Photo-Induced $FeCl_3$-catalysed direct denitrative chlorination of (hetero)nitroarenes at room temperature

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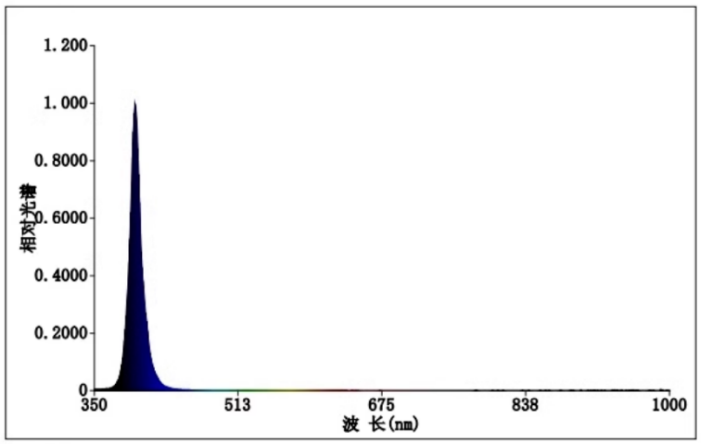
Content of the supporting information

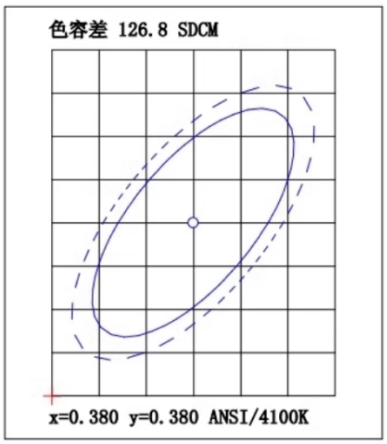
1. General Information

^{1}H NMR spectra were recorded on 600 MHz or 400 MHz spectrometers. The chemical shifts were reported in parts per million (δ) relative to internal standard TMS (0 ppm) for $CDCl_3$. The peak patterns are indicated as follows: s, singlet; d, doublet; dd, doublet of doublet; t, triplet; m, multiplet; q, quartet. The coupling constants, *J*, are reported in Hertz (Hz). ^{13}C NMR spectra were obtained at 151 MHz or 101 MHz spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ or d6-DMSO was used as the NMR solvent. High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectroMeter. The UV-Vis Spectroscopy was measured with Yoke UV-Vis Spectrophotometer with Holographic Blazed Grating C-T Monochromator. Melting points were determined with a MicroMelting point apparatus without corrections. Organic solutions were concentrated by rotary evaporation below 30 °C in vacuum. 4A MS was activated by heating at 200 degrees in a muffle furnace for 20 hours.

All the reagents and solvents were purchased as reagent grade and were used without further purification unless otherwise stated. Flash column chromatography was performed over silica gel 200-300 m and the eluent was a mixture of diethyl ether (Et_2O) and n-petane.

2. Light Source Test Report



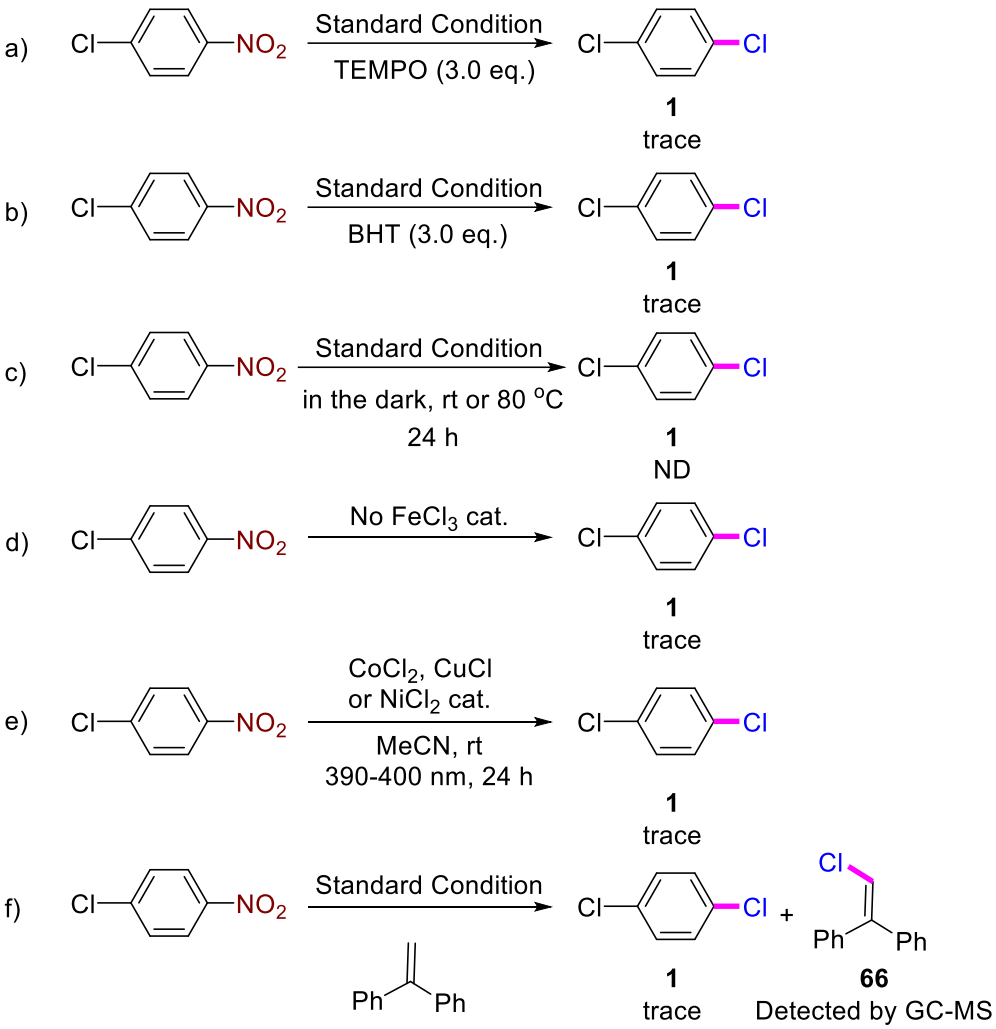


Chromaticity coordinates	X=0.1846	y=0.0454/u'=0.2325	V'=0.1287	Duv=-1.875e-001	
Correlated color temperature	Tc=100000 K	dominant wavelength	λd=436.9 nm	color purity	Purity =88.9 %
color ratio	R=10.3% G=69.8% B=19.9%	peak wavelength	λp=396.2 nm	half width	Δλd=13.1 nm
Color rendering index: Ra = 34.5					
R1 = 79.33	R2 = 37.93	R3 = -5.46	R4 = 10.42	R5 = 69.36	
R6 = 24.07	R7 = 25.89	R8 = 34.56	R9 = 39.27	R10 = -44.01	
R11 = 26.79	R12 = -86.57	R13 = 46.96	R14 = 45.93	R15 = 54.68	
TM30 parameters: Rf = 0.0， Rg: -70.4					
Photometric parameters:					
Luminous flux	Φ=0.8903 Lm	light micro 0.88 Lm/W 206.0 mW	Photovoltaic efficiency = 20.387%		
light quantum=6.914e-001 umol/s		Fluorescence blue light ratio = 0.00965	Fluorescent efficacy= 1.891e-003		
Electrical parameters					
Forward Voltage: VF = 6.738 V		Forward current: IF = 149.9 mA	Power P = 1011 mW		
Reverse current IR=0 uA (reverse voltage VR=5.003 V) Grading: **[out] White light classification: OUT					

Figure S1. LED Spectral Test Report

3. Experimental Section

3.1 Control Experiment to Explore the Mechanism.



Scheme S1. Control experiments to explore the possible mechanism. Conditions: The reaction was performed with standard condition unless otherwise noted. Substrate (0.1 mmol), cat. (10 mol%, 0.01 mmol), $MgCl_2$ (0.2 mmol), 4A MS (20 mg) in MeCN (1 mL, 0.1 M) under 390-400 nm light irradiation. f: Substrate (0.1 mmol,) 1,1-Diphenylethylene (0.2 mol, 2 equiv.), $MgCl_2$ (19 mg, 0.2 mmol, 2 equiv.), 4A MS (20 mg) was dissolved in MeCN (0.9 mL) in a quartz tube, then 100 µL of $FeCl_3$/MeCN (1.63 mg, 0.01 mmol, 10 mol%) was added to the reaction mixture. The product 65 was detected by GC-MS.

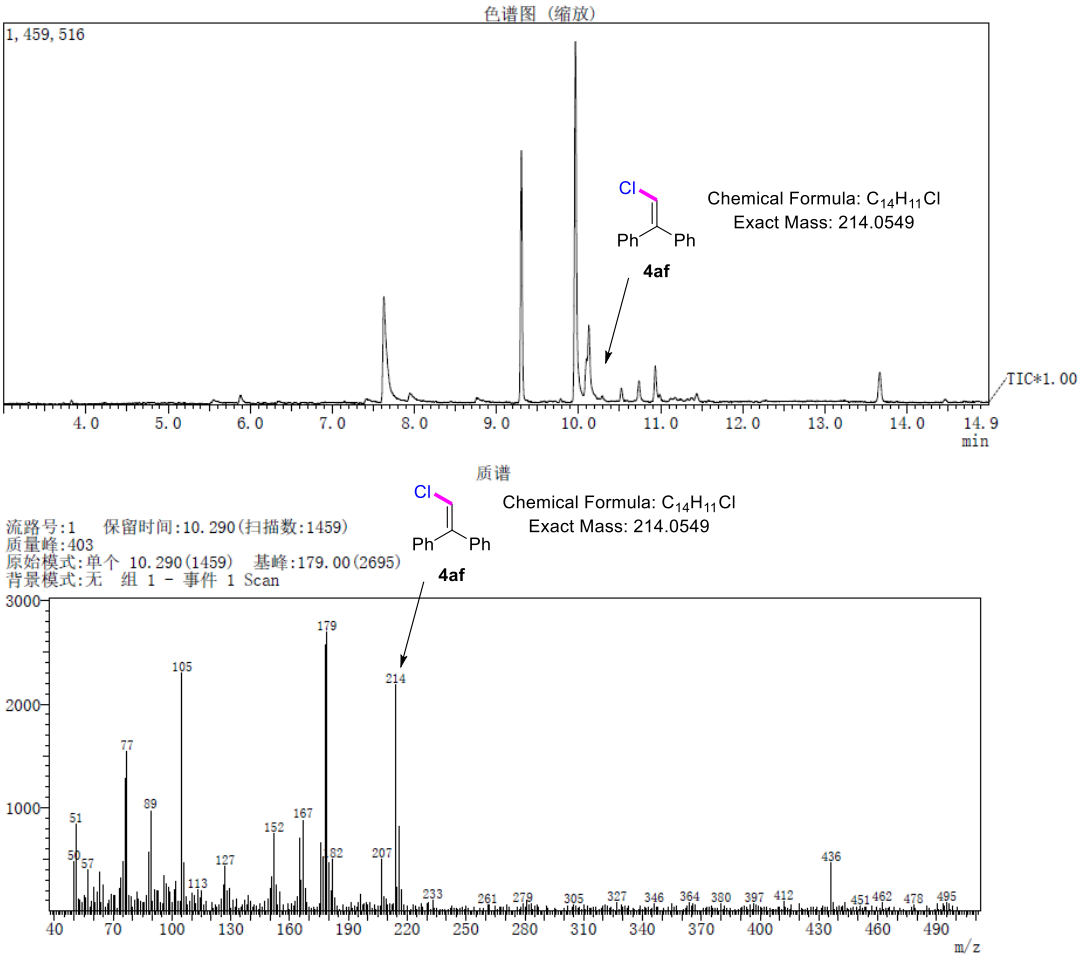


Figure S2. GC-MS trace of reaction in Scheme S1-f.

GC-MS method:

entry	Rate (°C/min)	Final Temperature (°C)	Keep time (min)
0	-	50	2
1	25.0	280	3.8
Total time			15

The column: Rtx-5MS, film thickness: 0.25 μm, length: 30 m, inside diameter: 0.25 mm

3.2 UV-Vis Spectroscopy

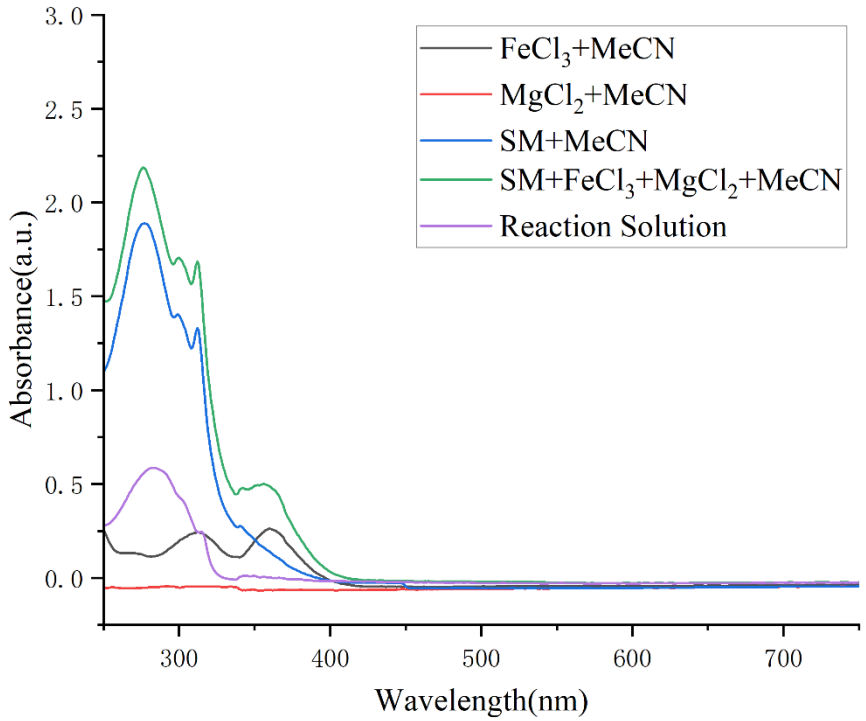


Figure S3. UV-Vis spectroscopy with 8-Nitroquinoline. SM is 8-Nitroquinoline (**60′**). Red line: $MgCl_2$/MeCN (1.0 mM); Black line: $FeCl_3$/MeCN (0.05 mM); Purple line: reaction mixture after 48 h and then diluted to 0.5 mM concertation; brown line: starting material 8-nitroquinoline/MeCN solution (0.5 mM); green line: SM/$FeCl_3$/$MgCl_2$ in MeCN (0.5 mM).

3.3 Light On/Off Experiments

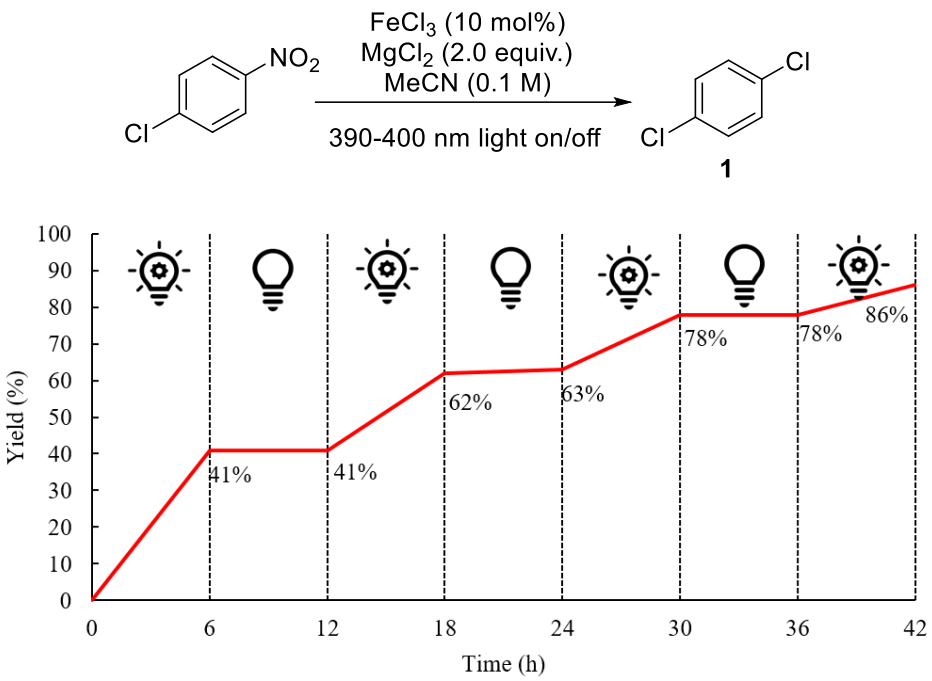
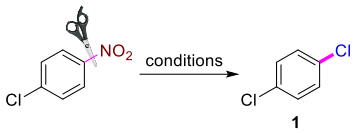


Figure S4. Light on/off experiment with 4-chloronitrobenzene.

3.4 Detailed optimization of the reaction conditions[a]



1

Entry	Cat. (10 mol%)	Cl Source	Solent	Light	Yield[b]
1	$NiCl_2$	NaCl	$CHCl_3$	365 nm	ND[c]
2	$CrCl_3$	NaCl	$CHCl_3$	365 nm	ND
3	$CuCl_2$	NaCl	$CHCl_3$	365 nm	trace
4	$FeCl_3$	NaCl	$CHCl_3$	365 nm	9%
5	$FeCl_3$	NaCl	acetone	365 nm	ND
6	$FeCl_3$	NaCl	dioxane	365 nm	ND
7	$FeCl_3$	NaCl	MeCN	365 nm	36%
8	$FeCl_3$	NaCl	DCE	365 nm	ND
9	$FeCl_3$	conc. HCl	MeCN	365 nm	12%
10	$FeCl_3$	NCS	MeCN	365 nm	33%
11	$FeCl_3$	$ZnCl_2$	MeCN	365 nm	20%
12	$FeCl_3$	$MgCl_2$	MeCN	365 nm	52%
13	$FeCl_3$	CCl_4	MeCN	365 nm	23%
14	$FeCl_3$	NH_4Cl	MeCN	365 nm	31%
15	$FeCl_3$	TBACl	MeCN	365 nm	ND
16	$FeCl_3$	$MgCl_2$	MeCN	370-380 nm	78%
17	$FeCl_3$	$MgCl_2$	MeCN	380-390 nm	73%
18	**$FeCl_3$**	**$MgCl_2$**	**MeCN**	**390-400 nm**	**86%**
19	$FeCl_3$	$MgCl_2$	MeCN	400-410 nm	76%
20	$CoCl_2·6H_2O$	$MgCl_2$	MeCN	390-400 nm	trace
21	CuCl	$MgCl_2$	MeCN	390-400 nm	10%
22	$NiCl_2·6H_2O$	$MgCl_2$	MeCN	390-400 nm	10%
23	$NiCl_2·DME$	$MgCl_2$	MeCN	390-400 nm	10%
24	$BiCl_3$	$MgCl_2$	MeCN	390-400 nm	trace
25	$CuCl_2·2H_2O$	$MgCl_2$	MeCN	390-400 nm	10%
26	$CeCl_3$	$MgCl_2$	MeCN	390-400 nm	15%
27	$TiCl_4$	$MgCl_2$	MeCN	390-400 nm	10%
28	Fe_2O_3	$MgCl_2$	MeCN	390-400 nm	trace
29	Ferrous Oxalate	$MgCl_2$	MeCN	390-400 nm	10%
30	Iron(II) gluconate	$MgCl_2$	MeCN	390-400 nm	trace
31	Ferric glycine	$MgCl_2$	MeCN	390-400 nm	trace
32	Fe_3O_4	$MgCl_2$	MeCN	390-400 nm	trace
33	$Fe(acac)_3$	$MgCl_2$	MeCN	390-400 nm	10%
34	$Fe(NO_3)_3$	$MgCl_2$	MeCN	390-400 nm	15%
35	$FeSO_4·7H_2O$	$MgCl_2$	MeCN	390-400 nm	trace
36	Ferrous fumarate	$MgCl_2$	MeCN	390-400 nm	trace
37[c]	$FeCl_3$	$MgCl_2$	MeCN	390-400 nm	86%
38[d]	$FeCl_3$	$MgCl_2$	MeCN	390-400 nm	86%
39[e]	$FeCl_3$	$MgCl_2$	MeCN	390-400 nm	86%
40	$FeCl_3$	/	MeCN	390-400 nm	trace
41	/	$MgCl_2$	MeCN	390-400 nm	ND

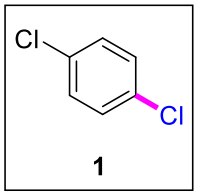
[a] Unless otherwise noted, the reaction was carried out with **1a** (0.10 mmol) and TM cat. (10 mol%) in solvent (1 mL, 0.1 M) under the irradiation of indicated light (5 W LED) cooling with fan. [b] Yields refer to the isolated products. ND means no desired product was detected by GC-MS. [c] 30 mol% $FeCl_3$ was used [d] 60 mol% $FeCl_3$ was used [e] 1 equiv. of $FeCl_3$ was used.

3.5 General Procedure for the Photoinduced $FeCl_3$-Catalyzed Chlorination.

The substrate nitroarene (0.10 mmol), $MgCl_2$ (19 mg, 0.2 mmol, 2 equiv.), 4A MS (20 mg) was dissolved in MeCN (0.9 mL) in a quartz tube, 100 μL of $FeCl_3$/MeCN (1.63 mg, 0.01 mmol, 10 mol%) was added to the reaction mixture, which was then stirred at room temperature with the irradiation under 390-400 nm light (5 W, 2 cm distance from the light). The process of the reaction was monitored by GC-MS (about 24 h-84 h). Upon completion, the solution was transferred to a random flask and was removed under vacuum and the residue was purified by silica gel chromatography with n-pentane or pentane/Et_2O as mobile phase to afford the desired chloroarenes **2** and **3**.

3.6 NMR Data.

1,4-Dichlorobenzene (1)[1]



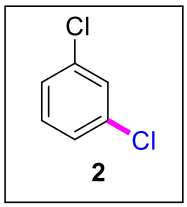
1

Compound 1 was prepared according to the general procedure in about 24 h. After standard work-up and purification, **1** was obtained (12.6 mg, 86% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (s, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 129.8.

1,3-Dichlorobenzene (2)[2]



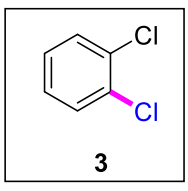
2

Compound 2 was prepared according to the general procedure in about 82 h. After standard work-up and purification, **2** was obtained (8.5 mg, 58% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 1H), 7.26 (d, *J* = 3.2 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 135.0, 130.5, 128.7, 126.9.

1,2-Dichlorobenzene (3)[3]

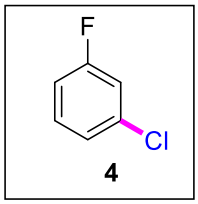


3

Compound 3 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **3** was obtained (11.5 mg, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 – 7.41 (m, 2H), 7.20 (dd, *J* = 6.0, 3.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 132.5, 130.5, 127.7.

1-Chloro-3-fluorobenzene (4)[4]



4

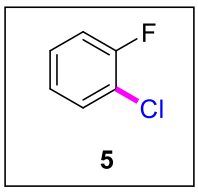
Compound 4 was prepared according to the general procedure in about 82 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **4** was obtained (8.1 mg, 62% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.29 (td, *J* = 8.2, 6.2 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.12 (dt, *J* = 8.8, 2.2 Hz, 1H), 7.00 (td, *J* = 8.5, 2.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 162.7 (d, *J* = 251.0 Hz), 135.1 (d, *J* = 11.0 Hz), 130.6 (d, *J* = 9.0 Hz), 124.5 (d, *J* = 3.0 Hz), 116.4 (d, *J* = 24.0 Hz), 113.8 (d, *J* = 21.0 Hz).

^{19}F NMR (565 MHz, $CDCl_3$) δ -110.92.

1-Chloro-2-fluorobenzene (5)[5]



5

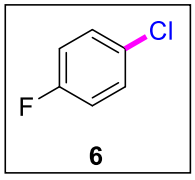
Compound 5 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **5** was obtained (9.7 mg, 74% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (td, *J* = 7.8, 1.6 Hz, 1H), 7.28 (d, *J* = 5.5 Hz, 1H), 7.20 – 7.06 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 130.7, 128.2, 128.0, 124.8 (d, *J* = 4.0 Hz), 116.7, 116.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.45.

1-Chloro-4-fluorobenzene (6)[4]



6

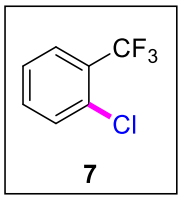
Compound 6 was prepared according to the general procedure in about 82 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **6** was obtained (6.5 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H).

13C NMR (151 MHz, $CDCl_3$) δ 161.3 (d, J = 246.0 Hz), 129.9 (d, J = 8.2 Hz), 129.1 (d, J = 3.3 Hz), 116.7 (d, J = 22.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -115.93 (m, 1F).

1-Chloro-2-(trifluoromethyl)benzene (7)[6]



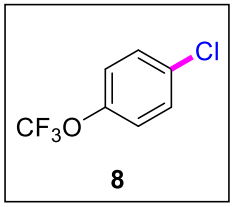
7

Compound 7 was prepared according to the general procedure in about 84 h. After standard work-up and purification, **7** was obtained (12.1 mg, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 – 7.65 (m, 1H), 7.53 – 7.44 (m, 2H), 7.39 – 7.32 (m, 1H).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.67.

1-Chloro-4-(trifluoromethoxy)benzene (8)[7]



8

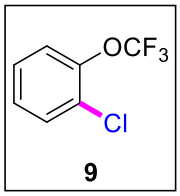
Compound 8 was prepared according to the general procedure in about 84 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **8** was obtained (10.4 mg, 53% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.33 (m, 2H), 7.18 – 7.12 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7 (d, *J* = 2.0 Hz), 132.5, 129.9, 122.4, 120.4 (q, *J* = 258.6 Hz)

^{19}F NMR (376 MHz, $CDCl_3$) δ -58.20.

1-Chloro-2-(trifluoromethoxy)benzene (9)[8]



9

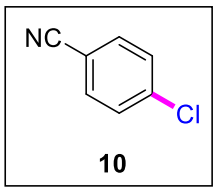
Compound 9 was prepared according to the general procedure in about 84 h. After standard work-up and purification, **9** was obtained (12.9 mg, 66% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.50 (dd, J = 7.7, 1.8 Hz, 1H), 7.43 – 7.31 (m, 2H), 7.31 – 7.23 (m, 1H).

^{13}C NMR (101 MHz, CDCl3) δ 145.3 (d, J = 2.0 Hz), 131.0, 127.8 (d, J = 5.0 Hz), 127.5, 122.6, 120.5 (q, J = 260.0 Hz).

^{19}F NMR (376 MHz, CDCl3) δ -57.9.

4-Chlorobenzonitrile (10)[9]



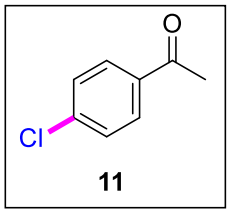
10

Compound 10 was prepared according to the general procedure in about 84 h. After standard work-up and purification, **10** was obtained (11.2 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.58 (m, 2H), 7.50 – 7.45 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 133.3, 129.7, 117.9, 110.7.

p-Chloroacetophenone (11)[1]

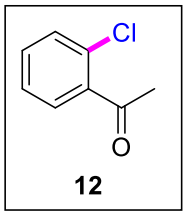


Compound 11 was prepared according to the general procedure in about 70 h. After standard work-up and purification, **11** was obtained (11.2 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 – 7.80 (m, 2H), 7.42 – 7.34 (m, 2H), 2.55 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 196.6, 139.3, 135.2, 129.5, 128.7, 26.3.

2-Chloroacetophenone (12)[10]

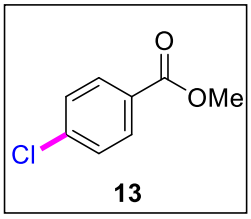


Compound 12 was prepared according to the general procedure in about 32 h. After standard work-up and purification, **12** was obtained (10.5 mg, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.42 – 7.24 (m, 3H), 2.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 200.2, 138.9, 131.8, 131.1, 130.5, 129.2, 126.8, 30.5.

Methyl 4-chlorobenzoate (13)[9]

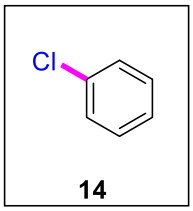


Compound 13 was prepared according to the general procedure in about 32 h. After standard work-up and purification, **13** was obtained (10.2 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 8.5 Hz, 2H), 3.92 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.1, 139.3, 130.9, 128.6, 128.5, 52.2.

Chlorobenzene (14)[3]

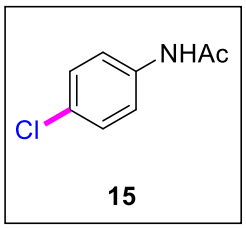


Compound 14 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **14** was obtained (9.2 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 6.98 (m, 5H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 134.2, 129.7, 128.6, 126.4.

N-(4-Chlorophenyl)acetamide (15)[11]

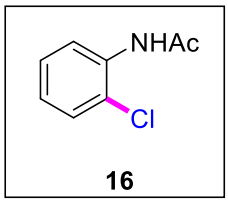


Compound 15 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **15** was obtained (13.6 mg, 80% yield).

^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 8.05 (d, *J* = 8.9 Hz, 2H), 7.78 (d, *J* = 8.9 Hz, 2H).

^{13}C NMR (101 MHz, DMSO) δ 169.0, 138.4, 128.8, 126.9, 120.9, 40.2, 38.9, 24.1.

N-(2-Chlorophenyl)acetamide (16)[12]

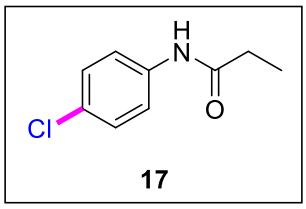


Compound 16 was prepared according to the general procedure in about 84 h. After standard work-up and purification, **16** was obtained (12.4 mg, 73% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.27 (d, *J* = 8.3 Hz, 1H), 7.28 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.23 – 7.17 (m, 1H), 6.96 (td, *J* = 7.7, 1.6 Hz, 1H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 168.2, 134.6, 128.9, 127.7, 124.6, 121.6, 24.8.

N-(4-Chlorophenyl)propanamide (17)[13]

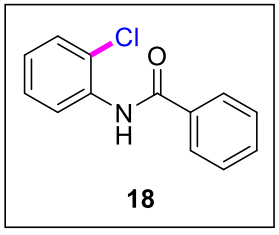


Compound 17 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **17** was obtained (13.6 mg, 74% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.52 – 7.46 (m, 2H), 7.31 – 7.24 (m, 2H), 2.41 (q, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 172.4, 136.5, 129.1, 128.9, 121.2, 30.6, 9.6.

N-(2-Chlorophenyl)benzamide (18)[12]

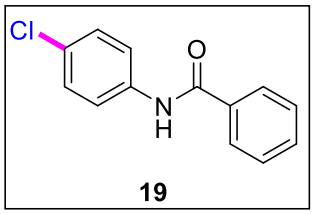


Compound 18 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **18** was obtained (15.5 mg, 67% yield).

^{1}H NMR (400 MHz, CDCl$_3$) δ 8.57 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.61 – 7.56 (m, 1H), 7.52 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.42 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.34 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.08 (td, *J* = 7.7, 1.6 Hz, 1H).

^{13}C NMR (101 MHz, CDCl$_3$) δ 165.2, 134.7, 134.6, 132.2, 129.0, 128.9, 127.9, 127.1, 124.7, 123.0, 121.4.

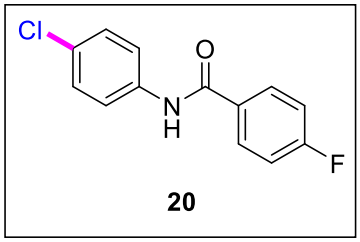
N-(4-Chlorophenyl)benzamide (19)[11]



19

Compound 19 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **19** was obtained (19.7 mg, 85% yield).
^{1}H NMR (400 MHz, DMSO-d6) δ 7.96 – 7.90 (m, 2H), 7.83 – 7.76 (m, 2H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.52 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.42 – 7.36 (m, 2H).
^{13}C NMR (101 MHz, DMSO) δ 166.1, 138.3, 134.8, 132.0, 128.8, 128.7, 127.9, 127.7, 122.2.

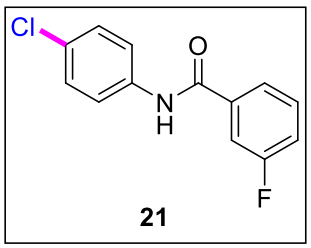
N-(4-Chlorophenyl)-4-fluorobenzamide (20)[14]



20

Compound 20 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **20** was obtained (19.5 mg, 78% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.7, 5.3 Hz, 2H), 7.57 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.8 Hz, 2H), 7.14 (t, *J* = 8.6 Hz, 2H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 166.5 (d, J = 154.5 Hz), 163.7, 136.3, 130.7, 129.7, 129.4 (d, *J* = 9.1 Hz), 129.1, 121.5, 115.9 (d, J = 22.2 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -106.93.

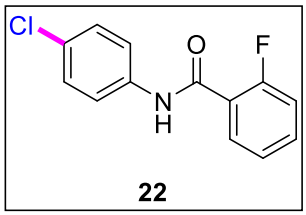
N-(4-Chlorophenyl)-3-fluorobenzamide (21)[15]



21

Compound 21 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **21** was obtained (18.0 mg, 72% yield).
^{1}H NMR (400 MHz, DMSO-d6) δ 7.75 (dddd, *J* = 20.5, 9.9, 3.0, 1.5 Hz, 4H), 7.57 (dd, *J* = 7.9, 5.8 Hz, 1H), 7.48 – 7.36 (m, 3H).
^{13}C NMR (101 MHz, DMSO) δ 164.6, 162.2 (d, J = 245.4 Hz), 138.0, 137.2 (d, J = 7.1 Hz), 131.0 (d, J = 8.1 Hz), 128.9, 127.9, 124.1, 122.3, 118.9 (d, J = 21.2 Hz), 114.7 (d, J = 22.2 Hz).
^{19}F NMR (376 MHz, DMSO) δ -112.44 (m, 1F).

N-(4-Chlorophenyl)-2-fluorobenzamide (22)[16]



22

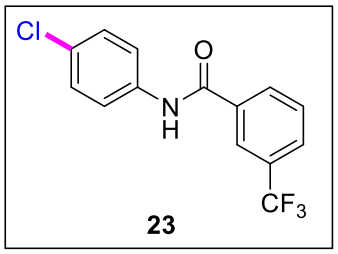
Compound 22 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **22** was obtained (22.0 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, *J* = 15.8 Hz, 1H), 8.07 (td, *J* = 8.0, 1.9 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.50 – 7.40 (m, 1H), 7.25 (dd, *J* = 8.5, 2.1 Hz, 2H), 7.15 – 7.05 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.5, 161.2 (d, *J* = 4.0 Hz), 159.1, 136.2, 134.0 (d, *J* = 9.1 Hz), 132.2 (d, *J* = 2.1 Hz), 129.7, 129.1, 125.2 (d, *J* = 3.0 Hz), 121.7, 121.0 (d, *J* = 11.1 Hz), 116.1 (d, *J* = 25.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-113.12 (m, 1F).

N-(4-Chlorophenyl)-3-(trifluoromethyl)benzamide (23)[2]



23

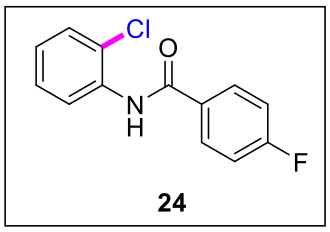
Compound 23 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **23** was obtained (24.6 mg, 82% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 1.8 Hz, 1H), 8.04 – 8.00 (m, 1H), 7.81 – 7.77 (m, 1H), 7.62 – 7.55 (m, 3H), 7.34 – 7.28 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 164.5, 135.7 (d, *J* = 61.6 Hz), 131.3 (d, *J* = 32.3 Hz), 130.4, 130.1, 129.5, 129.1, 128.6 (q, *J* = 4.0 Hz), 124.9, 124.0 (q, *J* = 4.0 Hz), 122.2, 121.8.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.74.

N-(2-Chlorophenyl)-4-fluorobenzamide (24)[14]



24

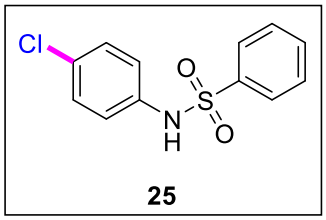
Compound 24 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **24** was obtained (16.2 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.52 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.96 – 7.90 (m, 2H), 7.41 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.33 (ddd, *J* = 8.5, 7.6, 1.5 Hz, 1H), 7.19 (t, *J* = 8.6 Hz, 2H), 7.09 (td, *J* = 7.7, 1.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 166.4, 164.2, 163.8, 134.5, 130.8 (d, *J* = 3.0 Hz), 129.5 (d, *J* = 10.1 Hz), 128.5 (d, *J* = 115.1 Hz), 124.9, 123.1, 121.5, 116.0 (d, *J* = 22.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-106.77 (m, 1F).

N-(4-Chlorophenyl)benzenesulfonamide (25)[17]



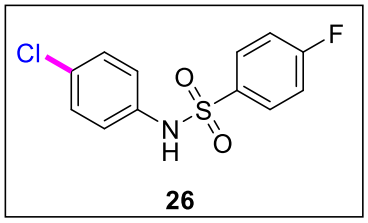
25

Compound 25 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **25** was obtained (18.7 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (ddt, *J* = 7.0, 5.0, 2.1 Hz, 1H), 7.56 (td, *J* = 7.3, 1.4 Hz, 1H), 7.49 – 7.41 (m, 1H), 7.23 – 7.16 (m, 1H), 7.03 (ddd, *J* = 8.8, 3.8, 2.1 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 138.6, 134.9, 133.3, 129.4, 129.2, 127.2, 123.1.

N-(4-Chlorophenyl)-4-fluorobenzenesulfonamide (26)[18]



26

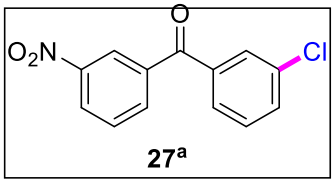
Compound 26 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **26** was obtained (20.0 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 1H), 7.25 – 7.18 (m, 1H), 7.13 (dd, *J* = 8.9, 8.2 Hz, 1H), 7.09 – 7.01 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 165.3 (d, *J* = 256.5 Hz), 134.7, 134.5 (d, *J* = 3.0 Hz), 131.4, 130.0 (d, *J* = 10.1 Hz), 129.5, 123.2, 116.5 (d, *J* = 2.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-103.70 (m, 1F).

(3-Chlorophenyl)(3-nitrophenyl)methanone(27^a)[16] and 3,3′-Dichlorobenzophenone (27^b)[19]

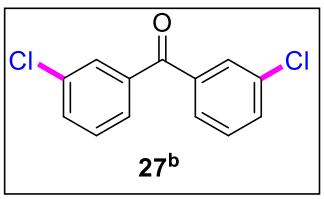


27^a

Compound 27^a and **27^b** was prepared according to the general procedure in about 72 h. After standard work-up and purification, **27^a** (13.1 mg, 50% yield) and **27^b** (5.0 mg, 20% yield) were obtained.

Compound 27^a ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (t, *J* = 1.9 Hz, 1H), 8.39 (ddd, *J* = 8.2, 2.3, 1.1 Hz, 1H), 8.05 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.71 (t, *J* = 1.9 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 7.61 – 7.53 (m, 2H), 7.41 (t, *J* = 7.9 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.8, 148.1, 138.4, 137.8, 135.3, 135.1, 133.3, 130.0, 129.8, 129.8, 128.0, 127.1, 124.6.

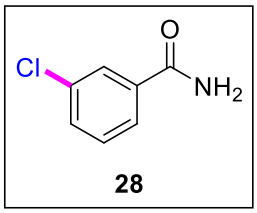


27^b

Compound 27^b ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (t, *J* = 1.9 Hz, 2H), 7.64 (dt, *J* = 7.7, 1.3 Hz, 2H), 7.58 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 2H), 7.44 (t, *J* = 7.9 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 193.8, 138.6, 134.8, 132.8, 129.8, 129.8, 128.0.

3-Chlorobenzamide (28)[1]



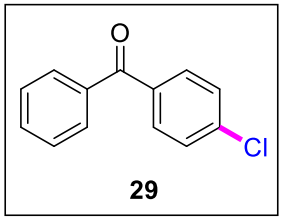
28

Compound 28 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **28** was obtained (7.8 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (t, *J* = 1.9 Hz, 1H), 7.69 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.51 (ddd, *J* = 8.0, 2.1, 1.1 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 134.9, 134.8, 132.2, 130.0, 127.7, 125.4.

4-Chlorobenzophenone (29)[9]



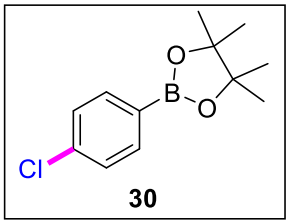
29

Compound 29 was prepared according to the general procedure in about 82 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **29** was obtained (15.6 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80 – 7.74 (m, 4H), 7.63 – 7.58 (m, 1H), 7.52 – 7.44 (m, 4H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.5, 138.9, 137.2, 135.8, 132.6, 131.4, 129.9, 128.6, 128.4.

4-Chlorophenylboronic acid pinacol ester (30)[20]



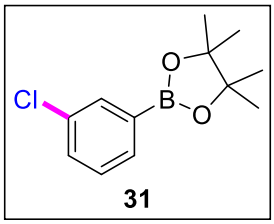
30

Compound 30 was prepared according to the general procedure in about 72 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **30** was obtained (14.3 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 – 7.61 (m, 2H), 7.31 – 7.22 (m, 2H), 1.26 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.5, 136.1, 128.0, 84.0, 24.8.

