

# Supporting Information

## A Three-Phase Four-Component Coupling Reaction: Selective Synthesis of *o*-Chloro Benzoates by KCl, Arynes, CO<sub>2</sub>, and Chloroalkanes

Huanfeng Jiang\*, Yu Zhang, Wenfang Xiong, Jinghe Cen, Lu Wang, Ruixiang Cheng,  
Chaorong Qi, and Wanqing Wu

School of Chemistry and Chemical Engineering, Key Lab of Functional Molecular Engineering of Guangdong  
Province South China University of Technology, Guangzhou 510640, P. R. China.

E-mail: [jianghf@scut.edu.cn](mailto:jianghf@scut.edu.cn)

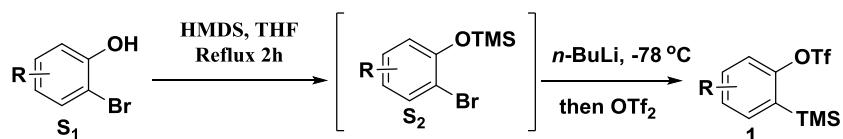
### Table of Contents

1. General information .....	1
2. General procedures for the preparation of aryne precursors.....	1
3. References.....	7
4. General procedures for the synthesis of alkyl benzoats.....	7
5. Reaction optimization for the synthesis of benzyl benzoates .....	8
6. General procedures for the synthesis of benzyl benzoates .....	11
7. Procedures for the synthesis 3ag in a 1 mmol scale.....	12
8. Transformations of product 3aa .....	12
9. Control experiments.....	14
10. Characterization data for all products .....	17
11. NMR Spectra.....	30

## 1. General information

All manipulations were carried out with standard Schlenk techniques in a N<sub>2</sub> glove box. KCl was dried at 100 °C for at least 8 h by vacuum drying oven and then stored in a N<sub>2</sub> glove box. Other commercially available reagents were used without further purification unless otherwise noted. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded by using a 400 MHz NMR spectrometer. The chemical shifts are referenced to signals at 7.26 and 77.0 ppm, respectively, and CDCl<sub>3</sub> is used as a solvent with TMS as the internal standard. Mass spectra were recorded on a gas chromatograph-mass spectrometer with an FID and equipped with an AT.SE-30 capillary column (internal diameter: 0.32 mm, length: 30 m). The data of HRMS was carried out on a high-resolution mass spectrometer (LCMS-IT-TOF). IR spectra were obtained either as potassium bromide plates or as liquid films between two potassium bromide plates with an infrared spectrometer. Melting points were determined with a digital melting point measuring instrument. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF254) using UV light as a visualizing agent. Flash column chromatography was conducted using silica gel (200–300 mesh) with solvent as indicated.

## 2. General procedures for the preparation of aryne precursors



Aryne precursors **1a**, **1b**, **1g**, **1i**, **1n** were commercially purchased and used without further purification. The other aryne precursors were prepared by using a modified literature procedure<sup>1</sup> as followed:

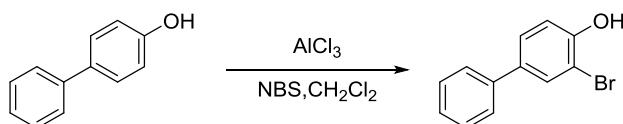
To a solution of *o*-bromophenol **S1** (10 mmol) in anhydrous THF (30 mL) was added HMDS (4.2 mL, 2 equiv) under N<sub>2</sub> atmosphere. The reaction mixture was refluxed for 2 h. After cooling to room temperature, the crude product **S2** was attained by removing the solvent *in vacuo* and used for the

next step without isolation.

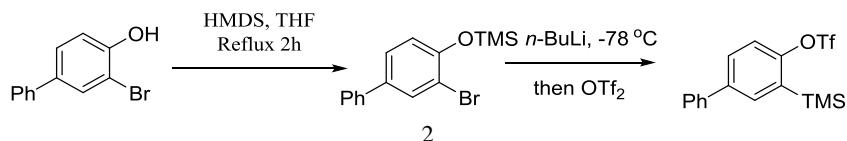
The crude product **S<sub>2</sub>** was dissolved in anhydrous THF (30 mL) under N<sub>2</sub> atmosphere and cooled to -78 °C, then *n*-BuLi (4.4 mL, 1.1 equiv, 2.5 M in hexane) was added dropwise to the mixture and the reaction was stirred for 40 min at -78 °C. After that, Tf<sub>2</sub>O (3.24 mL, 1.2 equiv) was added to the mixture dropwise at -78 °C and the reaction was stirred for another 40 min. The reaction mixture was quenched with cold sat. NaHCO<sub>3</sub> aq at -78 °C and warmed to room temperature. Then the aqueous layer was extracted with Et<sub>2</sub>O three times. The combined organic layers were dried over MgSO<sub>4</sub> and concentrated under reduced pressure. Finally, the residue was purified by silica gel column chromatography to afford aryne precursors **1**.



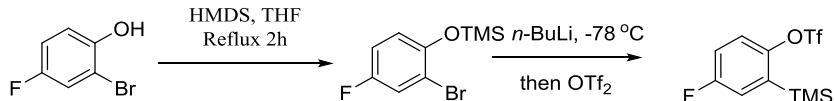
**3-Fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1c)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a clear oil (1.83 g, 58% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.39 - 7.44 (m, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.03 (t, *J* = 8.4 Hz, 1H), 0.44 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -73.2, -93.7; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.3 (d, *J* = 244.1 Hz), 154.15 (d, *J* = 14.8 Hz), 131.95 (d, *J* = 10.3 Hz), 120.5, 118.6 (q, *J* = 319 Hz, CF<sub>3</sub>), 116.14 (q, *J* = 1.4 Hz), 115.1 (d, *J* = 27.1 Hz), 0.29 (d, *J* = 3.6 Hz).



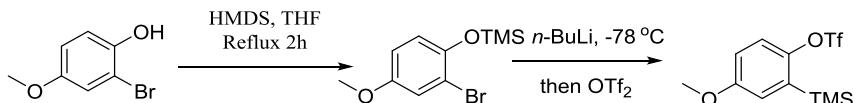
**3-Bromo-4-hydroxydiphenyl** was prepared by using a modified literature procedure.<sup>2</sup> 4-Phenylphenol (2.2 g, 13 mmol), *N*-bromosuccinimide (NBS) (2.3 g, 13 mmol) and AlCl<sub>3</sub> (314 mg, 1.3 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (70 ml) were stirred for 24 hours at room temperature. Then the aqueous layer was extracted with EtOAc three times. The combined organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. Finally, the residue was purified by silica gel column chromatography (PE: EtOAc = 100:1) to afford 3-bromo-4-hydroxydiphenyl (2.25 g, 91 %).



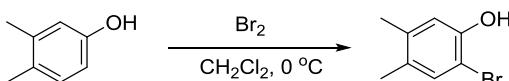
**3-(Trimethylsilyl)-[1,1'-biphenyl]-4-yl trifluoromethanesulfonate (1d)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a white solid (1.52 g, 41% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (d, *J* = 1.2 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.60 (d, *J* = 7.6 Hz, 2H), 7.53 – 7.42 (m, 4H), 0.49 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -73.9; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.5, 140.6, 139.8, 134.9, 133.0, 129.9, 128.9, 127.9, 127.2, 119.8, 118.6 (q, *J* = 318 Hz, CF<sub>3</sub>), -0.83.



**4-Fluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1e)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a yellow oil (1.52 g, 41% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33 – 7.31 (m, 1H), 7.21 – 7.19 (m, 1H), 7.12 – 7.08 (m, 1H), 0.39 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -74.0, -114.5; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 161.1 (d, *J* = 249 Hz), 150.3 (d, *J* = 2.4 Hz), 136.0 (d, *J* = 4.6 Hz), 122.4 (d, *J* = 21.8 Hz), 121.5 (d, *J* = 8.0 Hz), 118.5 (q, *J* = 318 Hz, CF<sub>3</sub>), 117.7 (d, *J* = 24.1 Hz), -1.08.

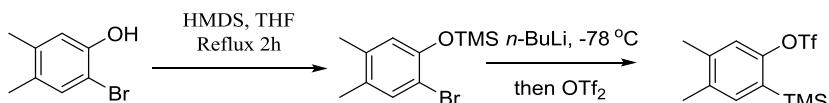


**4-Methoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1f)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a yellow oil (1.42 g, 43% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.15 (d, *J* = 8.8 Hz, 1H), 6.92 (d, *J* = 3.2 Hz, 1H), 6.77 - 6.80 (dd, *J* = 9.2, 3.2 Hz, 1H), 3.70 (s, 3H), 0.27 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -74.1; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.2, 148.4, 134.2, 121.5, 120.8 (d, *J* = 1.4 Hz), 118.6 (q, *J* = 318 Hz, CF<sub>3</sub>), 115.1, 113.80, 55.5, -0.9.

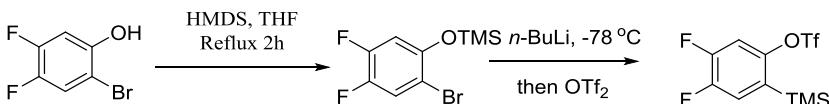


**2-Bromo-4,5-dimethylphenol** was prepared by using a modified literature procedure.<sup>3</sup> To a solution of 3,4-dimethylphenol (1.2 g, 10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (60 mL) was added a solution of bromine (0.51 mL, 10 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) dropwise at 0 °C. When the addition was completed, the reaction was quenched with sat. Na<sub>2</sub>SO<sub>3</sub> aq. at 0 °C and this mixture was warmed to room

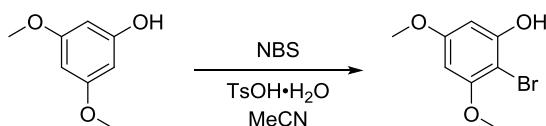
temperature. Then the aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  three times. The combined organic layers were washed with brine then dried over  $\text{MgSO}_4$ . The solvent was removed in vacuo, then the residue was recrystallized from pentane to afford 2-bromo-4,5-dimethylphenol as a white solid (1.36 g, 68% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.20 (s, 1H), 6.82 (s, 1H), 2.18 (s, 3H), 2.17 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.0, 137.9, 132.2, 130.2, 117.1, 106.5, 19.5, 18.6.



**4,5-Dimethyl-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1h)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a clear oil (0.684 g, 21% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.23 (s, 1H), 7.09 (s, 1H), 2.27 (s, 3H), 2.26 (s, 3H), 0.34 (s, 9H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -74.0;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  153.2, 140.3, 137.0, 136.0, 129.1, 120.5, 118.6 (q,  $J = 318$  Hz,  $\text{CF}_3$ ), 19.9, 19.1, -0.8.

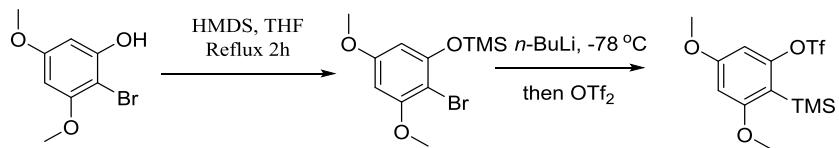


**4,5-Difluoro-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1j)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a clear oil (1.97 g, 59% yield).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30 (t,  $J = 9.6$  Hz, 1H), 7.23 (dd,  $J = 10.4, 6.0$  Hz, 1H), 0.37 (s, 9H);  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -73.8, -130.7 - 130.8 (m), -138.0 - -138.1 (m);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  150.6 (dd,  $J = 253.2, 14.5$  Hz), 149.3 (dd,  $J = 250.8, 11.5$  Hz), 149.0 (dd,  $J = 7.9, 3$  Hz), 130.1 (dd,  $J = 4.2, 2.7$  Hz), 123.5 (d,  $J = 17.1$  Hz), 118.5 (q,  $J = 318$  Hz,  $\text{CF}_3$ ), 110.4 (d,  $J = 20.7$  Hz), -1.06.

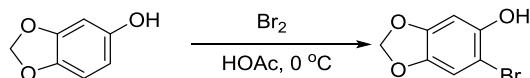


**2-Bromo-3, 5-dimethoxyphenol** was prepared by using a modified literature procedure.<sup>4</sup> 3,5-dimethoxyphenol (1.54 g, 10 mmol) and  $\text{TsOH}\cdot\text{H}_2\text{O}$  (11.9 g, 10 mmol) were dissolved in  $\text{CH}_3\text{CN}$  (50 mL) at room temperature, then NBS (1.78 g, 10 mmol) was added to the stirring solution slowly. After 24 h, the reaction was stopped and the solvents were evaporated. The residue was purified by

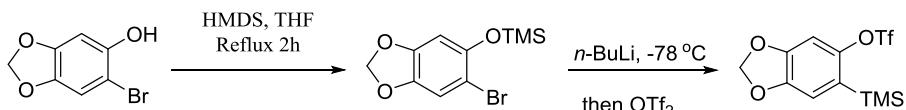
silica gel column chromatography (PE: EtOAc= 20:1) to afford the target as white solid (1.95 g, 84% yield).



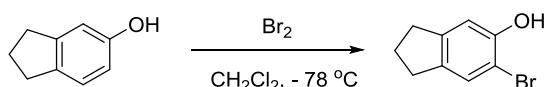
**3,5-Dimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1k)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a yellow oil (1.36 g, 38% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.51 (s, 1H), 6.41 (s, 1H), 3.81 (s, 3H), 3.80 (s, 3H), 0.35 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -72.8; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.2, 162.6, 155.3, 118.7 (q, *J*= 318 Hz, CF<sub>3</sub>), 112.1, 98.2, 97.3, 55.5 (d, *J*= 1.9 Hz), 55.4 (d, *J*= 1.8 Hz), 0.8.



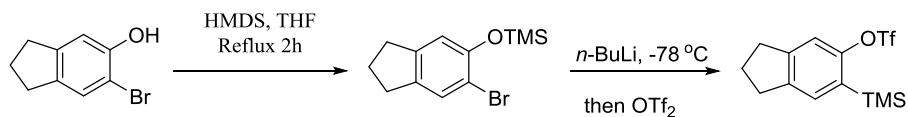
**5-Bromosesamol** was prepared by using literature procedure.<sup>2</sup> To a solution of sesamol (3.0 g, 21.7 mmol) in AcOH (7 mL) was added a solution of bromine (1.0 mL, 19.4 mmol) in HOAc (4 mL) dropwise at 0 °C and the reaction mixture was stirred for 30 min at this temperature. This mixture was poured into ice and filtered off. The residual solid was washed with water and dried to afford 5-bromosesamol as a faint green solid (2.43 g, 52%), which was used without further purification.



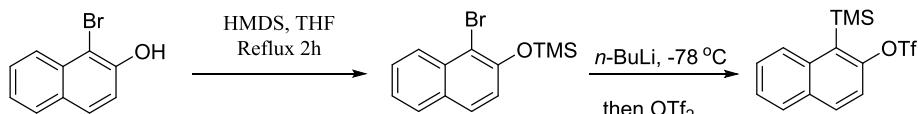
**6-(Trimethylsilyl)benzo[d][1,3]dioxol-5-yl trifluoromethanesulfonate (1l)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a yellow oil (2.2 g, 64% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.90 (s, 1H), 6.87 (s, 1H), 6.02 (s, 2H), 0.35 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -74.1; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 149.5, 148.6, 146.9, 124.9, 118.5 (q, *J*= 318 Hz, CF<sub>3</sub>), 113.1, 102.4, 102.3, -0.8.



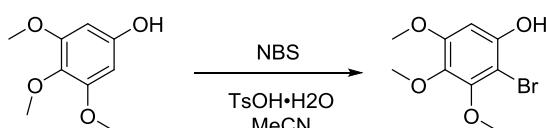
**6-Bromo-2,3-dihydro-1H-inden-5-ol** was prepared by using a modified literature procedure.<sup>5</sup> To a solution of 5-indanol (2.6 g, 20 mmol) in anhydrous CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was added a solution of bromine (1.0 mL, 19.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) dropwise at -78 °C under N<sub>2</sub> atmosphere and the reaction mixture was stirred for 1 h at this temperature. The reaction was then quenched with sat. Na<sub>2</sub>SO<sub>3</sub> aq. and extracted with CH<sub>2</sub>Cl<sub>2</sub> three times. The combined organic layers were washed with brine then dried over MgSO<sub>4</sub>. After that, the solvents were evaporated. The residue was purified by silica gel column chromatography (PE: EtOAc= 50:1) to afford the target as a clear oil (3.98g, 94% yield).



**6-(Trimethylsilyl)-2,3-dihydro-1H-inden-5-yl trifluoromethanesulfonate (1m)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a clear oil (2.28 g, 68% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (s, 1H), 7.20 (s, 1H), 2.97 – 2.90 (m, 4H), 2.18 – 2.10 (m, 2H), 0.37 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -74.0; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 154.0, 148.3, 143.6, 131.3, 129.5, 118.5 (q, *J*= 318 Hz, CF<sub>3</sub>), 115.7, 33.1, 32.1, 25.7, -0.7.

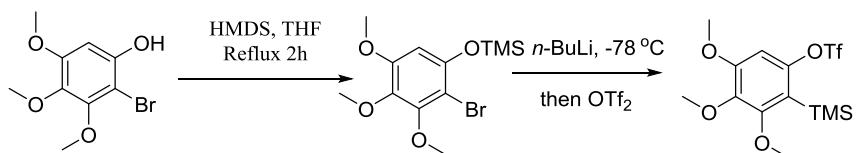


**1-(Trimethylsilyl)naphthalen-2-yl trifluoromethanesulfonate (1o)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a yellow oil (1.28 g, 37% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 8.4 Hz, 1H), 7.92 (t, *J* = 9.2 Hz, 2H), 7.63 - 7.54 (m, 2H), 7.46 (d, *J* = 9.2 Hz, 1H), 0.65 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -72.8; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 152.5, 137.6, 132.4, 132.4, 129.3, 129.0, 128.8, 126.7, 126.3, 119.1, 118.7 (q, *J*= 318 Hz, CF<sub>3</sub>), 2.2.



**2-Bromo-3,4,5-trimethoxyphenol** was prepared by using a modified literature procedure.<sup>4</sup> 3,4,5-trimethoxyphenol (1.84 g, 10 mmol) and TsOH•H<sub>2</sub>O (11.9 g, 10 mmol) were dissolved in CH<sub>3</sub>CN

(50 mL) at room temperature, then NBS (1.78 g, 10 mmol) was added to the stirring solution slowly. After 1 h, the reaction was stopped and the solvents were evaporated. The residue was purified by silica gel column chromatography (PE: EtOAc= 20:1) to afford the target as white solid (1.6 g, 61% yield).

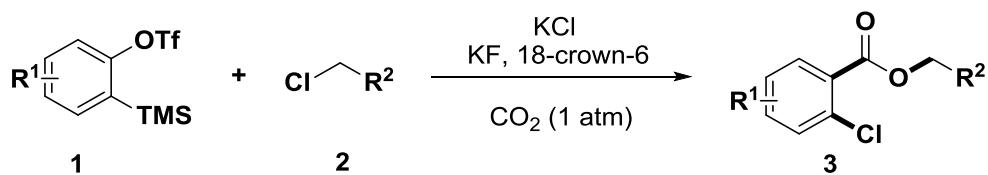


**3,4,5-Trimethoxy-2-(trimethylsilyl)phenyl trifluoromethanesulfonate (1p)** was prepared according to the general method. The crude mixture was purified by silica gel column chromatography with petroleum ether to afford the target as a yellow oil (1.26 g, 33% yield). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.65 (s, 1H), 3.90 (s, 3H), 3.84 (s, 3H), 3.82 (s, 3H), 0.34 (s, 9H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -73.0; <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 158.7, 155.1, 149.2, 141.0, 118.6 (q, *J*= 318 Hz, CF<sub>3</sub>), 117.5, 100.7, 60.9, 60.5, 56.1, 1.0.

### 3. References

1. D. Pena, A. Cobas, D. Perez, E. Guitian, *Synthesis* **2002**, *10*, 1454.
2. Bernini, R.; Cacchi, S.; Fabrizi, G. *Org. Lett.* **2008**, *10*, 3457.
3. Ueta, Y.; Mikami, K.; Ito, S. *Angew. Chem. Int. Ed.* **2016**, *55*, 7525.
4. Mesgar, M.; Daugulis, O. *Org. Lett.* **2017**, *19*, 4247.
5. Hermann, K.; Pratemyot, Y.; Polen, S.; Hardin, A. M.; Dalkilic, E.; Dastan, A.; Badjic, J. D. *Chem. Eur. J.* **2015**, *21*, 3550.

### 4. General procedures for the synthesis of alkyl benzoats



In a  $\text{N}_2$  glove box, a dried 25 mL Schlenk tube was charged with KCl (4 equiv, 59.6 mg), KF (4 equiv, 46.5 mg), 18-crown-6 (4 equiv, 211.5 mg) and **2** (0.5 mL) and filled with a rubber plug. Then the sealed tube was removed from the  $\text{N}_2$  glove box. The reaction mixture was evacuated and backfilled with  $\text{CO}_2$  (1 atm) for three times. To the stirring mixture was added the aryne precursor **1** (0.2 mmol, 49  $\mu\text{L}$ ) dropwise by a syringe and kept stirring under 1 atm  $\text{CO}_2$  at 46  $^\circ\text{C}$  for 12 h. After the reaction was completed, the reaction mixture was quenched by  $\text{H}_2\text{O}$  (10 mL) and extracted with ethyl acetate (30 mL). The organic layers were dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated. The crude residue was then separated by column chromatography on silica gel to afford corresponding *o*-chloro benzoates **3**.

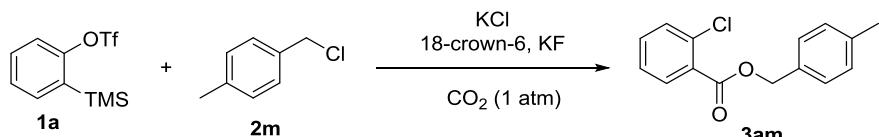
## 5. Reaction optimization for the synthesis of benzyl benzoates

### Screening of Solvents

Entry <sup>a</sup>	Solvent	Yield (%) <sup>b</sup>
<b>1</b>	<b>DCE</b>	<b>30</b>
2	THF	18
3	MeCN	10
4	DME	19
5	dioxane	28
6	$\text{CH}_2\text{Cl}_2$	26

Reaction conditions: **1a** (0.2 mmol), **2m** (1.2 equiv),  $\text{CO}_2$  (1 atm), KCl (4 equiv), 18-crown-6 (4 equiv), KF (4 equiv.), Solvent (0.5 mL), 46  $^\circ\text{C}$  for 12 h; <sup>b</sup> Yield based on **1a** and determined by  $^1\text{H}$  NMR analysis using  $\text{CH}_3\text{NO}_2$  as an internal standard.

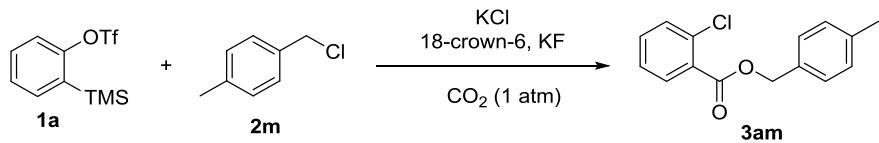
### Screening of Temperatures



Entry <sup>a</sup>	T (°C)	Yield (%) <sup>b</sup>
<b>1</b>	<b>46</b>	<b>28</b>
2	rt	26
3	70	20

Reaction conditions: **1a** (0.2 mmol), **2m** (1.2 equiv), CO<sub>2</sub> (1 atm), KCl (4 equiv), 18-crown-6 (4 equiv), KF (4 equiv), DCE (0.5 mL), 12 h; <sup>b</sup> Yield based on **1a** and determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard.

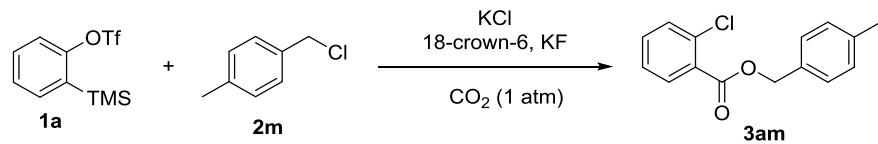
#### Screening the ratio of **1a** and **2m**



Entry <sup>a</sup>	<b>1a</b> (equiv)	<b>2m</b> (equiv)	Yield (%)
1	1	1.2	29 <sup>b</sup>
2	1	1.5	31 <sup>b</sup>
3	1	2	34 <sup>b</sup>
4	1	3	37 <sup>b</sup>
5	1.2	1	36 <sup>c</sup>
6	1.5	1	37 <sup>c</sup>
7	2	1	49 <sup>c</sup>
8	2.5	1	55 <sup>c</sup>
9	<b>3</b>	<b>1</b>	<b>56<sup>c</sup></b>
10	4	1	55 <sup>c</sup>

Reaction conditions: CO<sub>2</sub> (1 atm), KCl (4 equiv), 18-crown-6 (4 equiv), KF (4 equiv), DCE (0.5 mL), 46 °C for 12 h; <sup>b</sup> Yield based on **1a** and determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard. <sup>c</sup> Yield based on **2m** and determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard.

#### Screening of Time

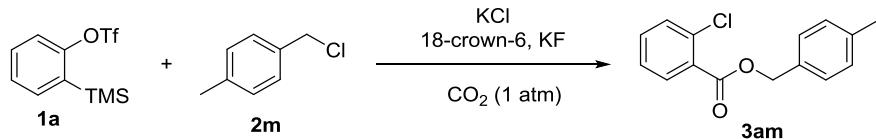


Entry <sup>a</sup>	t (h)	Yield (%) <sup>b</sup>
9		

1	12	56
<b>2</b>	<b>18</b>	<b>60</b>
3	24	60

Reaction conditions: **1a** (3 equiv), **2m** (0.2 mmol), CO<sub>2</sub> (1 atm), KCl (4 equiv), 18-crown-6 (4 equiv), KF (4 equiv), DCE (0.5 mL), 46 °C; <sup>b</sup> Yield based on **2r** and determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard.

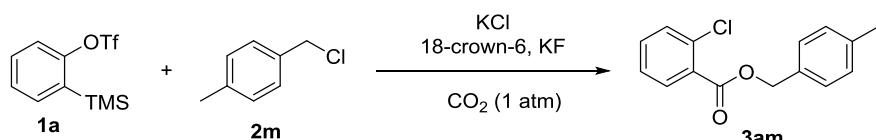
#### Screening of different parameters (KF, 18-crown-6, KCl, Temperature)



Entry <sup>a</sup>	KF (equiv)	18-crown-6 (equiv)	KCl (equiv)	T (°C)	Yield (%) <sup>b</sup>
1	4	4	4	rt	48
2	4	4	4	<b>40</b>	56
3	4	4	4	<b>46</b>	60
4	4	4	4	<b>50</b>	60
5	4	4	<b>3</b>	46	61
6	4	4	<b>2</b>	46	50
7	4	4	-	46	n.d.
8	<b>4</b>	<b>4</b>	<b>4</b>	46	60
9	<b>3</b>	<b>3</b>	4	46	49
10	<b>2</b>	<b>2</b>	4	46	28

Reaction conditions: **1a** (3 equiv), **2m** (0.2 mmol), DCE (0.5 mL), CO<sub>2</sub> (1 atm), 18 h; <sup>b</sup> Yield based on **2r** and determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard. n.d. = not detected.

#### Screening of the volume of DCE

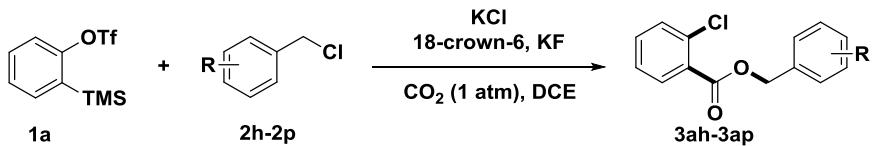


Entry <sup>a</sup>	DCE (mL)	Yield (%) <sup>b</sup>
1	-	57

2	0.1	80
<b>3</b>	<b>0.2</b>	<b>80</b>
4	0.25	73
5	0.3	71
6	0.4	70
7	0.5	60
8	1	42

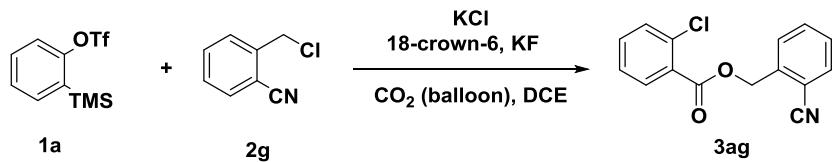
Reaction conditions: **1a** (3 equiv), **2m** (0.2 mmol), CO<sub>2</sub> (1 atm), KCl (4 equiv), 18-crown-6 (4 equiv), KF (4 equiv), 46 °C for 18 h; <sup>b</sup> Yield based on **2r** and determined by <sup>1</sup>H NMR analysis using CH<sub>3</sub>NO<sub>2</sub> as an internal standard.

## 6. General procedures for the synthesis of benzyl benzoates



In a N<sub>2</sub> glove box, a dried 25 mL Schlenk tube was charged with KCl (4 equiv, 59.6 mg), KF (4 equiv, 46.5 mg), 18-crown-6 (4 equiv, 211.5 mg), (benzyl chloride **2** (0.2 mmol), when benzyl chloride is solid.) and DCE (0.2 mL) and filled with a rubber plug. Then the sealed tube was removed from the N<sub>2</sub> glove box. The reaction mixture was evacuated and backfilled with CO<sub>2</sub> (1 atm) for three times. To the stirring mixture was added the benzyl chloride **2** (0.2 mmol) and aryne precursor **1a** (3 equiv, 147 µL) by a syringe in sequence and kept stirring under 1 atm CO<sub>2</sub> at 46 °C for 18 h. After the reaction was completed, the reaction mixture was quenched by H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (30 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The crude residue was then separated by column chromatography on silica gel to afford corresponding *o*-chloro benzoates **3**.

