Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

Photo-triggered Halodecarboxylation of Aliphatic Carboxylic Acids via Cerium-Mediated ligand-to-metal-charge-transfer in water

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I. General Information

^{1}H NMR spectra were recorded at 400 MHz using TMS as internal standard, ^{13}C NMR spectra were recorded at 100 MHz using TMS as internal standard. All chemical shifts were reported as δ values (ppm) relative to TMS and observed coupling constants (*J*) are given in Hertz (Hz). Mass spectra were measured with a HRMS-ESI instrument. The UV-Vis measurements were carried out using a UV-Vis spectrophotometer (ULN 2209003, MAPADA P6). The thin layer chromatography (TLC) was performed using glass plates covered with SiO_2. Spots were visualized by UV light irradiation or by staining of the TLC plate with iodine. Unless otherwise indicated, all reactions were carried out under air atmosphere at room temperature with magnetic stirring. All reagents were purchased from commercial source and without prior purification. Column chromatography was performed on silica gel (200-300 mesh) and the elution was performed with *n*-hexane/ethyl acetate.

The Material of the Irradiation Vessel

Manufacturer：Shenzhen Kelo Light Co., Ltd.

Model：Kelo A0100

Distance from the light source to the irradiation vessel：2.0 cm

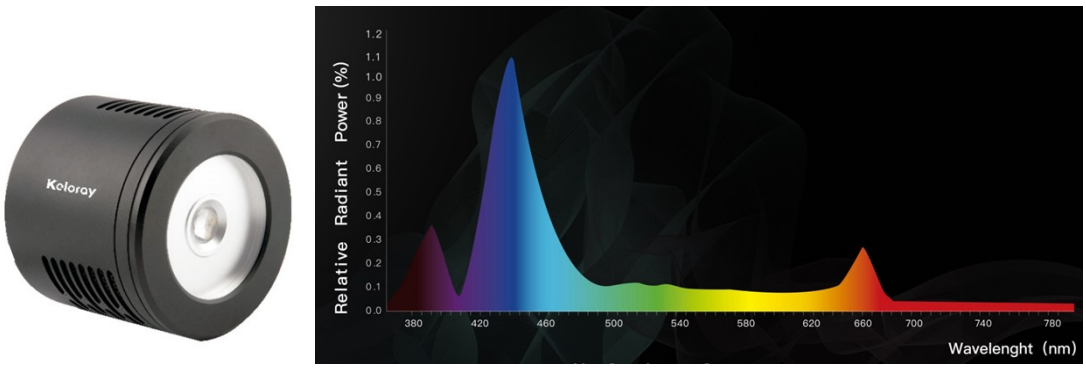
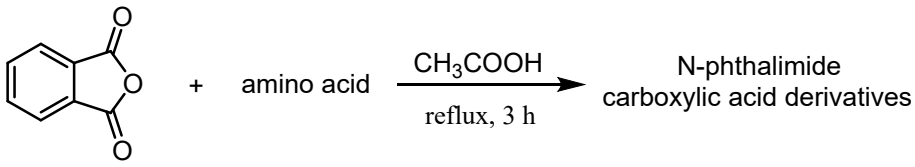


Figure S1. light setup and Broadband source.

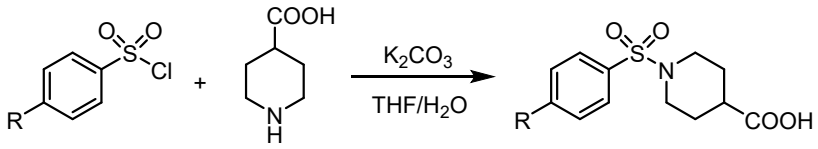
II. Preparation of substrate

General procedure for the synthesis of N-phthalimide carboxylic acid derivatives[1]



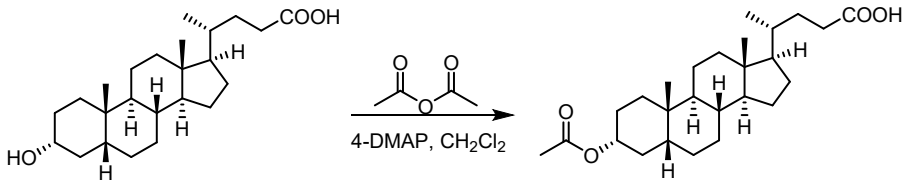
Reflux a solution of phthalic anhydride derivative (5 mmol) and amino acid (5 mmol) in acetic acid (20 mL) for 3 hours. Cool the reaction mixture to room temperature and then pour into ice water (50 mL). Stir the reaction mixture for 15 minutes. After that, a white crystalline product is obtained, filter the reaction mixture. Dry the reaction mixture in high vacuo to obtain the corresponding product.

General procedure for the synthesis of N-sulfoylpiperidinic acid derivatives[2]



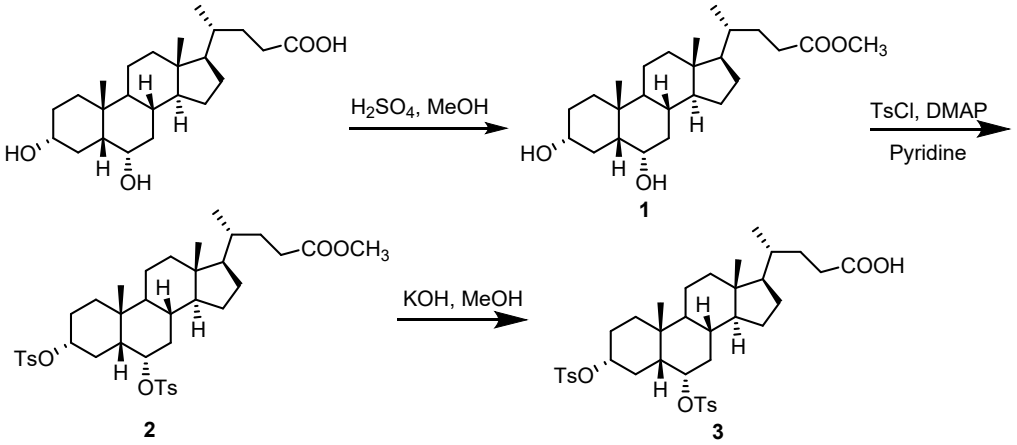
Piperidine 4-carboxylic acid (646 mg, 5.00 mmol, 1.0 eq) was stirred with potassium carbonate (970 mg, 7.0 mmol, 1.4 eq) in water (5 mL) at room temperature until a clear solution was obtained. Solution of benzene sulfonyl chloride (6.5 mmol, 1.3 equiv) in THF (5 mL) was added with the aid of a dropping funnel within 15 min. After stirring for 15 min, the cooling bath was removed and the reaction mixture was stirred for 24 h. After that, the reaction mixture was diluted with EtOAc (20 mL) and 2 N HCl (20 mL). Then, poured into an extraction funnel, the organic phase was washed with brine (1 x 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Dry the residues in high vacuo to obtain the corresponding product.

General procedure for the synthesis of lithocolic acid derivative[3]



Add acetic anhydride (26.43 mmol, 2.5 mL) dropwise to a solution of lithocholic (7.34 mmol, 2.764g) and 4,4-dimethylaminopyridine (1.47 mmol, 180 mg) in CH_2Cl_2 (30 mL). Stir the reaction mixture at room temperature under nitrogen atmosphere for 1 h. Wash the mixture with HCl 1 N aqueous solution (3×30 mL), 5% $NaHCO_3$ solution (3×30 mL), saturated NaCl solution (3×20 mL) and water (1×20 mL). Dry the organic layer over Na_2SO_4 and concentrate. Purify the crude product by column chromatography (silica gel, cyclohexane/ethyl acetate, 8:2) to obtain lithocolic acid derivative.

General procedure for the synthesis of hyodeoxycholic acid derivative.[4]

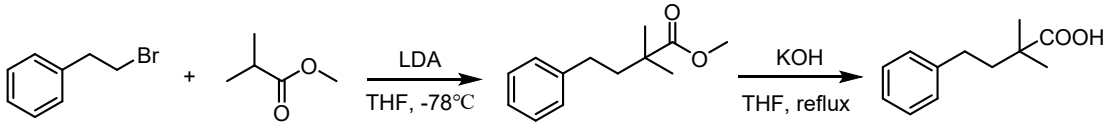


Hyodeoxycholic acid (20.0g, 51mmol, 1 equiv.) was added into methanol (100 mL) and stirred at room temperature for 5 min. After all dissolved, sulfuric acid (2.5 mL) was slowly added into the reaction solution and the reaction was carried out for 18 hours at room temperature under nitrogen atmosphere. The mixture was concentrated to obtain yellow oil, which was extracted by ethyl acetate. After that, saturated $NaHCO_3$ solution was added to adjust the pH to neutral and washed combined organic layers with brine. The organic phase was concentrated to obtain **1** (20.7g,99%).

1 (10.2g, 25 mmol, 1 equiv.), TsCl (14.1g, 75 mmol, 3 equiv.), DMAP (0.305 g, 2.5 mmol, 0.1 equiv.) were dissolved in pyridine (50 mL). The mixture was placed in an ice bath and stirred for 48 hours under nitrogen atmosphere. Subsequently, 250 mL 10 % HCl was added to the solution and then the white solid was precipitated, filtered under reduced pressure. The filter cake was washed with 5% HCl to neutral, and dried to obtain **2** (17.85 g, 99%).

2 (7.1g, 10 mmol, 1 equiv.), KOH (0.729g, 13 mmol, 1.3 equiv.) was dissolved in MeOH (50 mL). The mixture was stirred for 16 h at room temperature. Concentrated under reduced pressure The mixture was purified by silica gel column to obtain **3** (6.8g, 98%).

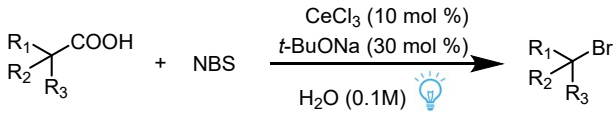
General procedure for the synthesis of 2,2-dimethyl-4-phenylbutanoic acid.[5]



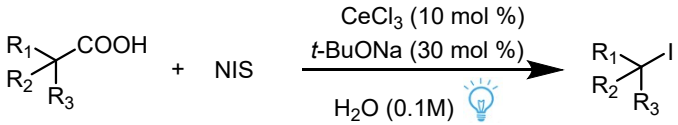
Methyl isobutyrate (10 mmol) and THF (20 mL) was added into an oven-dried 100 mL round-bottom flask and stirred at room temperature for 5 min. Submerge the flask in an acetone/dry ice bath (-78 °C) and stir the mixture vigorously for 5 minutes. Add LDA solution (20 ml, 0.5 M in THF, 10 mmol) dropwise to the mixture. Stir the mixture for 1 hours at -78 °C. Then, add corresponding halide (12 mmol) in THF (10 mL) dropwise to the mixture for 10 minutes. Remove the ice bath after stirring at -78 ° C for 1 hour. Allow the mixture to stir for 8 hours at room temperature. After that, the reaction mixture was diluted with EtOAc and 1 M HCl (aq.). Dry the organic layer over Na_2SO_4 and concentrate. Purify the crude product by column chromatography (silica gel, cyclohexane/ethyl acetate, 100:1) to obtain the ester (1.833 g, 89%).

Add a KOH solution (2.0 M in H_2O, 4.0 equiv.) to a solution of the alkylated ester (1.833g. 1.0 equiv.) in THF (0.2 M) at room temperature for 12 h. After washing the aqueous phase with DCM twice, adjust the pH to 1-2 with 4 N HCl. Extract the aqueous layer with DCM. Dry the combined organic layers over Na_2SO_4 and concentrate under reduced pressure to obtain 2,2-dimethyl-4-phenylbutanoic acid (1.505 g, 88 %).

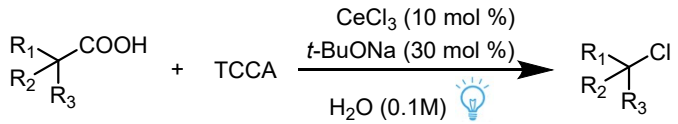
III. General procedure for decarboxylative halogenation



Procedure A: To a dried 8 mL vial was added acid (0.3 mmol), 1-bromopyrrolidine-2,5-dione (NBS) (1.0-1.5 equiv.), $CeCl_3$ (10 mol %), *t*-BuONa (30 mol %) in 3 mL H_2O under air atmosphere. The resulting solution was stirred under 100 W blue light for 6-12 h (25 ℃). After that, the reaction mixture was diluted with DCM. Then, poured into an extraction funnel, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA as an eluent gave the product.



Procedure B: To a dried 8 mL vial was added acid (0.3 mmol), 1-iodopyrrolidine-2,5-dione (NIS) (1.5 equiv.), $CeCl_3$ (10 mol %), *t*-BuONa (30 mol %) in 3 mL H_2O under air atmosphere. The resulting solution was stirred under 100 W blue light for 12 h (25 ℃). After that, the reaction mixture was diluted with DCM. Then, poured into an extraction funnel, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA as an eluent gave the product.

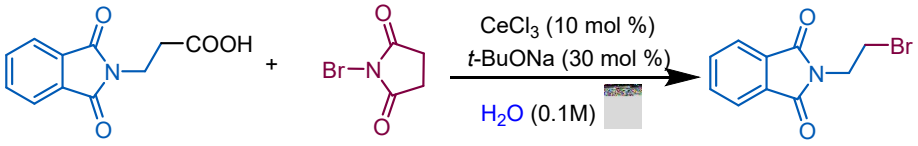


Procedure C: To a dried 8 mL vial was added acid (0.3 mmol), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (TCCA) (0.5 equiv.), $CeCl_3$ (10 mol %), *t*-BuONa (30 mol %) in 3 mL H_2O under air atmosphere. The resulting solution was stirred under 100 W blue light for 12 h (25 ℃). After that, the reaction mixture was diluted with DCM. Then, poured into an extraction funnel, the organic phase was dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA as an eluent gave the product.

Figure S2. 100 W blue LED light setup.

IV. Optimization of the reaction conditions

Table S1. Photocatalyst and base screening

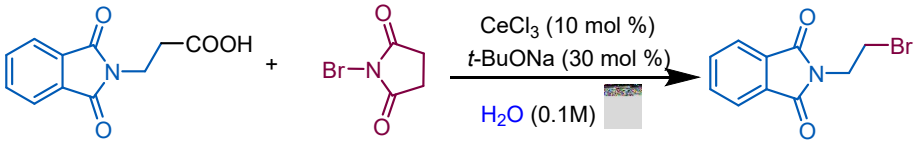


1 2

Entry	Deviation from standard conditions[a]	Yield[b] (%)
1	None	85
2	$CeBr_3$ as PC	65
3	Ce $(SO_4)_2$ as PC	32
4	5 mol % of $CeCl_3$	81
5	20 mol % of $CeCl_3$	84
6	CH_3ONa as base	46
7	K_2CO_3 as base	63
8	Cs_2CO_3 as base	32
9	10 mol % of *t*- BuONa	78
10	30 mol % of *t*- BuONa	82
11	1.0 equiv of *t*- BuONa	80
12	No base	trace

[a] Conditions: 3-Phthalimidopropionic acid (1) (0.2 mmol), NBS (1.5 equiv.), $CeCl_3$ (10 mol%), *t*-BuONa (30 mol %), H_2O (2 mL), room temperature, air atmosphere, 100W Blue LEDs, 12 h. [b] Determined by ^{1}HNMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard.

Table S2. Other parameter screening

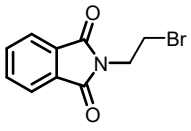


1 2

Entry	Deviation from standard conditions[a]	Yield[b] (%)
1	None	85
2	CH_3CN as solvent	84
3	DCE as solvent	71
4	DMSO as solvent	59
5	400 nm light instend of 100W Blue LEDs	37
6	435 nm light instend of 100W Blue LEDs	69
7	475 nm light instend of 100W Blue LEDs	32
8	Dark conditions	n.d.
9	No $CeCl_3$	n.d.
10	Nitrogen atmosphere	n.d.

[a] Conditions: 3-Phthalimidopropionic acid (1) (0.2 mmol), NBS (1.5 equiv.), $CeCl_3$ (10 mol%), *t*-BuONa (30 mol %), H_2O (2 mL), room temperature, air atmosphere, 100W Blue LEDs, 12 h. [b] Determined by ^{1}HNMR spectroscopy using 1,3,5-trimethoxybenzene as internal standard. n.d. No detected.

V. Characterization Data for the products



2

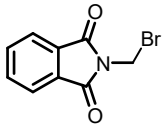
2-(2-bromoethyl)isoindoline-1,3-dione

According to general procedure A: using 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (0.3 mmol, 66 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (62.5 mg, 82% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 4.10 (t, *J* = 6.8 Hz 2H), 3.61 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.77, 134.19, 131.87, 123.49, 39.32, 28.08.

(Known compound: ACS Omega. 2021, 6, 33846).



3

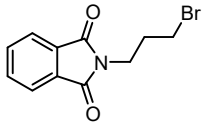
2-(bromomethyl)isoindoline-1,3-dione

According to general procedure A: using 2-(1,3-dioxoisoindolin-2-yl) acetic acid (0.3 mmol, 62 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (54 mg, 75% yield).

^{1}H NMR (400 MHz, DMSO-d6) δ 7.93 – 7.85 (m, 4H), 4.96 (s, 2H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.83, 135.21, 132.00, 123.77, 60.61.

(Known compound: *J. Am. Chem. Soc.* **2018**, 140, 15190).



4

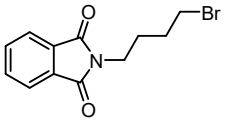
2-(3-bromopropyl)isoindoline-1,3-dione

According to general procedure A: using 4-(1,3-dioxoisoindolin-2-yl) butanoic acid (0.3 mmol, 70 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (65 mg, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.82 (m, 2H), 7.75 – 7.70 (m, 2H), 3.84 (t, *J* = 6.8 Hz, 2H), 3.41 (t, *J* = 6.7 Hz, 2H), 2.30 – 2.22 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.21, 134.03, 132.04, 123.32, 36.76, 31.66, 29.72.

(Known compound: *SynOpen.* **2017**; 1, 173).



5

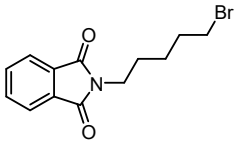
2-(4-bromobutyl)isoindoline-1,3-dione

According to general procedure A: using 5-(1,3-dioxoisoindolin-2-yl) pentanoic acid (0.3 mmol, 74 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (62 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.86 – 7.81 (m, 2H), 7.74 – 7.69 (m, 2H), 3.72 (t, *J* = 6.7 Hz, 2H), 3.44 (t, *J* = 6.3 Hz, 2H), 1.95 – 1.80 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.32, 133.95, 132.08, 123.24, 36.97, 32.69, 29.87, 27.25.

(Known compound: *J. Org. Chem.* **2004**, 69, 18, 6094).



6

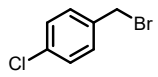
2-(5-bromopentyl)isoindoline-1,3-dione

According to general procedure A: using 6-(1,3-dioxoisoindolin-2-yl) hexanoic acid (0.3 mmol, 78 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as colorless oil (62 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 – 7.73 (m, 2H), 7.67 – 7.62 (m, 2H), 3.62 (t, *J* = 7.2 Hz, 2H), 3.32 (t, *J* = 6.7 Hz, 2H), 1.88 – 1.79 (m, 2H), 1.69 – 1.60 (m, 2H), 1.47 – 1.38 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.23, 133.84, 132.08, 123.10, 37.59, 33.32, 32.15, 27.66, 25.35.

(Known compound: *ChemPhysChem*. 2013, 14, 390).



7

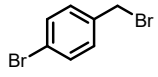
1-(bromomethyl)-4-chlorobenzene

According to general procedure A: using 2-(4-chlorophenyl) acetic acid (0.3 mmol, 51 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (50 mg, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.32 (s, 4H), 4.46 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.31, 134.32, 130.40, 129.02, 32.43.

(Known compound: *Green Chem.,* **2008**,10, 232).



8

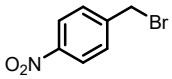
1-bromo-4-(bromomethyl)benzene

According to general procedure A: using 2-(4-bromophenyl) acetic acid (0.3 mmol, 65 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (62 mg, 83% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 (d, *J* = 7.5 Hz, 2H), 7.29 (d, *J* = 8.3 Hz, 2H), 4.46 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.80, 131.98, 130.68, 122.48, 32.40.

(Known compound: *Tetrahedron Lett.* **2009**. 65, 4429).



9

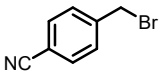
1-(bromomethyl)-4-nitrobenzene

According to general procedure A: using 2-(4-nitrophenyl) acetic acid (0.3 mmol, 54 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (45 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.23 (d, *J* = 8.7 Hz, 2H), 7.59 (d, *J* = 7.5 Hz, 2H), 4.54 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.67, 144.77, 129.93, 124.06, 30.94.

(Known compound: *Tetrahedron Lett.* **2009**. 65, 4429).



10

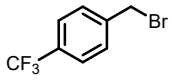
4-(bromomethyl)benzonitrile

According to general procedure A: using 2-(4-cyanophenyl) acetic acid (0.3 mmol, 49 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (41 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.64 (d, *J* = 7.9 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 4.48 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 142.83, 132.60, 129.73, 118.38, 112.22, 31.50.

(Known compound: *Eur. J. Med. Chem*. **2010**, 45, 5384).



11

1-(bromomethyl)-4-(trifluoromethyl)benzene

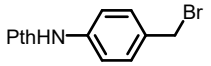
According to general procedure A: using 2-(4-(trifluoromethyl) phenyl) acetic acid (0.3 mmol, 61 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (54 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.63 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 4.53 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.63, 130.51 (q, *J* = 32.6 Hz), 129.36, 125.79 (q, *J* = 3.7 Hz), 123.88 (q, *J* = 273.4 Hz), 31.81.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.75.

(Known compound: *Org. Lett*. **2004**, 6, 3353).



12

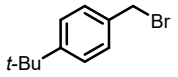
2-(4-(bromomethyl)phenyl)isoindoline-1,3-dione

According to general procedure A: using 2-(4-(1,3-dioxoisoindolin-2-yl) phenyl) acetic acid (0.3 mmol, 84 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (53 mg, 56% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 5.6, 2.9 Hz, 2H), 7.83 (dd, *J* = 5.9, 3.1 Hz, 2H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 8.6 Hz, 2H), 4.55 (d, *J* = 2.5 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.10, 137.49, 134.54, 131.68, 129.84, 126.70, 123.85, 32.59.

(Known compound: *Green Chem.* **2011**, 13, 928).



13

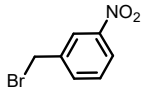
1-(bromomethyl)-4-(*tert*-butyl)benzene

According to general procedure A: using 2-(4-(tert-butyl) phenyl) acetic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (46 mg, 68% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.39 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.4 Hz, 2H), 4.51 (s, 2H), 1.33 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.60, 134.79, 128.81, 125.81, 34.68, 33.67, 31.30.

(Known compound: *Org. Lett.* **2013**, 15, 2210).



14

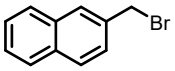
1-(bromomethyl)-3-nitrobenzene

According to general procedure A: using 2-(3-nitrophenyl) acetic acid (0.3 mmol, 54 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (45 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.30 – 8.24 (m, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 7.6 Hz, 1H), 7.54 (td, *J* = 8.0, 1.9 Hz, 1H), 4.54 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 148.37, 139.73, 135.02, 129.90, 123.94, 123.33, 31.13.

(Known compound: *Green Chem.* **2008**, 10, 232).



15

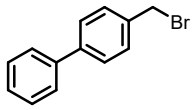
2-(bromomethyl)naphthalene

According to general procedure A: using 2-(naphthalen-2-yl) acetic acid (0.3 mmol, 56 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (47 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.84 (q, *J* = 4.1 Hz, 4H), 7.51 (dd, *J* = 8.2, 4.7 Hz, 3H), 4.68 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.10, 133.18, 133.09, 128.80, 127.99, 127.88, 127.75, 126.79, 126.60, 126.50, 34.10.

(Known compound: *J. Org. Chem.* **2006**, 71, 8276).



16

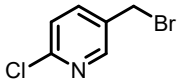
4-(bromomethyl)-1,1'-biphenyl

According to general procedure A: using 2-([1,1'-biphenyl]-4-yl) acetic acid (0.3 mmol, 64 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (53 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.56 (m, 4H), 7.47 (d, *J* = 7.2 Hz, 4H), 7.38 (d, *J* = 7.4 Hz, 1H), 4.56 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.41, 140.45, 136.77, 129.52, 128.85, 127.57, 127.13, 33.41. (one signal is missing due to overlapping).

(Known compound: *Bioorg. Med. Chem.* **2011**, 19, 1802).



17

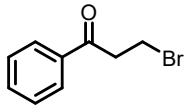
5-(bromomethyl)-2-chloropyridine

According to general procedure A: using 2-(6-chloropyridin-3-yl) acetic acid (0.3 mmol, 52 mg), 1-bromopyrrolidine-2,5-dione (0.33 mmol, 59 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as yellow solid (38 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.39 (d, *J* = 2.9 Hz, 1H), 7.69 (dd, *J* = 8.0, 2.7 Hz, 1H), 7.32 (dd, *J* = 8.3, 2.1 Hz, 1H), 4.43 (s, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 151.32, 149.55, 139.43, 132.68, 124.49, 28.40.

(Known compound: *Eur. J. Org. Chem.* **2015**, 8, 1764).



18

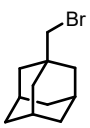
3-bromo-1-phenylpropan-1-one

According to general procedure A: using 4-oxo-4-phenylbutanoic acid (0.3 mmol, 54 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as colorless oil (45 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 2H), 7.63 – 7.56 (m, 1H), 7.52 – 7.46 (m, 2H), 3.75 (t, *J* =7.0 Hz 2H), 3.58 (t, *J* = 7.2 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.94, 136.29, 133.55, 128.75, 128.05, 41.56, 25.69.

(Known compound: *Org. Lett*. **2007**, 9, 1323).



19

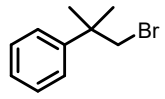
(3*r*,5*r*,7*r*)-1-(bromomethyl)adamantane

According to general procedure A: using 2-((3r,5r,7r)-adamantan-1-yl) acetic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (38 mg, 56% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.15 (s, 2H), 2.04 – 1.95 (m, 3H), 1.71 – 1.60 (m, 6H), 1.56 (d, *J* = 3.1 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 48.48, 40.69, 36.70, 33.57, 28.37.

(Known compound: *J. Med. Chem*. **2011**, 54, 2069).



20

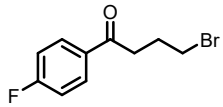
(1-bromo-2-methylpropan-2-yl)benzene

According to general procedure A: using 3-methyl-3-phenylbutanoic acid (0.3 mmol, 53 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (44 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.50 – 7.41 (m, 4H), 7.37 – 7.30 (m, 1H), 3.68 (s, 2H), 1.58 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.08, 128.43, 126.60, 125.90, 46.92, 39.22, 27.35.

(Known compound: *Bull. Chem. Soc. Jpn.* **1982**, 55, 255).



21

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

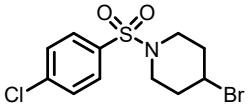
According to general procedure A: using 5-(4-fluorophenyl)-5-oxopentanoic acid (0.3 mmol, 63 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as colorless oil (64 mg, 88% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.97 (m, 2H), 7.19 – 7.10 (m, 2H), 3.55 (t, *J* = 6.3 Hz, 2H), 3.16 (t, *J* = 6.9 Hz, 2H), 2.37 – 2.26 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.21, 165.85 (d, *J* = 254.9 Hz), 133.18 (d, *J* = 3.0 Hz), 130.68 (d, *J* = 9.4 Hz), 115.78 (d, *J* = 21.9 Hz), 36.46, 33.59, 26.79.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.93.

(Known compound: *Green Chem.* **2020**, 22, 4357).



22

4-bromo-1-((4-chlorophenyl)sulfonyl)piperidine

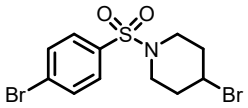
According to general procedure A: using 1-((4-chlorophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 91 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent:

PE/EA = 100/1) gave the title compound as white solid (72mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.70 (d, *J* = 6.3 Hz, 2H), 7.52 (d, *J* = 6.4 Hz, 2H), 4.34 – 4.21 (m, 1H), 3.24 – 3.10 (m, 4H), 2.25 – 2.12 (m, 2H), 2.12 – 2.01 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 139.52, 134.85, 129.52, 128.95, 47.58, 43.59, 34.56.

HRMS: $C_{11}H_{14}BrClNO_2S$ $[M+H]^+$; calculated: 337.9617, found: 337.9614.



23

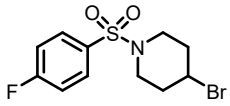
4-bromo-1-((4-bromophenyl)sulfonyl)piperidine

According to general procedure A: using 1-((4-bromophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 104 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (84 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.69 (d, *J* = 8.5 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 4.31 – 4.24 (m, 1H), 3.24 – 3.10 (m, 4H), 2.25 – 2.13 (m, 2H), 2.09 – 1.97 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.59, 132.48, 129.02, 127.97, 47.51, 43.60, 34.61.

HRMS: $C_{11}H_{14}Br_2NO_2S$ $[M+H]^+$; calculated: 383.9091, found: 383.9089.



24

4-bromo-1-((4-fluorophenyl)sulfonyl)piperidine

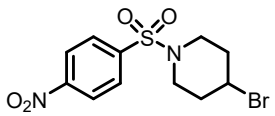
According to general procedure A: using 1-((4-fluorophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 86 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (75 mg, 78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 5.0 Hz, 2H), 7.29 (d, *J* = 10.4 Hz, 2H), 4.37 – 4.28 (m, 1H), 3.28 – 3.15 (m, 4H), 2.30 – 2.18 (m, 2H), 2.15 – 2.05 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.26 (d, *J* = 255.3 Hz), 132.37 (d, *J* = 3.3 Hz), 130.23 (d, *J* = 9.3 Hz), 116.48 (d, *J* = 22.5 Hz), 47.64, 43.59, 34.56.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -104.82.

HRMS: $C_{11}H_{14}BrFNO_2S$ $[M+H]^+$; calculated: 321.9907, found: 321.9900.



25

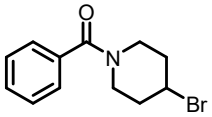
4-bromo-1-((4-nitrophenyl)sulfonyl)piperidine

According to general procedure A: using 1-((4-nitrophenyl) sulfonyl) piperidine-4-carboxylic acid (0.3 mmol, 94 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 20/1) gave the title compound as white solid (65 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.40 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.8 Hz, 2H), 4.36 – 4.29 (m, 1H), 3.32 – 3.16 (m, 4H), 2.25 – 2.03 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 150.28, 142.55, 128.70, 124.49, 47.29, 43.36, 34.43.

HRMS: $C_{11}H_{12}BrN_2O_4S$ [M-H] $^-$; calculated: 346.9701, found: 346.9694.



26

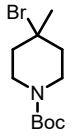
(4-bromopiperidin-1-yl)(phenyl)methanone

According to general procedure A: using 1-benzoylpiperidine-4-carboxylic acid (0.3 mmol, 70 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (58 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.34 (m, 5H), 4.43 (tt, *J* = 7.4, 3.7 Hz, 1H), 3.67 (t, *J* = 114.5 Hz, 4H), 2.25 – 1.86 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.49, 135.72, 129.76, 128.54, 126.85, 48.77.

(Known compound: *Org. Lett*. **2011**, 13, 2138).



27

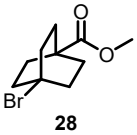
***tert*-butyl 4-bromo-4-methylpiperidine-1-carboxylate**

According to general procedure A: using 1-(tert-butoxycarbonyl)-4-methylpiperidine-4-carboxylic acid (0.3 mmol, 73 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as colorless oil (62 mg, 74% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.12 – 3.85 (m, 2H), 3.13 (t, *J* = 12.5 Hz, 2H), 1.97 (d, *J* = 14.4 Hz, 2H), 1.84 (s, 3H), 1.54 (td, *J* = 13.4, 12.0, 4.1 Hz, 2H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 154.63, 79.67, 67.82, 41.55, 35.01, 28.43. (one carbon signal is overlapped)

(Known compound: *J. Am. Chem. Soc.* **2017**, 139, 18037).



28

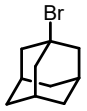
methyl 4-bromobicyclo[2.2.2]octane-1-carboxylate

According to general procedure A: using 4-(methoxycarbonyl) bicyclo [2.2.2] octane-1-carboxylic acid (0.3 mmol, 64 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100/1) gave the title compound as white solid (60 mg, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.63 (s, 3H), 2.37 – 2.14 (m, 6H), 2.00 – 1.91 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.12, 62.16, 51.89, 36.87, 36.83, 31.17.

(Known compound: *Org. Process Res. Dev.* **2020**, 24, 1328).



29

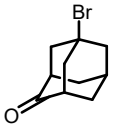
(3*s*,5*s*,7*s*)-1-bromoadamantane

According to general procedure A: using (3r,5r,7r)-adamantane-1-carboxylic acid (0.3 mmol, 52 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (54 mg, 83% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.37 (d, *J* = 3.0 Hz, 6H), 2.13 – 2.07 (m, 3H), 1.73 (t, *J* = 3.1 Hz, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 66.67, 49.35, 35.56, 32.62.

(Known compound: *F. Glorius, Chem. Eur. J.* **2016**, 22, 9971).



30

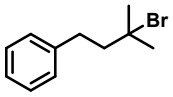
(1*R*,3*S*,5*s*,7*s*)-5-bromoadamantan-2-one

According to general procedure A: using (1s,3R,5S,7s)-4-oxoadamantane-1-carboxylic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (52 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.73 – 2.42 (m, 8H), 2.26 (s, 1H), 2.12 – 1.96 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 214.44, 59.94, 49.07, 49.00, 47.79, 37.52, 31.30.

(Known compound: *Org. Lett*. **2010**, 12, 332).



31

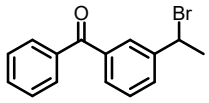
(3-bromo-3-methylbutyl)benzene

According to general procedure A: 2,2-dimethyl-4-phenylbutanoic acid (0.3 mmol, 58 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (49 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.21 (m, 3H), 2.91 – 2.84 (m, 2H), 2.14 – 2.07 (m, 2H), 1.84 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 141.62, 128.51, 128.45, 126.01, 67.55, 49.47, 34.31, 32.93.

(Known compound: *Science*. **2022**, 376, 410).



32

(3-(1-bromoethyl)phenyl)(phenyl)methanone

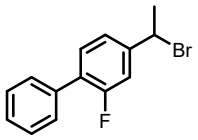
According to general procedure A: using ketoprofen (0.3 mmol, 76 mg), 1-bromopyrrolidine-2,5-dione

(0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as yellow oil (70 mg, 81% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.88 (s, 1H), 7.81 (d, *J* = 7.6 Hz, 2H), 7.69 (t, *J* = 7.6 Hz, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 7.54 – 7.44 (m, 3H), 5.25 (q, *J* = 7.0 Hz, 1H), 2.07 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 196.18, 143.67, 137.98, 137.32, 132.65, 130.87, 130.08, 130.05, 128.71, 128.40, 128.23, 48.40, 26.76.

(Known compound: *Org. Process Res. Dev.* **2020**, 24, 1328).



33

4-(1-bromoethyl)-2-fluoro-1,1'-biphenyl

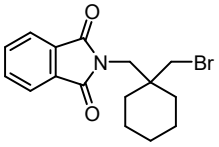
According to general procedure A: using flurbiprofen (0.3 mmol, 73 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (61 mg, 73% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.54 (m, 2H), 7.51 – 7.39 (m, 4H), 7.34 – 7.27 (m, 2H), 5.24 (q, *J* = 7.0 Hz, 1H), 2.10 (d, *J* = 6.9 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.54 (d, *J* = 249.2 Hz), 144.49 (d, *J* = 7.2 Hz), 135.23, 130.95 (d, *J* = 3.8 Hz), 129.13, 128.96 (d, *J* = 2.9 Hz), 128.51, 127.90, 47.94, 26.63.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -117.04.

(Known compound: *Org. Process Res. Dev.* **2020**, 24, 1328).



34

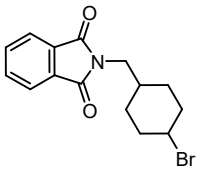
2-((1-(bromomethyl)cyclohexyl)methyl)isoindoline-1,3-dione

According to general procedure A: using 2-(1-((1,3-dioxoisoindolin-2-yl) methyl) cyclohexyl) acetic acid (0.3 mmol, 91 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as colorless oil (62 mg, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.76 – 7.70 (m, 2H), 3.70 (s, 2H), 3.53 (s, 2H), 1.72 – 1.60 (m, 4H), 1.58 – 1.43 (m, 2H), 1.41 – 1.24 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 169.09, 134.05, 131.99, 123.34, 45.55, 41.35, 39.07, 32.46, 25.51, 21.36.

HRMS: $C_{16}H_{19}BrNO_2$ $[M+H]^+$; calculated: 336.0599, found: 336.0596.



35

2-((4-bromocyclohexyl)methyl)isoindoline-1,3-dione

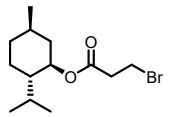
According to general procedure A: using 4-((1,3-dioxoisoindolin-2-yl) methyl) cyclohexane-1-carboxylic acid (0.3 mmol, 86 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as colorless oil (72 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 4.58 (p, *J* = 3.5 Hz, 0.62 H) (major), 4.00 – 3.93 (m, 0.40) (minor), 3.61 (d, *J* = 7.3 Hz, 1.32H) (major), 3.52 (d, *J* = 7.1 Hz, 1H), 2.36 – 2.26 (m, 1H), 2.14 – 2.05 (m, 1H), 1.94 – 1.69 (m, 4H), 1.62 – 1.52 (m, 2H), 1.28 – 1.09 (m, 1H).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.81 (m, 2H), 7.74 – 7.68 (m, 2H), 4.58 (p, *J* = 3.5 Hz, 0.62 H) (major), 4.00 – 3.93 (m, 0.40) (minor), 3.61 (d, *J* = 7.3 Hz, 1.32H) (major), 3.52 (d, *J* = 7.1 Hz, 0.76H) (minor), 2.36 – 2.26 (m, 1H), 2.14 – 2.05 (m, 1H), 1.94 – 1.69 (m, 4H), 1.62 – 1.52 (m, 2H), 1.28 – 1.09 (m, 1H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.62 (major), 168.57 (minor), 134.03 (minor), 133.97 (major), 132.00 (major), 131.93 (minor), 123.31 (minor), 123.27 (major), 53.67, 51.36, 43.35 (major), 43.30 (minor), 37.17, 36.04, 35.62, 33.96, 31.31, 25.40.

HRMS: $C_{15}H_{17}BrNO_2$ $[M+H]^+$; calculated: 322.0442, found: 322.0440.



36

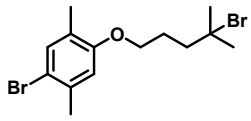
(1*R*,2*S*,5*R*)-2-isopropyl-5-methylcyclohexyl 3-bromopropanoate

According to general procedure A: using monomethylsuccinate (0.3 mmol, 77 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (68 mg, 78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.74 (td, *J* = 10.8, 4.0 Hz, 1H), 3.58 (t, *J* = 6.7 Hz, 2H), 2.89 (t, *J* = 6.9 Hz, 2H), 2.04 – 1.83 (m, 2H), 1.72 – 1.64 (m, 2H), 1.55 – 1.32 (m, 2H), 1.30 – 1.15 (m, 1H), 1.11 – 0.96 (m, 2H), 0.92 – 0.87 (m, 6H), 0.76 (d, *J* = 7.0 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.09, 46.96, 40.85, 38.13, 34.20, 31.40, 26.26, 23.36, 22.01, 20.76, 16.28.

HRMS: $C_{13}H_{23}BrNaO_2$ $[M+Na]^+$; calculated: 313.0779, found: 313.0775.



37

1-bromo-4-((4-bromo-4-methylpentyl)oxy)-2,5-dimethylbenzene

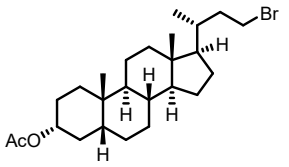
According to general procedure A: using gemfibrozil (0.3 mmol, 99 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O.

Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (69 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.28 (s, 1H), 6.70 (s, 1H), 3.98 (t, *J* = 6.1 Hz, 2H), 2.36 (s, 3H), 2.18 (s, 3H), 1.91 – 1.84 (m, 2H), 1.81 – 1.76 (m, 2H), 1.29 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 156.18, 135.68, 133.70, 126.27, 114.74, 113.75, 82.51, 68.49, 34.47, 24.00, 23.91, 22.89, 15.51.

HRMS: $C_{15}H_{21}Br_2O_3$ [M+HCOO] $^-$; calculated: 408.9837, found: 408.9832.



38

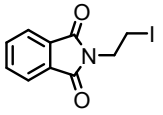
3α-Acetoxy-23-bromo-5β-norcholane

According to general procedure A: using 3-acetyllithocholic acid (0.3 mmol, 126 mg), 1-bromopyrrolidine-2,5-dione (0.45 mmol, 80 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as white solid (96 mg, 71% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.72 (tt, *J* = 11.6, 6.3, 5.5 Hz, 1H), 3.55 – 3.44 (m, 1H), 3.42 – 3.29 (m, 1H), 2.06 – 1.92 (m, 5H), 1.89 – 1.77 (m, 4H), 1.71 – 1.65 (m, 1H), 1.61 – 1.35 (m, 10H), 1.29 – 1.20 (m, 3H), 1.18 – 1.00 (m, 6H), 0.92 (s, 6H), 0.66 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.65, 74.40, 56.51, 56.13, 42.86, 41.89, 40.41, 40.16, 39.34, 35.78, 35.11, 35.04, 34.60, 32.26, 32.10, 28.25, 27.02, 26.65, 26.32, 24.17, 23.35, 21.51, 20.83, 18.11, 12.04.

(Known compound: *Org. Process Res. Dev.* **2020**, 24, 1328).



39

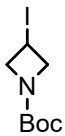
2-(2-iodoethyl)isoindoline-1,3-dione

According to general procedure B: using 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (0.3 mmol, 66 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as white solid (70 mg, 78% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.82 (m, 2H), 7.79 – 7.69 (m, 2H), 4.08 (t, *J* = 7.2 Hz, 2H), 3.40 (t, *J* = 7.3 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.67, 134.26, 131.85, 123.55, 40.06.

(Known compound: *Org. Biomol. Chem.* **2021**, 19, 6160).



40

tert-butyl 3-iodoazetidine-1-carboxylate

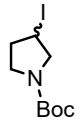
According to general procedure B: using 1-(tert-butoxycarbonyl) azetidine-3-carboxylic acid (0.3

mmol, 60 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (54 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.66 – 4.58 (m, 2H), 4.49 – 4.41 (m, 1H), 4.30 – 4.23 (m, 2H), 1.42 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 155.57, 80.13, 61.56, 28.32, 2.63.

(Known compound: *Org. Lett*. **2019**, 21, 2285).



41

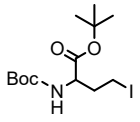
tert-butyl 3-iodopyrrolidine-1-carboxylate

According to general procedure B: using 1-(tert-butoxycarbonyl) pyrrolidine-3-carboxylic acid (0.3 mmol, 65 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (56 mg, 63% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.44 – 4.27 (m, 1H), 3.87 – 3.72 (m, 1.41H), 3.72 – 3.62 (m, 0.58H), 3.61 – 3.50 (m, 1H), 3.47 – 3.35 (m, 1H), 2.34 – 2.13 (m, 2H), 1.46 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ [154.27, 154.12], [79.78, 79.72], [57.39, 57.06], [45.07, 44.75], [38.39, 37.61], 28.48, 19.97.

(Known compound: *Org. Lett*. **2019**, 21, 2285).



42

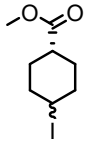
tert-butyl 2-((*tert*-butoxycarbonyl)amino)-4-iodobutanoate

According to general procedure B: using 5-(tert-butoxy)-4-((tert-butoxycarbonyl) amino)-5-oxopentanoic acid (0.3 mmol, 91 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (71 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 5.22 – 4.98 (m, 1H), 4.23 – 4.10 (m, 1H), 3.20 – 3.08 (m, 2H), 2.43 – 2.27 (m, 1H), 2.19 – 2.07 (m, 1H), 1.45 (s, 9H), 1.43 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 170.59, 155.34, 82.49, 79.98, 54.98, 37.66, 28.32, 27.99, -0.44.

(Known compound: *J. Med. Chem.* **2022**, 65, 9750).



43

methyl 4-iodocyclohexane-1-carboxylate

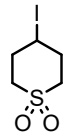
According to general procedure B: using 4-(methoxycarbonyl) cyclohexane-1-carboxylic acid (0.3 mmol, 56 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-

BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as colorless oil (58 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.69 – 4.60 (m, 0.64H) (major), 4.21 – 4.06 (m, 0.38H) (minor), 3.68 (d, *J* = 16.7 Hz, 3H), 2.43 – 2.38 (m, 1H), 2.17 – 1.88 (m, 4H), 1.88 – 1.49 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 175.63 (minor), 175.19 (major), 51.75 (major), 51.74 (minor), 41.49 (minor), 41.39 (major), 38.78, 35.88, 32.61, 30.63, 28.06, 26.15.

(Known compound: *Angew. Chem., Int. Ed.* **2018**, 57, 5492).



44

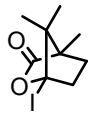
4-iodotetrahydro-2*H*-thiopyran 1,1-dioxide

According to general procedure B: using tetrahydro-2H-thiopyran-4-carboxylic acid 1,1-dioxide (0.3 mmol, 54 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as white solid (59 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 4.66 (p, *J* = 4.2 Hz, 1H), 3.43 – 3.29 (m, 2H), 3.08 – 2.94 (m, 2H), 2.48 (q, *J* = 4.4 Hz, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 50.36, 35.33, 24.62.

(Known compound: *PCT Int. Appl.* **2011**, 2011128455).



45

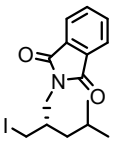
(1*S*,4*R*)-1-iodo-4,7,7-trimethyl-2-oxabicyclo[2.2.1]heptan-3-one

According to general procedure B: using camphorsulfonic acid (0.3 mmol, 59 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 100:1) gave the title compound as white solid (65 mg, 77% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.53 – 2.38 (m, 2H), 1.88 – 1.79 (m, 1H), 1.75 – 1.67 (m, 1H), 1.20 (s, 3H), 1.00 (s, 3H), 0.86 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.52, 56.43, 49.58, 40.70, 30.13, 18.86, 17.50, 10.62.

(Known compound: *PCT Int. Appl.* **2015**, 2015068159).



46

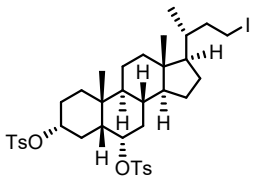
(*S*)-2-(2-(iodomethyl)-4-methylpentyl)isoindoline-1,3-dione

According to general procedure B: using (R)-3-((1,3-dioxoisoindolin-2-yl) methyl)-5-methylhexanoic acid (0.3 mmol, 87 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as yellow oil (85 mg, 76% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.75 (dd, *J* = 5.4, 3.1 Hz, 2H), 3.64 (dd, *J* = 6.8, 2.4 Hz, 2H), 3.30 – 3.17 (m, 2H), 1.96 – 1.84 (m, 1H), 1.76 – 1.67 (m, 1H), 1.41 – 1.32 (m, 1H), 1.21 – 1.12 (m, 1H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.90 (d, *J* = 6.6 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.50, 134.09, 131.92, 123.38, 42.72, 41.89, 36.07, 24.98, 22.95, 22.13, 12.03.

HRMS: $C_{15}H_{19}INO_2$ $[M+H]^+$; calculated: 372.0455, found: 372.0443.



47

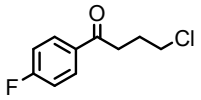
3α, 6α-Tos-23-iodo-5β-norcholane

According to general procedure B: using 3α, 6α-tos-hyodeoxycholic acid (0.3 mmol, 210 mg), 1-iodopyrrolidine-2,5-dione (0.45 mmol, 101 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as white solid (143 mg, 61% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.34 (t, *J* = 8.0 Hz, 4H), 4.78 (dt, *J* = 12.3, 4.9 Hz, 1H), 4.29 (tt, *J* = 11.1, 4.6 Hz, 1H), 3.29 (td, *J* = 9.2, 3.6 Hz, 1H), 3.08 (q, *J* = 8.4 Hz, 1H), 2.46 (s, 6H), 2.04 – 1.90 (m, 2H), 1.84 – 1.68 (m, 4H), 1.66 – 1.59 (m, 2H), 1.54 – 1.36 (m, 6H), 1.33 – 1.16 (m, 6H), 1.15 – 1.02 (m, 4H), 0.88 (d, *J* = 6.1 Hz, 3H), 0.80 (s, 3H), 0.61 (s, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 144.71, 144.68, 134.49, 134.47, 129.85, 129.81, 127.62, 127.54, 81.76, 55.82, 55.66, 46.32, 42.93, 40.10, 39.60, 39.45, 37.03, 36.15, 34.83, 34.81, 32.09, 27.98, 27.40, 26.46, 23.90, 22.90, 21.71, 21.69, 20.52, 17.76, 11.99, 5.12.

