

## **KOt-Bu/DMF Promoted Intramolecular Cyclization of (1,1')-Biphenyl**

### **Aldehydes and Ketones: An efficient Synthesis of Phenanthrenes**

Yan-yan Chen, Niu-niu Zhang, Lin-miao Ye, Jia-hua Chen, Xiang Sun, Xue-jing Zhang, Ming Yan\*

*Institute of Drug Synthesis and Pharmaceutical Process, School of Pharmaceutical Sciences, Sun Yat-sen University, Guangzhou 510006, China. E-mail: [yanming@mail.sysu.edu.cn](mailto:yanming@mail.sysu.edu.cn)*

#### **Supporting Information**

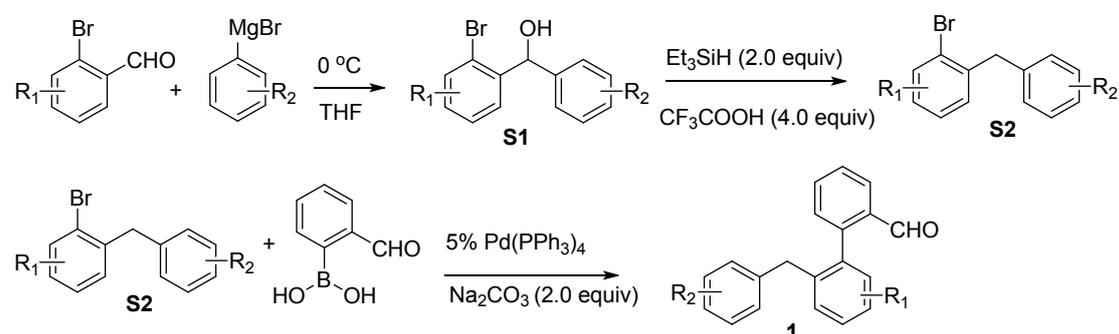
<b>1. General information</b>	<b>2</b>
<b>2. Procedures for the synthesis of substrates</b>	<b>2-7</b>
<b>3. Procedures for the synthesis of products</b>	<b>7</b>
<b>4. EPR experiment</b>	<b>7-8</b>
<b>5. Characterization data</b>	<b>8-24</b>
<b>6. References</b>	<b>25</b>
<b>7. Copies of NMR spectra</b>	<b>25-77</b>

## 1. General Information

$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker AVANCE 400 spectrometer. Chemical shifts of protons are reported in parts per million downfield from tetramethylsilane. Chemical shifts of carbon are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3$ ;  $\delta$  77.0). Peaks are labeled as singlet (s), broad singlet (br), doublet (d), triplet (t), double doublet (dd), multiplet (m). Melting points were measured on a WRS-2A melting point apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Bruker Tensor 37 spectrophotometer. Data are represented as frequency of absorption ( $\text{cm}^{-1}$ ). GC spectra were taken on an Agilent-6890A instrument. EPR spectra were recorded on a Bruker A300 spectrometer. *KOt*-Bu was purchased from Alfa Aesar chemical company and used without further purification. THF, DMF, Dichloromethane and  $\text{CH}_3\text{CN}$  and dioxane were dried and redistilled according to standard methods. DMSO was dried over  $4\text{\AA}$  molecular sieves.

## 2. Procedures for the synthesis of substrates

### 2.1 General procedure for the synthesis of substrates 1a- 1f, 1j-2n and 3f<sup>1, 2</sup>



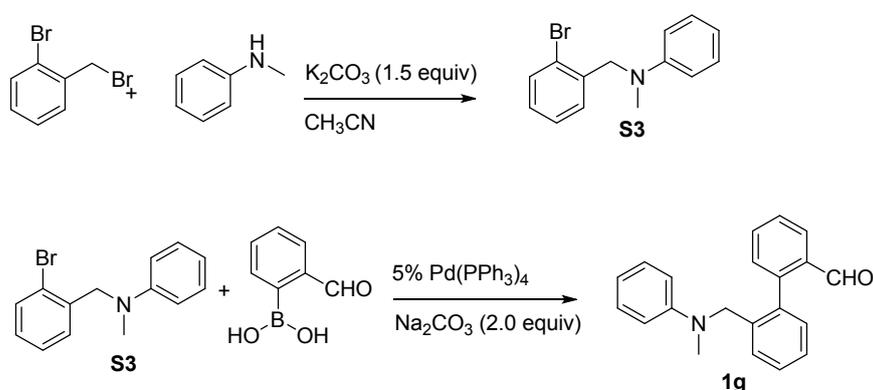
To a solution of 2-bromobenzaldehyde (552 mg, 3.0 mmol) in THF (10 mL) was added phenylmagnesium bromide (3.6 mL, 1M) at  $0\text{ }^\circ\text{C}$ . The mixture was stirred at rt for 0.5 h. Then saturated aqueous  $\text{NH}_4\text{Cl}$  (20 mL) was added and the reaction mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  2). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/ $\text{EtOAc}$ =10:1) to give the compound **S1** as a light yellow oil in 95% yield.

To a solution of **S1** (665 mg, 2.5 mmol) in  $\text{CH}_2\text{Cl}_2$  (15 mL) was added  $\text{Et}_3\text{SiH}$  (5.0 mmol) and  $\text{CF}_3\text{COOH}$  (10.0 mmol). The reaction mixture was stirred at rt for 2 h. Solid  $\text{Na}_2\text{CO}_3$  (530mg, 5.0 mmol) and water (20 mL) was successively added to the reaction mixture and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (2  $\times$  15 mL). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether) to give the compound **S2** as a colorless oil in 90%

yield.

To a mixture of **S2** (492 mg, 2.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.1 mmol), dioxane (10 mL) and aqueous Na<sub>2</sub>CO<sub>3</sub> (4.0 mL, 1 M), was added a solution of 2-formylphenylboronic acid (360 mg, 2.4 mmol) in MeOH (2 mL). The mixture was flushed with argon and stirred at 90 °C for 4 h. The reaction was quenched with water (10 mL) and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 2). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc =30:1 ) to give the compound **1a** as a white solid in 75% yield.

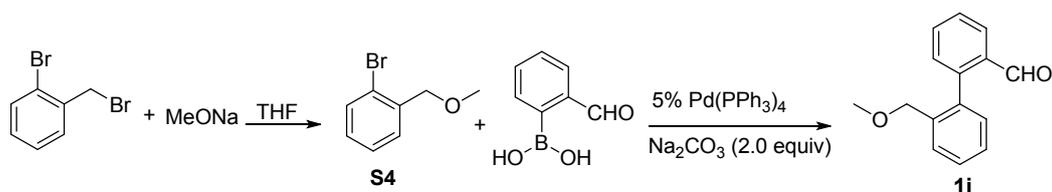
## 2.2 Procedure for the synthesis of substrates **1g** and **1h**



A mixture of 1-bromo-2-(bromomethyl)benzene (744 mg, 3.0 mmol), *N*-methylaniline (353 mg, 3.3 mmol), K<sub>2</sub>CO<sub>3</sub> (621 mg, 4.5 mmol) and CH<sub>3</sub>CN (15 mL) was stirred at 90 °C for 8 h. The reaction mixture was concentrated under vacuum and water (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL × 2). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=60:1 ) to give the compound **S3** as a yellow oil in 92% yield.

To a mixture of **S3** (550 mg, 2.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.1 mmol), dioxane (10 mL) and aqueous Na<sub>2</sub>CO<sub>3</sub> (4 mL, 1 M), was added a solution of 2-formylphenylboronic acid (360 mg, 2.4 mmol) in MeOH (2 mL). The reaction mixture was flushed with argon and stirred at 90 °C for 4 h. The reaction was quenched with water (10 mL) and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 2). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=30:1) to give the compound **1g** as a yellow solid in 70% yield.

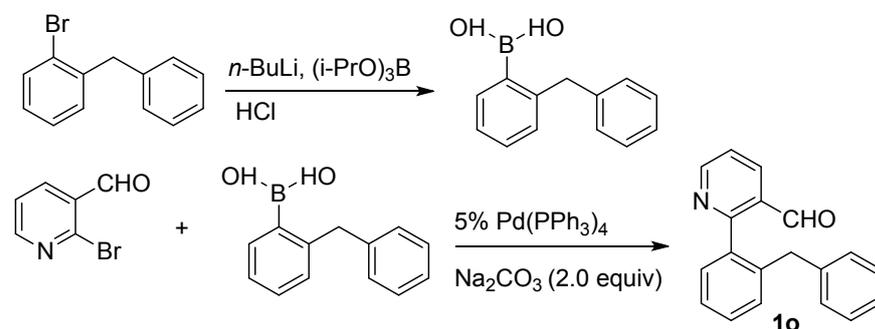
## 2.3 Procedure for the synthesis of substrate **1i**



To a solution of 1-bromo-2-(bromomethyl)benzene (744 mg, 3.0 mmol) in THF (15 mL) was added MeOK (252 mg, 3.6 mmol). The mixture was stirred at rt overnight. The reaction was quenched with water and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  2). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product **S4** was obtained.

To a mixture of **S4** (600 mg, 3.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (173 mg, 0.15 mol), dioxane (10 mL) and aqueous  $\text{Na}_2\text{CO}_3$  (6 mL, 1 M), was added a solution of 2-formylphenylboronic acid (540 mg, 3.6 mmol) in MeOH (2 mL). The mixture was flushed with argon and stirred at 90 °C for 4 h. The reaction was quenched with water (10 mL) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  2). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc =30:1) to give the compound **1i** as a colorless oil in 62 % yield.

#### 2.4 Procedure for the synthesis of substrate **1o** and **1p**.



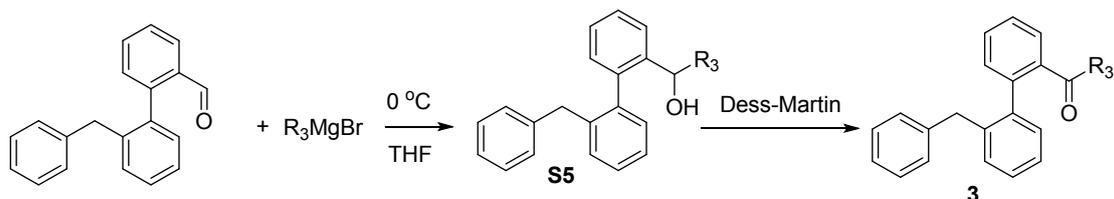
A solution of 1-benzyl-2-bromobenzene (10.0 mmol 2.46 g) in dry THF was cooled to -78 °C. To this solution was slowly added *n*-butyllithium (4.2 mL, 2.4 M, 10.0 mmol) over 15 min. The solution was stirred at -78 °C for 1 h whereupon triisopropyl borate (4.2 g, 15 mmol) dissolved in 10 mL of dry THF was dropped slowly to the reaction system. The solution was allowed to warm to room temperature for 3h. After that the reaction was quenched with dilute HCl (20%, 5 mL), and the reaction mixture was stirred for 1 h at room temperature. The mixture was extracted with  $\text{Et}_2\text{O}$  (20 mL  $\times$  2). After the evaporation of solvent under reduced pressure, the crude product (viscous liquid) was added petroleum ether 10 ml. The white boronic acid solid precipitated in petroleum ether was filtered and dried and used without further purification.

To a mixture of 2-bromonicotinaldehyde (370 mg, 2.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (116 mg, 0.1 mol), dioxane (10 mL) and aqueous  $\text{Na}_2\text{CO}_3$  (4 mL, 1 M), was added a solution of boronic acid (590 mg, 2.4 mmol) in MeOH (2 mL). The mixture was flushed with

argon and stirred at 90 °C for 4 h. The reaction was quenched with water (10 mL) and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10mL × 2). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc =30:1) to give the compound **1o** as a colorless oil in 62 % yield.

When 2-chloroquinoline-3-carbaldehyde was used as substrate to prepare **1p**, the solvent dioxane was changed to DMF.

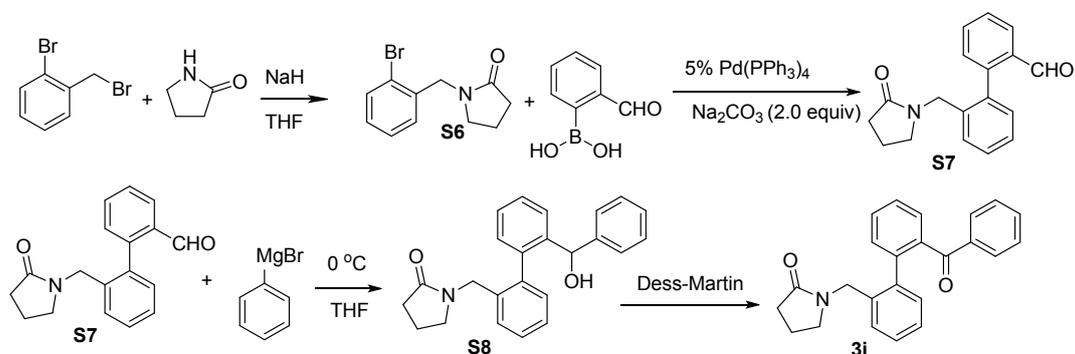
## 2.5 General procedure for the synthesis of substrates **3a - 3e, 3g-3h**



To a solution of **2a** (408 mg, 1.5 mmol) in THF (10 mL) was added phenylmagnesium bromide (1.8 mL, 1.0 M) at 0 °C. The reaction mixture was stirred at rt for 0.5 h. Then saturated aqueous NH<sub>4</sub>Cl (10 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL × 2). The combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=10:1) to give the compound **S5** as a light yellow oil in 87% yield.

To a solution of **S5** (420 mg, 1.2 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added Dess–Martin reagent (1.02 g, 2.4 mmol). The reaction mixture was stirred at rt for 0.5 h. The mixture was filtered through a sintered glass funnel to remove the solid. The filtrate was concentrated under vacuum. The crude product was purified by column chromatography (petroleum ether/EtOAc=30:1) to give the compound **3a** as a light yellow solid in 94 % yield.

## 2.6 Procedure for the synthesis of substrate **3i**



To a solution of pyrrolidin-2-one (425 mg, 5.0 mmol) in THF (10 mL) was added NaH (60% dispersion in mineral oil, 220 mg, 5.5 mmol). The reaction mixture was stirred at rt for 0.5 h. The mixture was added 1-bromo-2-(bromomethyl)benzene (1.24

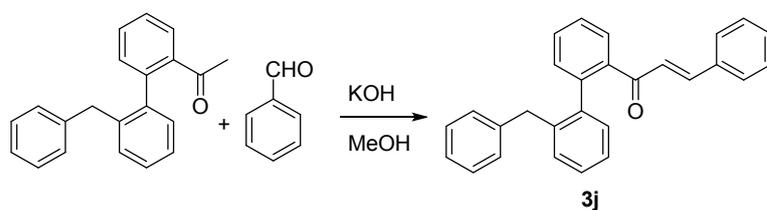
g, 5.0 mmol) and stirred for overnight. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (15 mL) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  2). The combined organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=1: 2) to give the compound **S6** as a yellow oil in 53% yield.

To a solution of **S6** (506 mg, 2.0 mmol),  $\text{Pd}(\text{PPh}_3)_4$  (116 mg, 0.01 mol), dioxane (10 mL) and aqueous  $\text{Na}_2\text{CO}_3$  (4 mL, 1 M) was added a solution of 2-formylphenylboronic acid (360 mg, 2.4 mmol) in MeOH (2 mL). The reaction mixture was flushed with argon and stirred at 90 °C for 4 h. The reaction was quenched with water (10 mL) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (10 mL  $\times$  2). The organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=1:2) to give the compound **S7** as a yellow oil in 65% yield.

To a solution of **S7** (335 mg, 1.2 mmol) in THF (10 mL) was added phenylmagnesium bromide (1.5 mL, 1.0 M) at 0 °C. The reaction mixture was stirred at rt for 0.5 h. The reaction was quenched with saturated aqueous  $\text{NH}_4\text{Cl}$  (10 mL) and the mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  2). The organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc =1:3.3) to give the compound **S8** as a yellow oil in 96 % yield.

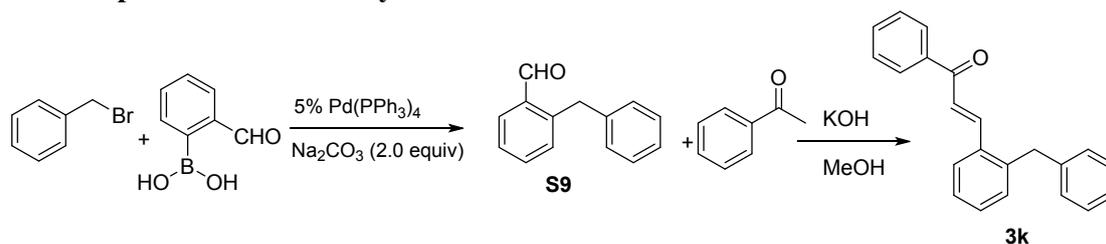
To a solution of **S8** (357 mg, 1.0 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 mL) was added Dess–Martin reagent (848 mg, 2.0 mmol). The reaction mixture was stirred at rt for 0.5 h. The mixture was filtered through a sintered glass funnel to remove the solid. The filtrate was concentrated under vacuum and the crude product was purified by column chromatography (petroleum ether/EtOAc=1:1.5) to give the compound **3a** as a light white solid in 88 % yield.

## 2.7 The procedure for the synthesis of substrate **3j**<sup>3</sup>



To a solution of **3f** (572 mg, 2.0 mmol) and benzaldehyde (212mg, 2.0 mmol) in MeOH (15 mL) was added KOH (224 mg, 4.0 mmol). The mixture was stirred at 70 °C for 6 h. After most of MeOH was evaporated under vacuum, water (20 mL) was added. The mixture was extracted with  $\text{CH}_2\text{Cl}_2$  (15 mL  $\times$  2). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$ . After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=30: 1) to give the compound **3j** as yellow oil in 93 % yield.

## 2.8 The procedure for the synthesis of substrate 3k



To a solution of (2-formylphenyl)boronic acid (300 mg, 2.0 mmol), Pd(PPh<sub>3</sub>)<sub>4</sub> (116 mg, 0.01 mol), Na<sub>2</sub>CO<sub>3</sub> (212 mg, 2.0 mmol) and toluene (15 mL) was added (bromomethyl)benzene (408 mg, 2.4 mmol). The reaction mixture was flushed with argon and stirred at 90 °C overnight. The reaction was quenched with water (10 mL) and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 mL × 2). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=30:1) to give the compound **S9** as a colorless oil in 90% yield.

To a solution of **S9** (294 mg, 1.5 mmol) and acetophenone (180 mg, 1.5 mmol) in MeOH (15 mL) was added KOH (168 mg, 3.0 mmol). The mixture was stirred at 70 °C for 6 h. After most of MeOH was evaporated under vacuum, water (20 mL) was added. The mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL × 2). The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the evaporation of the solvent under reduced pressure, the crude product was purified by column chromatography (petroleum ether/EtOAc=30: 1) to give the compound **3k** as a yellow oil in 86 % yield.

## 3. Procedures for the synthesis of products

### 3.1 General procedure for the synthesis of 2a-2n

A solution of **1a** (54 mg, 0.2 mmol) and KO*t*-Bu (22 mg, 0.2 mmol) in DMF (2.0 mL) was flushed with argon and stirred at rt for 1 h. Water (20.0 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL × 2). Then combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated under vacuum, the crude product was purified by column chromatography (petroleum ether) to give the product **2a** as a white solid in 93 % yield.

### 3.2 General procedure for the synthesis of 4a-4j

A solution of **3a** (70 mg, 0.2 mmol) and KO*t*-Bu (22 mg, 0.2 mmol) in DMF (2.0 mL) was flushed with argon and stirred at 80 °C for 1 h. Water (20.0 mL) was added and the mixture was extracted with CH<sub>2</sub>Cl<sub>2</sub> (15 mL × 2). Then combined organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the solvent was evaporated under vacuum, the crude product was purified by column chromatography (petroleum ether) to give the product **4a** as a white solid in 90% yield.

## 4. EPR experiment

### 4.1 EPR Studies of Interaction between DMF and KO*t*-Bu

A dried schlenk tube equipped with a stir bar was loaded with KO*t*-Bu (0.2 mmol) and DMF (2.0 mL), then the mixture was stirred at rt for one minute. The solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was

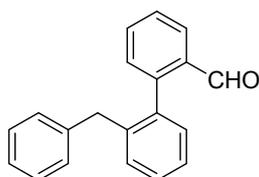
recorded at room temperature on EPR spectrometer operated at 9.869 GHz. Typical spectrometer parameters are shown as follows, scan range: 500 G; center field set: 3510 G; time constant: 81.92 ms; scan time: 40.96 s modulation amplitude: 5.0 G; modulation frequency: 100 kHz; receiver gain:  $1.00 \times 10^3$ ; microwave power: 10.11 mW.

#### 4.2 EPR Studies of Interaction between **1a** or triphenylmethane, DMF and KO $t$ -Bu

A dried schlenk tube equipped with a stir bar was loaded with **1a** or triphenylmethane (0.2 mmol), KO $t$ -Bu (0.2 mmol) and DMF (2.0 mL), then the mixture was stirred at rt for one minute. The solution sample was taken out into a small tube and analyzed by EPR. EPR spectra was recorded at room temperature on EPR spectrometer operated at 9.869 GHz. Typical spectrometer parameters are shown as follows, scan range: 500 G; center field set: 3510 G; time constant: 81.92 ms; scan time: 40.96 s modulation amplitude: 5.0 G; modulation frequency: 100 kHz; receiver gain:  $1.00 \times 10^3$ ; microwave power: 10.11 mW.

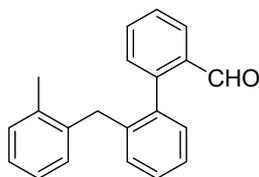
### 5. Characterization data

#### 2'-(benzyl)-(1,1'-biphenyl)-2-carbaldehyde (**1a**)



White solid. mp (70-72°C).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.51 (d,  $J = 0.7$  Hz, 1H), 7.92 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.56 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.46 (t,  $J = 7.5$  Hz, 1H), 7.38 (m, 1H), 7.34 – 7.27 (m, 2H), 7.23 – 7.17 (m, 2H), 7.14 – 7.07 (m, 3H), 6.79 – 6.78 (m, 2H), 3.84 – 3.75 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.6, 144.0, 139.1, 138.3, 136.7, 133.0, 132.4, 129.8, 129.7, 129.3, 127.7, 127.4, 127.2, 126.9, 125.9, 125.6, 125.0, 38.8. **HRMS (ESI)** calculated for  $\text{C}_{20}\text{H}_{16}\text{ONa}$  ( $\text{M}+\text{Na}$ ) $^+$ : 295.1083, found: 295.1093.

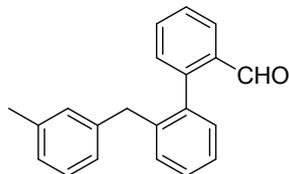
#### 2'-(2-methylbenzyl)-(1,1'-biphenyl)-2-carbaldehyde (**1b**)



White solid. mp (73-75°C).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.59 (d,  $J = 0.7$  Hz, 1H), 7.90 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.51 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.40 (t,  $J = 7.5$  Hz, 1H), 7.29 – 7.19 (m, 3H), 7.15– 7.12 (m, 1H), 7.09 – 6.86 (m, 4H), 6.81 – 6.72 (m, 1H), 3.70 – 3.60 (m, 2H), 1.85 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.7, 144.2,

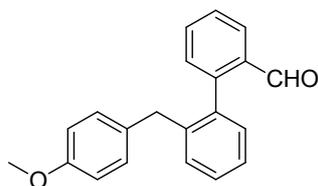
137.7, 137.1, 136.6, 135.3, 133.0, 132.5, 129.7, 129.5, 129.1, 128.8, 128.7, 127.4, 126.9, 126.1, 125.4, 125.0, 124.9, 36.2, 18.4. **HRMS (ESI)** calculated for  $C_{21}H_{18}ONa$  ( $M+Na$ )<sup>+</sup>: 309.1250, found: 309.1248.

### 2'-(3-methylbenzyl)-(1,1'-biphenyl)-2-carbaldehyde (1c)



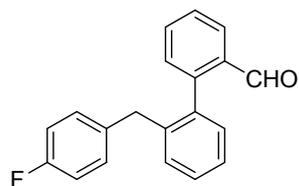
Yellow oil. **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  9.49 (d,  $J = 0.7$  Hz, 1H), 7.92 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.56 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.52 – 7.43 (m, 1H), 7.44 – 7.35 (m, 1H), 7.35 – 7.14 (m, 4H), 7.00 (t,  $J = 7.6$  Hz, 1H), 6.89 (d,  $J = 7.5$  Hz, 1H), 6.59 (d,  $J = 7.6$  Hz, 1H), 6.53 (s, 1H), 3.89 – 3.67 (m, 2H), 2.17 (s, 3H). **<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ ):  $\delta$  191.7, 145.1, 139.9, 139.5, 137.8, 137.7, 134.1, 133.4, 130.8, 130.7, 130.3, 129.6, 128.4, 128.1, 127.9, 126.9, 126.8, 126.1, 125.8, 39.8, 21.3. **HRMS (ESI)** calculated for  $C_{21}H_{18}O$  ( $M+H$ )<sup>+</sup>: 287.1430, found: 287.1426.

### 2'-(4-methoxybenzyl)-(1,1'-biphenyl)-2-carbaldehyde (1d)



Colorless oil. **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  9.54 (d,  $J = 0.8$  Hz, 1H), 7.97 – 7.90 (m, 1H), 7.56 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.50 – 7.43 (m, 1H), 7.41 – 7.33 (m, 1H), 7.33 – 7.26 (m, 2H), 7.23 – 7.14 (m, 2H), 6.74 – 6.59 (m, 4H), 3.77 – 3.67 (m, 5H). **<sup>13</sup>C NMR** (100 MHz,  $CDCl_3$ ):  $\delta$  191.7, 157.9, 145.1, 139.7, 137.6, 134.0, 133.4, 132.2, 130.8, 130.7, 130.1, 129.7, 128.4, 127.9, 127.0, 126.1, 113.7, 55.3, 38.9. **HRMS (ESI)** calculated for  $C_{21}H_{18}O_2$  ( $M+H$ )<sup>+</sup>: 303.1380, found: 303.1380.

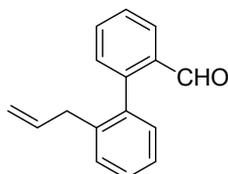
### 2'-(4-fluorobenzyl)-(1,1'-biphenyl)-2-carbaldehyde (1e)



Colorless oil. **<sup>1</sup>H NMR** (400 MHz,  $CDCl_3$ ):  $\delta$  9.55 (d,  $J = 0.7$  Hz, 1H), 7.94 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.55 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.50 – 7.44 (m, 1H), 7.42 – 7.35 (m, 1H), 7.33 – 7.27 (m, 2H), 7.22 – 7.13 (m, 2H), 6.82 – 6.77 (m, 2H), 6.75 – 6.66 (m,

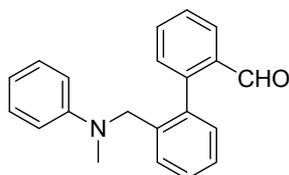
2H), 3.81– 3.70 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.6, 161.3 (d,  $J_{\text{CF}} = 243.0$  Hz), 144.9, 139.1, 137.7, 135.7 (d,  $J_{\text{CF}} = 3.2$  Hz), 133.9, 133.4, 130.8, 130.7, 130.2, 130.1 (d,  $J_{\text{CF}} = 7.8$  Hz), 128.5, 128.0, 127.1, 126.4, 115.0 (d,  $J_{\text{CF}} = 21.2$  Hz), 39.0. **HRMS (ESI)** calculated for  $\text{C}_{20}\text{H}_{15}\text{OF}$  ( $\text{M}+\text{H}$ ) $^+$ : 291.1180, found: 291.1166.

### 2'-allyl-(1,1'-biphenyl)-2-carbaldehyde (1f)



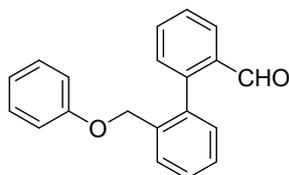
Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.73 (d,  $J = 0.7$  Hz, 1H), 8.02 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.65 – 7.58 (m, 1H), 7.55 – 7.47 (m, 1H), 7.42 – 7.36 (m, 1H), 7.35 – 7.26 (m, 3H), 7.19 (dd,  $J = 7.5, 1.2$  Hz, 1H), 5.81 – 5.67 (m, 1H), 4.95 – 4.91 (m, 1H), 4.79 – 4.74 (m, 1H), 3.24 – 3.11 (m, 2H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.2, 145.2, 138.1, 137.4, 136.4, 134.0, 133.5, 130.9, 130.6, 129.6, 128.5, 127.9, 127.1, 126.0, 116.3, 37.7. **HRMS (ESI)** calculated for  $\text{C}_{16}\text{H}_{14}\text{O}$  ( $\text{M}+\text{H}$ ) $^+$ : 223.1117, found: 223.1108.

### 2'-( (methyl (phenyl) amino ) methyl)-(1,1'-biphenyl)-2-carbaldehyde (1g)



Yellow solid. mp (93-95°C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.74 (s, 1H), 7.98 (dd,  $J = 7.8, 1.2$  Hz, 1H), 7.63 (td,  $J = 7.5, 1.4$  Hz, 1H), 7.49 (t,  $J = 7.6$  Hz, 1H), 7.40–7.31 (m, 4H), 7.25 – 7.19 (m, 1H), 7.17 – 7.06 (m, 2H), 6.68 (t,  $J = 7.2$  Hz, 1H), 6.51 (d,  $J = 8.2$  Hz, 2H), 4.19 (s, 2H), 2.82 (s, 3H).  $^{13}\text{C}$  NMR (1010 MHz,  $\text{CDCl}_3$ ):  $\delta$  191.5, 149.4, 144.4, 137.1, 136.9, 134.1, 133.7, 130.6, 130.4, 129.0, 128.5, 128.1, 127.5, 126.8, 117.0, 112.6, 55.6, 38.4. **HRMS (ESI)** calculated for  $\text{C}_{21}\text{H}_{19}\text{NO}$  ( $\text{M}+\text{H}$ ) $^+$ : 302.1539, found: 302.1537.

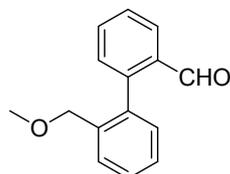
### 2'-(phenoxyethyl)-(1,1'-biphenyl)-2-carbaldehyde (1h)



Colorless oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.79 (d,  $J = 0.5$  Hz, 1H), 7.99 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.62 (dd,  $J = 7.5, 0.8$  Hz, 1H), 7.57 (td,  $J = 7.5, 1.4$  Hz, 1H), 7.49 – 7.41 (m, 3H), 7.36–7.34 (m, 1H), 7.27–7.25 (m, 1H), 7.21 – 7.15 (m, 2H), 6.90– 6.87 (m,

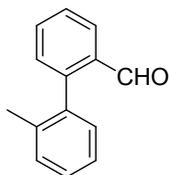
1H), 6.75– 6.72 (m, 2H), 4.79 – 4.72 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.8, 158.3, 143.9, 137.7, 135.1, 134.3, 133.4, 130.7, 130.6, 129.4, 128.7, 128.3, 128.1, 127.3, 121.1, 114.7, 68.0. HRMS (ESI) calculated for C<sub>20</sub>H<sub>16</sub>O<sub>2</sub> (M+Na)<sup>+</sup>: 311.1043, found: 311.1038.

### 2'-(methoxymethyl)-(1,1'-biphenyl)-2-carbaldehyde (1i)



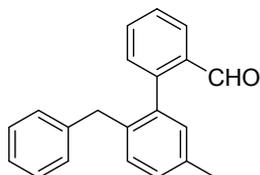
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.71 (d, *J* = 0.7 Hz, 1H), 8.04 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.63 (td, *J* = 7.5, 1.5 Hz, 1H), 7.57 – 7.49 (m, 2H), 7.44 (td, *J* = 7.5, 1.4 Hz, 1H), 7.38 (td, *J* = 7.4, 1.5 Hz, 1H), 7.33 (dd, *J* = 7.6, 0.8 Hz, 1H), 7.24 (dd, *J* = 7.4, 1.3 Hz, 1H), 4.18– 4.09 (m, 2H), 3.17 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 191.8, 144.2, 137.6, 136.4, 134.3, 133.3, 130.7, 130.4, 129.0, 128.4, 128.1, 127.6, 126.95, 72.5, 58.1. HRMS (ESI) calculated for C<sub>15</sub>H<sub>14</sub>O<sub>2</sub> (M+Na)<sup>+</sup>: 227.1067, found: 227.1060.

### 2'-methyl-(1,1'-biphenyl)-2-carbaldehyde (1j)



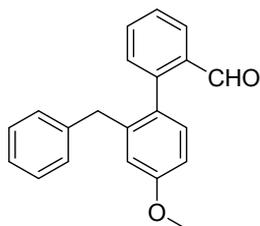
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.75 (d, *J* = 0.8 Hz, 1H), 8.03 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.66-7.62 (m, 1H), 7.52 – 7.47 (m, 1H), 7.34-7.25 (m, 4H), 7.19 (dd, *J* = 7.4, 1.2 Hz, 1H), 2.10 (s, 3H). data are consistent with the literature. (Iwasawa, T.; Kamei, T.; Watanabe, S.; Nishiuchi, M.; Kawamura, Y. *Tetrahedron Lett.* **2008**, *49*, 7430)

### 2'-benzyl-5'-methyl-(1,1'-biphenyl)-2-carbaldehyde (1k)



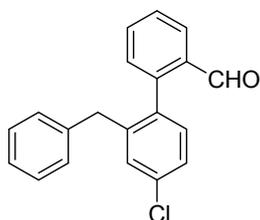
Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.45 (d, *J* = 0.7 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.46 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.15 – 7.06 (m, 3H), 7.05 – 6.95 (m, 3H), 6.91 (s, 1H), 6.74 – 6.65 (m, 2H), 3.85 – 3.49 (m, 2H), 2.27 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 190.8, 144.3, 139.4, 136.5, 135.2, 134.7, 133.0, 132.3, 130.4, 129.8, 129.2, 128.1, 127.7, 127.2, 126.7, 125.8, 124.9, 38.3, 19.9. HRMS (ESI) calculated for C<sub>21</sub>H<sub>18</sub>O (M+H)<sup>+</sup>: 287.1430, found: 287.1439.

### 2'-benzyl-4'-methoxy-(1,1'-biphenyl)-2-carbaldehyde (1l)



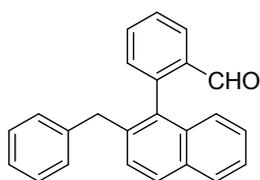
Colorless oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.54 (d, *J* = 0.7 Hz, 1H), 7.91 (dd, *J* = 7.8, 1.3 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (dd, *J* = 10.9, 4.2 Hz, 1H), 7.20 (dd, *J* = 7.6, 0.9 Hz, 1H), 7.14 – 7.04 (m, 4H), 6.90 – 6.72 (m, 4H), 3.84 – 3.72 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 191.9, 159.6, 144.9, 140.7, 139.9, 134.4, 133.4, 131.9, 131.3, 130.0, 128.7, 128.3, 127.8, 127.0, 126.1, 116.1, 111.2, 55.3, 40.0. **HRMS (ESI)** calculated for C<sub>21</sub>H<sub>18</sub>O<sub>2</sub> (M+Na)<sup>+</sup>: 325.1199, found: 325.1185.

### 2'-benzyl-4'-chloro-(1,1'-biphenyl)-2-carbaldehyde (1m)



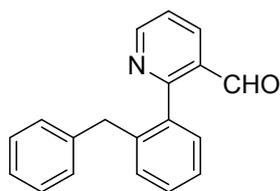
Yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>) δ 9.44 (s, 1H), 7.85 (d, *J* = 7.6 Hz, 1H), 7.49 (t, *J* = 7.4 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.19 (dd, *J* = 16.2, 7.7 Hz, 2H), 7.13 – 6.96 (m, 5H), 6.70 (d, *J* = 5.8 Hz, 2H), 3.71– 3.62 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 191.2, 143.6, 141.3, 139.1, 136.3, 134.3, 134.0, 133.6, 131.9, 130.8, 130.2, 128.8, 128.4, 128.3, 127.5, 126.4, 126.3, 36.7. **HRMS (ESI)** calculated for C<sub>20</sub>H<sub>15</sub>OCl (M+H)<sup>+</sup>: 307.0884, found: 307.0877.

### 2-(2-benzyl-naphthalen-1-yl)benzaldehyde (1n)



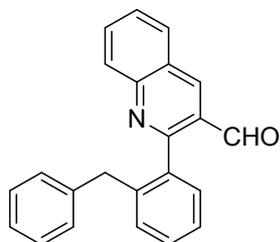
White solid. mp (134-135°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 9.31 (d, *J* = 0.7 Hz, 1H), 8.05 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.88 (dd, *J* = 8.2, 5.4 Hz, 2H), 7.68 (td, *J* = 7.5, 1.5 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.36 – 7.32 (m, 1H), 7.28 (dd, *J* = 7.5, 0.7 Hz, 1H), 7.20 – 7.08 (m, 4H), 6.90 – 6.82 (m, 2H), 3.86 (s, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 191.5, 143.0, 140.3, 137.1, 135.0, 134.0, 133.9, 133.5, 132.0, 131.7, 128.8, 128.6, 128.3, 128.2, 128.0, 127.1, 126.7, 126.1, 126.0, 125.6, 40.1. **HRMS (ESI)** calculated for C<sub>24</sub>H<sub>18</sub>O (M+Na)<sup>+</sup>: 345.1250, found: 345.1253.

### 2-(2-benzylphenyl)nicotinaldehyde (1o)



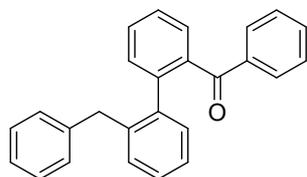
Light brown oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.43 (s, 1H), 8.84 (dd,  $J = 4.8, 1.8$  Hz, 1H), 8.11 (dd,  $J = 7.9, 1.8$  Hz, 1H), 7.48 – 7.37 (m, 3H), 7.34 (td,  $J = 7.4, 1.4$  Hz, 1H), 7.19 (dd,  $J = 7.5, 0.9$  Hz, 1H), 7.08 – 7.00 (m, 3H), 6.74 (dd,  $J = 7.1, 2.3$  Hz, 2H), 4.21 – 3.72 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 162.9, 153.2, 140.2, 140.0, 136.8, 134.9, 130.9, 130.8, 130.0, 129.4, 128.7, 128.2, 126.4, 126.0, 122.9, 39.5. **HRMS (ESI)** calculated for  $\text{C}_{19}\text{H}_{15}\text{NO}$  ( $\text{M}+\text{H}$ ) $^+$ : 274.1233, found: 274.1226.

### 2-(2-benzylphenyl)quinoline-3-carbaldehyde (1p)



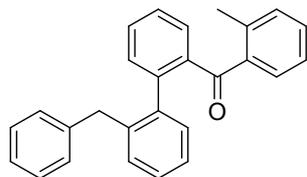
White solid, mp (102-104°C).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.53 (s, 1H), 8.64 (s, 1H), 8.19 (d,  $J = 8.5$  Hz, 1H), 7.99 (d,  $J = 8.1$  Hz, 1H), 7.91 – 7.87 (m, 1H), 7.70 – 7.60 (m, 1H), 7.50 – 7.41 (m, 2H), 7.38 (td,  $J = 7.2, 1.7$  Hz, 1H), 7.31 – 7.26 (m, 1H), 7.06 – 6.90 (m, 3H), 6.75 – 6.62 (m, 2H), 4.29 – 3.83 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.5, 160.9, 149.4, 140.2, 140.2, 137.4, 137.0, 132.7, 130.9, 130.4, 129.5, 129.5, 129.3, 128.8, 128.2, 128.0, 127.6, 126.6, 126.5, 126.0, 39.6. **HRMS (ESI)** calculated for  $\text{C}_{23}\text{H}_{17}\text{NO}$  ( $\text{M}+\text{H}$ ) $^+$ : 324.1391, found: 324.1383.

### (2'-benzyl-(1,1'-biphenyl)-2-yl)(phenyl)methanone (3a)



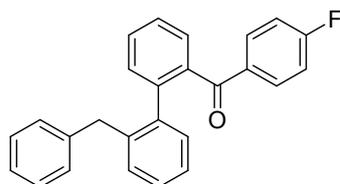
White solid. mp (79-81°C).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63 (dd,  $J = 5.2, 3.3$  Hz, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.37 (m, 3H), 7.34 – 7.26 (m, 2H), 7.24 – 6.95 (m, 10H), 3.88 – 3.77 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  198.0, 141.1, 140.6, 139.7, 139.3, 138.8, 137.8, 132.8, 131.0, 130.2, 130.1, 129.8, 129.7, 129.1, 128.5, 128.2, 128.12, 127.7, 126.8, 125.9, 125.6, 39.3. **HRMS (ESI)** calculated for  $\text{C}_{26}\text{H}_{20}\text{O}$  ( $\text{M}+\text{H}$ ) $^+$ : 349.1587, found: 349.1597.

**(2'-benzyl-(1,1'-biphenyl)-2-yl)(o-tolyl)methanone (3b)**



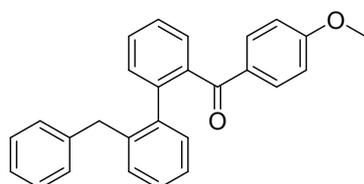
White solid. mp (93-95°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.61 – 7.55 (m, 1H), 7.46 – 7.37 (m, 2H), 7.24 – 6.91 (m, 14H), 3.82 – 3.67 (m, 2H), 2.27 (d, *J* = 3.8 Hz, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 200.5, 141.0, 140.7, 140.6, 139.9, 138.6, 138.5, 138.3, 131.2, 130.9, 130.8, 130.2, 130.1, 129.8, 129.6, 129.1, 129.0, 128.2, 127.5, 127.1, 125.8, 125.5, 124.8, 39.3, 20.4. **HRMS (ESI)** calculated for C<sub>27</sub>H<sub>22</sub>O (M+H)<sup>+</sup>: 363.1743, found: 363.1748.

**(2'-benzyl-(1,1'-biphenyl)-2-yl)(4-fluorophenyl)methanone (3c)**



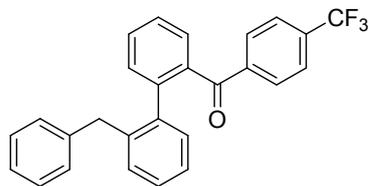
White solid. mp (98-100°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.69 – 7.57 (m, 2H), 7.52 – 7.38 (m, 3H), 7.26 – 6.92 (m, 12H), 3.89 – 3.73 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.5, 166.5 (d, *J*<sub>CF</sub> = 253.0 Hz), 141.0, 140.4, 139.6, 139.0, 138.7, 134.2 (d, *J*<sub>CF</sub> = 2.9 Hz), 132.3 (d, *J*<sub>CF</sub> = 9.3Hz), 131.0, 130.1, 129.9, 129.9, 129.0, 128.3, 128.2, 127.8, 126.9, 125.9, 125.6, 115.2 (d, *J*<sub>CF</sub> = 21.8Hz), 39.2. **HRMS (ESI)** calculated for C<sub>26</sub>H<sub>19</sub>FO (M+H)<sup>+</sup>: 367.1487, found: 367.1493.

