# Electronic Supporting Information
# For
# Graphene Oxide-Phenalenyl Composite: Transition Metal Free Recyclable and Catalytic C-H Functionalization

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**Contents:**

## General Methods:

All aryl/heteroaryl halides, $KO^tBu$ and other chemicals were purchased from easily available commercial sources and used without prior treatments or as otherwise mentioned. Spectroscopic grade organic solvents were used for all spectroscopic analysis. $^1$HNMR and $^{13}$CNMR data were acquired using $(CD_3)_2SO$, $CDCl_3$ and $CD_3OD$ as solvents. Analytical thin layer chromatography (TLC) was accomplished using pre-coated aluminium baked silica gel plates. The developed chromatogram was visualized by UV absorbance (254 nm). Column chromatography was executed on 230-400 mesh silica and neutral alumina.

## Instrumentation:

FT-IR spectroscopic studies were accomplished using a Perkin Elmer spectrum RX1. The spectroscopic grade KBr is used to prepare all the IR samples. UV-Vis absorption spectra were recorded at room temperature in DMF solution using Perkin Elmer UV-Vis spectrophotometer (LAMBDA 35). The measurement of absorption spectra is executed using a 1 cm long quartz cell. $^1$H NMR and $^{13}$C NMR data were collected in JEOL 400 MHz and BRUKER 500 MHz NMR spectrometer. Solid state $^{13}$C NMR (CP/MAS) data were collected in BRUKER 500 MHz NMR spectrometer. The Raman spectra were obtained at room temperature with a Horiba Jobin Yvon LABRAM HR800 Raman spectrometer using He-Ne (633 nm) laser. The powder X-Ray diffraction measurement is carried out with a Rigaku (mini flex II, Japan) diffractometer having Cu, Kα radiation (λ = 1.54059 Å) at a scan rate of 2°/min. The field emission scanning electron microscopy (FE-SEM) was used to investigate the surface morphologies. The images and energy-dispersive analysis of X-ray (EDAX) were recorded on FE-SEM apparatus (Carl Zeiss scanning microscope-ZSM-S 55 VP) equipped with an Oxford instrument X-Max having the INCA software. The High resolution transmission electron microscopy (HR-TEM) images were recorded by UHR-FEG-TEM system (JEOL, JEM 2100 F) operated at 200 kV electron source. Thermogravimetric analysis (TGA) is performed on a Mettler Toledo STARe under nitrogen atmosphere at a heating rate of 4°/min.

## Characterization experiments of GO-PLY:

## 1. SEM study of GO-PLY:

SEM study was carried out using GO-PLY powder dispersed in solvent using ultra sonication. Images obtained by scanning electron microscopy (SEM) reveal an agglomerated "fluffy" distribution (Fig. S1) of as-synthesized GO-PLY powder. To further clarify the appropriate morphology we have carried out the TEM analysis which is discussed in the main manuscript.

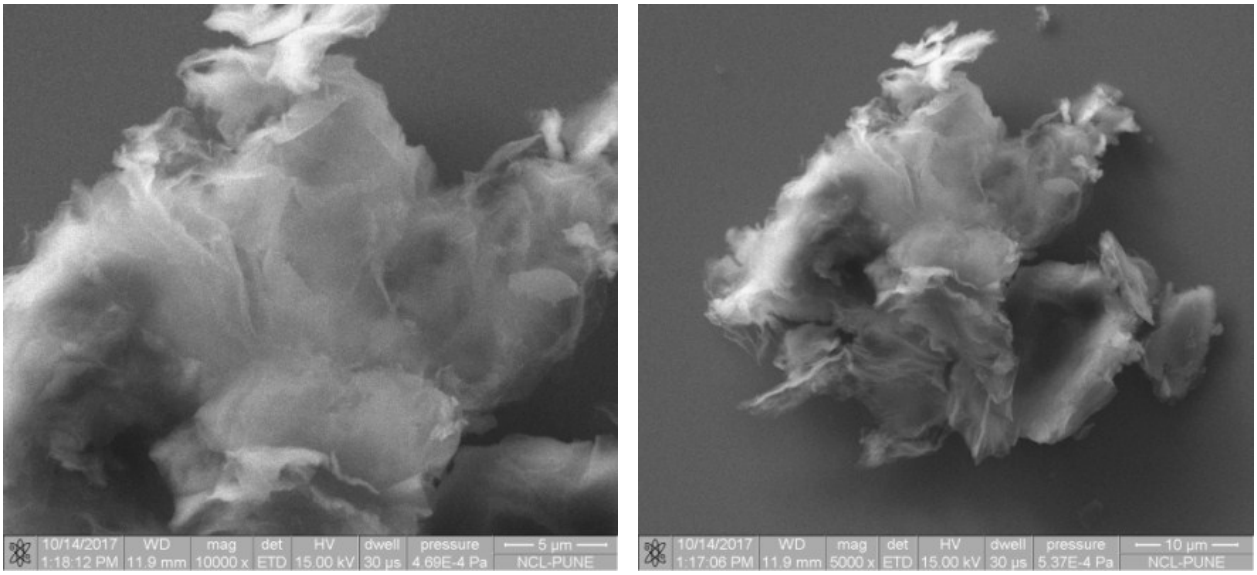



**Fig. S1** SEM images of GO-PLY compound showing fluffy distribution in isopropanol solution.

## 2. TEM study of GO-PLY:

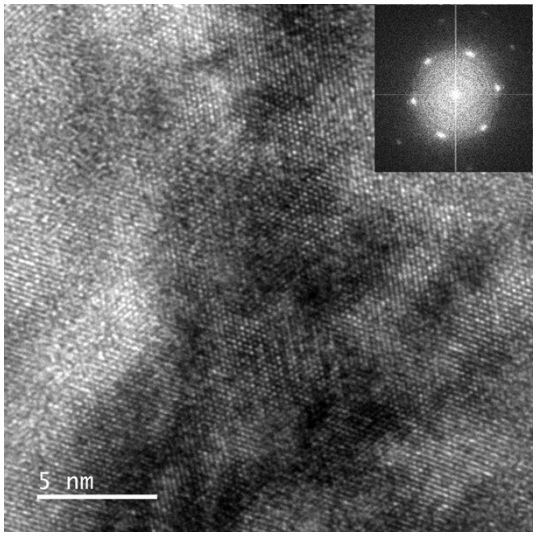



**Fig. S2** Fast Fourier transform spectrum indicates the presence of crystalline phases in GO-PLY.

## 3. TGA study of GO-PLY:

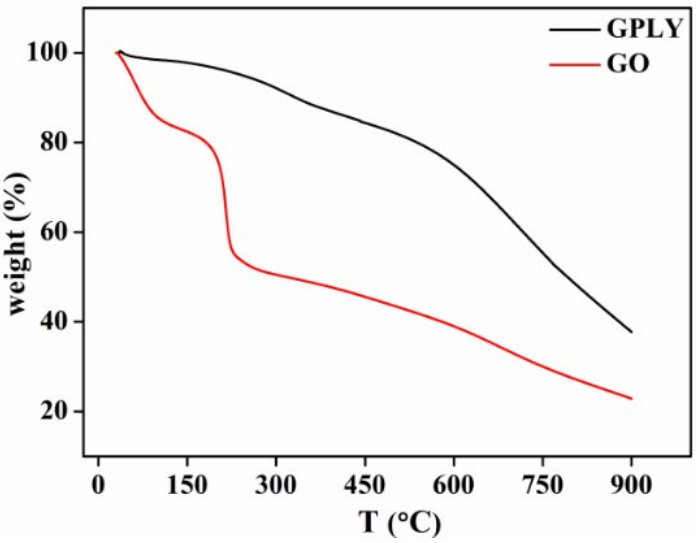
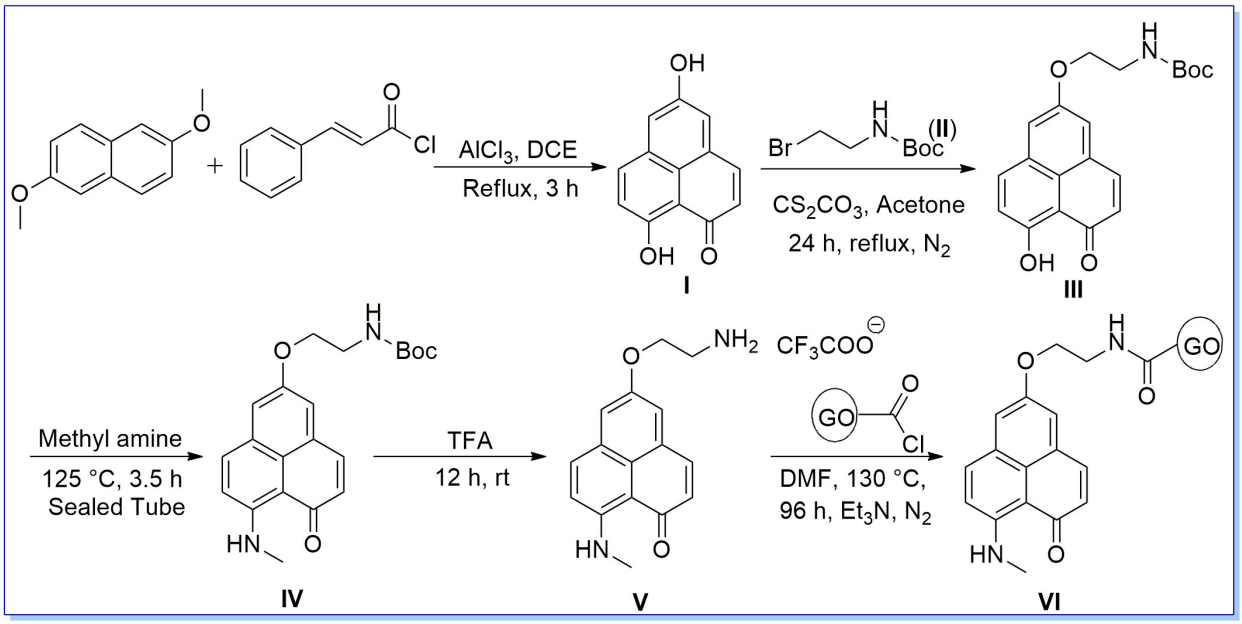



**Fig. S3** Gravimetric weight loss (%) of GO (red) and GO-PLY (black) samples as a function of temperature.

## Experimental Section:

**Scheme S1**. Synthetic scheme of GO-PLY




### Synthesis of 5,9-dihydroxyphenalenone (I):

The literature procedure for the preparation of 9-hydroxyphenalenone[1] was modified to prepare 5,9-dihydroxyphenalenone. In a 250 mL round bottom flask, cinnamoyl chloride (5.29 g, 0.03 mol) was added to a solution of 2, 6-dimethoxynaphthalene (5.0 g, 0.03 mol) in 1,2-dichloroethane (65 mL). The reaction flask was kept in an ice bath with slow addition of aluminum chloride (7.07 g, 0.05 mol), while the reaction mixture was mechanically stirred. After 1 h when the reaction temperature reached 30 ℃, a second portion of aluminum chloride (7.3 g) was added to the reaction mixture and stirred for 3 h at 95 ℃. After 3 h, the reaction mixture was cooled to room temperature and ice cold hydrochloric acid was added for quenching. The solution was filtered and the filtrate was extracted with dichloromethane. To the crude solid, obtained by filtration in the above step, DCM was added and repeatedly boiled and filtered. The boiling and filtration process was also performed with acetone and methanol, till the filtrate became colorless. All the organic fractions were combined, dried over anhydrous $Na_2SO_4$, the solution was filtered and concentrated to give a brown solid. The compound was purified via two sublimations supervened by a recrystallization from acetone to yield brown needles of **I** (3.1 g, 56%). 288-291 ℃, $^1$H NMR (500 MHz, $CDCl_3$): δ 7.18 (d, *J* = 9.46 Hz, 2H), 7.70 (s, 2H), 8.28 (d, *J* = 9.46 Hz, 2H), 10.09 (s, 1H), 15.81 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 110.3, 120.1, 120.3, 123.3, 126.5, 141.2, 154.4, 177.4. HRMS (ESI): calcd. for $C_{13}H_8O_3$ $[M + H]^+$ 213.0546; found 213.0555.

### Synthesis of tert-butyl (2-bromoethyl)carbamate (II):

In a 250 mL flask $(Boc)_2O$ (5.33 g, 0.0244 mol) was taken in dichloromethane (130 mL) at 0 ℃. In one portion, 2-bromoethylamin hydrobromide (5.56 g, 0.0271 mol) was added at 0 ℃, followed by the slow addition of triethylamine (5.08 mL, 0.0366 mol). The solution was then allowed to attain 30 ℃ and stirred for 20 h. The solution was diluted with dichloromethane (200 mL) and washed with sat aq. $NaHCO_3$ (2 x 100 mL), sat aq. $NH_4Cl$ (2 x 100 mL), and brine (2 x 100 mL). The organic fraction was dried using anhydrous $Na_2SO_4$, filtered and under reduced pressure was concentrated to obtain the crude mass, which was purified by column chromatography using 1:9 EtOAc/ hexane as eluent to afford the desired product as a colorless liquid[2] (5.57 g, 91%).

**Synthesis of tert-butyl (2-((9-hydroxy-1-oxo-1H-phenalen-5-yl)oxy)ethyl)carbamate (III):**

I (400 mg, 1.88 mmol) was dissolved in dry acetone (270 mL) and $Cs_2CO_3$ (6.1 g, 18.72 mmol) was added to it, which was then refluxed for 2 h. **II** (1.7 g, 7.6 mmol) was subsequently added to the reaction mixture in portion-wise for three times after every 2 h and refluxed for next 12 h. The reaction mixture was allowed to reach room temperature and filtered. The filtrate was concentrated under vacuum to obtain the desired product. The titled compound was then purified by column chromatography using EtOAc/ hexane (1:1) as an eluent, producing **III** as a yellow solid (565 mg, 84% yield). 158-160 ℃, $^1$H NMR (500 MHz, $CDCl_3$): δ 1.46 (s, 9H), 3.62-3.63 (m, 2H), 4.21 (t, *J* = 4.73, 2H), 5.03(b, 1H), 7.17 (d, *J* = 9.46 Hz, 2H), 7.55 (s, 1H), 8.00 (d, *J* = 9.46 Hz, 2H), 15.55 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 28.4, 40.1, 67.9, 79.7, 111.0, 118.4, 122.3, 124.4, 126.6, 140.0, 155.3, 155.9, 178.2. HRMS (ESI): calcd. for $C_{20}H_{21}NO_5$ $[M + H]^+$ 356.1492; found 356.1491.

**Synthesis of tert-butyl (2-((9-(methylamino)-1-oxo-1H-phenalen-5-yl)oxy)ethyl)carbamate (IV) :**

A mixture of aqueous methyl amine (4.5 mL, 40% solution) and compound **III** (630 mg, 1.77 mmol) were kept in a sealed tube and stirred for 3.5 h at 125 ℃. The sealed tube was then allowed to cool and the reaction mixture was diluted with 30 mL of distilled water and extracted with DCM. The organic part was dried over anhydrous magnesium sulfate. The solvent was concentrated using a rotary evaporator. The purification of the crude product was done through column chromatography on $Al_2O_3$ (eluent: EtOAc/hexane = 3:2) to give **IV** as an orange red solid[3] (522 mg, 80% yield). 139-142 ℃, $^1$H NMR (500 MHz, $CDCl_3$): δ 1.46 (s, 9H), 3.23 (d, *J* = 5.36 Hz, 3H), 3.60-3.61 (m, 2H), 4.19 (t, *J* = 5.04, 2H), 5.05 (br.s, 1H), 7.00 (d, *J* = 9.46 Hz, 1H), 7.21 (d, *J* = 9.46 Hz, 1H), 7.41 (d, *J* = 2.21 Hz, 1H), 7.49 (d, *J* = 2.21 Hz, 1H), 7.76 (d, *J* = 9.46 Hz, 1H), 7.93 (d, *J* = 9.46 Hz, 1H), 11.88 (s, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 28.3, 29.3, 40.2, 67.8, 79.5, 108.0, 114.7, 115.1, 119.3, 123.8, 125.0, 126.2, 129.7, 137.3, 137.4, 153.5, 155.7, 155.9, 183.9. HRMS (ESI): calcd. for $C_{21}H_{24}N_2O_4$ $[M + H]^+$ 369.1809; found 369.1810.

**Synthesis of 2-((9-(methylamino)-1-oxo-1H-phenalen-5-yl)oxy) ethanaminium 2,2,2-trifluoroacetate (V):**

In a 500 mL flask, trifluoroacetic acid (5 mL) was charged in a solution of compound **IV** (1.1 g, 2.98 mmol) in dry DCM (250 mL). The resulting reaction mixture was kept for stirring for 15 h at room temperature. After completion of the reaction, DCM was evaporated and the product was precipitated out using diethyl ether. The compound **V** was thus obtained as orange solid (1.1 g, 92% yield). 211-213 °C, $^1$H NMR (400 MHz, $CD_3OD$): δ 3.26 (s, 3H), 3.46 (t, 2H), 4.41 (t, *J* =, 2H), 6.92-6.95 (br.s, 1H), 7.36 (br.s, 1H), 7.67 (br.s, 2H), 7.89-7.91 (br.s, 1H), 8.08 (br.s, 1H). $^{13}$C NMR (100 MHz, $CD_3OD$): δ 29.7, 40.6, 66.2, 108.9, 116.5, 117.7, 120.6, 125.1, 127.0, 127.7, 129.7, 139.4, 139.9, 154.9, 158.2, 184.7. HRMS (ESI): calcd. for $C_{16}H_{17}N_2O_2^+$ [M ]$^+$ 269.1285; found 269.1284.

**Synthesis of GO-PLY (VI):**

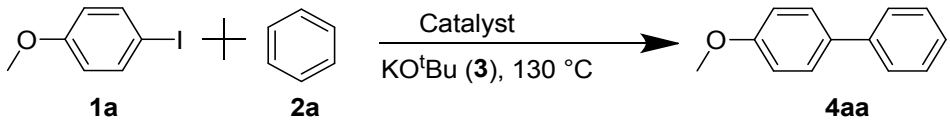
The graphene oxide was synthesized from graphite powder following a modified Hummers method.[4,5] The synthesized graphene oxide (300 mg) was then reacted with thionyl chloride (90 mL) in DMF (1.5 mL) and the reaction mixture was refluxed at 80 °C for 24 h under $N_2$ atmosphere. After the completion of the reaction, excess of thionyl chloride was removed under reduced pressure. **V** (441 mg, 1.15 mmol) was then added to a solution of above product in DMF (87 mL) in the presence of trimethylamine (7.5 mL) and heated at 130 °C for 4 days under nitrogen atmosphere. After the completion of the reaction, the reaction mixture was allowed to cool to room temperature and 0.2 µm PTFE membrane was used to isolate the product by filtration. The excess of phenalenyl **V** and other impurities were removed by washing the precipitate with different organic solvents. To ensure no free phenalenyl **V** existed in the desired product, thin-layer chromatography (TLC) and UV spectroscopy were performed on the filtrate obtained from final washing. Finally the product was dried under reduced pressure to yield the hybrid GO-PLY[6].

**Optimization of transition metal free catalysis:**

Next, with this phenalenyl-grafted graphene oxide composite (GO-PLY) in hand, we attempted to investigate its utility in the transition metal free arylation chemistry, where we choose 4-iodoanisole and benzene as the model coupling partner. Our Initial protocols in this regard, were mainly focused on catalyst loading. The coupling partners (**1a** and **2a**) along with GO-PLY (**VI**) and potassium tert-butoxide (**3**), under 25 mg catalyst loading conditions, were stirred at 130 °C in a sealed tube for 24 h, to produce the expected biaryl product (**4aa**) with 30% yield only (Table S1, entry 1). However, on increasing the catalyst loading to 50 mg, the yield of the desired product was increased to 41% (Table S1, entry 2), which was improved to 54 % (Table S1, entry 3) on increasing the amount of KO$^t$Bu from 4 equiv. to 8 equiv. and

maximized (95%, Table S1, entry 4) on using 12 equiv. KO$^t$Bu. The requirement of excess amount of base can be attributed to the fact that graphene oxide surface is enriched with acidic hydroxyl groups[7-8] and therefore it consumes the incoming potassium *tert*-butoxides, during the arylation reaction. We also found that lowering the reaction time up to 12 h does not decrease in the reaction yield (Table S1, entry 5). However, further shortening of the reaction time (Table S1, entry 6) lowers the yield to 65%. A control experiment without using any GO-PLY catalyst but in presence of 12 equiv. of KO$^t$Bu led to only 20% yield of the desired product under the optimized conditions (Table S1, entry 7), which explicitly proved the necessity of GO-PLY to perform the arylation effectively. Also, the fact that, only a trace amount of product was formed (<2%, Table S1, entry 8) under the optimized conditions, when GO was used as catalyst, which supports that GO-PLY is indeed essential for the arylation of benzene.

**Table S1.** Optimization of GO-PLY catalyzed direct arylation of benzene:[a]




**1a** **2a** **4aa**

| Entry | Catalyst | Base (equiv) | Time | Yield (%)[b] |
|---|---|---|---|---|
| 1 | GO-PLY (25 mg) | 4 | 24 | 30 |
| 2 | GO-PLY (50 mg) | 4 | 24 | 41 |
| 3 | GO-PLY (50 mg) | 8 | 24 | 54 |
| 4 | GO-PLY (50 mg) | 12 | 24 | 95[c] |
| **5** | **GO-PLY (50 mg)** | **12** | **12** | **95[c]** |
| 6 | GO-PLY (50 mg) | 12 | 6 | 65 |

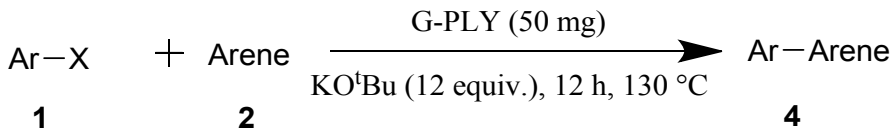
| | | | | |
|---|---|---|---|---|
| 7 | --- | 12 | 12 | 20 |
| 8 | GO (50 mg) | 12 | 12 | < 2 |

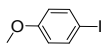
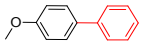
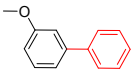
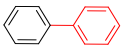
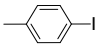
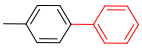
[a] Reactions were executed in a sealed tube using 4 mL benzene, 12 eqv. KO$^t$Bu, 0.21 mmol 4-iodoanisole at 130 °C. [b]The designated yields were calculated by $^1$H NMR spectroscopy. [c]Isolated yield.

