Supporting Information

Qi-Qi Hu,[1] Yao Xiang,[1] Zhaobo Ying,[1] Yu Zhou,[2]* Hui Zhou,[2]* & Youwei Xie[1]*

[1]Hubei Key Laboratory of Bioinorganic Chemistry and Materia Medica; Key Laboratory of Material Chemistry for Energy Conversion and Storage, Ministry of Education; Hubei Key Laboratory of Materials Chemistry and Service Failure; School of Chemistry and Chemical Engineering, Huazhong University of Science and Technology, 1037 Luoyu Road, Wuhan 430074, China.

[2]College of Chemistry, Central China Normal University (CCNU), 152 Luoyu Road, Wuhan, 430079, China.

Email: zhouyu@cuhk.edu.cn, huizhou@ccnu.edu.cn, xieyw@hust.edu.cn.

Table of Contents

1 General information 3

2 Synthesis and application of λ³-iodane III 4

2.1 Synthetic efforts towards λ³-iodane III by following established procedures for known I–Cl type λ³-iodane II 4

2.2 ^{1}H NMR study of the reaction progress during our synthetic attempts of III 5

2.3 Crystal Structure and Crystallographic Data for λ³-iodane III 13

2.4 Characterization for λ³-iodane III 16

2.5 Design and optimization of a catalytic C–H chlorination via catalytic formation of λ³-iodane III 19

2.6 Application of our procedure for the synthesis of the 1-chloro-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (BI-Cl) 23

3 Control experiments 25

3.1 In situ generation of λ³-iodane III for the chlorination of chlorobenzene 25

3.2 chlorination of chlorobenzene by the combination of λ³-iodane V and NaCl 25

4 Gram scale experiments 26

5 Comparison of chlorination methods 27

6 Mechanistic study 28

6.1 Syntheses of λ³-iodane V and λ⁵-iodane VIII (IBS) 28

6.2 Hydrolysis of λ³-iodane III 29

6.3 Reaction profile of λ⁵-iodane VIII (IBS) 31

6.4 Cyclic voltammetry studies 32

6.5 ^{1}H NMR study of hydrogen bonding interaction between λ³-iodane III and HFIP 33

6.6 Rate profile on the concentration of 2-iodobenzenesulphonic acid 35

6.7 Hammett plot 36

7 General procedure for the chlorination of arenes and characterization of chloroarene products 37

7.1 General procedure A for the chlorination of arenes 37

7.2 General procedure B for the chlorination of highly electron-deficient arenes 37

7.3 Spectroscopic data of reaction substrates 37

8 Reference 70

9 NMR spectroscopic data 71

10 Computational studies 162

1 General information

Unless otherwise stated, other chemicals used in this manuscript were purchased from Energy chemical company, Bide Pharmatech Ltd, Inno-Chem Ltd, Adamas Company, and Alfa Aesar Company. Other commercially available compounds and solvents were used as provided without further purification. Unless otherwise noted, all reactions were performed under air. Reactions were monitored by thin layer chromatography (TLC) on silica gel pre-coated plastic sheets (0.2 mm). Visualization was accomplished by irradiation with *p*-methoxybenzaldehyde, ultraviolet lamp (254 nm), alkaline potassium permanganate solution, iodine cylinder and phosphomolybdic acid solution. Flash column chromatography was performed over silica gel (200-300 mesh). The nuclear magnetic resonance data in this paper is measured by Bruker AVANCE III-400 or Bruker Ascend TM 600 MHz nuclear magnetic resonance instrument at room temperature. The chemical shifts are reported in parts per million (ppm) and coupling constants (J) are given in Hertz (Hz). ^{1}H NMR spectra are reported with the solvent resonance as the reference unless noted otherwise ($CDCl_3$ at 7.26 ppm, CD_3OD at 3.33 ppm, DMSO-d_6 at 2.50 ppm). Peaks are reported as s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, hept = heptet, br = broad signal, coupling constant (s) in Hz. ^{13}C NMR spectra were recorded with ^{1}H-decoupling and were reported with the solvent resonance as the reference unless noted otherwise ($CDCl_3$ at 77.16 ppm, CD_3OD at 49.00 ppm, d_6-DMSO at 40.00 ppm). High-resolution mass spectrometry data were measured by a Fourier transform high-resolution mass spectrometer Apex III (7.0 Tesla) FTMS (Bruker, Billerica, MA, USA) (ESI source) with FT-ICR-MS analyzer type. GC analyses were performed on Shimadzu GC 2010 Pro instrument. Infrared Spectroscopy IR (Nicolet IS10, USA) The heating source used in all heating reactions is an oil bath.

2 Synthesis and application of λ³-iodane III

2.1 Synthetic efforts towards λ³-iodane III by following established procedures for known I–Cl type λ³-iodane II

We tested various synthetic routes by mimicking the syntheses of known λ³-iodane **II**, however, these efforts did not lead to successful synthesis of λ³-iodane **III**, two examples are given as the following:

Synthetic attempt #1:

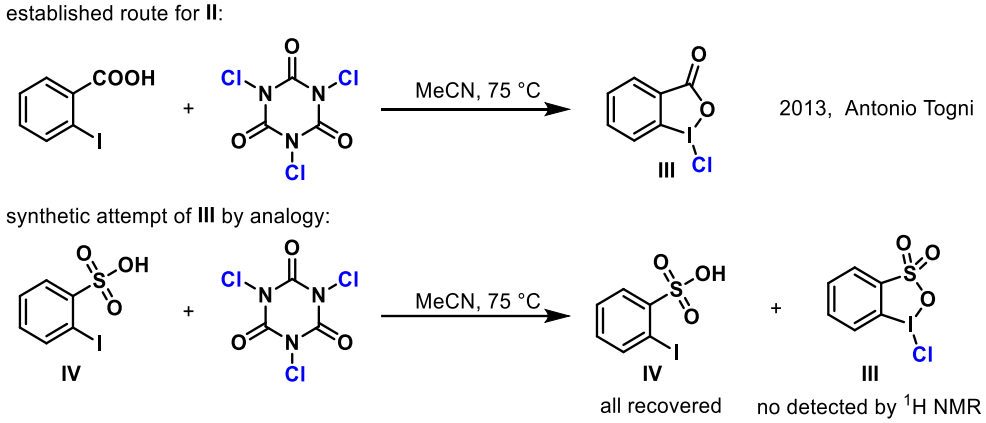


Figure S1. The attempted preparation of λ³-iodane **III** by TCCA

According to existing literature[1], to a 5 mL pressure Schlenk vial equipped with a magnetic stir bar was charged with 2-iodobenzenesulphonic acid (56 mg, 0.2 mmol, 1.0 eq.), trichloroisocyanuric acid TCCA (48 mg, 0.204 mmol, 1.02 eq.), anhydrous MeCN (1.0 mL). The reaction mixture was sealed and heated to 75 °C under N_2 for 4 hours. After the mixture was cooled to room temperature, through analysis of the crude ^{1}H NMR spectrum, no new species could be identified, only 2-iodobenzenesulphonic acid was observed in the reaction mixture.

Synthetic attempt #2:

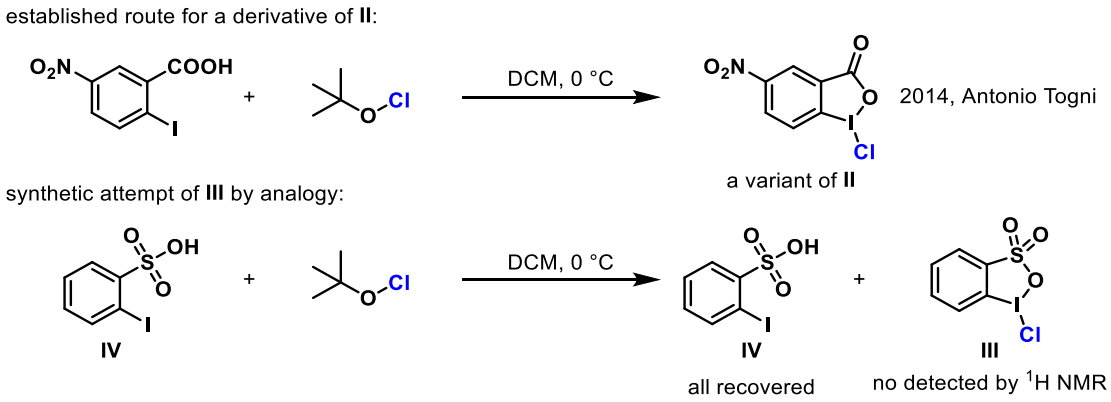


Figure S2. The attempted preparation of λ³-iodane **III** by t-BuOCl

According to existing literature[2], to a 5 mL pressure Schlenk vial equipped with a magnetic stir bar was charged with 2-iodobenzenesulphonic acid (56 mg, 0.2 mmol, 1.0 eq.), t-BuOCl (22 mg, 0.22 mmol, 1.1 eq.), DCM (1.0 mL). The reaction mixture was stirred at 0 °C for 4 hours. Through analysis of the crude ^{1}H NMR spectrum, no new species could be identified, only 2-iodobenzenesulphonic acid was observed in the reaction mixture.

2.2 ^{1}H NMR study of the reaction progress during our synthetic attempts of III

After various attempts, we are able to observe a new species that we speculated to be **III**, when DCE/HFIP (2/1) is used as the solvent, with 2-iodobenzenesulfonic acid (**IV**) as the starting compound.

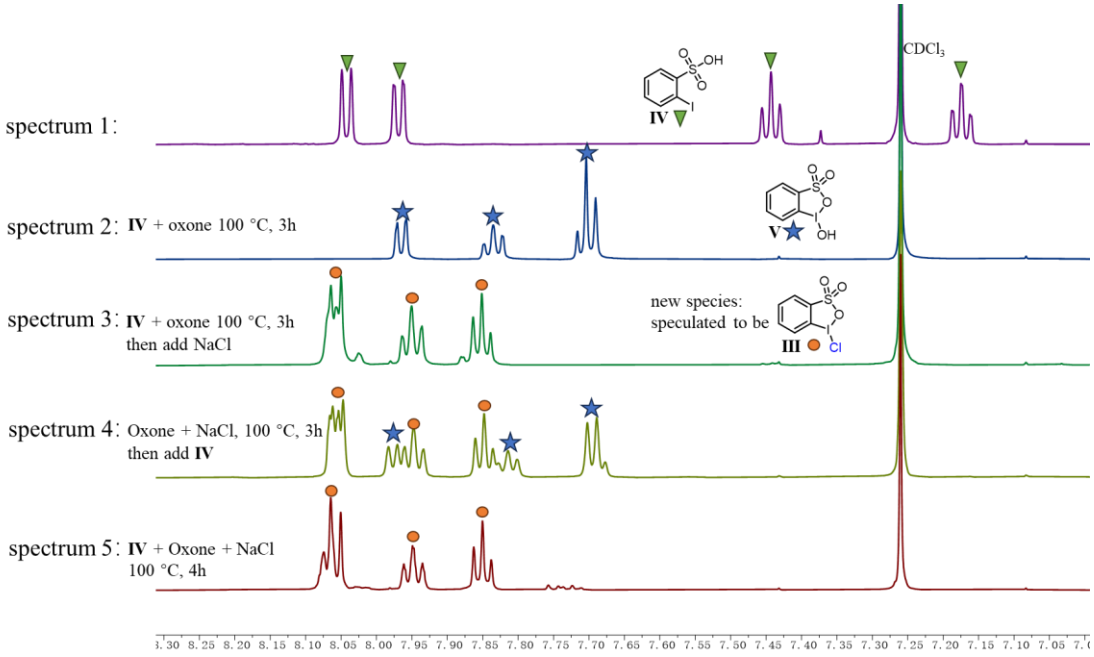


Figure S3. ^{1}H NMR spectra during a key synthetic attempt of **III** with DCE/HFIP (2/1) as the solvent (600 MHz, $CDCl_3$, 298.15 K)

For Clarity purpose, only sections from 7.0 ppm to 8.3 ppm are shown in the stacked ^{1}H NMR spectra in **Figure S3**, and the complete spectra are shown in the following pages.

Spectrum 1: ^{1}H NMR of 2-iodobenzenesulphonic acid (**IV**) in $CDCl_3$, add 50 µL of a mixture of DCE/HFIP (2/1) to increase the solubility of **IV**.

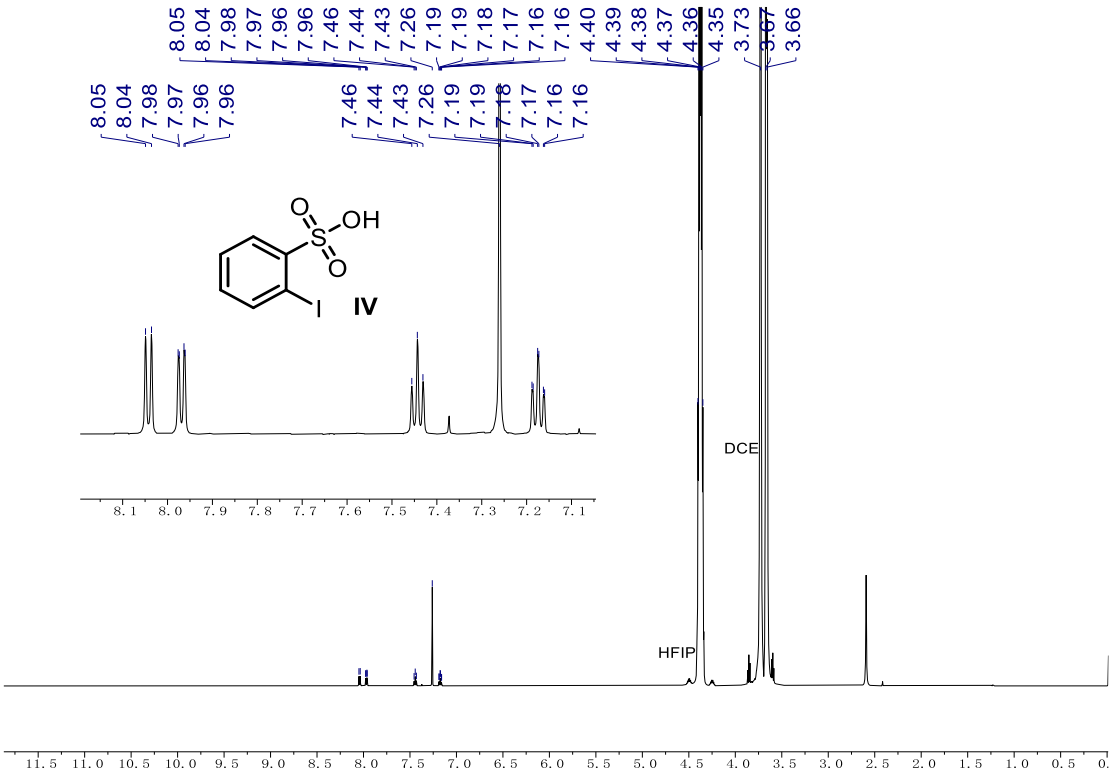
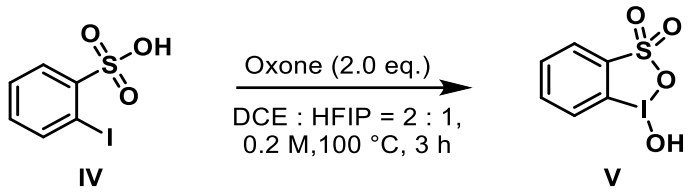


Figure S4. ^{1}H NMR spectrum of 2-iodobenzenesulphonic acid (**IV**) in DCE/HFIP (2/1) (600 MHz, $CDCl_3$, 298.15 K)

Spectrum 2: Stir a mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2 mmol) and oxone (246 mg, 2.0 eq.) in 1mL DCE/HFIP (2/1) under the air at 100 °C for 3 hours, after cooling down to room temperature, ^{1}H NMR was taken by adding an aliquot of the reaction mixture (50 μL) into 0.5 mL $CDCl_3$. Based on this ^{1}H NMR spectrum, complete conversion of **IV** to the known compound **V** was observed.



IV **V**

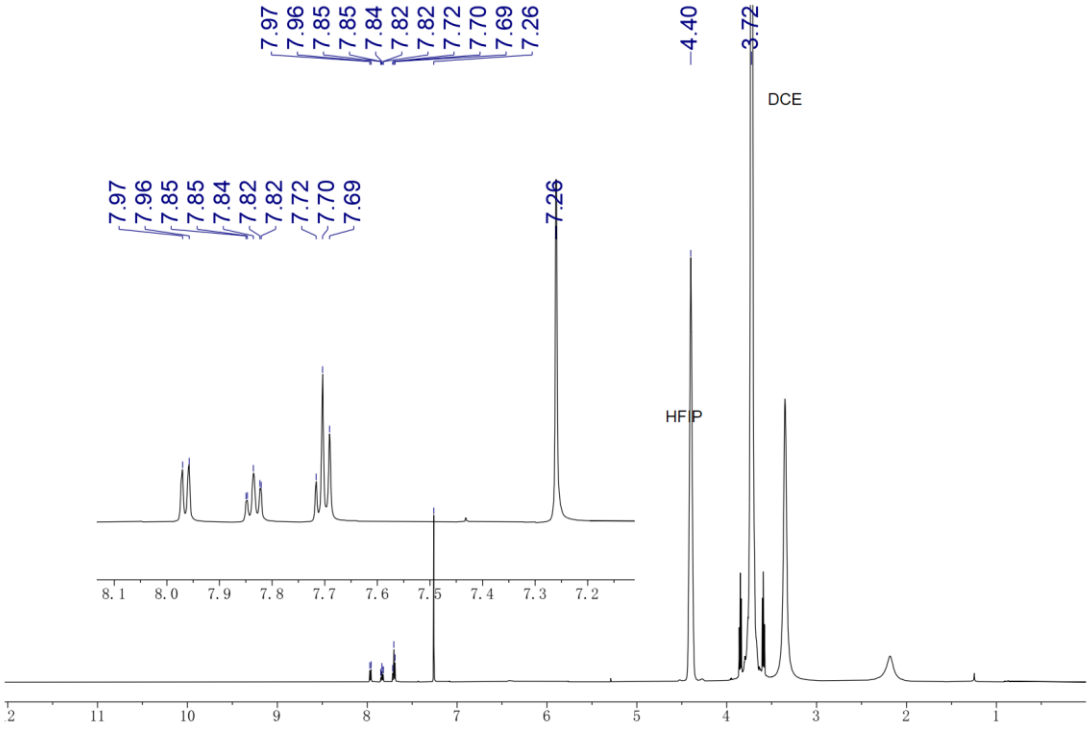


Figure S5. ^{1}H NMR spectrum of λ^3-iodane **V** (600 MHz, $CDCl_3$, 298.15 K)

Spectrum 3: Stir a mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2 mmol) and oxone (246 mg, 0.4 mmol) in 1mL DCE/HFIP (2/1) under the air at 100 °C for 3 hours, after cooling down to room temperature, NaCl (24 mg, 0.4 mmol) was added and the mixture was then heated at 100 °C for another 3 hours, after which ^{1}H NMR was taken by adding an aliquot of the reaction mixture (50 μL) into 0.5 mL $CDCl_3$. Based on this ^{1}H NMR spectrum, a new species was observed that we speculated to be **III**.

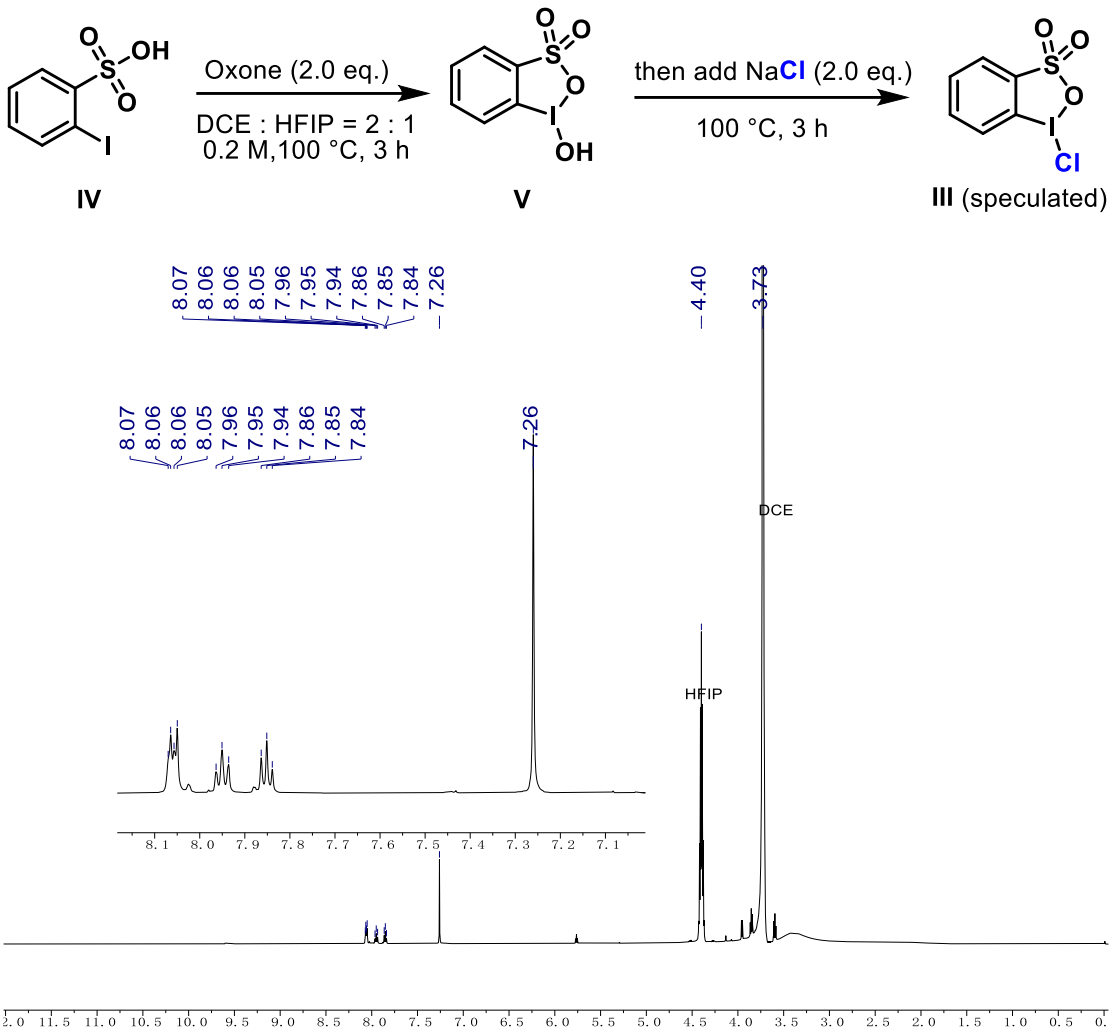


Figure S6. ^{1}H NMR spectrum of the speculated λ^3-iodane **III** by step-wise addition of reagents (600 MHz, $CDCl_3$, 298.15 K)

Spectrum 4: Stir a mixture of NaCl (24 mg, 0.4 mmol) and oxone (246 mg, 0.4 mmol) in 1 mL DCE/HFIP (2/1) under air at 100 °C for 3 hours, after cooling down to room temperature, 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2 mmol) was added and the mixture was then heated at 100 °C for another 3 hours, after which ^{1}H NMR was taken by adding an aliquot of the reaction mixture (50 μL) into 0.5 mL $CDCl_3$. ^{1}H NMR indicates that this order for adding the reagents leads to incomplete conversion of **IV** to give a mixture of the known compound species **V** and the new species that we speculated to be **III**, this result confirmed that the new set of peaks is due to formation of a new species rather than **V** complexed with NaCl that could potentially lead to downfield shift.

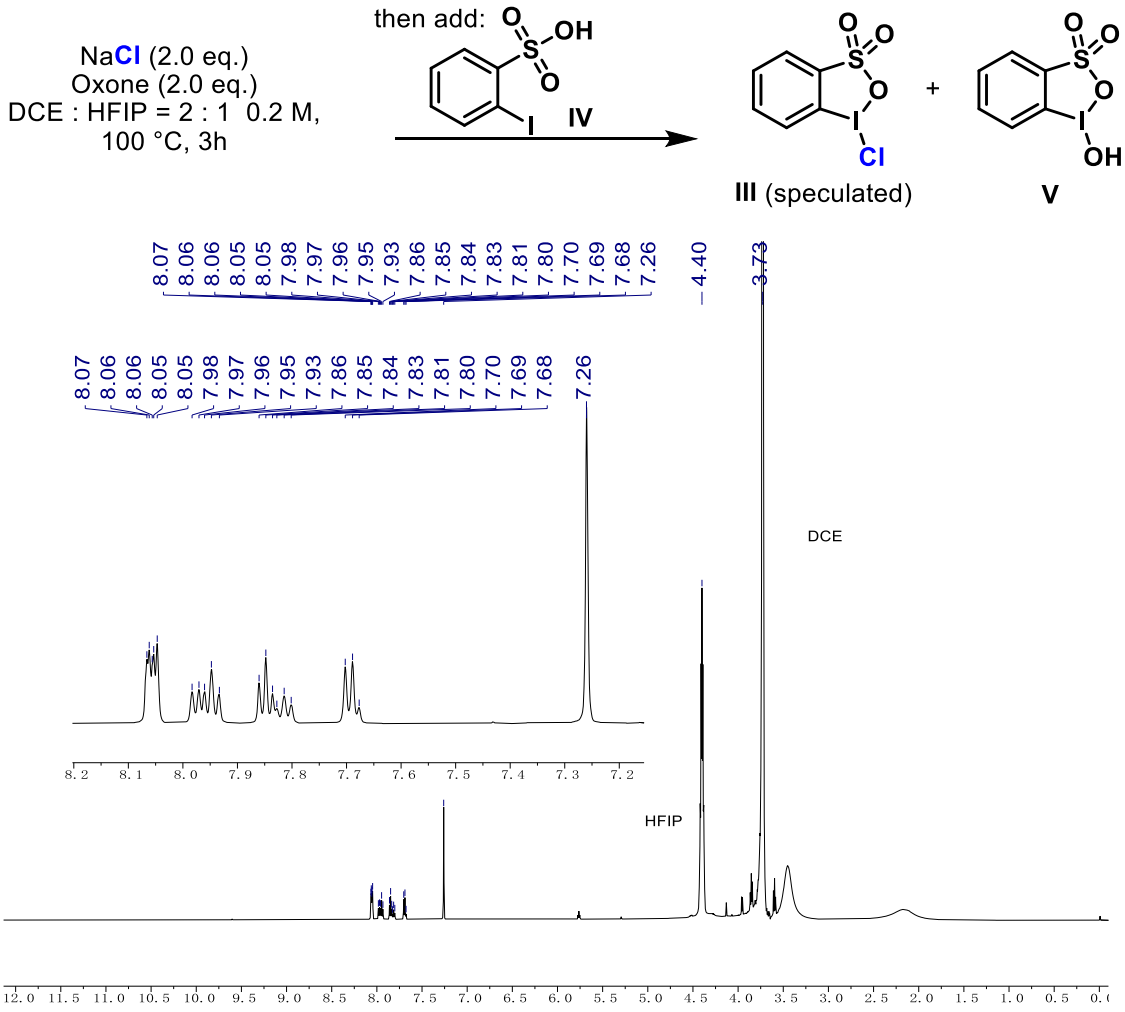


Figure S7. ^{1}H NMR spectrum of a mixture of the new species (speculated to be **III**) and λ^3-iodane **V** resulting from incomplete conversion of **IV** (600 MHz, $CDCl_3$, 298.15 K)

Spectrum 5: Stir a mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2mmol), NaCl (24 mg, 0.4 mmol) and oxone (246 mg, 0.4 mmol) in 1mL DCE/HFIP (2/1) under air at 100 °C for 4 hours, after cooling down to room temperature, ^{1}H NMR was taken by adding an aliquot of the reaction mixture (50 μL) into 0.5 mL $CDCl_3$. ^{1}H NMR showed that complete conversion of **IV** and formation of the new species (speculated to be **III**) could be achieved when all chemicals were added at once, sequential addition of reagents is not necessary.

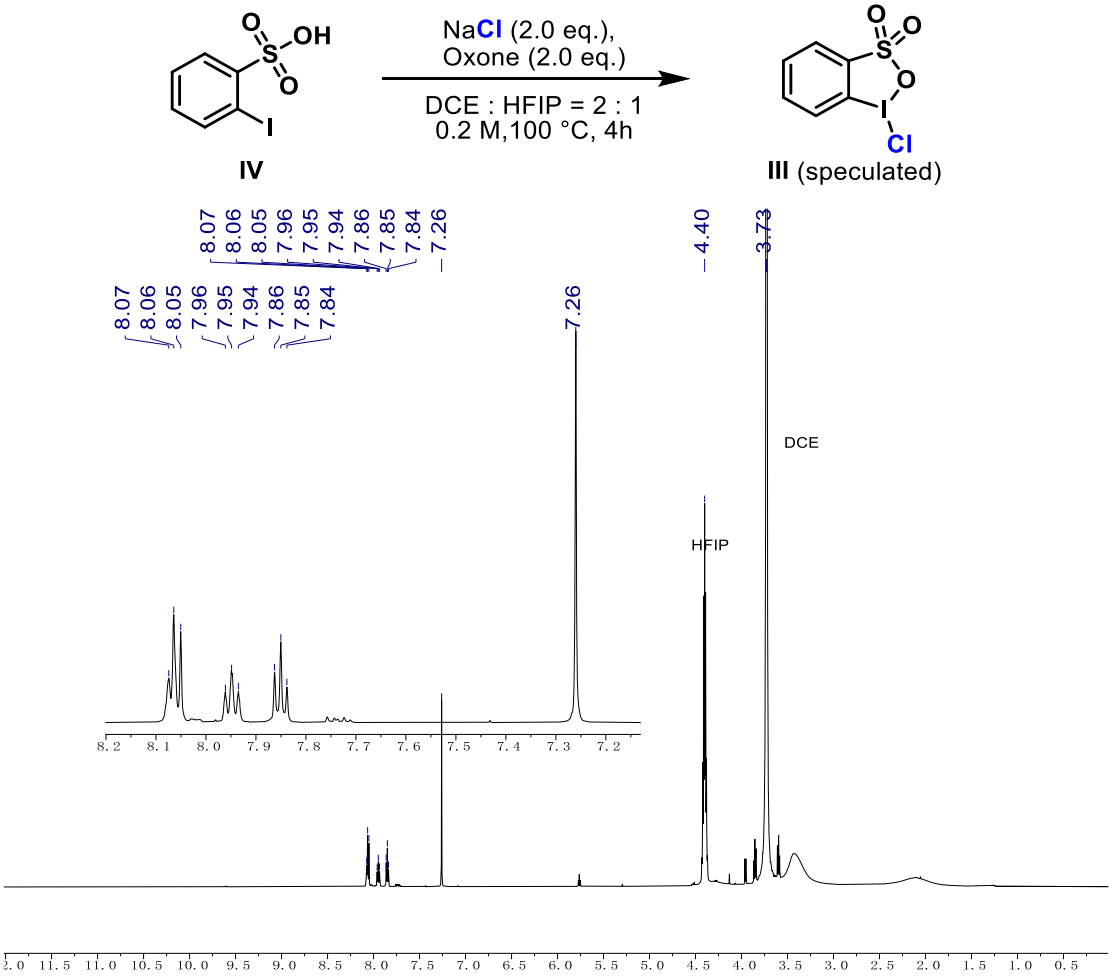


Figure S8. ^{1}H NMR spectrum of the speculated λ^3-iodane **III** by all-at-once addition of reagents (600 MHz, $CDCl_3$, 298.15 K)

Self-chlorination of the new species in the absence of arene substrates

Formation of the new species (speculated to be **III**) in pure HFIP was faster than in DCE/HFIP (2:1), however, prolonged heating of the newly formed species at 100 °C in the absence of an arene substrate leads to self-chlorination of the newly formed species.

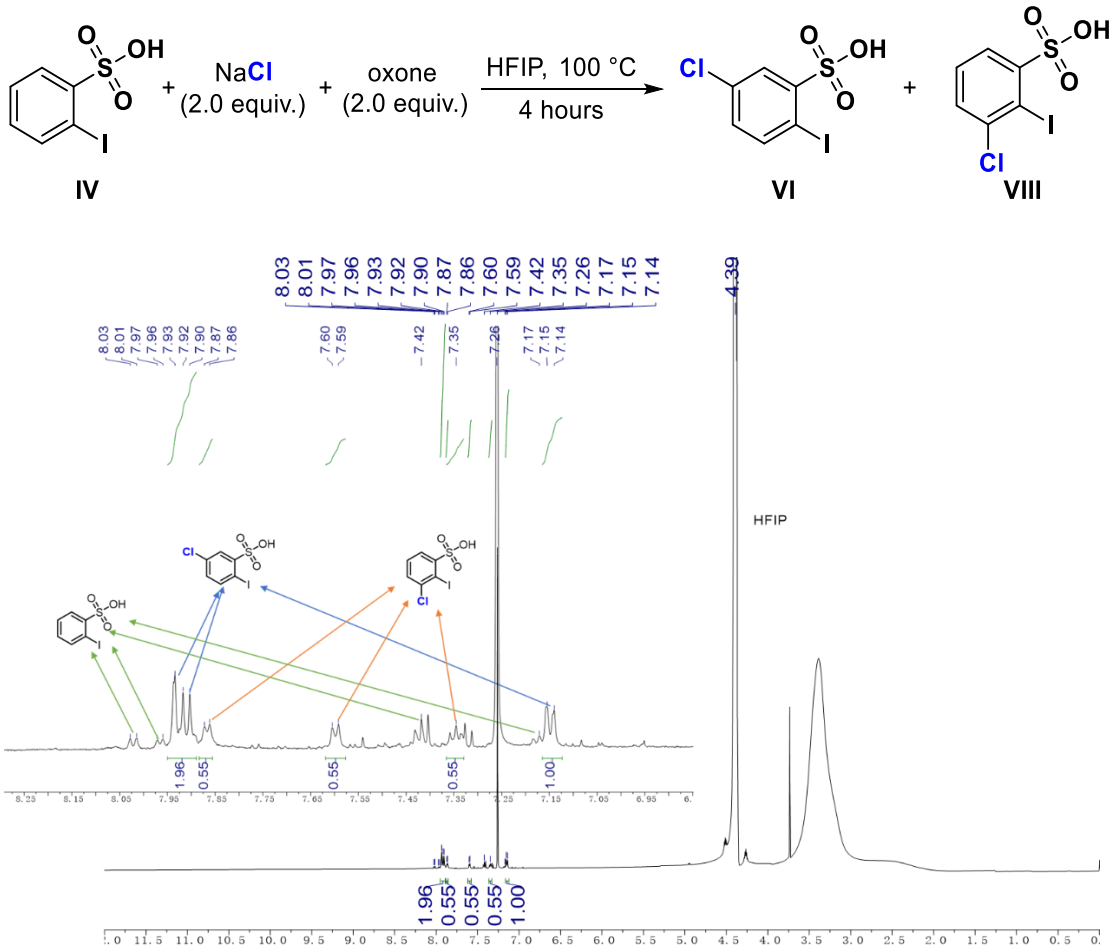


Figure S9. Chlorination of 2-iodobenzenesulphonic acid (600 MHz, $CDCl_3$, 298.15 K)

Protocol for taking the above ^{1}H NMR spectrum: a mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2mmol), NaCl (24 mg, 0.4 mmol) and oxone (246 mg, 0.4 mmol) in 1 mL HFIP was stirred under air at 100 °C for 4 hours, after cooling down to room temperature, ^{1}H NMR was taken by adding an aliquot of the reaction mixture (50 µL) into 0.5 mL $CDCl_3$.

Chlorination of chlorobenzene by new species

The observed new species (speculated to be **III**) can chlorinate electronically deactivated substrate chlorobenzene even at room temperature:

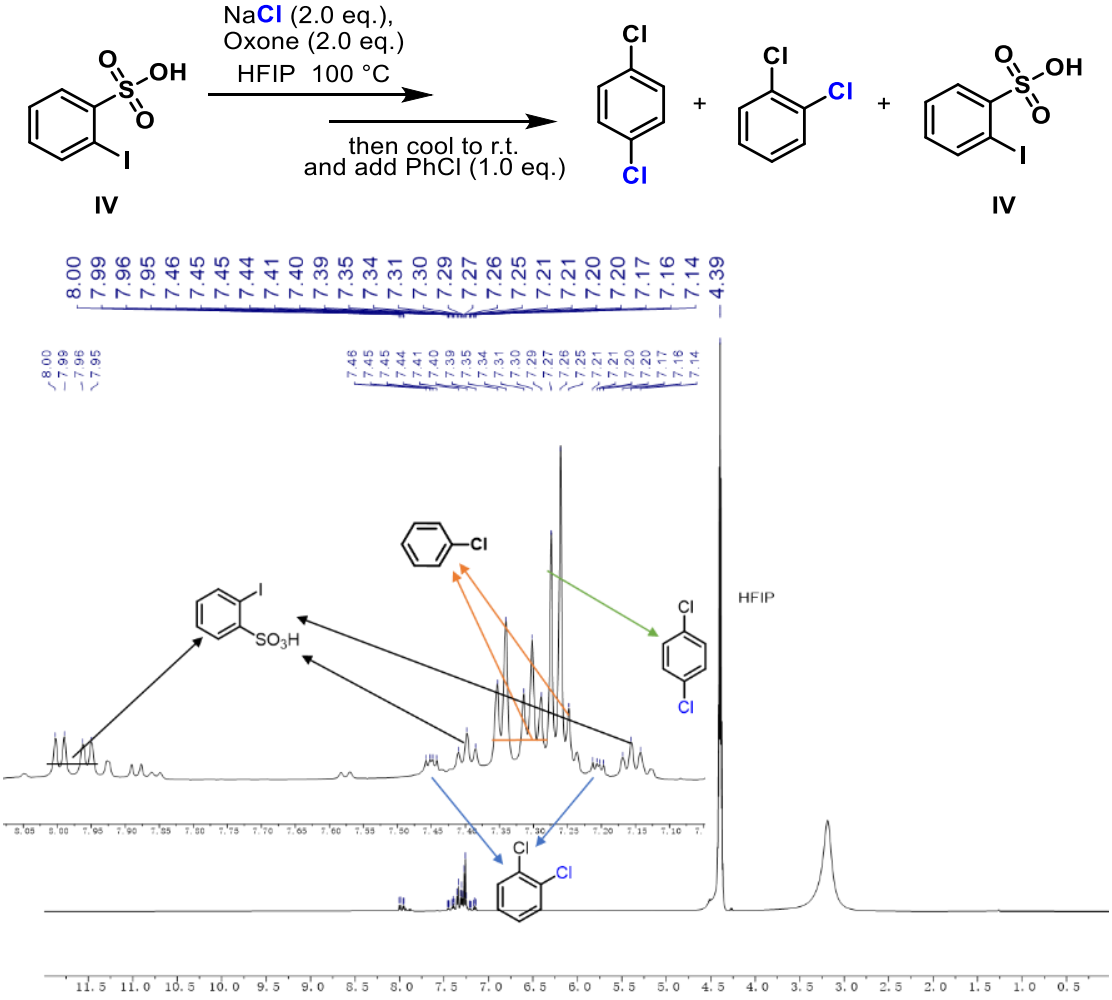


Figure S10. ^{1}H NMR spectrum of the reaction mixture of mixing the new species (speculated to be **III**) with chlorobenzene at room temperature (600 MHz, $CDCl_3$, 298.15 K)

Protocol for taking the above ^{1}H NMR spectrum: Stir a mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2 mmol), NaCl (24 mg, 0.4 mmol) and oxone (246 mg, 0.4 mmol) in 1mL HFIP under air at 100 °C for 3 hours, then cool to room temperature and add PhCl (22 mg, 0.2 mmol), and stir at room temperature for another 3 hours. Afterward, ^{1}H NMR was taken by an aliquot of the reaction mixture (50 μL) into 0.5 mL $CDCl_3$. ^{1}H NMR indicated that the new species (speculated to be **III**) is a highly reactive chlorinating reagent, and it could even chlorinate deactivated substrate chlorobenzene at room temperature without additional catalyst.

2.3 Crystal Structure and Crystallographic Data for λ^3-iodane III

Initial efforts to isolate the newly observed species (speculated to be **III**) from the reaction mixture via standard workup procedures, or via classic flash chromatography only leads to the decomposition of this new species, and 2-iodobenzenesulfonic acid (**IV**) was obtained as the main decomposition product. We speculate that the instability of the new species might due to its sensitivity to moisture, therefore, a careful workup under anhydrous condition was carried out and a recrystallization under N_2 atmosphere leads to the formation of crystals that are suitable for single crystal X-ray chromatography that leads to unambiguous assignment of the structure of the new species to be **III**, which agrees with our speculation.

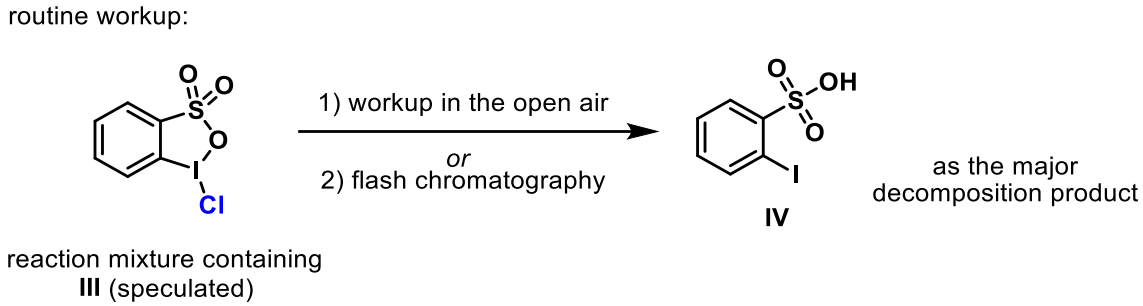
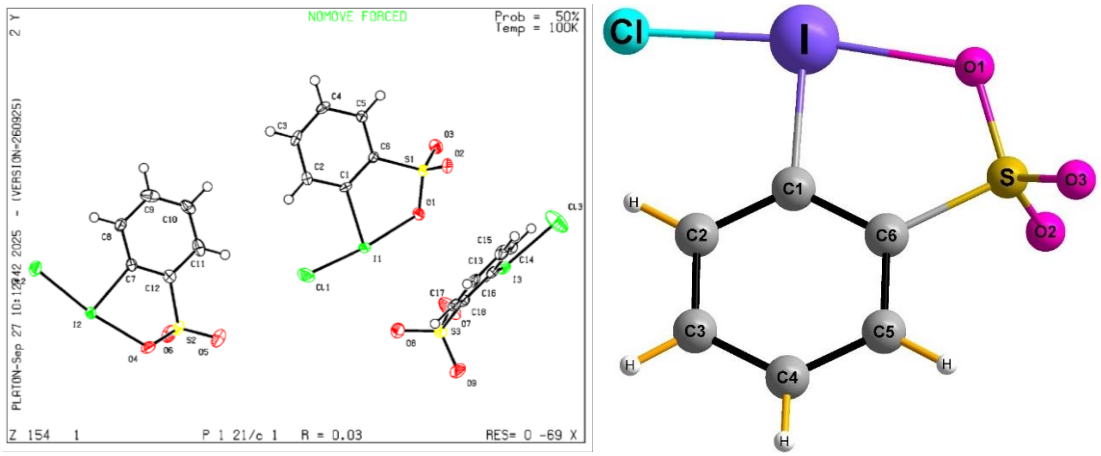


Figure S11. Isolate the newly observed species

Anhydrous workup: Stir a mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2mmol), NaCl (24 mg, 0.4 mmol) and oxone (246 mg, 0.4 mmol) in 1mL DCE/HFIP (2/1) under air at 100 °C for 4 hours. Cooling down to room temperature and filtration under N_2 atmosphere was performed to remove all solids to give a solution of **III** in DCE/HFIP (2/1), after which the solvent was removed under vacuum to give a pale yellow solid (pure **III**).

Method for single crystals cultivation: a pure solid sample was dissolved in $CHCl_3$ (0.5 mL) in a 5 mL vial at room temperature. The vial was properly sealed with a loose cap and kept at room temperature in N_2 atmosphere, to allow the slow evaporation of the solvent until single crystals were obtained.

Figure S12. X-ray crystal structure of λ^3-iodane **III**



Crystallographic data for compound (**CCDC-2491924**) has been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC.

Table S1. Crystal data for λ^3-iodane III

Identification code	1
Empirical formula	$C_6H_4ClIO_3S$
Formula weight	318.50
Temperature/K	100.03(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.5927(3)
b/Å	7.48490(10)
c/Å	22.9394(5)
α/°	90
β/°	103.646(2)
γ/°	90
Volume/Å^3	2601.68(9)
Z	12
ρ_{calc}g/cm^3	2.439
μ/mm^{-1}	4.201
F(000)	1800.0
Crystal size/mm^3	0.18 × 0.16 × 0.14
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	3.994 to 52.744
Index ranges	-19 ≤ h ≤ 19, -9 ≤ k ≤ 9, -28 ≤ l ≤ 28
Reflections collected	34770
Independent reflections	5206 [R_{int} = 0.0843, R_{sigma} = 0.0384]
Data/restraints/parameters	5206/0/325
Goodness-of-fit on F^2	1.171
Final R indexes [I>=2σ (I)]	R_1 = 0.0271, wR_2 = 0.0663
Final R indexes [all data]	R_1 = 0.0847, wR_2 = 0.1195
Largest diff. peak/hole / e Å^{-3}	4.31/-4.12

Bond precision: C-C = 0.0097 A Wavelength=0.71073

Cell: a=15.5927(3) b=7.4849(1) c=22.9394(5)
alpha=90 beta=103.646(2) gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	2601.68(9)	2601.68(9)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C6 H4 Cl I O3 S	C6 H4 Cl I O3 S
Sum formula	C6 H4 Cl I O3 S	C6 H4 Cl I O3 S
Mr	318.50	318.50
Dx,g cm-3	2.440	2.439
Z	12	12
Mu (mm-1)	4.201	4.201
F000	1800.0	1800.0
F000'	1798.32	
h,k,lmax	19,9,28	19,9,28
Nref	5330	5206
Tmin,Tmax	0.474,0.555	0.350,1.000
Tmin'	0.465	

Correction method= # Reported T Limits: Tmin=0.350 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.977 Theta(max)= 26.372

R(reflections)= 0.0271(4318) wR2(reflections)= 0.1195(5206)

S = 1.171 Npar= 325

2.4 Characterization for λ³-iodane III

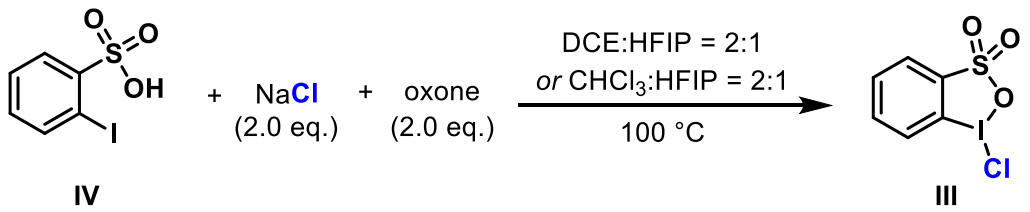


Figure S13. The synthetic procedure for λ³-iodane **III**

Protocol for making III for characterization: Stir the mixture of 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2mmol), NaCl (24 mg, 0.4 mmol) and oxone (246 mg, 0.4 mmol) in 1 mL DCE/HFIP(2/1) under air at 100 °C for 4 hours, after cooling down to room temperature, dilute the reaction mixture with $CHCl_3$, then filter off the solids and wash the residue with $CHCl_3$ (under N_2 atmosphere), removing the solvent under vacuum obtains yellow moisture-sensitive solid (25% NMR yield in DCE/HFIP = 2/1, 66% NMR yield in $CHCl_3$/HFIP = 2/1, 1,1,2,2-tetrachloroethane as the internal standard). **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.10 (dd, *J* = 7.5, 1.6 Hz, 1H), 8.06 (d, *J* = 8.9 Hz, 1H), 7.91 (ddd, *J* = 8.7, 7.2, 1.6 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 135.5, 133.0, 129.6, 126.9, 110.3.

HRMS *m/z* (ESI): calcd. for $C_6H_4ClIO_3S$ $[M-H]^-$:316.8542, found: 316.8536.

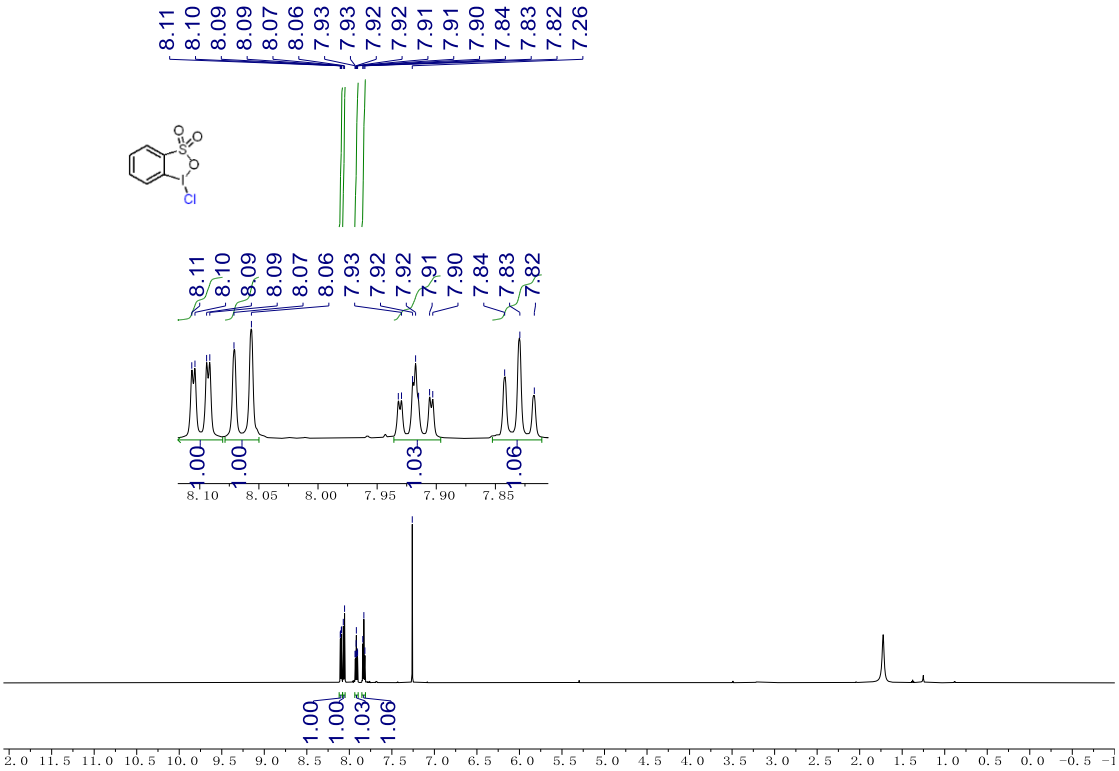


Figure S14. ^{1}H NMR spectrum of λ³-iodane **III** (600 MHz, $CDCl_3$, 298.15 K)

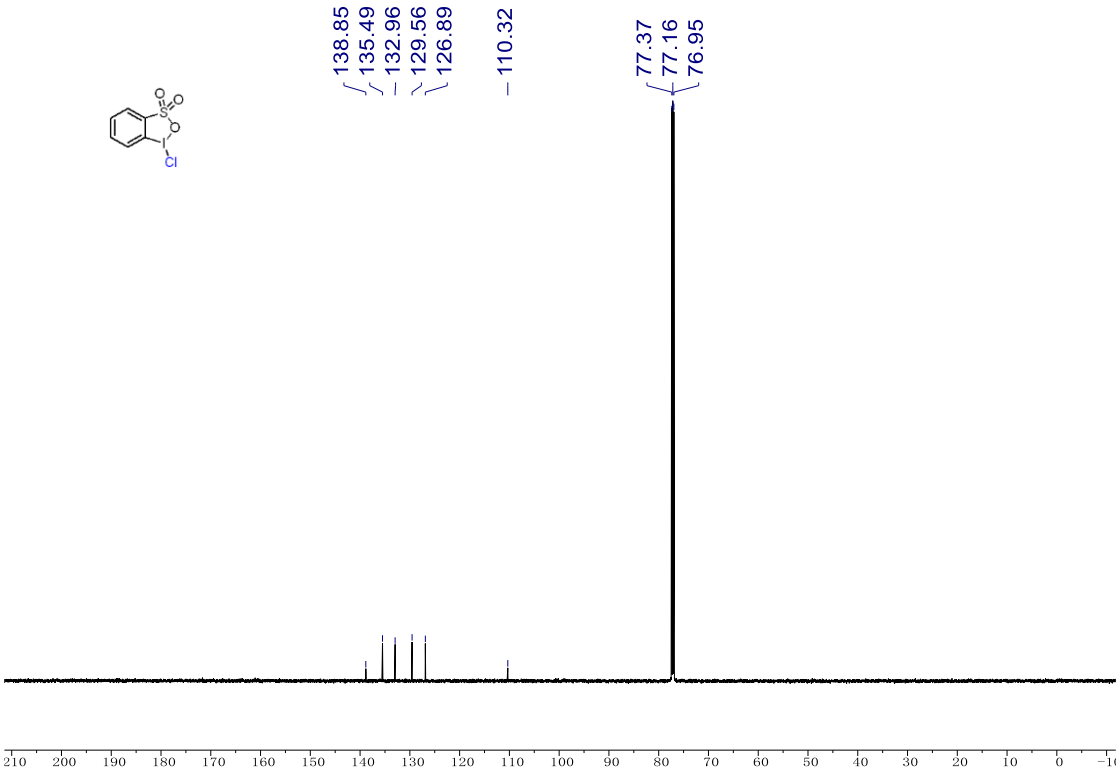


Figure S15. $^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of λ^3-iodane **III** (151 MHz, $CDCl_3$, 298.15 K)

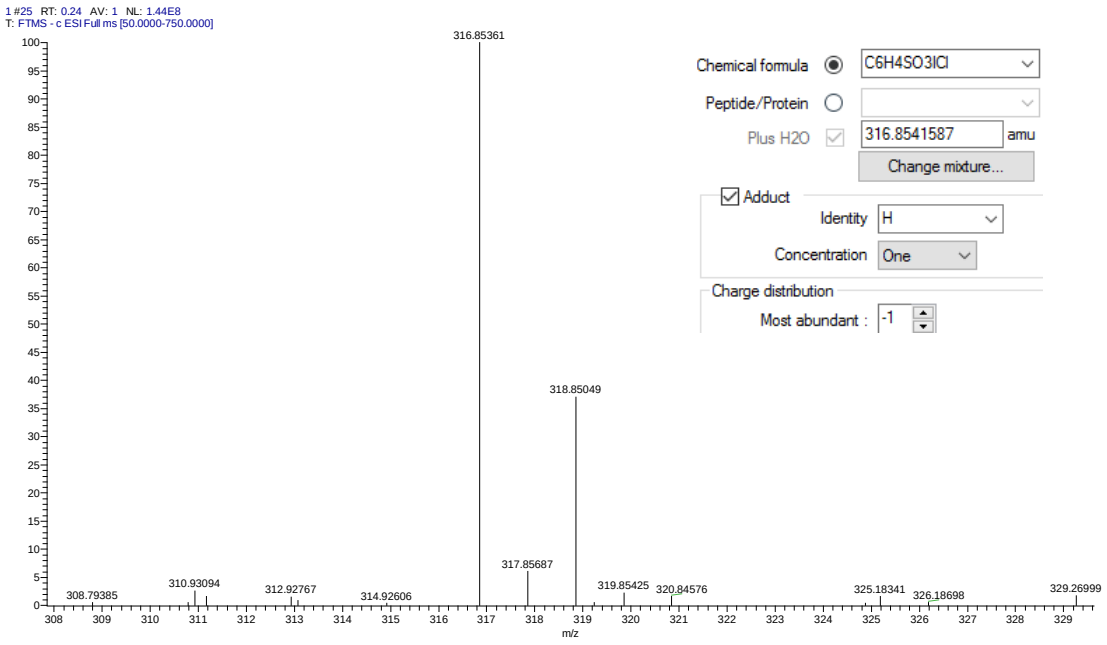


Figure S16. HR-MS spectrum for λ^3-iodane **III**

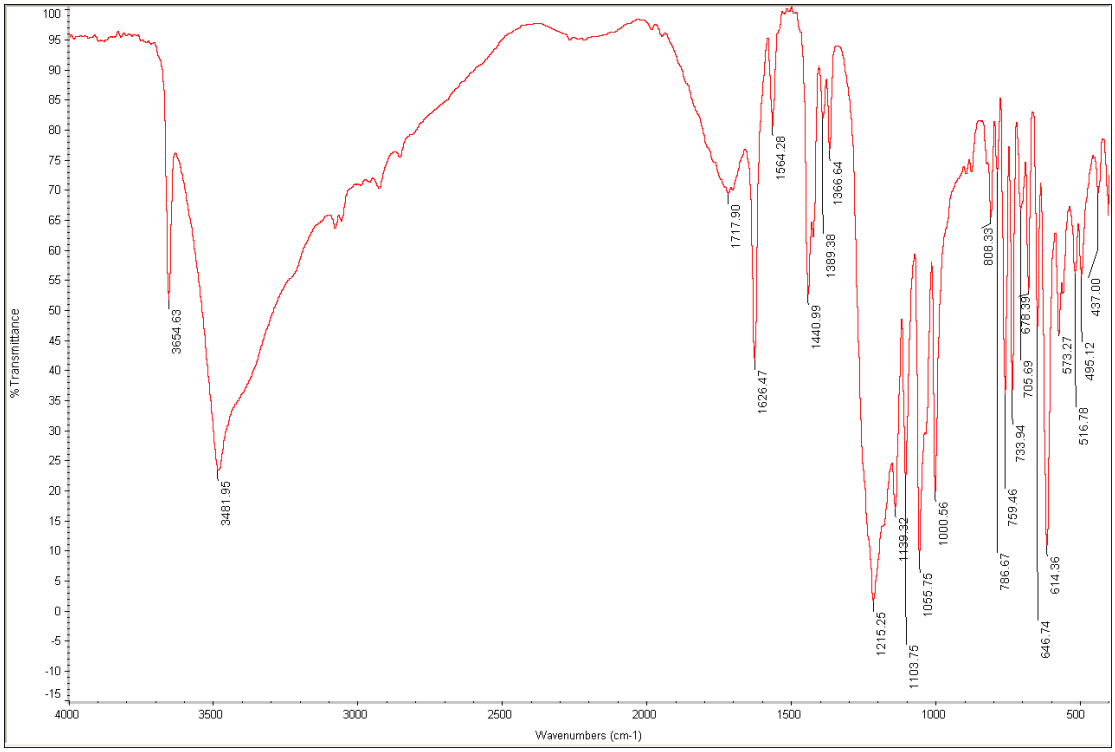


Figure S17. IR sprctrum for λ^3-iodane **III**

2.5 Design and optimization of a catalytic C–H chlorination via catalytic formation of λ³-iodane III

Considering the high electrophilicity of **III** and its sensitivity to moisture, we designed a catalytic arene C–H chlorination via *in situ* formation of **III** to address the problems associated with its preparation and handling:

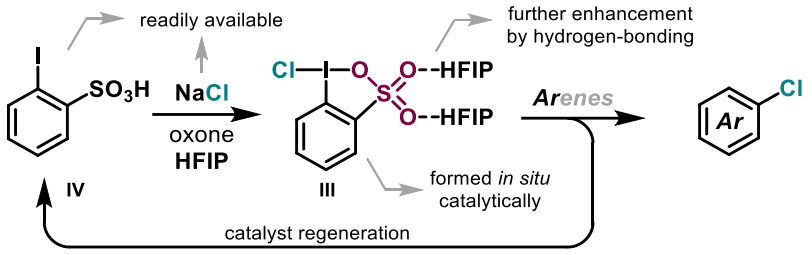
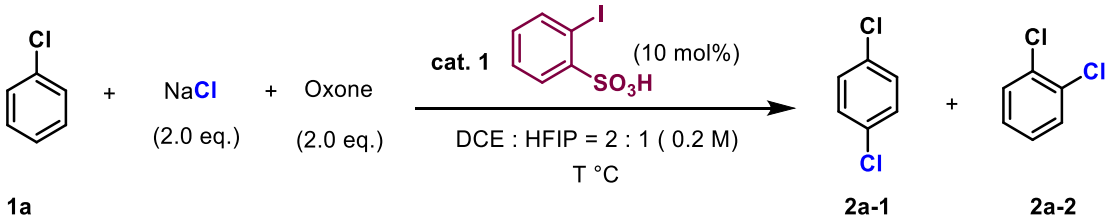


Figure S18. Design of a catalytic C–H chlorination for unactivated arenes via in situ formation of **III**

Reaction optimization:

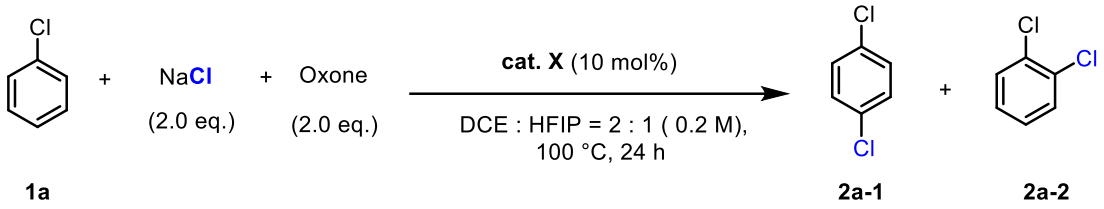
Table S2. Reaction condition optimization



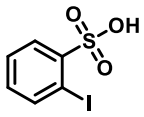
Entry	cat.	Oxone	T (°C)	2a-1/2a-2 / total yield (%)
1	cat.1	2.0 eq.	100	69/25/94
2	cat.1 (5 mol%)	2.0 eq	100	57/20/77
4	cat.1	no oxone	100	0/0/0
5	no cat.	2.0 eq.	100	8/1/9
6	cat.1	2.0 eq.	90	30/10/40
7	cat.1	2.0 eq.	80	trace

Unless otherwise specified, the reaction was carried out under air atmosphere, with **1a** (1.0 eq.), NaCl (2.0 eq.), oxone (2.0 eq.), DCE:HFIP=2:1 (0.2 M), cat.1 (5 ~ 10 mol%), chemical yield is determined by gas chromatography (GC) with dodecane as the internal standard.

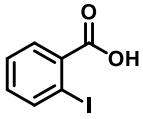
Table S3. Comparison of the catalytic activities of aryl iodides



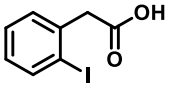
1a **2a-1** **2a-2**



cat. 1

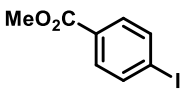


cat. 2

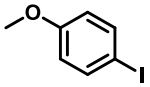


cat. 3

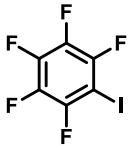
cat. 4



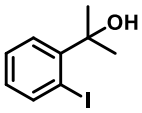
cat. 5



cat. 6



cat. 7

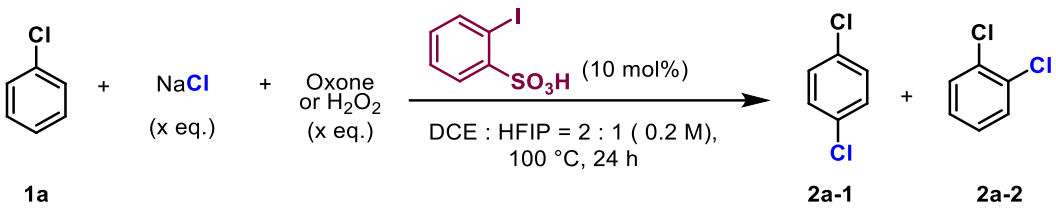


cat. 8

Entry	cat. (10 mol%)	2a-1/2a-2 / total yield (%)
1	cat.1	60/19/79
2	cat.2	24/8/32
3	cat.3	34/17/51
4	cat.4	20/11/31
5	cat.5	32/5/37
6	cat.6	51/8/59
7	cat.7	10/4/14
8	cat.8	0/0/0

Unless otherwise specified, the reaction was carried out under air atmosphere, with **1a** (1.0 eq.), NaCl (2.0 eq.), oxone (2.0 eq.), DCE:HFIP = 2:1 (0.2 M), **cat.1** ~ **cat.8** (10 mol%), chemical yield is determined by gas chromatography (GC) with dodecane as the internal standard.

Table S4. Optimization of the stoichiometry of NaCl and oxidants

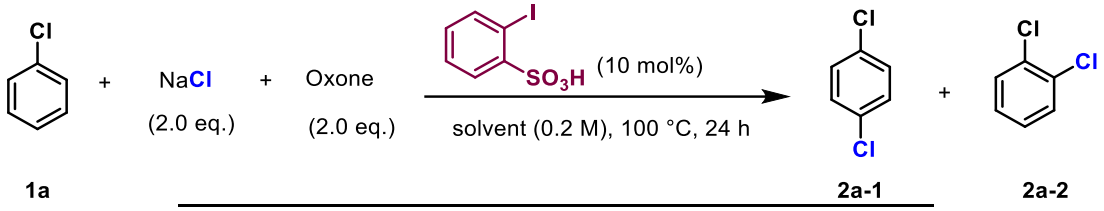


1a **2a-1** **2a-2**

Entry	NaCl loading	Oxidants/loadings	**2a-1**/**2a-2** / total yield (%)
1	1.0 eq.	Oxone/2.0 eq.	60/23/83
2	1.5 eq.	Oxone/2.0 eq.	63/25/88
3	2.0 eq.	Oxone/2.0 eq.	60/19/79
4	2.5 eq.	Oxone/2.0 eq.	63/25/88
5	2.0 eq.	H_2O_2/2.0 eq.	0/0/0
6	2.0 eq.	Oxone/1.5 eq.	51/18/69
7	2.0 eq.	Oxone/2.5 eq.	35/12/47

Unless otherwise specified, the reaction was carried out under air atmosphere, with **1a** (1.0 eq.), NaCl (1.0 ~ 2.5 eq.), oxidant source (1.5 ~ 2.5 eq.), DCE:HFIP = 2 : 1 (0.2 M), **cat.1** (10 mol%), chemical yield is determined by gas chromatography (GC) with dodecane as the internal standard.

Table S5. Optimization of the solvent



1a **2a-1** **2a-2**

Entry	solvent	**2a-1**/**2a-2** / total yield (%)
1	DCE	trace
2	HFIP	60/19/79
3	DMF	0/0/0
4	DMSO	0/0/0
5	MeOH	trace
6	1,4-dioxane	0/0/0
7	*i*Pr-OH	0/0/0
8	MeCN	trace
9	DCE:HFIP = 2:1	69/25/94
10	DMF:HFIP = 2:1	0/0/0
11	DMSO:HFIP = 2:1	0/0/0
12	$CHCl_3$:HFIP = 2:1	27/6/33
13	1,4-dioxane:HFIP = 2:1	0/0/0
14	MeCN:HFIP = 2:1	31/14/45

Unless otherwise specified, the reaction was carried out under air atmosphere, with **1a** (1.0 eq.), NaCl (2.0 eq.), oxone (2.0 eq.), solvent (0.2 M), **cat.1** (10 mol%), chemical yield is determined by gas chromatography (GC) with dodecane as the internal standard.

2.6 Application of our procedure for the synthesis of the 1-chloro-1λ³-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (BI-Cl)

The same protocol could also be applied to other I–Cl type λ³-iodane such as **II**, in contrast to **III**, **II** is less sensitive to moisture, which makes its isolation and characterization much easier, and that is why **II** is a commercially available chemical while **III** is not.

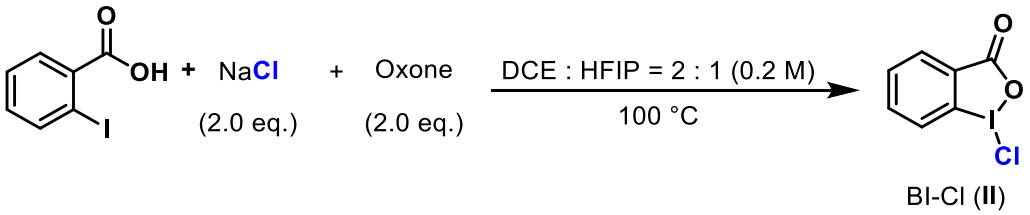


Figure S19. The synthetic procedure for **II**

Protocol for synthesizing II: to a 5 mL pressure vial equipped with a magnetic stir bar was charged with 2-iodobenzoic acid (50 mg, 0.2 mmol, 1.0 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), 1 mL DCE/HFIP (2/1). The reaction mixture was sealed and heated to 100 °C for 4 hours. After the mixture was cooled to room temperature, a small amount of the reaction solution was taken for NMR testing.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (d, *J* = 7.3 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 8.03 (t, *J* = 7.9 Hz, 1H), 7.82 (t, *J* = 7.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.1, 137.2, 133.6, 132.2, 128.5, 127.0, 117.2.

Known compound[1].

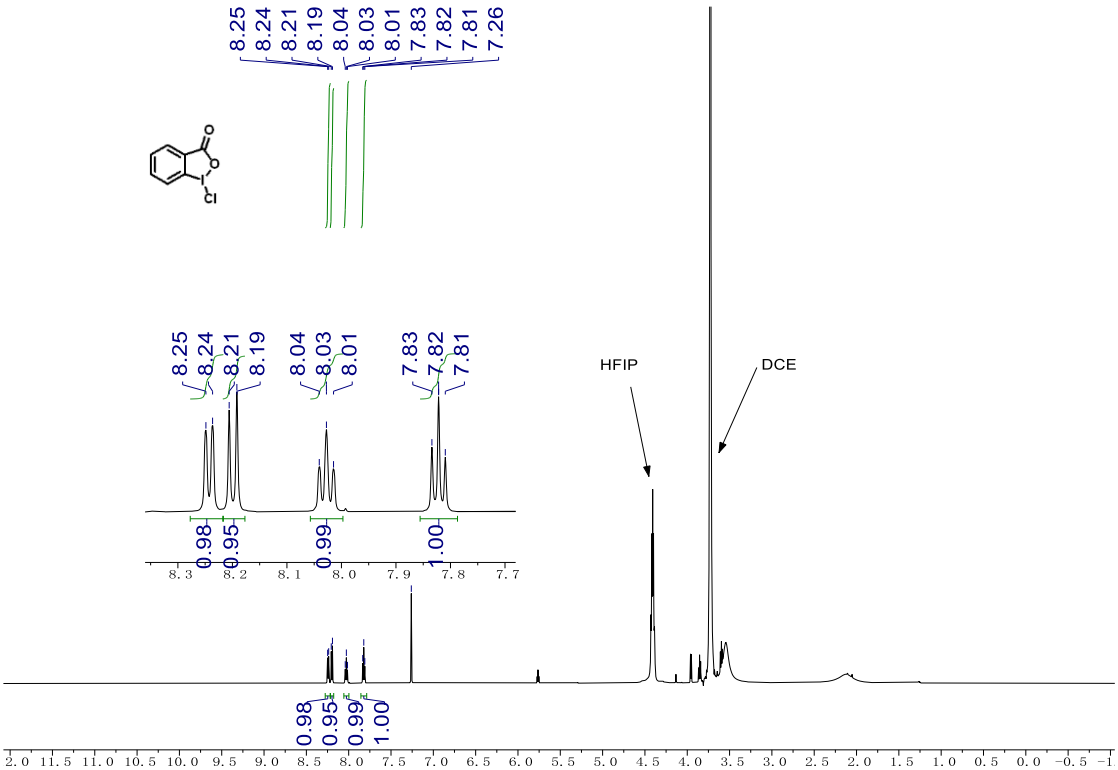


Figure S20. ^{1}H NMR spectrum of **BI-Cl** (600 MHz, $CDCl_3$, 298.15 K).

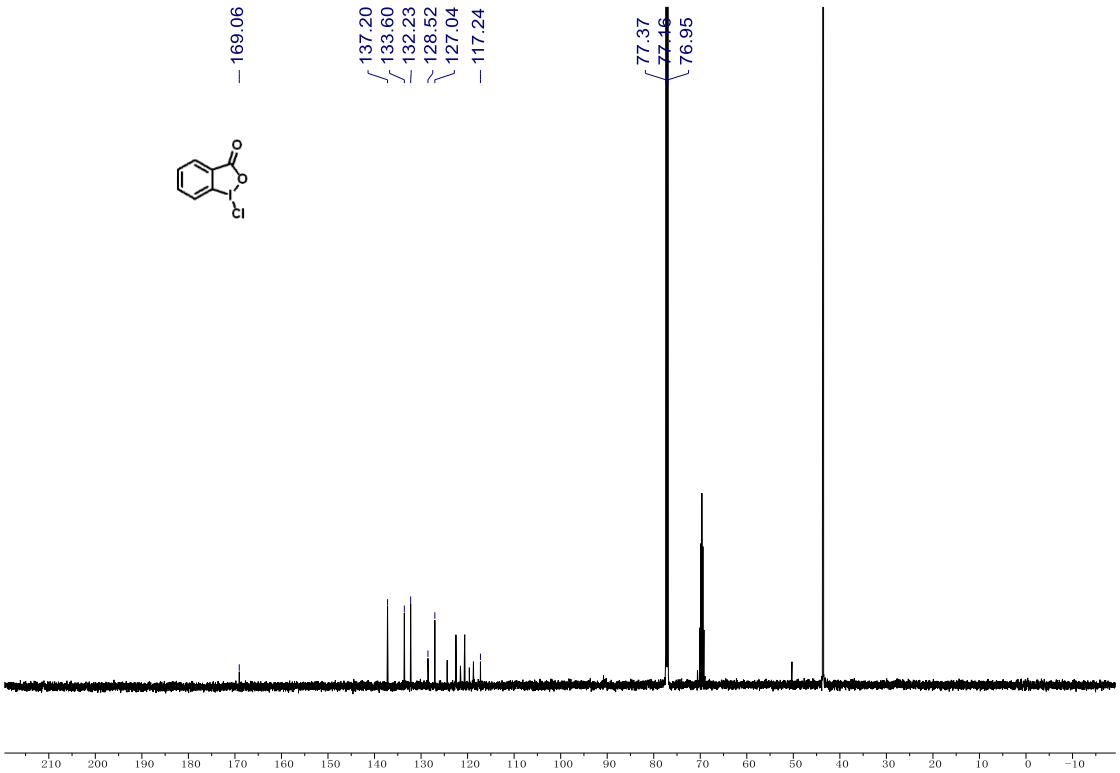


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of **BI-Cl** (151 MHz, $CDCl_3$, 298.15 K).

3 Control experiments

3.1 *In situ* generation of λ³-iodane III for the chlorination of chlorobenzene

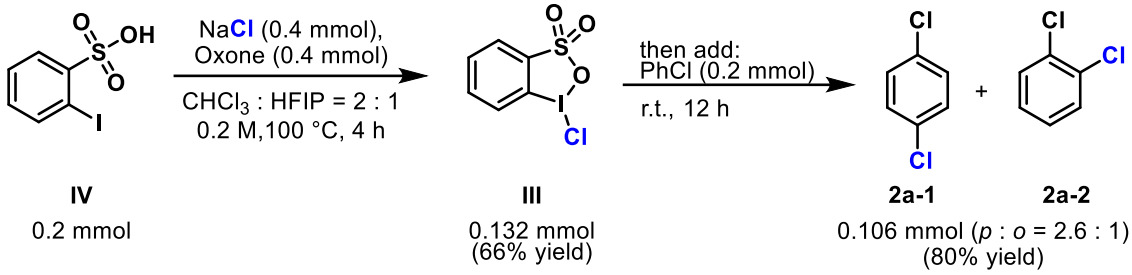


Figure S22. Chlorination of chlorobenzene by preparation of λ³-iodane **III** in situ

Experimental details: to a 5 mL pressure Schlenk vial equipped with a magnetic stir bar was charged with 2-iodobenzenesulphonic acid (**IV**, 56 mg, 0.2 mmol, 1.0 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), 1.0 mL $CHCl_3$/HFIP (2/1). The reaction mixture was sealed and heated to 100 °C for 4 hours. After the mixture was cooled to room temperature, the solid was removed by filtration (66% ^{1}H NMR yield, 1,1,2,2-tetrachloroethane as the internal standard) under N_2 and PhCl (22 mg, 0.2 mmol) was added, continue stirring at room temperature for another 12 hours. The GC detected 0.106 mmol of dichlorobenzene product (*p*: *o* = 2.6 : 1, dodecane as the internal standard). The chlorination conversion rate of the reactive intermediates is 80%.

3.2 chlorination of chlorobenzene by the combination of λ³-iodane V and NaCl

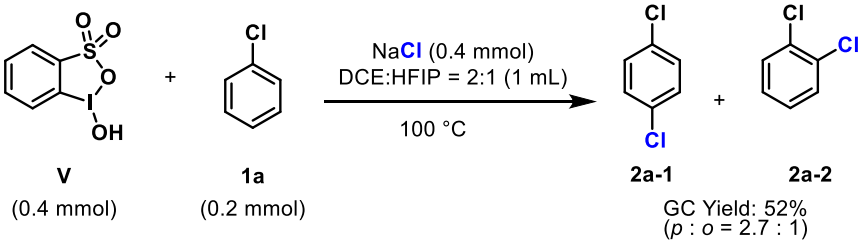


Figure S23. Chlorination of chlorobenzene by λ³-iodane **V** and NaCl

Experimental details: to a 5 mL pressure vial equipped with a magnetic stir bar was charged with 1-hydroxy-1*H*-1λ³-benzo[*d*][1,2,3]iodaoxathiole 3,3-dioxide (**V**, 120 mg, 0.4 mmol, 2.0 eq.), PhCl (22 mg, 0.2 mmol), NaCl (24 mg, 0.4 mmol, 2.0 eq.), 1 ml DCE/HFIP (2/1). The reaction mixture was sealed and heated to 100 °C for 24 hours. The GC yield of product was 52% (*p* : *o* = 2.7 : 1, dodecane as the internal standard).

4 Gram scale experiments

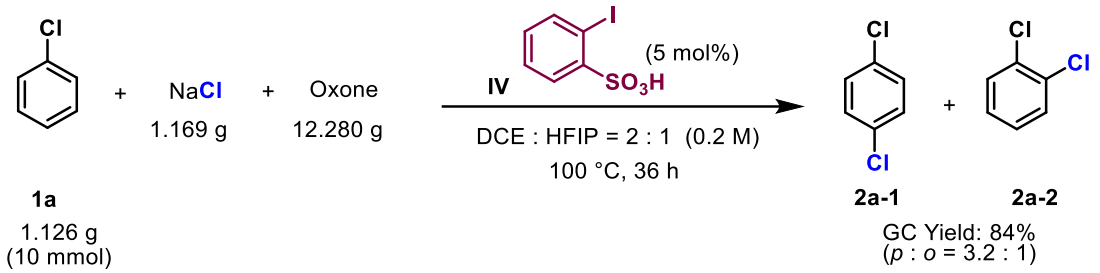


Figure S24. Gram reaction experiment of chlorobenzene

Experimental details: to a 500 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with chlorobenzene (1.126 g, 10.0 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (142 mg, 0.5 mmol, 0.05 equiv), NaCl (1.169 g, 20.0 mmol, 2.0 eq.), Oxone (12.280 g, 20 mmol, 2.0 eq.), 50 ml DCE/HFIP (2/1). The reaction mixture was stirred at 100 °C for 36 hours, the mixture was then cooled to room temperature. Then dodecane (2.27 mL) was added as an internal standard, the combined yield of **2a-1** and **2a-2** was determined to be 84% (GC, *p* : *o* = 3.2 : 1).

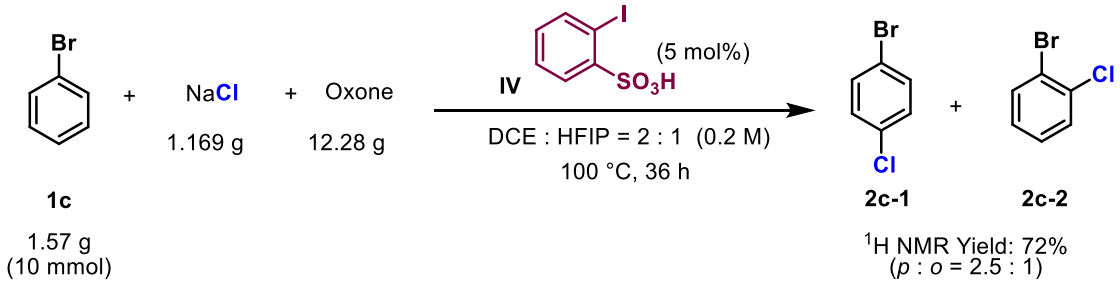


Figure S25. Gram reaction experiment of bromobenzene

Experimental details: to a 500 mL oven-dried Schlenk tube equipped with a magnetic stir bar was charged with bromobenzene (1.570 g, 10.0 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (142 mg, 0.5 mmol, 0.05 eq.), NaCl (1.169 g, 20.0 mmol, 2.0 eq.), Oxone (12.28 g, 20 mmol, 2.0 eq.), 50 ml DCE/HFIP (2/1). The reaction mixture was stirred at 100 °C for 36 hours, the mixture was then cooled to room temperature. Then 1,1,2,2-tetrachloroethane (1.058 mL) was added as an internal standard, the combined yield of **2c-1** and **2c-2** was determined to be 72% (^{1}H NMR, *p* : *o* = 3.2 : 1).

5 Comparison of chlorination methods

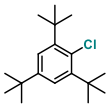
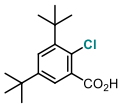
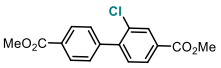
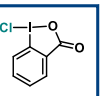
Our method:  III *in situ* formation (catalytically)	 2n	 2q	 2ii	 2yy	 BI-Cl (III)
Our Mehod:	**85%**	**85%**	**71%**	**86%**	 NCS
Mehod 1 (**BI-Cl**/DMF):	0%	trace	0%	0%	
Mehod 2 (**BI-Cl**/HFIP):	0%	**38%**	0%	0%	
Mehod 3 (**NCS**/HFIP):	0%	0%	0%	trace	
Mehod 4 (**NCS**/DMSO):	0%	**43%**	0%	0%	
Mehod 5 (**TCCA**/**TfOH**/HFIP):	**57%**	**15%**	**67%**	**85%**	 TCCA

Table S6. Comparison of chlorination methods

Method 1: According to existing literature[4], substrates (0.5 mmol), DMSO (0.1 mmol) and NCS (0.6 mmol) were dissolved in $CHCl_3$ (2 mL). The mixture was stirred at 25 °C for 12 hours. The yield of product was determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

Method 2: According to existing literature[5], substrates (0.5 mmol) and TCCA (0.2 mmol) were dissolved in HFIP (2 mL). The mixture was stirred at 60 °C for 24 hours. After cooling down to room temprature and concentrating in vacuum, the yield of product was determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

Method 3: According to existing literature[6], substrates (0.5 mmol) and NCS (0.5 mmol) were dissolved in HFIP (2 mL). The mixture was stirred at 25 °C for 24 hours. The yield of product was determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

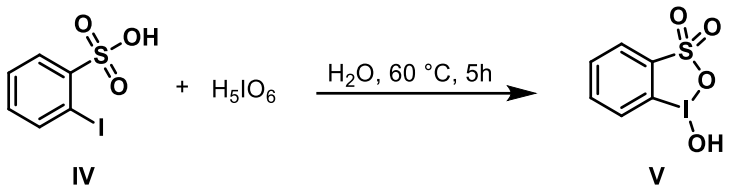
Method 4: According to existing literature[7], substrates (0.1 mmol) and BI-Cl (0.12 mmol) were dissolved in HFIP (1 mL). The mixture was stirred at 25 °C for 12 hours. The yield of product was determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

Method 5: According to existing literature[7], substrates (0.1 mmol) and BI-Cl (0.12 mmol) were dissolved in DMF (1 mL). The mixture was stirred at 25 °C for 24 hours. The yield of product was determined by ^1H NMR analysis of the crude reaction mixture using 1,1,2,2-tetrachloroethane as the internal standard.

6 Mechanistic study

6.1 Syntheses of λ³-iodane V and λ⁵-iodane VIII (IBS)

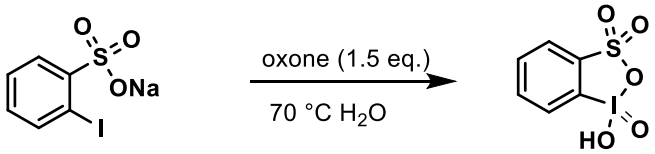
The known compounds λ³-iodane **V** and λ⁵-iodane **VIII** (IBS) that are used (or as references) in mechanistic studies are synthesized by using the following reported protocols:



IV V

Figure S26. The preparation of λ³-iodane **V**

Synthesis of V: according to existing literature[3], periodic acid (1.22 g, 5.35 mmol) in 2 mL of distilled water was added to 2-iodobenzenesulfonic acid (500 mg, 1.76 mmol) in 1 mL of distilled water by one portion. The reaction mixture was heated to 60 °C and was stirred for about 5 hours. After that, the reaction mixture was cooled to room temperature, and a precipitate was formed. The white precipitate of was collected by filtration, washed with cold distilled water and dried in vacuo to give 479 mg **V** (85%).



VIII

Figure S27. The preparation of λ⁵-iodane **VIII**

Synthesis of VIII: according to existing literature[3], to a 5 mL pressure vial equipped with a magnetic stir bar was charged with sodium 2-iodobenzenesulfononate (116 mg, 0.38 mmol, 1.0 eq.), oxone (350 mg, 0.57 mmol, 1.5 eq.), H_2O (1.0 mL). The reaction mixture was sealed and heated to 70 °C for 6 hours. After cooling the aqueous solution to room temperature, the product **VIII** precipitated out of the reaction mixture as a white crystal (55 mg, 46%).

6.2 Hydrolysis of λ³-iodane III

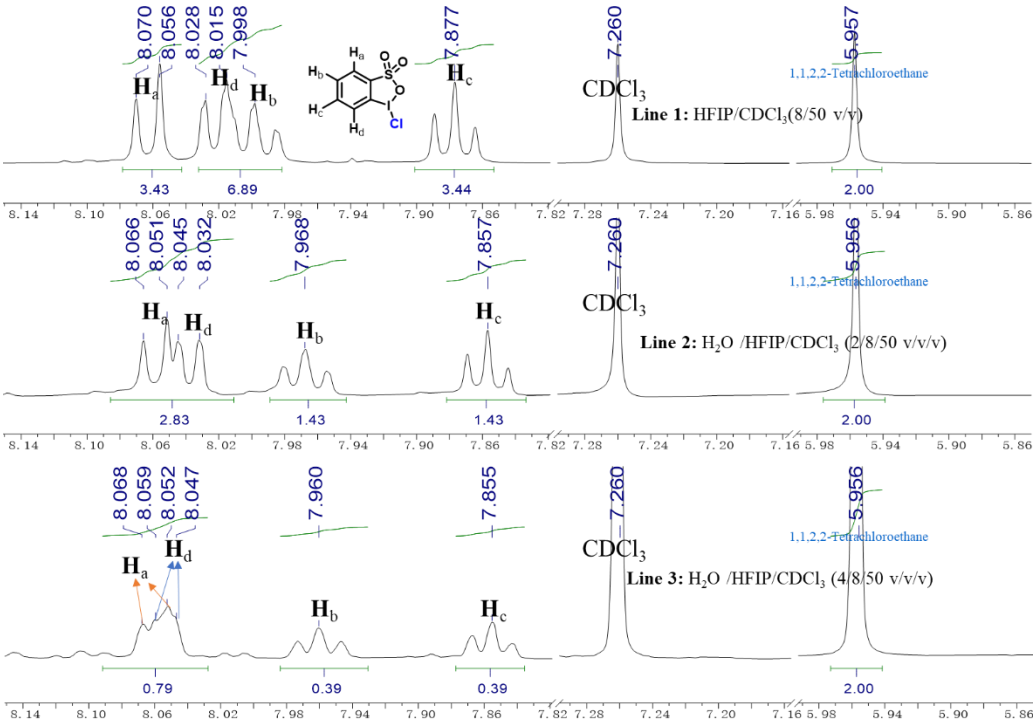


Figure S28. Crude ^{1}H NMR study of λ³-iodane III and H_2O (600 MHz, $CDCl_3$, 298.15 K)

Decomposition of III in the presence of water: after adding 20 μL H_2O to the NMR sample (HFIP/$CDCl_3$, 8/50, v/v), with 1,1,2,2-tetrachloroethane as the internal standard, the solution quickly decolorizes as the signal corresponding to **III** decreases, a white precipitate forms in the aqueous layer. Additional 20 μL of water was added to further consume λ³-iodane **III**.

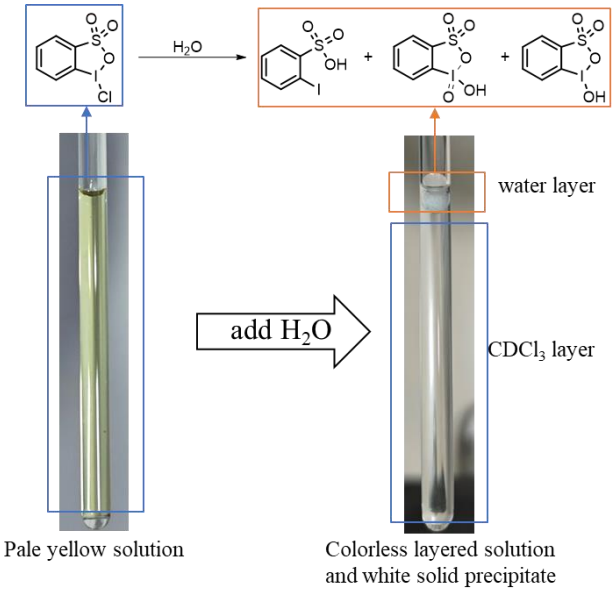


Figure S29. λ³-iodane **III** hydrolyzed in the NMR tube

The precipitate in the aqueous layer was collected and dissolved in D_2O for NMR analysis, which the decomposition product was a mixture of **IV**, **V** and **VIII** in a ratio of 6 : 1 : 1.5, determined by analyzing the ^1H NMR and compare it to the authentic sample synthesized with known protocols[3].

