

Electronic Supplementary Information

A General Electrochemical Strategy for Sandmeyer

Reaction

Qianyi Liu, Beiqi Sun, Zheng Liu, Yi Kao, Bo-Wei Dong, Shang-Da Jiang, Feng Li, Guoquan Liu, Yang Yang and Fanyang Mo*

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1. General information

The electrodes were purchased from AIDAHENGSHENG, Tianjin. Potentiostats (ITECH IT6720) were purchased on JD.COM. The IKA ElectraSyn 2.0 was purchased from IKA China agent. Solvents were purchased from TONGGUANG CHEMICAL, Beijing or BEIJING CHEMICAL, in GR (or CCER). Purification of products was conducted by column chromatography on silica gel (200-300 mesh, for some cases 300-400 mesh were used, from Qingdao, China). NMR spectra were measured on a Bruker ARX400 (^1H at 400 MHz, ^{13}C at 101 MHz) magnetic resonance spectrometer. Chemical shifts (δ) are reported in ppm using tetramethylsilane as internal standard (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), and coupling constants (J) were reported in Hertz (Hz). GC-MS or FID data were measured using the Agilent Technologies 7890B GC and the Agilent Technologies 5977B MSD. The FID yields were all based on standard curves with 5 points and minimum 0.996 R^2 value (or 4 points and minimum 0.997 R^2 value). The CV experiments were performed using electrochemical analyzer CHI627E (manufactured by Shanghai Chenhua Apparatus Company). *In situ* EPR experiments were conducted using Bruker Elexsys E580 Spectrometer.

Figure S1. Pt mesh electrodes (Photographed by Fanyang Mo)

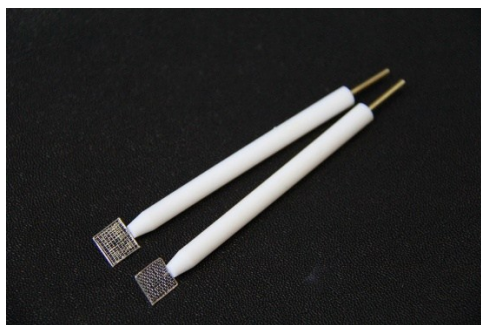


Figure S2. The potentiostat (Photographed by Fanyang Mo)

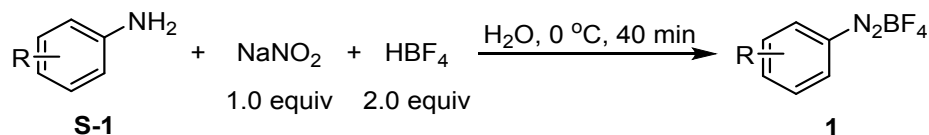


Figure S3. IKA ElectraSyn 2.0 (Photographed by Fanyang Mo)



2. Preparation of substrates

2.1 Preparation of diazonium salt (1a-1x)



The diazonium salts (**1**) were prepared according to literature procedure¹. Appropriate arylamine (**S-1**, 25 mmol) was dissolved in water (10 mL) and hydrofluoroboric acid (48% w/w in water, 10.5 mL, about 2.0 equiv). After the reaction mixture was cooled to 0 °C, sodium nitrile solution (1.73 g, 25 mmol in 6 mL water) was added dropwise. The reaction mixture was stirred at 0 °C for 40 min. The resulting precipitate was collected by filtration. The crude product was dissolved into acetone (about 20 mL, for some low solubility product, more acetone was used), and the solution was gently heated, and then diethyl ether was added until the recrystallized product precipitated completely. The diazonium salt **1** was collected by filtration, washed several times by cold diethyl ether and dried under vacuum.

4-ethoxycarbonylbenzenediazonium tetrafluoroborate (1a) 4.56 g, 69% yield. Pale-yellow solid. ¹H NMR (400 MHz, DMSO-d₆) δ 8.80 (d, *J* = 8.9 Hz, 2H), 8.44 (d, *J* = 8.9 Hz, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 1.36 (t, *J* = 7.1 Hz, 3H).²

3-ethoxycarbonylbenzenediazonium tetrafluoroborate (1b) 2.03 g, 51% yield (15 mmol of arylamine was used). White solid. ¹H NMR (400 MHz, DMSO-d₆) δ 9.27 (t, *J* = 1.9 Hz, 1H), 8.98 – 8.80 (m, 1H), 8.70 (dt, *J* = 8.1, 1.4 Hz, 1H), 8.13 (t, *J* = 8.1 Hz, 1H), 4.43 (q, *J* = 7.1 Hz, 2H), 1.37 (t, *J* = 7.1 Hz, 3H).³

2-ethoxycarbonylbenzenediazonium tetrafluoroborate (1c) 5.08 g, 64% yield (30 mmol of arylamine was used). White solid. ¹H NMR (400 MHz, DMSO-d₆) δ 8.98 – 8.91 (m, 1H), 8.48 – 8.34 (m, 2H), 8.30 – 8.22 (m, 1H), 4.50 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H).⁴

4-nitrobenzenediazonium tetrafluoroborate (1d) 3.39 g, 57% yield. Gray solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.93 (d, J = 9.3 Hz, 2H), 8.72 (d, J = 9.2 Hz, 2H).⁵

3-nitrobenzenediazonium tetrafluoroborate (1e) 4.32 g, 73% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6): δ 9.62 (t, J = 2.1 Hz, 1H), 9.01 (dddd, J = 10.9, 8.5, 2.2, 1.0 Hz, 2H), 8.24 (t, J = 8.4 Hz, 1H).⁵

2-nitrobenzenediazonium tetrafluoroborate (1f) 1.57 g, 27% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6): δ 9.10 (dd, J = 8.1, 1.4 Hz, 1H), 8.79 (dd, J = 8.3, 1.2 Hz, 1H), 8.53 (td, J = 8.0, 1.4 Hz, 1H), 8.41 (td, J = 7.9, 1.2 Hz, 1H).⁶

4-methyl-3-nitrobenzenediazonium tetrafluoroborate (1g) 2.20 g, 59% yield (15 mmol of arylamine was used). White solid. ^1H NMR (400 MHz, CD_3CN) δ 9.11 (d, J = 2.2 Hz, 1H), 8.60 (dd, J = 8.7, 2.3 Hz, 1H), 8.00 (d, J = 8.7 Hz, 1H), 2.82 (s, 3H).⁵

4-cyanobenzenediazonium tetrafluoroborate (1h) 4.50 g, 69% yield (30 mmol of arylamine). White solid. ^1H NMR (400 MHz, DMSO- d_6): δ 8.84 (d, J = 8.9 Hz, 2H), 8.46 (d, J = 8.9 Hz, 2H).⁷

2-cyanobenzenediazonium tetrafluoroborate (1i) 1.32 g, 24% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 9.00 (dd, J = 8.3, 1.1 Hz, 1H), 8.60 (dd, J = 7.8, 1.3 Hz, 1H), 8.46 (td, J = 7.8, 1.3 Hz, 1H), 8.32 (td, J = 8.1, 1.3 Hz, 1H).⁸

4-chlorobenzenediazonium tetrafluoroborate (1j) 4.14 g, 77% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.69 (d, J = 9.1 Hz, 2H), 8.12 (d, J = 9.1 Hz, 2H).⁵

4-bromobenzenediazonium tetrafluoroborate (1k) 5.18 g, 77% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.58 (d, J = 9.1 Hz, 2H), 8.26 (d, J = 9.1 Hz, 2H).⁵

4-iodobenzenediazonium tetrafluoroborate (1l) 4.74 g, 60% yield. Pale-yellow solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.43 (d, J = 8.9 Hz, 2H), 8.35 (d, J = 8.9 Hz, 2H).⁵

4-trifluoromethylbenzenediazonium tetrafluoroborate (1m) 4.17 g, 64% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.91 (d, J = 8.6 Hz, 2H), 8.42 (d, J = 8.8 Hz, 2H).⁹

4-mesylbenzenediazonium tetrafluoroborate (1n) 3.94 g, 58% yield. Pale-pink solid. ^1H NMR (400 MHz, DMSO- d_6): δ 8.92 (d, J = 8.9 Hz, 2H), 8.51 (d, J = 8.8 Hz, 2H), 3.47 (s, 3H).

4-methylbenzenediazonium tetrafluoroborate (1o) 4.60 g, 74% yield (30 mmol of arylamine). White solid. ^1H NMR (400 MHz, DMSO- d_6): δ 8.55 (d, J = 8.7 Hz, 2H), 7.80 (d, J = 8.4 Hz, 2H), 2.50 (s, 3H).¹⁰

3-methylbenzenediazonium tetrafluoroborate (1p) 3.09 g, 50% yield (30 mmol of arylamine). Pale-pink solid. ^1H NMR (400 MHz, MeCN- d_3) δ 8.38 – 8.23 (m, 2H), 8.15 – 7.95 (m, 1H), 7.92 – 7.69 (m, 1H), 2.52 (s, 3H).¹¹

2-methylbenzenediazonium tetrafluoroborate (1q) 2.78 g, 45% yield (30 mmol of arylamine). White solid. ^1H NMR (400 MHz, MeCN- d_3) δ 8.53 – 8.29 (m, 1H), 8.21 – 7.94 (m, 1H), 7.90 – 7.65 (m, 2H), 2.72 (s, 3H).¹¹

4-methoxybenzenediazonium tetrafluoroborate (1r) 4.66 g, 77% yield (27.4 mmol of arylamine). Pale-gray solid. ^1H NMR (400 MHz, DMSO- d_6): δ 8.62 (d, J = 9.4 Hz, 2H), 7.49 (d, J = 9.4 Hz, 2H), 4.04 (s, 3H).¹⁰

Benzenediazonium tetrafluoroborate (1s) 4.27 g, 74% yield (30 mmol of arylamine). White solid. ^1H NMR (400 MHz, DMSO- d_6): δ 8.79 – 8.51 (m, 2H), 8.35 – 8.17 (m, 1H), 8.12 – 7.91 (m, 2H).⁵

4-fluorobenzenediazonium tetrafluoroborate (1t) 3.45 g, 66% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 9.06 – 8.62 (m, 2H), 8.07 – 7.70 (m, 2H).⁵

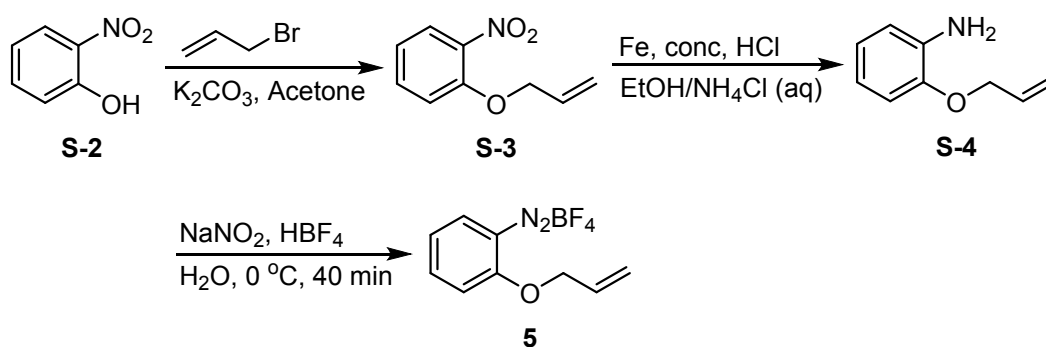
4-acetylbenzenediazonium tetrafluoroborate (1u) 3.49 g, 60% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.80 (d, J = 8.7 Hz, 2H), 8.41 (d, J = 8.8 Hz, 2H), 2.71 (s, 3H).⁵

2-acetylbenzenediazonium tetrafluoroborate (1v) 2.78 g, 48% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 8.94 (dd, J = 8.2, 1.2 Hz, 1H), 8.59 (dd, J = 7.9, 1.2 Hz, 1H), 8.41 (td, J = 7.7, 1.3 Hz, 1H), 8.23 (td, J = 7.9, 1.2 Hz, 1H), 2.77 (s, 3H).⁵

2-methyl-1,3-dioxoisindoline-5-diazonium tetrafluoroborate (1w) 0.46 g, 7% yield. White solid. ^1H NMR (400 MHz, DMSO- d_6) δ 9.11 (d, J = 1.7 Hz, 1H), 9.05 (dd, J = 8.1, 1.8 Hz, 1H), 8.41 (d, J = 8.1 Hz, 1H), 3.11 (s, 3H).

Quinoline-8-diazonium tetrafluoroborate (1x) 2.00 g, 83% yield (10 mmol of arylamine, 2.0 equiv of $^t\text{BuONO}$ was used, MeOH/water 1:1 was used as solvent). Brown solid. ^1H NMR (400 MHz, DMSO- d_6) δ 9.51 – 9.29 (m, 2H), 9.01 (dd, J = 8.3, 1.4 Hz, 1H), 8.91 (dd, J = 8.4, 1.6 Hz, 1H), 8.18 (t, J = 8.1 Hz, 1H), 8.05 (dd, J = 8.4, 4.4 Hz, 1H).¹²

2.2 Preparation of diazonium salt 5



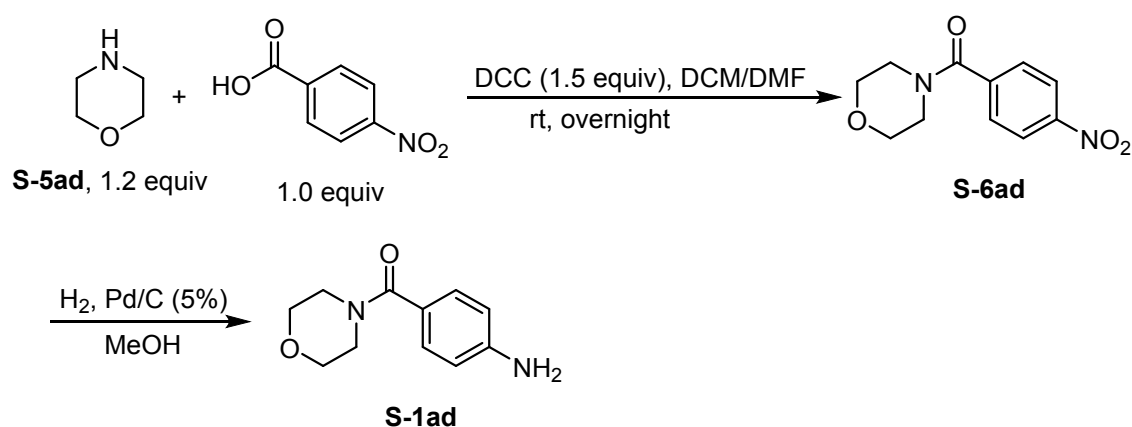
The amine **S-4** was prepared according to literature procedure.¹³ In a 250 mL dried flask, 2-nitrophenol (**S-2**, 4.17 g, 30 mmol) and K_2CO_3 (12.44 g, 90 mmol, 3.0 equiv) were added in acetone (60 mL), then allyl bromide (4.36 g, 36 mmol, 3.12 mL, 1.2 equiv) were added and the reaction mixture was stirred overnight at reflux temperature. Upon completion, the reaction mixture was cooled to room temperature, diluted with water and extracted with EtOAc. The combined

organic layers were dried over Na₂SO₄ and the solvent was removed under reduced pressure. After that, the crude product **S-3** and Fe powder (8.38 g, 150 mmol, 5.0 equiv) were suspended in a 1:1 mixture of EtOH/NH₄Cl(aq). Afterwards, a few drops of HCl (conc.) were added and the solution was stirred at reflux temperature for 5 h. Then the solution was filtered and extracted with EtOAc. The combined organic layers were dried over Na₂SO₄. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel) using a 30:1 mixture of PE/EA 20:1 as an eluent to provide **S-4** as a yellow oil (4.06 g, 91% yield from **S-2**). ¹H NMR (400 MHz, CDCl₃): δ 6.95 – 6.56 (m, 4H), 6.21 – 5.93 (m, 1H), 5.41 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.28 (dq, *J* = 10.5, 1.5 Hz, 1H), 4.57 (d, *J* = 5.3 Hz, 2H), 3.81 (brs, 2H).

After that, the diazonium salt **5** was prepared according to the procedure in Section 2.1. Yield: 2.44 g, 76% (from 13 mmol of **S-4**), white solid. ¹H NMR (400 MHz, DMSO-*d*₆) δ 8.53 (dd, *J* = 8.4, 1.7 Hz, 1H), 8.31 – 8.13 (m, 1H), 7.67 (dd, *J* = 8.9, 0.8 Hz, 1H), 7.54 – 7.37 (m, 1H), 6.21 – 6.01 (m, 1H), 5.62 – 5.48 (m, 1H), 5.42 (dq, *J* = 10.6, 1.4 Hz, 1H), 5.07 (dt, *J* = 5.3, 1.6 Hz, 2H).⁵

2.3 Preparation of amine (**S-1**)

Preparation of **S-1y**



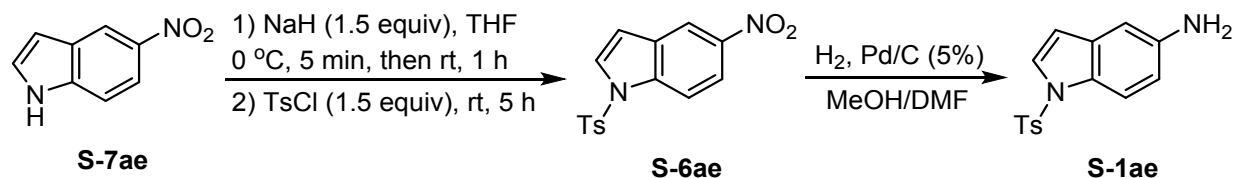
In a 250 mL dried flask, 4-nitrobenzoic acid (20 mmol, 3.34 g) and morpholine (2.09 g, 24 mmol, 2.1 mL) were dissolved in DCM (80 mL) and DMF (4 mL). DCC (30 mmol, 6.19 g) was added portion-wise. The reaction mixture was

purged and refilled with H₂ in balloon pressure, and the reaction mixture was stirred overnight at room temperature. Upon completion, the reaction mixture was filtered to remove the catalyst, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (silica gel).

S-1ac: using DCM/MeOH 40:1 as eluent. Yield: 4.23 g, 95% from **S-5ac**, white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, *J* = 8.7 Hz, 2H), 6.67 (d, *J* = 8.6 Hz, 2H), 6.49 (s, 1H), 4.25 (q, *J* = 7.2 Hz, 2H), 4.21 (d, *J* = 4.9 Hz, 2H), 3.99 (s, 2H), 1.31 (t, *J* = 7.1 Hz, 3H).¹⁵

S-1af: using PE/EA 10:1 ~ PE/EA/Et₃N 5:1:0.05 as eluent. Yield: 4.79 g, 87% from **S-5af** (Vitamin E), white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 8.6 Hz, 2H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.12 (d, *J* = 4.0 Hz, 2H), 2.61 (t, *J* = 6.8 Hz, 2H), 2.11 (s, 3H), 2.05 (s, 3H), 2.01 (s, 3H), 1.80 (tq, *J* = 13.1, 6.7 Hz, 2H), 1.62 – 1.01 (m, 24H), 0.99 – 0.60 (m, 12H).¹⁶

Preparation of **S-1ae**



The amine **S-1ae** was prepared according to literature procedure.¹⁷ 5-Nitro-1*H*-indole (**S-7ae**) (1.62 g, 10.0 mmol, 1.0 equiv) dissolved in THF (10 mL) was slowly added to a suspension of NaH (60% dispersion in mineral oil, 0.60 g, 15.00 mmol, 1.5 equiv) in THF (20 mL) at 0 °C over a period of 5 min. Then the reaction was allowed to warm up to room temperature and stirred for an additional 1 h. Tosyl chloride (2.86 g, 15.0 mmol, 1.5 equiv) dissolved in THF (10 mL) was added slowly. The reaction mixture was stirred for an additional 5 h at room temperature, after which it was poured into 5% NaHCO₃ aq. (100 mL) and extracted with EtOAc (3 × 50 mL). The combined organic layers were washed with brine, dried over anhydrous Na₂SO₄ and concentrated in vacuo. The

residue was crudely purified by column chromatography (silica gel) using PE/EA 10:1 as eluent.

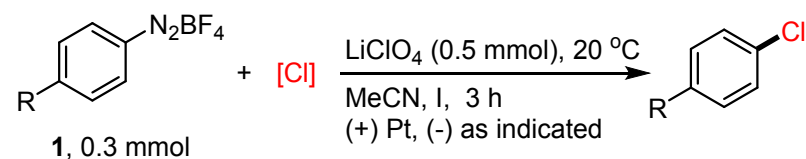
After that, under nitrogen atmosphere, the crude product **S-6ae** was dissolved in MeOH (55 mL) and DMF (45 mL), following with Pd/C (5%, 0.5 g) was added. The flask was purged and refilled with H₂ in balloon pressure, and the reaction mixture was stirred overnight at room temperature. After the reaction was complete, the catalyst was removed by filtration. The reaction mixture was poured into water (30 mL) and extracted with EtOAc (3 × 30 mL). The combined organic phase was washed with water (3 × 30 mL), washed with brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The amine **S-1ae** was purified by column chromatography (silica gel) using PE/EA 3:1 ~ 1:1 as eluent. Yield: 1.72 g (60%), yellow oil. ¹H NMR (400 MHz, CDCl₃) δ 7.77 (d, *J* = 8.7 Hz, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 3.6 Hz, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 6.76 (d, *J* = 2.3 Hz, 1H), 6.69 (dd, *J* = 8.8, 2.3 Hz, 1H), 6.47 (dd, *J* = 3.7, 0.8 Hz, 1H), 3.60 (s, 2H), 2.32 (s, 3H).¹⁷

3. Experimental procedures and characterization data

3.1 Conditions optimizing for chlorination

This part shows some of the experimental data of chlorination. If not noted, the experiments were conducted by adopting a procedure as described in Section 3.2. GC-FID yields were given.

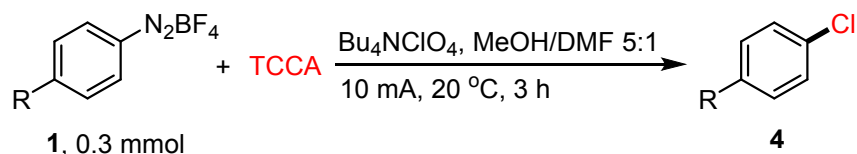
Table S1. Conditions optimizing for chlorination using metal chloride.



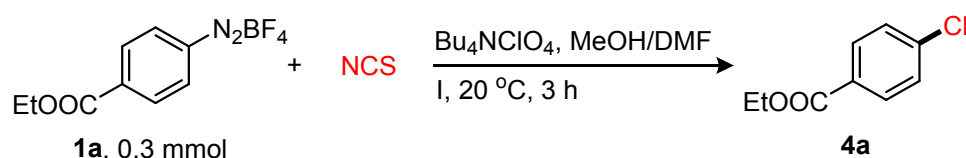
Entry	R	[Cl]	Equi v	I (mA)	Cathode	Additional conditions	Yield (FID)
1	CN	LiCl	3.0	10	Graphite		~ 20%
2	CN	CaCl ₂	3.0	10	Graphite		Trace
3	Br	CaCl ₂	3.0	10	Stainless steel (SS)		ND
4	Me	CaCl ₂	3.0	10	SS		ND
5	Me	CaCl ₂	3.0	10	Pt-plate	+ NCS (1.0 equiv)	ND
6	Me	CaCl ₂	5.0	10	Ni foam	+ 1M HCl (0.15 mL)	7.6%
7	Me	MgCl ₂	5.0	10	Ni foam		ND
8	Me	LiCl	6.0	10	Ni foam		41.5%
9	Br	LiCl	6.0	10	Ni foam		9.2%
10	Me	LiCl	6.0	15	Pt-plate	0.5 mmol	45.1%
11	OMe	LiCl	6.0	10	Ni foam		26.8%
12	Me	LiCl	6.0	15	Ni foam (old)		19.0%
13	Me	LiCl	6.0	15	Ni foam		47.2%
14	OMe	LiCl	6.0	15	Ni foam		ND
15	Me	LiCl	6.0	20	Ni foam		48.9%
16	Br	LiCl	6.0	20	Ni foam		36.8%
17	Me	LiCl	6.0	20	Ni foam	DMF as the solvent	Trace
18	Me	LiCl	6.0	20	Ni foam	MeOH as the solvent	9.1%
19	Me	LiCl	6.0	20	Ni foam	Acetone as the solvent	9.0%

Chlorination using NCS, TCCA, etc. For reactions conducted at 35 °C or higher, they were proceed in a 20 mL glass tube, 5 mL solvent was used. The tube was closed during the reaction, and an oil bath was used to control the reaction temperature.

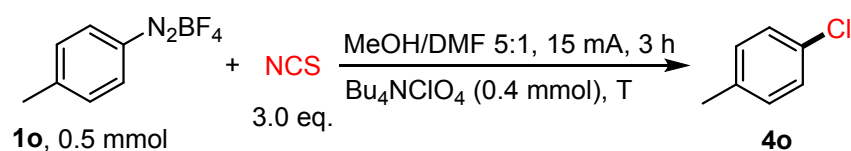
Table S2. Chlorination using NCS, TCCA, etc.



Entry	R	TCCA Equiv	Yield (FID)
1	COOEt	1.0	19.9%
2	COOEt	3.0	16.3%
3	Me	1.0	15.9%
4	Me	2.0	18.0%



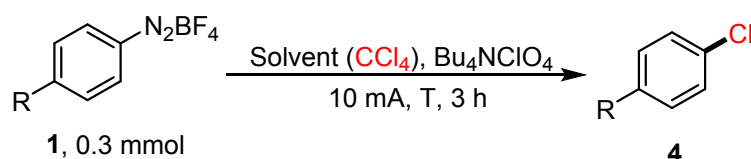
Entry	NCS Equiv	I (mA)	Yield (FID)
5	3.0	10	15.7%
6	5.0	10	15.7%
7	3.0	15	16.3%



Entry	Temperature (°C)	Yield (FID)
8	50	40.4%
9	35	41.0%
10	35 (10 mA, 2 h)	15.3%
11	20	25.6%
12	20 (2.0 equiv NCS)	24.6%

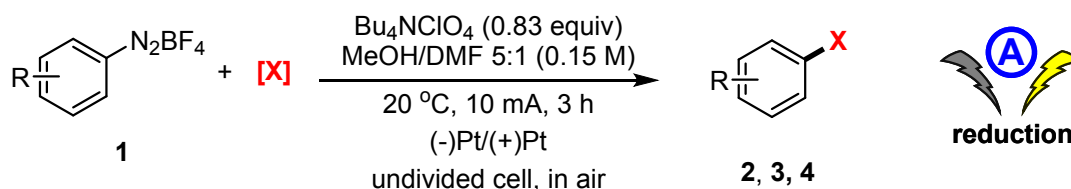
Chlorination using CCl_4 (as solvent). Conditions: **1** (0.3 mmol), 10 mA, 3 h. For cases running at 20 °C, 3 mL solvent and Bu_4NClO_4 (85.5 mg, 0.25 mmol) were used. For other cases, 5 mL solvent and Bu_4NClO_4 (171 mg, 0.5 mmol) were used and the reaction tube was closed.

Table S3. Chlorination using CCl₄ (as solvent).



Entry	R	Solvent	Temperature (°C)	Yield (FID)
1	COOEt	CCl ₄ (non-conducting)	20	0
2	COOEt	MeOH/CCl ₄ /DMF 3:2:1	20	31.5%
3	COOEt	CCl ₄ /DMF 5:1	20	42.1%
4	COOEt	CCl ₄ /DMF 5:1	50	57.6%
5	COOEt	CCl ₄ /DMF 5:1	75	39.7%
6	Br	CCl ₄ /DMF 5:1	20	43.6%
7	Br	CCl ₄ /DMF 5:1	50	41.4%
8	Br	CCl ₄ /DMF 5:1	75	37.4%
9	Me	MeOH/CCl ₄ /DMF 3:2:1	20	39.1%
10	Me	CCl ₄ /DMF 5:1	20	45.3%
11	Me	CCl ₄ /DMF 5:1	50	48.3%
12	OMe	MeOH/CCl ₄ /DMF 3:2:1	20	49.7%
13	OMe	CCl ₄ /DMF 5:1	20	13.9%

3.2 Electrochemical Sandmeyer reaction of diazonium salts.

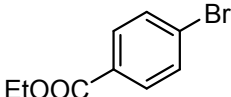


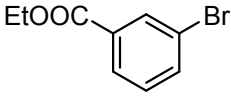
In a 10 mL tube equipped with a stir bar, diazonium salt (**1**, 0.3 mmol), halogenation reagent and Bu₄NClO₄ (0.25 mmol, 85.5 mg) were dissolved in a mixed solvent of MeOH (2.5 mL) and DMF (0.5 mL), following with two Pt net electrodes were immersed. The reaction mixture was stirred at 20 °C, with constant current was continuous given for 3 h. The slightly modified conditions were given in each case.

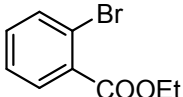
Upon completion, for cases given the isolated yields, the reaction mixture was poured into diethyl ether (60 mL), washed with water two times (20 mL * 2). The combined water phase was extracted with diethyl ether for another time,

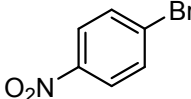
and the secondary organic phase was washed with water again. The combined organic phase was dried over Na₂SO₄, then the solvent was removed and the desired product was purified by column chromatography (silica gel).

For other cases, the salt in reaction mixture was removed by a small silica gel chromatography or extraction with diethyl ether and water. Then, internal standard substance was added (about 28 mg of n-decane for FID, or about 27 mg of 4-(Trifluoromethoxy)anisole for ¹⁹F NMR) and the yield was measured by GC-FID or ¹⁹F NMR directly.

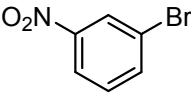
 **2a** 50.5 mg, 74% isolated yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.58 (d, *J* = 8.6 Hz, 2H), 4.37 (q, *J* = 7.1 Hz, 2H), 1.39 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.89, 131.65, 131.09, 129.39, 127.90, 14.31. *R*_f = 0.6 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.¹⁸

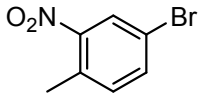
 **2b** 29.0 mg, 42% isolated yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 8.18 (t, *J* = 1.8 Hz, 1H), 7.98 (dt, *J* = 7.8, 1.3 Hz, 1H), 7.72 – 7.60 (m, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.27, 135.75, 132.55, 132.43, 129.90, 128.13, 122.41, 61.41, 14.29. *R*_f = 0.65 (PE/EA 10:1), using PE/EA 30:1 as eluent.¹⁹

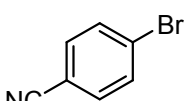
 **2c** 20.6 mg, 30% isolated yield. Colorless liquid. ¹H NMR (400 MHz, CDCl₃): δ 7.83 – 7.72 (m, 1H), 7.71 – 7.58 (m, 1H), 7.41 – 7.27 (m, 2H), 4.40 (q, *J* = 7.1 Hz, 2H), 1.41 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 166.27, 134.27, 132.60, 132.38, 131.16, 127.12, 121.54, 61.65, 14.22. *R*_f = 0.65 (PE/EA 10:1), using PE/EA 50:1 ~ 30:1 as eluent.²⁰

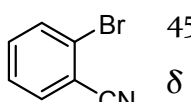
 **2d** MeOH/DMF 20:1 was used as the solvent, 1 h. 50.6 mg, 84% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 9.0 Hz, 2H), 7.70 (d, *J* = 9.0 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 132.63, 125.02. *R*_f = 0.55 (PE/EA 10:1), using PE/EA 40:1 ~ 30:1 as

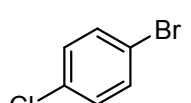
eluent.²¹

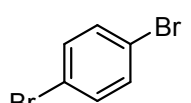
 MeOH/DMF 20:1 was used as the solvent. 32.9 mg, 54% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.39 (t, *J* = 2.1 Hz, 1H), 8.29 – 8.04 (m, 1H), 7.94 – 7.74 (m, 1H), 7.45 (t, *J* = 8.1 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 148.79, 137.62, 130.62, 126.78, 122.88, 122.15. *R*_f = 0.6 (PE/EA 10:1), using PE/EA 100:1 ~ 35:1 as eluent.²²

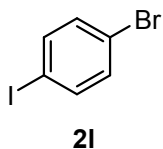
 48.6 mg, 76% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃): δ 8.11 (d, *J* = 1.9 Hz, 1H), 7.62 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 2.56 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 149.59, 135.97, 134.11, 132.55, 127.56, 119.66, 20.09. *R*_f = 0.6 (PE/EA 10:1), using PE/EA 30:1 as eluent.²³

 45.8 mg, 84% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃): δ 7.64 (d, *J* = 8.6 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 133.42, 132.65, 128.03, 118.07, 111.25. *R*_f = 0.55 (PE/EA 10:1), using PE/EA 30:1 as eluent.²⁴

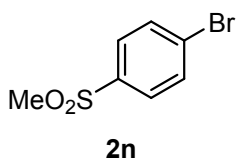
 45.8 mg, 84% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.84 – 7.57 (m, 2H), 7.57 – 7.34 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 134.34, 133.89, 133.22, 127.63, 125.36, 117.15, 115.91. *R*_f = 0.4 (PE/EA 10:1), using PE/EA 30:1 ~ 20:1 as eluent.²⁵

 MeOH/DMF 20:1 was used as the solvent, NBS (3.0 equiv) was used. 29.6 mg, 52% isolated yield. Pale-yellow solid. ¹H NMR (400 MHz, CDCl₃) δ 7.48 – 7.36 (m, 2H), 7.24 – 7.14 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 133.22, 132.77, 130.21, 120.27. *R*_f = 0.7 (PE), using PE as eluent.²⁶

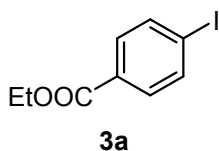
 MeOH/DMF 20:1 was used as the solvent, NBS (3.0 equiv) was used. 57.4 mg, 81% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.36 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 133.14, 121.06. *R*_f = 0.7 (PE), using PE as eluent.²⁷



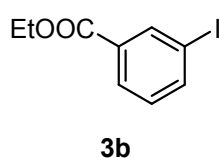
MeOH/DMF 20:1 was used as the solvent, NBS (3.0 equiv) was used. 57.8 mg, 68% isolated yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.64 – 7.46 (m, 2H), 7.25 – 7.17 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.07, 133.46, 122.21, 92.05. R_f = 0.75 (PE), using PE as eluent.²⁸



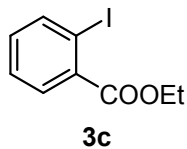
60.1 mg, 85% isolated yield. White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.82 (d, J = 8.6 Hz, 2H), 7.73 (d, J = 8.6 Hz, 2H), 3.06 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 139.55, 132.72, 129.04, 128.99, 44.54. R_f = 0.4 (PE/EA 3:1), using PE/EA 7:1 ~ 4:1 as eluent.²⁹



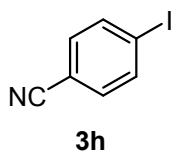
72.3 mg, 87% isolated yield. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.92 – 7.64 (m, 4H), 4.37 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.11, 137.66, 131.01, 129.97, 100.56, 61.24, 14.30. R_f = 0.6 (PE/EA 10:1). Using PE/EA 30:1 as eluent.³⁰



71.8 mg, 87% isolated yield. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 8.37 (s, 1H), 8.01 (d, J = 7.8 Hz, 1H), 7.87 (d, J = 7.9 Hz, 1H), 7.18 (t, J = 7.8 Hz, 1H), 4.38 (q, J = 7.1 Hz, 2H), 1.39 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 165.11, 141.63, 138.42, 132.39, 130.02, 128.73, 93.76, 61.39, 14.31. R_f = 0.65 (PE/EA 10:1). Using PE/EA 30:1 as eluent.³¹

