Photo-Induced $FeCl_3$-catalysed direct desulfurizative chlorination of thio-containing aromatics at room temperature

Mingjing Deng,[a,#] Zhaolun Ma,[a,#] Ke Liu,[a] Bingji Li,[a] Jing Wu[a] and Longyang Dian*[a]

a State Key Laboratory of Microbial Technology, Institute of Microbial Technology, Shandong University, No. 72 Binhai Avenue, Qingdao 266237 (P. R. China),

# M. Deng and Z. Ma contributed equally to this work

*Corresponding author: longyang_dian@sdu.edu.cn.

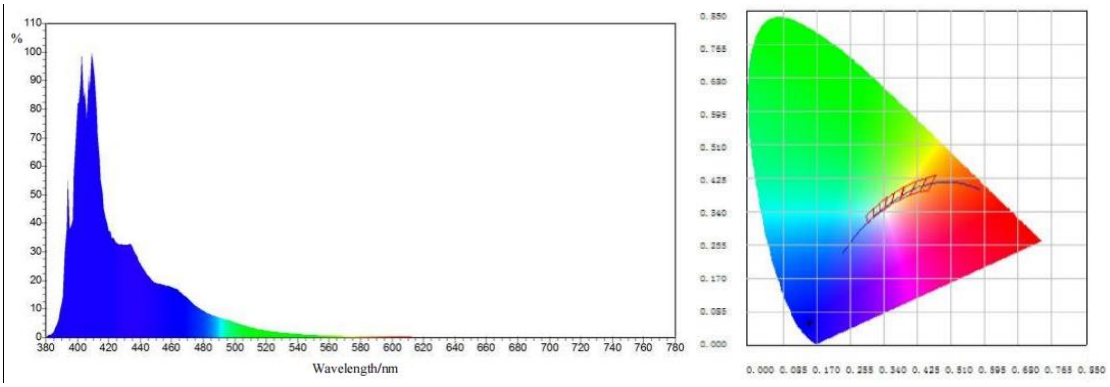
Content of the supporting information

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 100 MHz spectrometers and referenced to the internal solvent signals (central peak is 77.0 ppm in $CDCl_3$). $CDCl_3$ was used as the NMR solvent. Shimadzu GCMS-QP2010SE was used to monitor the reaction process. High resolution mass spectrometry (HRMS) was obtained on a Q-TOF micro spectroMeter. IR was measured with Nicolet™ iS50 FTIR Spectrometer. The reaction was performed in a Quartz sealed tube. Organic solutions were concentrated by rotary evaporation below 40 °C in vacuum with carefully control of the vacuum.

All the reagents (including the thiophenol compound) and solvents were purchased as reagent grade and were used without further purification.

2. Light source test report

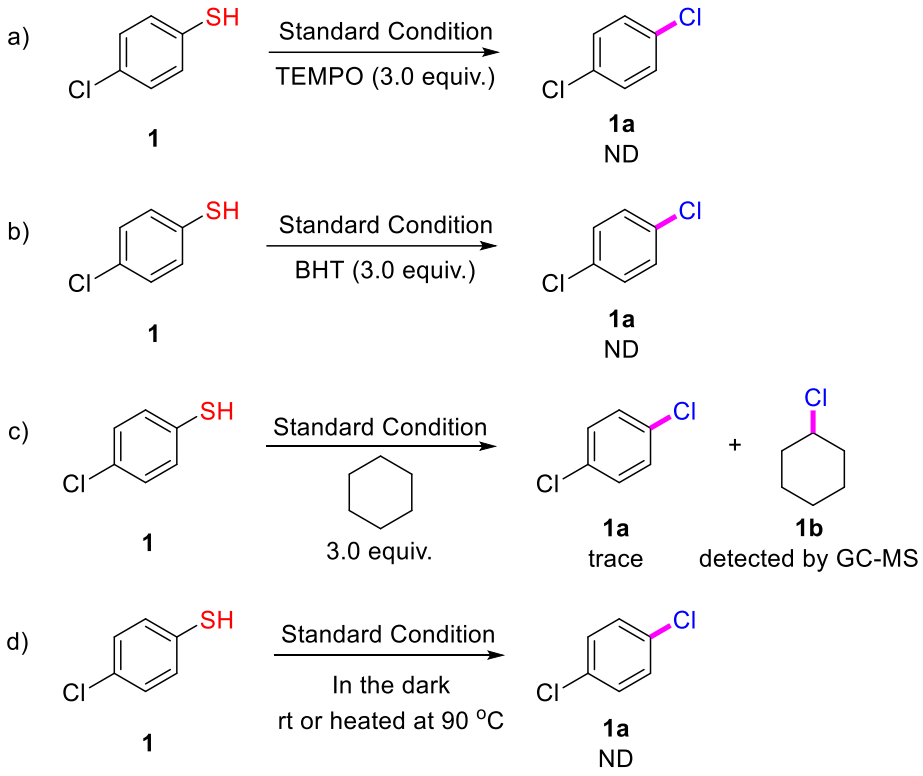


Chromaticity coordinates	X=0.1582	y=0.0607/u=01855	V=0.1067	Duv=-0.1085	
Correlated color temperature	Tc=100000 K	dominant wavelength	λd=462.1 nm	color purity	Purity-90.1%
color ratio	R=0.3% G=4.0% B=95.7%	peak wavelength	λp=409.6 nm	half width	Δλd=18.6 nm
Color rendering index: Ra=-2.5					
R1=9.2	R2 =37.9	R3 =-53.3	R4=-46.6	R5=20.5	
R6=10.4	R7 =13.7	R8=-11.4	R9 =-230.1	R10=-45.0	
R11=-75.5	R12=-69.4	R13=24.7	R14=15.2	R15=34.0	
Photometric parameters:					
Luminous flux	Φ=14.833Lm	light micro 5.606 Lm/W	5.606 Lm/W Φ*e* = 508.82 mW		
Electrical parameters					
Forward Voltage: VF=3.78 V		Forward current: IF=700.0 mA	Power P=2.646 W		

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 open to air unless otherwise noted. Substrate **1** (0.1 mmol), $FeCl_3$ (cat. 10 mol%, 0.01 mmol), $MgCl_2$ (0.2 mmol), 4A MS (20 mg) in MeCN (1 mL, 0.1 M) under 395-400 nm light irradiation. a) TEMPO (46.8 mg, 0.3 mmol) was added; b) BHT (66.1 mg, 0.3 mmol) was added; c) Cyclohexane (32.3 μL, 0.3 mmol) was added. The product **1b** was detected by GC-MS; d) The reaction was performed in the dark, at room temperature or heated at 90 °C for overnight.

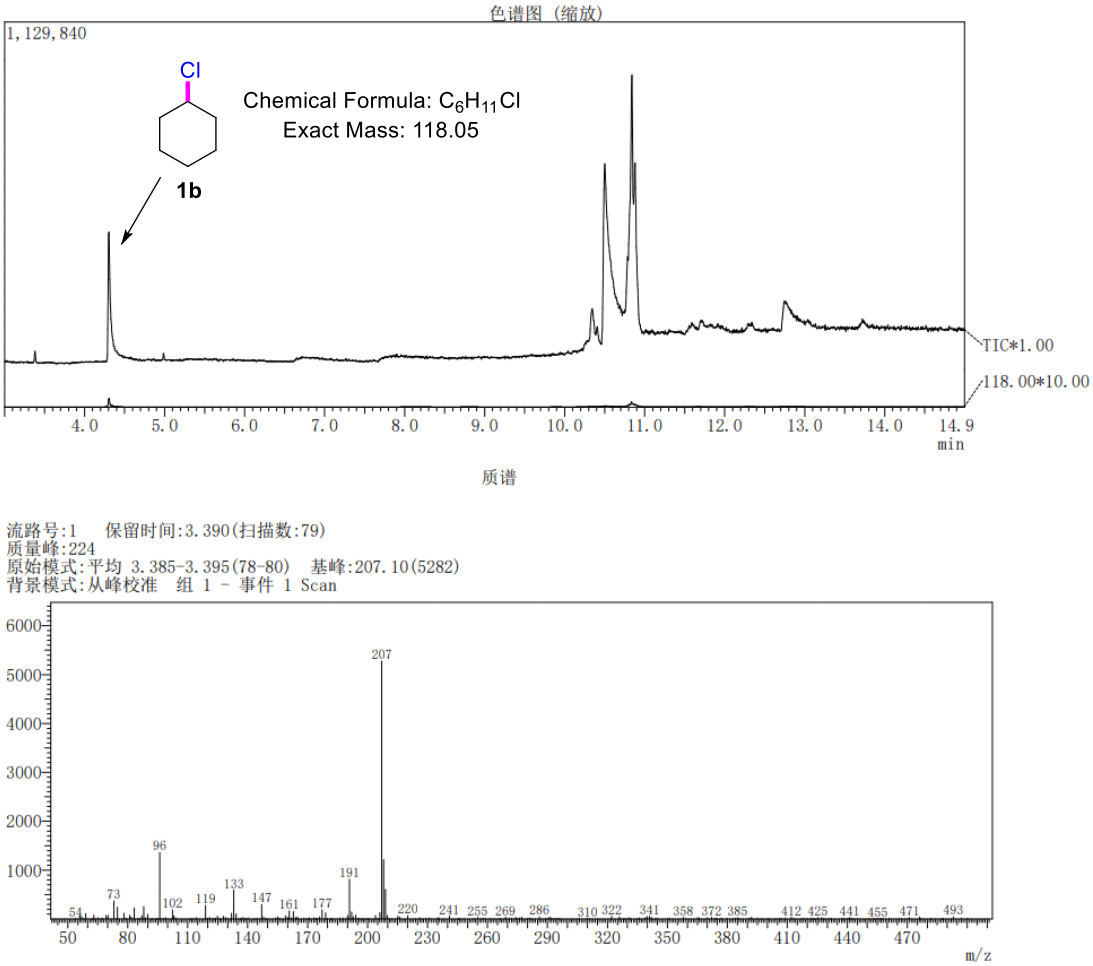


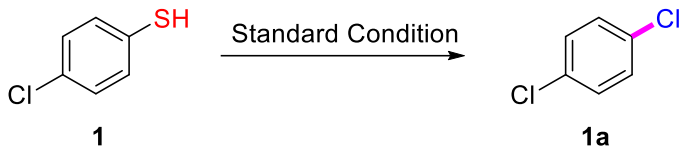
Figure S2. GC-MS trace of reaction in Scheme S1-d.

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 Light on/off experiment



1 **1a**

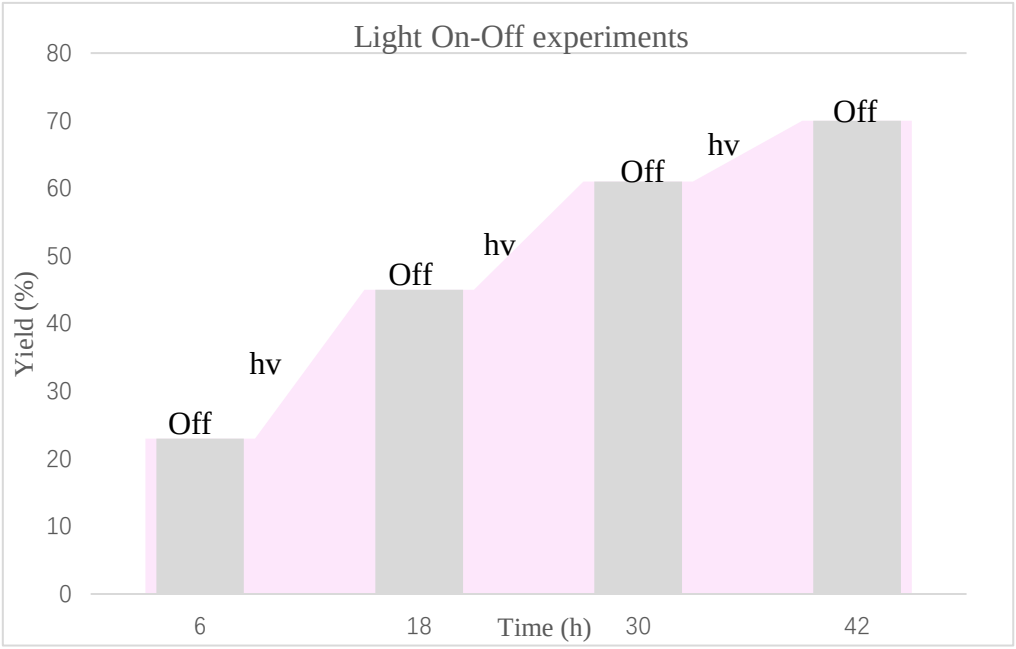
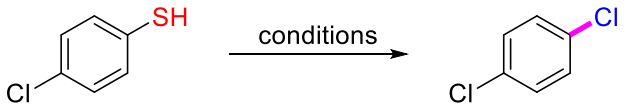


Figure S3. Light On-Off Experiments. The reaction was performed with **1** as substrate in MeCN for light on/off per 6 h. The reaction process was monitored by GC-MS.

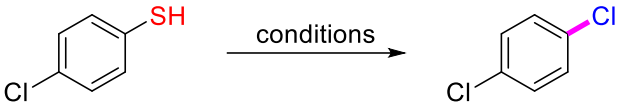
3.3 Detailed optimization of the reaction conditions

Table S1 optimization of conditions[a]



1 **1a**

Entry	Iron cat. (10 mol%)	Solvent	Cl source	Light source	Yields[b]
1	$Fe(OTf)_3$	MeCN	$MgCl_2$	395-400 nm	30%
2	$Fe(OTf)_2$	MeCN	$MgCl_2$	395-400 nm	trace
3	$Fe(acac)_3$	MeCN	$MgCl_2$	395-400 nm	trace
4	Fe_3O_4	MeCN	$MgCl_2$	395-400 nm	trace
5	**$FeCl_3$**	**MeCN**	**$MgCl_2$**	**395-400 nm**	**70%**
6	$FeCl_2·4H_2O$	MeCN	$MgCl_2$	395-400 nm	60%
7	$Fe(NO_3)_3·9H_2O$	MeCN	$MgCl_2$	395-400 nm	50%
8	$FeCl_3$	acetone	$MgCl_2$	395-400 nm	ND
9	$FeCl_3$	DMF	$MgCl_2$	395-400 nm	trace
10	$FeCl_3$	DCM	$MgCl_2$	395-400 nm	ND
11	$FeCl_3$	DCE	$MgCl_2$	395-400 nm	ND
12	$FeCl_3$	DMSO	$MgCl_2$	395-400 nm	ND
13	$FeCl_3$	DMA	$MgCl_2$	395-400 nm	ND
14	$FeCl_3$	HFIP	$MgCl_2$	395-400 nm	ND
15	$FeCl_3$	THF	$MgCl_2$	395-400 nm	ND
16	$FeCl_3$	*t*-BuCN	$MgCl_2$	395-400 nm	ND
17	$FeCl_3$	$MeNO_2$	$MgCl_2$	395-400 nm	40%
18	$FeCl_3$	MeCN	$ZnCl_2$	395-400 nm	ND
19	$FeCl_3$	MeCN	TBACl	395-400 nm	ND
20	$FeCl_3$	MeCN	NCS	395-400 nm	30%
21	$FeCl_3$	MeCN	C_2Cl_6	395-400 nm	30%
22[c]	$FeCl_3$	MeCN	DCE	395-400 nm	trace
23[c]	$FeCl_3$	MeCN	DCM	395-400 nm	30%
24[c]	$FeCl_3$	MeCN	$CHCl_3$	395-400 nm	30%
25	$FeCl_3$	MeCN	$MgCl_2$	390-395 nm	54%
26	$FeCl_3$	MeCN	$MgCl_2$	365 nm	40%
27	$FeCl_3$	MeCN	$MgCl_2$	385 nm	45%
28	$FeCl_3$	MeCN	$MgCl_2$	400-410 nm	63%
29	$FeCl_3$	MeCN	$MgCl_2$	5 W blue LED	ND
30	$FeCl_3$	MeCN	$MgCl_2$	5 W yellow LED	ND
31	$FeCl_3$	MeCN	$MgCl_2$	5 W white LED	ND

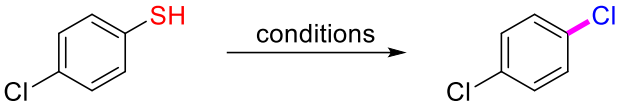


1 **1a**

Entry	Iron cat. (10 mol%)	Solvent	Cl source	Light source	Yields[b]
32	$FeCl_3$	MeCN	$MgCl_2$	5 W green LED	ND
33	$FeCl_3$	MeCN	$MgCl_2$	5 W red LED	ND
34	$FeCl_3$	MeCN	$MgCl_2$	Sun light	trace
35[d]	$FeCl_3$	MeCN	$MgCl_2$	395-400 nm	68%
36[e]	$FeCl_3$	MeCN	$MgCl_2$	395-400 nm	trace
37[f]	$FeCl_3$	MeCN	$MgCl_2$	395-400 nm	45%
38	/	MeCN	$MgCl_2$	395-400 nm	ND
39	$FeCl_3$	MeCN	/	395-400 nm	10%
40	$FeCl_3$	MeCN	$MgCl_2$	/	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. [b] Yields refer to the isolated products. [c] 0.1 mL chloro solvent DCE, DCM or $CHCl_3$ was used. [d] The concentration of reaction was 0.5 M, 0.20 mL of MeCN was used as the solvent. [e] The reaction is performed under argon atmosphere. [f] Reaction without 4 Å molecular sieve.

Table S2 the control experiments of active oxygen species inhibitors[a]

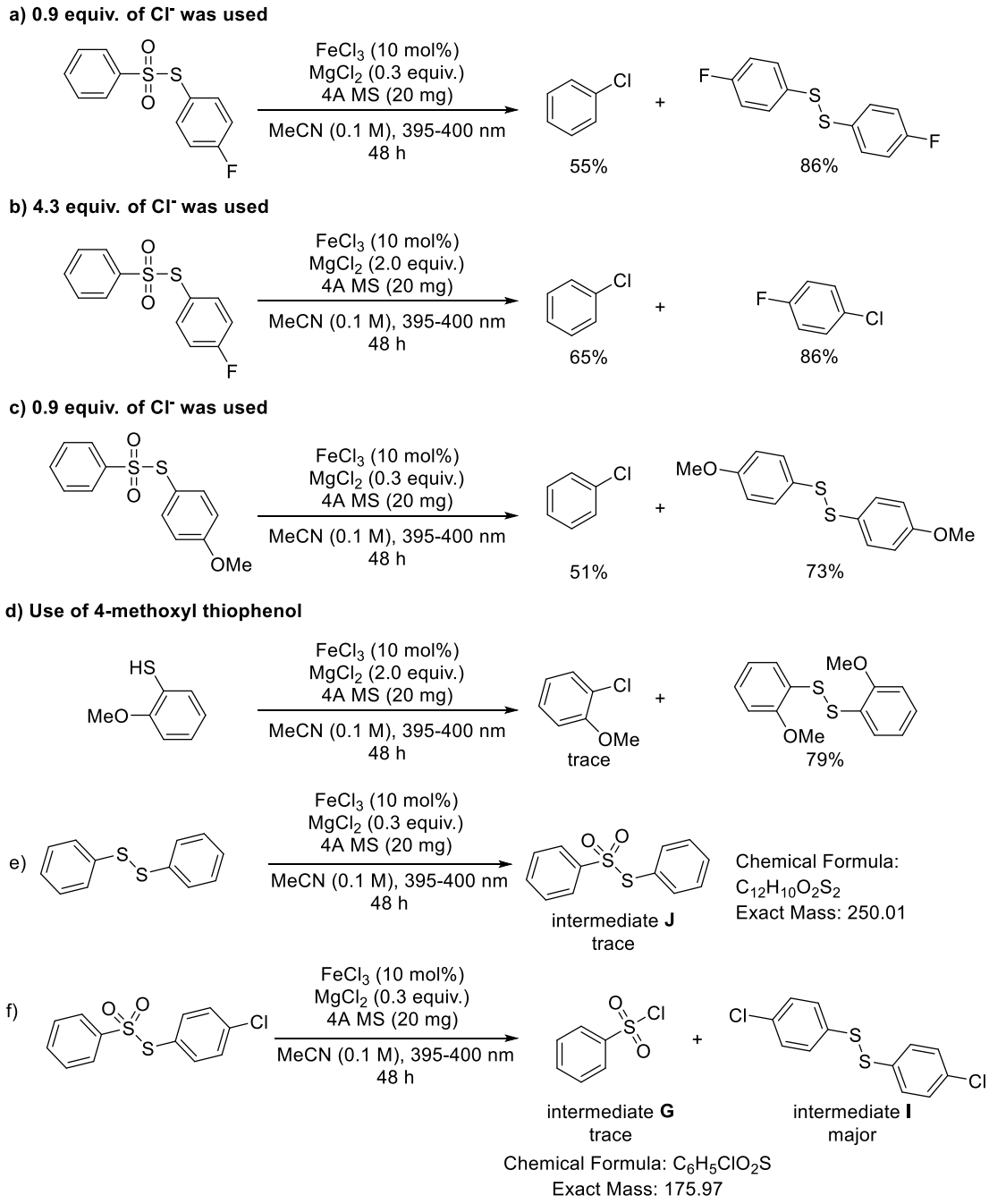


1 **1a**

Entry	Additives	Functions	Yields[b]
1	–	–	70%
2	NaN_3	$^1O_2$ Inhibitor	trace
3	9,10-dimethylanthracebe	$^1O_2$ Inhibitor	trace
4	*t*-BuOH	$OH^{\cdot}$ Inhibitor	60%
5	BQ	$O_2^{-\cdot}$ Inhibitor	trace
6	Luminol	$O_2^{-\cdot}$ Inhibitor	trace

[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. [b] Yields refer to the isolated products. Only trace amounts of product **1a** were detected in GC-MS with the addition of the additives NaN_3 and 9,10-dimethylanthracebe, which inhibit the singlet oxygen $^1O_2$; The addition of the additives BQ and Luminol, which inhibit $O_2^{-\cdot}$ radicals, only traces of product 1a were detected in GC-MS; The addition of the additive *t*-BuOH, which inhibits $OH^{\cdot}$ radicals, the reaction could be carried out normally and there was a 60% yield. This indicates that singlet oxygen $^1O_2$ and $O_2^{-\cdot}$ radicals may generated in the reaction.

3.4 Additional control experiments to explore the possible intermediates

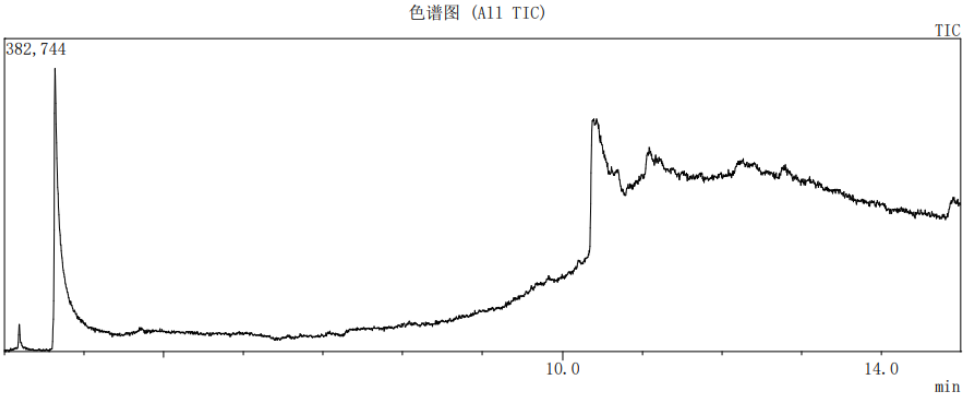


Scheme S2. Additional control experiments to explore the possible mechanism.

