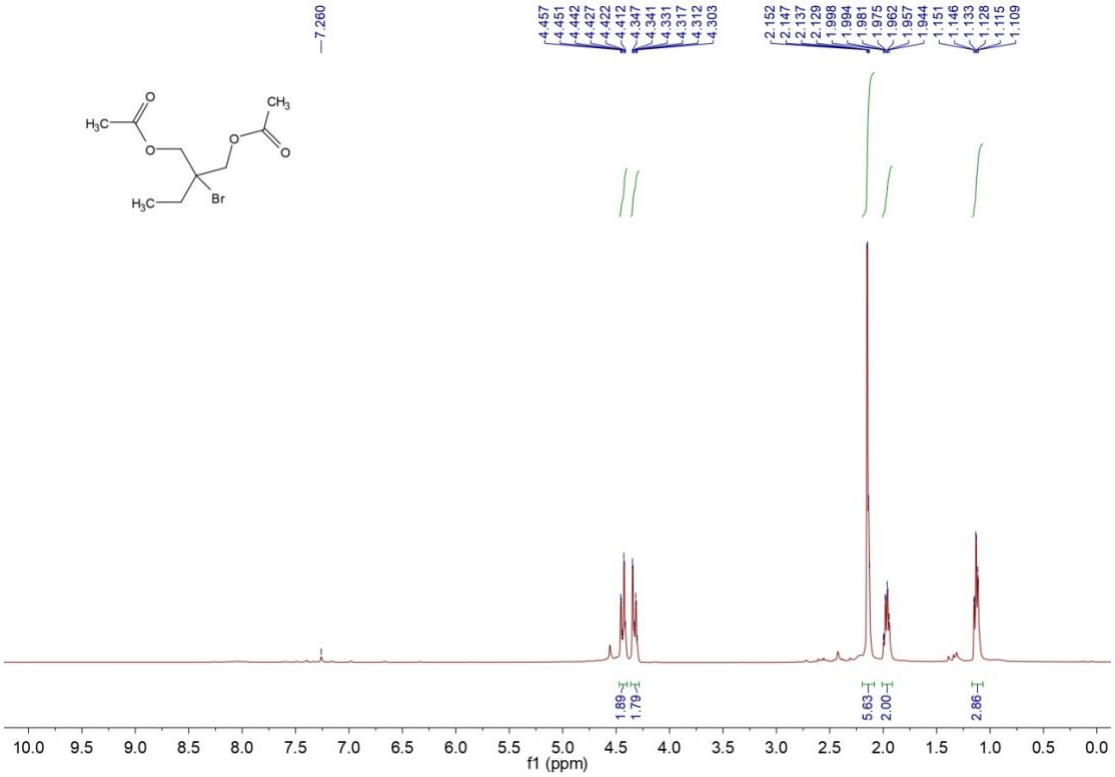
^{1}H NMR (400 MHz, $CDCl_3$) of product **38**



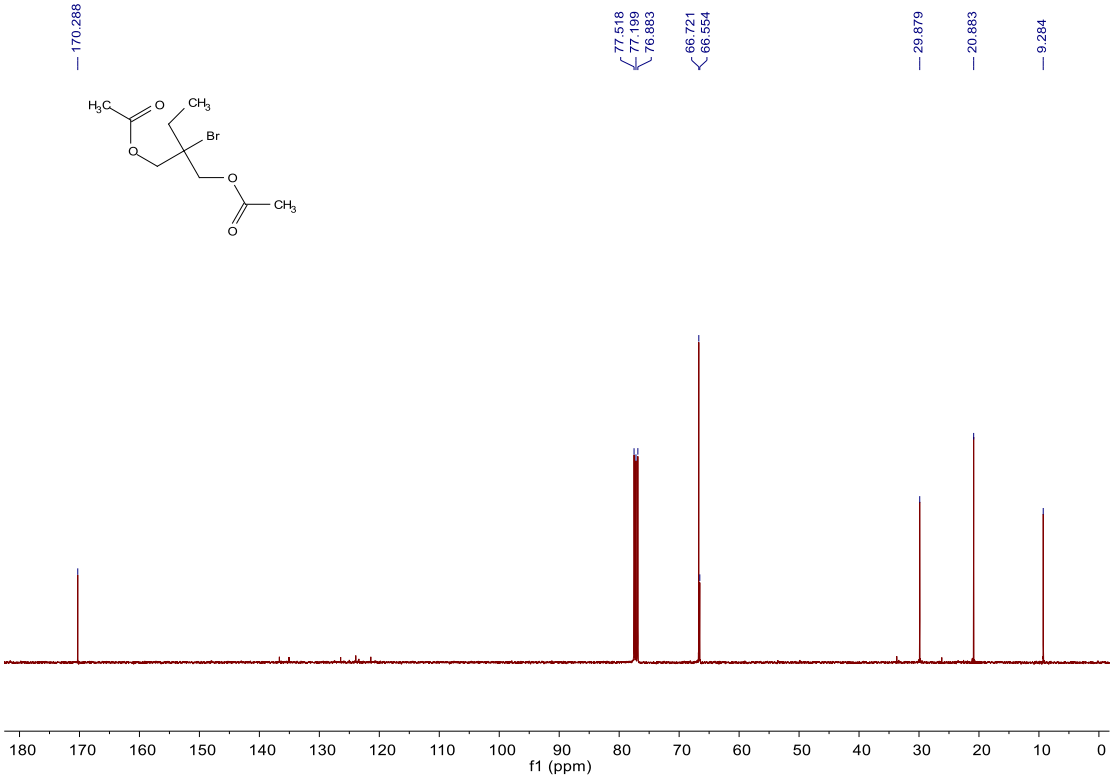
^{13}C NMR (101 MHz, $CDCl_3$) of product **38**



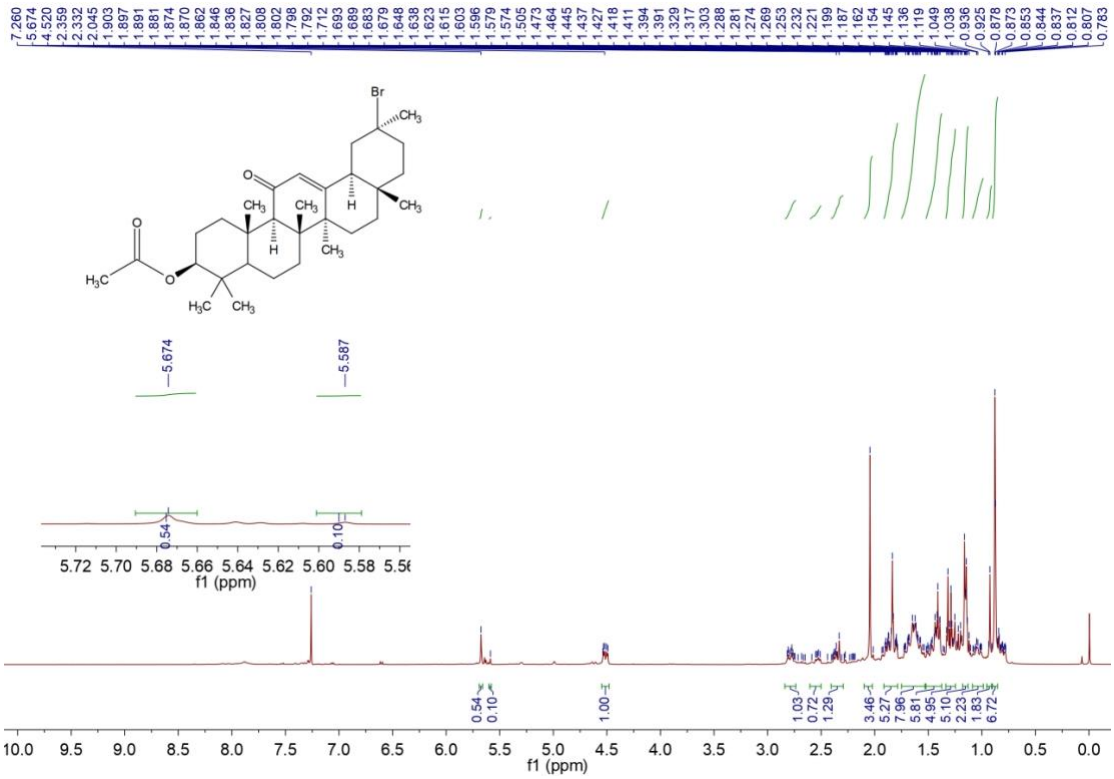
^{1}H NMR (400 MHz, $CDCl_3$) of product **42**



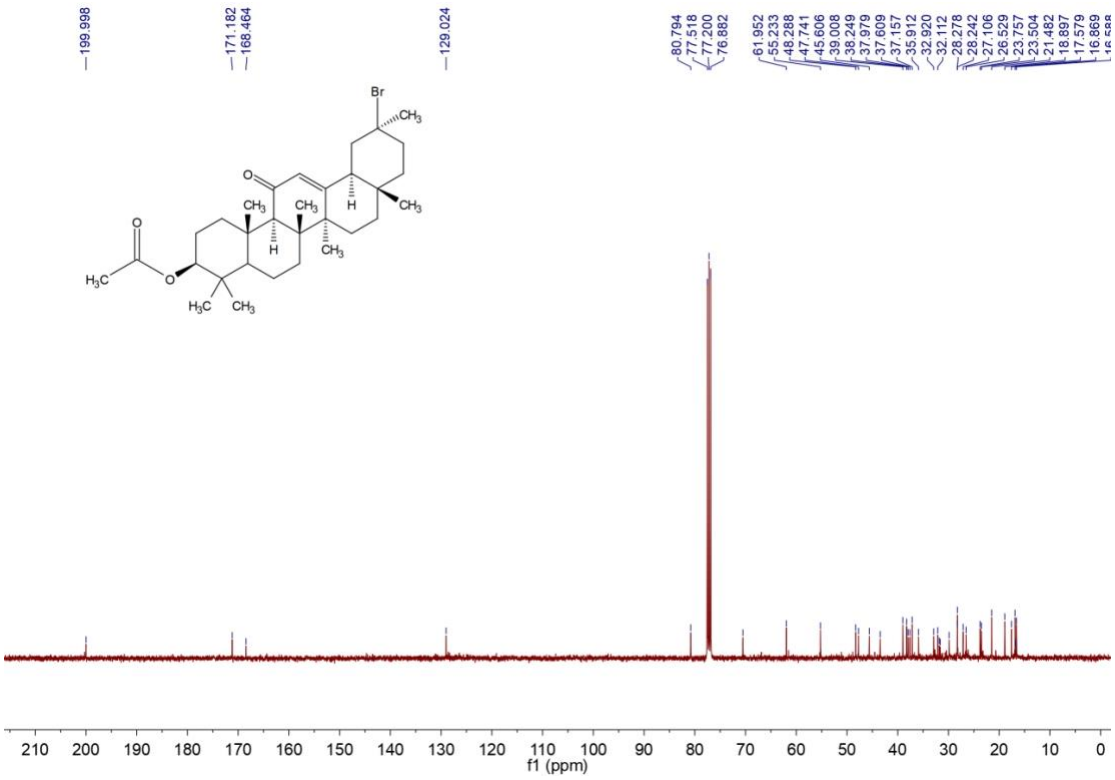
^{13}C NMR (101 MHz, $CDCl_3$) of product **42**



