Supporting Information

Sustainable Photoinduced Decarboxylative Chlorination Mediated by Halogen Atom Transfer

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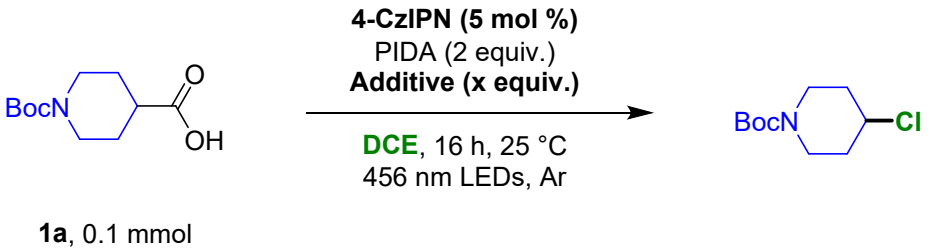
1. General Considerations

1.1 General: All chemical transformations requiring inert atmospheric conditions were carried out using Schlenk line techniques with a 4- or 5-port dual-bank manifold. For blue light irradiation, blue LED strips (light-emitting diode, λ_{max} = 456 nm) were employed at a distance of ~3-5 cm from the reaction vials. A fan was used to ensure reactions remained near room temperature. NMR spectra (^{1}H, ^{13}C, ^{19}F) were obtained at 298 K using 400, 500 and 600 MHz spectrometers. ^{1}H NMR spectra were referenced to residual, $CHCl_3$ (δ 7.26) in $CDCl_3$.^{13}C NMR spectra were referenced to $CDCl_3$ (δ 77.3). Reactions were monitored by ^{1}H NMR, GCMS, and/or TLC on silica gel plates (60 Å porosity, 250 μm thickness). TLC analysis was performed using hexanes/EtOAc as the eluent and visualized using phosphomolybdic acid stain and/or UV light. Flash chromatography was accomplished using an automated system (CombiFlash®, UV detector, λ = 254 nm and 280 nm) with RediSep® R_f silica gel disposable flash columns (60 Å porosity, 40–60 μm) or RediSep R_f Gold® silica gel disposable flash columns (60 Å porosity, 20–40 μm). Accurate mass measurement analyses were conducted using electrospray ionization (ESI). The signals were mass measured against an internal lock mass reference of perfluorotributylamine (PFTBA) for EI-GC/MS and leucine enkephalin for ESI-LC/MS. The utilized software calibrates the instruments and reports measurements by use of neutral atomic masses. The mass of the electron is not included. IR spectra were recorded on an FT-IR using either neat oil or solid products. Solvents were purified with drying cartridges through a solvent delivery system. UV/vis studies were measured in a 1 cm quartz cuvette using a Genesys 150 UV/vis spectrophotometer from Thermo Scientific.

1.2 Chemicals: Deuterated NMR solvents were purchased and stored over 4Å molecular sieves. Solvents were obtained from commercial suppliers and used as purchased. DMA (dimethylacetamide) 99.5% extra pure over molecular sieves was purchased from Acros Organics and used as received. All other reagents were purchased commercially and used as received. Photoredox-catalyzed reactions were performed using 8 mL Chemglass vials (2-dram, 17 x 60 mm, 15-425 Green Open Top Cap, TFE Septa).

2. Reaction Optimization

Table S1. Photocatalyst and base screening



1a, 0.1 mmol

Entry	Modifications from above	^{1}H NMR yield (%)[a]
1	**None (without additive)**	**62(58)[b](59)[b,c]**
2	10 mol % 4-CzIPN	48
3	MesAcr as PC	46
4	[IrdF(CF_3ppy)$_2$(dtbpy)][PF_6] as PC	33
5	Without PC	<4
6	390 nm instead of 456 nm irradiation	25
7	In the dark	N.R.
8	Addition of 2,6-lutidine (1.5 equiv) as base	60
9	Addition of Cs_2CO_3 (1.5 equiv) as base	15
10	48 h	64
11	35 °C	46

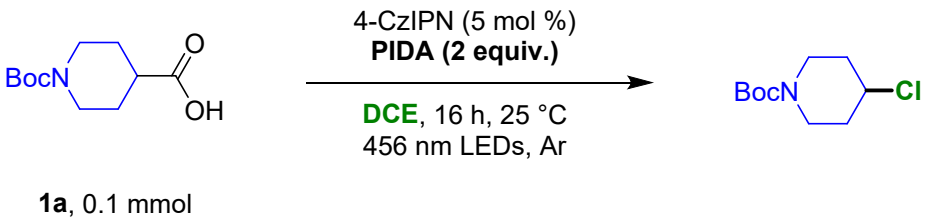
[a] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; [b] Isolated yield; [c] 0.3 mmol of **1a**;

4-CzIPN: 1,2,3,5-Tetrakis(carbazol-9-yl)-4,6-dicyanobenzene;

AcrMes: 9-Mesityl-10-methylacridinium tetrafluoroborate;

N.R.: No reaction.

Table S2. Hypervalent iodide screening



1a, 0.1 mmol

Entry	Modifications from above	^{1}H NMR yield (%)[a]
1	**none**	**62(58)[b](59)[b,c]**
2	0.5 equiv of PIDA	20
3	3.0 equiv of PIDA	59
4	Without PIDA	N.R.
5	PIFA (2 equiv) instead of PIDA	15
6	[BI-OH] (2 equiv) instead of PIDA	<10
7	[BI-OMe] (2 equiv) instead of PIDA	25
8	[BI-OAc] (2 equiv) instead of PIDA	24
9	Premixed (**1a** + PIDA)[d]	30

[a] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; [b] Isolated yield; [c] 0.3 mmol of **1a**; [d] The carboxylic acid and PIDA were dissolved in toluene (4 mL), and the solvent was then removed under reduced pressure at 50 °C (three times). The PC and DCE were added to the resulting mixture before irradiation with blue LEDs at 25 °C for 16 h.

PIDA: (Diacetoxyiodo)benzene

PIFA: [Bis(trifluoroacetoxy)iodo]benzene

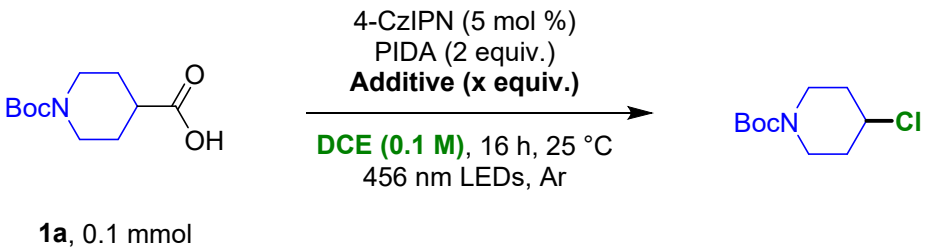
[BI-OH]: Hydroxybenziodoxole;

[BI-OMe]: Methoxybenziodoxole;

[BI-OAc]: Acetoxybenziodoxole;

N.R.: No reaction.

Table S3. Source of chloride screening



1a, 0.1 mmol

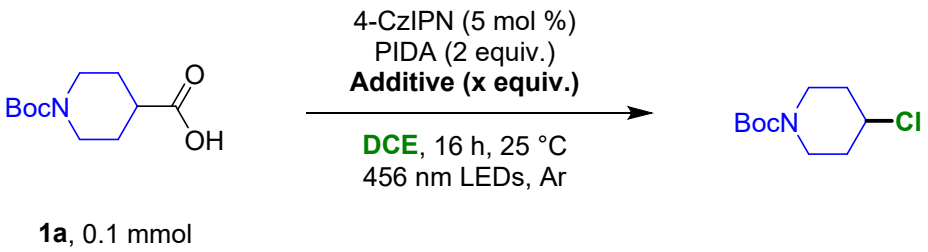
Entry	Modifications from above	^{1}H NMR yield (%)[a]
1	**None (without additive)**	**62(58)[b](59)[b,c]**
2	0.25 M	40
3	CH_2Cl_2	34
4	$CHCl_3$	24
5	Addition of TMSCl (4.0 equiv)	N.D.
6	Addition of NCS (0.5 equiv)	50
7	Addition of NCS (1.0 equiv)	50
8	Addition of *t*-BuOCl (0.5 equiv)	50
9	Addition of *t*-BuOCl (1.0 equiv)	53

[a] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; [b] Isolated yield; [c] 0.3 mmol of **1a**;

NCS: *N*-Chlorosuccinimide;

N.D.: Not Determined

Table S4. Oxidant screening



1a, 0.1 mmol

Entry	Modifications from above	^{1}H NMR yield (%)[a]
1	**None (without additive)**	**62(58)[b](59)[b,c]**
2	PIDA (0.5 equiv) + Oxone (2 equiv)	N.D.
3	PIDA (0.5 equiv) + Oxone (2 equiv) + DCE/HFIP (8/2)	N.D.
4	PIDA (0.5 equiv) + *m*CPBA (2 equiv)	11

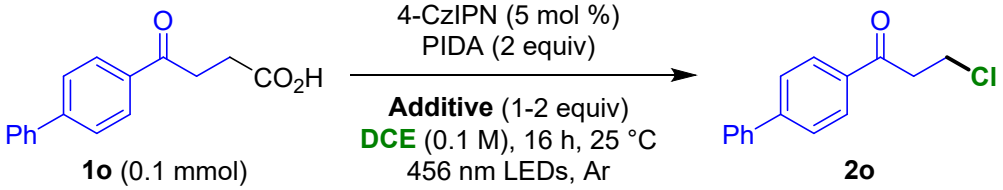
[a] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; [b] Isolated yield; [c] 0.3 mmol of **1a**;

Oxone: Potassium peroxymonosulfate;

*m*CPBA: *meta*-Chloroperoxybenzoic acid;

N.D.: Not Determined

Table S5. Second Optimization



Entry	Modifications from above	^{1}H NMR yield (%)[a]
1	None (without additive)	N.D.
2	**Addition of 2,6-lutidine (1.5 equiv)**	**77(72)[b]**
3	Addition of 2,6-lutidine (3 equiv)	75
4	Premixed **1o** and PIDA – Addition of 2,6-lutidine (1.5 equiv)	69
5	DIPEA (1.5 equiv)	54
6	Cs_2CO_3 (1.5 equiv)	33
7	[Ir[dF(CF_3)ppy]$_2$(dtbpy)]PF_6 as PC with 2,6-lutidine (1,5 equiv)	45
8	Ir(ppy)$_3$ as PC	N.D.
9	Ir(ppy)$_3$ as PC – Addition of 2,6-lutidine (1,5 equiv)	45
10	Addition of *t*-BuOCl (1 equiv)	57

[a] Yields were determined by ^{1}H NMR analysis using 1,3,5-trimethoxybenzene as an internal standard; [b] Isolated yield;

DIPEA: *N*,*N*-diisopropyléthylamine;

N.D.: Not Determined

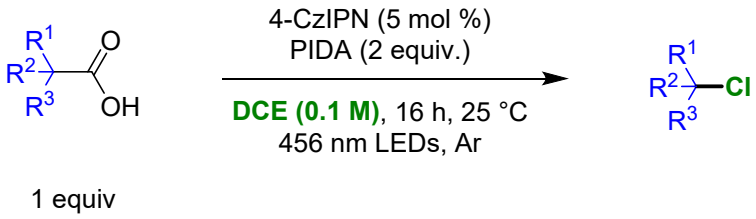
3. Synthesis of Fluorinated Compounds

A. Reaction Workflow

All photoredox reactions were performed with blue LED strips (light-emitting diode, λ_{max} = 456 nm) employed at a distance of ~3-5 cm from the reaction vials. A fan was used to ensure reactions remained near room temperature within a ventilated fume hood. A typical reaction setup is shown below.

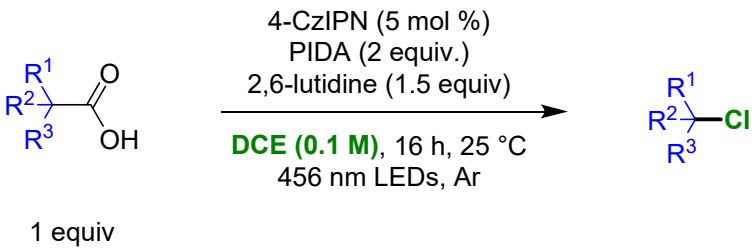
Figure S1. *Reaction setup for the photoinduced formation of chloroalkanes*

A. General Procedure A



To an 8 mL vial equipped with a magnetic stir bar and a rubber septum was added 4-CzIPN (11.8 mg, 0.015 mmol, 0.05 equiv), the corresponding carboxylic acid (0.3 mmol, 1 equiv), and PIDA (193.2 mg, 0.6 mmol, 2 equiv). DCE (3 mL) was then added *via* syringe under an argon atmosphere. The vial was sealed with Parafilm and irradiated with 456 nm LED strips for 16 h as described in the "Workflow" section. When the reaction was over, the solvent was removed under reduced pressure and the crude mixture was subjected purification by chromatography on silica gel (Hex:EtOAc, 95/5 to 80/20).

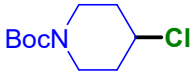
B. General Procedure B



To an 8 mL vial equipped with a magnetic stir bar and a rubber septum was added 4-CzIPN (11.8 mg, 0.015 mmol, 0.05 equiv), the corresponding carboxylic acid (0.3 mmol, 1 equiv), PIDA (193.2 mg, 0.6 mmol, 2 equiv) and 2,6-lutidine (48.2 mg, 52 µL, 0.45 mmol, 1.5 equiv). DCE (3 mL) was then added *via* syringe under an argon atmosphere. The vial was sealed with Parafilm and irradiated with 456 nm LED strips for 16 h as described in the "Workflow" section. When the reaction was over, the solvent was removed under reduced pressure and the crude mixture was subjected purification by chromatography on silica gel (Hex:EtOAc, 95/5 to 80/20).

C. Characterization Data

tert-Butyl 4-Chloropiperidine-1-carboxylate (2a)



Prepared according to the *General Procedure A* from 1-Boc-4-piperidinecarboxylic acid (68.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2a** was obtained as a colorless oil (38.6 mg, 0.18 mmol, 59%). All data was consistent with that previously reported.[1] **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.19 (tt, *J* = 7.5, 3.6 Hz, 1H), 3.70 (ddd, *J* = 13.9, 7.0, 3.8 Hz, 2H), 3.29 (ddd, *J* = 13.8, 7.9, 3.6 Hz, 2H), 2.02 (ddd, *J* = 14.1, 7.1, 3.6 Hz, 2H), 1.79 (dtd, *J* = 13.6, 7.7, 3.7 Hz, 2H), 1.46 (s, 9H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.8, 79.9, 57.1, 35.1 (2*C), 28.6 (3*C), 24.7 (2*C).

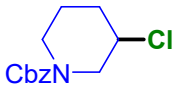
tert-Butyl 3-Chloropyrrolidine-1-carboxylate (2b)

2b **2b'**

Prepared according to the *General Procedure A* from 1-(*tert*-butoxycarbonyl)pyrrolidine-3-carboxylic acid (64.6 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), this compound was obtained as a colorless oil as a mixture of **2b** and **2b'** (85/15; 56,0 mg of the mixture including 47.6 mg, 0.23 mmol, 77% of **2b**, and 8.4 mg, 0.04 mmol, 12% of **2b'**). **^{1}H NMR** of **2b** (600 MHz, $CDCl_3$) δ 4.47 (s, 1H), 3.72 – 3.46

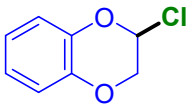
(m, 4H), 3.30 (m, 0.32H, **2b'**), 2.31 – 2.21 (m, 1H), 2.19 – 2.11 (m, 1H), 1.61 (m, 0.3, 1.81 (m, 0.58H, **2b'**), 1.47 (s, 9H), 1.46 (s, 0.44H, **2b'**). **^{13}C NMR** of **2b** (151 MHz, $CDCl_3$) δ 154.7 (**2b'**), 154.4, 79.7, 78.9 (**2b'**) 57.5, 57.0 (**2b'**), 55.3, 54.9 (**2b'**), 43.8, 43.5 (**2b'**), 35.9 (**2b'**), 35.1 (**2b'**), 29.7, 28.6 (3*C, **2b'**), 28.5 (3*C). **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 3002, 2972, 2773, 1703, 1462, 1418, 1357, 1297, 1262, 1221, 1217, 1190, 1142, 1122, 1047, 994. **HRMS (EI)** calcd for **2b**: $C_9H_{16}ClNO_2$ $[M]^+$: 205.0870, found 205.0875 and **2b'**: $C_{11}H_{20}ClNO_2$ $[M]^+$: 233.1183, found 233.1170.

Benzyl 3-chloropiperidine-1-carboxylate (2c)



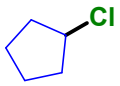
Prepared according to the *General Procedure A* from 1-((benzyloxy)carbonyl)piperidine-3-carboxylic acid (79.0 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2c** was obtained as a colorless oil (50.4 mg, 0.20 mmol, 66%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 5H), 5.14 (d, *J* = 8.9 Hz, 2H), 4.08 (m, 1H), 3.94 (m, 1H), 3.73 (s, 1H), 3.35 – 3.07 (m, 2H), 2.18 (d, *J* = 8.9 Hz, 1H), 1.92 – 1.73 (m, 2H), 1.54 (s, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 155.3, 136.7, 128.7 (2*C), 128.2, 128.1 (2*C), 67.5, 55.0, 51.4, 44.0, 34.5, 29.9 **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2948, 2873, 2849, 1698, 1467, 1426, 1363, 1287, 1258, 1229, 1217, 1189, 1145, 1119, 1072, 1027, 1003, 964. **HRMS (EI)** calcd for $C_{13}H_{16}ClNO_2$ $[M]^+$: 253.0870, found 253.0877.

2-Chloro-2,3-dihydrobenzo[b][1,4]dioxine (2d)



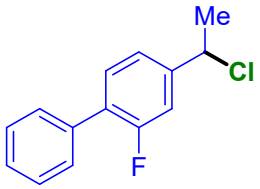
Prepared according to the *General Procedure B* from 1,4-benzodioxan-2-carboxylic acid (54.0 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2d** was obtained as a colorless oil (30.6 mg, 0.18 mmol, 60%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 6.99 – 6.82 (m, 4H), 6.33 (s, 1H), 4.41 – 4.31 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 142.6, 139.3, 123.7, 122.5, 118.3, 117.6, 84.2, 68.3. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2920, 2877, 1750, 1612, 1498, 1258, 1208, 1149, 1101. **HRMS (EI)** calcd for $C_8H_7O_2^{\cdot+}$ $[M\text{-}Cl]^+$: 135.0446, found 135.0450.

Chlorocyclopentane (2e)



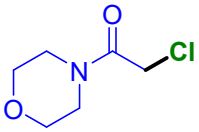
Prepared according to the *General Procedure B* from cyclopentanecarboxylic acid (34.2 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2e** was obtained as a colorless oil (25.3 mg, 0.24 mmol, 81%). All data was consistent with that previously reported.[2] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.39 (tt, *J* = 6.2, 3.3 Hz, 1H), 2.06 – 1.96 (m, 2H), 1.96 – 1.83 (m, 4H), 1.70 – 1.59 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 62.3, 37.2 (2*C), 23.2 (2*C).

4-(1-Chloroethyl)-2-fluoro-1,1'-biphenyl (2f)



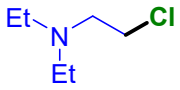
Prepared according to the *General Procedure B* from flurbiprofen (73.3 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2f** was obtained as a colorless oil (38.5 mg, 0.16 mmol, 55%). All data was consistent with that previously reported.[3] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 2H), 7.47 – 7.34 (m, 4H), 7.19 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.16 (dd, *J* = 11.4, 1.7 Hz, 1H), 5.89 (q, *J* = 6.6 Hz, 1H), 1.57 (d, *J* = 6.6 Hz, 3H). **^{19}F NMR** (565 MHz, $CDCl_3$) δ -117.52. **^{13}C NMR** (151 MHz, $CDCl_3$) δ 159.8 (d, *J* = 248.5 Hz), 143.4 (d, *J* = 7.4 Hz), 135.6, 131.0 (d, *J* = 3.9 Hz), 129.1 (d, *J* = 2.7 Hz, 2*C), 128.6 (2*C), 127.9 (2*C), 122.2, 113.9 (d, *J* = 24.0 Hz), 71.6, 22.3.

2-Chloro-1-morpholinoethan-1-one (2g)



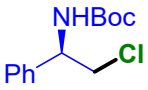
Prepared according to the *General Procedure A* from 3-morpholino-3-oxopropanoic acid (52.0 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2g** was obtained as a colorless oil (40.2 mg, 0.25 mmol, 82%). All data was consistent with that previously reported.[4] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.05 (s, 2H), 3.69 (dt, *J* = 16.2, 5.0 Hz, 4H), 3.61 (d, *J* = 5.4 Hz, 2H), 3.51 (t, *J* = 4.9 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 165.3, 66.7, 66.6, 46.8, 42.6, 40.7 (2*C).

2-Chloro-*N*,*N*-diethylethan-1-amine (2h)



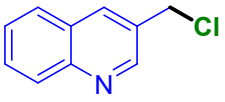
Prepared according to the *General Procedure A* from 3-(diethylamino)propanoic acid (43.6 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2h** was obtained as a colorless oil (30.7 mg, 0.23 mmol, 75%). All data was consistent with that previously reported.[5] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.04 (t, *J* = 6.8 Hz, 2H), 3.36 (td, *J* = 6.9, 5.0 Hz, 2H), 3.28 – 3.12 (m, 4H), 1.42 (t, *J* = 7.3 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 52.6, 47.2 (2*C), 36.7, 8.6 (2*C).

***tert*-Butyl (*R*)-(2-Chloro-1-phenylethyl)carbamate (2i)**



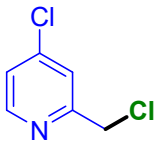
Prepared according to the *General Procedure A* from (*S*)-3-((*tert*-butoxycarbonyl)amino)-3-phenylpropanoic acid (132.7 mg, 0.50 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2i** was obtained as a colorless oil (99.0 mg, 0.39 mmol, 77%). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.34 (m, 2H), 7.34 – 7.27 (m, 3H), 5.14 (s, 1H), 5.01 (s, 1H), 3.84 (td, *J* = 11.1, 4.6 Hz, 2H), 1.44 (s, 9H). **^{13}C NMR** (101 MHz, CDCl3) δ 155.2, 139.2, 128.9 (2*C), 128.2, 126.7 (2*C), 80.3, 48.3, 29.9, 28.5 (3*C). **FT-IR** (cm^{-1}, neat, ATR), ṽ = 2982, 2864, 2802, 1663, 1635, 1585, 1437, 1260, 1211, 1086, 1029. **HRMS (EI)** calcd for $C_{13}H_{18}ClNO_2$ $[M]^+$: 255.1026, found 255.1032.

3-(Chloromethyl)quinoline (2j)



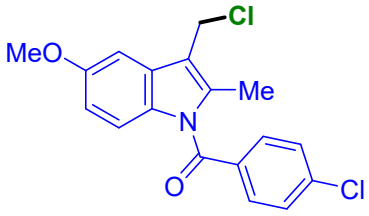
Prepared according to the *General Procedure A* from 2-(quinolin-3-yl)acetic acid (56.2 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2j** was obtained as a colorless oil (40.9 mg, 0.23 mmol, 77%). All data was consistent with that previously reported.[6] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.97 (d, *J* = 8.7 Hz, 1H), 8.86 (d, *J* = 8.6 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 8.09 – 8.04 (m, 2H), 7.90 (ddd, *J* = 8.2, 7.0, 1.1 Hz, 1H), 5.47 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 154.2, 145.8, 138.3, 135.3, 130.7, 128.3, 128.2, 122.5, 121.7, 40.1.

4-Chloro-2-(chloromethyl)pyridine (2k)



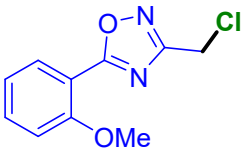
Prepared according to the *General Procedure A* from 2-(4-chloropyridin-2-yl)acetic acid (51.5 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2k** was obtained as a colorless oil (24.7 mg, 0.17 mmol, 57%). All data was consistent with that previously reported.[7] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.45 (d, *J* = 5.3 Hz, 1H), 7.32 (d, *J* = 1.9 Hz, 1H), 7.22 (dd, *J* = 5.4, 2.0 Hz, 1H), 4.75 (s, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 161.1, 149.6, 145.0, 123.0, 121.0, 64.1.

(3-(Chloromethyl)-5-methoxy-2-methyl-1H-indol-1-yl)(4-chlorophenyl)methanone (2l)



Prepared according to the *General Procedure A* from indomethacin (107.4 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2l** was obtained as a colorless oil (69.9 mg, 0.20 mmol, 67%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.05 (d, *J* = 2.6 Hz, 1H), 6.86 – 6.81 (m, 1H), 6.68 (dd, *J* = 9.0, 2.6 Hz, 1H), 5.30 (s, 2H), 3.85 (s, 3H), 2.46 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 168.3, 156.0, 139.4, 136.8, 133.9, 131.2 (2*C), 130.9, 130.6, 129.2 (2*C), 115.1, 114.7, 111.5, 101.2, 55.8, 48.1, 13.8. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2988, 2944, 2857, 1711, 1682, 1477, 1457, 1400, 1357, 1316, 1289, 1259, 1177, 1088, 1014, 927. **HRMS (EI)** calcd for $C_{18}H_{15}Cl_2NO_2$ $[M]^+$: 347.0480, found 347.0485.

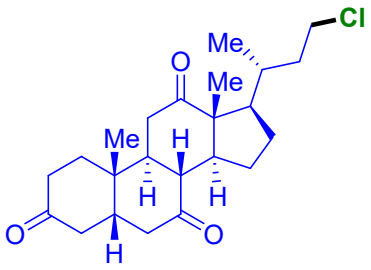
3-(Chloromethyl)-5-(2-methoxyphenyl)-1,2,4-oxadiazole (2m)



Prepared according to the *General Procedure A* from 2-(5-(2-methoxyphenyl)-1,2,4-oxadiazol-3-yl)acetic acid (70.3 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2m** was obtained as a colorless oil (37.3 mg, 0.17 mmol, 55%). All data was consistent with that

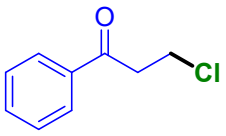
previously reported.[8] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.07 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.57 (ddd, *J* = 8.4, 7.4, 1.8 Hz, 1H), 7.12 – 7.05 (m, 2H), 4.69 (s, 2H), 3.99 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 176.1, 167.3, 158.7, 134.7, 131.8, 121.0, 113.0, 112.3, 56.2, 34.9.