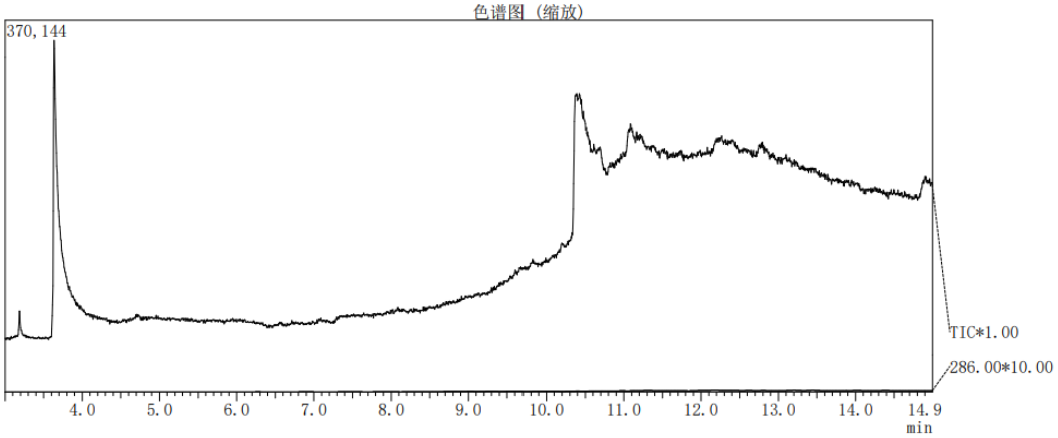
Crude GC-MS trace of Scheme S2-a

D:\data\202505\MZL04-19-4.qgd

色谱图 (All TIC)

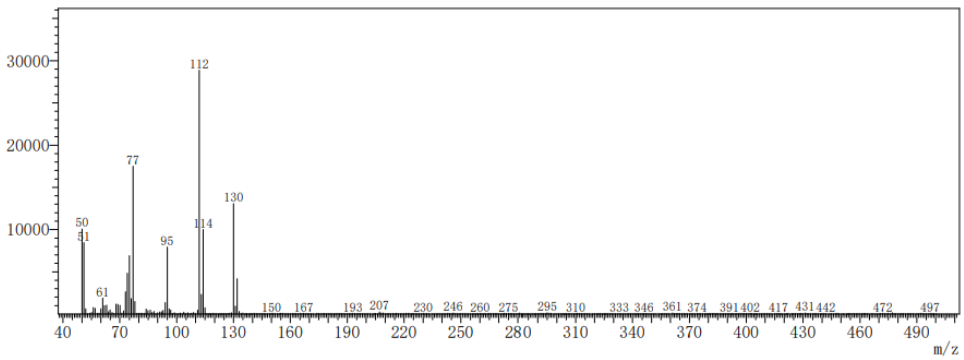


色谱图 (缩放)

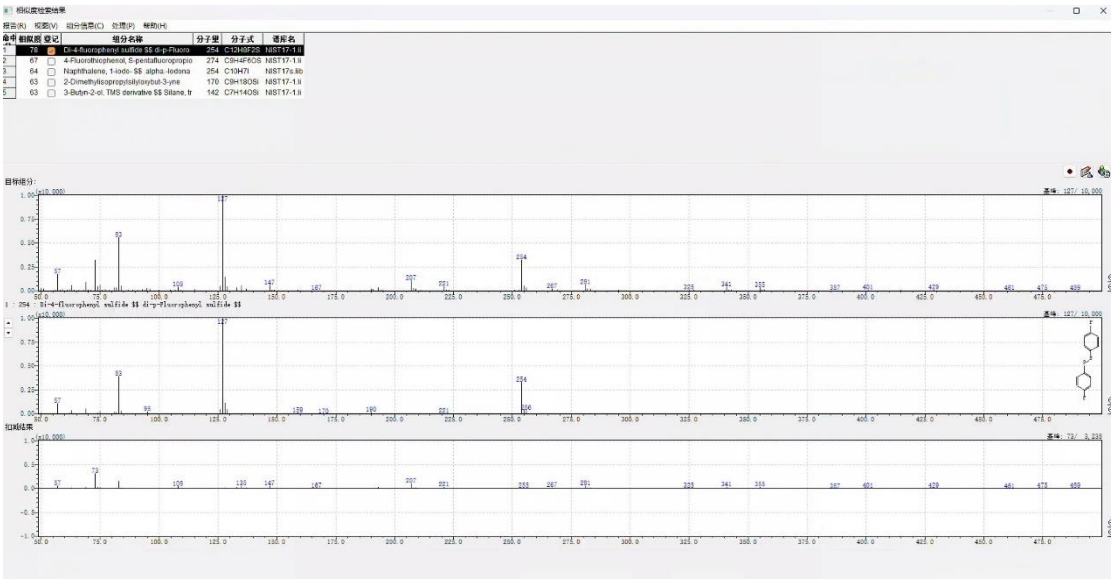


质谱

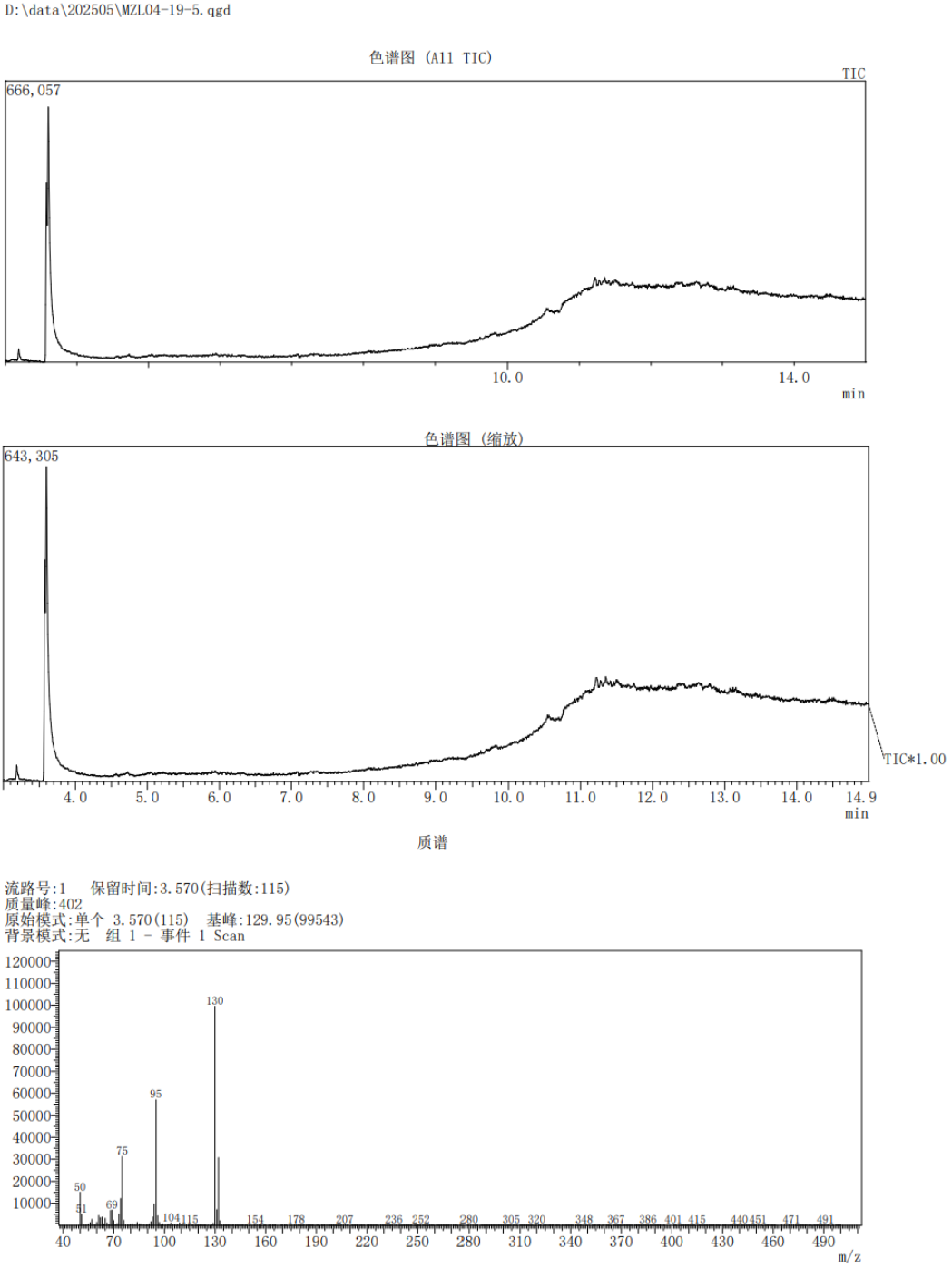
流路号:1　保留时间:3.625(扫描数:126)
质量峰:435
原始模式:单个 3.625(126)　基峰:111.95(28868)
背景模式:无　组 1 - 事件 1 Scan

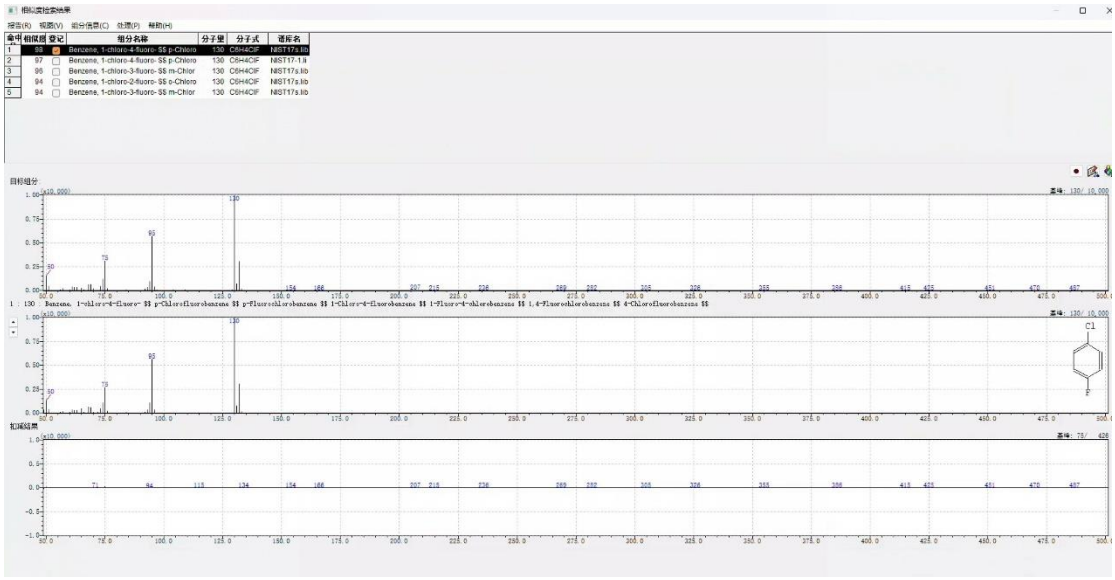


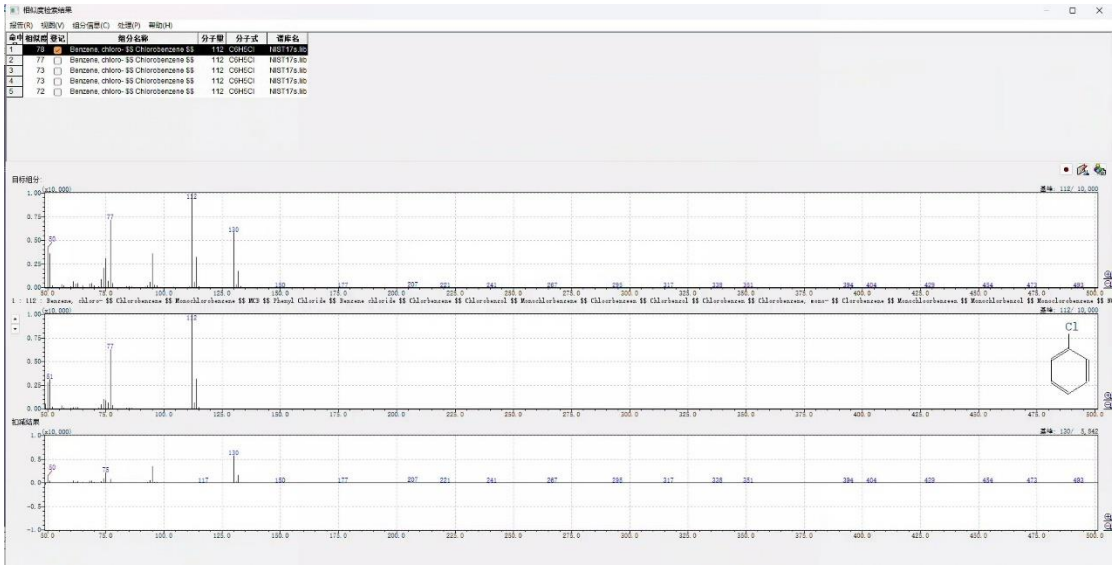

相似度检索结果
报告(R) 视图(V) 组分信息(C) 处理(P) 帮助(H)
命中 相似度 登记 组分名称 分子量 分子式 谱库名
1 81 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
2 81 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
3 77 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
4 77 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
5 75 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
目标组分:
扣除结果
Cl


相似度检索结果
报告(R) 视图(V) 组分信息(C) 处理(P) 帮助(H)
命中 相似度 登记 组分名称 分子量 分子式 谱库名
1 78 Di-4-fluorophenyl sulfide $$ di-p-Fluoro 254 C12H8F2S NIST17-1.li
2 67 4-Fluorothiophenol, S-pentafluoropropio 274 C9H4F6OS NIST17-1.li
3 64 Naphthalene, 1-iodo- $$ alpha.-Iodona 254 C10H7I NIST17s.lib
4 63 2-Dimethylisopropylsilyloxybut-3-yne 170 C9H18OSi NIST17-1.li
5 63 3-Butyn-2-ol, TMS derivative $$ Silane, tr 142 C7H14OSi NIST17-1.li
目标组分:
1 : 254 : Di-4-fluorophenyl sulfide $$ di-p-Fluorophenyl sulfide $$
扣除结果

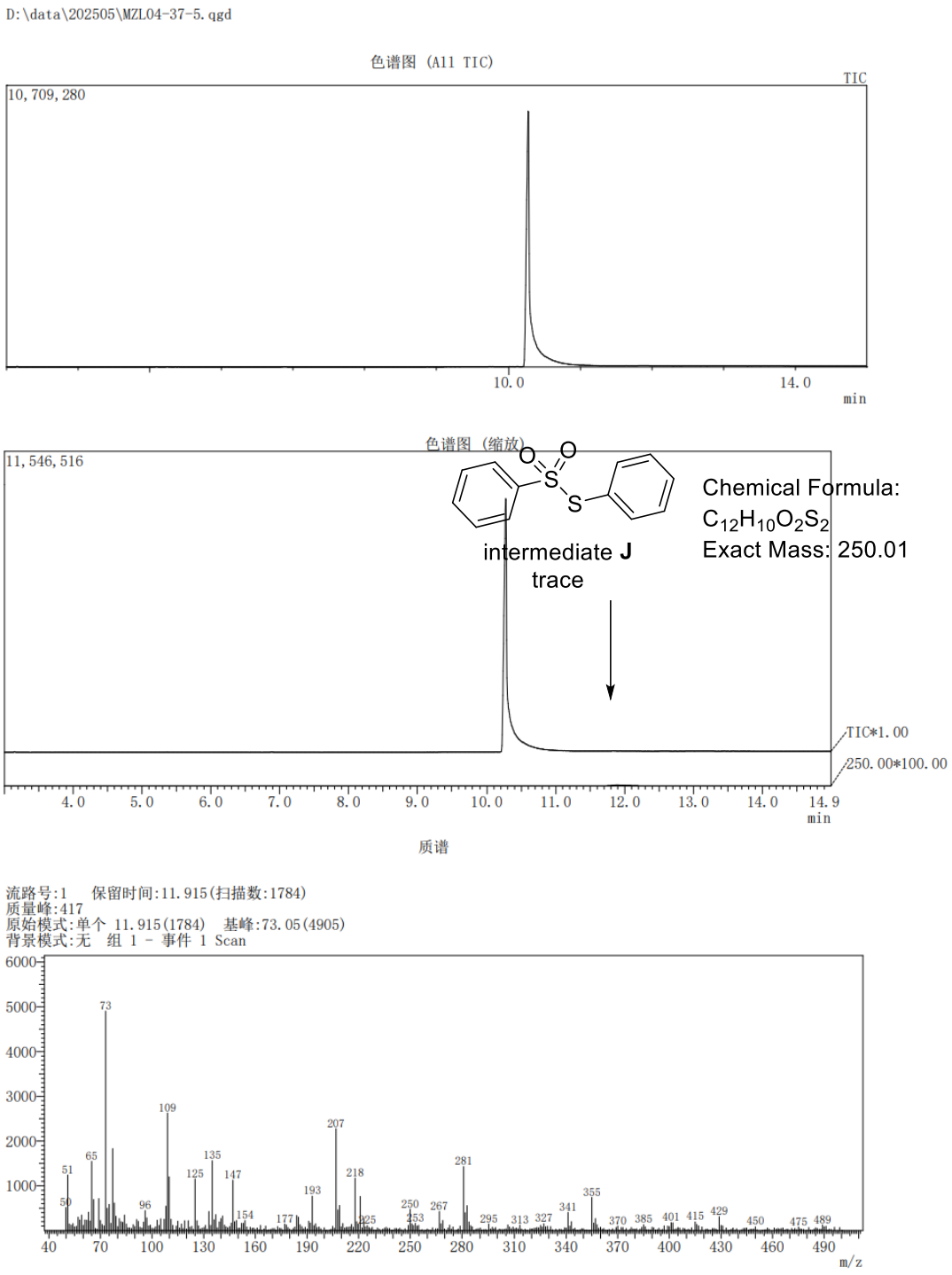
Crude GC-MS trace of Scheme S2-b



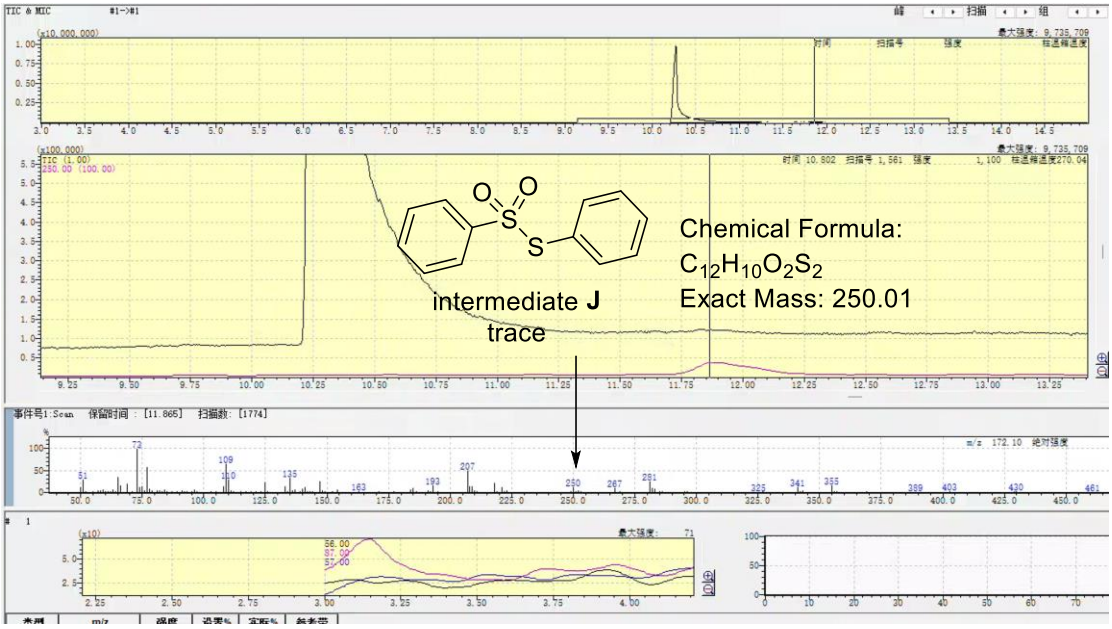

相似度检索结果
报告(R) 视图(V) 组分信息(C) 处理(P) 帮助(H)
命中 相似度 登记 组分名称 分子量 分子式 谱库名
1 88 Benzene, 1-chloro-4-fluoro- $$ p-Chloro 130 C6H4ClF NIST17s.lib
2 97 Benzene, 1-chloro-4-fluoro- $$ p-Chloro 130 C6H4ClF NIST17.lib
3 96 Benzene, 1-chloro-3-fluoro- $$ m-Chlor 130 C6H4ClF NIST17s.lib
4 94 Benzene, 1-chloro-2-fluoro- $$ o-Chloro 130 C6H4ClF NIST17s.lib
5 94 Benzene, 1-chloro-3-fluoro- $$ m-Chlor 130 C6H4ClF NIST17s.lib
目标组分
扣减结果


相似度检索结果
报告(R) 视图(V) 组分信息(C) 处理(P) 帮助(H)
命中 相似度 登记 组分名称 分子量 分子式 谱库名
1 78 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
2 77 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
3 73 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
4 73 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
5 72 Benzene, chloro- $$ Chlorobenzene $$ 112 C6H5Cl NIST17s.lib
目标组分
扣减结果

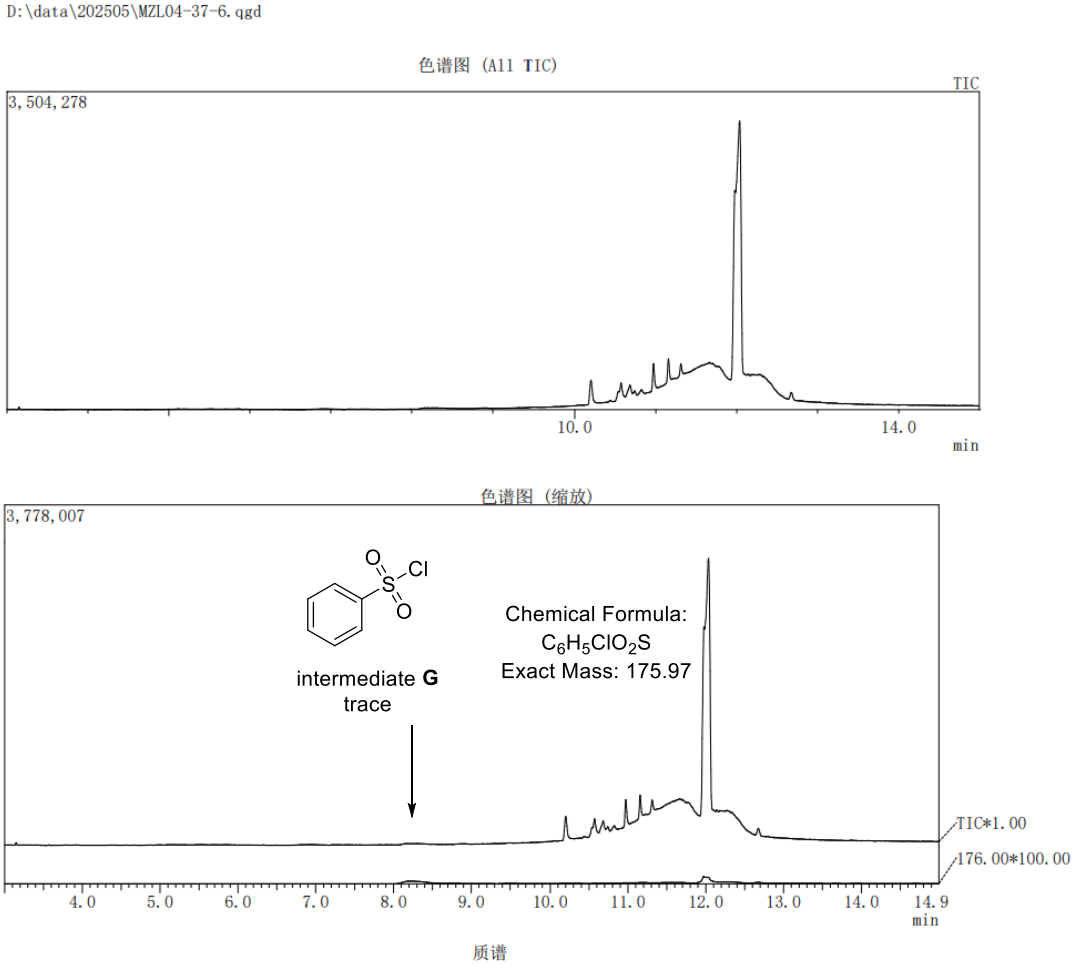
Crude GC-MS trace of Scheme S2-e



Enlarge of retention time 10-13 min



Crude GC-MS trace of Scheme S2-f

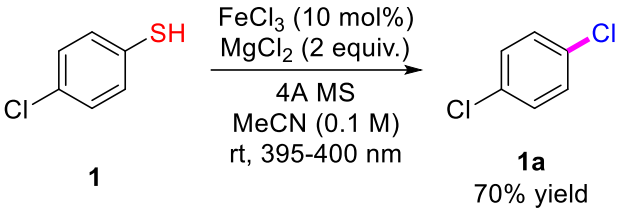


3.4 General procedure for the photo-induced $FeCl_3$-catalysed chlorination

The substrate thio-containing aromatic (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 395-400 nm light (5 W, 2 cm distance from the light). The process of the reaction was monitored by GC-MS (about 36 h-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 or pentane/Et_2O as mobile phase to afford the desired chloroarenes.