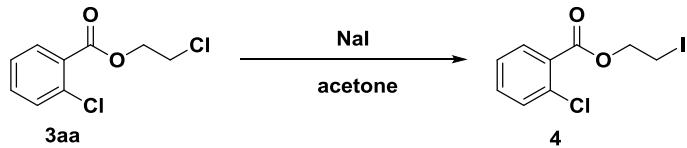
## 7. Procedures for the synthesis 3ag in a 1 mmol scale



In a  $\text{N}_2$  glove box, a dried 25 mL Schlenk tube was charged with KCl (4 equiv, 298 mg), KF (4 equiv, 232.5 mg), 18-crown-6 (4 equiv, 1057.5 mg), **2g** (1 mmol, 151.59 mg) and DCE (1 mL) and filled with a rubber plug. Then the sealed tube was removed from the  $\text{N}_2$  glove box. The reaction mixture was evacuated and backfilled with  $\text{CO}_2$  (1 atm) for three times. To the stirring mixture was added aryne precursor **1a** (3 equiv, 0.74 mL) dropwise by a syringe and the Schlenk tube was linked to a  $\text{CO}_2$  balloon, then the reaction kept stirring at 46  $^{\circ}\text{C}$  for 12 h. After the reaction was completed, the reaction mixture was quenched by  $\text{H}_2\text{O}$  (20 mL) and extracted with ethyl acetate ( $3 \times 30$  mL). The organic layers were dried over  $\text{Na}_2\text{SO}_4$  and the solvent was evaporated. The crude residue was then separated by column chromatography (PE: EtOAc = 10:1) to afford corresponding *o*-chloro benzoates **3ag** as a pale yellow solid (201 mg, 74 %).

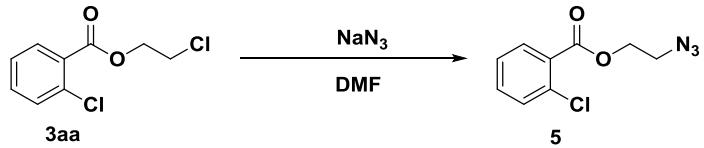
## 8. Transformations of product 3aa

### 2-Iodoethyl 2-chlorobenzoate (4)



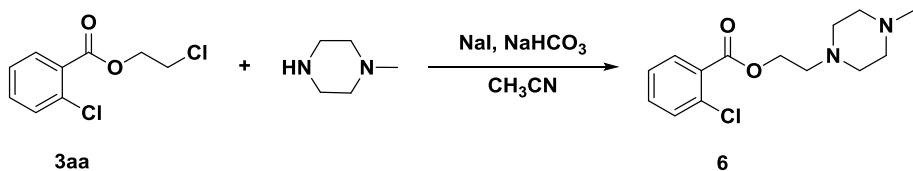
2-Chloroethyl 2-chlorobenzoate **3aa** (0.2 mmol, 43.6 mg), NaI (5 equiv, 149.9 mg) in acetone (1 mL) were suspended and the reaction mixture was stirred under reflux for 48 h. The reaction was then washed with sat.  $\text{NaCl}$  aq. and extracted with EtOAc three times. The combined organic layers were then dried over  $\text{Na}_2\text{SO}_4$ . After that, the solvents were evaporated. The residue was purified by silica gel column chromatography.

### 2-Azidoethyl 2-chlorobenzoate (5)



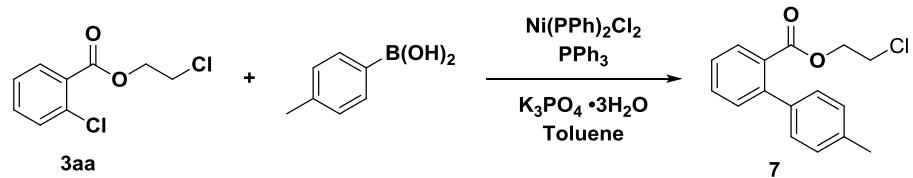
2-Chloroethyl 2-chlorobenzoate **3aa** (0.2 mmol, 43.6 mg), NaN<sub>3</sub> (2 equiv, 26 mg) in DMF (1 mL) were stirred under 70 °C for 12 h. After the reaction was completed, the reaction mixture was quenched by H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (30 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The crude residue was then separated by silica gel column chromatography.

### 2-(4-Methylpiperazin-1-yl)ethyl 2-chlorobenzoate (6)



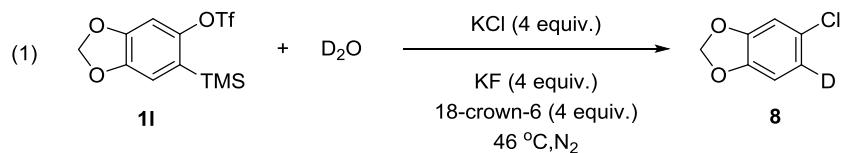
2-Chloroethyl 2-chlorobenzoate **3aa** (0.5 mmol, 109 mg), 1-methylpiperazine (2 equiv, 100.2 mg), NaI (6 mol %, 4.4 mg), NaHCO<sub>3</sub> (2 equiv, 84 mg) in CH<sub>3</sub>CN (3.5 mL) were stirred under 90 °C for 24 h. After the reaction was completed, the reaction mixture was quenched by H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (30 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The crude residue was then separated by silica gel column chromatography.

### 2-Chloroethyl 4'-methyl-[1,1'-biphenyl]-2-carboxylate (7)

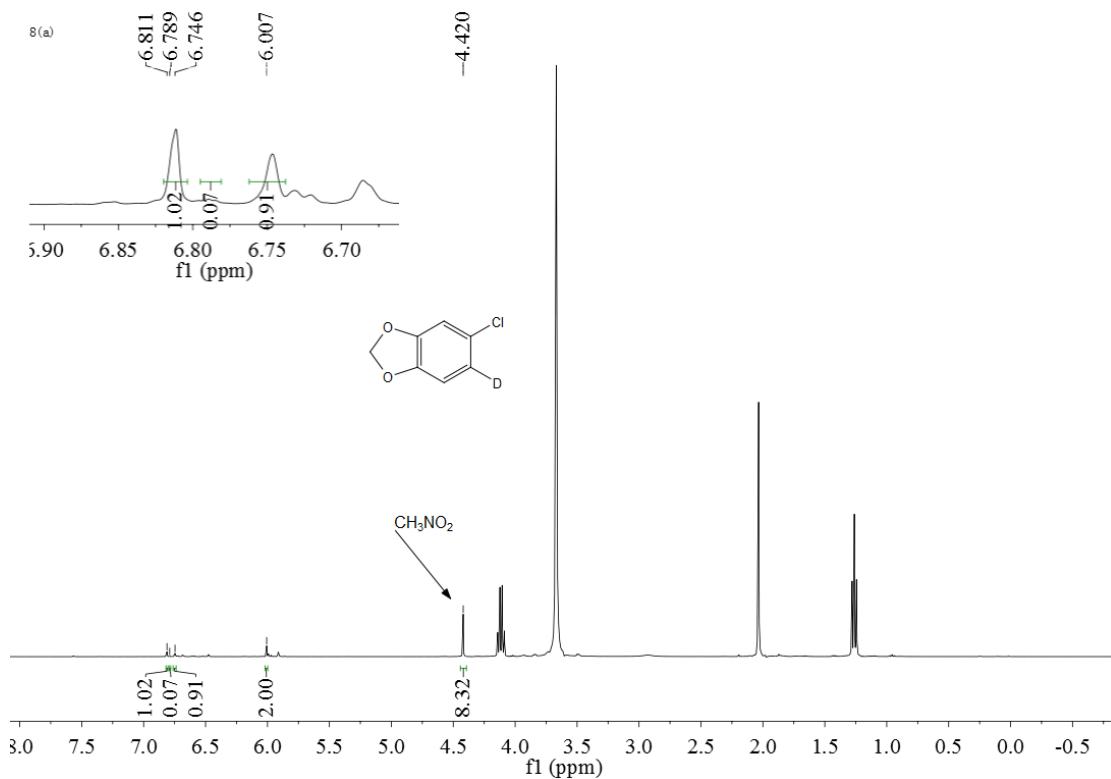


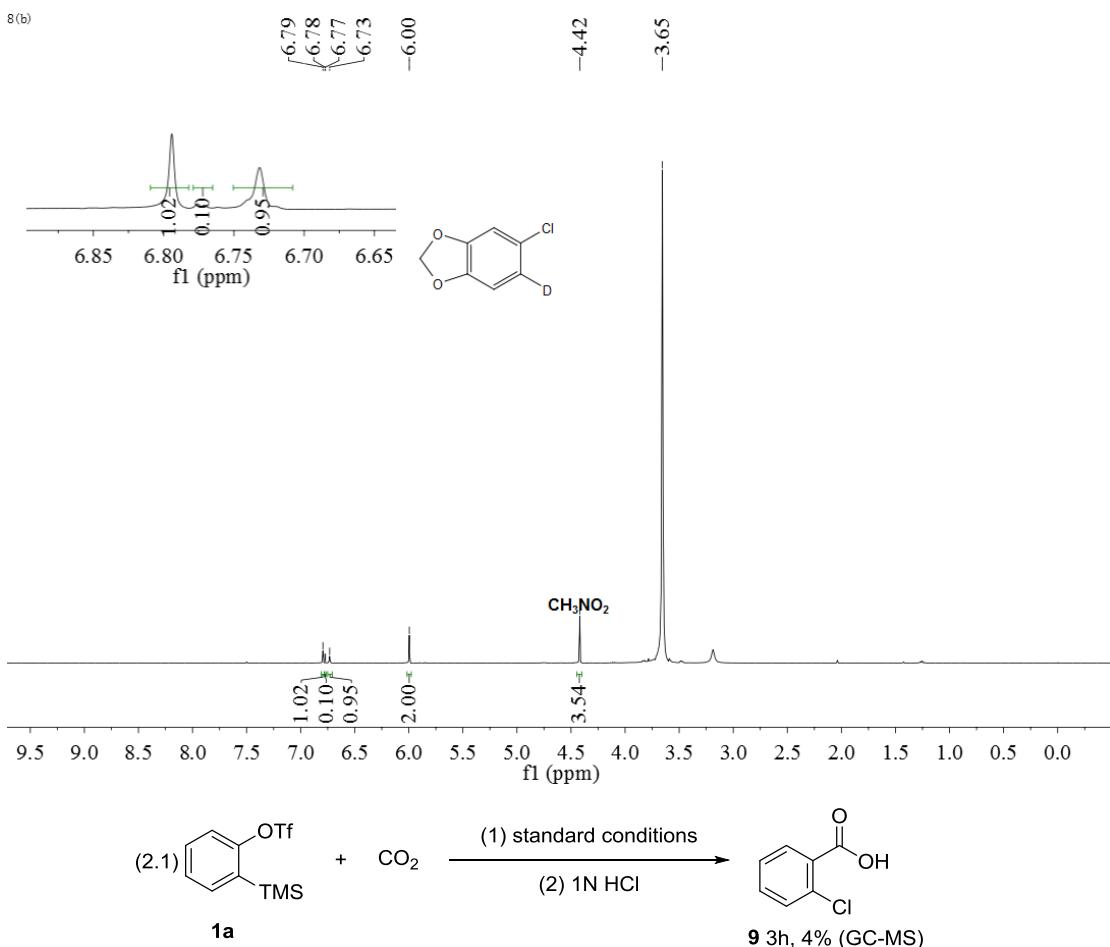
2-Chloroethyl 2-chlorobenzoate **3aa** (0.2 mmol, 43.6 mg), 4-tolylboronic acid (2.6 equiv), Ni(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (3 mol %), PPh<sub>3</sub> (6 mol %), K<sub>3</sub>PO<sub>4</sub> • 3H<sub>2</sub>O (2.6 equiv) in toluene (0.6 mL) were stirred under 120 °C for 12 h. After the reaction was completed, the reaction mixture was quenched by H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (30 mL). The organic layer were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The crude residue was then separated by silica gel column chromatography.

## 9. Control experiments



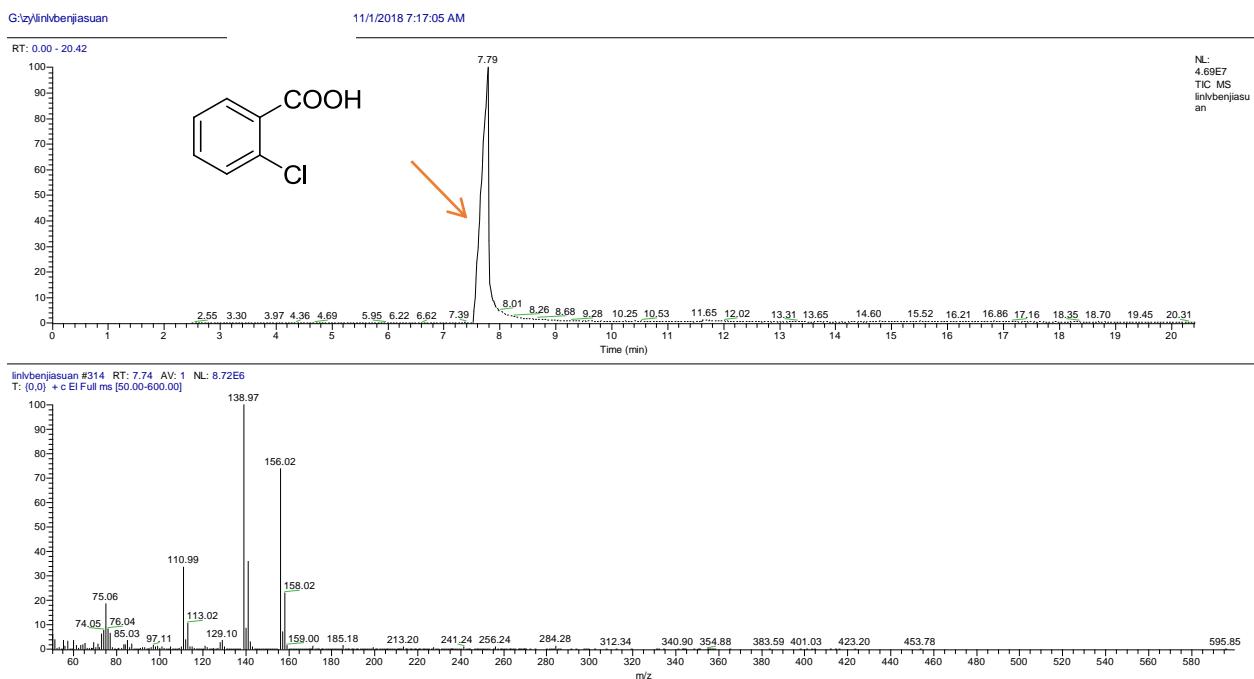
In a  $\text{N}_2$  glove box, a dried 25 mL Schlenk tube was charged with KCl (4 equiv, 59.6 mg), KF (4 equiv, 46.5 mg), 18-crown-6 (4 equiv, 211.5 mg) in DCE or THF (0.5 mL) and filled with a rubber plug. Then the sealed tube was removed from the  $\text{N}_2$  glove box. To the stirring mixture was added the aryne precursor **1q** (0.2 mmol, 52  $\mu\text{L}$ ) and  $\text{D}_2\text{O}$  (2 equiv, 8  $\mu\text{L}$ ) dropwise by a syringe in sequence and kept stirring under 1 atm  $\text{N}_2$  at 46  $^\circ\text{C}$  for 12 h. After the reaction was completed, the reaction mixture was filtered and concentrated. The crude residue was then added  $\text{CH}_3\text{NO}_2$  (0.2 mmol, 12.2 mg) by a syringe and dissolved in  $\text{CDCl}_3$  for  $^1\text{H}$  NMR spectrum analysis. When using THF as solvent, the product **8** was obtained in 36% yield (based on  $^1\text{H}$  NMR) with 93% deuterium incorporation (Scheme 6, 1a). In contrast, when using DCE as solvent, the product **8** could be improved to 85% yield (based on  $^1\text{H}$  NMR) with 90% deuteration.



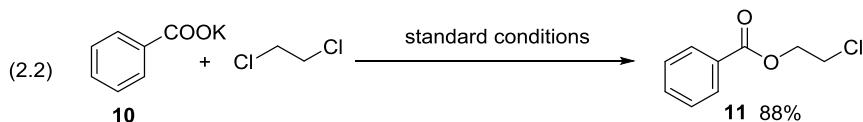
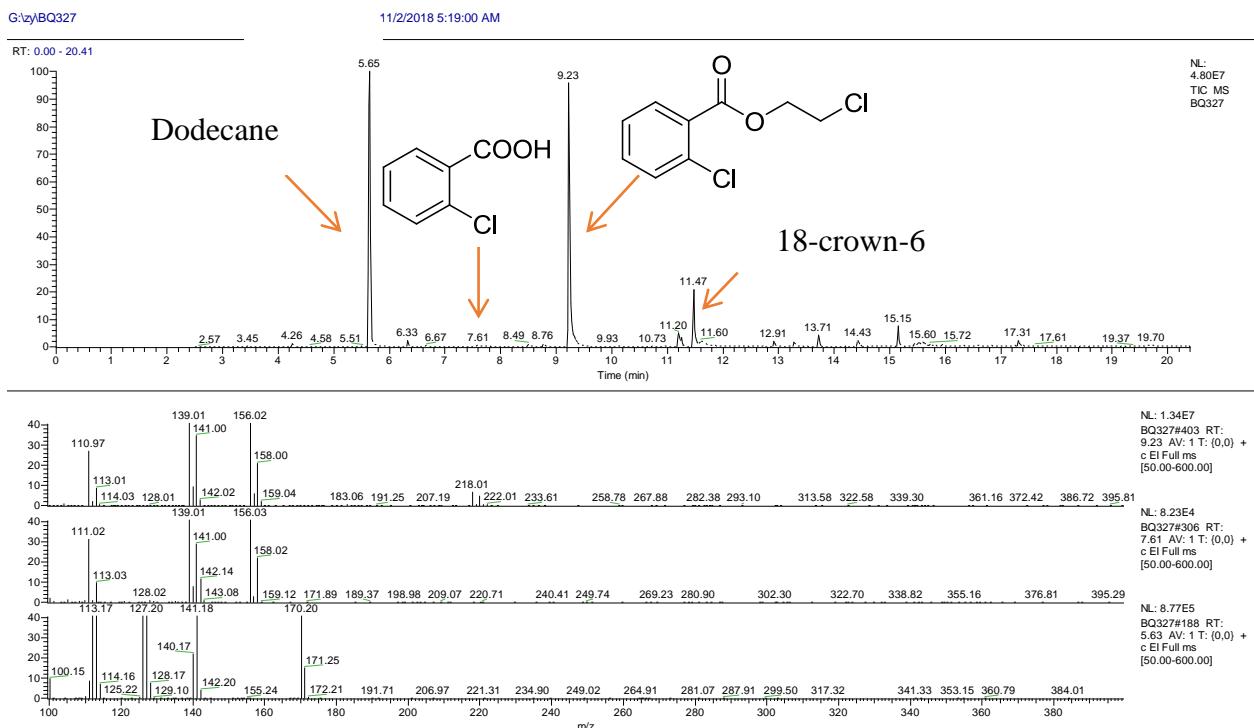


In a N<sub>2</sub> glove box, a dried 25 mL Schlenk tube was charged with KCl (4 equiv, 59.6 mg), KF (4 equiv, 46.5 mg), 18-crown-6 (4 equiv, 211.5 mg) and DCE (0.5 mL) and filled with a rubber plug. Then the sealed tube was removed from the N<sub>2</sub> glove box. The reaction mixture was evacuated and backfilled with CO<sub>2</sub> (1 atm) for three times. To the stirring mixture was added the aryne precursor **1a** (0.2 mmol, 49  $\mu$ L) dropwise by a syringe and kept stirring under 1 atm CO<sub>2</sub> at 46 °C for 3h. The reaction mixtures were quenched by HCl (1N, 4 mL) at the specified times and extracted with ethyl acetate (100 mL). The organic layers were dried over Na<sub>2</sub>SO<sub>4</sub> and concentrated under reduced pressure. The residue was added n-dodecane (0.2 mmol, 46  $\mu$ L) and determined by GC-MS.

#### GC-MS of 2-chlorobenzoic acid - Standard Sample



### GC-MS of 3h

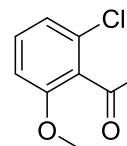


In a N<sub>2</sub> glove box, a dried 25 mL Schlenk tube was charged with KCl (4 equiv, 59.6 mg), KF (4 equiv, 46.5 mg), 18-crown-6 (4 equiv, 211.5 mg), potassium benzoate **10** (0.2 mmol, 32 mg) and DCE (0.5 mL) and filled with a rubber plug. Then the sealed tube was removed from the N<sub>2</sub> glove box. The reaction mixture was evacuated and backfilled with CO<sub>2</sub> (1 atm) for three times and kept

stirring under 1 atm CO<sub>2</sub> at 46 °C for 12 h. After the reaction was completed, the reaction mixture was quenched by H<sub>2</sub>O (10 mL) and extracted with ethyl acetate (30 mL). The organic layer were dried over Na<sub>2</sub>SO<sub>4</sub> and the solvent was evaporated. The ester **11** was then separated by silica gel column chromatography.

## 10. Characterization data for all products

### 2-Chloroethyl-2-chloro-6-methylbenzoate (3ba)

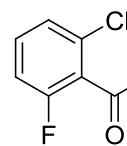


**3ba** was obtained after purification by column chromatography on silica gel

(petroleum ether / ethyl acetate = 30:1) as a yellow oil in 64% yield (31.6 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.28 (t, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 4.59 (t, *J* = 6.0 Hz, 2H), 3.83 (s, 3H), 3.79 (t, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 157.3, 131.5, 131.2, 123.1, 121.5, 109.5, 65.0, 56.2, 41.1; IR (KBr)/cm<sup>-1</sup> 3078, 2930, 1723, 1574, 1435, 1249, 1097, 1024, 792, 712, 665, 453; HRMS-ESI (*m/z*): calcd for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>3</sub><sup>+</sup> [M + Na]<sup>+</sup>: 270.9899; found 270.9990.

### 2-Chloroethyl-2-chloro-3-fluorobenzoate (3ca)

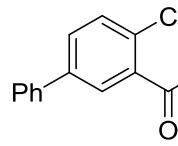
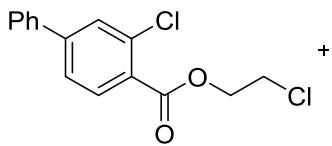


**3ca** was obtained after purification by column chromatography on silica gel

(petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in 34% yield (16.0 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.38- 7.33 (m, 1H), 7.24 (t, *J* = 9.6 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 1H), 4.63 (t, *J* = 6.0 Hz, 2H), 3.80 (t, *J* = 6.0 Hz, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -111.6- -111.7 (m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.7, 159.8 (d, *J* = 252.8 Hz), 132.6 (d, *J* = 4.6 Hz), 131.9 (d, *J* = 9.2 Hz), 125.6 (d, *J* = 3.5 Hz), 121.8 (d, *J* = 19.8 Hz), 114.5 (d, *J* = 21.2 Hz), 65.5, 40.9; IR (KBr)/cm<sup>-1</sup> 3082, 2914, 1736, 1590, 1446, 1263, 1184, 1105, 900, 753, 652, 541, 457; HRMS-ESI (*m/z*): calcd for C<sub>9</sub>H<sub>7</sub>Cl<sub>2</sub>FNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 258.9699; found 258.9694.

### 2-Chloroethyl 3-chloro-[1,1'-biphenyl]-4-carboxylate and 2-chloroethyl 4-chloro-[1,1'-biphenyl]-3-carboxylate (3da and 3da`)

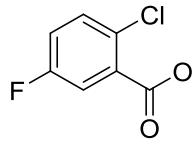
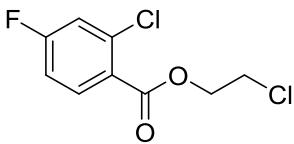


**3da and 3da`** were obtained after purification by column chromatography on silica gel

(petroleum ether / ethyl acetate = 50:1) as a yellow oil in 48% yield (regioisomer ratio= 1:1.5, 28.2 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 2.0 Hz, 0.4H), 7.87 (d, *J* = 8.0 Hz, 0.6H), 7.58 (s, 0.6H), 7.52 (dd, *J* = 8.0, 1.6 Hz, 0.4H), 7.47 – 7.45 (m, 2H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.37 – 7.26 (m, 3H), 4.52 – 4.47 (m, 2H), 3.72 (t, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 164.8, 146.0, 139.8, 138.7, 138.4, 134.6, 132.8, 132.2, 131.5, 131.2, 130.0, 129.6, 129.6, 129.0, 128.9, 128.6, 128.0, 127.4, 127.1, 126.9, 125.1, 64.9, 64.8, 41.4, 41.3; IR (KBr)/cm<sup>-1</sup> 3064, 2934, 1720, 1594, 1453, 1377, 1238, 1117, 1036, 827, 752, 682, 505; HRMS-ESI (*m/z*): calcd for C<sub>15</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 317.0107; found 317.0104.

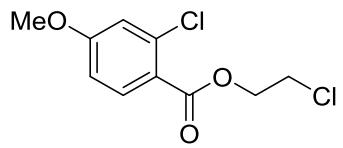
### 2-Chloroethyl 2-chloro-4-fluorobenzoate and 2-chloroethyl 2-chloro-5-fluorobenzoate (3ea and 3ea`)



**3ea and 3ea`** were obtained after purification by column chromatography on silica gel (petroleum ether / ethyl

acetate = 50:1) as a yellow oil in 60% yield (regioisomer ratio= 1:1.9, 28.3 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (dd, *J* = 8.4, 6.0 Hz, 0.34H), 7.58 (dd, *J* = 8.4, 2.8 Hz, 0.66H), 7.42 (dd, *J* = 8.8, 4.8 Hz, 0.66H), 7.21 – 7.13 (m, 1H), 7.06 – 7.01 (m, 0.34H), 4.59 – 4.55 (m, 2H), 3.81 (t, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.3 (d, *J* = 255.3 Hz), 164.0, 163.9 (d, *J* = 2.2 Hz), 160.6 (d, *J* = 246.8 Hz), 136.1 (d, *J* = 10.8 Hz), 133.75 (d, *J* = 9.6 Hz), 132.60 (d, *J* = 7.6 Hz), 130.59 (d, *J* = 7.3 Hz), 129.10 (d, *J* = 3.5 Hz), 125.38 (d, *J* = 3.5 Hz), 120.1 (d, *J* = 22.5 Hz), 118.7 (d, *J* = 24.6), 118.5 (d, *J* = 24.7), 114.1 (d, *J* = 21.2), 65.1, 64.9, 41.4, 41.3; IR (KBr)/cm<sup>-1</sup> 3083, 2925, 1730, 1589, 1466, 1401, 1253, 1195, 1111, 1040, 896, 821, 755, 653, 450; HRMS-ESI (*m/z*): calcd for C<sub>9</sub>H<sub>7</sub>Cl<sub>2</sub>FNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 258.9699; found 258.9695.

### 2-Chloroethyl 2-chloro-4-methoxybenzoate and 2-chloroethyl 2-chloro-5-methoxybenzoate (3fa and 3fa`)

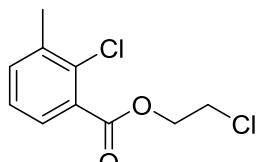
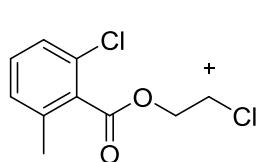


**3fa and 3fa`** were obtained after purification by column chromatography on silica gel

(petroleum ether / ethyl acetate = 30:1) as a yellow oil in 64% yield (regioisomer ratio= 1:1.3, 29.8 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.8 Hz, 0.44H), 7.36 (d, *J* = 3.3 Hz, 0.55H), 7.32 (d, *J* = 8.8 Hz, 0.55H), 6.97 – 6.94 (m, 1H), 6.82 – 6.79 (dd, *J* = 8.8, 2.4 Hz, 0.45H), 4.57 – 4.51 (m, 2H), 3.82 – 3.77 (m, 5H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.9, 164.4, 162.7, 157.9, 136.1, 133.5, 131.8, 129.9, 125.1, 120.8, 119.0, 116.5, 116.3, 112.5, 64.8, 64.5, 55.6, 55.6, 41.54, 41.34; IR (KBr)/cm<sup>-1</sup> 3084, 2941, 2845, 1721, 1591, 1465, 1399, 1239, 1115, 1029, 884, 824, 753, 655, 533; HRMS-ESI (*m/z*): calcd for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>3</sub><sup>+</sup> [M + Na]<sup>+</sup>: 270.9899; found 270.9900.

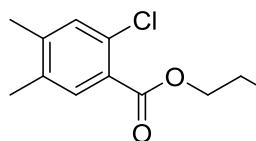
### 2-Chloroethyl 2-chloro-6-methylbenzoate and 2-chloroethyl 2-chloro-3-methylbenzoate (3ga and 3ga`)



**3ga and 3ga`** were obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in

48% yield (regioisomer ratio= 1:1.9, 22.3 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 (dd, *J* = 7.7, 0.7 Hz, 0.6H), 7.37 (d, *J* = 7.2 Hz, 0.6H), 7.23 – 7.19 (m, 1.4H), 7.11 (t, *J* = 4.4 Hz, 0.4H), 4.62 – 4.56 (m, 2H), 3.81 (t, *J* = 5.6 Hz, 2H), 2.42 (s, 1.9H), 2.35 (s, 1.1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.9, 165.8, 138.0, 137.0, 133.9, 133.1, 133.1, 130.7, 130.5, 130.4, 128.6, 128.4, 126.8, 126.1, 65.0, 64.8, 41.4, 41.2, 20.6, 19.5; IR (KBr)/cm<sup>-1</sup> 2926, 1729, 1583, 1441, 1268, 1149, 1043, 753, 452; HRMS-ESI (*m/z*): calcd for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 254.9950; found 254.9949.

### 2-Chloroethyl 2-chloro-4,5-dimethylbenzoate (3ha)

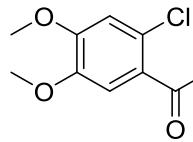


**3ha** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in 55% yield (27.1 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.66 (s, 1H), 7.22 (s, 1H), 4.55

(t, *J* = 6.0 Hz, 2H), 3.81 (t, *J* = 5.6 Hz, 2H), 2.26 (s, 3H), 2.25 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 142.7, 135.3, 132.6, 132.0, 131.1, 126.1, 64.6, 41.5, 19.6, 19.0; IR (KBr)/cm<sup>-1</sup> 2926, 1725, 1601,

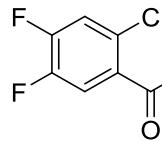
1444, 1381, 1260, 1219, 1122, 1015, 962, 876, 755, 664, 525, 452; HRMS-ESI (*m/z*): calcd for C<sub>11</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 269.0107; found 269.0109.

