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# Fe(III)-Catalyzed Decarboxylative Cycloaddition of β-Ketoacids and 2*H*-Azirines for the Synthesis of Pyrrole Derivatives

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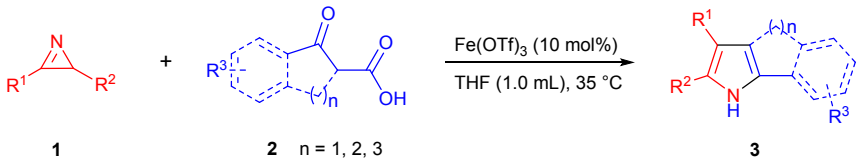
# Contents

## 1. General Information

**$^{1}$H NMR** spectra were recorded on commercial instruments (600 MHz). Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard. Spectra were reported as follows: chemical shift ($\delta$ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz), integration and assignment. **$^{13}$C{$^{1}$H} NMR** spectra were collected on commercial instruments (150 MHz) with complete proton decoupling. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard ($CDCl_3$, $\delta$ = 77.0). **$^{19}$F{$^{1}$H} NMR** spectra were collected at 565 MHz with complete proton decoupling. HRMS was recorded on a commercial apparatus (ESI Source). Solvents were dried according to standard procedures. The catalytic reactions were performed under nitrogen atmosphere. The β-ketoacids and 2*H*-azirines were prepared according to reported procedures.

## 2. General Procedure for the Domino Reaction of β-Ketoacids and 2*H*-Azirines



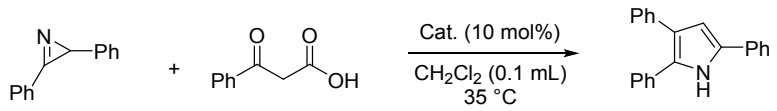

**1** **2** n = 1, 2, 3 **3**

**General procedure:**

A dry reaction tube was charged with β-ketoacid **1** (0.1 mmol), 2*H*-azirine **2** (0.1 mmol), $Fe(OTf)_3$ (5.0 mg, 10 mol%) in the glove-box, followed by adding dry THF (1.0 mL). The reaction mixture was stirred at 35 °C for the indicated time. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica gel, eluting with petroleum ether–ethyl acetate (v/v, 100:1 to 10:1) to afford the corresponding product **3**.

## 3. Optimization of Reaction Conditions

**Table S1. The screening of catalyst.**

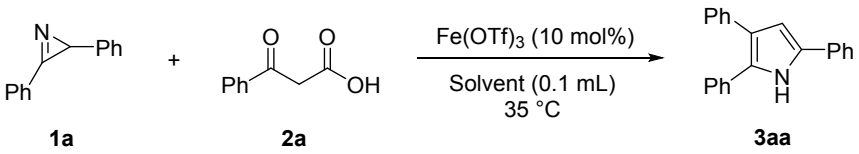



**1a** **2a** **3aa**

| Entry[a] | Cat. | Time (h) | Yield [%][b] |
|---|---|---|---|
| 1 | $Sc(OTf)_3$ | 36 | 18 |
| 2 | $Al(OTf)_3$ | 36 | 24 |
| 3 | $NiCl_2·6H_2O$ | 36 | 33 |
| 4 | $Cu(OTf)_2$ | 36 | 15 |
| 5 | $ZnCl_2$ | 36 | 45 |
| 6 | $Fe(OTf)_3$ | 36 | 60 |
| 7 | $Co(ClO_4)_2·6H_2O$ | 36 | 42 |
| 8 | $Fe(OTf)_2$ | 36 | 51 |
| 9 | $FeCl_2$ | 36 | 48 |
| 10 | $FeCl_3$ | 36 | 54 |
| 11 | TFA | 36 | NR |

[a] All the reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), Metal Salts (10 mol%) in $CH_2Cl_2$ (1.0 mL) at 35 °C under $N_2$ atmosphere for the indicated time. [b] The yield was determined by $^1H$ NMR by using dimethyl terephthalate as internal standard; NR = No Reaction.

## Table S2. The screening of solvents

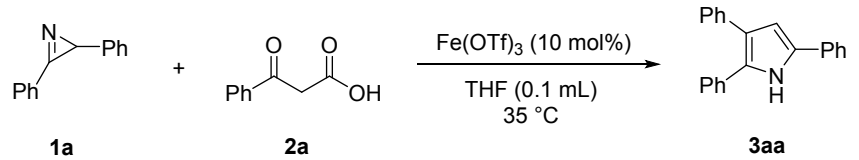



**1a** **2a** **3aa**

| Entry[a] | Solvent | Time (h) | Yield [%][b] |
|---|---|---|---|
| 1 | $CH_2Cl_2$ | 36 | 60 |
| 2 | THF | 36 | 90 |
| 3 | toluene | 36 | 33 |
| 4 | Acetone | 36 | 48 |
| 5 | 1,4-dioxane | 36 | 51 |
| 6 | DMF | 36 | 69 |
| 7[c] | THF | 36 | <5 |
| 8[d] | THF | 36 | 87 |

[a] All the reactions were performed with **1a** (0.10 mmol), **2a** (0.10 mmol), $Fe(OTf)_3$ (10 mol%) in solvent (1.0 mL) at 35 °C under $N_2$ atmosphere for 36 h. [b] The yield was determined by $^1H$ NMR by using dimethyl terephthalate as internal standard; NR = No Reaction. [c] The reaction temperature was 0 °C. [d] The reaction temperature was 50 °C.

## Table S3. The ratio of β-ketoacids to 2*H*-azirines



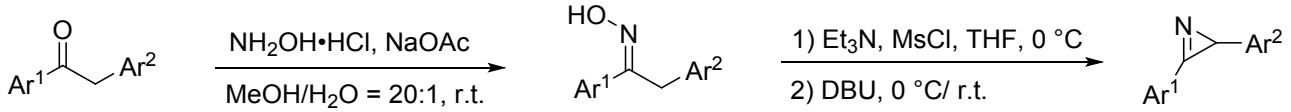

**1a** **2a** **3aa**

| Entry[a] | **1a**:**2a** (x:y) | Time (h) | Yield [%][b] |
|---|---|---|---|
| 1 | 1:1.2 | 36 | 87 |
| 2 | 1:1 | 36 | 90(88)[e] |
| 3 | 1.2:1 | 36 | 87 |
| 4[c] | 1:1 | 36 | 84 |
| 5[d] | 1:1 | 36 | 42 |

[a] All the reactions were performed with **1a** (x mmol), **2a** (y mmol), $Fe(OTf)_3$ (10 mol%) in solvent (1.0 mL) at 35 °C under $N_2$ atmosphere for 36 h. [b] The yield was determined by $^1H$ NMR by using dimethyl terephthalate as internal standard; NR = No Reaction. [c] The catalyst loading was 5 mol%. [d] The catalyst loading was 20 mol%. [e] Isolated yield.

# 4. Methods for the Synthesis of Substrates

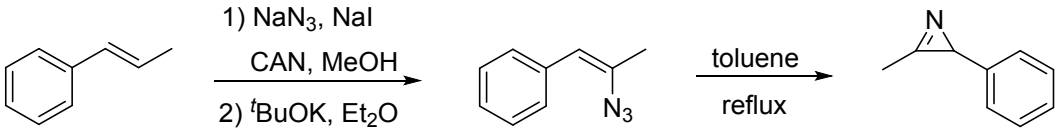
4.1 2*H*-azirines (**1a-1l, 1n-1q**) were prepared according to the following procedures.[1]




A dry reaction tube was charged with ketone (1.0 equiv), $NH_2OH{\cdot}HCl$ (1.5 equiv) and sodium acetate (1.5 equiv), followed by adding mixed solvent MeOH/$H_2O$ (20:1). The reaction mixture was stirred at room temperature and monitored by TLC. After the reaction completed, the solution was sequentially washed with $H_2O$, sat. $NaHCO_3$ and brine. The obtained organic layer was dried over $Na_2SO_4$ and the solvent was removed under reduced pressure. The obtained product **3** was used directly for the next step.

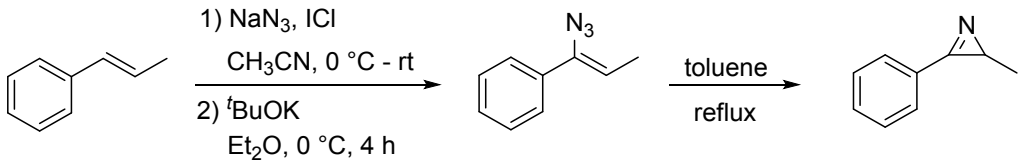
The MsCl (1.5 equiv) was added to the mixture of oxime (1.0 equiv) and $Et_3N$ (1.5 equiv) in dry THF at 0 °C. The resulting mixture was stirred for 30 minutes and DBU (1.5 equiv) was then added. After an additional 30 minutes, the reaction mixture was passed through a pad of silica gel, washing with EA. The mixture was concentrated in vacuo and the resulting residue was purified by column chromatography on silica gel to give the target 2*H*-azirine.

4.2 Procedures for the preparation of **1m.**[2]




A dry reaction tube was charged with $NaN_3$ (1.3 equiv), NaI (1.3 equiv) and *trans*-prophenylbenzene (1.0 equiv), followed by adding MeOH. Then, a solution of CAN in MeOH was added dropwise to the mixture at 0 °C. After completed, the reaction was quenched with sat. $NaHSO_3$ and extracted with $CH_2Cl_2$. The combined organic layer was washed with water, brine and dried over $Na_2SO_4$. The solvent was removed under reduced pressure and the obtained residue was purified by flash chromatography. The azide derivative was dissolved in toluene and heated to reflux for 4 h. The solvent was removed and the residue was purified by flash chromatography to give the 2*H*-azirine.

4.3 2*H*-azirine **1r/1u/1v** were synthesized according to the reported procedures.[2a]

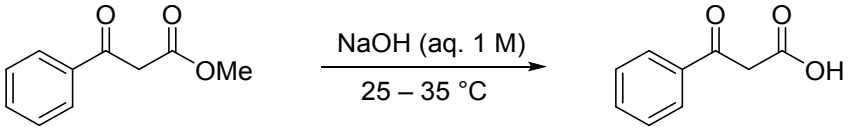



ICl (2.5 equiv) was added dropwise to the solution of $NaN_3$ (1.3 equiv) in $CH_3CN$ at 0 °C by using a dropping funnel. The resulting mixture was stirred for 10 minutes and the *trans*-prophenylbenzene (1.0 equiv) was added from another dropping funnel. The reaction mixture was monitored by TLC. After the reaction completed, the solution was poured into water and extracted with $Et_2O$. The combined organic solvent was washed with 5% thiosulfate, water and dried over $MgSO_4$. The solvent was removed under reduced pressure and the crude product was used directly without any further purification.

The obtained product was dissolved in dry $Et_2O$ and the mixture was cooled to 0 °C. Then, $^t$BuOK was added in portion and reaction mixture was stirred at 0 °C and monitored by TLC. After the reaction completed, the solution was washed with water. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. The resulting residue was purified by column chromatography to deliver the target product. The azide derivative was dissolved in toluene and heated to reflux for 4 h. The solvent was removed and the residue was purified by flash chromatography to give the 2*H*-azirine.

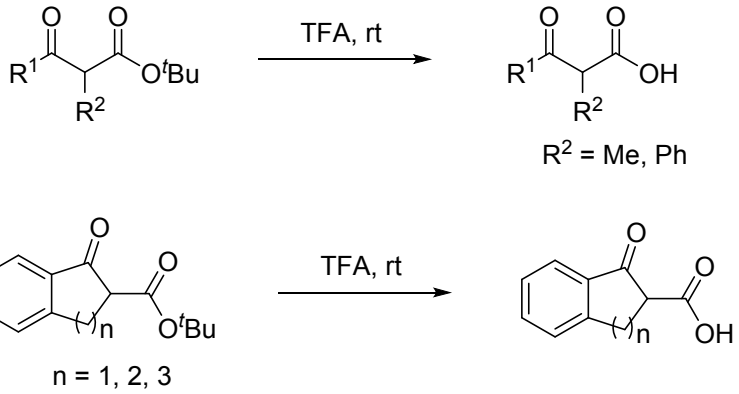
4.4 2*H*-azirine **1s/1t** was synthesized from the reflux of corresponding vinyl azides in toluene.[2b]

4.5 β-Ketoacids (**2a-2l**) were prepared according to the reported procedures.[3]




β-Ketoester was hydrolyzed by using NaOH (aq. 1M) at room temperature. After the β-ketoester consumed up, the resulting solution was extracted with $CH_2Cl_2$ for three times. The aqueous layer were combined and acidified at 0 °C until lots of white solid appeared. Then, the mixture was extracted with $CH_2Cl_2$ for three times, the combined organic layer was dried over $Na_2SO_4$ and the solvent was removed under reduced pressure to give the β-ketoacid.

4.6 Procedures for the preparation of β-ketoacids **2m-2q**.[4]




β-Ketoester was hydrolyzed by using TFA at room temperature. After the β-ketoester consumed up, TFA was removed under reduced pressure. The resulting residue was purified by flash chromatography to give the β-ketoacids.

## 5. References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1*H*-pyrroles by ligand-controlled site-selective dearomative C2-arylation and direct C3-arylation, *Org. Let*, 2019, **21**, 6972.

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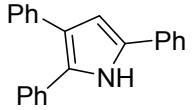
## 6. Characterization of the Products



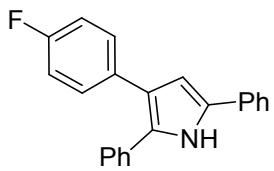

**2,3,5-triphenyl-1*H*-pyrrole (3aa)[5]**

Following the general procedure, the optimized time is 36 h. Yield: 88% (26.0 mg); **3aa** was obtained as a white solid; m.p. 128-131 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.41 (dt, *J* = 7.5, 3.8 Hz, 6H), 7.32 (dt, *J* = 21.0, 7.5 Hz, 5H), 7.22 (t, *J* = 7.5 Hz, 2H), 6.72 (s, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.37, 132.24, 129.01, 128.75, 128.45, 128.36, 127.50, 127.01, 126.56, 125.98, 123.86, 123.82, 108.61;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{17}N + H^+$]: 296.1439, found 296.1433.




**3-(4-fluorophenyl)-2,5-diphenyl-1*H*-pyrrole (3ba)[5]**

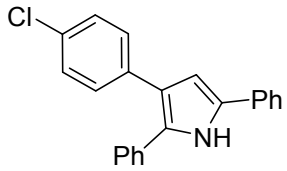
Following the general procedure, the optimized time is 36 h. Yield: 87% (27.2 mg); **3ba** was obtained as a white solid; m.p. 155-156 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.58 – 7.54 (m, 2H), 7.45 – 7.38 (m, 4H), 7.35 (ddd, *J* = 9.0, 6.5, 3.1 Hz, 4H), 7.32 – 7.26 (m, 2H), 7.03 – 6.97 (m, 2H), 6.67 (d, *J* = 2.9 Hz, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 161.52 (d, *J* = 242.7 Hz), 132.92, 132.42, 132.39, 132.31, 132.15, 129.93 (d, *J* = 7.6 Hz), 129.26, 129.05, 128.83, 127.47, 126.88 (d, *J* = 67.4 Hz), 123.84, 122.87, 115.24 (d, *J* = 21.5 Hz), 108.50;

**$^{19}$F{$^1$H} NMR** (565 MHz, $CDCl_3$) δ 117.02;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}FN + H^+$]: 314.1340, found 314.1338.



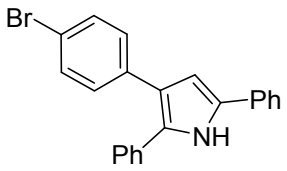

**3-(4-chlorophenyl)-2,5-diphenyl-1*H*-pyrrole (3ca)[5]**

Following the general procedure, the optimized time is 48 h. Yield: 83% (27.3 mg); **3ca** was obtained as a yellow solid; m.p. 131-132 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 7.56 – 7.53 (m, 2H), 7.43 – 7.27 (m, 10H), 7.25 (d, *J* = 6.5 Hz, 2H), 6.67 (d, *J* = 2.9 Hz, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 133.82, 131.76, 131.41, 131.01, 130.63, 128.58, 128.49, 128.00, 127.83, 127.48, 126.51, 126.21, 125.67, 122.80, 121.54, 107.24;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}ClN + H^+$]: 330.1044; Found: 330.1040.



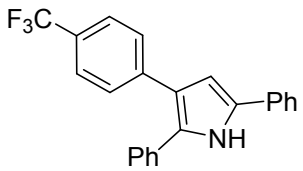

**3-(4-bromophenyl)-2,5-diphenyl-1*H*-pyrrole (3da)[5]**

Following the general procedure, the optimized time is 48 h. Yield: 78% (29.1 mg); **3da** was obtained as a white solid; m.p. 147-149 °C.

**$^1$H NMR** (600 MHz, Chloroform-d) δ 8.43 (s, 1H), 7.55 (d, *J* = 7.6 Hz, 2H), 7.41 (td, *J* = 9.7, 8.7, 6.6 Hz, 6H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.32 – 7.26 (m, 3H), 7.25 (d, *J* = 3.2 Hz, 1H), 6.67 (d, *J* = 2.9 Hz, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 135.34, 132.79, 132.48, 132.04, 131.47, 129.98, 129.55, 129.05, 128.89, 127.57, 127.28, 126.72, 123.85, 122.56, 119.77, 108.22;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}BrN + H^+$]: ($Br^{79}$) 374.0539, found 374.0531; ($Br^{81}$) 376.0518, found 376.0512.




**2,5-diphenyl-3-(4-(trifluoromethyl)phenyl)-1*H*-pyrrole (3ea)[6]**

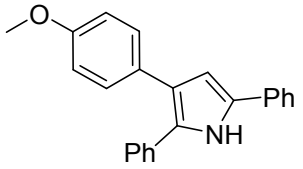
Following the general procedure, the optimized time is 24 h. Yield: 88% (32.2 mg); **3ea** was obtained as a yellow oil.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.46 (dd, *J* = 16.2, 8.0 Hz, 4H), 7.40 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.27 (m, 6H), 7.21 (dt, *J* = 25.1, 7.0 Hz, 2H), 6.63 (d, *J* = 2.9 Hz, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 139.03, 131.60, 130.89, 129.14, 128.03, 127.92, 127.26, 126.83, 126.70, 126.62, 126.48, 125.79, 124.24 (q, *J* = 3.4 Hz), 122.85, 122.54, 121.26, 107.16;

**$^{19}$F{$^1$H} NMR** (565 MHz, $CDCl_3$) δ -62.22;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{16}F_3N$ + $H^+$]: 364.1313, found 364.1313.



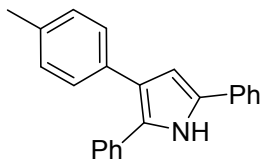

**3-(4-methoxyphenyl)-2,5-diphenyl-1*H*-pyrrole (3fa)[6]**

Following the general procedure, the optimized time is 36 h. Yield: 75% (24.5 mg); **3fa** was obtained as a white solid; m.p. 116-118 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.56 (s, 1H), 7.96 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.46 – 7.37 (m, 6H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 (s, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 3.90 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 158.06, 133.21, 132.14, 129.54, 129.00, 128.89, 128.73, 127.36, 126.84, 126.49, 123.80, 123.57, 113.84, 108.59, 55.26;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}NO$ + $H^+$]: 326.1539, found 326.1534.



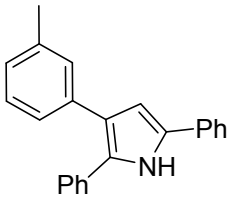

**2,5-diphenyl-3-(*p*-tolyl)-1*H*-pyrrole (3ga)[5]**

Following the general procedure, the optimized time is 36 h. Yield: 86% (26.7 mg); **3ga** was obtained as a yellow solid; m.p. 122-124 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.56 (d, *J* = 7.7 Hz, 2H), 7.41 (q, *J* = 7.8, 7.3 Hz, 4H), 7.36 – 7.29 (m, 4H), 7.28 (s, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 2H), 6.69 (d, *J* = 2.9 Hz, 1H), 2.36 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 135.55, 133.41, 133.21, 132.30, 132.18, 129.10, 129.00, 128.72, 128.32, 127.45, 126.90, 126.50, 123.82, 108.65, 21.19;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}NO$ + $H^+$]: 310.1590, found 310.1583.



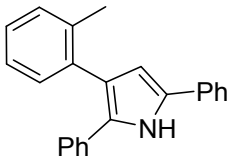

**2,5-diphenyl-3-(*m*-tolyl)-1*H*-pyrrole (3ha)[7]**

Following the general procedure, the optimized time is 48 h. Yield: 84% (26.1 mg); **3ha** was obtained as yellow oil.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.49 (s, 2H), 7.35 (d, *J* = 7.9 Hz, 4H), 7.28 (d, *J* = 8.0 Hz, 1H), 7.24 – 7.14 (m, 4H), 7.12 (d, *J* = 3.9 Hz, 2H), 6.99 (s, 1H), 6.64 (s, 1H), 2.27 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 137.89, 136.29, 133.16, 132.31, 129.15, 129.00, 128.70, 128.22, 127.43, 126.94, 126.76, 126.52, 125.61, 123.97, 123.81, 108.71, 21.50;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}NO + H^+$]: 310.1590, found 310.1590.



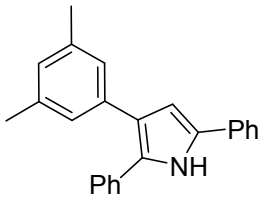

**2,5-diphenyl-3-(*o*-tolyl)-1*H*-pyrrole (3ia)[5]**

Following the general procedure, the optimized time is 72 h. Yield: 51% (15.8 mg); **3ia** was obtained as a white solid; m.p. 137-138 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.51 (s, 1H), 7.60 – 7.49 (m, 2H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.28 (m, 1H), 7.25 – 7.07 (m, 9H), 6.55 (s, 1H), 2.13 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.84, 130.89, 130.14, 129.01, 128.73, 126.88, 125.75, 123.71, 110.05, 20.39;

**HRMS (ESI-TOF)**: calcd for [$C_{24}H_{22}N_2O + Na^+$]: 310.1590, found 377.1589.



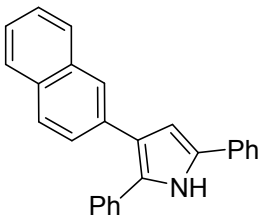

**3-(3,5-dimethylphenyl)-2,5-diphenyl-1*H*-pyrrole (3ja)**

Following the general procedure, the optimized time is 36 h. Yield: 90% (29.1 mg); **3ja** was obtained as a yellow oil.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.42 (q, *J* = 8.1, 7.6 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.27 (m, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.06 (d, *J* = 1.7 Hz, 2H), 6.90 (s, 1H), 6.71 (d, *J* = 2.9 Hz, 1H), 2.29 (s, 6H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 137.73, 128.97, 128.63, 127.69, 127.33, 127.31, 126.87, 126.84, 126.45, 126.30, 124.04, 123.77, 108.80, 21.34;

**HRMS (ESI-TOF)**: calcd for [$C_{24}H_{21}N + H^+$]: 324.1747, found 324.1747.



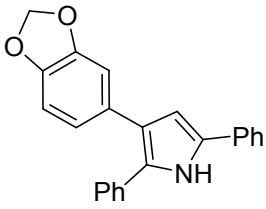
**3-(naphthalen-2-yl)-2,5-diphenyl-1*H*-pyrrole (3ka)**

Following the general procedure, the optimized time is 36 h. Yield: 92% (31.8 mg); **3ka** was obtained as a brown solid; m.p. 78-81 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.48 (s, 1H), 7.91 (s, 1H), 7.81 (d, *J* = 7.7 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.59 (d, *J* = 7.4 Hz, 2H), 7.49 (dd, *J* = 8.5, 2.7 Hz, 1H), 7.44 (s, 3H), 7.42 (d, *J* = 8.6 Hz, 3H), 7.35 – 7.31 (m, 2H), 7.27 (d, *J* = 5.6 Hz, 2H), 6.83 (s, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 133.99, 133.83, 133.05, 132.48, 132.25, 132.06, 129.68, 129.05, 128.80, 127.84, 127.71, 127.53, 127.50, 127.11, 126.63, 126.42, 125.92, 125.32, 123.88, 123.81, 108.82;

ESI-HRMS calcd for [$C_{26}H_{19}N + H^+$]: 346.1590, found 346.1583.



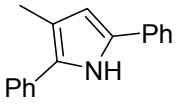
**3-(benzo[*d*][1,3]dioxol-5-yl)-2,5-diphenyl-1*H*-pyrrole (3la)**

Following the general procedure, the optimized time is 36 h. Yield: 87% (29.7 mg); **3la** was obtained as a white solid; m.p. 124-128 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.31 (s, 1H), 7.46 (d, *J* = 7.7 Hz, 2H), 7.33 (d, *J* = 7.7 Hz, 4H), 7.26 (q, *J* = 7.9 Hz, 2H), 7.17 (s, 2H), 6.84 – 6.75 (m, 2H), 6.70 – 6.66 (m, 1H), 6.55 (s, 1H), 5.87 (d, *J* = 2.7 Hz, 2H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 147.55, 145.92, 133.00, 132.22, 132.10, 130.44, 129.05, 129.01, 128.77, 127.44, 126.97, 126.55, 123.80, 123.62, 121.78, 109.14, 108.63, 108.38, 100.84;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{17}NO_2 + H^+$]: 340.1332, found 340.1331.



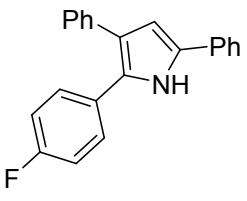
**3-methyl-2,5-diphenyl-1*H*-pyrrole (3ma)[8]**

Following the general procedure, the optimized time is 48 h. Yield: 58% (13.5 mg); **3ma** was obtained as a white solid; m.p. 98-100 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.36 – 8.19 (m, 1H), 7.49 (t, *J* = 8.0 Hz, 4H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.7 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.20 (t, *J* = 7.4 Hz, 1H), 6.45 (d, *J* = 2.9 Hz, 1H), 2.31 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 133.16, 132.50, 131.22, 128.93, 128.81, 126.30, 126.19, 123.66, 118.19, 110.01, 12.62;

**HRMS (ESI-TOF)**: calcd for [$C_{17}H_{15}N + H^+$]: 234.1277, found 234.1278.



**2-(4-fluorophenyl)-3,5-diphenyl-1*H*-pyrrole (3na)[5]**

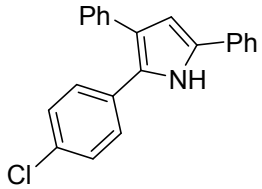
Following the general procedure, the optimized time is 33 h. Yield: 80% (25.1 mg); **3na** was obtained as a white solid; m.p. 113-115 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.56 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 8.4 Hz, 4H), 7.30 (d, *J* = 7.7 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.05 (s, 2H), 6.71 (s, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 162.00 (d, *J* = 244.5 Hz), 136.16, 132.22 (d, *J* = 9.0 Hz), 129.33 (d, *J* = 4.5 Hz), 129.30, 129.03, 128.41 (d, *J* = 9.0 Hz), 126.64, 126.06, 123.84, 115.78 (d, *J* = 21.0 Hz), 108.48;

**$^{19}$F{$^1$H} NMR** (565 MHz, $CDCl_3$) δ -114.66;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}FN + H^+$]: 314.1340, found 314.1342.



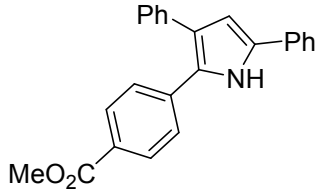

**2-(4-chlorophenyl)-3,5-diphenyl-1*H*-pyrrole (3oa)[5]**

Following the general procedure, the optimized time is 30 h. Yield: 82% (27.0 mg); **3oa** was obtained as a white solid; m.p. 107-109 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.56 (d, *J* = 7.5 Hz, 2H), 7.42 (d, *J* = 7.9 Hz, 2H), 7.38 (d, *J* = 7.6 Hz, 2H), 7.31 (q, *J* = 8.8, 8.3 Hz, 6H), 7.24 (s, 1H), 6.70 (s, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.09, 132.72, 132.69, 132.06, 131.52, 129.05, 128.97, 128.64, 128.49, 128.46, 128.05, 126.76, 126.22, 124.39, 123.90, 108.82;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}ClN + H^+$]: 330.1044, found 330.1032.



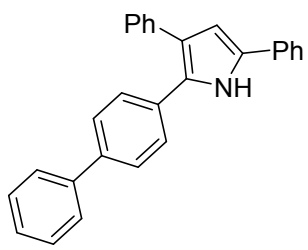

**methyl 4-(3,5-diphenyl-1*H*-pyrrol-2-yl)benzoate (3pa)**

Following the general procedure, the optimized time is 43 h. Yield: 72% (25.4 mg); **3pa** was obtained as a yellow solid; m.p. 220-225 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 8.01 – 7.93 (m, 2H), 7.63 – 7.56 (m, 2H), 7.45 – 7.37 (m, 6H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.26 (m, 1H), 7.24 (d, *J* = 1.6 Hz, 1H), 6.69 (d, *J* = 2.8 Hz, 1H), 3.90 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 166.89, 137.34, 136.03, 133.39, 131.87, 130.02, 129.02, 128.59, 128.49, 127.99, 127.91, 126.90, 126.67, 126.41, 125.69, 124.01, 109.35, 52.09;

**HRMS (ESI-TOF)**: calcd for [$C_{24}H_{19}NO_2 + H^+$]: 354.1489, found 354.1488.




**2-([1,1'-biphenyl]-4-yl)-3,5-diphenyl-1*H*-pyrrole (3qa)**

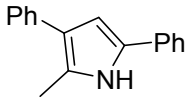
Following the general procedure, the optimized time is 48 h. Yield: 88% (32.6

mg); **3qa** was obtained as a white solid; m.p. 160-163 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.47 (s, 1H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.59 (d, *J* = 8.0 Hz, 4H), 7.48 (dd, *J* = 7.2, 4.3 Hz, 6H), 7.44 (dd, *J* = 13.8, 6.1 Hz, 3H), 7.37 (dt, *J* = 15.0, 7.5 Hz, 3H), 7.28 (d, *J* = 7.4 Hz, 2H), 6.75 (d, *J* = 3.0 Hz, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 140.43, 139.46, 136.36, 132.09, 131.90, 128.97, 128.80, 128.48, 128.37, 127.64, 127.33, 127.29, 126.84, 126.55, 126.02, 124.11, 123.80, 108.79;

**HRMS (ESI-TOF)**: calcd for [$C_{28}H_{21}N + H^+$]: 372.1747, found 372.1742.



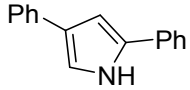

**2-methyl-3,5-diphenyl-1*H*-pyrrole (3ra)[10]**

Following the general procedure, the optimized time is 72 h. Yield: 47% (11.1 mg); **3ra** was obtained as a yellow oil.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.51 – 7.46 (m, 4H), 7.38 (dt, *J* = 15.3, 7.7 Hz, 4H), 6.64 (d, *J* = 2.9 Hz, 1H), 2.48 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.75, 132.57, 130.17, 129.05, 128.90, 128.43, 127.56, 125.98, 125.38, 123.44, 122.94, 106.30, 12.85;

**HRMS (ESI-TOF)**: calcd for [$C_{17}H_{15}N + H^+$]: 234.1277, found 234.1275.



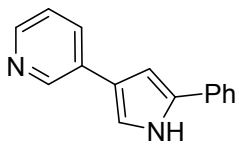

**2,4-diphenyl-1*H*-pyrrole (3sa)[9]**

Following the general procedure, the optimized time is 48 h. Yield: 60% (13.1 mg); **3sa** was obtained as a white solid; m.p. 178-179 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.42 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 2H), 7.50 (dt, *J* = 5.7, 2.6 Hz, 2H), 7.40 – 7.33 (m, 4H), 7.14 – 7.09 (m, 1H), 6.86 – 6.79 (m, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 135.53, 133.10, 132.50, 128.99, 128.70, 126.63, 126.53, 125.78, 125.21, 123.88, 115.61, 103.99;

**HRMS (ESI-TOF)**: [$C_{16}H_{13}N + H^+$]: 220.1121, found 220.1116.




**3-(5-phenyl-1*H*-pyrrol-3-yl)pyridine (3ta)**

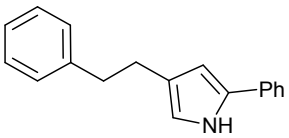
Following the general procedure, the optimized time is 48 h. Yield: 40% (8.9 mg); **3ta** was obtained as a white solid; m.p. 141-143 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.85 (d, *J* = 2.4 Hz, 1H), 8.79 (s, 1H), 8.43 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.84 (dt, *J* = 7.8, 1.9 Hz, 1H), 7.56 – 7.53 (m, 2H), 7.41 (t, *J* = 7.8 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.20 (dd, *J*

= 2.7, 1.7 Hz, 1H), 6.82 (dd, *J* = 2.8, 1.7 Hz, 1H);

**$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 146.57, 146.47, 132.39, 132.17, 129.04, 126.84, 124.02, 123.67, 116.01, 103.73;

**HRMS (ESI-TOF)**: [$C_{15}H_{12}N_2$ + $Na^+$]: 243.0893, found 243.0886.



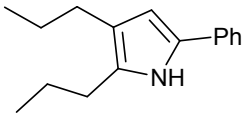

**4-phenethyl-2-phenyl-1*H*-pyrrole (3ua)**

Following the general procedure, the optimized time is 48 h. Yield: 17% (4.3 mg); **3ua** was obtained as a purple solid; m.p. 143-146 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.20 (s, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24 (d, *J* = 7.4 Hz, 2H), 7.20 (dt, *J* = 11.0, 5.3 Hz, 2H), 6.62 (s, 1H), 6.41 (s, 1H), 2.94 (dd, *J* = 9.8, 6.4 Hz, 2H), 2.83 (dd, *J* = 9.8, 6.4 Hz, 2H);

**$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 142.46, 128.86, 128.49, 128.27, 126.07, 125.77, 123.67, 116.24, 106.34, 37.50, 29.11;

**HRMS (ESI-TOF)**: [$C_{18}H_{17}N$ + $Na^+$]: 270.1253, found 270.1263.



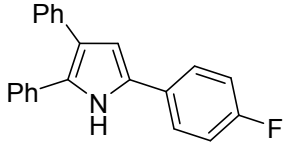

**5-phenyl-2,3-dipropyl-1*H*-pyrrole (3va)**

Following the general procedure, the optimized time is 48 h. Yield: 48% (11.6 mg); **3va** was obtained as a yellow oil.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.97 (s, 1H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.38 (d, *J* = 2.8 Hz, 1H), 2.61 (t, *J* = 7.7 Hz, 2H), 2.44 (t, *J* = 7.6 Hz, 2H), 1.66 (dq, *J* = 14.9, 7.4 Hz, 4H), 1.03 (td, *J* = 7.3, 3.2 Hz, 6H);

**$^{13}$C NMR** (150 MHz, $CDCl_3$) δ 133.13, 129.82, 129.30, 128.81, 125.41, 123.19, 121.63, 106.68, 36.15, 28.11, 28.03, 24.57, 23.63, 22.83, 14.23, 14.04;

**HRMS (ESI-TOF)**: [$C_{16}H_{21}N$ + $H^+$]: 228.1747, found 228.1749.




**5-(4-fluorophenyl)-2,3-diphenyl-1*H*-pyrrole (3ab)[5]**

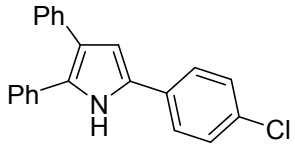
Following the general procedure, the optimized time is 36 h. Yield: 58% (18.2 mg); **3ab** was obtained as a white solid; m.p. 120-122 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.53 (d, *J* = 7.6 Hz, 2H), 7.39 (t, *J* = 7.7 Hz, 2H), 7.37 – 7.31 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 2H), 7.01 (t, *J* = 8.6 Hz, 2H), 6.68 (s, 1H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 161.73 (d, *J* = 244.5 Hz), 136.26, 133.01, 131.46, 129.36, 128.77, 128.65, 128.43, 128.39, 127.50, 127.07, 126.04, 125.51 (d, *J* = 7.5 Hz) 123.87, 115.99 (d, *J* = 21.0 Hz), 108.50;

**$^{19}F\{^1H\}$ NMR** (565 MHz, $CDCl_3$) δ -115.59;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}FN + H^+$]: 314.1340, found 314.1347.



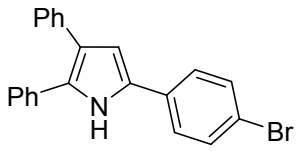

**5-(4-chlorophenyl)-2,3-diphenyl-1*H*-pyrrole (3ac)[5]**

Following the general procedure, the optimized time is 36 h. Yield: 60% (19.7 mg); **3ac** was obtained as a white solid; m.p. 109-111 °C.

**$^1H$ NMR** (600 MHz, Chloroform-*d*) δ 8.29 (s, 1H), 7.40 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 8.3 Hz, 5H), 7.29 (s, 1H), 7.25 – 7.13 (m, 6H), 6.61 (s, 1H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 136.13, 132.89, 132.08, 131.12, 130.75, 129.76, 129.17, 128.79, 128.41, 127.53, 127.18, 126.09, 124.95, 124.02, 109.01;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{16}ClN + H^+$]: 330.1044, found 330.1034.



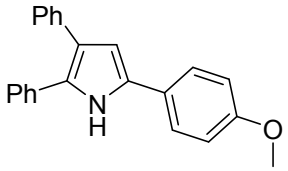

**5-(4-bromophenyl)-2,3-diphenyl-1*H*-pyrrole (3ad)[5]**

Following the general procedure, the optimized time is 36 h. Yield: 66% (24.6 mg); **3ad** was obtained as a yellow solid; m.p. 116-117 °C.

**$^1H$ NMR** (600 MHz, Chloroform-*d*) δ 8.37 (s, 1H), 7.55 – 7.50 (m, 2H), 7.40 (q, *J* = 8.5, 8.0 Hz, 6H), 7.35 – 7.32 (m, 2H), 7.29 (q, *J* = 7.2, 6.6 Hz, 3H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.70 (s, 1H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 136.10, 132.86, 132.09, 131.17, 131.10, 129.84, 128.79, 128.40, 127.52, 127.20, 126.10, 125.23, 124.06, 120.04, 109.07;

**HRMS (ESI-TOF)**: calcd for [$C_{17}H_{15}N + H^+$]: ($Br^{79}$) 374.0539, found 374.0540; ($Br^{81}$) 376.0518, found 376.0514.



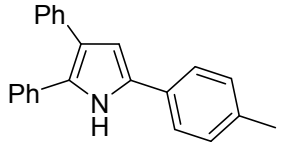

**5-(4-methoxyphenyl)-2,3-diphenyl-1*H*-pyrrole (3ae)[11]**

Following the general procedure, the optimized time is 96 h. Yield: 78% (25.4 mg); **3ae** was obtained as a white solid; m.p.183-184 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.32 (s, 1H), 7.54 – 7.44 (m, 2H), 7.40 (d, *J* = 6.2 Hz, 4H), 7.35 – 7.28 (m, 4H), 7.22 (d, *J* = 6.5 Hz, 2H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.59 (s, 1H), 3.85 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 157.53, 135.46, 127.68, 127.40, 127.29, 126.38, 125.79, 124.85, 124.23, 122.66, 113.44, 106.58, 54.34;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}NO + H^+$]: 326.1539, found 326.1535.