3.5 Data and references

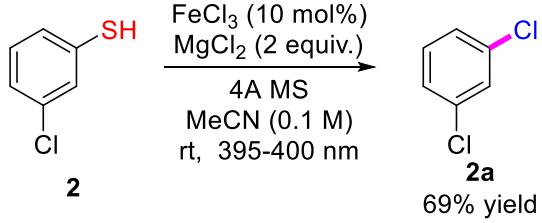
1,4-Dichlorobenzene (1a)[1]



Compound 1a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **1a** was obtained (10.2 mg, 70% 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.

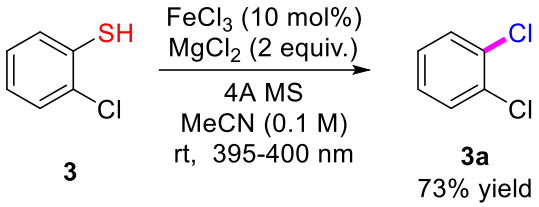
1,3-Dichlorobenzene (2a)[2]



Compound 2a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **2a** was obtained (10.1 mg, 69% 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 (3a)[3]

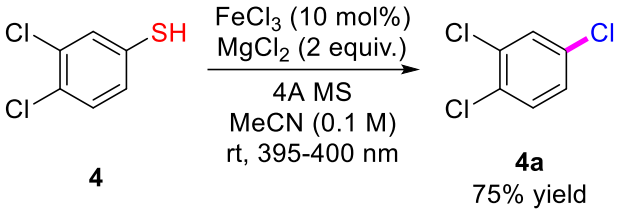


3 **3a** 73% yield

Compound 3a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **3a** was obtained (10.7 mg, 73% 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.

1,2,4-Trichlorobenzene (4a)[4]

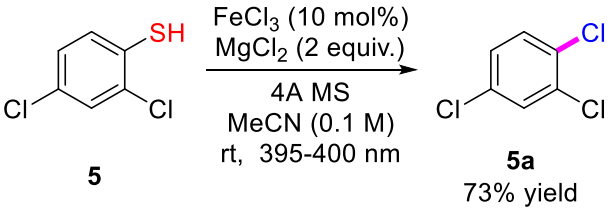


4 **4a** 75% yield

Compound 4a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **4a** was obtained (13.5 mg, 75% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ δ 7.87 – 7.71 (m, 2H), 7.51 – 7.41 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 133.4, 133.0, 131.1, 130.3, 128.7, 128.0.

1,2,4-Trichlorobenzene (5a)[4]

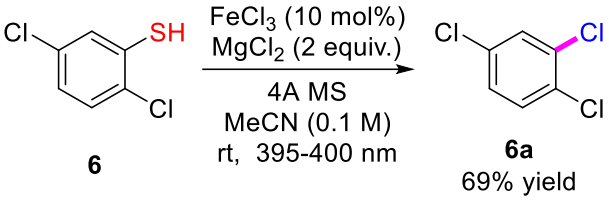


5 **5a** 73% yield

Compound 5a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **5a** was obtained (13.1 mg, 73% 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.

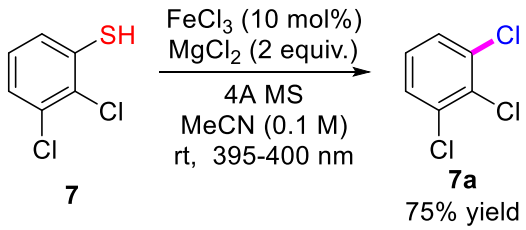
1,2,4-Trichlorobenzene (6a)[4]



Compound 6a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **6a** was obtained (12.4 mg, 69% 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 (7a)[4]

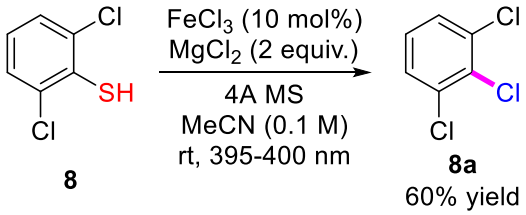


Compound 7a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **7a** was obtained (13.5 mg, 75% yield).

^{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-Trichlorobenzene (8a)[4]

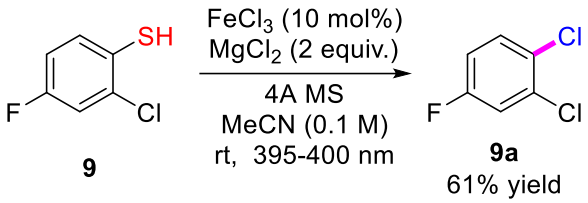


Compound 8a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **8a** was obtained (10.8 mg, 60% yield).

^{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.

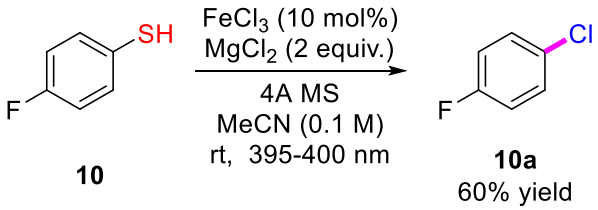
1,2-Dichloro-4-fluorobenzene (9a)[5]



Compound 9a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **9a** was obtained (10.0 mg, 61% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.43 – 7.37 (m, 1H), 7.20 (dd, *J* = 8.2, 2.9 Hz, 1H), 6.94 (ddd, *J* = 8.8, 7.6, 2.9 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 160.9 (d, *J* = 249.2 Hz), 133.3 (d, *J* = 10.6 Hz), 131.1 (d, *J* = 9.1 Hz), 128.0 (d, *J* = 4.5 Hz), 117.9 (d, *J* = 25.7 Hz), 115.1 (d, *J* = 22.7 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -113.25.

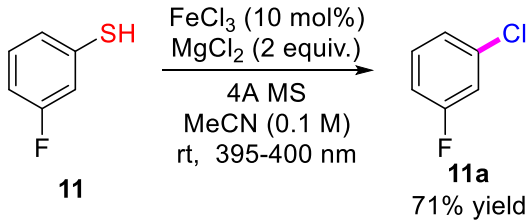
1-Chloro-4-fluorobenzene (10a)[6]



Compound 10a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **10a** was obtained (7.8 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H). **^{13}C 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-3-fluorobenzene (11a)[6]

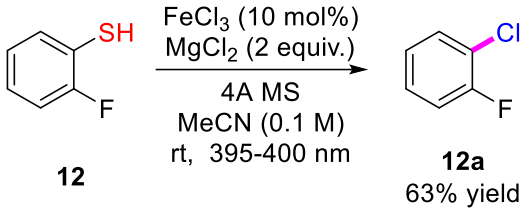


Compound 11a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **11a** was obtained (9.2 mg, 71% yield).

^{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.

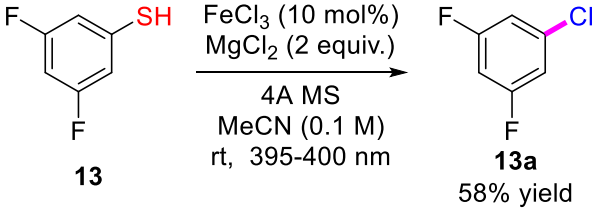
1-Chloro-2-fluorobenzene (12a)[7]



12 **12a** 63% yield

Compound 12a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **12a** was obtained (8.2 mg, 63% 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), 7.19 – 7.07 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2 (d, *J* = 249.5 Hz), 130.7, 128.1 (d, *J* = 7.1 Hz), 124.8 (d, *J* = 4.0 Hz), 121.0 (d, *J* = 18.2 Hz), 116.6 (d, *J* = 20.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -115.45.

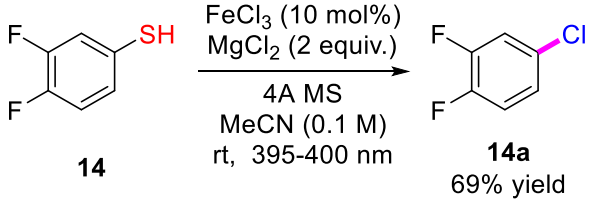
1-Chloro-3,5-difluorobenzene (13a)[8]



13 **13a** 58% yield

Compound 13a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **13a** was obtained (8.6 mg, 58% yield).
^{1}H NMR (600 MHz, $CDCl_3$) δ 6.95 (tt, *J* = 6.6, 3.5 Hz, 2H), 6.76 (tt, *J* = 8.9, 2.3 Hz, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.9 (dd, *J* = 252.2, 13.6 Hz), 135.8 (t, *J* = 12.1 Hz), 112.5 (dd, *J* = 22.7, 6.0 Hz), 102.8 (t, *J* = 24.2 Hz); **^{19}F NMR (565 MHz, $CDCl_3$)** δ -108.24.

1,2,4-Trifluorobenzene (14a)



14 **14a** 69% yield

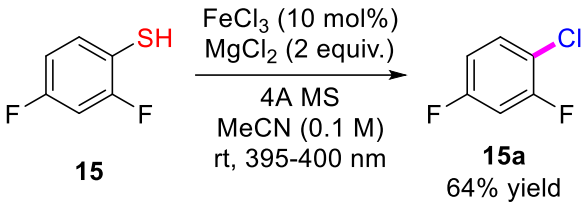
Compound 14a was prepared according to the general procedure in about 48 h. After

standard work-up and purification, **14a** was obtained (10.2 mg, 69% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (ddd, *J* = 9.5, 6.8, 2.3 Hz, 1H), 7.14 – 7.05 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 150.3 (dd, *J* = 252.2, 13.6 Hz), 149.4 (dd, *J* = 249.2, 12.1 Hz), 129.2 (dd, *J* = 7.6, 4.5 Hz), 124.7 (q, *J* = 3.0 Hz), 118.1 (d, *J* = 3.0 Hz), 118.0. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -134.60 (m, 1F), -139.75 (m, 1F).

HRMS (ESI) m/z calcd for $C_6H_3ClF_2Na$ [M + Na^+] 170.9784, found 170.9779.

1-Chloro-2,4-difluorobenzene (15a)

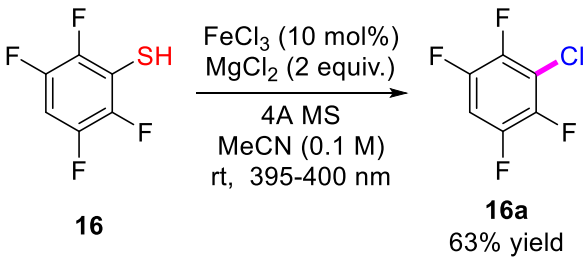


Compound 15a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **15a** was obtained (9.5 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (td, *J* = 8.6, 5.7 Hz, 1H), 6.96 – 6.82 (m, 2H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3 (dd, *J* = 249.7, 10.1 Hz), 158.1 (dd, *J* = 252.5, 12.1 Hz), 131.0 (d, *J* = 9.1 Hz), 116.5 (dd, *J* = 17.2, 4.0 Hz), 112.1 (dd, *J* = 23.2, 4.0 Hz), 105.2 (dd, *J* = 26.3, 24.2 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -110.5 (m, 1F), -111.2 (m, 1F).

HRMS (ESI) m/z calcd for $C_6H_3ClF_2Na$ [M + Na^+] 170.9784, found 170.9788.

3-Chloro-1,2,4,5-tetrafluorobenzene (16a)

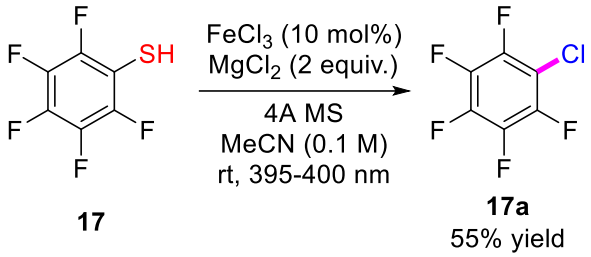


Compound 16a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **16a** was obtained (11.6 mg, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (tt, *J* = 9.7, 7.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.4 (m), 145.3 (m), 144.9 (m), 142.8 (q, *J* = 3.0 Hz), 104.6 (td, *J* = 44.4, 2.0 Hz). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -137.7 (m, 2F), -140.7 (m, 2F).

HRMS (ESI) m/z calcd for C_6HClF_4Na [M + Na^+] 206.9595, found 206.9586.

Chloropentafluorobenzene (17a)



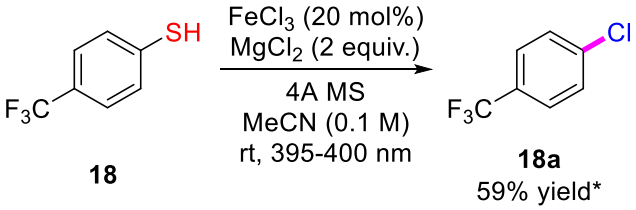
17 **17a** 55% yield

Compound 17a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **17a** was obtained (11.1 mg, 55% yield).

^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8 (m), 143.2 (m), 141.6 (m), 139.3 (m), 136.9 (m), 108.0 (m). **^{19}F NMR (376 MHz, $CDCl_3$)** δ -140.3 (m, 1F), -155.6 (t, 1F), -160.9 (m, 3F).

HRMS (ESI) m/z calcd for C_6HClF_4Na [M + Na^+] 224.9501, found 224.9510.

1-Chloro-4-(trifluoromethyl)benzene (18a)[9]

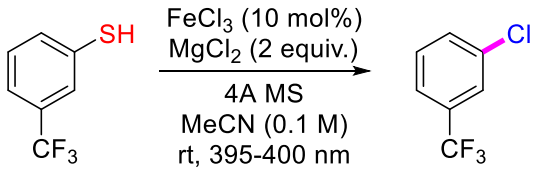


18 **18a** 59% yield*

Compound 18a was prepared according to the general procedure in about 48 h, during which 20 mol% of $FeCl_3$ was used. After standard work-up and purification, **18a** was obtained (10.6 mg, 59% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.35 – 7.30 (m, 2H), 7.05 – 7.00 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 162.1, 160.5, 129.9 (d, *J* = 7.6 Hz), 129.1 (d, *J* = 4.5 Hz), 116.7 (d, *J* = 22.7 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -115.93.

1-Chloro-3-(trifluoromethyl)benzene (19a)[10]



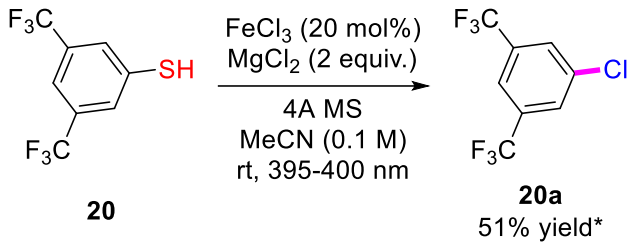
19 **19a** 54% yield

Compound 19a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **19a** was obtained (9.7 mg, 54% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.62 (d, *J* = 2.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.45 (dt, *J* = 15.8, 8.1 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.92, 132.3 (d, *J* = 33.2 Hz),

132.01, 130.17, 126.7 (q, *J* = 4.5 Hz), 125.7 (dd, *J* = 7.6, 4.5 Hz), 123.4 (dd, *J* = 7.6, 4.5 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -62.95.

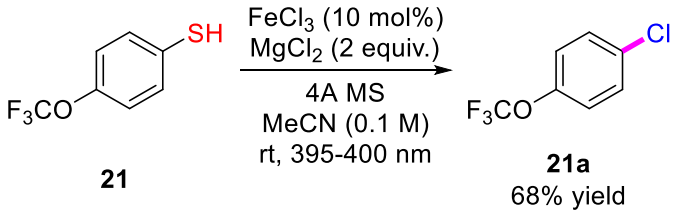
1-Chloro-3,5-bis(trifluoromethyl)benzene (20a)[9]



Compound 20a was prepared according to the general procedure in about 84 h, during which 20 mol% of $FeCl_3$ was used. After standard work-up and purification, **20a** was obtained (12.6 mg, 51% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.71 (d, *J* = 18.7 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 136.1, 133.3 (q, *J* = 34.7 Hz), 129.1 (q, *J* = 3.0 Hz), 125.3, 123.5, 121.7, 120.7 (m), 119.9. **^{19}F NMR (565 MHz, $CDCl_3$)** δ -63.31.

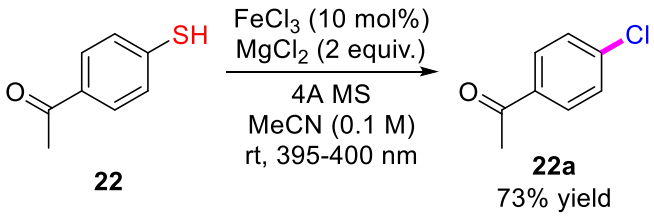
1-Chloro-4-(trifluoromethoxy)benzene (21a)[11]



Compound 21a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **21a** was obtained (13.3 mg, 68% 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.

***p*-Chloroacetophenone (22a)[1]**



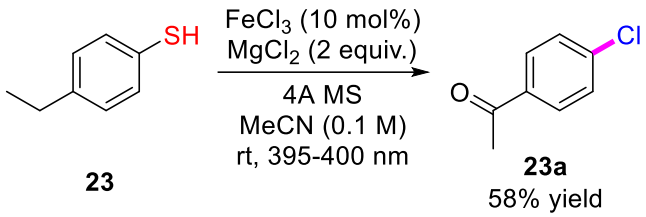
Compound 22a was prepared according to the general procedure in about 48 h. After

standard work-up and purification, **22a** 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.

***p*-Chloroacetophenone (23a)**[1]

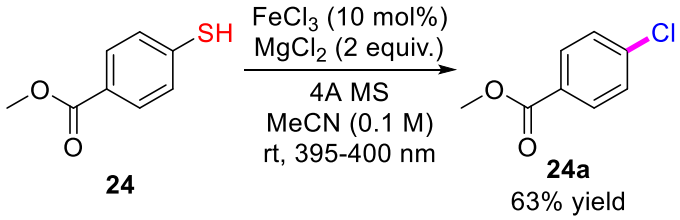


Compound 23a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **23a** was obtained (8.9 mg, 58% yield).

^{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.

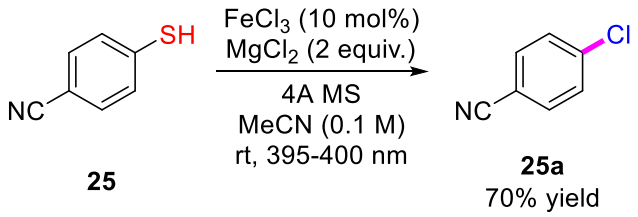
Methyl 4-chlorobenzoate (24a) [12]



Compound 24a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **24a** was obtained (10.7 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.

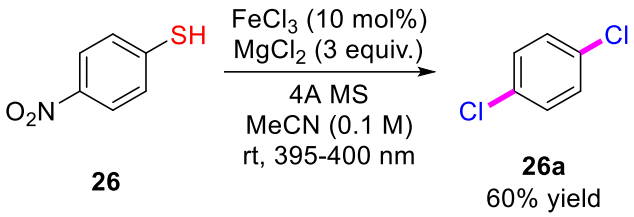
4-Chlorobenzonitrile (25a) [12]



Compound 25a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **25a** was obtained (9.6 mg, 70% 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.

1,4-Dichlorobenzene (26a) [1]

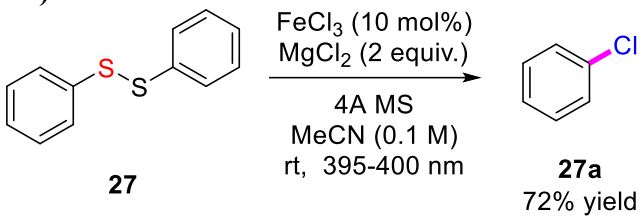


26 **26a** 60% yield

Compound 26a was prepared according to the general procedure in about 48 h, during which 0.3 mmol of $MgCl_2$ was used. After standard work-up and purification, **1** was obtained (8.8 mg, 60% 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.

Chlorobenzene (27a)[3]

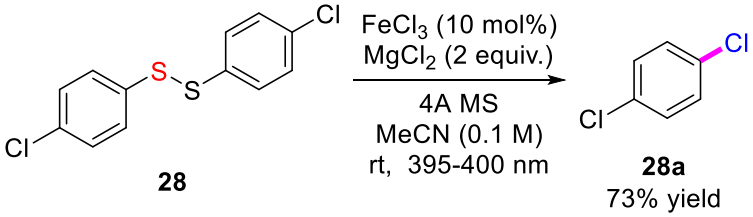


27 **27a** 72% yield

Compound 27a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **27a** was obtained (8.1 mg, 72% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.14 (d, J = 7.9 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.2, 129.7, 128.6, 126.4.

1,4-Dichlorobenzene (28a)[1]

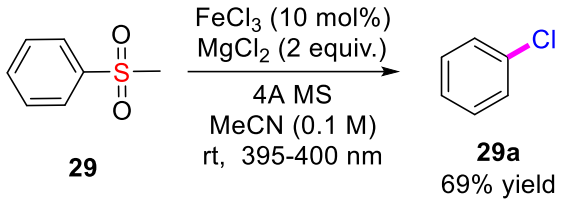


28 **28a** 73% yield

Compound 28a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **28a** was obtained (10.7 mg, 73% 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.

Chlorobenzene (29a)[3]

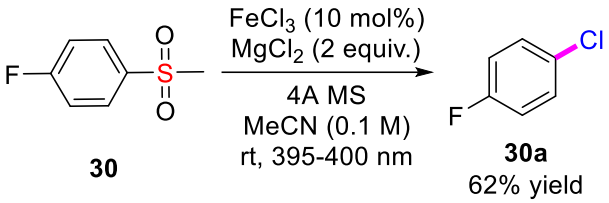


29 **29a** 69% yield

Compound 29a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **29a** was obtained (7.7 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.2, 129.7, 128.6, 126.4.

1-Chloro-4-fluorobenzene (30a)[6]

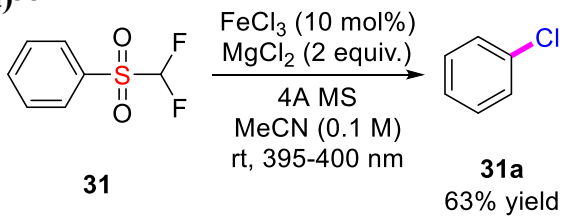


30 **30a** 62% yield

Compound 30a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **30a** was obtained (8.1 mg, 62% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H). **^{13}C 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).

Chlorobenzene (31a)[3]

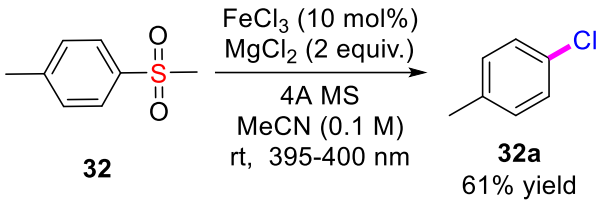


31 **31a** 63% yield

Compound 31a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **31a** was obtained (7.7 mg, 69% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.2, 129.7, 128.6, 126.4.

4-Chlorotoluene (32a)[13]

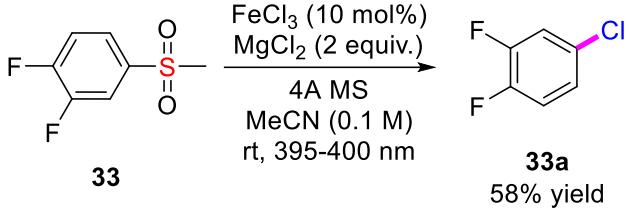


32 **32a** 61% yield

Compound 32a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **32a** was obtained (7.7 mg, 61% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.26 (d, *J* = 8.4 Hz, 2H), 7.18 – 7.08 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, $CDCl_3$)** δ 136.2, 131.1, 130.3, 128.3, 128.3, 20.8.