**(2'-benzyl-(1,1'-biphenyl)-2-yl)(4-methoxyphenyl)methanone (3d)**



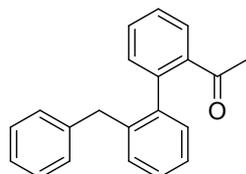
Yellow oil. **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 7.71 – 7.60 (m, 2H), 7.48 – 7.46 (m, 1H), 7.44 – 7.35 (m, 2H), 7.22 – 6.94 (m, 10H), 6.85 – 6.77 (m, 2H), 3.91 – 3.76 (m, 5H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 196.5, 163.4, 141.2, 140.2, 139.8, 139.6, 138.8, 132.3, 131.0, 130.7, 130.1, 129.7, 129.4, 129.2, 128.2, 128.1, 127.6, 126.7, 125.8, 125.5, 113.4, 55.5, 39.2. **HRMS (ESI)** calculated for C<sub>27</sub>H<sub>22</sub>O<sub>2</sub> (M+H)<sup>+</sup>: 379.1693, found: 379.1700.

**(2'-benzyl-(1,1'-biphenyl)-2-yl)(4-(trifluoromethyl)phenyl)methanone (3e)**



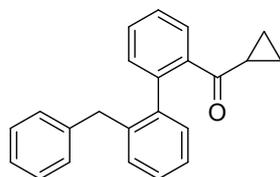
Yellow solid. mp (81-83°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.66 (d, *J* = 7.5 Hz, 2H), 7.59 – 7.41 (m, 5H), 7.28 – 6.85 (m, 10H), 3.85– 3.74 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 197.1, 140.9, 140.8, 140.7, 139.4, 138.7, 138.5, 133.7(q, *J*<sub>CF</sub> = 32.4Hz), 131.1, 130.5, 130.2, 129.9, 129.7, 129.0, 128.6, 128.3, 127.9, 127.1, 125.9, 125.7, 125.1(q, *J*<sub>CF</sub> = 3.7Hz), 123.6 (q, *J*<sub>CF</sub> = 271.7 Hz), 39.2. HRMS (ESI) calculated for C<sub>27</sub>H<sub>19</sub>OF<sub>3</sub> (M+H)<sup>+</sup>: 417.1461, found: 417.1461.

**1-(2'-benzyl-(1,1'-biphenyl)-2-yl)ethanone (3f)**



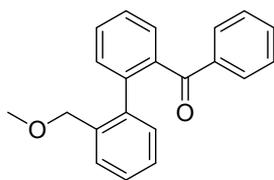
Yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.67 (dd, *J* = 6.9, 2.1 Hz, 1H), 7.46 – 7.37 (m, 2H), 7.34–7.30 (m, 1H), 7.26 – 7.23 (m, 2H), 7.18 – 7.08 (m, 5H), 6.89 (d, *J* = 6.9 Hz, 2H), 3.90–3.75 (m, 2H), 1.86 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 203.0, 140.7, 140.4, 140.1, 140.0, 138.7, 131.0, 130.8, 130.2, 130.0, 129.0, 128.3, 128.3, 128.2, 127.5, 126.3, 126.0, 39.4, 29.7. HRMS (ESI) calculated for C<sub>21</sub>H<sub>18</sub>O (M+H)<sup>+</sup>: 287.1430, found: 287.1444.

**(2'-benzyl-(1,1'-biphenyl)-2-yl)(cyclopropyl)methanone (3g)**



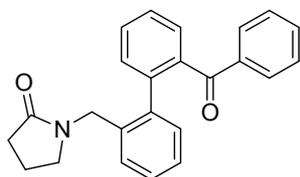
Colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.69 – 7.59 (m, 1H), 7.47 – 7.39 (m, 2H), 7.29 – 7.10 (m, 8H), 6.89–6.86 (m, 2H), 3.91–3.78 (m, 2H), 1.62– 1.56 (m, 1H), 0.98 – 0.86 (m, 2H), 0.53 – 0.50(m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 205.9, 141.3, 140.7, 140.6, 139.9, 138.8, 130.9, 130.4, 130.1, 129.0, 128.2, 128.0, 127.9, 127.4, 126.1, 125.9, 39.4, 21.5, 12.7, 12.4. HRMS (ESI) calculated for C<sub>23</sub>H<sub>20</sub>O (M+H)<sup>+</sup>: 313.1587, found: 313.1588.

**(2'-(methoxymethyl)-(1,1'-biphenyl)-2-yl)(phenyl)methanone (3h)**



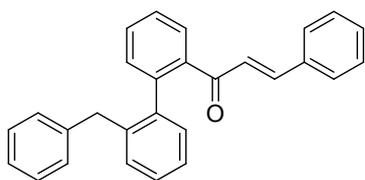
Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.65 – 7.36 (m, 7H), 7.35 (dd,  $J = 7.6, 0.7$  Hz, 1H), 7.31 – 7.25 (m, 2H), 7.19 (td,  $J = 7.5, 1.5$  Hz, 1H), 7.11 – 7.03 (m, 2H), 4.33 – 4.16 (m, 2H), 3.24 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.9, 139.9, 139.3, 137.8, 135.9, 132.8, 130.9, 130.1, 129.9, 129.7, 128.6, 128.4, 128.1, 127.7, 127.1, 127.0, 72.5, 58.1. **HRMS (ESI)** calculated for  $\text{C}_{21}\text{H}_{18}\text{O}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 303.1380, found: 303.1372.

### 1-((2'-benzoyl-(1,1'-biphenyl)-2-yl)methyl)pyrrolidin-2-one (3i)



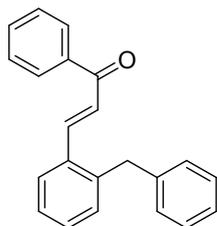
White solid. mp (132-133°C).  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.72 – 7.69 (m, 2H), 7.58 – 7.42 (m, 4H), 7.39 – 7.31 (m, 3H), 7.24 – 7.17 (m, 1H), 7.16 – 7.06 (m, 2H), 7.02 (dd,  $J = 7.5, 1.2$  Hz, 1H), 4.57– 4.13 (m, 2H), 3.31 – 3.04 (m, 2H), 2.38 – 2.32 (m, 2H), 1.97 – 1.88 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.5, 175.1, 139.7, 139.6, 138.8, 137.7, 134.4, 133.0, 131.0, 130.0, 129.9, 129.9, 128.8, 128.3, 127.9, 127.5, 127.0, 126.7, 46.67, 44.2, 30.8, 17.8. **HRMS (ESI)** calculated for  $\text{C}_{24}\text{H}_{21}\text{NO}_2$  ( $\text{M}+\text{H}$ ) $^+$ : 356.1645, found: 356.1656.

### (E)-1-(2'-benzyl-(1,1'-biphenyl)-2-yl)-3-phenylprop-2-en-1-one (3j)



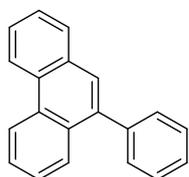
Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.79 – 7.70 (m, 1H), 7.48 – 7.43 (m, 3H), 7.34 – 7.05 (m, 13H), 6.97 – 6.87 (m, 2H), 6.51 (d,  $J = 15.8$  Hz, 1H), 3.93 – 3.81 (m, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  194.7, 143.2, 140.7, 140.3, 140.2, 140.0, 139.0, 134.8, 131.0, 130.6, 130.4, 130.2, 130.1, 129.0, 128.8, 128.7, 128.3, 128.2, 128.1, 127.5, 126.1, 125.9, 125.9, 39.3. **HRMS (ESI)** calculated for  $\text{C}_{28}\text{H}_{22}\text{O}$  ( $\text{M}+\text{Na}$ ) $^+$ : 397.1563, found: 397.1560.

### (E)-3-(2-benzylphenyl)-1-phenylprop-2-en-1-one (3k)



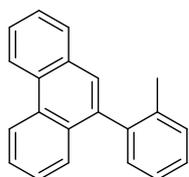
Yellow oil.  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.10 (d,  $J = 15.6$  Hz, 1H), 7.95 – 7.86 (m, 2H), 7.77 – 7.70 (m, 1H), 7.60 – 7.52 (m, 1H), 7.50 – 7.42 (m, 2H), 7.41 – 7.09 (m, 9H), 4.17 (s, 2H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 142.5, 140.7, 140.2, 138.1, 134.1, 132.7, 131.1, 130.4, 128.7, 128.6, 128.5, 127.0, 126.9, 126.2, 124.0, 39.2. **HRMS (ESI)** calculated for  $\text{C}_{22}\text{H}_{18}\text{O}$  ( $\text{M}+\text{H}$ ) $^+$ : 299.1430, found: 299.1436.

### 9-phenylphenanthrene (2a)



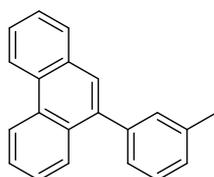
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.71 (dd,  $J = 21.9, 8.3$  Hz, 2H), 7.92– 7.85 (m, 2H), 7.73 – 7.40 (m, 10H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.9, 138.9, 131.6, 131.2, 130.7, 130.1, 130.0, 128.7, 128.4, 127.6, 127.4, 127.0, 126.9, 126.6, 126.5, 126.5, 123.0, 122.6. The data are consistent with that reported in the literature (Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6557).

### 9-(o-tolyl)phenanthrene (2b)



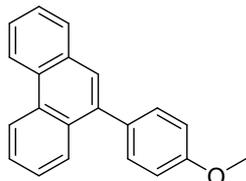
$^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.75 (d,  $J = 8.4$  Hz, 1H), 8.72 (d,  $J = 8.1$  Hz, 1H), 7.86 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.70 – 7.56 (m, 4H), 7.52 – 7.43 (m, 2H), 7.39 – 7.27 (m, 4H), 2.05 (s, 3H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  140.3, 138.5, 137.1, 131.7, 131.5, 130.4, 130.1, 130.0, 130.0, 128.7, 127.8, 127.2, 126.9, 126.8, 126.7, 126.6, 126.5, 125.8, 122.9, 122.6, 20.1. The data are consistent with that reported in the literature (Kawai, H.; Kobayashi, Y.; Oi, S.; Inoue, Y. *Chem. Commun.* **2008**, 1464).

### 9-(m-tolyl)phenanthrene (2c)



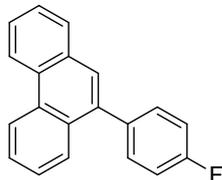
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.74 (d, *J* = 8.3 Hz, 1H), 8.68 (d, *J* = 8.1 Hz, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 7.7 Hz, 1H), 7.78 – 7.55 (m, 4H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.29 (m, 3H), 7.25 (d, *J* = 7.3 Hz, 1H), 2.43 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 140.8, 139.0, 138.0, 131.7, 131.3, 130.8, 130.7, 130.0, 128.7, 128.3, 128.2, 127.5, 127.2, 127.1, 126.9, 126.6, 126.5, 126.4, 123.0, 122.6, 21.6. The data are consistent with that reported in the literature (Xiao, T. B.; Dong, X. C.; Tang, Y. C.; Zhou, L. *Adv. Synth. Catal.* **2012**, 354, 3195).

#### 9-(4-methoxyphenyl)phenanthrene (2d)



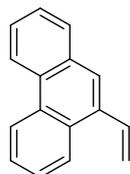
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.75 (d, *J* = 8.2 Hz, 1H), 8.69 (d, *J* = 8.2 Hz, 1H), 7.94 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.86 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.68 – 7.55 (m, 4H), 7.54 – 7.50 (m, 1H), 7.48 – 7.40 (m, 2H), 7.09 – 6.96 (m, 2H), 3.88 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 159.1, 138.5, 133.2, 131.7, 131.4, 131.2, 130.7, 129.9, 128.6, 127.5, 127.0, 126.9, 126.5, 126.5, 126.4, 122.9, 122.6, 113.8, 55.4. The data are consistent with that reported in the literature (Xiao, T. B.; Dong, X. C.; Tang, Y. C.; Zhou, L. *Adv. Synth. Catal.* **2012**, 354, 3195).

#### 9-(4-fluorophenyl)phenanthrene (2e)



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.73 (d, *J* = 8.2 Hz, 1H), 8.67 (d, *J* = 8.1 Hz, 1H), 7.88 – 7.77 (m, 2H), 7.66 – 7.55 (m, 4H), 7.53 – 7.41 (m, 3H), 7.22 – 7.11 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 162.4 (d, *J*<sub>CF</sub> = 244.7 Hz), 137.7, 136.8 (d, *J*<sub>CF</sub> = 3.3 Hz), 131.7 (d, *J*<sub>CF</sub> = 7.9 Hz), 131.5, 131.2, 130.7, 130.1, 128.7, 127.7, 127.0, 126.8, 126.7, 126.7, 126.6, 123.0, 122.6, 115.3 (d, *J*<sub>CF</sub> = 21.2 Hz). The data are consistent with that reported in the literature (Xiao, T. B.; Dong, X. C.; Tang, Y. C.; Zhou, L. *Adv. Synth. Catal.* **2012**, 354, 3195).

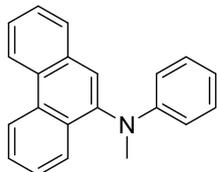
#### 9-vinylphenanthrene (2f)



**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.74 – 8.67 (m, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.14 – 8.12 (m, 1H), 7.88 – 7.85 (m, 1H), 7.82 (s, 1H), 7.69 – 7.52 (m, 4H), 7.45 (dd, *J* =

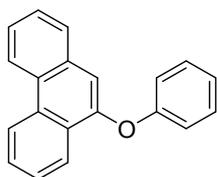
17.2, 10.9 Hz, 1H), 5.85 (dd,  $J = 17.2, 1.7$  Hz, 1H), 5.51 (dd,  $J = 10.9, 1.7$  Hz, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  135.1, 134.7, 131.8, 130.6, 130.4, 130.3, 128.7, 126.8, 126.7, 126.6, 126.5, 124.7, 123.1, 122.6, 117.6. The data are consistent with that reported in the literature (Katritzky, A. R.; Hitchings, J. G.; King, R. W.; Zhu, D. W. *Magn. Reson. Chem.* **1991**, *29*, 2).

### N-methyl-N-phenylphenanthren-9-amine (2g)



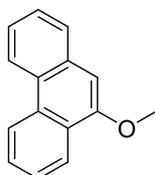
White solid. mp (97-99°C).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.61 (d,  $J = 8.3$  Hz, 1H), 8.56 (d,  $J = 8.2$  Hz, 1H), 7.84 (dd,  $J = 8.2, 0.9$  Hz, 1H), 7.71 – 7.64 (m, 1H), 7.57 – 7.37 (m, 5H), 7.07– 7.02 (m, 2H), 6.65– 6.57 (m, 3H), 3.31 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  150.1, 143.9, 132.6, 132.1, 130.4, 129.6, 129.1, 128.4, 127.0, 126.9, 126.7, 125.6, 124.7, 123.3, 122.7, 117.5, 113.9, 40.2. HRMS (ESI) calculated for  $\text{C}_{21}\text{H}_{18}\text{N}$  (M+H) $^+$ : 284.1429, found: 284.1934.

### 9-phenoxyphenanthrene (2h)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.68 (d,  $J = 8.2$  Hz, 1H), 8.61 (d,  $J = 7.8$  Hz, 1H), 8.34 (dd,  $J = 8.1, 1.1$  Hz, 1H), 7.70– 7.58 (m, 3H), 7.56– 7.48 (m, 2H), 7.40 – 7.30 (m, 2H), 7.16 – 7.03 (m, 4H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.4, 151.8, 132.4, 131.8, 130.0, 127.9, 127.8, 127.4, 127.1, 127.0, 126.8, 125.5, 123.6, 122.8, 122.7, 119.2, 111.5. The data are consistent with that reported in the literature (Toshihiko, O.; Koichi, S.; Naoki, M.; Yoshiyasu, K.; Shunji, N. *Chem. Pharm. Bull.* **1978**, *26*, 2014).

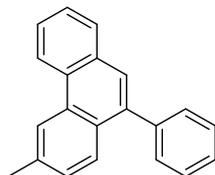
### 9-methoxyphenanthrene (2i)



$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.63 (d,  $J = 8.0$  Hz, 1H), 8.56 (d,  $J = 8.0$  Hz, 1H), 8.35 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.85 – 7.72 (m, 1H), 7.67– 7.58 (m, 2H), 7.54 – 7.46 (m, 2H), 6.96 (s, 1H), 4.06 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 133.0, 131.3, 127.3, 127.2, 126.9, 126.6, 126.5, 126.4, 124.2, 122.6, 122.6, 122.5, 102.0,

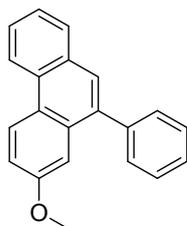
55.5. The data are consistent with that reported in the literature (Dreher, S. D.; Paruch, K.; Katz, T. J.; *J. Org. Chem.*, **2000**, *65*, 806).

### 3-methyl-10-phenylphenanthrene (2k)



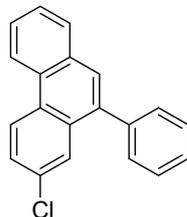
White solid. mp (82-84°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.67 (d, *J* = 8.2 Hz, 1H), 8.53 (s, 1H), 7.91 – 7.67 (m, 2H), 7.67 – 7.35 (m, 8H), 7.32 (dd, *J* = 8.4, 1.4 Hz, 1H), 2.58 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 141.1, 138.8, 136.2, 131.9, 130.8, 130.1, 129.8, 129.2, 128.7, 128.4, 128.3, 127.4, 126.9, 126.8, 126.7, 126.4, 122.8, 122.6, 22.0. **HRMS (EI)** calculated for C<sub>21</sub>H<sub>16</sub> (M)<sup>+</sup>: 268.1247, found: 268.1240.

### 2-methoxy-10-phenylphenanthrene (2l)



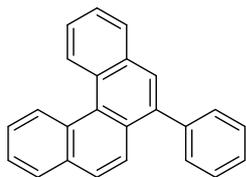
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.64 (d, *J* = 9.0 Hz, 1H), 8.58 (d, *J* = 8.3 Hz, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.65 (s, 1H), 7.60 (ddd, *J* = 8.4, 7.0, 1.4 Hz, 1H), 7.57 – 7.40 (m, 6H), 7.34 – 7.24 (m, 2H), 3.77 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 158.3, 141.0, 138.3, 132.6, 130.6, 130.1, 130.0, 128.7, 128.4, 128.2, 127.4, 126.7, 125.9, 125.0, 124.6, 122.1, 116.4, 107.9, 55.3. The data are consistent with that reported in the literature (Garcia-Cuadrado, D.; de Mendoza, P.; Braga, AAC; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2007**, *129*, 6880).

### 2-chloro-10-phenylphenanthrene (2m)



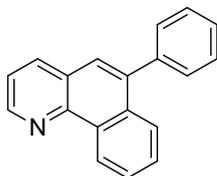
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.63– 8.58 (m, 2H), 7.85 (d, *J* = 11.7 Hz, 2H), 7.72 – 7.40 (m, 9H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 140.1, 137.9, 132.7, 132.4, 131.5, 130.0, 129.5, 129.0, 128.8, 128.7, 128.6, 127.7, 127.2, 127.1, 127.0, 126.1, 124.6, 122.5. The data are consistent with that reported in the literature (Garcia-Cuadrado, D.; Braga, AAC; Maseras, F.; Echavarren, A. M. *J. Am. Chem. Soc.* **2006**, *128*, 1066).

### 6-phenylbenzo[c]phenanthrene (2n)



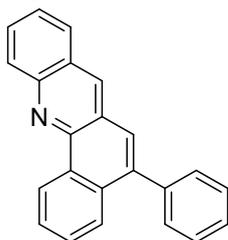
White solid. mp (113-115°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.11– 9.06 (m, 2H), 8.01 – 7.88 (m, 2H), 7.84 – 7.71 (m, 3H), 7.69 – 7.55 (m, 4H), 7.54 – 7.39 (m, 5H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 141.0, 138.7, 133.2, 132.9, 130.4, 130.2, 129.8, 129.7, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 127.5, 127.0, 126.3, 126.2, 126.1, 126.0, 124.7. HRMS (EI) calculated for C<sub>24</sub>H<sub>16</sub> (M)<sup>+</sup>: 304.1247, found: 304.1241.

### 6-phenylbenzo(h)quinoline (2o)



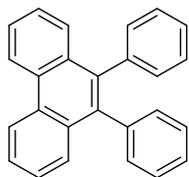
White solid, mp (140-141°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.41 (dd, *J* = 8.2, 0.6 Hz, 1H), 9.00 (dd, *J* = 4.4, 1.7 Hz, 1H), 8.14 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.70 (m, 1H), 7.67 – 7.57 (m, 2H), 7.57 – 7.41 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 148.8, 146.2, 140.2, 139.8, 135.9, 132.7, 131.8, 130.0, 128.4, 128.2, 127.7, 127.0, 126.4, 126.0, 125.8, 124.7, 122.1. HRMS (ESI) calculated for C<sub>19</sub>H<sub>13</sub>N (M + H)<sup>+</sup>: 256.1120, found: 256.1121.

### 5-phenylbenzo(c)acridine (2p)



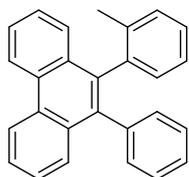
Yellow oil, mp (111-112°C). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.70 – 9.57 (m, 1H), 8.57 (s, 1H), 8.39 (d, *J* = 8.7 Hz, 1H), 7.98 (d, *J* = 8.2 Hz, 1H), 7.86 (d, *J* = 8.1 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.68 – 7.61 (m, 2H), 7.59 – 7.44 (m, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 147.7, 147.47, 140.2, 139.5, 135.0, 133.3, 131.8, 129.9, 129.8, 129.7, 129.0, 128.5, 127.8, 127.7, 127.3, 127.2, 126.6, 126.0, 125.9, 125.6, 124.8. HRMS (ESI) calculated for C<sub>23</sub>H<sub>15</sub>N (M + H)<sup>+</sup>: 306.1283, found: 306.1277.

### 9,10-diphenylphenanthrene (4a)



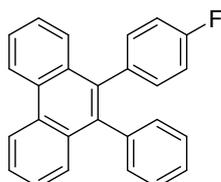
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.79 (d, *J* = 8.3 Hz, 2H), 7.65 (ddd, *J* = 8.3, 6.9, 1.4 Hz, 2H), 7.56 (dd, *J* = 8.3, 1.0 Hz, 2H), 7.47 (ddd, *J* = 8.1, 6.9, 1.1 Hz, 2H), 7.26 – 7.11 (m, 10H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 139.6, 137.2, 131.9, 131.1, 130.0, 127.9, 127.6, 126.7, 126.5, 126.4, 122.5. The data are consistent with that reported in the literature (Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6557).

#### 9-phenyl-10-(*o*-tolyl)phenanthrene (4b)



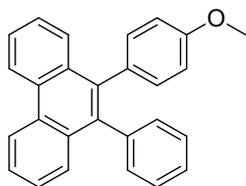
White solid. mp (211-213°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.78 (dd, *J* = 8.3, 2.2 Hz, 2H), 7.69 – 7.59 (m, 2H), 7.57 – 7.55 (m, 1H), 7.51 – 7.41 (m, 2H), 7.38 – 7.36 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.01 (m, 9H), 1.95 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 139.6, 139.0, 137.0, 136.7, 136.6, 132.2, 131.5, 131.4, 131.3, 130.2, 130.0, 129.5, 129.3, 127.8, 127.7, 127.6, 127.4, 127.2, 126.9, 126.7, 126.6, 126.5, 126.4, 125.2, 122.7, 122.6, 20.2. **HRMS (EI)** calculated for C<sub>27</sub>H<sub>20</sub> (M)<sup>+</sup>: 344.1560, found: 344.1565.

#### 9-(4-fluorophenyl)-10-phenylphenanthrene (4c)



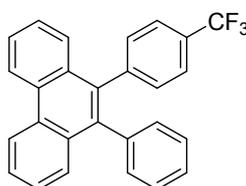
White solid. mp (245-248°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.80 (d, *J* = 8.3 Hz, 2H), 7.72 – 7.62 (m, 2H), 7.59 – 7.43 (m, 4H), 7.28 – 7.19 (m, 3H), 7.18 – 7.03 (m, 4H), 6.94– 7.90 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 161.5 (d, *J*<sub>CF</sub> = 244.0 Hz), 139.5, 137.7, 136.1, 135.4 (d, *J*<sub>CF</sub> = 3.5 Hz), 132.6 (d, *J*<sub>CF</sub> = 7.9 Hz), 131.9, 131.8, 131.0, 130.1, 127.9, 127.8, 127.6, 126.7, 126.7, 126.6, 126.6, 126.5, 122.6, 122.5, 114.6 (d, *J*<sub>CF</sub> = 21.2 Hz). **HRMS (EI)** calculated for C<sub>26</sub>H<sub>17</sub>F (M)<sup>+</sup>: 348.1309, found: 348.1306.

#### 9-(4-methoxyphenyl)-10-phenylphenanthrene (4d)



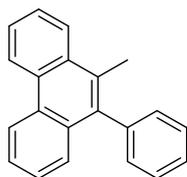
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.79 (d, *J* = 8.1 Hz, 2H), 7.75 – 7.37 (m, 6H), 7.30 – 7.10 (m, 5H), 7.05 (d, *J* = 7.0 Hz, 2H), 6.77 (d, *J* = 7.0 Hz, 2H), 3.76 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 158.1, 139.8, 137.5, 136.9, 132.3, 132.1, 132.0, 131.8, 131.1, 130.1, 130.0, 127.9, 127.9, 127.8, 126.6, 126.4, 126.4, 126.3, 122.5, 113.1, 55.1. The data are consistent with that reported in the literature (Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6557).

#### 9-phenyl-10-(4-(trifluoromethyl)phenyl)phenanthrene (4e)



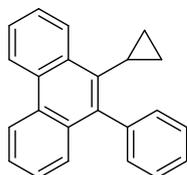
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.81 (dd, *J* = 8.1, 1.7 Hz, 2H), 7.67 (t, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.40 (m, 5H), 7.30 – 7.18 (m, 5H), 7.11 (d, *J* = 7.2 Hz, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 143.6, 139.0, 137.5, 135.7, 131.7, 131.5, 131.3, 130.9, 130.2, 130.1, 128.7 (q, *J*<sub>CF</sub> = 32.1 Hz), 128.0, 127.9, 127.4, 126.9, 126.9, 126.8, 126.7, 124.6 (q, *J*<sub>CF</sub> = 3.7), 124.2 (q, *J*<sub>CF</sub> = 270.4), 122.7, 122.6. The data are consistent with that reported in the literature (Shimizu, M.; Nagao, I.; Tomioka, Y.; Kadowaki, T.; Hiyama, Y. *Tetrahedron.* **2011**, *67*, 8014).

#### 9-methyl-10-phenylphenanthrene (4f)



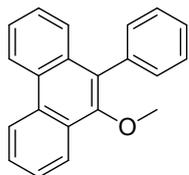
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.77– 7.70 (m, 2H), 8.20 – 8.09 (m, 1H), 7.72 – 7.60 (m, 2H), 7.58 – 7.33 (m, 6H), 7.32 – 7.24 (m, 2H), 2.44 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 140.8, 137.1, 132.4, 132.0, 130.4, 130.0, 129.9, 129.4, 128.5, 127.5, 127.1, 126.9, 126.4, 126.3, 125.7, 125.1, 122.9, 122.4, 17.4. The data are consistent with that reported in the literature (Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6557).

#### 9-cyclopropyl-10-phenylphenanthrene (4g)



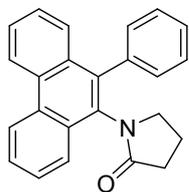
White solid. mp (135-137°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.80 – 8.61 (m, 3H), 7.69 – 7.53 (m, 4H), 7.51 – 7.33 (m, 6H), 2.08 – 2.01 (m, 1H), 0.80 – 0.75 (m, 2H), 0.34 – 0.30 (m, 2H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 140.3, 139.0, 134.0, 133.0, 132.0, 131.2, 130.1, 129.9, 128.0, 127.3, 126.8, 126.5, 126.5, 126.4, 126.2, 126.0, 122.8, 122.4, 13.4, 9.7. **HRMS (EI)** calculated for C<sub>23</sub>H<sub>18</sub> (M)<sup>+</sup>: 294.1403, found: 294.1398.

#### 9-methoxy-10-phenylphenanthrene (4h)



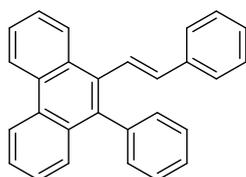
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.78 – 8.58 (m, 2H), 8.21 – 8.18 (m, 1H), 7.64 – 7.55 (m, 2H), 7.53 – 7.33 (m, 8H), 3.50 (s, 3H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 151.2, 136.5, 132.7, 131.5, 130.9, 128.4, 128.3, 128.2, 127.8, 127.4, 127.0, 127.0, 126.7, 126.7, 125.5, 123.2, 122.9, 122.6, 61.3. The data are consistent with that reported in the literature (Kitamura, T.; Kobayashi, S.; Taniguchi, H. *J. Org. Chem.* **1984**, *49*, 3167).

#### 1-(10-phenylphenanthren-9-yl)pyrrolidin-2-one (4i)



White solid. mp (258-260°C). **<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.78– 8.74 (m, 2H), 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.76 – 7.61 (m, 3H), 7.60 – 7.41 (m, 6H), 7.37 – 7.28 (m, 1H), 3.64 – 3.59 (m, 1H), 3.21 – 3.25 (m, 1H), 2.59– 2.51 (m, 1H), 2.28 – 2.05 (m, 2H), 1.81 – 1.66 (m, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 176.1, 137.8, 137.0, 131.8, 131.5, 131.2, 130.4, 129.9, 129.5, 128.8, 128.4, 127.9, 127.7, 127.7, 127.6, 127.2, 127.2, 126.8, 123.46, 123.3, 122.6, 50.1, 31.0, 19.5. **HRMS (ESI)** calculated for C<sub>24</sub>H<sub>19</sub>NO (M+H)<sup>+</sup>: 338.1539, found: 338.1536.

#### (E)-9-phenyl-10-styrylphenanthrene (4j)



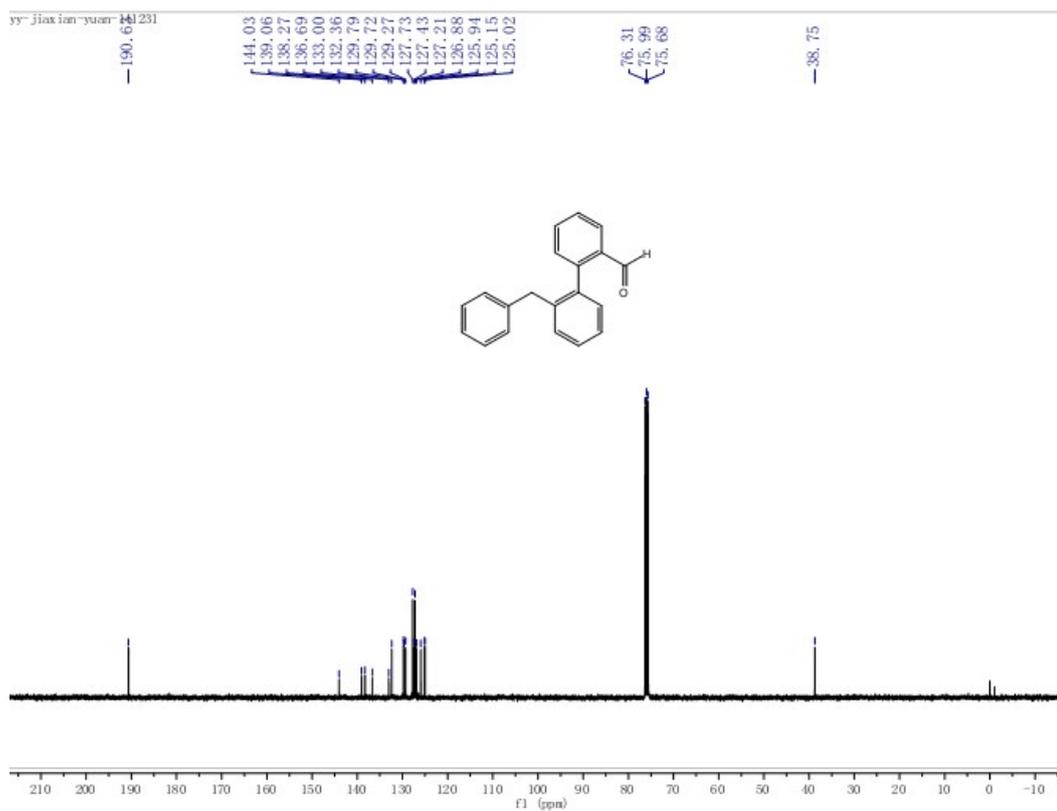
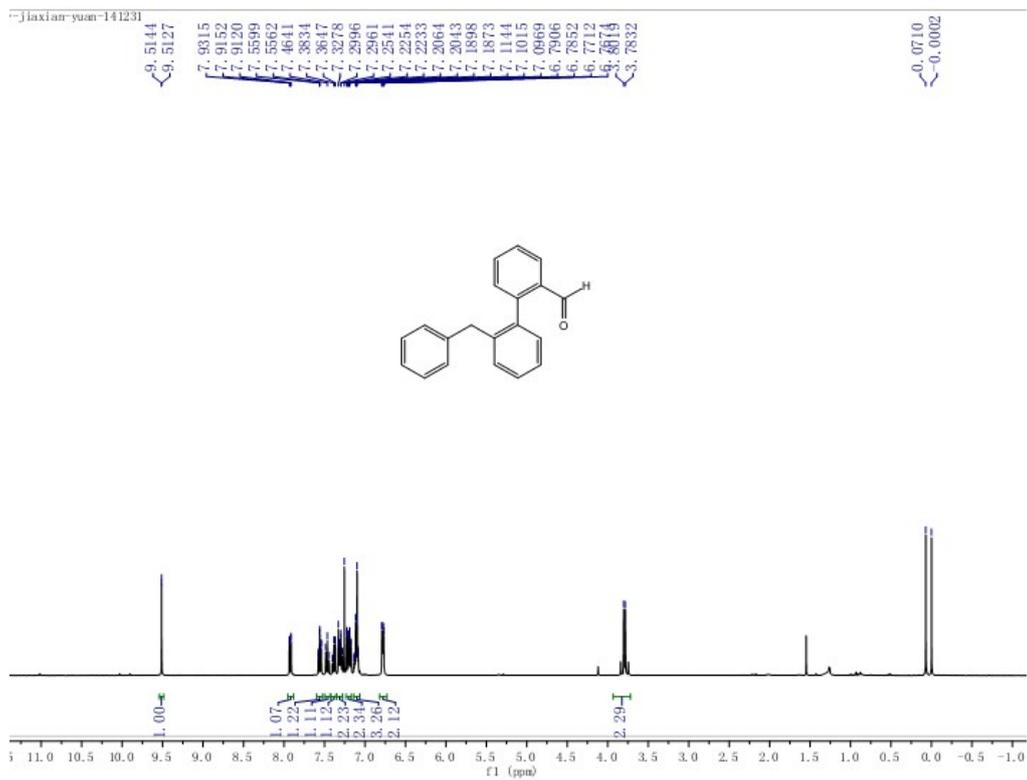
**<sup>1</sup>H NMR** (400 MHz, CDCl<sub>3</sub>): δ 8.76 (d, *J* = 8.0 Hz, 1H), 8.72 (d, *J* = 8.3 Hz, 1H), 8.38 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.63 – 7.56 (m, 2H), 7.53 (dd, *J* = 8.2, 0.9 Hz, 1H), 7.46 – 7.42 (m, 3H), 7.39 – 7.35 (m, 1H), 7.33 – 7.31 (m, 2H), 7.29 – 7.19 (m, 5H), 7.11 (d, *J* = 16.7 Hz, 1H), 6.61 (d, *J* = 16.7 Hz, 1H). **<sup>13</sup>C NMR** (100 MHz, CDCl<sub>3</sub>): δ 139.8, 137.7, 136.8, 135.9, 132.5, 131.9, 131.0, 130.8, 130.5, 129.9, 128.6, 128.3, 127.7, 127.6, 127.1, 126.9, 126.8, 126.8, 126.6, 126.5, 126.4, 126.4, 122.9, 122.5. The data are consistent with that reported in the literature (Matsumoto, A.; Ilies, L.; Nakamura, E. *J. Am. Chem. Soc.* **2011**, *133*, 6557).

## 6. References

1. C. Shu, C. B. Chen, W.X. Chen, L. W. Ye, *Org. Lett.*, 2013, **15**, 5542.
2. A. R. Jagdale, J. H. Park, S. W. Youn, *J. Org. Chem.*, 2011, **76**, 7204.
3. M. Y. Chang, C. Y. Tsai, M. H. Wu, *Tetrahedron.*, 2013, **69**, 6364.