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



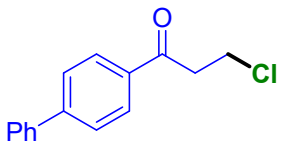
Prepared according to the *General Procedure B* from dehydrocholic acid (120.8 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2n** was obtained as a colorless oil (78.8 mg, 0.20 mmol, 67%). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.65 (ddd, *J* = 11.2, 7.4, 3.9 Hz, 1H), 3.57 – 3.49 (m, 1H), 2.95 – 2.86 (m, 2H), 2.86 (t, *J* = 12.8 Hz, 1H), 2.37 – 2.30 (m, 3H), 2.30 – 2.20 (m, 3H), 2.18 – 2.11 (m, 2H), 2.05 – 2.00 (m, 1H), 1.97 (ddd, *J* = 14.4, 5.4, 3.2 Hz, 2H), 1.86 (td, *J* = 11.3, 7.1 Hz, 1H), 1.65 – 1.58 (m, 2H), 1.54 (s, 3H), 1.41 (s, 3H), 1.37 – 1.23 (m, 4H), 1.10 – 1.06 (m, 1H), 0.87 (d, *J* = 6.5 Hz, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 212.1, 209.1, 208.8, 57.1, 51.9, 49.1, 47.0, 45.9, 45.7, 45.1, 43.4, 42.9, 38.8, 38.5, 36.6, 36.2, 35.4, 33.8, 27.9, 25.3, 22.1, 18.6, 12.0. **FT-IR** (cm^{-1}, neat, ATR), $\tilde{\nu}$ = 2961, 2855, 1704, 1438, 1383, 1205, 1142, 725. **HRMS (EI)** calcd for $C_{23}H_{33}ClO_3$ $[M]^+$: 392.2118, found 392.2125.

3-Chloro-1-phenylpropan-1-one (2o)



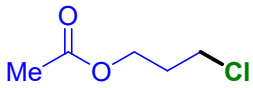
Prepared according to the *General Procedure B* from 4-oxo-4-phenylbutanoic acid (53.5 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2o** was obtained as a colorless oil (42.6 mg, 0.25 mmol, 84%). All data was consistent with that previously reported.[9] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 2H), 7.63 – 7.57 (m, 1H), 7.52 – 7.46 (m, 2H), 3.93 (t, *J* = 6.8 Hz, 2H), 3.47 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.9, 136.5, 133.7, 128.9 (2*C), 128.2 (2*C), 41.4, 38.8.

1-([1,1'-Biphenyl]-4-yl)-3-chloropropan-1-one (2p)



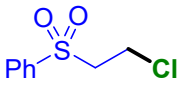
Prepared according to the *General Procedure B* from Fenbufen (76.3 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2p** was obtained as a colorless oil (52.9 mg, 0.22 mmol, 72%). All data was consistent with that previously reported.[9] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.3 Hz, 2H), 7.63 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H), 3.96 (t, *J* = 6.8 Hz, 2H), 3.50 (t, *J* = 6.8 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 196.5, 146.4, 139.9, 135.2, 129.2 (2*C), 128.8 (2*C), 128.5, 127.5 (2*C), 127.4 (2*C), 41.5, 38.9.

3-Chloropropyl acetate (2q)



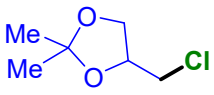
Prepared according to the *General Procedure B* from 4-acetoxybutanoic acid (43.8 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2q** was obtained as a colorless oil (26.5 mg, 0.19 mmol, 65%). All data was consistent with that previously reported.[10] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.21 (t, *J* = 6.1 Hz, 2H), 3.61 (t, *J* = 6.4 Hz, 2H), 2.09 (m, 2H), 2.05 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.1, 61.3, 41.3, 31.7, 21.0.

((2-Chloroethyl)sulfonyl)benzene (2r)



Prepared according to the *General Procedure B* from 3-(phenylsulfonyl)propanoic acid (64.3 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2r** was obtained as a colorless oil (36.3 mg, 0.18 mmol, 59%). All data was consistent with that previously reported.[11] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.96 – 7.90 (m, 2H), 7.73 – 7.67 (m, 1H), 7.64 – 7.57 (m, 2H), 3.78 – 3.72 (m, 2H), 3.56 – 3.50 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 138.8, 134.5, 129.7 (2*C), 128.3 (2*C), 58.2, 35.7.

4-(Chloromethyl)-2,2-dimethyl-1,3-dioxolane (2s)

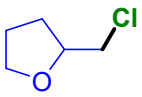


Prepared according to the *General Procedure B* from 2-(2,2-dimethyl-1,3-dioxolan-4-yl)acetic acid (48.1 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2s** was obtained as a colorless oil (30.7 mg, 0.20 mmol, 68%). All data was consistent with that previously reported.[12] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.29 (ddt, *J* = 7.6, 6.2, 4.9 Hz, 1H), 4.10 (dd, *J* = 8.4, 6.0 Hz, 1H), 3.86 (dd, *J* = 8.7, 5.1 Hz, 1H), 3.56 (dd, *J* = 10.9, 4.7 Hz, 1H), 3.45 (dd, *J* = 10.9, 7.6 Hz, 1H), 1.42 (s, 3H), 1.34 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 110.3, 75.5, 67.6, 44.7, 27.0, 25.4.

4-Chlorobutanenitrile (2t)

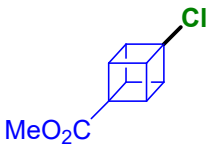
Prepared according to the *General Procedure B* from 4-cyanobutanoic acid (33.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2t** was obtained as a colorless oil (24.3 mg, 0.23 mmol, 78%). All data was consistent with that previously reported.[13] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 3.67 (td, *J* = 6.0, 2.0 Hz, 2H), 2.58 (td, *J* = 7.1, 2.0 Hz, 2H), 2.17 – 2.08 (m, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 118.6, 42.7, 28.4, 14.9.

2-(Chloromethyl)tetrahydrofuran (2u)



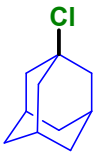
Prepared according to the *General Procedure B* from 2-(tetrahydrofuran-2-yl)acetic acid (39.0 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2u** was obtained as a colorless oil (25.2 mg, 0.21 mmol, 70%). All data was consistent with that previously reported.[14] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.14 (m, 1H), 3.92 (dt, *J* = 8.0, 6.6 Hz, 1H), 3.81 (dt, *J* = 8.1, 6.6 Hz, 1H), 3.58 – 3.47 (m, 2H), 2.10 – 2.01 (m, 1H), 2.00 – 1.86 (m, 2H), 1.76 (ddt, *J* = 13.1, 8.4, 6.8 Hz, 1H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 78.6, 69.0, 47.1, 29.5, 25.9.

Methyl-4-Chlorocubane-1-carboxylate (2v)



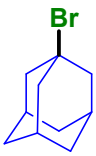
Prepared according to the *General Procedure B* from 4-(methoxycarbonyl)cubane-1-carboxylic acid (61.9 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2v** was obtained as a colorless oil (35.9 mg, 0.18 mmol, 61%). All data was consistent with that previously reported.[15] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 4.37 (dd, *J* = 5.8, 4.2 Hz, 3H), 4.28 (dd, *J* = 5.7, 4.2 Hz, 3H), 3.70 (s, 3H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.9, 56.1, 54.9 (3*C), 51.7, 50.3 (2*C), 49.5, 45.2.

1-Chloroadamantane (2w)



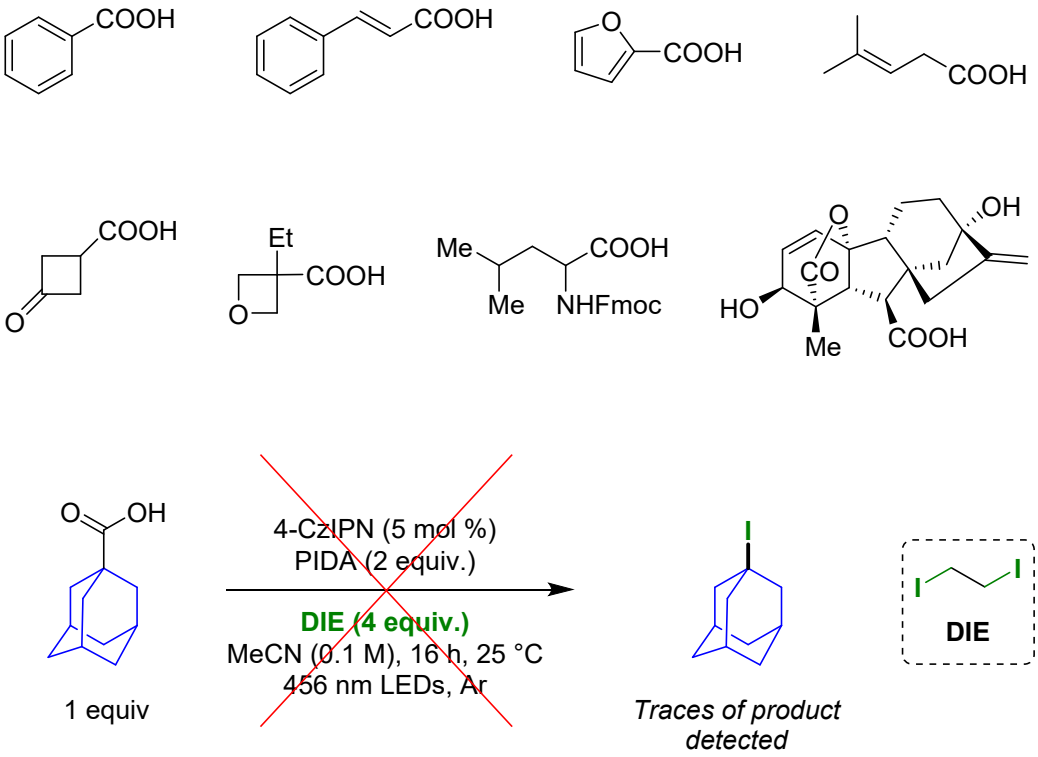
Prepared according to the *General Procedure B* from adamantane-1-carboxylic acid (54.7 mg, 0.30 mmol, 1.0 equiv). After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2w** was obtained as a colorless oil (43.7 mg, 0.26 mmol, 85%). All data was consistent with that previously reported.[16] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.14 (s, 9H), 1.68 (s, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 69.1, 47.9 (3*C), 35.7 (3*C), 31.9 (3*C).

1-Bromoadamantane (2x)

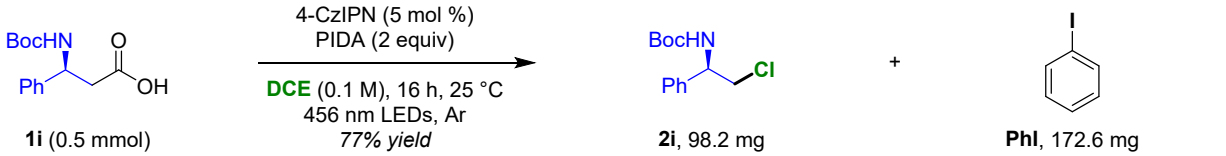


Prepared according to the *General Procedure B* from adamantane-1-carboxylic acid (54.7 mg, 0.30 mmol, 1.0 equiv) and the use of 1,2-dibromoethane as solvent. After chromatographic purification (5–20% EtOAc in hexanes), the title compound **2x** was obtained as a colorless oil (43.8 mg, 0.20 mmol, 68%). All data was consistent with that previously reported.[16] **^{1}H NMR** (600 MHz, $CDCl_3$) δ 2.37 (d, *J* = 3.1 Hz, 6H), 2.13 – 2.08 (m, 3H), 1.73 (t, *J* = 3.1 Hz, 6H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 67.0, 49.5 (3*C), 35.7 (3*C), 32.8 (3*C).

D. Unsuccessful Substrates Examples



4. Green Chemistry Metrics Calculations



1i (0.5 mmol)
Chemical Formula: $C_{14}H_{19}NO_4$
Molecular Weight: 265.31 g/mol

2i, 98.2 mg
Chemical Formula: $C_{13}H_{18}ClNO_2$
Molecular Weight: 255.74 g/mol

PhI, 172.6 mg
Chemical Formula: C_6H_5I
Molecular Weight: 204.01 g/mol

To a 12 mL vial equipped with a magnetic stir bar and a rubber septum was added 4-CzIPN (19.7 mg, 0.025 mmol, 0.05 equiv), the corresponding carboxylic acid **1i** (0.5 mmol, 132.7 mg, 1 equiv) and PIDA (322.1 mg, 1.0 mmol, 2 equiv). DCE (M = 98.95 g/mol, 5 mL, 6.25 g) was then added *via* syringe under an argon atmosphere. The vial was sealed with Parafilm and irradiated with 456 nm LED strips for 16 h as described in the "Workflow" section. When the reaction was over, the solvent was recovered by distillation (3.7 mL, 4.6 g) and the crude mixture was subjected to purification by chromatography on silica gel (Hex:EtOAc, 95/5 to 80/20) to afford the desired product **2i** as yellow oil (98.2 mg, 77% yield) and the major byproduct **PhI** (172.6 mg, 85% yield).

A. E factor evaluation

$$\text{Completed } E \text{ Factor (cEF)} = \frac{\sum m(\text{raw materials}) + \sum m(\text{reagents}) + \sum m(\text{solvents}) - m(\text{product})}{m(\text{product})}$$

$$\text{cEF} = \frac{0.1327 + 0.0197 + 0.3221 - 0.1726 + 6.25 - 4.6 - 0.0982}{0.0982} = 18.9 \text{ kg waste per kg product}$$

$$\text{Traditionnal } E\text{-factor (tEF)} = \frac{\sum m(\text{raw materials}) + \sum m(\text{reagents}) + 0.1\text{x} \sum m(\text{solvents}) - m(\text{product})}{m(\text{product})}$$

10% of solvent

$$\text{tEF} = \frac{0.1327 + 0.0197 + 0.3221 - 0.1726 + (0.1 * 6.25) - 0.0982}{0.0982} = 8.4 \text{ kg waste per kg product}$$

$$\text{Simple } E \text{ Factor (sEF)} = \frac{\sum m(\text{raw materials}) + \sum m(\text{reagents}) - m(\text{product})}{m(\text{product})}$$

Solvents not included

$$\text{sEF} = \frac{0.1221 + 0.0197 + 0.3221 - 0.1726 - 0.0982}{0.0982} = 2.1 \text{ kg waste per kg product}$$

B. Atom and Carbon Efficiencies evaluations

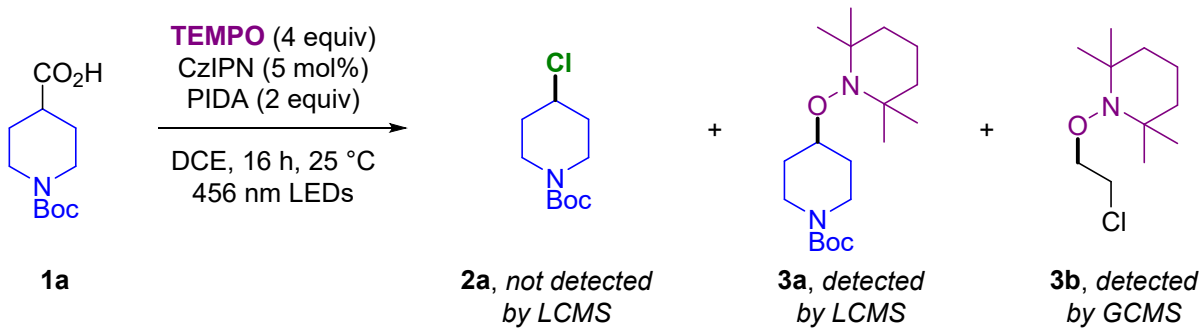
$$\textit{Atom Economy (AE)} = \frac{\text{M(product)}}{\text{M(reactants)}} \times 100 = \frac{\text{M(}\mathbf{2i}\text{)}}{\text{M(}\mathbf{1i}\text{) + M(DCE)}} \times 100 = \frac{255.7}{265.3 + 99} \times 100 = 70\%$$

$$\textit{Atom Efficiency} = \frac{\text{AE x Yield}}{100} = \frac{70 \times 77}{100} = 54\%$$

$$\textit{Carbon Efficiency} = \frac{\text{C(product)}}{\text{C(reactants)}} = \frac{\text{C(}\mathbf{2i}\text{)}}{\text{C(}\mathbf{1i}\text{) + C(DCE)}} = \frac{13}{14 + 2} = 81\%$$

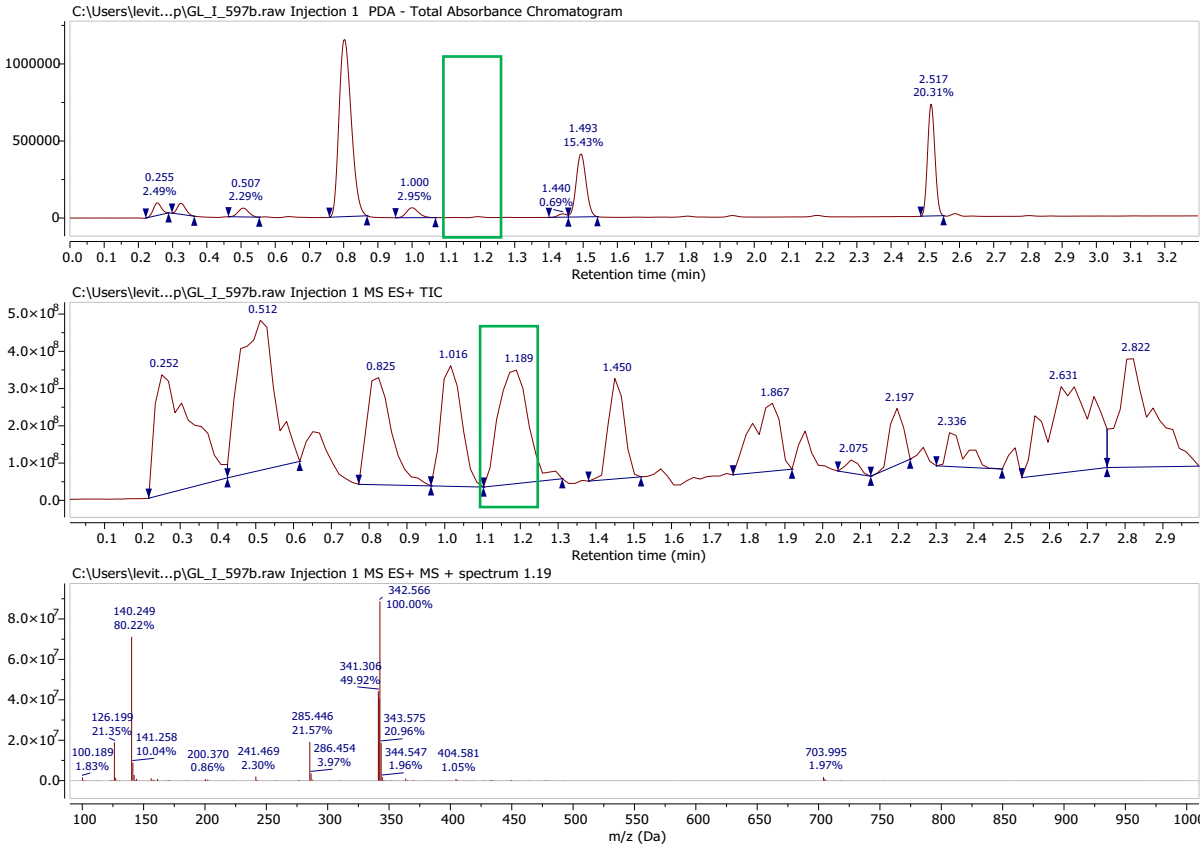
5. Mechanistic Investigations

A. TEMPO Trapping Experiment



To test the intermediacy of radical species, a trapping experiment was performed using TEMPO [(2,2,6,6-tetramethylpiperidin-1-yl)oxyl] as a radical scavenger. The reaction was performed according to the *General Procedure A* using 1-(*tert*-butoxycarbonyl)piperidine-4-carboxylic acid as substrate. The trapping of the 1-Boc-piperidinyl radical and the •CH_2CH_2Cl radical by TEMPO (**3a** and **3b**) was detected by LCMS and GCMS.

*Figure S2. LCMS of crude mixture containing compound **3a***



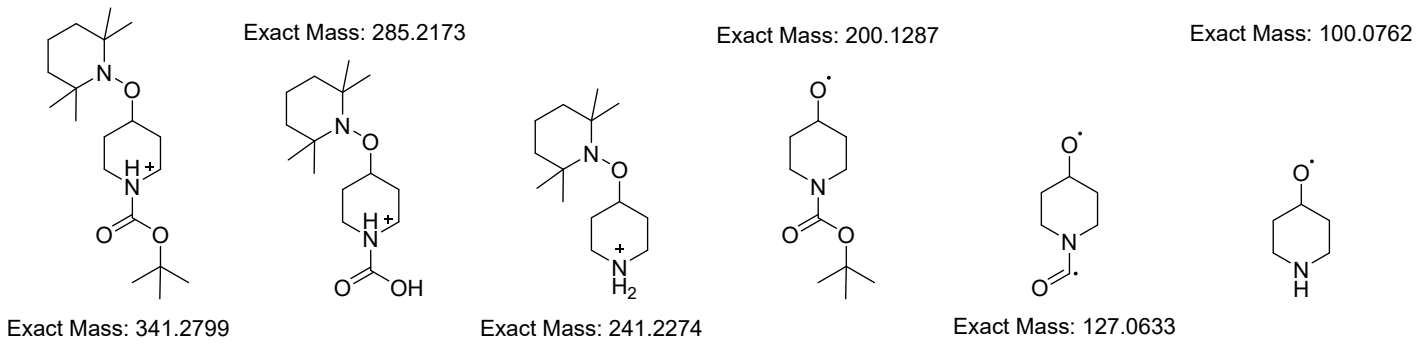
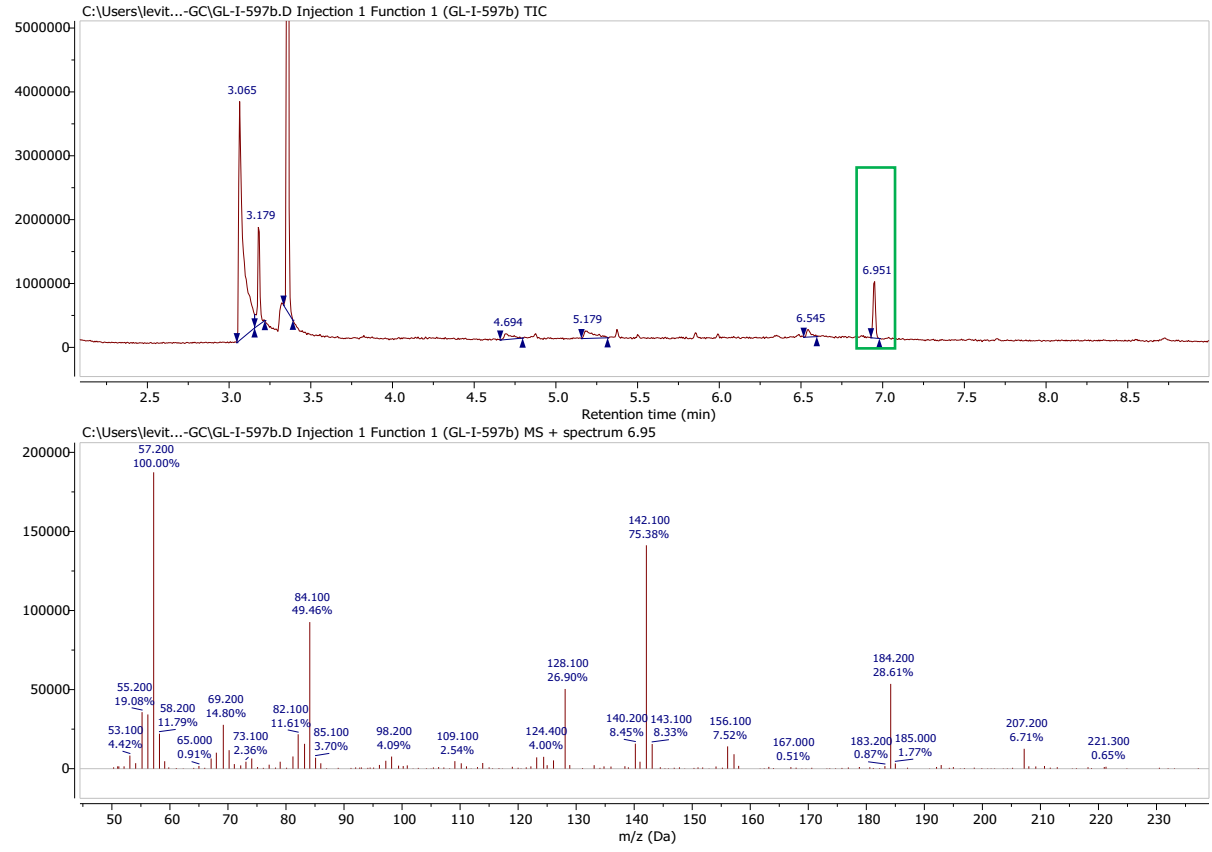
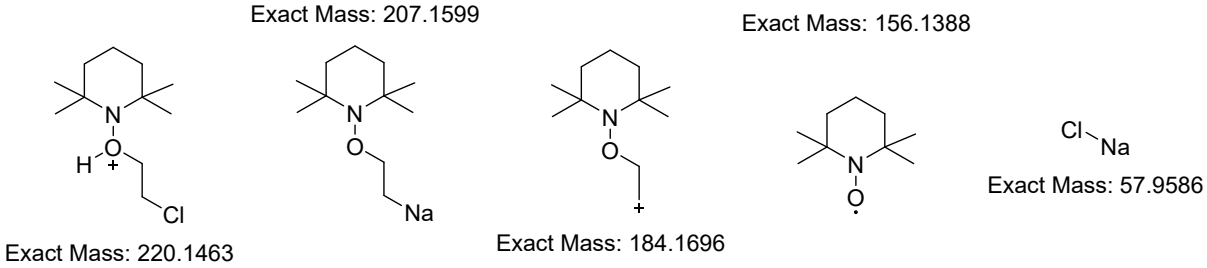
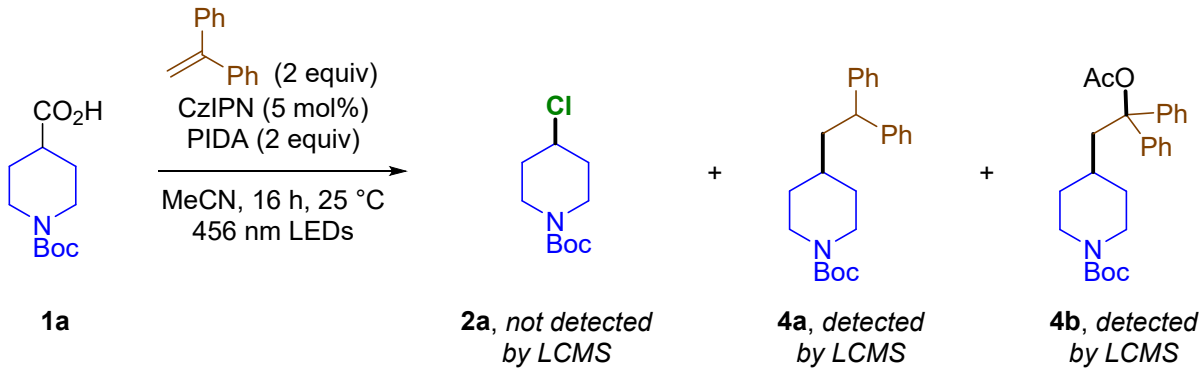