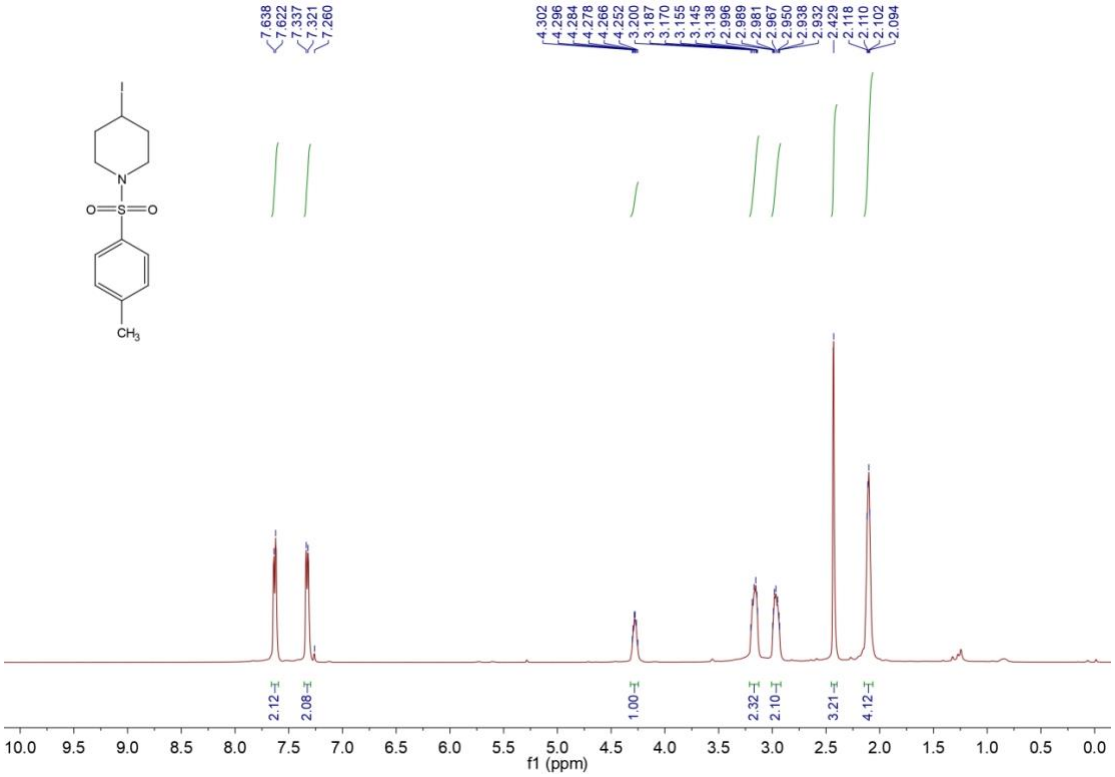
^{1}H NMR (400 MHz, $CDCl_3$) of product **48**



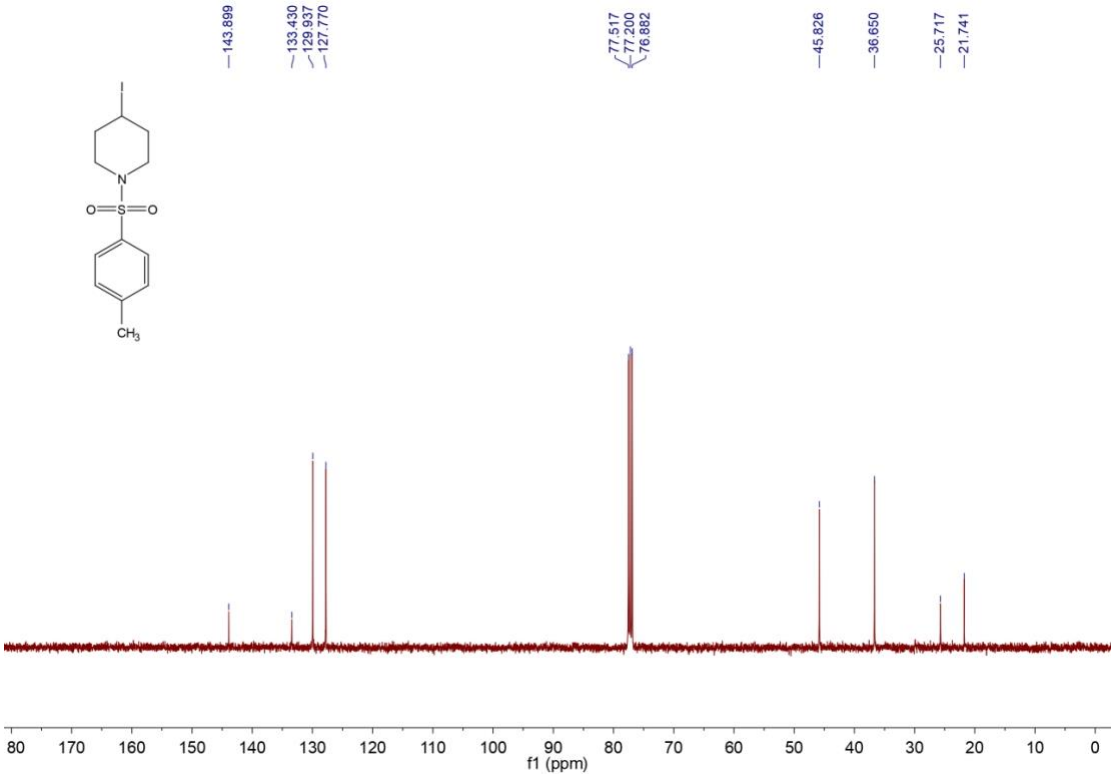
^{13}C NMR (101 MHz, $CDCl_3$) of product **48**



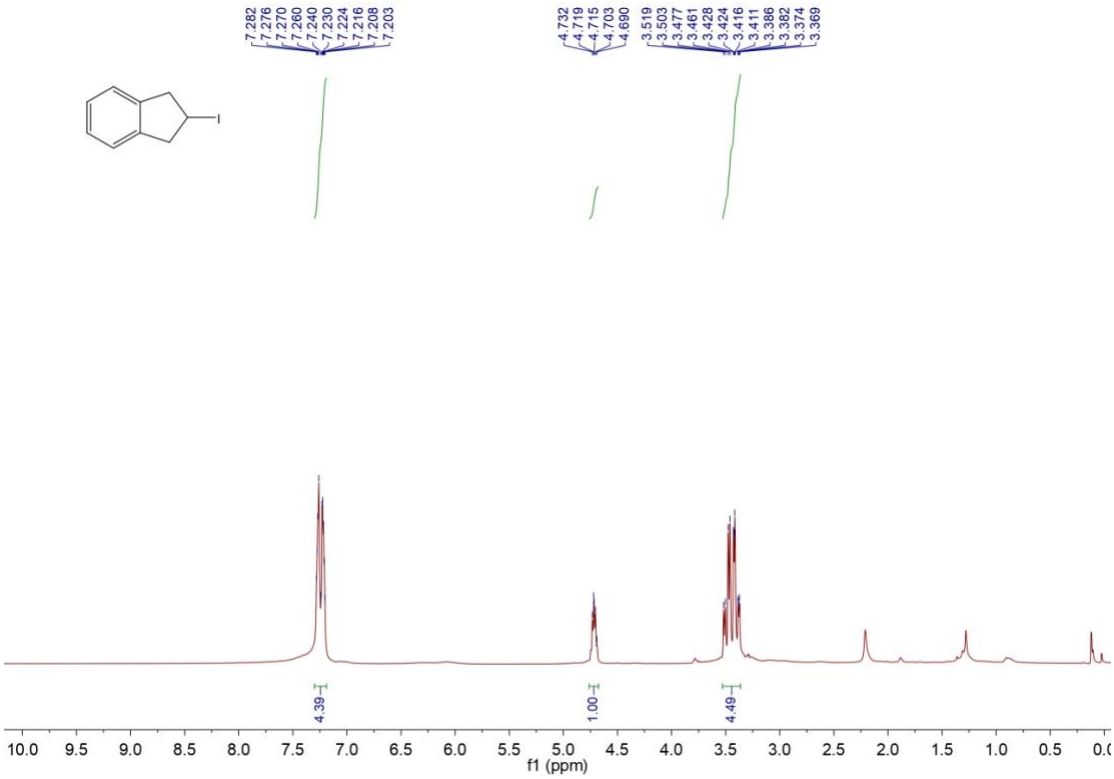
^{1}H NMR (400 MHz, $CDCl_3$) of product **3**



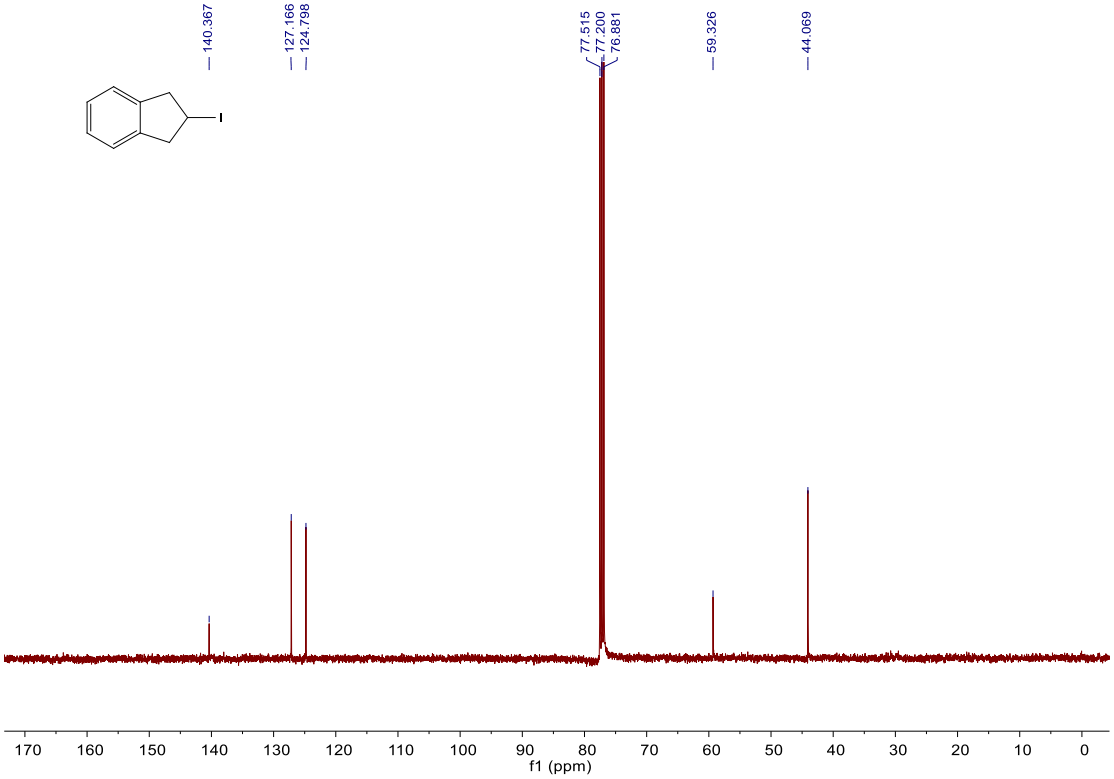
^{13}C NMR (101 MHz, $CDCl_3$) of product **3**