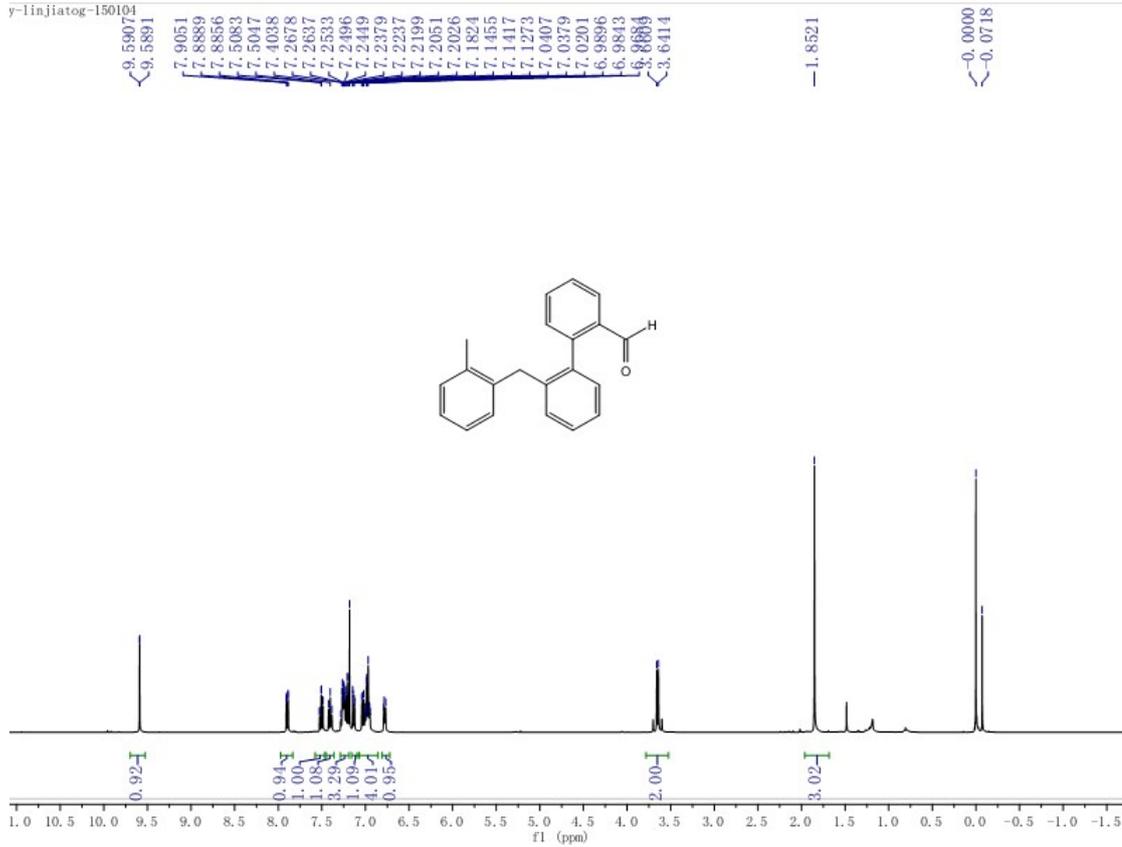
## 7. Copies of NMR spectra of products

**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 1a**

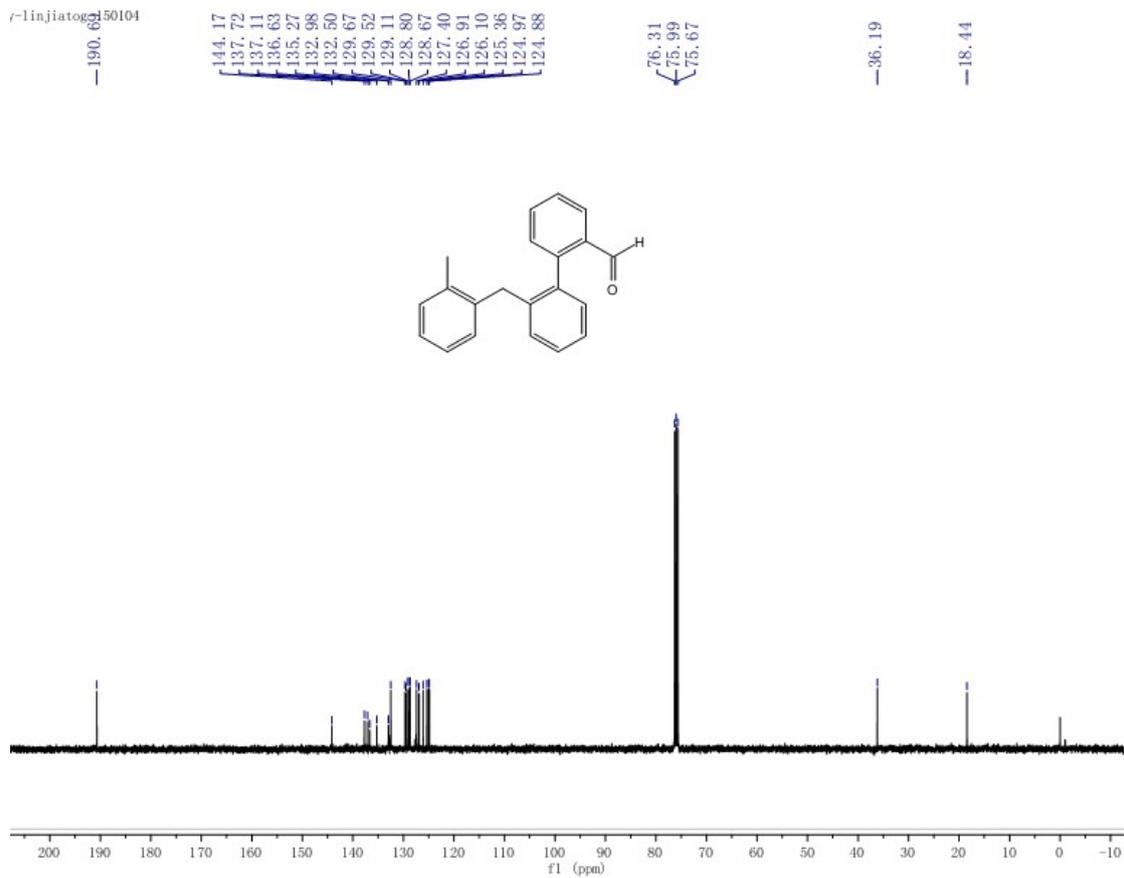


$^1\text{H}$  NMR and  $^{13}\text{C}$  NMR of 1b

y-linjiatog-150104

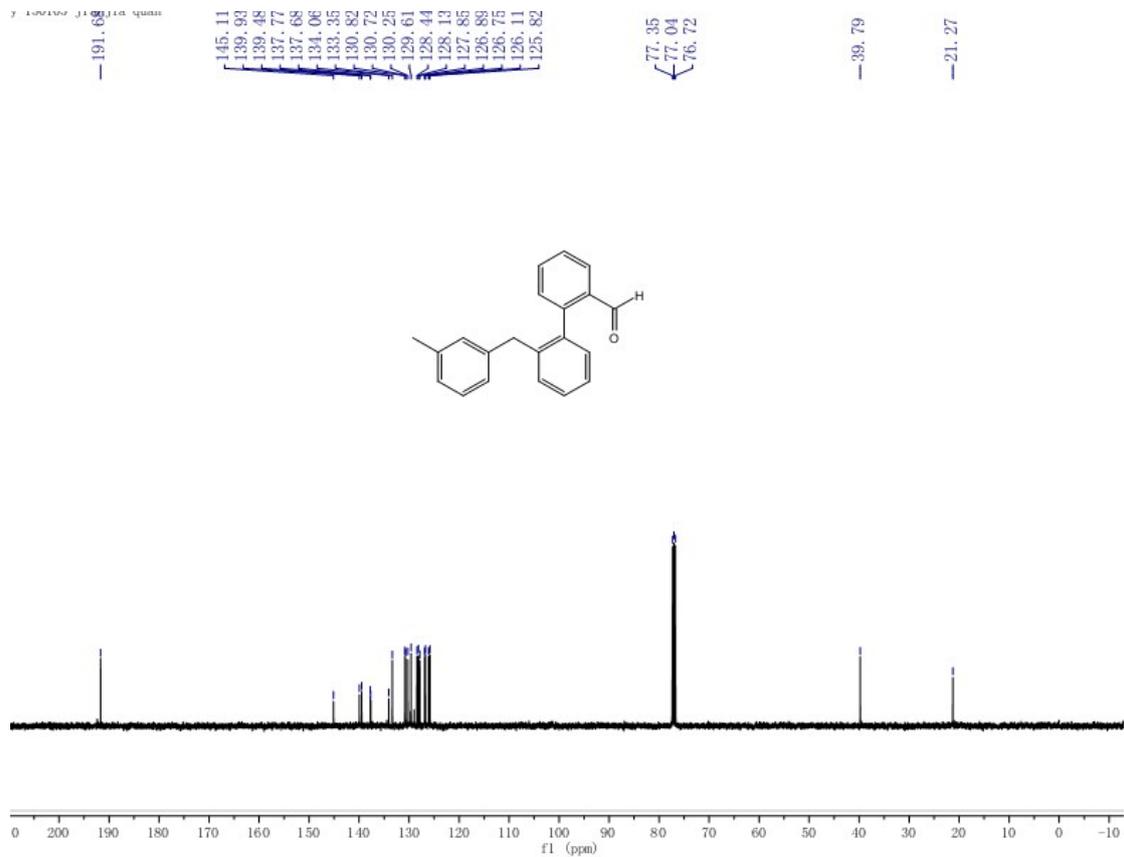
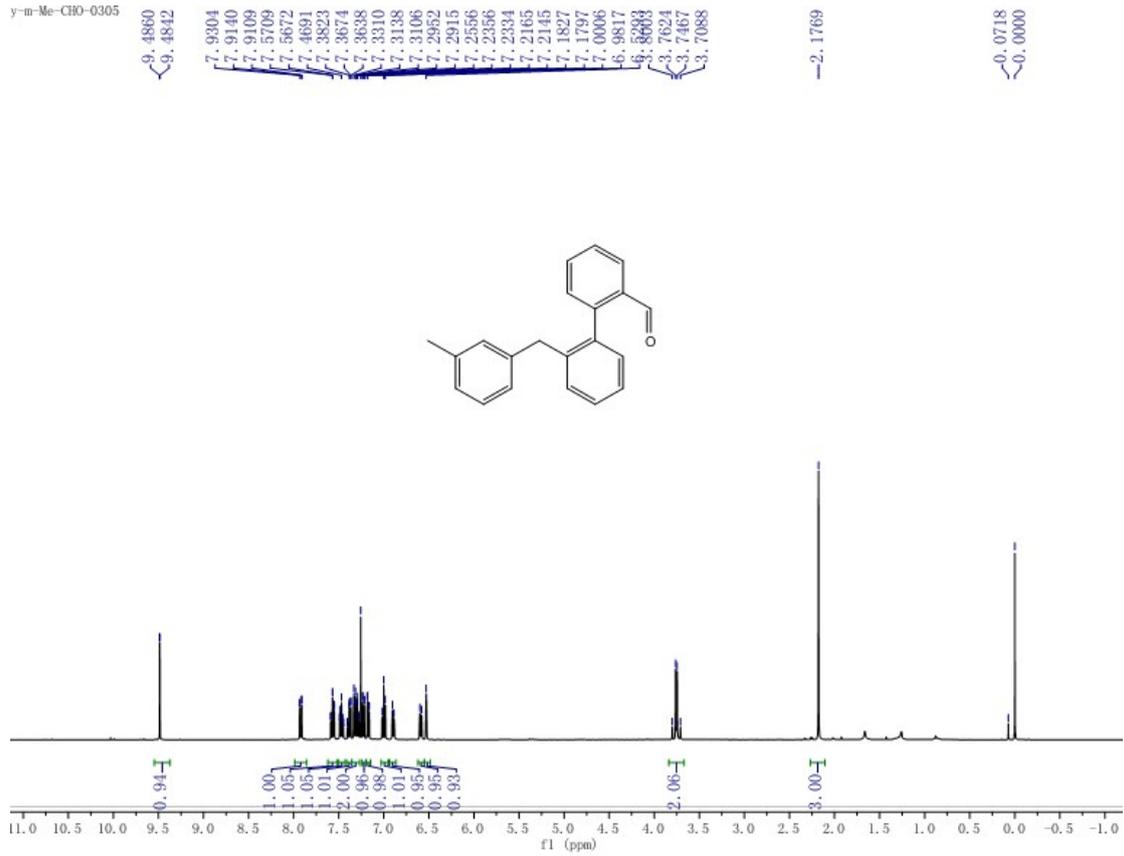


r-linjiatog-150104

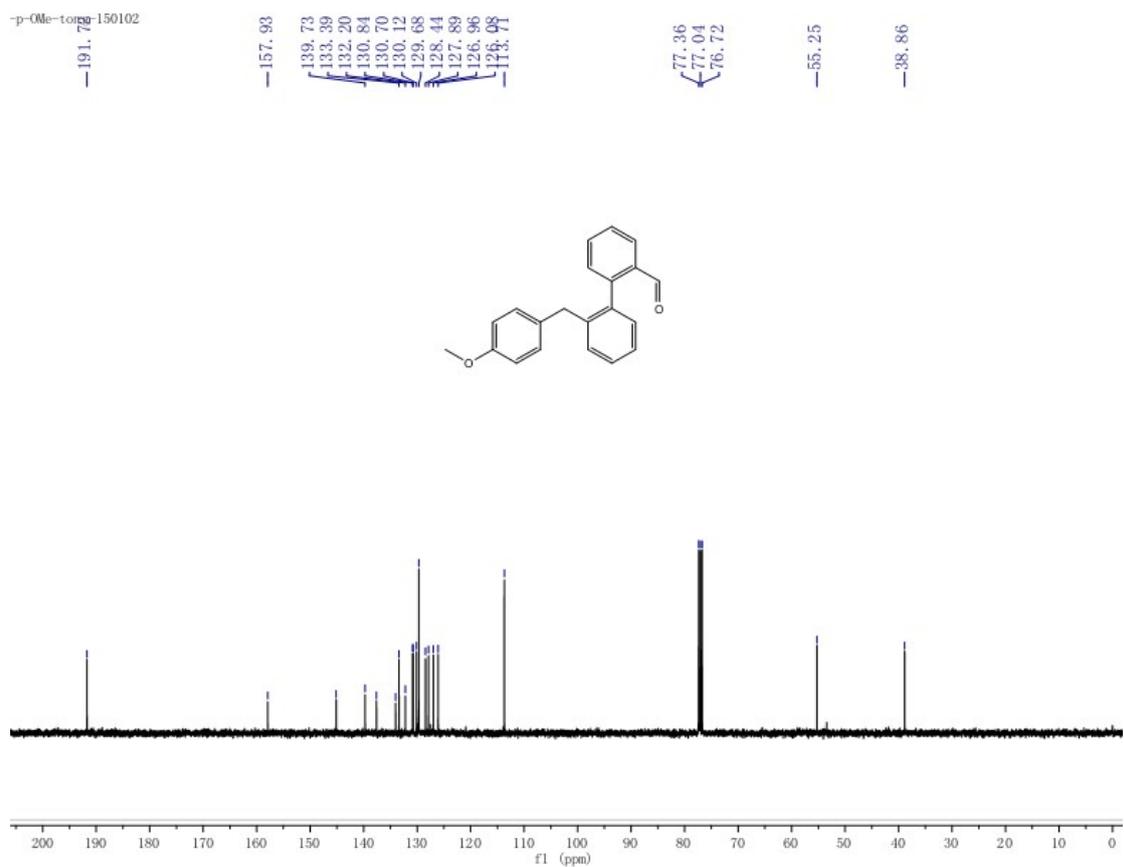
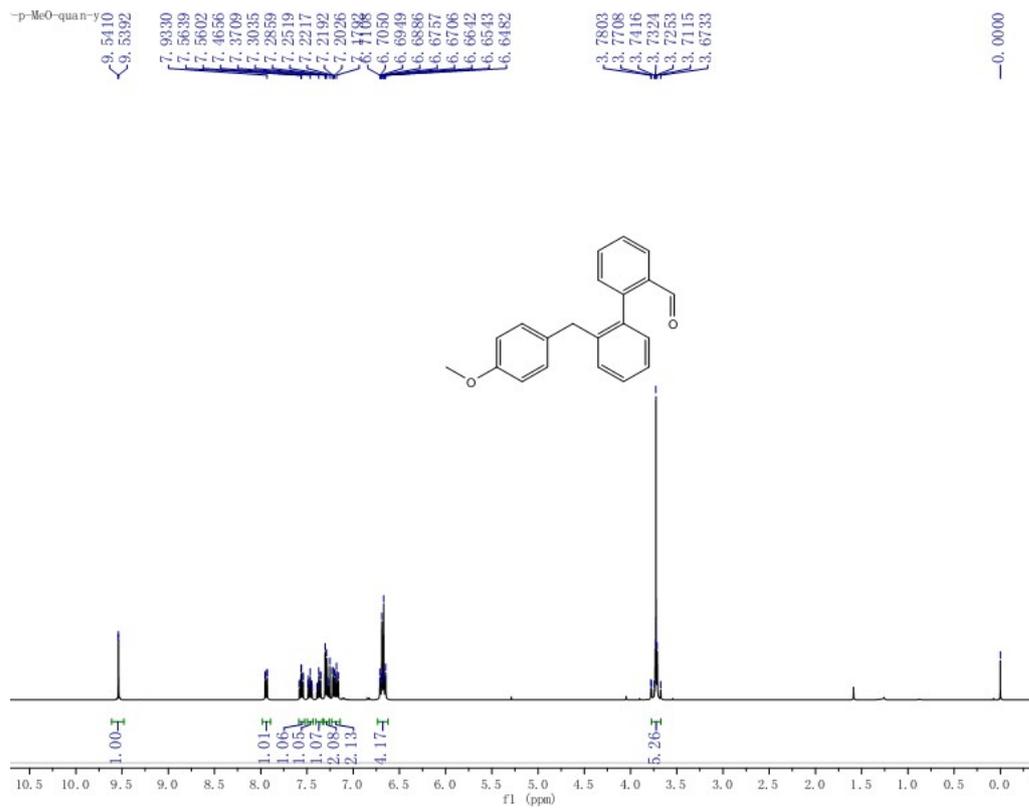


<sup>1</sup>H NMR and <sup>13</sup>CNMR of 1c

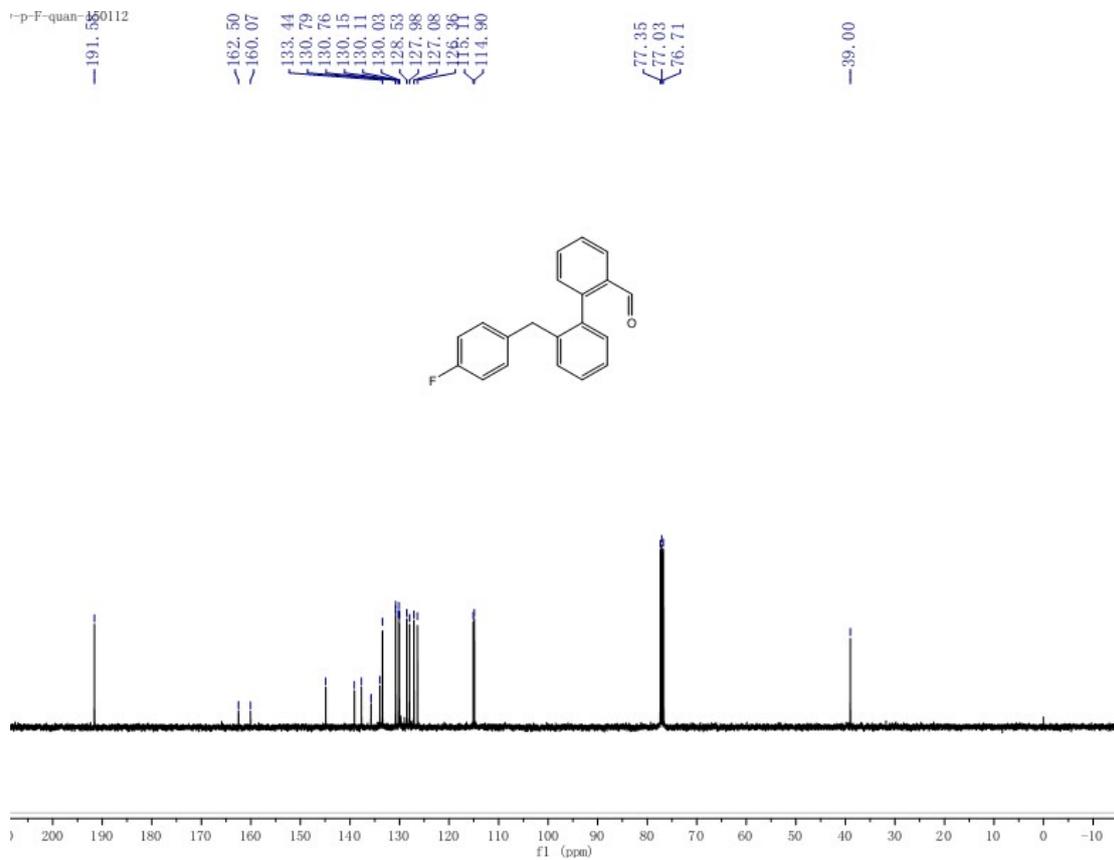
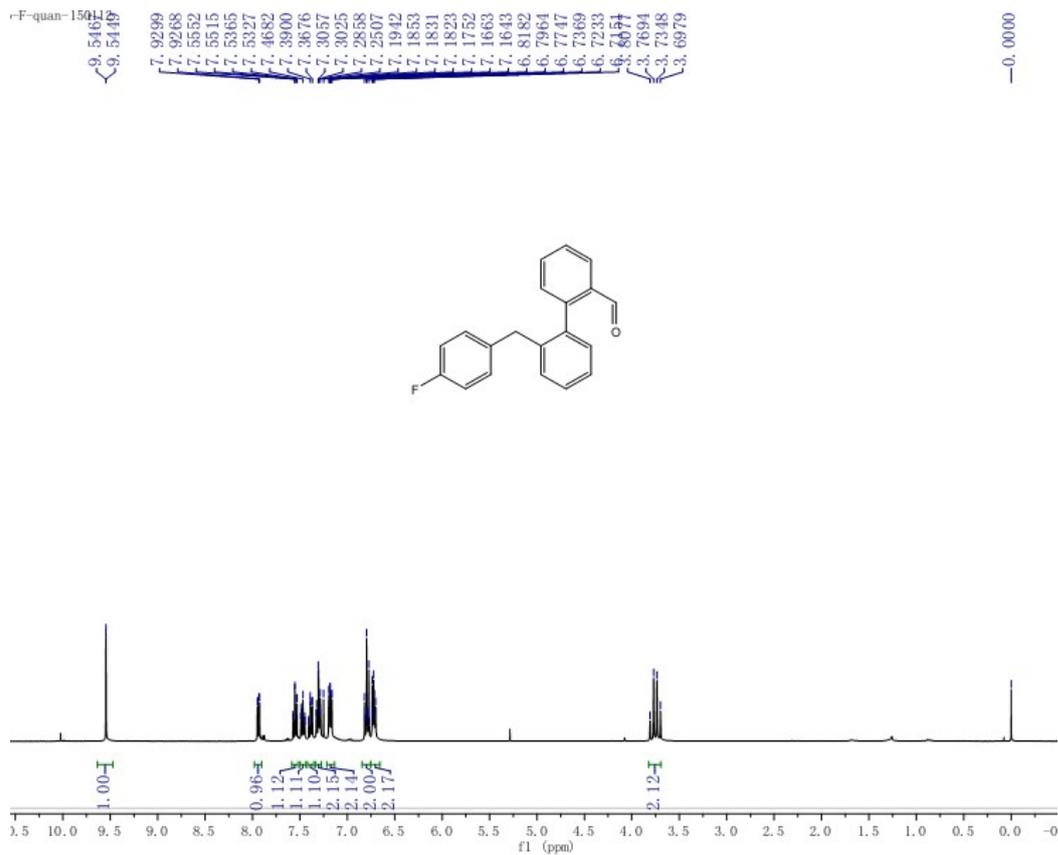
y-m-Me-CHO-0305



<sup>1</sup>H NMR and <sup>13</sup>C NMR of 1d

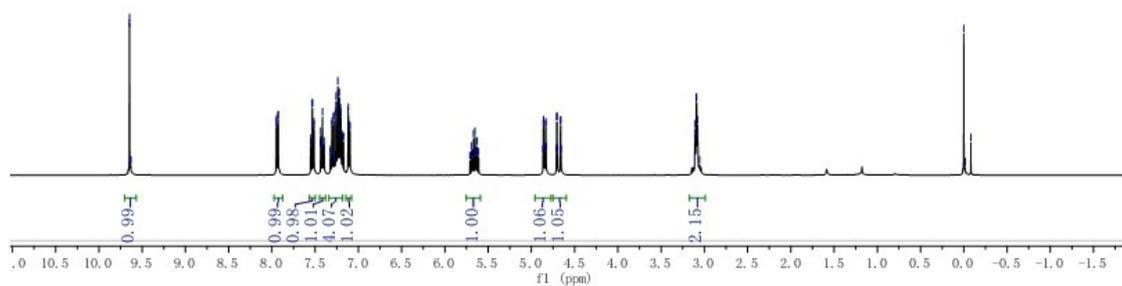
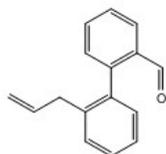


**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 1e**



**<sup>1</sup>H NMR and <sup>13</sup>C NMR of 1f**

9.6482, 9.6463, 7.9487, 7.9458, 7.9293, 7.9264, 7.5634, 7.5497, 7.5347, 7.5310, 7.5160, 7.5123, 7.4373, 7.4346, 7.4322, 7.4157, 7.3984, 7.3969, 7.3943, 7.3081, 7.3028, 7.2881, 7.2846, 7.2605, 7.2577, 7.2375, 7.2356, 7.2239, 7.2196, 7.2165, 7.2053, 7.2016, 7.1873, 7.1835, 7.1707, 7.1193, 7.1161, 7.1005, 7.0974, 5.6939, 5.6680, 5.6518, 5.6262, 4.8621, 4.8581, 4.8546, 4.8405, 4.8369, 4.8329, 4.8294, 4.7073, 4.7030, 4.6989, 4.6647, 4.6605, 3.1069, 3.0935, 3.0902, 3.0817, 3.0781, 0.0000, -0.0810



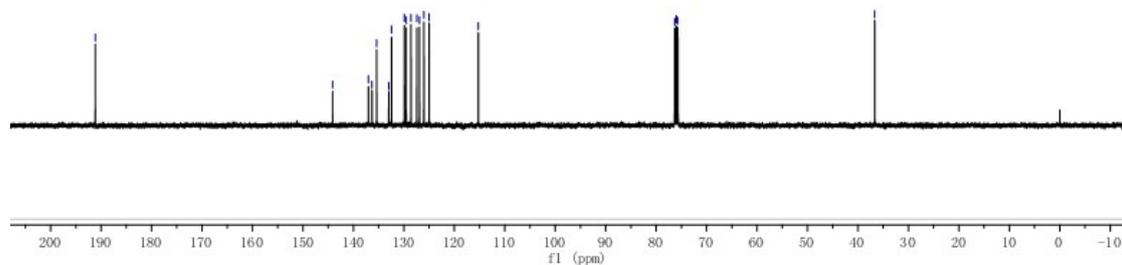
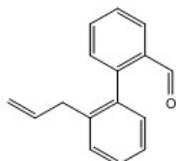
xy-xibingj1-quanyuan-0303

191.14

144.11, 137.02, 136.31, 135.40, 132.98, 132.43, 129.91, 129.53, 128.59, 127.43, 126.89, 126.03, 124.99, 115.23

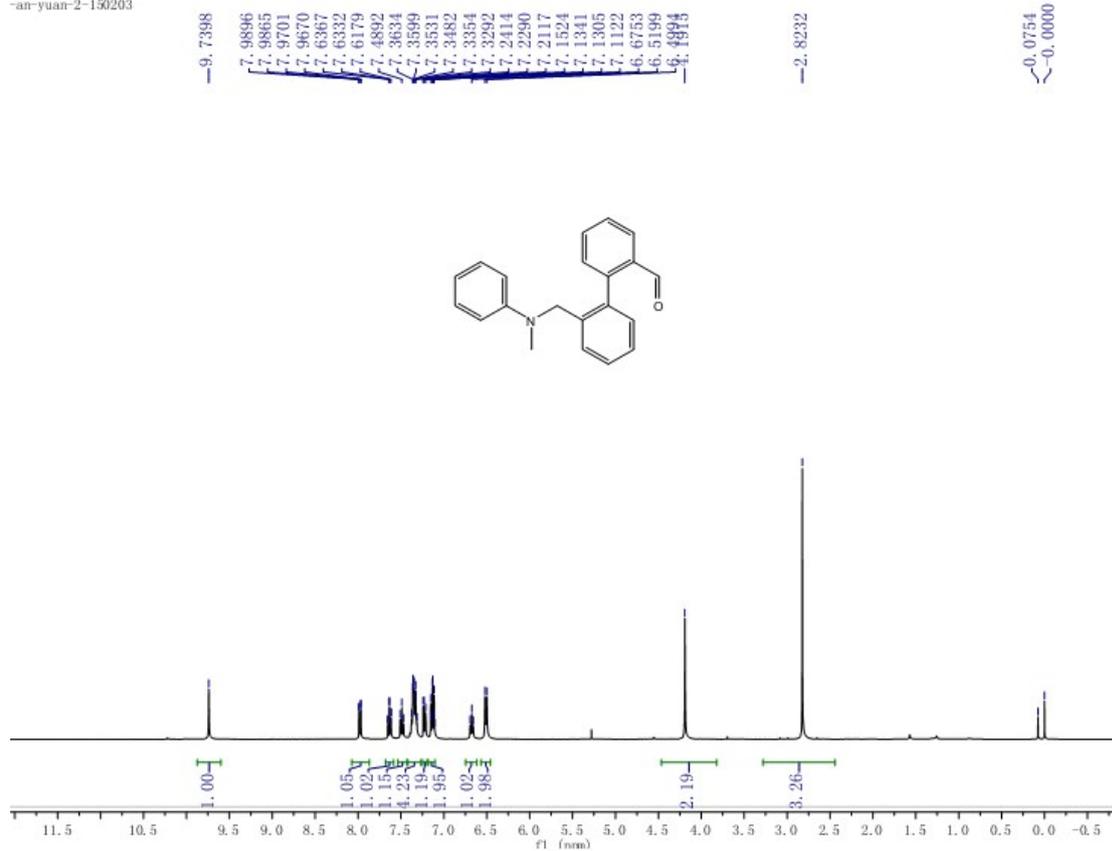
76.33, 76.01, 75.69

36.68

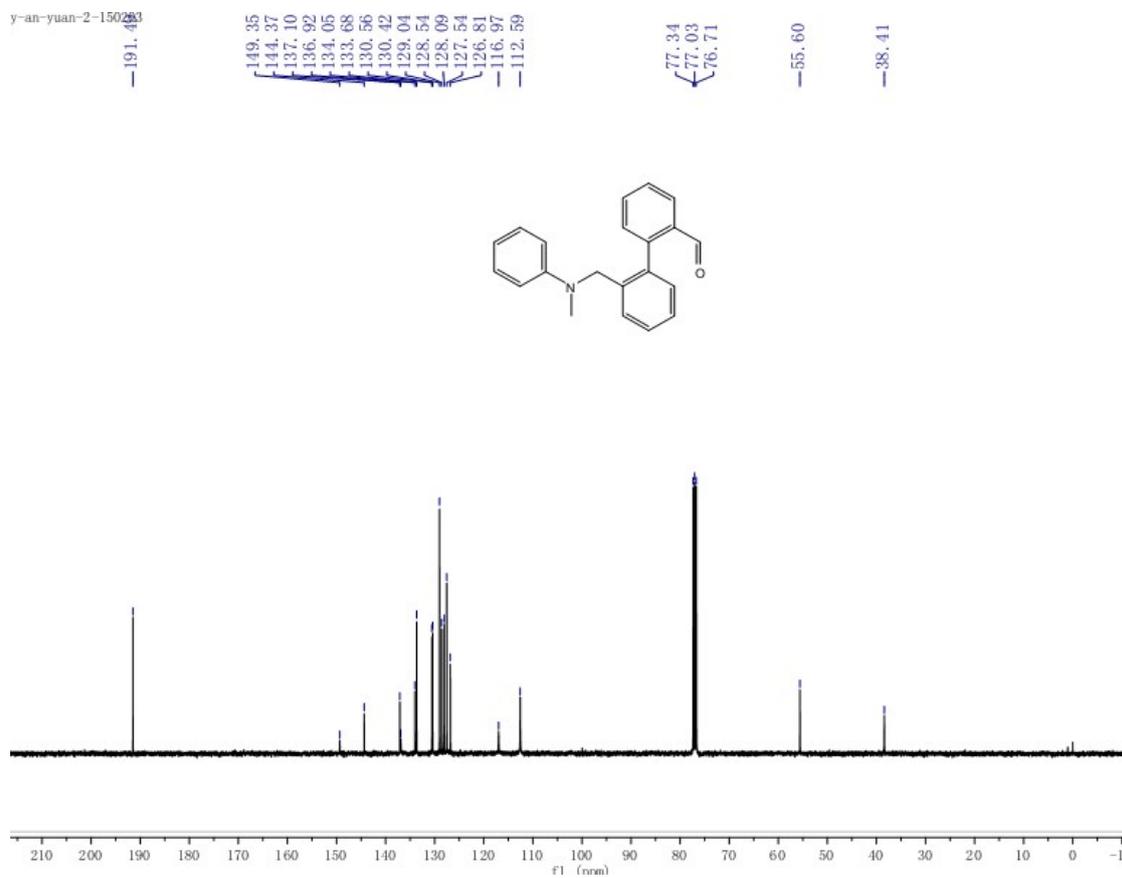


**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 1g**

-an-yuan-2-150203

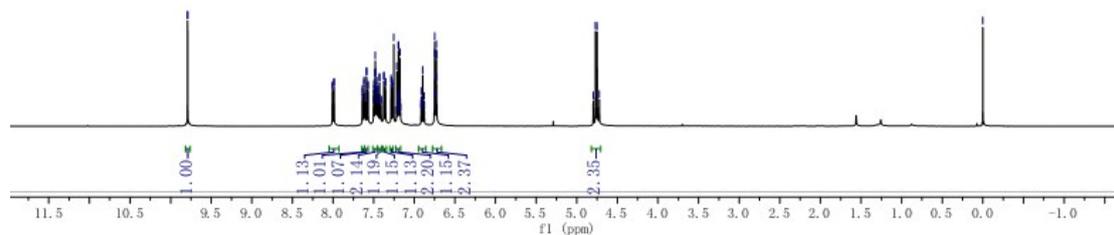
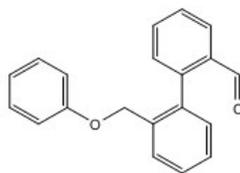


y-an-yuan-2-150203



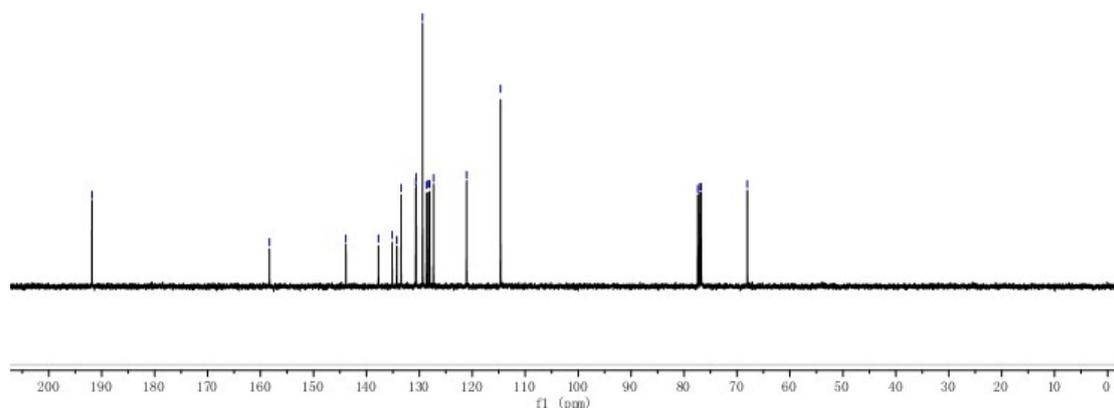
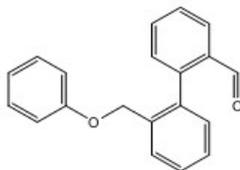
<sup>1</sup>H NMR and <sup>13</sup>C NMR of 1h

9.7929  
9.7910  
8.0091  
8.0063  
7.9897  
7.9868  
7.6402  
7.6376  
7.6212  
7.6189  
7.6088  
7.6051  
7.5901  
7.5864  
7.5713  
7.5676  
7.5031  
7.4990  
7.4962  
7.4936  
7.4844  
7.4804  
7.4772  
7.4658  
7.4615  
7.4585  
7.4557  
7.4483  
7.4445  
7.4296  
7.4260  
7.4109  
7.4074  
7.3749  
7.3729  
7.3569  
7.3539  
7.2862  
7.2829  
7.2677  
7.2642  
7.2524  
7.2155  
7.2102  
7.1970  
7.1937  
7.1803  
7.1753  
6.9150  
6.8966  
6.8782  
6.7511  
6.7485  
6.7433  
6.7317  
6.7291  
6.7268  
4.7972  
4.7693  
4.7498  
4.7219  
-0.0000



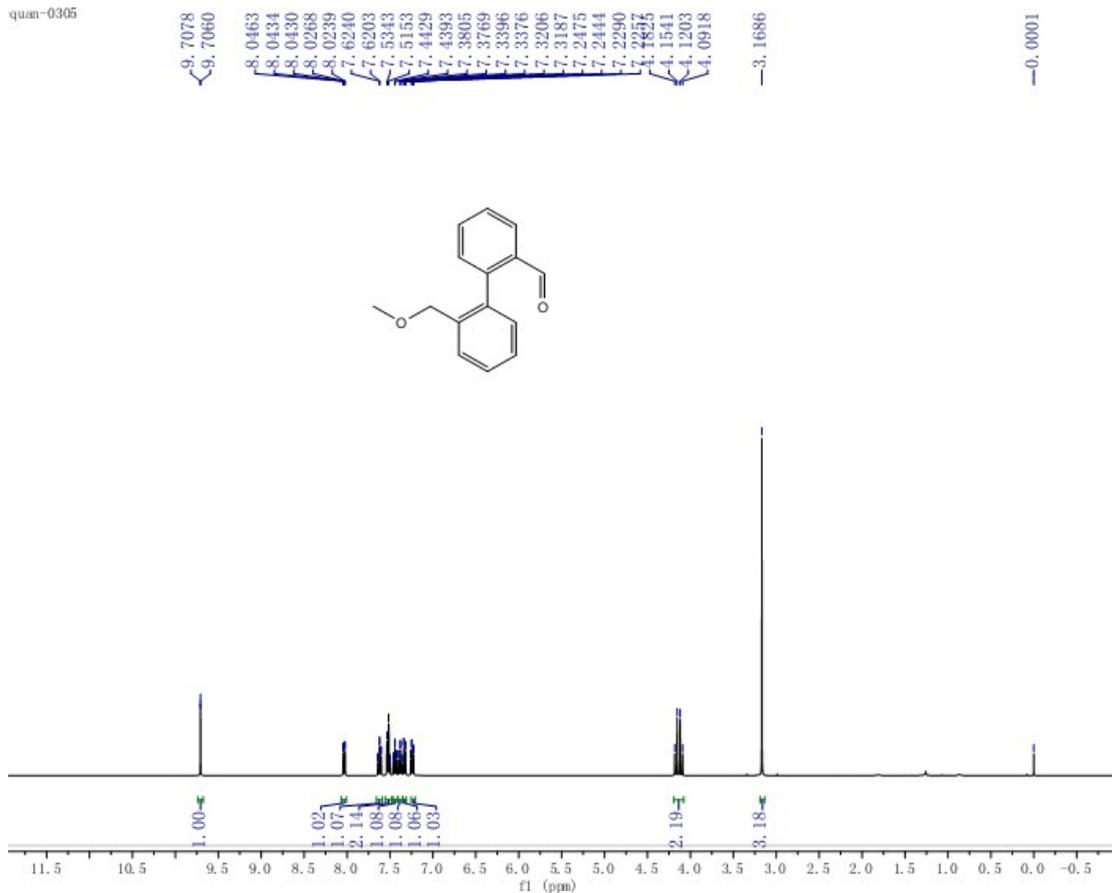
7-PhO-quan-150204

191.8  
158.32  
143.88  
137.73  
135.13  
134.26  
133.65  
130.69  
130.60  
129.41  
128.66  
128.27  
128.06  
127.31  
121.08  
114.66  
77.42  
77.10  
76.78  
68.04

