

## Supporting Information

### Visible-light-mediated dehalogenative Borylation of inactivated aryl and alkyl

#### halides with a palladium complex

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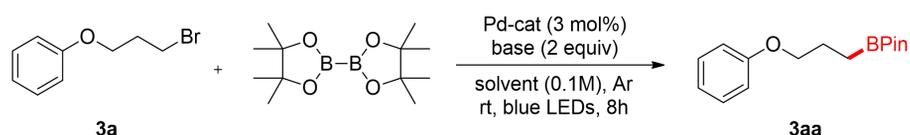
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## 1. General Information and Materials

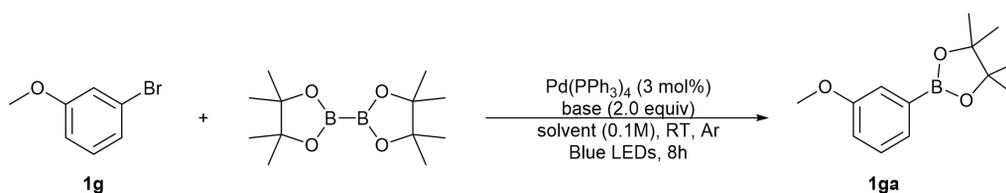
Silica products was purified by flash column chromatography on silica gel (Innochem SilicaFlashP60, 230-400 mesh) and GF<sub>254</sub> TLC. Reactions were stirred using Teflon - coated magnetic stir bars, Organic solutions were concentrated using a rotary evaporator with a diaphragm vacuum pump. The reaction apparatus for the common blue light transmission straight glass reaction tube, light wavelength is 75W, 445 nm Kessil LEDs lights, The temperature of reaction system is controlled between 25°C and 30°C by box reactor and fan. <sup>1</sup>H NMR spectra were recorded on 400 MHz in CDCl<sub>3</sub>, <sup>13</sup>C NMR spectra were recorded on 100 MHz in CDCl<sub>3</sub>, <sup>19</sup>F NMR spectra were recorded on 376 MHz in CDCl<sub>3</sub> using TMS as internal standard. Melting points were determined on a microscopic apparatus and were uncorrected. All products were further characterized by HRMS (high resolution mass spectra). Copies of their <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were provided. The yield was calculated by GC-MS, with 0.1mmol dodecane as internal standard. The starting materials were purchased from Sigma-Aldrich, Acros, TCI, Adamas or J&K Chemicals and used without further purification.

## 2. Optimization of Reaction Conditions of alkyl/aryl boronates



| entries         | catalyst   | ligand           | solvent     | base                               | Yield <sup>a</sup>          |
|-----------------|--|------------------|-------------|------------------------------------|-----------------------------|
| 1               | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | DMF         | K <sub>3</sub> PO <sub>4</sub>     | 43%                         |
| 2               | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | THF         | K <sub>3</sub> PO <sub>4</sub>     | 30%                         |
| 3               | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | dioxane     | K <sub>3</sub> PO <sub>4</sub>     | 36%                         |
| 4               | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | PhMe        | K <sub>3</sub> PO <sub>4</sub>     | 41%                         |
| 5               | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 54%                         |
| 6               | Pd(OAc) <sub>2</sub>                               | Xantphos         | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | none                        |
| 7               | Pd(OAc) <sub>2</sub>                               | DPEphos          | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 33%                         |
| 8               | Pd(OAc) <sub>2</sub>                               | dipy             | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | none                        |
| 9               | Pd(OAc) <sub>2</sub>                               | BINAP            | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | Trace                       |
| 10              | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | MeCN        | CsCO <sub>3</sub>                  | 28%                         |
| 11              | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | MeCN        | K <sub>2</sub> CO <sub>3</sub>     | 42%                         |
| 12              | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | MeCN        | <sup>t</sup> BuOK                  | Trace                       |
| 13              | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | MeCN        | KOMe                               | 33%                         |
| 14              | Pd(OAc) <sub>2</sub>                               | PPh <sub>3</sub> | MeCN        | DBU                                | 24%                         |
| 15              | <b>Pd(PPh<sub>3</sub>)<sub>4</sub></b>             | -                | <b>MeCN</b> | <b>K<sub>3</sub>PO<sub>4</sub></b> | <b>75%(55%<sup>b</sup>)</b> |
| 16              | Pd <sub>2</sub> (dba) <sub>3</sub>                 | -                | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | none                        |
| 17              | Pd(PPh <sub>3</sub> ) <sub>2</sub> Cl <sub>2</sub> | -                | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 15%                         |
| 18              | -  | -                | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | none                        |
| 19              | Pd(PPh <sub>3</sub> ) <sub>4</sub>                 | -                | MeCN        | -                                  | none                        |
| 20 <sup>c</sup> | Pd(PPh <sub>3</sub> ) <sub>4</sub>                 | -                | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | none                        |

a. Reaction conditions: 1a (0.2 mmol), catalyst (3 mol %), ligand (6 mol %), base (2.0 equiv), B<sub>2</sub>pin<sub>2</sub> (2.0 equiv), solvent (2 mL), blue LEDs light, Ar, 25°C, 8h. The conversions and yields were determined by GC-MS using n-dodecane as an internal standard. b. Isolated yield. c. Without light.



| entry             | catalyst                               | solvent     | base                               | Yield <sup>a</sup>          |
|-------------------|--|-------------|------------------------------------|-----------------------------|
| 1                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | CsCO <sub>3</sub>                  | 42%                         |
| 2                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | THF         | CsCO <sub>3</sub>                  | 0                           |
| 3                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | DCE         | CsCO <sub>3</sub>                  | 0                           |
| 4                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeOH        | CsCO <sub>3</sub>                  | Trace                       |
| 5                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | DMF         | CsCO <sub>3</sub>                  | Trace                       |
| 6                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | DMA         | CsCO <sub>3</sub>                  | 0                           |
| 7                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | K <sub>2</sub> CO <sub>3</sub>     | 21%                         |
| 8                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 52%                         |
| 9                 | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | NaOAc                              | Trace                       |
| 10                | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | DBU                                | 38%                         |
| 11                | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | NaO <sup>t</sup> Bu                | 20%                         |
| 12                | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | Et <sub>3</sub> N                  | 13%                         |
| 13                | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | -                                  | Trace                       |
| 14 <sup>b,c</sup> | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 57%                         |
| 15 <sup>b,d</sup> | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 74%                         |
| 16 <sup>b,e</sup> | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | 31%                         |
| 17 <sup>b</sup>   | <b>Pd(PPh<sub>3</sub>)<sub>4</sub></b> | <b>MeCN</b> | <b>K<sub>3</sub>PO<sub>4</sub></b> | <b>95%(75%<sup>f</sup>)</b> |
| 18 <sup>b,g</sup> | Pd(PPh <sub>3</sub> ) <sub>4</sub>     | MeCN        | K <sub>3</sub> PO <sub>4</sub>     | None                        |

a) Reactions were carried out using 0.2 mmol of aryl halide, catalyst (3 mol %), 2.0 equiv of B<sub>2</sub>pin<sub>2</sub>, 1.0 equiv of base in 2.0 mL of solvent. The yields were determined by GC-MS analysis versus a calibrated internal standard and are averages of two experiments. b) 2.0 equiv of base. c) 1.0 equiv of B<sub>2</sub>pin<sub>2</sub>. d) 3.0 equiv of B<sub>2</sub>pin<sub>2</sub>. e) MeCN:H<sub>2</sub>O=19:1. f) Yield of isolated product. g) Without light.

### 3. General Procedure for the Photooxidation boronizing of Aryl and Alkyl Halides (GP1)

In a 5.0 mL reaction tube with Teflon cover and magnetic stirring bar the alkyl/aryl bromides or chlorides **1a-3c**, **4a**, **4b** (0.2 mmol, 1.0 equiv), palladium catalyst (0.006 mmol, 3 mol %), Bis(pinacolato)diboronand (0.4 mmol, 2.0 equiv) and base (0.4 mmol, 2.0 equiv) were dissolved in 2.0 mL of dry MeCN. After degassing with argon by syringe needle for 5 minutes, the reaction mixture was then irradiated in reactor with cooling device using a 440 (± 15) nm LED (75 W) for 8 hours. The reaction progress was monitored by GC-MS analysis. After full conversion, the reaction mixture was transferred into a flask and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petroleum ether/ethyl acetate as eluents on silica gel.

### 4. General Procedure for the Photooxidation boronizing of the secondary and tertiary Alkyl Bromides (GP2)

In a 5.0 mL reaction tube with Teflon cover and magnetic stirring bar the secondary and tertiary alkyl bromides **3d-3h** (0.2 mmol, 1.0 equiv), palladium catalyst (0.006 mmol, 3 mol %), bis(catecholato)diboron (0.4

mmol, 2.0 equiv) and base (0.4 mmol, 2.0 equiv) were dissolved in 2.0 mL of dry MeCN. After degassing with argon by syringe needle for 5 minutes, the reaction mixture was then irradiated in reactor with cooling device using a 440 ( $\pm$  15) nm LED (75 W) for 8 hours. The reaction progress was monitored by GC-MS analysis. After full conversion, a solution of pinacol (95 mg, 0.80 mmol) in triethylamine (0.7 mL) was added to the mixture. After 1 hour, water (15 mL) was added and the aqueous layer was extracted with ethyl acetate (3 x 15 mL). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and concentrated. The reaction mixture was added transferred into a flask and concentrated in vacuum. Purification of the crude product was achieved by flash column chromatography using petroleum ether/ethyl acetate as eluents on silica gel.

## 5. The synthesis procedure of compound 6aa, 6ba, 6ca and 6da

**6aa:** To a stirred solution of 2-naphthaleneboronic acid pinacol ester (1.0 mmol, 1.0 equiv) in methanol or acetonitrile solvent (1 mL) was added Urea-Hydrogen peroxide (UHP) (1.0 mmol, 1.0 equiv) at room temperature and the progress of the reaction was monitored by TLC after 15 minutes. After completion, the reaction mixture was diluted with water and extracted with dichloromethane (DCM). The combined organic layer was dried over anhydrous sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>). The resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel using the mixture of PE and EtOAc as eluents to give the product.

**6ba:** In a nitrogen-filled glovebox, a 10-mL vial was charged with 2-naphthaleneboronic acid pinacol ester (0.2 mmol), LiOtBu (0.22 mmol, 1.1 equiv), Lil (0.10 mmol, 10 mol%), CuI (0.02 mmol, 5.0 mol%), DMI (0.3 mL), PO(OMe)<sub>3</sub> (0.22 mmol, 1.1 equiv) and a magnetic stir bar. The vial was sealed with a Teflon-lined cap. The reaction mixture was heated at 50°C with stirring for 16 h in an aluminum block outside the glovebox. The reaction was quenched by H<sub>2</sub>O (10 mL) and extracted with toluene (10 mL  $\times$  3). The organic layer was condensed, and the resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel using the mixture of PE and EtOAc as eluents to give the product.

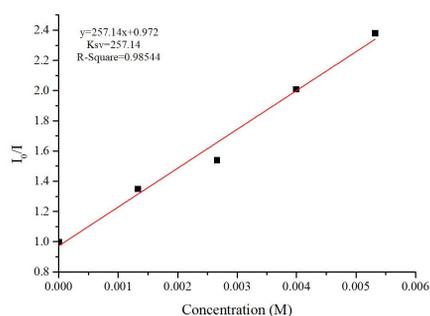
**6ca:** 2-naphthaleneboronic acid pinacol ester (0.4 mmol, 2.0 equiv), piperidine (0.20 mmol, 1 equiv), Cu(OAc)<sub>2</sub> (0.20 mmol, 1.0 equiv), Et<sub>3</sub>N (0.40 mmol, 2.0 equiv) and powdered activated 4 Å molecular sieves (200 mg) in DCM (0.8 mL). After 24 h, the resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel using the mixture of PE and EtOAc as eluents to give the product.

**6da:** To an oven-dried Schlenk tube was charged 2-naphthaleneboronic acid pinacol ester (1.5 mmol, 2.0 equiv.), N,N'-dimethylenediamine (0.9 mmol, 1.2 equiv.), Cu<sub>2</sub>O (0.3 mmol, 40 mol%), and a magnetic bar. The tube was evacuated three times under vacuum and backfilled with O<sub>2</sub>, and then connected to an oxygen balloon via a needle. Dried CH<sub>3</sub>CN (3 mL) and TMSCN (0.75 mmol, 1.0 equiv.) were injected via syringe. The mixture was stirred at 25°C for 12 h. The resultant mixture was evaporated under reduced pressure and the residue was purified by flash column chromatography on a silica gel using the mixture of PE and EtOAc as eluents to give the product.

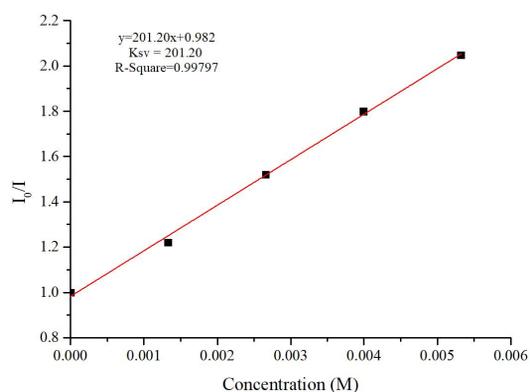
## 6. Mechanism characterization

### a) Radical capture experiments



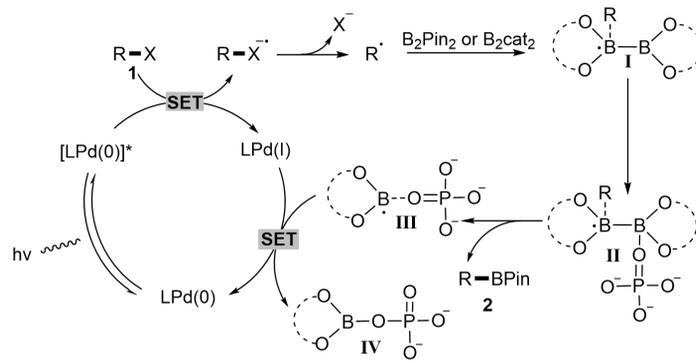


**Figure 2.** Fluorescence quenching plots of mixed solution  $\text{Pd}(\text{PPh}_3)_4$  ( $2.00 \times 10^{-3}$  M) and 3-bromoanisole (0 M,  $1.30 \times 10^{-3}$  M,  $2.60 \times 10^{-3}$  M,  $3.90 \times 10^{-3}$  M,  $5.20 \times 10^{-3}$  M) in MeCN. Stern–Volmer plots of the mixed solution of  $\text{Pd}(\text{PPh}_3)_4$  and 3-bromoanisole are presented.  $I_0$  is the luminescence intensity without the quencher, and  $I$  is the intensity with the quencher.  $K_{\text{SV}}=257.14$

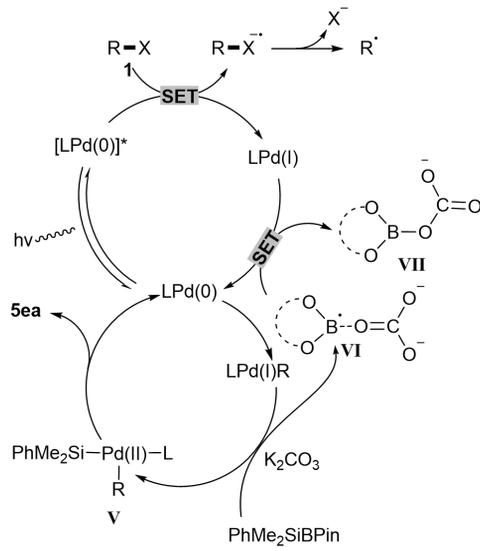


**Figure 3.** Fluorescence quenching plots of mixed solution  $\text{Pd}(\text{PPh}_3)_4$  ( $2.00 \times 10^{-3}$  M) and 3-phenoxypropyl bromide (0 M,  $1.30 \times 10^{-3}$  M,  $2.60 \times 10^{-3}$  M,  $3.90 \times 10^{-3}$  M,  $5.20 \times 10^{-3}$  M) in MeCN. Stern–Volmer plots of the mixed solution of  $\text{Pd}(\text{PPh}_3)_4$  and 3-phenoxypropyl bromide are presented.  $I_0$  is the luminescence intensity of the solvent without quencher, and  $I$  represents the intensity after adding the indicated concentration of the corresponding quencher.  $K_{\text{SV}}=201.20$

d) Propose mechanism

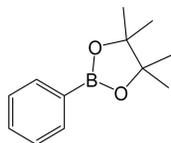


a) proposed mechanism of boronylation



b) Proposed mechanism of silylation.

## 7. Characterization Data of Products

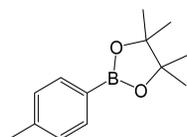


**1aa:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.82-7.80 (m, 2H), 7.48-7.44 (m, 1H), 7.39-7.34 (m, 2H), 1.35 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 134.7, 131.2, 127.7, 83.8, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 24388-23-6.<sup>[1]</sup>

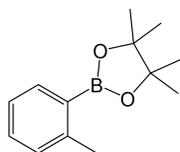


**1ba:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.71-7.69 (d, *J* = 7.8 Hz, 2H), 7.19-7.17 (d, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.33 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 141.4, 134.8, 128.5, 83.6, 24.8, 21.7;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 195062-57-8.<sup>[1]</sup>

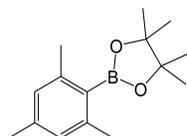


**1ca:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.77-7.75 (d, *J* = 7.8 Hz, 1H), 7.33-7.29 (m, 1H), 7.17-7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 144.8, 135.8, 130.7, 129.7, 124.7, 83.4, 24.9, 22.2;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 195062-59-0.<sup>[1]</sup>

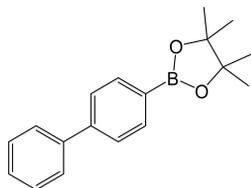


**1da:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 6.77 (s, 2H), 2.36 (s, 6H), 2.24 (s, 3H), 1.37 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 142.1, 138.9, 127.4, 83.4, 24.9, 22.2, 21.2;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 171364-84-4.<sup>[1]</sup>

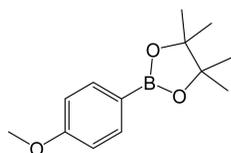


**1ea:** according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.90-7.88 (d, *J* = 8.1 Hz, 2H), 7.62-7.60 (d, *J* = 7.8 Hz, 4H), 7.44-7.40 (t, *J* = 7.5 Hz, 2H), 7.35-7.32 (t, *J* = 7.3 Hz, 1H), 1.35 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 143.8, 141.0, 135.2, 128.7, 127.5, 127.2, 126.4, 83.8, 24.8;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 144432-80-4. <sup>[3]</sup>

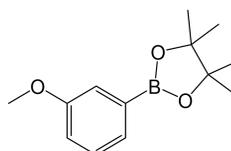


**1fa:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.77-7.75 (m, 1H), 6.90-6.88 (m, 1H), 3.82 (s, 3H), 1.33 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 162.1, 136.5, 113.3, 83.5, 55.0, 24.8;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 171364-79-7. <sup>[1]</sup>

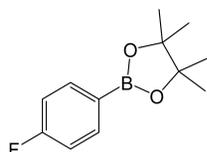


**1ga:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.41-7.39 (m, 1H), 7.33-7.28 (m, 2H), 7.02-7.00 (m, 1H), 3.83 (s, 3H), 1.35 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 159.0, 128.9, 127.2, 118.7, 117.9, 83.8, 55.2, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 325142-84-5. <sup>[3]</sup>



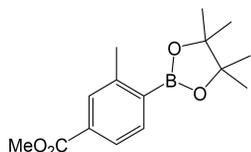
**1ha:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.82-7.77 (m, 2H), 7.07-7.02 (m, 2H), 1.34 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 165.07 (d, *J*<sub>C-F</sub> = 248.0 Hz), 137.0, 136.9, 114.9, 114.7, 83.9, 24.9;

**<sup>19</sup>F NMR** (376 MHz, CDCl<sub>3</sub>, δ ppm) -108.44;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 214360-58-4. <sup>[1]</sup>

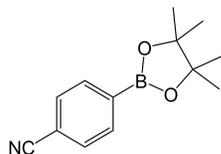


**1ia**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.82-7.80 (m, 3H), 3.91 (s, 3H), 2.57 (s, 3H), 1.36 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 167.3, 144.9, 135.7, 131.7, 130.4, 125.5, 83.8, 52.1, 24.9, 22.1;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 473596-87-1. <sup>[4]</sup>

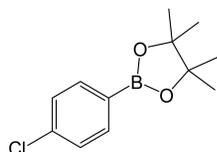


**1ja**: according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.90-7.88 (d, *J* = 8.1 Hz, 2H), 7.65-7.63 (d, *J* = 8.2 Hz, 2H), 1.35 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 135.0, 131.1, 118.8, 114.5, 84.4, 24.8;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 171364-82-2. <sup>[1]</sup>

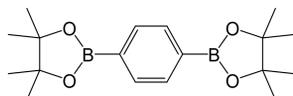


**1ka**: according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.74-7.72 (m, 2H), 7.35-7.33 (m, 2H), 1.34 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 137.5, 136.1, 128.0, 84.0, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 195062-61-4. <sup>[1]</sup>

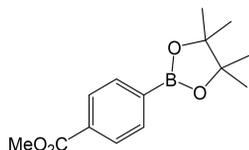


**1kb**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.80 (s, 4H), 1.35 (s, 24H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 133.9, 83.8, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 99770-93-1. <sup>[1]</sup>

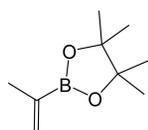


**1a**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 8.03-8.01 (d, *J* = 8.1 Hz, 2H), 7.88-7.86 (d, *J* = 8.1 Hz, 2H), 3.93 (s, 3H), 1.36 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 167.1, 134.6, 132.3, 128.6, 84.2, 52.2, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 171364-80-0. <sup>[1]</sup>

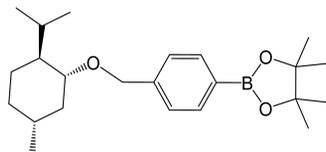


**1ma**: according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 5.76-5.63 (m, 2H), 1.82 (t,  $J = 1.5$  Hz, 3H), 1.27 (s, 12H);

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 130.0, 83.4, 24.8, 21.2;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 126726-62-3.



**1na**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

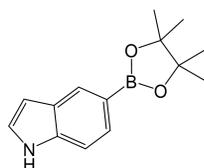
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 7.78-7.77 (d,  $J = 8.0$  Hz, 2H), 7.35-7.33 (d,  $J = 8.0$  Hz, 2H), 4.68-4.65 (d,  $J = 12.0$  Hz, 1H), 4.44-4.41 (d,  $J = 12.0$  Hz, 1H), 3.19-3.12 (m, 1H), 2.33-2.25 (m, 1H), 2.20-2.14 (m, 1H), 1.67-1.60 (m, 2H), 1.34 (s, 12H), 1.32-1.25 (m, 2H), 0.94-0.86 (dd,  $J_1 = 13.7$  Hz,  $J_2 = 6.8$  Hz, 8H), 0.71-0.69 (d,  $J = 6.9$  Hz, 3H);

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 142.4, 134.8, 126.9, 83.7, 78.8, 70.2, 48.3, 40.3, 34.6, 31.5, 25.5, 24.9, 24.8, 23.3, 22.4, 21.0, 16.1;

IR: 2977.1, 2925.7, 2868.5, 1454.5, 1281.7, 1170.7, 1123.9, 851.4.

HRMS (ESI<sup>+</sup>)  $m/z$  373.2919 (373.2909 calcd for  $\text{C}_{23}\text{H}_{37}\text{BO}_3^+$ ,  $[\text{M}+\text{H}]^+$ )

Carbon bearing boron not observed.