Figure S3. GCMS of crude mixture containing compound ***3b***



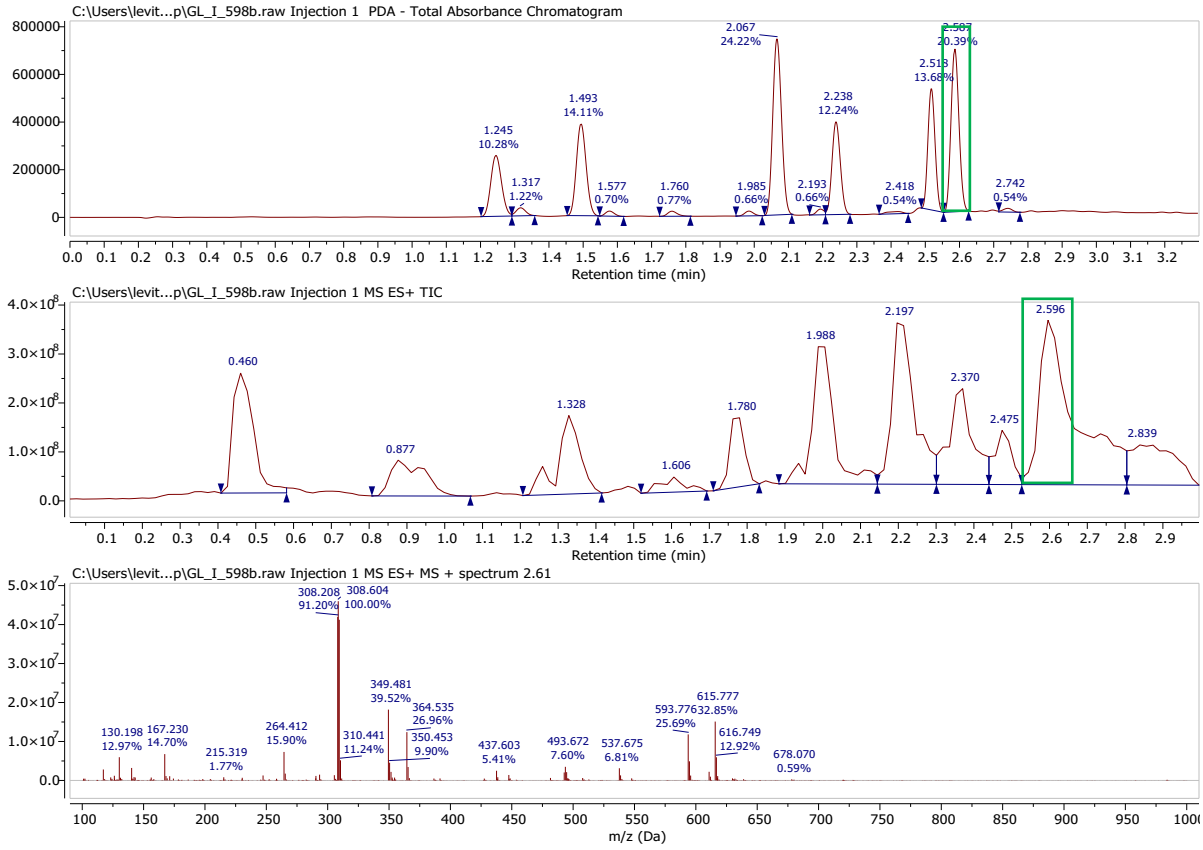


B. 1,1-Diphenylethylene Trapping Experiment



To test the intermediacy of radical species, a trapping experiment was performed using 1,1-diphenylethylene as a radical scavenger. The reaction was performed according to the *General Procedure A* using 1-(tert-butoxycarbonyl)piperidine-4-carboxylic acid as substrate. The trapping of the 1-Boc-piperidinyl radical by 1,1-diphenylethylene (**4a** and **4b**) was detected by LCMS.

*Figure S4. LCMS of crude mixture containing compound **4a***



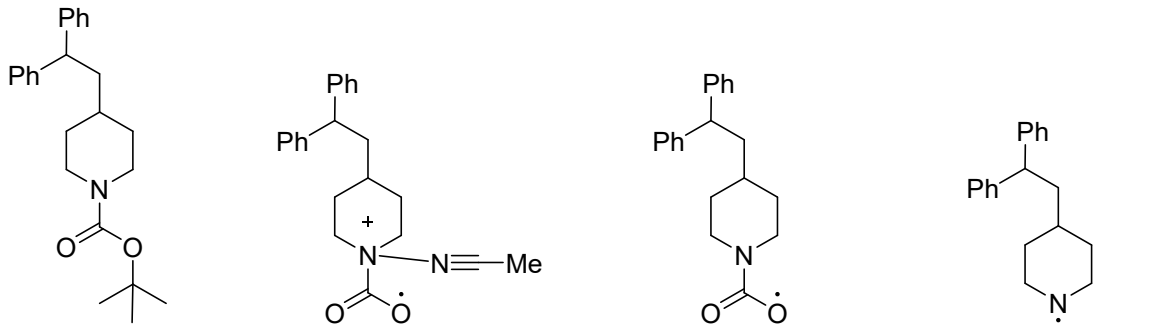
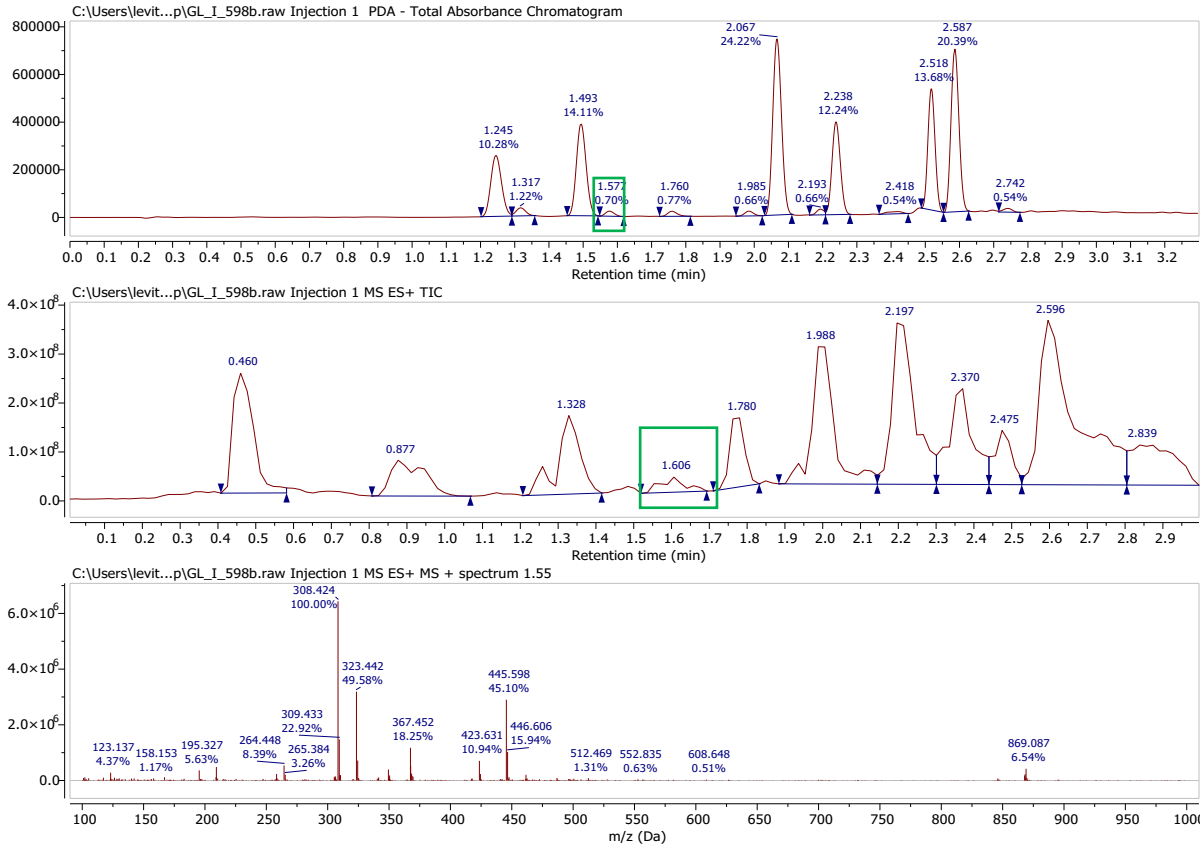
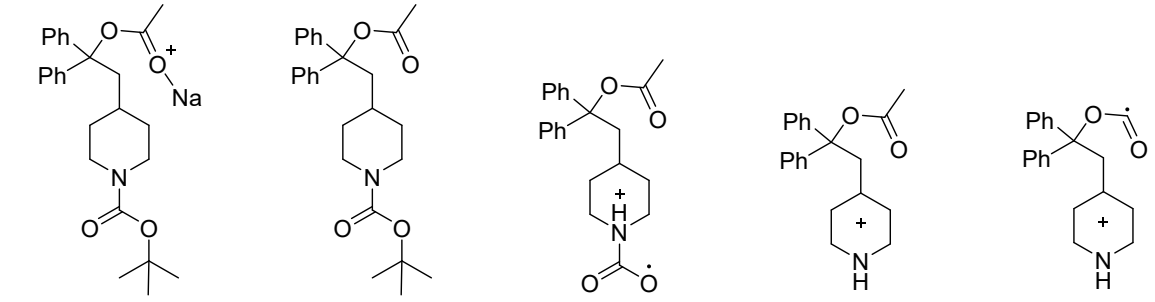


*Figure S5. LCMS of crude mixture containing compound **4b***



Exact Mass: 423.2410

Exact Mass: 323.1885



Exact Mass: 446.2302

Exact Mass: 367.1778

Exact Mass: 308.1651

6. References

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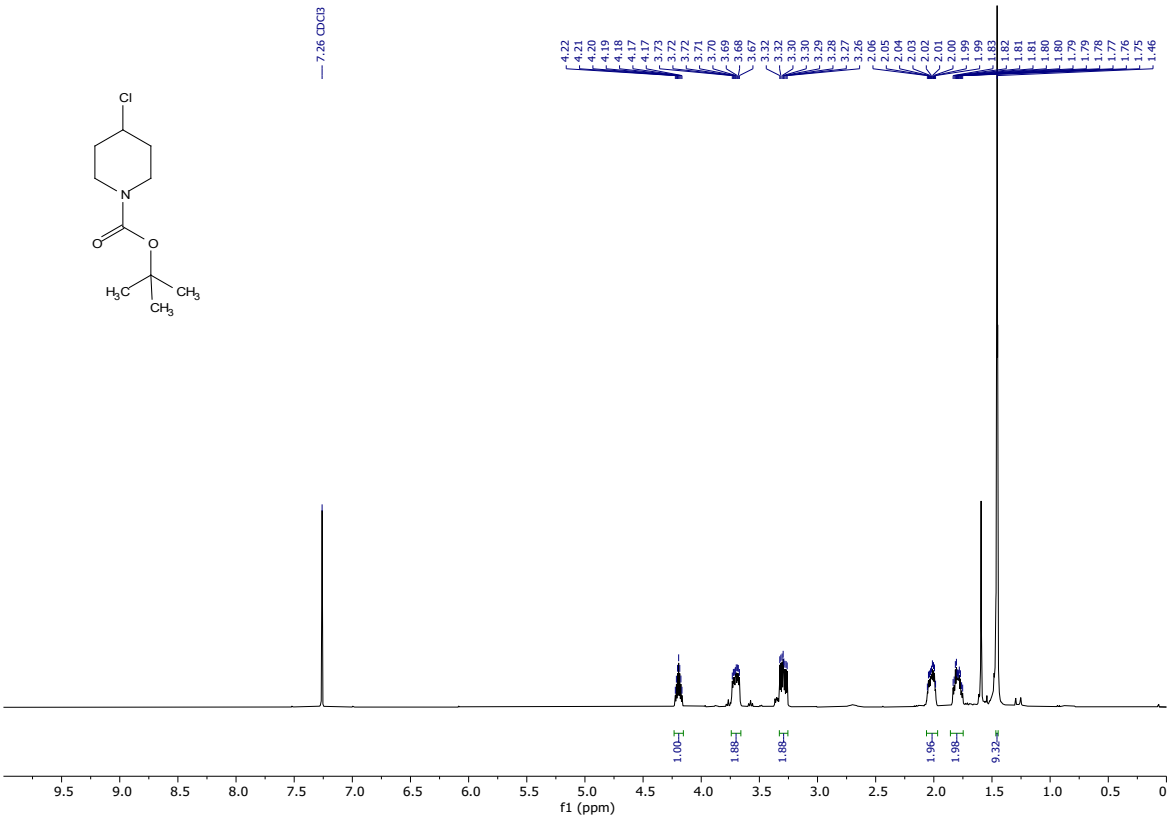
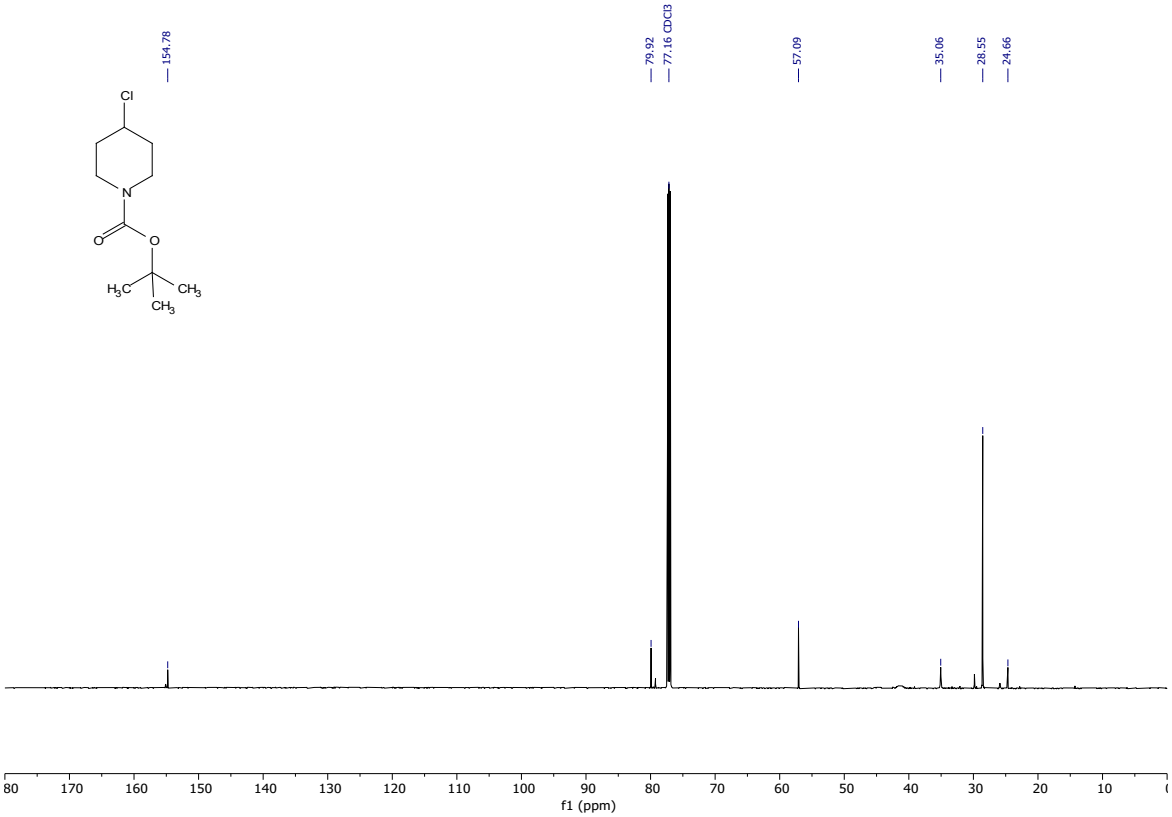
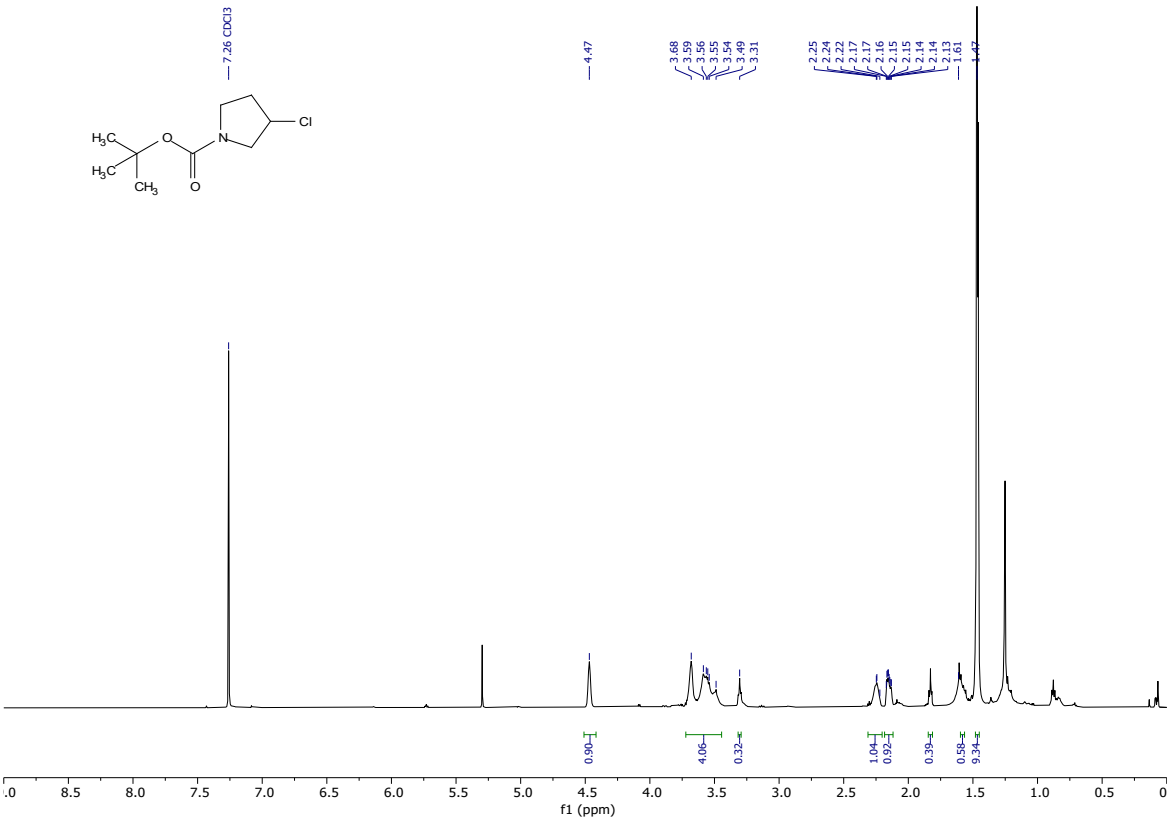
7. NMR Spectra



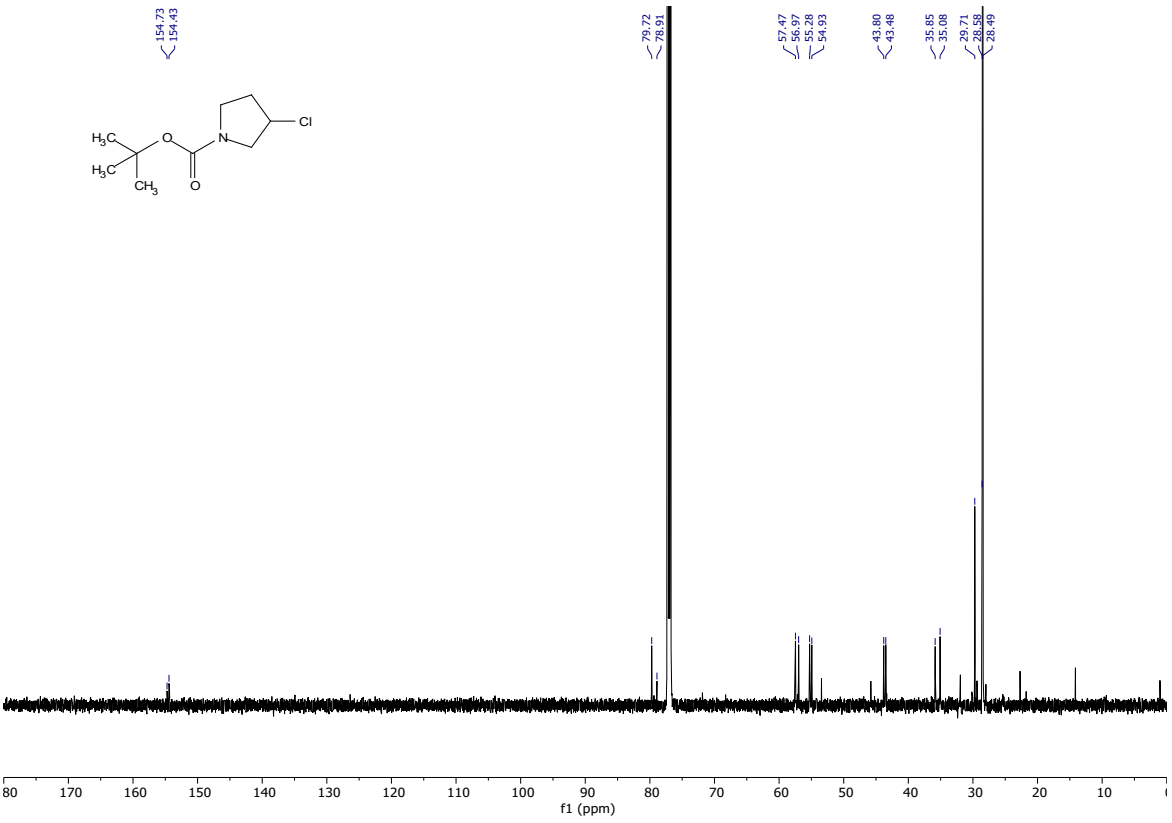
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2a**.



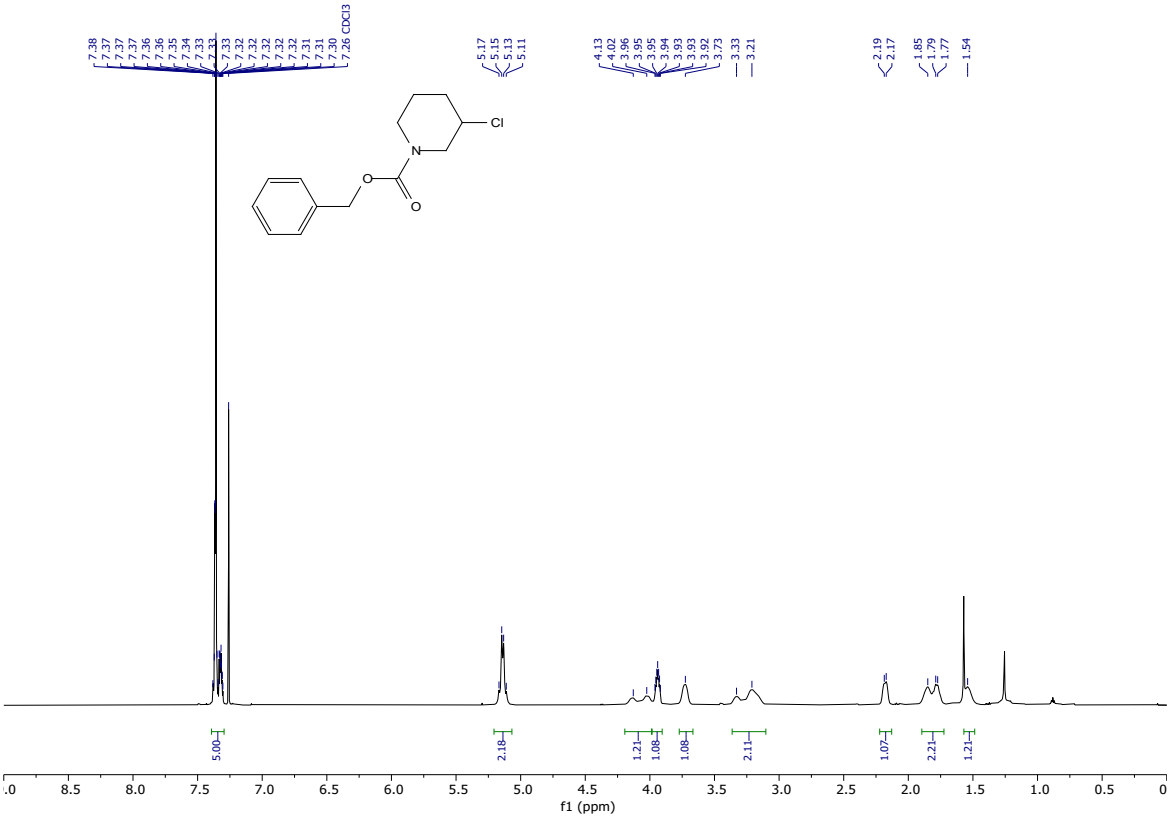
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2a.**



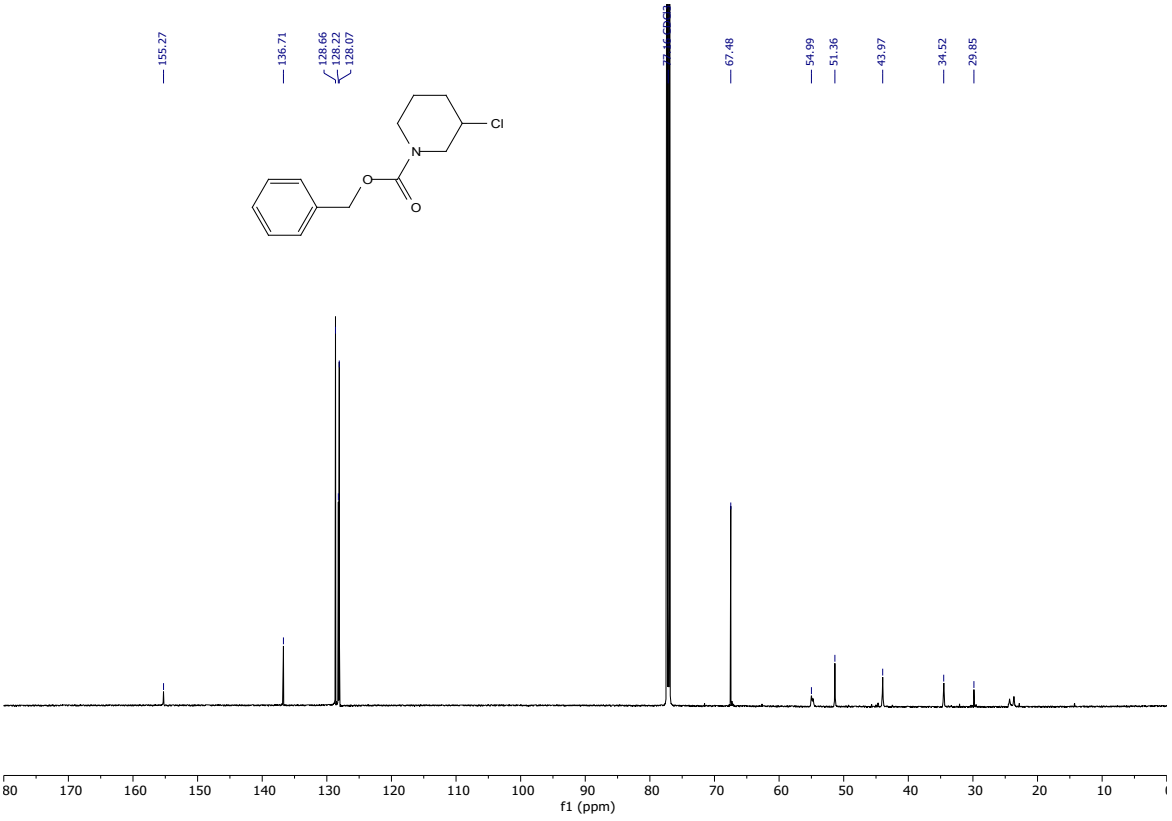
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2b** and **2b'**.