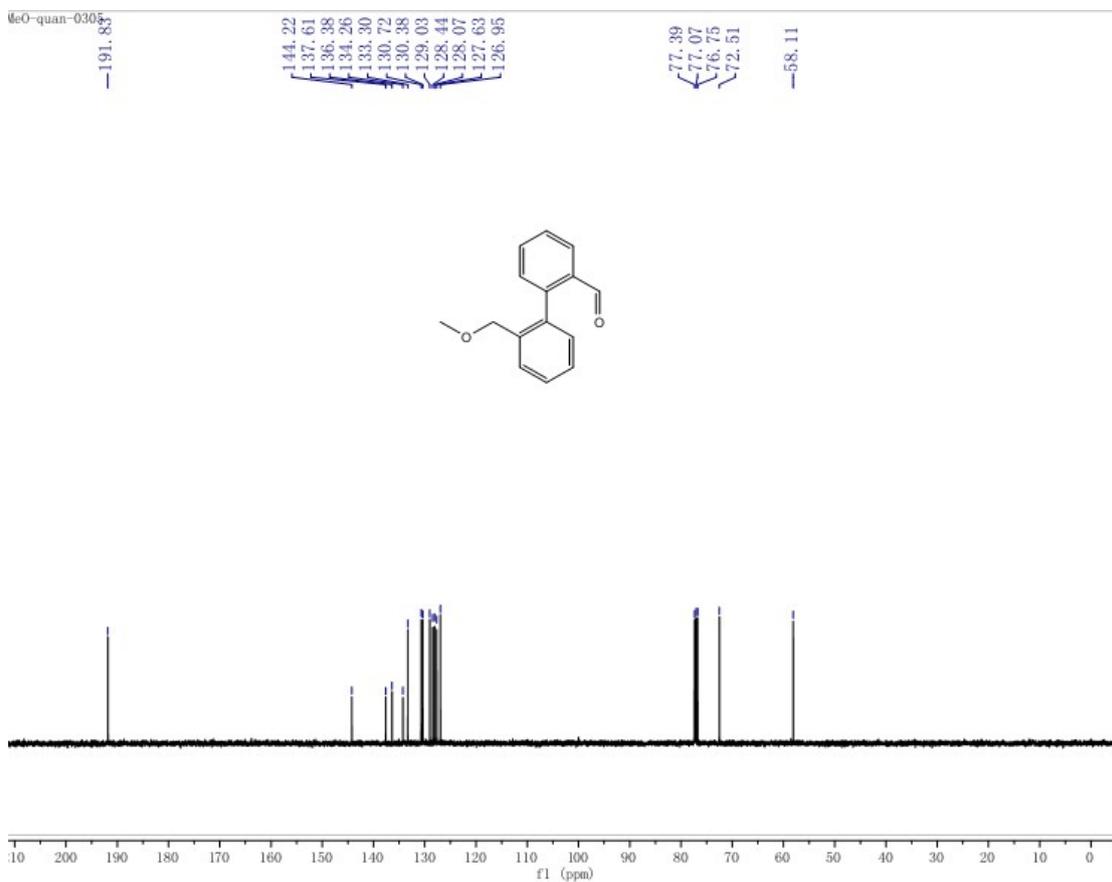


**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 1i**

quan-0305

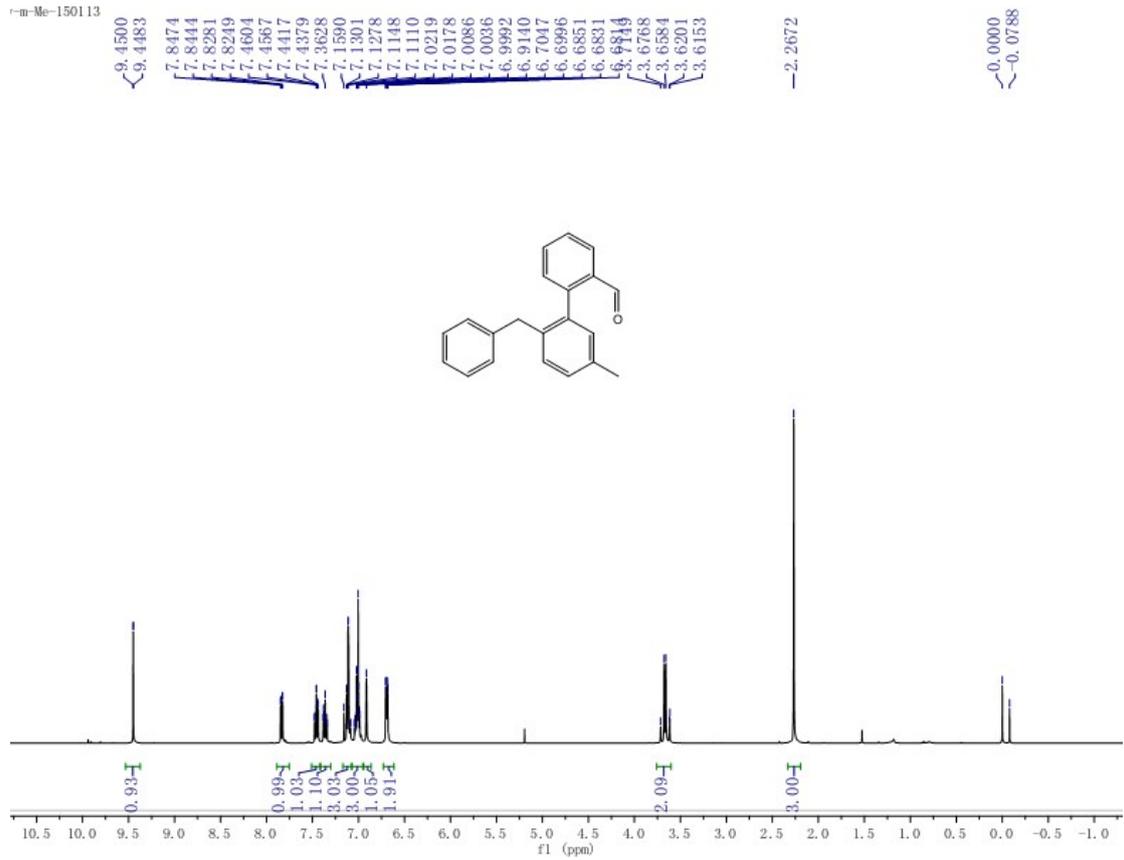


MeO-quant-0305

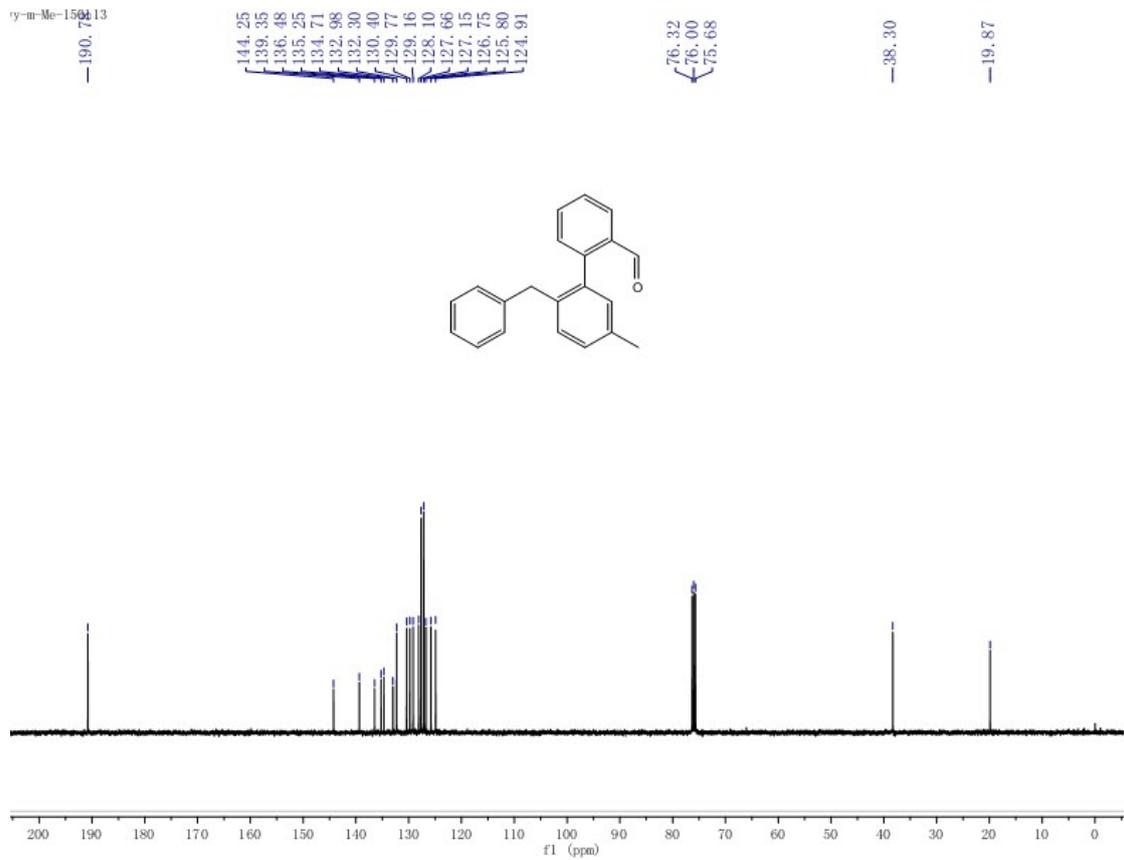


# <sup>1</sup>H NMR and <sup>13</sup>CNMR of 1k

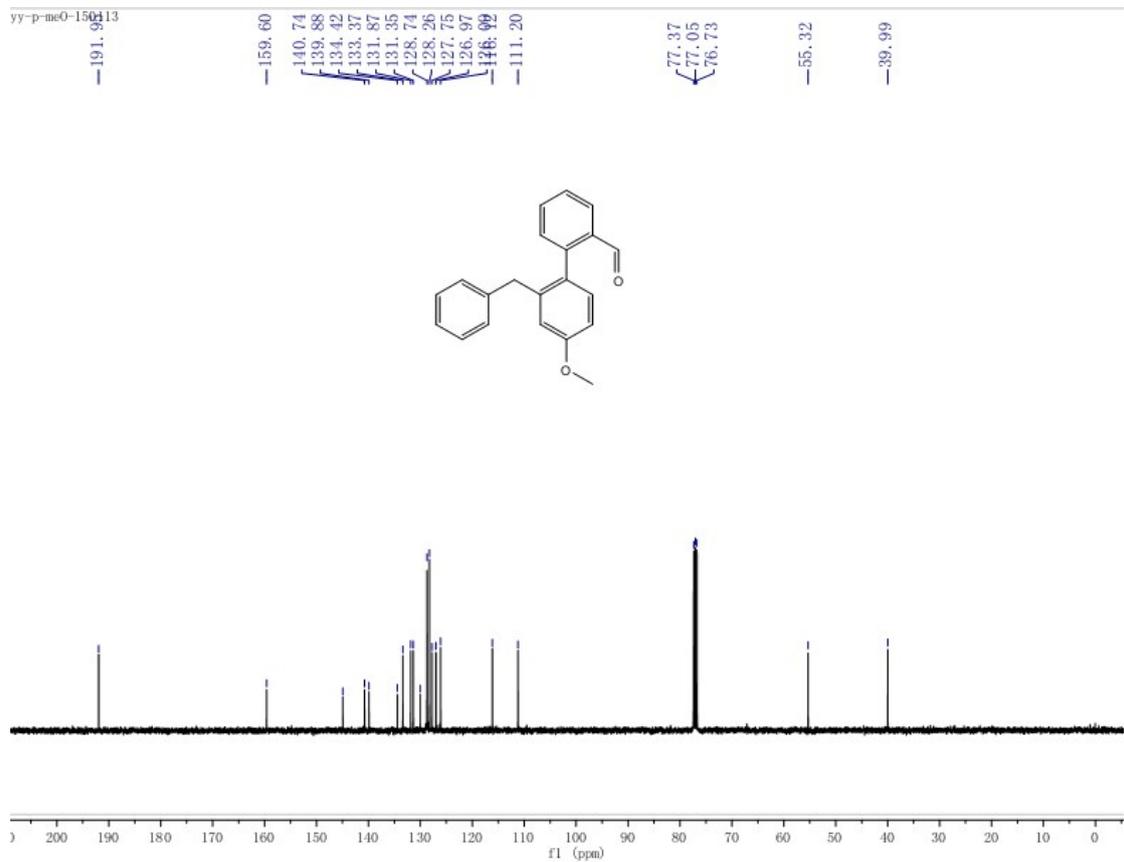
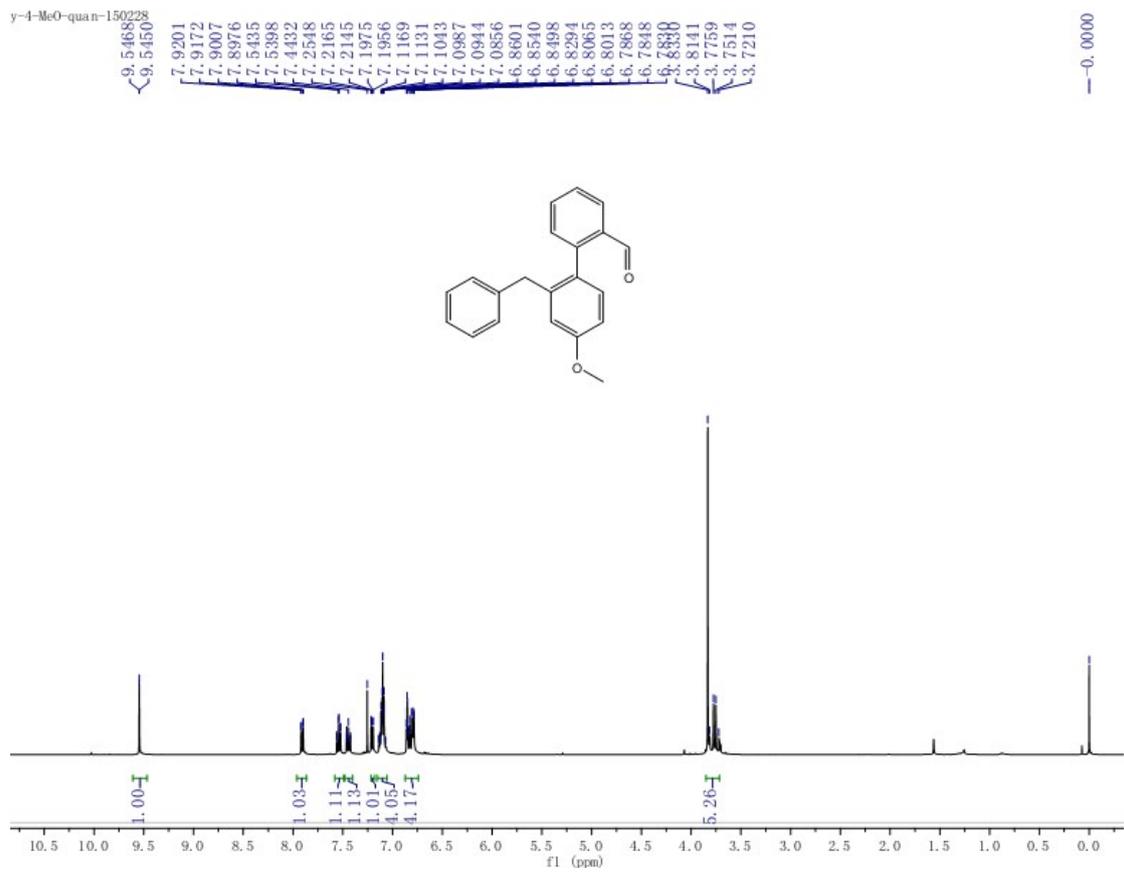
γ-m-Me-150113



γ-m-Me-150113

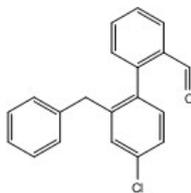
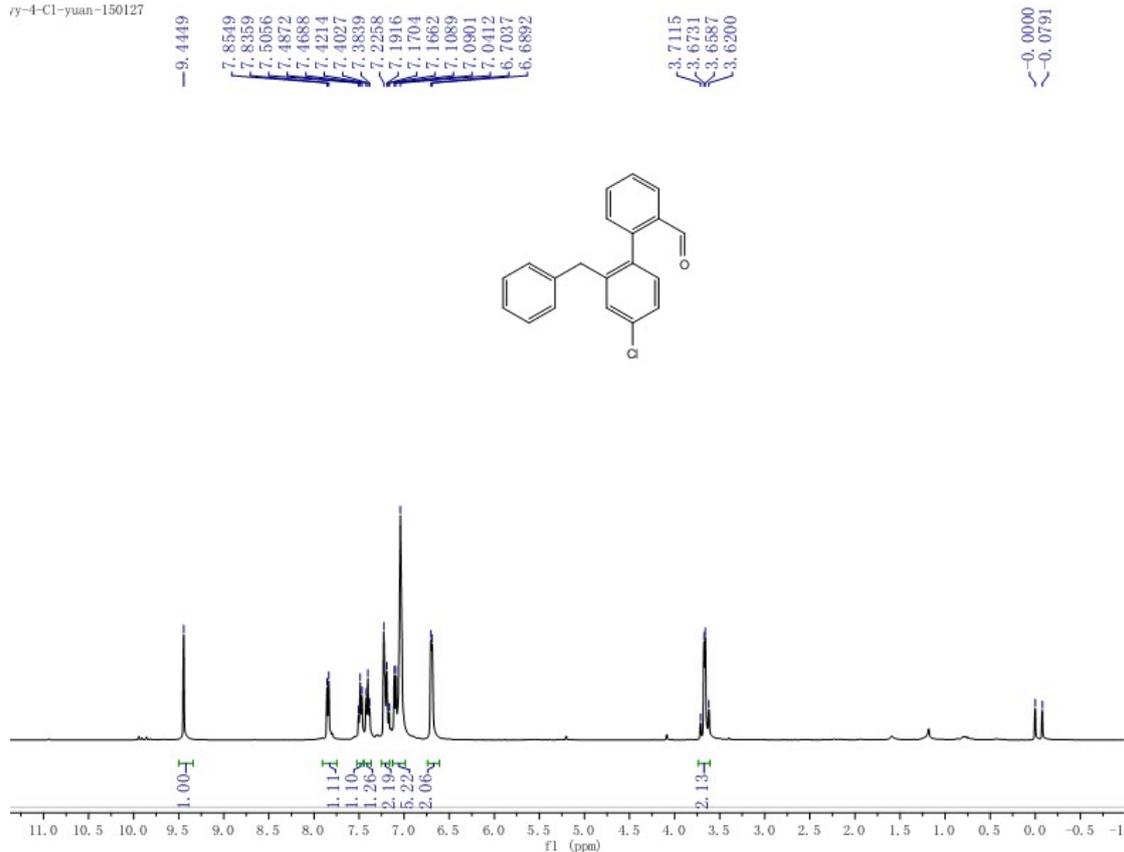


# <sup>1</sup>H NMR and <sup>13</sup>CNMR of 11

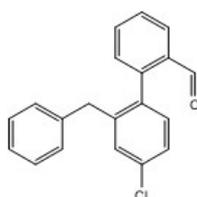
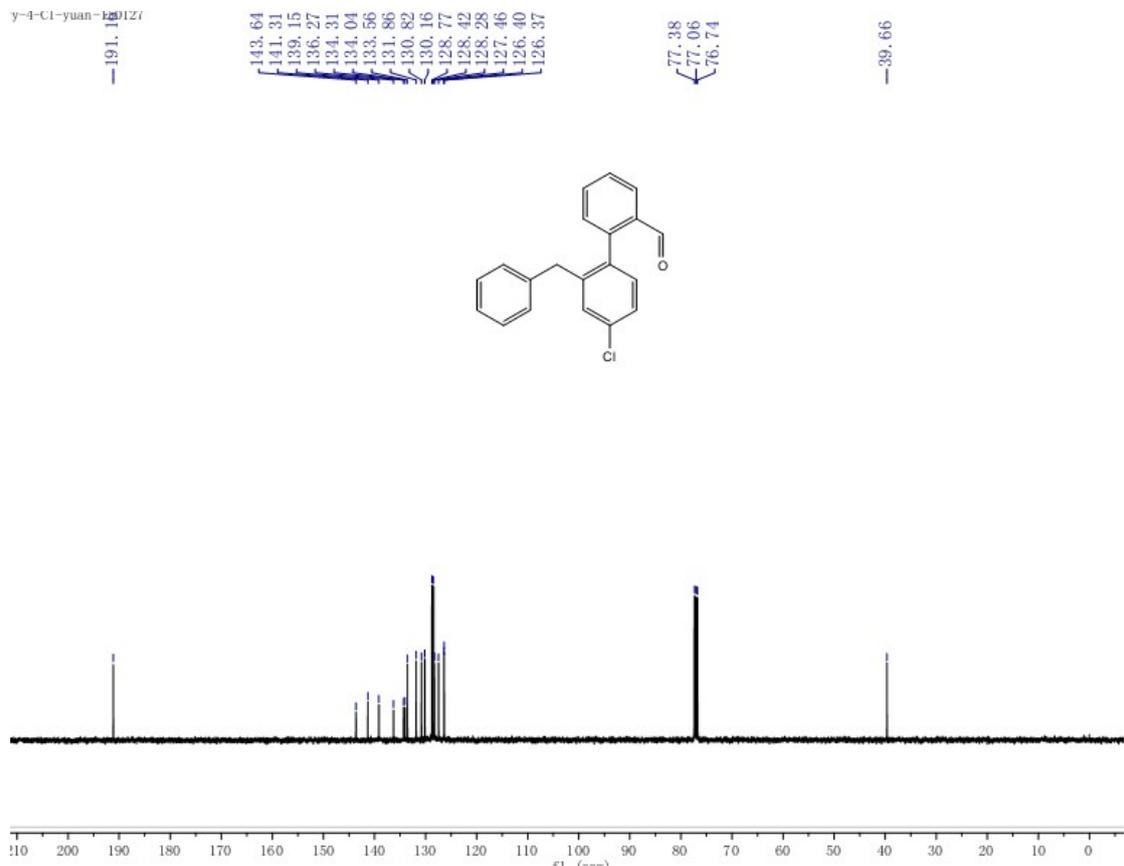


# <sup>1</sup>H NMR and <sup>13</sup>CNMR of 1m

zy-4-Cl-yuan-150127



zy-4-Cl-yuan-150127

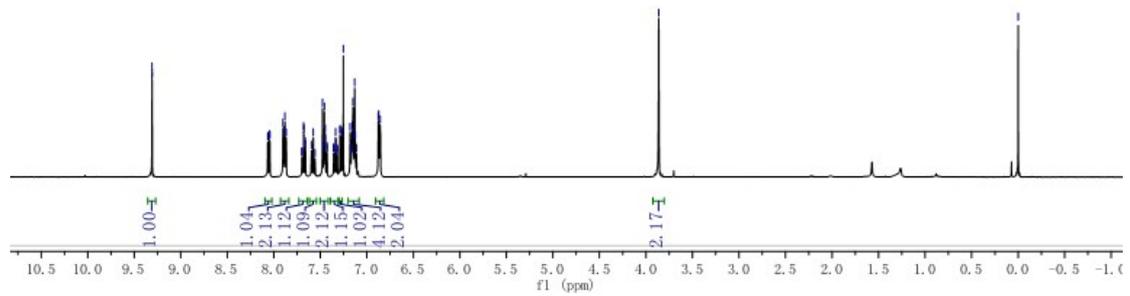
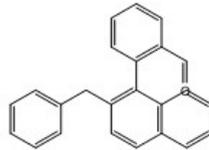


# <sup>1</sup>H NMR and <sup>13</sup>CNMR of 1n

naph-quant-150112

9.3091  
9.3072  
8.0453  
7.9015  
7.8874  
7.8804  
7.8673  
7.6799  
7.6762  
7.5758  
7.4766  
7.4553  
7.4468  
7.3366  
7.2882  
7.2864  
7.2694  
7.2675  
7.2525  
7.1791  
7.1564  
7.1491  
7.1452  
7.1309  
6.8721  
6.8665

-0.0000



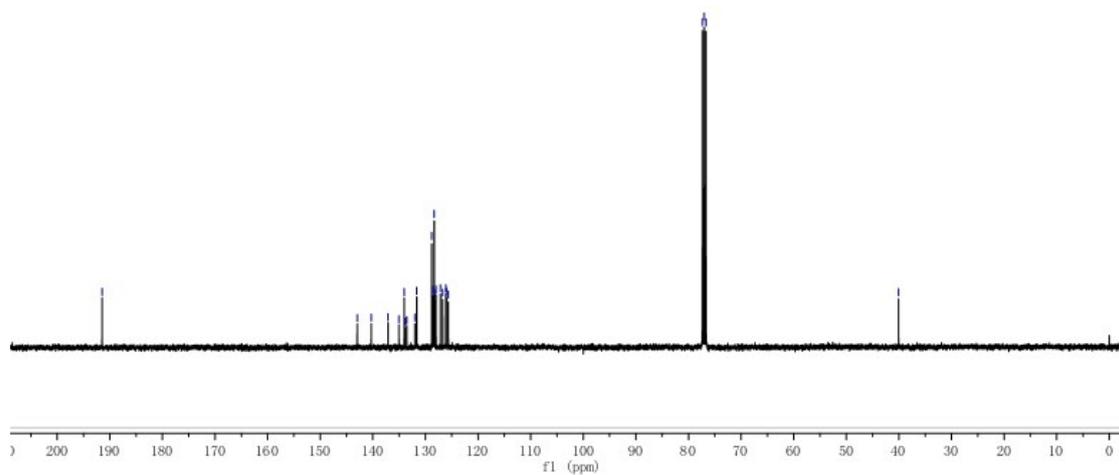
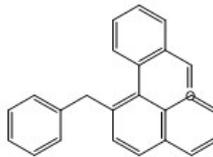
Y-naph-quant-150112

-191.45

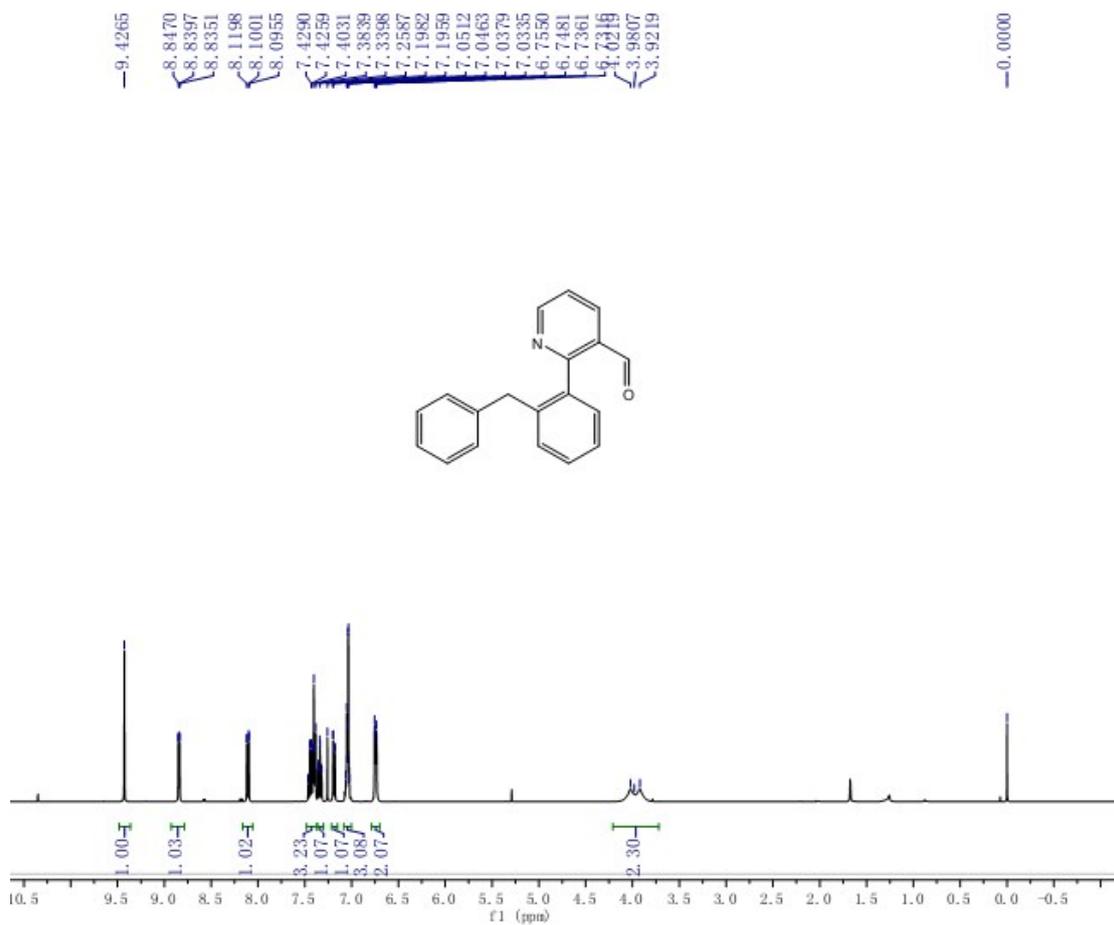
142.96  
140.30  
137.11  
135.04  
134.02  
133.87  
133.51  
132.00  
131.66  
128.79  
128.58  
128.32  
128.19  
128.00  
127.13  
126.69  
126.12  
126.00  
125.64

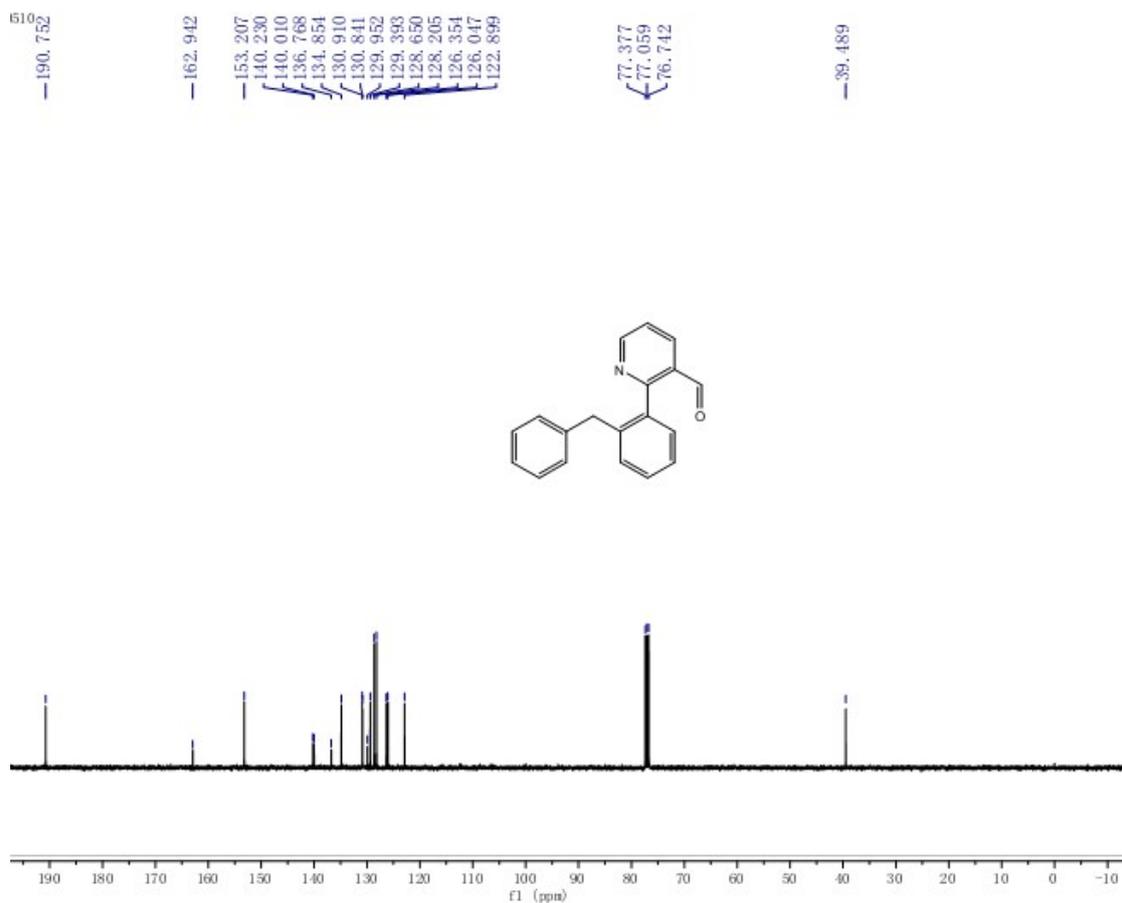
77.33  
77.01  
76.70

-40.07

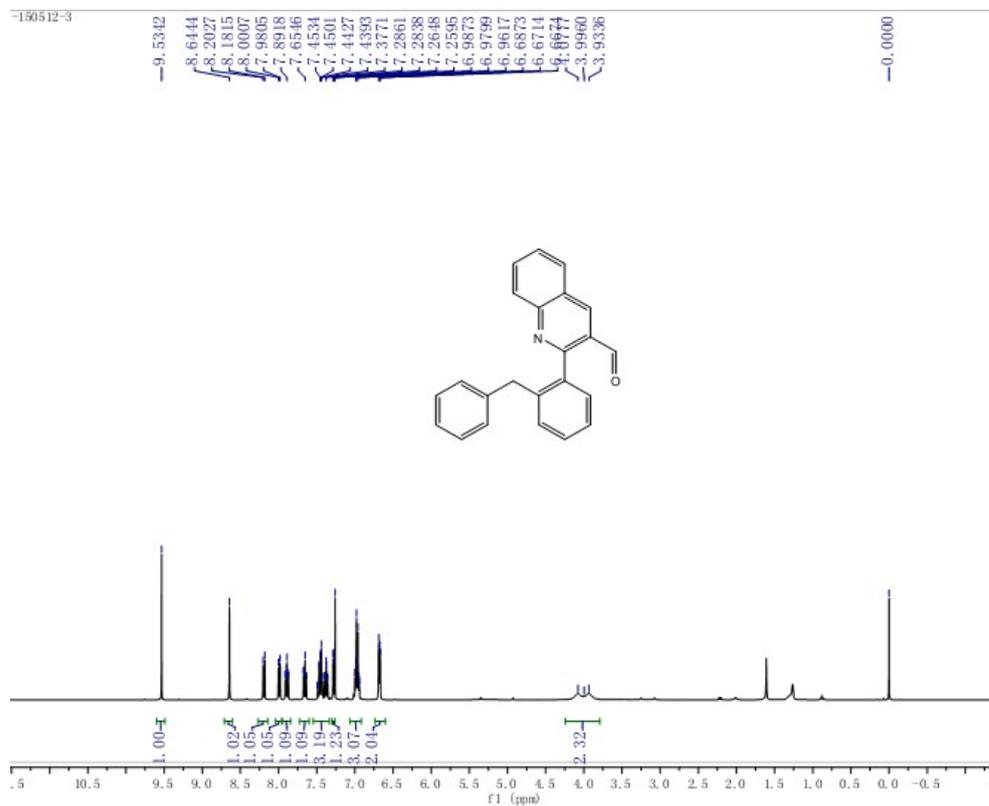


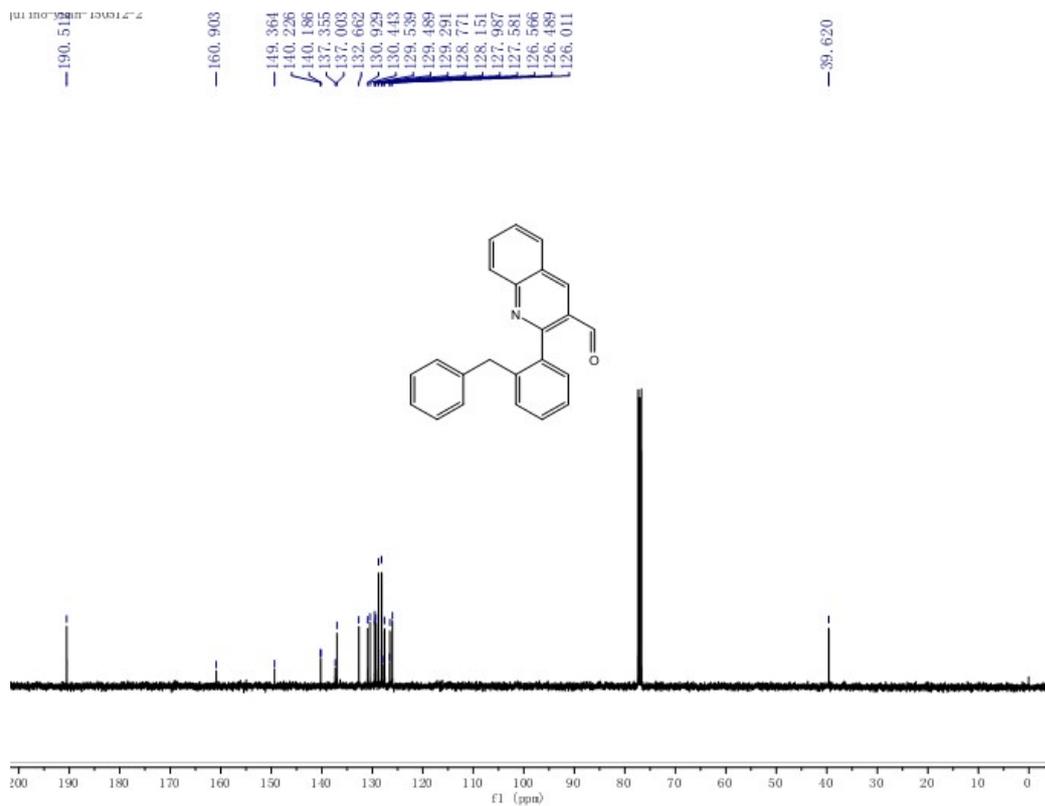
# <sup>1</sup>H NMR and <sup>13</sup>CNMR of 1o



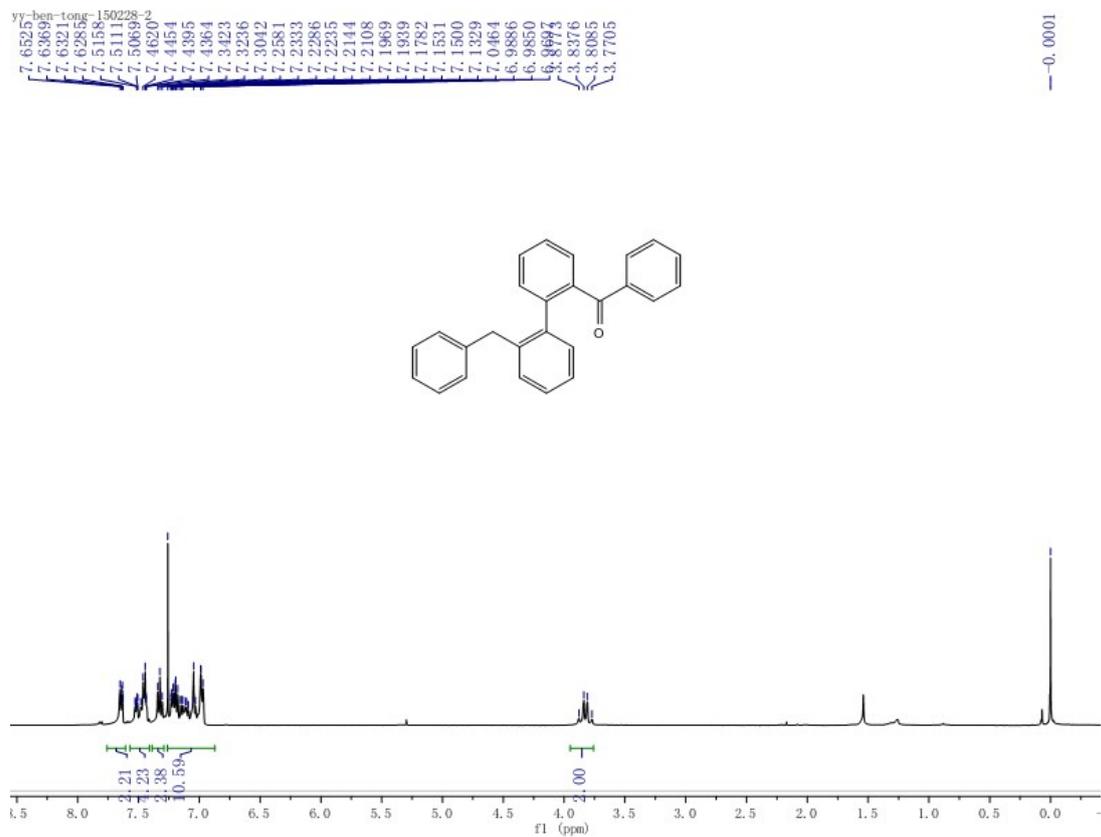


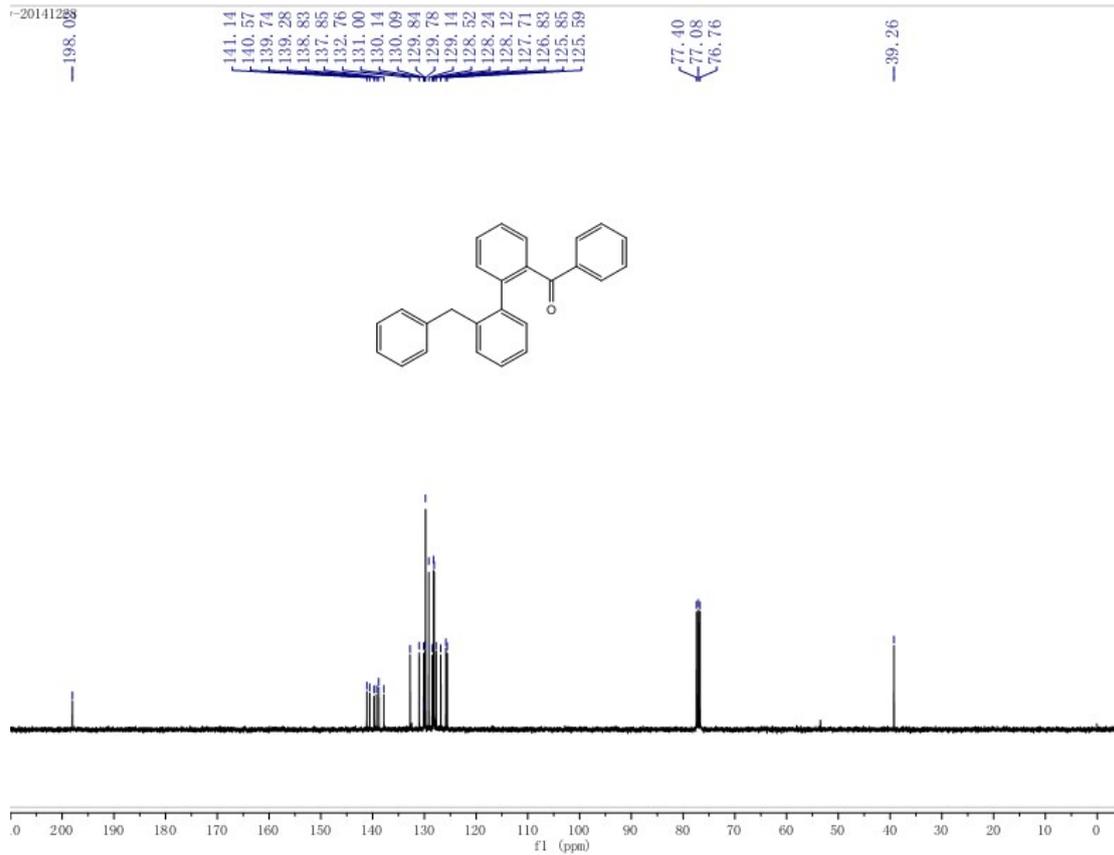
### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 1p



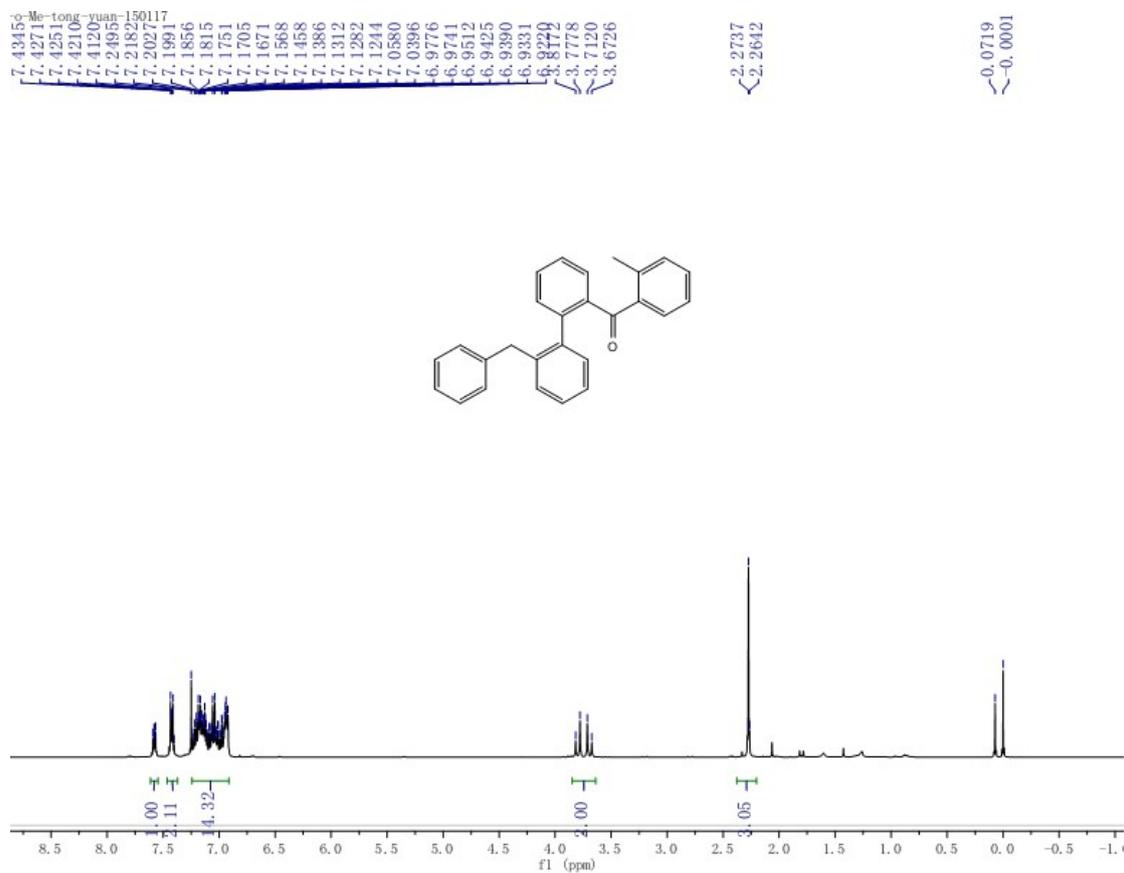


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3a

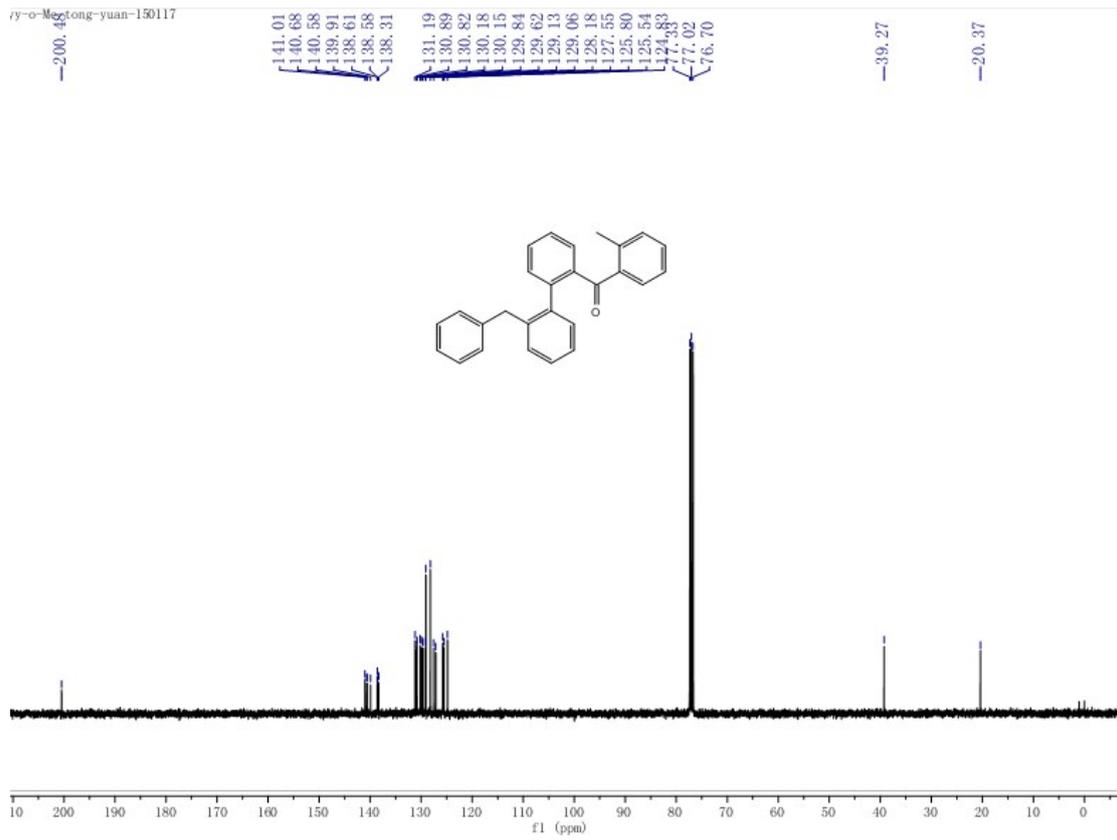




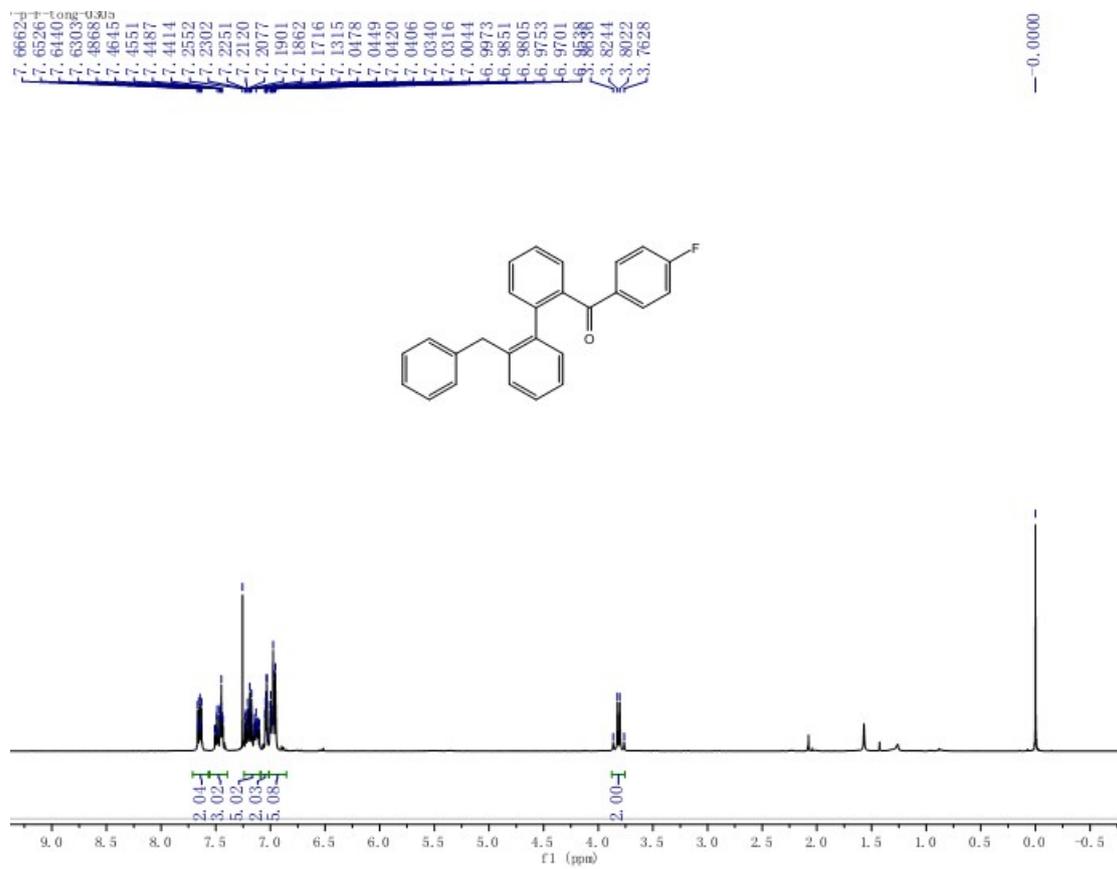
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3b