HRMS: $C_{37}H_{52}INaO_6S_2$ $[M+Na]^+$; calculated: 805.2069, found: 805.2069.



48

4-chloro-1-(4-fluorophenyl)butan-1-one

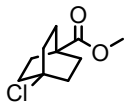
According to general procedure C: using 5-(4-fluorophenyl)-5-oxopentanoic acid (0.3 mmol, 63 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 50:1) gave the title compound as yellow oil (43 mg, 72% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.96 (m, 2H), 7.13 (t, *J* = 8.6 Hz, 2H), 3.67 (t, *J* = 6.2 Hz, 2H), 3.15 (t, *J* = 7.0 Hz, 2H), 2.22 (p, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 197.34, 165.82 (d, *J* = 254.9 Hz), 133.19 (d, *J* = 3.0 Hz), 130.66 (d, *J* = 9.2 Hz), 115.76 (d, *J* = 21.8 Hz), 44.64, 35.19, 26.69.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.03.

(Known compound: *J. Am. Chem. Soc.* **2022**, 144, 13895).



49

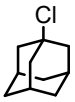
methyl 4-chlorobicyclo[2.2.2]octane-1-carboxylate

According to general procedure C: using 4-(methoxycarbonyl) bicyclo [2.2.2] octane-1-carboxylic acid (0.3 mmol, 64 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE/EA = 30:1) gave the title compound as colorless oil (42 mg, 69% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.63 (s, 3H), 2.10 – 2.01 (m, 6H), 1.98 – 1.90 (m, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 177.07, 66.23, 51.86, 37.51, 35.54, 30.36.

(Known compound: *J. Org. Chem.* **1985**, 50, 1079).



50

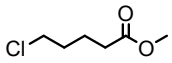
(3*s*,5*s*,7*s*)-1-chloroadamantane

According to general procedure C: using (3r,5r,7r)-adamantane-1-carboxylic acid (0.3 mmol, 54 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (36 mg, 70% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 2.14 (s, 9H), 1.67 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 68.94, 47.75, 35.59, 31.72.

(Known compound: *Chem. Eur. J.* **2016**, 22, 9971).



51

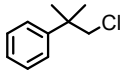
methyl 5-chloropentanoate

According to general procedure C: using 6-methoxy-6-oxohexanoic acid (0.3 mmol, 48 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (28 mg, 62% yield).

^{1}H NMR (400 MHz, Chloroform-*d*) δ 3.67 (s, 3H), 3.54 (t, *J* = 6.3 Hz, 2H), 2.35 (t, *J* = 6.7 Hz, 2H), 1.87 – 1.72 (m, 4H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 173.63, 51.61, 44.45, 33.18, 31.84, 22.23.

(Known compound: *Russ. Chem. Bull.* **2004**, 53, 2200).



52

(1-chloro-2-methylpropan-2-yl)benzene

According to general procedure C: using 6-methoxy-6-oxohexanoic acid (0.3 mmol, 54 mg), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (0.15 mmol, 35 mg), $CeCl_3$ (0.03 mmol, 7.4 mg), *t*-BuONa (0.09 mmol, 8.6 mg) and 3 mL H_2O. Purification by flash column chromatography (eluent: PE) gave the title compound as colorless oil (31 mg, 61% yield).

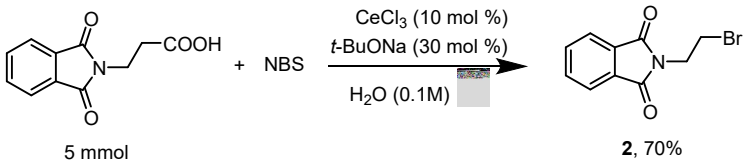
^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.35 (m, 4H), 7.31 – 7.26 (m, 1H), 3.70 (s, 2H), 1.48 (s, 6H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 146.03, 128.35, 126.50, 125.93, 56.36, 39.80, 26.45.

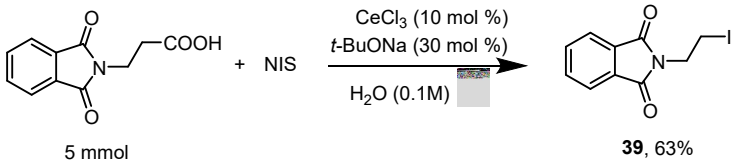
(Known compound: *Org. Lett*. **2017**, 19, 4560).

VI. Application of the methodology

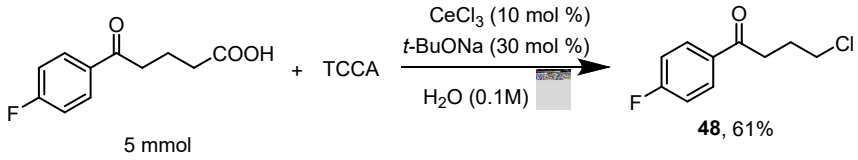
Gram-scale synthesis



In a dry 100 mL round-bottom flask was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (5 mmol), 1-bromopyrrolidine-2,5-dione (7.5 mmol) in 20 mL H_2O under air atmosphere. The resulting solution was stirred for 12 h at room temperature under 100W Blue lights. On completion, the resulting solution was diluted with DCM (30 mL). Then, poured into an extraction funnel, the organic phase was washed with brine (1 x 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA (100/1) as eluent gave the compound **37** as white solid (0.889 g, 70% yield)



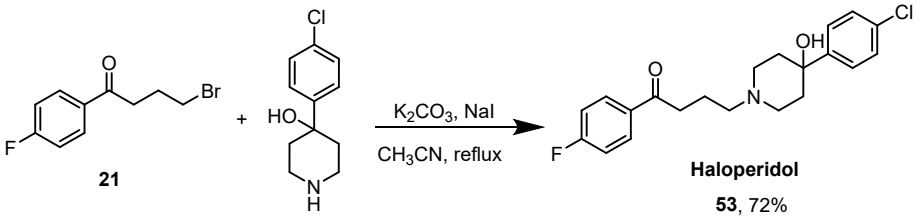
In a dry 100 mL round-bottom flask was added 5-(4-fluorophenyl)-5-oxopentanoic acid (5 mmol), 1,3,5-trichloro-1,3,5-triazinane-2,4,6-trione (2.5 mmol) in 20 mL H_2O under air atmosphere. The resulting solution was stirred for 12 h at room temperature under 100W Blue lights. On completion, the resulting solution was diluted with DCM (30 mL). Then, poured into an extraction funnel, the organic phase was washed with brine (1 x 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA (100/1) as eluent gave the compound **46** as yellow oil (0.948 g, 63% yield)



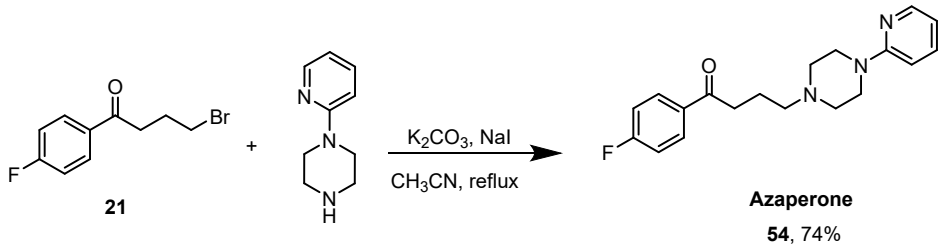
In a dry 100 mL round-bottom flask was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (5 mmol), 1-iodopyrrolidine-2,5-dione (7.5 mmol) in 20 mL H_2O under air atmosphere. The resulting solution was stirred for 12 h at room temperature under 100W Blue lights. On completion, the resulting solution was diluted with DCM (30 mL). Then, poured into an extraction funnel, the organic phase was washed with brine (1 x 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. Purification by flash column chromatography with PE/EA (100/1) as eluent gave the compound **2** as white solid (0.662 g, 61% yield)

Figure S3. 100 W blue LED light setup for gram-scale reaction.

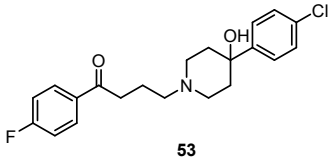
Synthesis of drug[6]



In a dry 100 mL round-bottom flask were added 4-bromo-1-(4-fluorophenyl) butan-1-one **20** (1 mmol, 1.0 equiv.), 4-(4-chlorophenyl) piperidin-4-ol (1.5 mmol, 1.5 equiv.), NaI (15 mg, 0.1 mmol, 0.1 equiv), K_2CO_3 (207 mg, 1.5 mmol, 1.5 equiv.), and anhydrous MeCN (20 mL) in an N_2 glovebox. The vial was sealed and transferred out of glovebox. The reaction mixture was reflux for 4 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the desired product haloperidol **51** (271 mg, 72%) (eluent: PE/EA = 1/1): yellow solid.



In a dry 100 mL round-bottom flask were added 4-bromo-1-(4-fluorophenyl) butan-1-one **20** (1 mmol, 1.0 equiv.), 1-(pyridin-2-yl) piperazine (1.5 mmol, 1.5 equiv.), NaI (15 mg, 0.1 mmol, 0.1 equiv), K_2CO_3 (207 mg, 1.5 mmol, 1.5 equiv.), and anhydrous MeCN (20 mL) in an N_2 glovebox. The vial was sealed and transferred out of glovebox. The reaction mixture was reflux for 4 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the desired product azaperone **52** (242 mg, 74%) (eluent: PE/EA = 1/1): yellow solid.

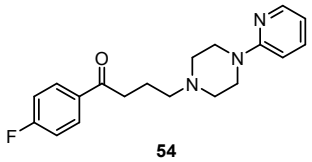


^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.43 – 7.37 (m, 2H), 7.34 – 7.29 (m, 2H), 7.19 – 7.11 (m, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.85 – 2.75 (m, 2H), 2.54 – 2.38 (m, 4H), 2.07 – 1.95 (m, 4H), 1.72 – 1.65 (m, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.39, 165.63 (d, *J* = 254.5 Hz), 146.94, 133.68 (d, *J* = 3.0 Hz), 132.73, 130.69 (d, *J* = 9.2 Hz), 128.37, 126.11, 115.62 (d, *J* = 21.9 Hz), 71.08, 57.85, 49.33, 38.38, 36.26, 21.90.

^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.65.

(Known compound: *ACS Catal.* **2020**, 10, 7543).



54

Azaperone

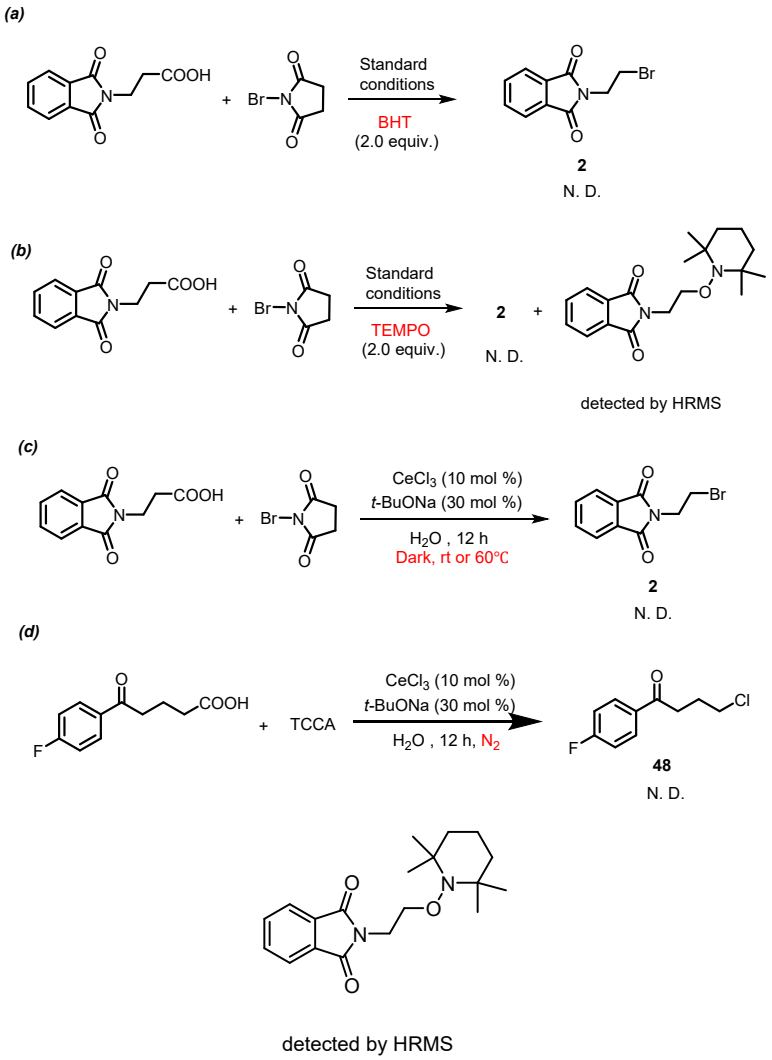
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.17 (dd, *J* = 4.9, 1.9 Hz, 1H), 8.00 (dd, *J* = 8.6, 5.4 Hz, 2H), 7.52 – 7.41 (m, 1H), 7.12 (t, *J* = 8.5 Hz, 2H), 6.68 – 6.55 (m, 2H), 3.51 (t, *J* = 5.0 Hz, 4H), 3.01 (t, *J* = 7.0 Hz, 2H), 2.57 (t, *J* = 5.0 Hz, 4H), 2.48 (t, *J* = 7.1 Hz, 2H), 2.00 (p, *J* = 7.0 Hz, 2H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 198.39, 165.66 (d, *J* = 254.3 Hz), 159.49, 147.97, 137.44, 130.67 (d, *J* = 9.2 Hz), 115.63 (d, *J* = 21.8 Hz), 113.31, 107.06, 57.70, 52.89, 45.06, 36.13, 21.42.

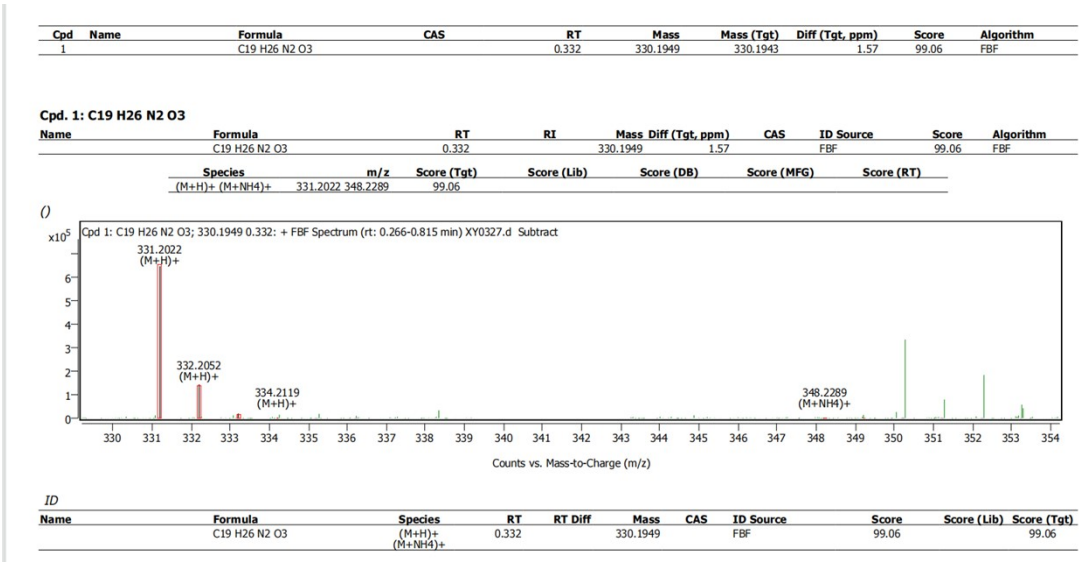
^{19}F NMR (376 MHz, Chloroform-*d*) δ -105.58.

(Known compound: *J. Org. Chem.* **2019**, 84, 15315).

VII. Control experiments



The reaction was completely inhibited by free radical inhibitors, and the radical adducts was detected by HRMS ($[M+H]^+$=331.2022)



Cpd	Name	Formula	CAS	RT	Mass	Mass (Tgt)	Diff (Tgt, ppm)	Score	Algorithm
1		C19 H26 N2 O3		0.332	330.1949	330.1943	1.57	99.06	FBF

Cpd. 1: C19 H26 N2 O3

Name	Formula	RT	RI	Mass	Diff (Tgt, ppm)	CAS	ID Source	Score	Algorithm
	C19 H26 N2 O3	0.332		330.1949	1.57		FBF	99.06	FBF

Species	m/z	Score (Tgt)	Score (Lib)	Score (DB)	Score (MFG)	Score (RT)
(M+H)+ (M+NH4)+	331.2022 348.2289	99.06				

Name	Formula	Species	RT	RT Diff	Mass	CAS	ID Source	Score	Score (Lib)	Score (Tgt)
	C19 H26 N2 O3	(M+H)+ (M+NH4)+	0.332		330.1949		FBF	99.06		99.06

Figure S4. HRMS data of TEMPO adduct

VIII. UV-visible absorption Spectra

UV-Vis experiments were performed to analyse the ligand-to-metal-charge-transfer (LMCT) process between cerium catalyst and alkyl carboxylic acids. For verification, $(n\text{-}Bu_4N)_2Ce^{IV}Cl_6$ was chosen as a Ce(IV) source accoding to one reported by Zuo et al.[7] In order to ensure the solubility, acetonitrile (similar yield to the model reaction) was selected as the solvent.

Preparation of a stock solution (solution A): In a glass vial equipped with a teflon-coated stirring bar and a septum, $(n\text{-}Bu_4N)_2Ce^{IV}Cl_6$ (25.1 mg, 0.03 mmol) were dissolved in MeCN (3 mL). Dilute 66 μL of the above solution to 6 mL to obtain solution A.

Preparation of a stock solution (solution B): In a glass vial equipped with a teflon-coated stirring bar and a septum, $(n\text{-}Bu_4N)_2Ce^{IV}Cl_6$ (25.1 mg, 0.03 mmol) and 1-adamantane carboxylic acid (54.1 mg, 0.3 mmol) were dissolved in MeCN (3 mL). Dilute 66 μL of the above solution to 6 mL to obtain solution B.

UV-Visible absorption spectra of solution A

UV-Vis spectra were recorded after irradiation the cuvette solution A with 100 W blue LED light.

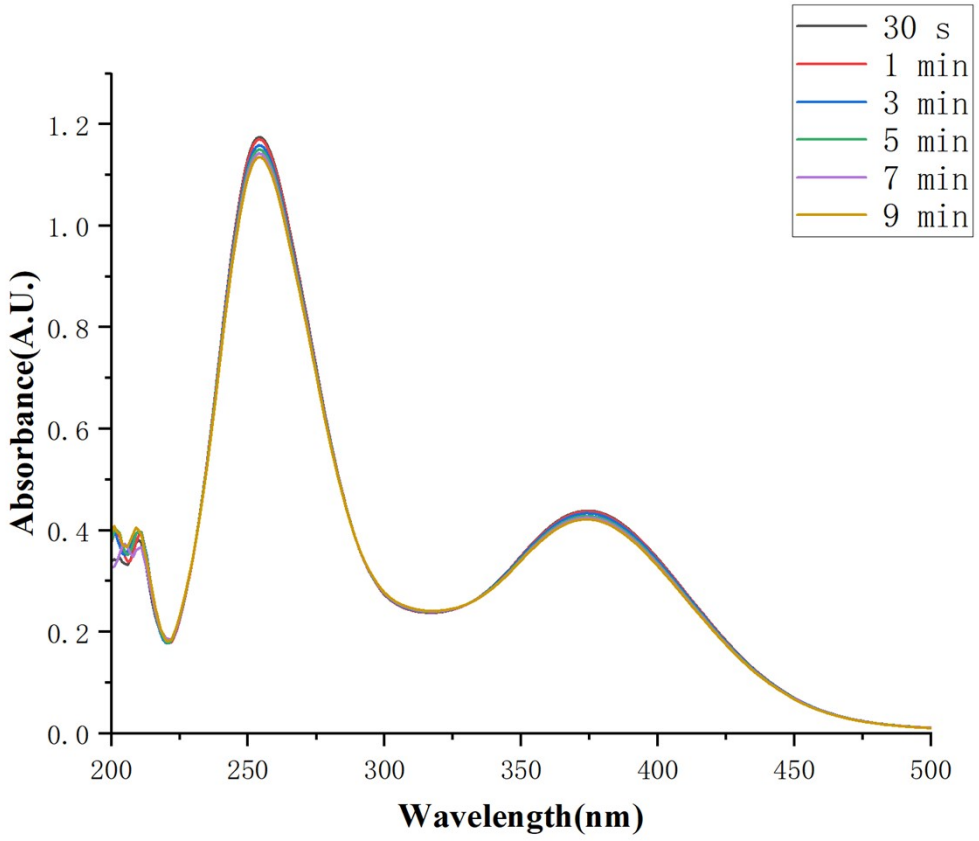


Figure S5. UV-Visible spectra of a solution of $(n\text{-}Bu_4N)_2Ce^{IV}Cl_6$ without acid after irradiation with 100 W blue LED light

As show in Figure S5, in the absence of acid, Ce^{IV} ($\lambda_{max} \approx 380$ nm) absorbance hardly changed with the increase of irradiation time.

UV-Visible absorption spectra of solution B

UV-Vis spectra were recorded after irradiation the cuvette solution B with 100 W blue LED light.

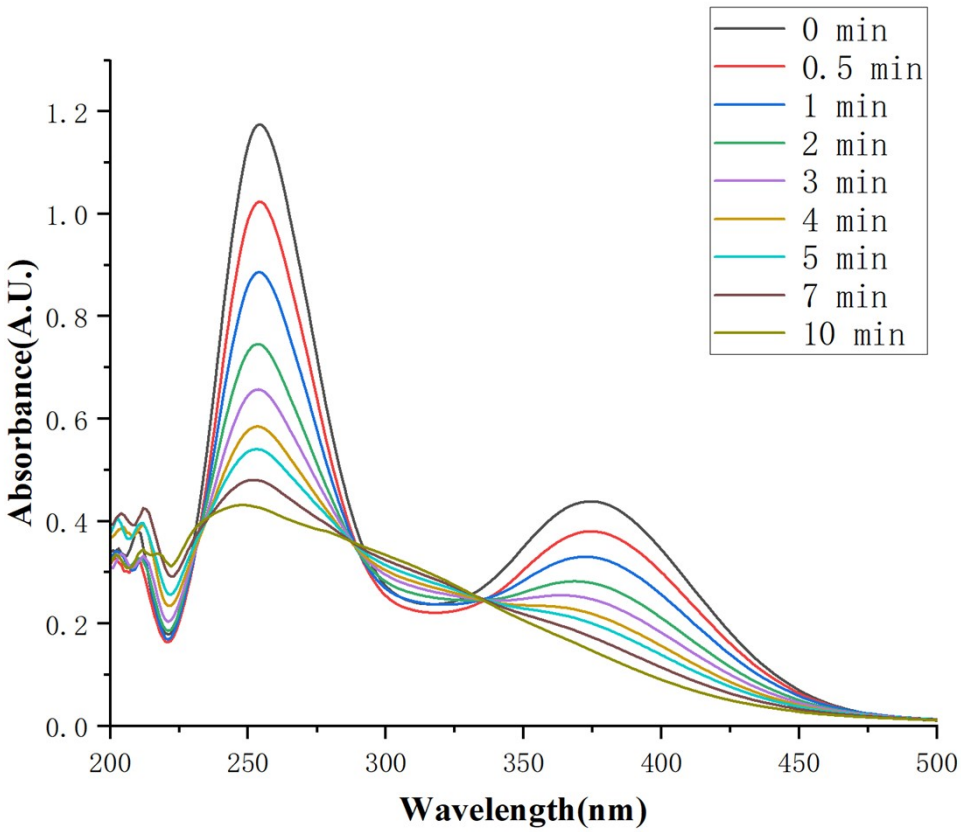


Figure S6. UV-Visible spectra of a solution of (n-$Bu_4N)_2Ce^{IV}Cl_6$ with acid after irradiation with 100 W blue LED light

When the 100 W blue LED was switched-on, the fast consumption of Ce^{IV} ($\lambda_{max} \approx 380$ nm) was observed and the absorbance of Ce^{III} ($\lambda_{max} \approx 330$ nm) gradually increases, which demostrated that in the presence of carboxylic acid, the Ce^{IV} was rapidly reduced to Ce^{III} after gradually increasing the illumination time.

In order to investigate the effect of the strong oxidant TCCA on the reaction, the following UV-VIS experiments were performed.

Preparation of a stock solution (solution C): In a glass vial equipped with a teflon-coated stirring bar and a septum, $CeCl_3$ (7.4 mg, 0.03 mmol) were dissolved in H_2O (3 mL). Dilute 66 μL of the above solution to 6 mL to obtain solution C.

Preparation of a stock solution (solution D): In a glass vial equipped with a teflon-coated stirring bar and a septum, TCCA (34.9 mg, 0.15 mmol) were dissolved in H_2O (3 mL). Dilute 66 μL of the above solution to 6 mL to obtain solution D.

Preparation of a stock solution (solution E): In a glass vial equipped with a teflon-coated stirring bar and a septum, $CeCl_3$ (7.4 mg, 0.03 mmol), TCCA (34.9mg, 0.15 mmol) were dissolved in H_2O (3 mL). The solution was stirred for 10 h at room temperature. Dilute 66 μL of the above solution to 6 mL to obtain solution E.

UV-Visible absorption spectra of solution C, solution D and solution E

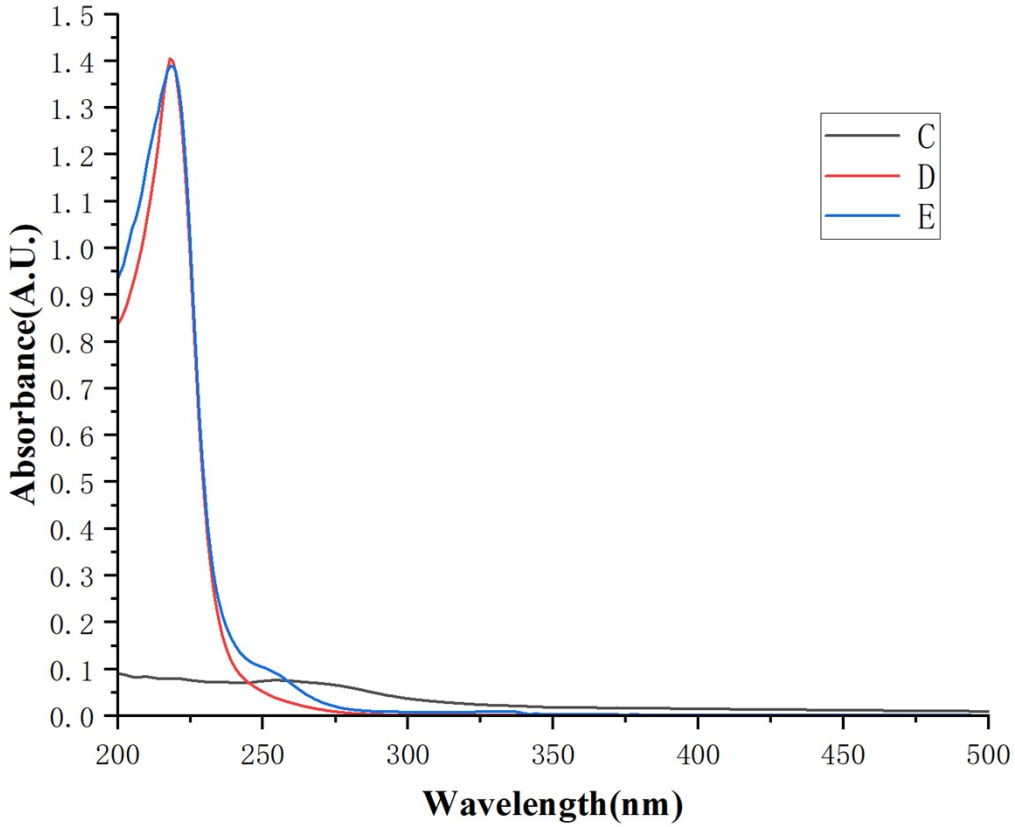


Figure S7. UV-Visible spectra of a solution C, solution D and solution E

As show in Figure S7, no absorption of Ce^{IV} ($\lambda_{max} \approx 380$ nm) was observed at 380 nm. Thus, it could be speculated that Ce^{III} cannot be oxidized to Ce^{IV} by TCCA.

IX. Electron paramagnetic resonance (EPR) experiment

In order to determine the active species of oxygen involved in the present reaction, 5,5-dimethylpyrroline-N-oxide (DMPO) were employed to capture $O2^{-}\cdot$ (g = 2.0069).

To a dried 8 mL vial was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (0.3 mmol), 1-bromopyrrolidine-2,5-dione (NBS) (1.0-1.5 equiv.), $CeCl_3$ (10 mol %), *t*-BuONa (30 mol %), DMPO (5,5-dimethyl-1-pyrroline N-oxide, 15 μL) in 3 mL H_2O under air atmosphere. The resulting solution was stirred under 100 W blue light for 30 min (25 ℃). After that, the solution sample was taken out into a small tube and analyzed by EPR. As show in Figure S6, there was a strong characteristic signal of $O_2^{-}\cdot$ adduct with DMPO when the DMPO was added into model reaction.

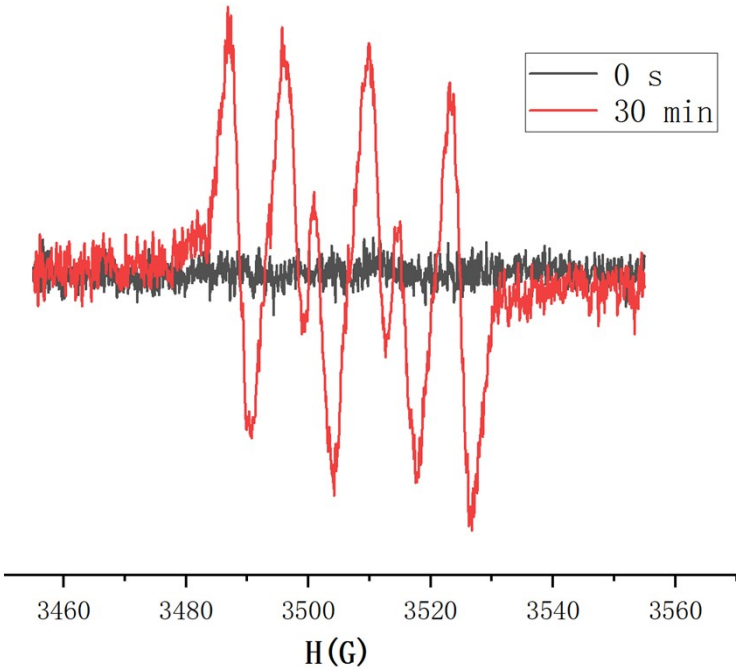


Figure S8 . Electron spin resonance (ESR) spectra of DMPO with $O_2^{-}\cdot$

X. KI-starch test for the detection of hydrogen peroxide (H_2O_2) in the reaction

It was anticipated that H_2O_2 may be one of the reasonable by-products of the photo-induced halodecarboxylation reaction, which was confirmed by KI/starch test.

To a dried 8 mL vial was added 3-(1,3-dioxoisoindolin-2-yl) propanoic acid (0.3 mmol), 1-bromopyrrolidine-2,5-dione (NBS) (1.0-1.5 equiv.), $CeCl_3$ (10 mol %), *t*-BuONa (30 mol %) in 3 mL H_2O under air atmosphere. The resulting solution was stirred under 100 W blue light for 12 h (25 ℃). After that, the KI-starch paper was immersed in the reaction solution and quickly turned into dark purple colour (Figure S7), which confirms the formation of H_2O_2.

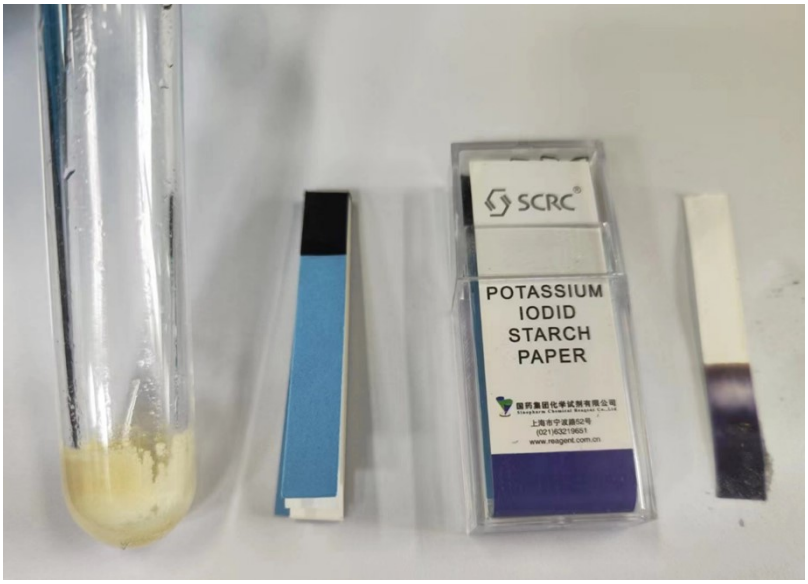


Figure S9 . Detection of hydrogen peroxide (H_2O_2) using KI-starch paper

Reference:

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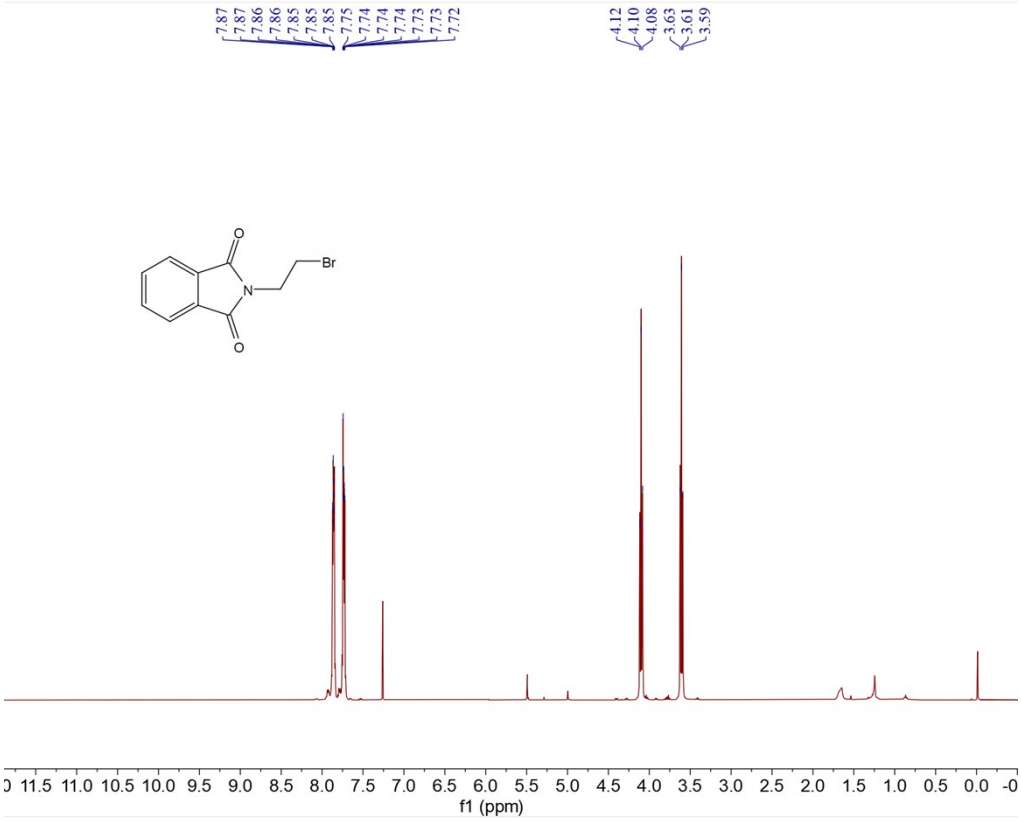
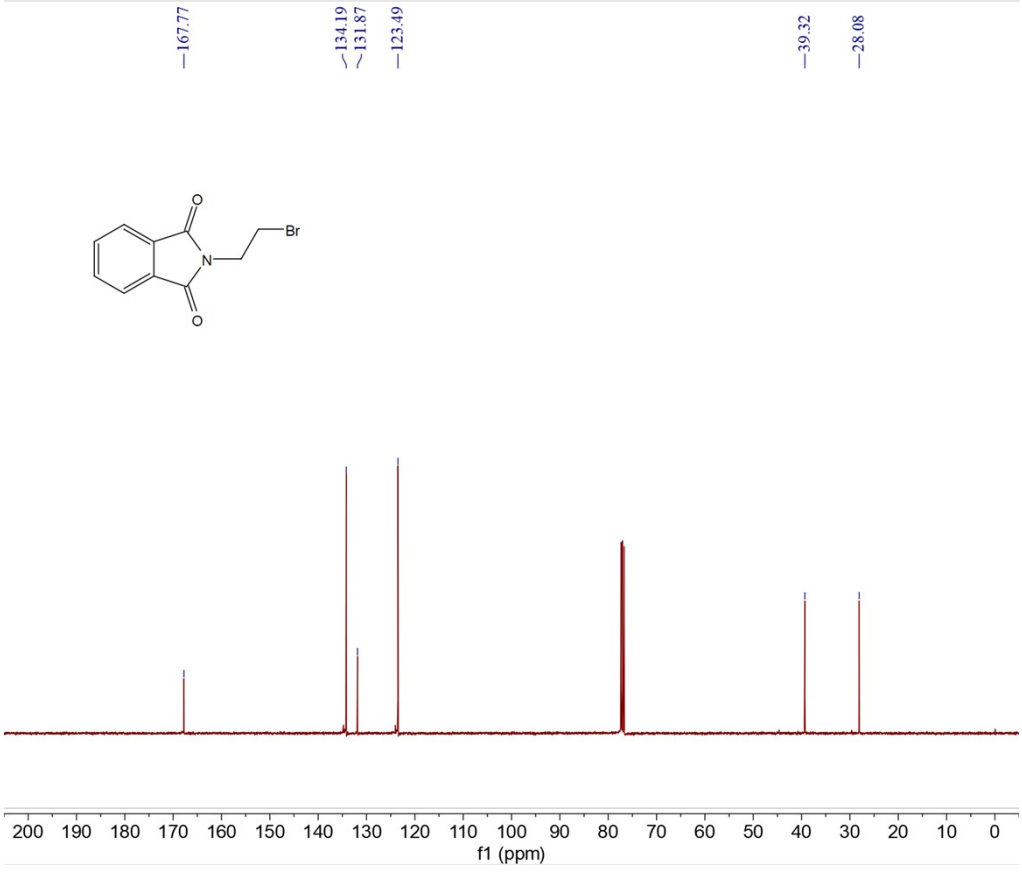
XI. Copied of NMR spectra