**2-Chloroethyl-2-chloro-4,5-dimethoxybenzoate (3ia)**



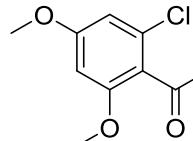
**3ia** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a pale yellow solid in 51% yield (28.4 mg, 51%, m.p. = 81- 82 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.44 (s, 1H), 6.89 (s, 1H), 4.55 (t, *J* = 5.6 Hz, 2H), 3.90 (s, 3H), 3.89 (s, 3H), 3.80 (t, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.5, 152.4, 147.3, 127.5, 120.2, 113.9, 113.8, 64.6, 56.2, 56.1, 41.5; IR (KBr)/cm<sup>-1</sup> 2960, 1722, 1659, 1593, 1509, 1445, 1351, 1262, 1188, 1117, 1019, 955, 863, 760, 671; HRMS-ESI (*m/z*): calcd for C<sub>11</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>4</sub><sup>+</sup> [M + Na]<sup>+</sup>: 301.0005; found 301.0004.

**2-Chloroethyl-2-chloro-4,5-difluorobenzoate (3ja)**



**3ja** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in 47% yield (23.9 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (dd, *J* = 10.4, 8.4 Hz, 1H), 7.31 (dd, *J* = 9.6, 6.8 Hz, 1H), 4.58 (t, *J* = 6.0 Hz, 2H), 3.81 (t, *J* = 6.0 Hz, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -128.2 - -128.3 (m), -137.6 - -137.7 (m); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.0, 152.2 (dd, *J* = 257.8, 13.4 Hz), 148.5 (dd, *J* = 249.5, 12.5 Hz), 130.3 (dd, *J* = 8.4, 3.7 Hz), 125.5 (dd, *J* = 5.0, 4.0 Hz), 120.7 (dd, *J* = 20.1, 1.8 Hz), 120.4 (d, *J* = 20.3 Hz), 65.2, 41.3; IR (KBr)/cm<sup>-1</sup> 3068, 2931, 1734, 1598, 1498, 1393, 1303, 1235, 1174, 1106, 1009, 893, 771, 665, 454; HRMS-ESI (*m/z*): calcd for C<sub>9</sub>H<sub>6</sub>Cl<sub>2</sub>F<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 276.9605; found 276.9603.

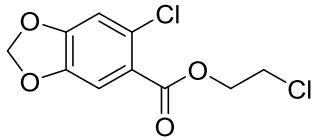
**2-Chloroethyl 2-chloro-4,6-dimethoxybenzoate (3ka)**



**3ka** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a yellow oil in 54% yield (30.0 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.50 (s, 1H), 6.36 (s, 1H), 4.54 (t, *J* = 5.6 Hz, 2H), 3.78 – 3.75 (m, 8H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 161.8, 158.5, 132.6, 115.9,

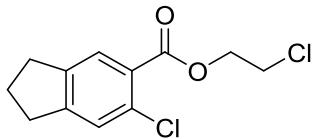
106.0, 97.5, 64.9, 56.1, 55.6, 41.1; IR (KBr)/cm<sup>-1</sup> 3091, 2928, 1721, 1579, 1431, 1257, 1139, 1019, 936, 821, 750, 620; HRMS-ESI (*m/z*): calcd for C<sub>11</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>4</sub><sup>+</sup> [M + Na]<sup>+</sup>: 301.0005; found 301.0010.

### 2-Chloroethyl-6-chlorobenzo[d][1,3]dioxole-5-carboxylate (3la)



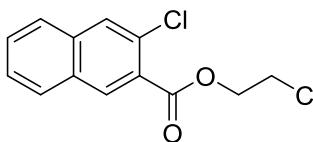
**3la** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a yellow oil in 40% yield (21.0 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.36 (s, 1H), 6.88 (s, 1H), 6.04 (s, 2H), 4.53 (t, *J* = 5.6 Hz, 2H), 3.79 (t, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.2, 151.2, 146.5, 128.8, 121.7, 111.3, 110.8, 102.6, 64.7, 41.5; IR (KBr)/cm<sup>-1</sup> 3076, 2910, 1720, 1614, 1480, 1401, 1240, 1126, 1029, 931, 854, 747, 654, 536; HRMS-ESI (*m/z*): calcd for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>NaO<sub>4</sub><sup>+</sup> [M + Na]<sup>+</sup>: 284.9692; found 284.9694.

### 2-Chloroethyl-6-chloro-2,3-dihydro-1*H*-indene-5-carboxylate (3ma)



**3ma** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale white solid in 44% yield (22.7 mg, m.p. = 60- 61 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.72 (s, 1H), 7.28 (s, 1H), 4.56 (t, *J* = 6.0 Hz, 2H), 3.81 (t, *J* = 5.6 Hz, 2H), 2.90 (q, *J* = 6.8 Hz, 4H), 2.14 - 2.07 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.4, 150.3, 143.0, 131.7, 127.0, 126.8, 126.6, 64.6, 41.5, 32.8, 32.0, 25.4; IR (KBr)/cm<sup>-1</sup> 2948, 1725, 1606, 1449, 1390, 1254, 1197, 1110, 1009, 950, 878, 753, 662, 520; HRMS-ESI (*m/z*): calcd for C<sub>12</sub>H<sub>12</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 281.0107; found 281.0112.

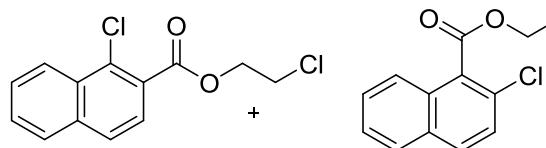
### 2-Chloroethyl-3-chloro-2-naphthoate (3na)



**3na** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow solid in 50% yield (26.8 mg, m.p. = 109- 110 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 8.43 (s, 1H), 7.92 (s, 1H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.4 Hz, 1H), 7.60 (t, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 4.65 (t, *J* = 5.6 Hz, 2H), 3.87 (t, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 165.2, 135.0, 132.9, 130.7, 129.4, 129.3, 129.1, 128.8, 127.0, 126.9, 126.8, 65.0, 41.5; IR (KBr)/cm<sup>-1</sup>

3055, 2924, 1719, 1620, 1439, 1378, 1261, 1194, 1108, 996, 883, 749, 656, 465; HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 290.9950; found 290.9954.

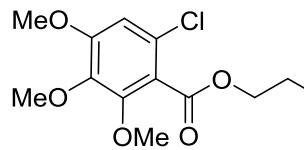
**2-Chloroethyl 1-chloro-2-naphthoate and 2-chloroethyl 2-chloro-1-naphthoate (3oa and 3oa`)**



3oa and 3oa` were obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate =

50:1) as a yellow oil in 57% yield (regioisomer ratio = 1:1.4, 30.5 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.42 (d, *J* = 8.4 Hz, 0.39H), 7.83 – 7.72 (m, 3H), 7.63 – 7.54 (m, 1.5H), 7.48 (t, *J* = 7.6 Hz, 0.61H), 7.40 (d, *J* = 8.8 Hz, 0.5H), 4.76 (t, *J* = 5.6 Hz, 1.2H), 4.65 (t, *J* = 5.6 Hz, 0.8H), 3.88 – 3.84 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.5, 165.7, 135.2, 132.4, 131.3, 131.0, 130.9, 130.3, 129.6, 128.9, 128.3, 128.1, 127.9, 127.9, 127.7, 126.9, 126.8, 126.5, 126.5, 125.7, 125.5, 124.2, 65.2, 64.9, 41.4, 41.2; IR (KBr)/cm<sup>-1</sup> 3066, 2952, 1729, 1588, 1502, 1444, 1381, 1266, 1224, 1130, 1012, 873, 811, 749, 663, 540; HRMS-ESI (*m/z*): calcd for C<sub>13</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 290.9950; found 290.9954.

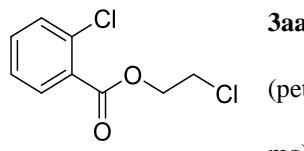
**2-Chloroethyl 6-chloro-2,3,4-trimethoxybenzoate (3pa)**



3pa was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a pale yellow oil in 34% yield (20.9 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.68 (s, 1H),

4.56 (t, *J* = 5.6 Hz, 2H), 3.92 (s, 3H), 3.84 (s, 3H), 3.83 (s, 3H), 3.77 (t, *J* = 5.6 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.7, 155.0, 151.6, 141.0, 125.6, 121.0, 108.8, 65.1, 61.9, 60.9, 56.3, 41.1; IR (KBr)/cm<sup>-1</sup> 2931, 1728, 1582, 1452, 1389, 1266, 1151, 1103, 1015, 944, 825, 751, 656, 573; HRMS-ESI (*m/z*): calcd for C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>NaO<sub>5</sub><sup>+</sup> [M + Na]<sup>+</sup>: 331.0110; found 331.0115.

**2-Chloroethyl-2-chlorobenzoate (3aa)**

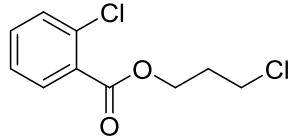


3aa was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in 60% yield (26.1 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 7.6 Hz, 1 H), 7.47 – 7.41 (m, 2

H), 7.34 – 7.30 (m, 1 H), 4.58 (t, *J* = 6.0 Hz, 2 H), 3.81 (t, *J* = 6.0 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)

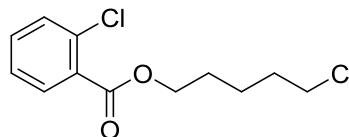
$\delta$  165.1, 133.9, 132.8, 131.6, 131.1, 129.4, 126.6, 64.8, 41.4; IR (KBr)/cm<sup>-1</sup> 3071, 1715, 1574, 1436, 1373, 1246, 1110, 1035, 749, 655, 543, 474; HRMS-ESI (*m/z*): calcd for C<sub>9</sub>H<sub>8</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 240.9794; found 240.9791.

### 3-Chloropropyl-2-chlorobenzoate (3ac)



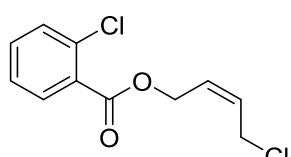
**3ac** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in 53% yield (24.6 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.31 (t, *J* = 7.6 Hz, 1H), 4.49 (t, *J* = 6.4 Hz, 2H), 3.71 (t, *J* = 6.4 Hz, 2H), 2.26 – 2.20 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.6, 133.5, 132.6, 131.4, 131.0, 130.0, 126.6, 62.2, 41.2, 31.5; IR (KBr)/cm<sup>-1</sup> 2950, 1722, 1586, 1441, 1259, 1119, 1039, 898, 749, 651; HRMS-ESI (*m/z*): calcd for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 254.9950; found 254.9954.

### 5-Chloropentyl-2-chlorobenzoate (3ad)



**3ad** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale yellow oil in 16% yield (8.3 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.40 (m, 2H), 7.32 (t, *J* = 8.0 Hz, 1H), 4.36 (t, *J* = 6.4 Hz, 2H), 3.56 (t, *J* = 6.8 Hz, 2H), 1.89 – 1.78 (m, 4H), 1.66 – 1.58 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.8, 133.5, 132.4, 131.3, 131.0, 130.3, 126.6, 65.2, 44.7, 32.1, 27.9, 23.4; IR (KBr)/cm<sup>-1</sup> 3071, 2934, 1723, 1589, 1451, 1385, 1258, 1122, 1039, 953, 837, 744, 649, 455; HRMS-ESI (*m/z*): calcd for C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 283.0263; found 283.0266.

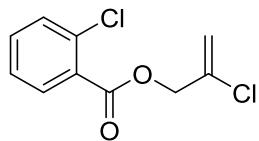
### (Z)-4-Chlorobut-2-en-1-yl 2-chlorobenzoate (3ae)



**3ae** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 46% yield (22.4 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.81 (d, *J* = 7.6 Hz, 1H), 7.42 (q, *J* = 8.0 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 5.94 – 5.83 (m, 2H), 4.93 (d, *J* = 6.0 Hz, 2H), 4.20 (d, *J* = 7.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  165.2, 133.7, 132.6, 131.4, 131.0, 130.3, 129.7, 127.4, 126.5,

60.2, 38.6; IR (KBr)/cm<sup>-1</sup> 3080, 2933, 1729, 1587, 1455, 1255, 1121, 1042, 948, 834, 747, 465; HRMS-ESI (*m/z*): calcd for C<sub>11</sub>H<sub>10</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 266.9950; found 266.9948.

### 2-Chlorallyl 2-chlorobenzoate (3af)

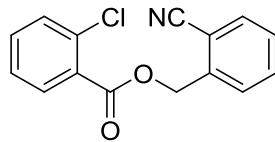


**3af** was obtained after purification by column chromatography on silica gel

(petroleum ether / ethyl acetate = 50:1) as a yellow oil in 28% yield (12.9 mg).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (d, *J* = 7.6 Hz, 1H), 7.45 (q, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.2 Hz, 1H), 5.60 (s, 1H), 5.47 (s, 1H), 4.90 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.6, 135.5, 134.0, 132.9, 131.6, 131.2, 129.2, 126.6, 115.5, 66.8; IR (KBr)/cm<sup>-1</sup> 2926, 1731, 1642, 1588, 1440, 1368, 1255, 1113, 1043, 966, 895, 749, 643; HRMS-ESI (*m/z*): calcd for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 252.9794; found 252.9792.

### 2-Cyanobenzyl 2-chlorobenzoate (3ag)

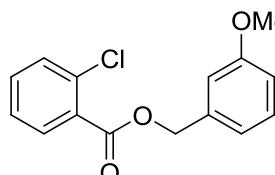


**3ag** was obtained after purification by column chromatography on silica gel

(petroleum ether / ethyl acetate = 10:1) as a pale yellow solid in 78% yield

(42.3 mg, m.p. = 68- 69 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.71 (d, *J* = 7.6 Hz, 1H), 7.64 (q, *J* = 8.0 Hz, 2H), 7.48 – 7.41 (m, 3H), 7.32 (t, *J* = 7.2 Hz, 1H), 5.56 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.8, 138.8, 133.8, 132.9, 132.9, 132.8, 131.6, 131.0, 129.6, 129.1, 128.8, 126.6, 116.9, 112.1, 64.6; IR (KBr)/cm<sup>-1</sup> 3071, 2937, 2226, 1730, 1590, 1446, 1375, 1253, 1118, 1044, 953, 888, 823, 750, 603, 551, 457; HRMS-ESI (*m/z*): calcd for C<sub>15</sub>H<sub>11</sub>ClNO<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup>: 272.0473; found 272.0475.

### 3-Methoxybenzyl 2-chlorobenzoate (3ah)



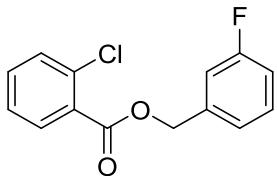
**3ah** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 30:1) as a yellow oil in 74% yield

(40.8 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.88 (d, *J* = 7.2 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.35 – 7.30 (m, 2H), 7.08 – 7.05 (m, 2H), 6.93 – 6.90 (dd, *J* = 8.4, 1.6 Hz, 1H), 5.39 (s, 2H), 3.84 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.3, 159.7, 137.0, 133.7,

132.5, 131.4, 131.0, 129.9, 129.6, 126.5, 120.4, 113.8, 113.6, 67.0, 55.2; IR (KBr)/cm<sup>-1</sup> 3073, 2942, 1722,

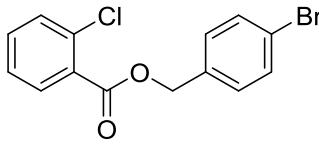
1592, 1447, 1370, 1258, 1114, 1038, 949, 858, 749, 691, 543; HRMS-ESI (*m/z*): calcd for C<sub>15</sub>H<sub>13</sub>ClNaO<sub>3</sub><sup>+</sup> [M + Na]<sup>+</sup>: 299.0445; found 299.0450.

### 3-Fluorobenzyl 2-chlorobenzoate (3ai)



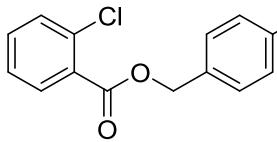
**3ai** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 100:1) as a pale yellow oil in 79% yield (41.7 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.50 – 7.43 (m, 2H), 7.40 – 7.32 (m, 2H), 7.25 (d, *J* = 7.6 Hz, 1H), 7.20 (d, *J* = 9.6 Hz, 1H), 7.06 (t, *J* = 8.4 Hz, 1H), 5.39 (s, 2H); <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -112.6 – -112.7 (q, *J* = 9.6 Hz); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.3, 162.8 (d, *J* = 245 Hz), 138.0 (d, *J* = 7.4 Hz), 133.9, 132.7, 131.5, 131.1, 130.2 (d, *J* = 8.1 Hz), 129.7, 126.6, 123.6 (d, *J* = 2.9 Hz), 115.11 (d, *J* = 17.6 Hz), 115.0 (d, *J* = 18.6 Hz), 66.3; IR (KBr)/cm<sup>-1</sup> 3070, 1725, 1588, 1442, 1369, 1249, 1117, 1041, 940, 864, 747, 689, 528; HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>10</sub>ClFNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 287.0246; found 287.0245.

### 4-Bromobenzyl 2-chlorobenzoate (3aj)



**3aj** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 100:1) as a pale purple solid in 88% yield (57.0 mg, m.p. = 54- 55 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 8.1 Hz, 2H), 7.46 – 7.39 (m, 2H), 7.34 – 7.28 (m, 3H), 5.32 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.3, 134.6, 133.8, 132.7, 131.7, 131.5, 131.1, 130.0, 129.7, 126.6, 122.4, 66.4; IR (KBr)/cm<sup>-1</sup> 3066, 2930, 1723, 1587, 1465, 1366, 1257, 1116, 1042, 947, 746, 488; HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>10</sub>BrClNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 346.9445; found 346.9441.

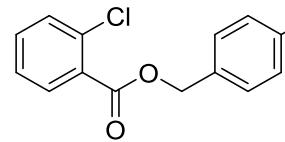
### 4-Nitrobenzyl 2-chlorobenzoate (3ak)



**3ak** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 10:1) as a yellow solid in 58% yield (33.8 mg, m.p. = 108- 109 °C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (d, *J* = 8.4 Hz, 2H), 7.87 (d, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 8.4 Hz, 2H), 7.48 – 7.43 (m, 2H), 7.36 – 7.32 (m, 1H), 5.46 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 147.8, 142.8, 133.9, 133.0, 131.6,

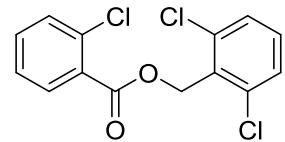
131.2, 129.3, 128.5, 126.7, 123.8, 65.7; IR (KBr)/cm<sup>-1</sup> 2922, 1721, 1591, 1516, 1451, 1342, 1249, 1115, 1042, 982, 836, 740, 547, 452; HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>10</sub>ClNNaO<sub>4</sub><sup>+</sup> [M + Na]<sup>+</sup>: 314.0191; found 314.0190.

#### 4-Methylbenzyl 2-chlorobenzoate (3al)



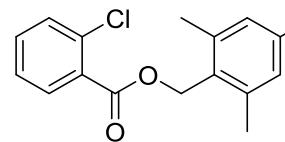
**3al** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a gray oil in 80% yield (41.6 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.0 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.35 (d, *J* = 7.6 Hz, 2H), 7.29 – 7.25 (m, 1H), 7.19 (d, *J* = 7.6 Hz, 2H), 5.33 (s, 2H), 2.35 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.5, 138.2, 133.8, 132.6, 132.5, 131.5, 131.0, 130.1, 129.3, 128.5, 126.5, 67.2, 21.2; IR (KBr)/cm<sup>-1</sup> 2922, 1723, 1590, 1441, 1370, 1258, 1115, 1041, 939, 804, 747, 570, 471; HRMS-ESI (*m/z*): calcd for C<sub>15</sub>H<sub>13</sub>ClNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 283.0496; found 283.0497.

#### 2,6-Dichlorobenzyl 2-chlorobenzoate (3am)



**3am** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a pale green oil in 85% yield (53.4 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.45 (d, *J* = 7.2 Hz, 1H), 7.42 – 7.40 (m, 1H) 7.37 (d, *J* = 8.0 Hz, 2H), 5.67 (s, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 137.0, 133.8, 132.6, 131.5, 131.1, 131.0, 130.6, 129.6, 128.4, 126.4, 62.1; IR (KBr)/cm<sup>-1</sup> 3077, 2913, 1724, 1575, 1436, 1366, 1248, 1112, 1038, 956, 881, 747, 554, 470; HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>9</sub>Cl<sub>3</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 336.9560; found 336.9565.

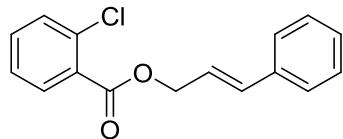
#### 2,4,6-Trimethylbenzyl 2-chlorobenzoate (3an)



**3an** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a purple oil in 78% yield (44.9 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.40 (m, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 6.95 (s, 2H), 5.49 (s, 2H), 2.47 (s, 6H), 2.34 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.8, 138.5, 138.3, 133.6, 132.3, 131.3, 130.9, 130.2, 129.0, 128.7, 126.4, 62.0,

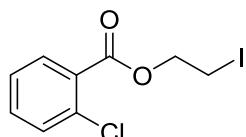
21.0, 19.5; IR (KBr)/cm<sup>-1</sup> 2921, 1722, 1592, 1442, 1368, 1246, 1116, 1039, 930, 849, 745, 584, 472; HRMS-ESI (*m/z*): calcd for C<sub>17</sub>H<sub>17</sub>ClNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 311.0809; found 311.0812.

### Cinnamyl 2-chlorobenzoate (3ao)



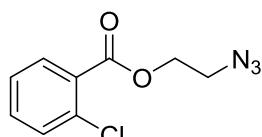
**3ao** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 75% yield (40.8 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.46 – 7.38 (m, 4H), 7.34 – 7.24 (m, 4H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.43 – 6.35 (m, 1H), 4.99 (d, *J* = 6.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.4, 136.1, 134.7, 133.7, 132.5, 131.4, 131.0, 130.1, 128.6, 128.1, 126.6, 126.5, 122.7, 66.0; IR (KBr)/cm<sup>-1</sup> 3028, 2926, 1720, 1585, 1437, 1367, 1244, 1115, 1039, 954, 743, 690, 459; HRMS-ESI (*m/z*): calcd for C<sub>16</sub>H<sub>13</sub>ClNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 295.0496; found 295.0494.

### 2-Iodoethyl 2-chlorobenzoate (4)



**4** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a brown oil in 79% yield (49.0 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.44 (q, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 6.8 Hz, 1H), 4.59 (t, *J* = 6.8 Hz, 2H), 3.43 (t, *J* = 6.8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.8, 133.9, 132.8, 131.6, 131.1, 129.4, 126.6, 65.4, -0.1; IR (KBr)/cm<sup>-1</sup> 2935, 1723, 1590, 1439, 1373, 1255, 1125, 1047, 958, 750; HRMS-ESI (*m/z*): calcd for C<sub>9</sub>H<sub>8</sub>ClNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 332.9150; found 332.9148.

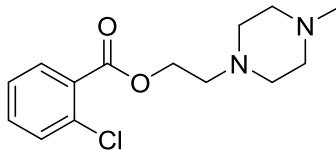
### 2-Azidoethyl 2-chlorobenzoate (5)



**5** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 95% yield (42.7 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.47 – 7.40 (m, 2H), 7.34 – 7.30 (m, 1H), 4.48 (t, *J* = 5.2 Hz, 2H), 3.61 (t, *J* = 5.2 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.1, 133.9, 132.8, 131.5, 131.1, 129.2, 126.6, 63.7, 49.7; IR (KBr)/cm<sup>-1</sup> 3075, 2922, 2857, 2094,

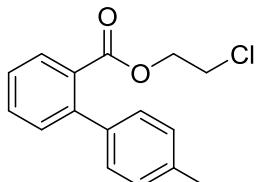
1722, 1586, 1439, 1362, 1243, 1114, 1038, 842, 746, 641, 544, 462; HRMS-ESI (*m/z*): calcd for C<sub>9</sub>H<sub>8</sub>ClN<sub>3</sub>NaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 248.0197; found 248.0199.

### 2-(4-Methylpiperazin-1-yl)ethyl 2-chlorobenzoate (6)



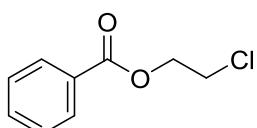
**6** was obtained after purification by column chromatography on silica gel (Hexane: EtOAc = 1:1) as a yellow oil in 42% yield (59.2 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.79 (d, *J* = 7.2 Hz, 1H), 7.40 (q, *J* = 8.0 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 1H), 4.45 (t, *J* = 6.0 Hz, 2H), 2.76 (t, *J* = 5.6 Hz, 2H), 2.59 (s, 4H), 2.44 (s, 4H), 2.26 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.5, 133.5, 132.4, 131.2, 130.9, 130.2, 126.4, 62.8, 56.3, 54.9, 53.2, 45.9; IR (KBr)/cm<sup>-1</sup> 3070, 2936, 2798, 1727, 1591, 1451, 1370, 1286, 1124, 1045, 941, 750, 646, 461; HRMS-ESI (*m/z*): calcd for C<sub>14</sub>H<sub>20</sub>ClN<sub>2</sub>O<sub>2</sub><sup>+</sup> [M + H]<sup>+</sup>: 283.1208; found 283.1206.

### 2-Chloroethyl 4'-methyl-[1,1'-biphenyl]-2-carboxylate (7)



**7** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 38% yield (21.0 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.40 (q, *J* = 7.6, 2H), 7.22 (s, 4H), 4.32 (t, *J* = 6.0 Hz, 2H), 3.45 (t, *J* = 6.0 Hz, 2H), 2.41 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.2, 142.8, 138.4, 137.0, 131.5, 130.8, 130.2, 129.9, 128.8, 128.2, 127.0, 64.3, 41.0, 21.2; IR (KBr)/cm<sup>-1</sup> 3026, 2923, 1724, 1591, 1449, 1372, 1259, 1119, 956, 823, 753, 523; HRMS-ESI (*m/z*): calcd for C<sub>16</sub>H<sub>15</sub>ClNaO<sub>2</sub><sup>+</sup> [M + Na]<sup>+</sup>: 297.0653; found 297.0648.

### 2-Chloroethyl benzoate (11)

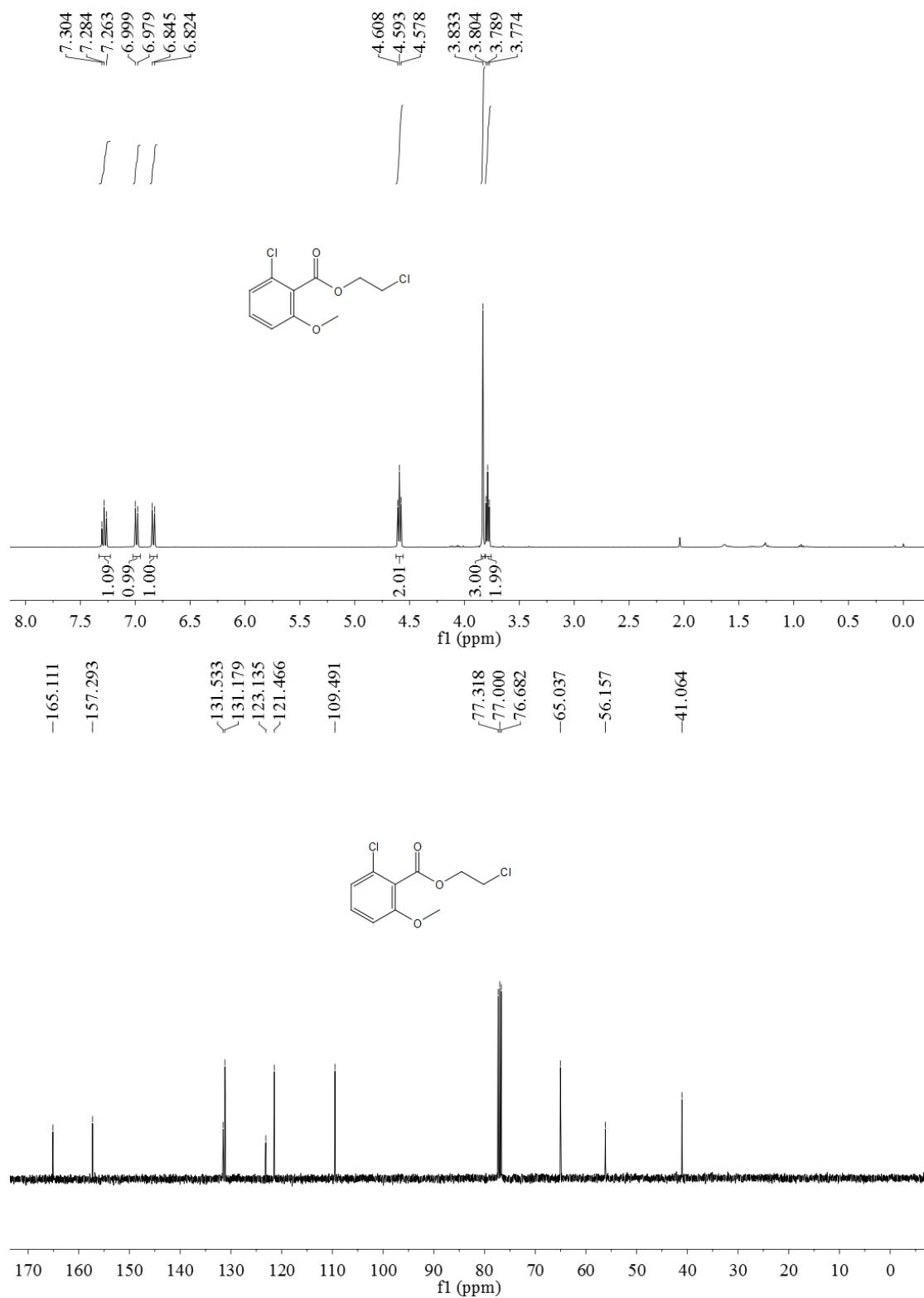


**11** was obtained after purification by column chromatography on silica gel (petroleum ether / ethyl acetate = 50:1) as a yellow oil in 88% yield (32.4 mg). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.07 (d, *J* = 8.0 Hz, 2H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.44 (t, *J* = 7.6 Hz, 2H), 4.56 (t, *J* = 5.6 Hz, 2H), 3.80 (t, *J* = 6.0 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 166.0, 133.2, 129.6, 129.5, 128.3, 64.4, 41.6; IR (KBr)/cm<sup>-1</sup> 3068, 2945, 1723, 1595, 1448,