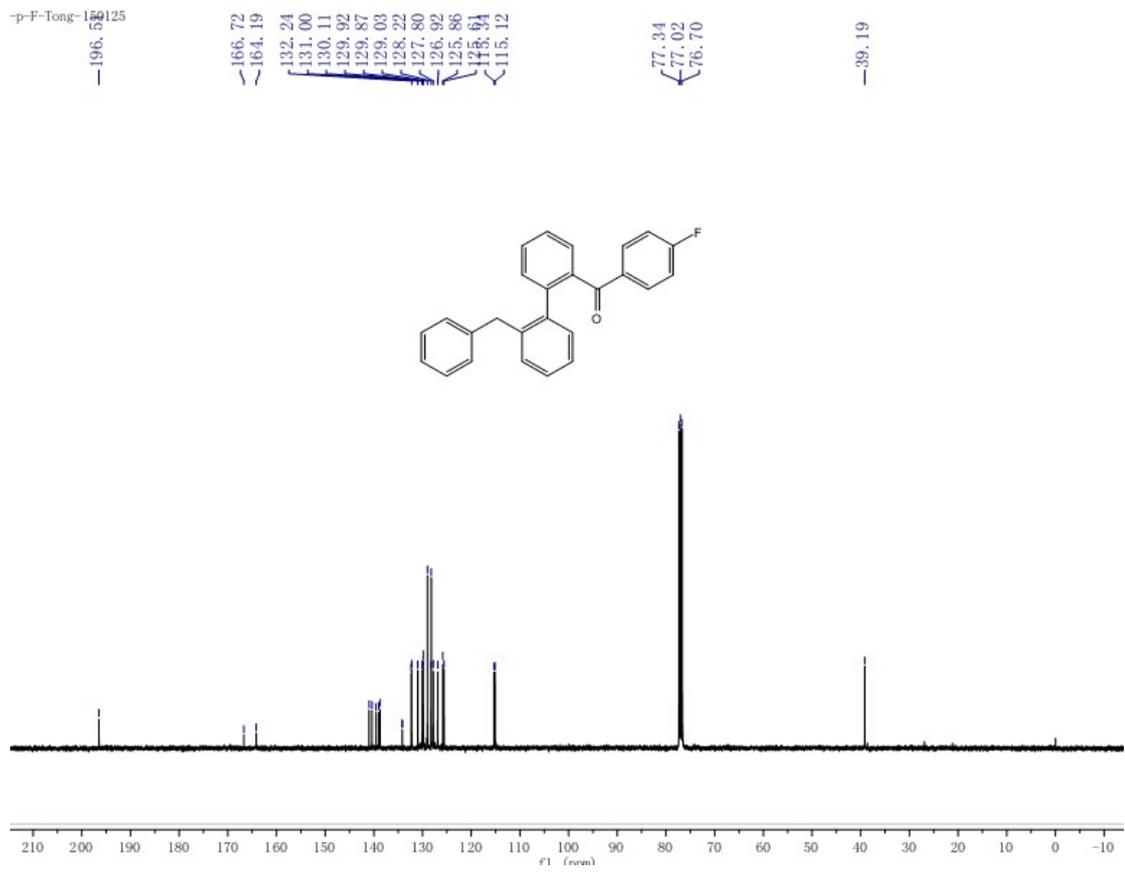
ry-o-Meotong-yuan-150117



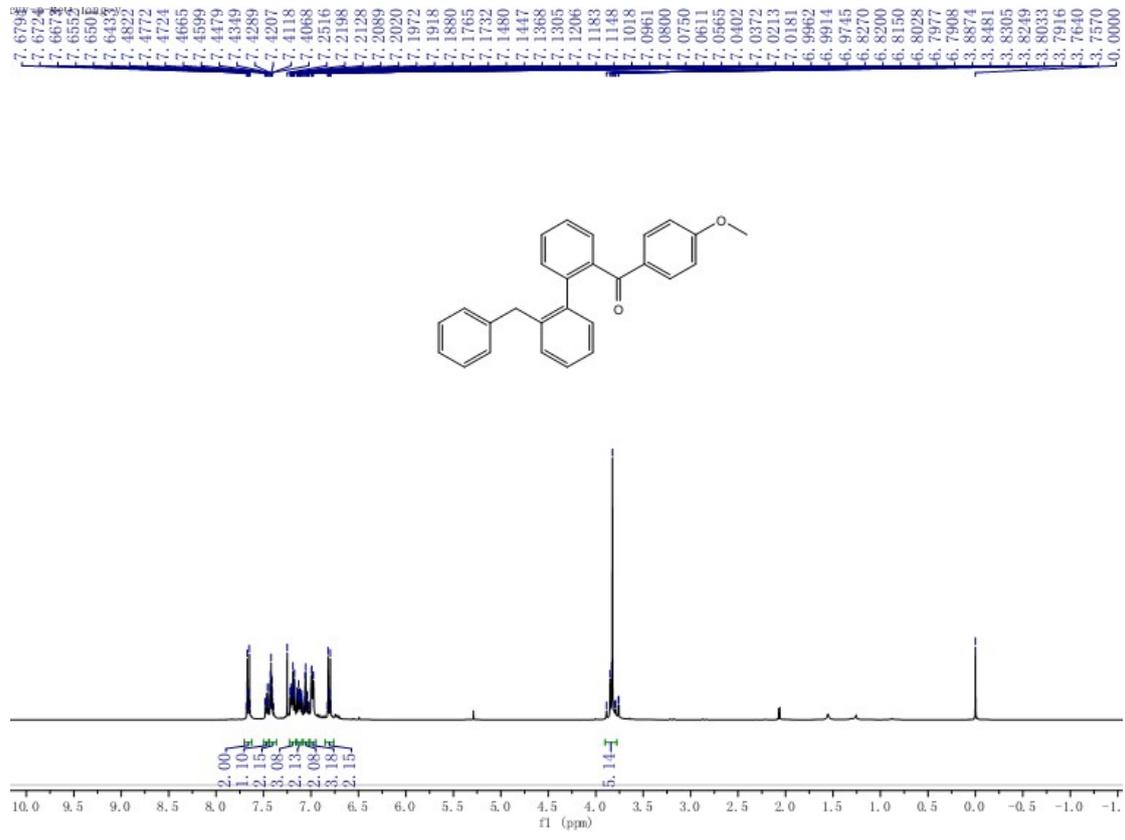
### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 3c



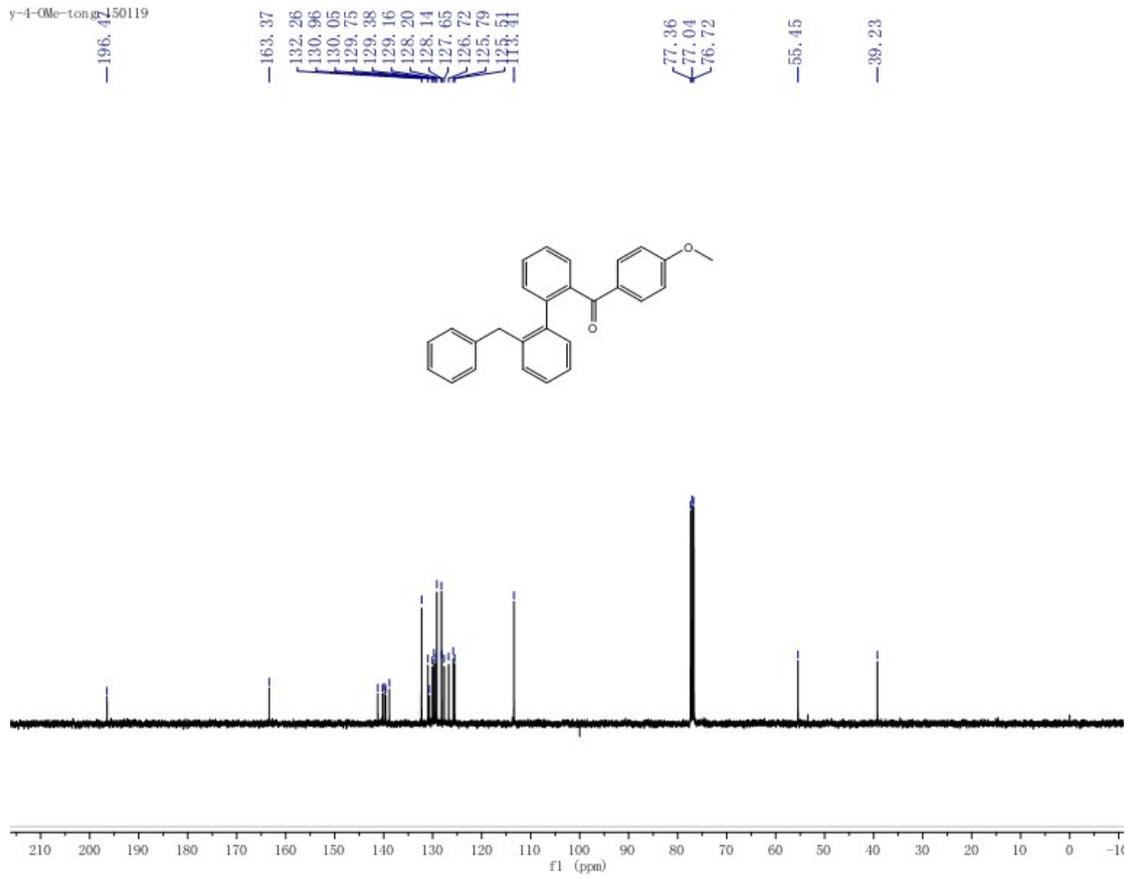
p-F-Tong-150



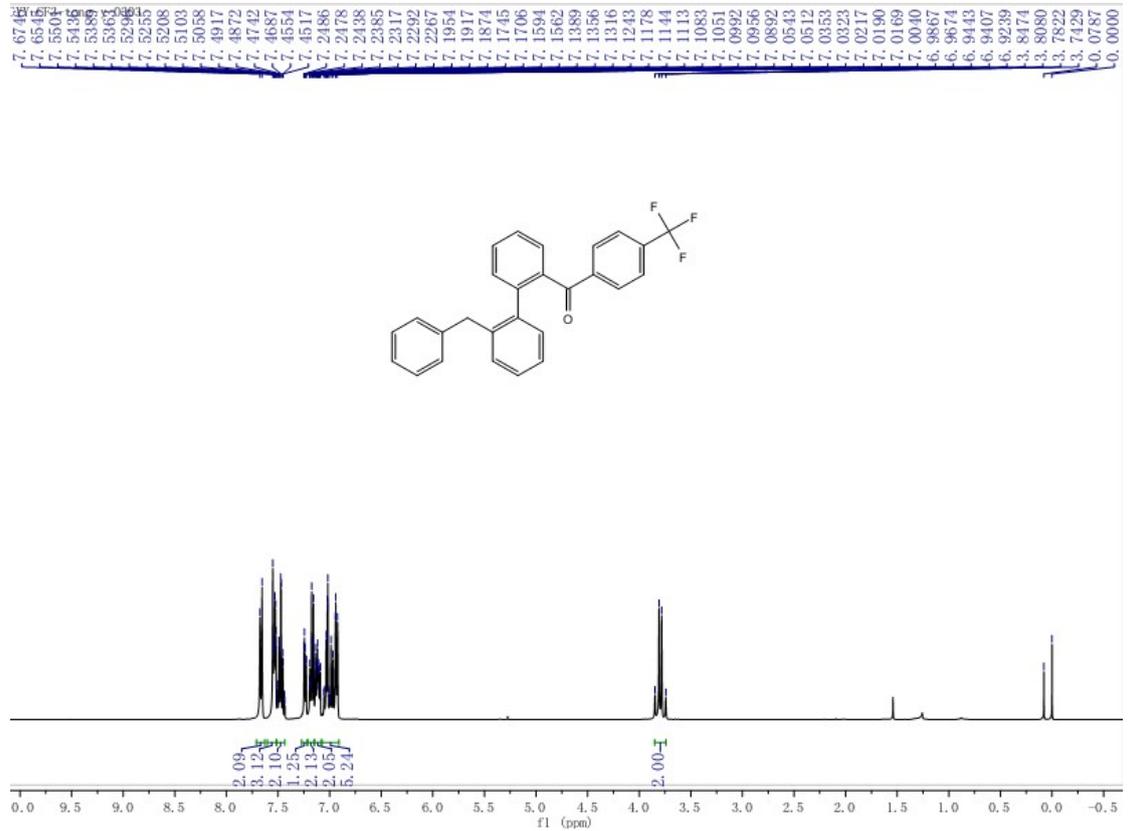
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3d



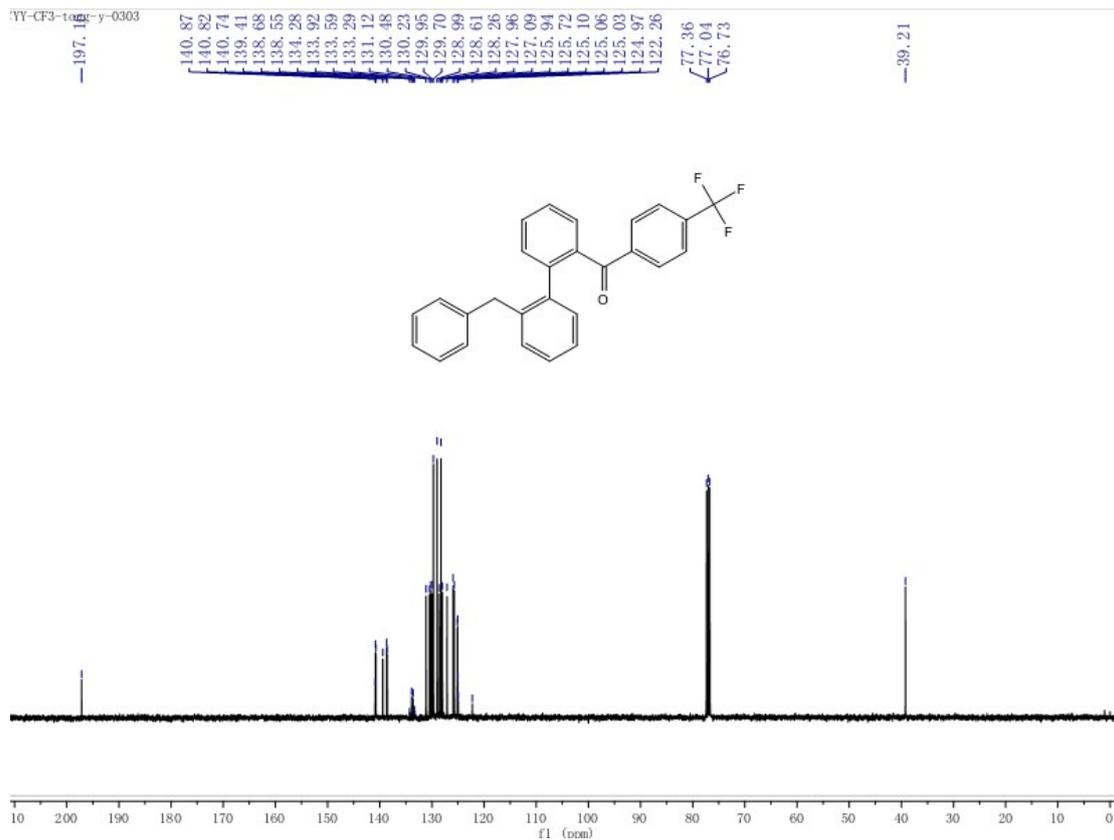
y-4-OMe-tonig-150119



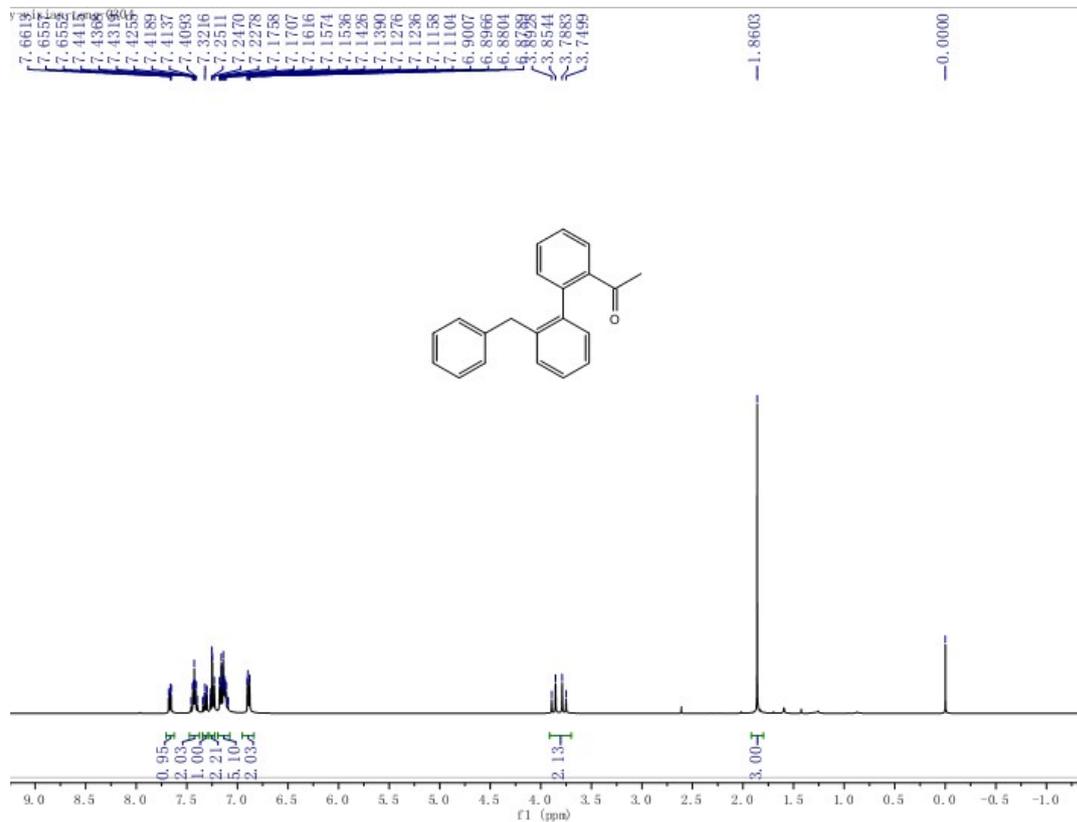
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3e



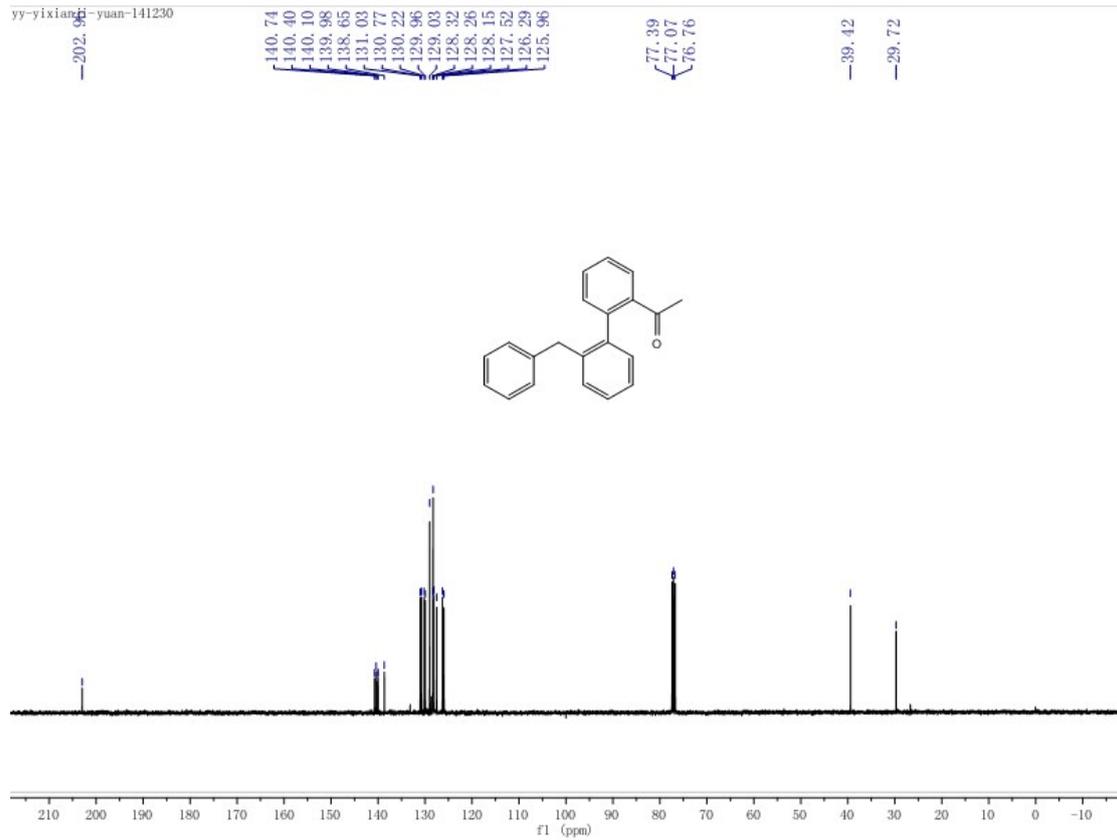
YY-CF3-to-r-y-0303



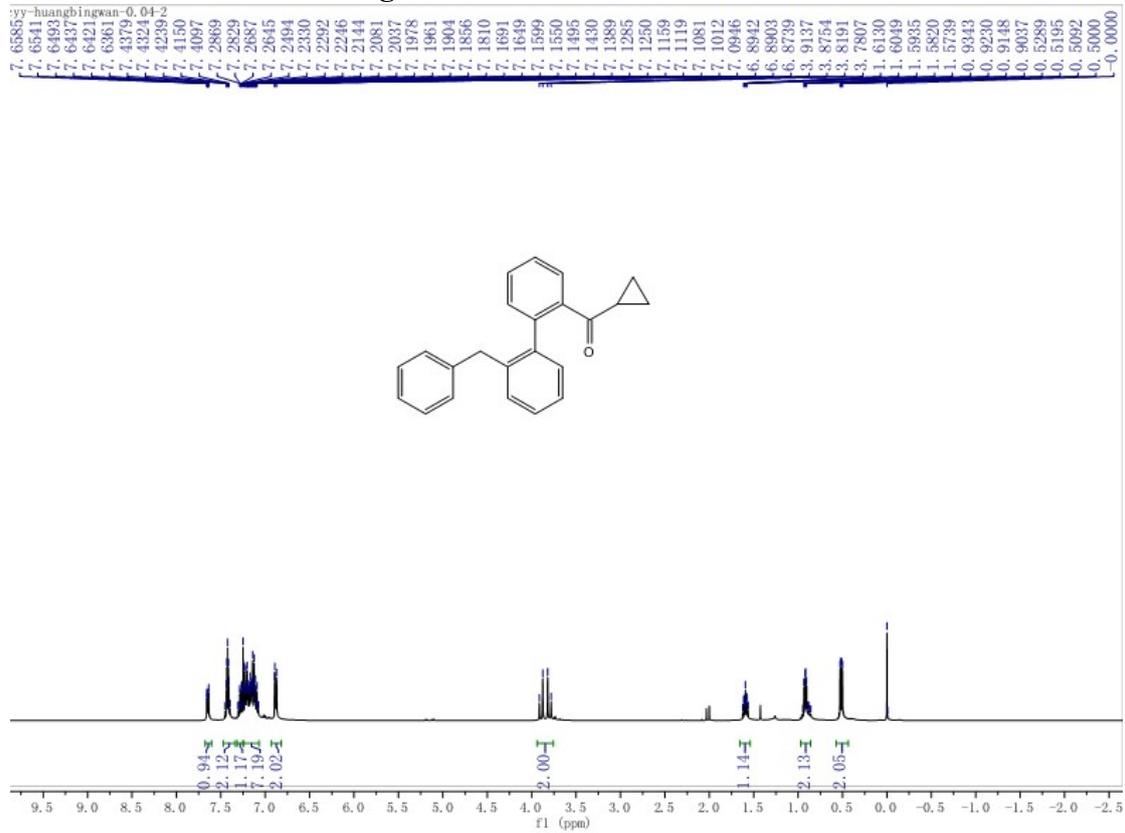
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3f



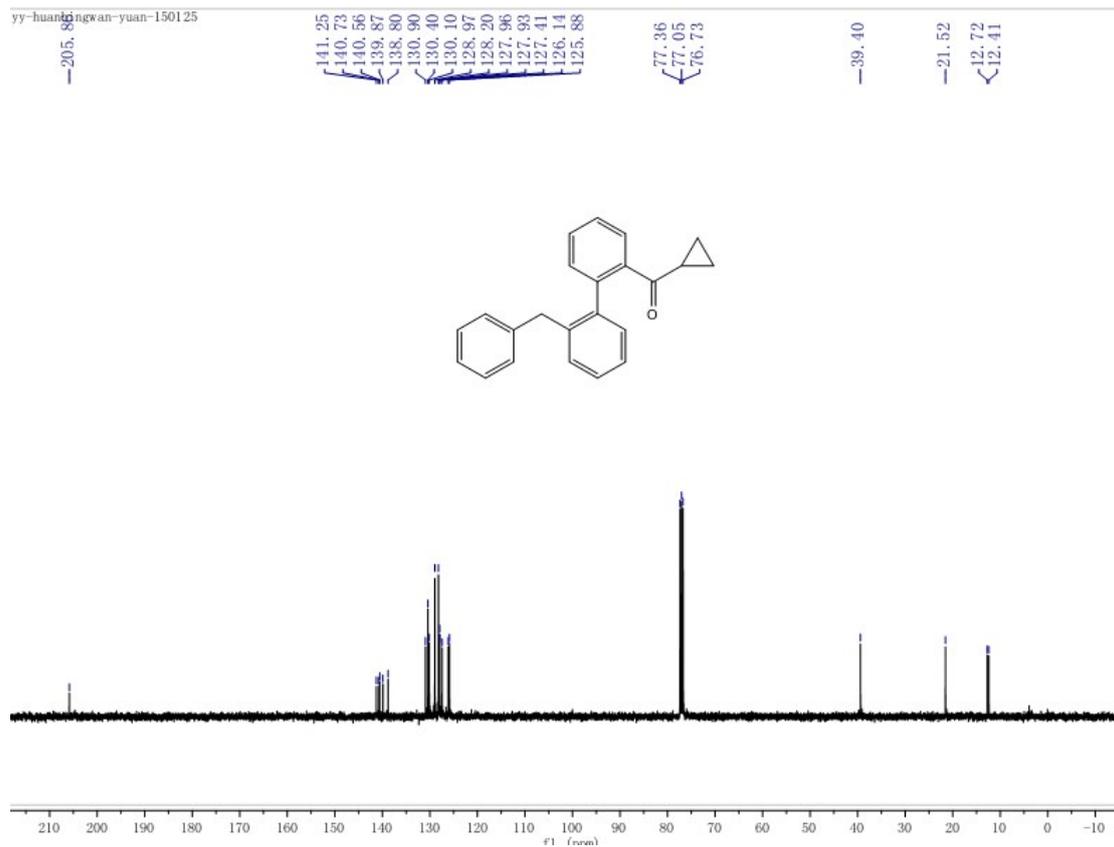
yy-yixiang-yuan-141230



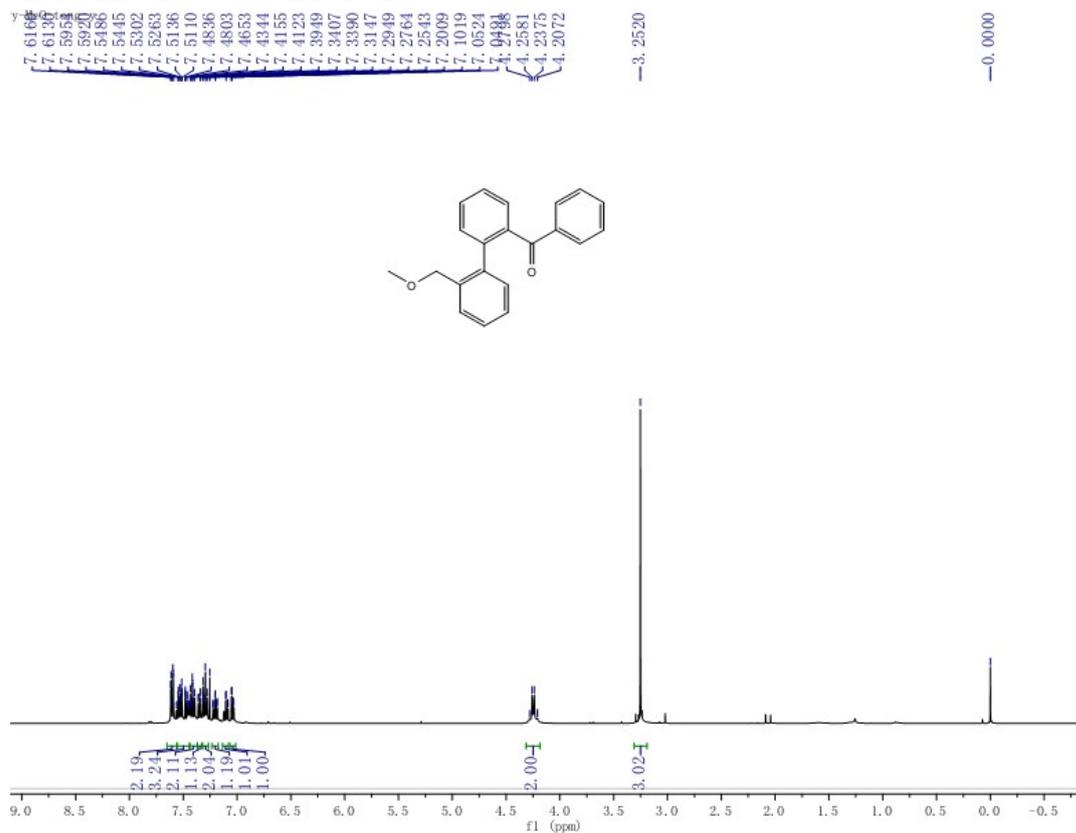
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3g



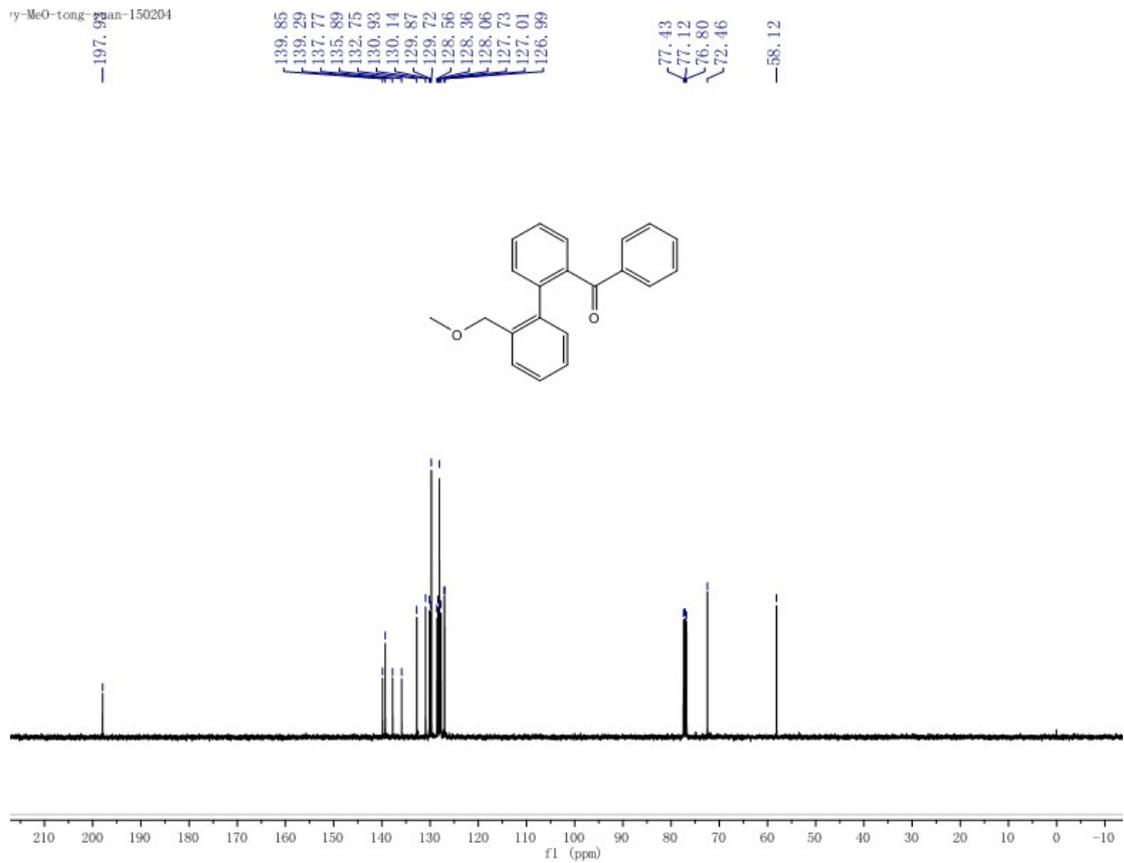
yy-huangwang-yuan-150125



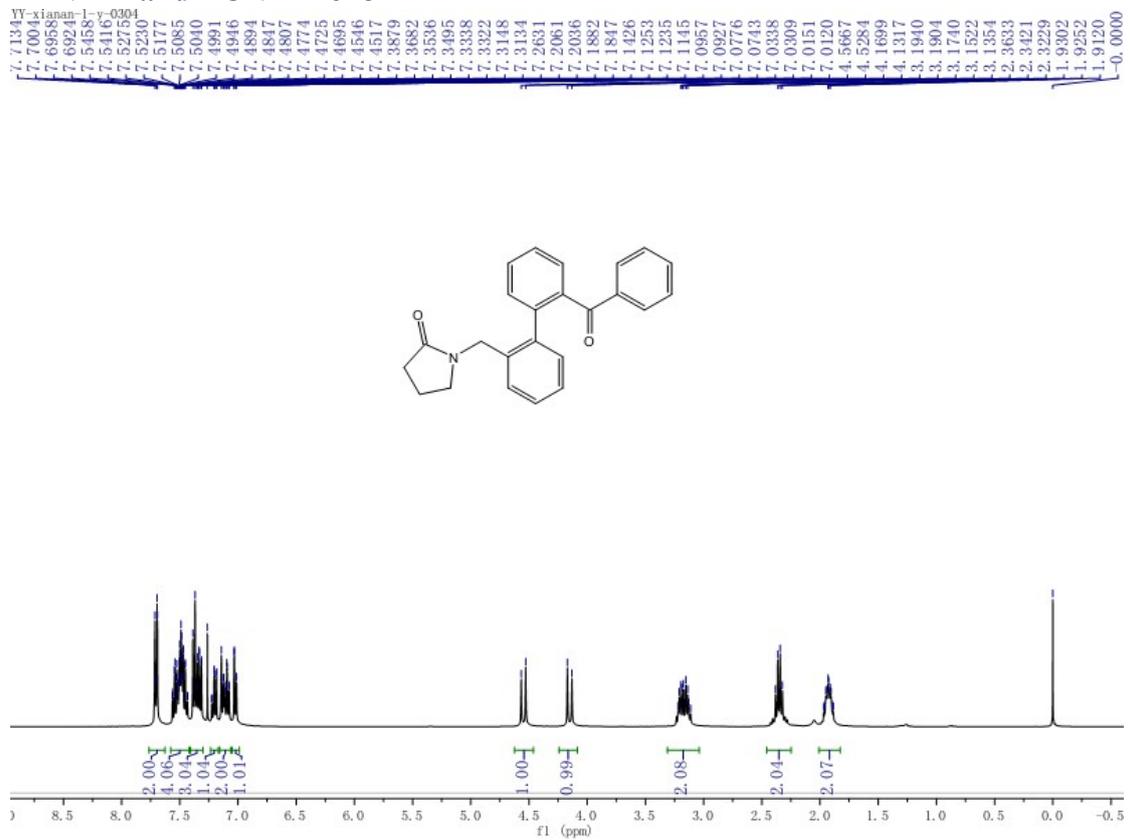
### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 3h



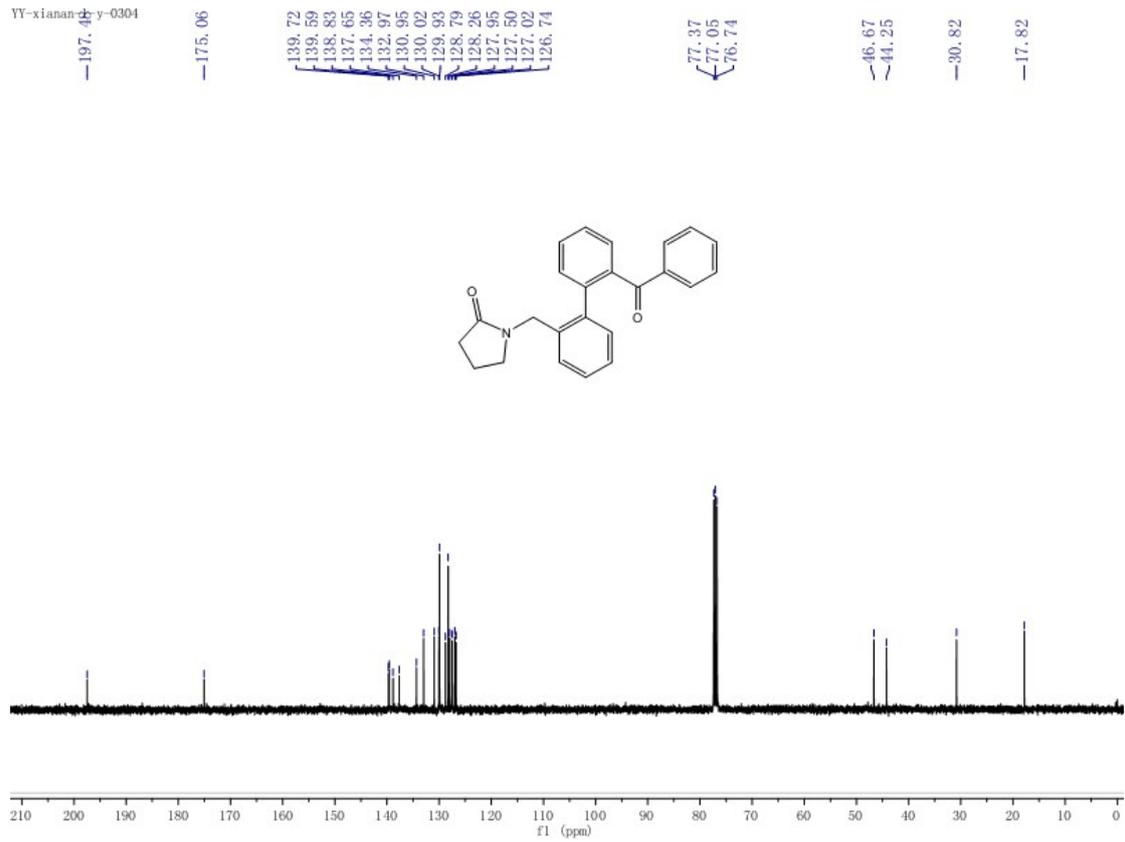
yy-MeO-tong-an-150204



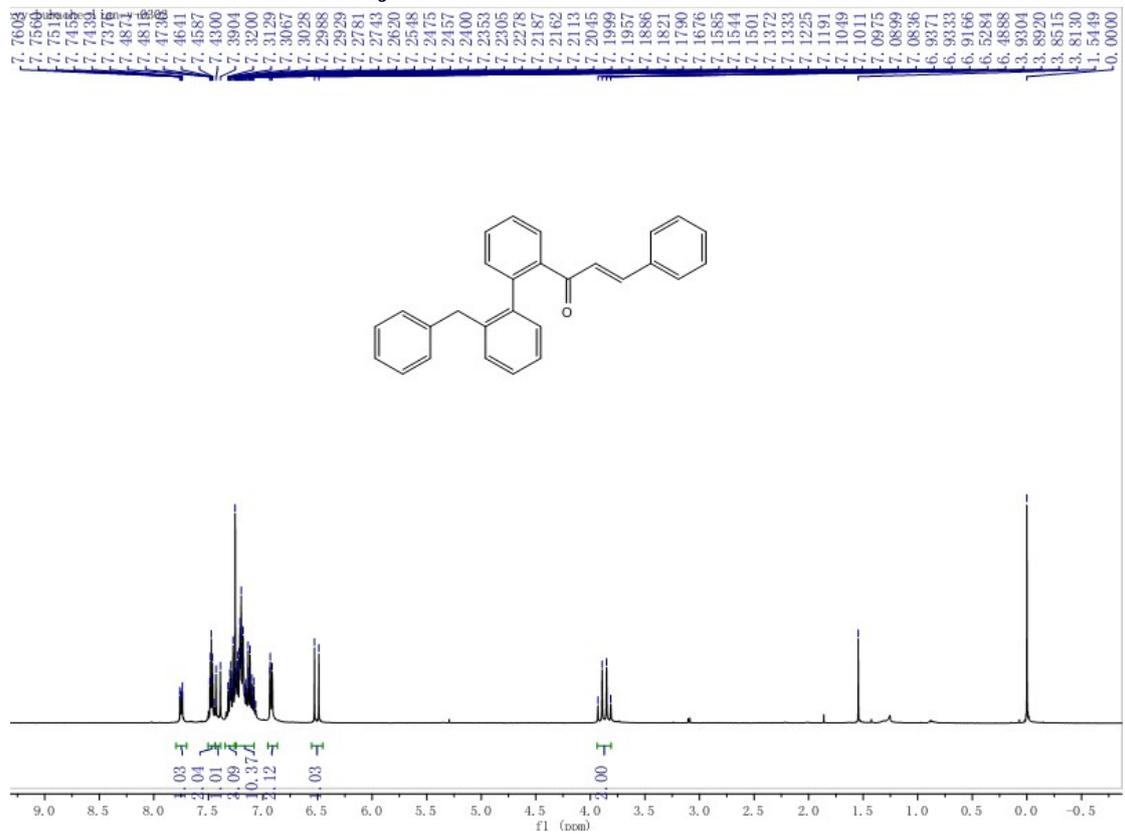
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 3i