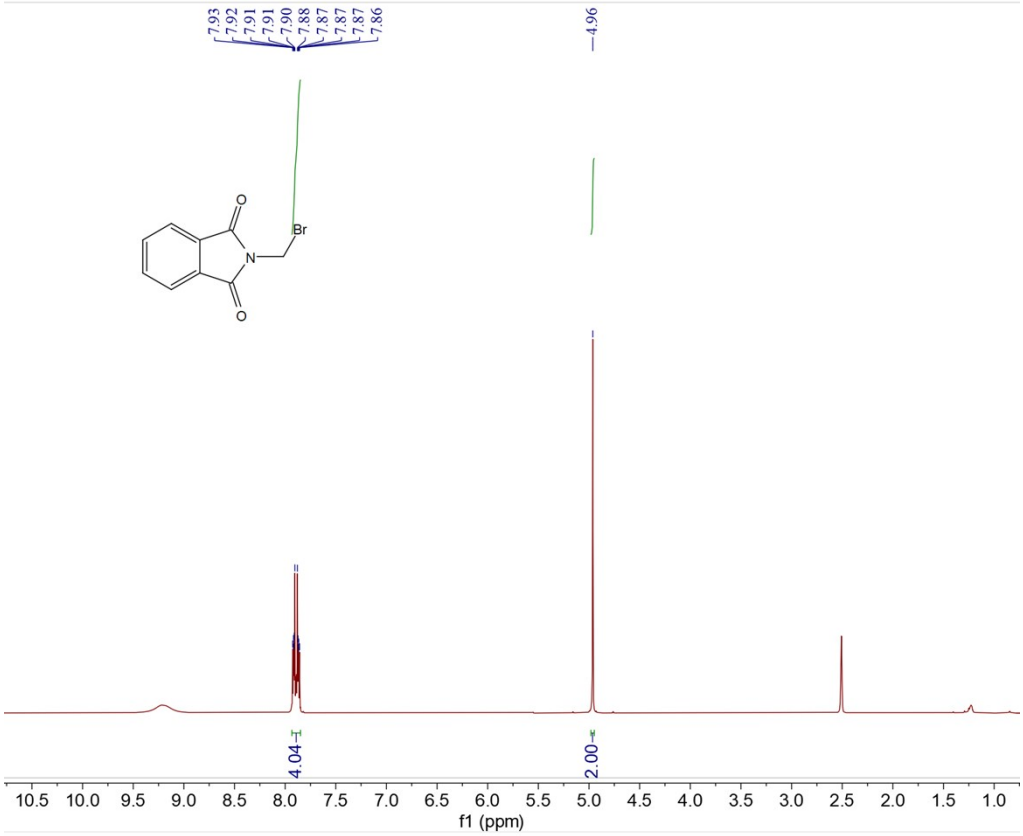
^{1}H NMR of compound **2**



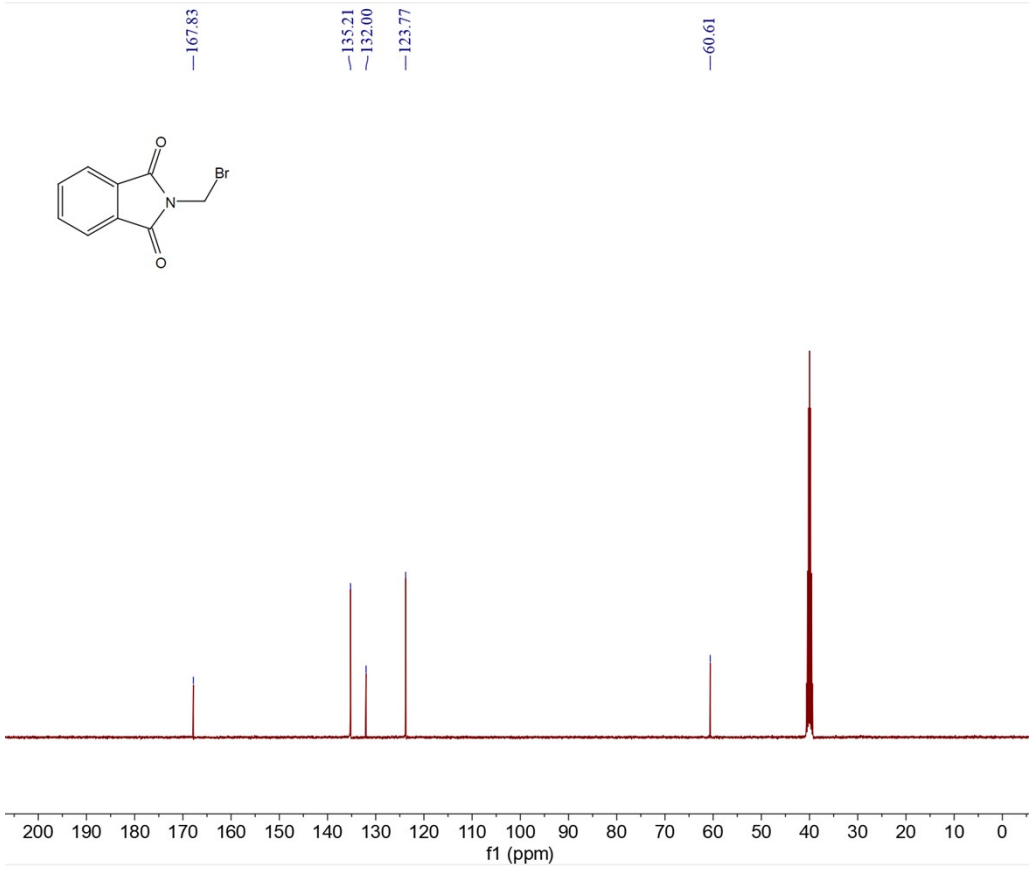
^{13}C NMR of compound **2**



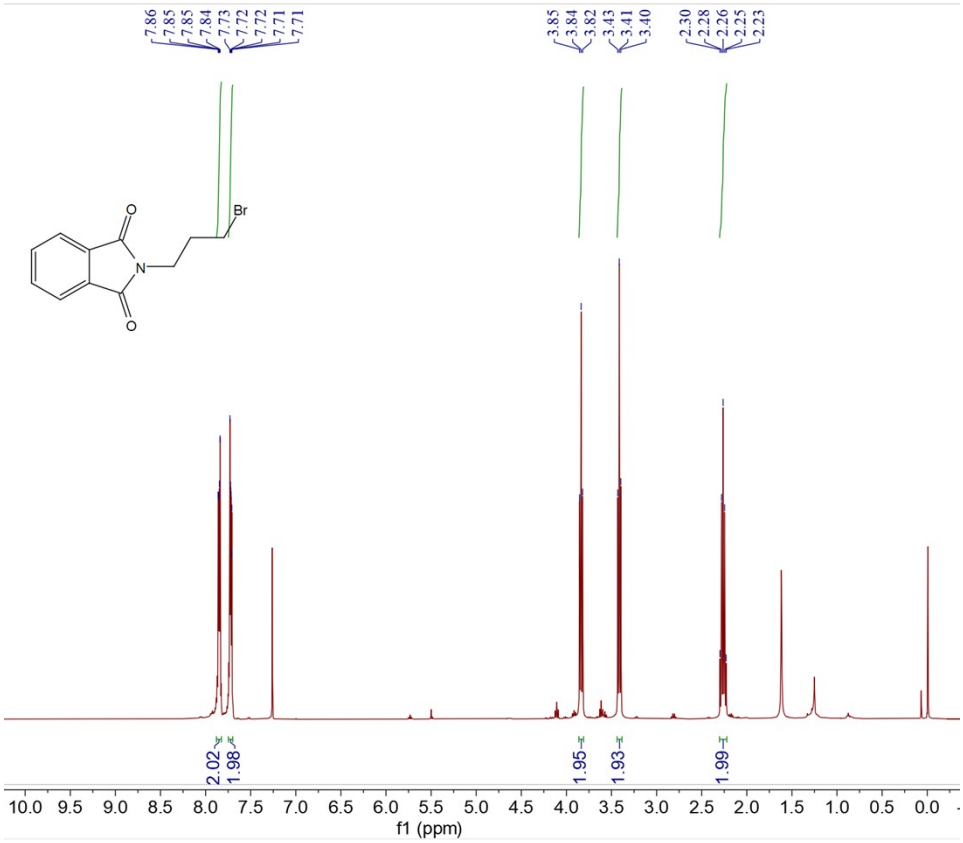
^{1}H NMR of compound **3**



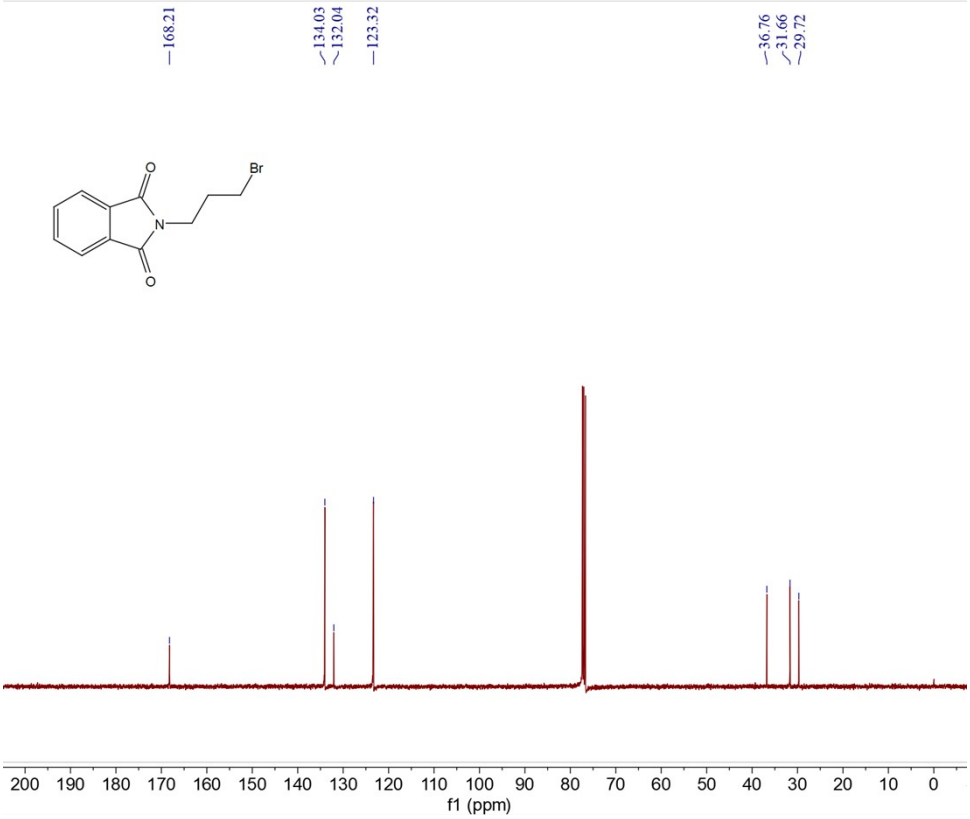
^{13}C NMR of compound **3**



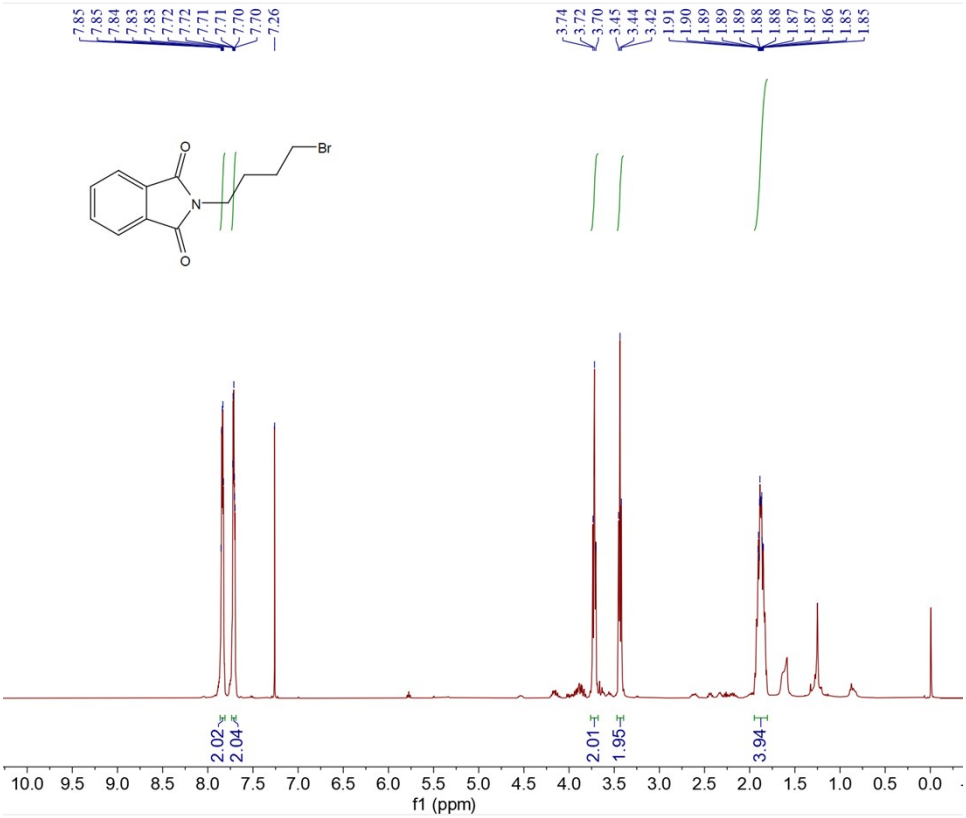
^{1}H NMR of compound **4**



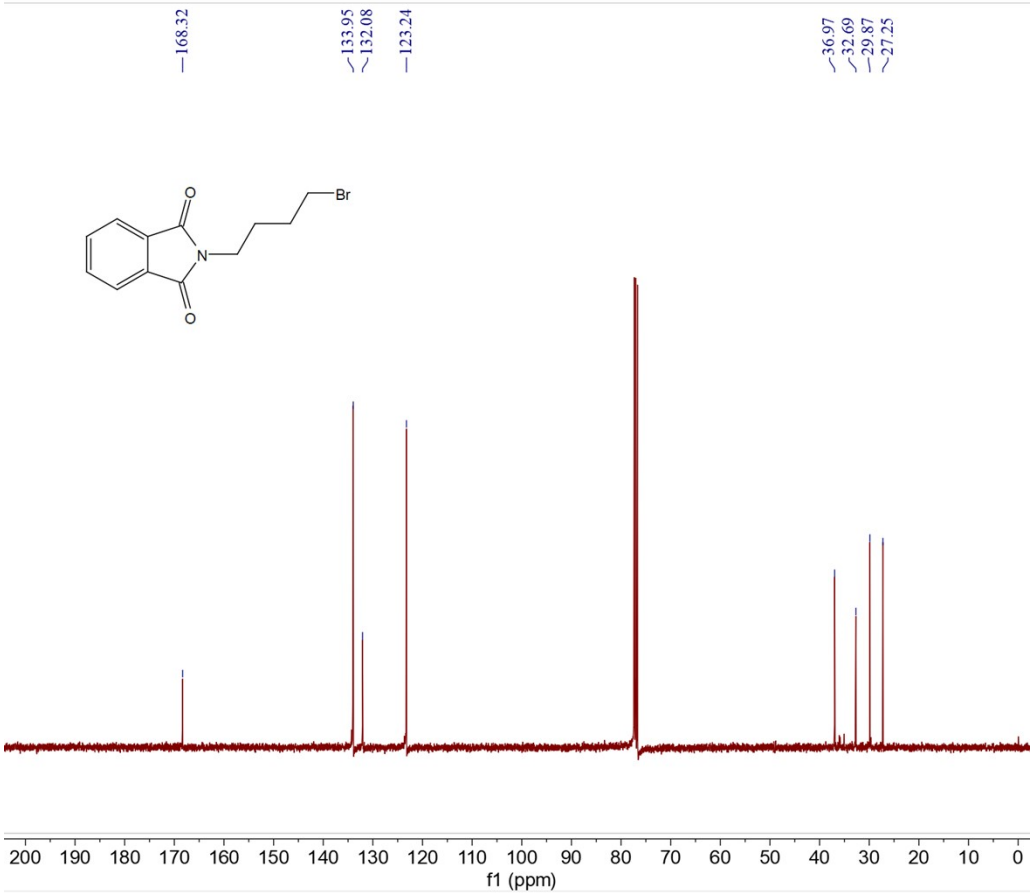
^{13}C NMR of compound **4**



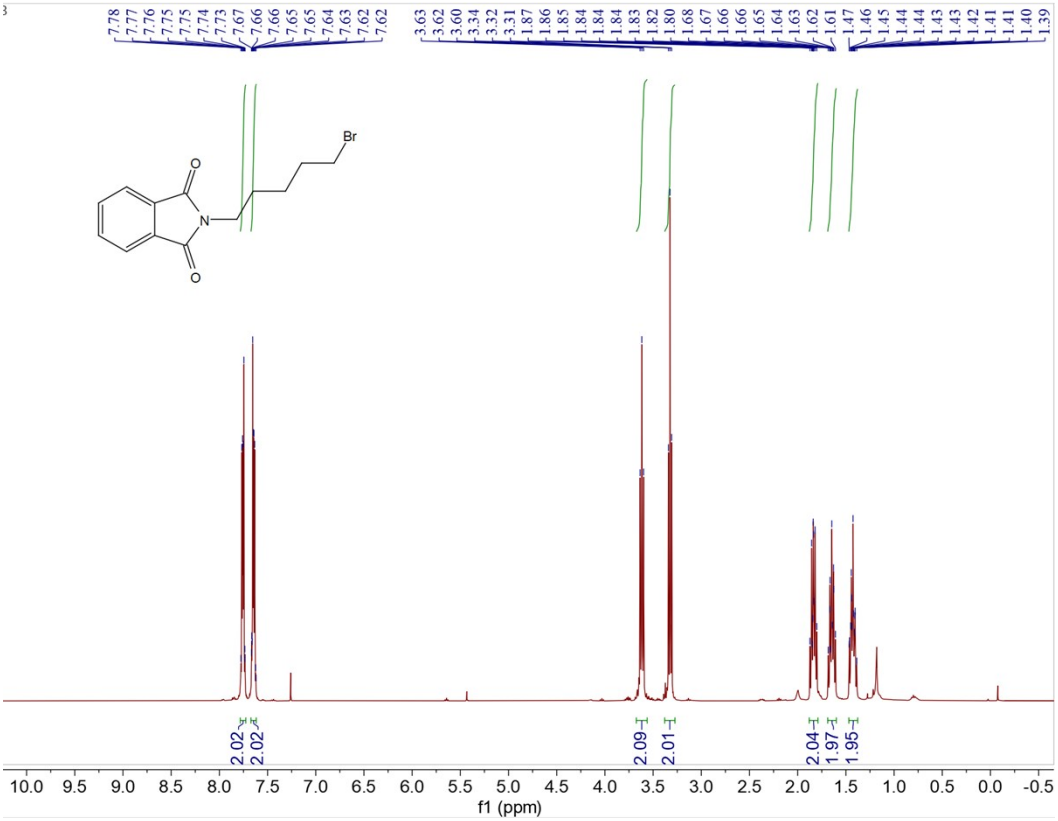
^{1}H NMR of compound **5**



^{13}C NMR of compound **5**



^{1}H NMR of compound **6**



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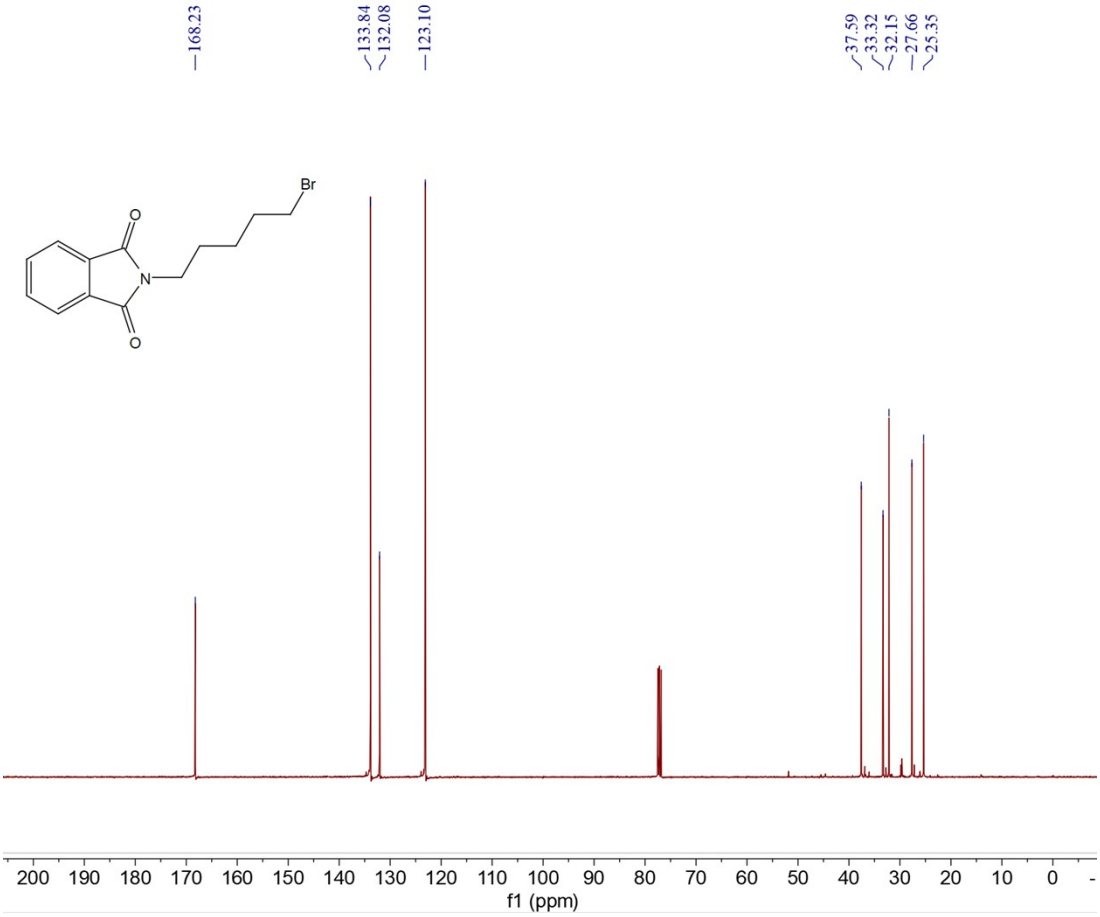

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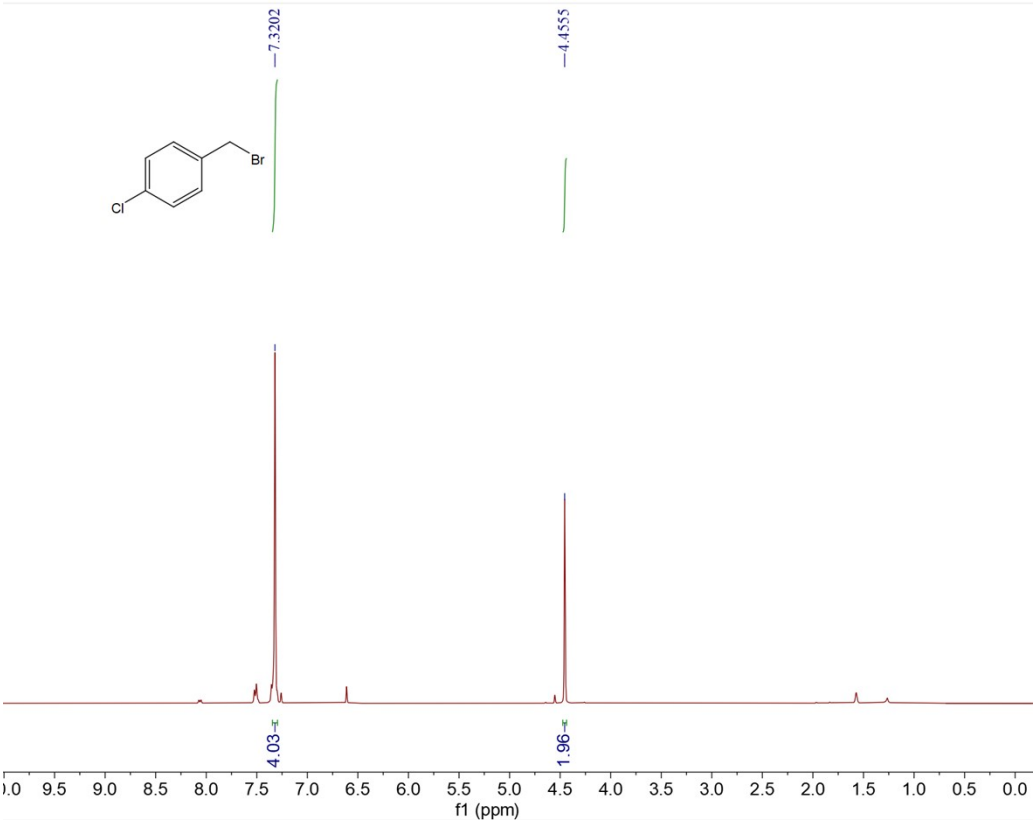

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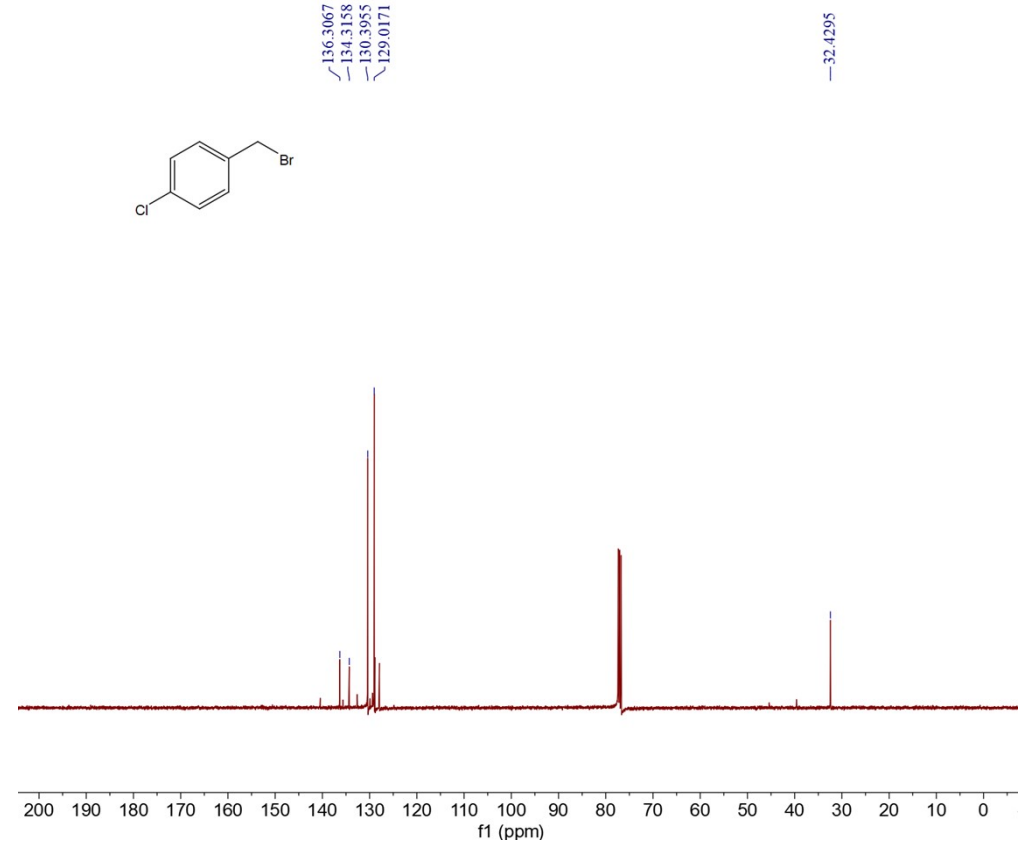
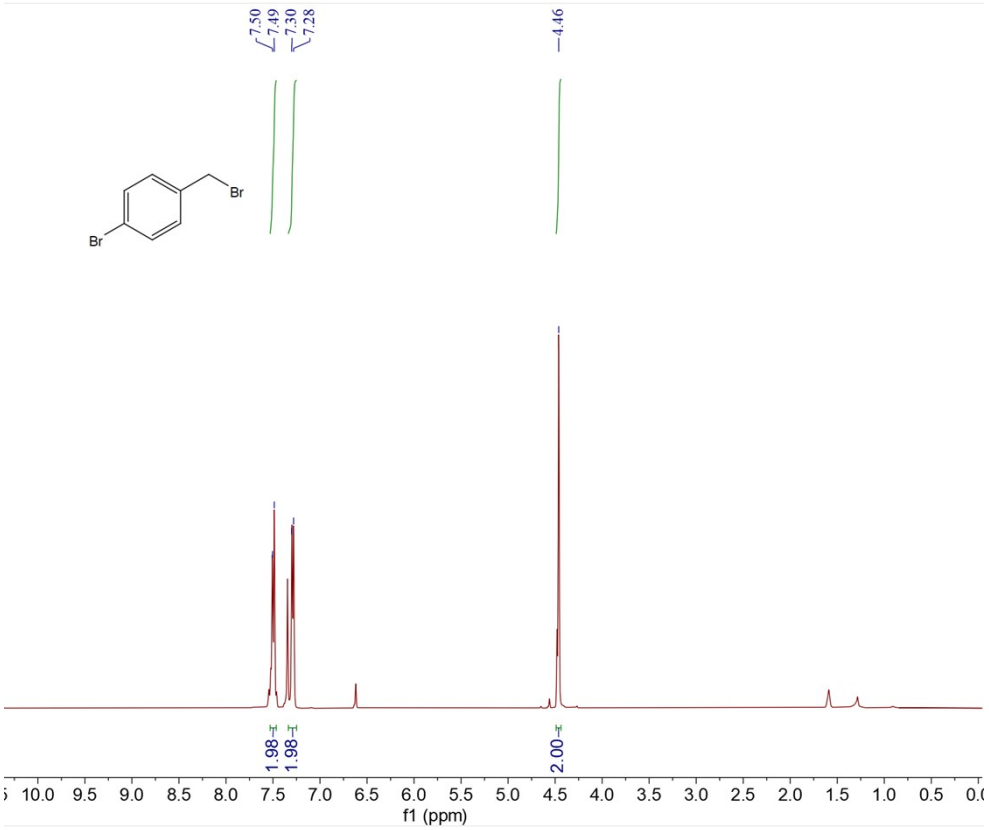


^{1}H NMR of compound **8**



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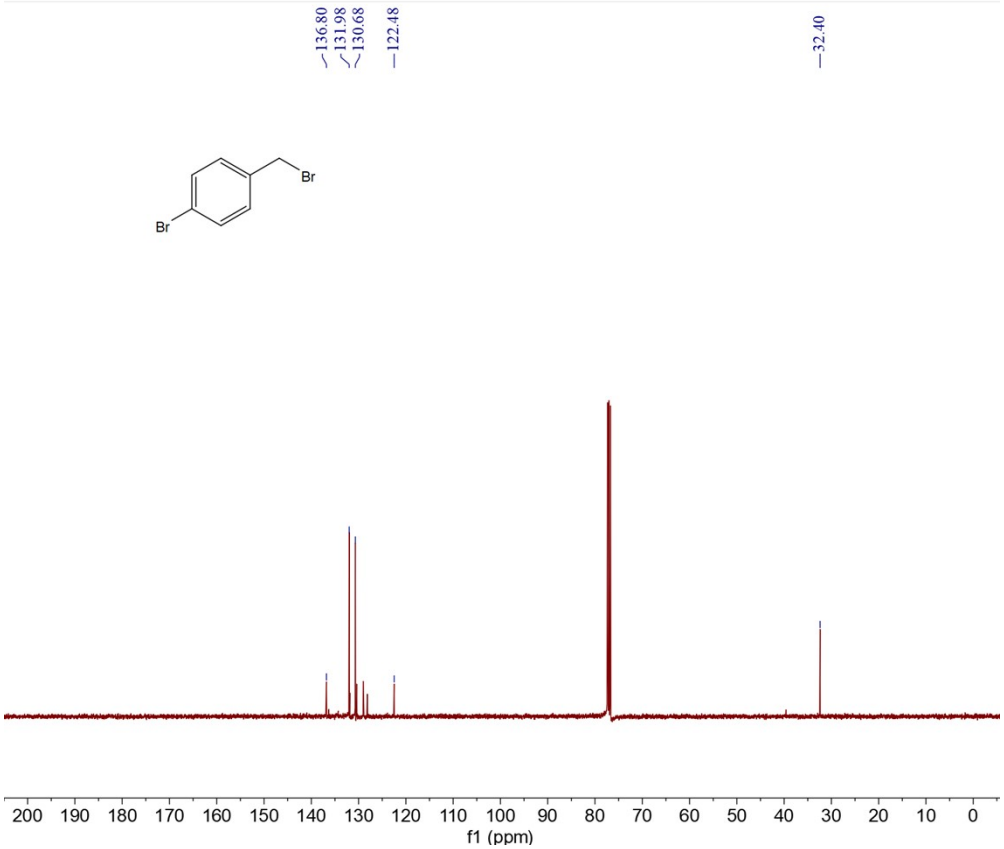

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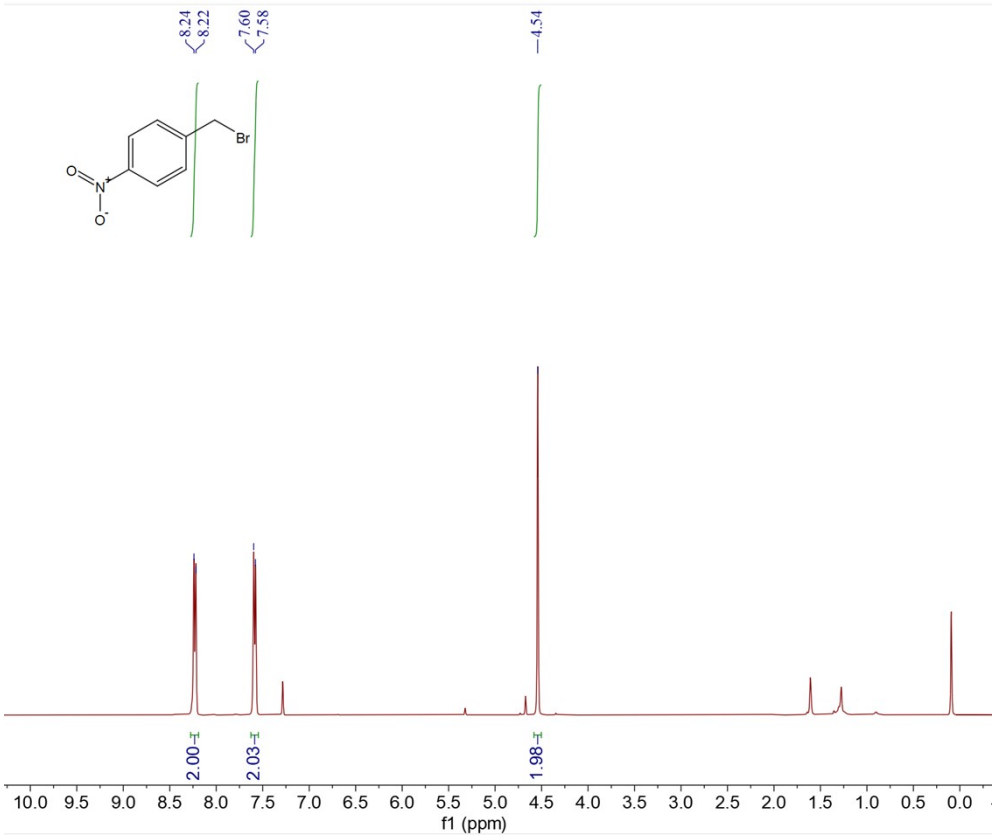

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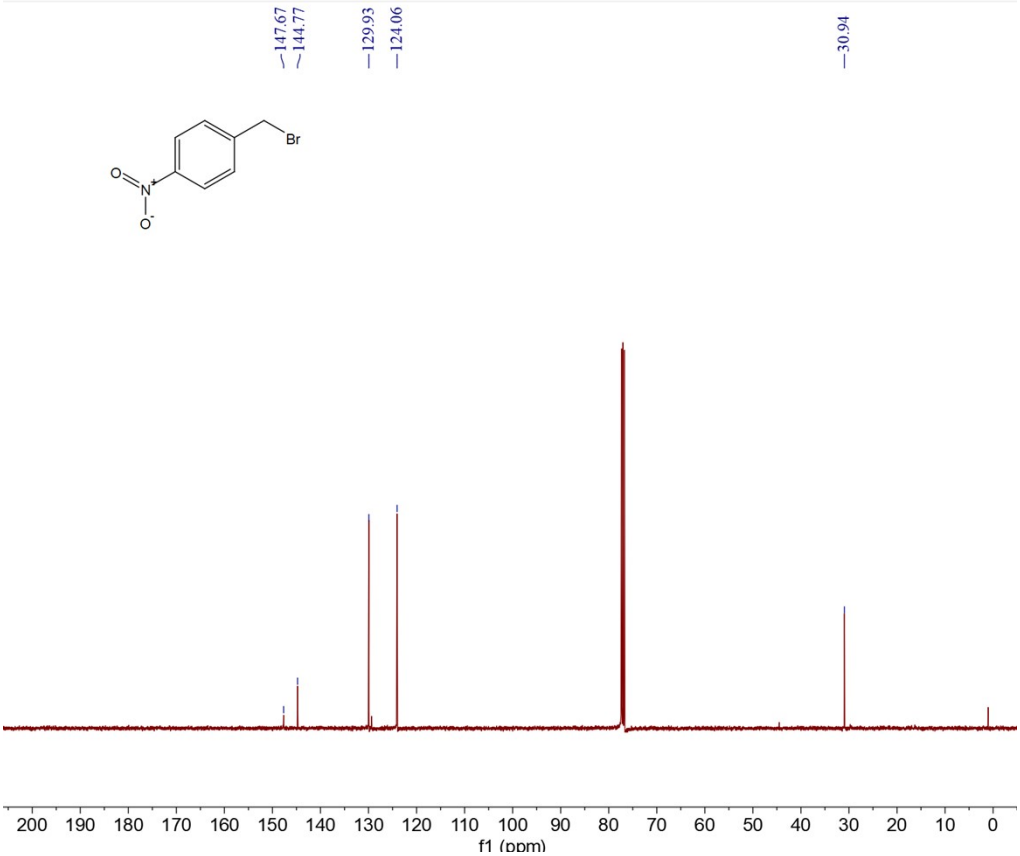

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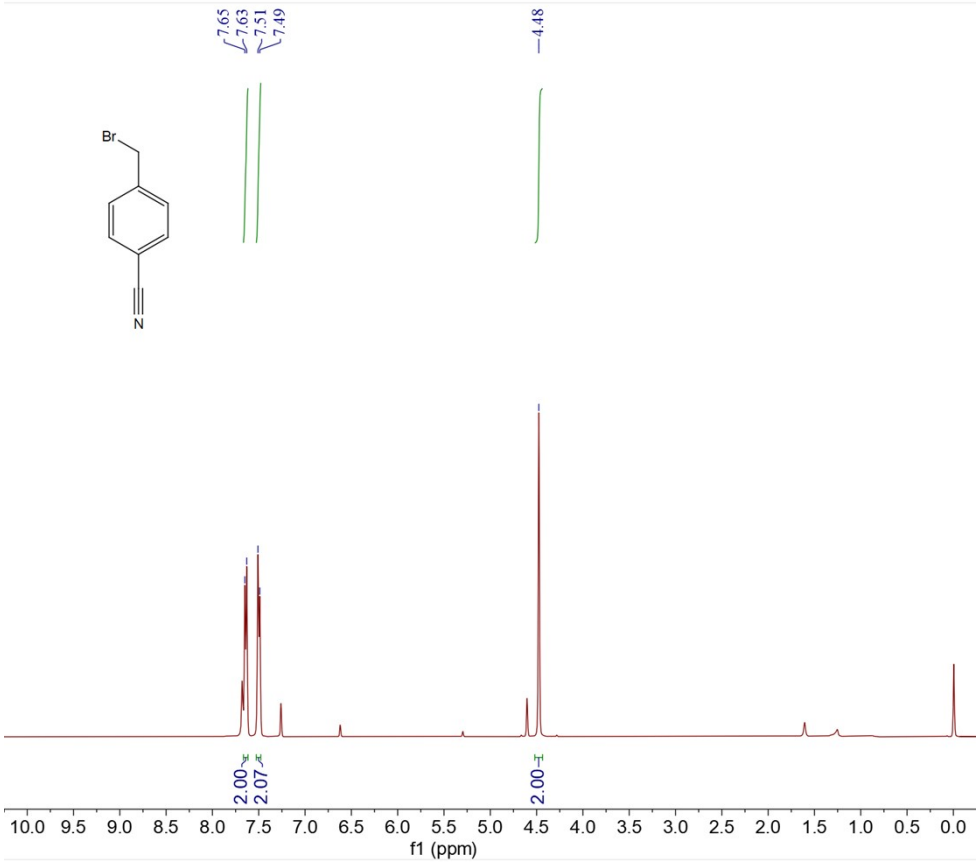

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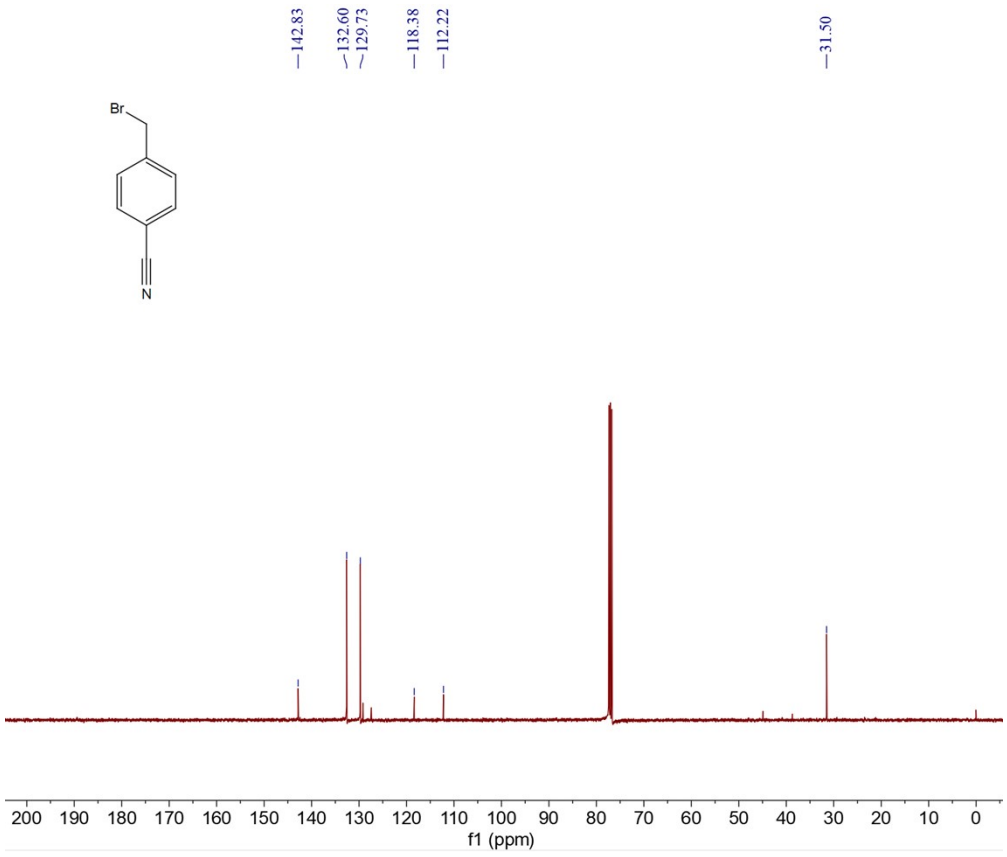

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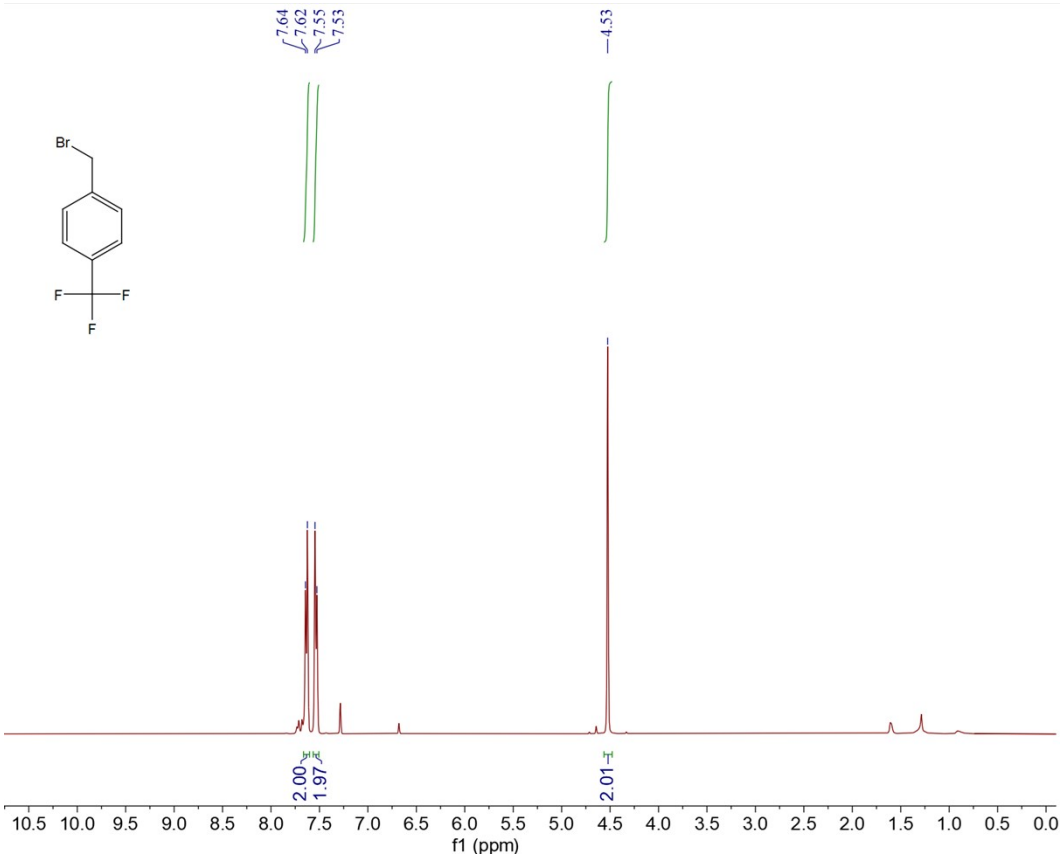

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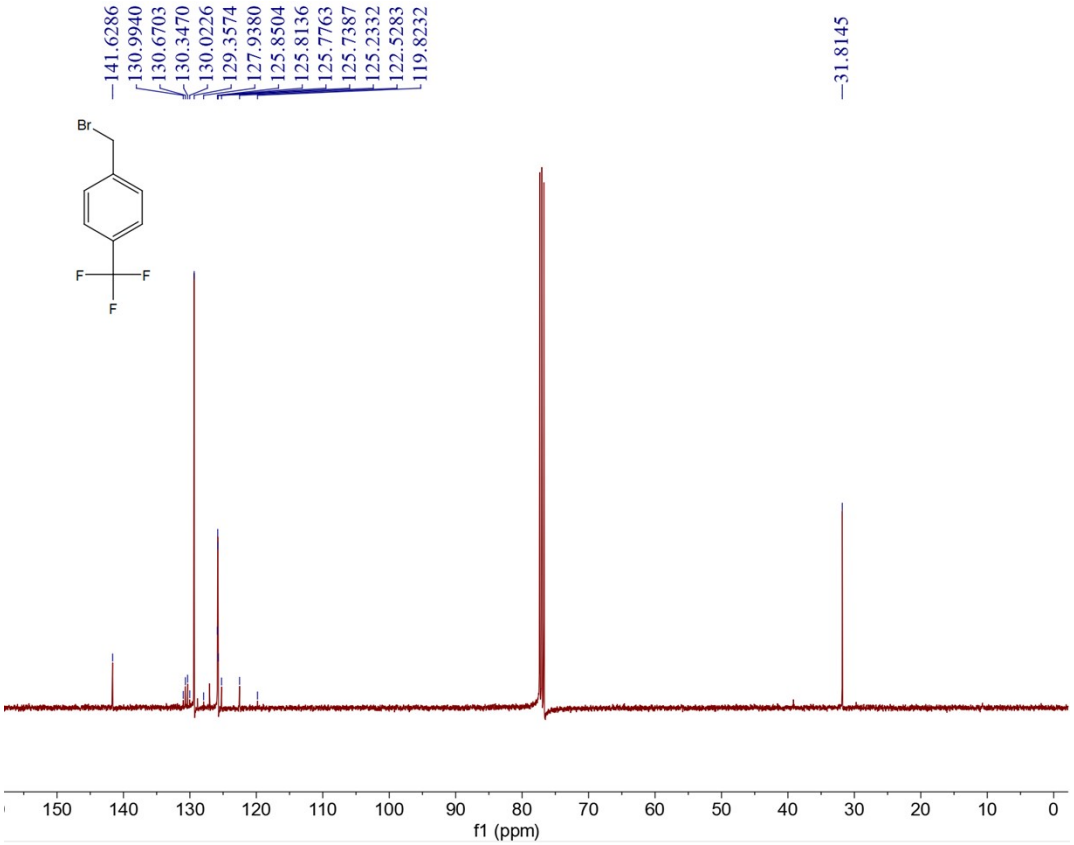

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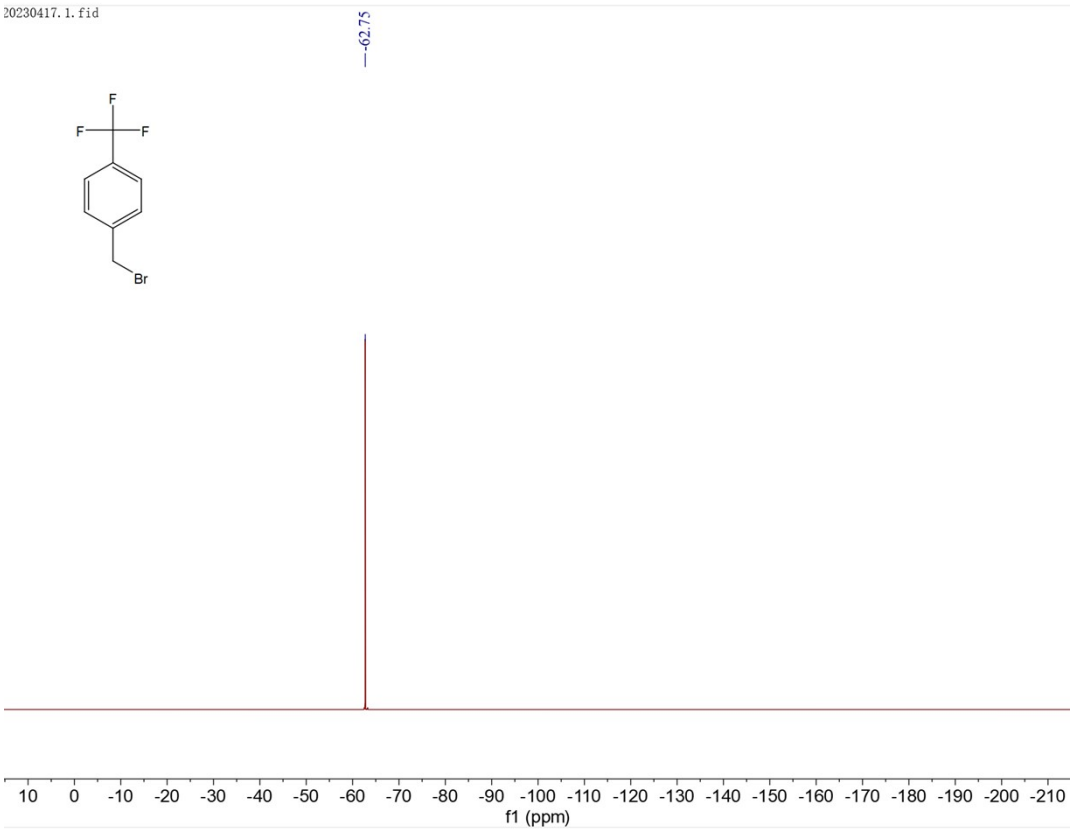

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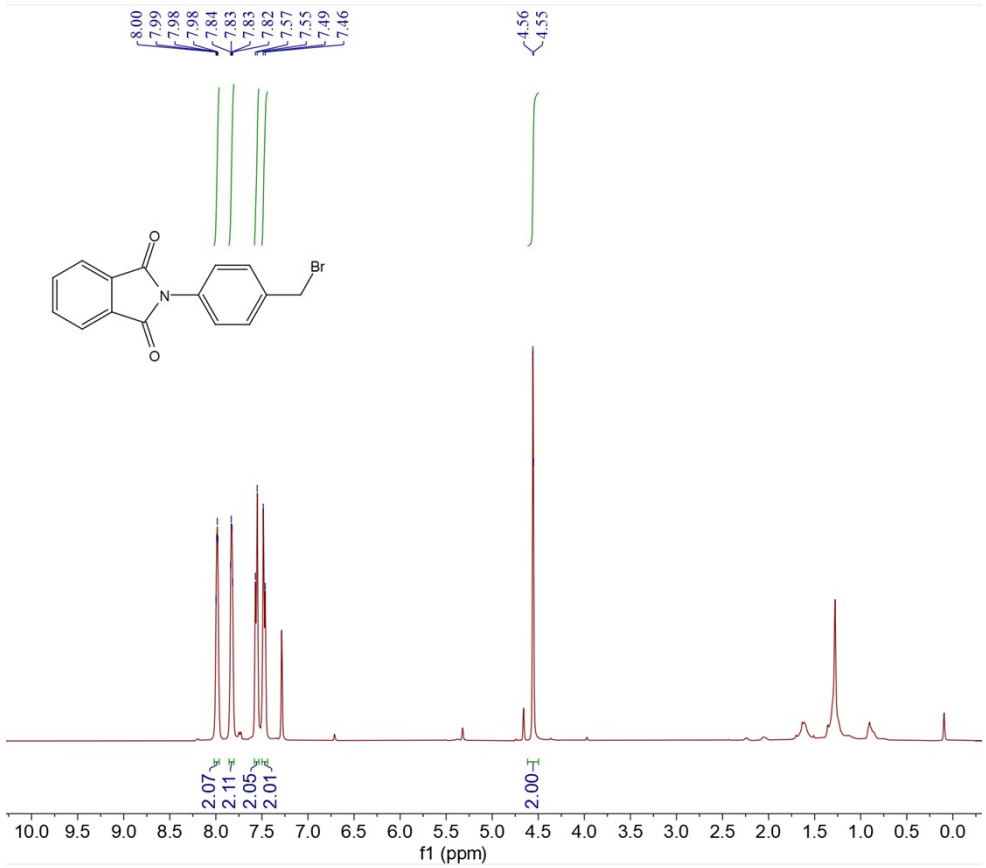

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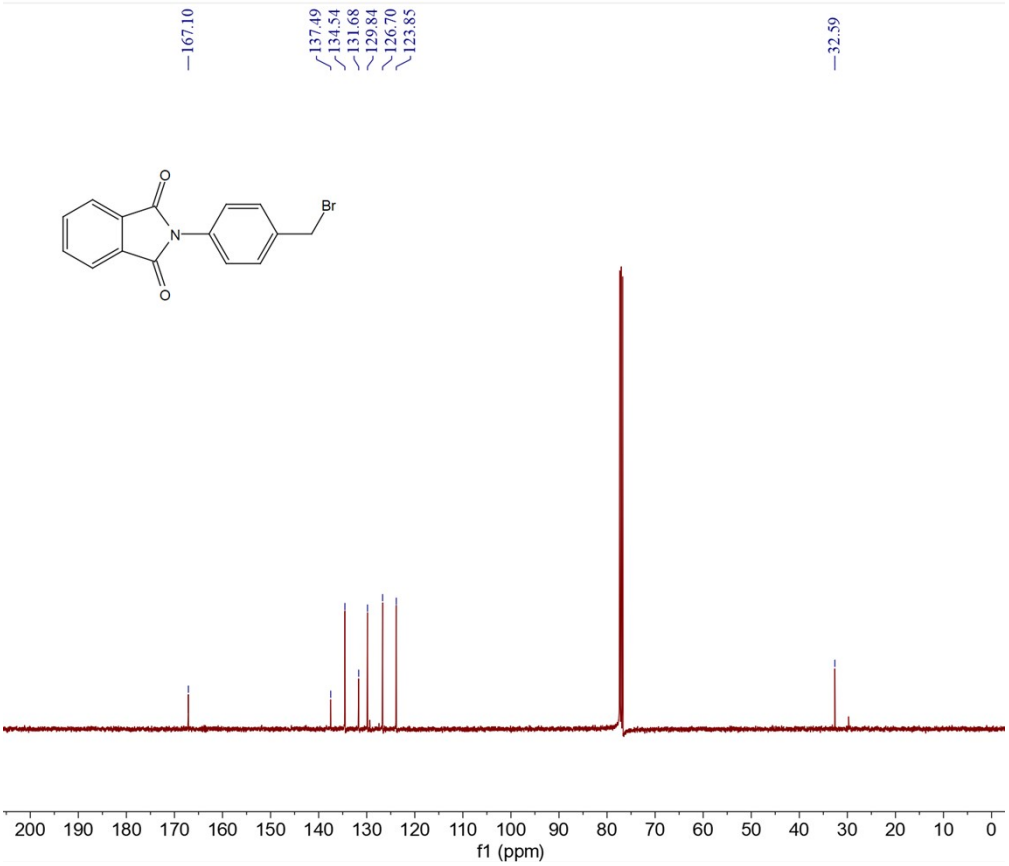