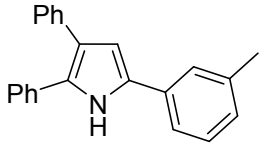

**2,3-diphenyl-5-(*p*-tolyl)-1*H*-pyrrole (3af)[5]**

Following the general procedure, the optimized time is 96 h. Yield: 81% (25.1 mg); **3af** was obtained as a white solid; m.p. 97-99 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.38 (s, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.42 (dt, *J* = 8.1, 1.5 Hz, 4H), 7.36 – 7.26 (m, 5H), 7.25 – 7.20 (m, 3H), 6.67 (d, *J* = 2.8 Hz, 1H), 2.39 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.48, 136.36, 133.20, 132.46, 129.69, 129.50, 128.93, 128.74, 128.45, 128.35, 127.48, 126.90, 125.92, 123.81, 123.76, 108.12, 21.21;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}N + H^+$]: 310.1590, found 310.1590.



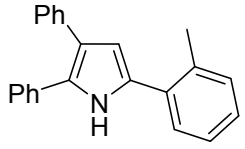

**2,3-diphenyl-5-(*m*-tolyl)-1*H*-pyrrole (3ag)[12]**

Following the general procedure, the optimized time is 40 h. Yield: 60% (18.5 mg); **3ag** was obtained as a white solid; m.p. 105-107 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.36 (s, 1H), 7.39 (dt, *J* = 8.0, 1.6 Hz, 4H), 7.36 – 7.22 (m, 8H), 7.21 – 7.17 (m, 1H), 7.05 (d, *J* = 7.4 Hz, 1H), 6.67 (d, *J* = 2.8 Hz, 1H), 2.39 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 138.62, 136.47, 133.19, 132.43, 132.20, 129.21, 128.93, 128.76, 128.72, 128.68, 128.47, 128.38, 127.53, 127.43, 126.97, 125.96, 124.60, 123.83, 121.02, 108.56, 21.61;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}N + H^+$]: 310.1590, found 310.1590.



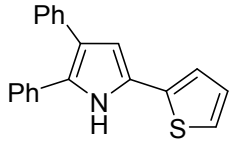

**2,3-diphenyl-5-(*o*-tolyl)-1*H*-pyrrole (3ah)[12]**

Following the general procedure, the optimized time is 42 h. Yield: 43% (13.3 mg); **3ah** was obtained as yellow solid; m.p. 131-132 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.42 (dd, *J* = 11.8, 7.4 Hz, 4H), 7.31 (ddt, *J* = 20.7, 14.4, 7.4 Hz, 7H), 7.23 (q, *J* = 7.3, 6.3 Hz, 2H), 6.55 (d, *J* = 2.9 Hz, 1H), 2.58 (s, 3H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 136.56, 135.13, 133.19, 132.26, 131.62, 131.26, 128.75, 128.50, 128.44, 128.37, 127.64, 127.43, 127.04, 126.87, 126.22, 125.88, 123.02, 111.56, 21.46;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{19}N + H^+$]: 310.1590, found 310.1594.



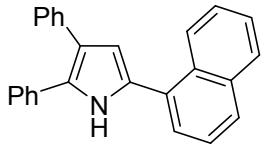
**2,3-diphenyl-5-(thiophen-2-yl)-1*H*-pyrrole (3ai)[11]**

Following the general procedure, the optimized time is 28 h. Yield: 68% (20.5 mg); **3ai** was obtained as a white solid; m.p. 92-94 °C.

**$^1H$ NMR** (600 MHz, Chloroform-*d*) δ 8.26 (s, 1H), 7.37 (d, *J* = 1.6 Hz, 2H), 7.36 (t, *J* = 1.3 Hz, 2H), 7.33 – 7.27 (m, 3H), 7.26 – 7.21 (m, 2H), 7.21 – 7.18 (m, 1H), 7.16 (dd, *J* = 5.1, 1.1 Hz, 1H), 7.09 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.02 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.58 (d, *J* = 2.9 Hz, 1H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 136.13, 135.68, 132.87, 129.01, 128.78, 128.47, 128.40, 127.83, 127.54, 127.11, 126.97, 126.08, 123.72, 123.07, 121.23, 109.27;

**HRMS (ESI-TOF)**: calcd for [$C_{20}H_{15}NS + H^+$]: 302.0998, found 302.0995.



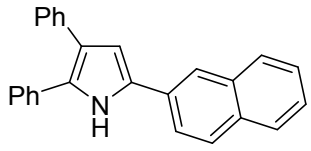
**5-(naphthalen-1-yl)-2,3-diphenyl-1*H*-pyrrole (3aj)[11]**

Following the general procedure, the optimized time is 48 h. The yield of **3aj** was detected through $^1H$ NMR by using dimethyl terephthalate as internal standard (48%).

**$^1H$ NMR** (600 MHz, Chloroform-*d*) δ 8.49 – 8.46 (m, 1H), 8.44 (s, 1H), 7.93 – 7.88 (m, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.61 (d, *J* = 7.0 Hz, 1H), 7.54 (td, *J* = 7.9, 4.8 Hz, 3H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.44 (d, *J* = 7.6 Hz, 2H), 7.33 (dt, *J* = 11.3, 7.5 Hz, 4H), 7.27 (d, *J* = 7.3 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 6.71 (d, *J* = 2.7 Hz, 1H);

**$^{13}C$ NMR** (150 MHz, $CDCl_3$) δ 136.51, 134.14, 133.17, 131.26, 130.96, 130.91, 128.96, 128.78, 128.53, 128.40, 127.79, 127.48, 126.94, 126.54, 126.11, 125.96, 125.94, 125.74, 125.51, 123.25, 112.16;

**HRMS (ESI-TOF)**: [$C_{26}H_{19}N + H^+$]: 346.1590, found 346.1597.



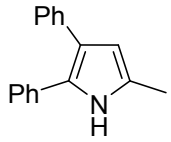
**5-(naphthalen-2-yl)-2,3-diphenyl-1*H*-pyrrole (3ak)[5]**

Following the general procedure, the optimized time is 36 h. Yield: 82% (28.3 mg). **3ak** was obtained as a yellow solid; m.p. 182-184 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.58 (s, 1H), 7.93 (s, 1H), 7.89 – 7.82 (m, 3H), 7.74 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.50 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 7.48 – 7.43 (m, 5H), 7.39 – 7.29 (m, 5H), 7.24 (t, *J* = 7.4 Hz, 1H), 6.84 (d, *J* = 2.8 Hz, 1H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.33, 133.81, 132.29, 128.79, 128.76, 128.47, 128.40, 127.83, 127.75, 127.56, 127.10, 126.62, 126.04, 125.58, 124.06, 123.06, 121.08, 109.30;

**HRMS (ESI-TOF)**: [$C_{26}H_{19}N + H^+$]: 346.1590, found 346.1594.



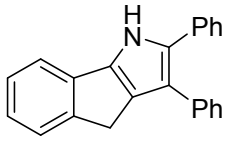

**5-methyl-2,3-diphenyl-1*H*-pyrrole (3al)[13]**

Following the general procedure, the optimized time is 36 hours. Yield: 51% (11.8mg); **3al** was obtained as a purple oil.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 7.94 (s, 1H), 7.35 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.33 (d, *J* = 1.4 Hz, 1H), 7.32 – 7.31 (m, 1H), 7.31 – 7.27 (m, 3H), 7.25 (d, *J* = 1.6 Hz, 1H), 7.22 – 7.19 (m, 1H), 7.18 (ddt, *J* = 8.7, 6.8, 1.5 Hz, 1H), 6.11 (dd, *J* = 2.9, 1.1 Hz, 1H), 2.36 (s, 3H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 136.82, 133.50, 128.57, 128.35, 128.21, 128.18, 127.20, 126.79, 126.37, 125.55, 122.21, 108.98, 12.97;

**HRMS (ESI-TOF)**: calcd for [$C_{17}H_{15}N + H^+$]: 234.1277, found 234.1275.



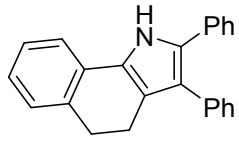

**2,3-diphenyl-1,4-dihydroindeno[1,2-*b*]pyrrole (3ao)**

Following the general procedure, the optimized time is 20 h. Yield: 43% (13.2 mg); **3ao** was obtained as an off-white solid; m.p. 107-110 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.41 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 4H), 7.37 – 7.26 (m, 6H), 7.25 (s, 4H), 3.67 (s, 2H);

**$^{13}$C{$^1$H} NMR** (150 MHz, $CDCl_3$) δ 128.63, 128.54, 128.41, 125.87, 29.74;

**HRMS (ESI-TOF)**: calcd for [$C_{23}H_{17}N + H^+$]: 308.1434, found 308.1439.



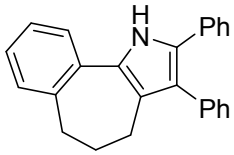

**2,3-diphenyl-4,5-dihydro-1*H*-benzo[*g*]indole (3ap)**

Following the general procedure, the optimized time is 24 h. Yield: 64% (20.5 mg); **3ap** was obtained as a white solid; m.p. 165-169 °C.

**$^1$H NMR** (600 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.35 – 7.23 (m, 10H), 7.21 (t, *J* = 7.0 Hz, 3H), 7.08 (t, *J* = 7.3 Hz, 1H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.76 (s, 2H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 135.54, 135.14, 133.01, 129.83, 129.21, 128.82, 128.59, 128.35, 128.26, 128.06, 127.08, 126.54, 125.98, 125.39, 121.25, 121.05, 118.36, 29.94, 20.72;

**HRMS (ESI-TOF)**: calcd for [$C_{24}H_{19}N + H^+$]: 322.1590, found 322.1600.



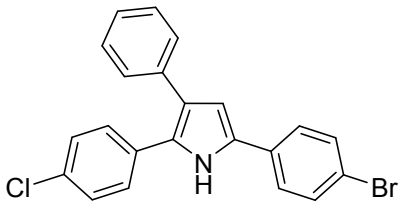
**2,3-diphenyl-1,4,5,6-tetrahydrobenzo[6,7]cyclohepta[1,2-*b*]pyrrole (3aq)**

Following the general procedure, the optimized time is 36 h. Yield: 56% (18.8 mg); **3aq** was obtained as a white solid; m.p. 140-147 °C.

**$^1H$ NMR** (600 MHz, Chloroform-*d*) δ 8.25 (s, 1H), 7.47 (s, 1H), 7.36 – 7.22 (m, 10H), 7.20 – 7.07 (m, 3H), 2.92 – 2.83 (m, 2H), 2.70 (s, 2H), 2.03 (dt, *J* = 11.8, 6.7 Hz, 2H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 140.95, 136.14, 132.77, 130.55, 129.70, 128.53, 128.30, 126.73, 126.40, 126.36, 126.26, 125.82, 124.02, 123.77, 122.77, 35.16, 27.68, 26.99;

**HRMS (ESI-TOF)**: calcd for [$C_{25}H_{21}N + H^+$]: 336.1747, found 336.1750.



**5-(4-bromophenyl)-2,3-diphenyl-1*H*-pyrrole (3od)[14]**

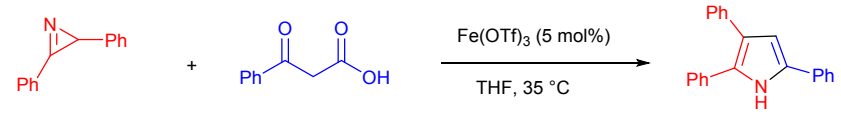
Following the general procedure, the optimized time is 36 h. Yield: 83% (33.8 mg); **3od** was obtained as a yellow solid; m.p. 172-174 °C.

**$^1H$ NMR** (600 MHz, Chloroform-*d*) δ 8.34 (s, 1H), 7.54 – 7.50 (m, 2H), 7.42 – 7.39 (m, 2H), 7.37 – 7.34 (m, 2H), 7.32 – 7.28 (m, 6H), 7.26 – 7.22 (m, 1H), 6.68 (d, *J* = 2.8 Hz, 1H);

**$^{13}C\{^1H\}$ NMR** (150 MHz, $CDCl_3$) δ 135.81, 132.93, 132.13, 131.49, 131.28, 130.98, 129.01, 128.67, 128.52, 128.42, 126.34, 125.30, 124.56, 120.27, 109.26;

**HRMS (ESI-TOF)**: calcd for [$C_{22}H_{15}BrClN + H^+$]: ($Br^{81}$) 410.0129, found 410.0131; ($Br^{79}$) 408.0149, found 408.0147.

## 7. Procedure for the Scale-up Version.




**1a** (5 mmol, 0.95 g) **2a** (5 mmol, 0.85 g) **3aa** 73% yield, 1.07 g

**Procedure**: A dry reaction tube was charged with **1a** (5 mmol, 0.95 g), **2a** (5 mmol, 0.85 g) and

$Fe(OTf)_3$ (0.25 mmol, 125 mg), followed by adding THF (25 mL). The reaction mixture was stirred at 35 °C for the 3 days. The solvent was removed under reduced pressure and the residue was subjected to column chromatography on silica gel, eluting with petroleum ether–ethyl acetate (100:1 to 30:1) to afford the corresponding product **3aa**.

## 8. X-ray Structure of 3od.


Single crystal of compound **3od** [$C_{22}H_{15}BrClN$] was obtained in PE and $CH_2Cl_2$. CCDC 2021744 contains the supplementary crystallographic data which can be obtained free of charge from the Cambridge Crystallographic Data Center via https://www.ccdc.cam.ac.uk/structures/.

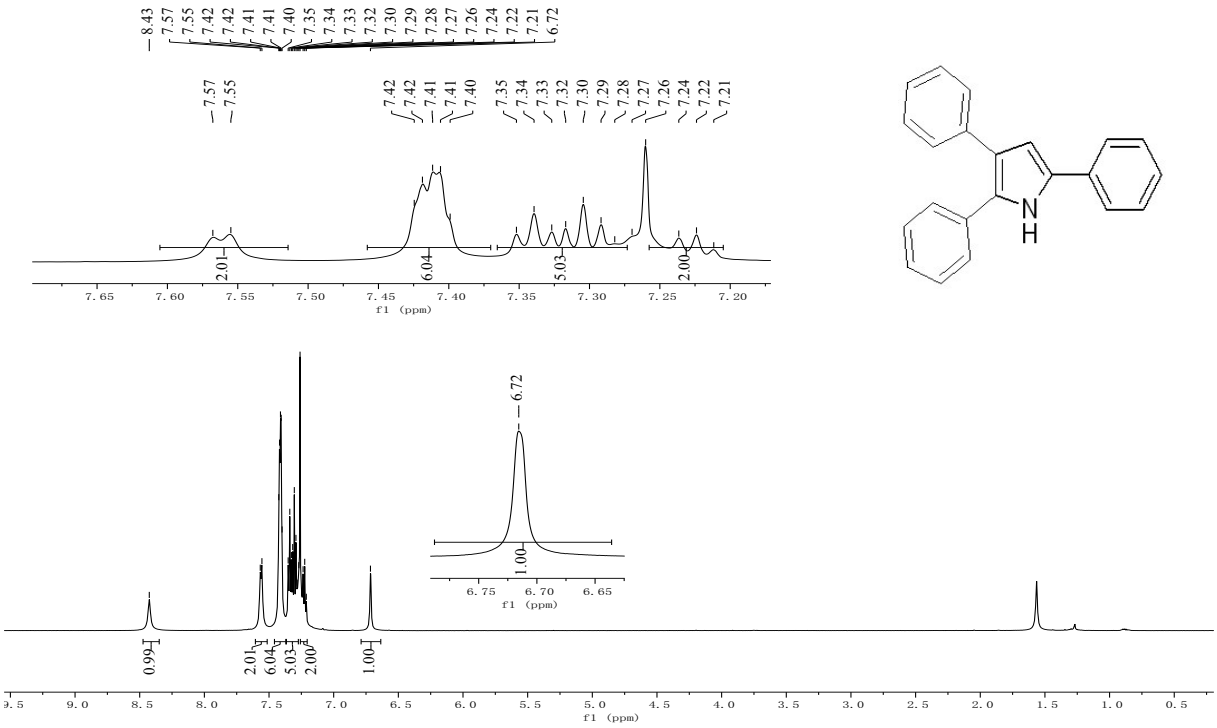
**Table 1 Crystal data and structure refinement for exp_280.**

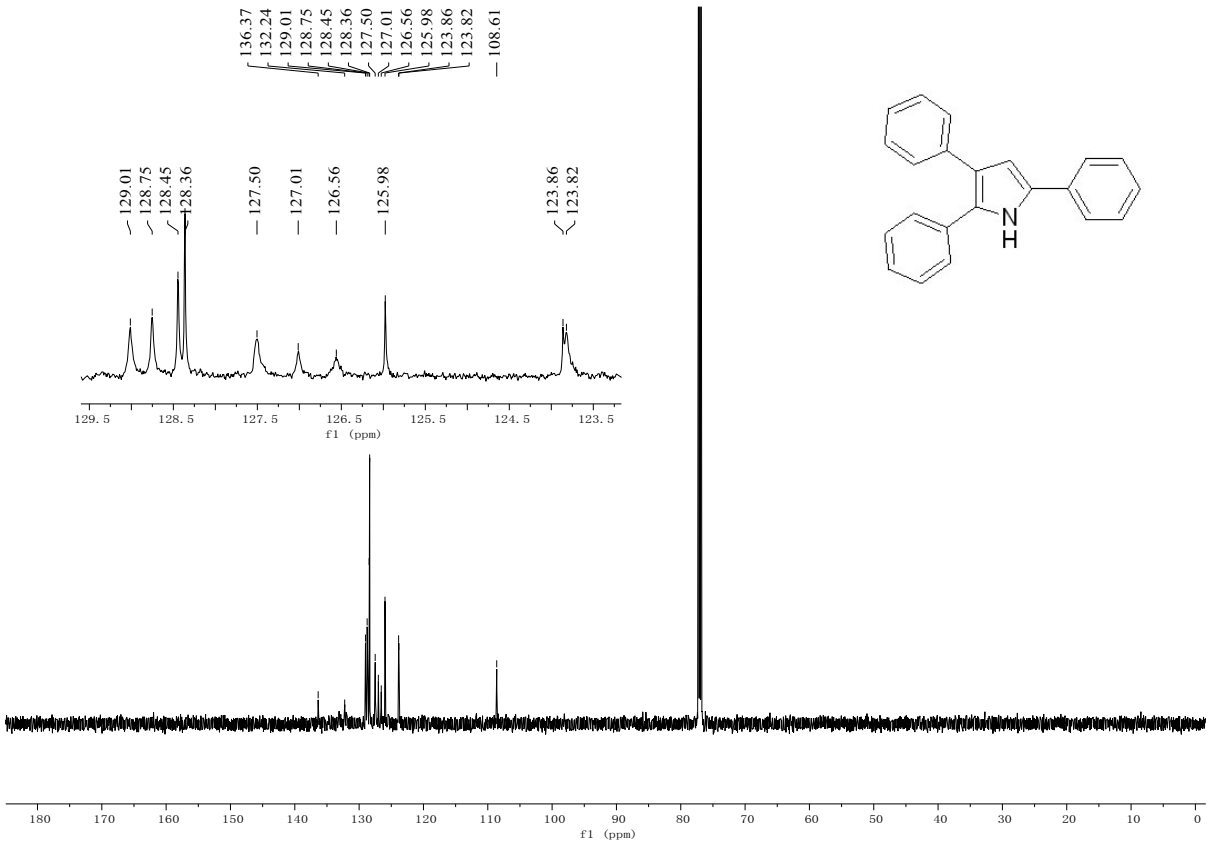
| | |
|---|---|
| Identification code | exp_280 |
| Empirical formula | $C_{22}H_{15}BrClN$ |
| Formula weight | 410.21 |
| Temperature/K | 298.56(10) |
| Crystal system | orthorhombic |
| Space group | $Pca2_1$ |
| a/Å | 8.52520(10) |
| b/Å | 11.9586(2) |
| c/Å | 17.5059(3) |
| α/° | 90 |
| β/° | 90 |
| γ/° | 90 |
| Volume/Å$^3$ | 1784.72(5) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.527 |
| μ/mm$^{-1}$ | 4.519 |
| F(000) | 827.0 |
| Crystal size/mm$^3$ | 0.2 × 0.1 × 0.1 |
| Radiation | Cu Kα (λ = 1.54184) |
| 2Θ range for data collection/ | 7.392 to 153.228 |
| Index ranges | $-10 \le h \le 10$, $-13 \le k \le 15$, $-20 \le l \le 22$ |

| | |
|---|---|
| Reflections collected | 8560 |
| Independent reflections | 3105 [$R_{int}$ = 0.0316, $R_{sigma}$ = 0.0351] |
| Data/restraints/parameters | 3105/1/227 |
| Goodness-of-fit on $F^2$ | 1.113 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0360, $wR_2$ = 0.0956 |
| Final R indexes [all data] | $R_1$ = 0.0387, $wR_2$ = 0.0978 |
| Largest diff. peak/hole / e $Å^{-3}$ | 0.30/-0.38 |
| Flack parameter | -0.029(18) |

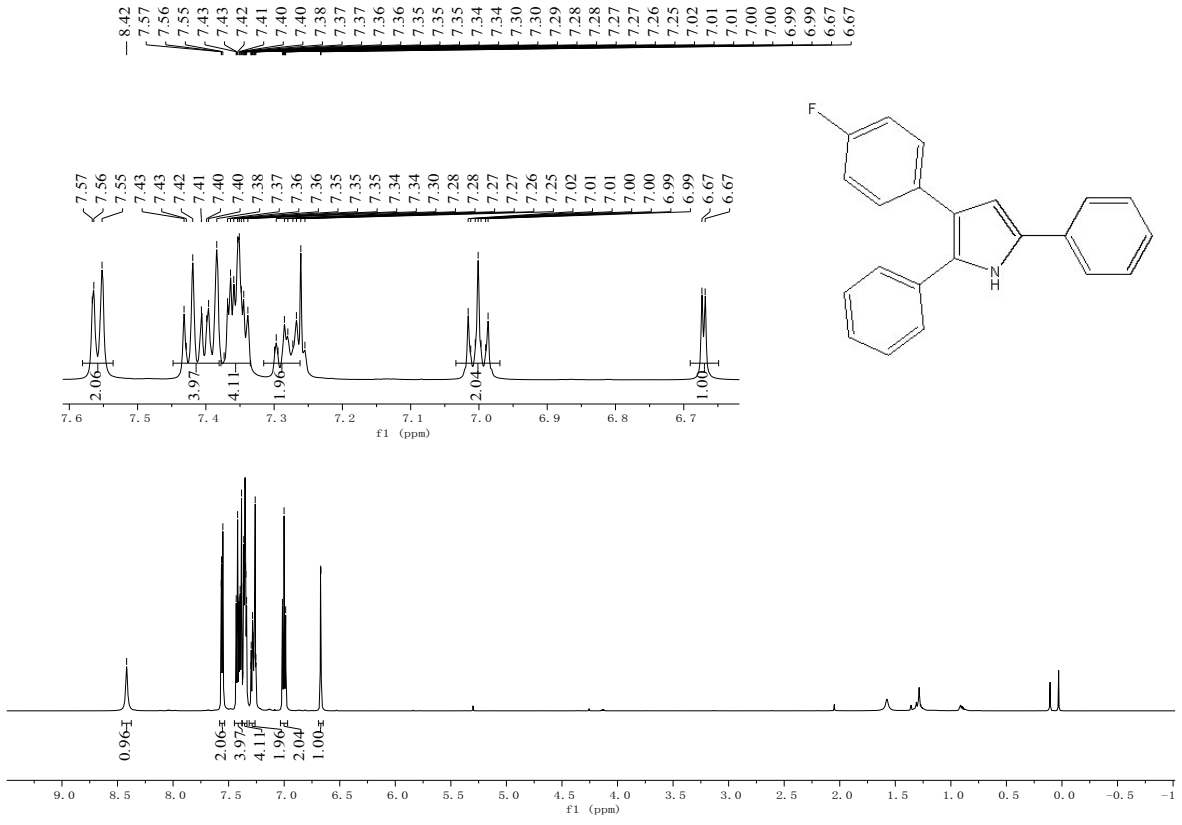
## 9. Copy of $^{1}H$, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR Spectra

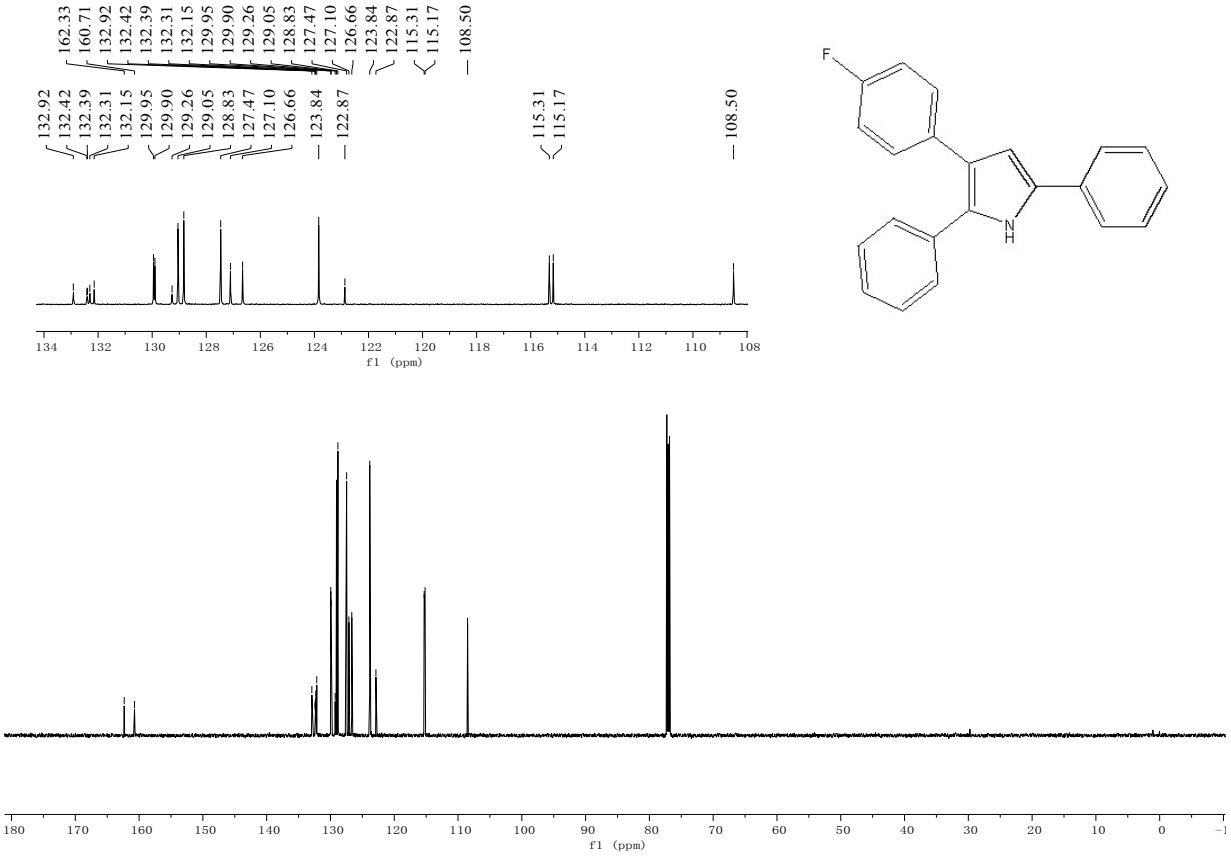
## Compound 3aa



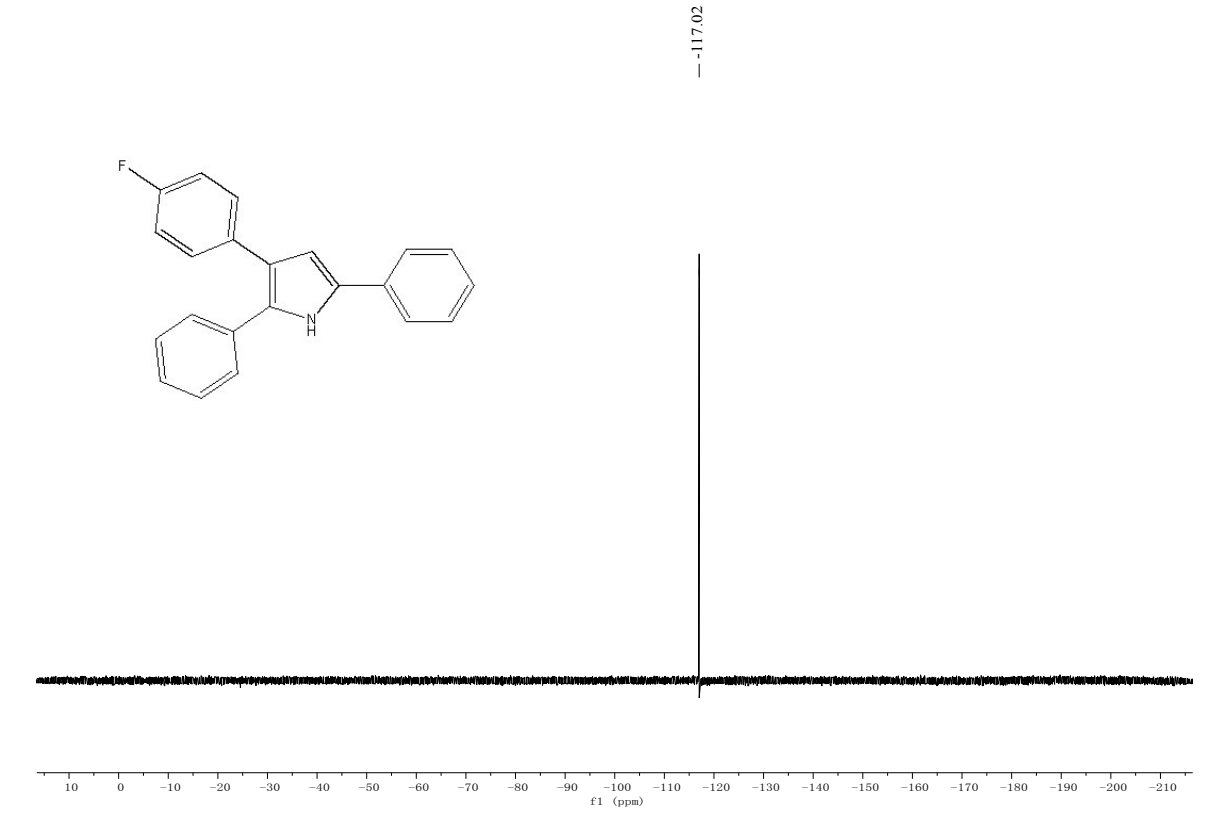



## Compound 3ba

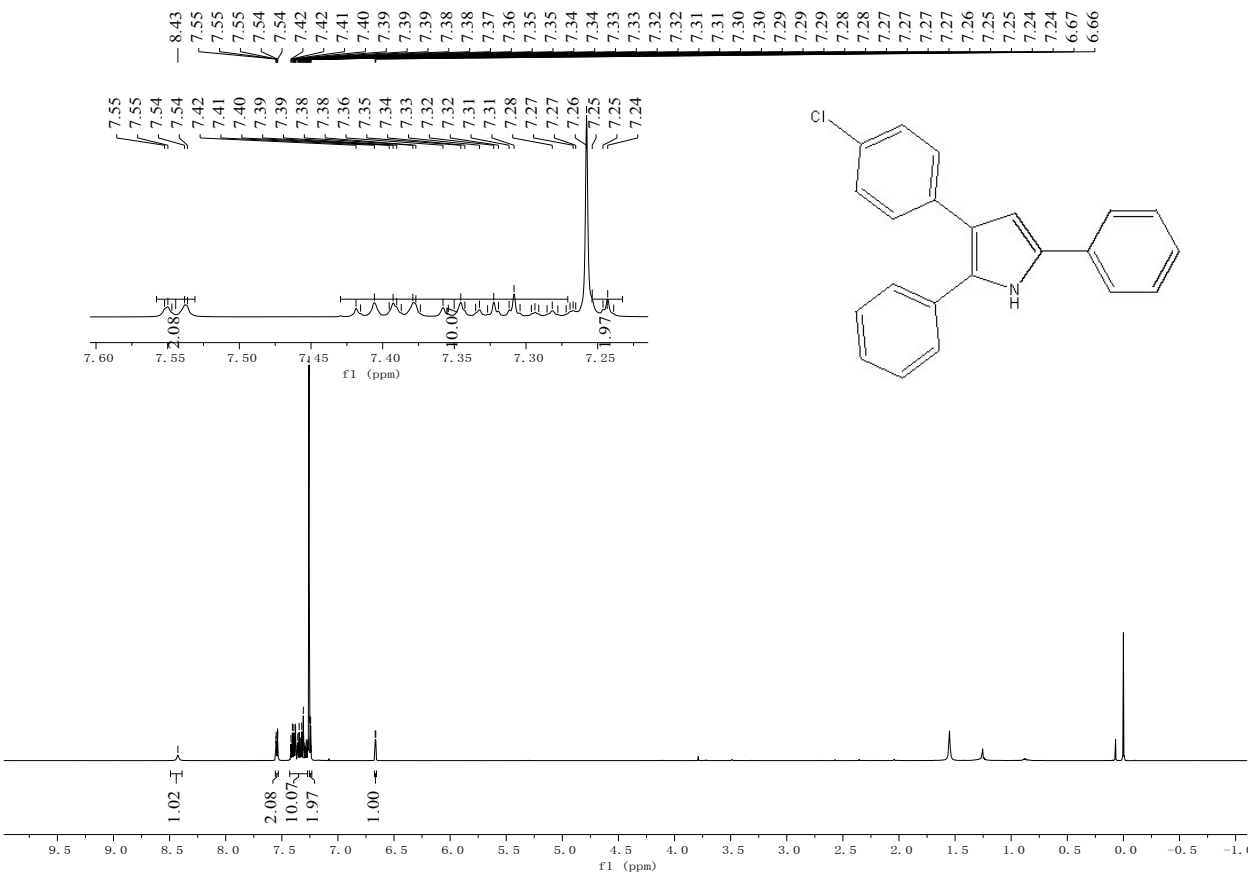


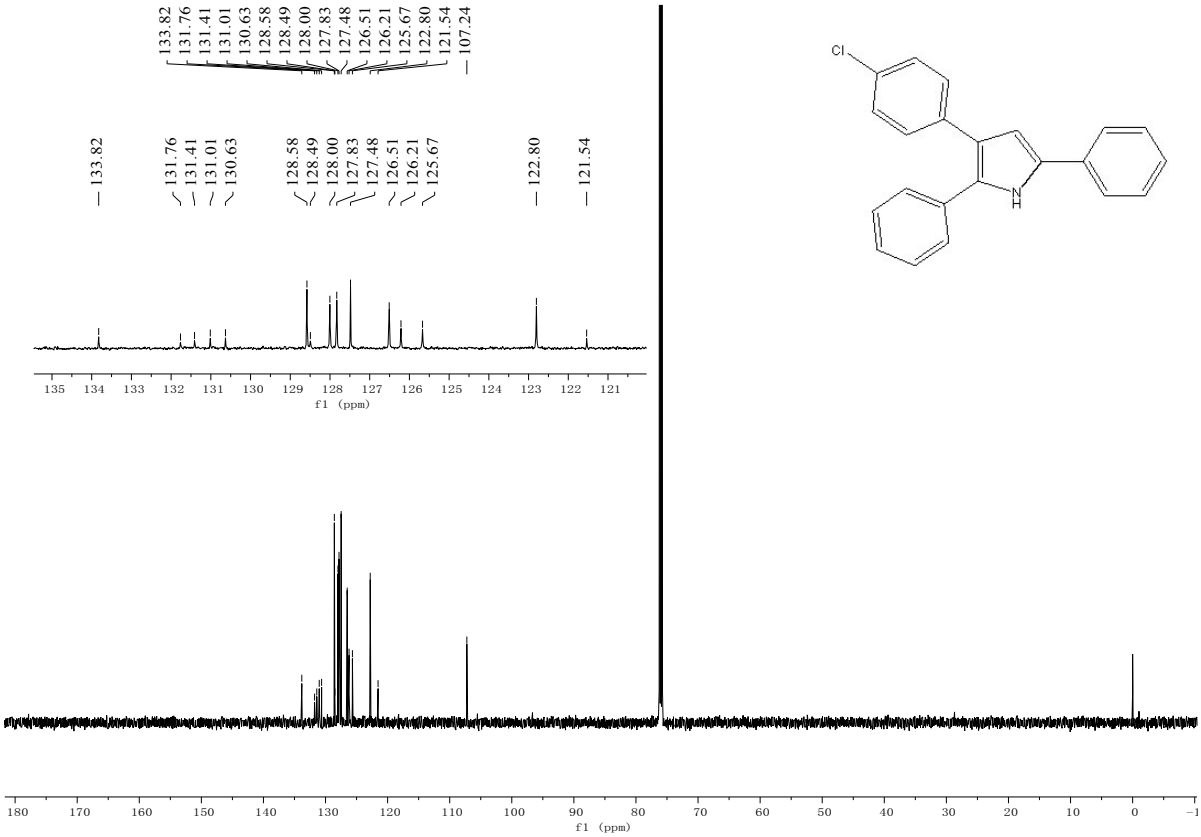

162.33
160.71
132.92
132.42
132.39
132.31
132.15
129.95
129.90
129.26
129.05
128.83
127.47
127.10
126.66
123.84
122.87
115.31
115.17
108.50
F
N
H
f1 (ppm)


f1 (ppm)

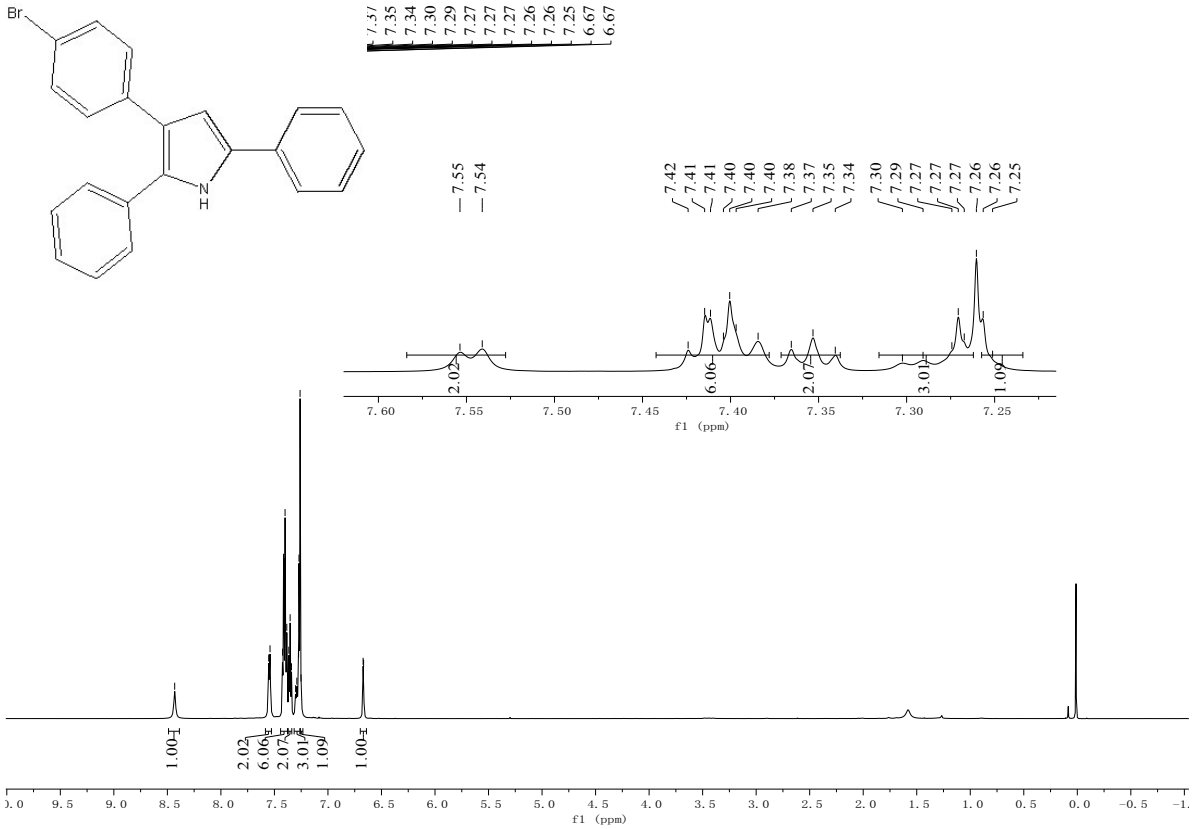

-117.02
F
N
H
f1 (ppm)