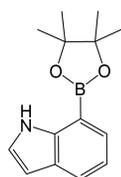


**2aa**: according to **GP1**; Pale brown solid; Eluent: petroleum ether/EtOAc = 25/1;

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 8.26 (s, 1H), 8.19 (s, 1H), 7.65-7.63 (d,  $J = 8.2$  Hz, 1H), 7.35-7.33 (d,  $J = 8.2$  Hz, 1H), 7.15-7.13 (m, 1H), 6.55-6.54 (m, 1H), 1.36 (s, 12H);

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 137.8, 128.6, 128.0, 127.6, 124.2, 110.5, 103.0, 83.4, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 269410-24-4; CCDC: No.2000793. <sup>[1]</sup>

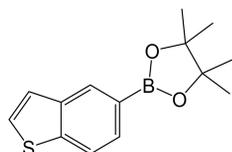


**2ba**: according to **GP1**; Pale brown solid; Eluent: petroleum ether/EtOAc = 25/1;

$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 9.23 (s, 1H), 7.78-7.75 (m, 1H), 7.66-7.64 (m, 1H), 7.26-7.24 (m, 1H), 7.15-7.10 (m, 1H), 6.55-6.53 (m, 1H), 1.38 (s, 12H);

$^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ,  $\delta$  ppm) 140.9, 129.2, 126.8, 124.2, 124.1, 119.2, 101.9, 83.8, 24.97, 24.82;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 642494-37-9. <sup>[5]</sup>

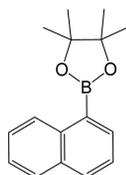


**2ca**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 8.31 (s, 1H), 7.90-7.88 (m, 1H), 7.76-7.74 (m, 1H), 7.42-7.41 (d, *J* = 5.5 Hz, 1H), 7.36-7.34 (m, 1H), 1.37 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 142.7, 139.2, 130.7, 129.7, 126.0, 124.1, 121.8, 83.8, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 501945-71-7. <sup>[5]</sup>

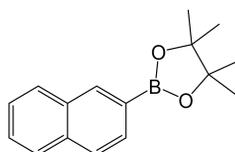


**2da**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 8.78-8.76 (d, *J* = 8.3 Hz, 1H), 8.09-8.07 (d, *J* = 8.2 Hz, 1H), 7.93-7.91 (d, *J* = 8.3 Hz, 1H), 7.83-7.81 (d, *J* = 7.9 Hz, 1H), 7.55-7.51 (m, 1H), 7.48-7.44 (m, 2H), 1.41 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 136.9, 135.6, 133.2, 131.6, 128.4, 128.3, 126.3, 125.6, 124.9, 83.7, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 68716-52-9. <sup>[2]</sup>

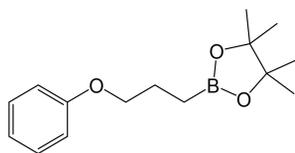


**2ea**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 8.38 (s, 1H), 7.89-7.81 (m, 4H), 7.52-7.44 (m, 2H), 1.38 (s, 12H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 136.2, 135.0, 132.8, 130.4, 128.6, 127.7, 127.0, 126.9, 125.8, 83.9, 24.9;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 256652-04-7. <sup>[3]</sup>

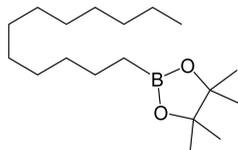


**3aa**: according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.28-7.24 (m, 2H), 6.94-6.89 (m, 3H), 3.95-3.92 (t, *J* = 6.7 Hz, 2H), 1.93-1.86 (m, 2H), 1.25 (s, 12H), 0.94-0.90 (t, *J* = 7.9 Hz, 2H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 159.1, 129.3, 120.3, 114.6, 83.1, 69.5, 24.8, 23.8;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 177950-03-7. <sup>[6]</sup>

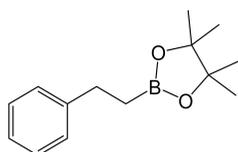


**3ba**: according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 1.25-1.24 (m, 32H), 0.89-0.86 (t, *J* = 6.8 Hz, 3H), 0.78-0.74 (t, *J* = 7.7 Hz, 2H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 82.8, 32.4, 31.9, 29.7, 29.7, 29.6, 29.4, 29.4, 24.8, 24.0, 22.7, 14.1;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 177035-82-4.<sup>[7]</sup>

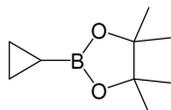


**3ca:** according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.28-7.20 (m, 4H), 7.17-7.13 (m, 1H), 2.77-7.72 (t, *J* = 8.2 Hz, 2H), 1.22 (s, 12H), 1.16-1.12 (t, *J* = 8.2 Hz, 2H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 144.4, 128.2, 128.0, 125.5, 83.1, 29.9, 24.8;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 165904-22-3.<sup>[6]</sup>

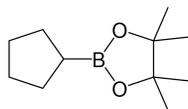


**3da:** according to **GP2**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 1.22 (s, 12H), 0.65-0.58 (m, 2H), 0.53-0.48 (m, 2H), -0.15- -0.23 (m, 1H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 82.8, 24.7, 3.8;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 126689-01-8.<sup>[8]</sup>

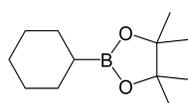


**3ea:** according to **GP2**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 1.71-1.62 (m, 2H), 1.54-1.35 (m, 6H), 1.17 (s, 12H), 1.15-1.04 (m, 1H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 82.7, 28.5, 26.8, 24.7;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 66217-55-8.<sup>[8]</sup>

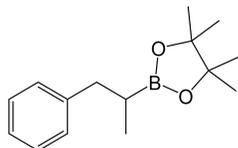


**3fa:** according to **GP2**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 1.68-1.57 (m, 5H), 1.35-1.23 (m, 5H), 1.23 (s, 12H), 0.98 (s, 1H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 82.7, 27.9, 27.1, 26.7, 24.7;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 87100-15-0.<sup>[8]</sup>

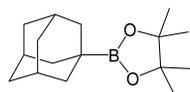


**3ga:** according to **GP2**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.26-7.23 (m, 2H), 7.20-7.19 (m, 2H), 7.17-7.13 (m, 1H), 5.30 (s, 1H) 2.83-2.51 (m, 2H), 1.19-1.18 (d, *J* = 4.6 Hz, 12H), 0.97-0.95 (d, *J* = 7.4 Hz, 3H);

**<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>, δ ppm) 142.3, 128.9, 128.0, 125.5, 83.0, 38.9, 24.7, 24.7, 15.2;

Carbon bearing boron not observed, CAS: 916658-74-7. <sup>[8]</sup>

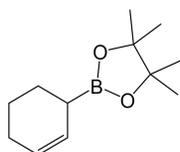


**3ha**: according to **GP2**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 1.85 (s, 3H), 1.75 (d, *J* = 3.1 Hz, 12H), 1.21 (s, 12H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 82.6, 38.0, 37.5, 27.6, 24.6;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 1357000-33-9. <sup>[8]</sup>

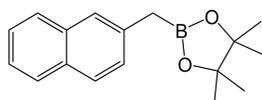


**4aa**: according to **GP1**; Colorless oil; Eluent: petroleum ether/EtOAc = 25/1;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 5.74-5.64 (m, 2H), 2.01-1.96 (m, 2H), 1.80-1.73 (m, 2H), 1.69-1.57 (m, 3H), 1.25 (s, 12H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 127.6, 126.0, 83.1, 25.0, 24.8, 24.7, 24.1, 22.5;

Carbon bearing boron not observed, CAS: 167773-14-0. <sup>[8]</sup>

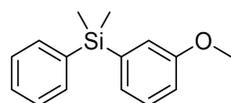


**4ba**: according to **GP1**; White solid; Eluent: petroleum ether/EtOAc = 25/1;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.78-7.71 (m, 3H), 7.61 (m, 1H), 7.41-7.32 (m, 3H), 2.45 (s, 2H), 1.22 (s, 12H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 136.3, 133.8, 131.4, 128.2, 127.6, 127.5, 127.2, 126.6, 125.6, 124.6, 83.5, 24.7;

Carbon bearing boron not observed. The chemical shifts were consistent with those reported in the literature, CAS: 1379610-55-5. <sup>[9]</sup>

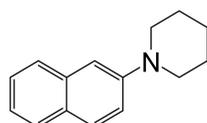


**5ea**: White solid; Eluent: petroleum ether/EtOAc = 25/1;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.54-7.50 (m, 2H), 7.36-7.33 (m, 3H), 7.11-7.09 (m, 1H), 7.06-7.05 (m, 1H), 6.91-6.88 (m, 1H), 3.77 (s, 3H), 0.54 (s, 6H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 159.0, 139.9, 138.1, 134.1, 129.1, 129.0, 127.8, 126.4, 119.8, 114.2, 55.0, -2.4;

The chemical shifts were consistent with those reported in the literature, CAS: 1006715-18-9. <sup>[10]</sup>

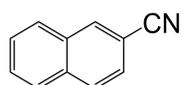


**6aa**: White solid; Eluent: petroleum ether/EtOAc = 25/1

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.71-7.66 (m, 3H), 7.39-7.35 (m, 1H), 7.29-7.24 (m, 2H), 7.12-7.11 (d, *J* = 2.4 Hz, 1H), 3.26-3.24 (m, 4H), 1.79-1.73 (m, 4H), 1.64-1.58 (m, 2H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 150.1, 134.7, 128.5, 128.3, 127.4, 126.6, 126.1, 123.1, 120.2, 110.3, 51.0, 25.9, 24.4;

CAS: 5465-85-0.

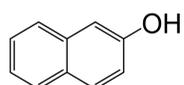


**6ba**: White solid; Eluent: petroleum ether/EtOAc = 50/1

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 8.18 (s, 1H), 7.98-7.93 (m, 2H), 7.90-7.88 (m, 2H), 7.55-7.48 (m, 2H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 138.4, 133.7, 132.7, 128.5, 128.2, 127.8, 127.7, 126.4, 126.1, 126.0, 125.7;

CAS: 613-46-7.

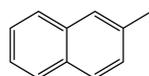


**6ca**: White solid; Eluent: petroleum ether/EtOAc = 25/1

<sup>1</sup>H NMR (400 MHz, MeOD, δ ppm) 7.71-7.68 (m, 2H), 7.63-7.61 (m, 1H), 7.37-7.33 (m, 1H), 7.25-7.21 (m, 1H), 7.13-7.12 (m, 1H), 7.10-7.07 (m, 1H), 4.92 (s, 1H);

<sup>13</sup>C NMR (100 MHz, MeOD, δ ppm) 156.3, 136.4, 130.4, 129.9, 128.6, 127.1, 127.1, 123.9, 119.2, 109.9;

CAS: 135-19-3.



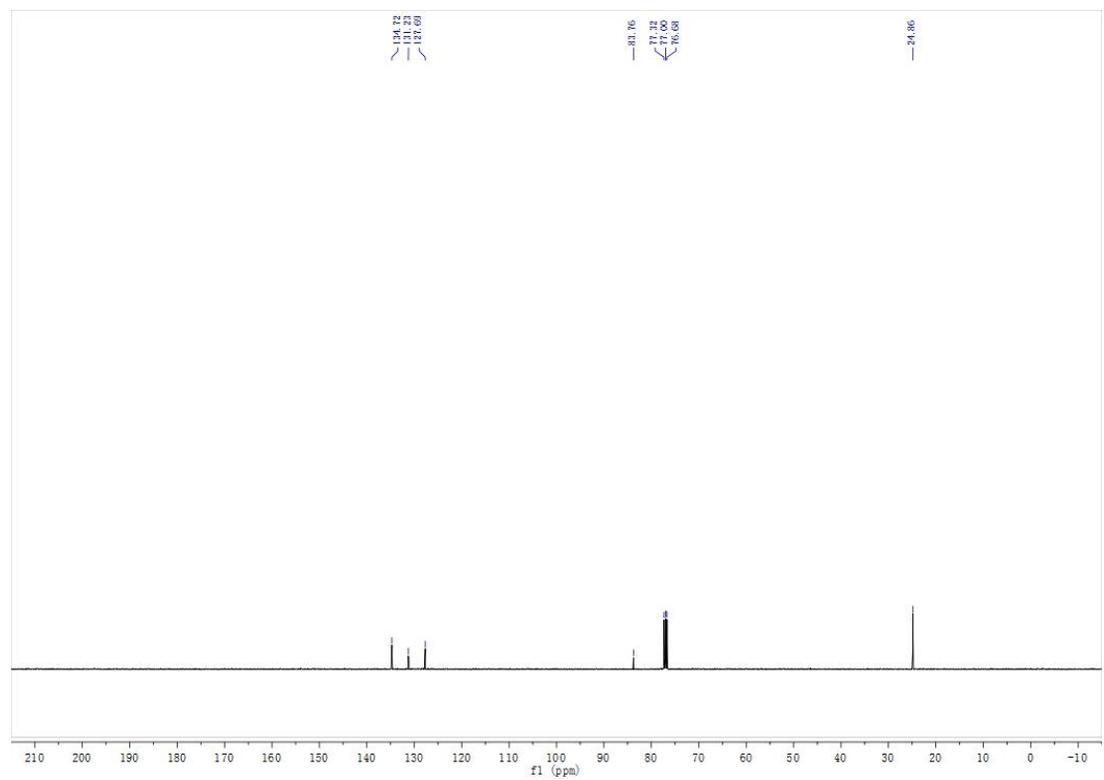
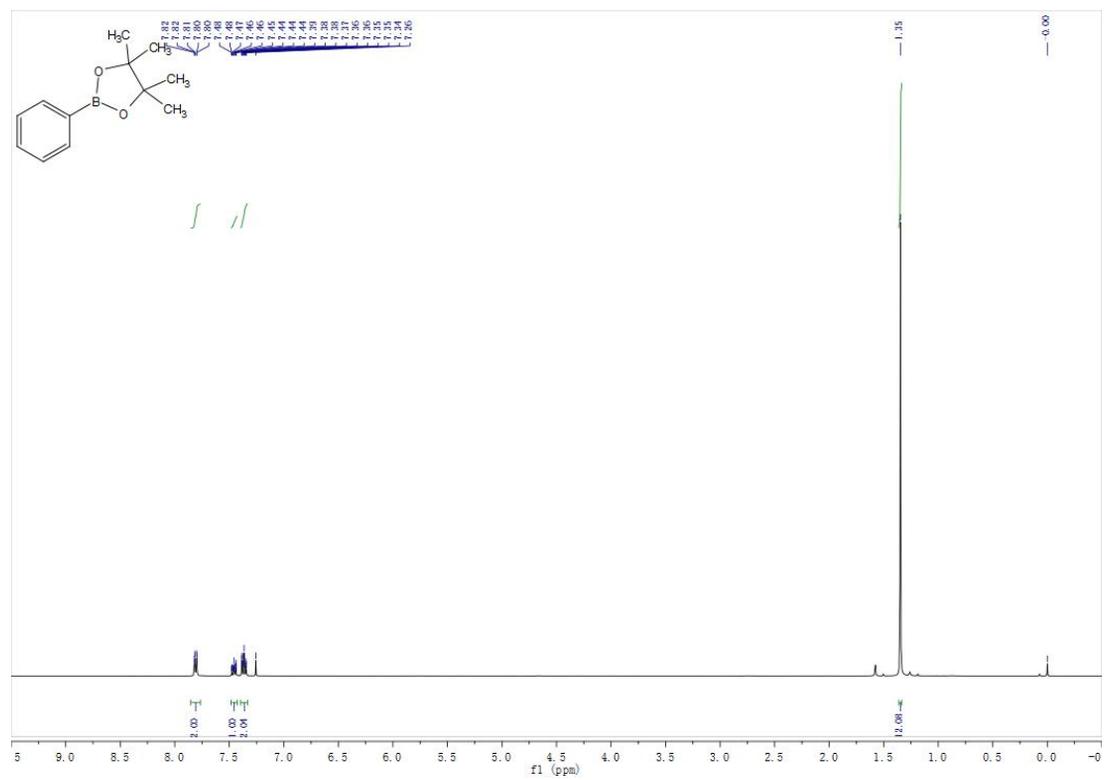
**6da**: White solid; Eluent: petroleum ether

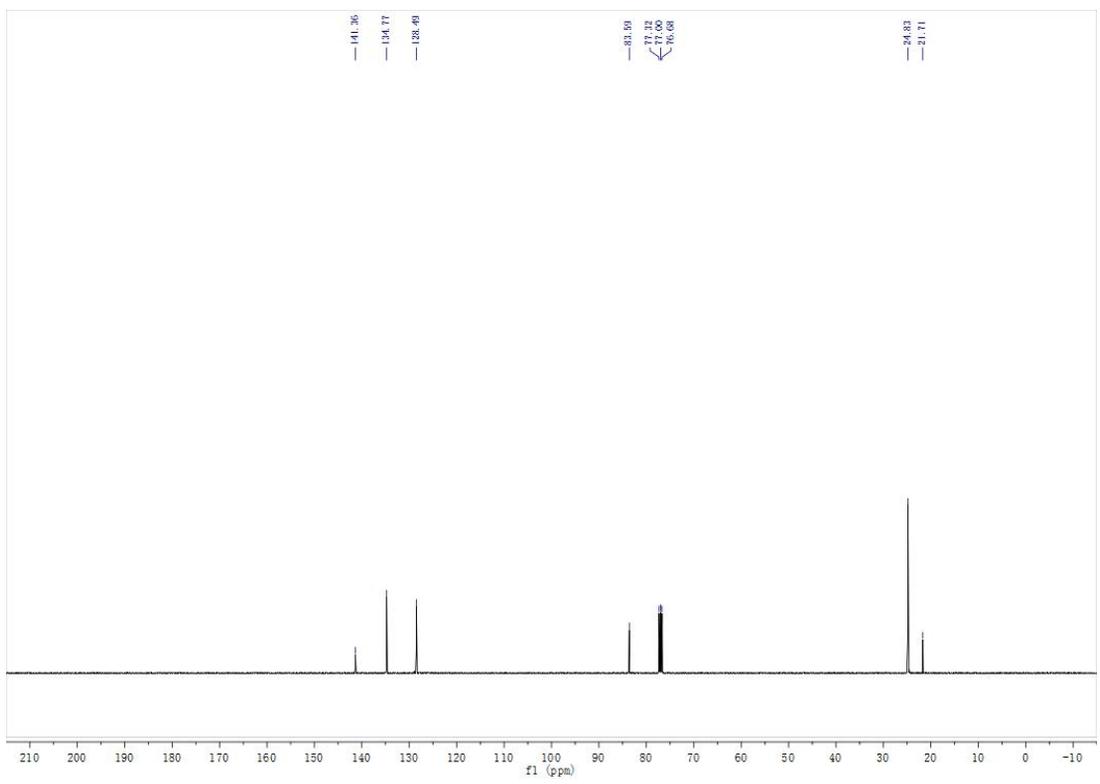
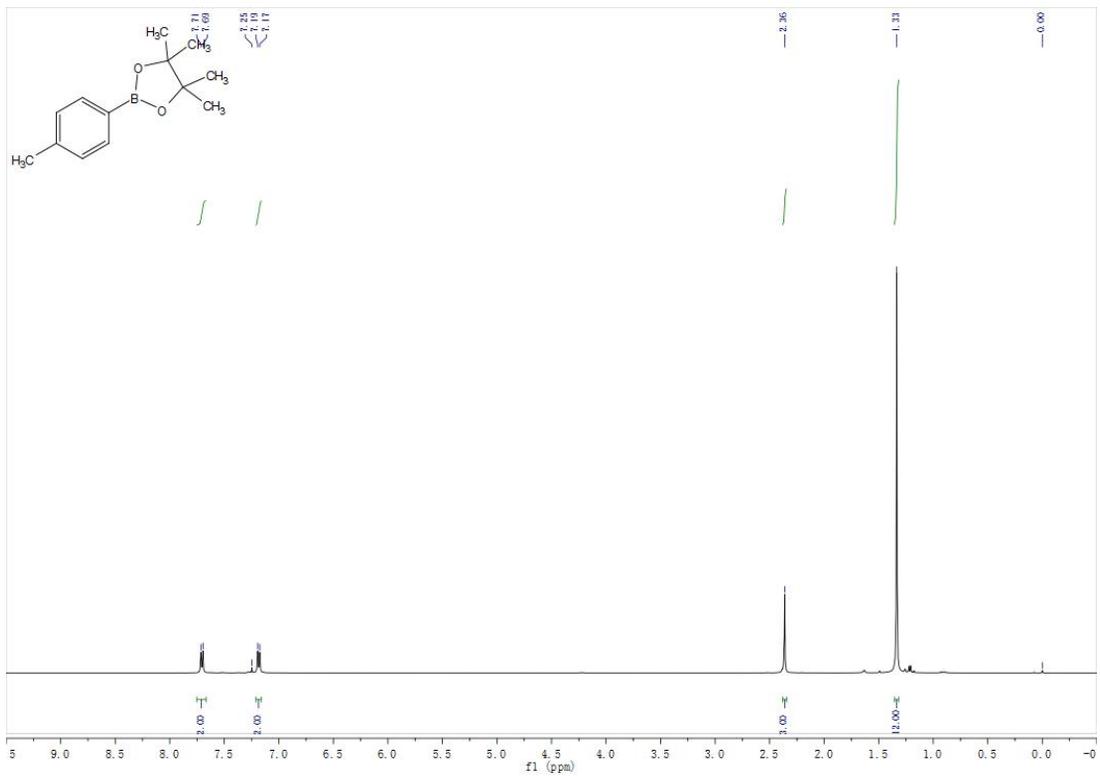
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, δ ppm) 7.81-7.79 (m, 1H), 7.76-7.74 (m, 2H), 7.62 (s, 1H), 7.44-7.40 (m, 2H), 7.33-7.31 (m, 1H), 2.52 (s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, δ ppm) 138.4, 133.7, 132.7, 128.5, 127.7, 127.6, 127.2, 126.8, 125.7, 124.9, 29.7;

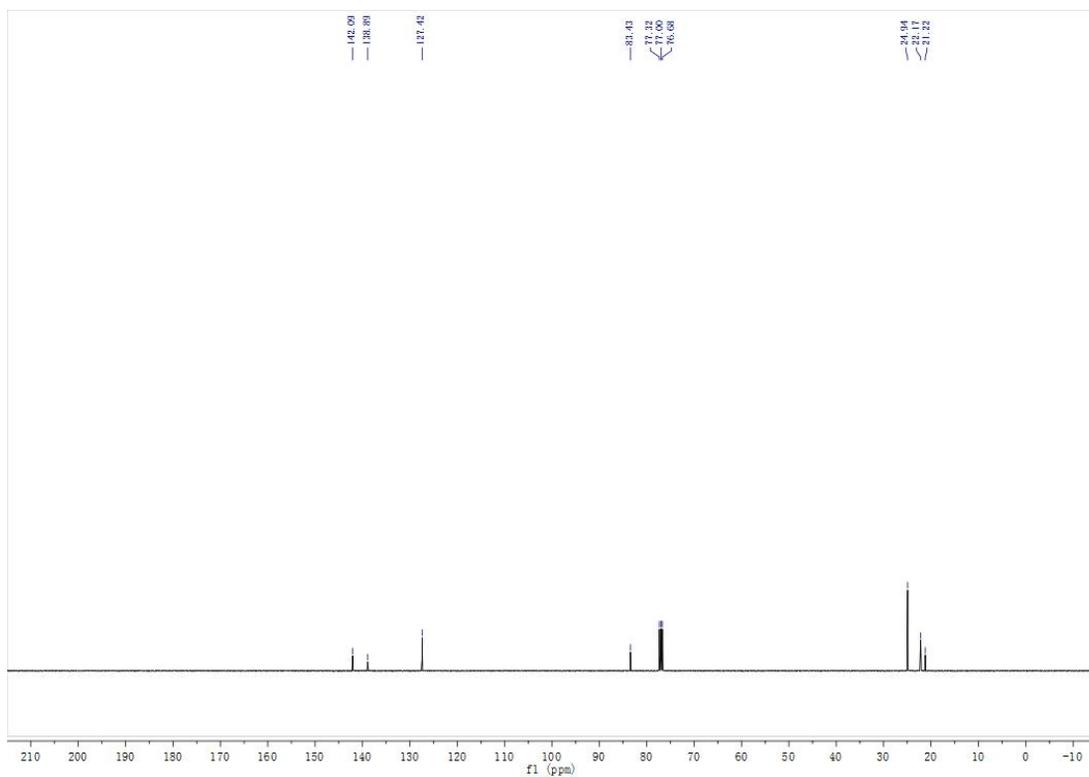
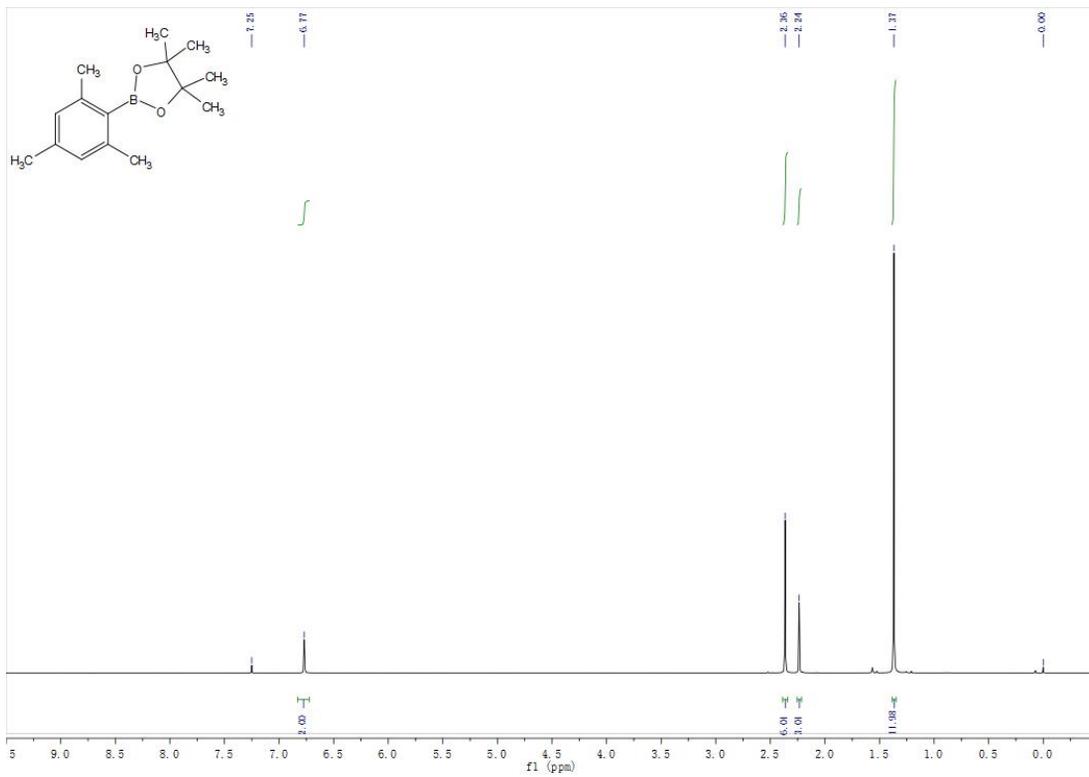
CAS: 91-57-6.