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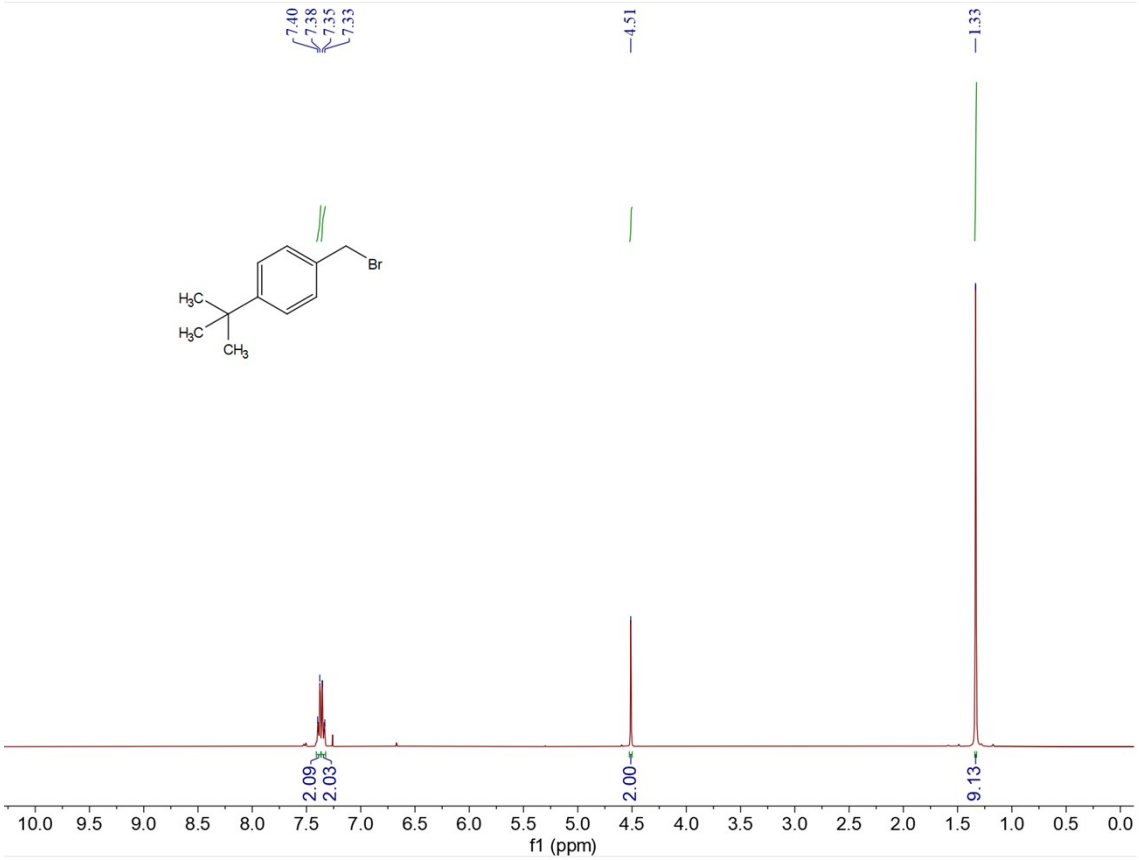

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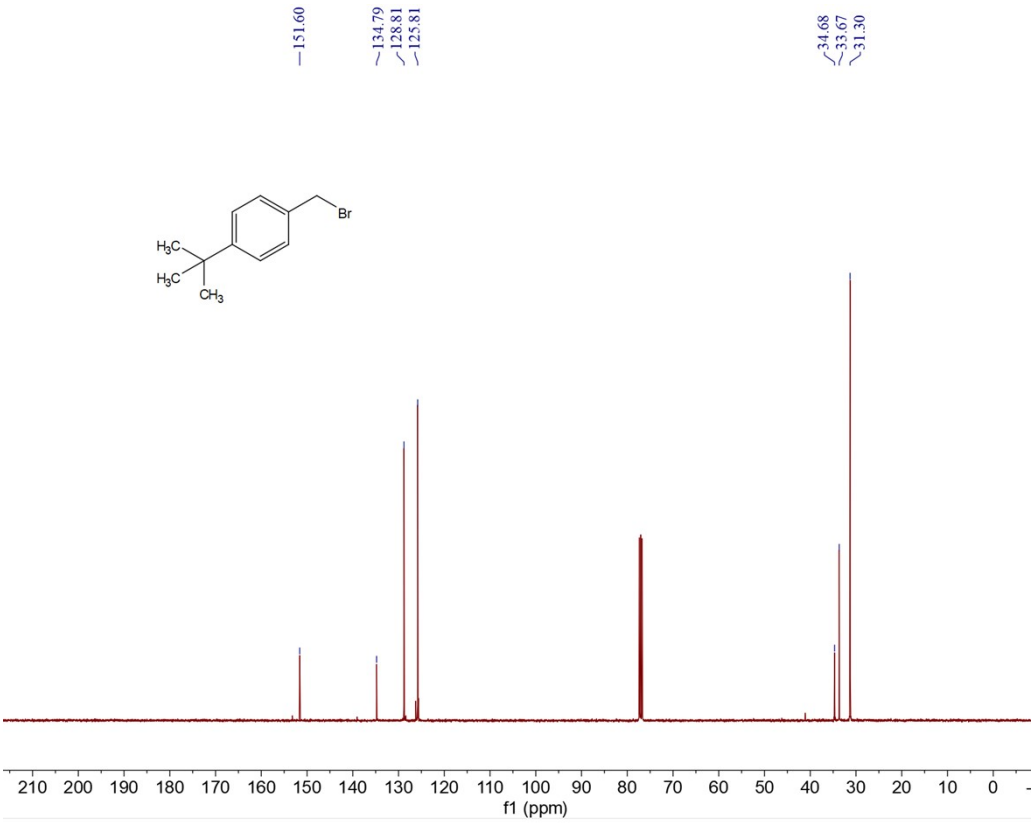

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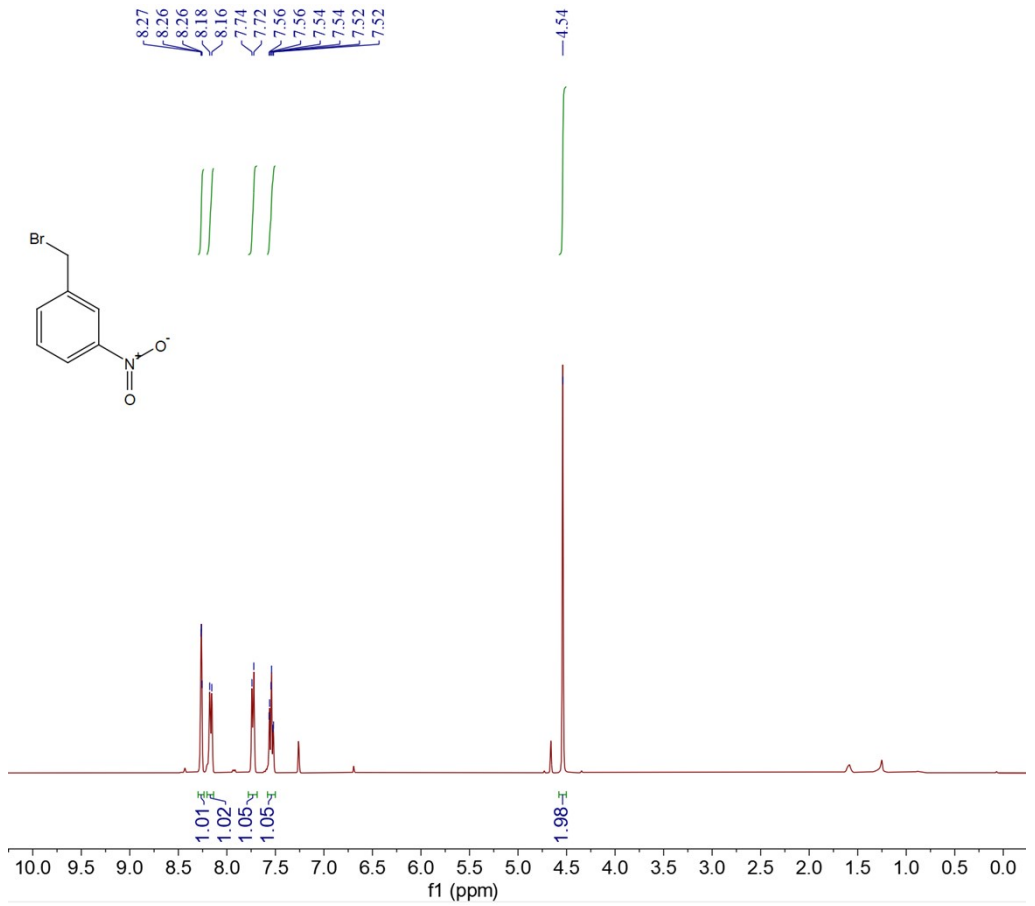

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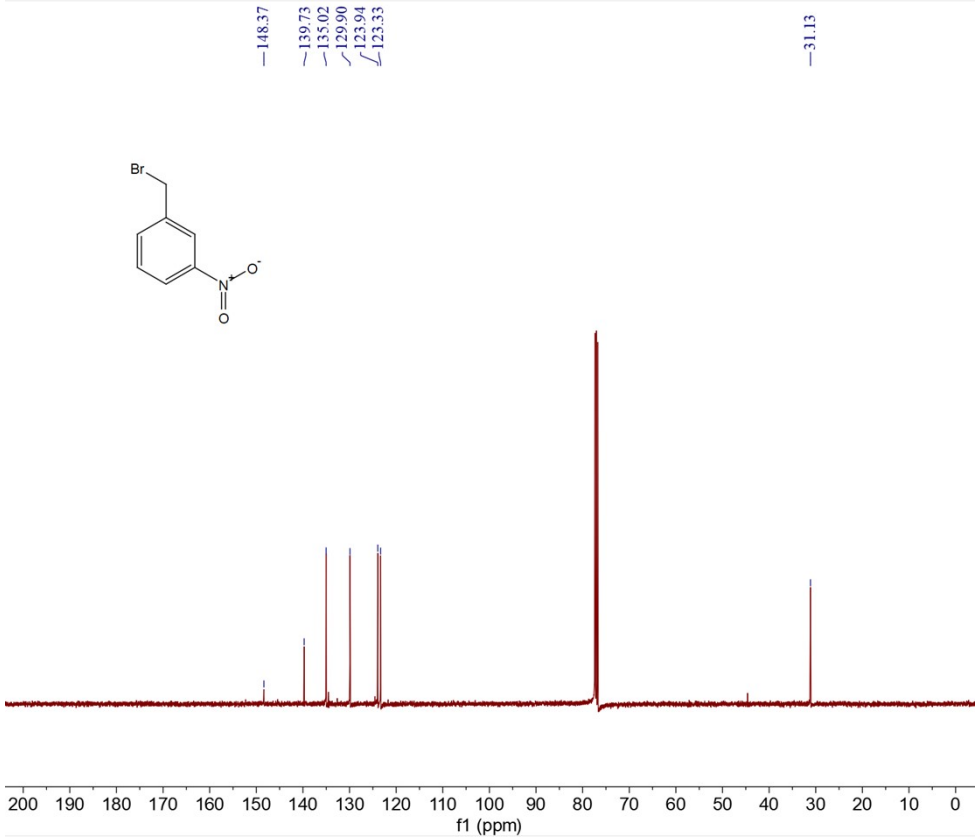

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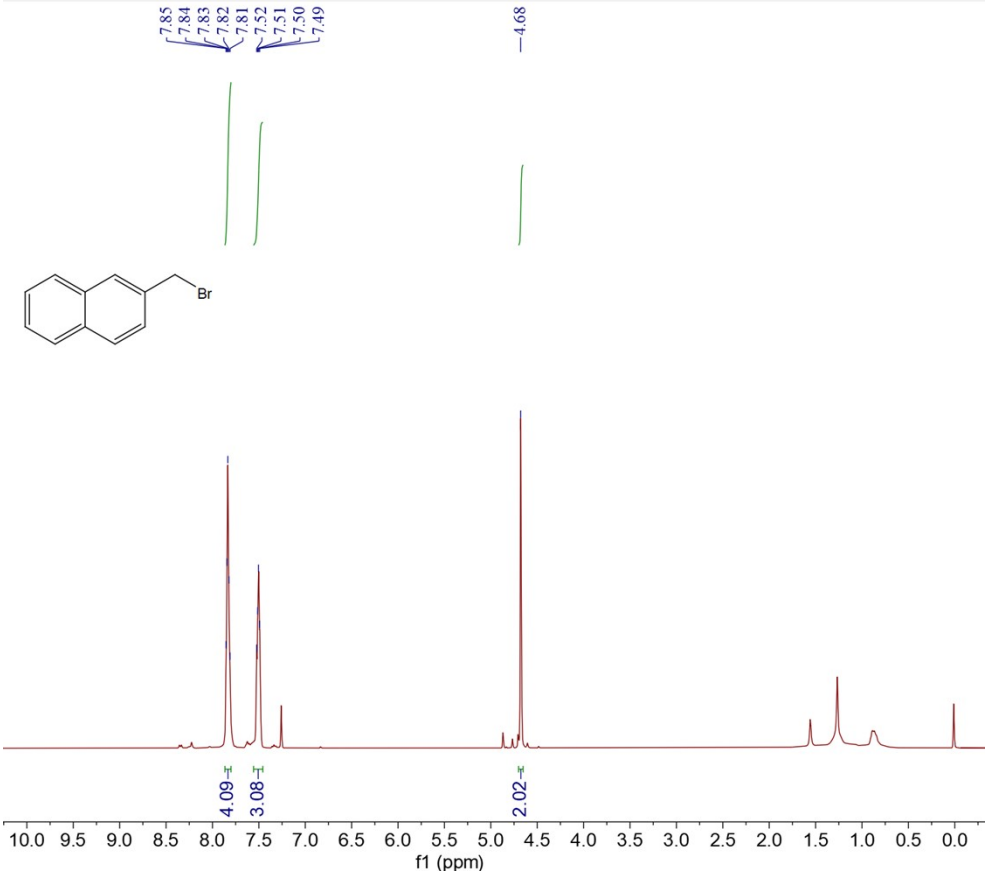

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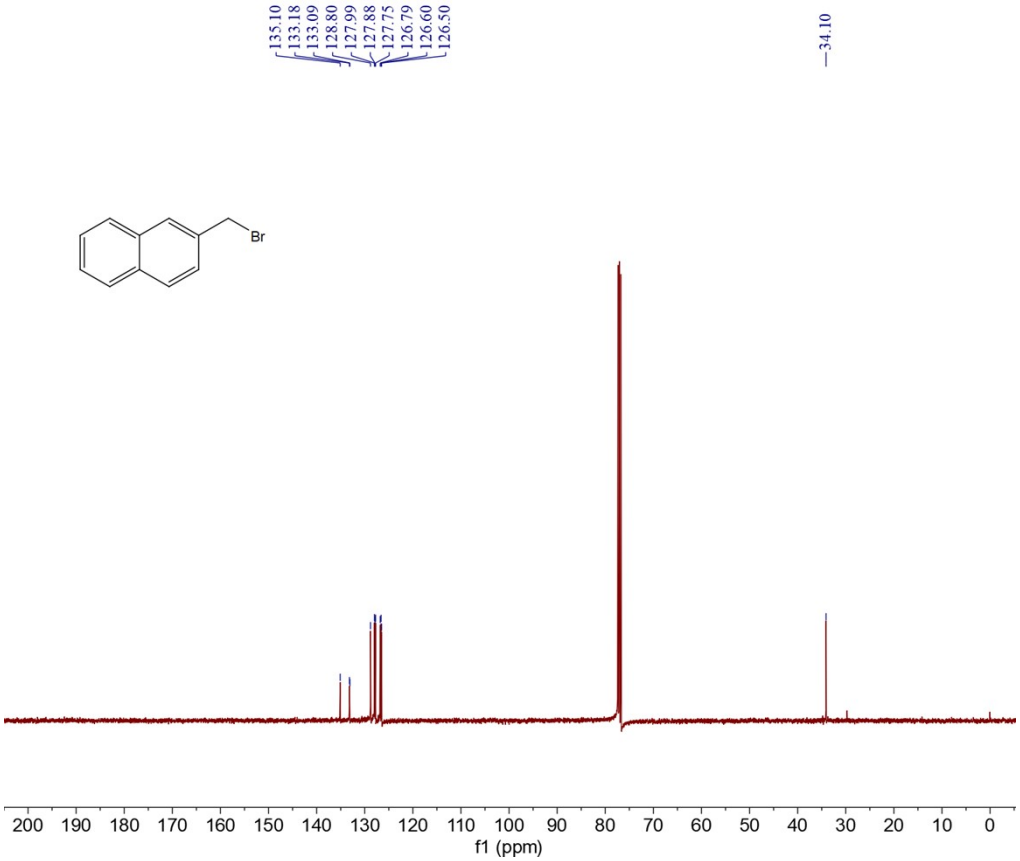

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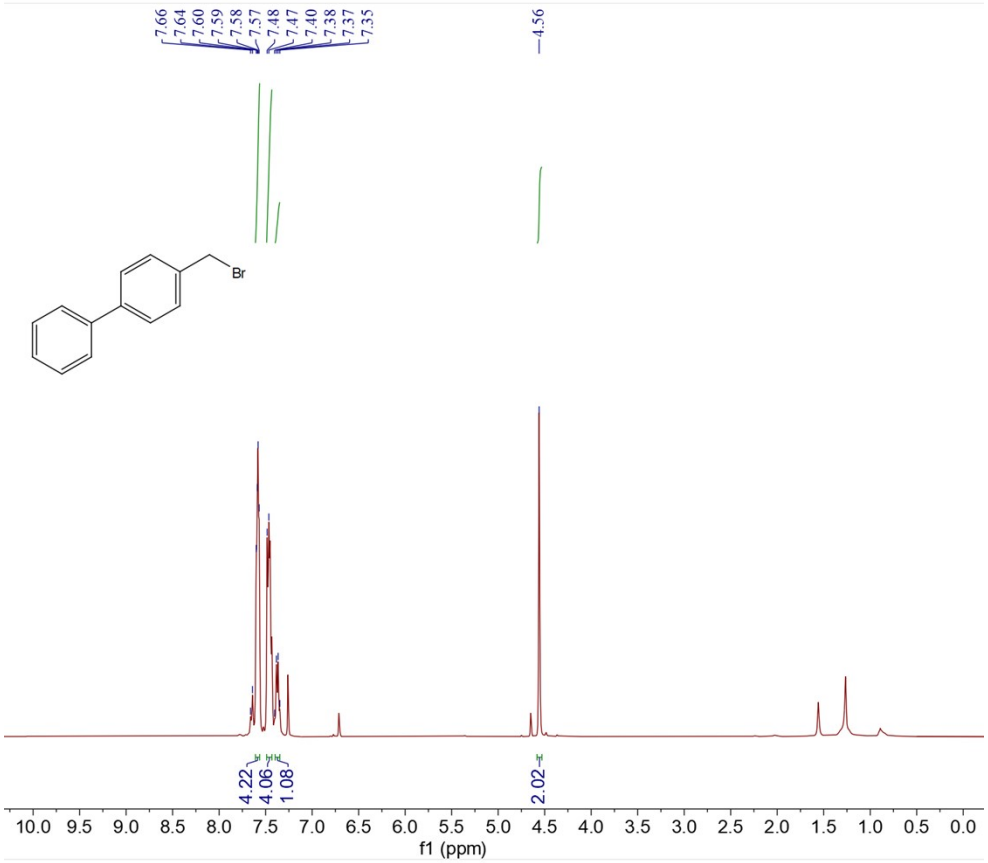

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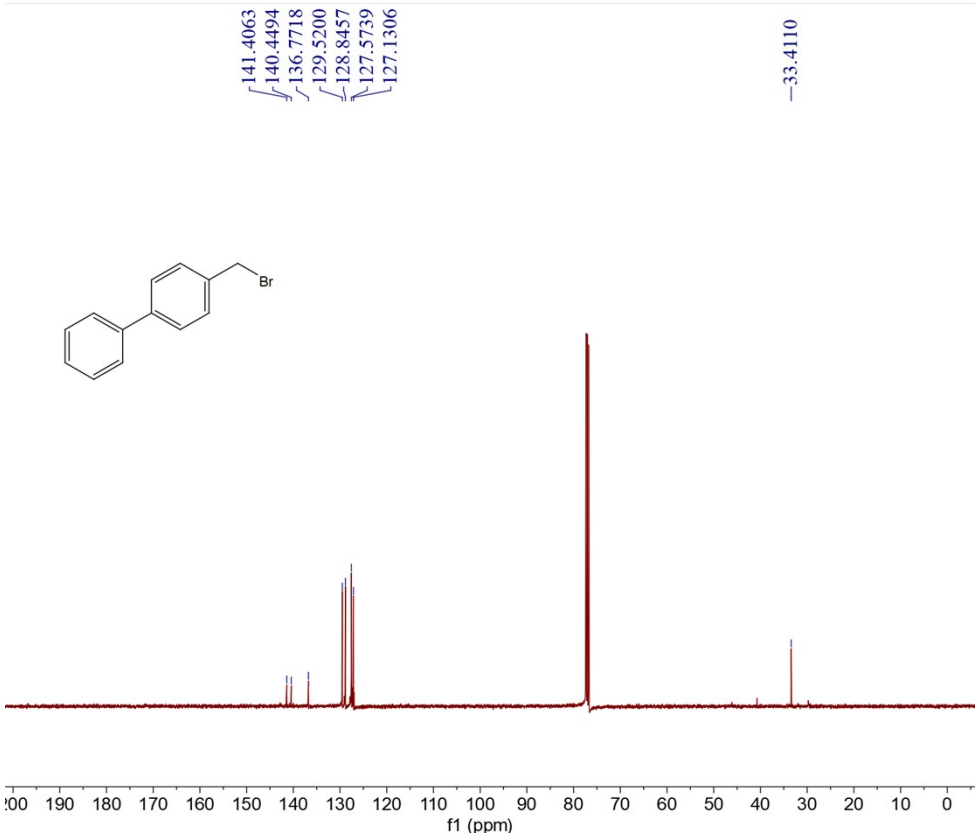

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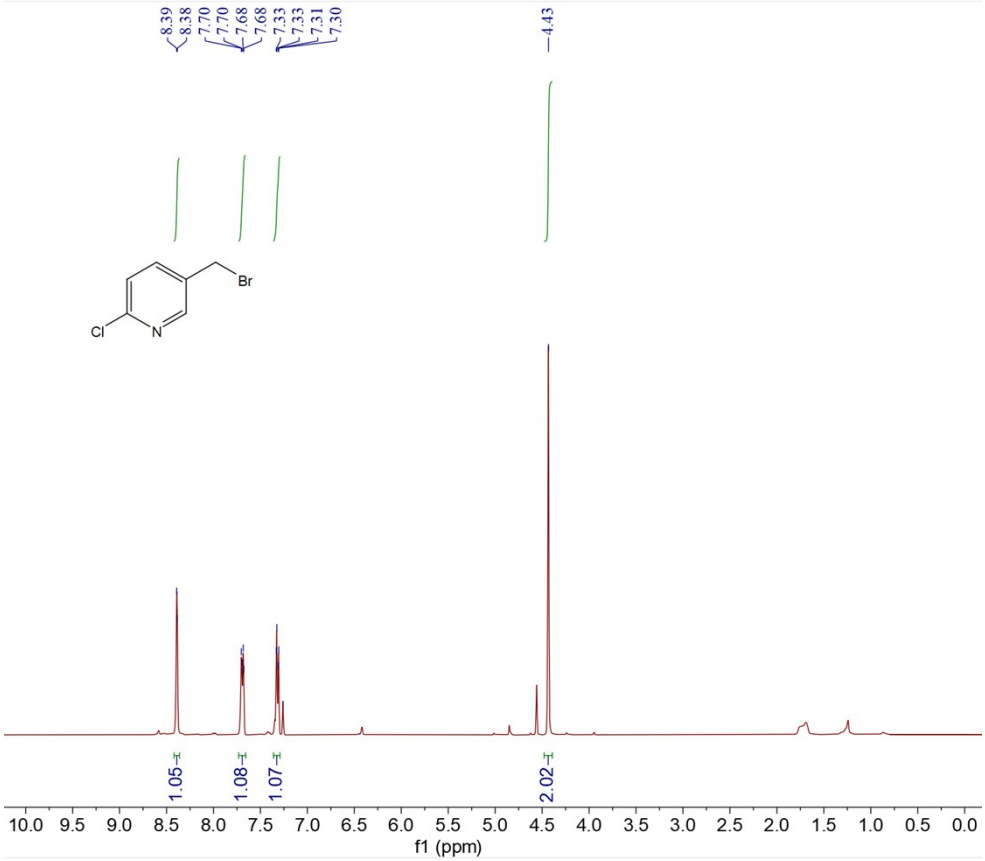

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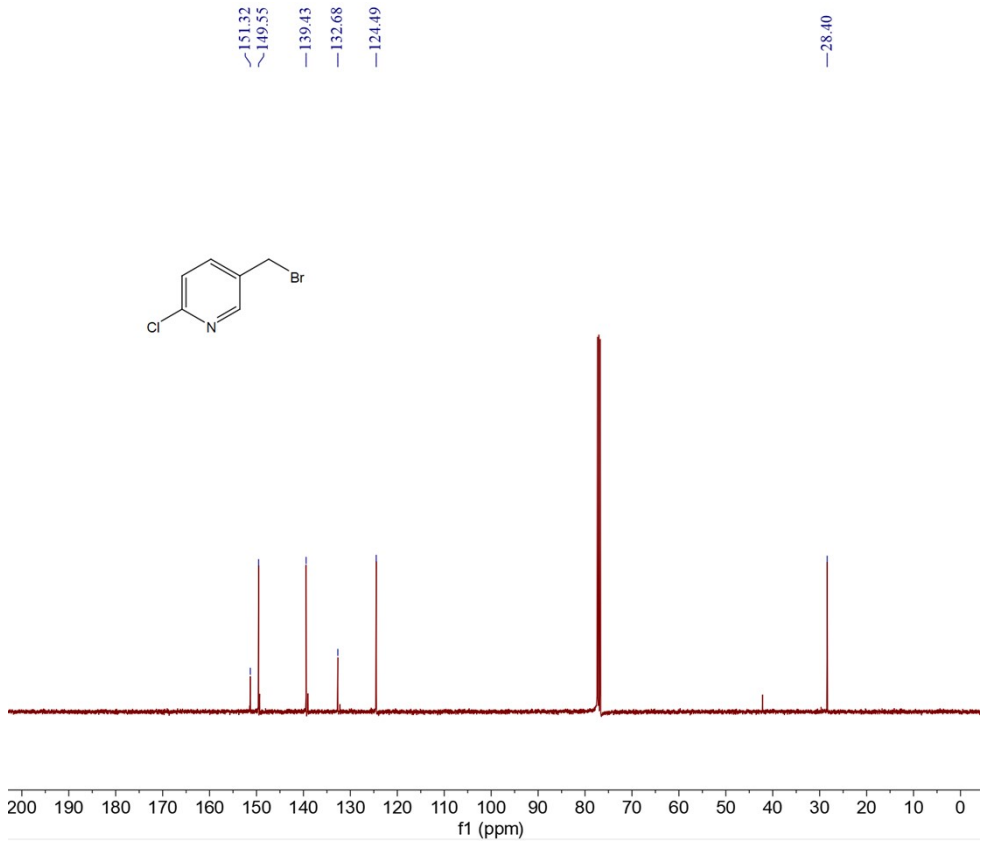

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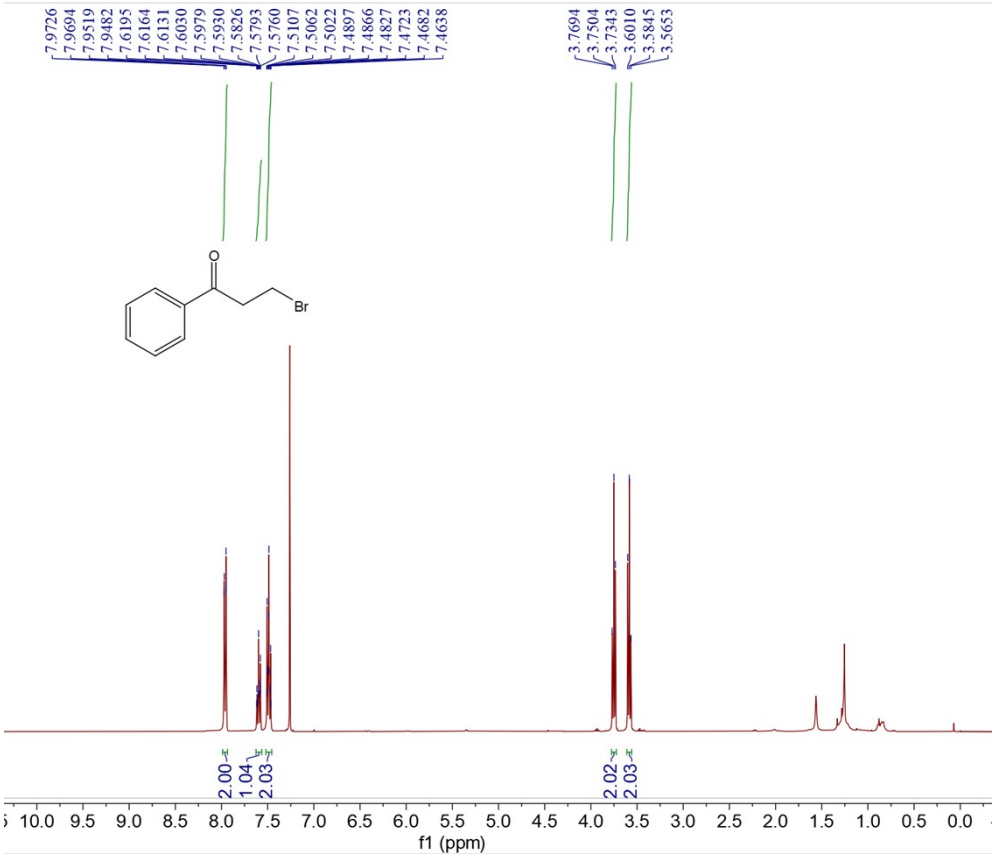

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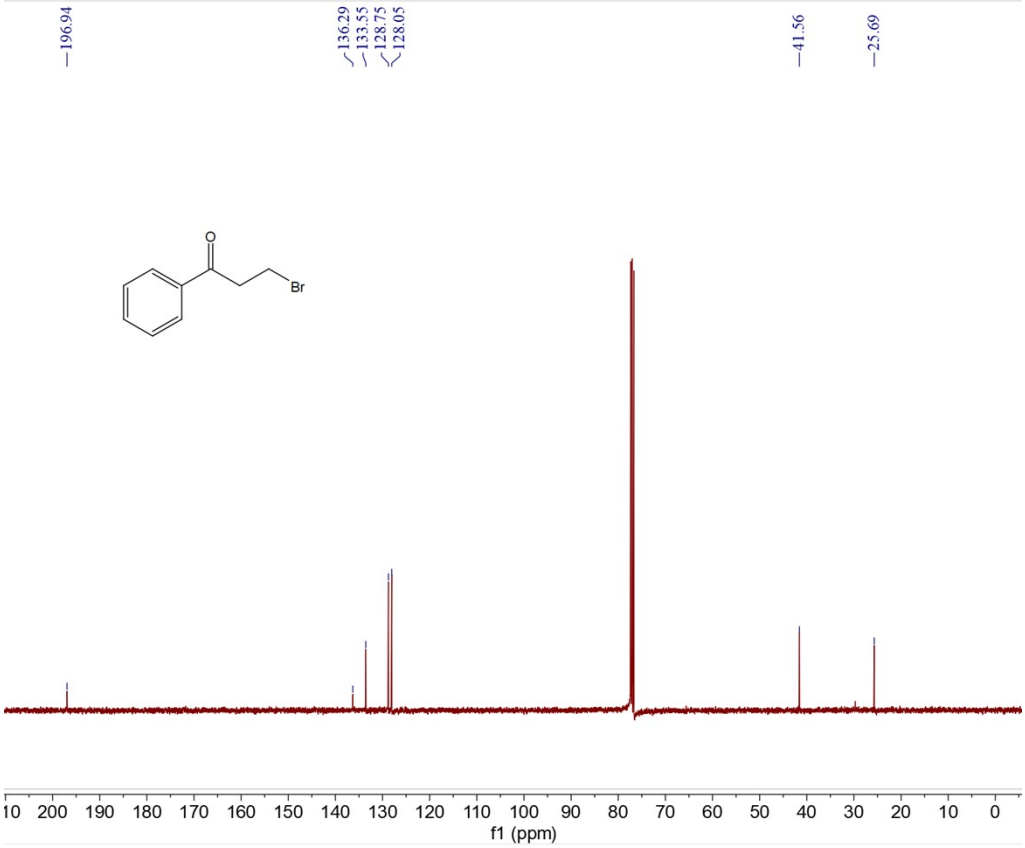

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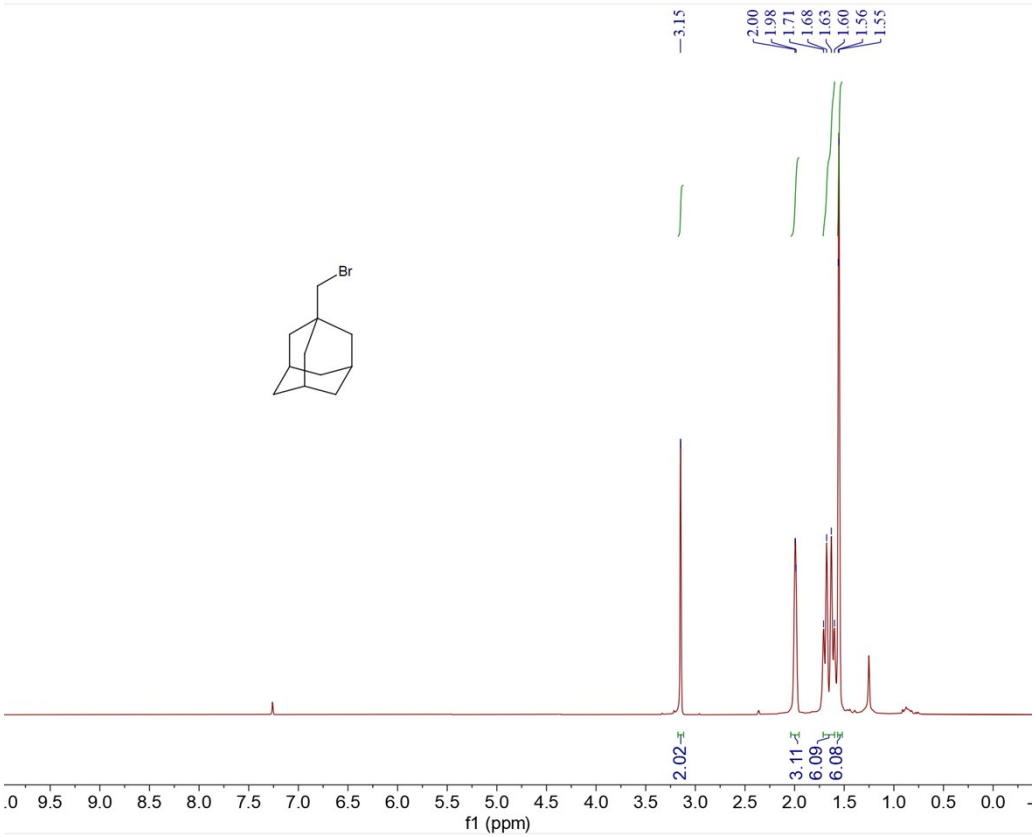

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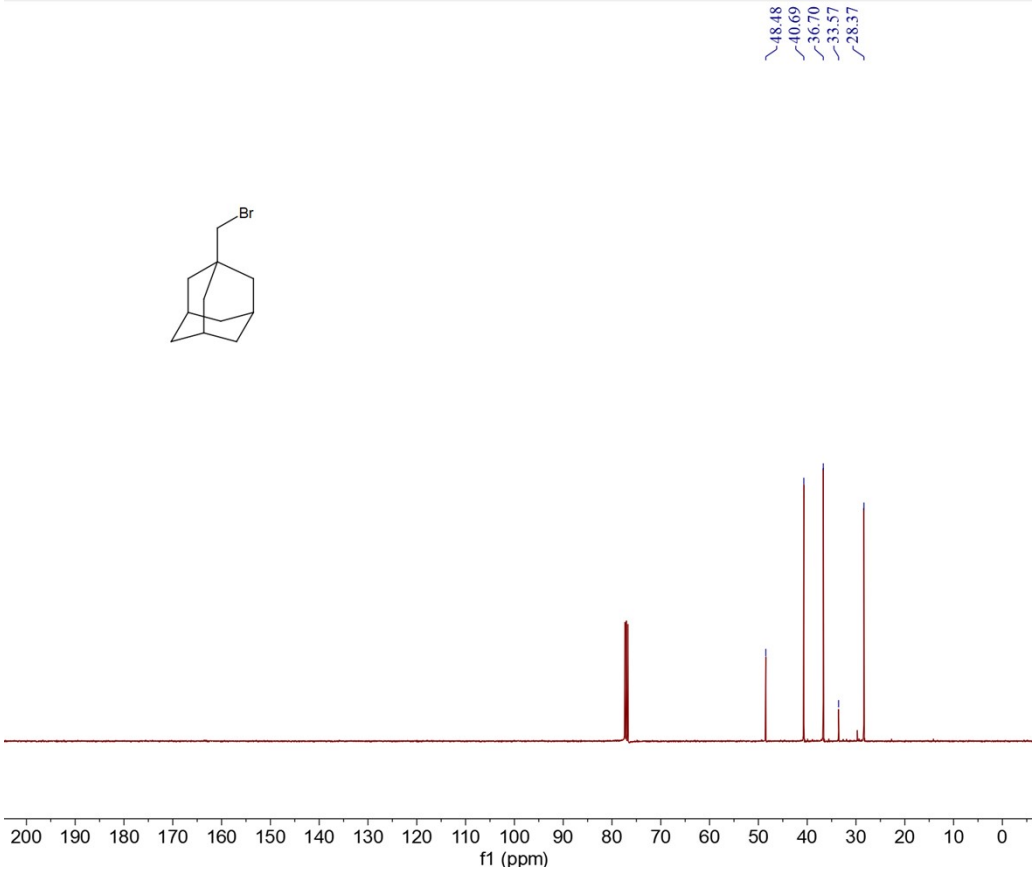

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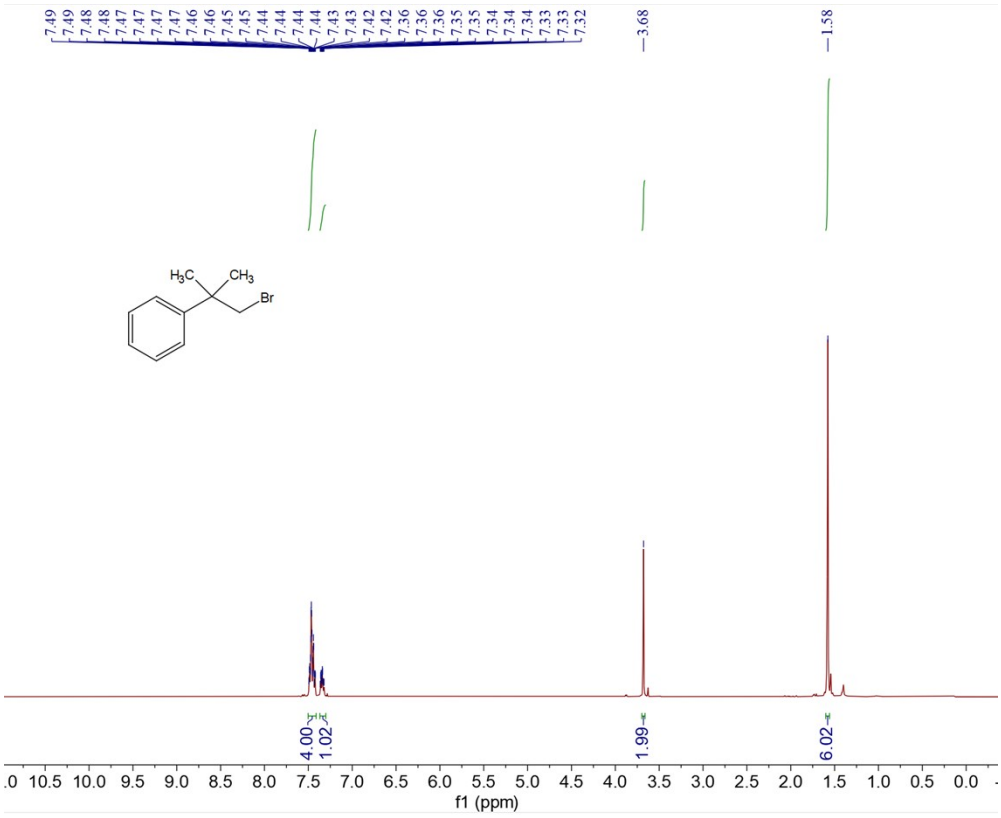

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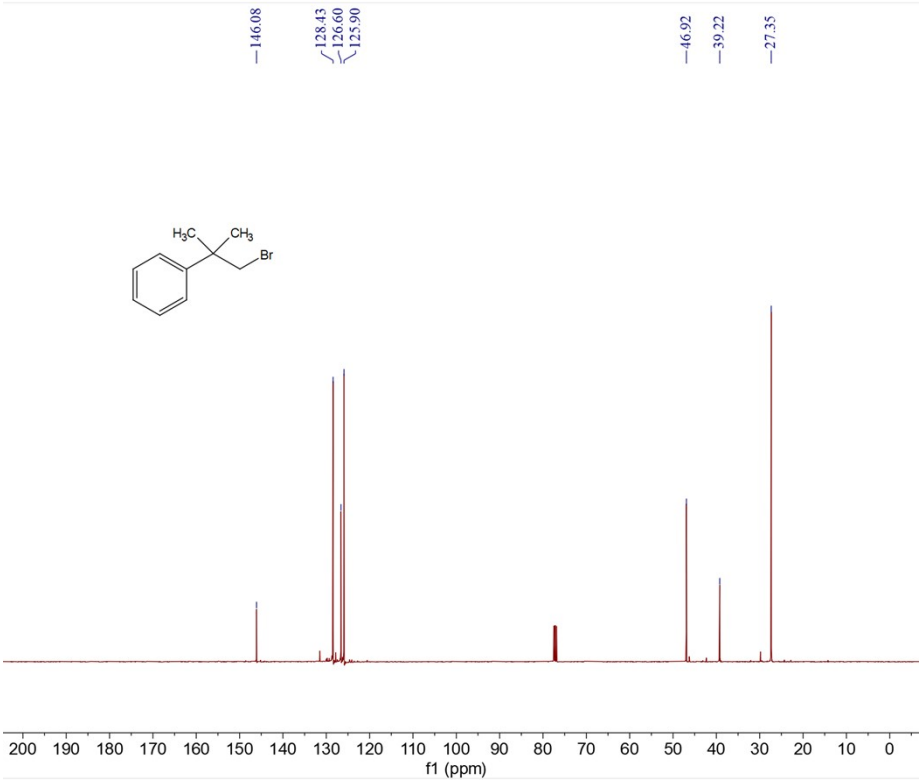

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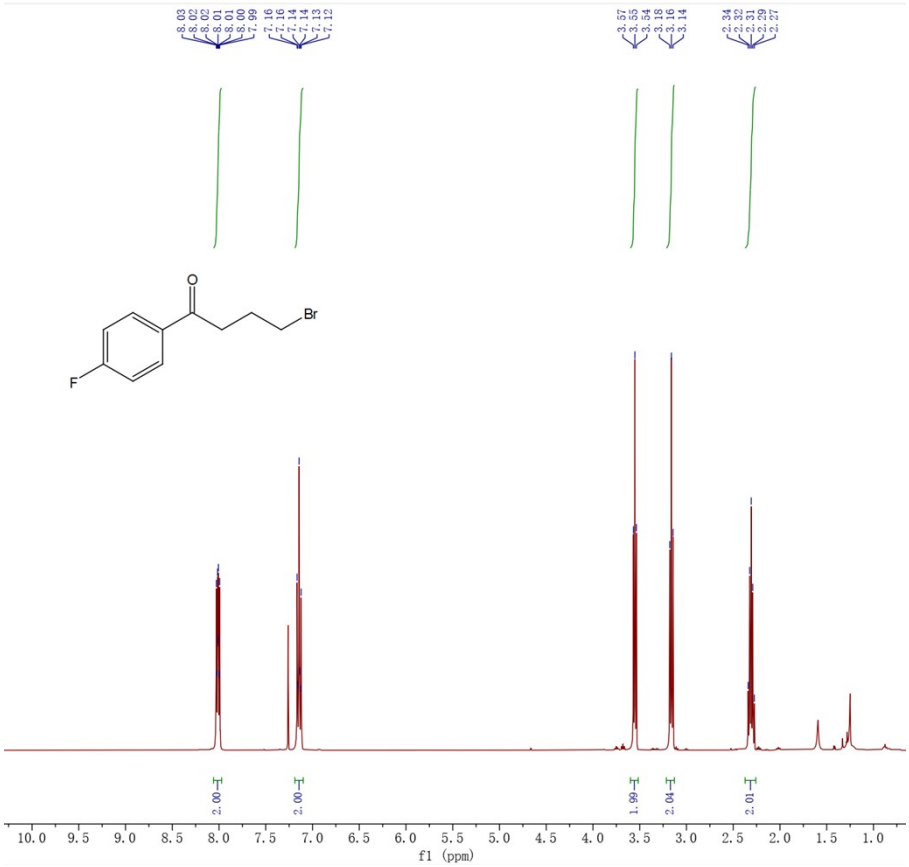

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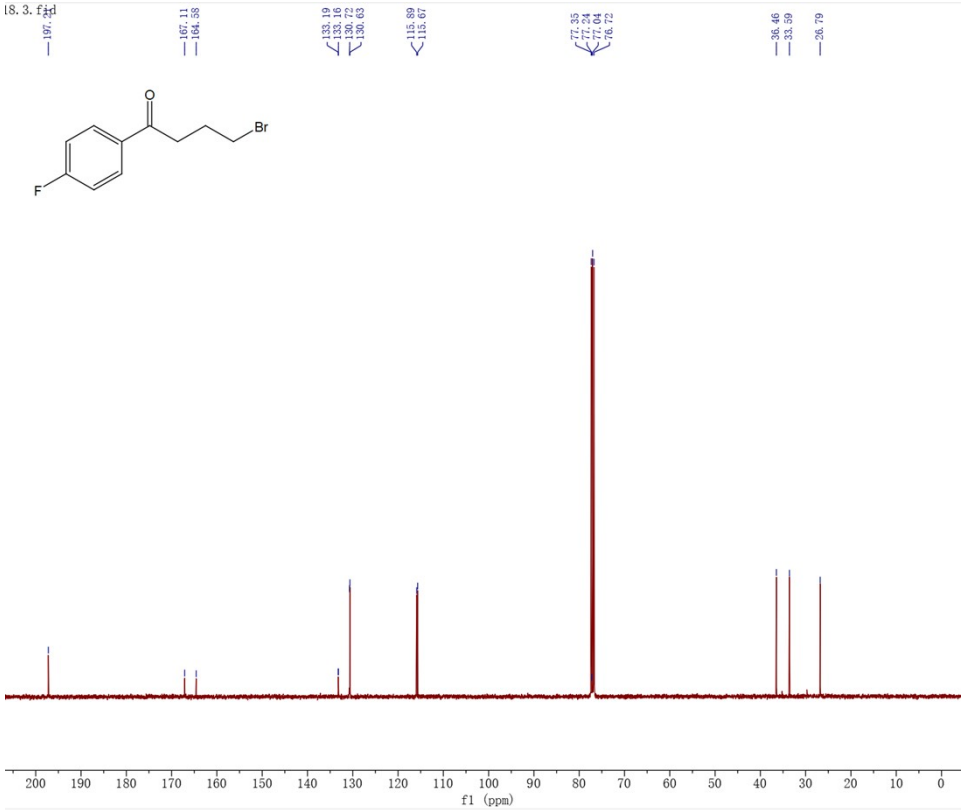