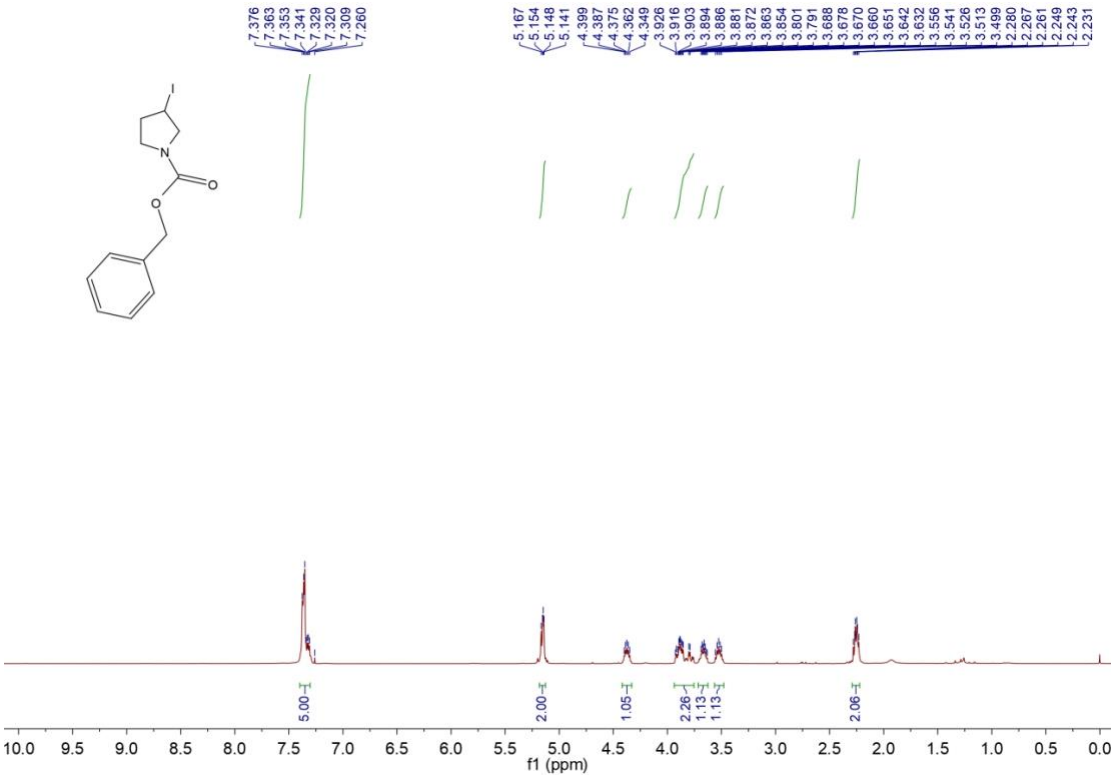
^{1}H NMR (400 MHz, $CDCl_3$) of product **6**



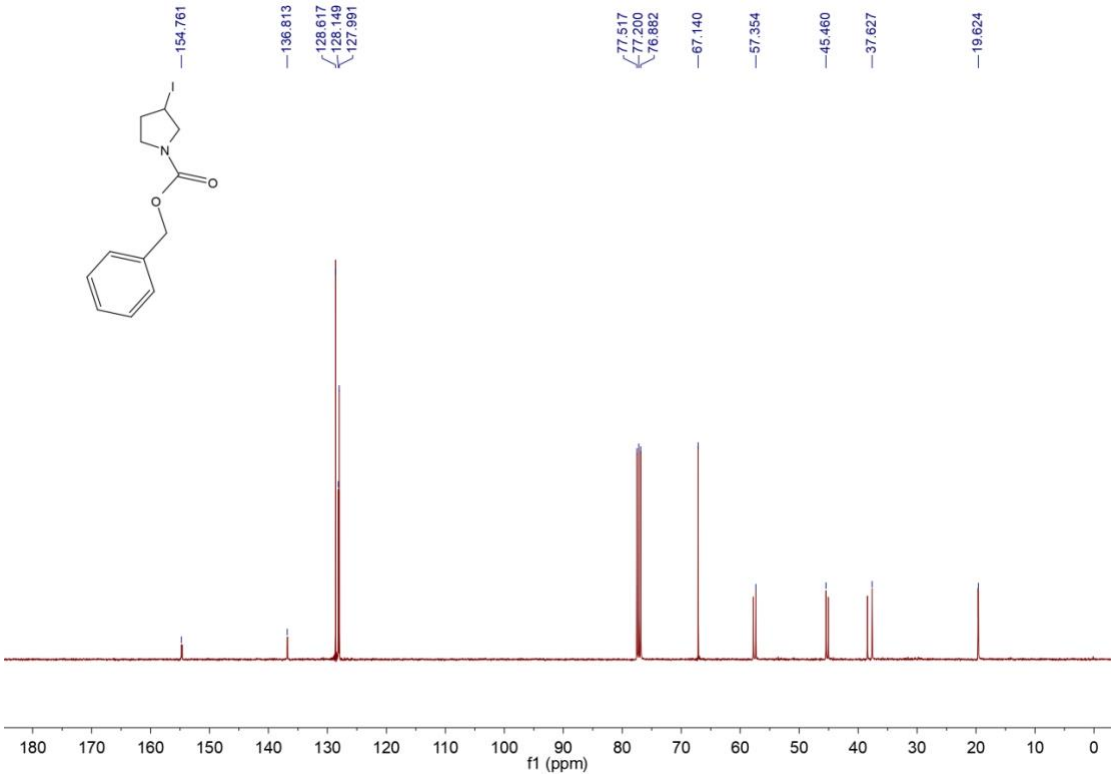
^{13}C NMR (101 MHz, $CDCl_3$) of product **6**



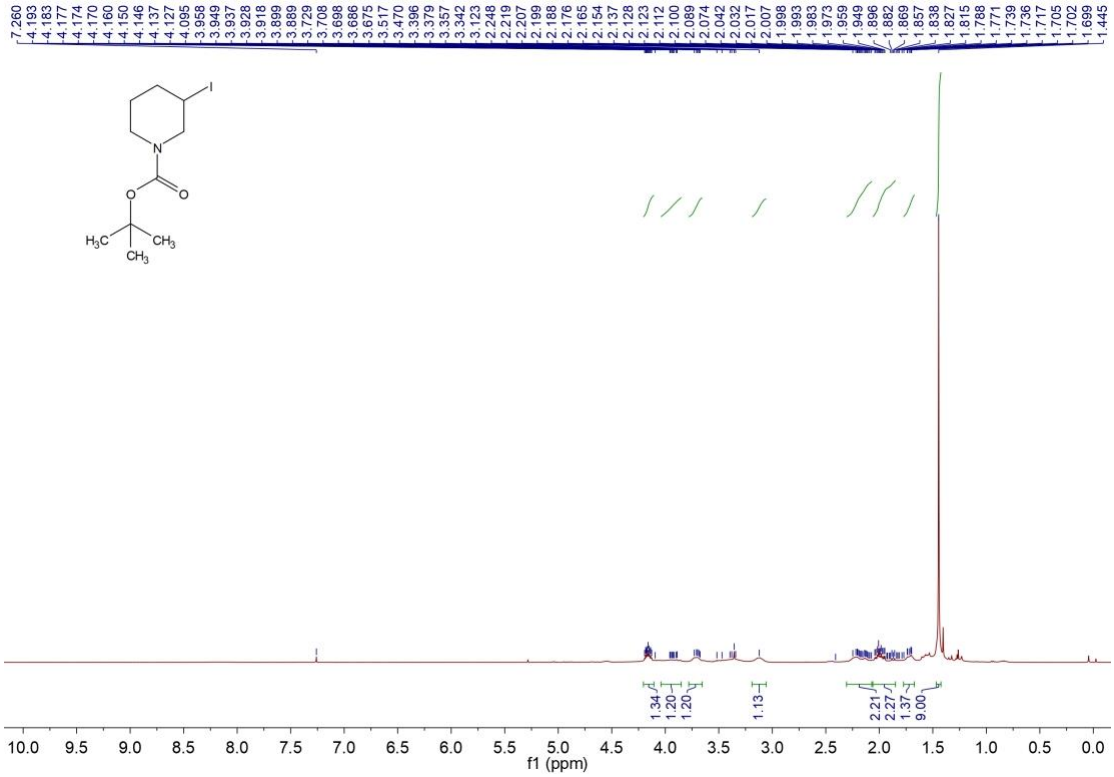
^{1}H NMR (400 MHz, $CDCl_3$) of product **7**