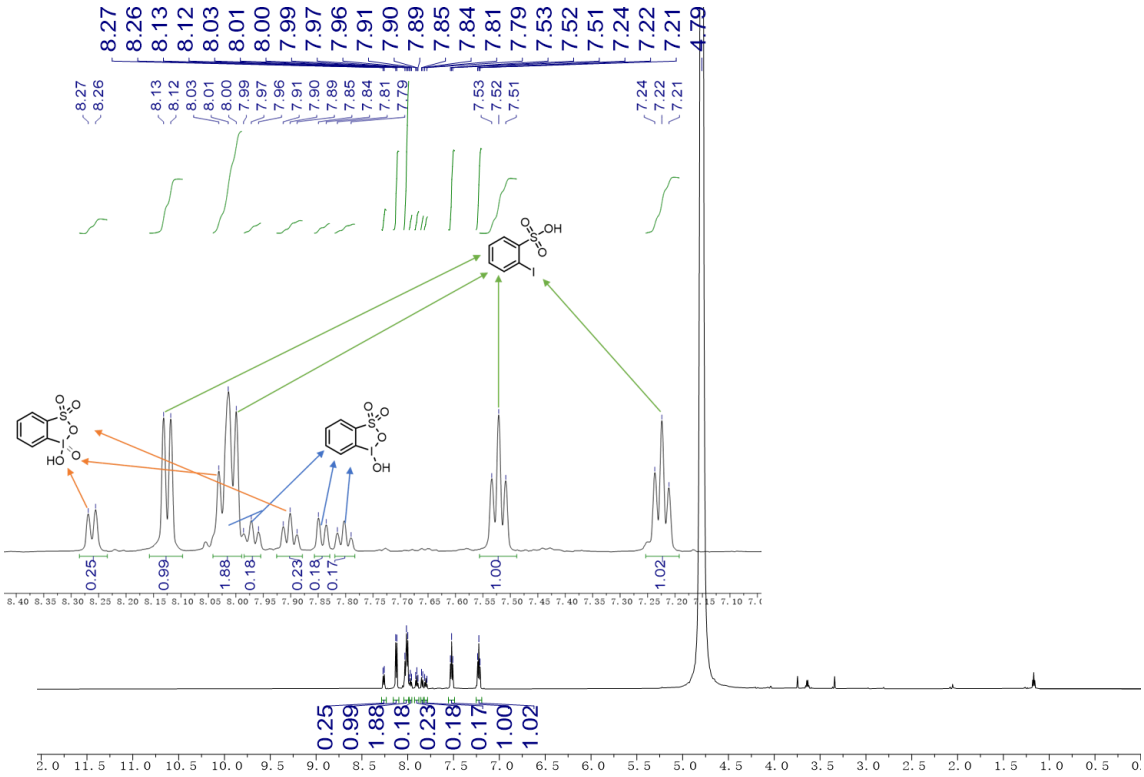


Figure S30. ^1H NMR spectrum of the hydrolysis products of λ^3-iodane **III** (600 MHz, D_2O, 298.15 K)

6.3 Reaction profile of λ^5-iodane VIII (IBS)

Experimental details: to a 5 mL pressure vial equipped with a magnetic stir bar was charged with **VIII** (IBS, 32 mg, 0.1 mmol, 1.0 eq.), 2-iodobenzenesulfonic acid (**IV**, 28 mg, 0.1 mmol, 1.0 eq.), 1 mL DCE/HFIP (2/1). The reaction mixture was sealed and heated to 100 °C for 7 hours. After cooling, crude ^{1}H NMR spectrum analysis shows that the product is completely converted to **IV**.

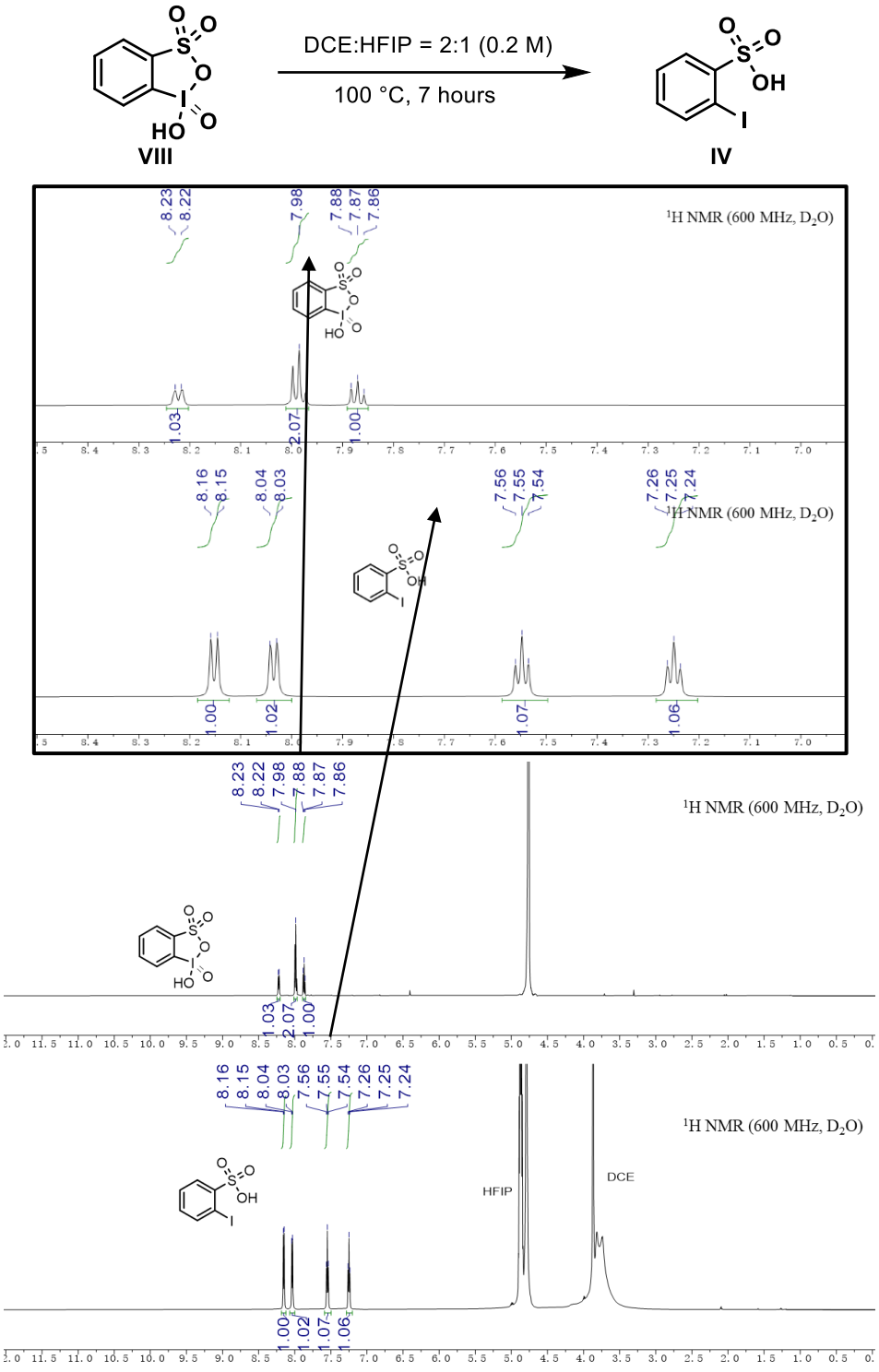


Figure S31. The transformation of λ^5-iodane VIII in the reaction system (600 MHz, D_2O, 298.15 K)

6.4 Cyclic voltammetry studies

Cyclic voltammograms were obtained on a CHI830C potentiostation. CV measurement was performed in a three-electrode cell (volume 20 mL); HFIP or DCE/HFIP (2/1) as solvent, *n*-Bu_4NPF_6 (0.1 M) as the supporting electrolyte; 1×10^{-2} M concentration of cat.; 1×10^{-1} M concentration of PhCl; NaCl has poor solubility in the two solvents; a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode (1.0*5.0 mm) and a saturated calomel reference electrode (SCE). The scan rate was 100 mV s^{-1}.

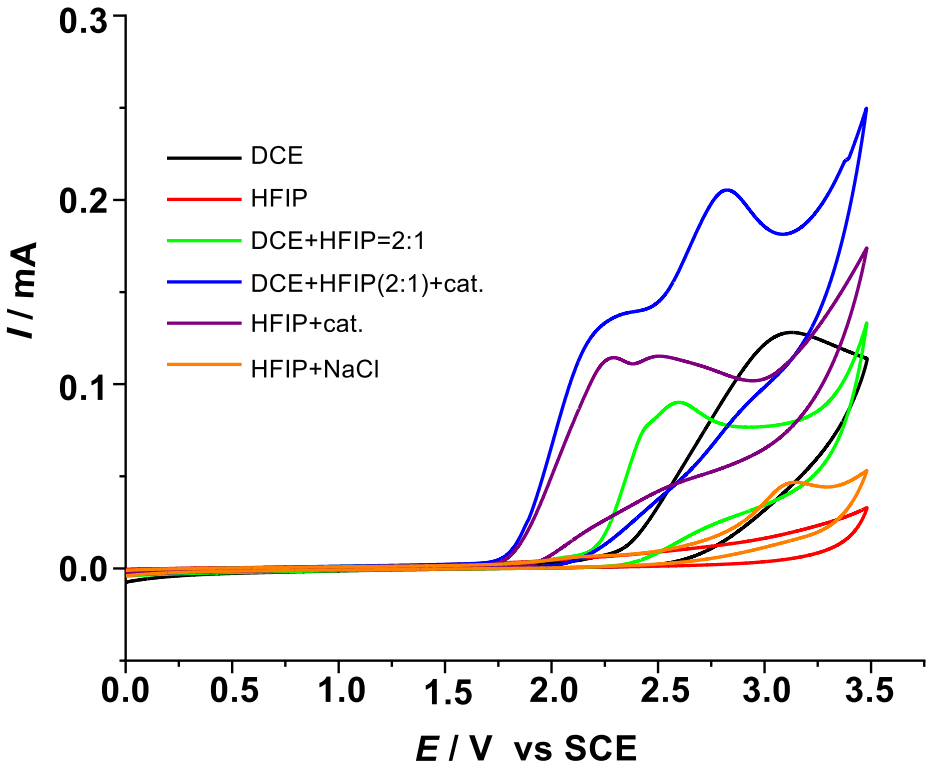


Figure S32. Cyclic voltammetry studies

6.5 ^{1}H NMR study of hydrogen bonding interaction between λ^3-iodane III and HFIP

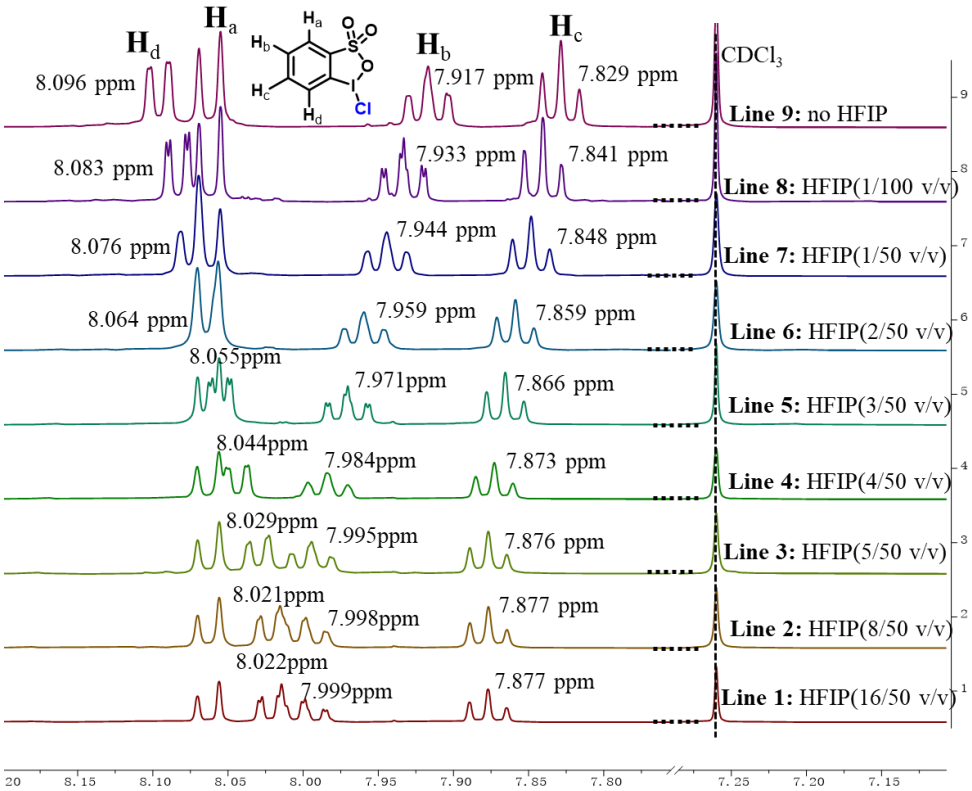


Figure S33. ^{1}H NMR of λ^3-iodane **III** in the presence of varying amounts of HFIP (600 MHz, $CDCl_3$, 298.15 K)

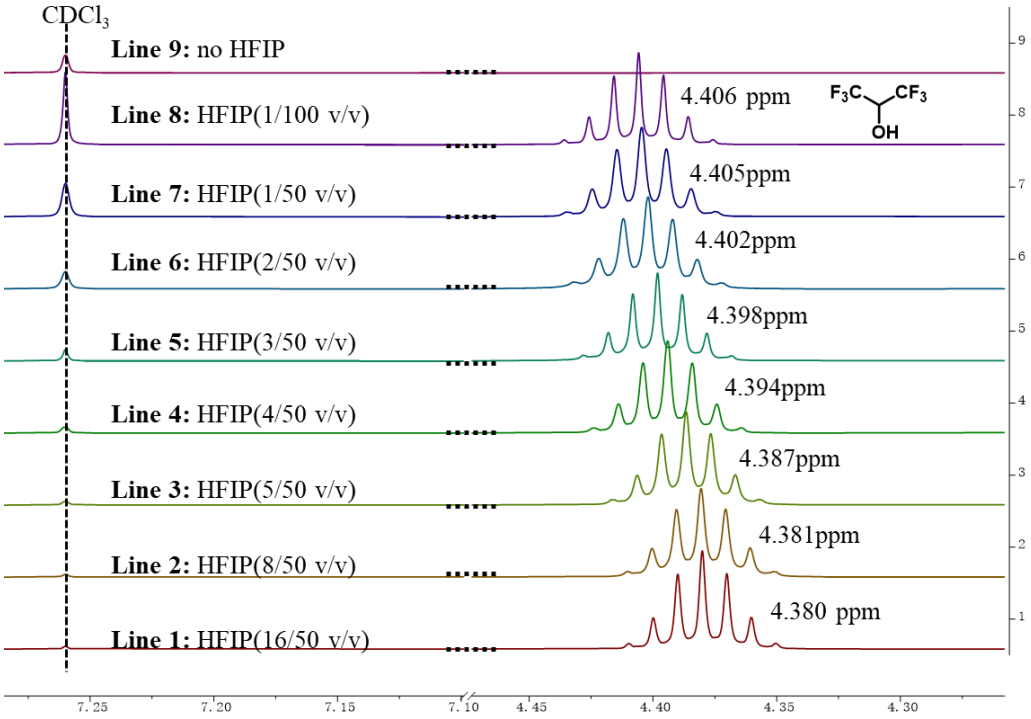
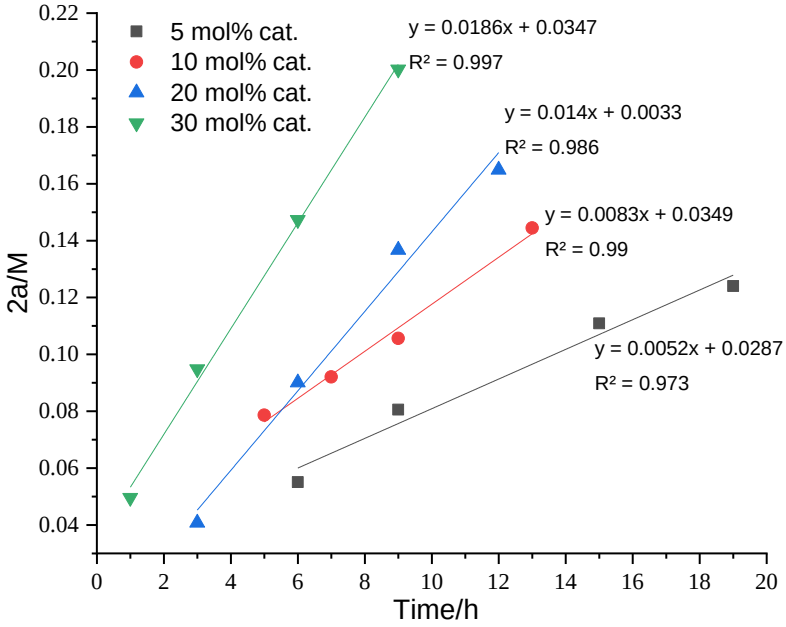


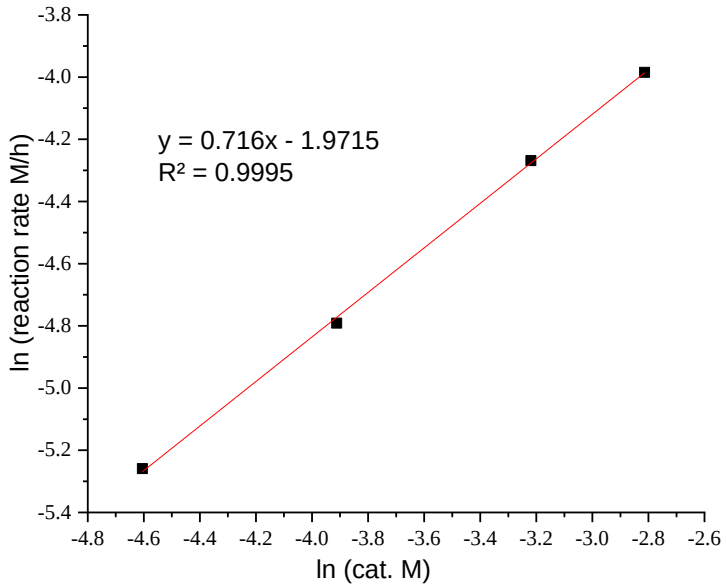
Figure S34. ^{1}H NMR of HFIP in the presence of λ^3-iodane **III** (600 MHz, $CDCl_3$, 298.15 K)

Line 9: λ^3-iodane III in $CDCl_3$ (no HFIP) for ^1H NMR.
Line 8: λ^3-iodane III in $CDCl_3$ (add HFIP 1/100 v/v) for ^1H NMR.
Line 7: λ^3-iodane III in $CDCl_3$ (add HFIP 1/50 v/v) for ^1H NMR.
Line 6: λ^3-iodane III in $CDCl_3$ (add HFIP 2/50 v/v) for ^1H NMR.
Line 5: λ^3-iodane III in $CDCl_3$ (add HFIP 3/50 v/v) for ^1H NMR.
Line 4: λ^3-iodane III in $CDCl_3$ (add HFIP 4/50 v/v) for ^1H NMR.
Line 3: λ^3-iodane III in $CDCl_3$ (add HFIP 5/50 v/v) for ^1H NMR.
Line 2: λ^3-iodane III in $CDCl_3$ (add HFIP 8/50 v/v) for ^1H NMR.
Line 1: λ^3-iodane III in $CDCl_3$ (add HFIP 16/50 v/v) for ^1H NMR.

6.6 Rate profile on the concentration of 2-iodobenzenesulphonic acid

Experimental details: chlorobenzene (0.2 mmol), 2-iodobenzenesulphonic acid (5 mol%, 10 mol%, 20 mol%, 30 mol%), NaCl (2.0 eq.) and oxone (2.0 eq.) were dissolved in 1 mL DCE/HFIP (2/1). The reaction mixture heated at 100 °C for the indicated periods of time, dodecane (45 μL, 0.2 mmol) was added as an internal standard, and the mixture was monitored by GC to determine the product formation rate. Kinetic profiles of different initial concentration of 2-iodobenzenesulphonic acid (from 0.01 M to 0.06 M) were shown as the following.





2-iodobenzenesulphonic acid/M	Reaction rate/(M/h)
0.01	0.0052
0.02	0.0083
0.04	0.014
0.06	0.0186

Figure S35. Dependence of the reaction rate on concentration of 2-iodobenzenesulphonic acid

6.7 Hammett plot

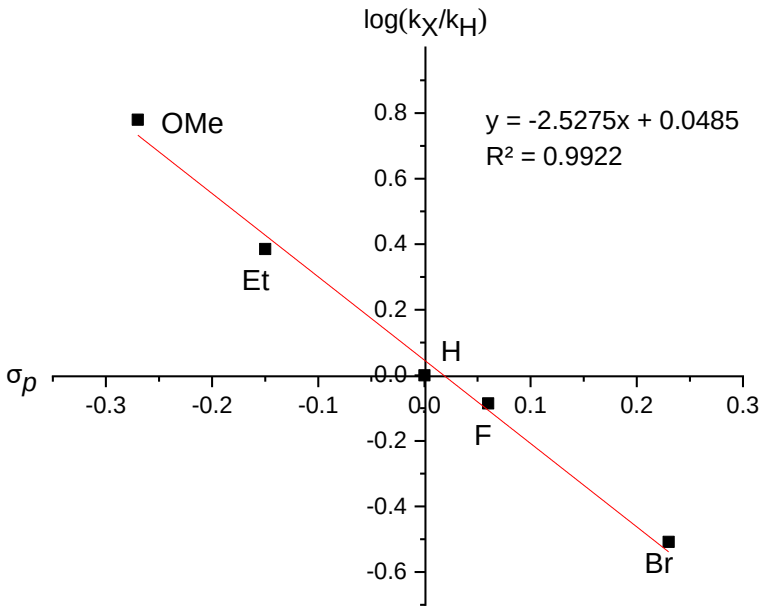
Experimental details: to a 5 mL oven-dried vial equipped with a magnetic stir bar was charged with mixture two different *p*-substituted substrates (**1u** and **1e**; **1g** and **1e**; **1i** and **1e**; **1k** and **1e**, 0.2 mmol each, 1.0 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), 2-iodobenzenesulphonic acid (**IV**, 5.6 mg, 0.02 mmol), oxone (246 mg, 0.4 mmol), 1 mL DCE/HFIP (2/1). The reaction mixture was heated at 100 °C for the indicated periods of time, then dodecane (45 μL, 0.2 mmol) was added as an internal standard, and immediately added EtOAc to dilute the reaction. The composition of mixture was analyzed by GC to determine the reduced molar amount of **1**. The k_X/k_H data was calculated based on the reduced molar amount of **1** and the results were summarized as follows equation:

$$\frac{k_X}{k_H} = \frac{\frac{c_{X0} - c_{Xt}}{t}}{\frac{c_{H0} - c_{Ht}}{t}} = \frac{\frac{n_{X0} - n_{Xt}}{V}}{\frac{n_{H0} - n_{Ht}}{V}} = \frac{n_{X0} - n_{Xt}}{n_{H0} - n_{Ht}}$$

Table S7. The datas of k_X/k_H

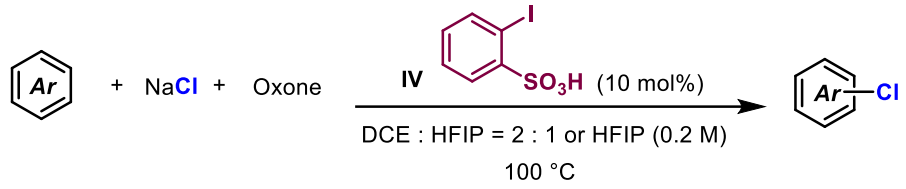
entry	*p*-substituted X	k_X/k_H	$\sigma_p{}^a$	log(k_X/k_H)
1	OMe	6.021	-0.27	0.779680
2	Et	2.427	-0.15	0.384998
3	H	1	0	0
4	F	0.821	0.06	-0.085530
5	Br	0.310	0.23	-0.507994

Figure S36. Hammett plots of log(k_X/k_H) vs σ_p



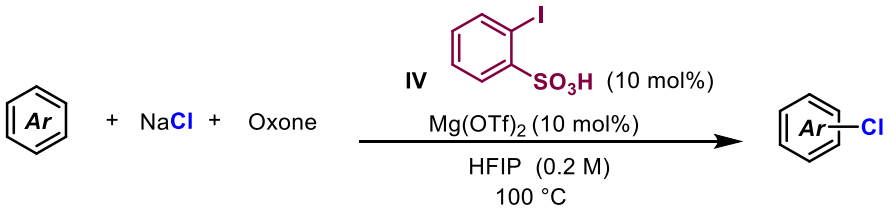
7 General procedure for the chlorination of arenes and characterization of chloroarene products

7.1 General procedure A for the chlorination of arenes



Experimental details: to a 5 mL pressure vial equipped with a magnetic stir bar was charged with aromatic compound (0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (**IV**, 5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), 1.0 mL DCE/HFIP (2/1) or HFIP. The reaction mixture was sealed and heated to the indicated temperature for the indicated period of time. After the mixture was cooled to room temperature, the solid was removed by filtration and washed with DCM, the combined organic layer was concentrated under reduced pressure, and the product was purified by flash column chromatography on silica gel to give the desired product.

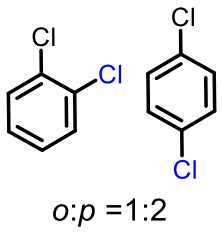
7.2 General procedure B for the chlorination of highly electron-deficient arenes



Experimental details: to a 5 mL pressure vial equipped with a magnetic stir bar was charged with aromatic compound (0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (**IV**, 5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL). The reaction mixture was sealed and heated to the indicated temperature for the indicated period of time. After the mixture was cooled to room temperature, the solid was removed by filtration and washed with DCM, the combined organic layer was concentrated under reduced pressure, and the product was purified by flash column chromatography on silica gel to give the desired product.

7.3 Spectroscopic data of reaction substrates

2a: 1,4-dichlorobenzene and 1,2-dichlorobenzene



2a was synthesized according to the general procedure **A** with chlorobenzene (22 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Due to the volatile nature of the corresponding chlorination product, 94% yield (*p* : *o* = 2 : 1) was determined by GC, using dodecane (46 μL) as internal standard.

2a-1: Para chlorination product (1,4-dichlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (s, 4H).

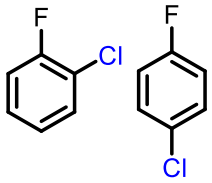
2a-2: Ortho chlorination product (1,2-dichlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 6.0, 3.6 Hz, 1H), 7.20 (dd, *J* = 6.0, 3.6 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 132.71, 132.66, 130.7, 130.0, 127.9.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi:10.1021/jacs.2c06440

2b: 1-chloro-4-fluorobenzene and 1-chloro-2-fluorobenzene



o:*p*=1:10

2b was synthesized according to the general procedure **A** with fluorobenzene (19 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 equiv), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 99% yield (*p* : *o* = 10 : 1) was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

2b-1: Para chlorination product (1-Chloro-4-fluorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 – 7.23 (m, 2H), 7.01 – 6.95 (m, 2H).

2b-2: Ortho chlorination product (2-Chlorofluorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.38 (td, *J* = 7.8, 1.8 Hz, 0.09H), 7.23 – 7.20 (m, 0.1H) 7.12 (td, *J* = 9.6, 1.8 Hz, 0.1H), 7.07 (t, *J* =7.8 Hz, 0.1H).

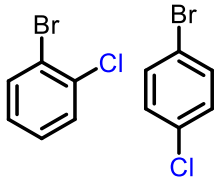
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.5 (d, $^1J_{C-F}$ = 245.6 Hz), 130.1 (d, $^3J_{C-F}$ = 8.1 Hz), 129.3 (d, $^4J_{C-F}$ = 3.2 Hz), 116.8 (d, $^2J_{C-F}$ = 23.1 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -115.5, -116.0.

Known compound, data are consistent with those reported in the literature:

Yamamoto K, Li J, Garber J A O, et al. Palladium-catalysed electrophilic aromatic C–H fluorination[J]. Nature, 2018, 554(7693): 511-514. doi: 10.1038/nature25749

2c: 1-bromo-4-chlorobenzene and 1-bromo-2-chlorobenzene



o:*p*=1:2

2c was synthesized according to the general procedure **A** with bromobenzene (31 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give an inseparable mixture of 1-bromo-4-chlorobenzene and 1-bromo-2-chlorobenzene (2:1, 29 mg, 78%) as a colorless oil.

2c-1: Para chlorination product (1-bromo-4-chlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.42 (d, *J* = 9.0 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H).

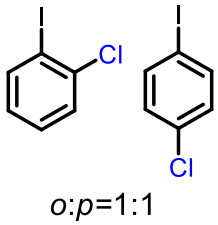
2c-2: Ortho chlorination product (1-bromo-2-chlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.62 (dd, *J* = 8.0, 1.6 Hz, 0.5H), 7.45 (dd, *J* = 8.0, 1.6 Hz, 0.5 H), 7.26 – 7.23 (m, 0.5H), 7.12 (td, *J* = 7.7, 1.6 Hz, 0.5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.9, 133.4, 133.3, 132.9, 130.6, 130.3, 128.6, 128.0, 122.7, 120.4.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi:10.1021/jacs.2c06440

2d: 1-chloro-4-iodobenzene and 1-chloro-2-iodobenzene



2d was synthesized according to the general procedure **A** with iodobenzene (31 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give an inseparable mixture of 1-chloro-4-iodobenzene and 1-chloro-2-iodobenzene (1:1, 29 mg, 72%) as a colorless oil.

2d-1: Para chlorination product (1-chloro-4-iodobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ7.61 (d, *J* = 9.0 Hz, 2H), 7.08 (d, *J* = 9.0 Hz, 2H).

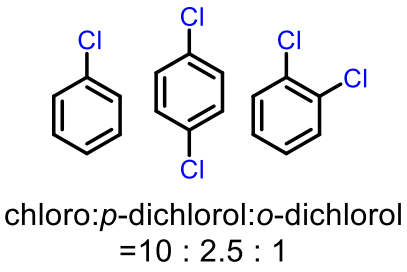
2d-2: Ortho chlorination product (1-chloro-2-iodobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.45 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.28 (td, *J* = 7.8, 1.2 Hz, 1H), 6.95 (td, *J* = 7.7, 1.5 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 140.4, 138.9, 138.6, 134.4, 130.7, 129.5, 128.0, 98.3, 91.3.

Known compound, data are consistent with those reported in the literature:

Fu Z, Hao G, Fu Y, et al. Transition metal-free electrocatalytic halodeborylation of arylboronic acids with metal halides MX (X= I, Br) to synthesize aryl halides[J]. Organic Chemistry Frontiers, 2020, 7(3): 590-595. doi:10.1002/adsc.201100145

2e: chlorobenzene, 1,4-dichlorobenzene and 1,2-dichlorobenzene



2e was synthesized according to the general procedure **A** with benzene (21 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 95% yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

2e-1: Monosubstituted chlorination product (chlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.0 Hz, 1H).

2e-2: Double substituted chlorination (1,4-dichlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.27 (s, 1.1H).

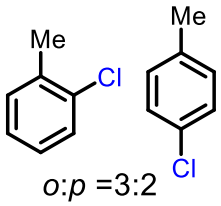
2e-3: Double substituted chlorination (1,2-dichlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (dd, *J* = 6.0, 3.6 Hz 0.2H), 7.20 (dd, *J* = 6.0, 3.6 Hz, 0.2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.4, 132.7, 130.7, 130.0, 129.9, 128.8, 127.9, 126.6.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi:10.1021/jacs.2c06440

2f: 4-chlorotoluene and 2-chlorotoluene



2f was synthesized according to the general procedure **A** with toluene (18 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 91% yield (*p* : *o* = 2 : 3) was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

2f-1: Para chlorination product (4-chlorotoluene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20 (d, *J* = 8.2 Hz, 1.34H), 7.12 (d, *J* = 8.2 Hz, 1.36H), 2.30 (s, 2H).

2f-2: Ortho chlorination product (2-chlorotoluene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.7 Hz, 1H), 7.22 – 7.21 (m, 1H), 7.15 – 7.11 (m, 2H), 2.36 (s, 3H).

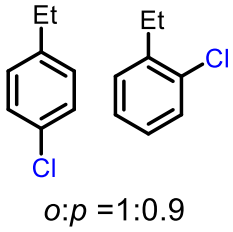
^{13}C NMR (151 MHz, $CDCl_3$) δ 136.2, 134.4, 131.11, 131.06, 130.50, 129.1, 128.4, 127.2, 126.7, 20.8, 20.0.

Known compound, data are consistent with those reported in the literature:

Xiao J, Ma Y, Wu X, et al. Phosphonic acid mediated practical dehalogenation and benzylation with benzyl halides[J]. RSC advances, 2019, 9(39): 22343-22347. doi: 10.1039/c9ra04770k

He W, Zhang R, Cai M. A highly efficient heterogeneous copper-catalyzed chlorodeboronation of arylboronic acids leading to chlorinated arenes[J]. RSC Advances, 2017, 7(2): 764-770. doi: 10.1039/C6RA25666J

2g:1-chloro-4-ethylbenzene and 1-chloro-2-ethylbenzene



2g was synthesized according to the general procedure **A** with ethylbenzene (21 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 95% yield (*p* : *o* = 0.9 : 1) was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

2g-1: Para chlorination product (1-chloro-4-ethylbenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 – 7.23 (m, 1.46H), 7.15 – 7.14 (m, 1.43H), 2.64 (q, *J* = 7.6 Hz, 1.75H), 1.24 (t, *J* = 7.6 Hz, 2.63H).

2g-2: Ortho chlorination product (1-chloro-2-ethylbenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.35 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.15 – 7.14 (m, 1H), 2.78 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 7.8 Hz, 3H).

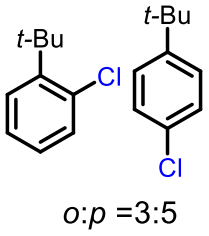
^{13}C NMR (151 MHz, $CDCl_3$) δ 129.7, 129.5, 129.4, 128.5, 127.2, 127.0, 28.4, 26.8, 15.6, 14.1. four carbon is missing due to low intensity because of high dilution

Known compound, data are consistent with those reported in the literature:

Cummings S P, Le T N, Fernandez G E, et al. Tetrahydroxydiboron-mediated palladium-catalyzed transfer hydrogenation and deuteriation of alkenes and alkynes using water as the stoichiometric H or D atom donor[J]. Journal of the American Chemical Society, 2016, 138(19): 6107-6110. doi: 10.1021/jacs.6b02132

Zobernig D P, Stöger B, Veiros L F, et al. Hydrogenation of Alkenes Catalyzed by Mn (I) Alkyl Complexes Bearing NHC Phosphine Ligands[J]. ChemCatChem, 2024, 16(22): e202401172. doi: 10.1002/cctc.202401172

2h: 1-*tert*-Butyl-4-chlorobenzene and 1-(*tert*-butyl)-2-chlorobenzene



2h was synthesized according to the general procedure **A** with tert-butylbenzene (27 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give an inseparable mixture of 1-*tert*-Butyl-4-chlorobenzene and 1-(*tert*-butyl)-2-chlorobenzene (5:3, 27 mg, 80%) as a colorless oil.

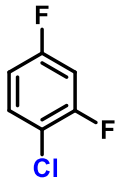
2h-1: Para chlorination product (1-*tert*-Butyl-4-chlorobenzene) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.7 Hz, 2H), 7.27 (d, *J* = 7.4 Hz, 2H), 1.32 (s, 9H).

2h-2: Ortho chlorination product (1-(*tert*-butyl)-2-chlorobenzene) **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.46 – 7.39 (m, 0.65H), 7.32 – 7.37 (m, 0.6H), 7.23 – 7.19 (m, 0.67H), 7.16 – 7.08 (m, 0.66H), 1.50 (s, 7.74H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 149.7, 146.6, 133.1, 132.1, 131.3, 128.2, 127.8, 127.3, 126.9, 126.8, 36.2, 34.6, 31.4, 29.7.

Known compound, data are consistent with those reported in the literature:

Molander G A, Cavalcanti L N. Metal-free chlorodeboronation of organotrifluoroborates[J]. The Journal of organic chemistry, 2011, 76(17): 7195-7203. doi: 10.1021/jo201313a

2i: 1-chloro-2,4-difluorobenzene



2i was synthesized according to the general procedure **A** with 1,3-difluorobenzene (23 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 99% yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 (td, *J* = 8.6, 5.7 Hz, 1H), 6.91 (td, *J* = 8.8, 2.8 Hz, 1H), 6.85 – 6.82 (m, 1H).

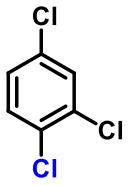
^{13}C NMR (151 MHz, $CDCl_3$) δ 161.4 (dd, $^{1,3}J_{C-F}$ = 248.8, 10.5 Hz), 158.2 (dd, $^{1,3}J_{C-F}$ = 251.1, 12.4 Hz), 131.1 (d, $^{3}J_{C-F}$ = 9.4 Hz), 116.6 (dd, $^{2,4}J_{C-F}$ = 18.0, 4.3 Hz), 112.3 (dd, $^{2,4}J_{C-F}$ = 22.7, 4.0 Hz), 105.3 (dd, $^{2,2}J_{C-F}$ = 26.4, 24.8 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -82.56 (HFIP), -110.6, -111.3.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi: 10.1021/jacs.2c06440

2j: 1,2,4-trichlorobenzene



2j was synthesized according to the general procedure **A** with 1,3-dichlorobenzene (29 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 32 mg (87%) of 1,2,4-trichlorobenzene as white solid.

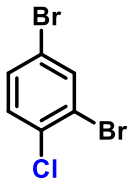
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (s, 1H), 7.37 (d, *J* = 8.8 Hz, 1H), 7.19 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.4, 133.0, 131.1, 130.3, 128.0.

Known compound, data are consistent with those reported in the literature:

Sharp-Bucknall L, Sceney M, White K F, et al. Synthesis, structural characterization, reactivity and catalytic activity of mixed halo/triflate ArI (OTf)(X) species[J]. Dalton Transactions, 2023, 52(11): 3358-3370. doi: 10.1039/d3dt00275f

2k: 2,4-dibromo-1-chlorobenzene



2k was synthesized according to the general procedure **A** with 1,3-dibromobenzene (47 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 46 mg (86%) of 2,4-dibromo-1-chlorobenzene as white solid.

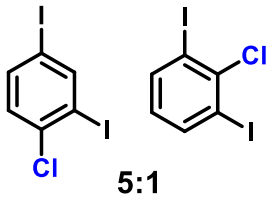
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.37 (d, *J* = 9.0 Hz, 1H), 7.31 (d, *J* = 9.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 136.2, 133.8, 131.7, 131.4, 123.5, 120.7.

Known compound, data are consistent with those reported in the literature:

Sharp-Bucknall L, Sceney M, White K F, et al. Synthesis, structural characterization, reactivity and catalytic activity of mixed halo/triflate ArI (OTf)(X) species[J]. Dalton Transactions, 2023, 52(11): 3358-3370. doi: 10.1039/d3dt00275f

2l: 1-chloro-2,4-diiodobenzene and 2-chloro-1,3-diiodobenzene 415



2l was synthesized according to the general procedure **A** with 1,3-diiodobenzene (66 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give an inseparable mixture of 1-chloro-2,4-diiodobenzene and 2-chloro-1,3-diiodobenzene (5:1, 68 mg, 94%) as white solid.

2l-1: (1-chloro-2,4-diiodobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.17 (s, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H).

2l-2: (2-chloro-1,3-diiodobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 0.40H), 6.58 (t, *J* = 7.8 Hz, 0.2H).

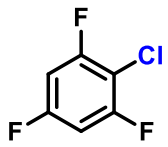
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 141.9, 140.4, 138.7, 138.5, 130.7, 129.3, 99.7, 97.1, 91.7.

Known compound, data are consistent with those reported in the literature:

Naka H, Uchiyama M, Matsumoto Y, et al. An aluminum ate base: Its design, structure, function, and reaction mechanism[J]. Journal of the American Chemical Society, 2007, 129(7): 1921-1930. doi: 10.1021/ja064601n

Feng Y, Yukioka T, Matsuyama M, et al. Deprotonative generation and trapping of haloaryllithium in a batch reactor[J]. Organic Letters, 2023, 25(17): 3013-3017. doi: 10.1021/acs.orglett.3c00800

2m: 2-chloro-1,3,5-trifluorobenzene



2m was synthesized according to the general procedure **A** with 1,3-difluorobenzene (27mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (36 mg, 0.6 mmol, 3.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), DCE/HFIP (2/1, 1.0 mL)under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 80% yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

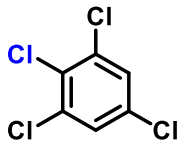
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.80 – 6.76 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 161.9 (dt, $^{1,3}J_{C-F}$ = 247.6, 14.1 Hz), 159.2 (ddd, $^{1,3,4}J_{C-F}$ =250.7, 14.8, 5.5 Hz), 106.2 (td, $^{2,4}J_{C-F}$ = 21.2, 5.4 Hz), 101.2 (t, $^{2}J_{C-F}$ = 26.5 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -82.5 (HFIP), -109.1, -109.8.

HRMS *m/z* (ESI): calcd. for $C_6H_2ClF_3$ $[M+H]^+$:166.9870, found: 166.9870.

2n: 1,2,3,5-tetrachlorobenzene



2n was synthesized according to the general procedure **A** with 1,2,3-trichlorobenzene (36 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), HFIP (1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 37 mg (89%) of 1,2,3,5-tetrachlorobenzene as white solid.

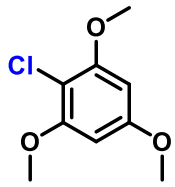
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.39 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.9, 132.9, 130.5, 128.8.

Known compound, data are consistent with those reported in the literature:

Sharp-Bucknall L, Sceney M, White K F, et al. Synthesis, structural characterization, reactivity and catalytic activity of mixed halo/triflate ArI (OTf)(X) species[J]. Dalton Transactions, 2023, 52(11): 3358-3370. doi: 10.1039/d3dt00275f

2o: 2-chloro-1,3,5-trimethoxybenzene



2o was synthesized according to the general procedure **A** with 1,3,5-trimethoxybenzene (34 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 25 mg (62%) of 2-chloro-1,3,5-trimethoxybenzene as a white solid.

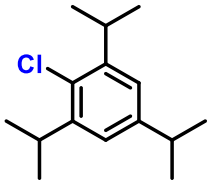
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.18 (s, 2H), 3.88 (s, 6H), 3.81 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.5, 156.6, 102.7, 91.6, 56.4, 55.7.

Known compound, data are consistent with those reported in the literature:

van der Werf A, Selander N. Para-selective halogenation of nitrosoarenes with copper (ii) halides[J]. Organic Letters, 2015, 17(24): 6210-6213. doi: 10.1021/acs.orglett.5b03198

2p: 2-chloro-1,3,5-triisopropylbenzene



2p was synthesized according to the general procedure **A** with 1,3,5-triisopropylbenzene (41 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 38 mg (81%) of 2-chloro-1,3,5-triisopropylbenzene as a white solid.

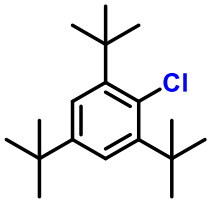
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.00 (s, 2H), 3.47 (heptet, *J* = 6.9 Hz, 2H), 2.87 (heptet, *J* = 6.9 Hz, 1H), 1.24 - 1.26 (m, 18H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.2, 145.7, 122.1, 34.2, 30.8, 24.2, 23.0.

Known compound, data are consistent with those reported in the literature:

Granados A, Jia Z, del Olmo M, et al. In situ generation of hypervalent iodine reagents for the electrophilic chlorination of arenes[J]. European Journal of Organic Chemistry, 2019, 2019(17): 2812-2818. doi: 10.1002/ejoc.201900237

2q: 1,3,5-tri-tert-butyl-2-chlorobenzene



2q was synthesized according to the general procedure **A** with 1,3,5-tri-tert-butylbenzene (50 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 47 mg (85%) of 1,3,5-tri-tert-butyl-2-chlorobenzene as a colorless oil.

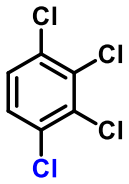
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 1.53 (s, 18H), 1.32 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.9, 147.2, 131.5, 123.3, 37.4, 35.1, 31.6, 30.7.

Known compound, data are consistent with those reported in the literature:

Hoshi T, Honma T, Mori A, et al. An active, general, and long-lived palladium catalyst for cross-couplings of deactivated (hetero) aryl chlorides and bromides with arylboronic acids[J]. The Journal of Organic Chemistry, 2013, 78(22): 11513-11524. doi: 10.1021/jo402089r.

2r: 1,2,3,4-tetrachlorobenzene



2r was synthesized according to the general procedure **A** with 1,2,3-trichlorobenzene (36 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), HFIP (1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 38 mg (89%) of 1,2,3,4-tetrachlorobenzene as a white solid.

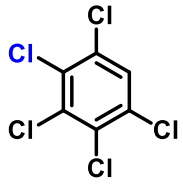
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.3, 132.7, 128.6.

Known compound, data are consistent with those reported in the literature:

Deng M, Liu K, Ma Z, et al. Photo-Induced $FeCl_3$-catalysed direct denitrative chlorination of (hetero) nitroarenes at room temperature[J]. Green Chemistry, 2024, 26(23): 11556-11562. doi: 10.1039/D4GC04210G

2s: 1,2,3,4,5-pentachlorobenzene



2s was synthesized according to the general procedure **B** with 1,2,3,5-tetrachlorobenzene (43 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 44 mg (88%) of 1,2,3,4,5-pentachlorobenzene as a white solid.

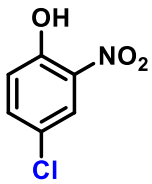
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.54 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.5, 132.5, 131.8, 129.1.

Known compound, data are consistent with those reported in the literature:

Takeuchi Y, Furuyama H, Fukushi S, et al. Carbon-13 nuclear magnetic resonance spectra of polychloro- and polybromo-benzenes[J]. Journal of the Chemical Society, Perkin Transactions 2, 1985 (2): 175-177. doi: 10.1039/P29850000175

2t: 4-chloro-2-nitrophenol



2t was synthesized according to the general procedure **A** with 2-nitrophenol (28 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 21 mg (60%) of 4-chloro-2-nitrophenol as yellow solid.

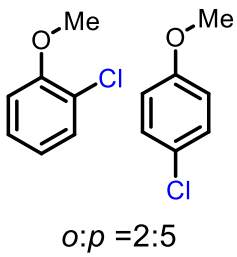
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.48 (s, 1H), 8.11 (d, *J* = 2.6 Hz, 1H), 7.54 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.14 (d, *J* = 9.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.7, 137.6, 125.2, 124.3, 121.4.

Known compound, data are consistent with those reported in the literature:

Clewley R G, Cross G G, Fischer A, et al. Formation of 4-Halo-4-nitrocyclohexa-2, 5-dienones on nitration of p-halophenols and p-halophenyl acetates[J]. Tetrahedron, 1989, 45(5): 1299-1310. doi: 10.1016/0040-4020(89)80128-0

2u: 4-chloroanisole and 2-chloroanisole



2u was synthesized according to the general procedure **A** with anisole (22 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give an inseparable mixture of 4-chloroanisole and 2-chloroanisole (5:2, 25 mg, 80%) as

colorless oil.

2u-1: Para chlorination product (4-chloroanisole) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.24 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 8.0 Hz, 2H), 3.79 (s, 3H).

2u-2: Ortho chlorination product (2-chloroanisole) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 7.8, 1.7 Hz, 0.47H), 7.25 – 7.19 (m, 0.40H), 6.93 (dd, *J* = 8.2, 1.4 Hz, 0.45H), 6.90 (td, *J* = 7.7, 1.4 Hz, 0.48H), 3.90 (s, 1.42H).

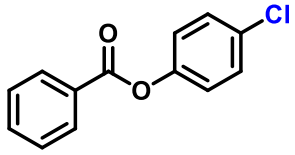
^{13}C NMR (151 MHz, $CDCl_3$) δ 158.3, 155.1, 130.40, 129.4, 127.90, 125.7, 122.6, 121.4, 115.30, 112.2, 56.2, 55.6.

Known compound, data are consistent with those reported in the literature:

Molander G A, Cavalcanti L N. Metal-free chlorodeboronation of organotrifluoroborates[J]. The Journal of organic chemistry, 2011, 76(17): 7195-7203. doi: 10.1021/jo201313a

Barker G, Webster S, Johnson D G, et al. Gold-catalyzed proto-and deuterodeboronation[J]. The Journal of Organic Chemistry, 2015, 80(20): 9807-9816. doi: 10.1021/acs.joc.5b01041

2v: 4-chlorophenyl benzoate



2v was synthesized according to the general procedure **A** with phenyl benzoate (40 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 39 mg (86%) of 4-chlorophenyl benzoate as white solid.

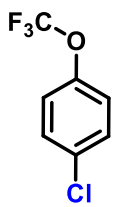
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.8 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.57 – 7.53 (m, 2H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.1, 149.6, 133.9, 131.4, 130.3, 129.7, 129.3, 128.8, 123.2.

Known compound, data are consistent with those reported in the literature:

Arisawa M, Tazawa T, Tanii S, et al. Rhodium-Catalyzed Synthesis of Unsymmetric Di (heteroaryl) Sulfides Using Heteroaryl Ethers and S-Heteroaryl Thioesters via Heteroarylthio Exchange[J]. The Journal of Organic Chemistry, 2017, 82(1): 804-810. doi: 10.1021/acs.joc.6b02585

2w: 1-chloro-4-(trifluoromethoxy)benzene



2w was synthesized according to the general procedure **A** with (trifluoromethoxy)benzene (33 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours. Due to the volatile nature of the corresponding chlorination product, 99% yield was determined by ^{1}H NMR using 1,1,2,2-tetrachloroethane (22 μL) as internal standard.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.5 Hz, 2H).

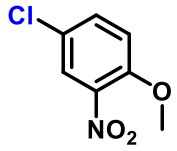
^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7 (q, $^4J_{C-F}$ = 3.0 Hz) 129.9, 124.3, 122.5, 120.3 (q, $^1J_{C-F}$ = 256.7 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -58.2.

Known compound, data are consistent with those reported in the literature:

Chatalova-Sazepin C, Binayeva M, Epifanov M, et al. Xenon difluoride mediated fluorodecarboxylations for the syntheses of di-and trifluoromethoxyarenes[J]. Organic Letters, 2016, 18(18): 4570-4573. doi: 10.1021/acs.orglett.6b02208

2x: 4-chloro-1-methoxy-2-nitrobenzene



2x was synthesized according to the general procedure **A** with 1-methoxy-2-nitrobenzene (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 26 mg (68%) of 4-chloro-1-methoxy-2-nitrobenzene as white solid.

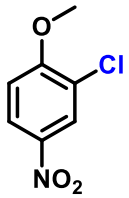
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.84 (d, *J* = 2.6 Hz, 1H), 7.50 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.04 (d, *J* = 9.0 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.8, 139.9, 134.1, 125.7, 125.4, 114.9, 57.0.

Known compound, data are consistent with those reported in the literature:

Matsuoka J, Yano Y, Hirose Y, et al. Elemental sulfur-mediated aromatic halogenation[J]. The Journal of Organic Chemistry, 2023, 89(1): 770-777. doi: 10.1021/acs.joc.3c02259

2y: 2-chloro-1-methoxy-4-nitrobenzene



2y was synthesized according to the general procedure **A** with 1-methoxy-4-nitrobenzene (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 27 mg (72%) of 2-chloro-1-methoxy-4-nitrobenzene as yellow solid.

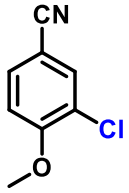
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1H), 8.16 (d, *J* = 9.2 Hz, 1H), 7.00 (d, *J* = 9.0 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.2, 141.4, 126.2, 124.2, 123.4, 111.1, 57.0.

Known compound, data are consistent with those reported in the literature:

Zhang L, Hu X. Room temperature C (sp^2)–H oxidative chlorination via photoredox catalysis[J]. Chemical science, 2017, 8(10): 7009-7013. doi: 10.1039/C7SC03010J

2z: 3-chloro-4-methoxybenzonitrile



2z was synthesized according to the general procedure **A** with 4-methoxybenzonitrile (27 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 25 mg (75%) of 3-chloro-4-methoxybenzonitrile as white solid.

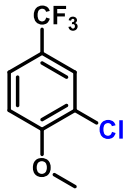
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.67 (s, 1H), 7.58 (d, *J* = 8.6 Hz, 1H), 7.00 (d, *J* = 8.6 Hz, 1H), 3.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 158.7, 133.7, 132.6, 123.7, 118.0, 112.3, 104.9, 56.6.

Known compound, data are consistent with those reported in the literature:

McManus J B, Nicewicz D A. Direct C–H cyanation of arenes via organic photoredox catalysis[J]. Journal of the American Chemical Society, 2017, 139(8): 2880-2883. doi: 10.1021/jacs.6b12708

2aa: 2-chloro-1-methoxy-4-(trifluoromethyl)benzene



2aa was synthesized according to the general procedure **A** with 1-methoxy-4-(trifluoromethyl)benzene (35 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (100% petroleum ether) on silica gel to give 33 mg (78%) of 2-chloro-1,3,5-trimethoxybenzene as white solid.

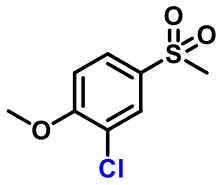
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.63 (d, *J* = 2.2 Hz, 1H), 7.50 (dd, *J* = 8.7, 1.7 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 127.6 (q, $^4J_{C-F}$ = 3.03 Hz), 125.3 (q, $^4J_{C-F}$ = 3.03 Hz), 123.8 (q, $^1J_{C-F}$ = 271.7 Hz), 123.7 (q, $^2J_{C-F}$ = 33.3 Hz), 123.1, 111.8, 56.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -61.7.

HRMS *m/z* (ESI): calcd. for $C_8H_7ClF_3O$ $[M+H]^+$: 211.0132, found: 211.0132.

2bb: 2-chloro-1-methoxy-4-(methylsulfonyl)benzene



2bb was synthesized according to the general procedure **A** with 1-methoxy-4-(methylsulfonyl)benzene (37 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 10:1) on silica gel to give 39 mg (88%) of 2-chloro-1-methoxy-4-(methylsulfonyl)benzene as white solid.

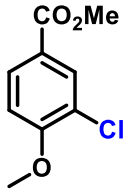
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 2.3 Hz, 1H), 7.81 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H), 3.98 (s, 3H), 3.04 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 159.3, 133.1, 129.6, 128.0, 123.8, 112.0, 56.7, 44.9.

Known compound, data are consistent with those reported in the literature:

Zhang L, Du W, Wu J, et al. Au (I)/Au (III)-Catalyzed Sulfonylation of Aryl Iodides for the Synthesis of Various Functionalized Aryl Sulfones[J]. Organic Letters, 2024, 26(43): 9413-9418. doi: 10.1021/acs.orglett.4c03724

2cc: methyl 3-chloro-4-methoxybenzoate



2cc was synthesized according to the general procedure **A** with methyl 4-methoxybenzoate (33 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 31 mg (78%) of methyl 3-chloro-4-methoxybenzoate as white solid.

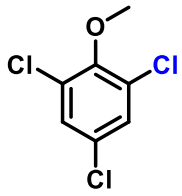
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (s, 1H), 7.92 (d, *J* = 8.4 Hz, 1H), 6.93 (d, *J* = 8.6 Hz, 1H), 3.94 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.9, 158.7, 131.7, 130.0, 123.4, 122.6, 111.3, 56.4, 52.2.

Known compound, data are consistent with those reported in the literature:

Zhang L, Hu X. Room temperature C (sp^2)–H oxidative chlorination via photoredox catalysis[J]. Chemical science, 2017, 8(10): 7009-7013. doi: 10.1039/C7SC03010J

2dd: 1,3,5-trichloro-2-methoxybenzene



2dd was synthesized according to the general procedure **A** with 2,4-dichloro-1-methoxybenzene (35 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 23 mg (54%) of 1,3,5-trichloro-2-methoxybenzene as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.30 (s, 2H), 3.88 (s, 3H).

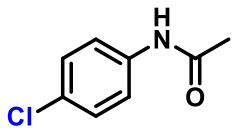
^{13}C NMR (151 MHz, $CDCl_3$) δ 151.6, 130.2, 129.7, 128.9, 61.0.

Known compound, data are consistent with those reported in the literature:

Maraš N, Polanc S, Kočevar M. Microwave-assisted methylation of phenols with tetramethylammonium chloride in the presence of K_2CO_3 or Cs_2CO_3[J]. Tetrahedron, 2008, 64(51): 11618-11624. doi: 10.1016/j.tet.2008.10.024

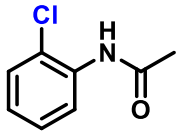
2ee: *N*-(4-chlorophenyl)acetamide and *N*-(2-chlorophenyl)acetamide

2ee was synthesized according to the general procedure **A** with *N*-phenylacetamide (27 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 11 mg (34%) *N*-(4-chlorophenyl)acetamide and 15 mg (45%) of *N*-(2-chlorophenyl)acetamide as white solid.



2ee-1: (*N*-(4-chlorophenyl)acetamide) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.8 Hz, 2H), 7.37 (s, 1H), 7.27 (d, *J* = 8.6 Hz, 2H), 2.17 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.5, 136.6, 129.4, 129.1, 121.2, 24.7.



2ee-2: (*N*-(2-chlorophenyl)acetamide) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.36 (d, *J* = 8.4 Hz, 1H), 7.61 (s, 1H), 7.36 (d, *J* = 8.1 Hz, 1H), 7.30 – 7.26 (m, 1H), 7.04 (t, *J* = 7.8 Hz, 1H), 2.24 (s, 3H).

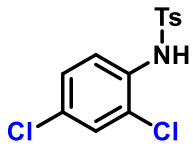
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.4, 134.7, 129.1, 127.9, 124.7, 122.6, 121.7, 25.0.

Known compound, data are consistent with those reported in the literature:

Mahajan P S, Humne V T, Tanpure S D, et al. Radical Beckmann rearrangement and its application in the formal total synthesis of antimalarial natural product isocryptolepine via C–H activation[J]. Organic letters, 2016, 18(14): 3450-3453. doi: 10.1021/acs.orglett.6b01634

Xiong X, Yeung Y Y. Highly ortho-Selective Chlorination of Anilines Using a Secondary Ammonium Salt Organocatalyst[J]. Angewandte Chemie International Edition, 2016, 55(52): 16101-16105. doi: 10.1002/anie.201607388

2ff: *N*-(2,4-dichlorophenyl)-4-methylbenzenesulfonamide



2ff was synthesized according to the general procedure **A** with 4-methyl-*N*-phenylbenzenesulfonamide (50 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/Et_3N = 100:20:1) on silica gel to give 39 mg (63%) of *N*-(2,4-dichlorophenyl)-4-methylbenzenesulfonamide as yellow solid.

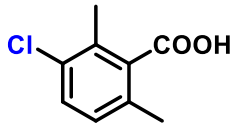
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.3 Hz, 2H), 7.61 (d, *J* = 8.8 Hz, 1H), 7.26 (s, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.91 (s, 1H), 2.39 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.7, 135.7, 132.4, 130.9, 129.9, 129.3, 128.3, 127.4, 126.0, 123.5.

Known compound, data are consistent with those reported in the literature:

Patil D B, Gámez-Montaño R, Ordoñez M, et al. Iodine (III)-Mediated Electrophilic Chlorination and Catalytic Nitration of N-Tosyl Anilines[J]. European Journal of Organic Chemistry, 2022, 2022(47): e202201295. doi: 10.1002/ejoc.202201295

2gg: 3-chloro-2,6-dimethylbenzoic acid



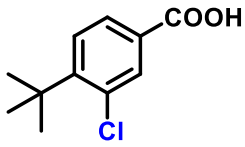
2gg was synthesized according to the general procedure **A** with 2,6-dimethylbenzoic acid (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 23 mg (62%) of 3-chloro-2,6-dimethylbenzoic acid as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 8.1 Hz, 1H), 2.42 (s, 3H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 133.5, 132.8, 132.6, 130.5, 129.0, 19.7, 17.6.

HRMS *m/z* (ESI): calcd. for $C_9H_8ClO_2$ $[M-H]^-$:183.0218, found: 183.0218.

2hh: 4-(tert-butyl)-3-chlorobenzoic acid



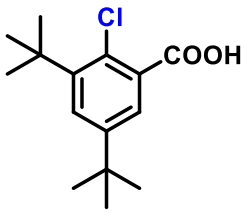
2hh was synthesized according to the general procedure **A** with 4-(tert-butyl)benzoic acid (36 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 29 mg (68%) of 4-(tert-butyl)-3-chlorobenzoic acid as white solid.

^{1}H NMR (600 MHz, CDCl3) δ 8.07 (s, 1H), 7.91 (d, *J* = 8.3 Hz, 1H), 7.54 (d, *J* = 8.2 Hz, 1H), 1.51 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 134.2, 133.7, 128.5, 128.1, 36.8, 29.5.

HRMS *m/z* (ESI): calcd. for $C_{11}H_{12}ClO_2$ $[M-H]^-$: 211.0531, found: 211.0530.

2ii: 3,5-di-*tert*-butyl-2-chlorobenzoic acid



2ii was synthesized according to the general procedure **A** with 3,5-di-*tert*-butylbenzoic acid (46 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 31 mg (57%) of 3,5-di-*tert*-butyl-2-chlorobenzoic acid as white solid.

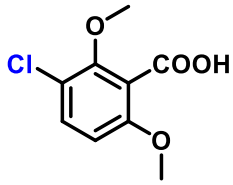
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.59 (s, 1H), 7.55 (s, 1H), 1.51 (s, 9H), 1.31 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.3, 147.2, 128.6, 127.8, 125.1, 37.0, 34.9, 31.3, 30.0.

HRMS *m/z* (ESI): calcd. for $C_{15}H_{20}ClO_2$ $[M-H]^-$: 267.1157, found: 267.1156.

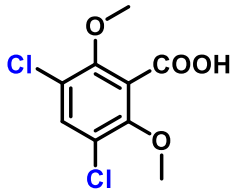
2jj: 3-chloro-2,6-dimethoxybenzoic acid and 3,5-dichloro-2,6-dimethoxybenzoic acid

2jj was synthesized according to the general procedure **A** with 2,6-dimethoxybenzoic acid (36 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 5 mg (12%) of 3-chloro-2,6-dimethoxybenzoic acid and 33 mg (66%) 3,5-dichloro-2,6-dimethoxybenzoic acid as a white solid.



2jj-1: 3-chloro-2,6-dimethoxybenzoic acid **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.40 (d, J = 8.9 Hz, 1H), 6.70 (d, J = 9.0 Hz, 1H), 3.96 (s, 3H), 3.88 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 168.1, 156.2, 154.2, 132.2, 119.9, 118.5, 108.0, 62.2, 56.5.



2jj-2: 3,5-dichloro-2,6-dimethoxybenzoic acid **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.68 (s, 1H), 7.51 (s, 1H), 3.96 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.6, 152.7, 132.8, 125.3, 124.1, 62.57.

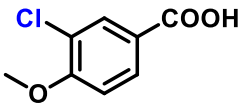
Known compound, data are consistent with those reported in the literature:

Song S, Li X, Wei J, et al. DMSO-catalysed late-stage chlorination of (hetero) arenes[J]. Nature Catalysis, 2020, 3(2): 107-115. doi: 10.1038/s41929-019-0398-0

Maraš, N., Kočevar, M. Effects of tertiary amine catalysis on the regioselectivity of anisole chlorination with trichloroisocyanuric acid. Monatsh Chem 146, 697–704 (2015). doi: 10.1007/s00706-014-1383-6

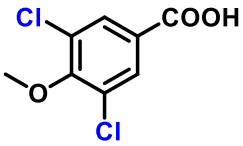
2kk: 3-chloro-4-methoxybenzoic acid and 3,5-dichloro-4-methoxybenzoic acid

2kk was synthesized according to the general procedure **A** with 4-methoxybenzoic acid (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 8 mg (21%) 3-chloro-4-methoxybenzoic acid and 25 mg (55%) of 3,5-dichloro-4-methoxybenzoic acid as white solid.



2kk-1: 3-chloro-4-methoxybenzoic acid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 2.1 Hz, 1H), 8.02 (dd, *J* = 8.7, 2.1 Hz, 1H), 6.99 (d, *J* = 8.8 Hz, 1H), 3.99 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.2, 159.5, 132.4, 130.8, 122.9, 122.4, 111.4, 56.6.



2kk-2: 3,5-dichloro-4-methoxybenzoic acid: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.04 (s, 2H), 3.98 (s, 3H).

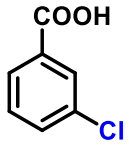
^{13}C NMR (151 MHz, $CDCl_3$) δ 157.0, 131.0, 129.9, 61.1.

Known compound, data are consistent with those reported in the literature:

Mostafa M A B, Bowley R M, Racys D T, et al. Iron (III)-catalyzed chlorination of activated arenes[J]. The Journal of organic chemistry, 2017, 82(14): 7529-7537. doi: 10.1021/acs.joc.7b01225

Schlosser M, Heiss C, Marzi E, et al. Proton Mobility in 2-Substituted 1, 3-Dichlorobenzenes:"ortho" or "meta" Metalation?[J]. European Journal of Organic Chemistry, 2007, 2007(3): 416-428. doi: 10.1002/ejoc.200600350

2ll: 3-chlorobenzoic acid



2ll was synthesized according to the general procedure **B** with benzoic acid (24 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 20 mg (64%) of 3-chlorobenzoic acid as white solid.

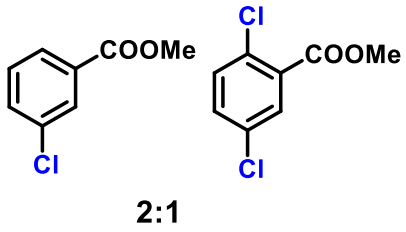
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (t, *J* = 1.9 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 1H), 7.60 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H), 7.43 (t, *J* = 7.9 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.2, 134.9, 134.1, 131.1, 130.4, 130.0, 128.5.

Known compound, data are consistent with those reported in the literature:

Murray A T, Matton P, Fairhurst N W G, et al. Biomimetic flavin-catalyzed aldehyde oxidation[J]. Organic Letters, 2012, 14(14): 3656-3659. doi: 10.1021/ol301496m

2mm: methyl 3-chlorobenzoate and methyl 2,5-dichlorobenzoate



2mm was synthesized according to the general procedure **B** with methyl benzoate (34 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give an inseparable mixture of methyl 3-chlorobenzoate and methyl 2,5-dichlorobenzoate (2:1, 27 mg, 74%) as a colorless oil.

2mm-1: methyl 3-chlorobenzoate **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.02 (t, *J* = 1.9 Hz, 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.53 (ddd, *J* = 8.0, 2.2, 1.1 Hz, 1H),7.38 (t, *J* = 7.8 Hz, 1H), 3.93 (s, 3H).

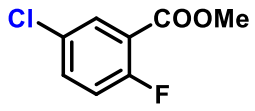
2mm-2: methyl 2,5-dichlorobenzoate **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.82 (t, *J* = 1.5 Hz, 0.5H), 7.40 – 7.39 (m, 1H), 3.94 (s, 1.5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.1, 165.1, 134.7, 133.1, 132.8, 132.7, 132.4, 132.3, 132.0, 131.7, 131.5, 131.3, 129.8, 127.9, 52.9, 52.6.

Known compound, data are consistent with those reported in the literature:

Gassmann J, Voss J. Electroreduction of Organic Compounds, 36 [1]. Electroreduction of Chlorinated Methyl Benzoates[J]. Zeitschrift für Naturforschung B, 2008, 63(11): 1291-1299. doi: 10.1515/znb-2008-1107

2nn: methyl 5-chloro-2-fluorobenzoate



2nn was synthesized according to the general procedure **B** with methyl 2-fluorobenzoate (31 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 29 mg (77%) of methyl 5-chloro-2-fluorobenzoate as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.91 (dd, J = 6.2, 2.8 Hz, 1H), 7.47 (ddd, J = 8.8, 4.1, 2.8 Hz, 1H), 7.09 (dd, J = 10.0, 8.8 Hz, 1H), 3.93 (s, 3H).

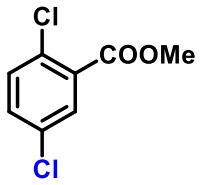
^{13}C NMR (151 MHz, $CDCl_3$) δ 163.8 (d, $^{4}J_{C-F}$ = 4.1 Hz), 160.5 (d, $^{1}J_{C-F}$ = 260.3 Hz), 134.4 (d, $^{3}J_{C-F}$ = 9.2 Hz), 131.9, 129.4 (d, $^{4}J_{C-F}$ = 3.8 Hz), 120.0 (d, $^{3}J_{C-F}$ = 11.5 Hz), 118.6 (d, $^{2}J_{C-F}$ = 24.2 Hz), 52.8.

^{19}F NMR (565 MHz, $CDCl_3$) δ -112.1.

Known compound, data are consistent with those reported in the literature:

Sato A, Sakauchi N, Shirai J, et al. Structure determination, synthesis, and biological evaluation of a metabolite of the selective α1D adrenoceptor antagonist TAK-259[J]. Tetrahedron, 2016, 72(41): 6334-6339. doi: 10.1016/j.tet.2016.08.013

2oo: methyl 2,5-dichlorobenzoate



2oo was synthesized according to the general procedure **B** with methyl 2-chlorobenzoate (34 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.8 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 35 mg (87%) of methyl 2,5-dichlorobenzoate acid as white solid.

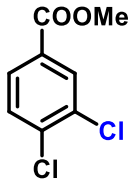
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.81 (t, J = 1.5 Hz, 1H), 7.38 (d, J = 1.5 Hz, 2H), 3.93 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.0, 132.8, 132.7, 132.4, 132.3, 131.5, 131.3, 52.8.

Known compound, data are consistent with those reported in the literature:

Gassmann J, Voss J. Electroreduction of Organic Compounds, 36 [1]. Electroreduction of Chlorinated Methyl Benzoates[J]. Zeitschrift für Naturforschung B, 2008, 63(11): 1291-1299. doi: 10.1515/znb-2008-1107

2pp: methyl 3,4-dichlorobenzoate



2pp was synthesized according to the general procedure **B** with methyl 4-chlorobenzoate (34 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 21 mg (51%) of methyl 3,4-dichlorobenzoate acid as white solid.

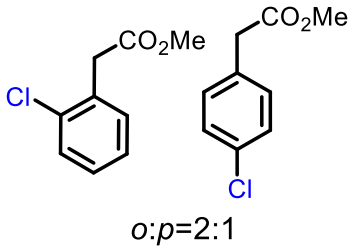
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.12 (d, *J* = 2.0 Hz, 1H), 7.86 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.4, 137.7, 133.1, 131.7, 130.7, 130. 1, 128.8, 52.7.

Known compound, data are consistent with those reported in the literature:

Golding W A, Pearce-Higgins R, Phipps R J. Site-selective cross-coupling of remote chlorides enabled by electrostatically directed palladium catalysis[J]. Journal of the American Chemical Society, 2018, 140(42): 13570-13574. doi:10.1021/jacs.8b08686

2qq: methyl 2-(2-chlorophenyl)acetate and methyl 2-(4-chlorophenyl)acetate



2qq was synthesized according to the general procedure **A** with methyl 2-phenylacetate (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give an inseparable mixture of methyl 2-(2-chlorophenyl)acetate and methyl 2-(4-chlorophenyl)acetate (2:1, 33 mg, 91%) as colorless oil.

2qq-1: methyl 2-(2-chlorophenyl)acetate: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.39 – 7.38 (m, 1H), 7.30 – 7.28 (m, 1H), 7.25 – 7.21 (m, 2H), 3.78 (s, 2H), 3.71 (s, 3H).

2qq-2: methyl 2-(4-chlorophenyl)acetate: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.4Hz, 1H), 7.24 – 7.22 (m, 1H), 3.78 (s, 1H), 3.71 (s, 1H), 3.69 (s, 1.5H), 3.60 (s, 1H).

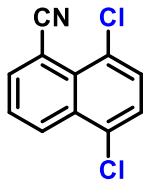
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 171.2, 134.7, 133.2, 132.50, 132.48, 131.6, 130.8, 129.6, 128.8, 127.0, 52.3, 52.2, 40.5, 39.1.

Known compound, data are consistent with those reported in the literature:

Sun X, Shan G, Sun Y, et al. Regio-and Chemoselective C- H Chlorination/Bromination of Electron-Deficient Arenes by Weak Coordination and Study of Relative Directing-Group Abilities[J]. Angewandte Chemie, 2013, 125(16): 4536-4540. doi: 10.1002/anie.201300176

Yamamoto N, Obora Y, Ishii Y. Iridium-catalyzed oxidative methyl esterification of primary alcohols and diols with methanol[J]. The Journal of Organic Chemistry, 2011, 76(8): 2937-2941. doi: 10.1021/jo2003264

2rr: 5,8-dichloro-1-naphthonitrile



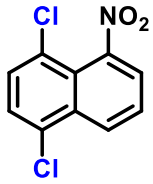
2rr was synthesized according to the general procedure **A** with 1-naphthonitrile (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (36 mg, 0.6 mmol, 3.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 34 mg (77%) of 5,8-dichloro-1-naphthonitrile as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.6 Hz, 1H), 8.14 (d, *J* = 7.3 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.66 – 7.57 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.8, 132.4, 132.3, 130.9, 130.3, 130.1, 129.7, 127.8, 126.8, 119.1, 109.3.

HRMS *m/z* (ESI): calcd. for $C_{11}H_6Cl_2N$ $[M+H]^+$: 221.9872, found: 221.9872.

2ss: 1,4-dichloro-5-nitronaphthalene



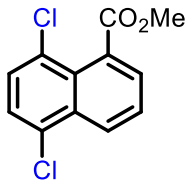
2ss was synthesized according to the general procedure **A** with 1-nitronaphthalene (34 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (36 mg, 0.6 mmol, 3.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), DCE/HFIP (2/1, 1.0 mL)under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 36 mg (74%) of 1,4-dichloro-5-nitronaphthalene as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.51 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.76 (d, *J* = 7.4 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.63 – 7.57 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 147.7, 132.9, 132.0, 130.7, 129.0, 127.9, 127.2, 126.6, 124.1, 122.6.

HRMS *m/z* (ESI): calcd. for $C_{10}H_6Cl_2NO_2$ $[M+H]^+$: 241.9770, found: 241.9770.

2tt: methyl 5,8-dichloro-1-naphthoate



2tt was synthesized according to the general procedure **A** with methyl 1-naphthoate (37 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 39 mg (78%) of methyl 5,8-dichloro-1-naphthoate as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.42 (dd, *J* = 8.4, 1.3 Hz, 1H), 7.67 (dd, *J* = 7.1, 1.4 Hz, 1H), 7.65 – 7.61 (m, 1H), 7.54 (s, 2H), 3.98 (s, 3H).

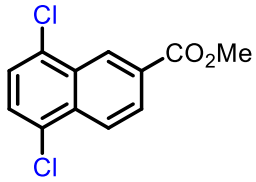
^{13}C NMR (151 MHz, $CDCl_3$) δ 170.7, 132.4, 131.8, 131.4, 129.2, 128.8, 128.7, 128.2, 127.6, 126.9, 126.7, 53.1.

Known compound, data are consistent with those reported in the literature:

Chen J, Smith V J, Huffman J W. 8-Chloro-and 5, 8-Dichloro-1-naphthoic Acids[J]. Organic preparations and procedures international, 2010, 42(5): 490-493.

doi: 10.1080/00304948.2010.514799

2uu: methyl 5,8-dichloro-2-naphthoate



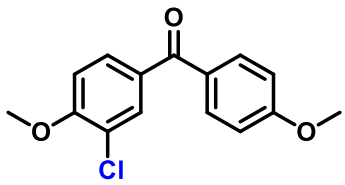
2uu was synthesized according to the general procedure **A** with methyl 2-naphthoate (37mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 36 mg (71%) of methyl 5,8-dichloro-2-naphthoate as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 9.00 (d, *J* = 1.8 Hz, 1H), 8.32 (d, *J* = 8.9 Hz, 1H), 8.21 (dd, *J* = 8.8, 1.6 Hz, 1H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 8.0 Hz, 1H), 4.02 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.6, 133.8, 132.4, 131.2, 131.1, 129.4, 128.2, 127.9, 127.4, 126.9, 125.7, 52.7.

HRMS *m/z* (ESI): calcd. for $C_{15}H_{14}ClO_3$ $[M+H]^+$:254.9974, found: 254.9975.

2vv: (3-chloro-4-methoxyphenyl)(4-methoxyphenyl)methanone



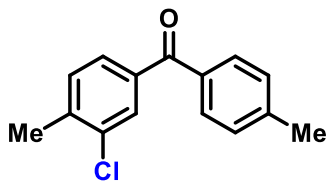
2vv was synthesized according to the general procedure **A** with bis(4-methoxyphenyl)methanone (48 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL)under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 40 mg (71%) of (3-chloro-4-methoxyphenyl)(4-methoxyphenyl)methanone as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.1 Hz, 1H), 7.79 – 7.76 (m, 2H), 7.71 (dd, *J* = 8.5, 2.2 Hz, 1H), 6.99 (d, *J* = 8.6 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.99 (s, 3H), 3.89 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.4, 163.3, 158.2, 132.4, 132.3, 131.5, 130.5, 130.2, 122.6, 113.8, 111.2, 56.5, 55.7.

HRMS *m/z* (ESI): calcd. for $C_{15}H_{14}ClO_3$ $[M+H]^+$: 277.0626, found: 277.0625.

2ww: (3-chloro-4-methylphenyl)(p-tolyl)methanone



2ww was synthesized according to the general procedure **A** with di-*p*-tolylmethanone (42 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 36 mg (73%) of (3-chloro-4-methylphenyl)(p-tolyl)methanone as white solid.

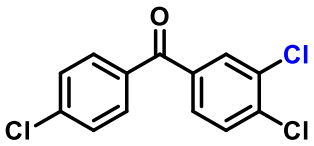
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.77 (d, *J* = 1.7 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.58 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.33 (d, *J* = 7.9 Hz, 1H), 7.29 (d, *J* = 7.8 Hz, 2H), 2.46 (s, 3H), 2.44 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 195.1, 143.6, 140.9, 137.2, 134.7, 134.6, 130.9, 130.7, 130.3, 129.2, 128.3, 21.8, 20.5.

HRMS *m/z* (ESI): calcd. for $C_{15}H_{14}ClO$ $[M+H]^+$:245.0728, found: 245.0727.

2xx: (4-chlorophenyl)(3,4-dichlorophenyl)methanone and bis(3,4-dichlorophenyl)methanone

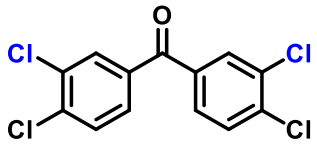
2xx was synthesized according to the general procedure **B** with bis(4-chlorophenyl)methanone (50 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 28 mg (49%) of (4-chlorophenyl)(3,4-dichlorophenyl)methanone and 10 mg (16%) of bis(3,4-dichlorophenyl)methanone as white solid.



2xx-1: (4-chlorophenyl)(3,4-dichlorophenyl)methanone **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 1.9 Hz, 1H), 7.72 (d, *J* = 8.5 Hz, 2H), 7.60 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.49 (d, *J* = 8.5 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.2, 139.7, 137.5, 136.9, 135.1, 133.3, 131.9, 131.4, 130.7, 129.09, 129.05.

HRMS *m/z* (ESI): calcd. for $C_{16}H_{14}ClO_4$ $[M+H]^+$:284.9635, found: 284.9636.

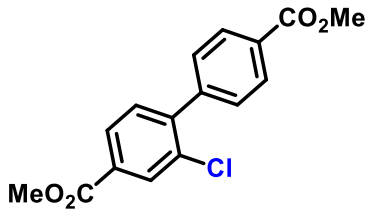


2xx-2: bis(3,4-dichlorophenyl)methanone **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.87 (s, 2H), 7.60 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 192.0, 137.9, 136.4, 133.6, 131.8, 130.9, 129.0.

HRMS *m/z* (ESI): calcd. for $C_{16}H_{14}ClO_4$ $[M+H]^+$: 318.9246, found: 318.9247.

2yy: dimethyl 2-chloro-[1,1'-biphenyl]-4,4'-dicarboxylate



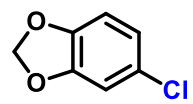
2yy was synthesized according to the general procedure **A** with dimethyl [1,1'-biphenyl]-4,4'-dicarboxylate (54 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 5:1) on silica gel to give 53 mg (86%) of dimethyl 2-chloro-[1,1'-biphenyl]-4,4'-dicarboxylate as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (s, 1H), 8.12 (d, *J* = 7.6 Hz, 2H), 7.98 (d, *J* = 8.1 Hz, 1H), 7.52 (d, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 1H), 3.95 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 166.9, 165.8, 143.9, 143.1, 132.8, 131.4, 131.3, 131.2, 130.0, 129.6, 129.5, 128.1, 52.6, 52.4.

HRMS *m/z* (ESI): calcd. for $C_{16}H_{14}ClO_4$ $[M+H]^+$: 305.0575, found: 305.0575.

2zz: 5-chlorobenzo[*d*][1,3]dioxole



2zz was synthesized according to the general procedure **A** with benzo[*d*][1,3]dioxole (24 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was

concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 25 mg (82%) of 5-chlorobenzo[*d*][1,3]dioxole as a white solid

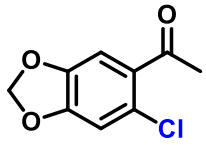
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 – 6.78 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 1H), 5.97 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 148.5, 146.6, 126.4, 121.5, 109.8, 109.0, 101.8.

Known compound, data are consistent with those reported in the literature:

Moon B S, Choi H Y, Koh H Y, et al. The Use of Sodium Chlorate/Hydrochloric Acid Mixtures as a Novel and Selective Chlorination Agent[J]. Bulletin of the Korean Chemical Society, 2011, 32(2): 472-476. doi:10.5012/bkcs.2011.32.2.472

2aaa: 1-(6-chlorobenzo[*d*][1,3]dioxol-5-yl)ethan-1-one



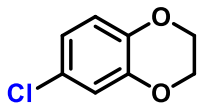
2aaa was synthesized according to the general procedure **A** with 1-(benzo[*d*][1,3]dioxol-5-yl)ethan-1-one (32 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 24 mg (61%) of 1-(6-chlorobenzo[*d*][1,3]dioxol-5-yl)ethan-1-one as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (s, 1H), 6.85 (s, 1H), 6.04 (s, 2H), 2.62 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 198.6, 150.8, 147.0, 132.3, 126.2, 110.9, 109.5, 102.6, 31.0.

HRMS *m/z* (ESI): calcd. for $C_9H_8ClO_3$ $[M+H]^+$: 199.0157, found: 199.0156.

2bbb: 6-chloro-2,3-dihydrobenzo[*b*][1,4]dioxine



2bbb was synthesized according to the general procedure **A** with 2,3-dihydrobenzo[*b*][1,4]dioxine (28 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 23 mg (68%) of 6-chloro-2,3-dihydrobenzo[*b*][1,4]dioxine as white solid.

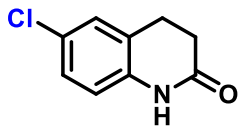
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.79 – 6.78 (m, 2H), 4.24 (s, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 144.1, 142.5, 125.9, 121.5, 118.2, 117.5, 64.5, 64.3.

Known compound, data are consistent with those reported in the literature:

Togo H, Muraki T, Hoshina Y, et al. Formation and synthetic use of oxygen-centred radicals with (diacetoxyiodo) arenes[J]. Journal of the Chemical Society, Perkin Transactions 1, 1997 (5): 787-794. doi: 10.1039/A603446B

2ccc: 6-chloro-3,4-dihydroquinolin-2(1*H*)-one



2ccc was synthesized according to the general procedure **A** with 3,4-dihydroquinolin-2(1*H*)-one (25 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced

pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 25 mg (69%) of 6-chloro-3,4-dihydroquinolin-2(1*H*)-one as yellow solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 7.19 – 7.10 (m, 2H), 6.70 (d, *J* = 8.2 Hz, 1H), 2.97 – 2.93 (m, 2H), 2.65 – 2.60 (m, 2H).

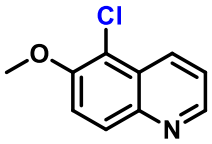
^{13}C NMR (151 MHz, $CDCl_3$) δ 171.3, 135.9, 128.20, 128.19, 127.6, 125.5, 116.5, 30.5, 25.4.

Known compound, data are consistent with those reported in the literature:

Li B, Park Y, Chang S. Regiodivergent access to five-and six-membered benzo-fused lactams: Ru-catalyzed olefin hydrocarbamoylation[J]. Journal of the American Chemical Society, 2014, 136(3): 1125-1131. doi: 10.1021/ja411913e

2ddd: 5-chloro-6-methoxyquinoline and 5-chloro-6-methoxyquinoline-1-oxide

2ddd was synthesized according to the general procedure **A** with 6-methoxyquinoline (34 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (123 mg, 0.2 mmol, 1.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 5:1) on silica gel to give 16 mg (35%) of 5-chloro-6-methoxyquinoline as yellow solid and 10 mg (24%) of 5-chloro-6-methoxyquinoline 1-oxide as white solid.

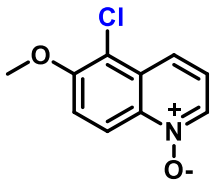


2ddd-1: 5-chloro-6-methoxyquinoline **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.83 (dd, *J* = 4.3, 1.6 Hz, 1H), 8.54 (d, *J* = 8.6 Hz, 1H), 8.07 (d, *J* = 9.3 Hz, 1H), 7.54 (d, *J* = 9.3 Hz, 1H), 7.48 (dd, *J* = 8.6, 4.2 Hz, 1H), 4.07 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.9, 148.9, 144.1, 132.1, 129.6, 127.5, 122.3, 116.8, 116.0, 57.1.

Known compound, data are consistent with those reported in the literature:

Tse M H, Zhong R L, Kwong F Y. Palladium-Catalyzed Miyaura Borylation of Overly Crowded Aryl Chlorides Enabled by a Complementary Localized/Remote Steric Bulk of Ligand Chassis[J]. ACS Catalysis, 2022, 12(6): 3507-3515. doi: 10.1021/acscatal.2c00263

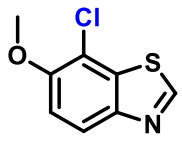


2ddd-2: 5-chloro-6-methoxyquinoline-1-oxide **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.72 (d, *J* = 9.6 Hz, 1H), 8.44 (d, *J* = 5.9 Hz, 1H), 8.08 (d, *J* = 8.8 Hz, 1H), 7.52 (d, *J* = 9.7 Hz, 1H), 7.35 (dd, *J* = 8.8, 6.0 Hz, 1H), 4.08 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 154.8, 137.5, 134.2, 130.1, 122.3, 122.2, 120.1, 116.9, 116.6, 57.1.

HRMS *m/z* (ESI): calcd. for $C_{10}H_9ClNO_2$ $[M+H]^+$: 210.0136, found: 210.0136.

2eee: 7-chloro-6-methoxybenzo[*d*]thiazole



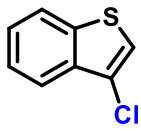
2eee was synthesized according to the general procedure **A** with 6-methoxybenzo[*d*]thiazole (33 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 26 mg (65%) of 7-chloro-6-methoxybenzo[*d*]thiazole as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.86 (s, 1H), 7.99 (d, *J* = 8.9 Hz, 1H), 7.20 (d, *J* = 9.1 Hz, 1H), 4.01 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 153.3, 152.8, 147.9, 136.3, 122.3, 114.5, 112.2, 57.3.

HRMS *m/z* (ESI): calcd. For C_8H_7ClNOS $[M+H]^+$: 199.9931, found: 199.9931.

2fff: 3-chlorobenzo[*b*]thiophene



2fff was synthesized according to the general procedure **A** with benzo[*b*]thiophene (27 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 12 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 100:1) on silica gel to give 13 mg (43%) of 3-chlorobenzo[*b*]thiophene as colorless oil.

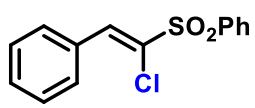
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.0 Hz, 1H), 7.84 (d, *J* = 8.1 Hz, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 1H), 7.32 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.5, 136.2, 125.5, 125.0, 123.0, 122.0, 121.3, 120.9.

Known compound, data are consistent with those reported in the literature:

Kuriyama M, Hamaguchi N, Yano G, et al. Deuterodechlorination of aryl/heteroaryl chlorides catalyzed by a palladium/unsymmetrical NHC system[J]. The Journal of Organic Chemistry, 2016, 81(19): 8934-8946. doi: 10.1021/acs.joc.6b01609

2ggg: (*Z*)-(2-chloro-2-(phenylsulfonyl)vinyl)benzene



2ggg was synthesized according to the general procedure **A** with (*E*)-(2-(phenylsulfonyl)vinyl)benzene (49 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 33 mg (60%) of (*Z*)-(2-chloro-2-(phenylsulfonyl)vinyl)benzene as white solid.

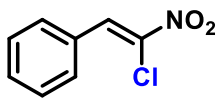
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 (s, 1H), 8.00 (d, *J* = 7.1 Hz, 2H), 7.80 – 7.79 (m, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.58 (t, *J* = 7.9 Hz, 2H), 7.45 – 7.42 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.5, 135.2, 134.2, 131.4, 131.2, 130.6, 130.4, 129.4, 129.2, 128.9.