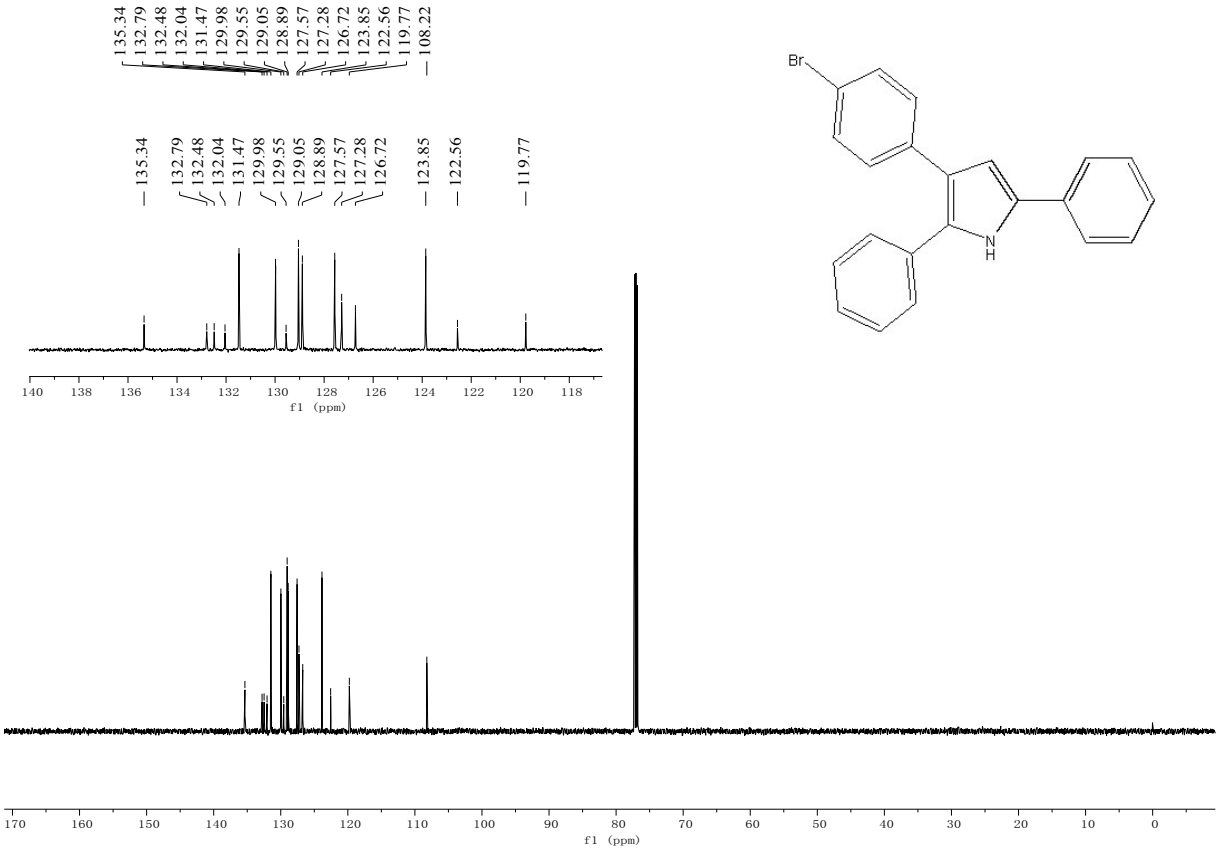
## Compound 3ca



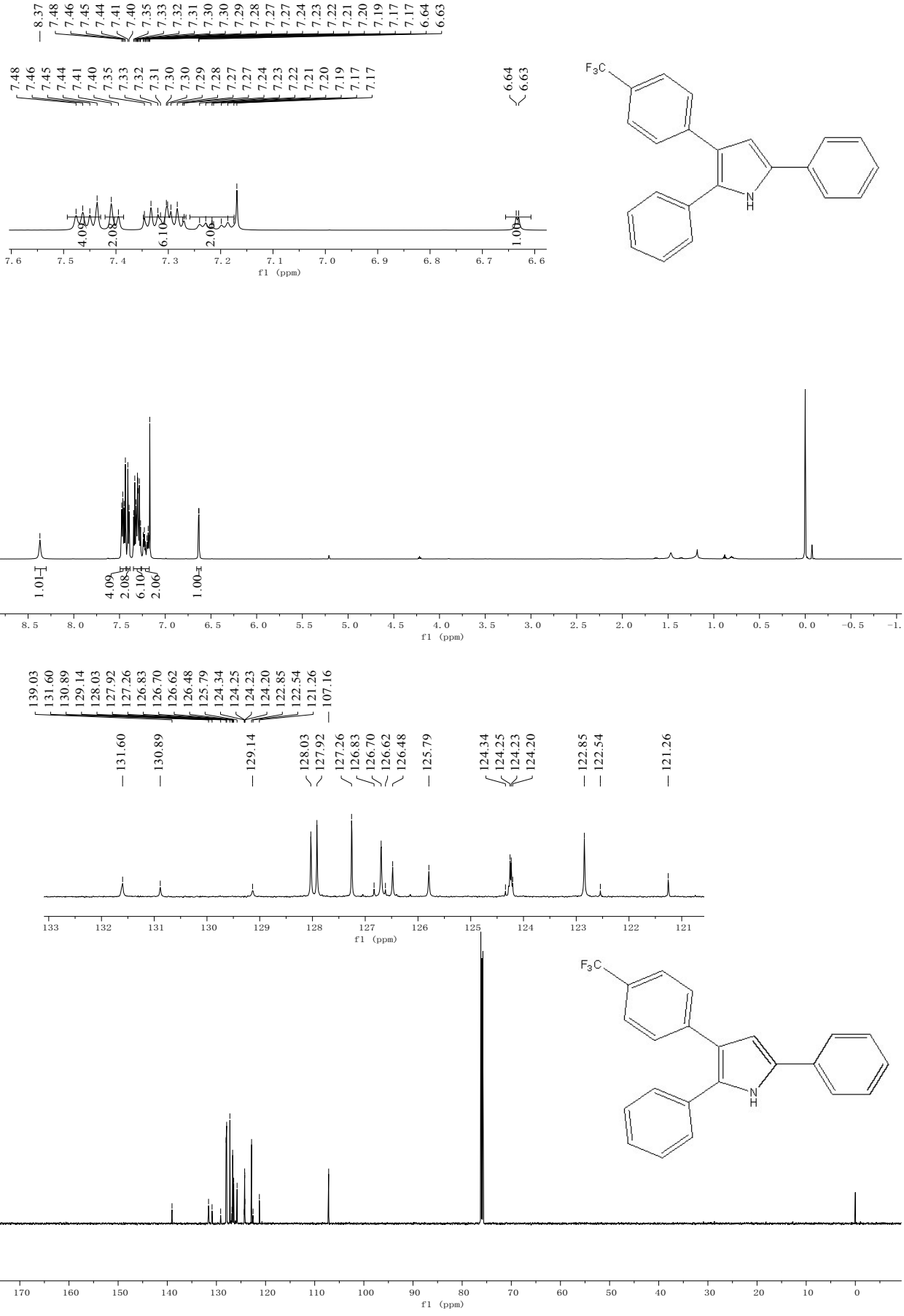



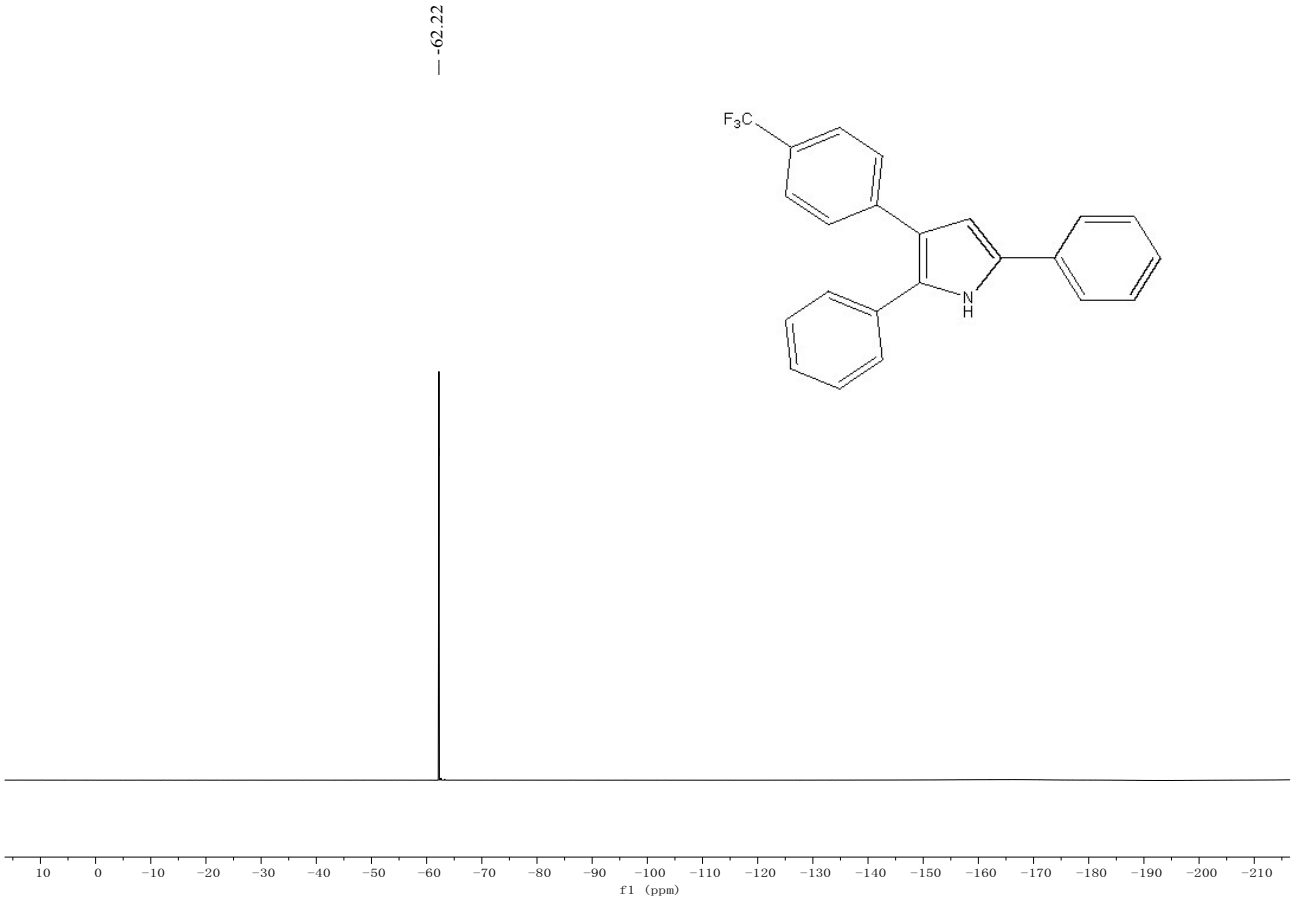
## Compound 3da



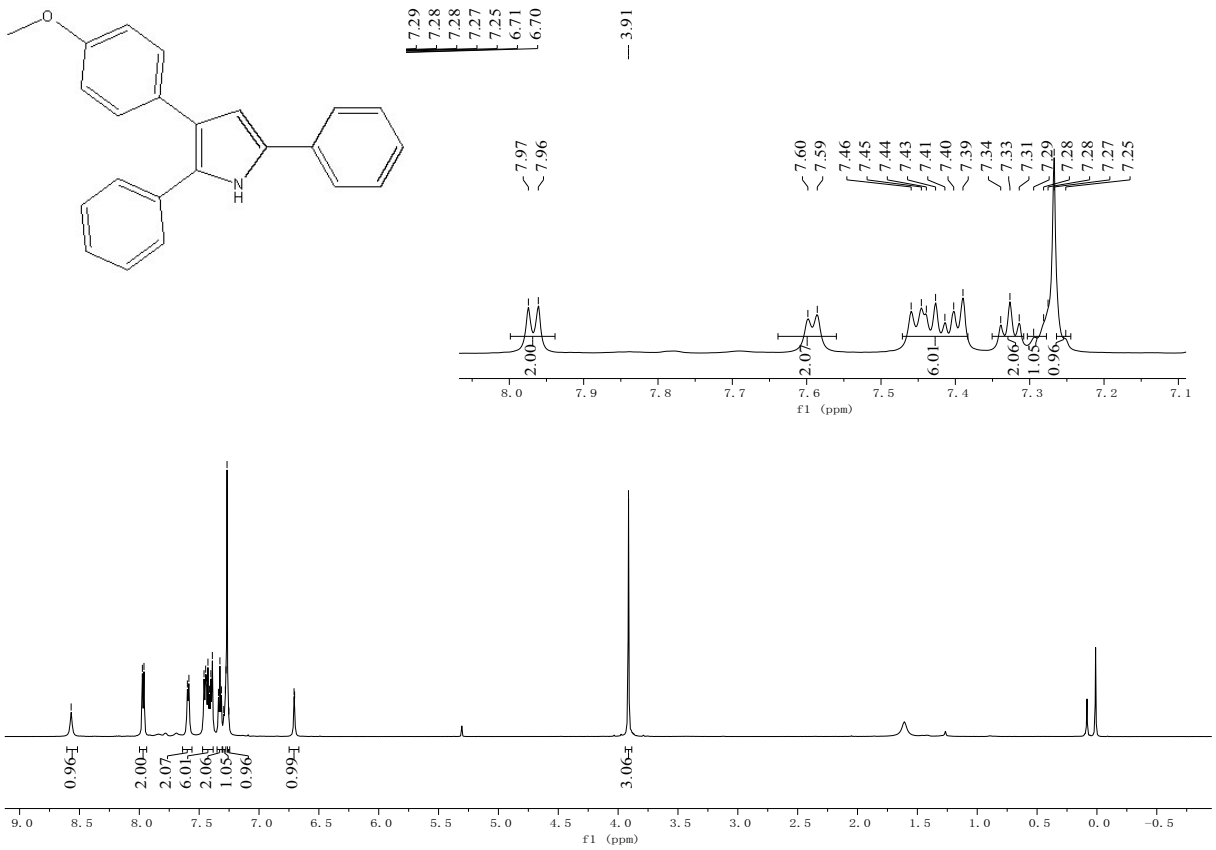



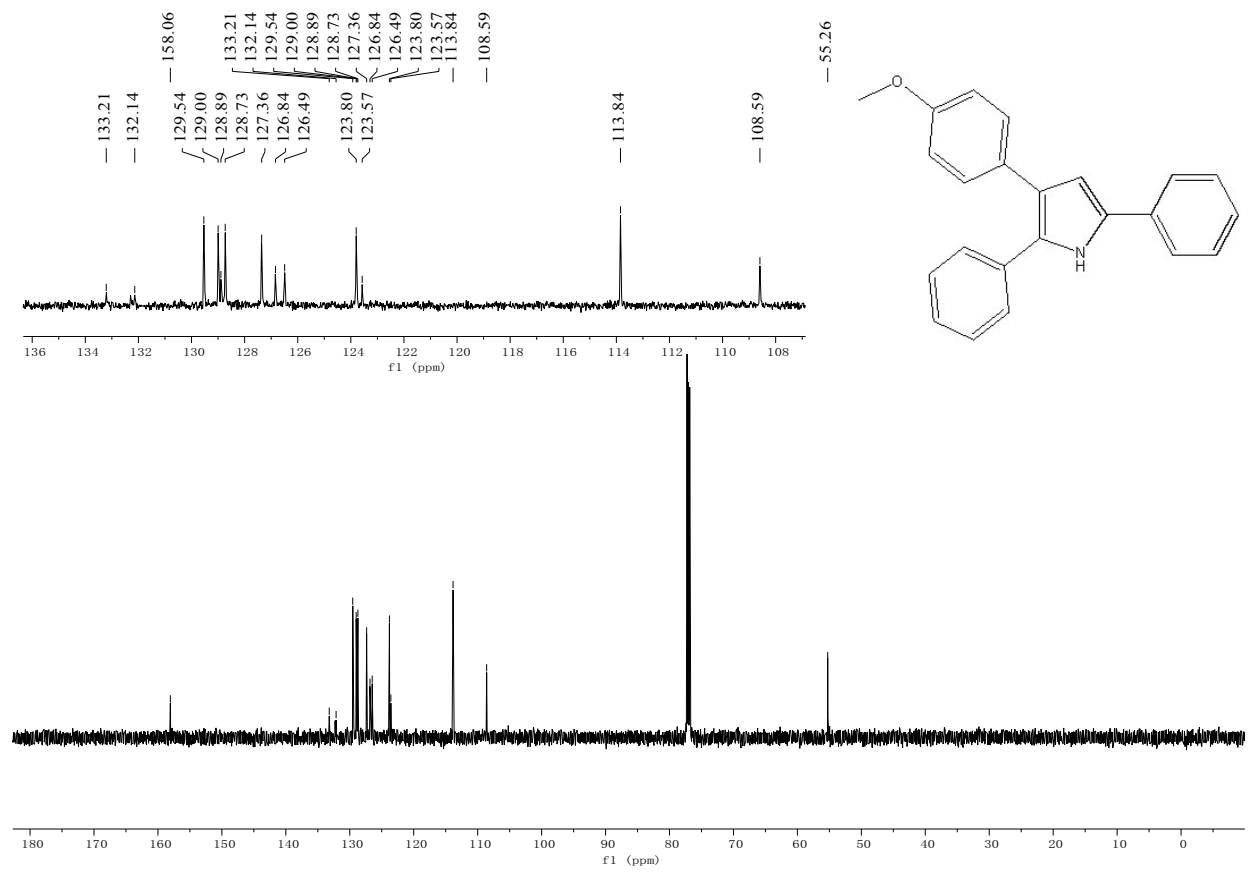
## Compound 3ea



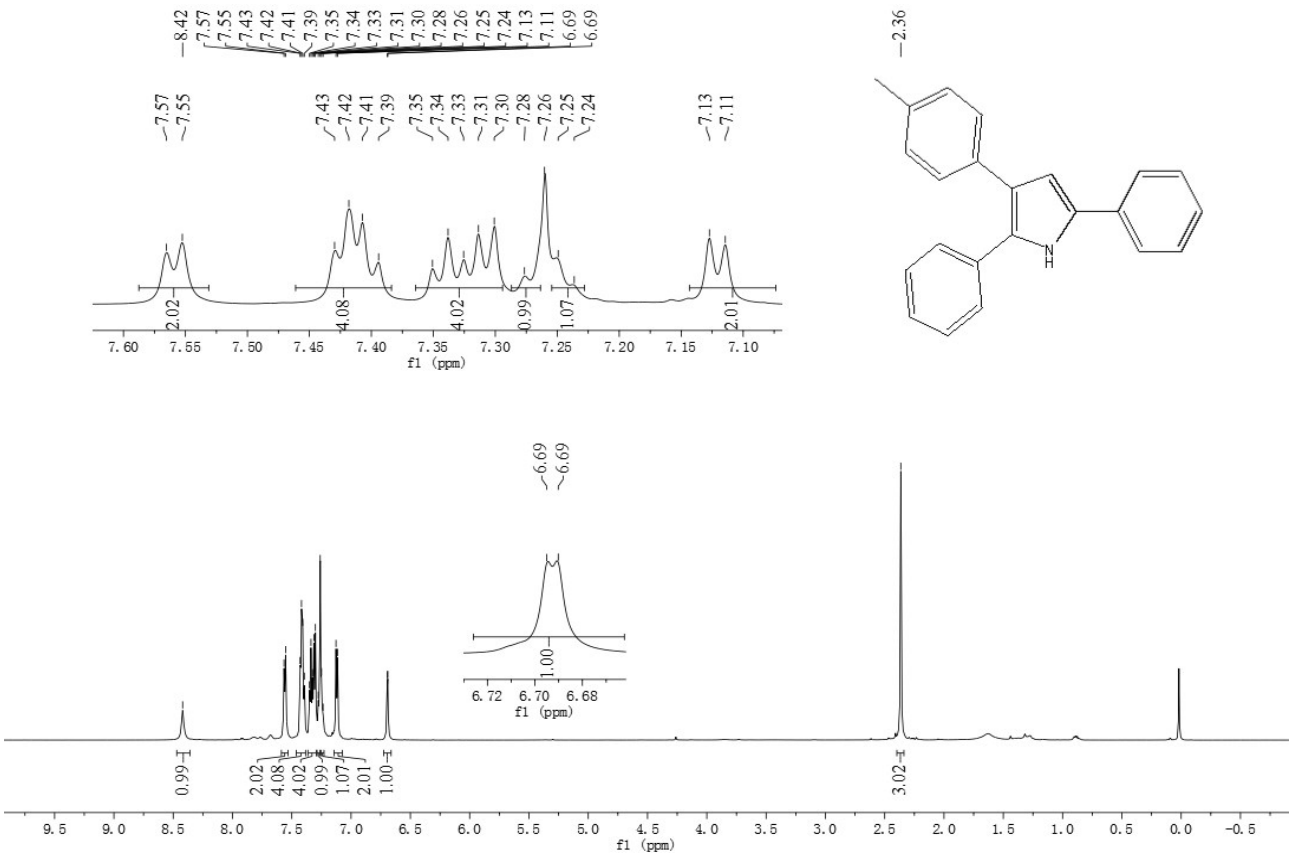


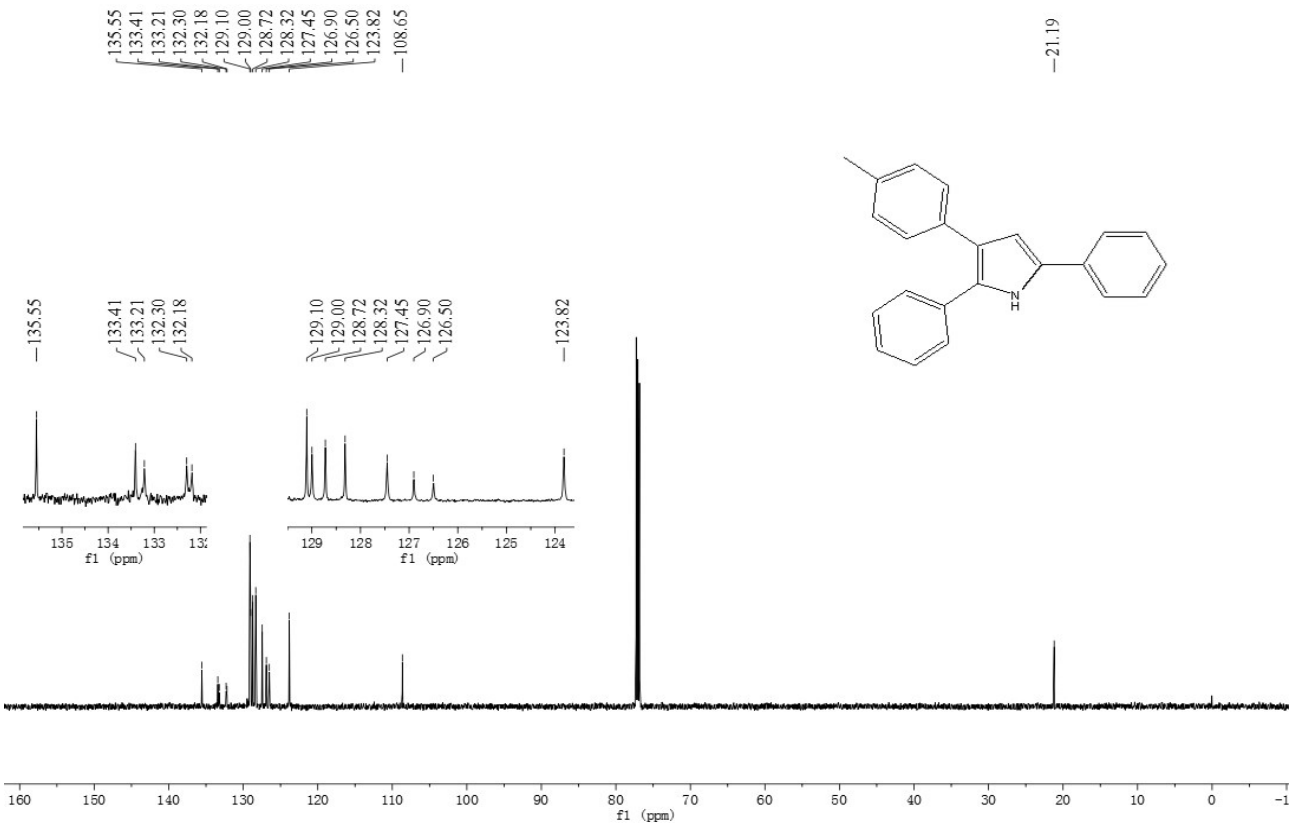

## Compound 3fa



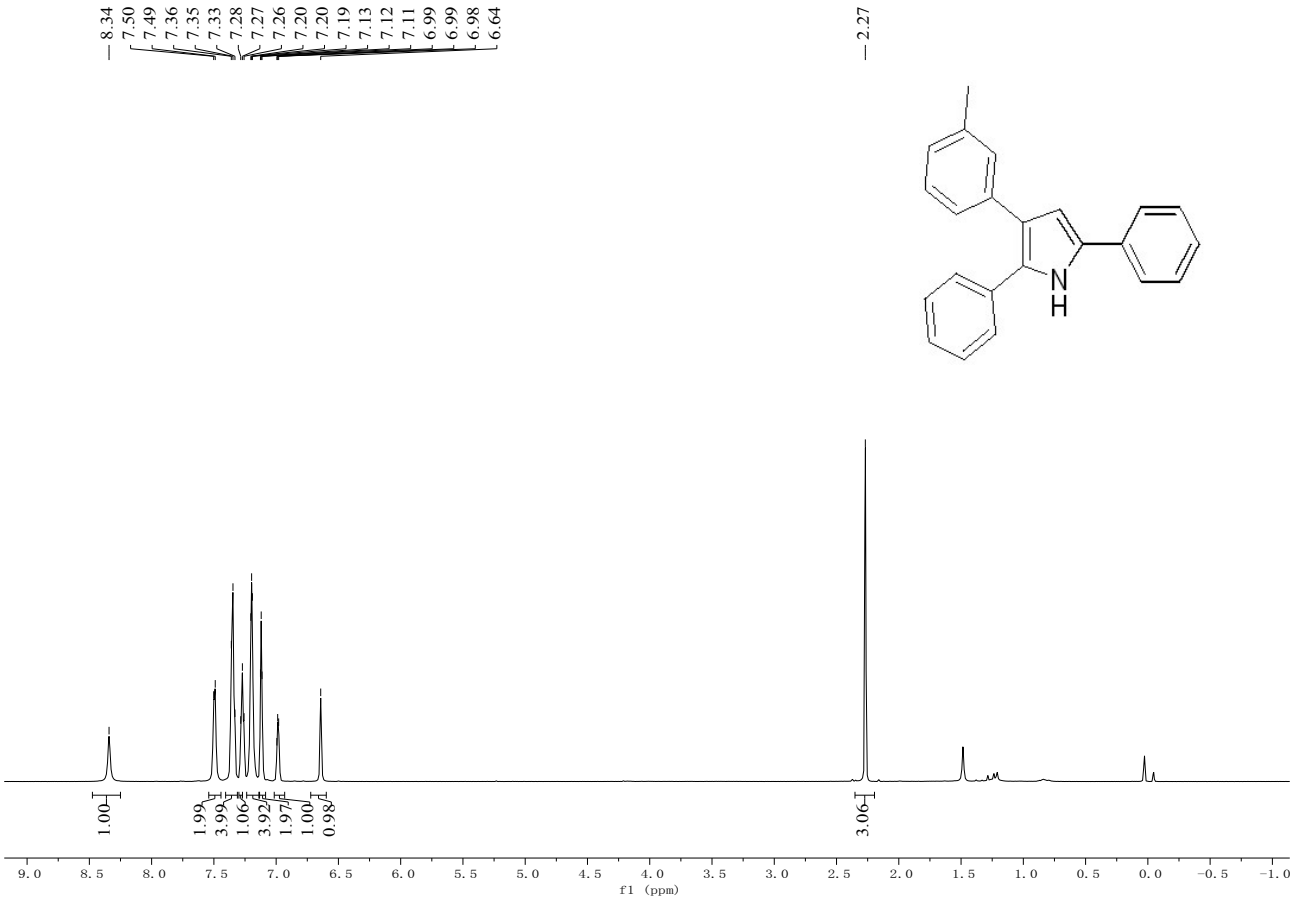


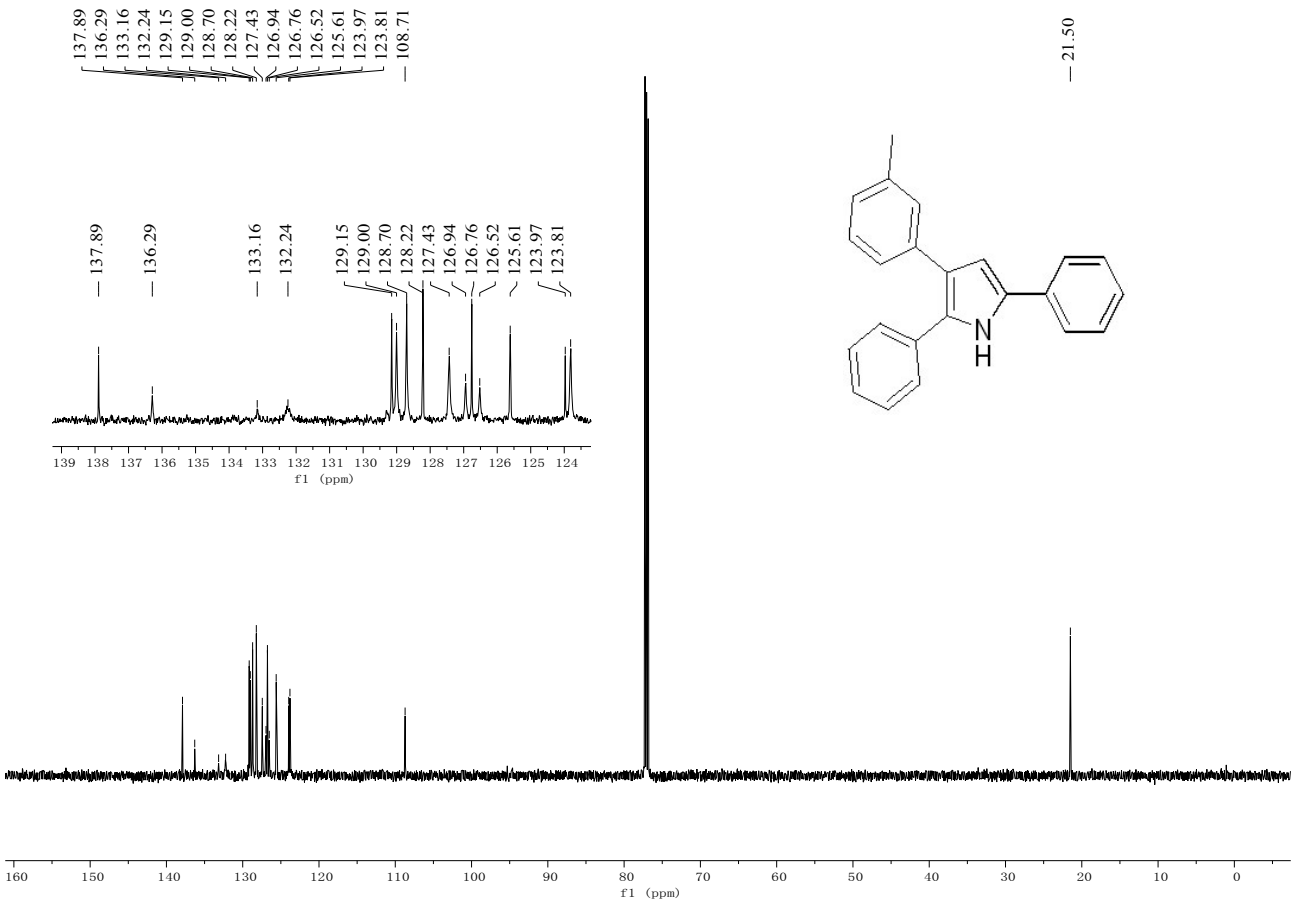

## Compound 3ga



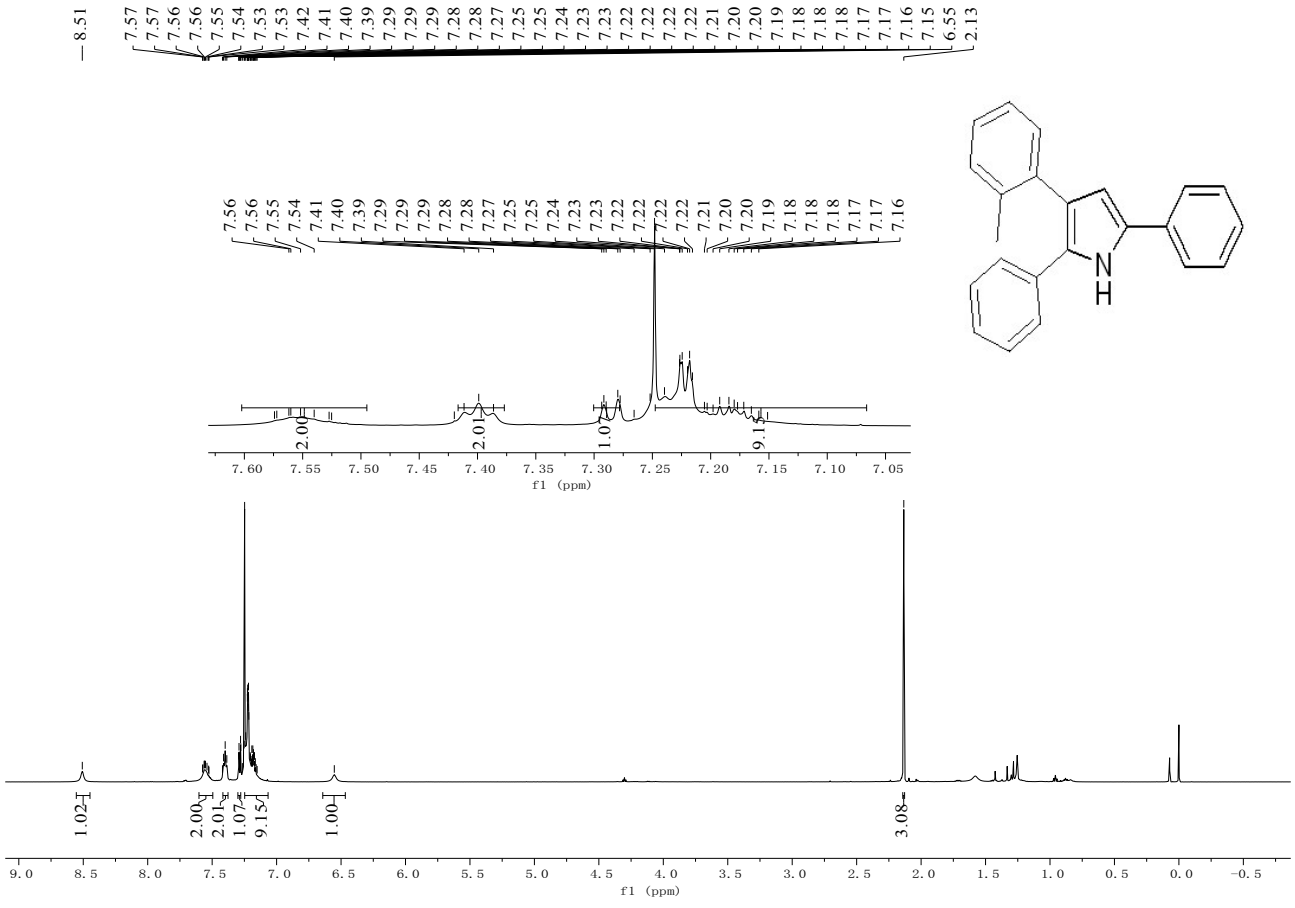


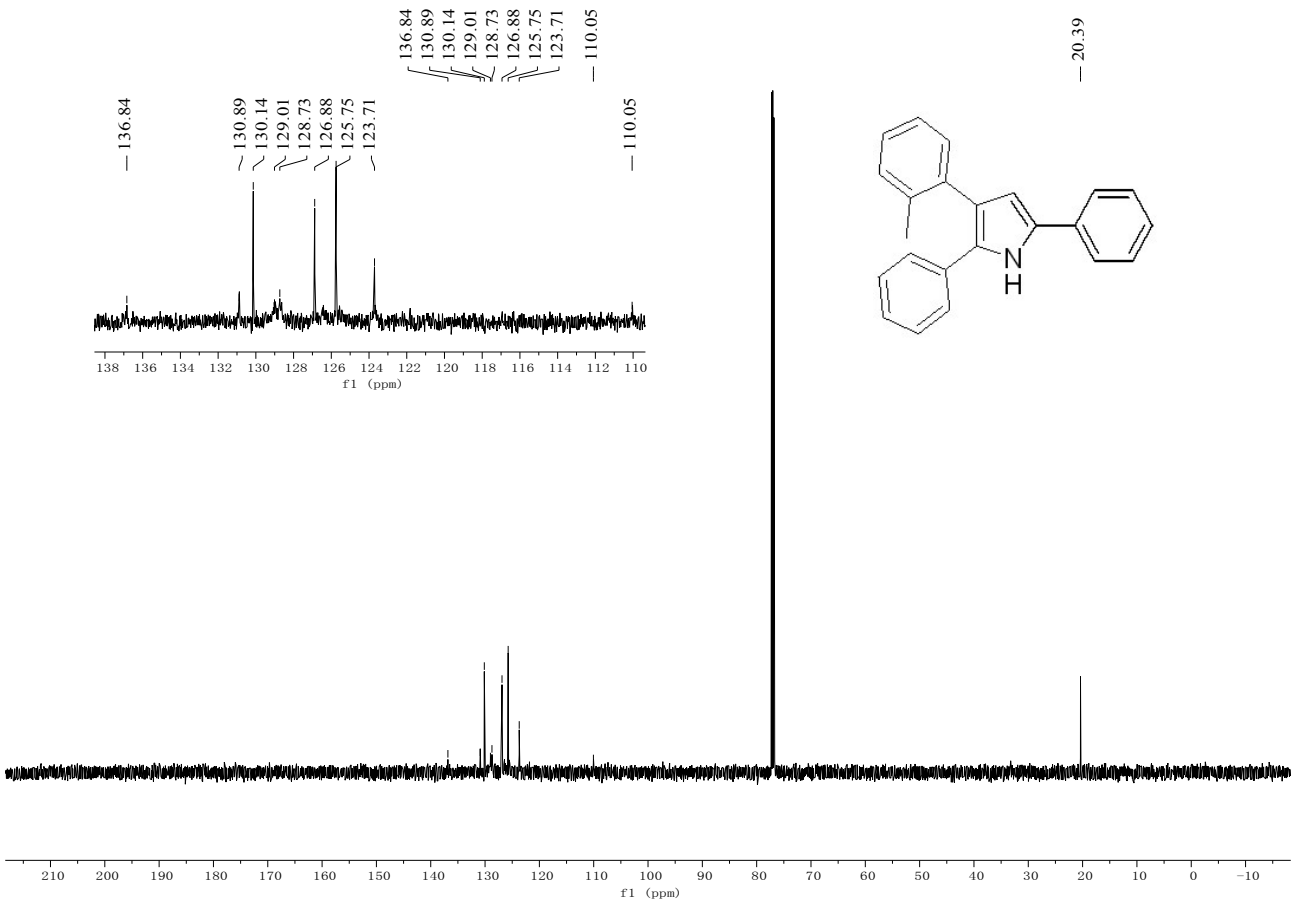

## Compound 3ha



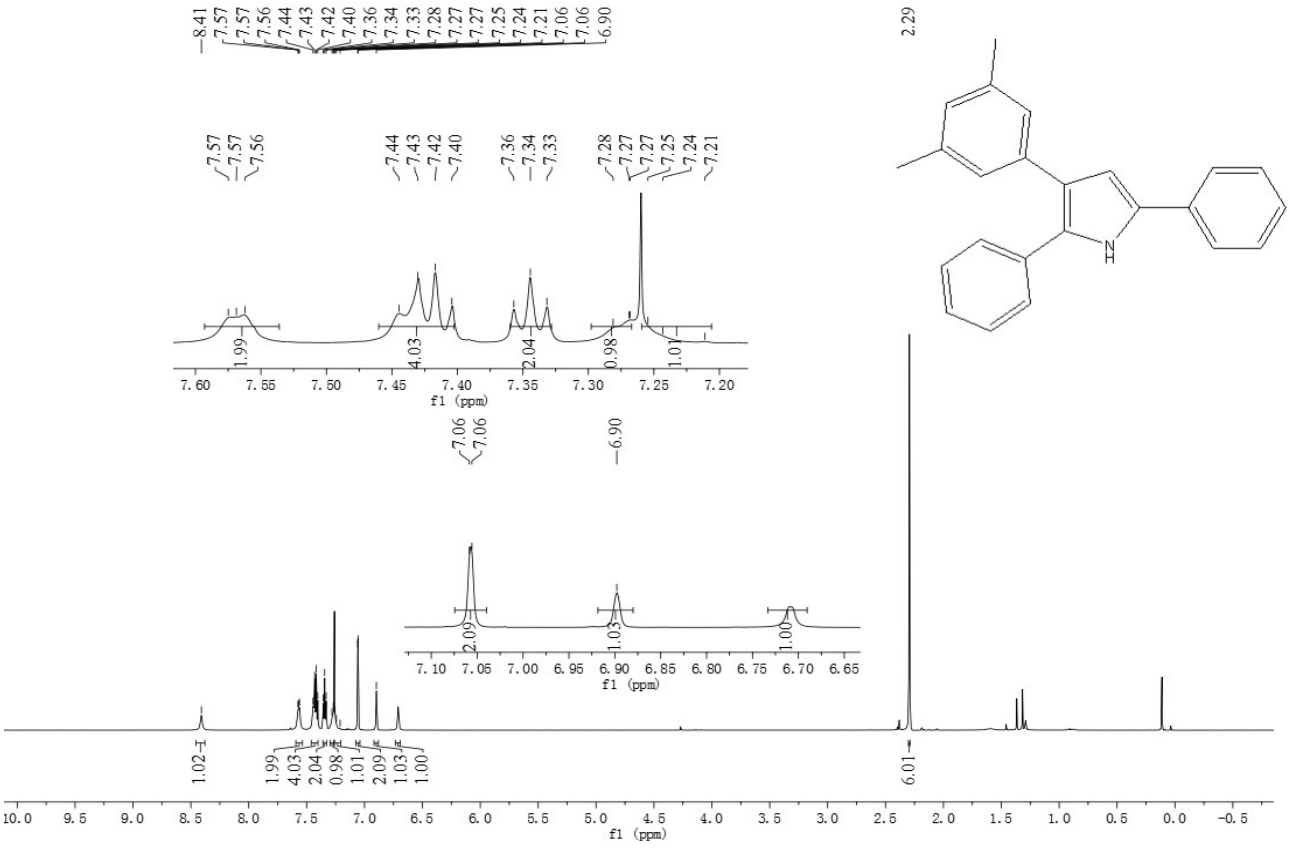


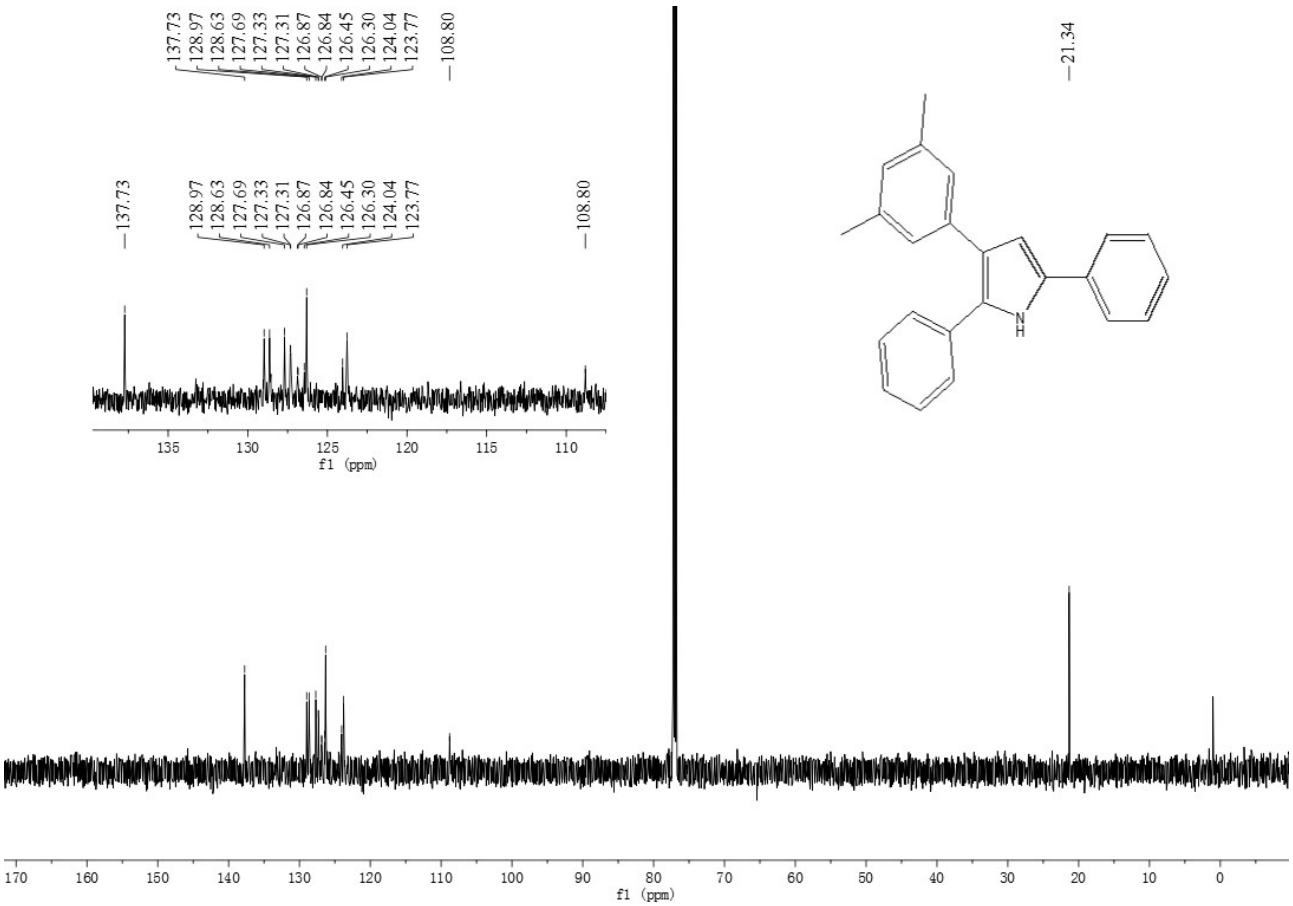

## Compound 3ia



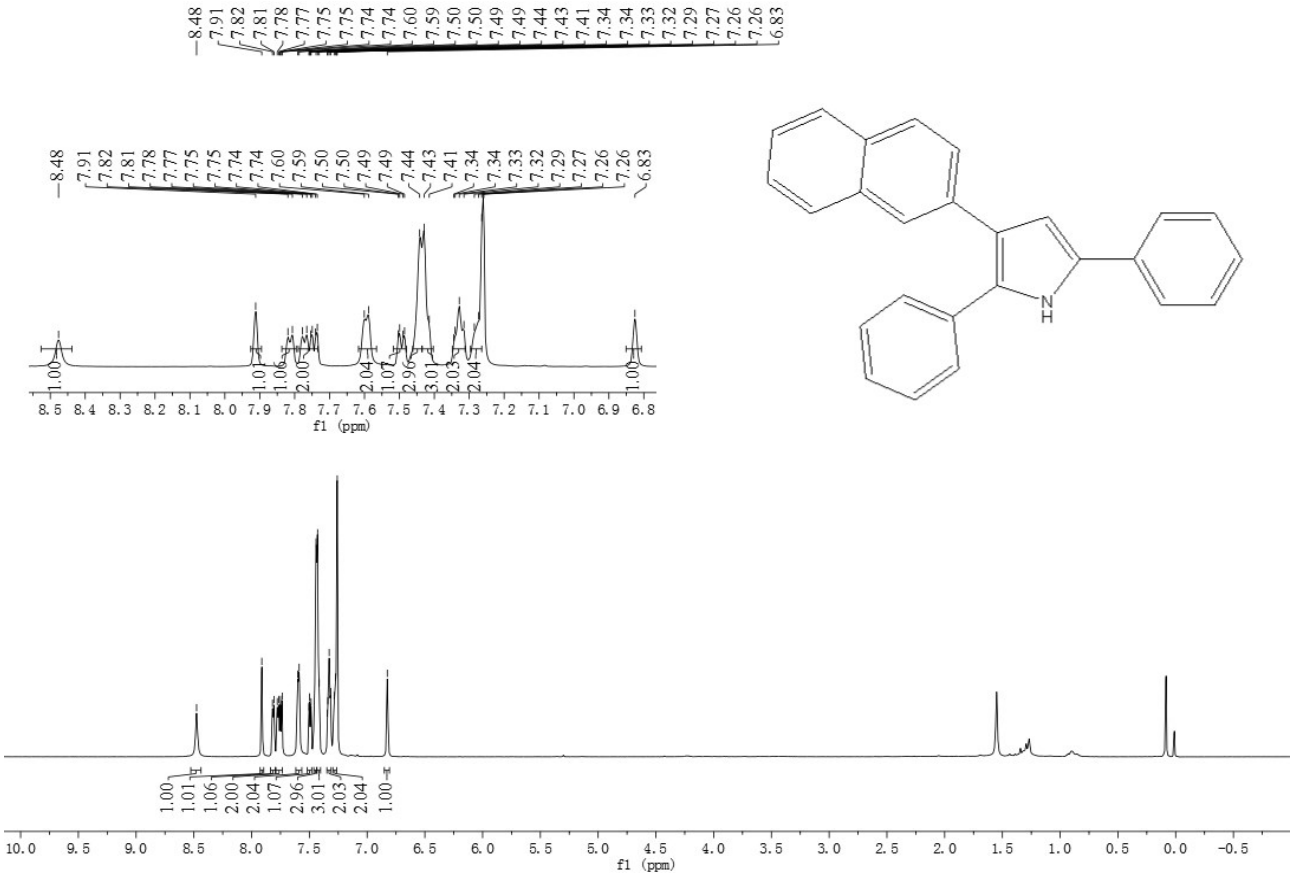


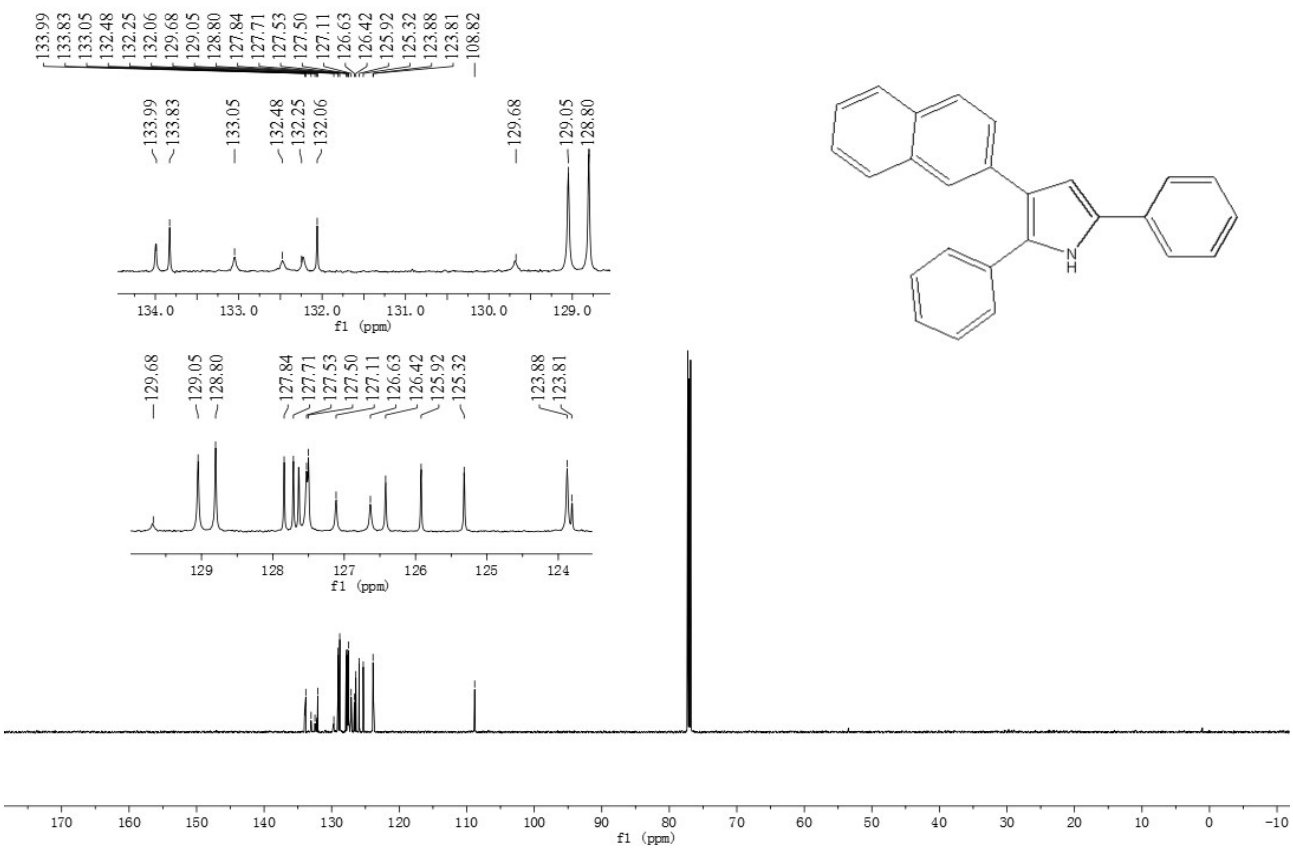