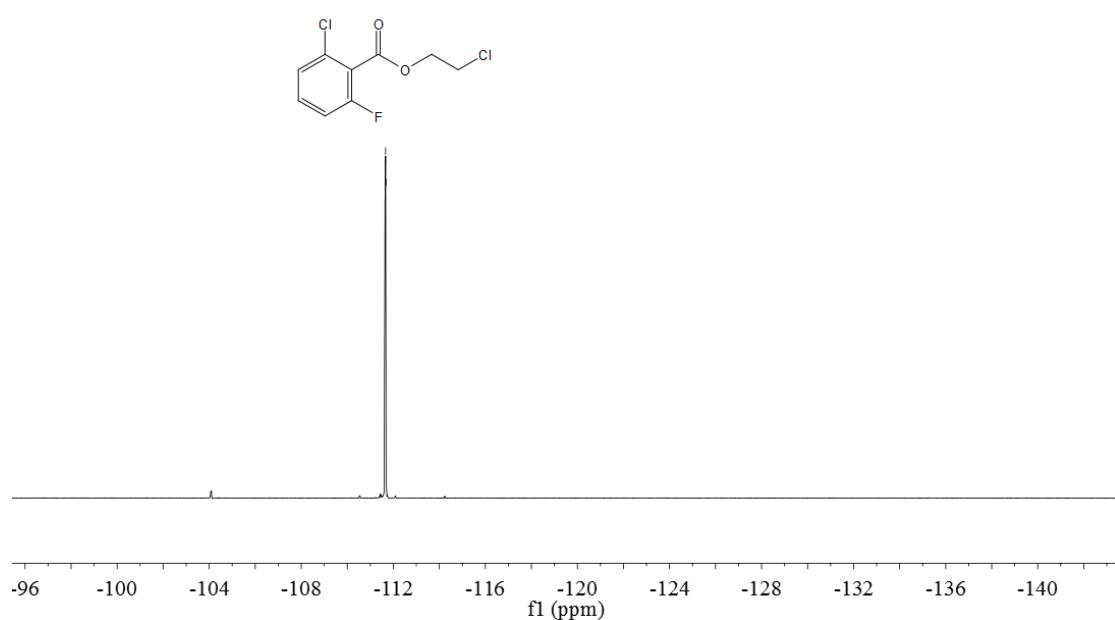
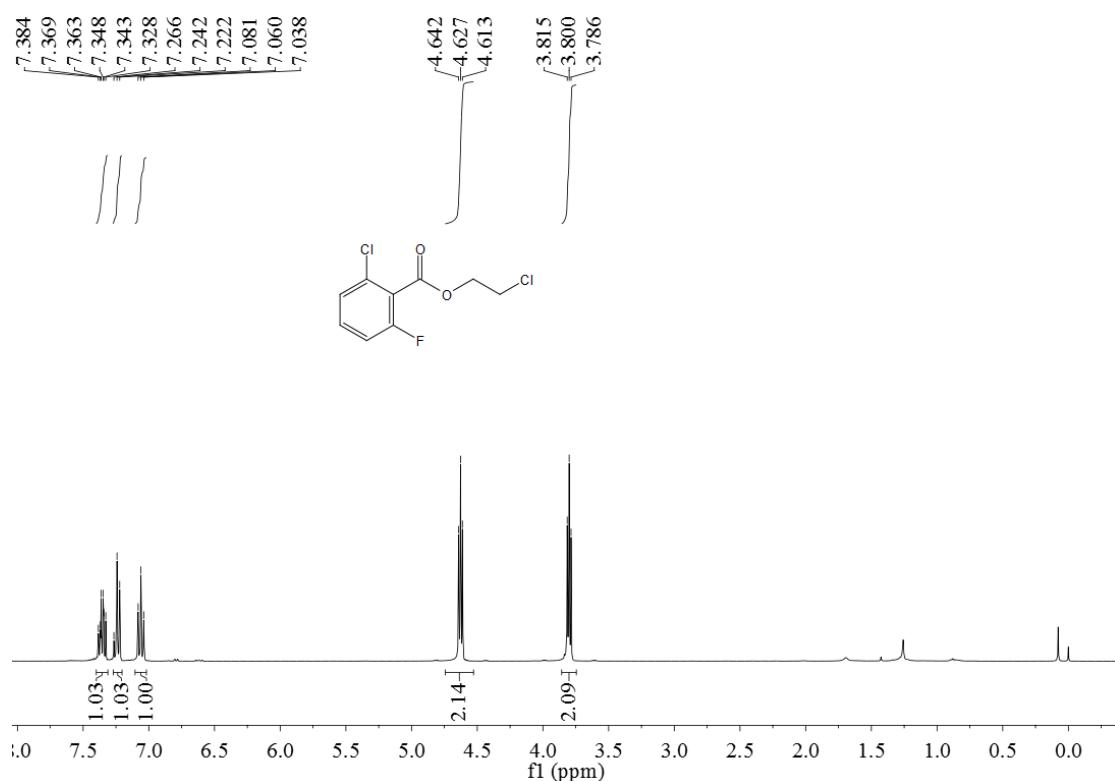
1379, 1266, 1180, 1111, 1026, 953, 707, 505; HRMS-ESI (*m/z*): calcd for  $C_9H_9ClNaO_2^+$  [M + Na]<sup>+</sup>: 207.0183; found 207.0181.

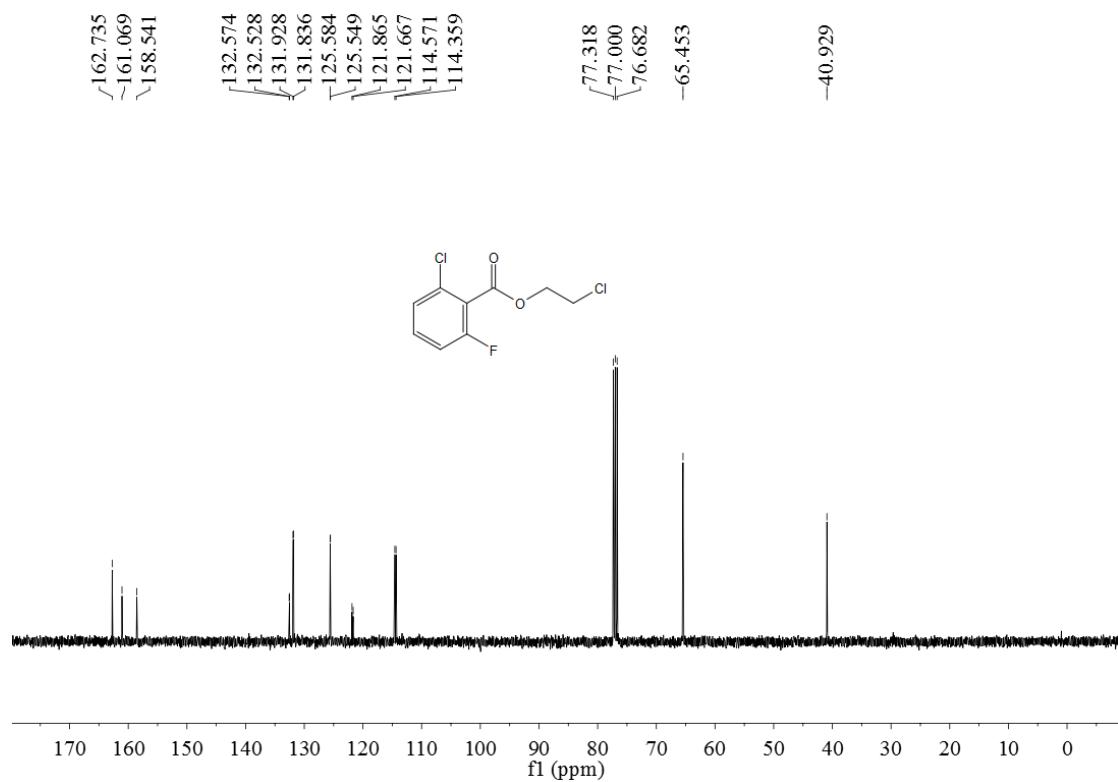
## 11. NMR Spectra

**3ba**

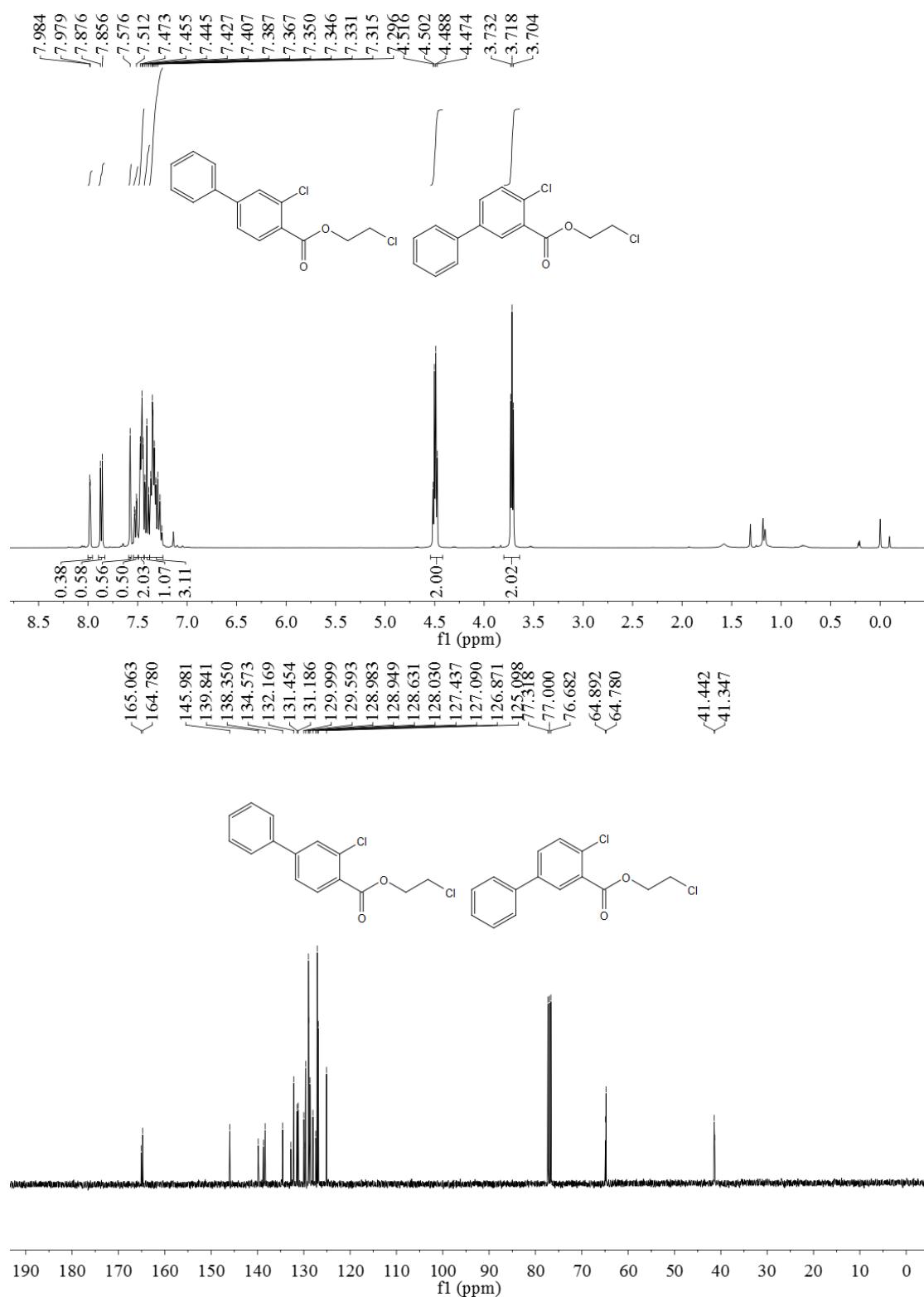


**3ca**

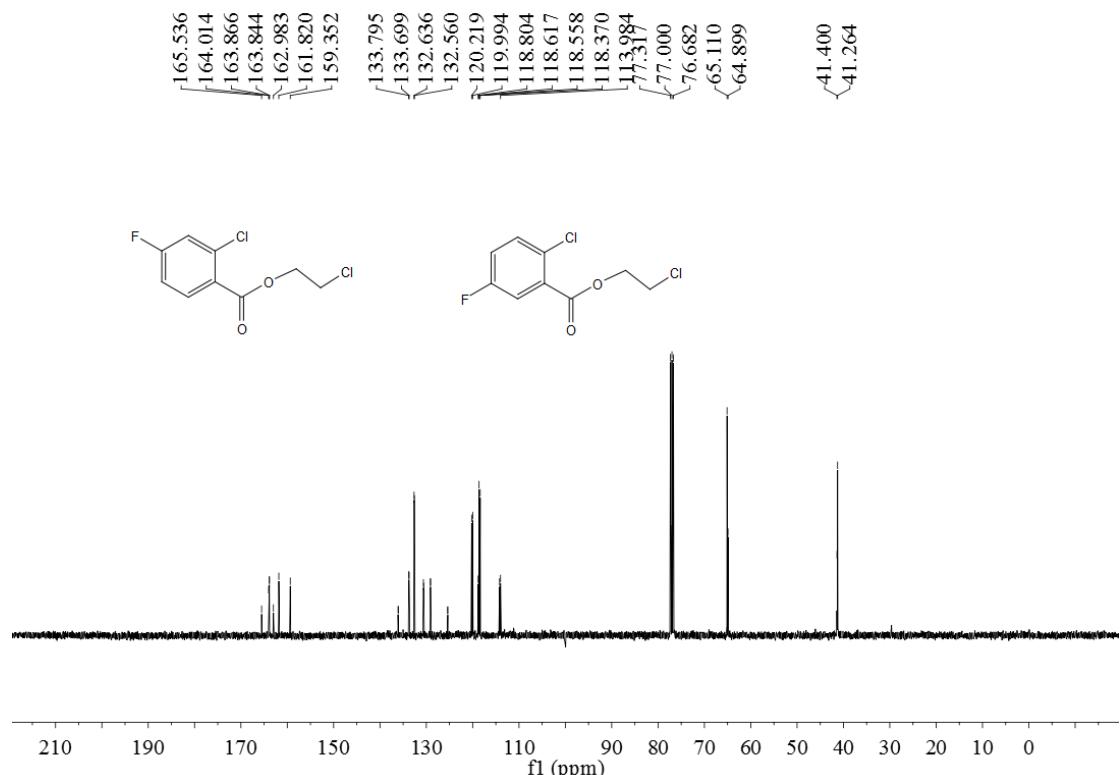
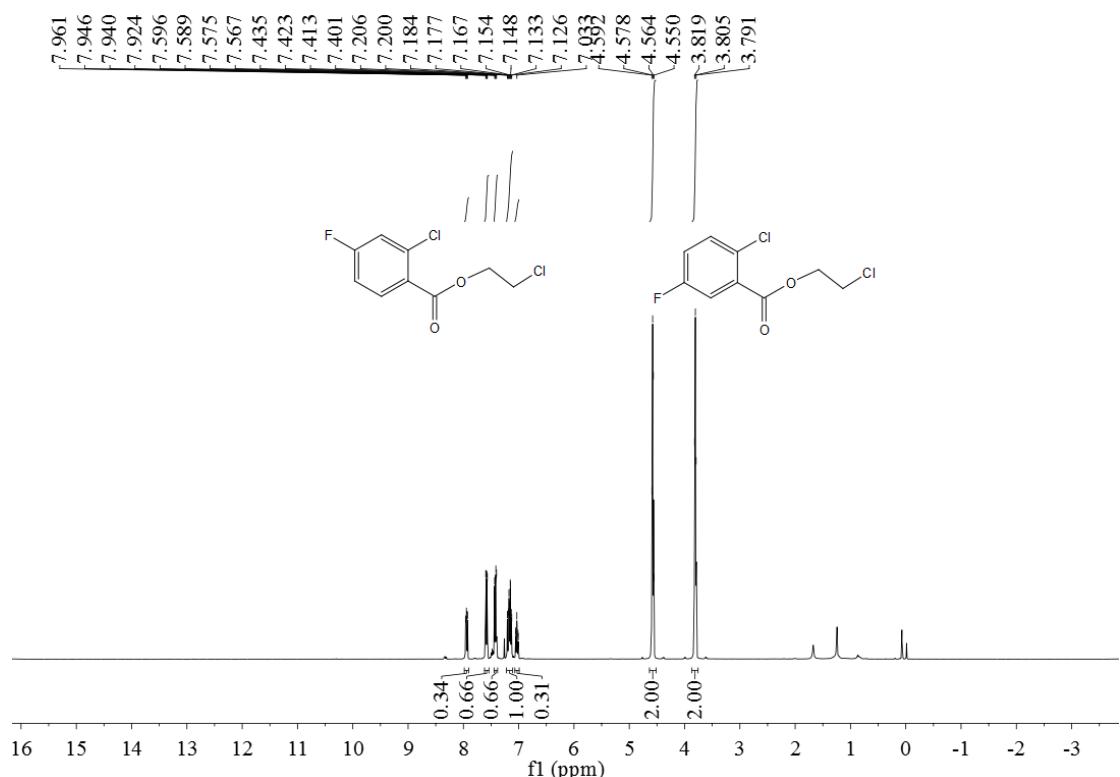




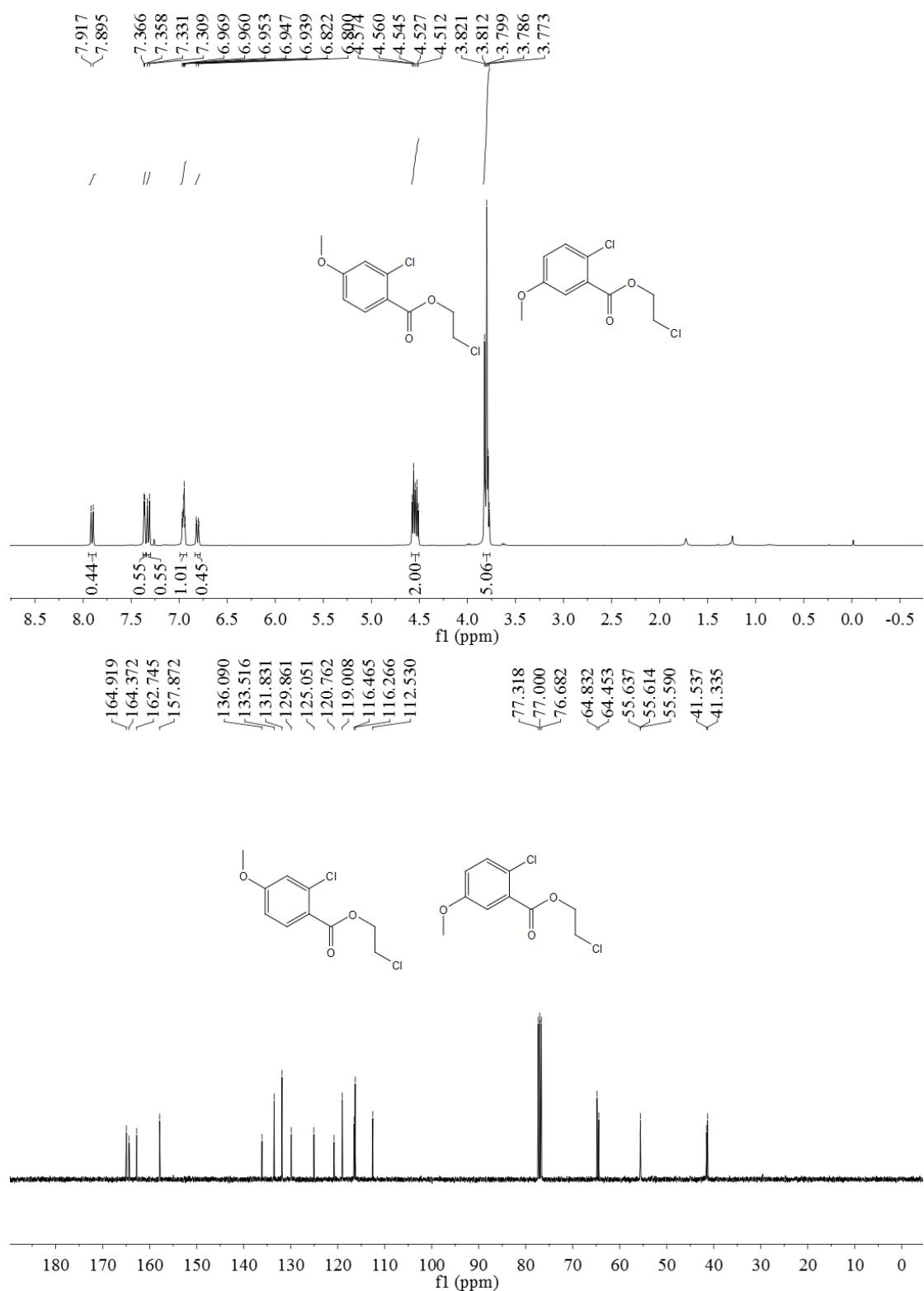
## 3da and 3da`



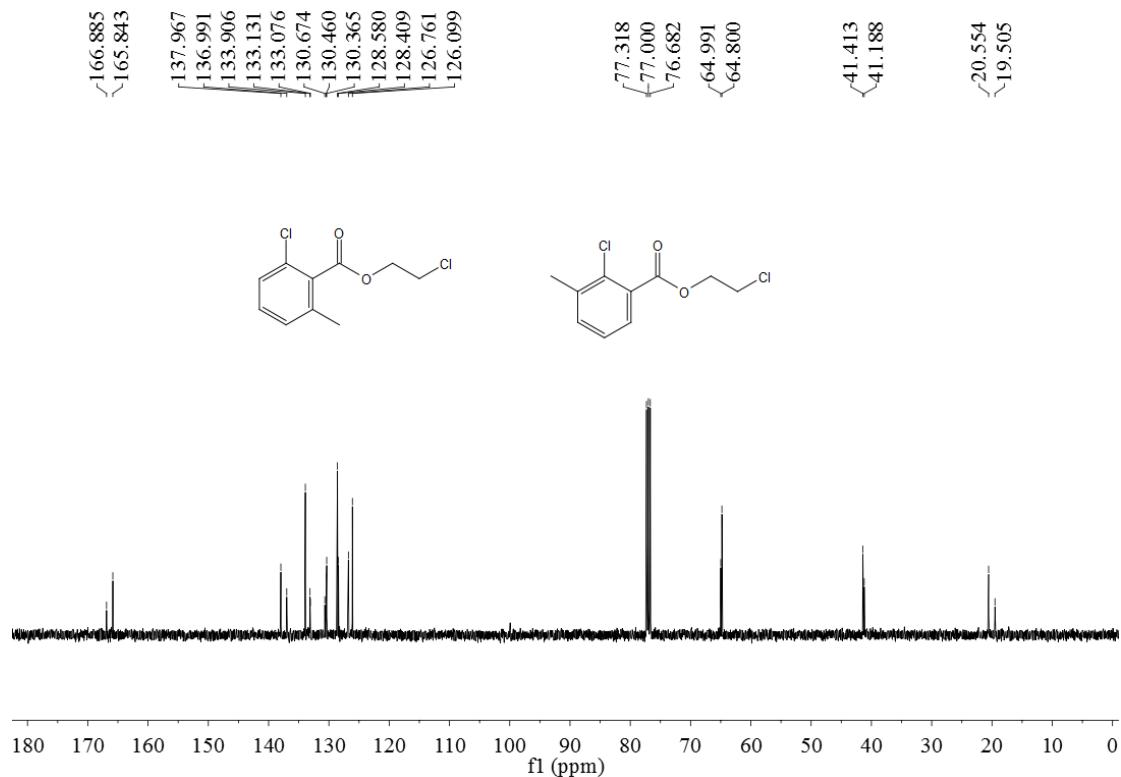
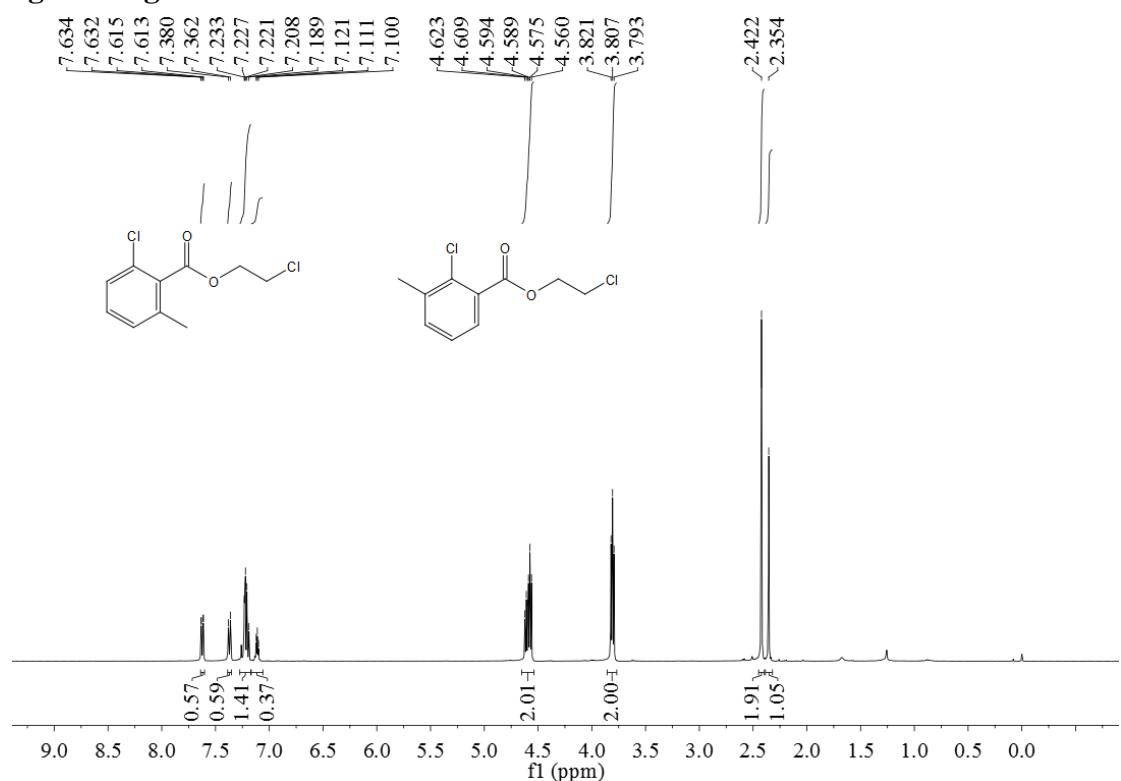
**3ea and 3ea'**



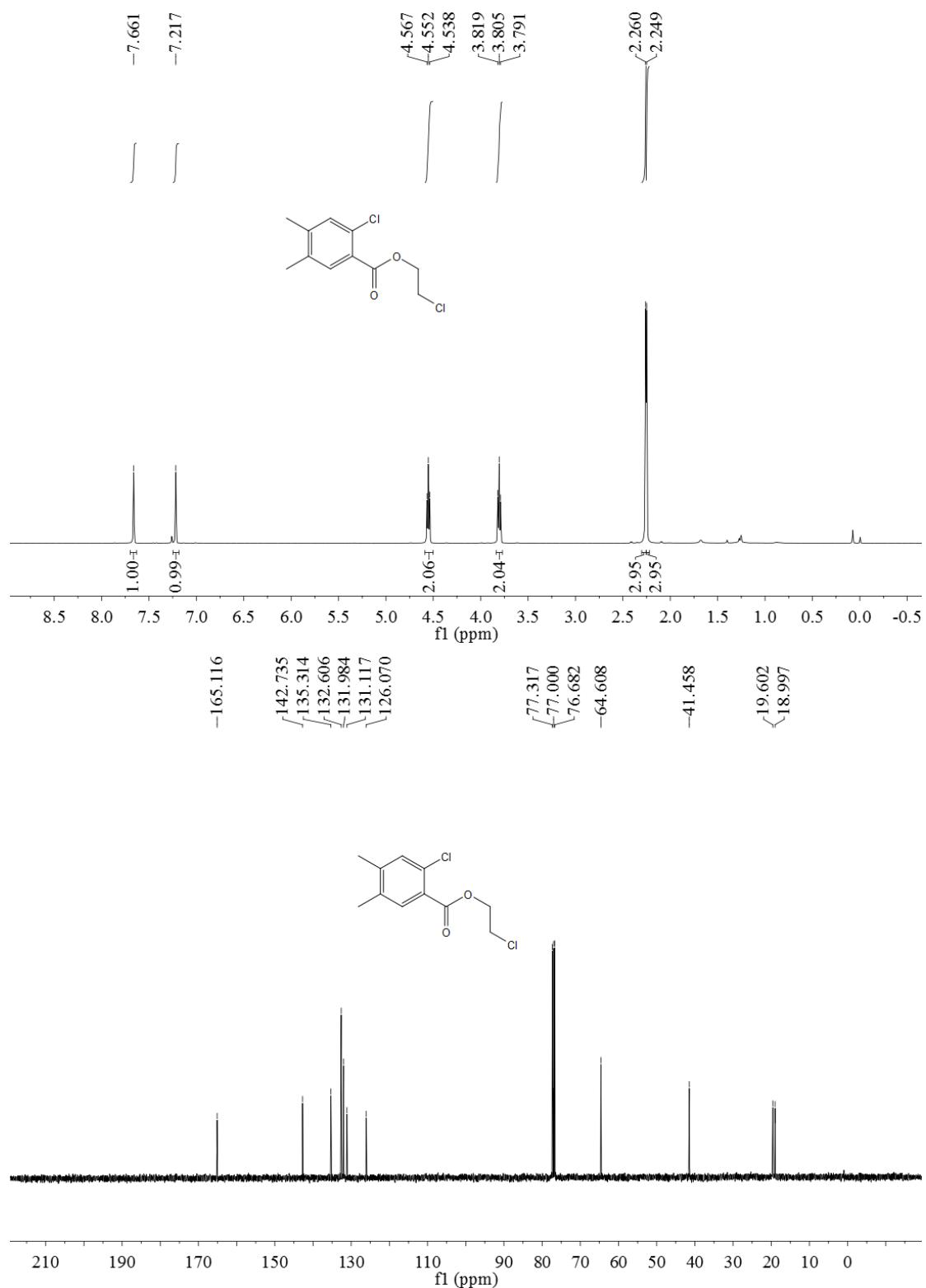
**3fa and 3fa`**



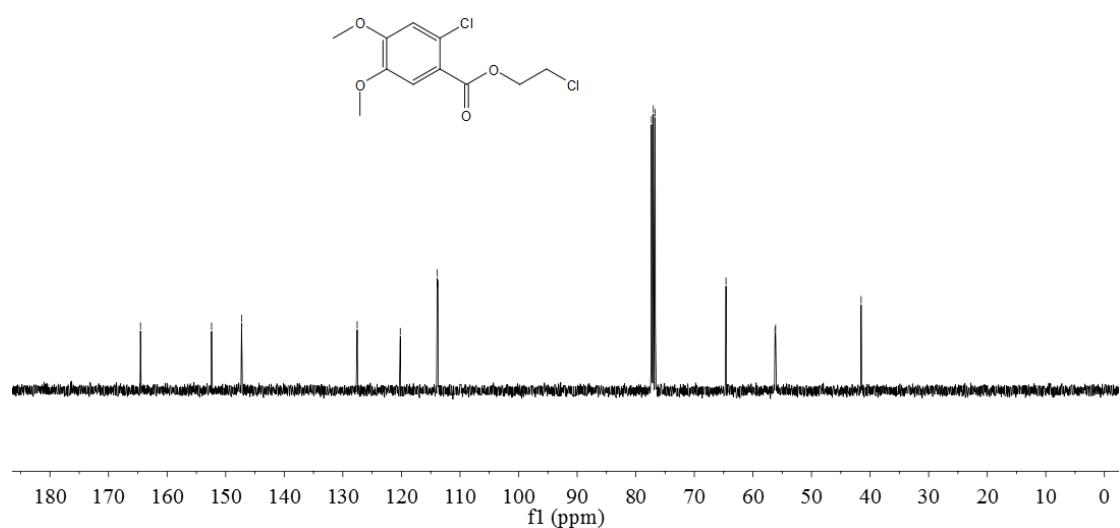
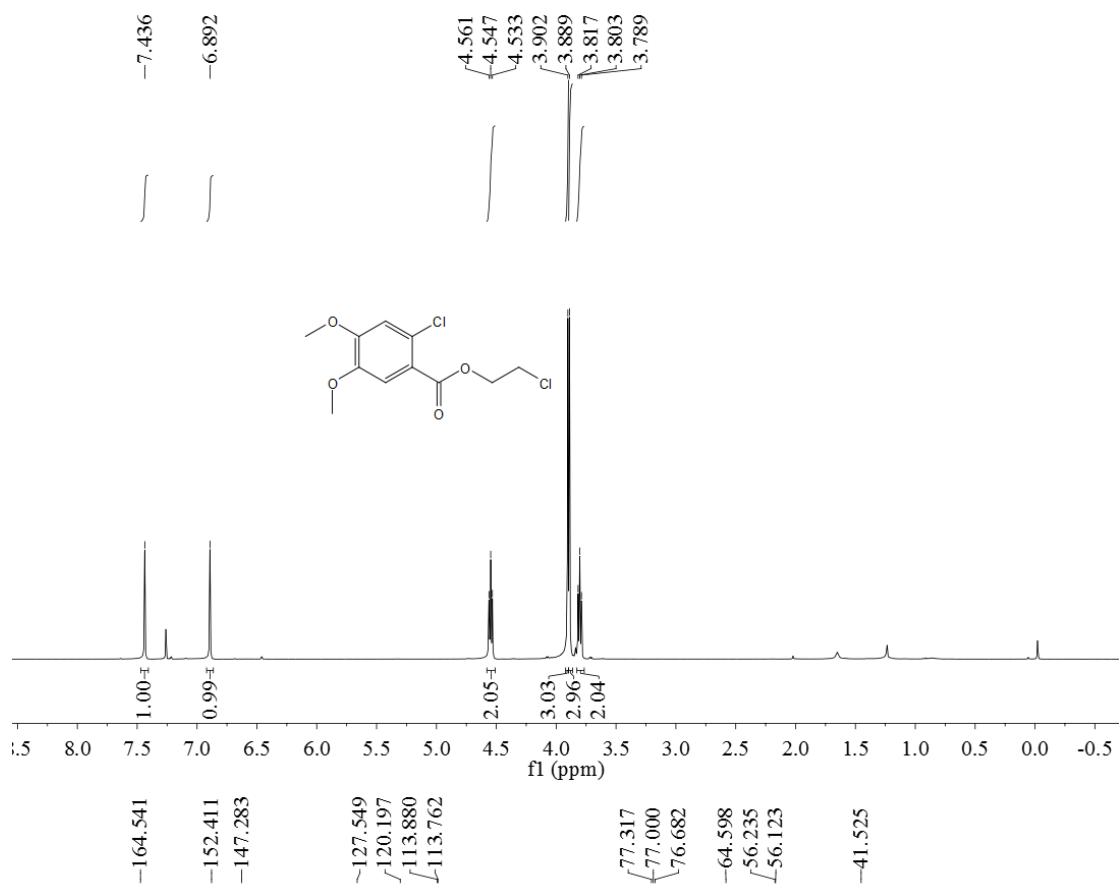
**3ga and 3ga'**