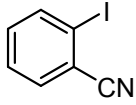


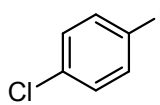
61.1 mg, 74% isolated yield. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (dd, J = 7.9, 1.2 Hz, 1H), 7.79 (dd, J = 7.8, 1.7 Hz, 1H), 7.40 (td, J = 7.6, 1.2 Hz, 1H), 7.14 (td, J = 7.7, 1.7 Hz, 1H), 4.40 (q, J = 7.2 Hz, 2H), 1.41 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 166.63, 141.23, 135.51, 132.48, 130.82, 127.88, 93.97, 61.72, 14.23. R_f = 0.65 (PE/EA 10:1). Using PE/EA 30:1 as eluent.³²

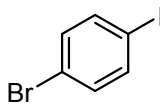


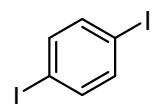
63.7 mg, 93% isolated yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 7.94 – 7.75 (m, 2H), 7.47 – 7.31 (m, 2H). ^{13}C NMR (101

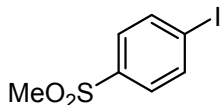
MHz, CDCl₃) δ 138.52, 133.17, 118.23, 111.76, 100.31. R_f = 0.5 (PE/EA 10:1), using PE/EA 30:1 as eluent.³⁰

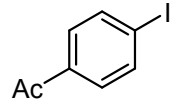
 52.1 mg, 76% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 8.06 – 7.81 (m, 1H), 7.78 – 7.56 (m, 1H), 7.54 – 7.39 (m, 1H), 7.38 – 7.19 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.56, 134.28, 133.74, 128.33, 120.62, 119.34, 98.41. R_f = 0.45 (PE/EA 10:1), using PE/EA 30:1 ~ 20:1 as eluent.³³

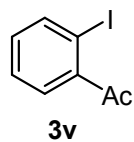
 42.9 mg, 60% isolated yield. White solid. ¹H NMR δ 7.67 – 7.45 (m, 2H), 7.14 – 6.94 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 138.73, 134.22, 130.55, 91.19. R_f = 0.7 (PE), using PE/EA 1:0 ~ 50:1 as eluent.³⁴

 51.4 mg, 61% isolated yield. White solid. 57.8 mg, 68% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.64 – 7.46 (m, 2H), 7.25 – 7.17 (m, 2H). ¹³C NMR (101 MHz, CDCl₃) δ 139.07, 133.46, 122.21, 92.05. R_f = 0.75 (PE), using PE as eluent.²⁸

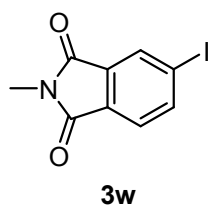
 55.7 mg, 56% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.40 (s, 4H). ¹³C NMR (101 MHz, CDCl₃) δ 139.34, 93.41. R_f = 0.75 (PE), using PE as eluent.³⁵

 53.6 mg, 63% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.94 (dd, *J* = 8.7, 2.1 Hz, 2H), 7.66 (dd, *J* = 8.7, 2.0 Hz, 2H), 3.05 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 140.19, 138.69, 128.79, 101.60, 77.36, 77.34, 77.05, 44.50. R_f = 0.4 (PE/EA 3:1), using PE/EA 7:1 ~ 4:1 as eluent.³⁶

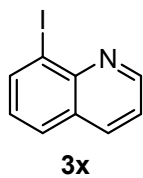
 64.4 mg, 87% isolated yield. White solid. ¹H NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 8.6 Hz, 2H), 7.66 (d, *J* = 8.4 Hz, 2H), 2.57 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 197.31, 137.91, 136.34, 129.73, 101.12, 26.51. R_f = 0.4 (PE/EA 10:1), using PE/EA 30:1 ~ 25:1 as eluent.³⁷



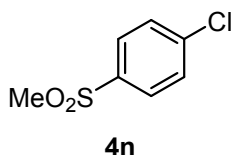
51.6 mg, 70% isolated yield. Colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.94 (dd, $J = 7.9, 1.1$ Hz, 1H), 7.47 (dd, $J = 7.7, 1.8$ Hz, 1H), 7.41 (td, $J = 7.5, 1.1$ Hz, 1H), 7.13 (td, $J = 7.6, 1.8$ Hz, 1H), 2.62 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 201.82, 144.01, 140.89, 131.85, 128.35, 128.09, 90.99, 29.53. $R_f = 0.45$ (PE/EA 10:1), using PE/EA 30:1 ~ 20:1 as eluent.³⁸



58.8 mg, 68% isolated yield. White solid. ^1H NMR (400 MHz, CDCl_3) δ 8.18 (d, $J = 1.4$ Hz, 1H), 8.07 (dd, $J = 7.8, 1.4$ Hz, 1H), 7.57 (d, $J = 7.8$ Hz, 1H), 3.18 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.86, 167.02, 142.87, 133.52, 132.33, 131.34, 124.48, 100.75, 24.11. $R_f = 0.4$ (PE/EA 10:1), using PE/EA 30:1 ~ 25:1 as eluent.³⁹

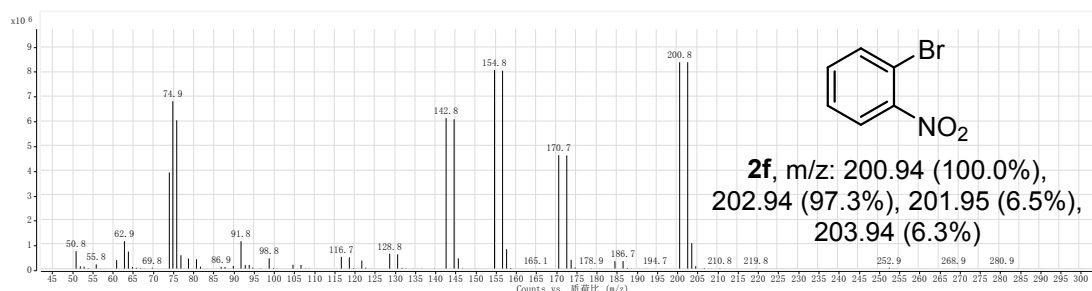


29.5 mg, 39% isolated yield. Pale-yellow solid. ^1H NMR (400 MHz, CDCl_3) δ 9.10 – 8.80 (m, 1H), 8.46 – 8.18 (m, 1H), 8.14 – 7.94 (m, 1H), 7.88 – 7.67 (m, 1H), 7.51 – 7.34 (m, 1H), 7.27 – 7.04 (m, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 151.45, 147.06, 140.06, 136.79, 128.83, 127.70, 121.94, 103.45. $R_f = 0.6$ (PE/EA 3:1), using PE/EA 20:1 ~ 10:1 as eluent.⁴⁰

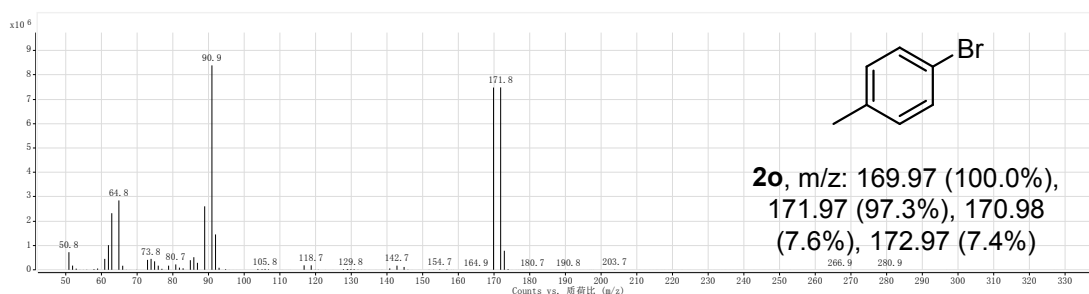
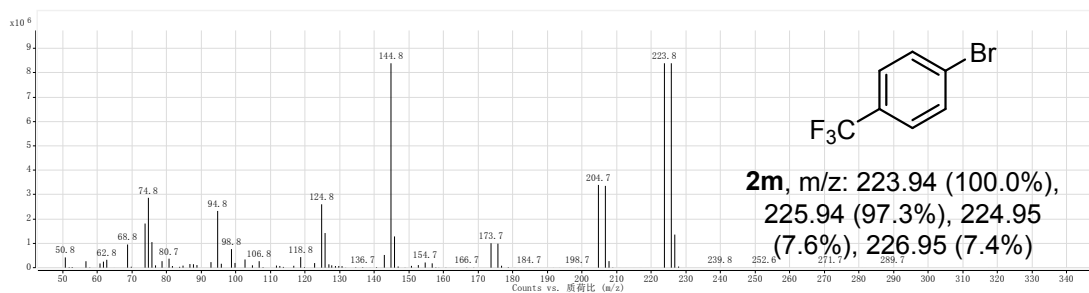
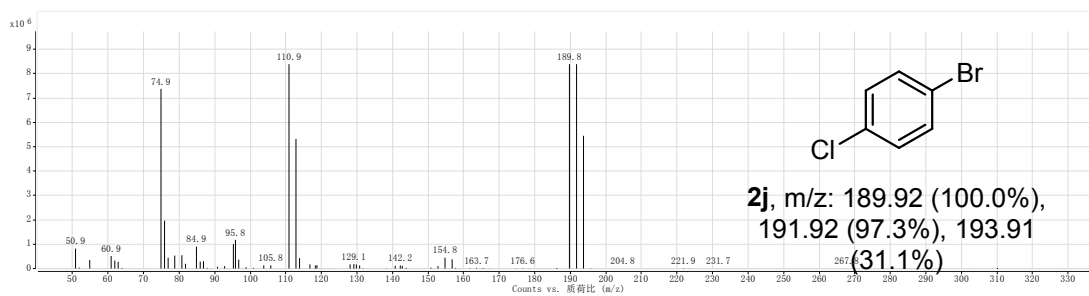


MeCN was used as the solvent, 20 mA, Ni foam as the cathode. 36.2 mg, 64% isolated yield. White solid. ^1H NMR (400 MHz, CDCl_3): δ 7.89 (d, $J = 8.7$ Hz, 2H), 7.56 (d, $J = 8.6$ Hz, 2H), 3.06 (s, 3H). ^{13}C NMR (101 MHz, CDCl_3) δ 140.49, 139.04, 129.72, 128.93, 44.57. $R_f = 0.5$ (PE/EA 3:1), using PE/EA 6:1 ~ 4:1 as eluent.⁴¹

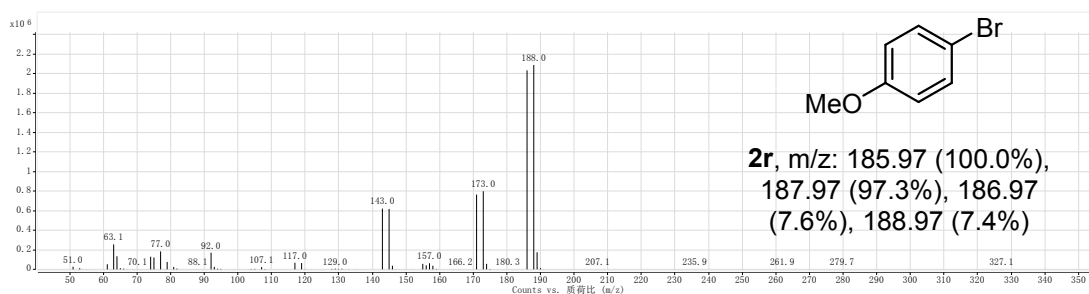
MS data for cases given GC-FID or NMR yields.



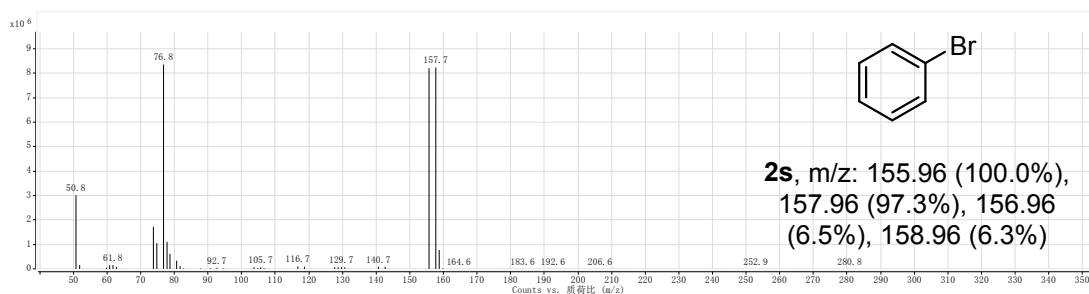
Conditions for **2f**: MeOH/DMF 20:1, 1 h. NBS (3.0 equiv) was used.



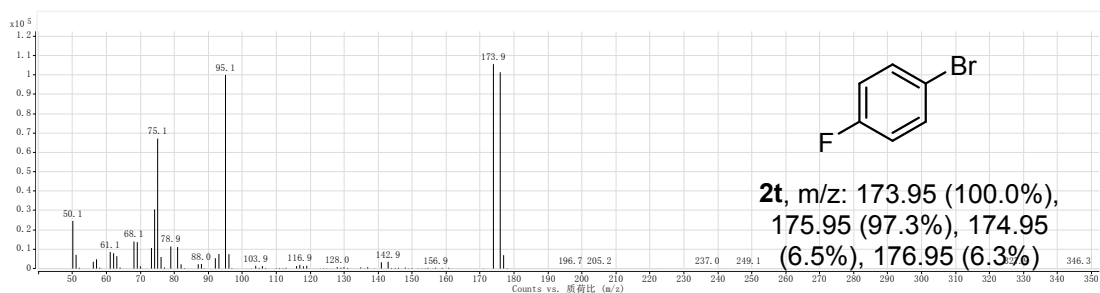
Conditions for **2o**: DMF, 4.5 h.



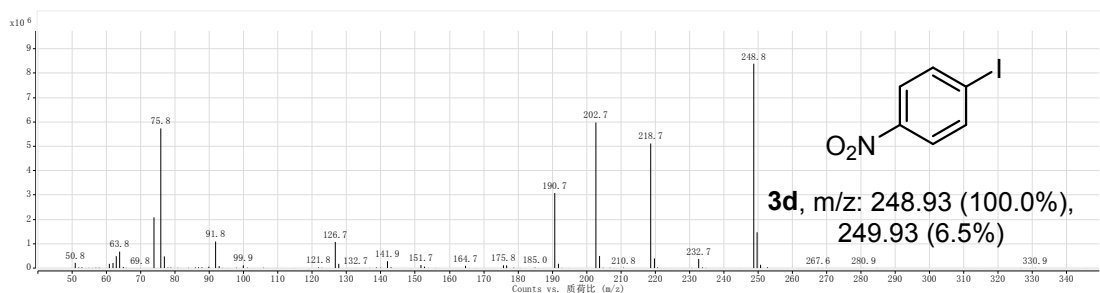
Conditions for **2r**: DMF, 2 h.



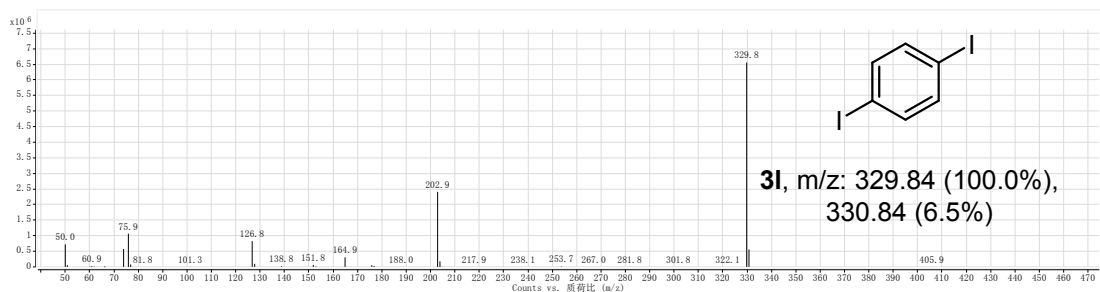
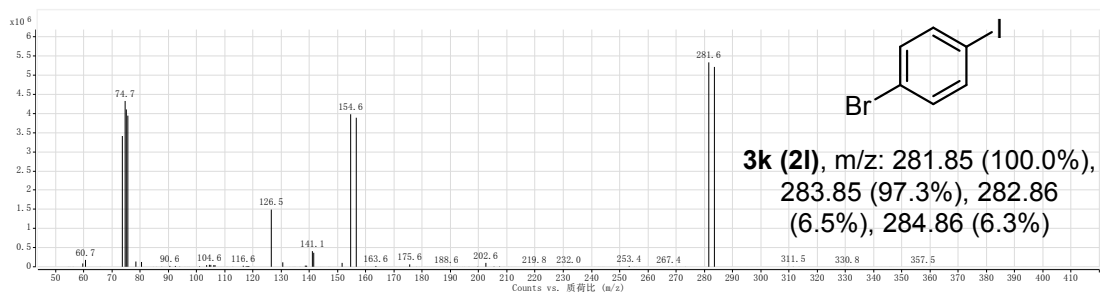
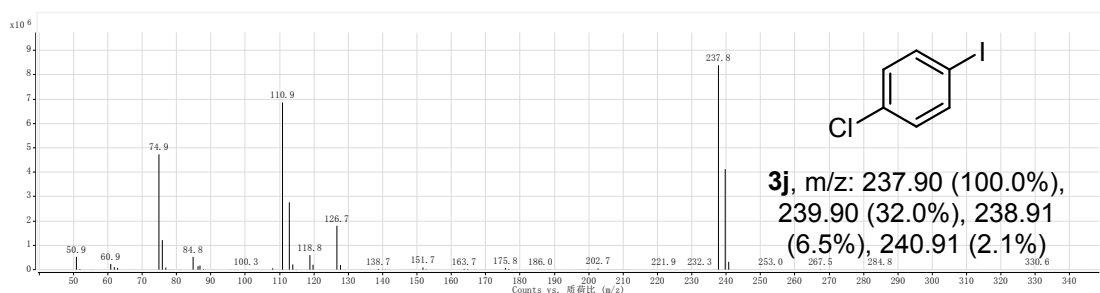
Conditions for **2s**: DMF.

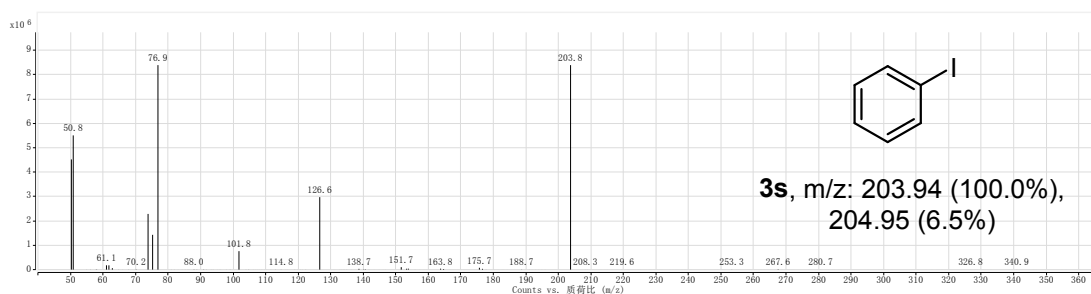
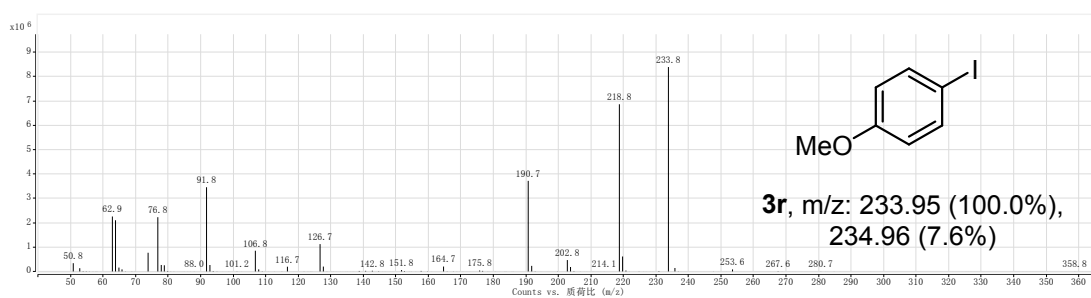
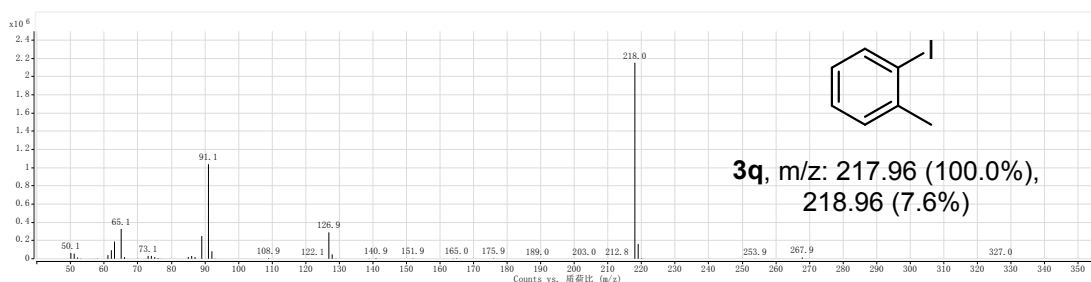
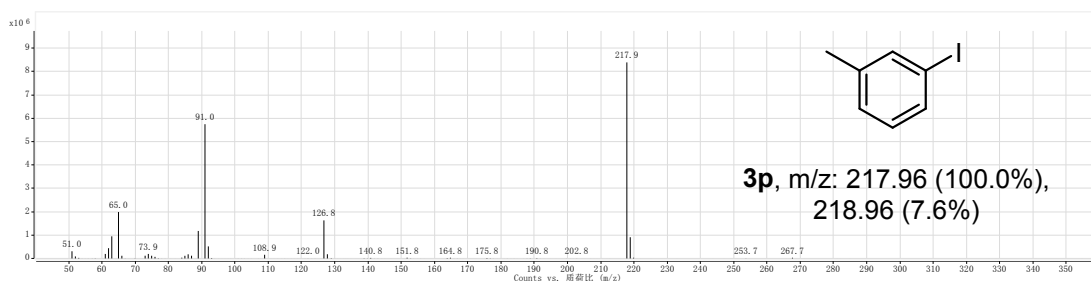
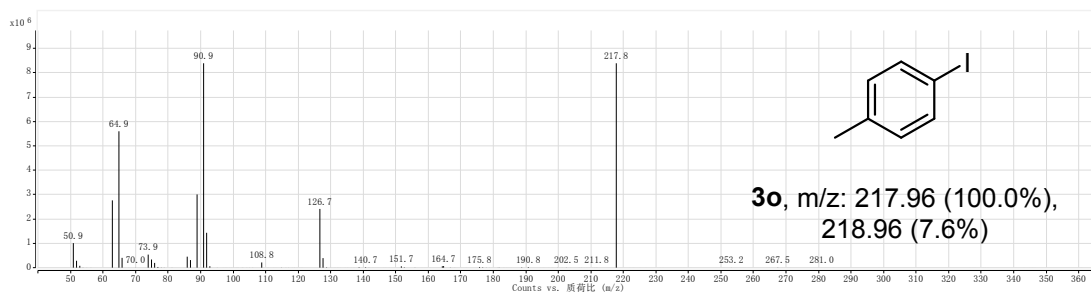
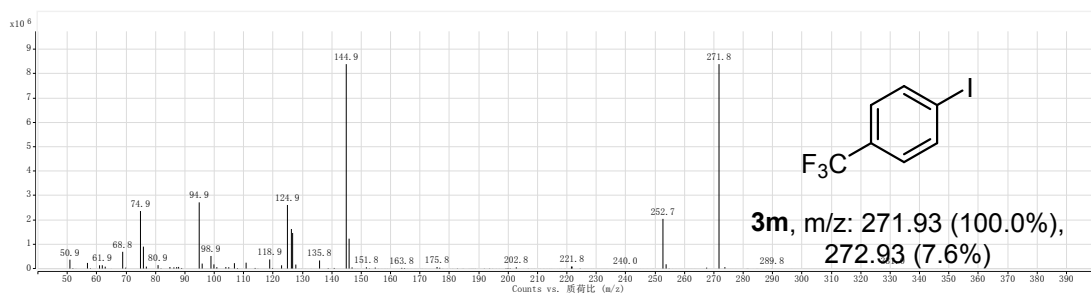


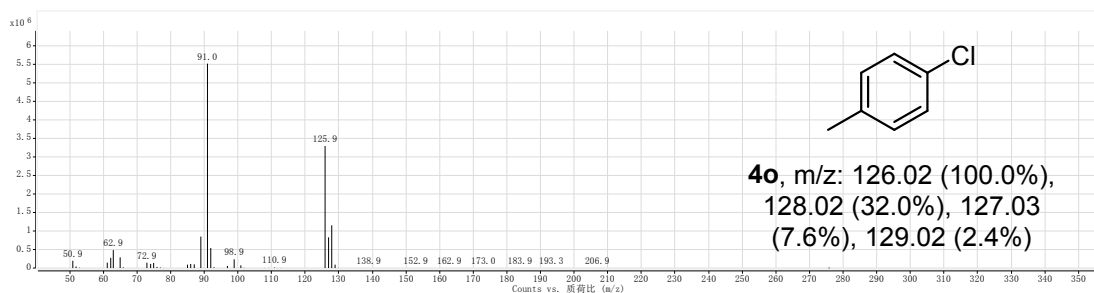
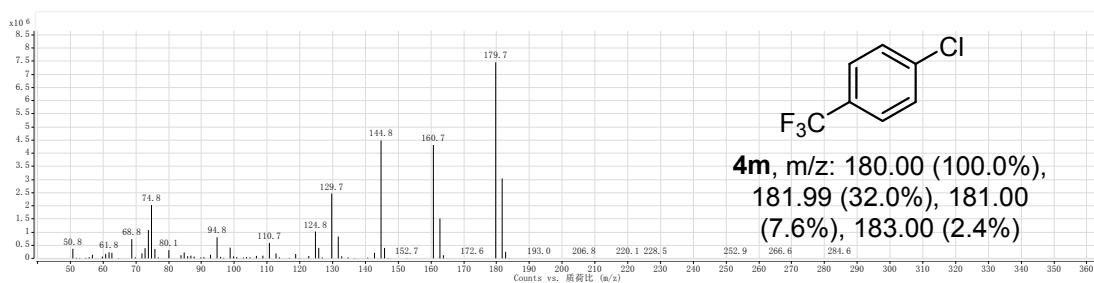
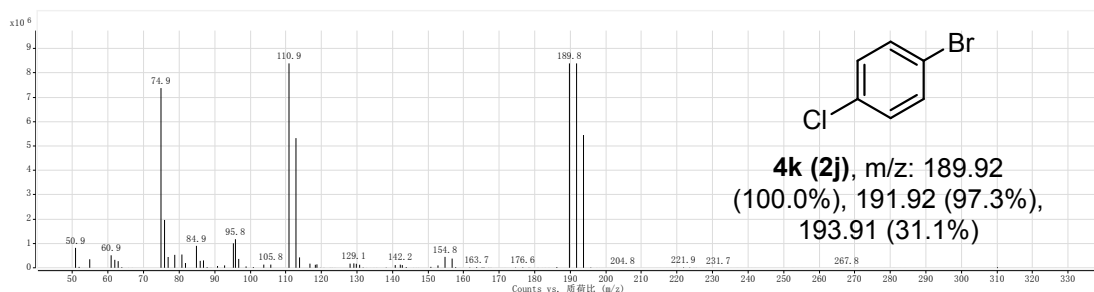
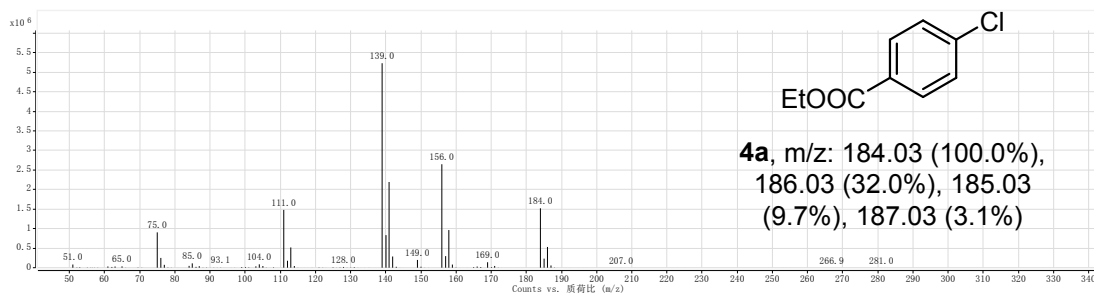
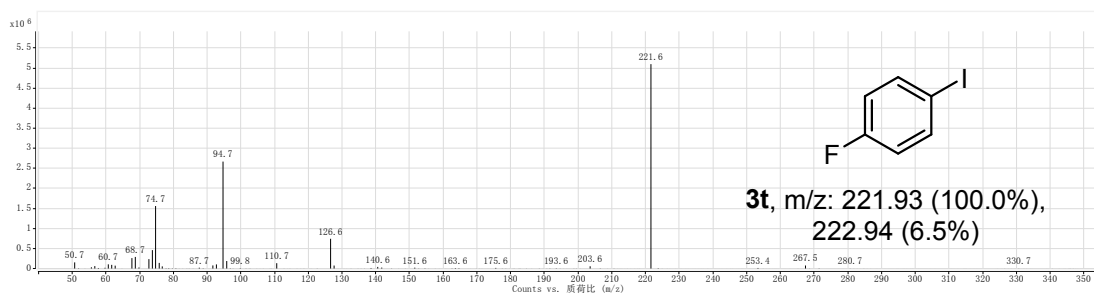
Conditions for **2t**: DMF.



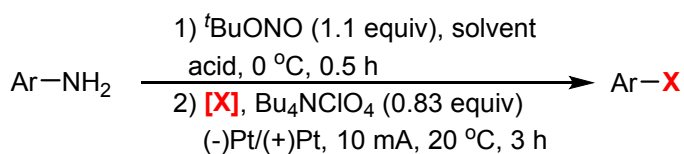
Conditions for **3d**: 2 h.



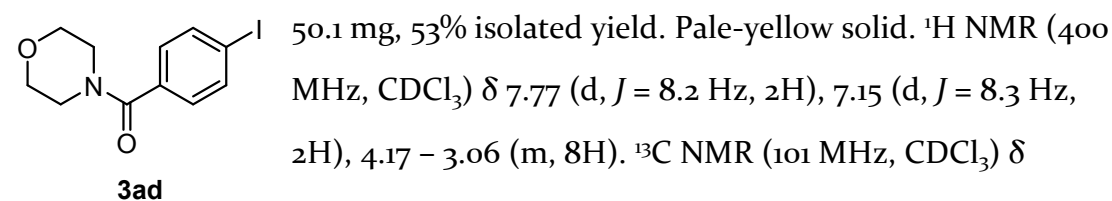
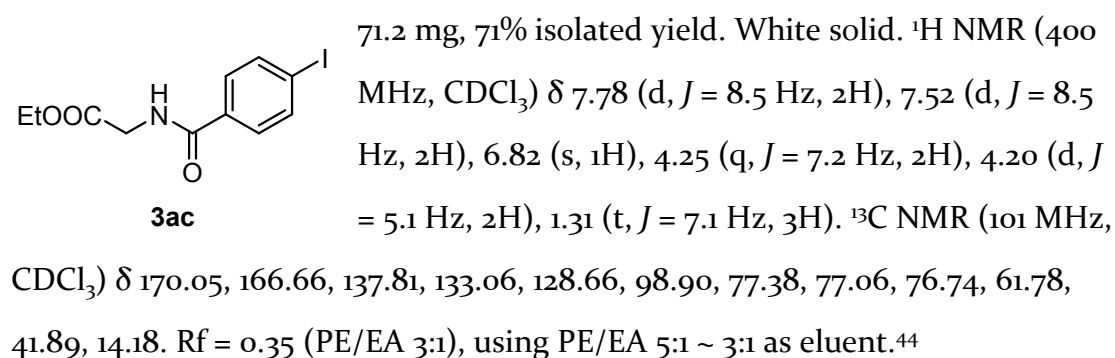
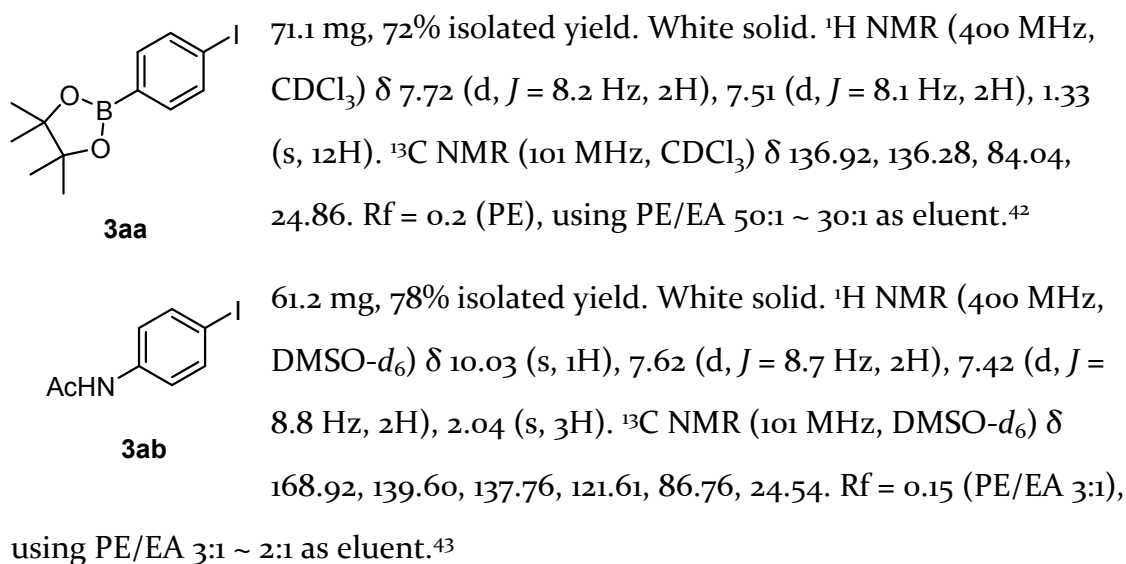




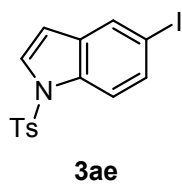
3.3 Electrochemical Sandmeyer reaction of in situ formed diazonium salt



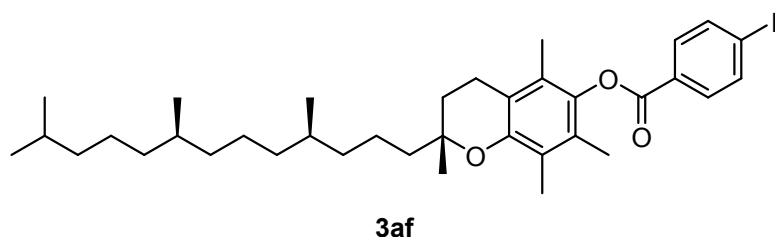
In a 10 mL tube equipped with a stir bar, aryl amine (0.3 mmol) was dissolved in given solvent. The reaction mixture was cooled to 0 °C, then acid and ^tBuONO (90%, 1.1 equiv, 45 µl) was added and the reaction mixture was stirred at 0 °C for 30 min. After that, Bu₄NClO₄ (0.25 mmol, 85.5 mg) and halogenation reagent was added, following with two Pt net electrodes were immersed into the solvent. The reaction mixture was stirred at 20 °C for 3 h, with 10 mA constant current was continuous given. Finally, the desired product was measured by GC-FID or purified according to the procedure described in Section 3.1.