3-Chlorophenylboronic acid pinacol ester (31)[20]



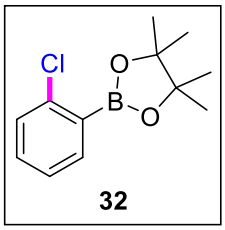
31

Compound 31 was prepared according to the general procedure in about 72 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **31** was obtained (13.1 mg, 55% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 2.3 Hz, 1H), 7.59 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.34 (ddd, *J* = 8.0, 2.3, 1.2 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 1.26 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.5, 134.0, 132.6, 131.2, 129.2, 84.1, 24.8.

2-Chlorophenylboronic acid pinacol ester (32)[20]

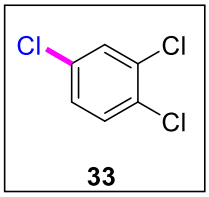


Compound 32 was prepared according to the general procedure in about 72 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **32** was obtained (14.7 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.25 (dd, *J* = 6.1, 1.9 Hz, 2H), 7.20 – 7.12 (m, 1H), 1.28 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 139.5, 136.4, 131.8, 129.3, 125.8, 84.1, 24.7.

1,2,4-Trichlorobenzene (33)[21]

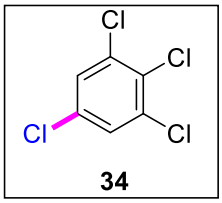


Compound 33 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **33** was obtained (11.8 mg, 65% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.4 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 133.0, 131.1, 130.3, 128.7, 128.0.

1,2,3,5-Tetrachlorobenzene (34)[21]

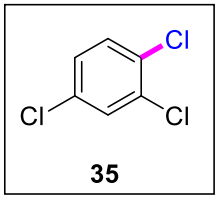


Compound 34 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **34** was obtained (15.1 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.8, 132.7, 130.3, 128.7.

1,2,4-Trichlorobenzene (35)[21]

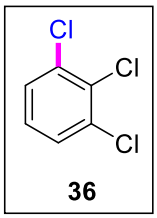


Compound 35 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **35** was obtained (13.6 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.4 Hz, 1H), 7.36 (d, *J* = 8.6 Hz, 1H), 7.18 (dd, *J* = 8.6, 2.4 Hz, 1H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.4, 133.0, 131.1, 130.3, 128.7, 128.0.

1,2,3-Trichlorobenzene (36)[22]



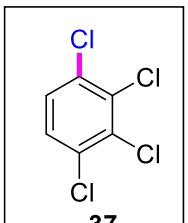
36

Compound 36 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **36** was obtained (19.8 mg, 66% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J* = 8.1 Hz, 2H), 7.14 (dd, *J* = 8.4, 7.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 134.3, 131.5, 128.7, 127.5.

1,2,3,4-Tetrachlorobenzene (37)[23]



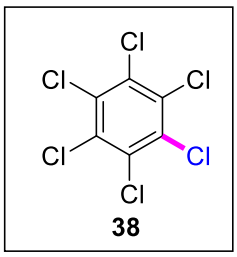
37

Compound 37 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **37** was obtained (17.3 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.1, 132.5, 128.4.

Hexachlorobenzene (38)

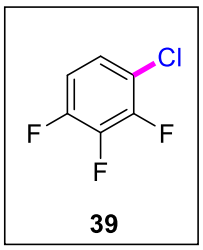


38

Compound 35 was prepared according to the general procedure in about 72 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **38** was obtained (11.4 mg, 40% yield).

^{13}C NMR (101 MHz, $CDCl_3$) δ 132.3.

1-Chloro-2,3,4-trifluorobenzene (39)[23]



39

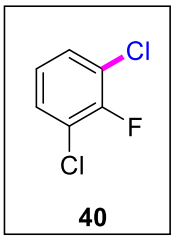
Compound 39 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **39** was obtained (14.2 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 1H), 6.95 (tdd, *J* = 9.4, 7.4, 2.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4-149.2 (m), 148.9-146.7 (m), 140.8 (dt, *J* = 255.5 Hz), 123.9 (dd, *J* = 7.1, 4.0 Hz), 177.8 (dd, *J* = 15.2, 4.0 Hz), 122.3 (dd, *J* = 19.2, 4.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-133.33 (m, 1F), -134.99 (m, 1F), -156.48 (m, 1F).

1,3-Dichloro-2-fluorobenzene (40)[24]



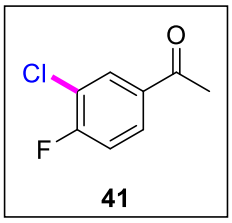
Compound 40 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **40** was obtained (11.6 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.03 (td, *J* = 8.1, 1.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.3 (d, *J* = 251.5 Hz), 129.0, 124.7 (d, *J* = 3.0 Hz), 122.5 (d, *J* = 18.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-115.76 (t, 1F).

1-(3-Chloro-4-fluorophenyl)ethanone (41)



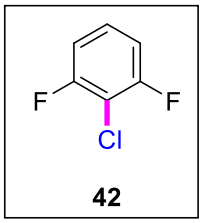
Compound 41 was prepared according to the general procedure in about 36 h. After standard work-up and purification, **41** was obtained (14.7 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (dt, *J* = 7.1, 1.6 Hz, 1H), 7.88 (ddd, *J* = 8.5, 4.6, 2.2 Hz, 1H), 7.25 (q, *J* = 8.6 Hz, 1H), 2.60 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 195.3, 161.0 (d, *J* = 258.6 Hz), 134.2 (d, *J* = 3.0 Hz), 131.2, 128.7 (d, *J* = 8.1 Hz), 121.8 (d, *J* = 18.2 Hz), 116.8 (d, *J* = 21.2 Hz), 26.5.

^{19}F NMR (376 MHz, $CDCl_3$) δ-107.67 (m, 1F).

2-Chloro-1,3-difluorobenzene (42)



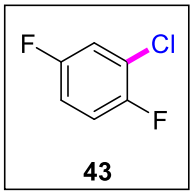
Compound 42 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **42** was obtained (12.2 mg, 82% yield).

^{1}H NMR (400 MHz, CDCl3) δ 7.25 – 7.17 (m, 1H), 7.02 – 6.94 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.1 (dd, J = 249.0, 3.0 Hz), 127.5 (t, J = 9.0 Hz), 112.0 (dt, J = 19.0, 3.0 Hz), 109.9 (d, J = 21.0 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -113.1 (2F).

2-Chloro-1,4-difluorobenzene (43)[25]



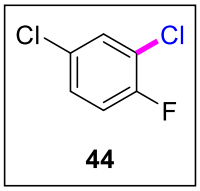
Compound 43 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **43** was obtained (12.3 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.07 (m, 2H), 6.95 (ddt, *J* = 9.1, 7.6, 3.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.4 - 156.9 (m), 155.9 - 153.5 (m), 121.7 (dd, J = 20.2, 11.1 Hz), 117.7 (d, J = 27.3 Hz), 117.1 (dd, J = 24.2, 9.1 Hz), 114.8 (dd, J = 24.2, 7.1 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-117.00 (m, 1F), -121.44 (m, 1F).

2,4-Dichlorofluorobenzene (44)[5]



44

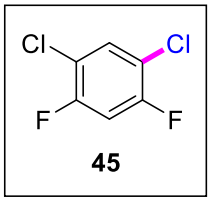
Compound 44 was prepared according to the general procedure in about 42 h. After standard work-up and purification, **44** was obtained (14.9 mg, 90% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (dd, *J* = 6.4, 2.6 Hz, 1H), 7.21 (ddd, *J* = 8.8, 4.1, 2.5 Hz, 1H), 7.08 (t, *J* = 8.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.0 (d, *J* = 250.5 Hz), 130.4, 129.5 (d, *J* = 4.0 Hz), 128.2 (d, *J* = 7.1 Hz), 122.0 (d, *J* = 19.2 Hz), 117.5 (d, *J* = 22.2 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-117.77 (m, 1F).

1,5-Dichloro-2,4-difluorobenzene (45)



45

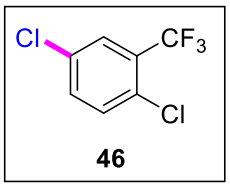
Compound 45 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **45** was obtained (13.2 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (t, *J* = 7.4 Hz, 1H), 7.02 (t, *J* = 8.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.7 (dd, *J* = 253.5, 11.1 Hz), 131.1, 117.1 (dd, *J* = 15.2, 8.1 Hz), 106.0(t, *J* = 26.3 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ-112.02 (t, 2F).

1,4-Dichloro-2-(trifluoromethyl)benzene (46)[26]



46

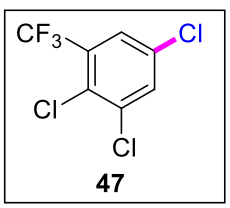
Compound 46 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **46** was obtained (13.3 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.46 (s, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 132.8, 132.6, 130.7 (q, *J* = 2.0 Hz), 129.8 (q, *J* = 32.3 Hz), 127.8 (q, *J* = 6.1 Hz), 122.1 (q, *J* = 277.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.18.

1,2,5-Trichloro-3-(trifluoromethyl)benzene (47)



47

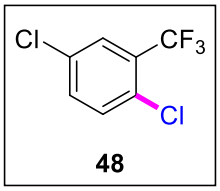
Compound 47 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **47** was obtained (21.2 mg, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (s, 1H), 7.67 – 7.60 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 137.1, 132.8, 131.6, 131.1, 129.1 (q, *J* = 6.0 Hz), 128.1 (d, *J* = 33.3 Hz), 121.8 (d, *J* = 274.7 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.84 (m, 3F).

1,4-Dichloro-2-(trifluoromethyl)benzene (48)[26]



48

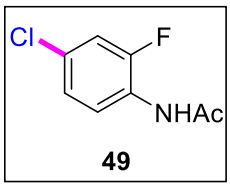
Compound 48 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **48** was obtained (10.8 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.46 (s, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 133.0, 132.8, 132.6, 130.7 (q, *J* = 2.0 Hz), 129.8 (q, *J* = 32.3 Hz), 127.8 (q, *J* = 6.1 Hz), 122.1 (q, *J* = 277.8 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -63.18.

N-(4-Chloro-2-fluorophenyl)acetamide (49)[27]



49

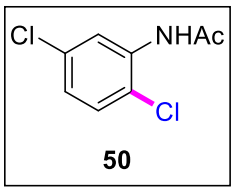
Compound 49 was prepared according to the general procedure in about 48 h. After standard work-up and purification,**49** was obtained (14.1 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (t, *J* = 8.5 Hz, 1H), 7.17 – 7.05 (m, 2H), 2.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 152.0 (d, *J* = 302.0 Hz), 126.9 (dd, *J* = 369.7, 10.1 Hz)126.9 (d, *J* = 369.7 Hz), 124.7 (d, *J* = 3.0 Hz), 122.5 (d, *J* = 2.0 Hz), 115.6 (d, *J* = 23.2 Hz), 24.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -128.46 (m, 1F).

N-(2,5-Dichlorophenyl)acetamide (50)[28]



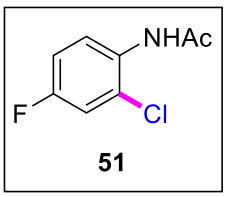
50

Compound 50 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **50** was obtained (16.3 mg, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (t, *J* = 2.8 Hz, 1H), 7.32 – 7.28 (m, 1H), 7.03 (dt, *J* = 8.7, 2.1 Hz, 1H), 2.26 (d, *J* = 1.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 135.3, 133.5, 129.5, 124.5, 121.3, 24.9.

N-(2-Chloro-4-fluorophenyl)acetamide (51)[29]



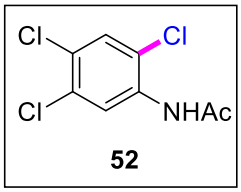
51

Compound 51 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **51** was obtained (16.5 mg, 88% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 9.2, 5.7 Hz, 1H), 7.11 (dd, *J* = 8.0, 2.9 Hz, 1H), 6.99 (ddd, *J* = 9.1, 7.8, 2.9 Hz, 1H), 2.22 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 158.4 (d, *J* = 247.5 Hz), 131.0(d, *J* = 3.0 Hz), 123.1 (d, *J* = 8.1 Hz), 116.2 (d, *J* = 26.3 Hz), 144.6 (d, *J* = 21.2 Hz), 24.6.
^{19}F NMR (376 MHz, $CDCl_3$) δ-116.28 (m, 1F).

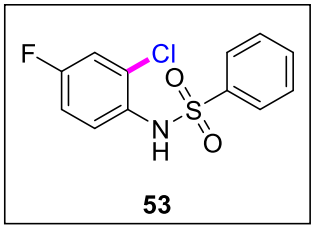
N-(2,4,5-Trichlorophenyl)acetamide (52)



52

Compound 52 was prepared according to the general procedure in about 60 h. After standard work-up and purification, **52** was obtained (17.2 mg, 72% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (s, 1H), 7.46 (s, 1H), 2.25 (s, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 168.2, 133.9, 131.9, 129.7, 122.3, 120.7, 24.9.

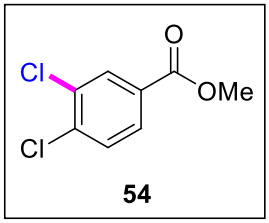
N-(2-Chloro-4-fluorophenyl)benzenesulfonamide (53)



53

Compound 53 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **53** was obtained (20.0 mg, 70% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.70 (m, 2H), 7.66 (dd, *J* = 9.9, 5.3 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.43 (t, *J* = 7.8 Hz, 2H), 6.99 (dd, *J* = 5.5, 2.5 Hz, 1H), 6.86 (s, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8 (d, *J* = 249.5 Hz), 138.6, 133.4, 129.6 (d, *J* = 3.0 Hz), 129.1, 127.2 (t, *J* = 5.1 Hz), 125.4 (d, *J* = 9.1 Hz), 116.6 (d, *J* = 26.3 Hz), 115.1 (d, *J* = 22.2 Hz).
^{19}F NMR (376 MHz, $CDCl_3$) δ -113.80 (m, 1F).

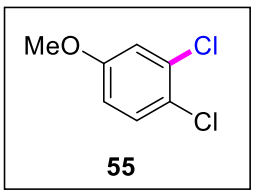
Benzoic acid, 3,4-dichloro-, methyl ester (54)[17]



54

Compound 54 was prepared according to the general procedure in about 48 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **54** was obtained (11.3 mg, 55% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (t, *J* = 2.1 Hz, 1H), 7.98 – 7.77 (m, 1H), 7.66 – 7.43 (m, 1H), 3.92 (d, *J* = 0.9 Hz, 3H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 165.2, 137.6, 132.9, 131.5, 130.5, 129.9, 128.6, 52.5.

1,2-Dichloro-4-methoxybenzene (55)[9]

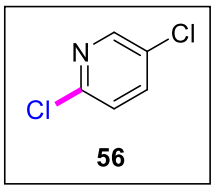


55

Compound 55 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **55** was obtained (5.3 mg, 30% yield).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.9 Hz, 1H), 6.99 (d, *J* = 2.9 Hz, 1H), 6.75 (dd, *J* = 8.9, 2.9 Hz, 1H), 3.79 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 158.6, 132.8, 130.6, 123.9, 115.7, 114.1, 55.7.

2,5-Dichloropyridine (56)[30]



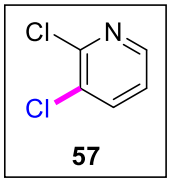
56

Compound 56 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **56** was obtained (10.1 mg, 68% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (d, *J* = 2.5 Hz, 1H), 7.55 (dd, *J* = 8.5, 2.6 Hz, 1H), 7.21 (d, *J* = 8.5 Hz, 1H)

^{13}C NMR (151 MHz, $CDCl_3$) δ 149.4, 148.4, 138.4, 130.9, 125.1.

2,3-Dichloropyridine (57)[31]



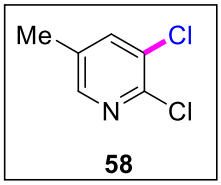
57

Compound 57 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **57** was obtained (8.9 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dq, *J* = 4.2, 1.8 Hz, 1H), 7.77 (dq, *J* = 8.0, 1.6 Hz, 1H), 7.32 – 7.12 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 149.2, 147.2, 138.7, 130.6, 123.2.

2,3-Dichloro-5-methylpyridine (58)



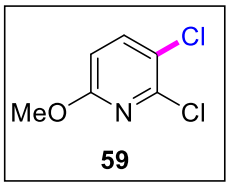
58

Compound 58 was prepared according to the general procedure in about 82 h, during which 1 equiv. of $FeCl_3$ (16.3 mg) was used. After standard work-up and purification, **58** was obtained (8.1 mg, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 – 8.01 (m, 1H), 7.59 (dt, *J* = 1.5, 0.7 Hz, 1H), 2.31 (d, *J* = 0.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 147.5, 146.2, 139.3, 133.7, 129.8, 77.3.

2,3-Dichloro-6-methoxypyridine (59)[32]



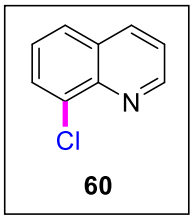
59

Compound 59 was prepared according to the general procedure in about 72 h. After standard work-up and purification, **59** was obtained (11.2 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.6, 0.9 Hz, 1H), 6.64 (dd, *J* = 8.5, 0.9 Hz, 1H), 3.92 (d, *J* = 0.9 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.8, 145.5, 140.8, 121.5, 110.6, 54.4.

8-Chloroquinoline (60)[33]

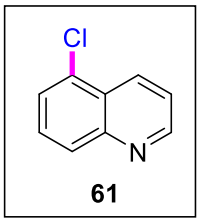


Compound 60 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **60** was obtained (11.5 mg, 70% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (dd, *J* = 4.2, 1.5 Hz, 1H), 8.05 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.72 (d, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.29 (m, 2H)

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.7, 144.0, 136.3, 133.0, 129.3, 129.3, 126.8, 126.2, 121.6.

5-Chloroquinoline (61)[34]

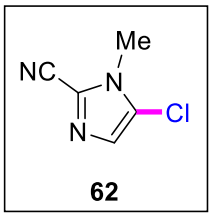


Compound 61 was prepared according to the general procedure in about 82 h. After standard work-up and purification, **61** was obtained (13.6 mg, 83% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (d, *J* = 4.0 Hz, 1H), 8.44 (d, *J* = 8.5 Hz, 1H), 7.94 (dd, *J* = 5.6, 3.9 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.37 (dd, *J* = 8.5, 4.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 148.6, 132.8, 131.2, 129.1, 128.5, 126.5, 126.2, 121.8.

5-Chloro-1-methyl-1*H*-imidazole-2-carbonitrile (62)



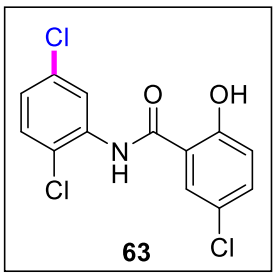
Compound 62 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **62** was obtained (6.9 mg, 49% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (s, 1H), 3.78 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 128.6, 122.5, 121.6, 110.4, 32.1.

HRMS (ESI) m/z calcd for $C_5H_5ClN_3Na$ [M + Na^+] 142.0167, found 142.0159.

5-Chloro-*N*-(2,5-dichlorophenyl)-2-hydroxybenzamide (63)[35]



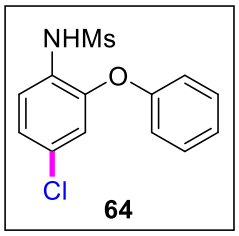
Compound 63 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **63** was obtained (16.1 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.7 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.26 (s, 1H), 7.25 – 7.22 (m, 1H), 7.09 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.04 – 7.01 (m, 2H), 6.84 – 6.79 (m, 2H), 3.01 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 155.0, 148.3, 130.8, 130.4, 126.4, 125.1, 124.0, 122.6, 119.2, 117.8, 39.6.

HRMS (ESI) m/z calcd for $C_{13}H_8Cl_3NO_2Na$ [M + Na^+] 337.9513, found 337.9508.

N-(4-chloro-2-phenoxyphenyl)methanesulfonamide (64)



64

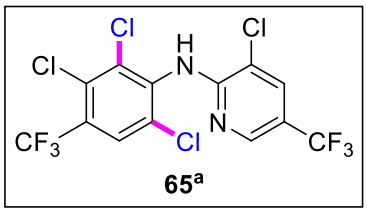
Compound 64 was prepared according to the general procedure in about 48 h. After standard work-up and purification, **64** was obtained (15.4 mg, 52% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (dd, *J* = 8.9, 1.3 Hz, 1H), 7.44 (d, *J* = 2.4 Hz, 1H), 7.41 (d, *J* = 2.3 Hz, 1H), 7.36 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.27 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.19 (s, 2H), 6.94 (dd, *J* = 8.9, 1.3 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 167.0, 160.4, 135.1, 132.1, 130.5, 129.1, 128.1, 125.1, 124.6, 124.1, 123.1, 120.7, 115.3.

HRMS (ESI) m/z calcd for $C_{13}H_{12}ClNO_3SNa$ [M + Na^+] 320.0119, found 320.0126.

3-Chloro-N-(2,3,6-trichloro-4-(trifluoromethyl)phenyl)-5-(trifluoromethyl)pyridin-2-amine (65)



65^{a}

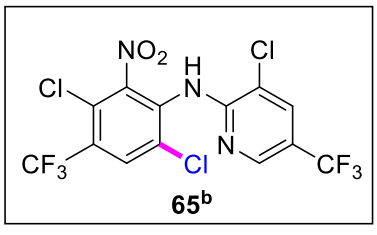
Compound 65^{a} was prepared according to the general procedure in about 48 h. After standard work-up and purification, **65^{a}** (8.8 mg, 20% yield), **65^{b}** (11.3 mg, 25% yield) and **65^{c}** (18.2 mg, 40% yield) were obtained.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (dd, *J* = 2.1, 1.1 Hz, 1H), 7.88 (d, *J* = 2.1 Hz, 1H), 7.80 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 143.5 (q, *J* = 4.0 Hz), 136.4 (d, *J* = 345.4 Hz), 134.3 (q, *J* = 3.0 Hz), 131.5, 130.7, 128.4 (d, *J* = 33.3 Hz), 126.7 (q, *J* = 6.1 Hz), 123.8 (d, *J* = 137.4 Hz), 121.1 (d, *J* = 140.4 Hz), 120.3, 119.9, 116.6.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.48, -62.97.

HRMS (ESI) m/z calcd for $C_{13}H_4Cl_4F_6N_2O_2Na$ [M + Na^+] 464.8925, found 464.8918.



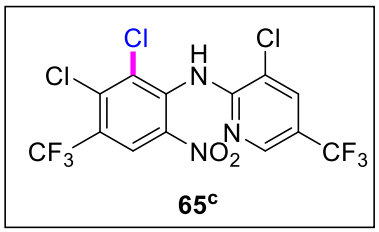
65^{b}

Compound 65^{b} ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (s, 1H), 8.27 (dd, *J* = 2.1, 1.0 Hz, 1H), 8.21 (s, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 150.8, 142.8 (q, *J* = 4.0 Hz), 139.1 (d, *J* = 410.1 Hz), 134.9 (q, *J* = 3.0 Hz), 134.3, 131.5, 125.3 (d, *J* = 34.3 Hz), 123.5 (d, *J* = 126.3 Hz), 122.6 (q, *J* = 4.0 Hz), 122.0, 121.5 (d, *J* = 25.3 Hz), 120.1, 118.0.

^{19}F NMR (376 MHz, $CDCl_3$) δ -61.68, -62.86.

HRMS (ESI) m/z calcd for $C_{13}H_4Cl_3F_6N_3O_2Na$ [M + Na^+] 475.9165, found 475.9158.



65c

Compound 65c ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 2.1, 1.0 Hz, 1H), 7.98 (s, 1H), 7.87 (d, *J* = 2.1 Hz, 1H).
^{13}C NMR (101 MHz, $CDCl_3$) δ 152.1, 143.3 (q, *J* = 4.0 Hz), 134.7 (q, *J* = 4.0 Hz), 133.2, 132.2, 130.0 (q, *J* = 5.1 Hz), 128.4 (d, *J* = 33.3 Hz), 124.1 (d, *J* = 24.2 Hz), 122.1 (d, *J* = 115.1 Hz), 121.3, 120.9, 119.9, 116.7.
^{19}F NMR (376 MHz, $CDCl_3$) δ -61.59, -62.54.
HRMS (ESI) m/z calcd for $C_{13}H_4Cl_3F_6N_3O_2Na$ [M + Na^+] 475.9165, found 475.9168.

3.7 Gram-Scale of the denitrative chlorination reaction.

The 4-nitrochloroarene (1.57 g, 10 mmol), $MgCl_2$ (1.90 g, 20 mmol, 2 equiv.), 4A MS (2.0 g) was dissolved in MeCN (90 mL) in a quartz tube, 10 mL of $FeCl_3$/MeCN (163 mg, 1 mmol, 10 mol%) was added to the reaction mixture, which was then stirred at room temperature with the irradiation under 390-400 nm light (two of 10 W LED , 2 cm distance from the light), the reaction system was cooling with fan, which is shown as below. The process of the reaction was monitored by GC-MS (about 48 h). Upon completion, the solution was transferred to a random flask and was removed under vacuum and the residue was purified by silica gel chromatography with n-pentane as mobile phase to afford the desired 1,4-dichloroarene (1.17 g, 80% yield) as white solid.

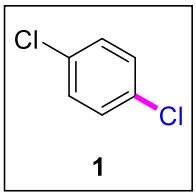
4. References

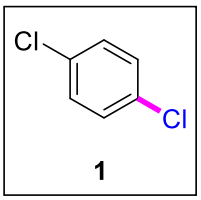
[1] G. A. Molander, L. N. Cavalcanti, *J. Org Chem.* **2011**, *76*, 7195–7203.

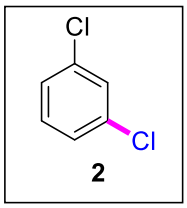
[2] R. Mészáros, S. B. Ötvös, *Green Chem.* **2021**, *23*, 4685–4696.
[3] X. Min, Q Chen, *J. Am. Chem. Soc.* **2022**, *144*, 11081−11087.
[4] S. D. Schimler, M. S. Sanford, *J. Am. Chem. Soc.* **2017**, *139*, 1452−1455.
[5] Z. Yu, W. Su, *Tetrahedron Lett*. **2013**, *54*, 1261–1263.
[6] Y. Li, C. Duan, *Synlett.* **2011**, *12*, 1713–1716.
[7] W. Zheng, C. A. Morales-Rivera, J. W. Lee, P. Liu, M.-Y. Ngai, *Angew. Chem. Int. Ed.* **2018**, *57*, 9645–9649.
[8] W. Zheng, M. Ngai, *Angew. Chem. Int. Ed.* **2018**, *57*, 13795–13799.
[9] R. Hernandez-Ruiz, S. Gomez-Gil, M. R. Pedrosa, S. Suarez-Pantiga, S. Roberto, *Org. Biomol. Chem*. **2023**, *21*, 7791–7798.
[10] Y.-F. Wang, Y.-R. Gao, S. Mao, Y.-L. Zhang, D.-D. Guo, Z.-L. Yan, S.-H. Guo, Y.-Q. Wang, *Org. Lett.* **2014**, *16*, 1610–1613.
[11] S. Josef, S. Düsel, B. König, *Eur. J. Org. Chem.* **2020**, 1491–1495.
[12] X. Wan, Z. Ma, B. Li, K. Zhang, S. Cao, S. Zhang, Z. Shi, *J. Am. Chem. Soc.* **2006**, *128*, 7416–7417.
[13] N. B. Kilimciler, N. M. Palavecino, N. Gruber, D. R. Vega, L. R. Orelli, J. E. Díaz, *J. Org. Chem.* **2023**, doi/10.1021/acs.joc.2c02558
https://pubs.acs.org/doi/10.1021/acs.joc.2c02558
[14] S. K. Nayak, M. K. Reddy, T. N. G. Row, D. Chopra, *Cryst. Growth Des*. **2011**, *11*, 1578–1596.
[15] Y.-C. Teo, F.-F. Yong, I. K. Ithnin, S.-H. T.Yio, Z. Lin, *Eur. J. Org. Chem*. **2013**, 515–524.
[16] M. S. Crocker, Z. Deng, J. N. Johnston, *J. Am. Chem. Soc.* **2022**, *144*, 16708–16714.
[17] W. Zhang, J. Xie, B. Rao, M. Luo, *J. Org. Chem.* **2015**, *80*, 3504–3511.
[18] S. Kikkawa, M. Okayasu, H. Hikawa, I. Azumaya, *Cryst. Growth Des*. **2021**, *21*, 1148–1158.
[19] L. Yang, T. Zeng, Q. Shuai, X. Guo, C.-J. Li, *Chem. Commun*. **2011**, *47*, 2161–2163.
[20] L. Candish, M. Teders, F. Glorius, *J. Am. Chem. Soc.* **2017**, *139*,7440-7443.
[21] L. Sharp-Bucknall, M. Sceney, K. F. White, J. L. Dutton, *Dalton Trans*. **2023**, *52*, 3358–3370.
[22] V. A. Kallepalli, M. R. Smith, *J. Org. Chem*. **2015**, *80*, 8341−8353.
[23] W. Wang, X. Yang, R. Dai, Z. Yan, J. Wei, X. Dou, X. Qiu, H. Zhang, C. Wang, Y. Liu, S. Song, N. Jiao, J. Am. Chem. Soc. **2022**, *144*, 13415–13425.
[24] S. Yamada, P. Knochel, *Angew. Chem. Int. Ed.* **2010**, *49*, 2215–2218.
[25] H. Zhang, J. Wu, X. Zhang, M. Fan, *J. Org. Chem*. **2023**, *88*, 12826–12834.
[26] J. Qi, J. Xu, H. T. Ang, B. Wang, N. K. Gupta, S. R. Dubbaka, P. O., X. Mao, Y. Lum, J. Wu, *J. Am. Chem. Soc*. **2023**, *145*, 24965–24971.
[27] L. Jin, X. Zeng, S. Li, G. Qiu, P. Liu, *Eur. J. Org. Chem.* **2022**, e202200399.
[28] S. Strekalova, A. Kononov, V. Morozov, O. Babaeva, E. Gavrilova, Y. Budnikova, *Adv. Synth. Catal.* **2023**, *365*, 3375–3381.
[29] F. Liu, N. Wu, X. Cheng, *Org. Lett*. **2021**, 23, 3015−3020.
[30] X. Feng, Y. Qu, Y. Han, X. Yu, M. Bao, Y. Yamamoto, *Chem. Commun*. **2012**, *48*,

9468–9470.
[31] X. Zhang, X. Feng, H. Zhang, Y. Yamamoto, M. Bao, *Green Chem*. **2019**, 21, 5565–5570.
[32] B. Bartels, P. Cueni, D. Muri, M. Koerner, *Bioorg. Med. Chem*. **2018**, *26*, 970–976.
[33] C. Wang, D. M. Flanigan, L. N. Zakharov, P. R. Blakemore, *Org. Lett*. **2011**, *13*, 4024–4027.
[34] A. L. Ware, S. S. Pekamwar, *Indo Am. J. Pharm. Res*. **2019**, *9*, 3040–3043.
[35] R. A. Mook, J. Wang, X.-R. Ren, M. Chen, I. Spasojevic, L. S. Barak, H. K. Lyerly, W. Chen, *Bioorg. Med. Chem*. **2015**, *23*, 5829–5838.

5. ^{1}H NMR and ^{13}C NMR Spectra of the Products.



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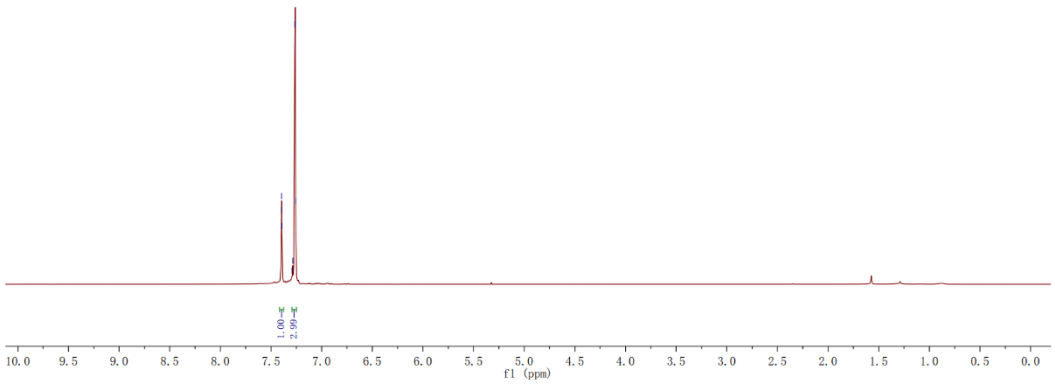
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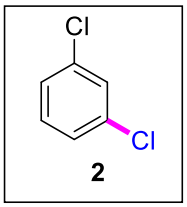
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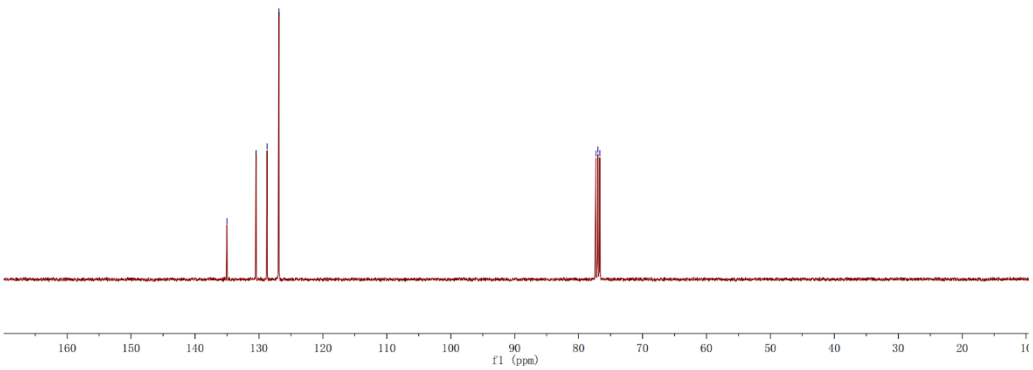
76.68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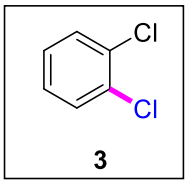
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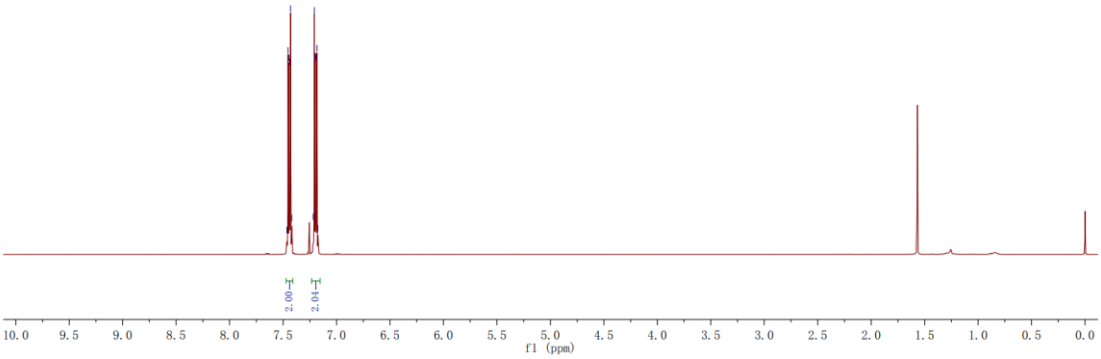
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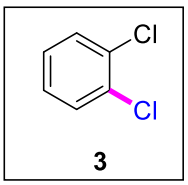
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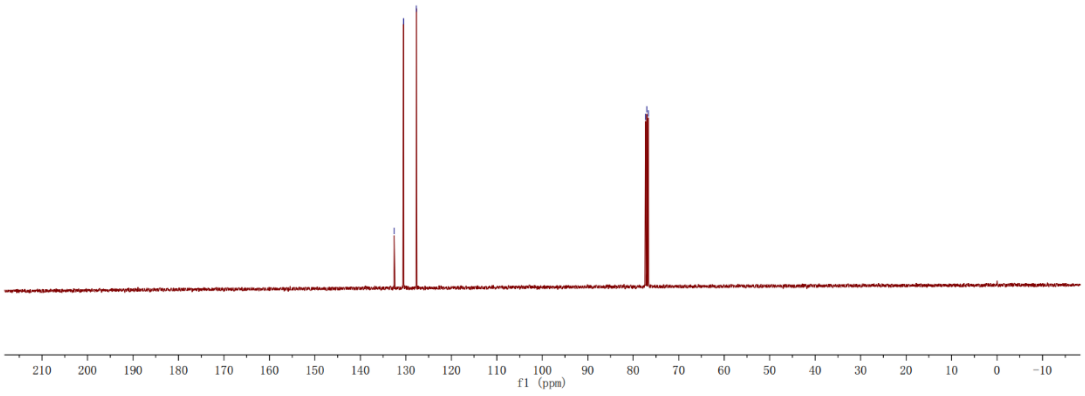
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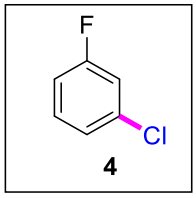
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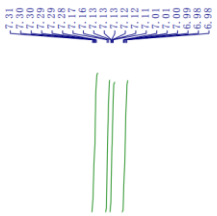
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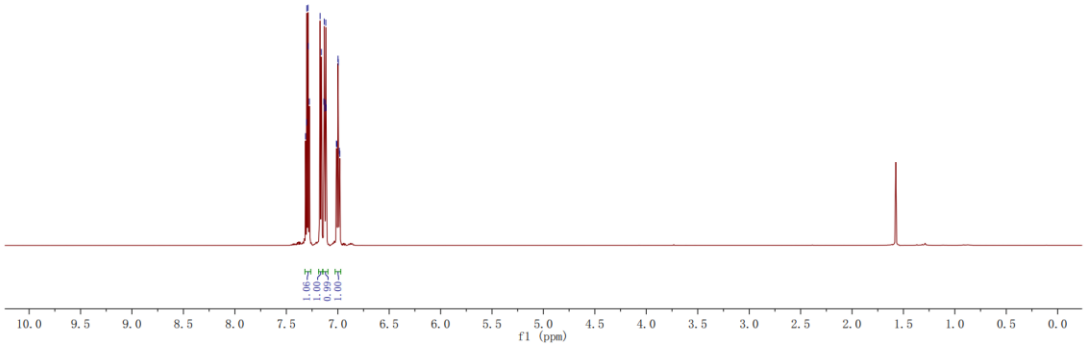
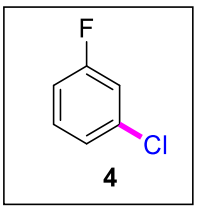
6.98
6.98

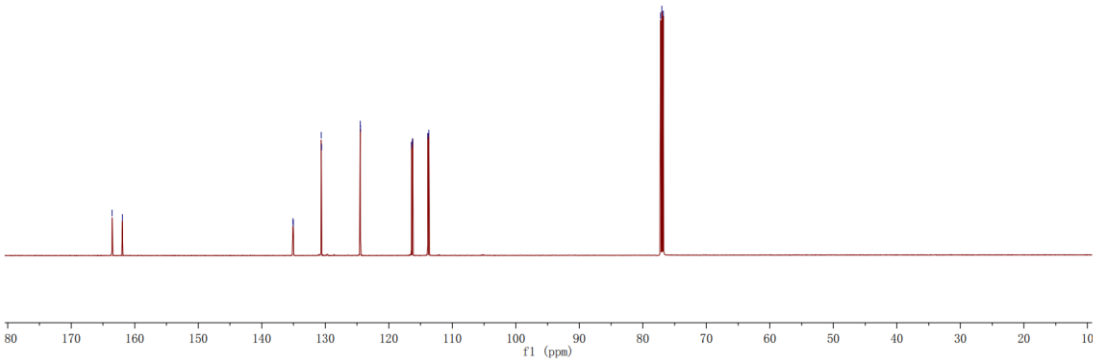

1.06
1.09
0.99
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

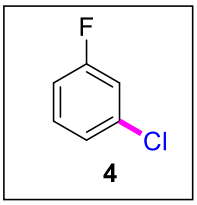

163.57
161.91

135.09
135.02
130.64
130.58
124.50
124.48
116.41
116.25
113.84
113.76


77.21
77.00
76.79


F
Cl
4

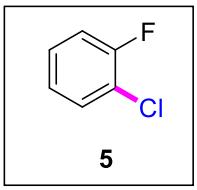

80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


F
Cl

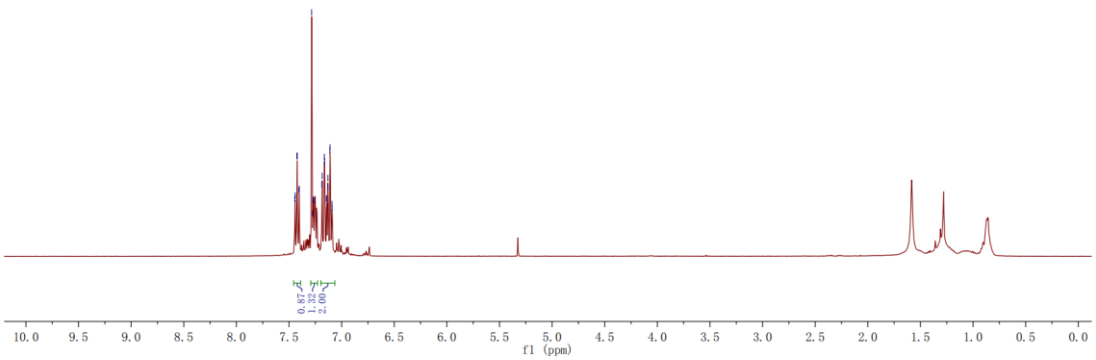
4

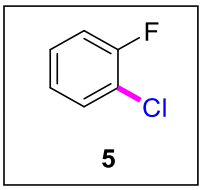
-110.92
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)


7.45
7.44
7.43
7.42
7.41
7.40
7.29
7.28
7.27
7.19
7.18
7.16
7.15
7.14
7.13
7.11
7.10
7.09