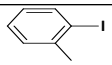
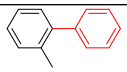
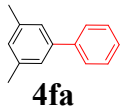
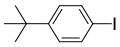
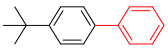
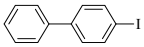
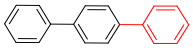
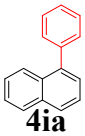
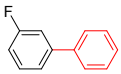
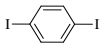
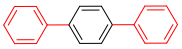
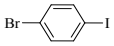
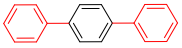
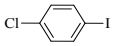
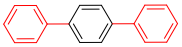
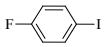
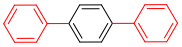
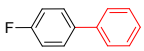
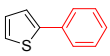
**General representative procedure for the catalytic reaction with benzene:**

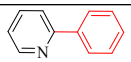
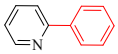
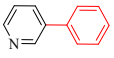
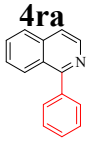
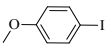
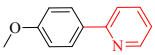
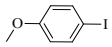
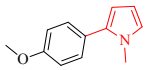
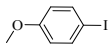
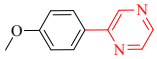
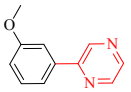
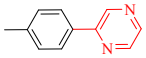
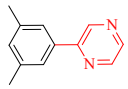
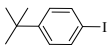
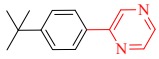
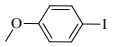
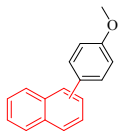
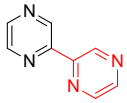
Aryl iodide / heteroaryl iodide (0.21 mmol), KO$^t$Bu (12 equiv.), GO-PLY (50 mg), and benzene (4 mL) were charged in a sealed tube and the tube was sealed with a Teflon Plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered through 0.2 µm PTFE membrane, washed with DCM and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (eluent: hexane/EtOAc = 99/ 1 to 85/ 15) to give pure product.

**Table S2.** GO-PLY catalyzed C-H arylation of arene with aryl or heteroaryl iodide precursors




| Entry | (Hetero)Aryl halide | Product | Yield (%) |
|---|---|---|---|
| 1 |  **1a** |  **4aa** | 95 |
| 2 |  **1b** |  **4ba** | 79 |
| 3 |  **1c** |  **4ca** | 94 |
| 4 |  **1d** |  **4da** | 81 |

| | | | |
|---|---|---|---|
| 5 |  **1e** |  **4ea** | 71 |
| 6 |  **1f** |  **4fa** | 79 |
| 7 |  **1g** |  **4ga** | 93 |
| 8 |  **1h** |  **4ha** | 96 |
| 9 |  **1i** |  **4ia** | 73 |
| 10 |  **1j** |  **4ja** | 74 |
| 11 |  **1k** |  **4ha** | 72 |
| 12 |  **1l** |  **4ha** | 85 |
| 13 |  **1m** |  **4ha** | 83 |
| 14 |  **1n** |  **4ha** | 13[b] |
| | |  **4na** | 64 |
| 15 |  **1o** |  **4oa** | 82 |

| | | | |
|---|---|---|---|
| 16 |  **1p** |  **4pa** | 81 |
| 17 |  **1q** |  **4pa** | 22 |
| 18 |  **1r** |  **4ra** | 67 |
| 19 |  **1s** |  **4sa** | 55 |
| 20[c] |  **1a** |  **4ab** | 54 |
| 21[d] |  **1a** |  **4ac** | 53 |
| 22[e] |  **1a** |  **4ad** | 72 |
| 23[e] |  **1b** |  **4bd** | 69 |
| 24[e] |  **1d** |  **4dd** | 71 |
| 25[e] |  **1f** |  **4fd** | 79 |
| 26[e] |  **1g** |  **4gd** | 73 |
| 27[f] |  **1a** |  **4ae+4ae'** | 64 |
| 28[e] |  **1t** |  **4td** | 42 |

[a]Reactions were executed in the sealed tubes without using inert or dry conditions and the yields are isolated yields. [b]Yield of terphenyl (**10ga**). [c]Pyridine, [d]N-methylpyrrole, [e]pyrazine, [f]napthalene were used as arene partners.

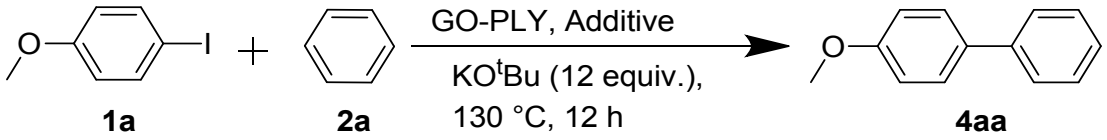
**Recyclability experiment:**

4-Iodoanisole (100 mg, 0.43 mmol), KO$^t$Bu (574 mg, 5.12 mmol), GO-PLY (100 mg), and benzene (8 mL) were charged in a sealed tube and the tube was sealed with a Teflon Plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered and washed with DCM. The filtrate was concentrated under reduced pressure and the product was purified by column chromatography. The recovered GO-PLY was washed several times with distilled water, acetone, and methanol and finally dried under vacuum. This dried recovered catalyst was then used again for the next cycle, maintaining the same catalyst to substrate ratio. Even after ten successive catalytic cycles, the yield of the biaryl product (**4aa**) was still found to be as high as 80%.

**Catalytic efficiency experiment for the physical mixing:**

4-Iodoanisole (58 mg, 0.247 mmol), KO$^t$Bu (333 mg, 2.97 mmol), GO (24 mg), compound **IV** (34 mg), and benzene (4.6 mL) were charged in a sealed tube and the tube was sealed with a Teflon Plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered and washed with DCM. The filtrate was concentrated under reduced pressure and the yield was calculated by $^1$H NMR spectroscopy. The recovered solid was washed several times with distilled water, acetone, and methanol and finally dried under vacuum. This dried and recovered catalyst was then used again for the next cycle, maintaining the same catalyst to substrate ratio.

**Table S3.** Radical quenching experiment




**1a** **2a** **4aa**

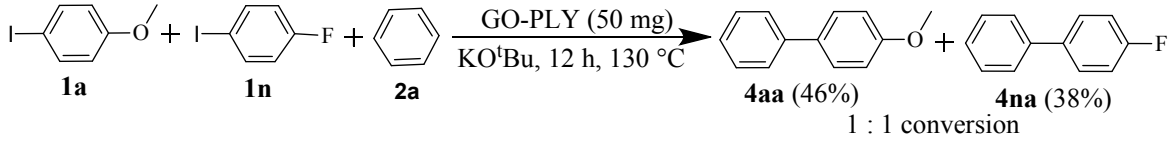
| Entry | Additive | Time (h) | Yield (%) |
|---|---|---|---|
| 1 | TEMPO (1 equiv) | 12 | < 3 |
| 2 | TEMPO (1 equiv) | 24 | < 3 |

[a] The reactions were executed in the sealed tubes without using inert or dry conditions. The indicated yields were calculated by $^1$H NMR spectroscopy.

**Procedure for radical scavenger experiment:**

4-Iodoanisole (50 mg, 0.21 mmol), KO$^t$Bu (287 mg, 2.56 mmol), GO-PLY (50 mg), benzene (2 mL) and TEMPO (33 mg, 0.21 mmol) were charged in a sealed tube and the tube was sealed with a teflon plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered and washed with DCM and concentrated under reduced pressure. The resulting product was purified by column chromatography (eluent: hexane/EtOAc = 99/ 1 to 97/ 3) to give a mixture of less than 3% 4-methoxybiphenyl with remaining unreacted 4-iodoanisole.

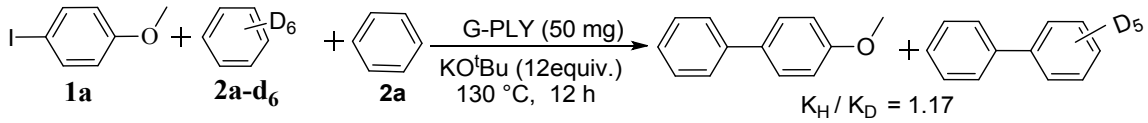
**Procedure for the competition reaction**:




**Scheme S2.** Competition reaction between different iodoarenes

4-Fluoroiodobenzene (25 mg, 0.11 mmol), 4-iodoanisole (26 mg, 0.11 mmol), GO-PLY (51 mg), KO$^t$Bu (172 mg, 1.53 mmol), and benzene (4 mL) were charged in a sealed tube and the tube was sealed with a teflon plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered and washed with DCM and concentrated under reduced pressure. The resulting product was purified by column chromatography (eluent: hexane/EtOAc = 99/ 1 to 97/ 3) to obtain the mixture of 4-methoxy-biphenyl and 4-fluoro-biphenyl. The $^1$H NMR spectroscopy was used to obtain the relative yields.

**Procedure for kinetic isotopic effect experiment:**




**Scheme S3.** KIE experiment utilizing benzene-$d_6$ and benzene, revealing a Low $K_H/K_D$ value

4-Iodoanisole (50 mg, 0.21 mmol), KO$^t$Bu (287 mg, 2.56 mmol), GO-PLY (50 mg), benzene (2 mL) and benzene-$d_6$ (2 mL) were charged in a tube and the tube was sealed with a teflon plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered and washed with DCM and concentrated under reduced pressure. The resulting product was purified by column chromatography (eluent: hexane/EtOAc = 99/ 1 to 97/ 3) to give a mixture of 4-methoxybiphenyl and its deuterated analogue as a white solid. The KIE value was found to be 1.17, as calculated from $^1$H NMR spectroscopy.

**Procedure for large scale catalysis experiment:**

4-Iodoanisole (2.13 mmol), KO$^t$Bu (12 equiv.), GO-PLY (500 mg), and benzene (60 mL) were charged in a sealed tube and the tube was sealed with a Teflon Plug. The resulting mixture was heated at 130 ℃ for 12 h. The reaction mixture was allowed to cool, filtered through 0.2 μm PTFE membrane, washed with DCM and concentrated under reduced pressure. The resulting crude product was purified by column chromatography (eluent: hexane/EtOAc = 97/ 3) to give pure product (**4aa**).

## Analytical and Spectral Characterization Data of the Biaryl Products:

**4- Methoxy-biphenyl (4aa).**[9] Yield 38 mg (95%), $^1$H NMR (400 MHz, $CDCl_3$): δ 3.86 (s, 3H), 7.00 (d, *J* = 8.39 Hz, 2H), 7.32 (t, *J* = 6.87 Hz, 1H), 7.43 (t, *J* = 8.39 Hz, 2H), 7.56 (t, *J* = 7.63 Hz, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 55.3, 114.2, 126.6, 126.7, 128.1, 128.7, 133.7, 140.5, 159.1.

**3- Methoxy-biphenyl (4ba).**[9] Yield 31 mg (79%), $^1$H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 6.90 (dd, *J* = 8.39 Hz, 1.53 Hz, 1H), 7.13 (t, *J* = 2.29 Hz, 1H), 7.19 (d, *J* = 7.63 Hz, 1H), 7.33-7.38 (m, 2H), 7.44 (t, *J* = 8.39, 2H), 7.56 (dd, *J* = 8.39 Hz, 1.53 Hz, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 55.3, 112.7, 112.7, 119.7, 127.2, 127.4, 128.7, 129.7, 141.1, 142.8, 159.9.

**Biphenyl (4ca).**[9] Yield 36 mg (94%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.34-7.38 (m, 2H), 7.44-7.47 (m, 4H), 7.60-7.62 (m, 4H).$^{13}$C NMR (100 MHz, $CDCl_3$): δ 127.2, 127.2, 128.7, 141.2.

**4-Methyl-biphenyl (4da).**[9] Yield 31 mg (81%), $^1$H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 3H), 7.26 (d, *J* = 7.63 Hz, 2H), 7.33 (t, *J* = 7.63Hz, 1H), 7.44 (t, *J* = 7.63 Hz, 2H), 7.51 (d, 8.39 2H), 7.59 (d, *J* = 7.63, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.1, 127.0, 128.7, 129.4, 137, 138.3, 141.1.

**2-Methyl-biphenyl (4ea).**[9] Yield 27 mg (71%), $^1$H NMR (400 MHz, $CDCl_3$): δ 2.30 (s, 3H), 7.25-7.30 (m, 4H), 7.34-7.37 (m, 3H), 7.41-7.46 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 20.4, 125.7, 126.7, 127.2, 128.0, 128.7, 129.1, 129.7, 130.2, 135.3, 141.9.

**3,5-Dimethyl-biphenyl (4fa).**[10] Yield 35 mg (89%), $^1$H NMR (400 MHz, $CDCl_3$): δ 2.39 (s, 6H), 7.01 (s, 1H), 7.22 (s, 2H), 7.31-7.35(m, 1H), 7.40-7.45 (m, 2H), 7.57-7.60 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.4, 126.0, 127.1, 127.2, 128.6, 128.9, 138.2, 141.3, 141.5.

**4-t-butyl-biphenyl (4ga).**[11] Yield 38 mg (93%), $^1$H NMR (400 MHz, $CDCl_3$): δ 1.39 (s, 9H), 7.34(tt, *J* = 6.87 Hz, 1.53 Hz, 1H), 7.42-7.47 (m, 2H), 7.47-7.51 (m, 2H), 7.55-7.58 (m, 2H), 7.60-7.62 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 31.4, 34.5, 125.7, 126.8, 127.0, 127.0, 128.7, 138.3, 141.1, 150.2.

**Terephenyl (4ha).**[12] Yield 39 mg (96%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35-7.39 (m, 2H), 7.45-7.49 (m, 4H), 7.64-7.66 (m, 4H), 7.69 (s, 4H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 127.1, 127.3, 127.5, 128.8, 140.1, 140.7.

**1-Phenyl-naphthalene (4ia).**[13] Yield 30 mg (73%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.41-7.46 (m, 3H), 7.48-7.52 (m, 5H), 7.53-7.55, (m, 1H), 7.87 (d, *J* =8.39 Hz, 1H), 7.91 (d, *J* = 7.63, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 125.4, 125.7, 126.0, 12.9, 127.2, 127.6, 128.2, 130.1, 131.6, 133.8, 140.3, 140.8.

**3-Fluoro-biphenyl (4ja).**[14] Yield 29 mg (74%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.01-7.06 (m, 1H), 7.28-7.31 (m, 1H), 7.35-7.41 (m, 3H), 7.45(td, *J* = 7.63 Hz, 2.29 Hz, 2H), 7.58 (d, *J* = 7.63 Hz, 2H).

$^{13}$C NMR (100 MHz, $CDCl_3$): δ 113.9, 114.1, 122.8 (d, $J_{C-F}$ = 1.92 Hz),127.1, 127.8, 128.9, 130.2 (d, $J_{C-F}$ = 8.63 Hz),139.2, 143.5 (d, $J_{C-F}$ = 7.67 Hz), 163.2 (d, $J_{C-F}$ = 245 Hz).

**4-Fluoro-biphenyl (4na).**[15] Yield 25 mg (64%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.11-7.15 (m, 2H), 7.35 (t, *J* = 8 Hz, 1H), 7.44 (t, *J* = 8 Hz, 2H), 7.53-7.57 (m, 4H), $^{13}$C NMR (100 MHz, $CDCl_3$): δ 115.5, 115.7, 127.0, 127.2, 128.7 (t, $J_{C-F}$ = 8.63 Hz), 137.3 (d, $J_{C-F}$ = 2.87 Hz), 140.3, 162.5 (d, $J_{C-F}$ = 246 Hz).

**2-Phenyl-thiophene (4oa).**[16] Yield 32 mg (82%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.07-7.09 (m, 1H), 7.27-7.32 (m, 3H), 7.38 (t, *J* = 6.87 Hz 2H), 7.62 (m, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 123.1, 124.8, 125.9, 127.4, 128.0, 128.9, 134.4, 144.4.

**2-Phenyl-pyridine (4pa).**[12] Yield 30 mg (81%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.21-7.25 (m, 1H), 7.42 (tt, *J* = 6.10 Hz, 1.53 Hz, 1H), 7.46-7.50 (m, 2H), 7.72-7.77 (m, 2H), 7.98-8.0 (m, 2H), 8.69-8.71 (m, 1H).$^{13}$C NMR (100 MHz, $CDCl_3$): δ 120.5, 122.1, 126.9, 128.7, 128.9, 136.7, 139.4, 149.7, 157.5.

**3-Phenyl-pyridine (4ra).**[12] Yield 25 mg (67%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7.35-7.43 (m, 2H), 7.49 (tt, *J* = 6.87 Hz, 1.53 Hz, 2H), 7.58-7.60 (m, 2H), 7.87-7.90 (m, 1H), 8.60 (dd, *J* = 5.34 Hz, 1.53 Hz, 1H ), 8.86 (m, 1H).$^{13}$C NMR (100 MHz, $CDCl_3$): δ 123.6, 127.2, 128.1, 129.1, 134.4, 136.7, 137.8, 148.3, 148.4.

**1-Phenyl-isoquinoline (4sa).**[17] Yield 22 mg (55%), $^1$H NMR (400 MHz, $CDCl_3$): δ 7. 7.50-7.56 (m, 4H), 7.65-7.72 (m, 4H), 7.89 (d, *J* = 8.39 Hz, 1H), 8.11 (d, *J* = 7.63 Hz, 1H), 8.62 (d, *J* = 5.34 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 119.9, 126.7, 127.0, 127.1, 127.6, 128.3, 128.6, 129.9, 130.0, 136.6, 142.2, 160.7.

**2-(4-Methoxyphenyl)-pyridine (4ab).**[18] Yield 21 mg (54%), $^1$H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 7.00 (dt, *J* = 9.92 Hz, 3.05 Hz, 2H), 7.16-7.19 (m, 1H), 7.66-7.74 (m, 2H), 7.95 (dt, *J* = 9.92 Hz, 3.05 Hz, 2H), 8.65 (d, *J* = 4.58 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 55.5, 114.1, 119.8, 122.0, 128.2, 132.1, 136.7, 149.6, 157.2, 160.5.

**1-Methyl-2-(4-anisyl)-pyrrole (4ac).**[10,19] Yield 21 mg (53%), $^1$H NMR (500 MHz, $CDCl_3$): δ 3.64 (s, 3H), 3.85 (s, 3H), 6.16-6.17 (m, 1H), 6.19-6.20 (m, 1H), 6.69-6.70 (m, 1H), 6.94-6.96 (m, 2H), 7.32-7.34 (m, 2H). $^{13}$C NMR (125 MHz, $CDCl_3$): δ 34.8, 55.2, 107.5, 107.9, 113.7, 122.9, 125.9, 129.9, 134.3, 158.6.

**2-(4-Methoxyphenyl)-pyrazine (4ad).**[20-21] Yield 29 mg (72%), $^1$H NMR (400 MHz, $CDCl_3$): δ 3.87 (s, 3H), 7.02-7.04 (m, 2H), 7.97-7.99 (m, 2H), 8.43 (d, *J* = 3.05 Hz, 1H), 8.57-8.58 (m, 1H), 8.97 (d, *J* = 1.53 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 55.3, 114.4, 128.2, 128.8, 141.5, 142.0, 143.9, 152.4, 161.1.

**2-(3-Methoxyphenyl)-pyrazine (4bd).**[20,22] Yield 27 mg (69%), $^1$H NMR (400 MHz, $CDCl_3$): δ 3.90 (s, 3H), 7.03 (dd, *J* = 8.39 Hz, 1.53 Hz, 1H), 7.43 (t, 8.39 Hz, 1H), 7.57-7.60 (m, 2H), 8.51 (d, *J* = 2.29 Hz, 1H), 8.63-8.64 (m, 1H), 9.02 (d, *J* = 1.53 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 55.4, 112.0, 116.0, 119.2, 130.0, 137.7, 142.3, 143.0, 144.0, 152.6, 160.2.

**2-(p-Tolyl)-pyrazine (4dd).**[20] Yield 28 mg (71%), $^1$H NMR (400 MHz, $CDCl_3$): δ 2.43 (s, 3H), 7.32 (d, *J* = 7.63 Hz, 2H), 7.92 (d, 8.39 Hz, 2H), 8.74 (d,2.29 Hz, 1H), 8.61-8.61 (m, 1H), 9.01 (d, *J* = 1.53 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.3, 126.7, 129.7, 133.5, 140.0, 141.9, 142.5, 144.0, 152.8.

**2-(3,5-Dimethylphenyl)-pyrazine (4fd).**[23] Yield 31 mg (79%), $^1$H NMR (400 MHz, $CDCl_3$): δ 2.41 (s, 6H), 7.12 (s, 1H), 7.62 (s, 2H), 8.49 (d,2.29 Hz, 1H), 8.61-8.62 (m, 1H), 9.00 (d, *J* = 1.53 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 21.3, 124.7, 131.5, 136.2, 138.6, 142.3, 142.7, 144.0, 153.1.

**2-(4-(tert-butyl)phenyl)-pyrazine (4gd).**[20] Yield 30 mg (73%), $^1$H NMR (400 MHz, $CDCl_3$): δ 1.37 (s, 9H), 7.55-7.53 (m, 2H), 7.95-7.97 (m, 2H), 8.48 (d, *J* = 2.29 Hz, 1H), 8.61-8.62 (m, 1H), 9.02 (d, *J* = 1.53 Hz, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 31.2, 34.8, 126.0, 126.6, 133.5, 142.0, 142.5, 144.1, 152.8, 153.2.