169.48, 137.76, 134.68, 128.86, 96.15, 66.83. $R_f = 0.3$ (PE/EA 3:1), using PE/EA 5:1 ~ PE/EA/Et₃N 3:1:0.08 as eluent.⁴⁵



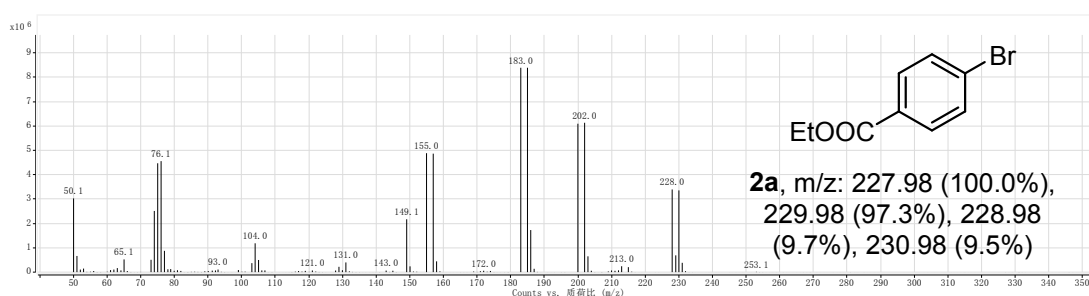
53.8 mg, 45% isolated yield. Gray solid. ¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, $J = 1.7$ Hz, 1H), 7.74 (dd, $J = 8.5, 6.8$ Hz, 3H), 7.57 (dd, $J = 8.7, 1.7$ Hz, 1H), 7.52 (d, $J = 3.7$ Hz, 1H), 7.26 – 7.11 (m, 2H), 6.57 (d, $J = 3.7$ Hz, 1H), 2.35 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 145.27, 134.99, 133.03, 130.25, 129.99, 127.18, 126.80, 117.76, 115.35, 108.00, 87.44, 21.61. $R_f = 0.6$ (PE/EA 5:1), using PE/EA 20:1 as eluent.⁴⁶

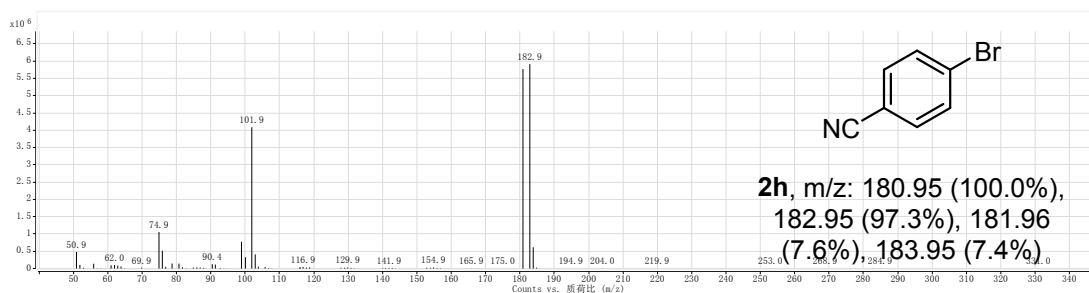


117.6 mg, 59% isolated yield. Pale-yellow oil. ¹H NMR (400 MHz, CDCl₃): δ 8.16 – 7.58 (m, 4H), 2.61 (t, $J =$

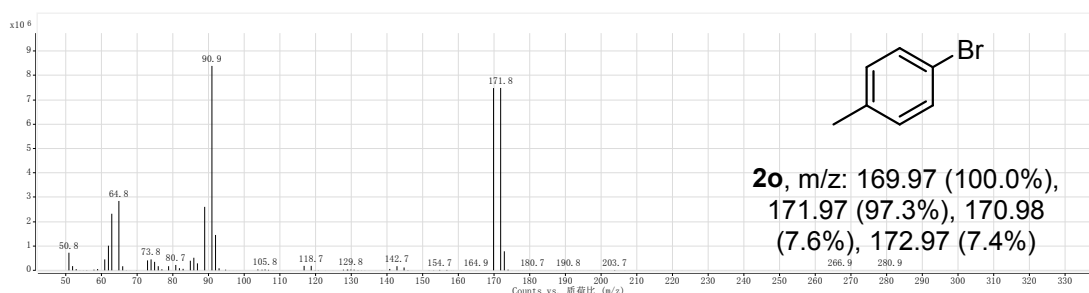
6.8 Hz, 2H), 2.17 – 0.76 (m, 47H). ¹³C NMR (101 MHz, CDCl₃) δ 164.73, 149.58, 140.47, 137.98, 131.56, 129.10, 126.78, 125.02, 123.22, 117.54, 101.34, 75.14, 39.40, 37.47, 37.31, 32.82, 31.02, 29.73, 28.01, 24.83, 24.48, 22.75, 22.66, 21.05, 20.65, 19.78, 19.69, 13.06, 12.22, 11.88. IR: $\nu = 2923, 2866, 1735, 1586, 1480, 1460, 1414, 1392, 1377, 1334, 1267, 1237, 1174, 1090, 1007, 912, 863, 843, 750, 735, 677, 636, 463, 412$ cm⁻¹. HRMS: Calcd. C₃₆H₅₄IO₃⁺ [M+H]⁺: 661.3112. Found: 661.3127. Calcd. C₃₆H₅₇INO₃⁺ [M+NH₄]⁺: 678.3378. Found: 678.3383. $R_f = 0.65$ (PE/EA 10:1), using PE ~ PE/EA 50:1 as eluent.

MS data for cases given GC-FID or NMR yields.

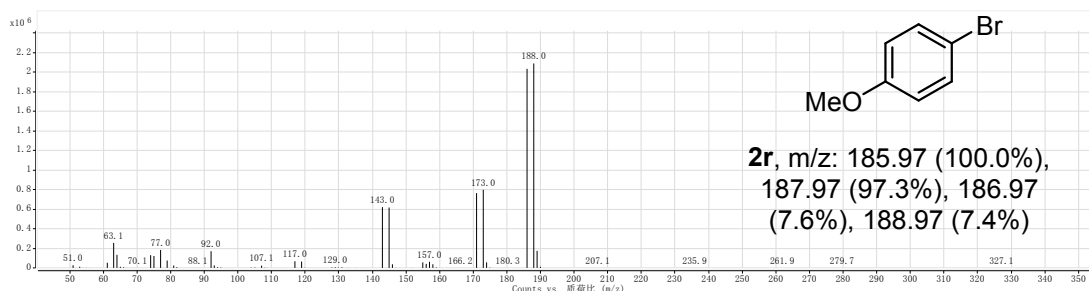




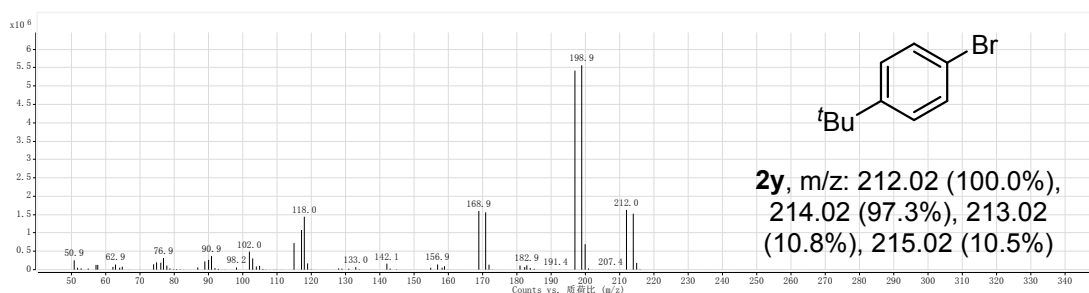
Conditions for **2h**: NaNO_2 (1.1 equiv), HBF_4 (2.0 equiv), H_2O (0.05 mL). Then, MeOH/DMF 5:1 (3 mL), Na_2SO_4 (10 equiv), NBS (2.0 equiv), 10 mA, 3 h.



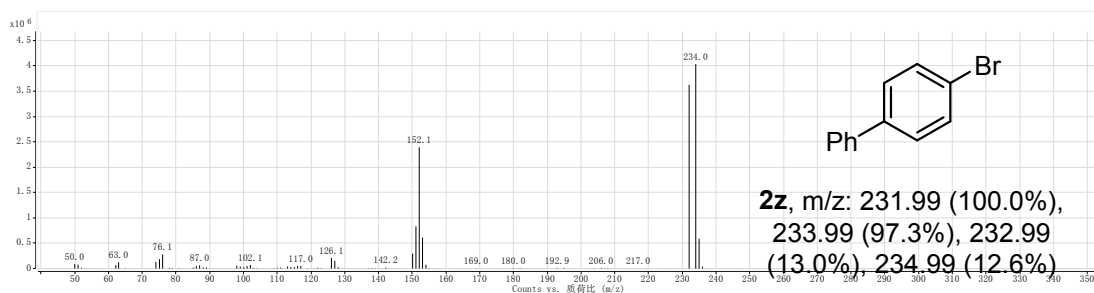
Conditions for **2o**: DMF, HBr (1.5 equiv, 6.5 M in aqueous), Na_2SO_4 (6.0 equiv).



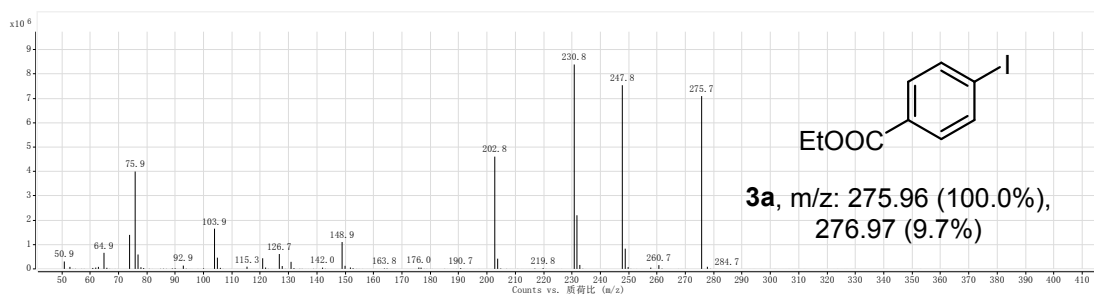
Conditions for **2r**: DMF, HBr (1.5 equiv, 6.5 M in aqueous), Na_2SO_4 (6.0 equiv).



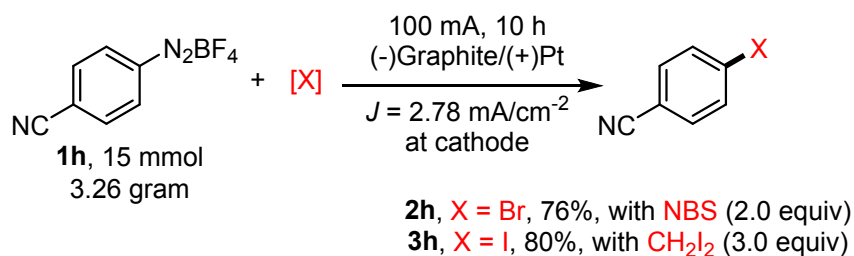
Conditons for **2y**: DMF, HBr (1.5 equiv, 6.5 M in aqueous), Na_2SO_4 (6.0 equiv).



Conditons for **2z**: DMF, HBr (1.5 equiv, 6.5 M in aqueous), Na₂SO₄ (6.0 equiv).



3.4 Bromination and iodination of 15 mmol scale



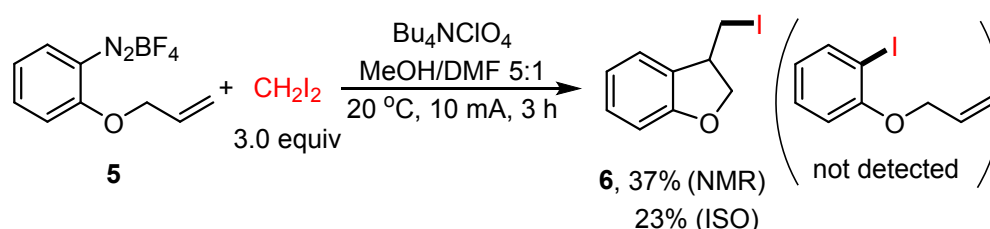
In a 200 mL well dried beaker equipped with a stir bar, diazonium salt **1h**, (3.26 g, 15 mmol), and Bu₄NClO₄ (3.42 g, 10 mmol) were dissolved in a mixed solvent of MeOH (100 mL) and DMF (20 mL). Then NBS (5.34 g, 30 mmol, 2.0 equiv) or CH₂I₂ (12.03 g, 45 mmol, 3.63 mL, 3.0 equiv) was added, following with a Pt net electrode in the center as the anode, and 4 graphite plates (10 cm * 3 cm * 1 mm each, about 3 cm immersed in the solution) in each side of a square as the cathode in parallel were stretched into the solvent (as **Scheme 3** shown). The reaction mixture was stirred at 20 °C for 3 h, with 100 mA constant current was continuous given. Upon completion, most of methanol was removed using a rotary evaporator, then the residual solution was poured into diethyl ether (150 mL) and washed with water two times (50 mL * 2). The combined water phase

was extracted by diethyl ether (100 mL) for another time, following with the second organic phase was washed with water (50 mL). The organic phase was combined and dried over Na_2SO_4 , then the solvent was removed under reduced pressure and the desired product **2h** or **3h** was purified by column chromatography (silica gel) using PE/EA 30:1 as eluent.

Bromination (**2h**): 2.08 g, 76% yield. Iodination (**3h**): 2.74 g, 80% yield.

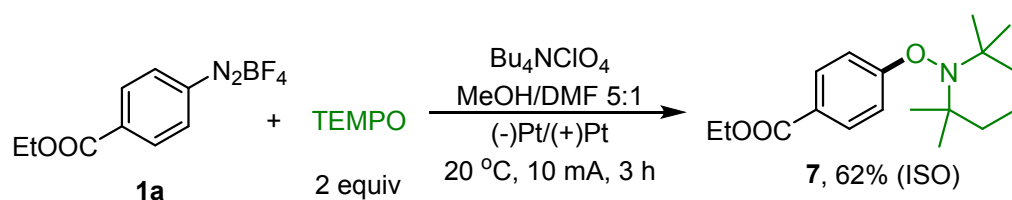
4. Mechanism study experiments

4.1 Electrochemical Clock reaction



In a 10 mL tube equipped with a stir bar, **1t** (0.3 mmol, 79.2 mg), CH_2I_2 (0.9 mmol, 73 μL , 3.0 equiv) and Bu_4NClO_4 (0.25 mmol, 85.5 mg) were dissolved in a mixed solvent of MeOH (2.5 mL) and DMF (0.5 mL), following with two Pt net electrodes immersed into the solvent. The reaction mixture was stirred at room temperature for 3 h, with 10 mA constant current was continuous given. After that, most of MeOH was removed under reduced pressure and the residue was poured into diethyl ether (60 mL), washed with water two times (20 mL * 2) and dried over Na_2SO_4 . The product **6** was measured by ^1H NMR or purified by preparation thin-layer chromatography (silica gel) using PE/EA 20:1 as eluent. Yield: 37% according to ^1H NMR, 18.2 mg (23%) isolated as a colorless liquid. ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.14 (m, 2H), 6.95 – 6.85 (m, 1H), 6.81 (d, J = 8.0 Hz, 1H), 4.72 – 4.58 (m, 1H), 4.34 (dd, J = 9.4, 5.5 Hz, 1H), 3.85 (dt, J = 9.2, 4.5 Hz, 1H), 3.51 – 3.39 (m, 1H), 3.21 (t, J = 9.8 Hz, 1H). ^{13}C NMR (101 MHz, CDCl_3) δ 160.18, 129.36, 128.77, 124.35, 120.69, 110.26, 77.68, 44.85, 9.00.⁴⁷

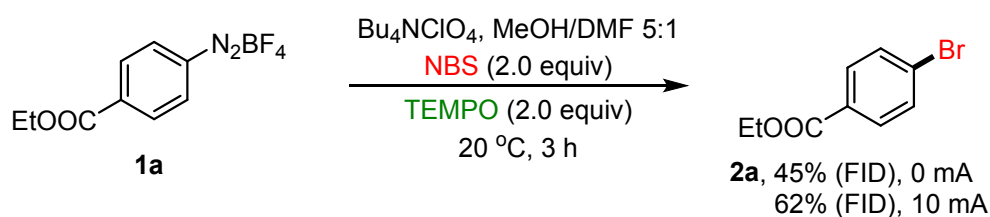
4.2 Electrochemical reaction with TEMPO



In a 10 mL tube equipped with a stir bar, **1a** (0.3 mmol, 79.2 mg), TEMPO (0.6 mmol, 93.8 mg, 2.0 equiv) and Bu_4NClO_4 (0.25 mmol, 85.5 mg) were dissolved in a mixed solvent of MeOH (2.5 mL) and DMF (0.5 mL), following with two Pt net electrodes immersed into the solvent. The reaction mixture was stirred at room temperature for 1 h, with 10 mA constant current was continuous given.

After that, the reaction mixture was poured into diethyl ether (60 mL), washed with water two times (20 mL * 2) and dried via Na_2SO_4 . The diethyl ether was then removed, and the desired product was purified by column chromatography (silica gel) using PE/EA 40:1~30:1 as an eluent to give the product **7** as a colorless oil. Yield: 56.3 mg (62%). ^1H NMR (400 MHz, CDCl_3) δ 8.01 – 7.84 (m, 2H), 7.24 (d, J = 20.1 Hz, 2H), 4.33 (q, J = 7.2 Hz, 2H), 1.72 – 1.52 (m, 5H), 1.46 – 1.39 (m, 1H), 1.36 (t, J = 7.2 Hz, 3H), 1.23 (s, 6H), 0.99 (s, 6H). ^{13}C NMR (101 MHz, CDCl_3) δ 167.39, 166.55, 131.02, 122.36, 113.71, 60.58, 60.42, 39.71, 32.38, 20.45, 16.98, 14.44.⁴⁸

4.3 Electrochemical reaction with TEMPO and NBS



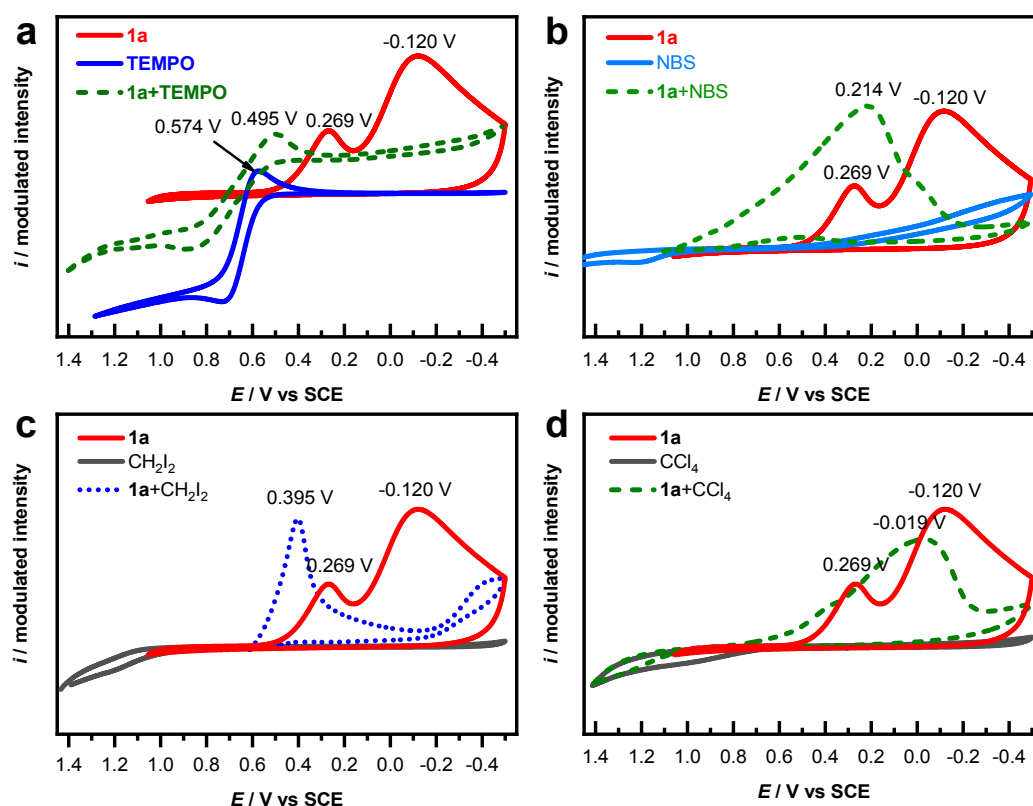
In a 10 mL tube equipped with a stir bar, **1a** (0.3 mmol, 79.2 mg), TEMPO (0.6 mmol, 93.8 mg, 2.0 equiv), NBS (0.6 mmol, 107 mg, 2.0 equiv) and Bu_4NClO_4 (0.25 mmol, 85.5 mg) were dissolved in a mixed solvent of MeOH (2.5 mL) and DMF (0.5 mL), following with two Pt net electrodes stretched into the solvent. The reaction mixture was stirred at room temperature for 3 h, with no current

or 10 mA constant current was continuous given. After that, the reaction mixture was analyzed by GC-MS and the yield of **2a** was measured by GC-FID.

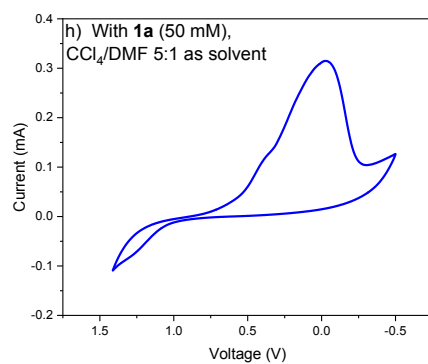
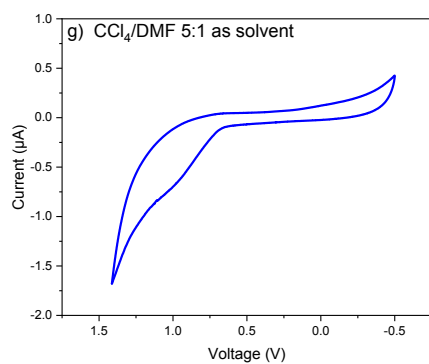
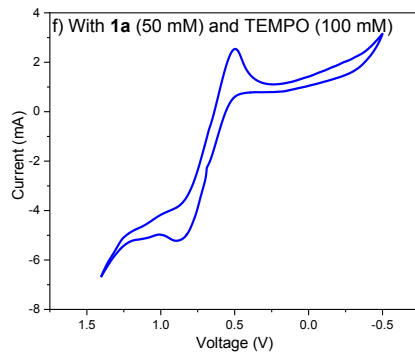
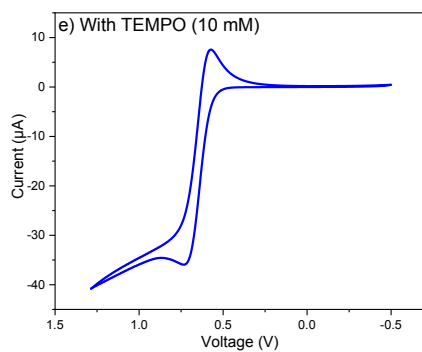
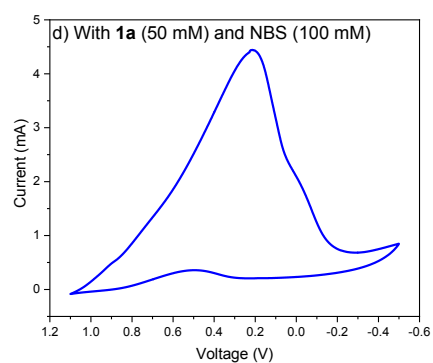
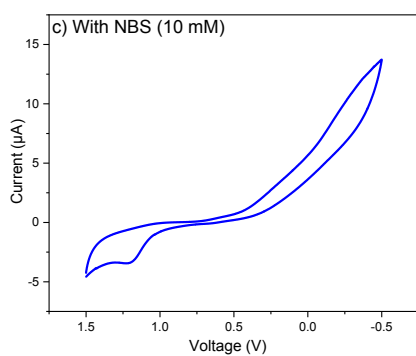
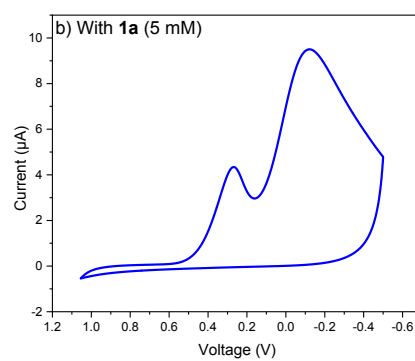
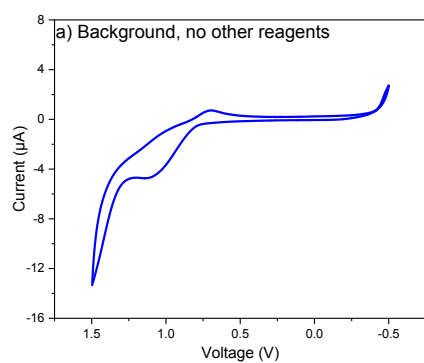
4.4 Cyclic voltammetry (CV) experiments

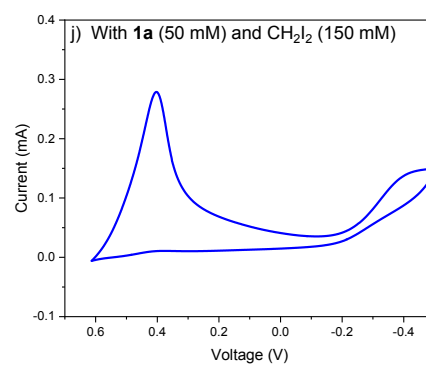
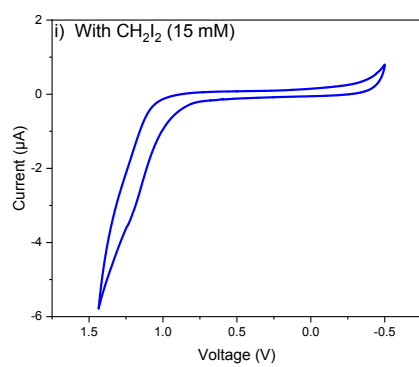
In all cases, a mixture solvent of MeOH and DMF (5:1 v/v) contented Bu_4NClO_4 (0.1 M) as electrolyte was used. The experiments used an L-shape glassy carbon electrode as the working electrode, a Pt wire as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The electric potential was between +1.5 and -0.5 V vs SCE, with 0.01 V/s scan rate. For cases with a single reagent, the concentration was 5 mM (for **1a**) or 10 mM (for NBS and TEMPO), while for cases with two reagents a tenfold concentration was required to increase the signal for their cooperative process.

Figure S4. Cyclic voltammetry curves



Original data:





5. EPR experiments and data

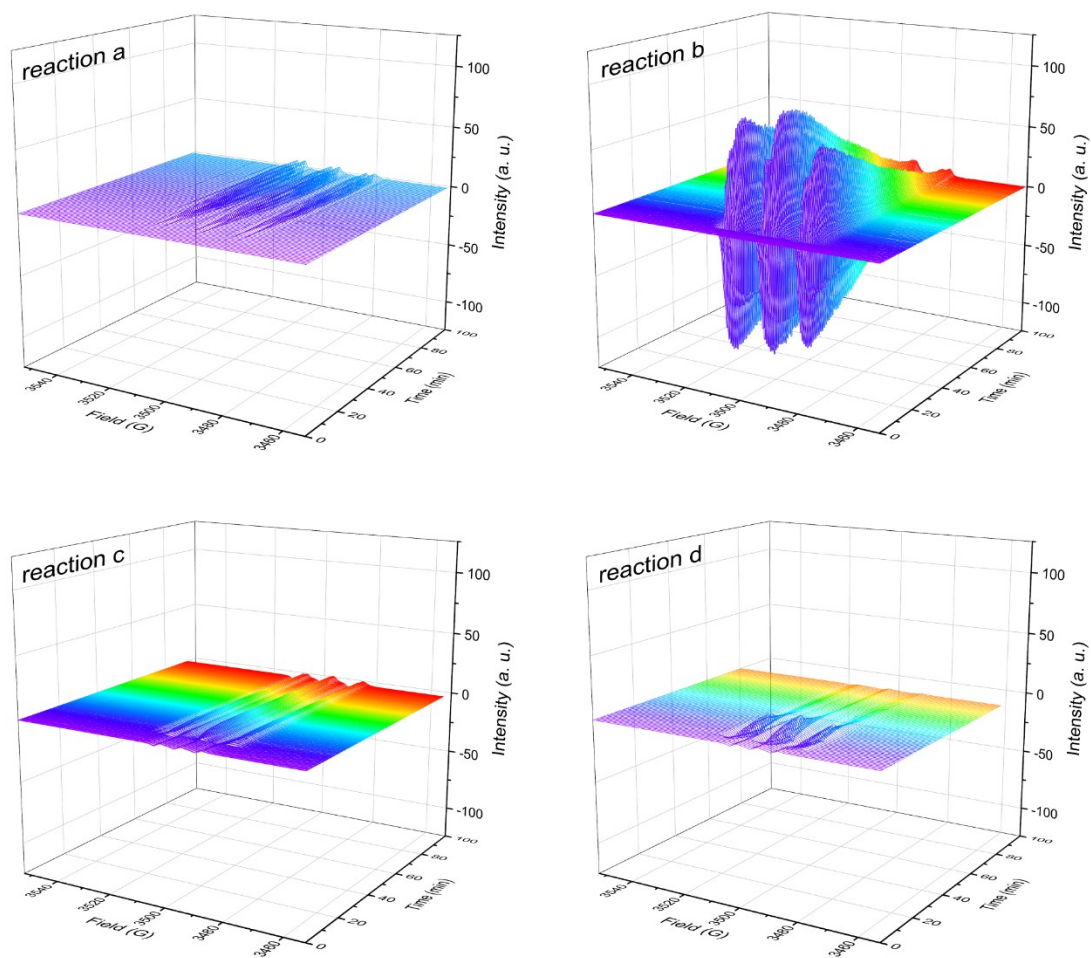
Bu₄NClO₄ (513 mg, 1.5 mmol) was dissolved in a mixed solvent of MeOH (12.5 mL) and DMF (2.5 mL). Two Teflon plugs were drilled 3 mm hole, Two Pt wires (0.2 mm diameter) were welded with general electric wires and passed through each plug.

For each case, PBN (21.3 mg, 0.12 mmol, 1.2 equiv), **1a** (if necessary, 26.4 mg, 0.1 mmol, 1.0 equiv) and NBS (if necessary 35.6 mg, 0.2 mmol, 2.0 equiv) were dissolved in 1 mL of the prepared electrolyte solution. Then, the reaction mixture was added into a glass flat cell (0.3 mm thickness in the working area, with a liquid storage pot above, about 0.2 mL of solvent was required). The flat cell was closed using the plugs as mentioned above, meanwhile the Pt wires were stretched from each side as electrodes.

X-band cw-EPR spectra were measured on a Bruker Elexsys E580 spectrometer with a super-high-Q resonator at room temperature. In all cases, the Q values after sample loading were similar (1500 ± 300). The magnetic field scanning region was between 3420 and 3620 G and contained 1024 points. MW power was 9.464 mW and modulation amplitude was 1 G. A total of 300 spectra were acquired in a time course of ~ 100 min. In each case, the current was given in a constant voltage of 16 V since about 6 min after the experiment was began (in order to obtain a blank control at the beginning). The EPR spectra were simulated using the EasySpin-5.2.14 running in Matlab (R2017a).

5.1 Time-dependent 2D EPR profile of reaction a-d

Figure S5. Time-dependent 2D EPR profile of reaction a-d

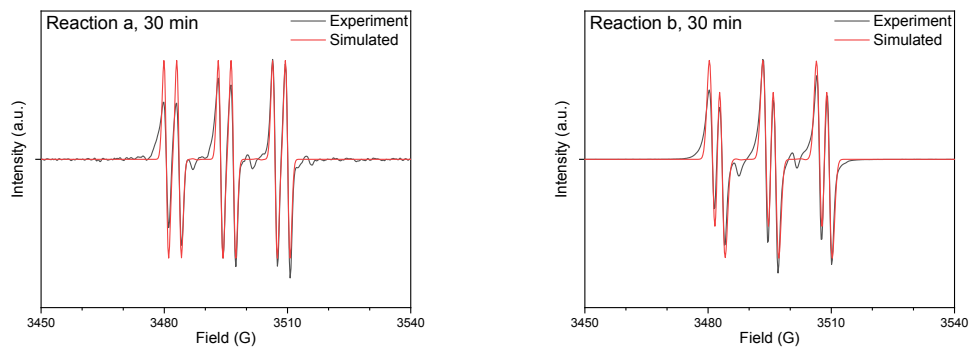


5.2 Simulations

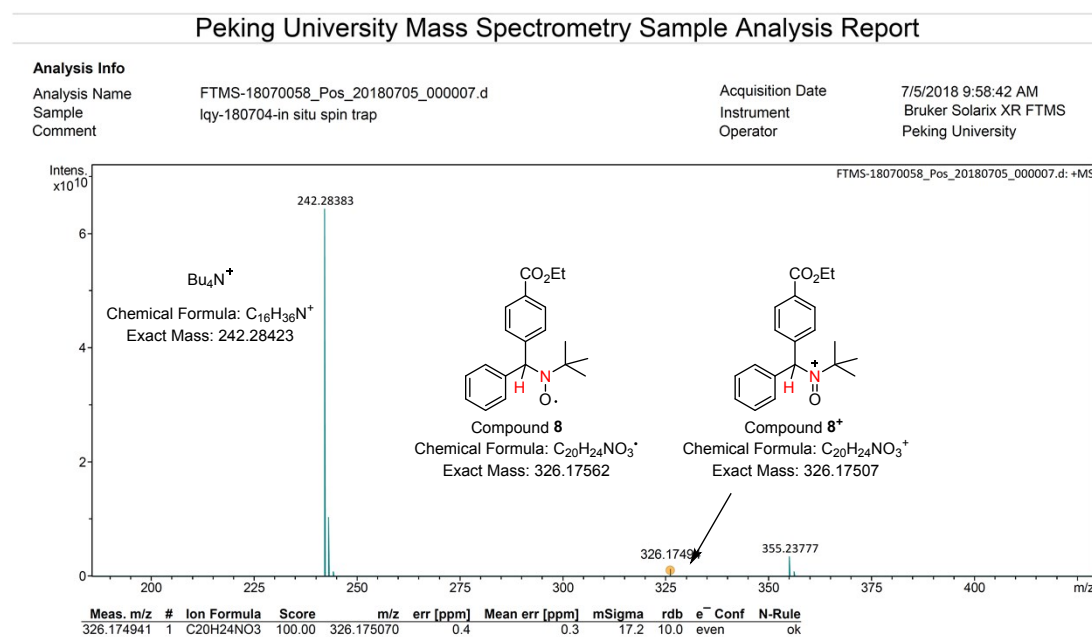
Table S4. Simulation of reaction a, b at 30 min.