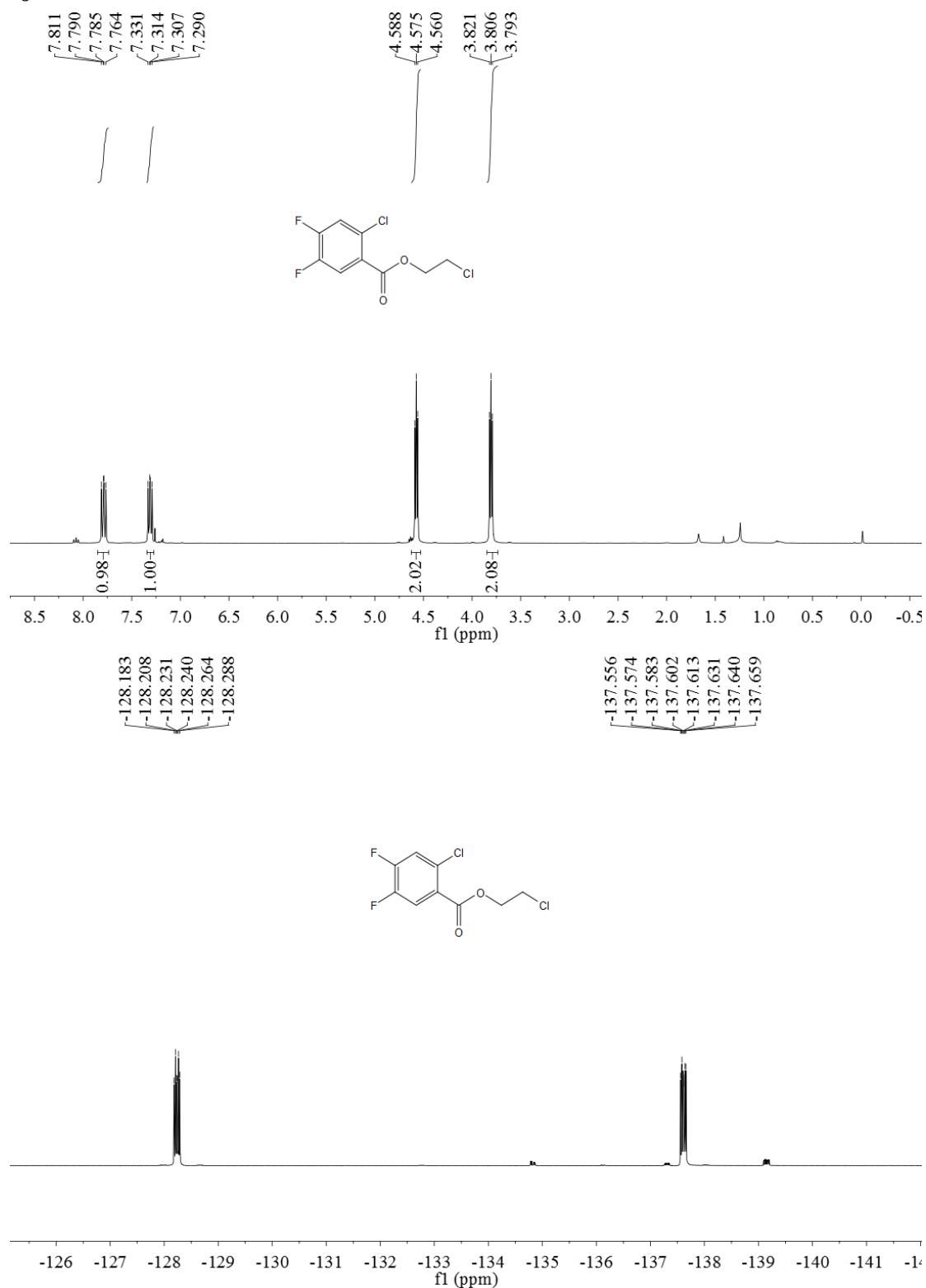
**3ha**

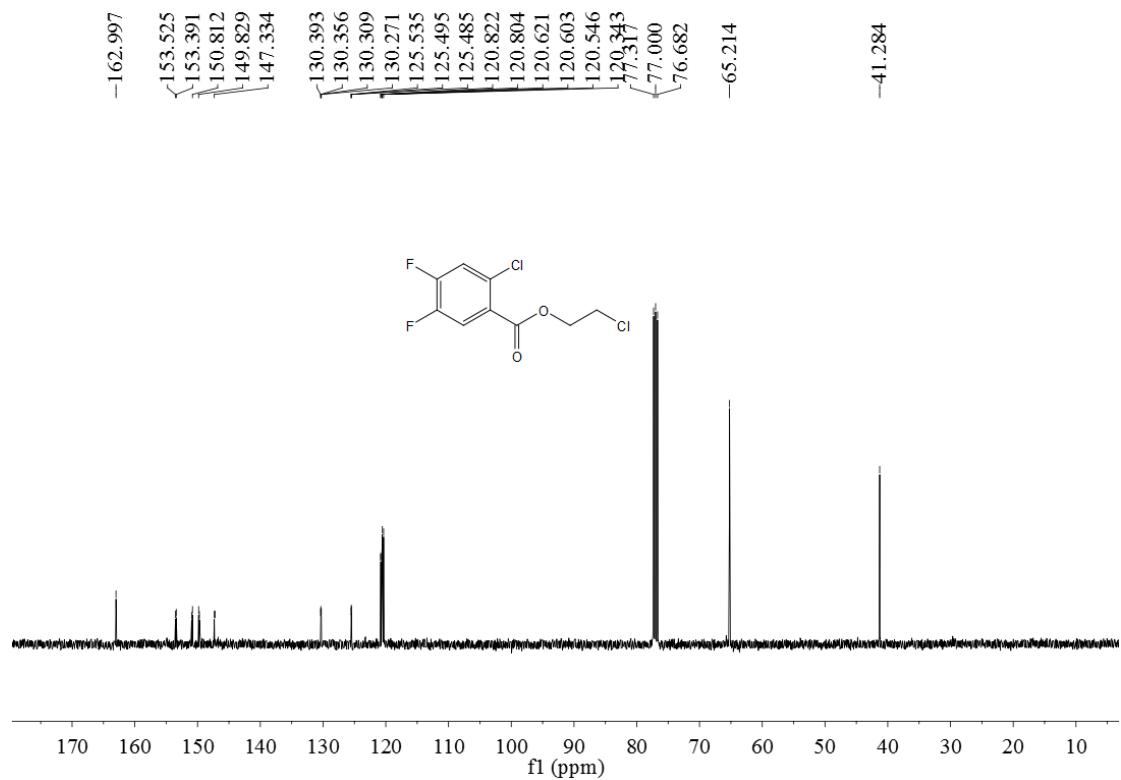


**3ia**

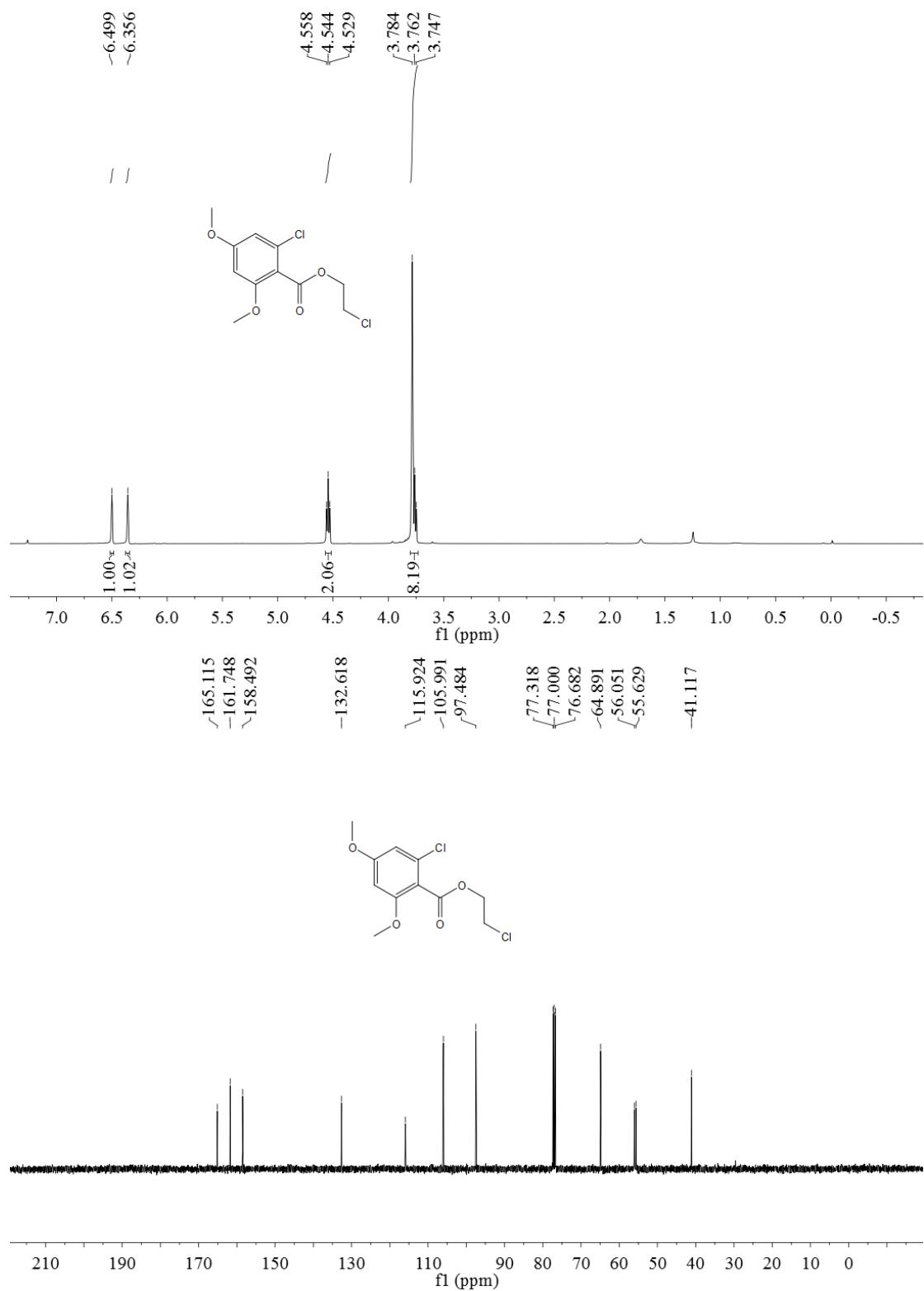


**3ja**

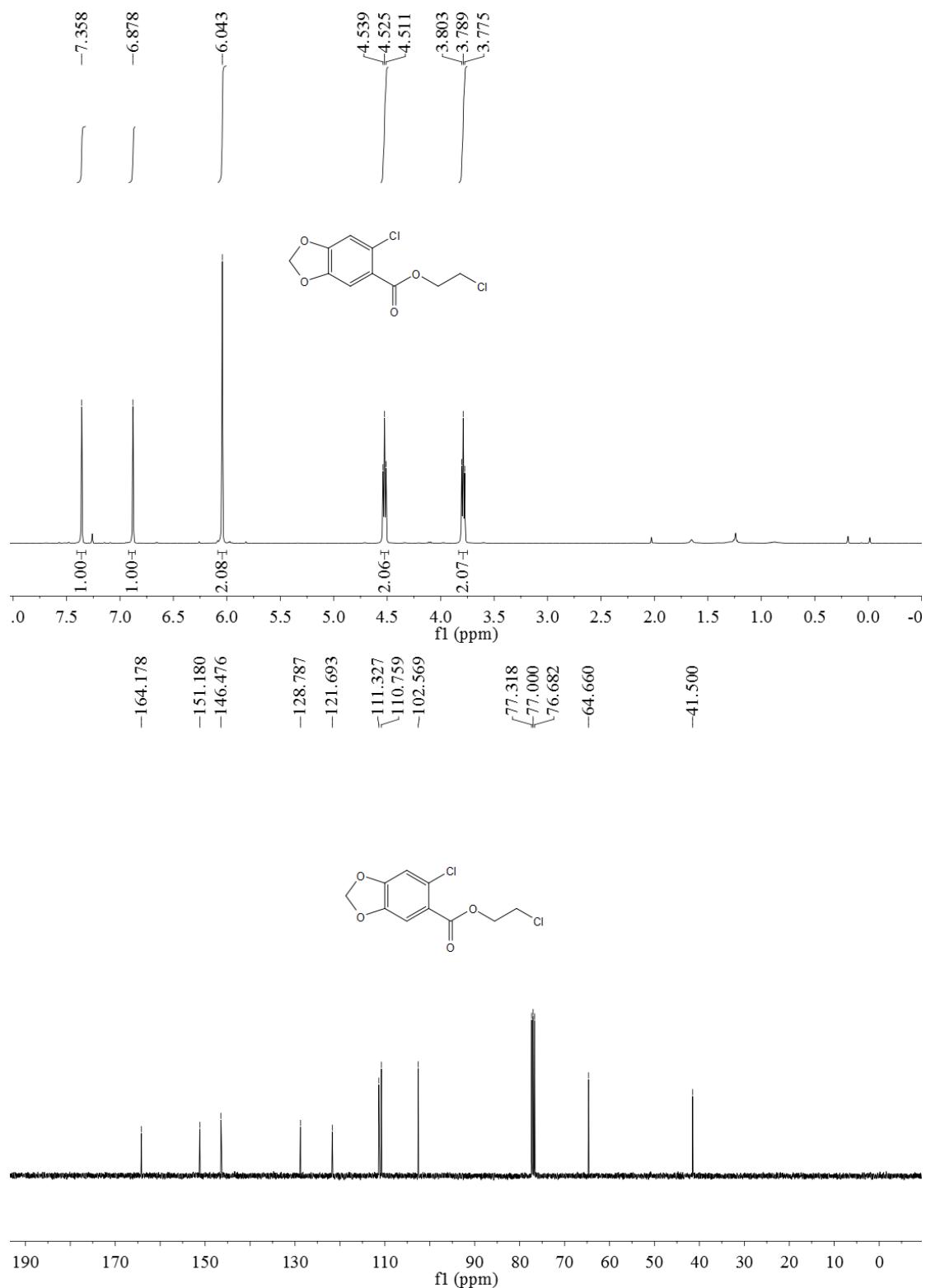




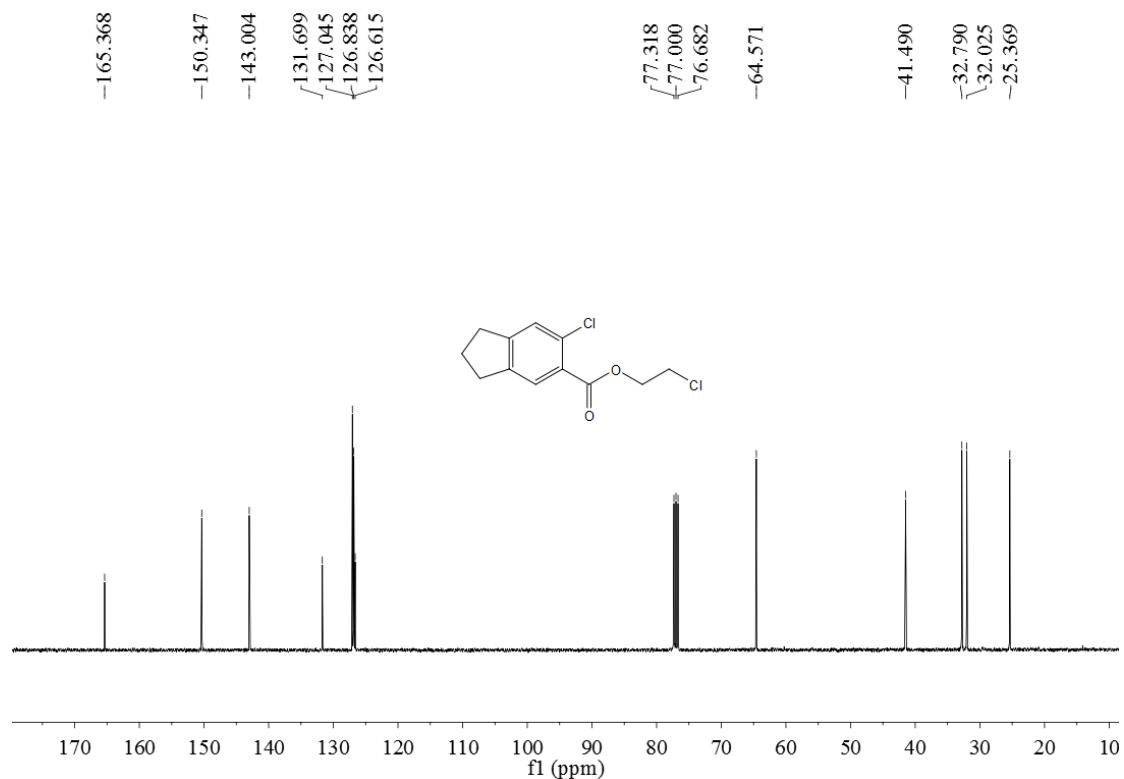
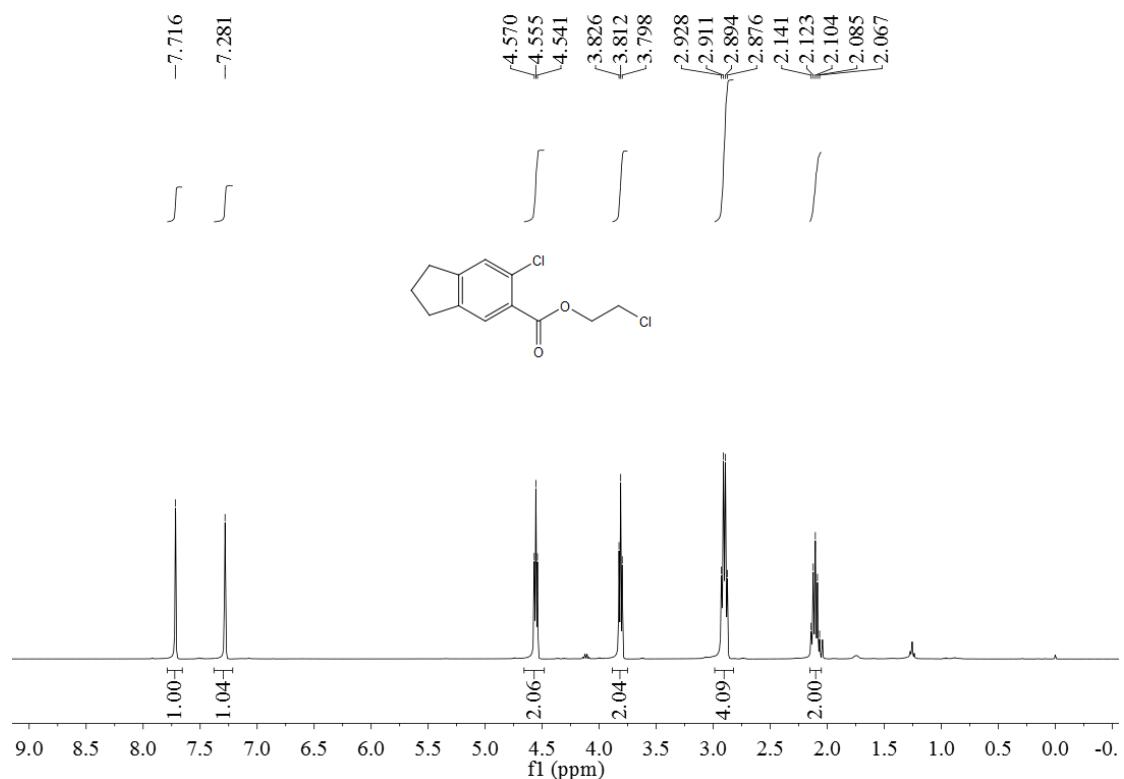
3ka



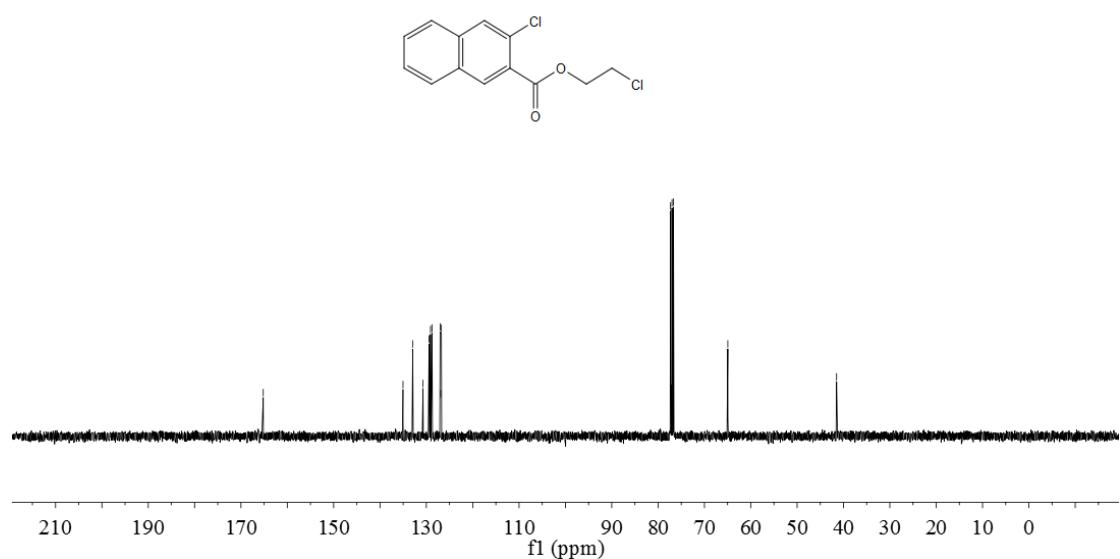
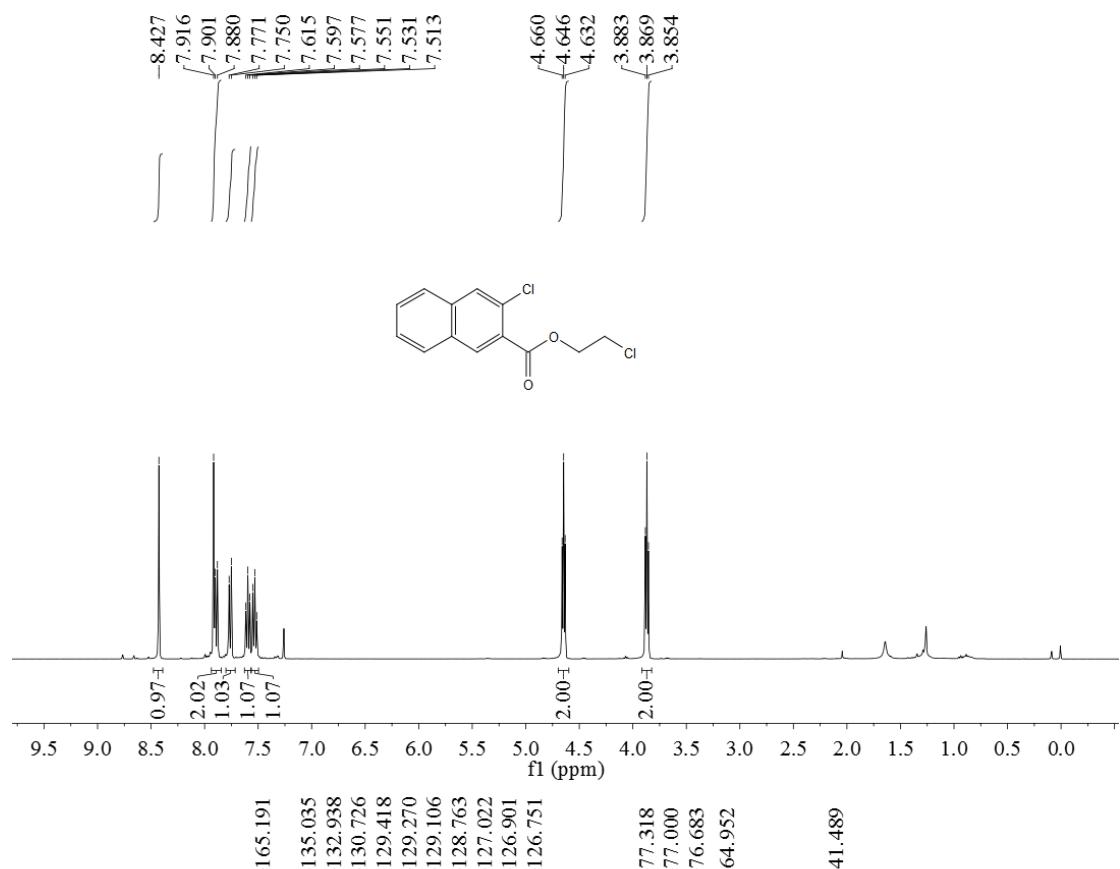
**3la**