## Compound 3ja



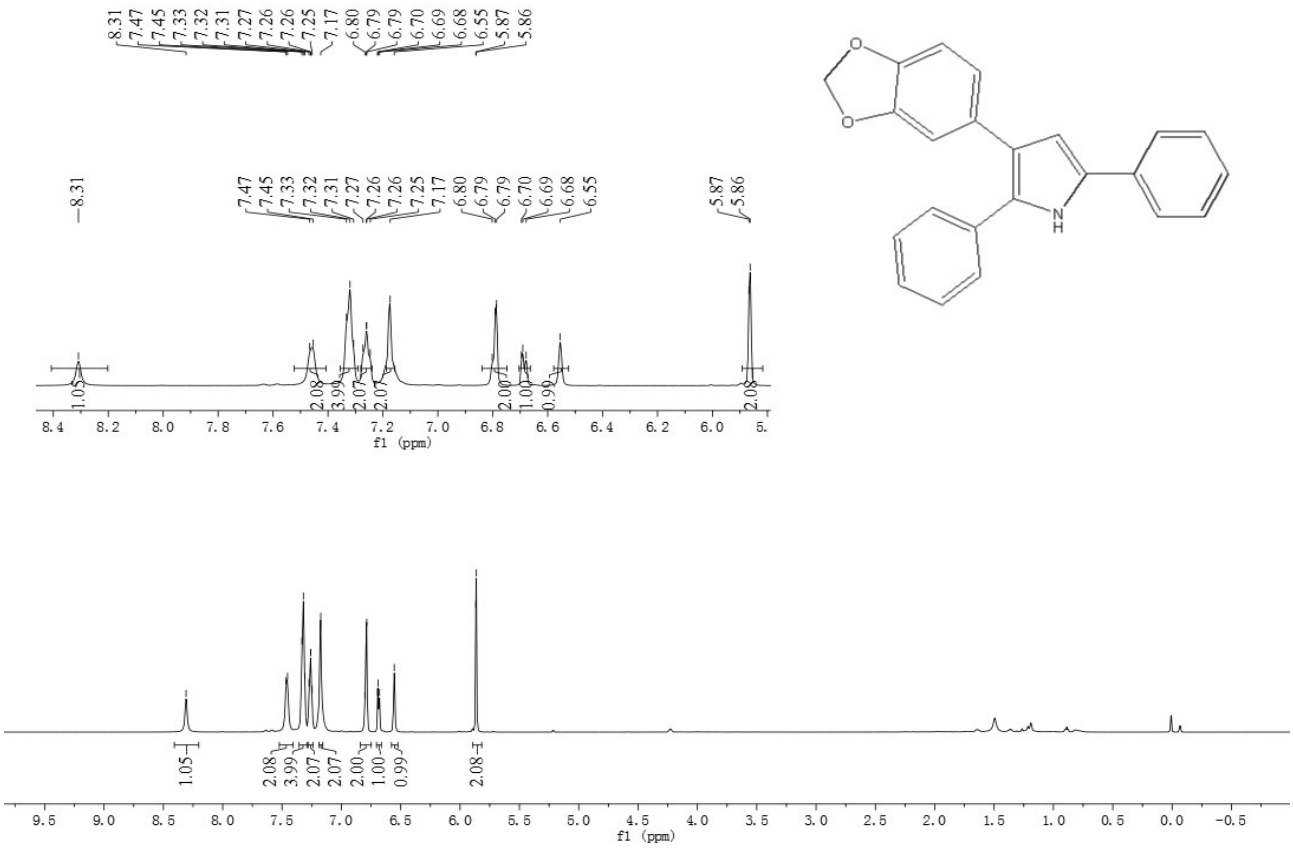


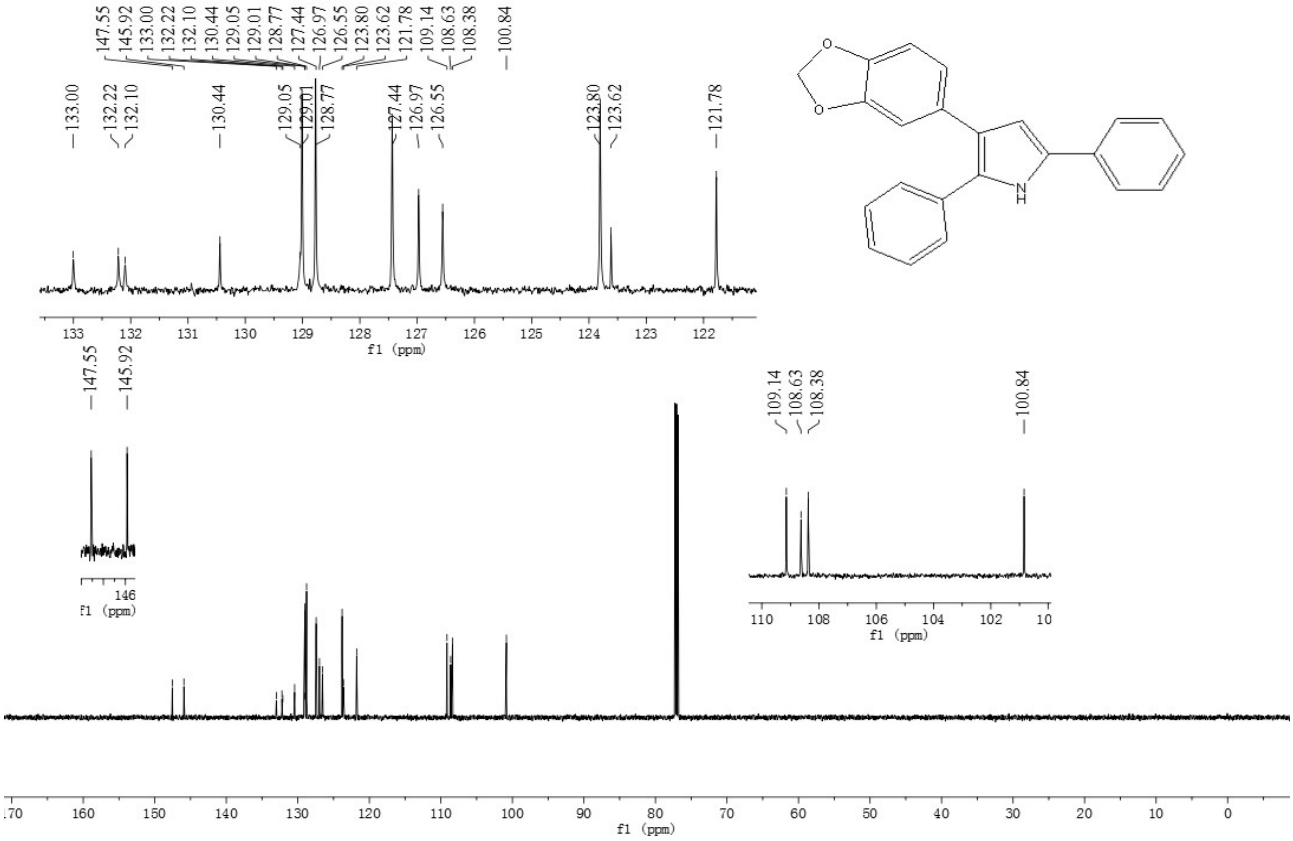

## Compound 3ka



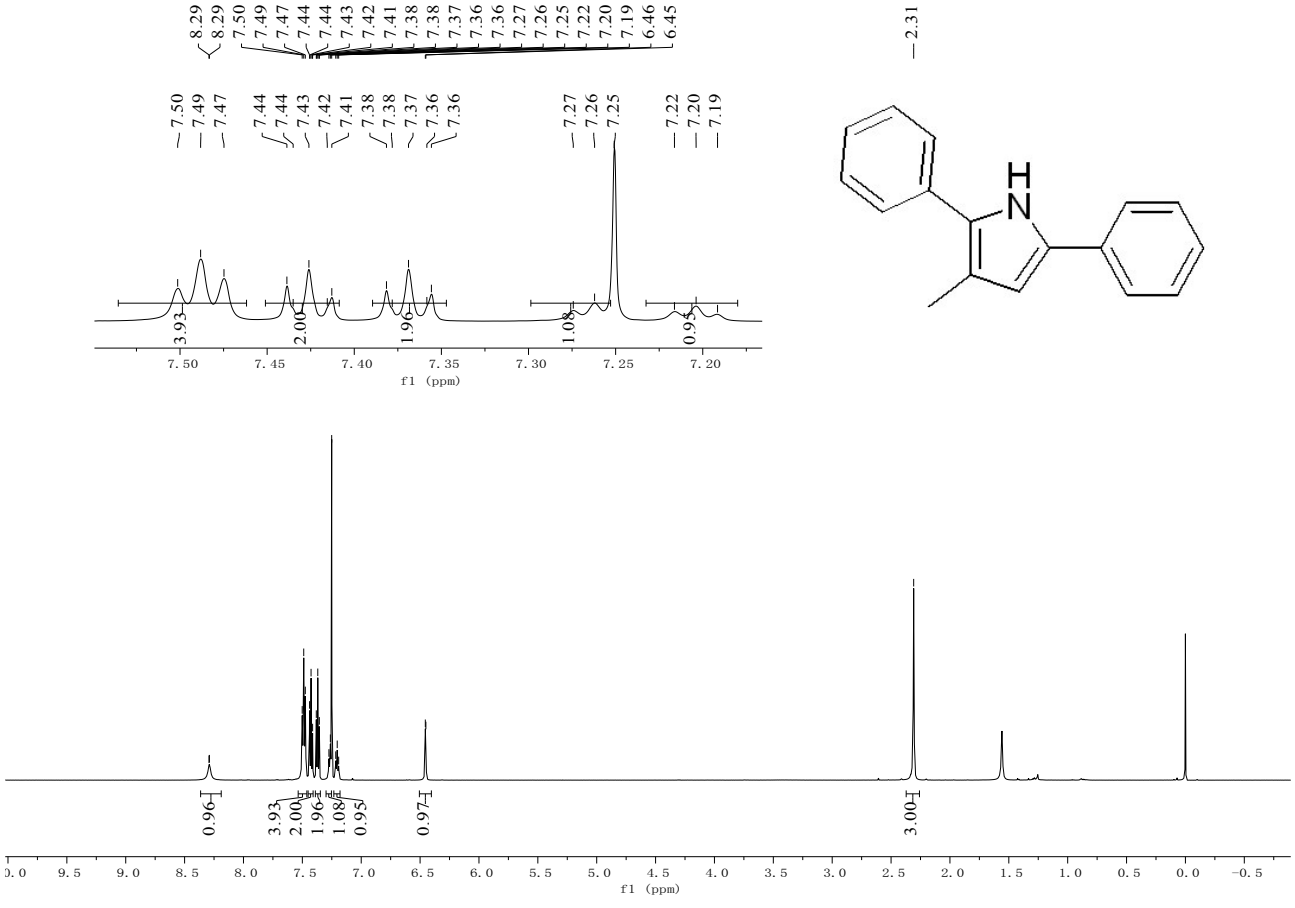


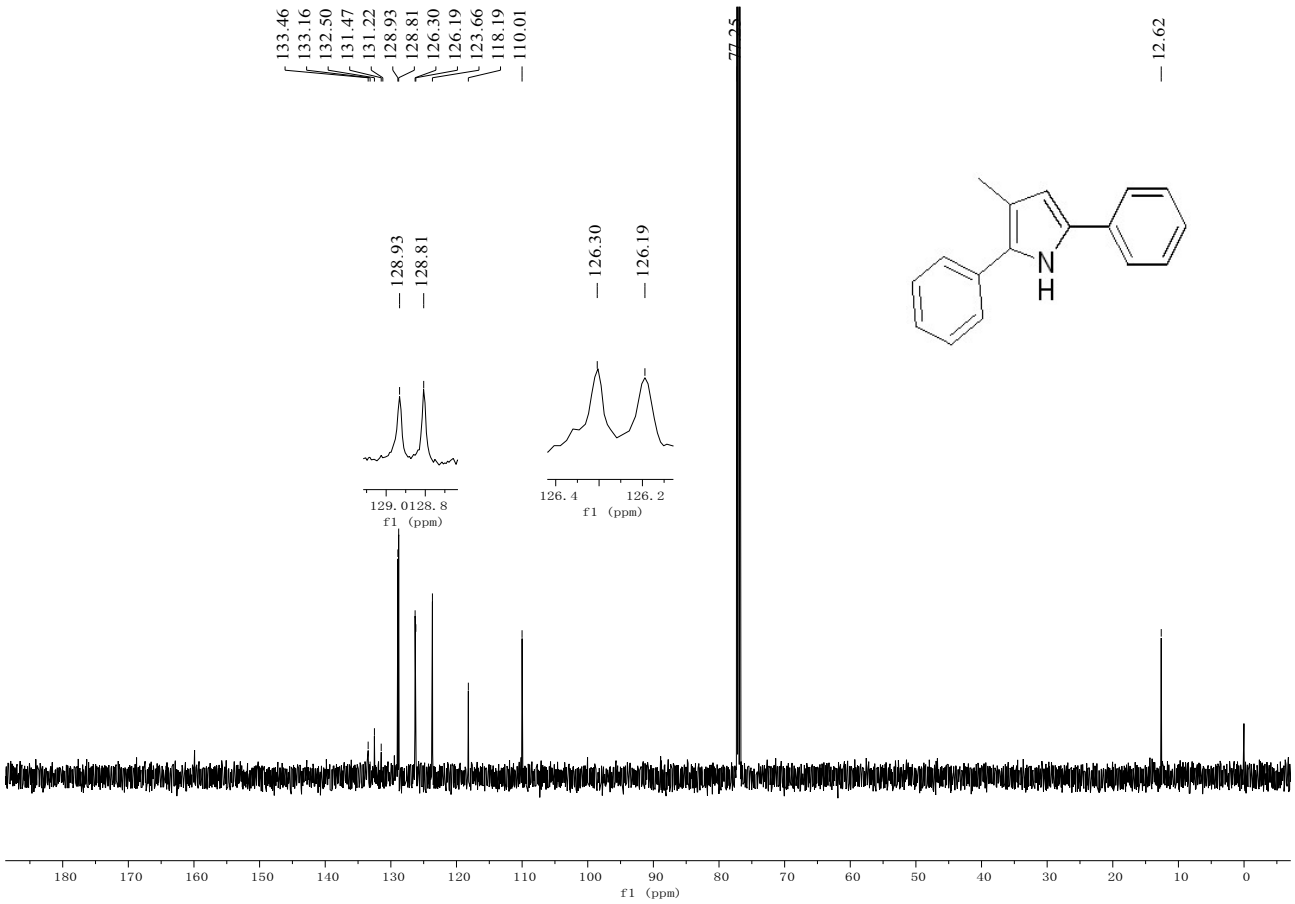
## Compound 3la



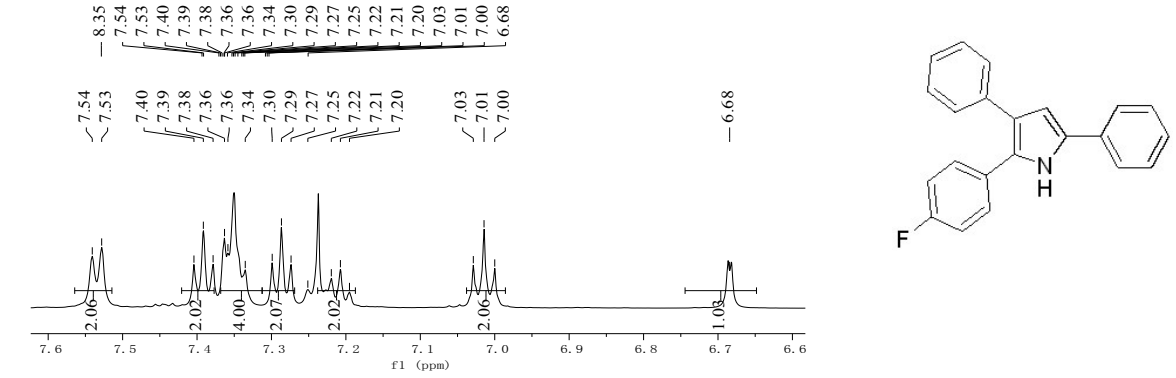


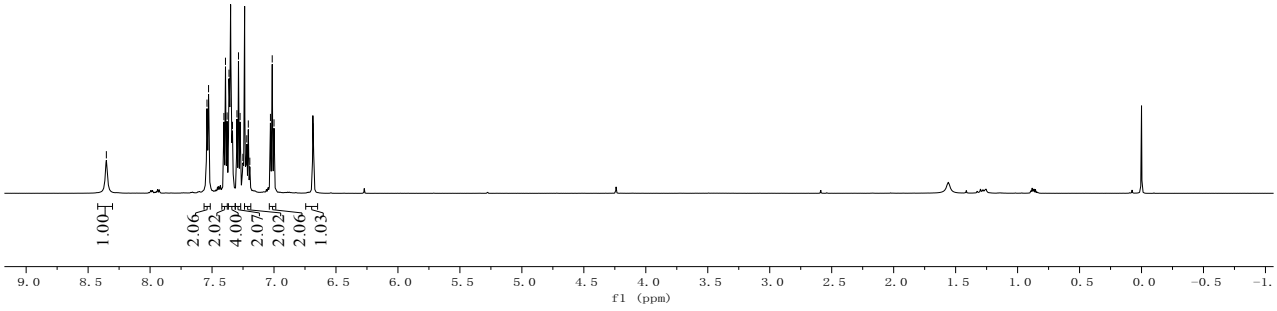
## Compound 3ma

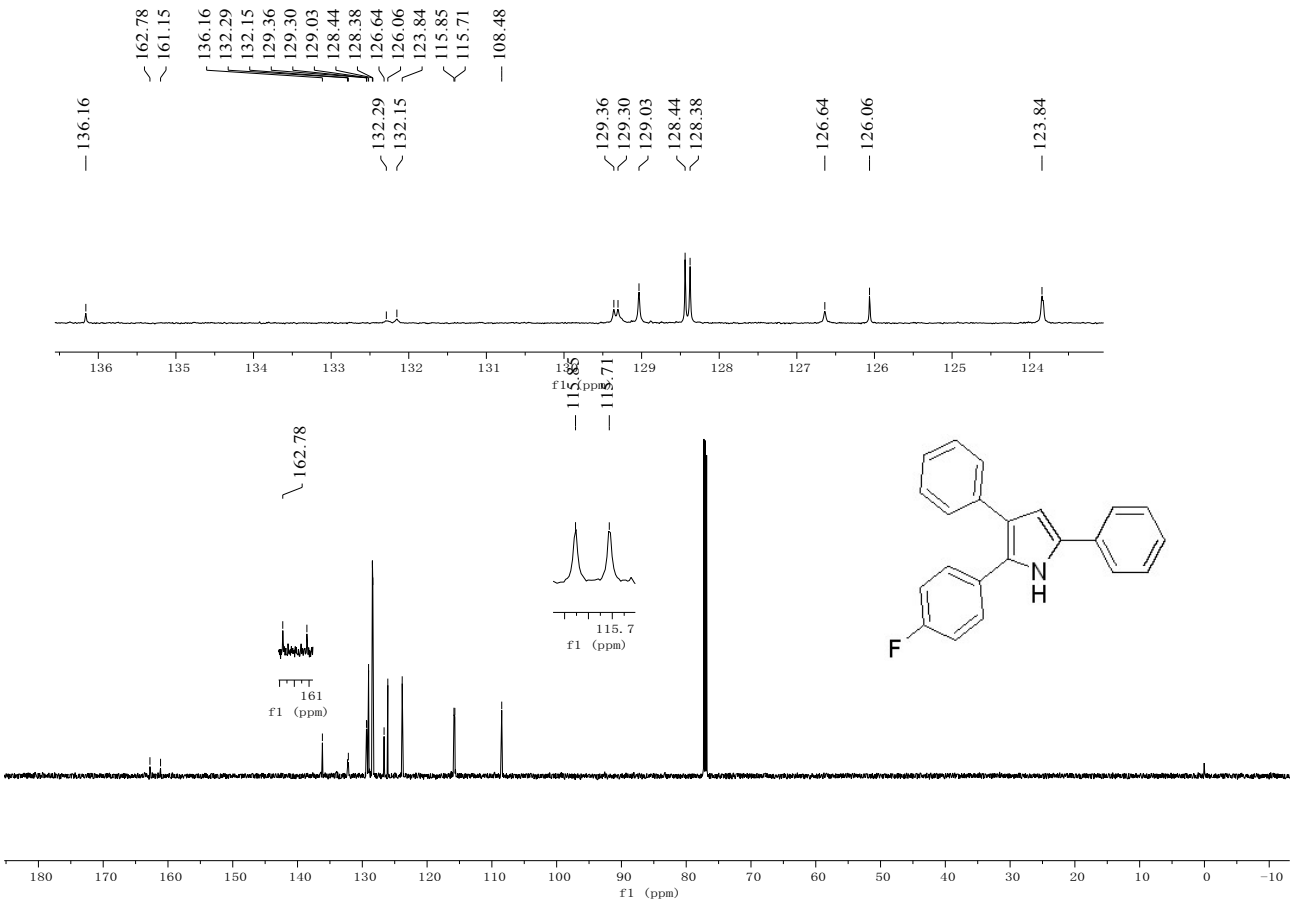





## Compound 3na




162.78
161.15
136.16
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129.36
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129.03
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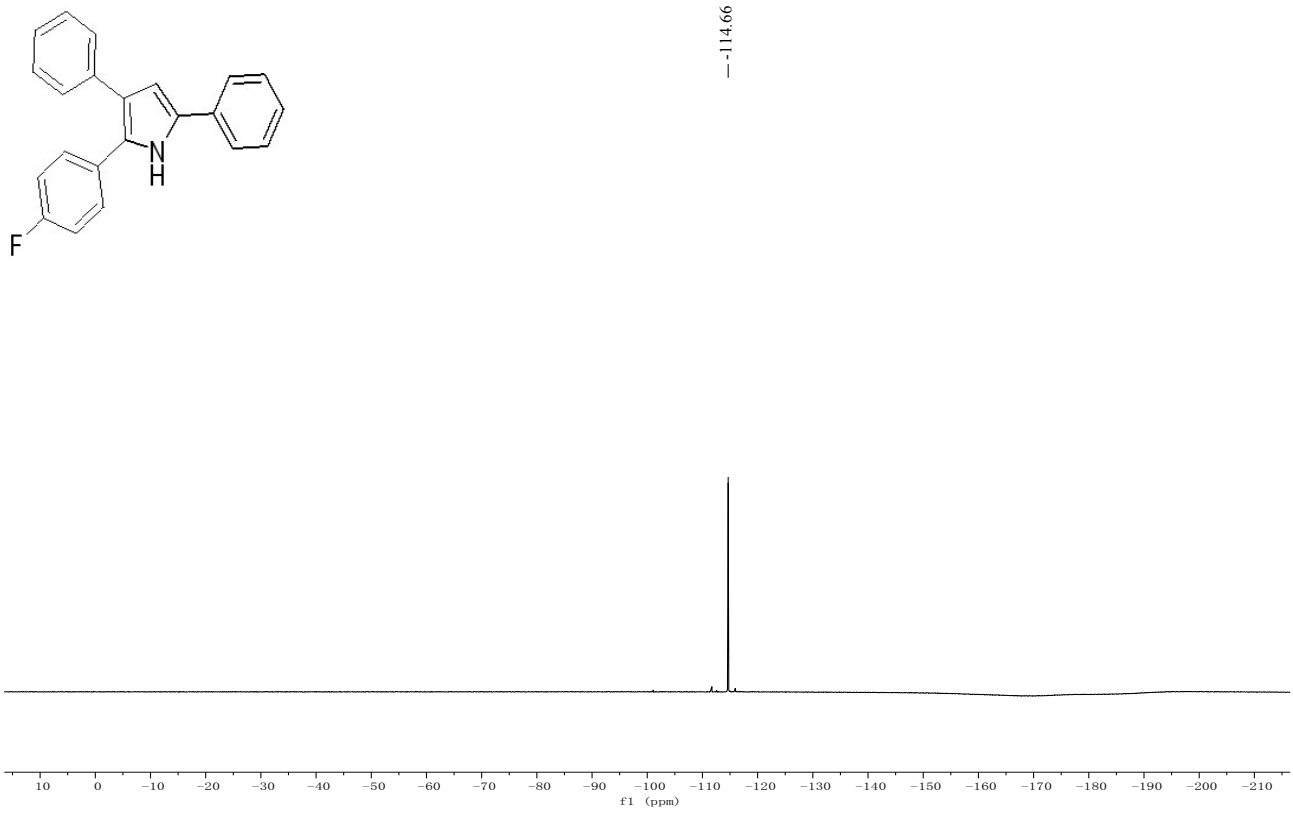
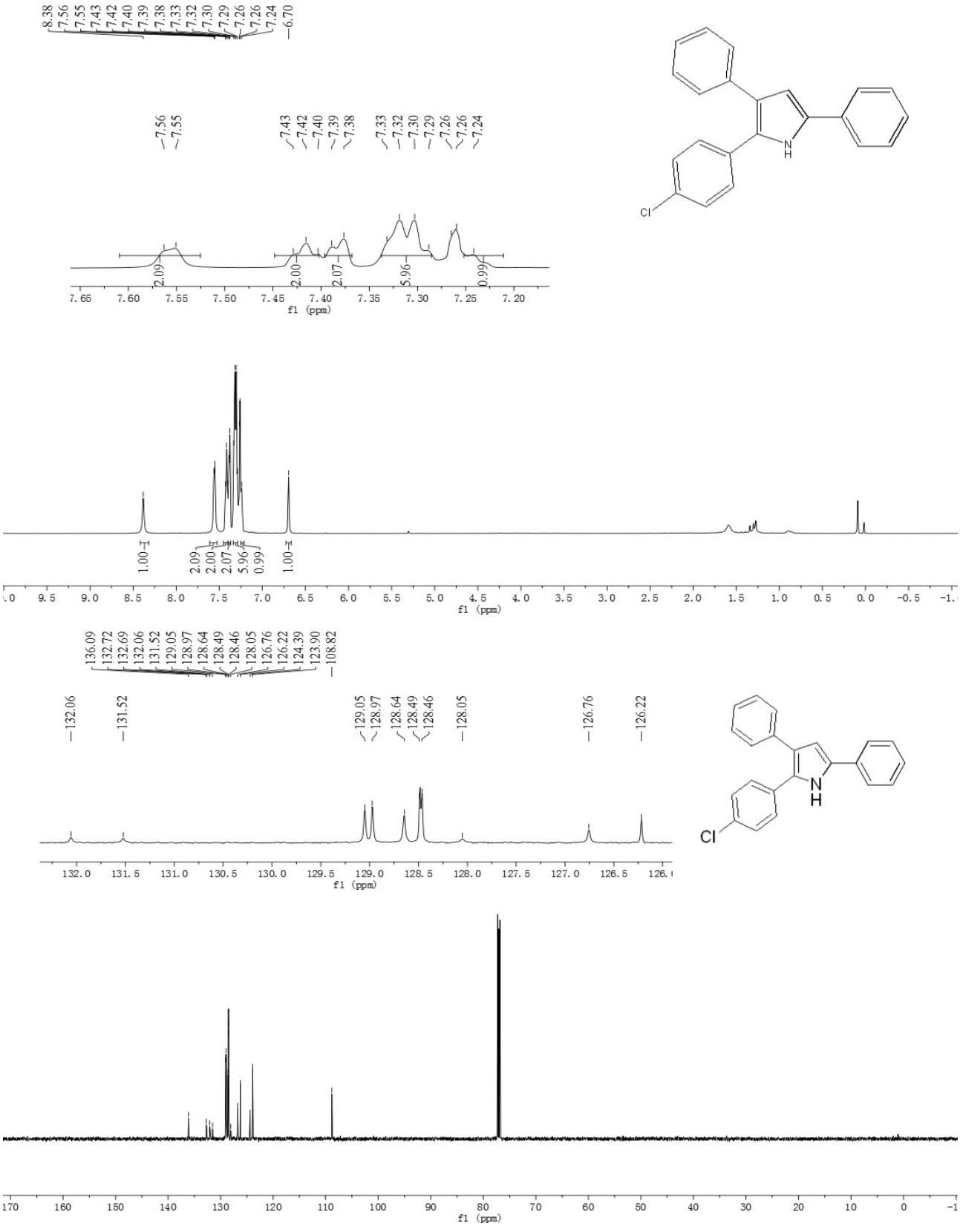
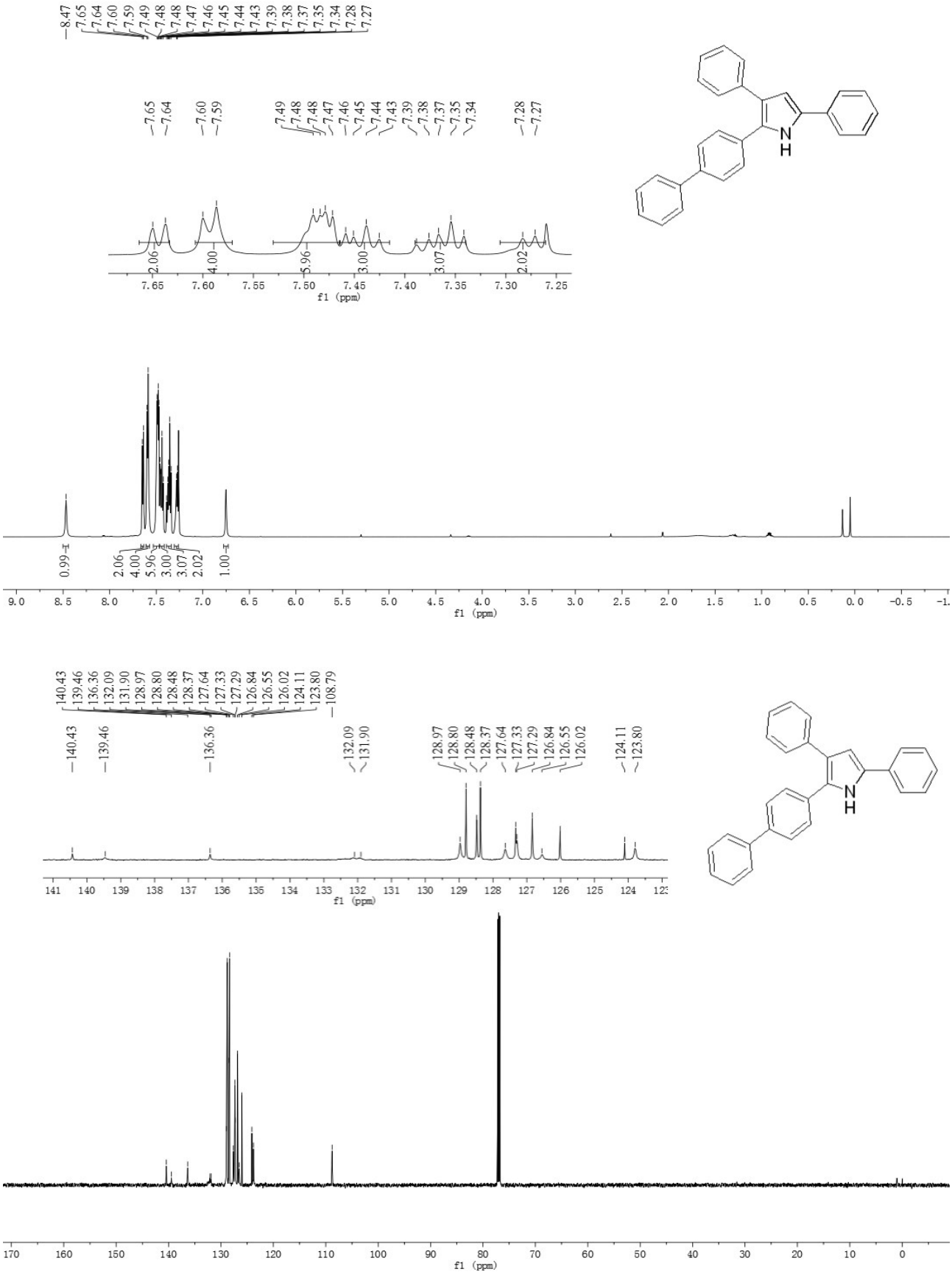
126.64
126.06
123.84
115.85
115.71
108.48
f1 (ppm)
N
H
F


-114.66
f1 (ppm)