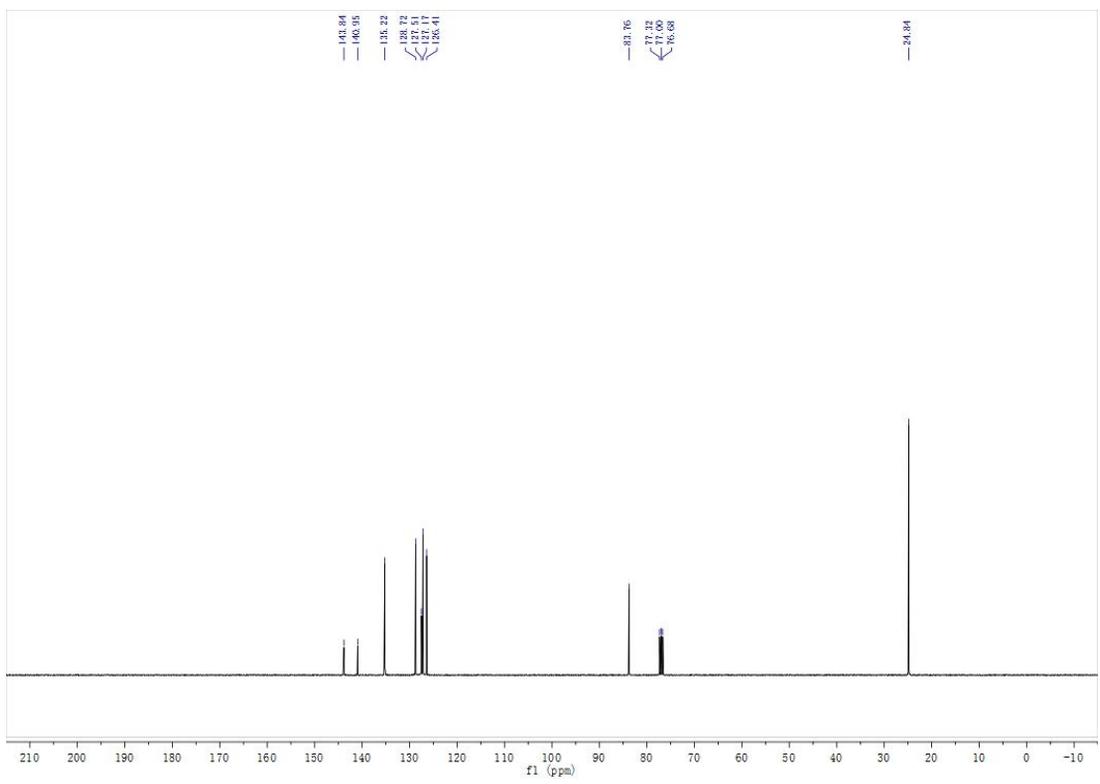
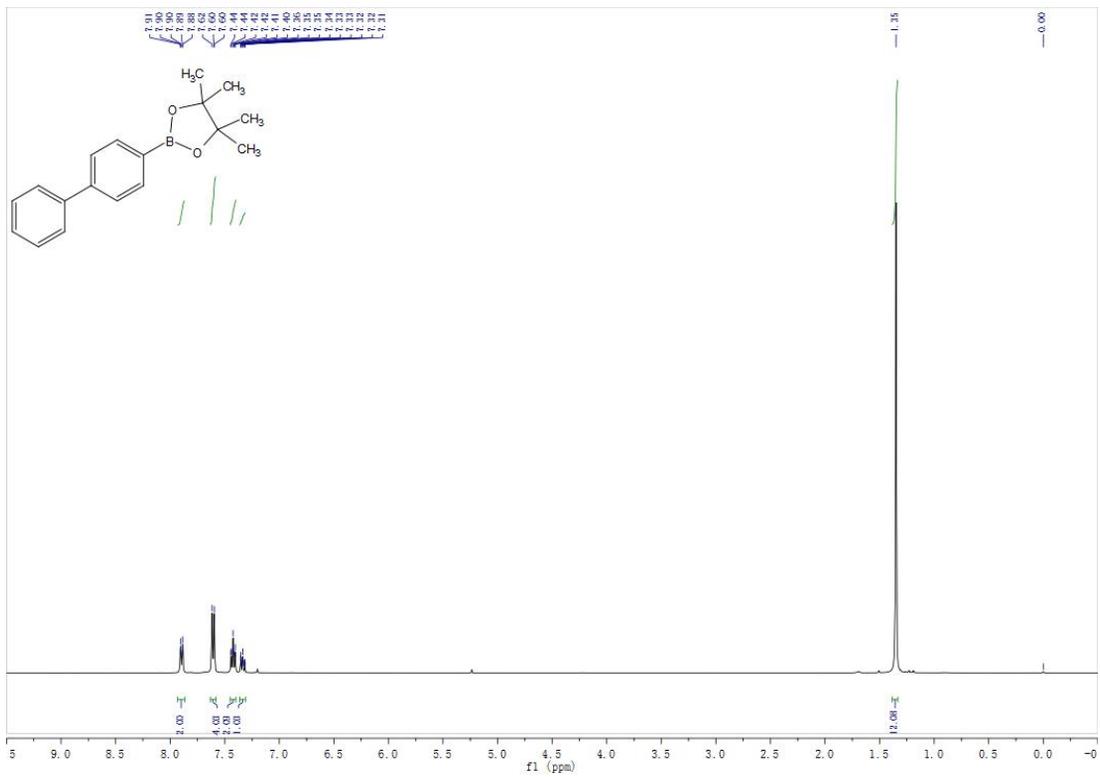
## 8. NMR Spectra data for Products:

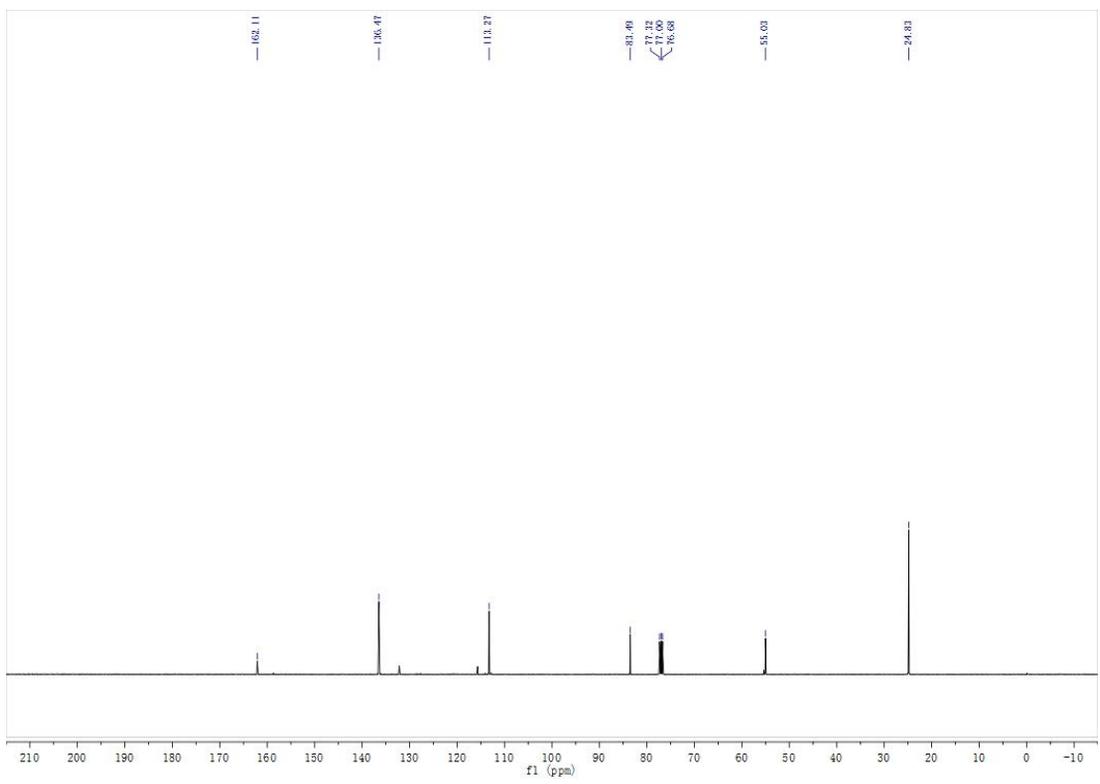
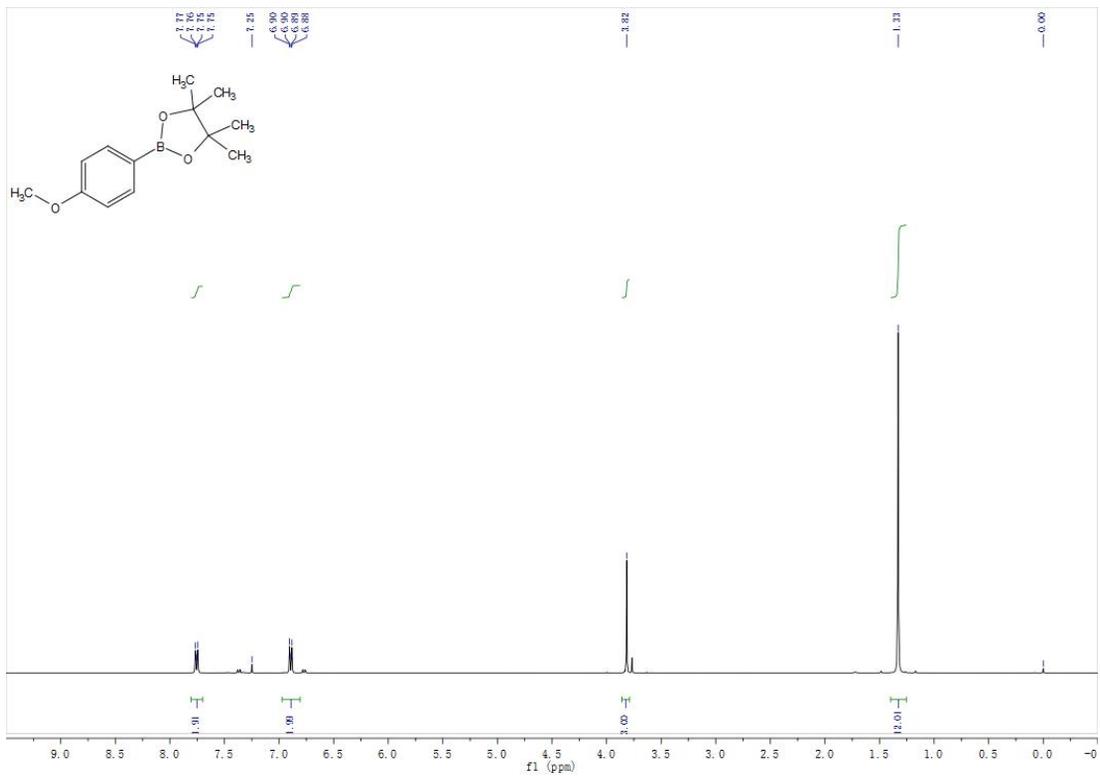


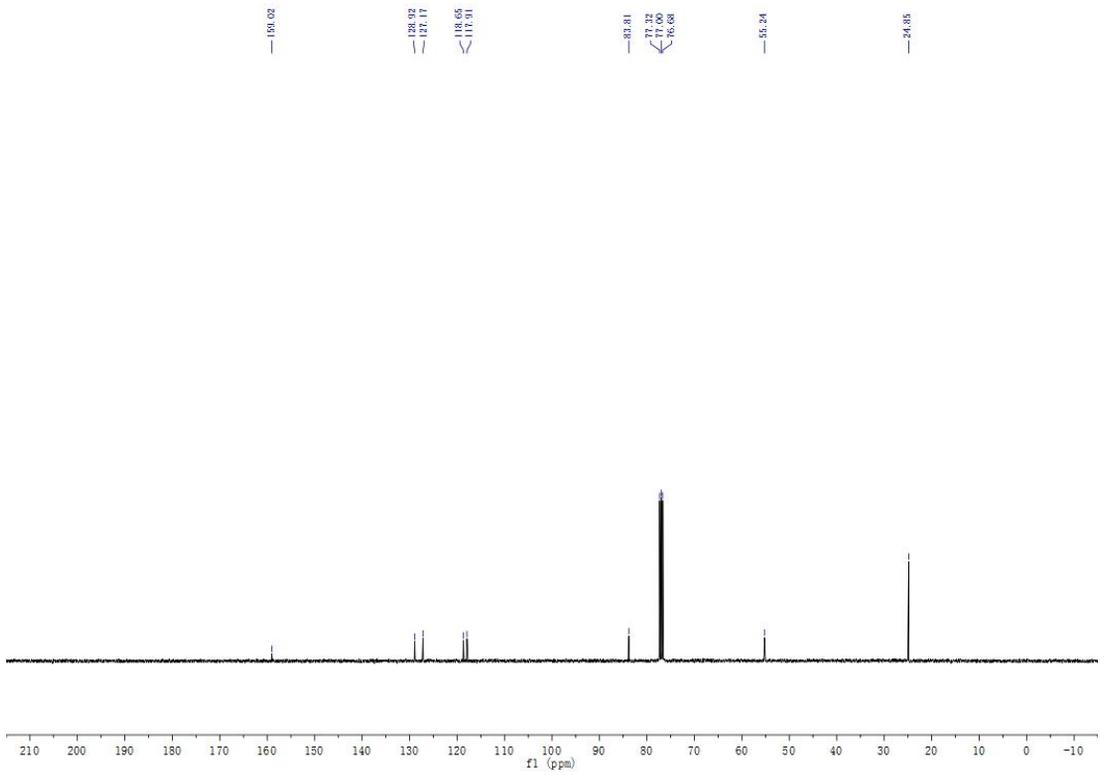
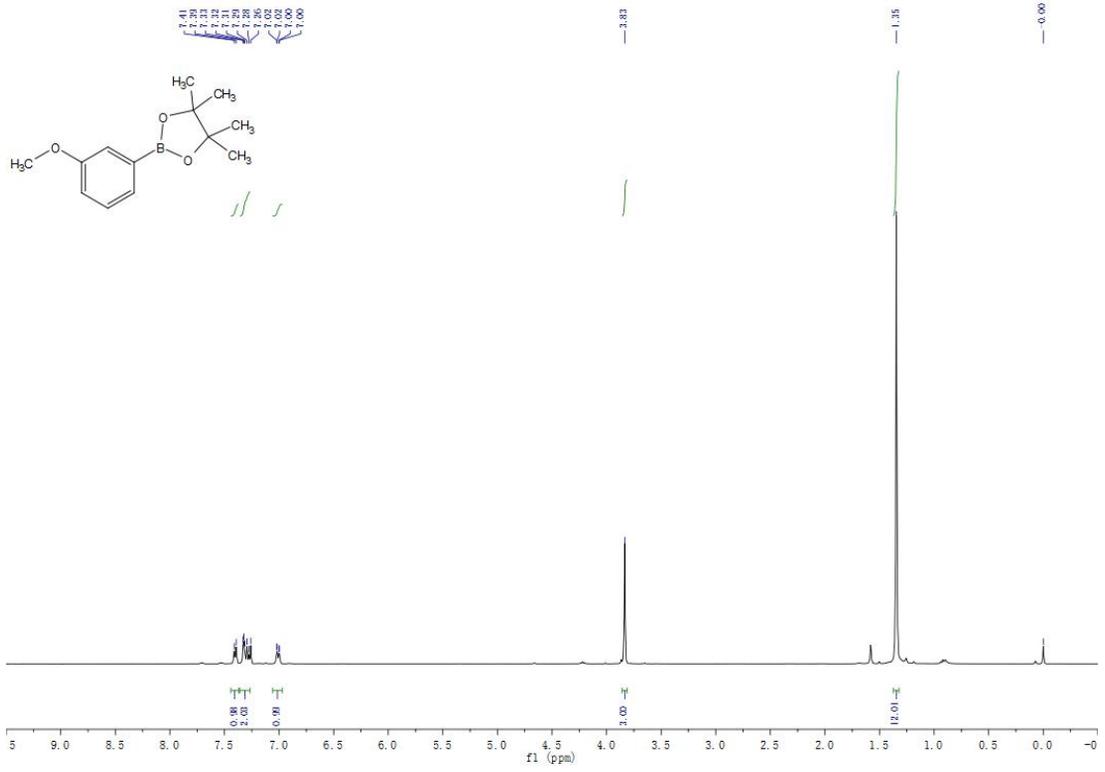


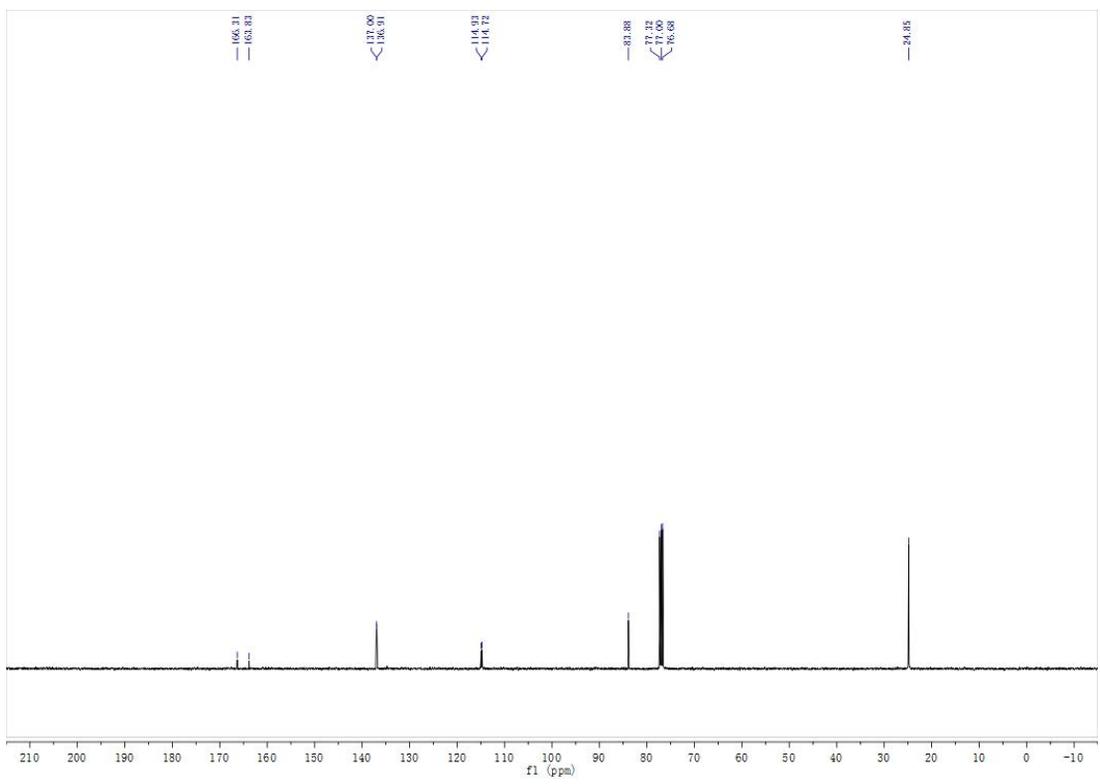
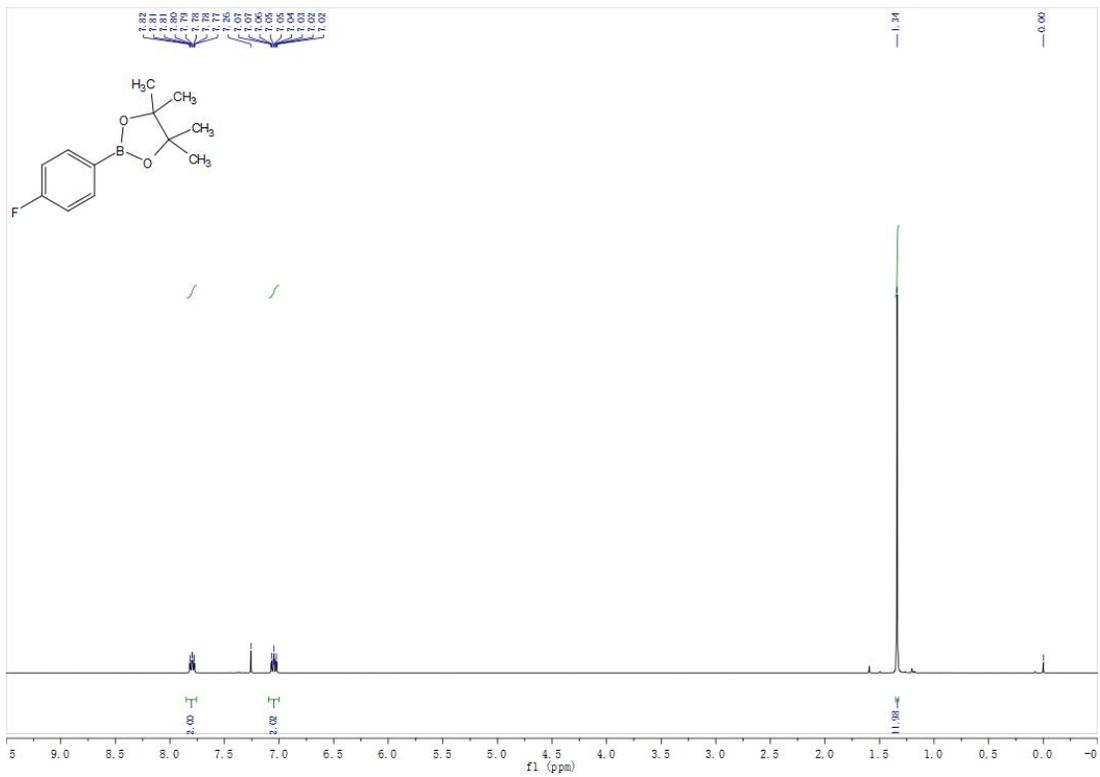


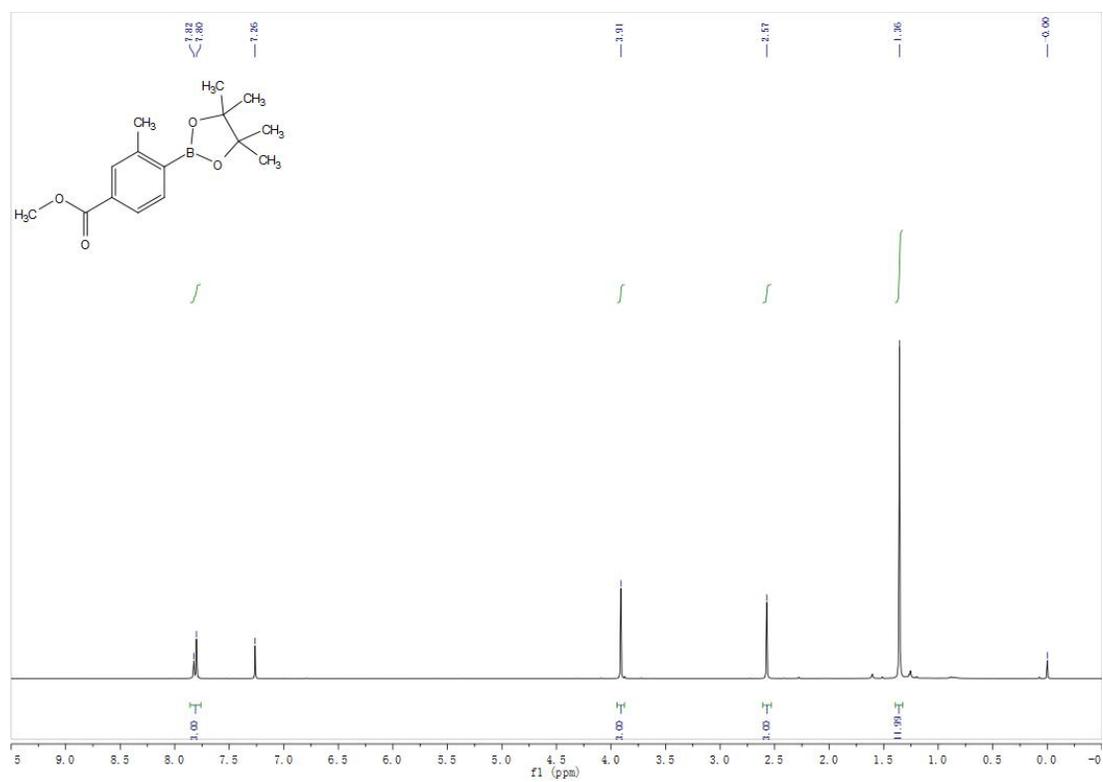
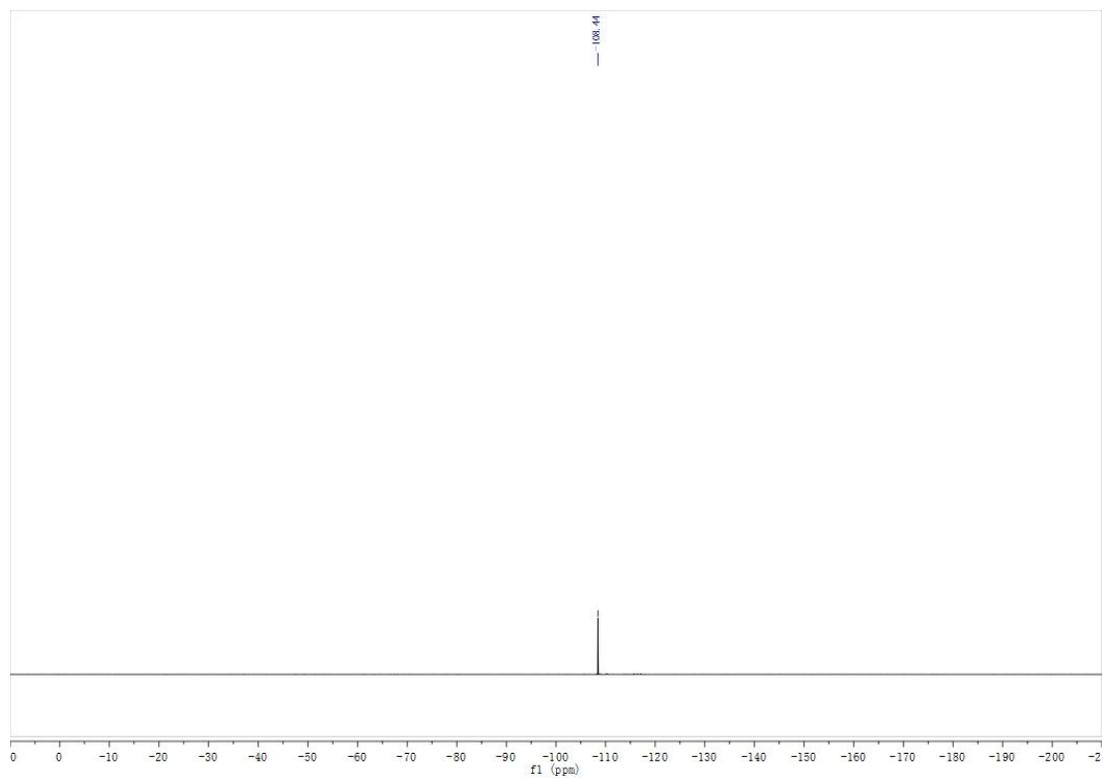