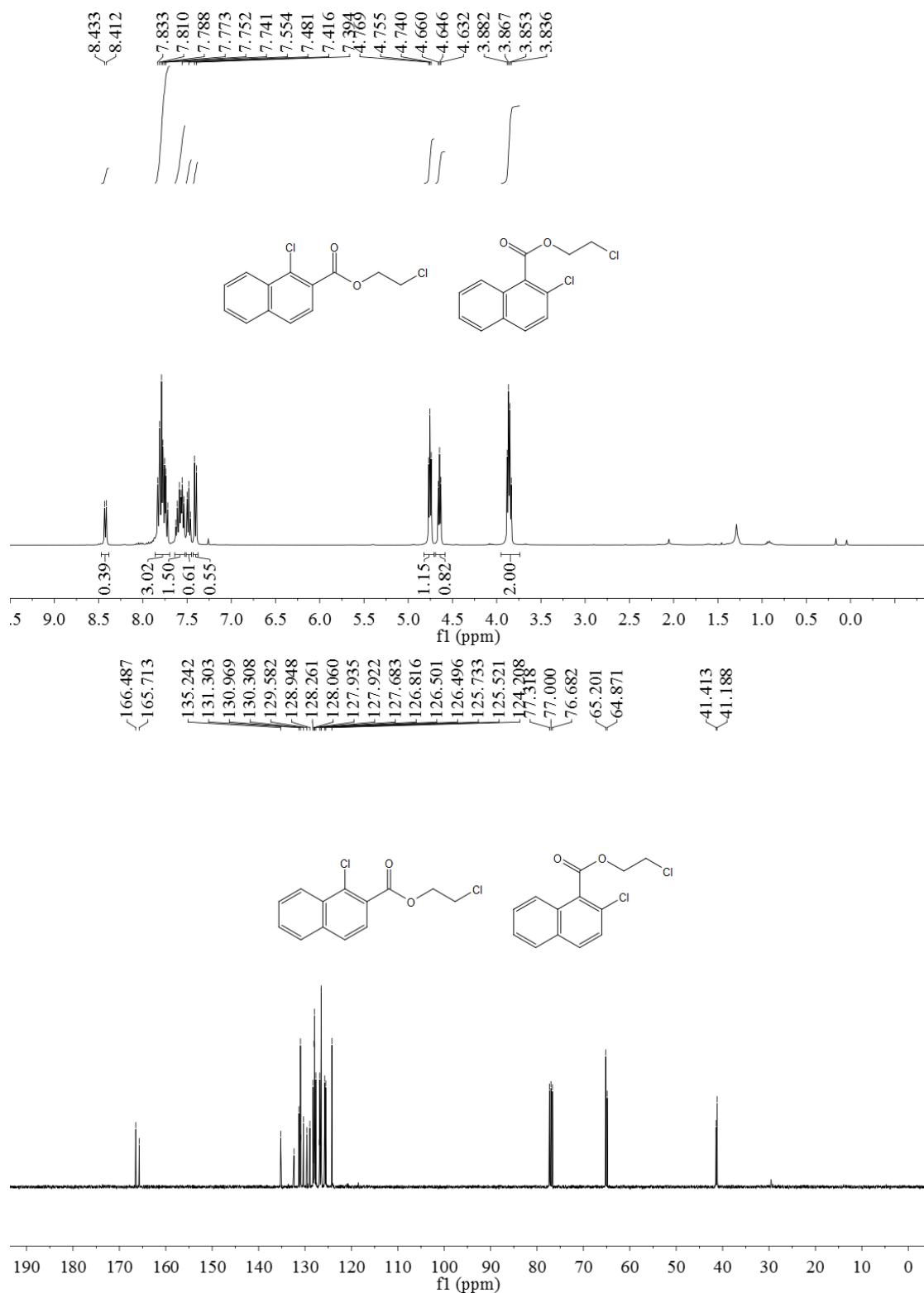
**3ma**



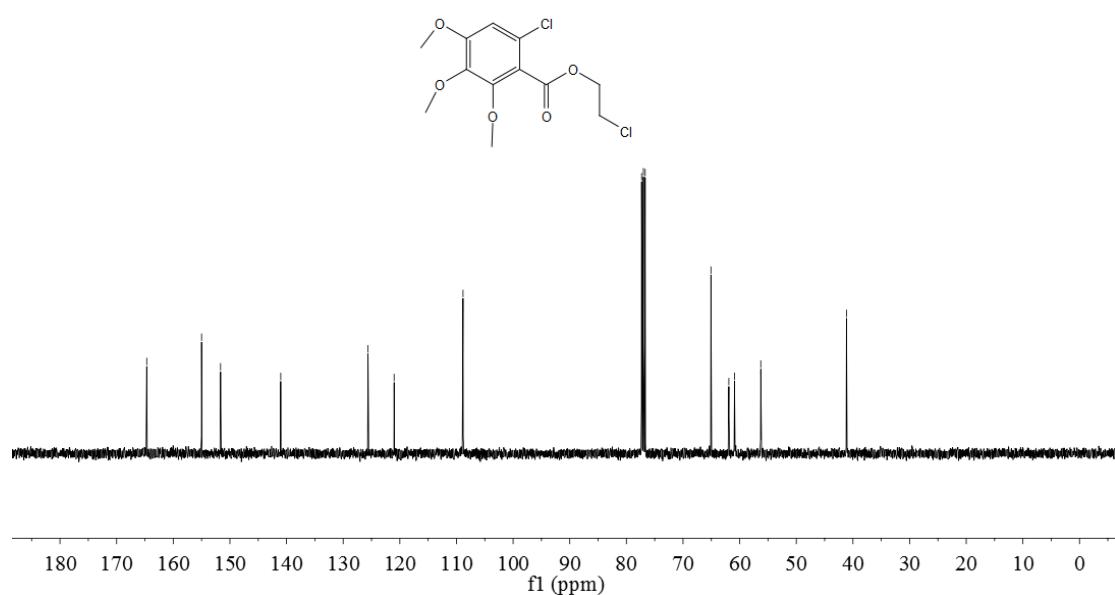
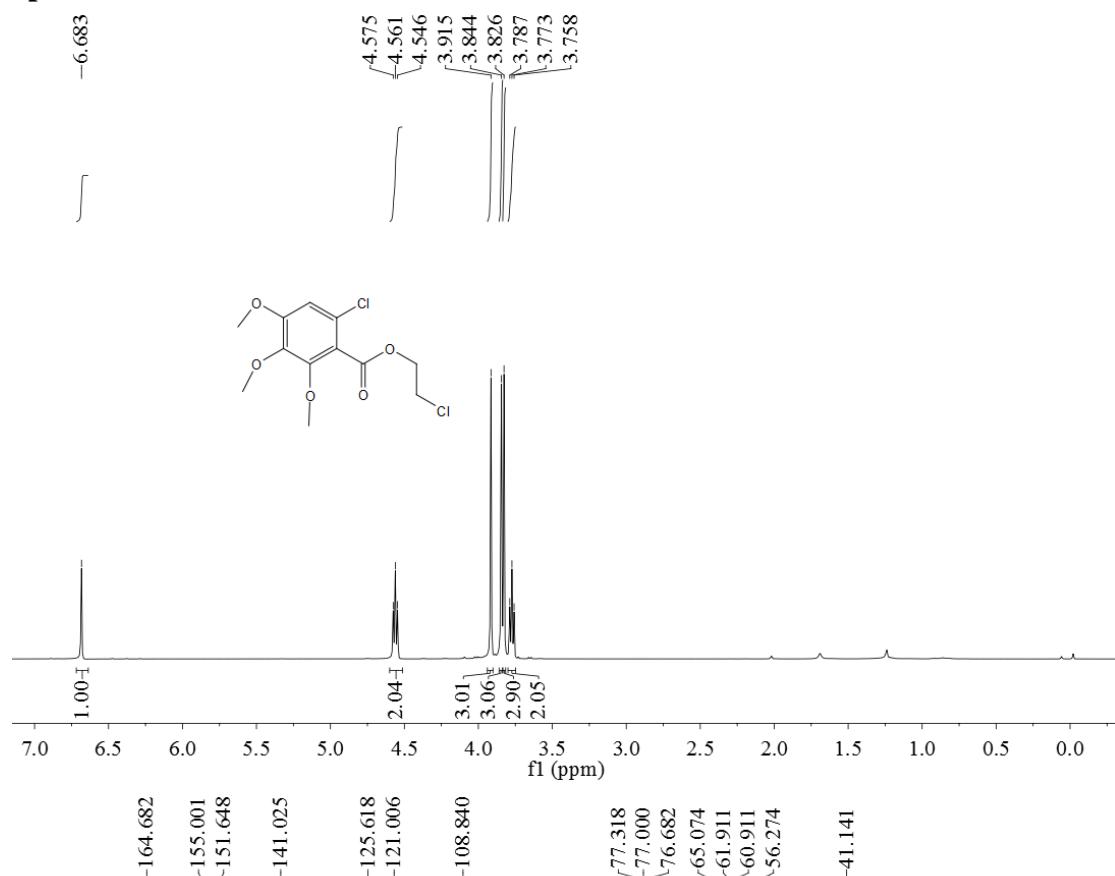
**3na**



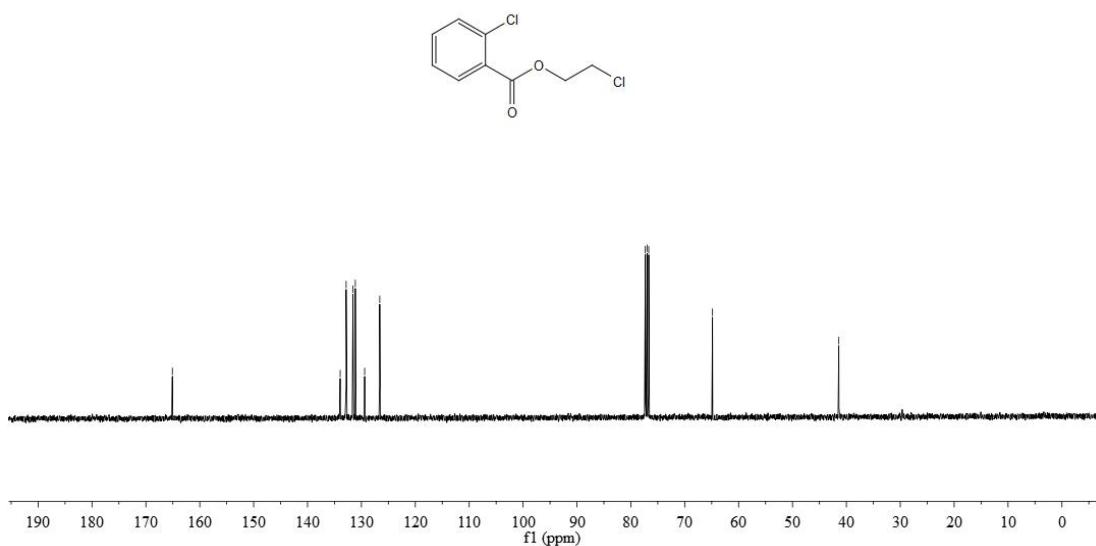
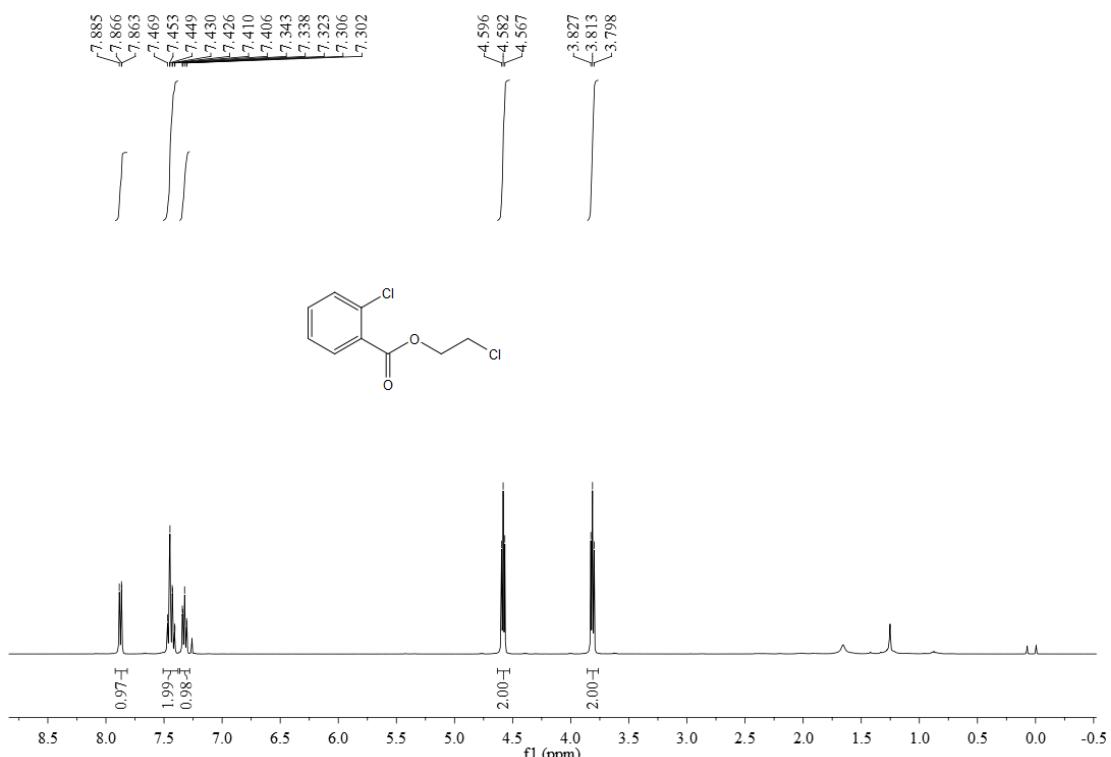
30a



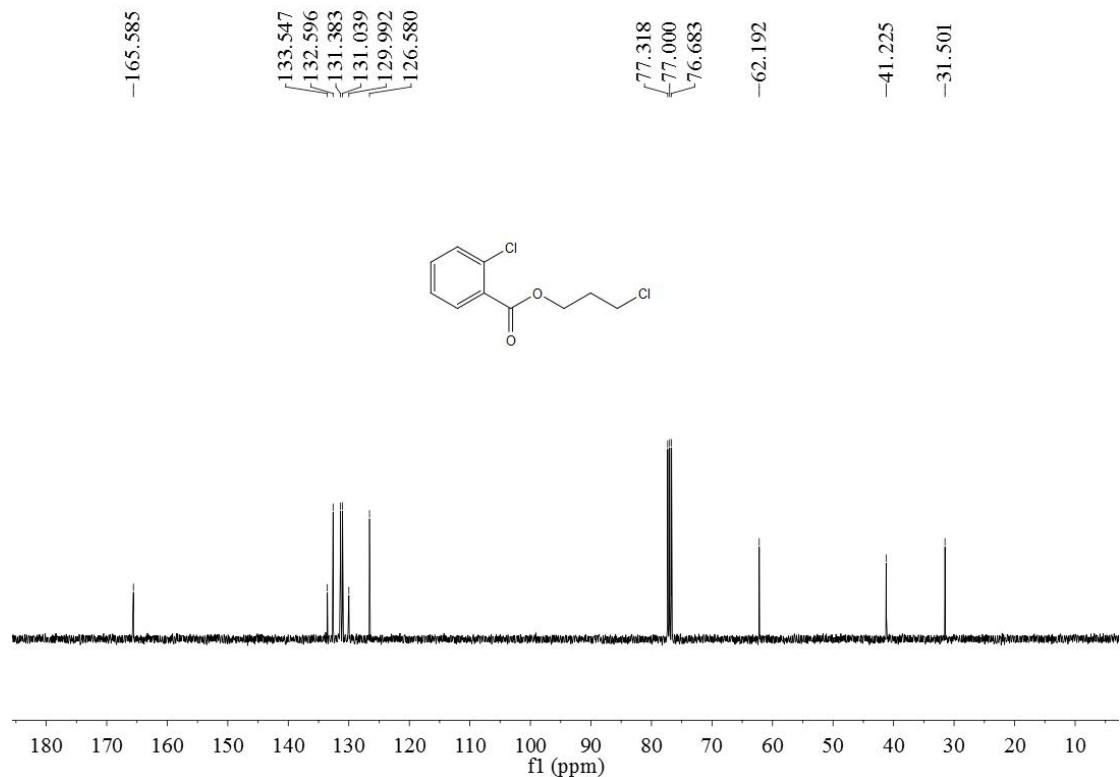
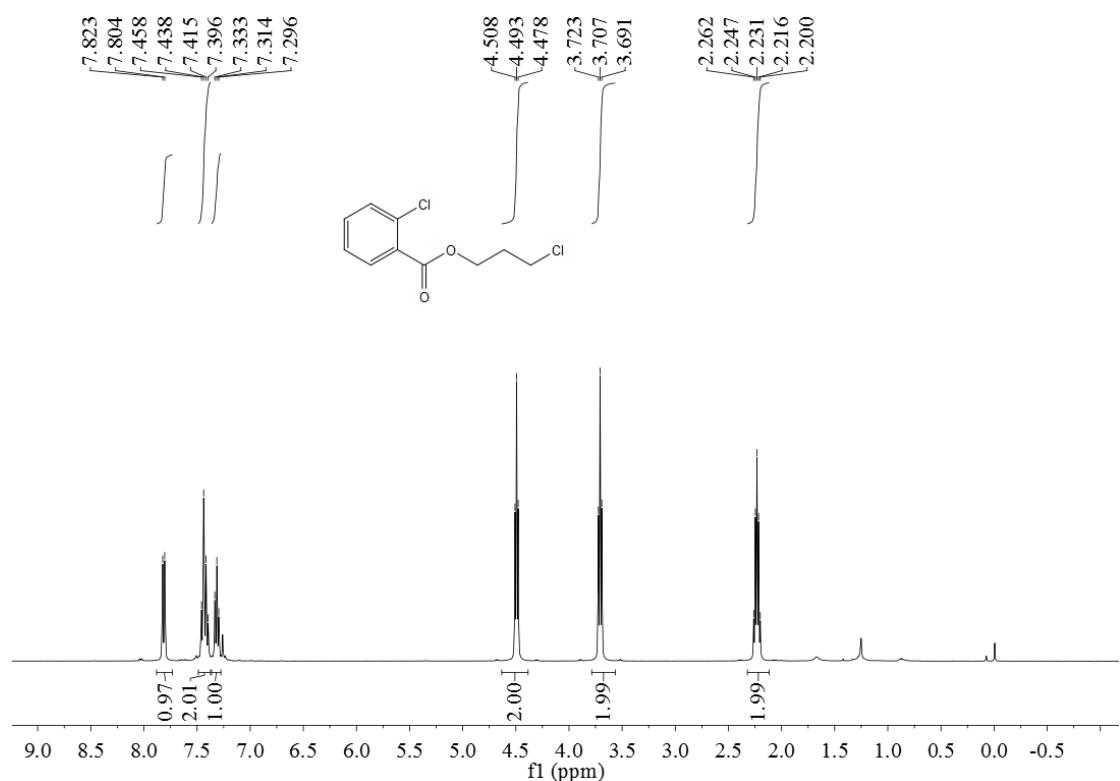
**3pa**



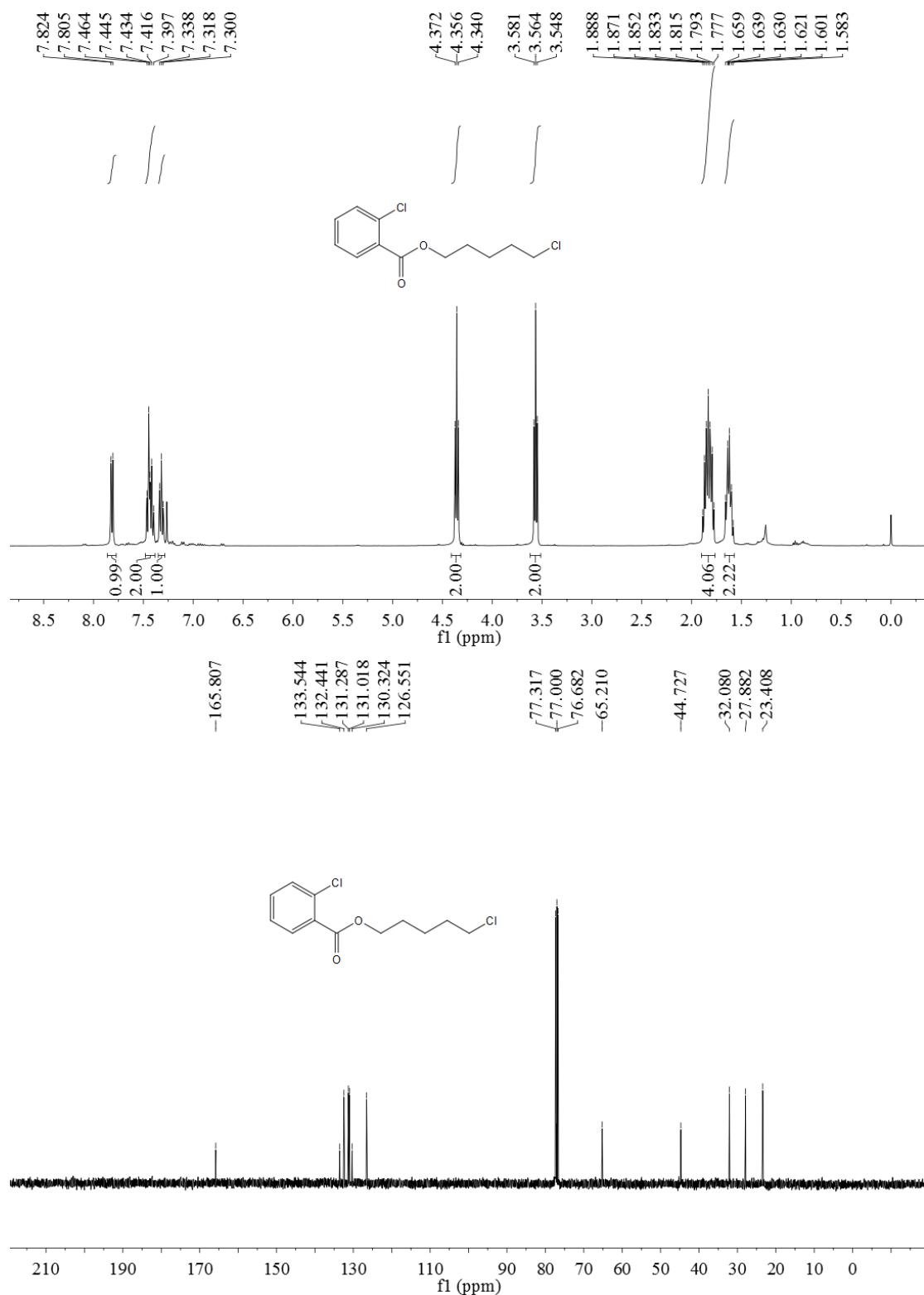
**3aa**



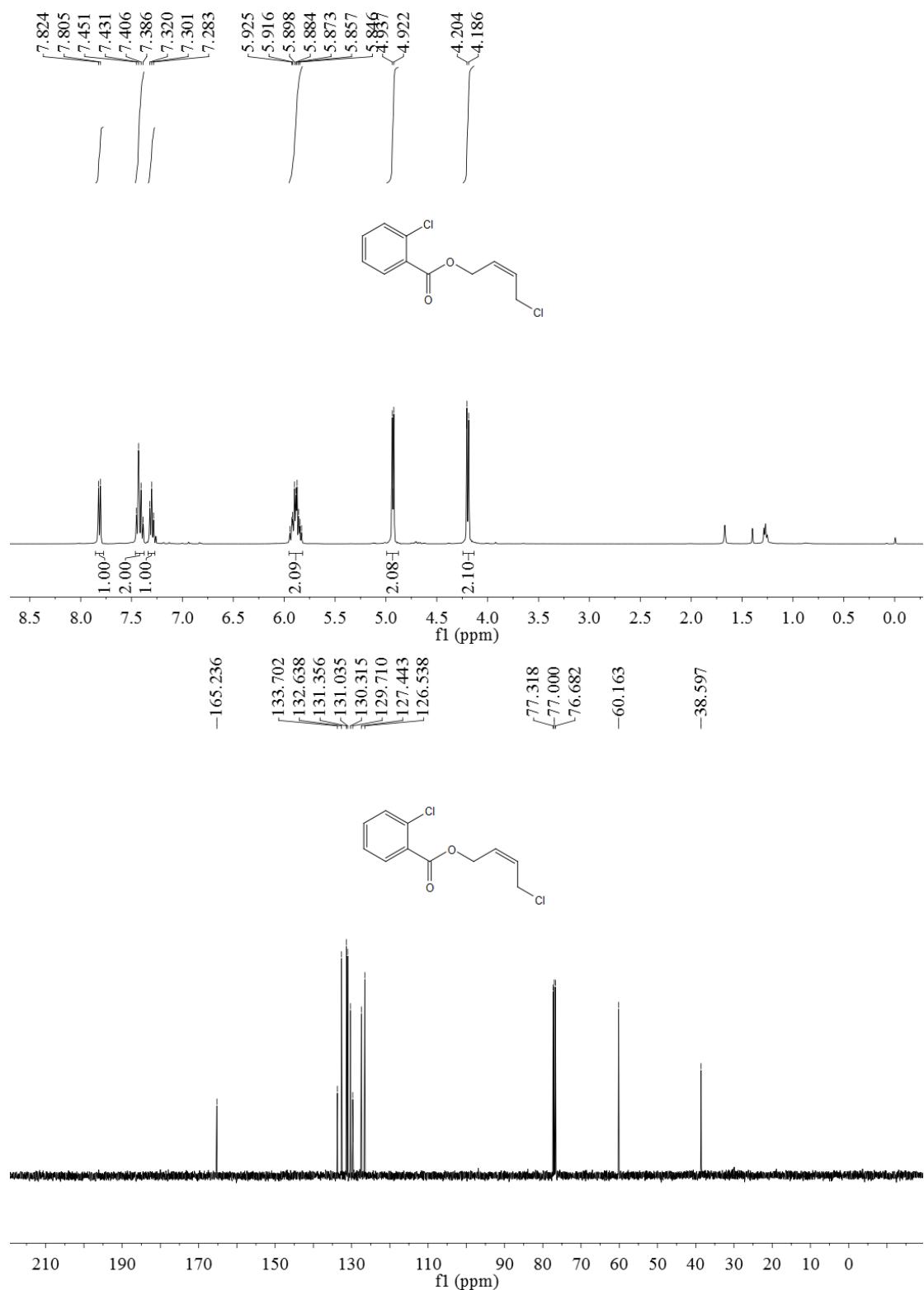
**3ac**



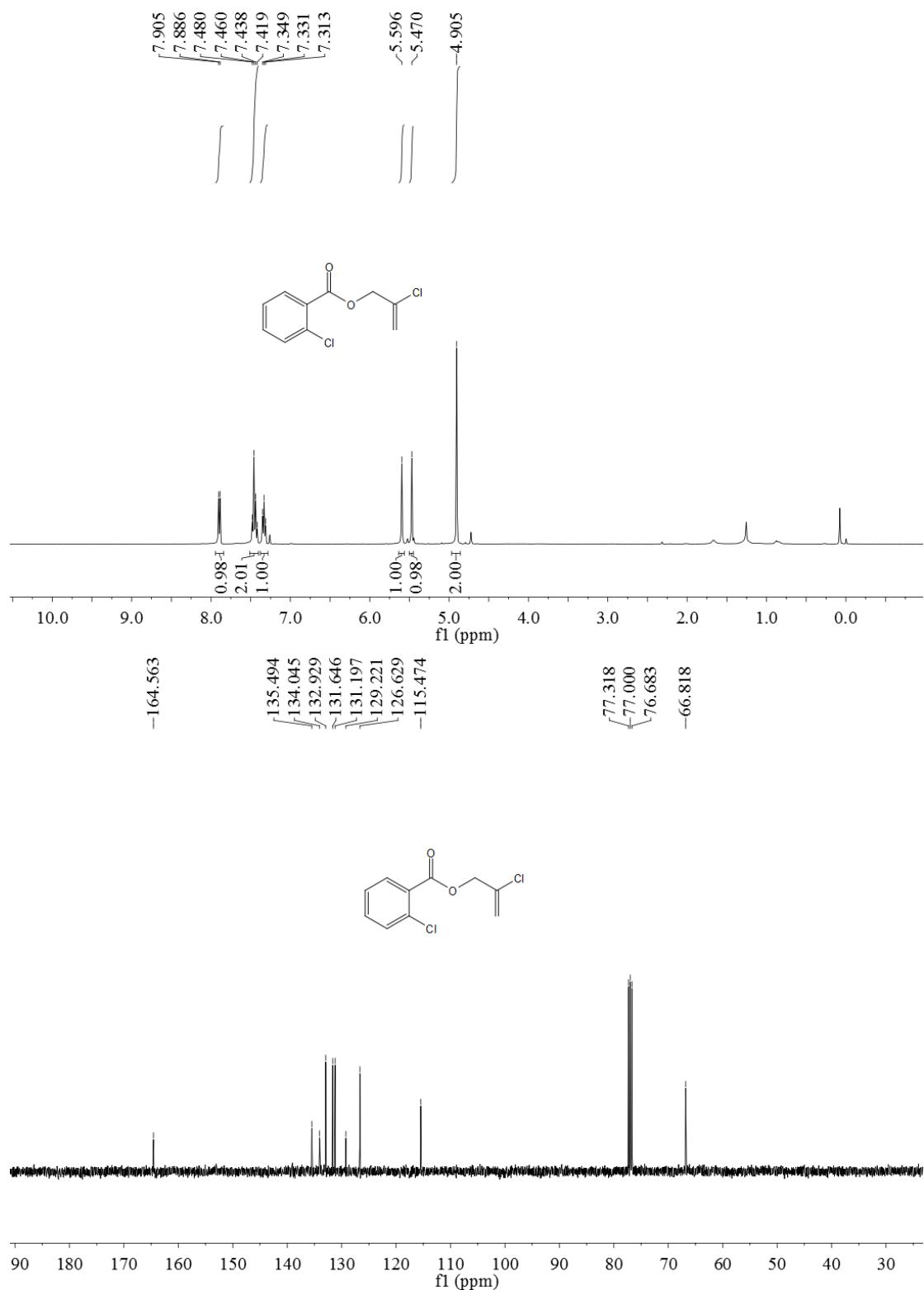
**3ad**



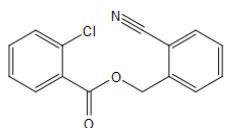
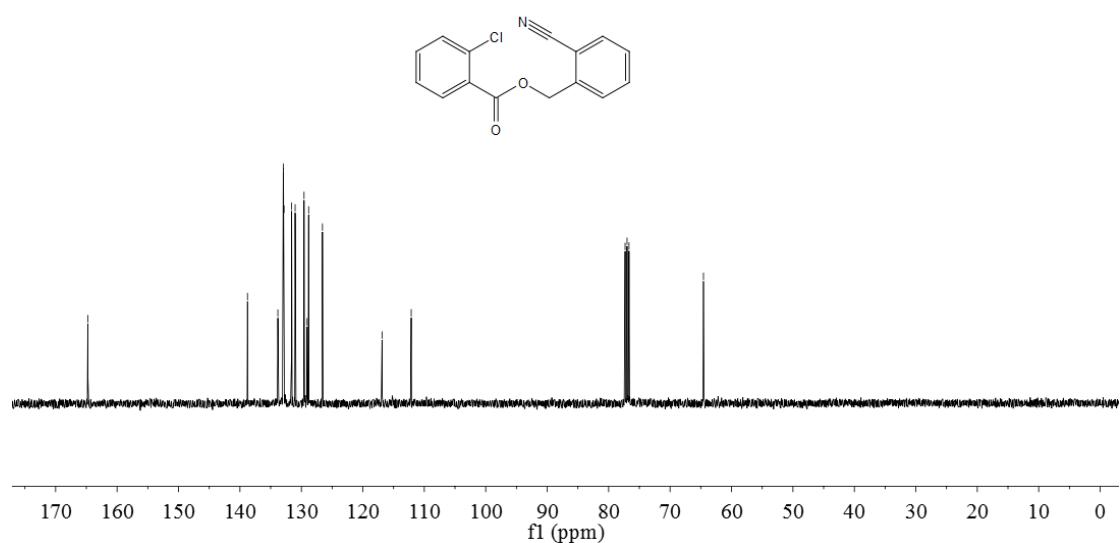
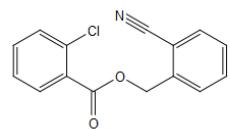
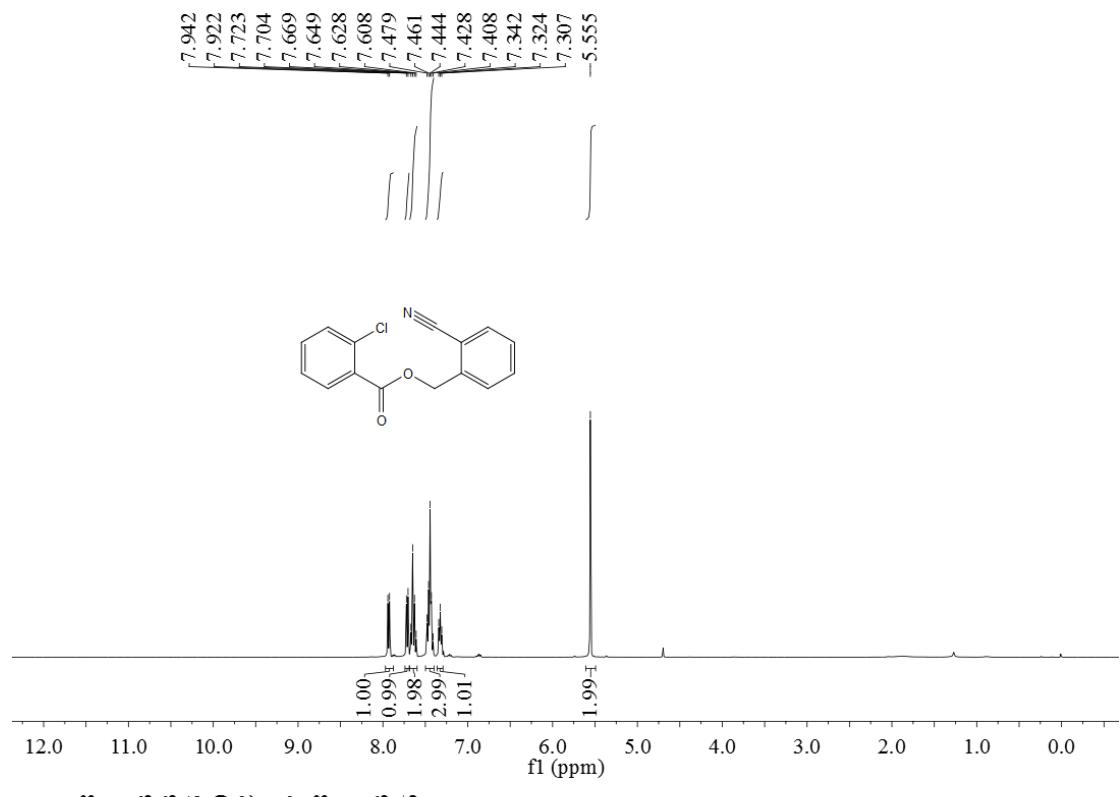
3ae