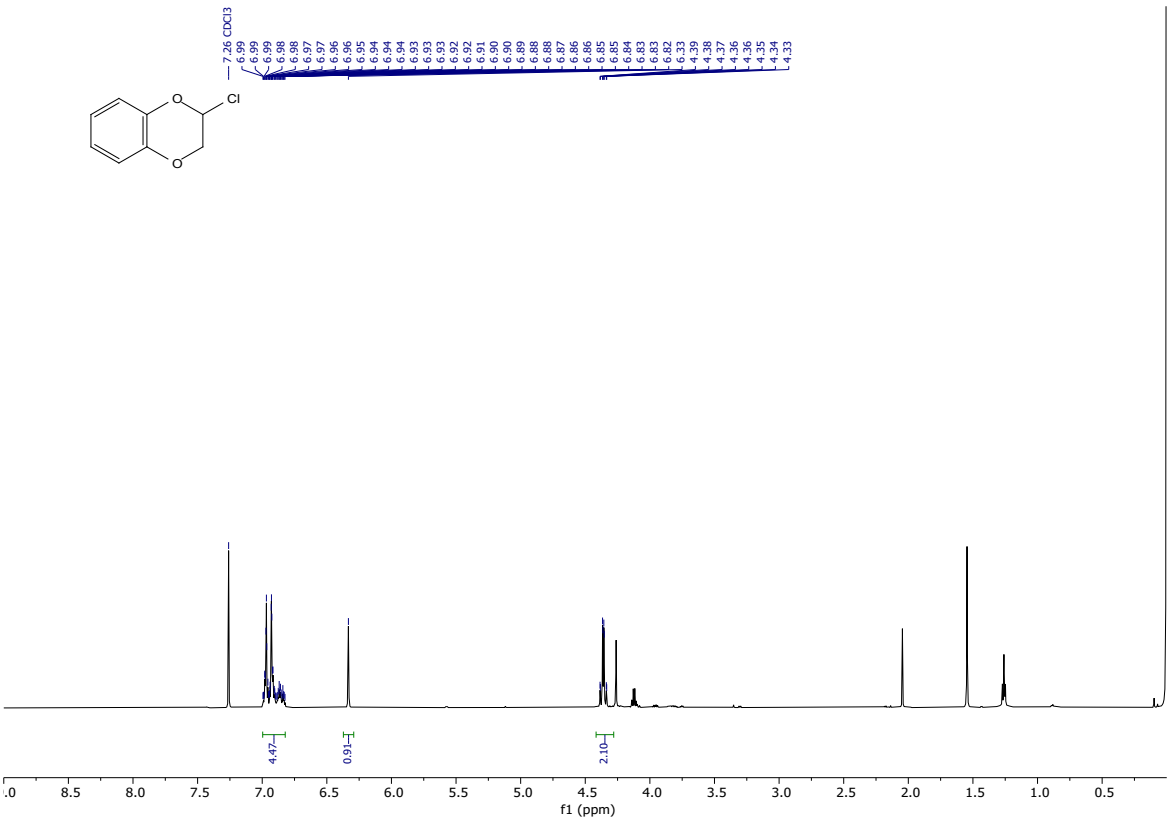
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2b** and **2b'.**



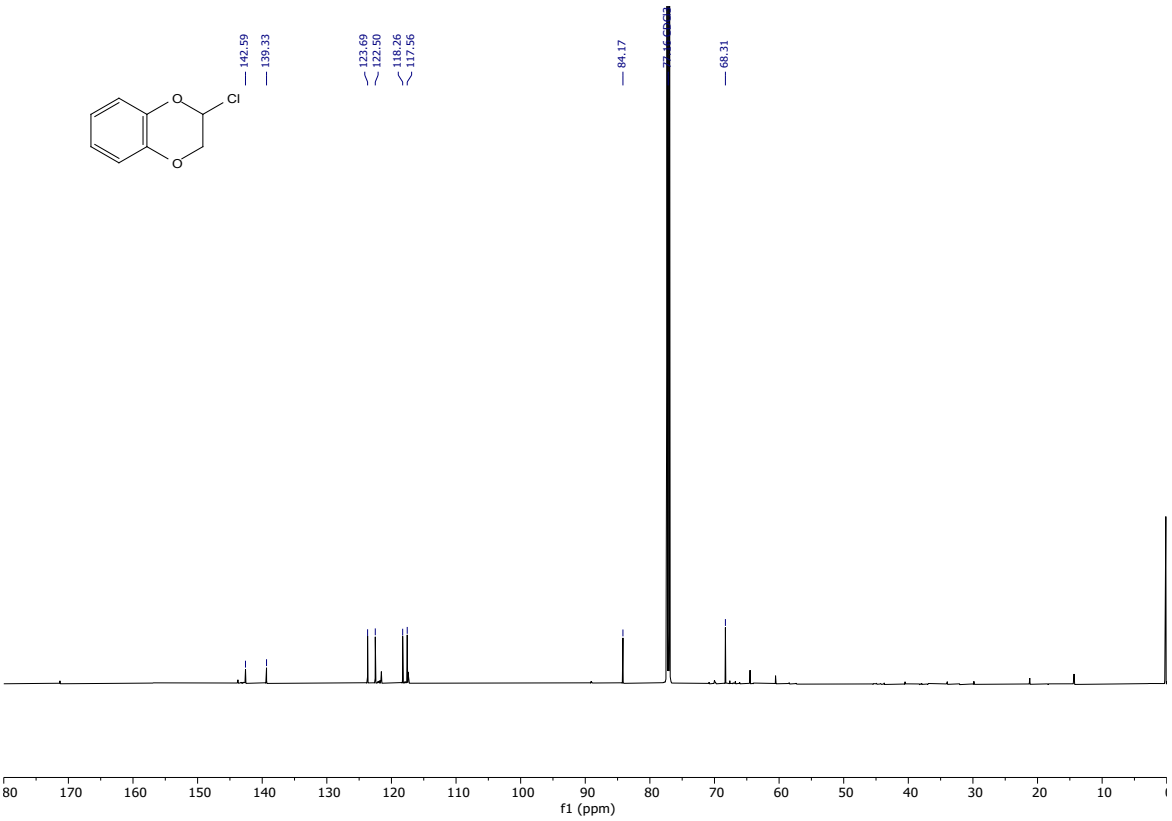
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2c**.



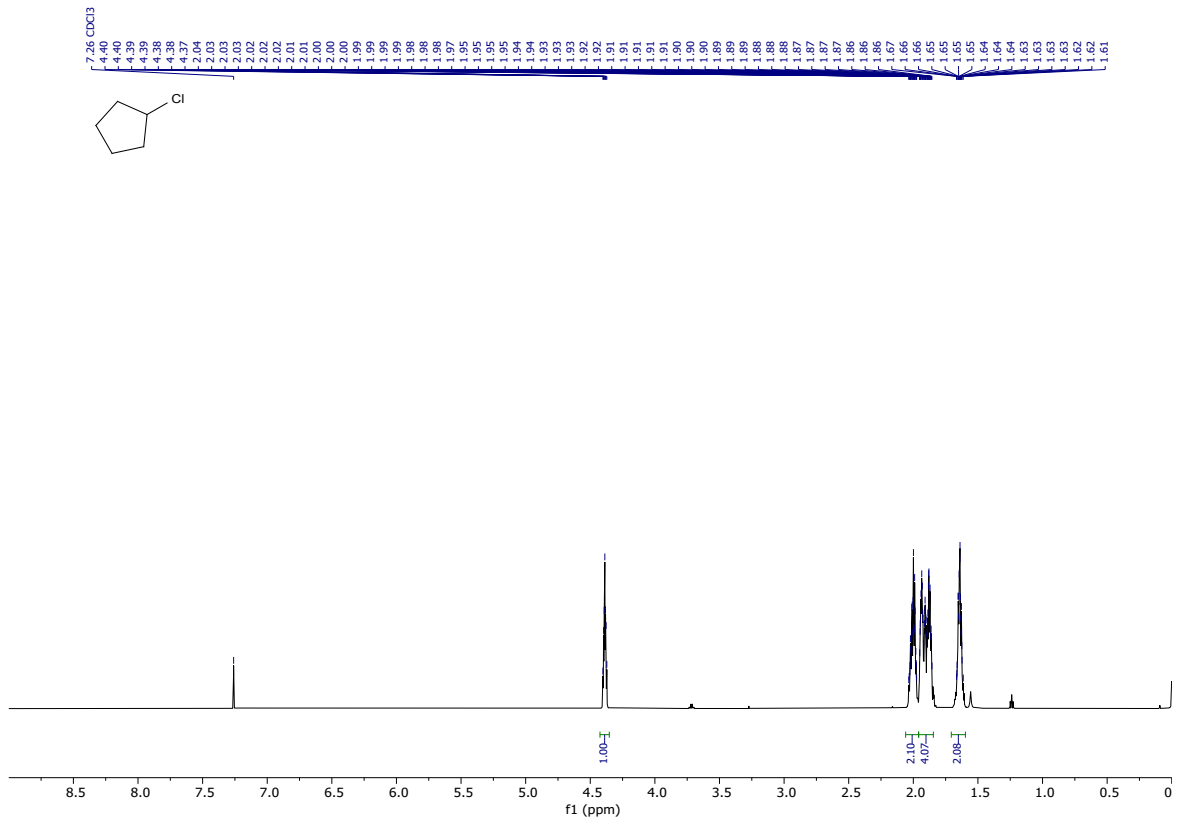
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2c.**



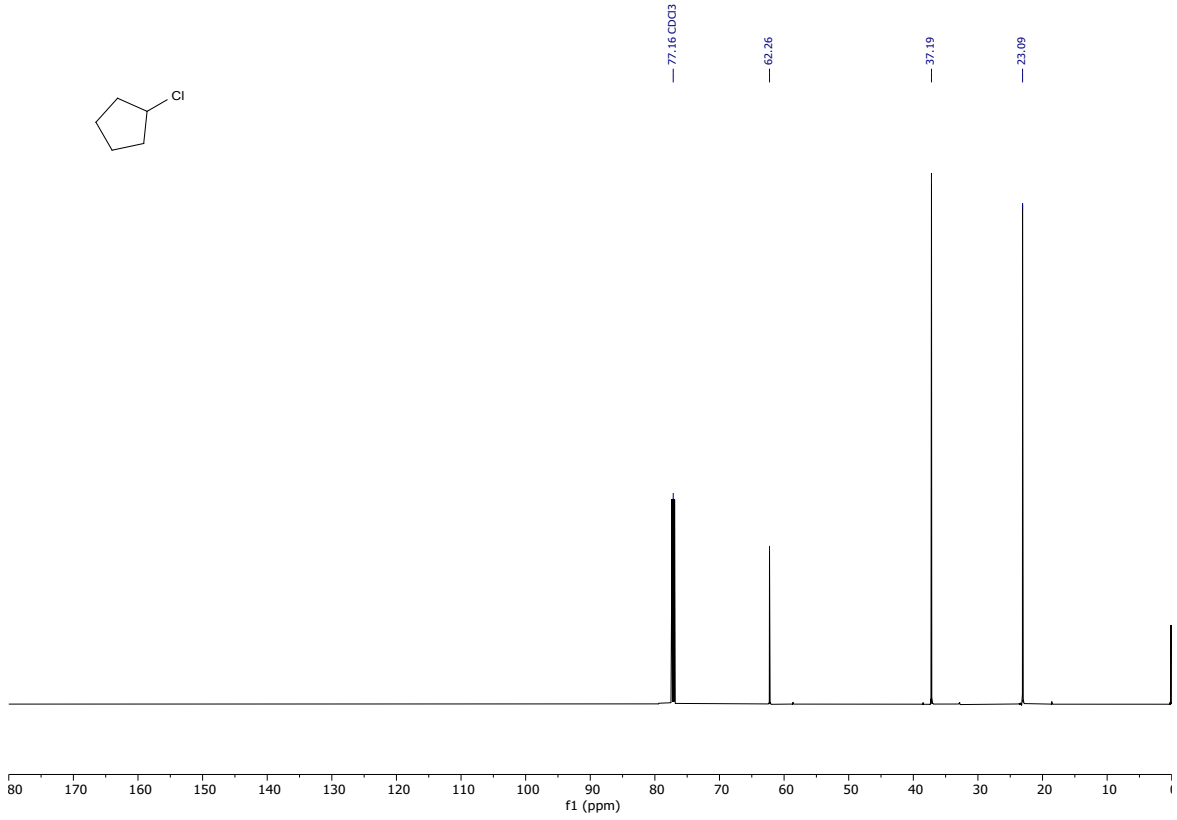
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2d**.



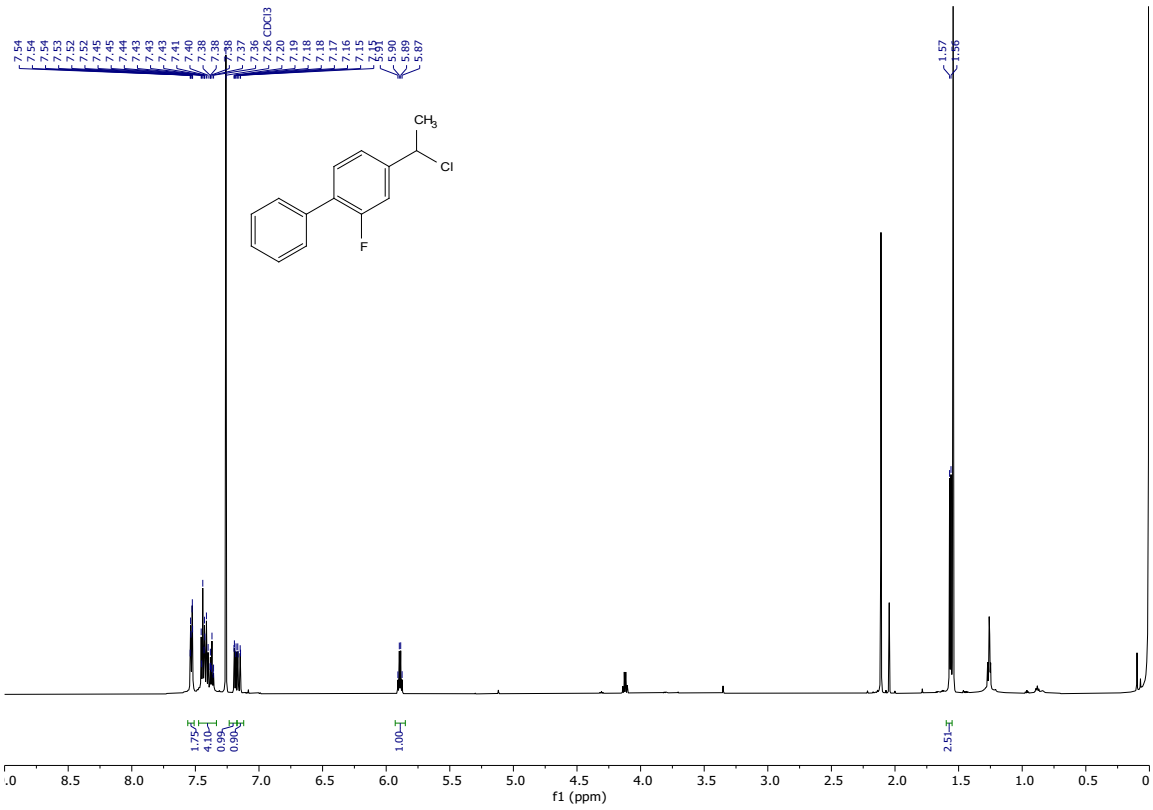
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2d.**



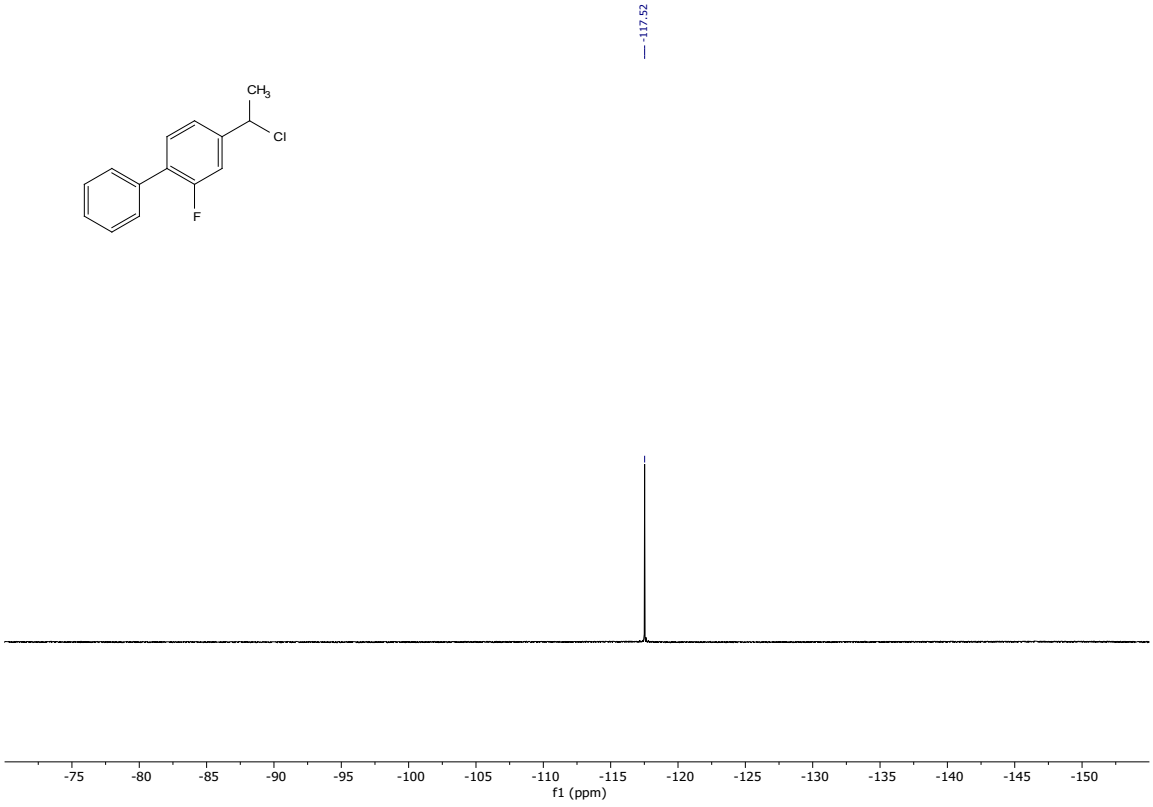
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2e**.



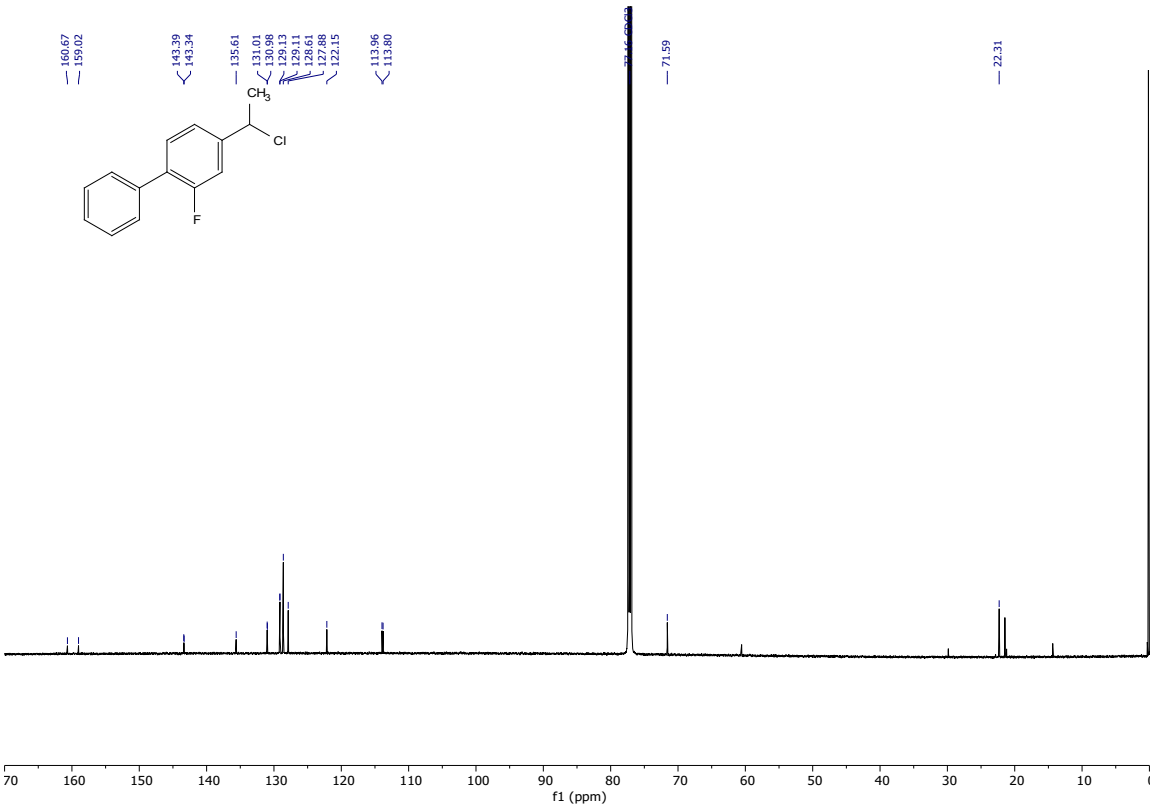
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2e.**



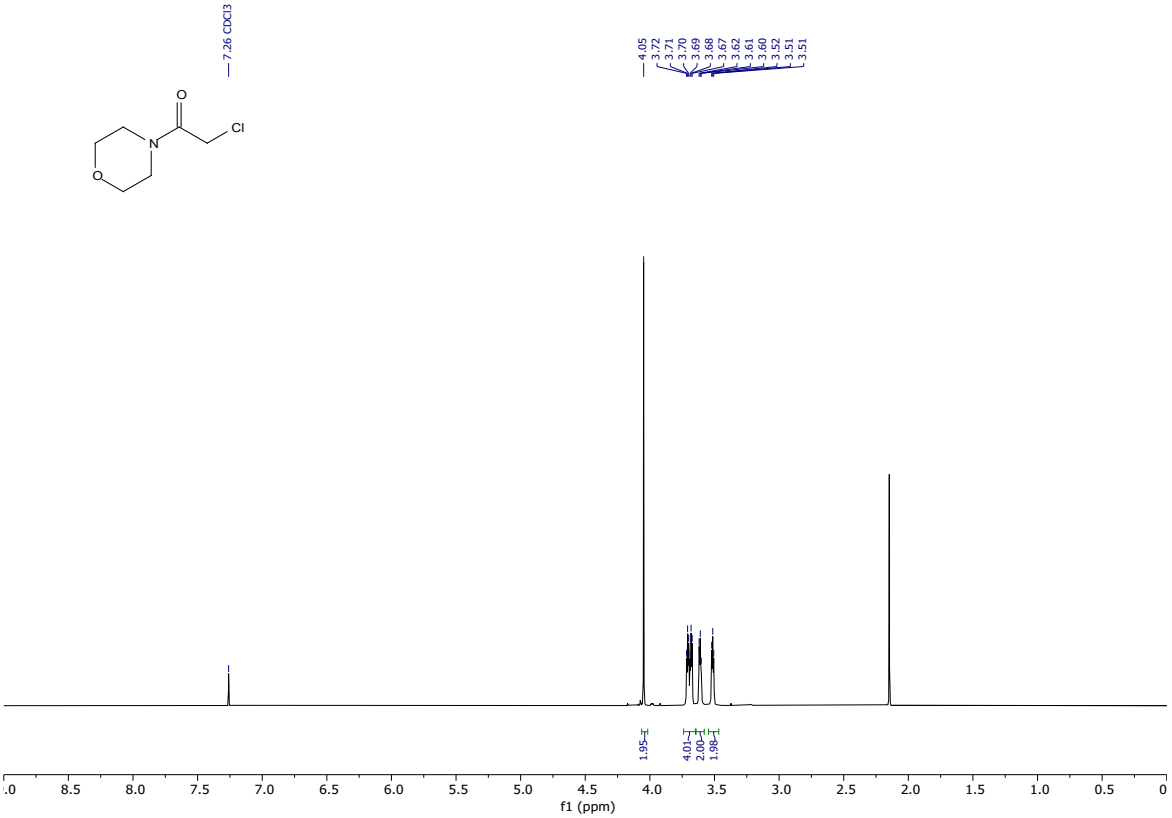
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2f**.