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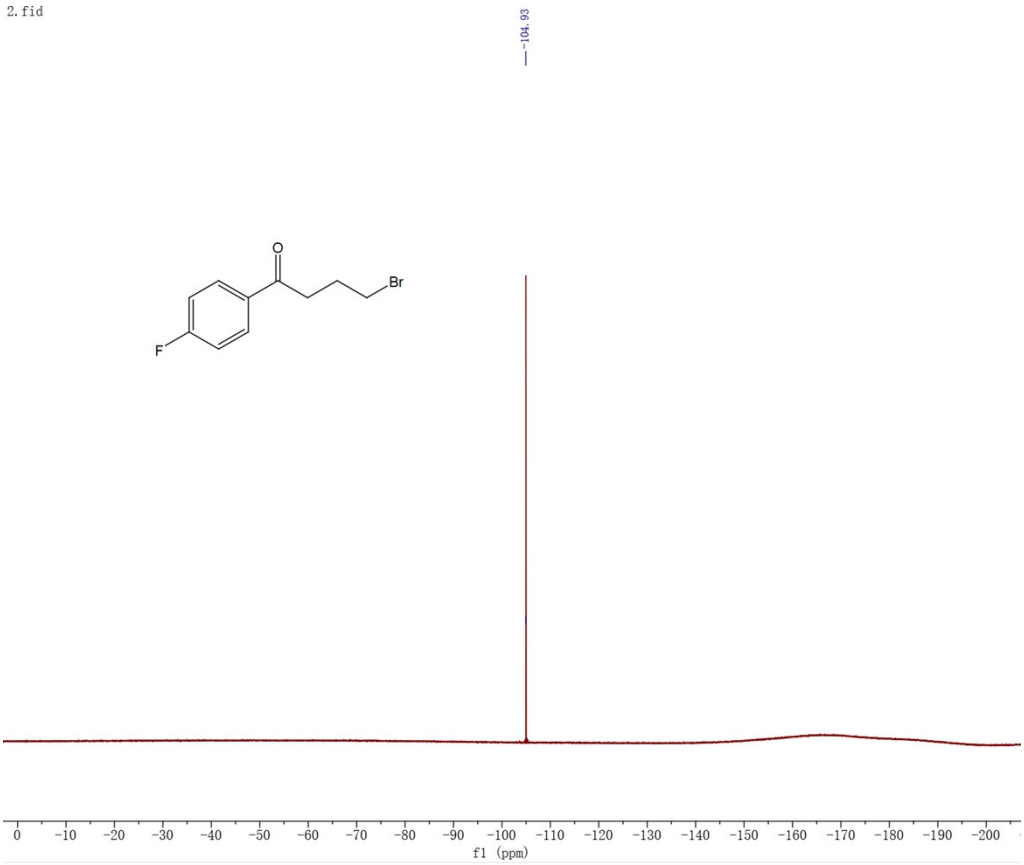

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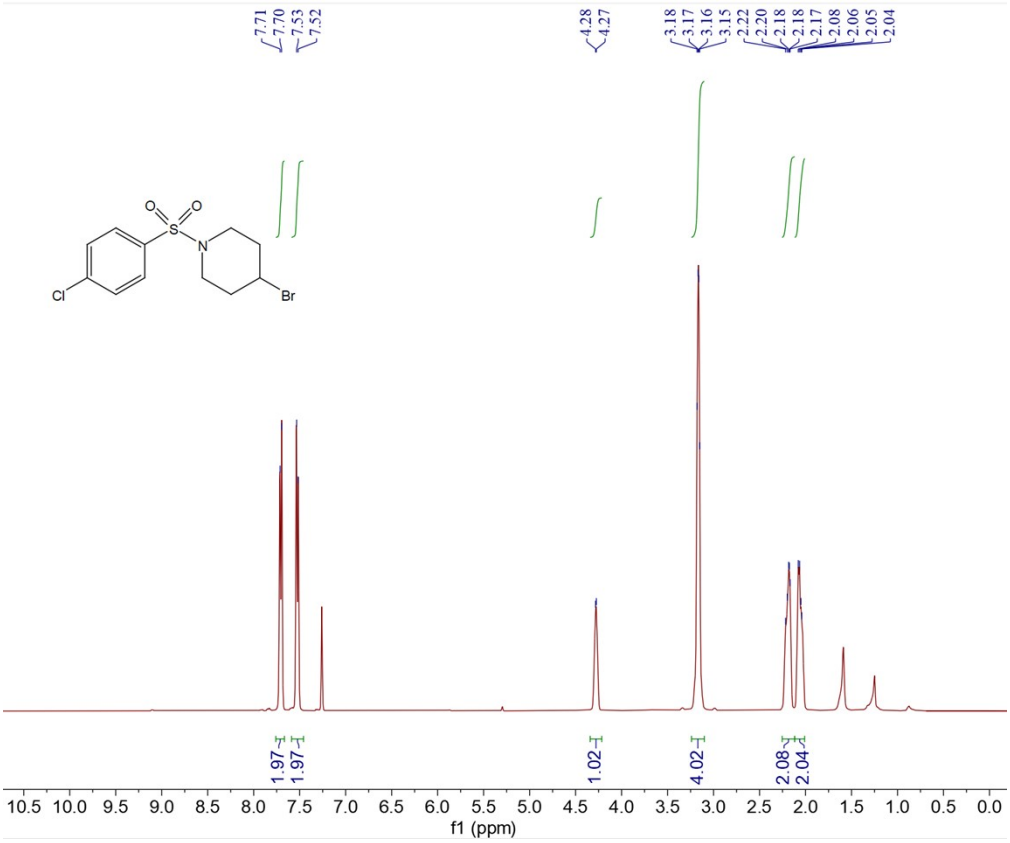

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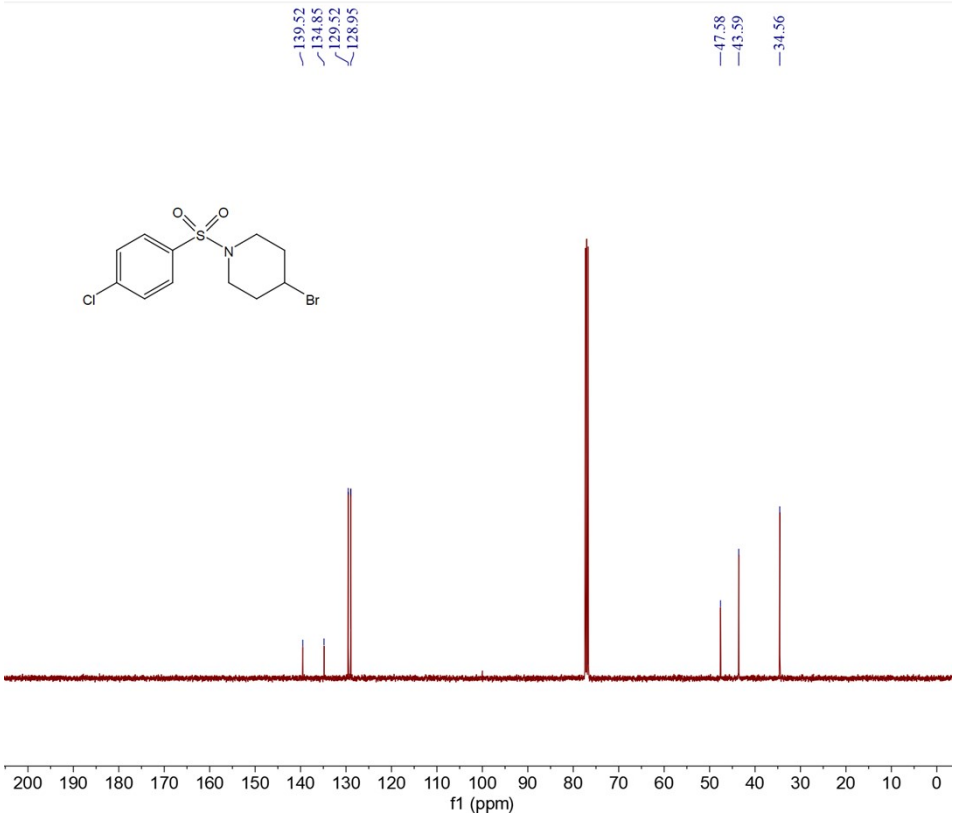
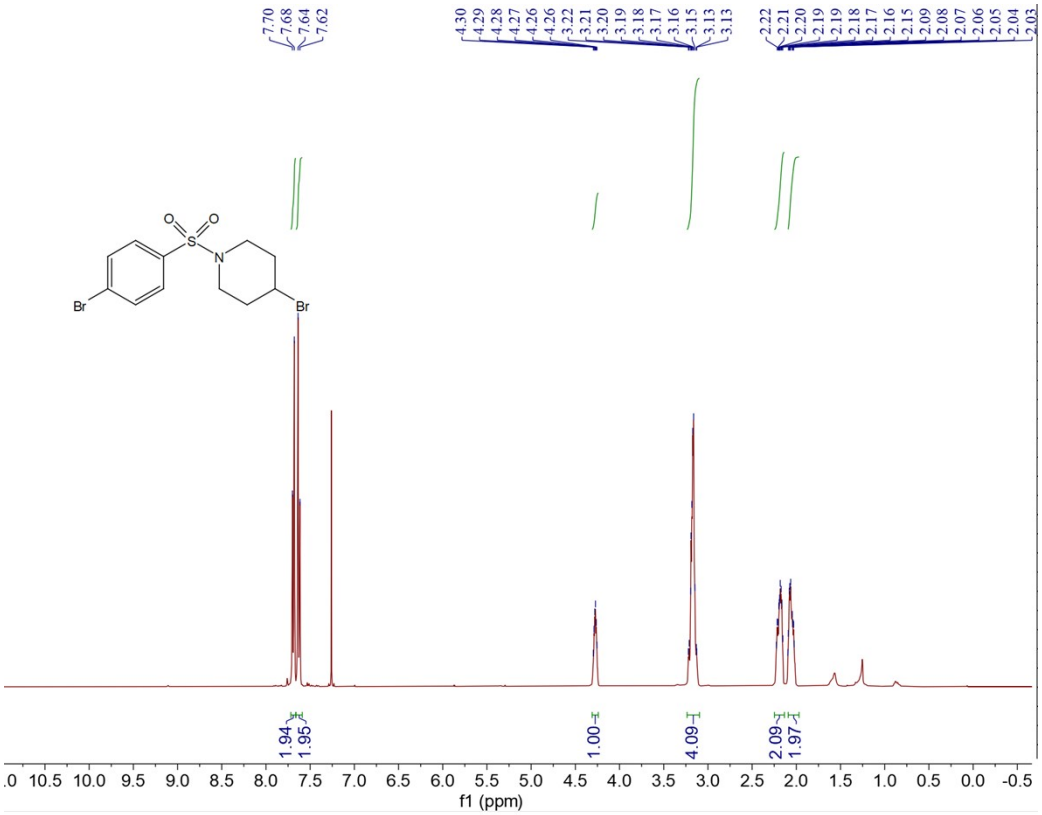
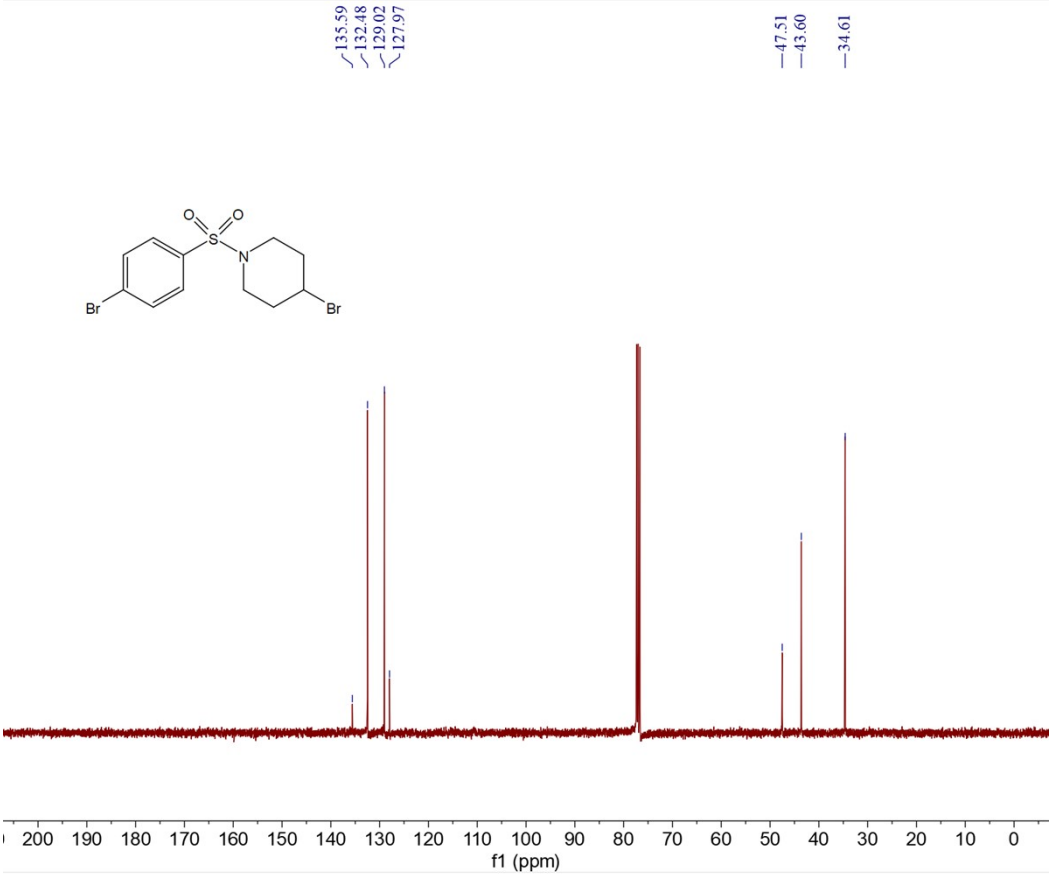