Exp	g value	linewidth (G)	a_N (G)	a_H (G)	Residual
a	2.0039	1.346	13.27	3.14	0.0660
b	2.0039	1.796	13.02	2.37	0.0547

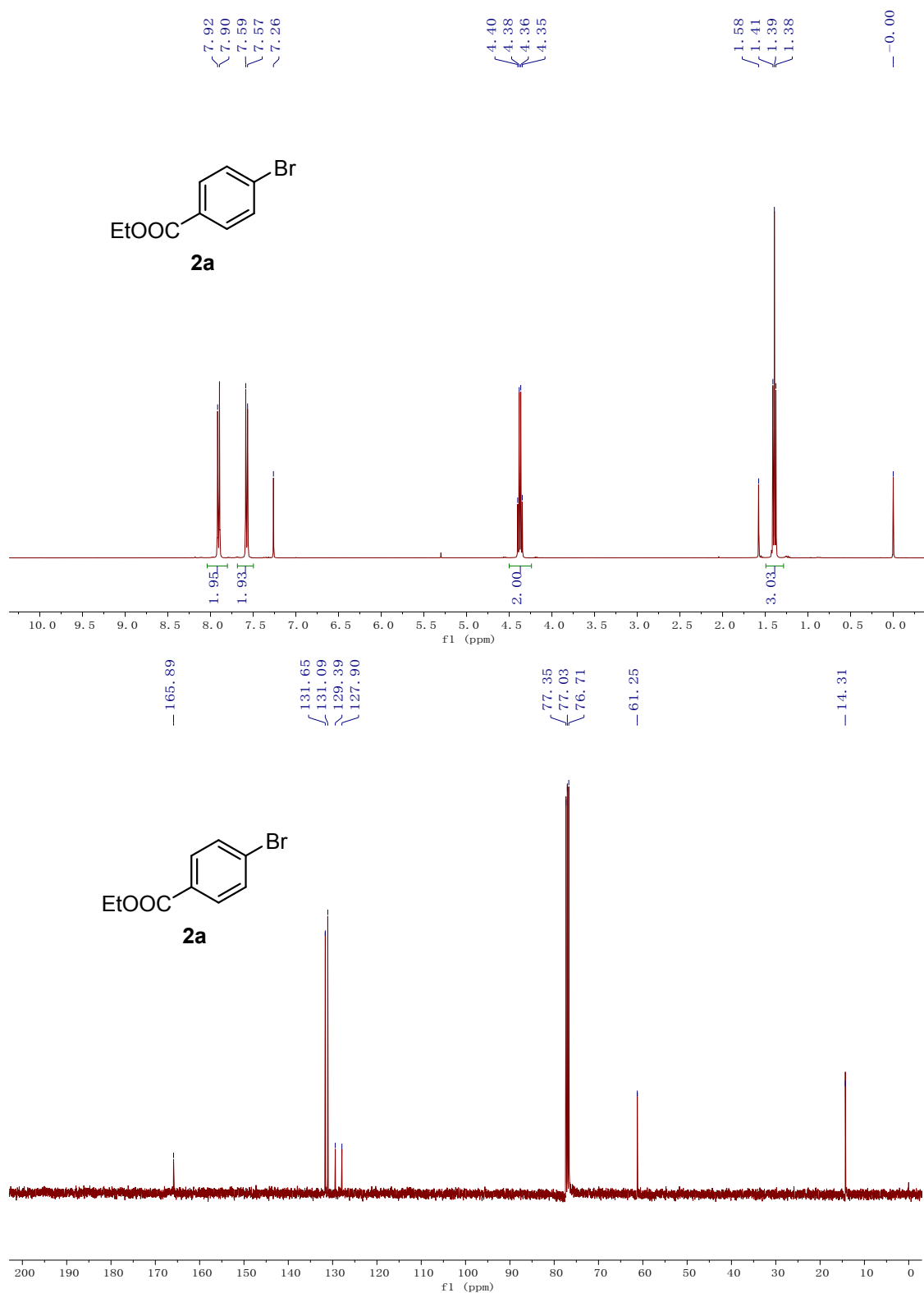
Figure S6. Comparison of simulation and experimental data

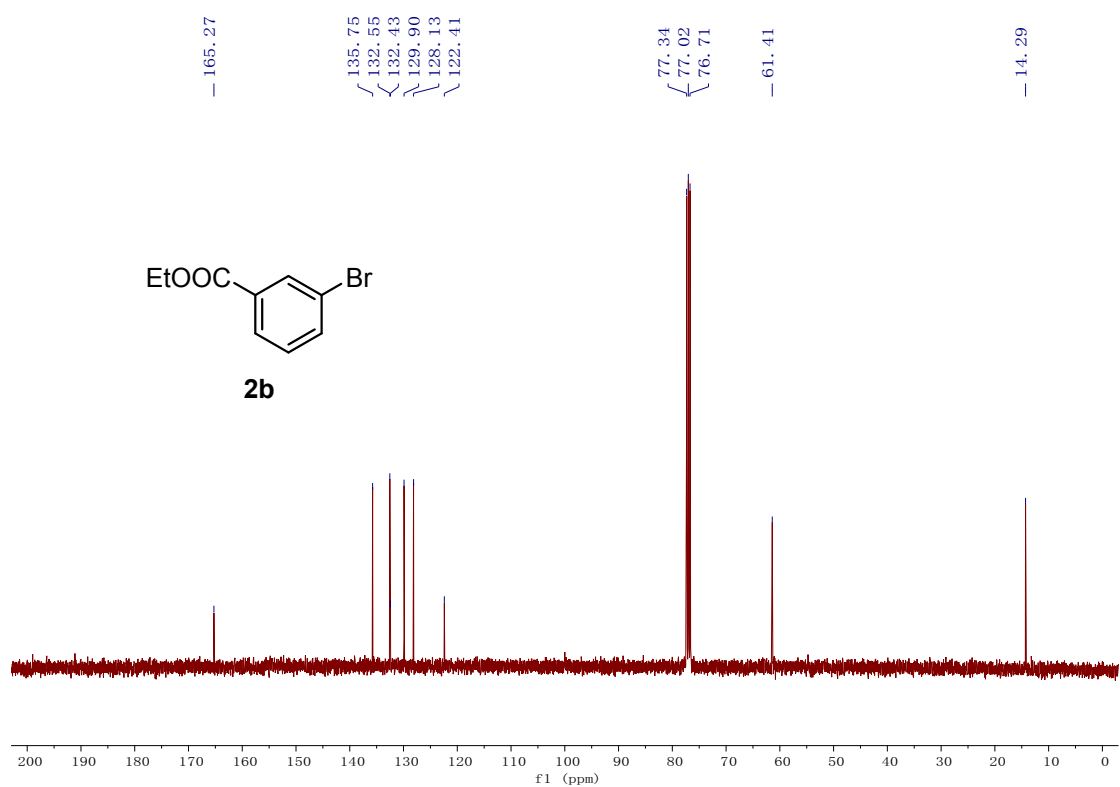
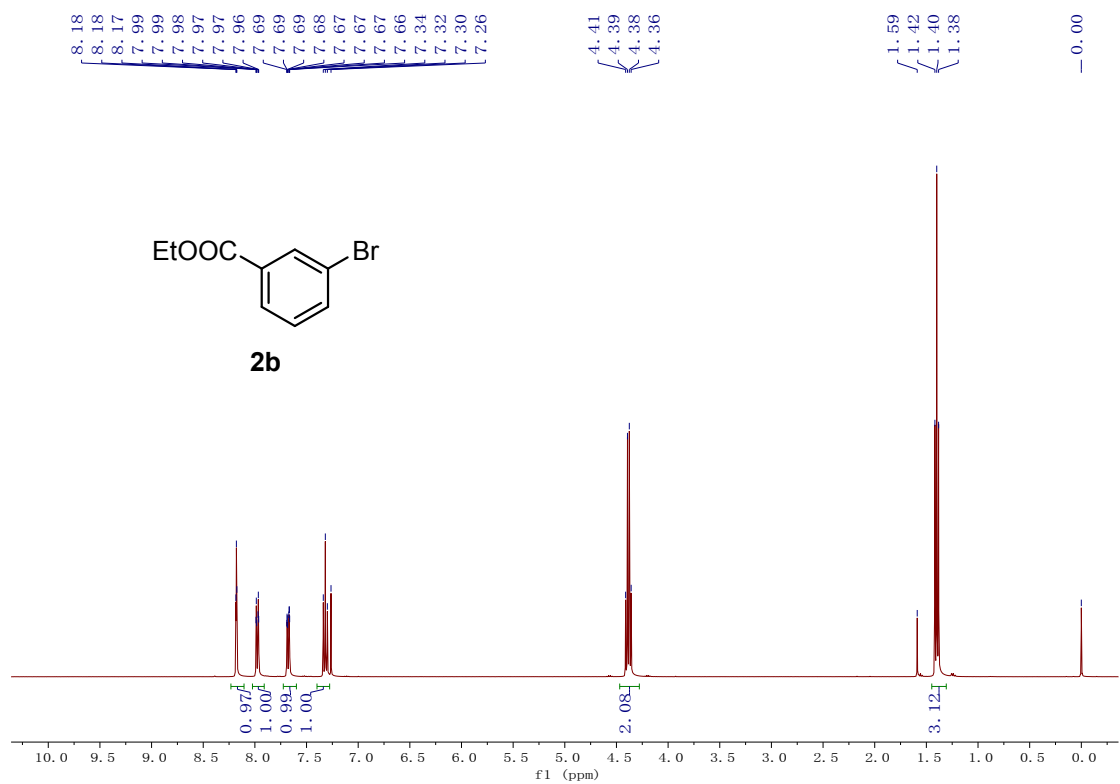


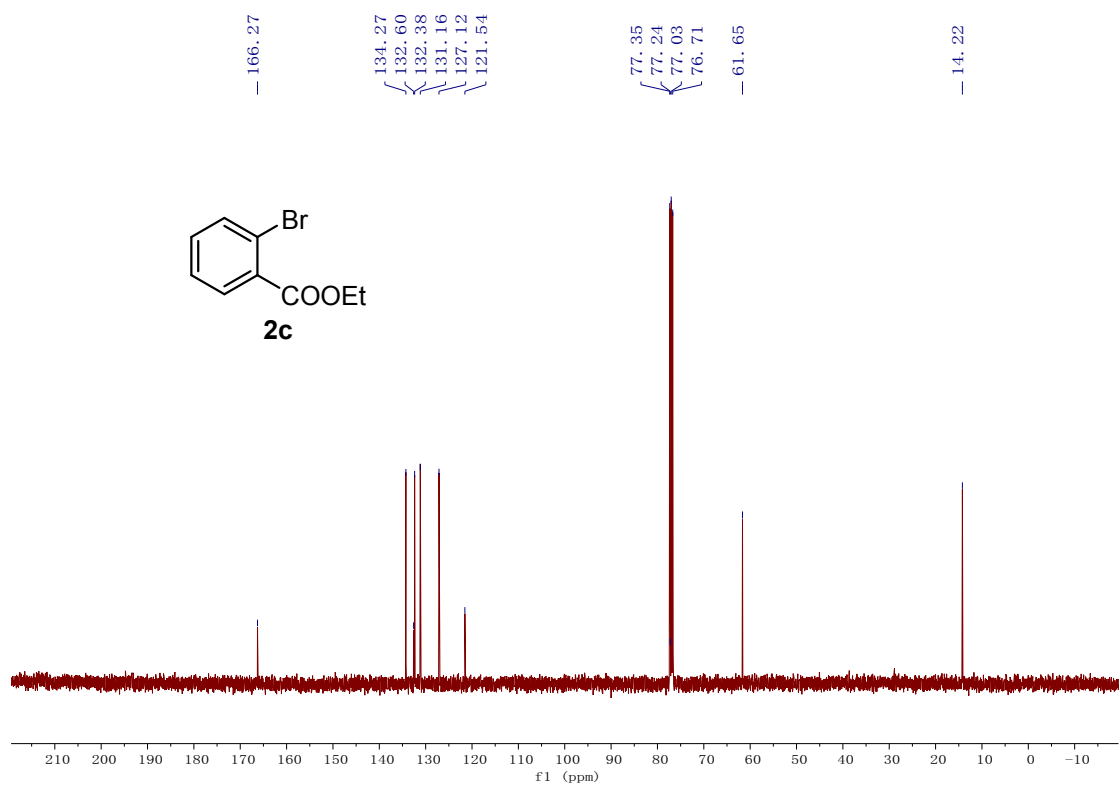
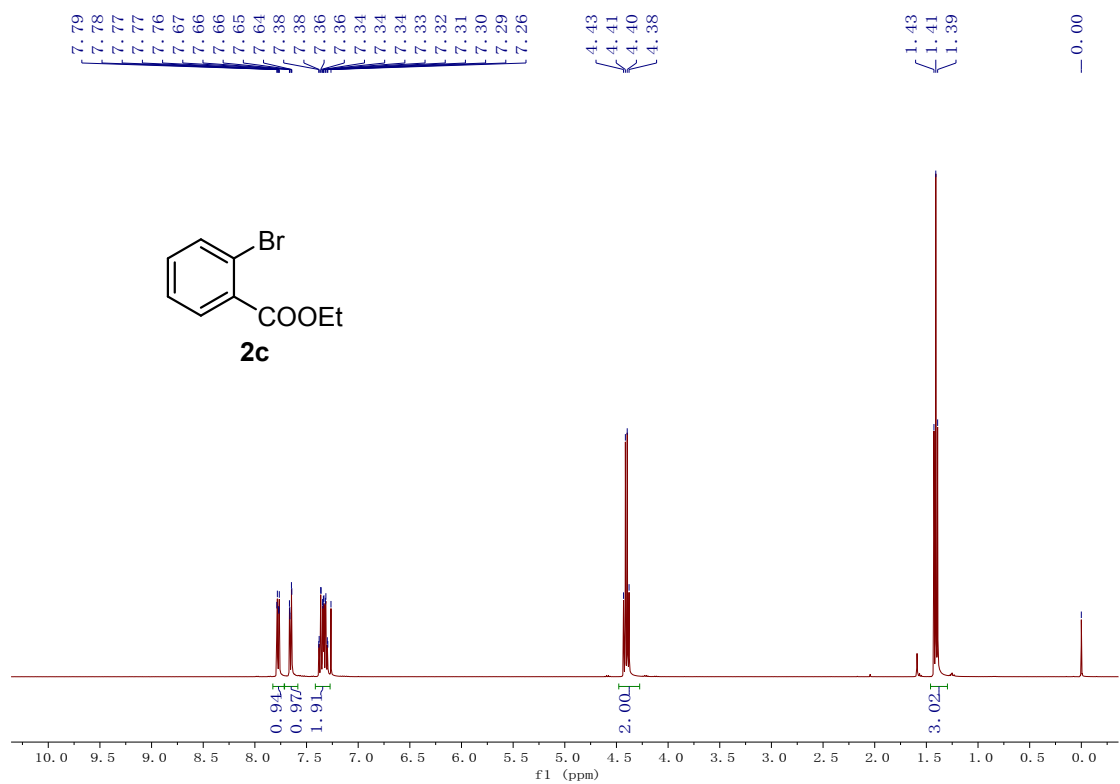
5.3 HRMS of compound 8

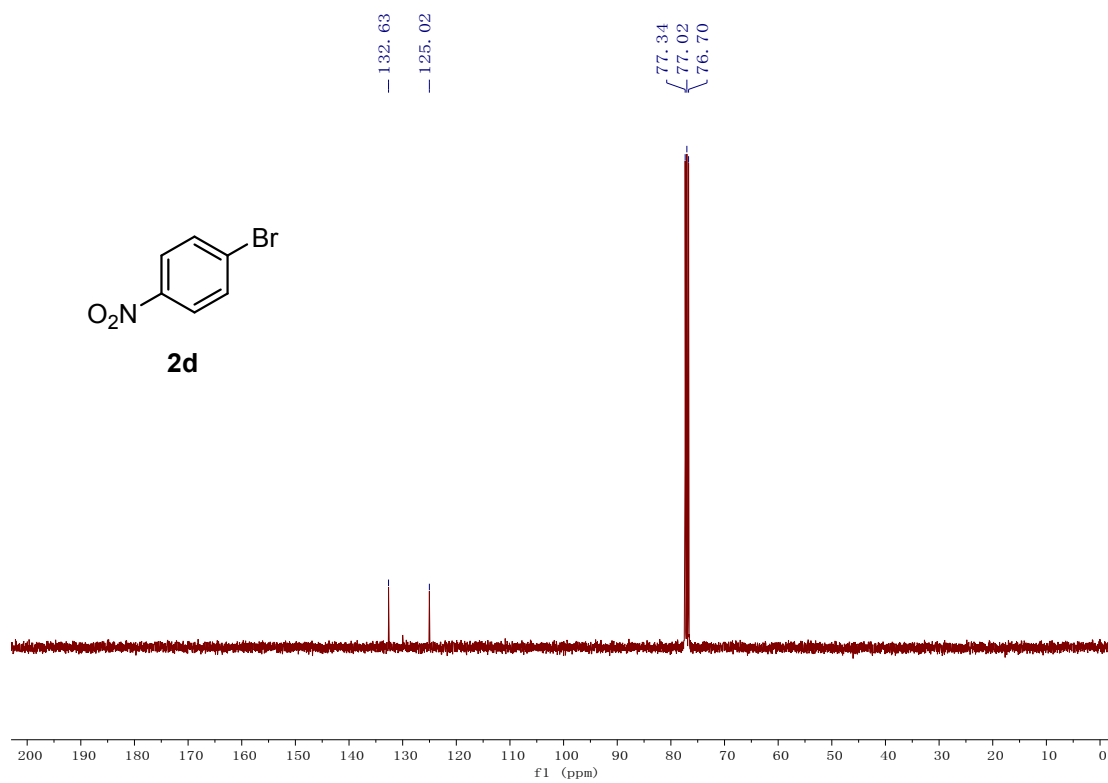
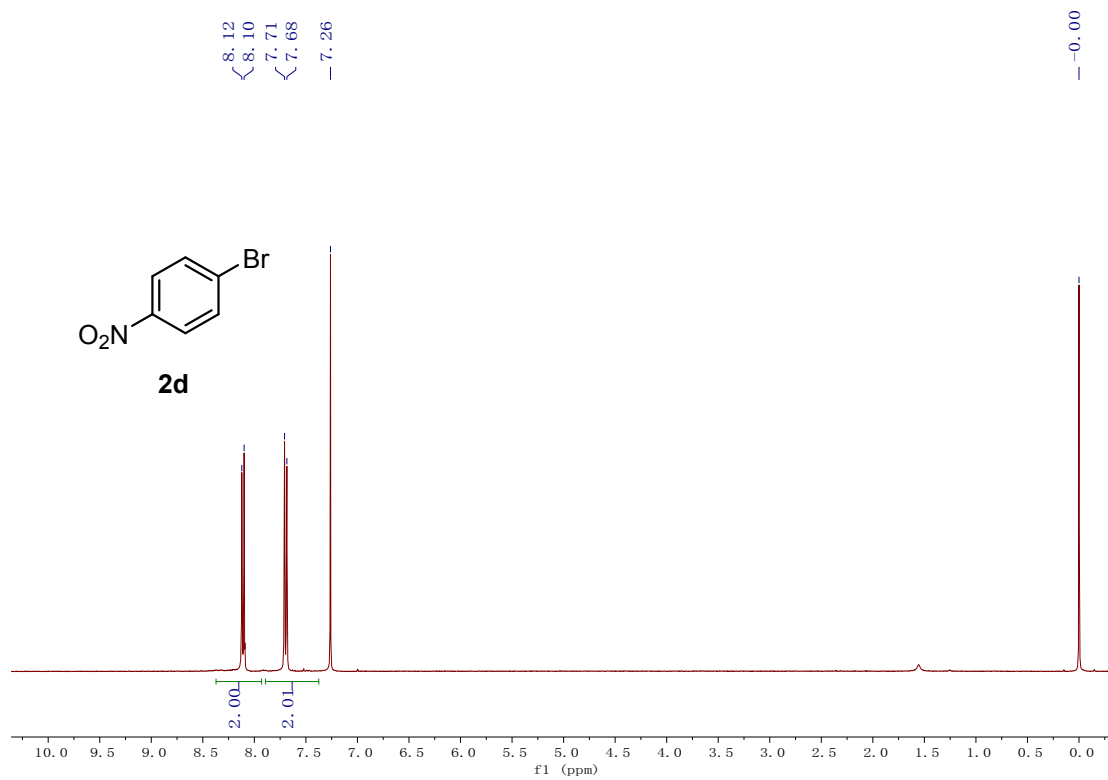


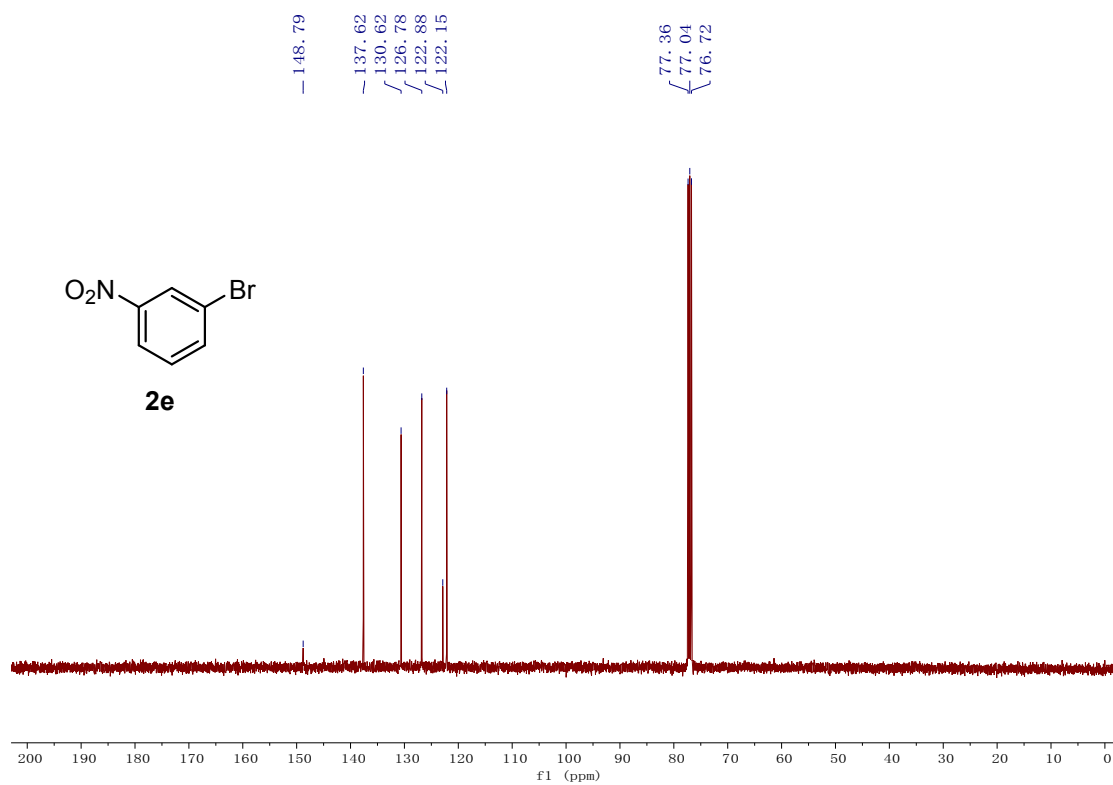
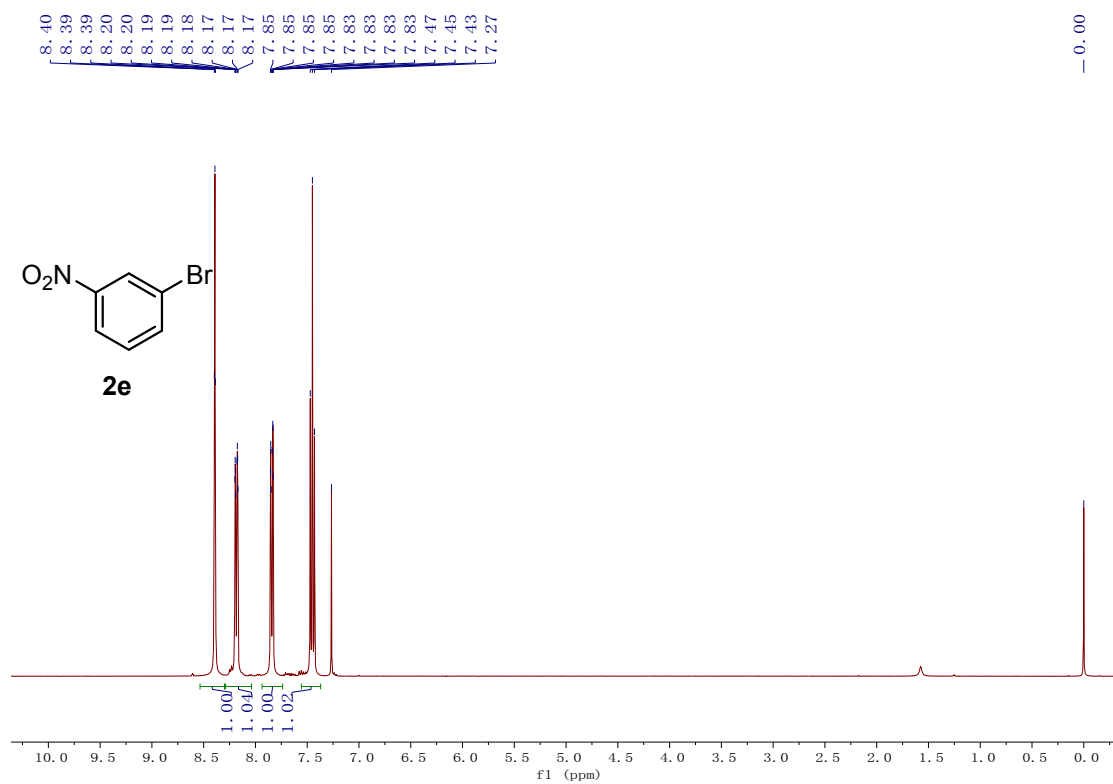
6. NMR charts

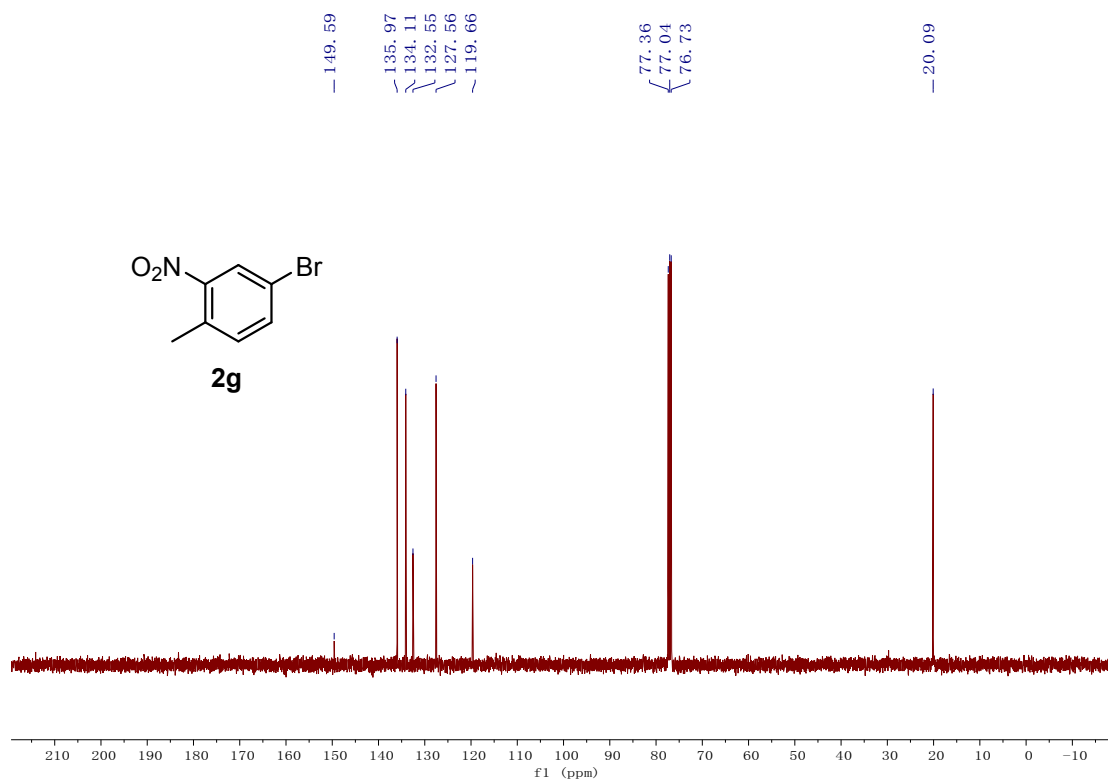
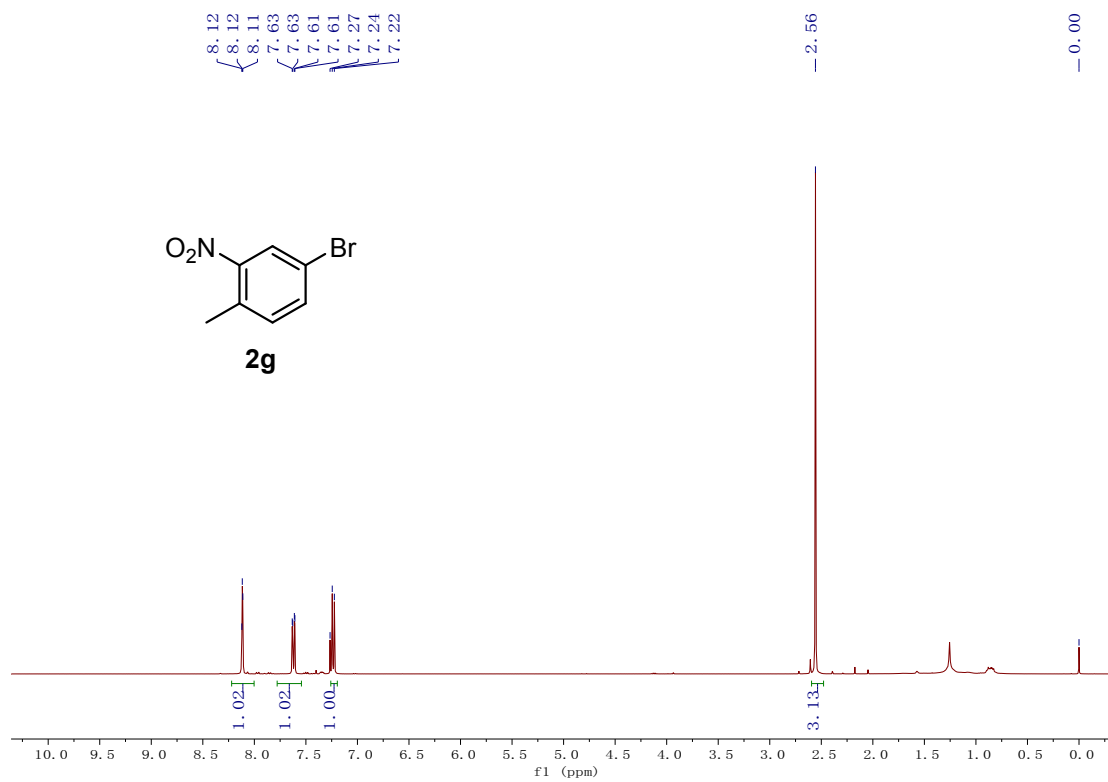


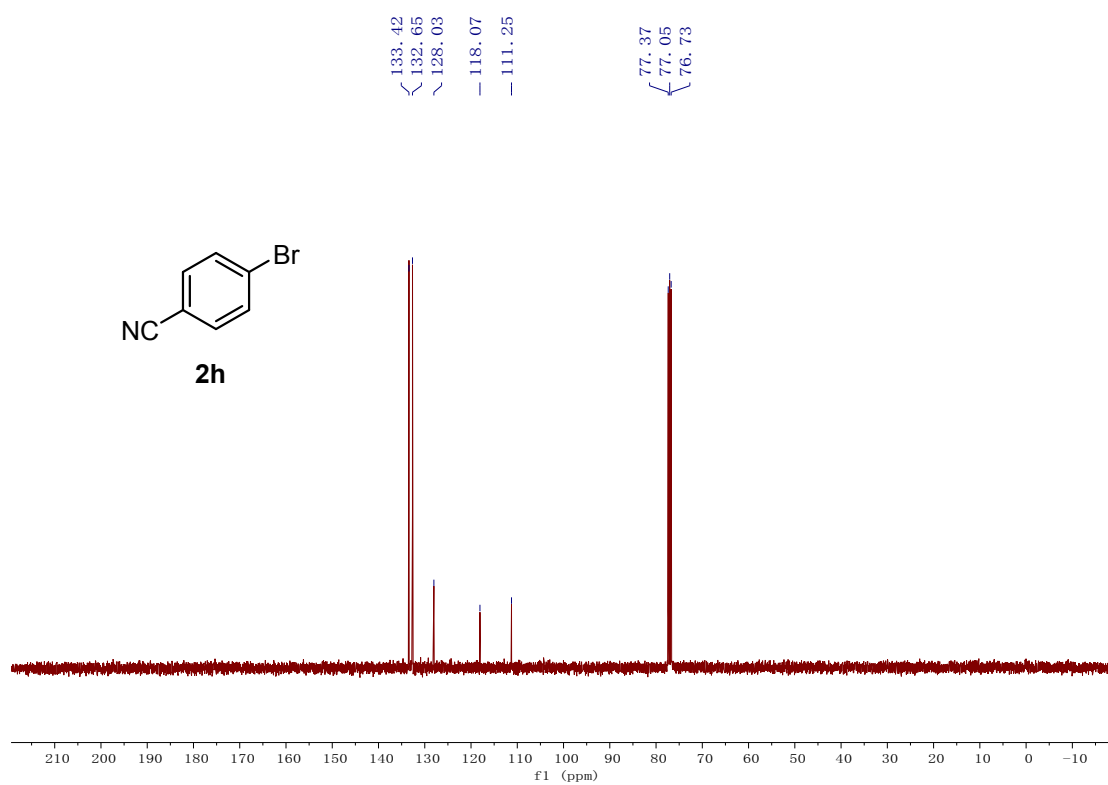
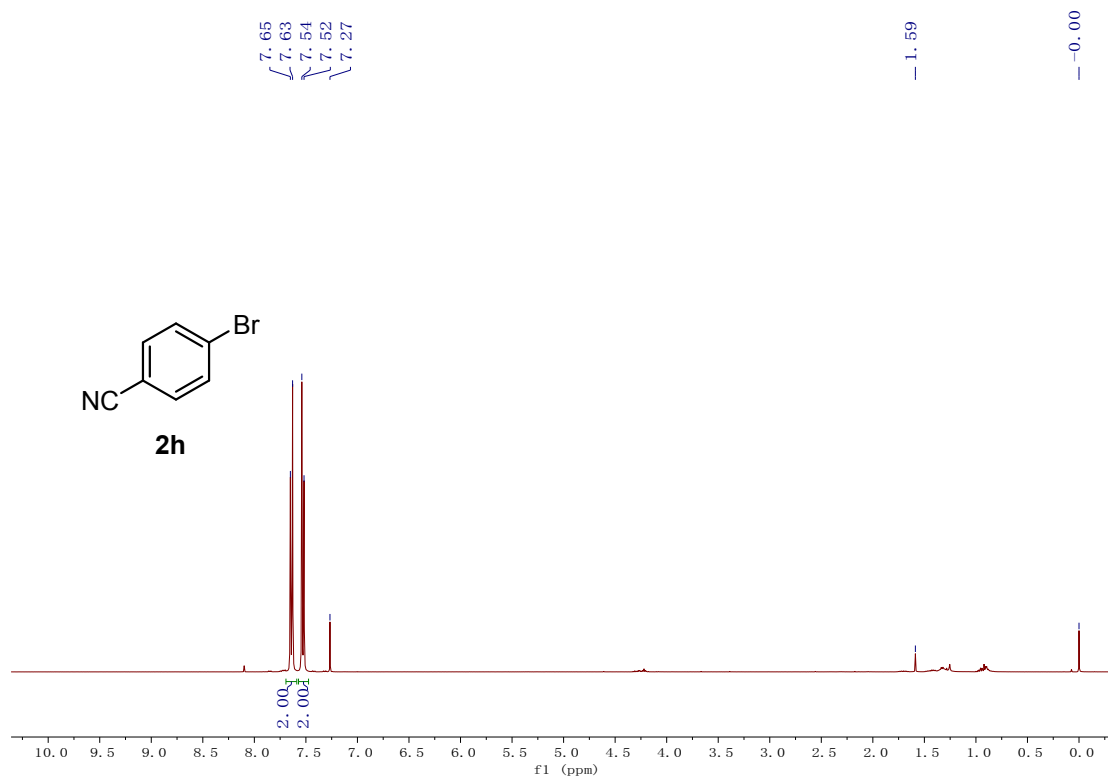