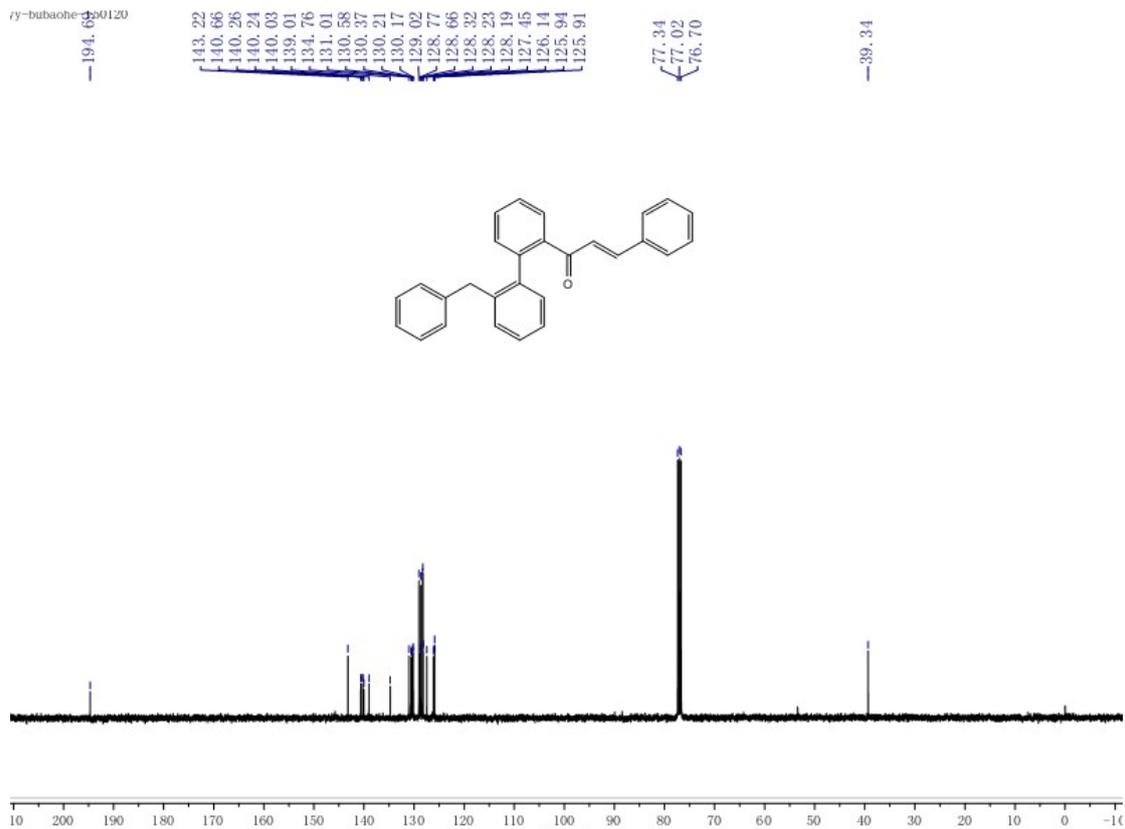


YY-xianan-4-y-0304

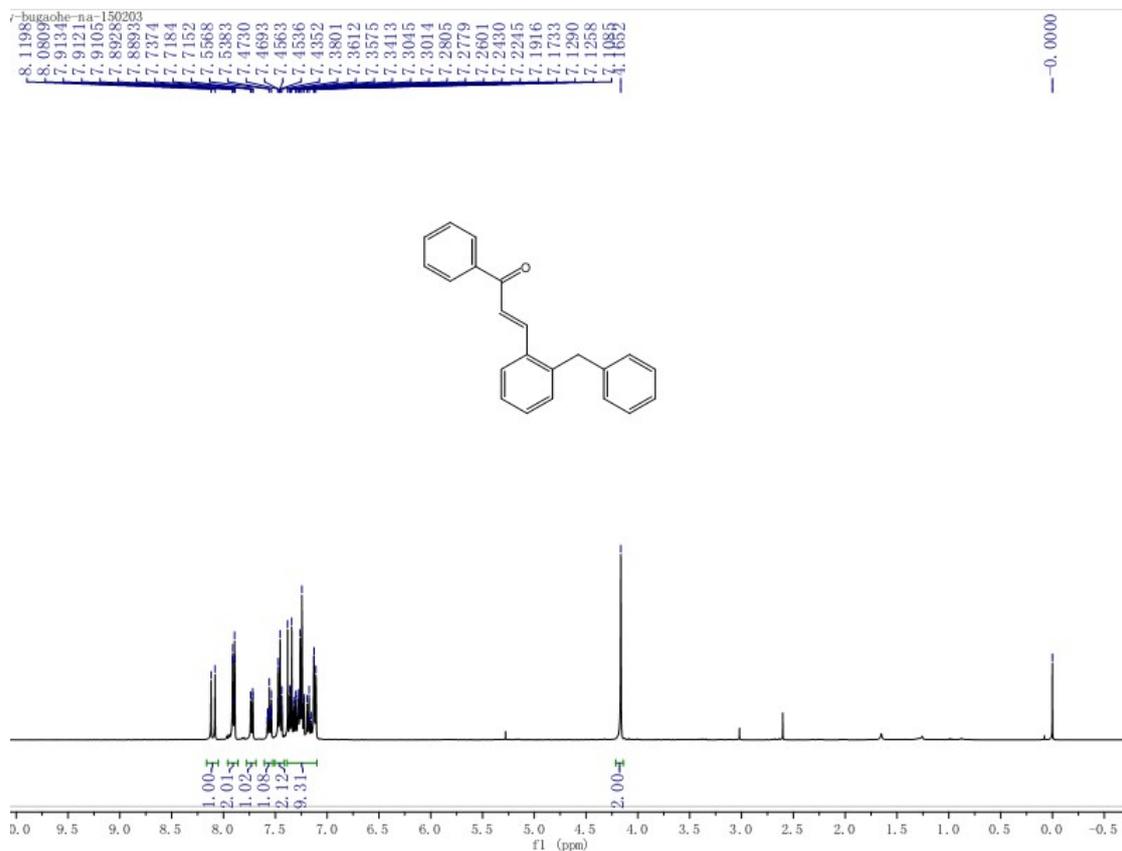


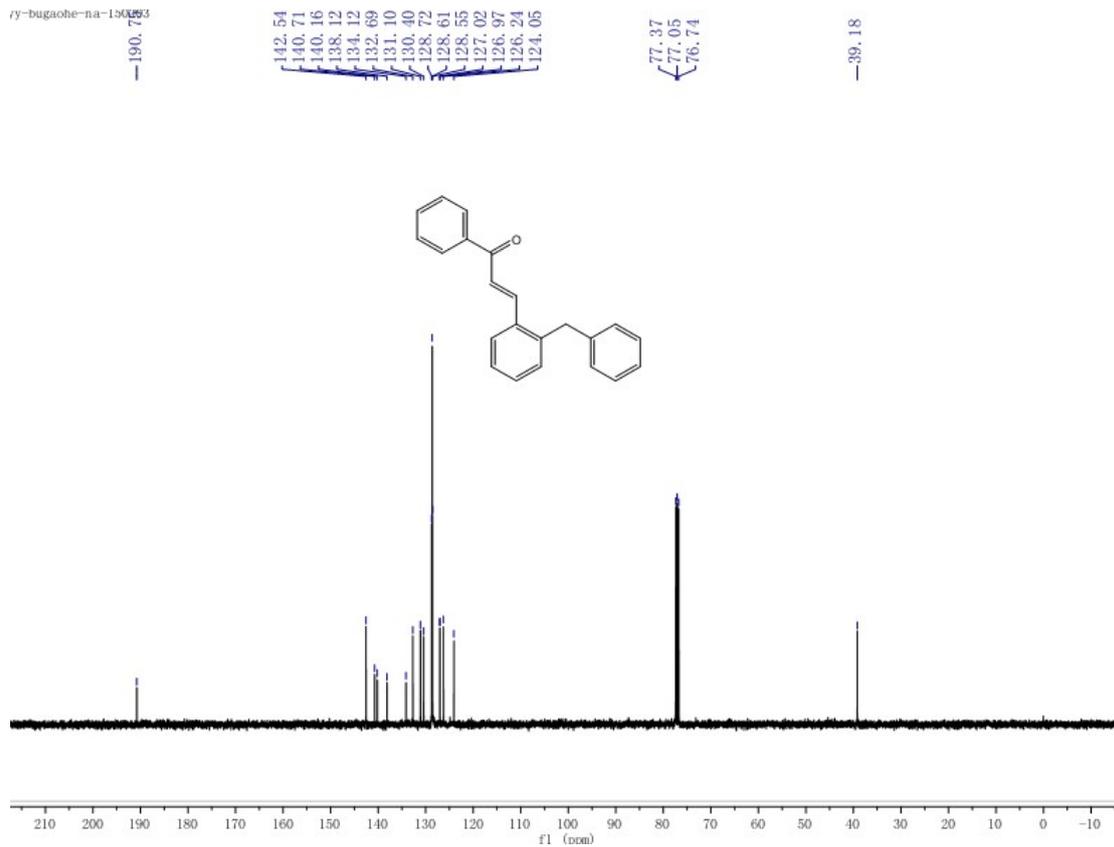
### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 3j



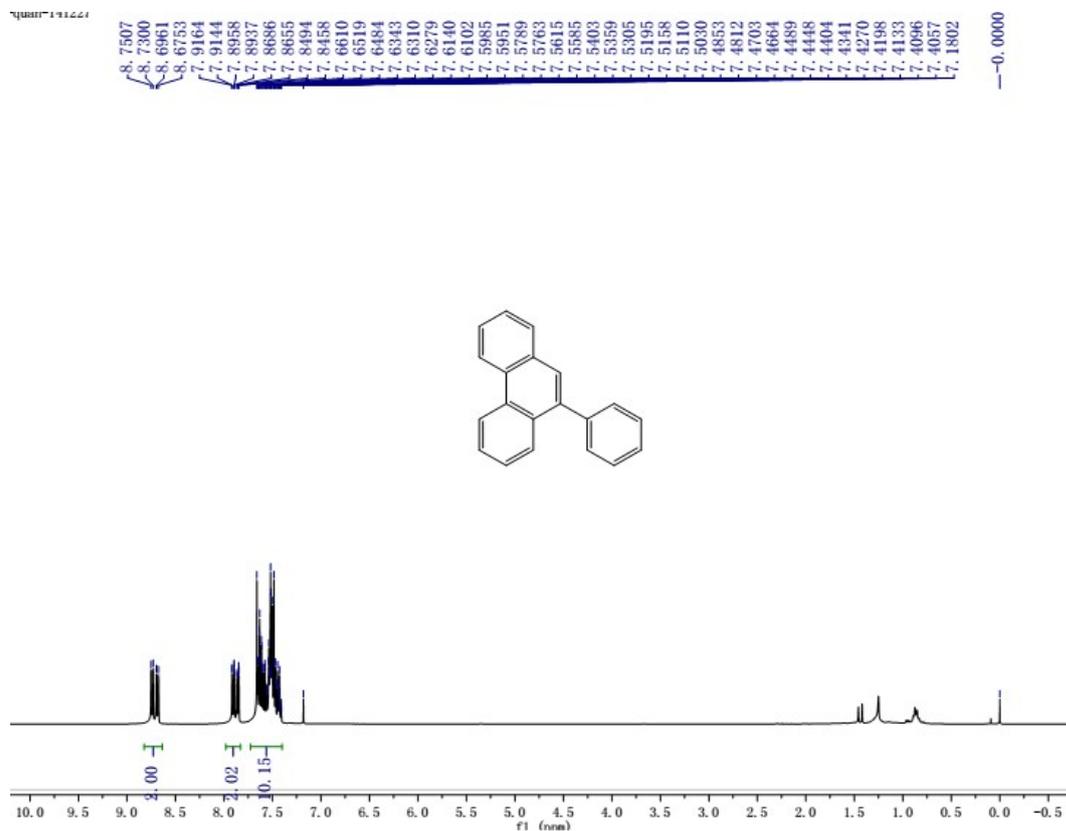


### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 3k



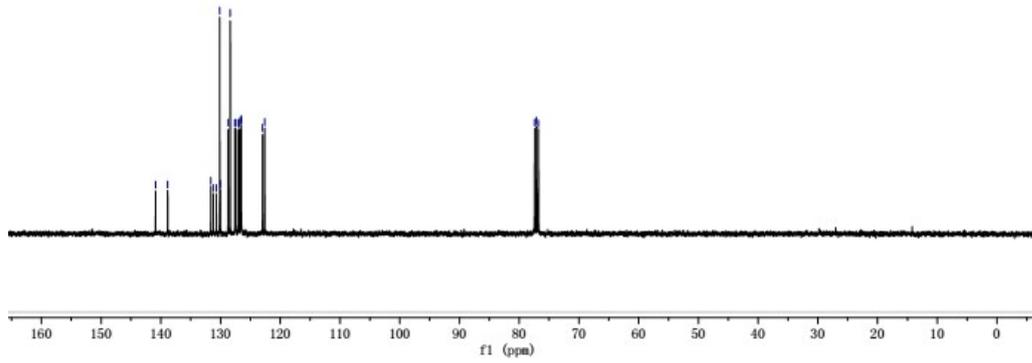
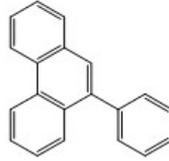


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2a



141227

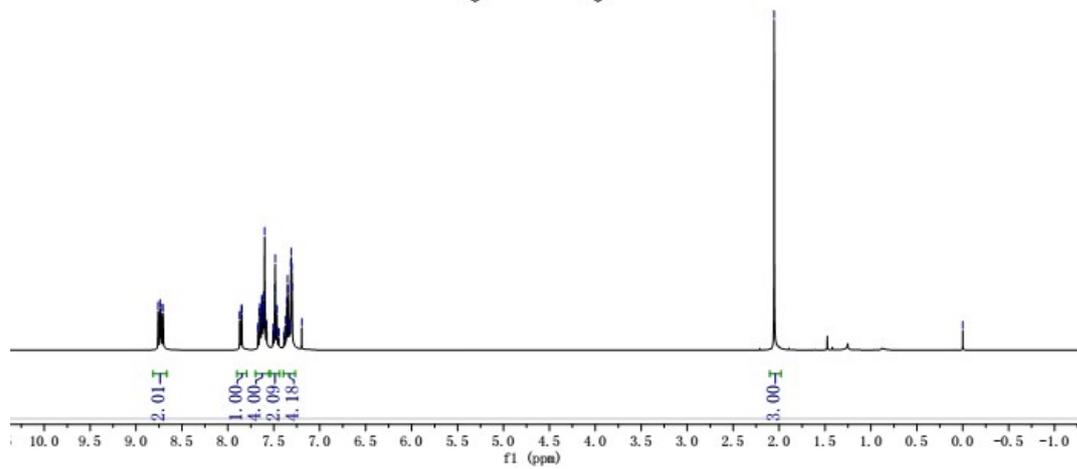
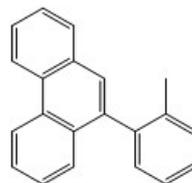
140.88  
138.85  
131.64  
131.21  
130.70  
130.14  
130.03  
128.73  
128.38  
127.59  
127.43  
127.00  
126.91  
126.65  
126.57  
126.52  
122.97  
122.60  
77.42  
77.10  
76.78

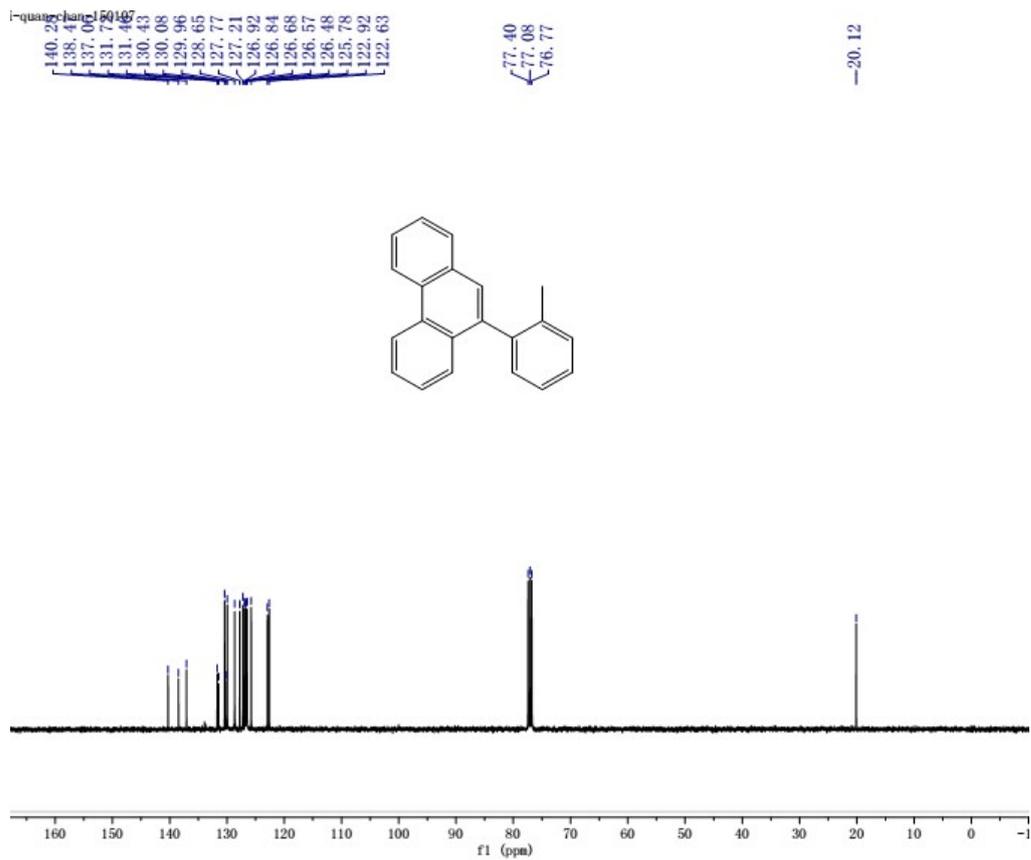


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2b

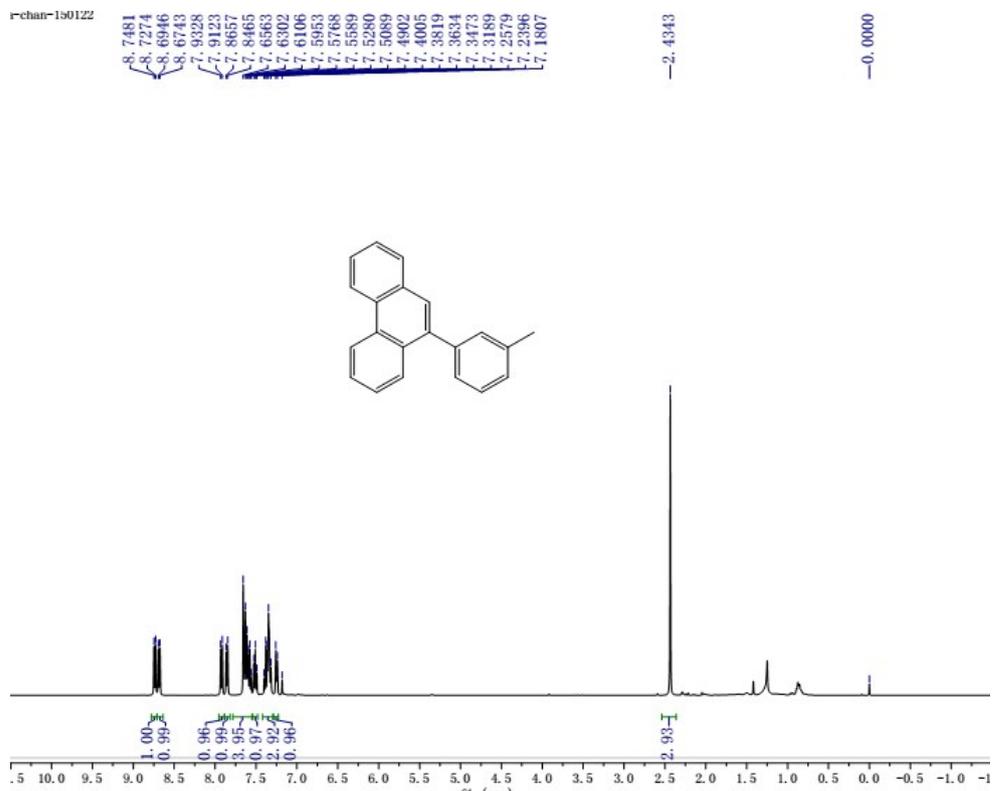
141227

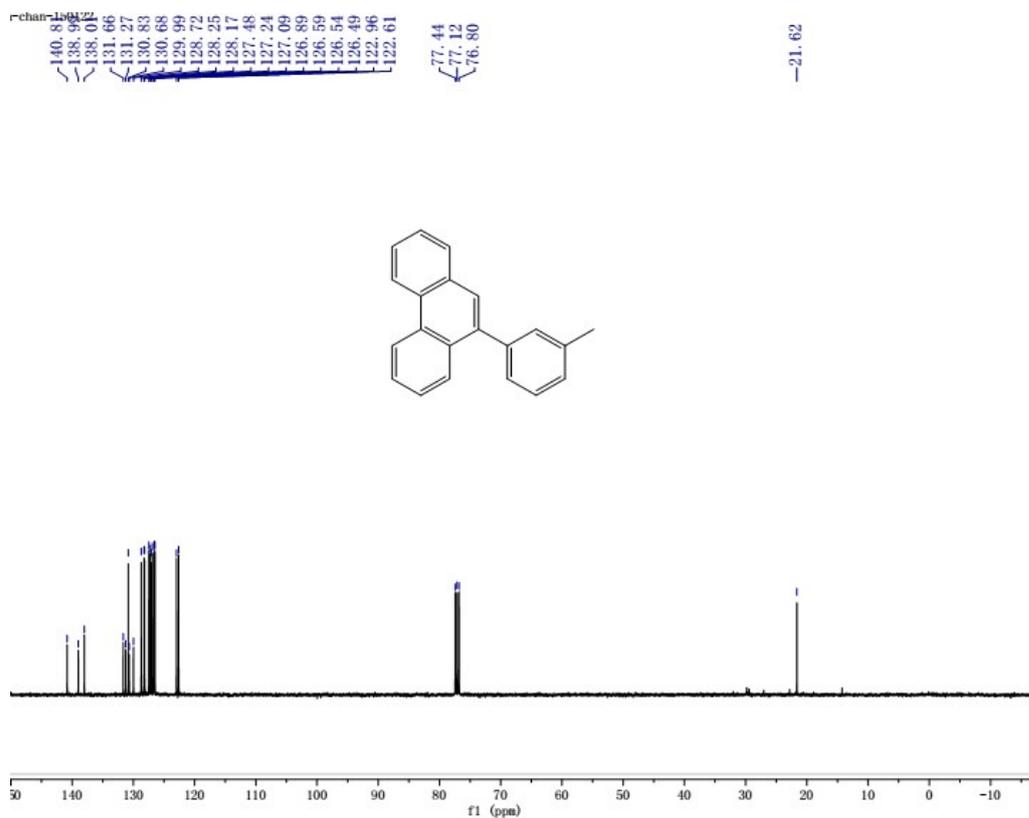
8.7592  
8.7382  
8.7267  
8.7063  
7.8711  
7.8679  
7.8518  
7.8484  
7.8484  
7.6561  
7.6527  
7.6490  
7.6430  
7.6358  
7.6323  
7.6276  
7.6224  
7.6166  
7.6130  
7.6067  
7.6001  
7.4908  
7.4858  
7.4702  
7.4674  
7.3710  
7.3608  
7.3509  
7.3464  
7.3283  
7.3124  
7.3102  
7.3037  
7.3008  
7.0368  
0.0000



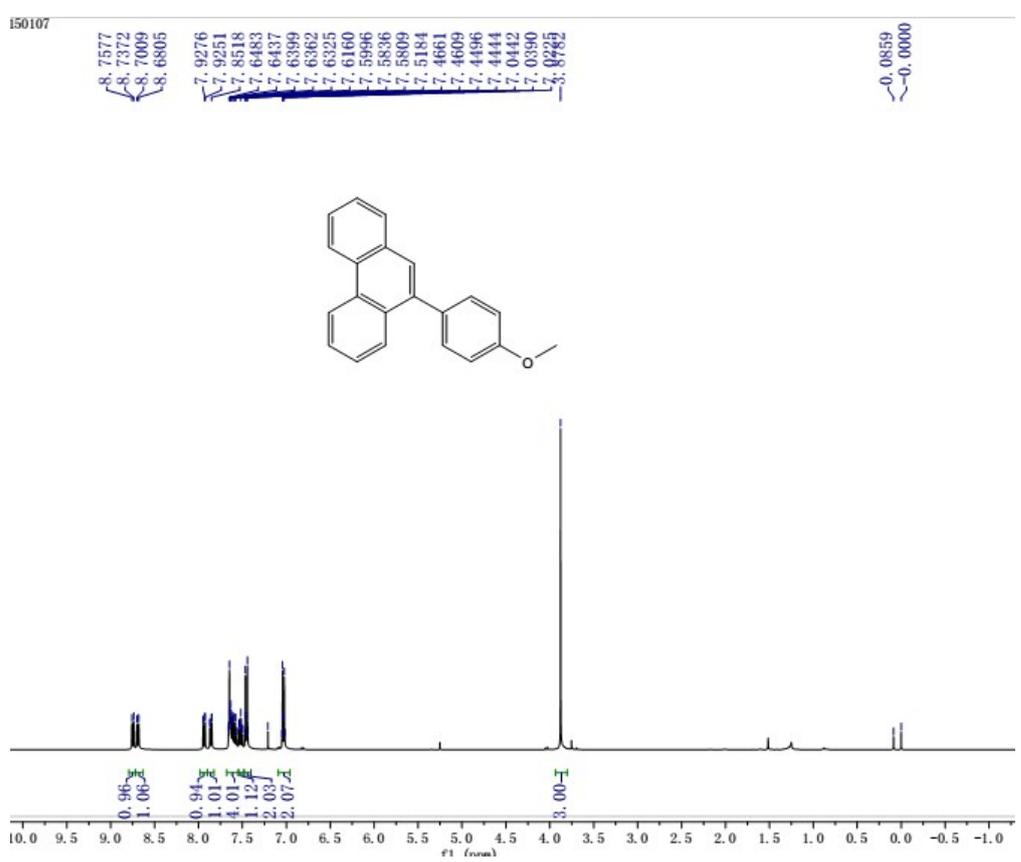


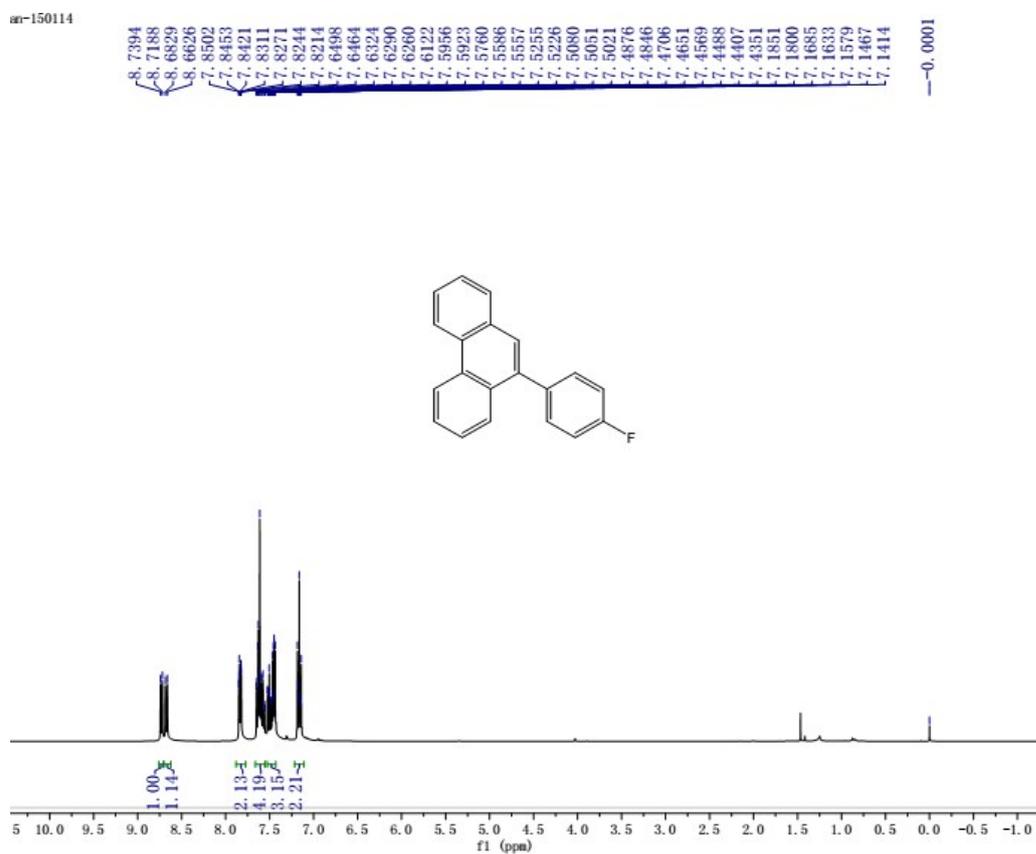
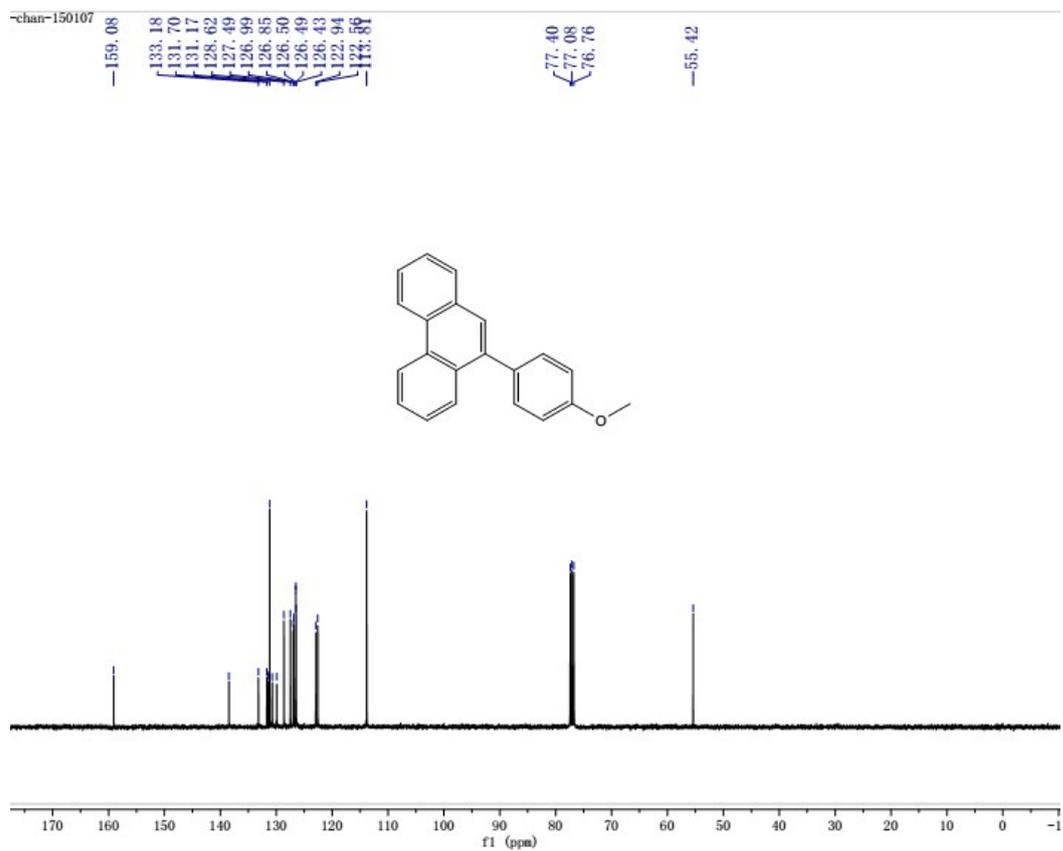
**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 2c**



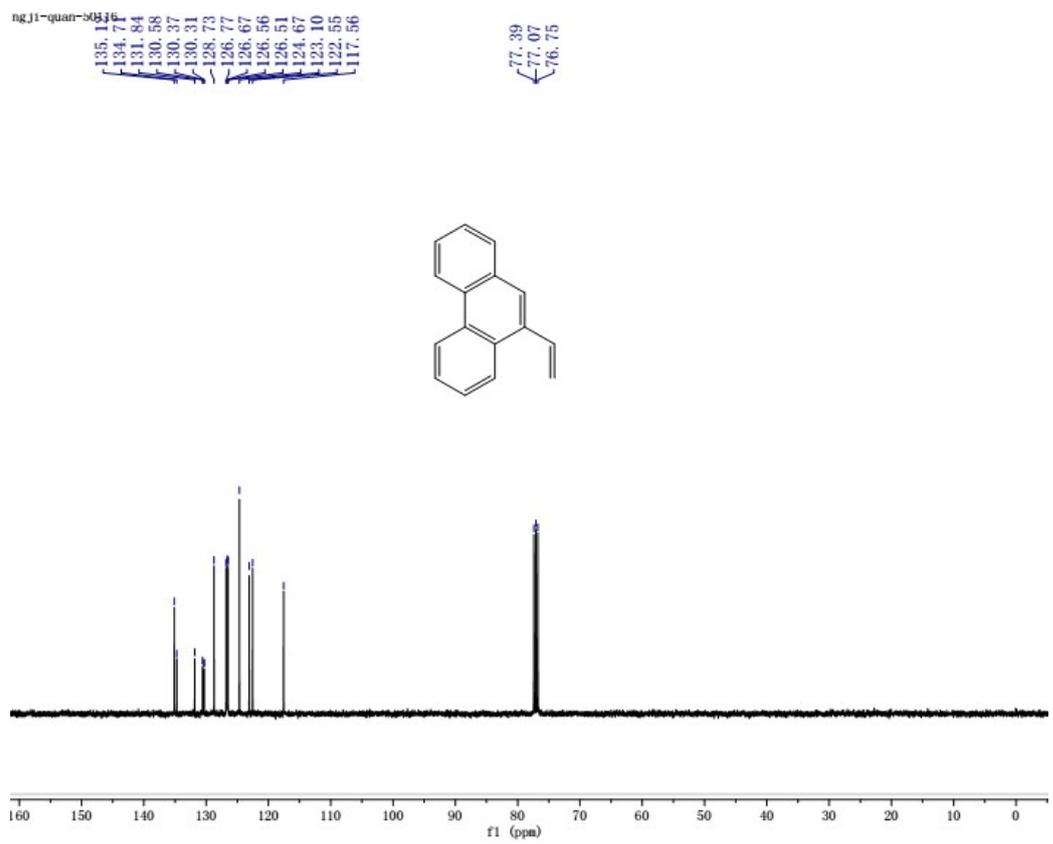


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2d

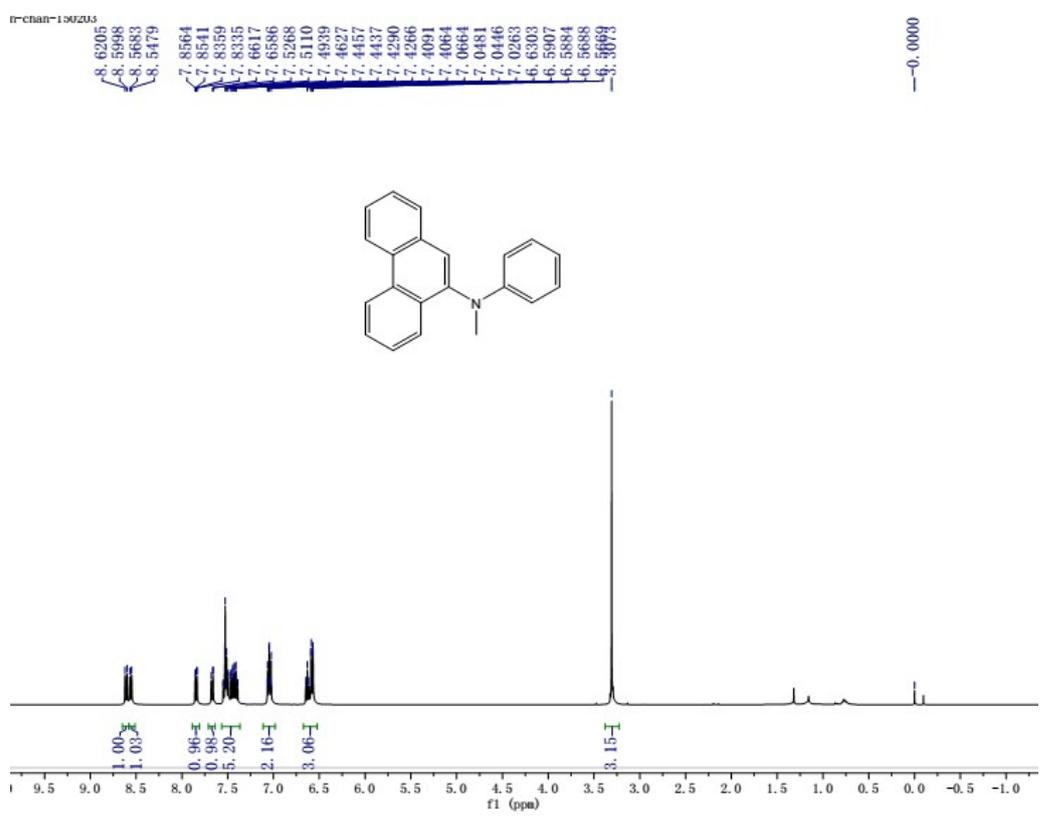




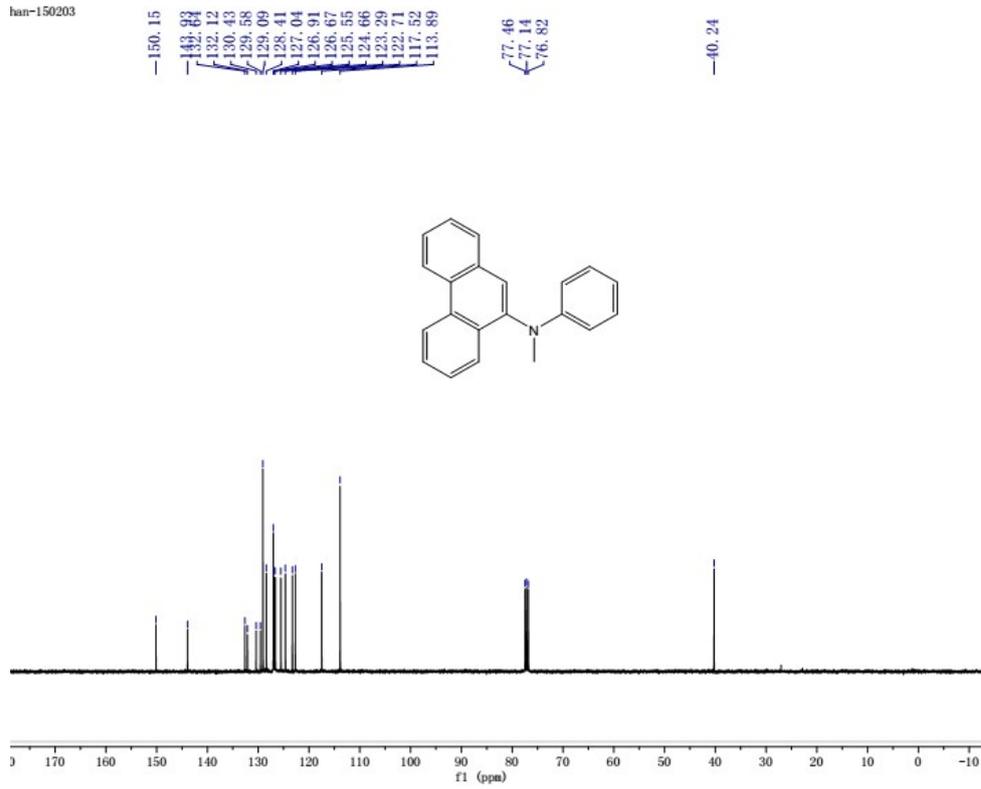




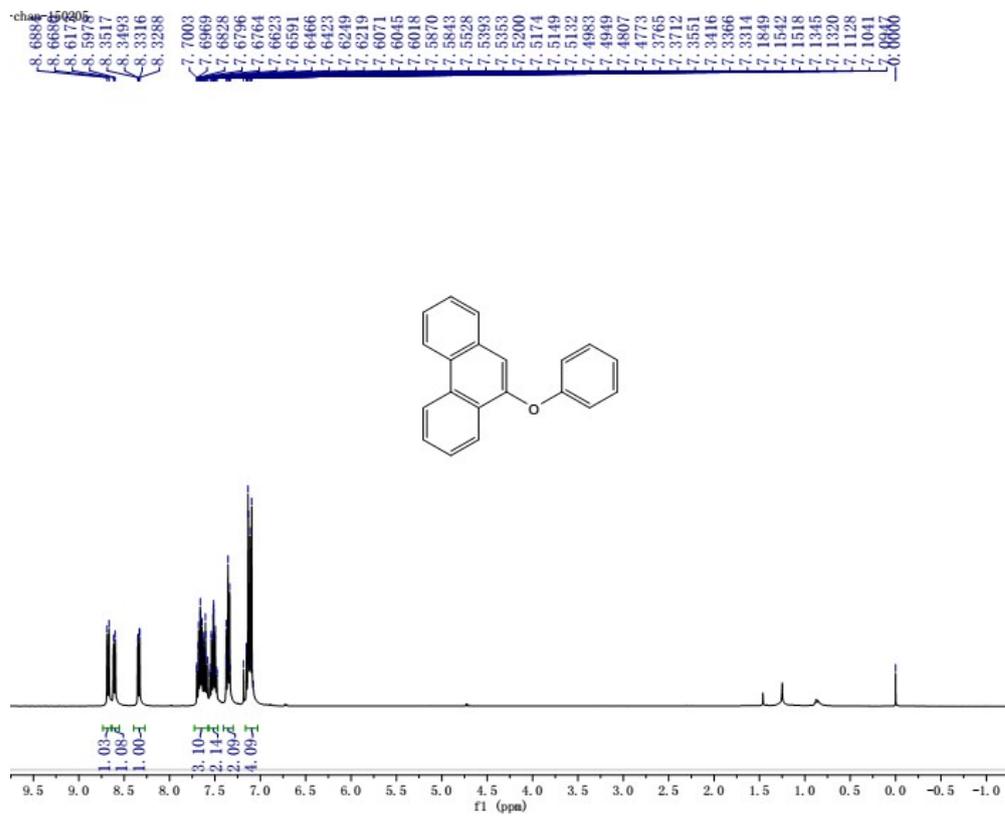
**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 2g**



han-150203

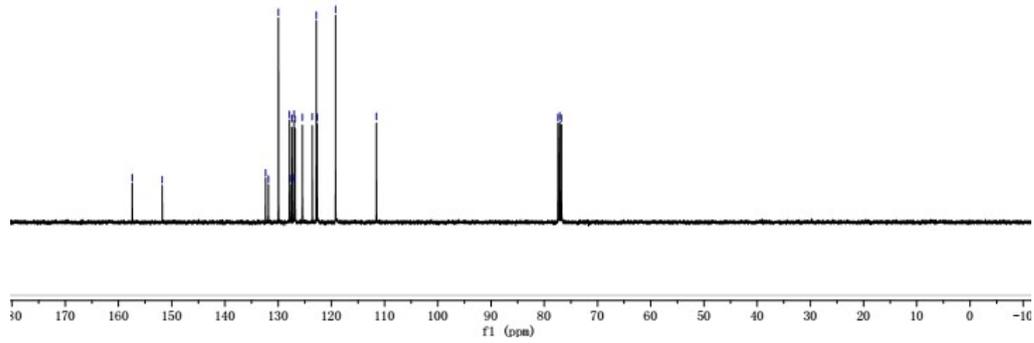
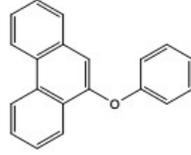