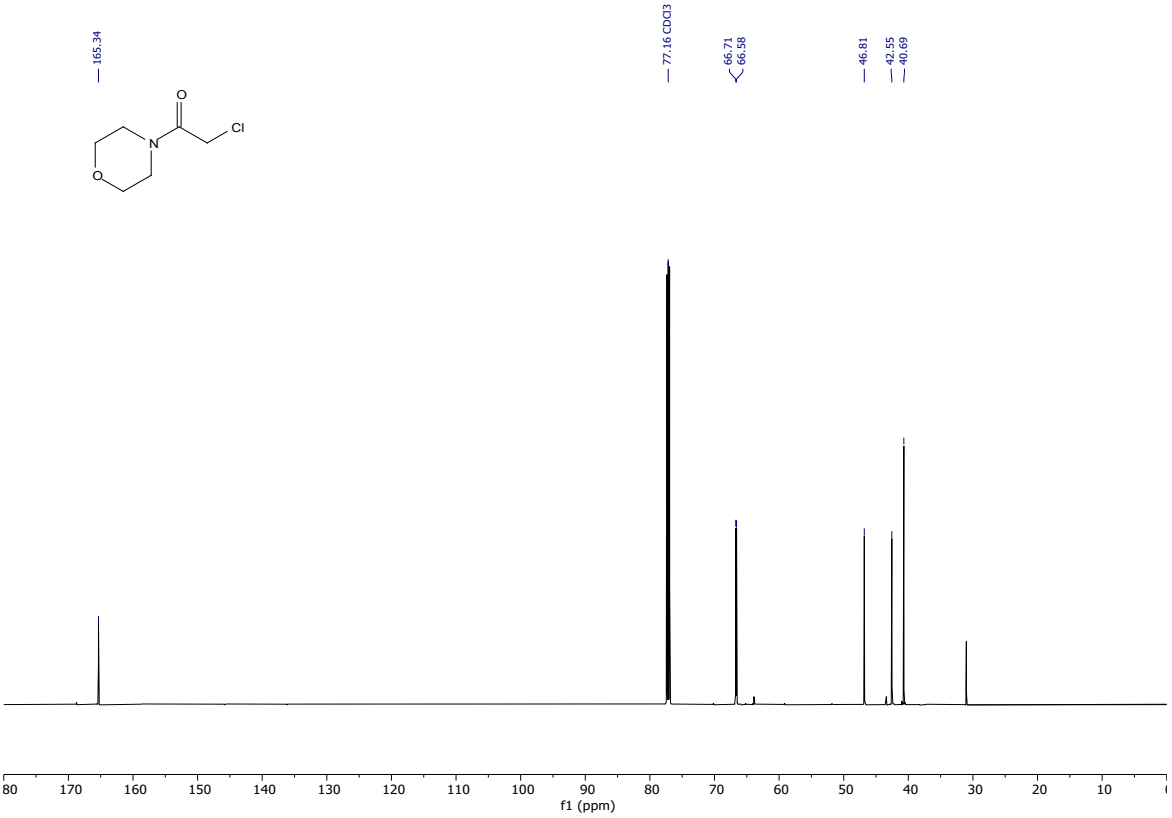
^{19}F NMR (565 MHz, $CDCl_3$) of compound **2f**.



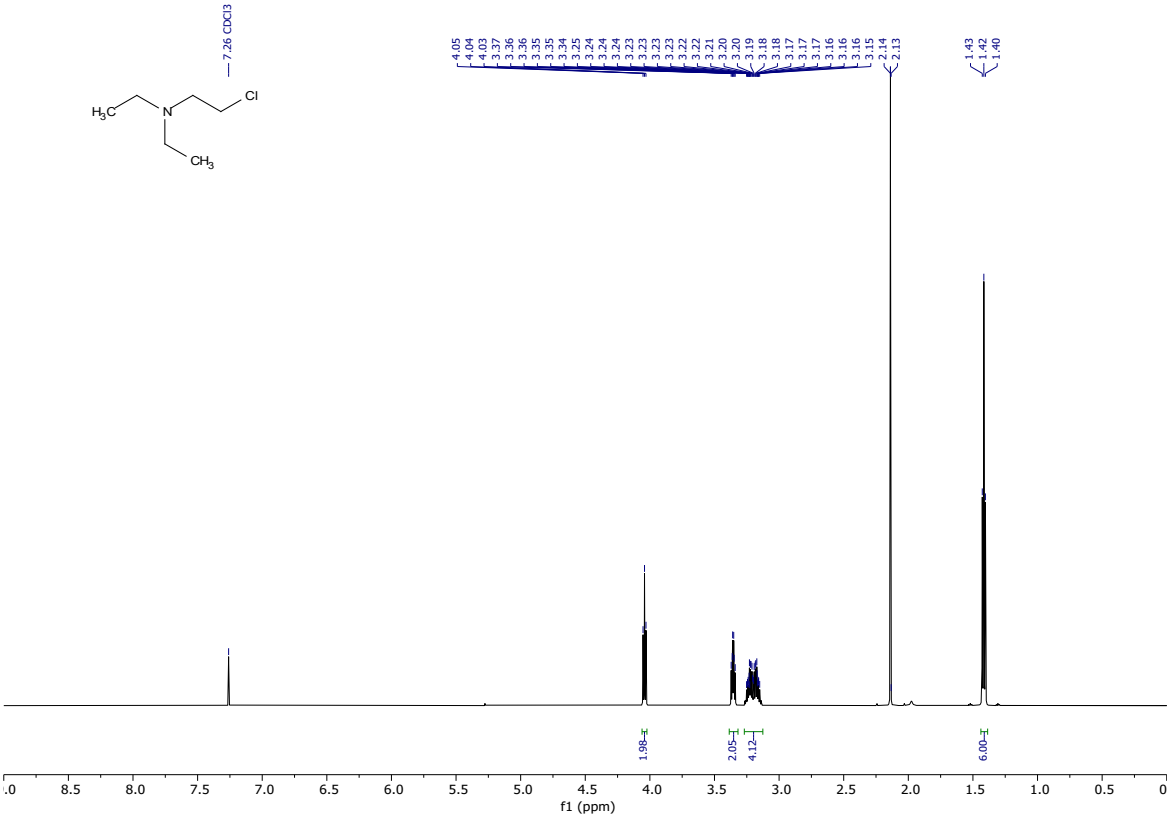
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2f.**



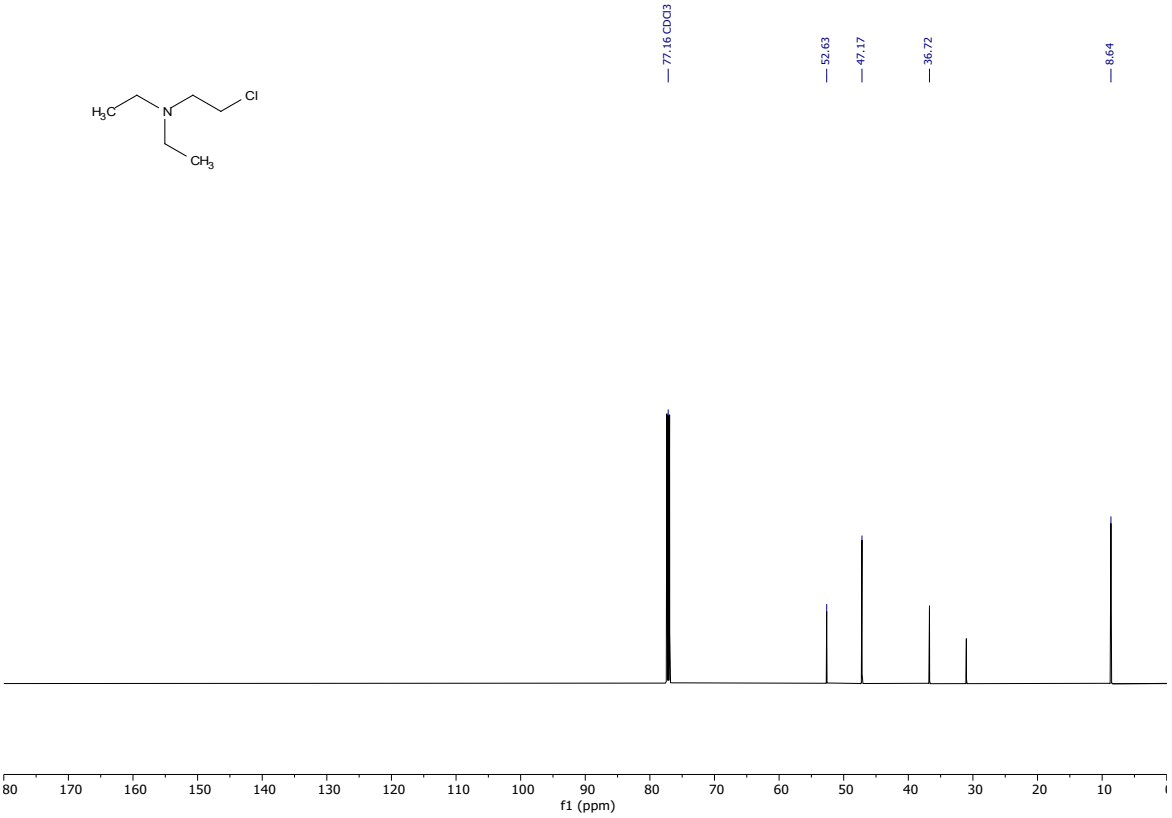
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2g**.



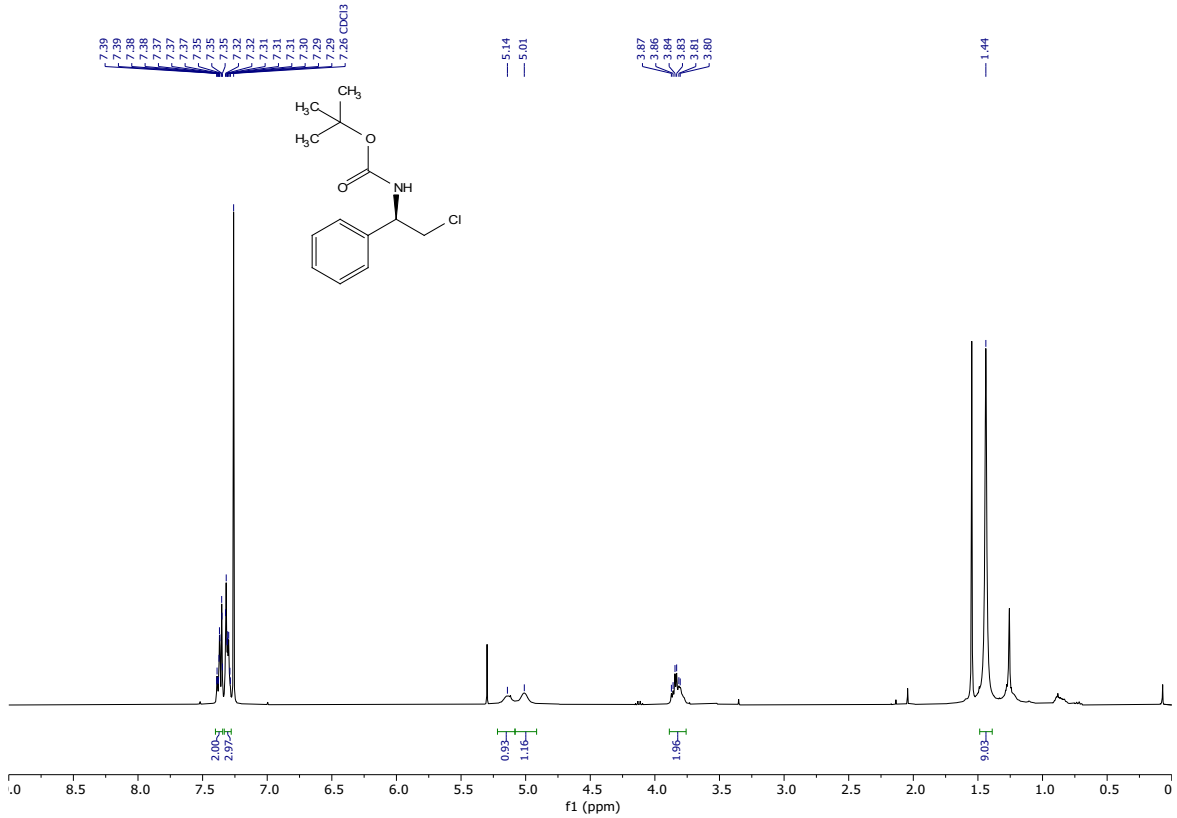
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2g.**



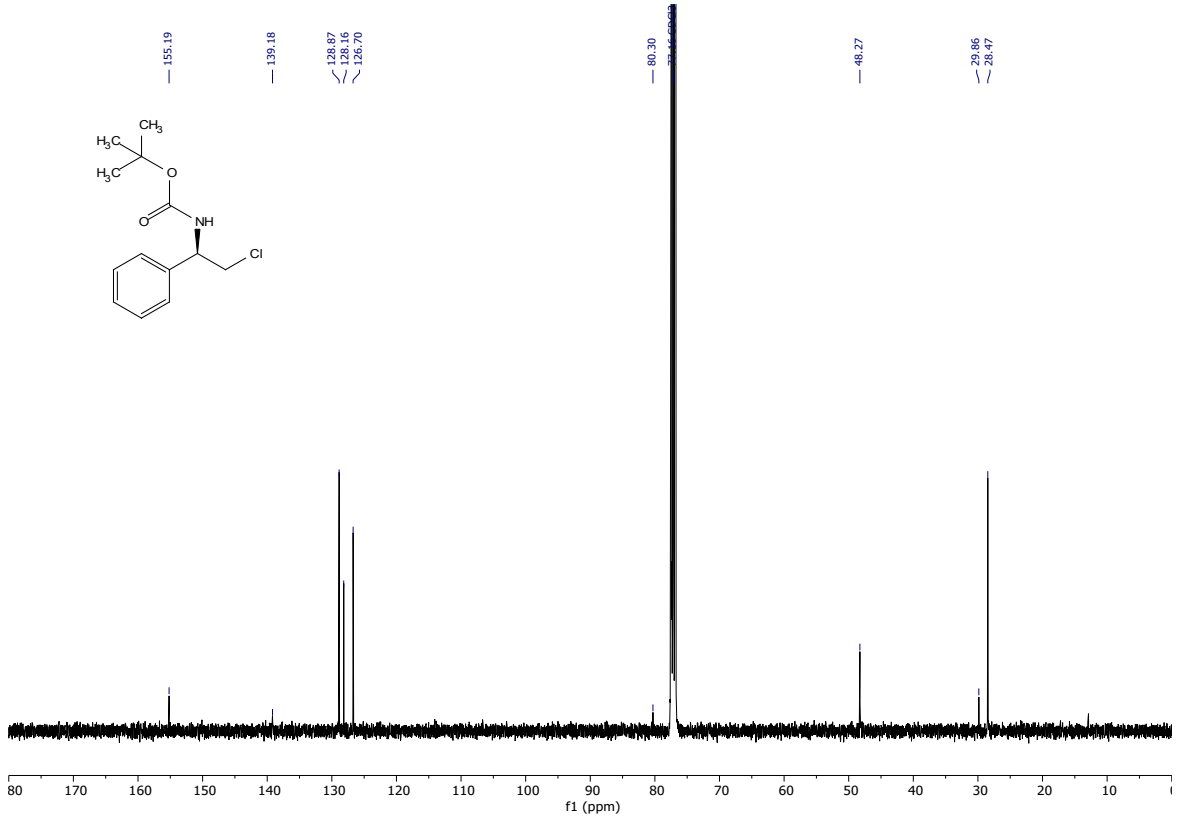
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2h**.



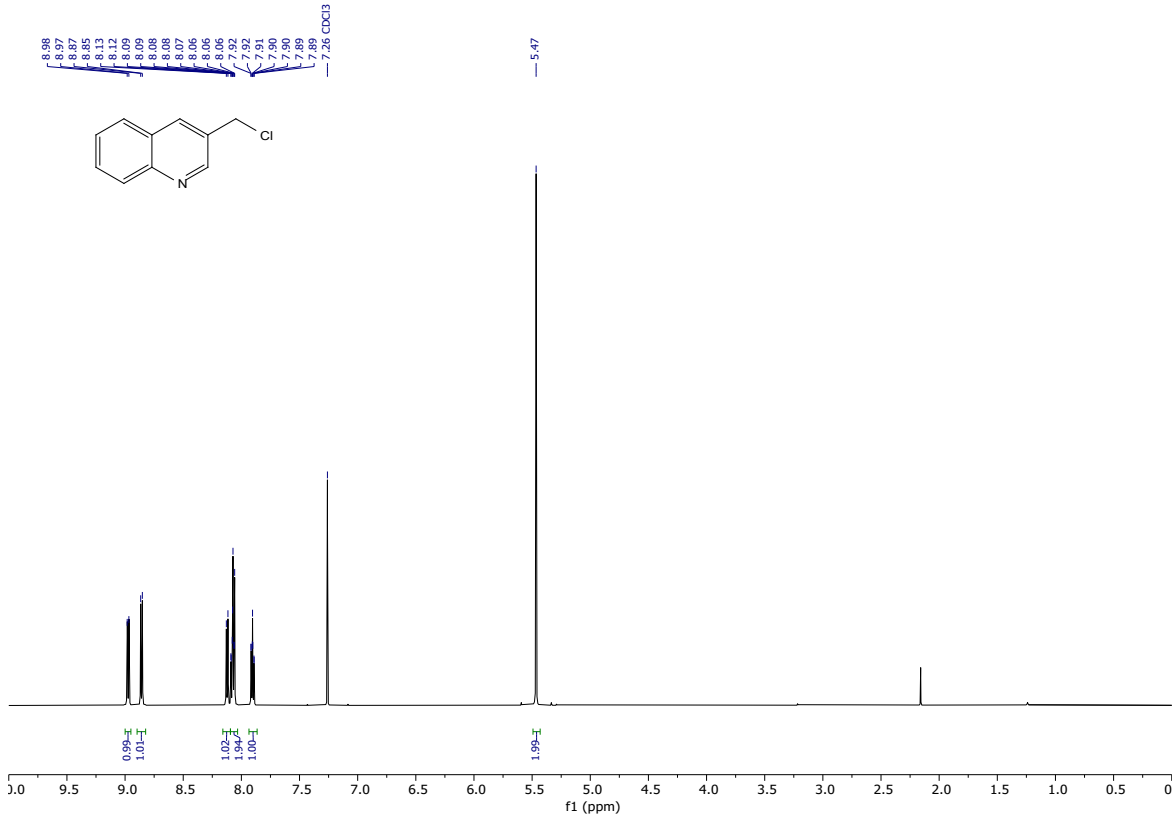
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2h.**



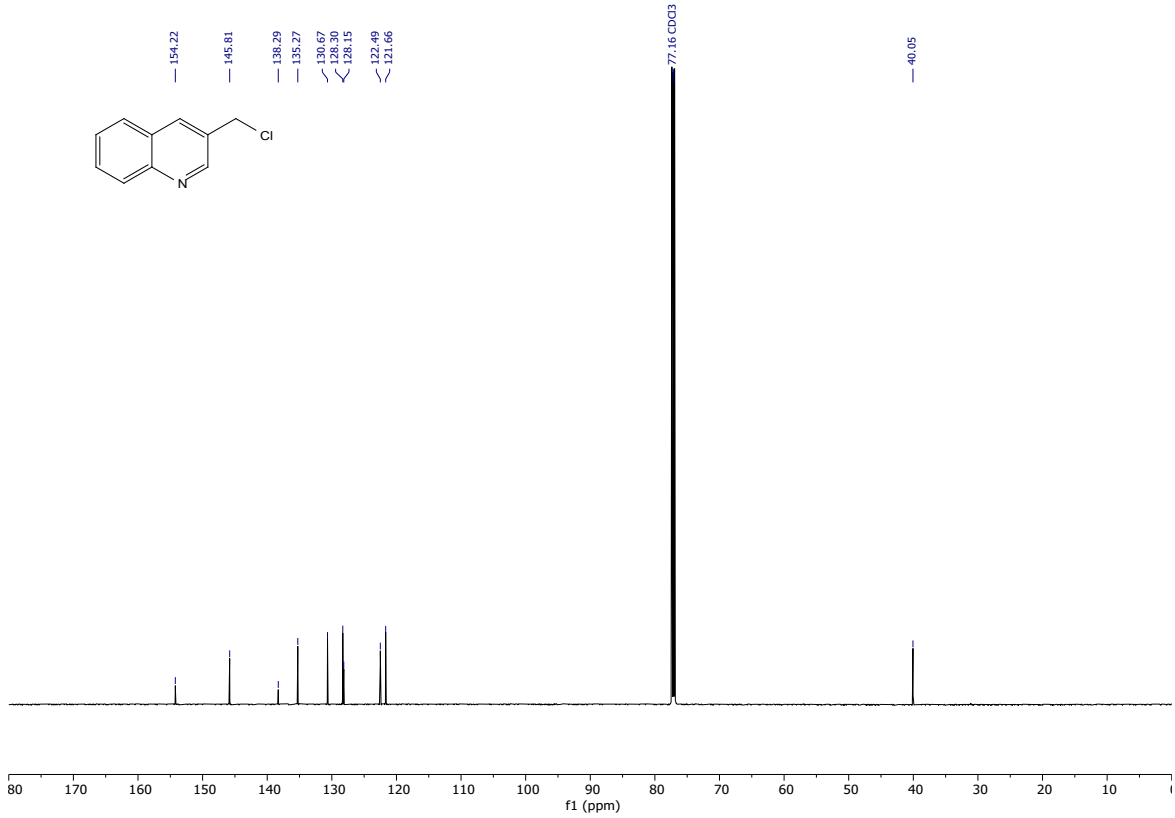
^{1}H NMR (400 MHz, $CDCl_3$) of compound **2i**.



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



^{1}H NMR (600 MHz, $CDCl_3$) of compound **2j**.



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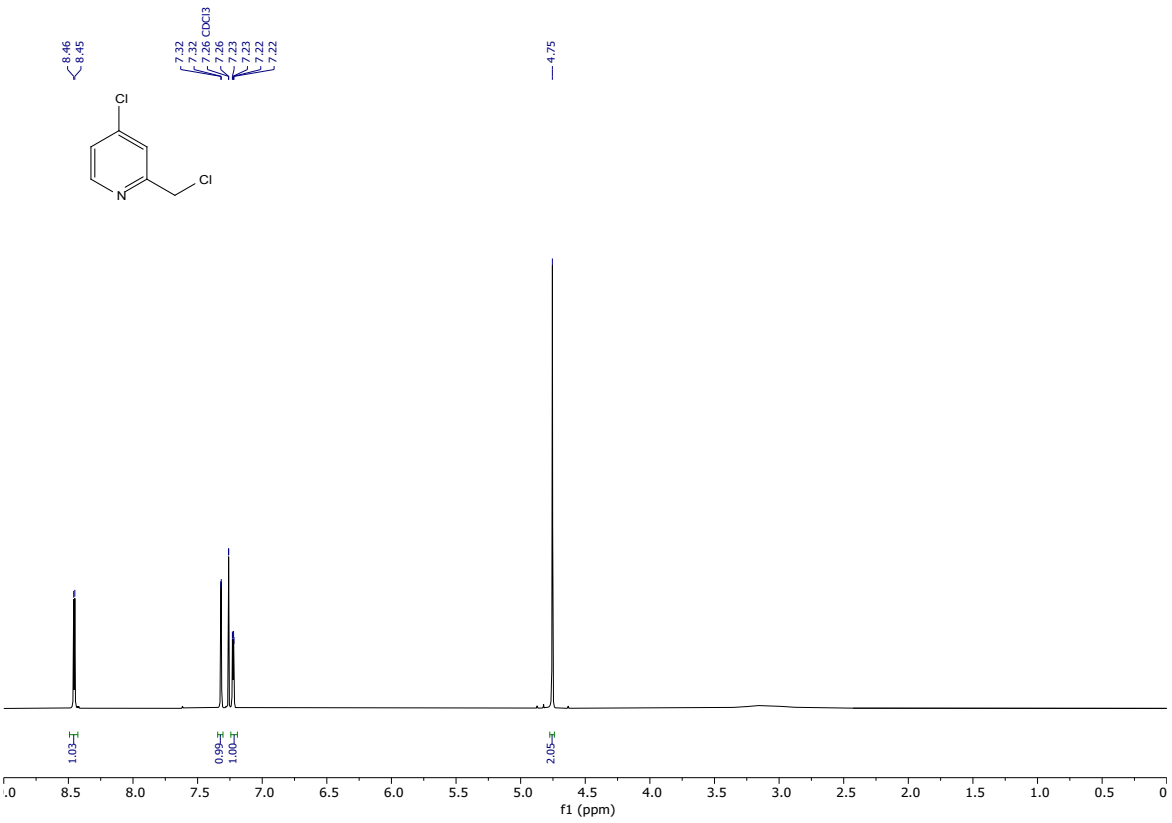
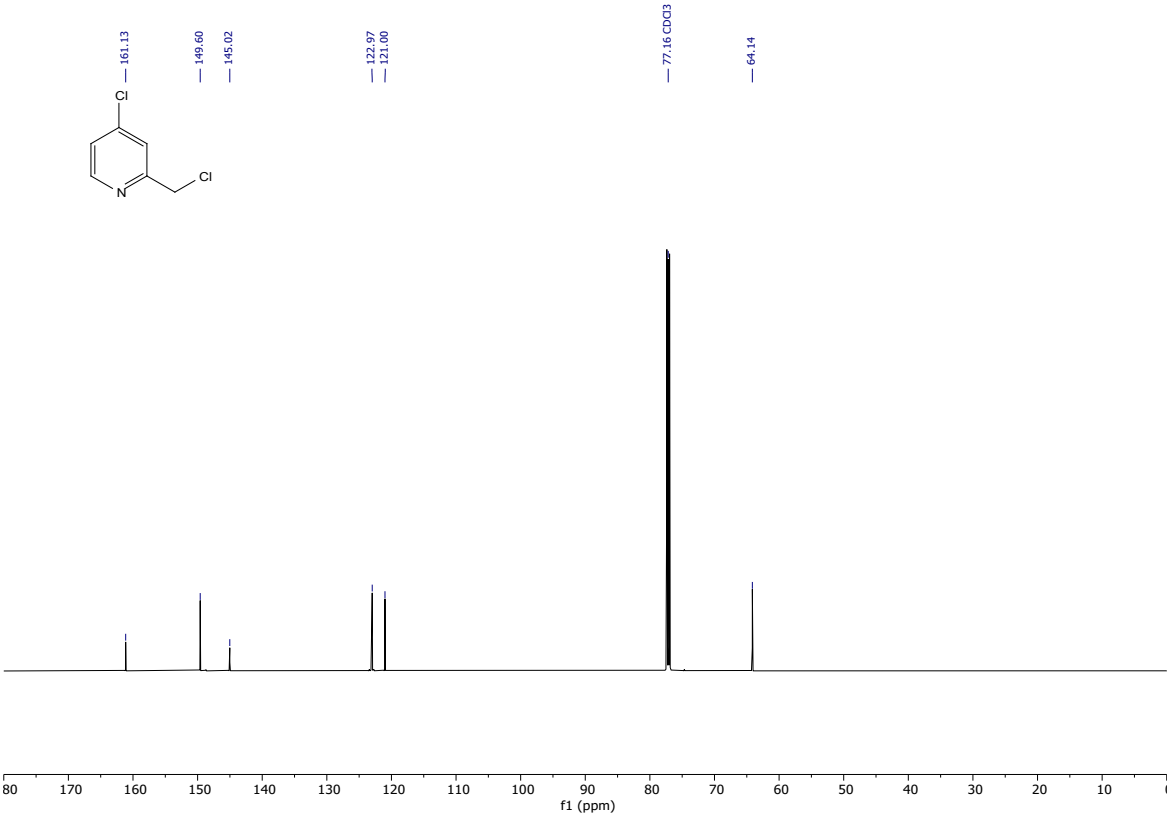
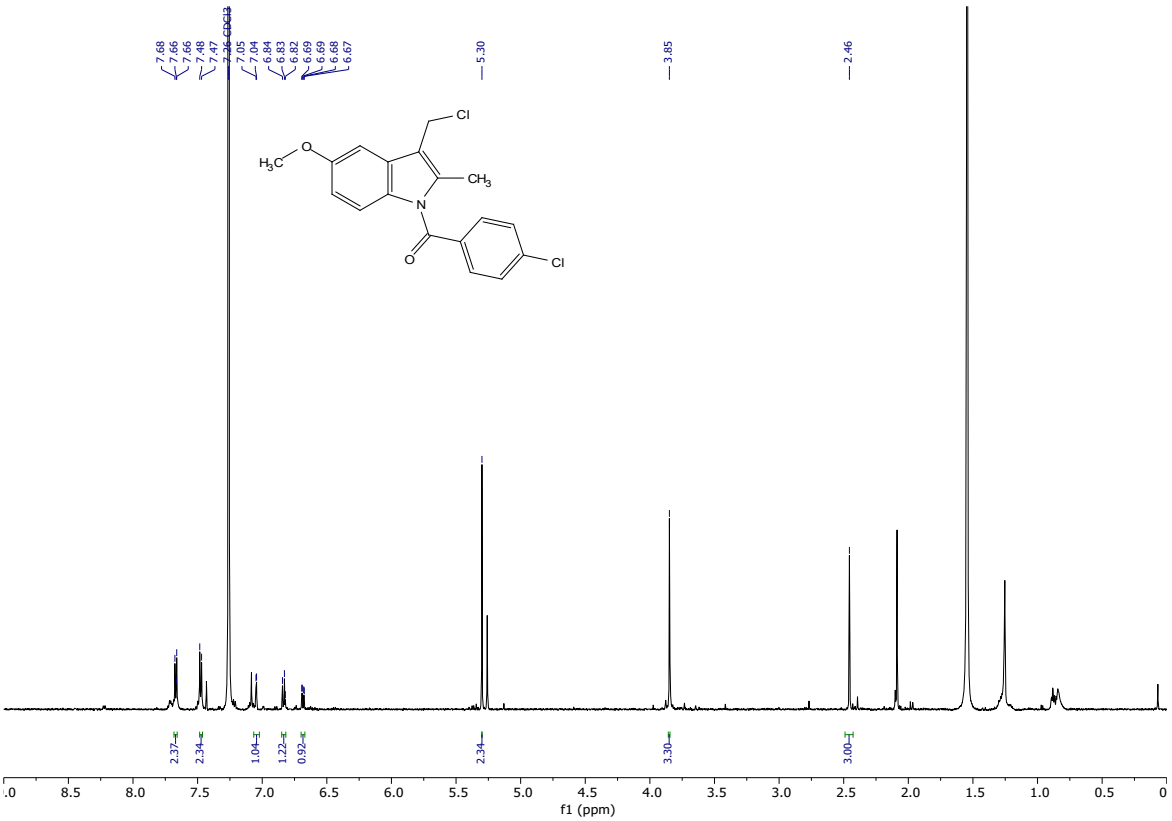