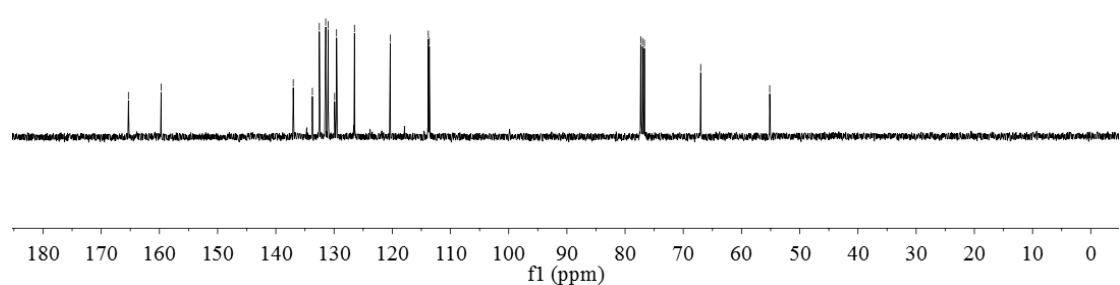
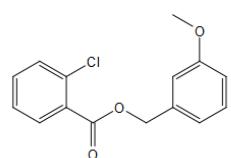
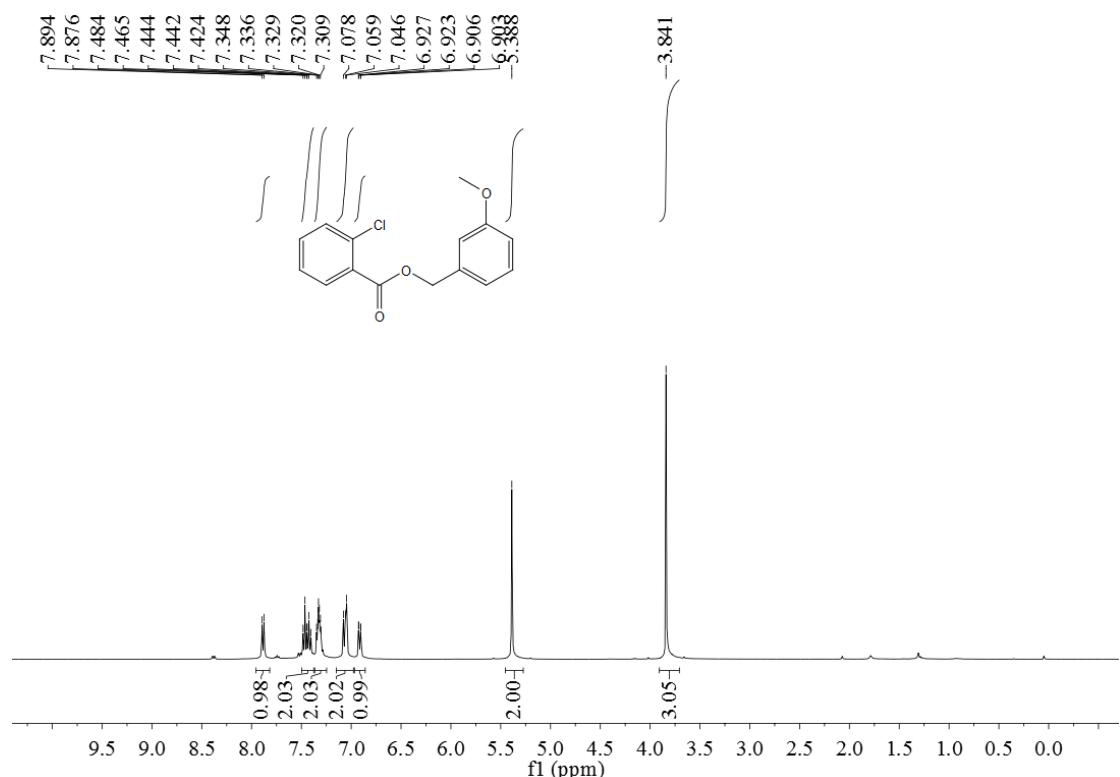
3af



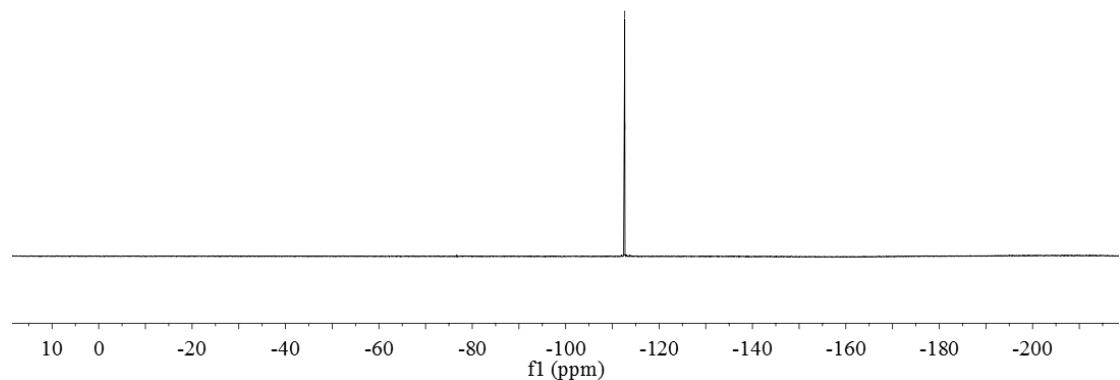
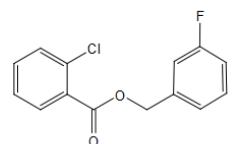
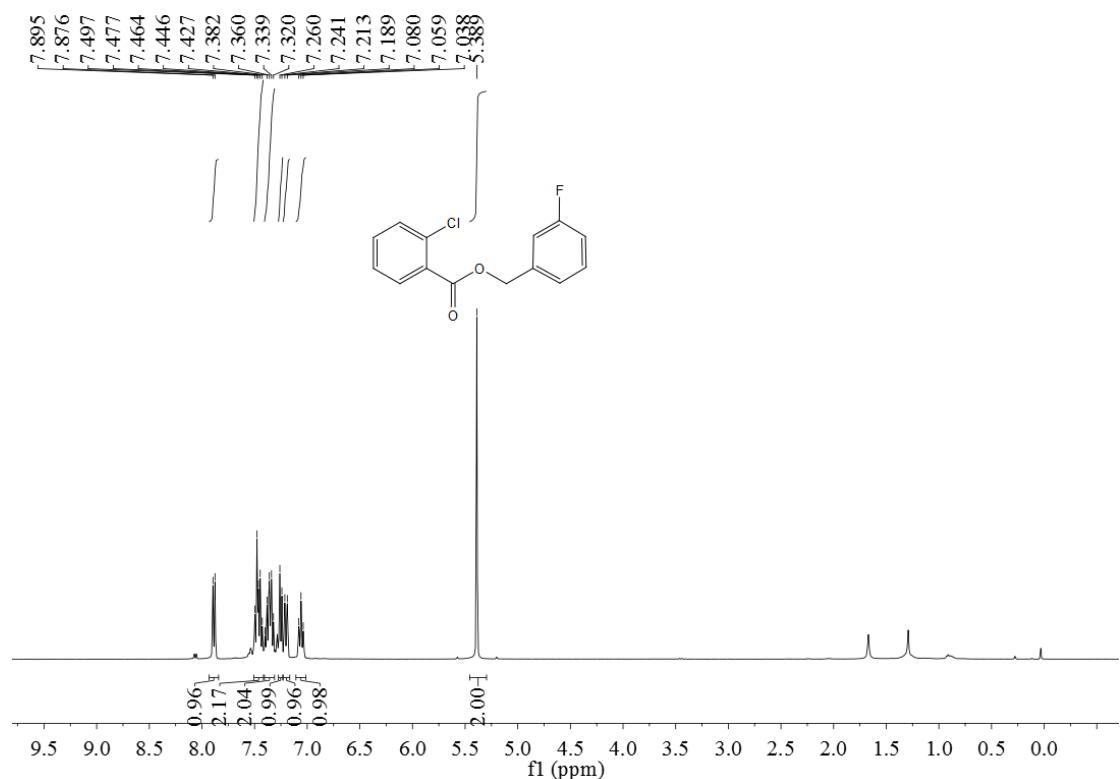
3ag

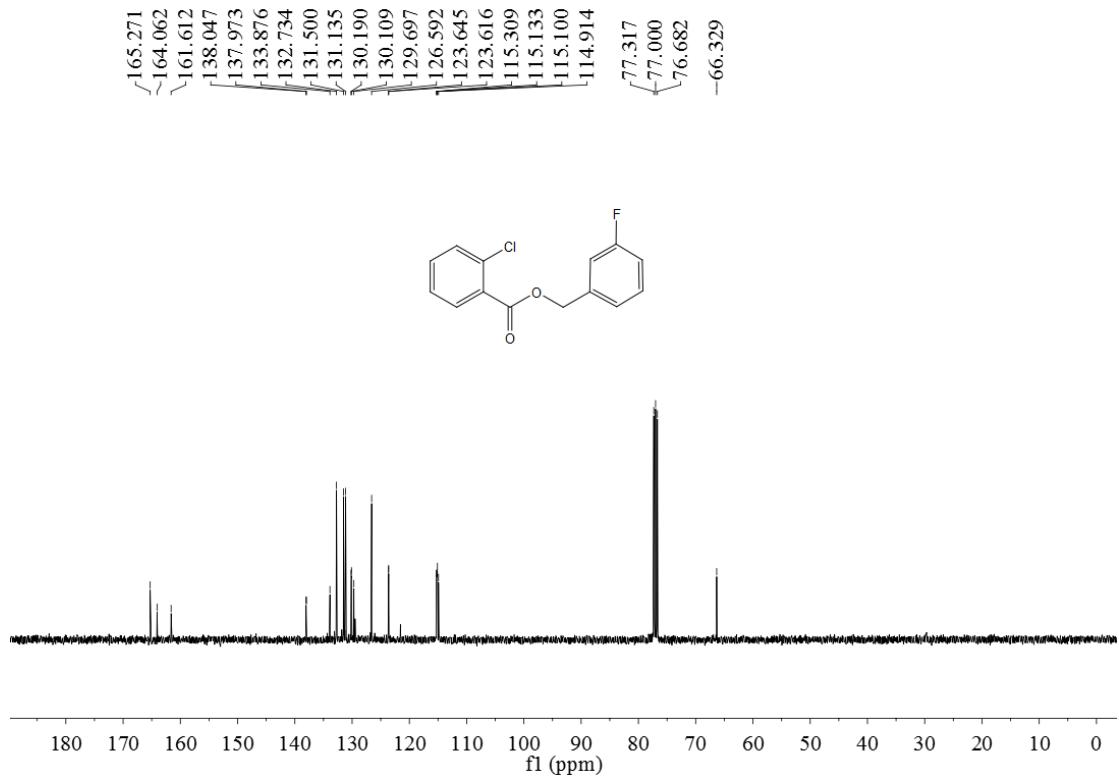


3ah

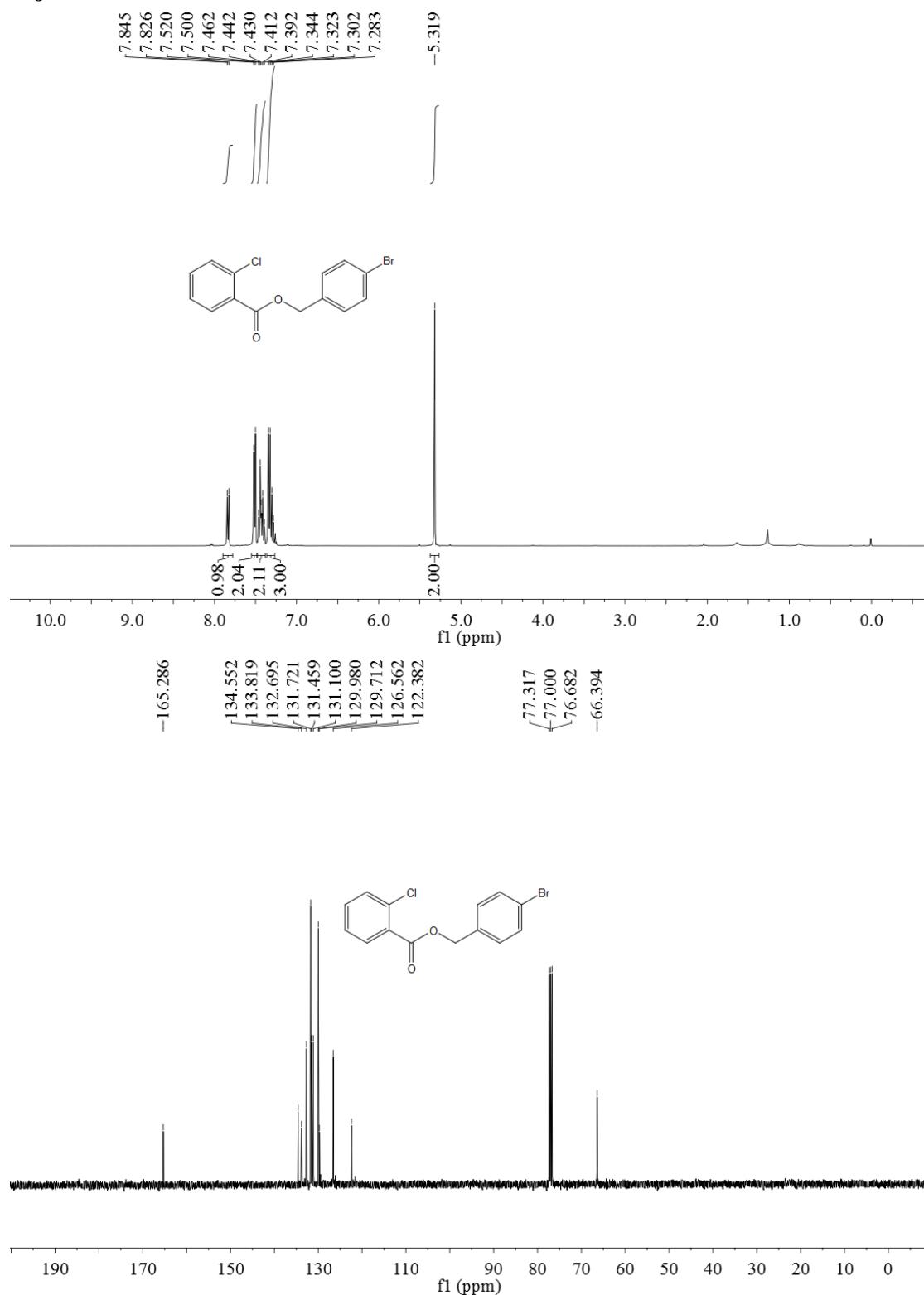


3ai

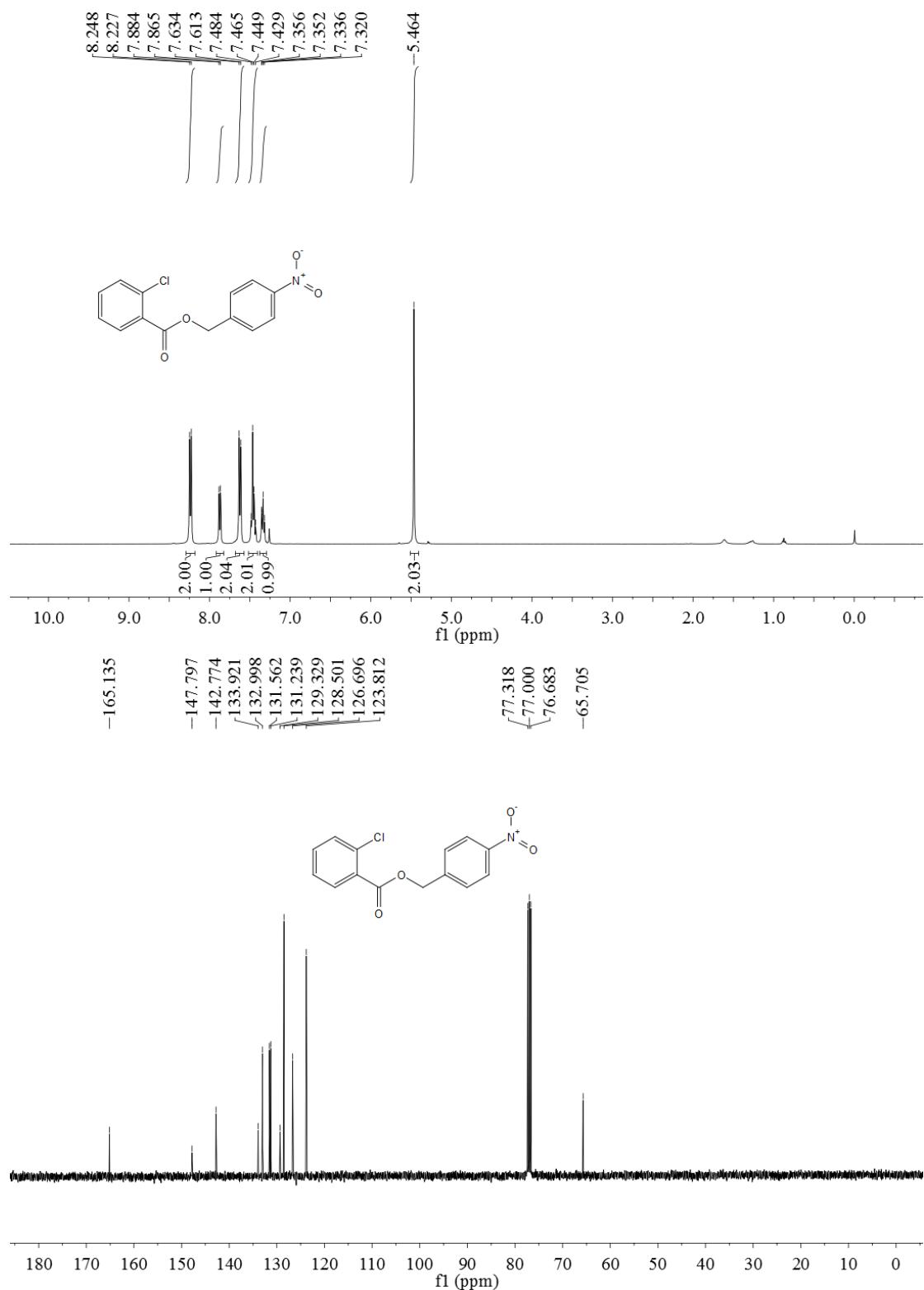




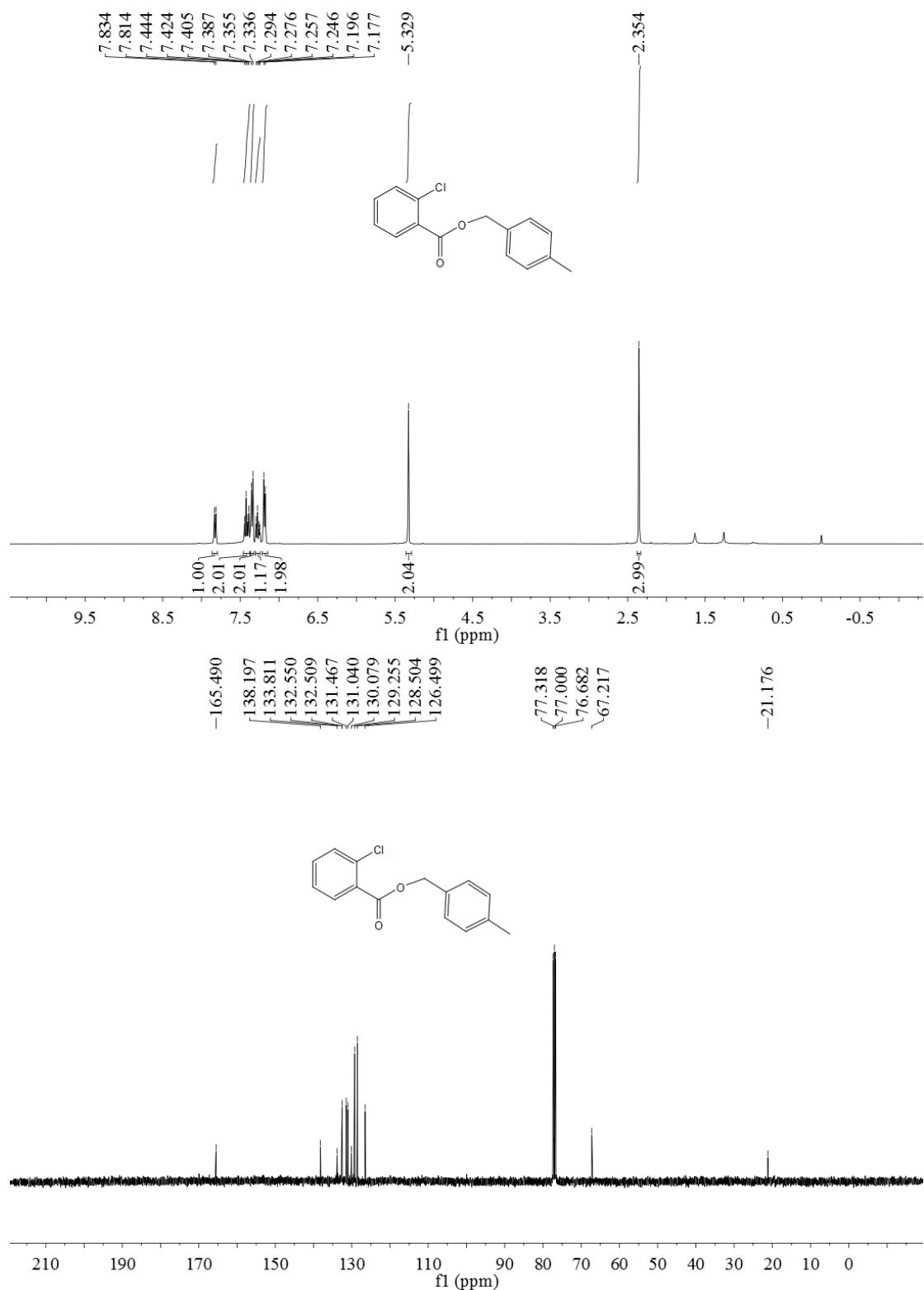
3aj



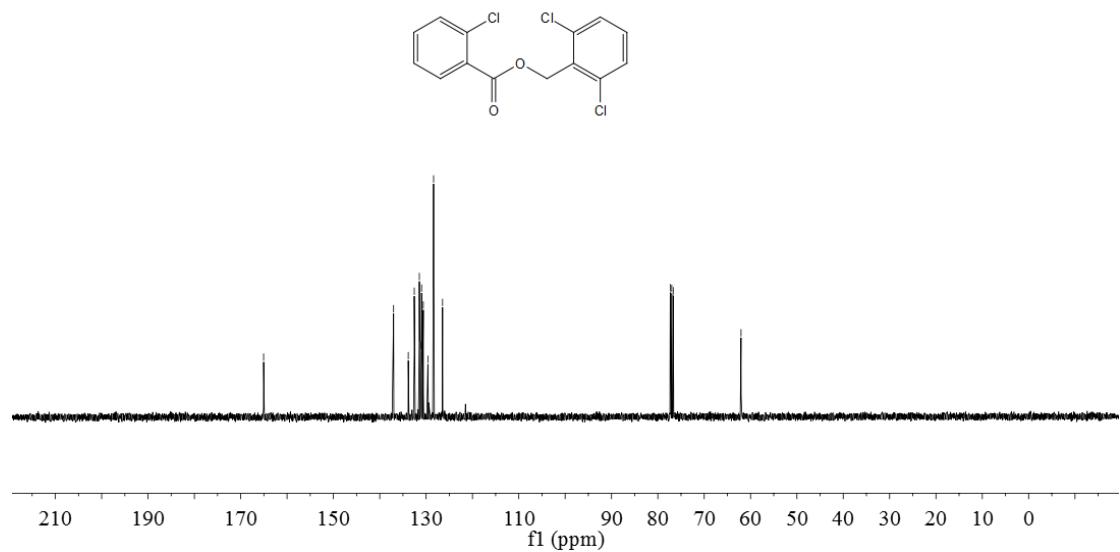
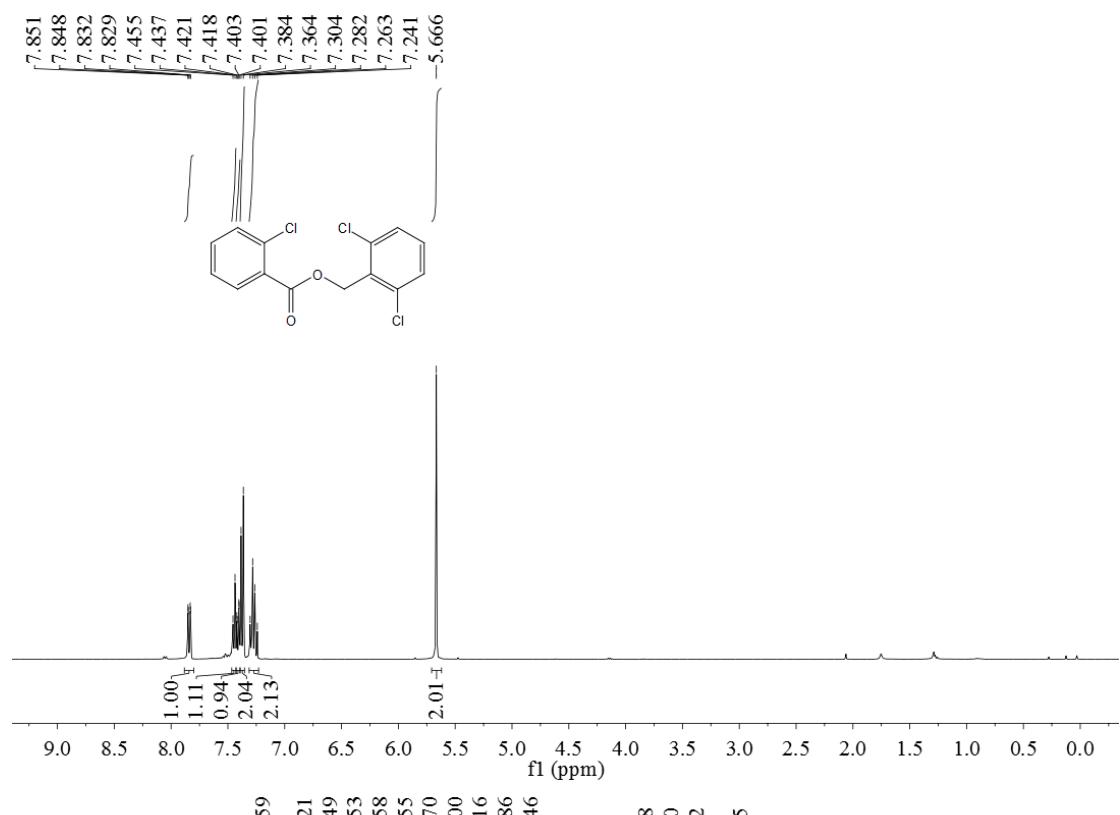
**3ak**