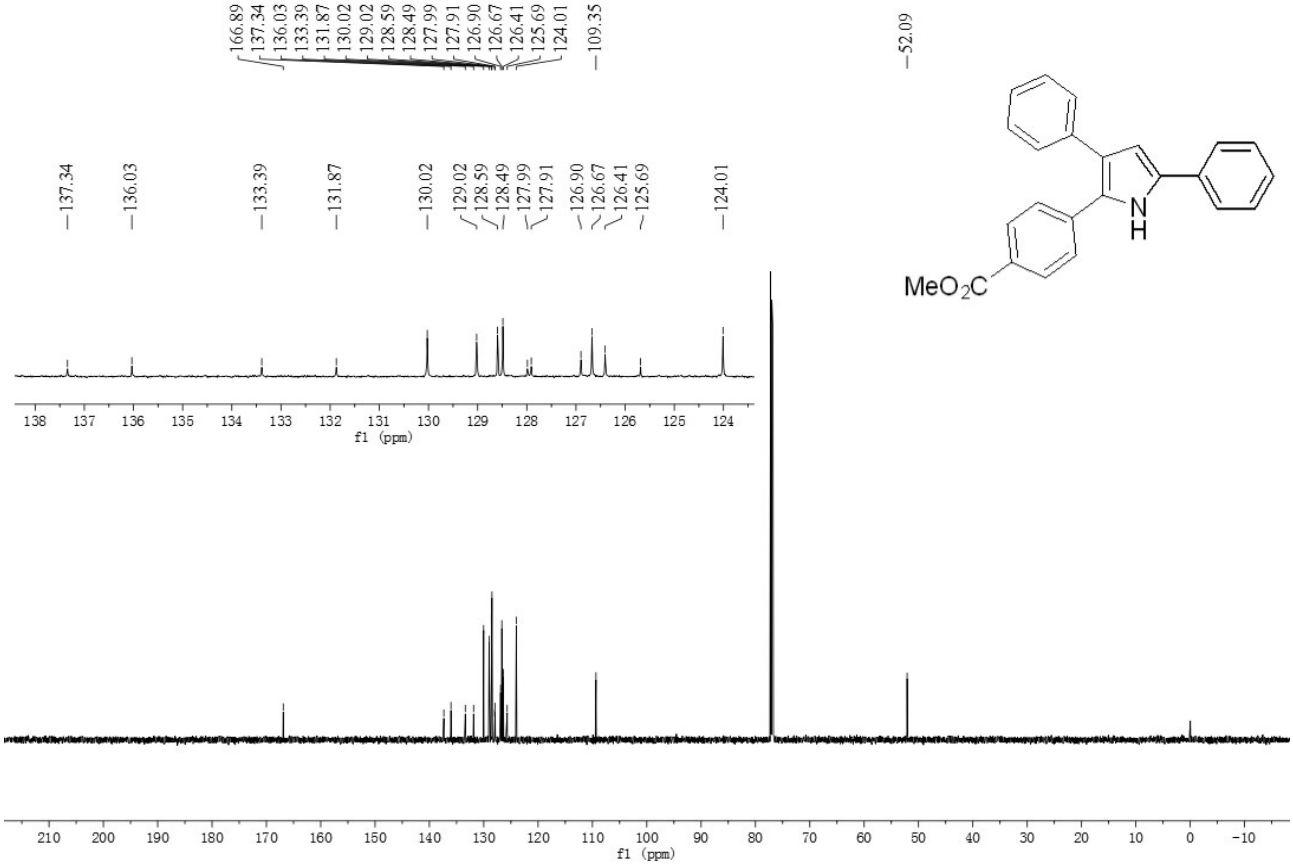
## Compound 3oa

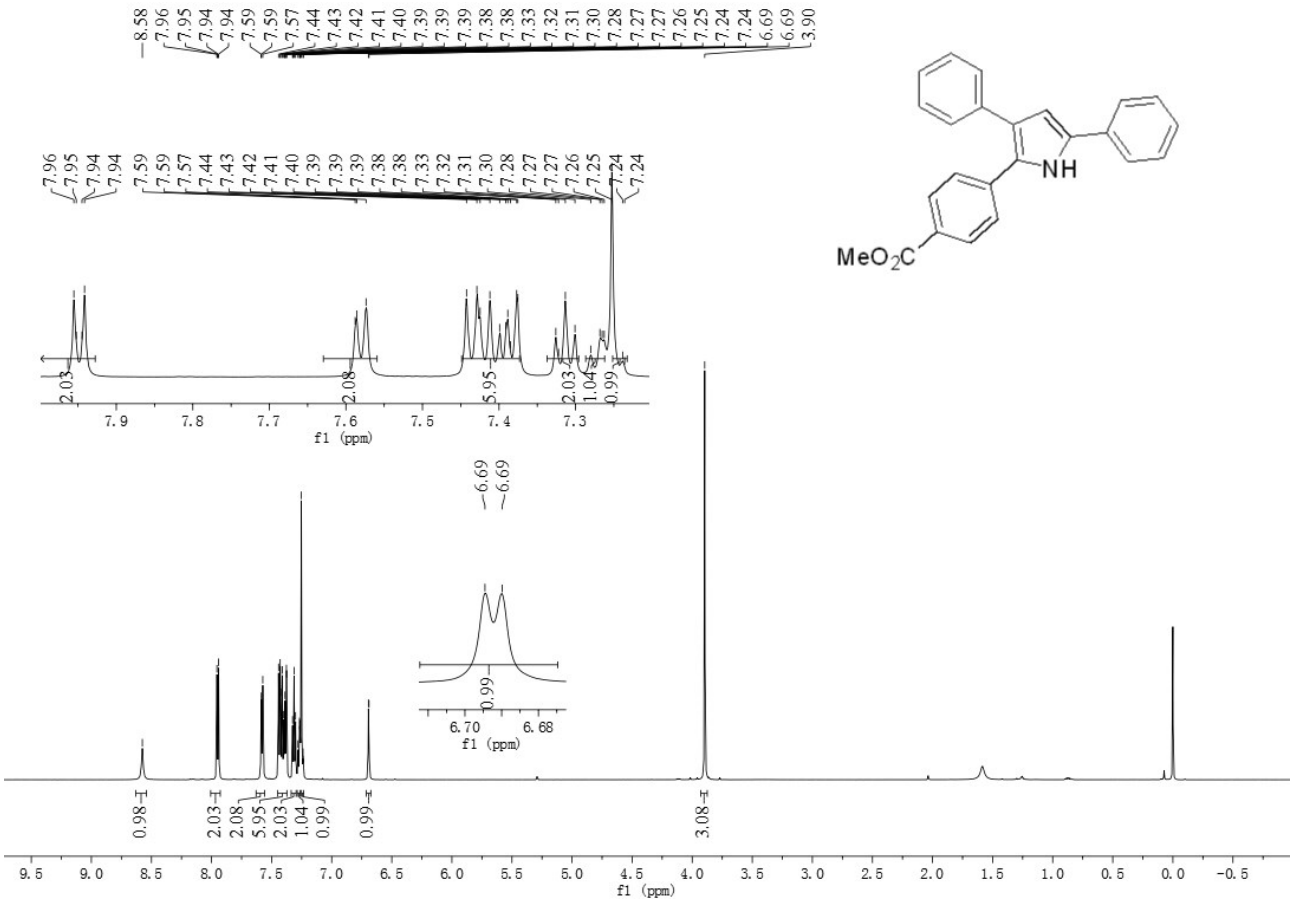


## Compound 3pa

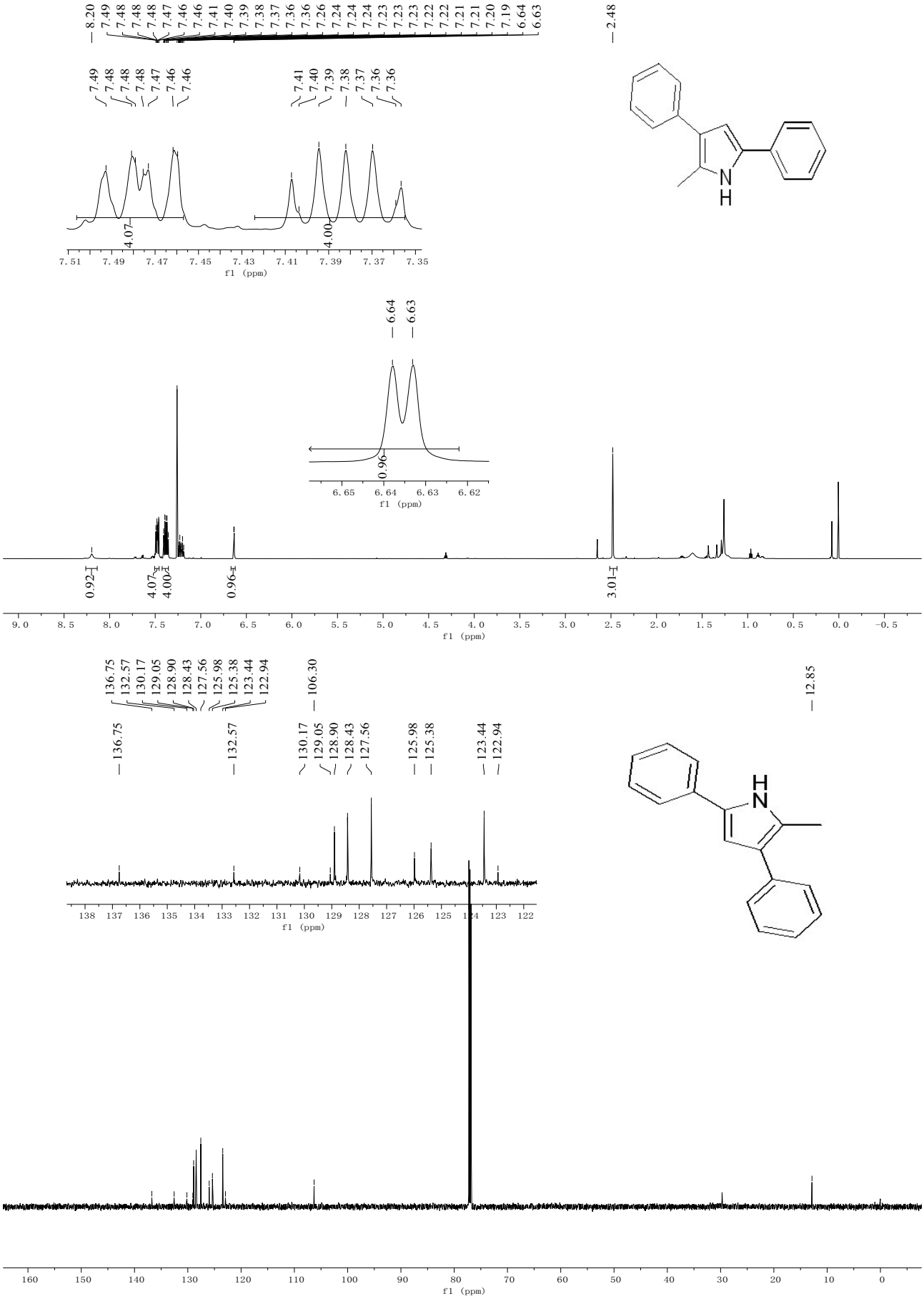


. **Compound 3qa**

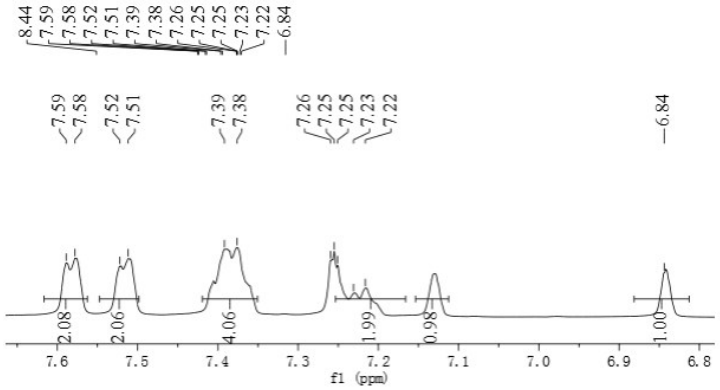


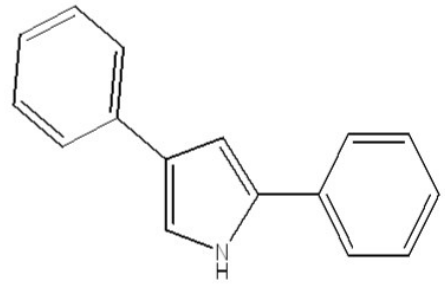



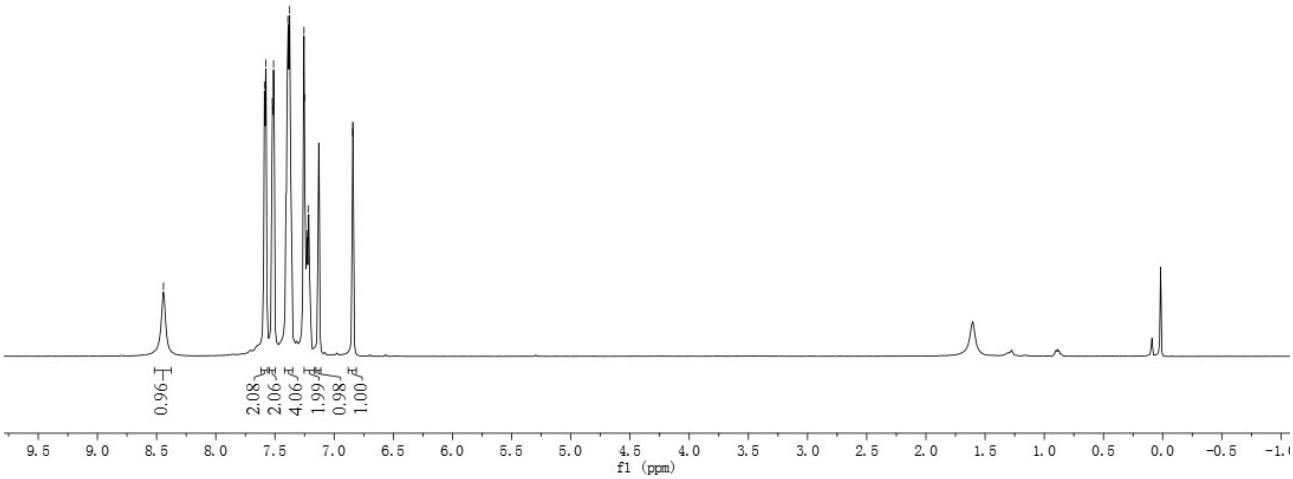
## Compound 3ra

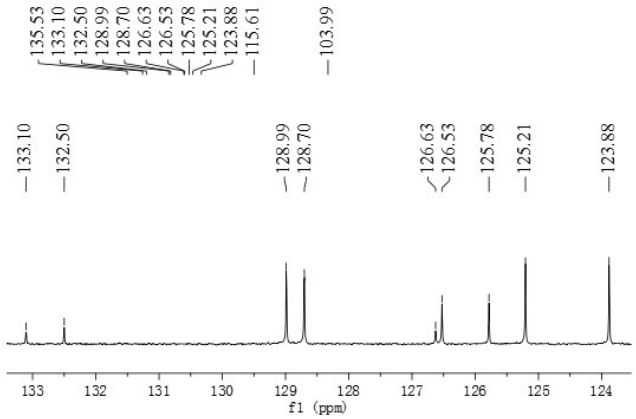


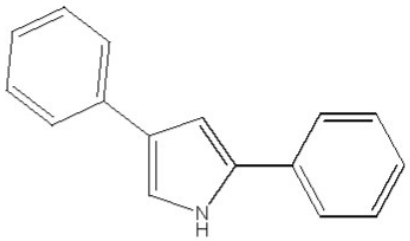
## Compound 3sa

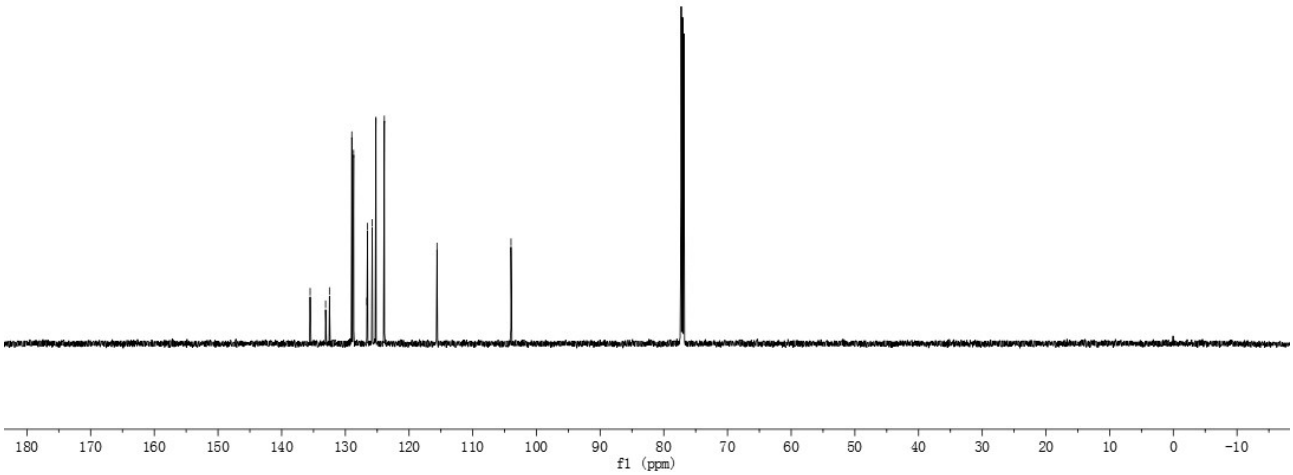


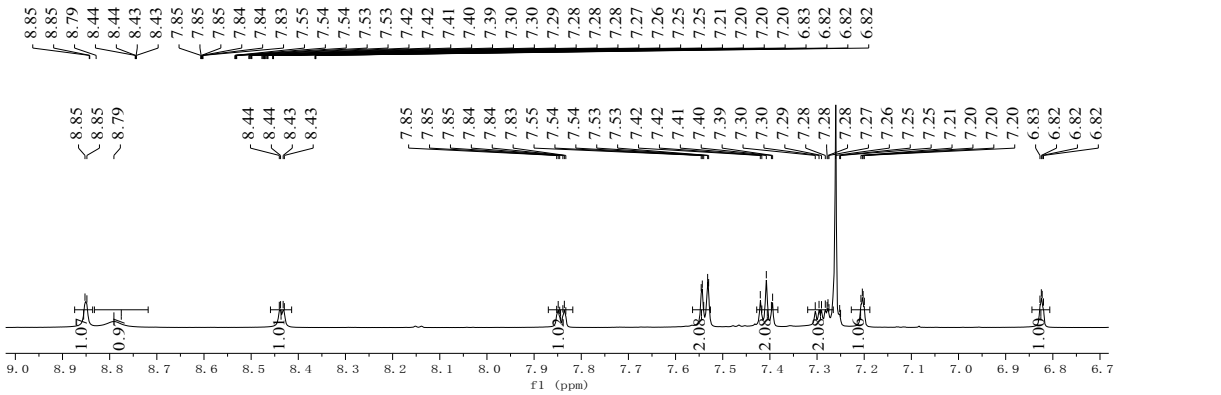


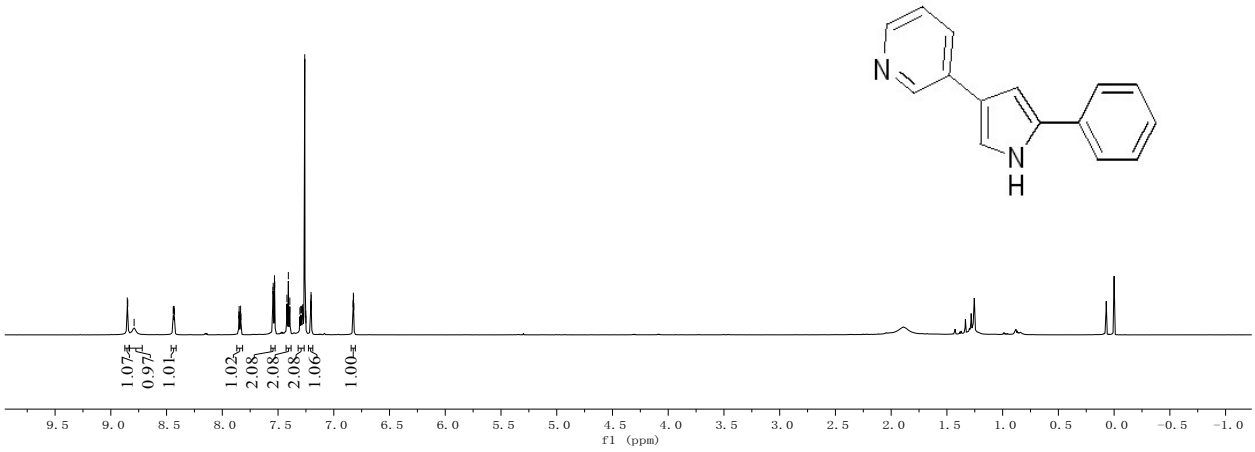



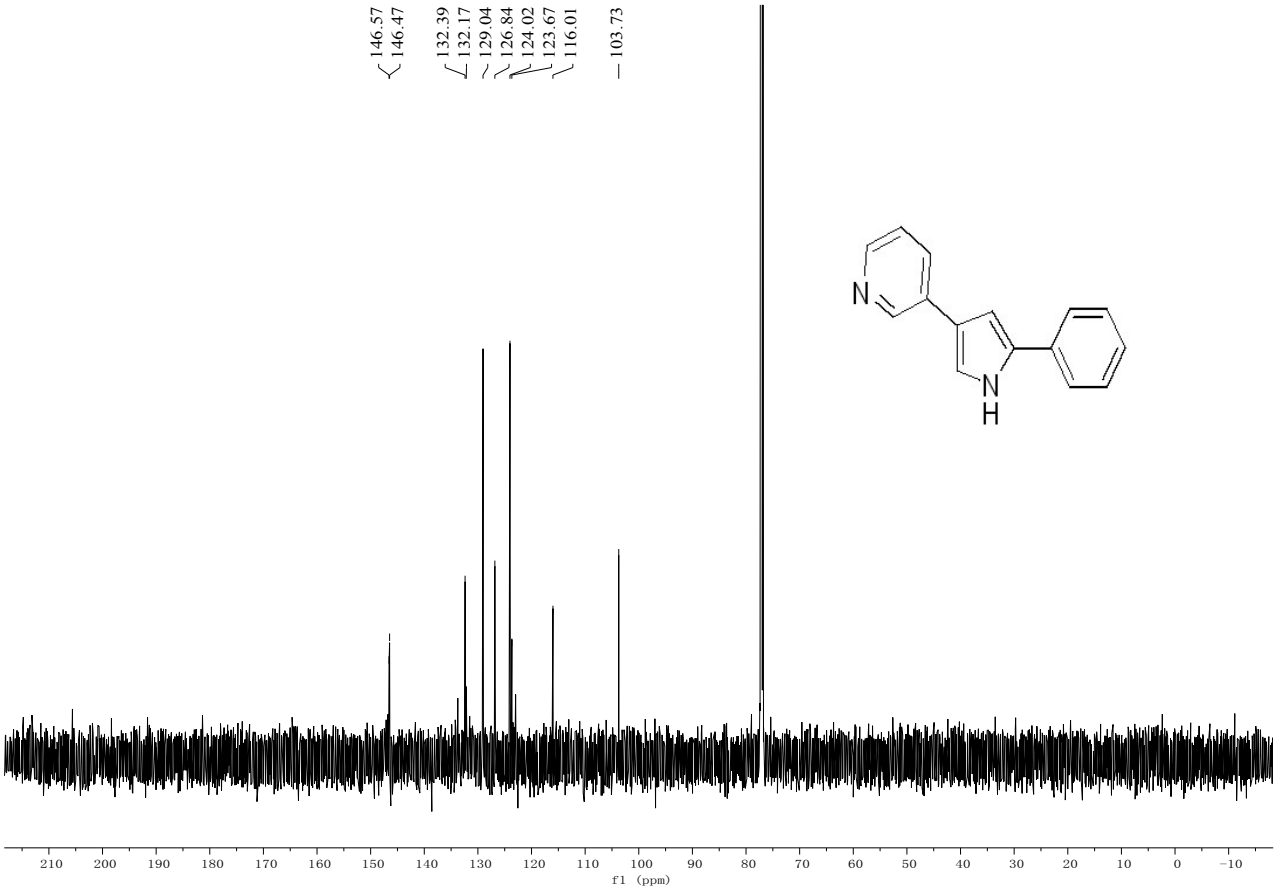