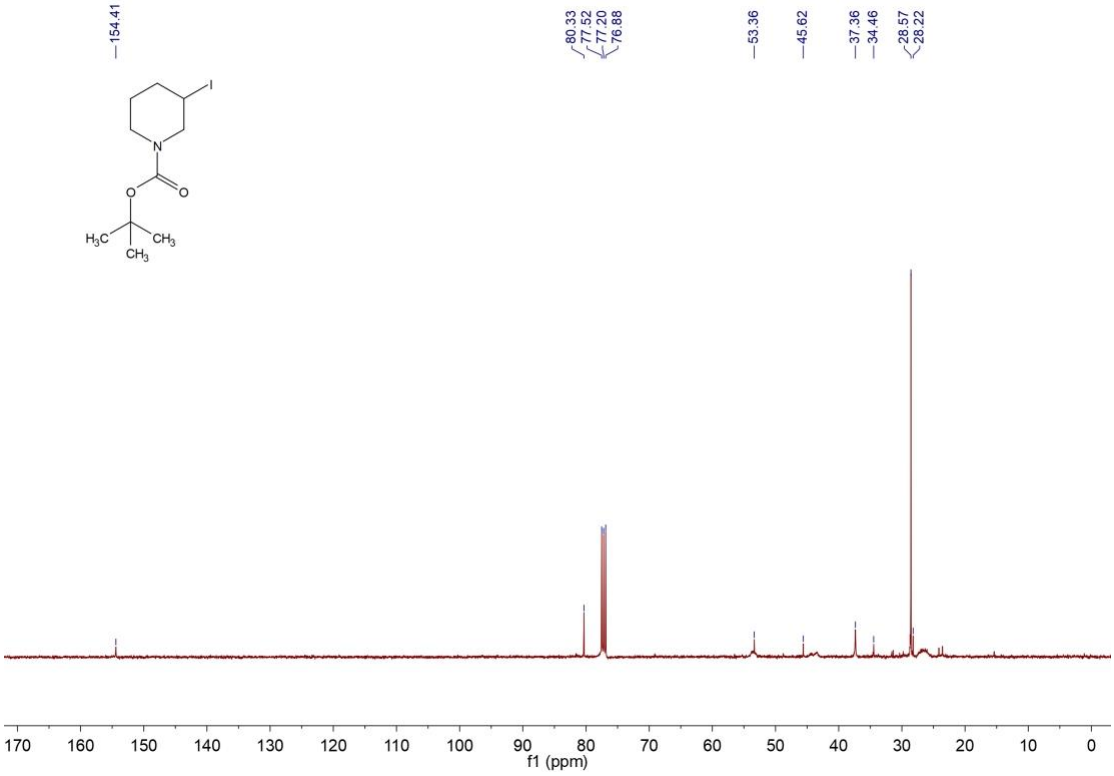
^{13}C NMR (101 MHz, $CDCl_3$) of product **7**



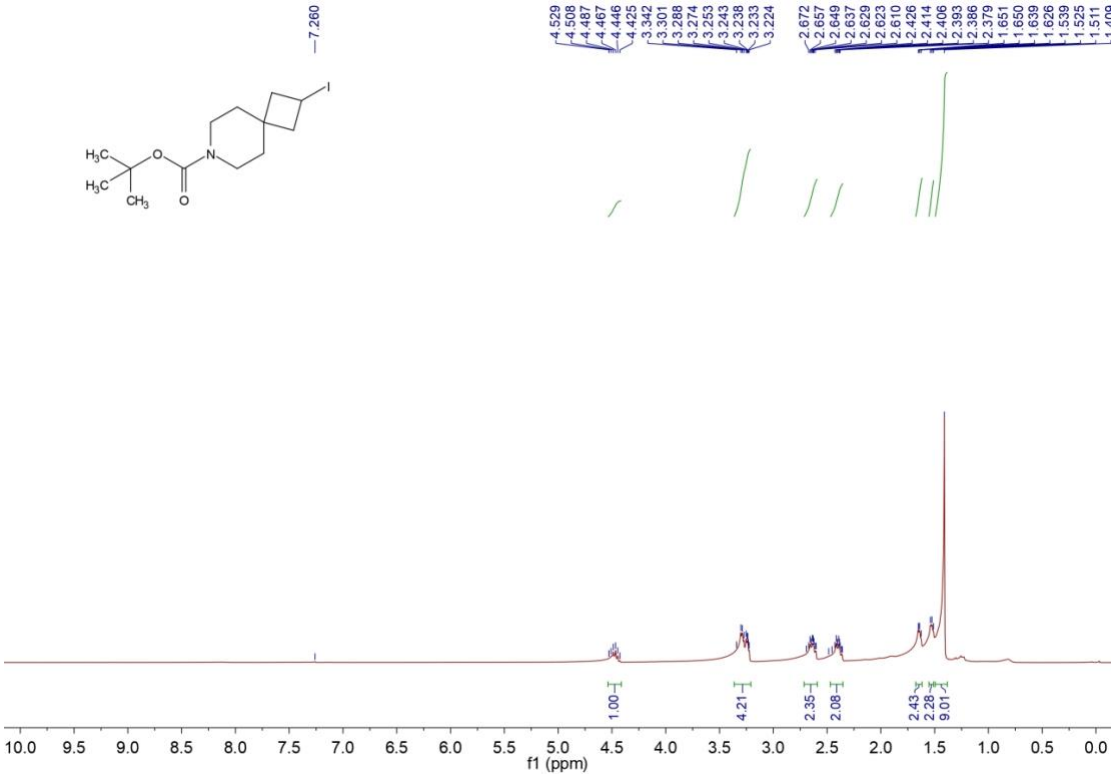
^{1}H NMR (400 MHz, $CDCl_3$) of product **11**



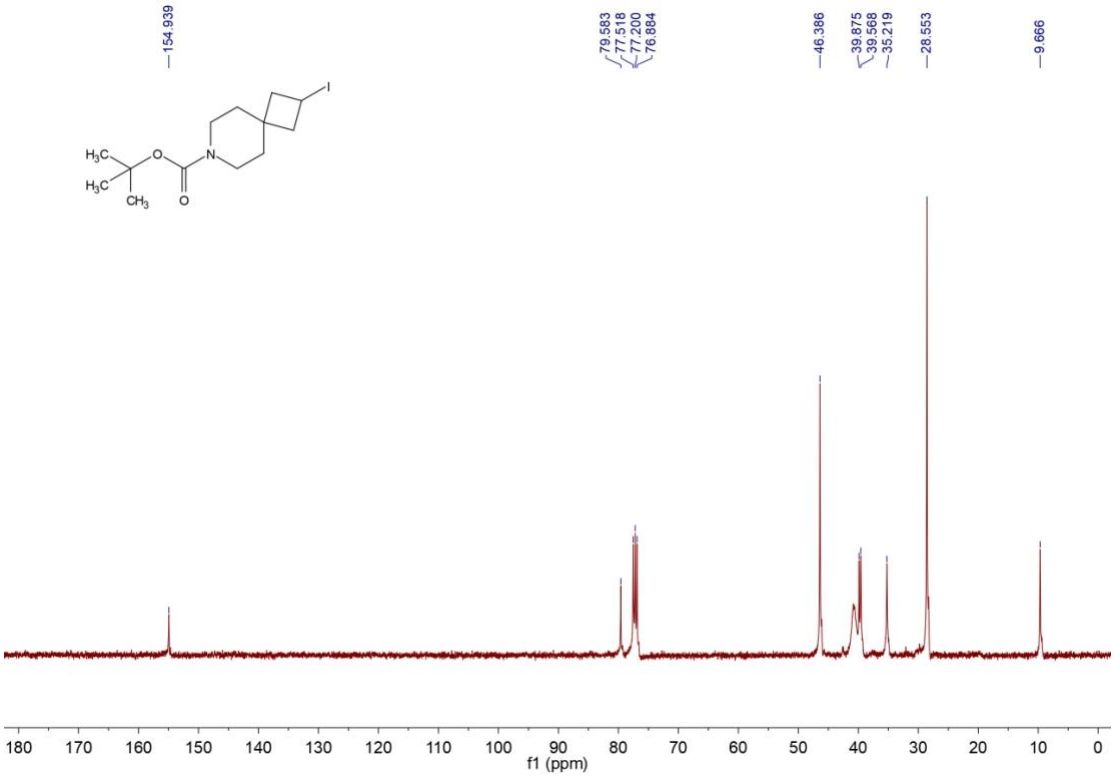
^{13}C NMR (101 MHz, $CDCl_3$) of product **11**



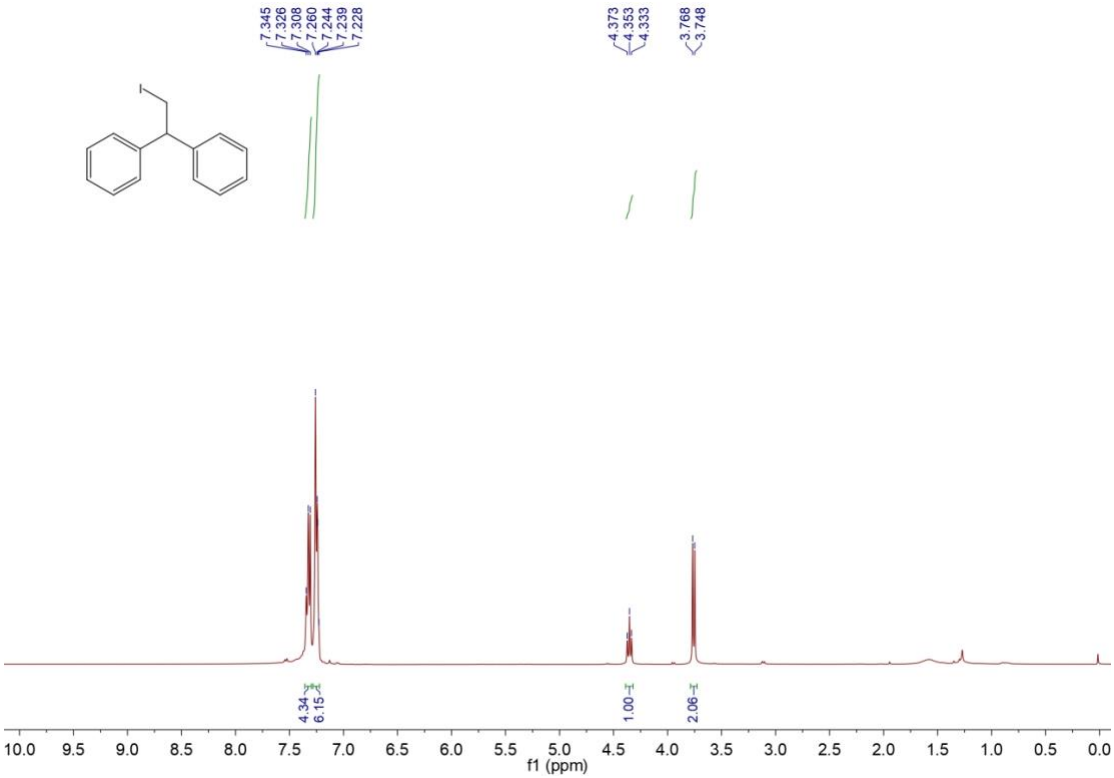
^{1}H NMR (400 MHz, $CDCl_3$) of product **14**