F
Cl

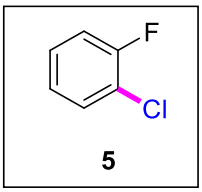
5


0.87
1.32
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
Cl

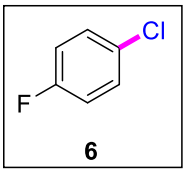
5

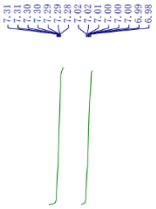
130.70
128.15
128.08
124.84
124.80
116.74
116.53
77.32
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

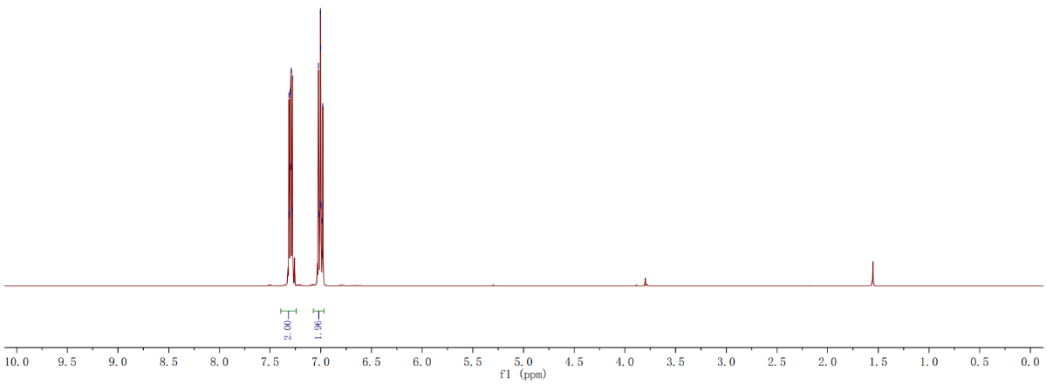

F
Cl

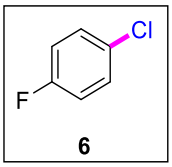
5

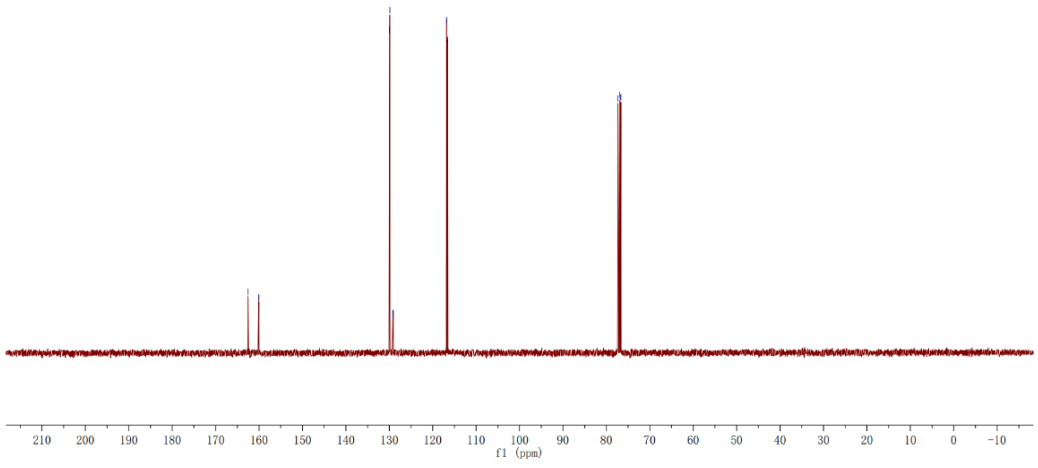
-115.45
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165 -170 -175 -180 -185 -190 -195
f1 (ppm)

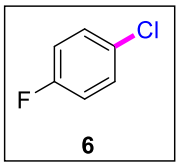

Cl
F
6

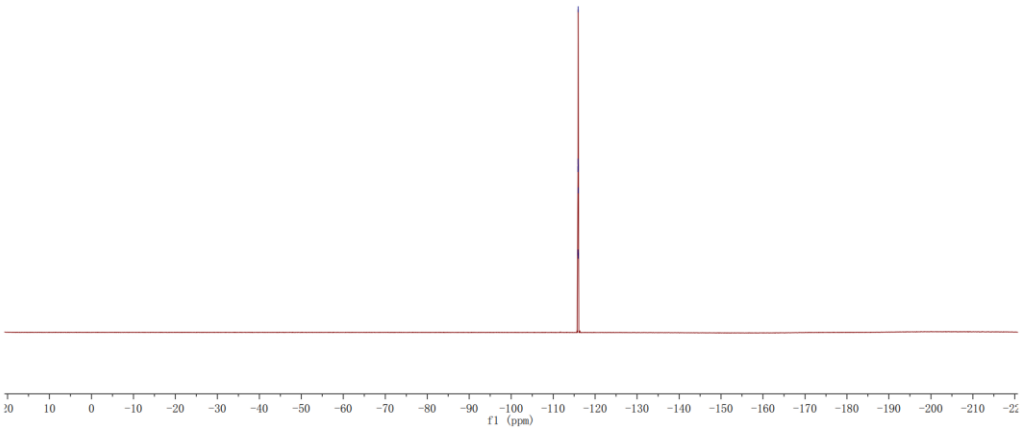


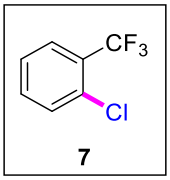

2.00
1.96
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

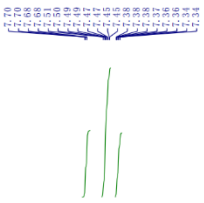

Cl
F
6

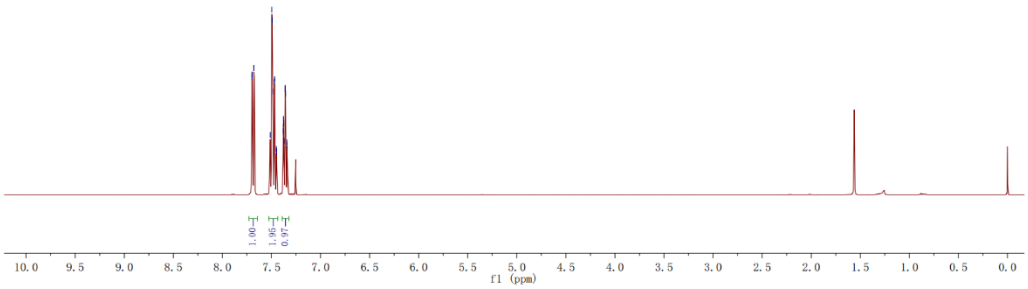

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

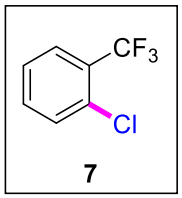

Cl
F
6


f1 (ppm)

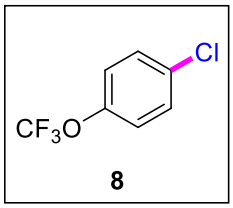

CF3
Cl
7



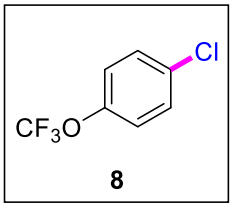

1.00
1.95
0.97
f1 (ppm)



7

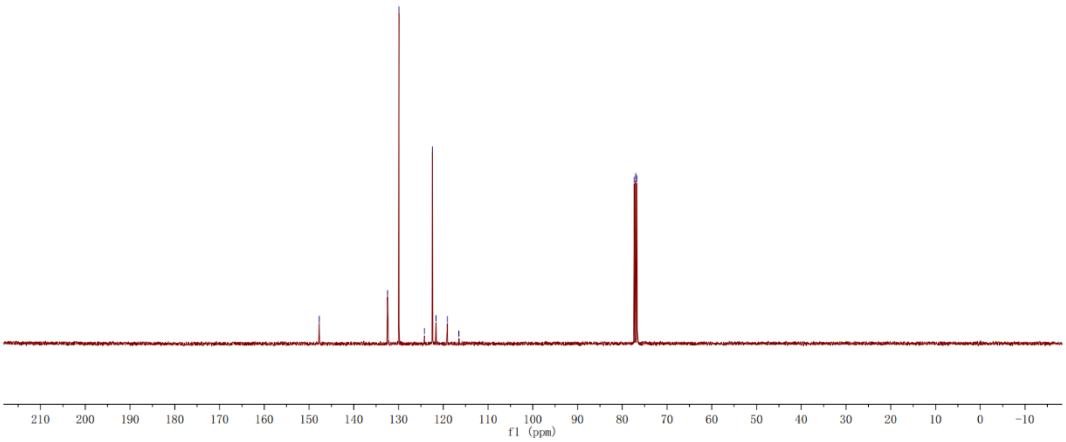


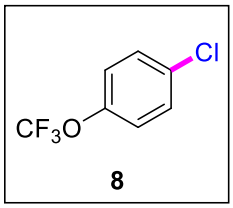
8


Cl
CF3O

8

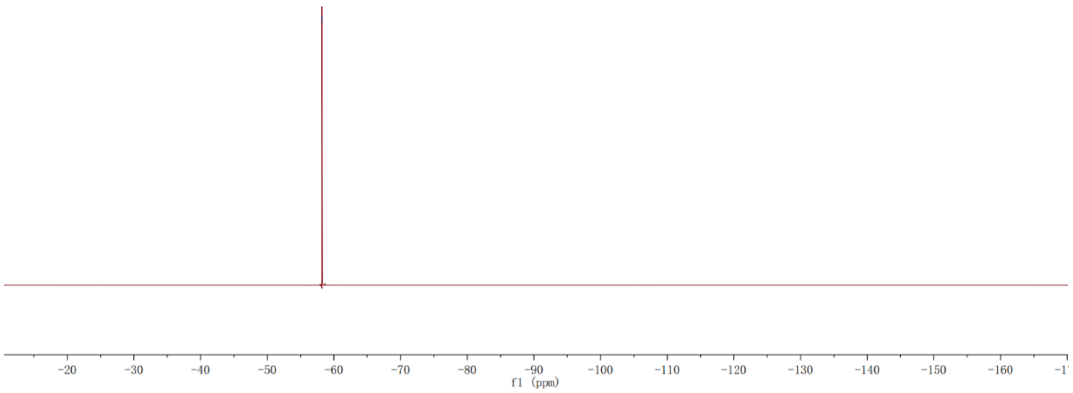

147.71
147.69
132.46
129.90
123.20
122.38
121.64
119.08
116.51
77.32
77.00
76.68

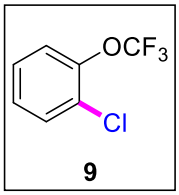

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

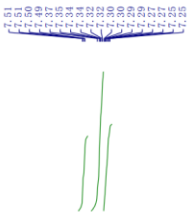

Cl
CF3O

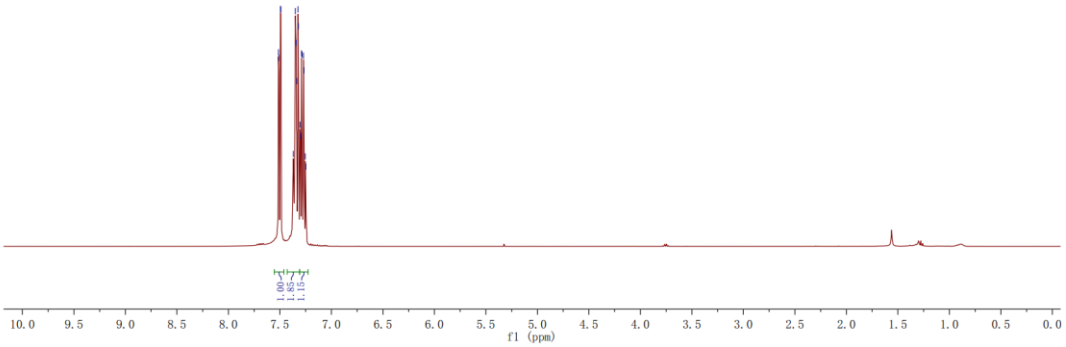
8

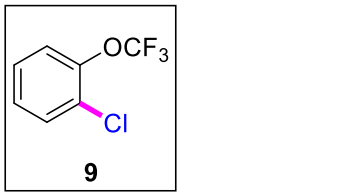
-58.20

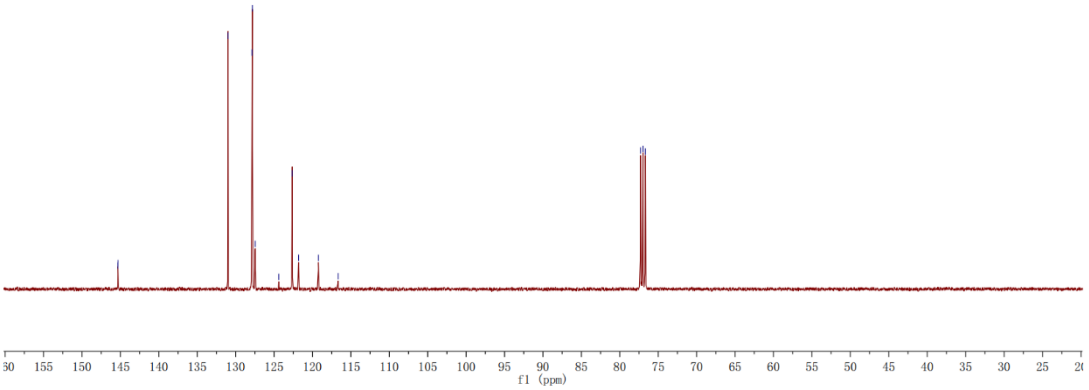

-20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

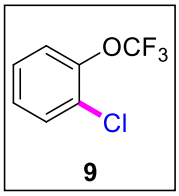

OCF3
Cl
9




10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

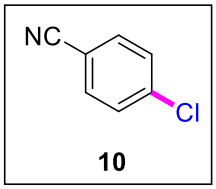

OCF3
Cl
9


f1 (ppm)

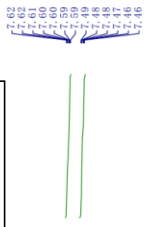

OCF3
Cl

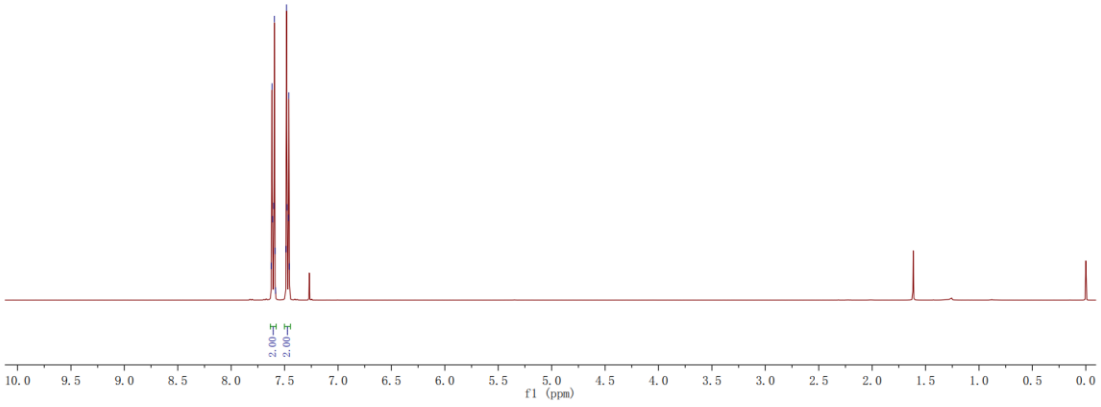
9

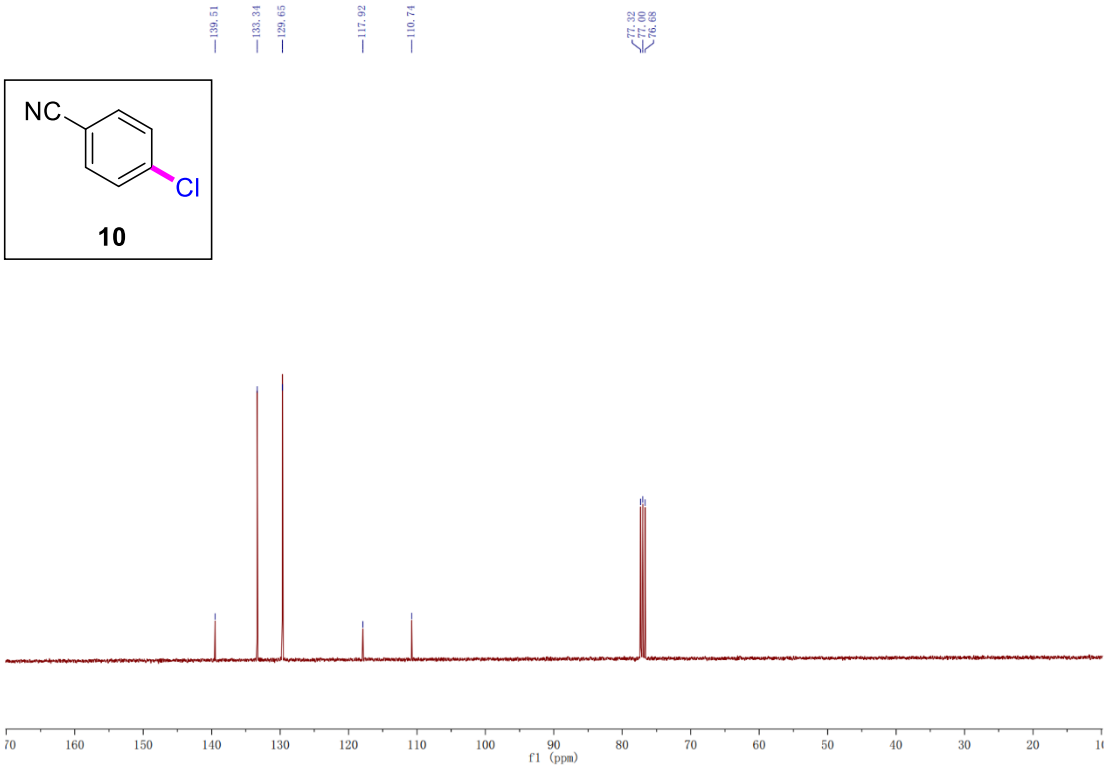
-57.91
25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

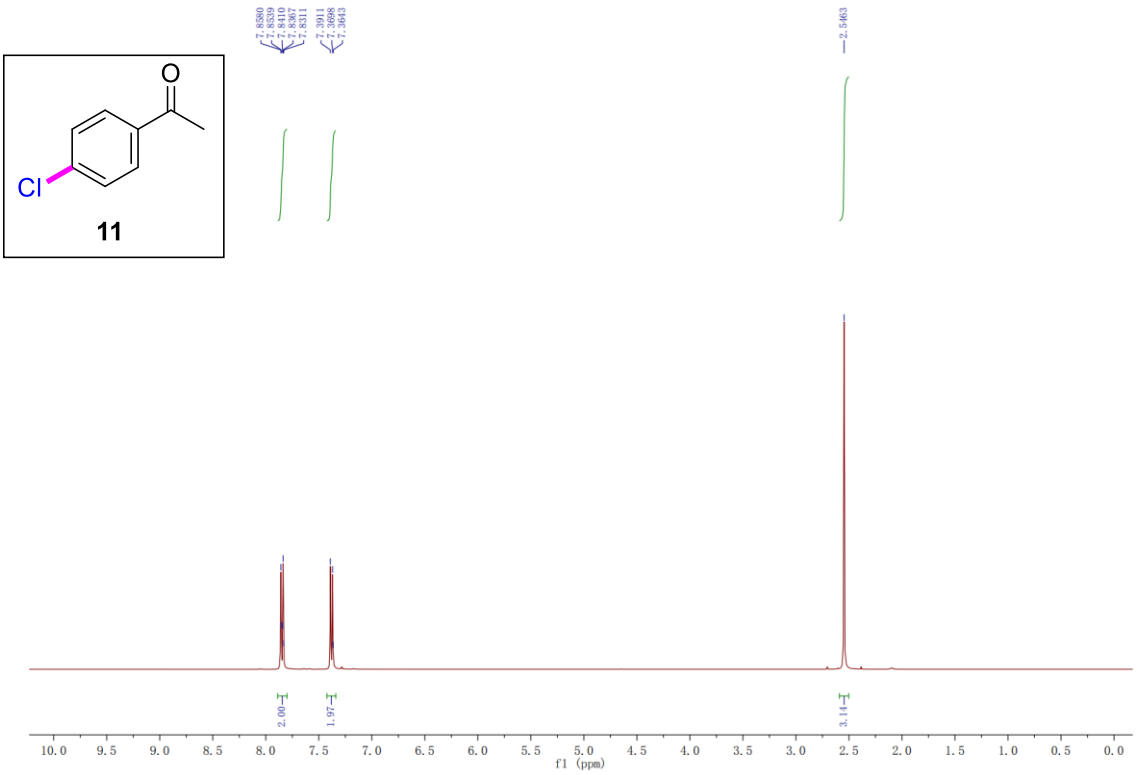

NC
Cl

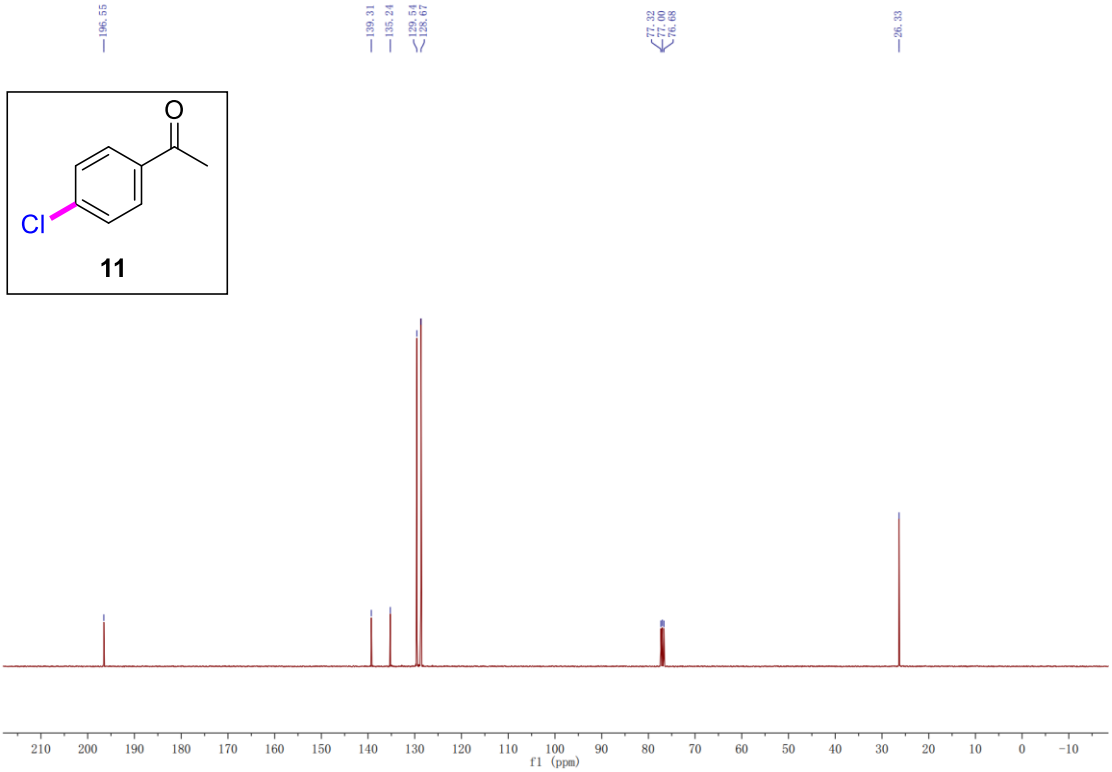
10

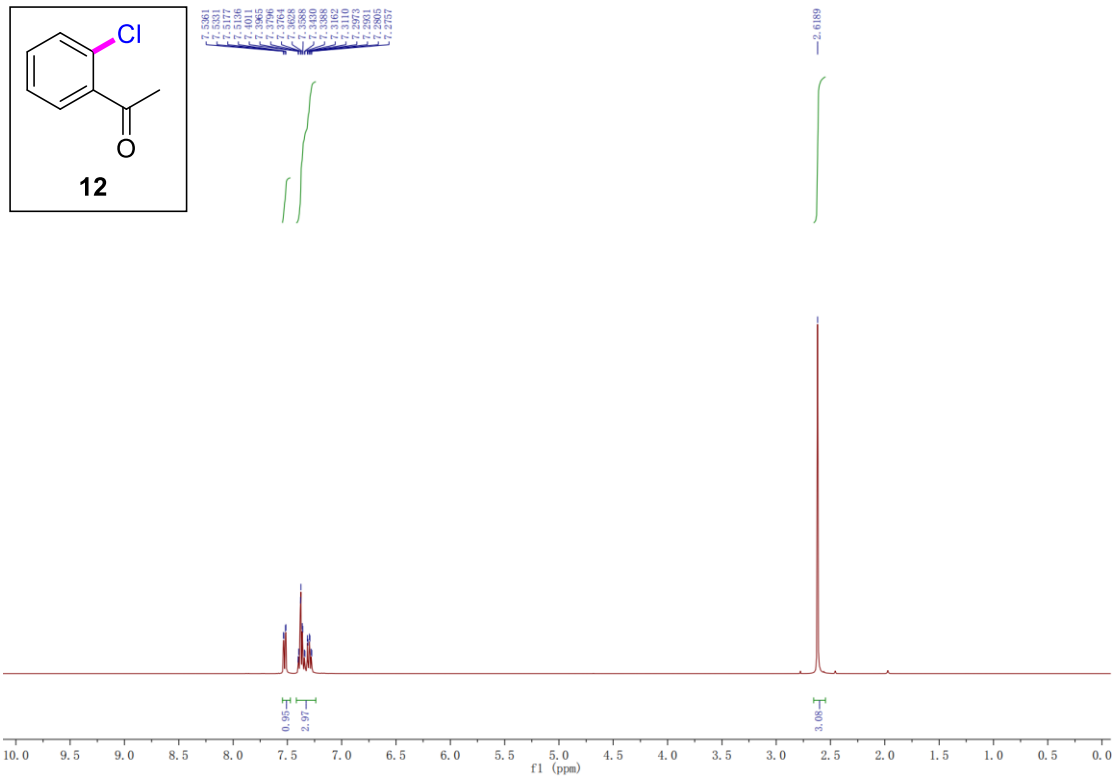


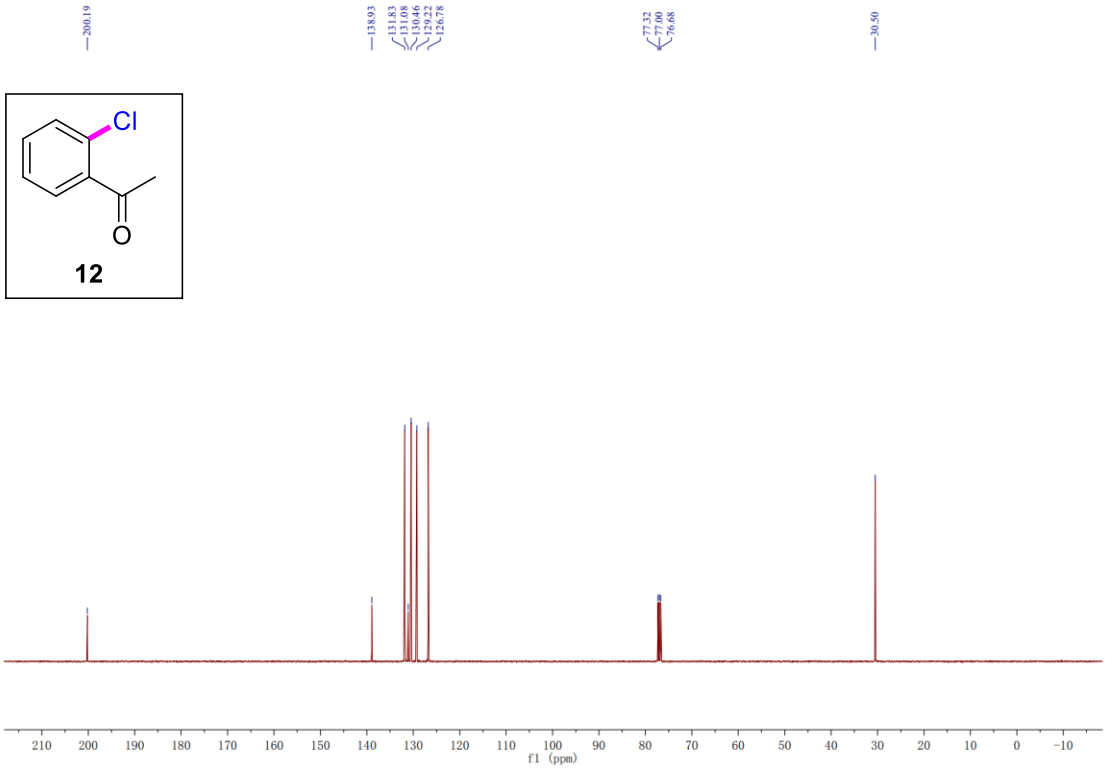

2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

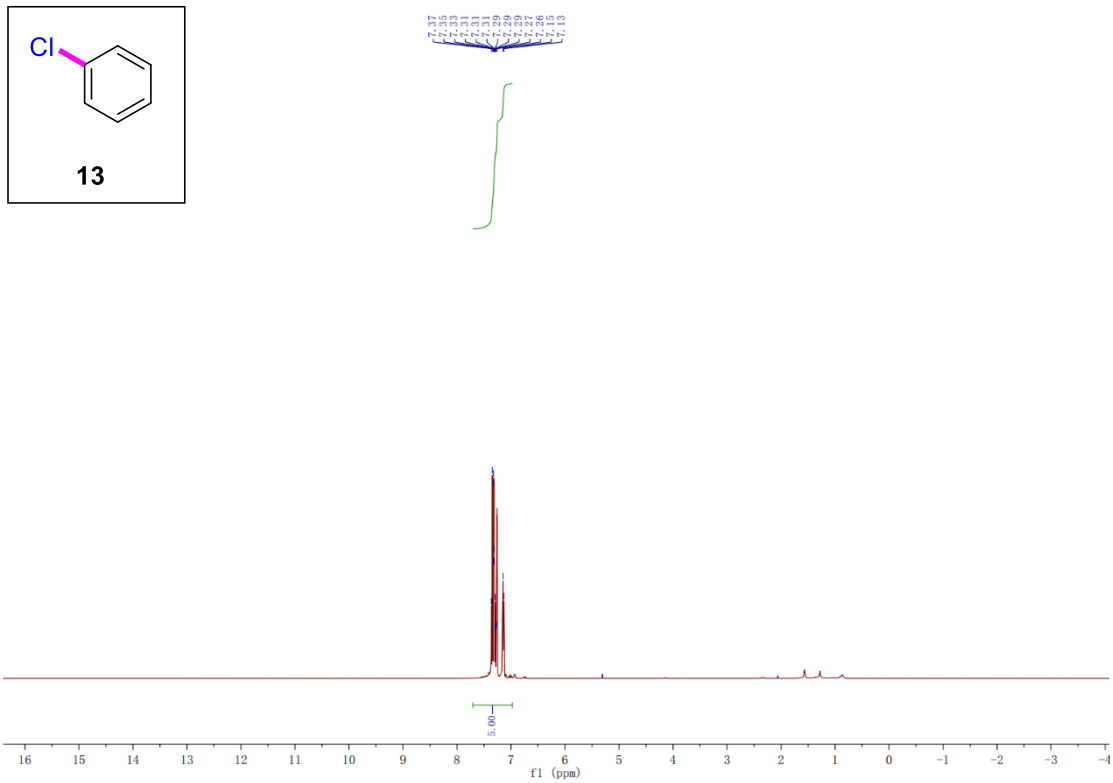

139.51
133.34
129.65
117.92
110.74
77.32
77.00
76.68
NC
Cl
10
f1 (ppm)

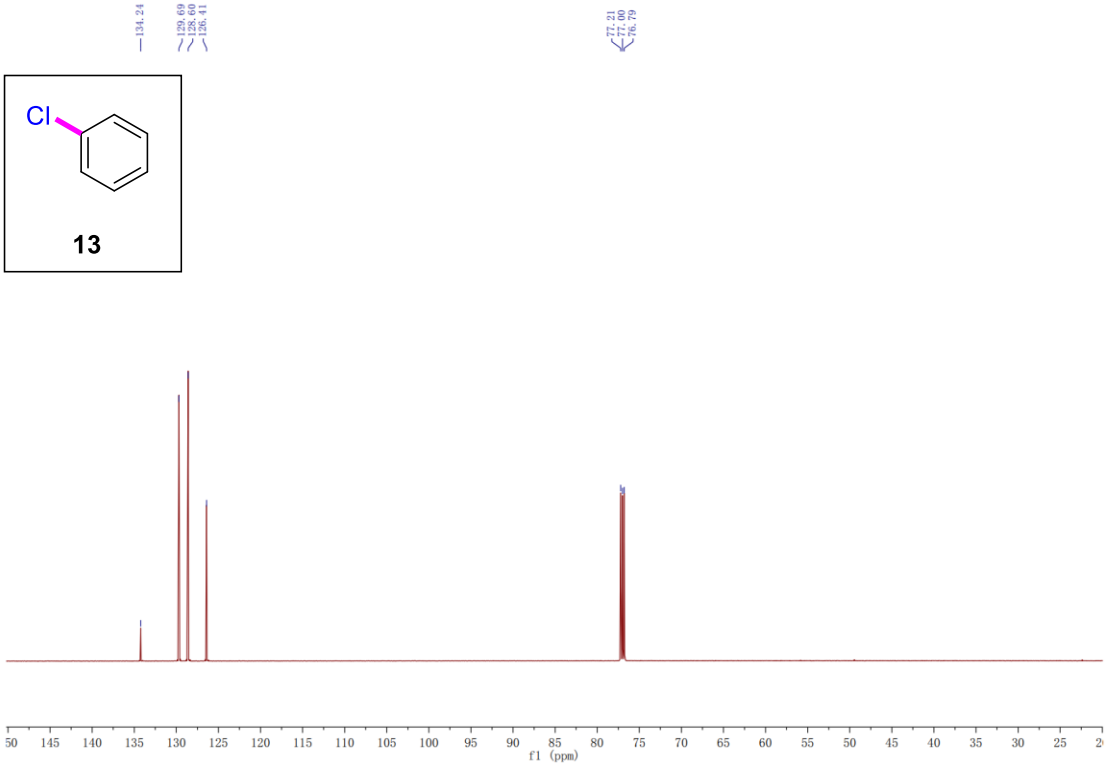

7.8380
7.8339
7.8410
7.8387
7.8311
7.3911
7.3698
7.3643
2.5463
O
Cl
11
2.60
1.97
3.14
f1 (ppm)

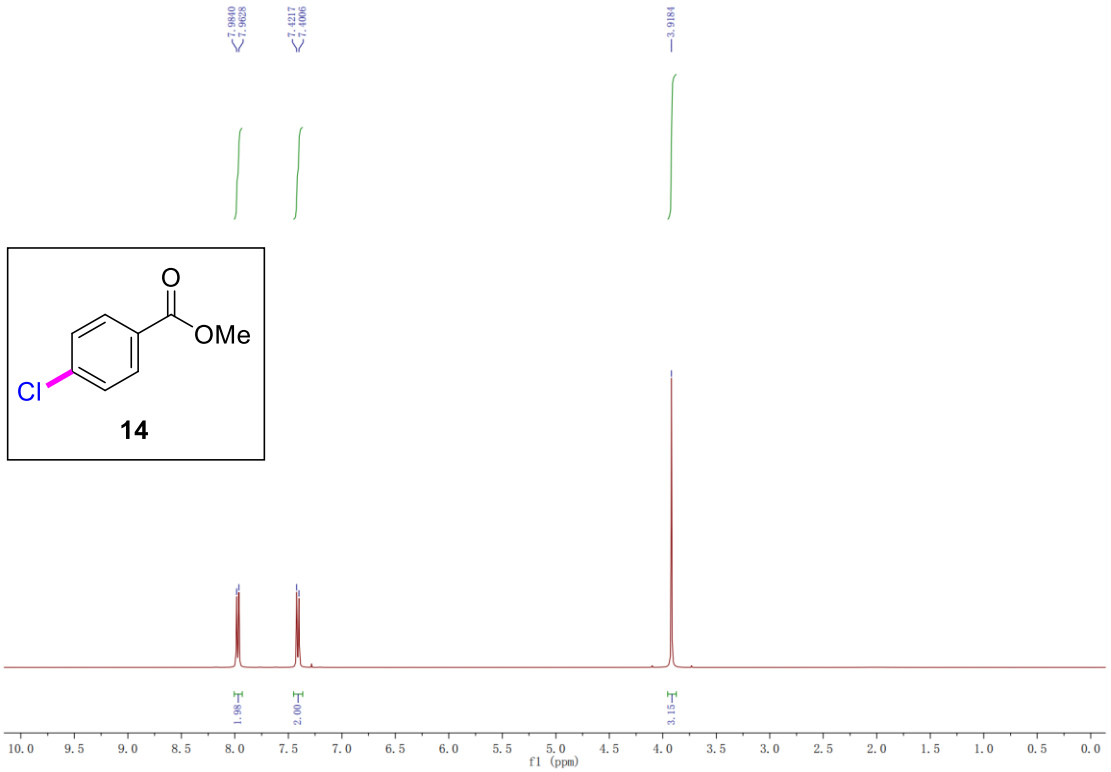

196.55
139.31
135.24
129.54
128.67
77.32
77.00
76.68
26.33
O
Cl
11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

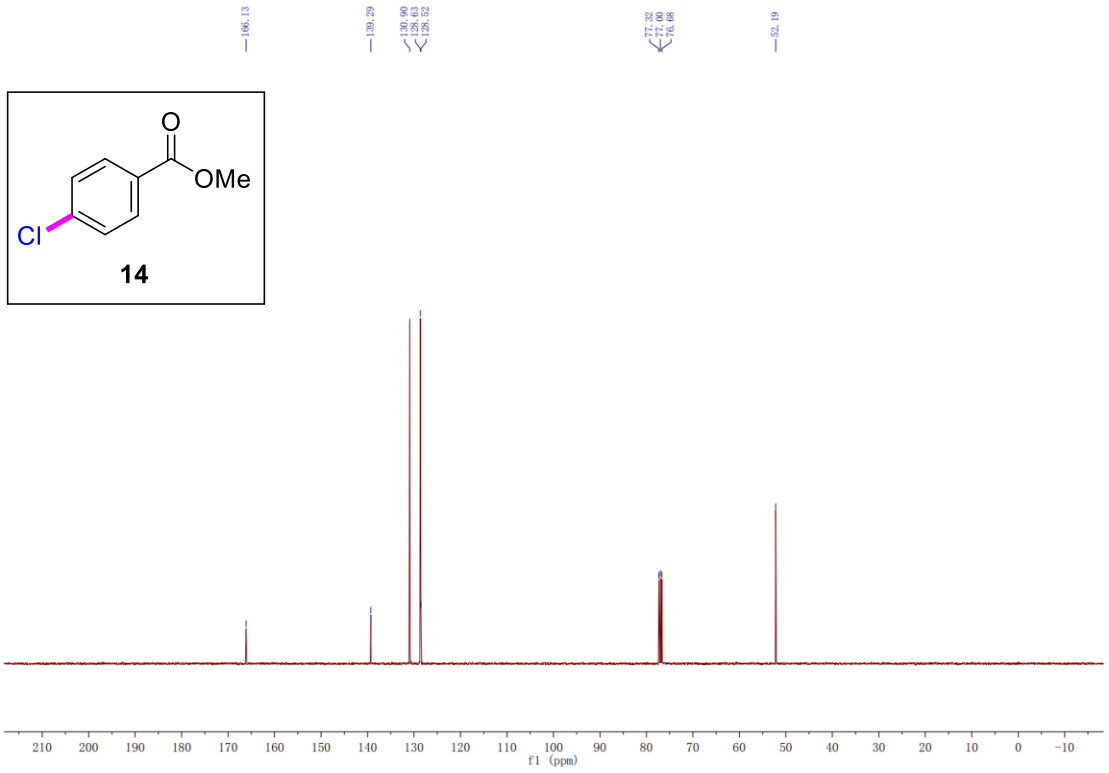

Cl
O
12
2.6189
0.95
2.97
3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

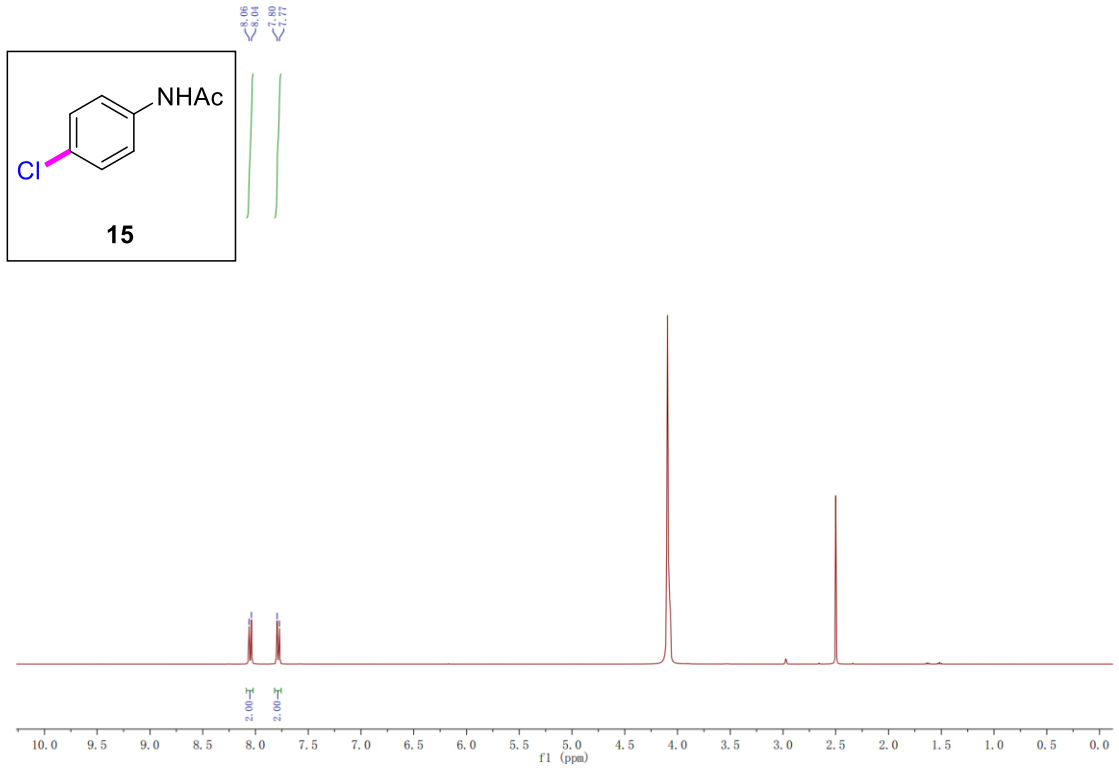

200.19
138.93
131.83
131.08
130.46
129.22
126.78
77.32
77.00
76.68
30.50
Cl
O
12
f1 (ppm)