1,2,4-Trifluorobenzene (33a)

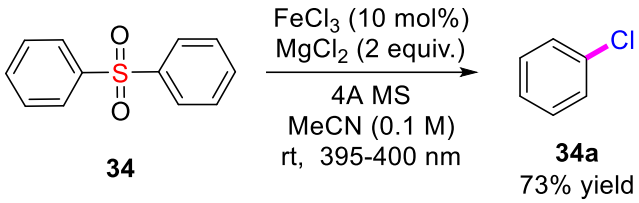


33 **33a** 58% yield

Compound 33a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **33a** was obtained (8.6 mg, 69% yield).

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 (ddd, *J* = 9.5, 6.8, 2.3 Hz, 1H), 7.14 – 7.05 (m, 2H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 150.6 (dd, *J* = 145.0, 13.6 Hz), 149.4 (d, *J* = 13.6 Hz), 148.5 (d, *J* = 12.0 Hz), 129.2 (dd, *J* = 7.6, 4.5 Hz), 124.7 (dd, *J* = 6.0, 3.0 Hz), 118.1 (dd, *J* = 21.1, 3.0 Hz). **^{19}F NMR (565 MHz, $CDCl_3$)** δ -134.60 (m, 1F), -139.75 (m, 1F).

Chlorobenzene (34a)[3]

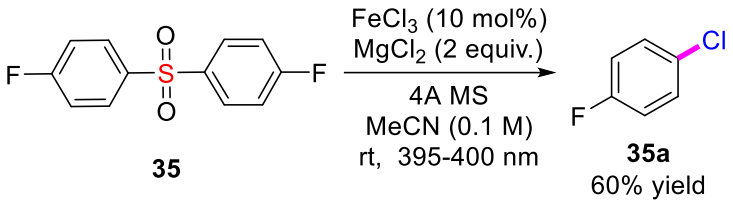


34 **34a** 73% yield

Compound 34a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **34a** was obtained (8.2 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.2, 129.7, 128.6, 126.4.

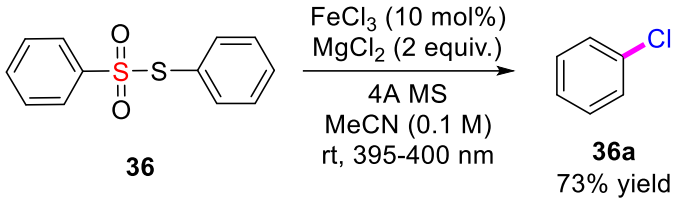
1-Chloro-4-fluorobenzene (35a)[6]



Compound 35a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **35a** was obtained (7.8 mg, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H). **^{13}C 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).

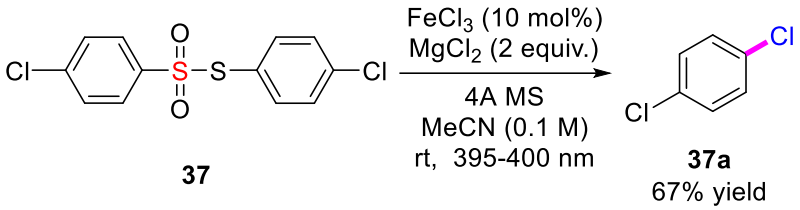
Chlorobenzene (36a)[3]



Compound 36a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **36a** was obtained (8.2 mg, 73% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.24 (m, 4H), 7.14 (d, *J* = 7.9 Hz, 1H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 134.2, 129.7, 128.6, 126.4.

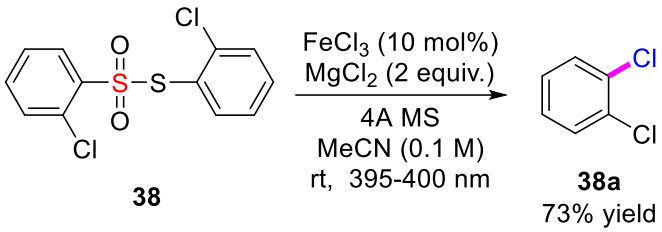
1,4-Dichlorobenzene (37a)[1]



Compound 37a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **37a** was obtained (9.8 mg, 67% 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.

1,2-Dichlorobenzene (38a)[3]

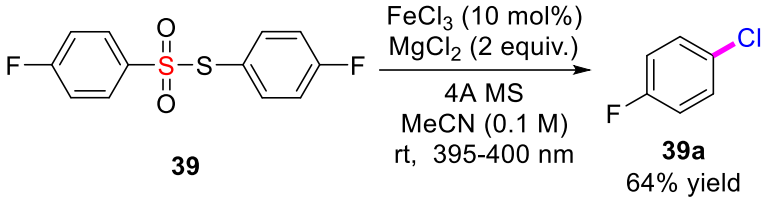


38 **38a** 73% yield

Compound 38a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **38a** was obtained (10.7 mg, 73% 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-4-fluorobenzene (39a)[6]



39 **39a** 64% yield

Compound 39a was prepared according to the general procedure in about 48 h. After standard work-up and purification, **39a** was obtained (8.3 mg, 64% yield).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.24 (m, 2H), 7.07 – 6.97 (m, 2H). **^{13}C 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).

3.6 Gram-scale reaction

The substrate 4-chlorothiophenol (1.44 g, 10 mmol) was dissolved in MeCN (100 mL, 0.10 M) in a flask, $FeCl_3$ (163 mg, 1 mmol), $MgCl_2$ (1.90 g, 20 mmol) and 4A MS (500 mg) was added also to the flask. The reaction mixture was then stirred with air atmosphere at room temperature with the irradiation of two lamps (20 W, 2 cm distance from the light, 395-400 nm) at room temperature. The process of the reaction was monitored by TLC and GC-MS (about 24-36 h). Upon completion, the solution was filtered and the filtrate transferred to a random flask. Then the solvent was removed under vacuum and the residue was purified by silica gel chromatography with petroleum ether (PE)/diethyl ether (Et_2O) as mobile phase to afford the corresponding product 1a (0.95 g, 65% yield).

4. References

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

[2] J. Cornella, C. Sanchez, D. Banawa, I. Larrosa, *Chem. Commun.* **2009**, *46*, 7176–7178.

[3] J. Wu, J.-P. Zhou, Y.-L. Shi, J.-T. Zhu, *Synthetic Commun.* **2016**, *46*, 1619–1624.

[4] L. Sharp-Bucknall, M. Sceney, K. F. White, J. L. Dutton, *Dalton Trans*. **2023**, *52*, 3358–3370.

[5] J.-K. Li, J.-T. Chen, R.-C. Sang, W.-S. Ham, M. B. Plutschack, F. Berger, S. Chabbra, A. Schnegg, C. Genicot, T. Ritter, *Nat. Chem.* **2020**, *12*, 56–62.

[6] S. D. Schimler, M. S. Sanford, *J. Am. Chem. Soc.* **2017**, *139*, 1452−1455.

[7] Z. Yu, W. Su, *Tetrahedron Lett*. **2013**, *54*, 1261–1263.

[8] M.-J. Deng, L. Liu, S.-Y. Yuan, G.-Z. Luo, L.-Y. Dian, *Org. Let.* **2023**, *25*, 4576–4580.

[9] X.-Y. Chen, W.-Q. Hu, F.-L. Qing, Org. Let. **2024**, *26*, 7966–7970.

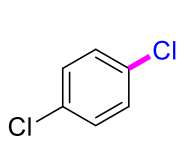
[10] J.-Y. Yang, X.-H. Xu, F.-L. Qing, *J. Fluor. Chem.* **2015**, *180*, 175–180.

[11] W. Zheng, C. A. Morales-Rivera, J. W. Lee, P. Liu, M.-Y. Ngai, *Angew. Chem. Int. Ed.* **2018**, *57*, 9645–9649.

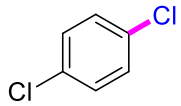
[12] R. Hernandez-Ruiz, S. Gomez-Gil, M. R. Pedrosa, S. Suarez-Pantiga, S. Roberto, *Org. Biomol. Chem*. **2023**, *21*, 7791–7798.

[13] S.-G. Wang, P. Zhou, L. Jiang, Z.-H. Zhang, K.-J. Deng, Y.-H. Zhang, Y.-X. Zhao, J.-L. Li, S. Bottle, H.-Y. Zhu, *J. Catal.* **2018**, *368*, 207–216.

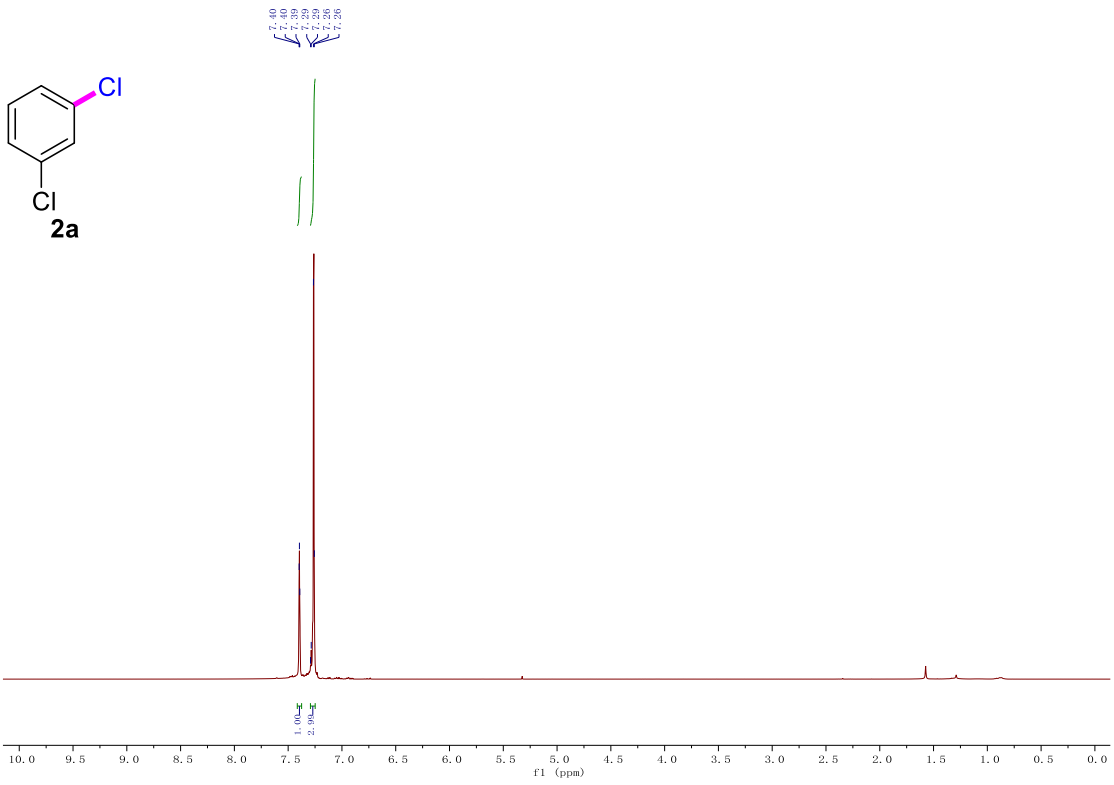
5. NMR Spectra of the Products

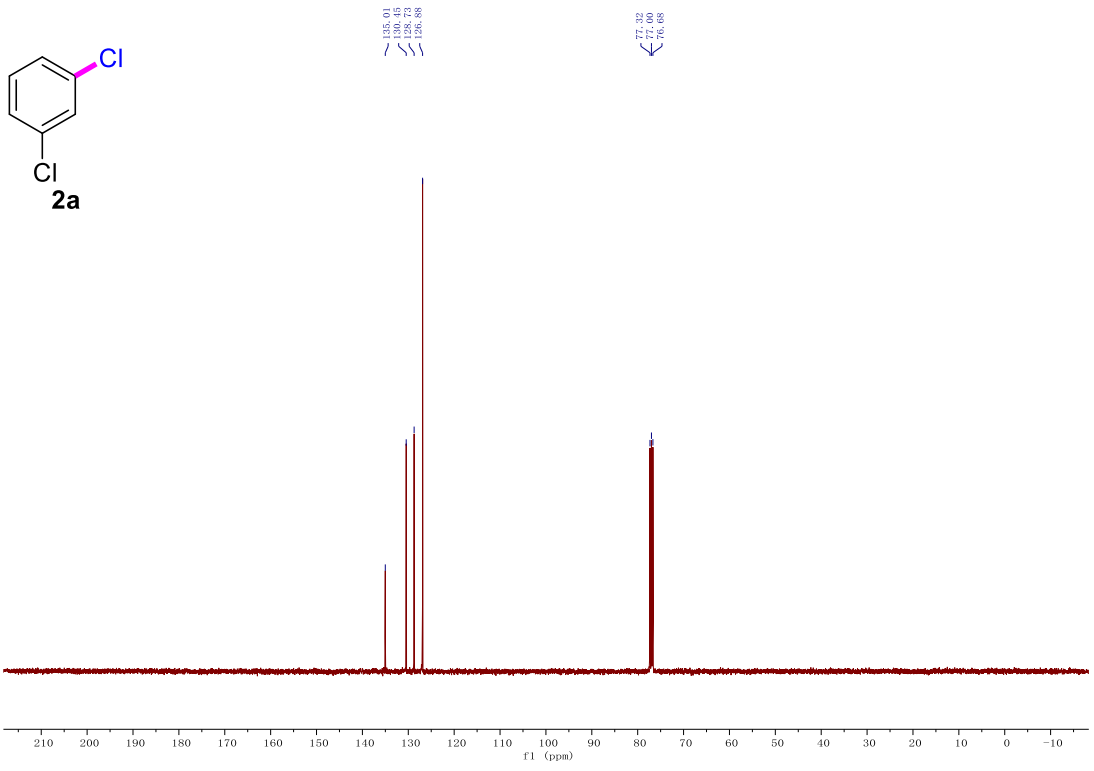


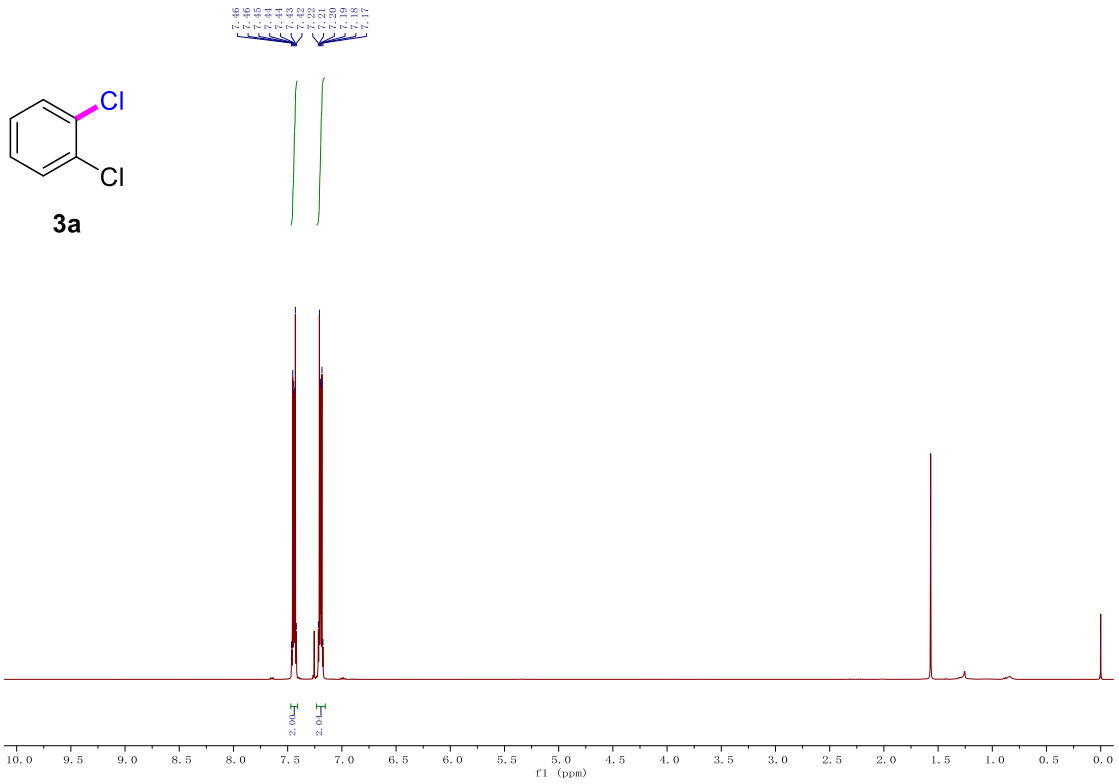
1a

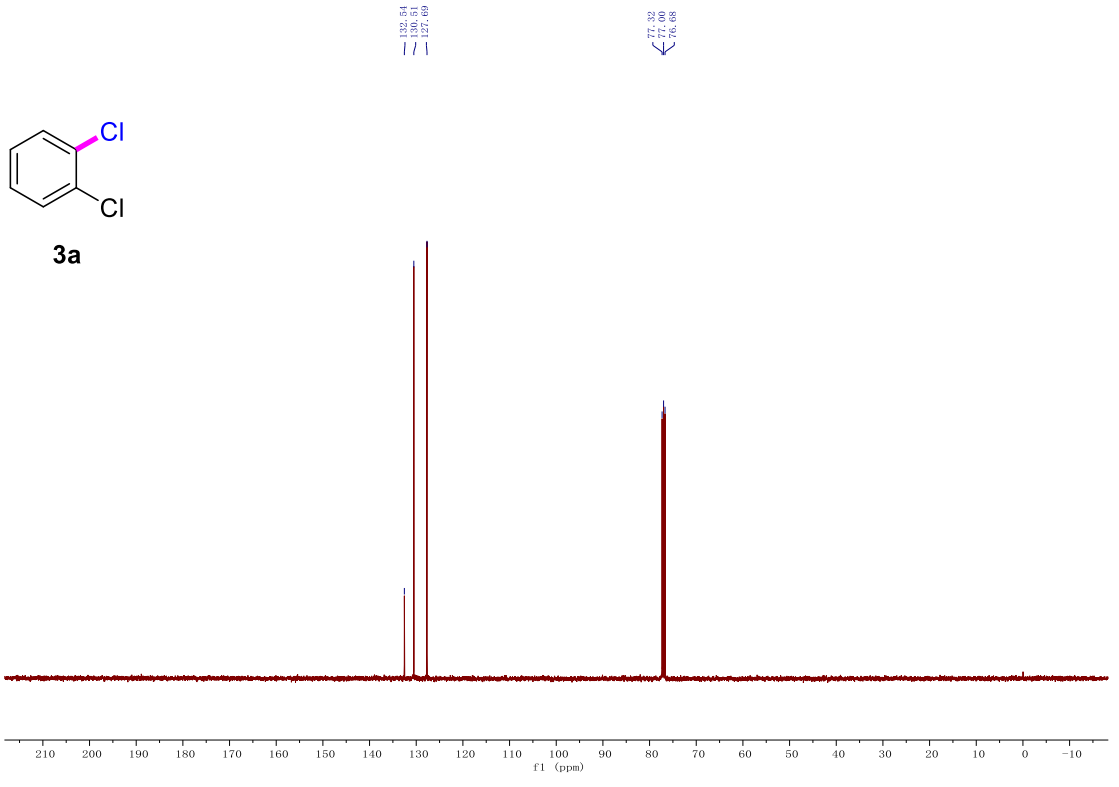


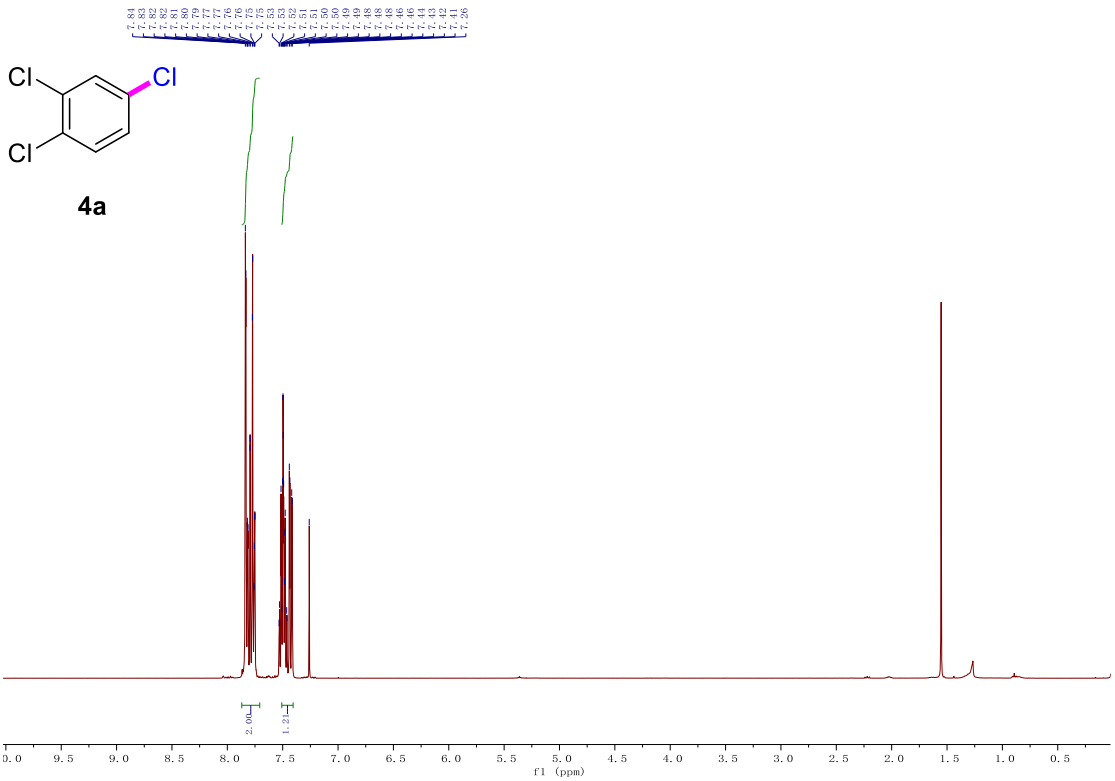
1a

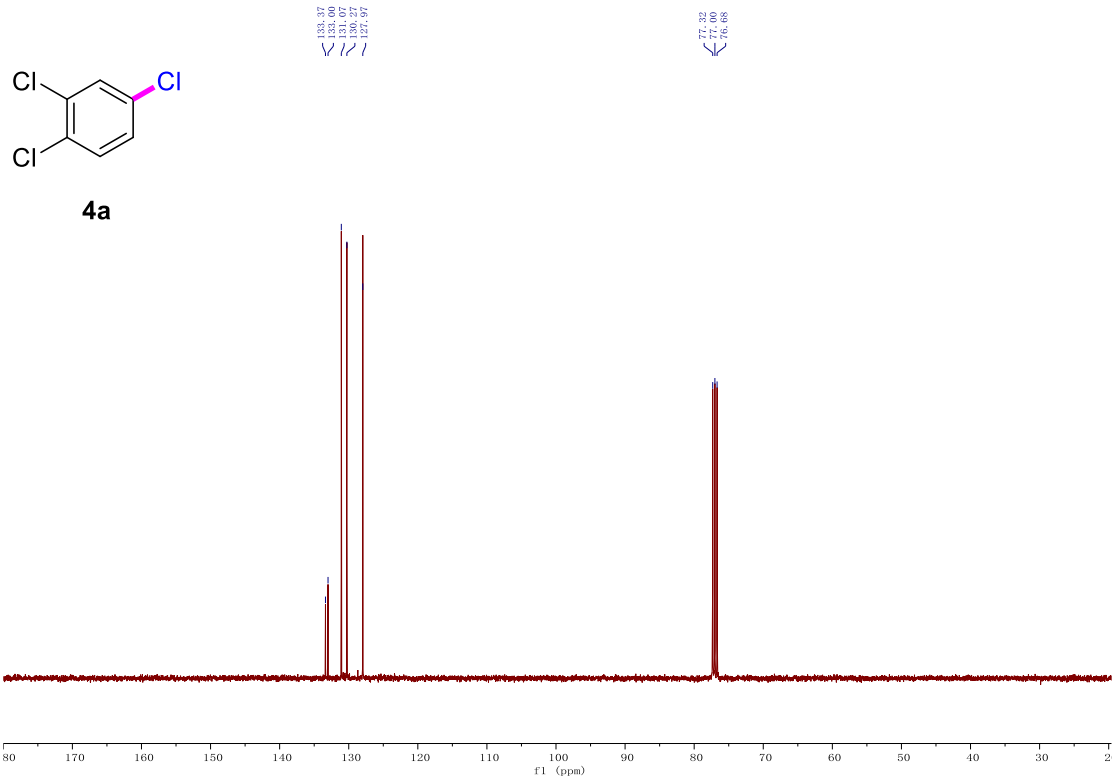

Cl
Cl
2a
7.40
7.40
7.39
7.39
7.29
7.26
7.26
1.00
2.09
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