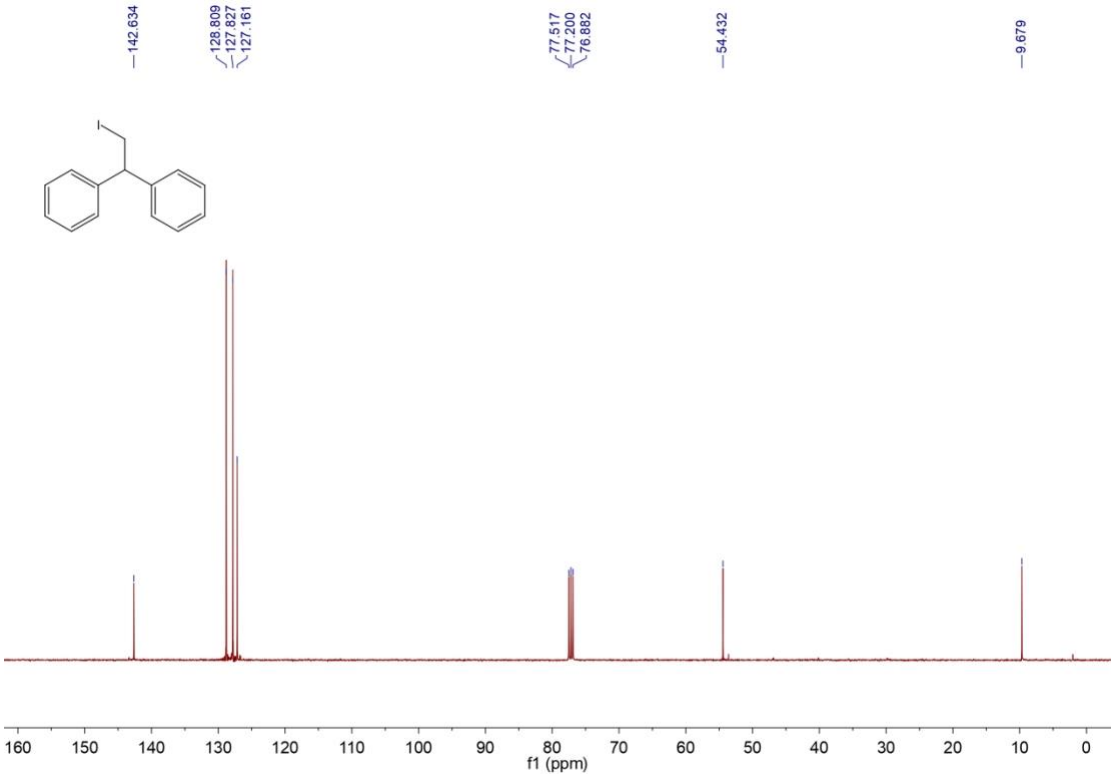
^{13}C NMR (101 MHz, $CDCl_3$) of product **14**



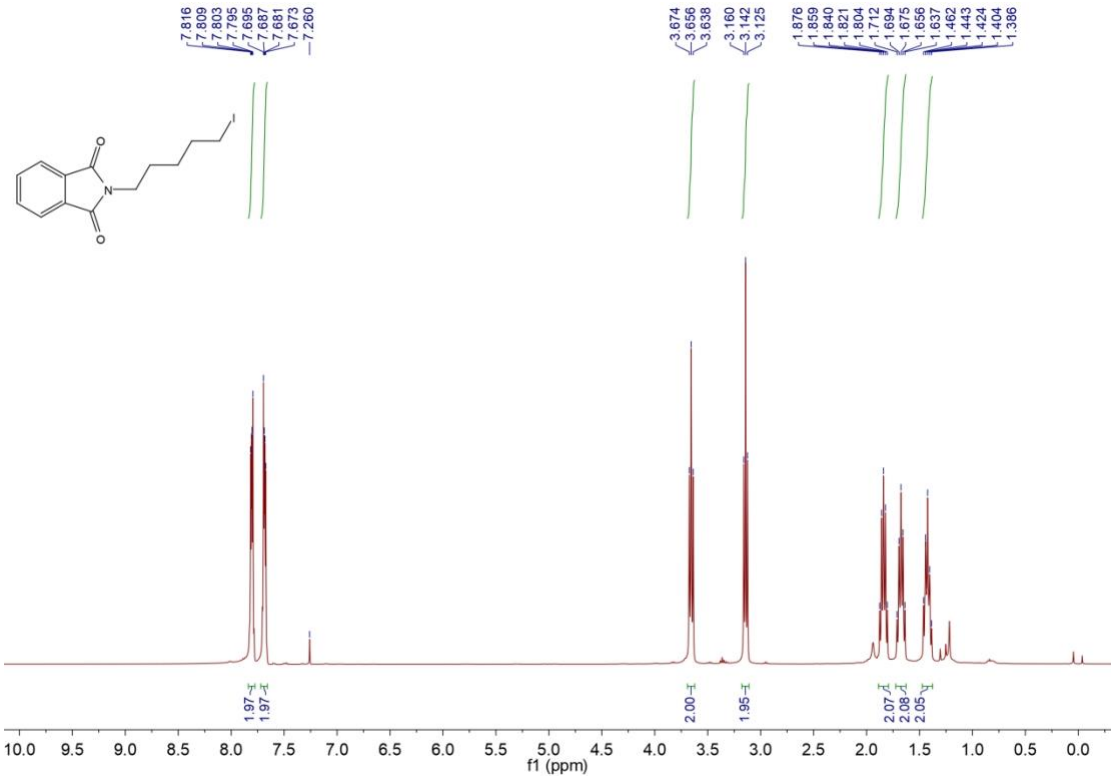
^{1}H NMR (400 MHz, $CDCl_3$) of product **17**



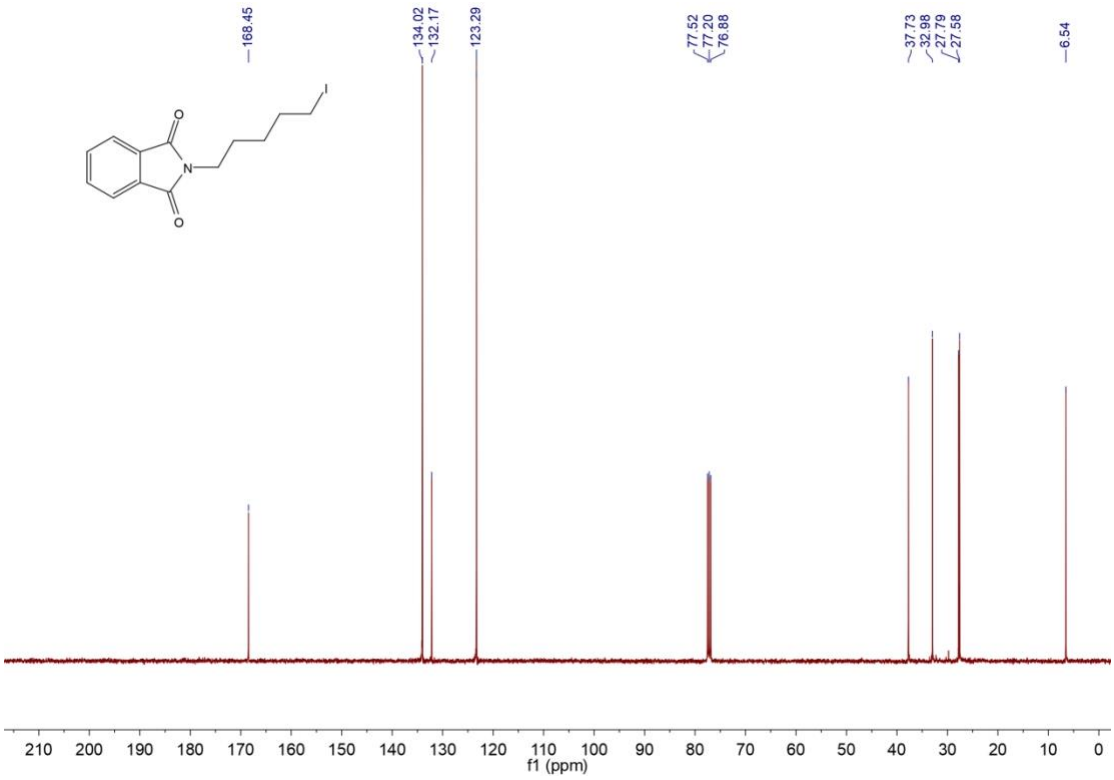
^{13}C NMR (101 MHz, $CDCl_3$) of product **17**



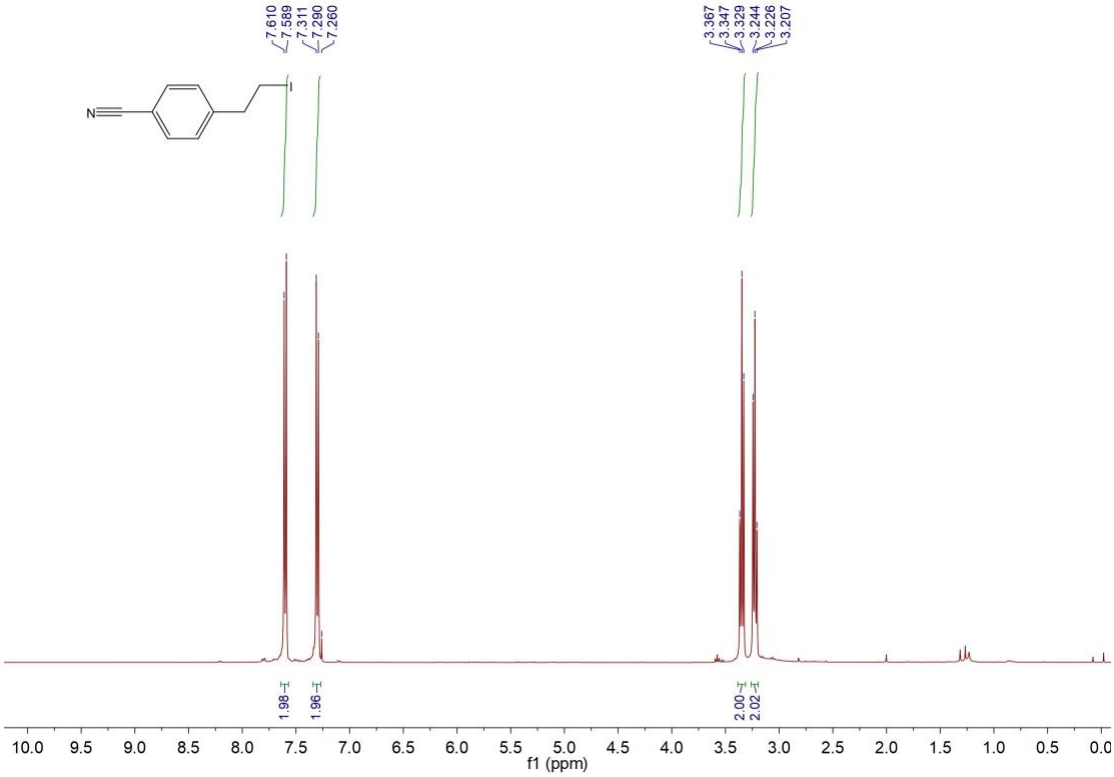
^{1}H NMR (400 MHz, $CDCl_3$) of product **20**