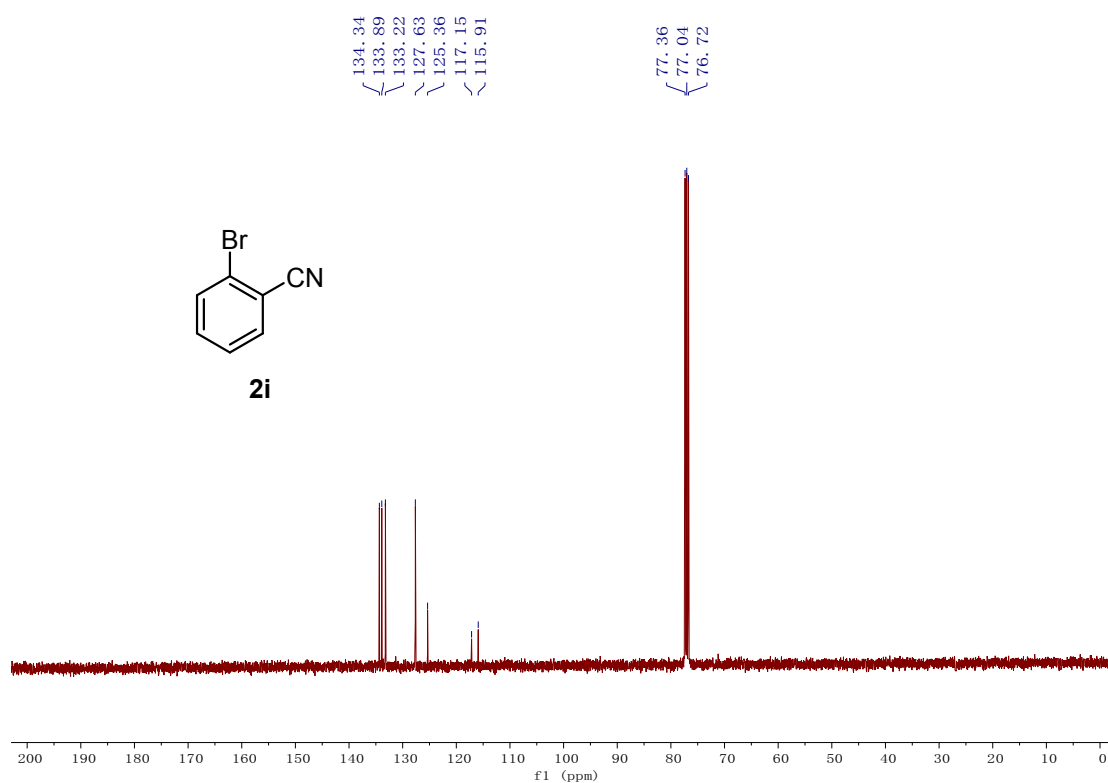
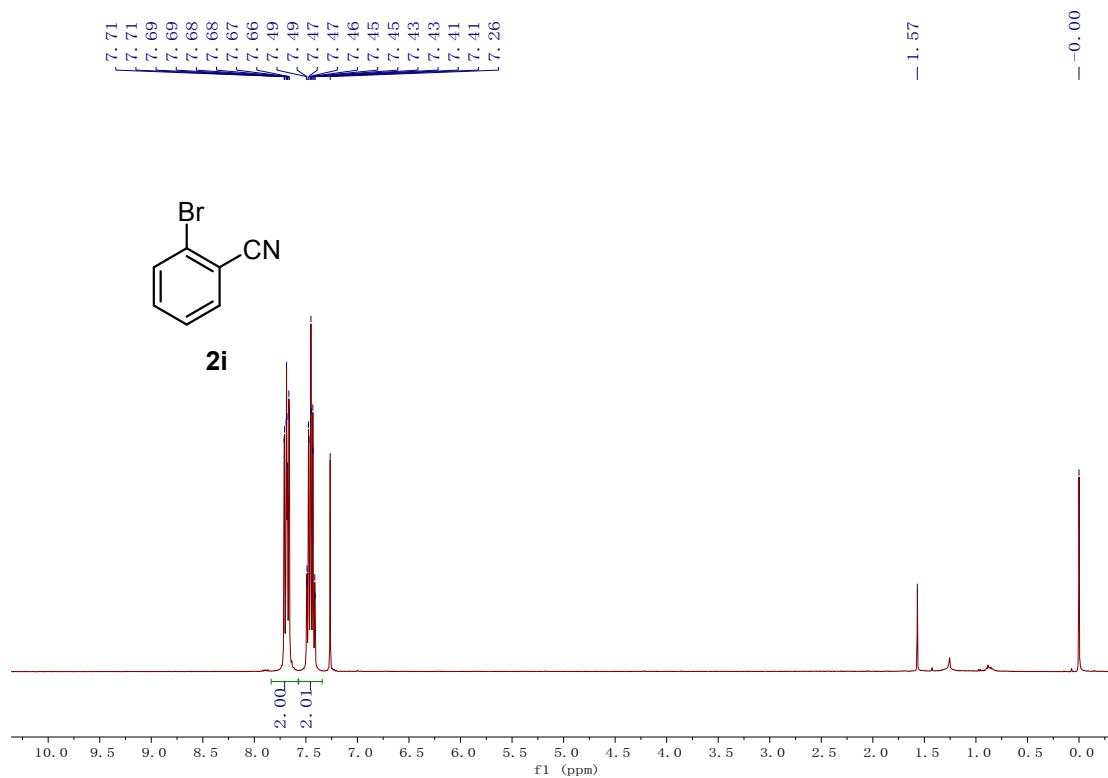


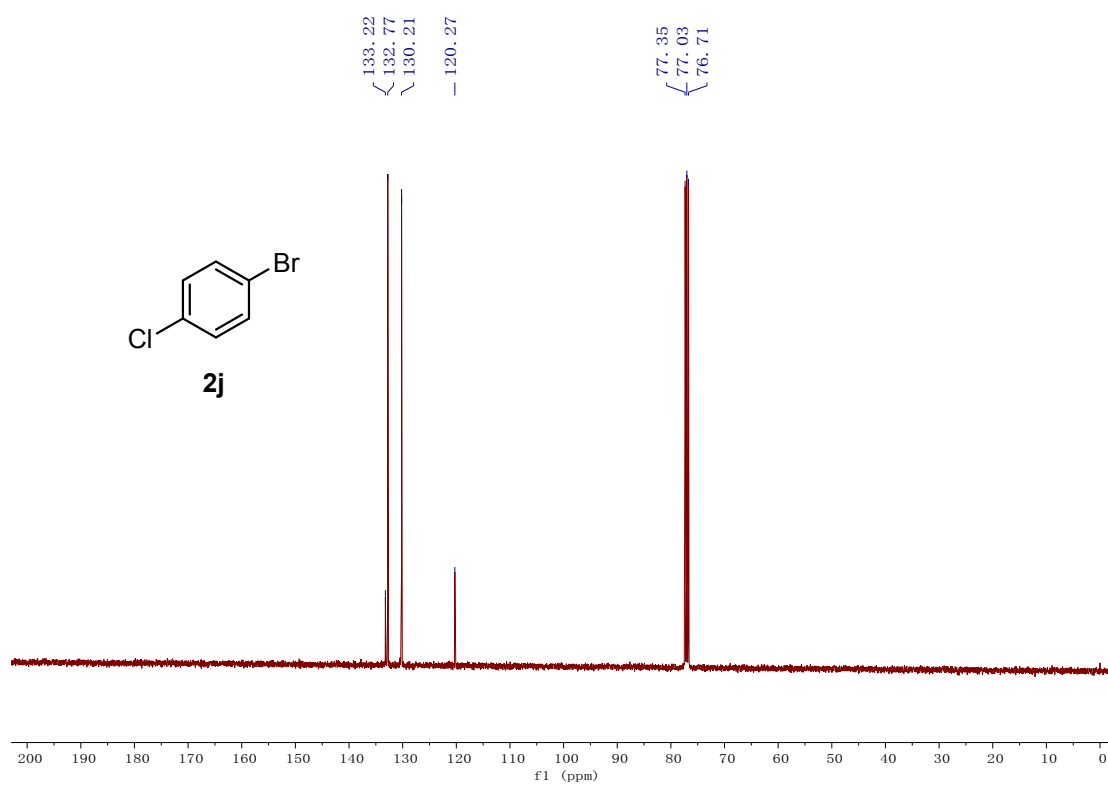
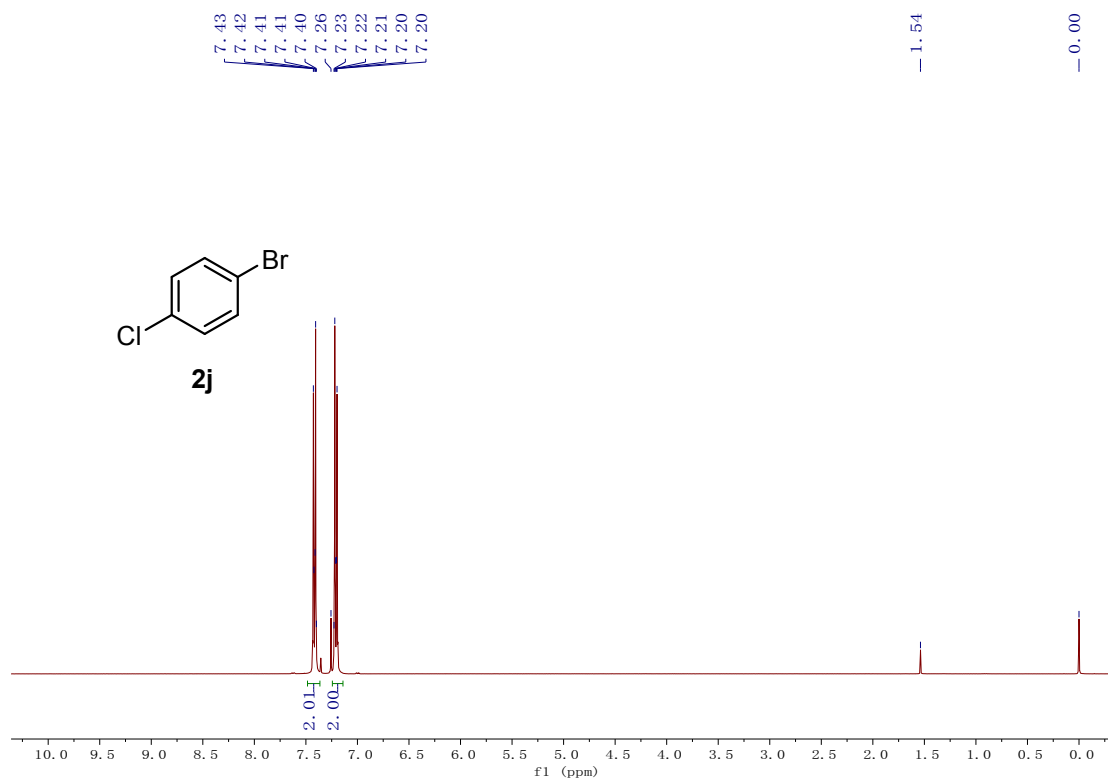


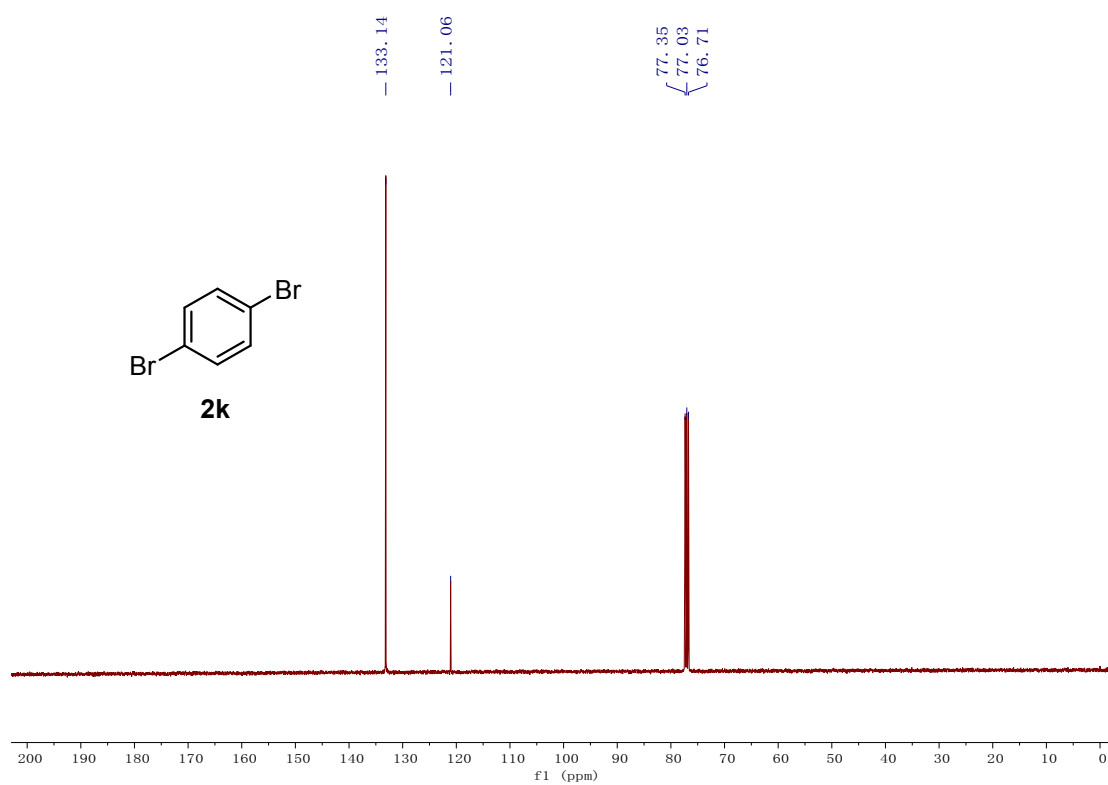
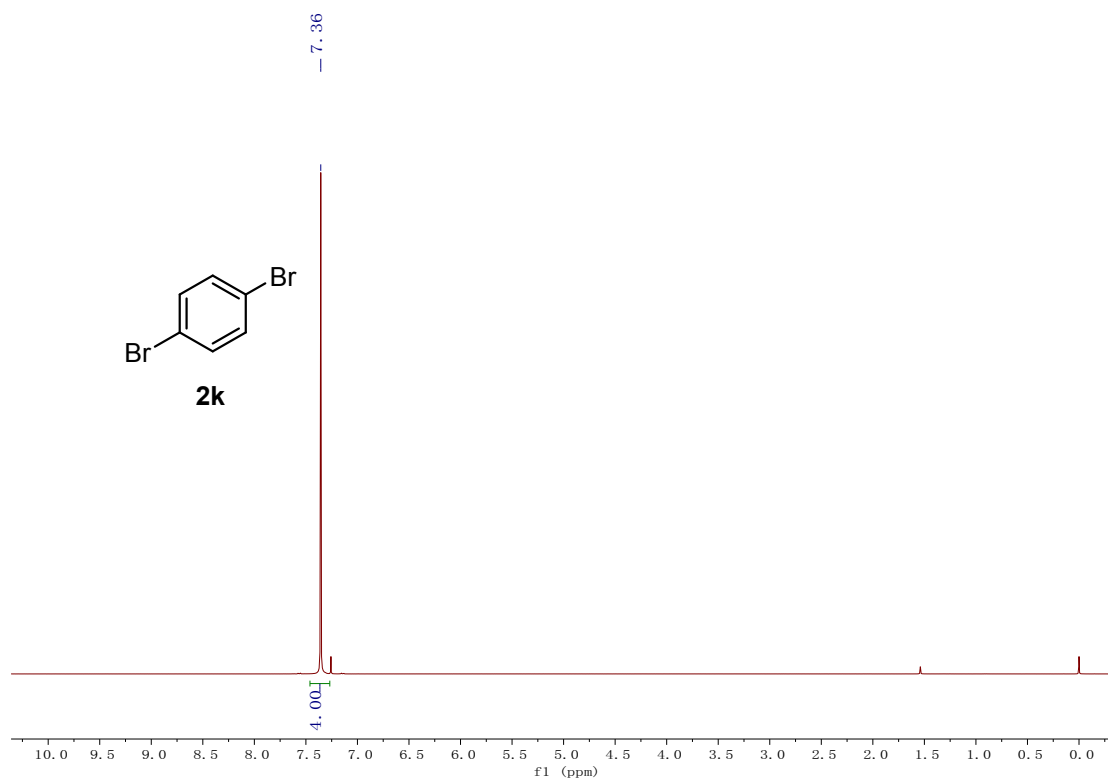


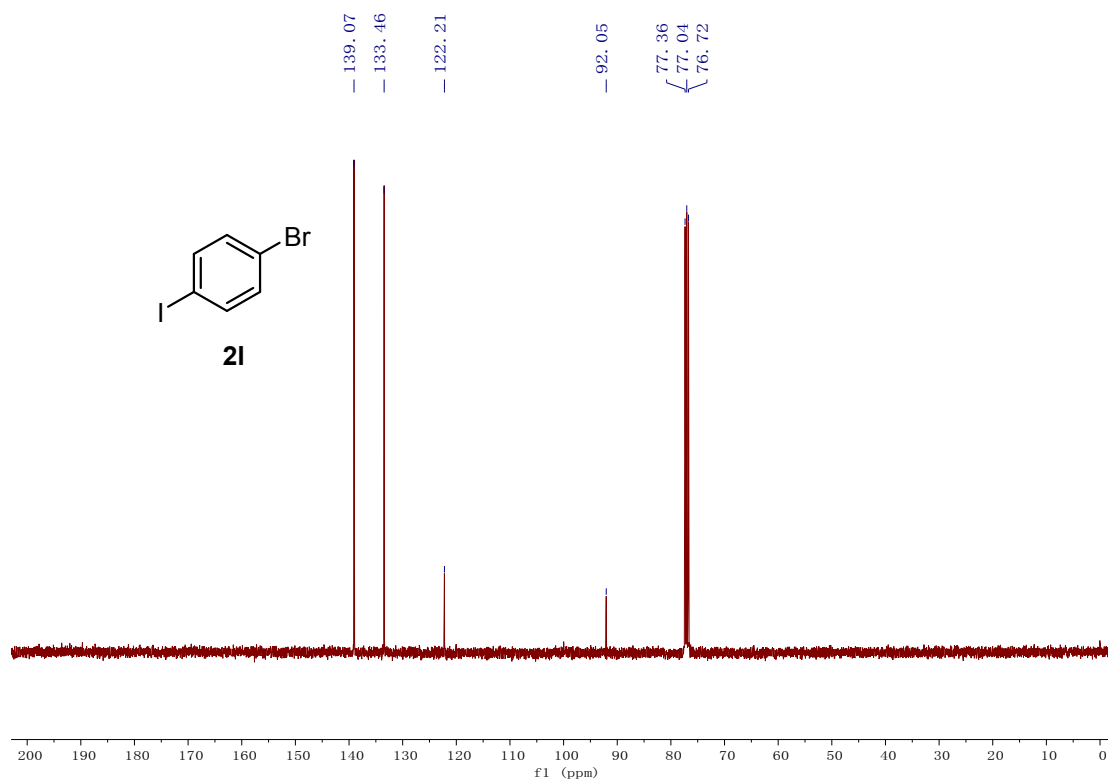
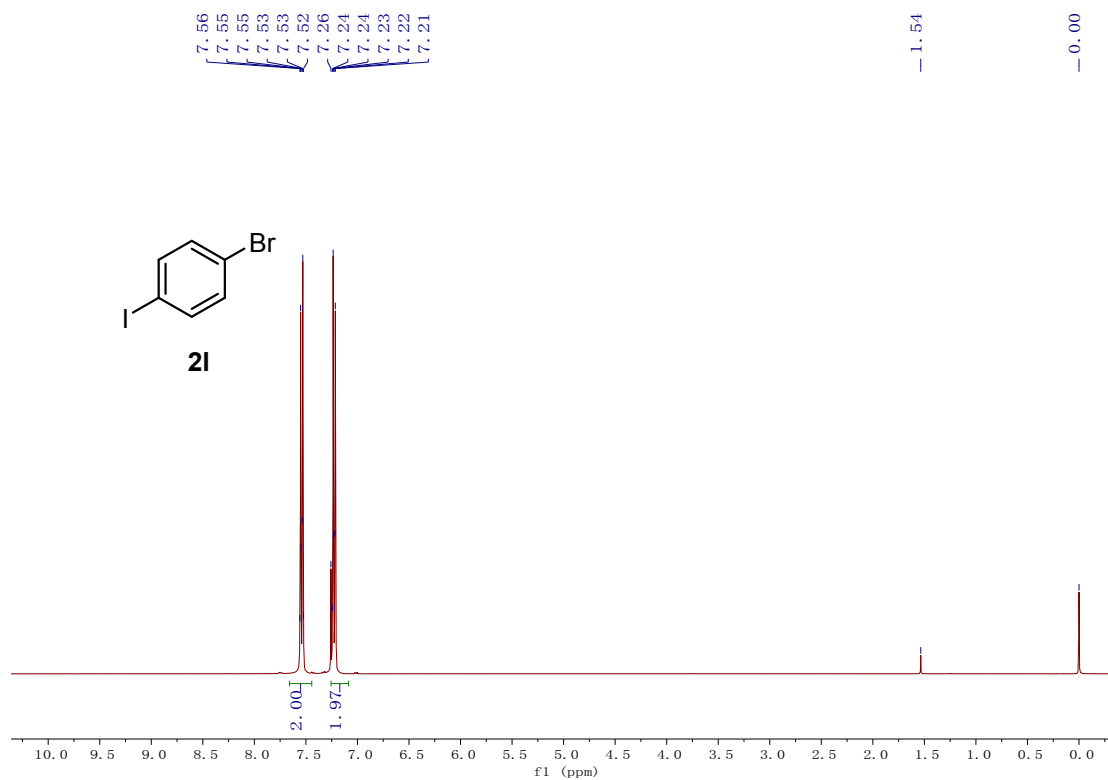


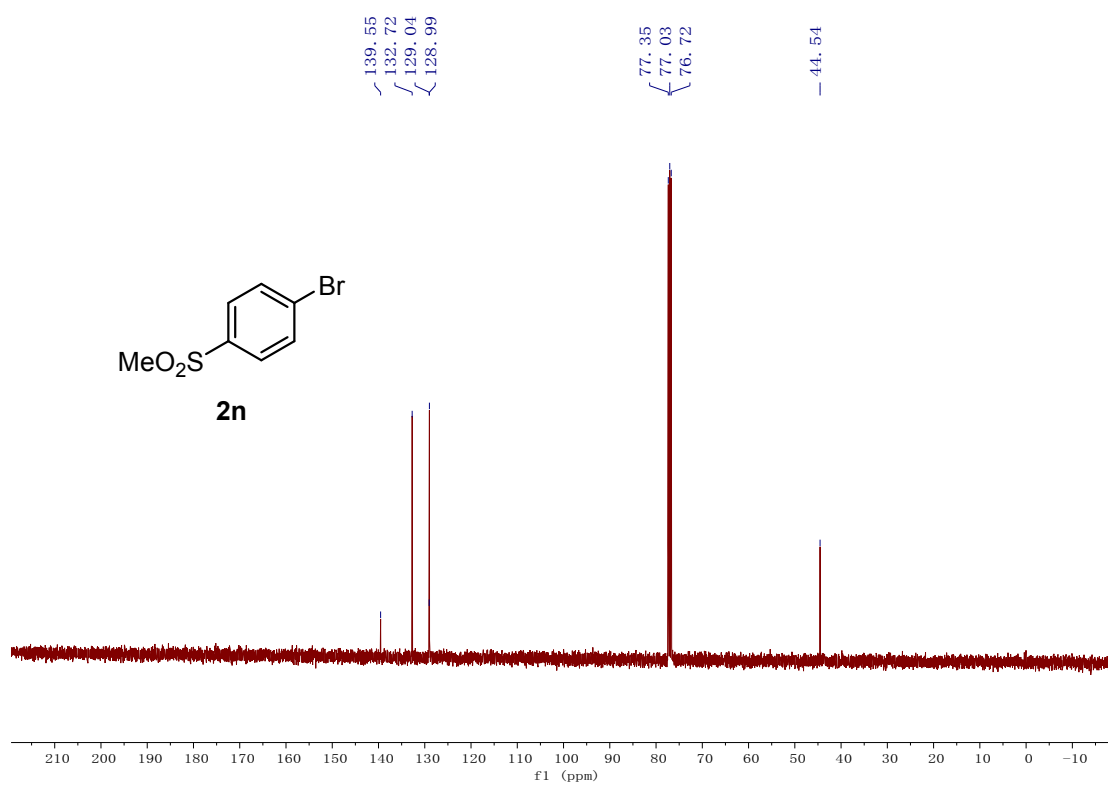
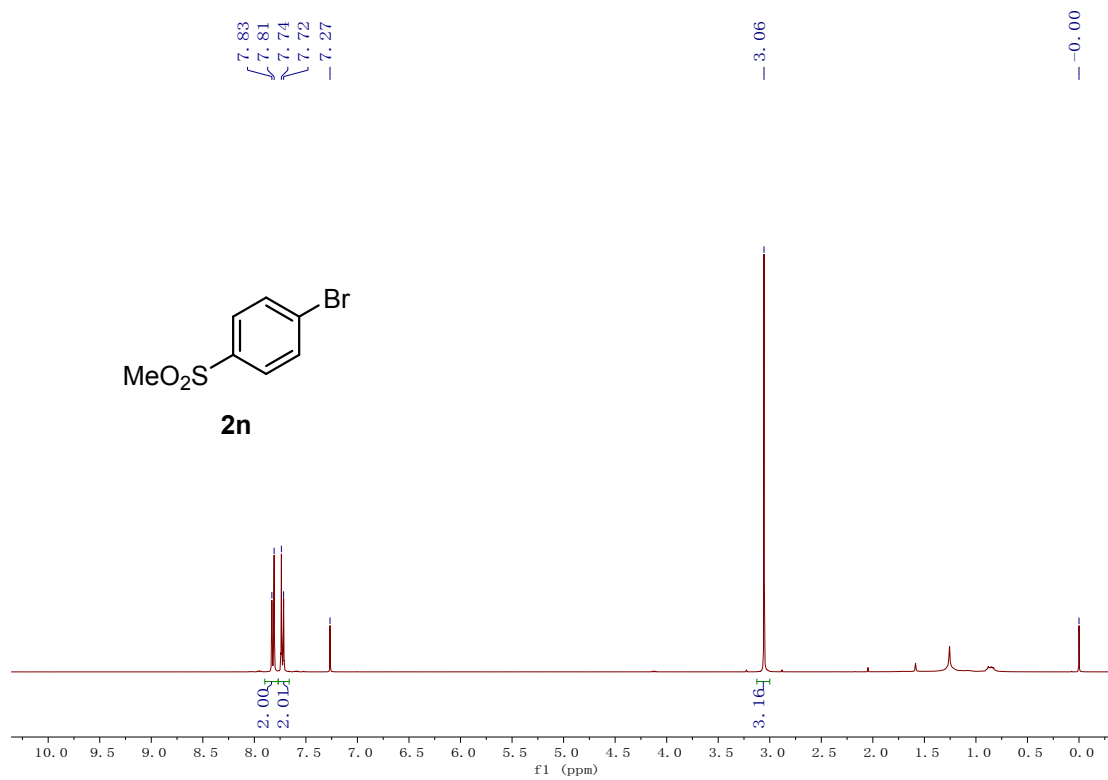


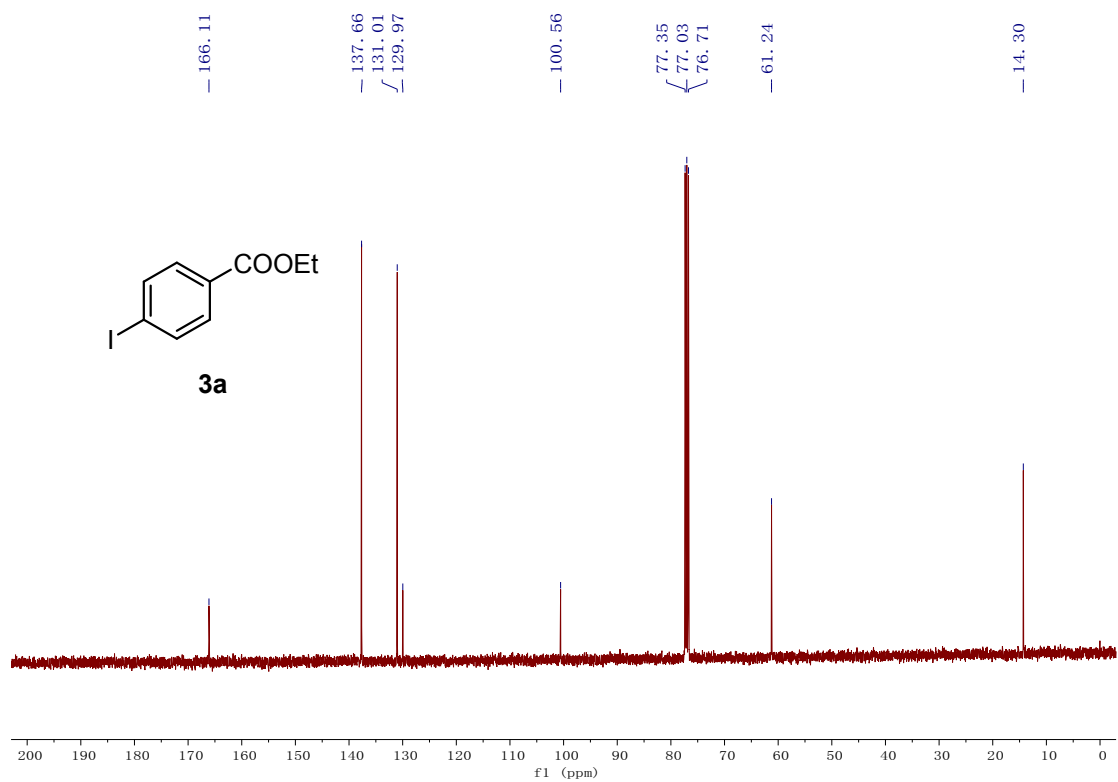
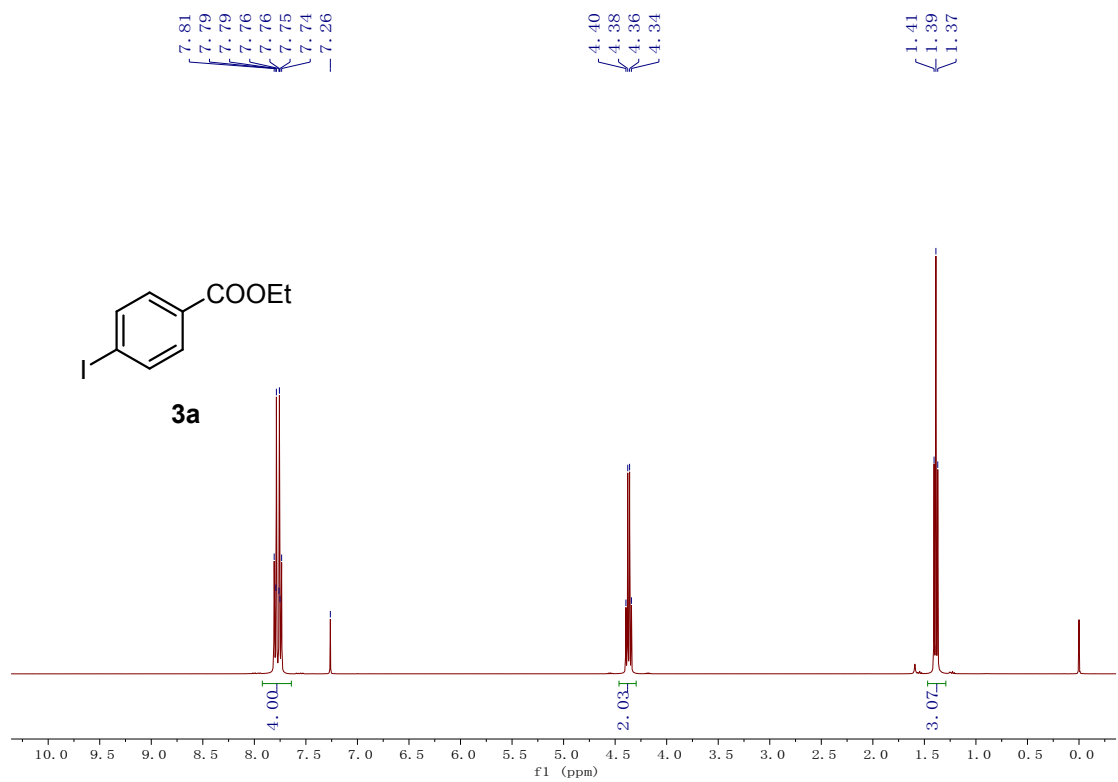