Known compound, data are consistent with those reported in the literature:

Liu L, Zhang-Negrerie D, Du Y, et al. $PhICl_2$ and wet DMF: An efficient system for regioselective chloroformyloxylation/α-chlorination of alkenes/α, β-unsaturated compounds[J]. Organic Letters, 2014, 16(2): 436-439. doi: 10.1021/ol403321n

2hhh: (*Z*)-(2-chloro-2-nitrovinyl)benzene



2hhh was synthesized according to the general procedure **A** with (*E*)-(2-nitrovinyl)benzene (30 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column

chromatography (PE/EA = 50:1) on silica gel to give 19 mg (60%) of (*Z*)-(2-chloro-2-nitrovinyl)benzene as yellow solid.

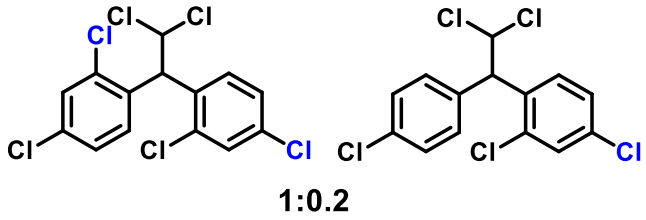
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.38 (s, 1H), 7.86 – 7.85 (m, 2H), 7.52 – 7.49 (m, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 137.7, 132.1, 131.8, 131.3, 129.8, 129.2.

Known compound, data are consistent with those reported in the literature:

Liu L, Zhang-Negrerie D, Du Y, et al. $PhICl_2$ and wet DMF: An efficient system for regioselective chloroformyloxylation/α-chlorination of alkenes/α, β-unsaturated compounds[J]. Organic Letters, 2014, 16(2): 436-439. doi: 10.1021/ol403321n

4a: 4,4'-(2,2-dichloroethane-1,1-diyl)bis(1,3-dichlorobenzene) and 2,4-dichloro-1-(2,2-dichloro-1-(4-chlorophenyl)ethyl)benzene



4a was synthesized according to the general procedure **A** with Mitotane (64 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (36 mg, 0.6 mmol, 3.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 100:1) on silica gel to give an inseparable mixture of 4,4'-(2,2-dichloroethane-1,1-diyl)bis(1,3-dichlorobenzene) and 2,4-dichloro-1-(2,2-dichloro-1-(4-chlorophenyl)ethyl)benzene (1:0.2, 40 mg, 52%) as colorless oil.

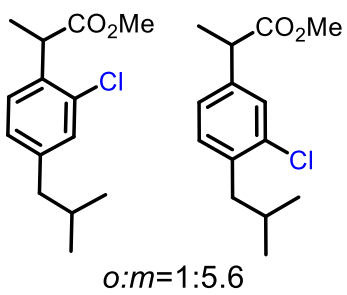
4a-1: 4,4'-(2,2-dichloroethane-1,1-diyl)bis(1,3-dichlorobenzene) **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.44 – 7.42 (m, 2H), 7.40 (d, *J* = 2.3 Hz, 1H), 7.34 (d, *J* = 8.5 Hz, 1H), 7.23 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.21 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.29 (d, *J* = 8.4 Hz, 1H), 5.10 (d, *J* = 8.4 Hz, 1H).

4a-2: 2,4-dichloro-1-(2,2-dichloro-1-(4-chlorophenyl)ethyl)benzene **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 2.5 Hz, 0.2H), 7.34 (d, *J* = 8.5 Hz, 0.2H), 7.33 – 7.32 (m, 0.4H), 7.29 (d, *J* = 8.5 Hz, 0.4H), 7.22 – 7.19 (m, 0.2H), 6.31 (d, *J* = 8.6 Hz, 0.2H), 5.13 (d, *J* = 8.6 Hz, 0.2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 138.9, 138.3, 137.7, 136.17, 134.1, 133.4, 133.2, 133.0, 132.6, 132.5, 131.5, 131.4, 131.0, 130.8, 130.3, 129.4, 129.11, 129.10, 128.68, 128.66, 128.3, 73.4, 72.9, 57.3, 57.0.

HRMS *m/z* (ESI): calcd. for $C_{14}H_8Cl_6$ and $C_{14}H_9Cl_5$ $[M+H]^+$:386.8830 and 352.9220, found: 386.8830 and 352.9220.

4b: methyl 2-(3-chloro-4-isobutylphenyl)propanoate and methyl 2-(2-chloro-4-isobutylphenyl)propanoate



4b was synthesized according to the general procedure **A** with Ibuprofen methyl ester (44 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (123 mg, 0.2 mmol, 1.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give an inseparable mixture of methyl

2-(3-chloro-4-isobutylphenyl)propanoate and methyl 2-(2-chloro-4-isobutylphenyl)propanoate (1:5.6, 33 mg, 65%) as colorless oil.

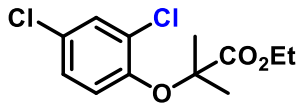
4b-1: chlorination at *m*-position methyl 2-(3-chloro-4-isobutylphenyl)propanoate: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.28 (d, *J* = 1.8 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.09 (dd, *J* = 7.9, 1.8 Hz, 1H), 3.68 (s, 3H), 2.56 (d, *J* = 7.2 Hz, 2H), 1.99 – 1.92 (m, 1H), 1.48 (d, *J* = 7.2 Hz, 3H), 0.92 (d, *J* = 6.6 Hz, 6H).

4b-2: chlorination at *o*-position methyl 2-(2-chloro-4-isobutylphenyl)propanoate: **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 8.0, 1.8 Hz, 0.18H), 7.16 (d, *J* = 1.8 Hz, 0.17H), 7.02 (dd, *J* = 7.9, 1.8 Hz, 0.18H), 3.68 (s, 0.7H), 2.42 (d, *J* = 7.2 Hz, 0.35H), 1.90 – 1.77 (m, 0.18H), 1.48 (d, *J* = 7.2 Hz, 0.67H), 0.90 (d, *J* = 6.6 Hz, 1.28H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.9, 174.8, 142.4, 139.7, 138.3, 135.6, 134.4, 133.3, 131.6, 130.2, 129.5, 129.4, 128.6, 128.2, 128.1, 127.3, 125.7, 52.3, 44.82, 44.75, 42.5, 41.8, 30.2, 28.8, 22.53, 22.46, 18.6, 17.8.

HRMS *m/z* (ESI): calcd. for $C_{14}H_{20}ClO_2$ $[M+H]^+$: 255.1146, found: 255.1146.

4c: ethyl 2-(2,4-dichlorophenoxy)-2-methylpropanoate



4c was synthesized according to the general procedure **A** with Clofibrate (48 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 41 mg (75%) of Clofibrate-Cl as a white solid.

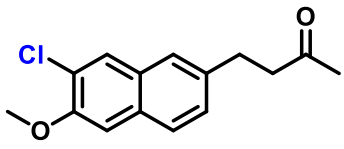
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 2.6 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.6 Hz, 1H), 6.85 (d, *J* = 8.8 Hz, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.59 (s, 6H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.8, 150.6, 130.2, 127.9, 127.7, 127.3, 120.9, 81.4, 61.7, 25.2, 14.2.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi: 10.1021/jacs.2c06440

4d: 4-(7-chloro-6-methoxynaphthalen-2-yl)butan-2-one



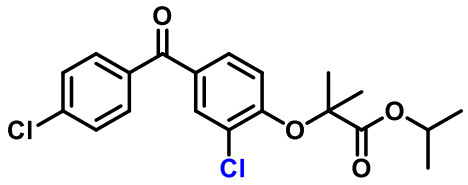
4d was synthesized according to the general procedure **A** with Nabumetone (45 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 50:1) on silica gel to give 29 mg (55%) of 4-(7-chloro-6-methoxynaphthalen-2-yl)butan-2-one as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.9 Hz, 1H), 7.57 (s, 1H), 7.40 (d, *J* = 8.7 Hz, 1H), 7.28 (d, *J* = 8.8 Hz, 1H), 4.02 (d, *J* = 1.6 Hz, 3H), 3.04 (t, *J* = 7.6 Hz, 2H), 2.84 (t, *J* = 7.5 Hz, 2H), 2.15 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 207.9, 152.3, 137.1, 130.7, 129.8, 128.8, 127.6, 126.7, 123.9, 117.0, 114.1, 57.1, 45.0, 30.3, 29.6.

HRMS *m/z* (ESI): calcd. for $C_{15}H_{16}ClO_2$ $[M+H]^+$:263.0833, found: 263.0833.

4e: isopropyl 2-(2-chloro-4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate



4e was synthesized according to the general procedure **A** with Fenofibrate (72 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 74 mg (94%) of isopropyl 2-(2-chloro-4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoate as white solid.

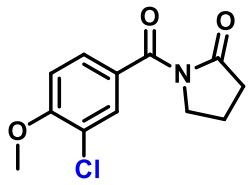
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.85 (d, *J* = 2.2 Hz, 1H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.58 (dd, *J* = 8.6, 2.2 Hz, 1H), 7.46 (d, *J* = 8.5 Hz, 2H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.09 (heptet, *J* = 6.3 Hz, 1H), 1.68 (s, 6H), 1.22 (d, *J* = 6.3 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 193.3, 172.8, 155.6, 138.9, 135.9, 132.6, 131.26, 131.25, 129.6, 128.8, 125.7, 117.0, 81.2, 69.6, 25.4, 21.6.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi: 10.1021/jacs.2c06440

4f: 1-(3-chloro-4-methoxybenzoyl)pyrrolidin-2-one



4f was synthesized according to the general procedure **A** with Aniracetam (0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (123 mg, 0.2 mmol, 1.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 80 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 5:1) on silica gel to give 39 mg (76%) of 1-(3-chloro-4-methoxybenzoyl)pyrrolidin-2-one as white solid.

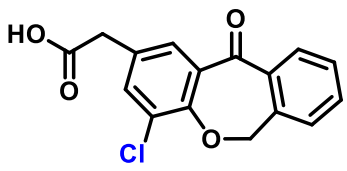
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.1 Hz, 1H), 7.56 (dd, *J* = 8.6, 2.2 Hz, 1H), 6.92 (d, *J* = 8.6 Hz, 1H), 3.95 (s, 3H), 3.92 (t, *J* = 7.1 Hz, 2H), 2.61 (t, *J* = 8.0 Hz, 2H), 2.14 (p, *J* = 7.6 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 174.8, 169.0, 158.2, 131.8, 130.0, 127.1, 122.1, 110.8, 56.4, 46.9, 33.4, 17.8.

Known compound, data are consistent with those reported in the literature:

Shi H, Zhang J, Li X, et al. Thianthrene/TfOH-catalyzed electrophilic halogenations using N-halosuccinimides as the halogen source[J]. Chemical Science, 2024, 15(32): 13058-13067. doi: 10.1039/D4SC04461D

4g: 2-(4-chloro-11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid



4g was synthesized according to the general procedure **A** with Isoxepac (74 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated

under reduced pressure and the residue was purified using flash column chromatography (PE/EA/AcOH = 100:2:1) on silica gel to give 31 mg (51%) of 2-(4-chloro-11-oxo-6,11-dihydrodibenzo[*b,e*]oxepin-2-yl)acetic acid as white solid.

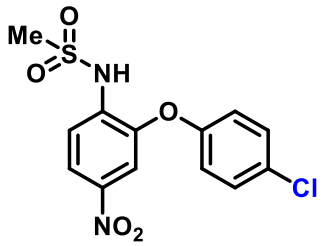
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 2.3 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.40 (d, *J* = 7.4 Hz, 1H), 5.30 (s, 2H), 3.66 (s, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 190.3, 156.2, 140.1, 136.6, 135.1, 133.2, 131.6, 129.69, 129.68, 128.1, 127.5, 126.7, 125.8, 125.7, 74.3, 39.7.

Known compound, data are consistent with those reported in the literature:

Kona C N, Oku R, Nakamura S, et al. Aromatic halogenation using carborane catalyst[J]. Chem, 2024, 10(1): 402-413. doi: 10.1016/j.chempr.2023.10.006

4h: *N*-(2-(4-chlorophenoxy)-4-nitrophenyl)methanesulfonamide



4h was synthesized according to the general procedure **A** with Nimesulide (54 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 5:1) on silica gel to give 58 mg (82%) of *N*-(2-(4-chlorophenoxy)-4-nitrophenyl)methanesulfonamide as yellow solid.

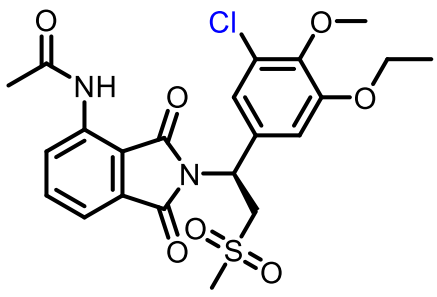
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 9.0, 2.5 Hz, 1H), 7.77 (d, *J* = 9.0 Hz, 1H), 7.64 (d, *J* = 2.5 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 7.36 (s, 1H), 7.03 (d, *J* = 8.9 Hz, 2H), 3.18 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 152.8, 146.0, 143.7, 134.1, 131.4, 130.9, 121.2, 119.9, 117.5, 111.9, 40.8.

Known compound, data are consistent with those reported in the literature:

Kona C N, Oku R, Nakamura S, et al. Aromatic halogenation using carborane catalyst[J]. Chem, 2024, 10(1): 402-413. doi: 10.1016/j.chempr.2023.10.006

4i: *N*-(2-(1-(3-chloro-5-ethoxy-4-methoxyphenyl)-2-(methylsulfonyl)ethyl)-1,3-dioxoisoindolin-4-yl)acetamide



4i was synthesized according to the general procedure **A** with Apremilas (92 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (12 mg, 0.2 mmol, 1.0 eq.), oxone (123 mg, 0.2 mmol, 1.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/Et_3N = 100:20:1) on silica gel to give 43 mg (44%) of *N*-(2-(1-(3-chloro-5-ethoxy-4-methoxyphenyl)-2-(methylsulfonyl)ethyl)-1,3-dioxoisoindolin-4-yl)acetamide as white solid.

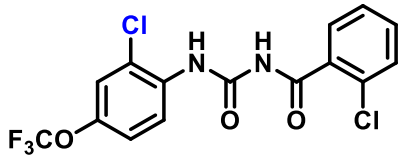
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 8.77 (d, *J* = 8.4 Hz, 1H), 7.71 – 7.63 (m, 1H), 7.54 – 7.47 (m, 1H), 7.29 (s, 1H), 6.86 (s, 1H), 6.35 (dd, *J* = 11.8, 3.0 Hz, 1H), 4.54 – 4.49 (m, 1H), 4.16 – 4.04 (m, 2H), 3.85 (s, 3H), 3.49 (dd, *J* = 14.6, 3.0 Hz, 1H), 3.02 (s, 3H), 2.26 (s, 3H), 1.46 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 169.8, 169.4, 168.1, 150.3, 147.8, 137.8, 136.3, 131.2, 126.1, 125.2, 124.2, 118.5, 115.2, 113.5, 112.8, 65.1, 56.3, 53.8, 46.0, 41.1, 25.1, 14.7.

Known compound, data are consistent with those reported in the literature:

Duan Y, Luo S. Phase-Transfer Catalysis for Electrochemical Chlorination and Nitration of Arenes[J]. Angewandte Chemie, 2024, 136(17): e202319206. doi: 10.1002/anie.202319206

4j: 2-chloro-*N*-((2-chloro-4-(trifluoromethoxy)phenyl)carbamoyl)benzamide



4j was synthesized according to the general procedure **A** with Triflumuron (72 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/Et_3N = 100:20:1) on silica gel to give 56 mg (71%) of 2-chloro-*N*-((2-chloro-4-(trifluoromethoxy)phenyl)carbamoyl)benzamide as white solid.

^{1}H NMR (600 MHz, CDCl3) δ 11.13 (s, 1H), 8.80 (s, 1H), 8.33 (d, *J* = 9.1 Hz, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.51 (d, *J* = 6.2 Hz, 2H), 7.43 (t, *J* = 6.9 Hz, 1H), 7.34 (s, 1H), 7.15 (d, *J* = 9.2 Hz, 1H).

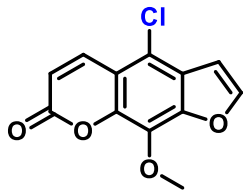
^{13}C NMR (151 MHz, $CDCl_3$) δ 167.8, 150.8, 145.0, 133.6, 133.2, 132.7, 131.4, 131.0, 130.6, 127.5, 124.3, 122.4 (2 peaks overlapped), 120.5 (q, $^{1}J_{C-F}$ = 258.2 Hz), 120.3.

^{19}F NMR (565 MHz, $CDCl_3$) δ -58.2.

Known compound, data are consistent with those reported in the literature:

Wang Y, Bi C, Kawamata Y, et al. Discovery of N–X anomeric amides as electrophilic halogenation reagents[J]. Nature Chemistry, 2024, 16(9): 1539-1545. doi: 10.1038/s41557-024-01539-4

4k: 4-chloro-9-methoxy-7*H*-furo[3,2-*g*]chromen-7-one



4k was synthesized according to the general procedure **A** with Xanthotoxin (43 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 37 mg (73%) of 4-chloro-9-methoxy-7*H*-furo[3,2-*g*]chromen-7-one as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, *J* = 9.8 Hz, 1H), 7.71 (d, *J* = 2.2 Hz, 1H), 6.92 (d, *J* = 2.2 Hz, 1H), 6.45 (d, *J* = 9.9 Hz, 1H), 4.27 (s, 3H).

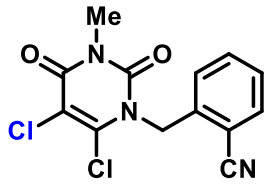
^{13}C NMR (151 MHz, $CDCl_3$) δ 159.8, 147.3, 147.1, 143.8, 140.4, 132.1, 125.8, 116.3, 115.7, 114.4, 105.9, 61.6.

Known compound, data are consistent with those reported in the literature:

Su J, Zhang Y, Chen M, et al. A copper halide promoted regioselective halogenation of coumarins using N-halosuccinimide as halide source[J]. Synlett, 2019, 30(05): 630-634. doi: 10.1055/s-0037-1612080

4l: 2-((5,6-dichloro-3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)methyl)benzonitrile

4l was synthesized according to the general procedure **A** with Alogliptin Intermediate (55 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C, then the mixture was



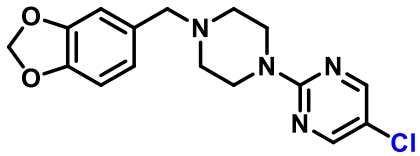
cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 52 mg (83%) of 2-((5,6-dichloro-3-methyl-2,4-dioxo-3,4-dihydropyrimidin-1(2*H*)-yl)methyl)benzonitrile as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.57 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 5.57 (s, 2H), 3.45 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 157.5, 150.2, 142.6, 138.7, 133.6, 133.5, 128.7, 126.6, 116.8, 111.2, 109.6, 49.3, 29.9.

HRMS *m/z* (ESI): calcd. for $C_{13}H_{10}Cl_2N_3O_2$ $[M+H]^+$: 310.0145, found: 310.0145.

4m: 2-(4-(benzo[*d*][1,3]dioxol-5-ylmethyl)piperazin-1-yl)-5-chloropyrimidine



4m was synthesized according to the general procedure **A** with Piribedil (45 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (36 mg, 0.6 mmol, 3.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20: 1) on silica gel to give 41 mg (61%) of 2-(4-(benzo[*d*][1,3]dioxol-5-ylmethyl)piperazin-1-yl)-5-chloropyrimidine as white solid.

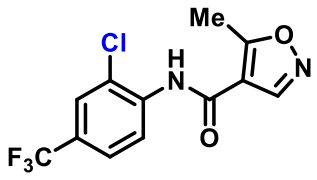
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 2H), 6.88 (s, 1H), 6.75 (s, 2H), 5.95 (s, 2H), 3.80 – 3.76 (t, *J* = 5.4 Hz, 4H), 3.45 (s, 2H), 2.47 (t, *J* = 5.1 Hz, 4H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 160.0, 155.9, 147.8, 146.8, 131.9, 122.4, 118.2, 109.6, 108.0, 101.1, 63.0, 52.8, 44.1.

Known compound, data are consistent with those reported in the literature:

Wang Y, Bi C, Kawamata Y, et al. Discovery of N–X anomeric amides as electrophilic halogenation reagents[J]. Nature Chemistry, 2024, 16(9): 1539-1545. doi: 10.1038/s41557-024-01539-4

4n: *N*-(2-chloro-4-(trifluoromethyl)phenyl)-5-methylisoxazole-4-carboxamide



4n was synthesized according to the general procedure **A** with Leflunomide (54 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 5:1) on silica gel to give 50 mg (82%) of *N*-(2-chloro-4-(trifluoromethyl)phenyl)-5-methylisoxazole-4-carboxamide as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.7 Hz, 1H), 8.51 (s, 1H), 8.04 (s, 1H), 7.68 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 2.79 (s, 3H).

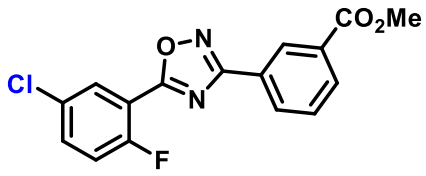
^{13}C NMR (151 MHz, $CDCl_3$) δ 173.6, 159.1, 147.9, 137.2, 127.1 (q, $^2J_{C-F}$ = 33.7 Hz), 126.4 (q, $^4J_{C-F}$ = 4.0 Hz), 125.3 (q, $^4J_{C-F}$ = 3.7 Hz), 123.5 (q, $^1J_{C-F}$ = 206.9 Hz), 122.8, 121.3, 112.1, 12.9.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.4.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi: 10.1021/jacs.2c06440

4o: methyl 3-(5-(5-chloro-2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzoate



4o was synthesized according to the general procedure **B** with Ataluren methyl ester (60 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), $Mg(OTf)_2$ (6.4 mg, 0.02 mmol, 0.1 eq.), NaCl (48 mg, 0.8 mmol, 4.0 eq.), oxone (369 mg, 0.6 mmol, 3.0 eq.), HFIP (1.0 mL) under air at 100 °C for 36 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 10:1) on silica gel to give 29 mg (43%) of methyl 3-(5-(5-chloro-2-fluorophenyl)-1,2,4-oxadiazol-3-yl)benzoate as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.83 (t, *J* = 1.7 Hz, 1H), 8.36 (dt, *J* = 7.8, 1.5 Hz, 1H), 8.23 (dd, *J* = 5.9, 2.7 Hz, 1H), 8.21 (dt, *J* = 7.8, 1.5 Hz, 1H), 7.61 (t, *J* = 7.8 Hz, 1H), 7.57 (ddd, *J* = 8.9, 4.2, 2.7 Hz, 1H), 7.26 (t, *J* = 8.3Hz, 1H), 3.98 (s, 3H).

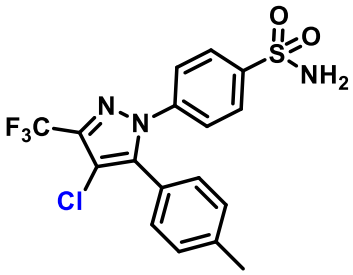
^{13}C NMR (151 MHz, $CDCl_3$) δ 172.1 (d, $^4J_{C-F}$ = 4.5 Hz), 168.3, 166.5, 159.4 (d, $^1J_{C-F}$ = 261.3 Hz), 134.6 (d, $^3J_{C-F}$ = 8.5 Hz), 132.5, 131.9, 131.2, 130.6 (d, $^4J_{C-F}$ = 1.4 Hz), 130.3(d, $^4J_{C-F}$ = 3.7 Hz), 128.9, 127.1, 118.8 (d, $^2J_{C-F}$ = 22.7 Hz), 114.1 (d, $^3J_{C-F}$ = 13.0 Hz), 52.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.8.

Known compound, data are consistent with those reported in the literature:

Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425. doi: 10.1021/jacs.2c06440

4p: 4-(4-chloro-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide



4p was synthesized according to the general procedure **A** with Celecoxib (76 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA/Et_3N = 100:20:1) on silica gel to give 71 mg (85%) of 4-(4-chloro-5-(p-tolyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.24 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.9 Hz, 2H), 5.18 (s, 2H), 2.40 (s, 3H).

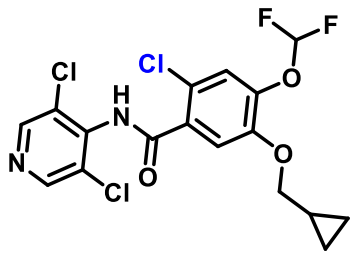
^{13}C NMR (151 MHz, $CDCl_3$) δ 142.3, 142.0, 141.7, 140.7 (q, $^2J_{C-F}$ = 37.8 Hz), 140.7, 130.1, 129.8, 127.7, 125.2, 123.4, 120.5 (q, $^1J_{C-F}$ = 270.1 Hz), 109.9, 21.6.

^{19}F NMR (565 MHz, $CDCl_3$) δ -62.7.

Known compound, data are consistent with those reported in the literature:

Wang Y, Bi C, Kawamata Y, et al. Discovery of N–X anomeric amides as electrophilic halogenation reagents[J]. Nature Chemistry, 2024, 16(9): 1539-1545. doi: 10.1038/s41557-024-01539-4

4q: 2-chloro-5-(cyclopropylmethoxy)-*N*-(3,5-dichloropyridin-4-yl)-4-(difluoromethoxy)benzamide



4q was synthesized according to the general procedure **A** with Roflumilast (0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 5:1) on silica gel to give 43 mg (49%) of 2-chloro-5-(cyclopropylmethoxy)-*N*-(3,5-dichloropyridin-4-yl)-4-(difluoromethoxy)benzamide as white solid

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.57 (s, 2H), 8.39 (s, 1H), 7.53 (s, 1H), 7.29 (s, 1H), 6.74 (t, *J* = 74.4 Hz, 1H), 3.93 (d, *J* = 6.9 Hz, 2H), 1.32 – 1.27 (m, 1H), 0.69 – 0.66 (m, 2H), 0.38 – 0.36 (m, 2H).

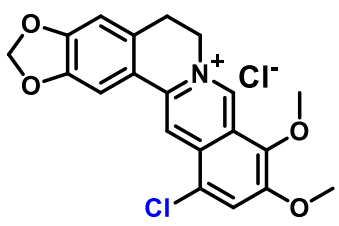
^{13}C NMR (151 MHz, $CDCl_3$) δ 162.2, 149.8, 148.5, 142.9, 139.5, 130.0, 129.6, 124.4, 122.4, 116.9, 115.6 (t, $^1J_{C–F}$ = 264 Hz), 74.7, 10.1, 3.5.

^{19}F NMR (565 MHz, $CDCl_3$) δ -82.3, -82.4.

Known compound, data are consistent with those reported in the literature:

Wang Y, Bi C, Kawamata Y, et al. Discovery of N–X anomeric amides as electrophilic halogenation reagents[J]. Nature Chemistry, 2024, 16(9): 1539-1545. doi: 10.1038/s41557-024-01539-4

4r: 12-chloro-9,10-dimethoxy-5,6-dihydro-[1,3]dioxolo[4,5-*g*]isoquinolino[3,2-*a*]isoquinolin-7-ium



4r was synthesized according to the general procedure **A** with Berberine (74 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 equiv), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (DCM/MeOH = 20:1) on silica gel to give 49 mg (60%) of 12-chloro-9,10-dimethoxy-5,6-dihydro-[1,3]dioxolo[4,5-*g*]isoquinolino[3,2-*a*]isoquinolin-7-ium as yellow solid.

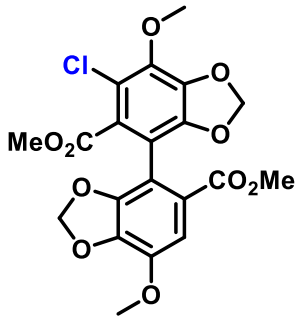
^{1}H NMR (600 MHz, $CDCl_3$) δ 10.86 (s, 1H), 8.36 (s, 1H), 7.85 (s, 1H), 7.36 (s, 1H), 6.83 (s, 1H), 6.10 (s, 2H), 5.41 (t, *J* = 6.2 Hz, 2H), 4.34 (s, 3H), 4.06 (s, 3H), 3.31 (t, *J* = 5.8 Hz, 2H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 151.2, 150.7, 148.9, 148.7, 145.8, 138.9, 131.3, 130.5, 126.0, 125.7, 122.8, 120.2, 116.2, 108.9, 105.3, 102.4, 63.5, 57.5, 55.9, 27.7.

Known compound, data are consistent with those reported in the literature:

Li W, Huang S, Jiang M, et al. An Efficient and Eco-Friendly Synthesis of Protoberberine and 13-Me Protoberberine Alkaloids via Electrochemical Acceptorless Dehydrogenation[J]. ChemCatChem, 2023, 15(7): e202201553. doi: 10.1002/anie.202100897

4s: 6-chloro-7,7'-dimethoxy-[4,4'-bibenzo[*d*][1,3]dioxole]-5,5'-dicarboxylate



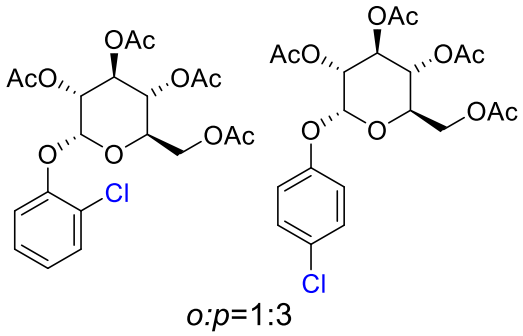
4s was synthesized according to the general procedure **A** with Bifendate (83 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 eq.), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give 54 mg (60%) of dimethyl 6-chloro-7,7'-dimethoxy-[4,4'-bibenzo[*d*][1,3]dioxole]-5,5'-dicarboxylate as white solid.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.31 (s, 1H), 6.04 – 5.98 (m, 4H), 4.07 (s, 3H), 3.95 (s, 3H), 3.70 (s, 3H), 3.60 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 165.8, 147.0, 140.0, 138.1, 127.8, 117.9, 108.0, 102.5, 60.4, 52.5.

HRMS *m/z* (ESI): calcd. for $C_{20}H_{18}ClO_{10}$ $[M+H]^+$:453.0583, found: 453.0576.

4t: 2-(acetoxymethyl)-6-(2-chlorophenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate and 2-(acetoxymethyl)-6-(4-chlorophenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate



4t was synthesized according to the general procedure **A** with 2-(acetoxymethyl)-6-phenoxytetrahydro-2*H*-pyran-3,4,5-triyl triacetate (84 mg, 0.2 mmol, 1.0 eq.), 2-iodobenzenesulphonic acid (5.6 mg, 0.02 mmol, 0.1 equiv), NaCl (24 mg, 0.4 mmol, 2.0 eq.), oxone (246 mg, 0.4 mmol, 2.0 eq.), DCE/HFIP (2/1, 1.0 mL) under air at 100 °C for 24 hours, then the mixture was cooled to room temperature. Following filtration and washing of the solid with DCM, the combined organic phase was concentrated under reduced pressure and the residue was purified using flash column chromatography (PE/EA = 20:1) on silica gel to give an inseparable mixture of 2-(acetoxymethyl)-6-(2-chlorophenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate and 2-(acetoxymethyl)-6-(2-chlorophenoxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (3:1, 83 mg, 91%) as colorless oil.

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.39 (m, 0.21H), 7.24 (d, *J* = 8.9 Hz, 1.26H),7.17 – 7.13 (m, 0.42H), 7.09 (d, *J* = 9.0 Hz, 0.18H) 7.00 (d, *J* = 9.0 Hz, 1.26H), 5.73 -5.63 (d, *J* = 59.8 Hz, 2H), 5.14 – 5.11 (m, 1H), 5.02 – 5.98 (m, 1H), 4.25 – 4.20 (m, 1.34H), 4.09 – 4.20 (m, 1.77H), 2.06 – 2.02 (m, 12H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 170.54, 170.52, 170.48, 170.43, 170.37, 170.18, 170.16, 170.03, 170.01, 169.71, 169.66, 169.61, 154.66, 152.08, 150.89, 130.64, 130.34, 129.65, 128.82, 128.21, 127.92, 125.46, 124.62, 124.23, 118.43, 118.01, 117.76, 95.96, 95.75, 94.48, 70.63, 70.54, 70.41, 70.00, 69.98, 69.86, 68.65, 68.50, 68.33, 68.30, 68.22, 61.68, 61.64, 61.62, 20.76, 20.74, 20.70, 20.68, 20.66, 20.63.

Known compound, data are consistent with those reported in the literature:

Kumar V, Talisman I J, Bukhari O, et al. Dual role of ionic liquids as phase transfer catalyst and solvent for glycosidation reactions[J]. RSC Advances, 2011, 1(9): 1721-1727. DOI: 10.1039/C1RA00385B

8 Reference

1. Matousek V, Pietrasiak E, Schwenk R, et al. One-pot synthesis of hypervalent iodine reagents for electrophilic trifluoromethylation[J]. The Journal of organic chemistry, 2013, 78(13): 6763-6768.

2. Santschi N, Sarott R C, Otth E, et al. Synthesis, characterization and initial evaluation of 5-nitro-1-(trifluoromethyl)-3*H*-1λ^3, 2-benziodaoxol-3-one[J]. Beilstein journal of organic chemistry, 2014, 10(1): 1-6.

3. Mironova I A, Postnikov P S, Yusubova R Y, et al. Preparation and X-ray structure of 2-iodoxybenzenesulfonic acid (IBS)–a powerful hypervalent iodine (V) oxidant[J]. Beilstein Journal of Organic Chemistry, 2018, 14(1): 1854-1858.

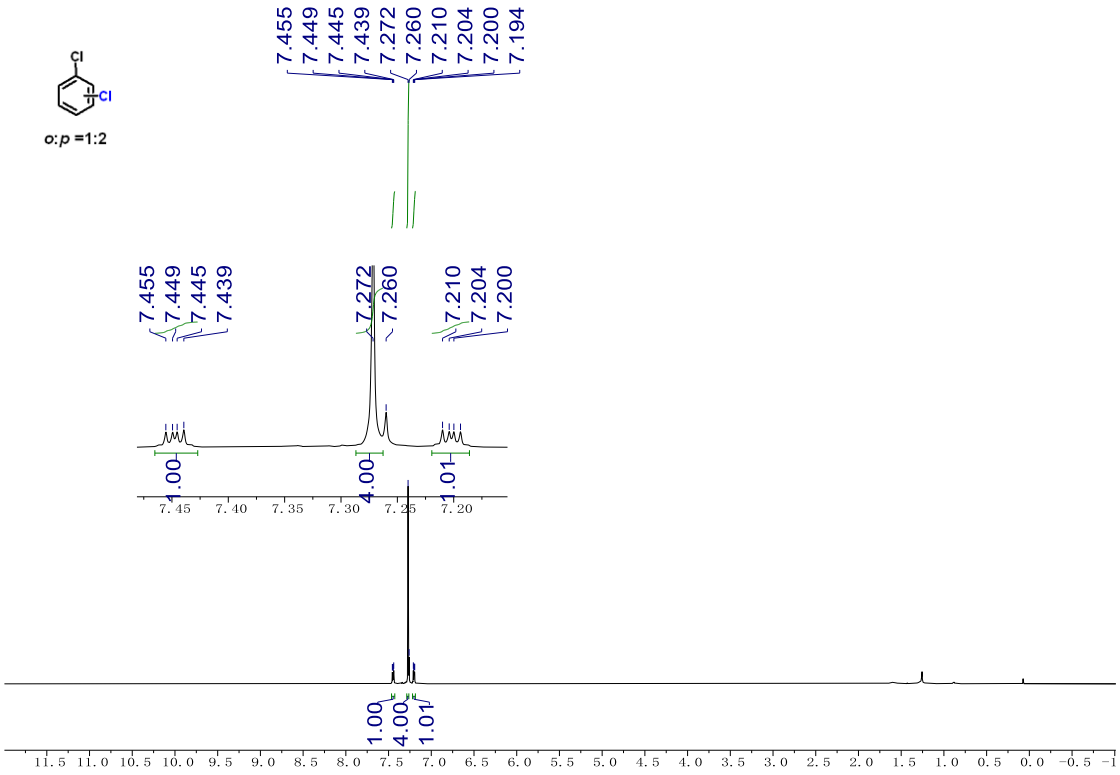
4. Song S, Li X, Wei J, et al. DMSO-catalysed late-stage chlorination of (hetero) arenes[J]. Nature Catalysis, 2020, 3(2): 107-115.

5. Wang W, Yang X, Dai R, et al. Catalytic electrophilic halogenation of arenes with electron-withdrawing substituents[J]. Journal of the American Chemical Society, 2022, 144(29): 13415-13425.

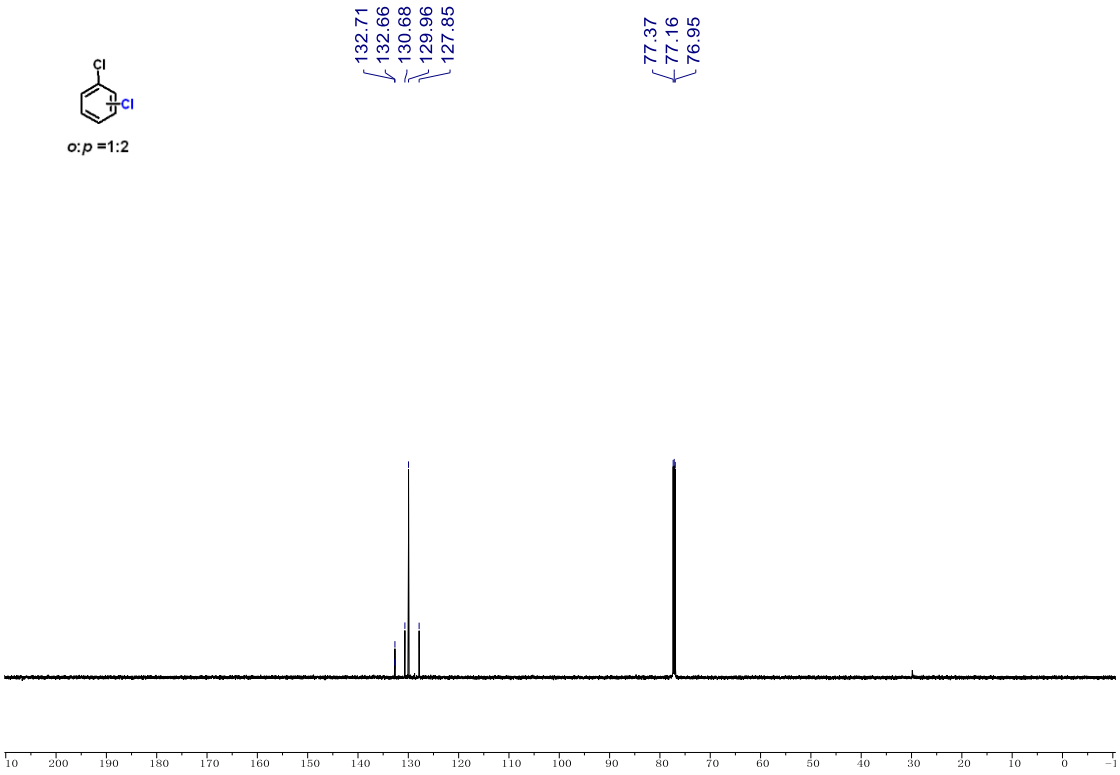
6. Tang R J, Milcent T, Crousse B. Regioselective halogenation of arenes and heterocycles in hexafluoroisopropanol[J]. The Journal of organic chemistry, 2018, 83(2): 930-938.

7. Wang M, Zhang Y, Wang T, et al. Story of an age-old reagent: an electrophilic chlorination of arenes and heterocycles by 1-chloro-1, 2-benziodoxol-3-one[J]. Organic letters, 2016, 18(9): 1976-1979.

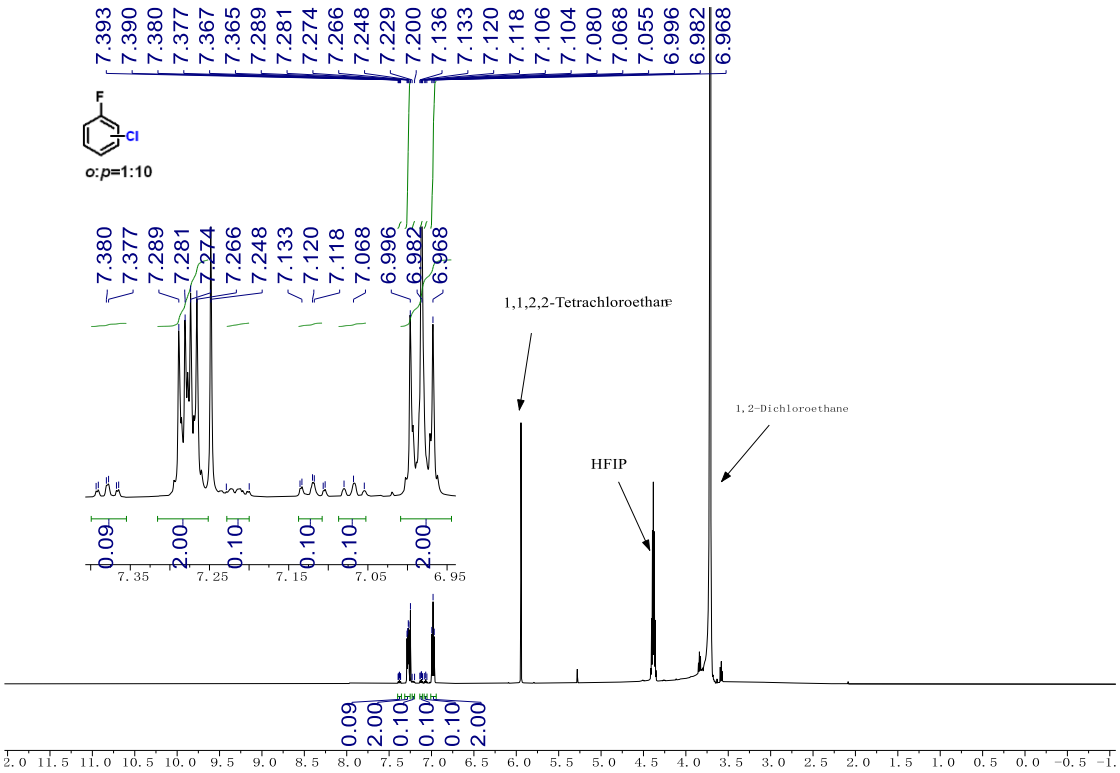
9 NMR spectroscopic data



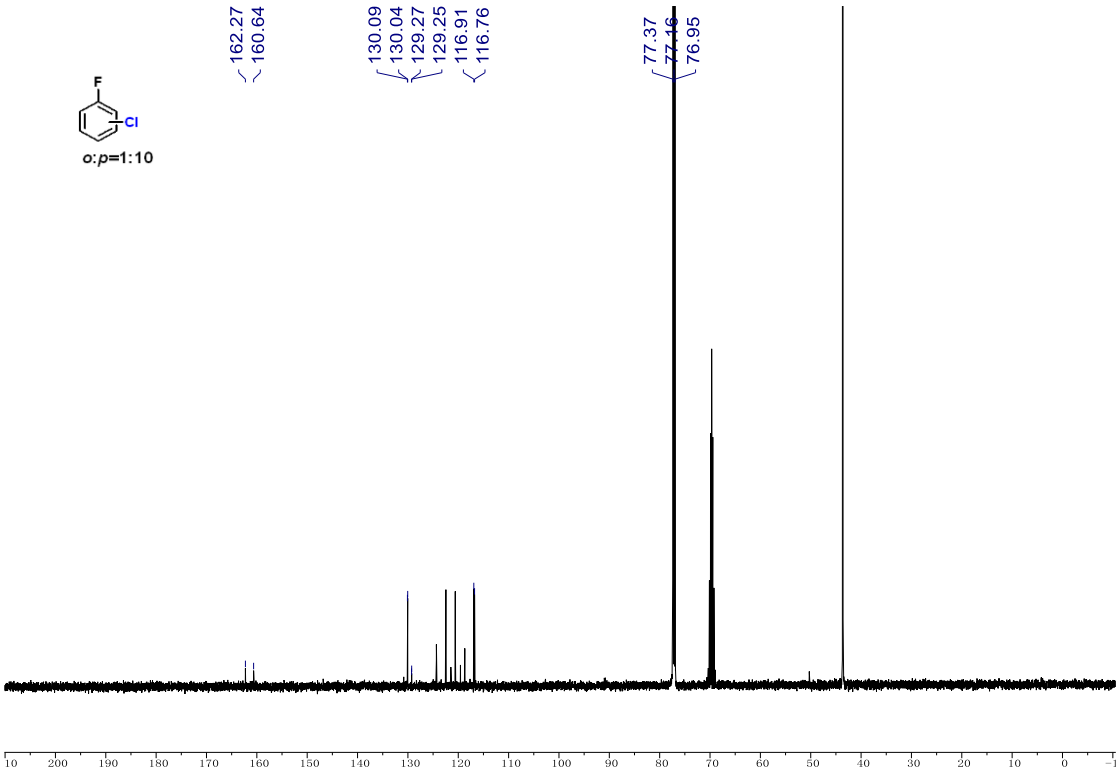
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2a**.



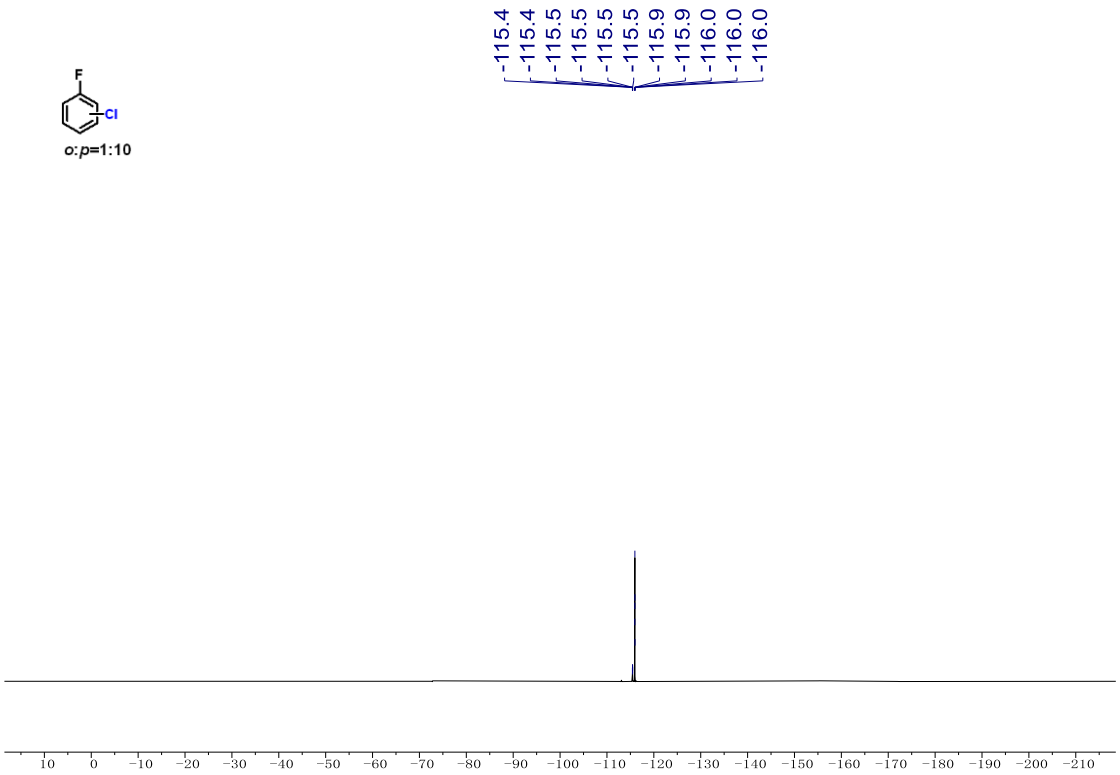
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2a**.



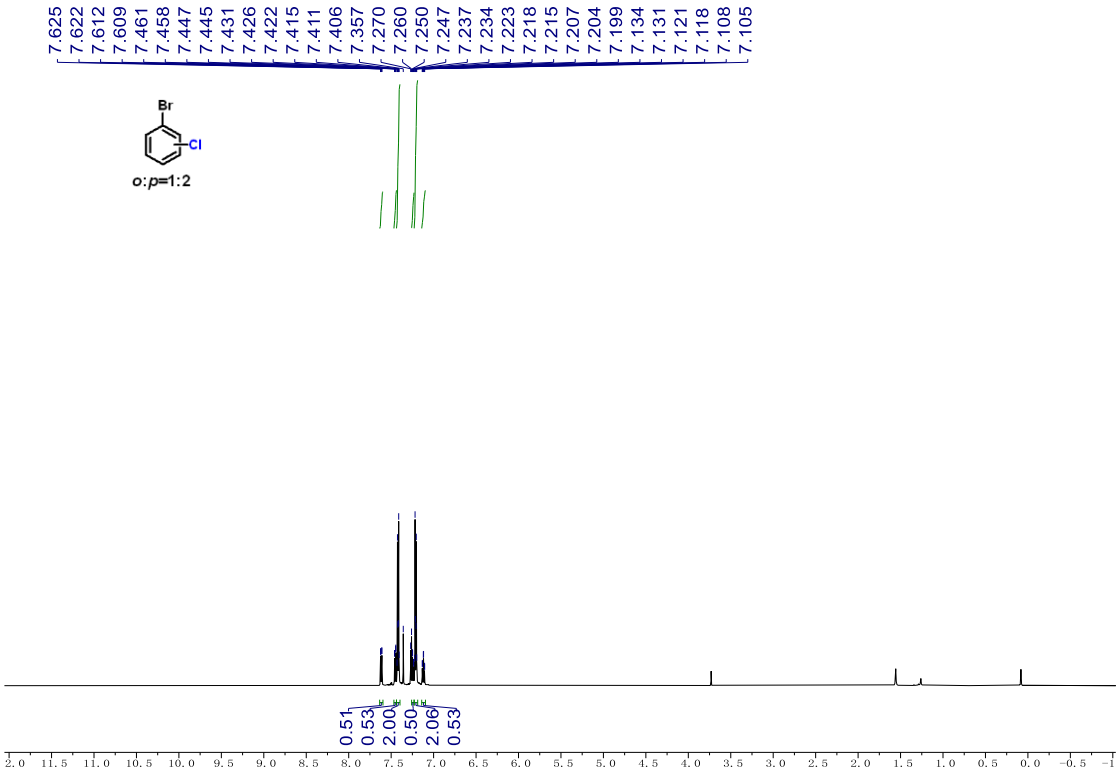
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2b**.



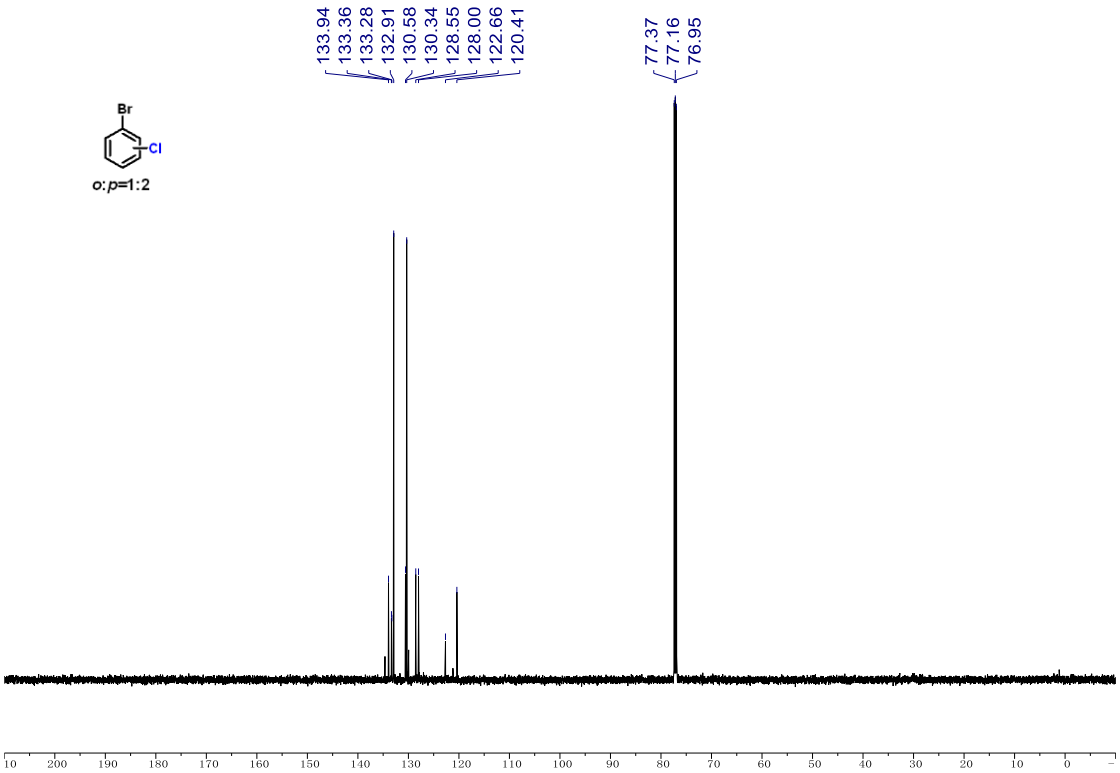
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2b**.



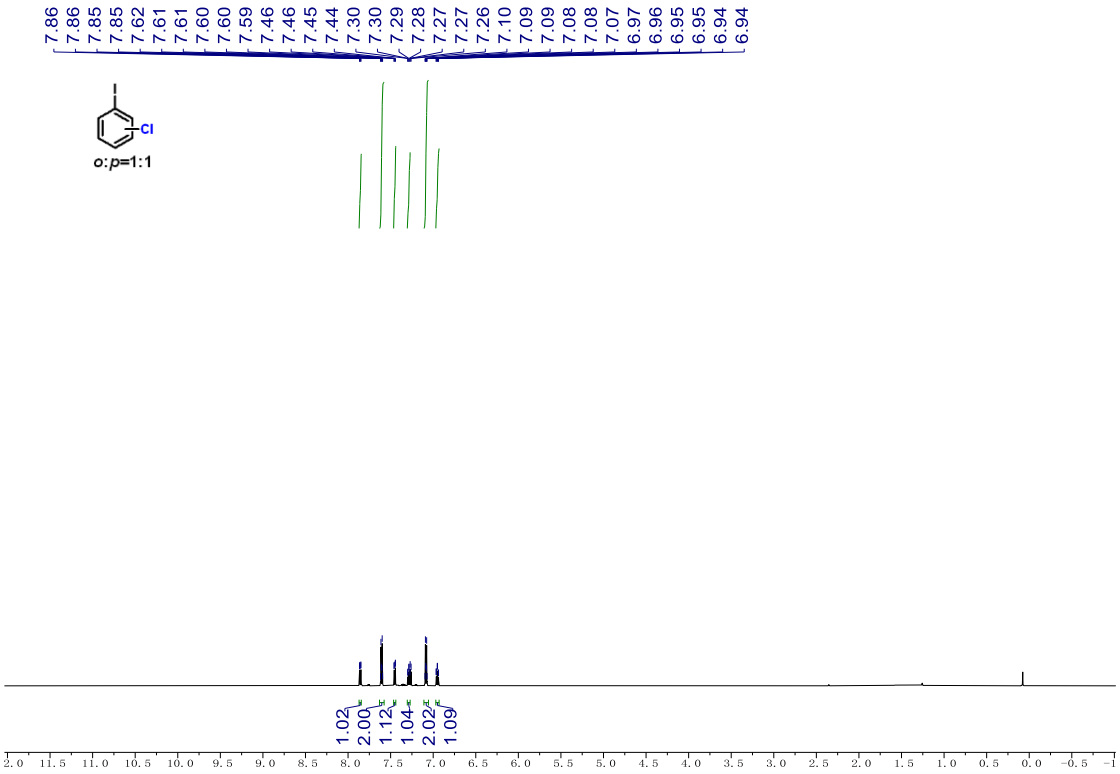
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **2b**



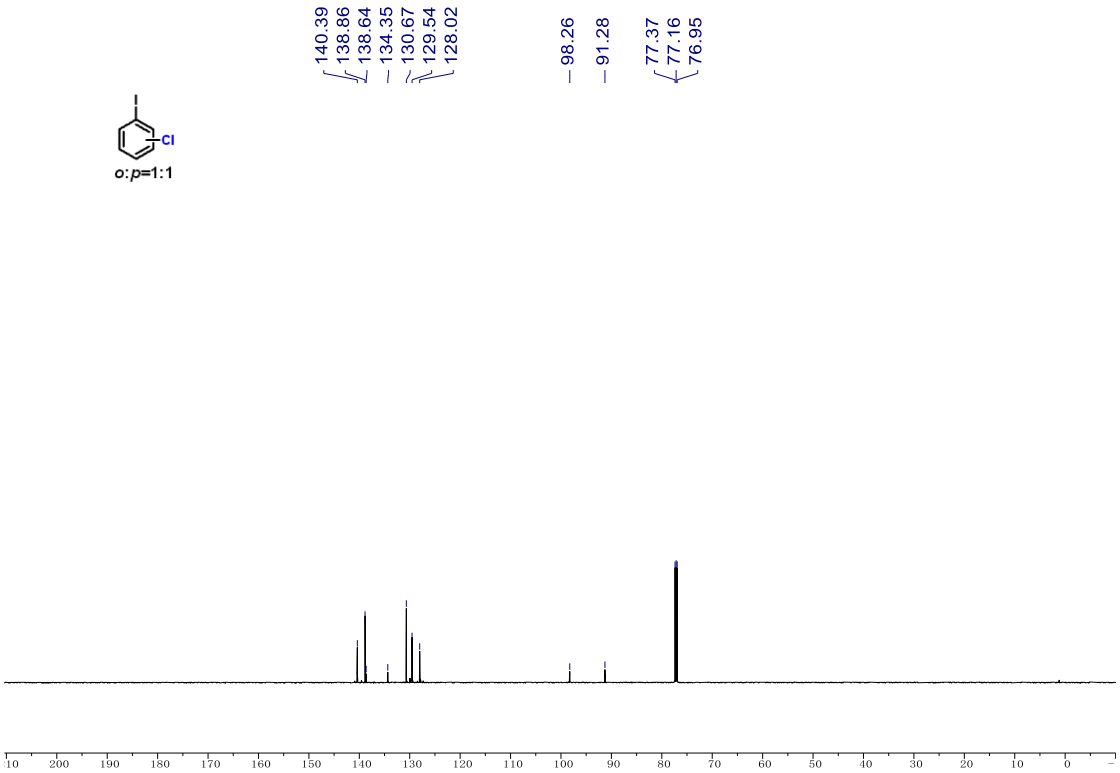
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2c**.



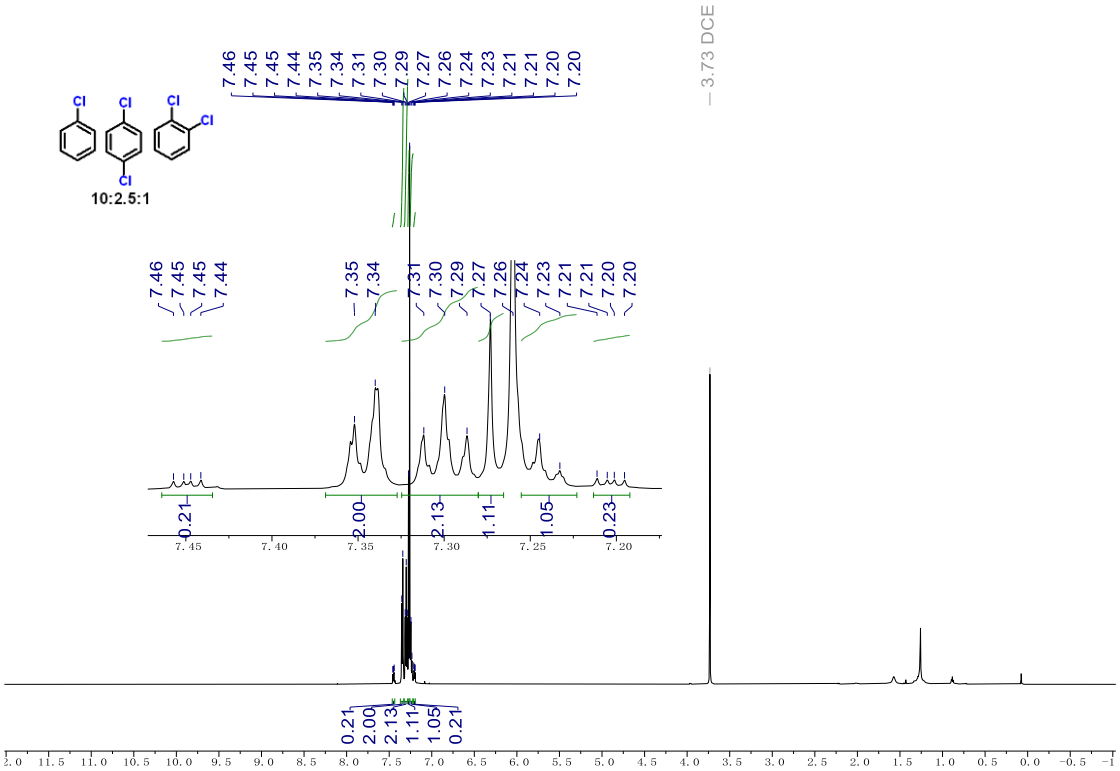
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2c**.



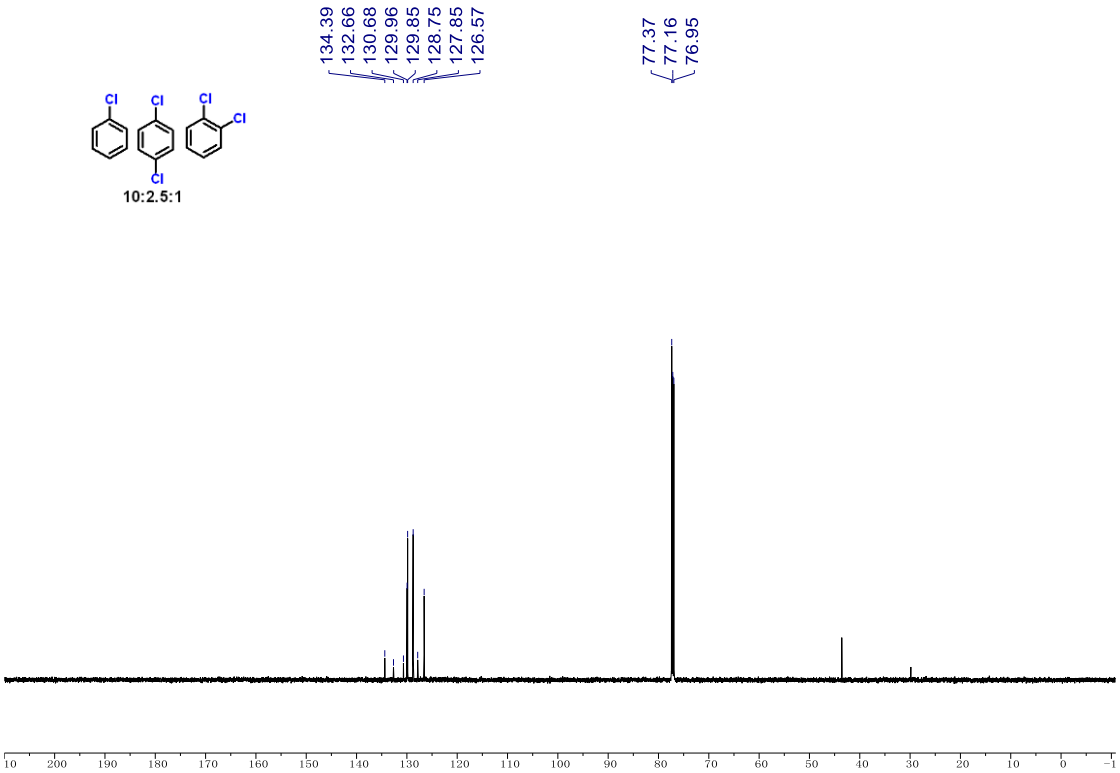
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2d**.



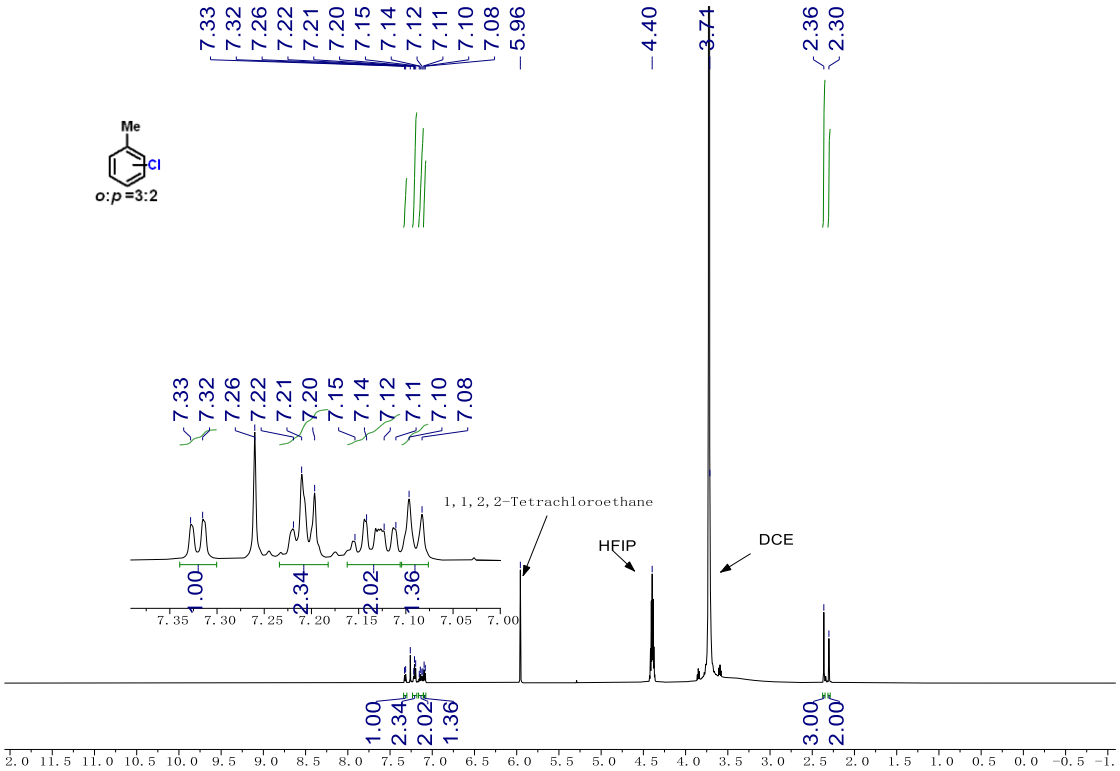
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2d**.



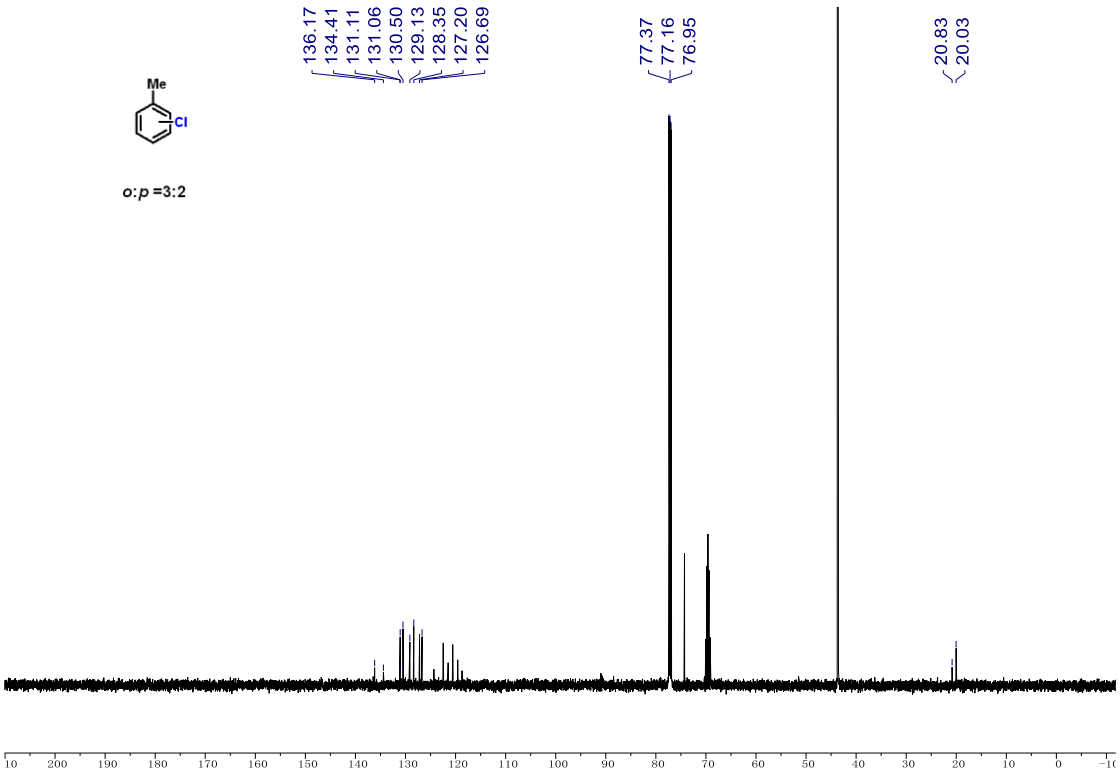
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2e**.



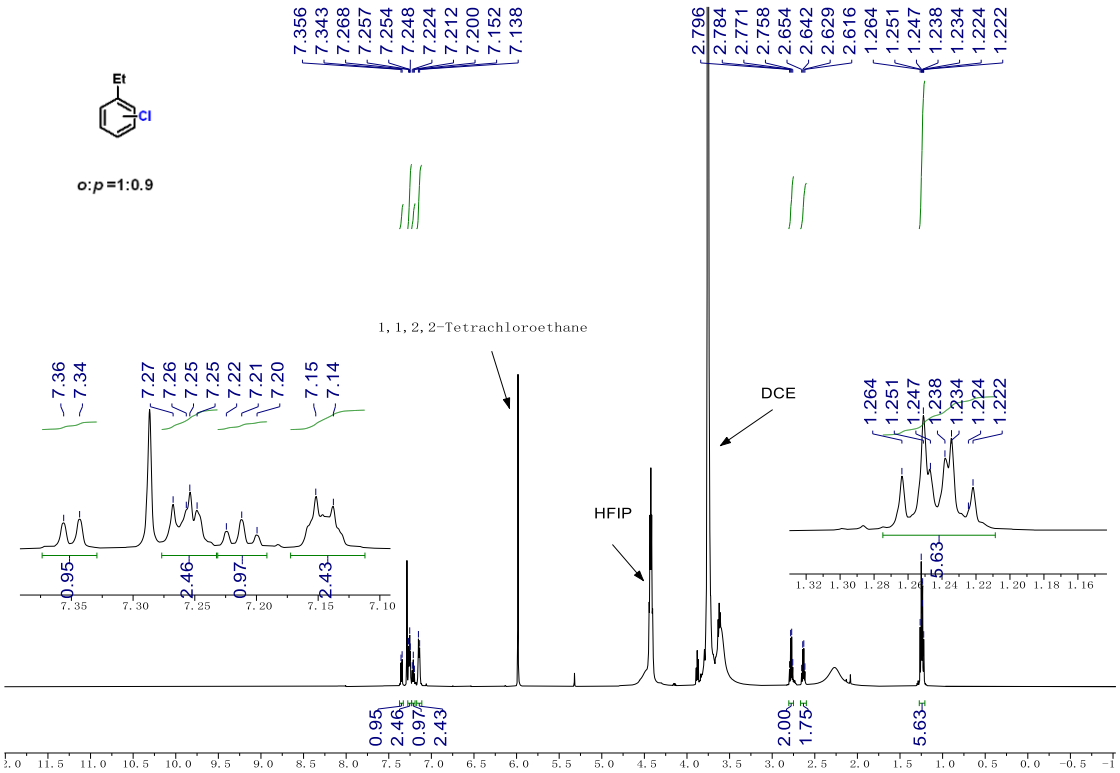
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2e**.



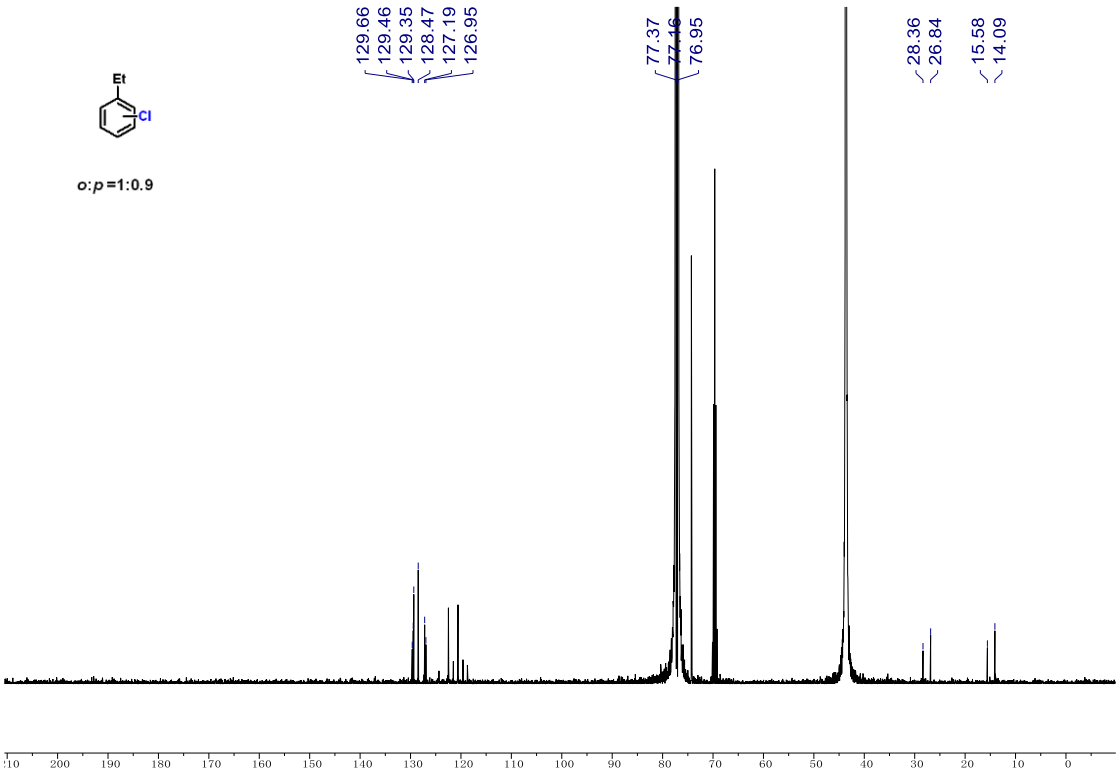
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2f**.



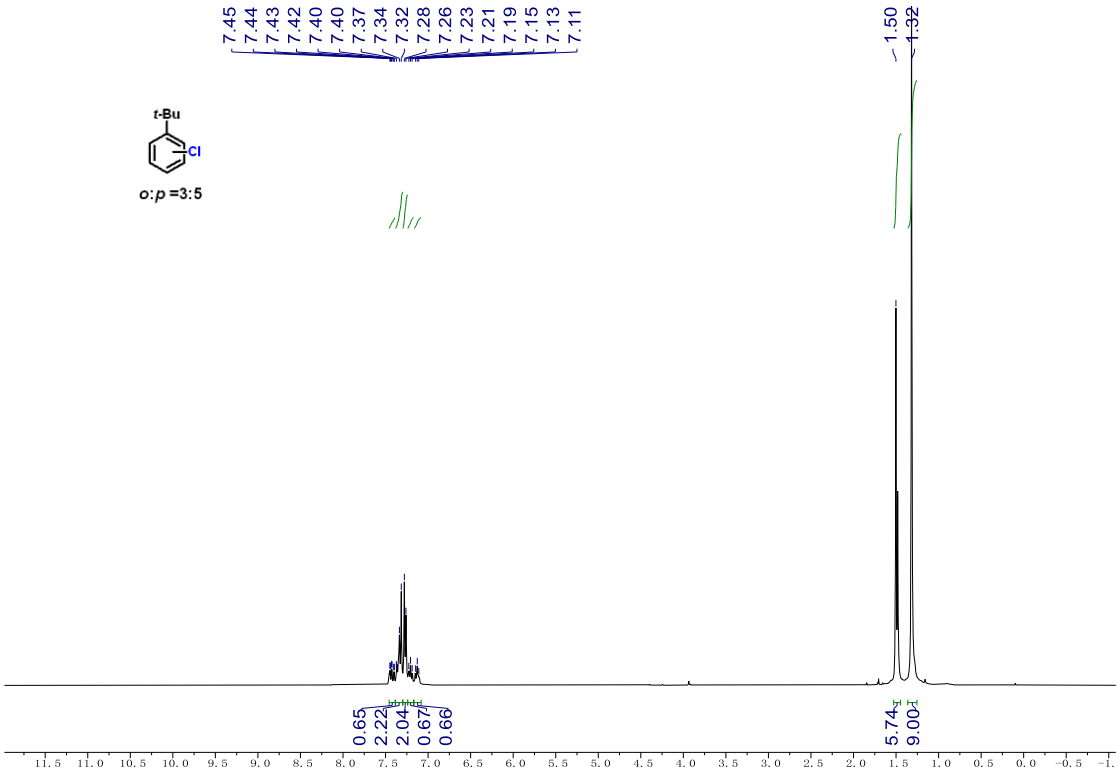
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2f**.



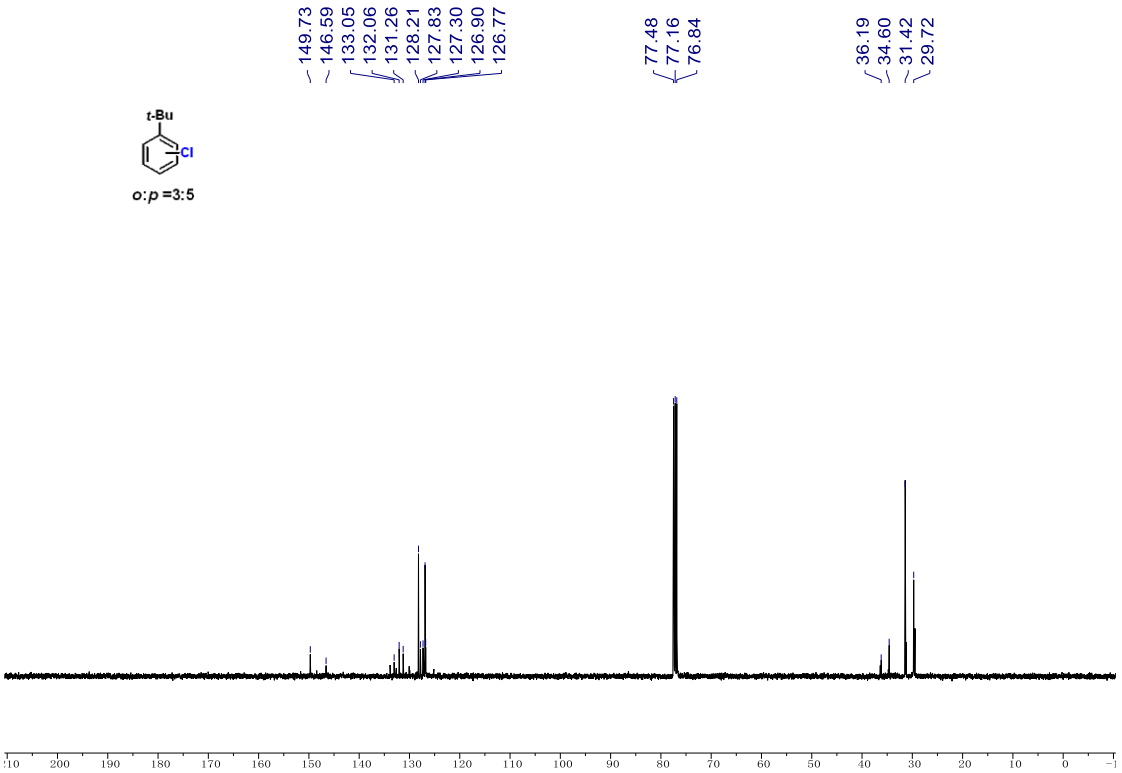
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2g**.



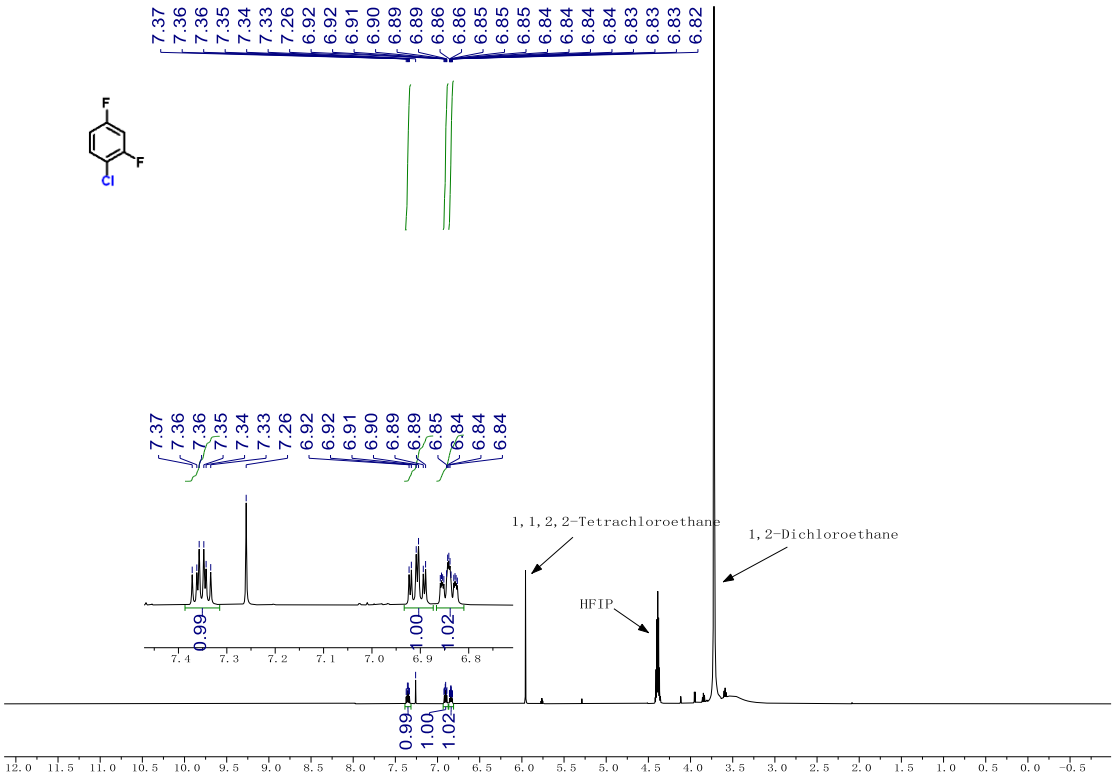
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2g**.



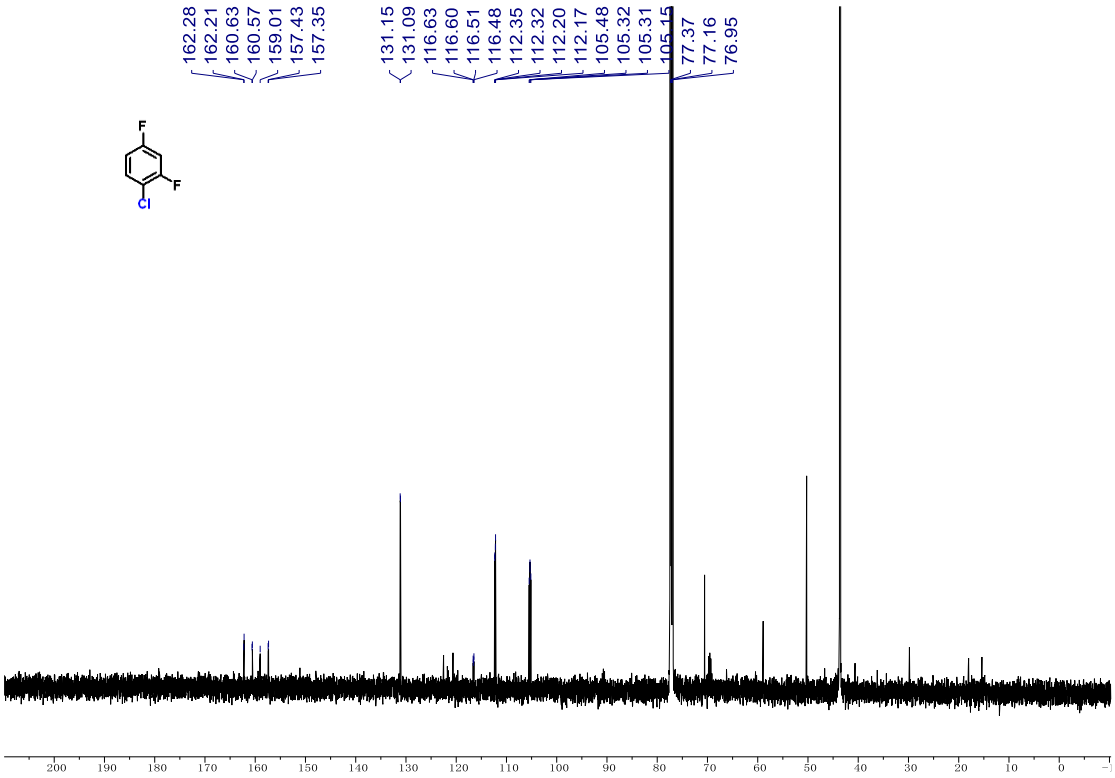
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2h**.



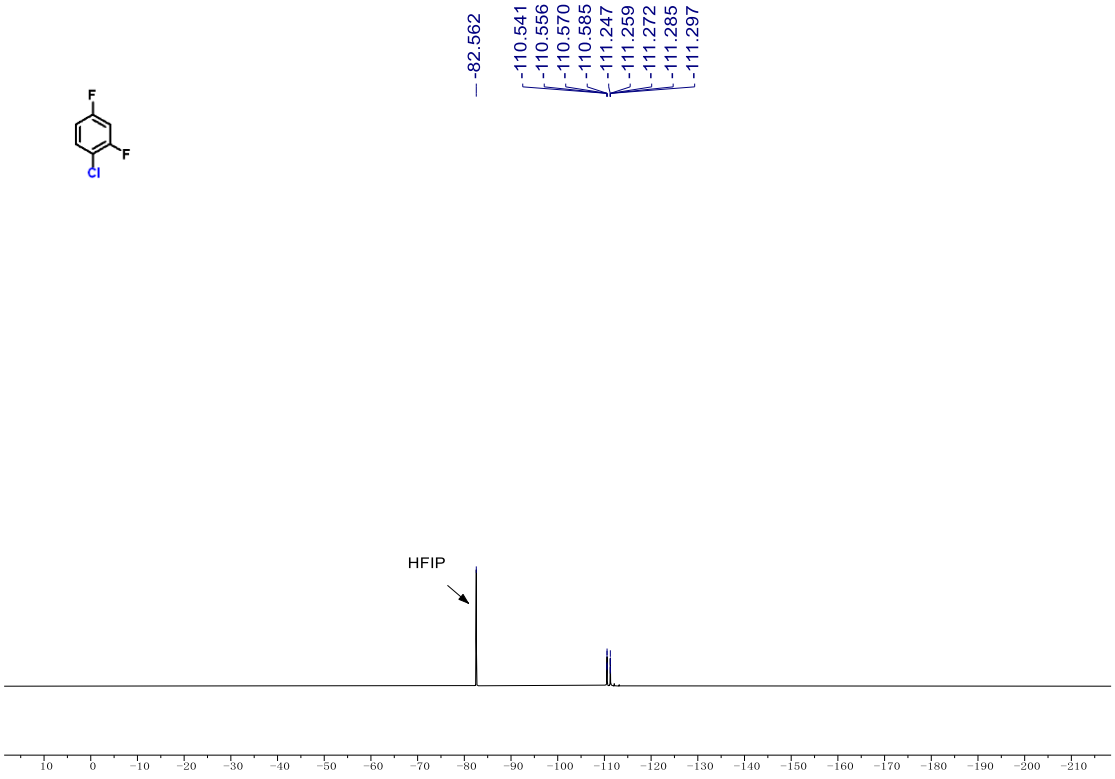
$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) spectrum of **2h**.