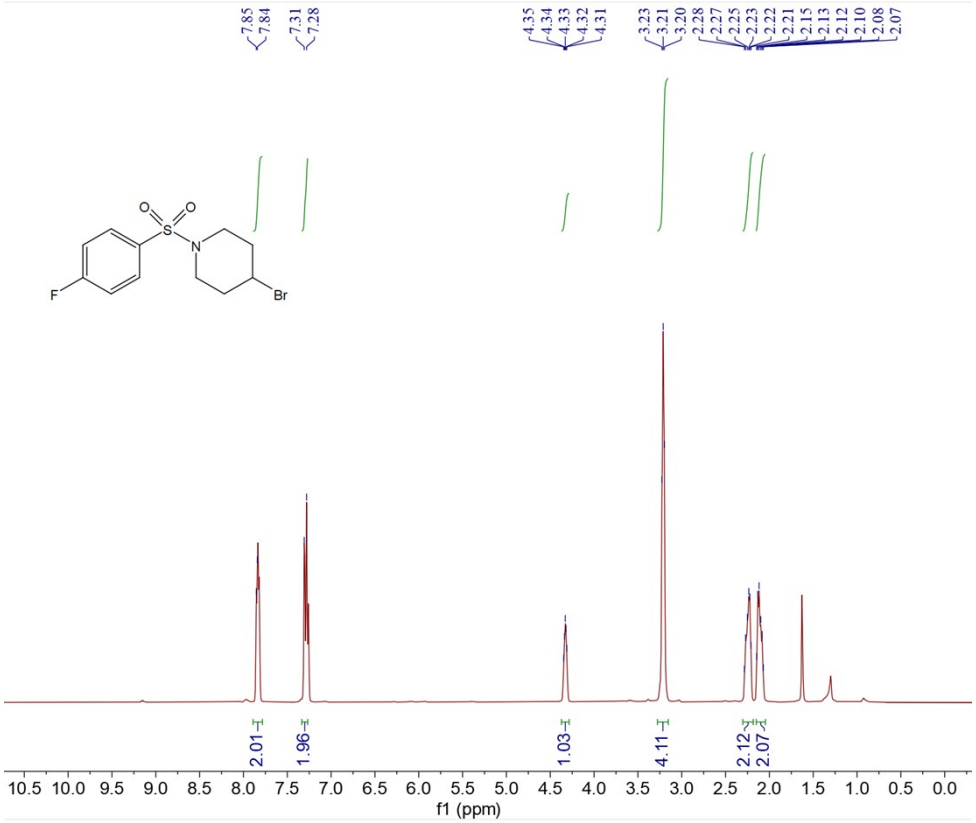
^{1}H NMR of compound **23**



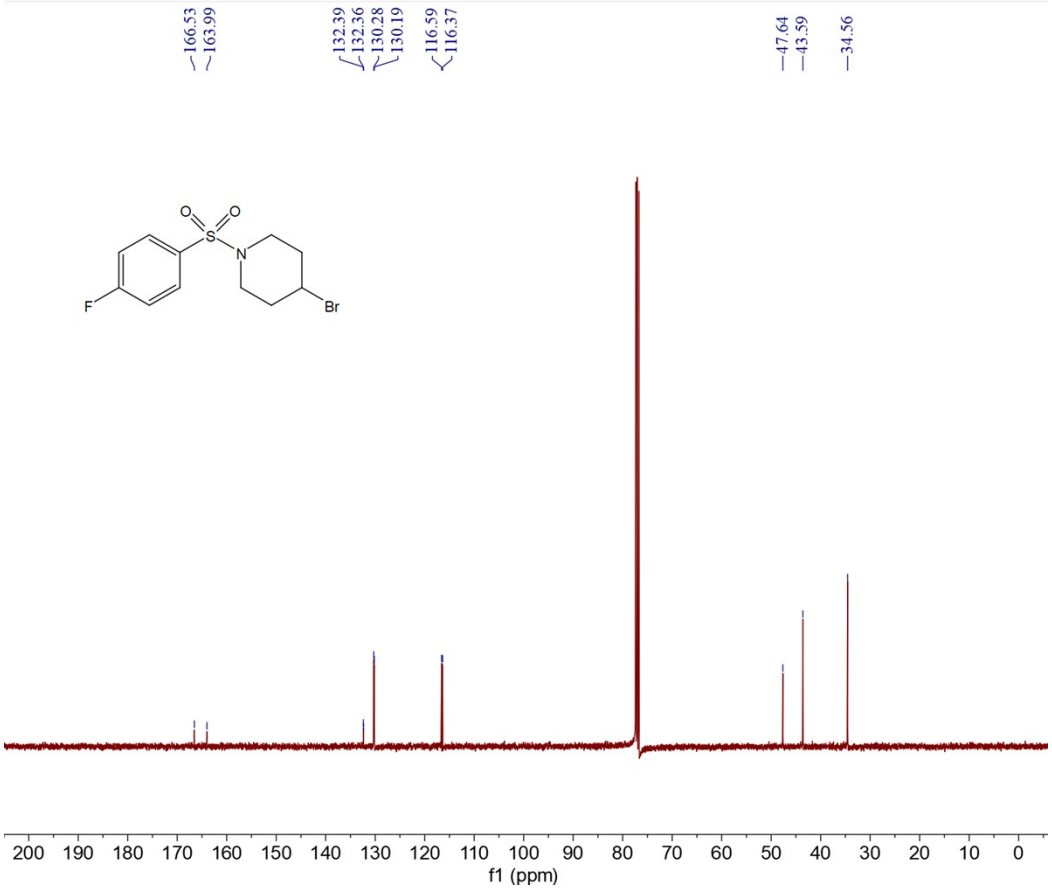
^{13}C NMR of compound **23**



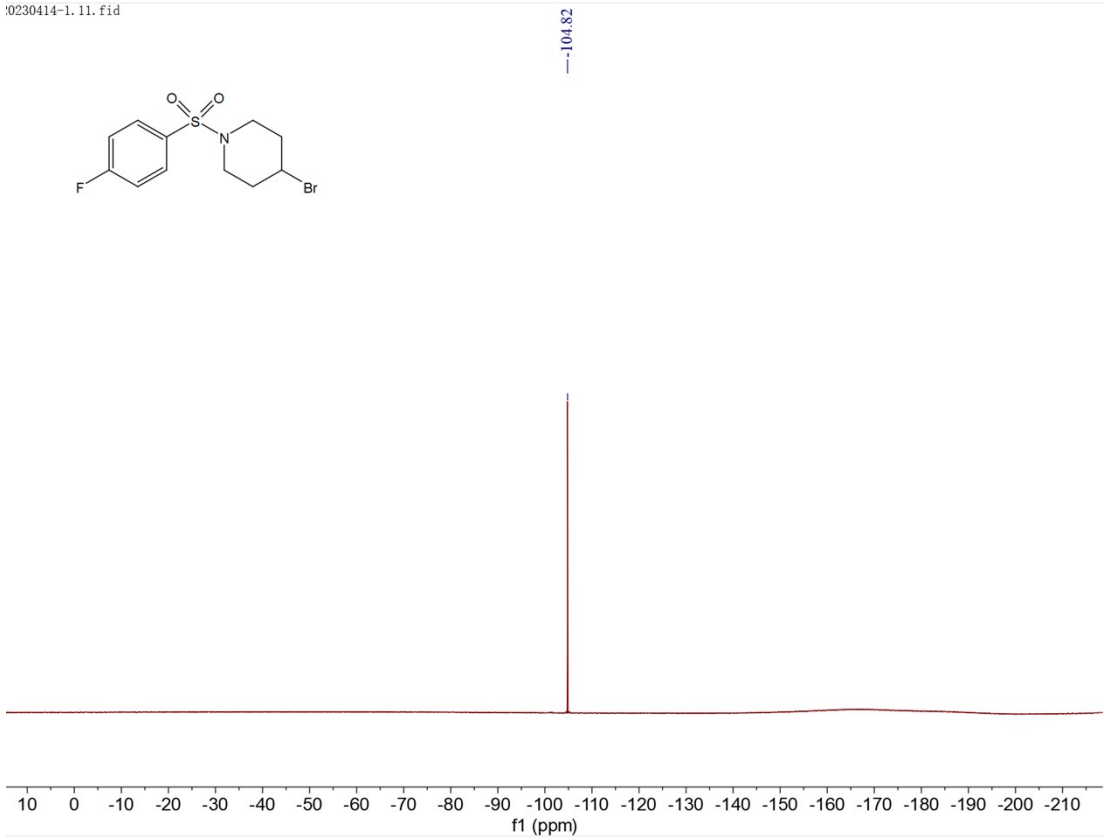
^{1}H NMR of compound **24**



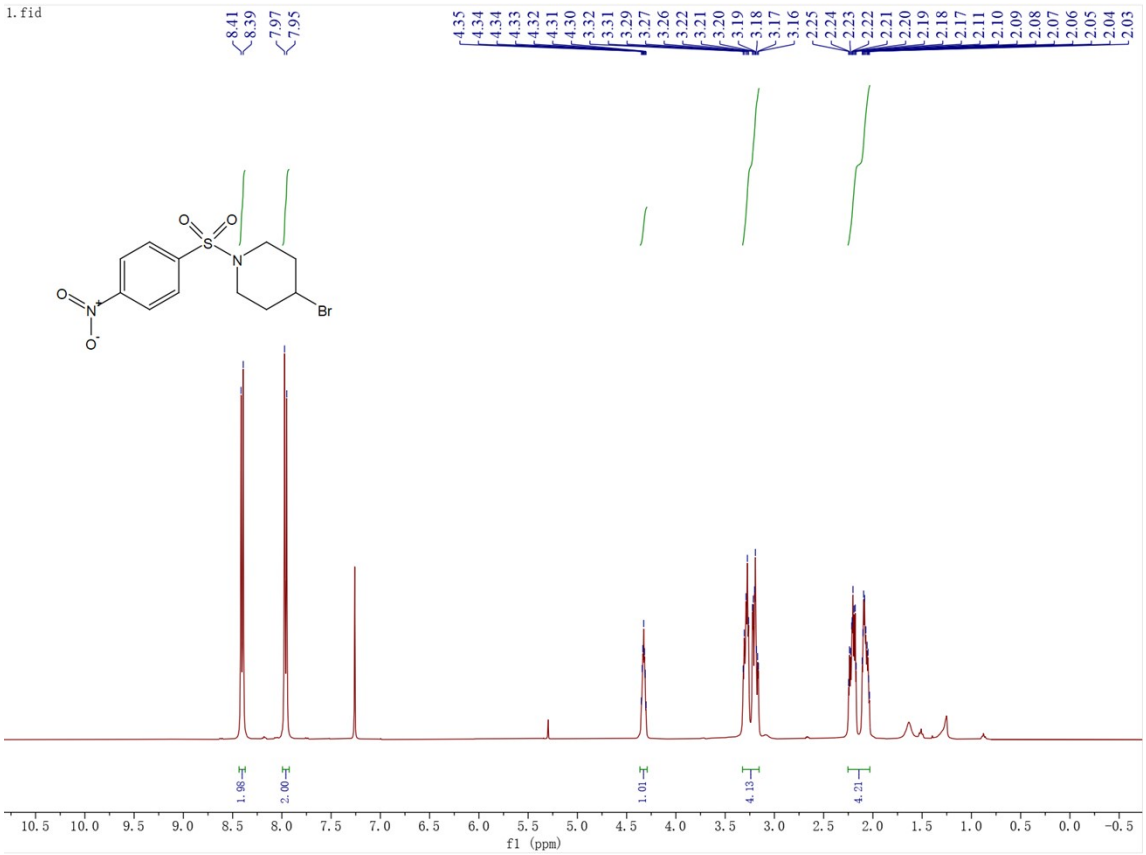
^{13}C NMR of compound **24**



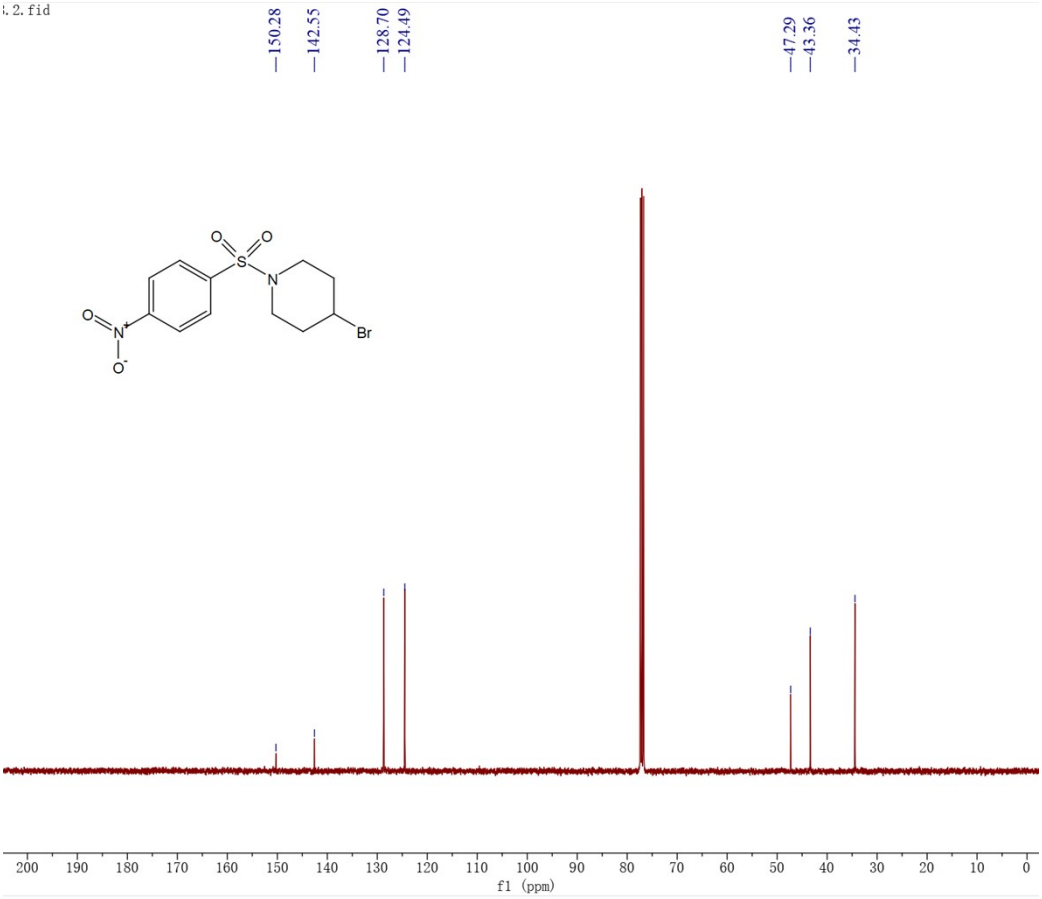
^{19}F NMR of compound **24**



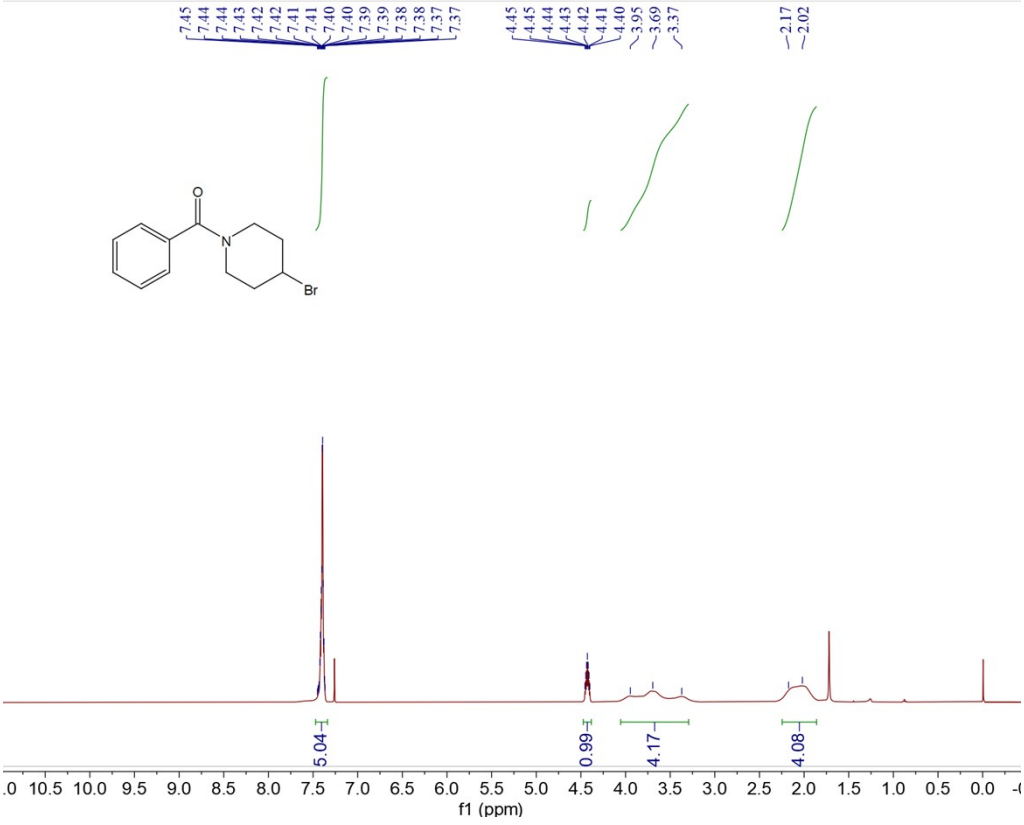
^{1}H NMR of compound **25**



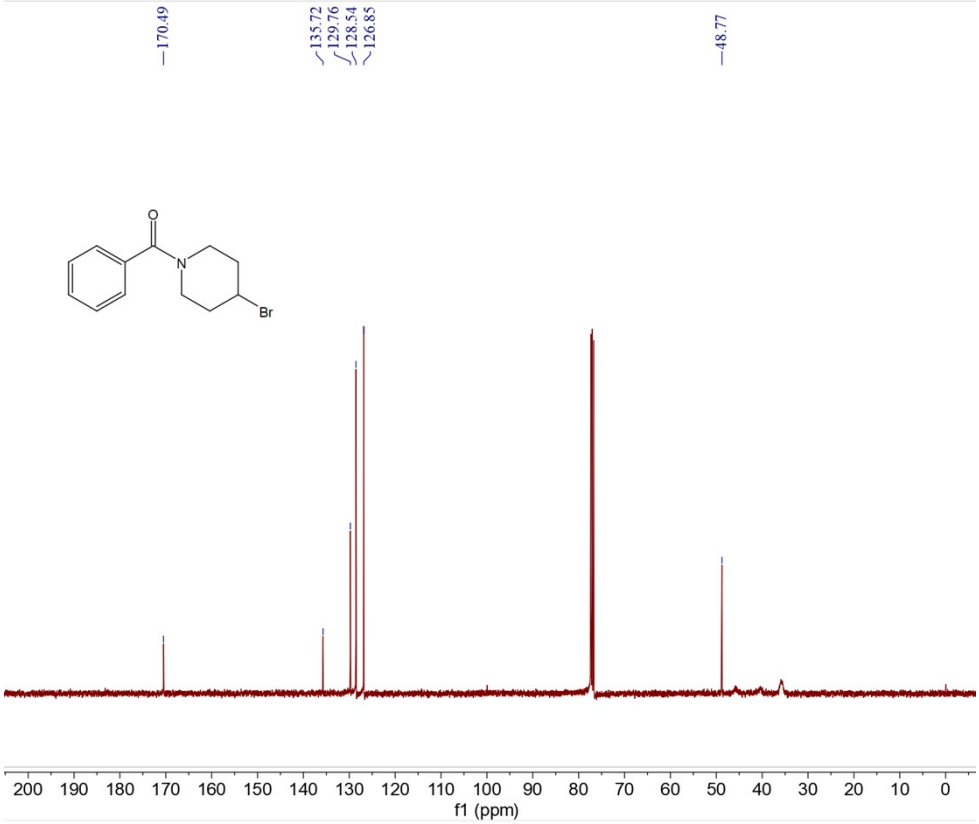
^{13}C NMR of compound **25**



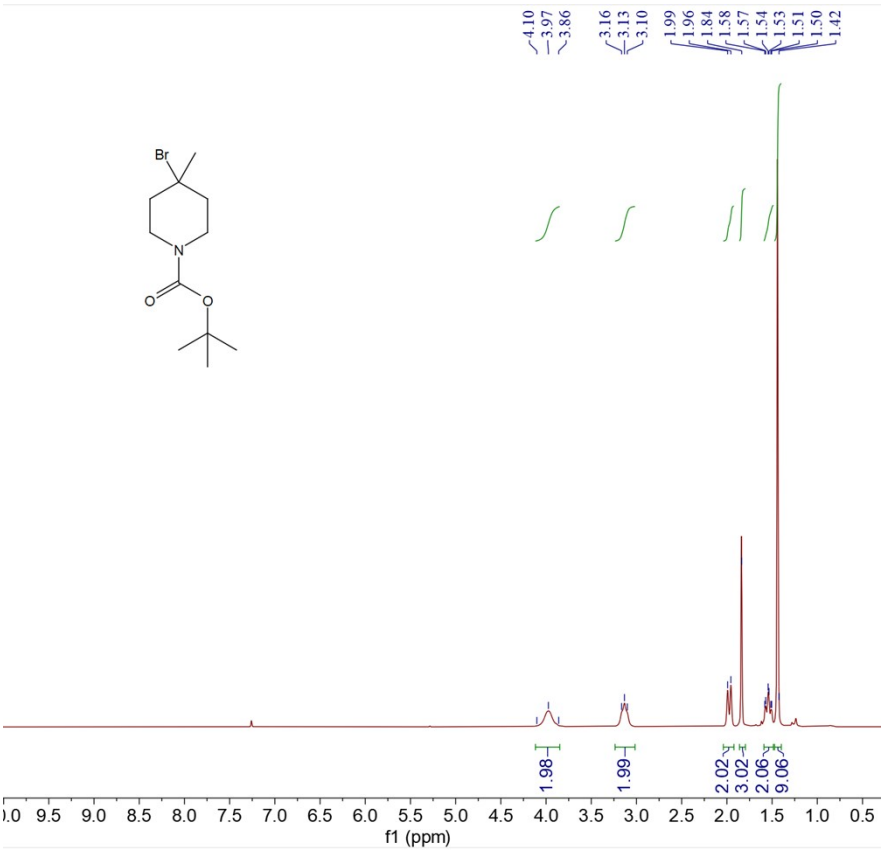
^{1}H NMR of compound **26**



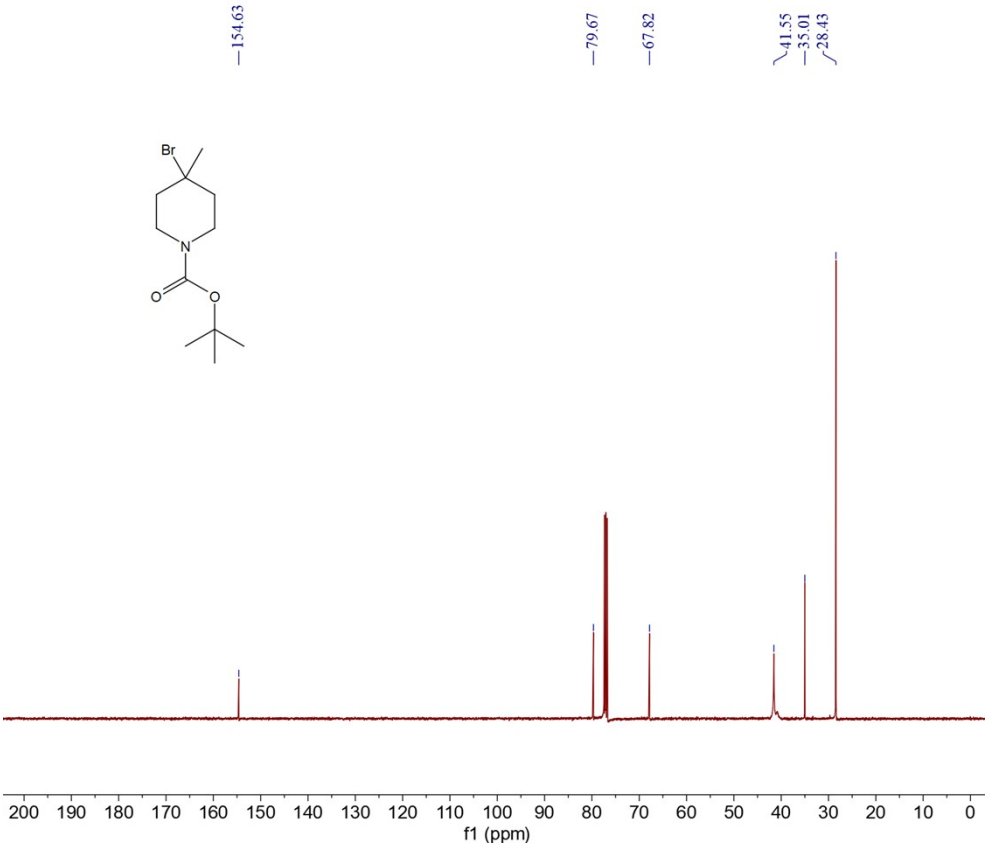
^{13}C NMR of compound **26**



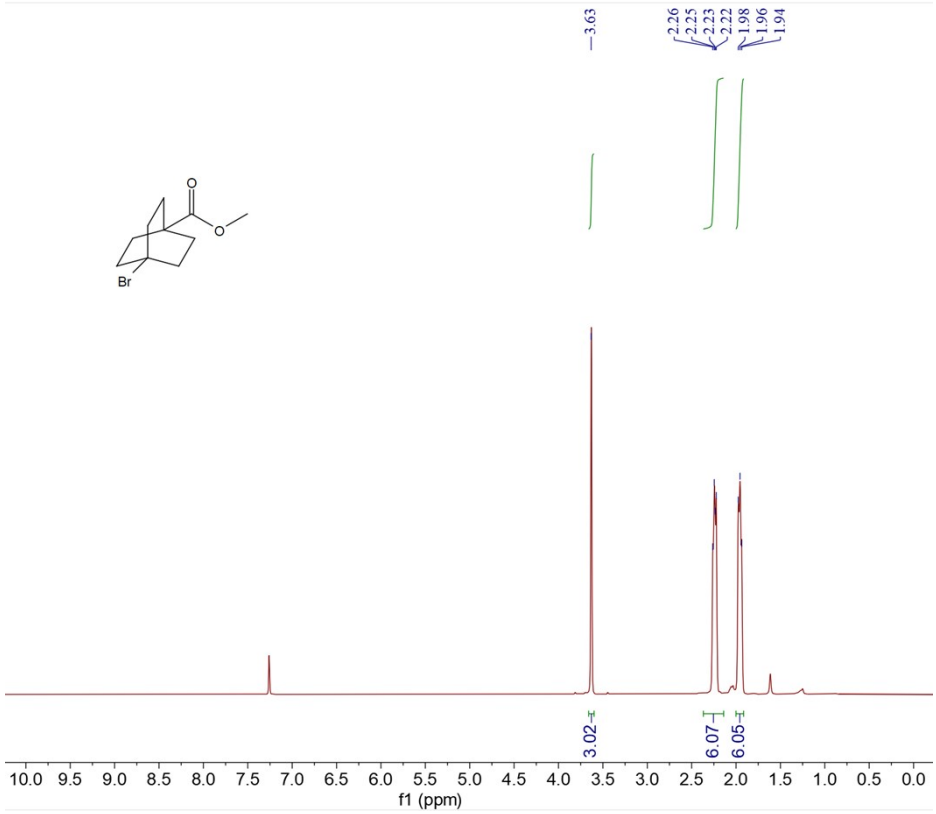
^{1}H NMR of compound **27**



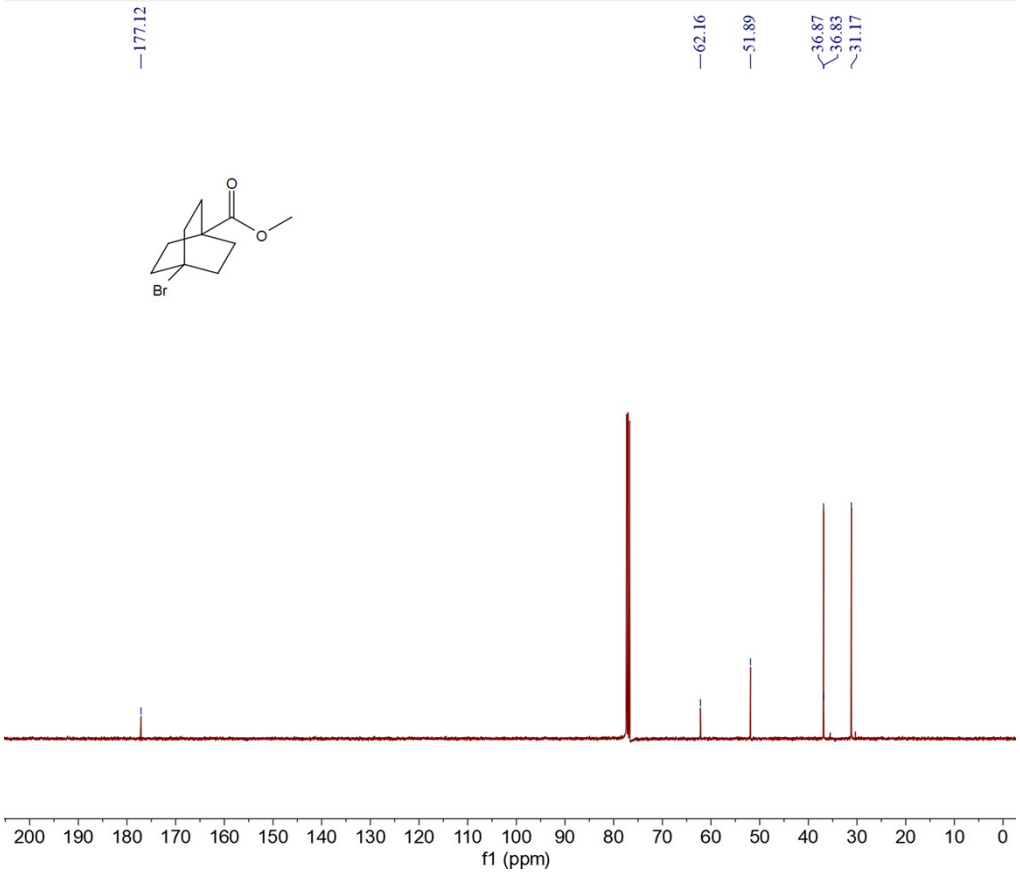
^{13}C NMR of compound **27**



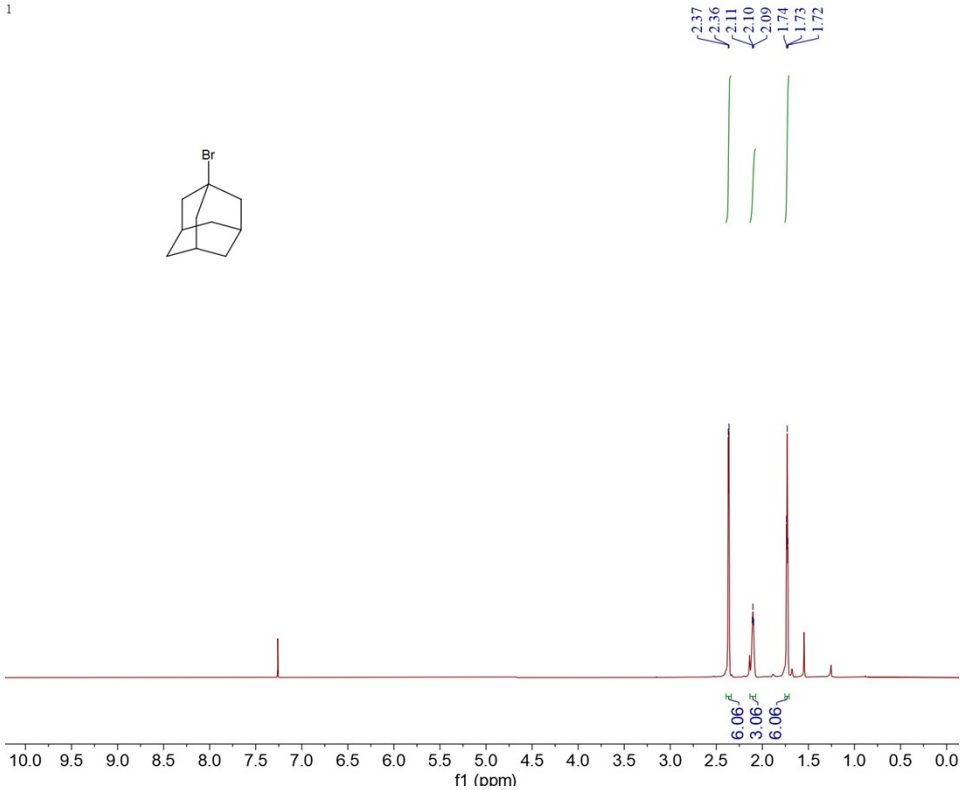
^{1}H NMR of compound **28**



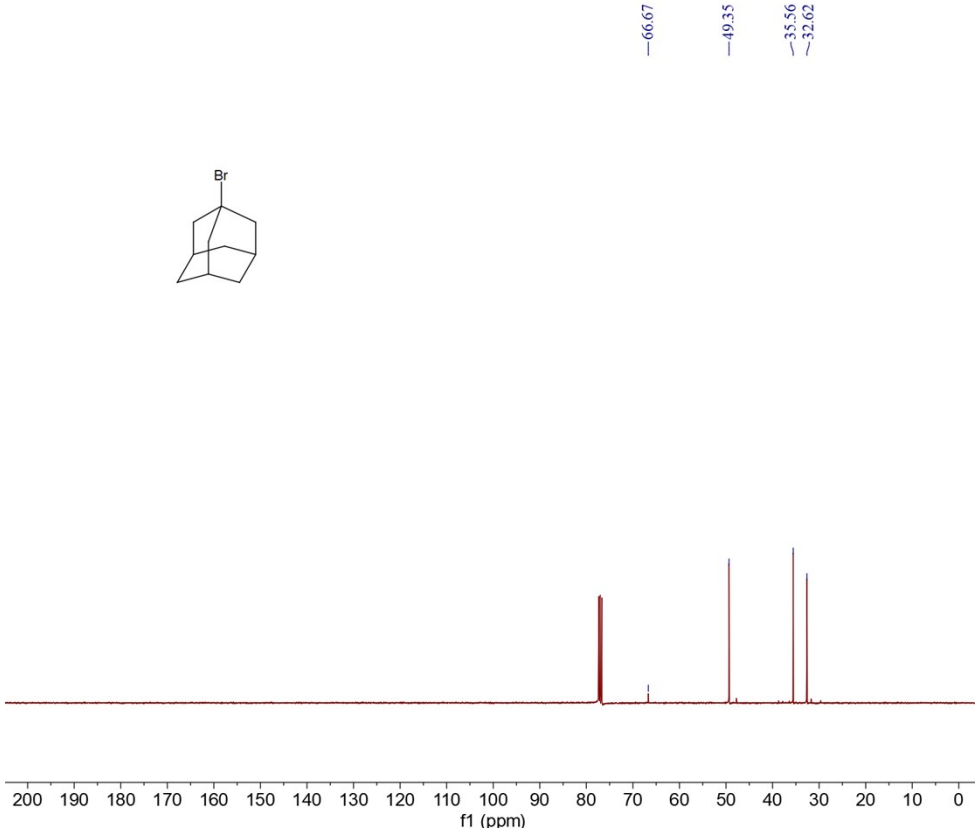
^{13}C NMR of compound **28**



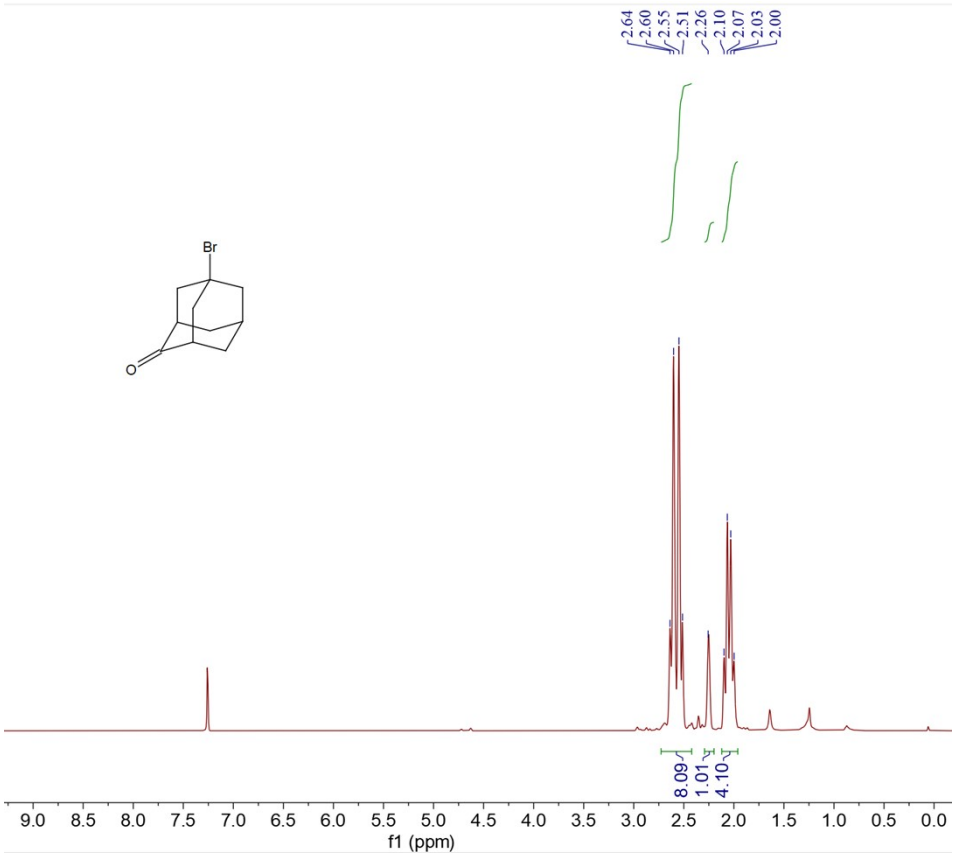
^{1}H NMR of compound **29**



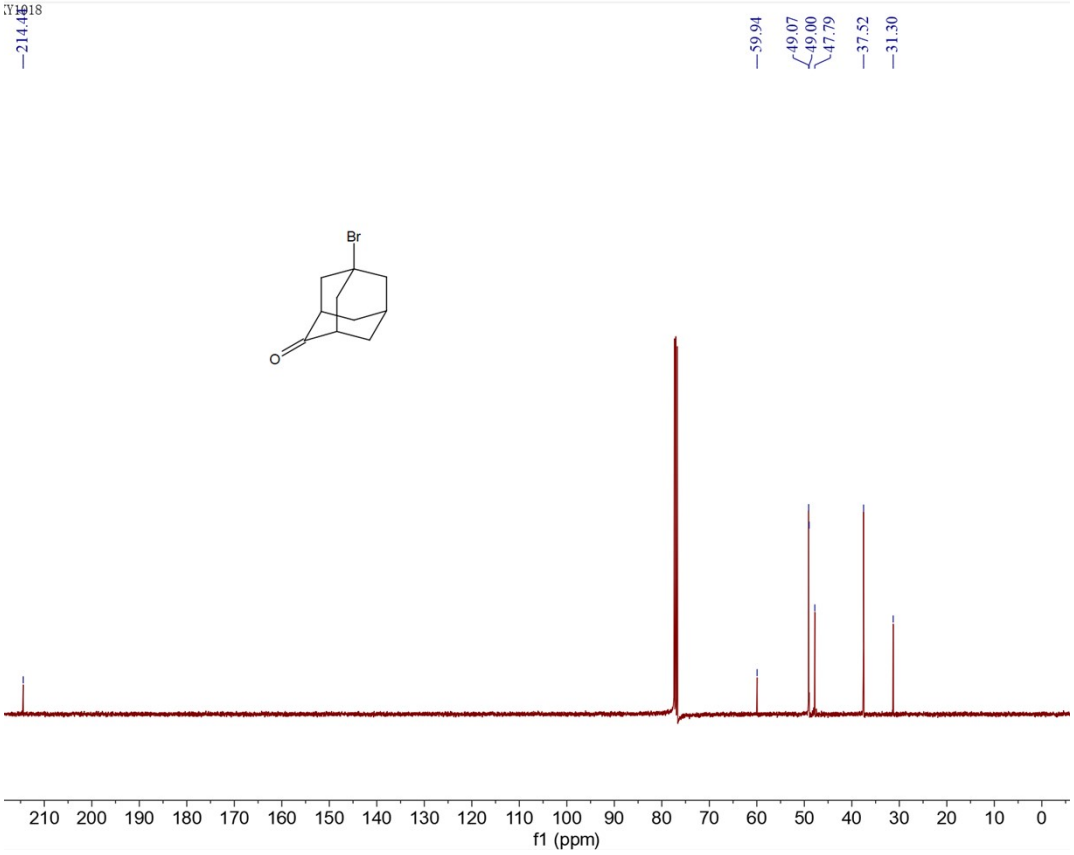
^{13}C NMR of compound **29**



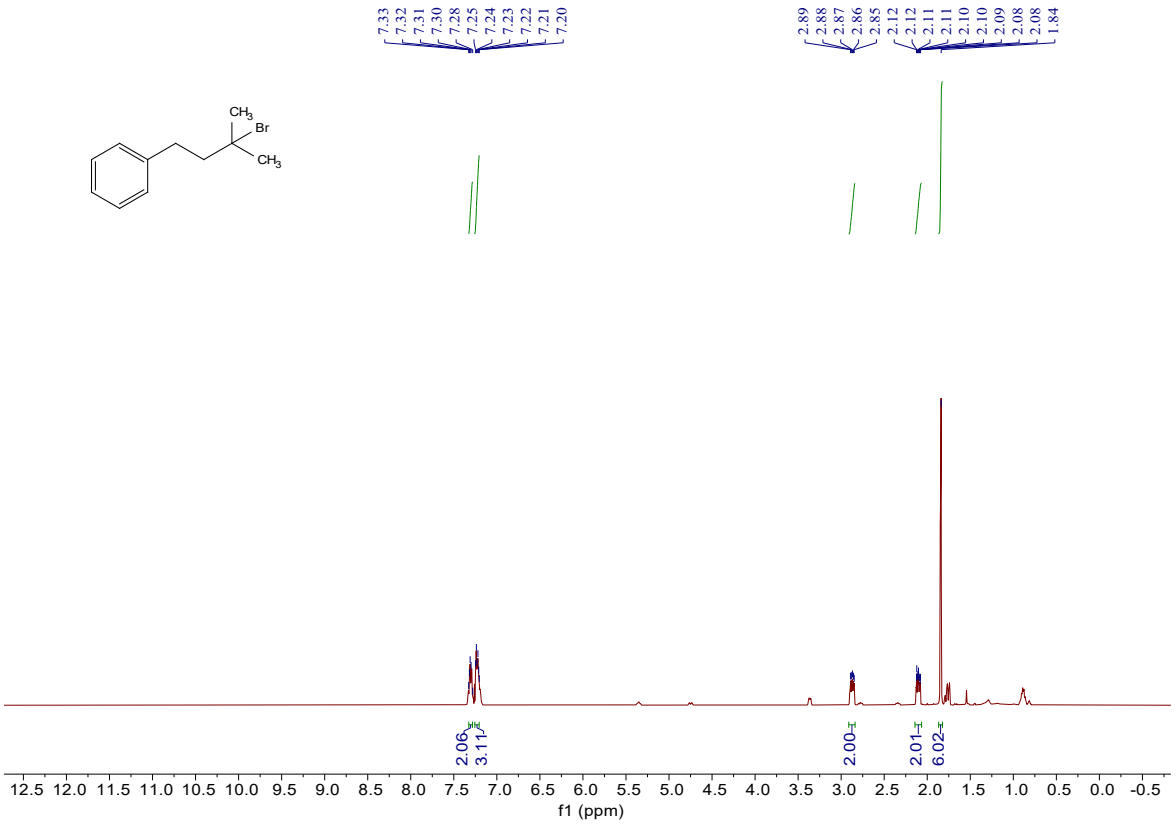
^{1}H NMR of compound **30**



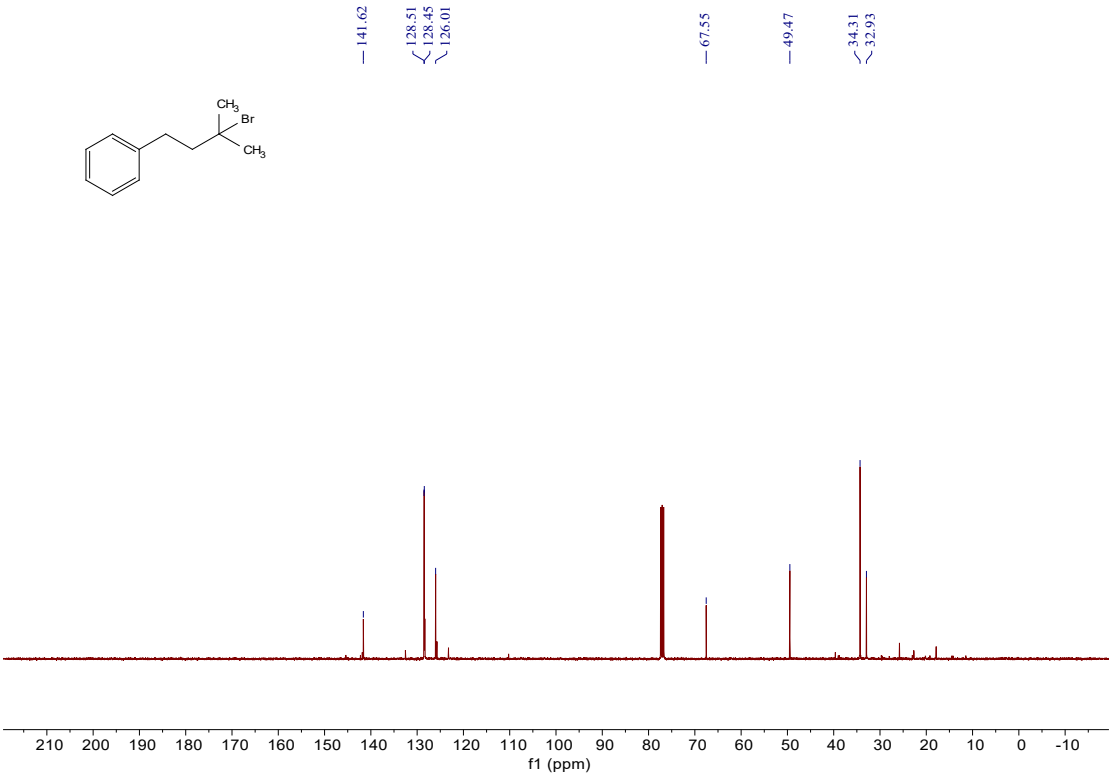
^{13}C NMR of compound **30**



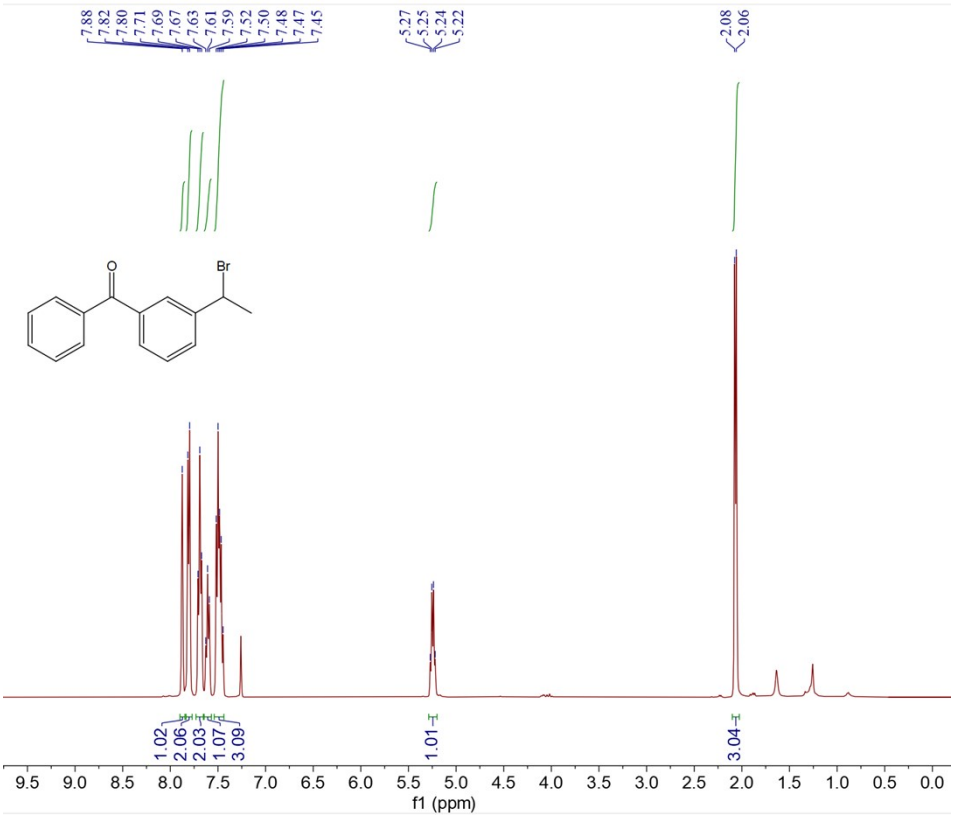
^{1}H NMR of compound **31**



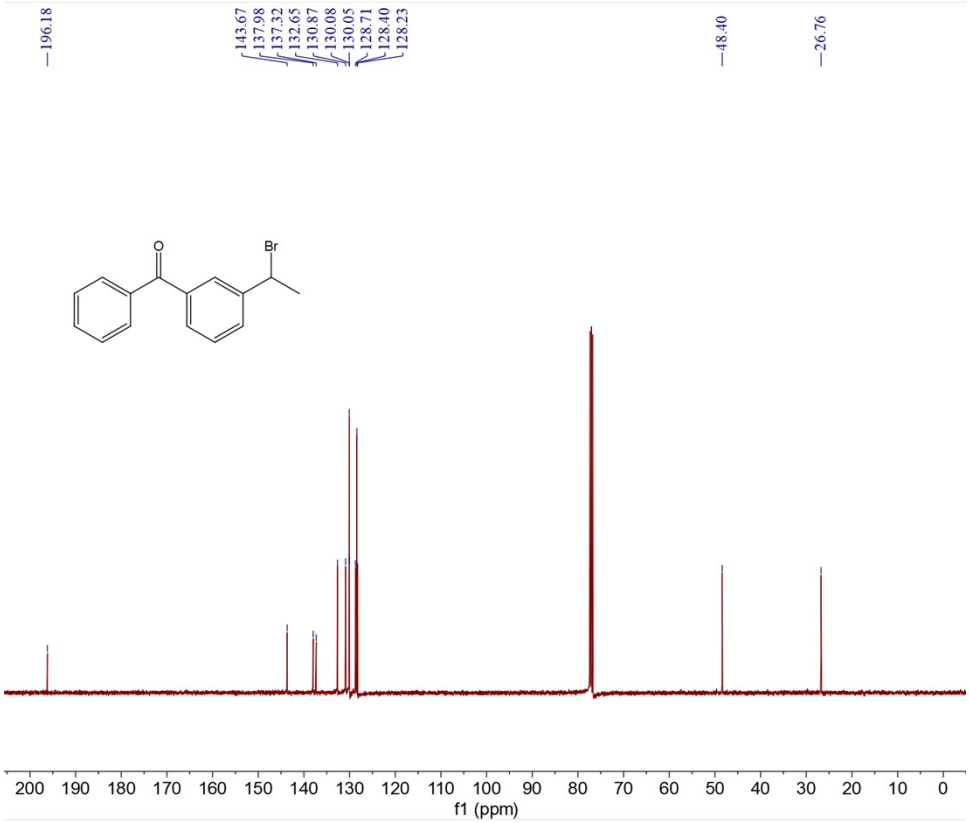
^{13}C NMR of compound **31**



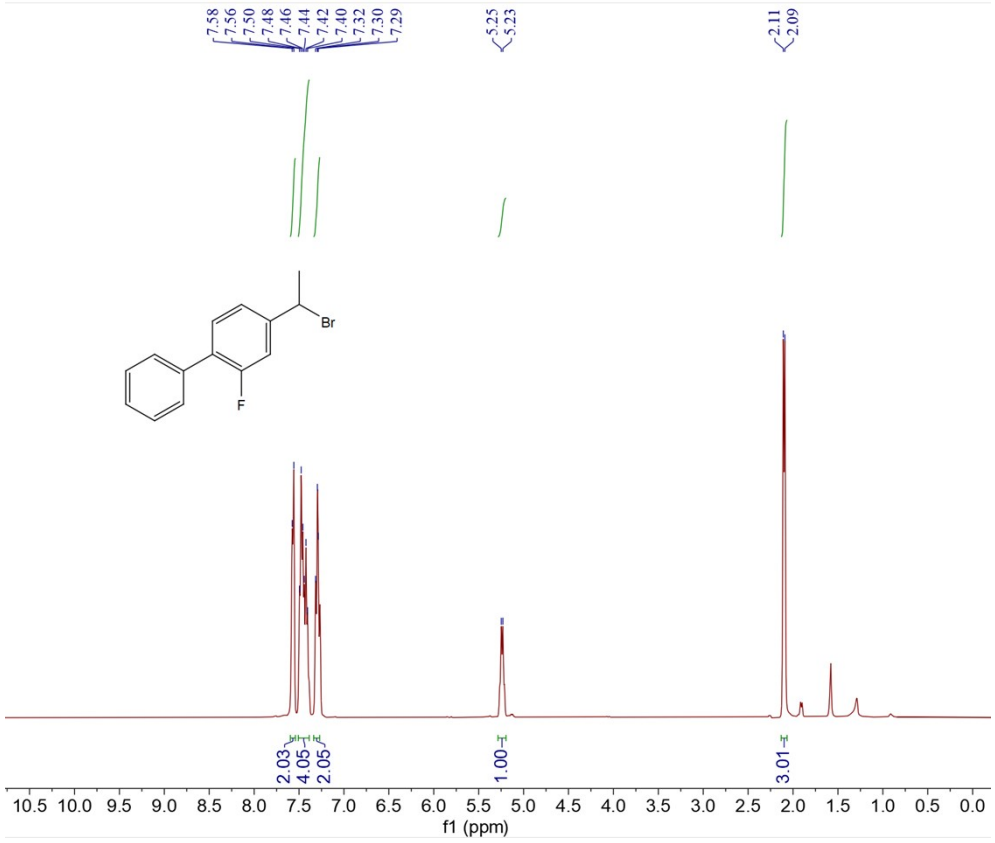
^{1}H NMR of compound **32**



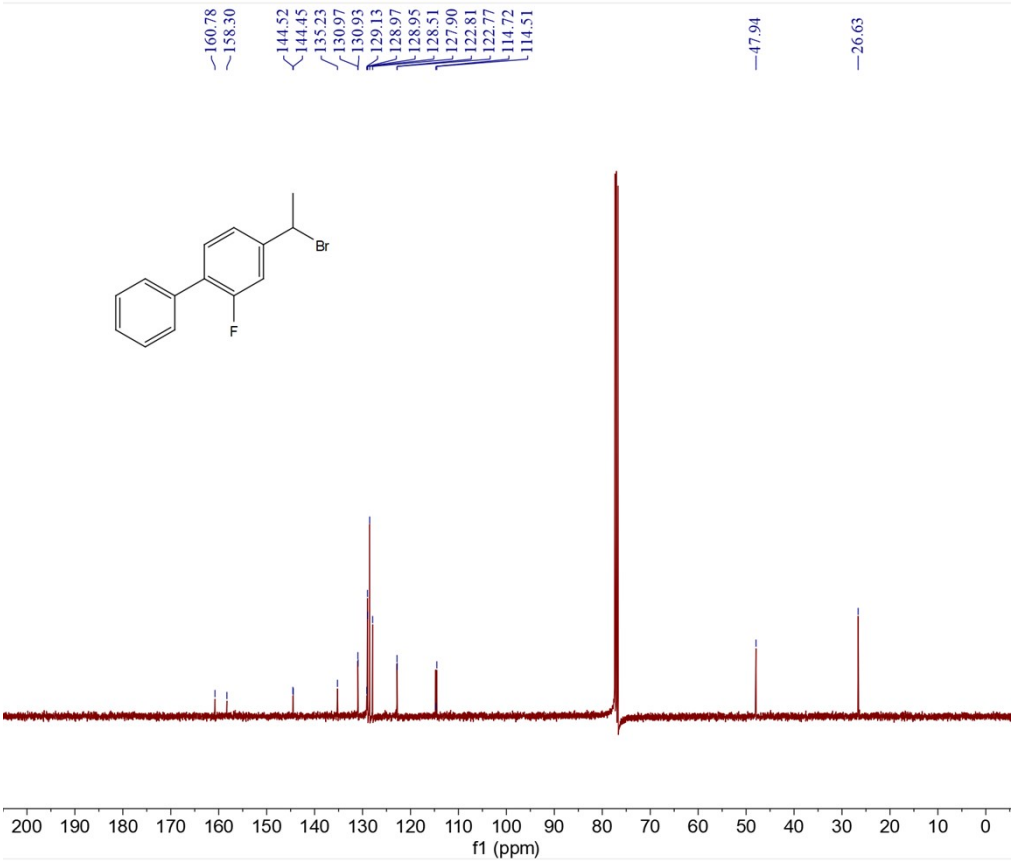
^{13}C NMR of compound **32**



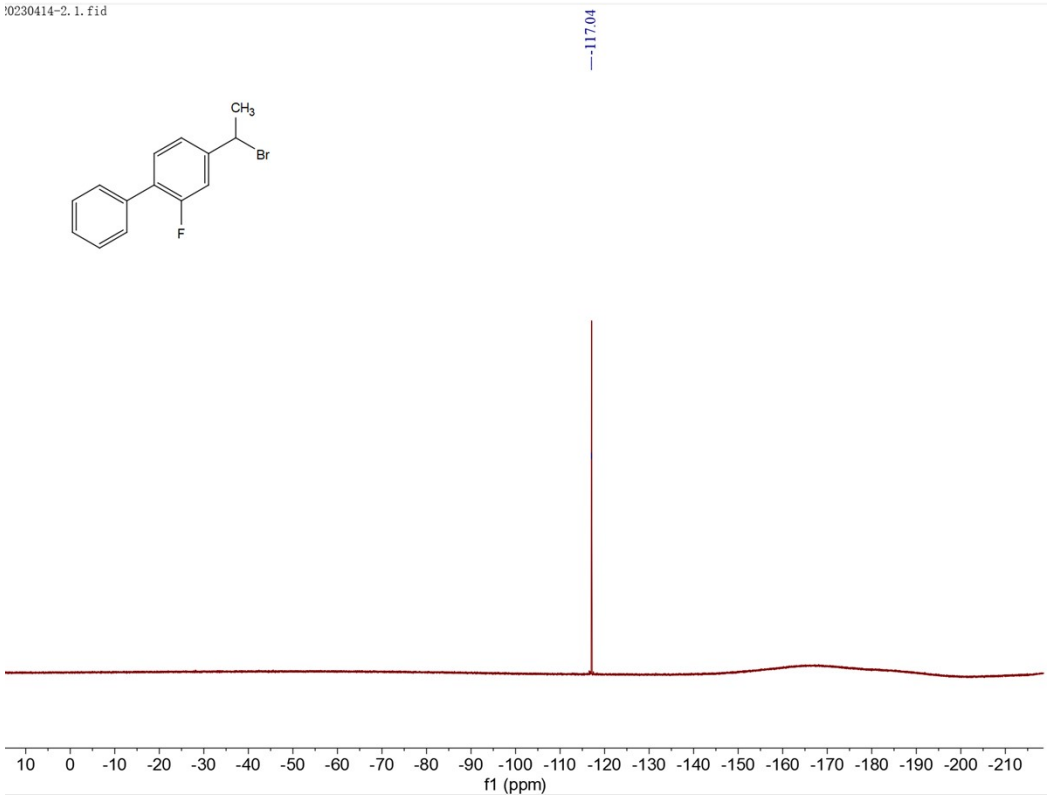
^{1}H NMR of compound **33**



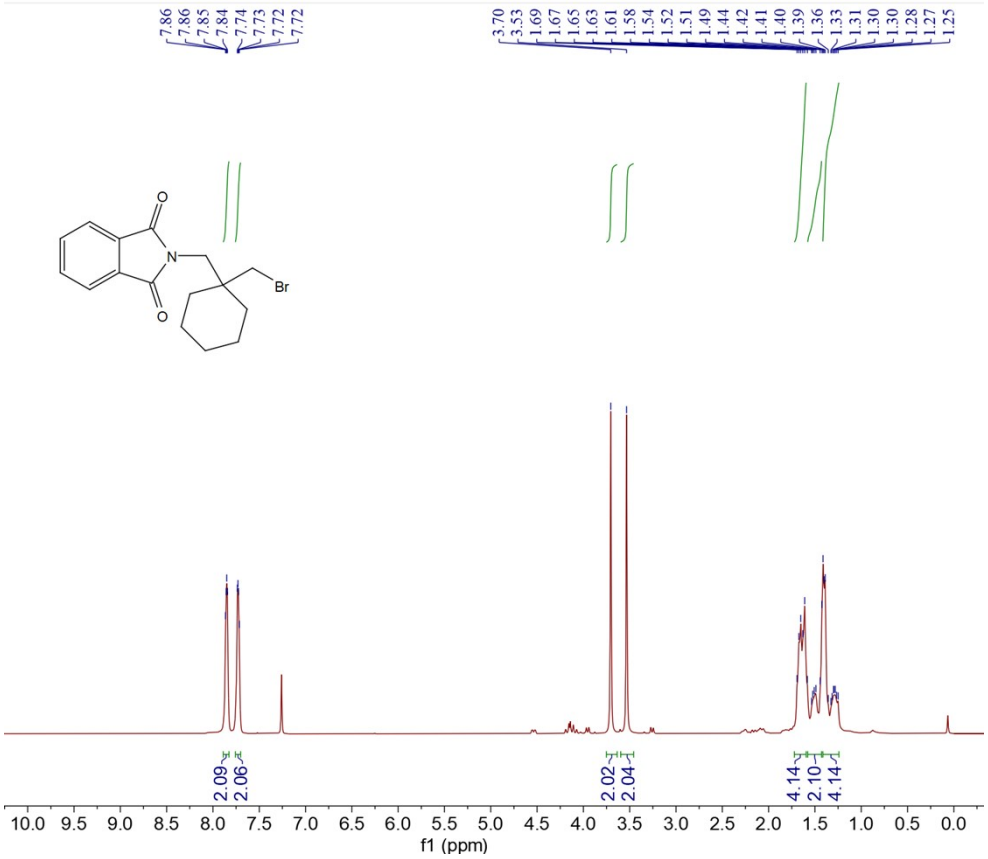