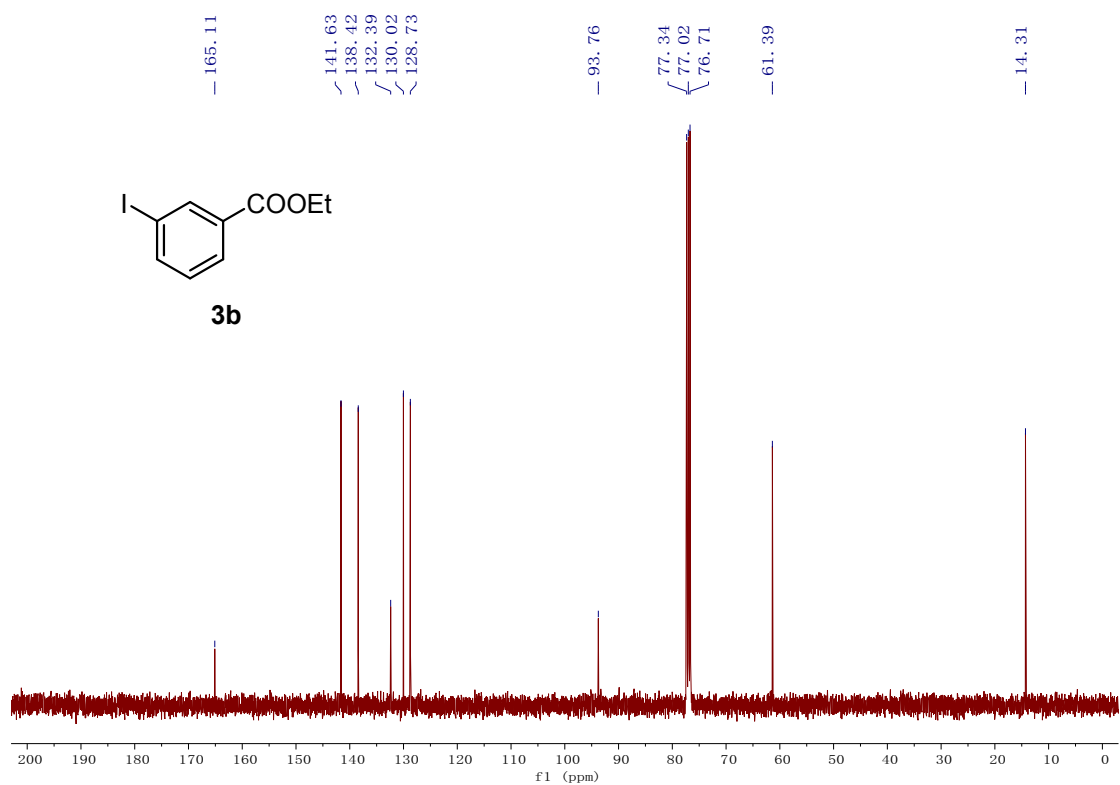
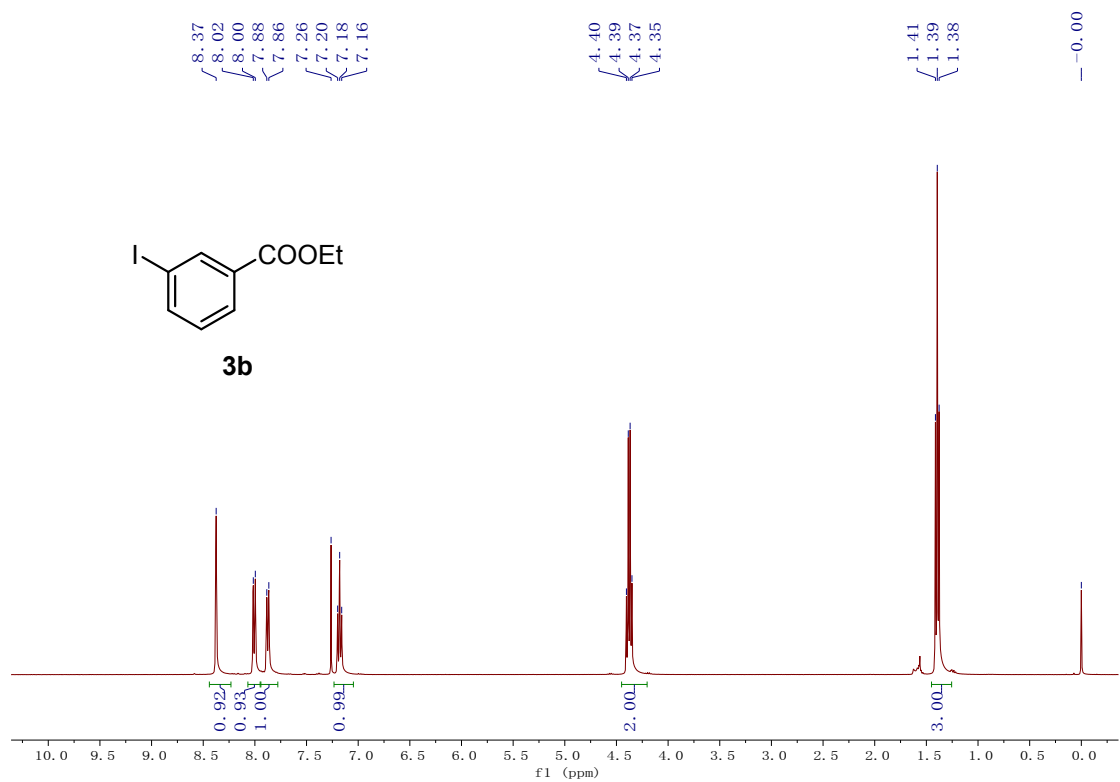


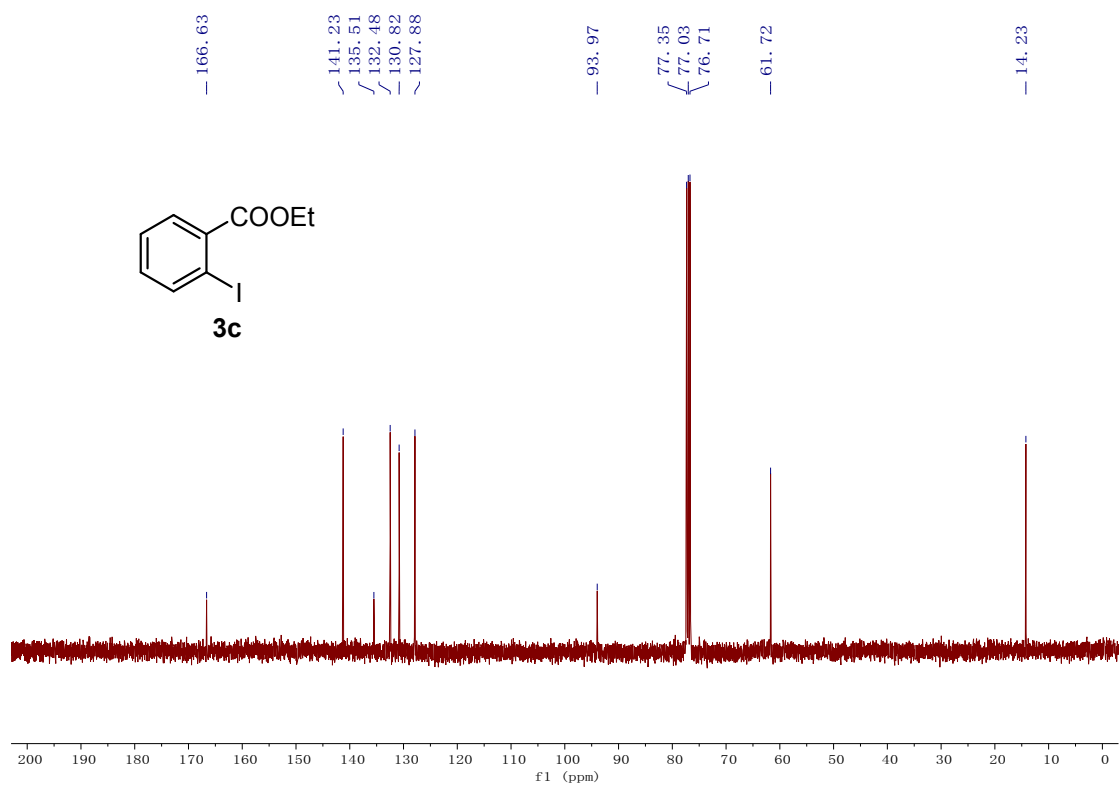
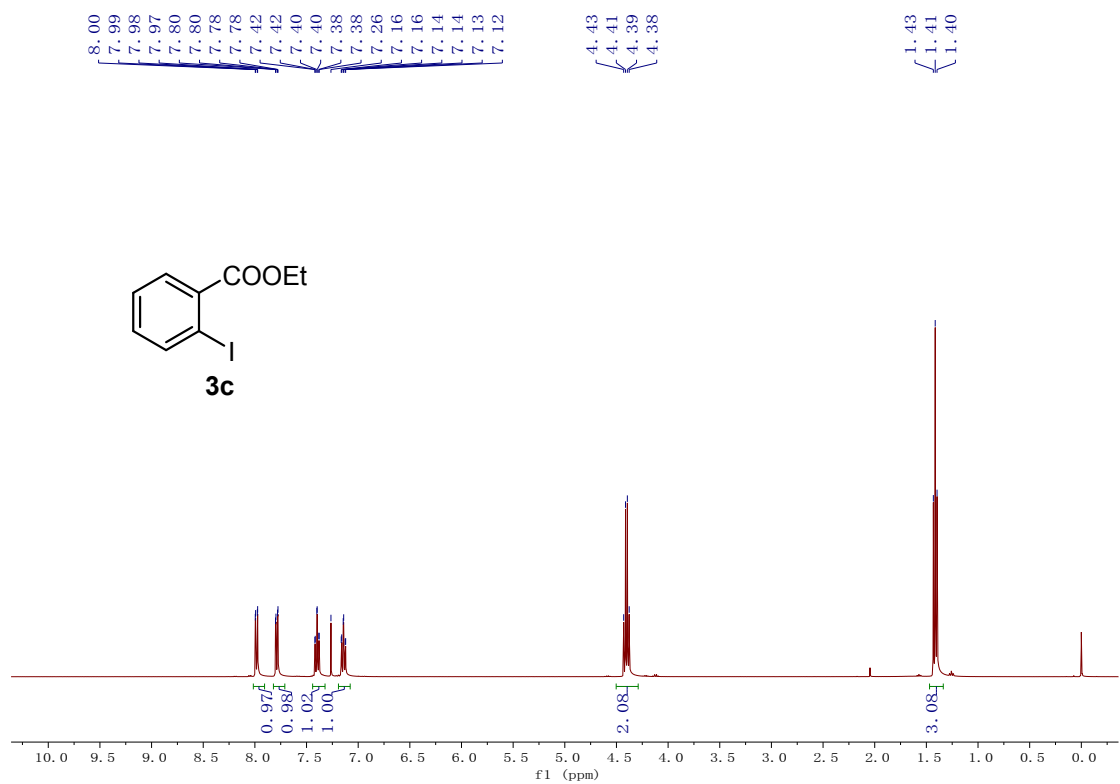


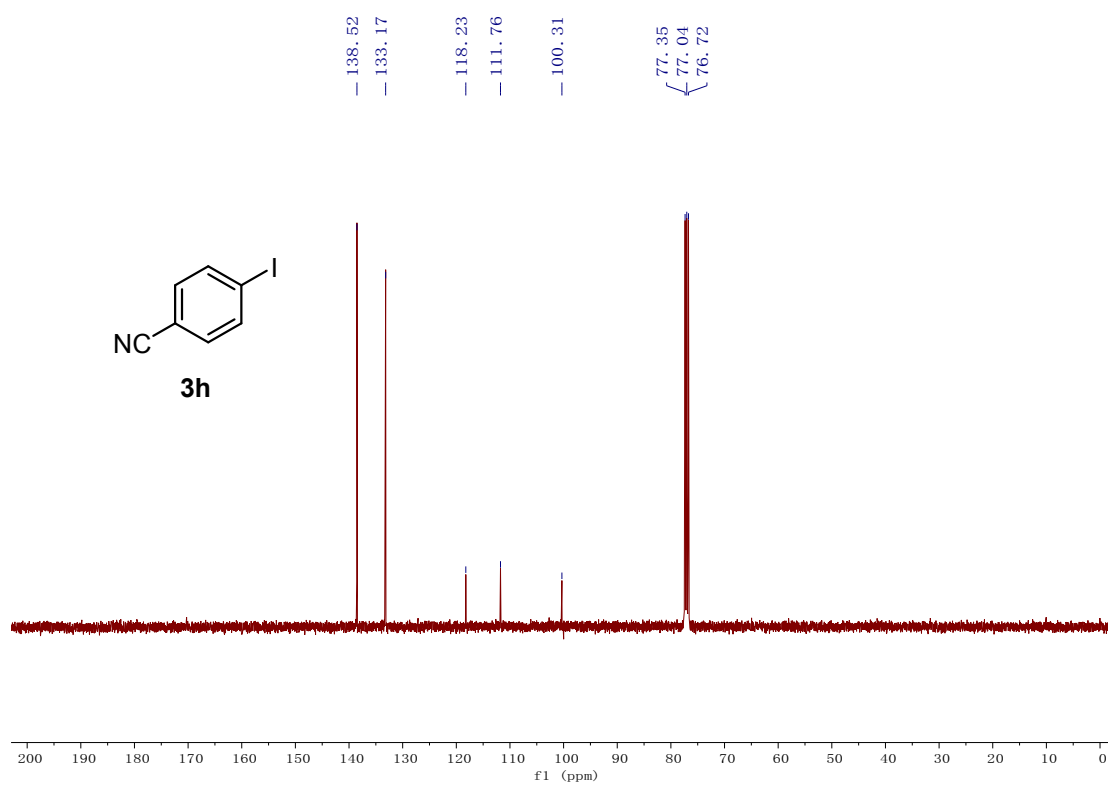
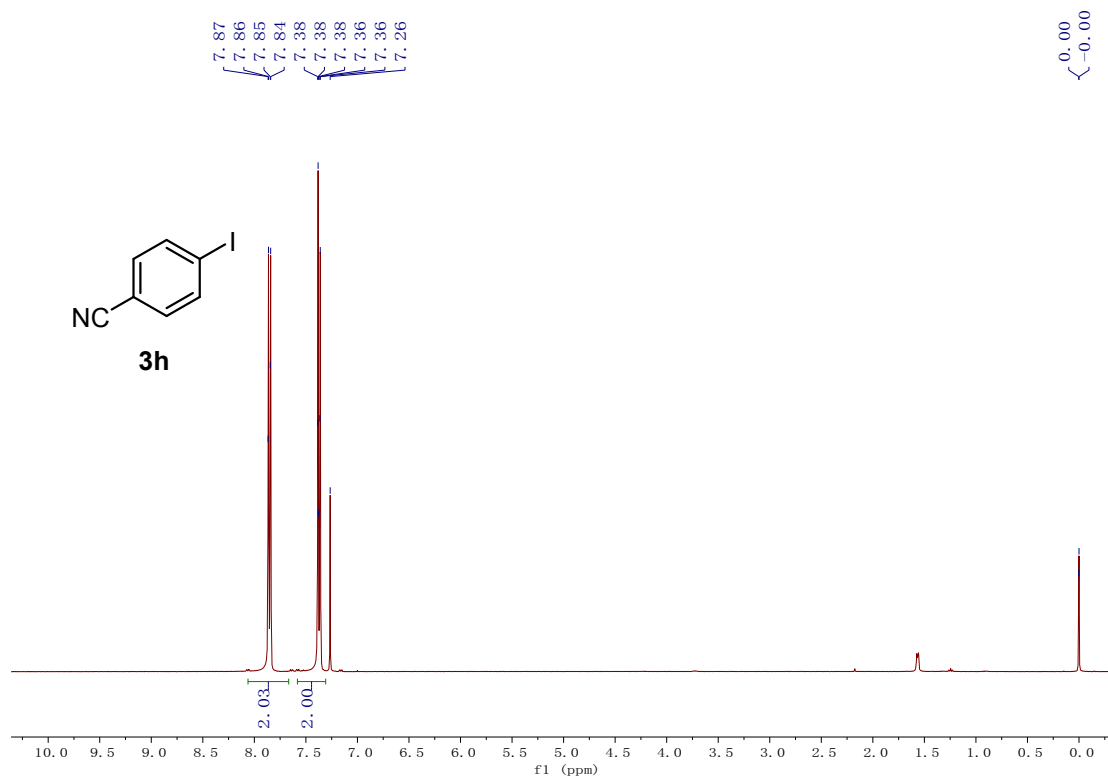


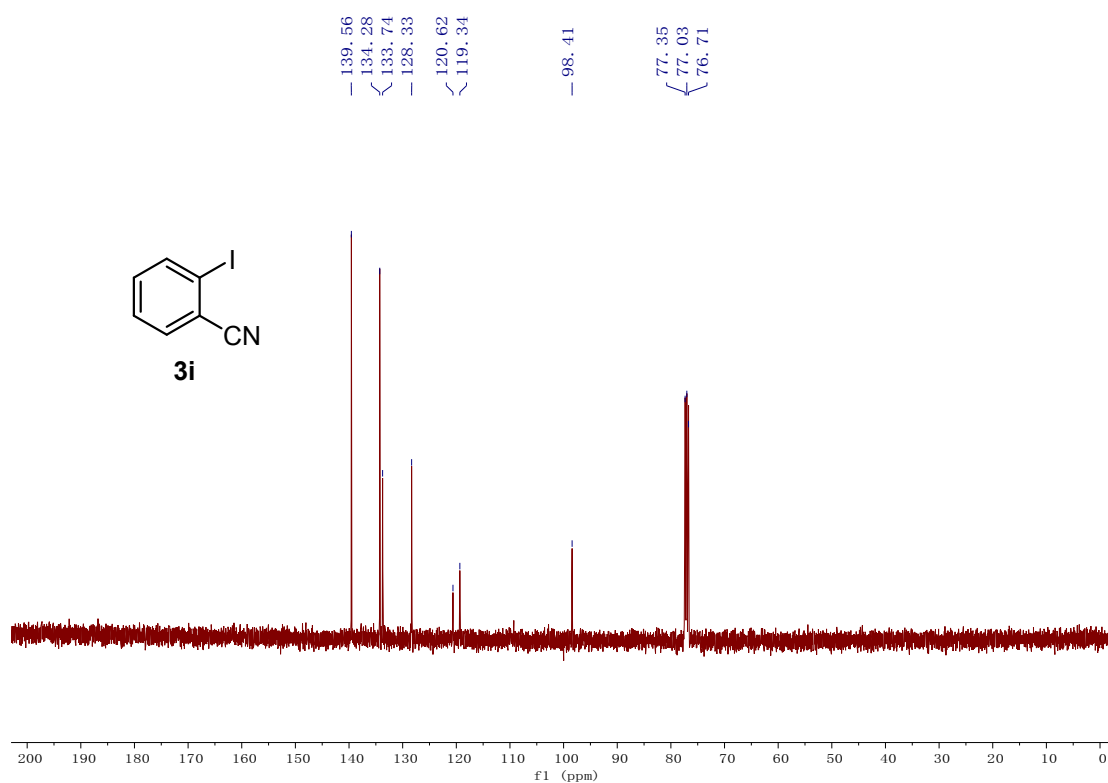
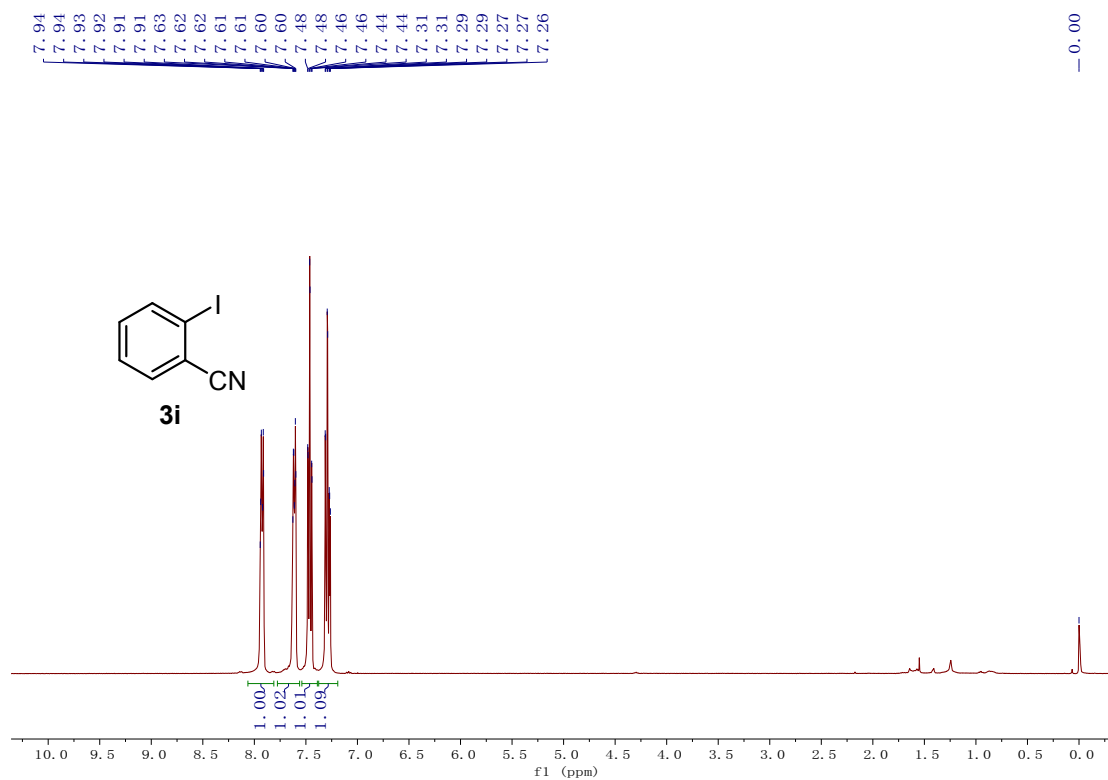


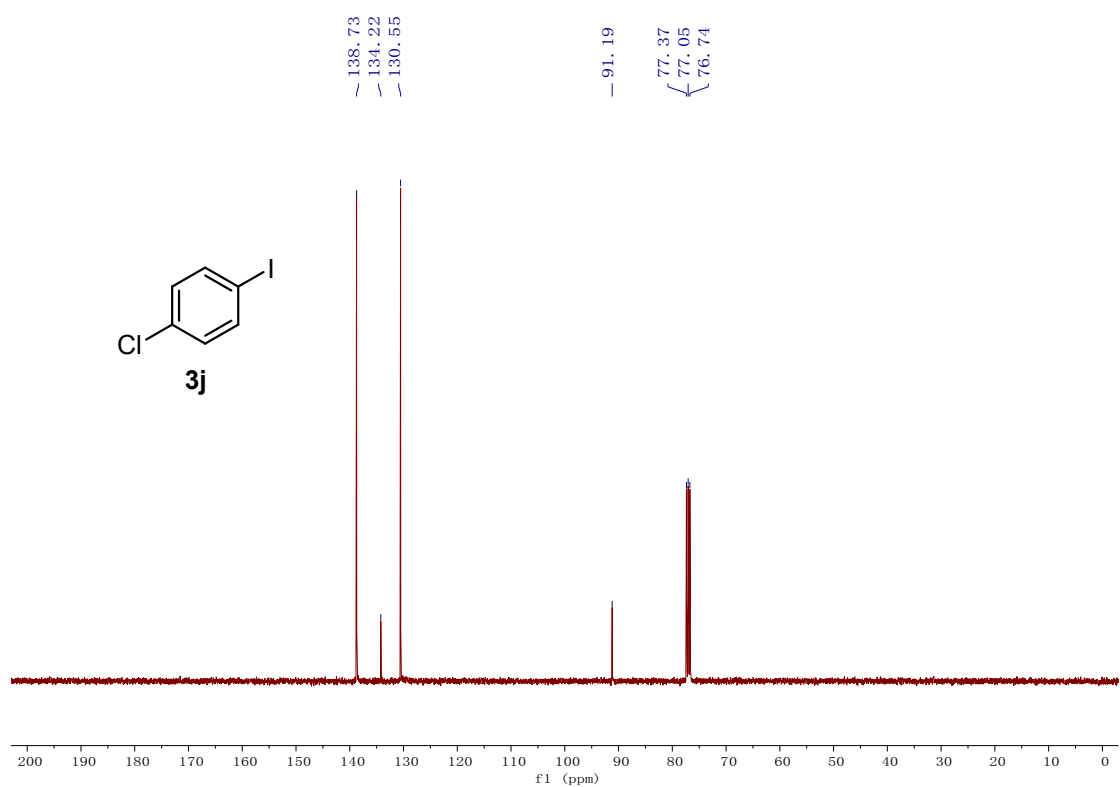
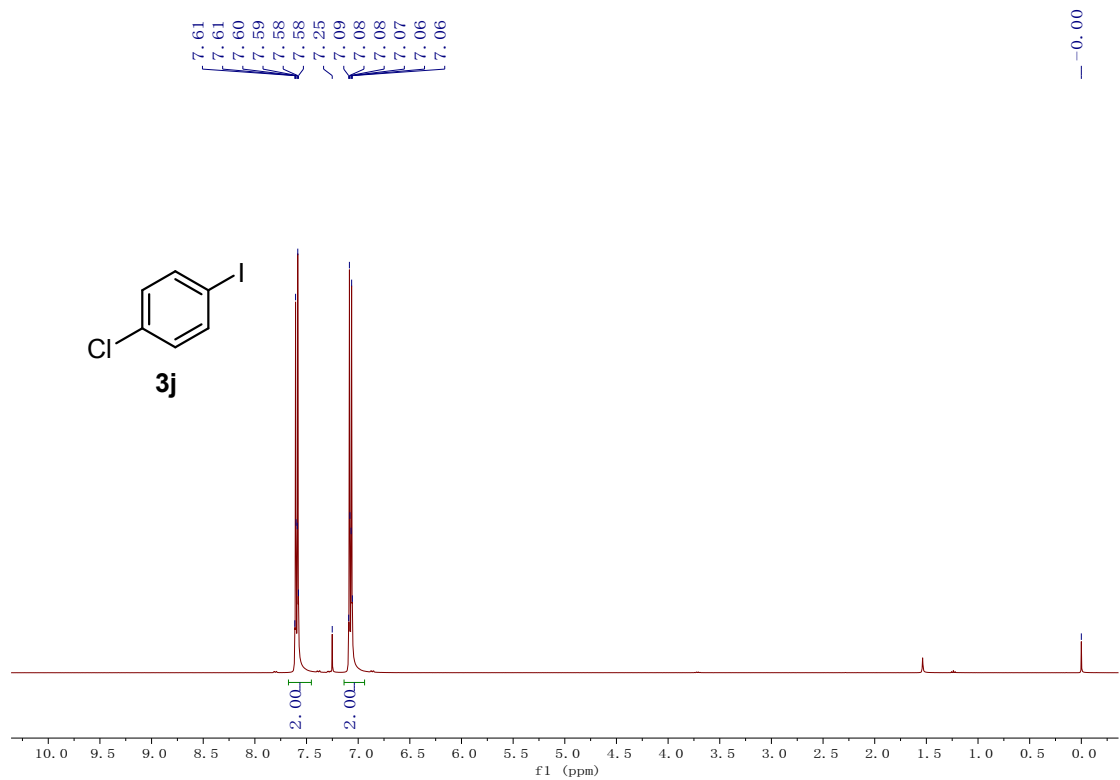


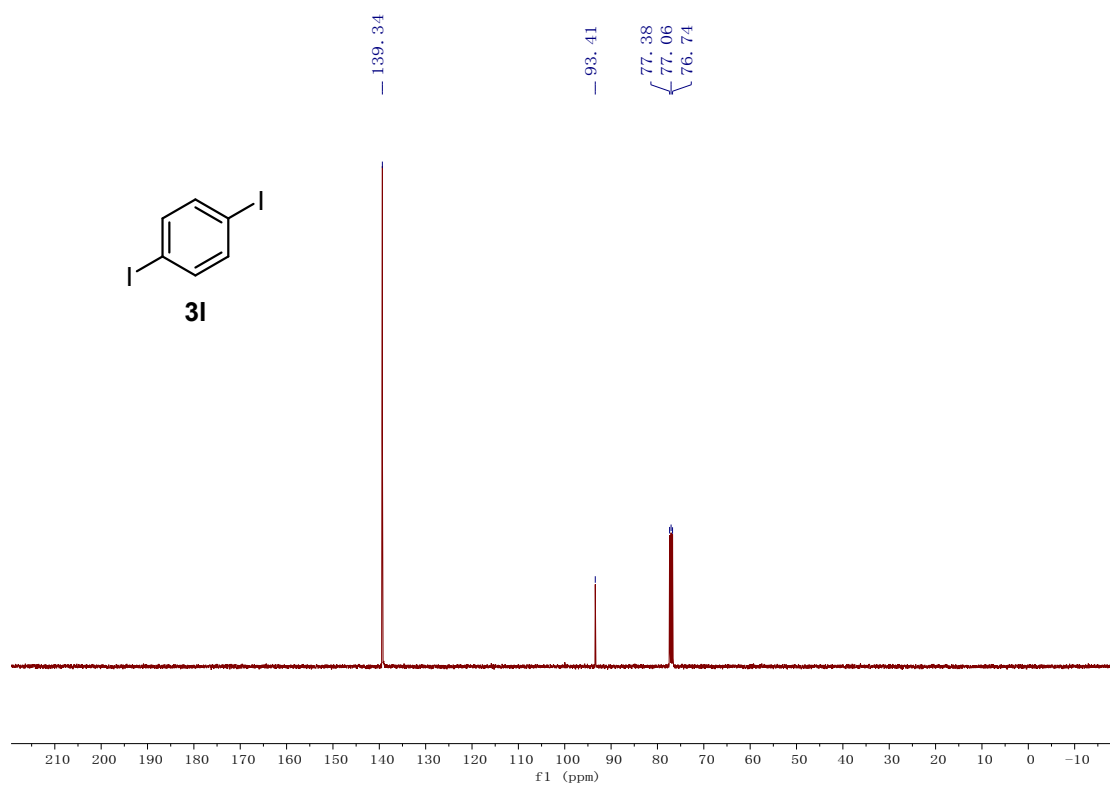
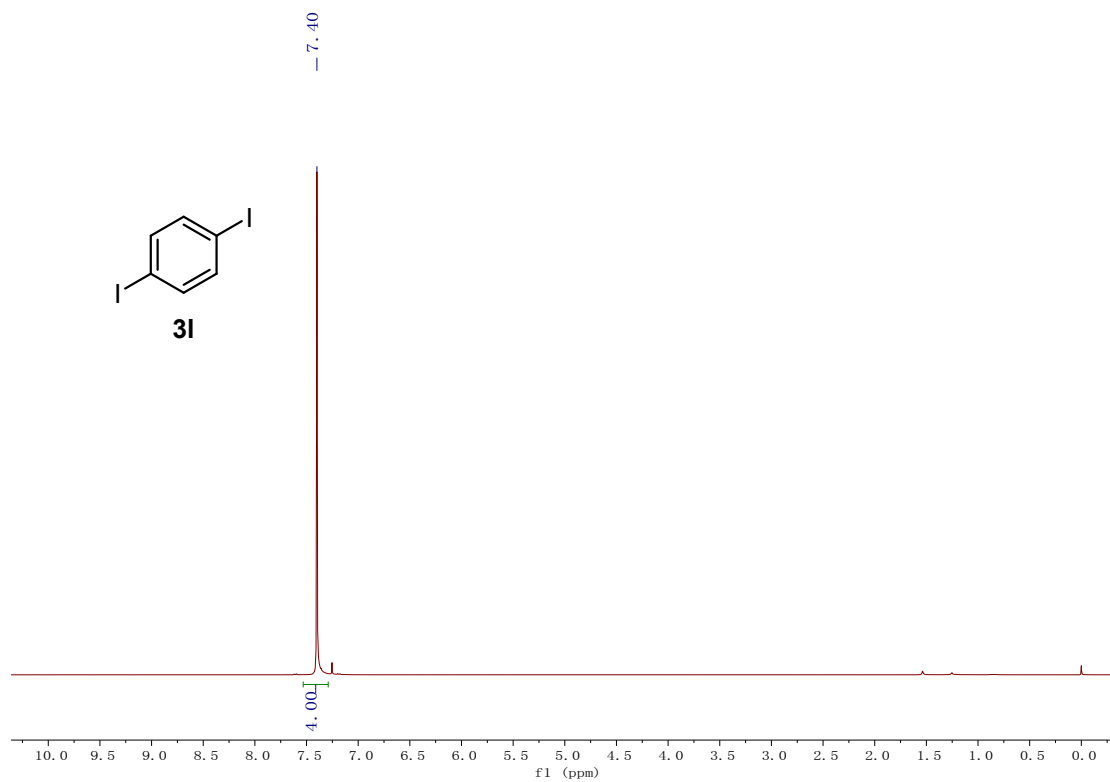


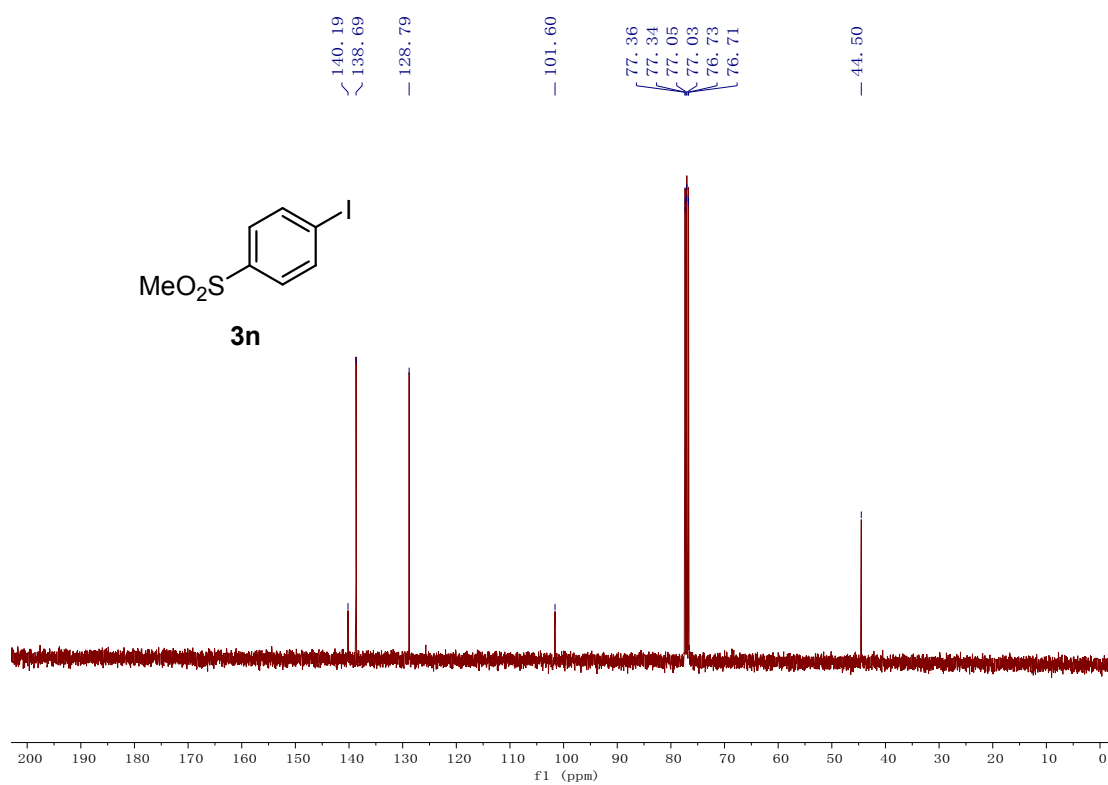
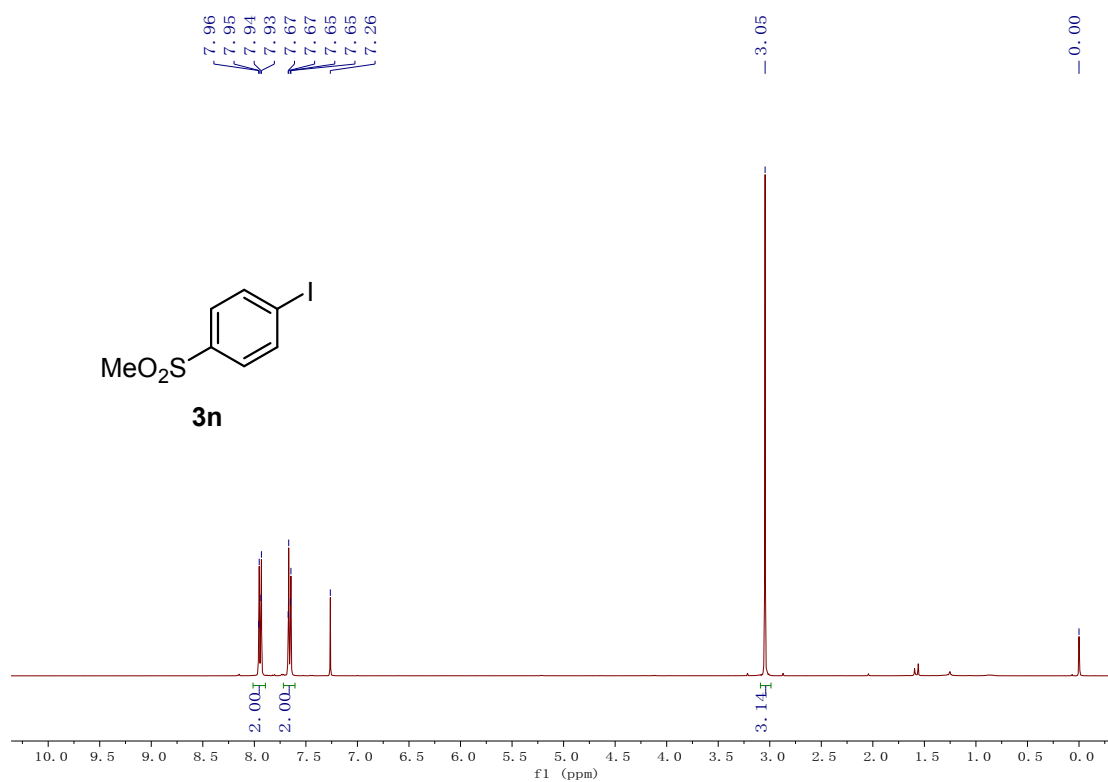