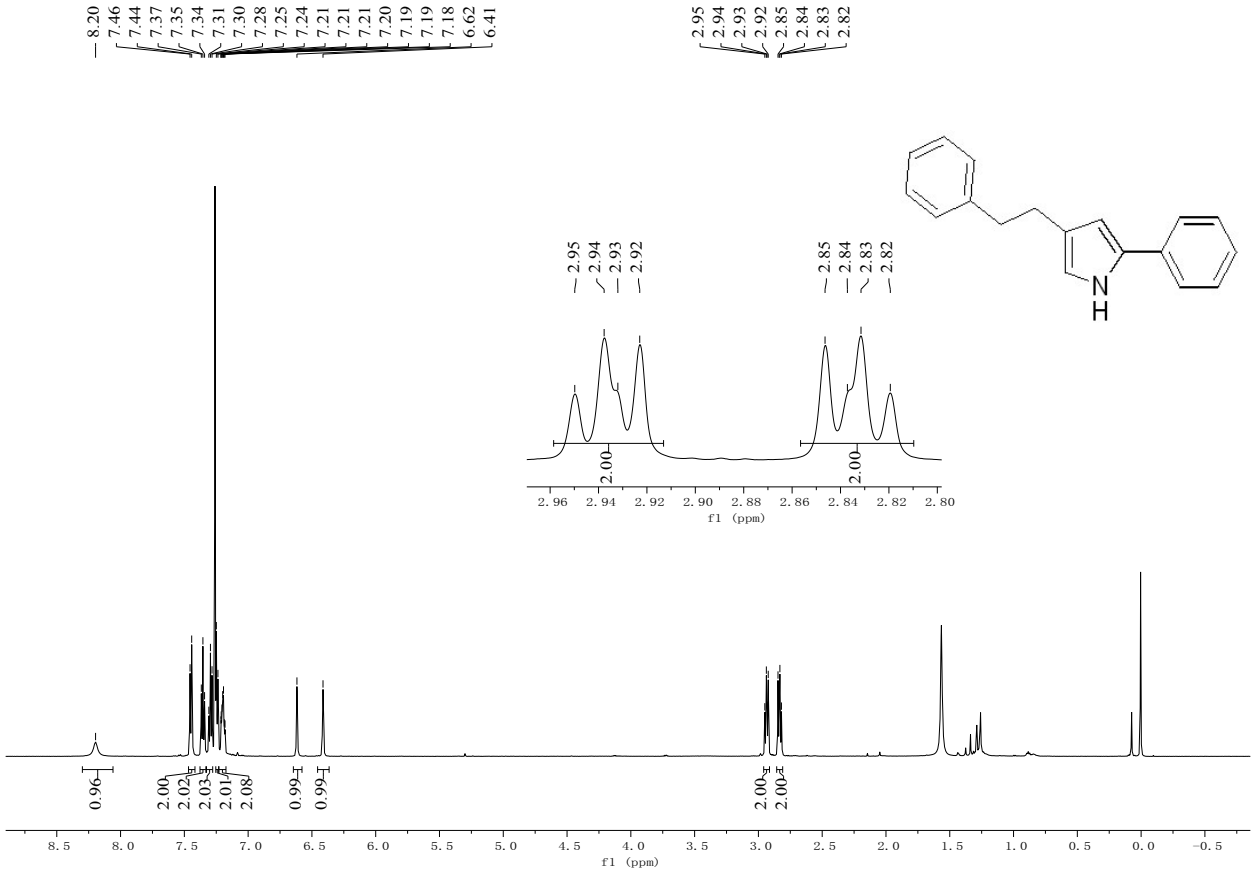
## Compound 3ta

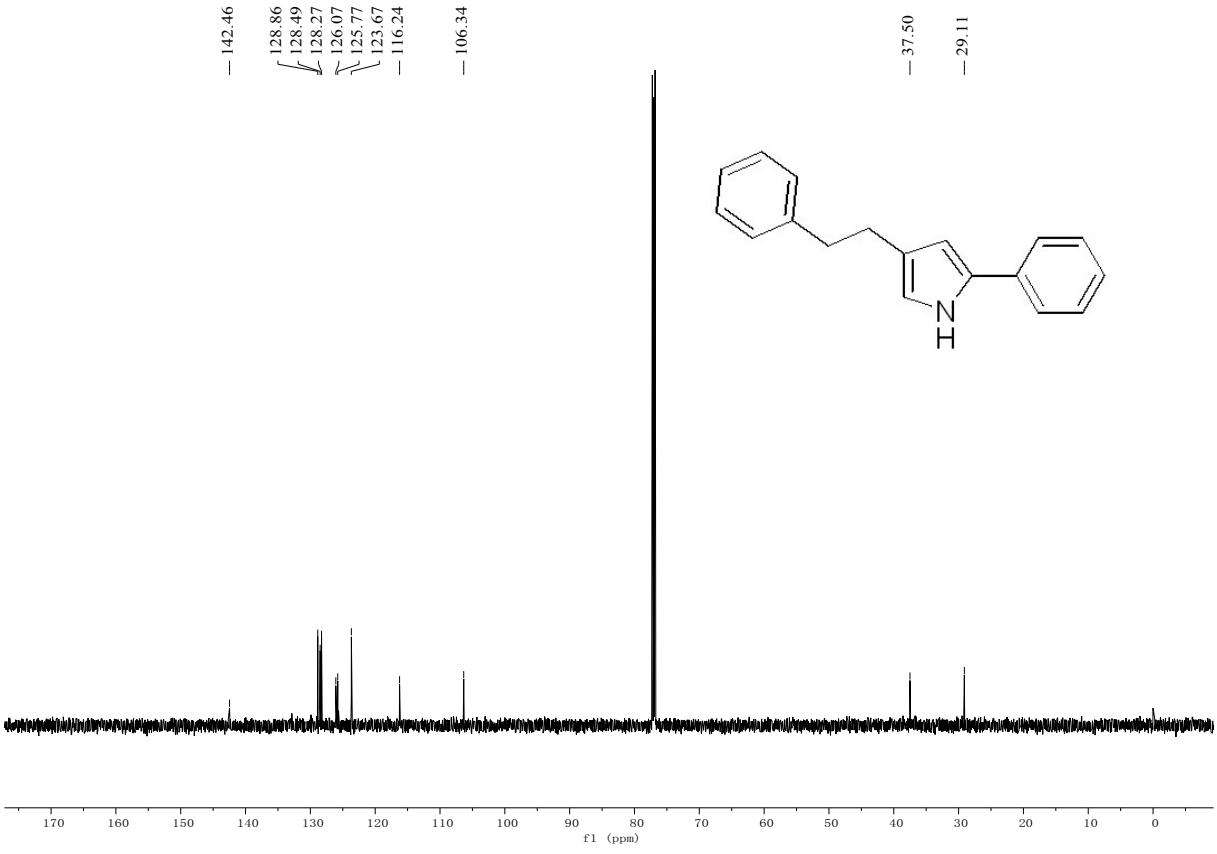


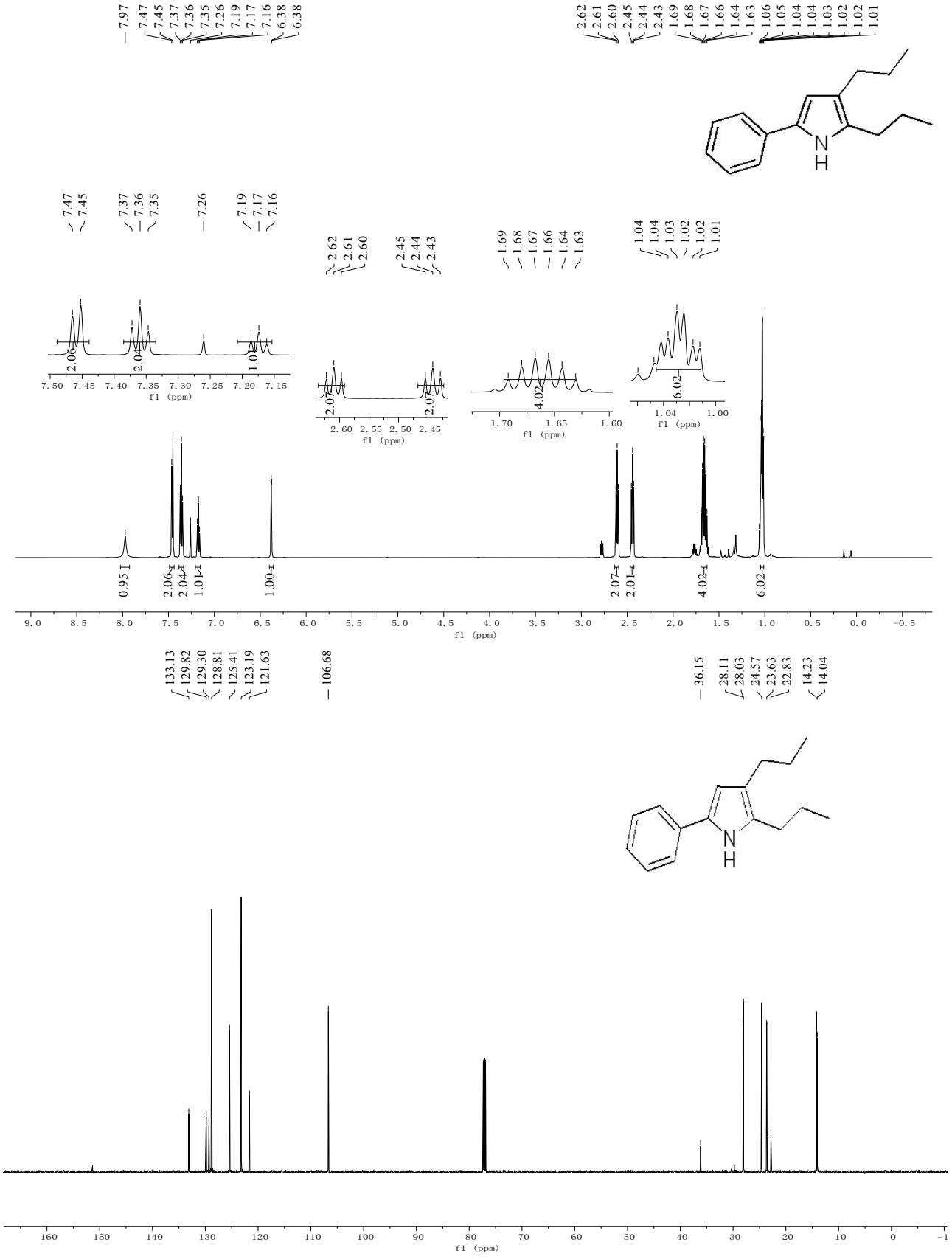



## Compound 3ua

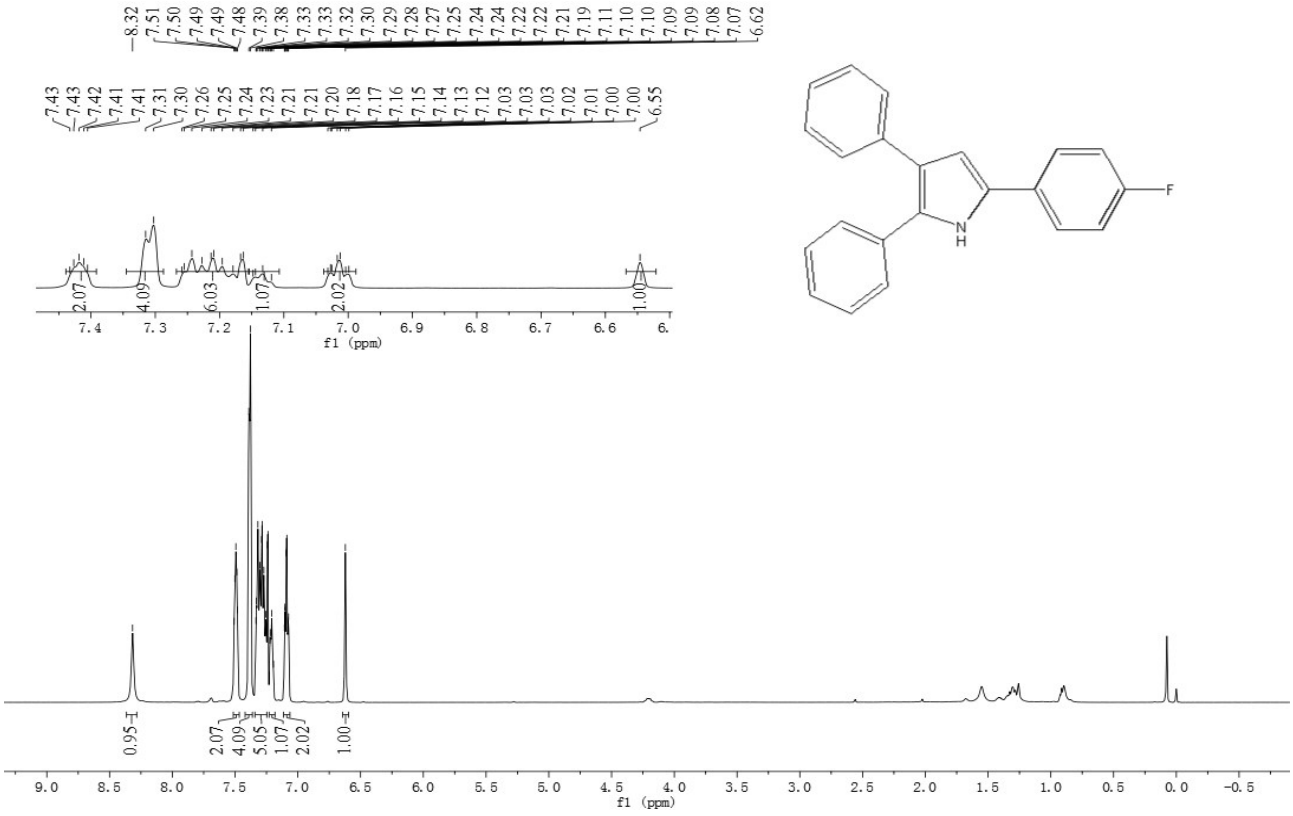


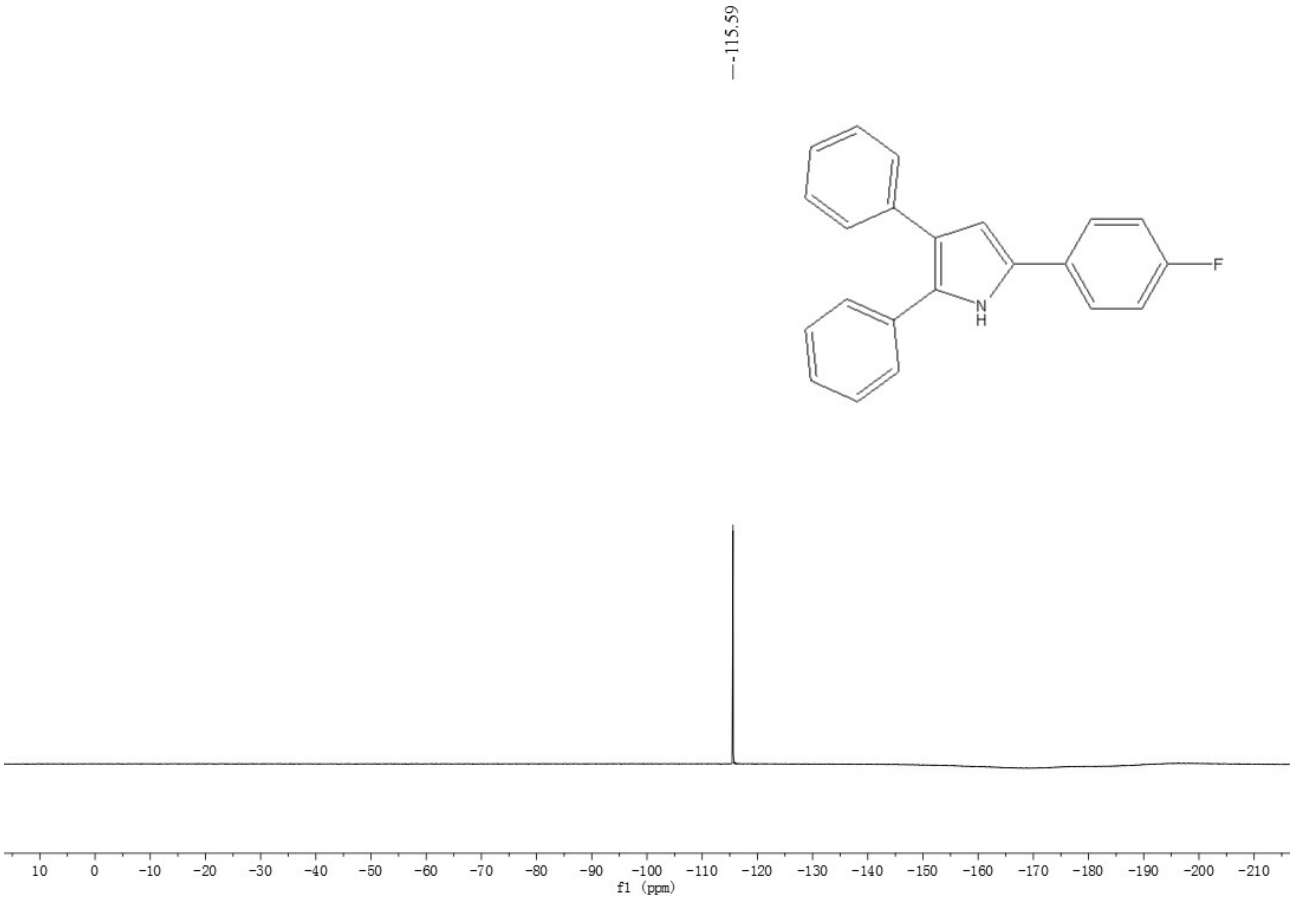



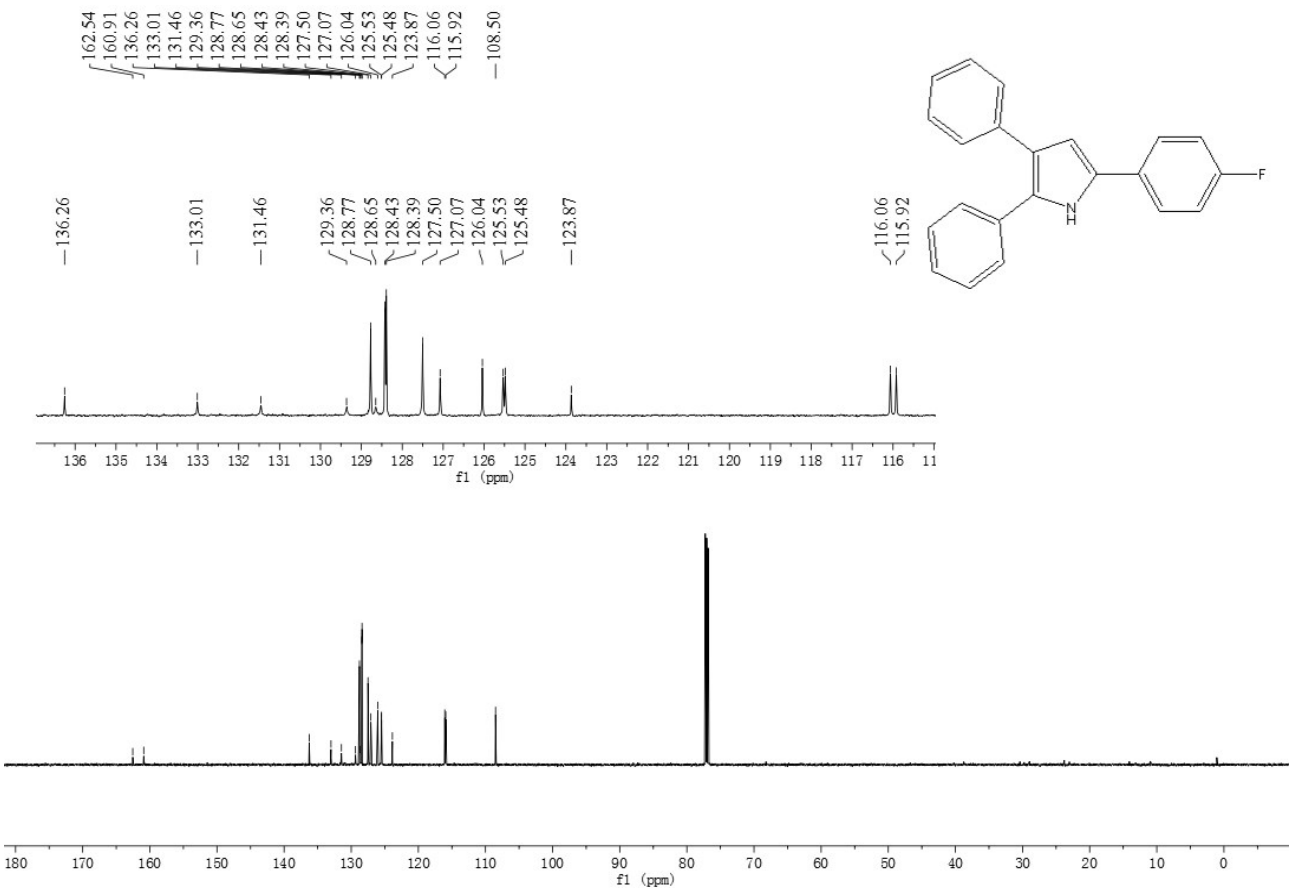
## Compound 3va



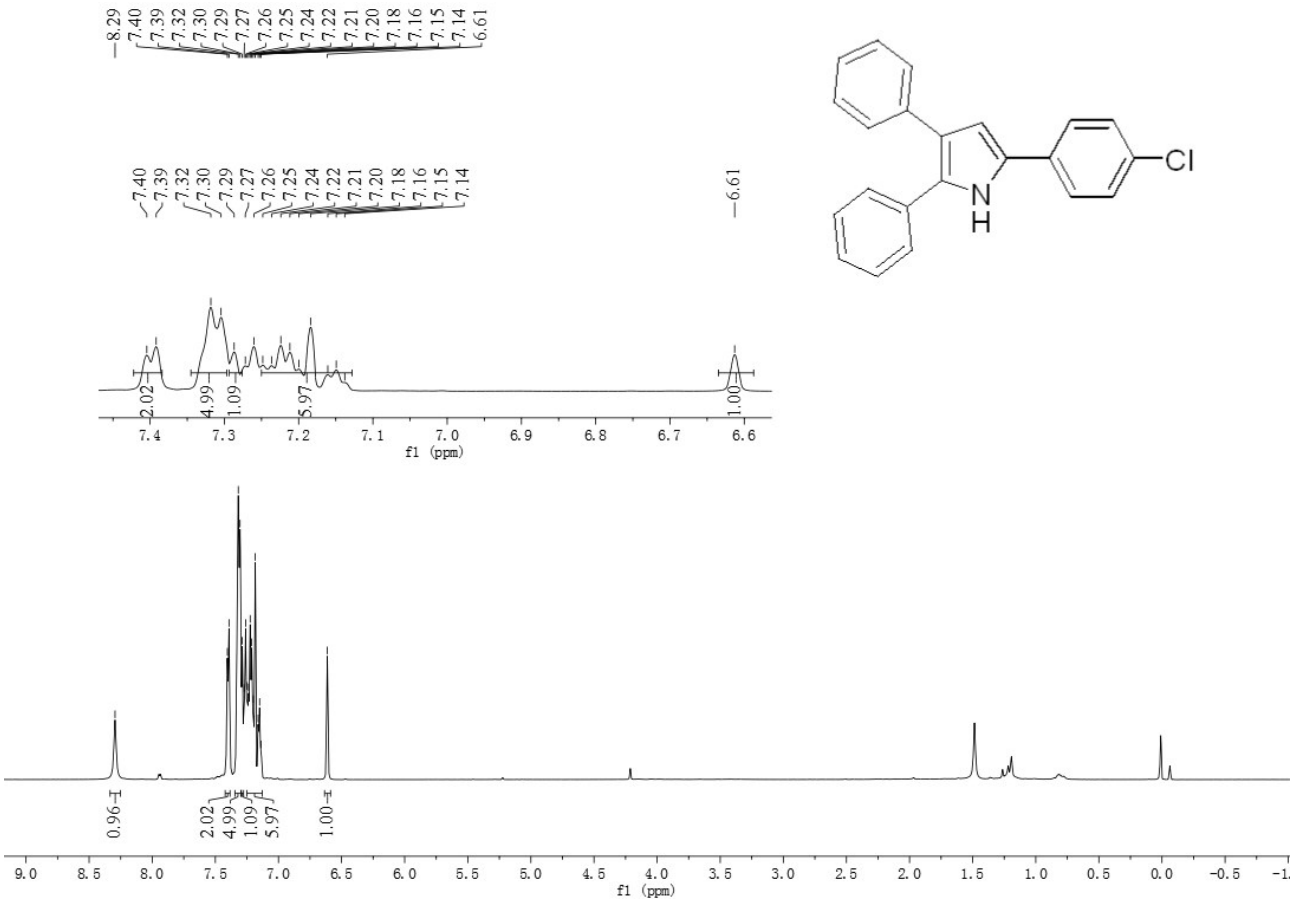
## Compound 3ab

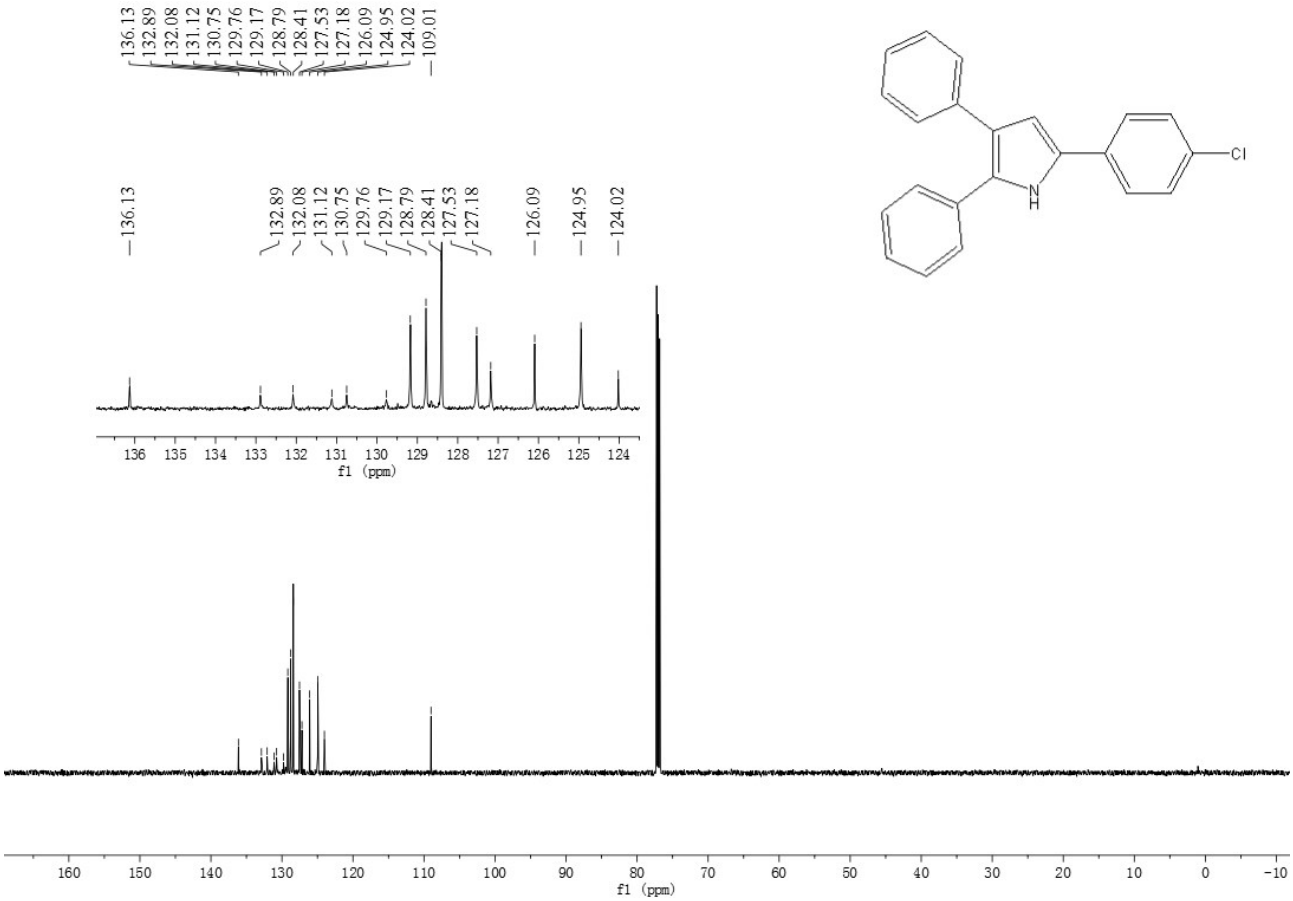


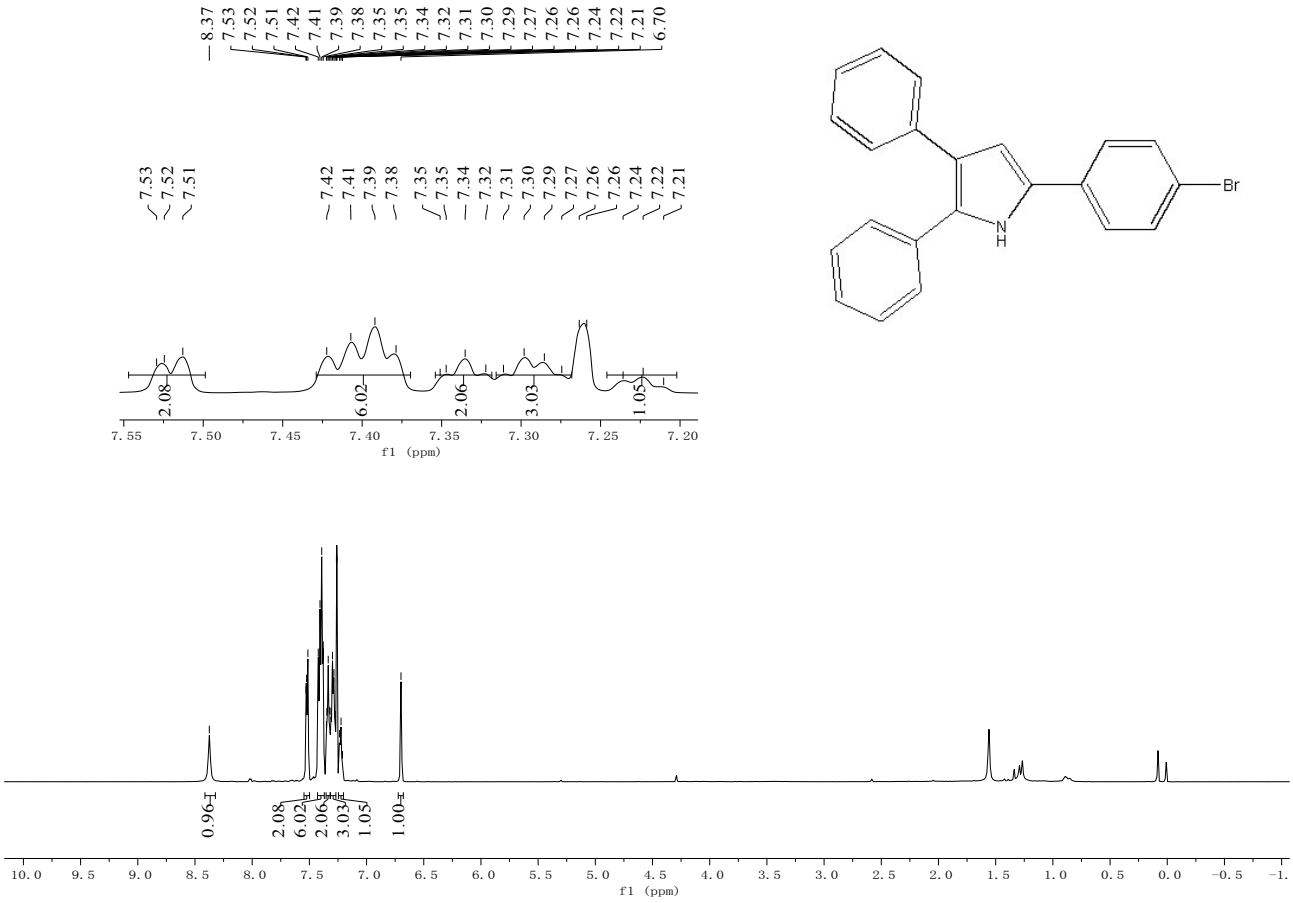


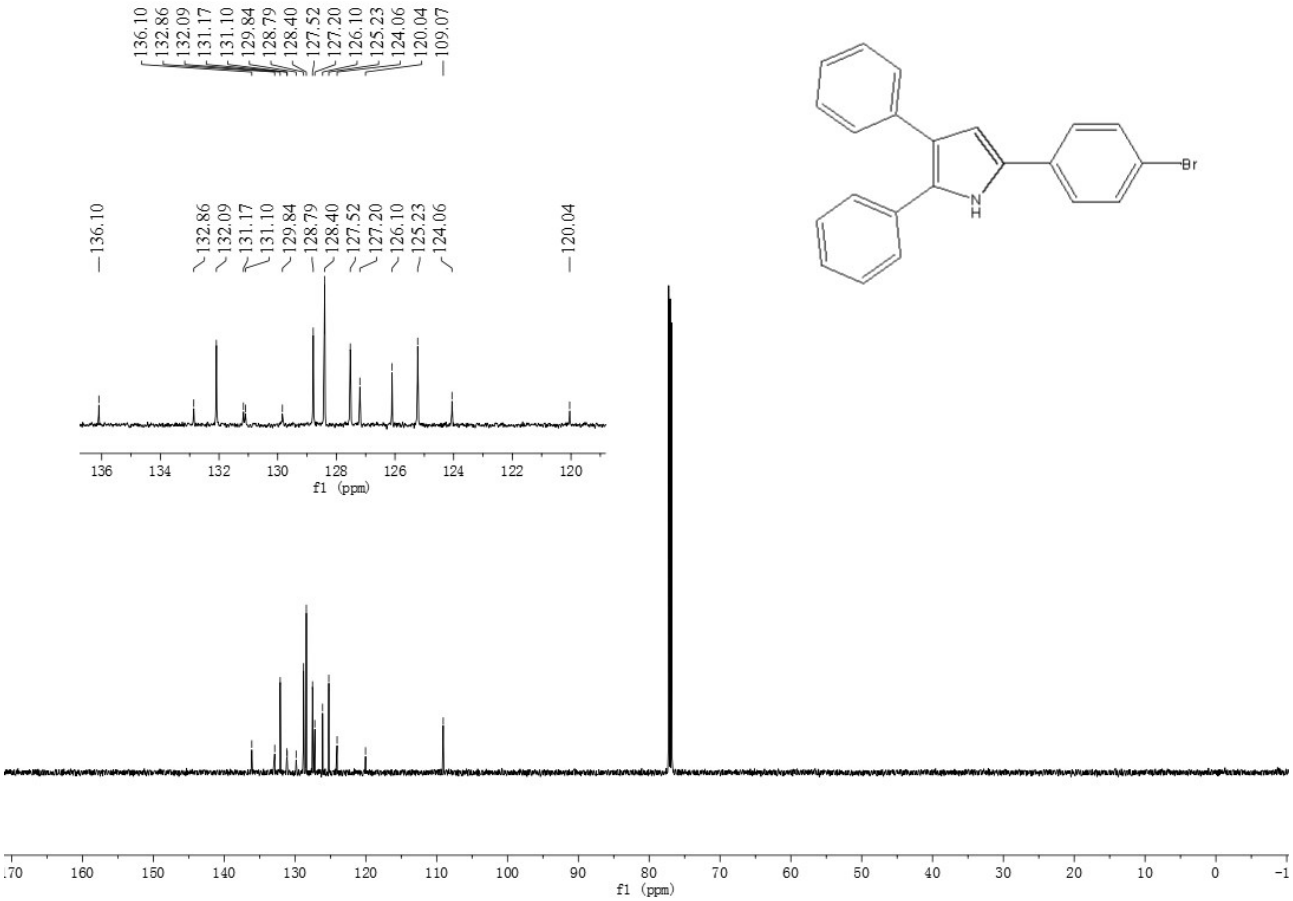

## Compound 3ac



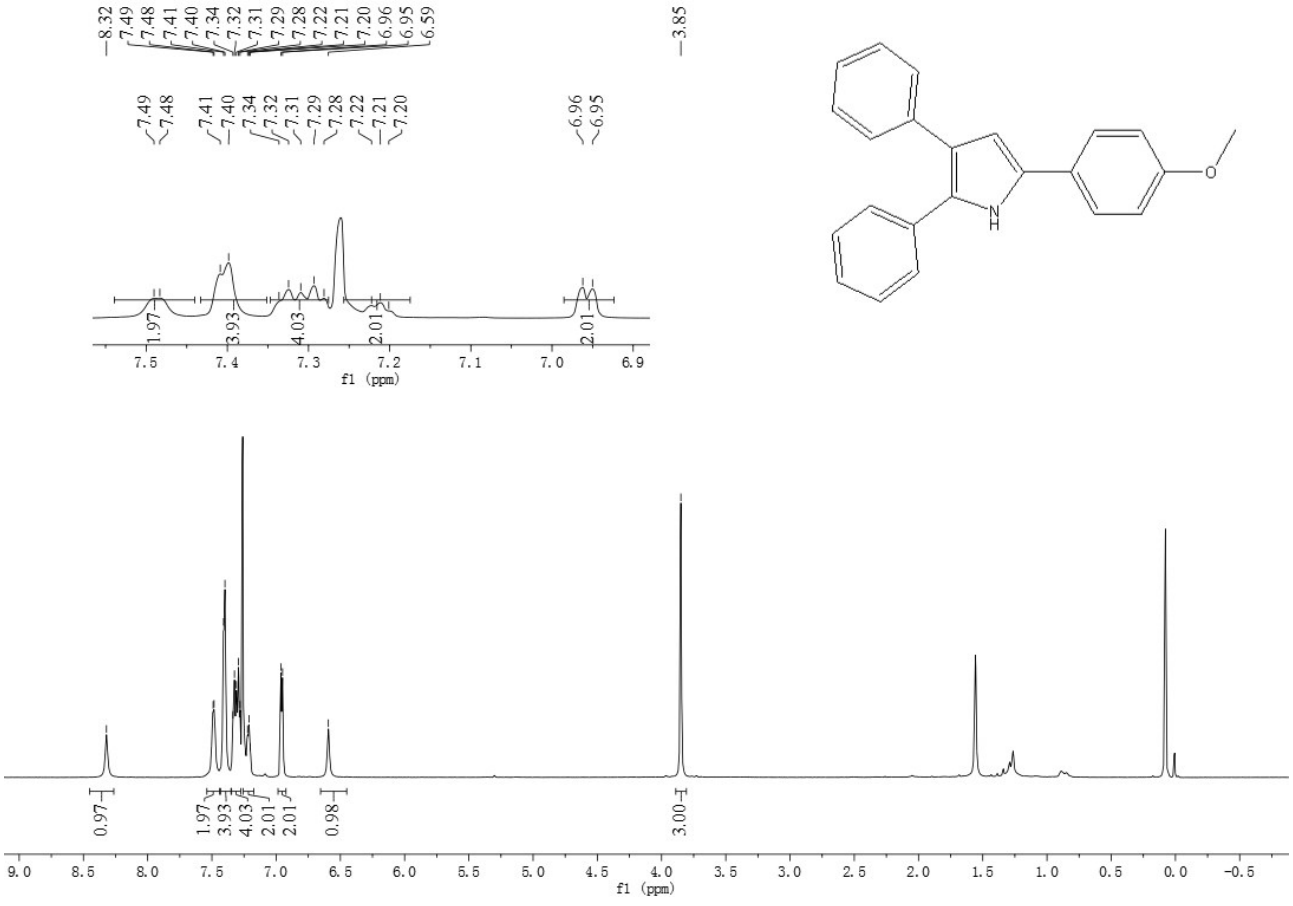


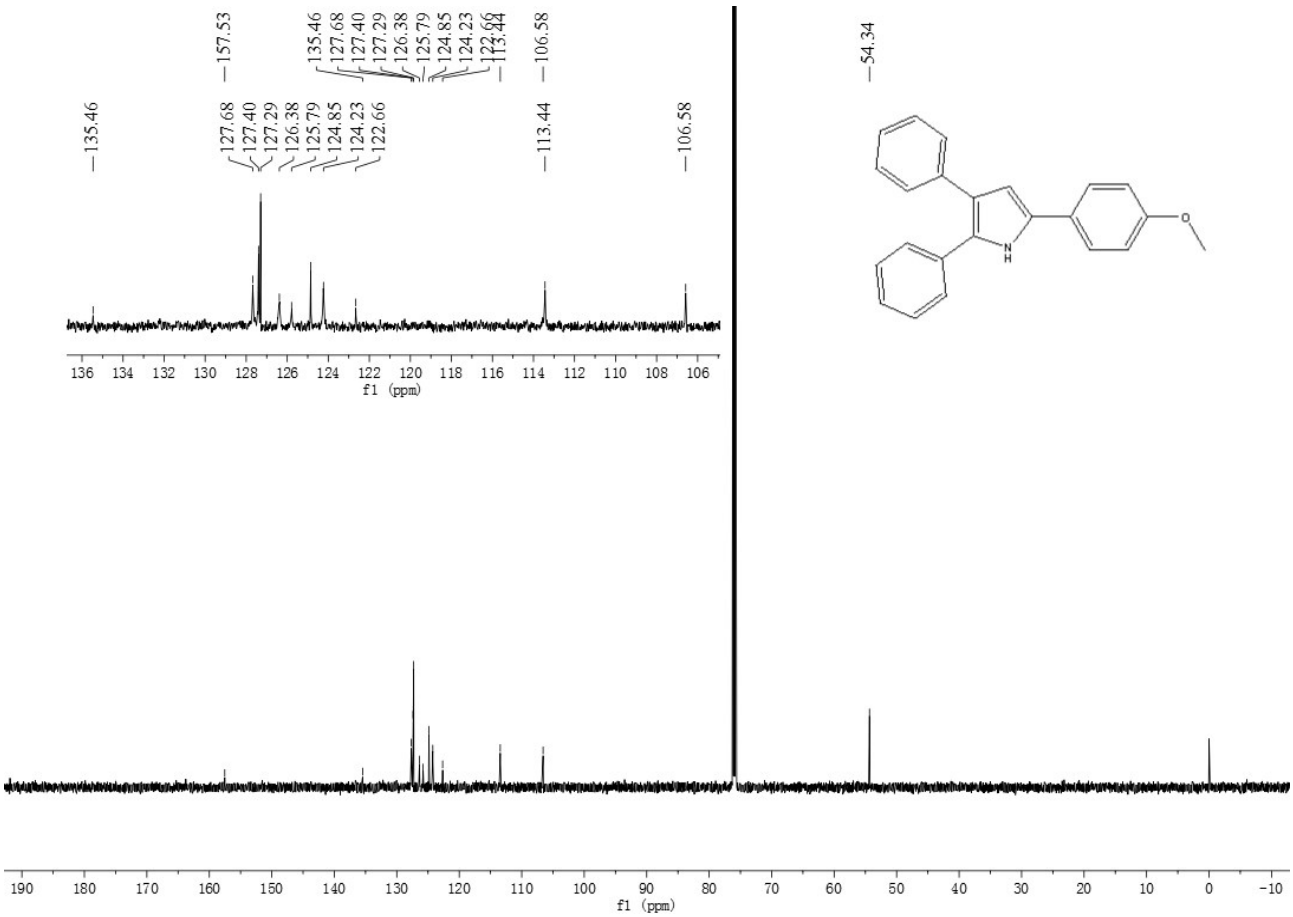