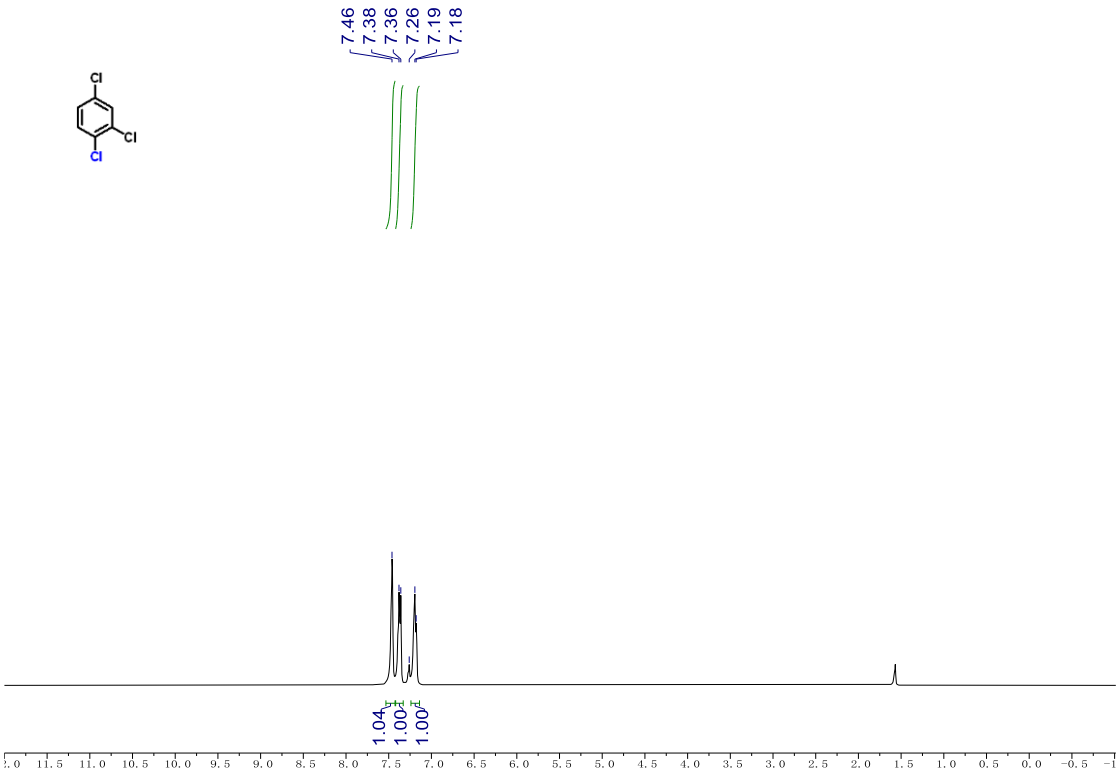
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2i**.



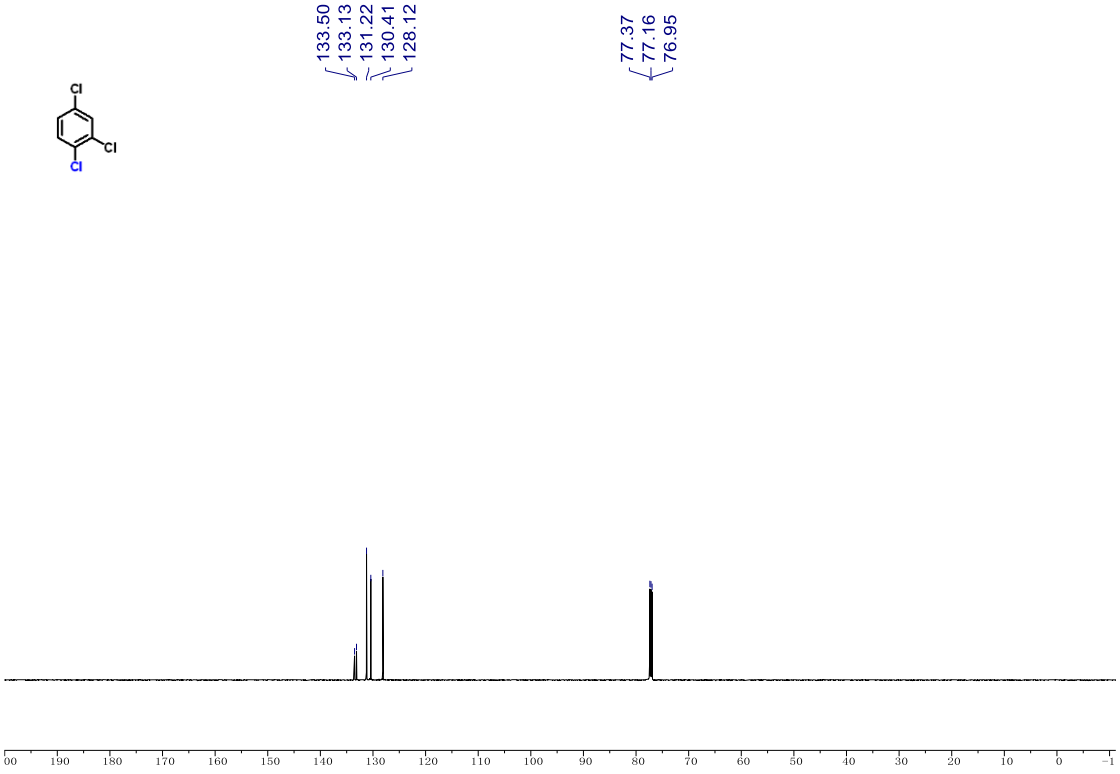
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2i**.



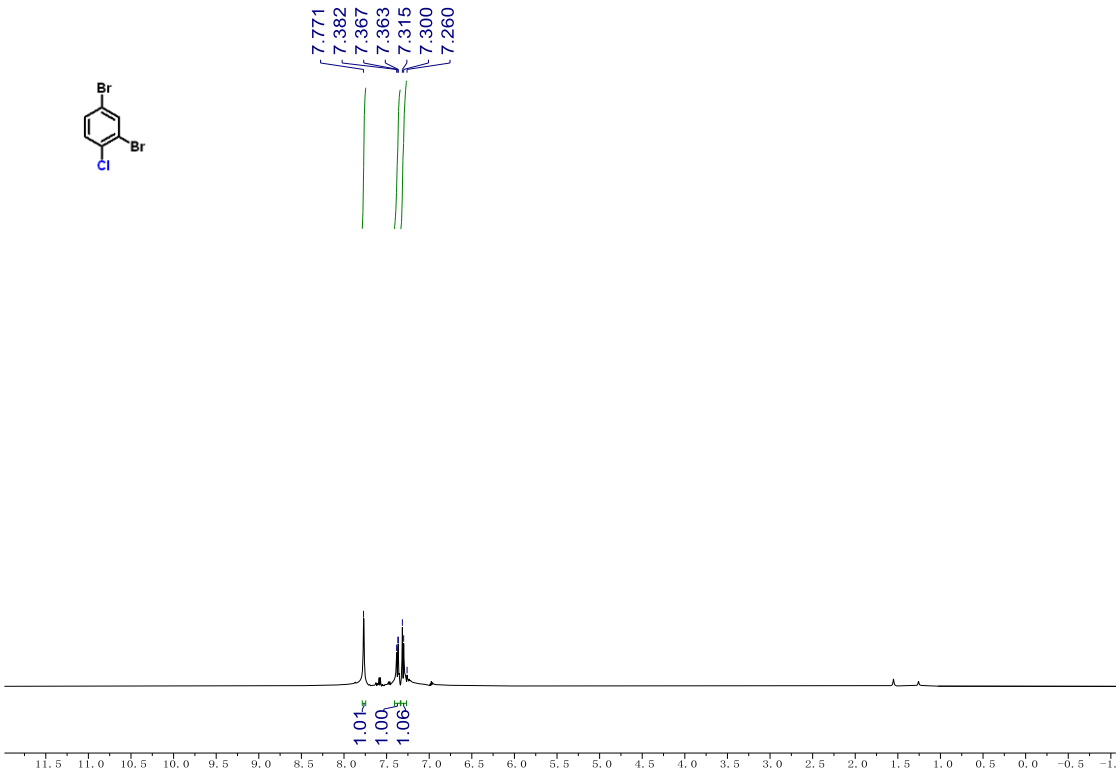
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **2i**



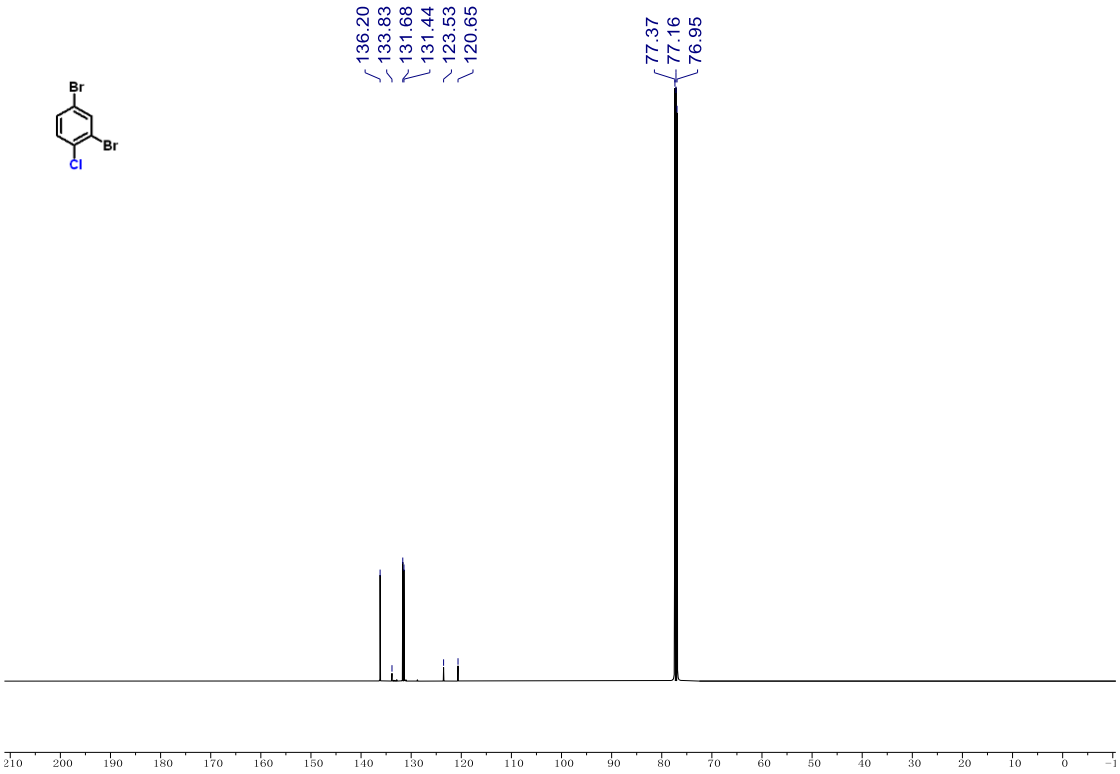
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2j**.



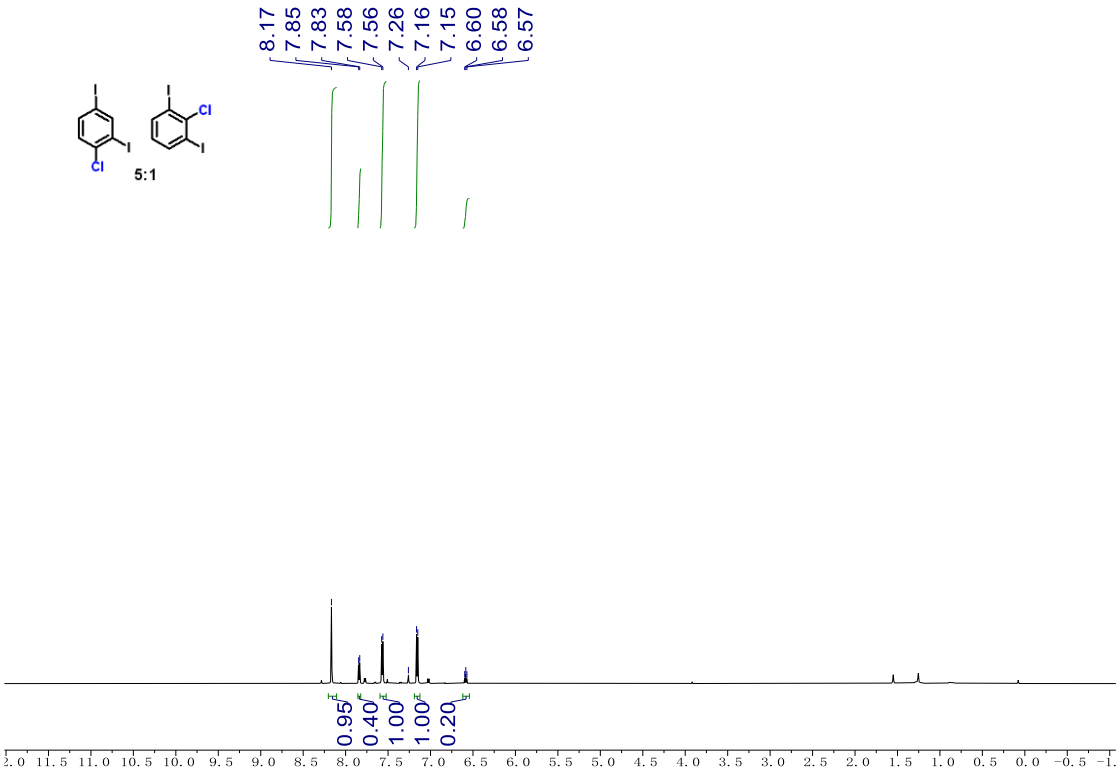
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2j**.



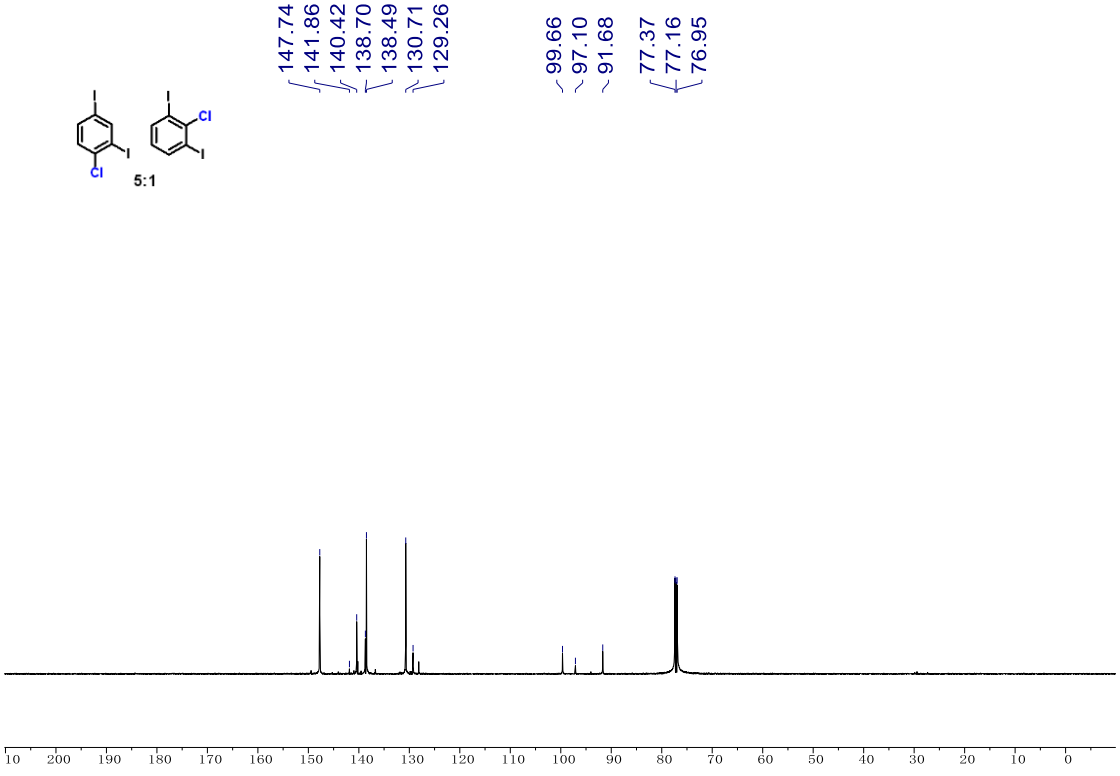
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2k**.



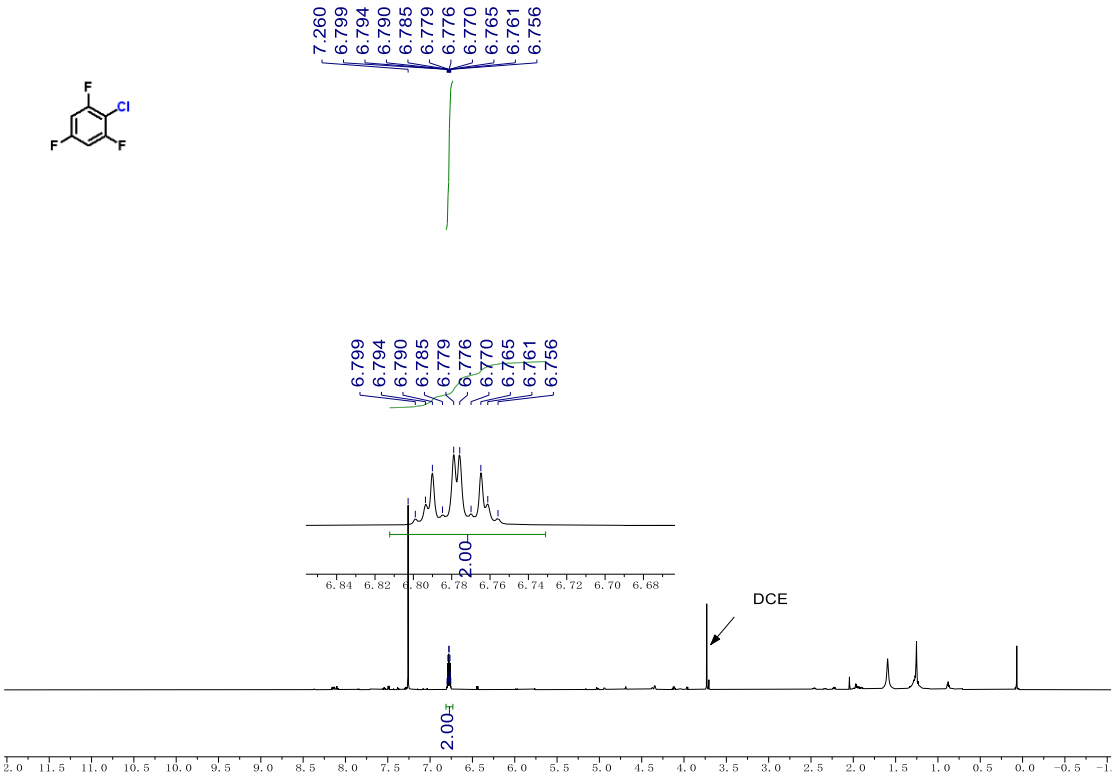
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2k**.



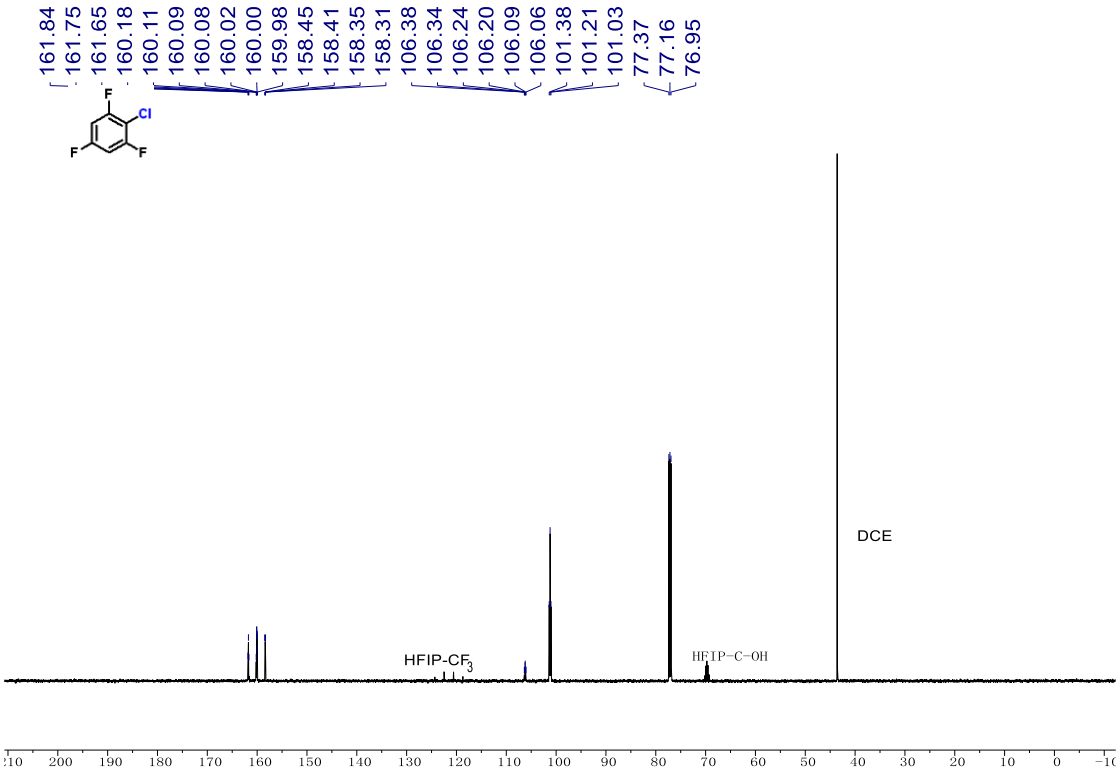
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2l**.



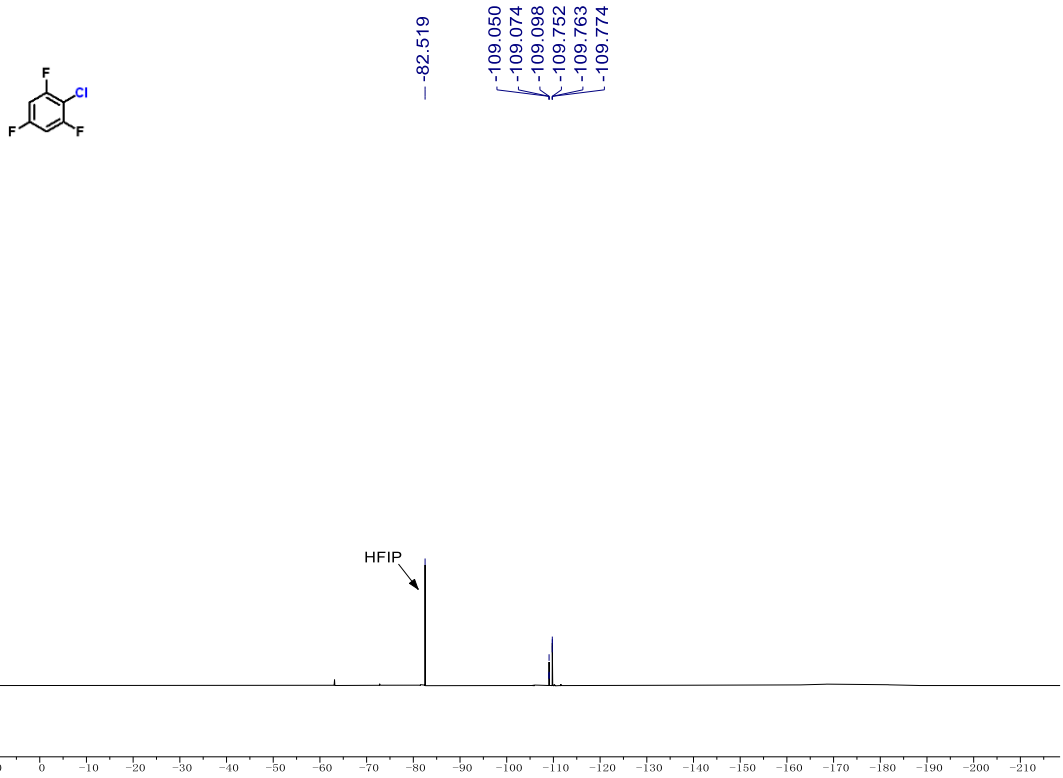
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2l**.



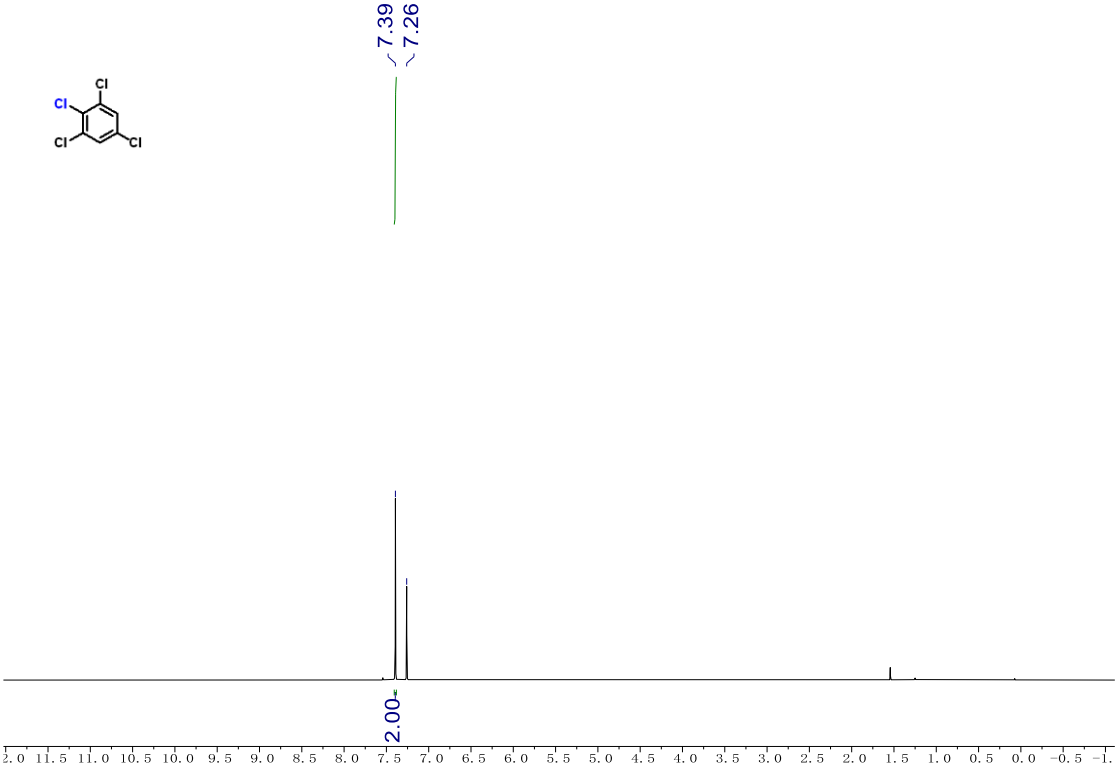
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2m**.



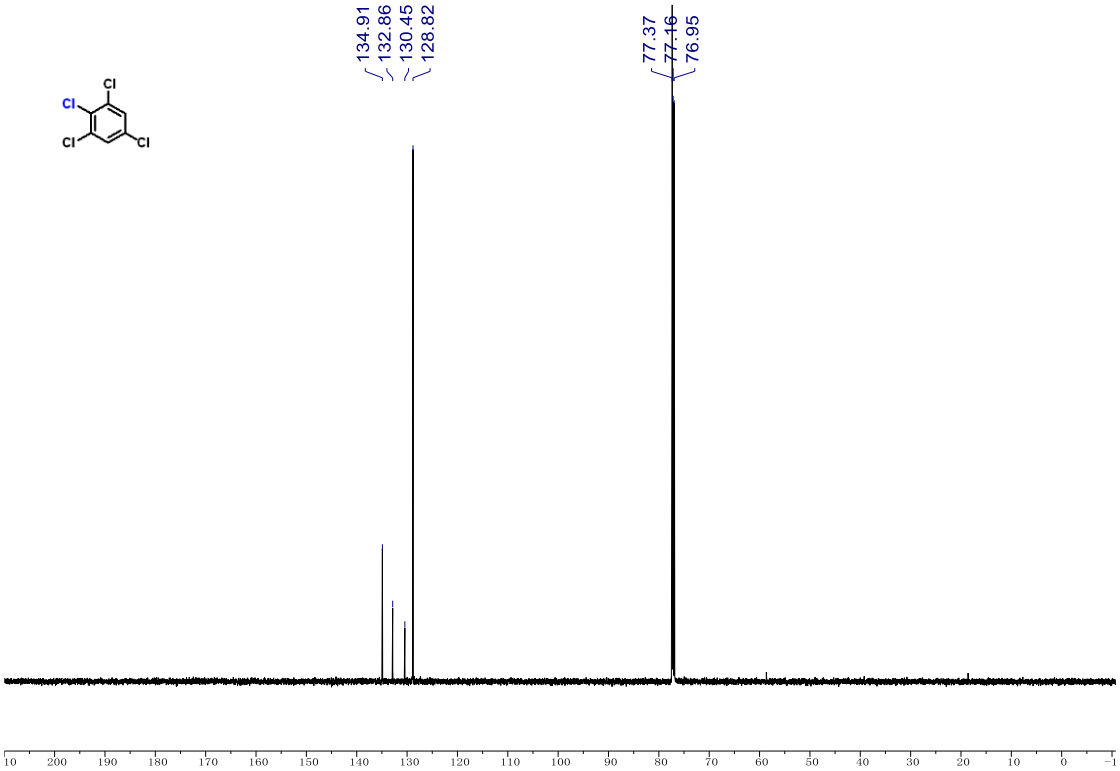
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2m**.



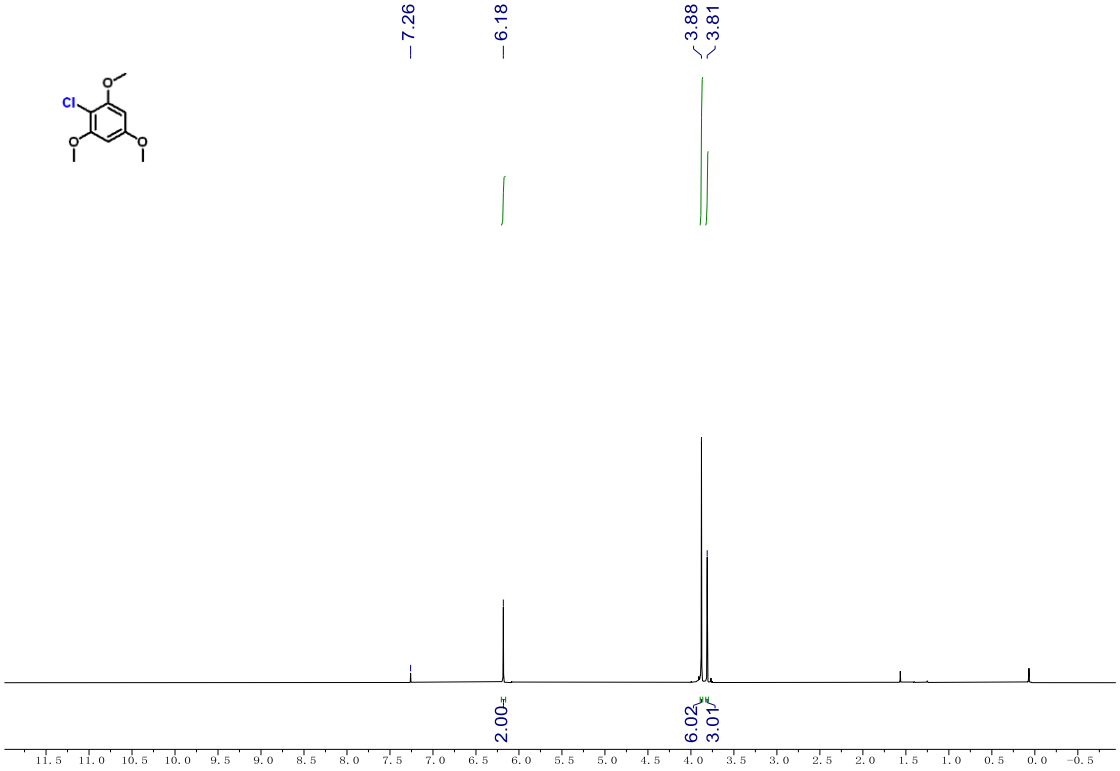
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **2m**



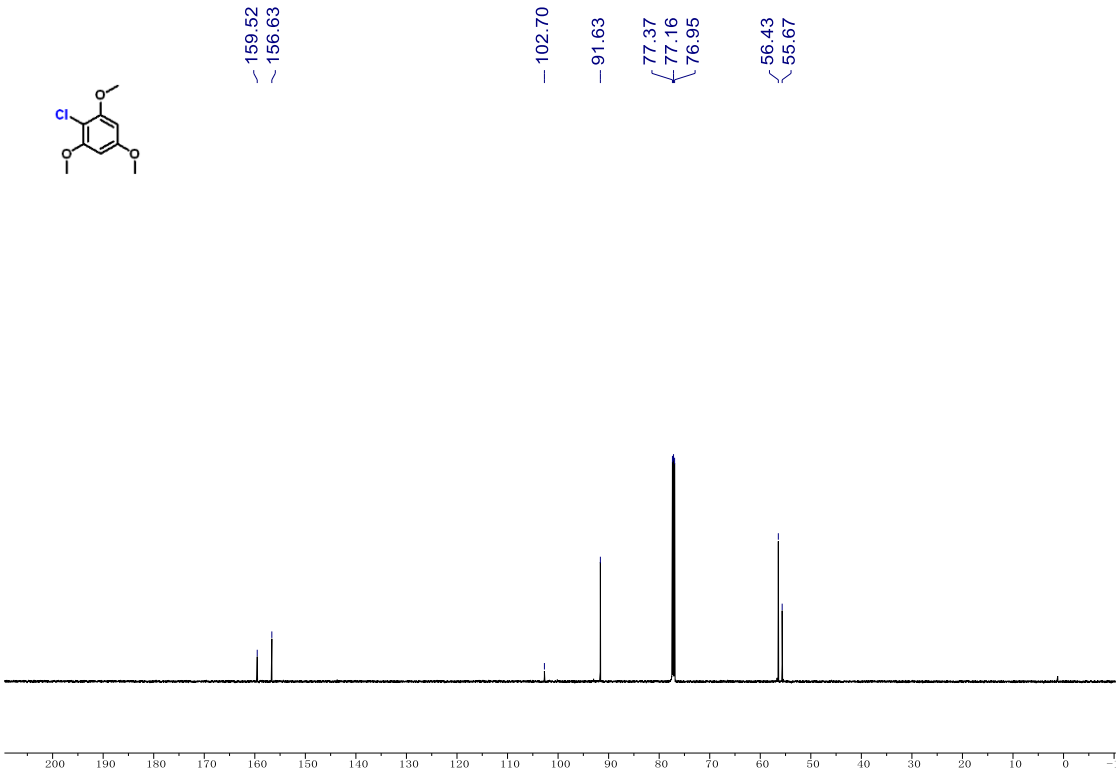
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2n**.



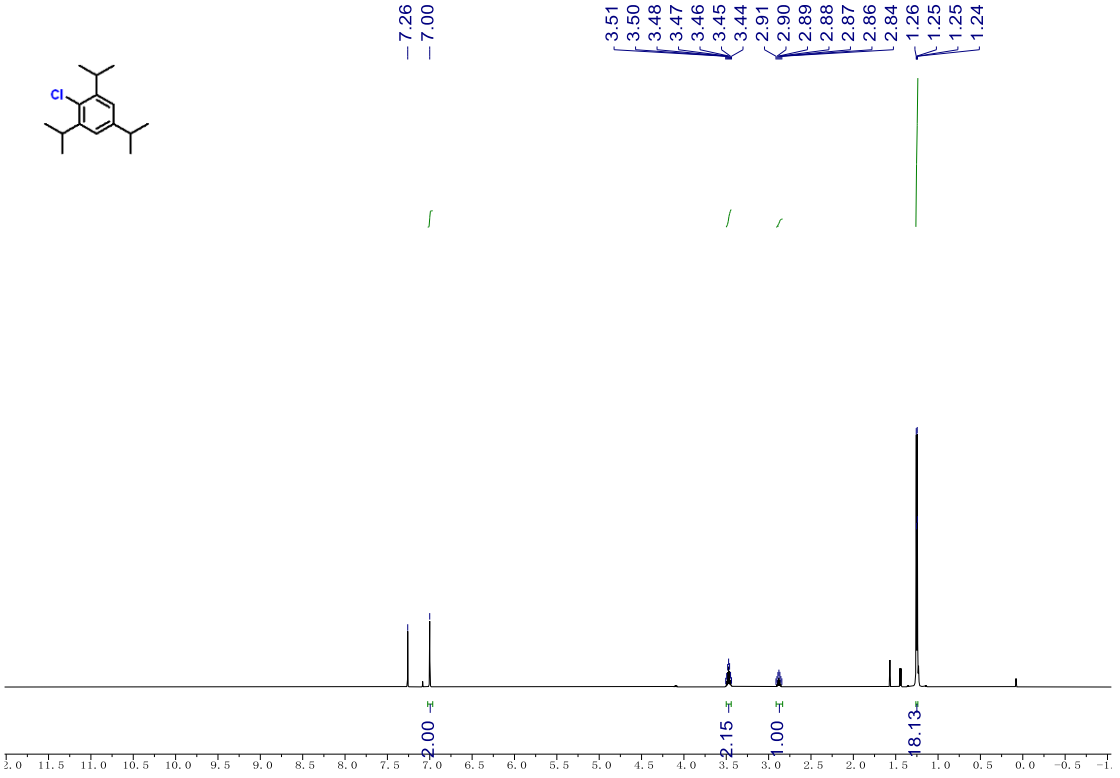
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2n**.



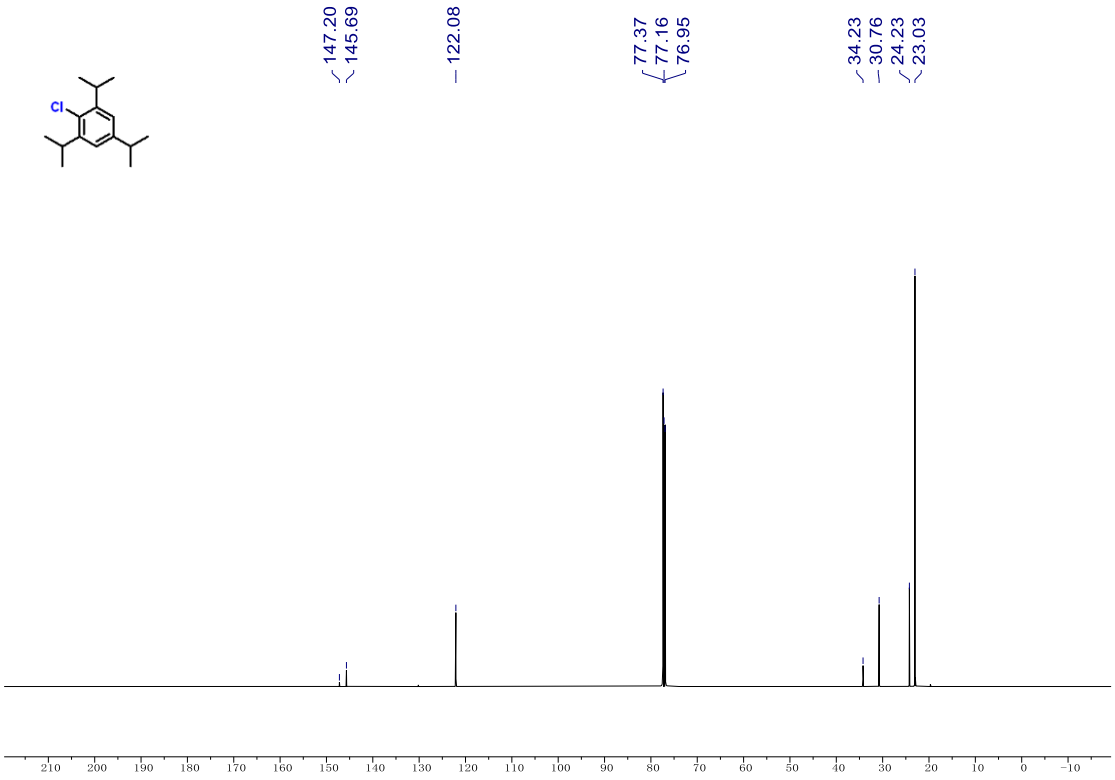
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2o**.



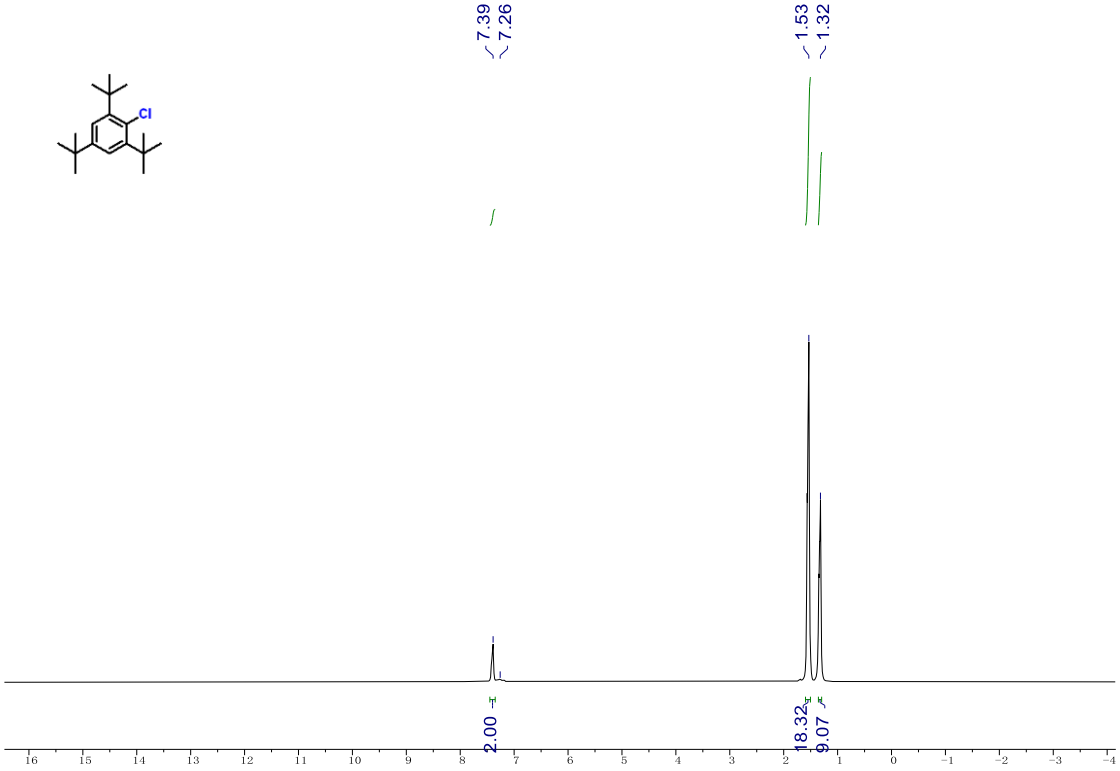
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2o**.



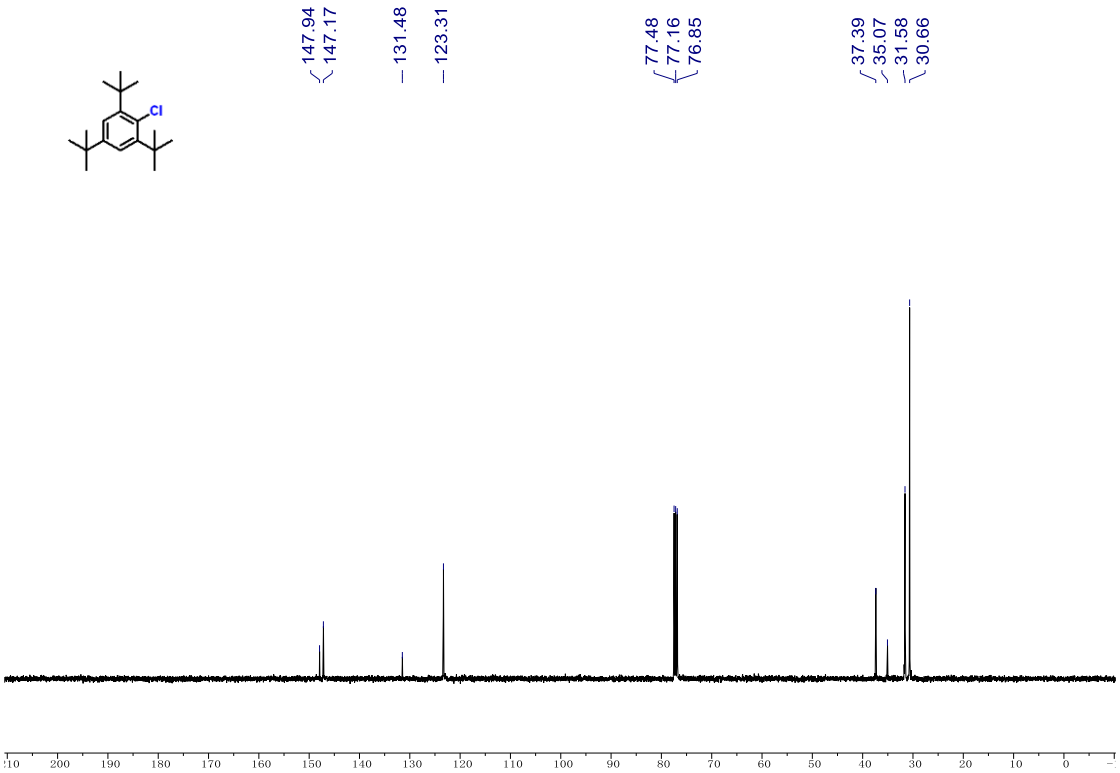
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2p**.



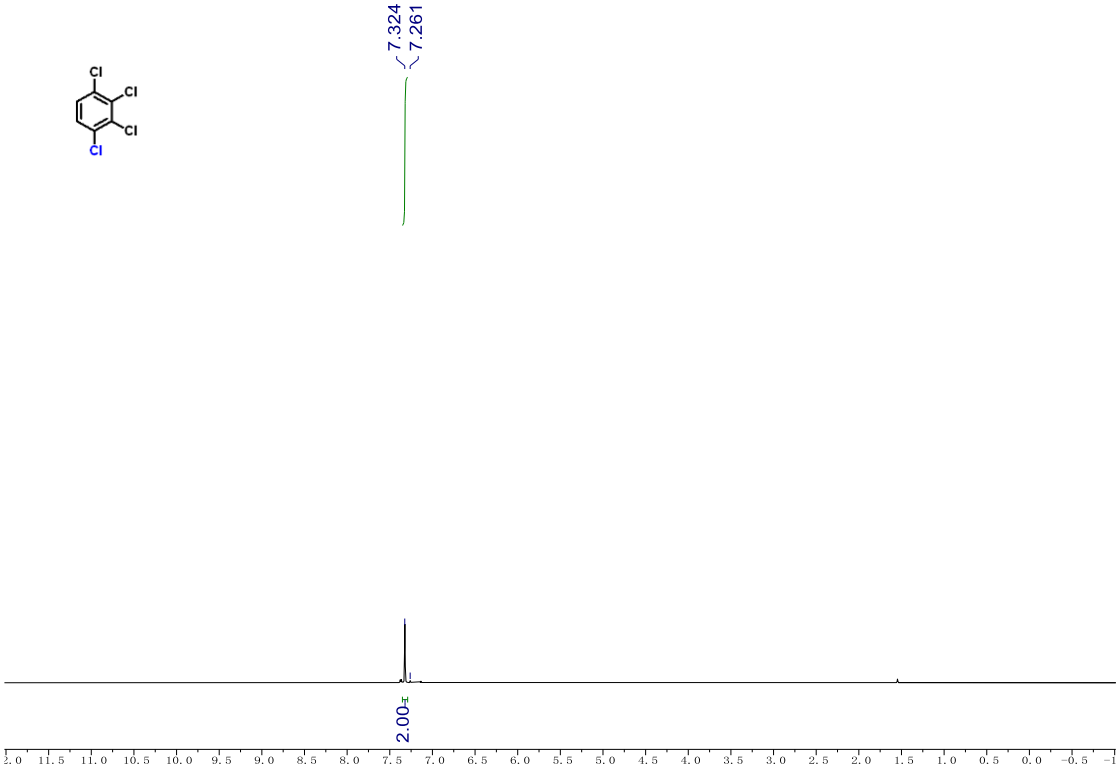
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2p**.



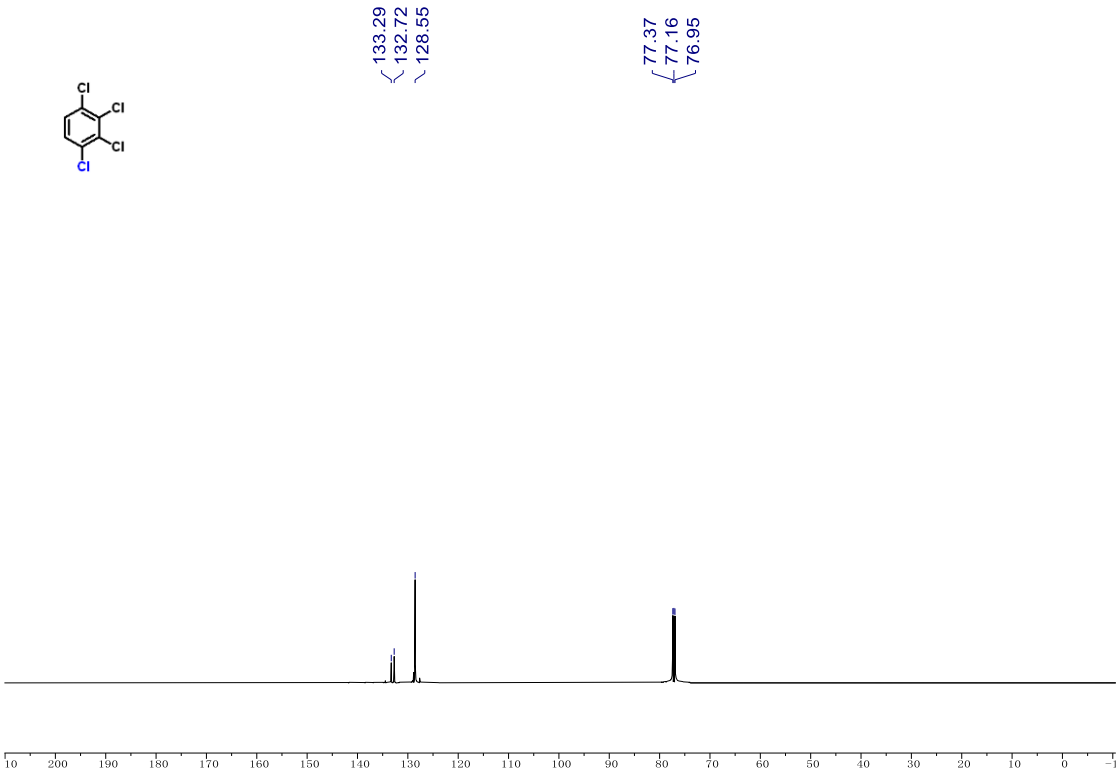
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2q**.



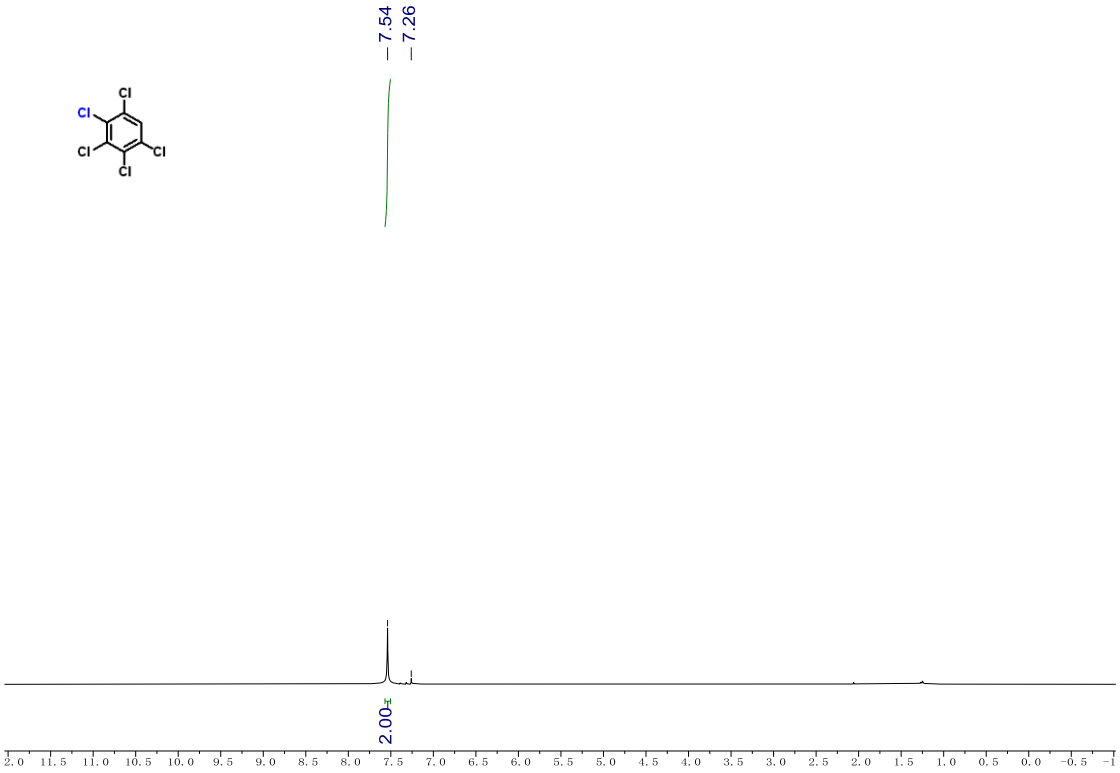
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2q**.



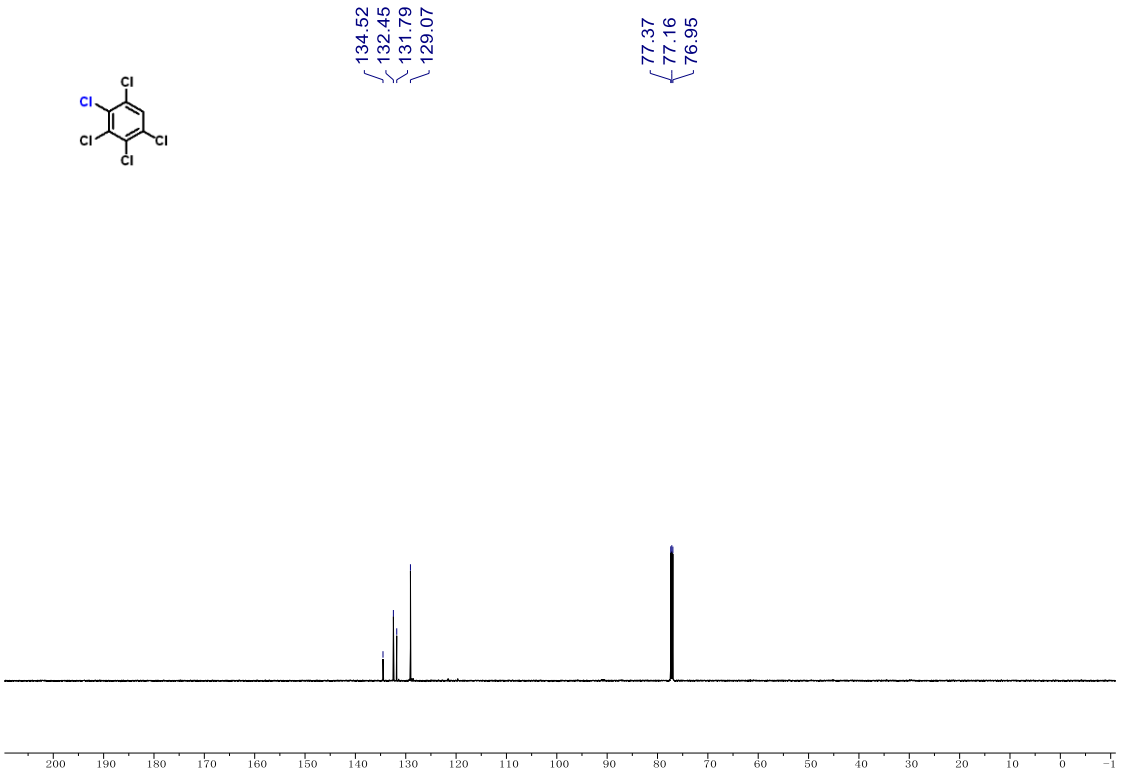
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2r**.



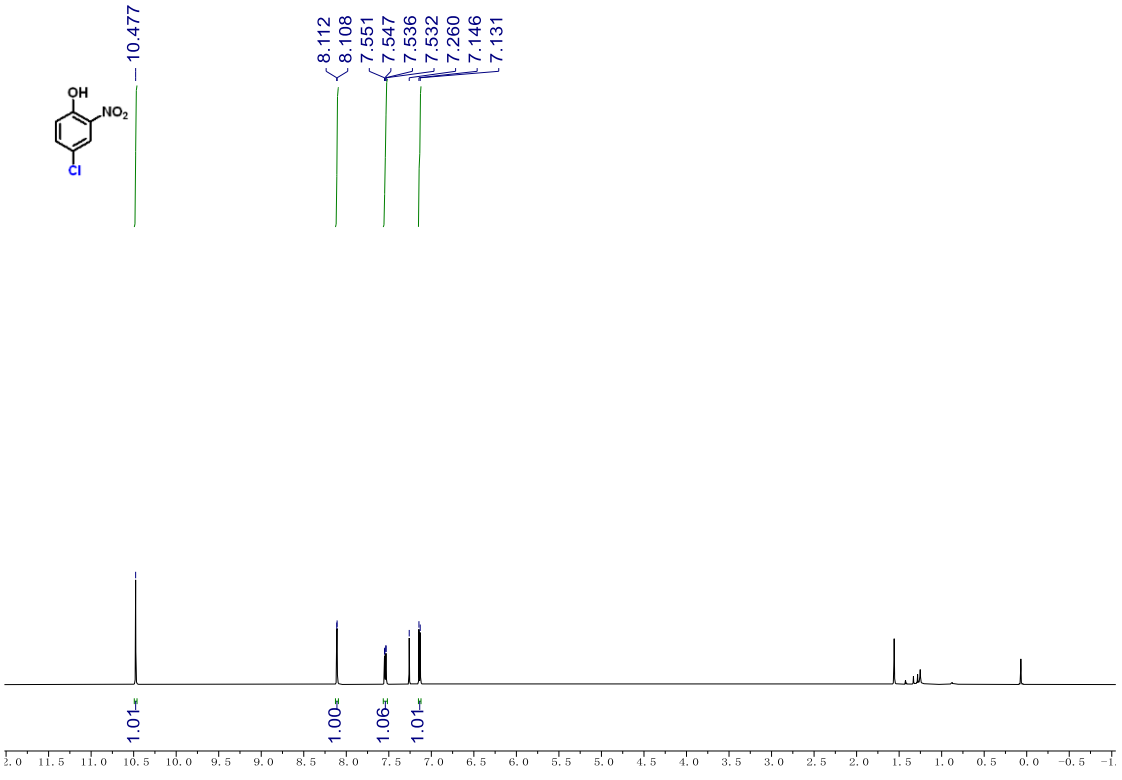
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2r**.



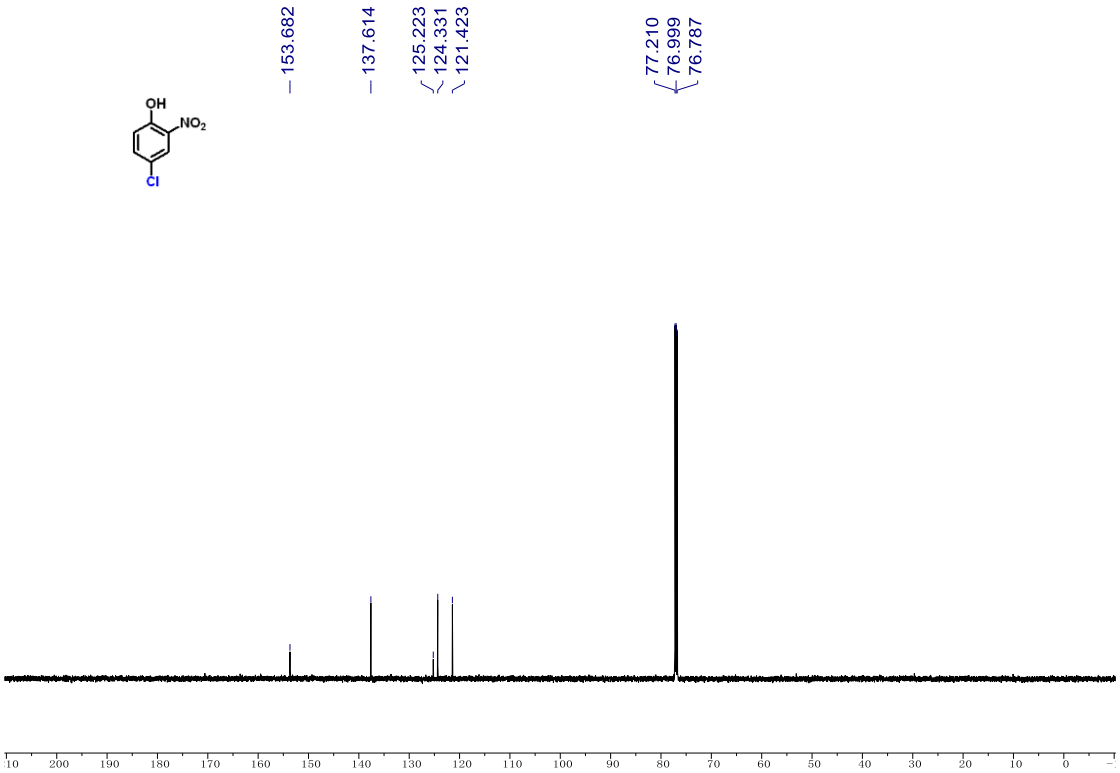
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2s**.



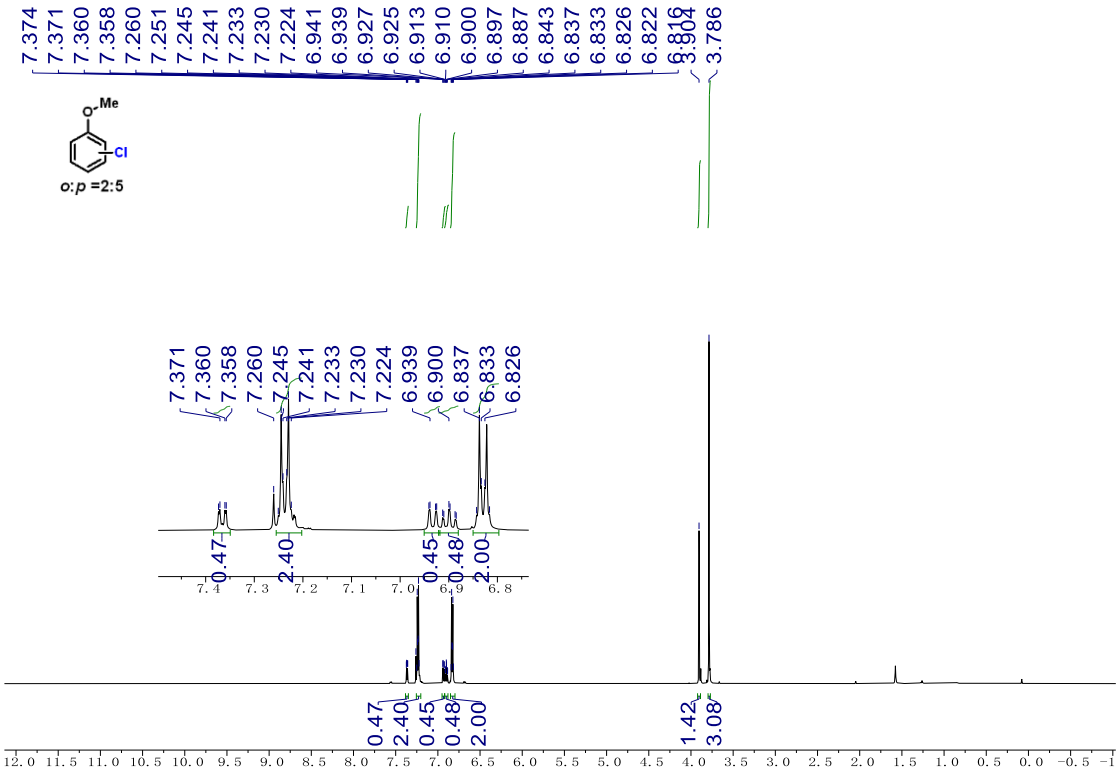
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2s**.



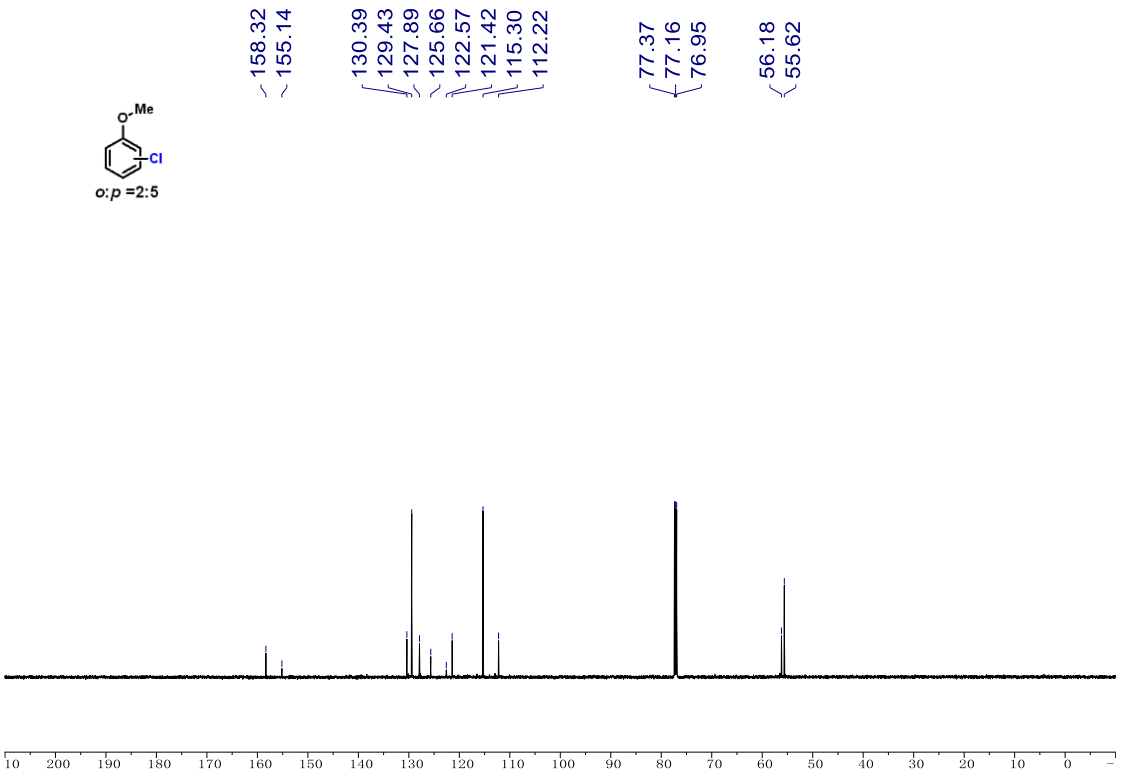
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2t**.



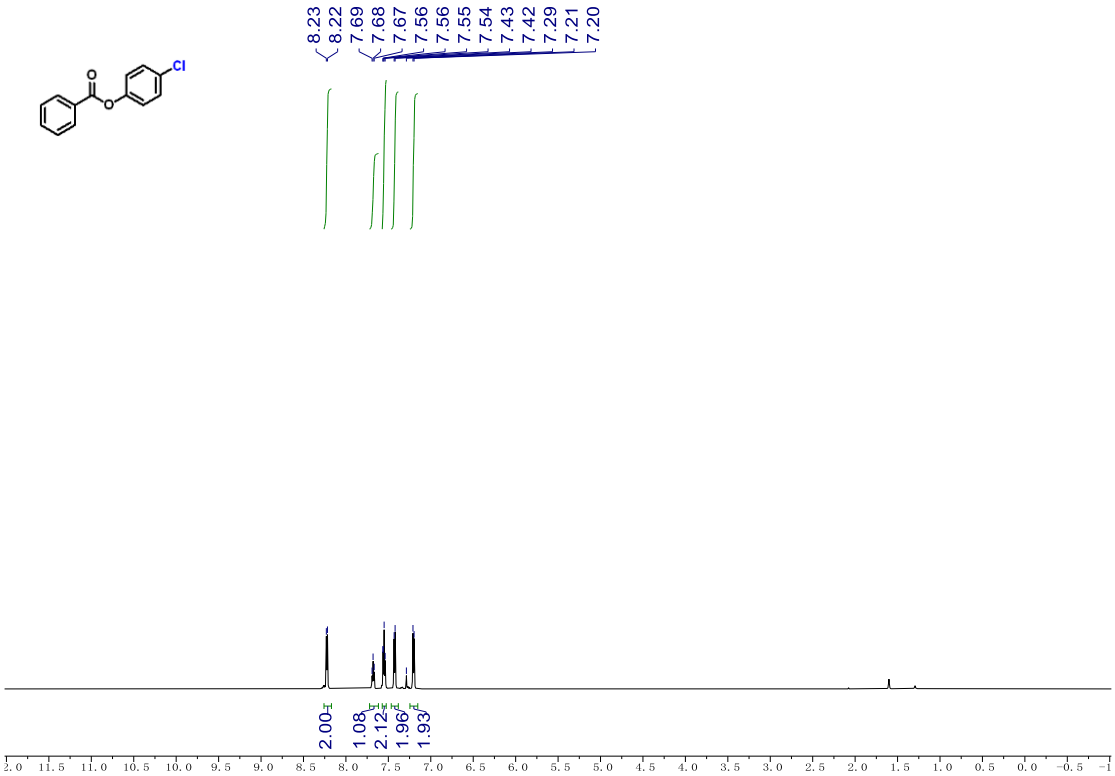
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2t**.



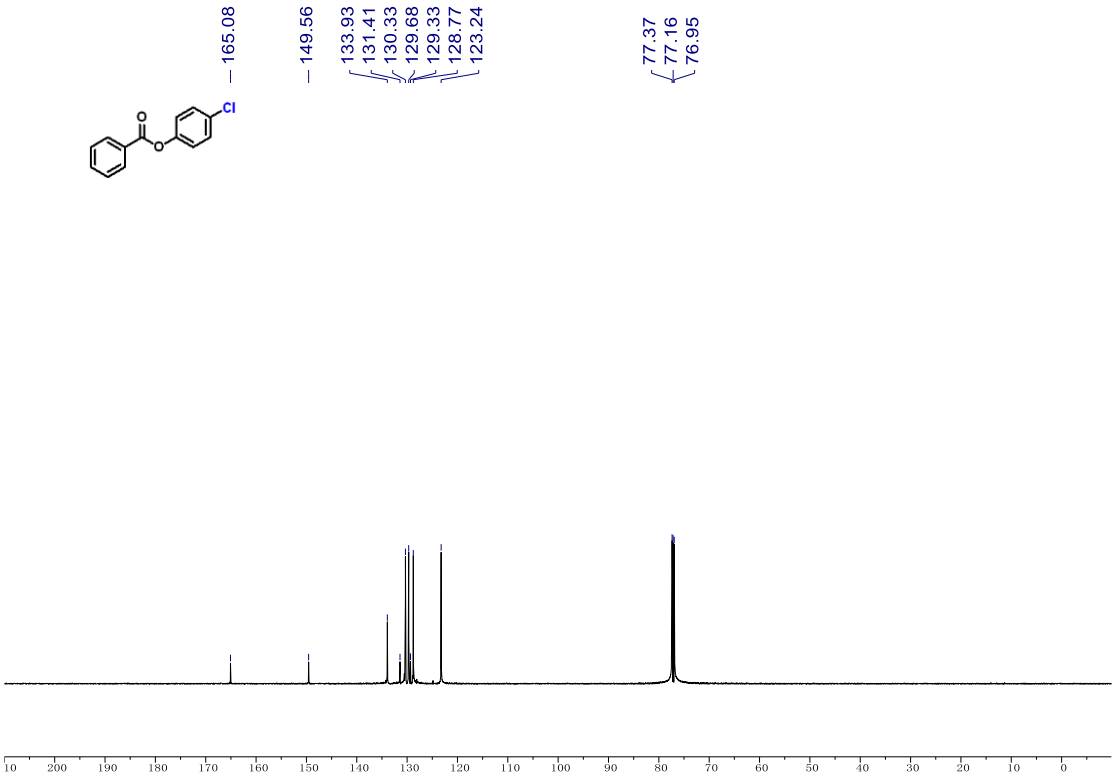
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2u**.



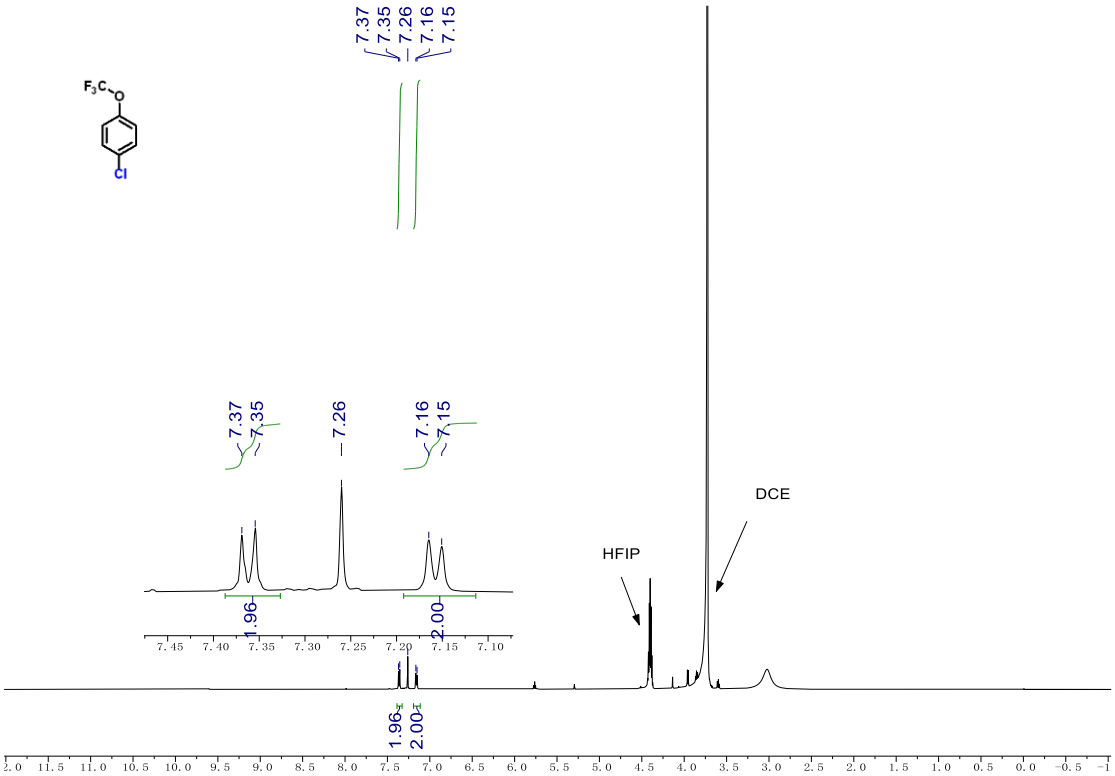
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2u**.



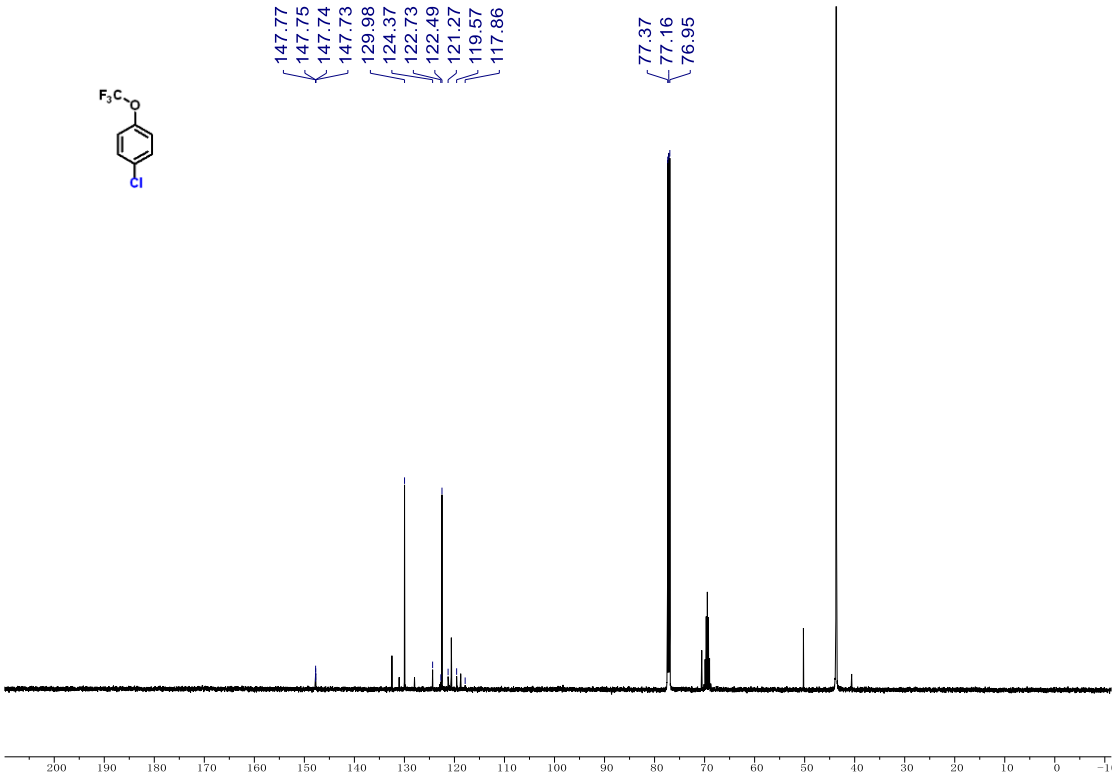
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2v**.



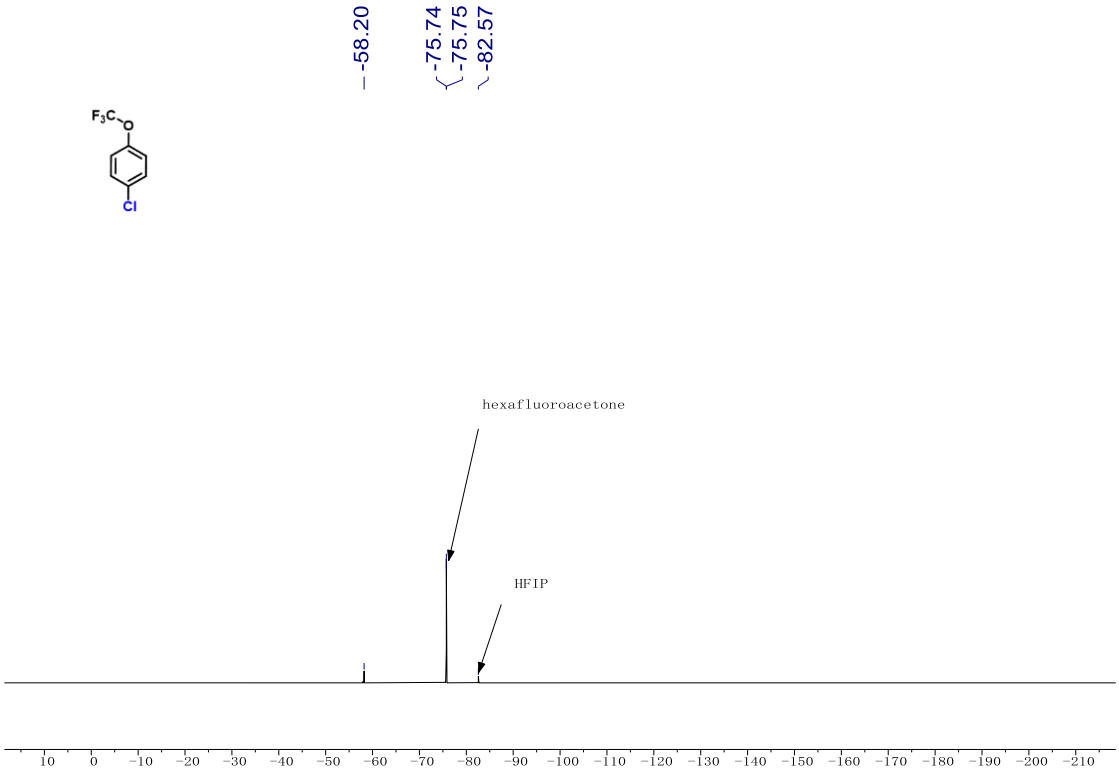
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2v**.



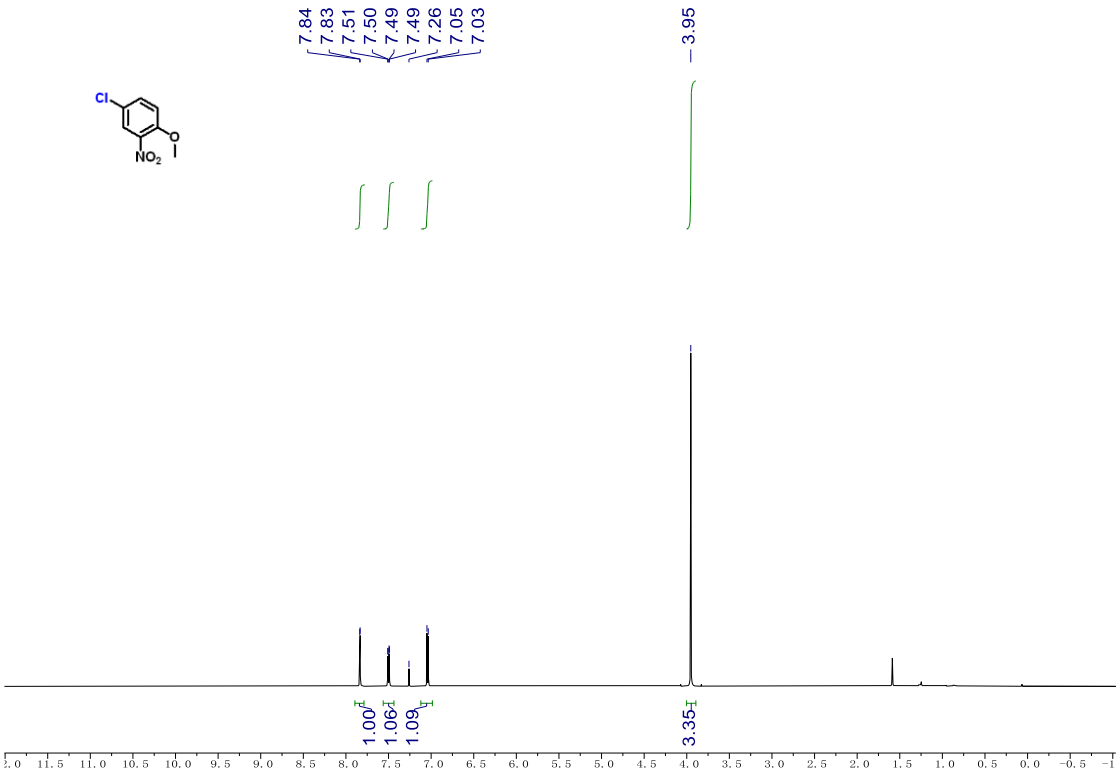
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2w**.



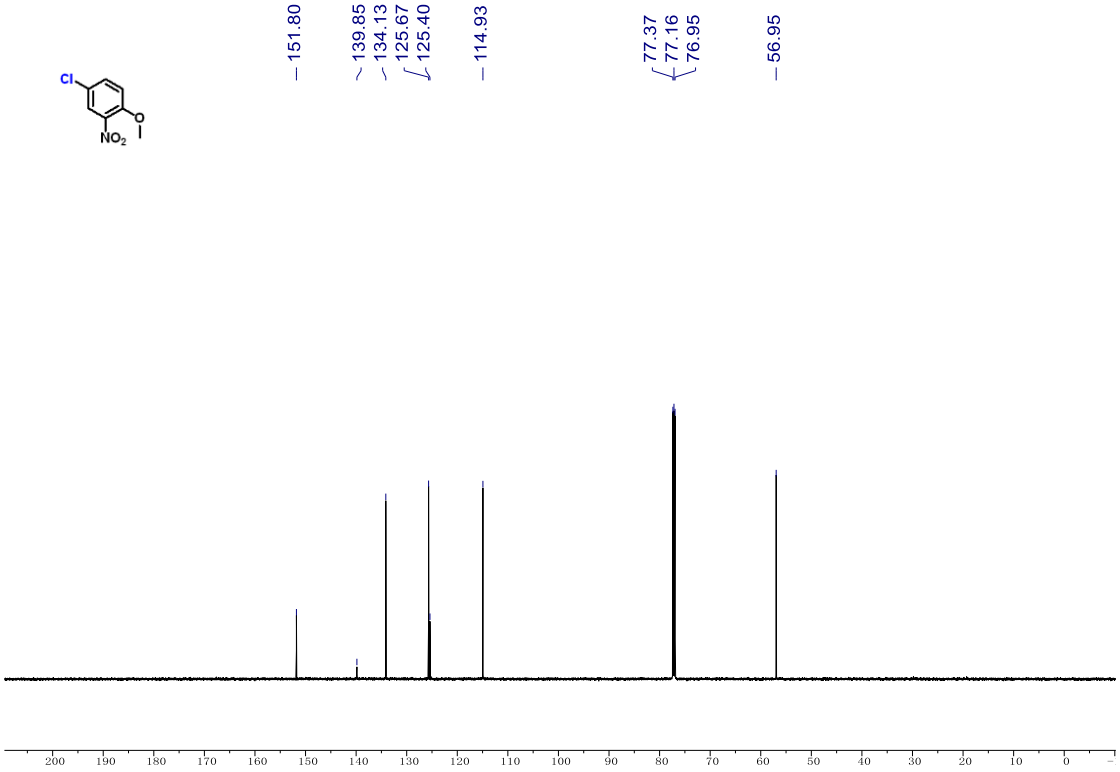
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2w**.



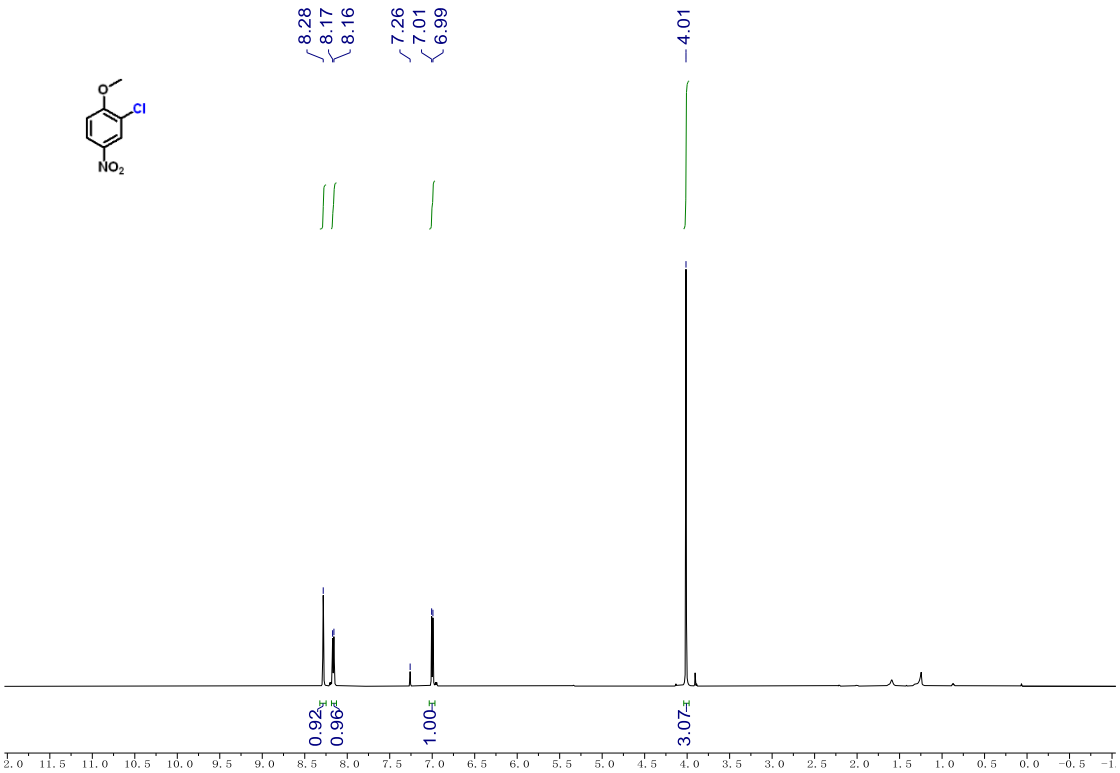
^{19}F NMR ($CDCl_3$) spectrum of **2w**



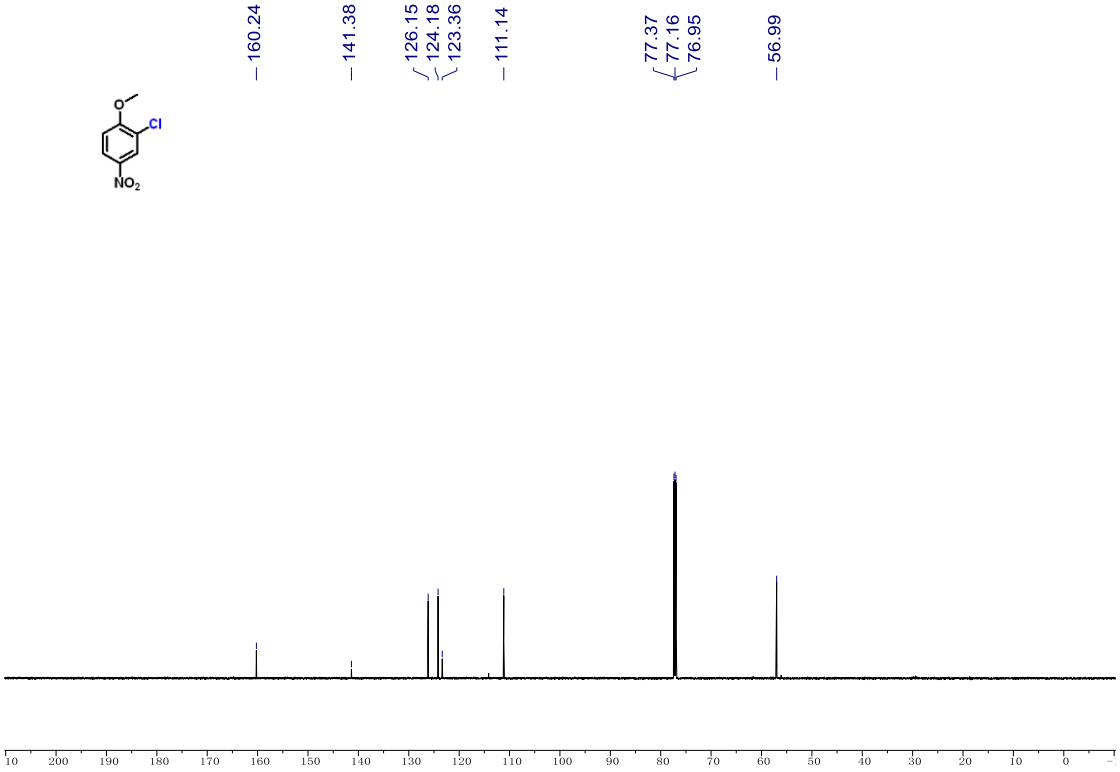
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2x**.