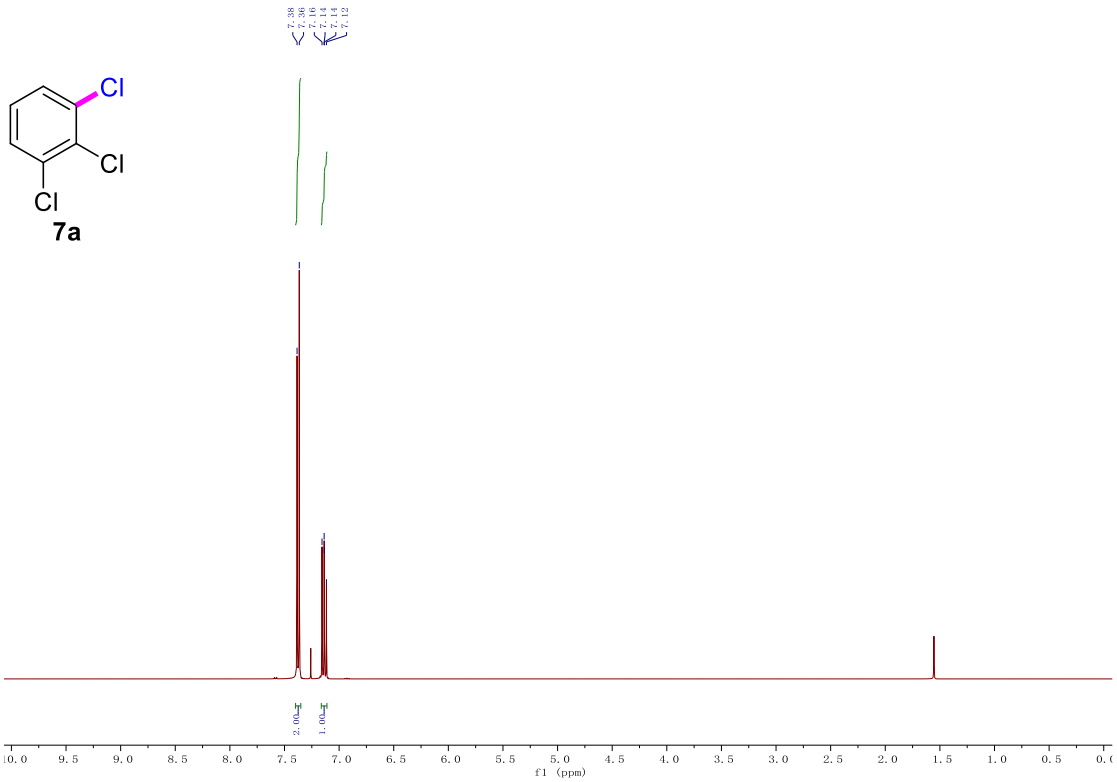

Cl
Cl
2a
135.01
130.45
128.73
128.58
77.32
77.00
76.68
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

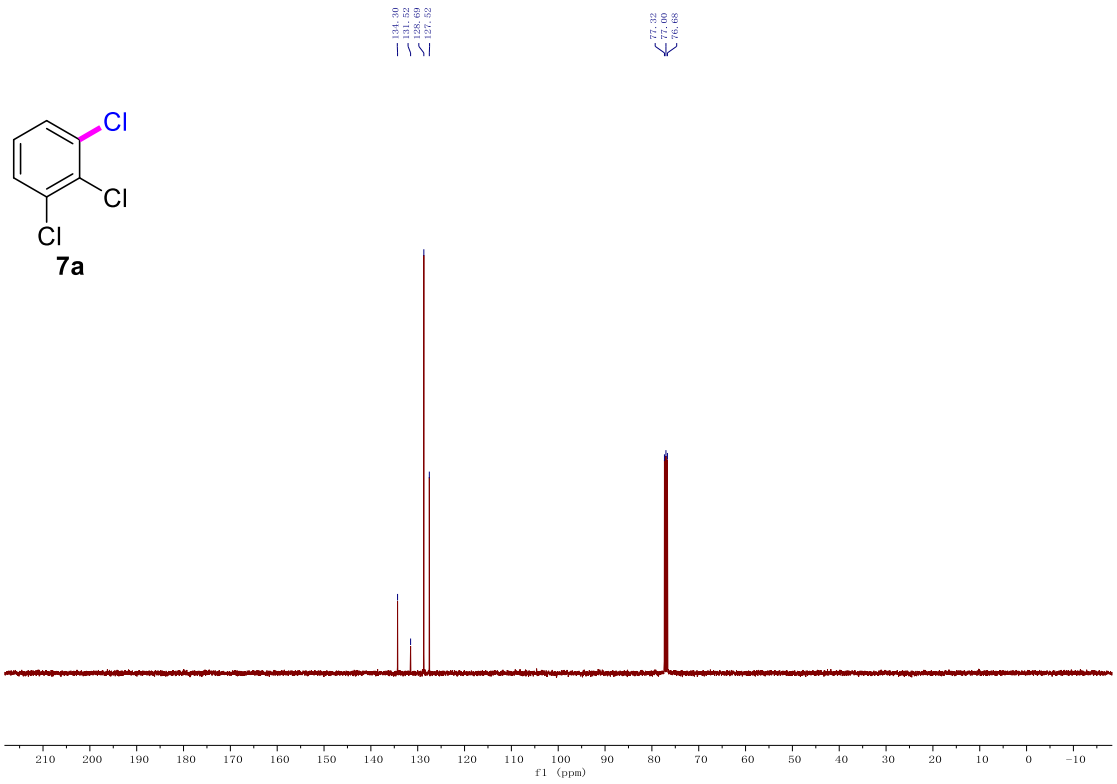

7.46
7.46
7.45
7.44
7.44
7.43
7.42
7.22
7.21
7.20
7.19
7.18
7.17
Cl
Cl
3a
2.00
2.04
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

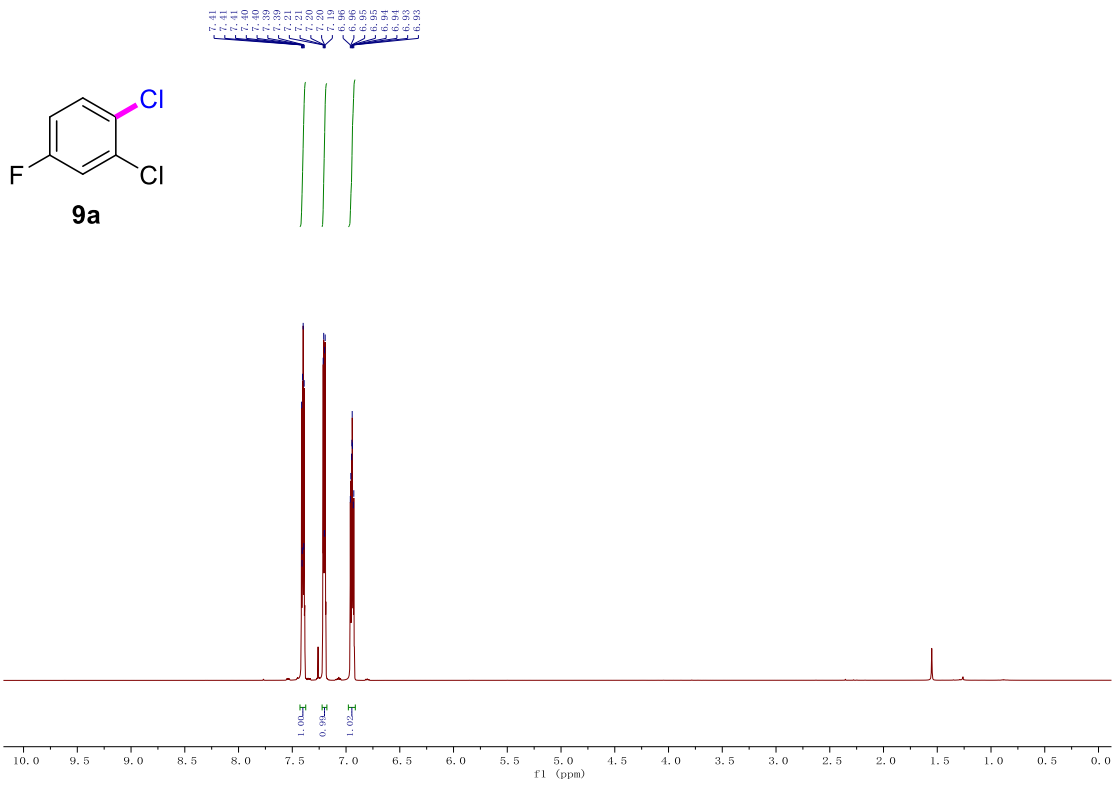

132.54
130.51
127.69
77.32
77.00
76.68
Cl
Cl
3a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

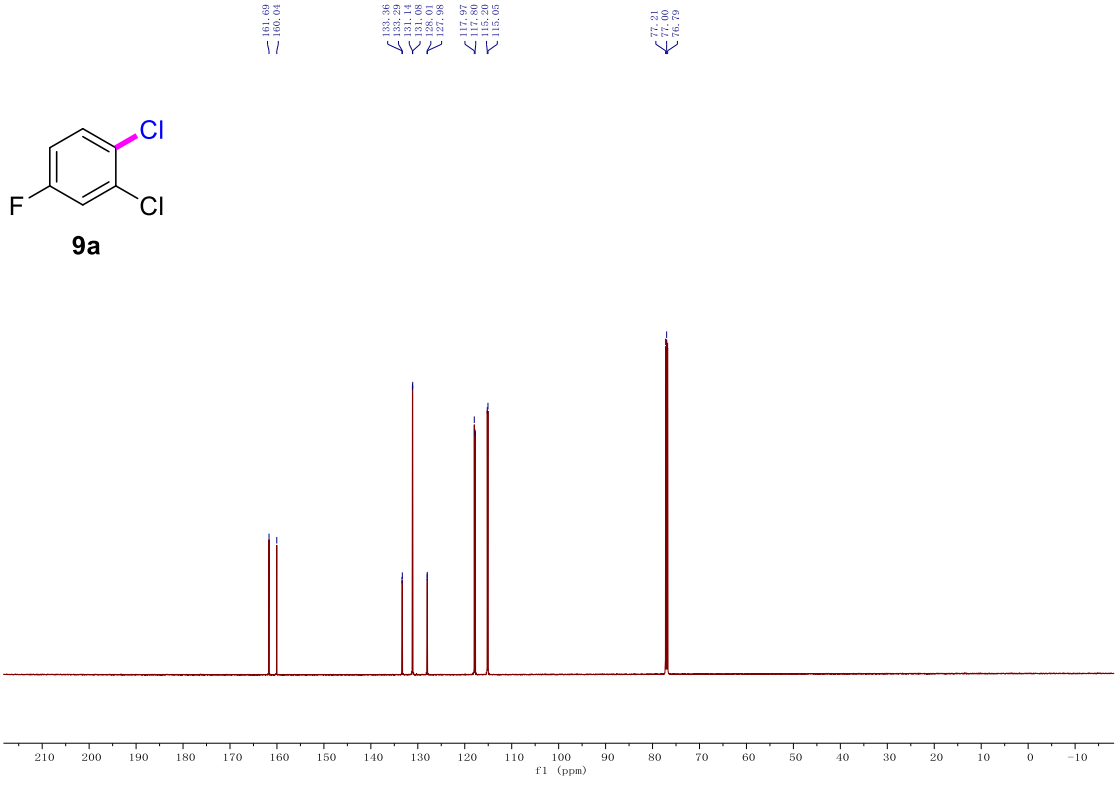

Cl
Cl
4a
2.00
1.21
f1 (ppm)

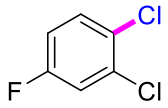

133.37
133.00
131.07
130.27
127.97
77.32
77.00
76.68
Cl
Cl
4a
f1 (ppm)


7.38
7.36
7.16
7.14
7.14
7.12
Cl
Cl
Cl
7a
2.00
1.00
f1 (ppm)


134.30
131.52
128.69
127.32
77.32
77.00
76.68
Cl
Cl
Cl
7a
f1 (ppm)

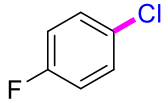

Cl
F
Cl
9a
7.41
7.41
7.41
7.40
7.40
7.39
7.39
7.21
7.21
7.20
7.20
7.19
6.96
6.96
6.95
6.95
6.94
6.94
6.93
6.93
1.00
0.99
1.02
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


161.69
160.04
133.36
133.29
131.14
131.06
128.01
127.98
117.97
117.80
115.20
115.05
77.21
77.00
76.79
Cl
F
Cl
9a
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

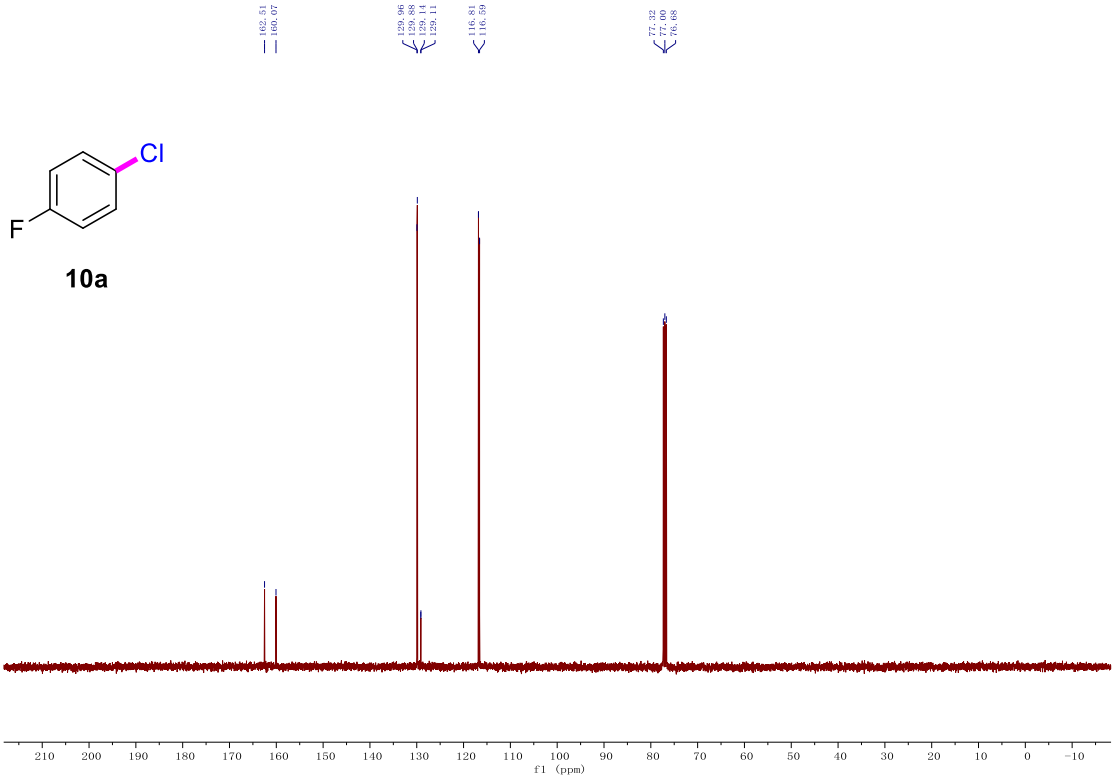
9a

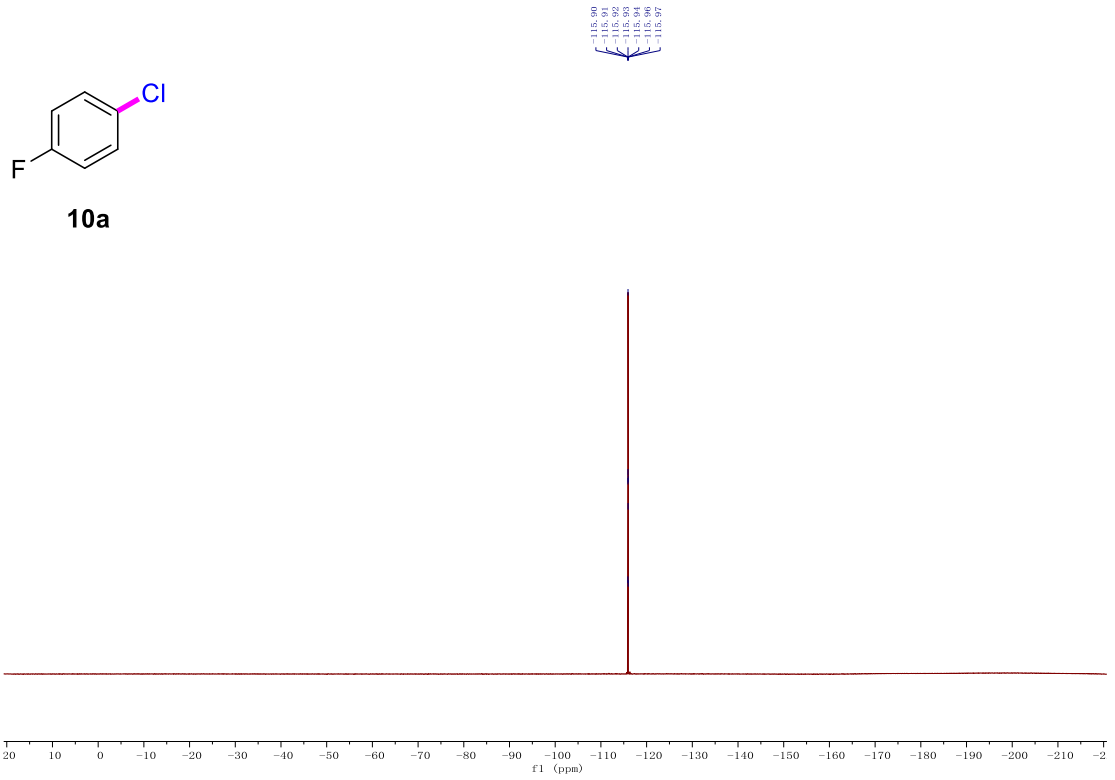
-113.25
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

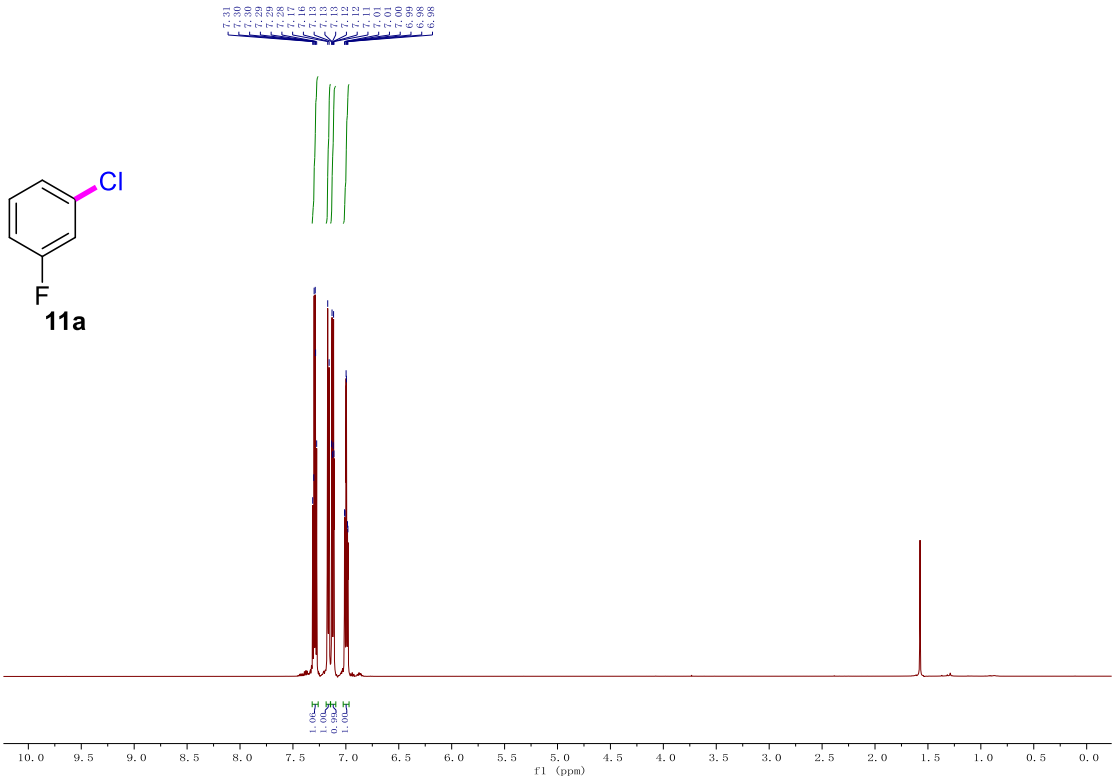

Cl
F

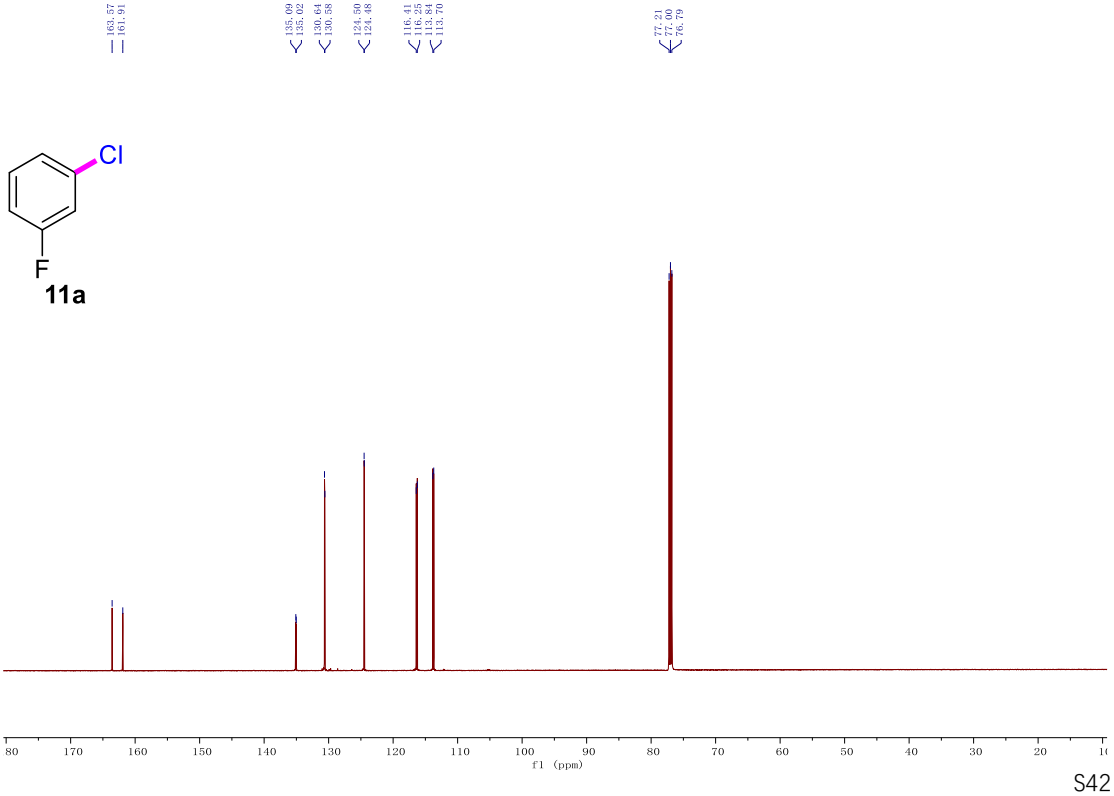
10a

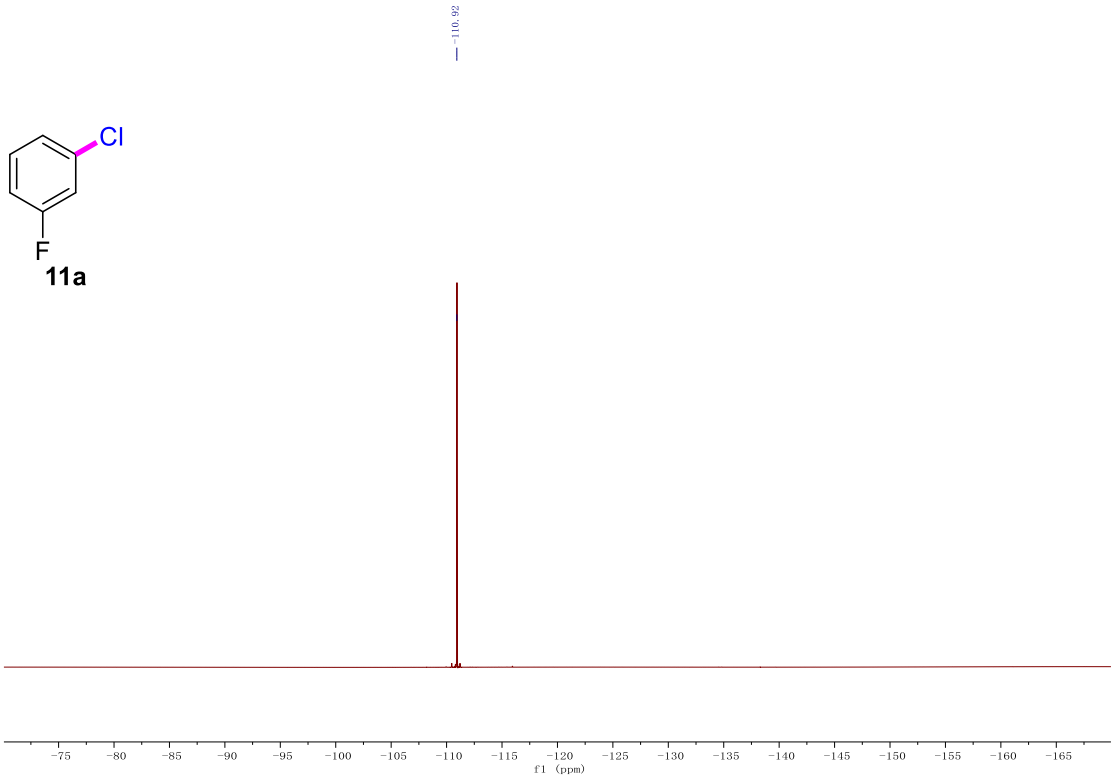
7.31
7.31
7.30
7.30
7.29
7.29
7.28
7.02
7.01
7.00
7.00
6.99
6.98
1.00
0.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