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2h



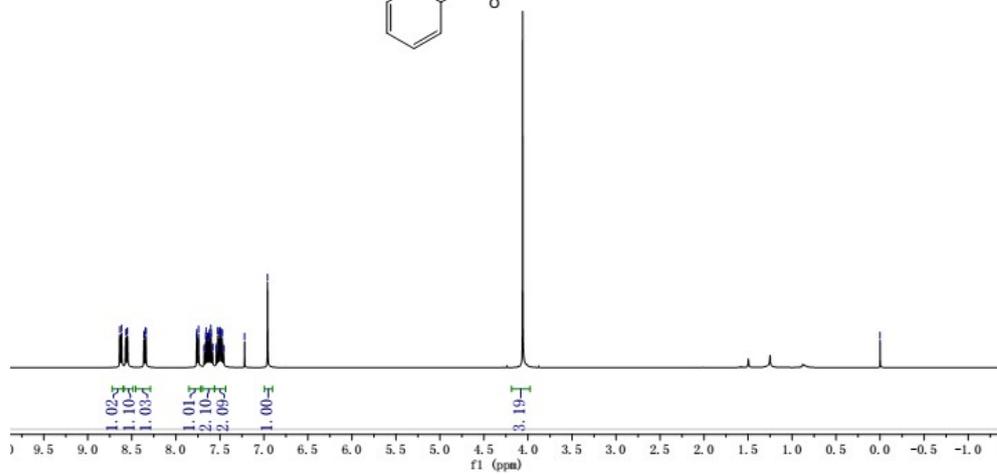
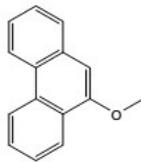
M-nan-130203

157.42  
151.78  
132.36  
129.95  
127.88  
127.43  
127.02  
126.82  
125.45  
123.58  
122.84  
122.67  
119.54  
77.41  
77.10  
76.78

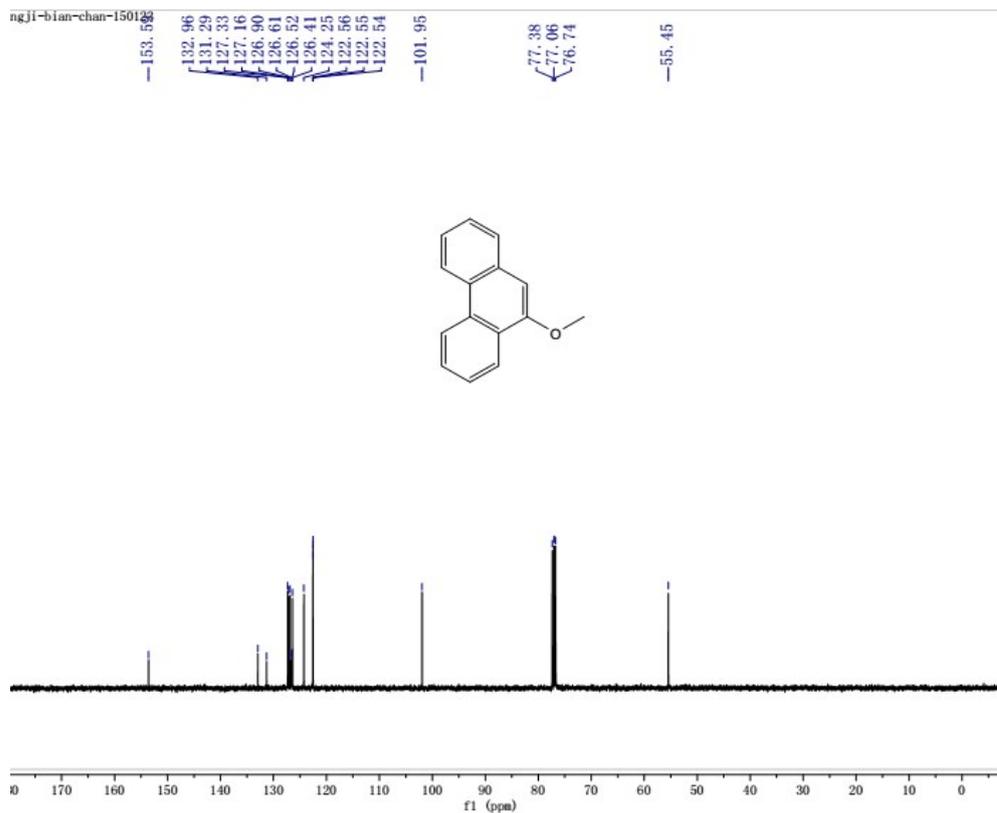


### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 2i

8.6363  
8.6168  
8.5703  
8.5503  
8.3641  
8.3612  
8.3442  
8.3403  
7.7645  
7.7609  
7.7418  
7.6778  
7.6741  
7.6603  
7.6569  
7.6402  
7.6361  
7.6232  
7.6197  
7.6027  
7.6000  
7.5855  
7.5825  
7.5413  
7.5379  
7.5236  
7.5204  
7.5049  
7.5008  
7.4977  
7.4933  
7.4773  
7.4738  
7.4599  
7.4562  
7.2192  
6.9584  
0.0000

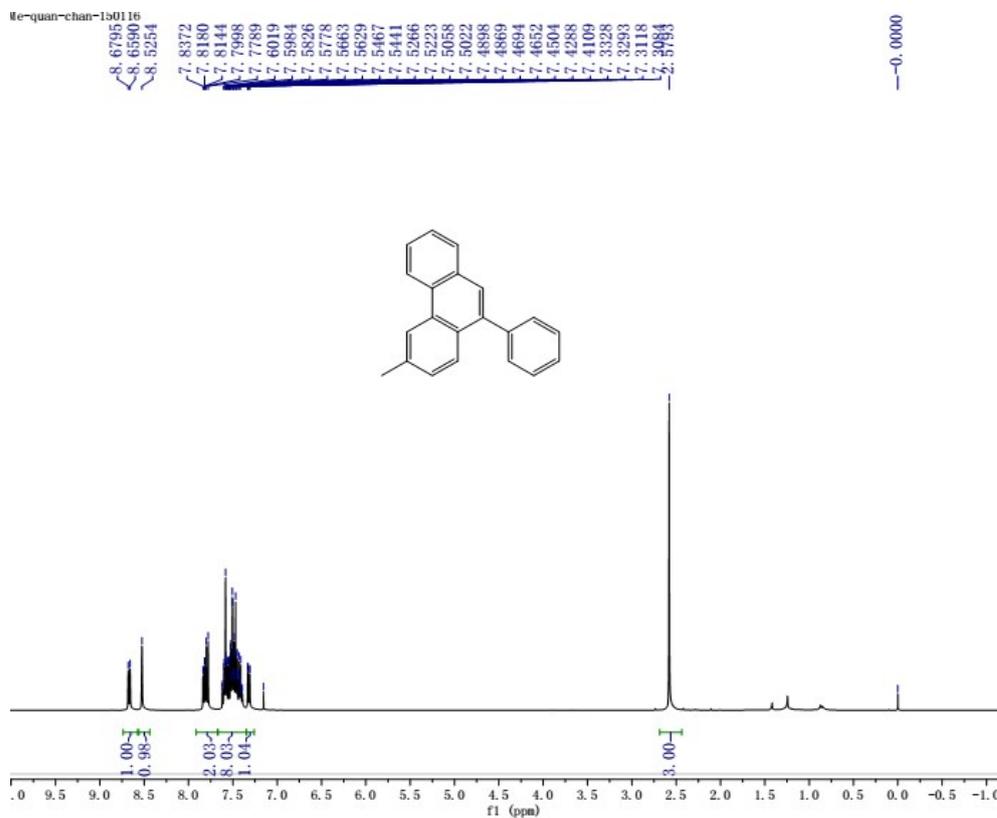


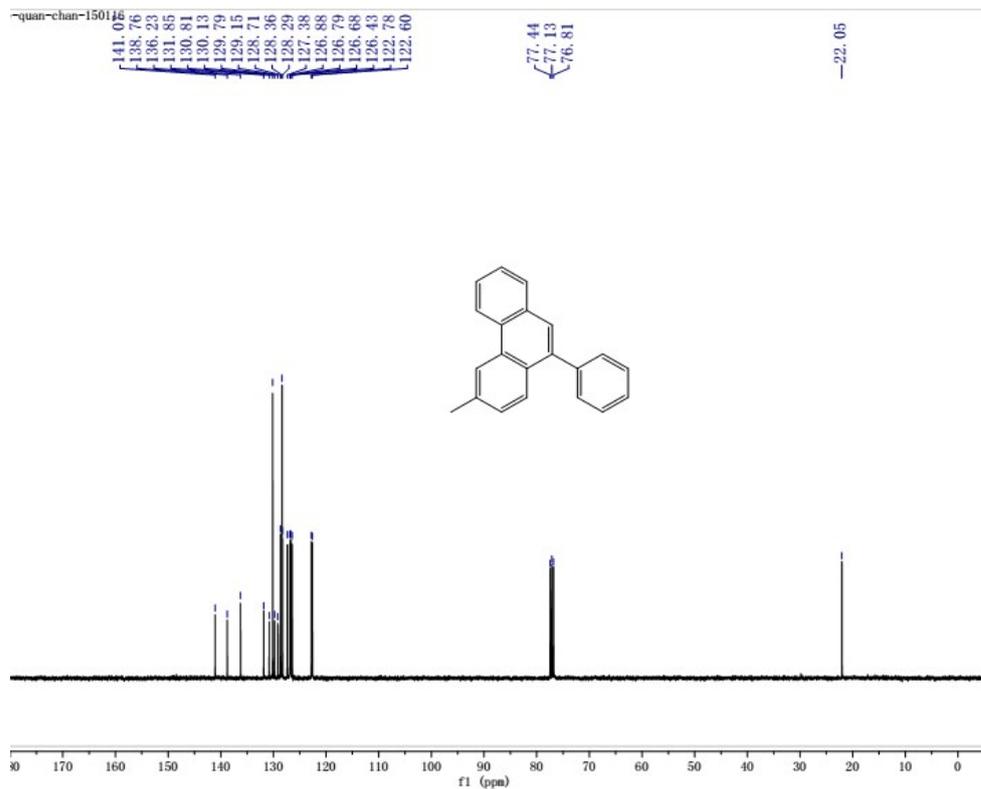
ngji-bian-chan-150123



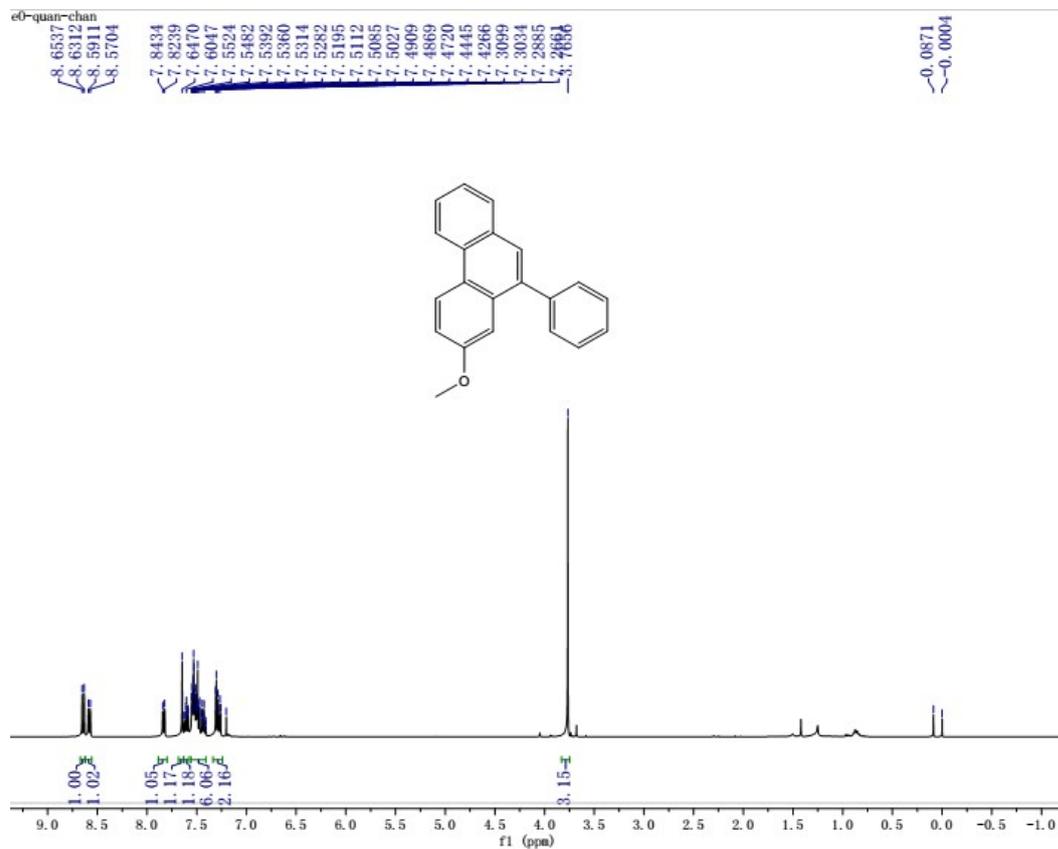
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2k

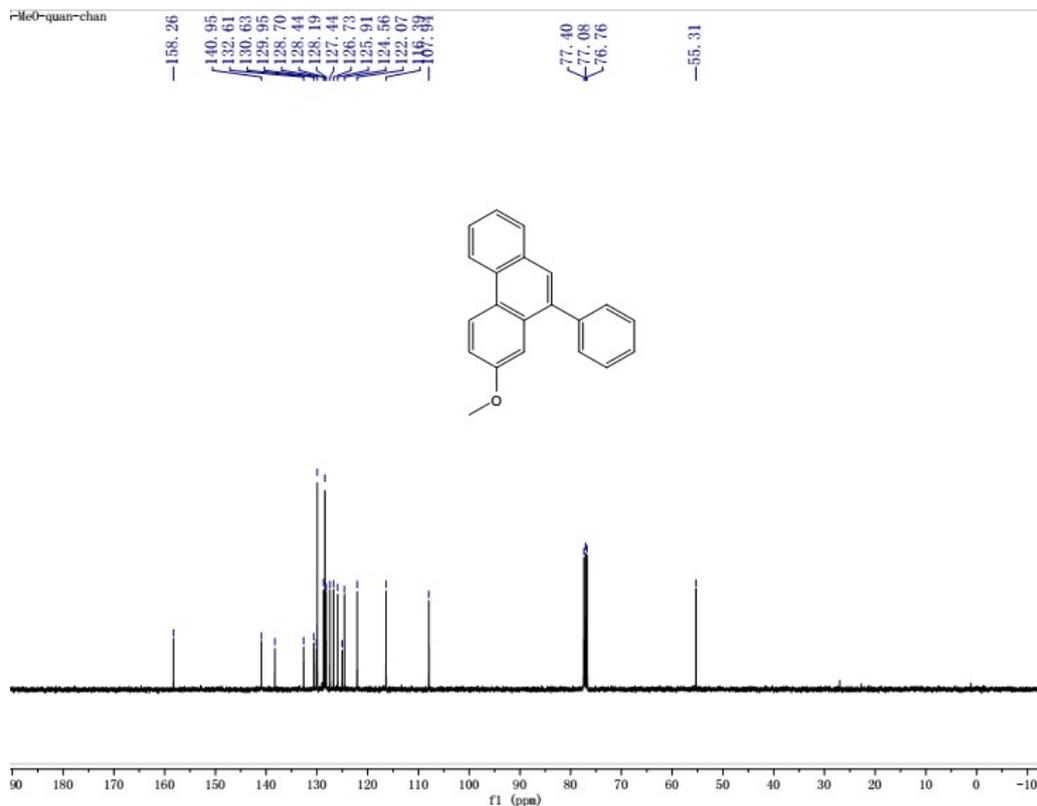
Me-quan-chan-150116



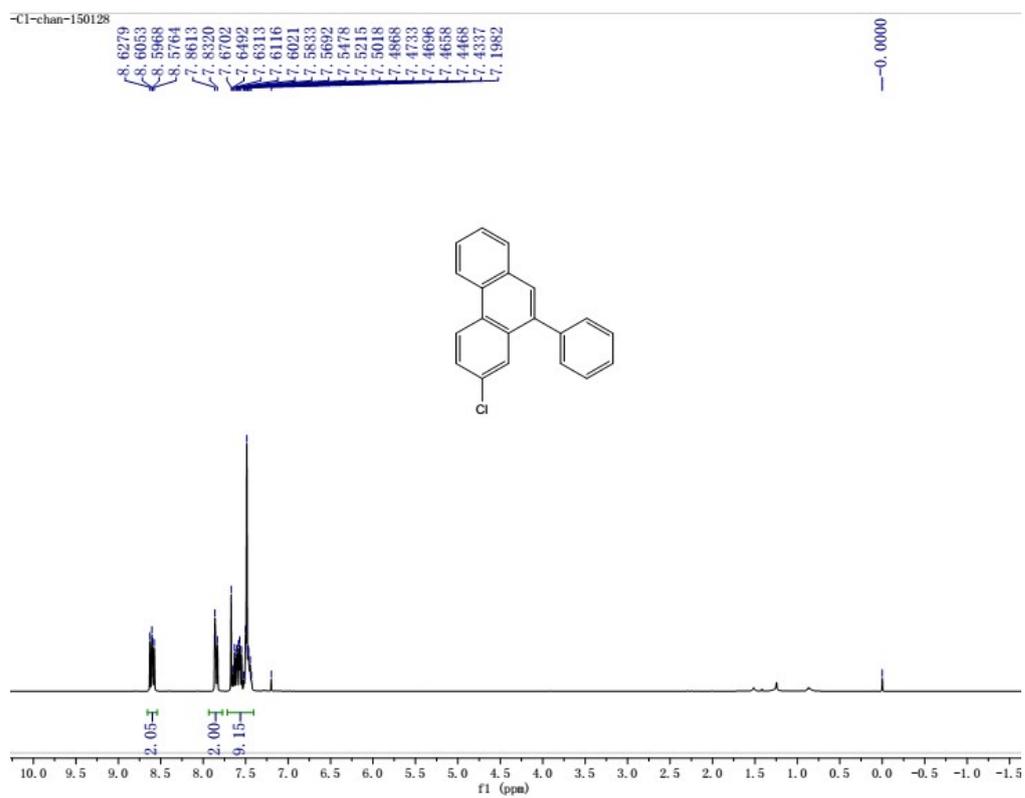


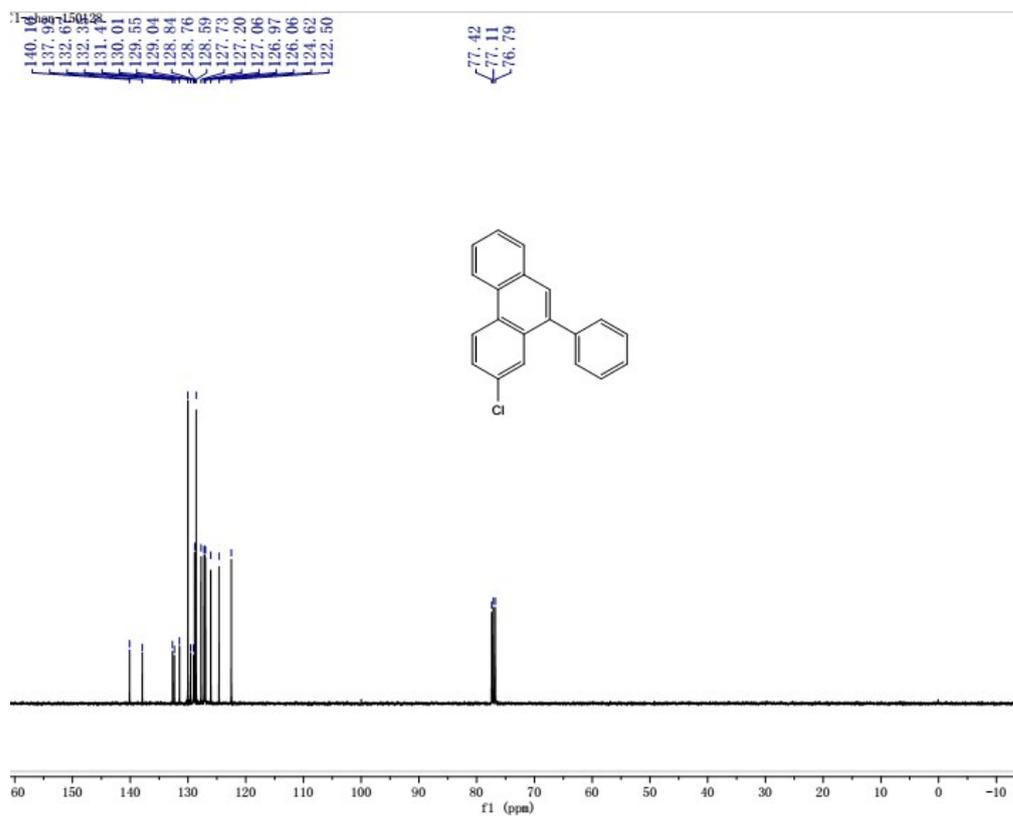
**<sup>1</sup>H NMR and <sup>13</sup>CNMR of 2l**



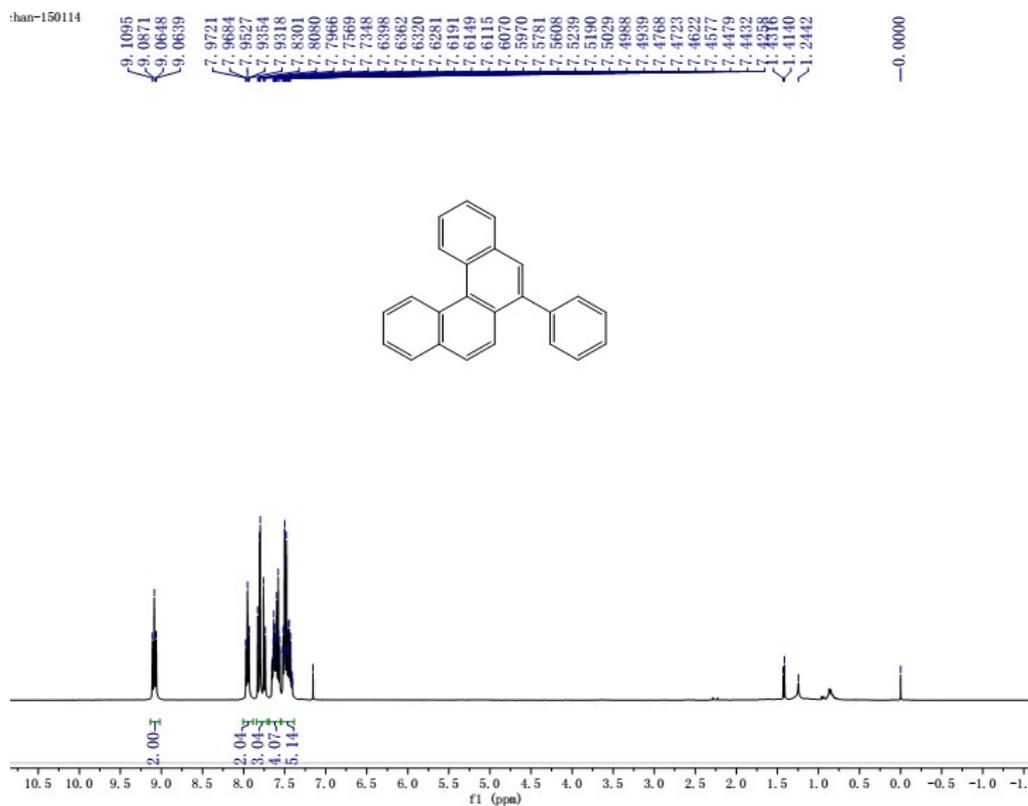


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2m

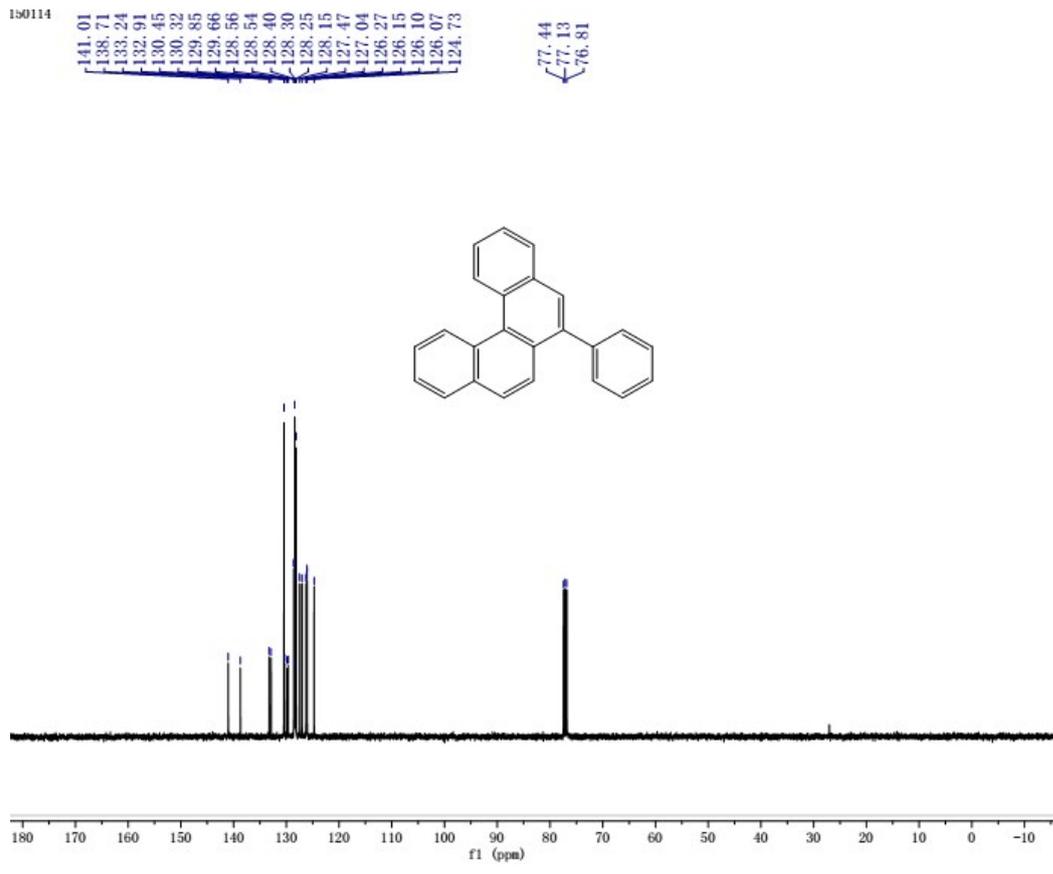




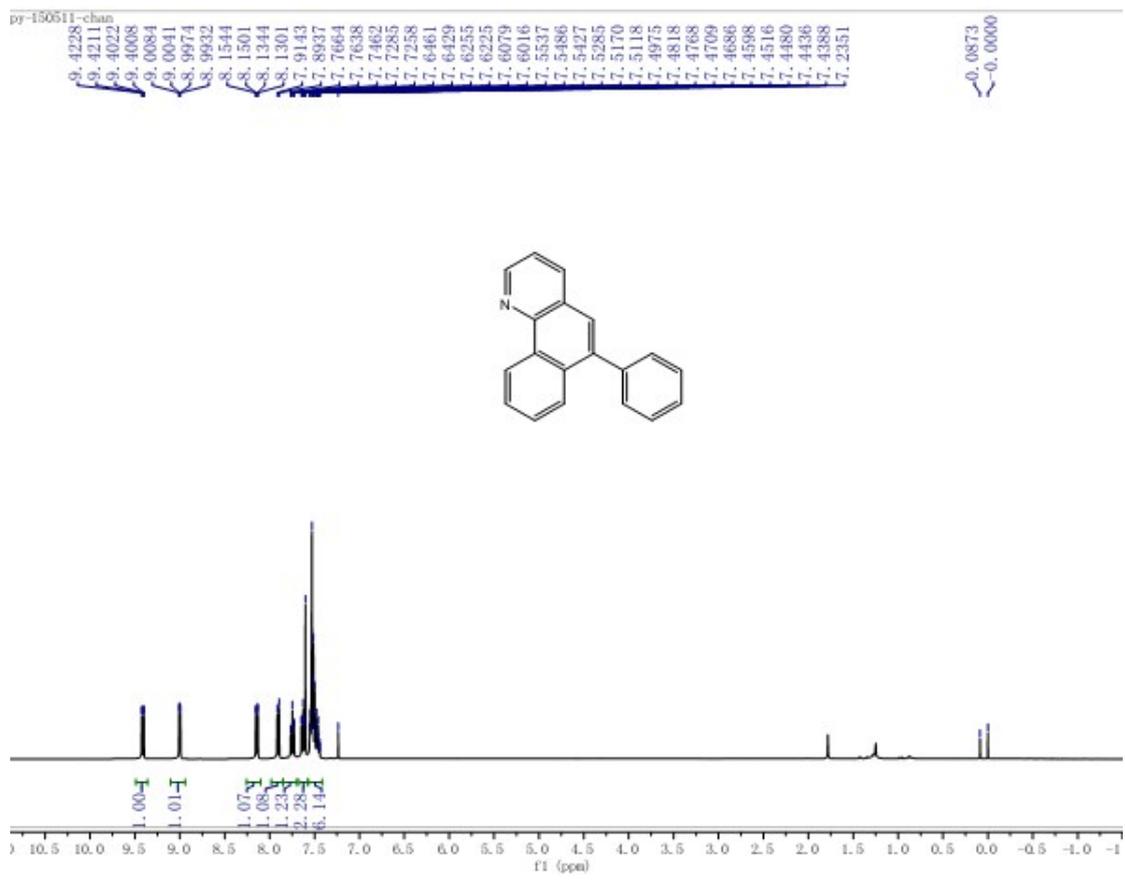
### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2n

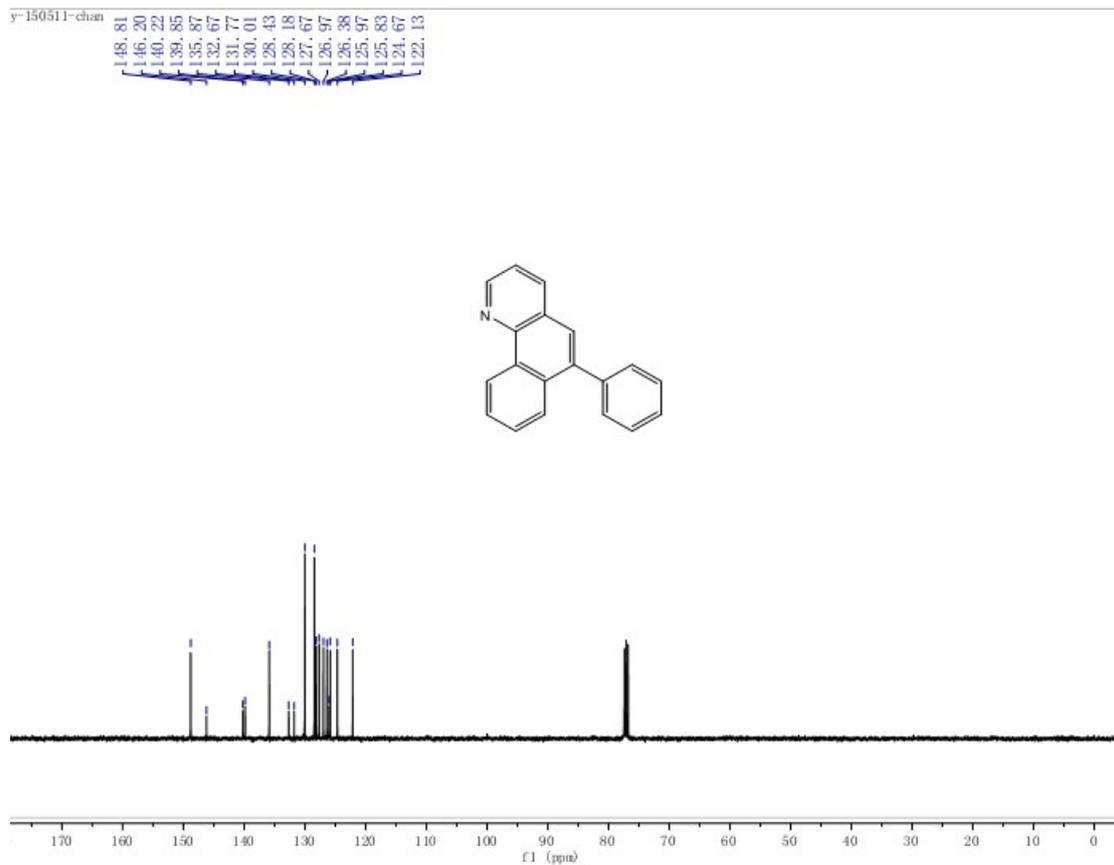


150114

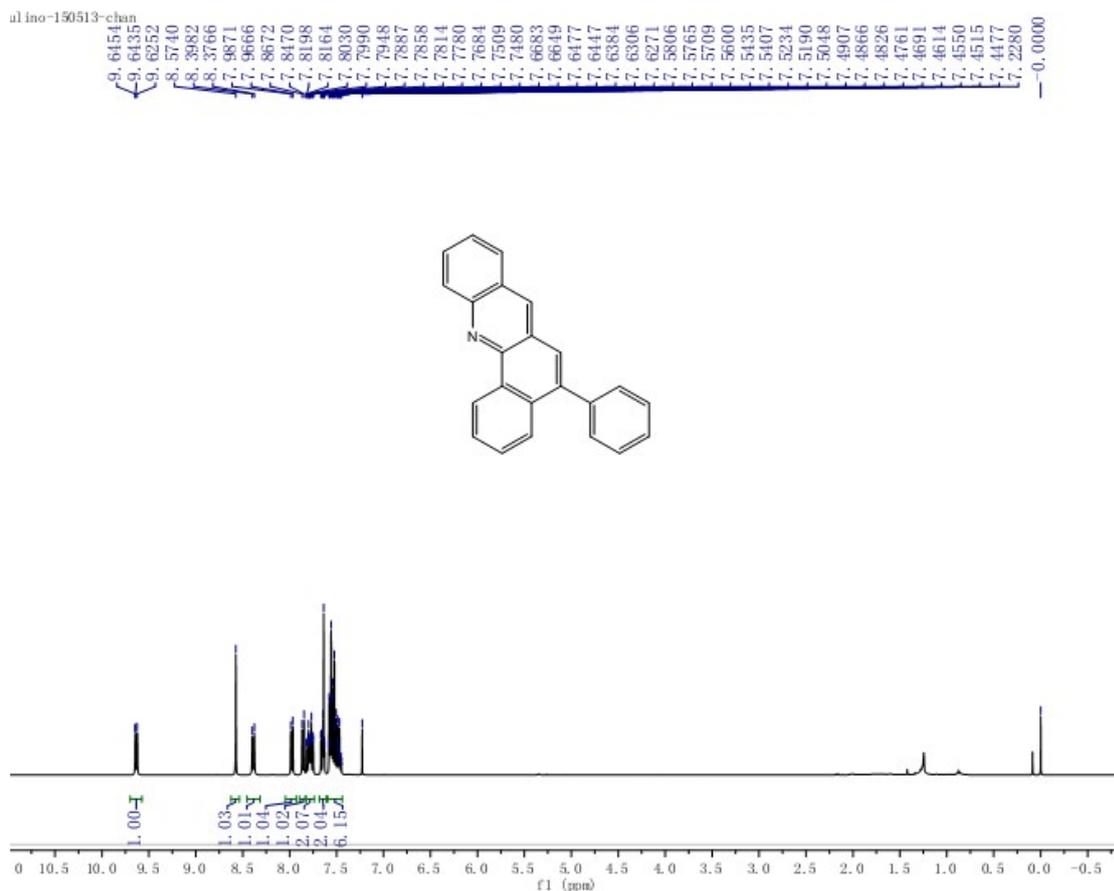


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 20



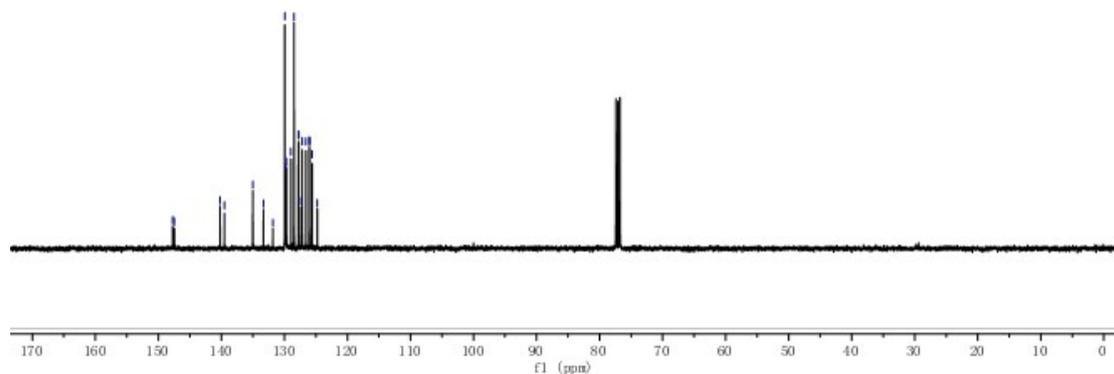
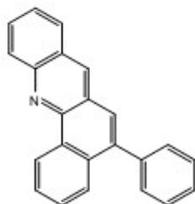


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 2p



ulino-150513-chan

147.72  
147.47  
140.21  
139.52  
135.01  
133.32  
131.83  
129.95  
129.82  
129.68  
128.96  
128.47  
127.79  
127.72  
127.30  
127.18  
126.57  
126.05  
125.90  
125.61  
124.78

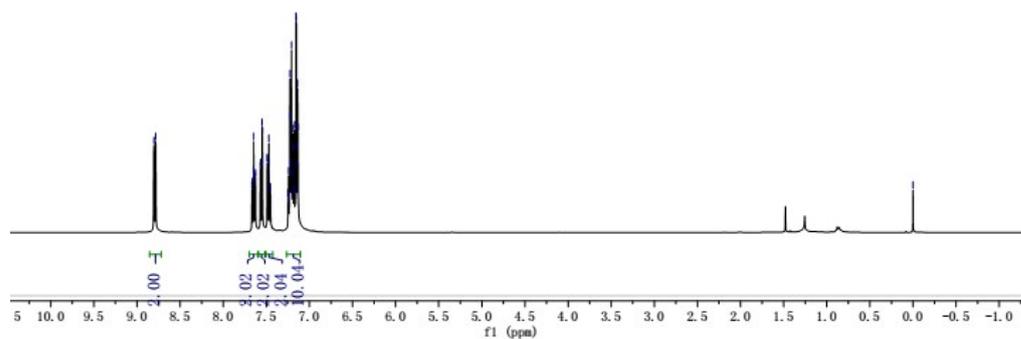


### <sup>1</sup>H NMR and <sup>13</sup>CNMR of 4a

ntong-141228

8.8048  
8.7841  
7.6671  
7.6636  
7.6499  
7.6464  
7.6429  
7.6291  
7.6257  
7.5694  
7.5669  
7.5488  
7.5463  
7.4909  
7.4881  
7.4737  
7.4707  
7.4676  
7.4531  
7.4504  
7.2482  
7.2437  
7.2397  
7.2271  
7.2229  
7.2164  
7.2088  
7.1968  
7.1926  
7.1885  
7.1818  
7.1751  
7.1662  
7.1564  
7.1521  
7.1465  
7.1401  
7.1361  
7.1326

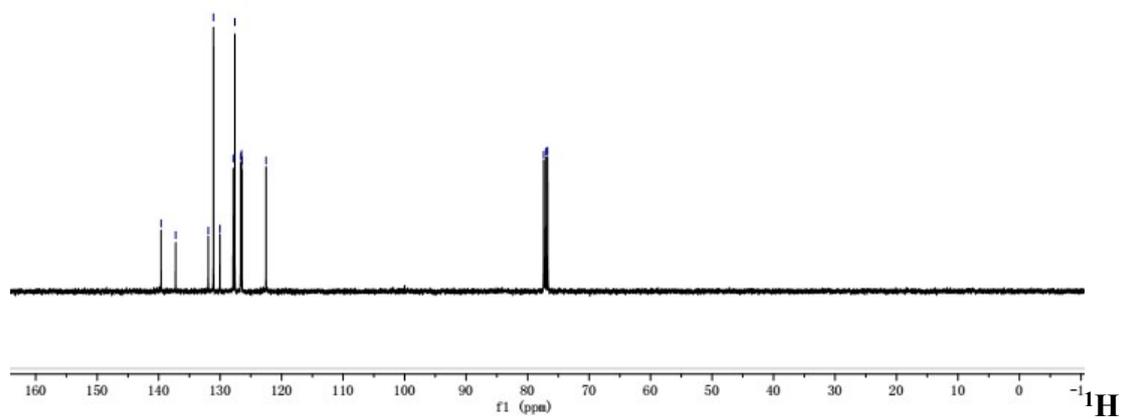
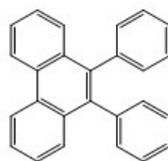
0.0001



ong-141228

139.61  
137.24  
131.92  
131.08  
130.04  
127.89  
127.62  
126.66  
126.51  
126.43  
122.53