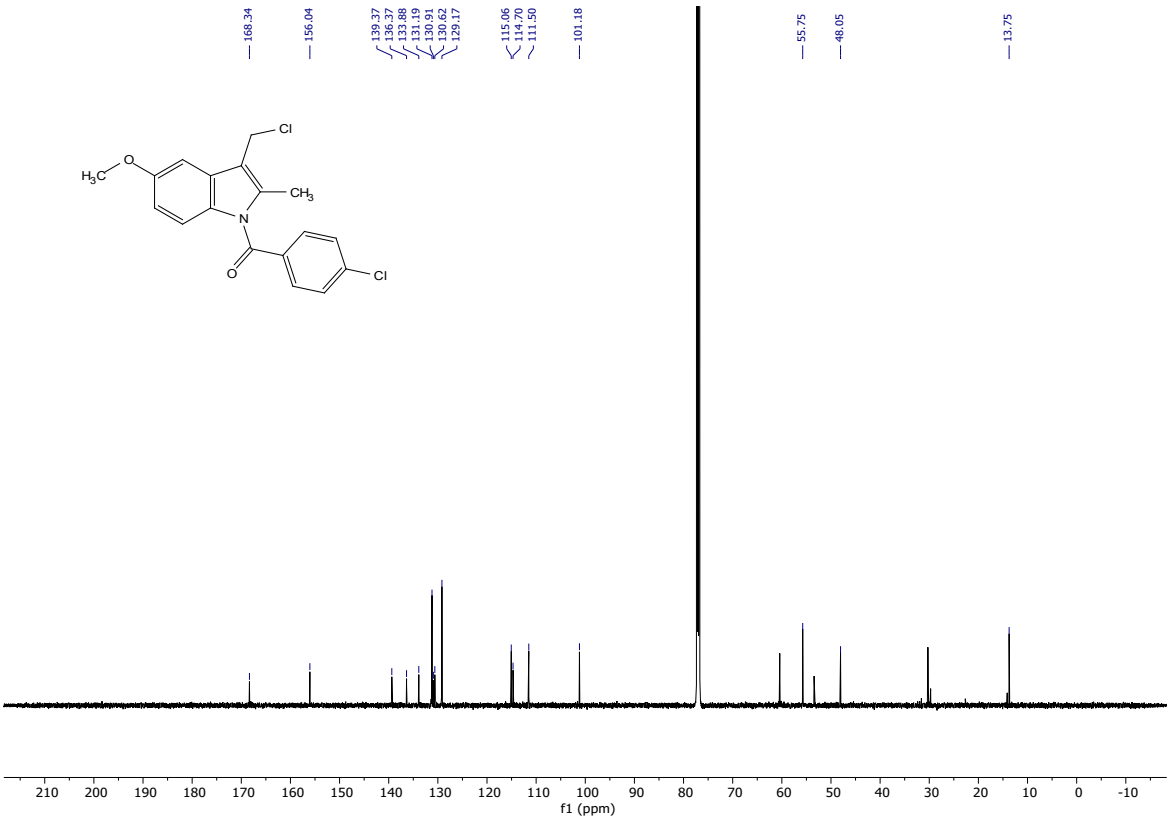
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2k**.



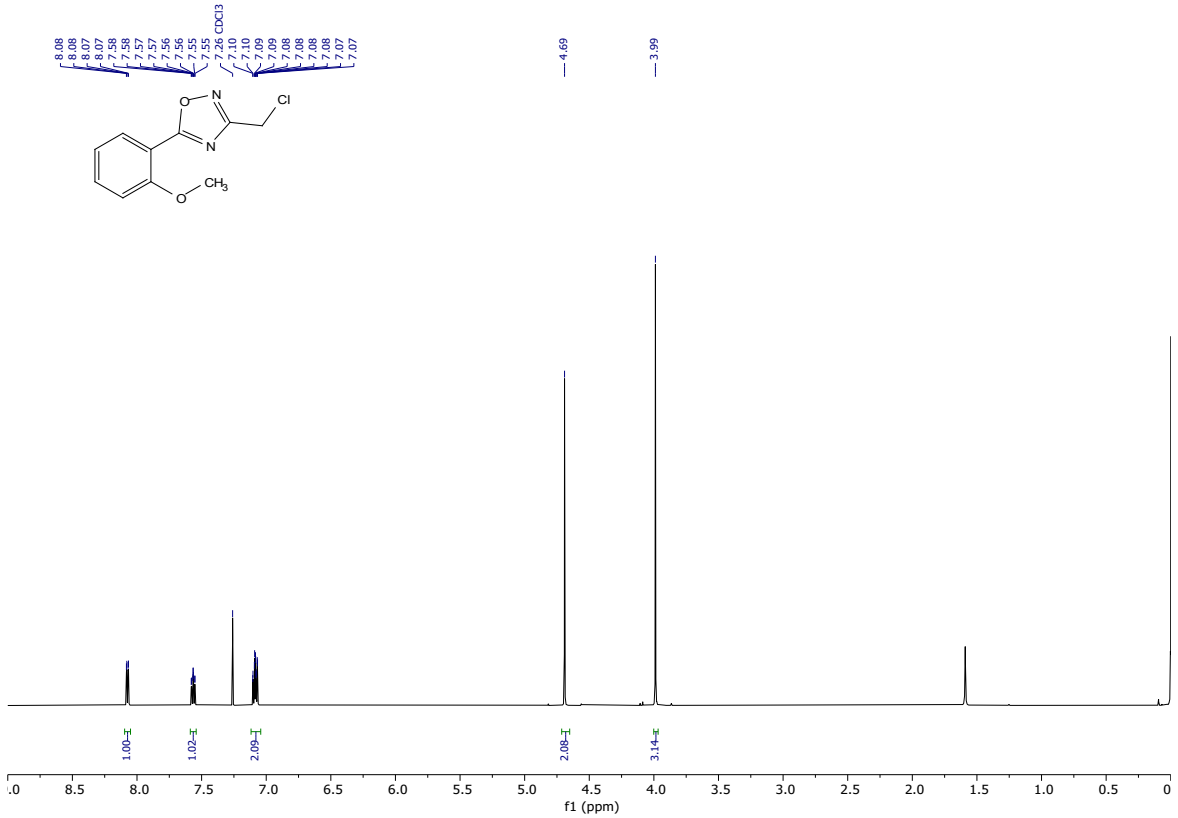
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2k.**



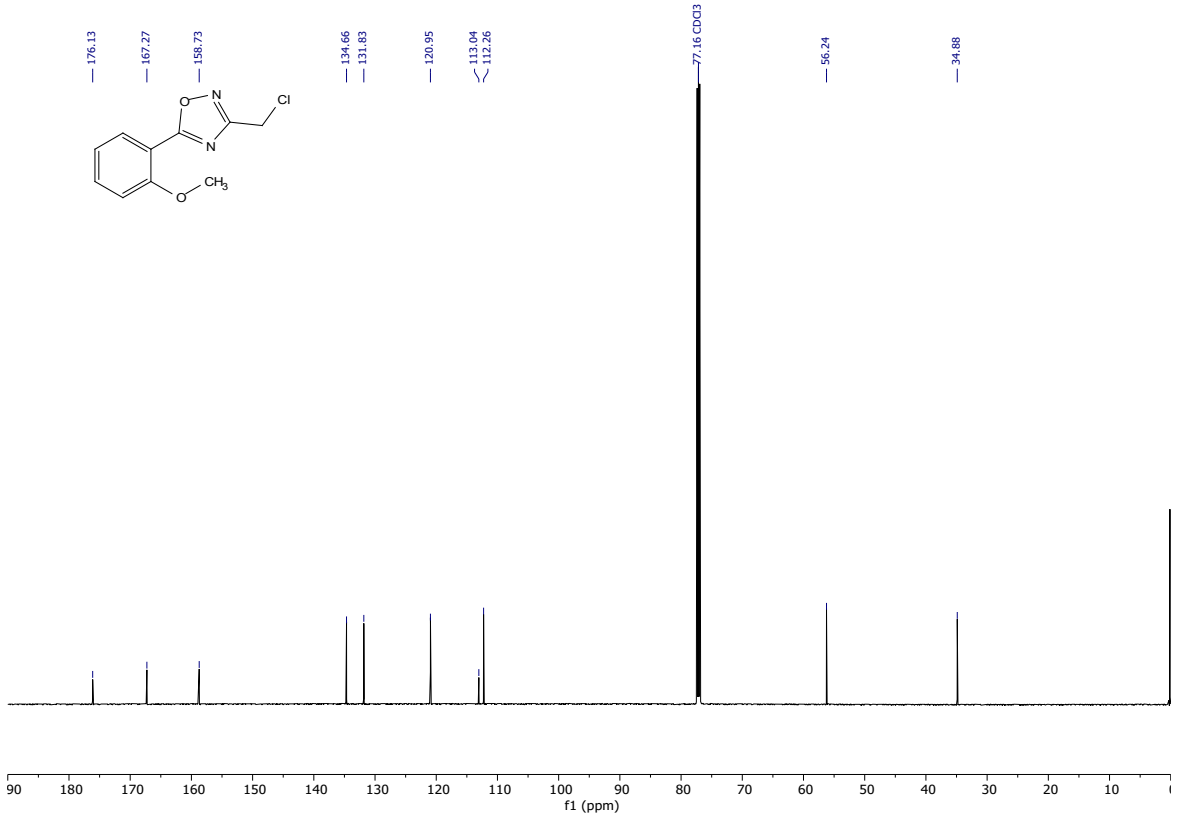
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2l**.



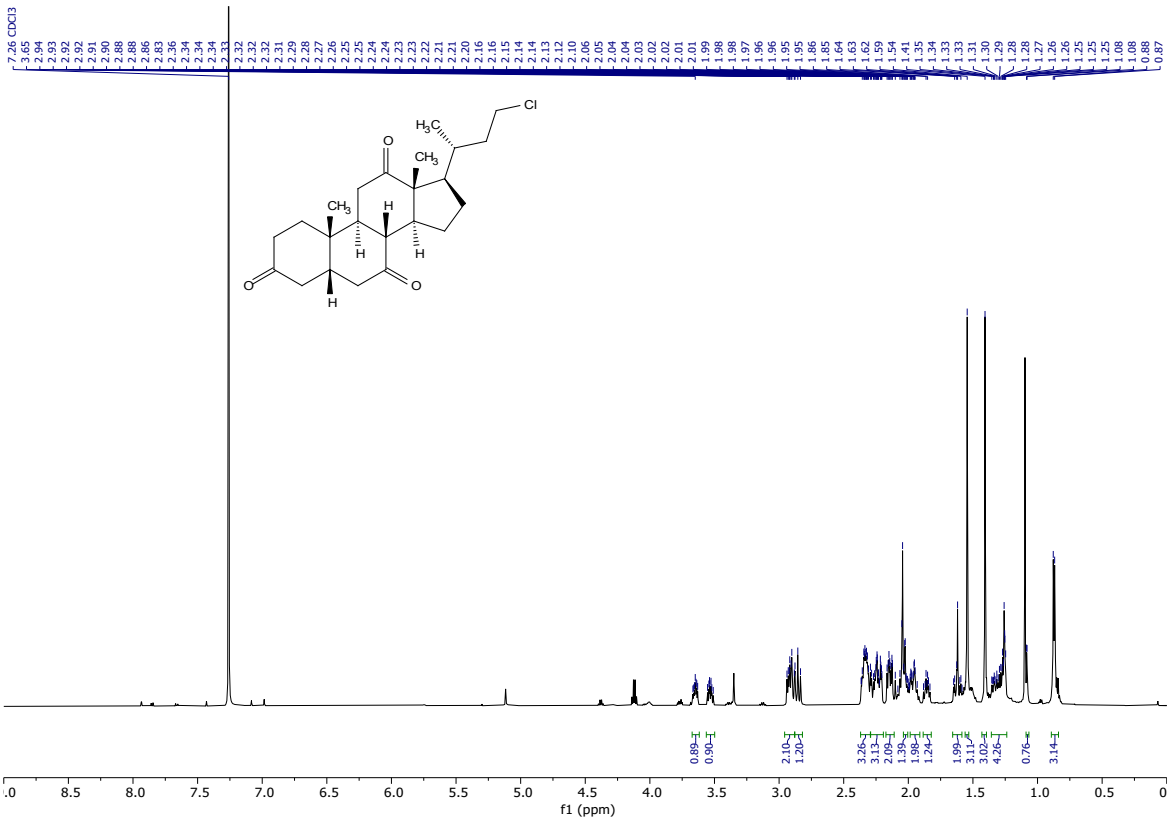
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2l.**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **2m**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **2m.**



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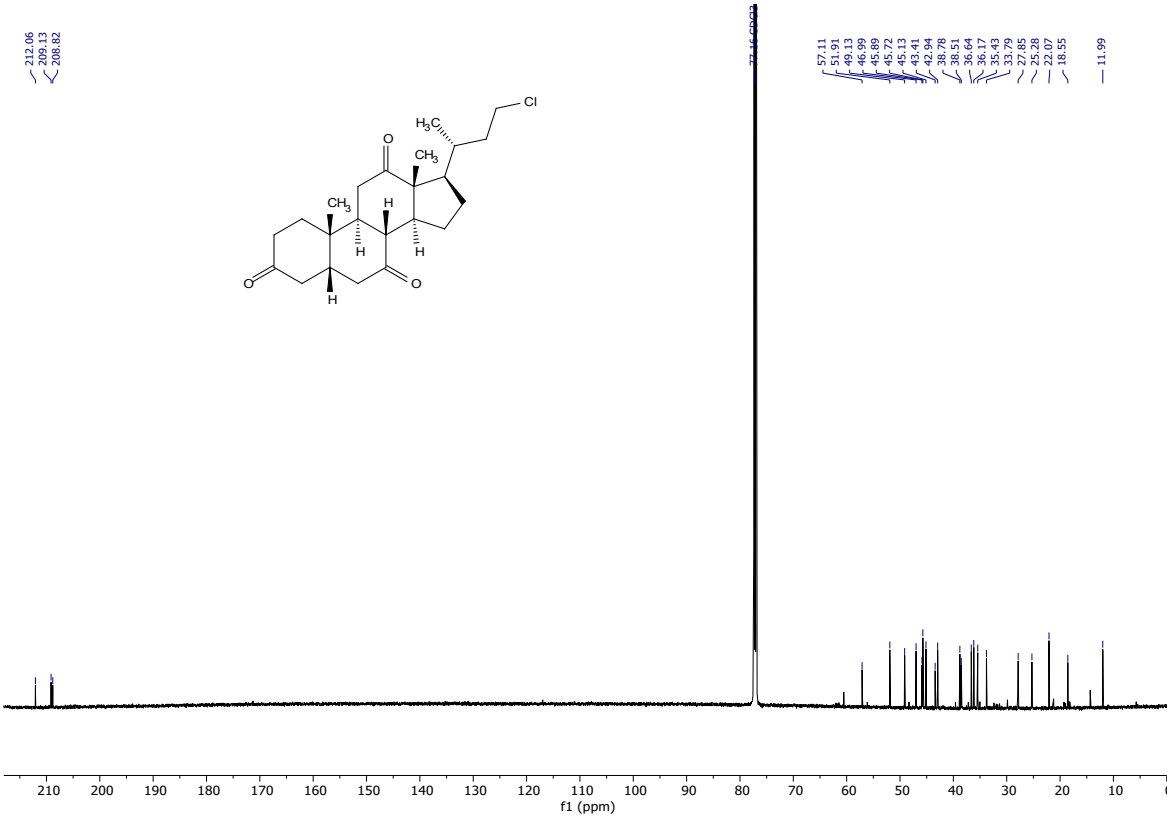
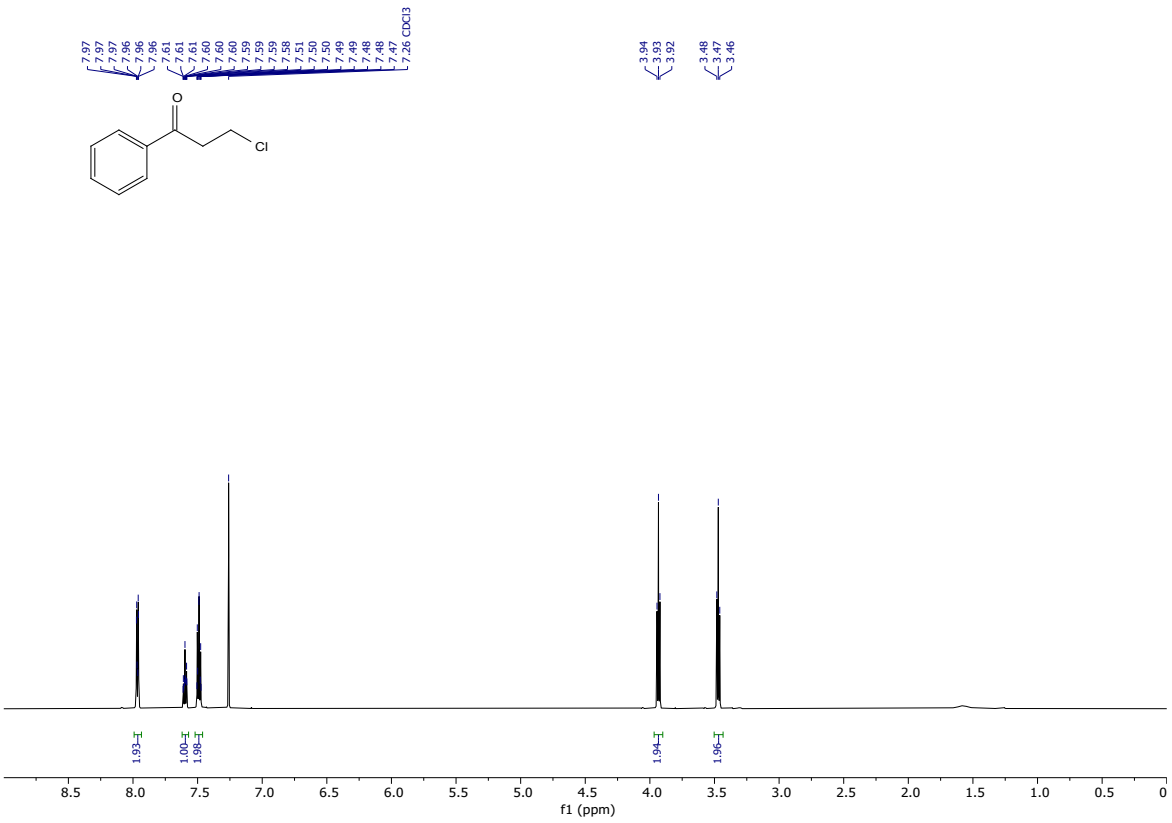
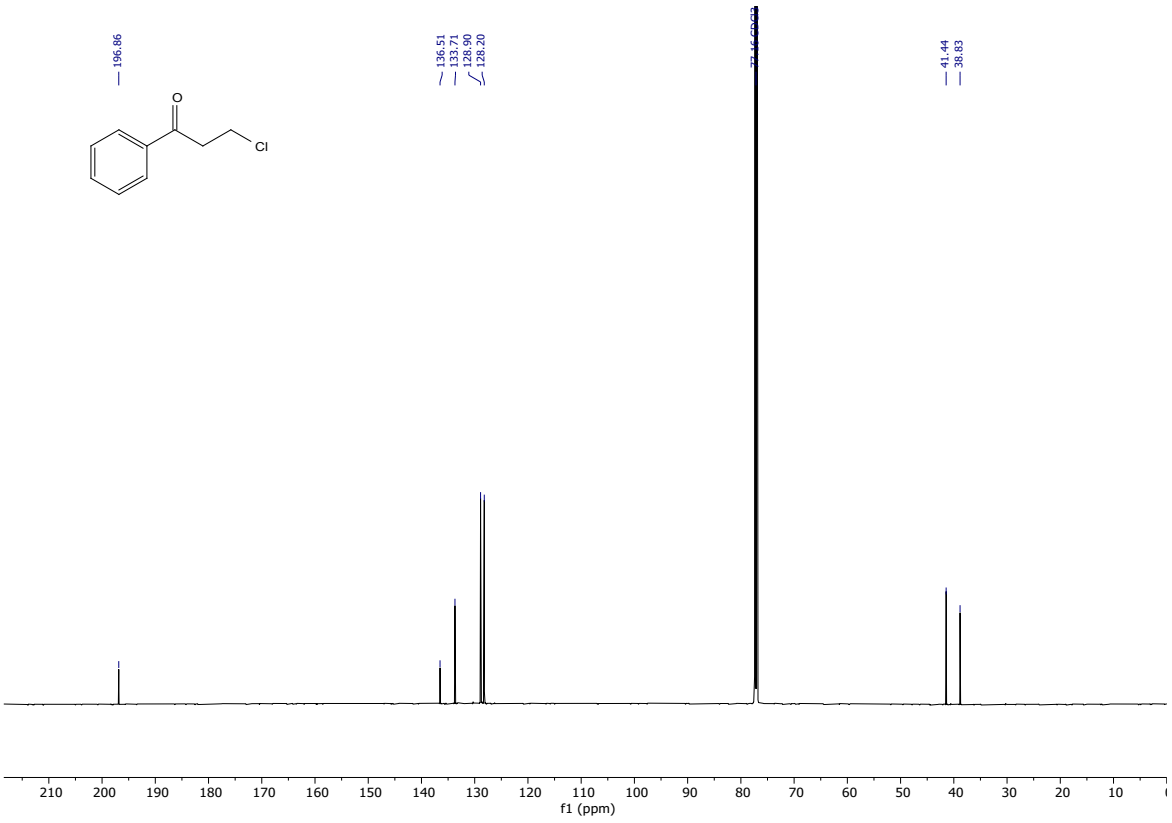


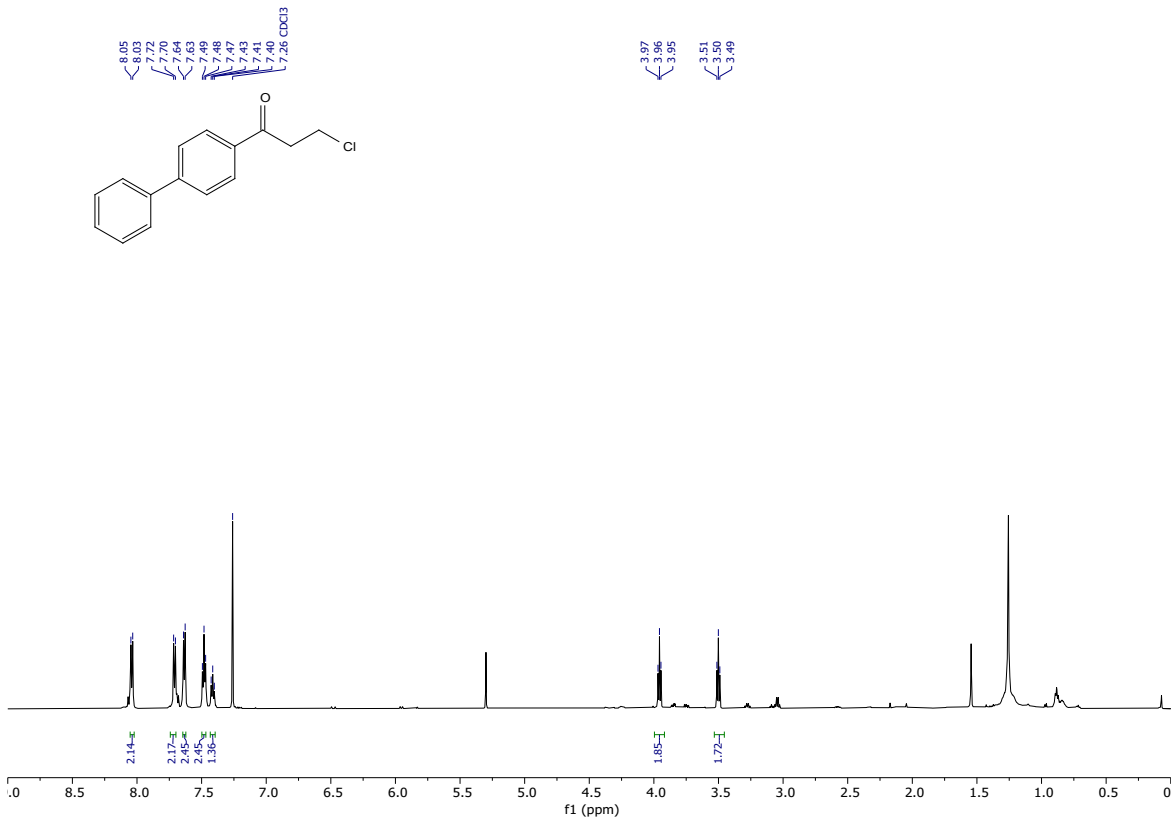
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2n.**