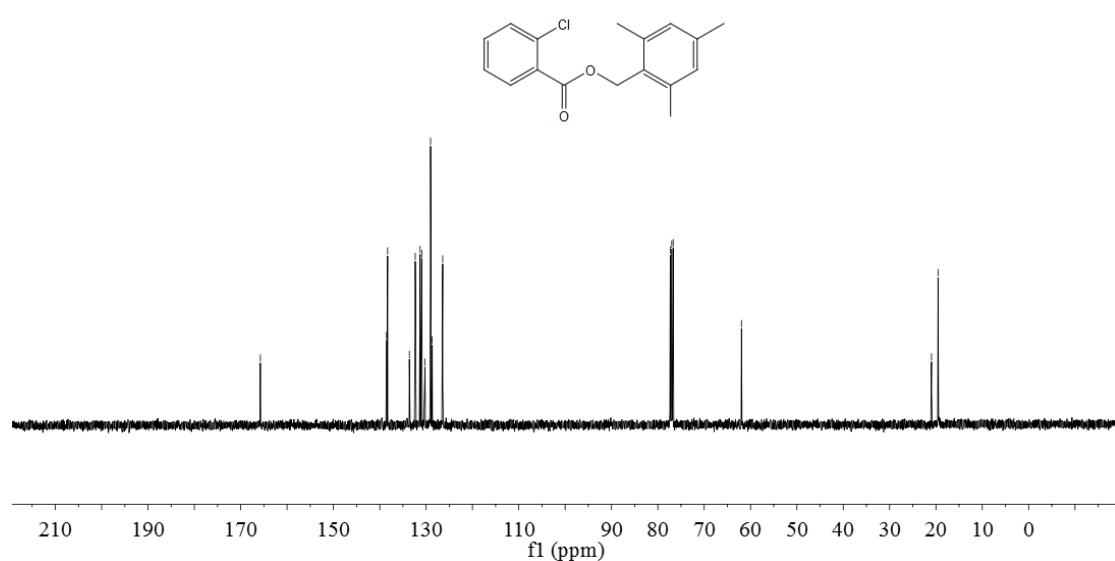
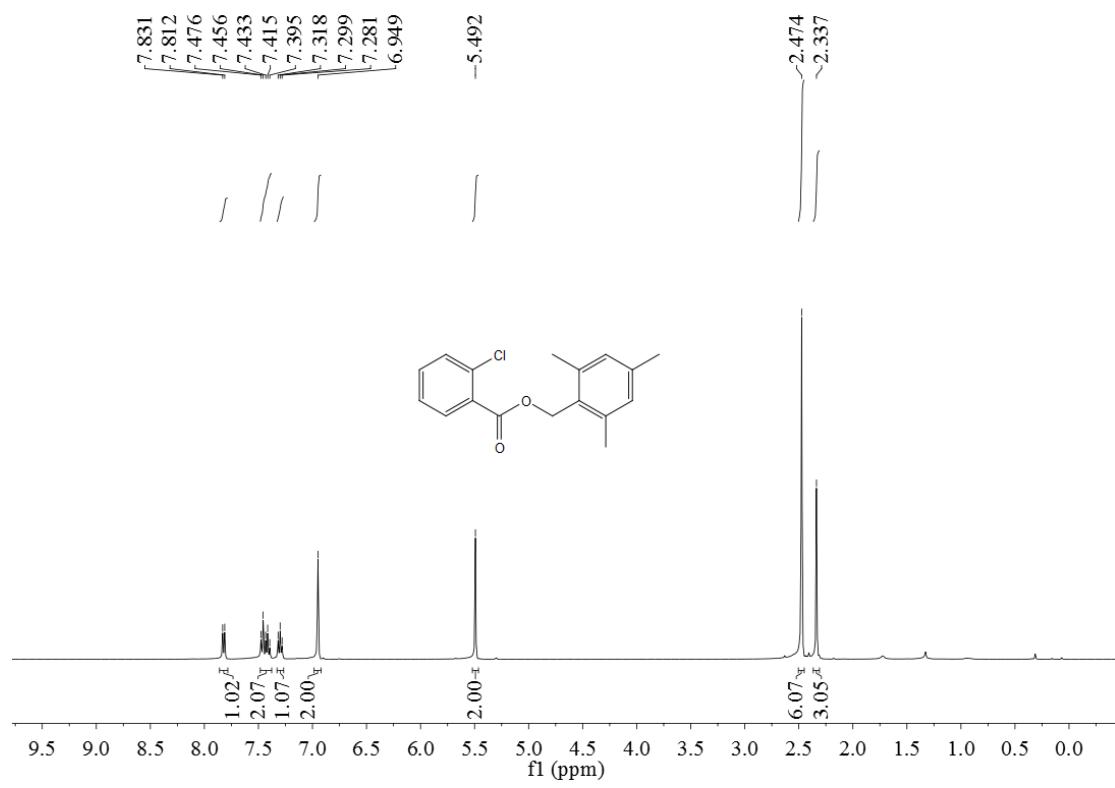
3al



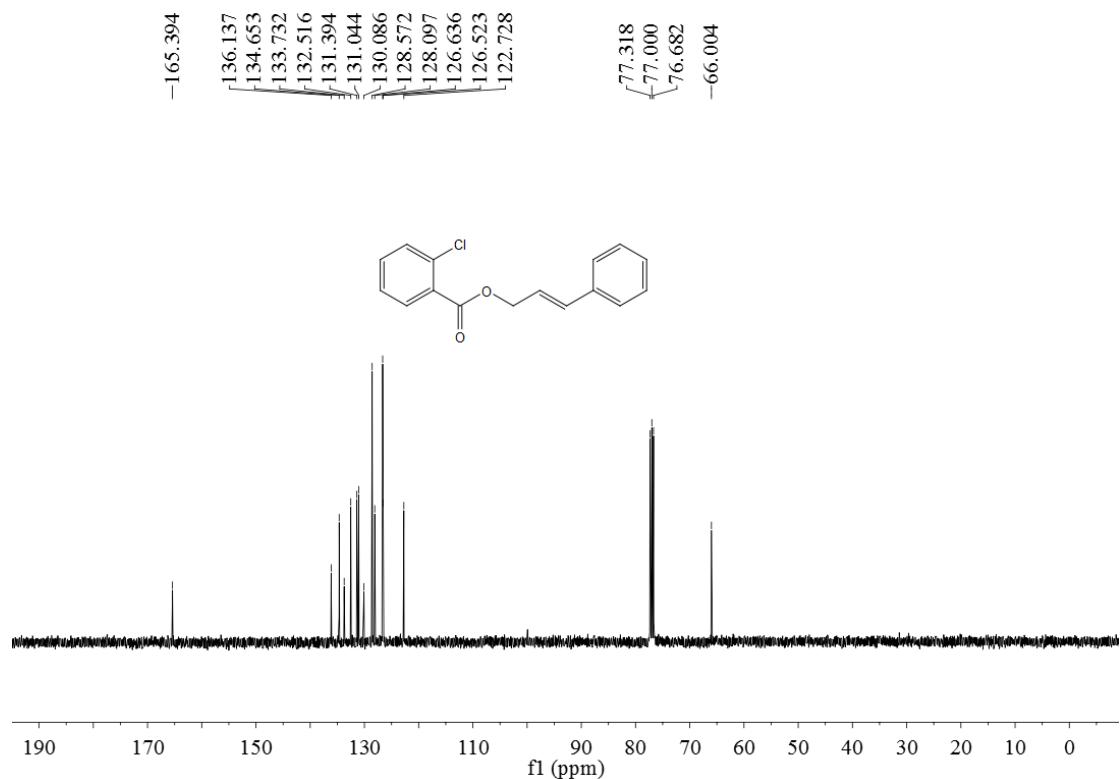
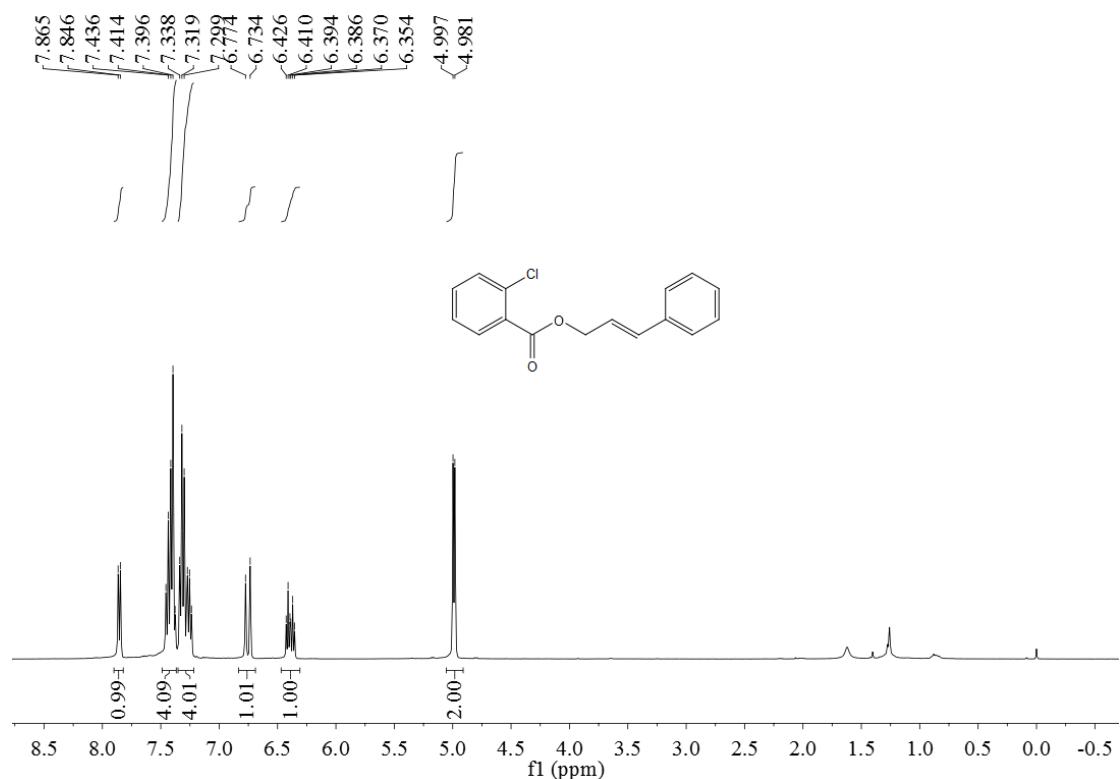
**3am**



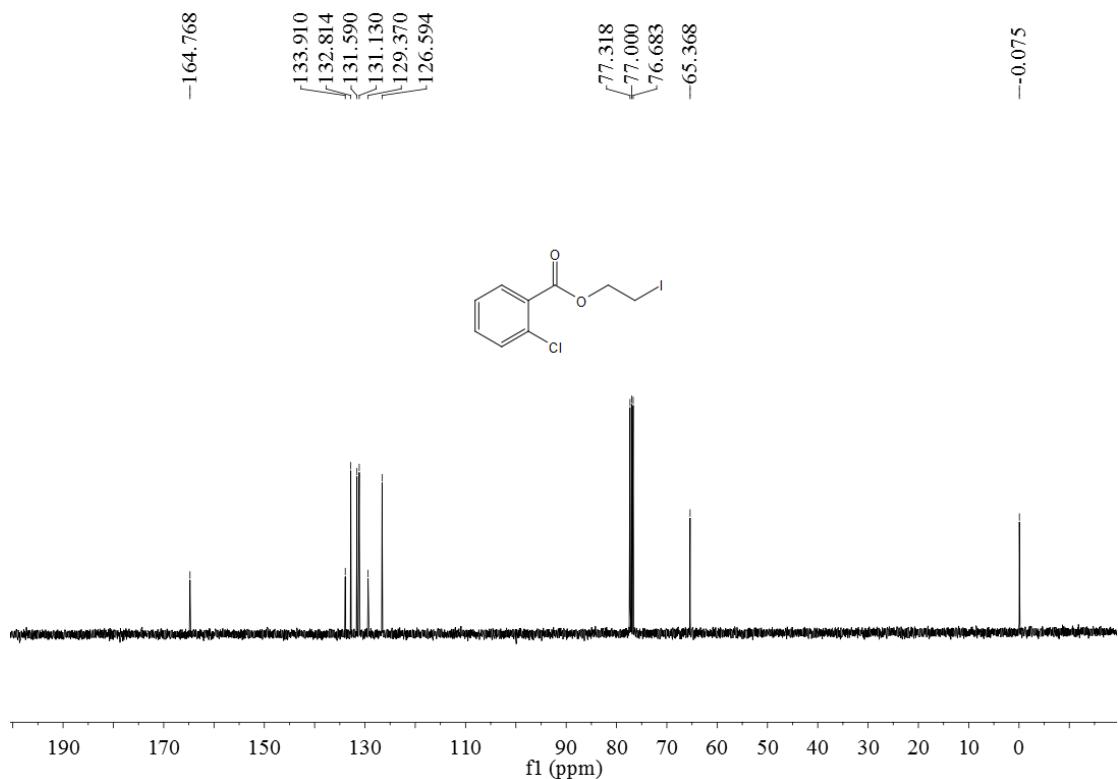
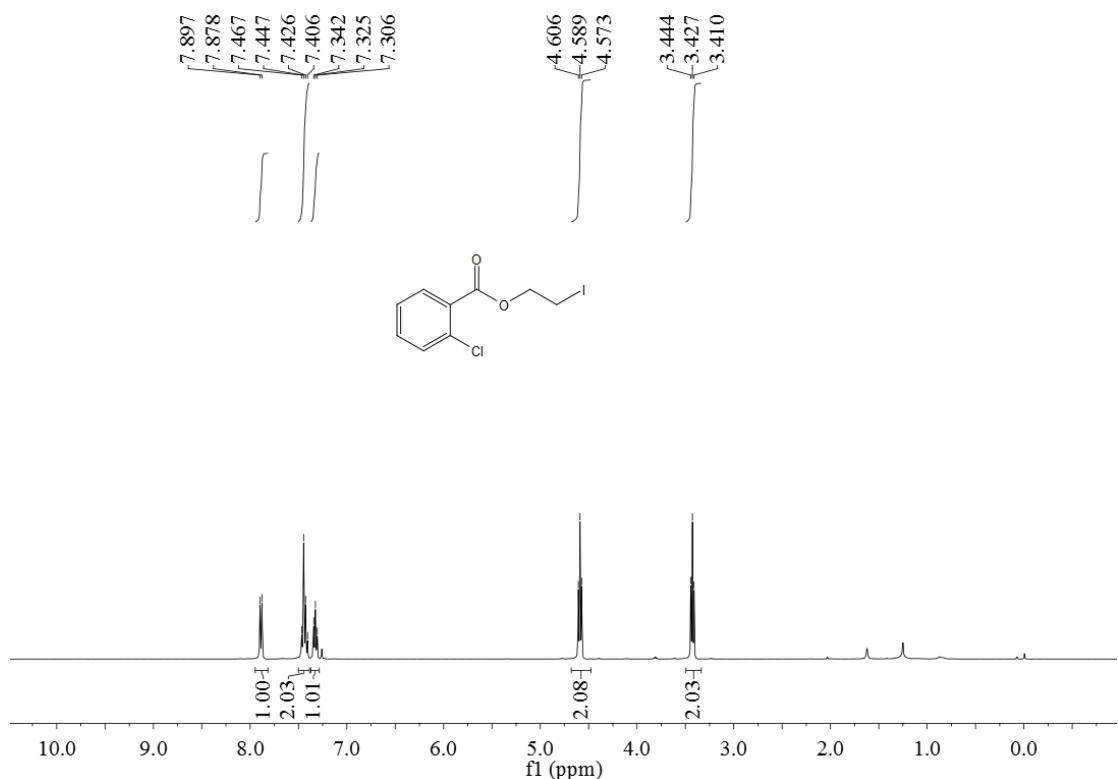
**3an**



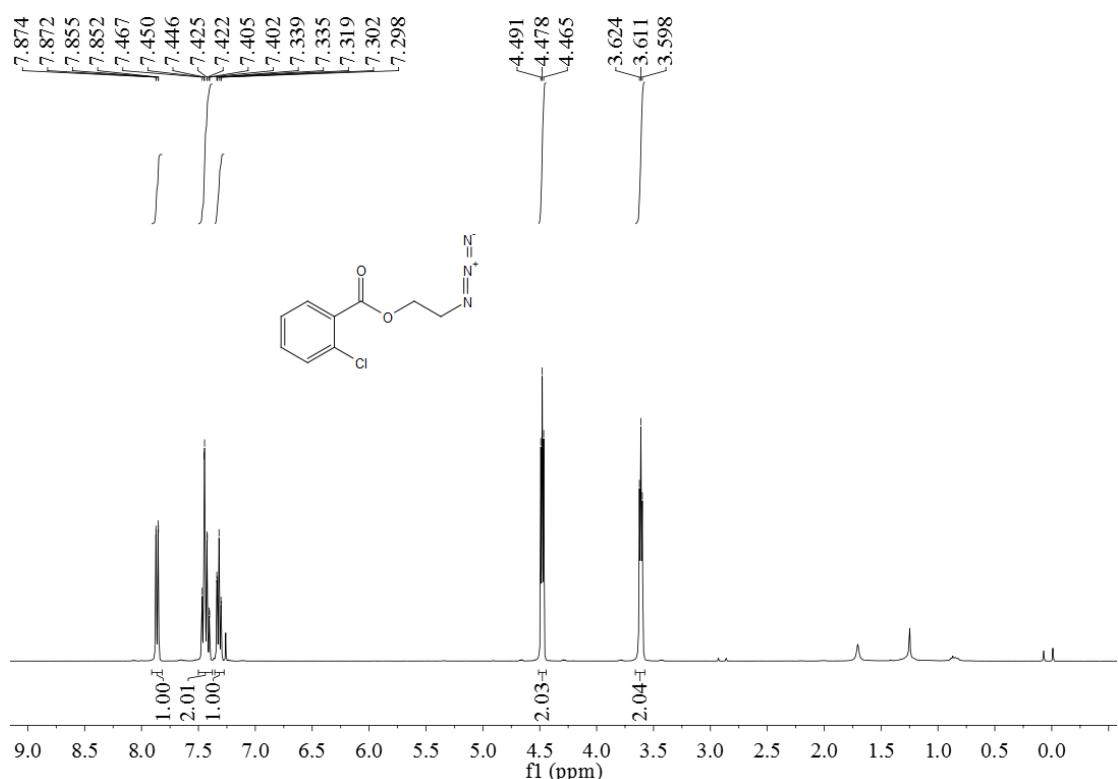
**3ao**



4



5



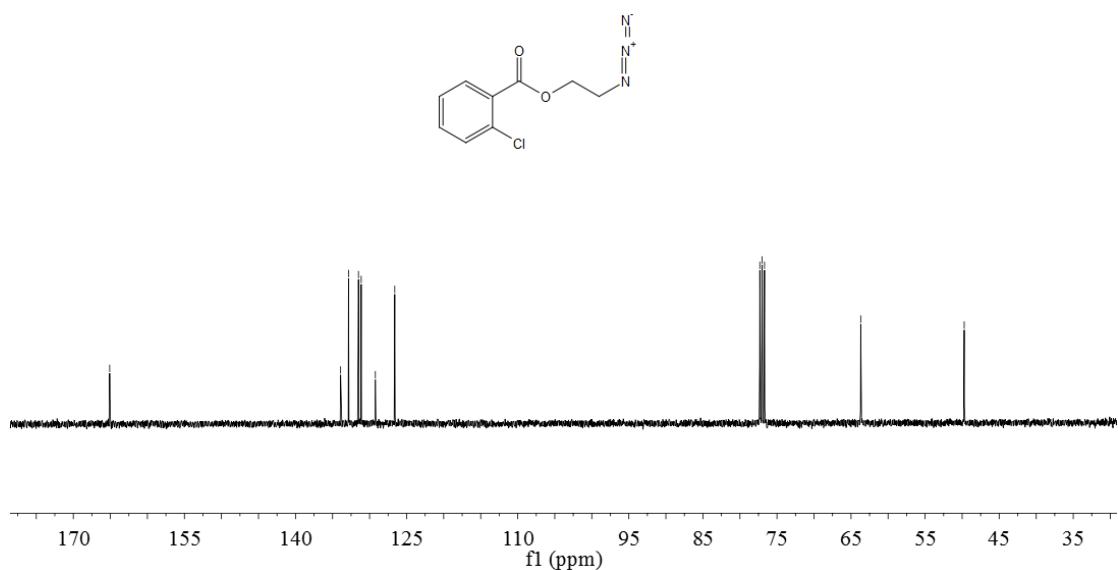
-165.089

133.911  
132.844  
131.503  
131.132  
129.222  
126.601

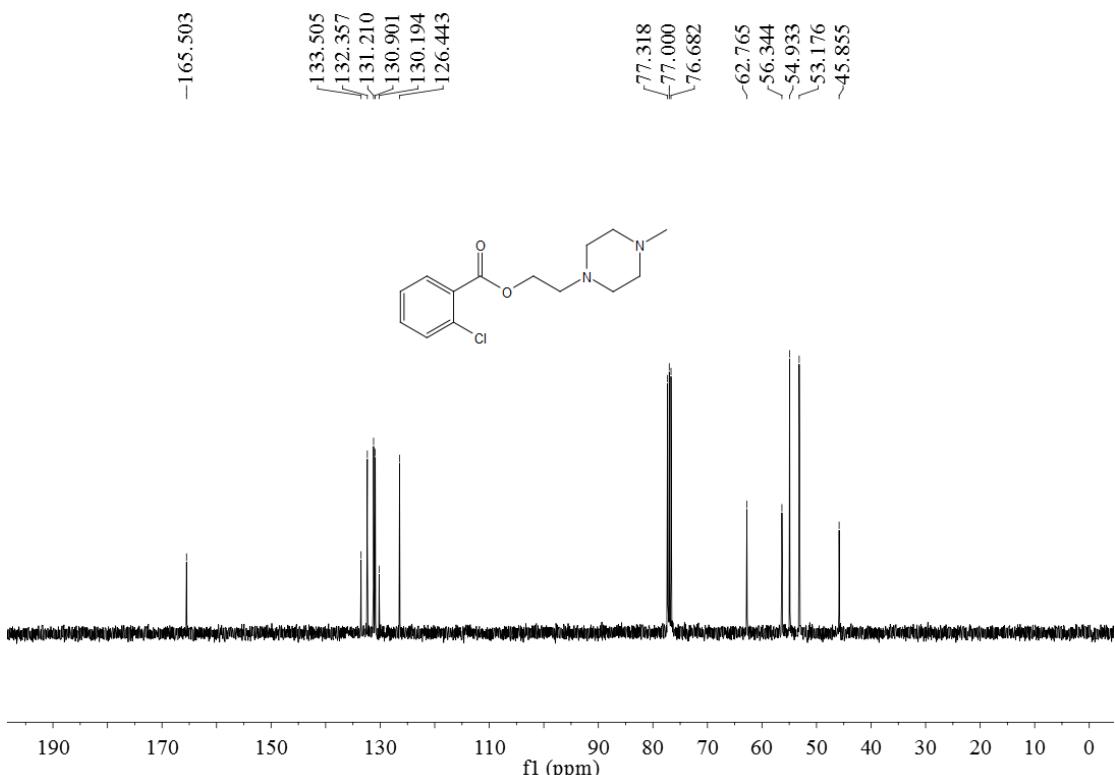
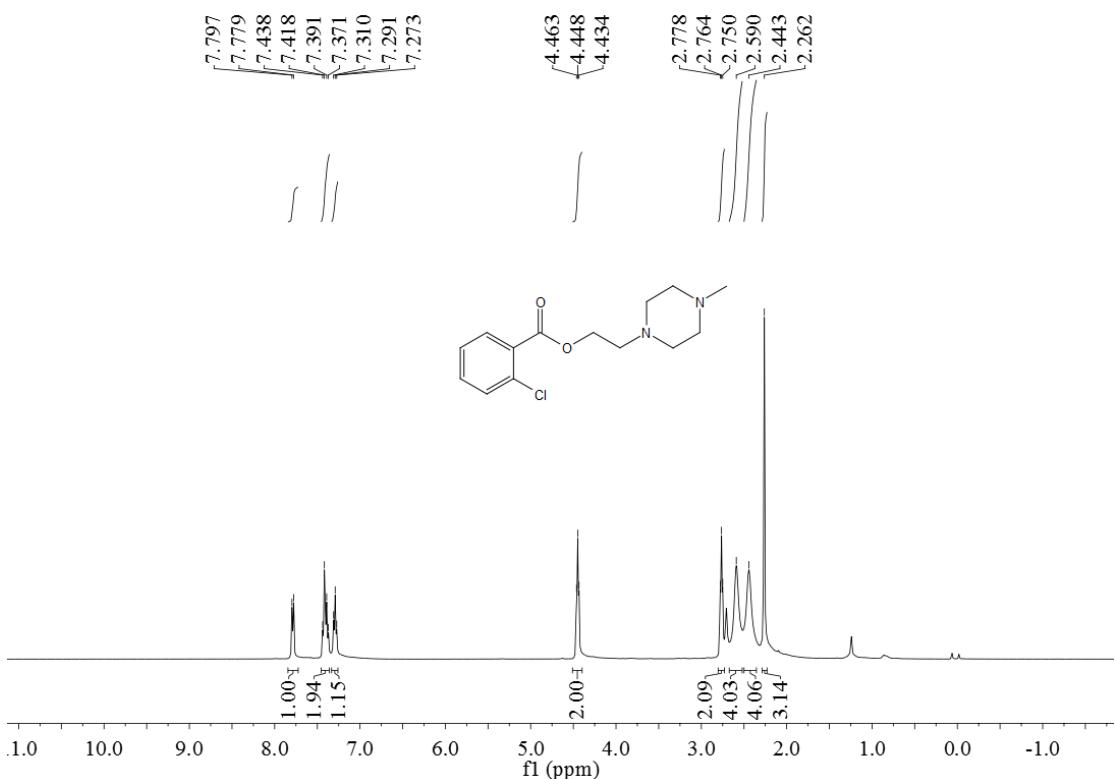
77.318  
77.000  
76.683

-63.694

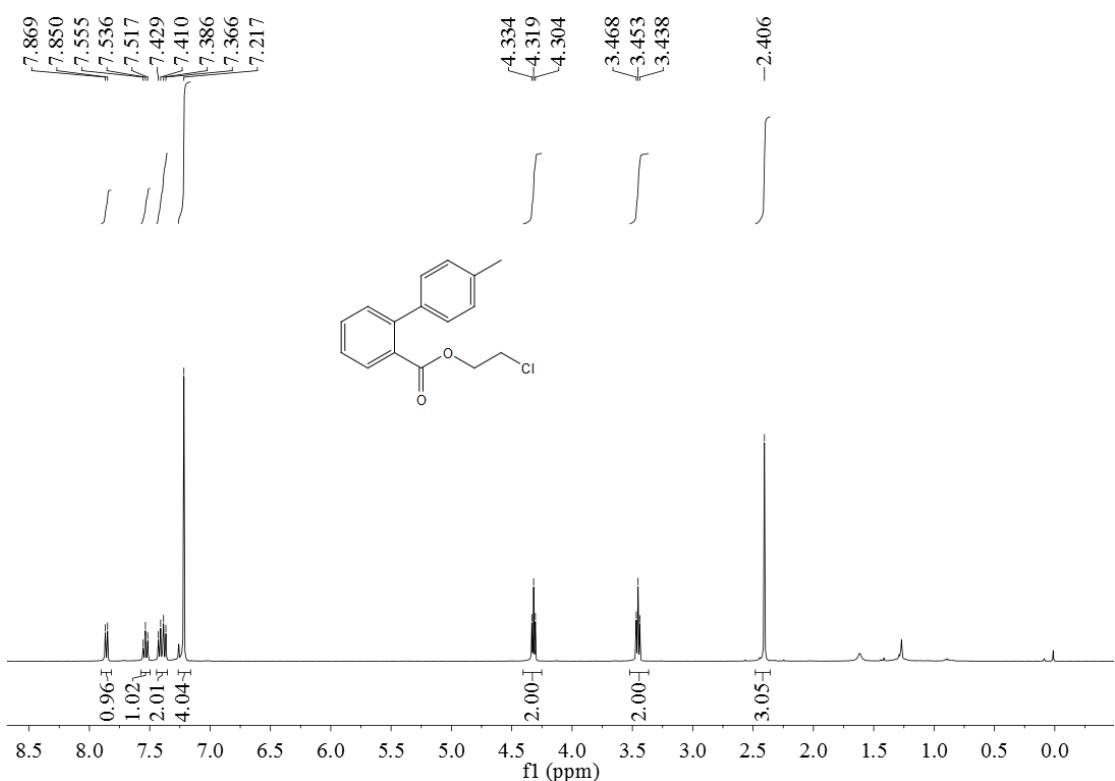
-49.721



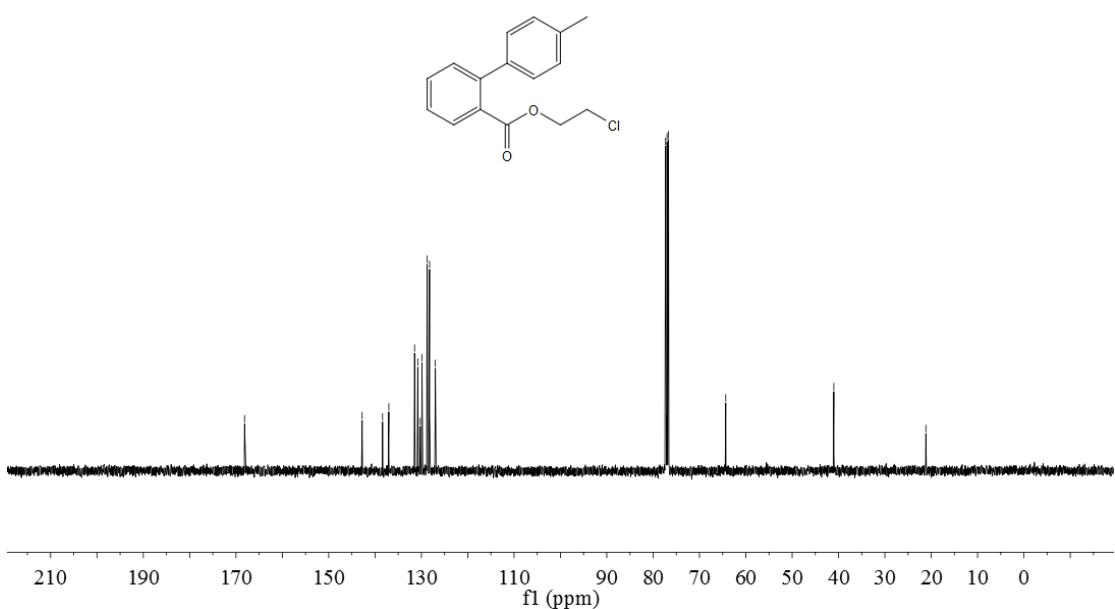
6



7



-168.155, -142.786, -138.376, -137.024, -131.468, -130.782, -130.249, -129.867, -128.778, -128.238, -126.985, -77.318, -77.000, -76.683, -64.330, -41.014, -21.160



11