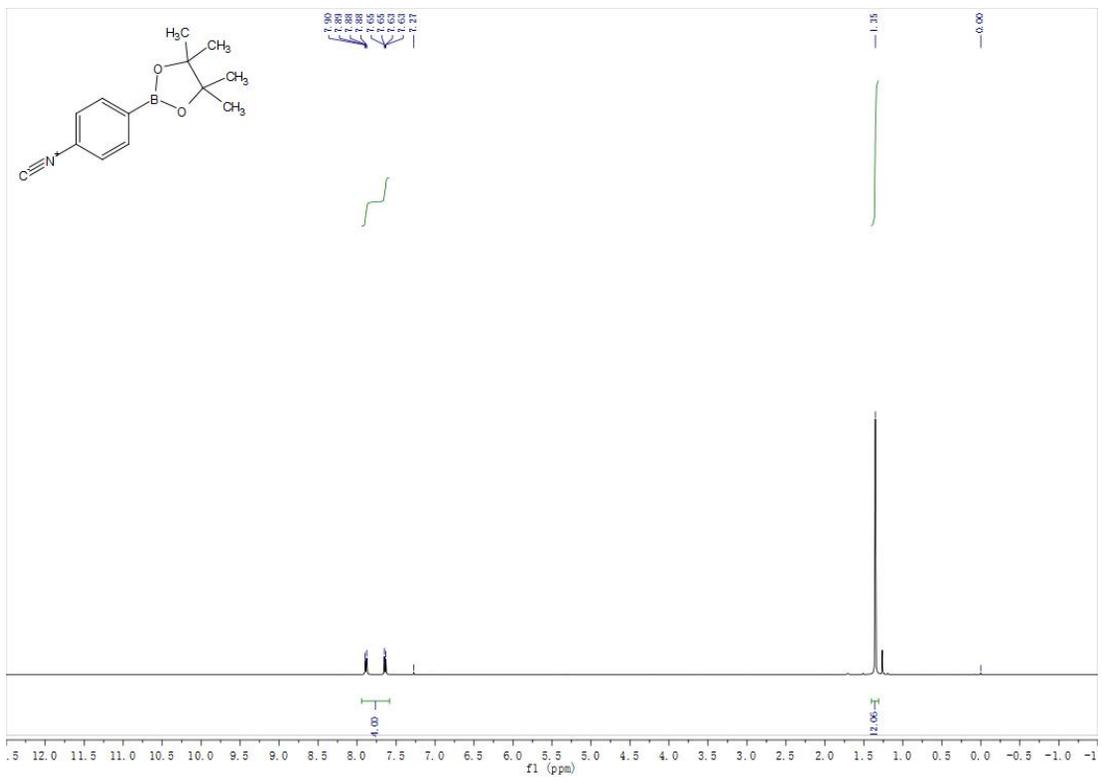
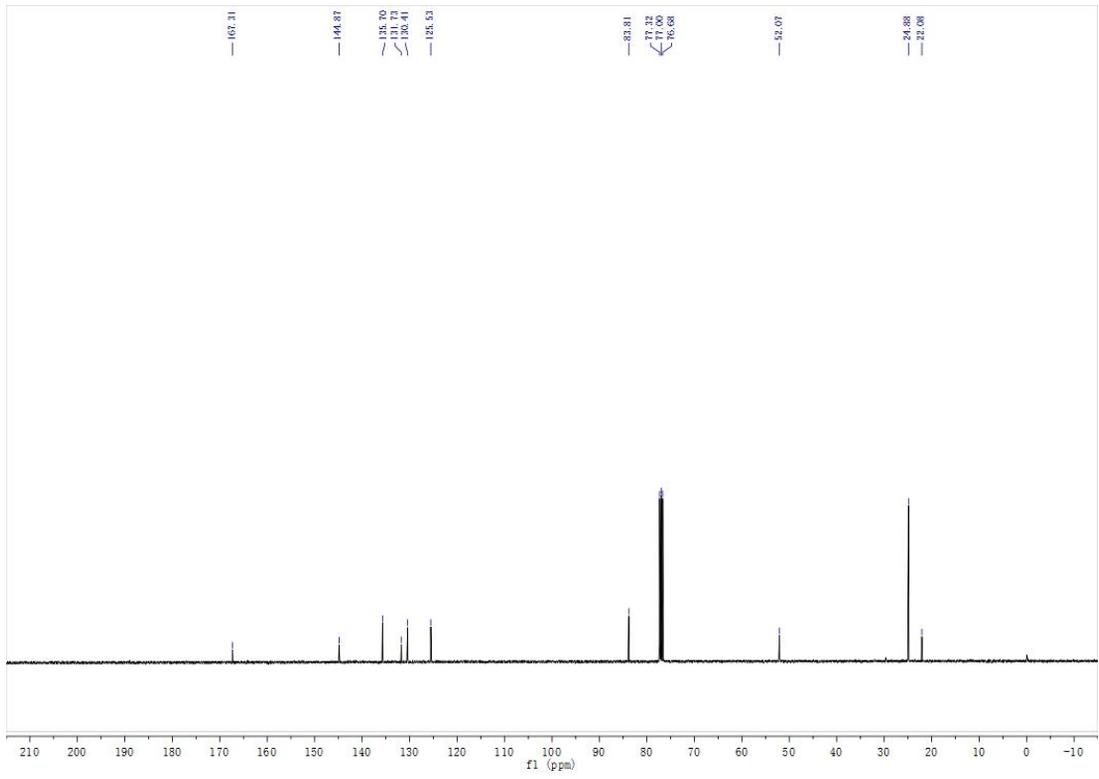


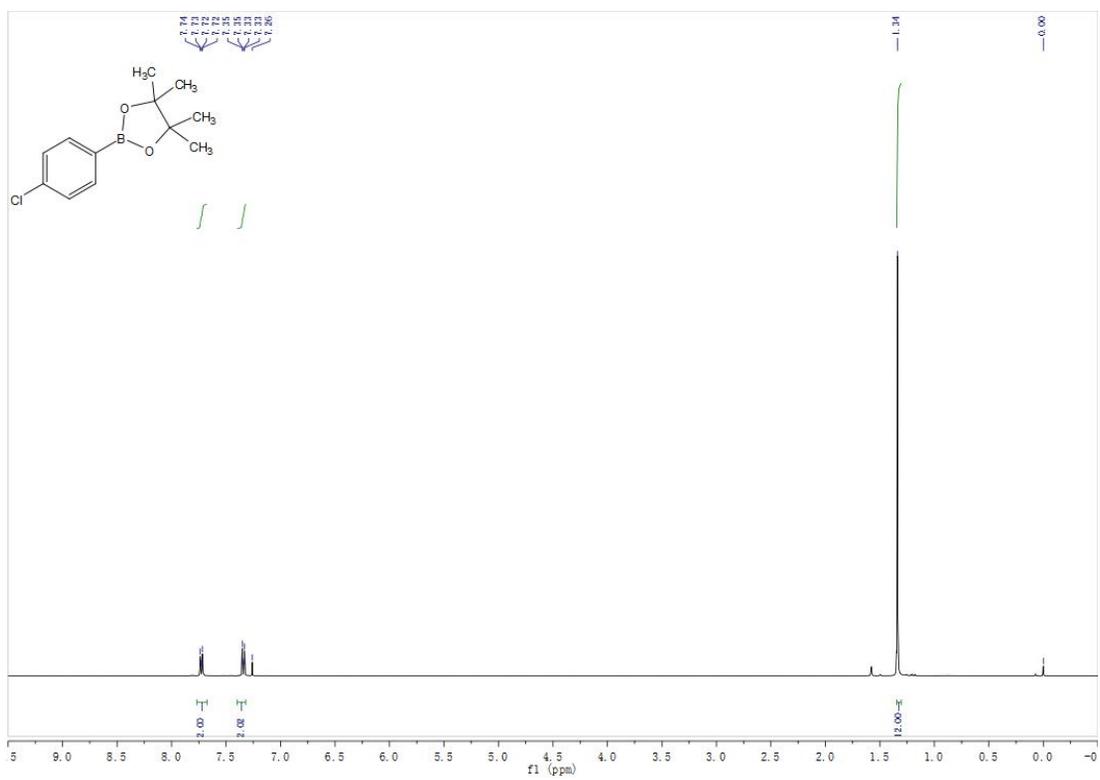
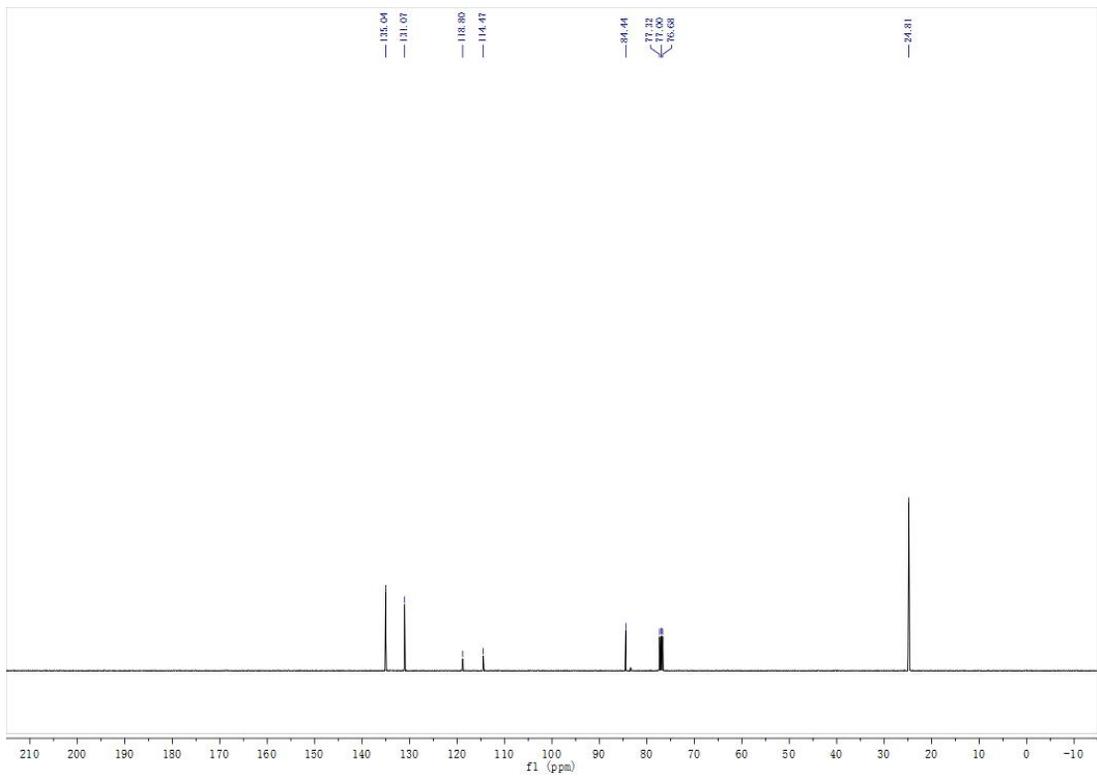


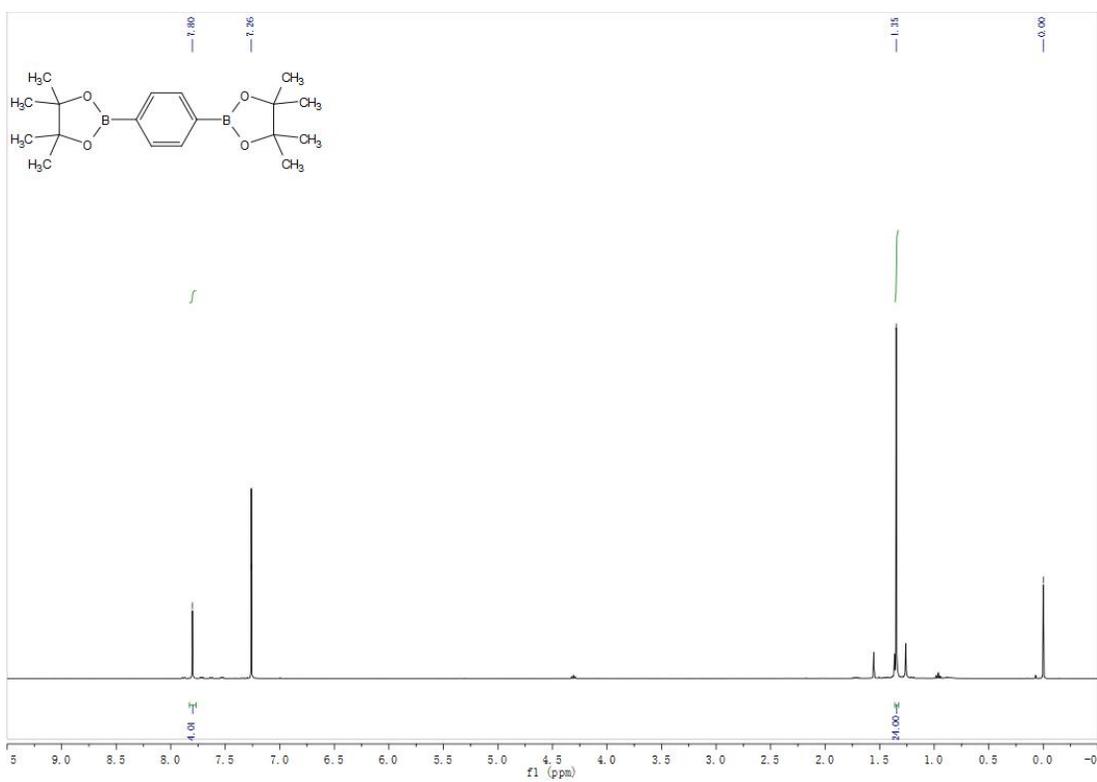
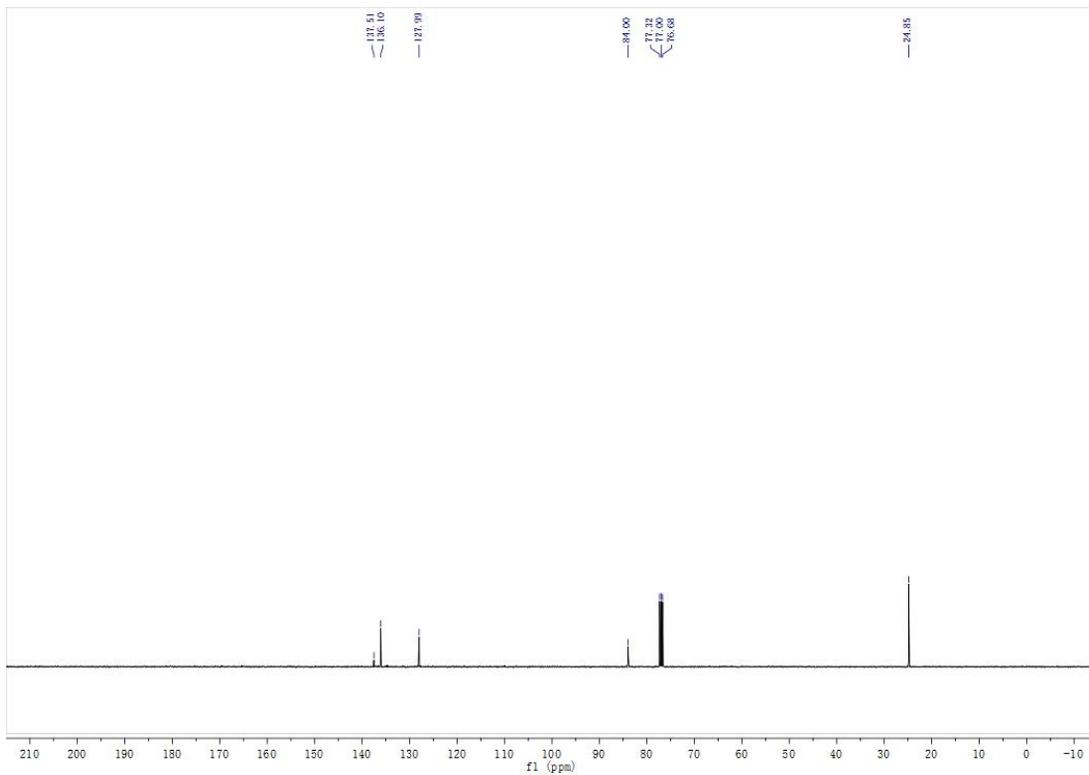


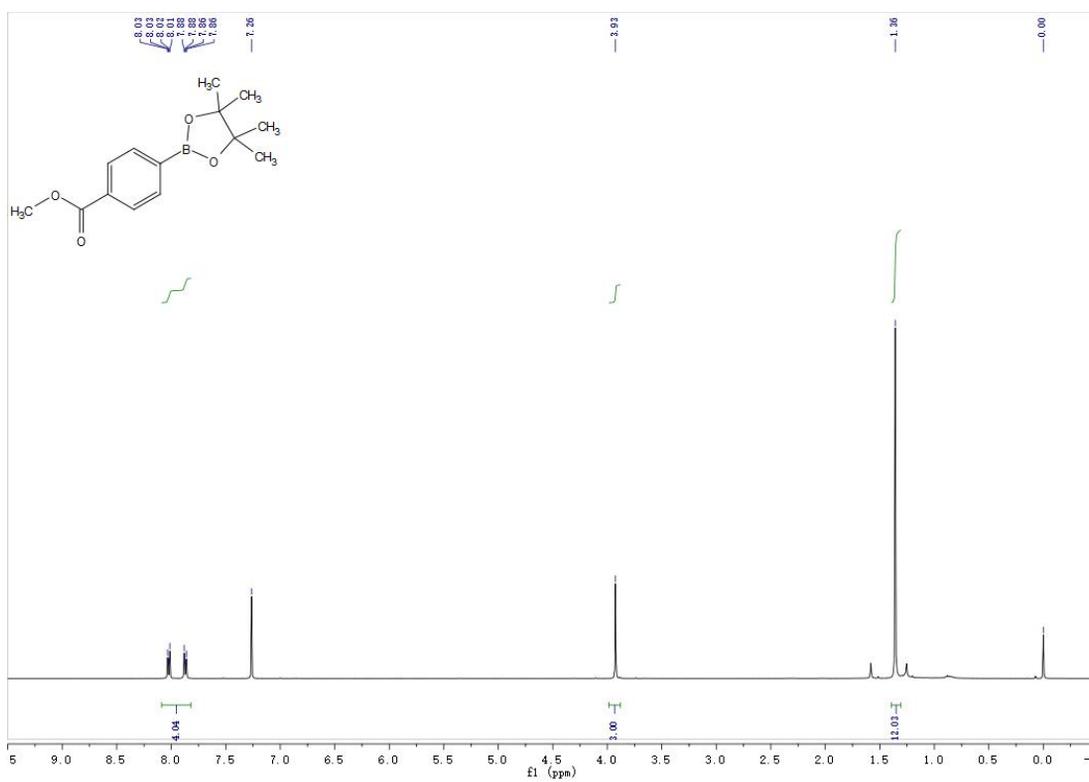
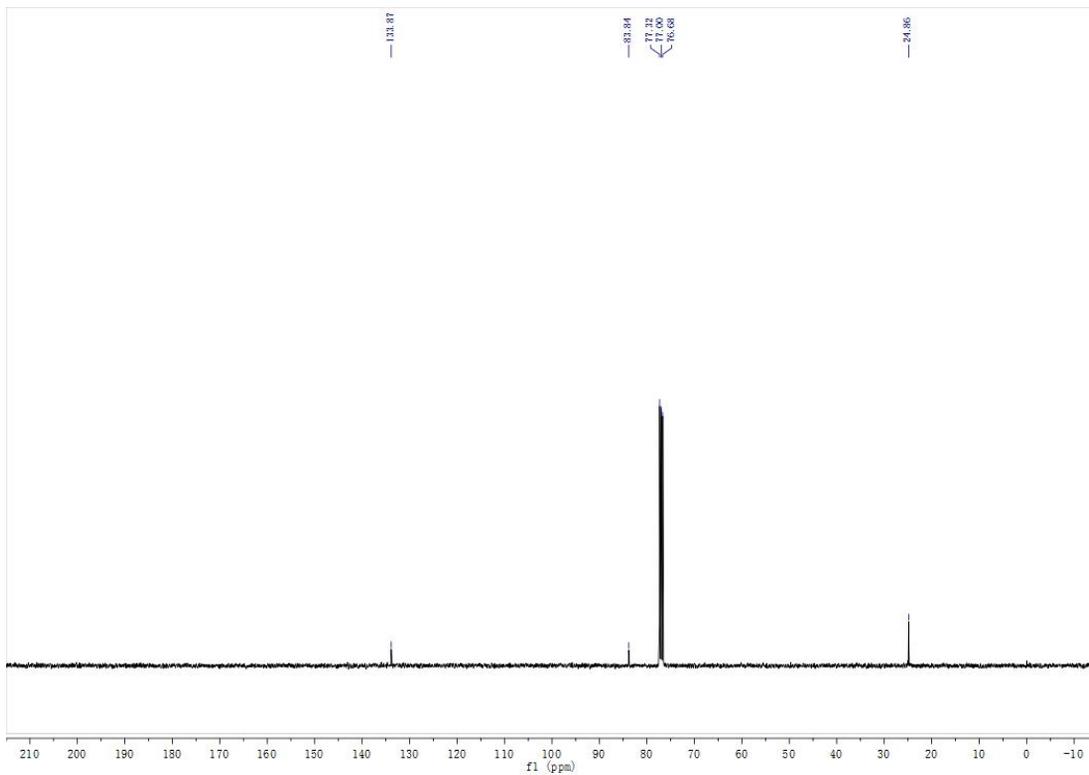


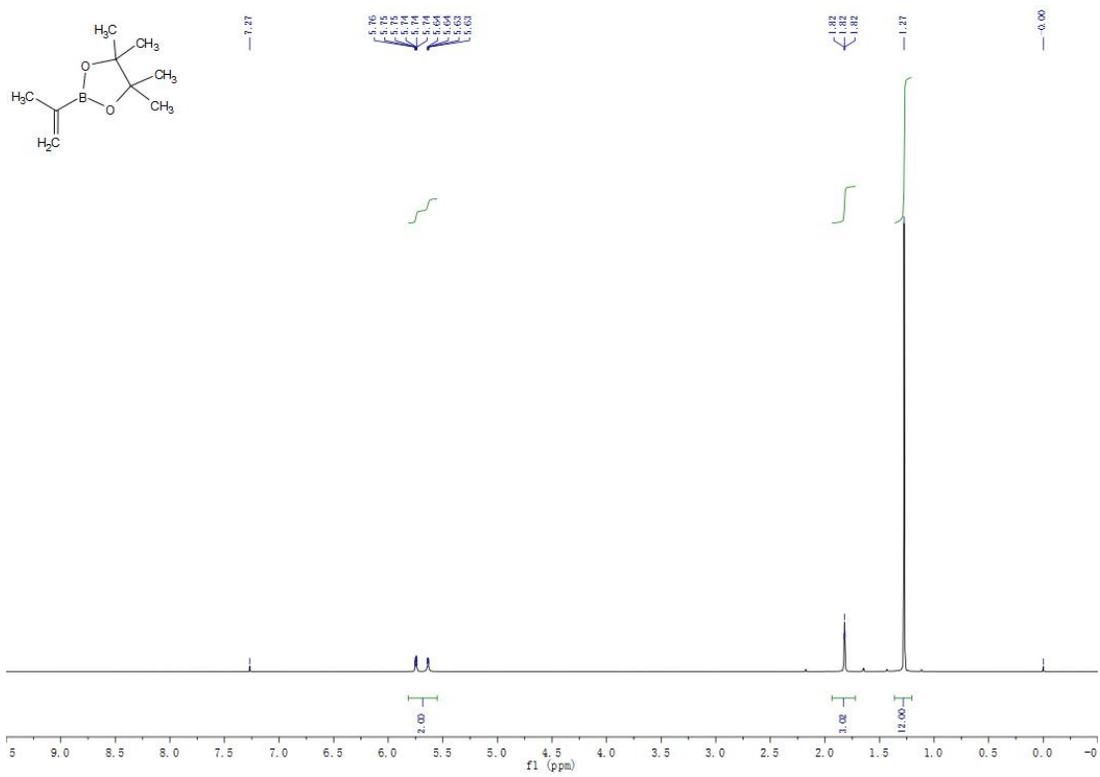
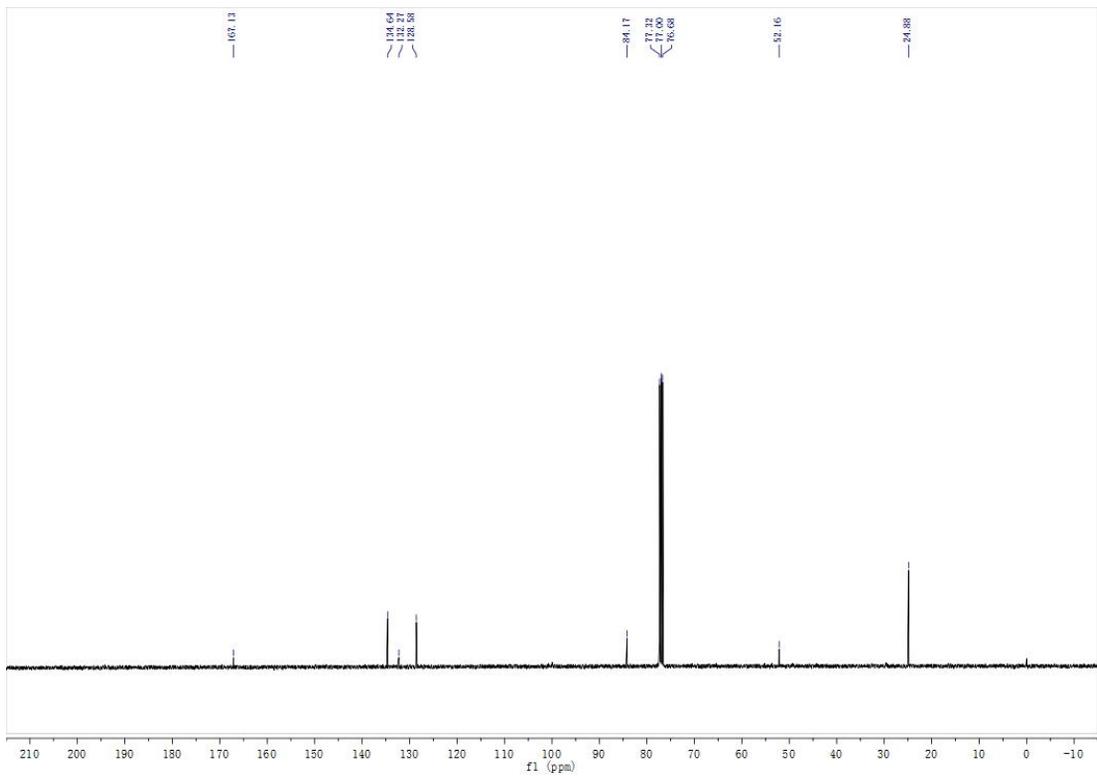