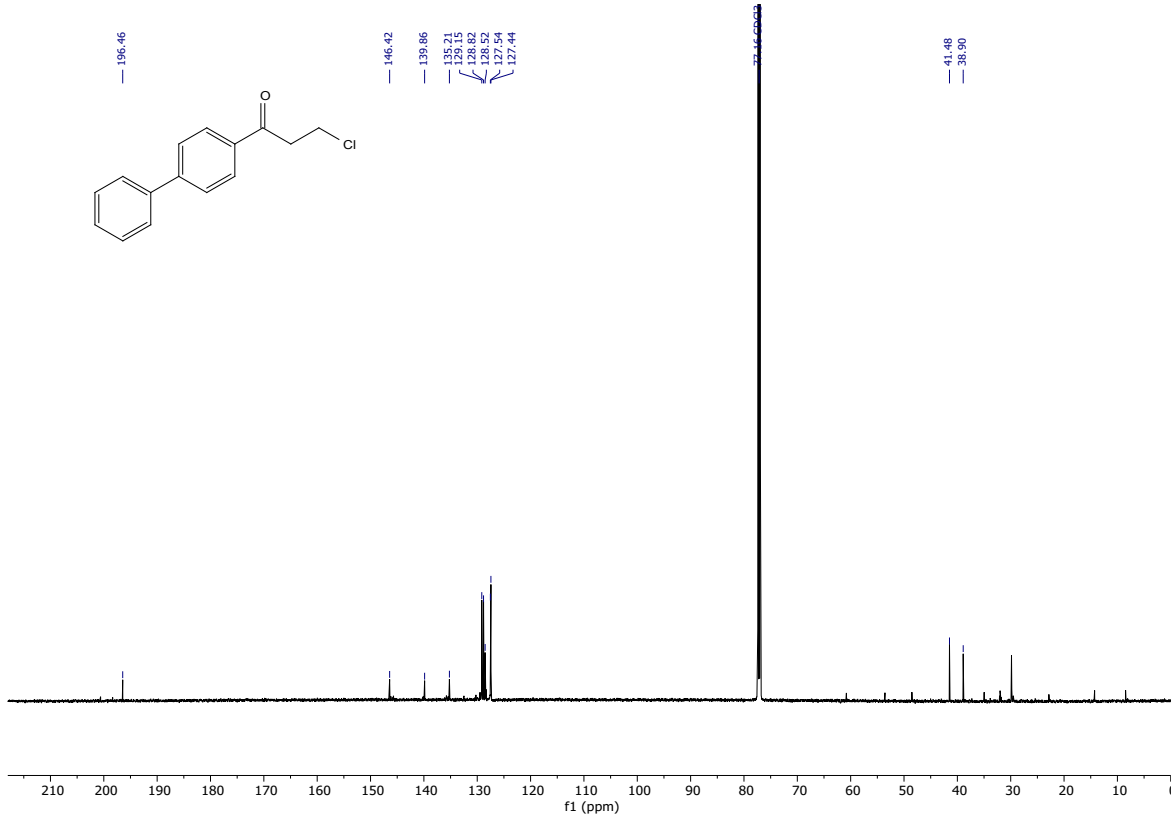
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2o**.



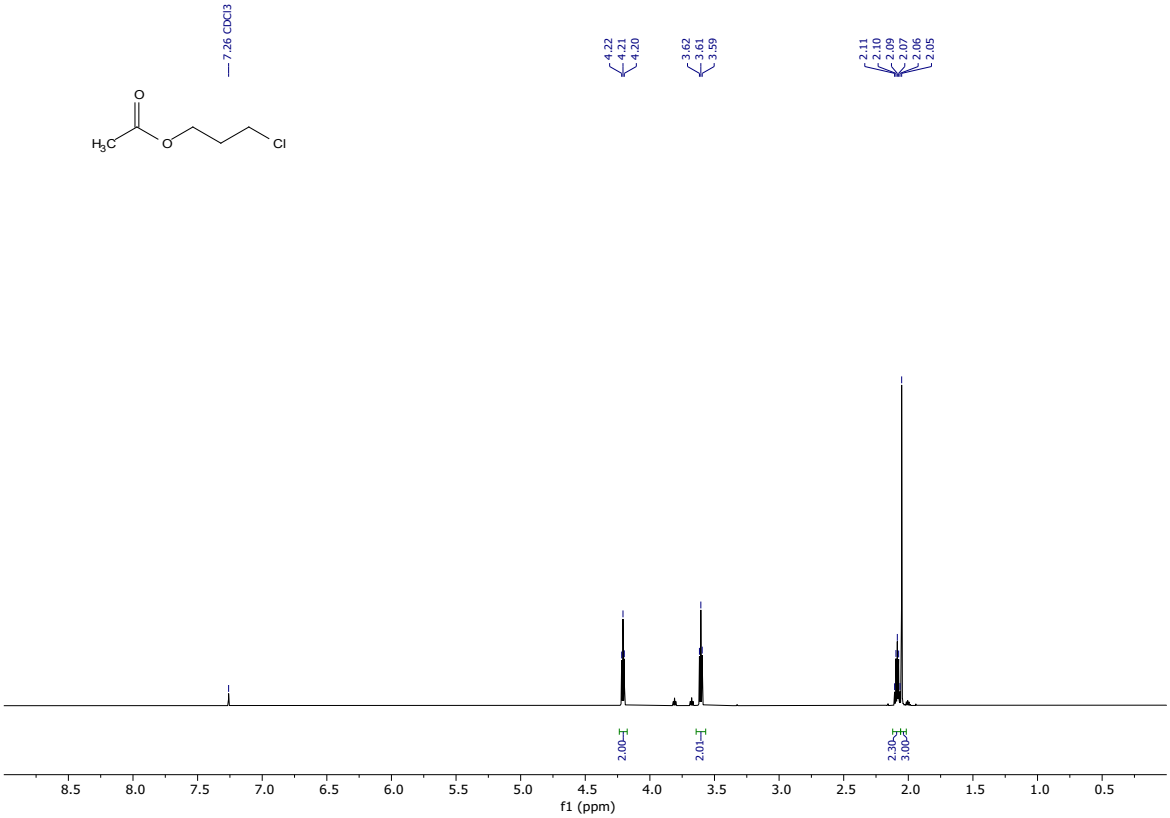
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2o.**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **2p**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **2p.**



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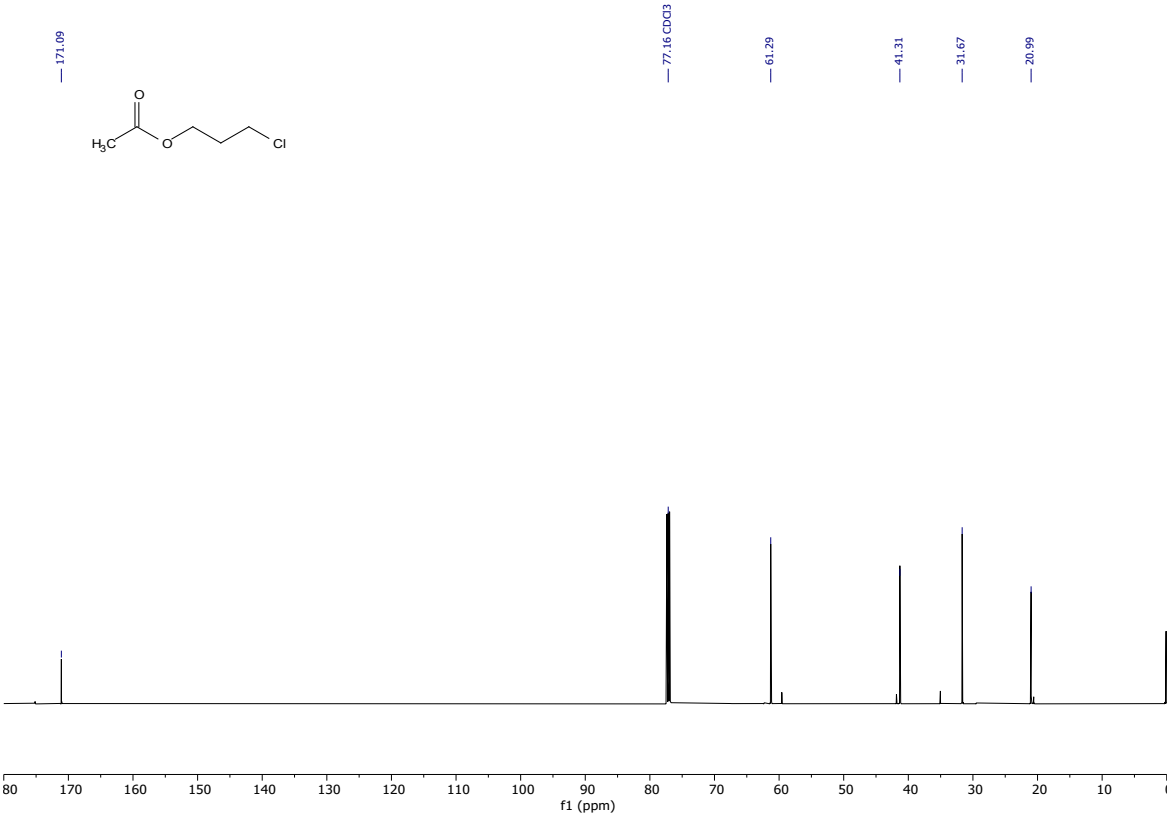
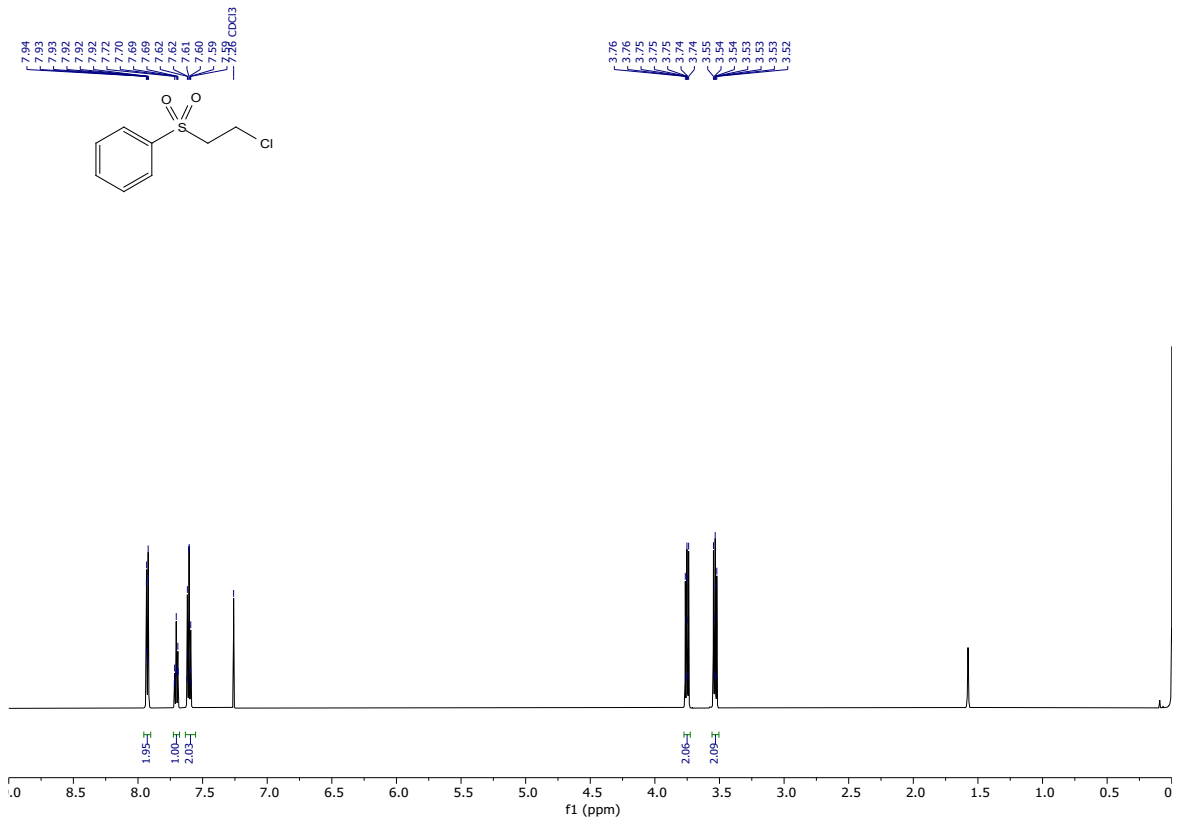
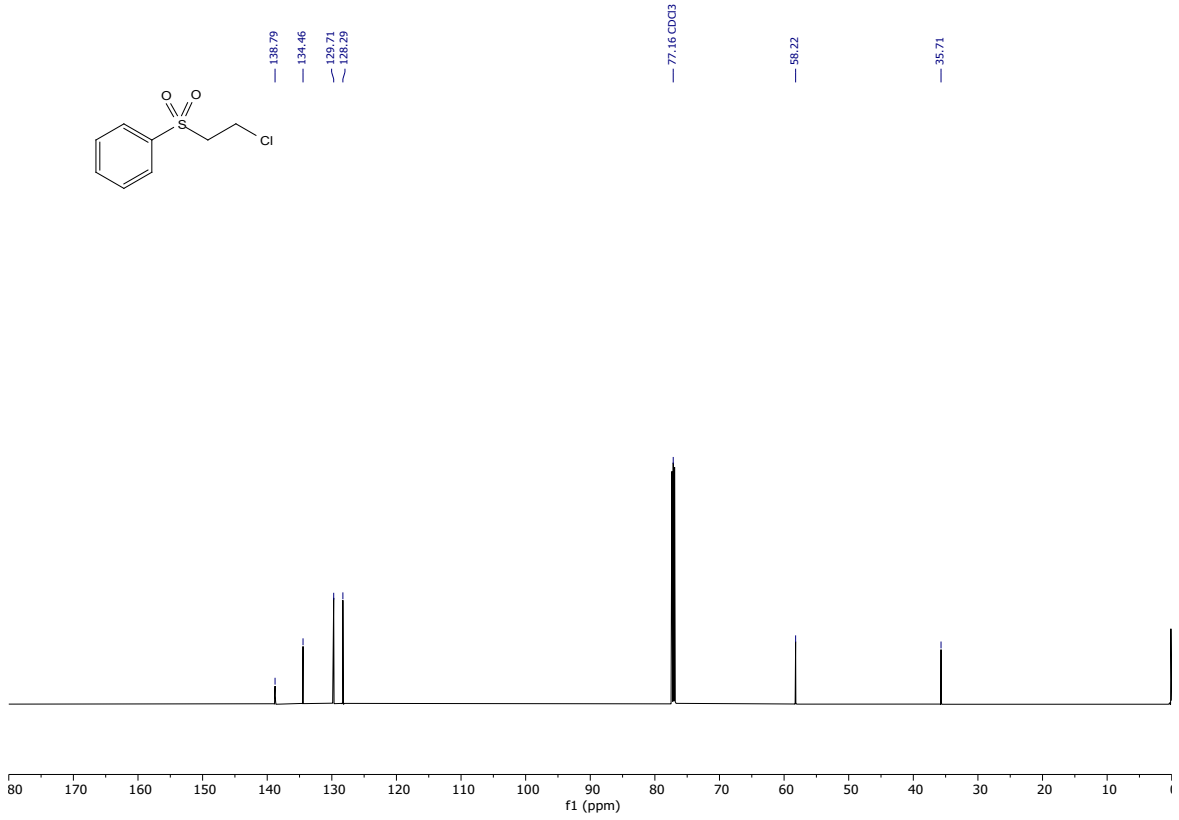


^{13}C NMR (151 MHz, $CDCl_3$) of compound **2q.**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **2r**.



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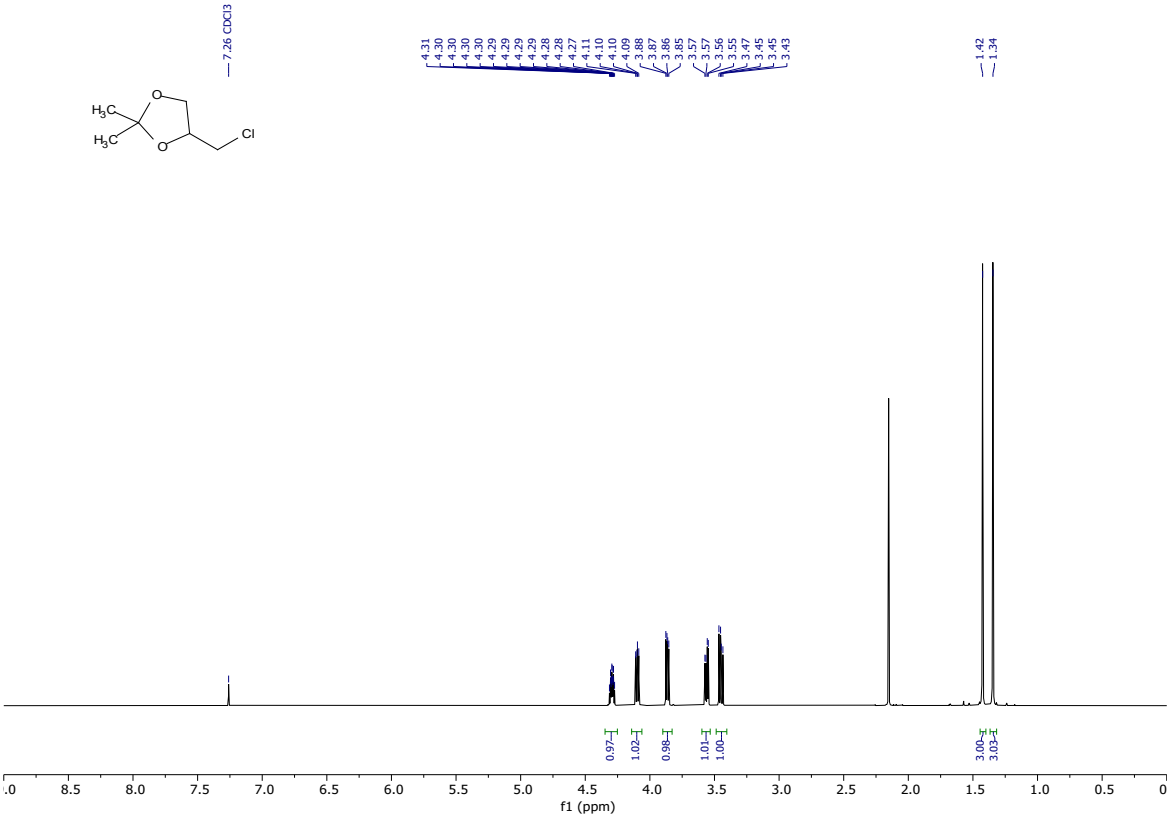

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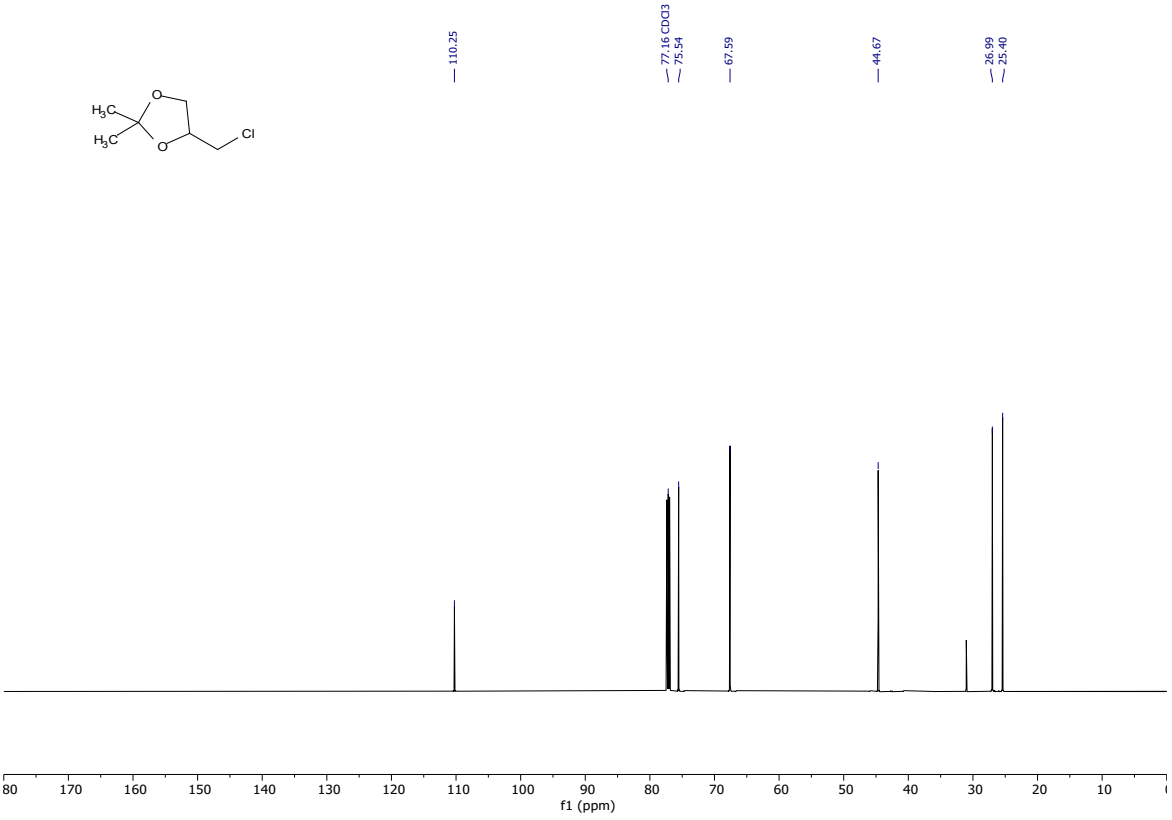
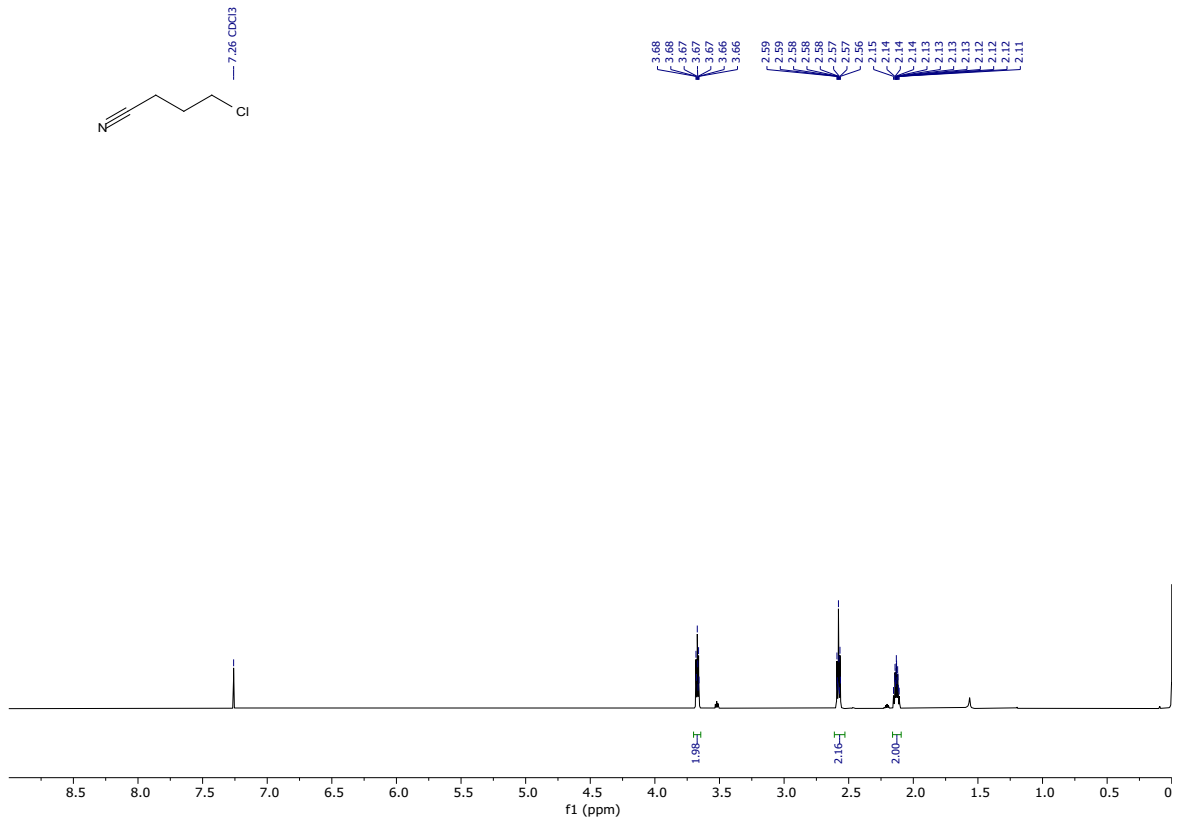
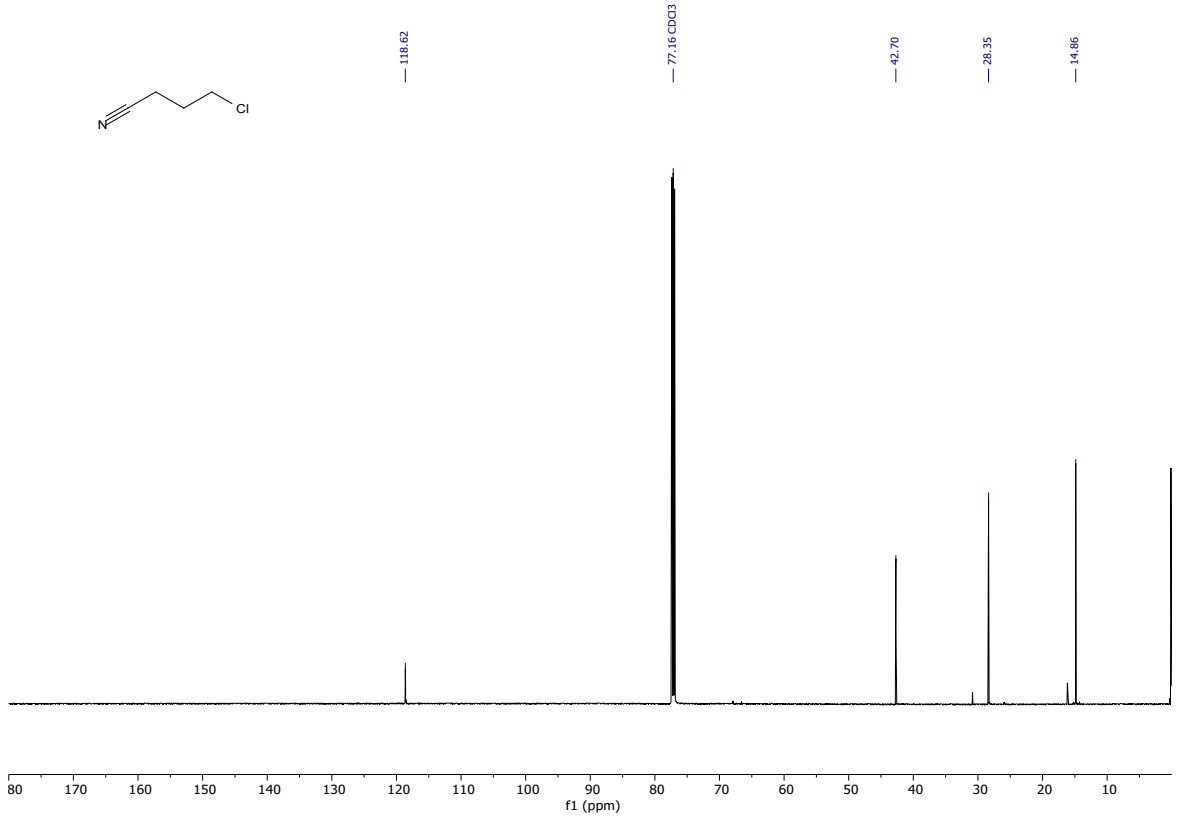