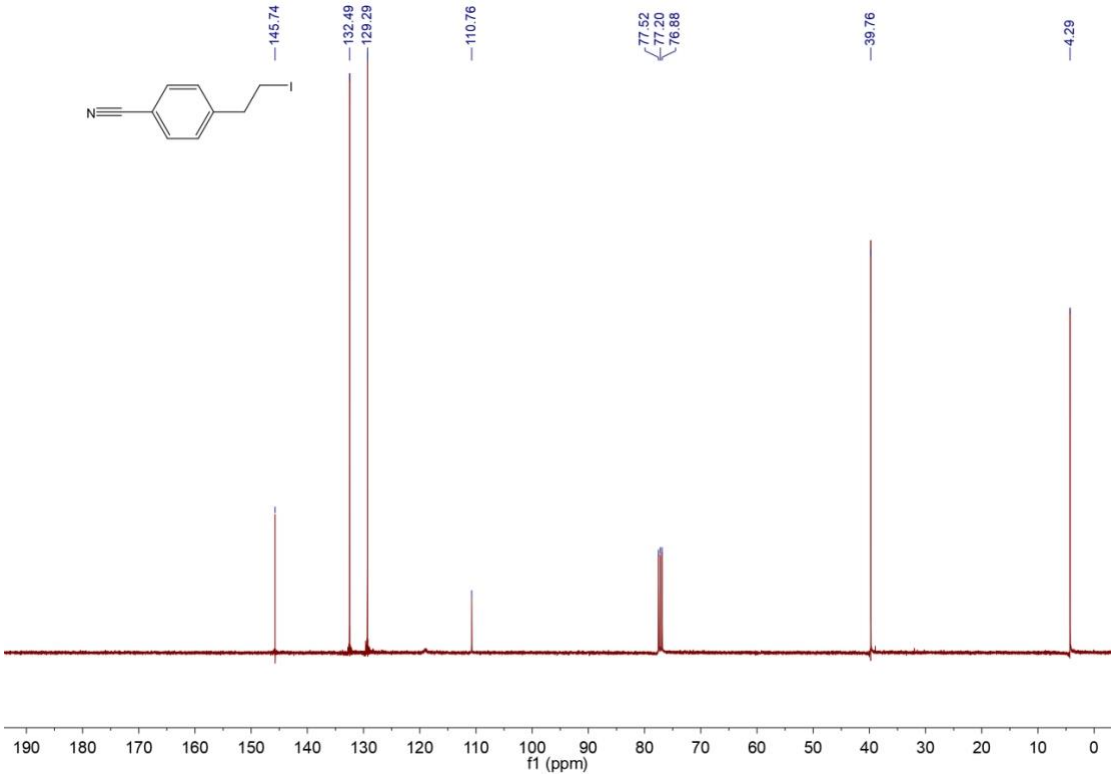
^{13}C NMR (101 MHz, $CDCl_3$) of product **20**



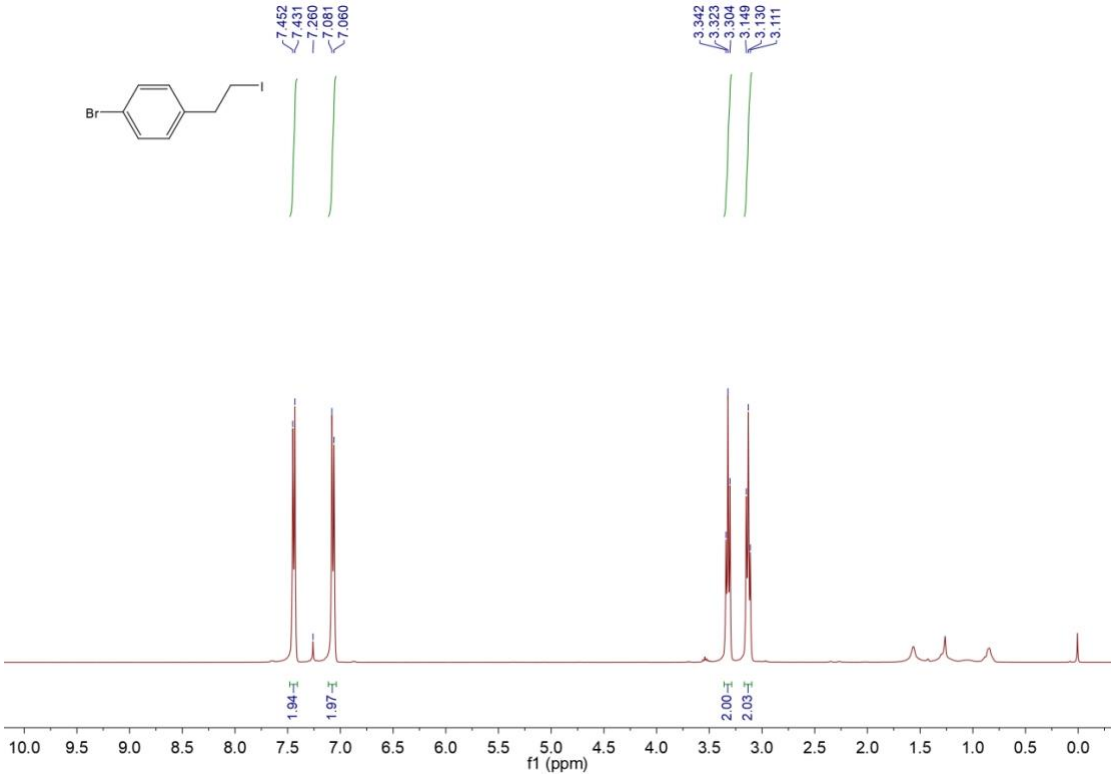
^{1}H NMR (400 MHz, $CDCl_3$) of product **26**



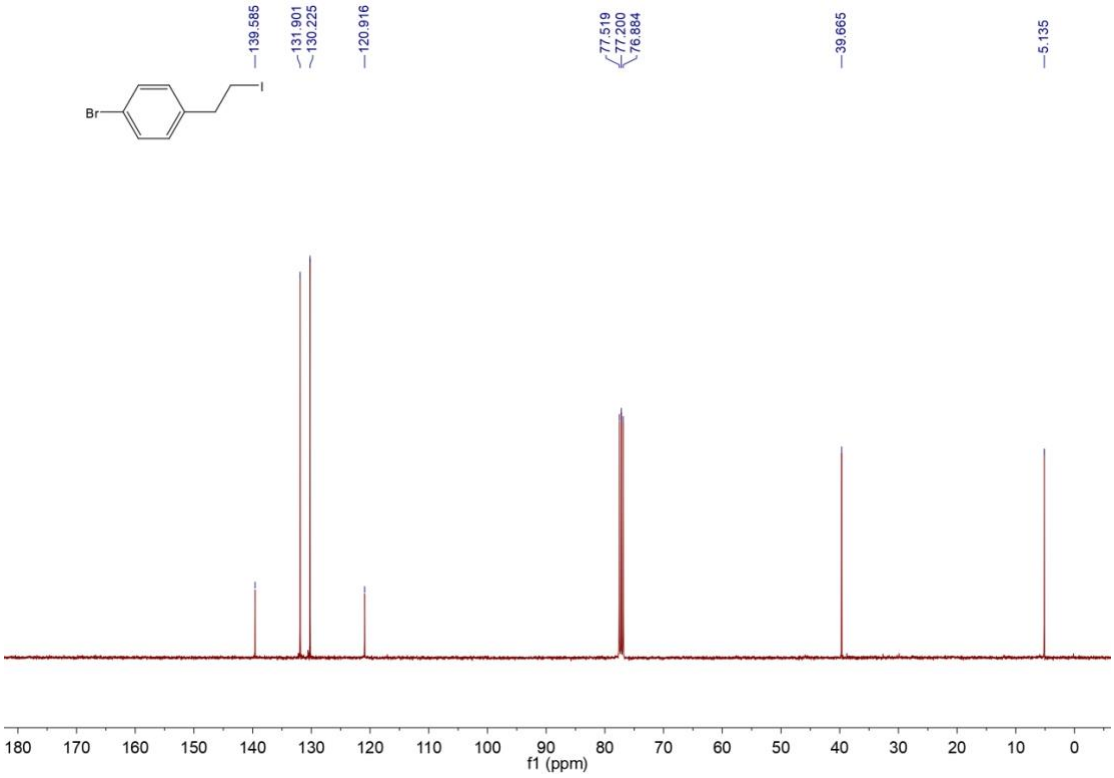
^{13}C NMR (101 MHz, $CDCl_3$) of product **26**



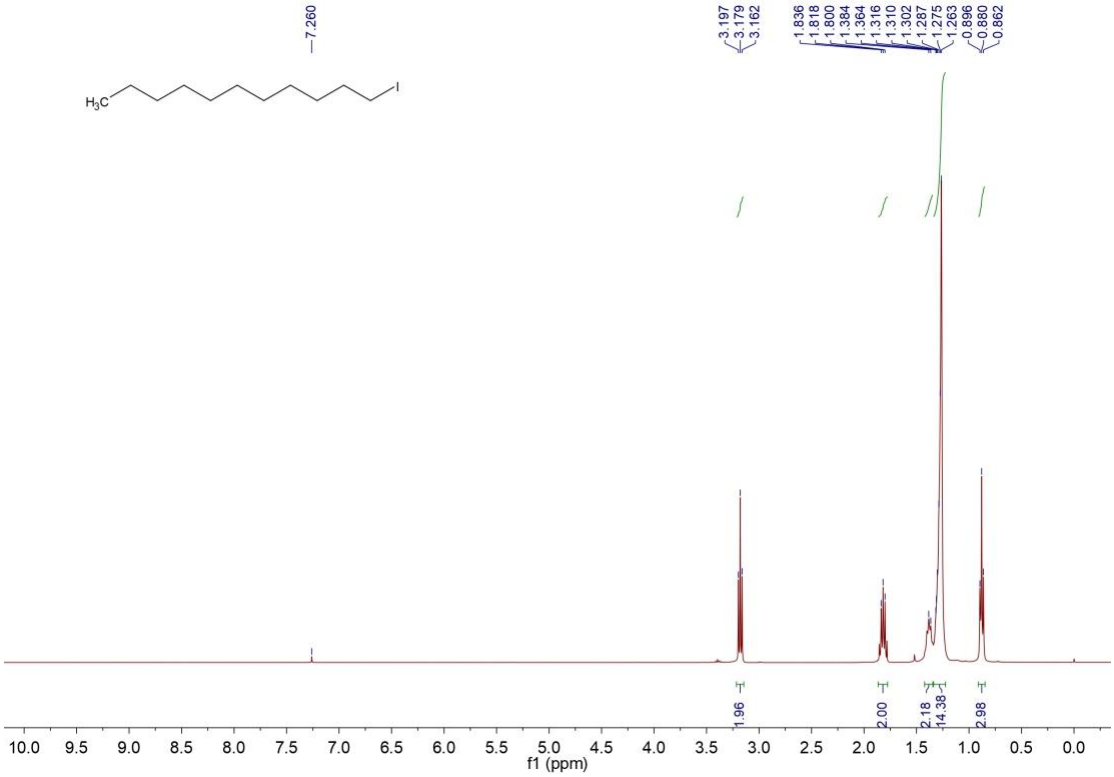
^{1}H NMR (400 MHz, $CDCl_3$) of product **28**