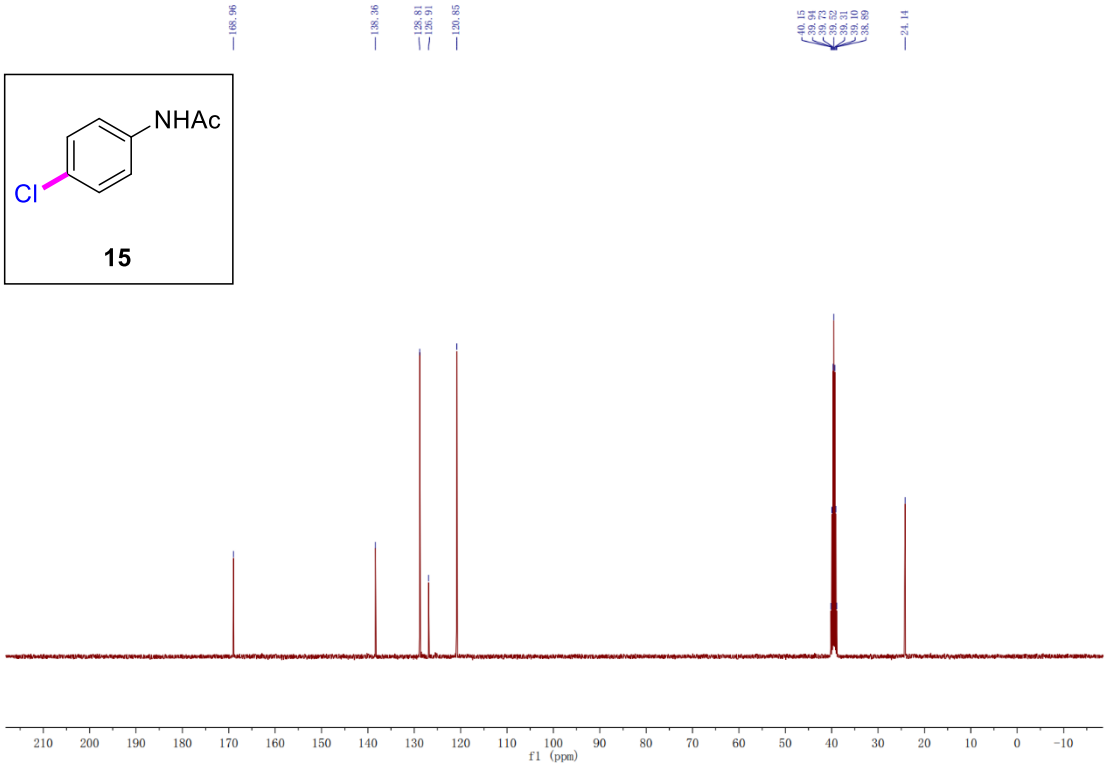

Cl
13
7.37
7.35
7.33
7.31
7.31
7.31
7.29
7.29
7.27
7.26
7.15
7.13
5.00
f1 (ppm)

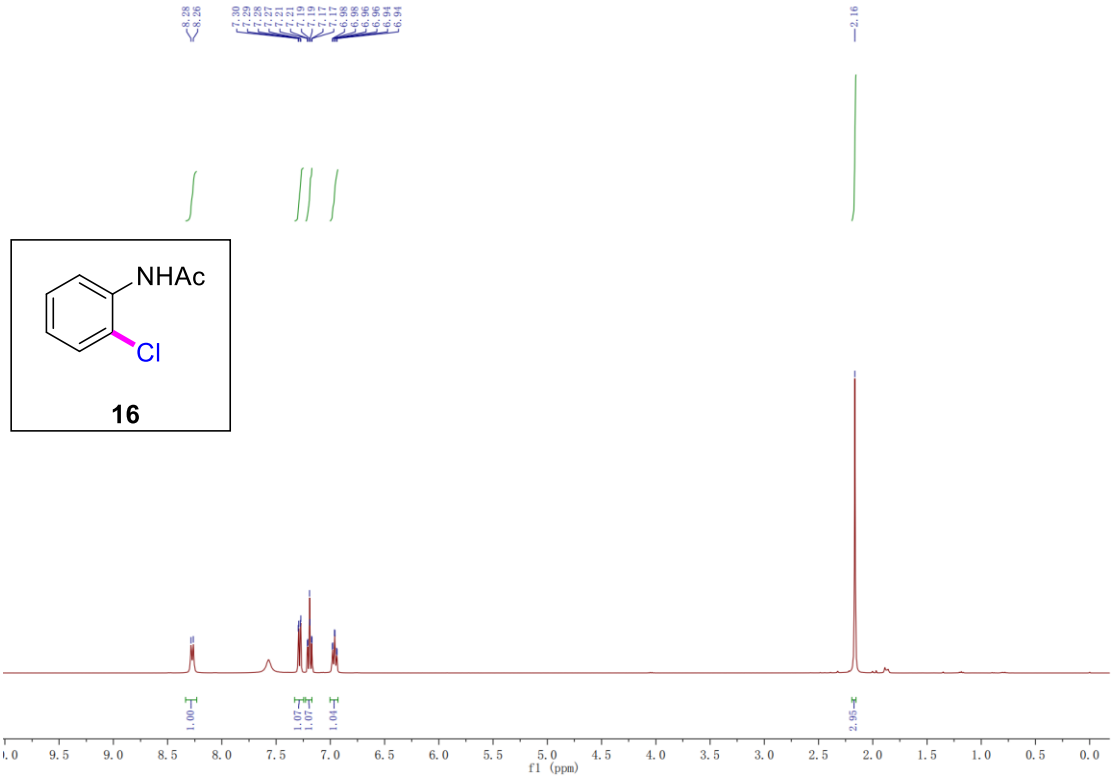

134.24
129.69
128.60
126.41
77.21
77.00
76.79
Cl
13
f1 (ppm)

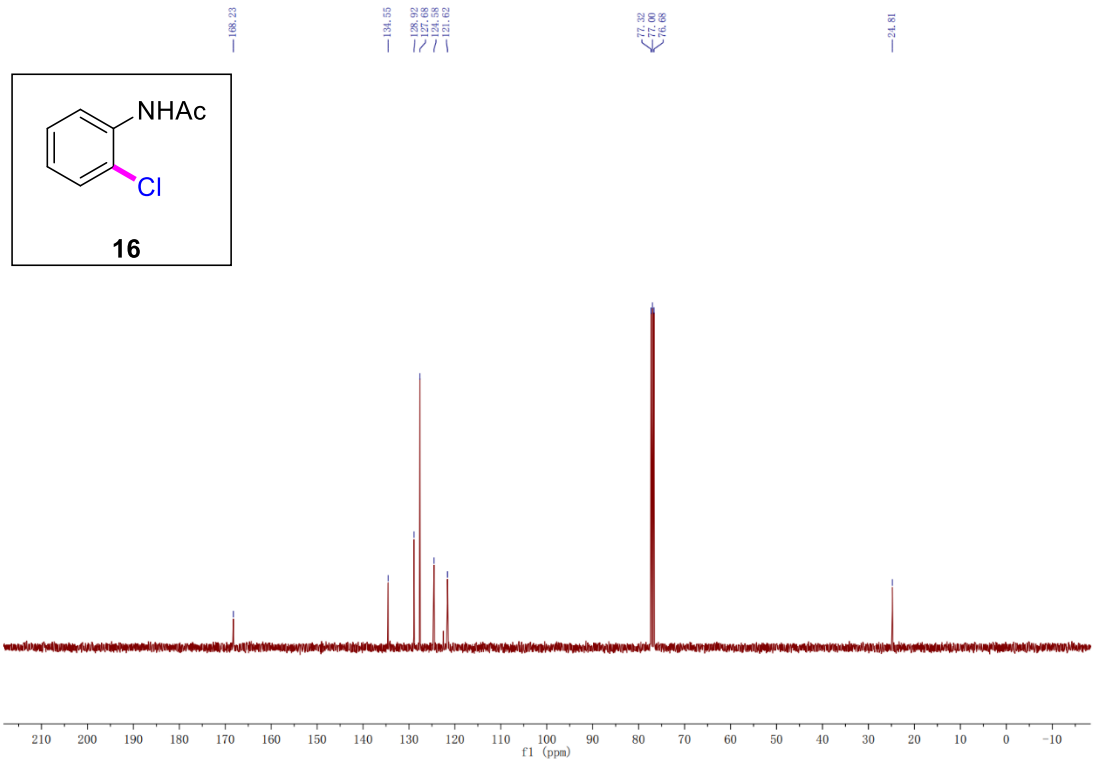

7.9840
7.9628
7.4217
7.4006
3.9184
O
OMe
Cl
14
1.98
2.00
3.15
f1 (ppm)

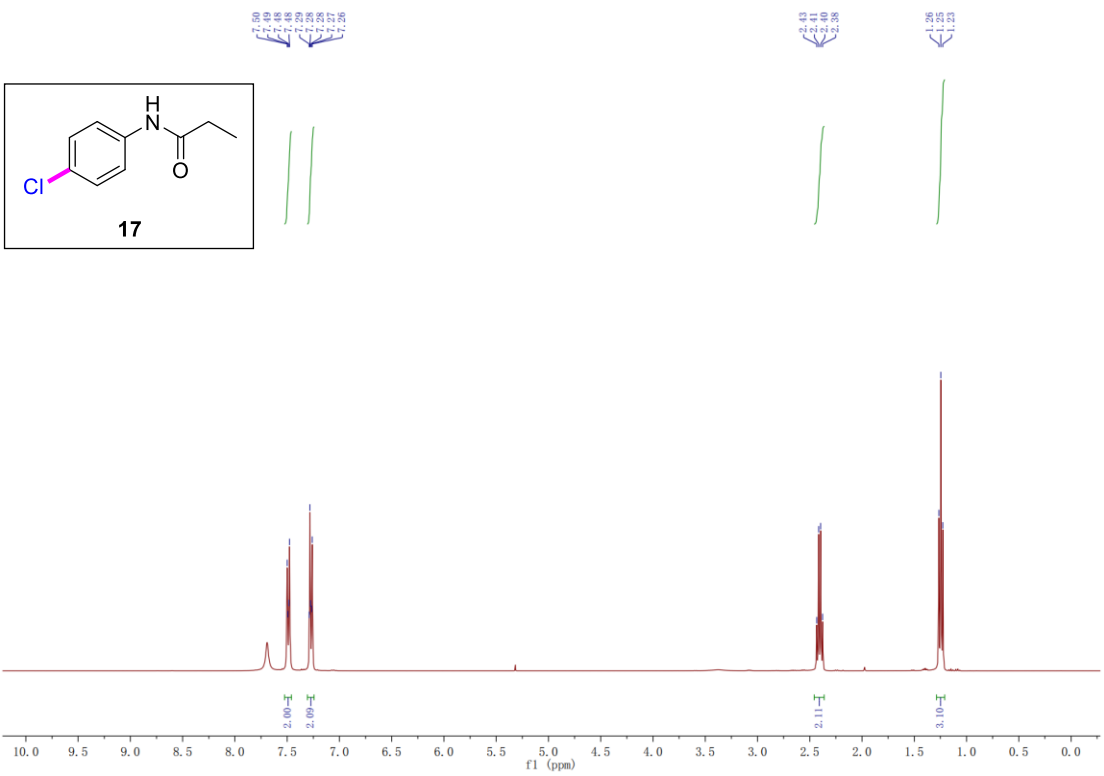

166.13
139.29
130.90
128.63
128.52
77.32
77.00
76.68
52.19
O
OMe
Cl
14
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

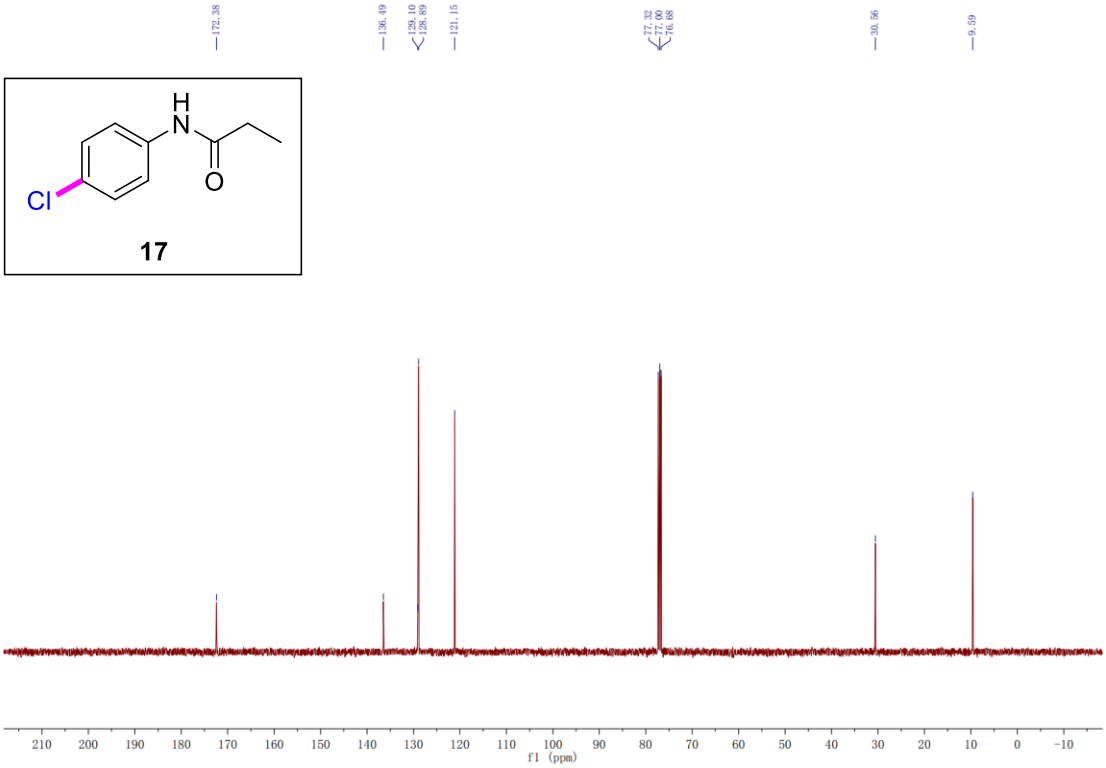

8.06
8.04
7.80
7.77
NHAc
Cl
15
2.00
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

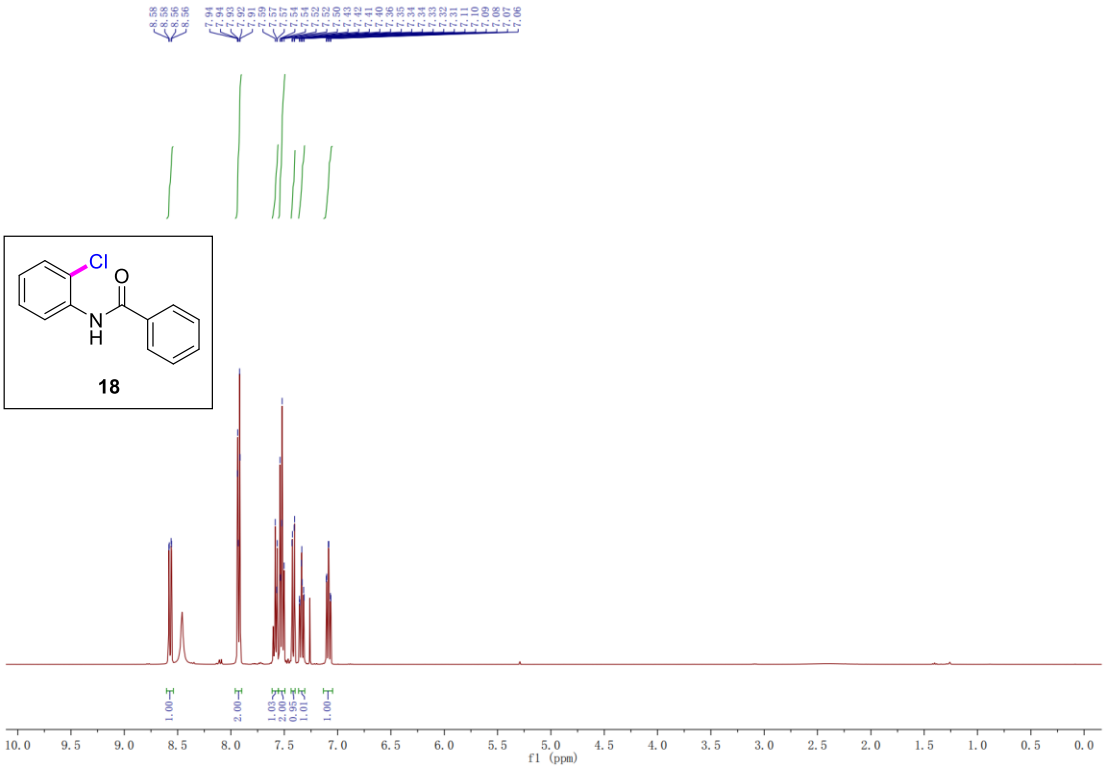

NHAc
Cl
15
168.96
138.36
128.81
126.91
120.85
40.15
39.94
39.73
39.52
39.31
39.10
38.89
24.14
f1 (ppm)

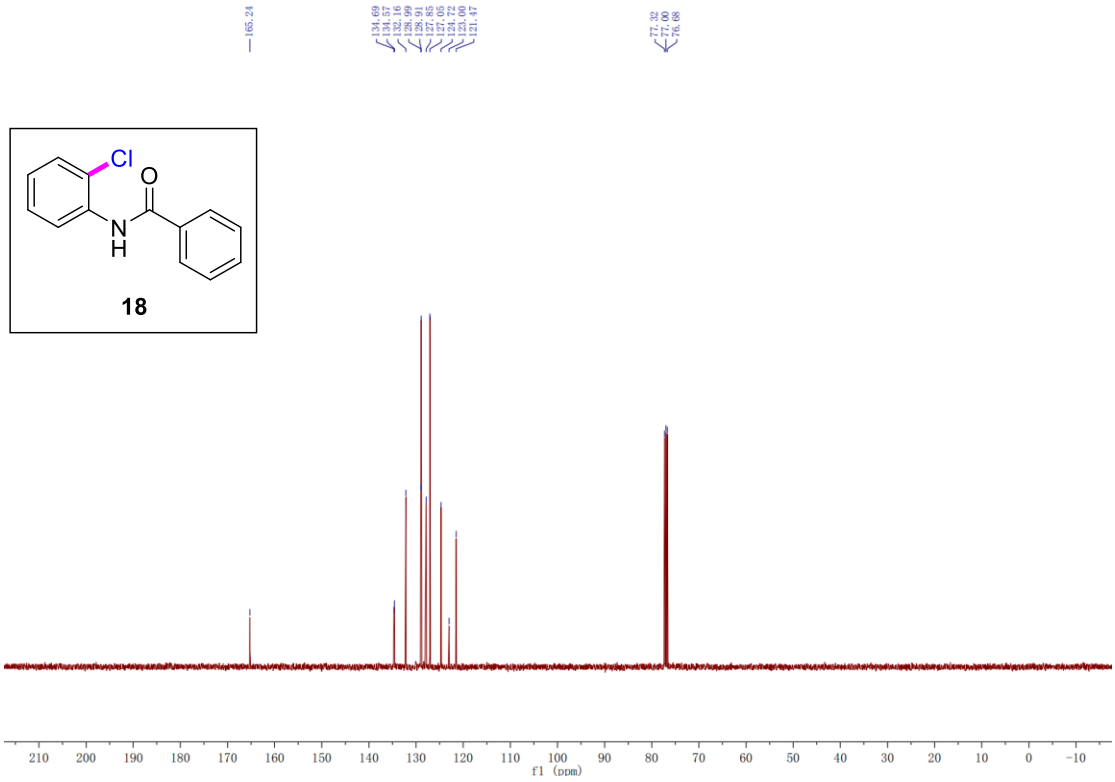

NHAc
Cl
16
8.28
8.26
7.30
7.29
7.28
7.27
7.21
7.19
7.17
6.98
6.96
6.94
2.16
1.00
1.07
1.07
1.04
2.95
f1 (ppm)

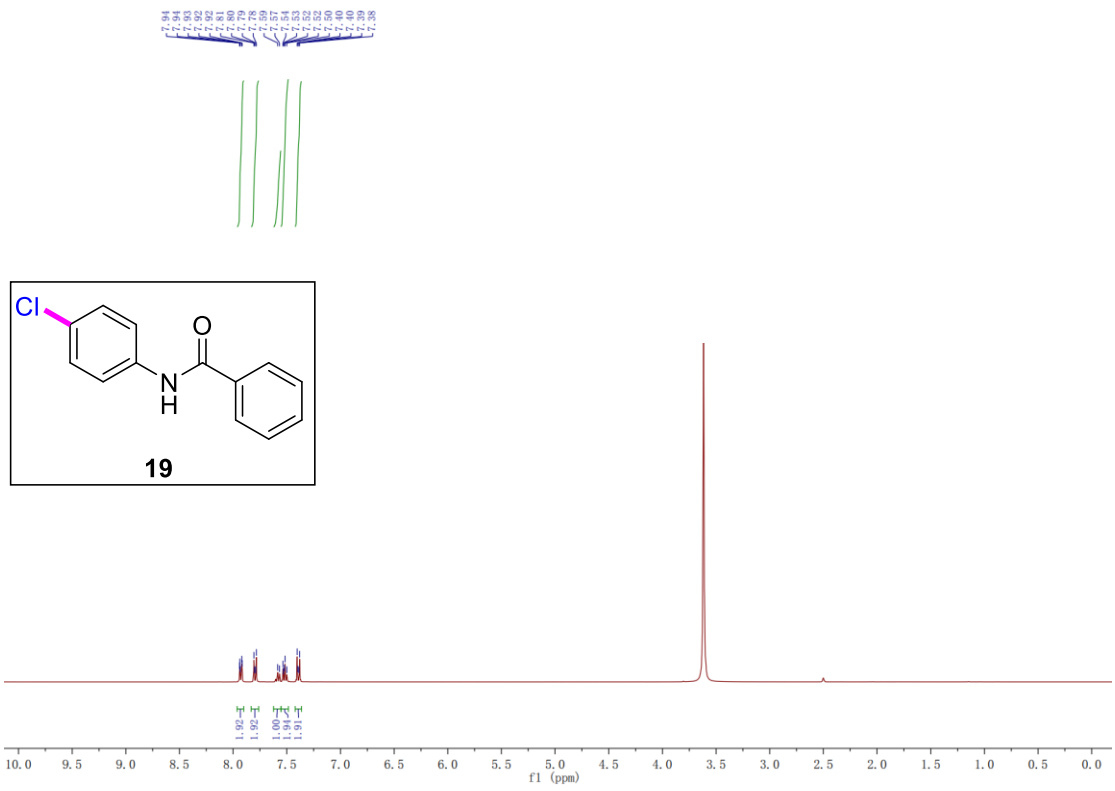

NHAc
Cl
16
168.23
134.55
128.92
127.68
124.58
121.62
77.32
77.00
76.68
24.81
f1 (ppm)

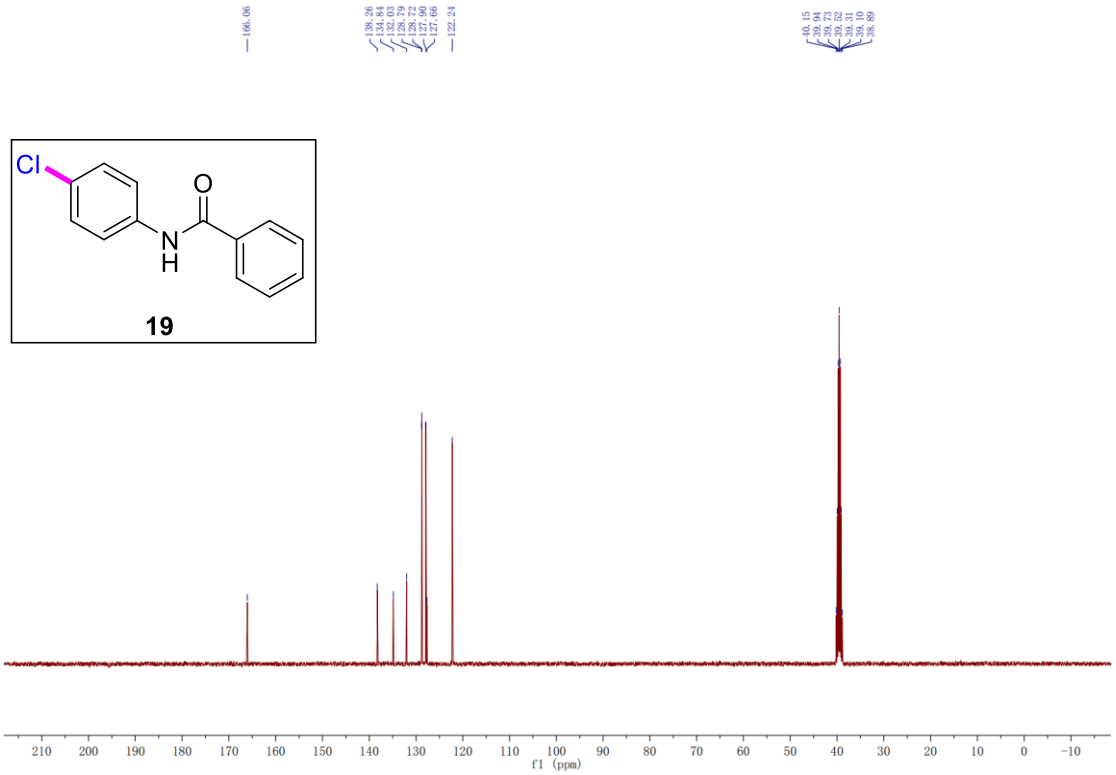

H
N
O
Cl
17
7.50
7.49
7.48
7.48
7.29
7.28
7.28
7.27
7.26
2.43
2.41
2.40
2.38
1.26
1.25
1.23
2.00
2.09
2.11
3.10
f1 (ppm)

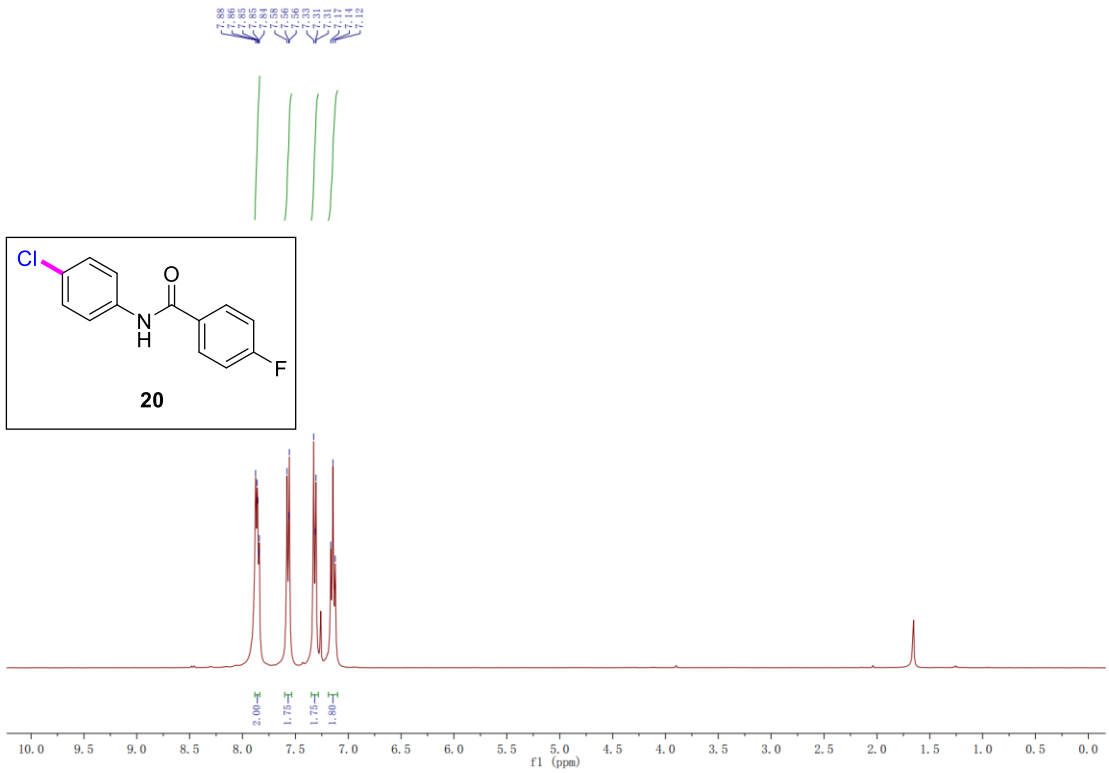

172.38
136.49
129.10
128.89
121.15
77.32
77.00
76.68
30.56
9.59
H
N
O
Cl
17
f1 (ppm)

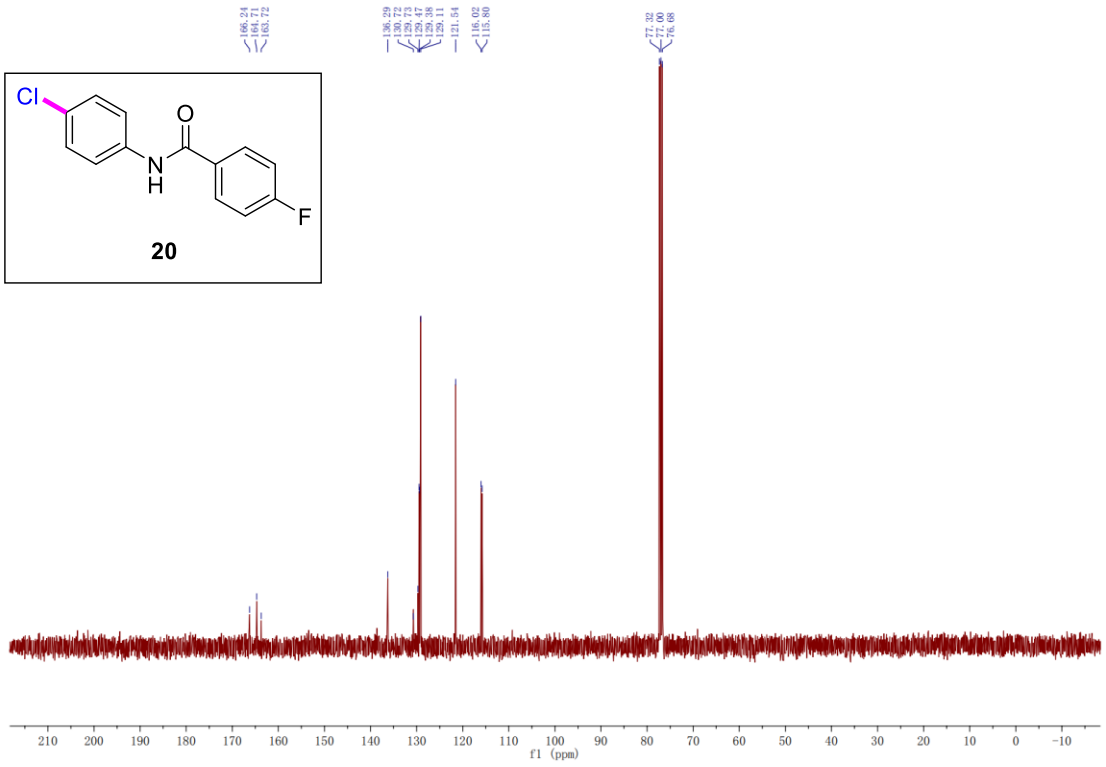

Cl
O
N
H
18
f1 (ppm)

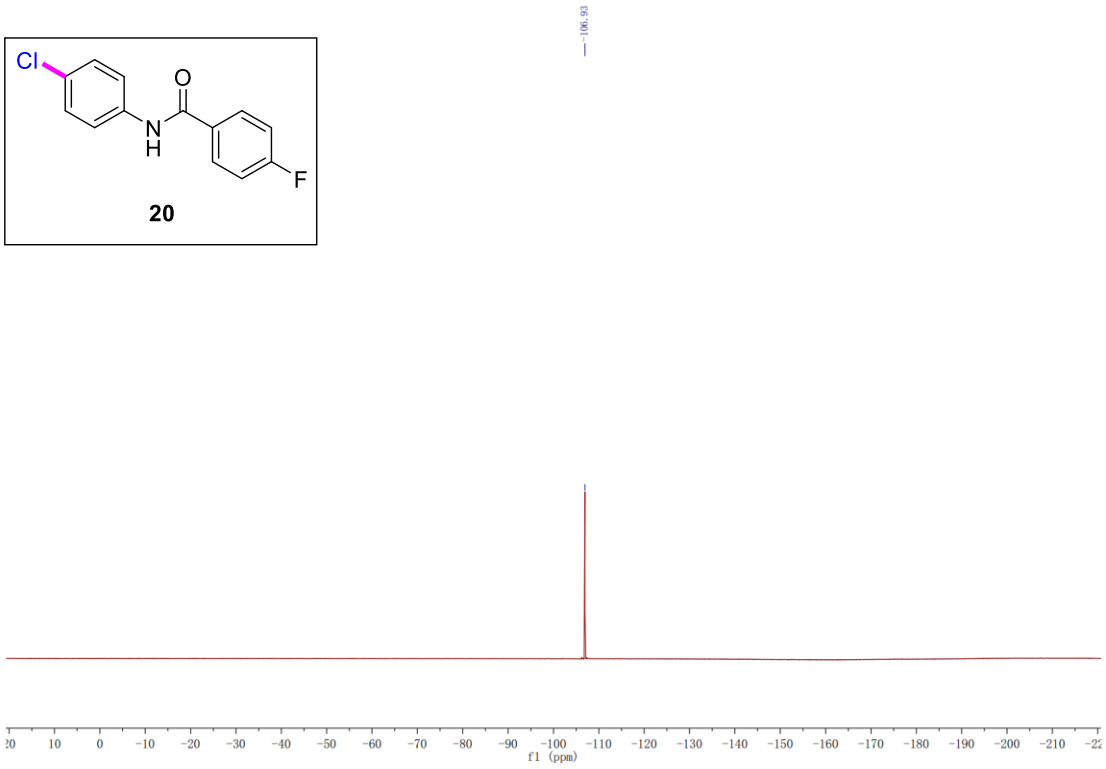

165.24
134.69
134.57
132.16
128.99
128.91
127.85
127.05
124.72
123.09
121.47
77.32
77.00
76.68
Cl
O
N
H
18
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

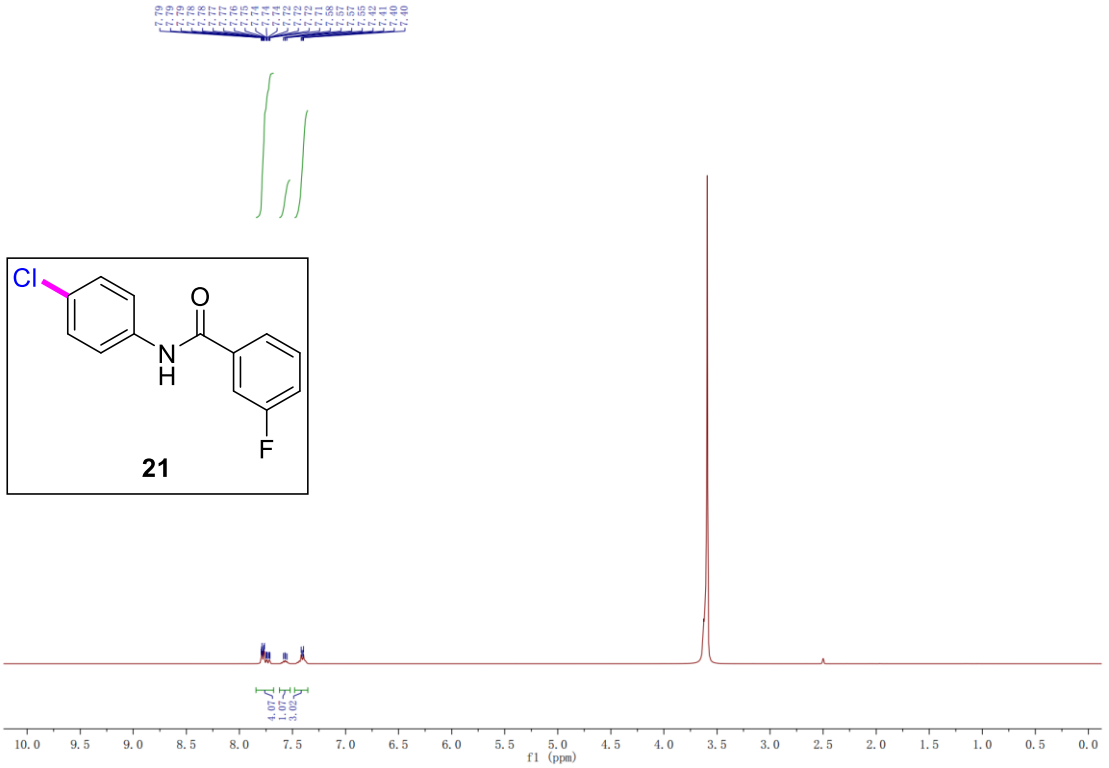

7.94
7.94
7.93
7.92
7.92
7.81
7.80
7.79
7.78
7.59
7.57
7.54
7.53
7.52
7.52
7.50
7.40
7.40
7.39
7.38
Cl
O
N
H
19
1.92
1.92
1.00
1.94
1.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

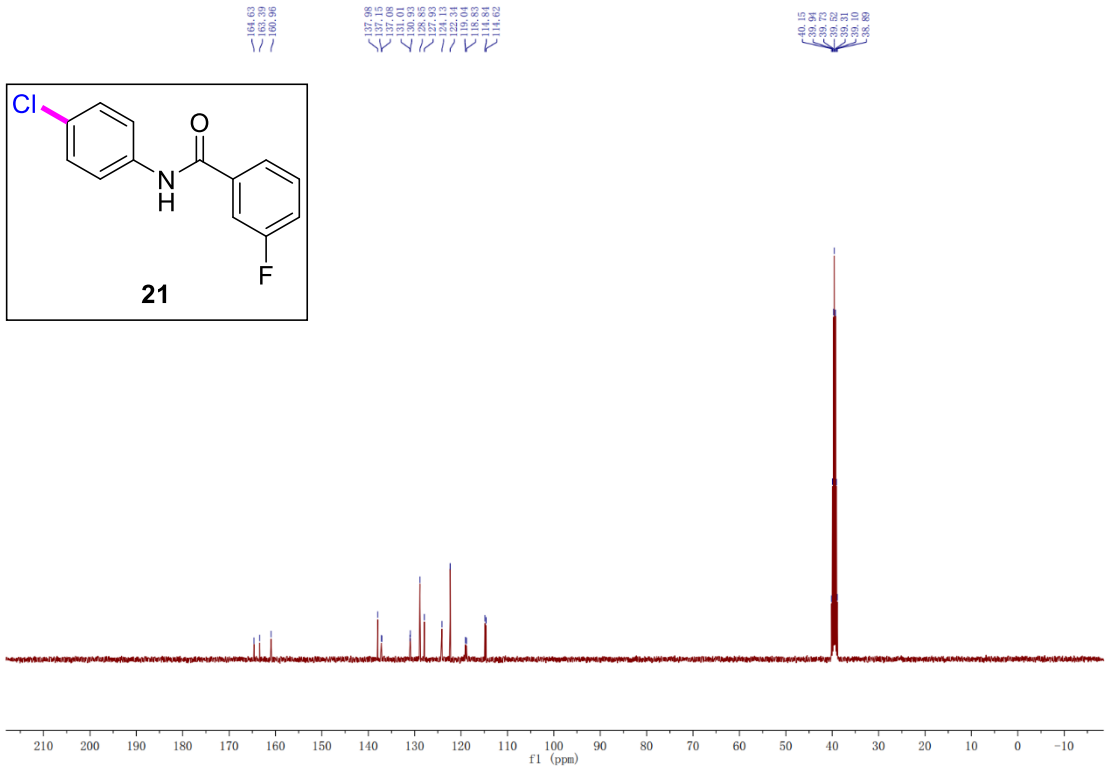

166.06
138.26
134.84
132.03
129.79
128.72
127.90
127.66
122.24
40.15
39.94
39.73
39.52
39.31
39.10
38.89
Cl
O
N
H
19
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

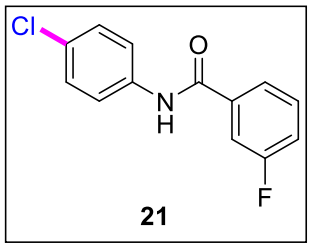

7.88
7.86
7.85
7.84
7.58
7.56
7.56
7.33
7.31
7.17
7.14
7.12
Cl
O
N
H
F
20
2.00
1.75
1.75
1.80
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


166.24
164.71
163.72
136.29
130.72
129.73
129.47
129.36
129.11
121.54
116.02
115.80
77.32
77.00
76.68
Cl
O
N
H
F
20
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