## Compound 3ad



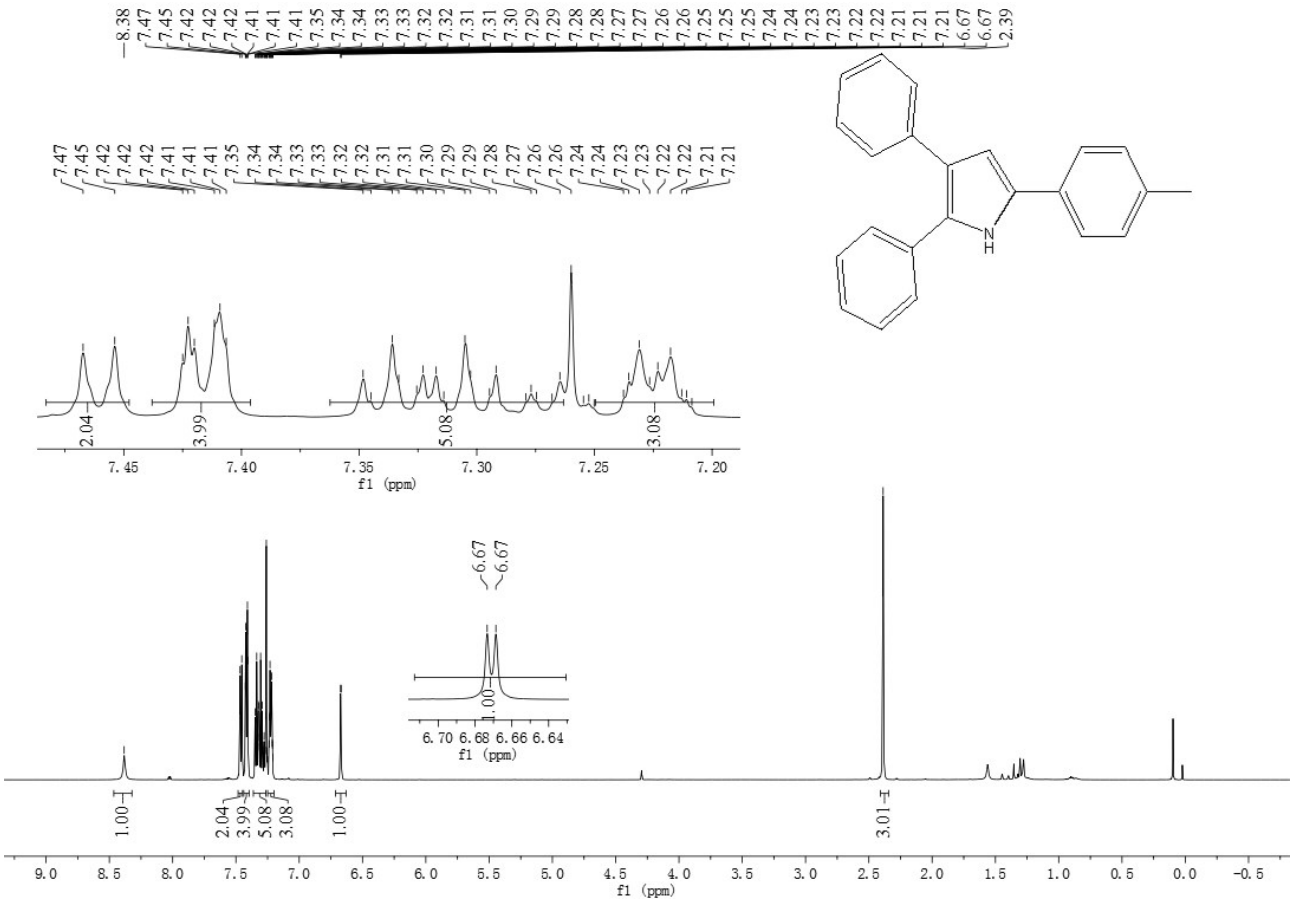


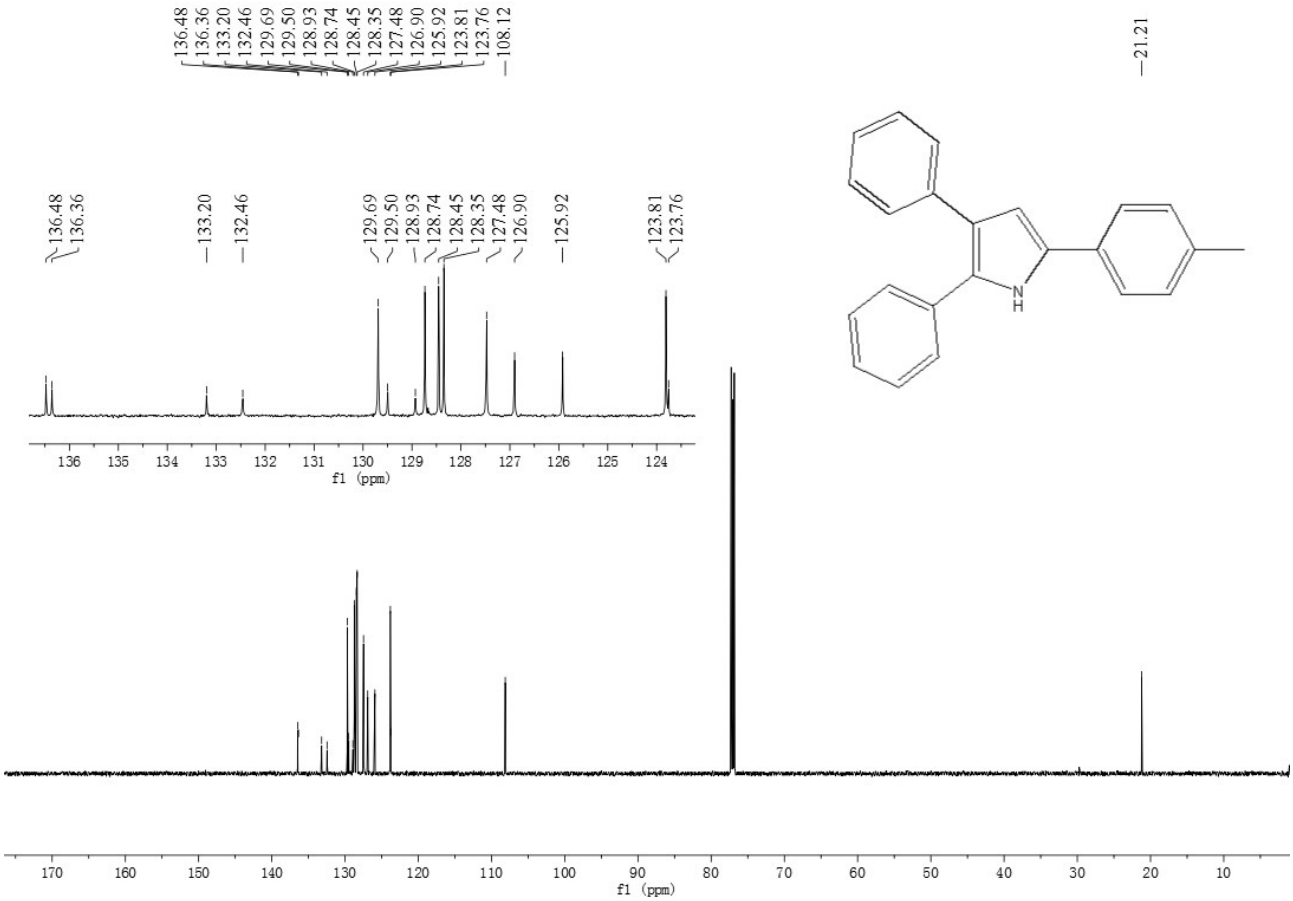

**Compound 3ae**



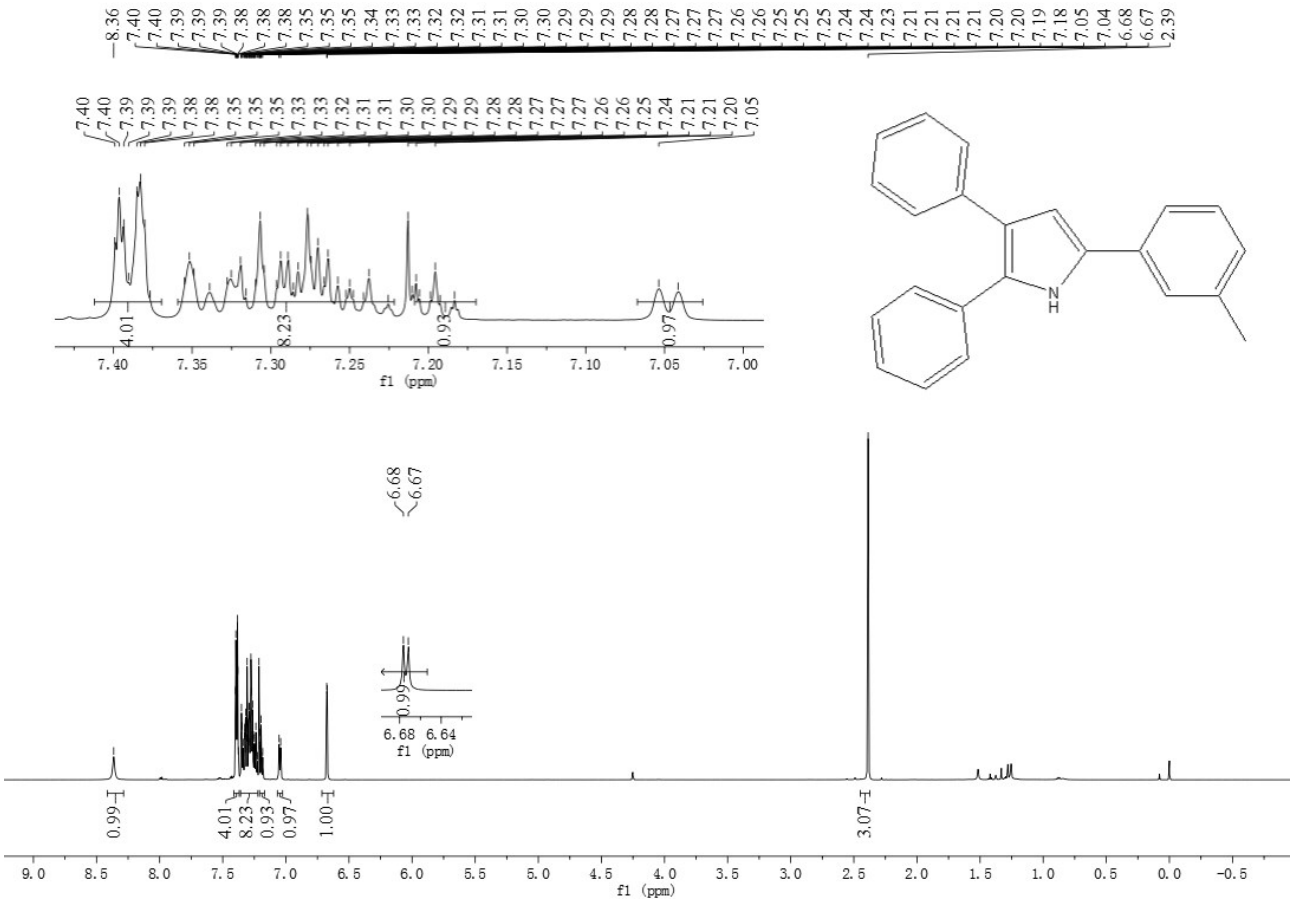


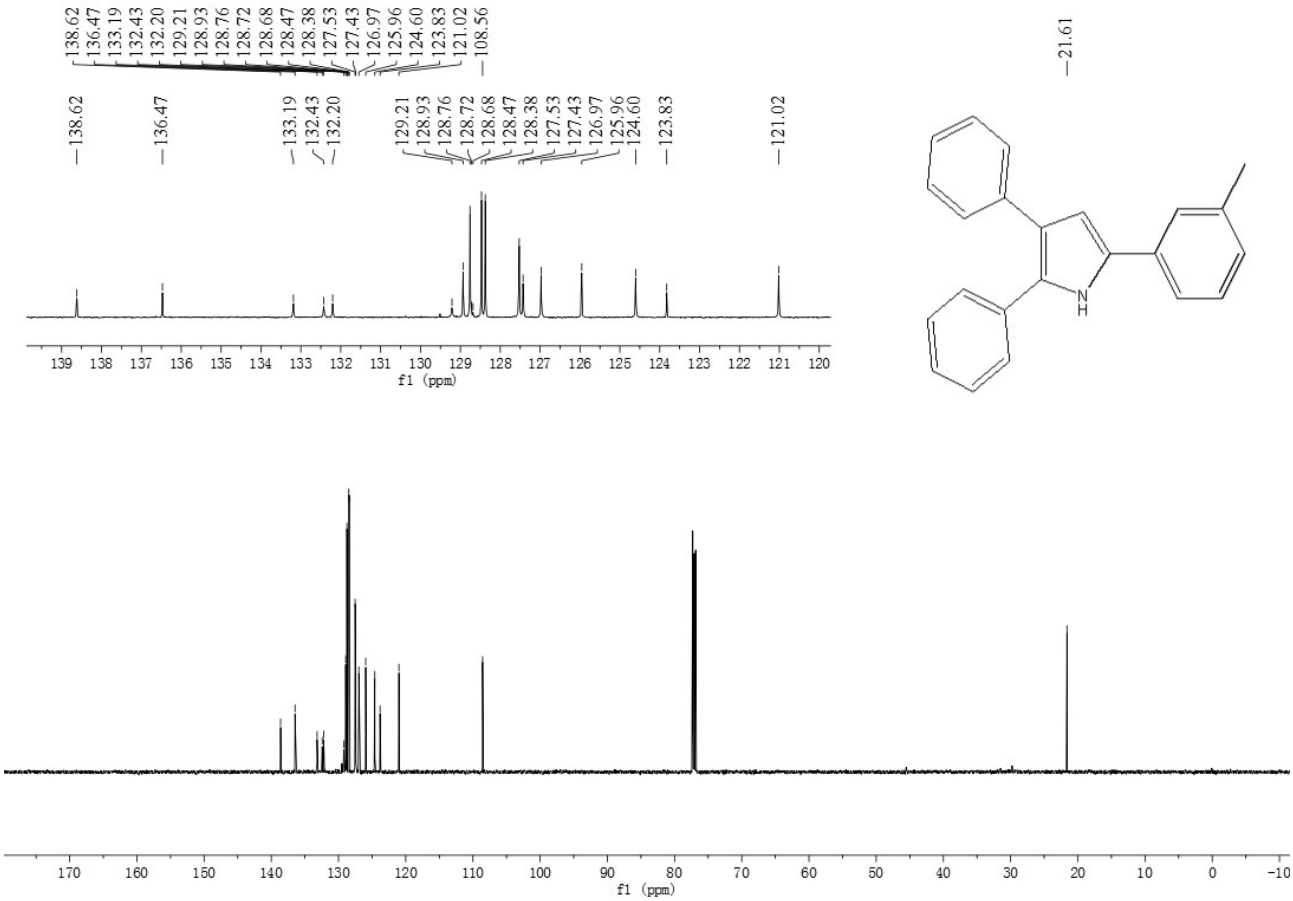

## Compound 3af






## Compound 3ag



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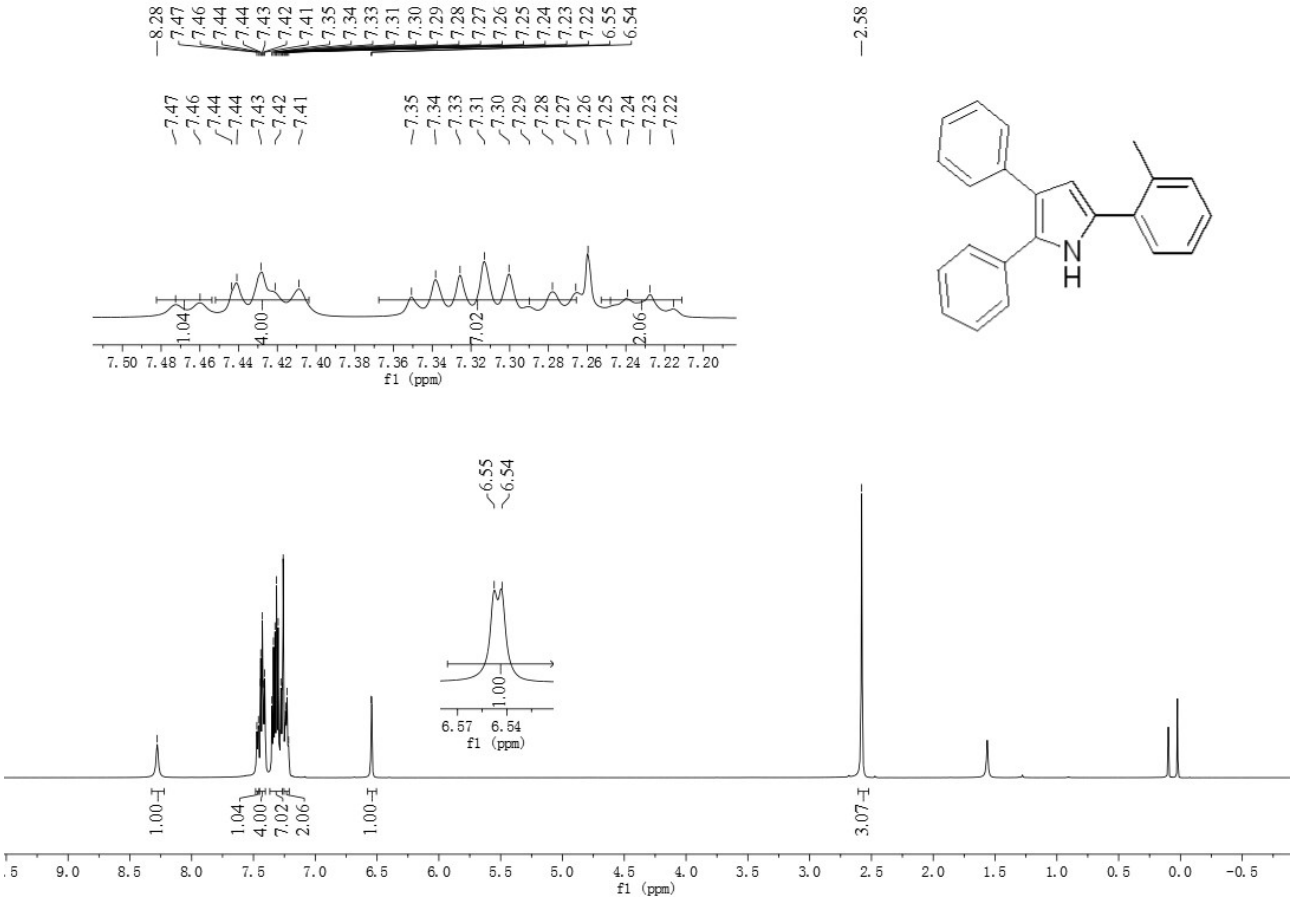

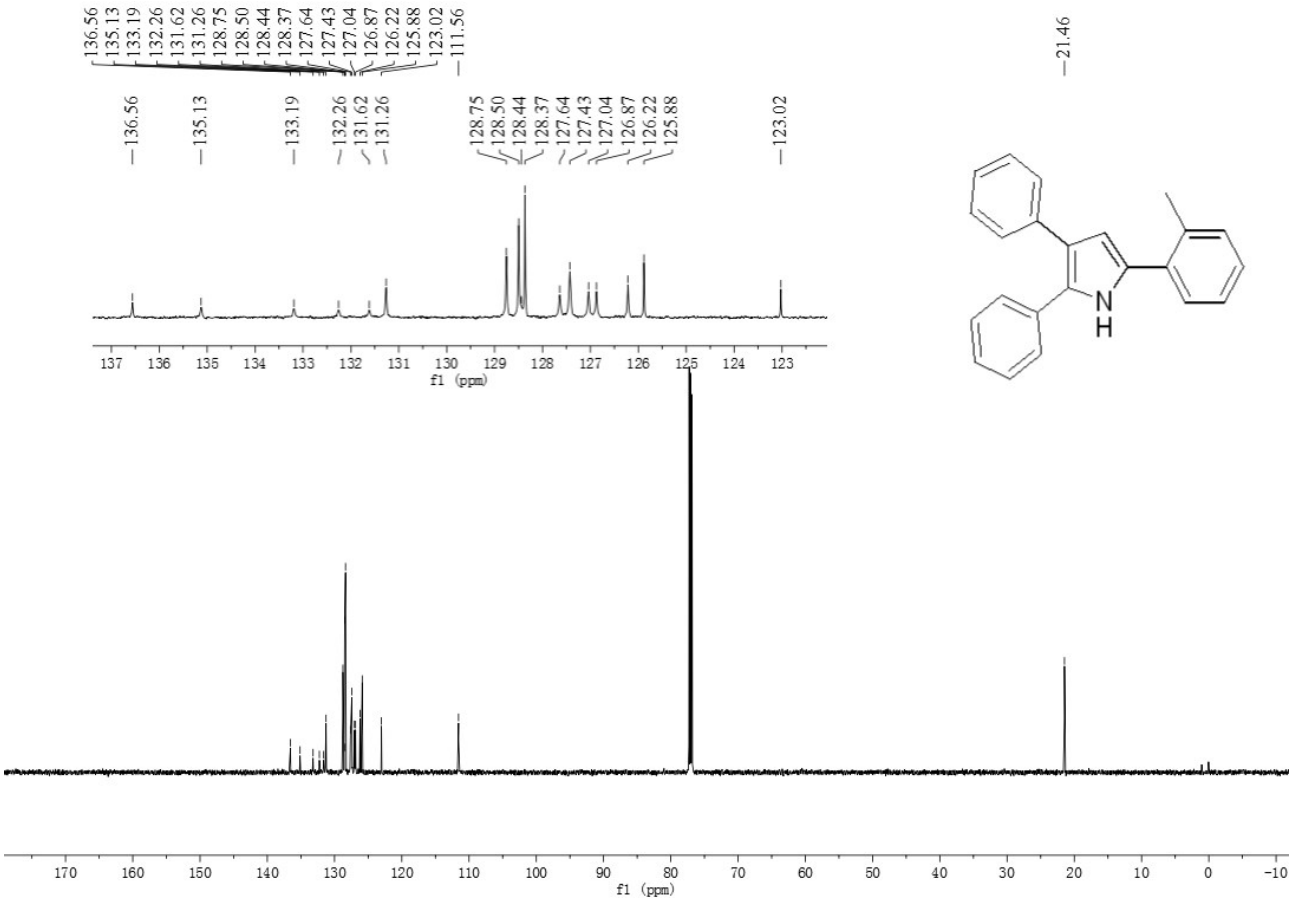


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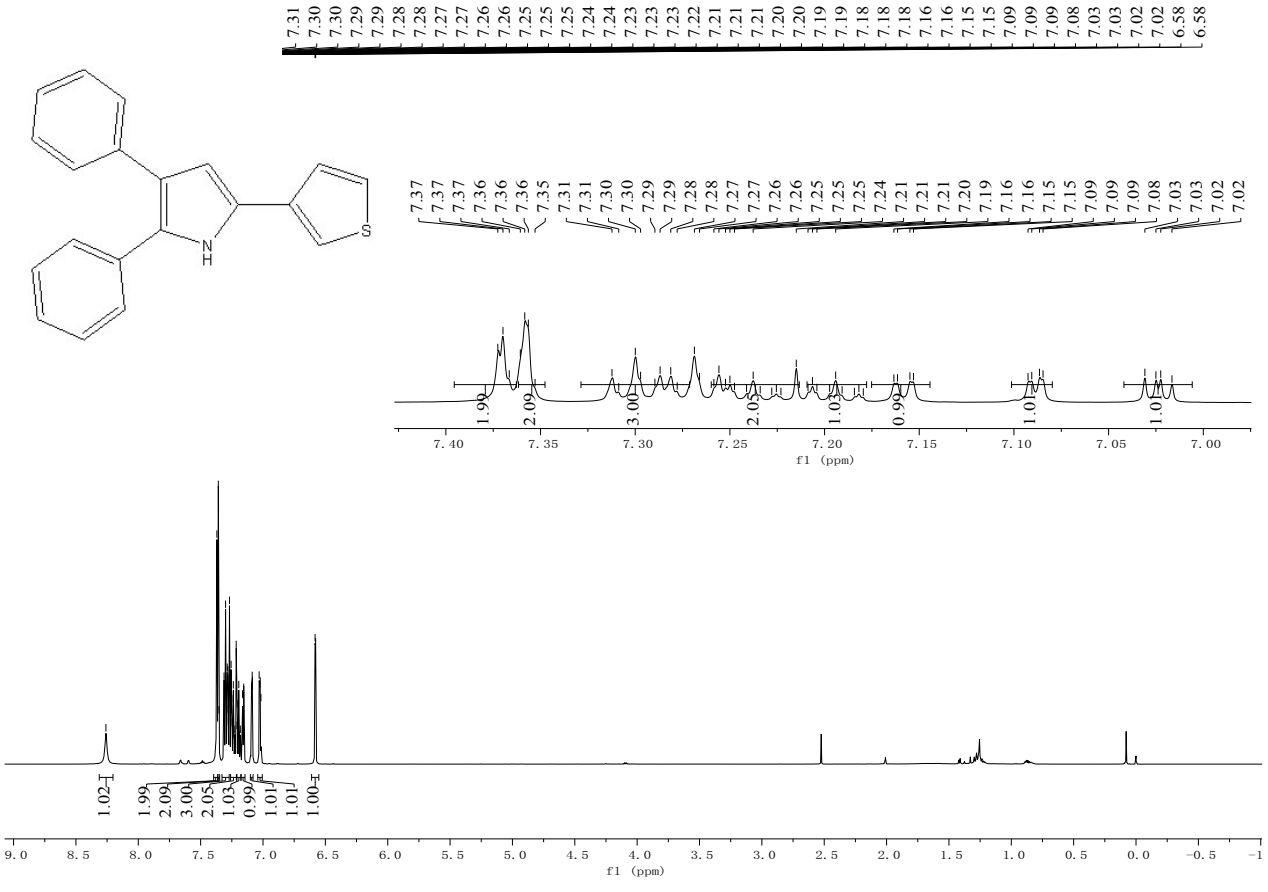

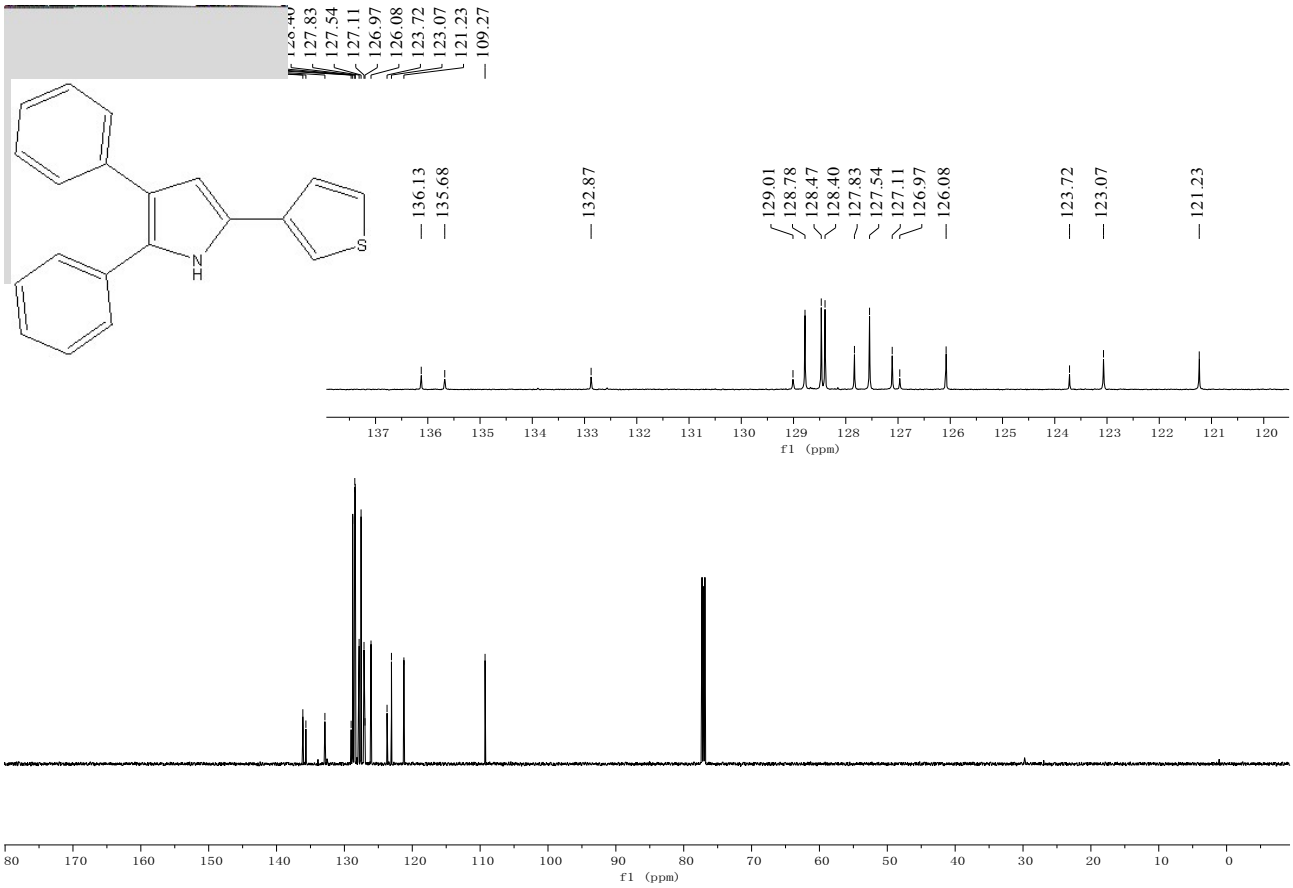

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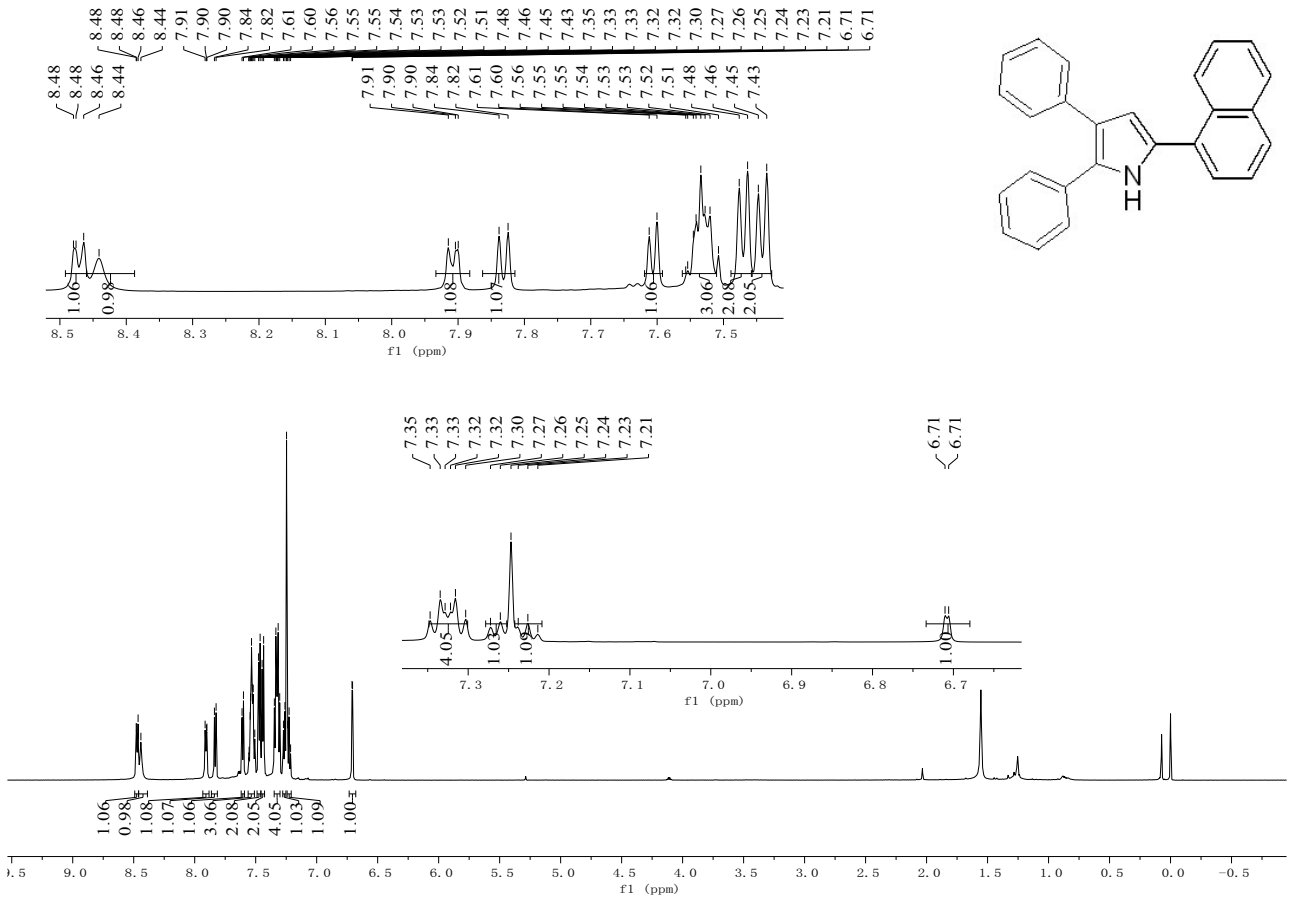