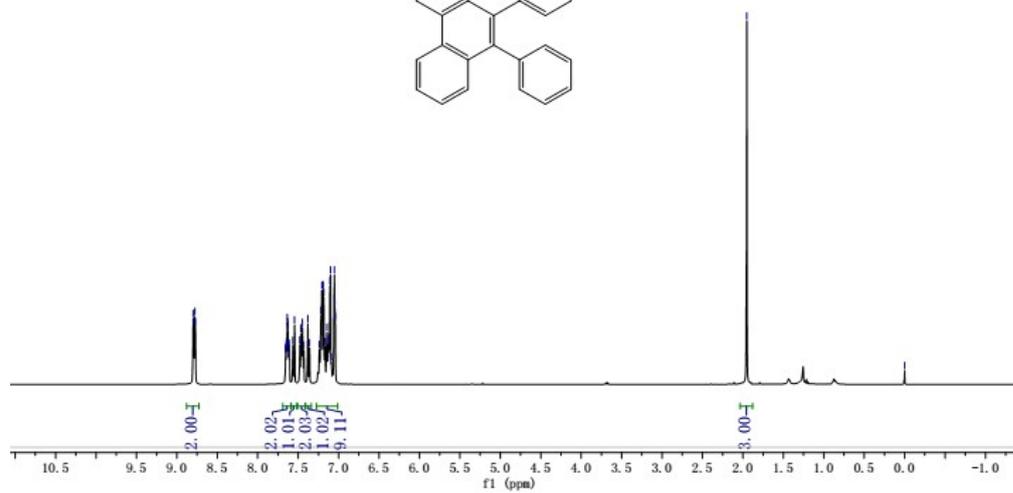
77.38  
77.06  
76.74

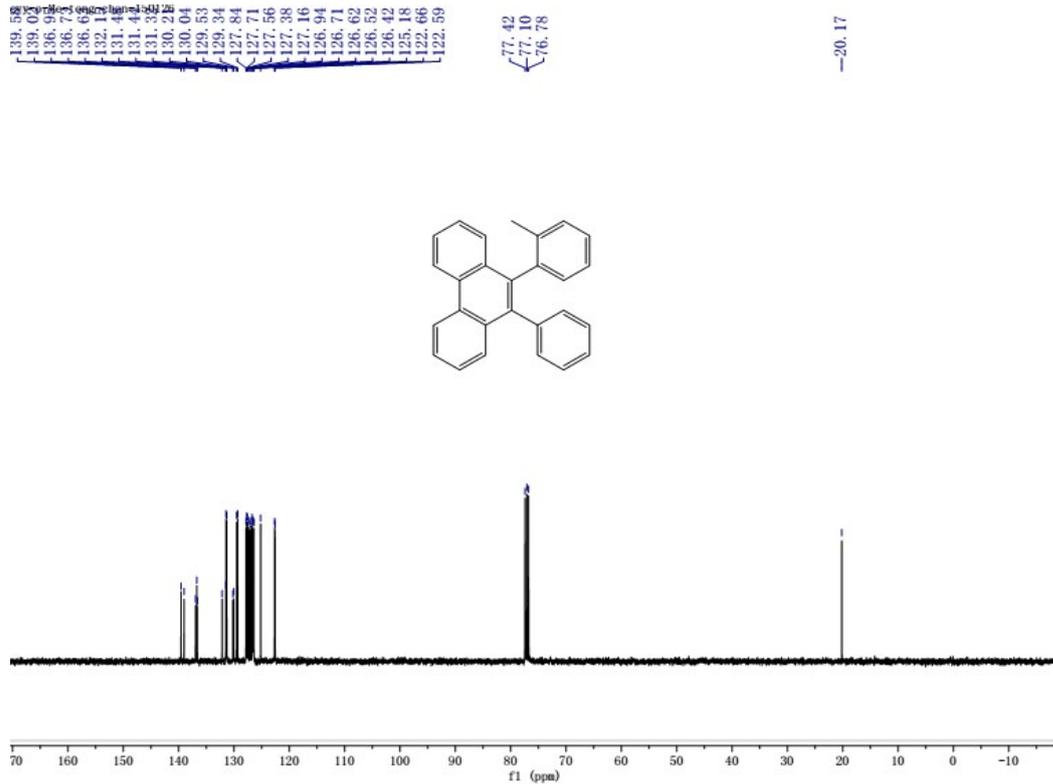


### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4b

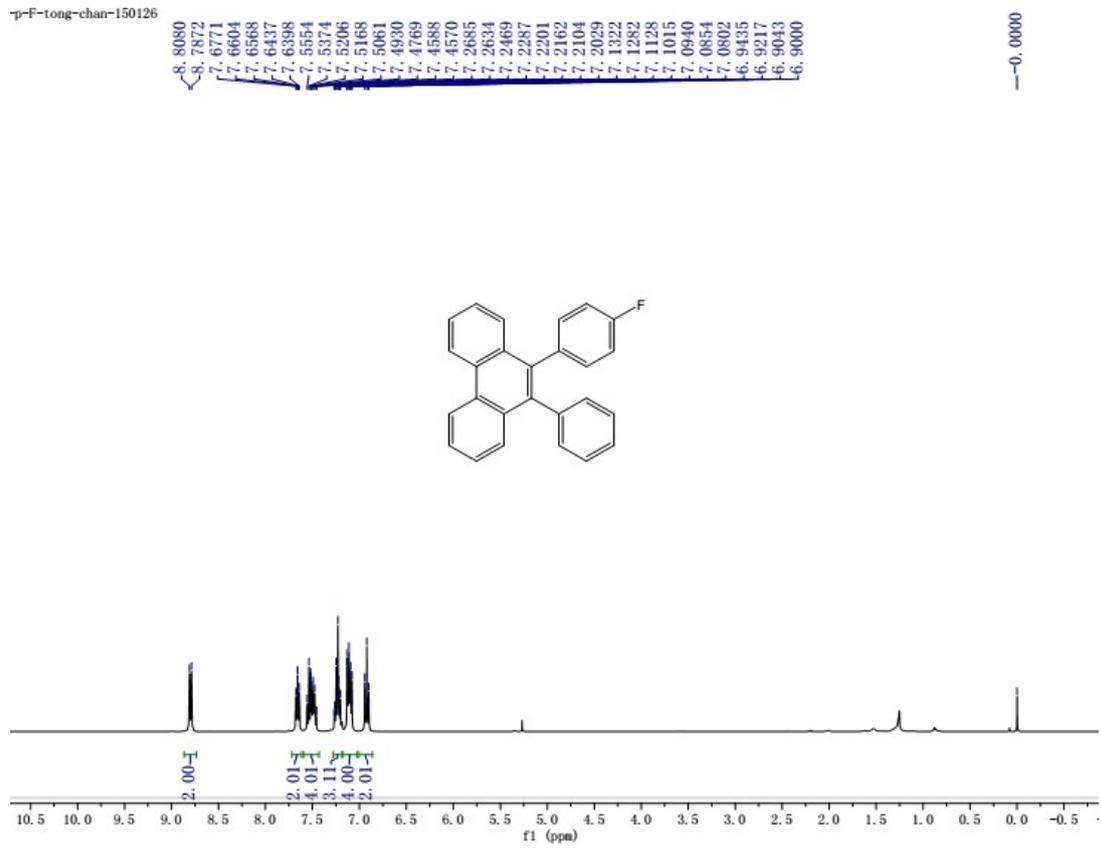
Me-tong-chan-150126

8.7980  
8.7925  
8.7774  
8.7718  
7.6472  
7.6441  
7.6354  
7.6313  
7.6271  
7.6180  
7.6149  
7.5661  
7.5656  
7.4798  
7.4639  
7.4601  
7.4475  
7.3808  
7.3603  
7.2384  
7.2185  
7.2082  
7.1901  
7.1843  
7.1801  
7.1835  
7.1253  
7.1175  
7.1078  
7.0999  
7.0516  
7.0461  
7.0416  
-0.0001



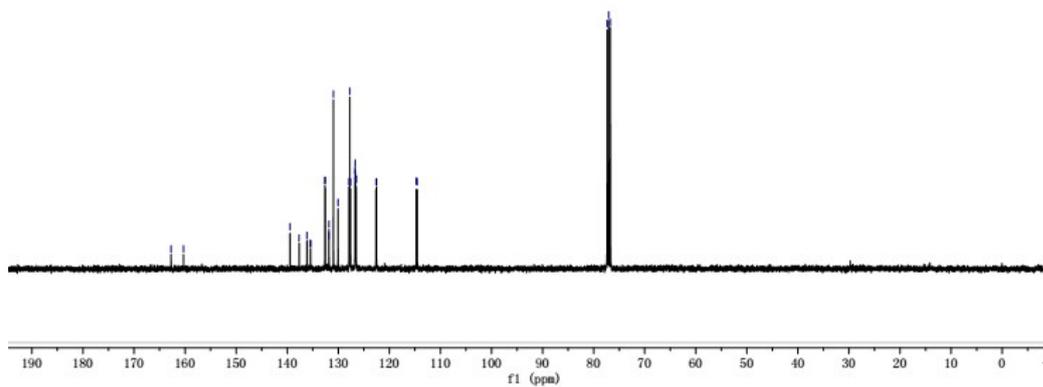
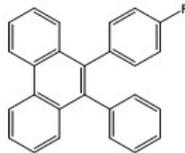


### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4c



$\gamma$ -p-F-TONG-150126

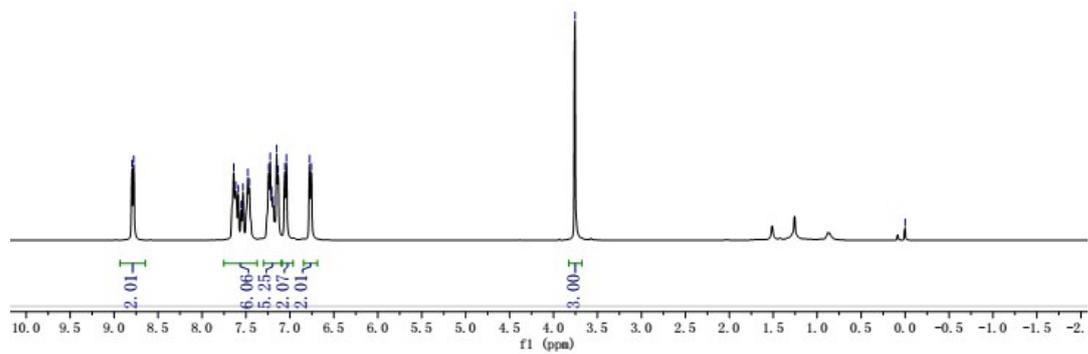
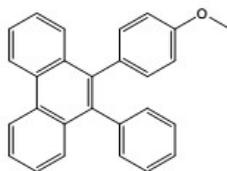
162.75  
160.31  
132.62  
130.54  
130.97  
127.90  
127.75  
126.73  
126.72  
126.63  
126.57  
126.52  
122.89  
114.54  
77.36  
77.04  
76.73

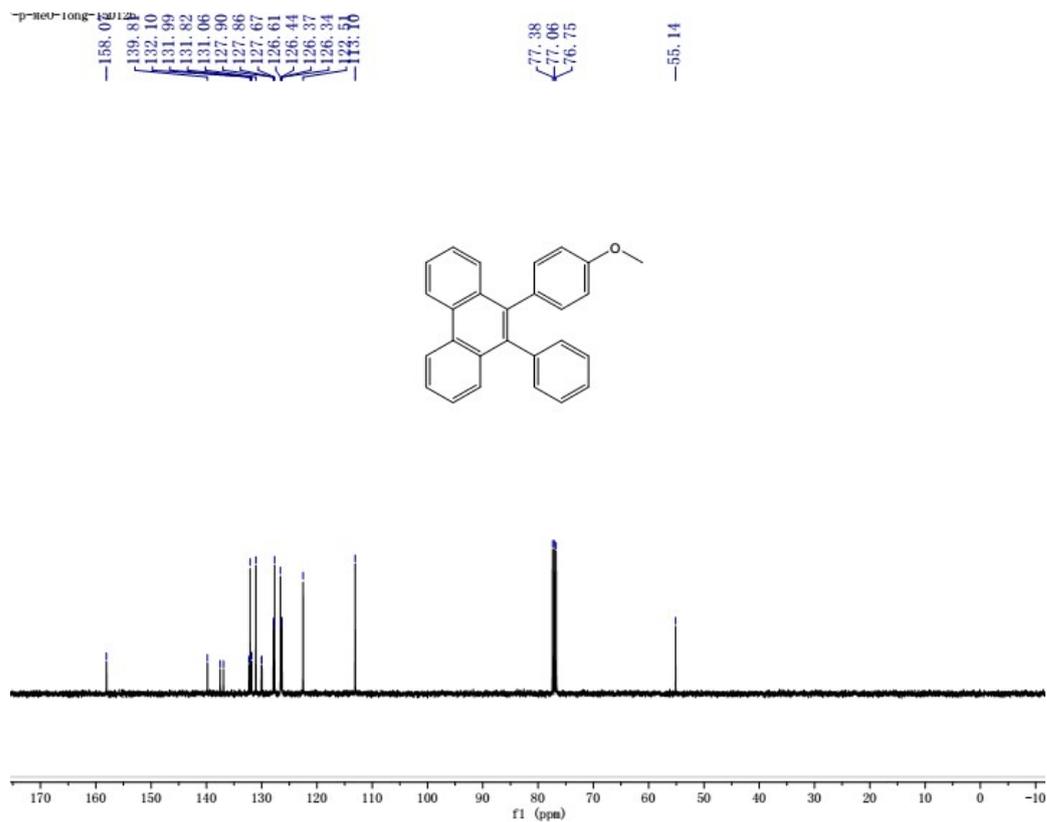


### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 4d

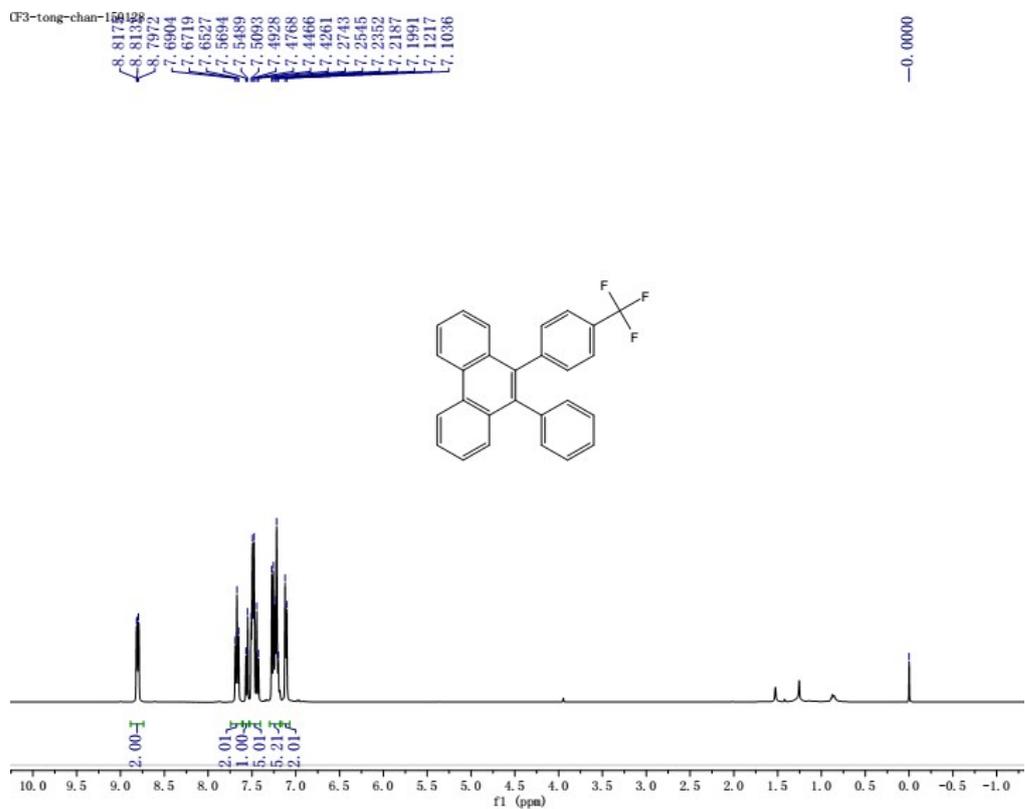
$\gamma$ -MeO-Tong-150126

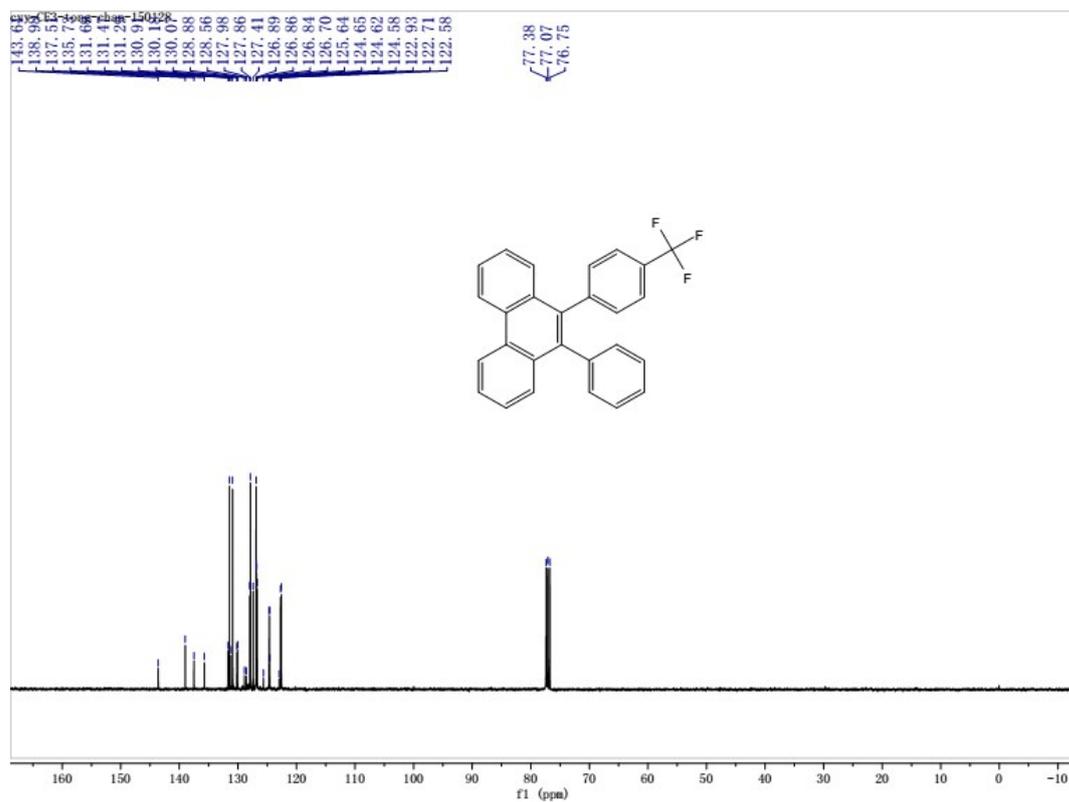
8.79536  
8.7756  
7.6390  
7.6152  
7.5865  
7.5528  
7.5324  
7.4782  
7.4618  
7.2417  
7.2244  
7.2072  
7.1919  
7.1501  
7.1337  
7.0573  
6.7744  
6.7568  
3.7555  
0.0000



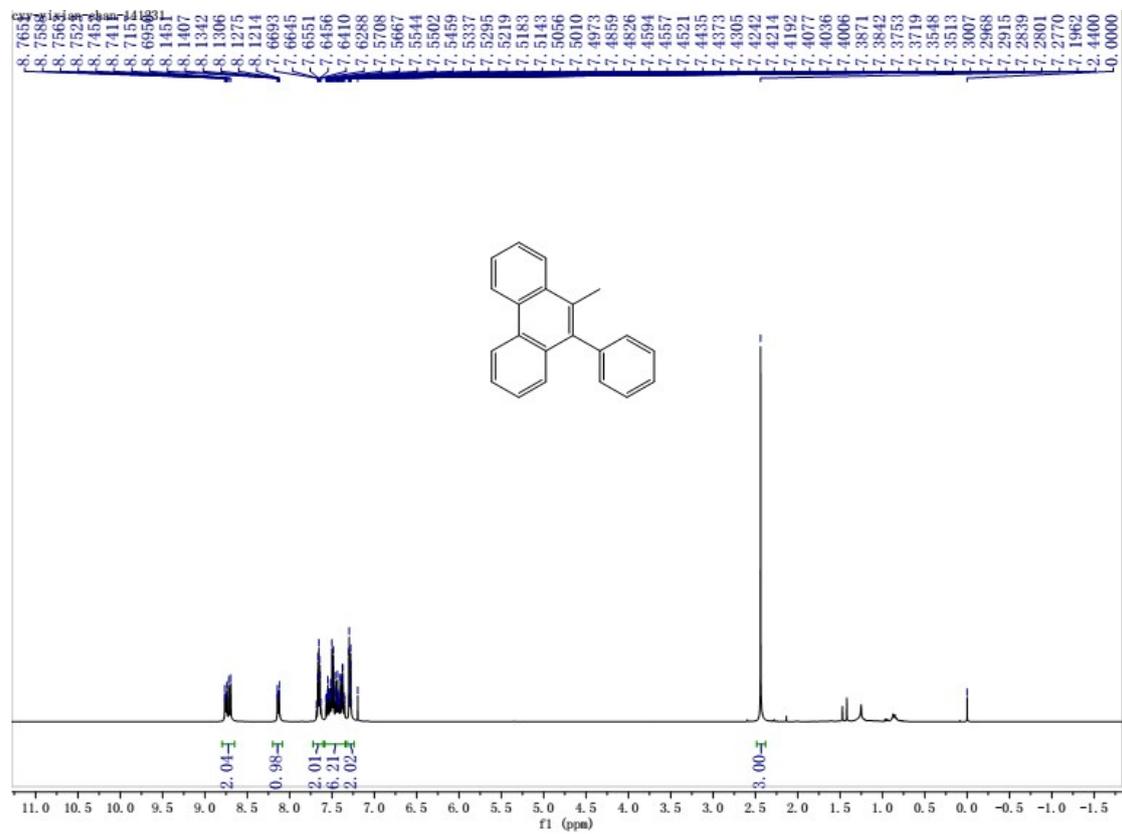


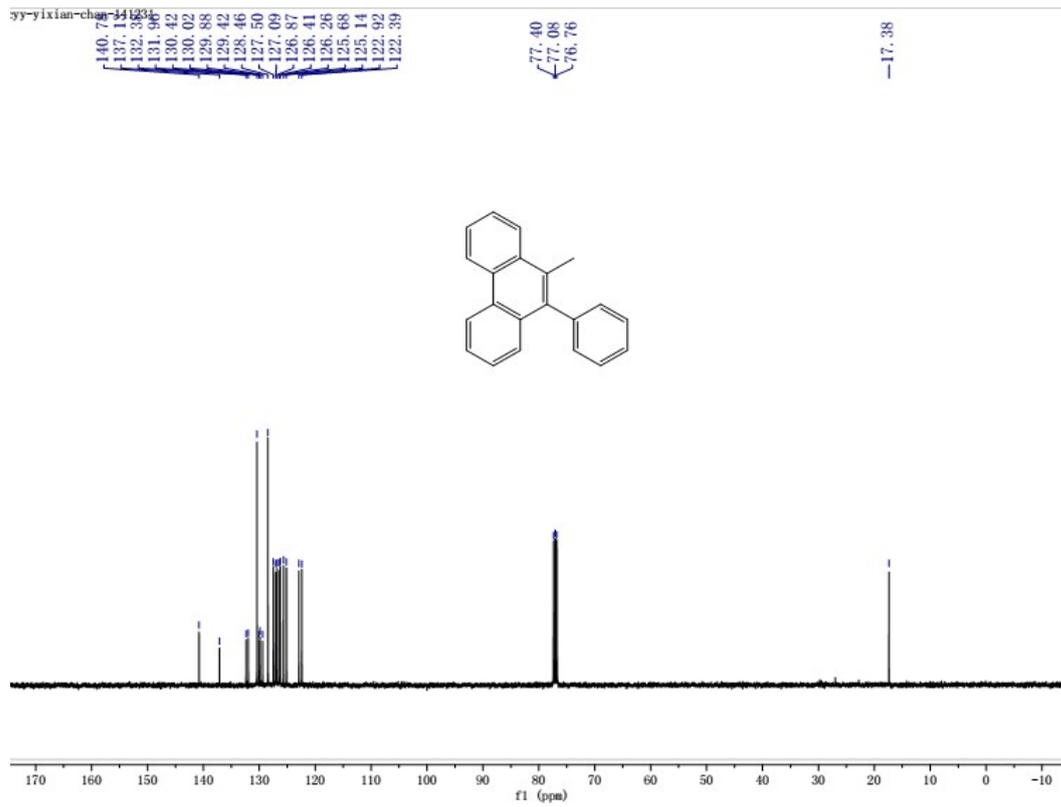
### <sup>1</sup>H-NMR and <sup>13</sup>C-NMR of 4e



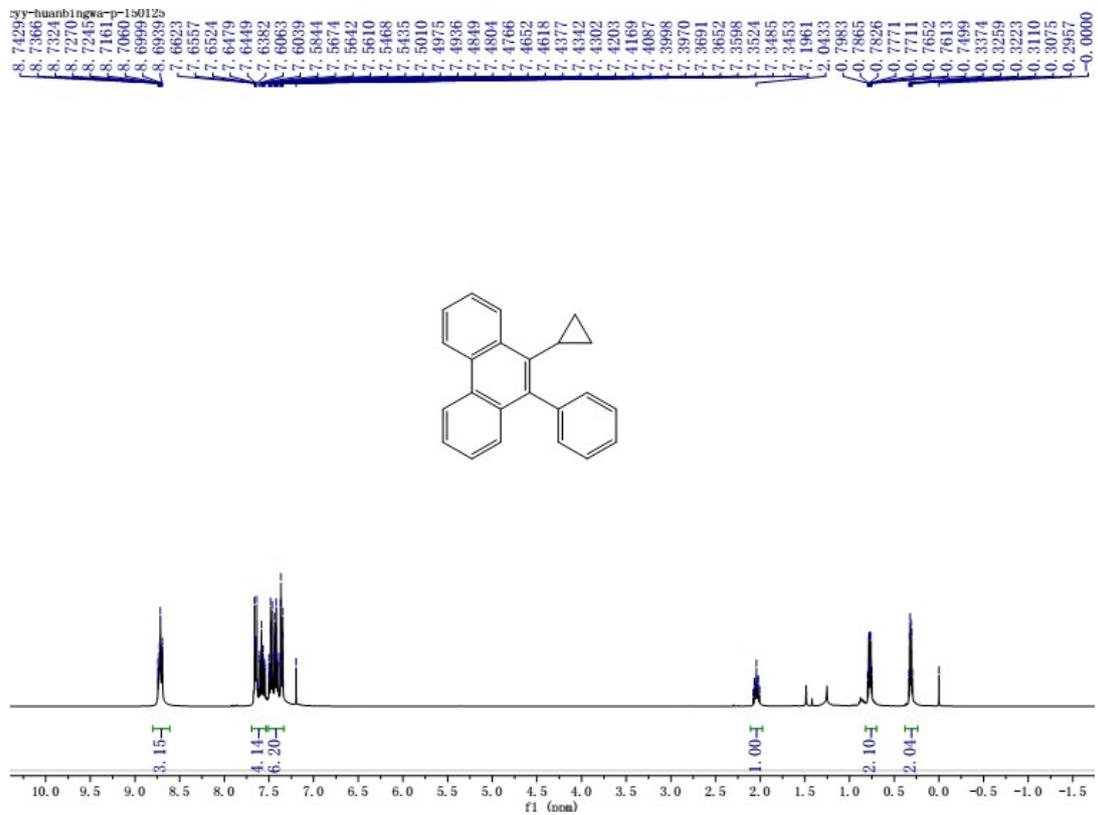


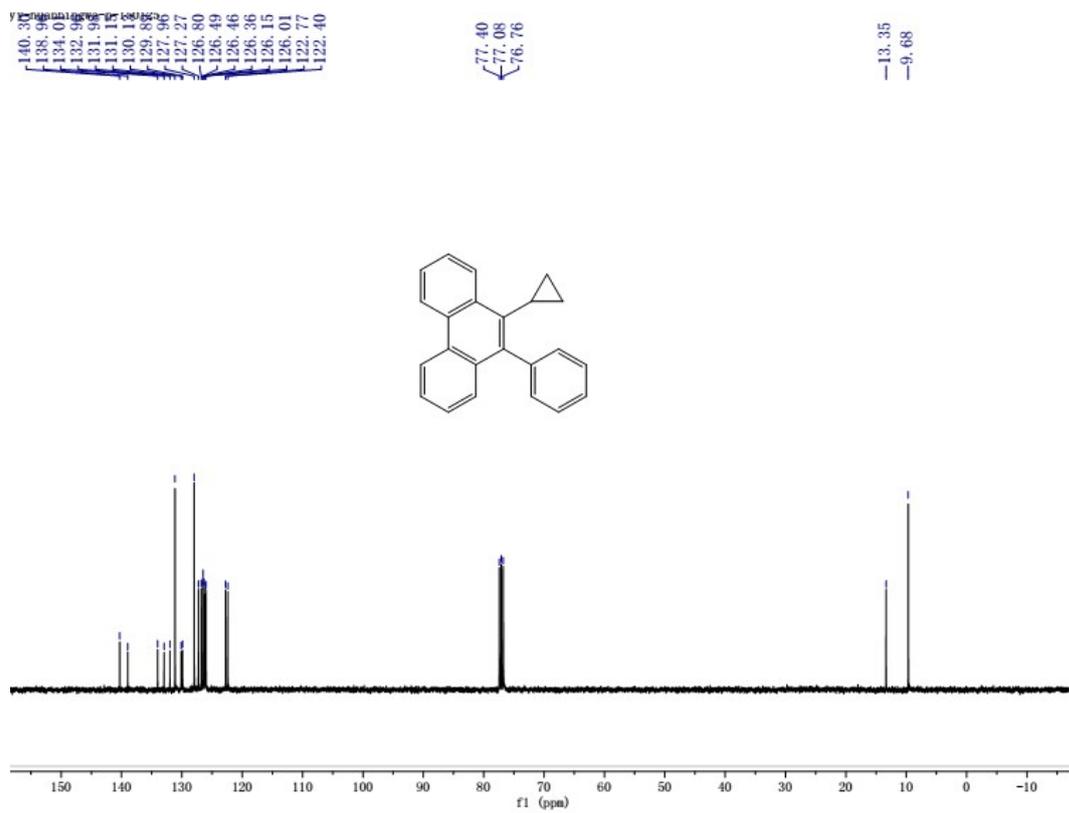
**<sup>1</sup>H NMR and <sup>13</sup>C NMR of 4f**



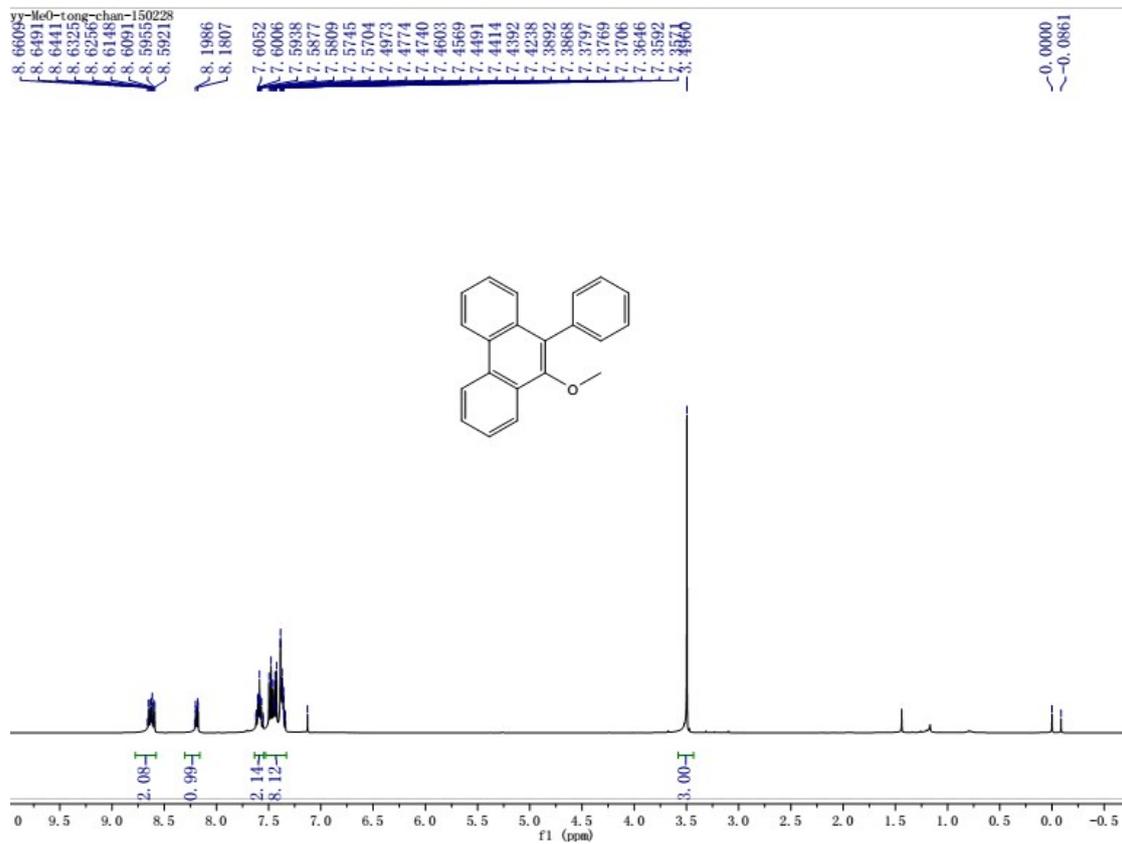


### $^1\text{H}$ NMR and $^{13}\text{C}$ NMR of 4g





### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4h

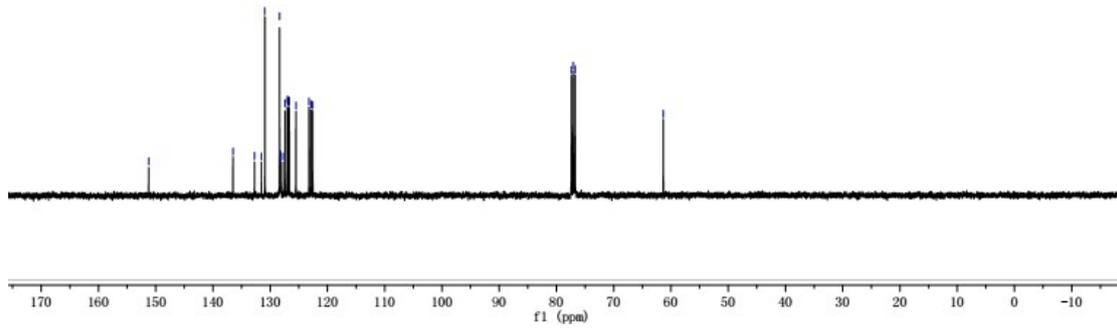
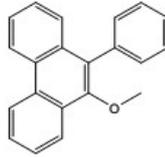


py-MeO-tong-cha-10877

151.21  
136.54  
132.74  
131.94  
130.93  
128.36  
128.27  
128.20  
127.83  
127.40  
127.01  
126.95  
126.72  
126.66  
125.51  
123.22  
122.89  
122.57

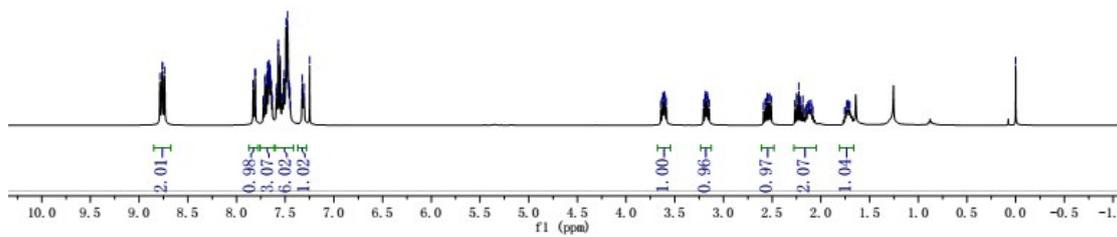
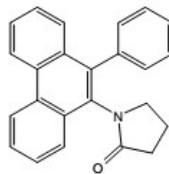
77.39  
77.07  
76.75

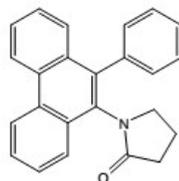
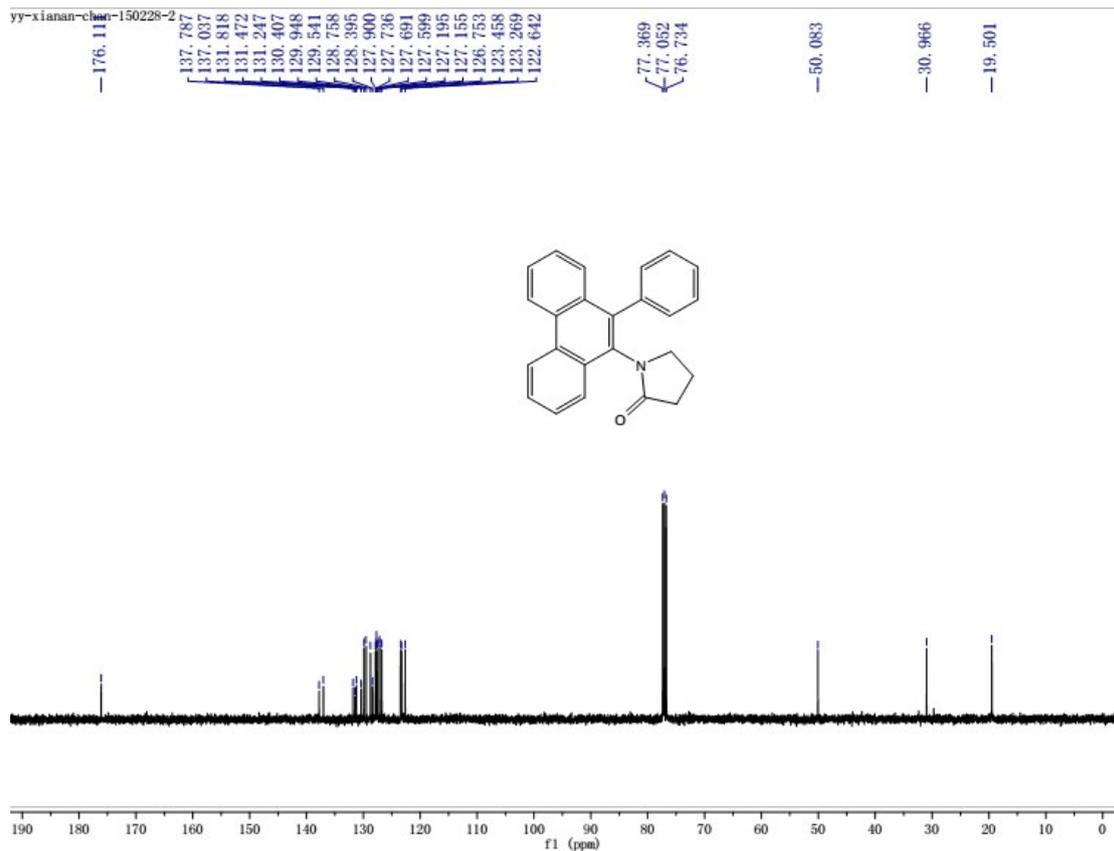
-61.32



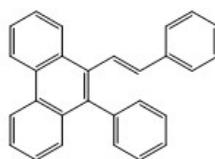
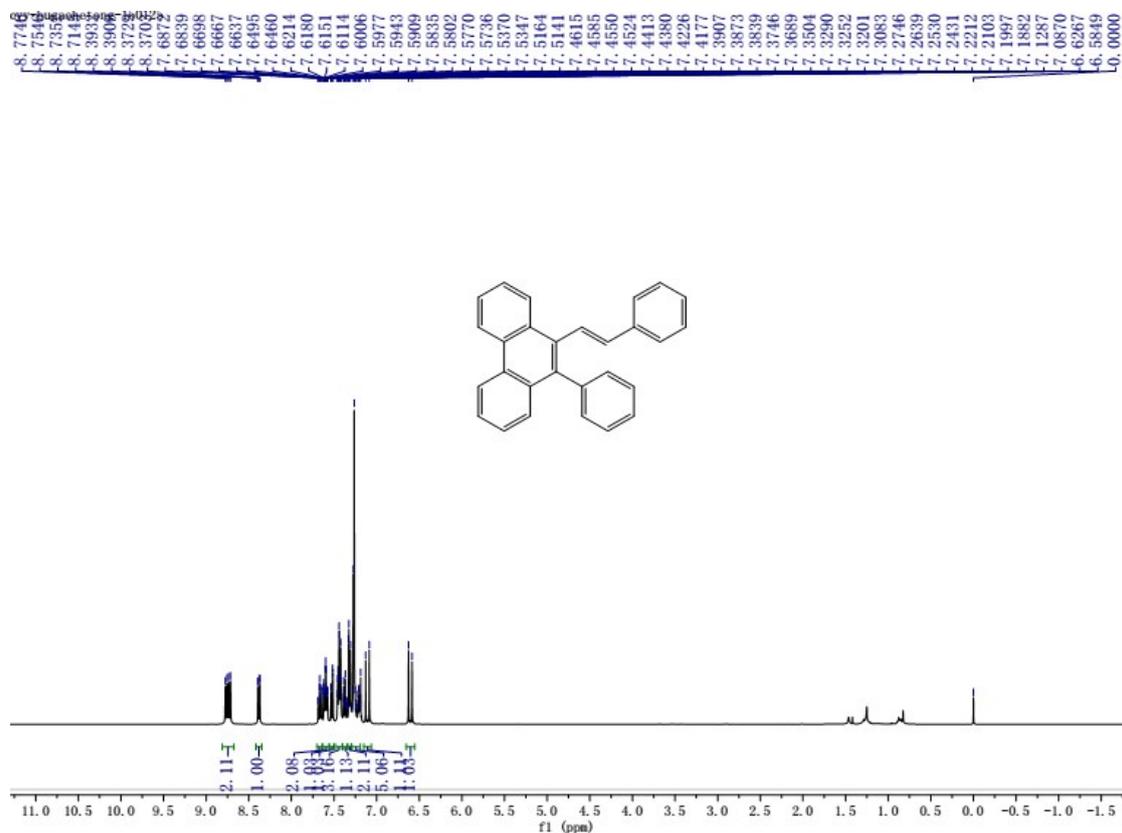
### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4i

8.7844  
8.7634  
8.7593  
8.7375  
8.8233  
8.8277  
8.8104  
8.8088  
8.7088  
8.7054  
8.6885  
8.6843  
8.6808  
8.6731  
8.6695  
8.6673  
8.6634  
8.6589  
8.6528  
8.6503  
8.6462  
8.6427  
8.6356  
8.5901  
8.5873  
8.5733  
8.5704  
8.5525  
8.5502  
8.5325  
8.5283  
8.5247  
8.5169  
8.5109  
8.4920  
8.4839  
8.4771  
8.4732  
8.4630  
8.4591  
8.4554  
8.4526  
8.4285  
8.4239  
8.3194  
8.3062  
8.2490  
8.6228  
8.6197  
8.6096  
8.6062  
8.1858  
8.1826  
8.1707  
8.1674  
8.5504  
8.5479  
8.5321  
8.5245  
8.2495  
8.2259  
0.0000





### <sup>1</sup>H NMR and <sup>13</sup>C NMR of 4j



yy-bugaohetong