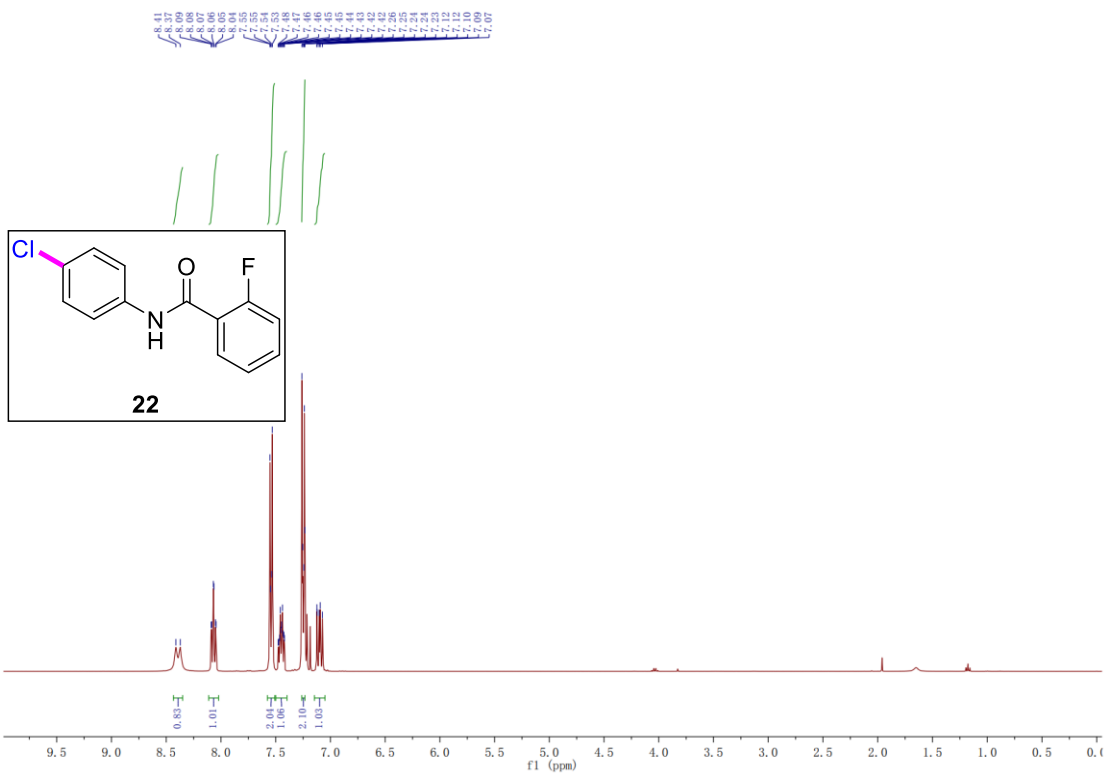

-106.93
Cl
O
N
H
F
20
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

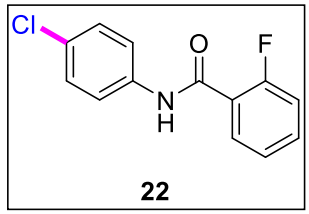

Cl
O
N
H
F
21
4.07
1.07
2.13
3.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

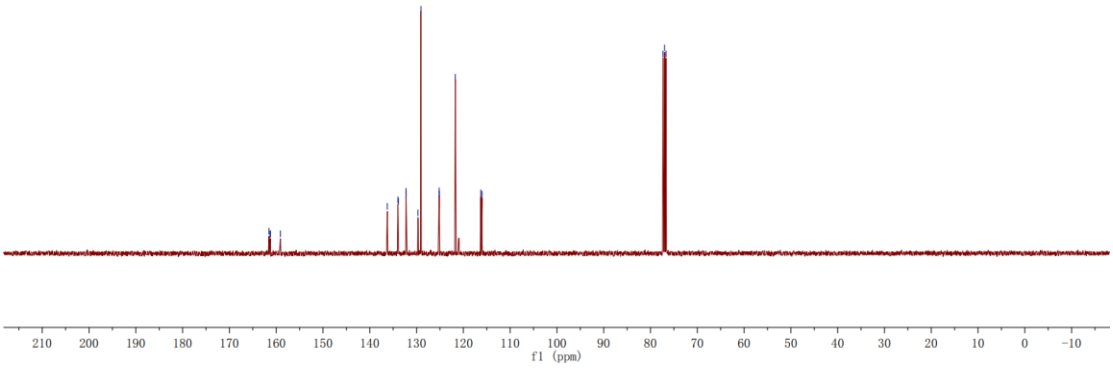

Cl
O
N
H
F
21
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

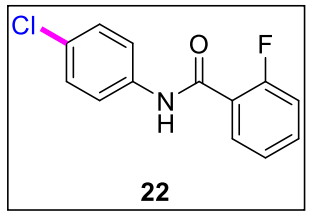

Cl
O
N
H
F
21

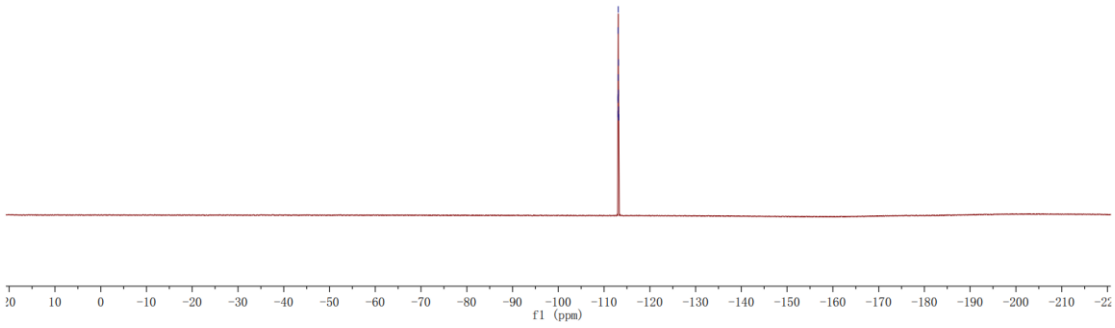
f1 (ppm)

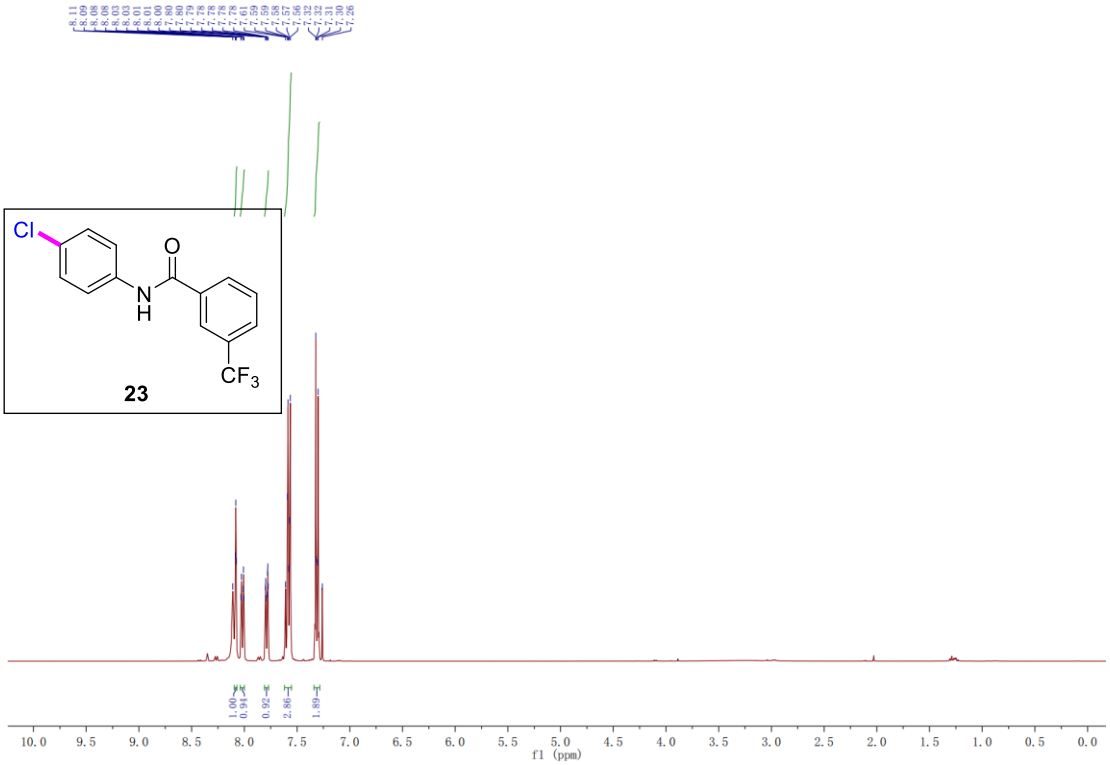

Cl
O
F
N
H
22
f1 (ppm)

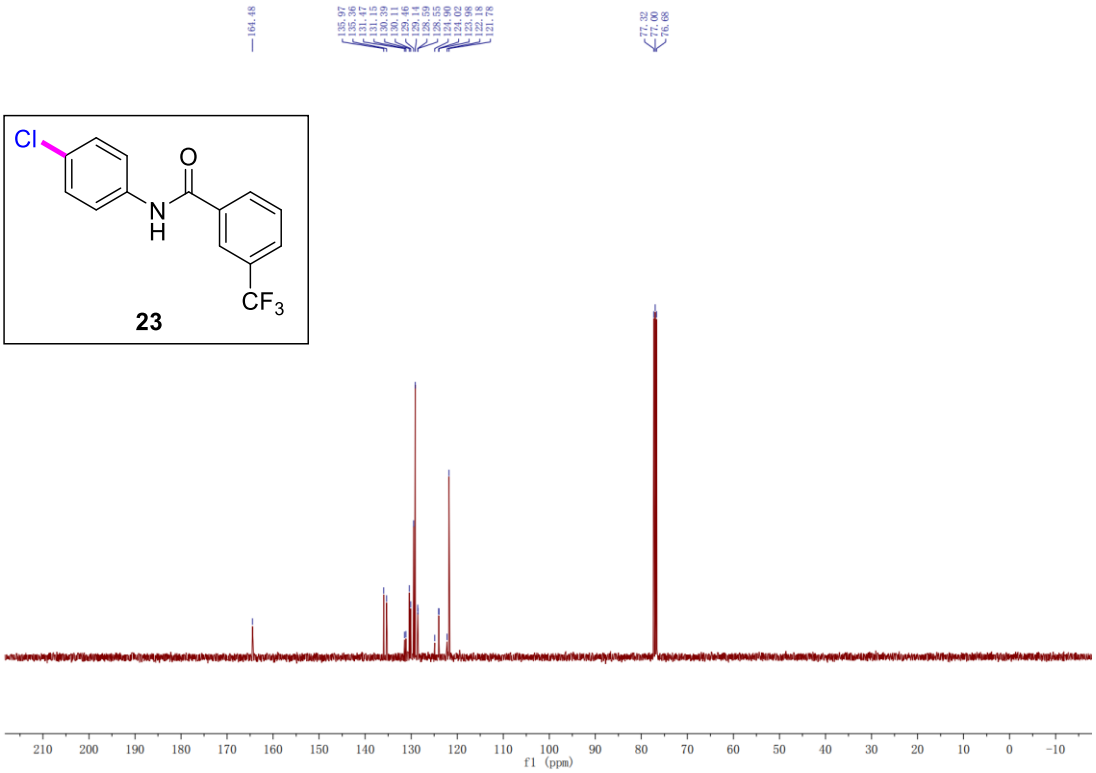

Cl
O
F
N
H
22

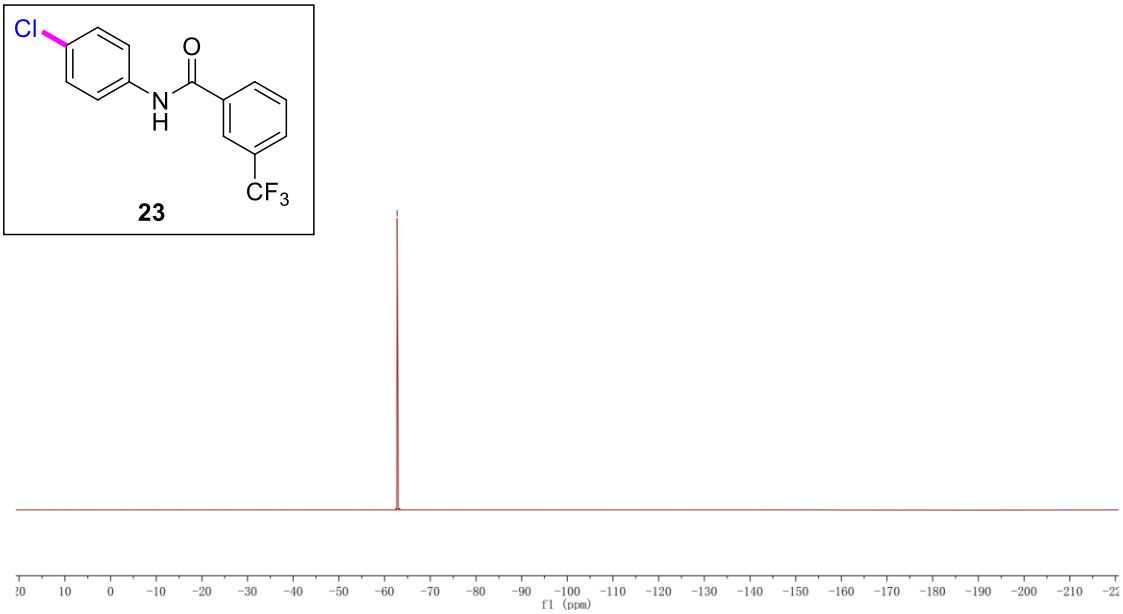

f1 (ppm)

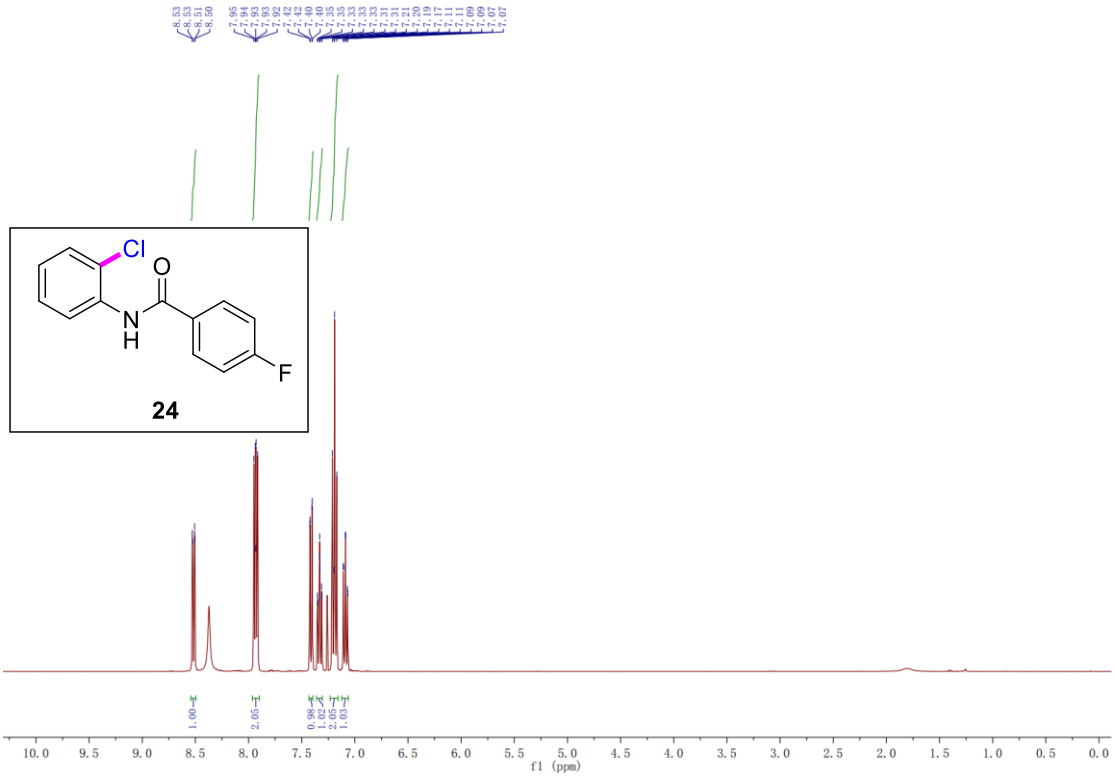

Cl
O
F
N
H
22

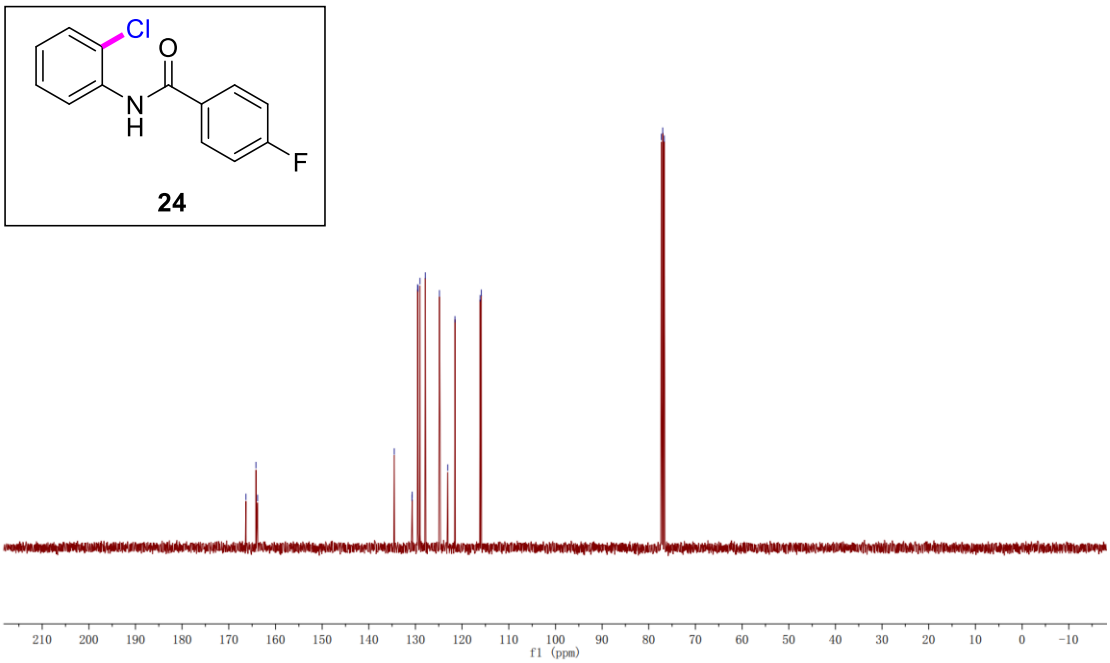

f1 (ppm)

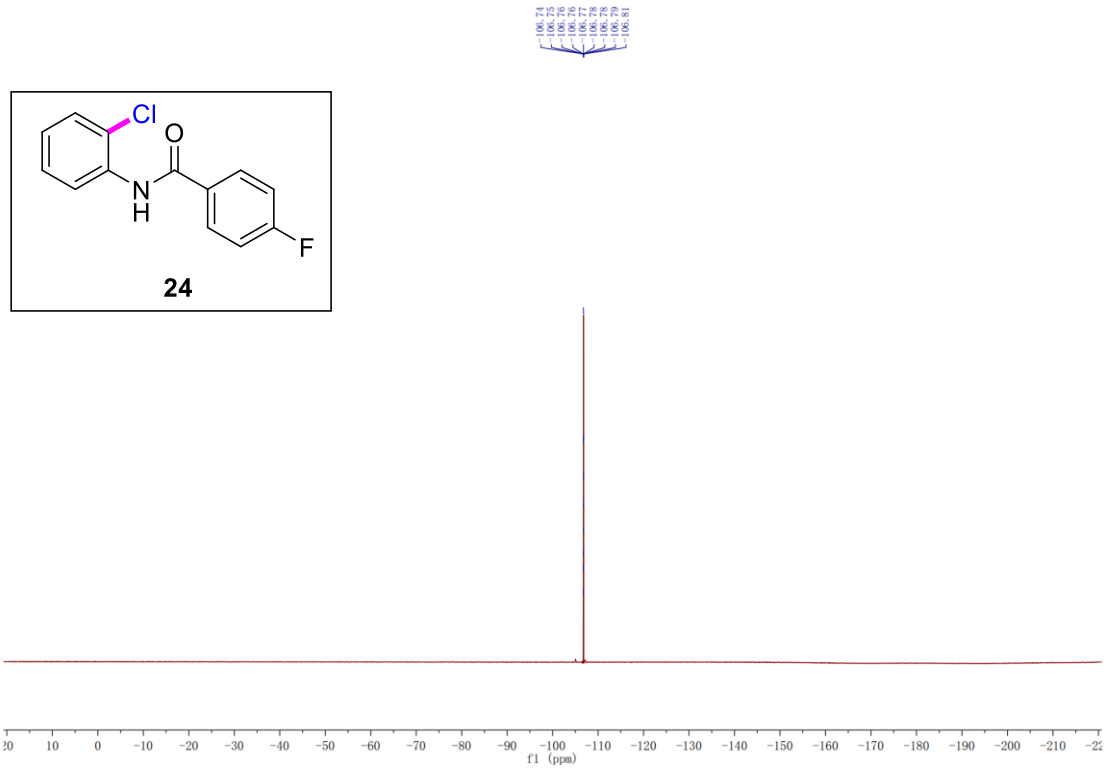

Cl
O
N
H
CF3
23
f1 (ppm)

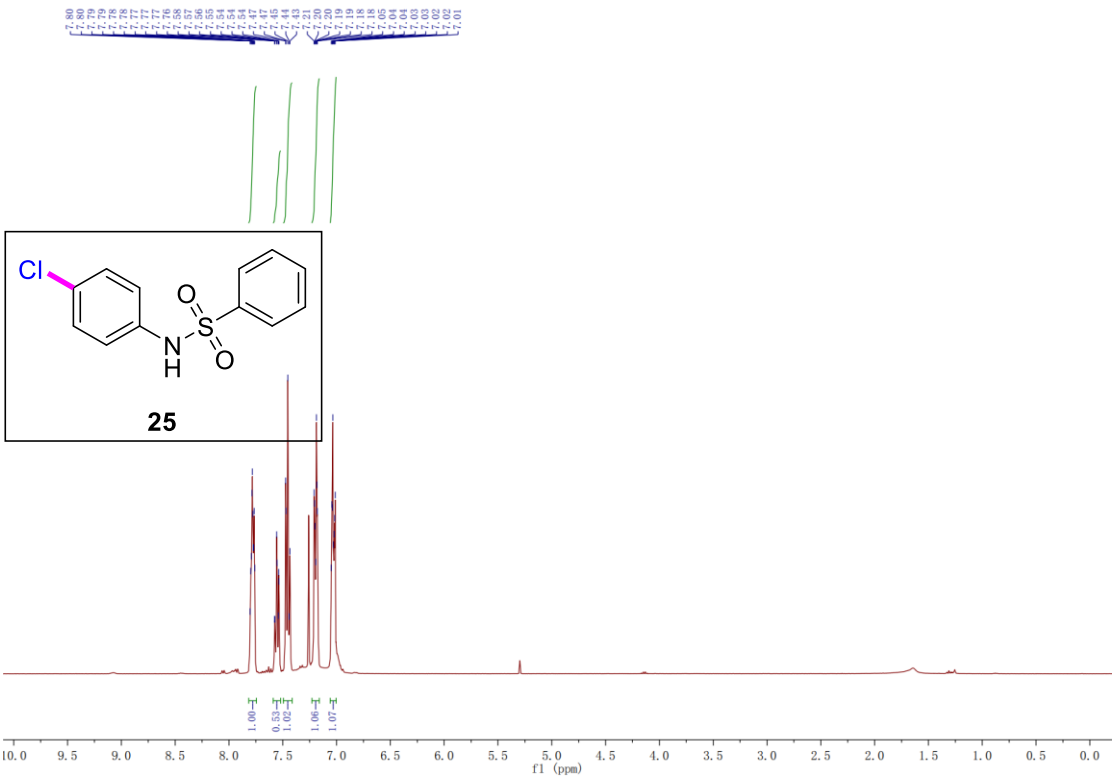

Cl
O
N
H
CF3
23
f1 (ppm)

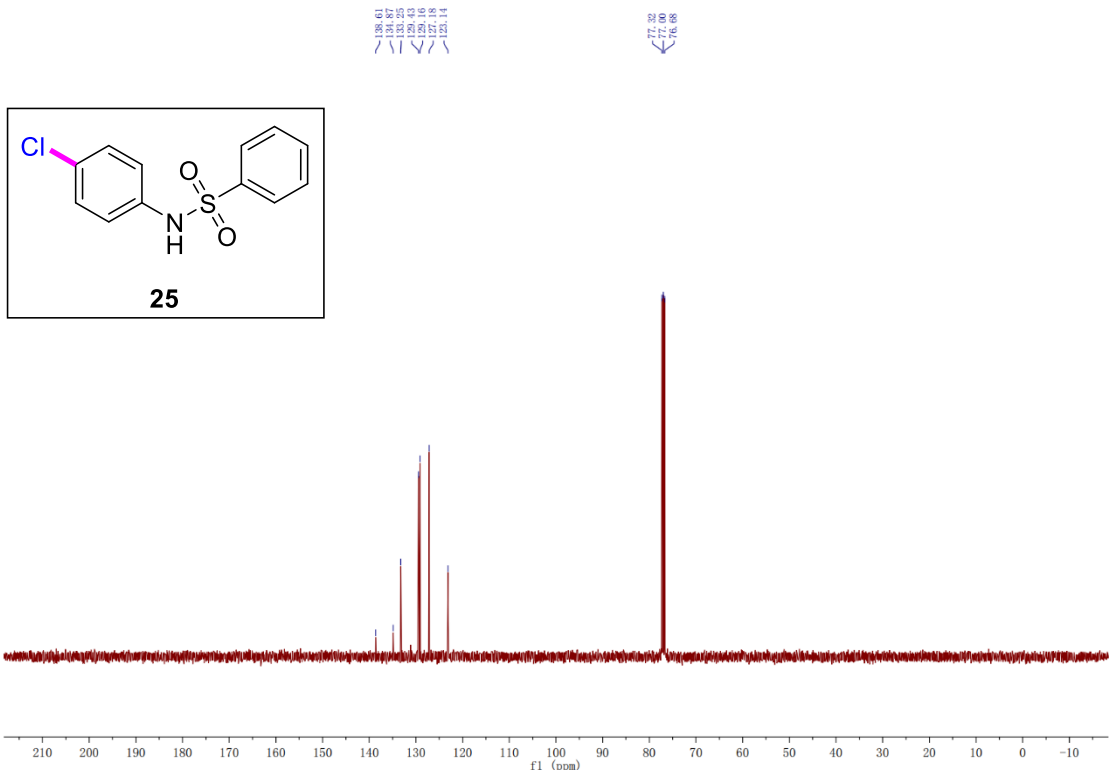

Cl
O
N
H
CF3
23
-62.74
f1 (ppm)

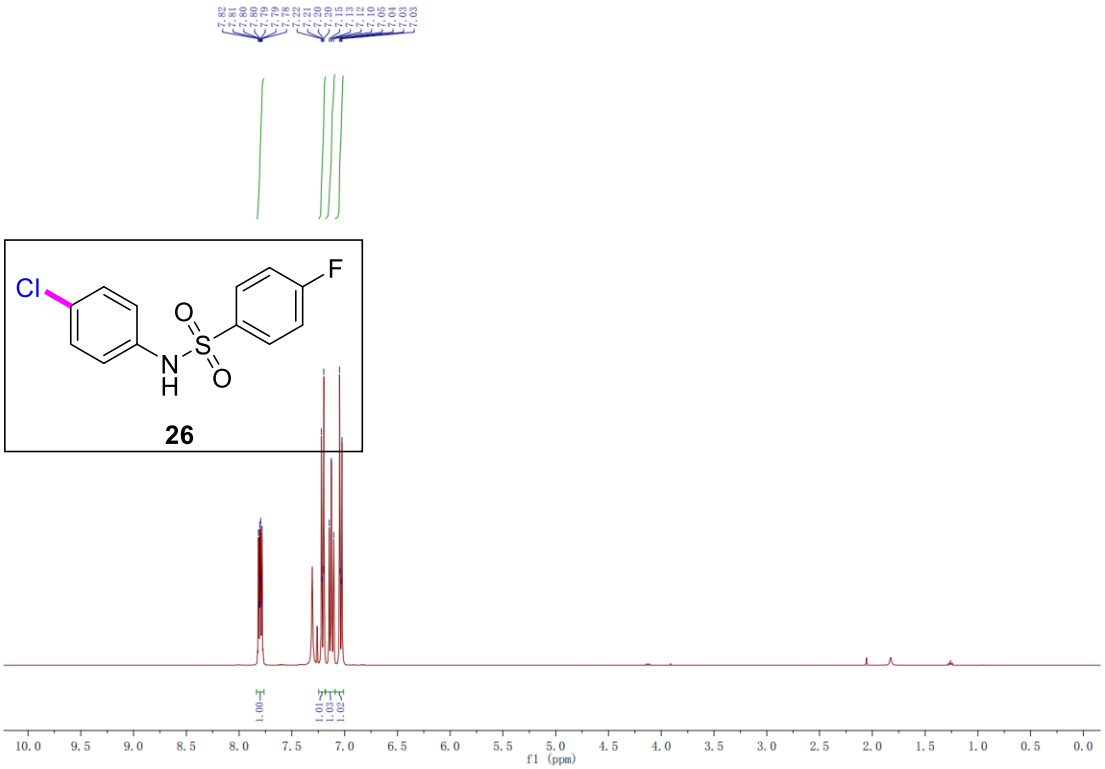

Cl
O
N
H
F
24
f1 (ppm)

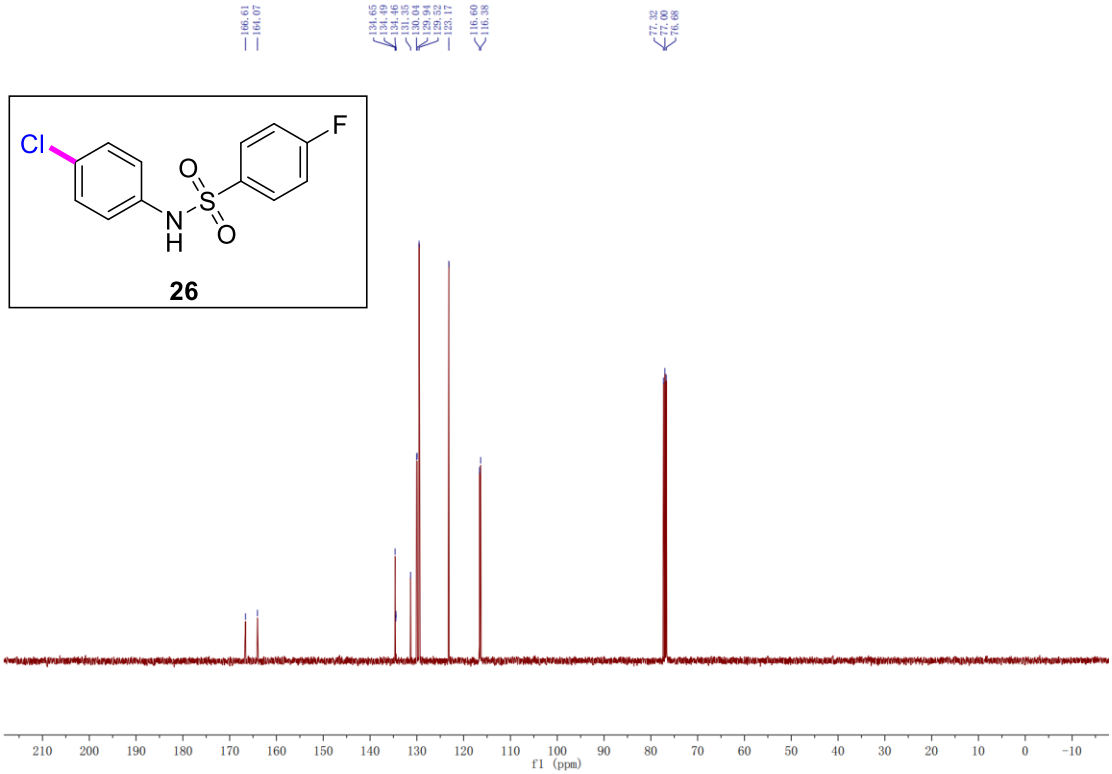

Cl
O
N
H
F
24
f1 (ppm)

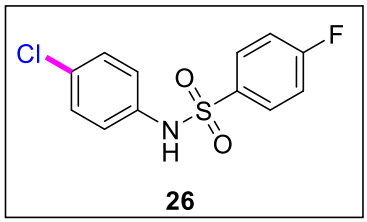

Cl
O
N
H
F
24
f1 (ppm)


Cl
O
S
O
N
H
25
1.00
0.53
1.02
1.06
1.07
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

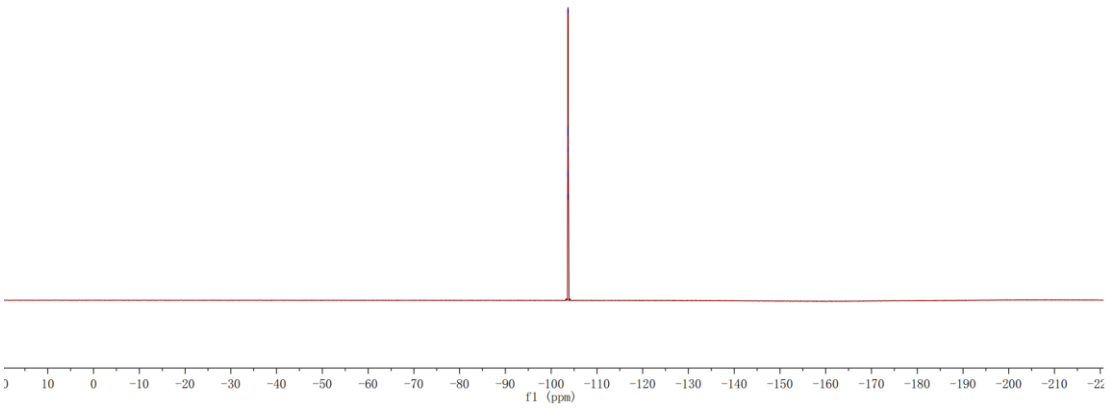

138.61
134.57
133.25
129.43
129.16
127.38
121.14
77.32
77.00
76.68
Cl
O
S
O
N
H
25
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

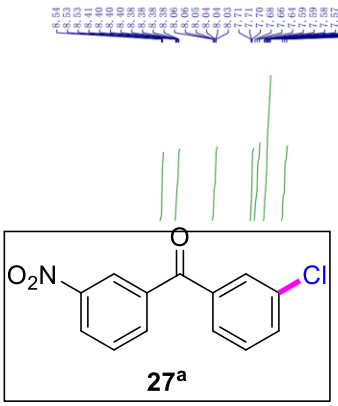

Cl
F
O
S
N
H
O
26
f1 (ppm)


Cl
F
O
S
N
H
O
26
f1 (ppm)

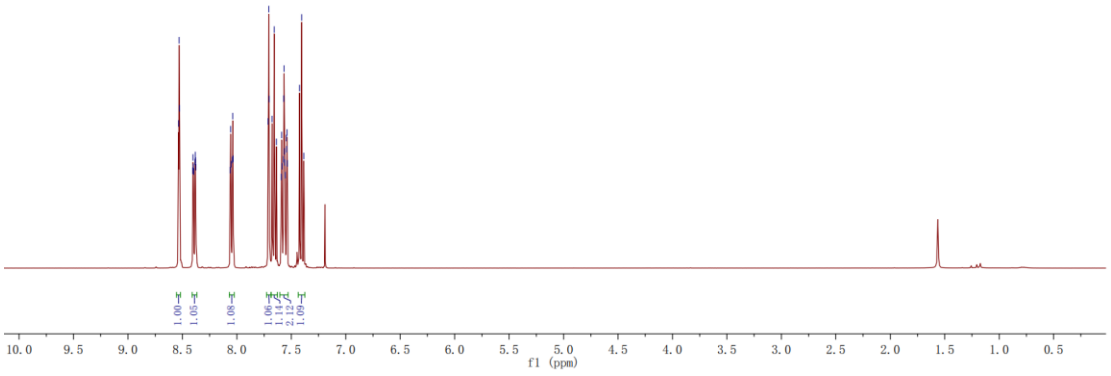


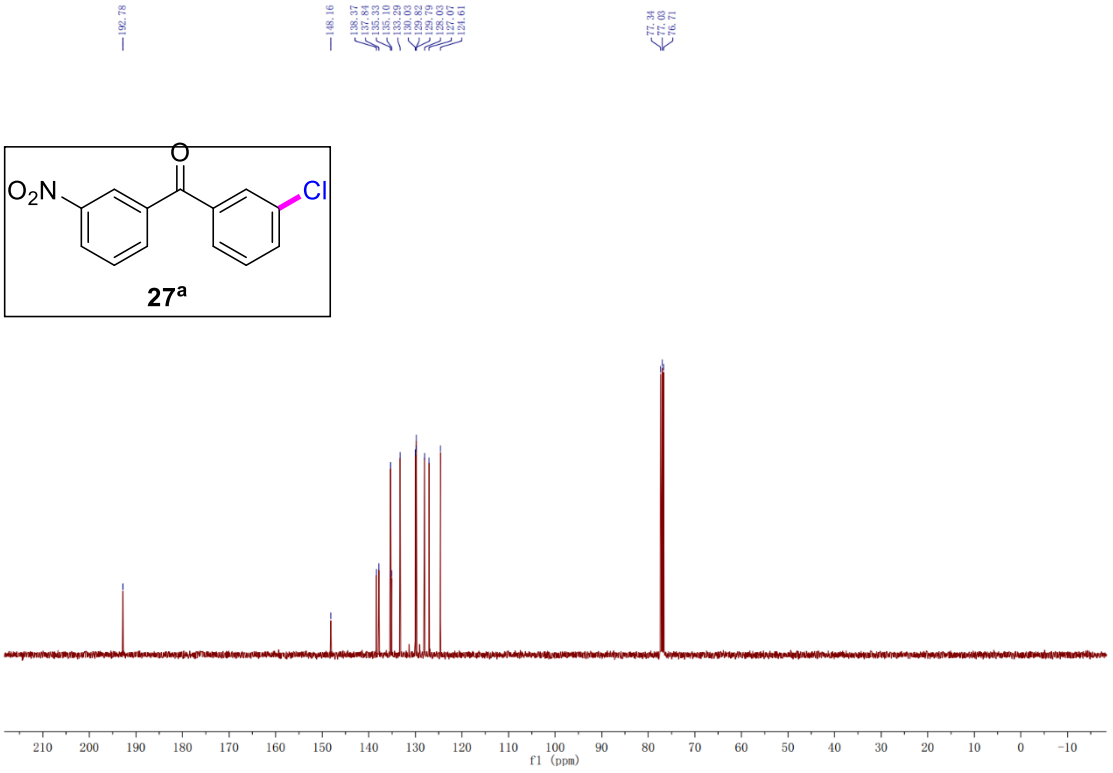
26

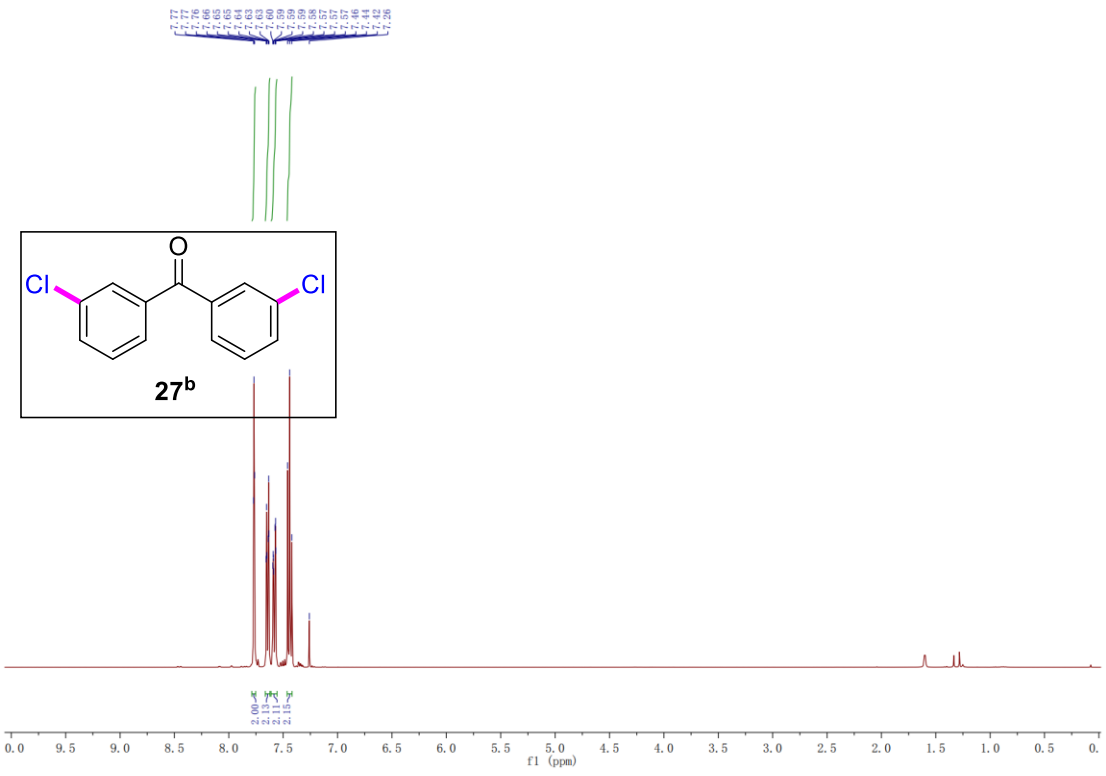


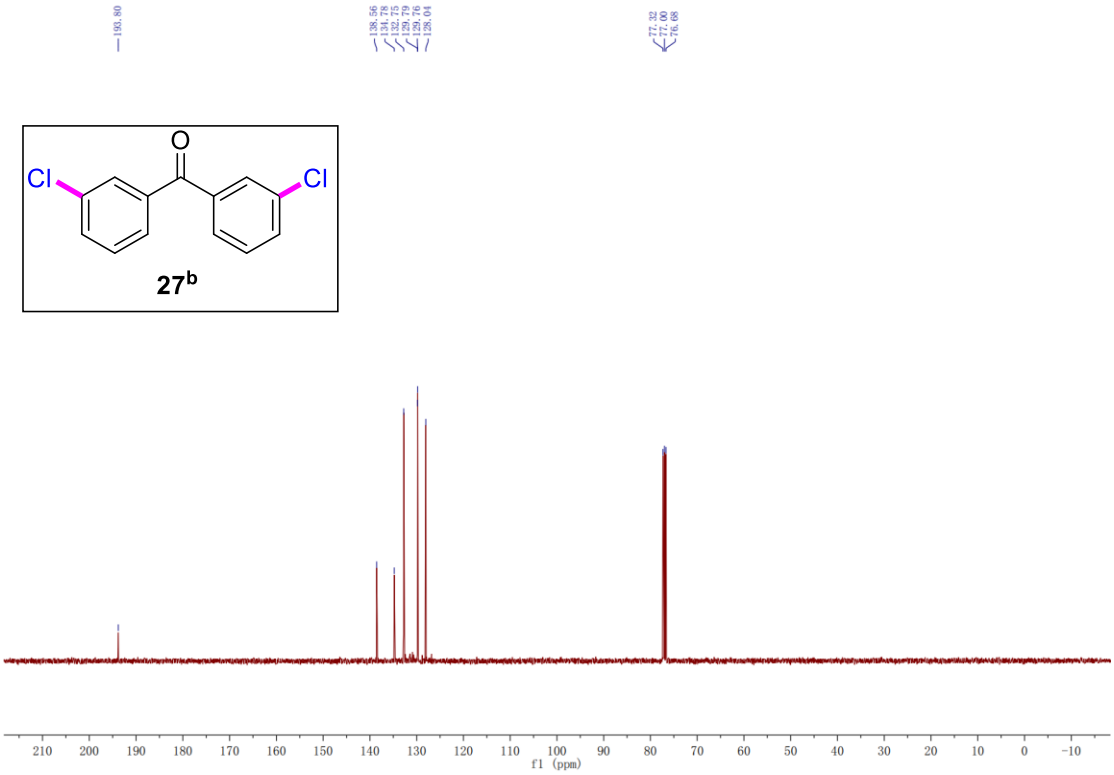


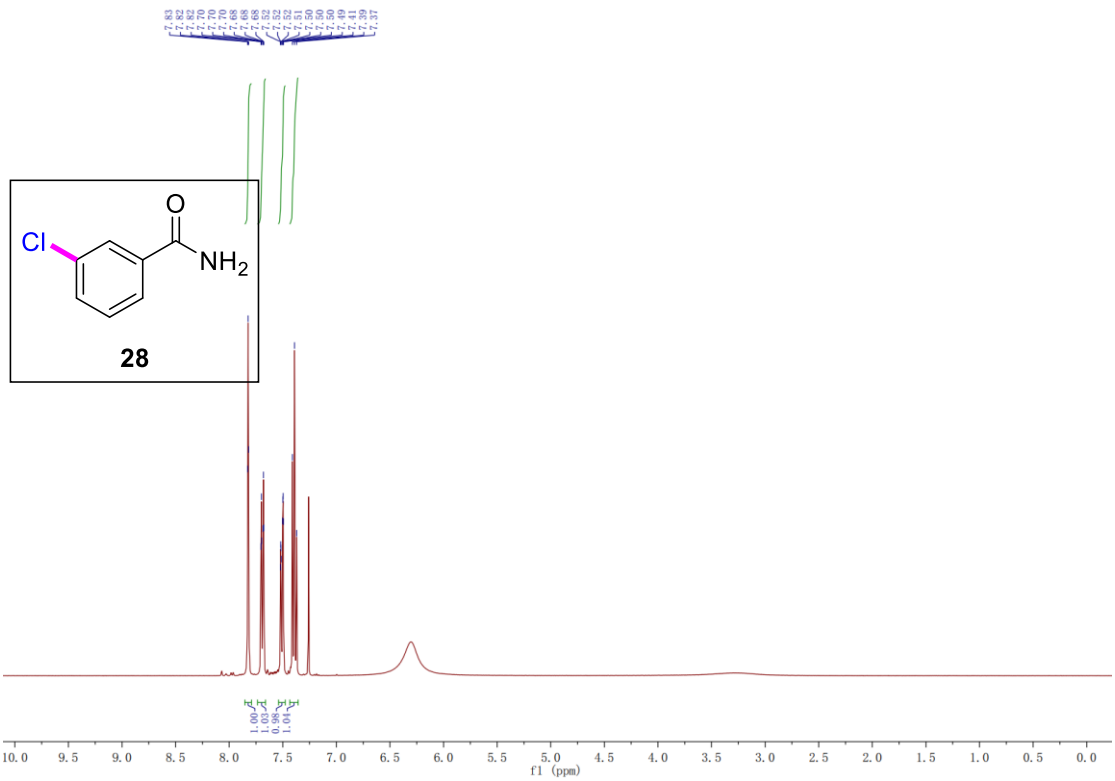
27[a]