^{13}C NMR of compound **33**



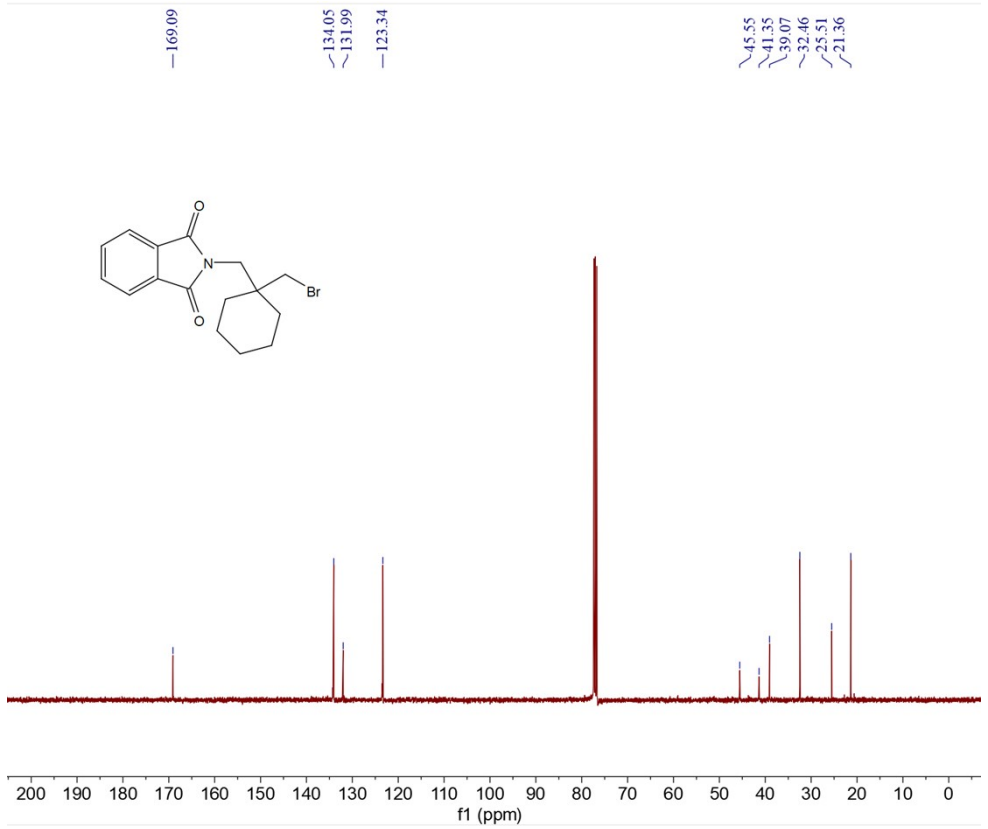
^{19}F NMR of compound **33**



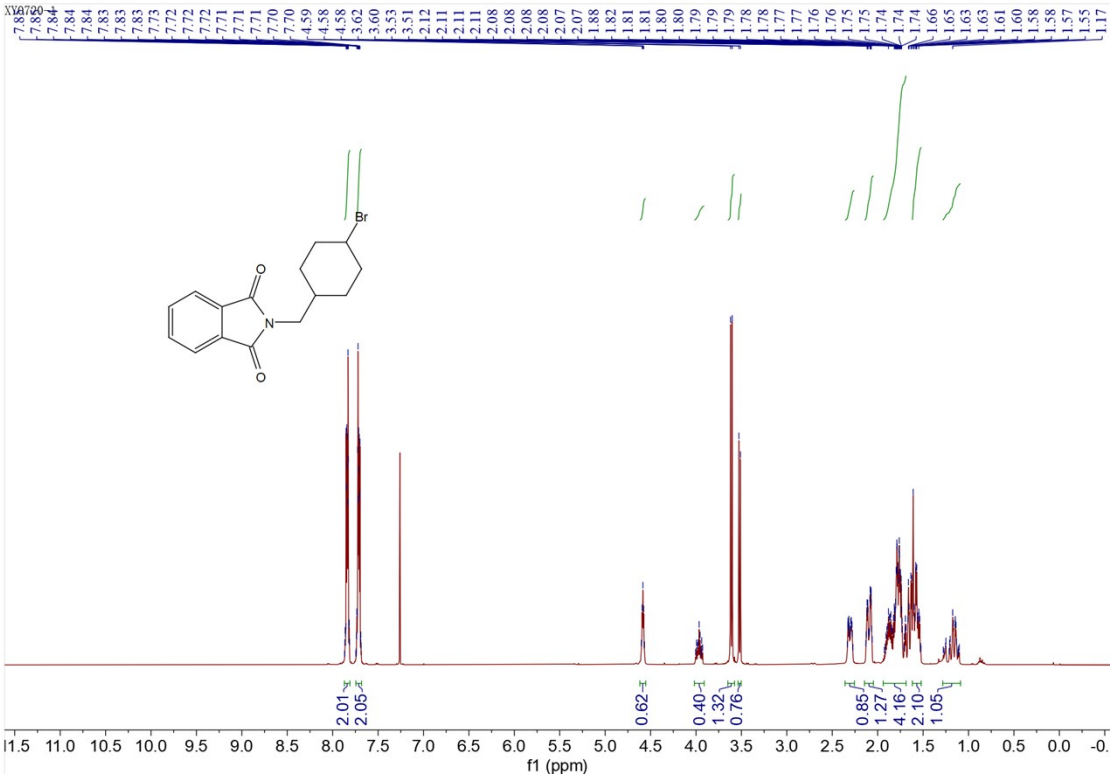
^{1}H NMR of compound **34**



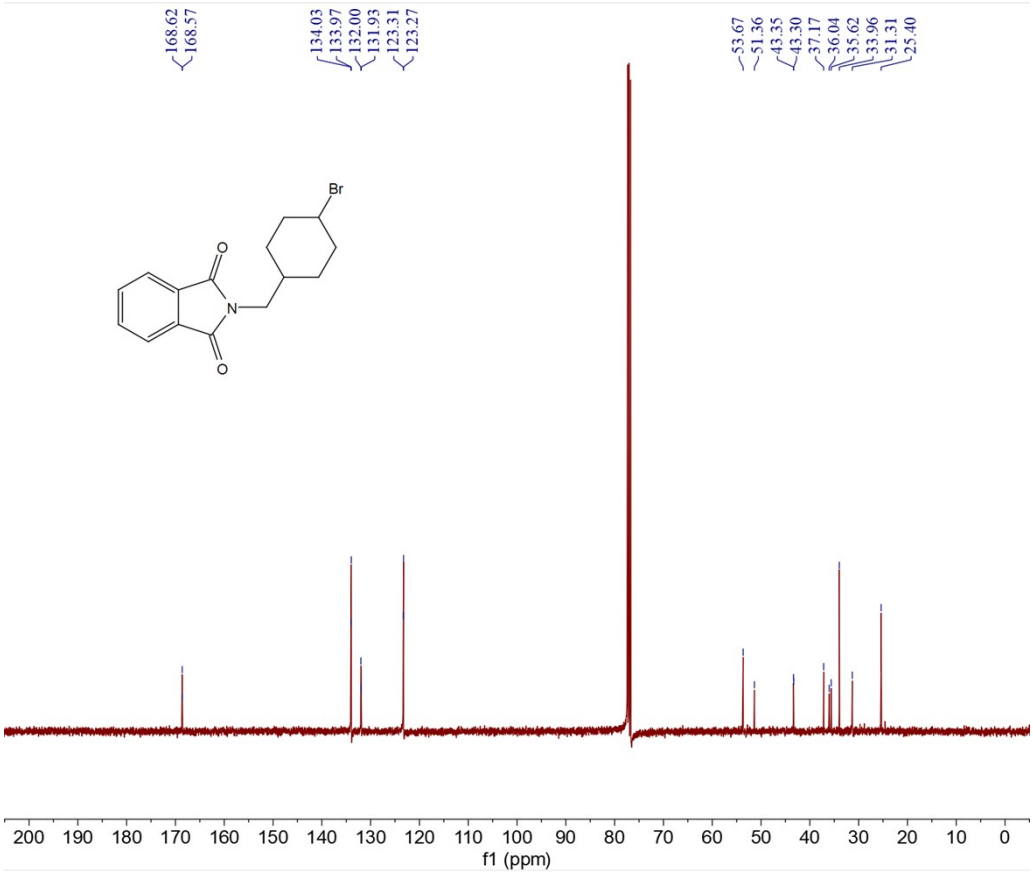
^{13}C NMR of compound **34**



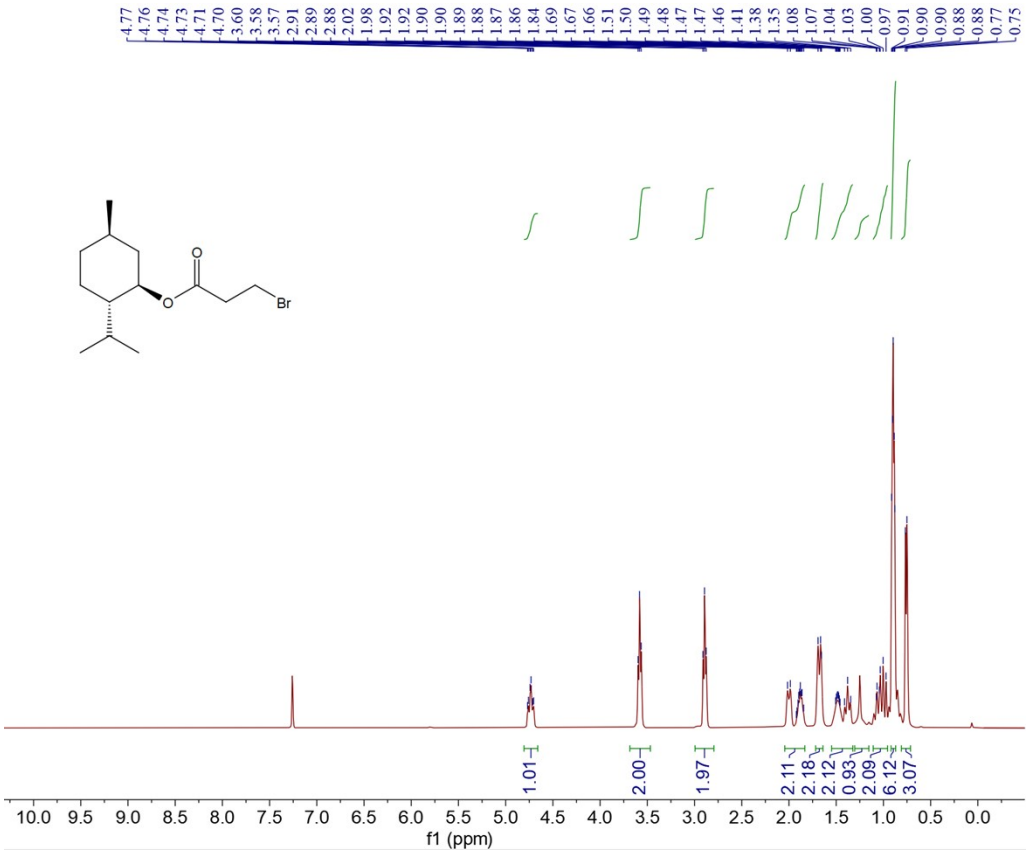
^{1}H NMR of compound **35**



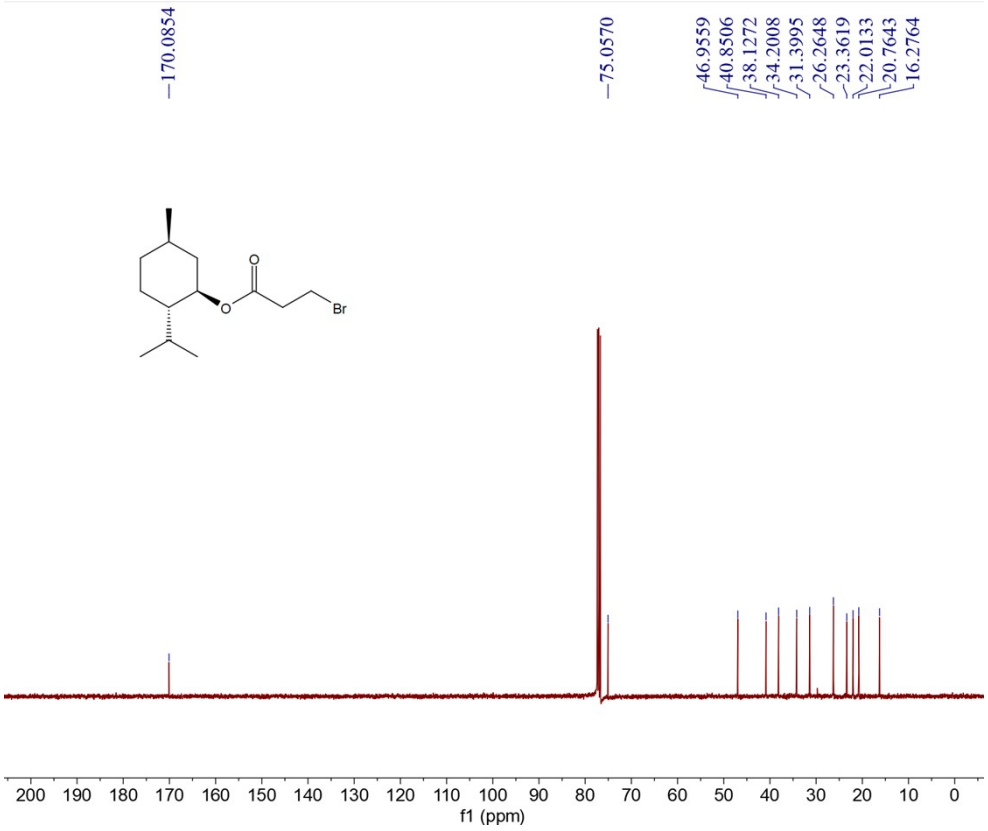
^{13}C NMR of compound **35**



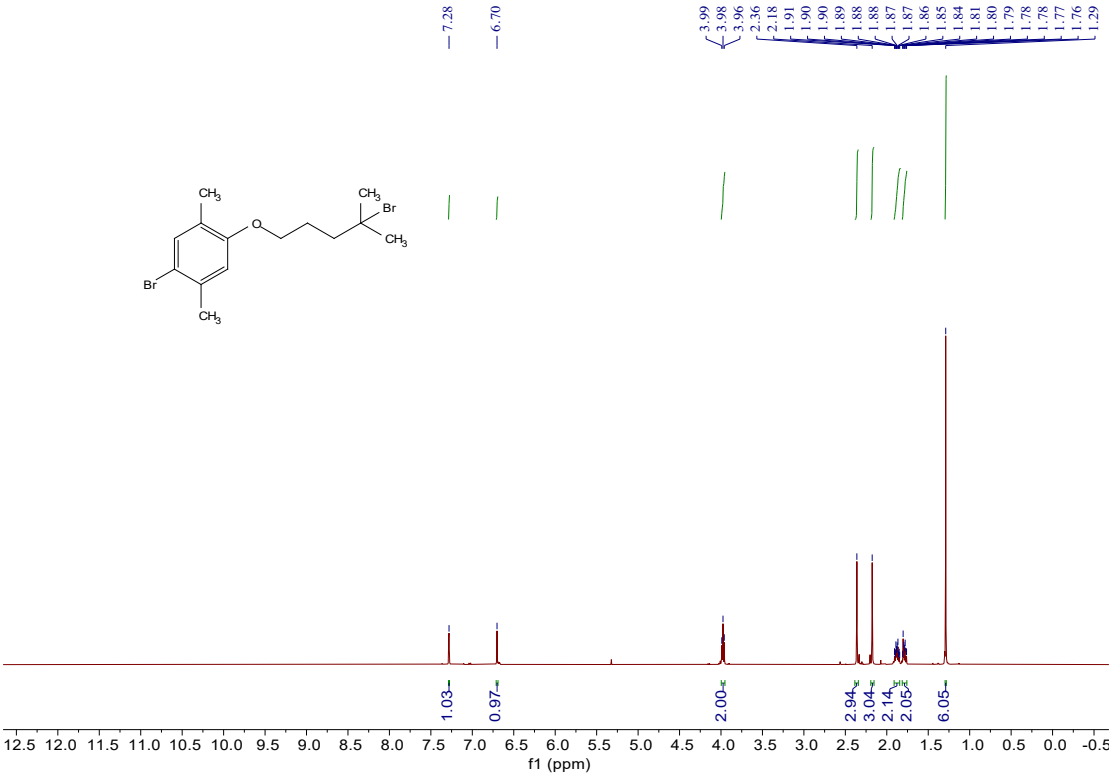
^{1}H NMR of compound **36**



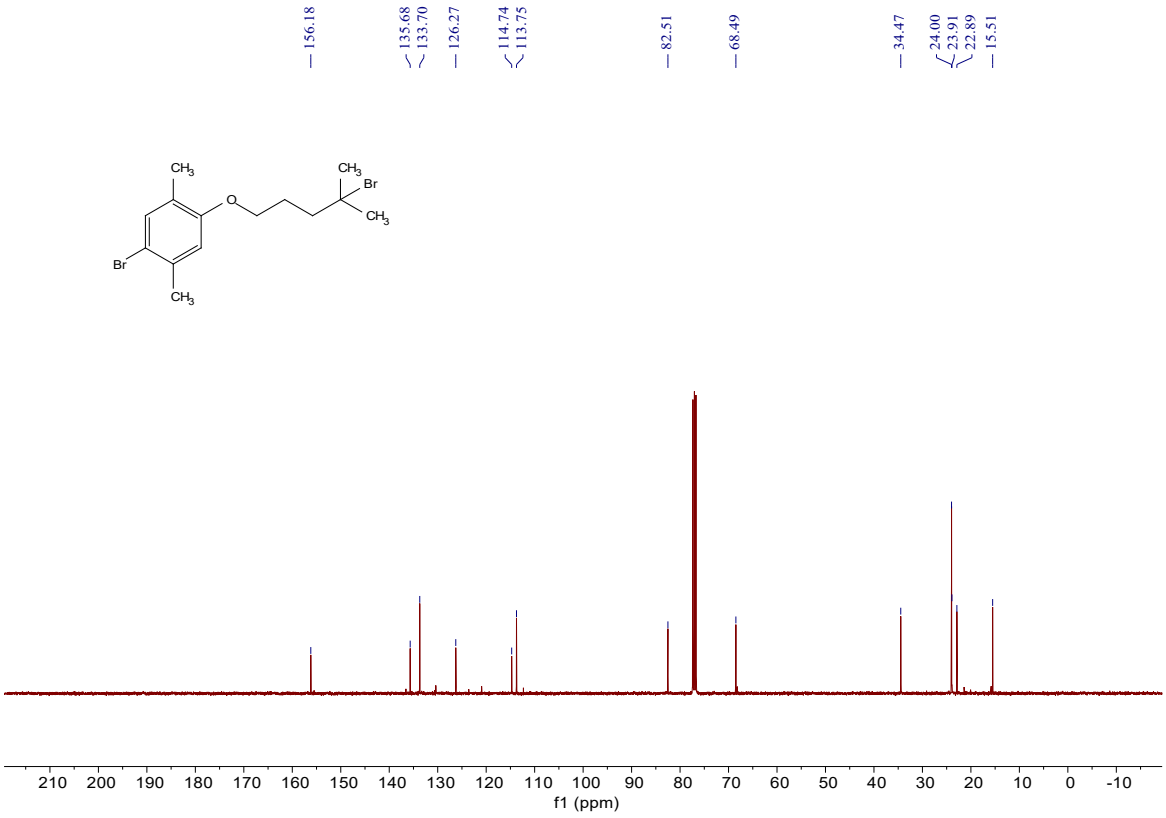
^{13}C NMR of compound **36**



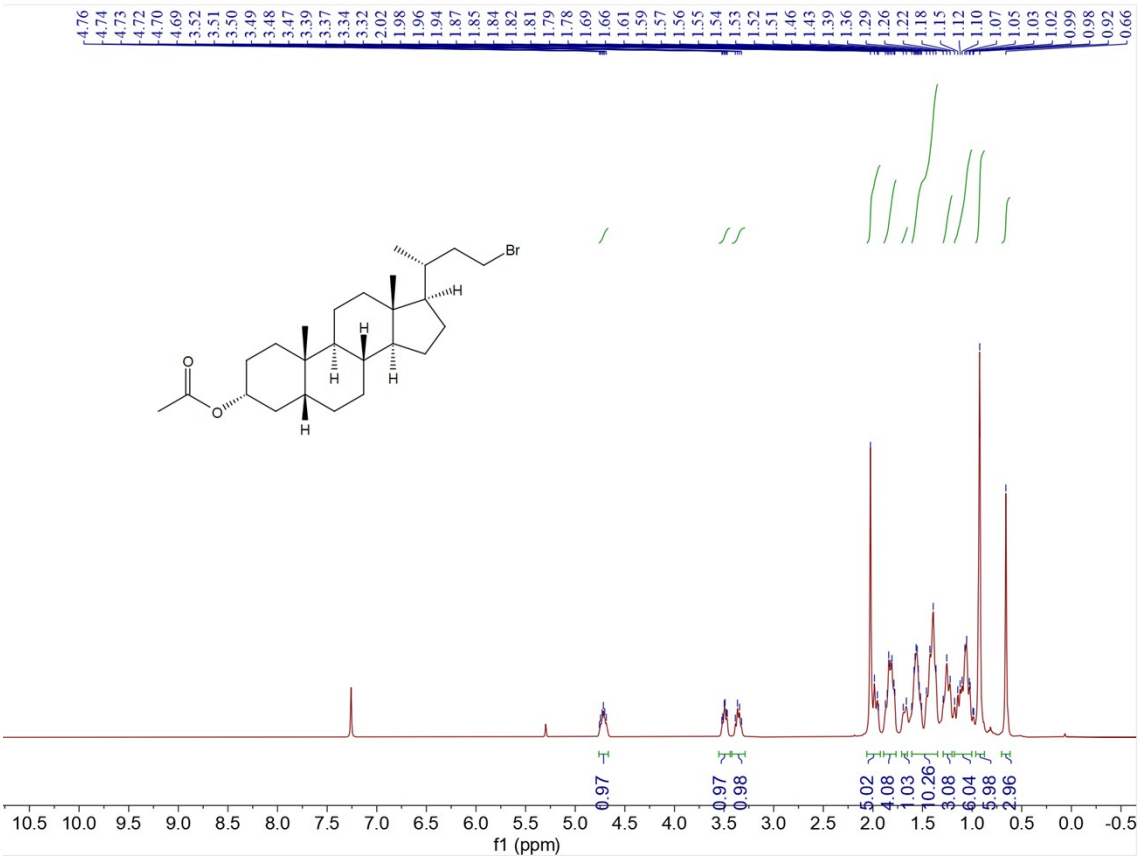
^{1}H NMR of compound **37**



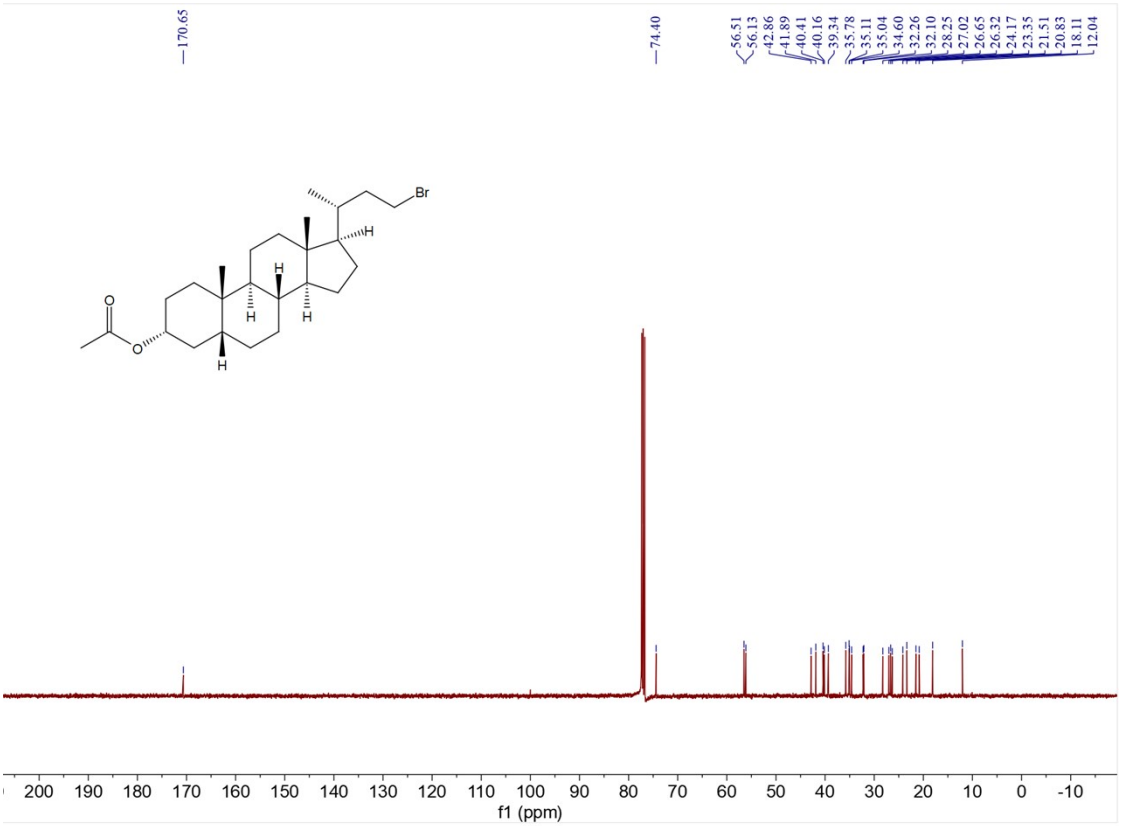
^{13}C NMR of compound **37**



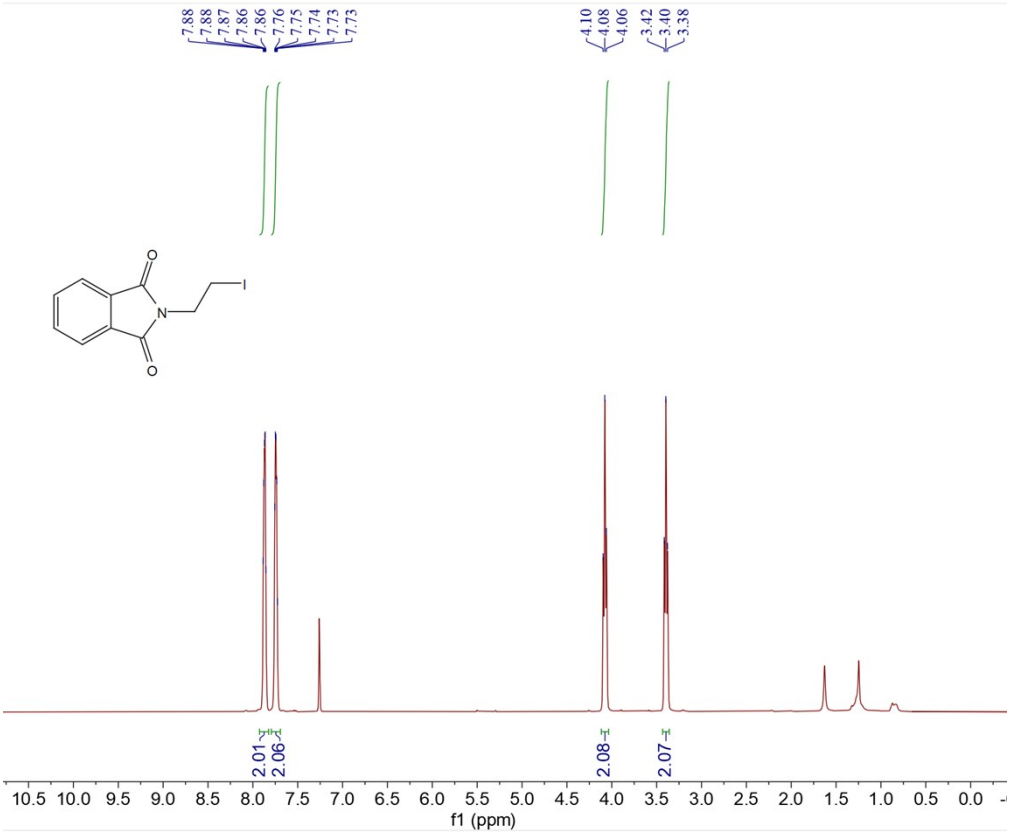
^{1}H NMR of compound **38**



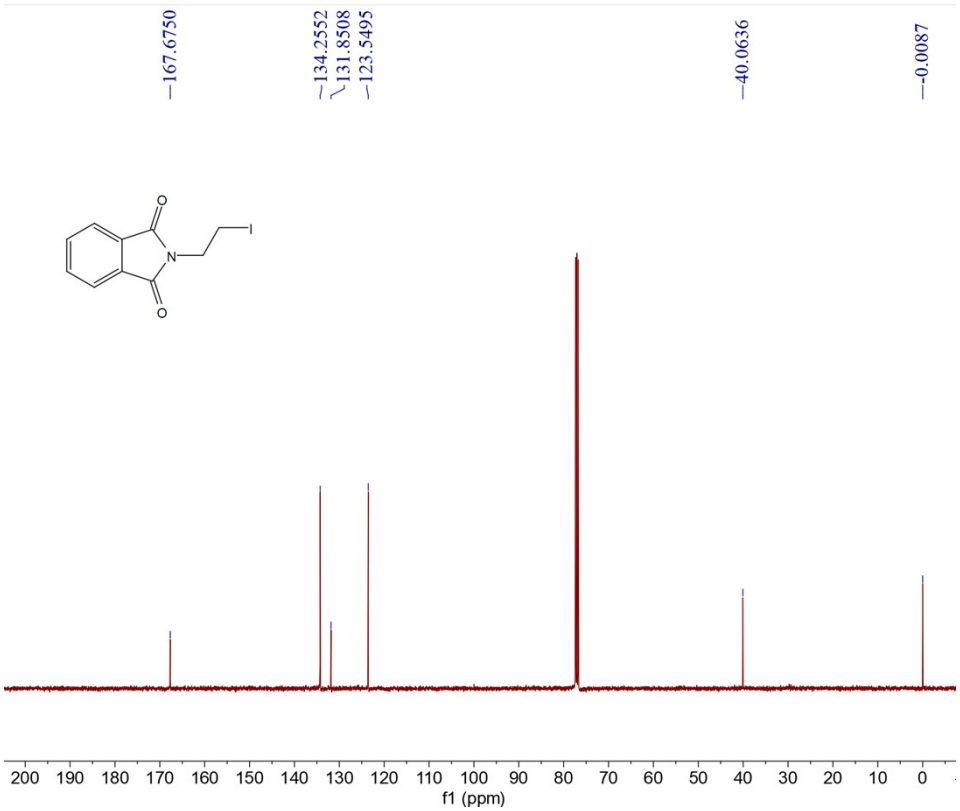
^{13}C NMR of compound **38**



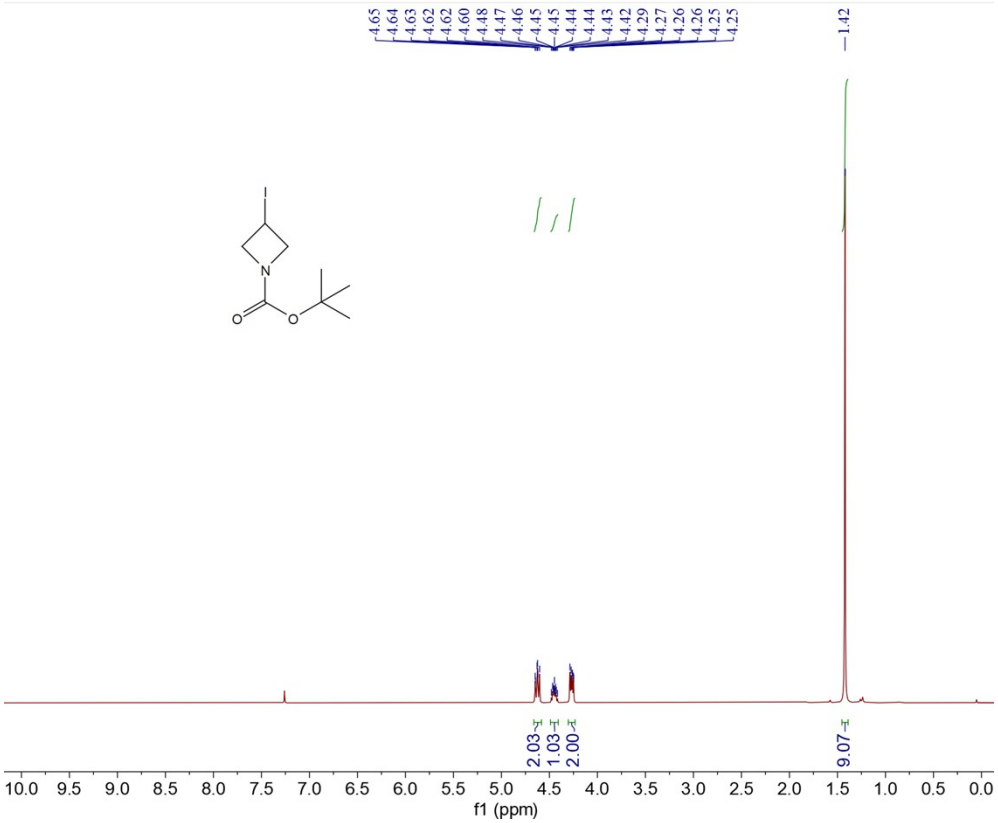
^{1}H NMR of compound **39**



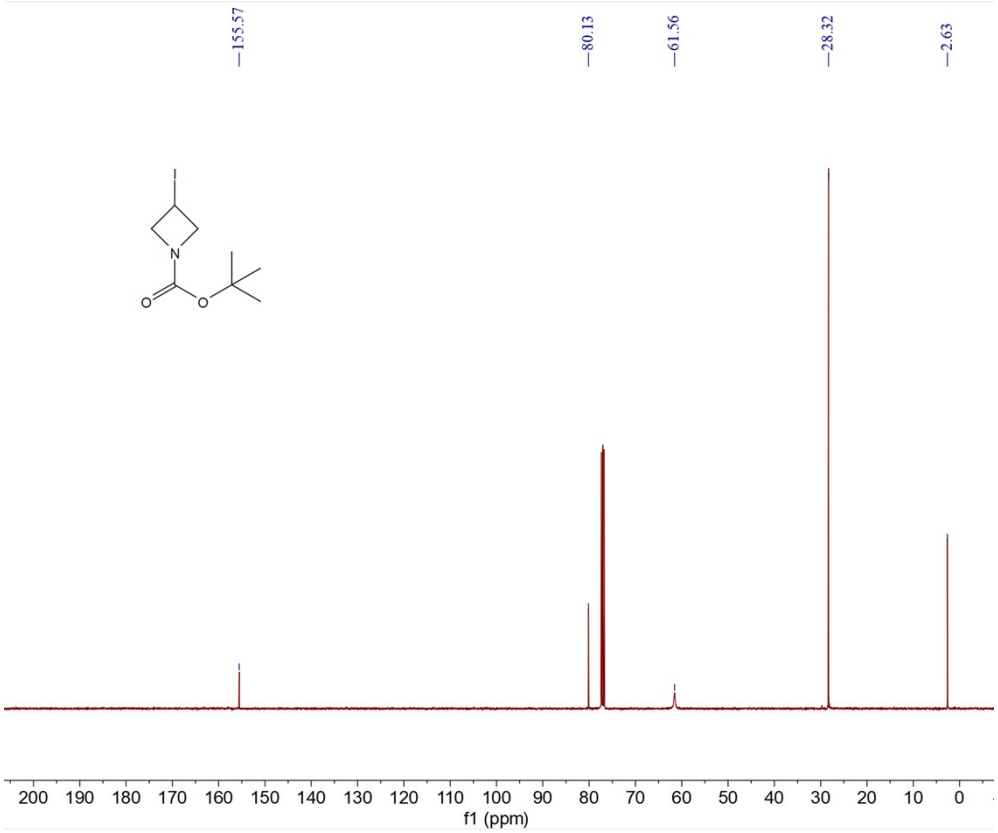
^{13}C NMR of compound **39**



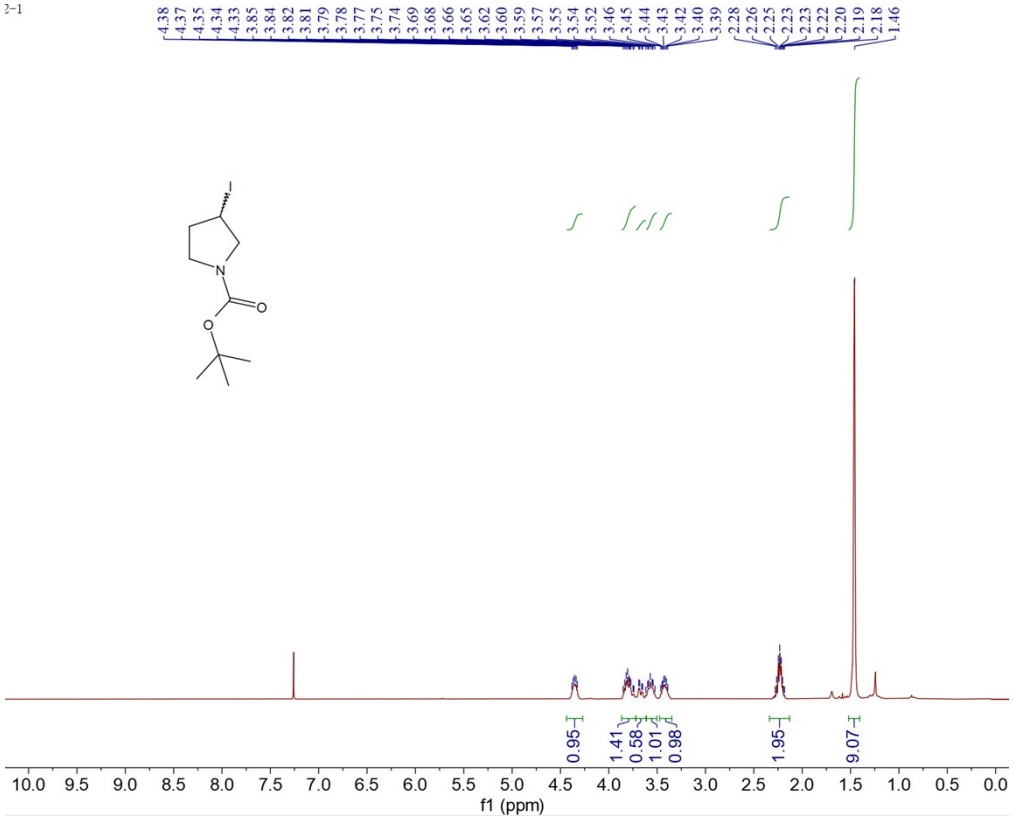
^{1}H NMR of compound **40**



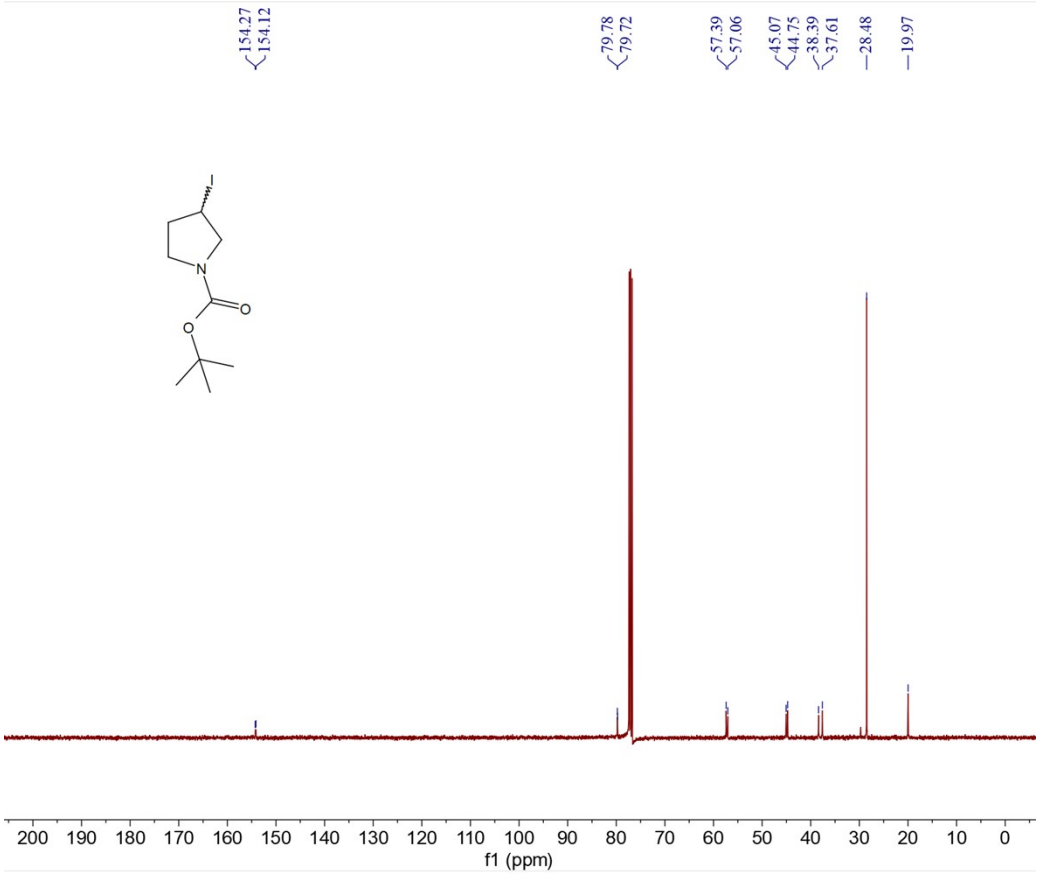
^{13}C NMR of compound **40**



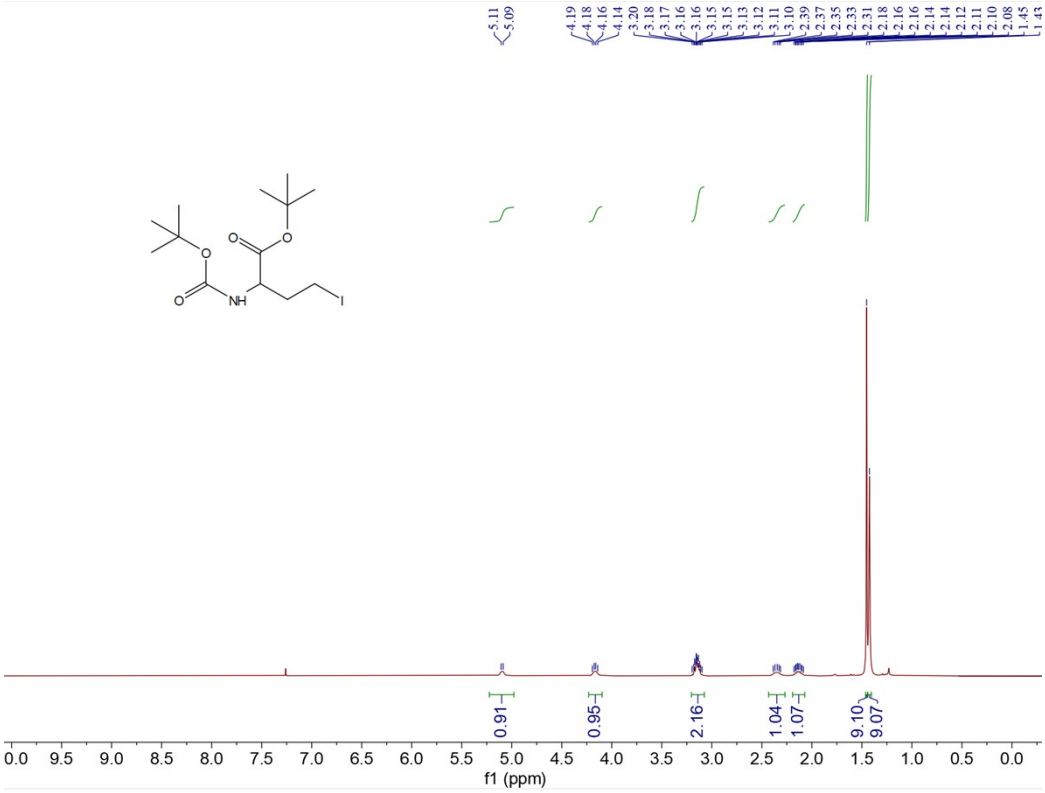
^{1}H NMR of compound **41**



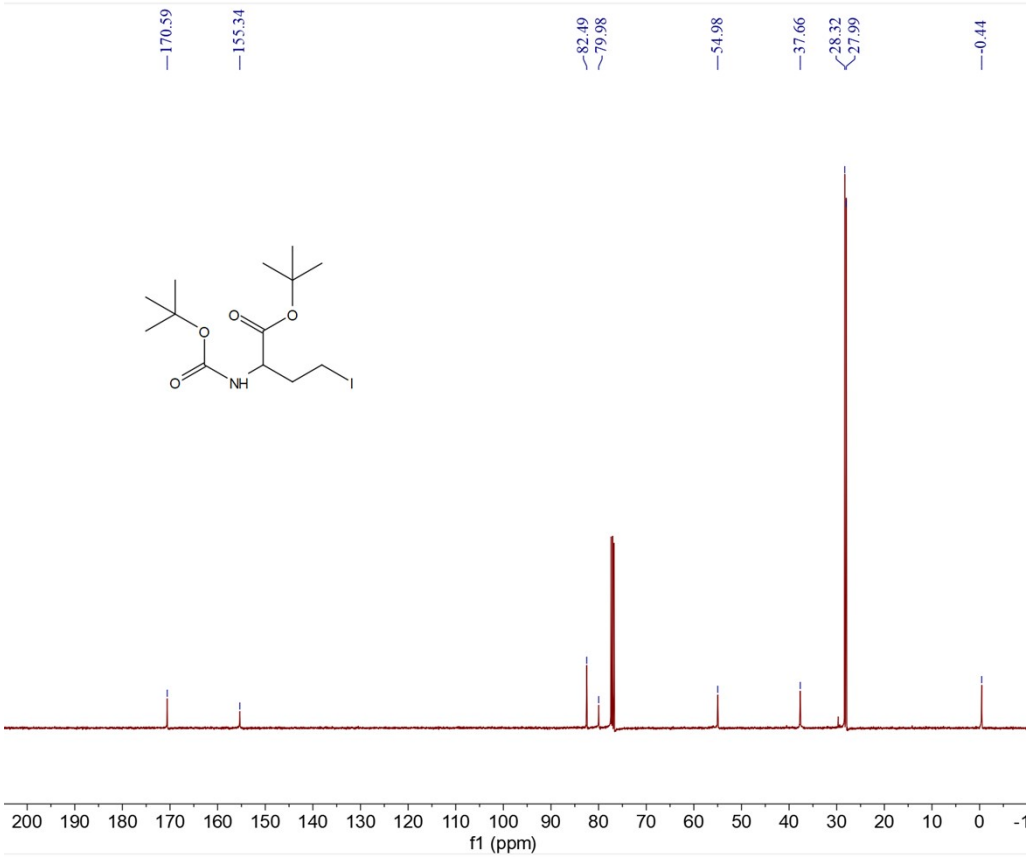
^{13}C NMR of compound **41**



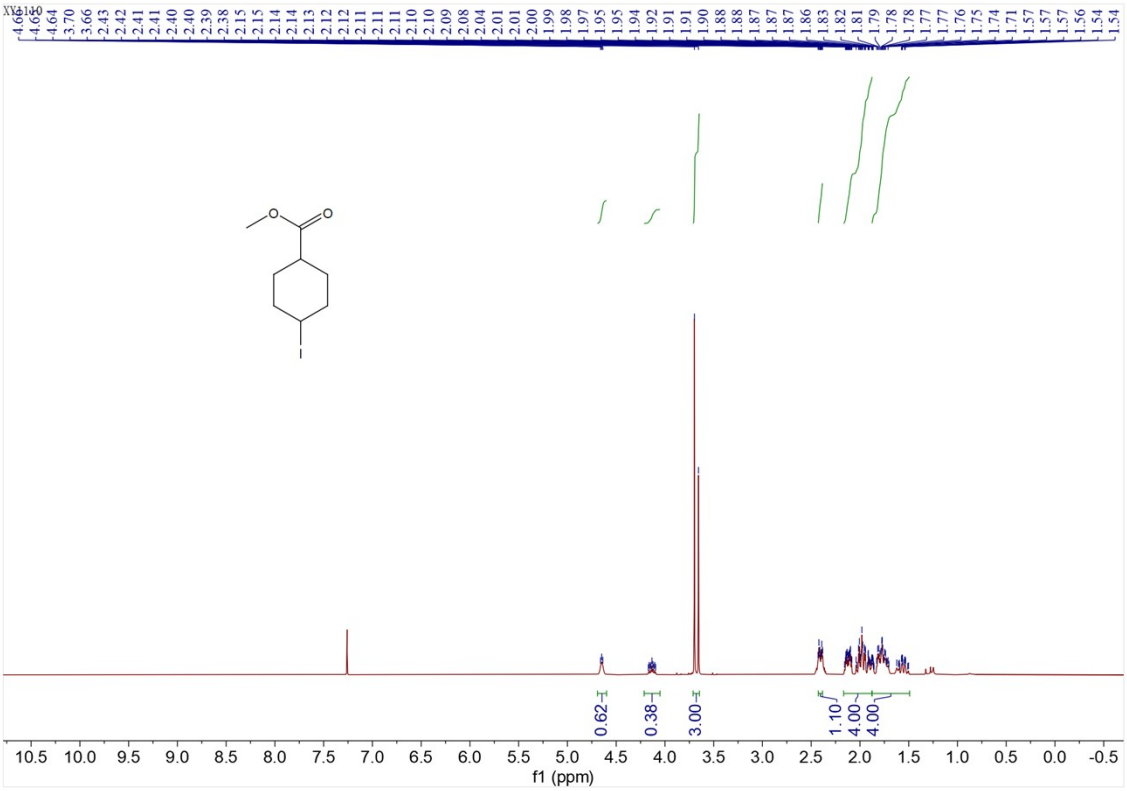
^{1}H NMR of compound **42**



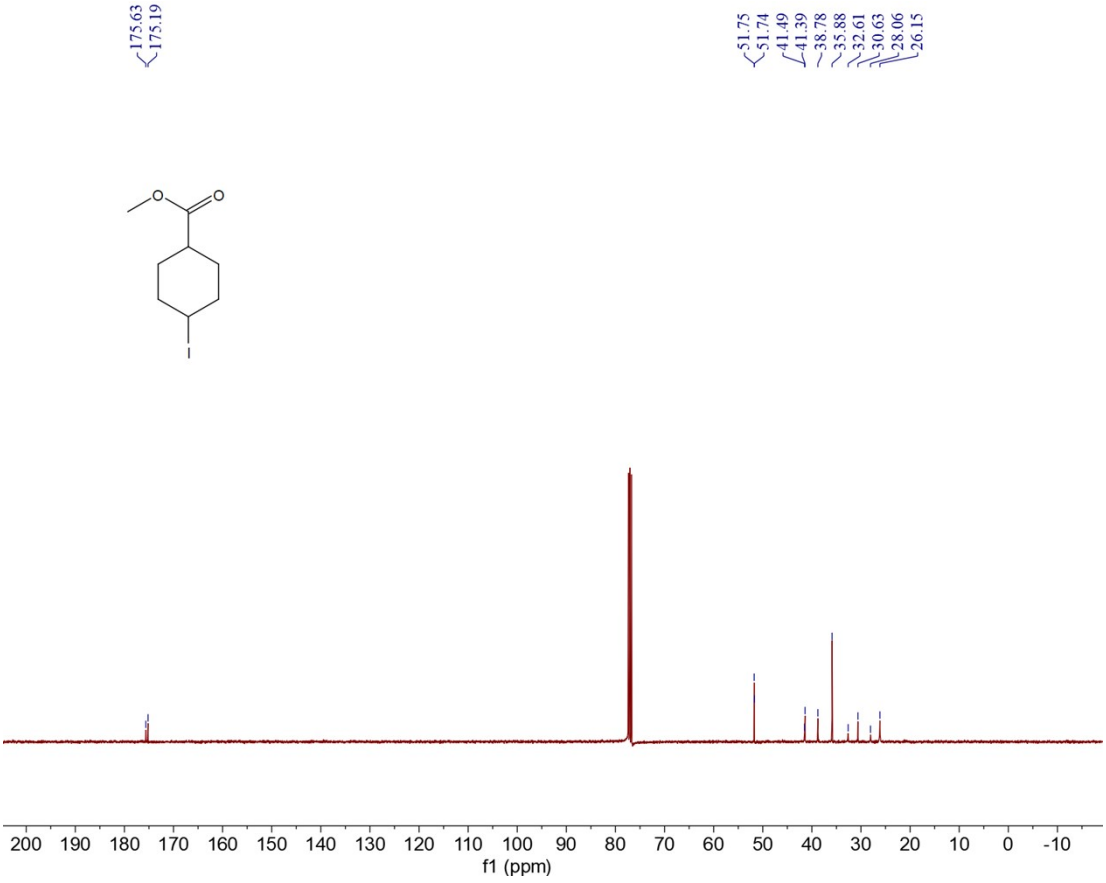
^{13}C NMR of compound **42**



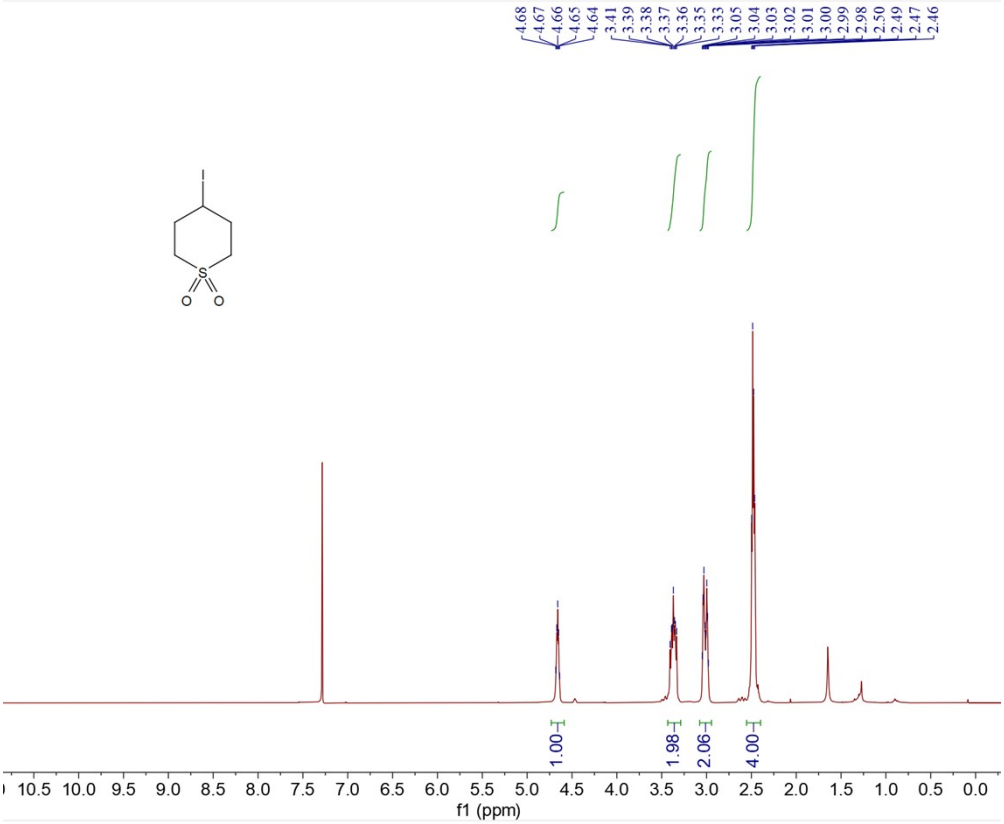
^{1}H NMR of compound **43**



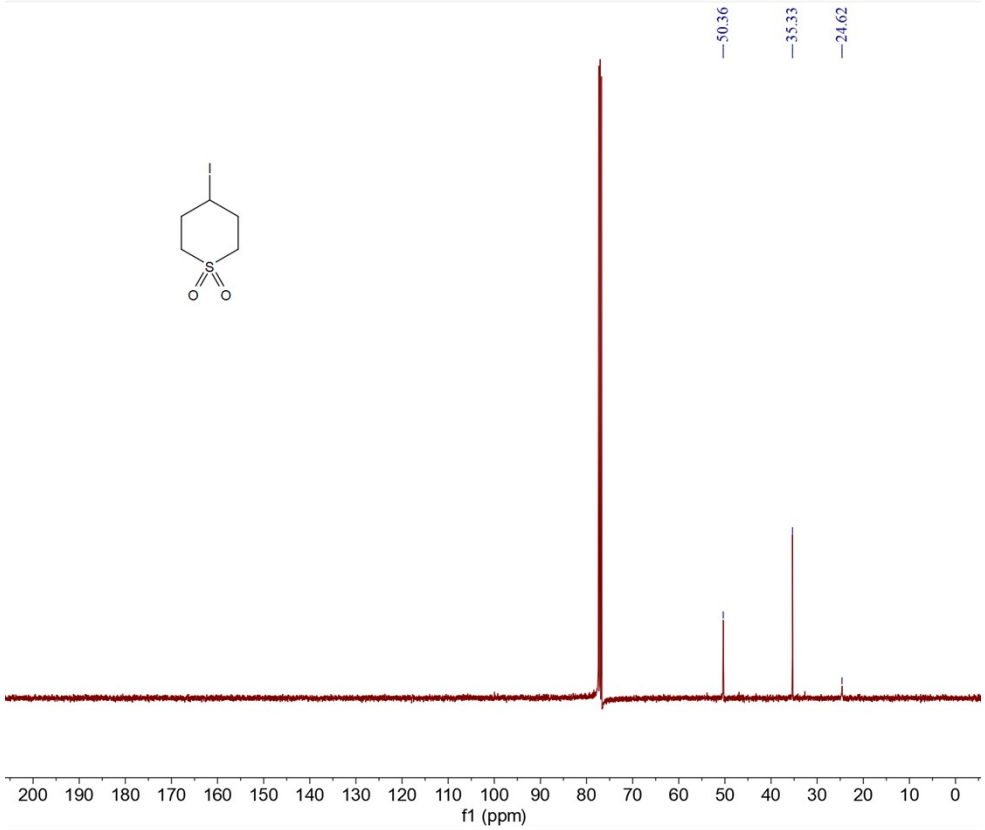
^{13}C NMR of compound **43**



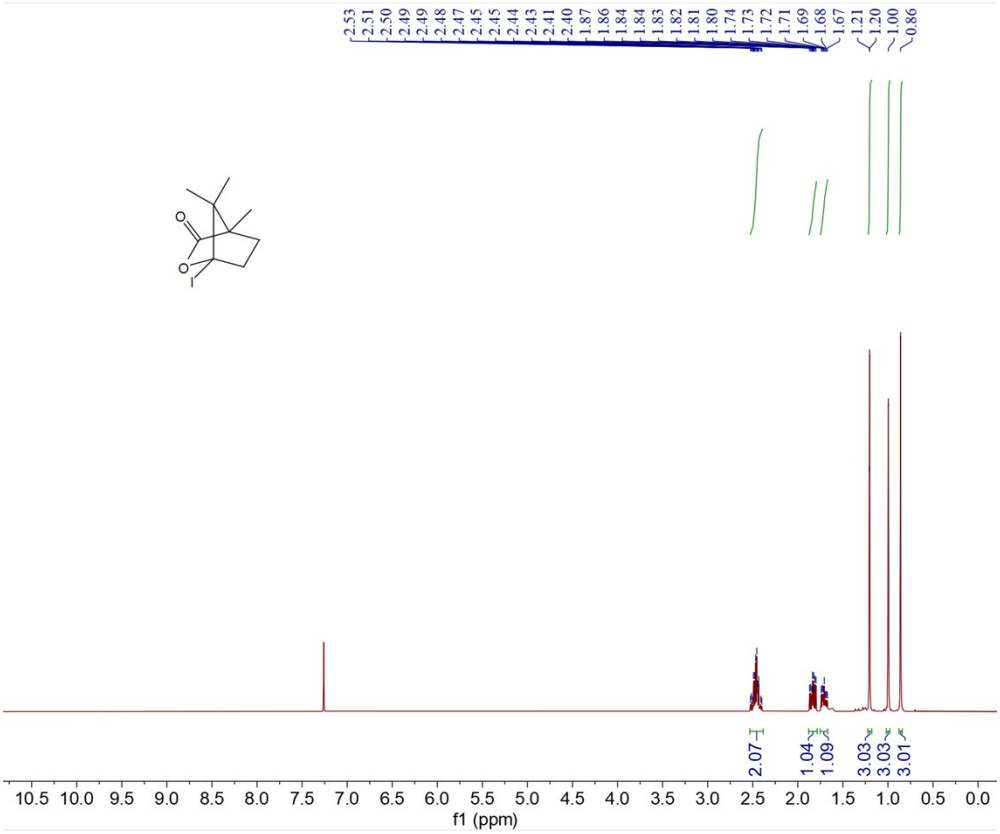
^{1}H NMR of compound **44**