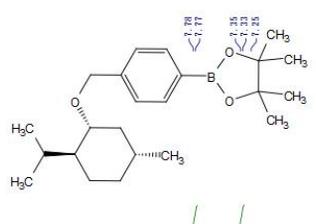
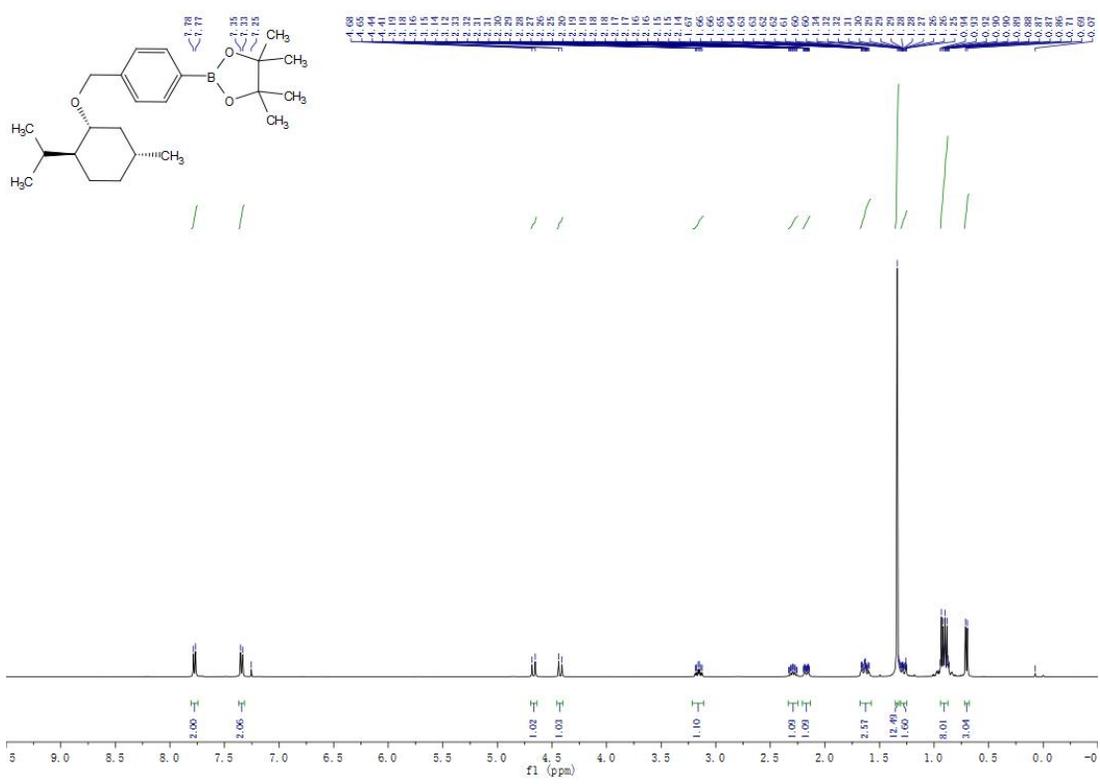
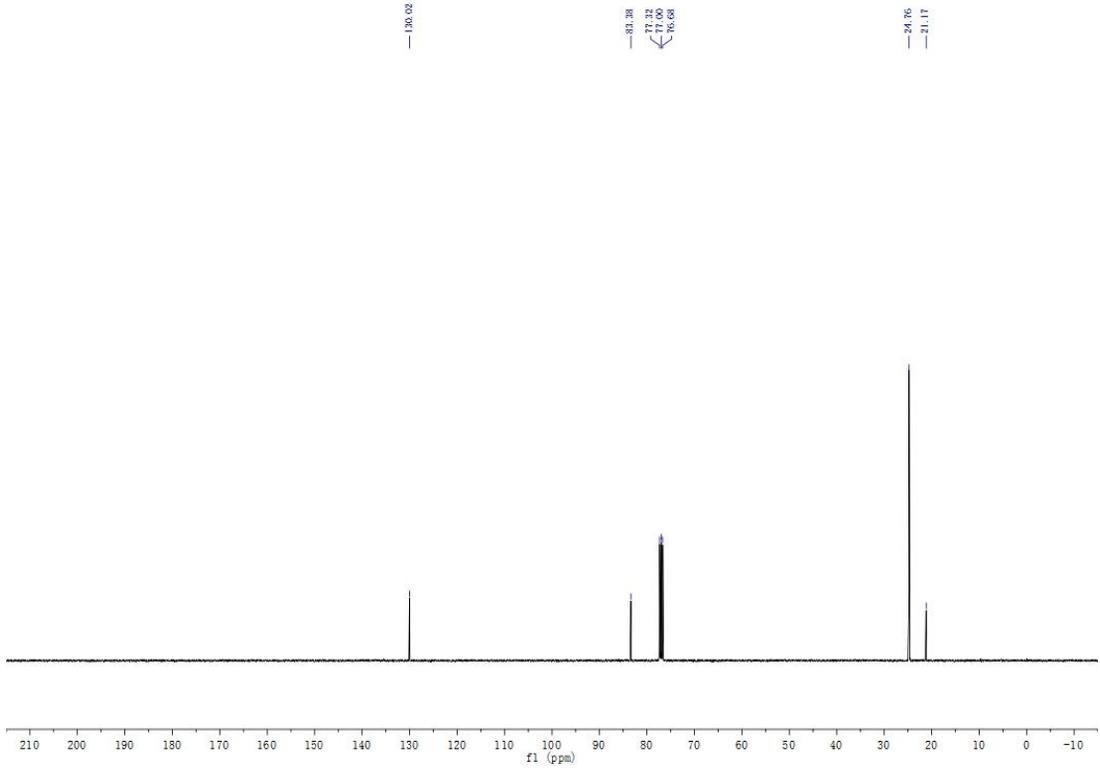


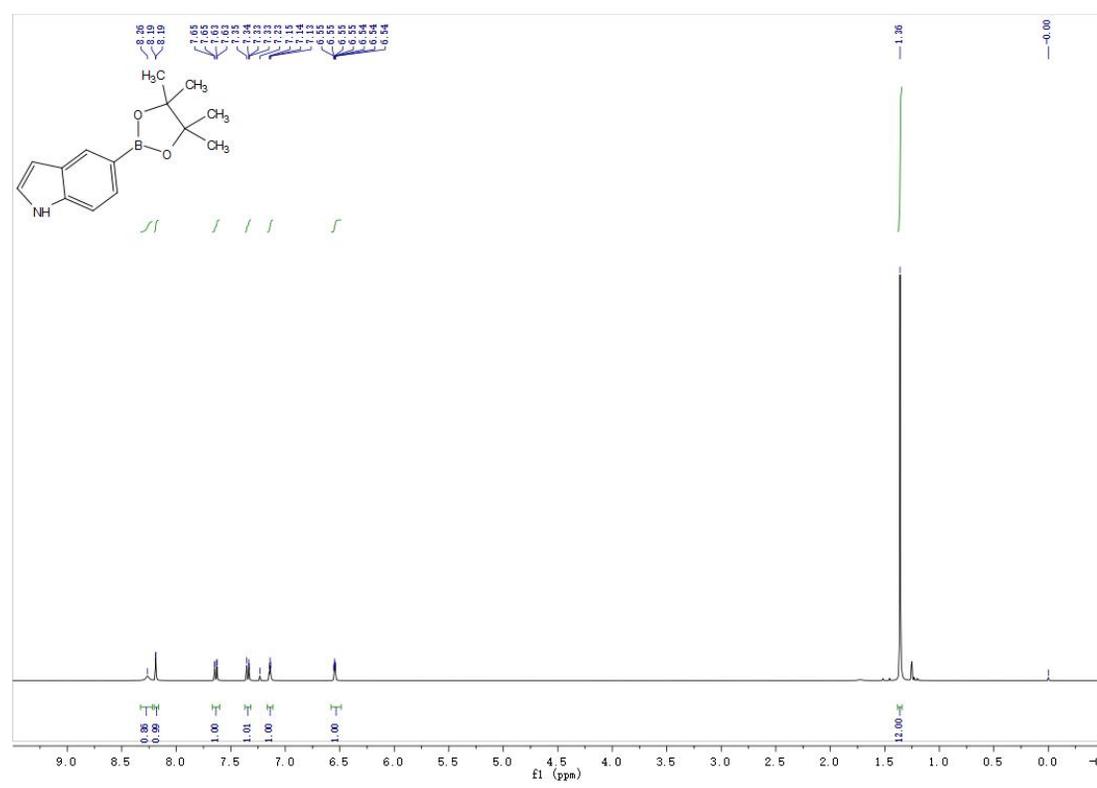
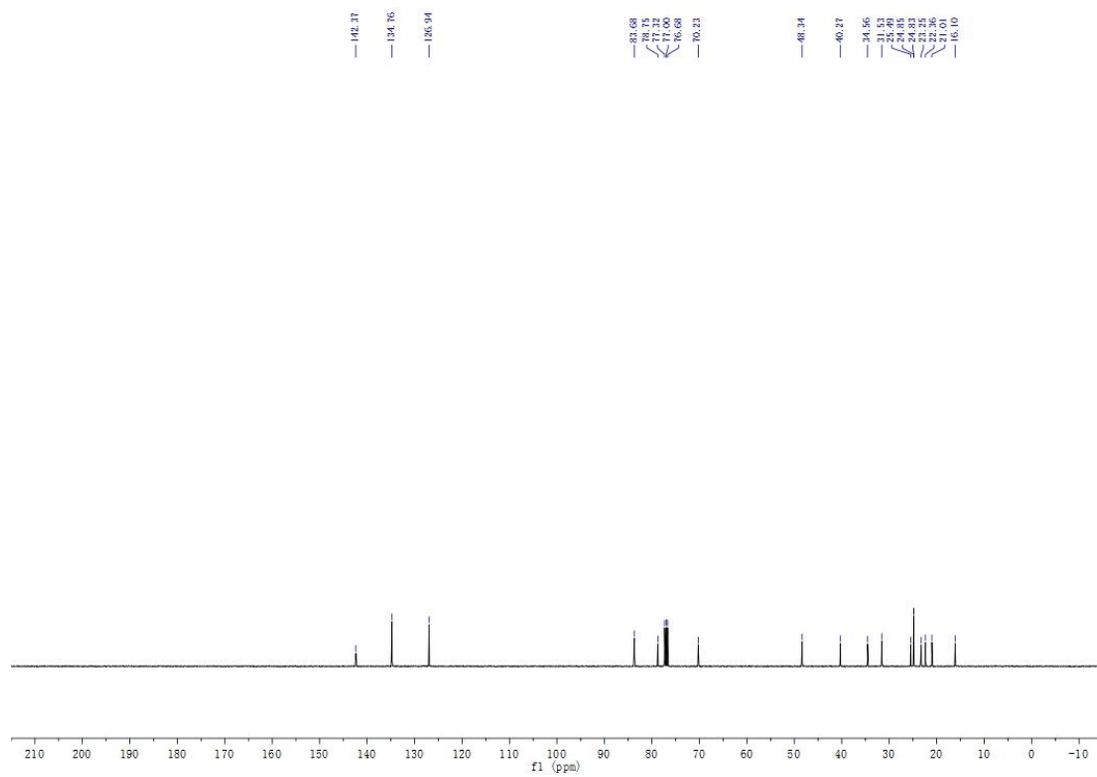


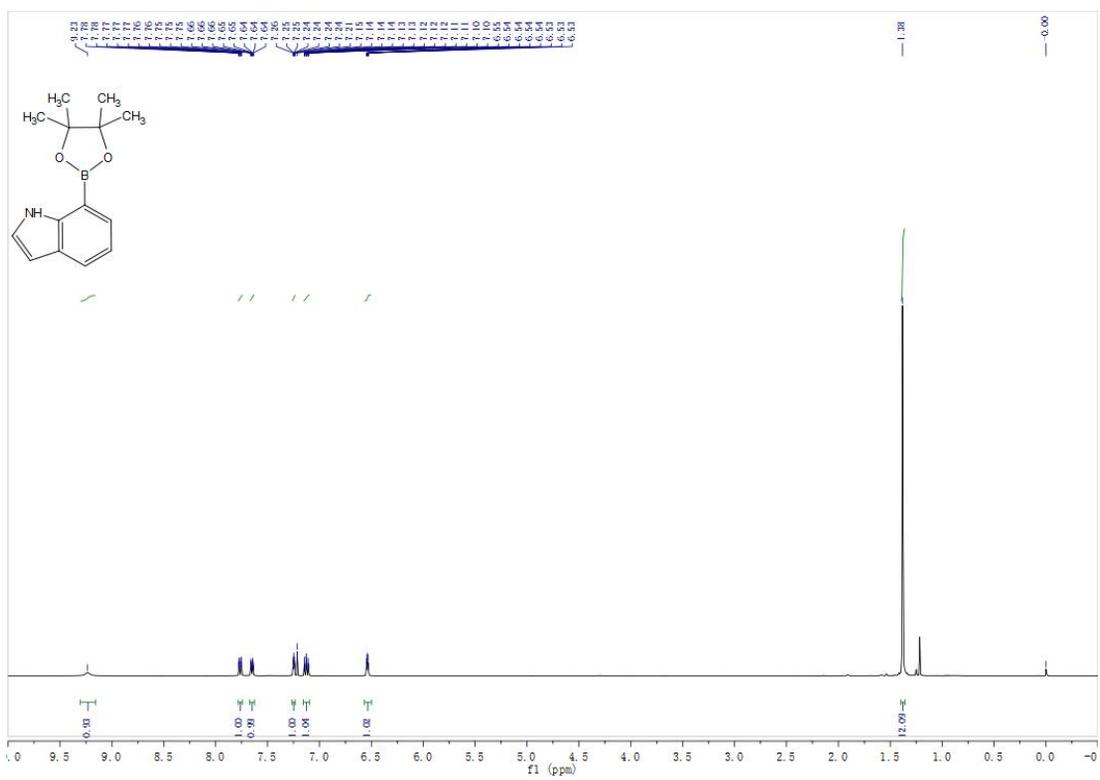
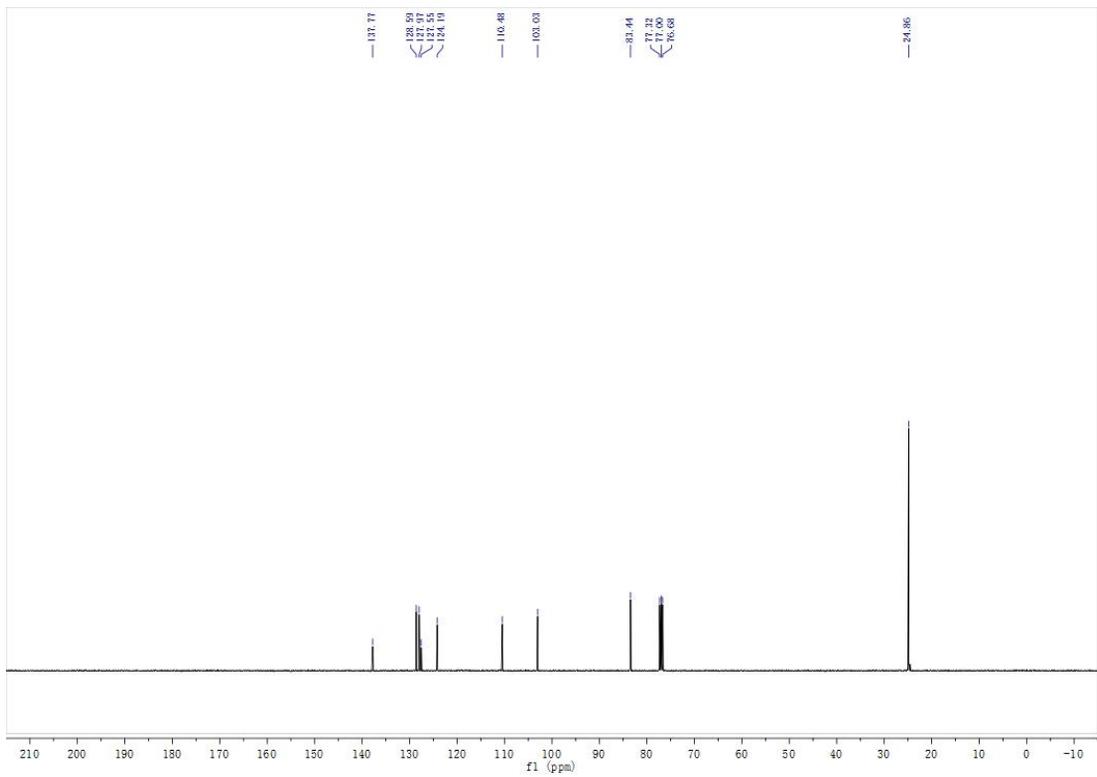


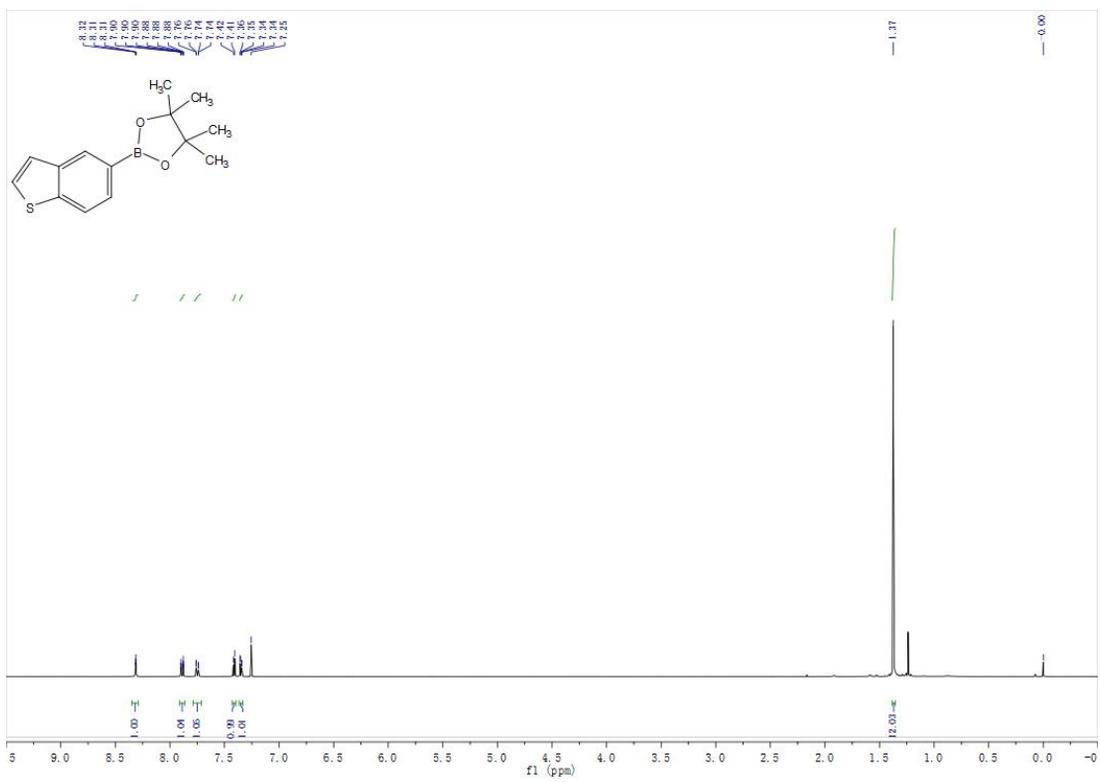
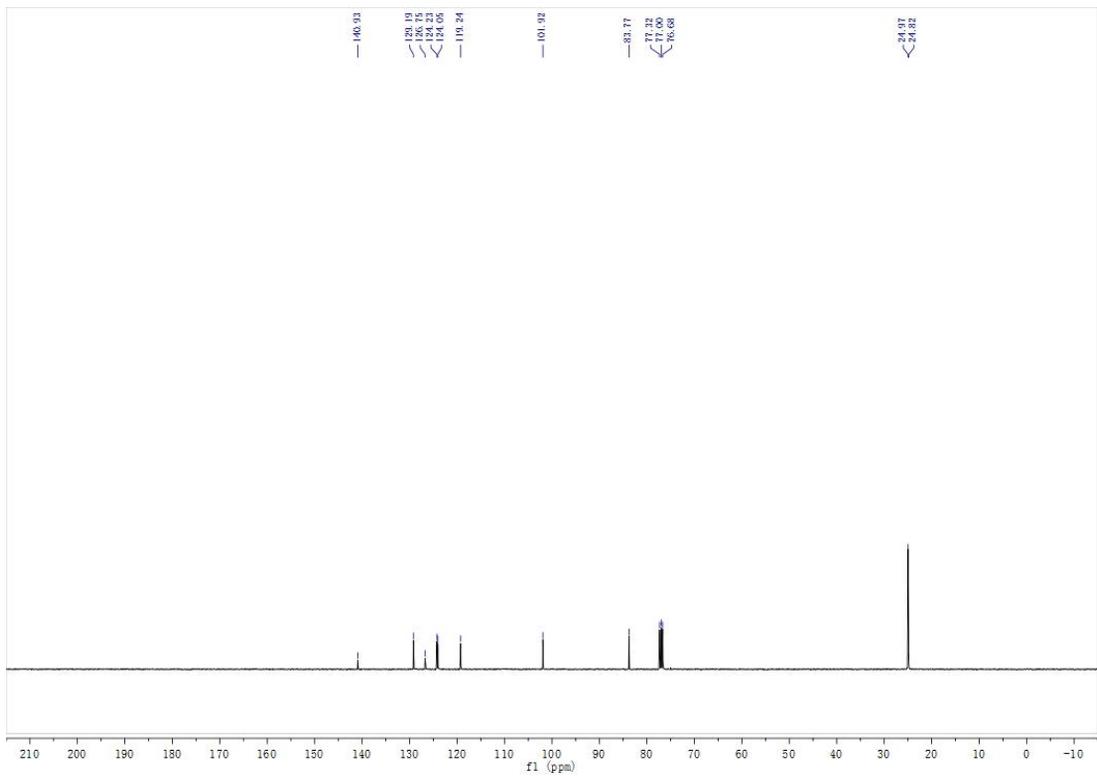