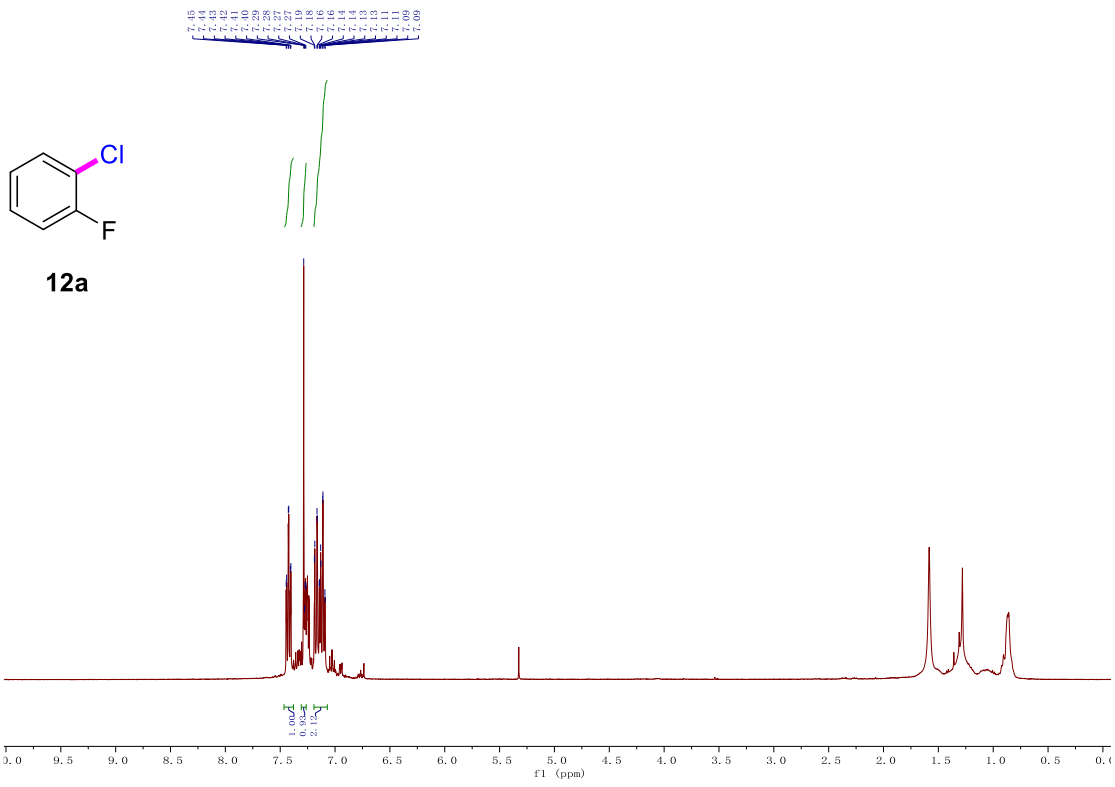

162.51
160.07
129.96
129.88
129.41
129.11
116.81
116.59
77.32
77.00
76.68
Cl
F
10a
f1 (ppm)

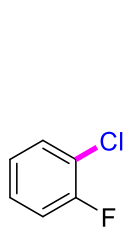

115.90
115.91
115.92
115.93
115.94
115.96
115.97
Cl
F
10a
f1 (ppm)


Cl
F
11a
7.31
7.30
7.30
7.29
7.29
7.28
7.17
7.16
7.13
7.13
7.13
7.12
7.11
7.01
7.01
7.00
6.99
6.98
6.98
1.00
1.00
0.98
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
113.70
77.21
77.00
76.79
Cl
F
11a
80 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20
f1 (ppm)

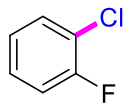

Cl
F
11a
-110.92
-75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150 -155 -160 -165
f1 (ppm)


Cl
F
12a
7.45
7.44
7.43
7.42
7.41
7.40
7.29
7.28
7.27
7.19
7.18
7.16
7.14
7.14
7.13
7.11
7.11
7.09
7.09
1.00
0.93
2.18
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)


Cl
F

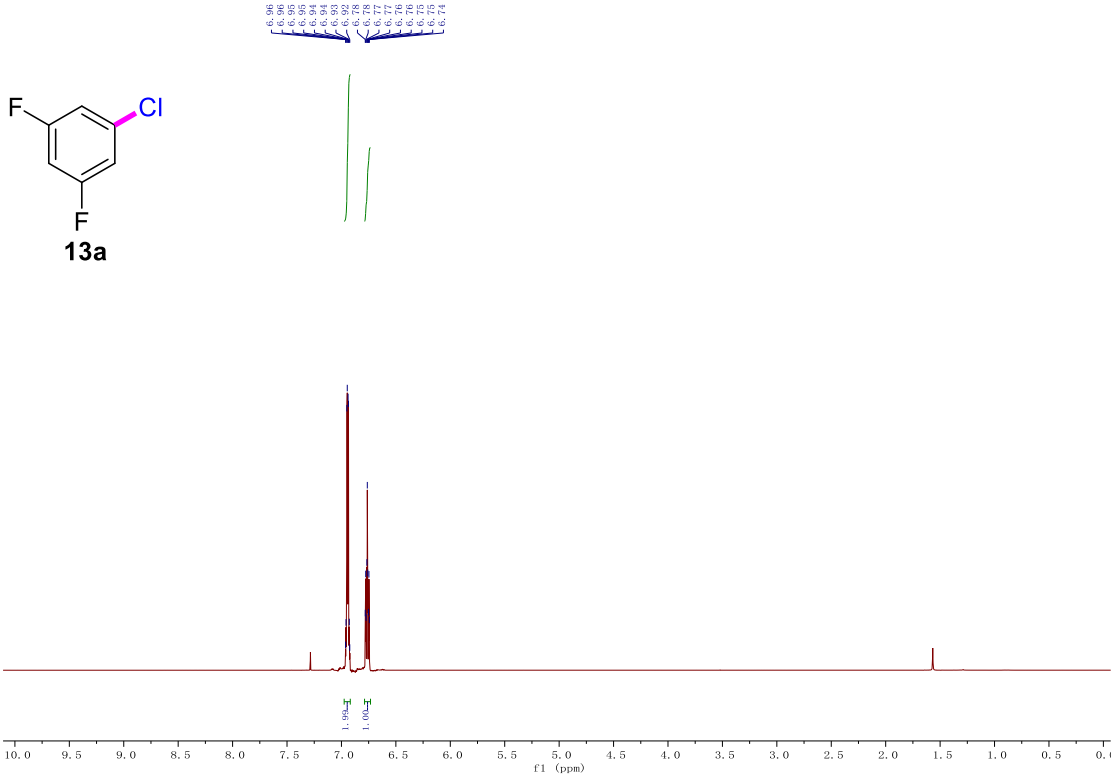
12a

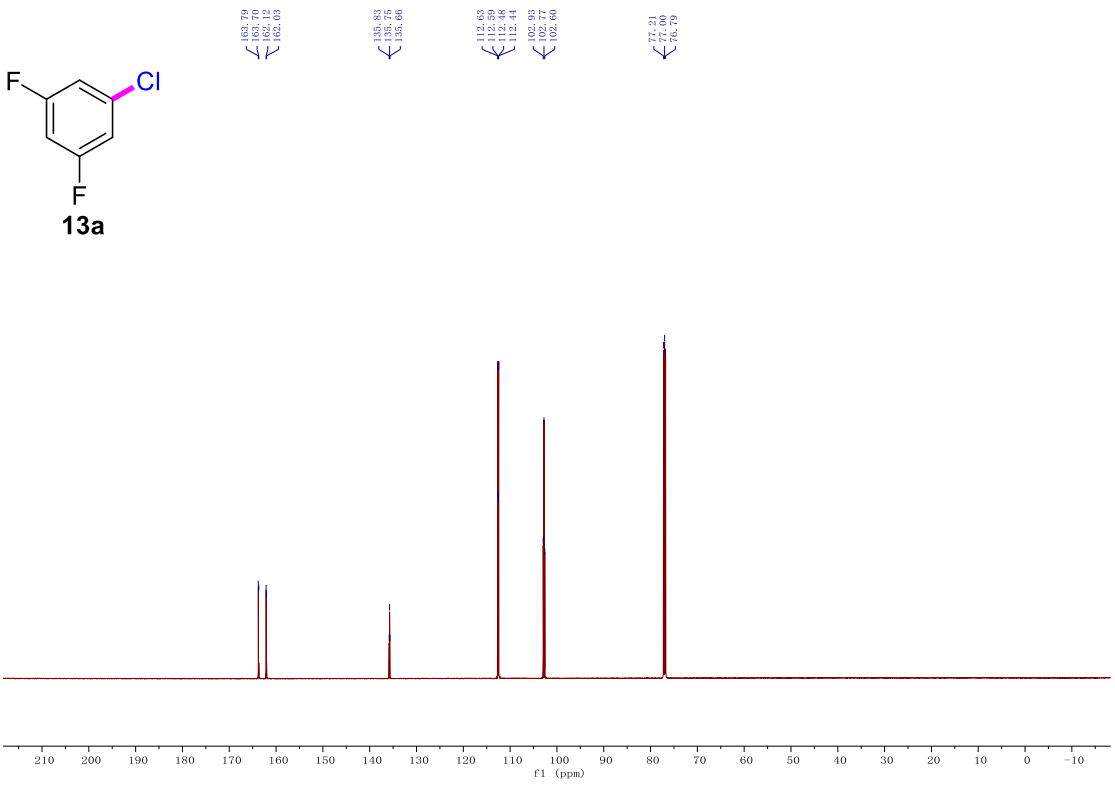
159.39
156.92
130.66
128.14
126.07
124.83
124.79
121.06
120.88
116.69
116.49
77.32
77.00
76.68
f1 (ppm)

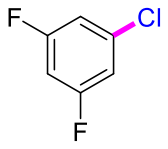

Cl
F

12a

-115.45
f1 (ppm)

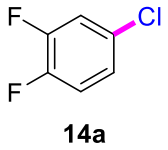

F
Cl
F
13a
6.96
6.96
6.95
6.95
6.94
6.94
6.93
6.92
6.78
6.78
6.77
6.77
6.76
6.76
6.75
6.75
6.74
1.99
1.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


F
Cl
F
13a
163.79
163.70
162.13
162.03
135.83
135.75
135.66
112.63
112.59
112.48
112.44
102.93
102.77
102.60
77.21
77.00
76.79
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
F

13a

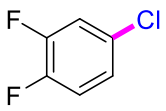
-108.24
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


F
Cl
F

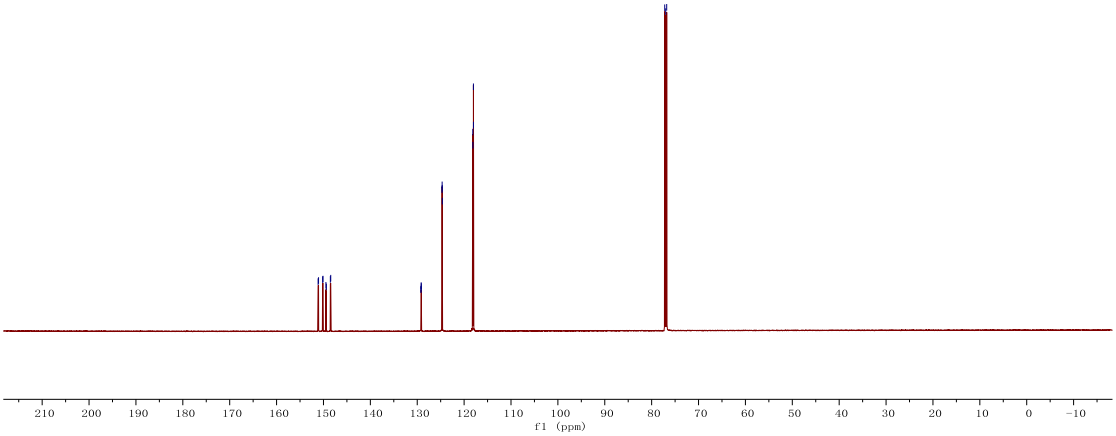
14a

7.21
7.20
7.20
7.19
7.19
7.18
7.18
7.17
7.13
7.12
7.11
7.11
7.10
7.10
7.09
7.09
7.08
7.08
7.08
7.08
7.07
7.07
7.07
7.07
7.07
7.07
7.06
7.06
1.00
2.02
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)

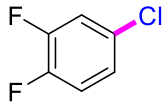

151.14
151.05
150.18
150.10
149.47
149.38
148.53
148.45
129.21
129.18
129.16
129.13
124.71
124.69
124.67
124.65
118.15
118.13
118.01
118.00
77.21
77.00
76.79


F
Cl
F

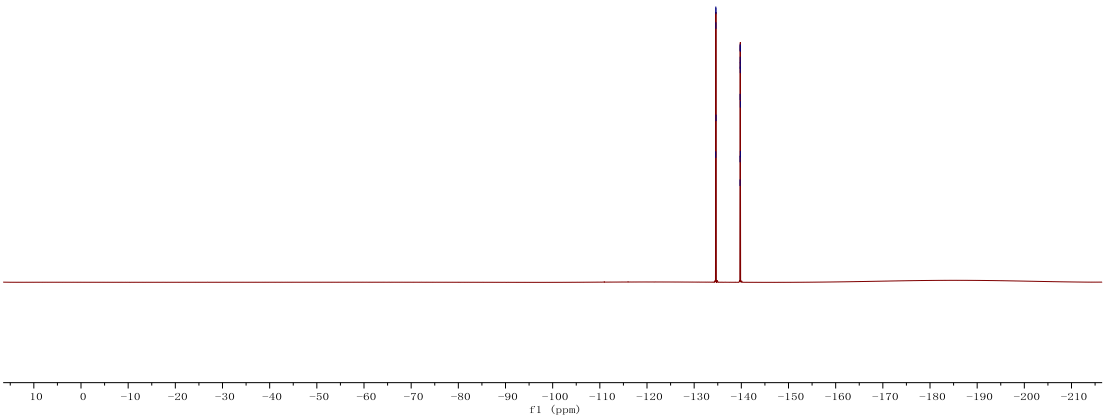
14a

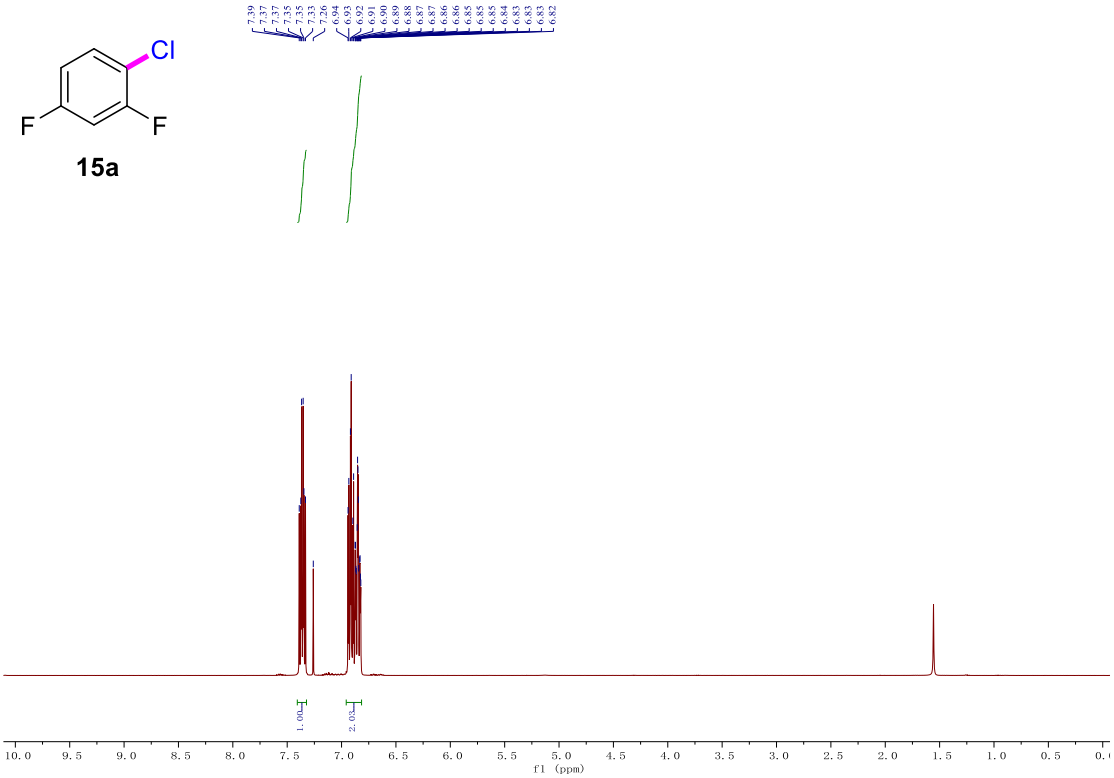

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)

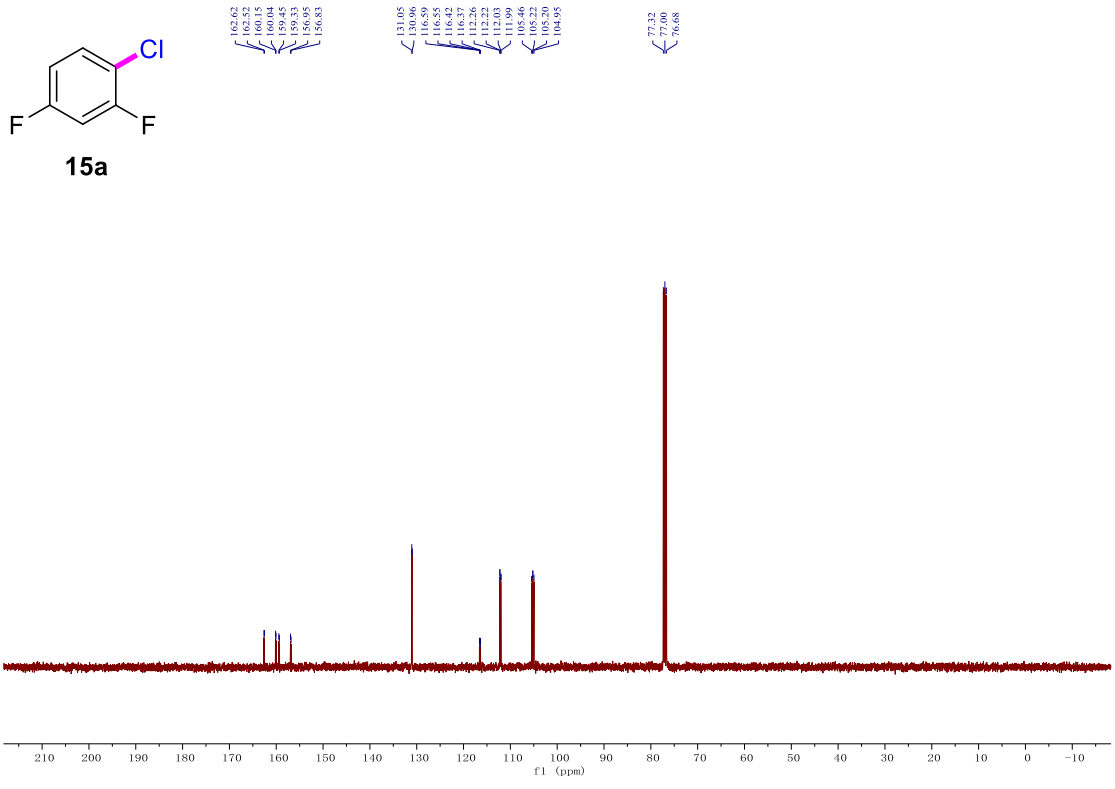

−134.57
−134.58
−134.60
−134.62
−134.64
−139.72
−139.73
−139.73
−139.73
−139.74
−139.75
−139.76
−139.77
−139.78
−139.79
−139.80

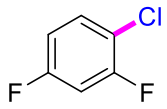

F
Cl
F

14a


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)

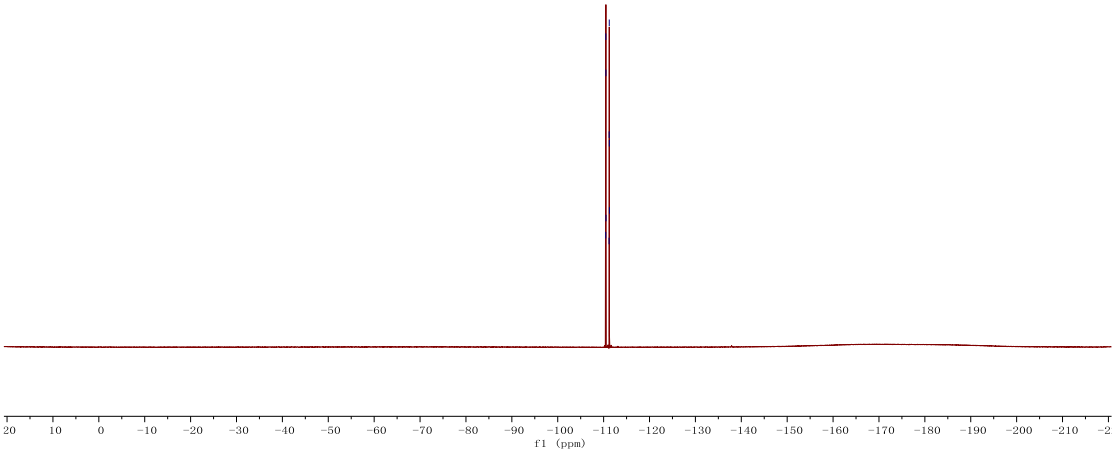

Cl
F
F
15a
7.39
7.37
7.37
7.35
7.35
7.33
7.26
7.04
6.94
6.93
6.92
6.91
6.90
6.89
6.88
6.87
6.87
6.86
6.86
6.85
6.85
6.84
6.84
6.83
6.83
6.82
1.00
2.03
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