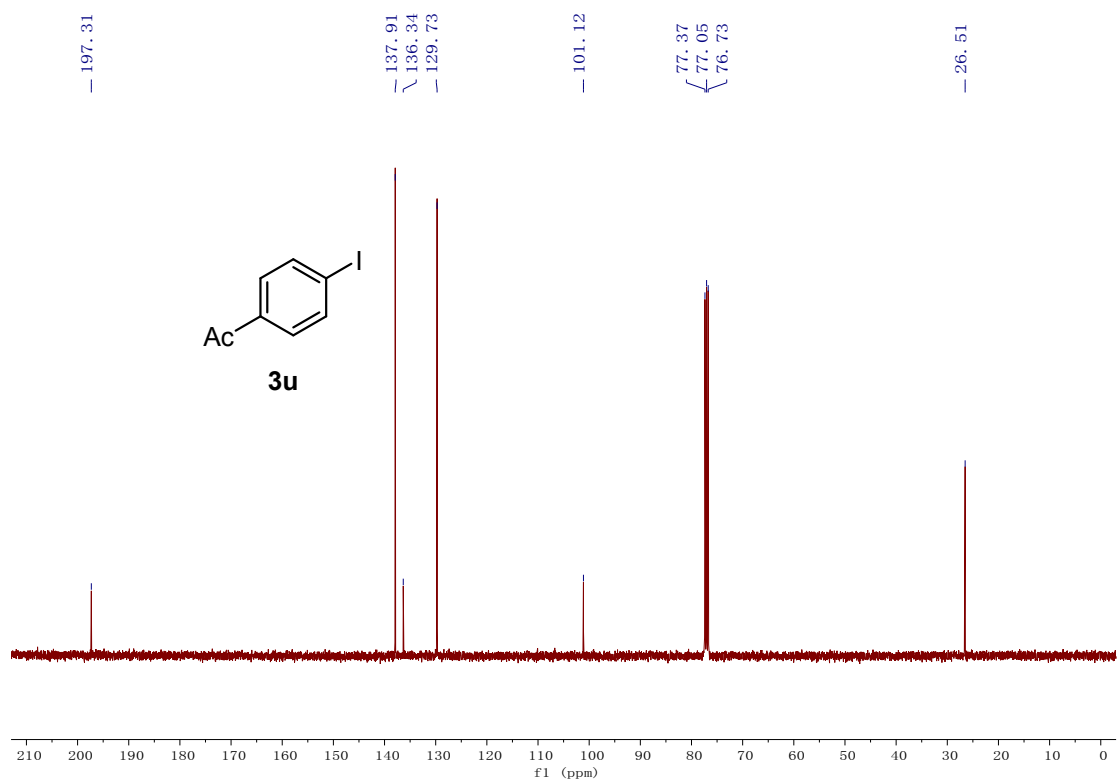
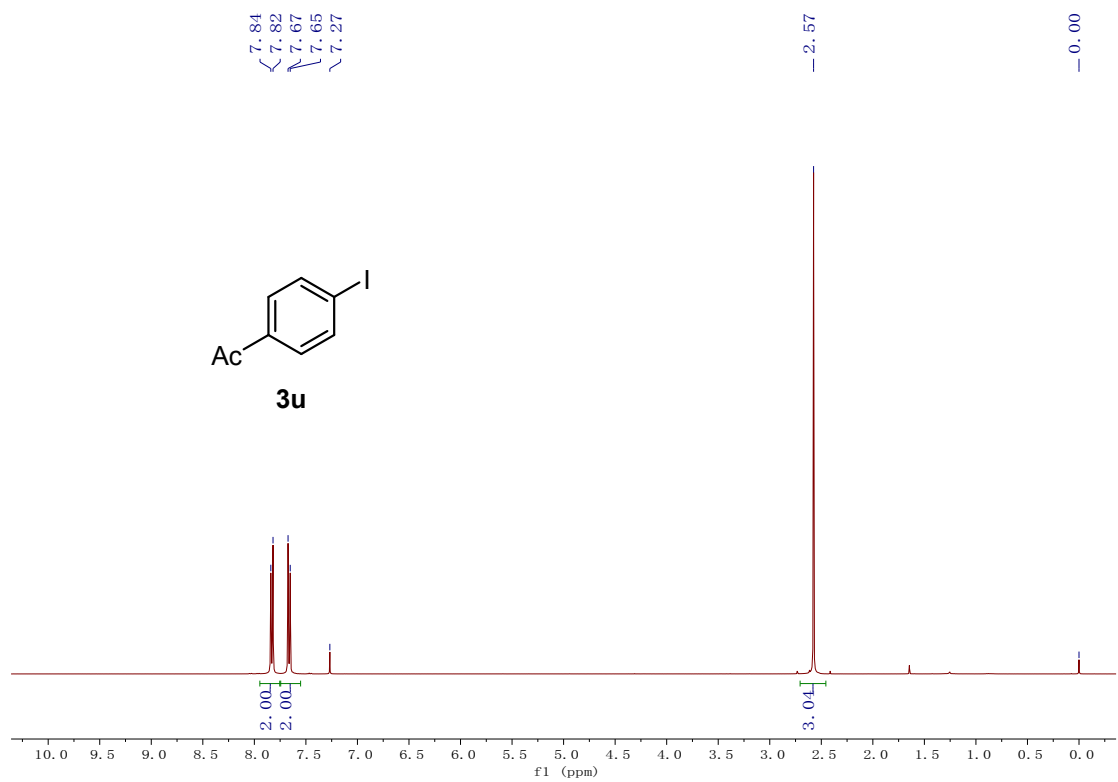


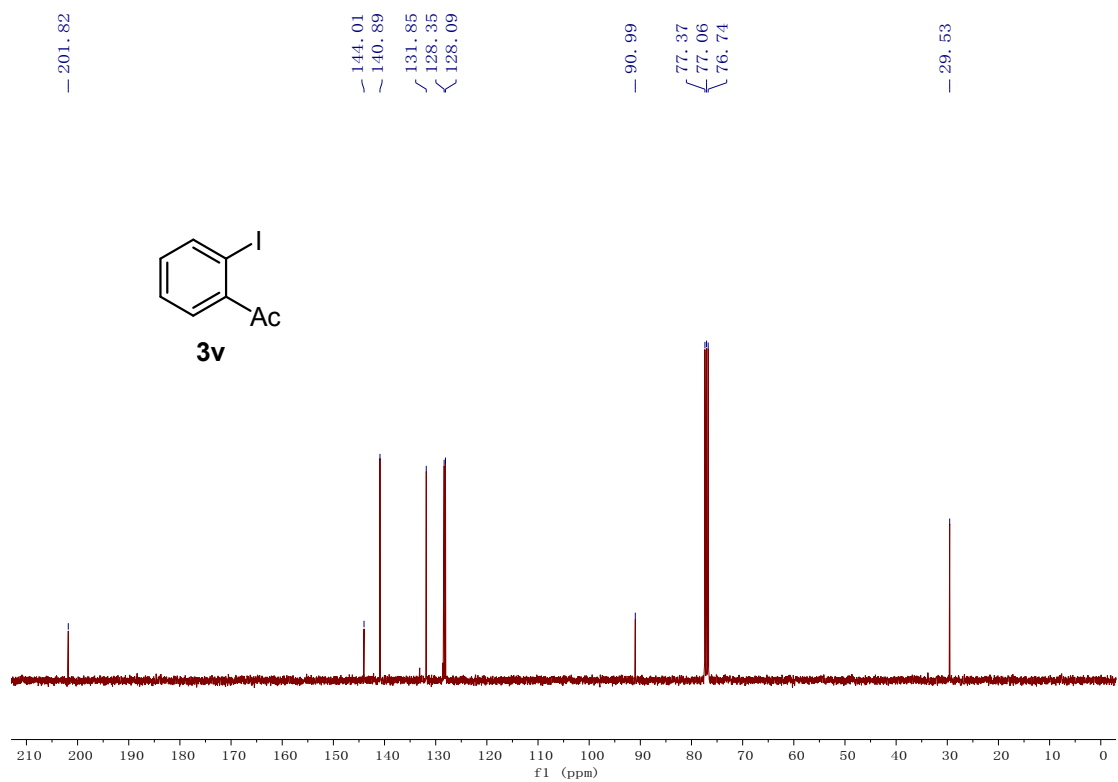
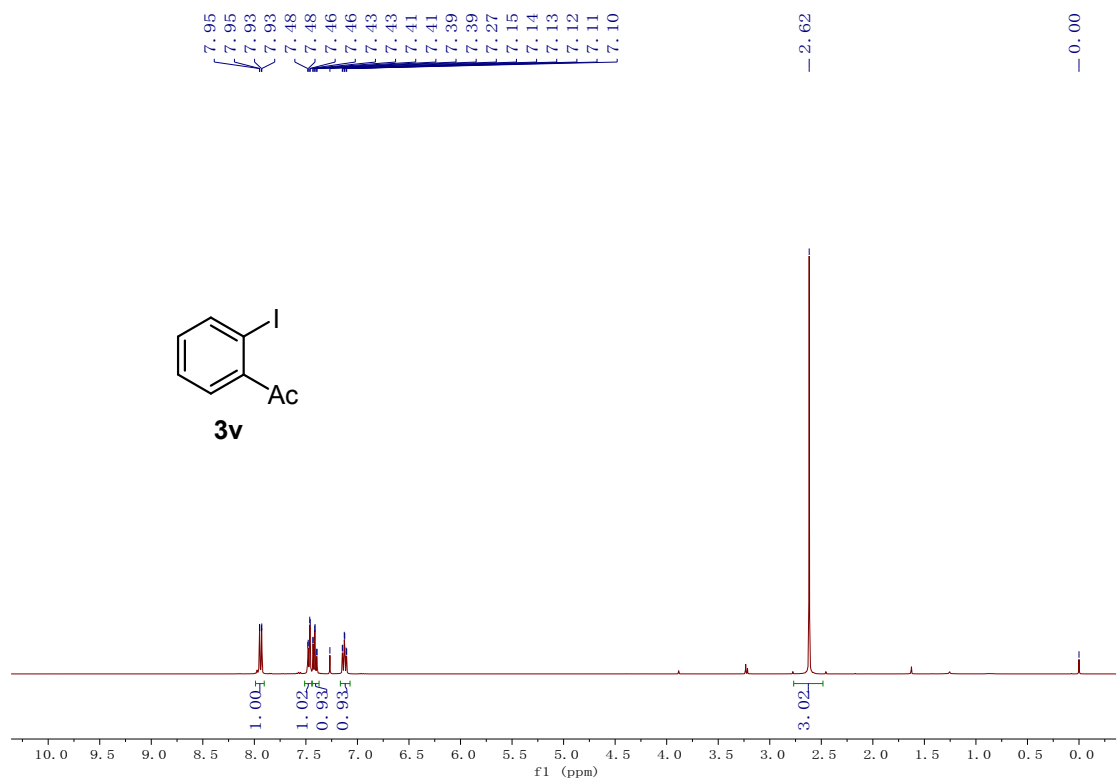


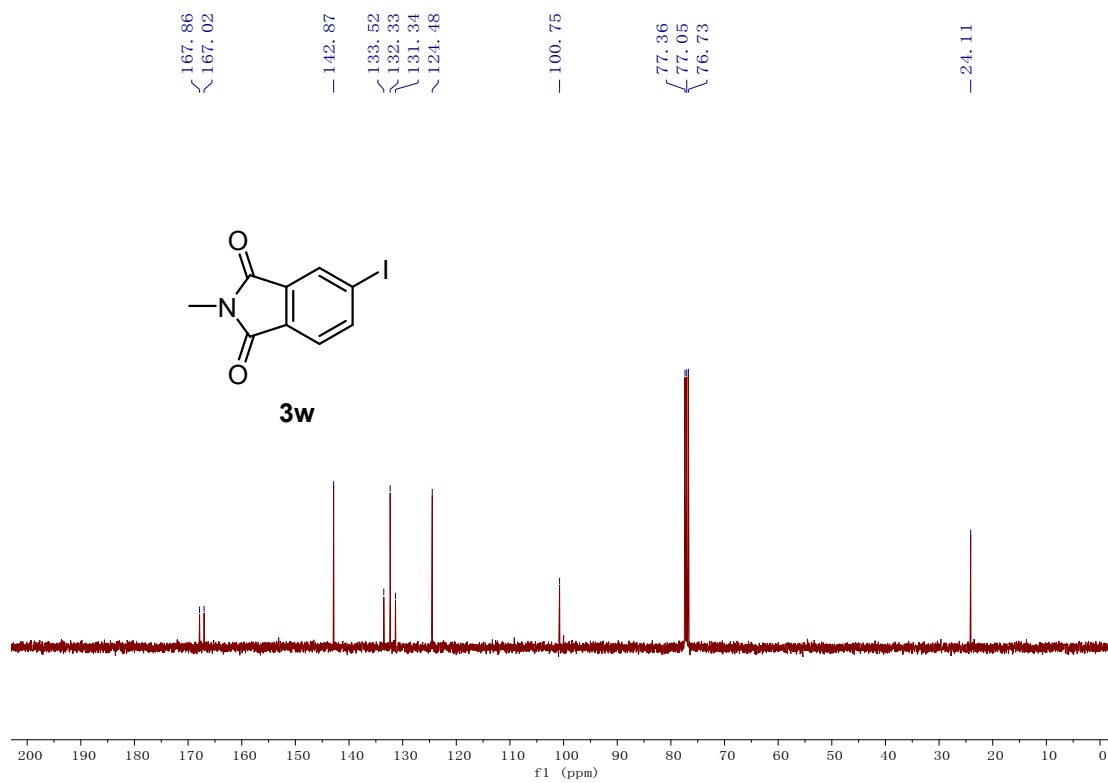
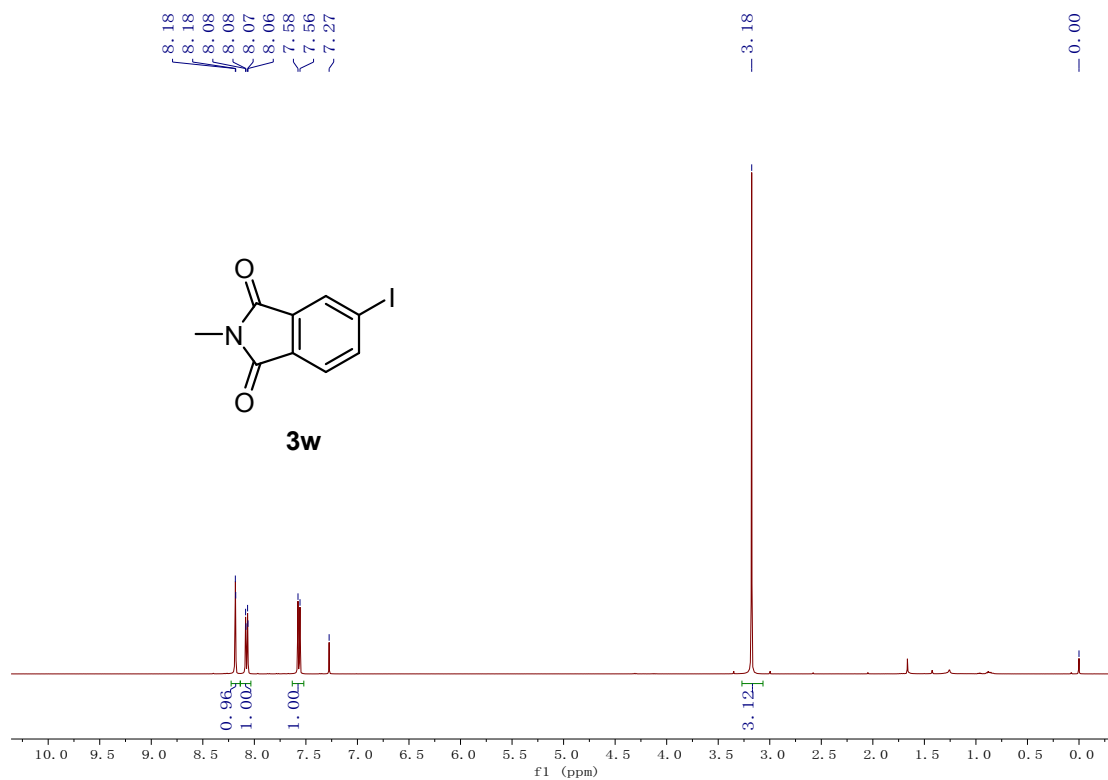


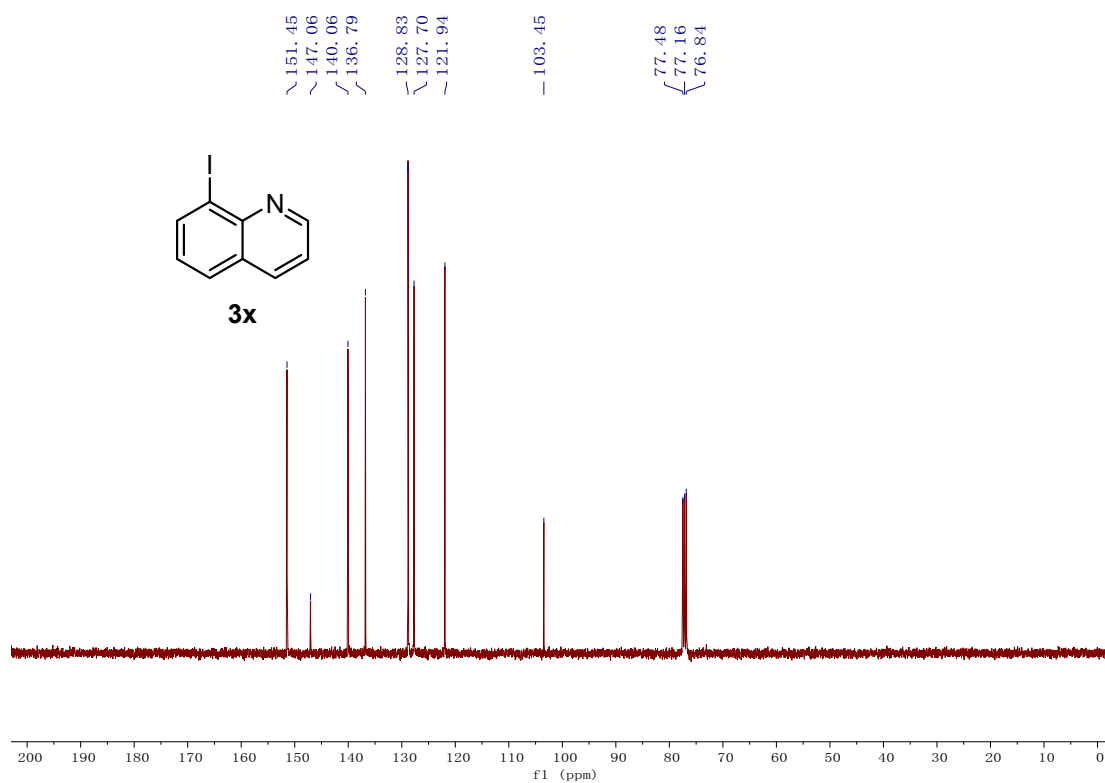
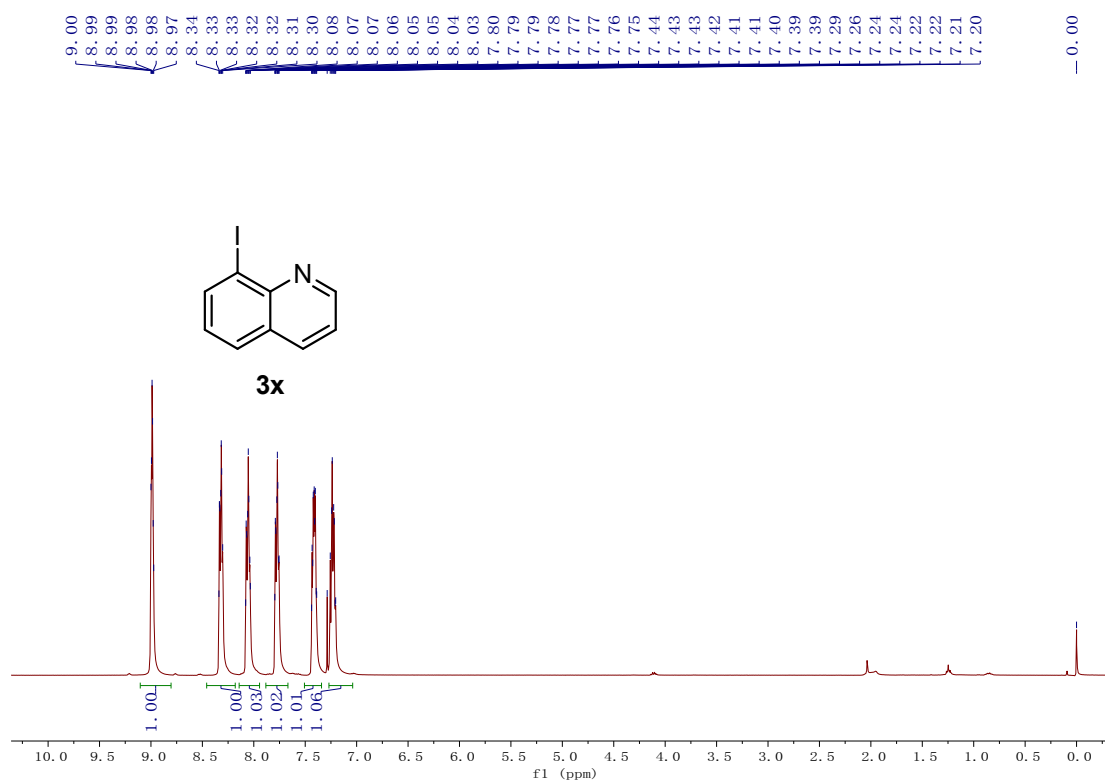


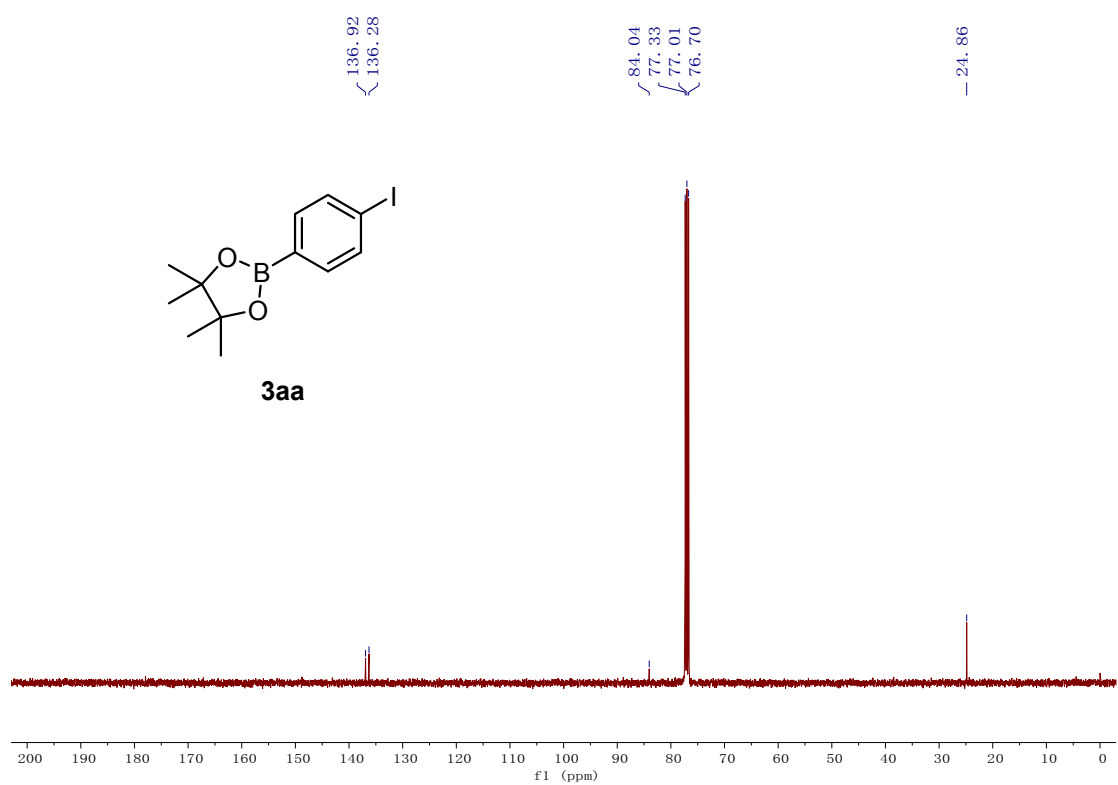
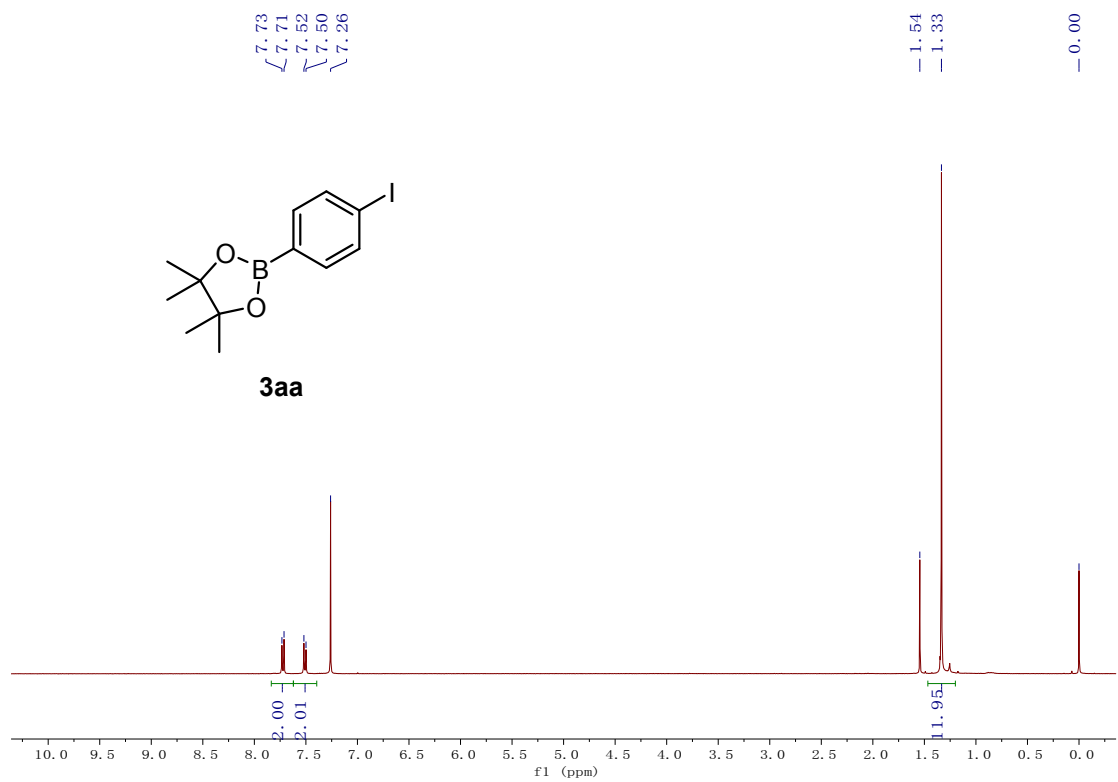


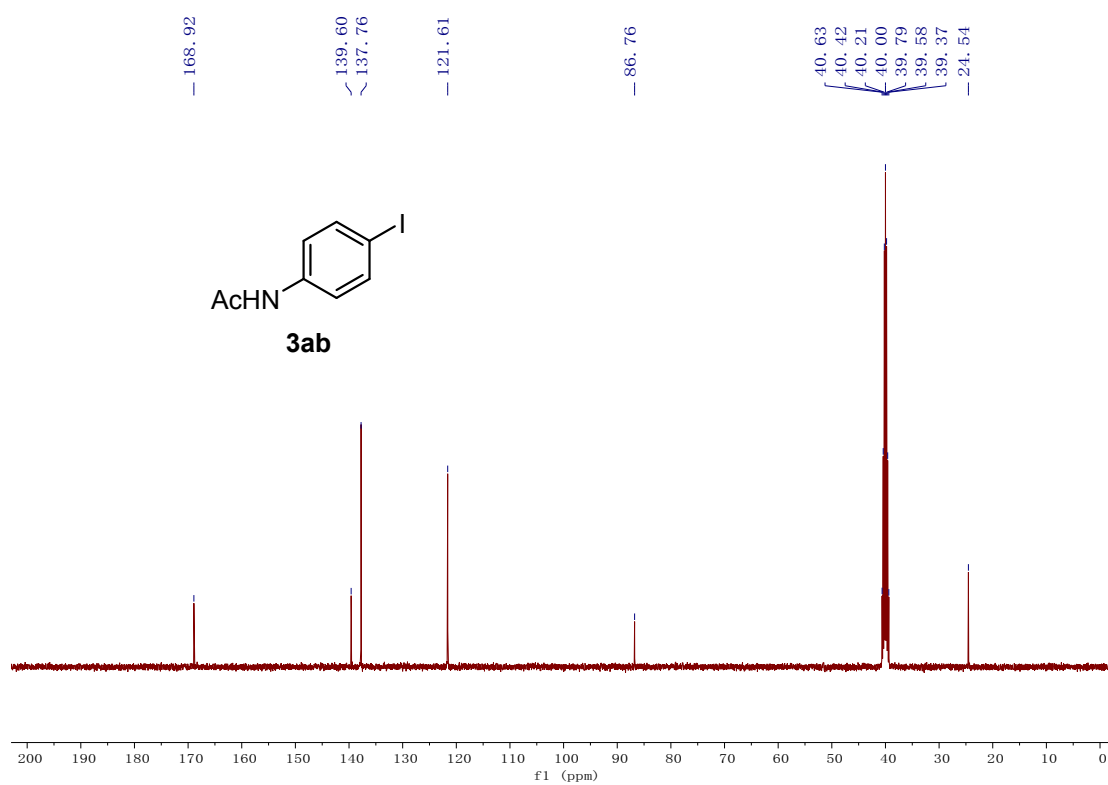
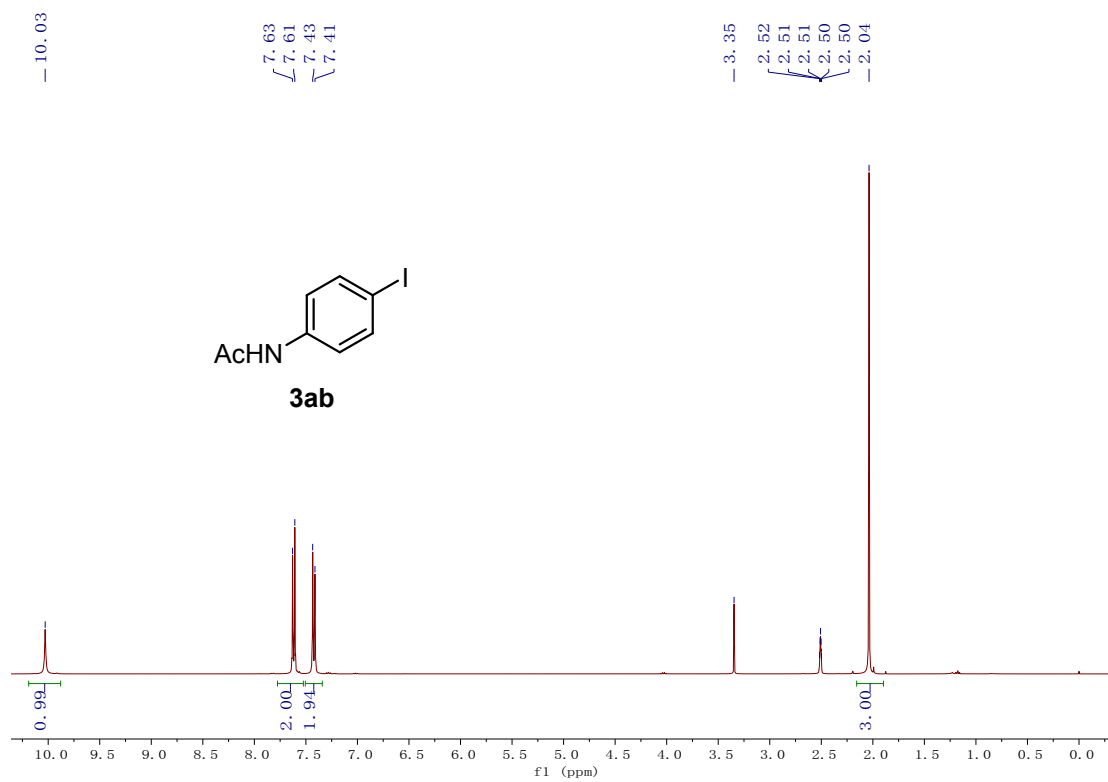