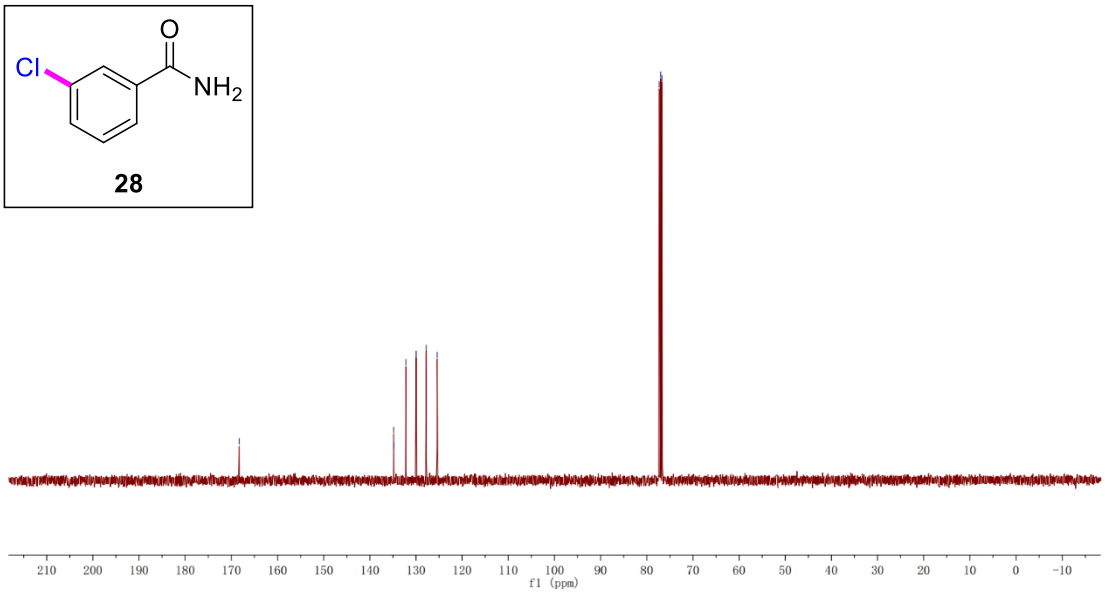


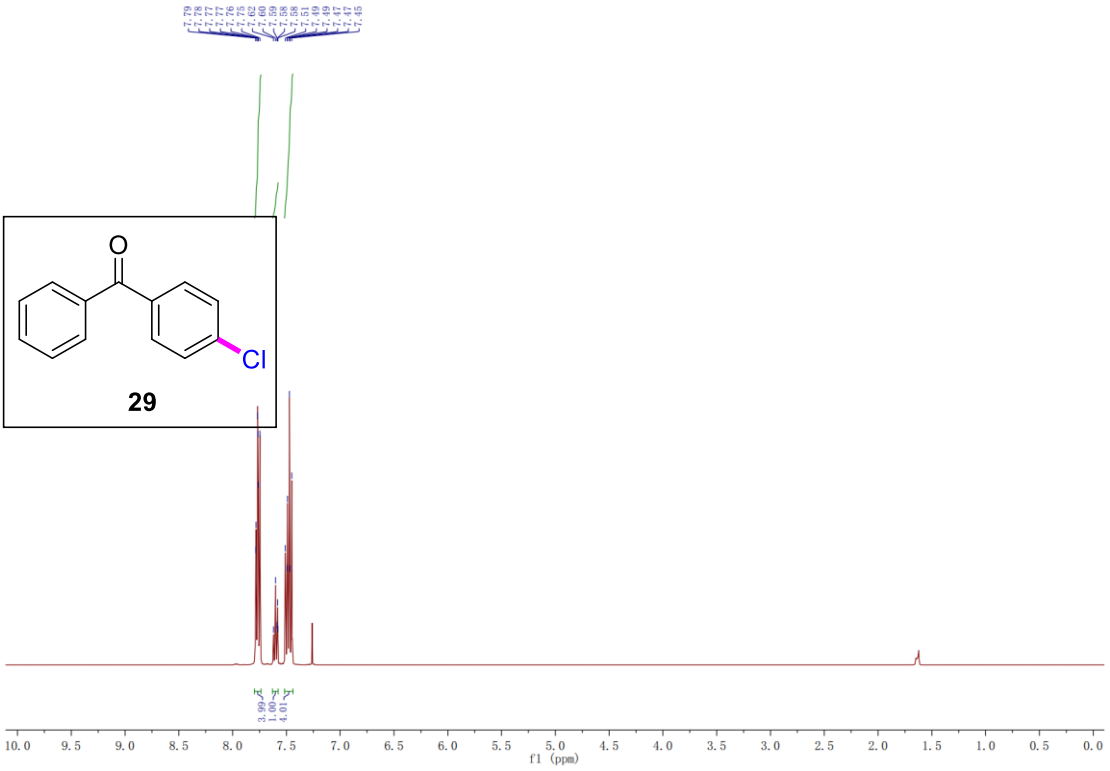

192.78
148.16
138.37
137.84
135.33
135.10
133.29
130.05
129.82
129.79
128.03
127.07
124.61
77.34
77.03
76.71
O
O2N
Cl
27a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

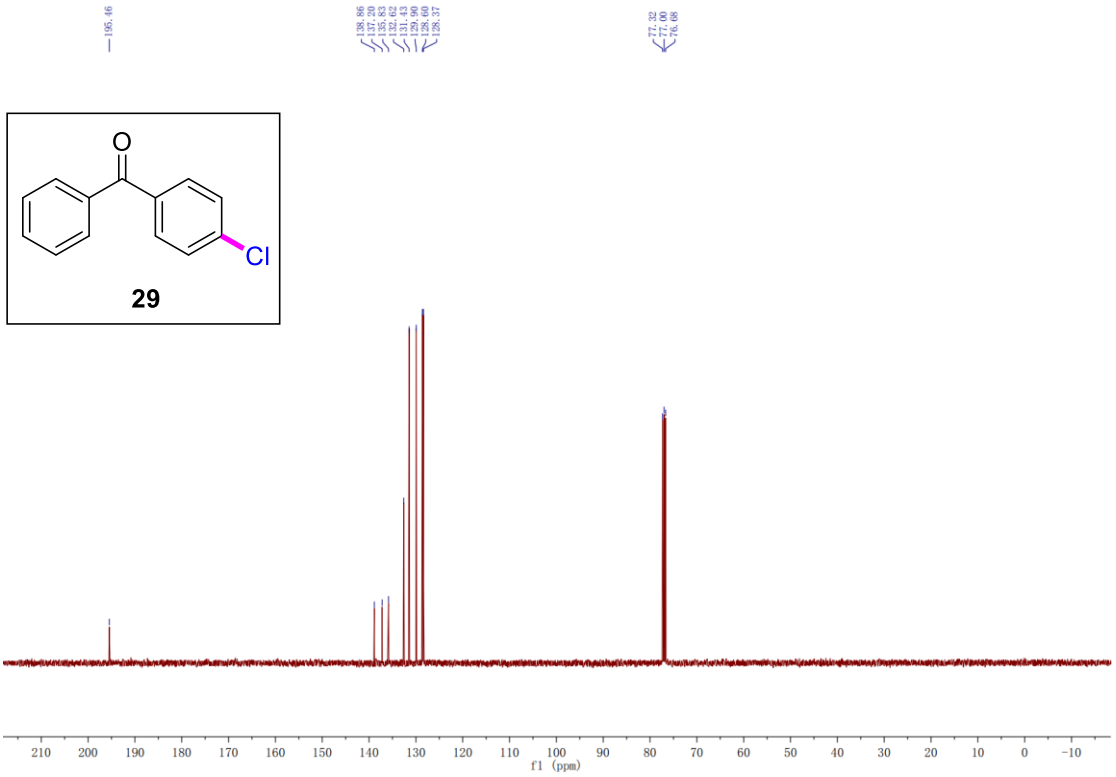

7.77
7.76
7.66
7.65
7.64
7.63
7.60
7.59
7.58
7.57
7.46
7.44
7.43
7.26
O
Cl
Cl
27b
2.00
1.13
2.11
2.15
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.
f1 (ppm)

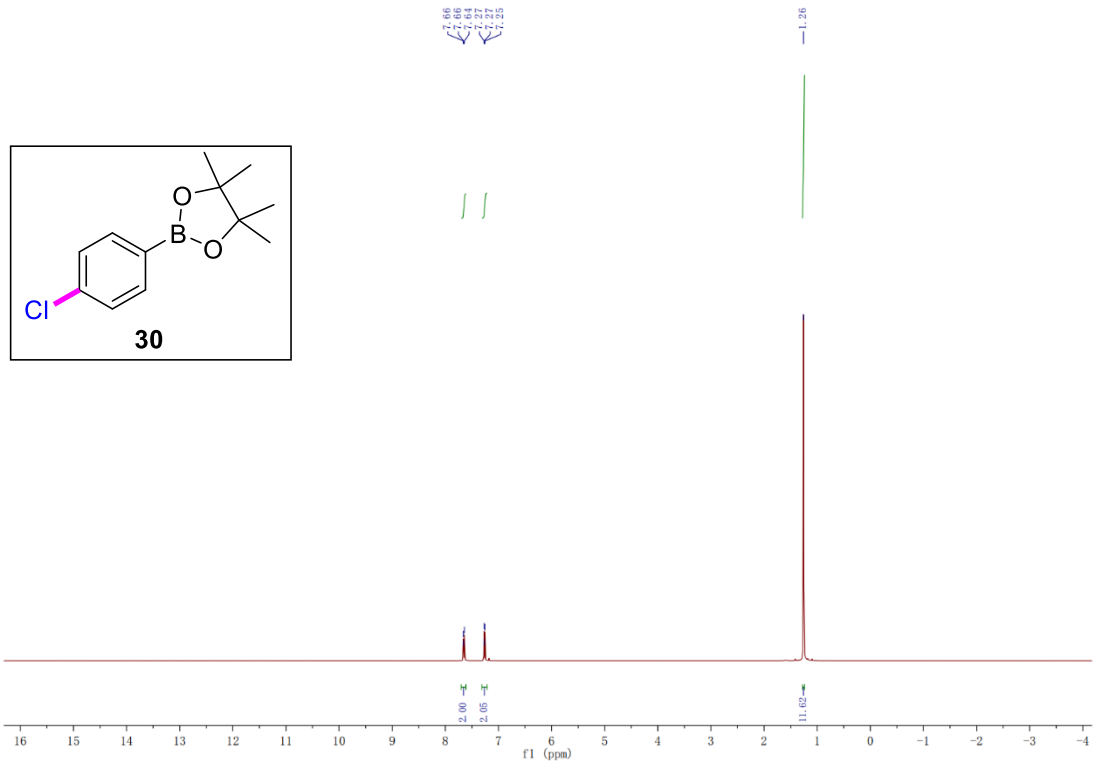

190.80
138.56
134.78
132.75
131.79
129.76
128.04
77.32
77.00
76.68
O
Cl
Cl
27b
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

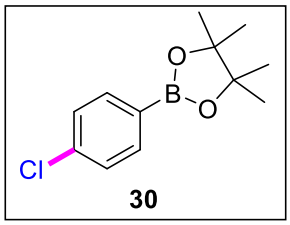

7.83
7.82
7.82
7.70
7.70
7.70
7.68
7.68
7.68
7.52
7.52
7.52
7.51
7.50
7.50
7.49
7.41
7.39
7.37
O
Cl
NH2
28
1.00
1.02
1.00
0.98
1.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


168.32
134.85
134.82
132.17
129.97
127.76
125.43
77.32
77.00
76.68
O
Cl
NH2
28
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


7.79
7.78
7.77
7.77
7.77
7.76
7.75
7.62
7.60
7.59
7.58
7.58
7.51
7.49
7.47
7.47
7.45
O
Cl
29
3.99
1.00
4.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

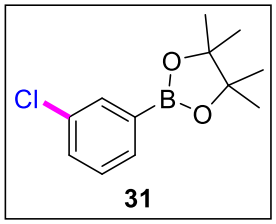

195.46
138.86
137.20
135.83
132.62
131.43
129.90
128.60
126.57
77.32
77.00
76.68
O
Cl
29
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


7.66
7.66
7.64
7.64
7.27
7.25
1.26
O
B
O
Cl
30
2.00
2.05
11.62
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)


O
B
O
Cl

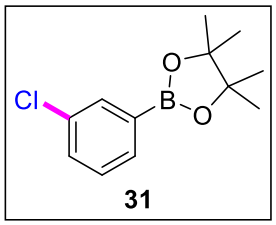
30

137.50
136.10
127.98
83.98
77.32
77.00
76.68
24.83
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


O
B
O
Cl

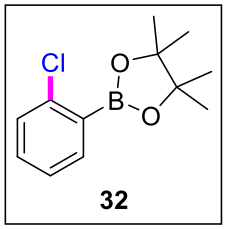
31

7.70
7.70
7.60
7.60
7.59
7.58
7.58
7.57
7.35
7.35
7.34
7.34
7.33
7.33
7.32
7.23
7.22
7.20
1.26
1.00
1.02
1.06
1.20
12.32
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0 −1 −2 −3 −4
f1 (ppm)


Cl
O
B
O

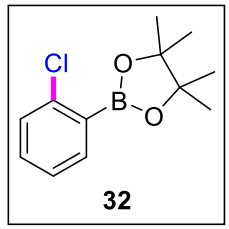
31

134.53
134.00
132.62
131.23
129.16
84.10
77.32
77.00
76.68
24.82
f1 (ppm)


Cl
O
B
O

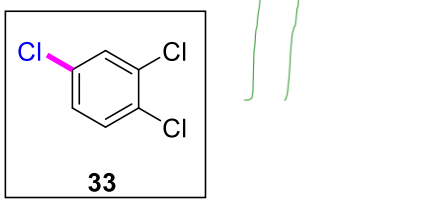
32

7.61
7.61
7.61
7.59
7.59
7.59
7.25
7.24
7.24
7.15
7.15
7.14
7.14
7.14
7.13
7.12
1.28
1.00
1.89
1.00
12.06
f1 (ppm)


Cl
O
B
O

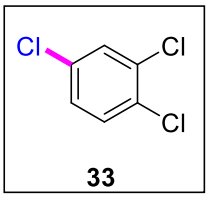
32

139.49
136.56
131.78
129.32
125.75
84.08
77.32
77.00
76.68
24.74
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
Cl
Cl

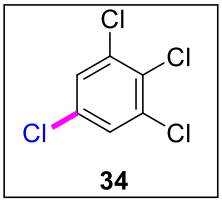
33

7.85
7.84
7.84
7.82
7.82
7.81
7.80
7.78
7.76
7.74
7.74
7.73
7.71
7.52
7.50
7.49
7.49
7.48
7.48
7.47
7.46
7.45
7.45
7.43
7.42
7.41
7.40
4.00
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
Cl
Cl

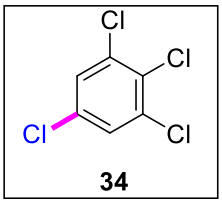
33

133.37
133.00
131.07
130.27
127.97
77.32
77.00
76.68
f1 (ppm)


Cl
Cl
Cl
Cl

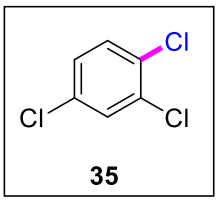
34

7.41
7.40
7.40
7.40
2.00
f1 (ppm)


Cl
Cl
Cl
Cl

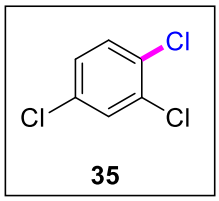
34

134.77
132.71
130.31
128.66
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
Cl
Cl

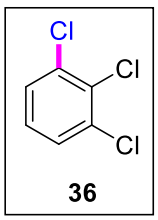
35

7.85
7.84
7.84
7.82
7.82
7.81
7.80
7.78
7.76
7.74
7.74
7.73
7.71
7.52
7.50
7.50
7.49
7.48
7.47
7.46
7.45
7.43
7.42
7.41
7.40
4.00
2.89
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


Cl
Cl
Cl

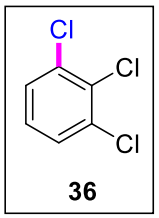
35

133.37
133.00
131.07
130.27
127.97
77.32
77.00
76.68
f1 (ppm)


Cl
Cl
Cl

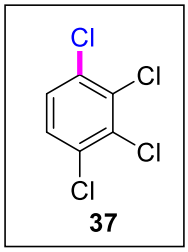
36

7.38
7.36
7.16
7.14
7.14
7.12
2.00
1.00
f1 (ppm)


Cl
Cl
Cl

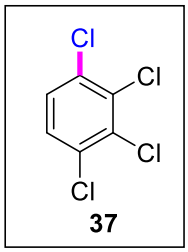
36

134.30
131.62
130.69
127.52
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
Cl
Cl
Cl

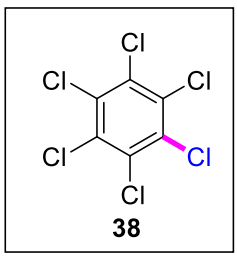
37

7.34
2.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0 -1.5 -2.0
f1 (ppm)


Cl
Cl
Cl
Cl

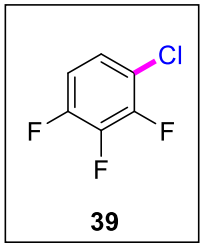
37

133.12
132.54
128.38
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
Cl
Cl
Cl
Cl
Cl

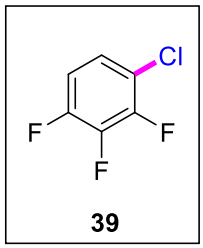
38

132.31
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Cl
F
F
F

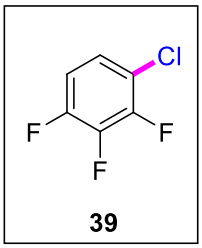
39

7.17
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.13
7.12
7.11
6.99
6.98
6.97
6.96
6.96
6.95
6.94
6.92
1.00
1.01
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

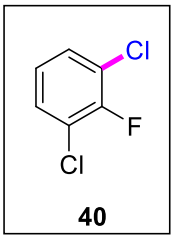

Cl
F
F
F

39

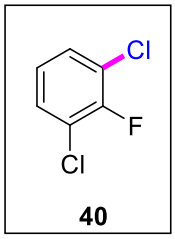
151.35
151.25
149.36
149.24
148.86
148.84
148.76
146.82
146.73
142.16
142.01
141.85
139.63
139.48
139.32
123.98
123.94
123.91
123.86
117.88
117.84
117.73
117.69
112.36
112.32
112.17
112.13
77.32
77.00
76.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



39

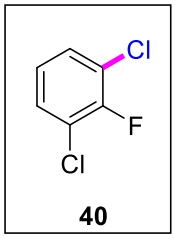


40


Cl
F
Cl

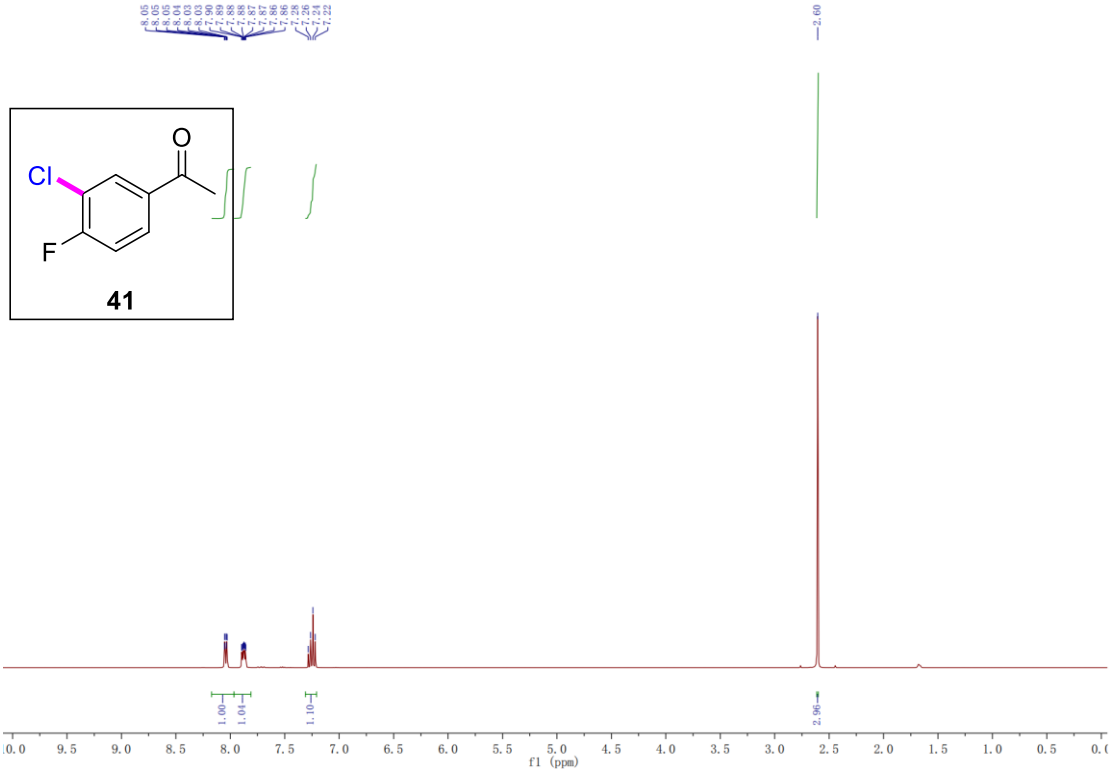
40

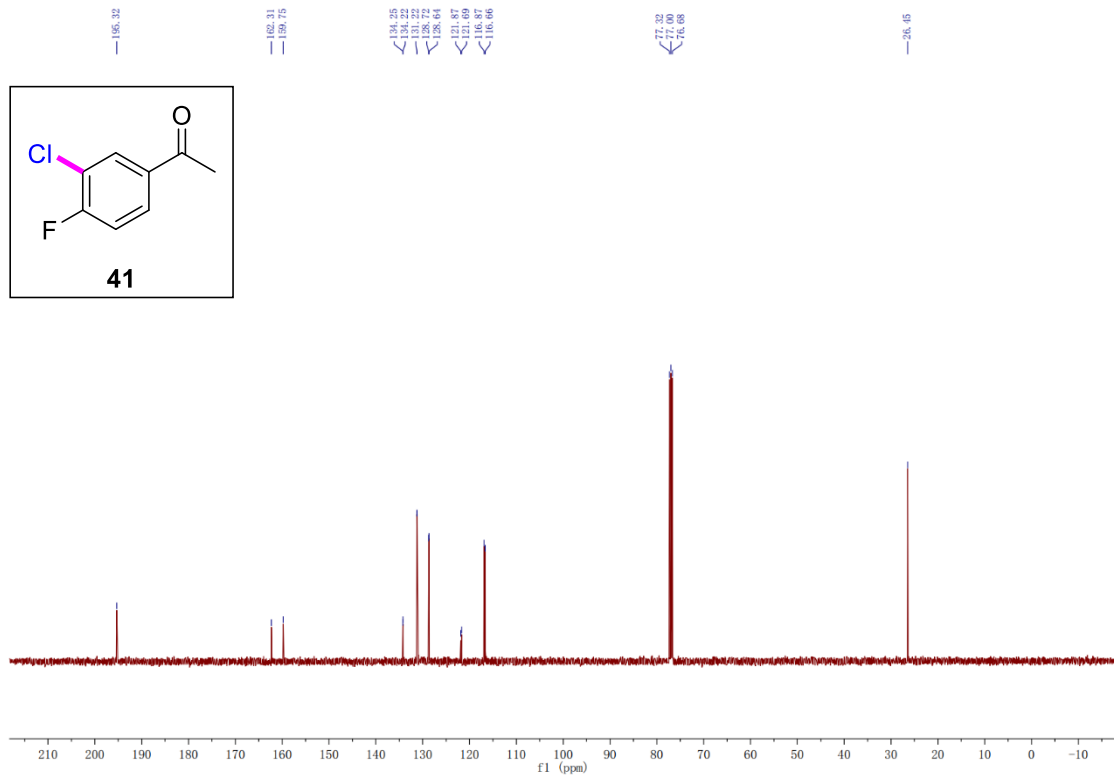
155.49
153.00
128.97
124.70
124.64
123.55
122.37
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

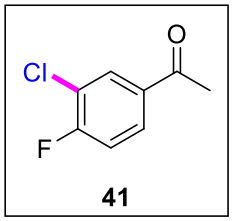

Cl
F
Cl

40

-115.74
-115.76
-115.77
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

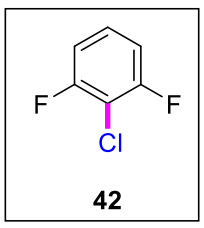

Cl
O
F
41
f1 (ppm)


Cl
O
F
41
f1 (ppm)

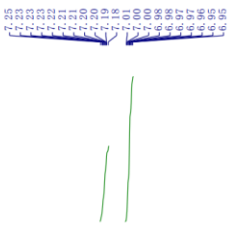

O
Cl
F

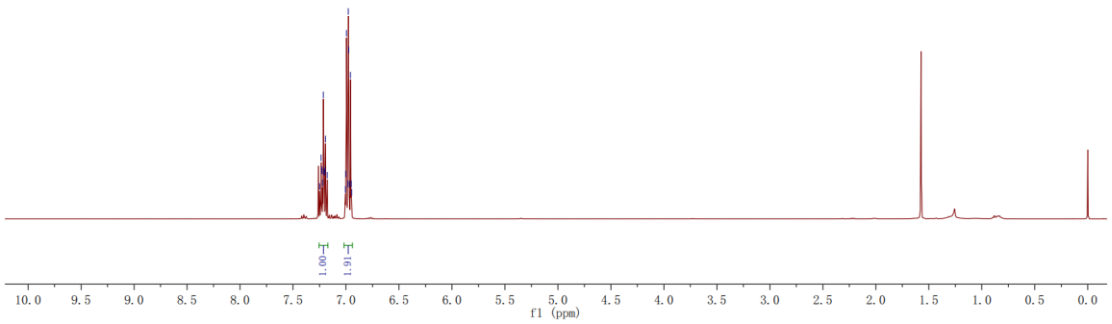
41

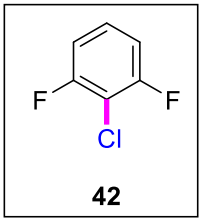
-113.08
50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)


F
F
Cl

42

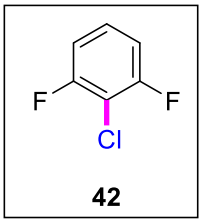

7.25
7.23
7.23
7.23
7.23
7.22
7.21
7.21
7.21
7.20
7.20
7.19
7.18
7.01
7.00
7.00
6.98
6.98
6.97
6.97
6.96
6.95
6.95


1.00
1.91
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
F
Cl

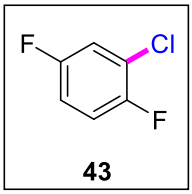
42

160.36
160.33
157.87
157.84
127.62
127.53
127.44
112.10
112.07
112.05
111.91
111.88
111.85
109.99
109.78
77.32
77.00
76.68
70 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25
f1 (ppm)

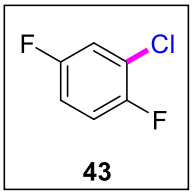

F
F
Cl

42

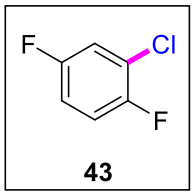
-113.08
50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)


F
Cl
F
43

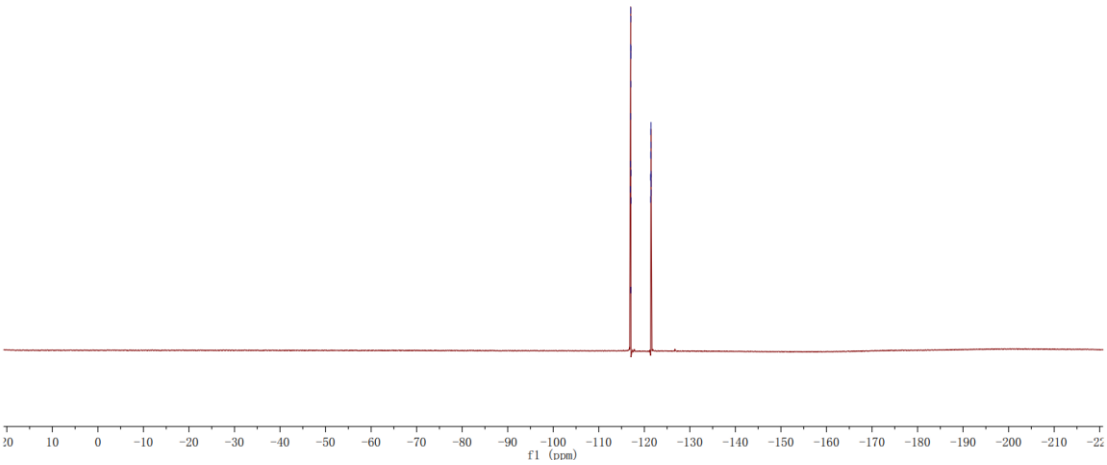
f1 (ppm)

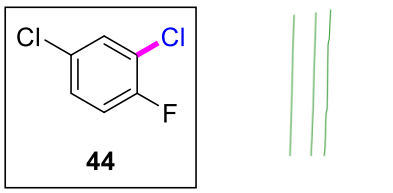

F
Cl
F
43

f1 (ppm)

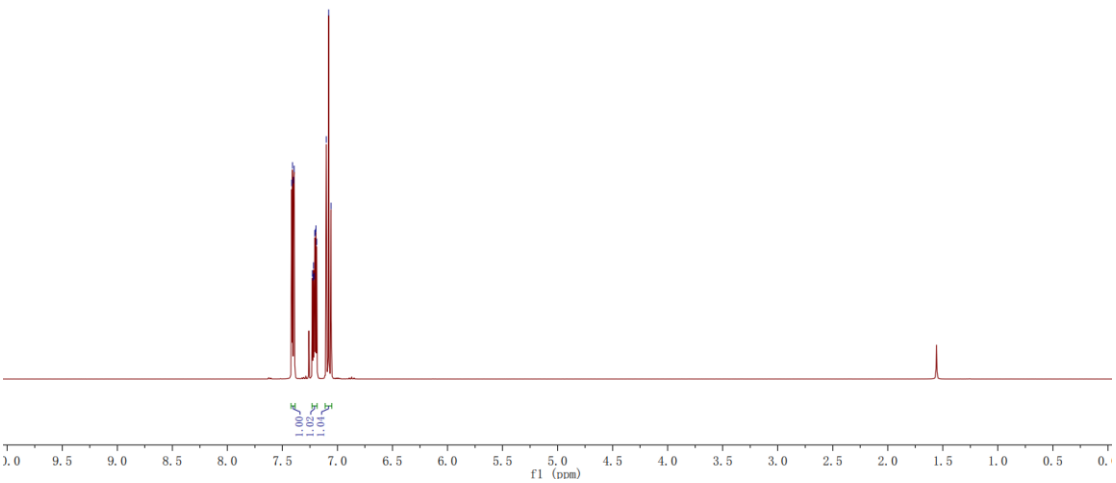


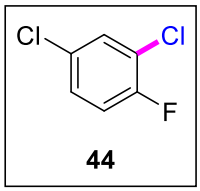
43





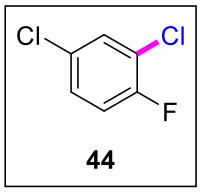
44




Cl
Cl
F

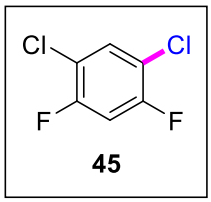
44

158.17
155.69
130.40
129.55
129.31
128.22
128.15
122.07
121.98
117.56
117.34
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

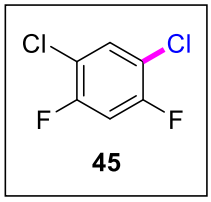

Cl
Cl
F

44

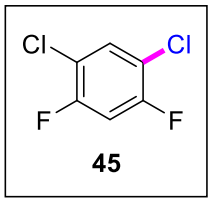
117.74
117.75
117.76
117.77
117.77
117.78
117.78
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


Cl
Cl
F
F
45

7.49
7.47
7.45
7.04
7.02
7.00
1.00
1.01
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

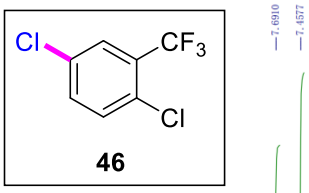

Cl
Cl
F
F
45

157.96
157.85
155.45
155.35
131.14
117.21
117.14
117.06
116.98
106.26
106.00
105.74
77.32
77.00
76.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
Cl
F
F

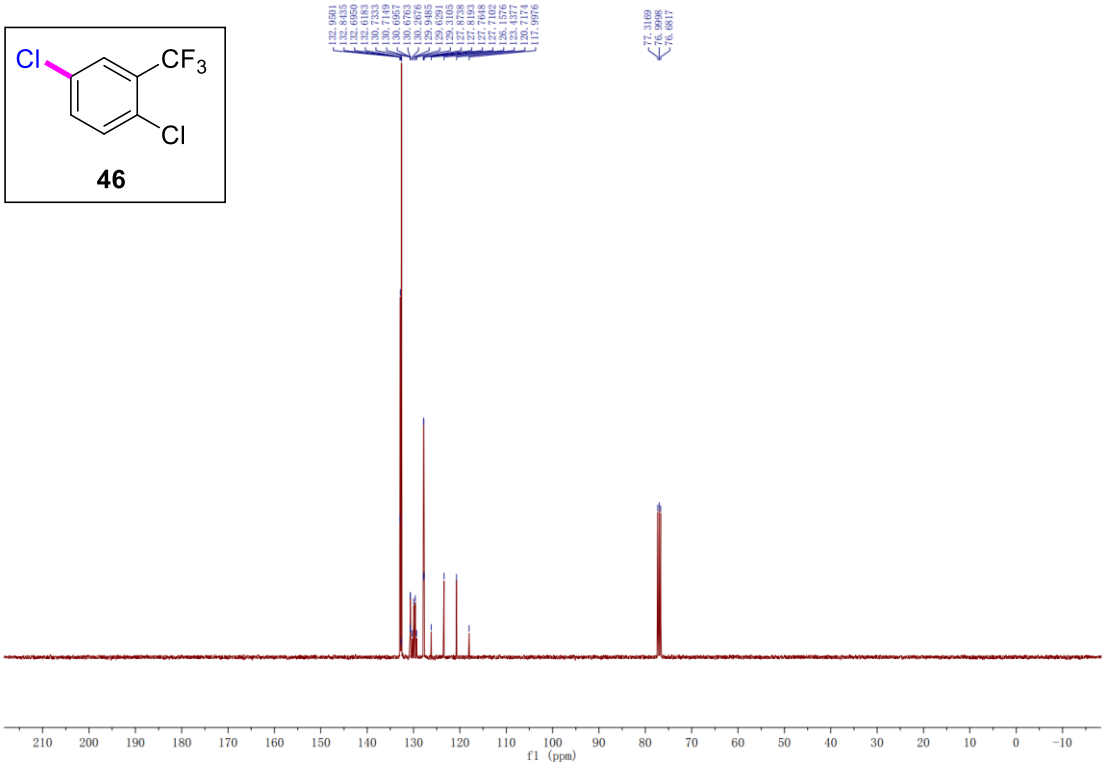
45

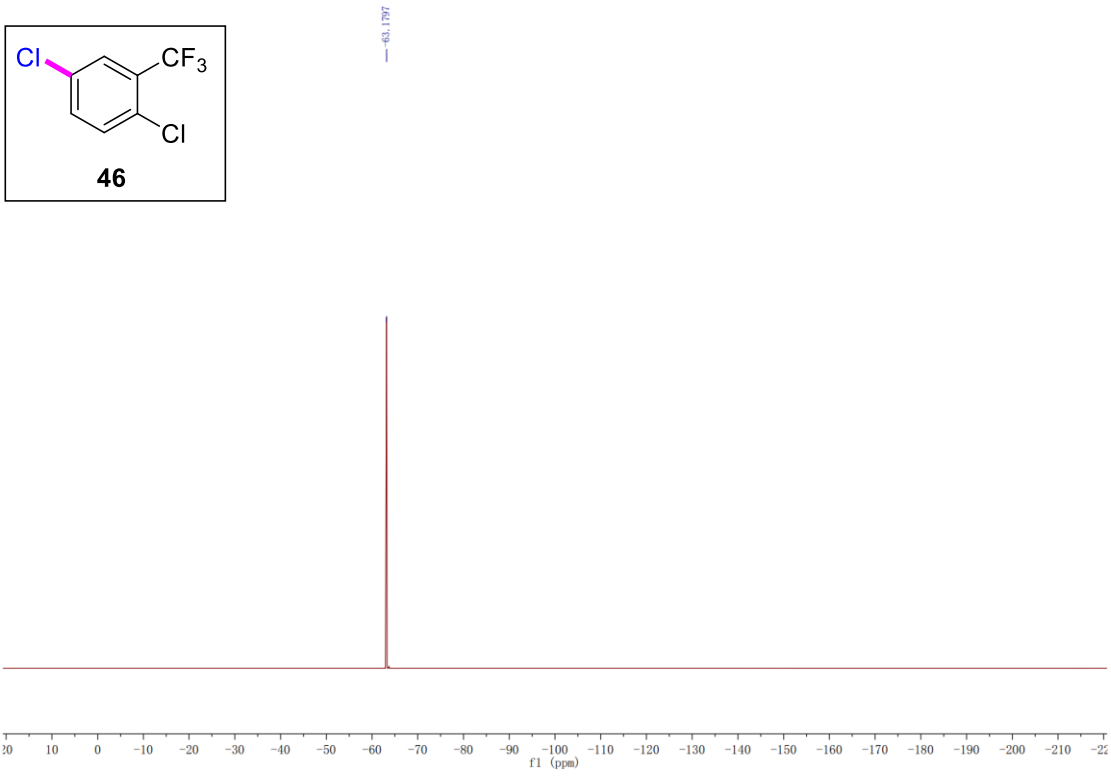
-112.00
-112.00
-112.02
-112.04
f1 (ppm)