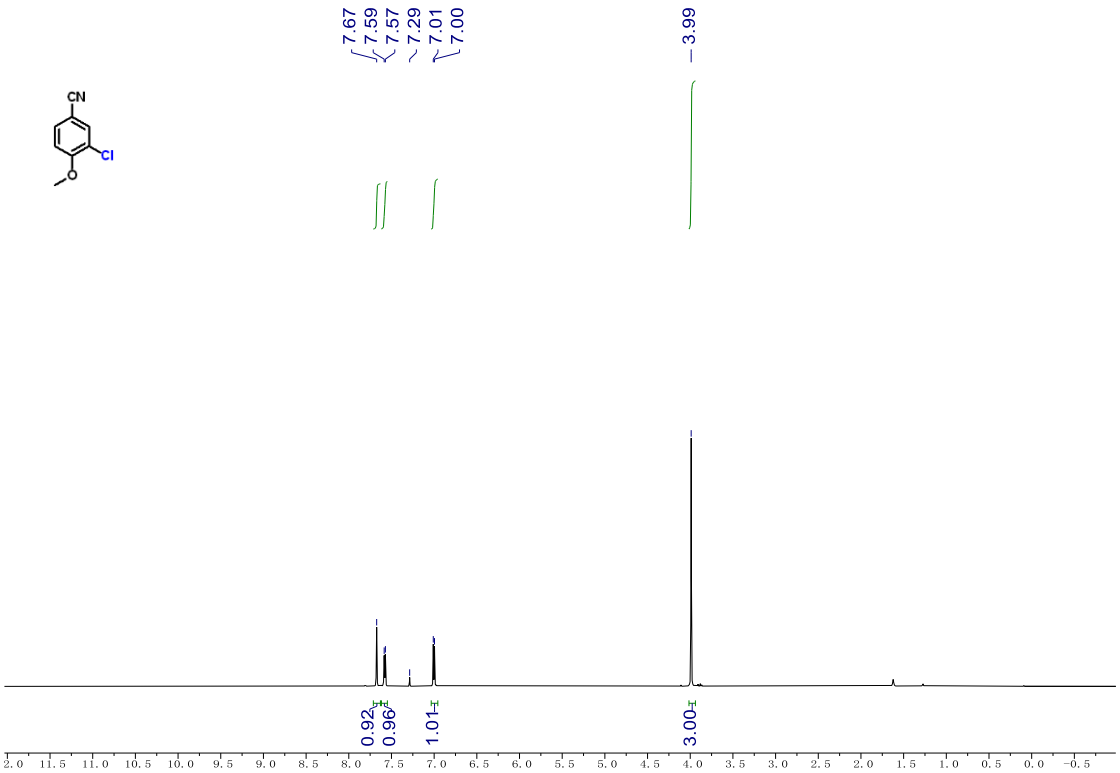
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2x**.



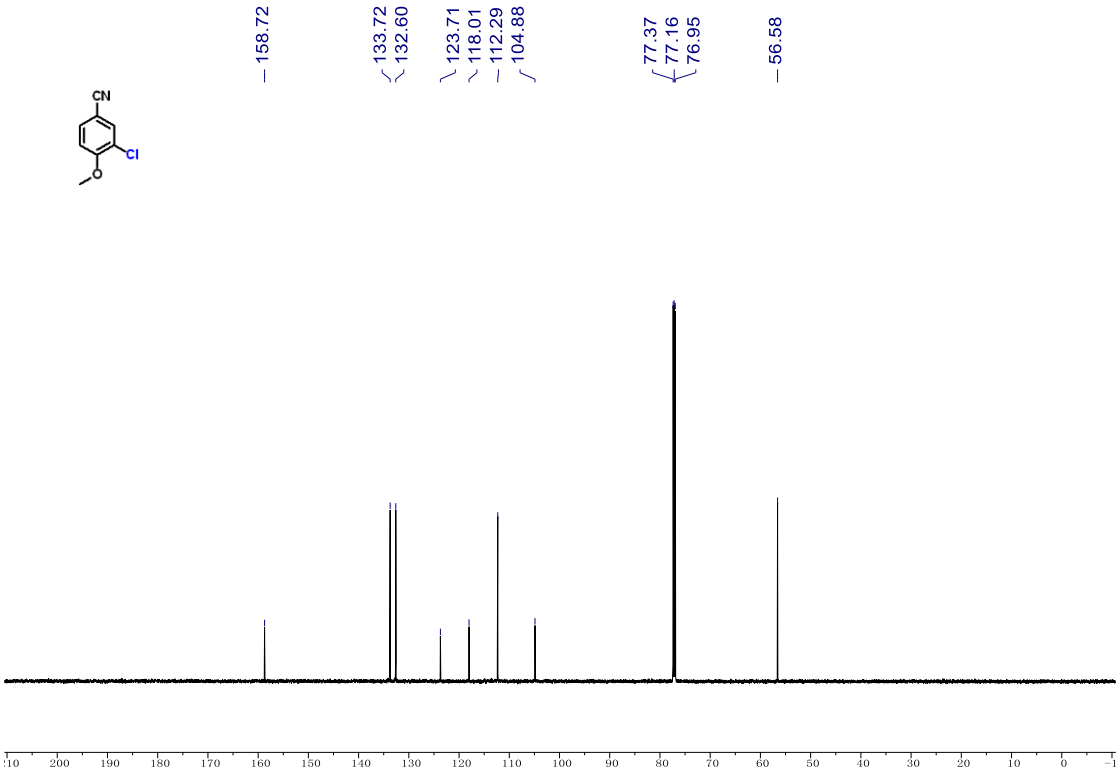
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2y**.



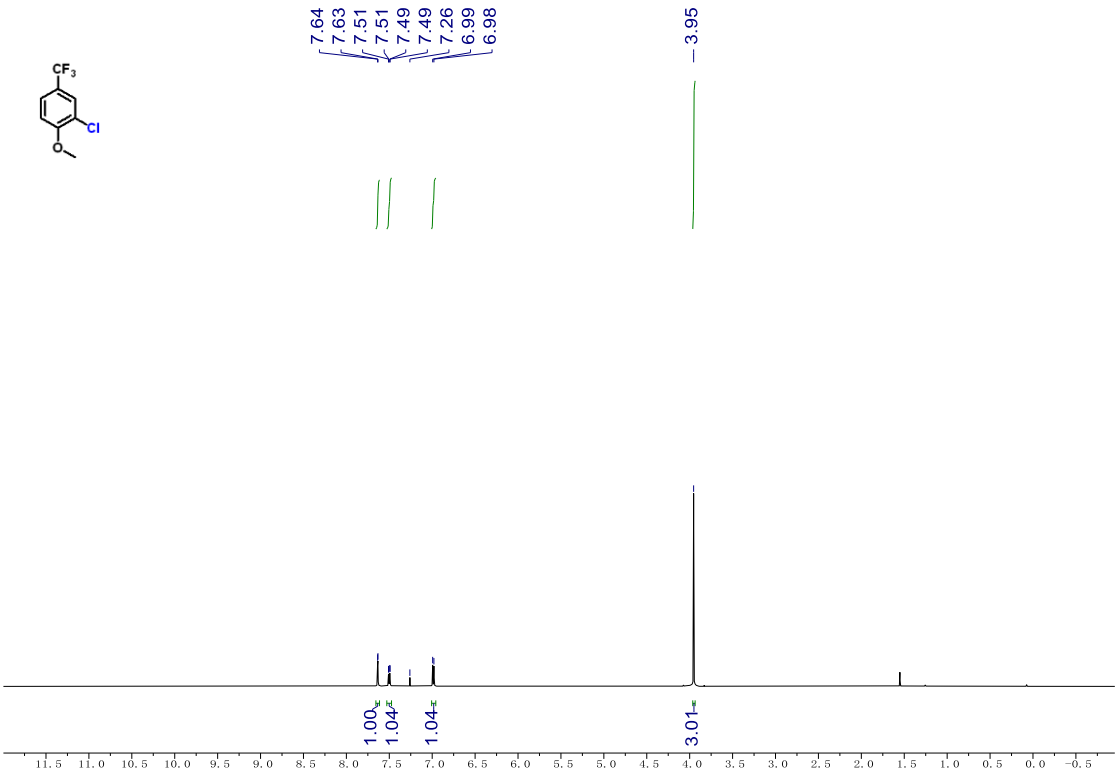
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2y**.



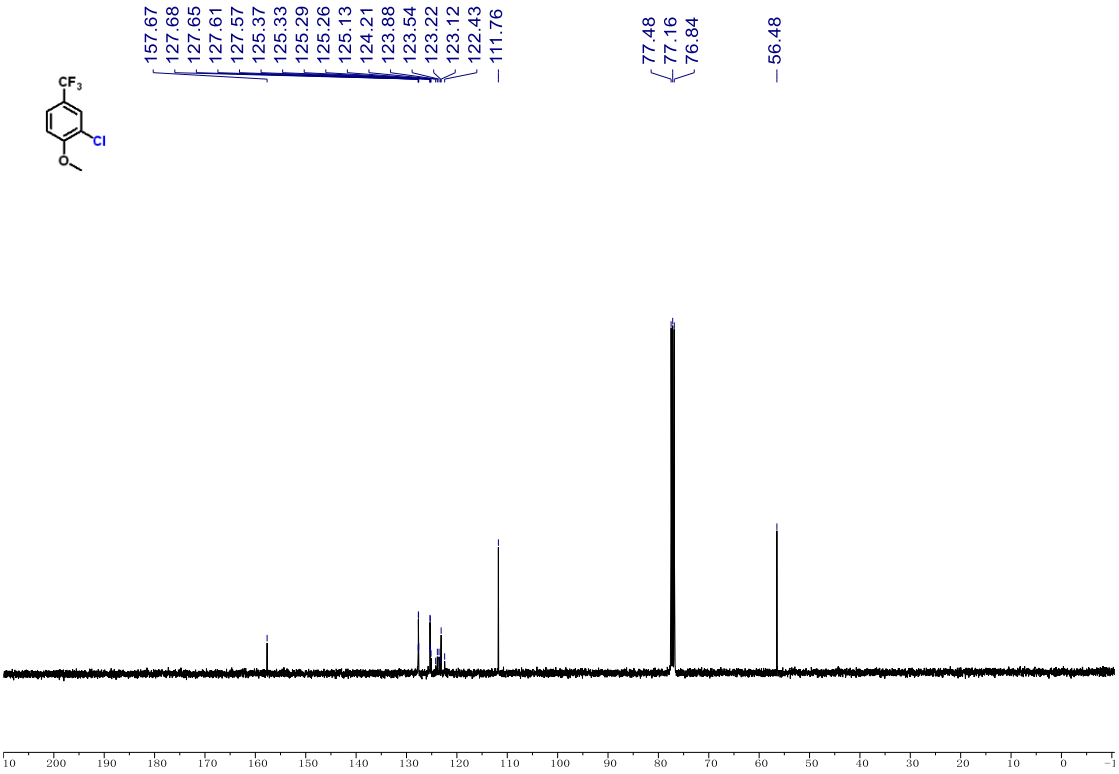
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2z**.



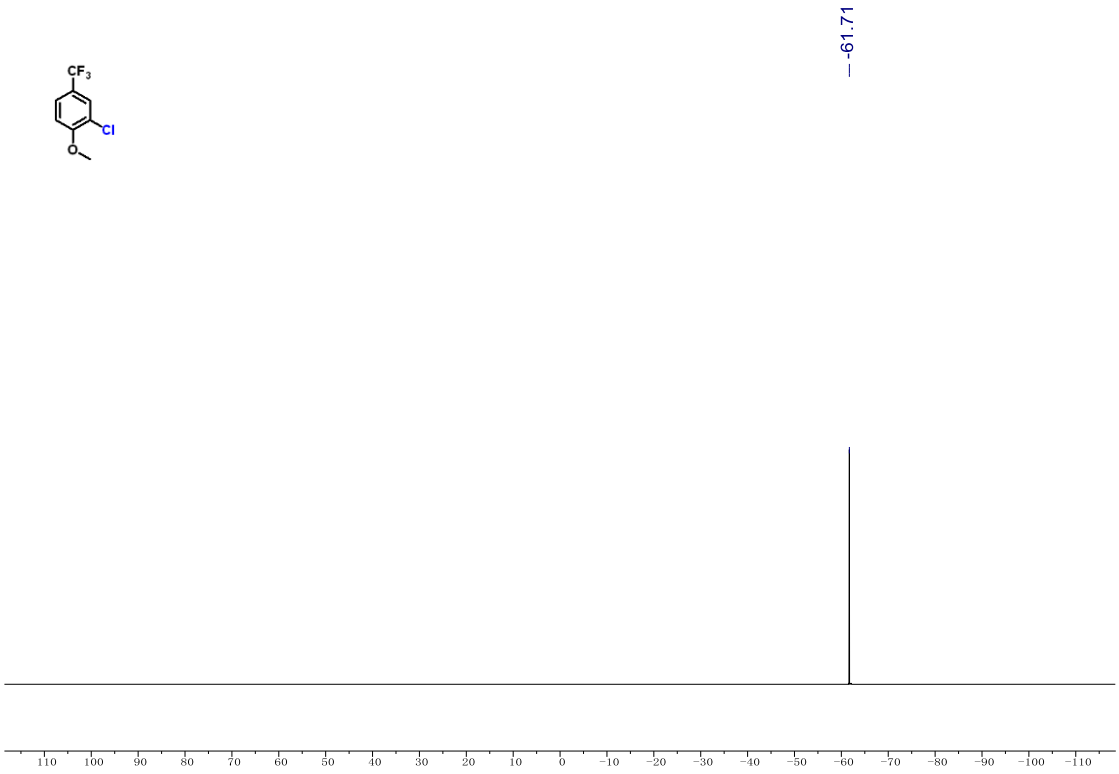
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2z.**



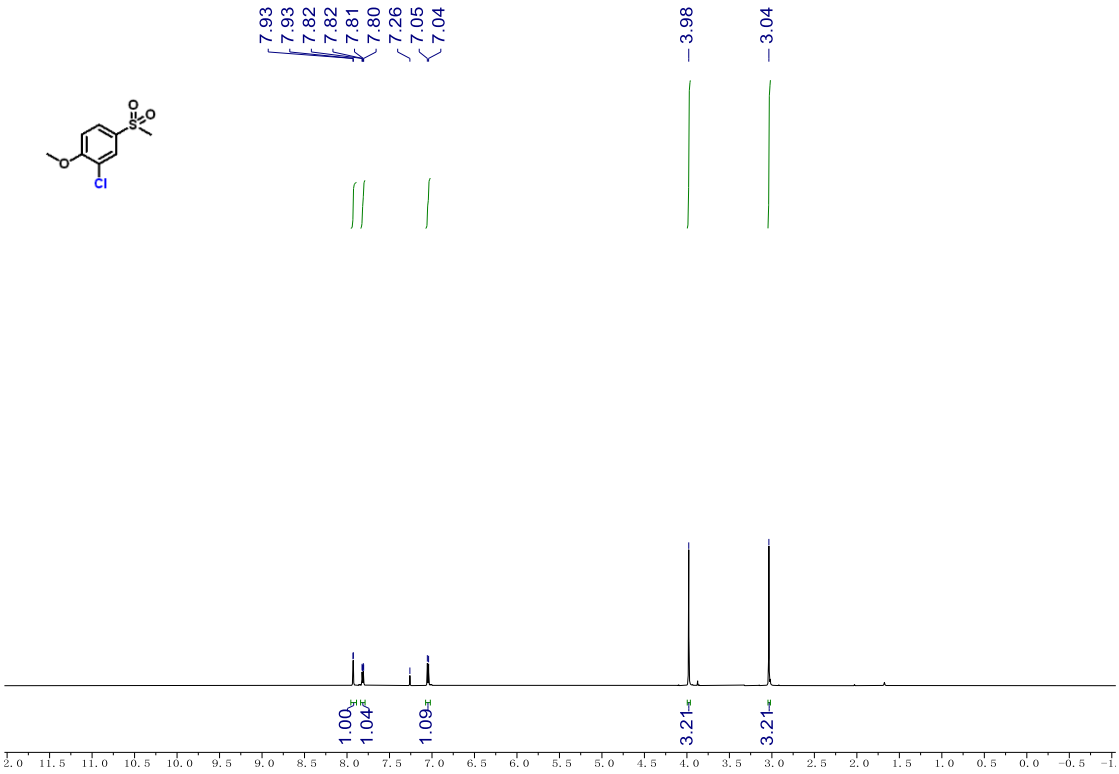
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aa**.



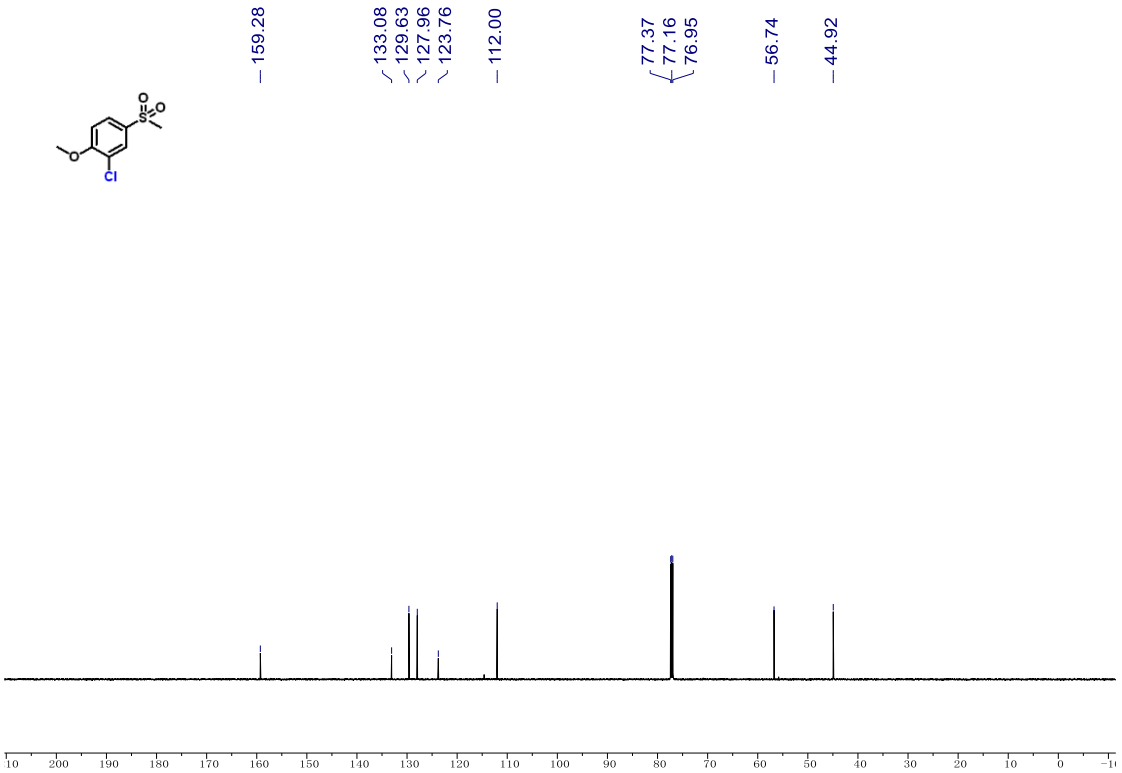
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2aa**



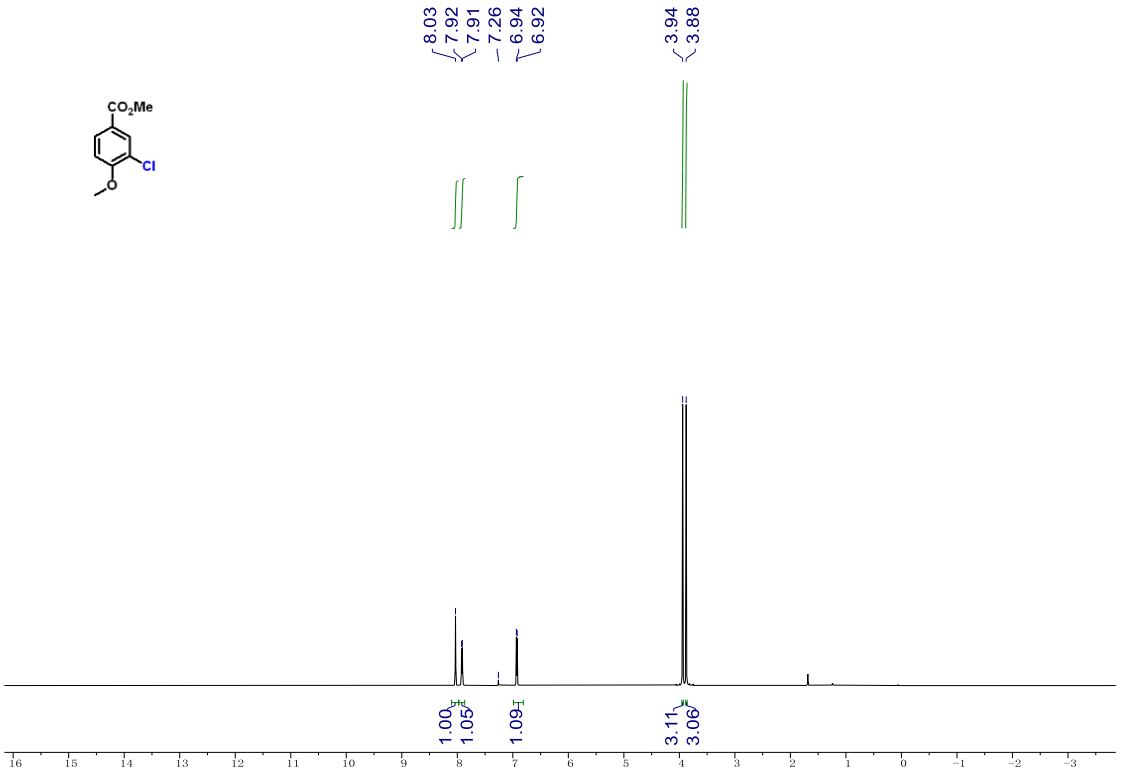
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **2aa**



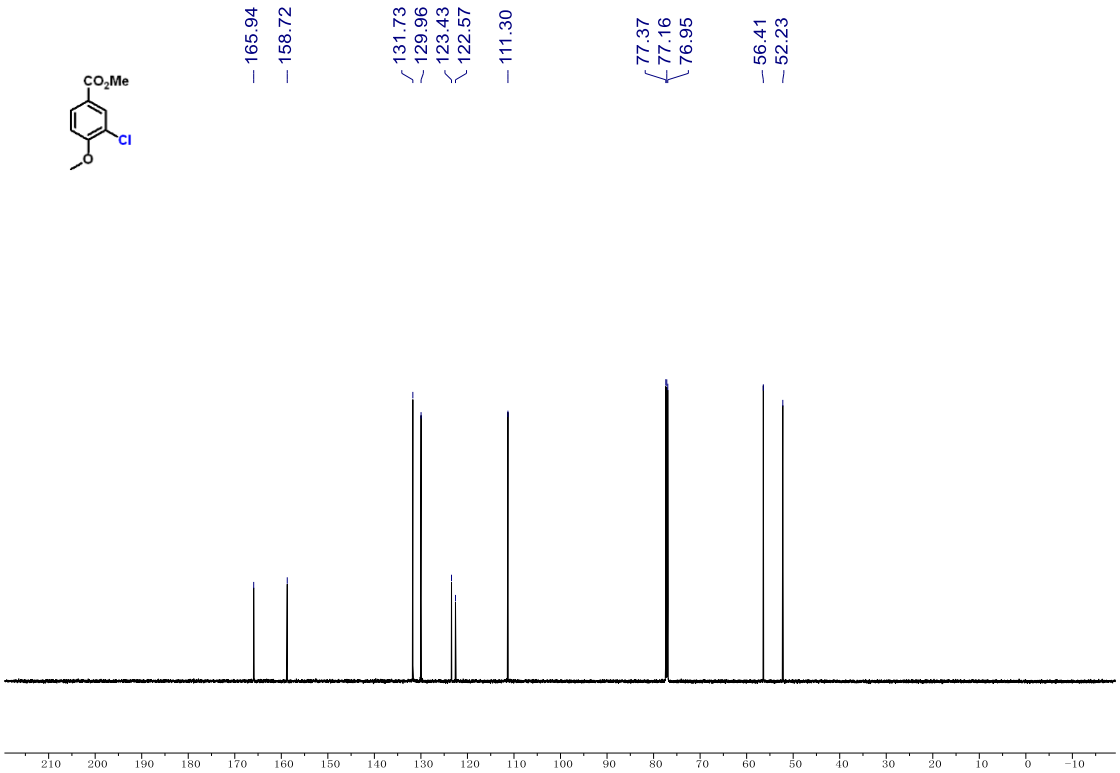
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2bb**.



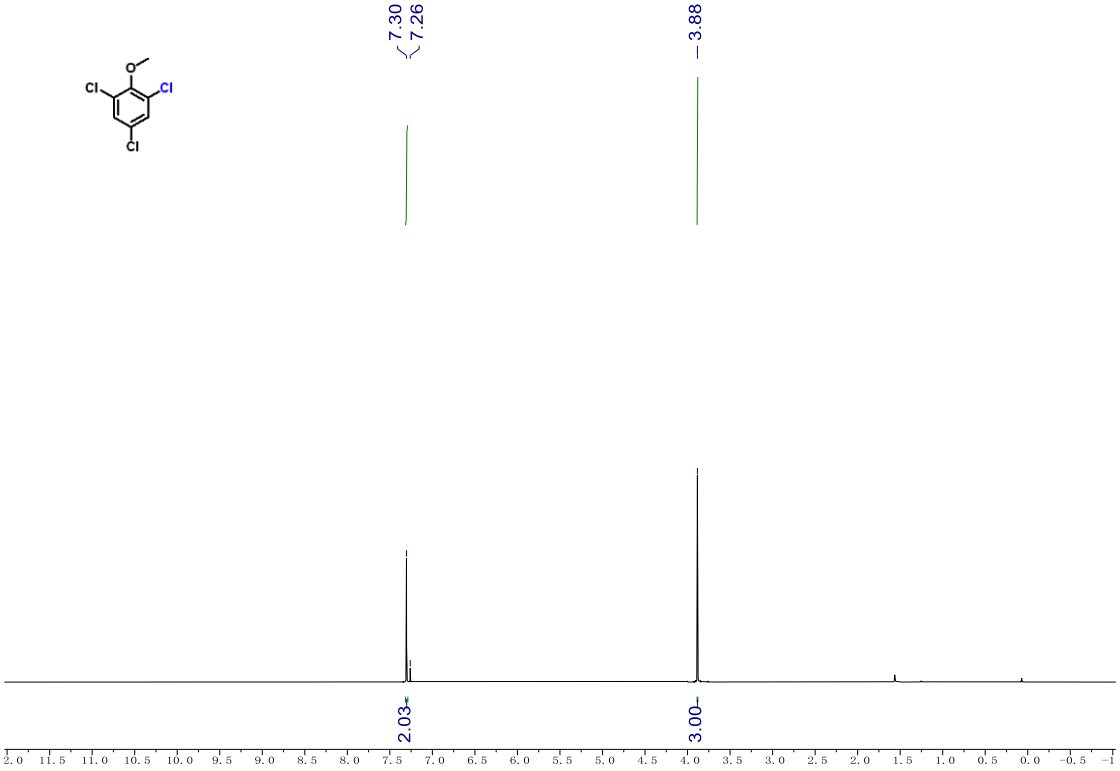
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2bb**.



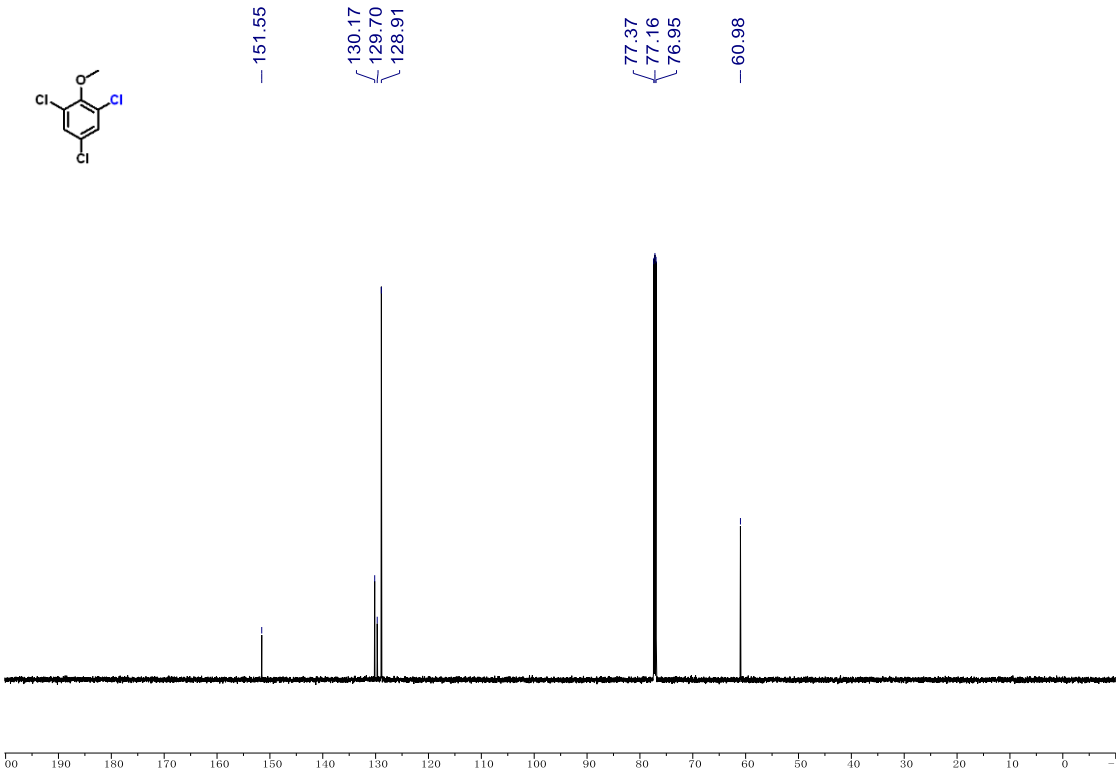
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2cc**.



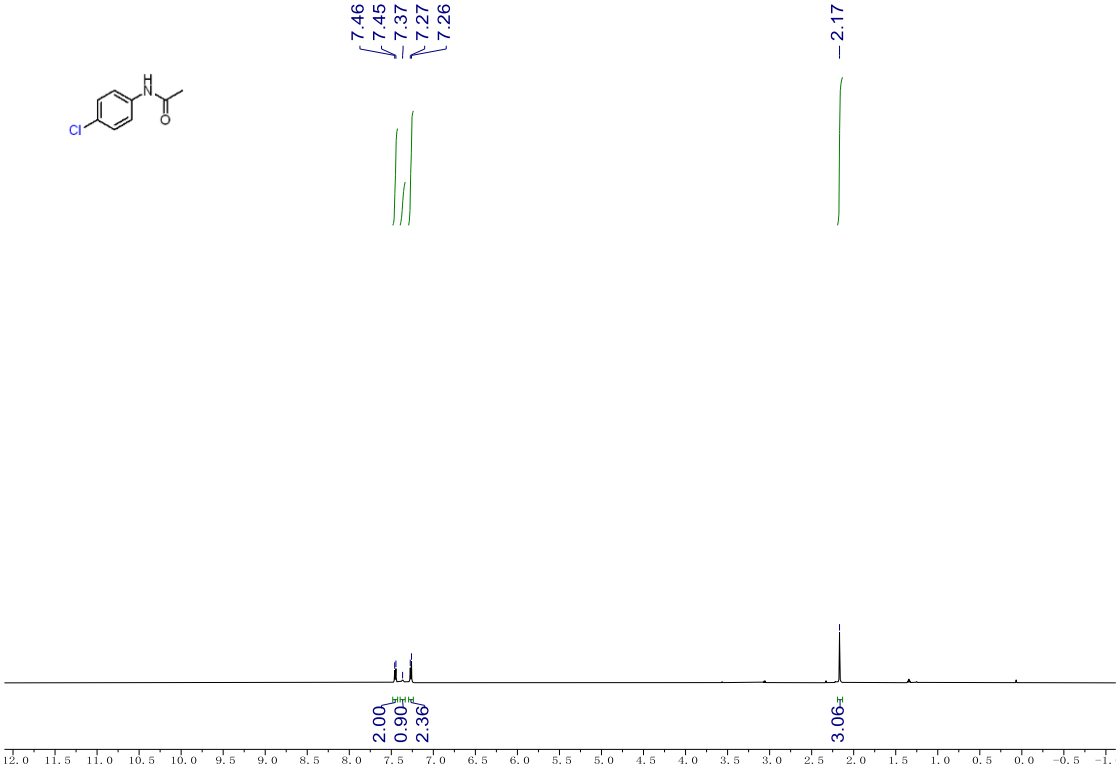
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2cc**.



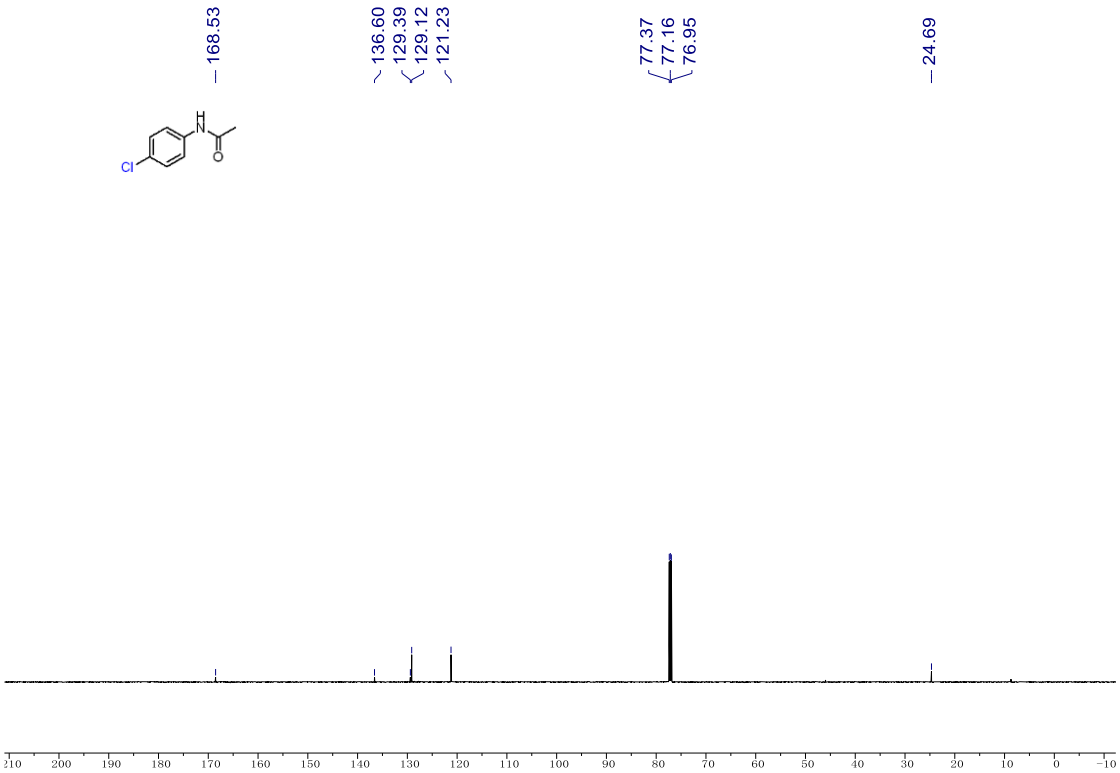
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2dd**.



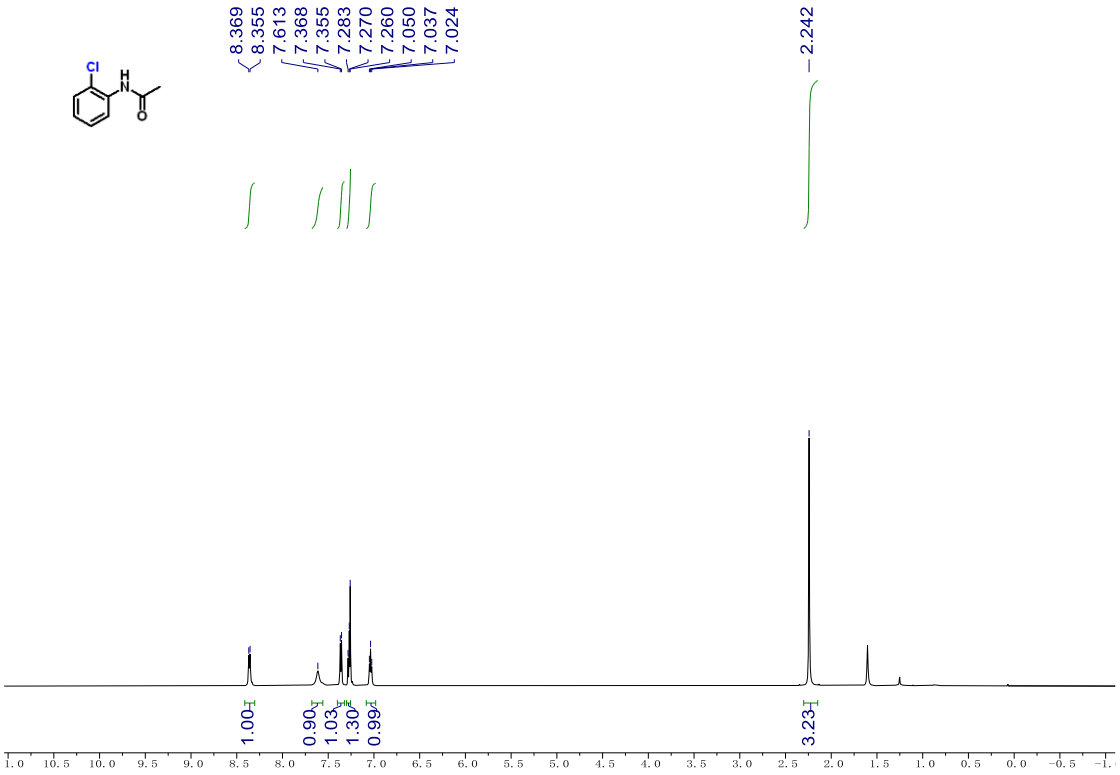
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2dd**.



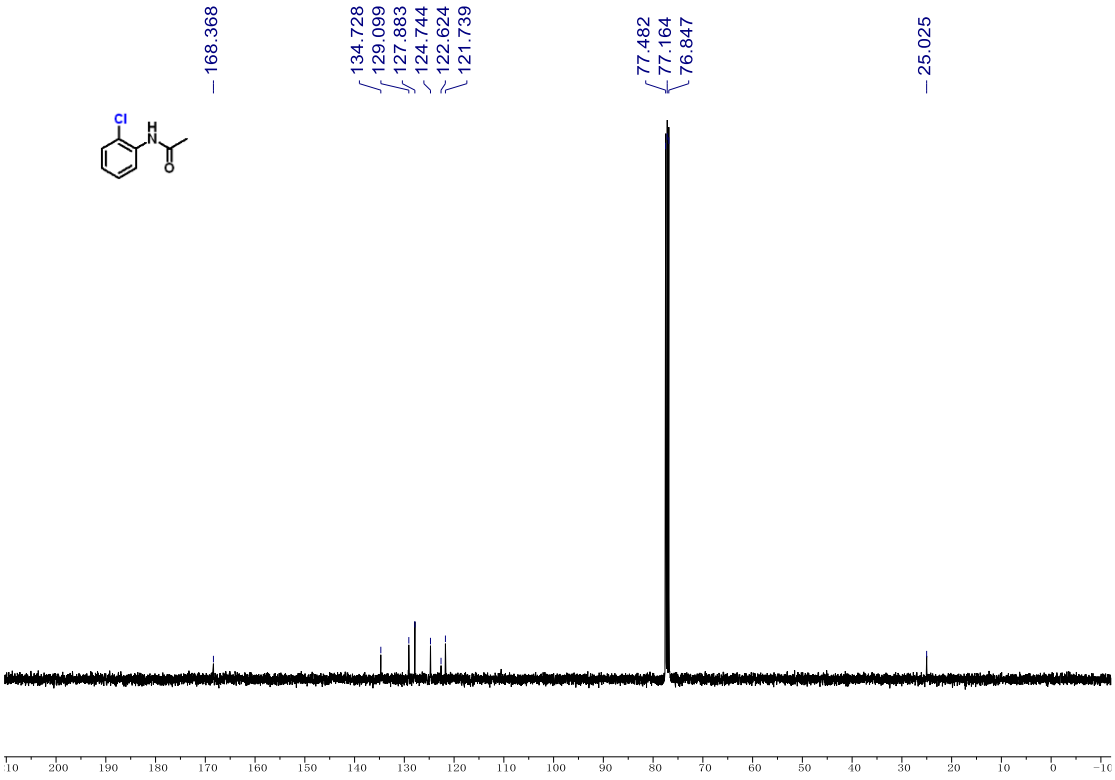
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ee-1**.



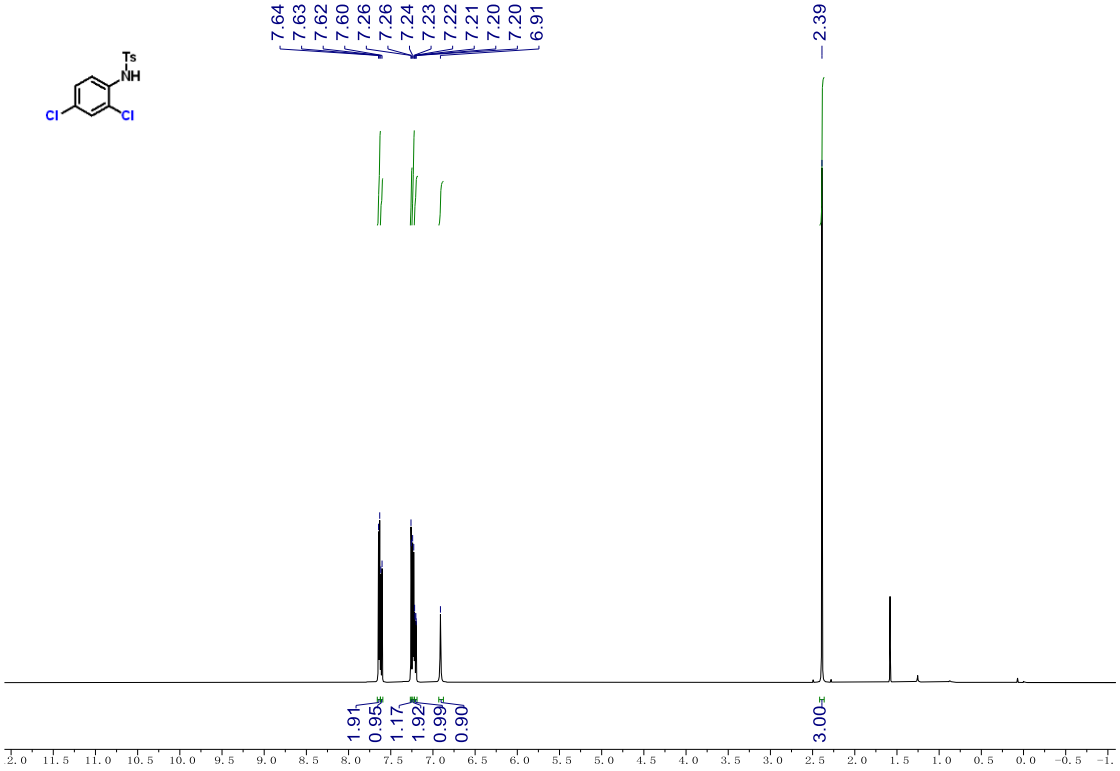
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2ee-1**.



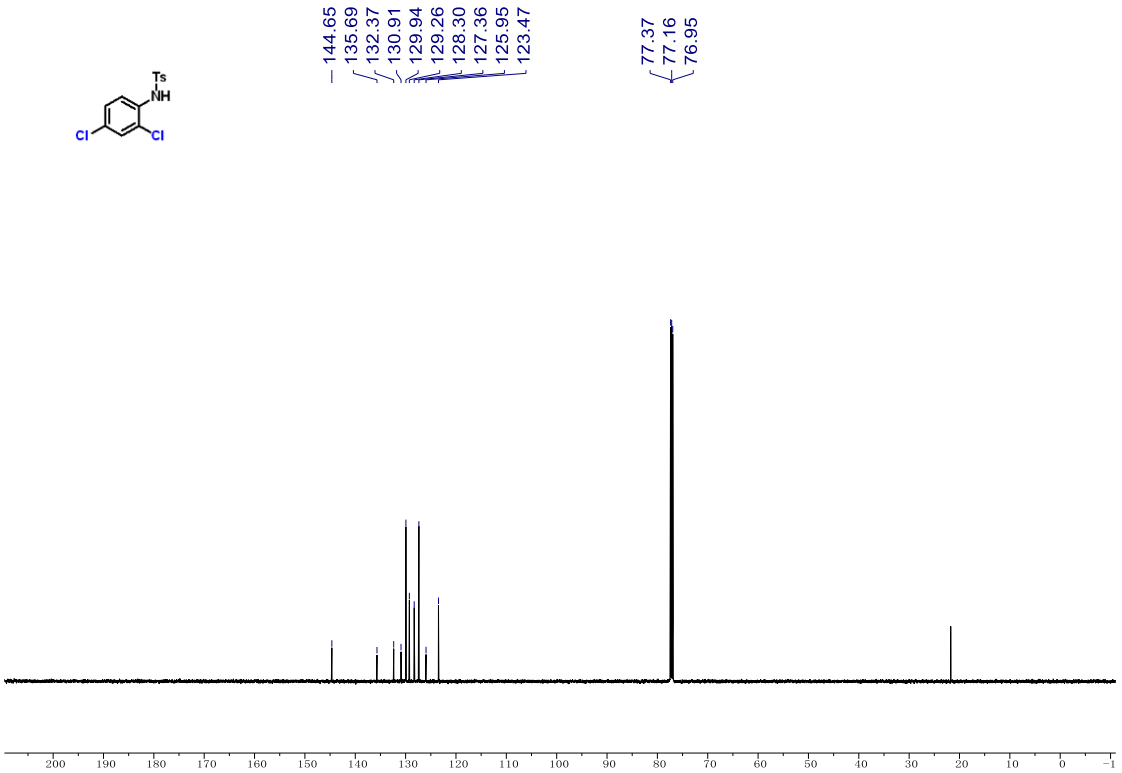
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ee-2**.



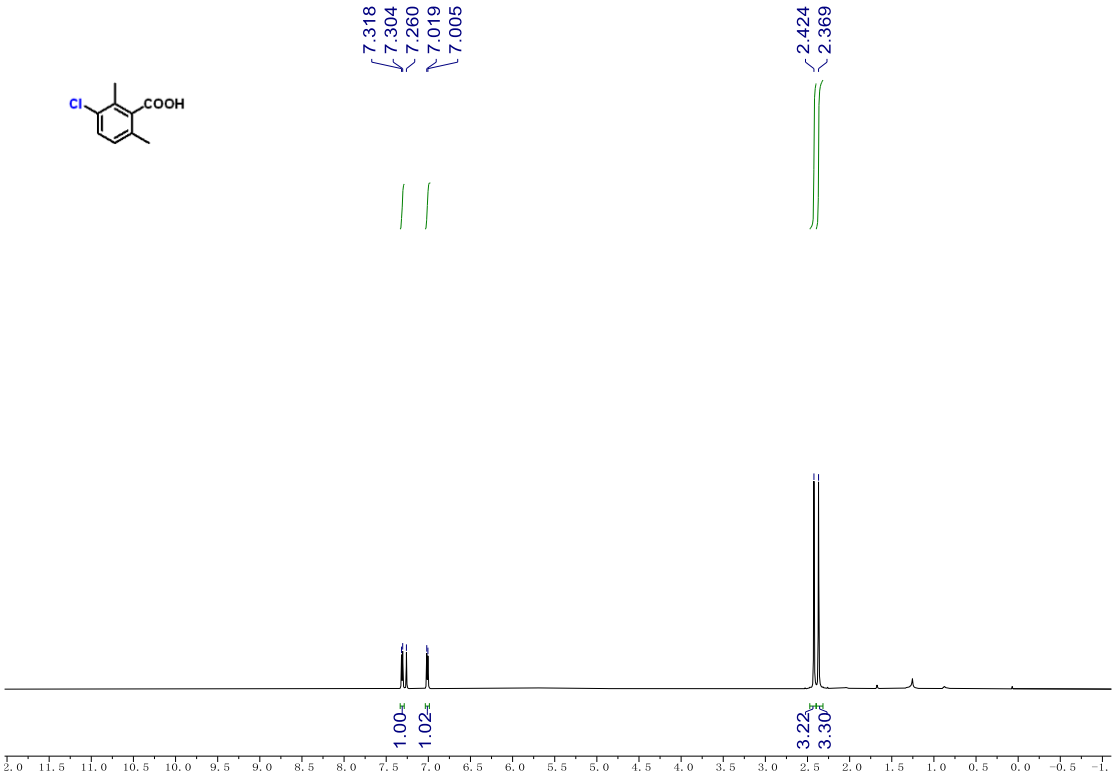
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2ee-2**.



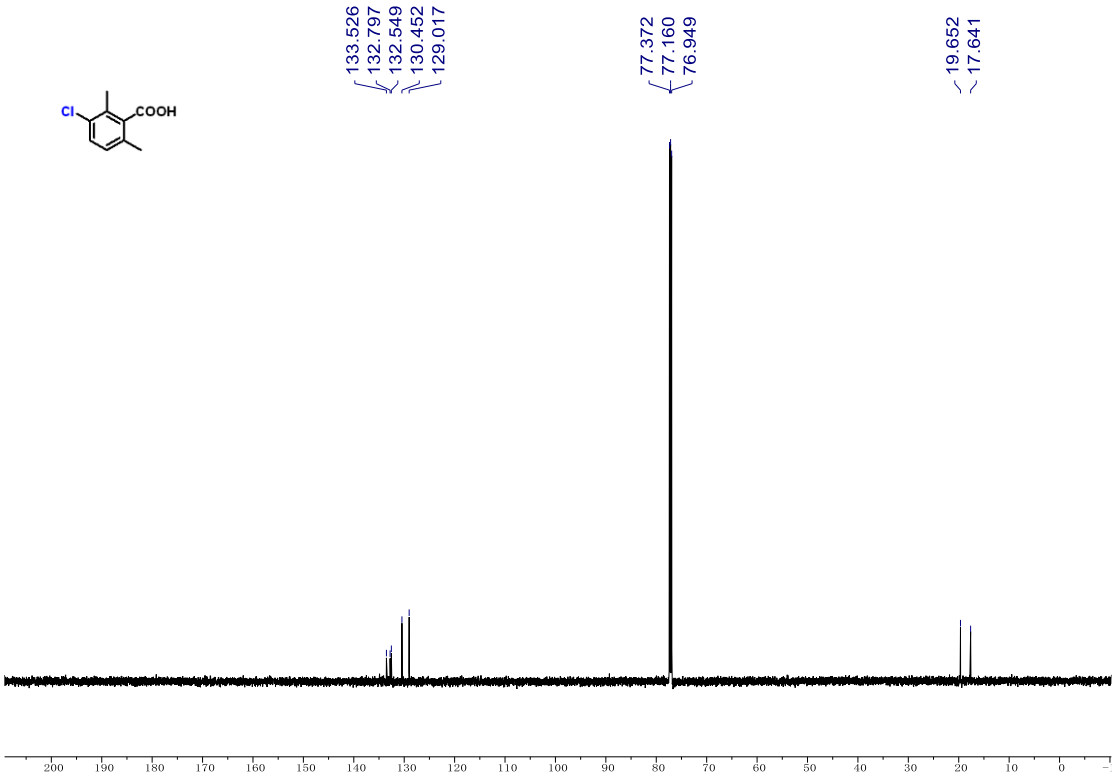
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ff**.



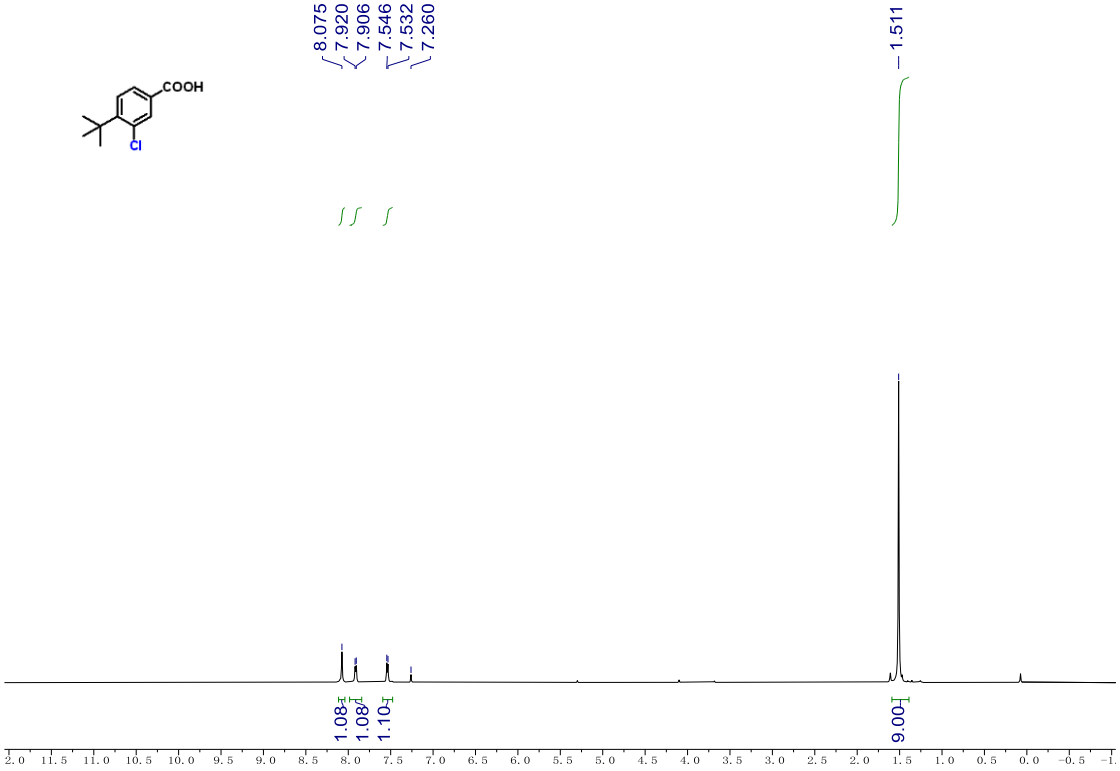
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2ff**



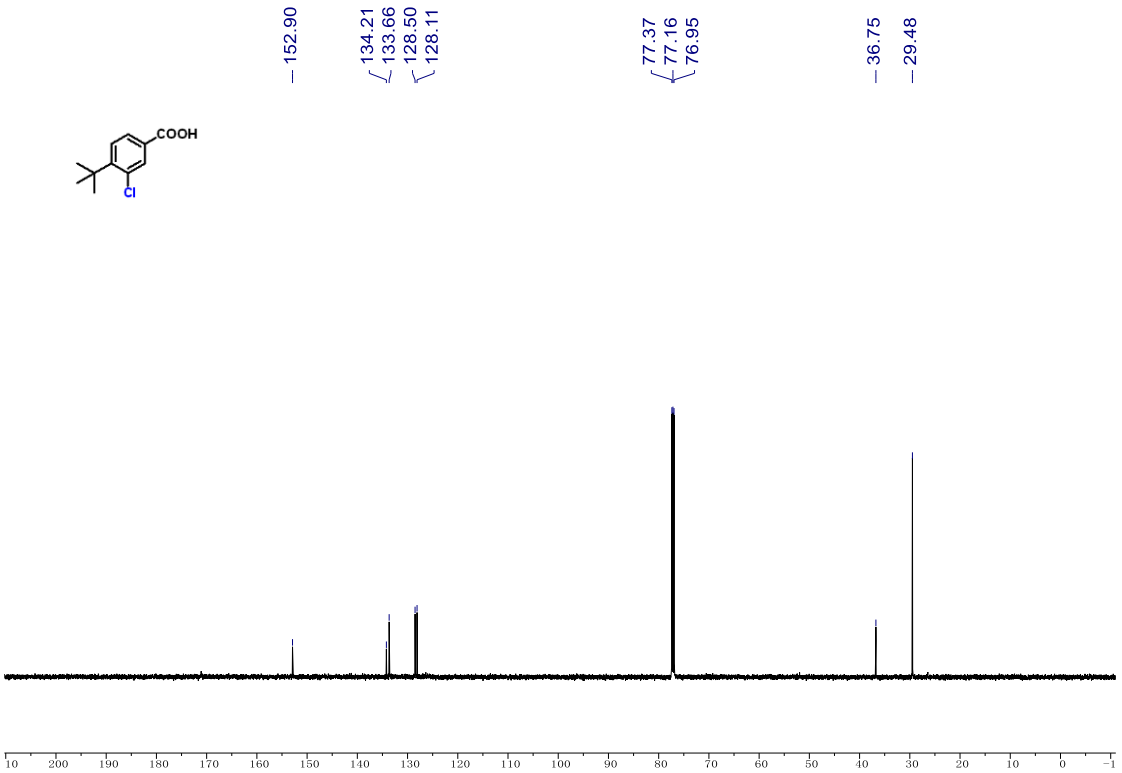
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2gg**.



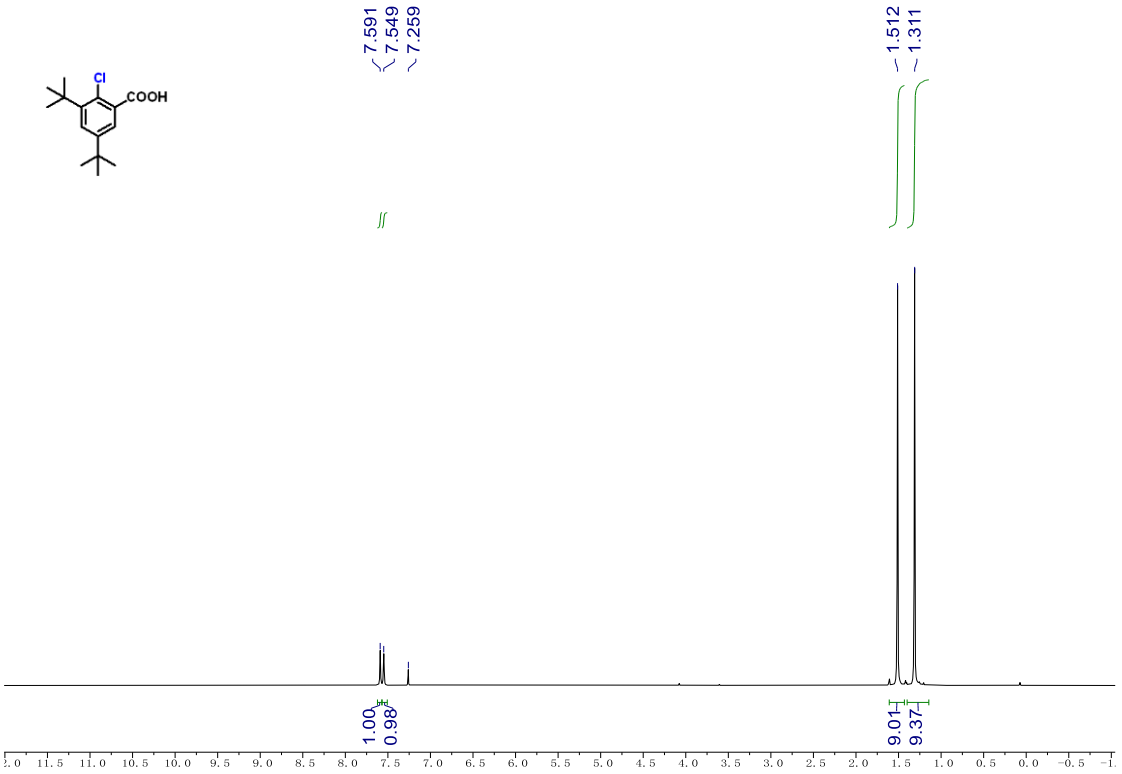
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2gg**.



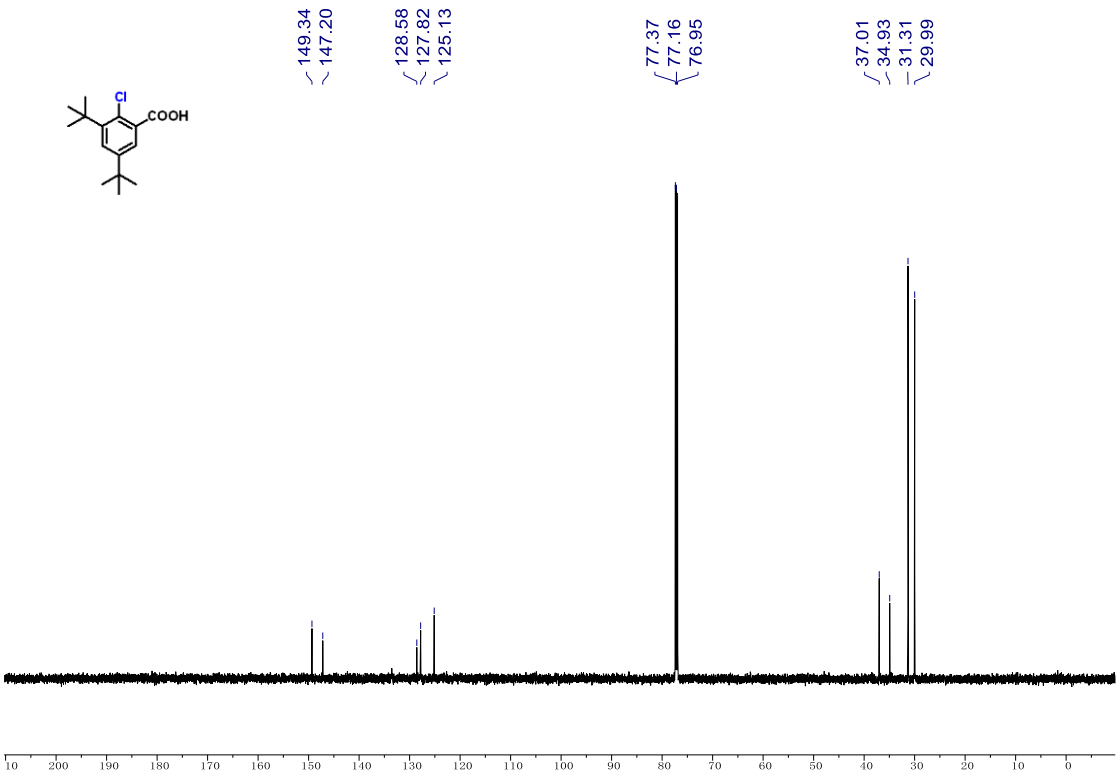
^{1}H NMR ($CDCl_3$) spectrum of **2hh**.



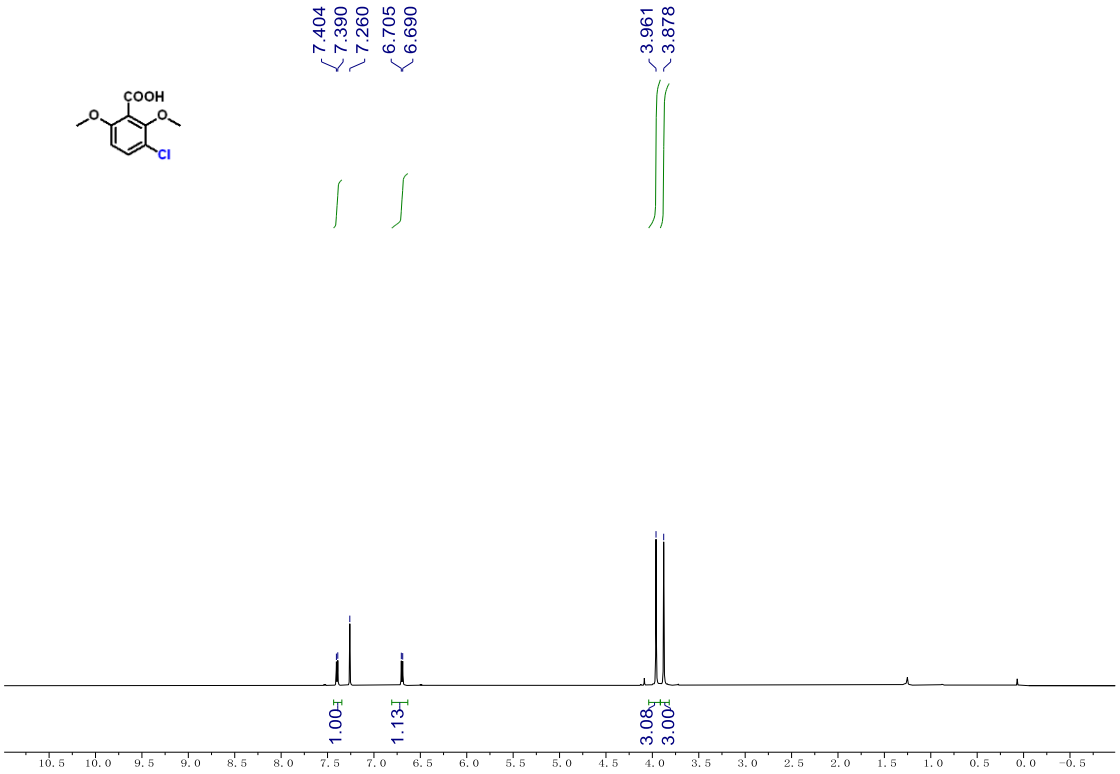
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2hh**.



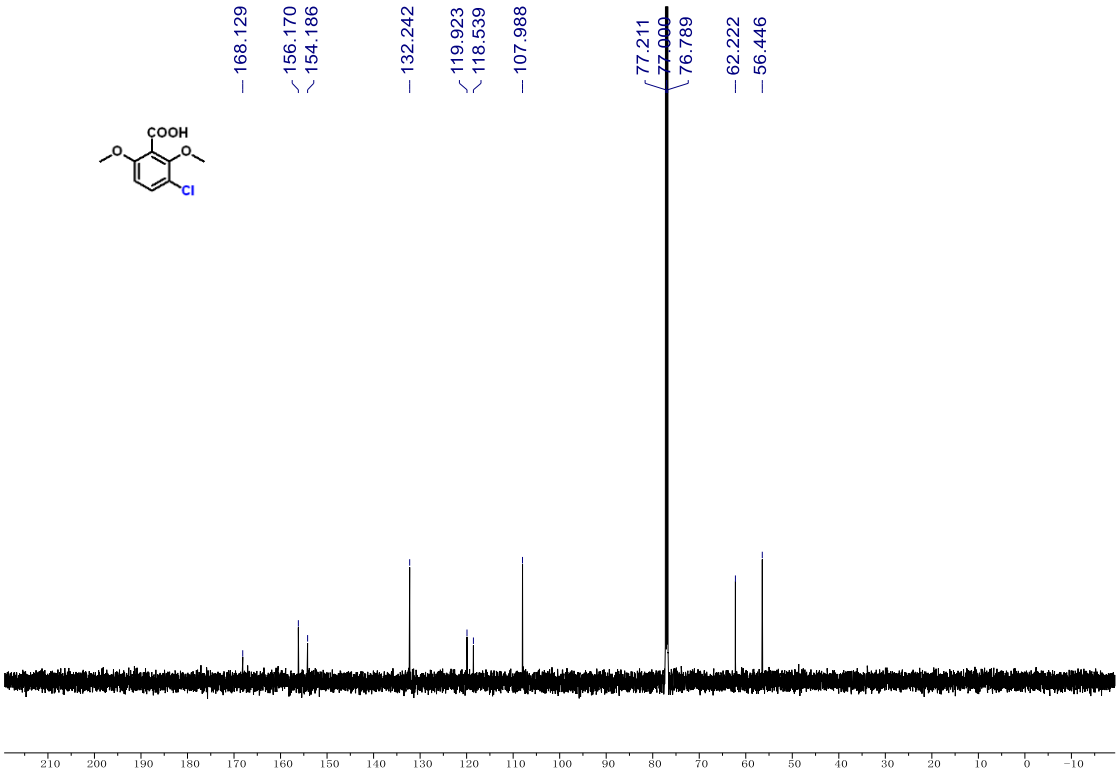
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ii**.



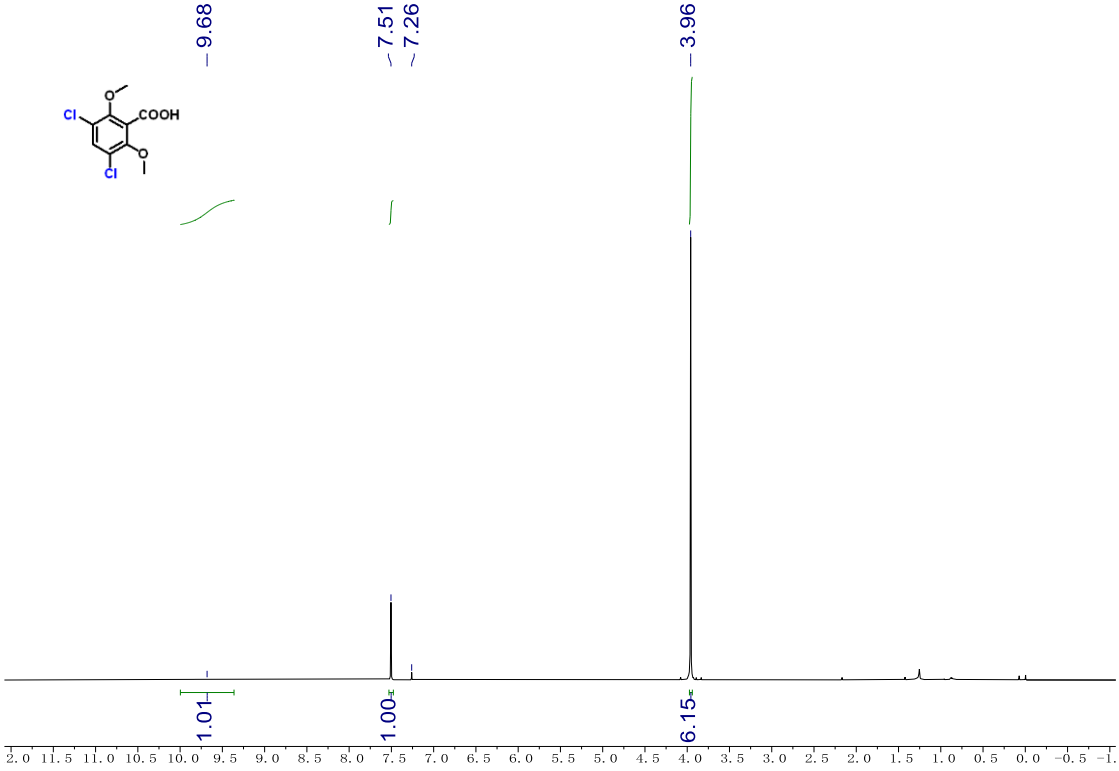
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ii**.



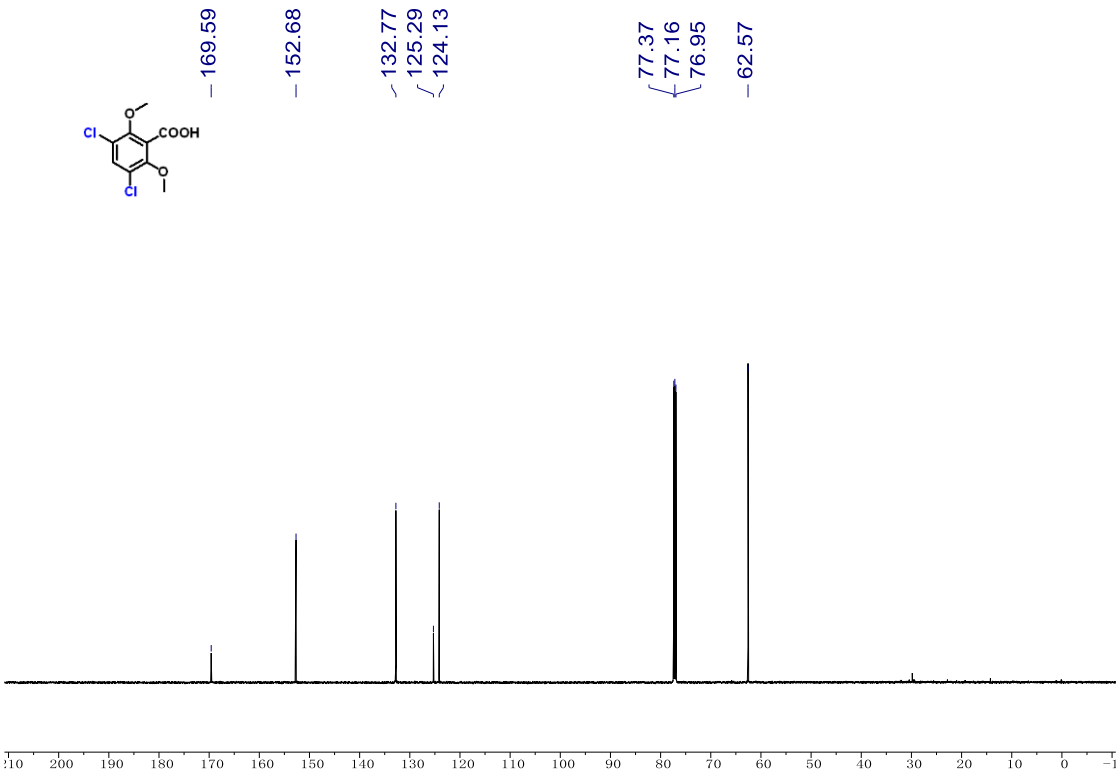
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2jj-1**.



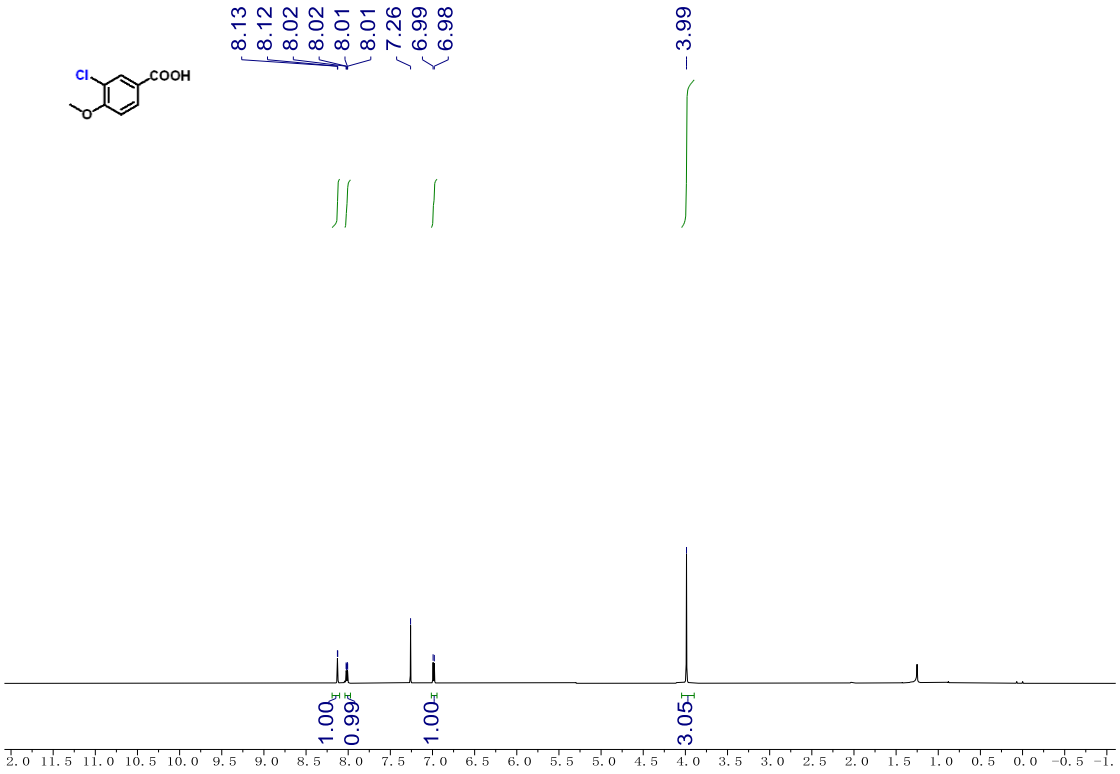
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2jj-1**.



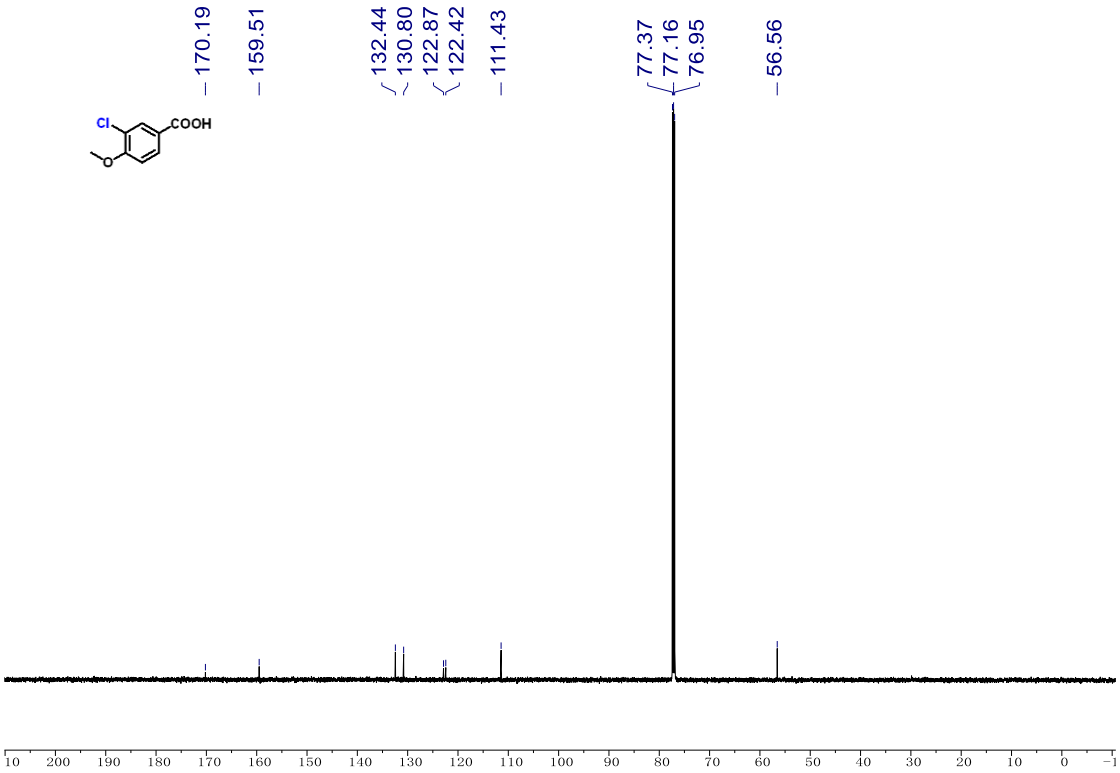
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2jj-2**.



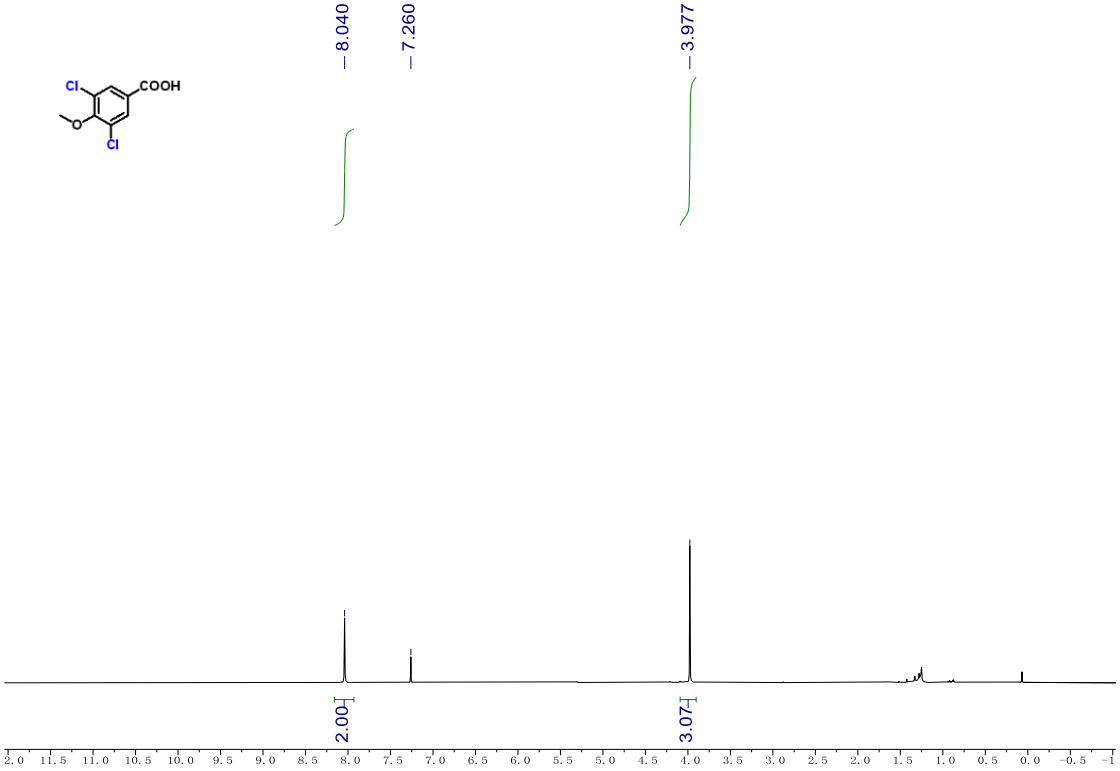
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2jj-2**



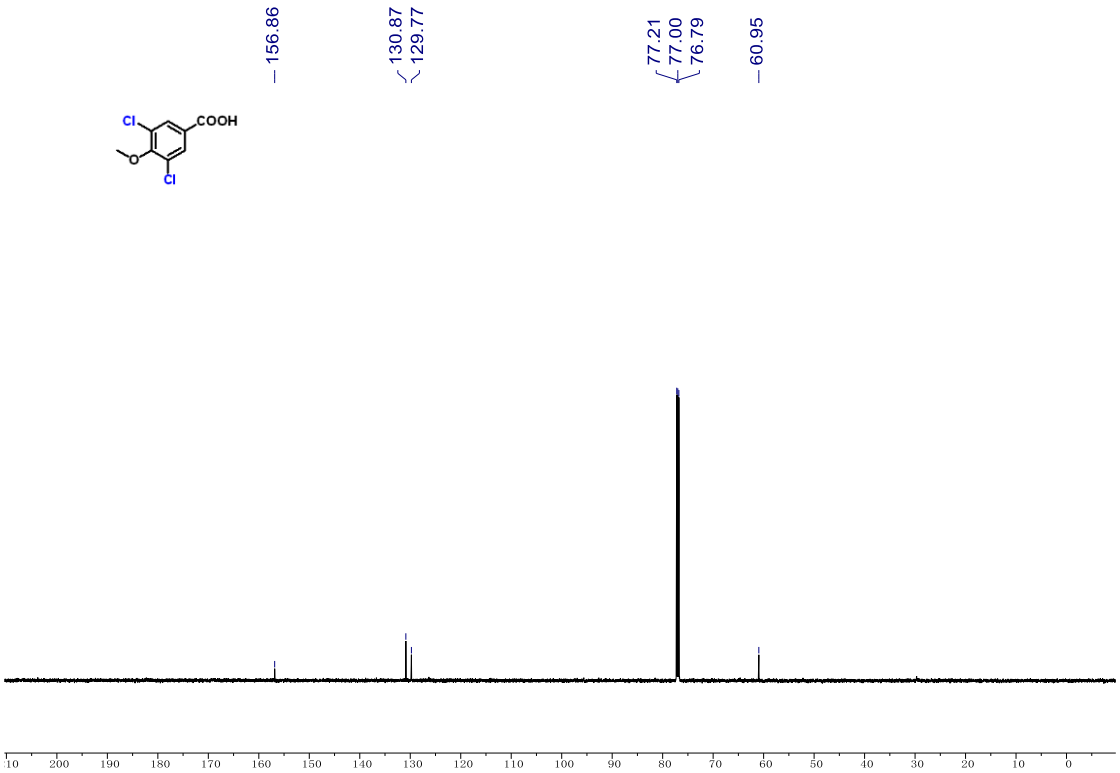
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2kk-1**.



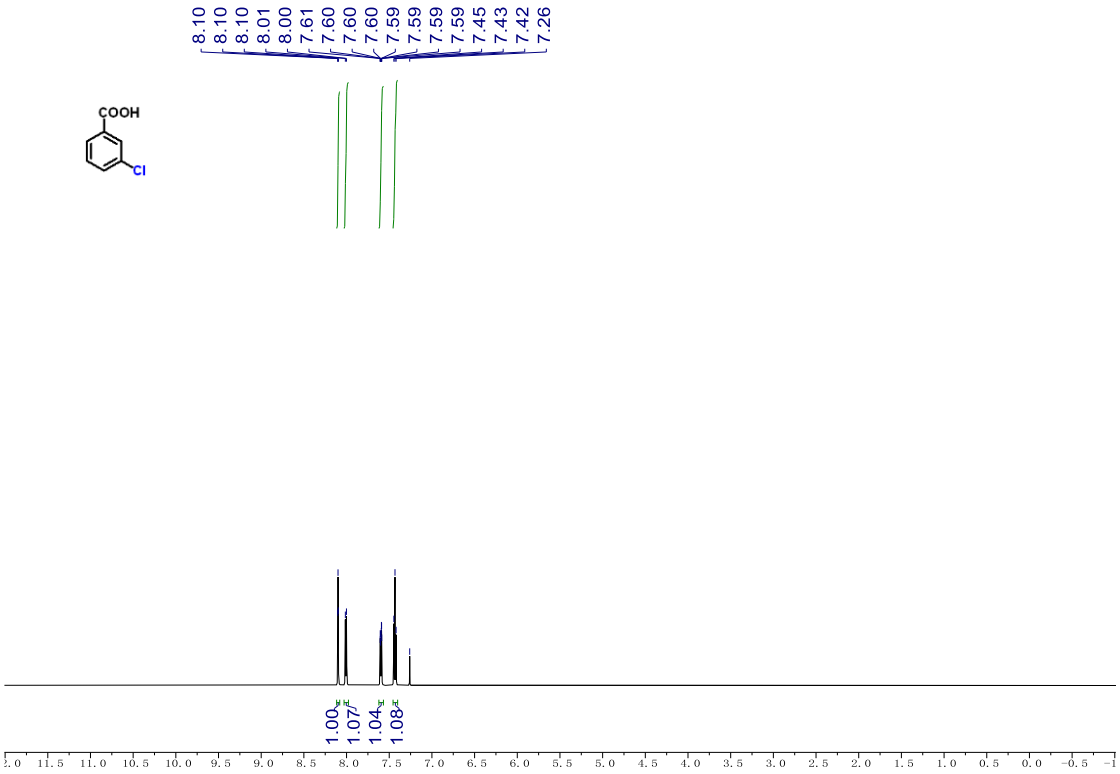
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2kk-1**.



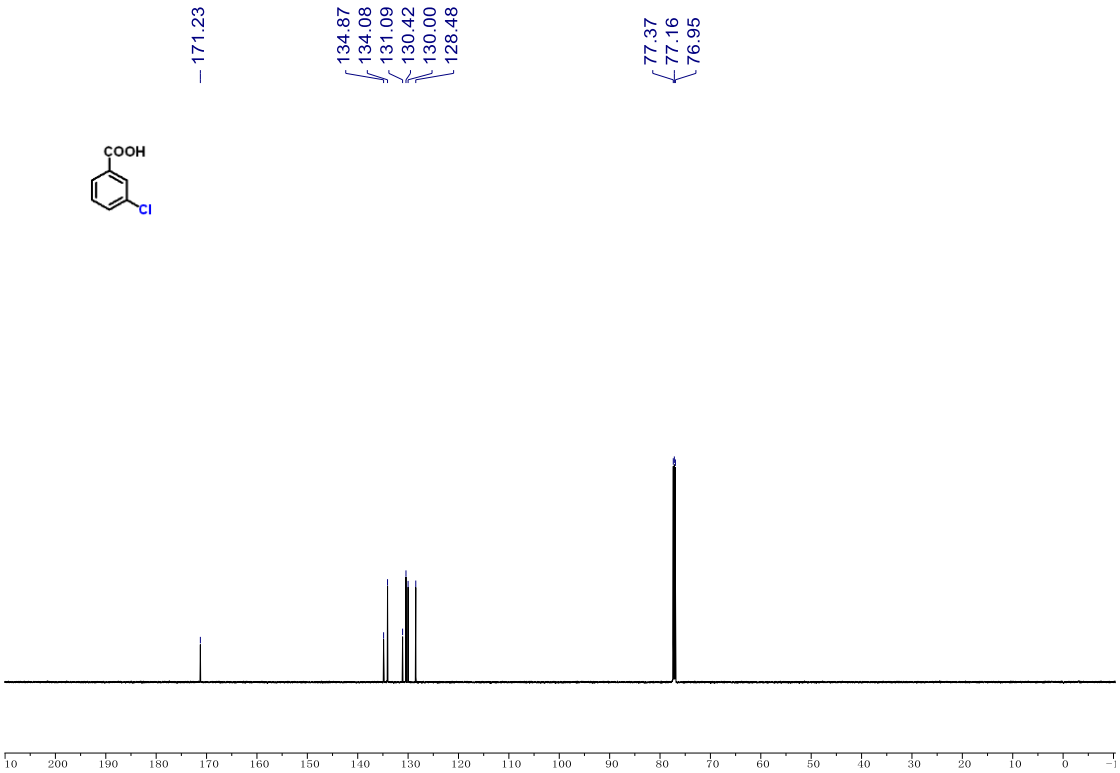
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2kk-2**.