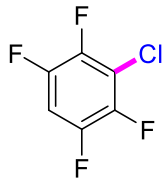

Cl
F
F
15a
162.62
162.52
160.15
160.04
159.45
159.33
156.95
156.83
131.05
130.96
116.59
116.55
116.42
116.37
112.26
112.22
112.03
111.99
105.46
105.22
105.20
104.95
77.32
77.00
76.68
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


Cl
F
F

15a

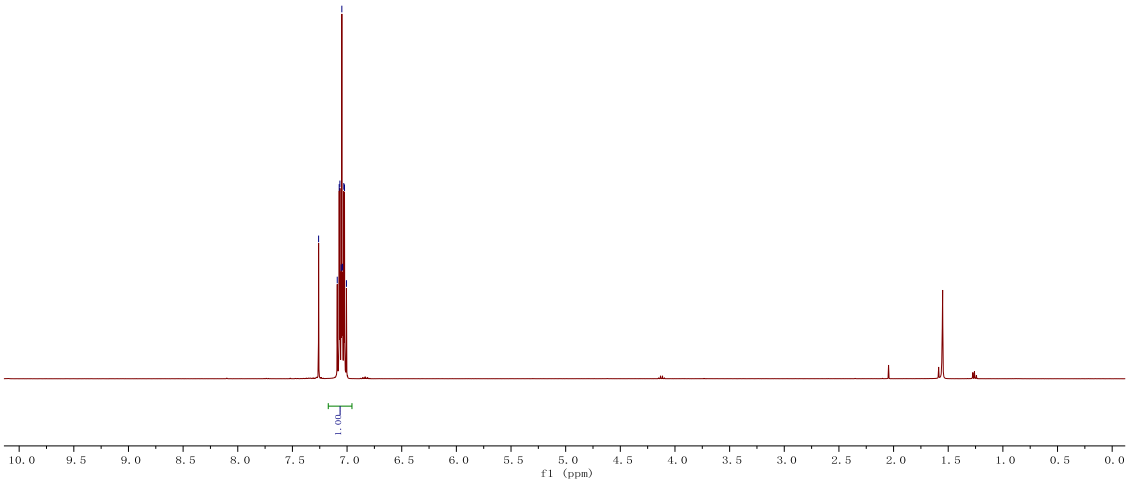

-110.45
-110.47
-110.49
-110.52
-111.19
-111.21
-111.23
-111.25
-111.27

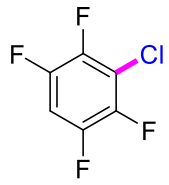

20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


F
F
Cl
F
F

16a

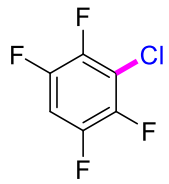

7.26
7.09
7.07
7.07
7.07
7.05
7.05
7.04
7.03
7.02
7.01


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)


F
F
Cl
F
F

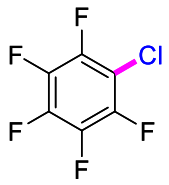
16a

147.48
147.38
147.20
145.40
145.20
145.00
144.89
144.71
142.87
142.75
142.72
104.79
104.58
104.56
104.53
104.33
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)


F
F
Cl
F
F

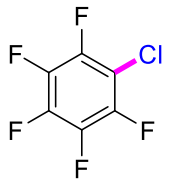
16a

-137.59
-137.62
-137.65
-137.66
-137.68
-137.69
-137.70
-137.71
-137.74
-137.75
-137.76
-137.77
-140.58
-140.59
-140.61
-140.62
-140.63
-140.65
-140.66
-140.67
-140.68
-140.70
-140.71
-140.73
-140.75
-140.76
-140.77
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2
f1 (ppm)


F
F
Cl
F
F
F

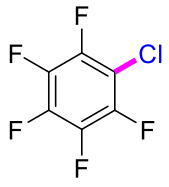
17a

7.26
1.52
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
F
F
F

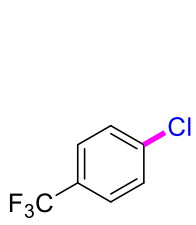
17a

145.82
145.58
145.70
143.30
143.16
141.55
139.52
139.36
139.15
139.01
136.98
136.80
107.96
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)

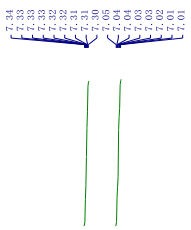

F
F
Cl
F
F
F

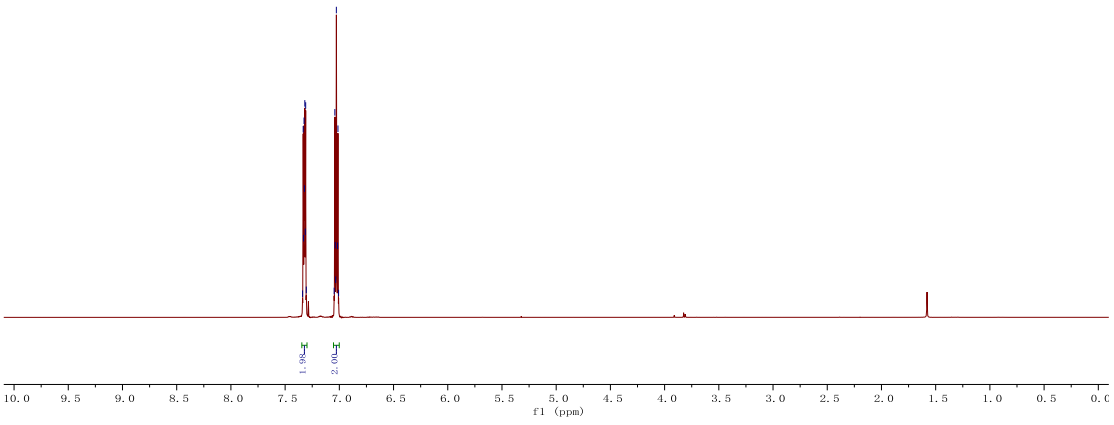
17a

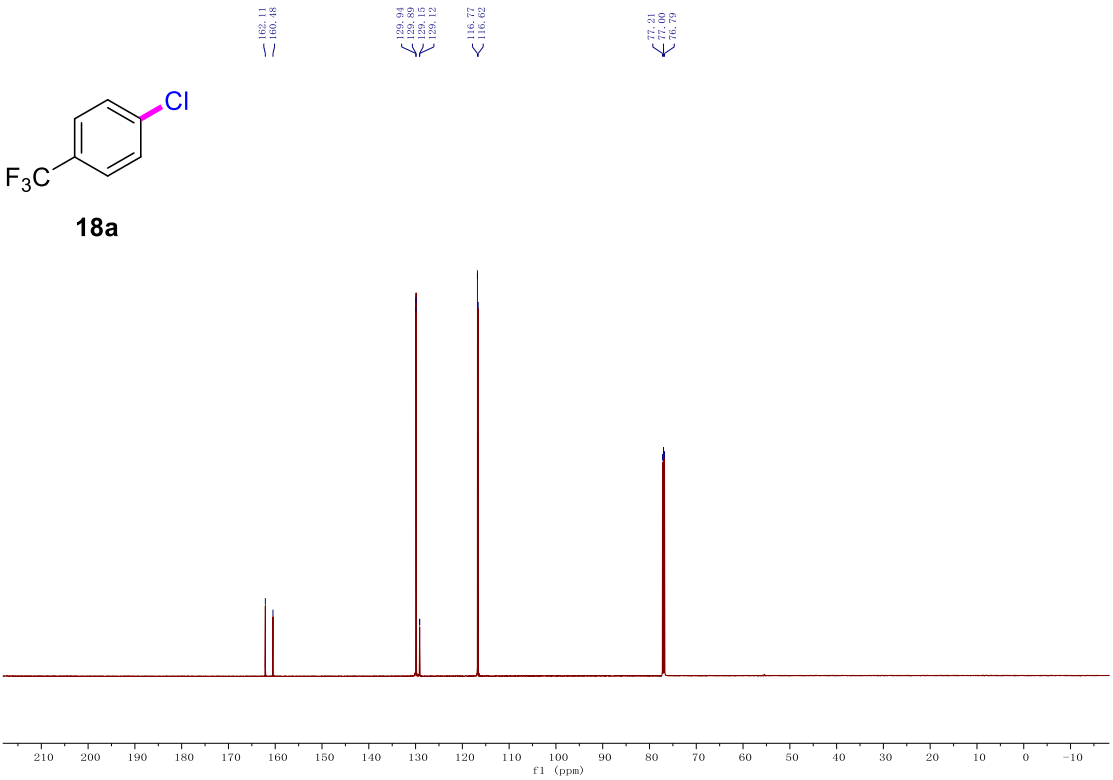
-140.25
-140.25
-140.26
-140.27
-140.27
-140.32
-140.32
-140.33
-140.34
-140.34
-155.56
-155.62
-155.67
-160.80
-160.81
-160.81
-160.82
-160.87
-160.88
-160.89
-160.92
-160.93
-160.93
-160.94
f1 (ppm)

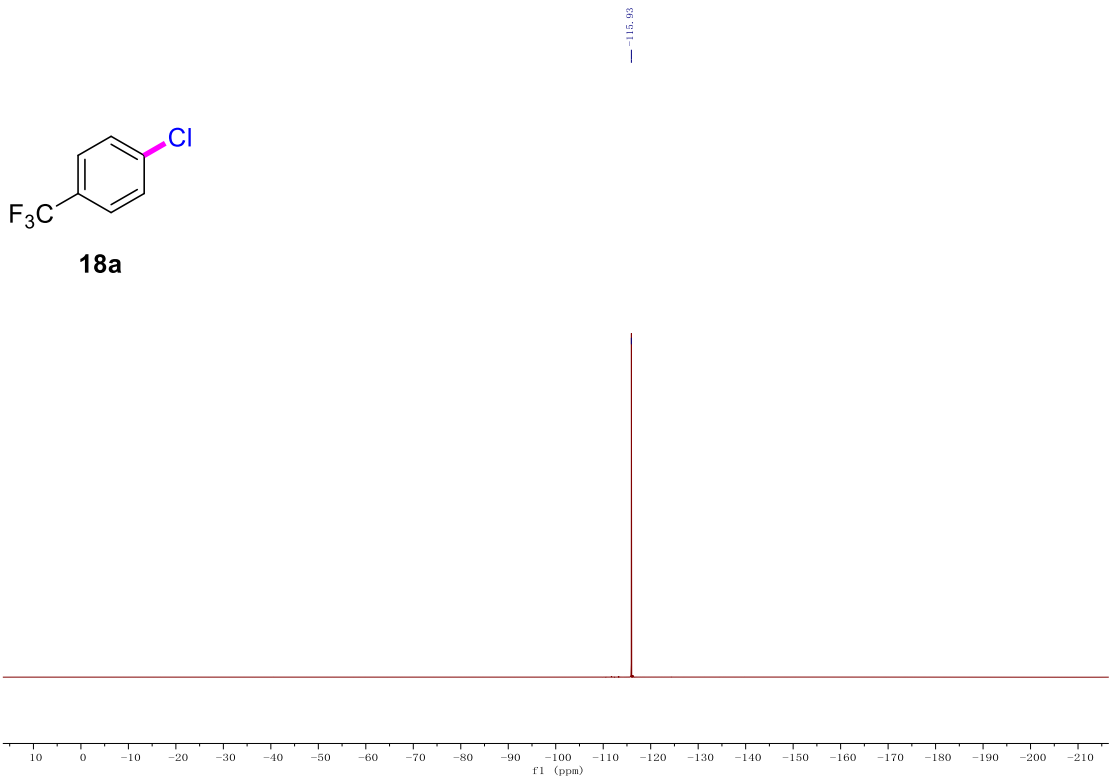

Cl
F3C

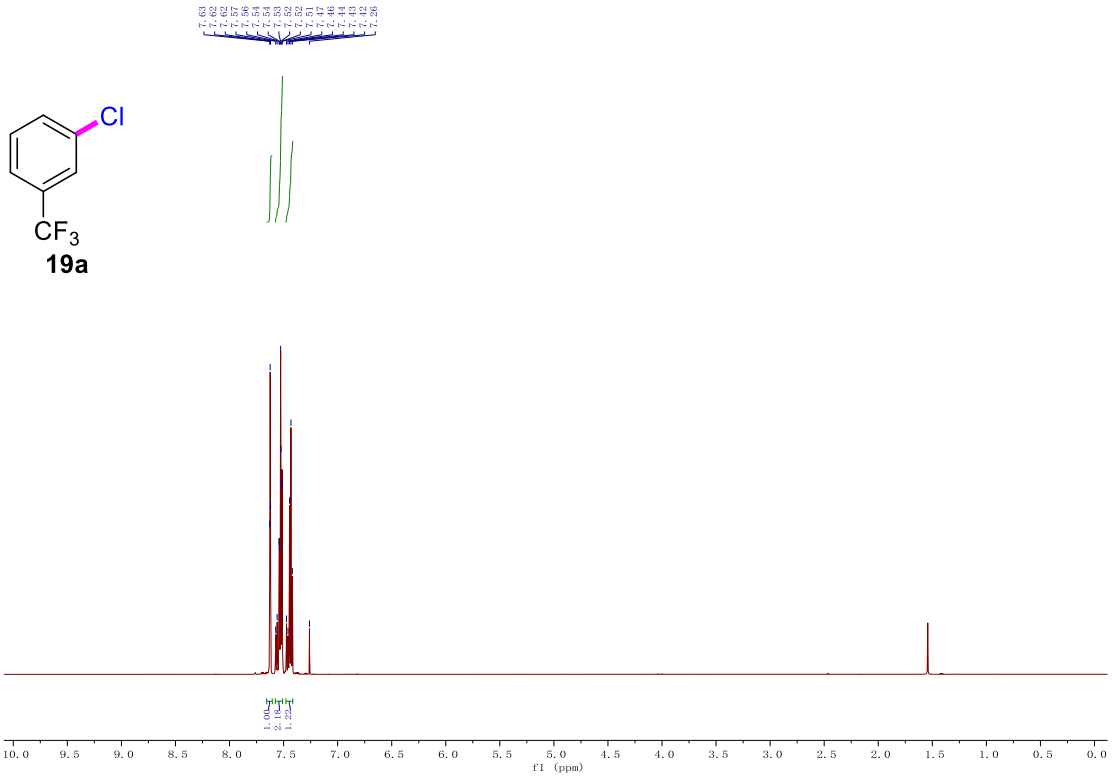
18a

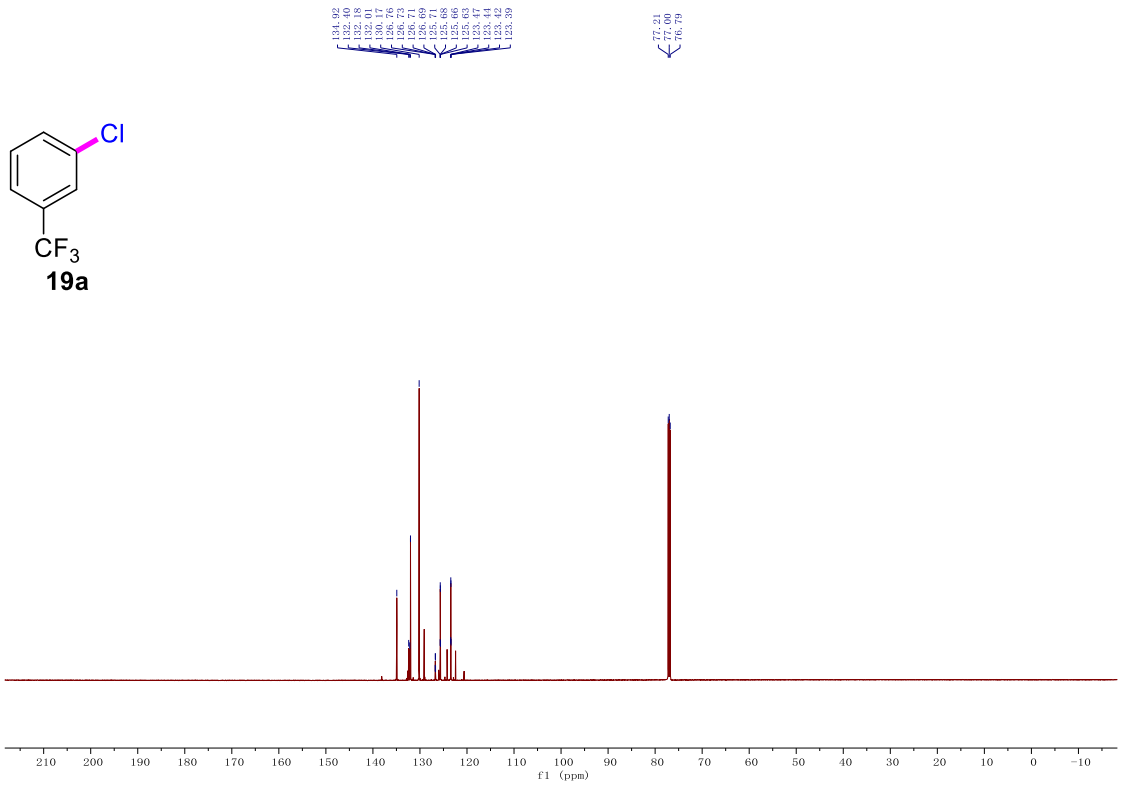

7.34
7.33
7.33
7.33
7.32
7.32
7.31
7.31
7.30
7.05
7.04
7.04
7.03
7.03
7.02
7.02
7.01
7.01

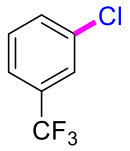

1.98
2.00
f1 (ppm)


162.11
160.48
129.94
129.89
129.15
129.12
116.77
116.62
77.21
77.00
76.79
Cl
F3C
18a
f1 (ppm)


-115.93
Cl
F3C
18a
f1 (ppm)

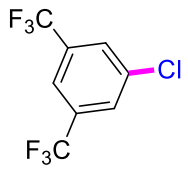

Cl
CF3
19a
f1 (ppm)


Cl
CF3
19a
f1 (ppm)


Cl
CF3

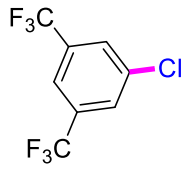
19a

-62.95
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)


F3C
Cl
F3C

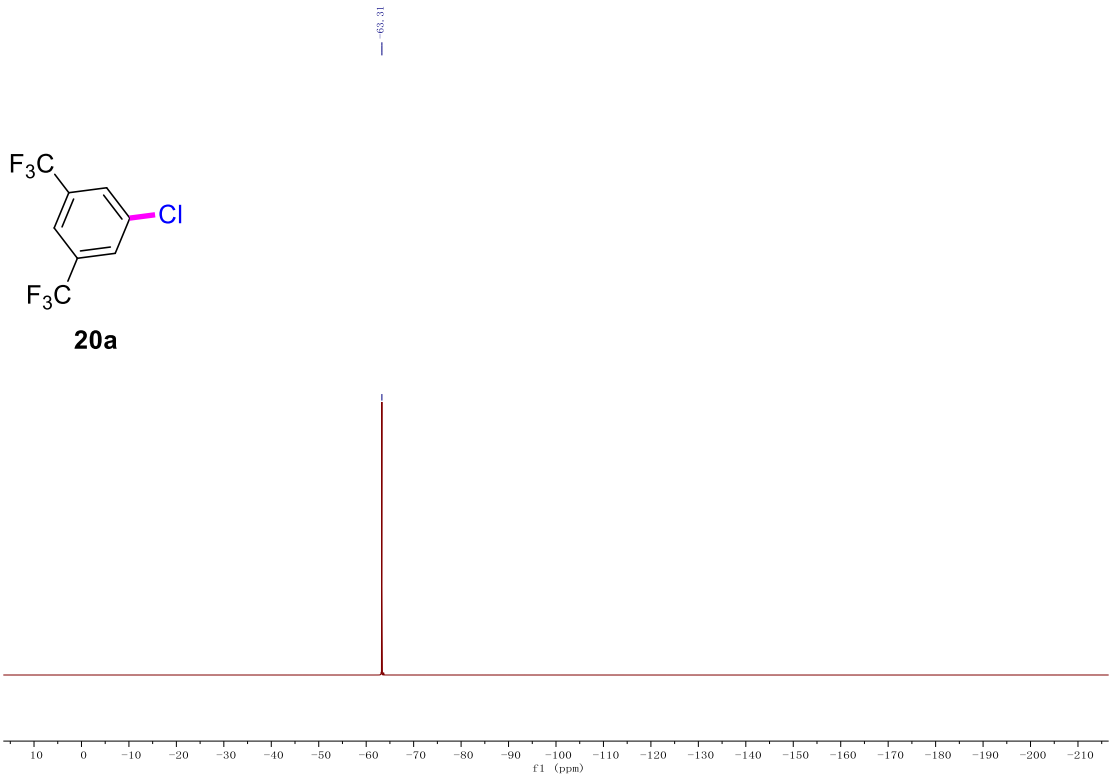
20a

7.72
7.69
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)


F3C
Cl
F3C

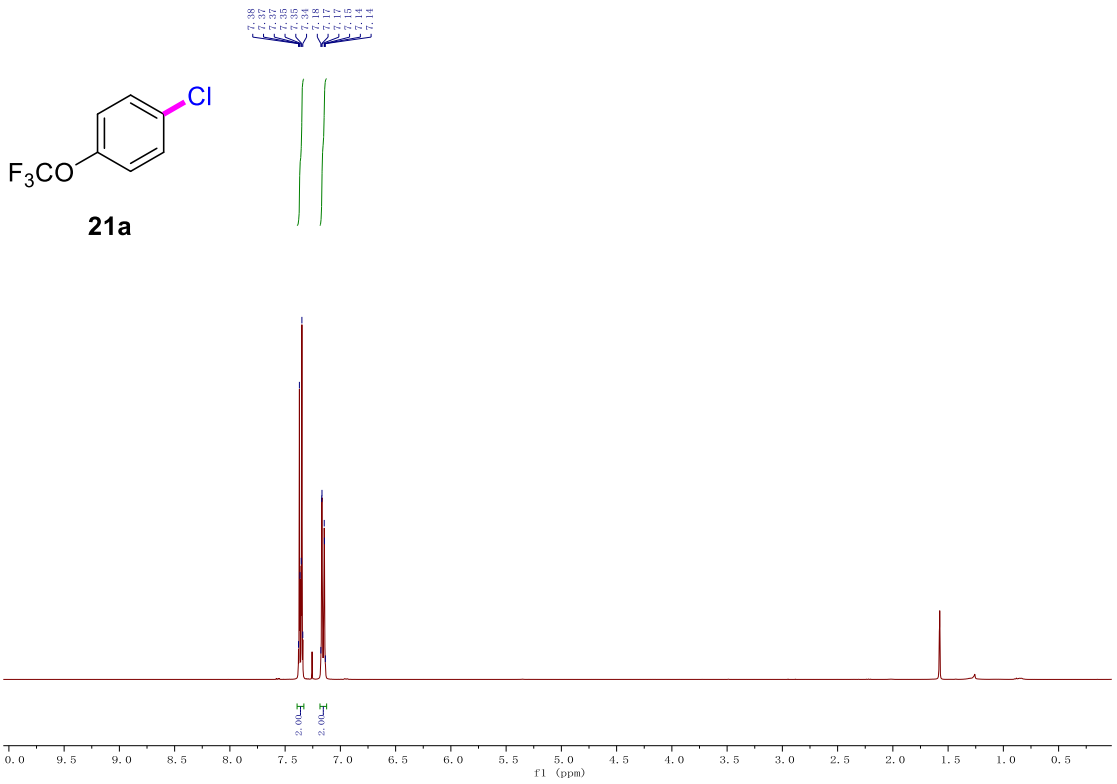
20a

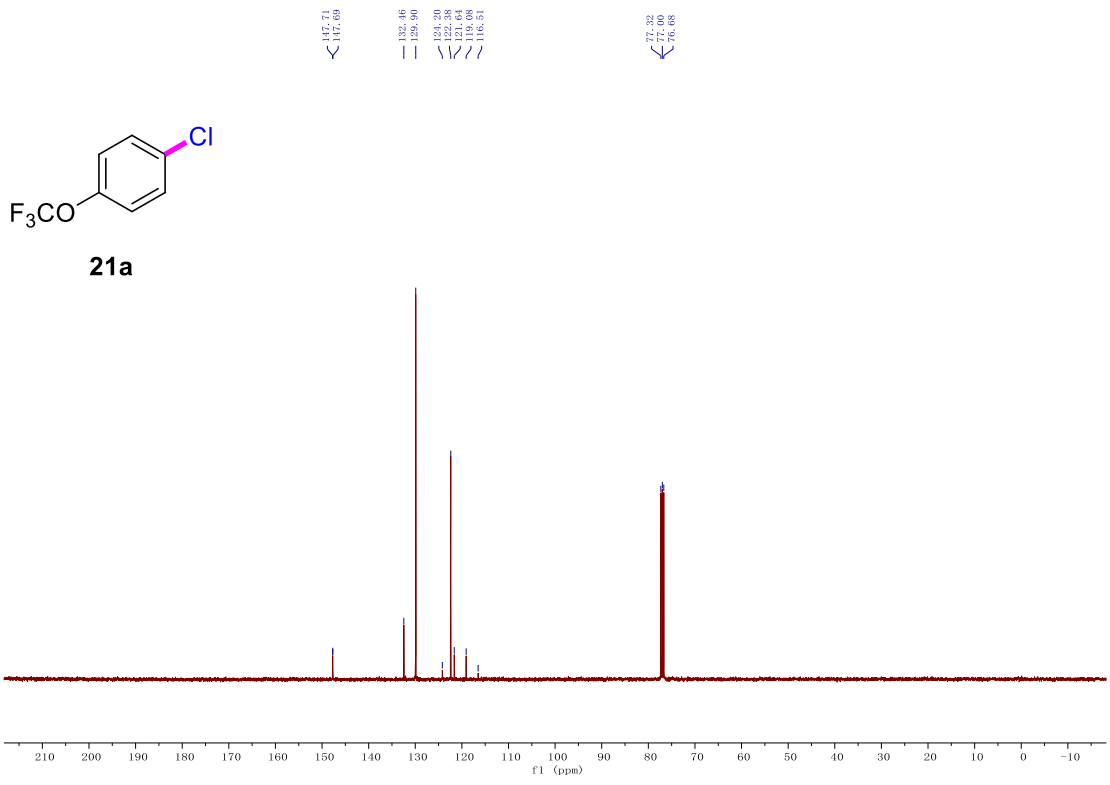
136.06
133.61
133.38
133.16
132.93
129.15
129.13
129.10
129.08
125.39
123.48
121.67
120.78
120.76
120.73
120.71
120.68
120.66
120.63
119.87
77.21
77.00
76.79
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