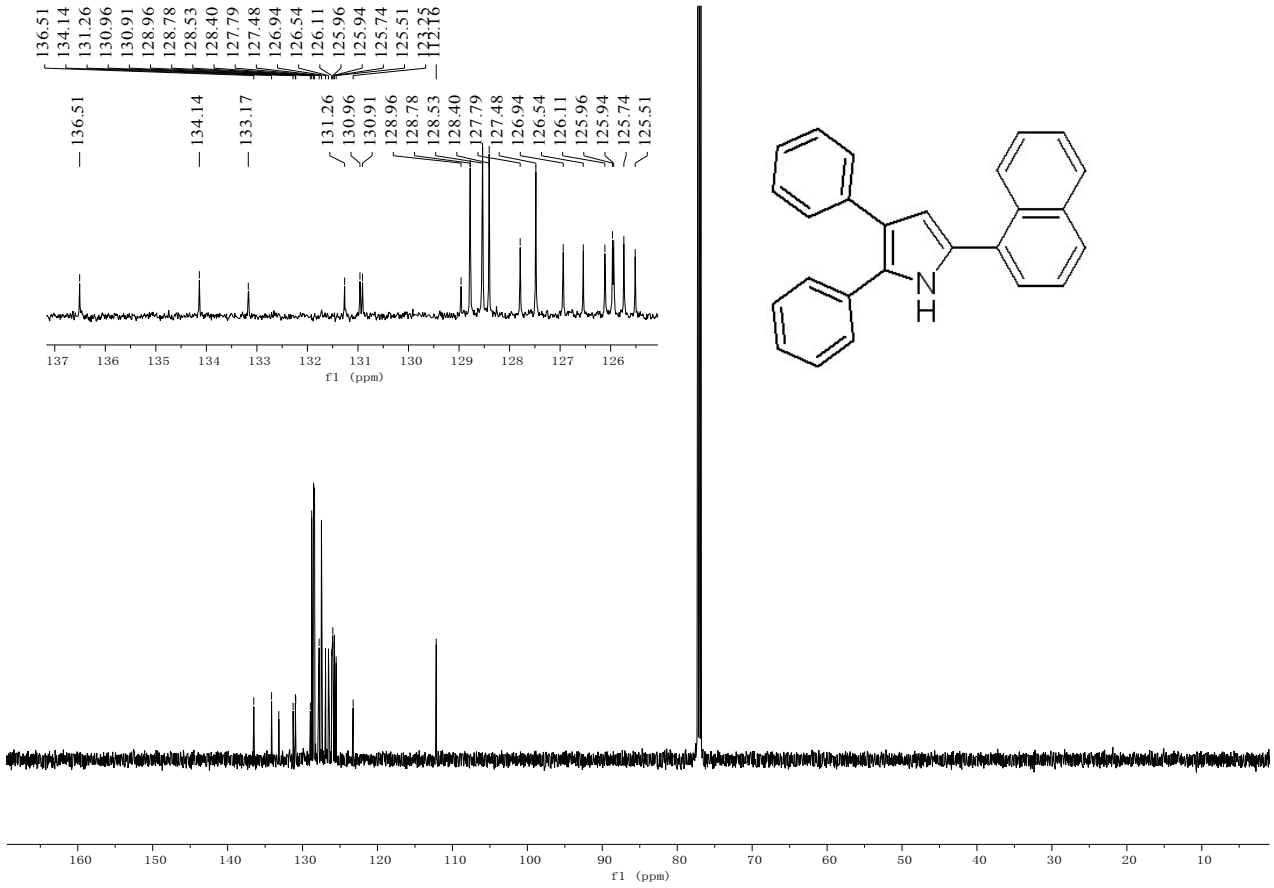


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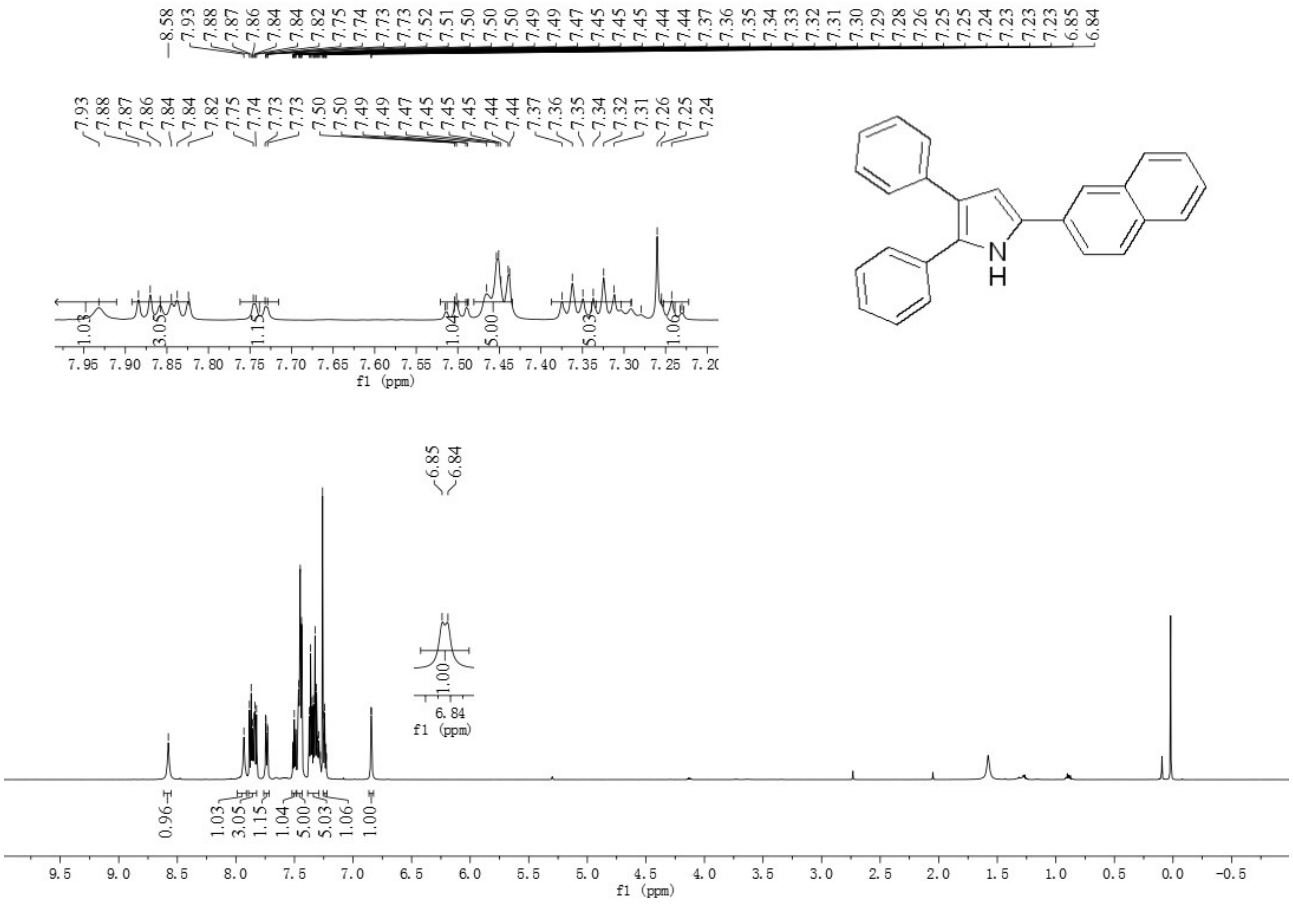
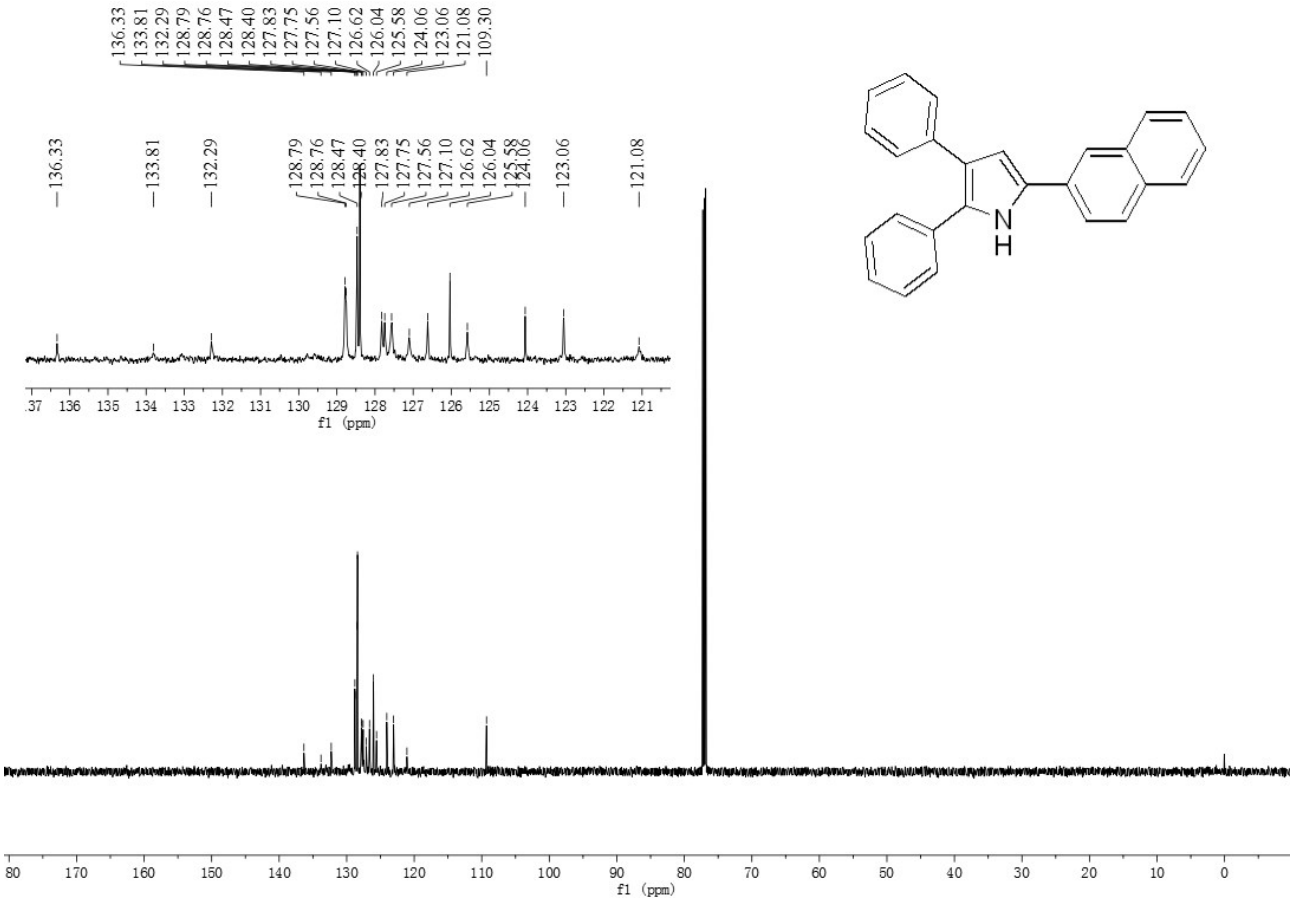
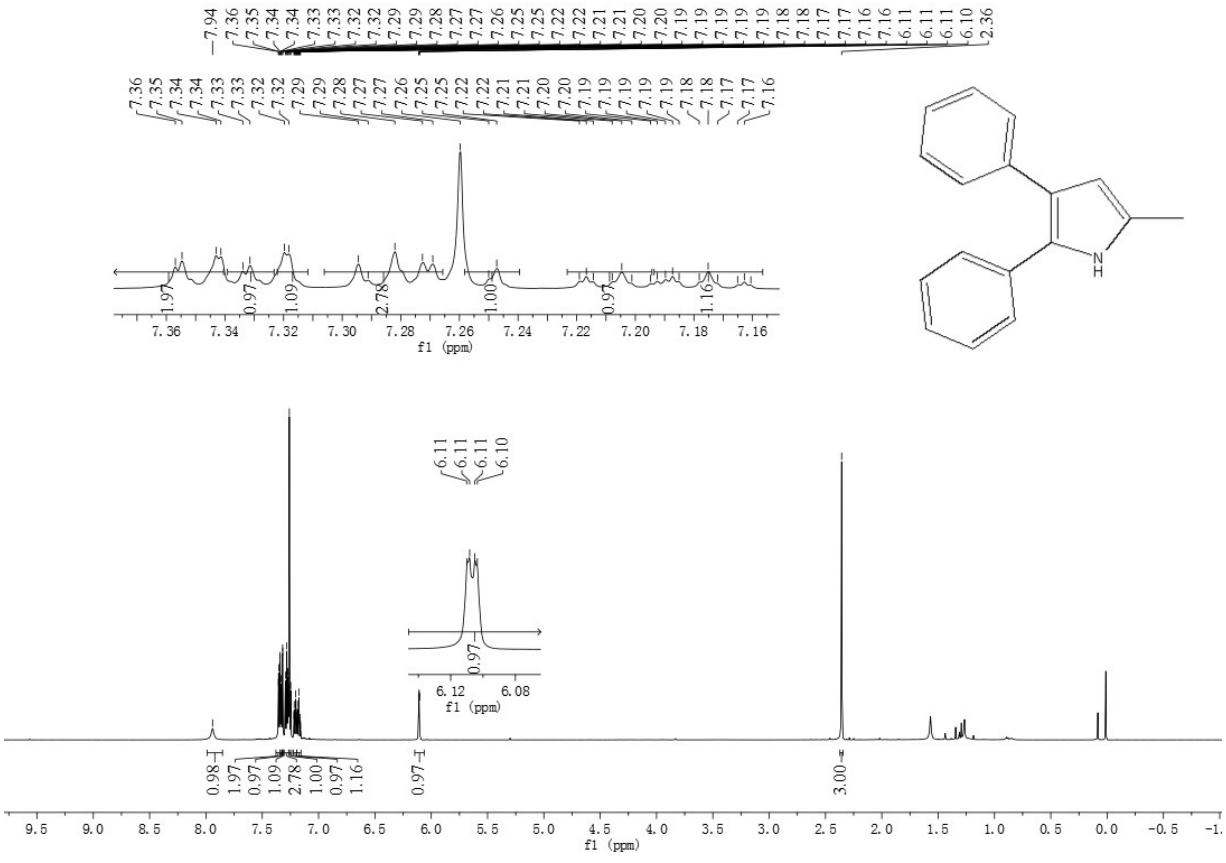
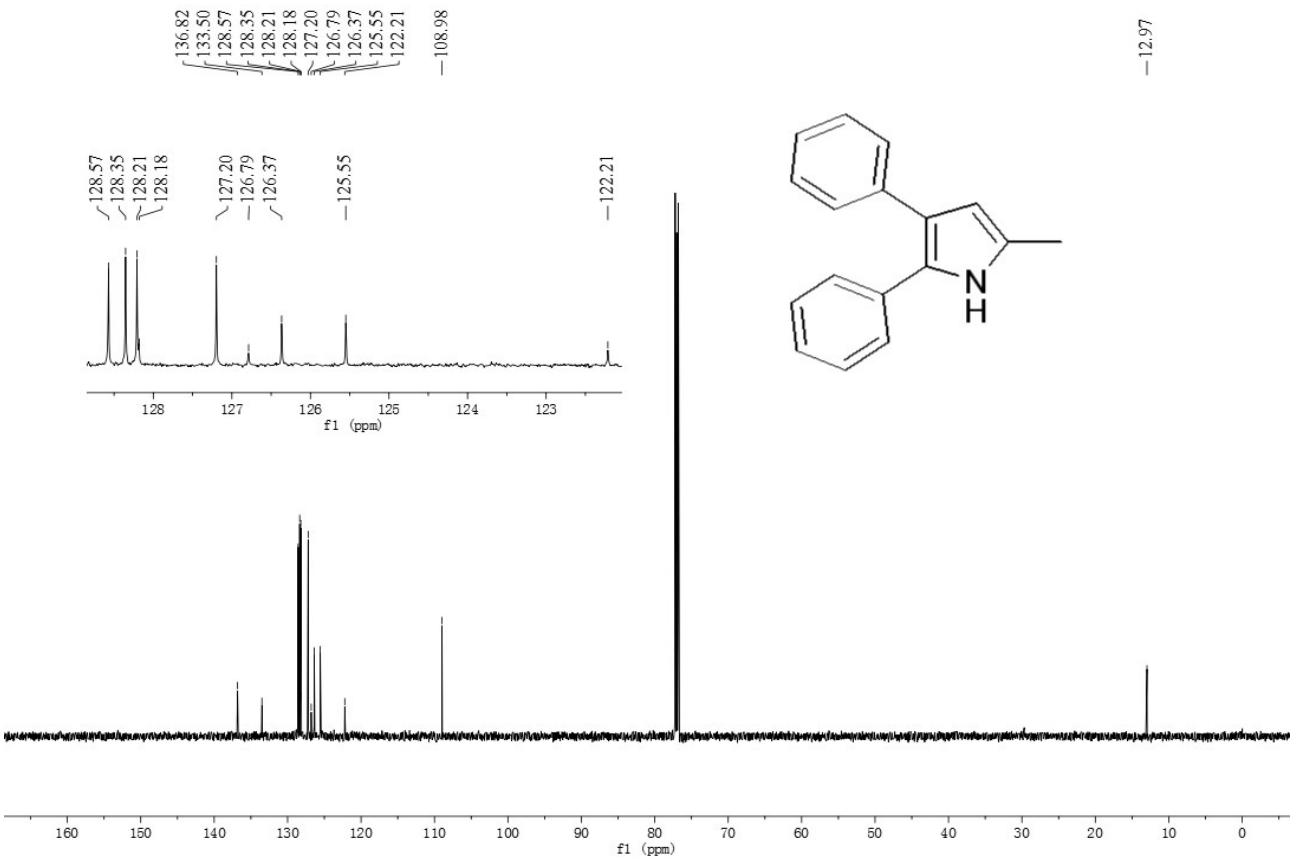


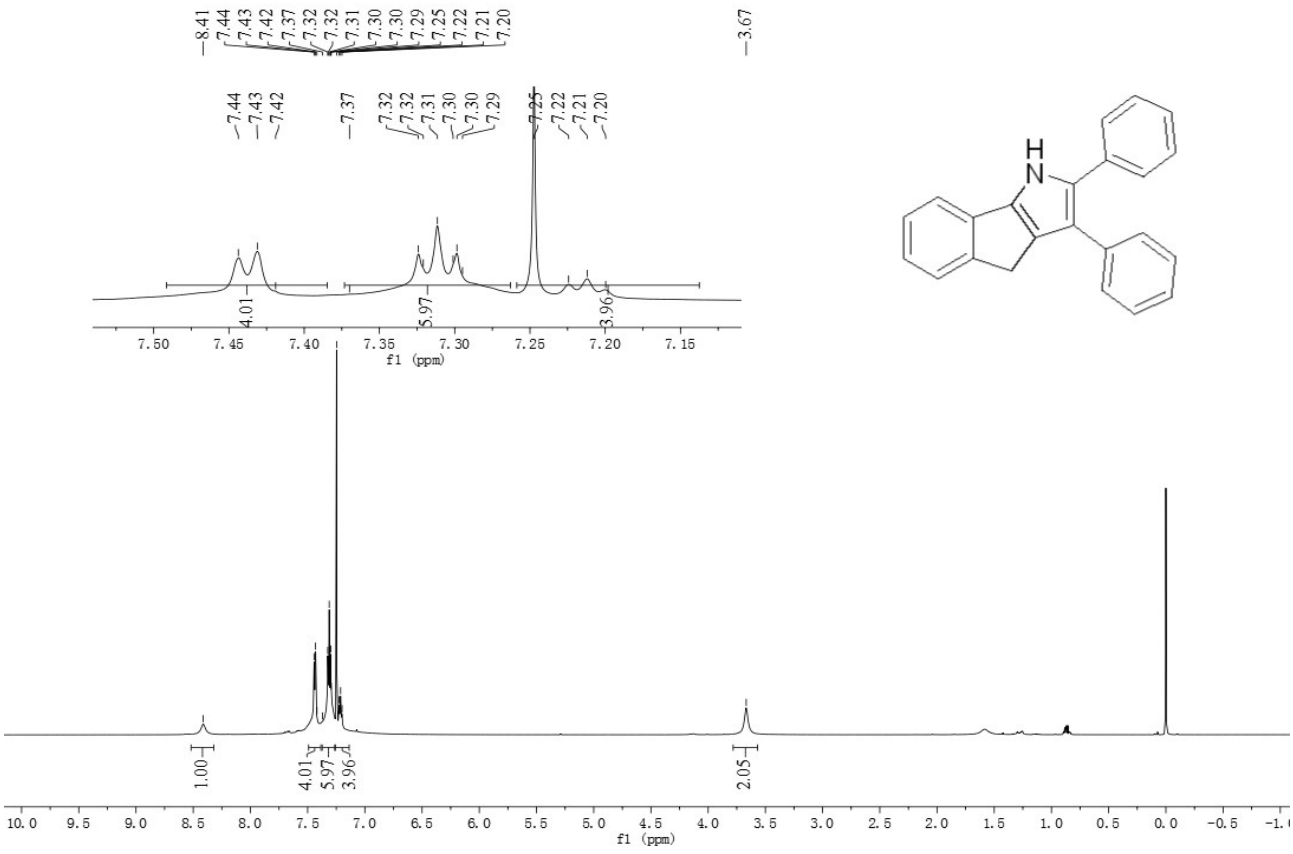


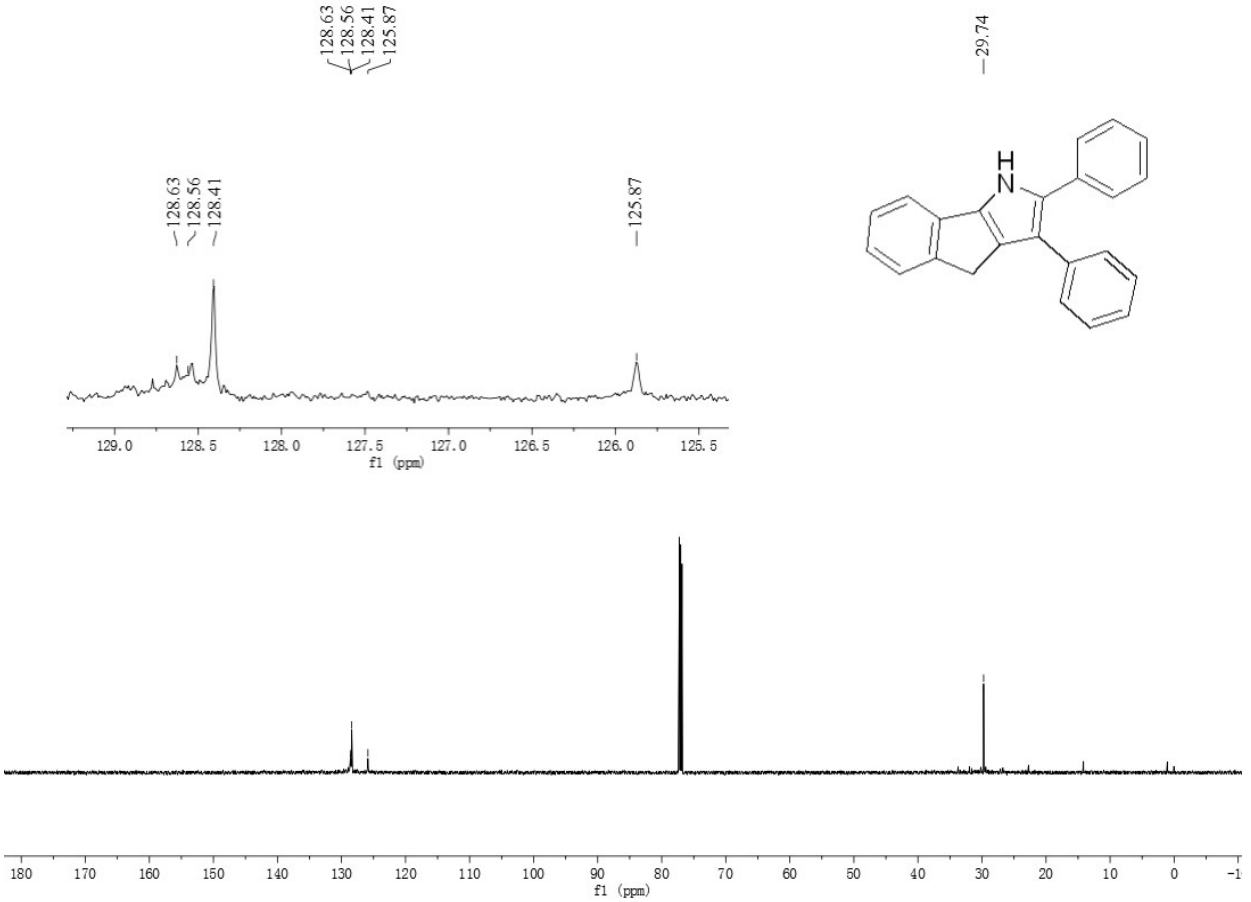
## Compound 3al






## Compound 3ao



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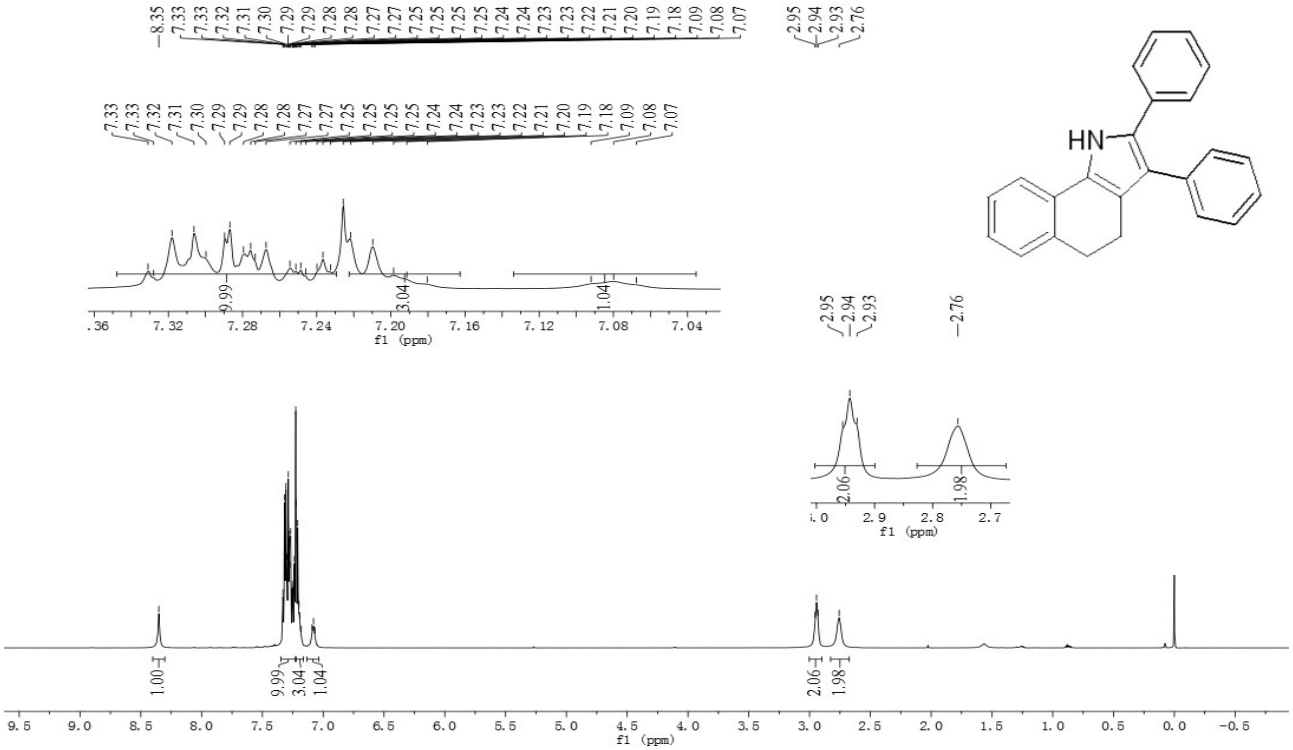

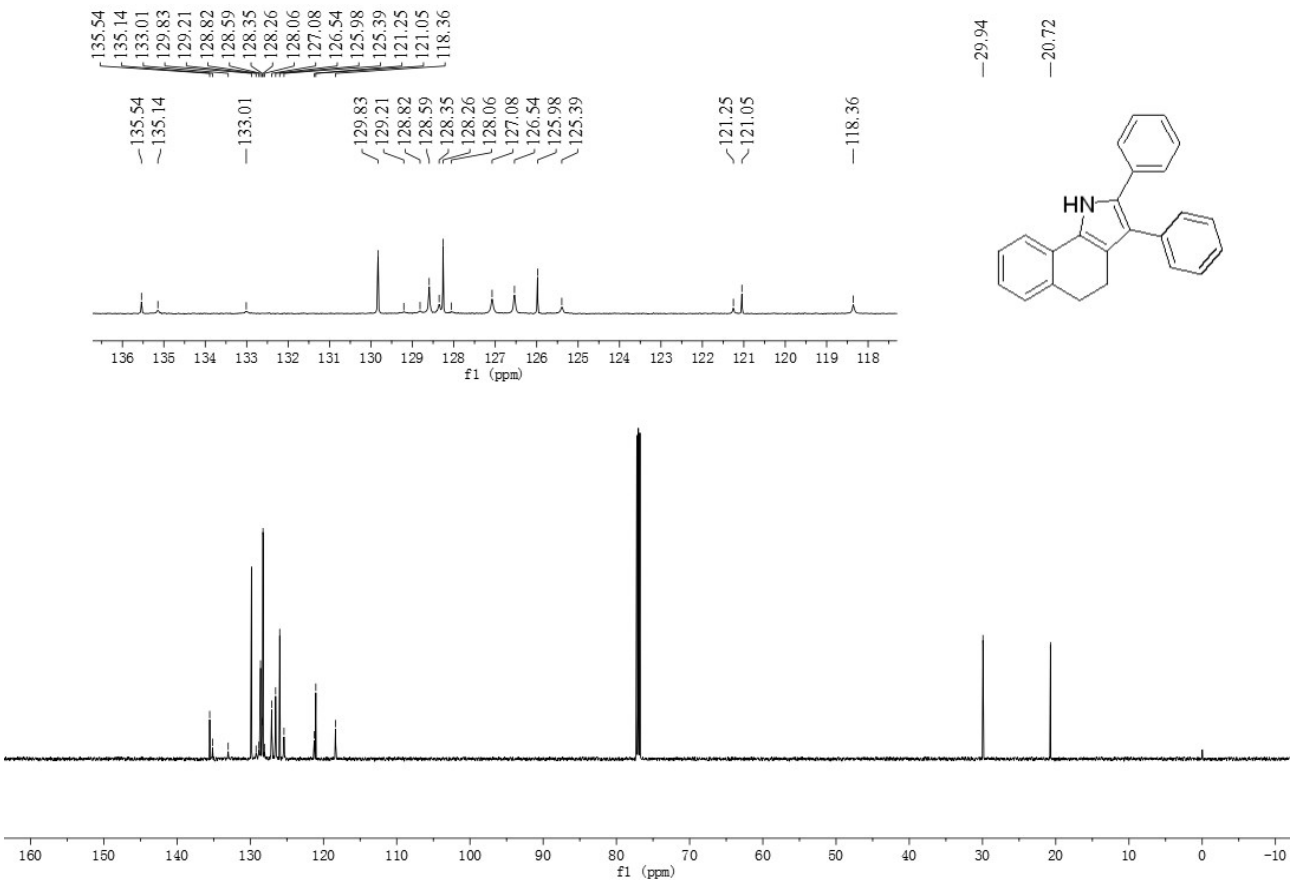


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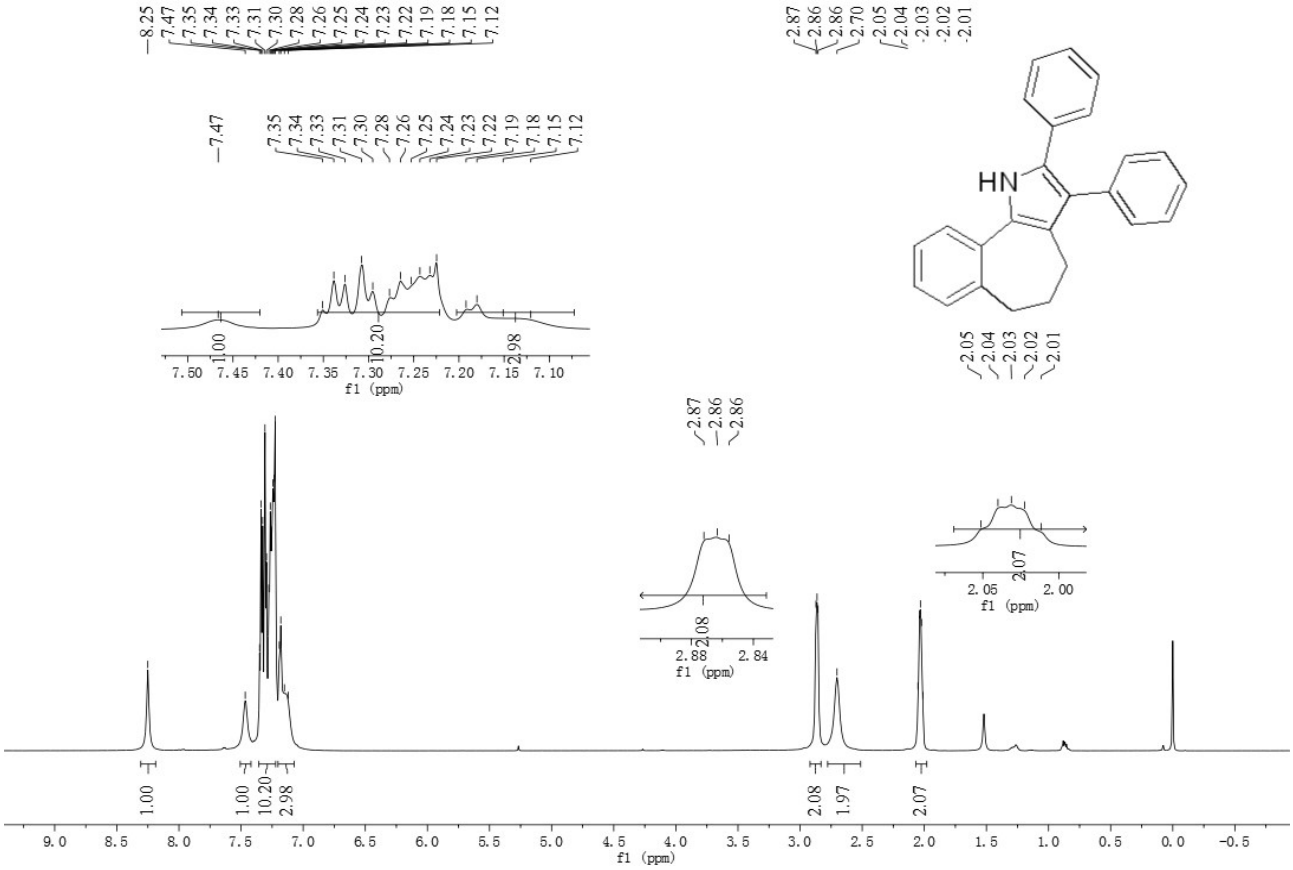
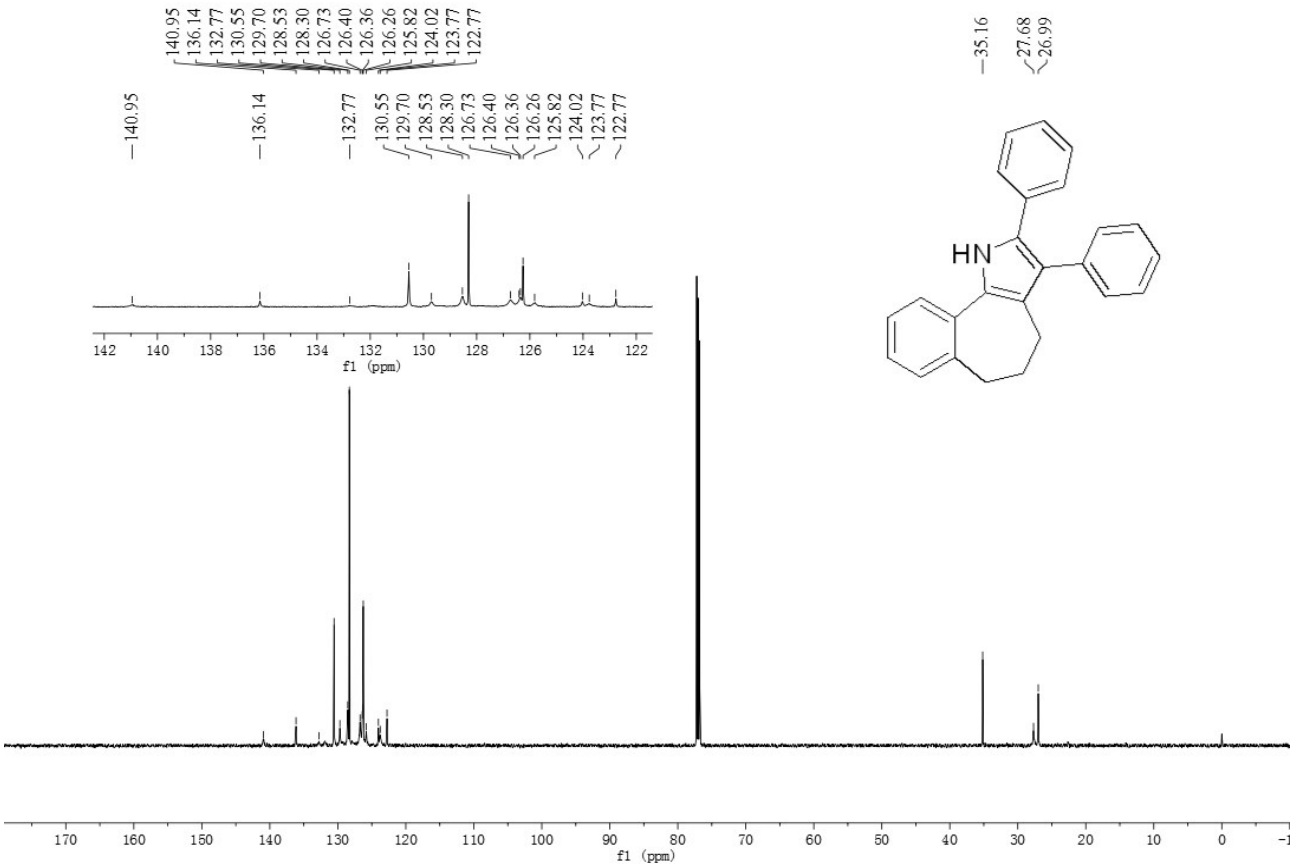
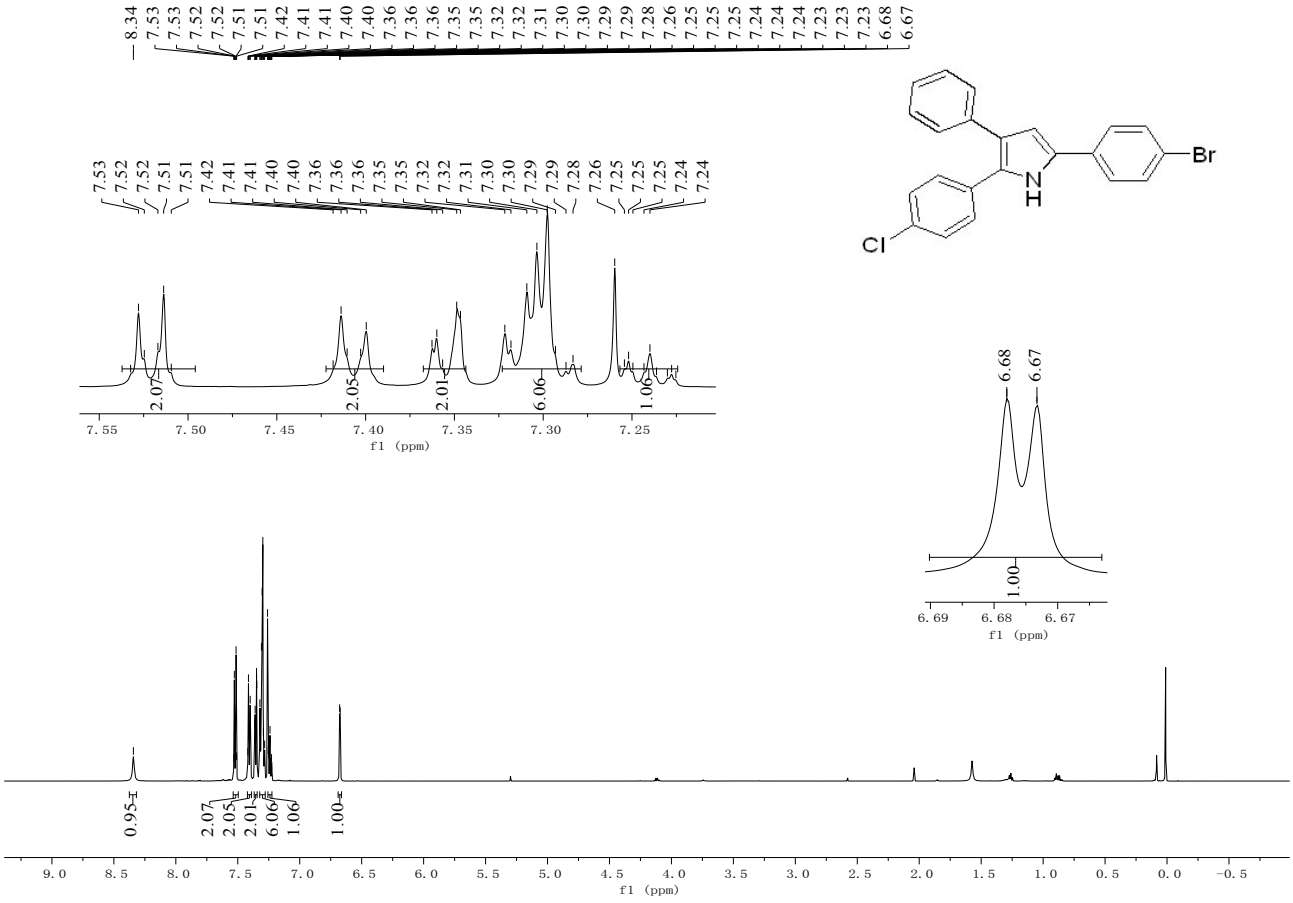
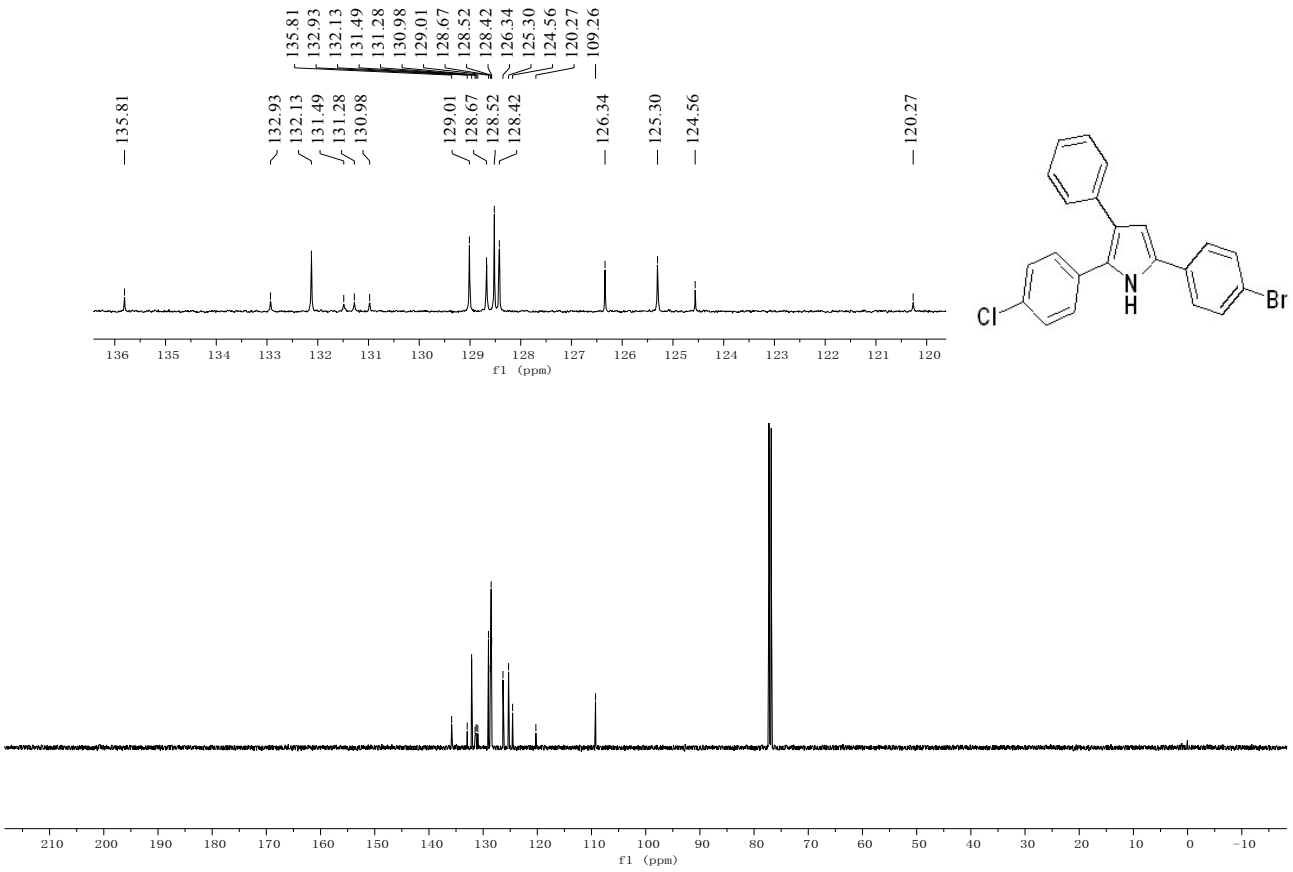





## Compound 3od

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f1 (ppm)
Cl
N
H
Br