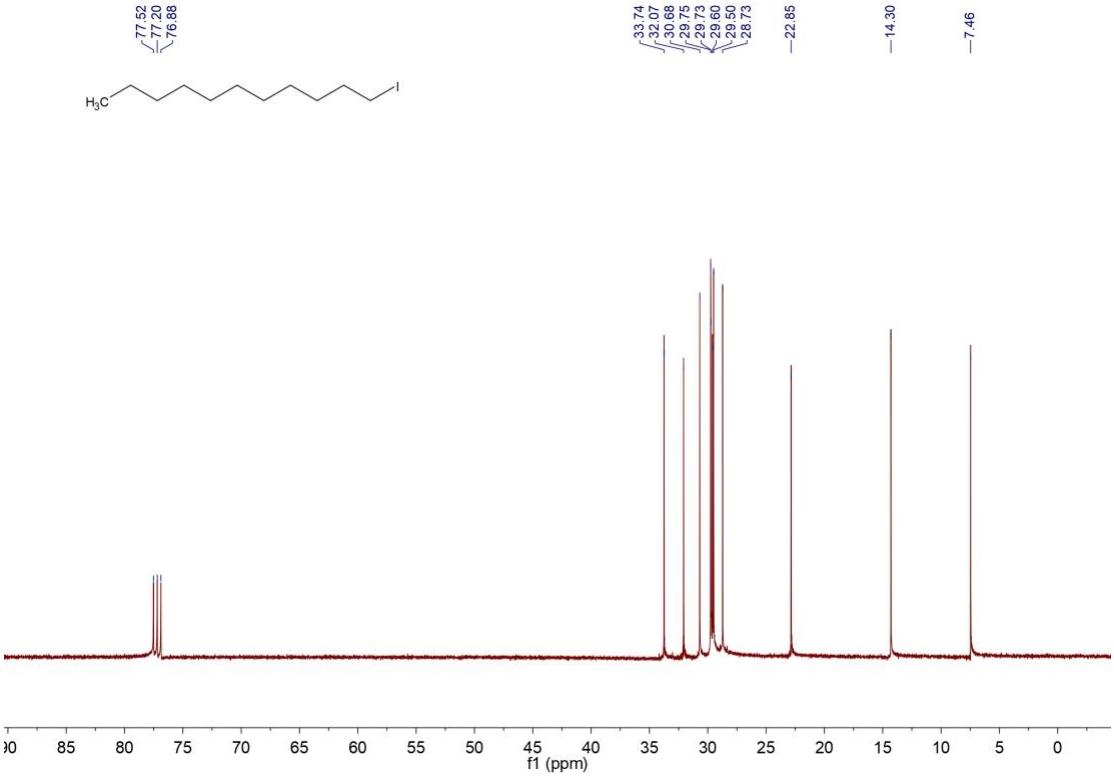
^{13}C NMR (101 MHz, $CDCl_3$) of product **28**



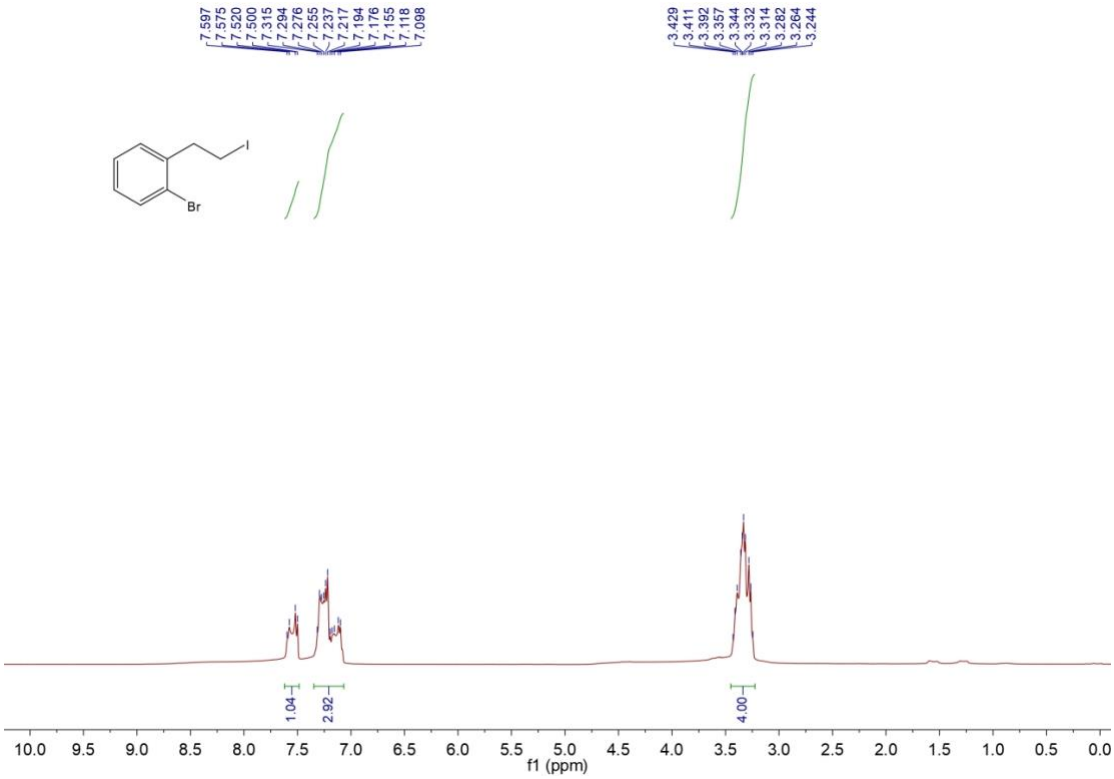
^{1}H NMR (400 MHz, $CDCl_3$) of product **31**



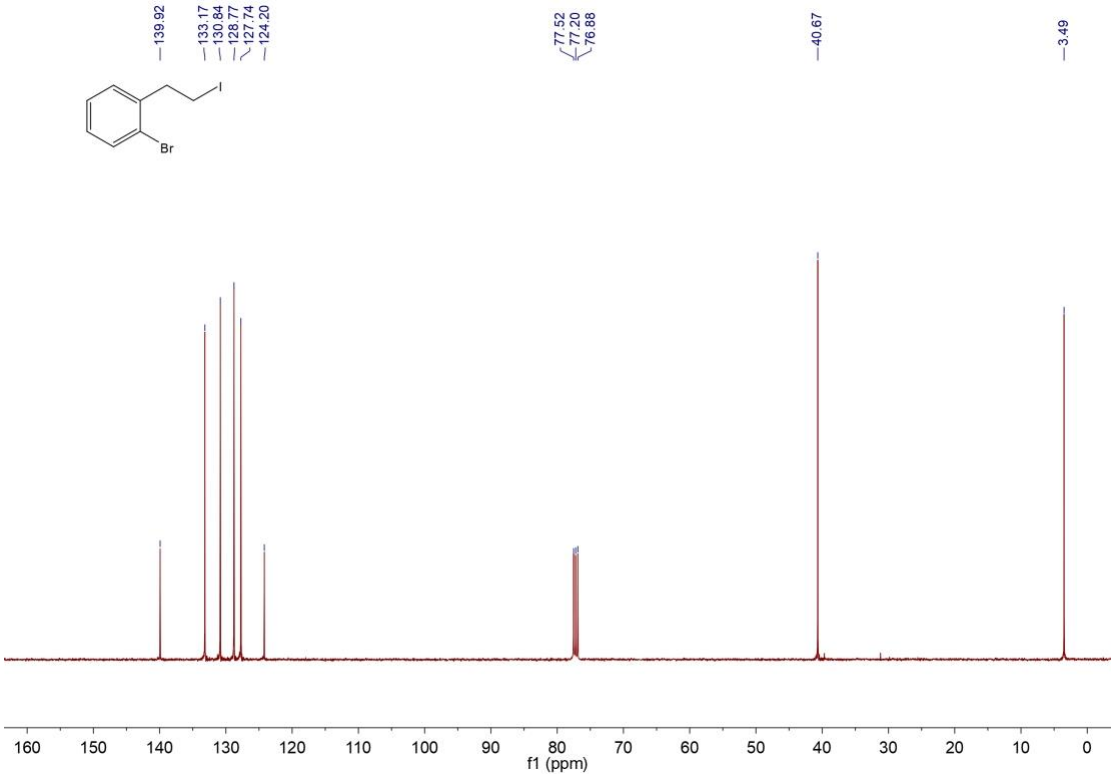
^{13}C NMR (101 MHz, $CDCl_3$) of product **31**