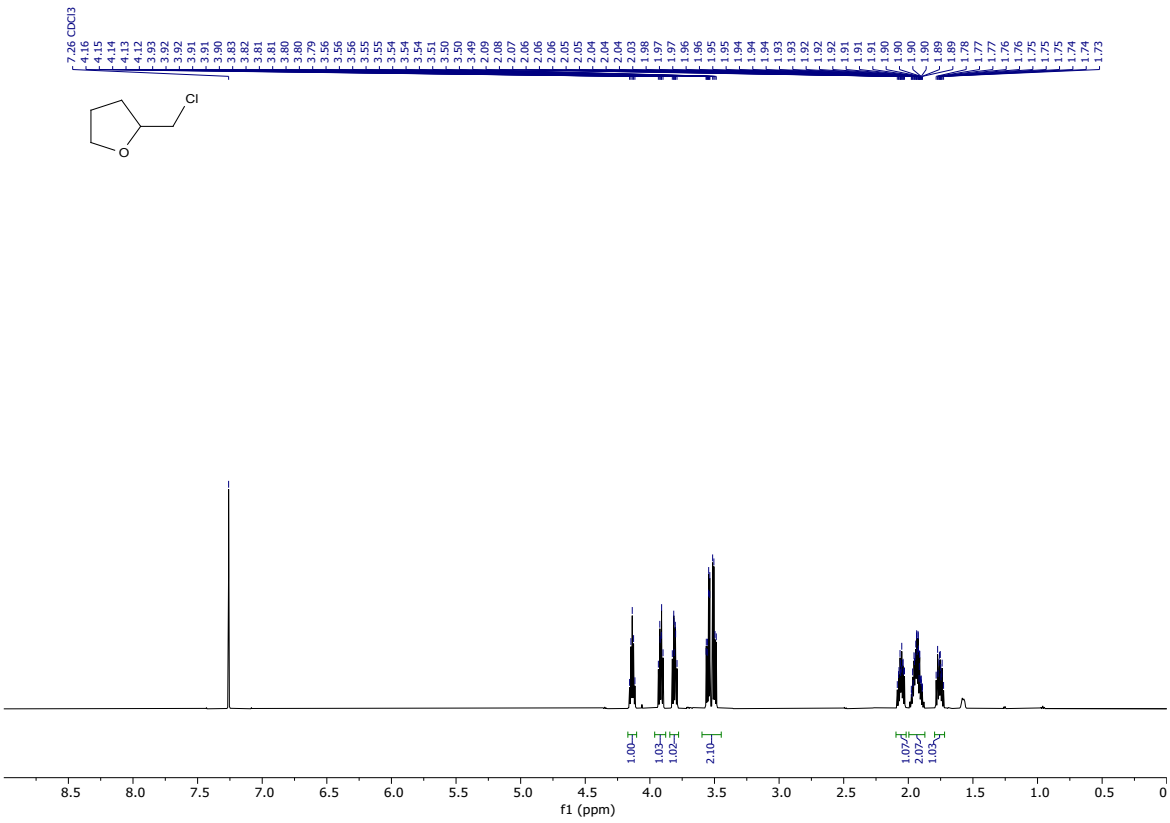
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2s.**



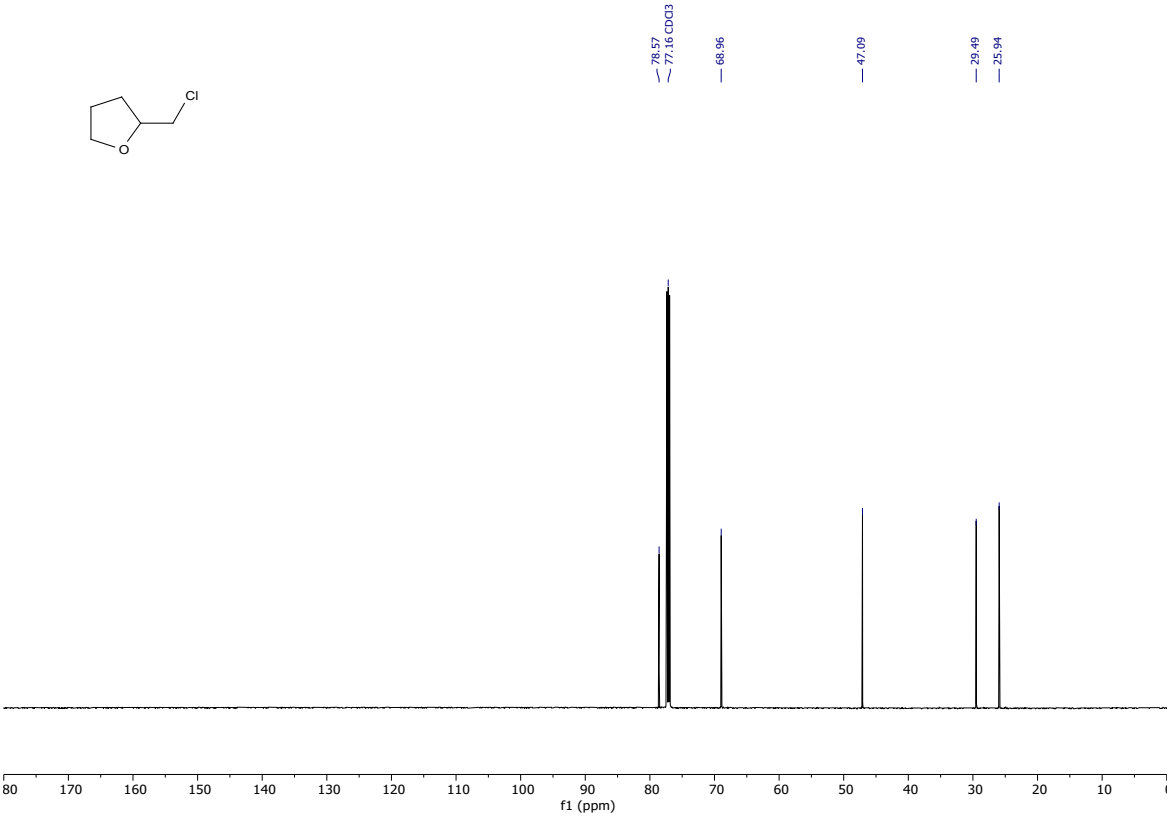
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2t**.



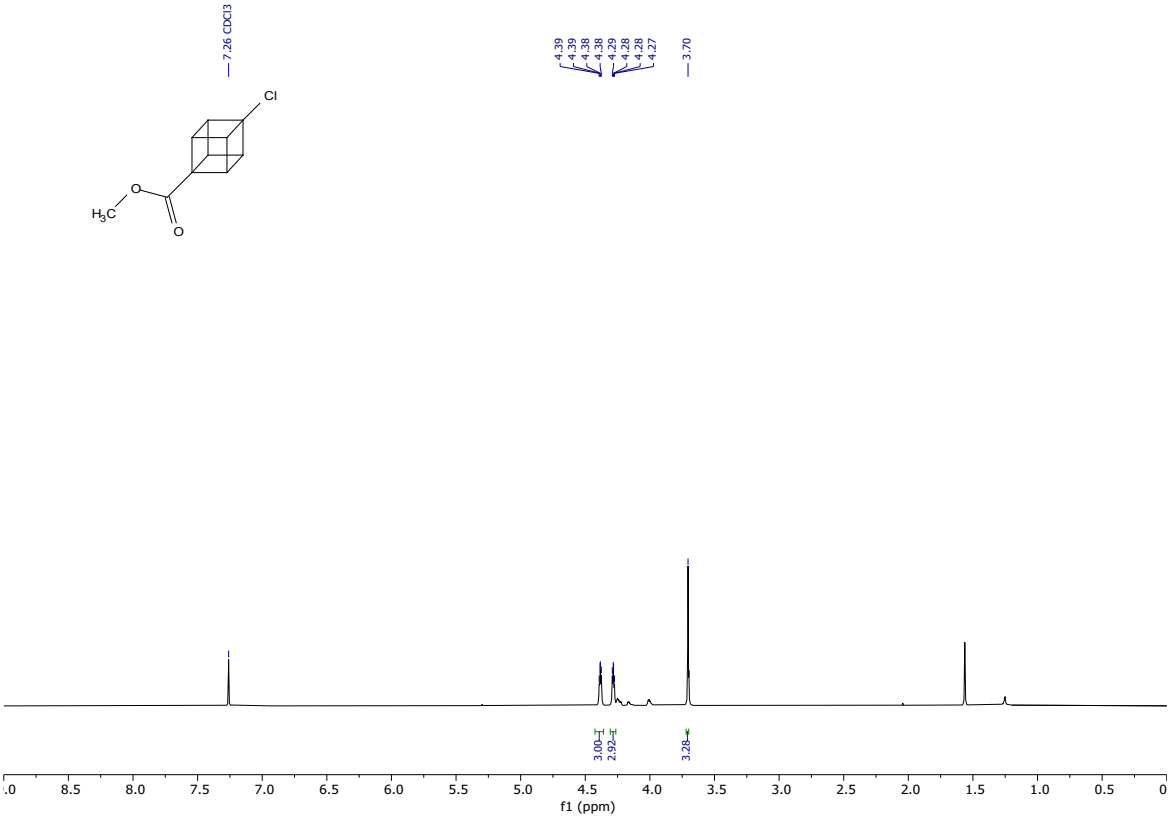
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2t.**



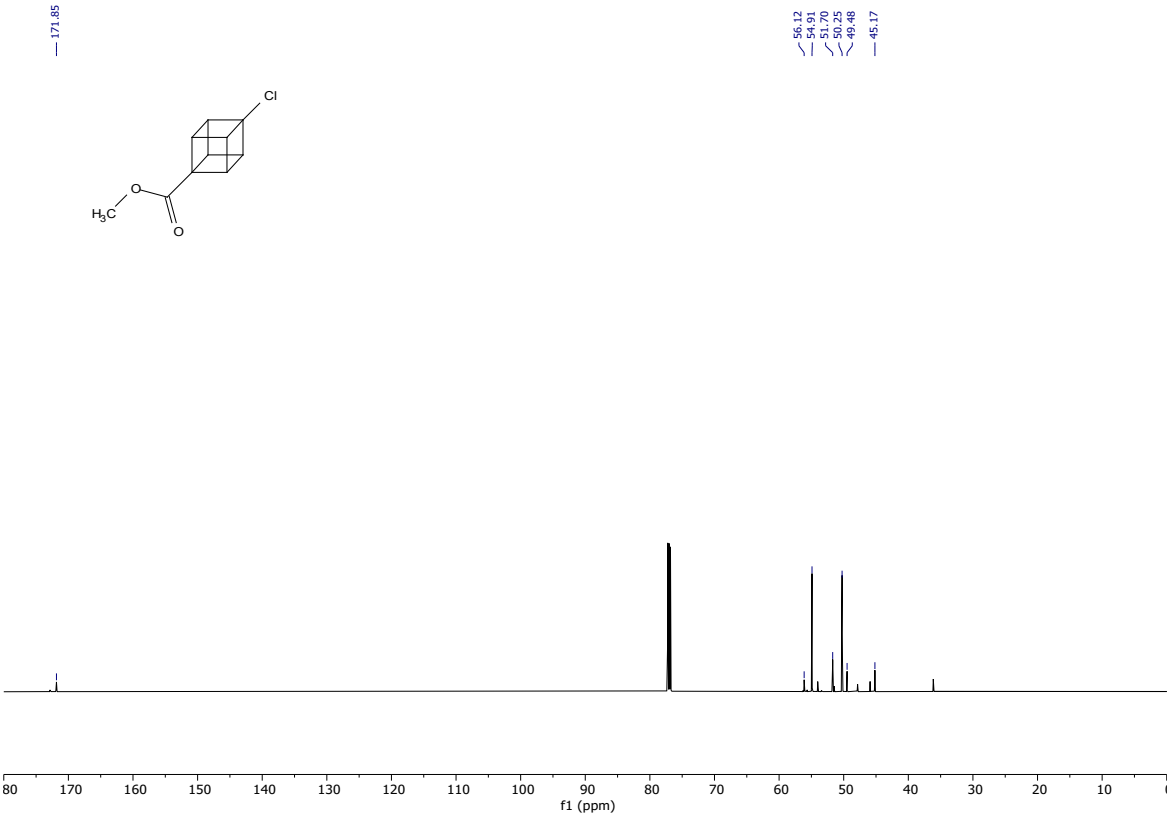
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2u**.



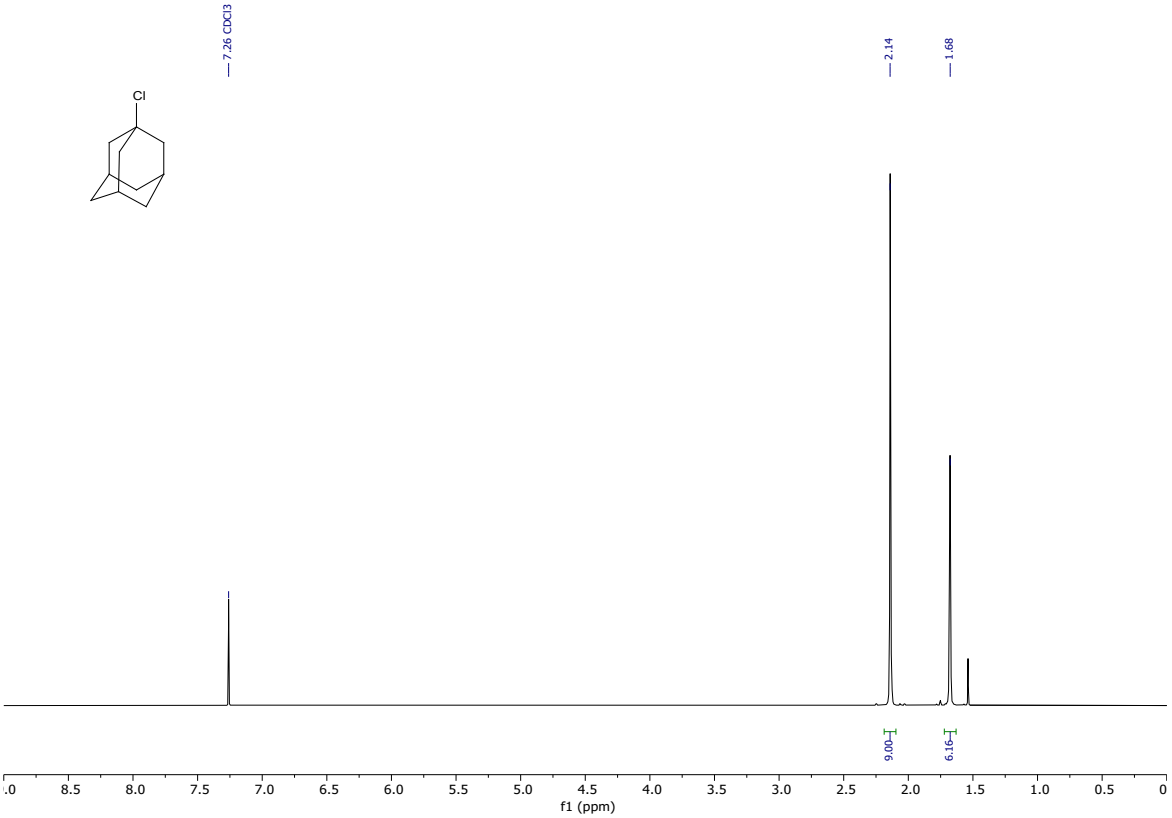
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2u.**



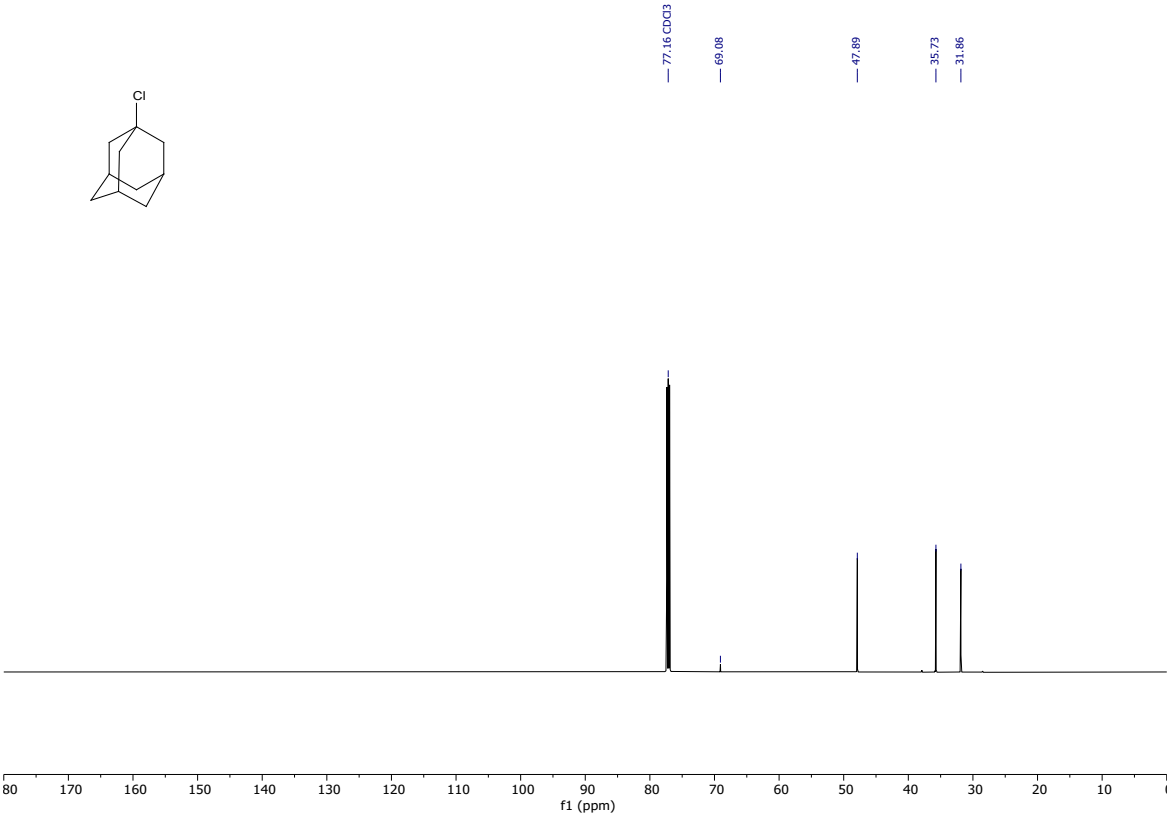
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2v**.



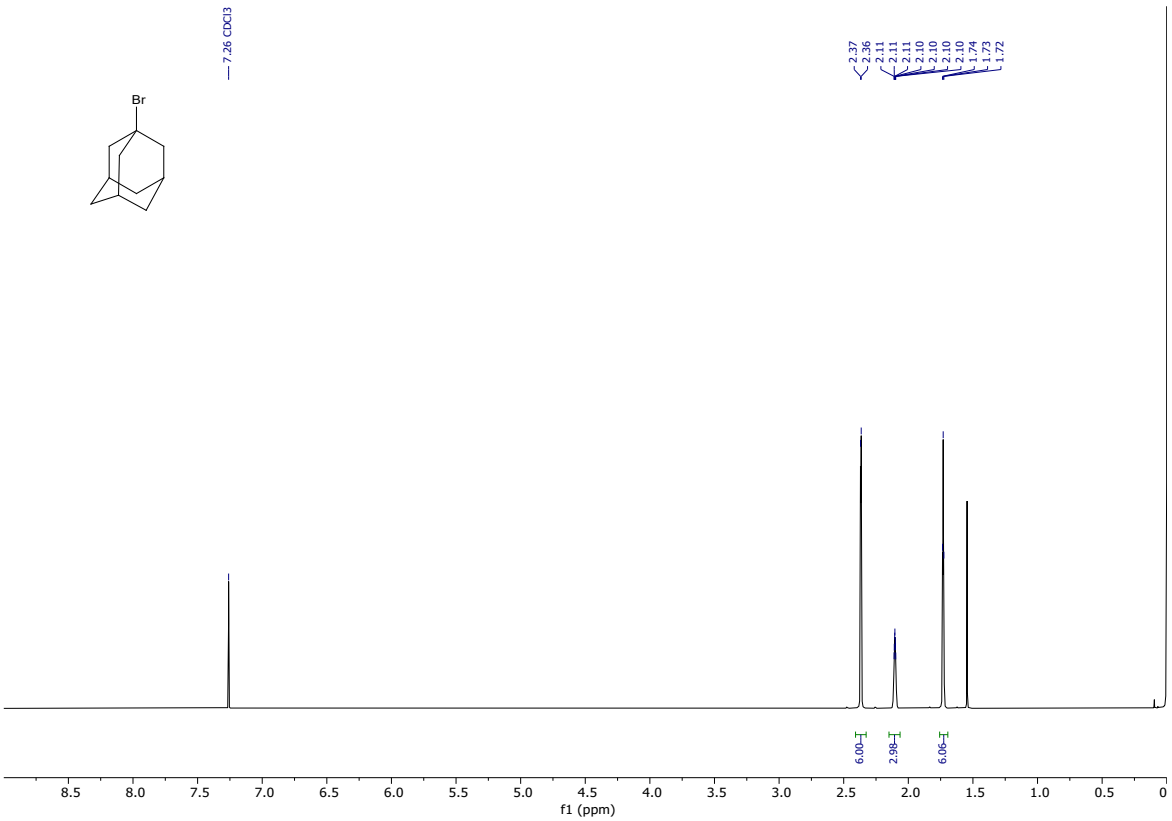
^{13}C NMR (151 MHz, $CDCl_3$) of compound **2v.**



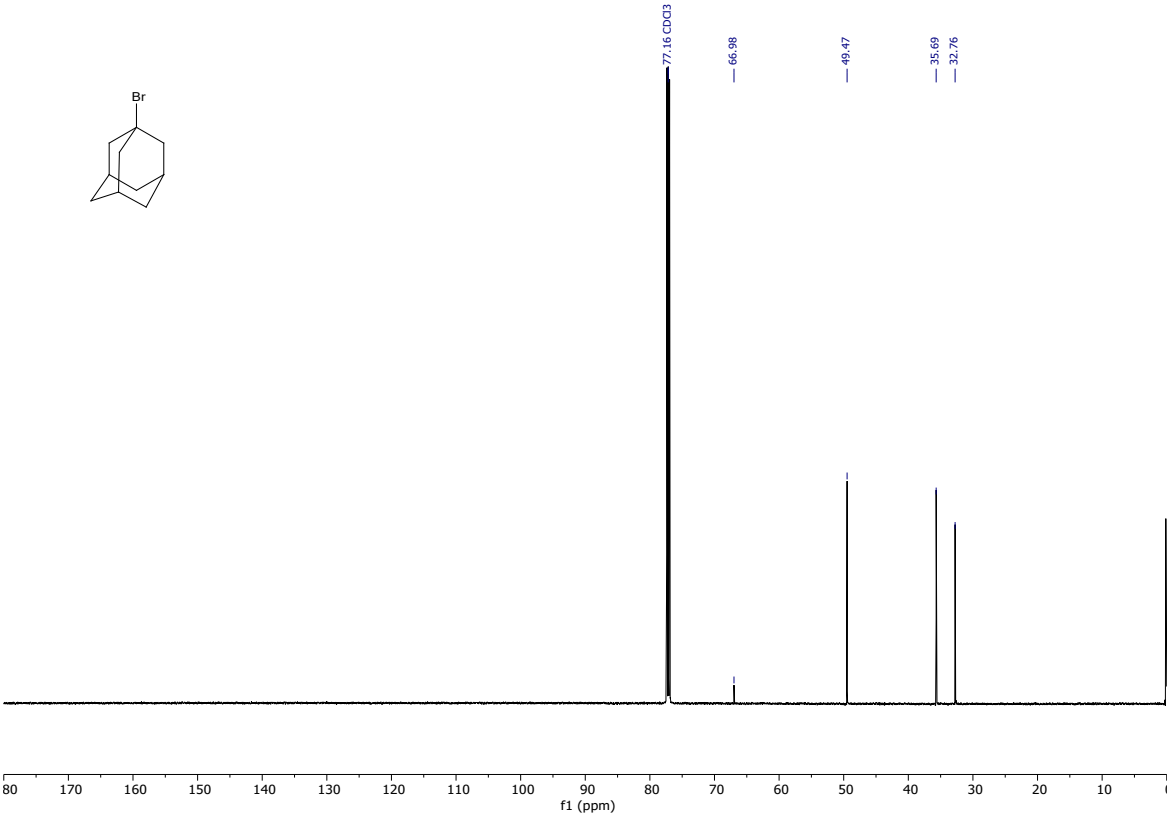
^{1}H NMR (600 MHz, $CDCl_3$) of compound **2w**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **2w.**



^{1}H NMR (600 MHz, $CDCl_3$) of compound **2x**.



^{13}C NMR (151 MHz, $CDCl_3$) of compound **2x.**