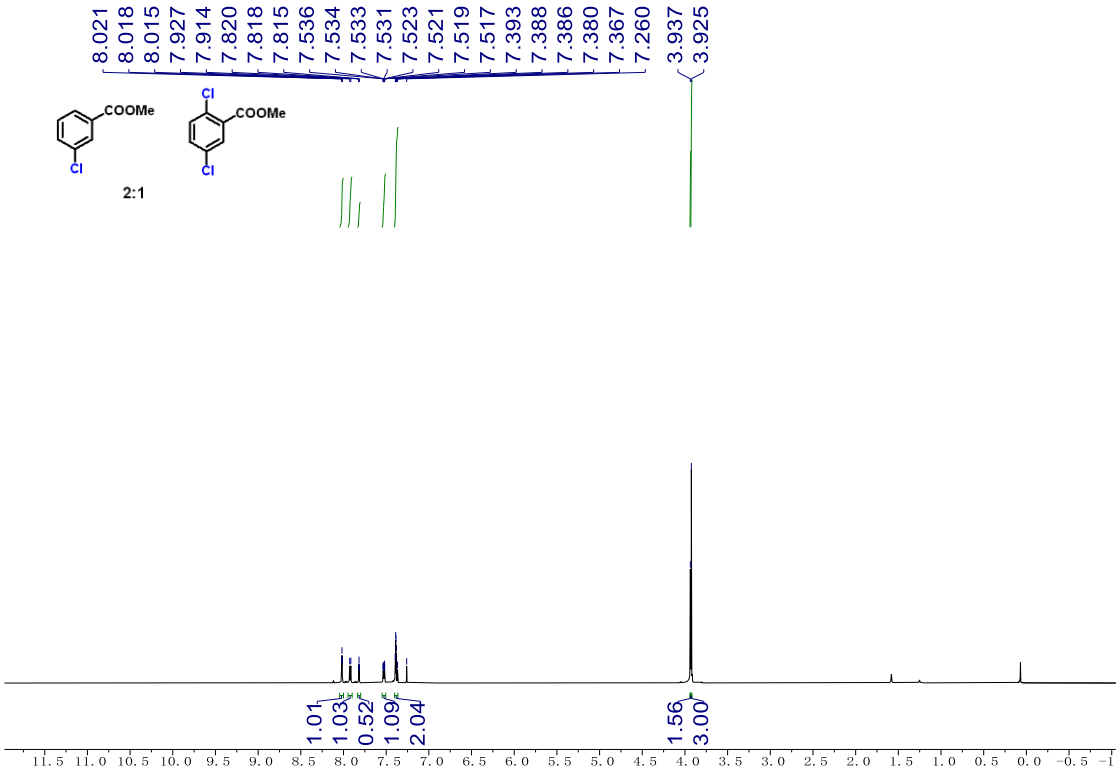
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2kk-2**.



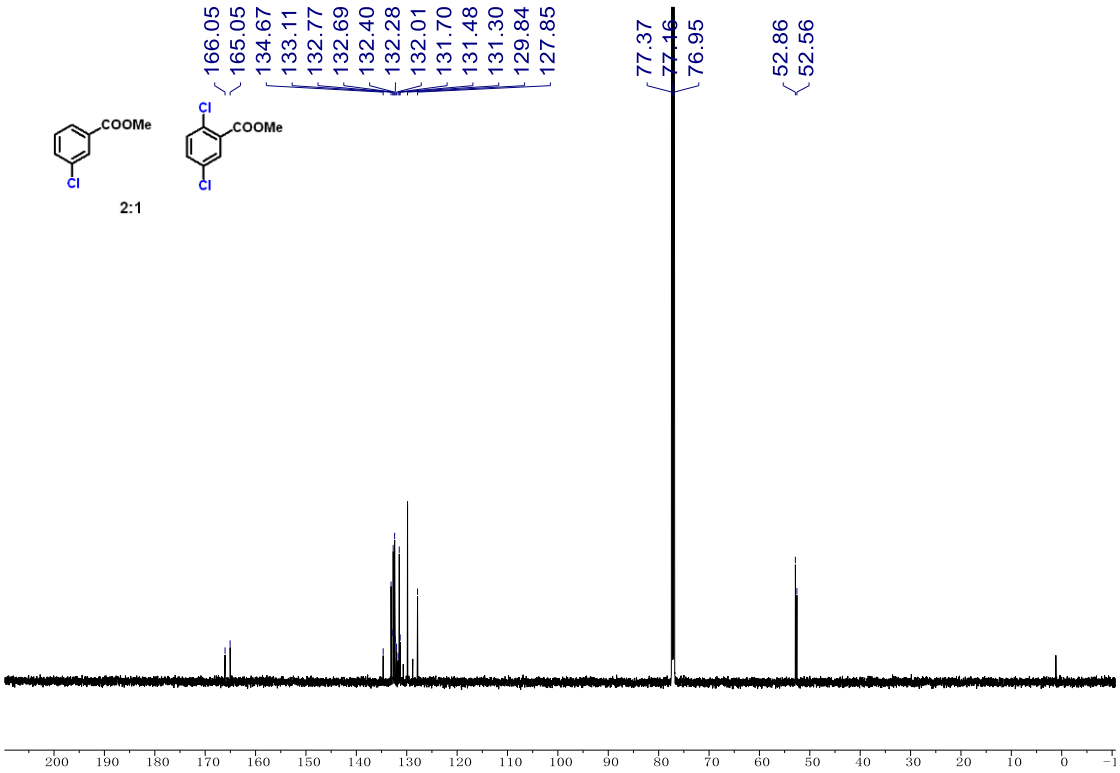
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ll**.



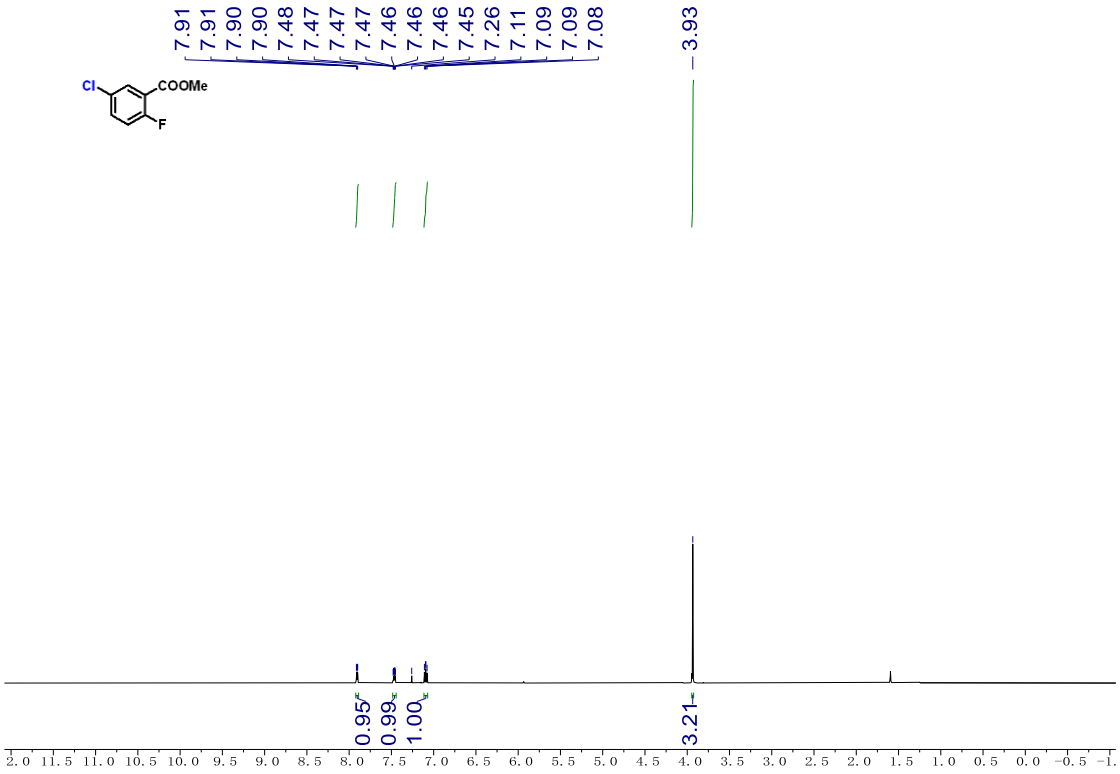
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2ll**.



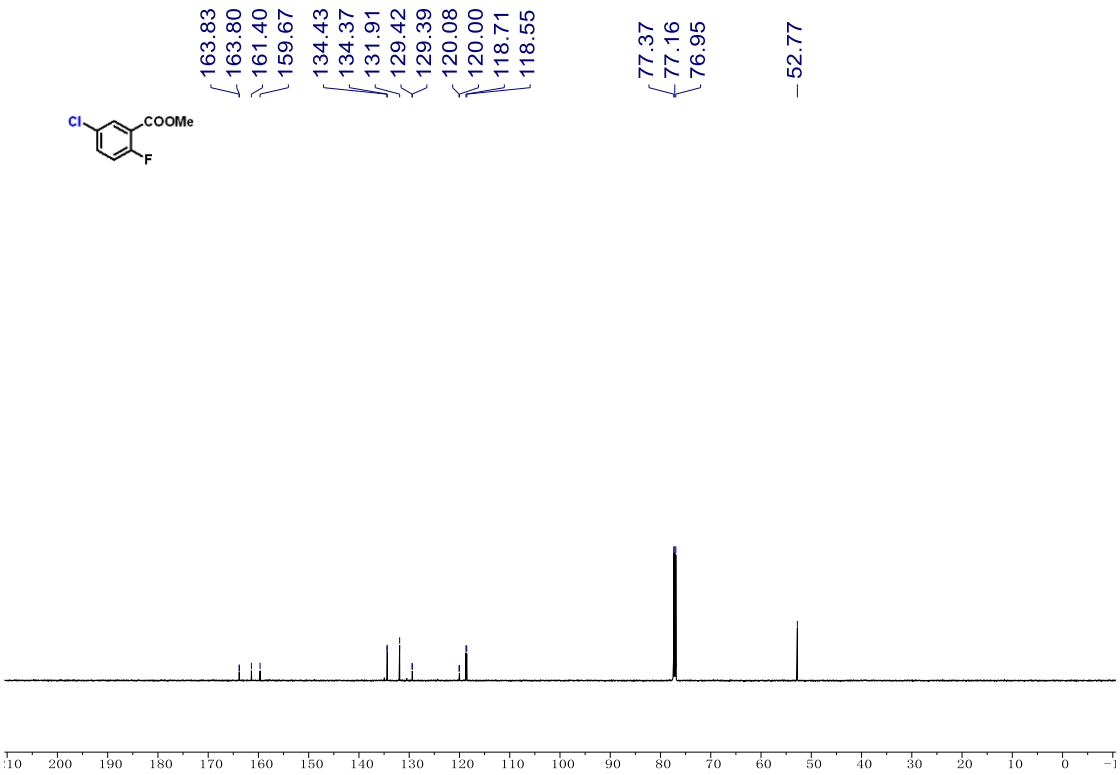
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2mm**.



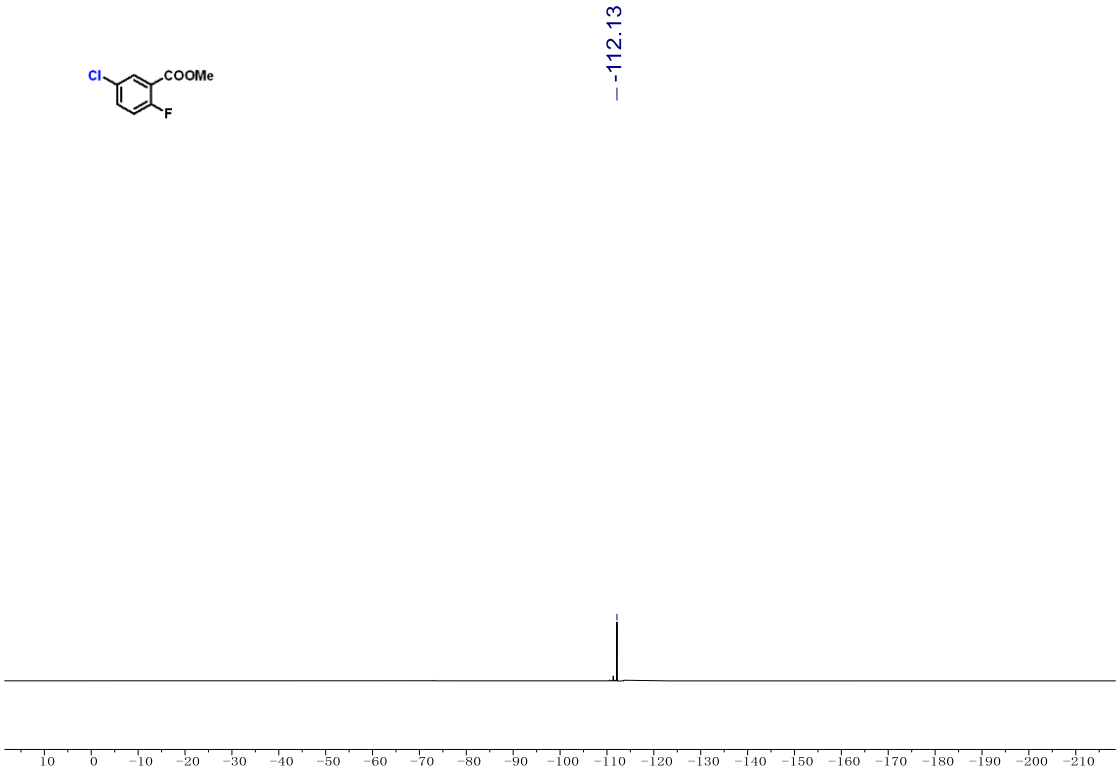
$^{13}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **2mm**.



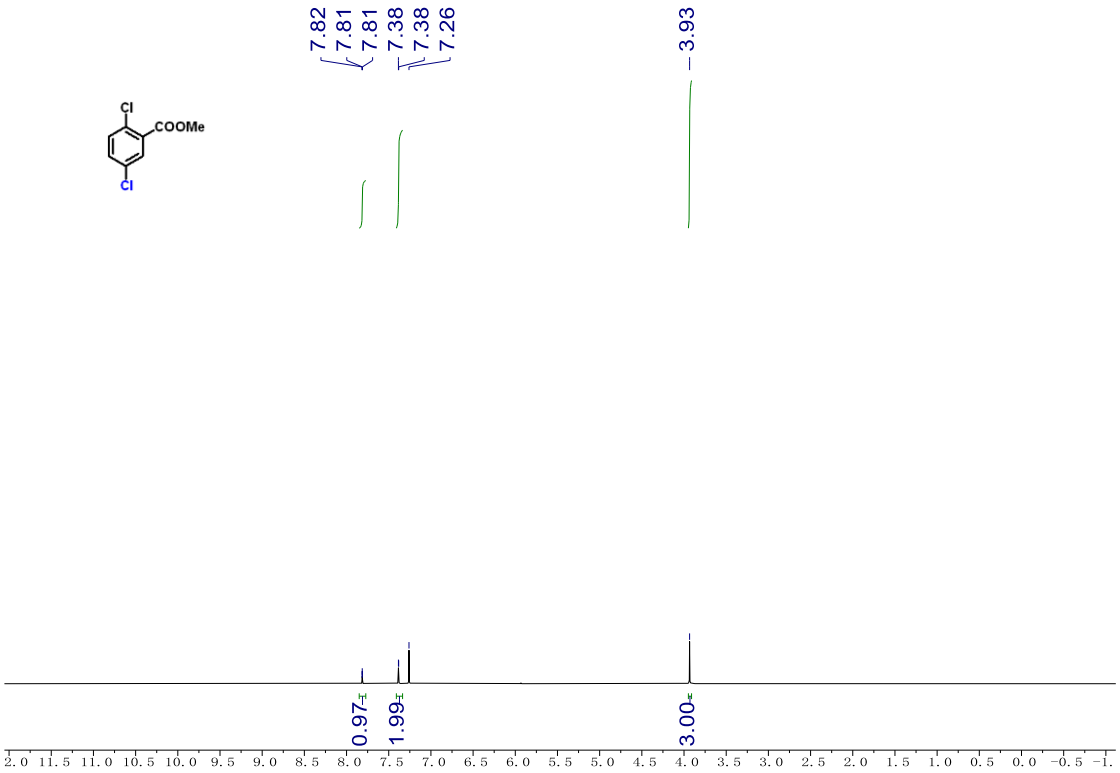
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2nn**.



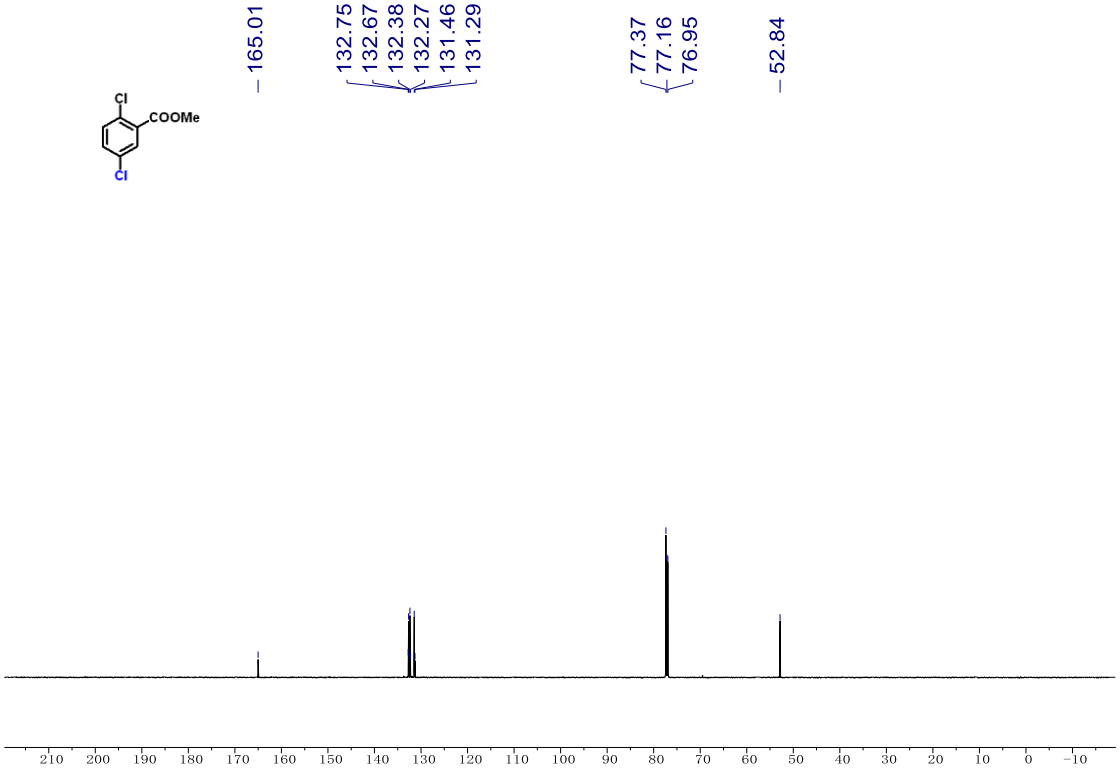
$^{13}C\{^{1}H\}$ NMR ($CDCl_3$) spectrum of **2nn**.



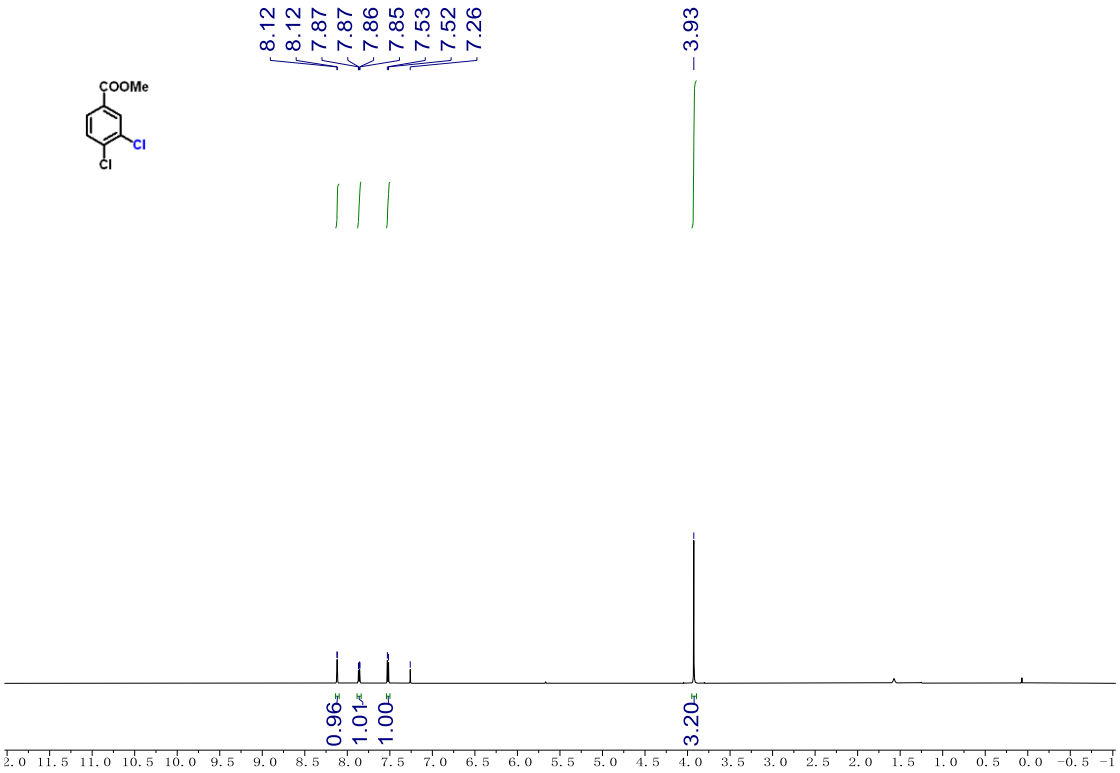
^{19}F NMR ($CDCl_3$) spectrum of **2nn.**



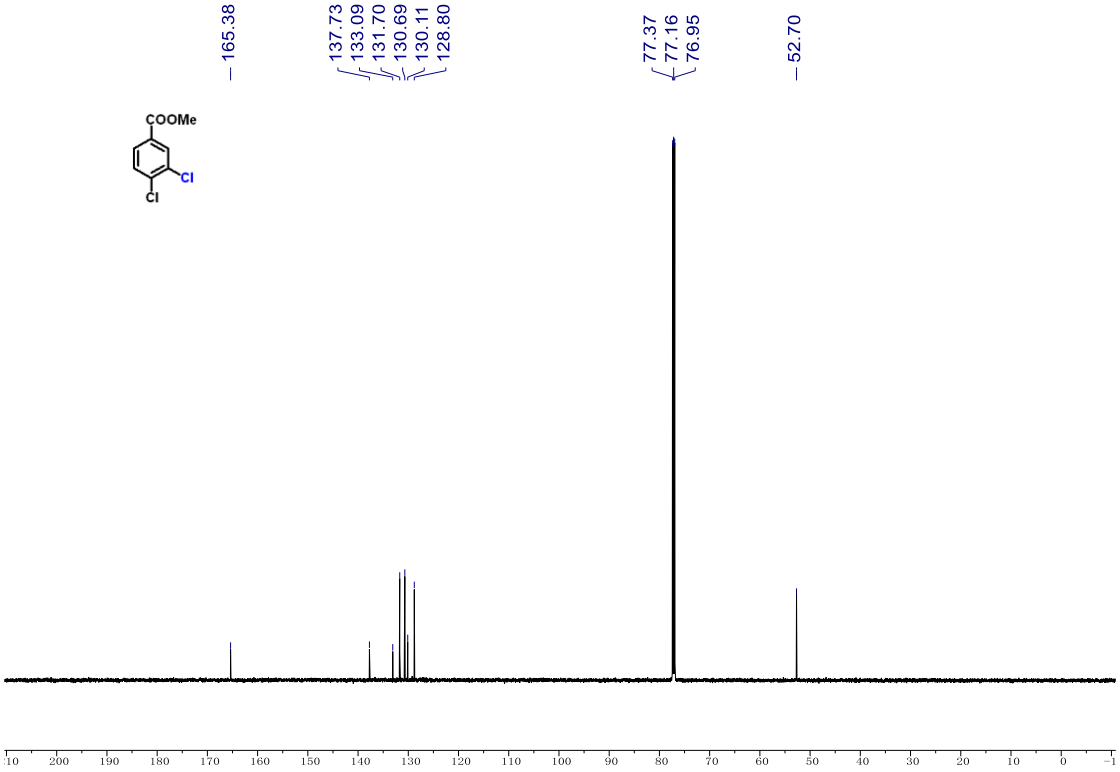
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2oo**.



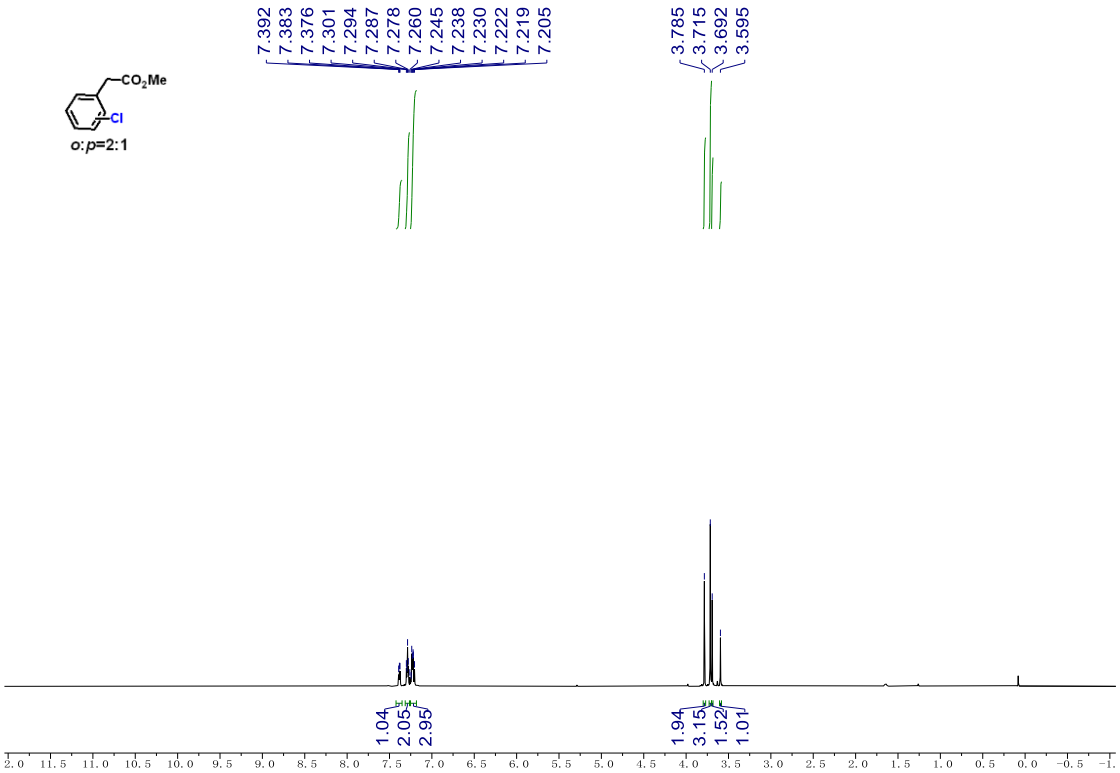
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2oo**



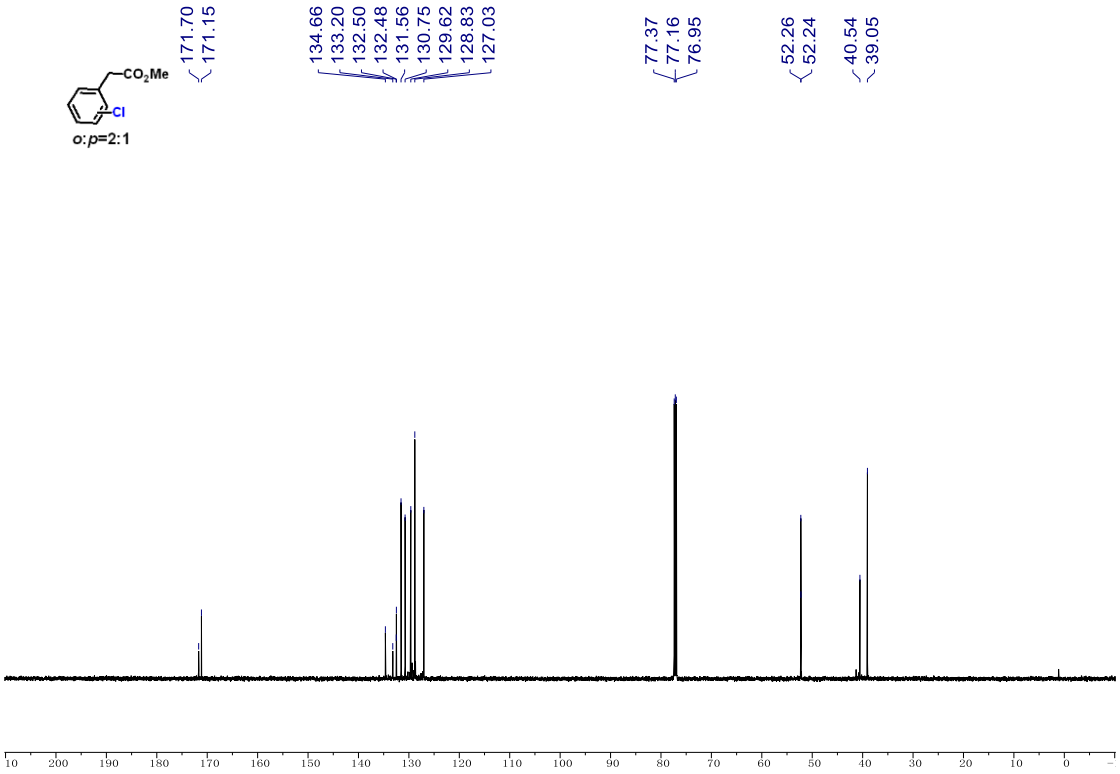
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2pp**.



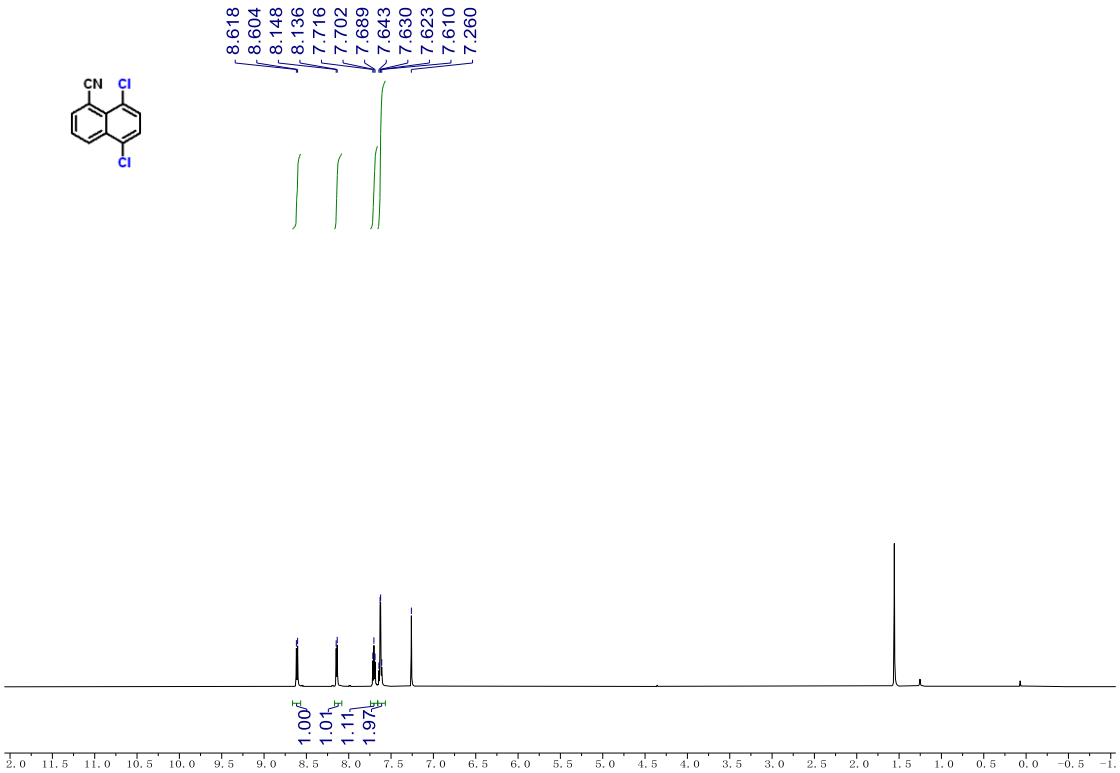
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2pp**.



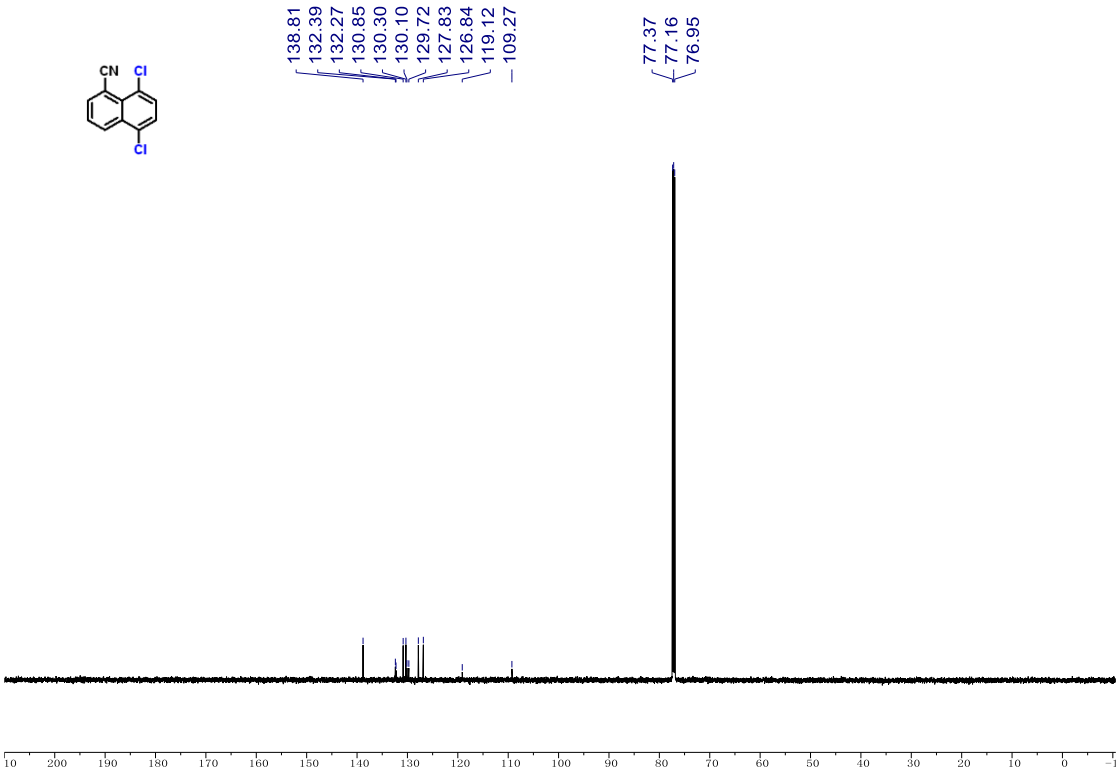
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2qq**.



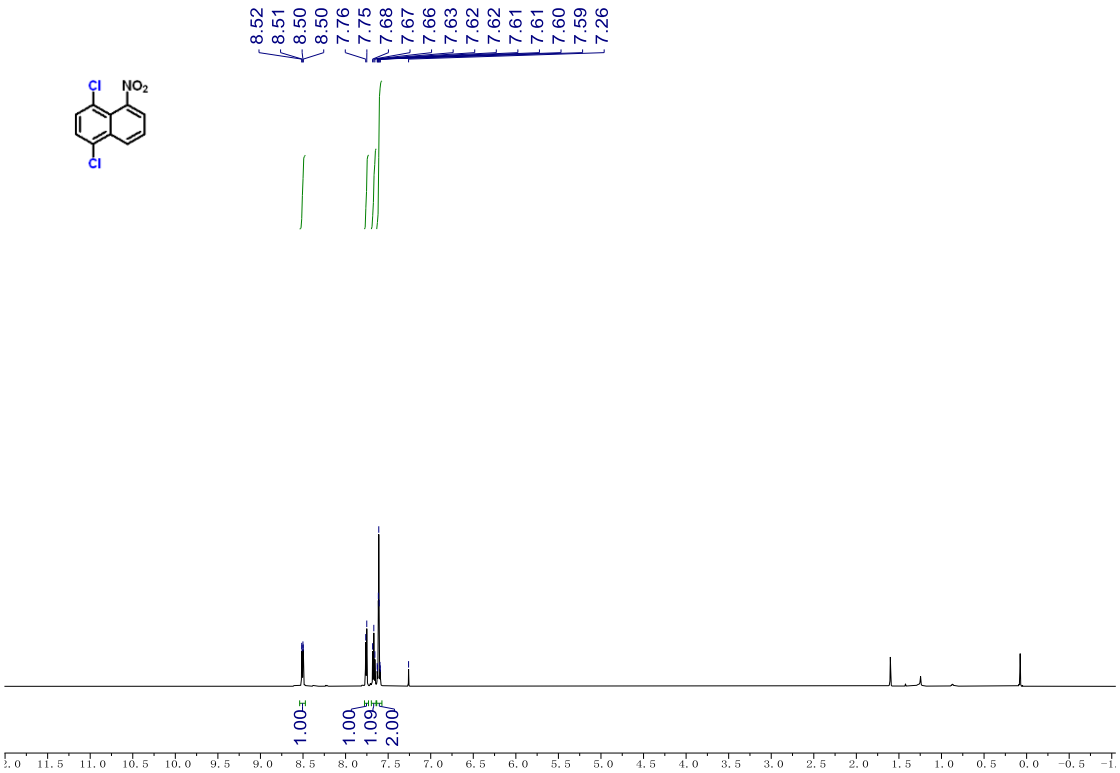
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2qq**.



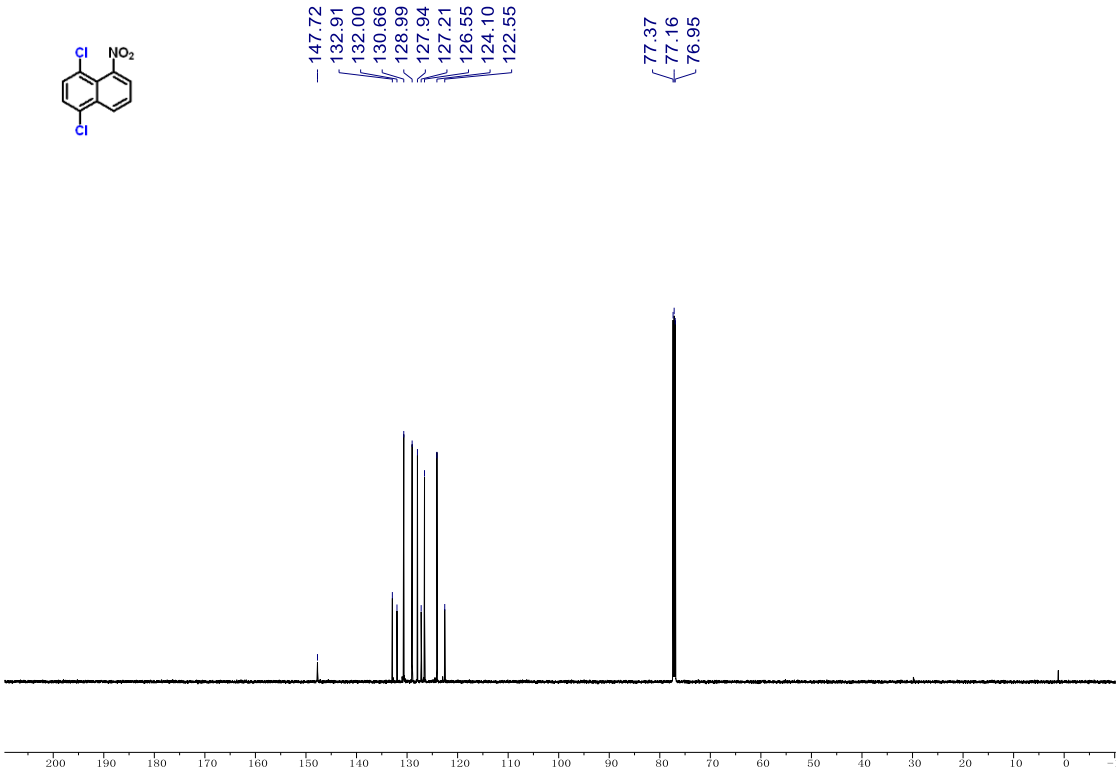
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2rr**.



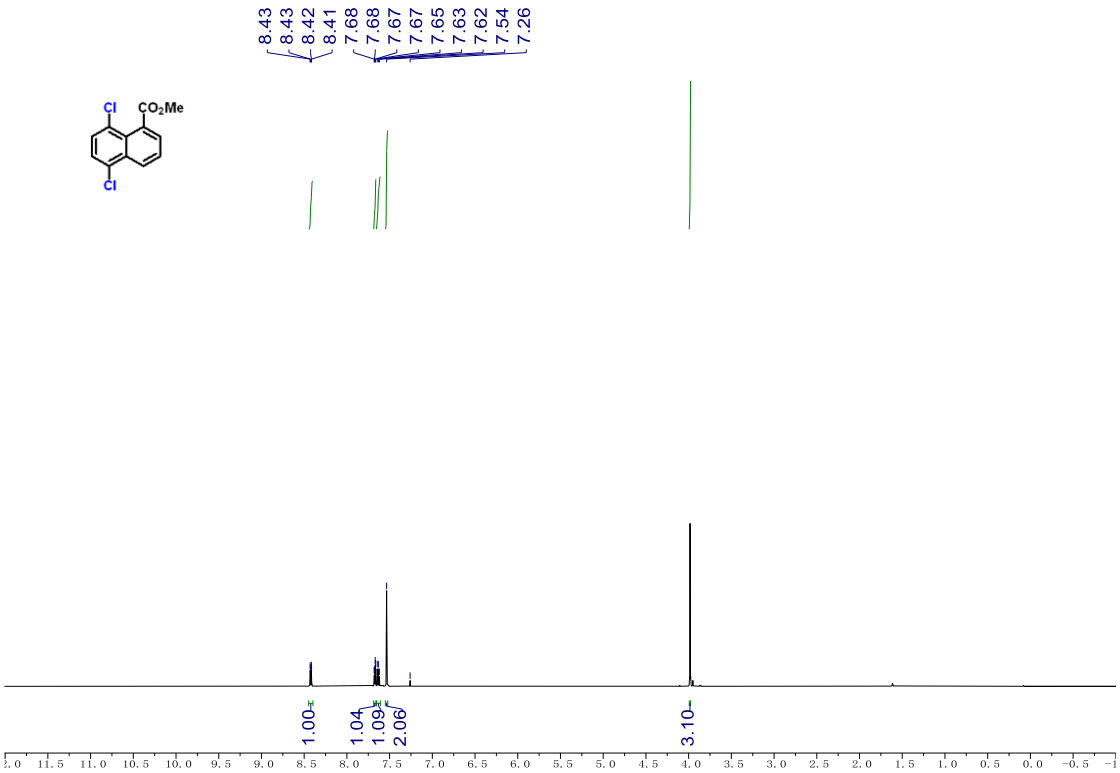
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2rr**.



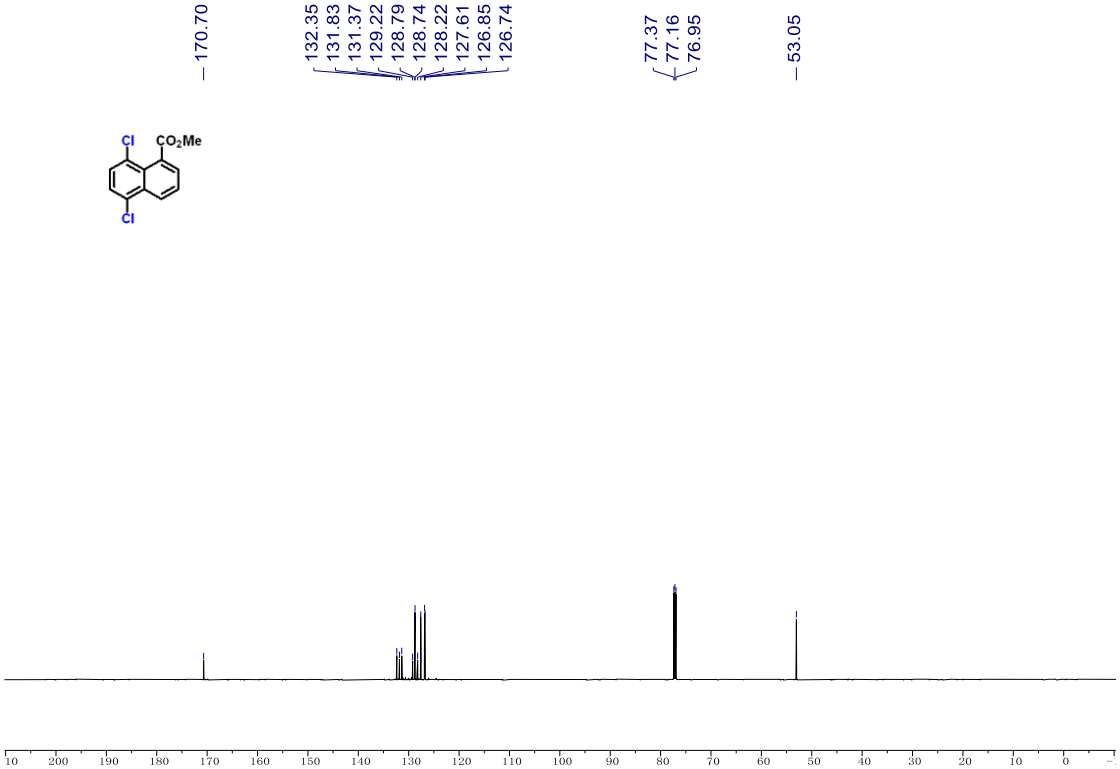
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ss**.



^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ss**.

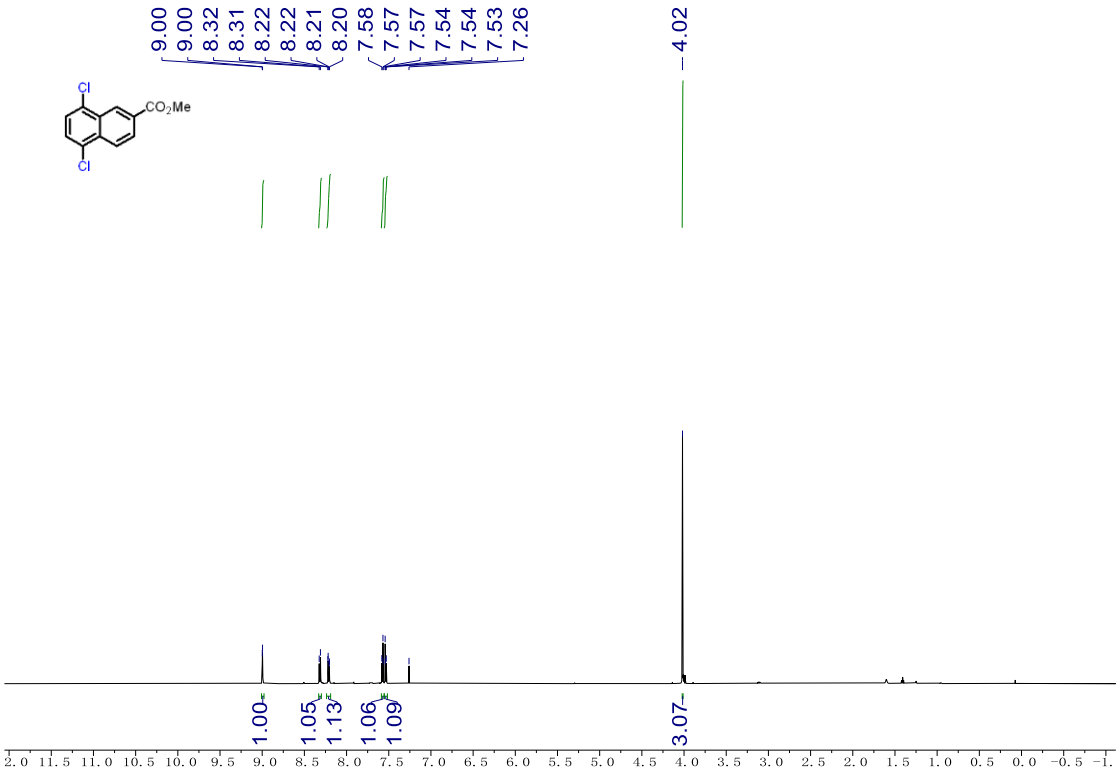


^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2tt**.

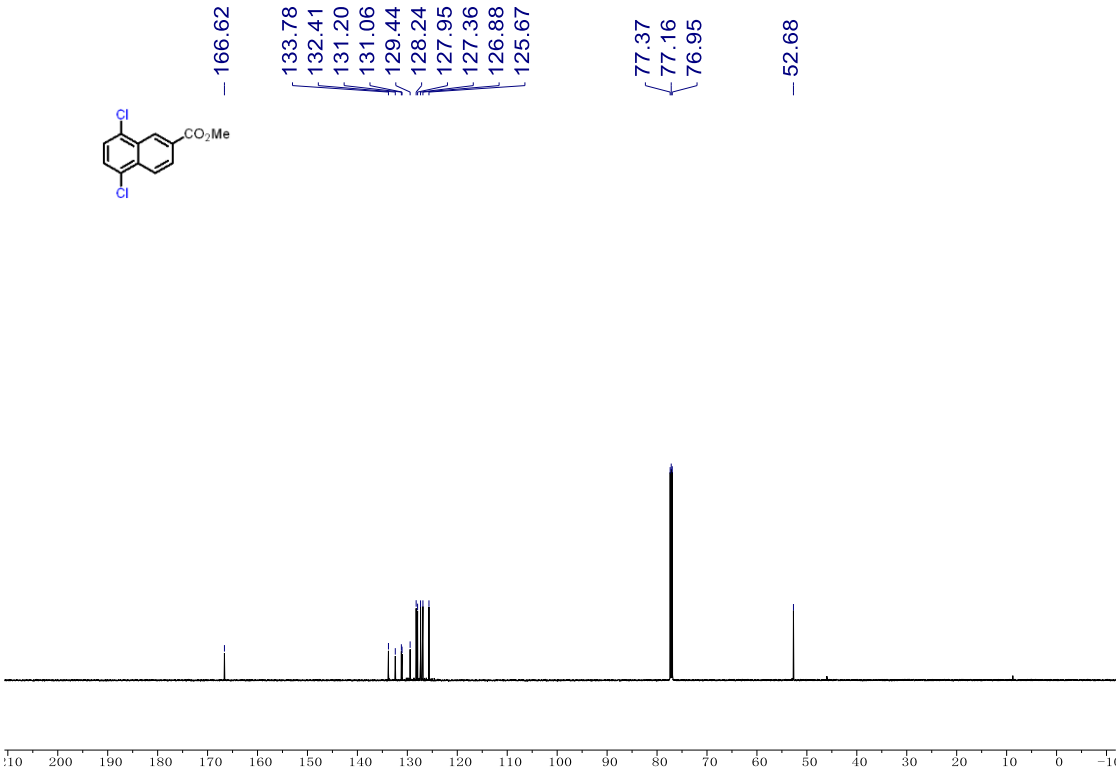


^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2tt**.

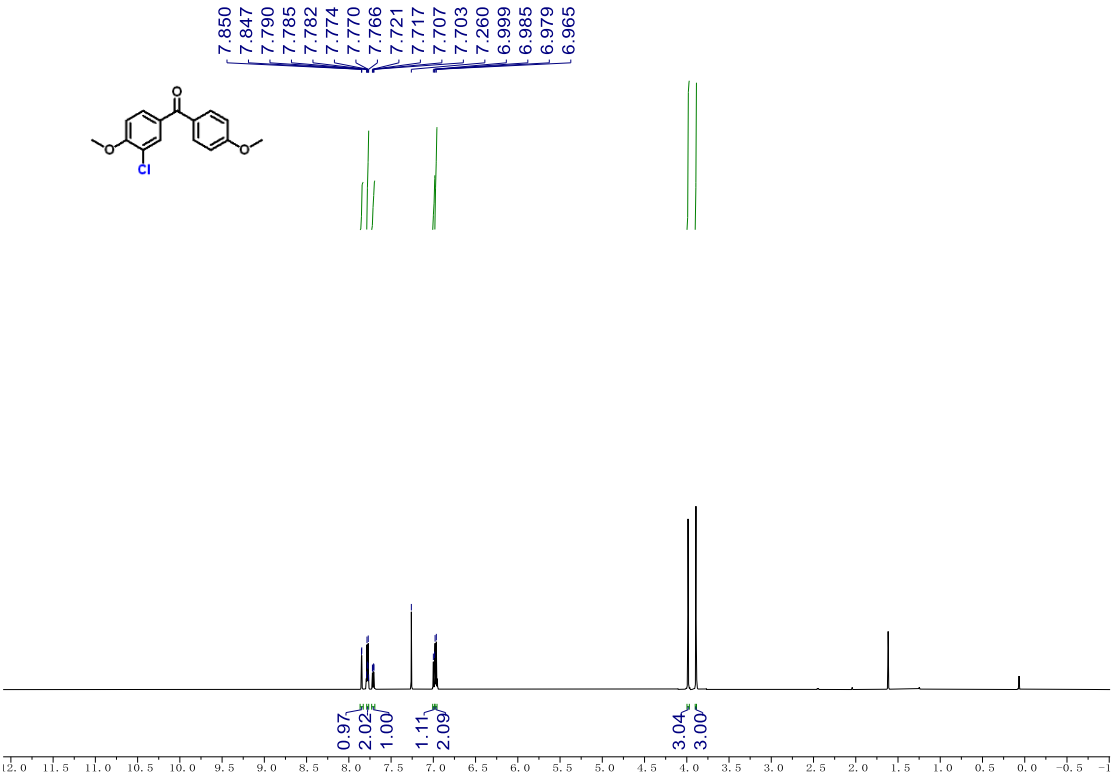
.



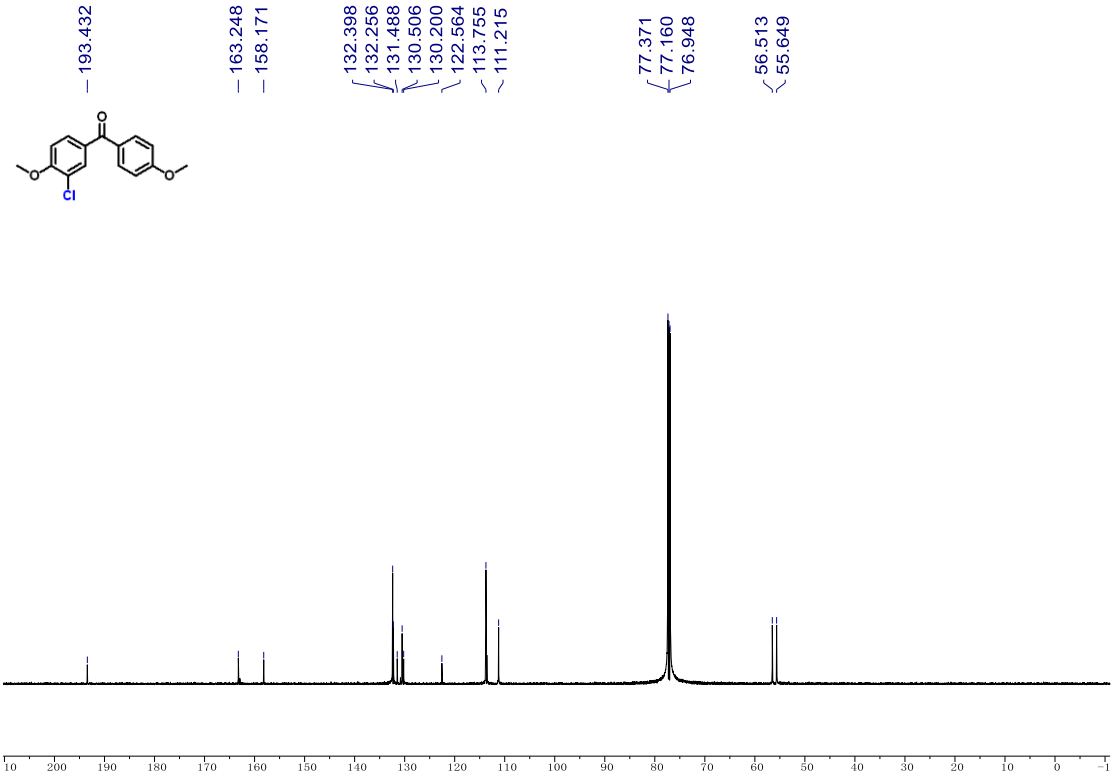
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2uu**.



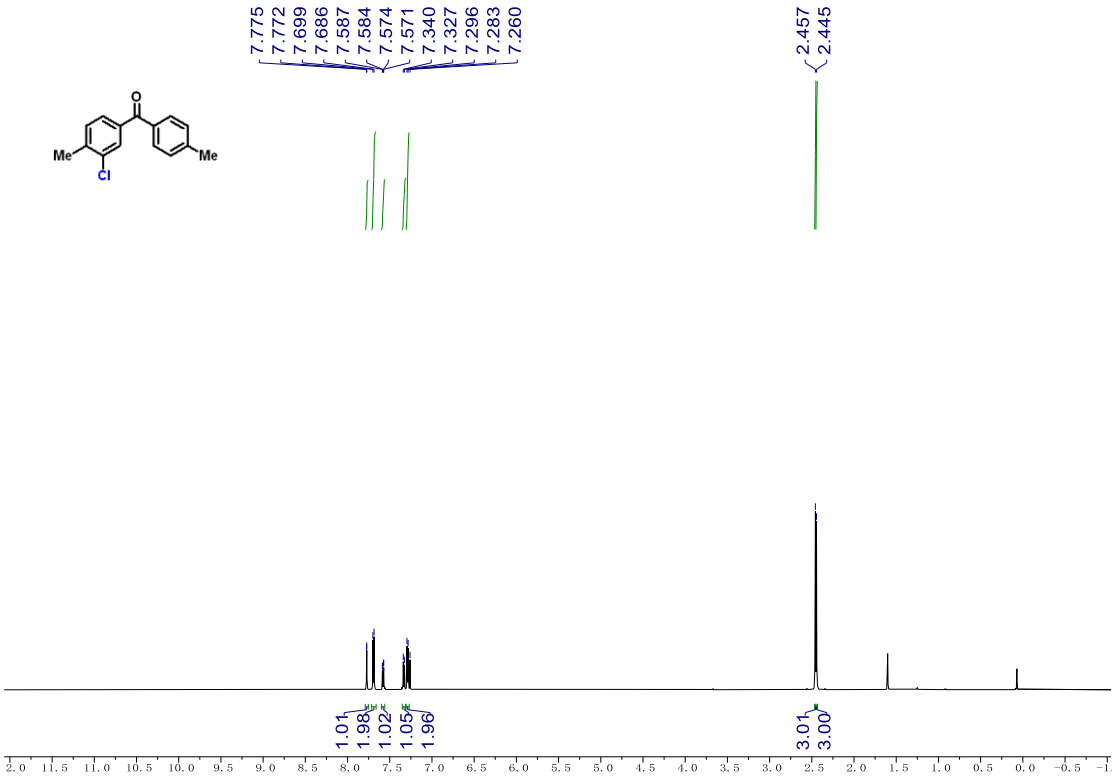
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2uu**.



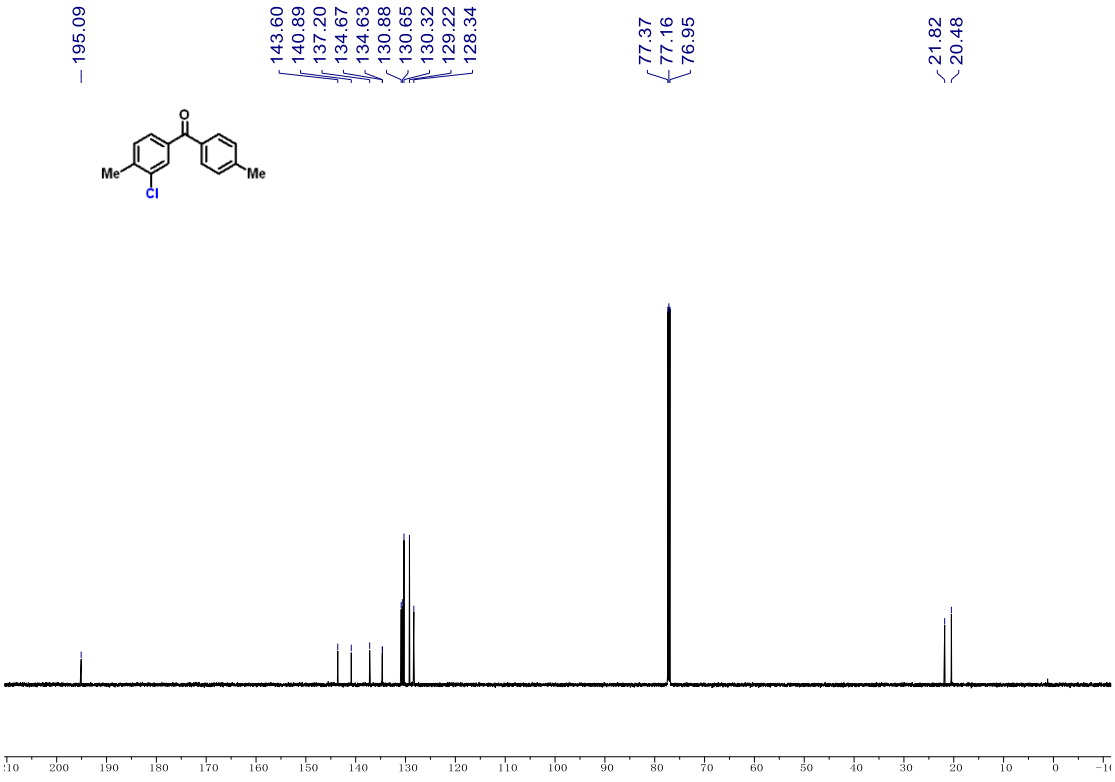
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2vv**.



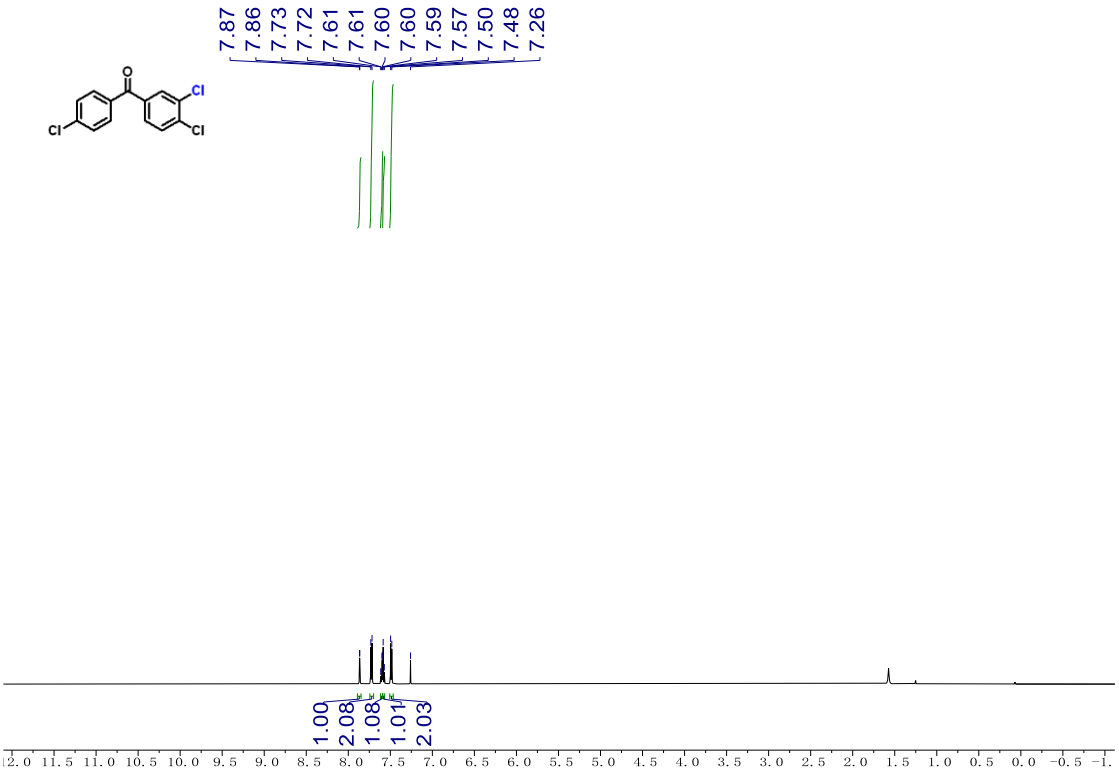
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2vv**.



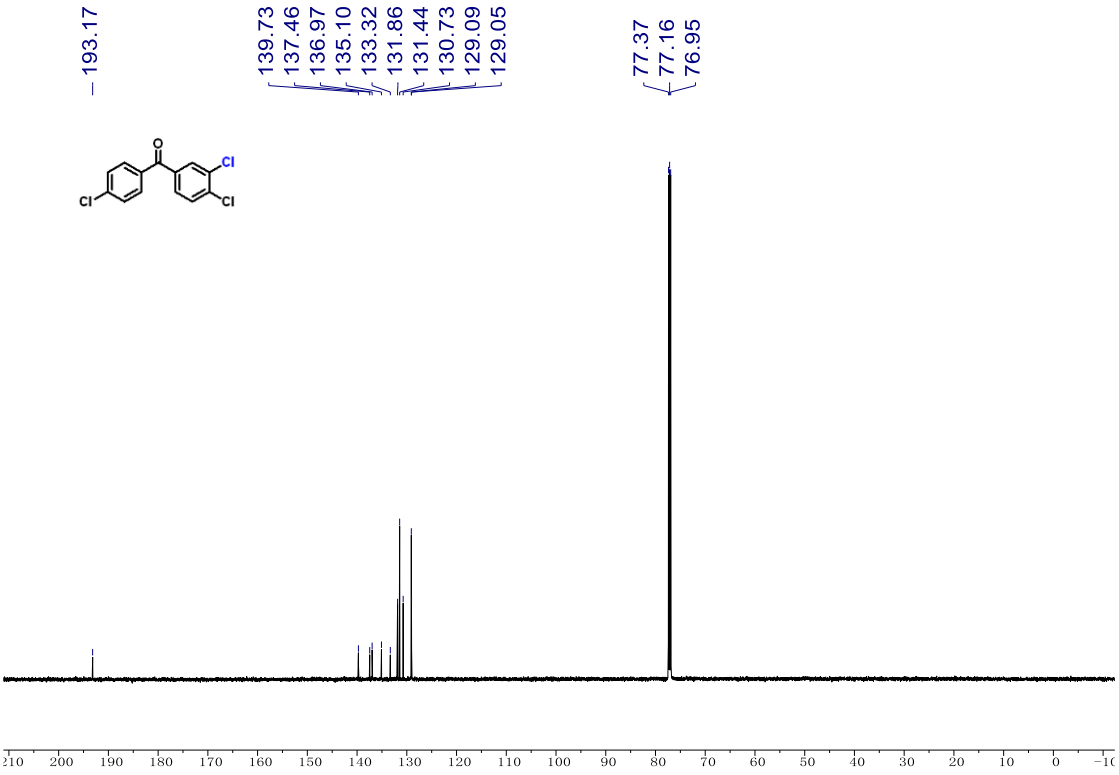
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ww**.



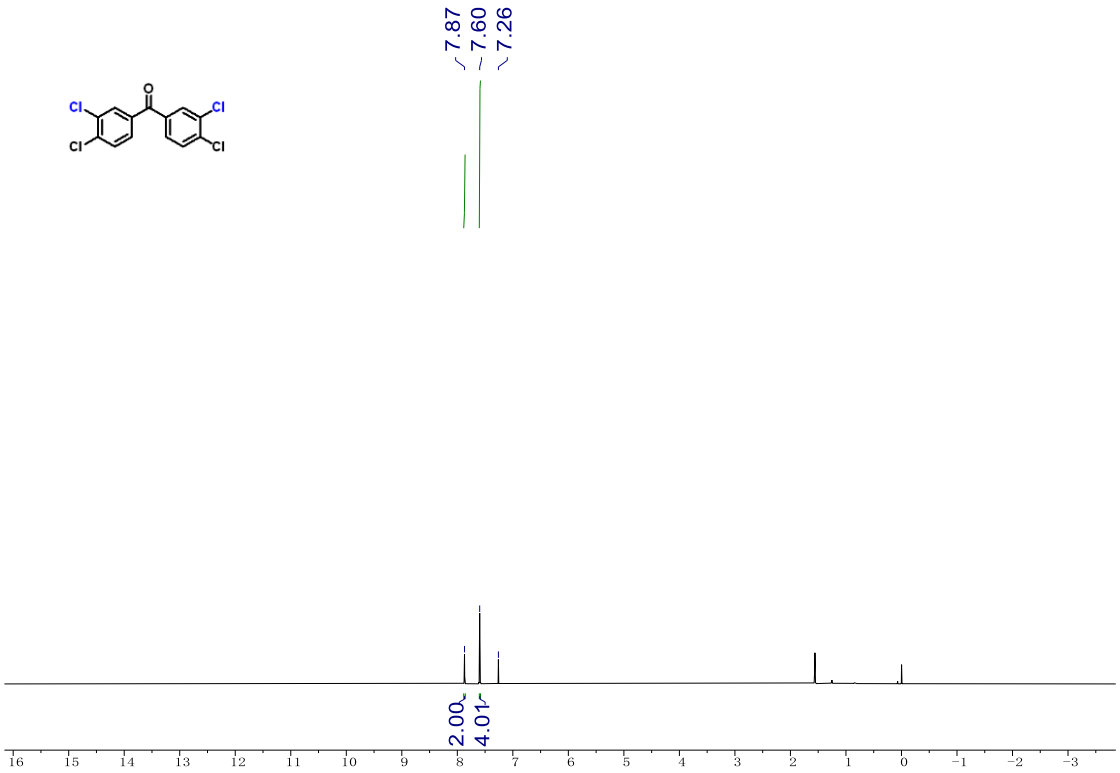
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ww**.



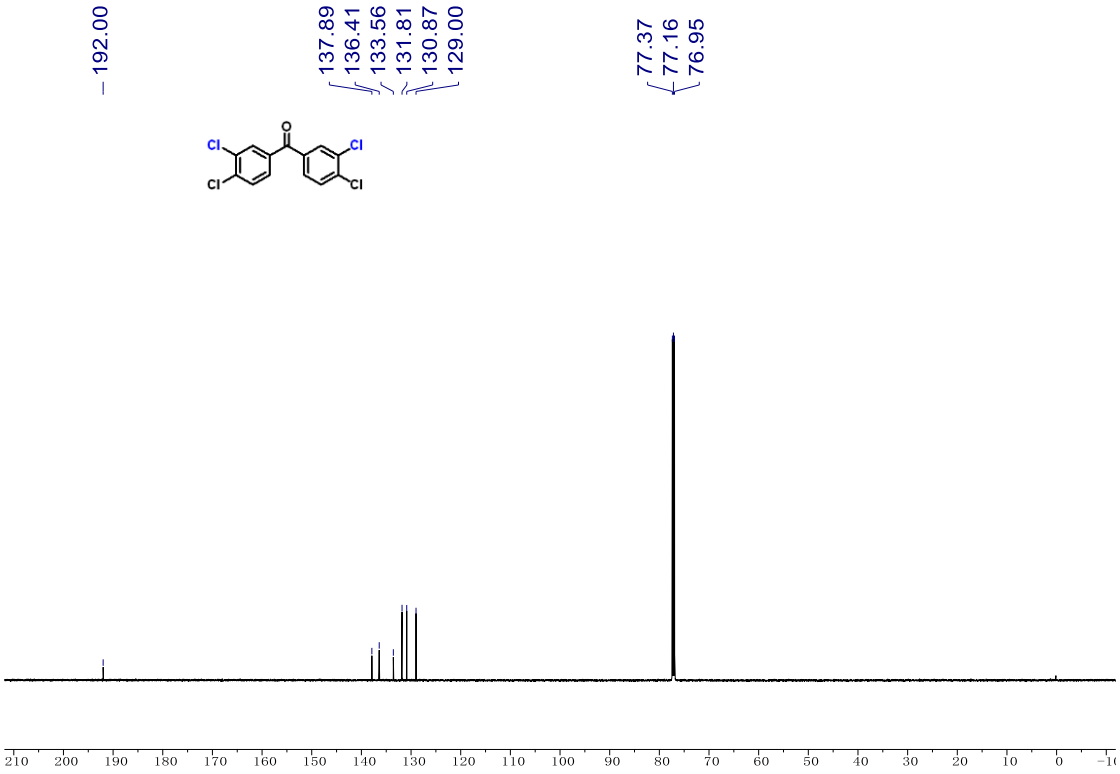
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2xx-1**.



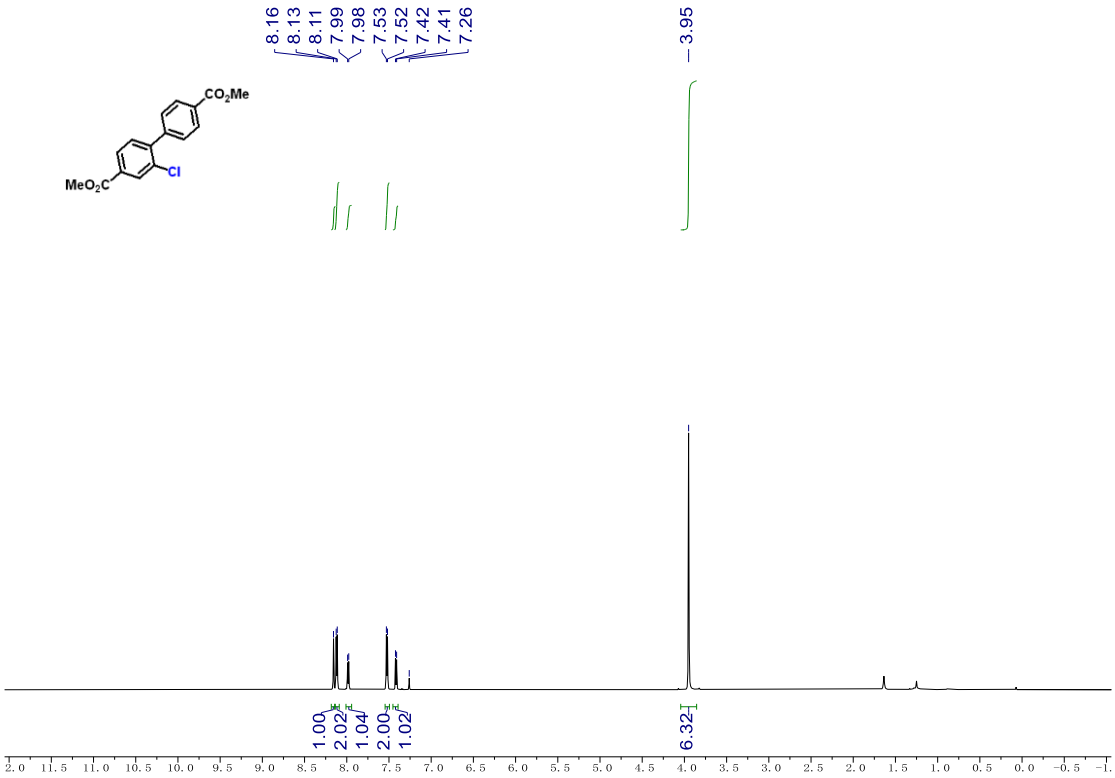
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2xx-1**.



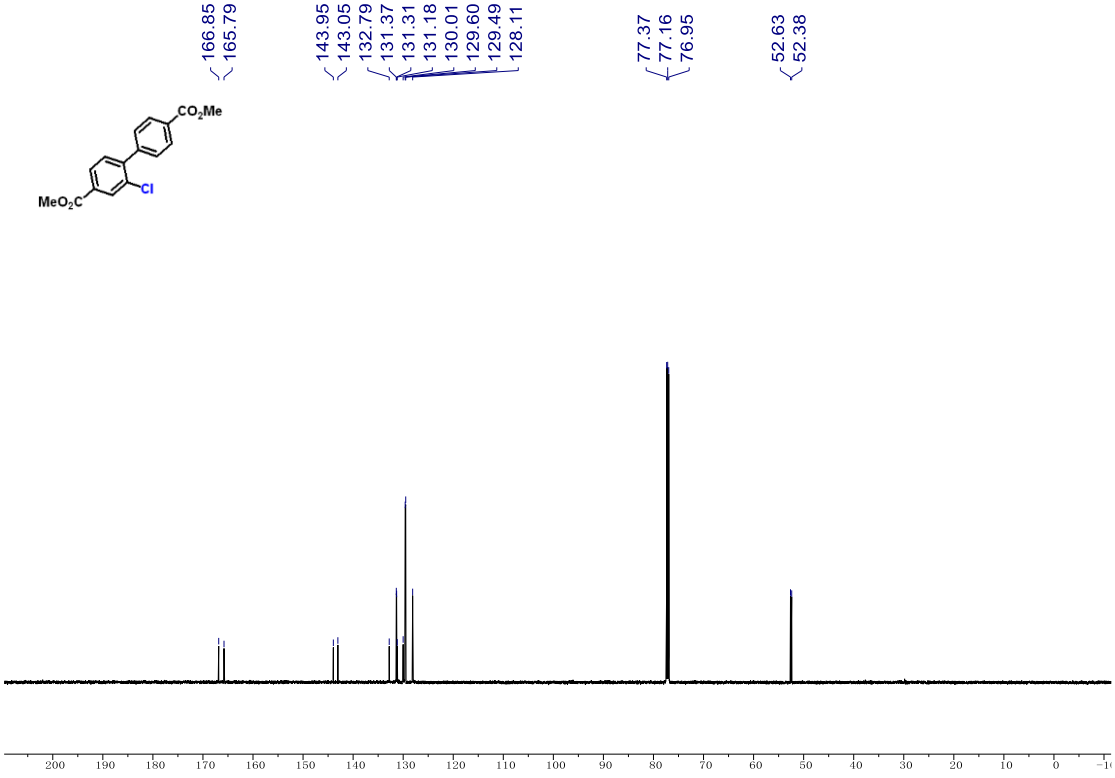
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2xx-2**.



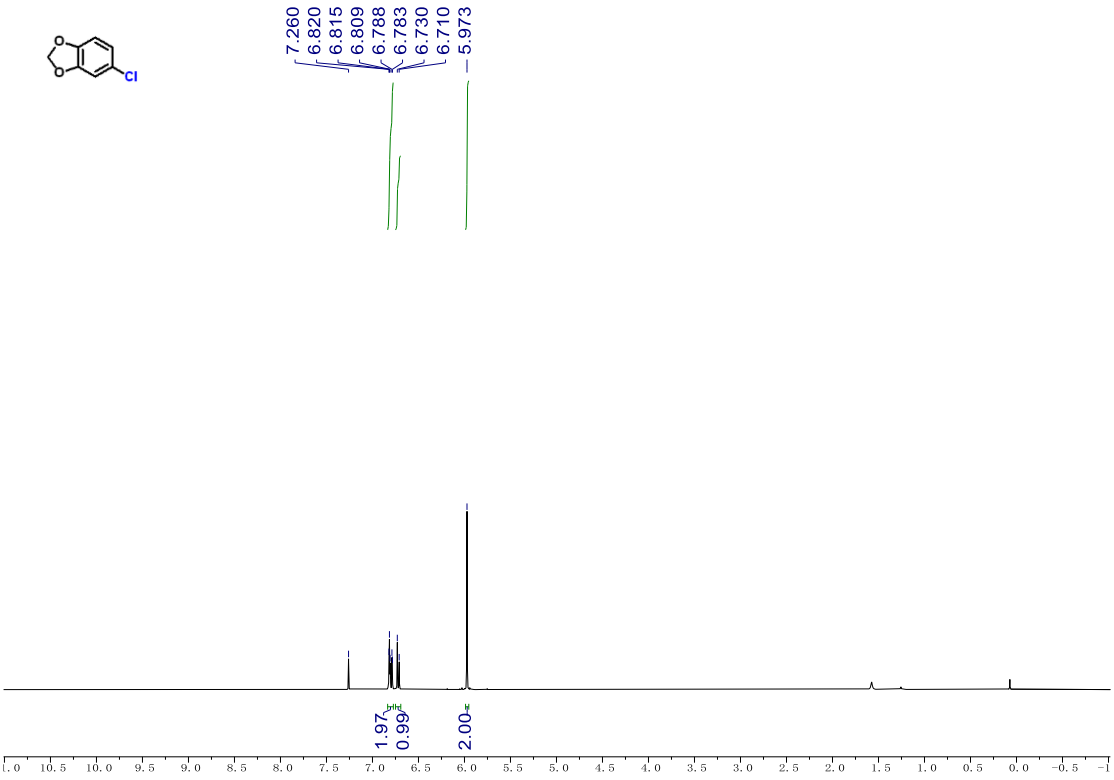
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2xx-2**.



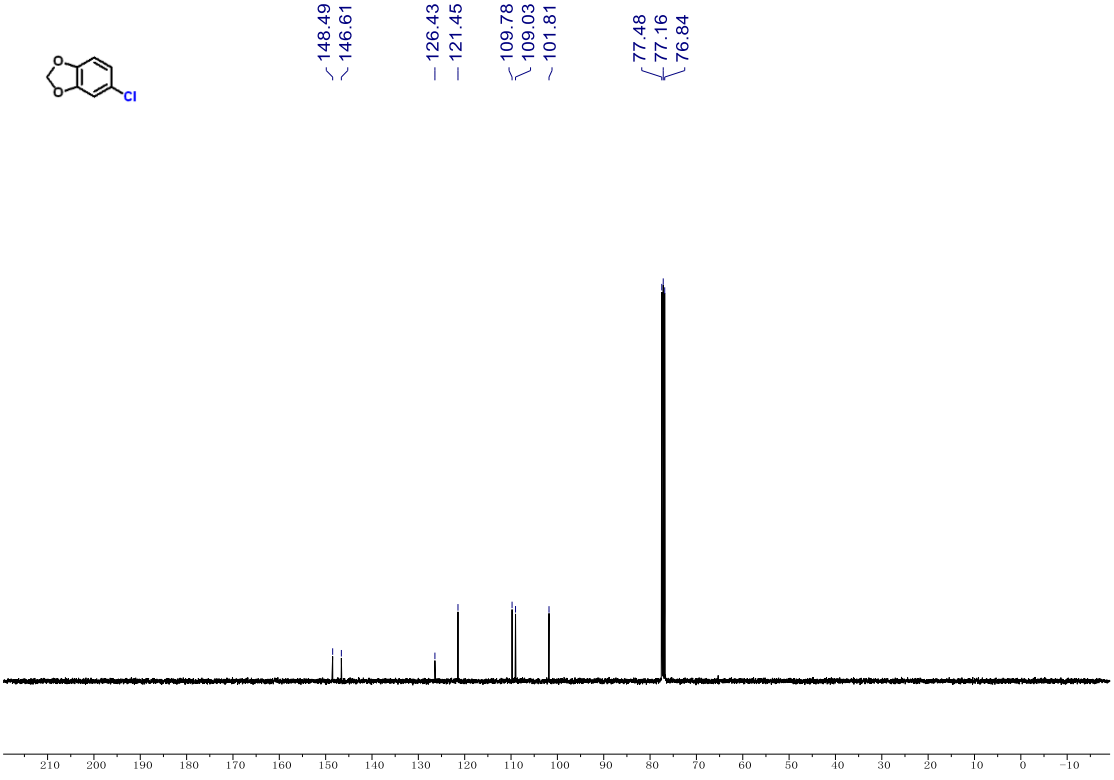
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2yy**.



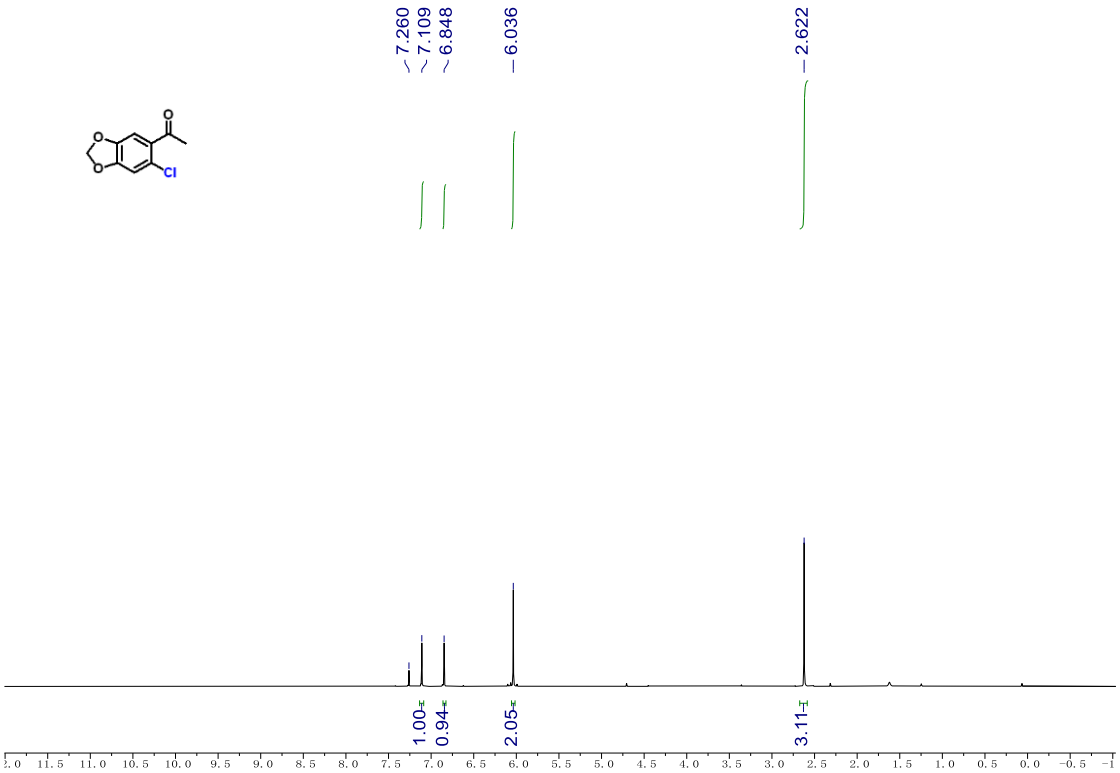
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2yy**.



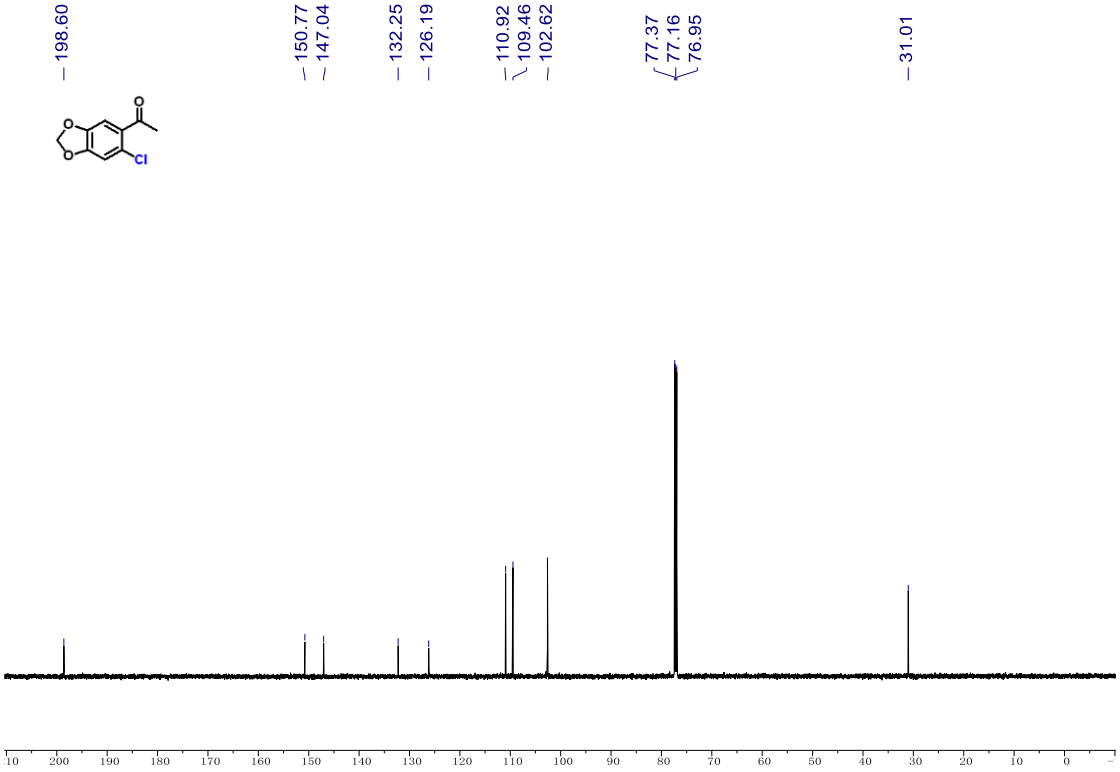
^{1}H NMR (400 MHz, $CDCl_3$) spectrum of **2zz**.