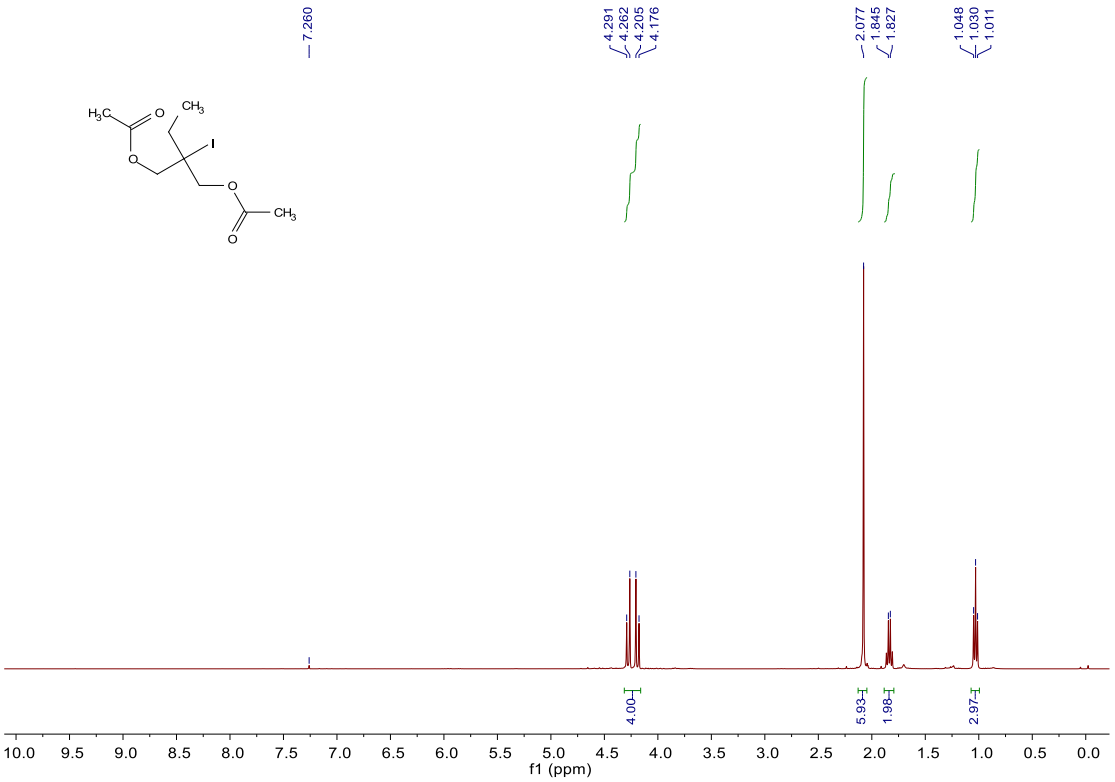
^{1}H NMR (400 MHz, $CDCl_3$) of product **34**



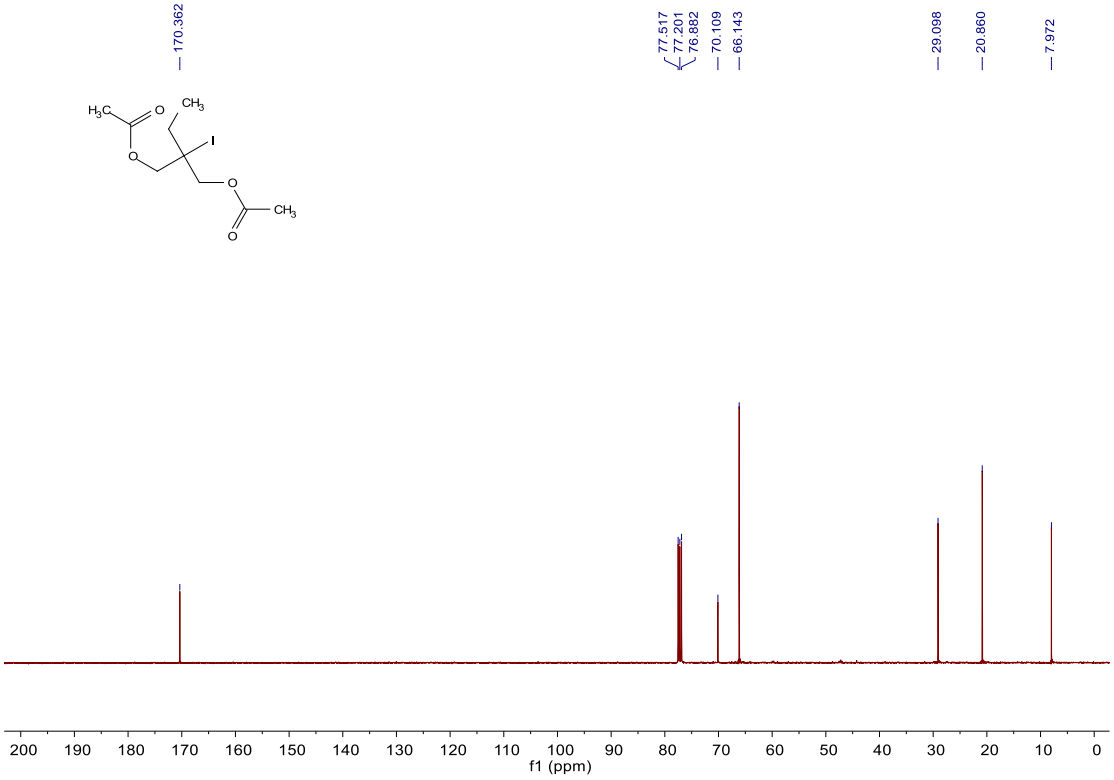
^{13}C NMR (101 MHz, $CDCl_3$) of product **34**



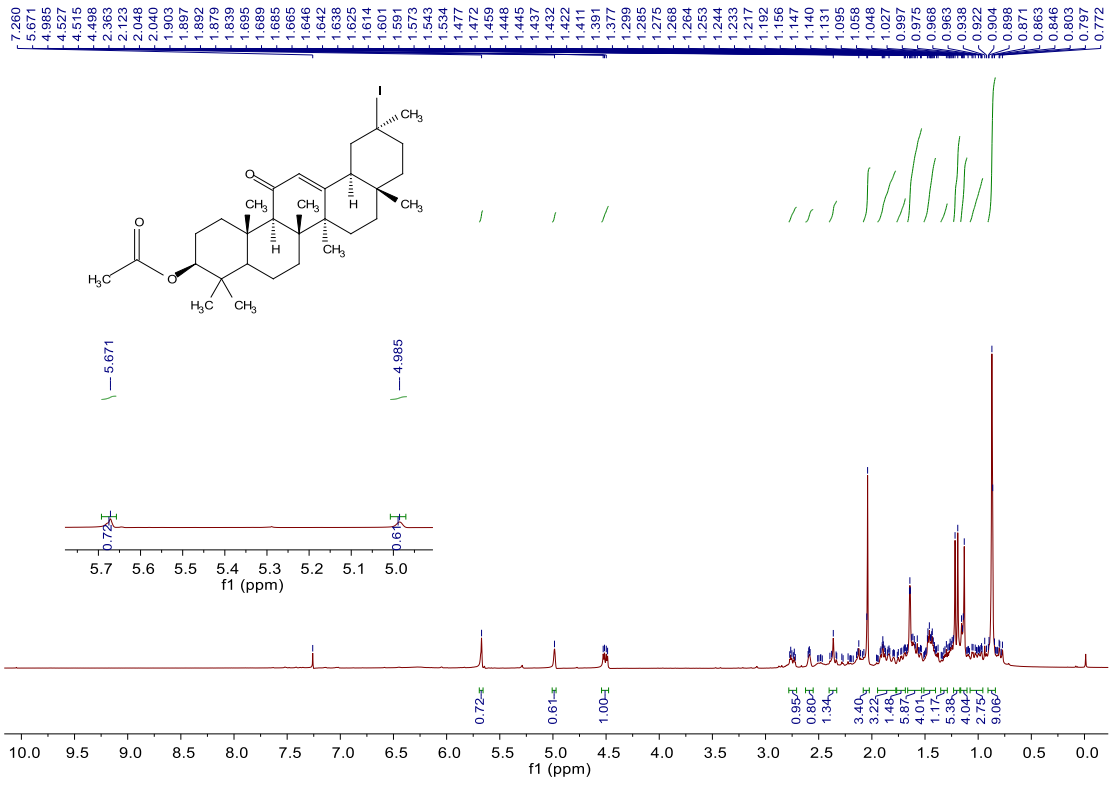
^{1}H NMR (400 MHz, $CDCl_3$) of product **43**



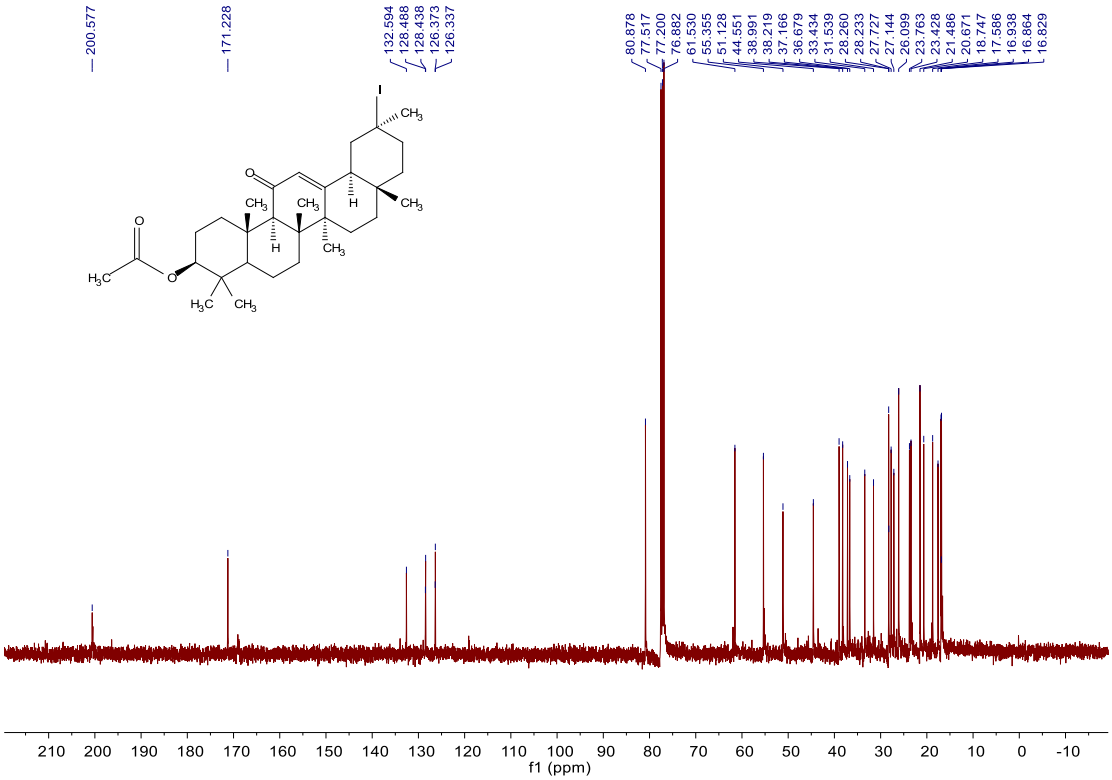
^{13}C NMR (101 MHz, $CDCl_3$) of product **43**



^{1}H NMR (400 MHz, $CDCl_3$) of product **49**



^{13}C NMR (101 MHz, $CDCl_3$) of product **49**



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