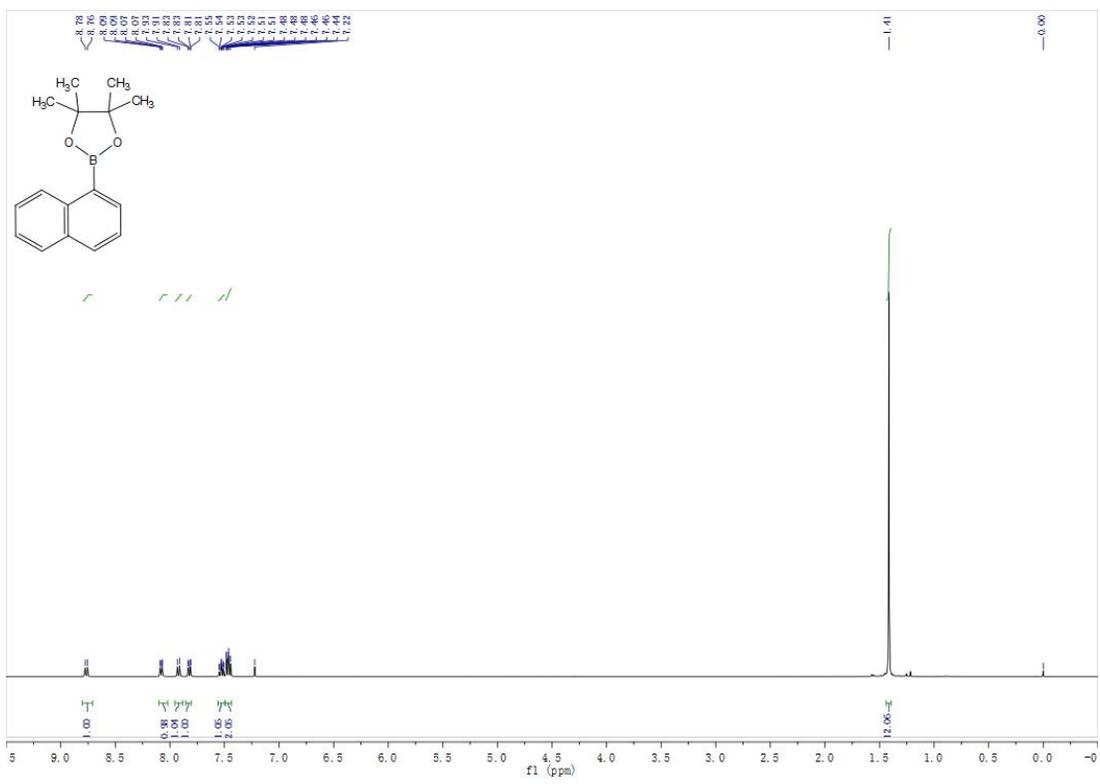
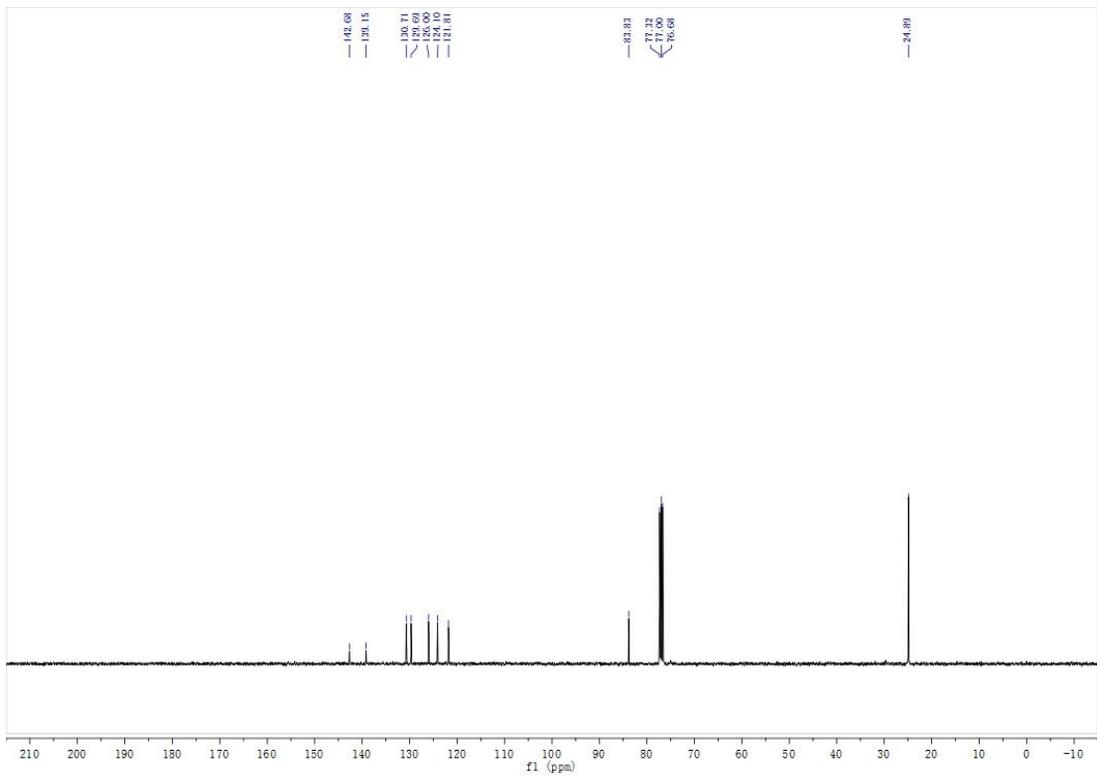


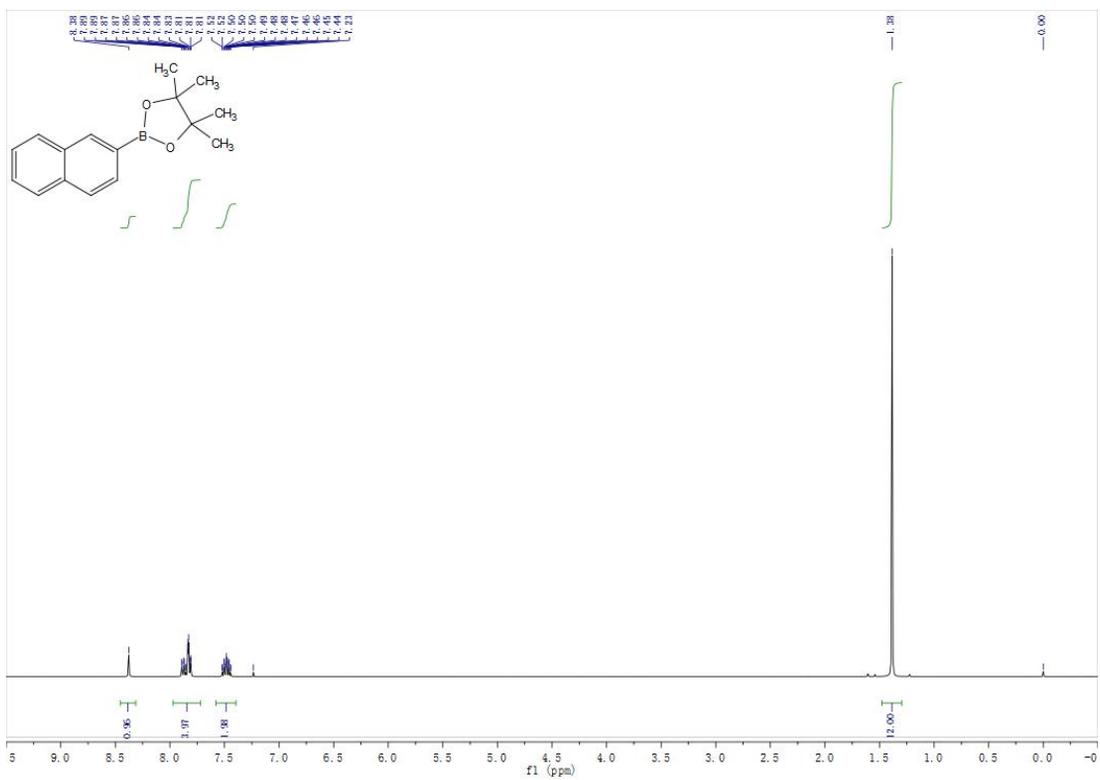
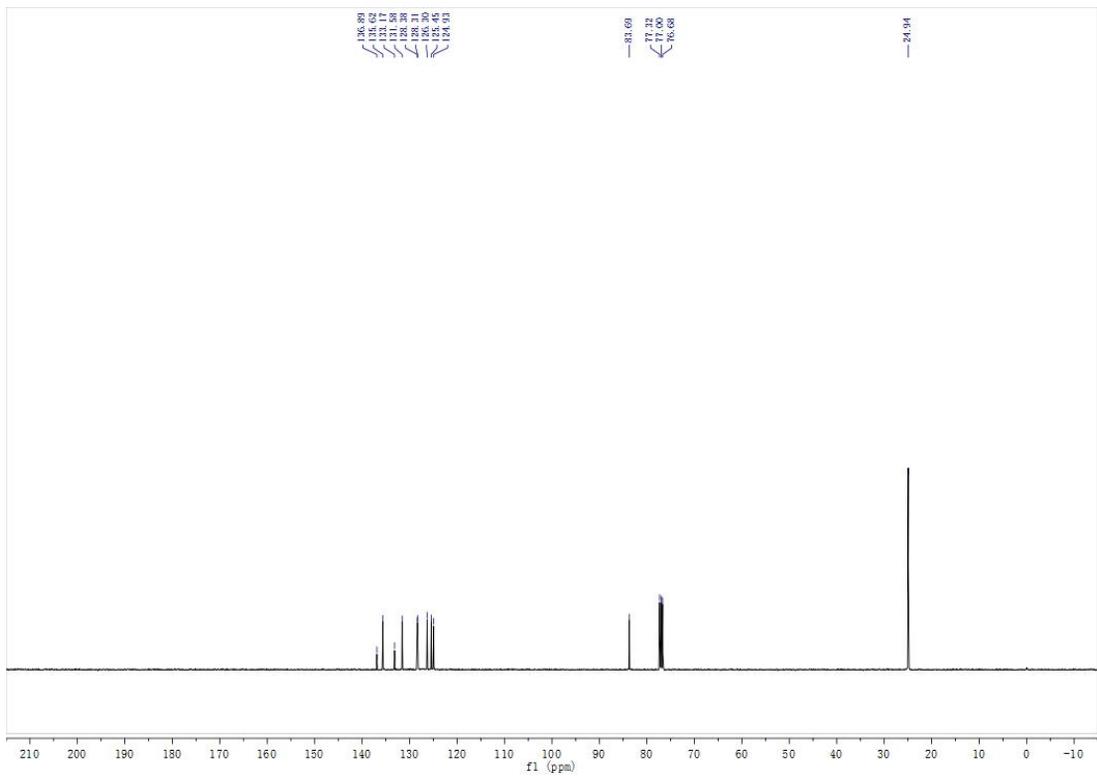




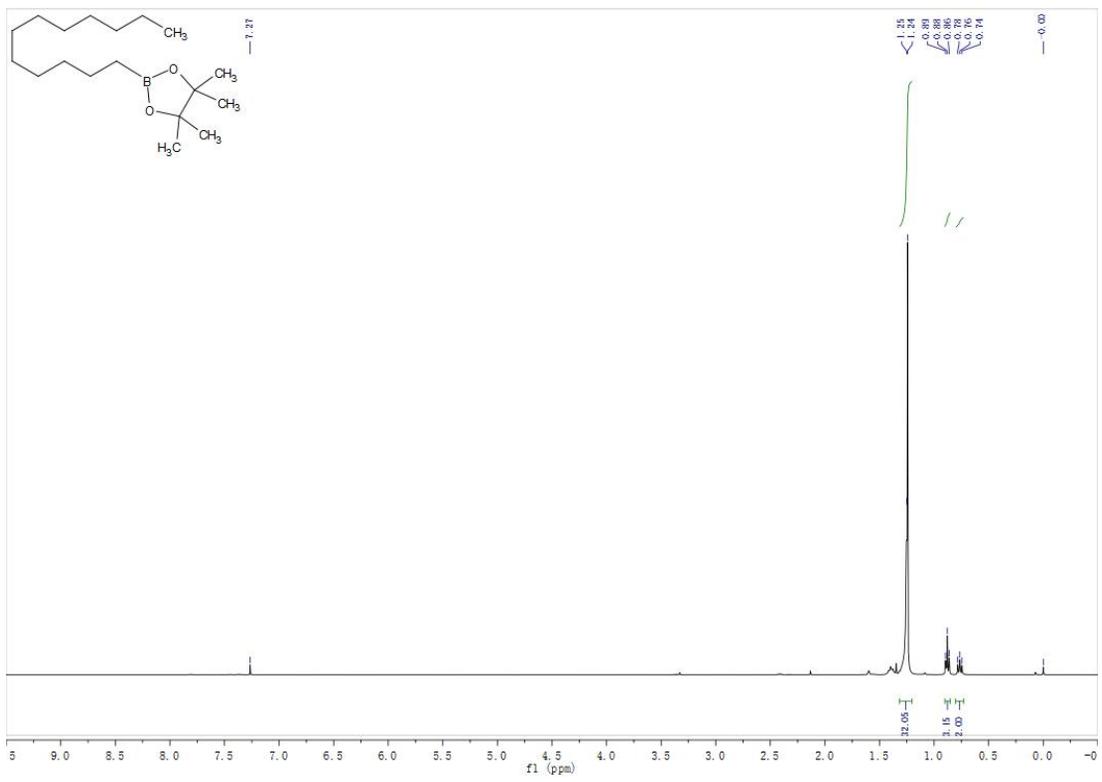
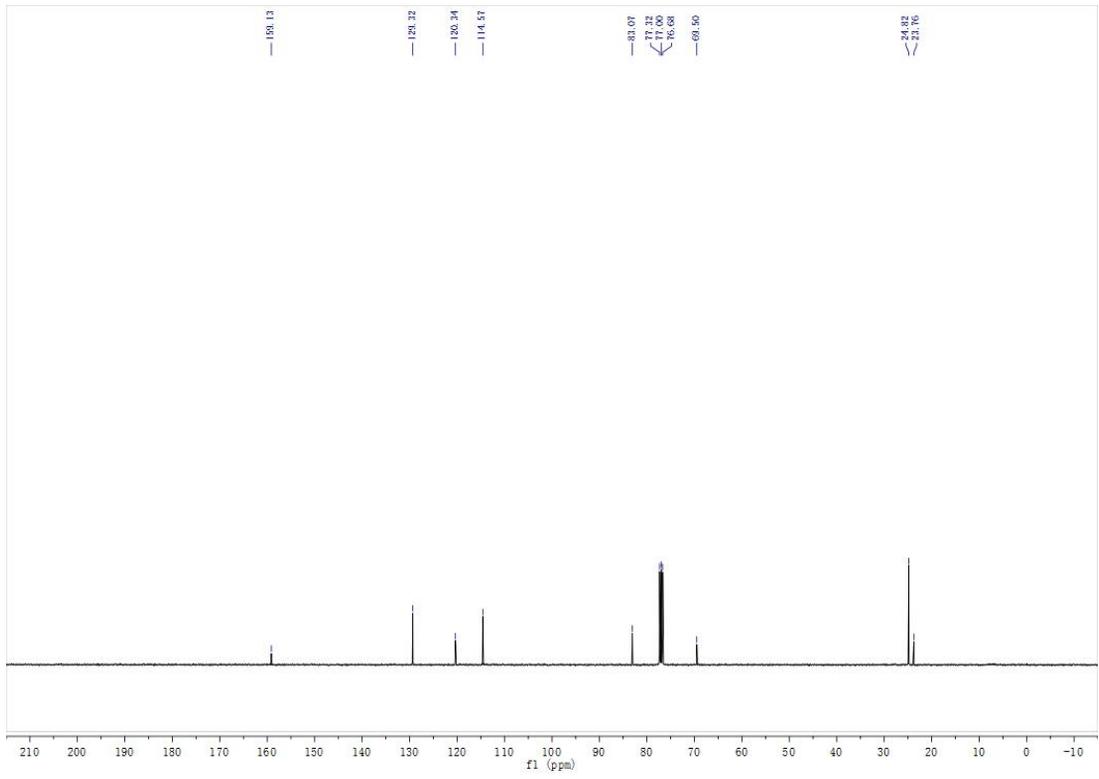


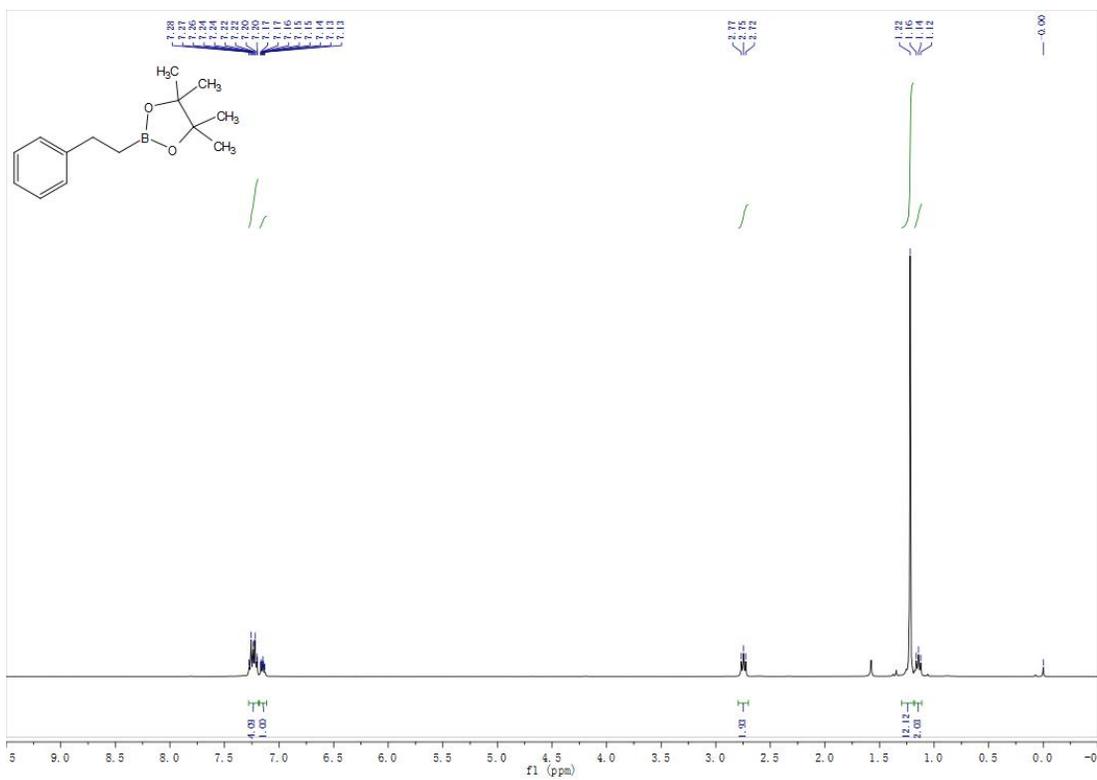
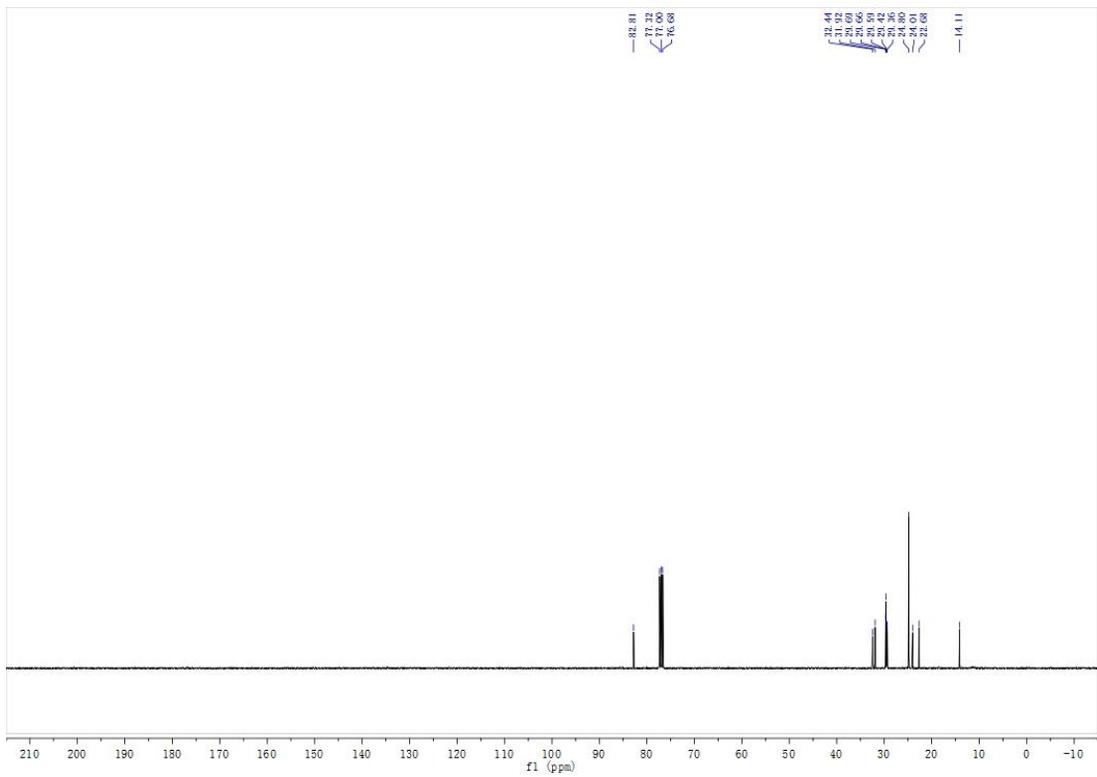




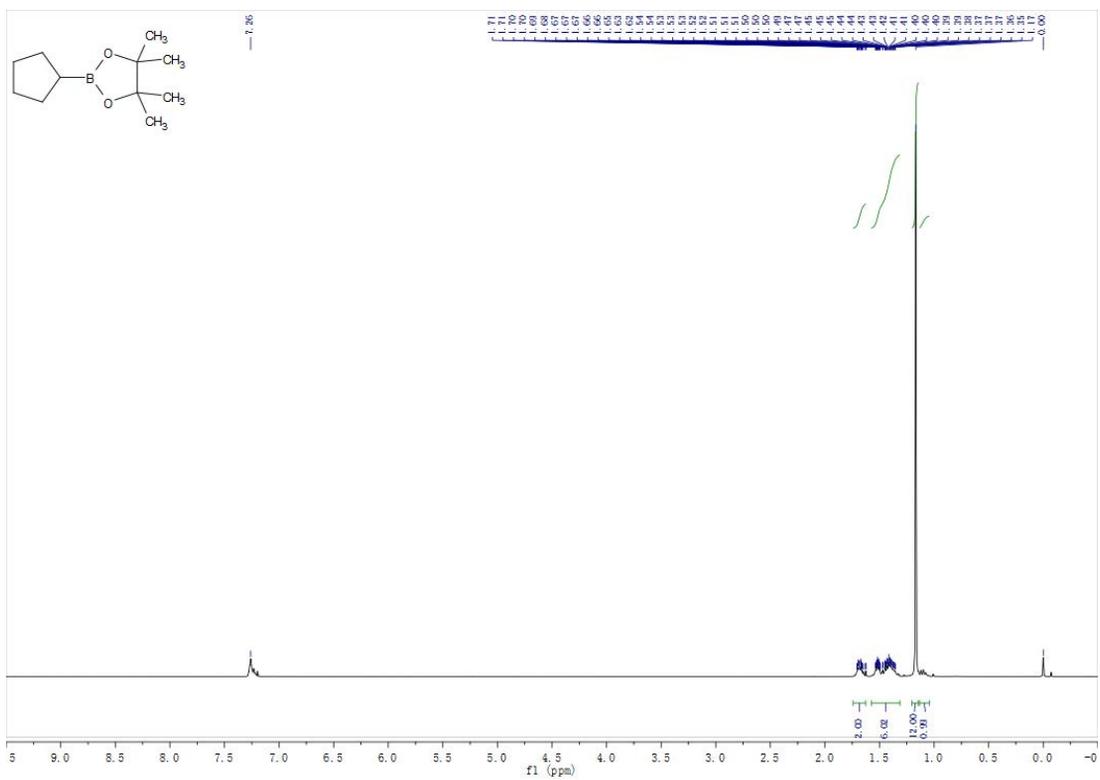
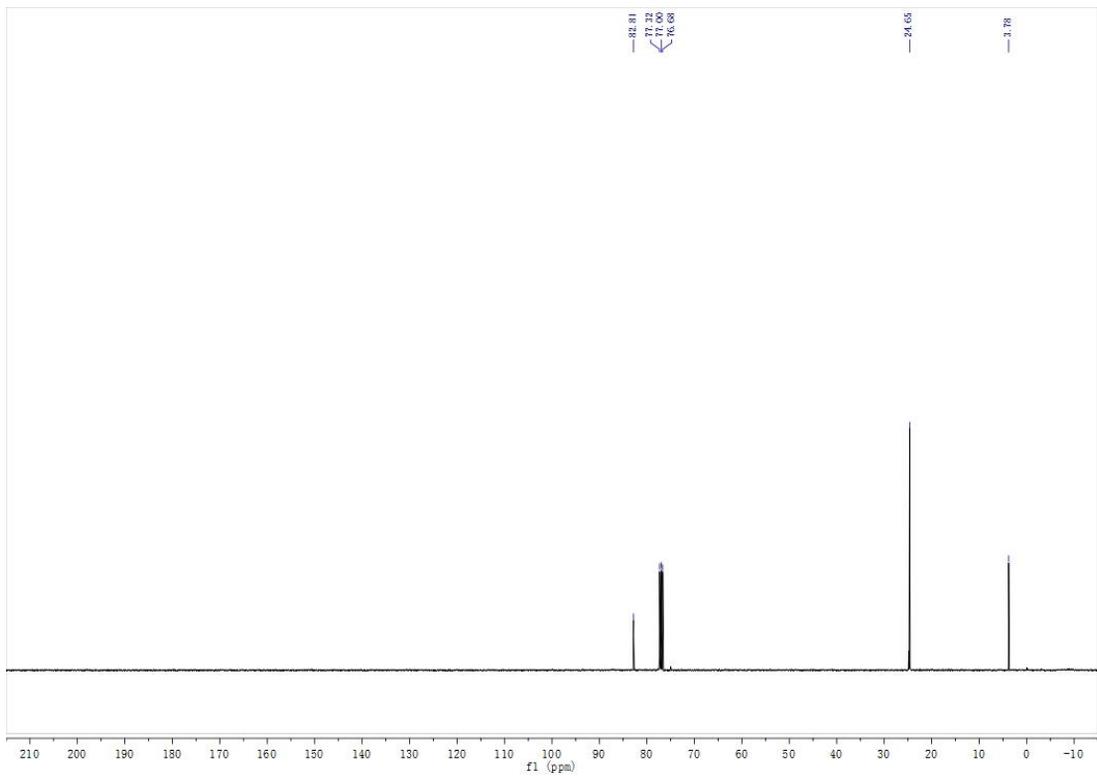