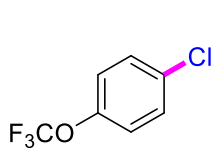

-63.31
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

F3C
Cl
F3C

20a

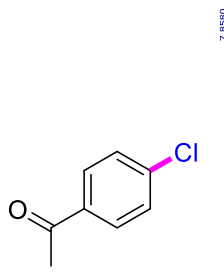

7.38
7.37
7.37
7.35
7.35
7.34
7.18
7.17
7.17
7.15
7.14
7.14
Cl
F3CO
21a
2.00
2.00
f1 (ppm)


147.71
147.69
132.46
129.90
124.20
122.38
121.64
119.08
116.51
77.32
77.00
76.68
Cl
F3CO
21a
f1 (ppm)


Cl
F3CO

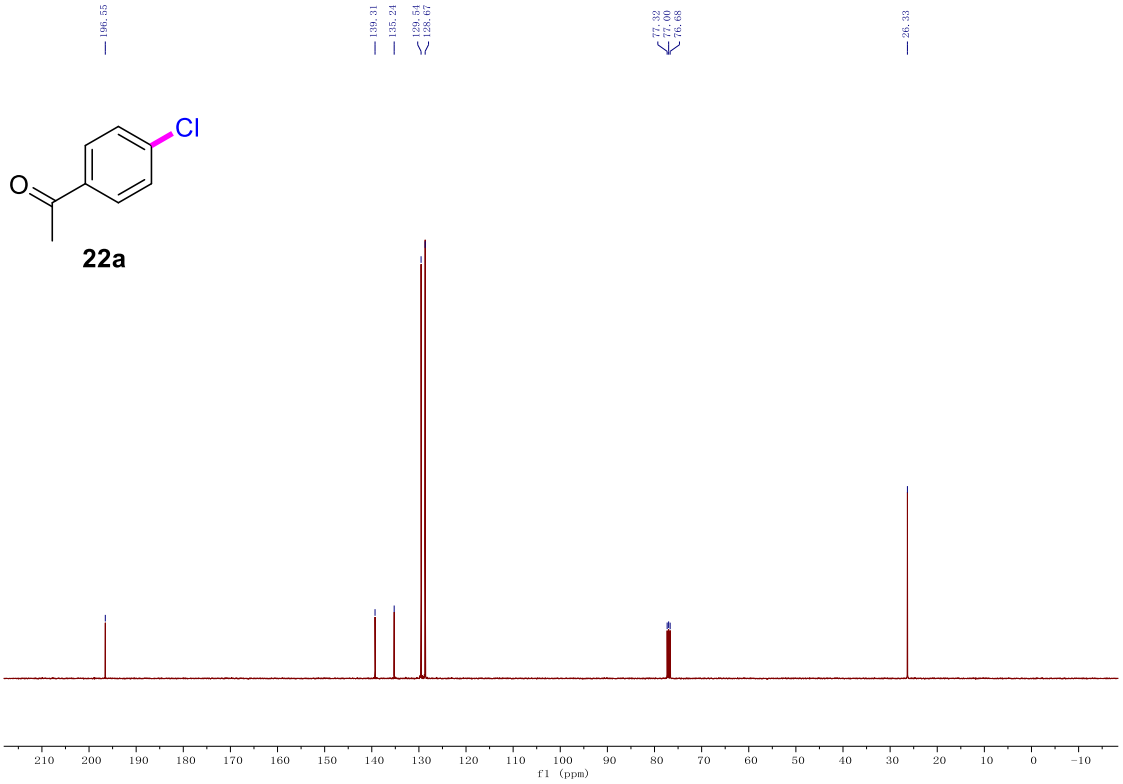
21a

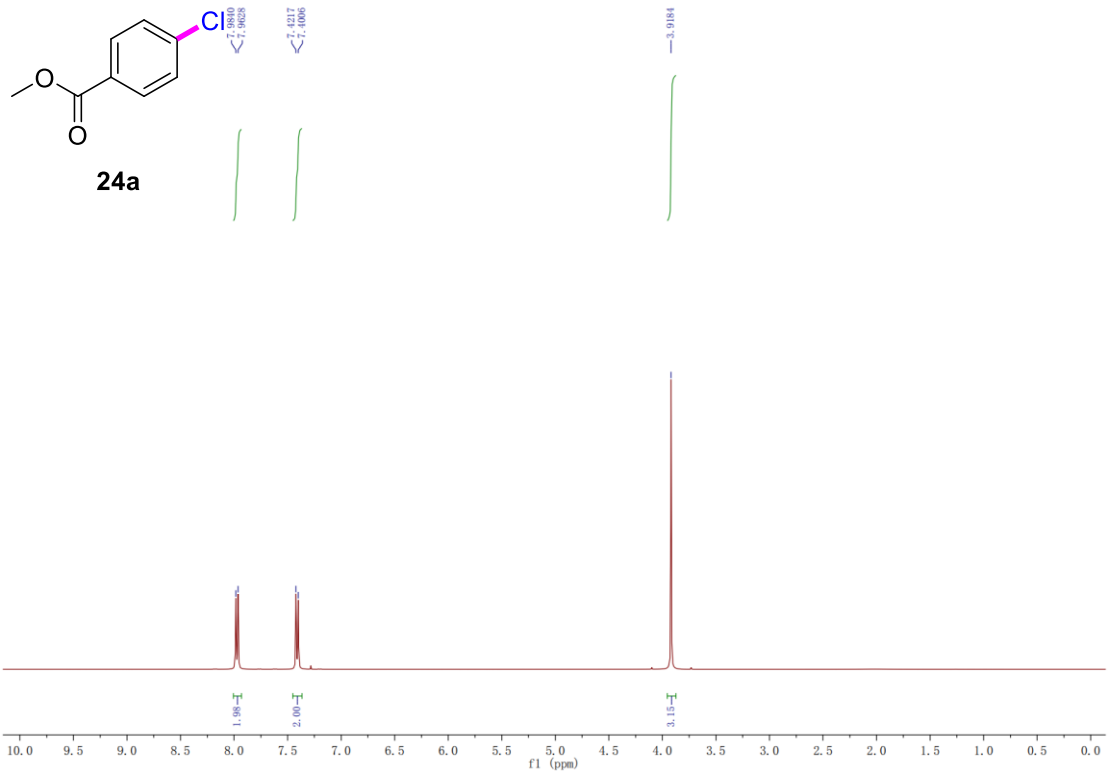
-58.20
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
f1 (ppm)

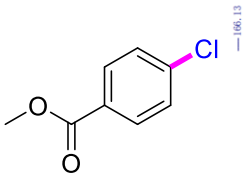

Cl
O

22a

7.8580
7.8539
7.8410
7.8367
7.8311
7.3911
7.3698
7.3643
2.5463
2.00
1.97
3.14
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
f1 (ppm)

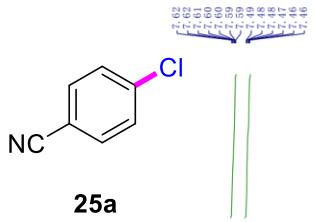

196.55
139.31
135.24
129.54
128.67
77.32
77.00
76.68
26.33
Cl
O
22a
f1 (ppm)


7.9840
7.9628
7.4217
7.4006
3.9184
Cl
O
O
24a
1.98
2.00
3.15
f1 (ppm)


Cl
O
O

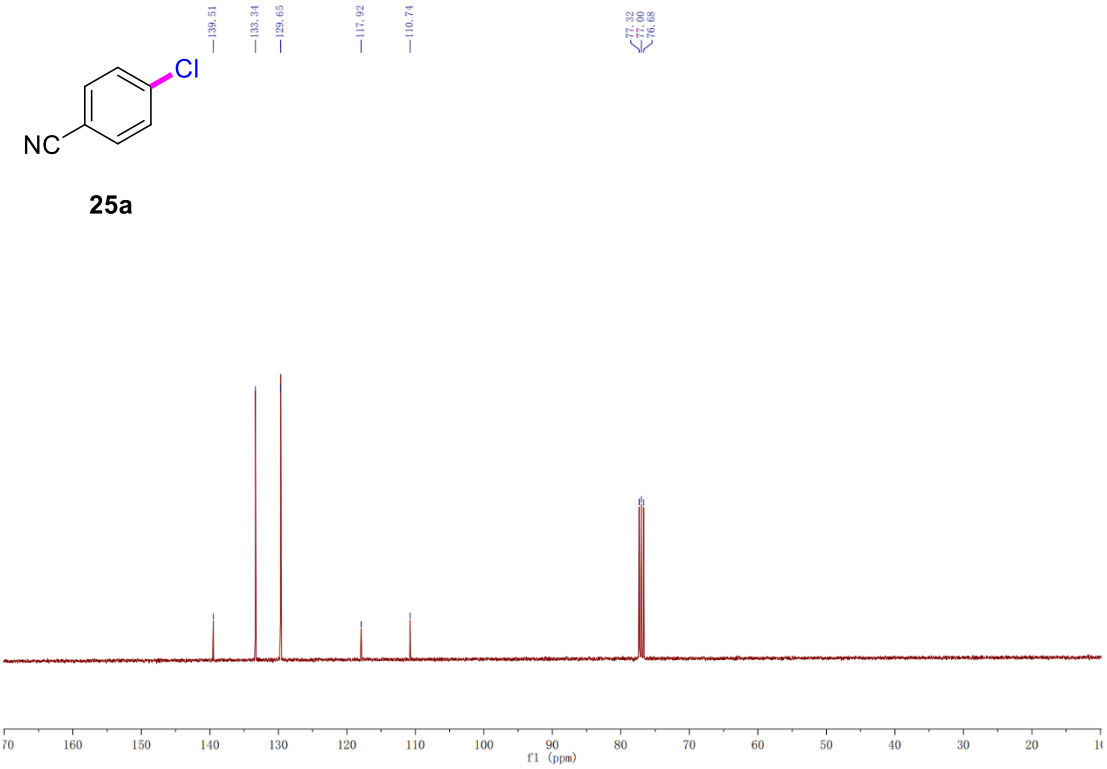
24a

166.13
139.29
130.90
128.63
128.52
77.32
77.00
76.68
52.19
f1 (ppm)

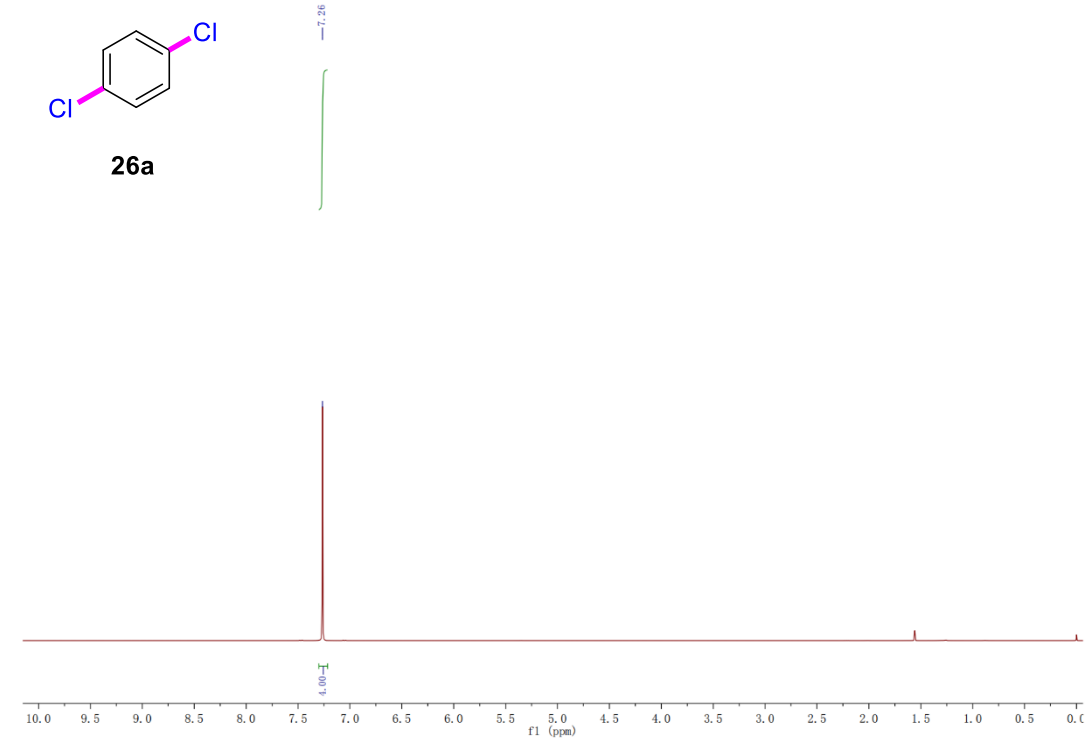

Cl
NC

25a

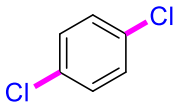
7.62
7.61
7.60
7.59
7.49
7.48
7.47
7.46
2.00
2.00
f1 (ppm)


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

25a

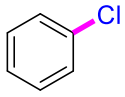

7.26
Cl
Cl
4.00
f1 (ppm)

26a


Cl
Cl

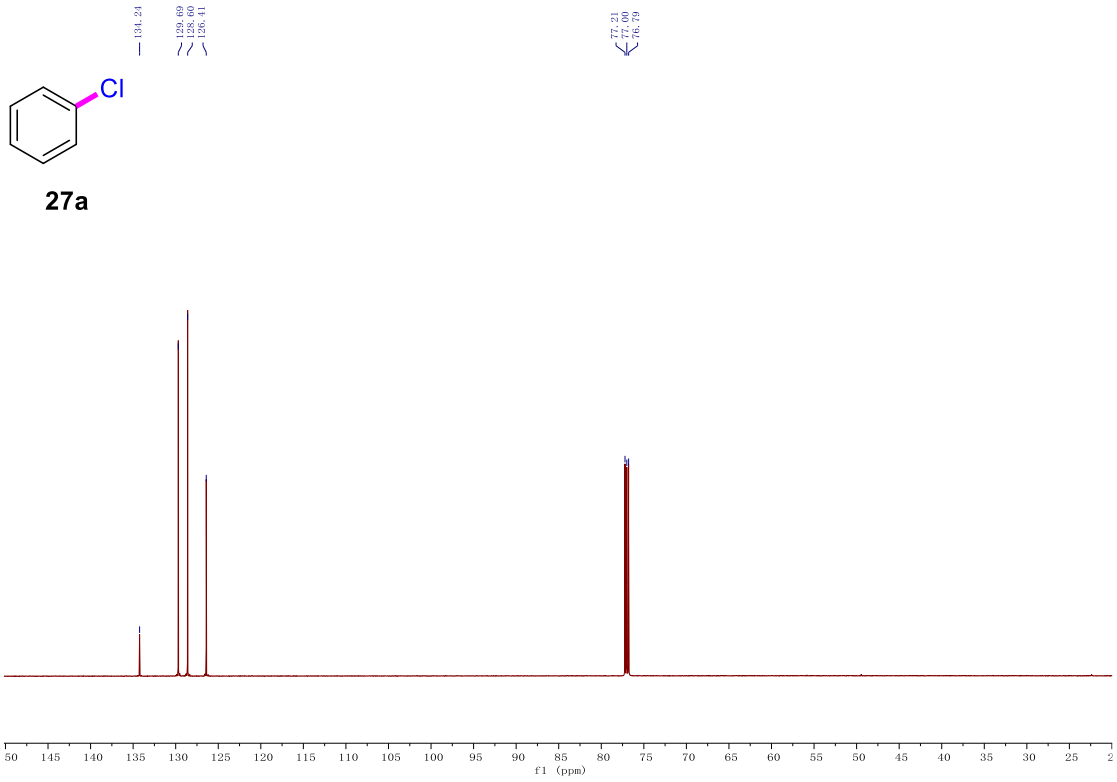
26a

132.59
129.79
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)

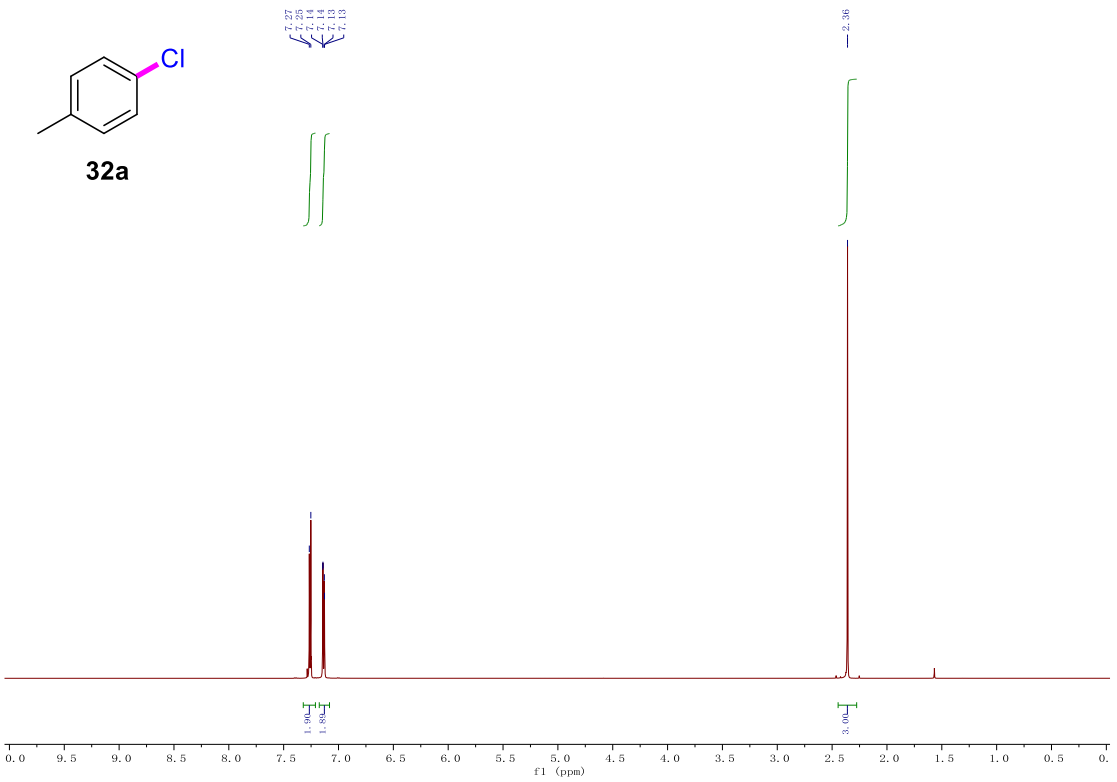

Cl

27a

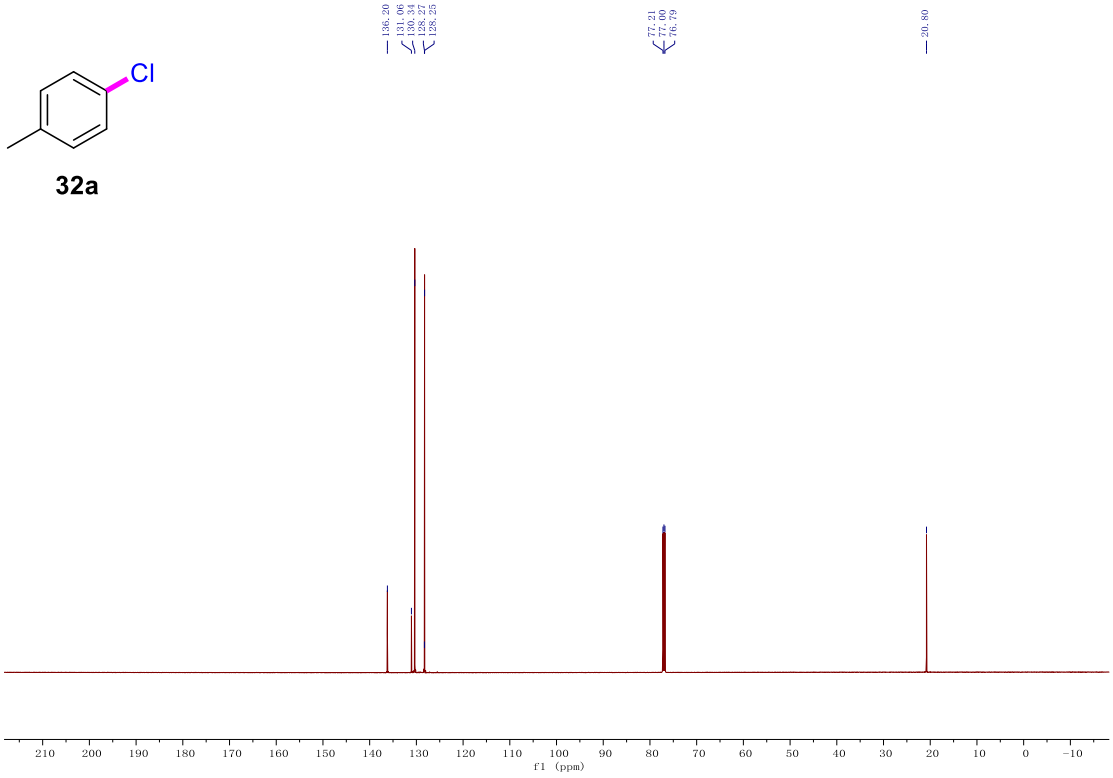
7.37
7.35
7.33
7.31
7.31
7.29
7.29
7.27
7.26
7.15
7.13
3.16
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


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

27a


7.27
7.25
7.14
7.14
7.13
7.13
2.36
Cl
1.90
1.89
3.00
f1 (ppm)

32a


136.20
131.06
130.34
128.27
126.25
77.21
77.00
76.79
20.80
Cl
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)

32a