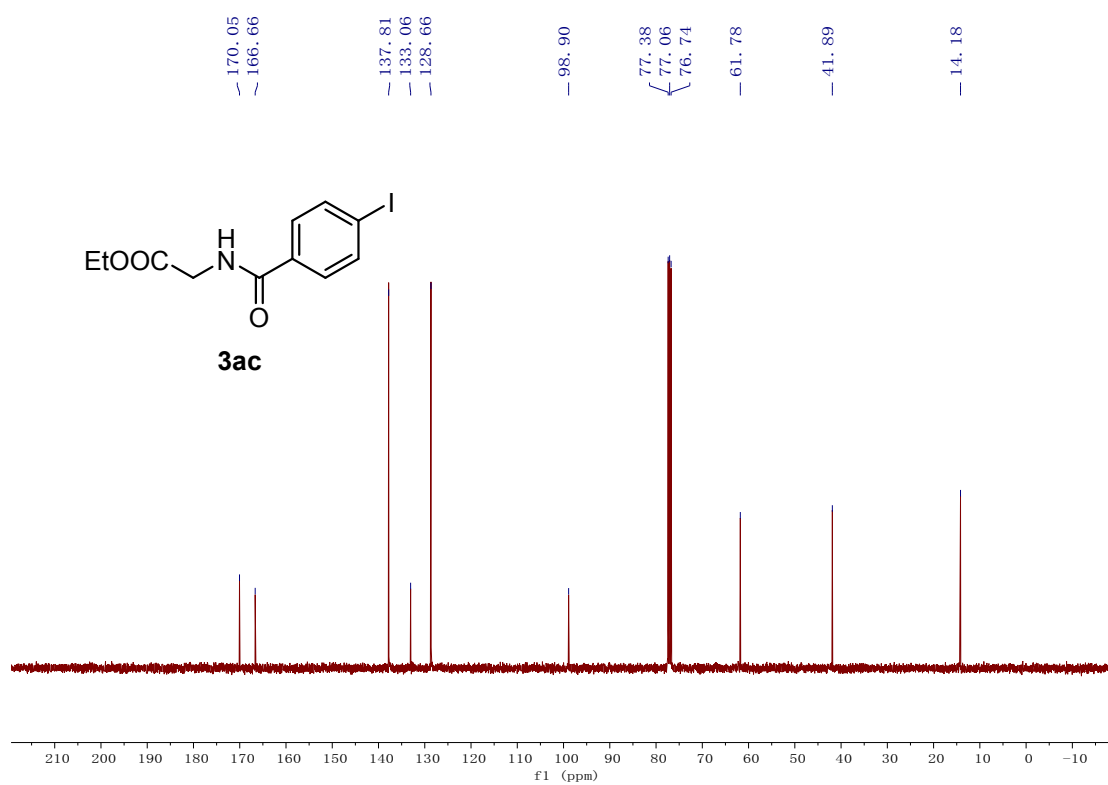
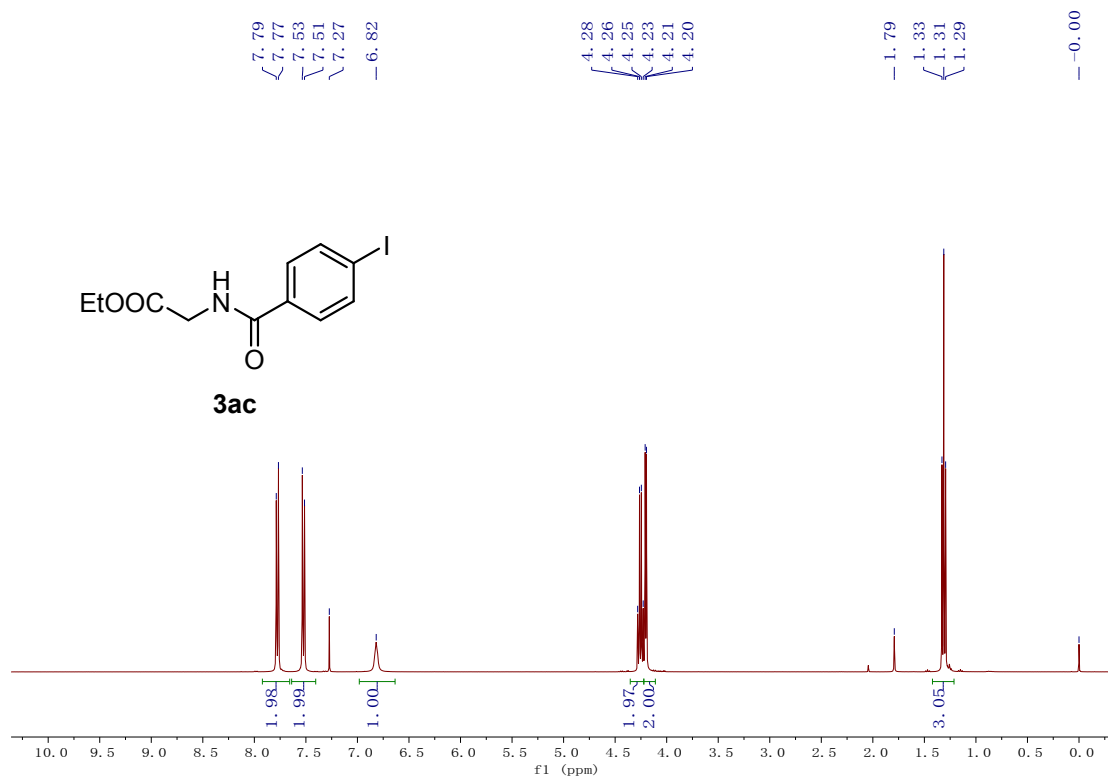


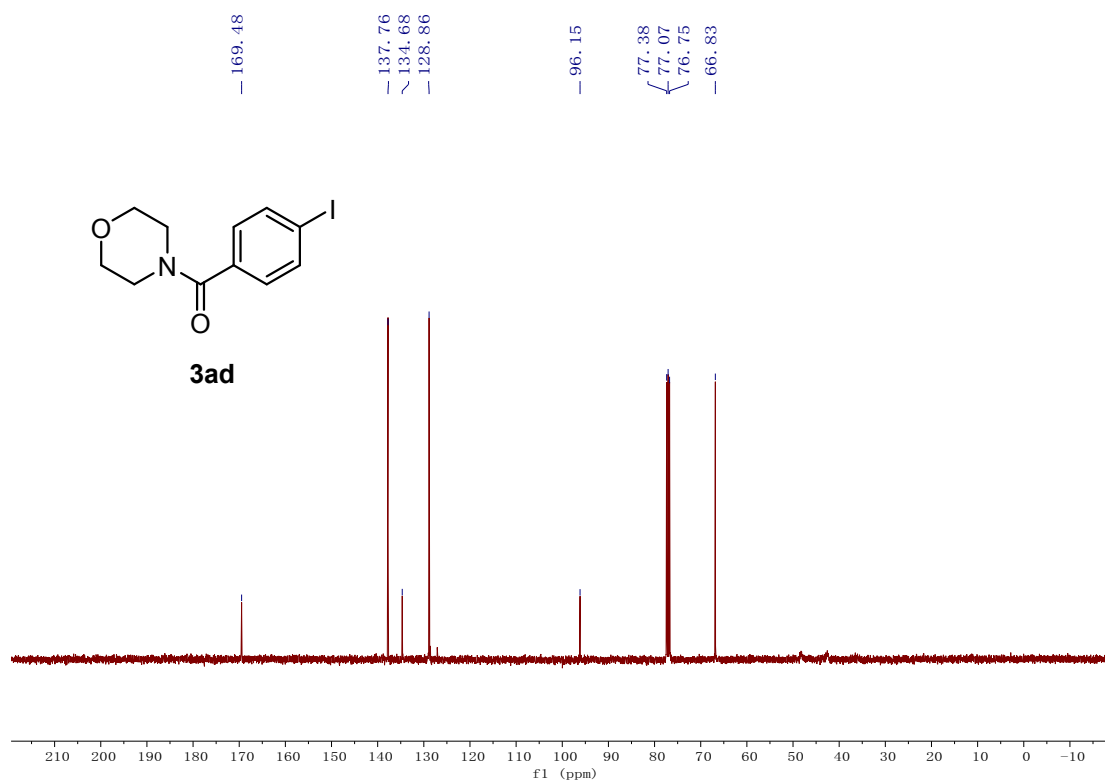
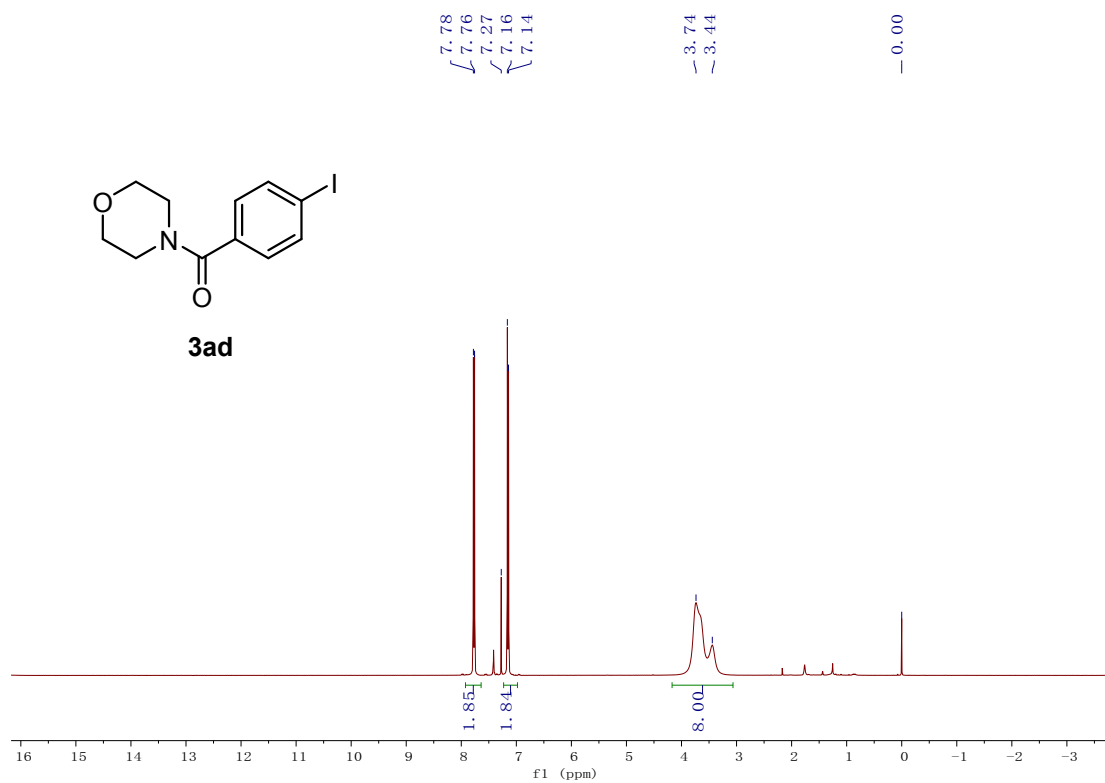


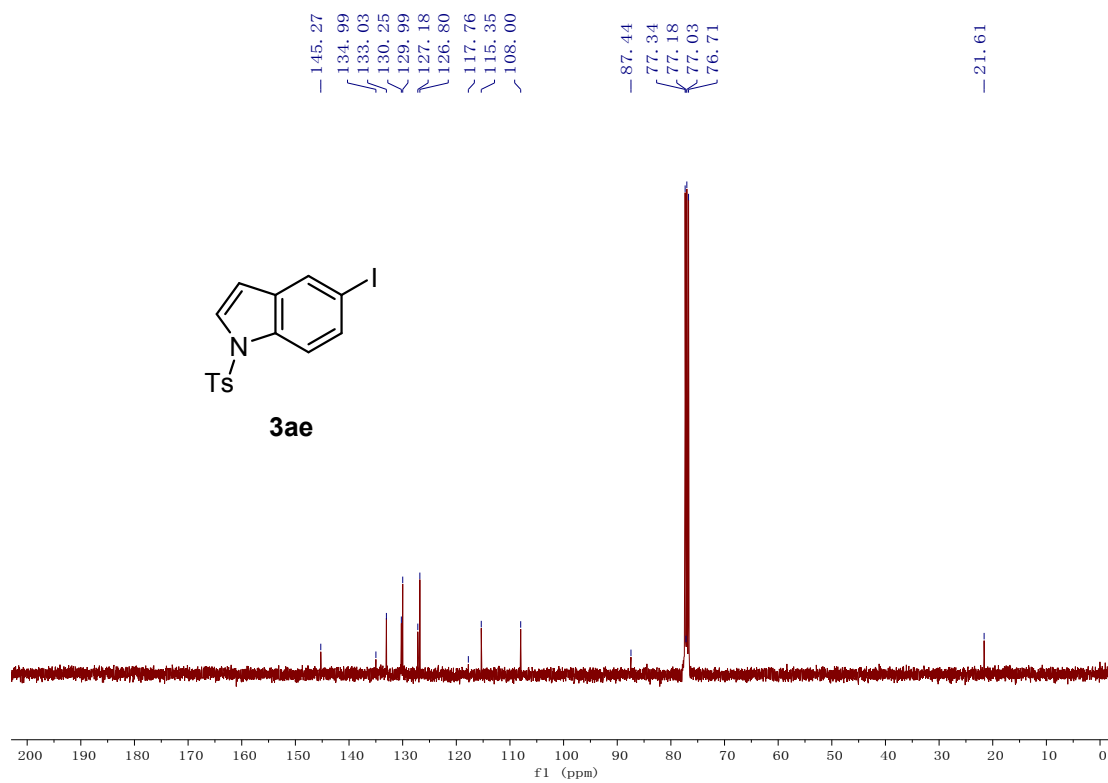
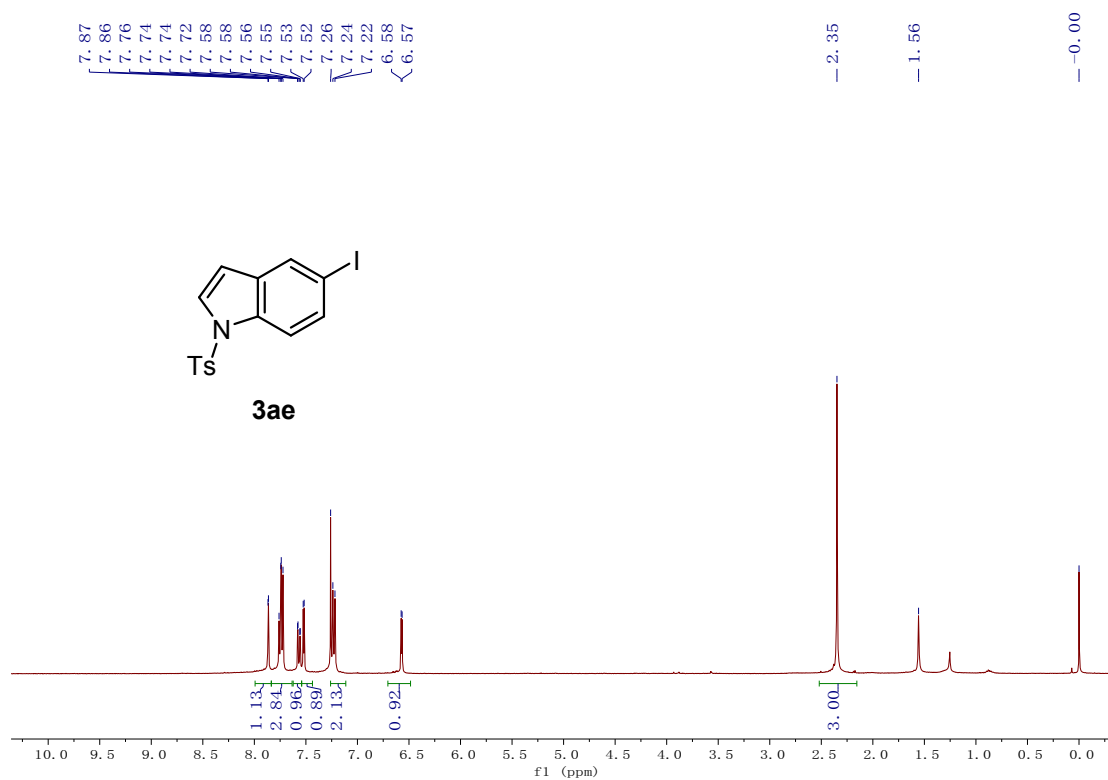


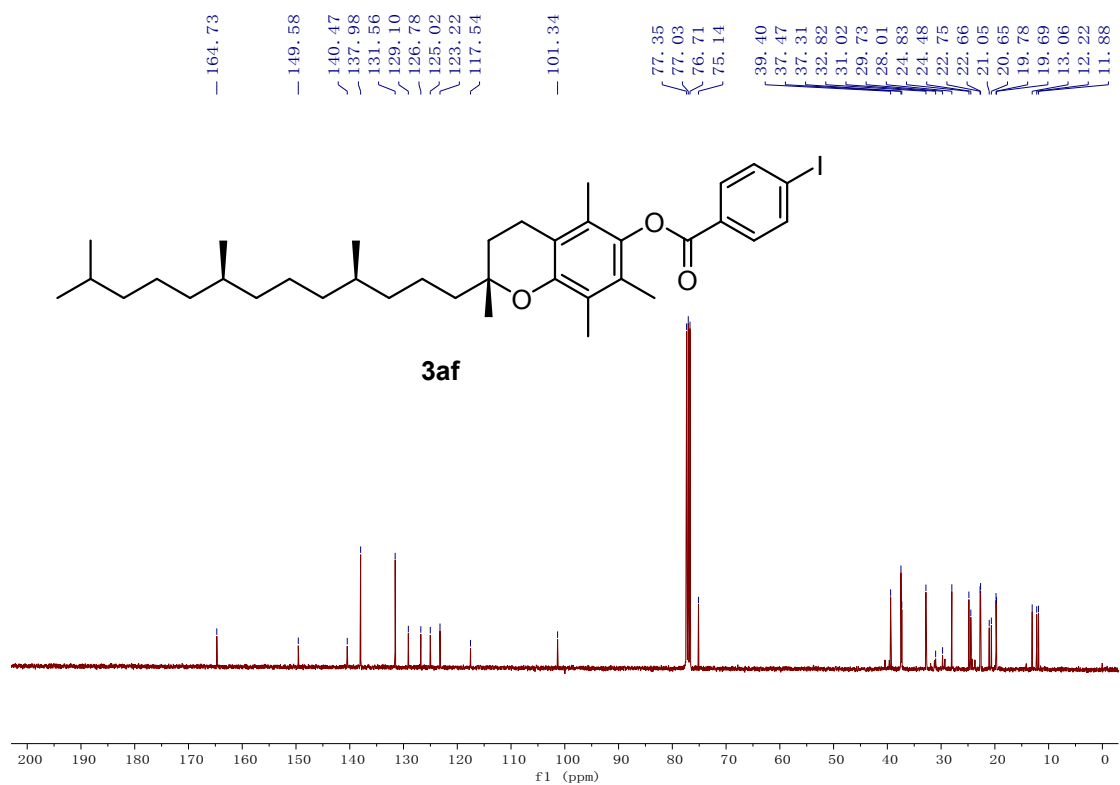
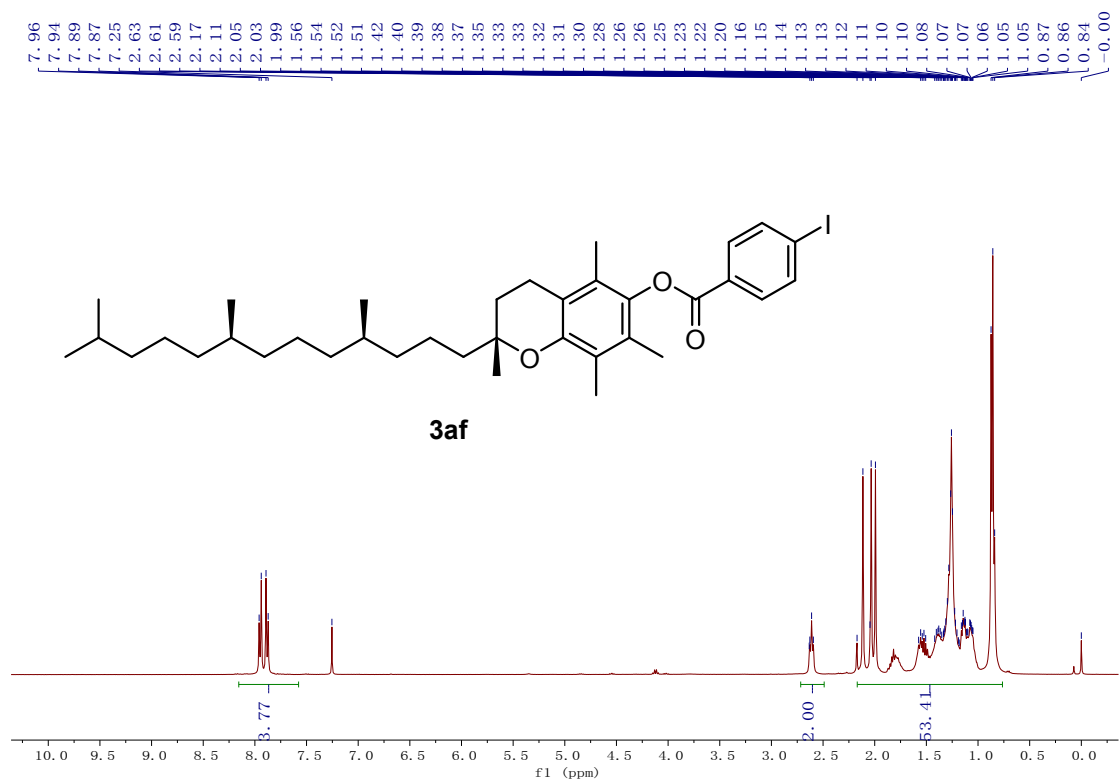


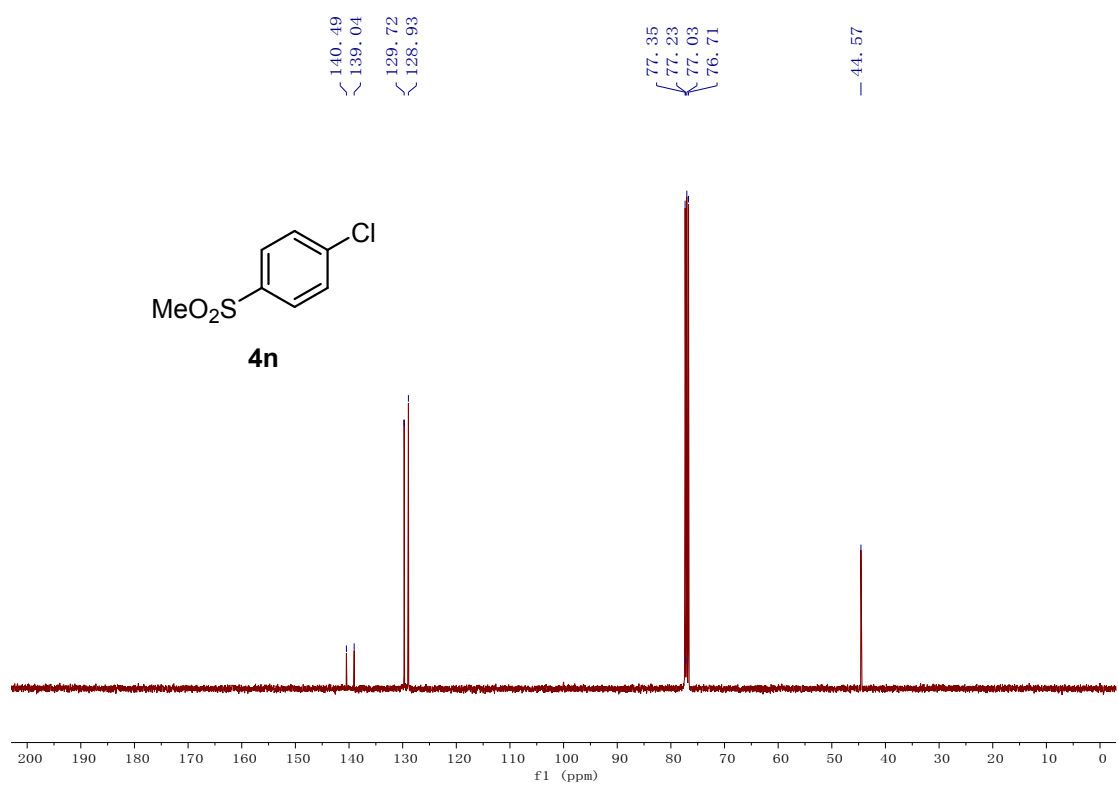
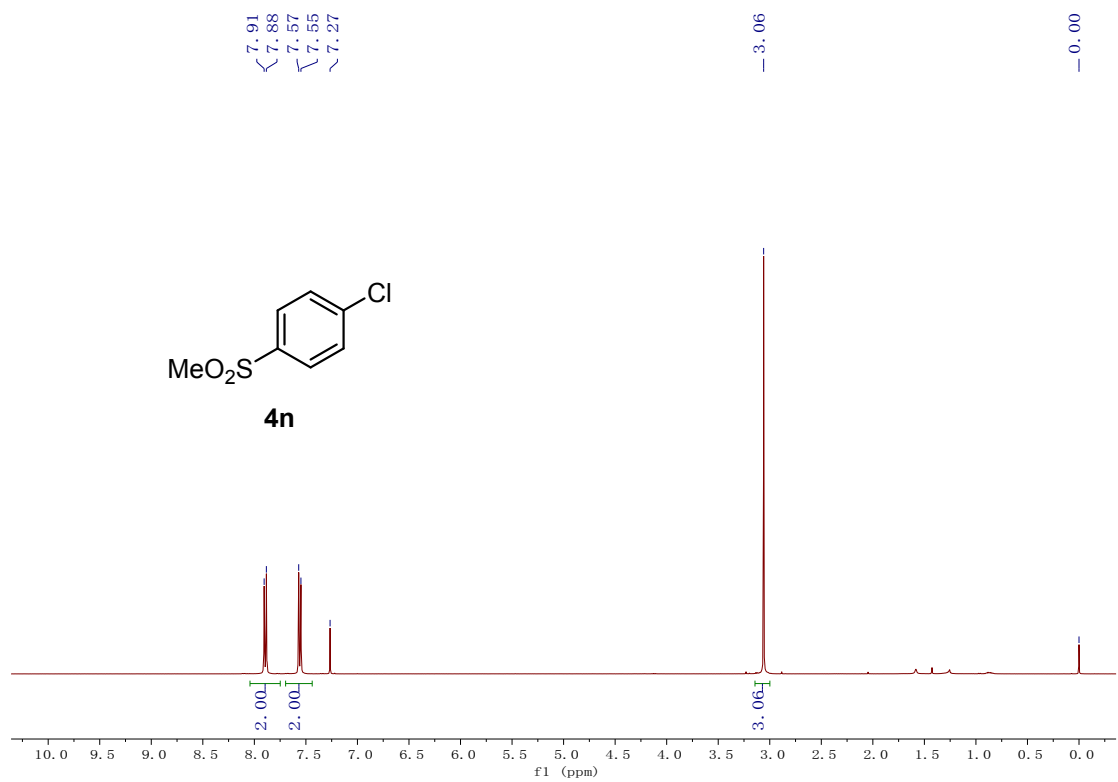


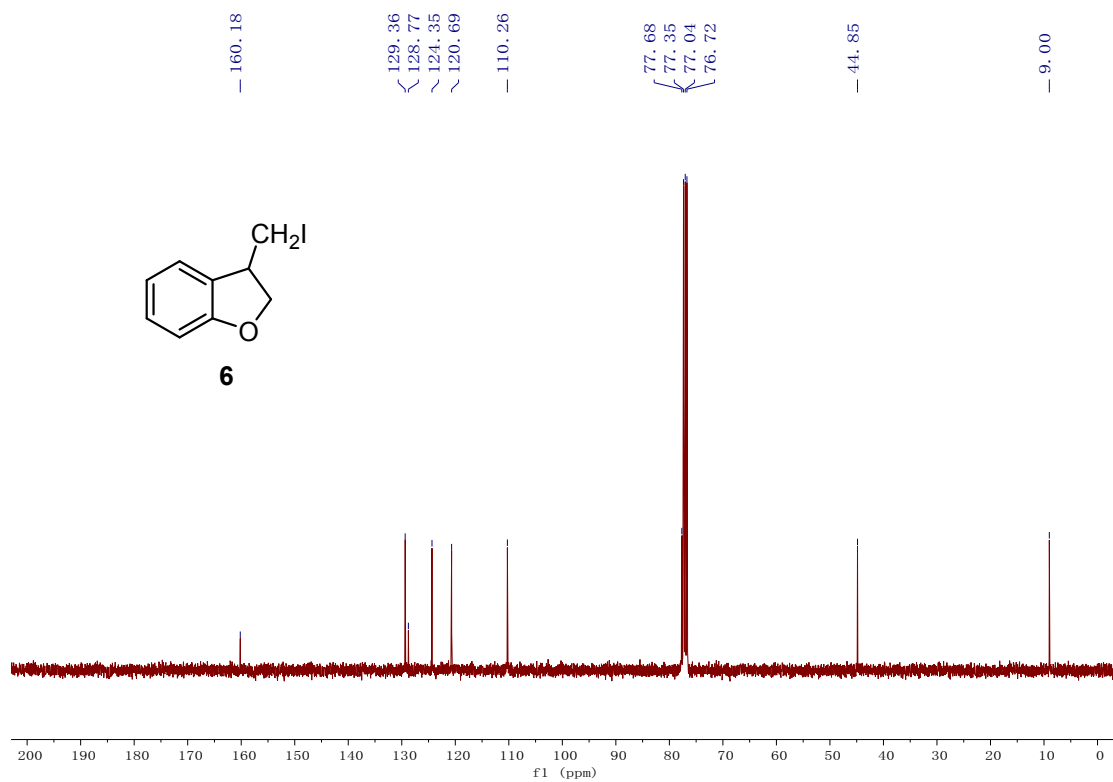
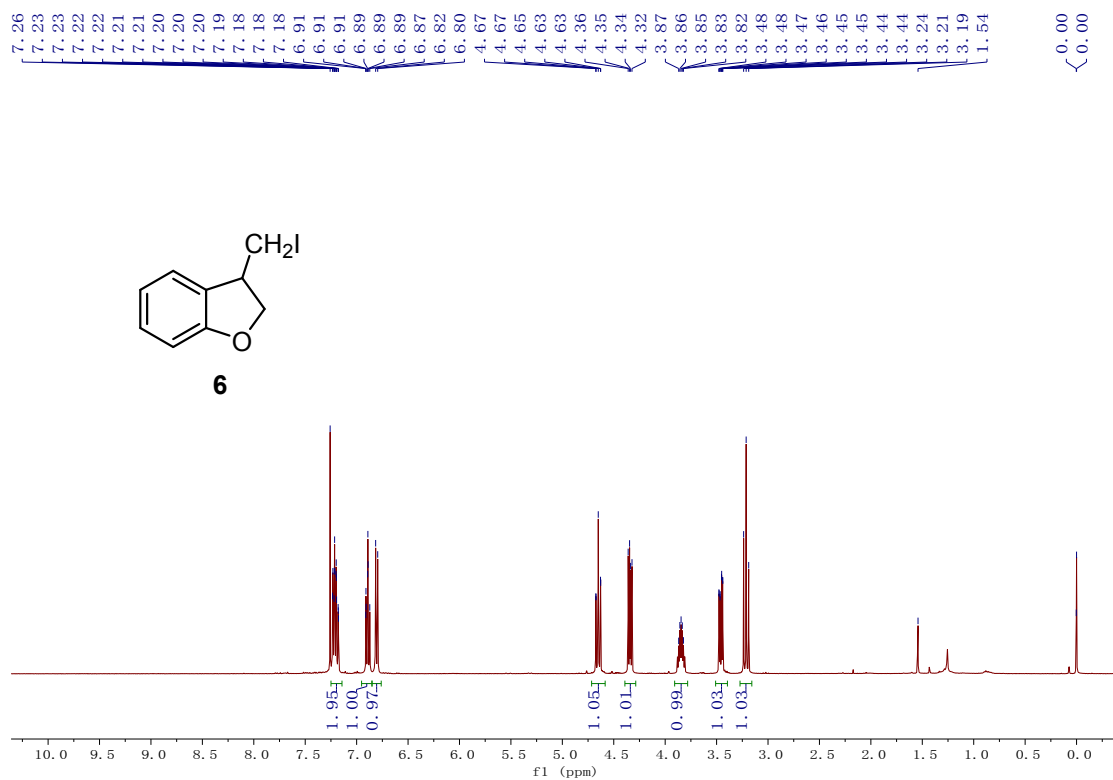


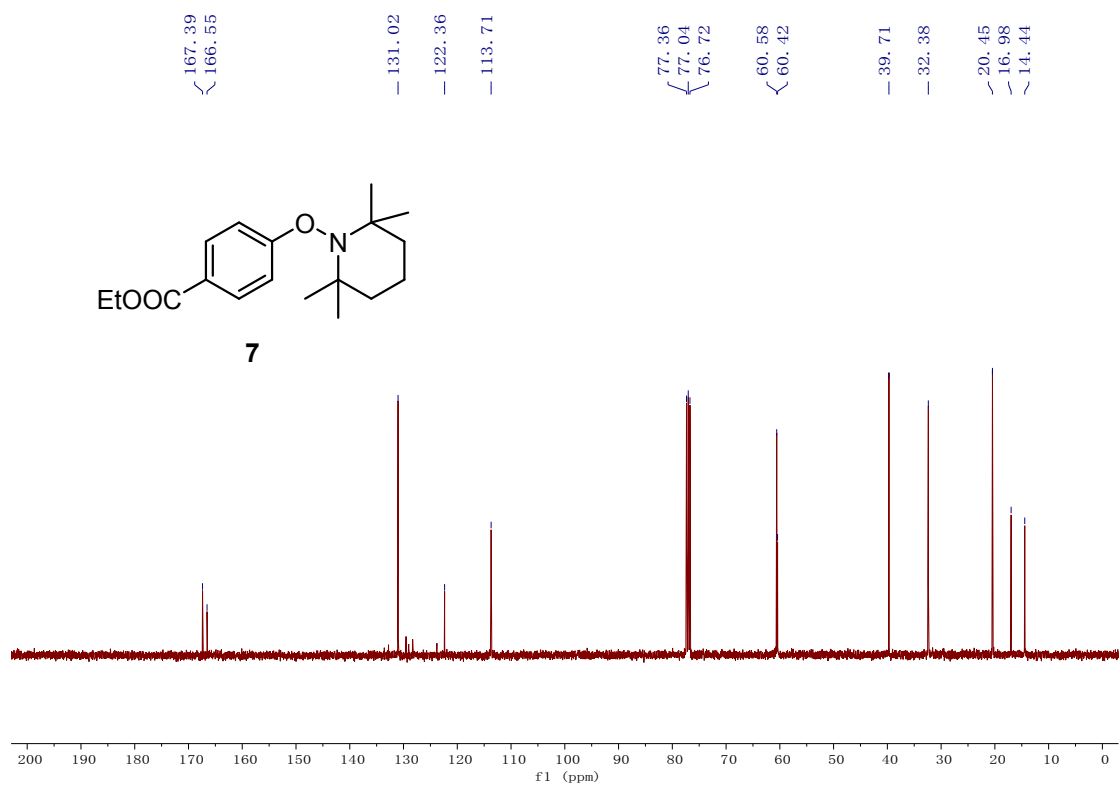
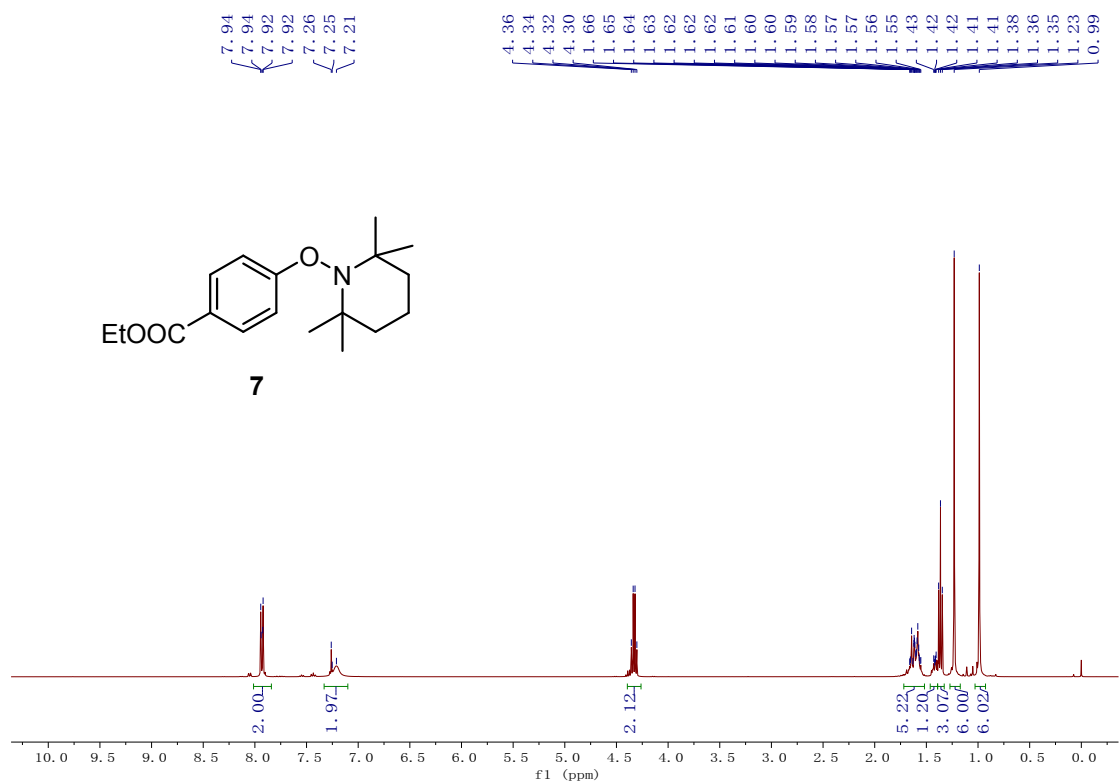












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