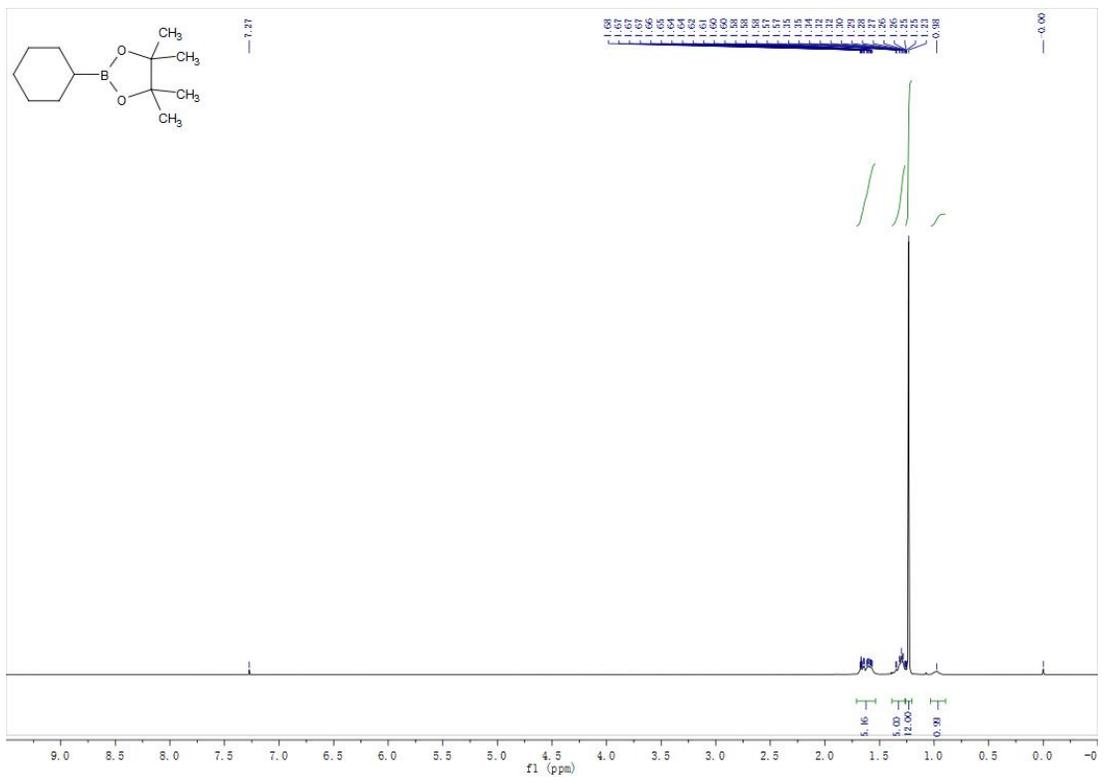
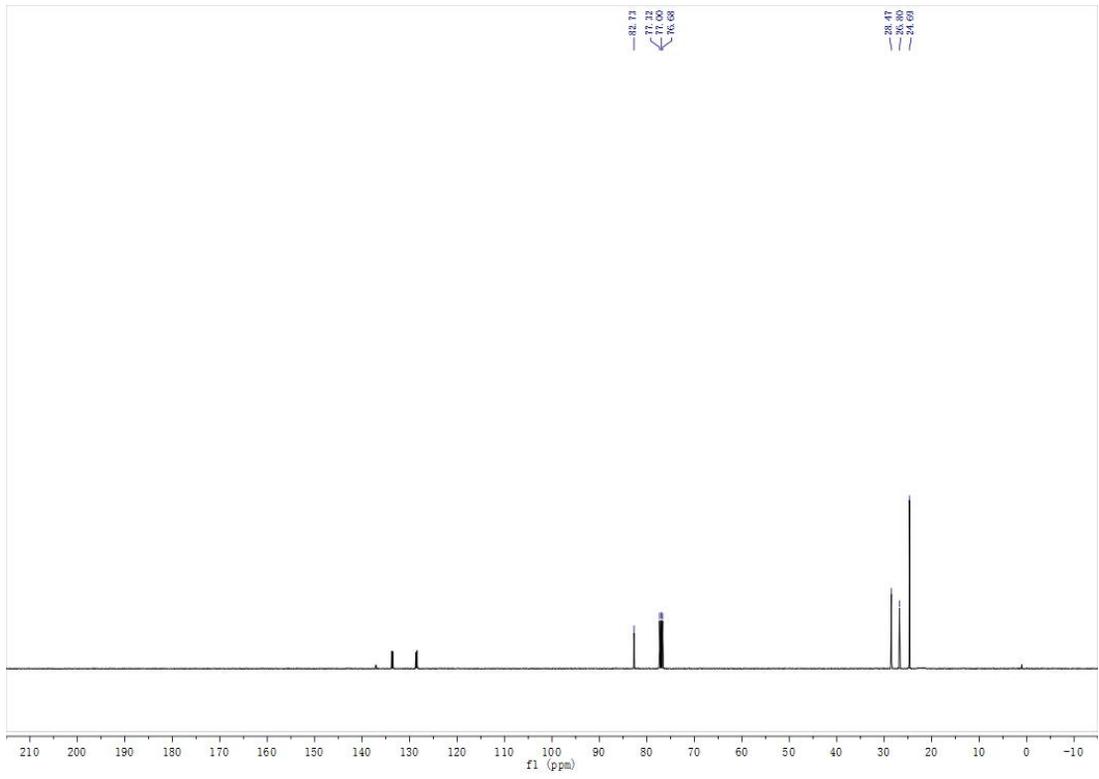


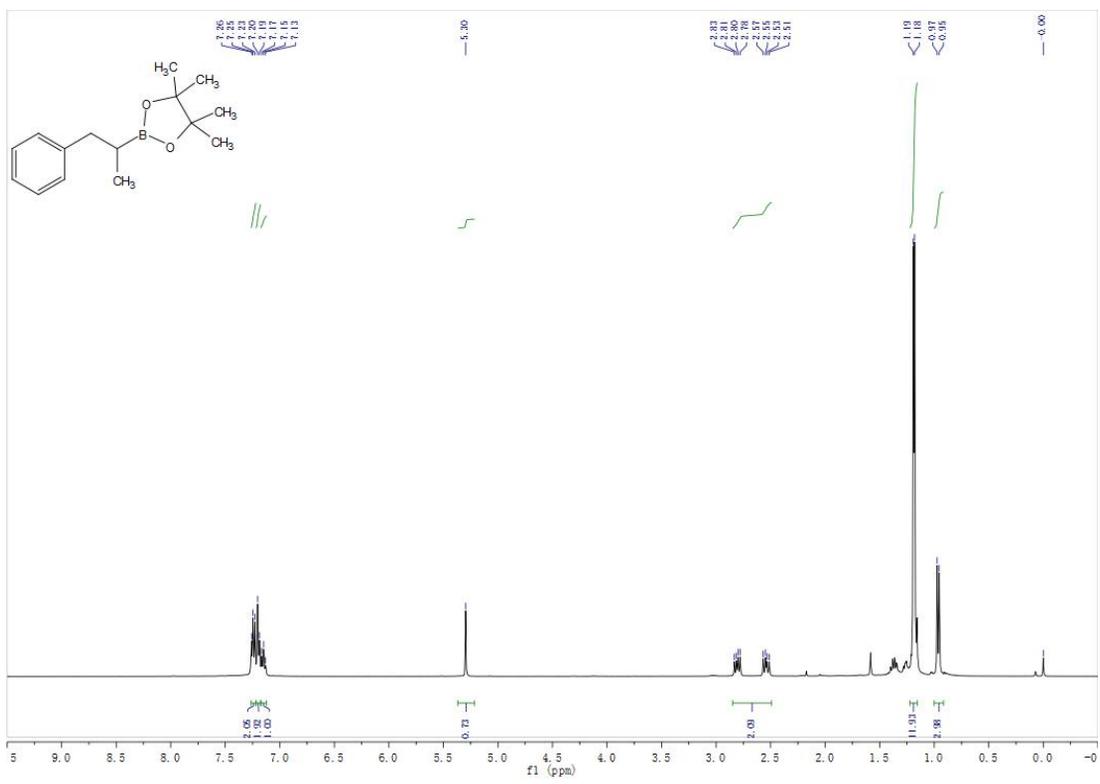
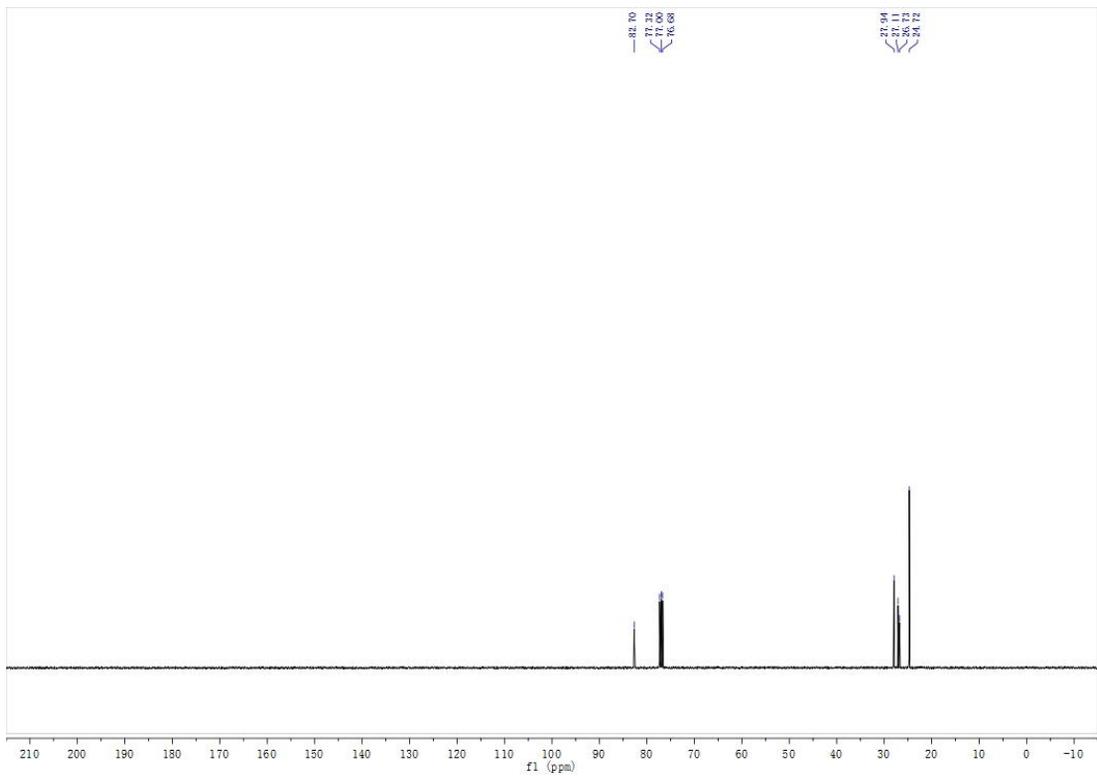


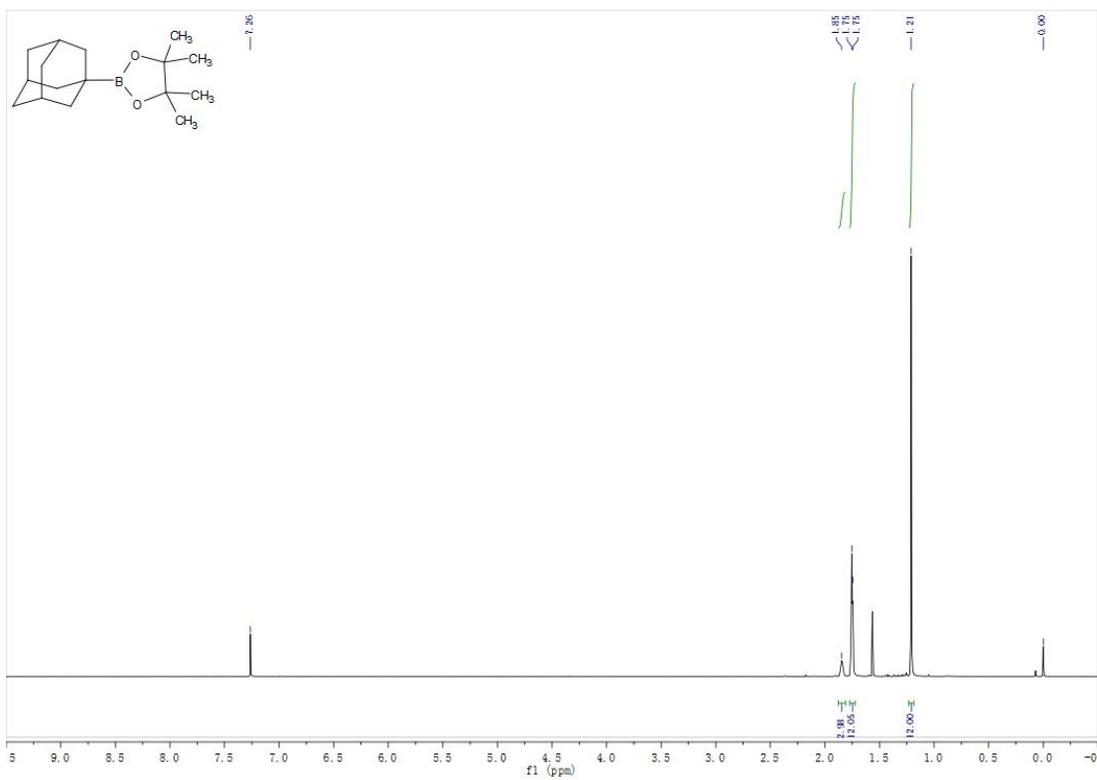
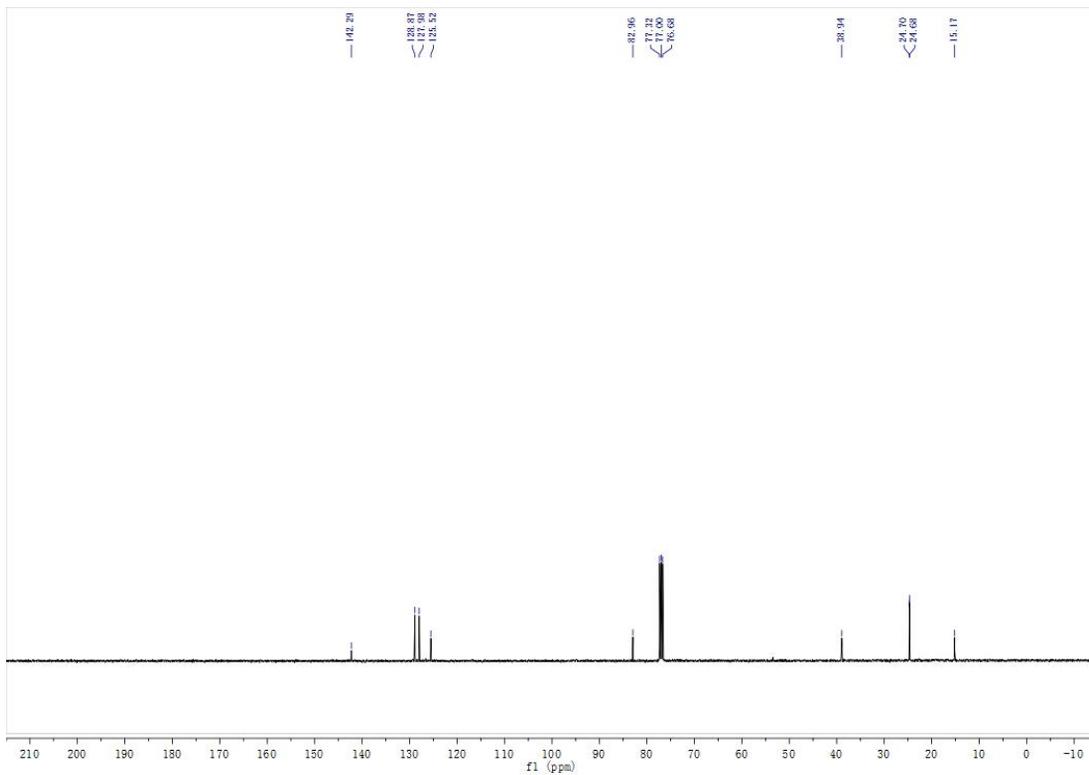




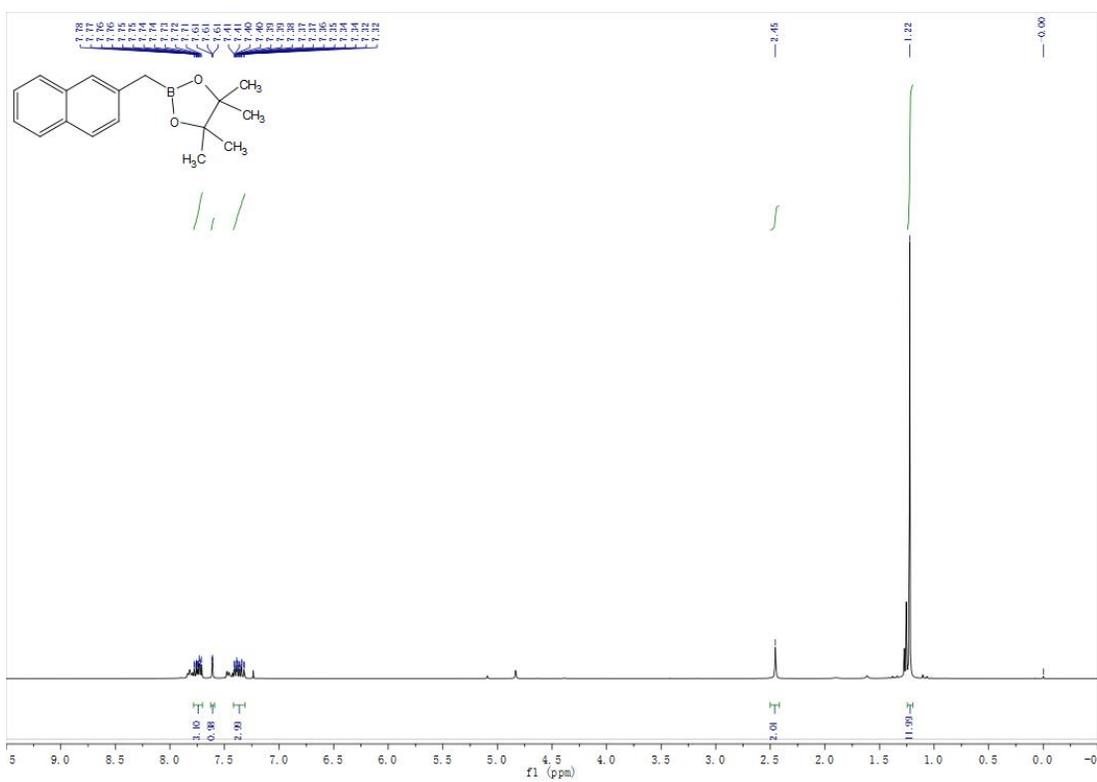
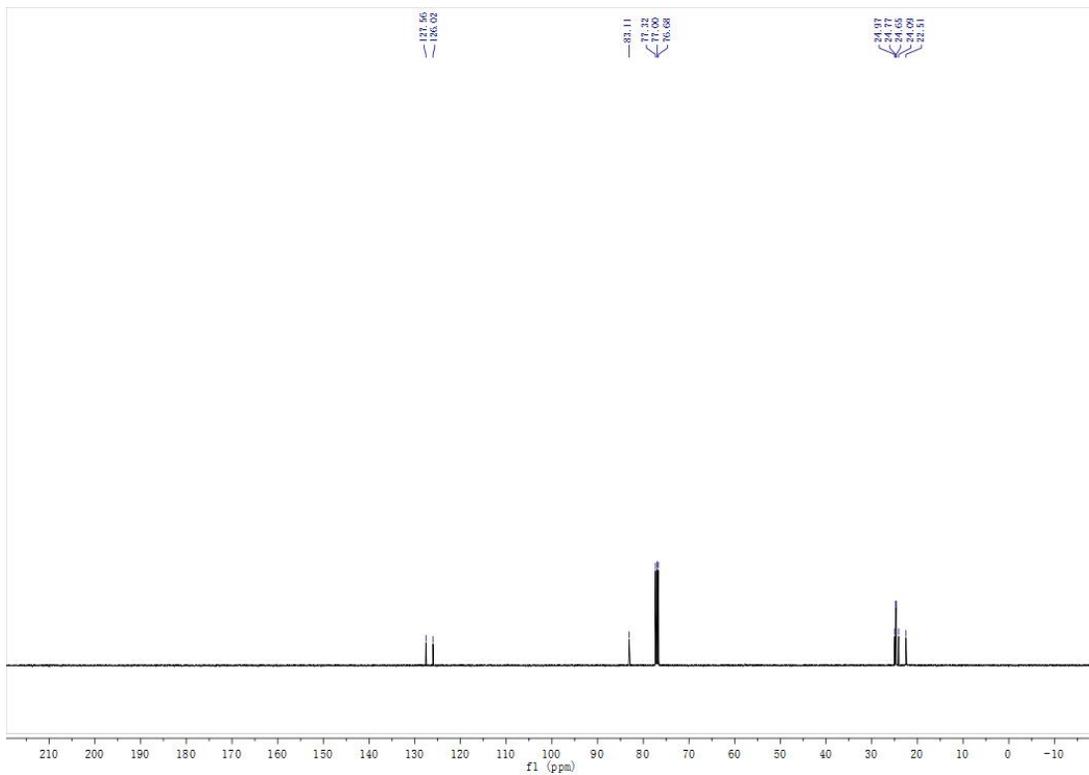


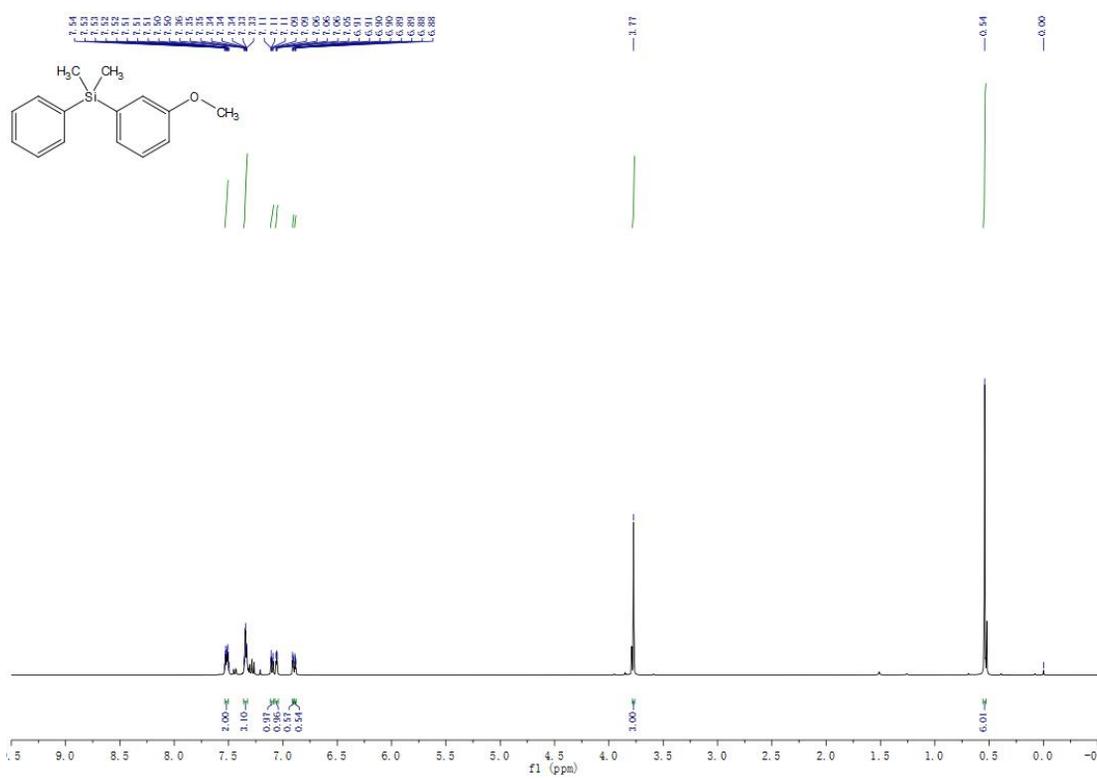
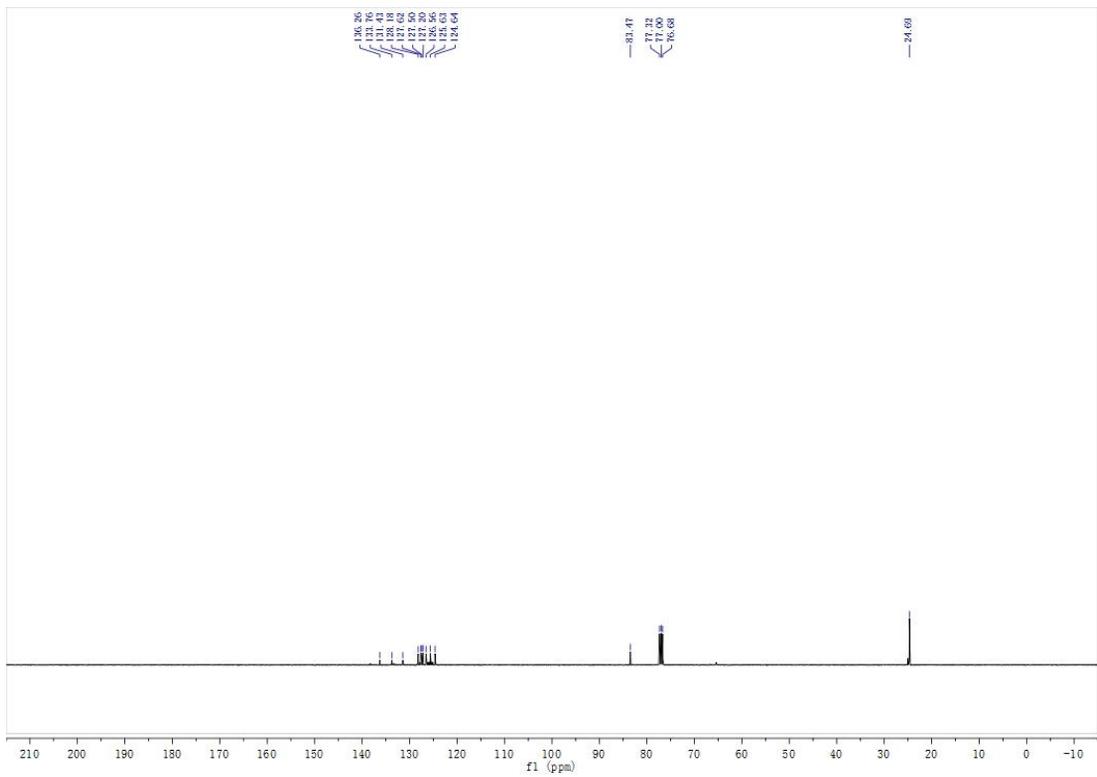