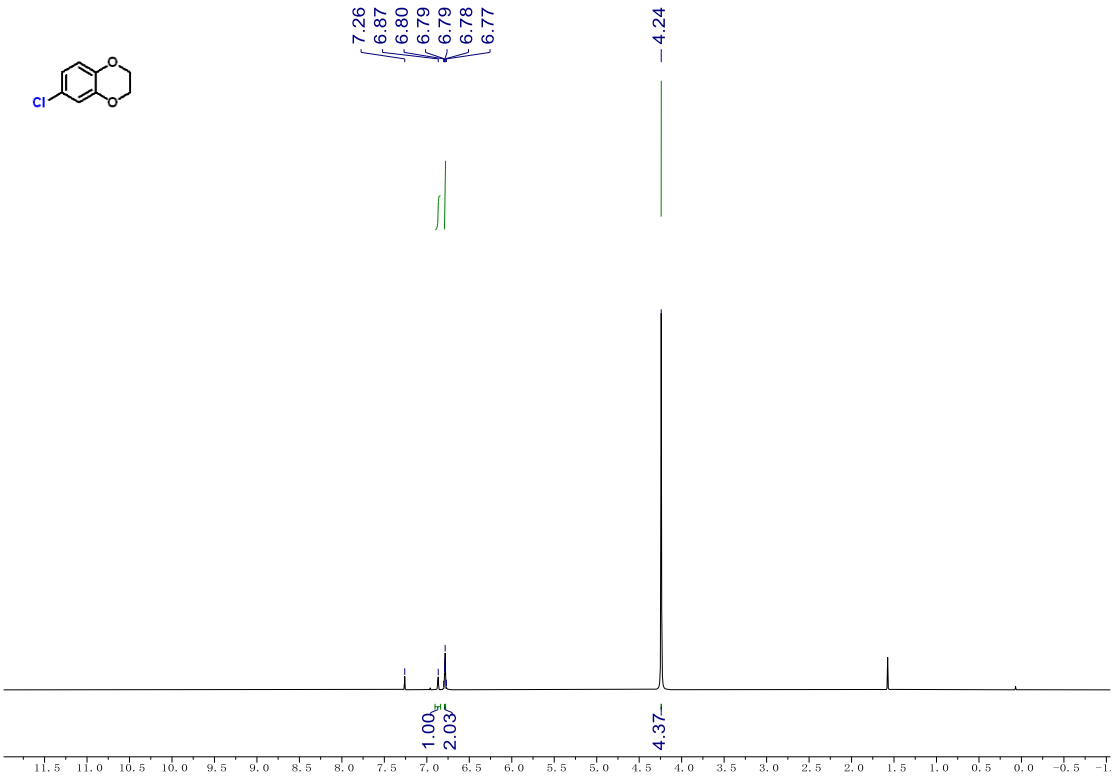
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **2zz**.



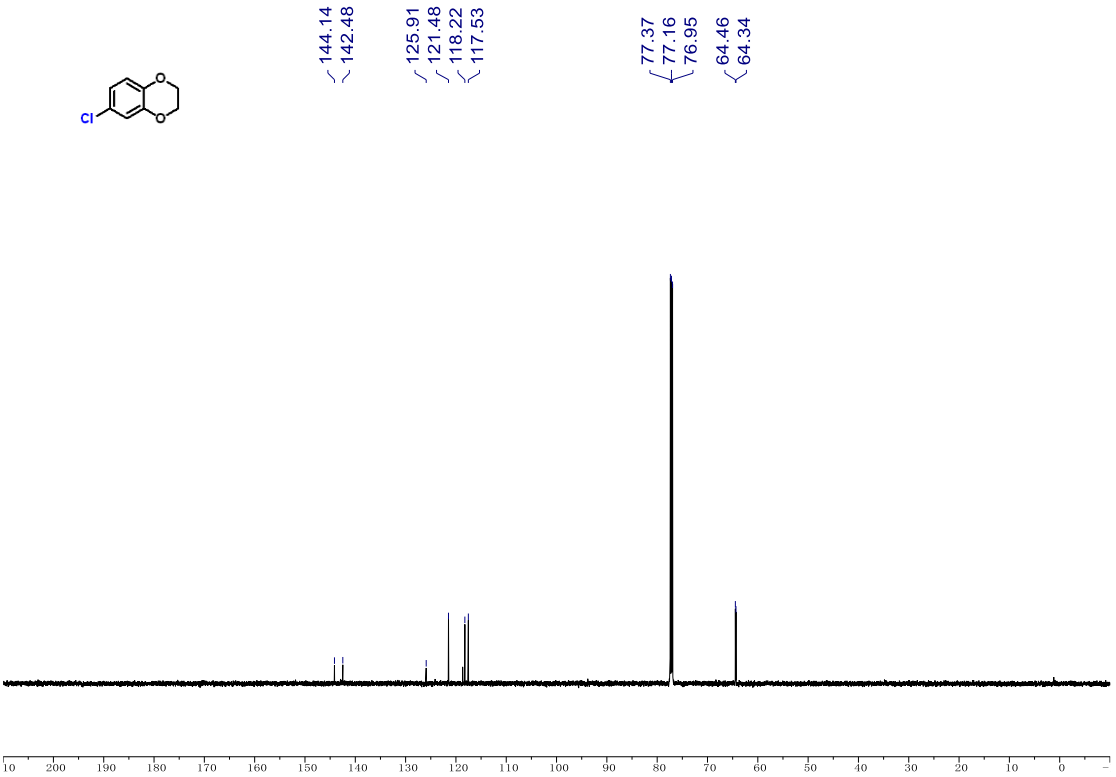
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2aaa**.



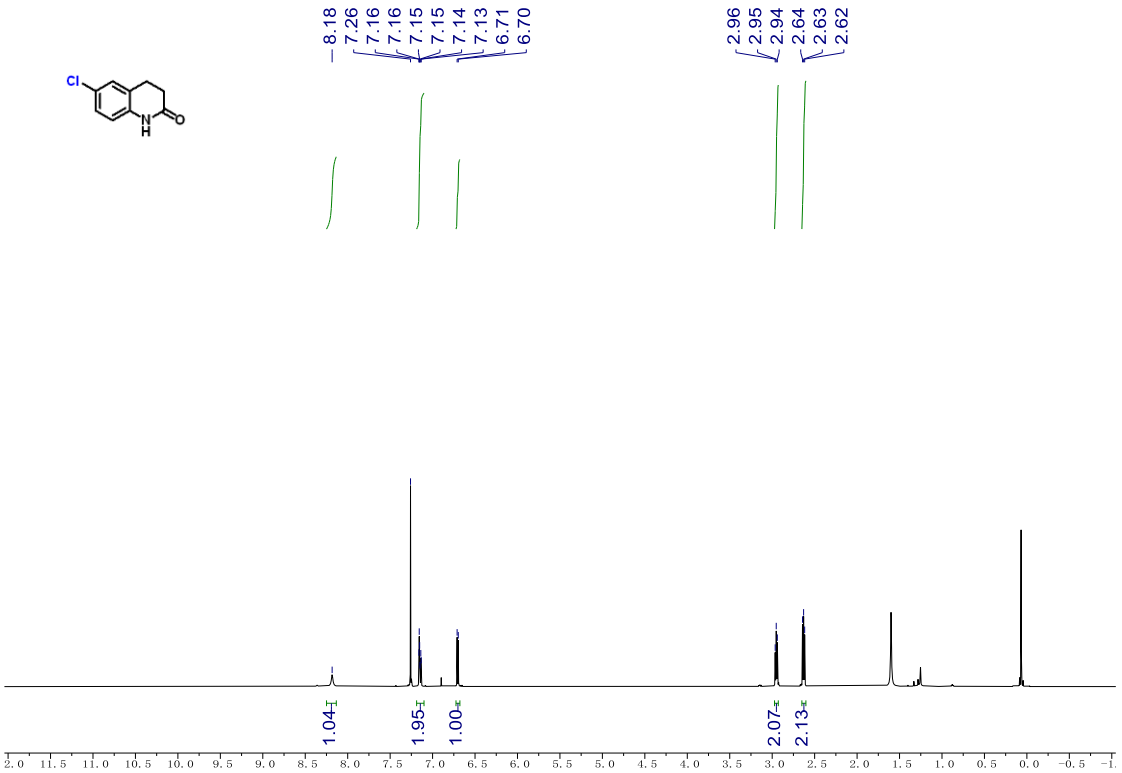
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2aaa**.



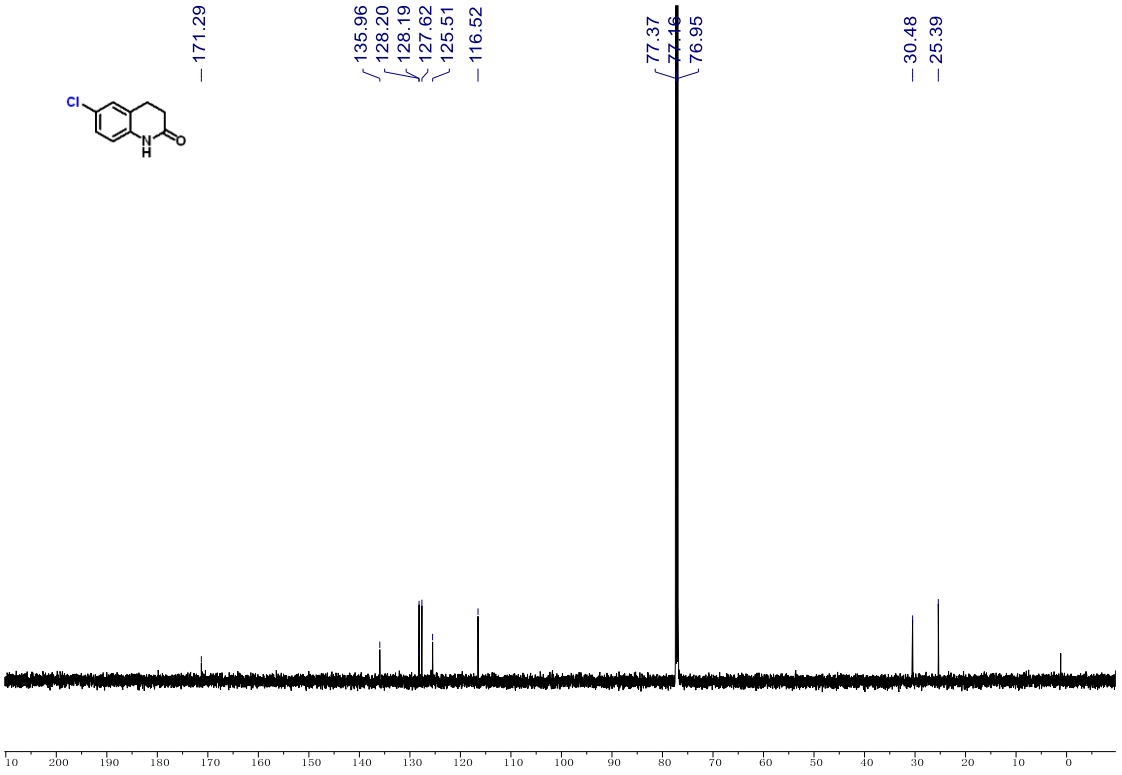
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2bbb**.



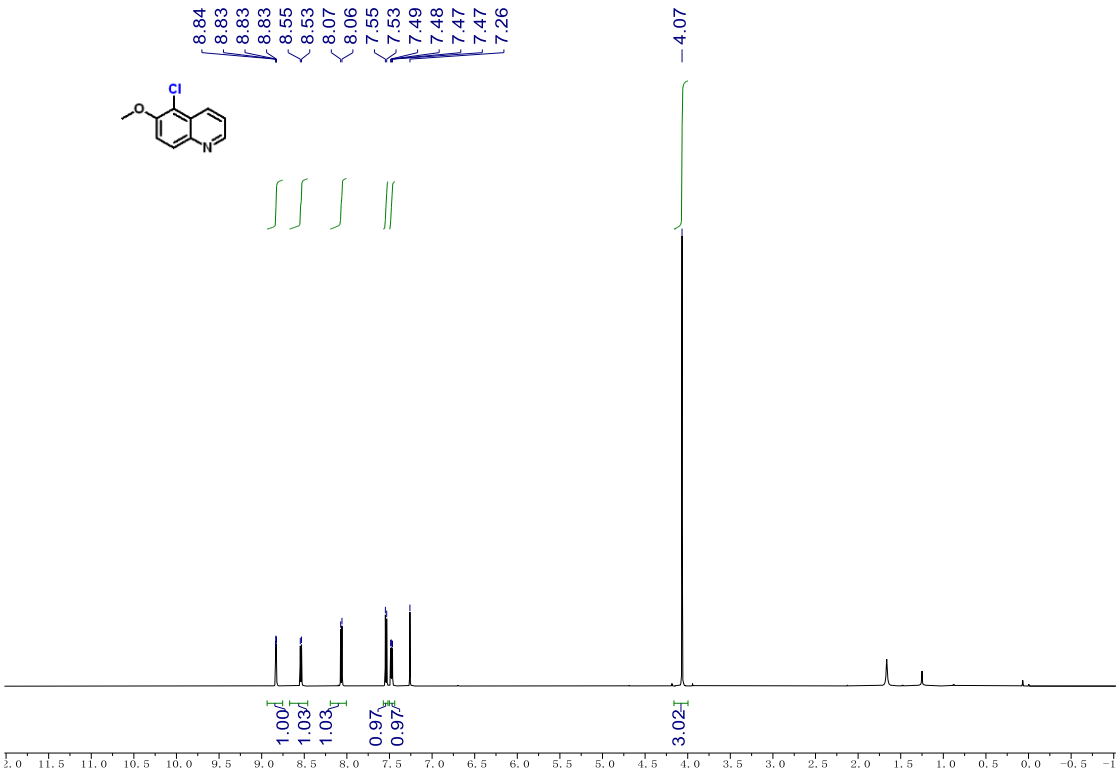
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2bbb**.



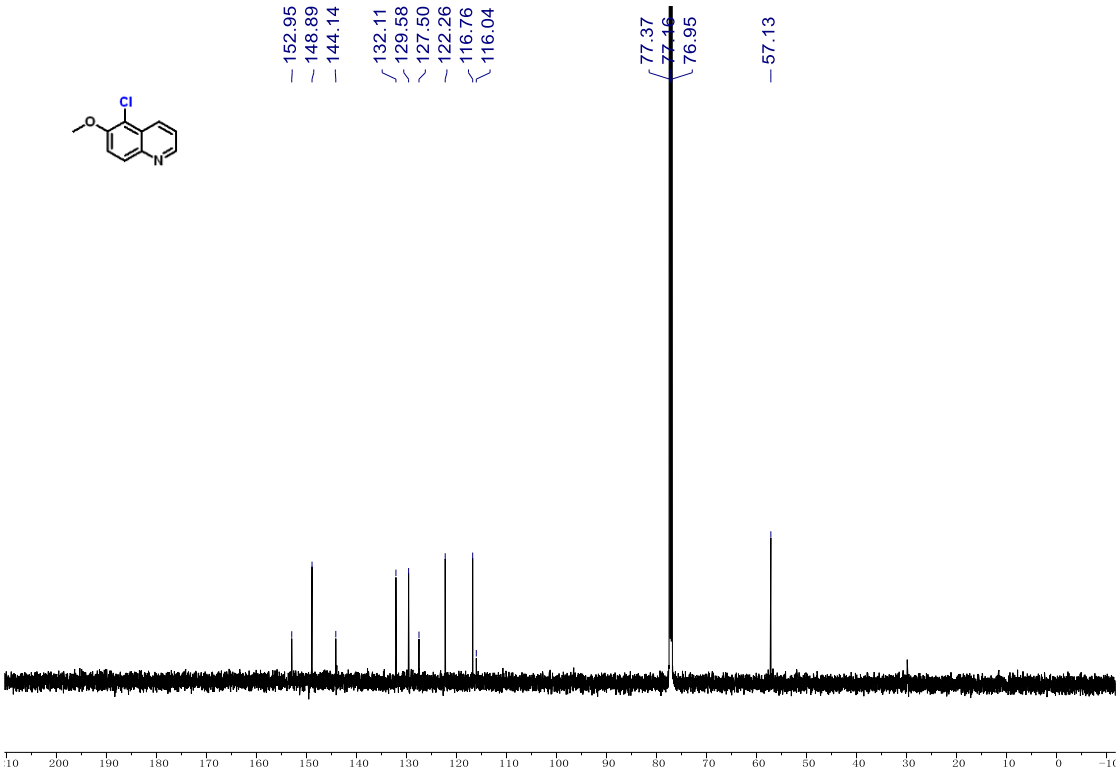
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ccc**.



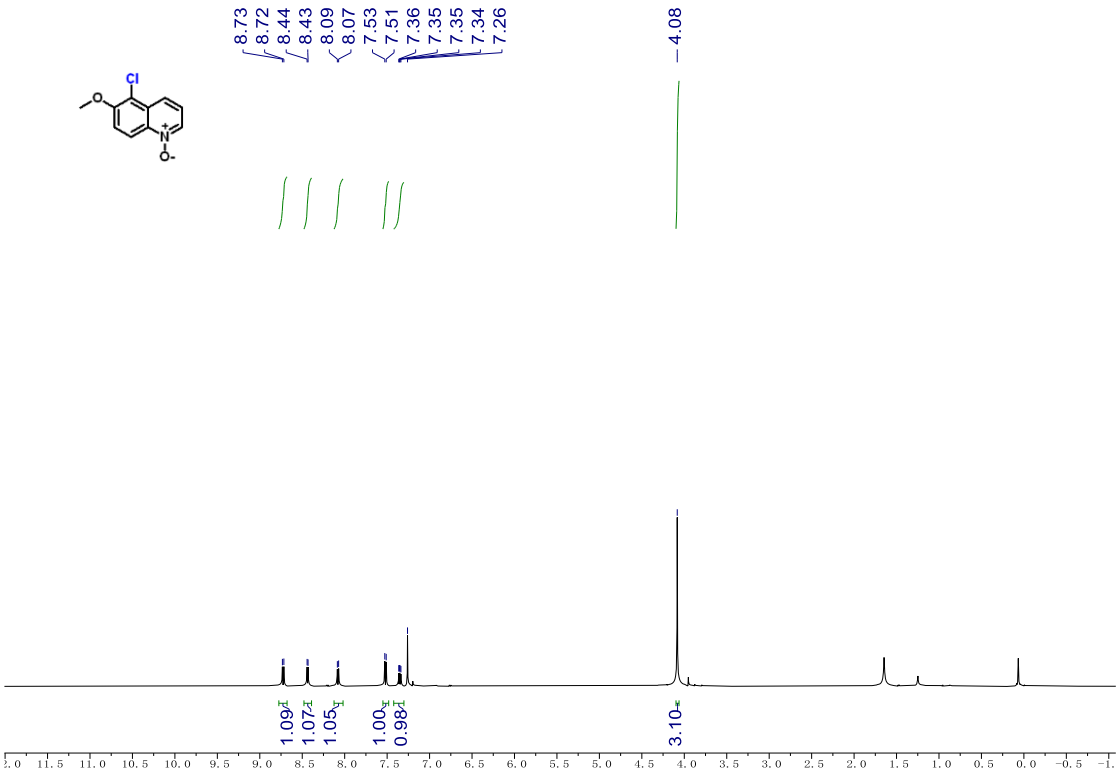
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ccc**.



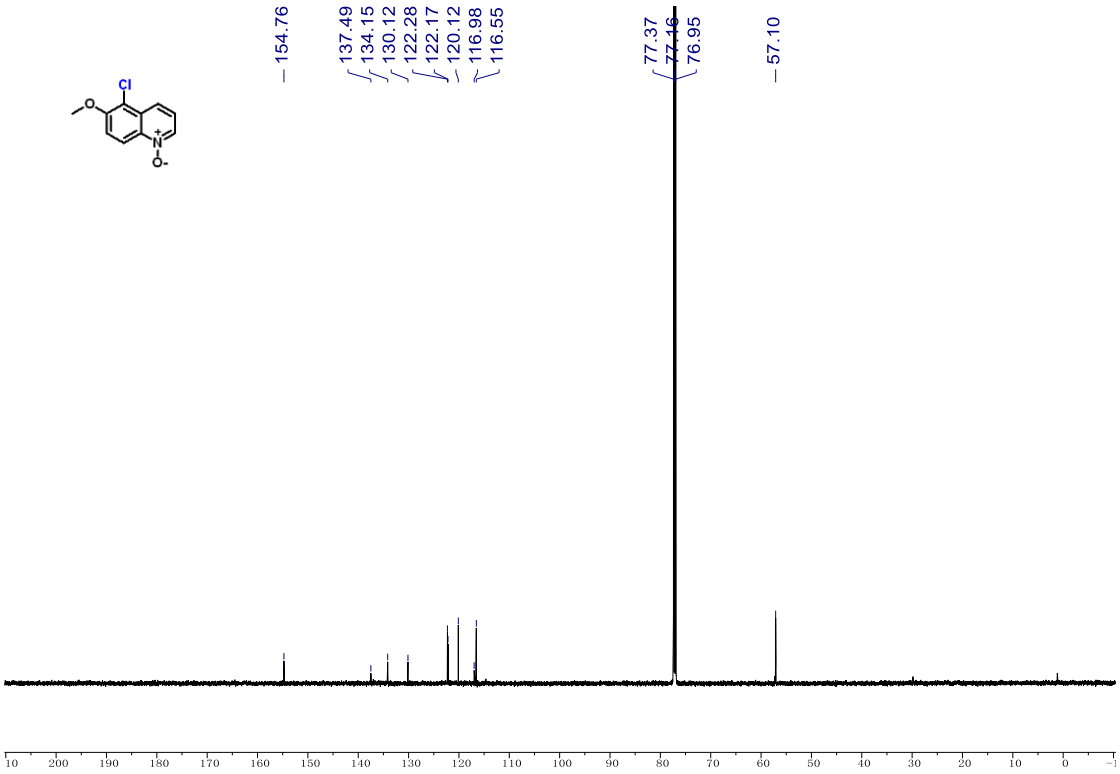
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ddd-1**.



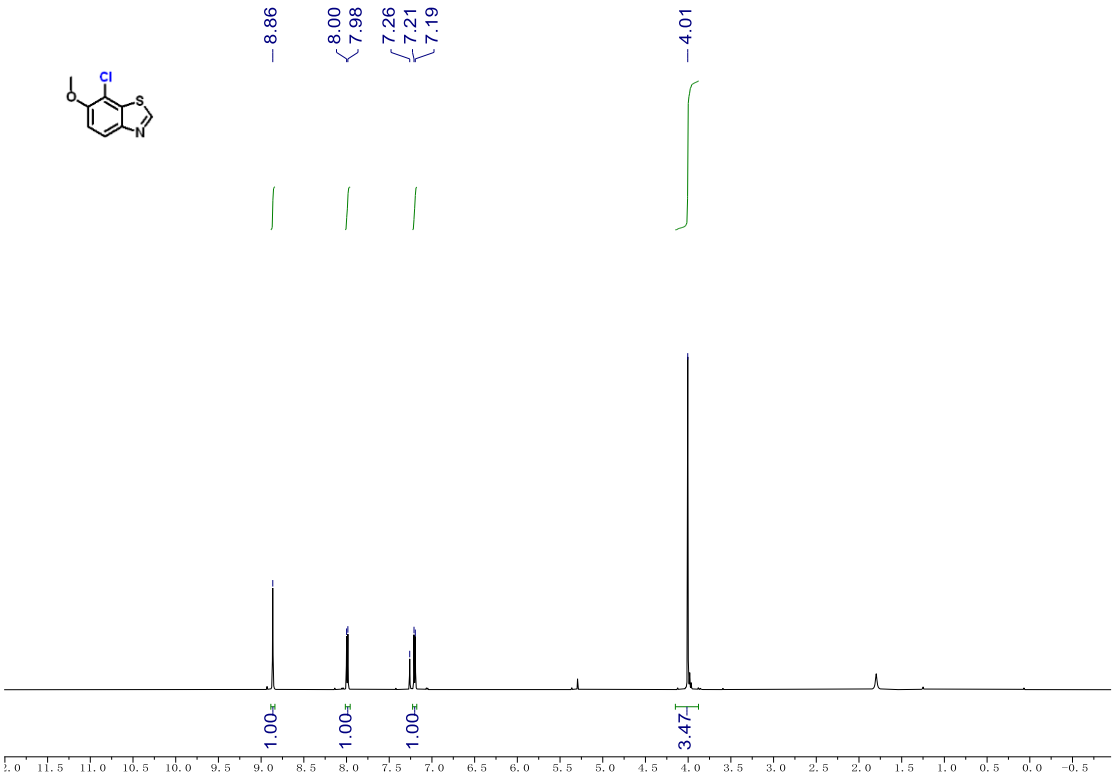
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ddd-1**.



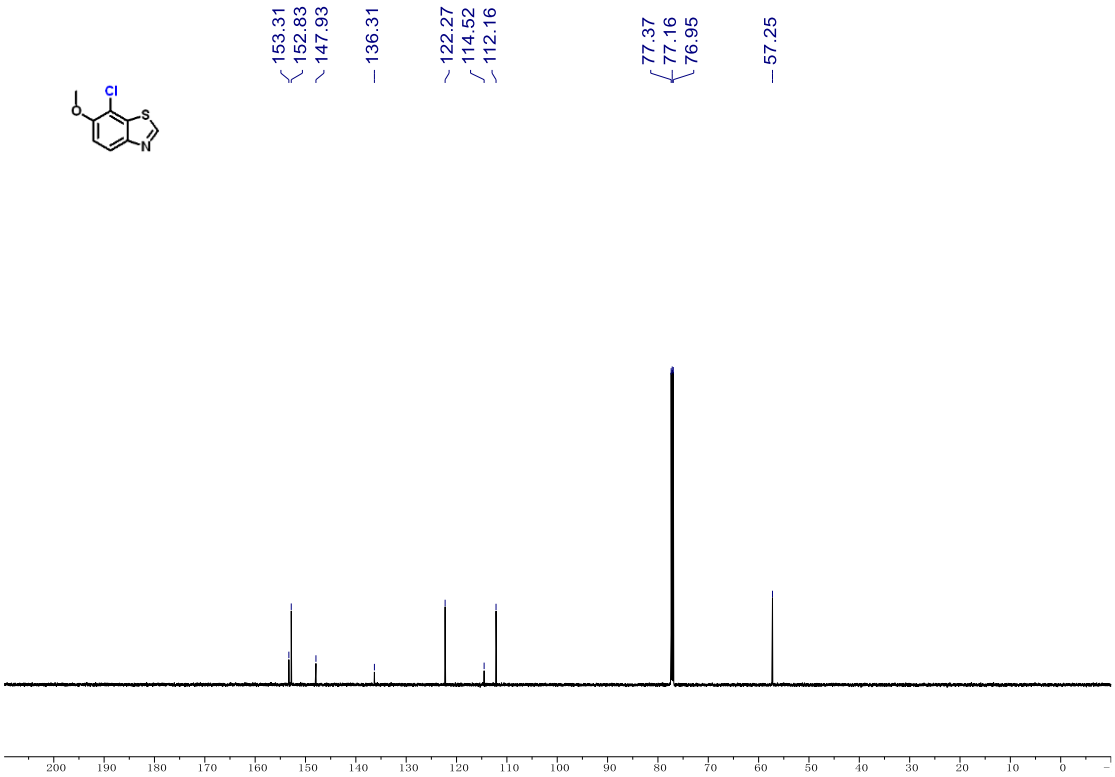
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ddd-2**.



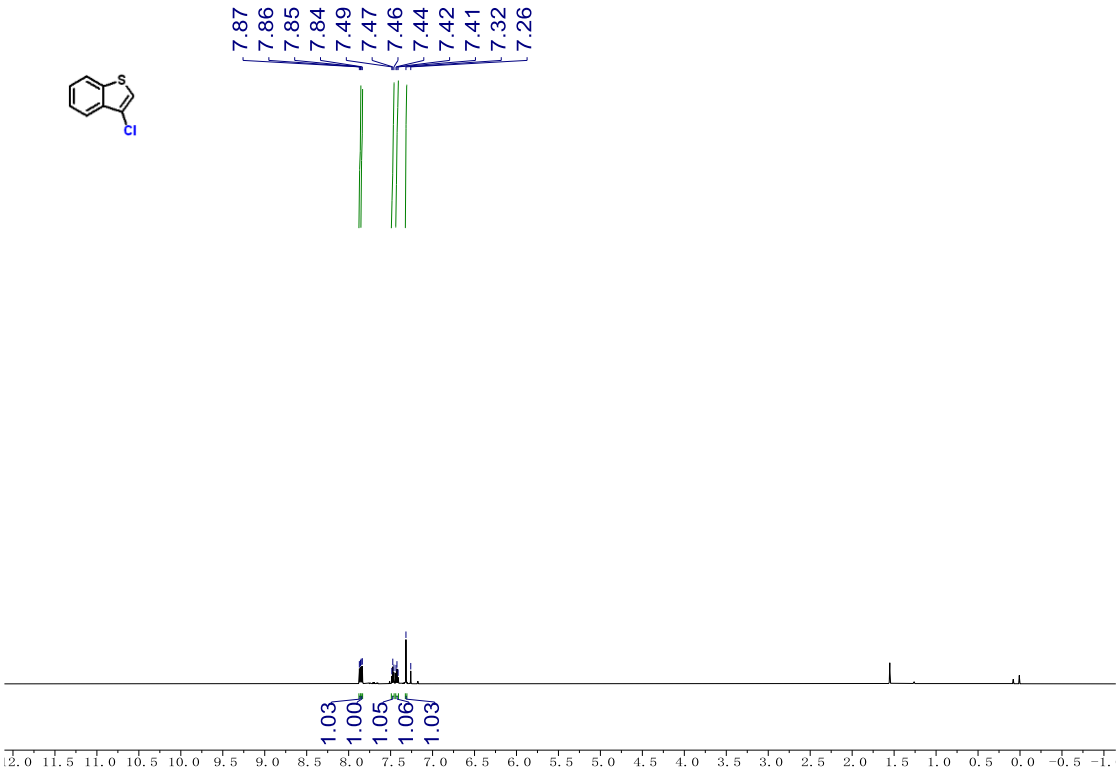
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ddd-2**.



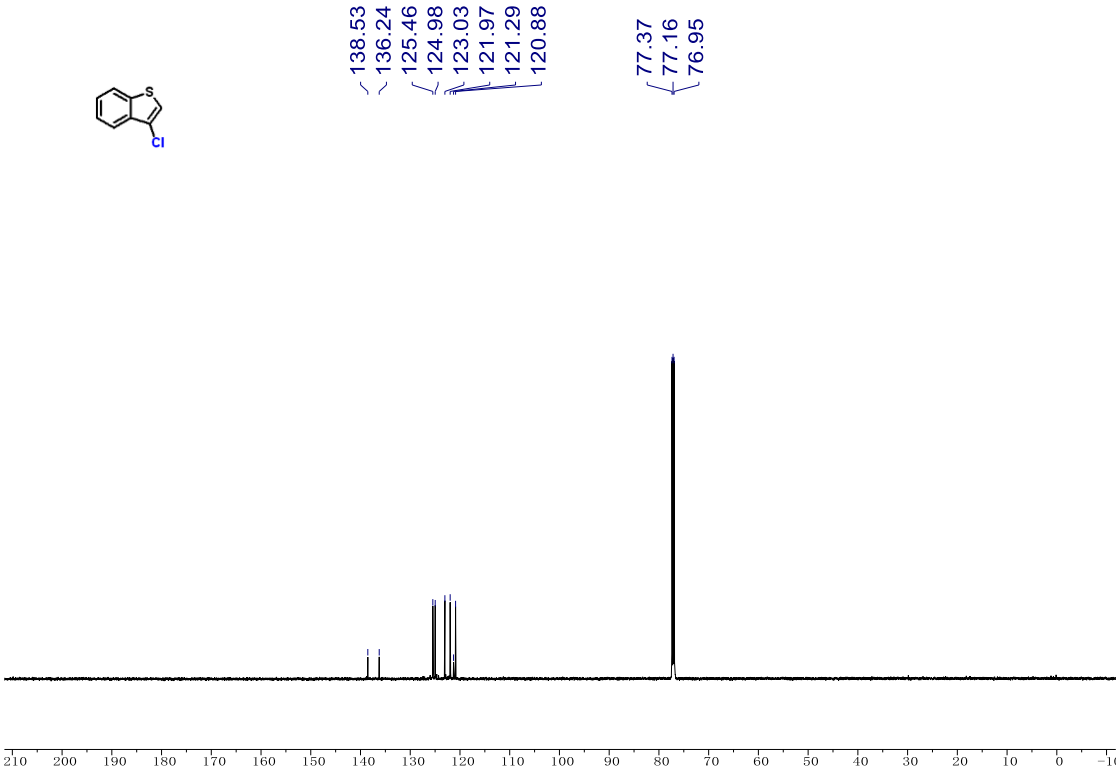
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2eee**.



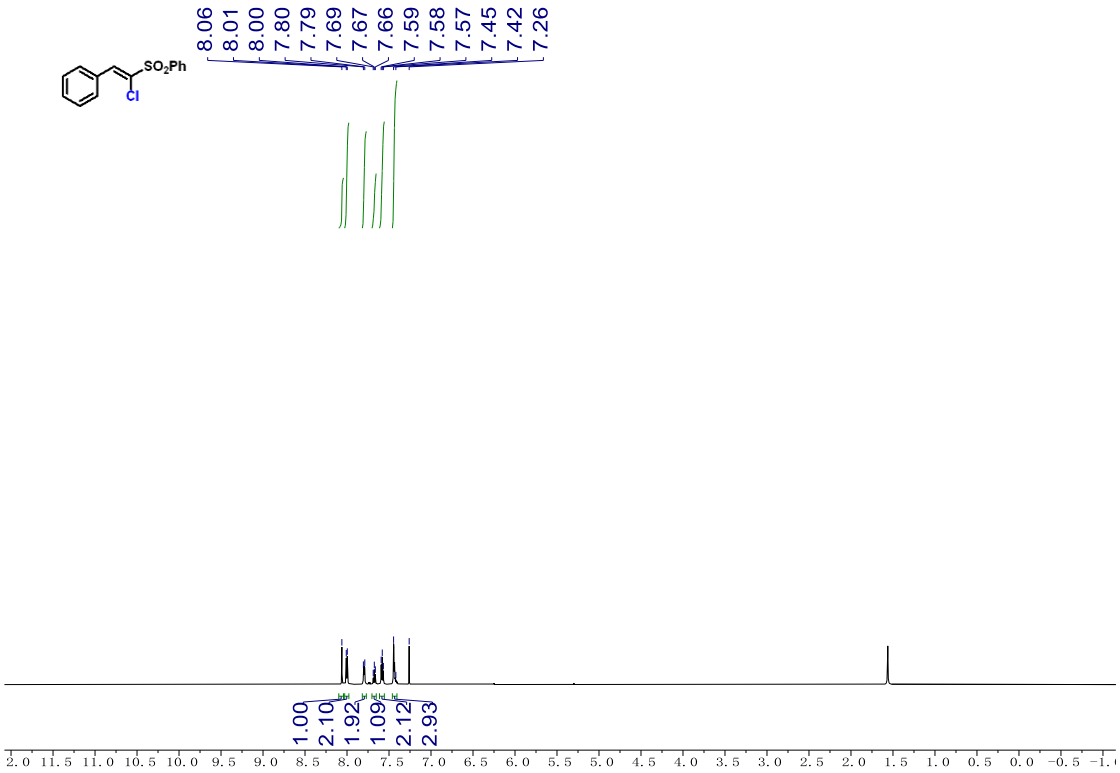
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2eee**.



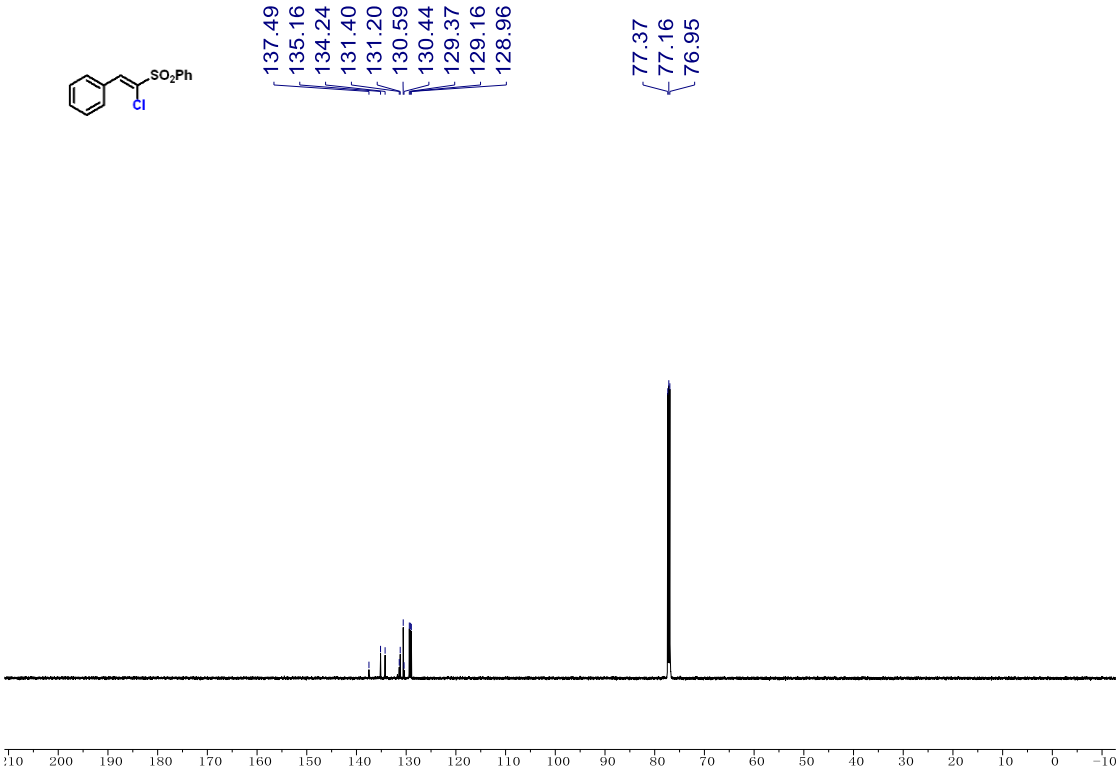
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2fff**.



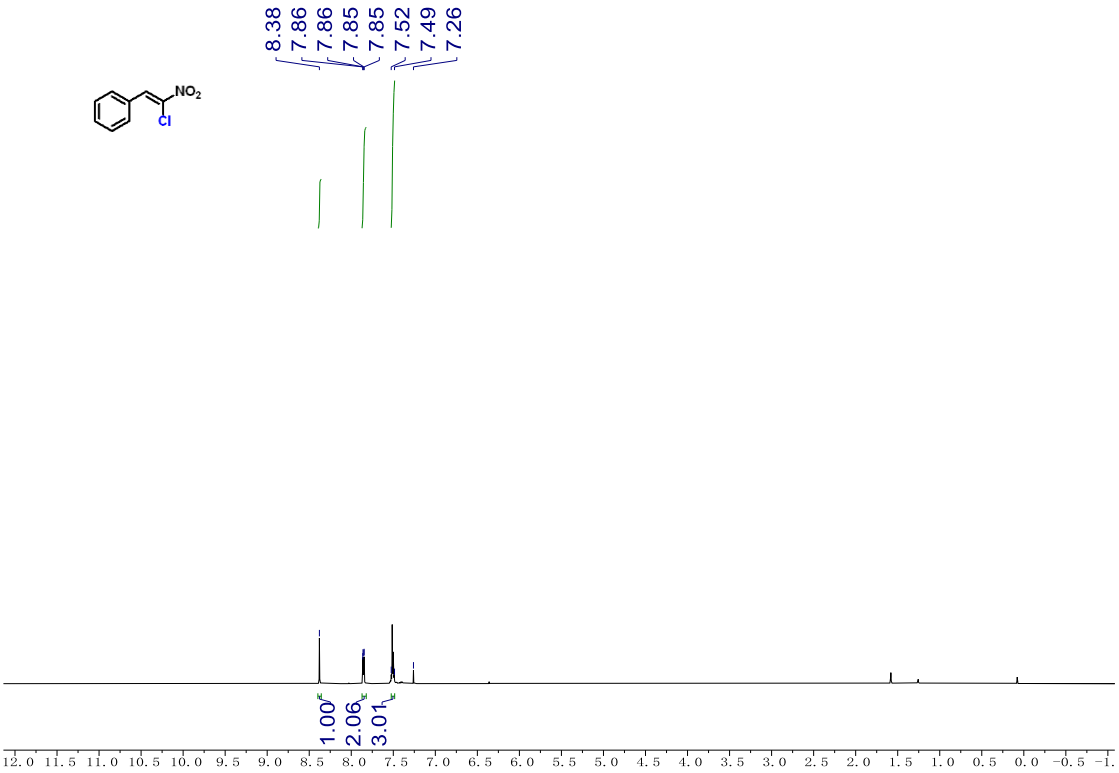
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2fff**.



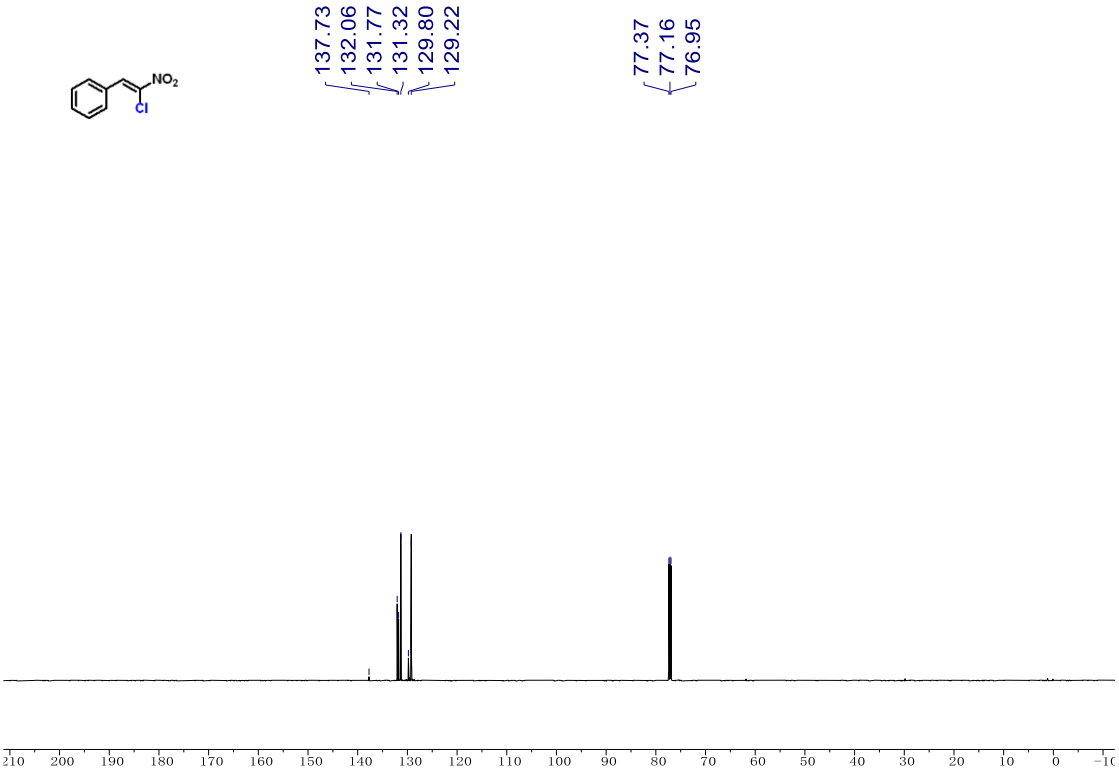
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2ggg**.



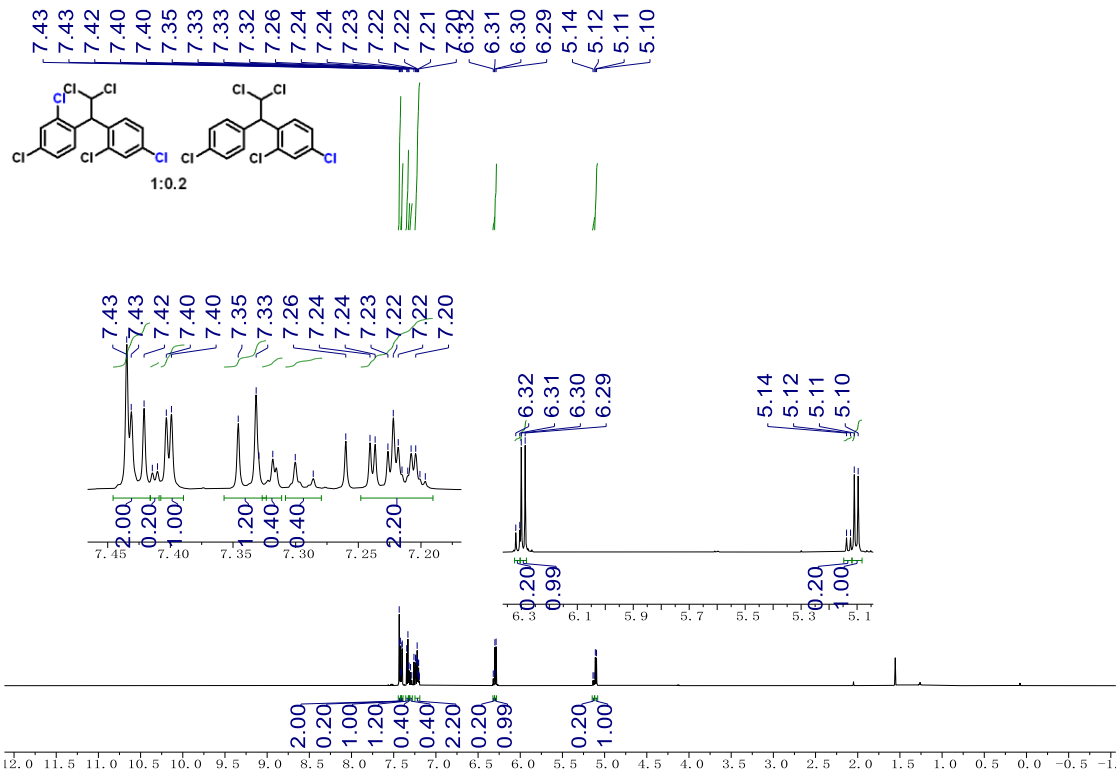
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2ggg**.



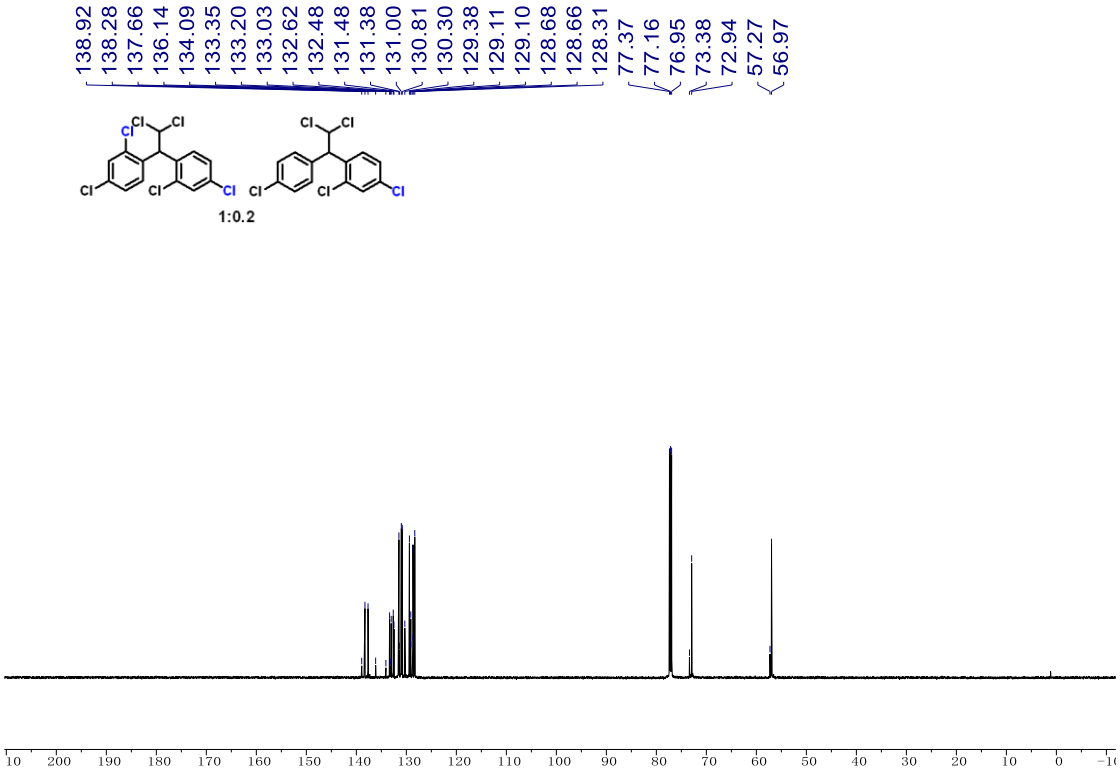
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **2hhh**.



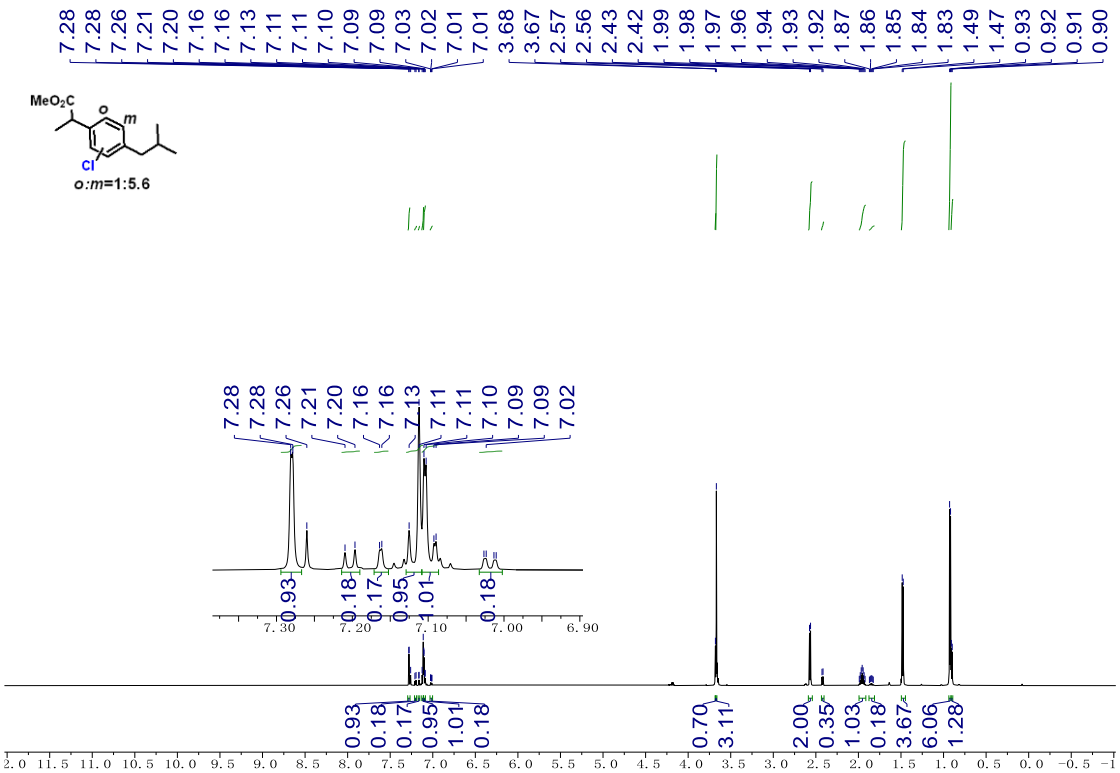
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **2hhh**.



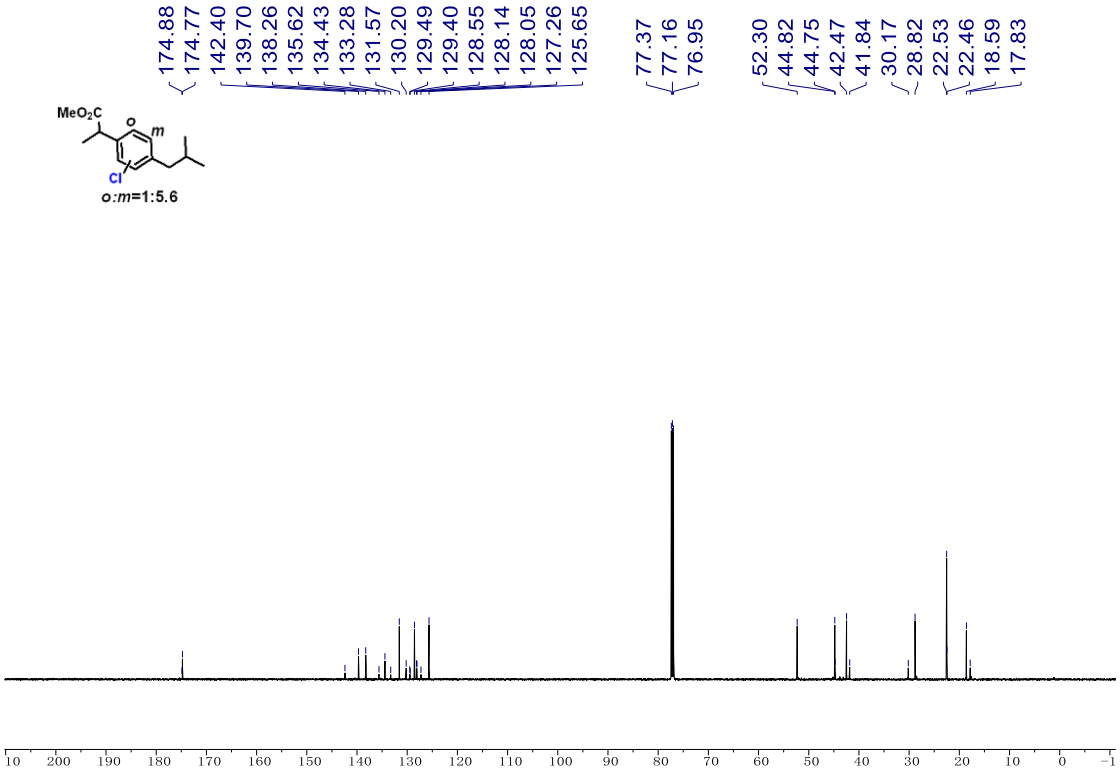
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4a**.



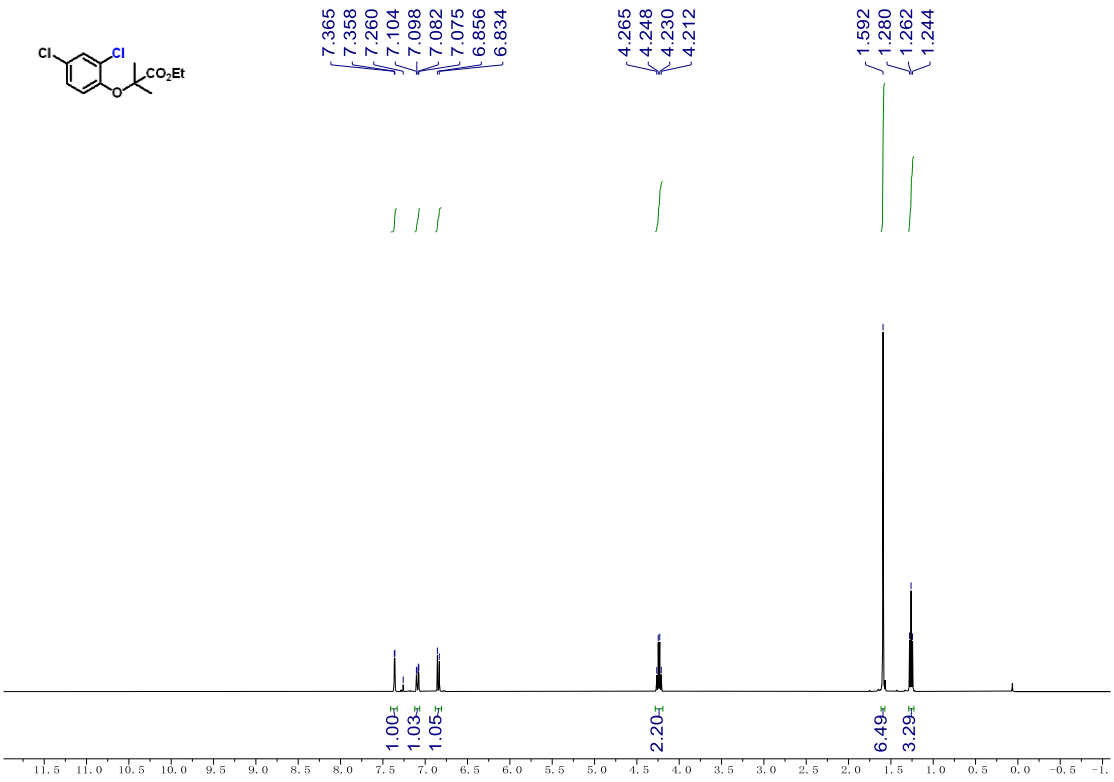
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4a**.



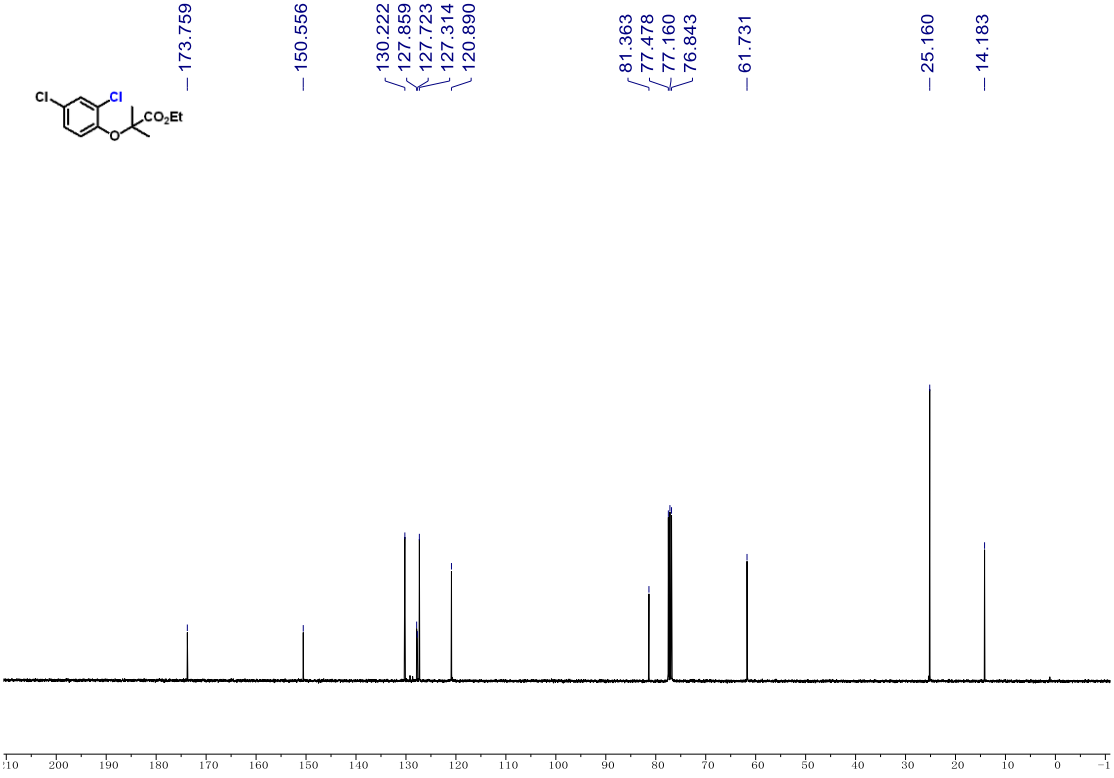
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4b**.



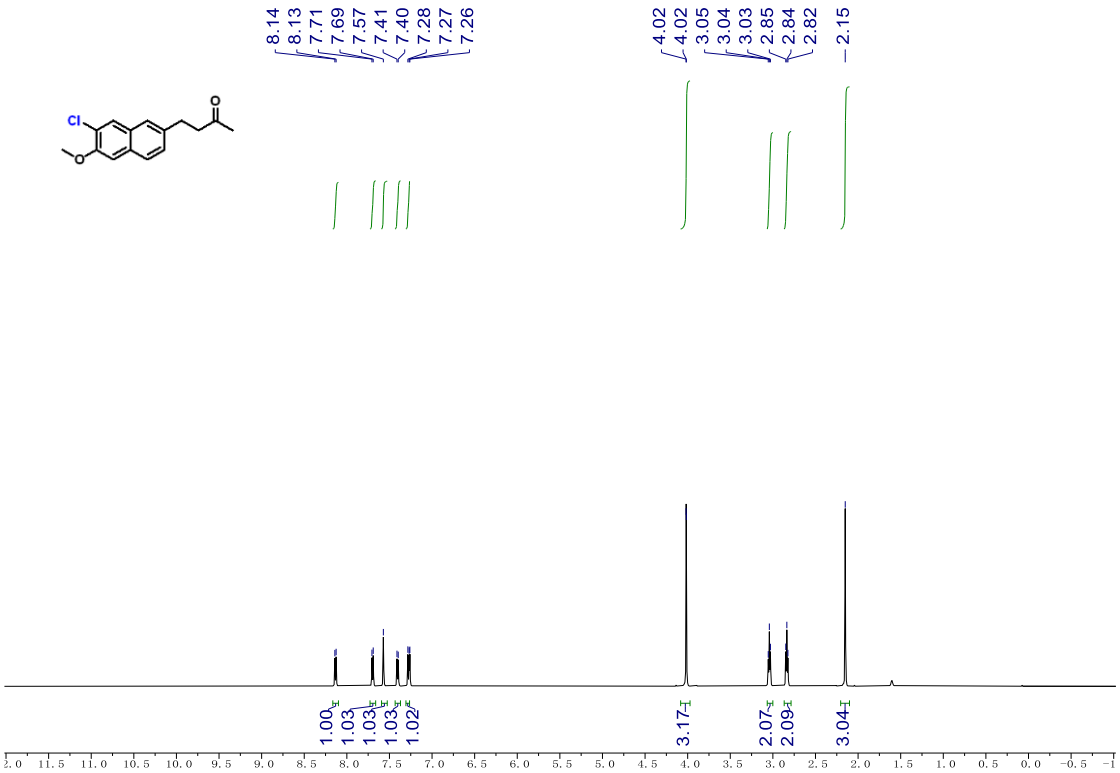
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4b**.



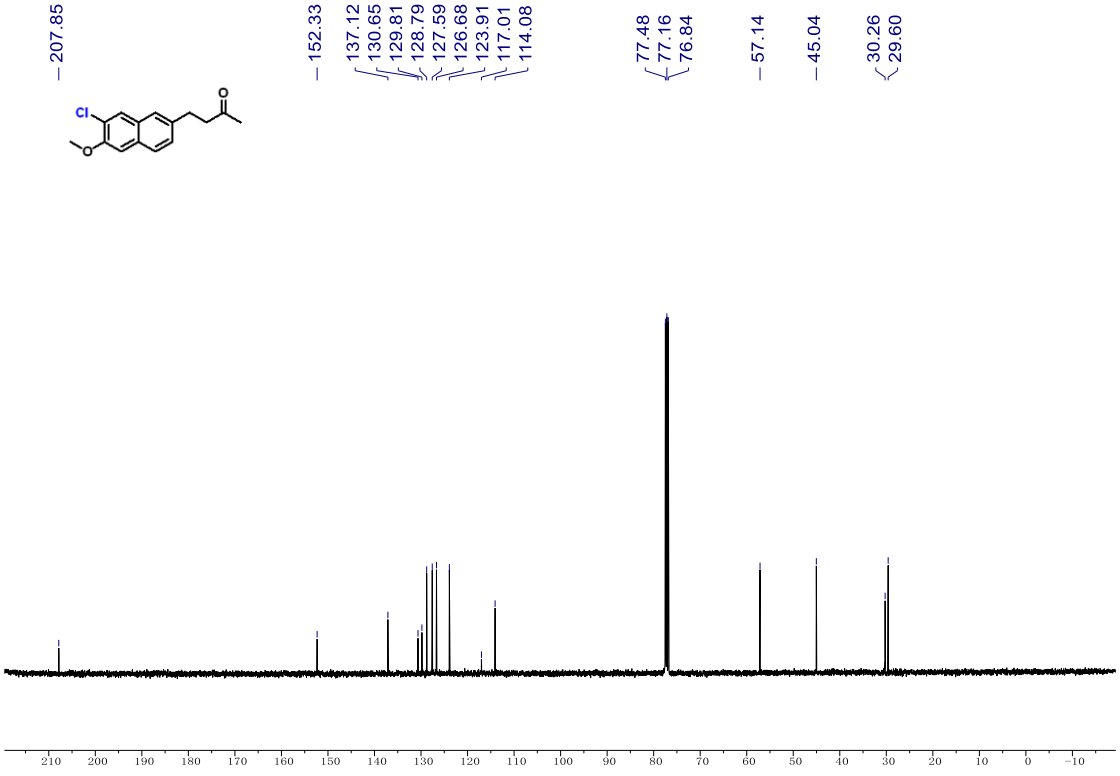
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4c**.



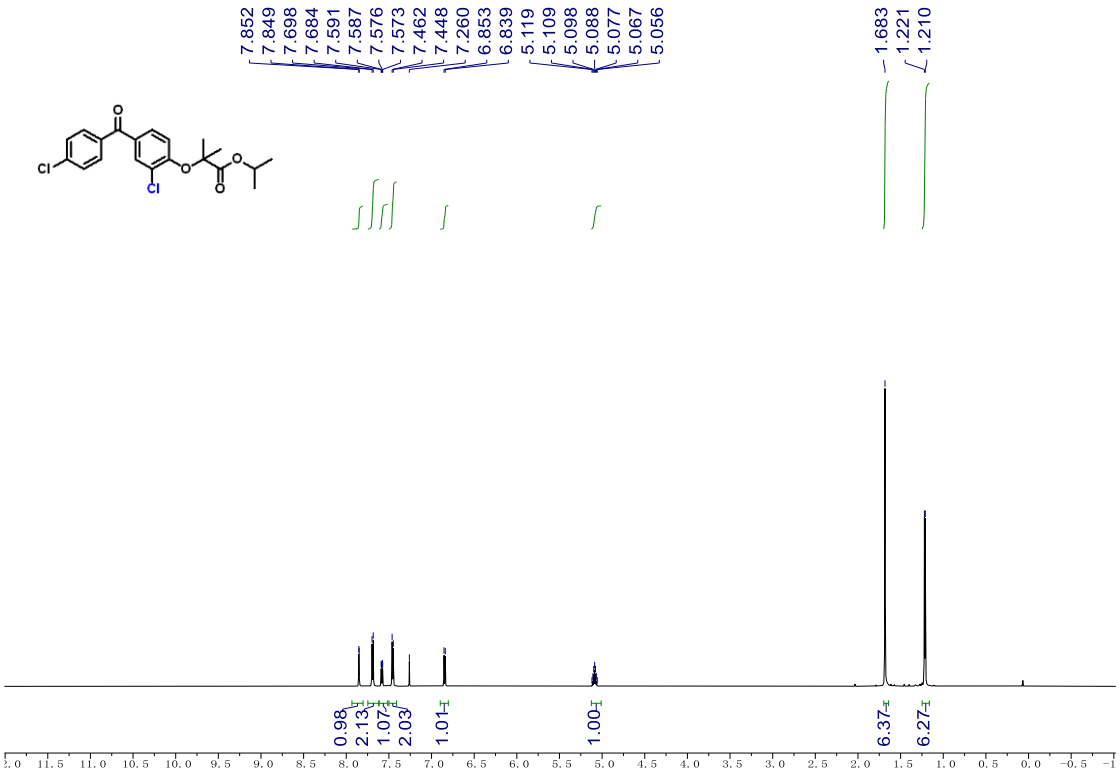
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4c**.



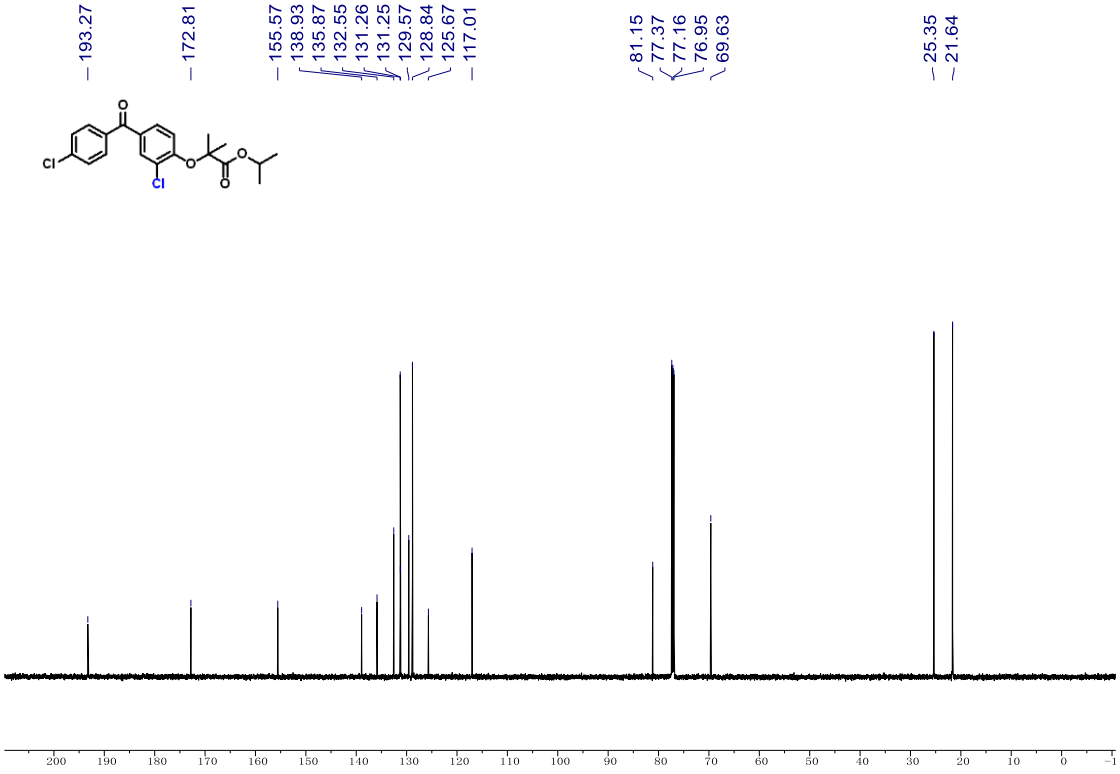
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4d**.



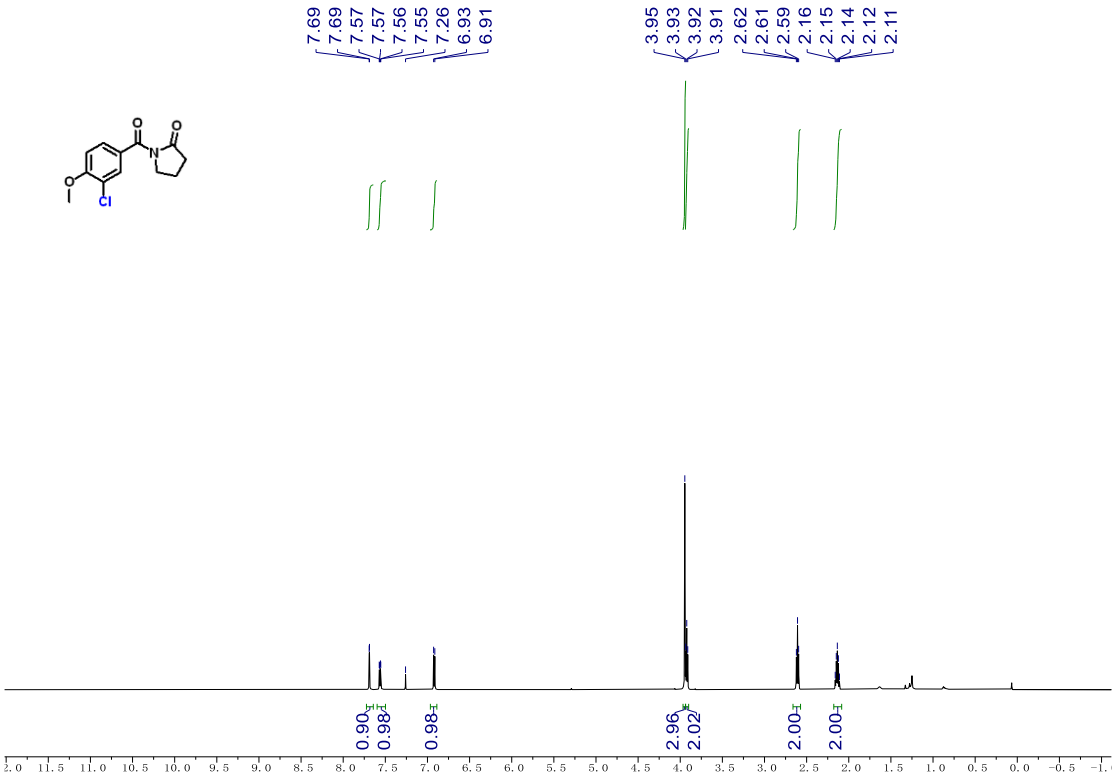
^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) spectrum of **4d**.



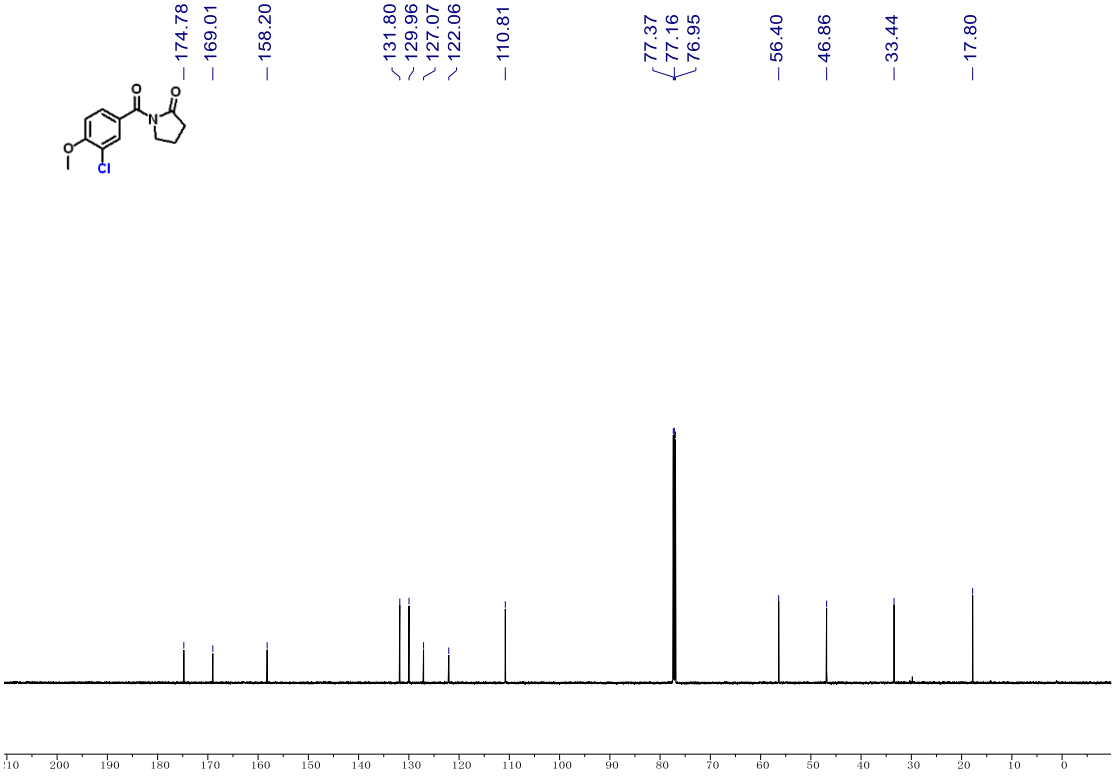
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4e**.



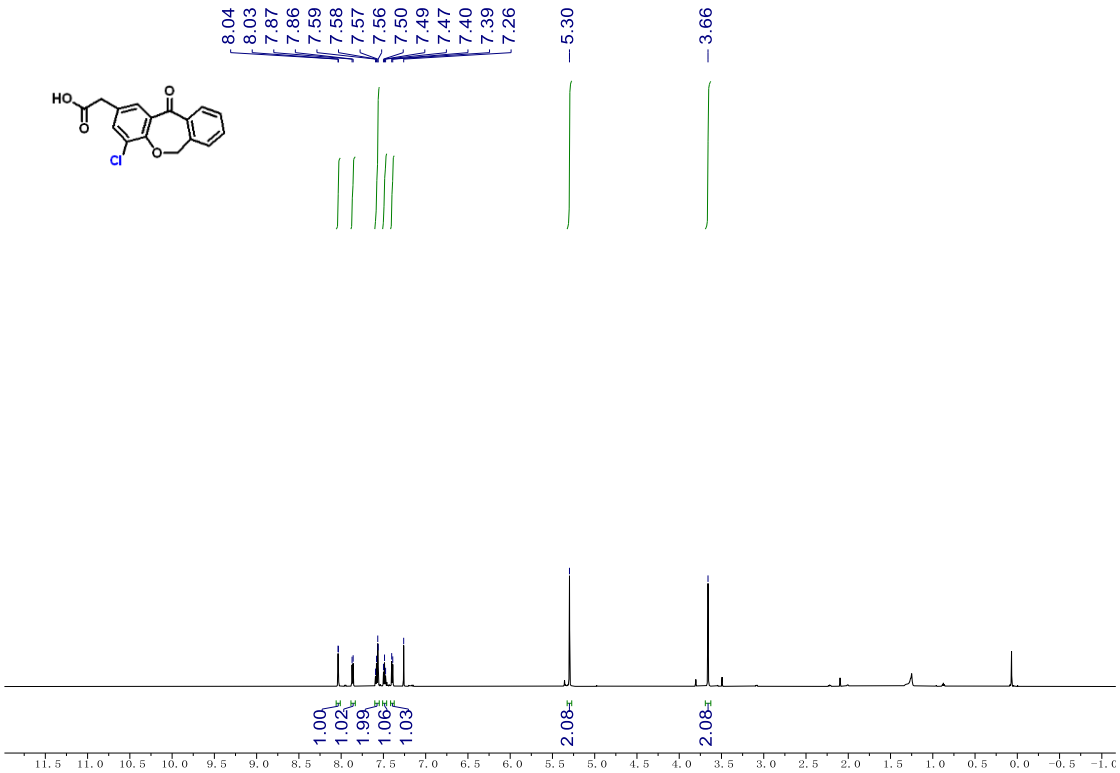
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4e**.



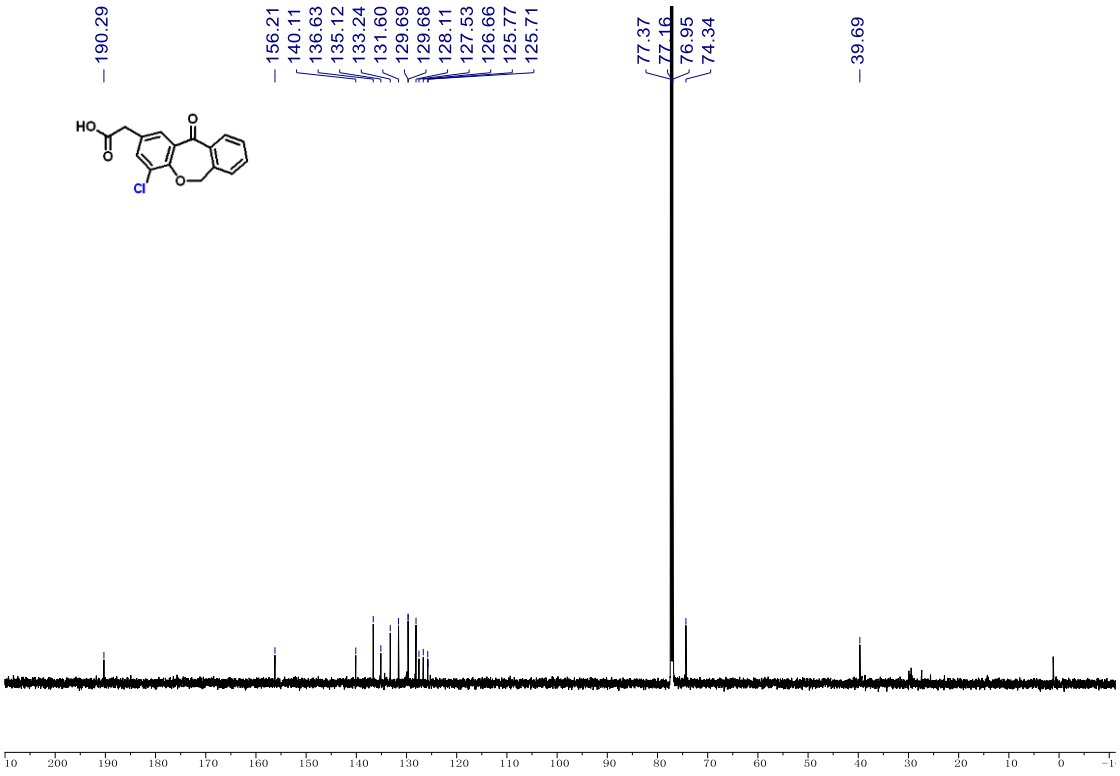
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4f**.



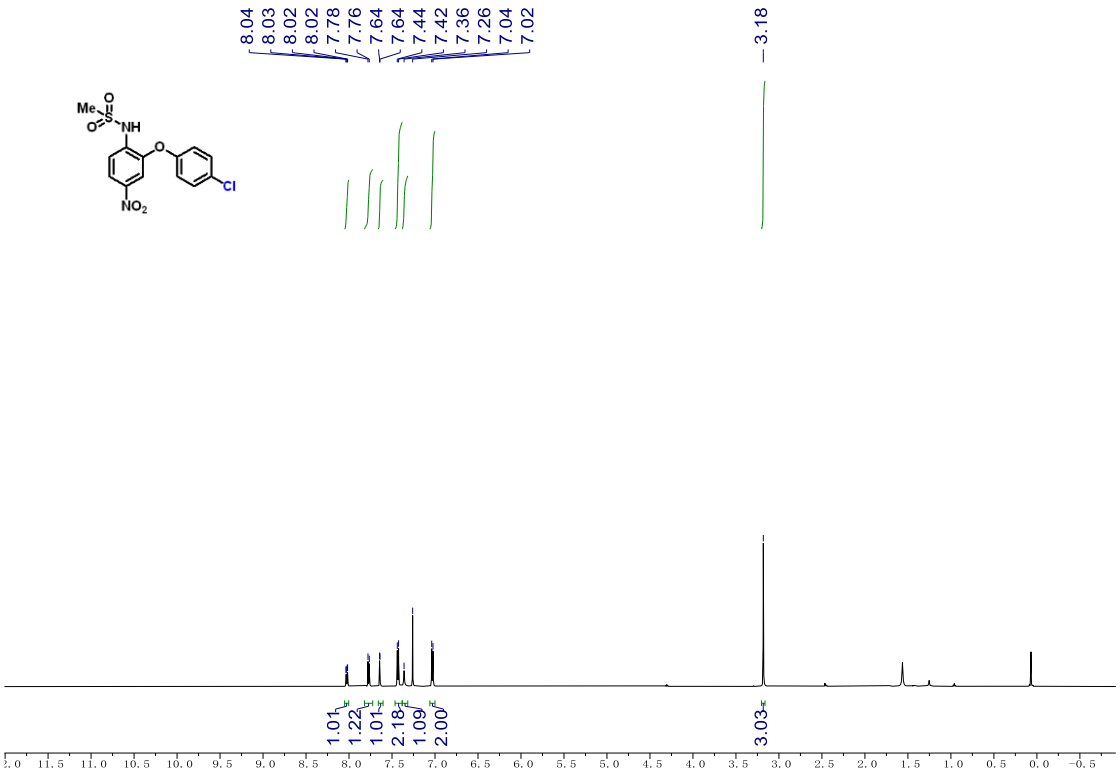
^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4f**.



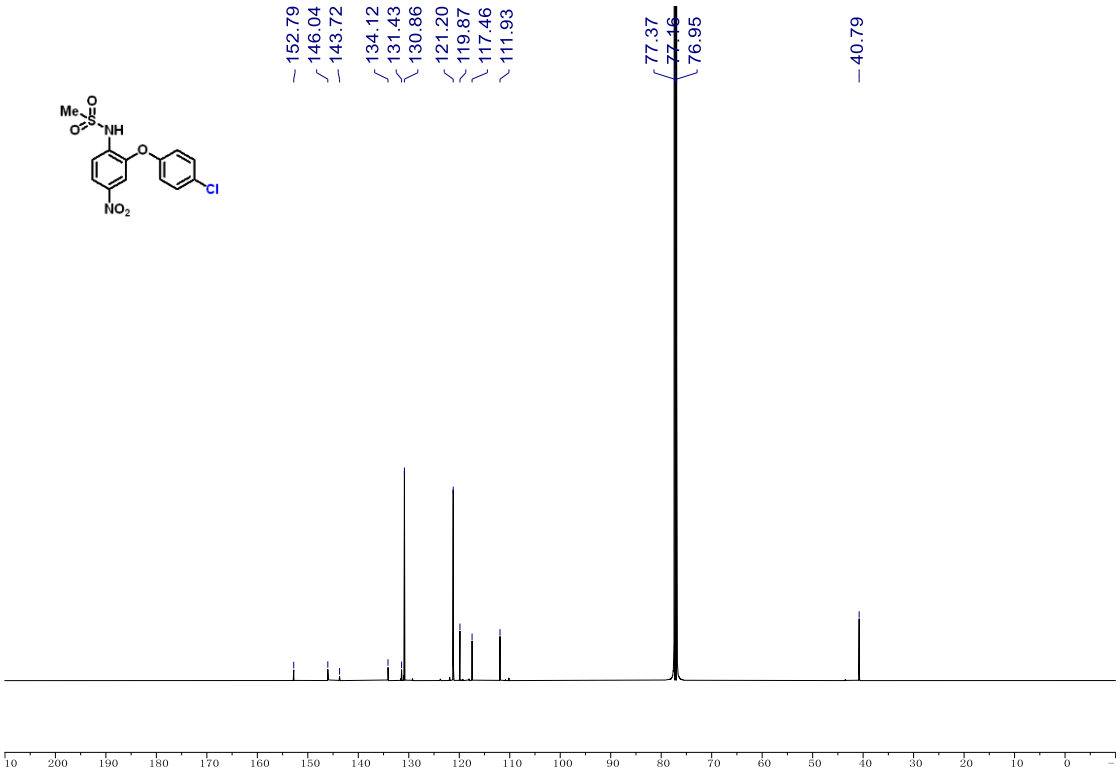
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4g**.



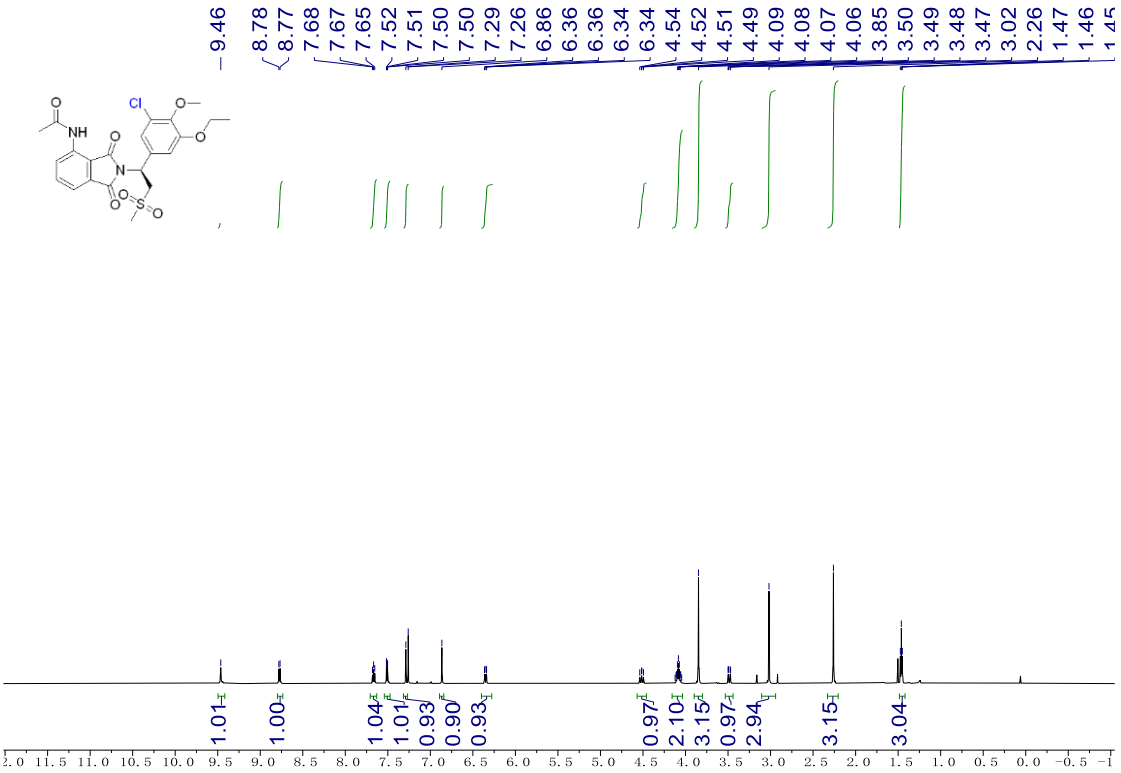
^{3}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4g**.