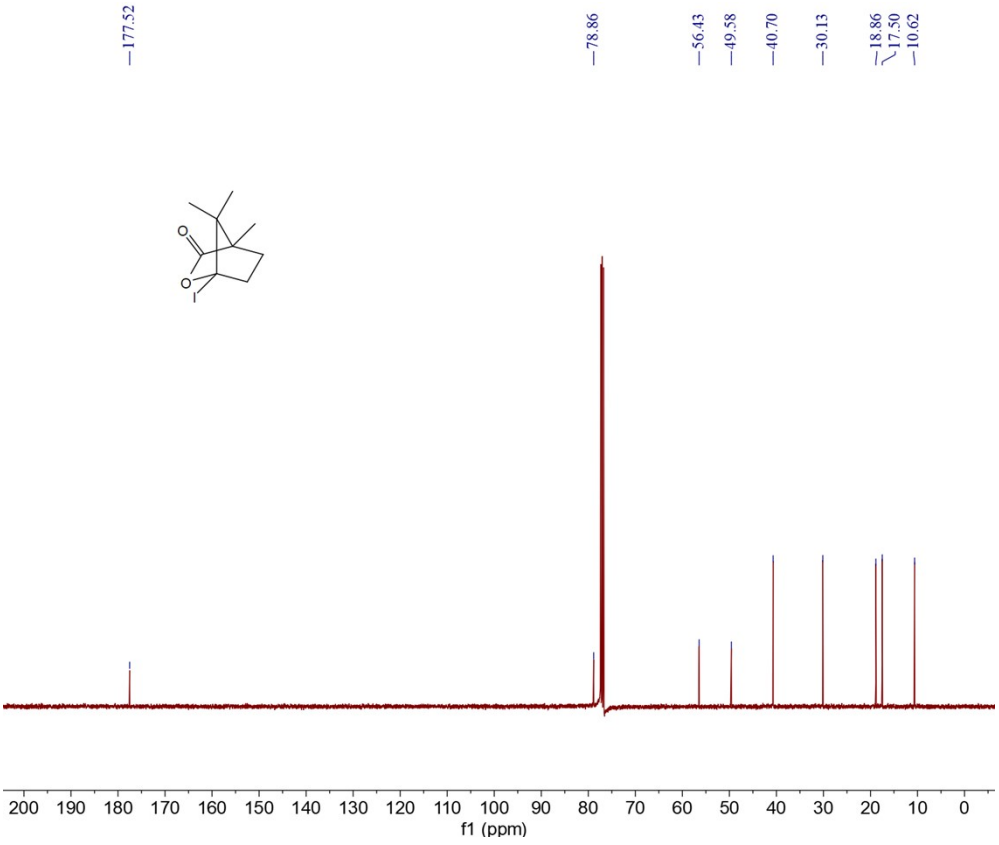
^{13}C NMR of compound **44**



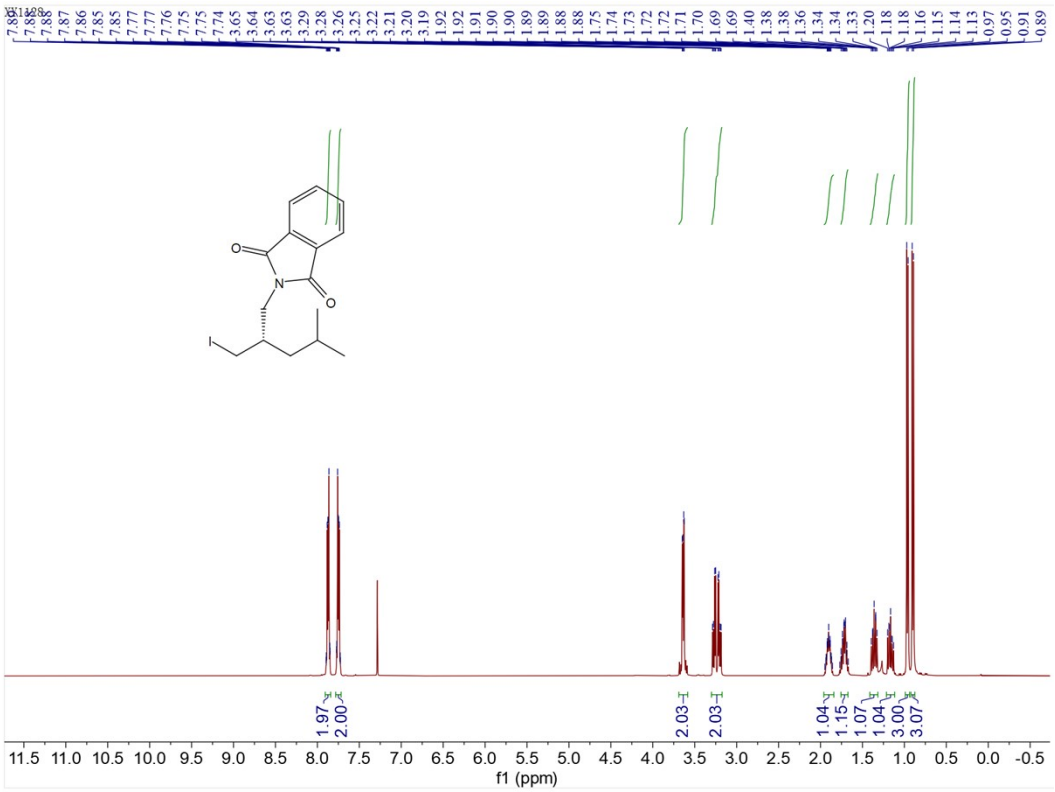
^{1}H NMR of compound **45**



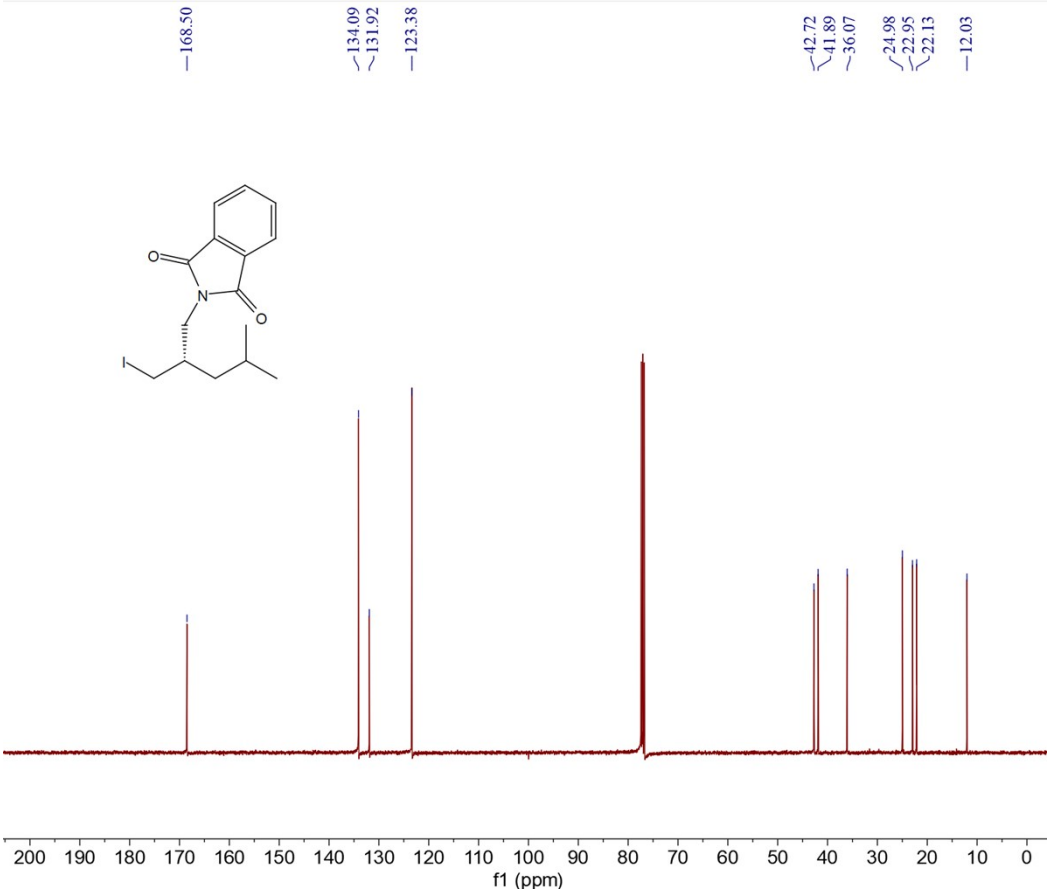
^{13}C NMR of compound **45**



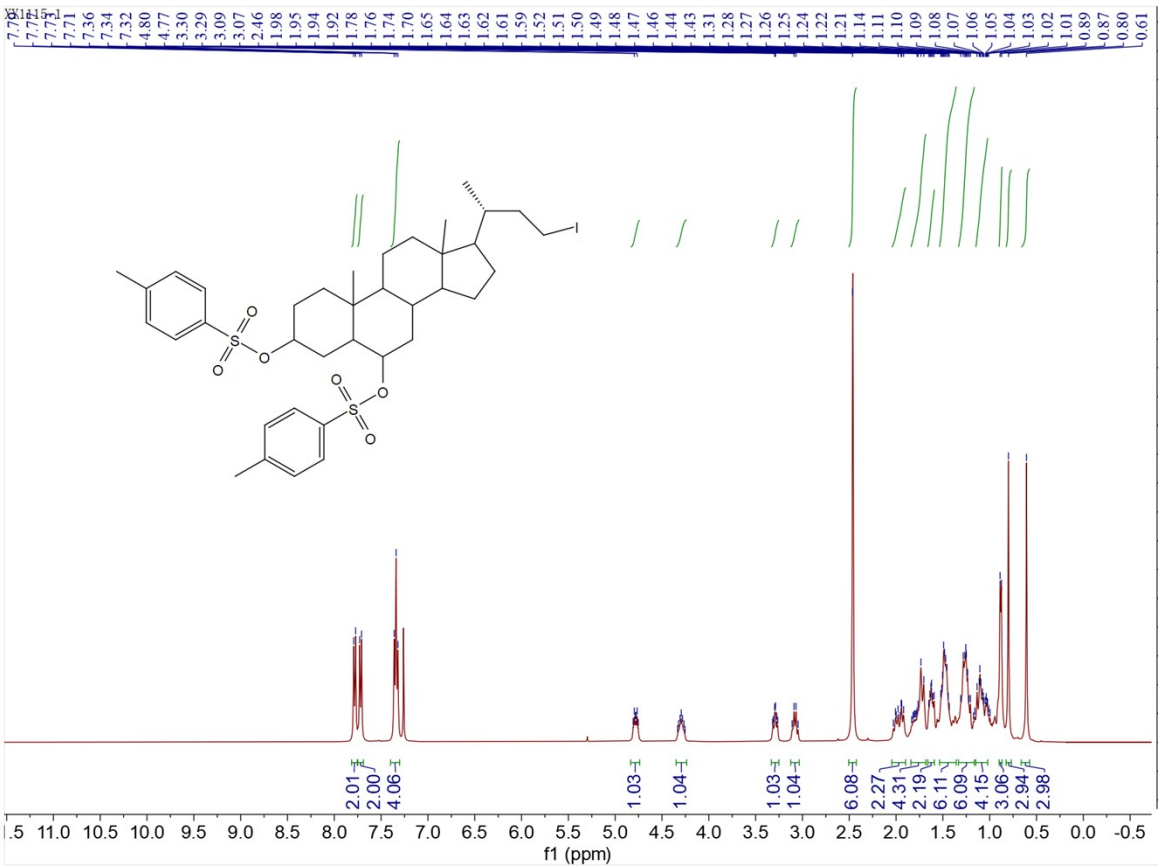
^{1}H NMR of compound **46**



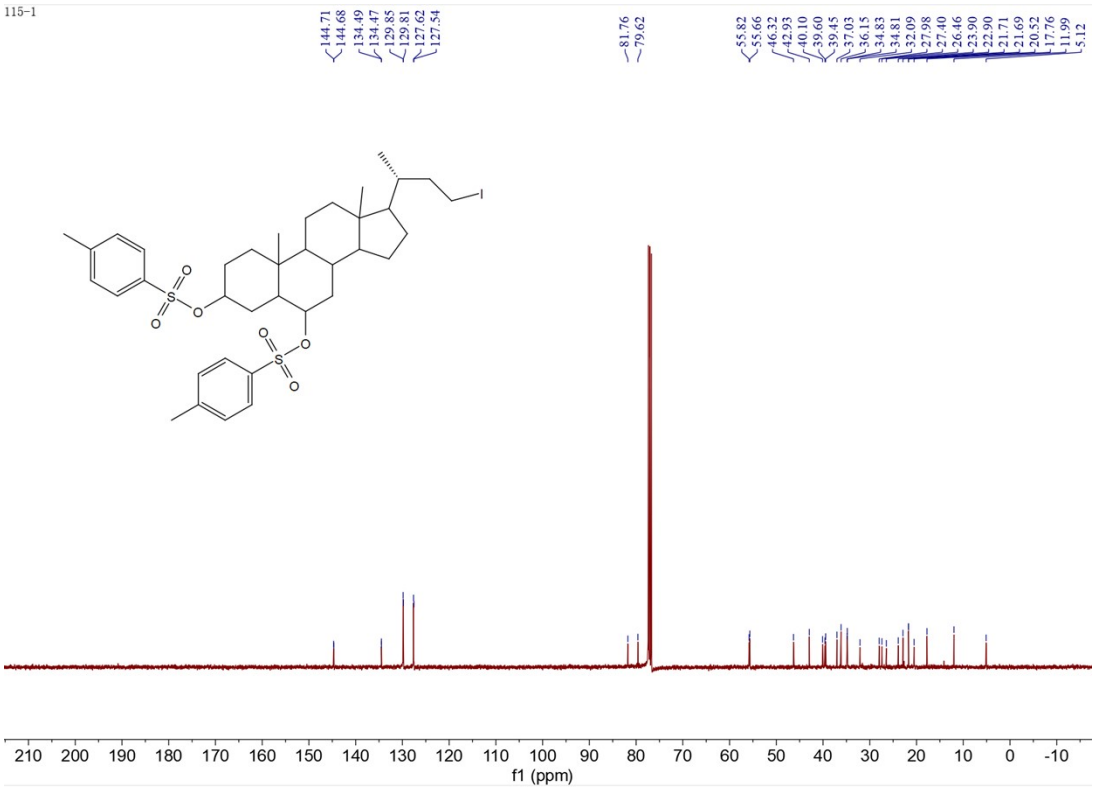
^{13}C NMR of compound **46**



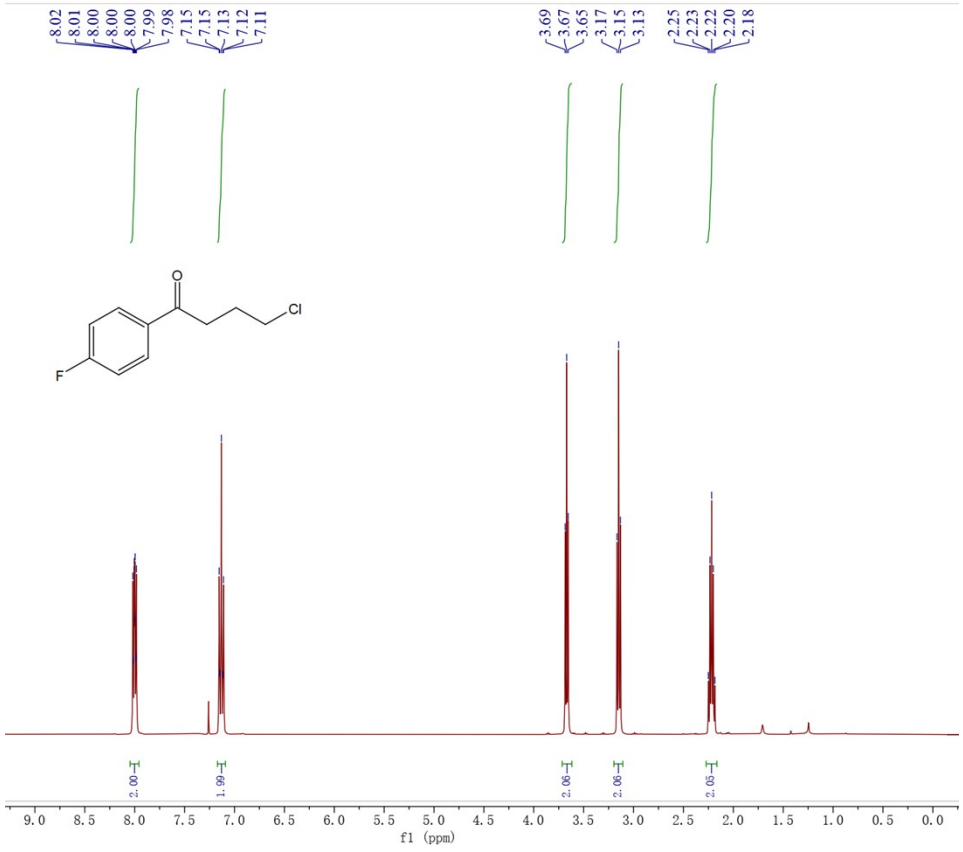
^{1}H NMR of compound **47**



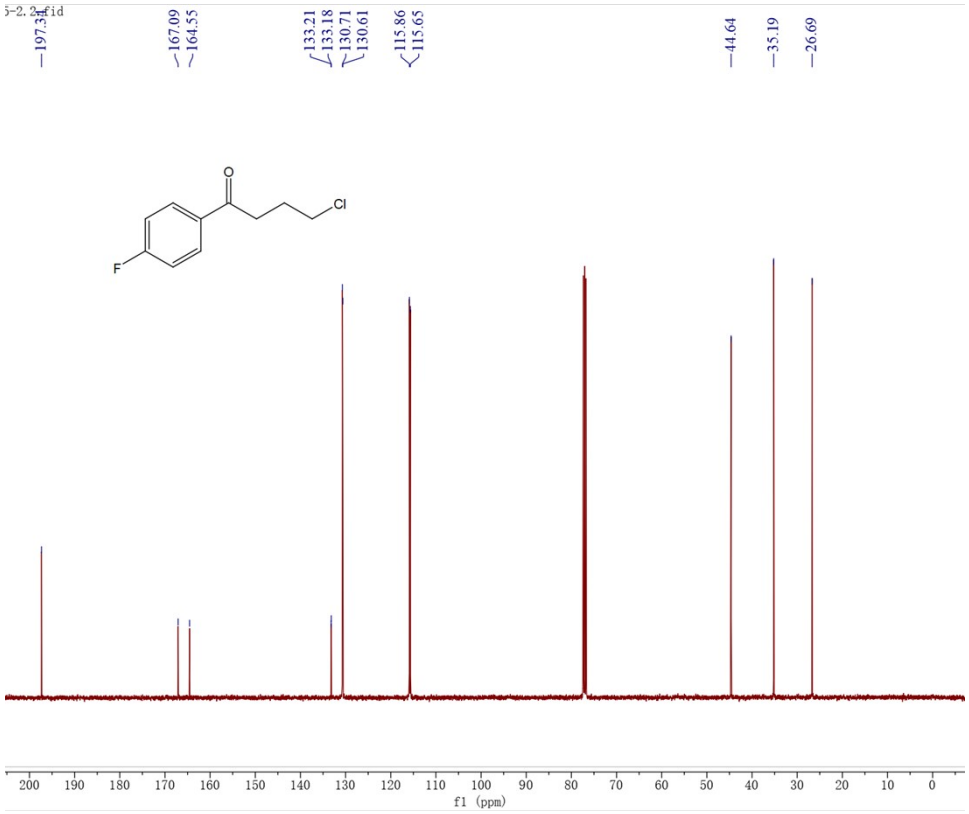
^{13}C NMR of compound **47**



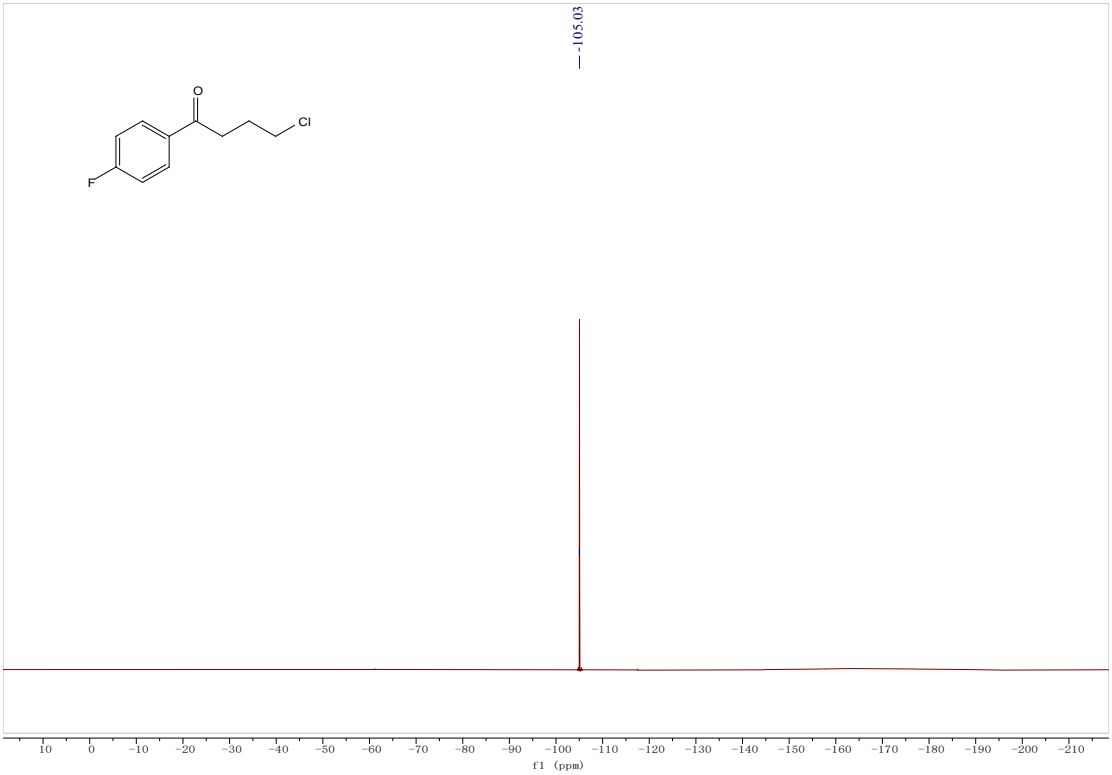
^{1}H NMR of compound **48**



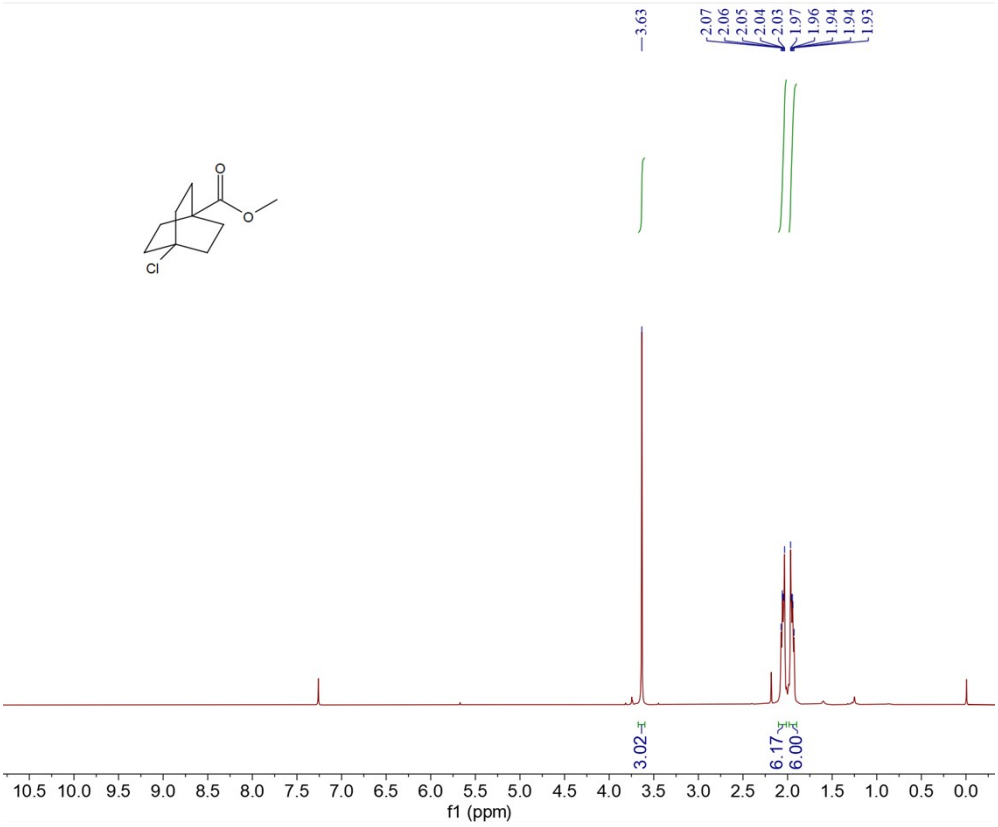
^{13}C NMR of compound **48**



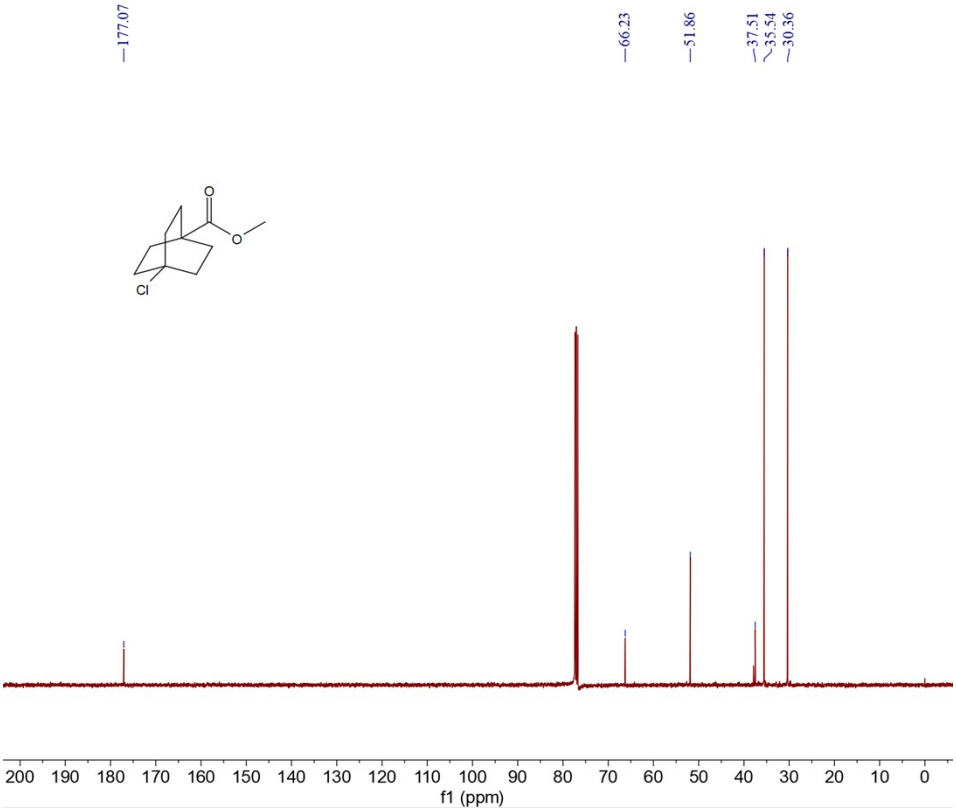
^{19}F NMR of compound **48**



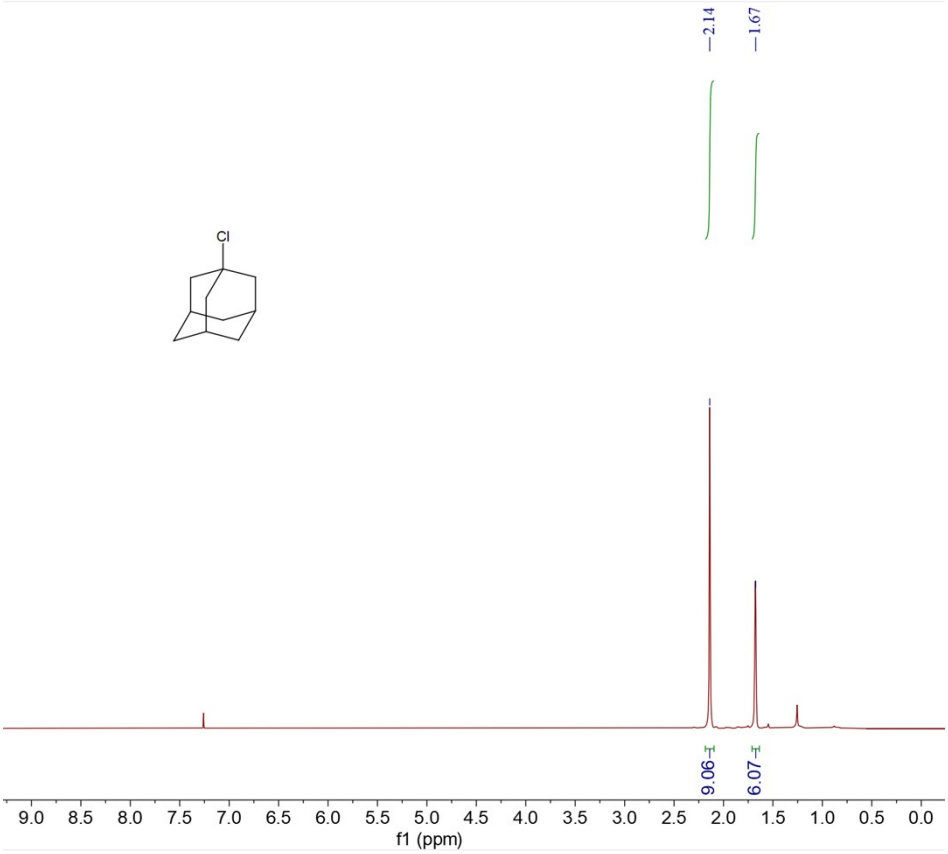
^{1}H NMR of compound **49**



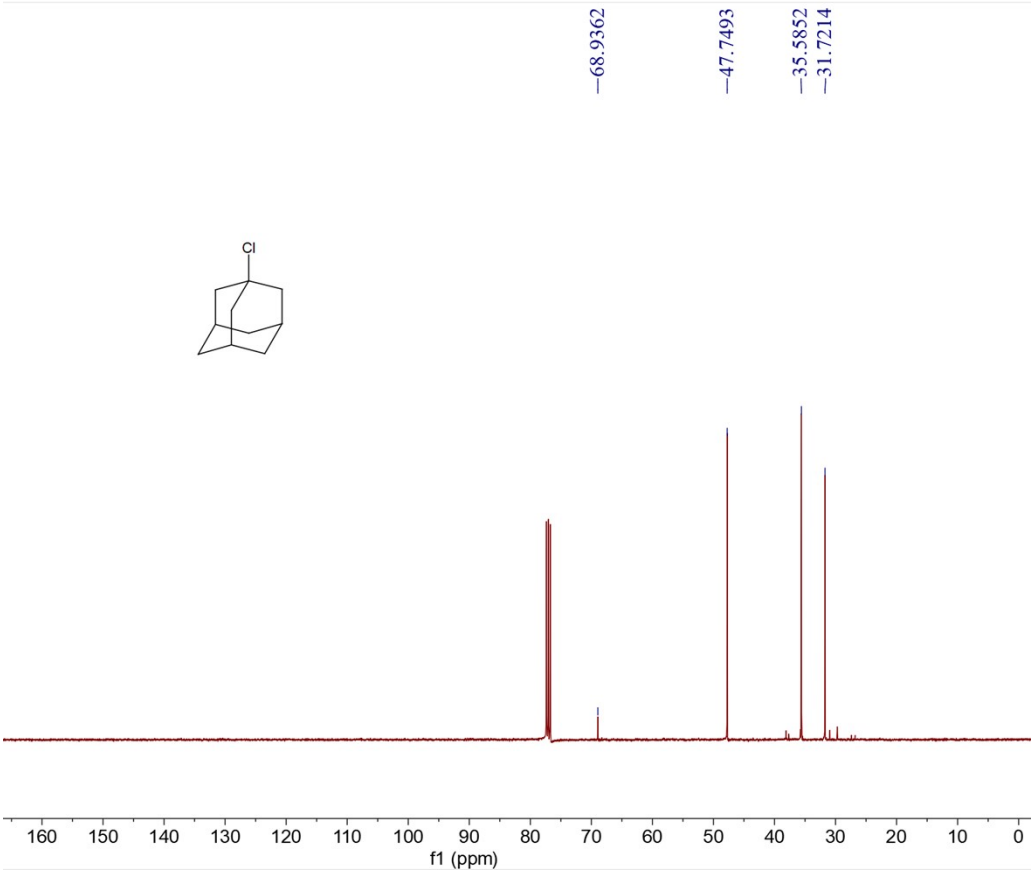
^{13}C NMR of compound **49**



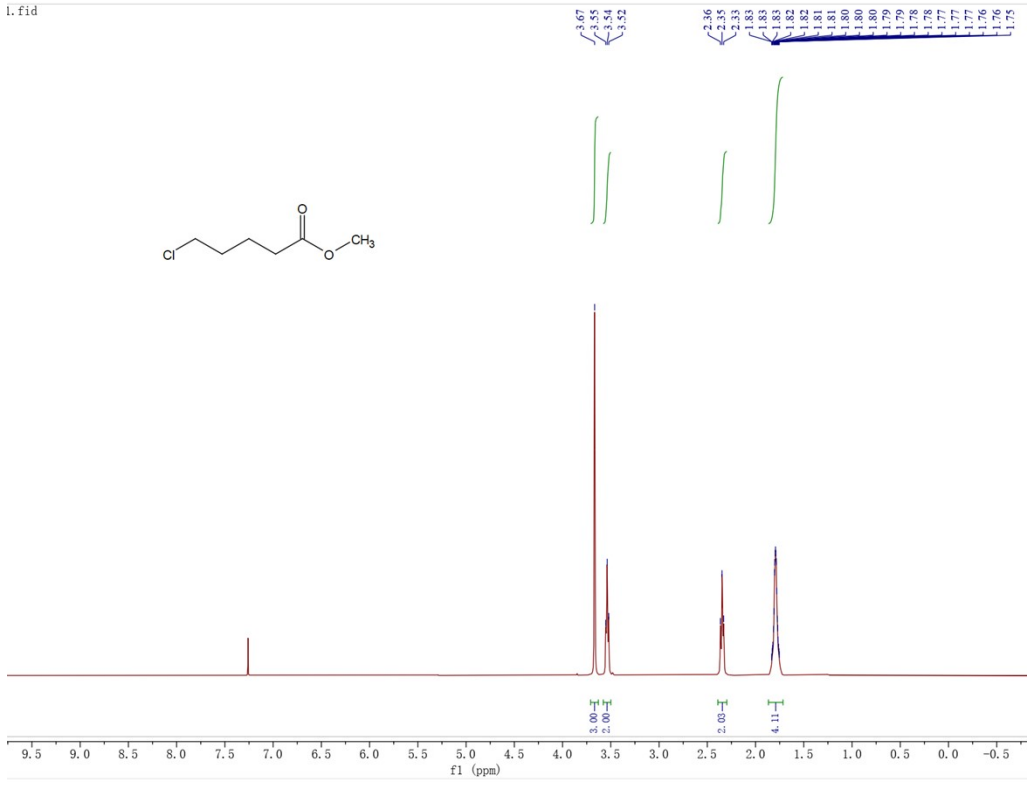
^{1}H NMR of compound **50**



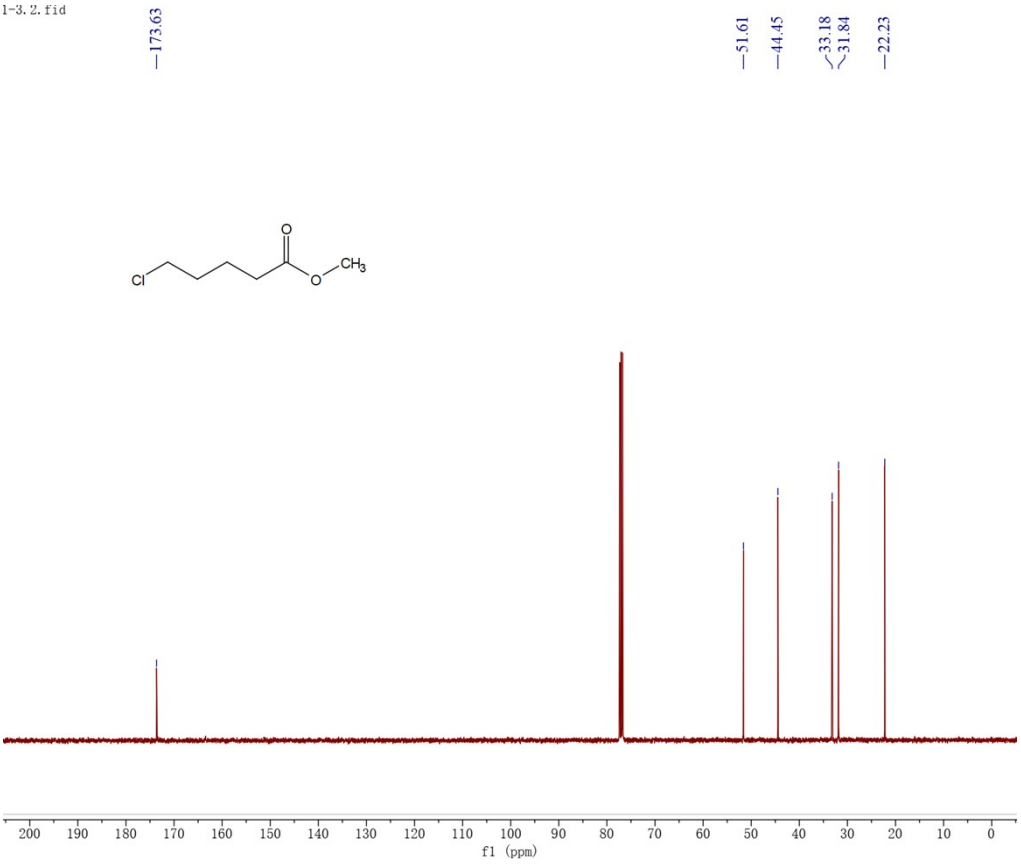
^{13}C NMR of compound **50**



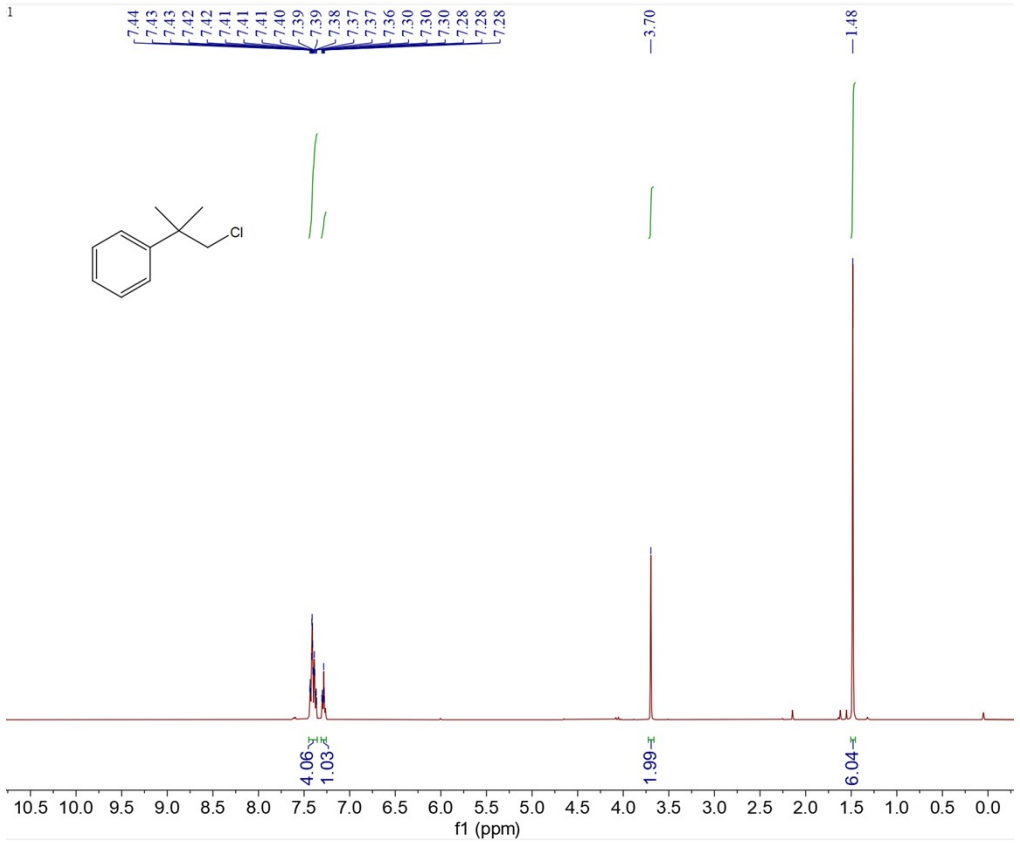
^{1}H NMR of compound **51**



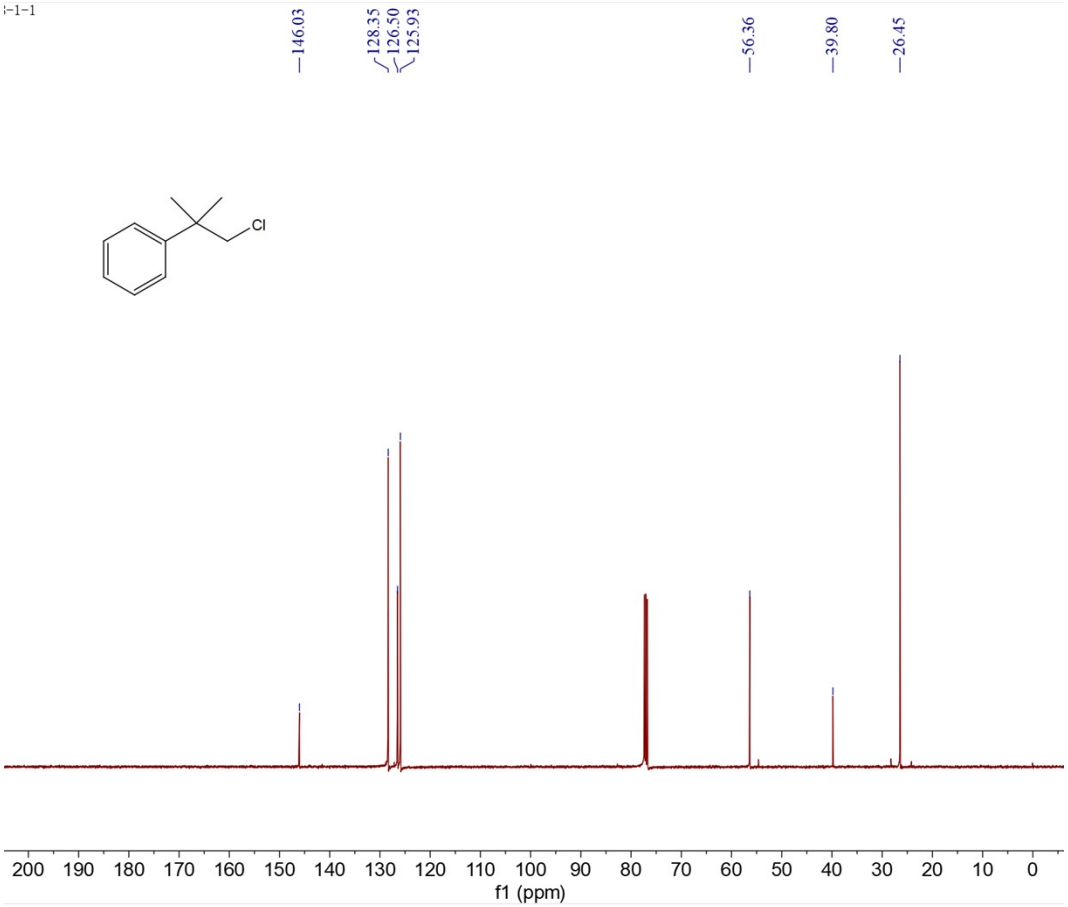
^{13}C NMR of compound **51**



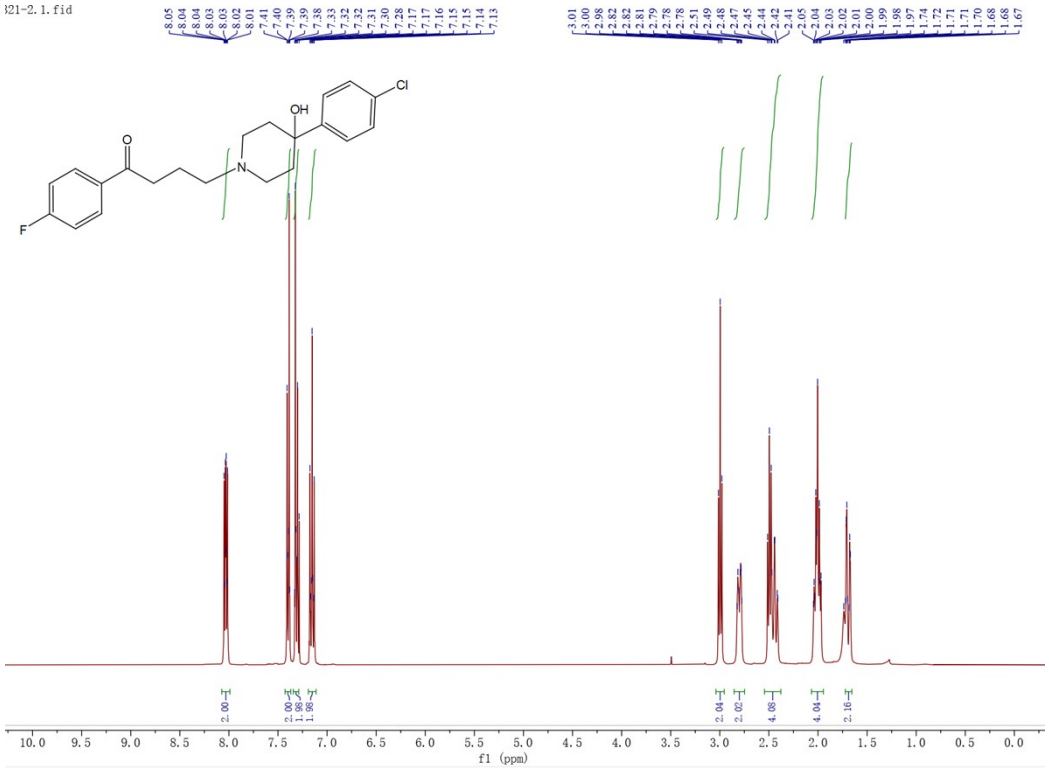
^{1}H NMR of compound **52**



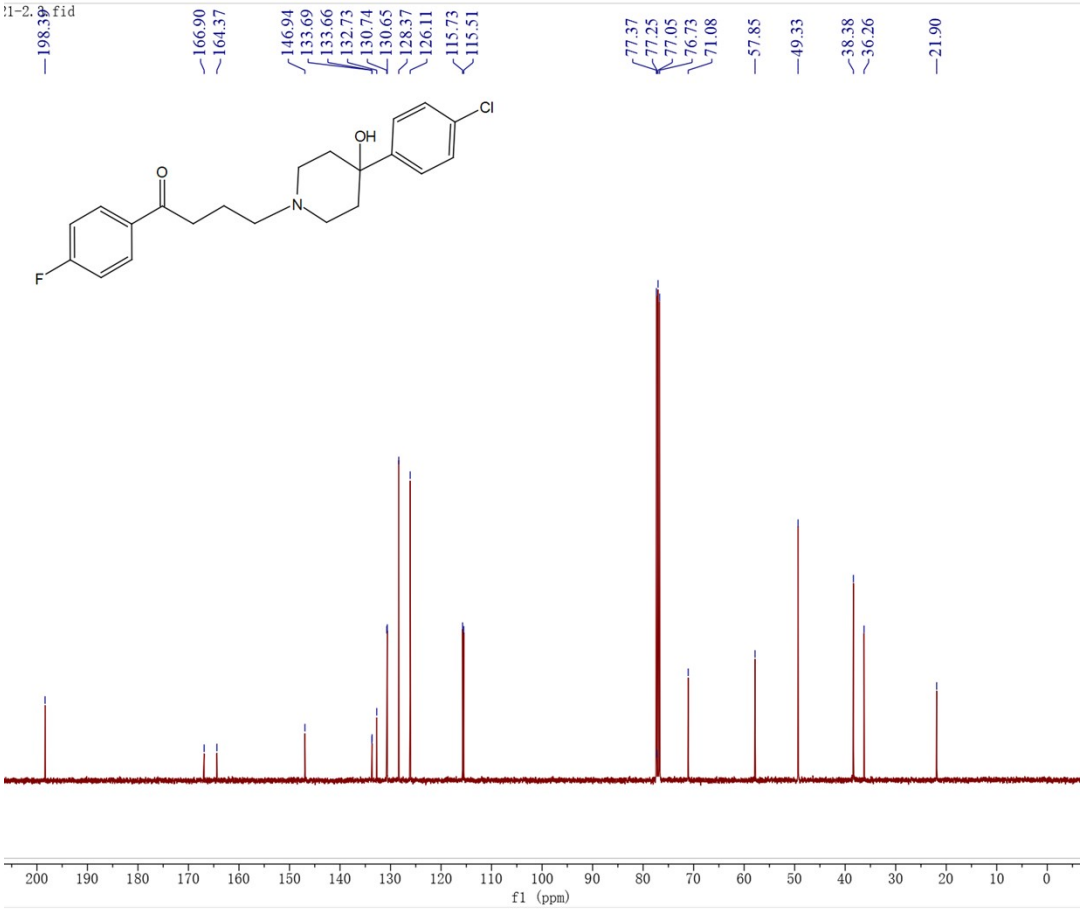
^{13}C NMR of compound **52**



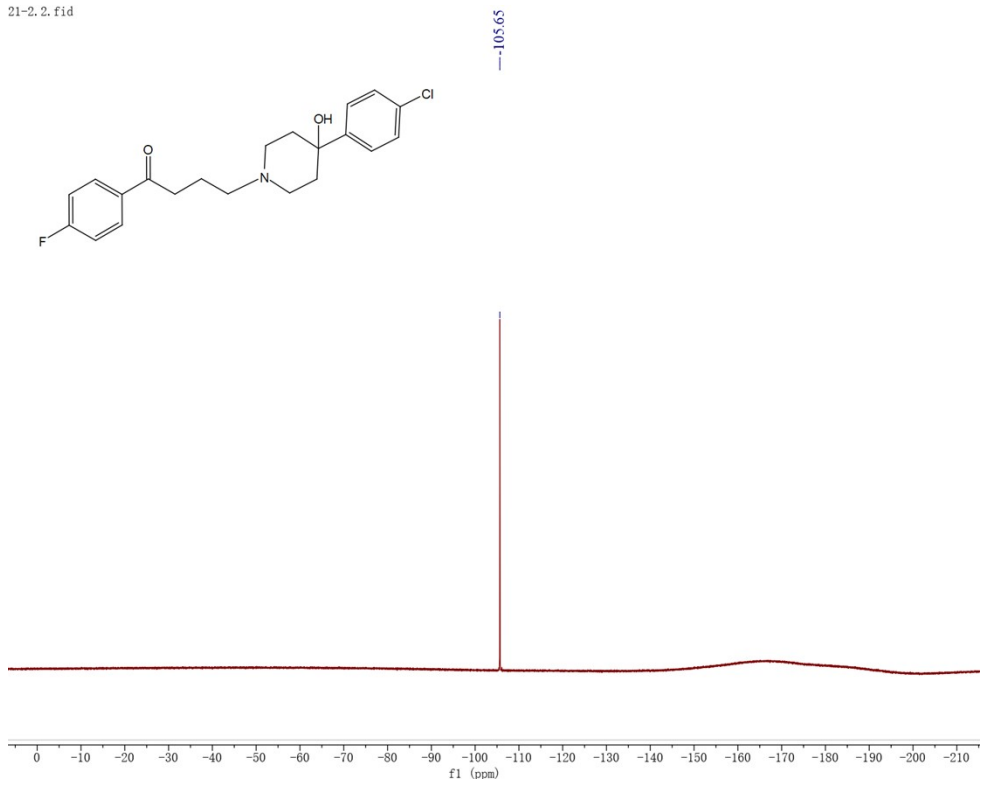
^{1}H NMR of compound **53**



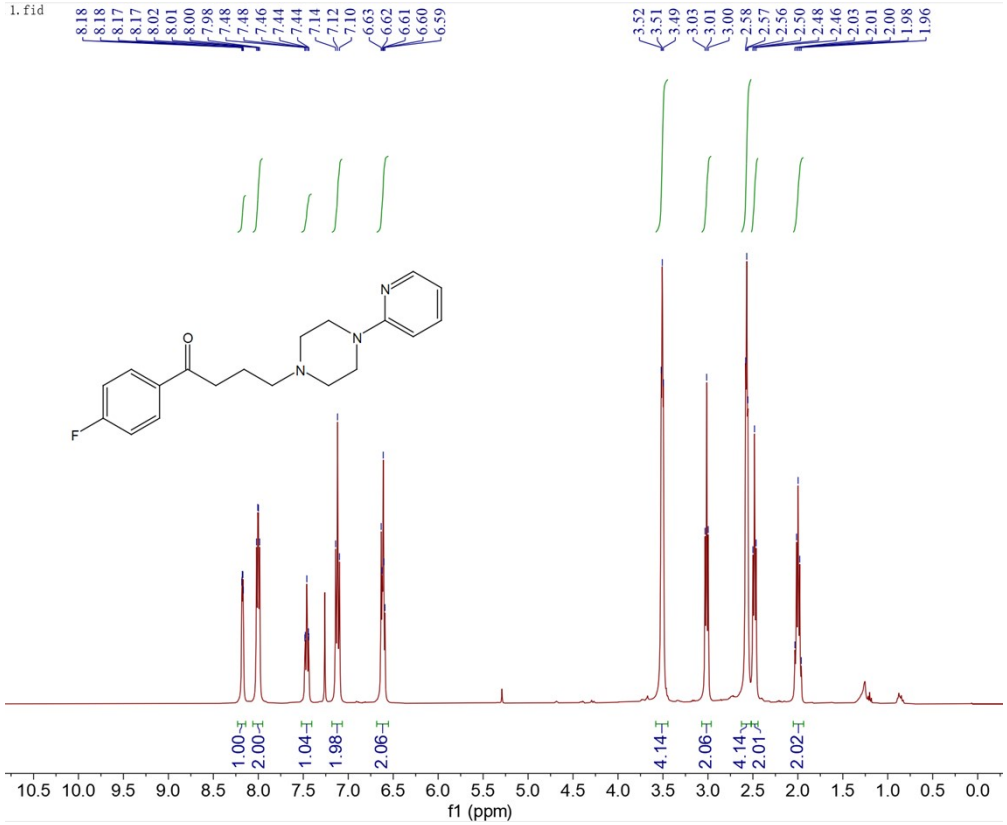
^{13}C NMR of compound **53**



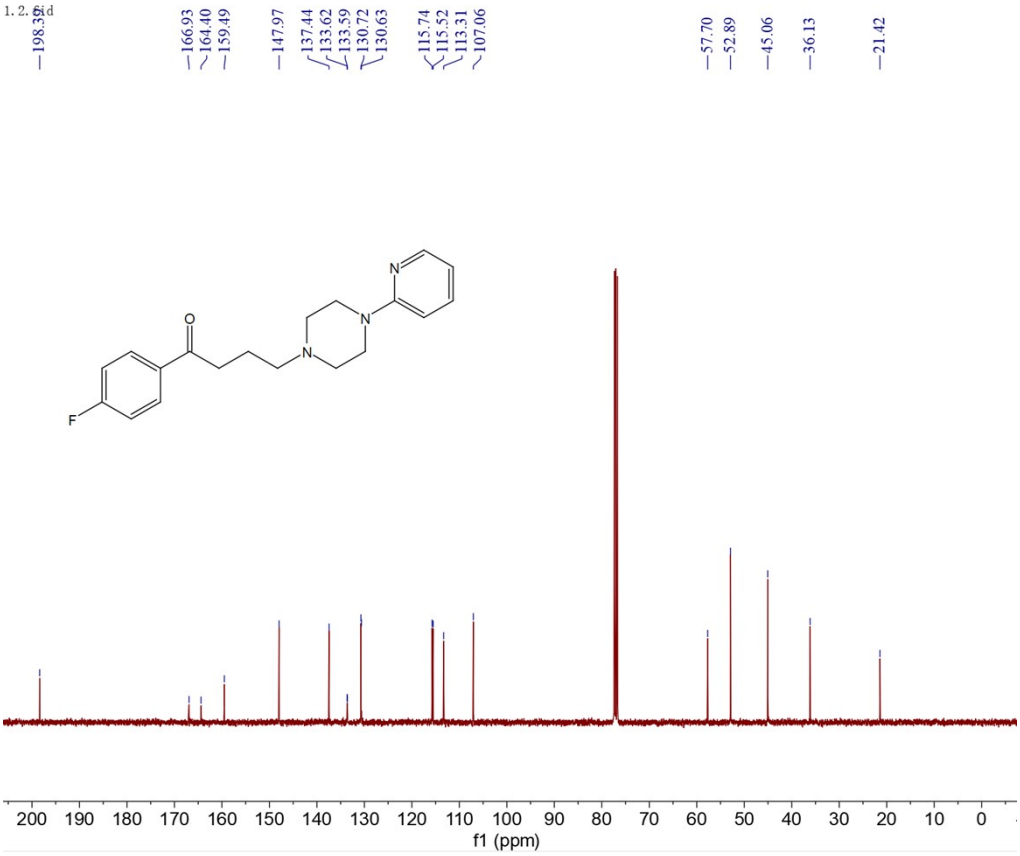
^{19}F NMR of compound **53**



^{1}H NMR of compound **54**



^{13}C NMR of compound **54**



^{19}F NMR of compound **54**