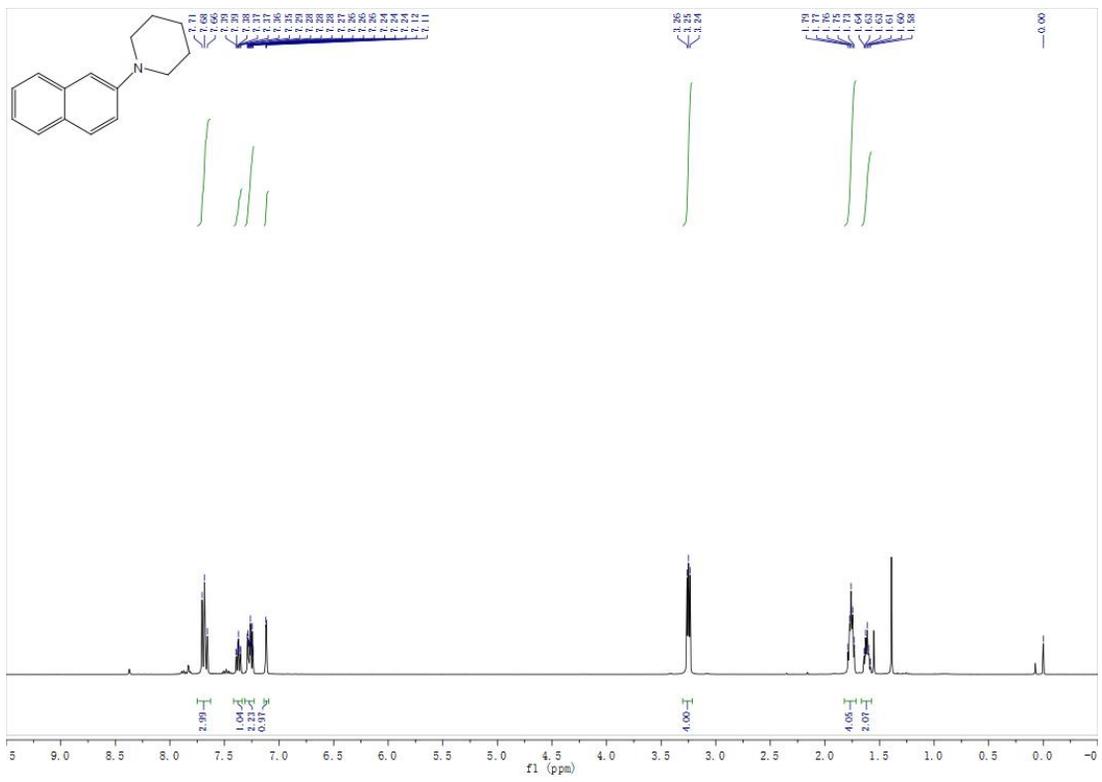
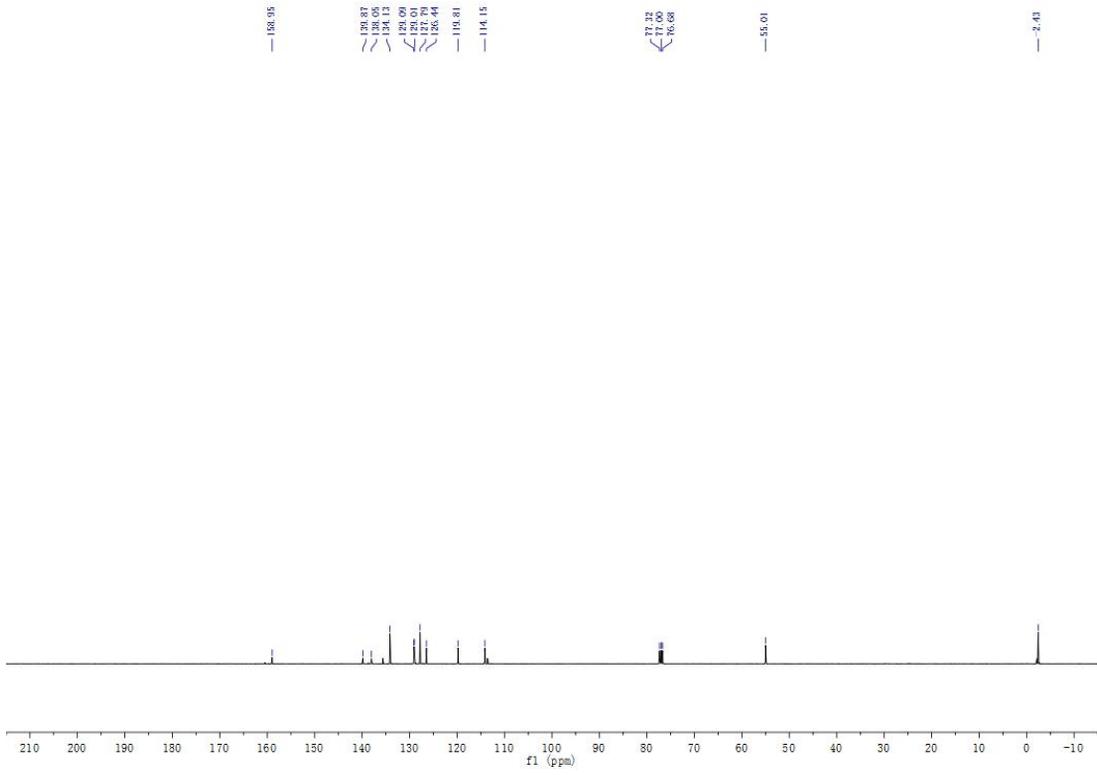


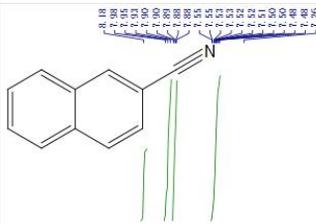
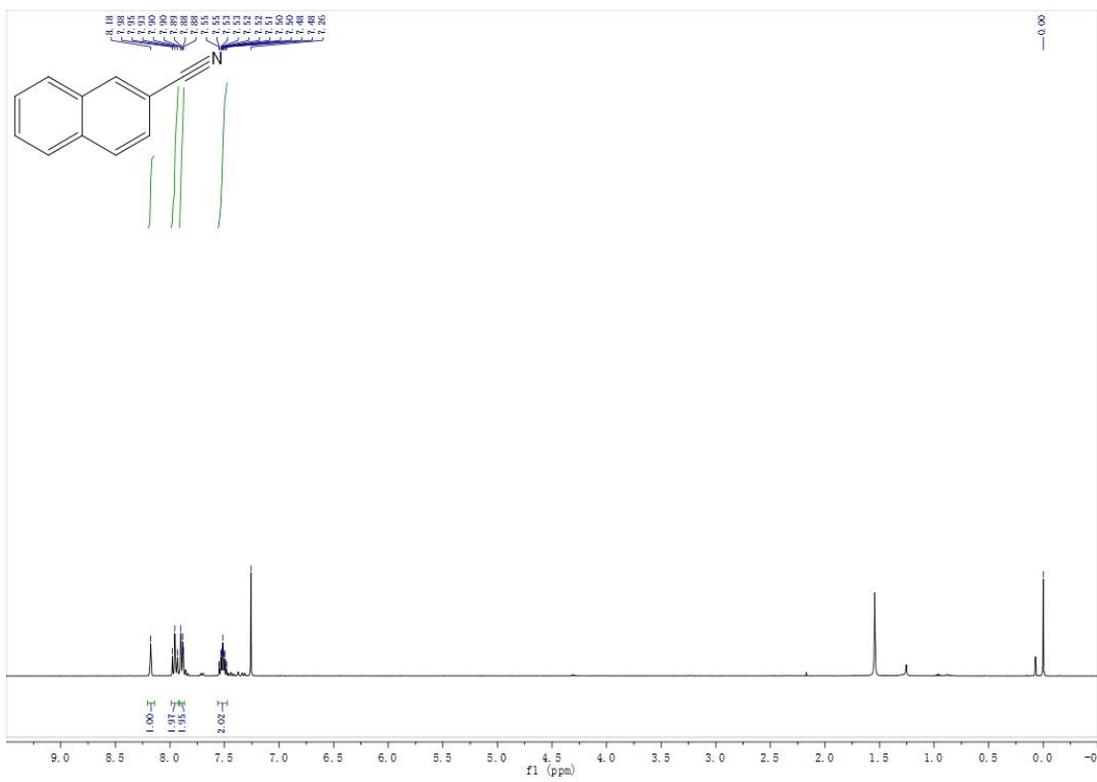
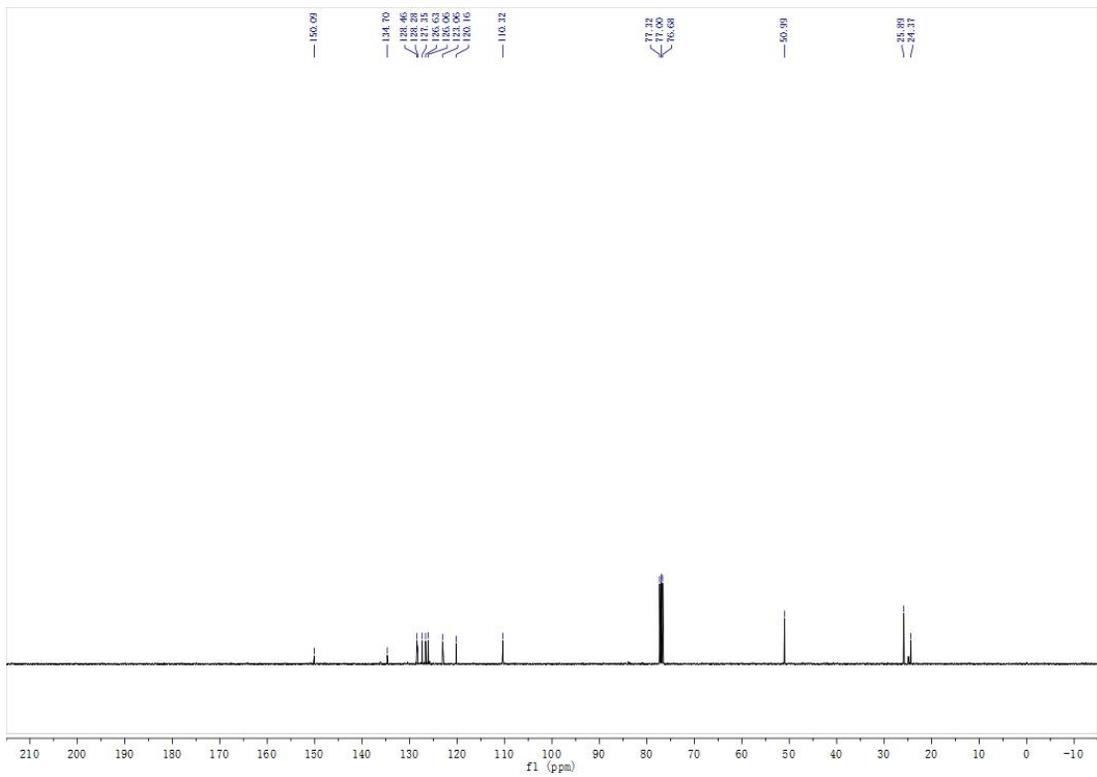


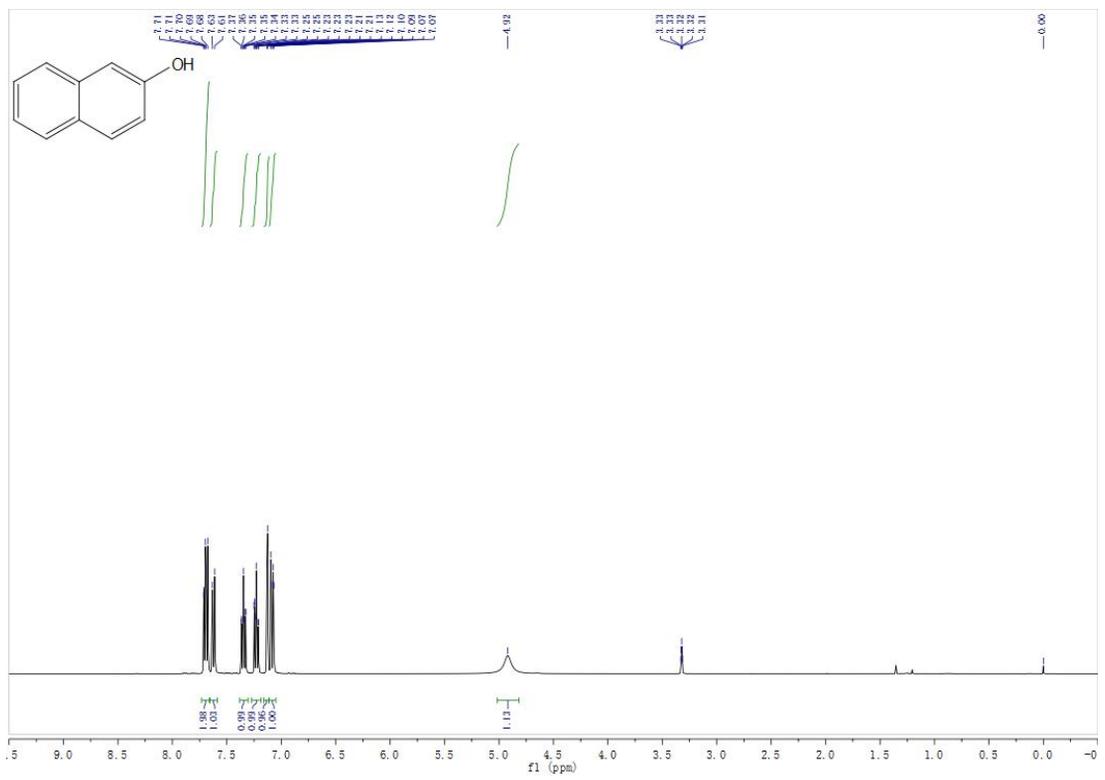
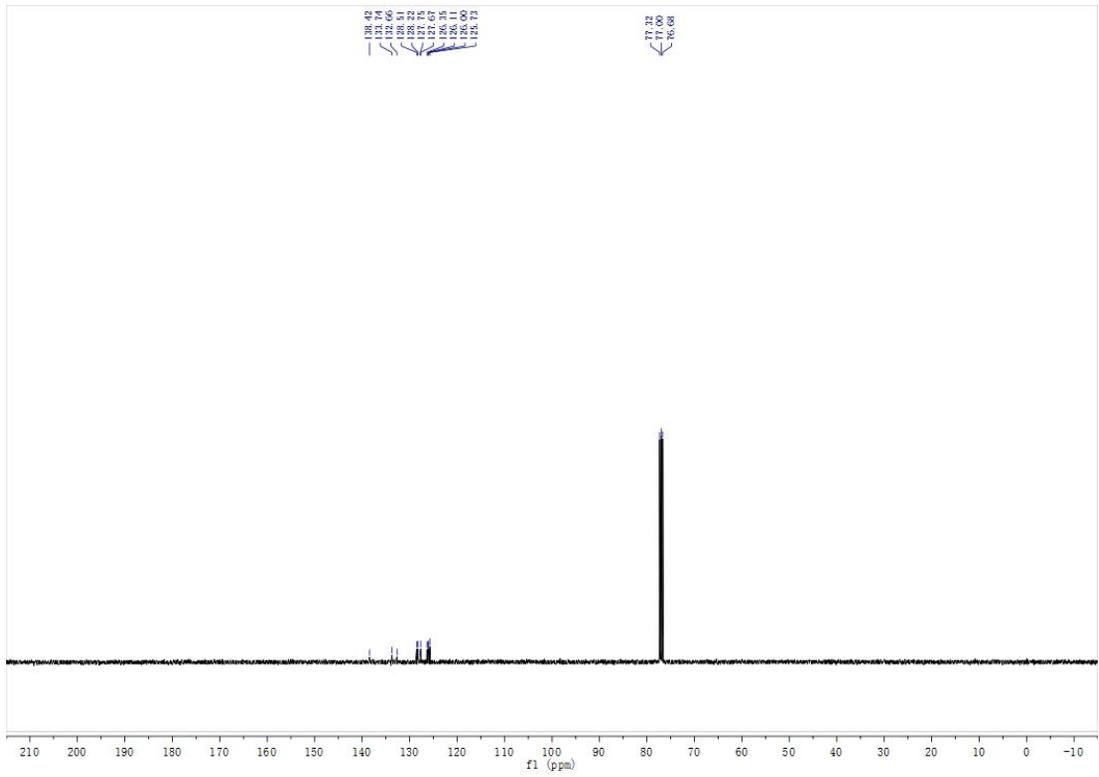


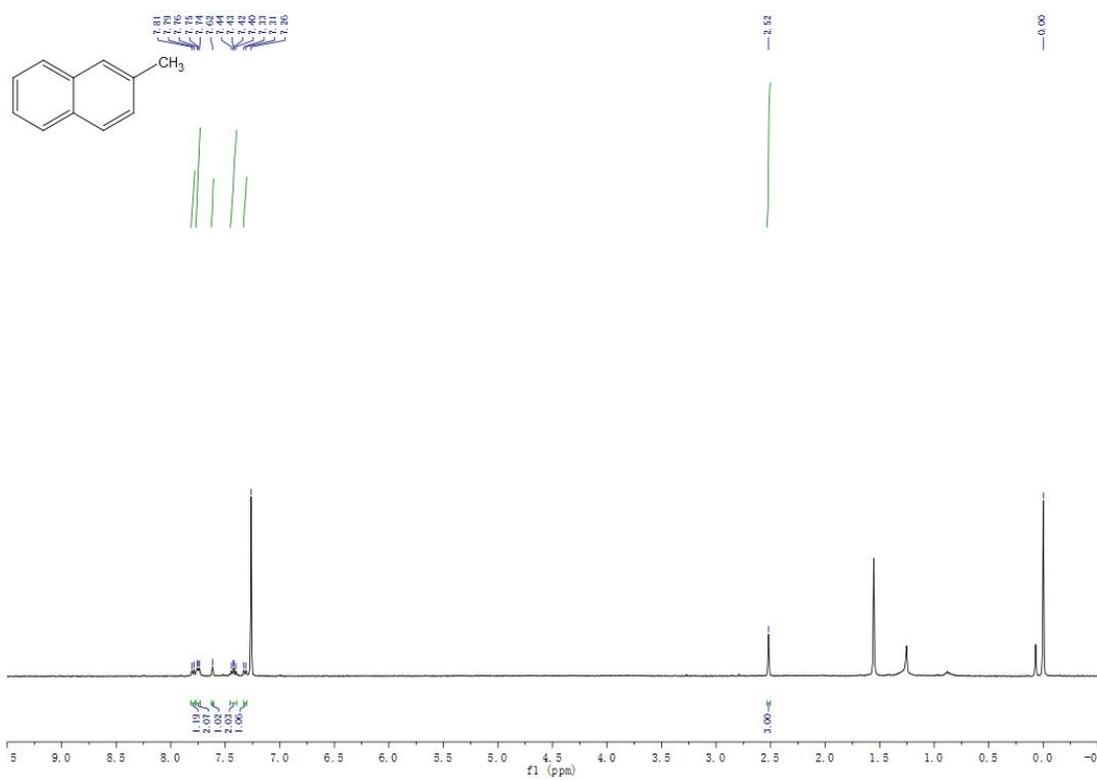
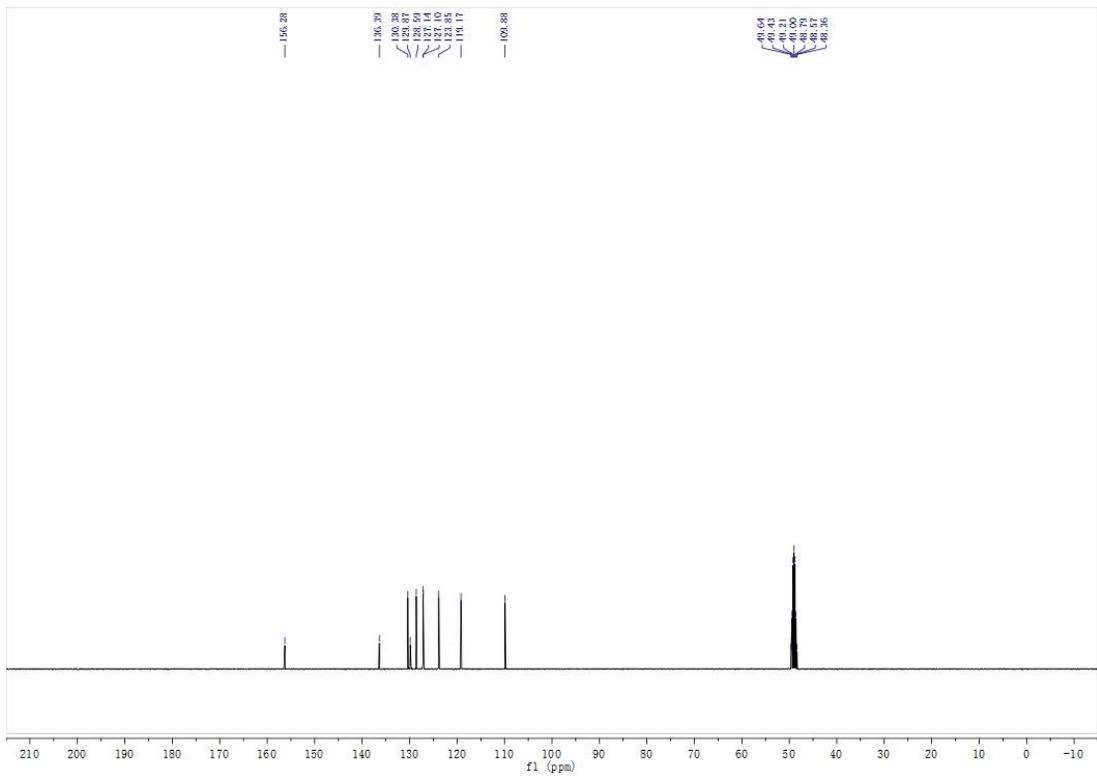


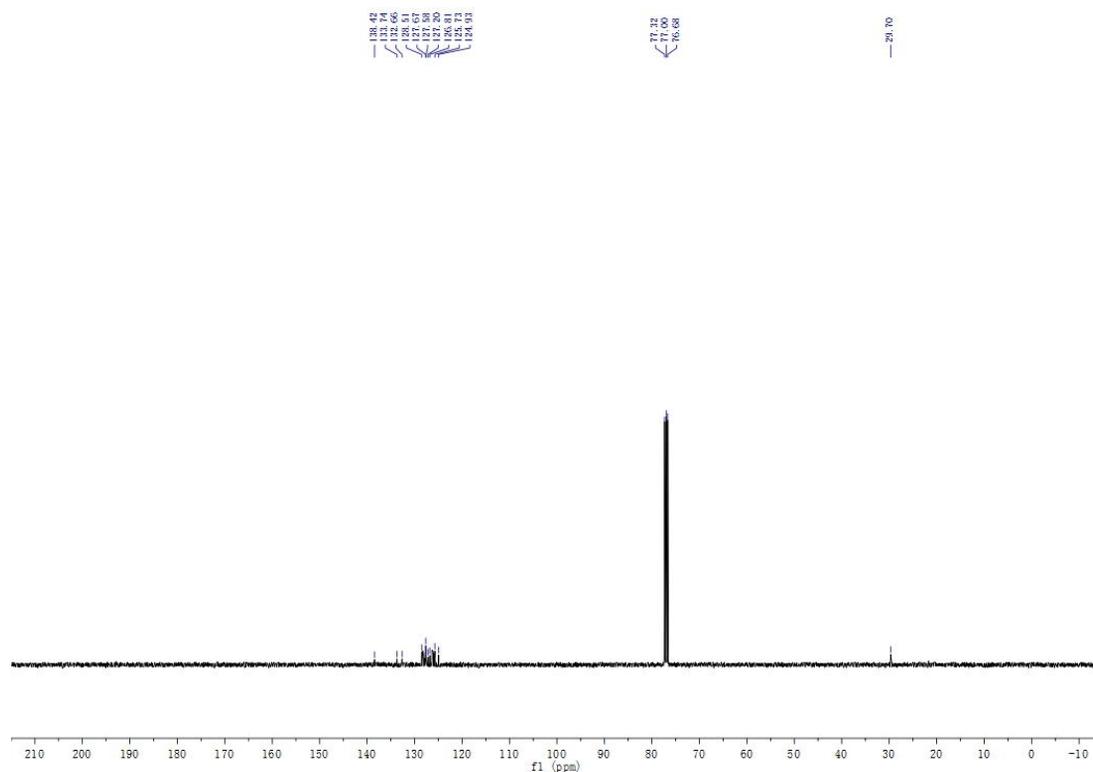












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