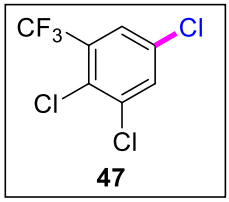

Cl
CF3
Cl

46

7.6910
7.4577
0.99
1.97
f1 (ppm)

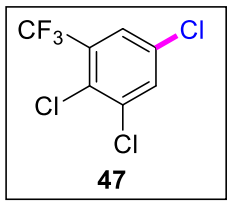

Cl
CF3
Cl
46
f1 (ppm)


Cl
CF3
Cl
46
-63.1797
f1 (ppm)


CF3
Cl
Cl
Cl

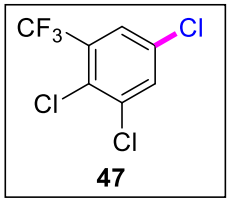
47

7.77
7.63
7.63
7.63
7.62
1.00
0.97
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


CF3
Cl
Cl
Cl

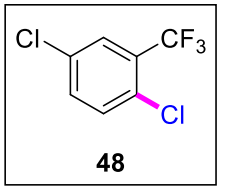
47

137.11
132.87
131.59
131.12
129.16
128.19
128.27
127.94
125.14
120.42
77.32
77.00
76.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


CF3
Cl
Cl
Cl

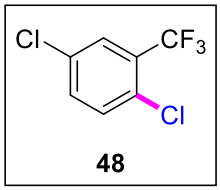
47

62.82
62.83
62.84
62.85
62.86
f1 (ppm)


Cl
CF3
Cl

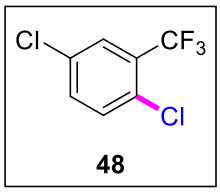
48

7.6910
7.4577
0.99
1.97
f1 (ppm)


Cl
CF3
Cl

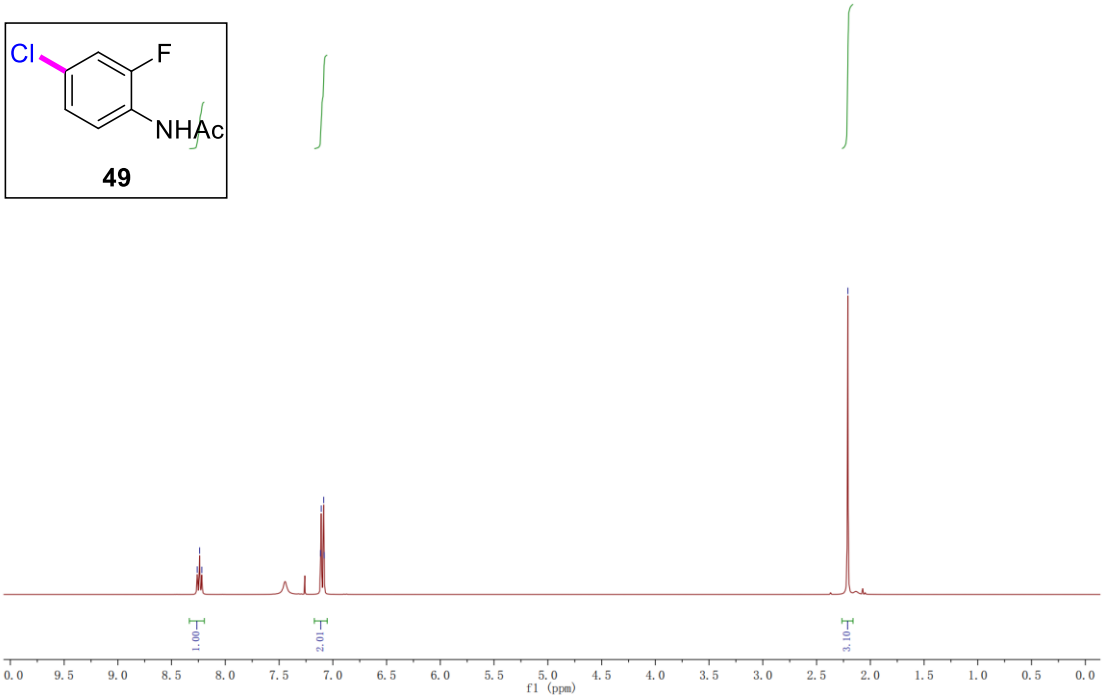
48

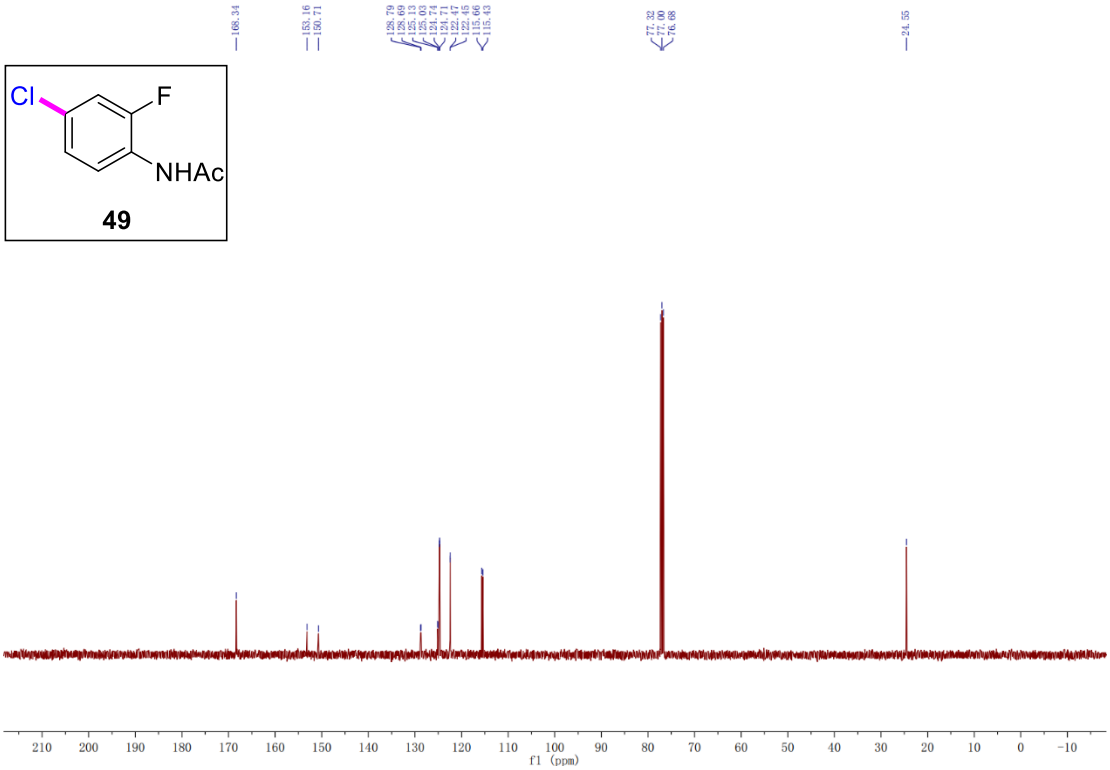
132.9601
132.8435
132.6183
130.7333
130.7149
130.6993
130.3676
129.9485
129.6291
129.3106
127.8738
127.8193
127.7648
127.7102
126.1576
123.4377
120.7174
117.9996
77.3169 CDCl3
76.9998 CDCl3
76.6817 CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

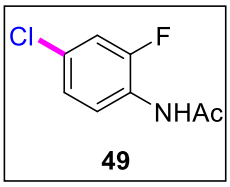

Cl
CF3
Cl

48

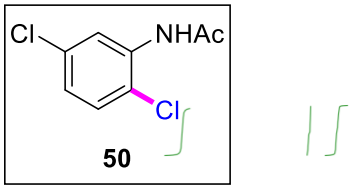
-63.1797
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.26
8.24
8.22
7.11
7.11
7.09
7.08
2.21
Cl
F
NHAc
49
1.00
2.01
3.10
0.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

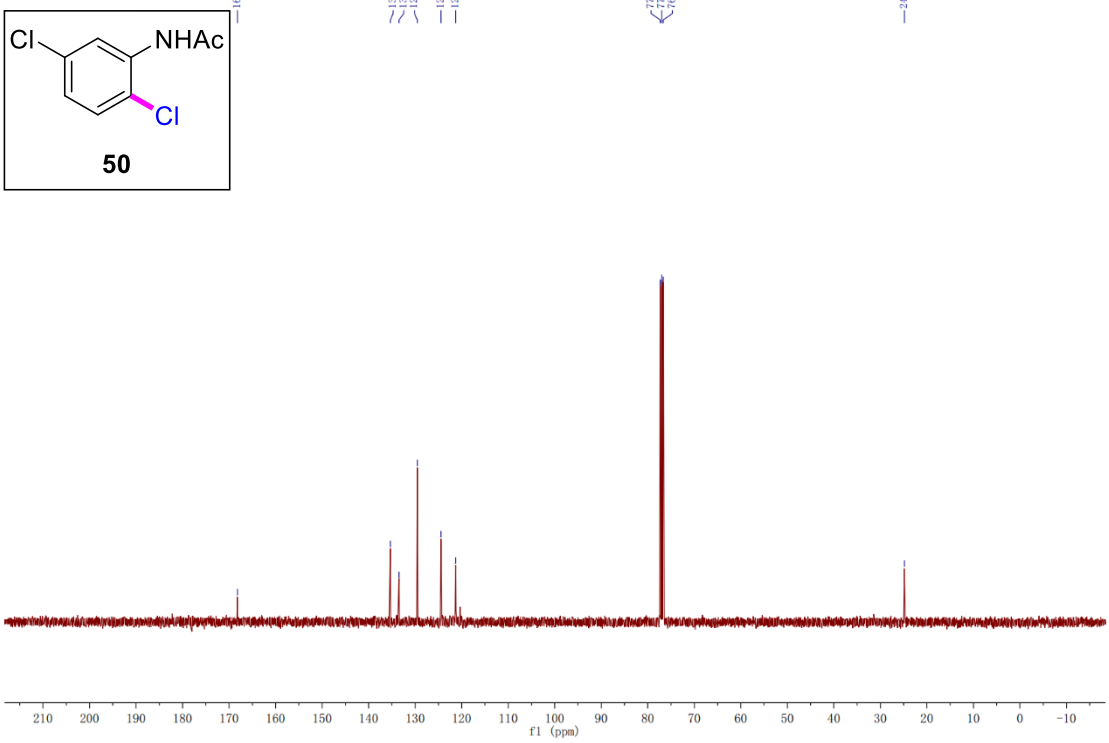

166.34
153.16
150.71
128.79
128.69
125.13
125.03
121.74
121.71
122.47
122.45
115.66
115.43
77.32
77.00
76.68
24.55
Cl
F
NHAc
49
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

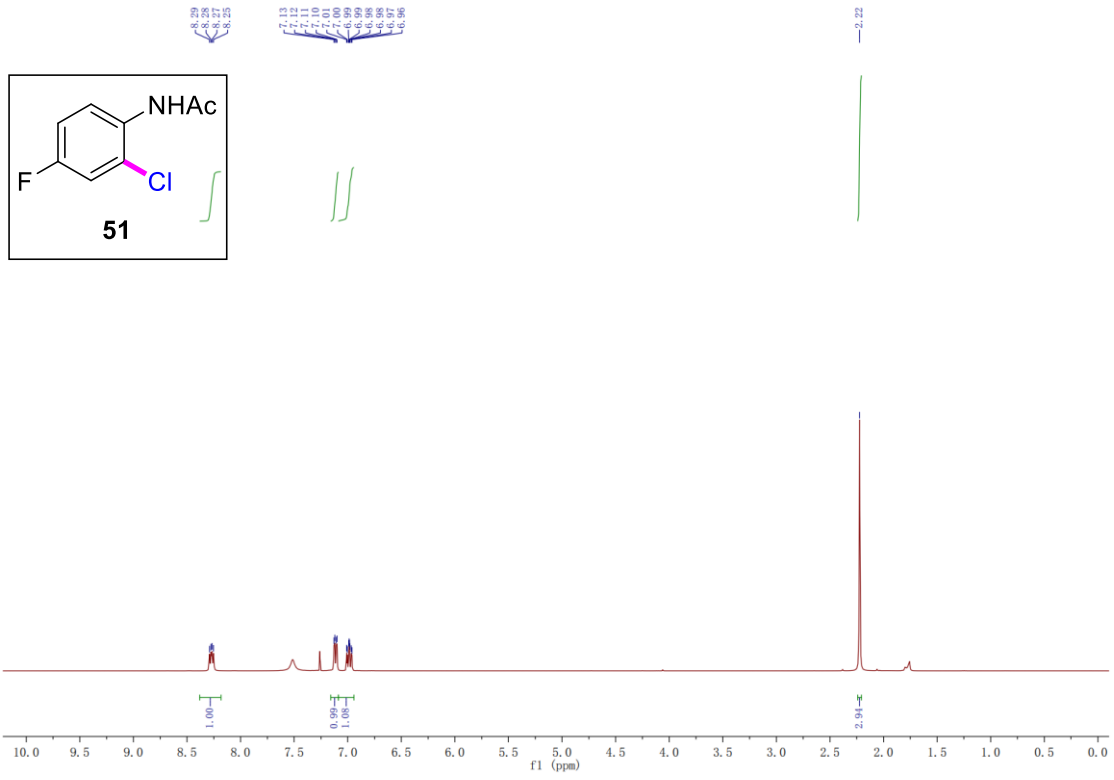


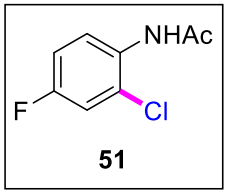
49



50

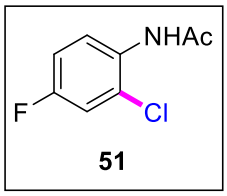

Cl
NHAc
Cl
50
168.22
135.34
133.49
129.94
124.45
121.29
77.32
77.00
76.68
24.84
f1 (ppm)


NHAc
F
Cl
51
8.29
8.28
8.27
8.25
7.13
7.12
7.11
7.10
7.01
7.00
6.99
6.99
6.98
6.98
6.97
6.96
2.22
1.00
0.99
1.08
2.94
f1 (ppm)


NHAc
F
Cl

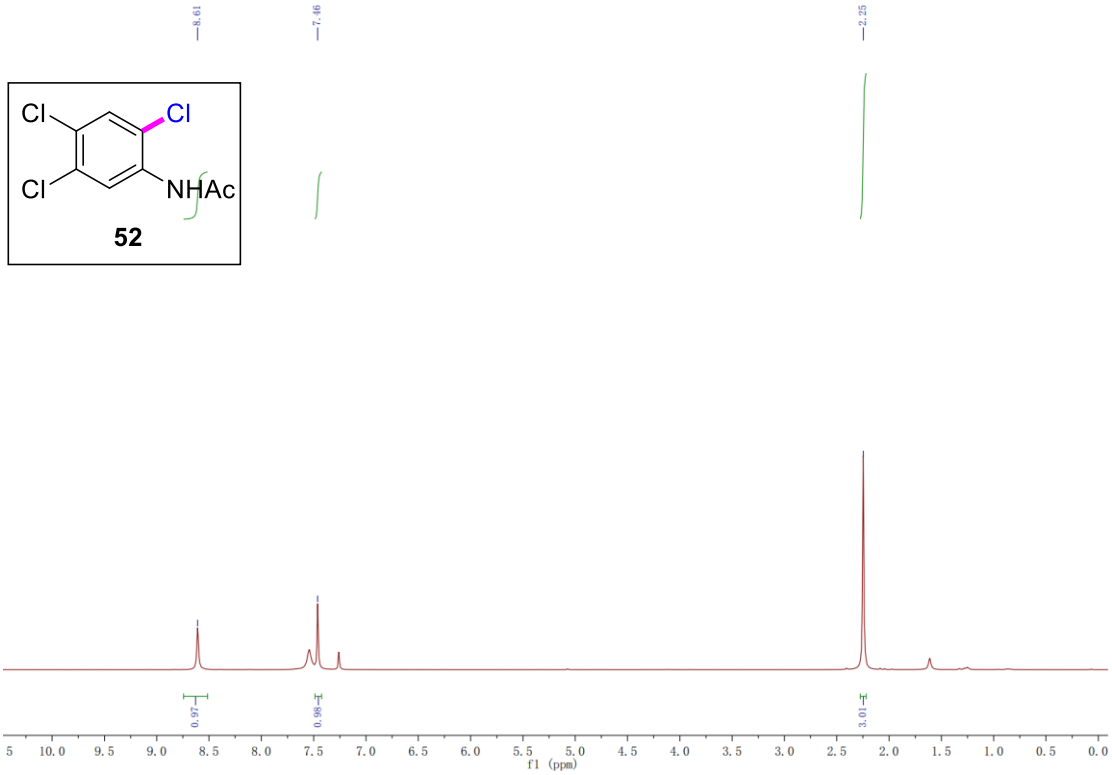
51

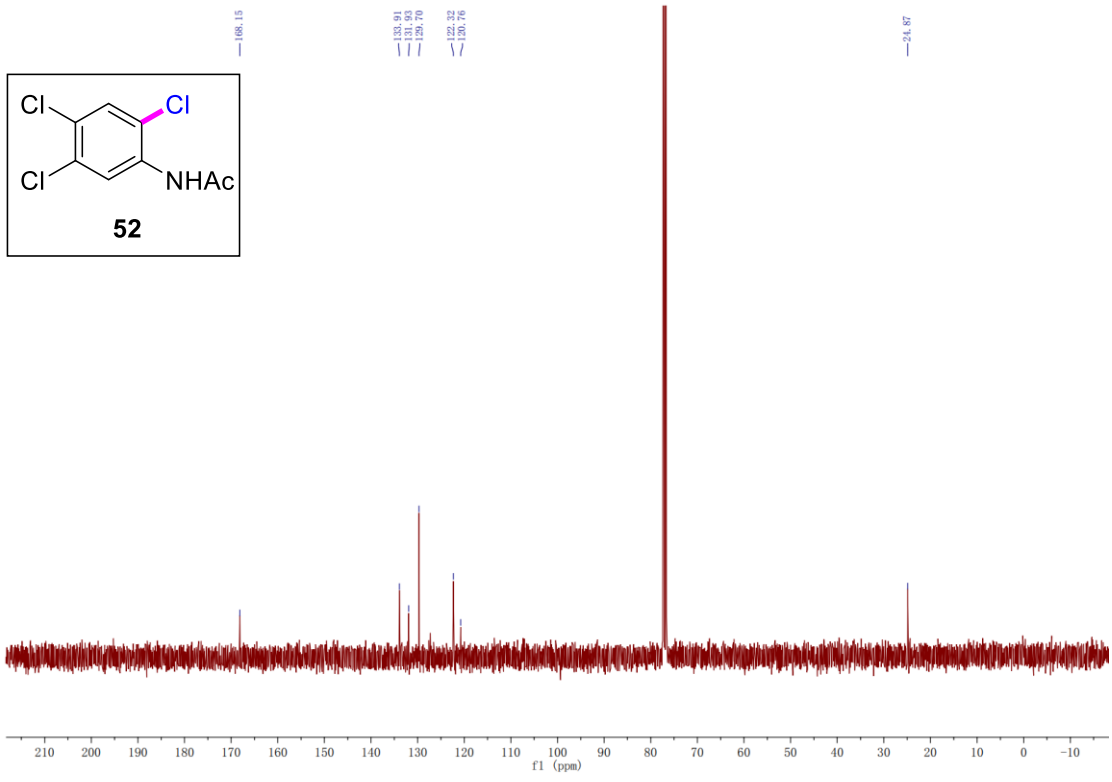
168.21
159.57
157.12
130.99
130.96
123.09
123.01
116.32
116.06
114.68
114.47
77.32
77.00
76.68
24.62
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

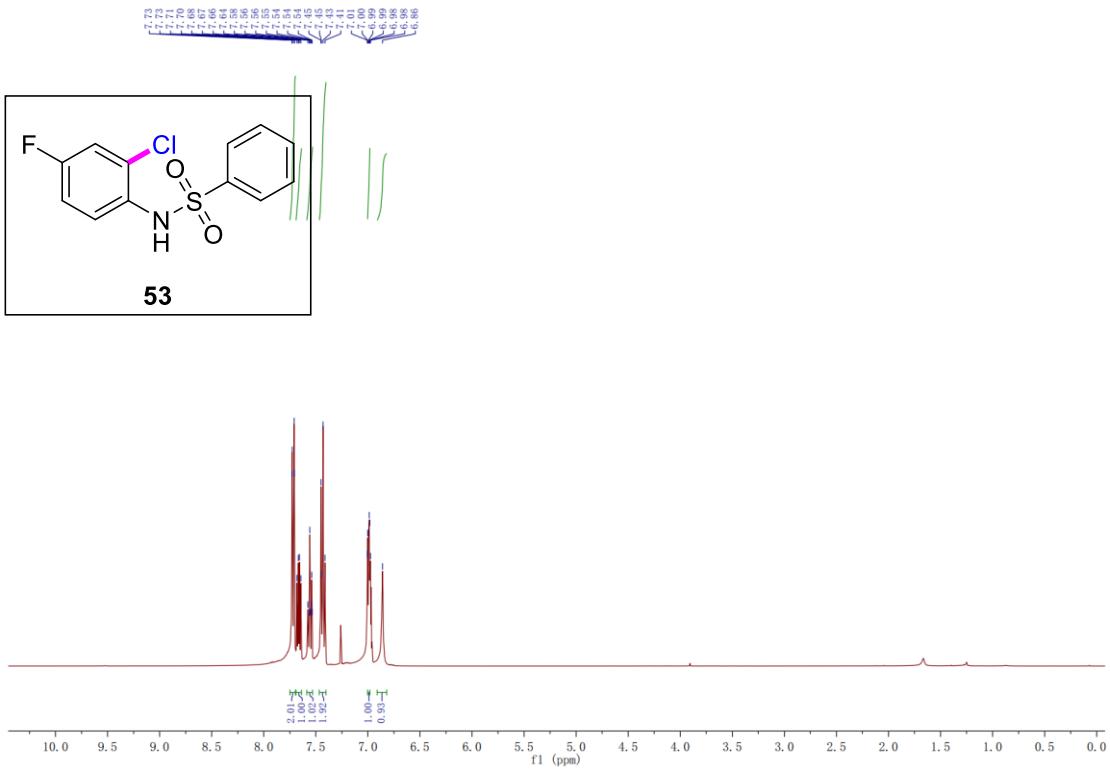

NHAc
F
Cl

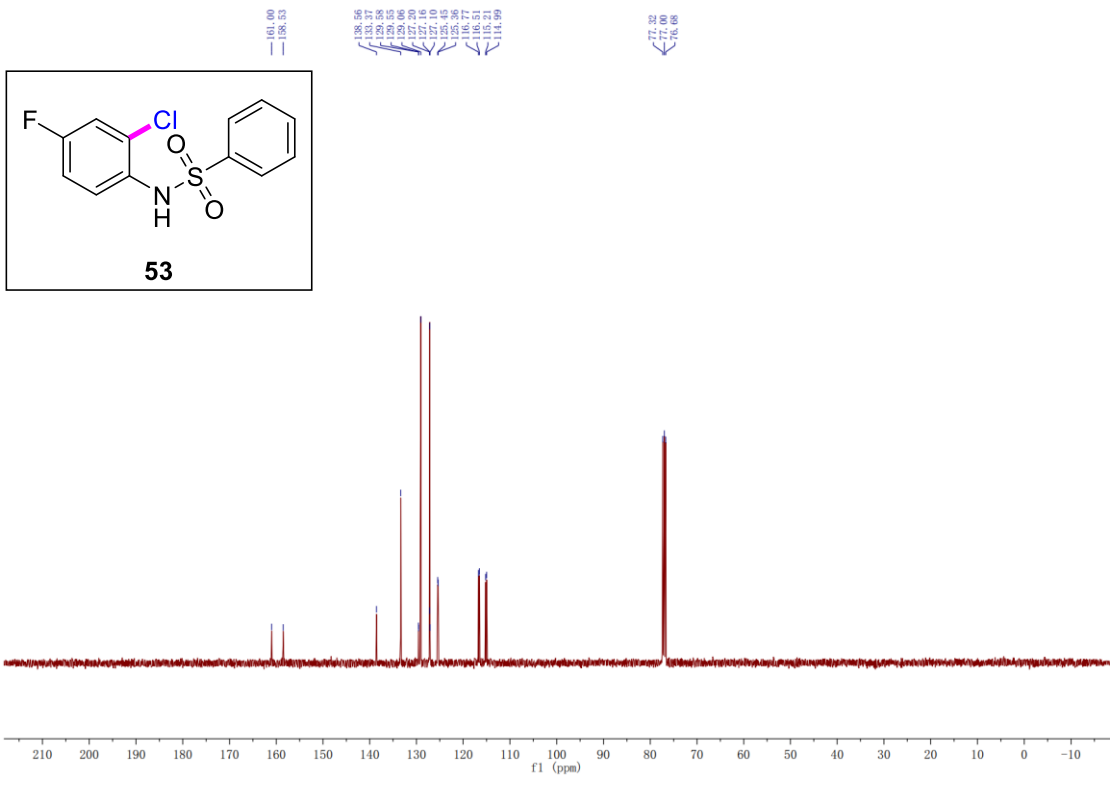
51

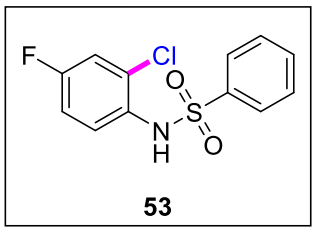
116.26
116.27
116.28
116.29
116.31
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


8.61
7.46
2.25
Cl
Cl
Cl
NHAc
52
0.97
0.98
3.01
5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


168.15
133.91
131.93
129.70
122.32
120.76
24.87
Cl
Cl
Cl
NHAc
52
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

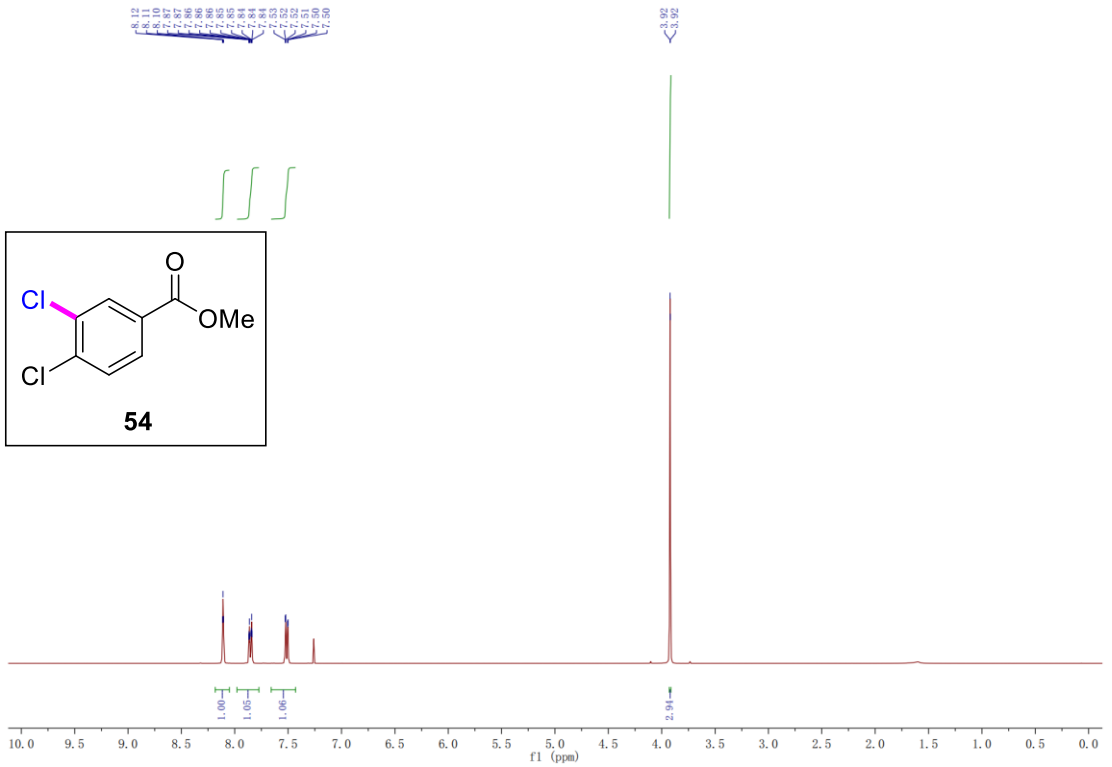

F
Cl
O
S
O
N
H
53
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


F
Cl
O
S
O
N
H
53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)


F
Cl
O
S
N
H
O

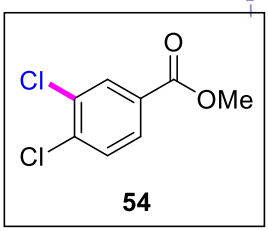
53

113.76
113.77
113.78
113.80
113.82
f1 (ppm)


8.12
8.11
8.10
7.87
7.86
7.85
7.84
7.53
7.52
7.51
7.50
3.92
1.00
1.05
1.06
2.94
f1 (ppm)

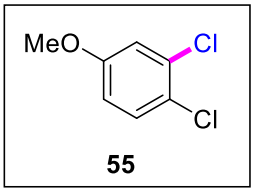
O
Cl
OMe
Cl

54


O
Cl
OMe
Cl

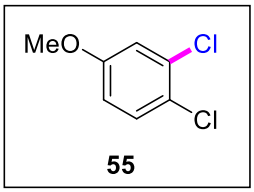
54

165.19
137.55
132.91
131.82
130.51
129.93
128.62
77.32
77.00
76.68
52.53
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


MeO
Cl
Cl

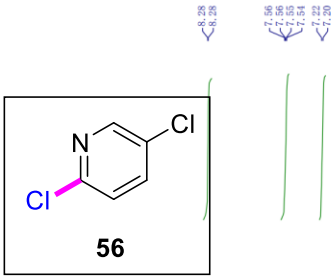
55

7.33
7.30
6.99
6.98
6.77
6.76
6.75
6.74
3.79
1.00
0.94
0.96
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


MeO
Cl
Cl

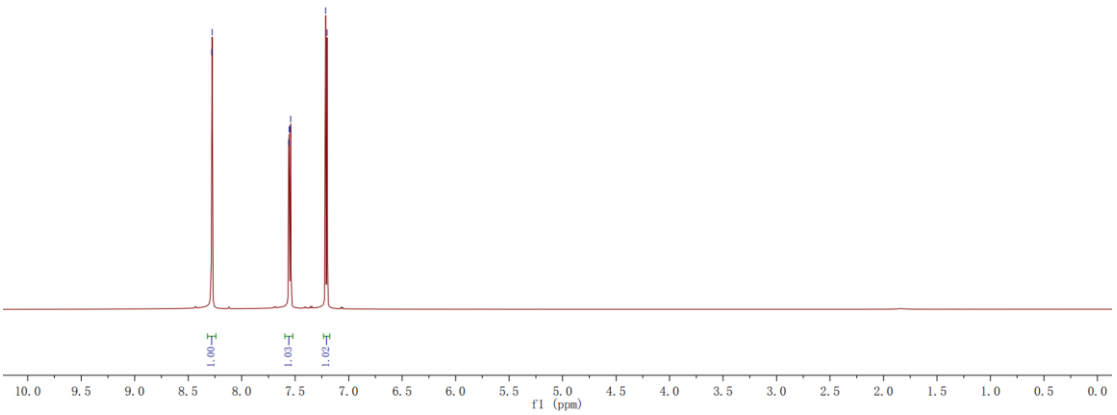
55

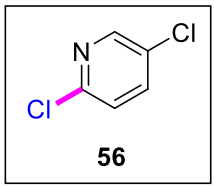
158.62
132.81
130.62
123.86
115.67
114.08
77.32
77.00
76.68
55.70
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


N
Cl
Cl

56

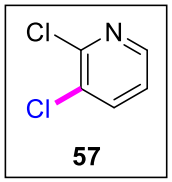
8.28
8.28
7.56
7.56
7.55
7.54
7.22
7.20


1.00
1.03
1.02
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


N
Cl
Cl

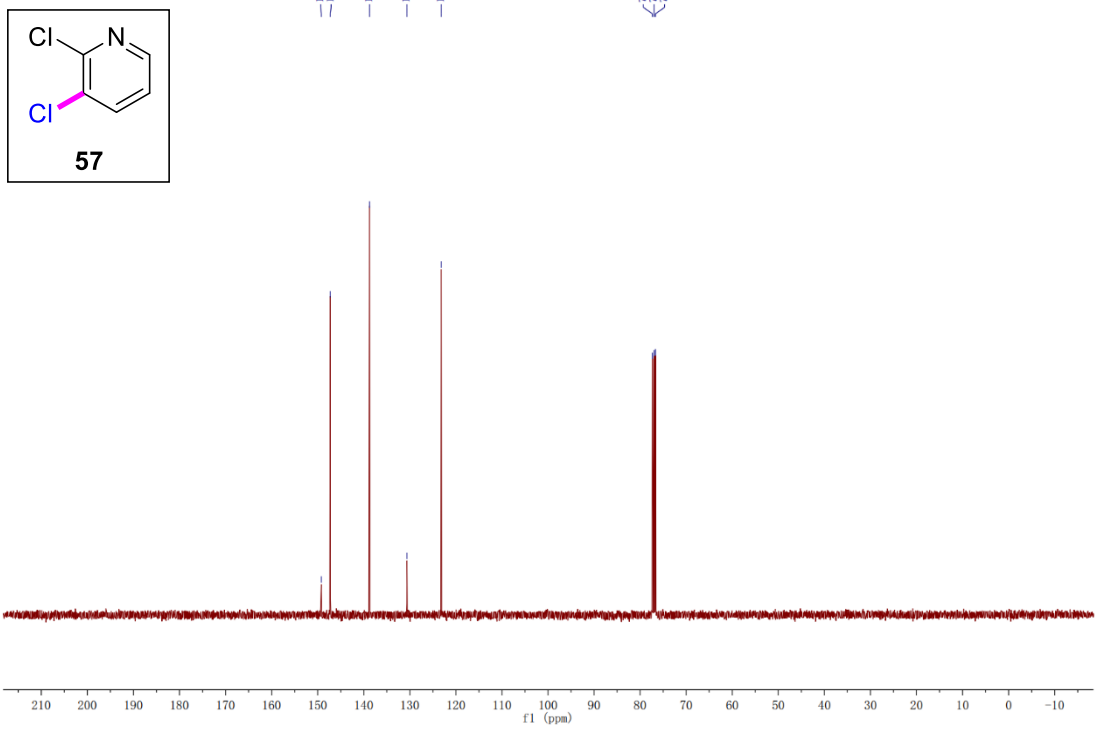
56

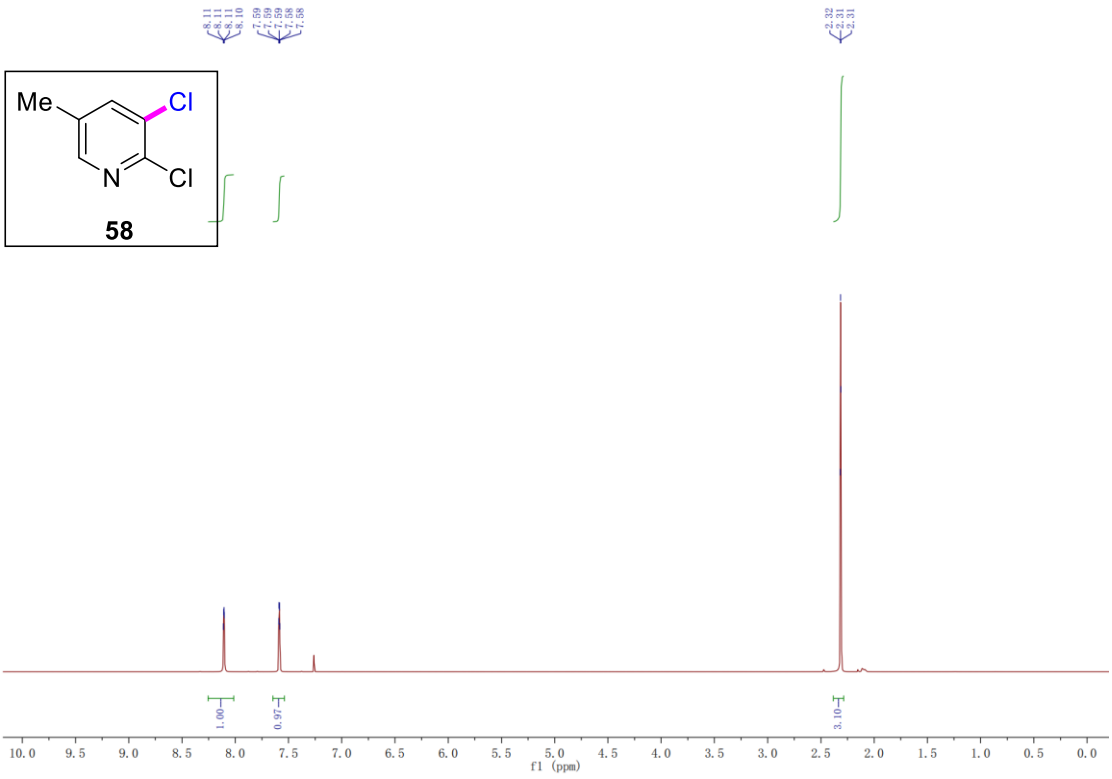
149.38
148.39
138.36
130.85
125.05
77.21
77.00
76.79
f1 (ppm)

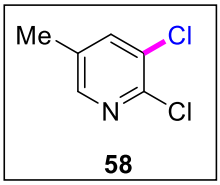

Cl
N
Cl

57

1.00
1.00
1.06
f1 (ppm)

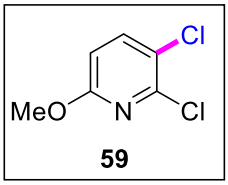

Cl
N
Cl
57
149.20
147.24
138.76
130.64
123.19
77.32
77.00
76.68
f1 (ppm)


Me
Cl
N
Cl
58
8.11
8.11
8.10
7.59
7.59
7.59
7.58
7.58
2.32
2.31
2.31
1.00
0.97
3.10
f1 (ppm)