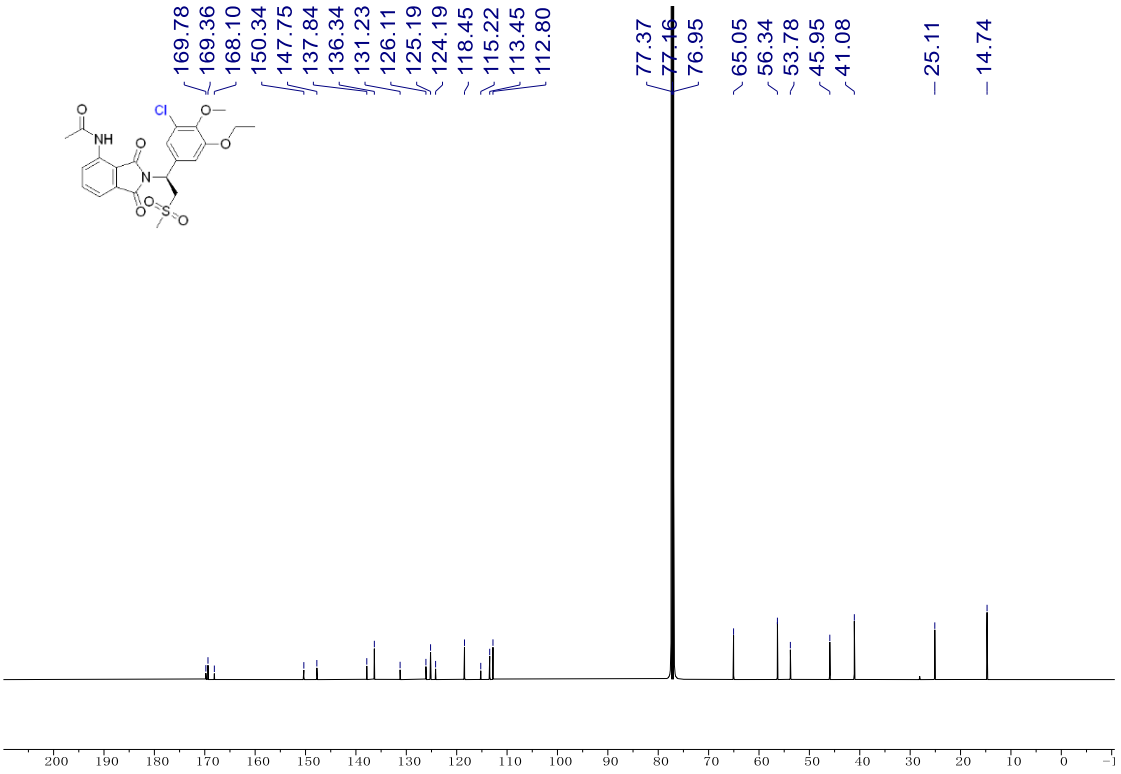
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4h**.



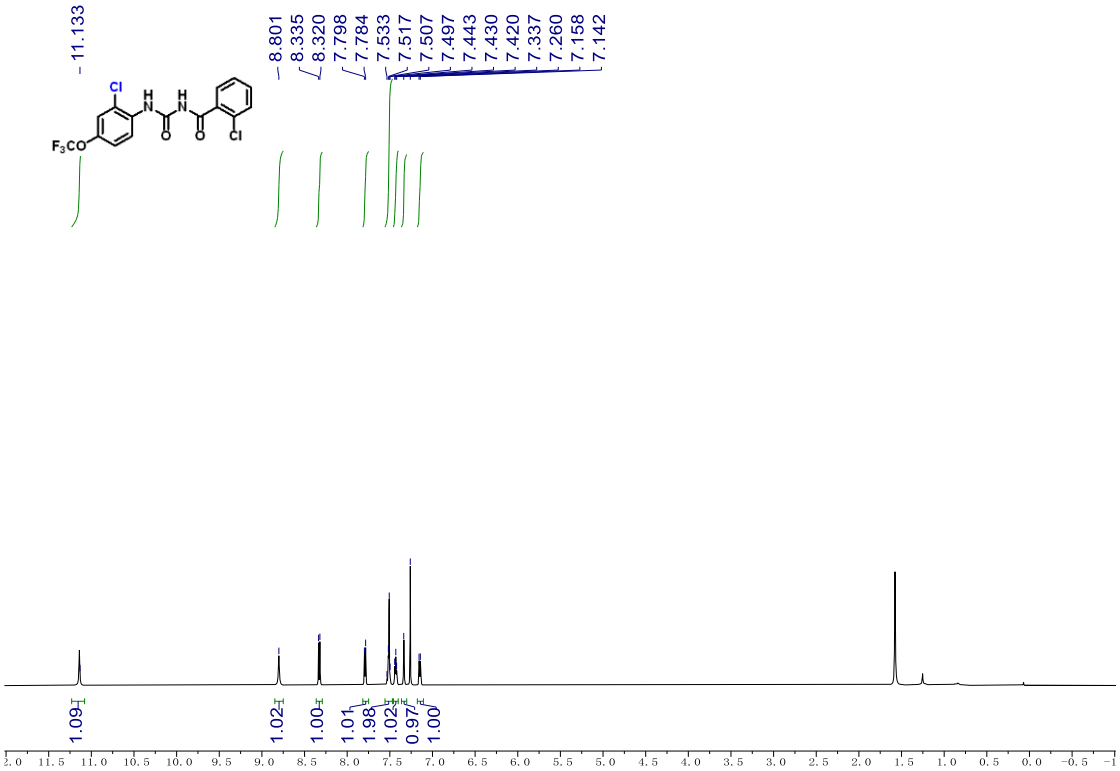
^{3}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4h**.



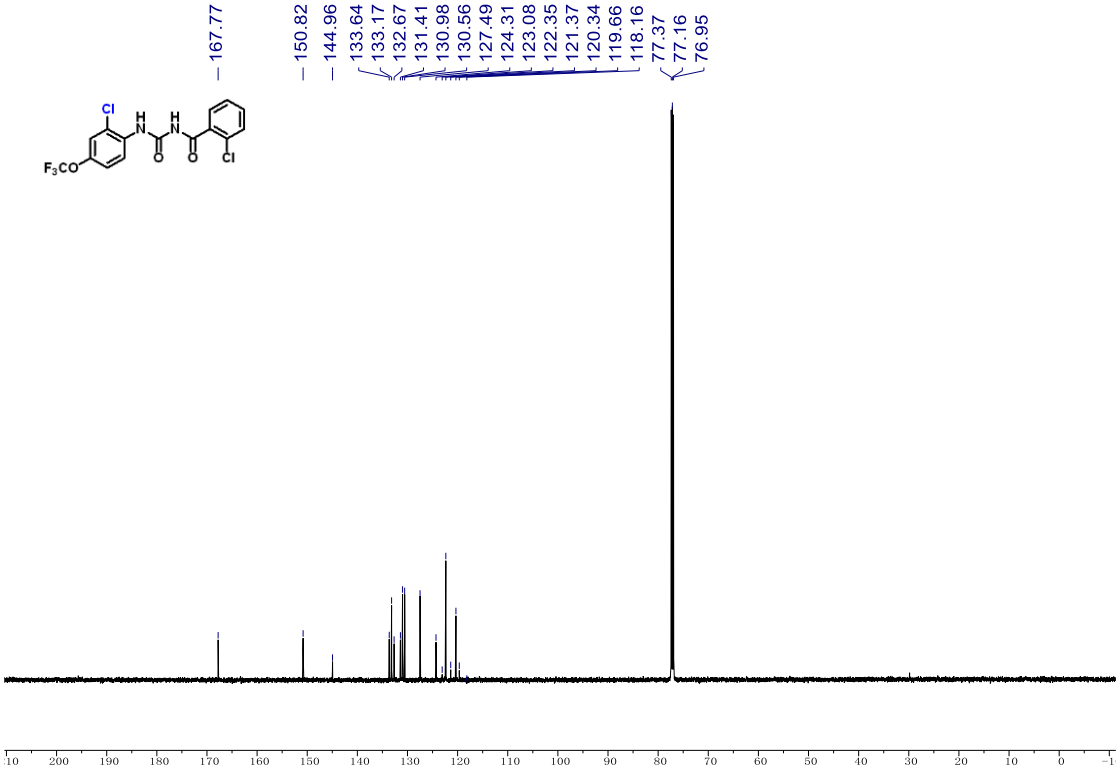
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4i**.



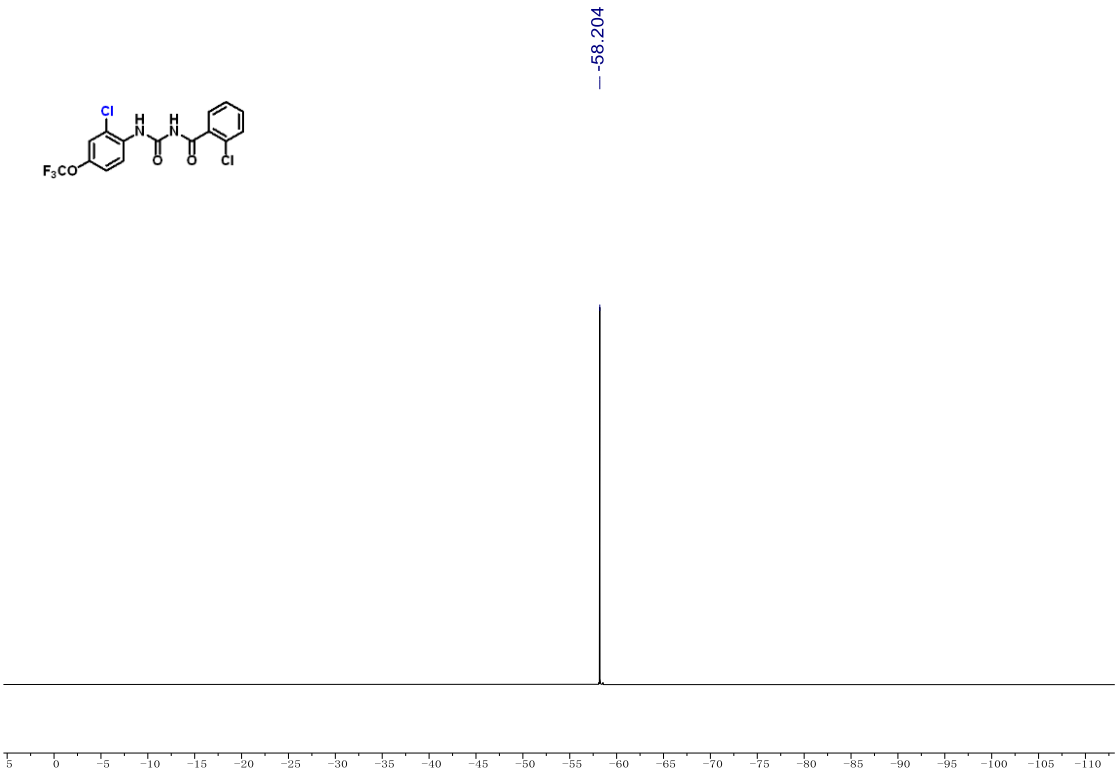
^{3}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4i**.



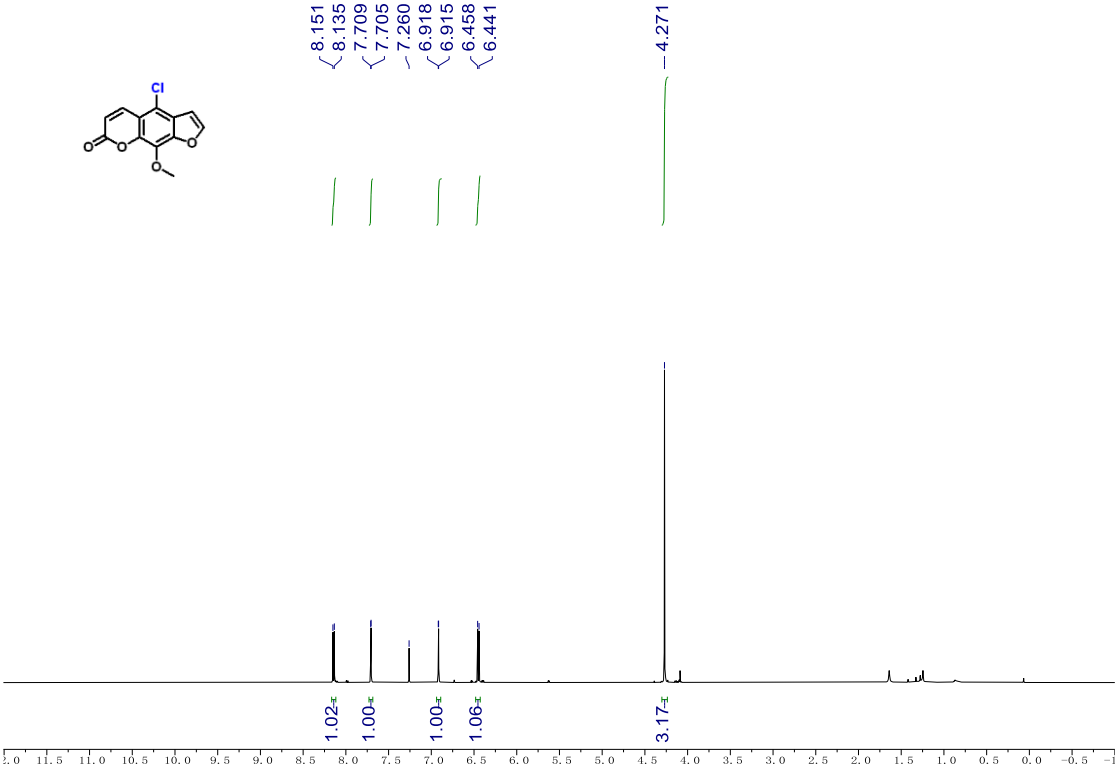
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4j**.



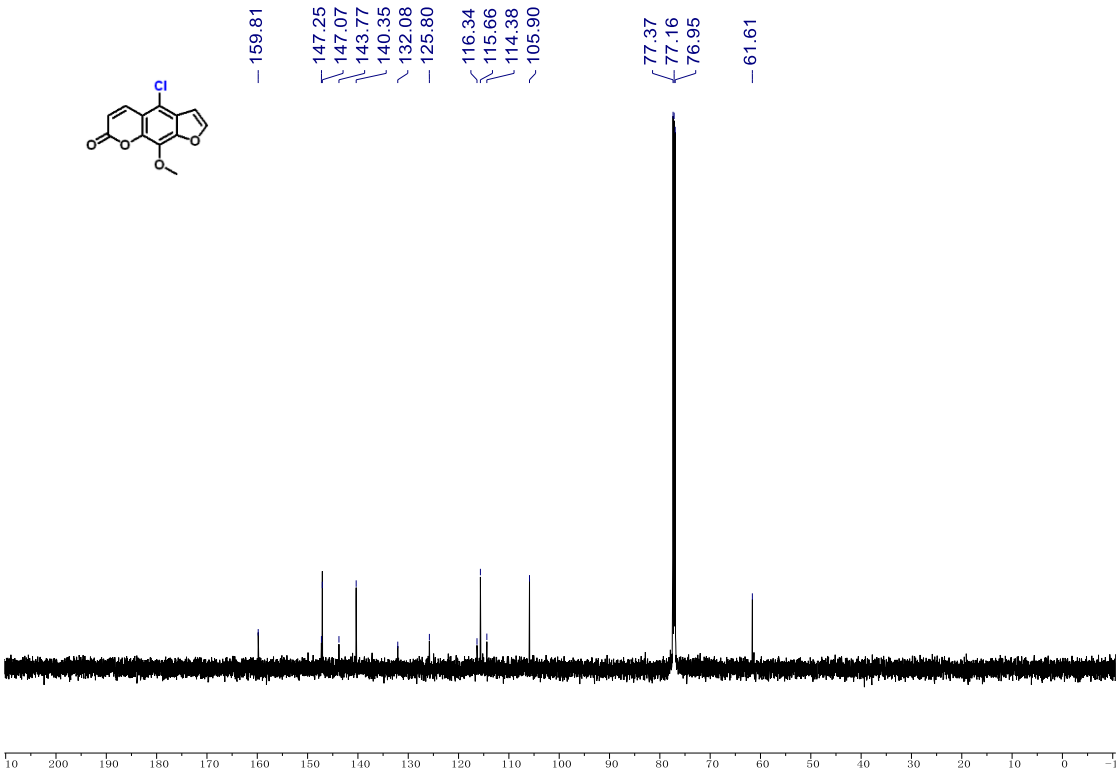
^{3}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4j**.



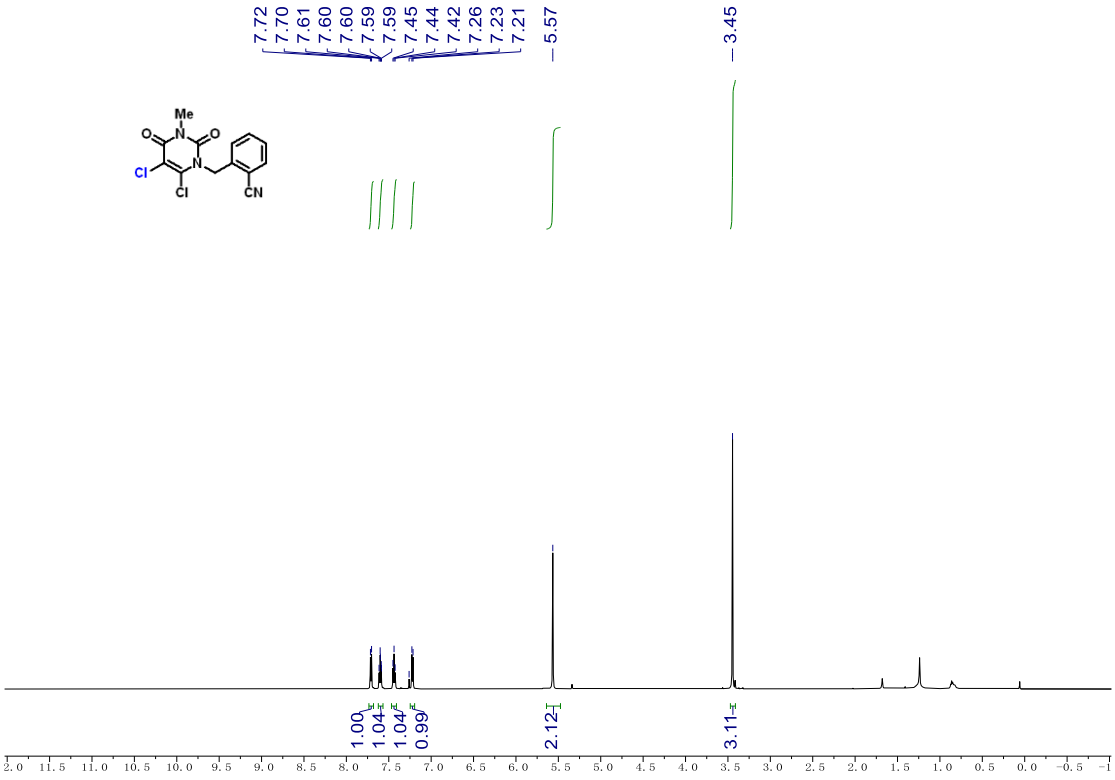
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **4j.**



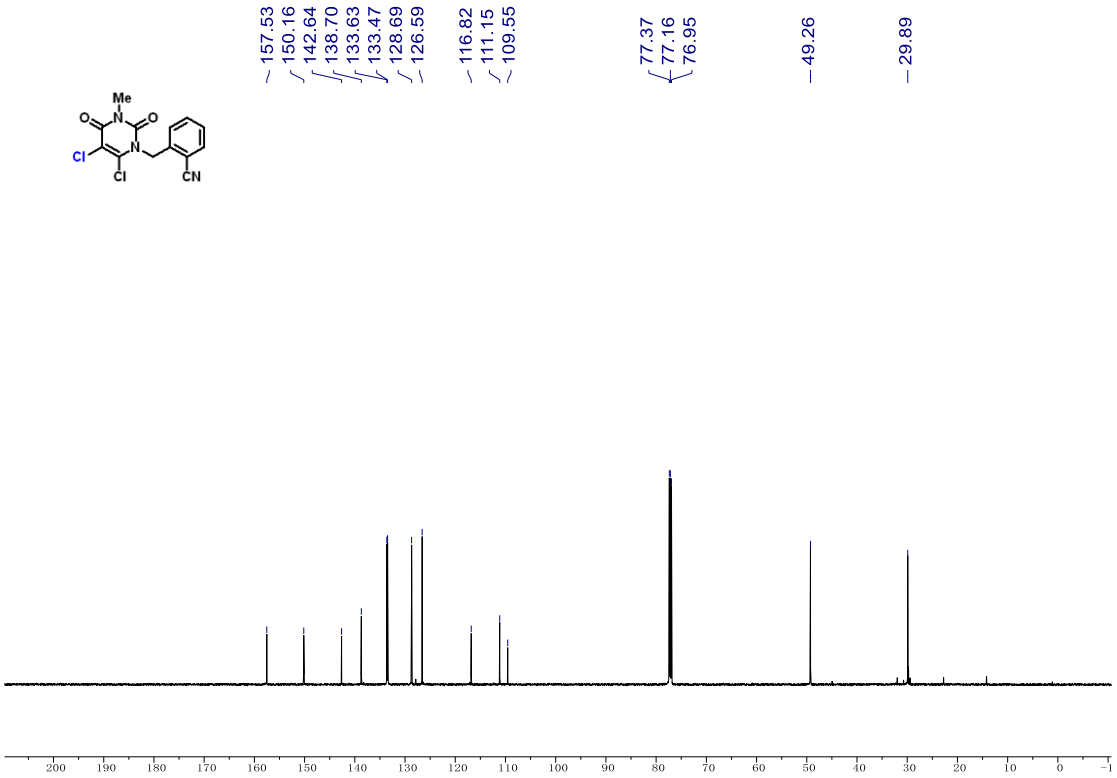
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4k**.



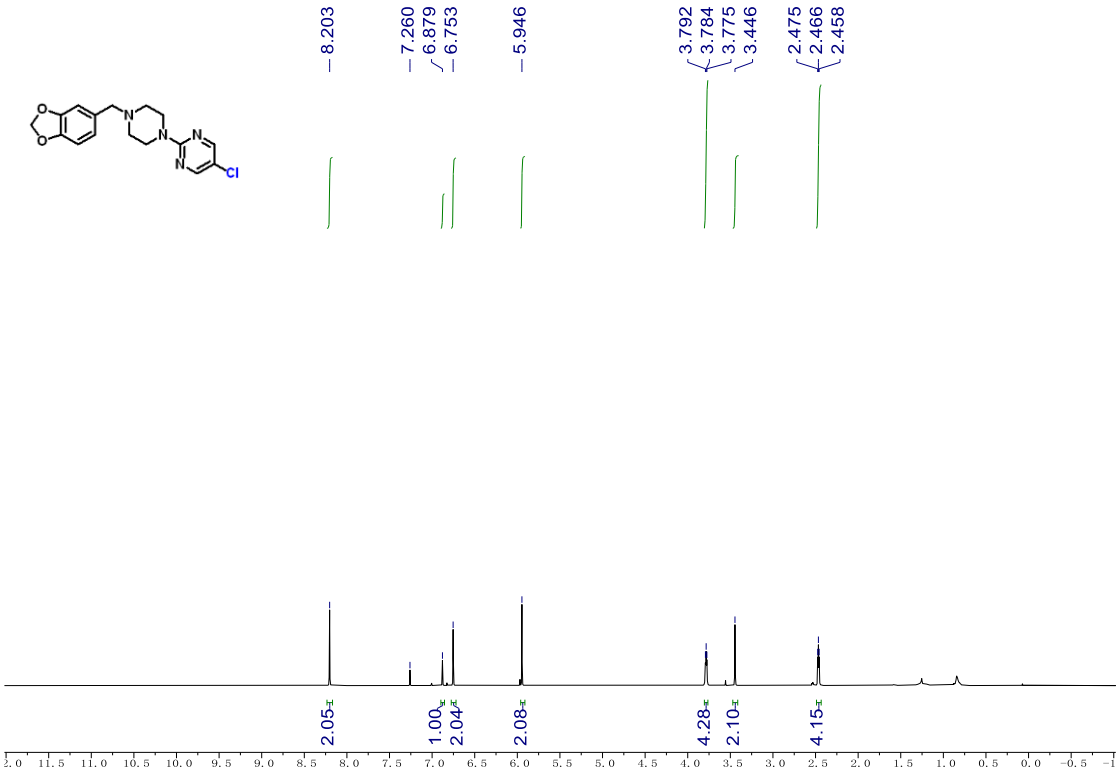
$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4k**.



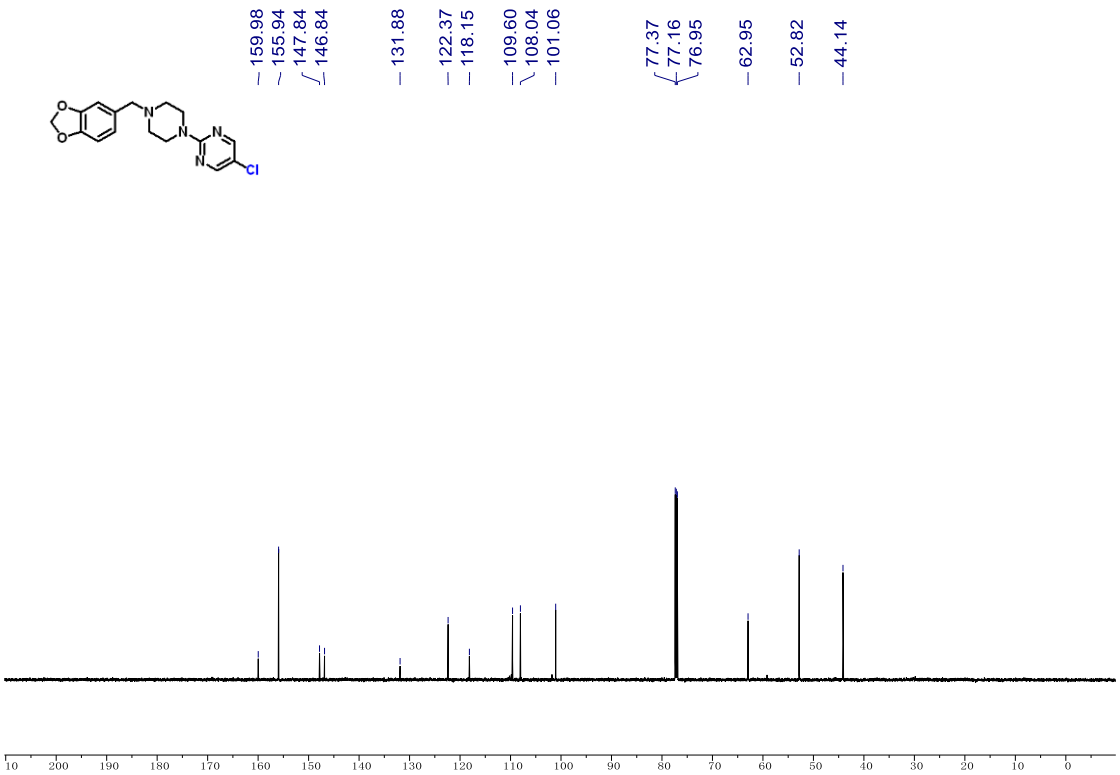
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4l**.



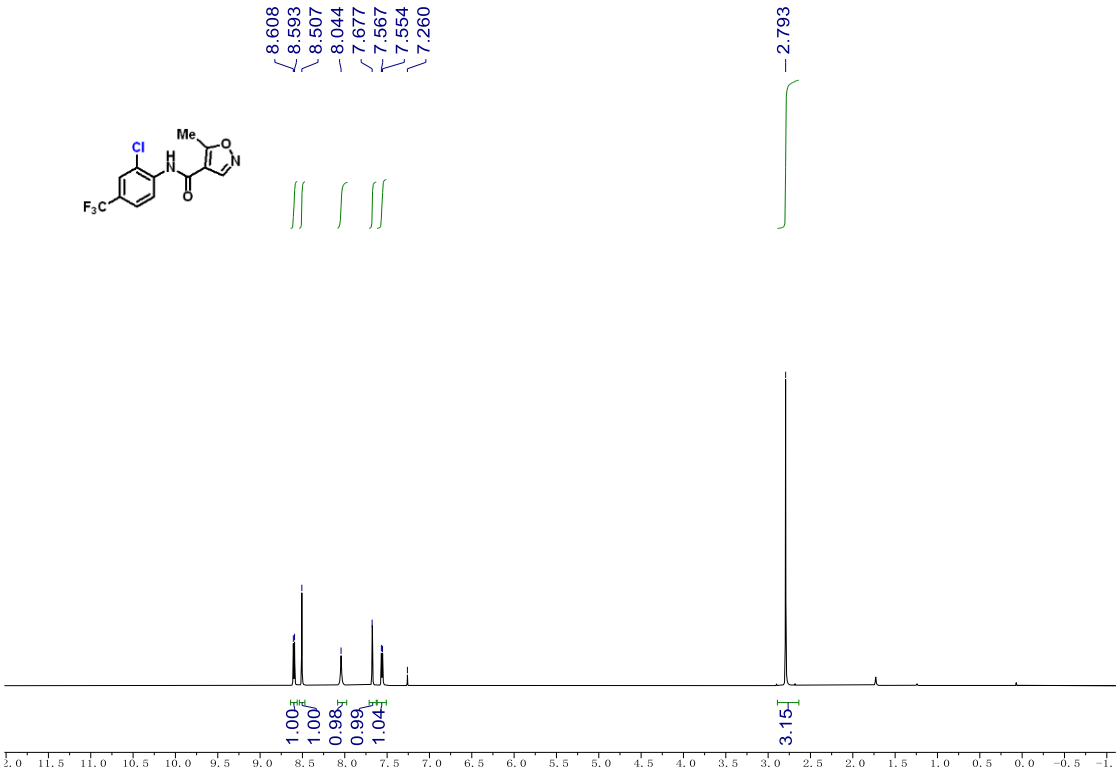
$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4l**.



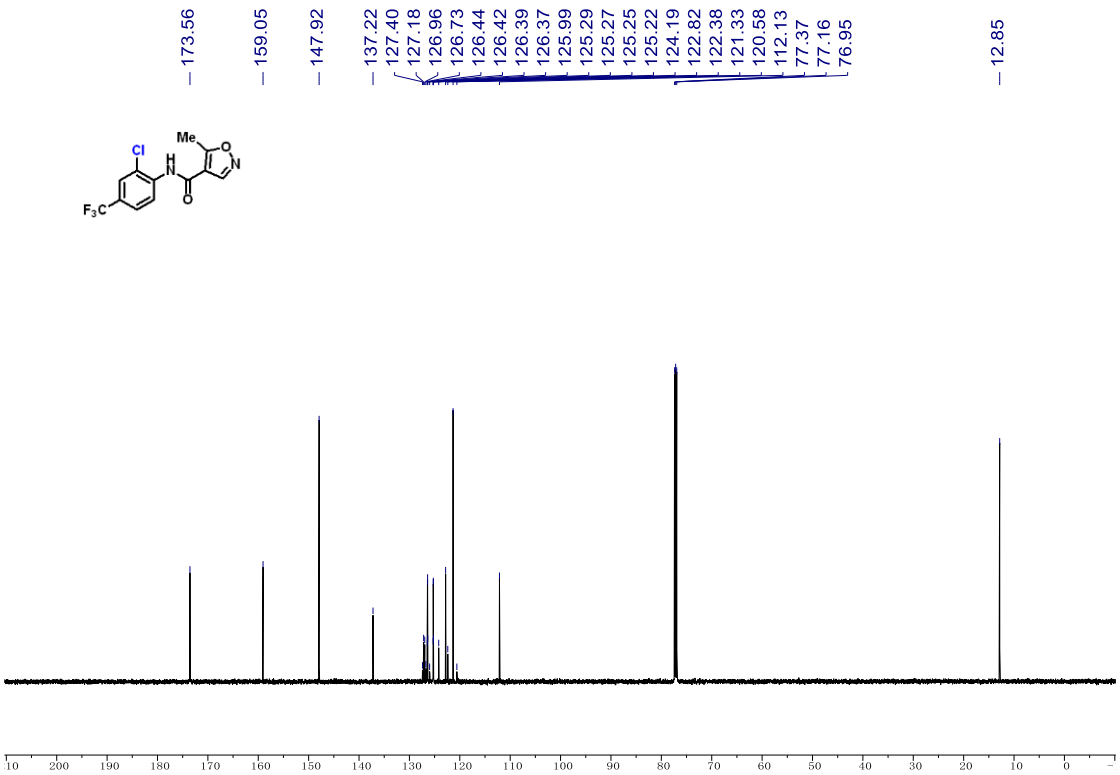
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4m**.



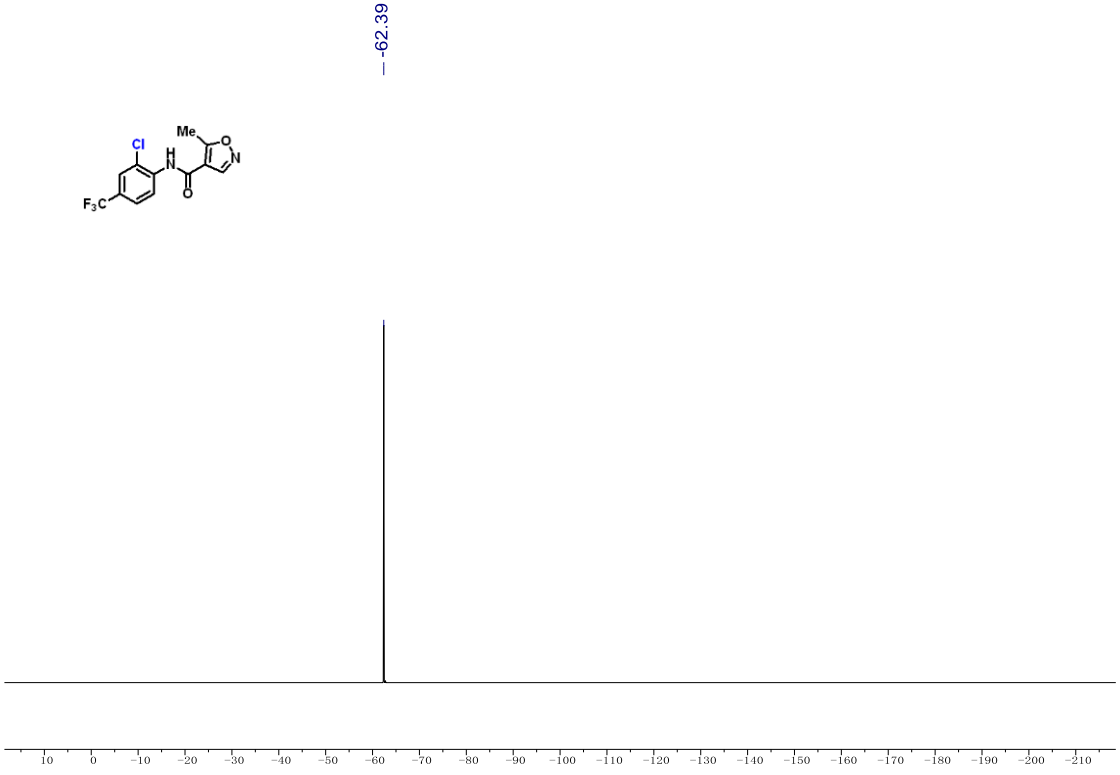
$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4m**.



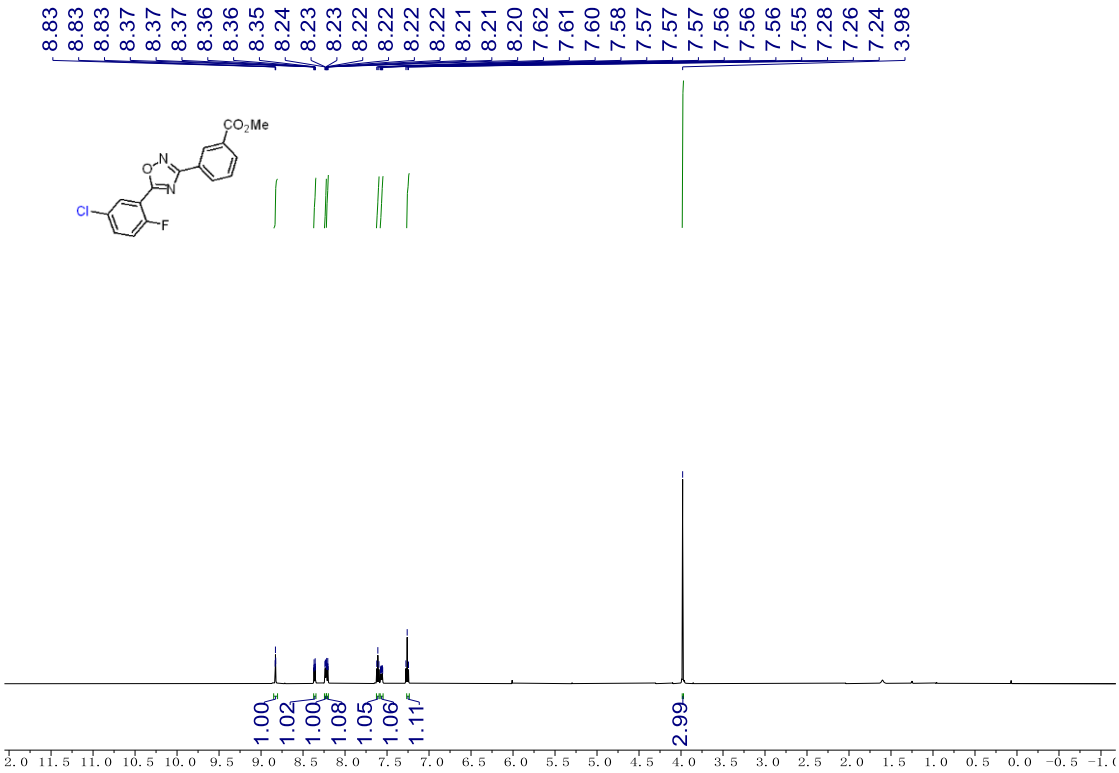
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4n**.



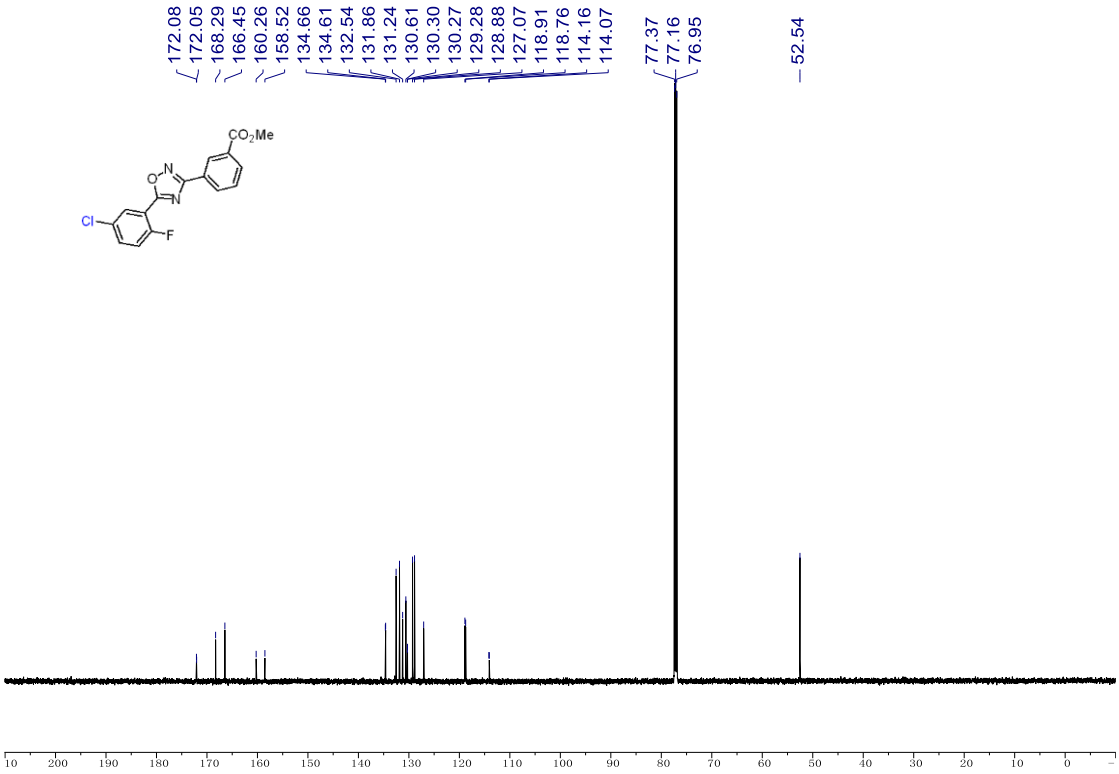
$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4n**.



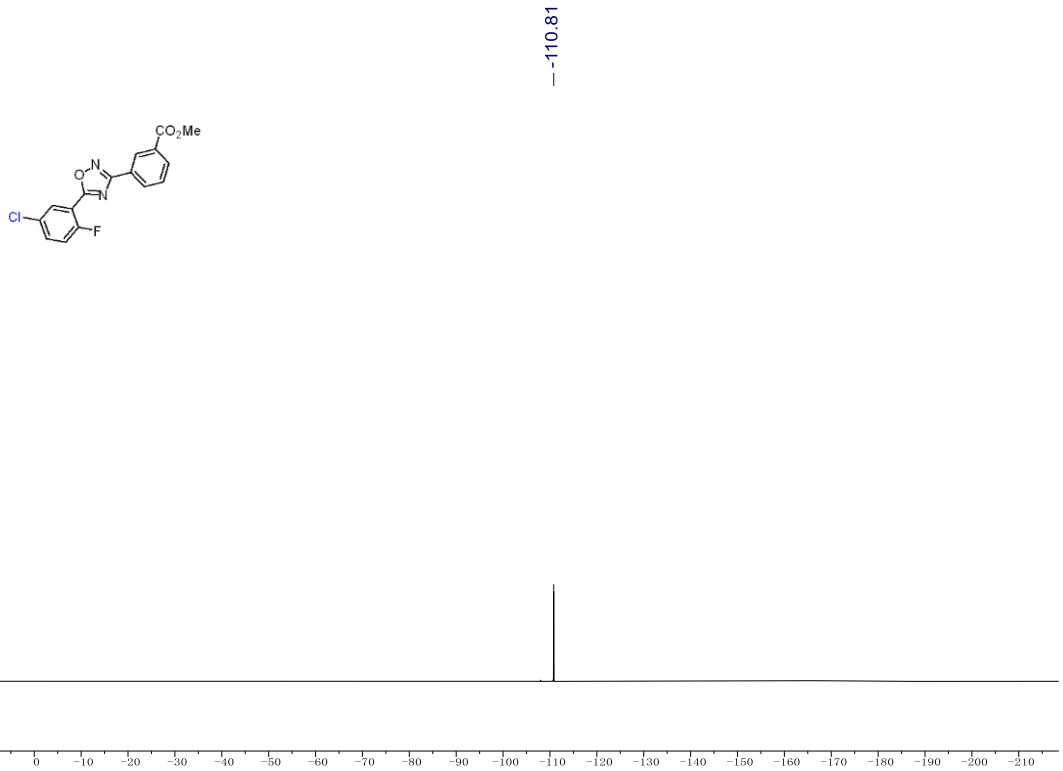
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **4n.**



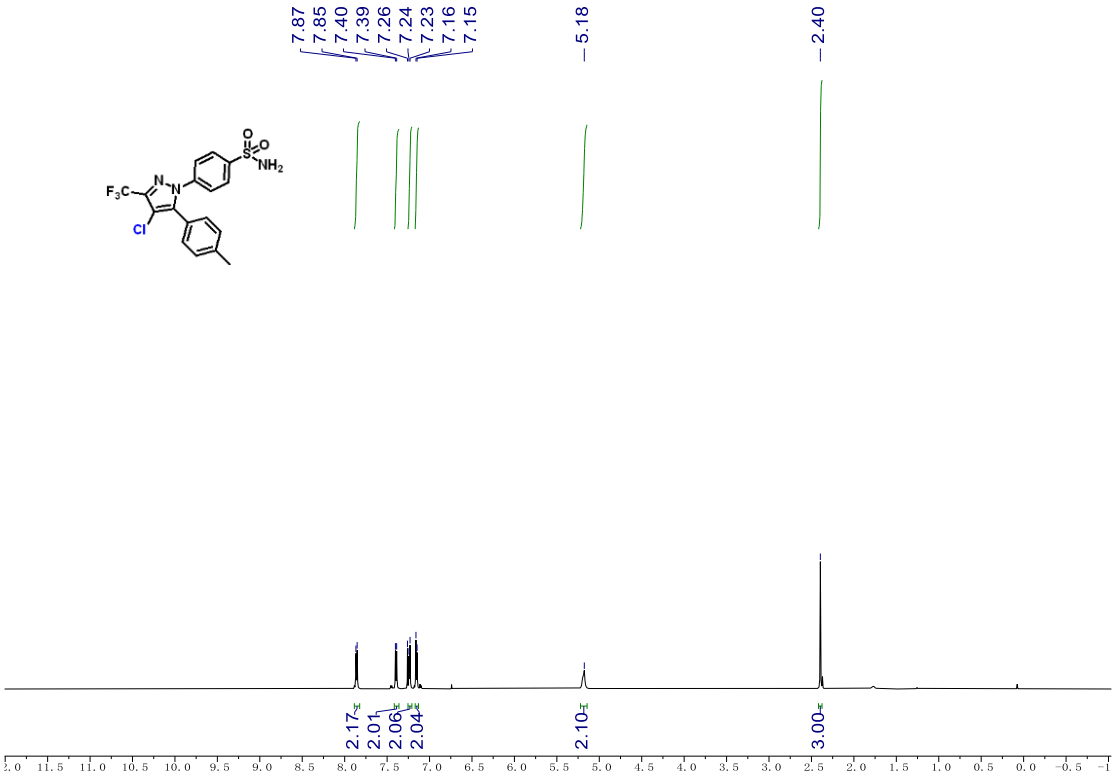
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4o**.



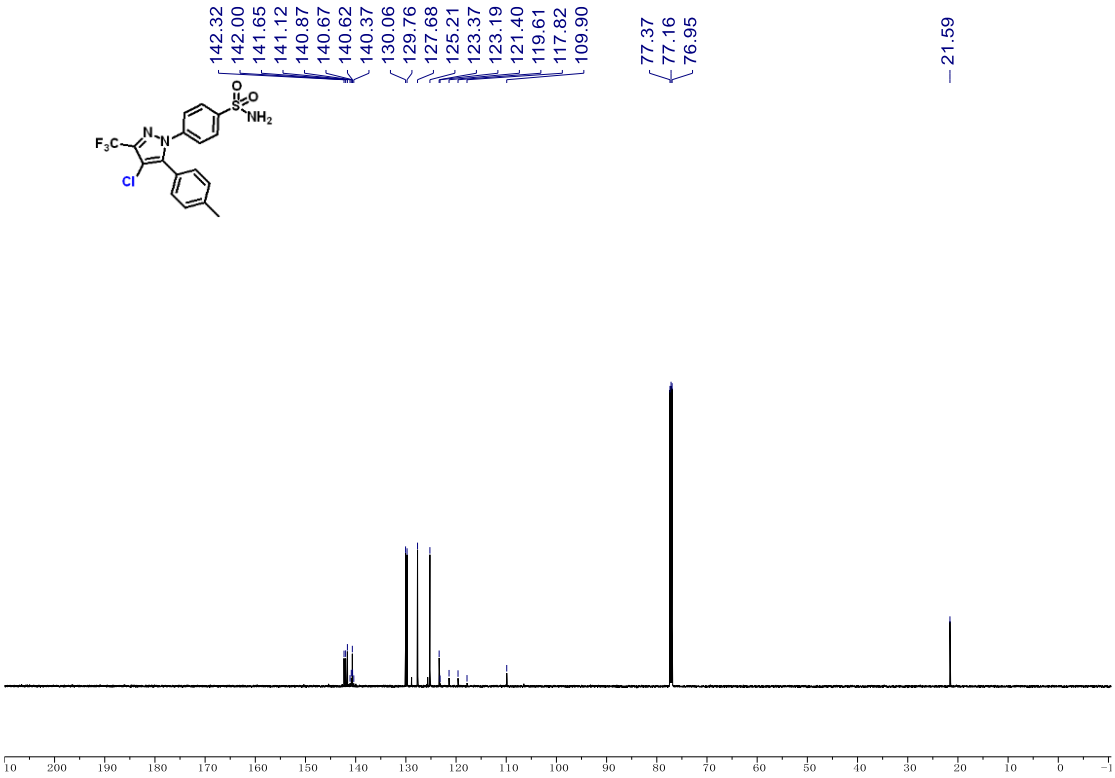
^{3}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4o**.



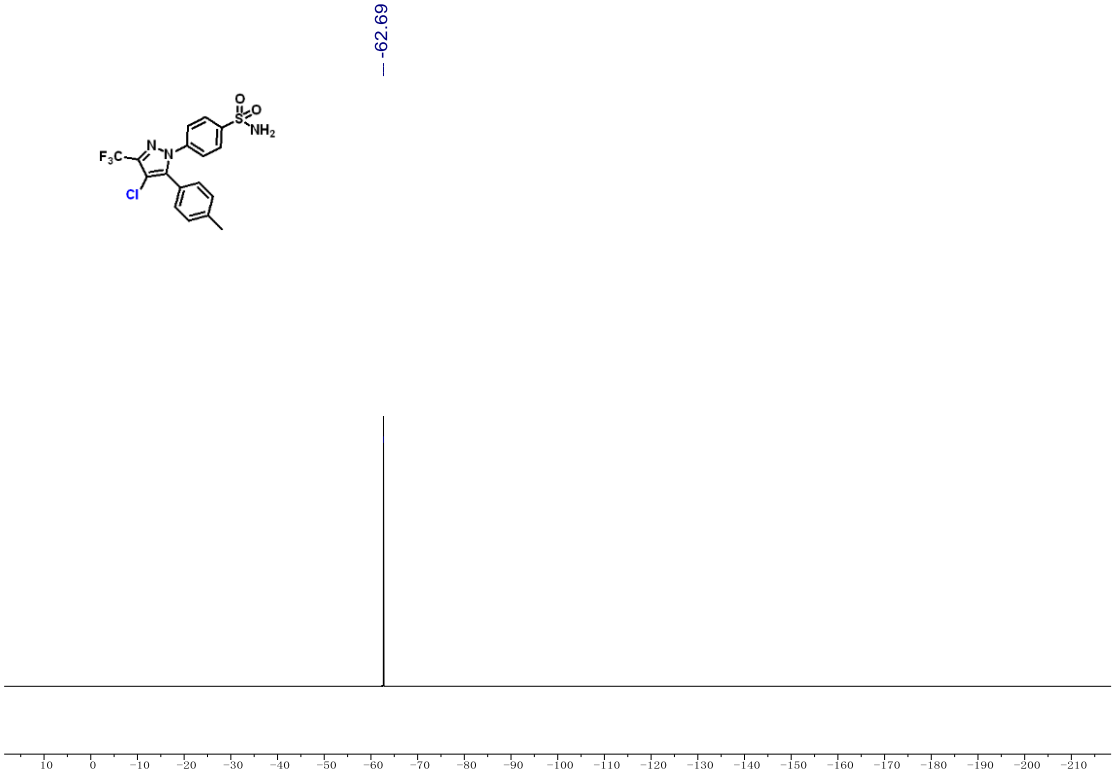
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **4o.**



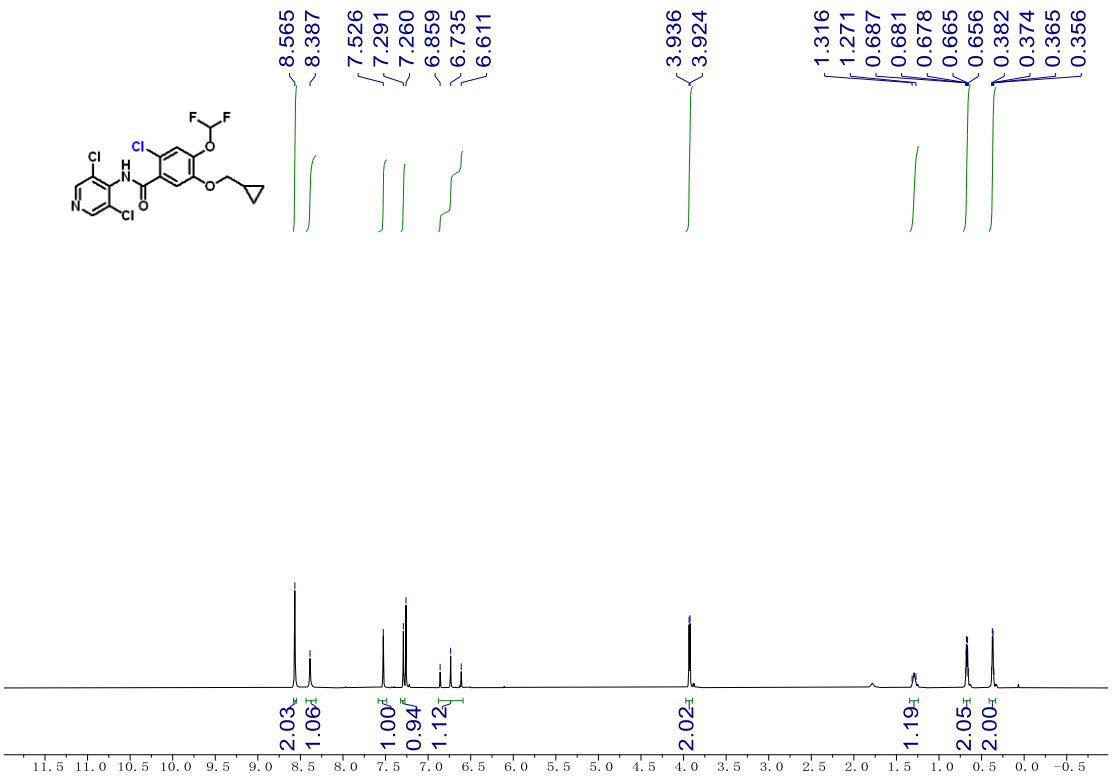
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4p**.



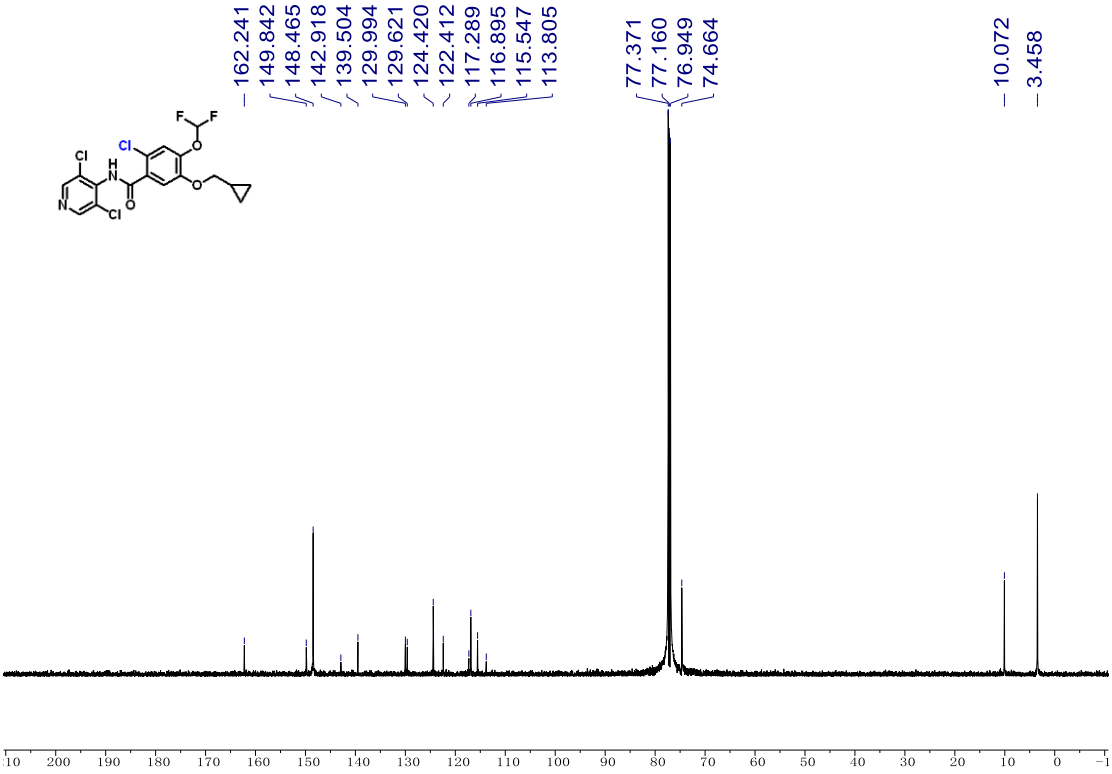
$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4p**.



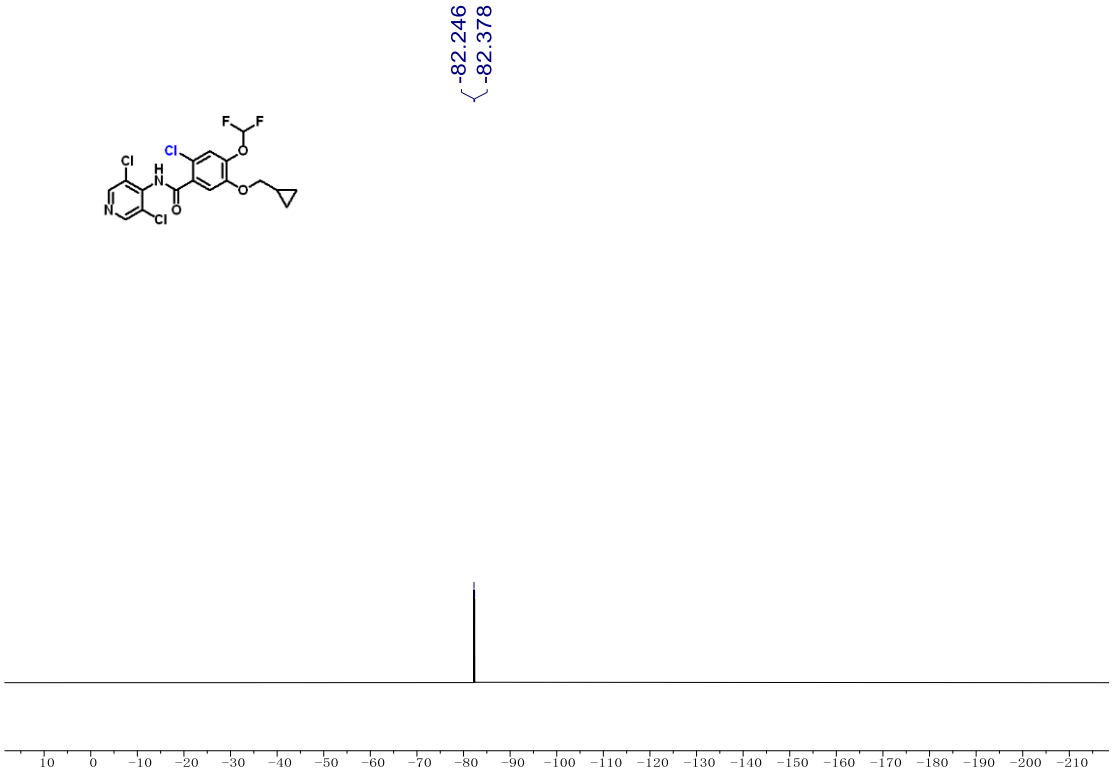
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **4p.**



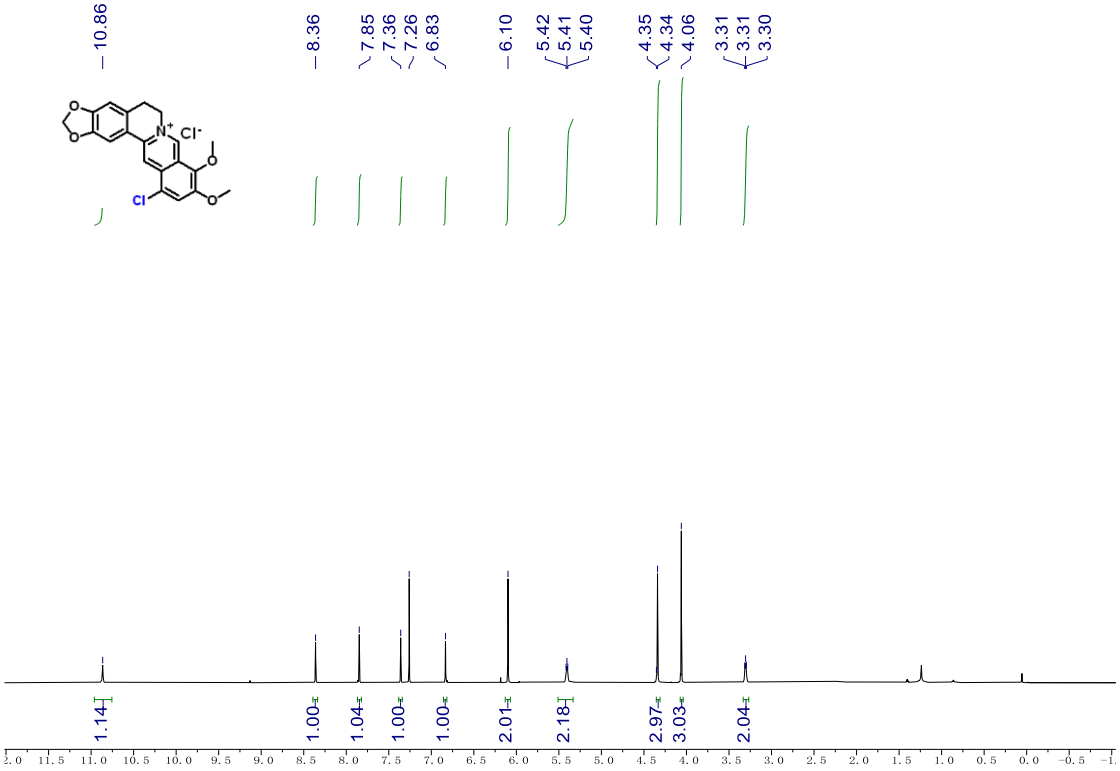
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4q**.



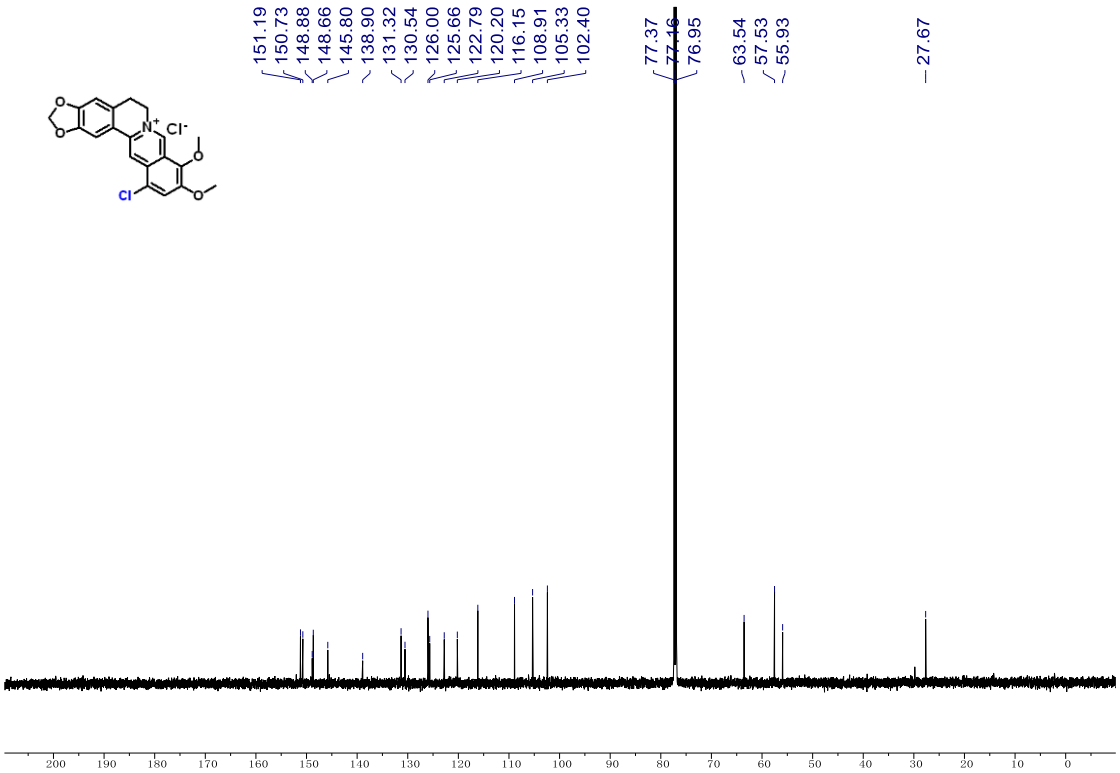
^{3}C{^{1}H} NMR (151 MHz, $CDCl_3$) spectrum of **4q**.



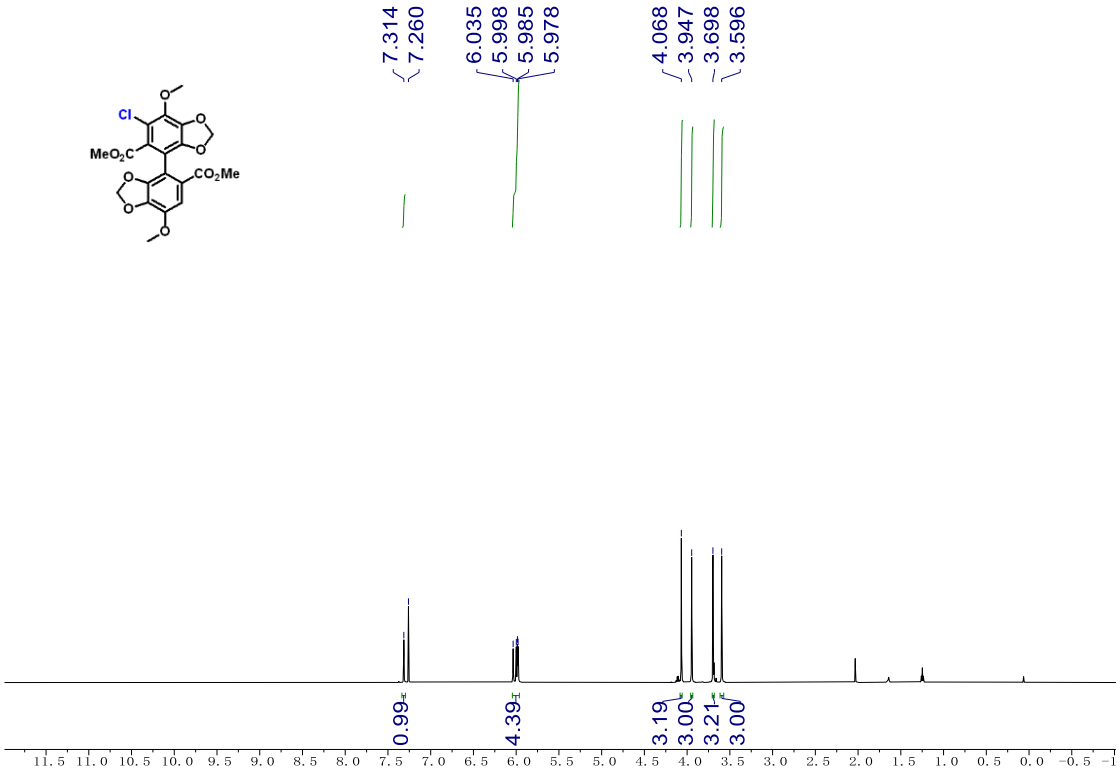
^{19}F NMR (565 MHz, $CDCl_3$) spectrum of **4q.**



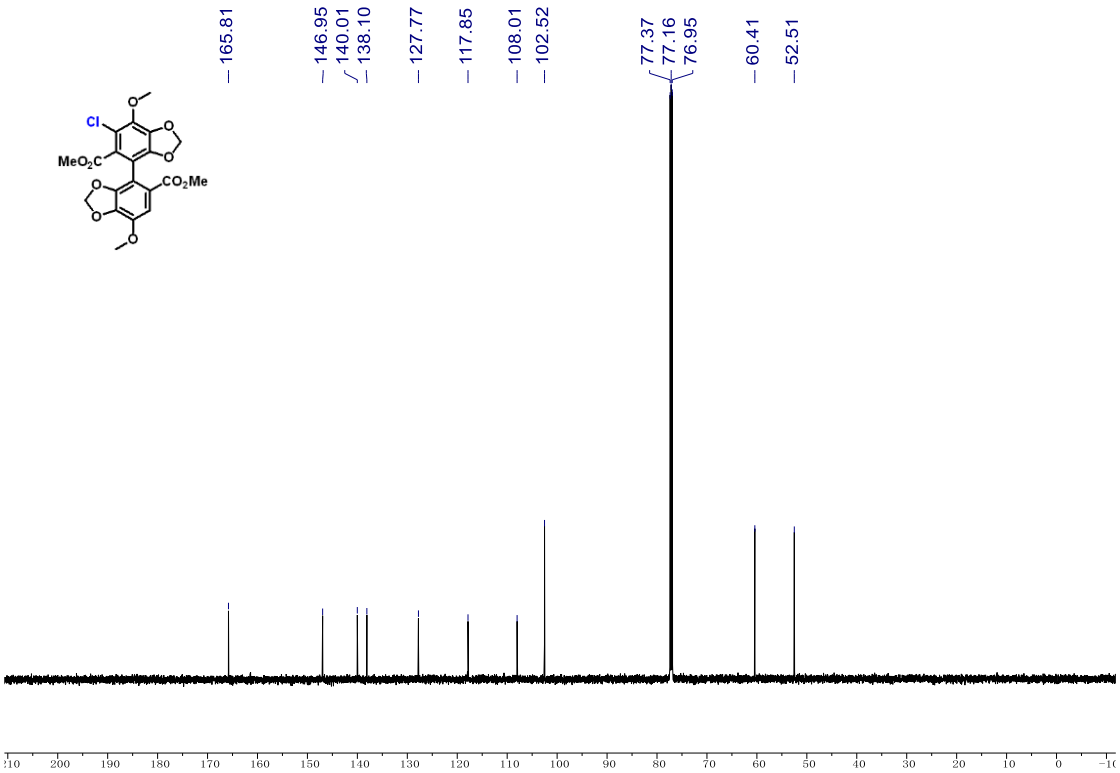
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4r**.



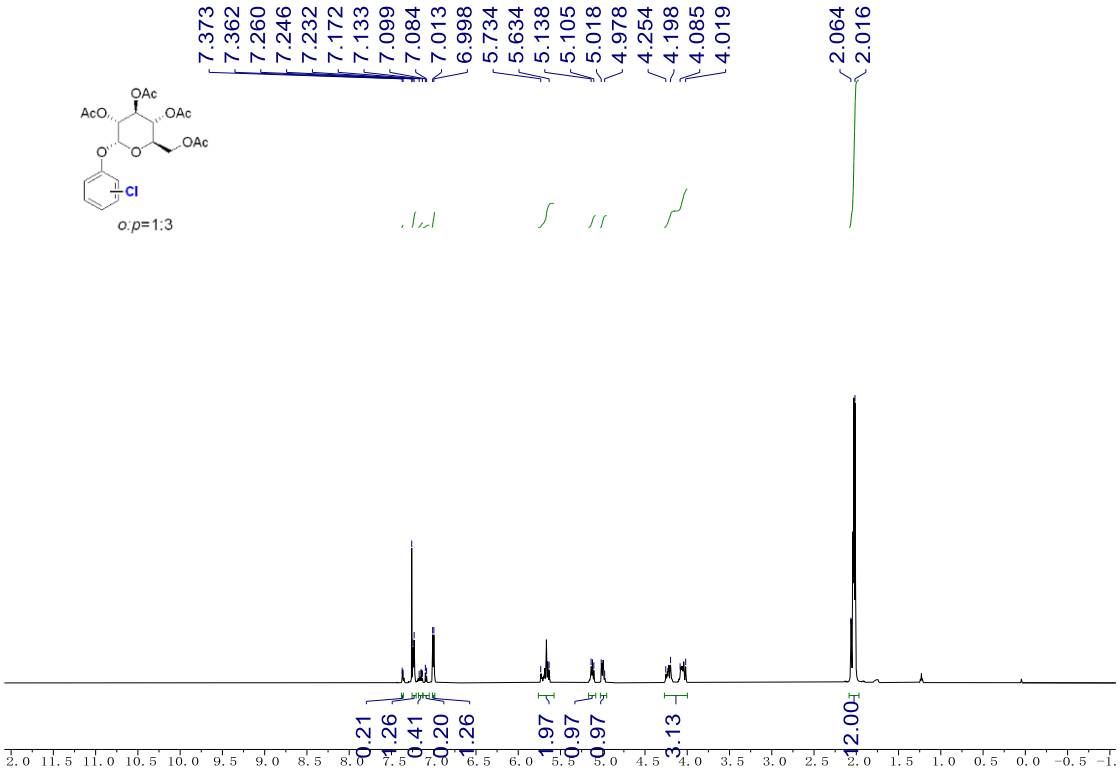
$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4r**.



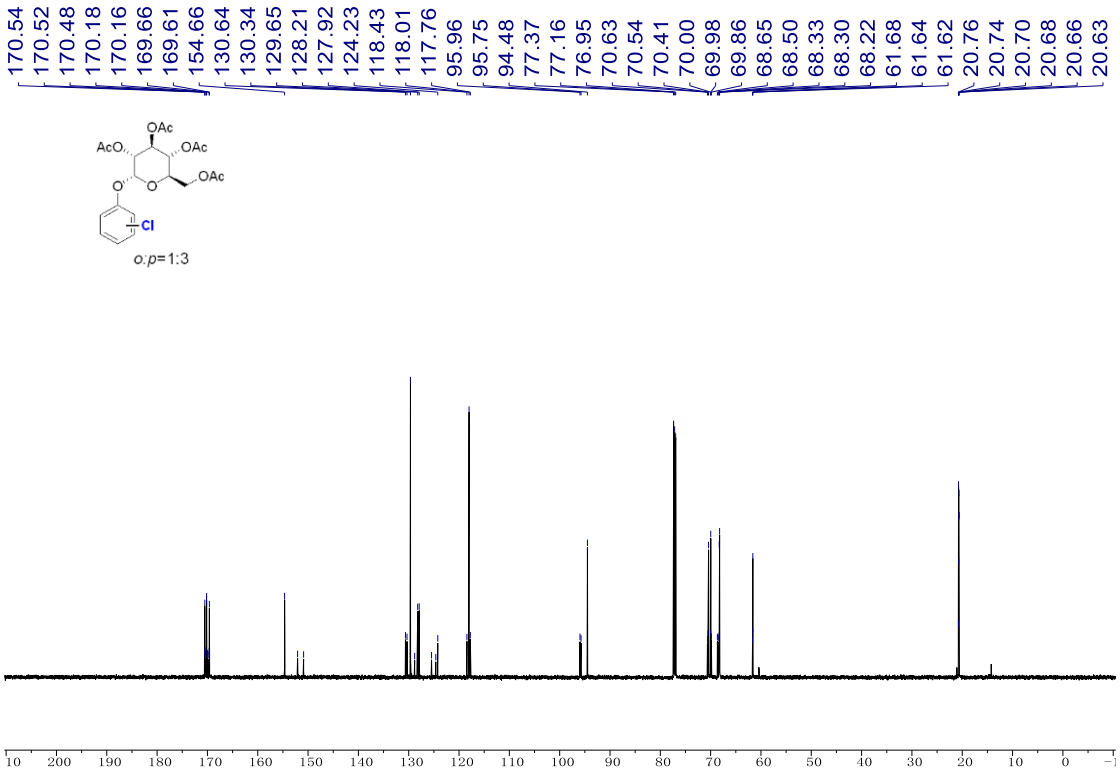
^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4s**.



$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4s**.



^{1}H NMR (600 MHz, $CDCl_3$) spectrum of **4t**.

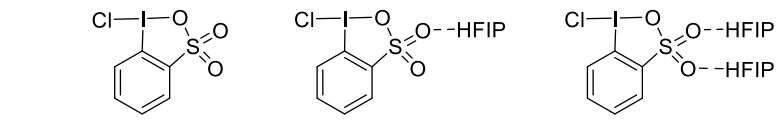


$^{3}C\{^{1}H\}$ NMR (151 MHz, $CDCl_3$) spectrum of **4t**.

10 Computational studies

Computational details

DFT calculations were performed with the Gaussian software (Gaussian 16 C01).[1] Geometry optimizations were carried out at the M06-2x[2-3]/def2-TZVP[4] level, as recommended by the previous studies[5-6]. Solvent effect with the SMD model[7] in dichloroethane is also taken into consideration during the geometry optimization. Frequency analysis was employed to ensure that the intermediates have no imaginary frequency and the transition states have only one imaginary frequency. Intrinsic reaction coordinates (IRCs)[8-9] are calculated to ensure that the transition states indeed connect the two corresponding intermediates. Corrections[10-11] of -2.6 (or 2.6) kcal/mol were made for transformations involving two molecules to one molecule (or one molecule to two molecules), as employed in many earlier studies to reduce the overestimation of entropy contribution. Multiwfn software[12] was used for the generation of .cub files, and the plots of molecular electrostatic potential were rendered in VMD[13].



Reagents	I-Cl bond (Å)
III	2.398
III_1	2.381
III_2	**2.374**

Figure S37. The relative free energy and the corresponding I-Cl bond distances of reagent **III** and HFIP-activated **III**.

(These results showed that hydrogen-bonding with HFIP can further decrease I–Cl bond length of **III** and increase its electrophilicity.)

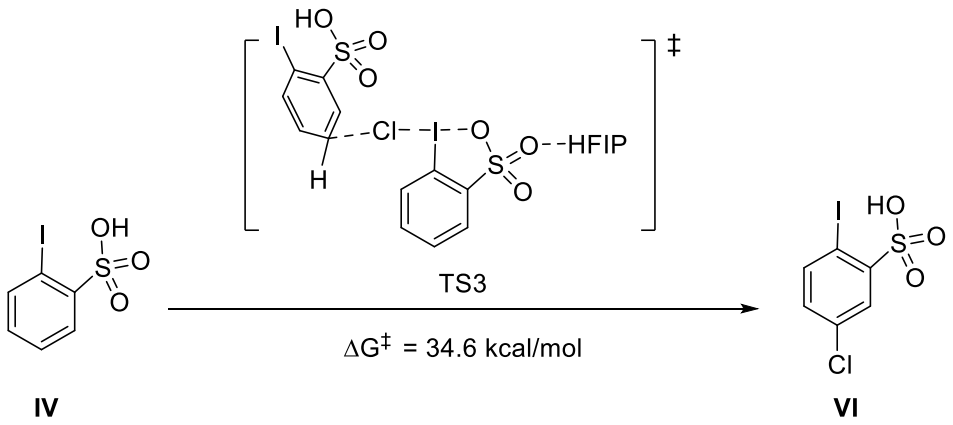


Figure S38. Chlorination for the very electron-deficient arene **IV** in the absence of substrate.

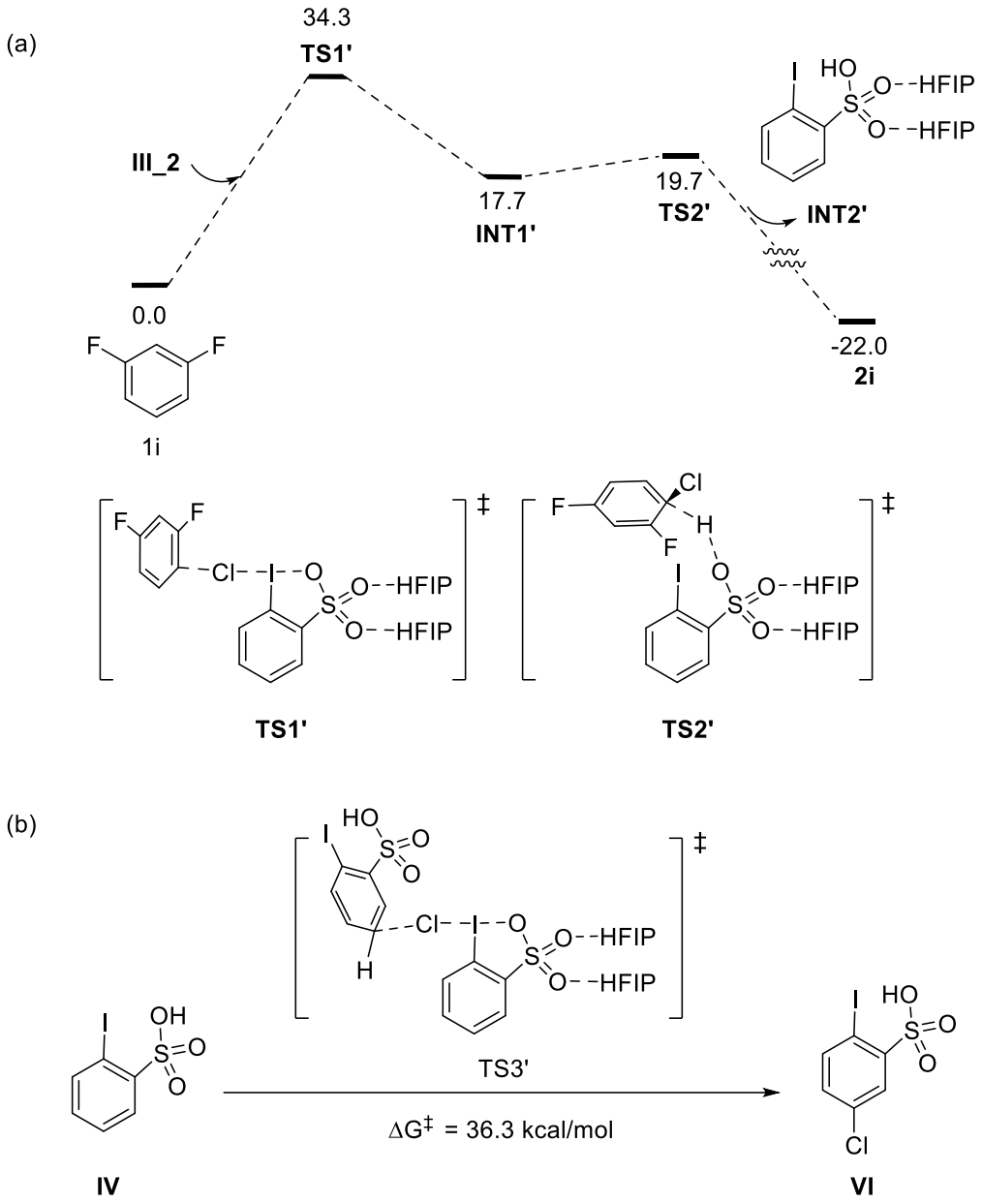
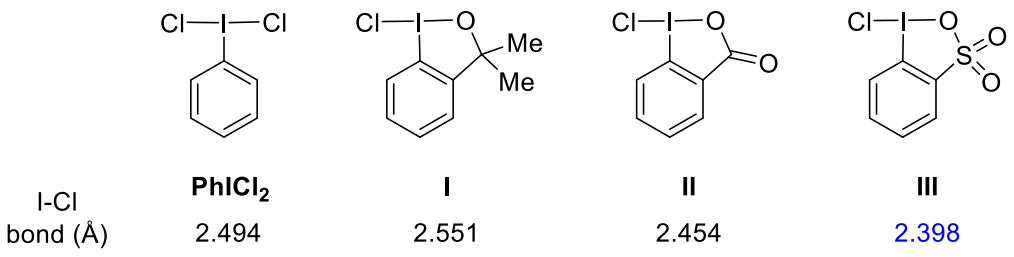


Figure S39. Energy profile for the chlorination process by **III_2**, formed by two HFIP molecules assisted by **III**.



	$PhICl_2$	**I**	**II**	**III**
I-Cl bond (Å)	2.494	2.551	2.454	2.398

Figure S40. I-Cl bond distances in the optimized structures of chlorination reagents.

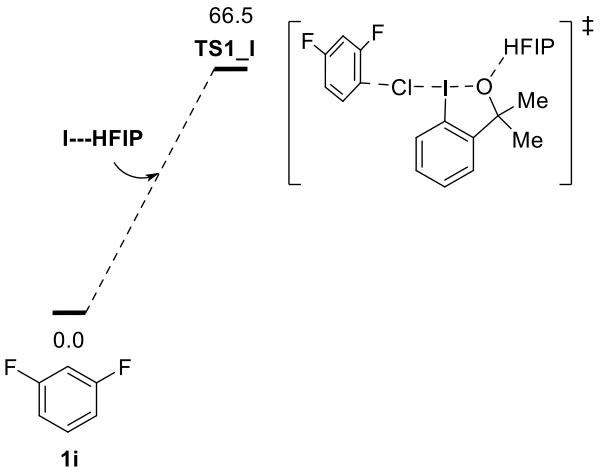


Figure S41. Prohibitively high barrier for the chlorination of the very electron-deficient arene **1i** by reagent **I**.

References

[1]. Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams; Ding, F.; Lipparini, F.; Egidi, F.; Goings, J.; Peng, B.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16 Rev. C.01*, Wallingford, CT, 2016.

[2]. Zhao, Y.; Truhlar, D. G., Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008,** *41* (2), 157-167.

[3]. Zhao, Y.; Truhlar, D. G., The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008,** *120* (1), 215-241.

[4]. Weigend, F.; Ahlrichs, R., Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005,** *7* (18), 3297-3305.

[5]. Sun, T.-Y.; Chen, K.; Zhou, H.; You, T.; Yin, P.; Wang, X., Revisiting the effect of f-functions in predicting the right reaction mechanism for hypervalent iodine reagents. *J. Comput. Chem.* **2021,** *42* (7), 470-474.

[6]. Jiang, H.; Sun, T.-Y.; Chen, Y.; Zhang, X.; Wu, Y.-D.; Xie, Y.; Schaefer, H. F., Designing new Togni reagents by computation. *Chem. Commun.* **2019,** *55* (39), 5667-5670.

[7]. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009,** *113* (18), 6378-6396.

[8]. Fukui, K., The path of chemical reactions - the IRC approach. *Acc. Chem. Res.* **1981,** *14* (12), 363-368.

[9]. Fukui, K., Formulation of the reaction coordinate. *J. Phys. Chem.* **1970,** *74* (23), 4161-4163.

[10]. Wang, Z.; Zhou, Y.; Lam, W. H.; Lin, Z., DFT Studies of Ru-Catalyzed C–O versus C–H Bond Functionalization of Aryl Ethers with Organoboronates. *Organometallics* **2017,** *36* (12), 2354-2363.

[11]. Fan, T.; Sheong, F. K.; Lin, Z., DFT Studies on Copper-Catalyzed Hydrocarboxylation of Alkynes Using CO2 and Hydrosilanes. *Organometallics* **2013,** *32* (18), 5224-5230.

[12]. Lu, T.; Chen, F., Multiwfn: A multifunctional wavefunction analyzer. *J. Comput. Chem.* **2012,** *33*

(5), 580-592.
[13]. Humphrey, W.; Dalke, A.; Schulten, K., VMD: visual molecular dynamics. *J. Mol. Graphics* **1996,** *14* (1), 33-38.

Energy table

Table S8. Zero-point energy (ZPE), thermal correction to Enthalpy (Hcorr), thermal correction to Gibbs Free Energy (Gcorr), and imaginary frequency (cm^{-1}) of transition states of optimized structures. Energies are given in Hartree.

Structures	ZPE	Hcorr	Gcorr	Imaginary frequency
1i	0.084742	0.091552	0.054653	/
HFIP	0.063083	0.07311	0.028079	/
$PhICl_2$	0.092957	0.10366	0.054449	/
I	0.169152	0.182195	0.129938	/
II	0.095177	0.105831	0.058098	/
III	0.096104	0.108122	0.057214	/
IV	0.106104	0.116968	0.068973	/
III_1	0.160134	0.183255	0.10108	/
TS1	0.245481	0.275713	0.178897	-268.3
INT1	0.246855	0.277176	0.181117	/
TS3	0.265534	0.299449	0.193897	-288.0
III_2	0.224883	0.258656	0.150907	/
TS1'	0.309889	0.351094	0.225097	-267.0
INT2'	0.311562	0.352638	0.228993	/
TS2'	0.306923	0.347119	0.225001	-105.2
2i	0.075343	0.083341	0.043124	/
TS3'	0.33058	0.375406	0.242569	-281.3
TS1_1	0.316124	0.346508	0.248363	-267.8