Me
Cl
N
Cl

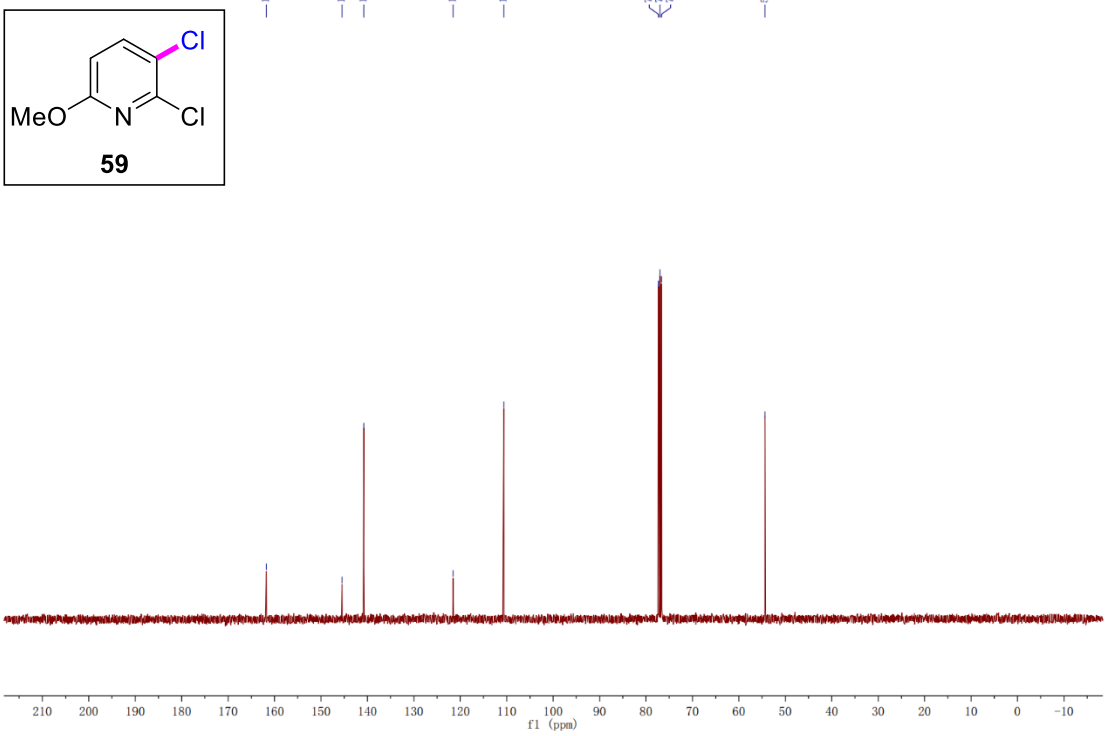
58

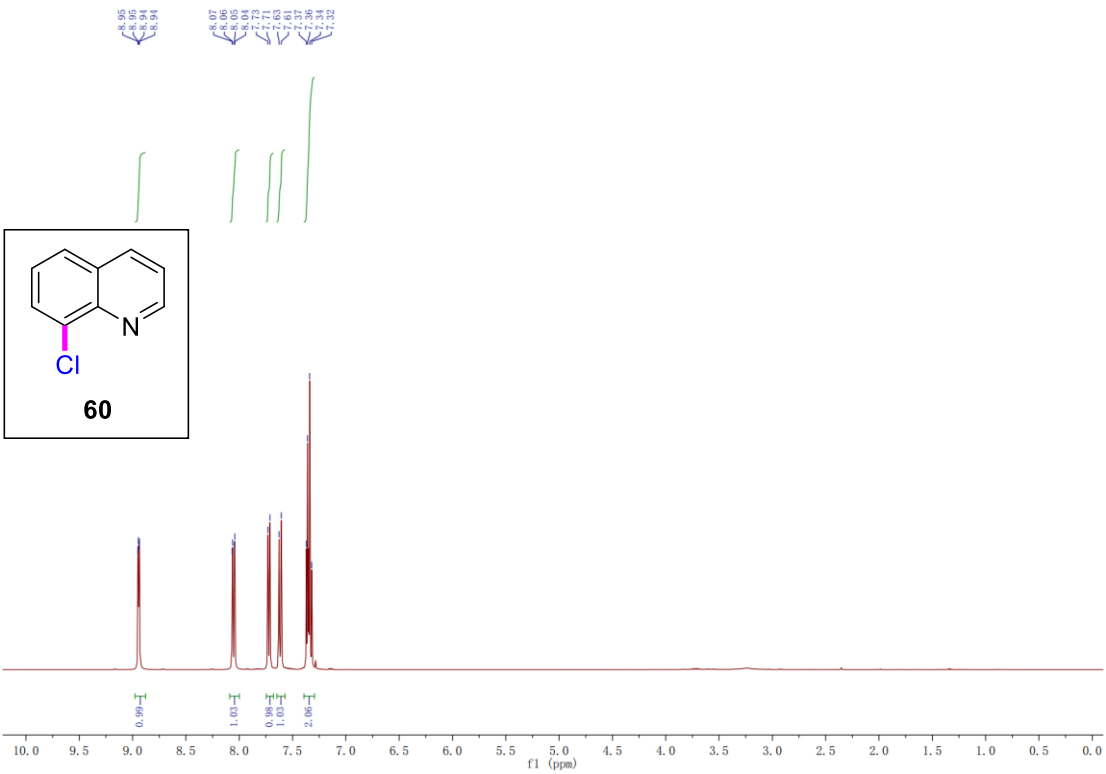
147.51
146.16
139.26
133.66
129.82
77.32
77.00
76.68
17.36
f1 (ppm)

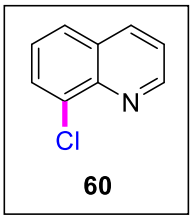

Cl
MeO
N
Cl

59

7.61
7.60
7.58
7.58
6.65
6.65
6.63
6.63
3.92
3.92
1.00
1.01
3.08
f1 (ppm)

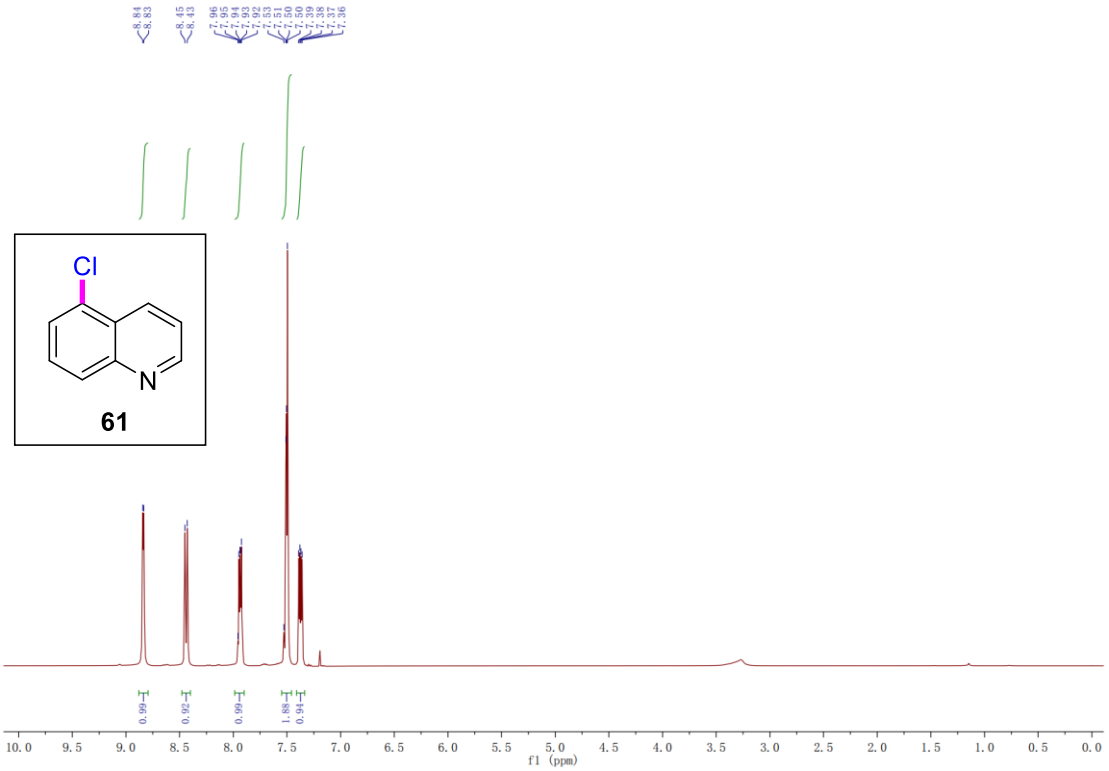

Cl
MeO
N
Cl
59
161.78
145.47
140.76
121.54
110.64
77.32
77.00
76.68
54.37
f1 (ppm)


8.95
8.95
8.94
8.94
8.07
8.06
8.05
8.04
7.73
7.71
7.63
7.61
7.37
7.36
7.34
7.32
N
Cl
60
0.99
1.03
0.98
1.03
2.06
f1 (ppm)


Cl
N

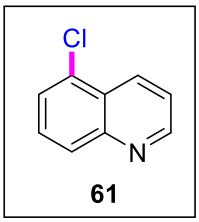
60

150.66
144.03
136.29
133.03
129.32
129.25
126.75
126.22
121.64
77.32
77.00
76.68
f1 (ppm)


8.84
8.83
8.45
8.43
7.96
7.95
7.94
7.93
7.92
7.53
7.51
7.50
7.39
7.38
7.37
7.36
0.99
0.92
0.99
1.88
0.94
f1 (ppm)

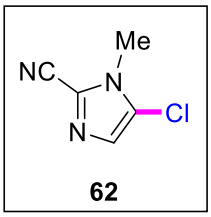
Cl
N

61


Cl
N

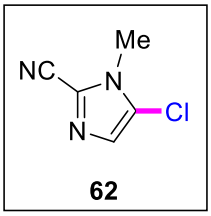
61

150.79
148.64
132.79
131.18
130.67
128.50
126.53
126.24
121.75
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
NC
N
N
Cl

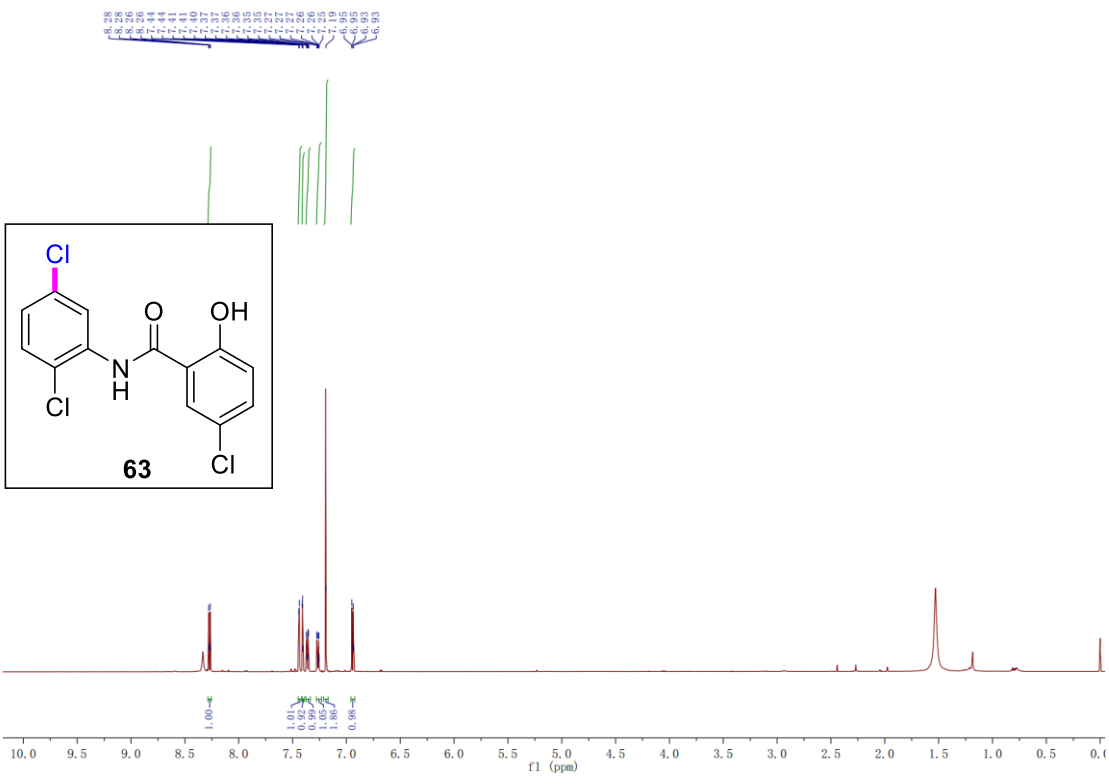
62

7.11
3.78
1.00
3.04
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


Me
NC
N
N
Cl

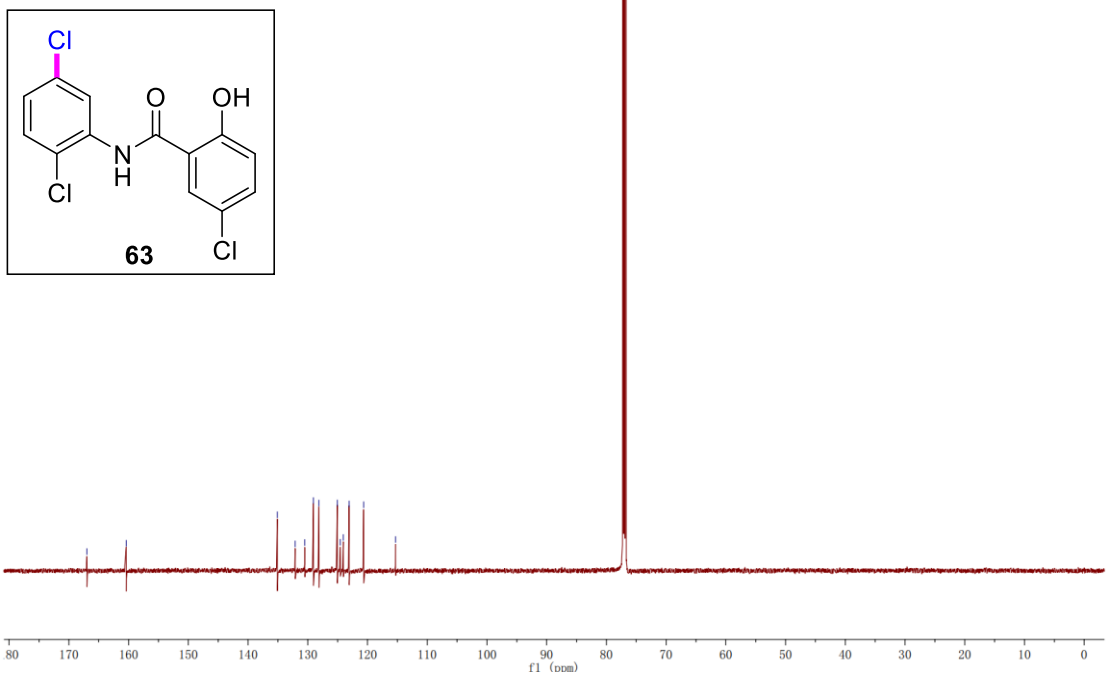
62

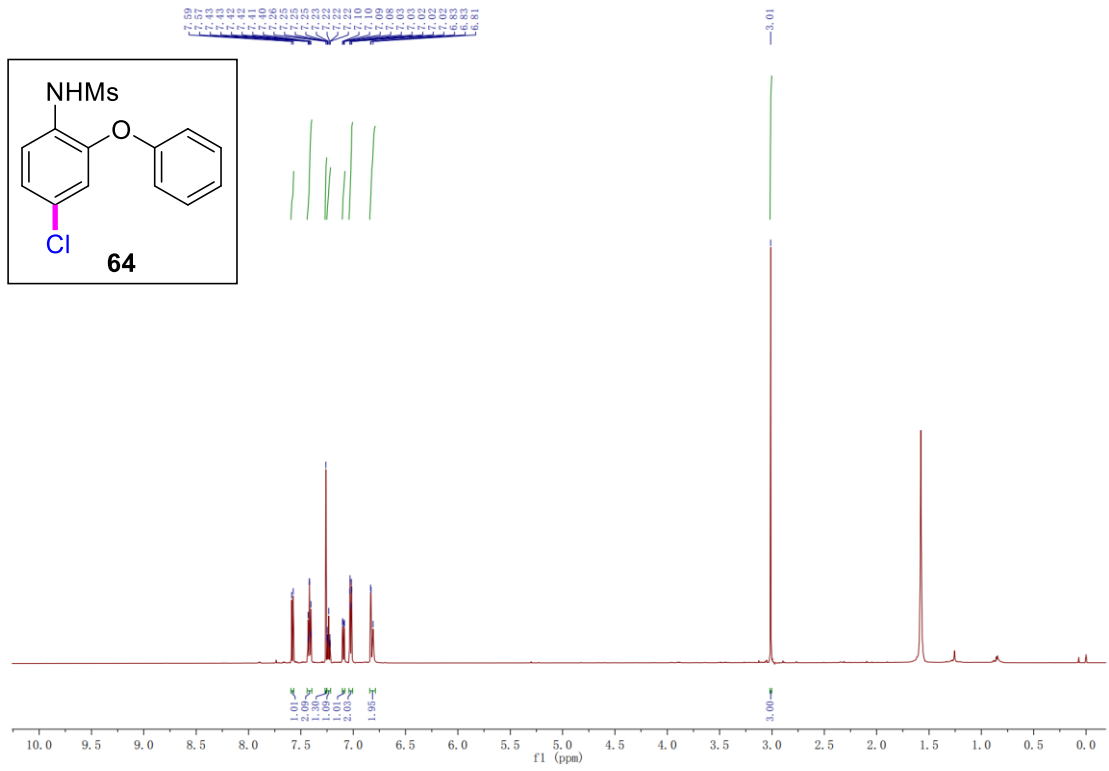
128.56
122.48
121.60
110.43
77.32
77.00
76.68
32.07
f1 (ppm)

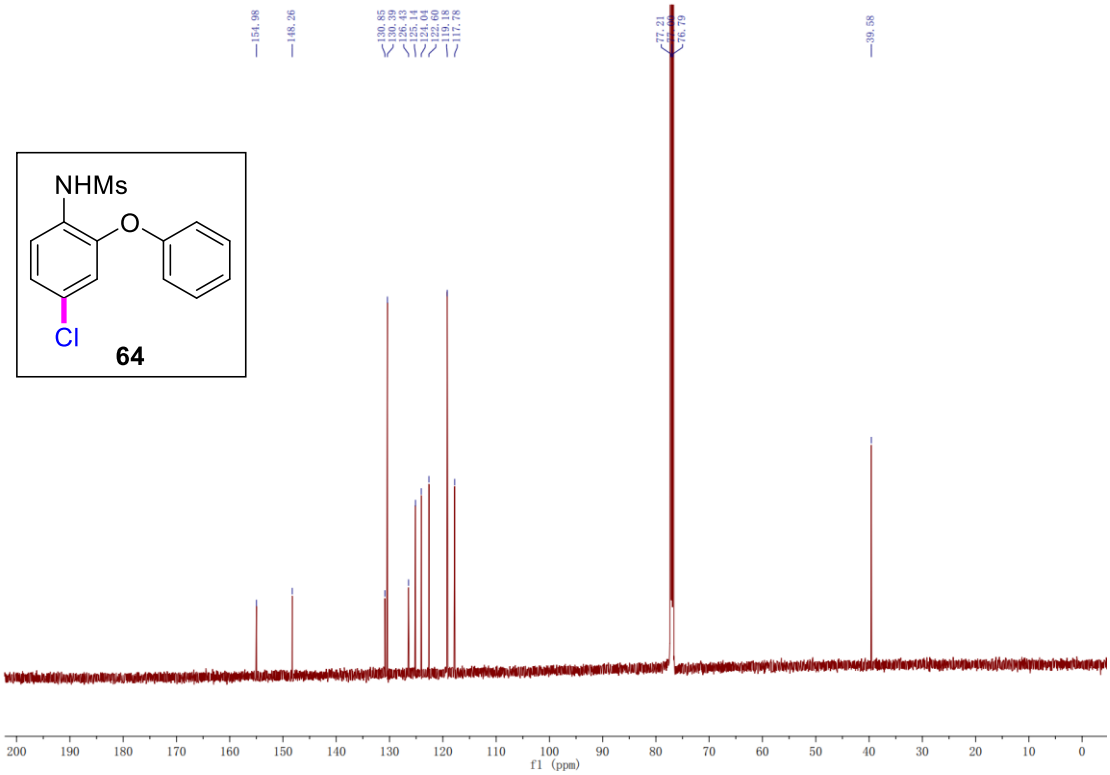

8.28
8.26
7.44
7.41
7.40
7.37
7.36
7.35
7.27
7.26
7.25
7.19
6.95
6.93
1.00
1.01
0.92
0.99
1.05
1.86
0.98
f1 (ppm)

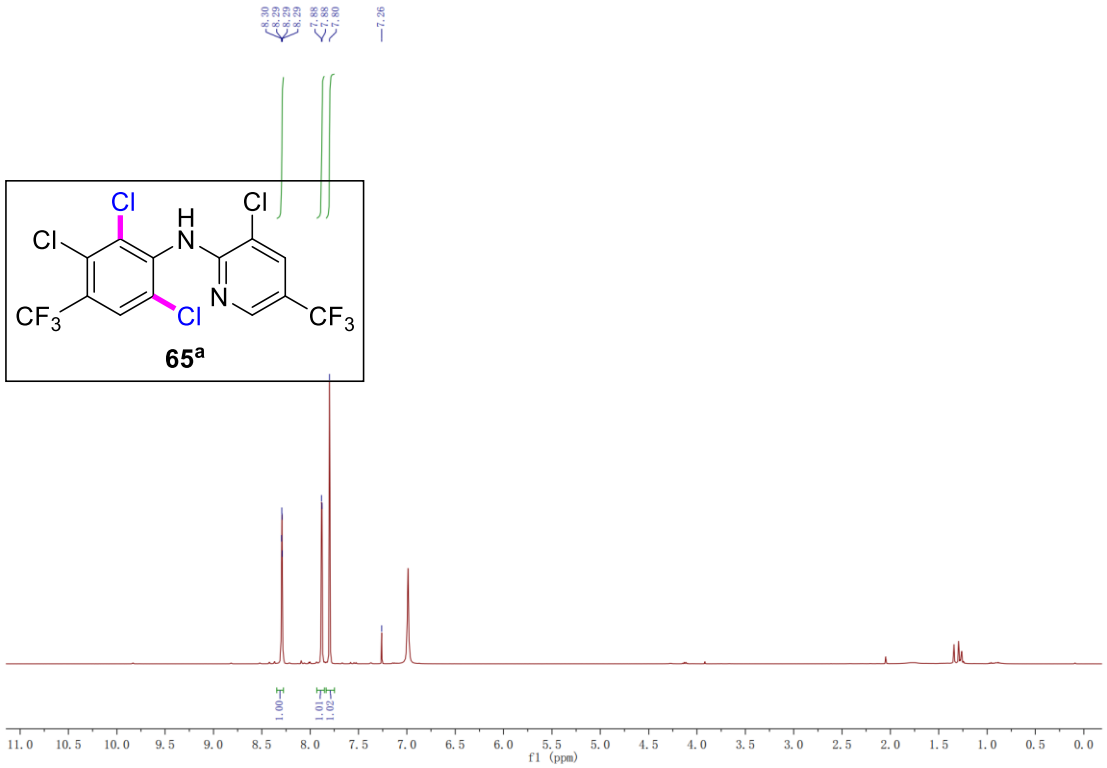
Cl
O
OH
N
H
Cl
Cl

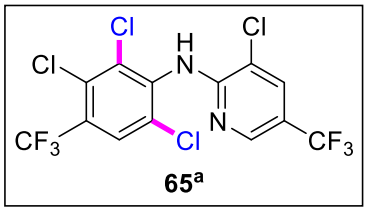
63


Cl
O
OH
N
H
Cl
Cl
63

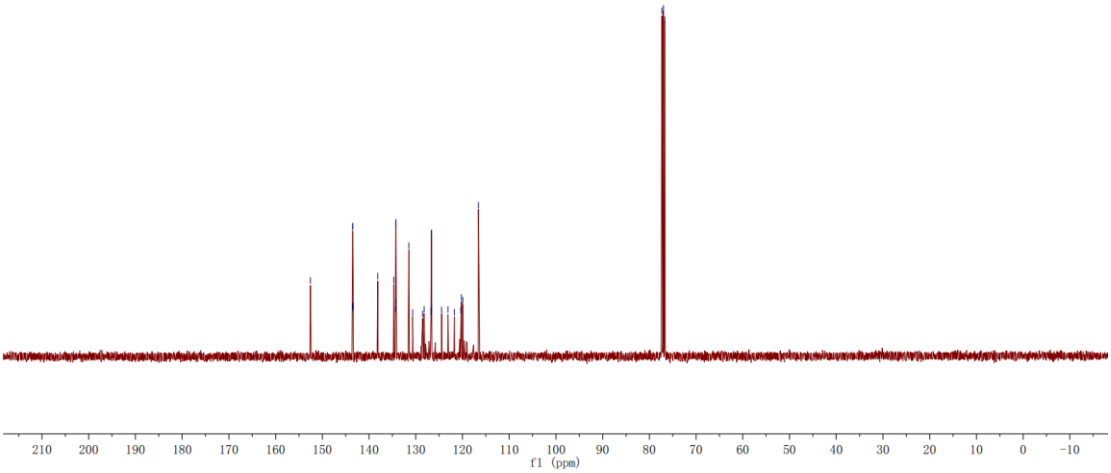

NHMs
O
Cl
64

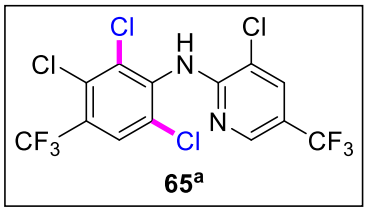

NHMs
O
Cl
64
154.98
148.26
130.85
130.39
126.43
125.14
124.04
122.60
119.18
117.78
77.21
76.79
39.58
f1 (ppm)


Cl
H
N
Cl
Cl
N
CF3
Cl
CF3
65a
8.30
8.29
8.29
8.29
7.88
7.88
7.80
7.26
1.00
1.01
1.02
f1 (ppm)

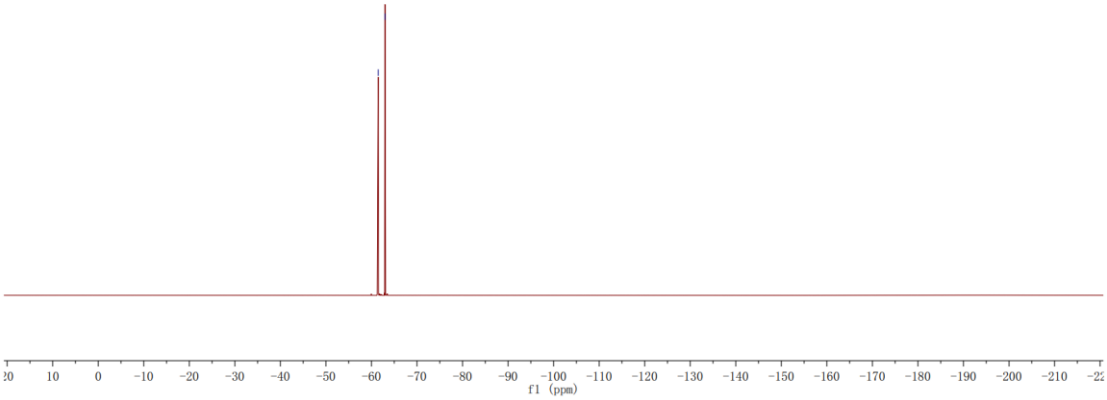


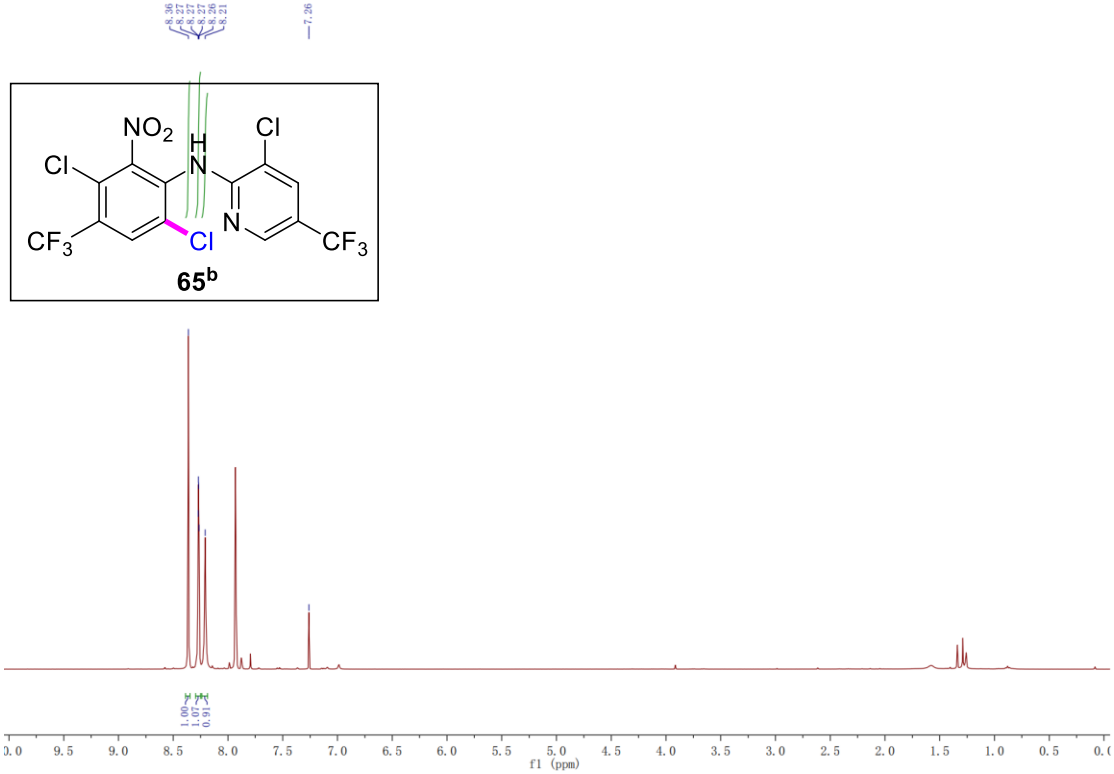
65[a]

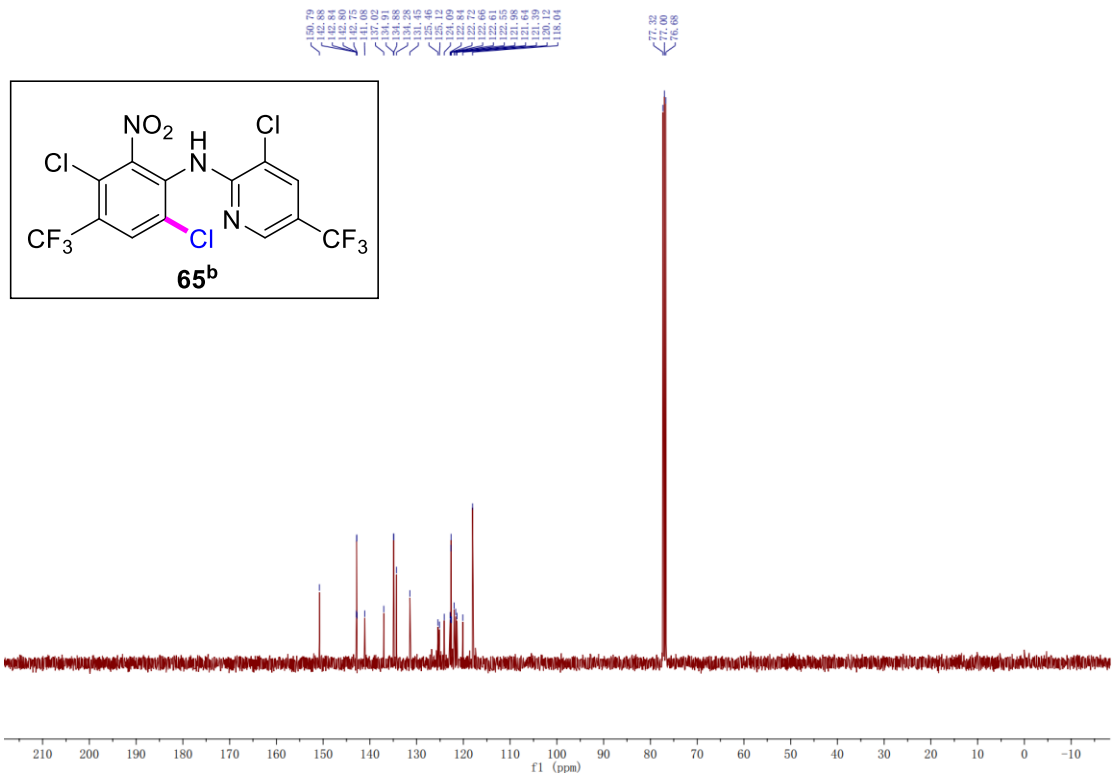


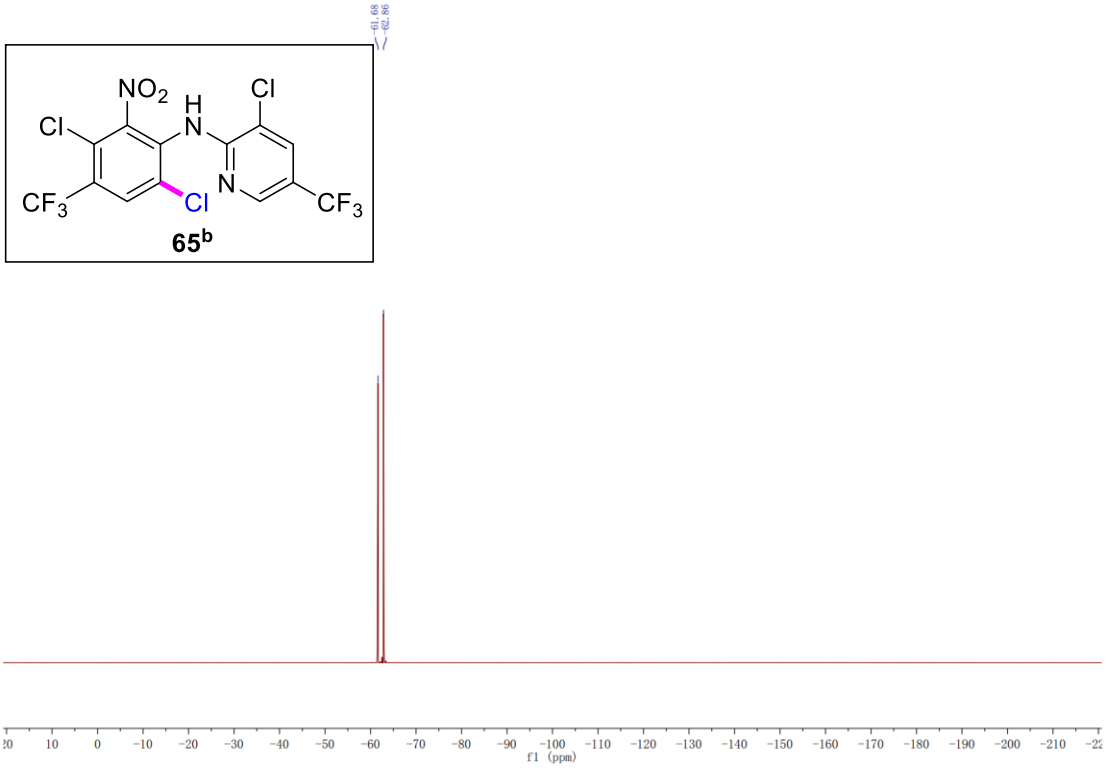


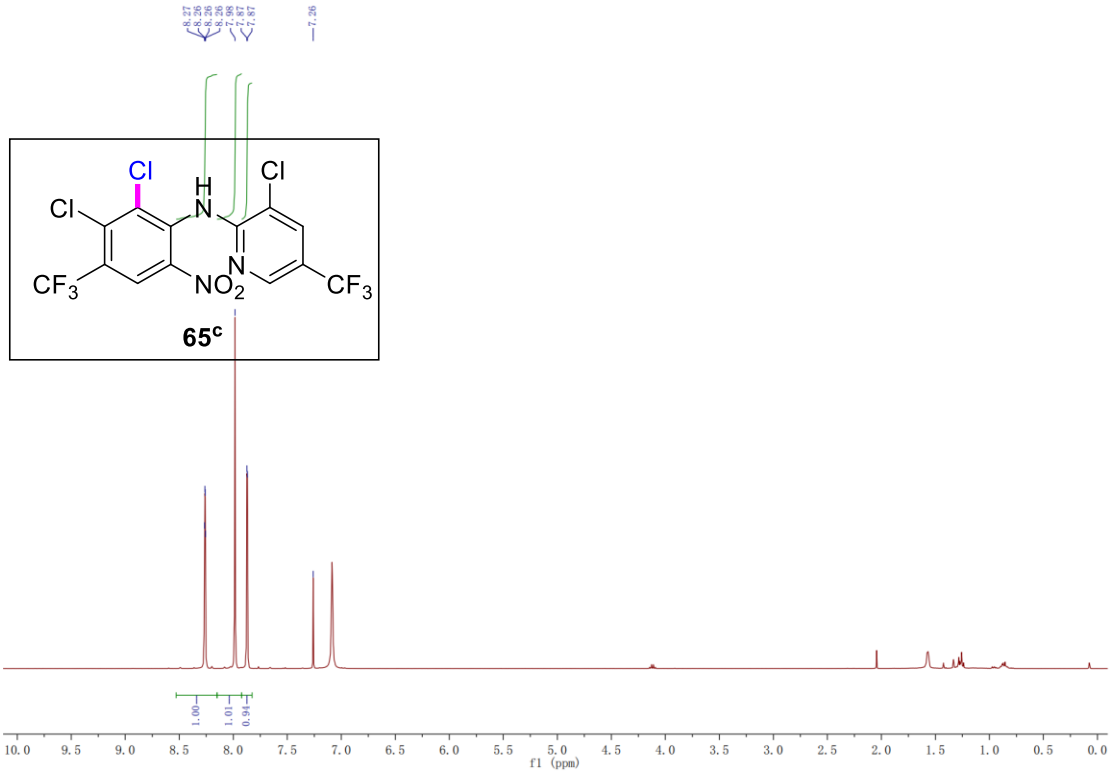
65[a]

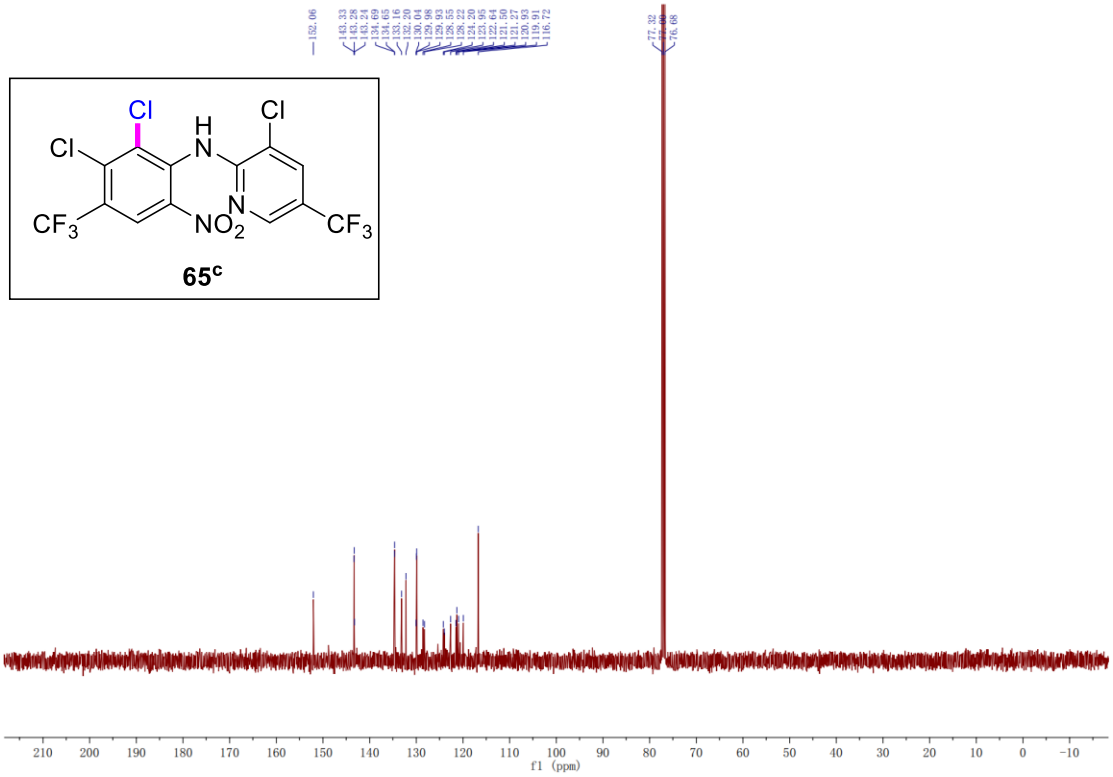


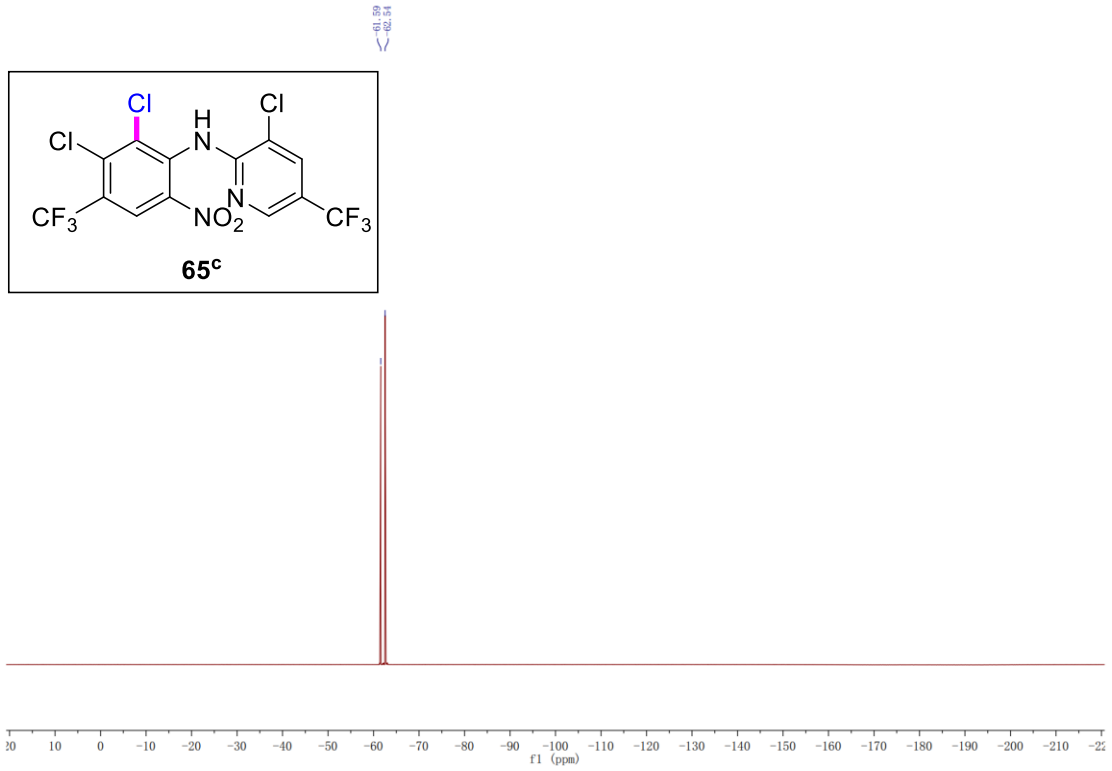

NO2
H
N
Cl
Cl
N
CF3
Cl
CF3
65b
f1 (ppm)


NO2
H
N
Cl
Cl
N
CF3
Cl
CF3
65b
f1 (ppm)


NO2
H
N
Cl
Cl
N
CF3
Cl
CF3
65b
-61.68
-62.86
f1 (ppm)


8.27
8.26
8.26
8.26
7.88
7.87
7.87
7.26
Cl
H
N
Cl
Cl
N
CF3
NO2
CF3
65c
1.00
1.01
0.94
f1 (ppm)


Cl
H
N
Cl
Cl
N
CF3
NO2
CF3
65c
f1 (ppm)


Cl
H
N
Cl
Cl
N
CF3
NO2
CF3
65c
f1 (ppm)