**Mixture of 1-(4-anisyl)-naphthalene, 2-(4-anisyl)-naphthalene (4ae+4ae').**[24] Yield 32 mg (64%). Ratio of α and β isomers were calculated from the $^1$H NMR spectroscopy by analyzing the peaks of methoxy groups for both isomers. 1-(4-anisyl)-naphthalene **(4ae):** $^1$H NMR (400 MHz, $CDCl_3$): δ 3.91 (s, 3H), 7.85 (d, *J* = 8.39 Hz, 1H). However, the following peaks of α isomer were merging with the peaks of β isomer **(4ae')** due to which these signals are not clearly distinguishable at δ 7.04-7.06 (m), 7.42-7.55 (m), 7.90-7.96 (m).

**2,2'-Bipyrazine (4td).**[25] Yield 16 mg (42%), $^1$H NMR (400 MHz, $CDCl_3$): δ 8.67 (s, 4H), 9.61 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$): δ 143.4, 143.7, 145.2, 149.3.

**$^{1}$H NMR and $^{13}$C NMR spectra of phenalenyl derivatives:**

$^{1}$H NMR and $^{13}$C NMR spectra of **1** in DMSO-$d_6$:

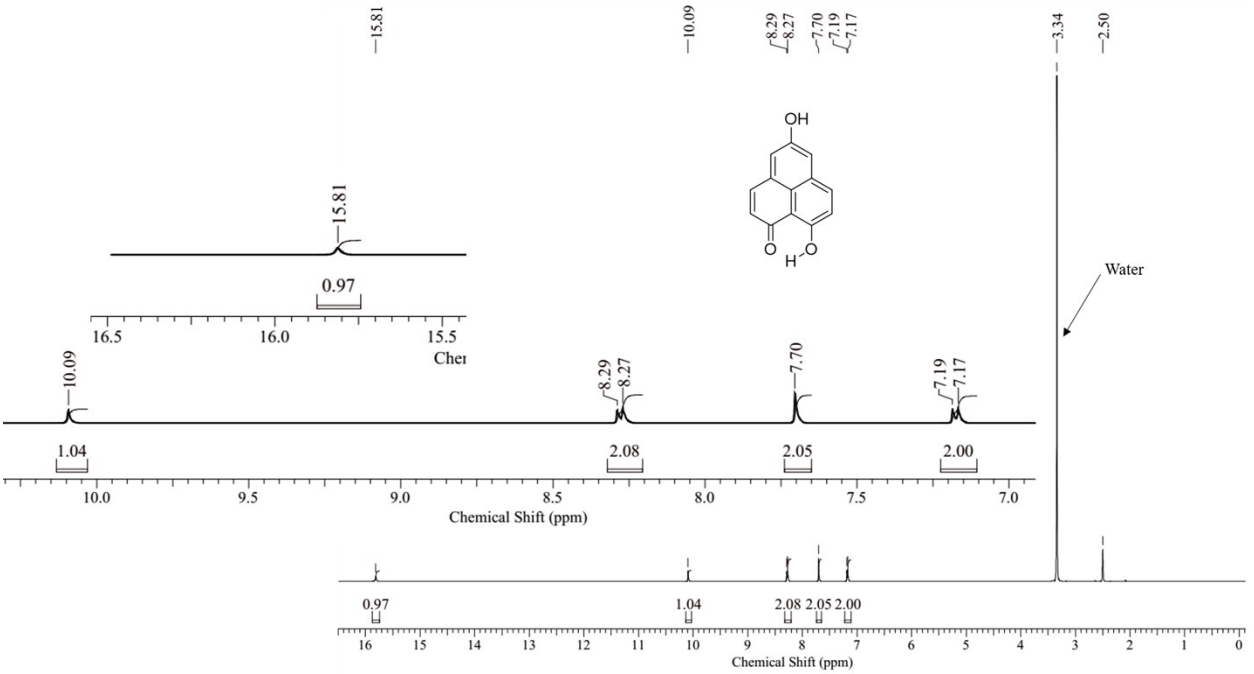



**Fig. S4** $^{1}$H NMR spectrum of 5,9-dihydroxyphenalenone (**1**) in DMSO-$d_6$

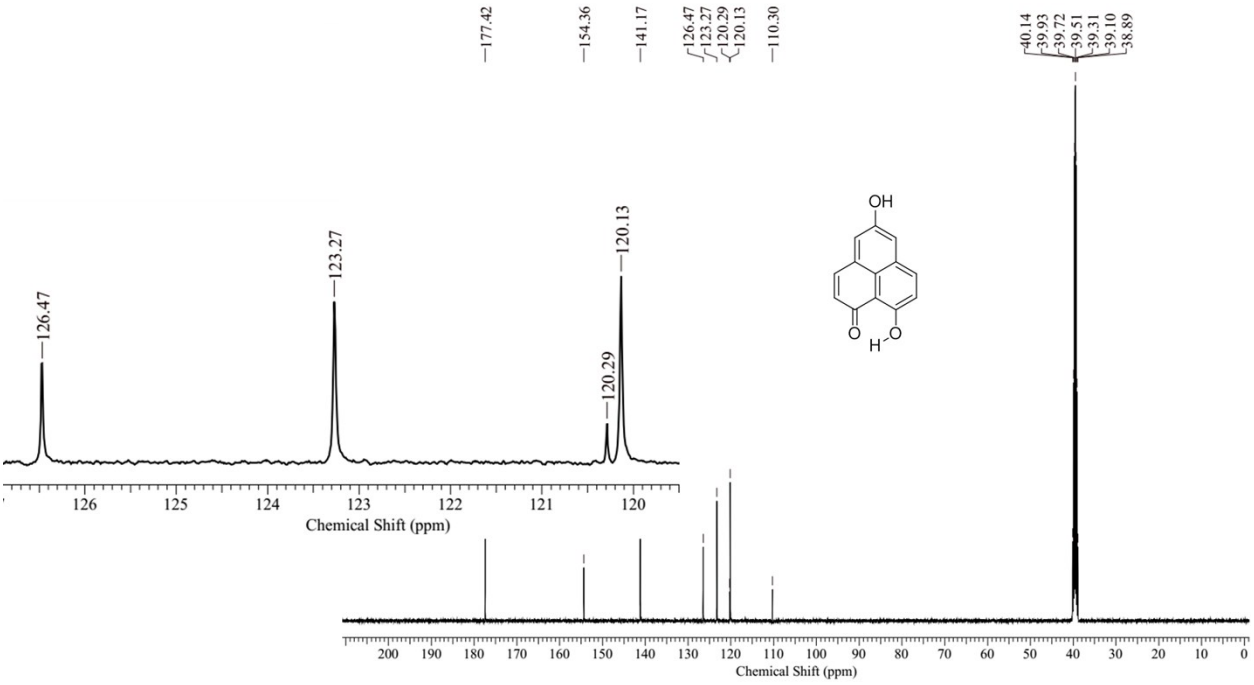



**Fig. S5** $^{13}$C NMR spectrum of 5,9-dihydroxyphenalenone (**1**) in DMSO-$d_6$

$^{1}$H NMR and $^{13}$C NMR spectra of **3** in $CDCl_3$:

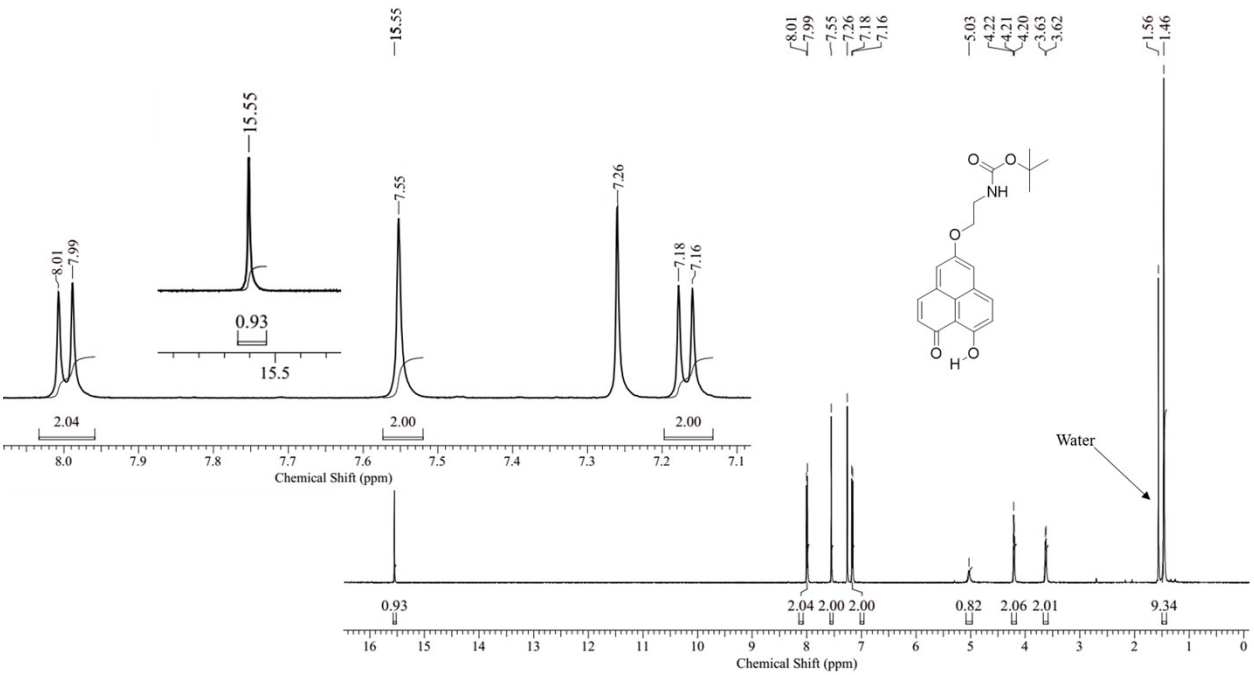



**Fig. S6** $^{1}$H NMR spectrum of **3** in $CDCl_3$

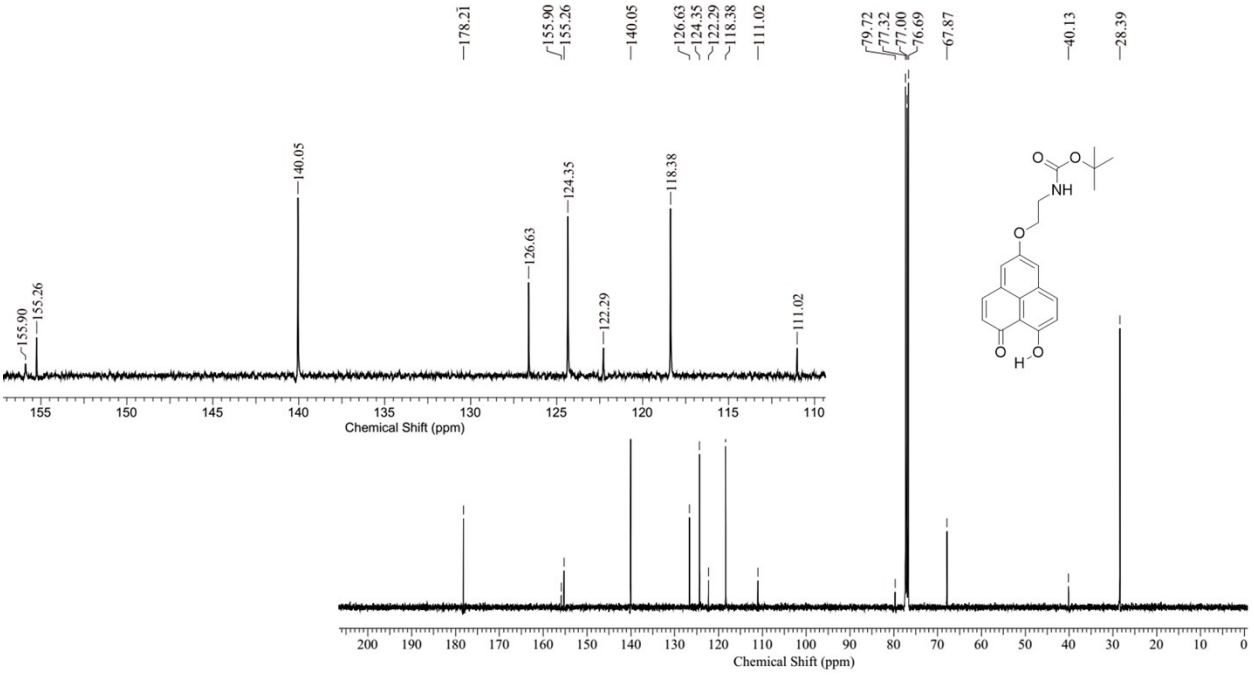



**Fig. S7** $^{13}$C NMR spectrum of **3** in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4** in $CDCl_3$:

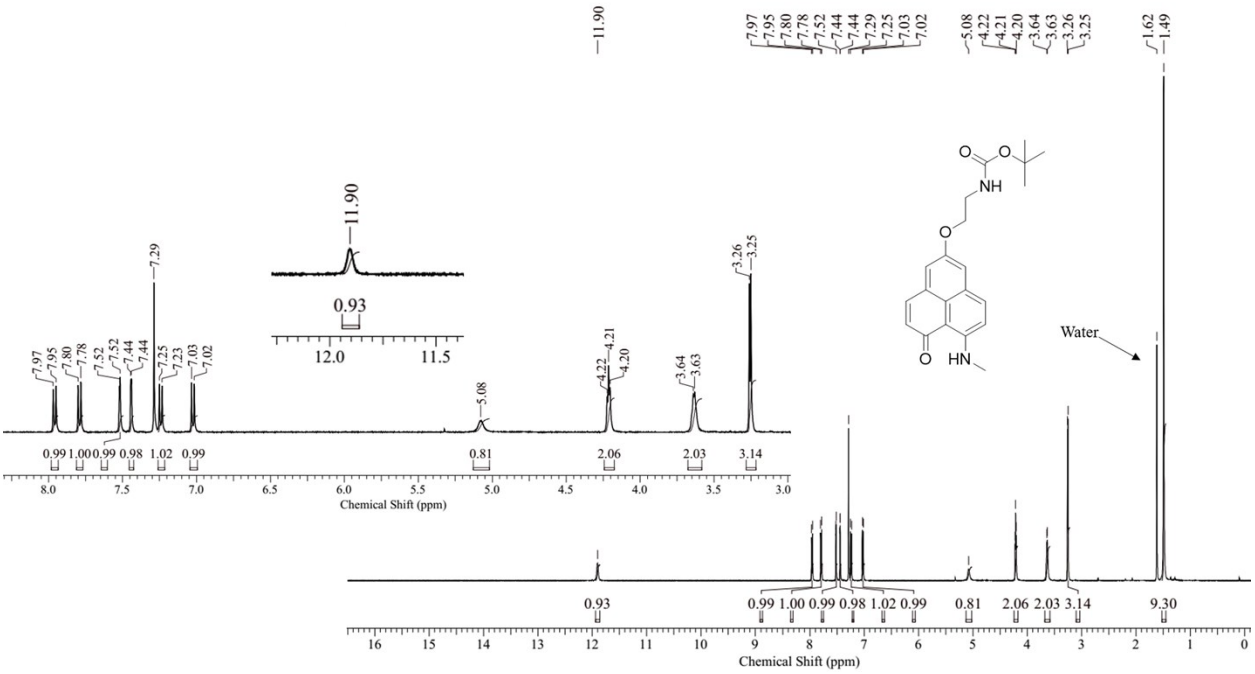



**Fig. S8** $^{1}$H NMR spectrum of **4** in $CDCl_3$

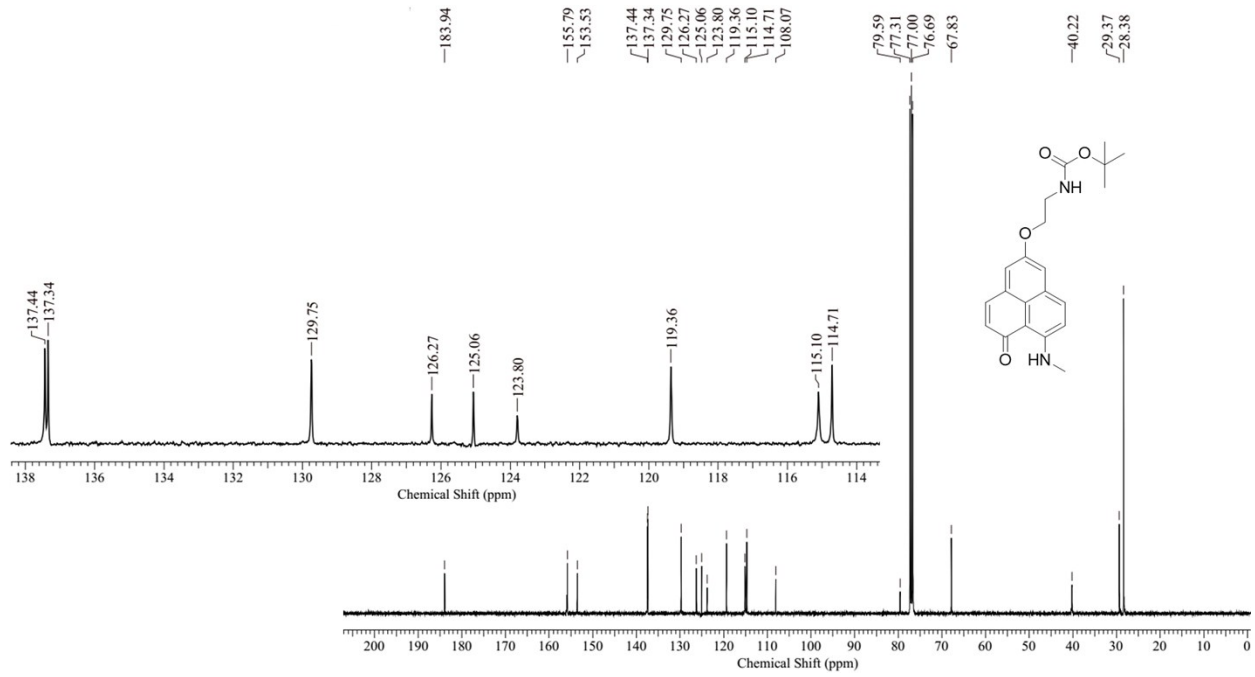



**Fig. S9** $^{13}$C NMR spectrum of **4** in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **5** in $CD_3OD$:

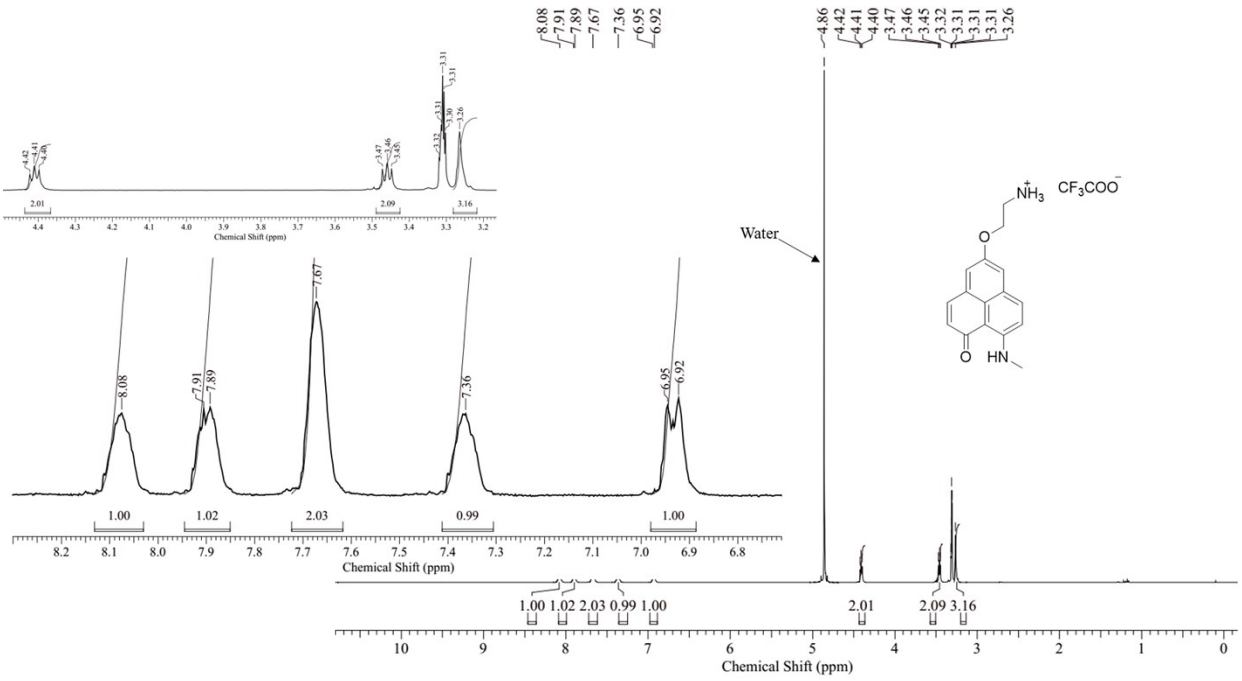



**Fig. S10** $^{1}$H NMR spectrum of **5** in $CD_3OD$

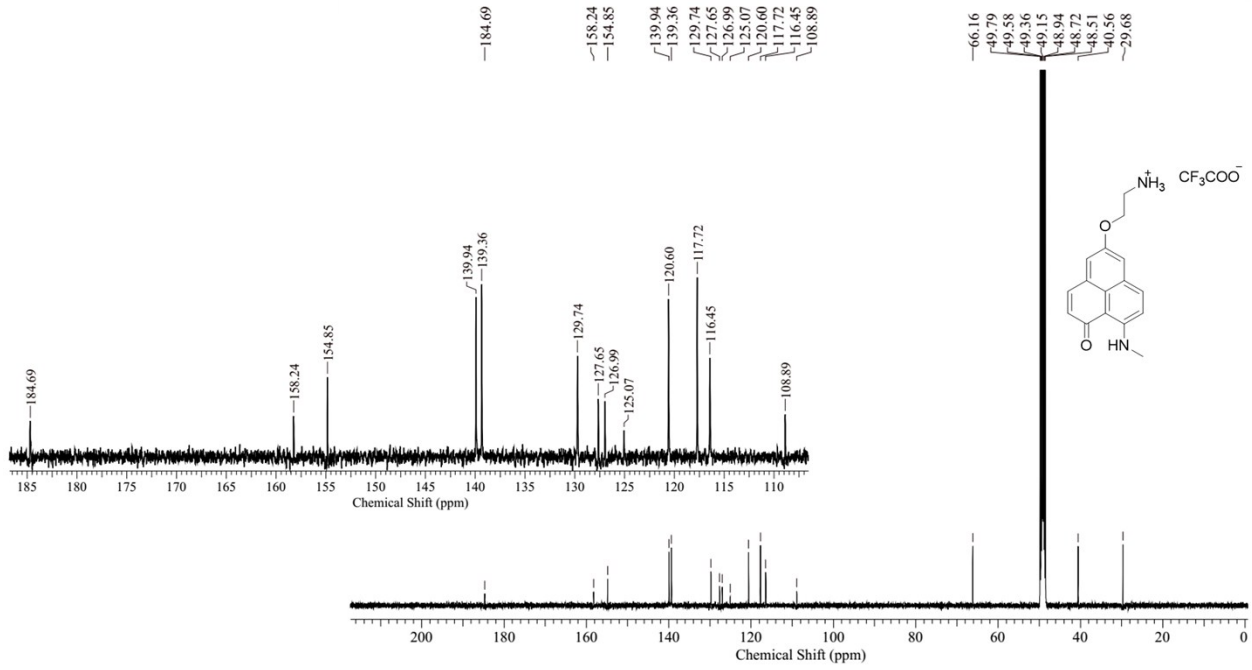



**Fig. S11** $^{13}$C NMR spectrum of **5** in $CD_3OD$

**$^{1}$H NMR and $^{13}$C NMR spectra of biaryl products:**

$^{1}$H NMR and $^{13}$C NMR spectra of **4aa** in $CDCl_3$:

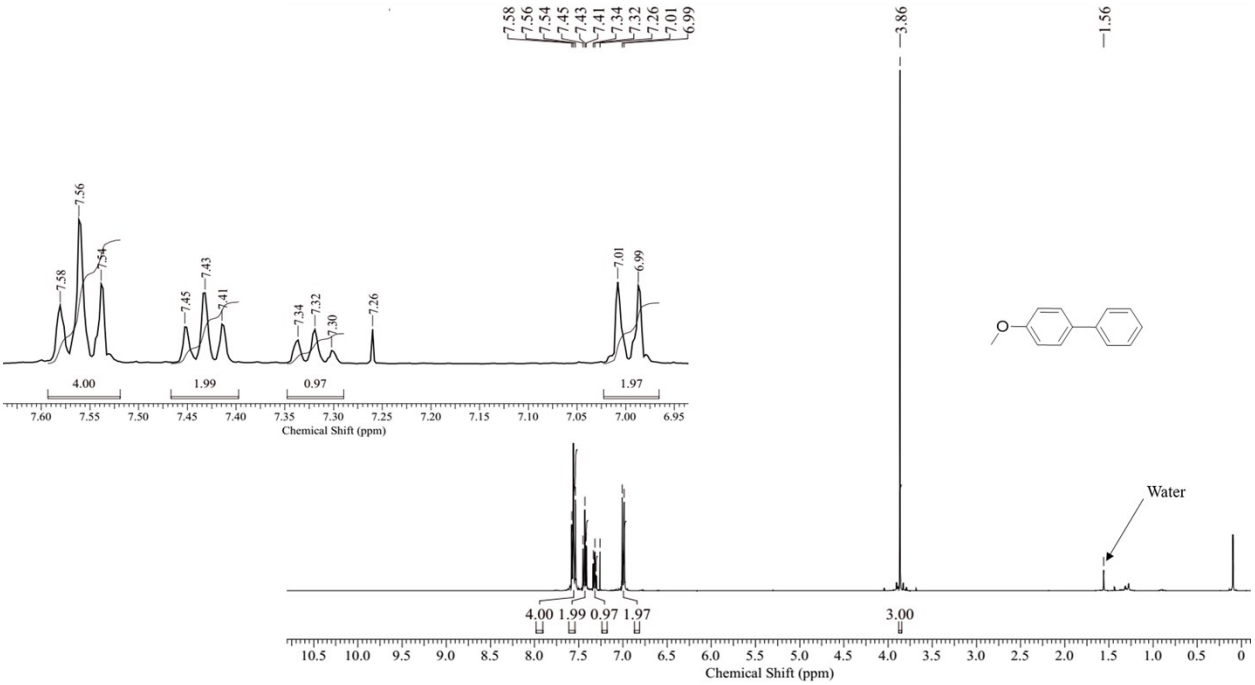



**Fig. S12** $^{1}$H NMR spectrum of 4- methoxy-biphenyl (**4aa**) in $CDCl_3$

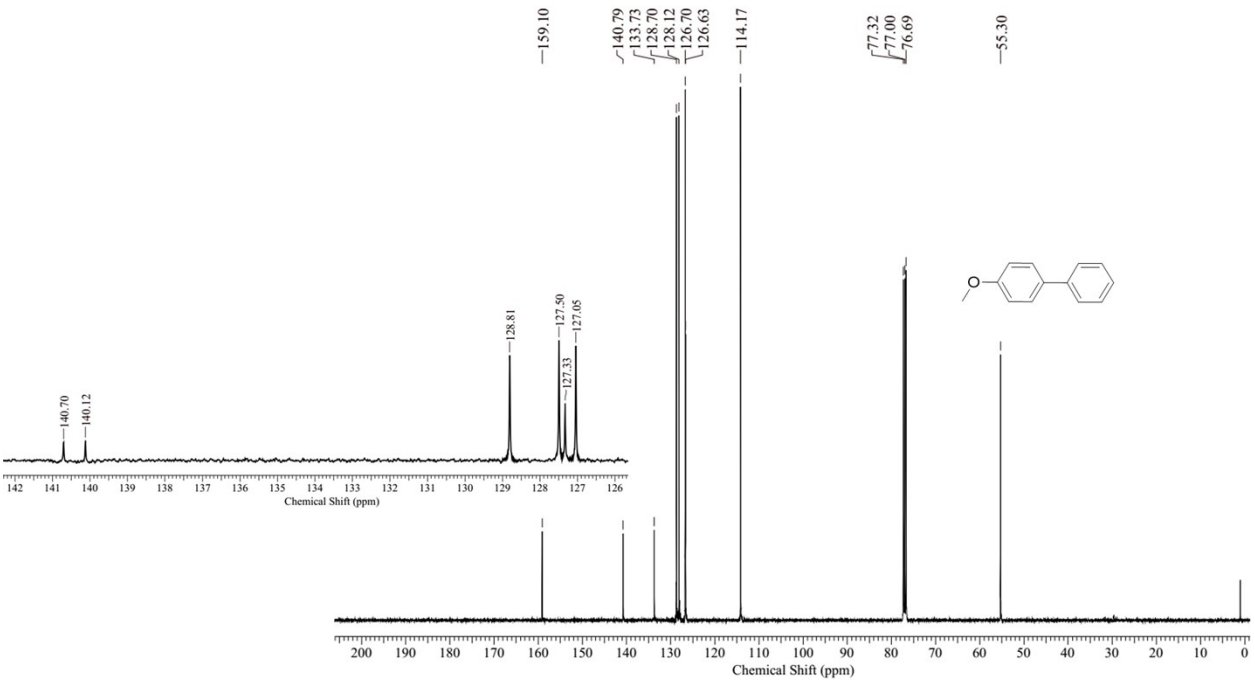



**Fig. S13** $^{13}$C NMR spectrum of 4- methoxy-biphenyl (**4aa**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ba** in $CDCl_3$:

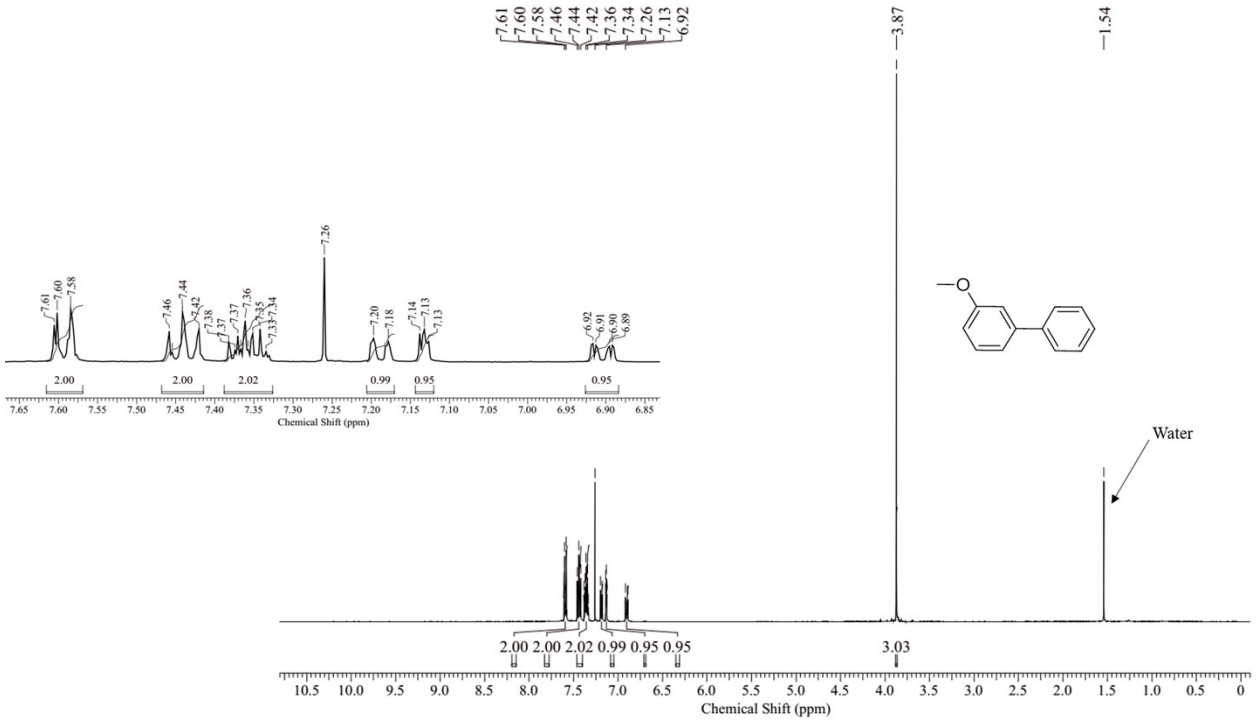



**Fig. S14** $^{1}$H NMR spectrum of 3- methoxy-biphenyl (**4ba**) in $CDCl_3$

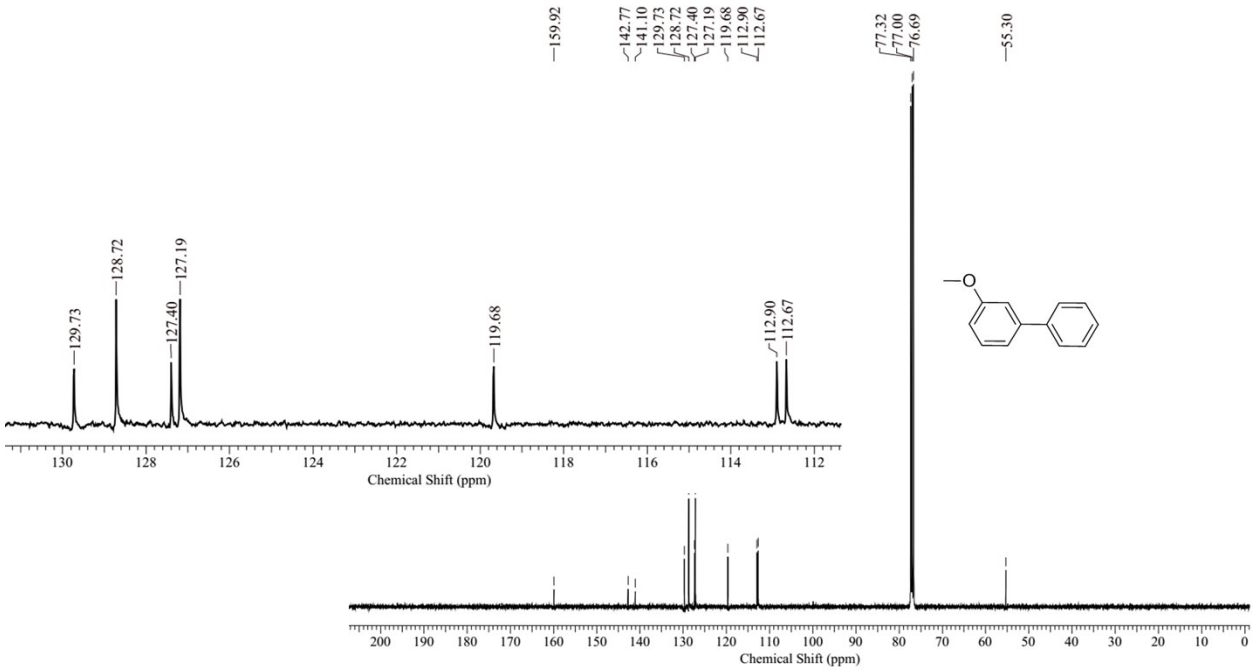



**Fig. S15** $^{13}$C NMR spectrum of 3- methoxy-biphenyl (**4ba**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ca** in $CDCl_3$:

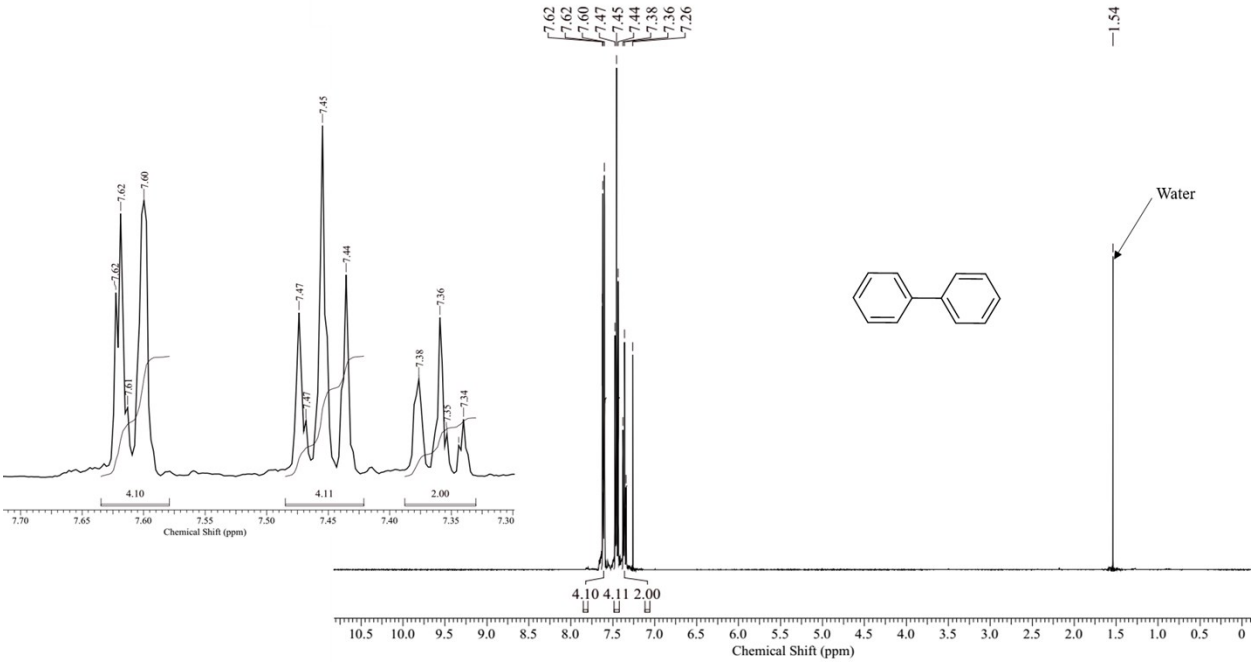



**Fig. S16** $^{1}$H NMR spectrum of biphenyl (**4ca**) in $CDCl_3$

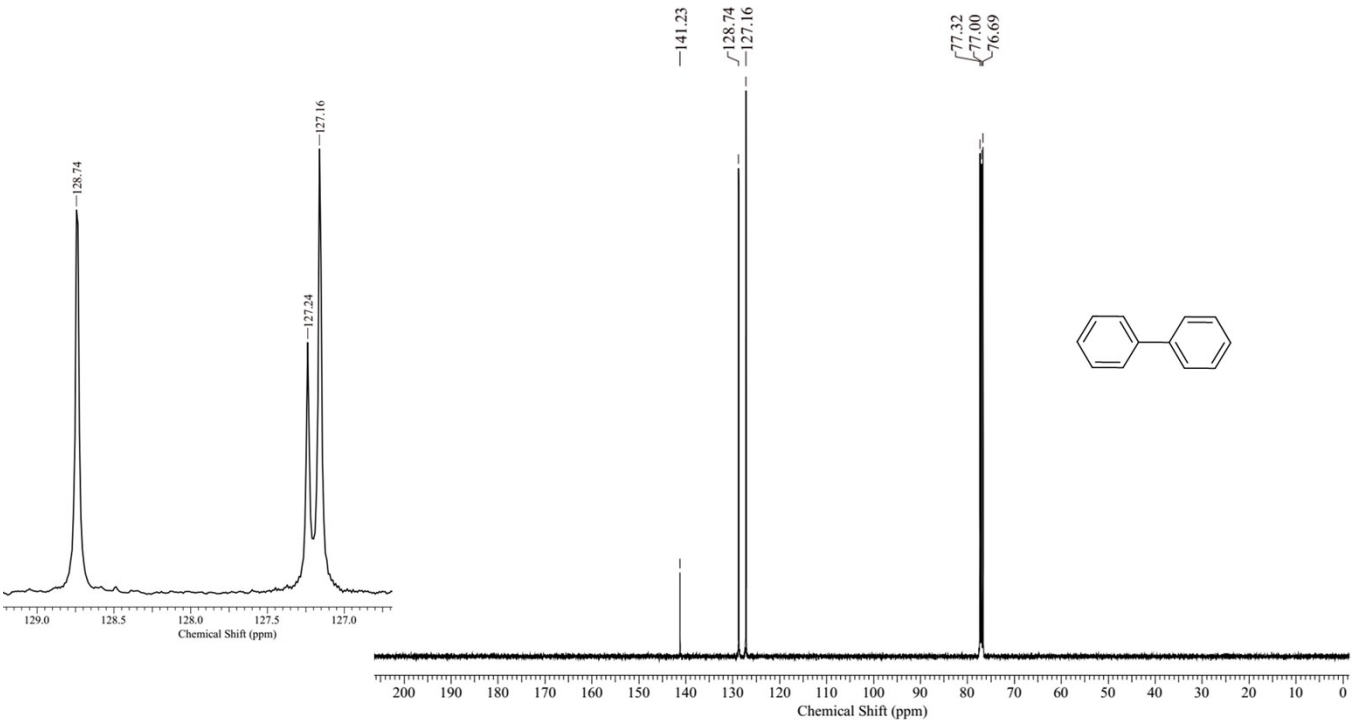



**Fig. S17** $^{13}$C NMR spectrum of biphenyl (**4ca**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4da** in $CDCl_3$:

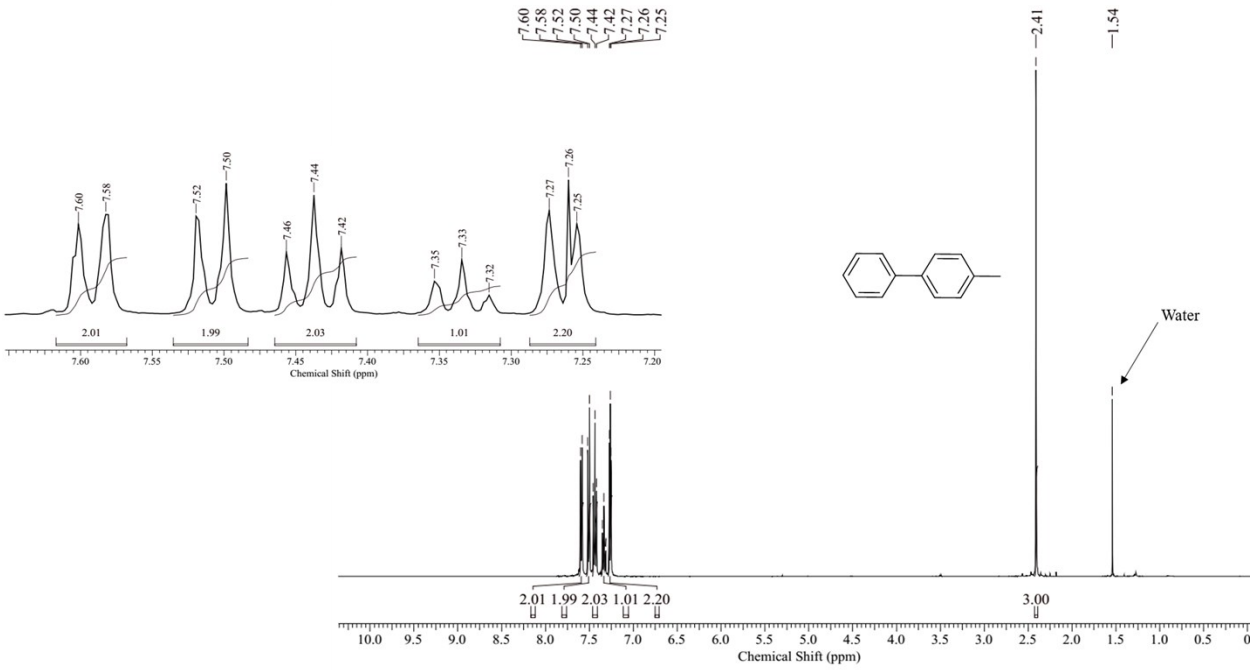



**Fig. S18** $^{1}$H NMR spectrum of 4-methyl-biphenyl (**4da**) in $CDCl_3$

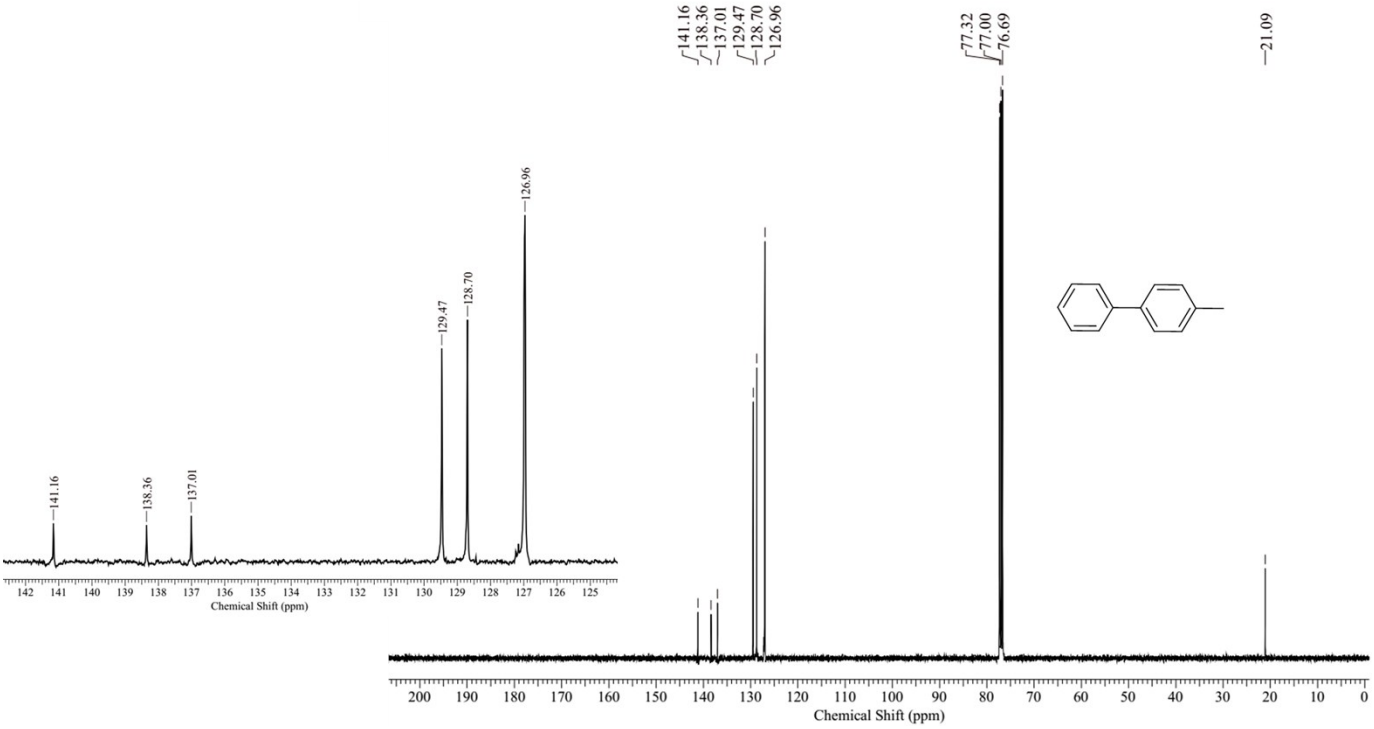



**Fig. S19** $^{13}$C NMR spectrum of 4-methyl-biphenyl (**4da**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ea** in $CDCl_3$:

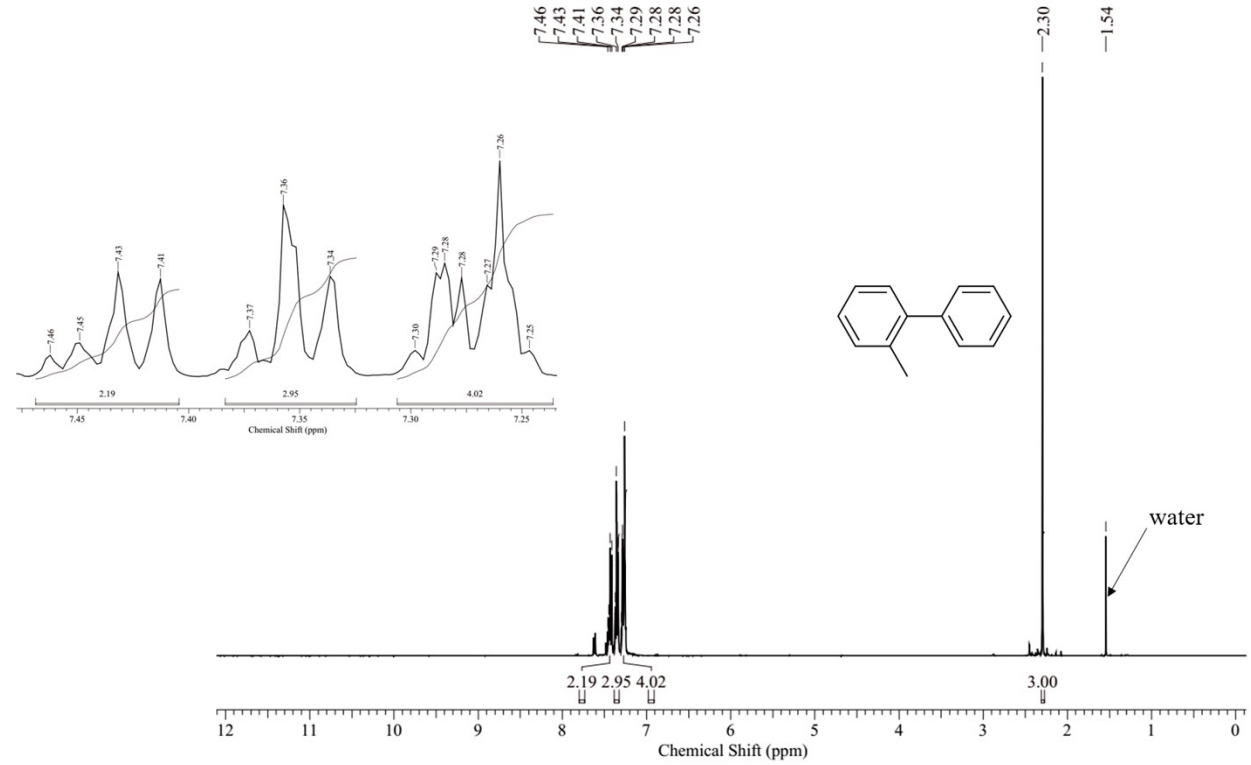



**Fig. S20** $^{1}$H NMR spectrum of 2-methyl-biphenyl (**4ea**) in $CDCl_3$

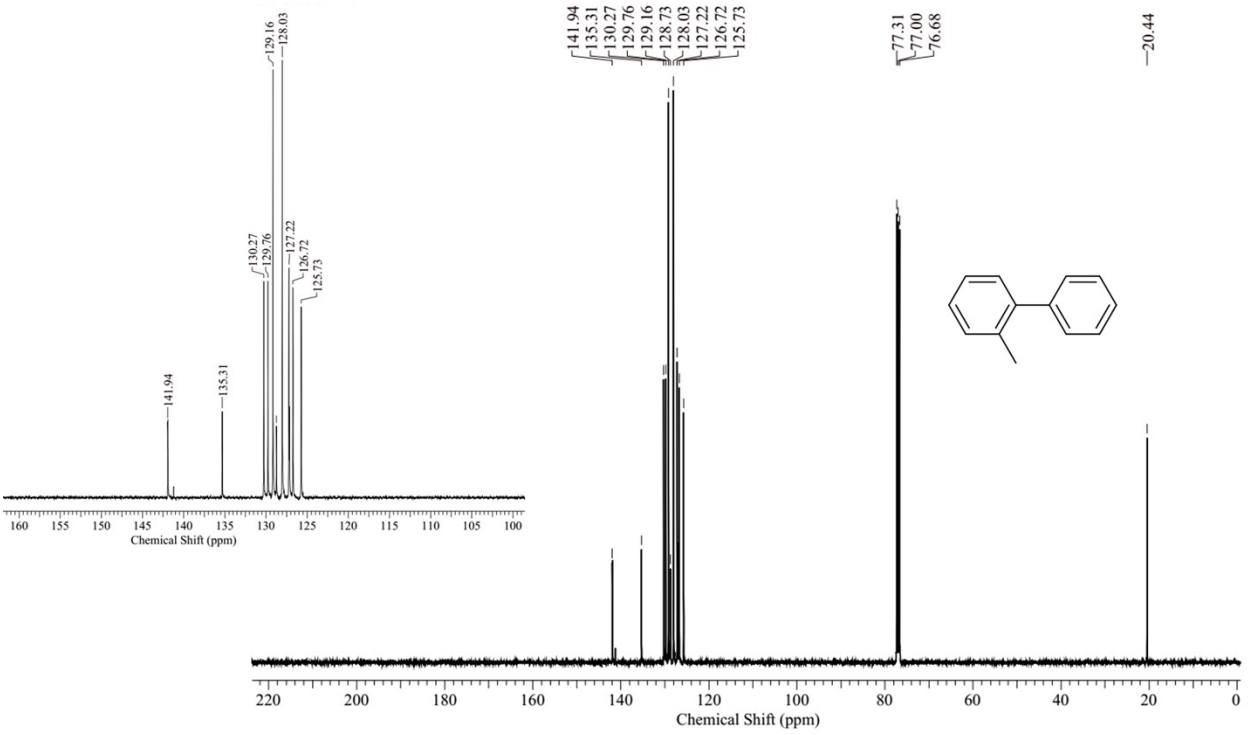



**Fig. S21** $^{13}$C NMR spectrum of 2-methyl-biphenyl (**4ea**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4fa** in $CDCl_3$:

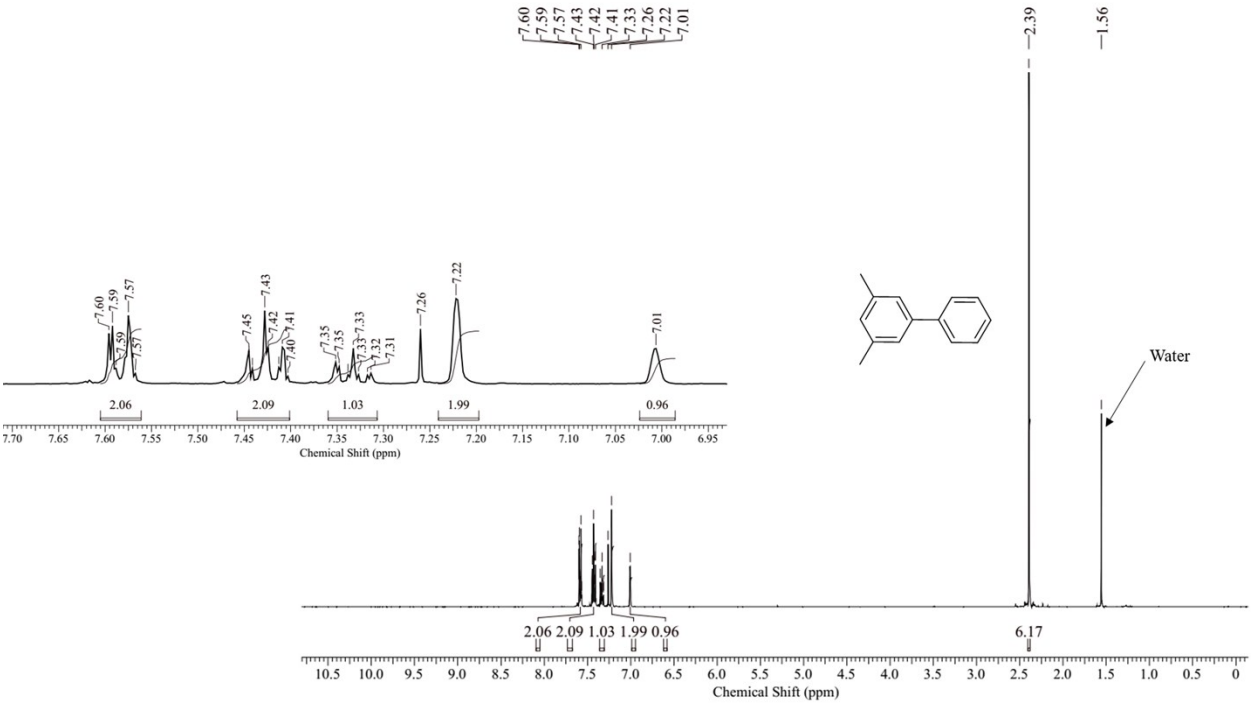



**Fig. S22** $^{1}$H NMR spectrum of 3,5-dimethyl-biphenyl (**4fa**) in $CDCl_3$

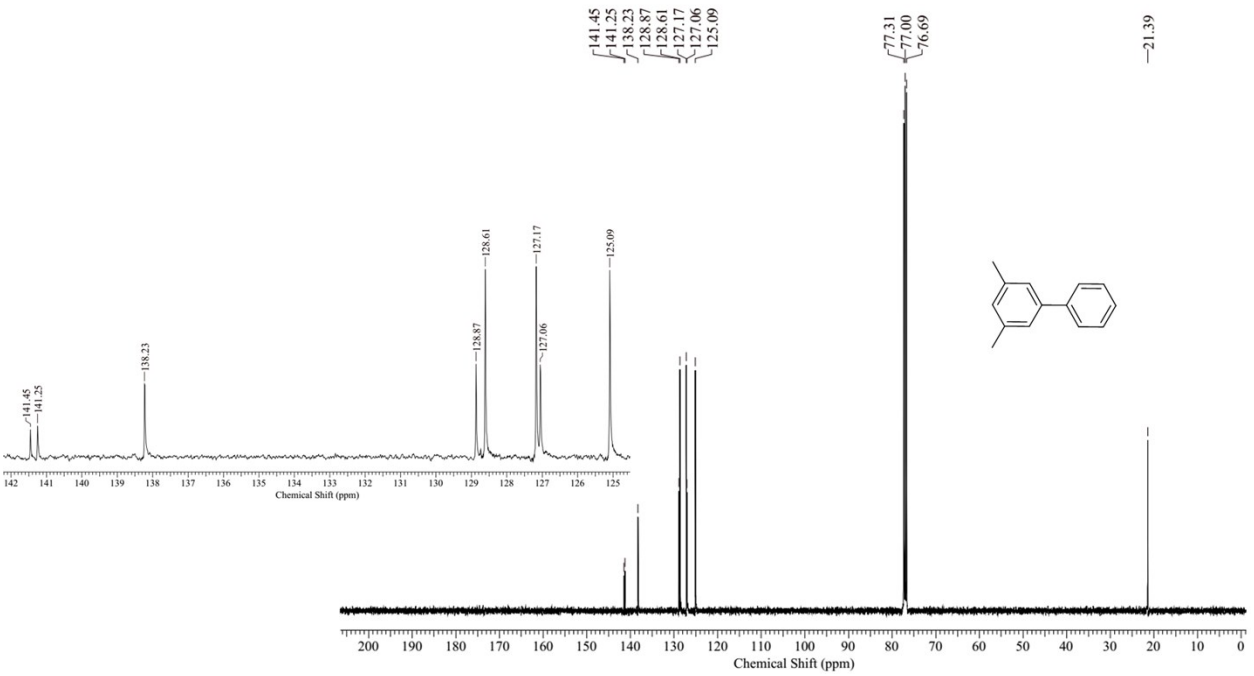



**Fig. S23** $^{13}$C NMR spectrum of 3,5-dimethyl-biphenyl (**4fa**) in $CDCl_3$

$^{1}H$ NMR and $^{13}C$ NMR spectra of **4ga** in $CDCl_3$:

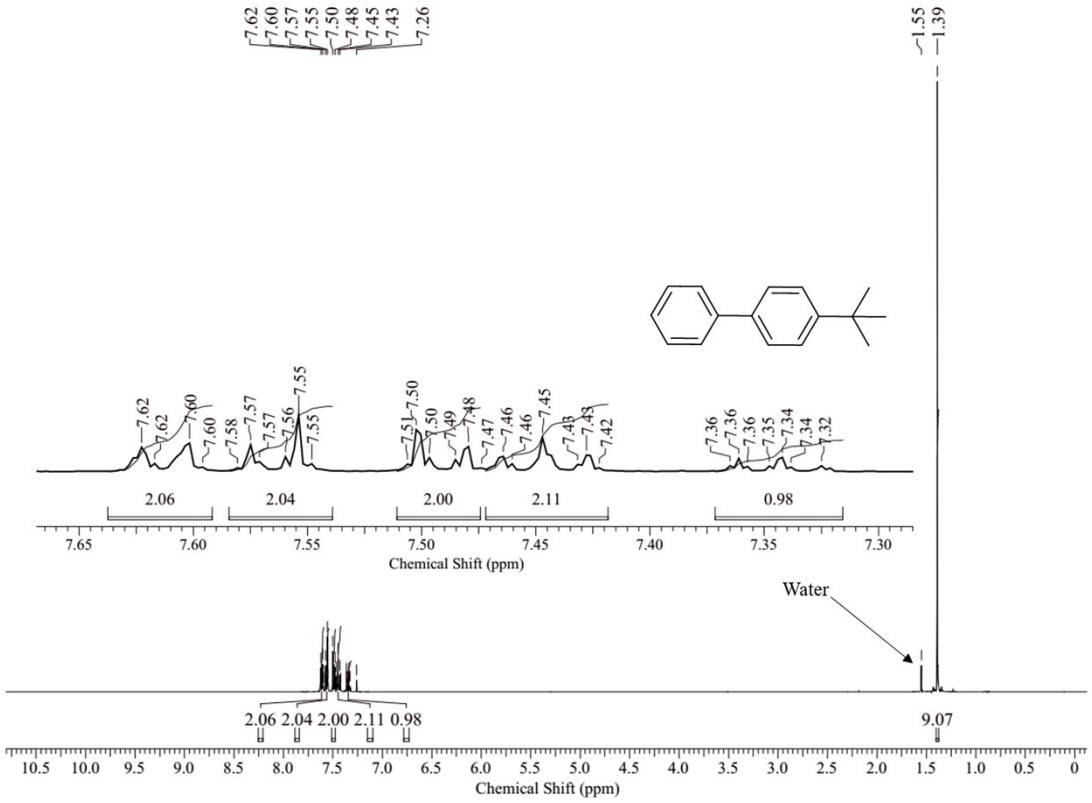



**Fig. S24** $^{1}H$ NMR spectrum of 4-t-butyl-biphenyl (**4ga**) in $CDCl_3$

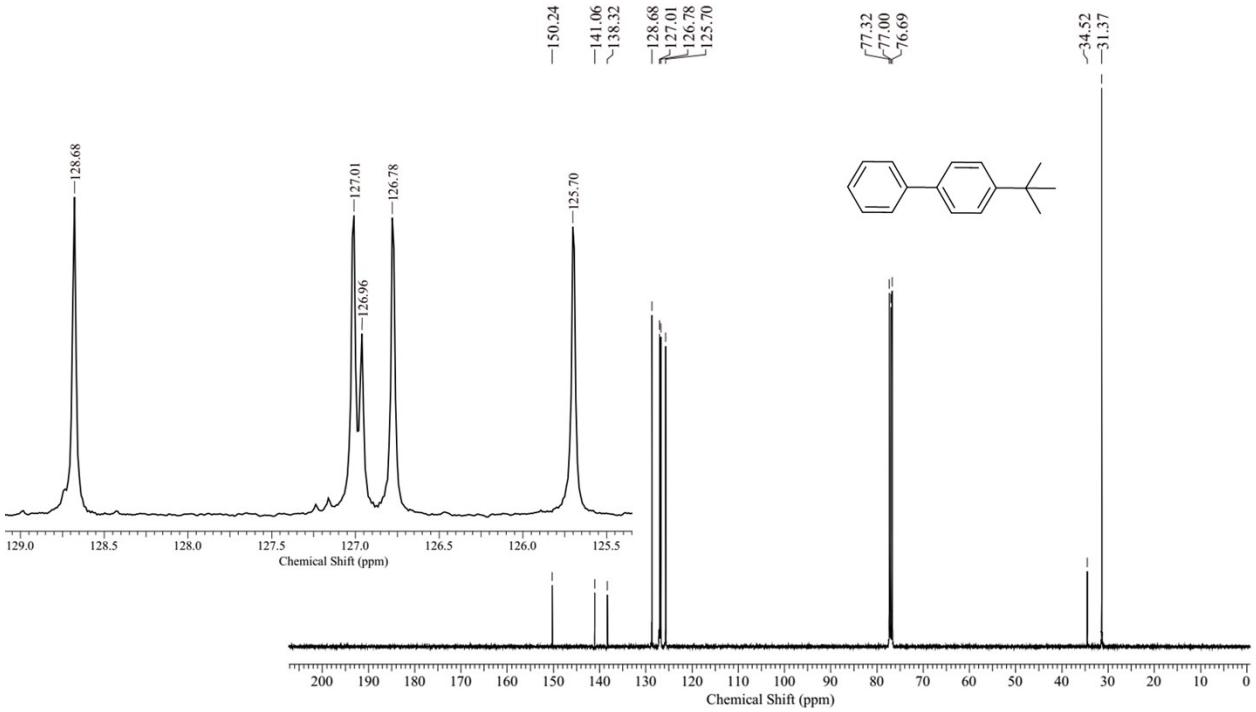



**Fig. S25** $^{13}C$ NMR spectrum of 4-t-butyl-biphenyl (**4ga**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ha** in $CDCl_3$:

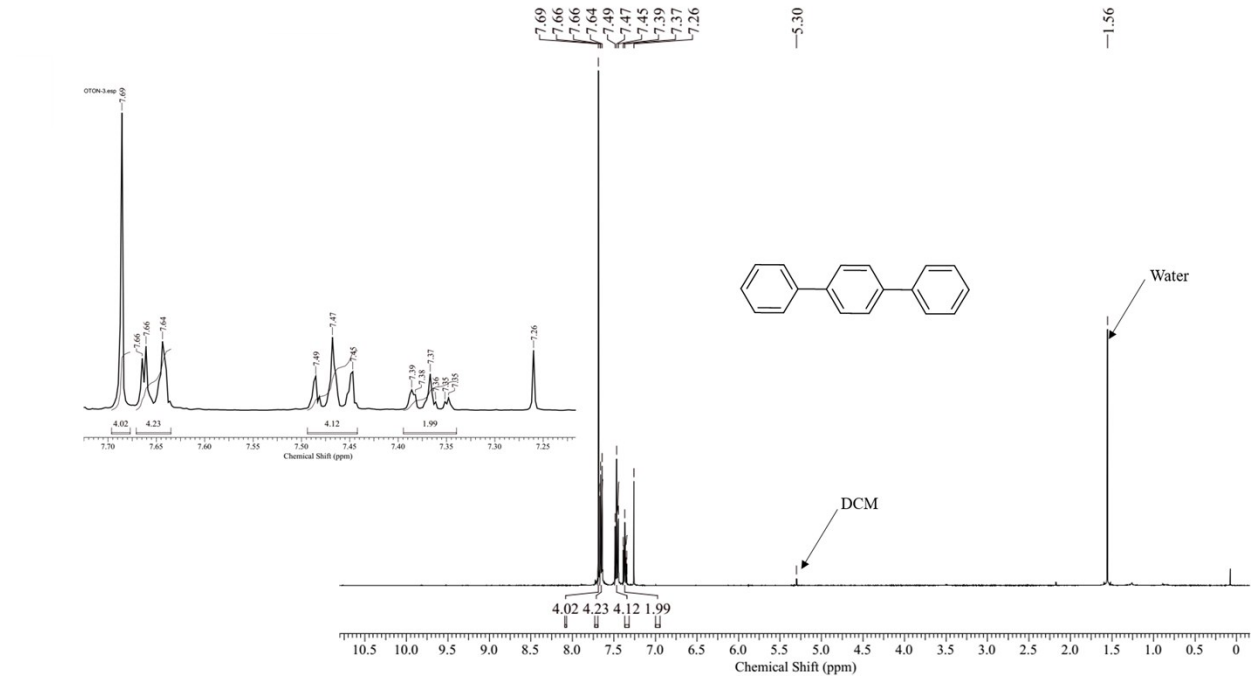



**Fig. S26** $^{1}$H NMR spectrum of terephenyl (**4ha**) in $CDCl_3$

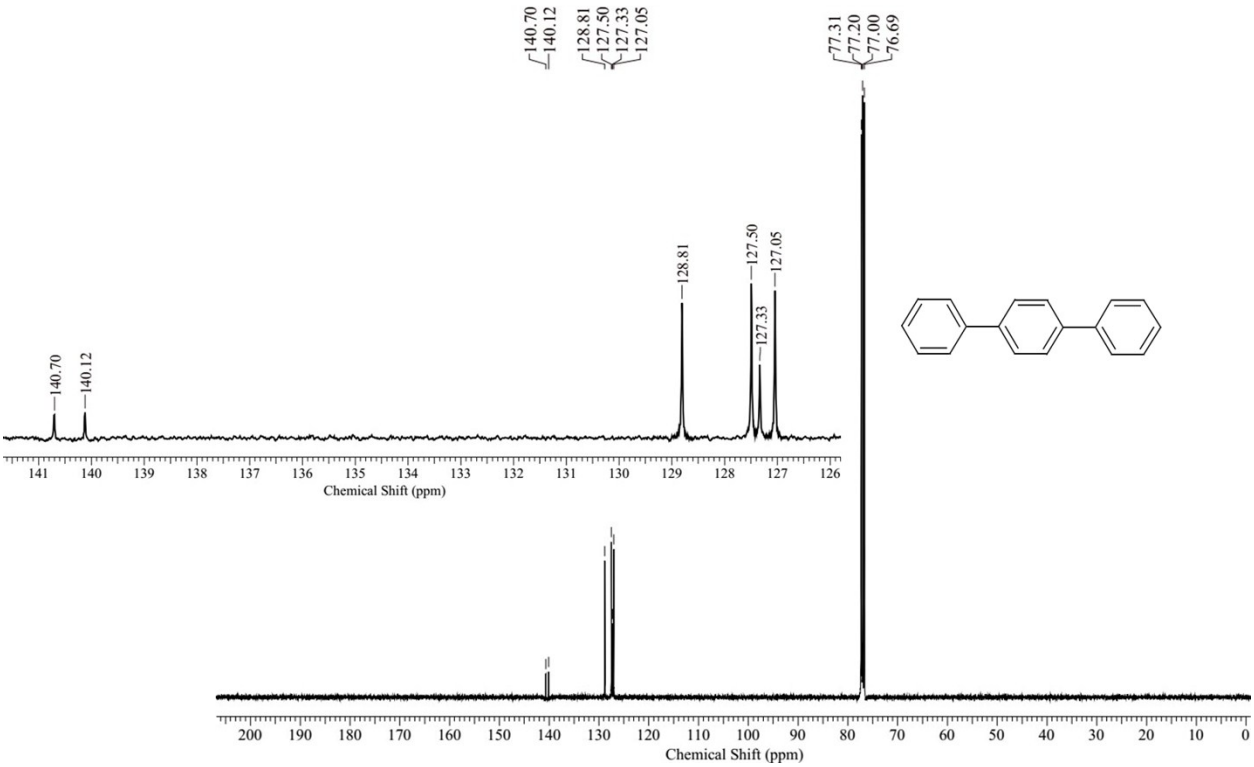



**Fig. S27** $^{13}$C NMR spectrum of terephenyl (**4ha**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ia** in $CDCl_3$:

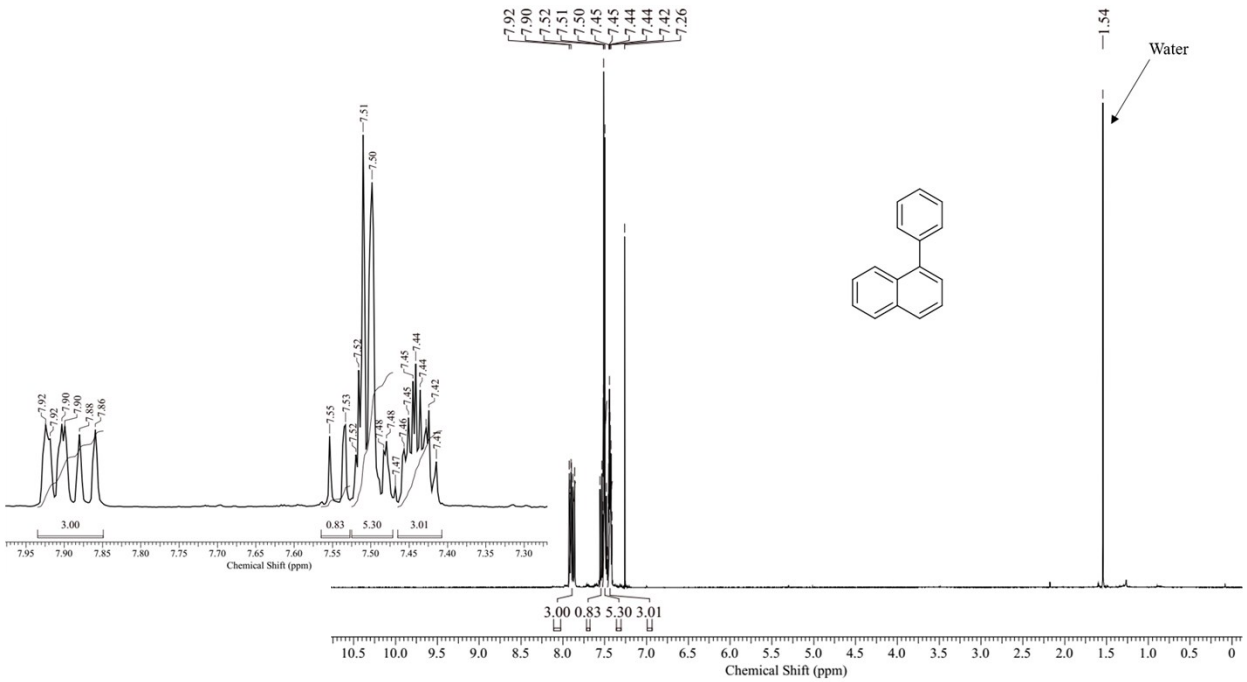



**Fig. S28** $^{1}$H NMR spectrum of 1-phenyl-naphthalene (**4ia**) in $CDCl_3$

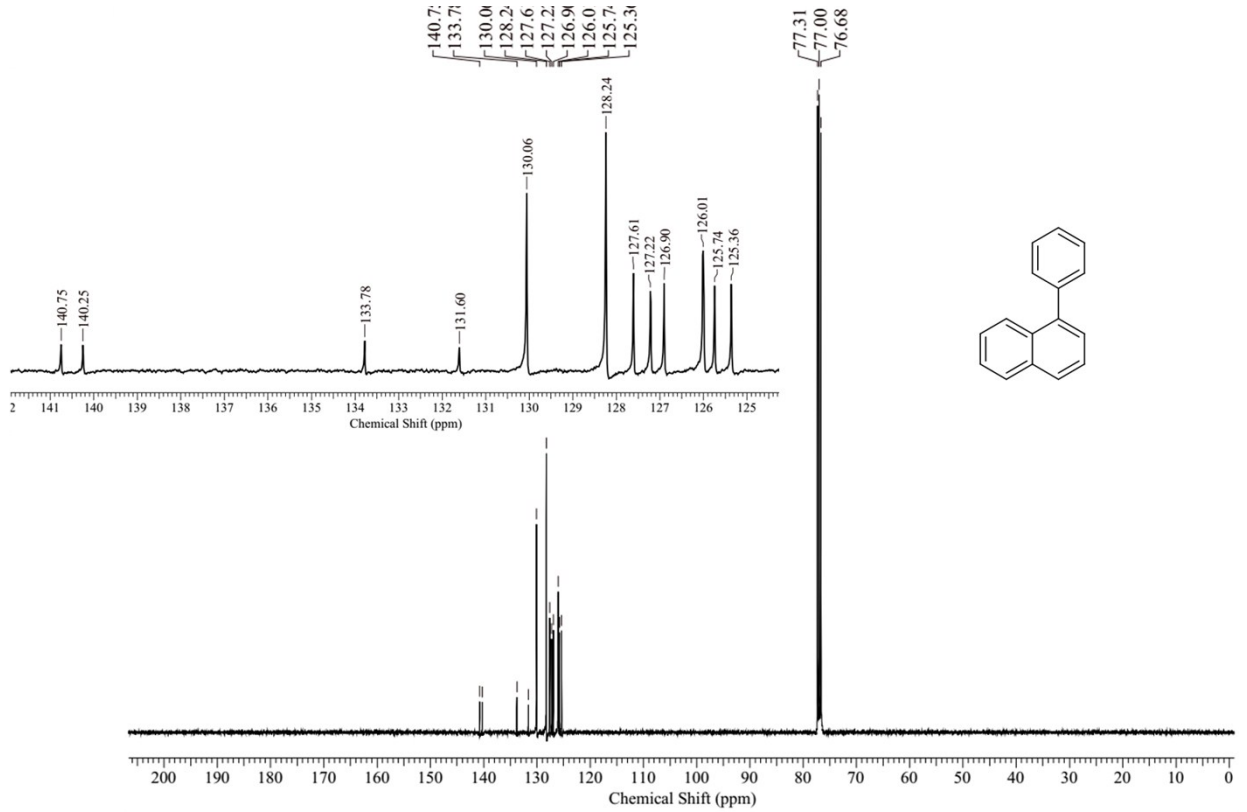



**Fig. S29** 13C NMR spectrum of 1-phenyl-naphthalene (**4ia**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ja** in $CDCl_3$:

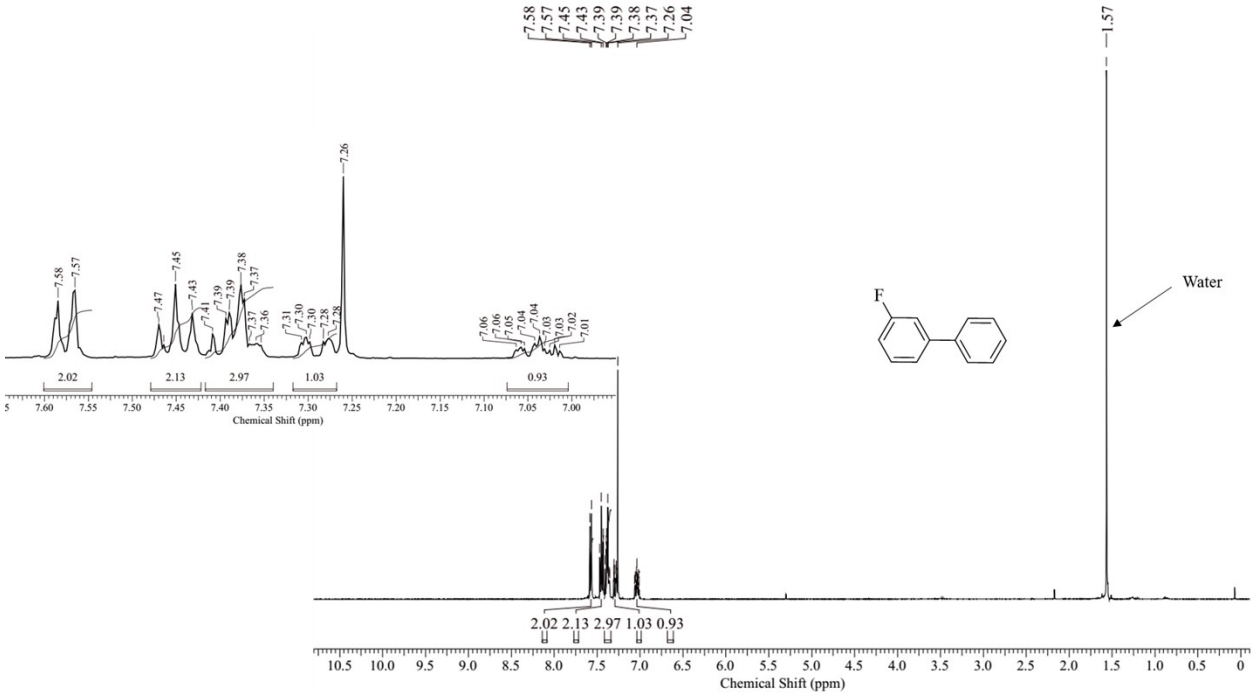



**Fig. S30** $^{1}$H NMR spectrum of 3-fluoro-biphenyl (**4ja**) in $CDCl_3$

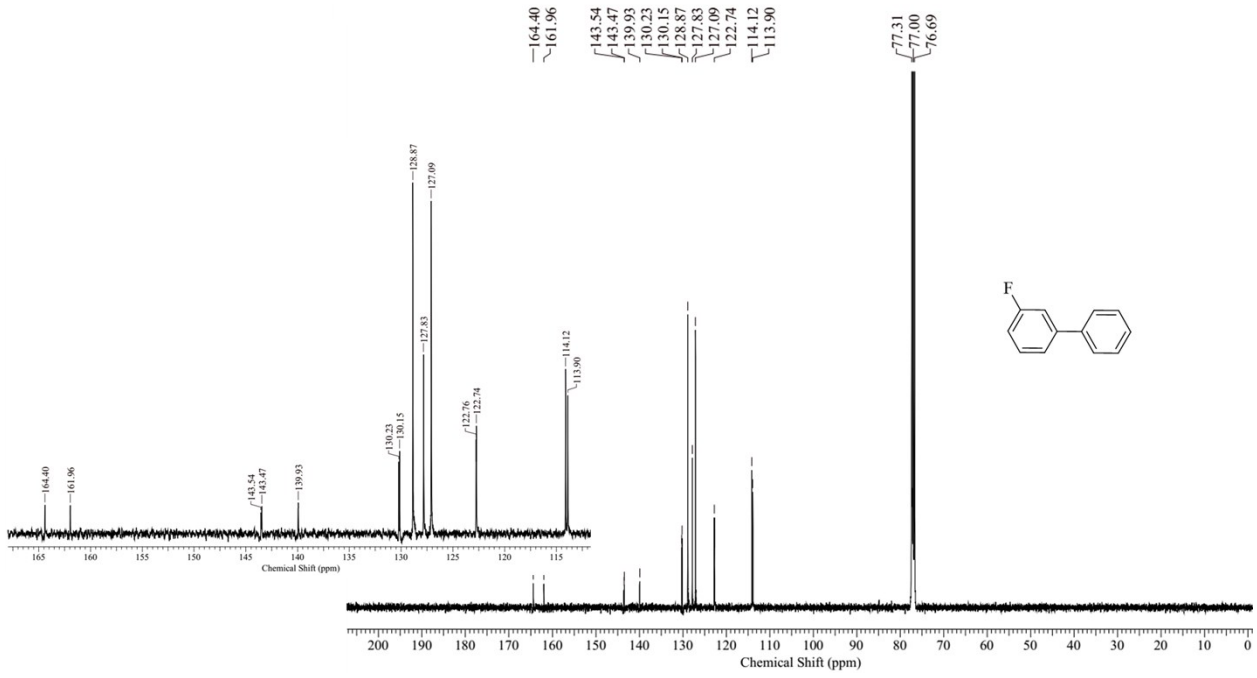



**Fig. S31** $^{13}$C NMR spectrum of 3-fluoro-biphenyl (**4ja**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4na** in $CDCl_3$:

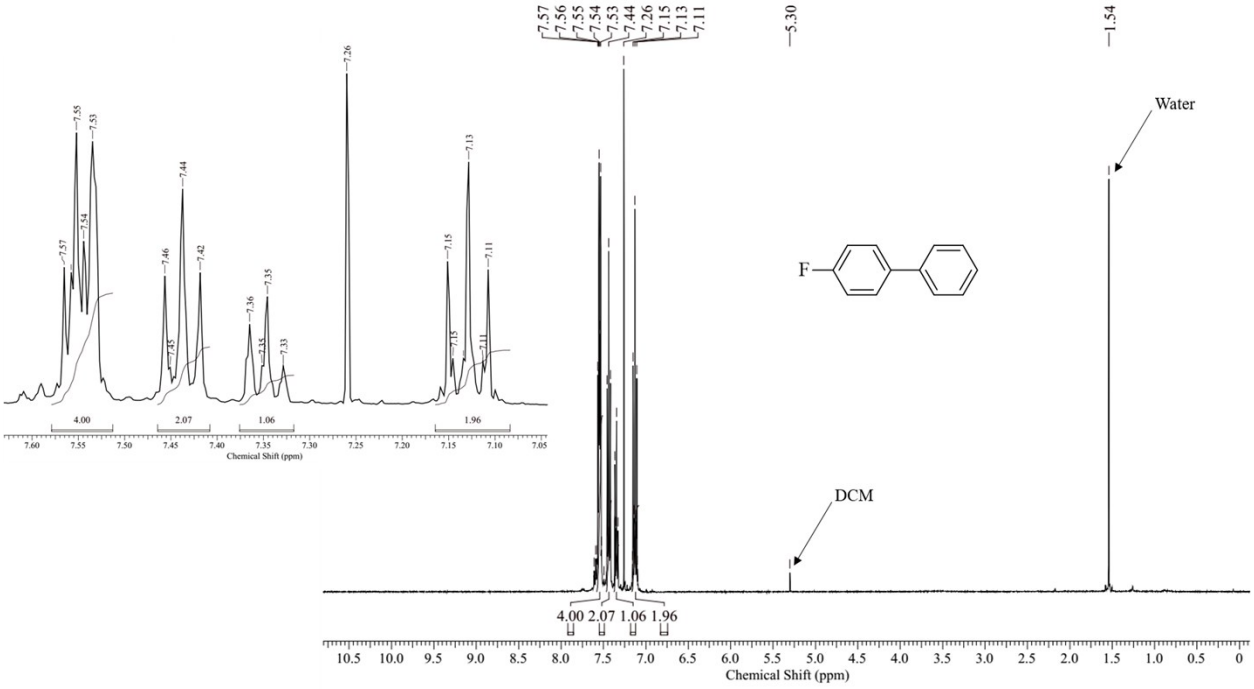



**Fig. S32** $^{1}$H NMR spectrum of 4-fluoro-biphenyl (**4na**) in $CDCl_3$

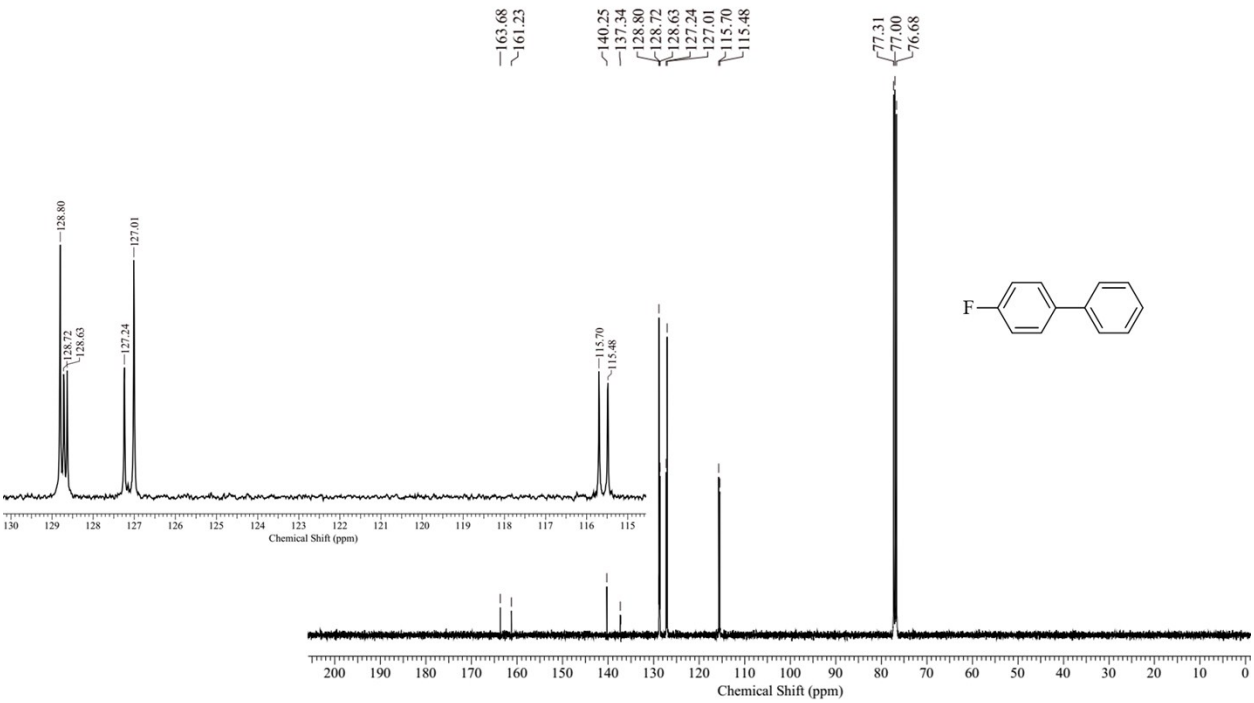



**Fig. S33** $^{13}$C NMR spectrum of 4-fluoro-biphenyl (**4na**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4oa** in $CDCl_3$:

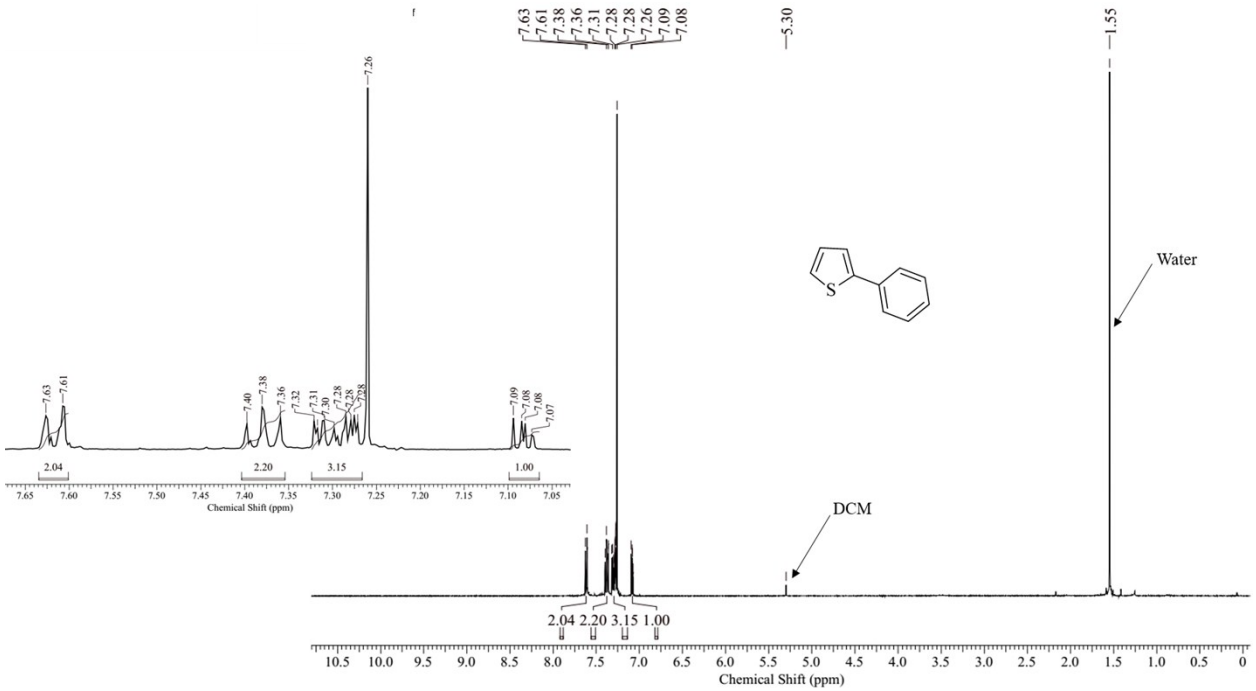



**Fig. S34** $^{1}$H NMR spectrum of 2-phenyl-thiophene (**4oa**) in $CDCl_3$

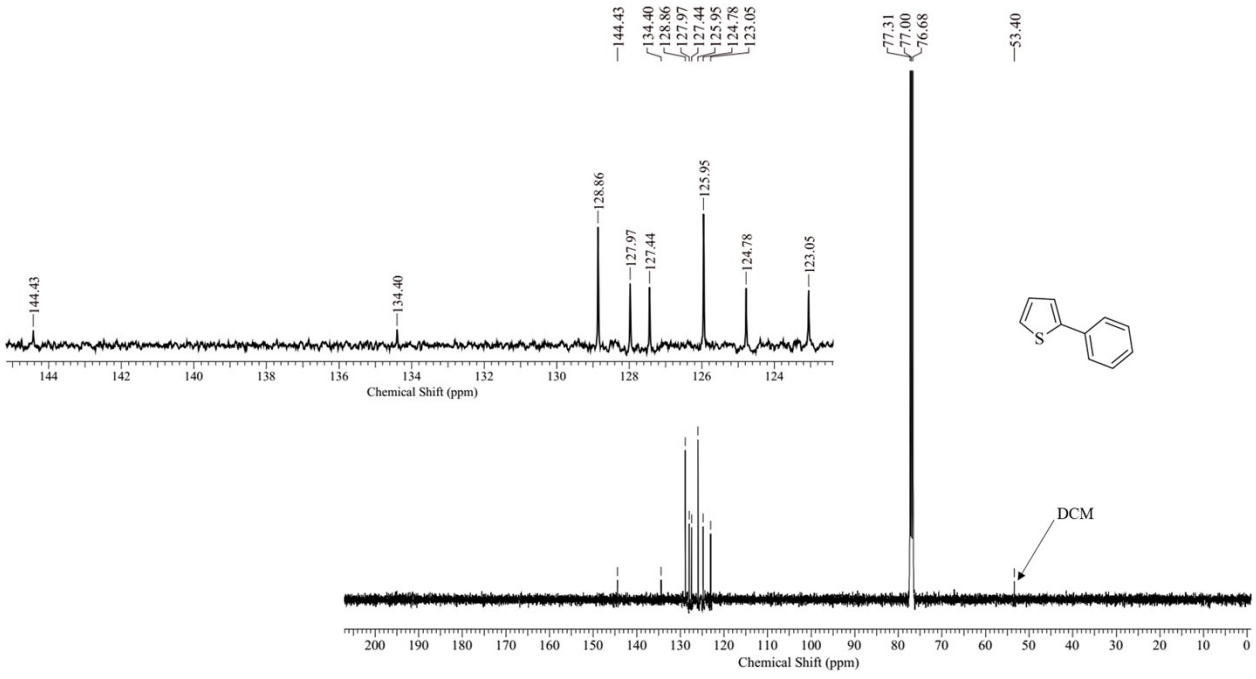



**Fig. S35** $^{13}$C NMR spectrum of 2-phenyl-thiophene (**4oa**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4pa** in $CDCl_3$:

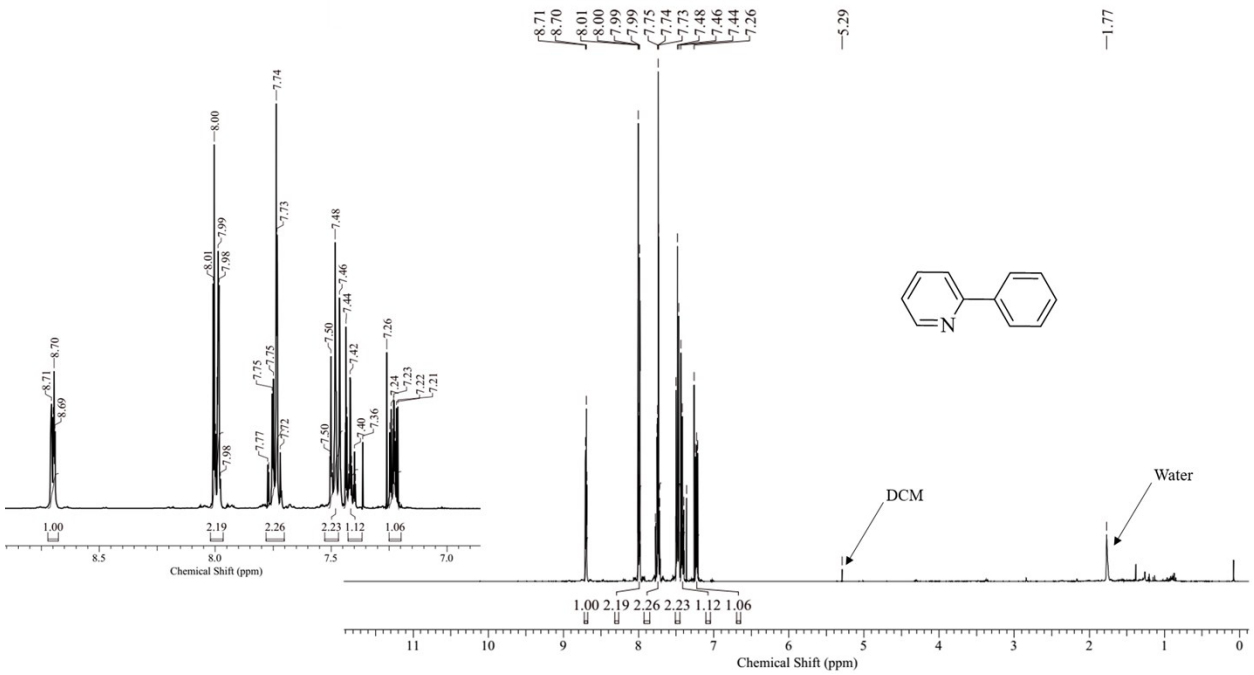



**Fig. S36** $^{1}$H NMR spectrum of 2-phenyl-pyridine (**4pa**) in $CDCl_3$

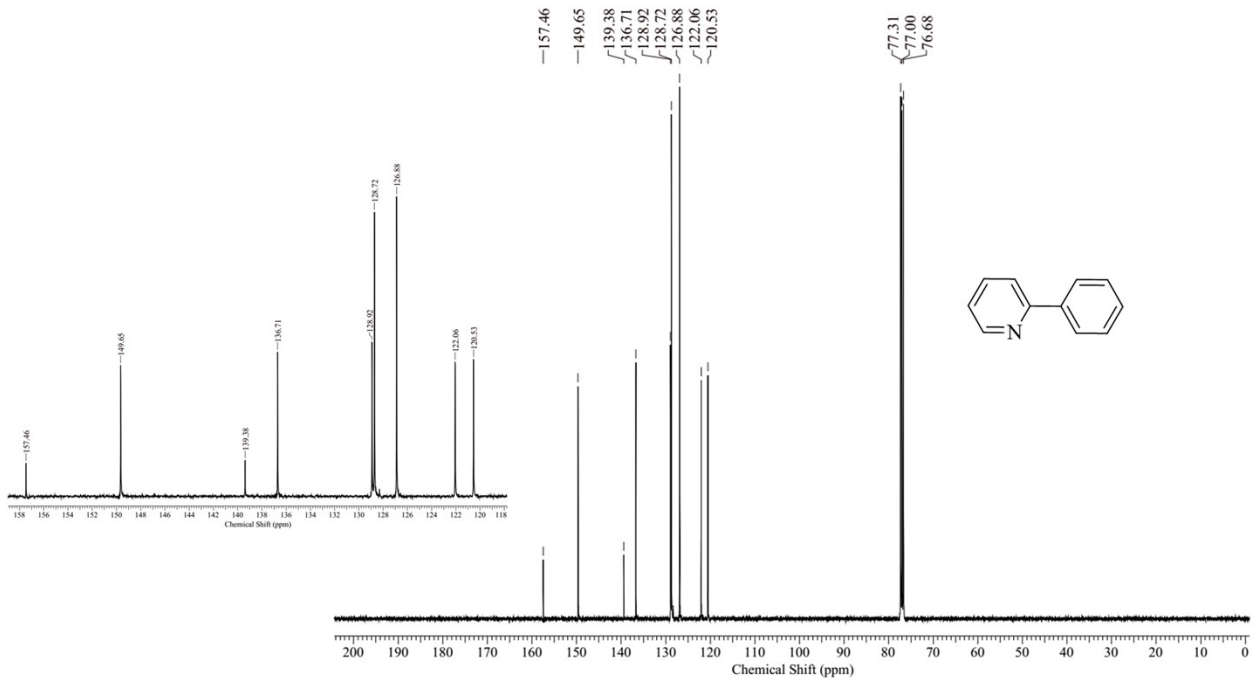



**Fig. S37** $^{13}$C NMR spectrum of 2-phenyl-pyridine (**4pa**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ra** in $CDCl_3$:

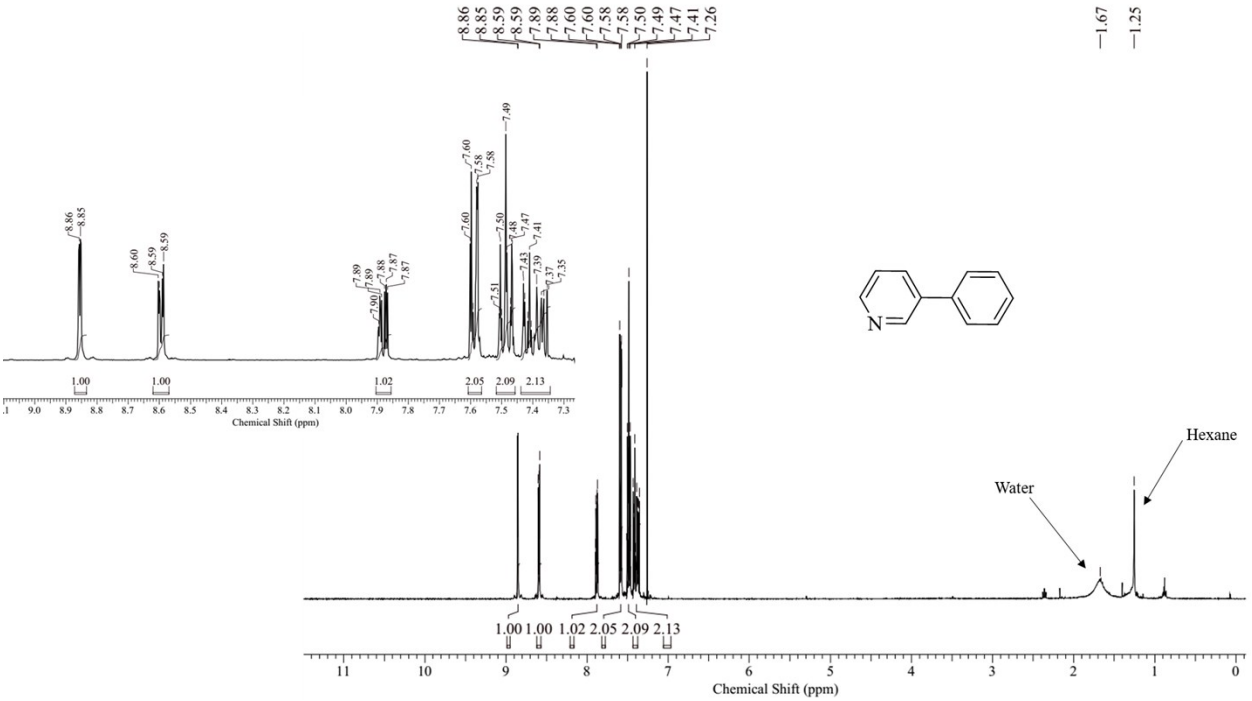



**Fig. S38** $^{1}$H NMR spectrum of 3-phenyl-pyridine (**4ra**) in $CDCl_3$

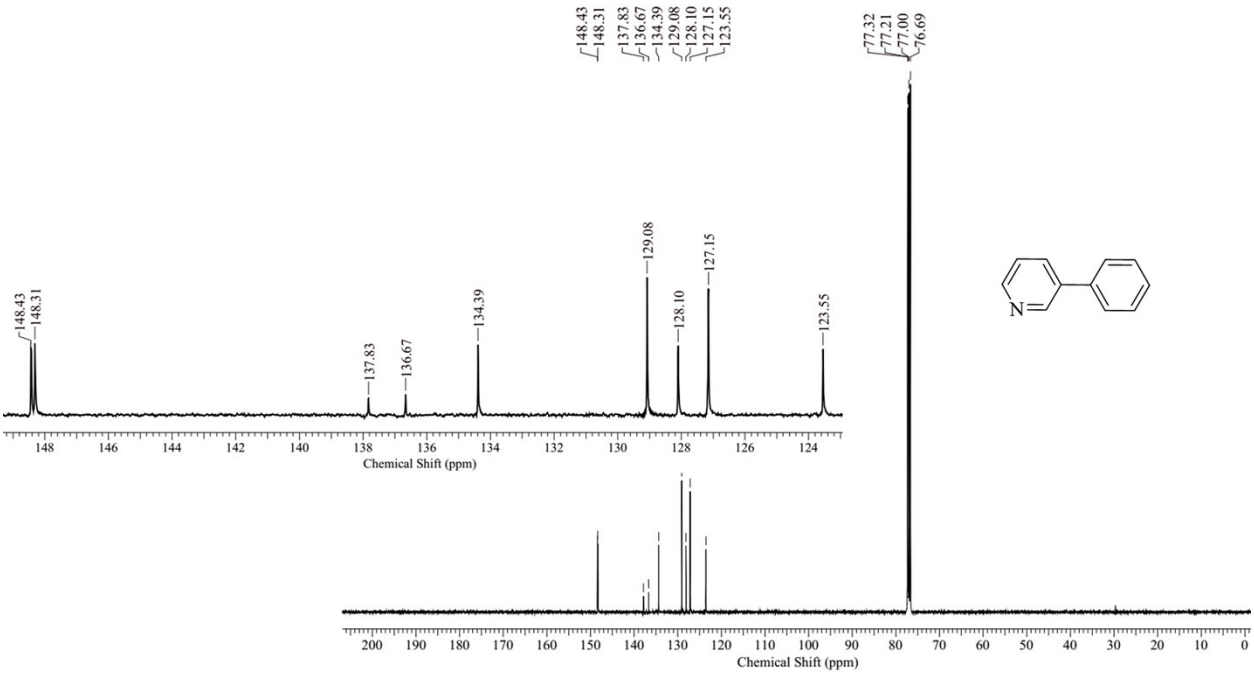



**Fig. S39** $^{13}$C NMR spectrum of 3-phenyl-pyridine (**4ra**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4sa** in $CDCl_3$:

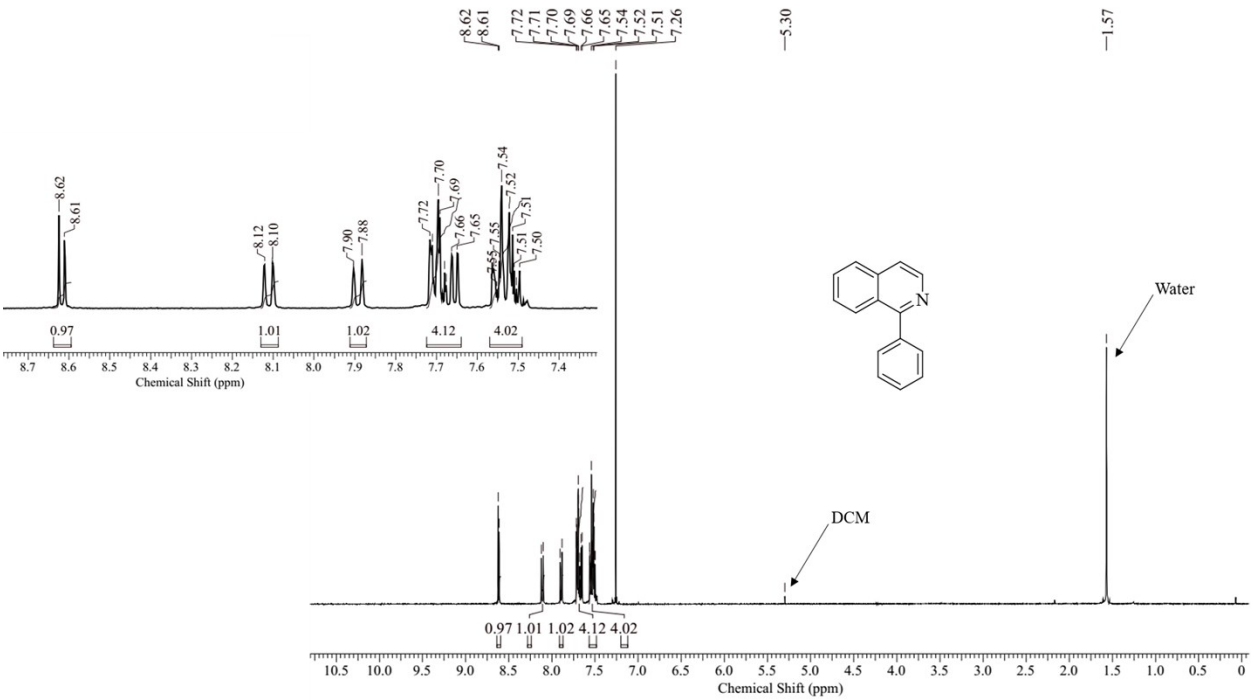



**Fig. S40** $^{1}$H NMR spectrum of 1-phenyl-isoquinoline (**4sa**) in $CDCl_3$

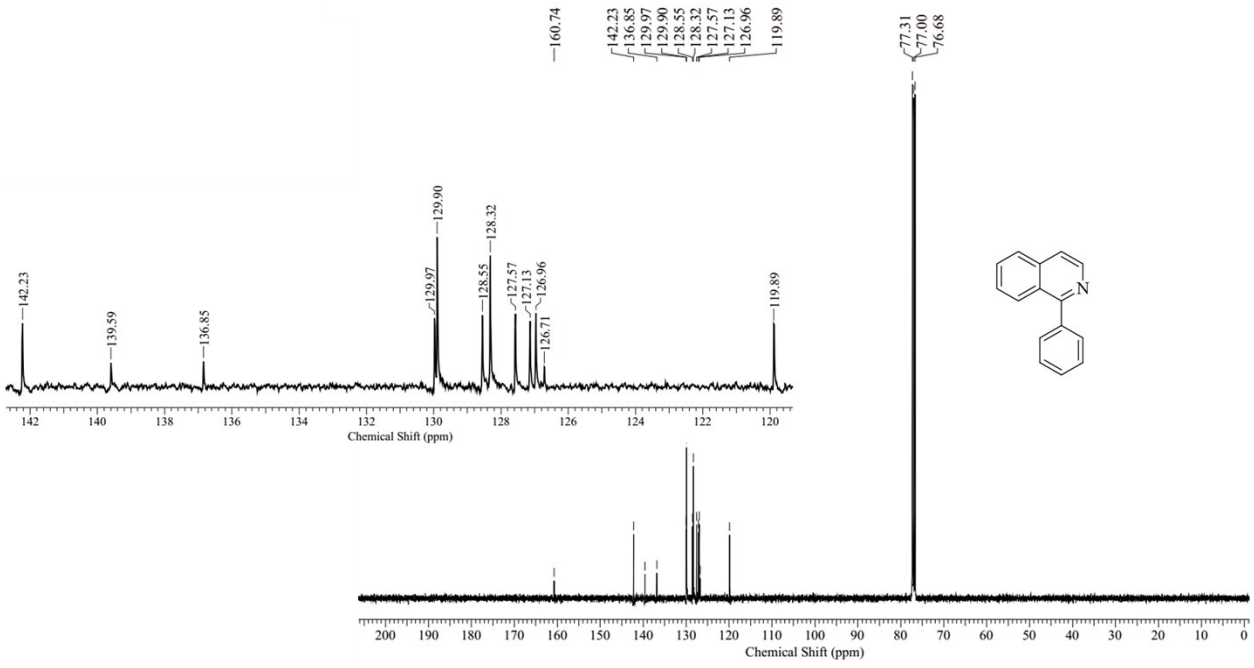



**Fig. S41** $^{13}$C NMR spectrum of 1-phenyl-isoquinoline (**4sa**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ab** in $CDCl_3$:

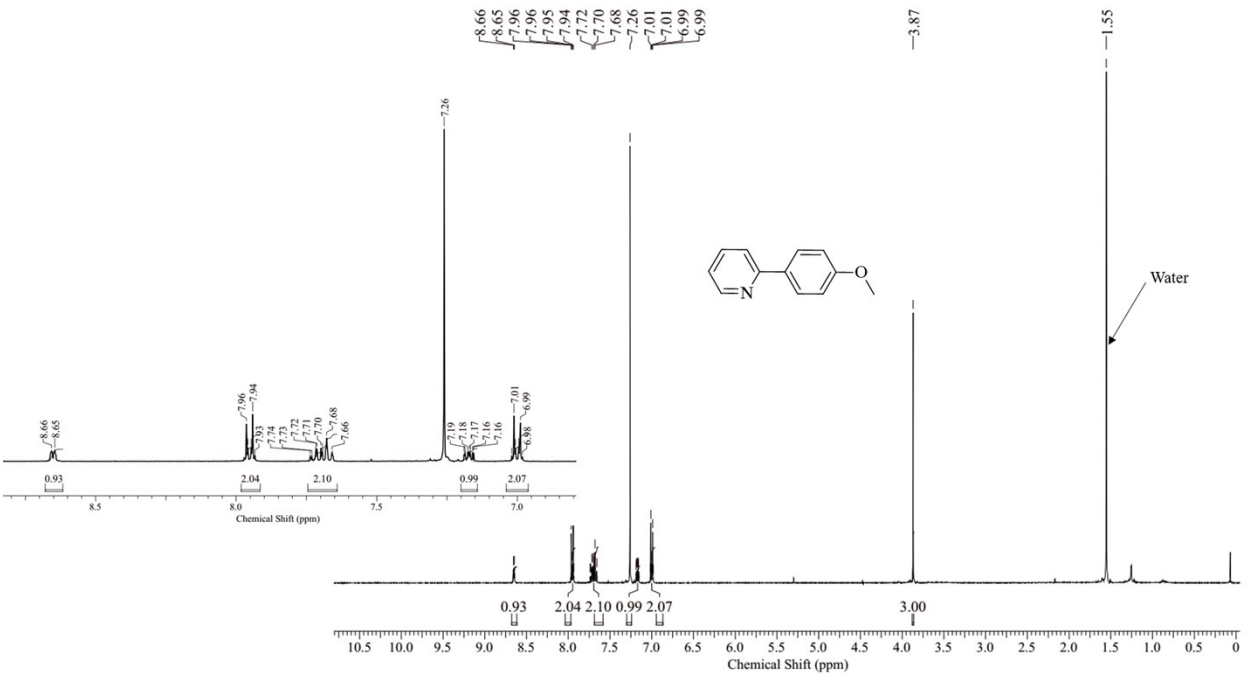



**Fig. S42** $^{1}$H NMR spectrum of 2-(4-methoxyphenyl)-pyridine (**4ab**) in $CDCl_3$

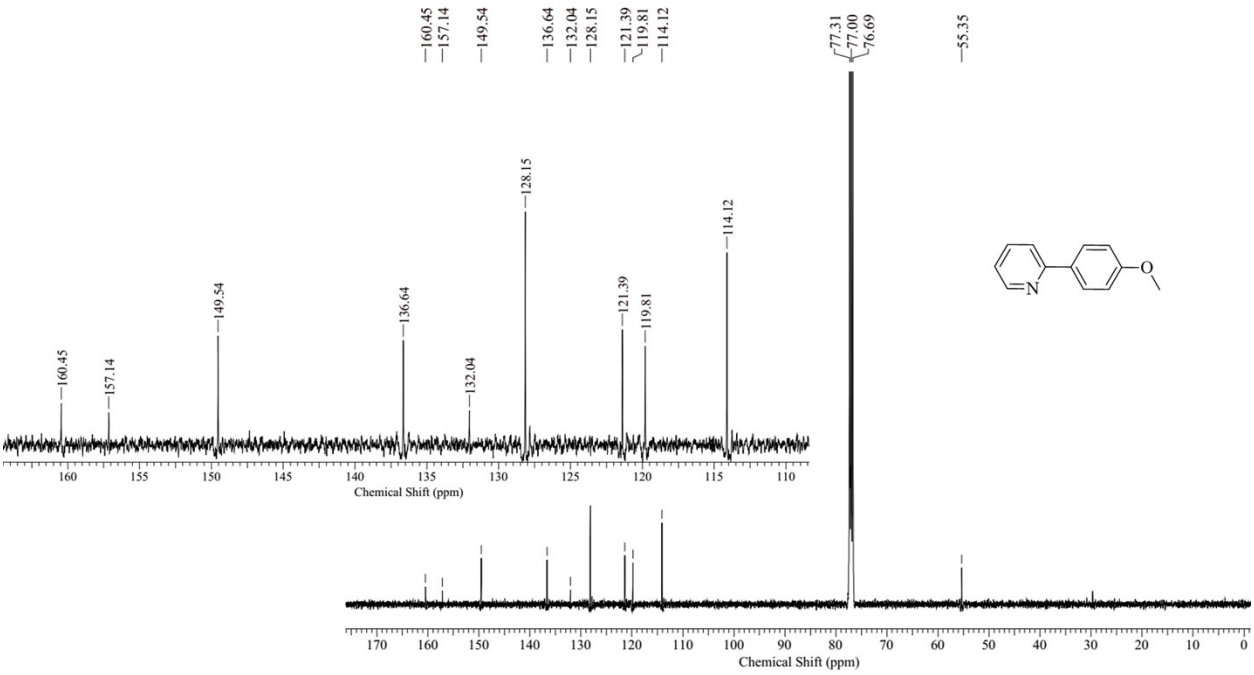



**Fig. S43** $^{13}$C NMR spectrum of 2-(4-methoxyphenyl)-pyridine (**4ab**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ac** in $CDCl_3$:

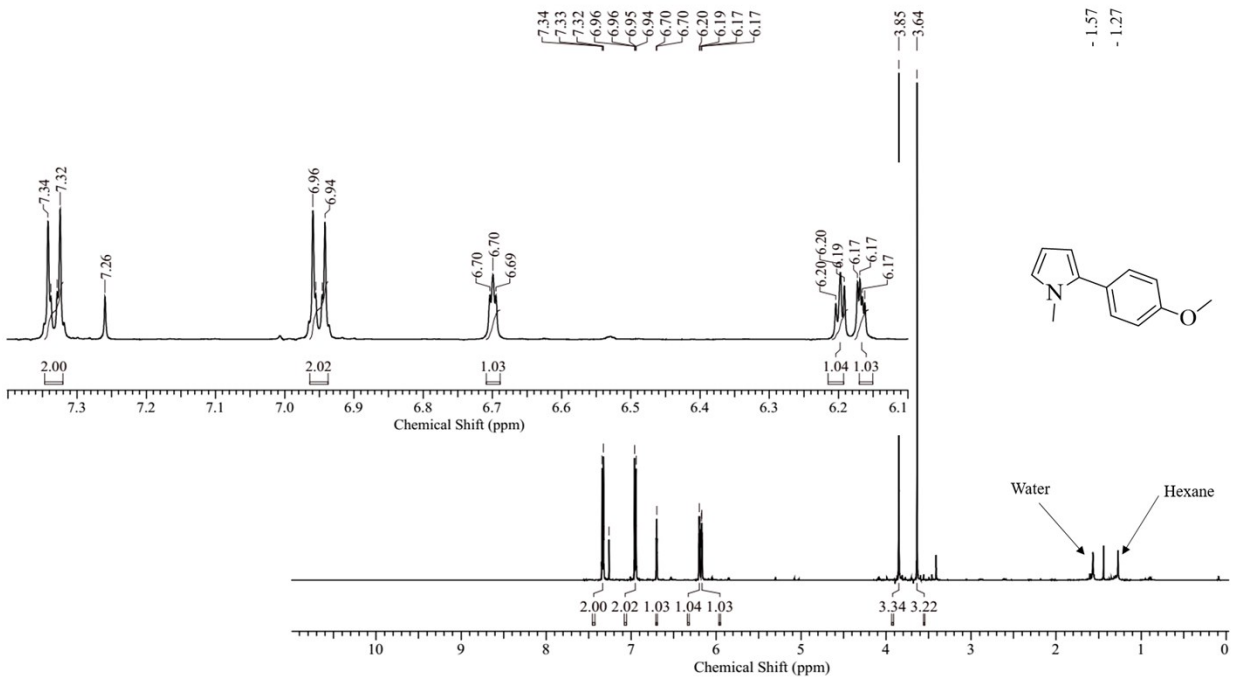



**Fig. S44** $^{1}$H NMR spectrum of 1-methyl-2-(4-anisyl)-pyrrole (**4ac**) in $CDCl_3$

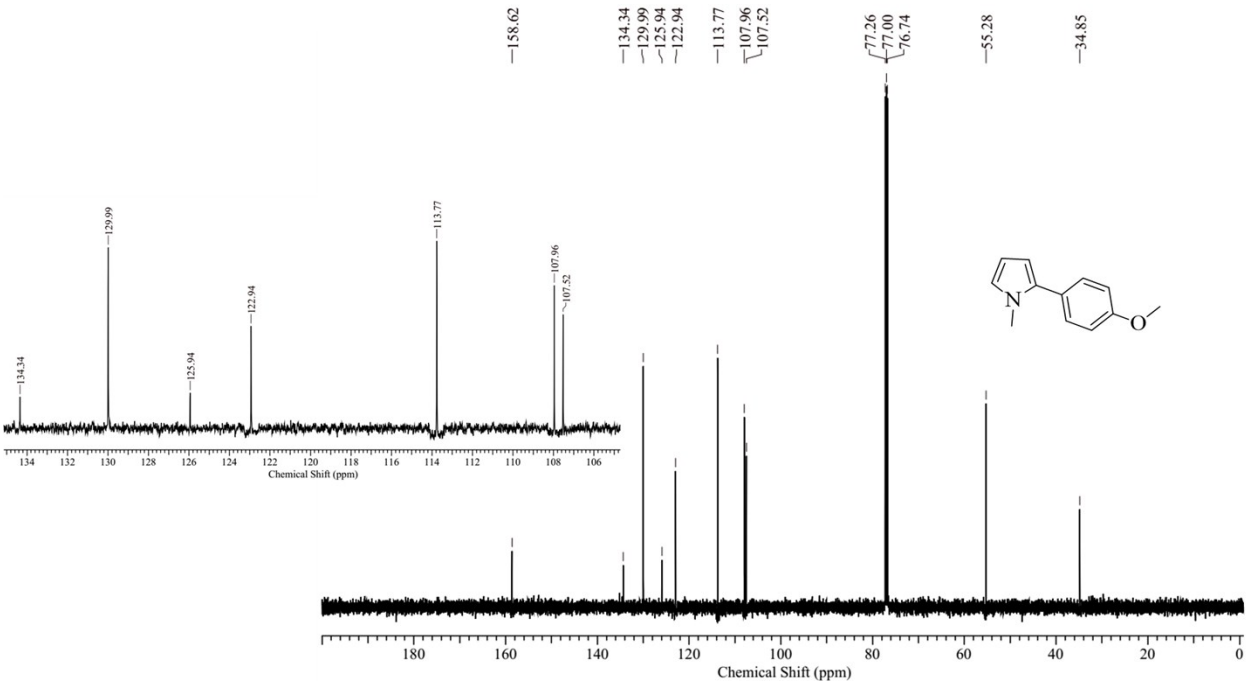



**Fig. S45** $^{13}$C NMR spectrum of 1-methyl-2-(4-anisyl)-pyrrole (**4ac**) in $CDCl_3$

$^{1}H$ NMR and $^{13}C$ NMR spectra of **4ad** in $CDCl_3$:

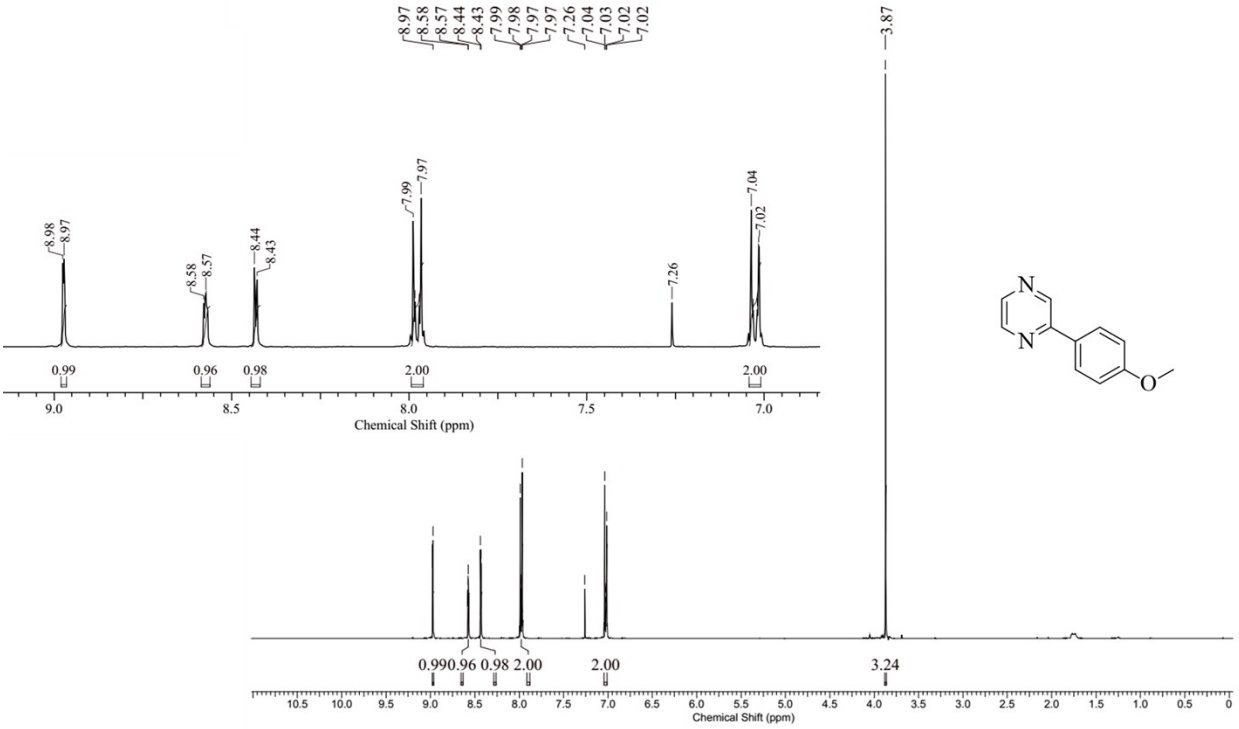



**Fig. S46** $^{1}H$ NMR spectrum of 2-(4-Methoxyphenyl)-pyrazine (**4ad**) in $CDCl_3$

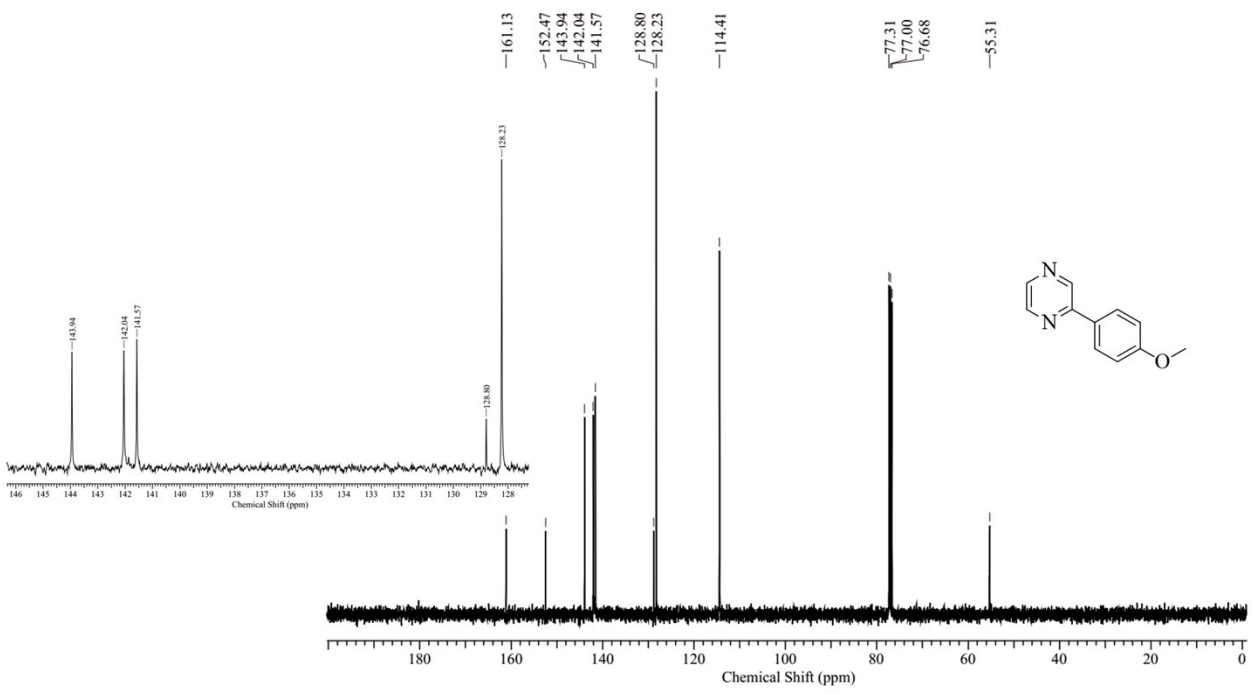



**Fig. S47** 13C NMR spectrum of 2-(4-Methoxyphenyl)-pyrazine (**4ad**) in CDCl3

$^{1}$H NMR and $^{13}$C NMR spectra of **4bd** in $CDCl_3$:

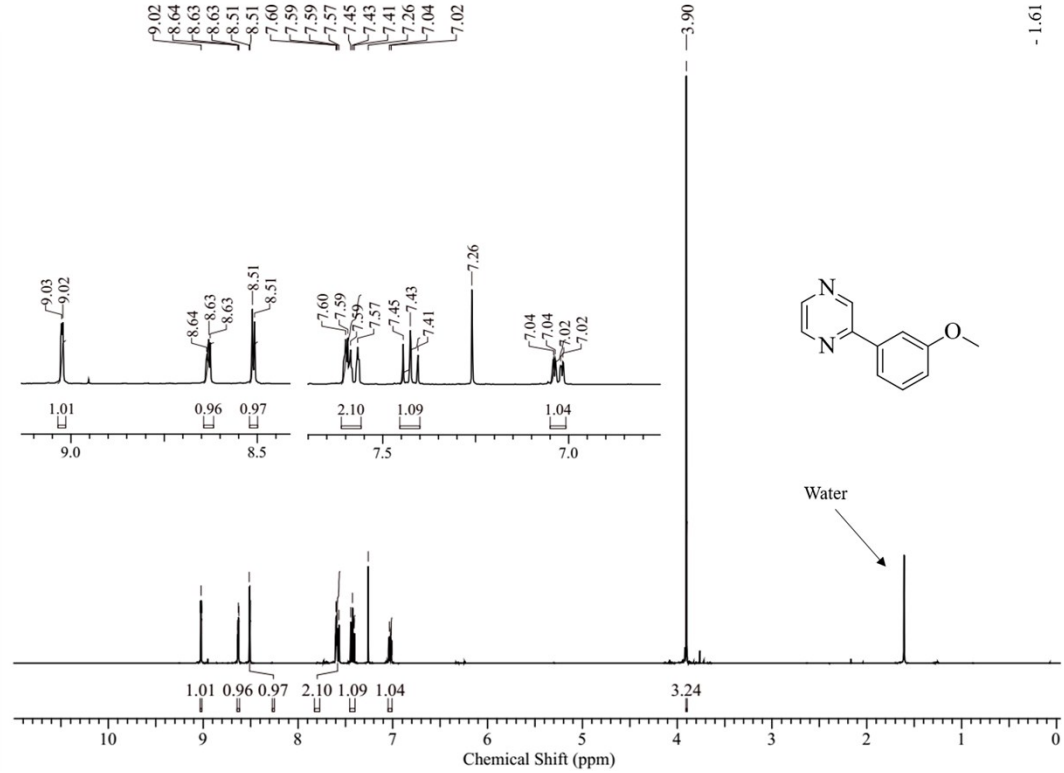



**Fig. S48** $^{1}$H NMR spectrum of 2-(3-Methoxyphenyl)-pyrazine (**4bd**) in $CDCl_3$

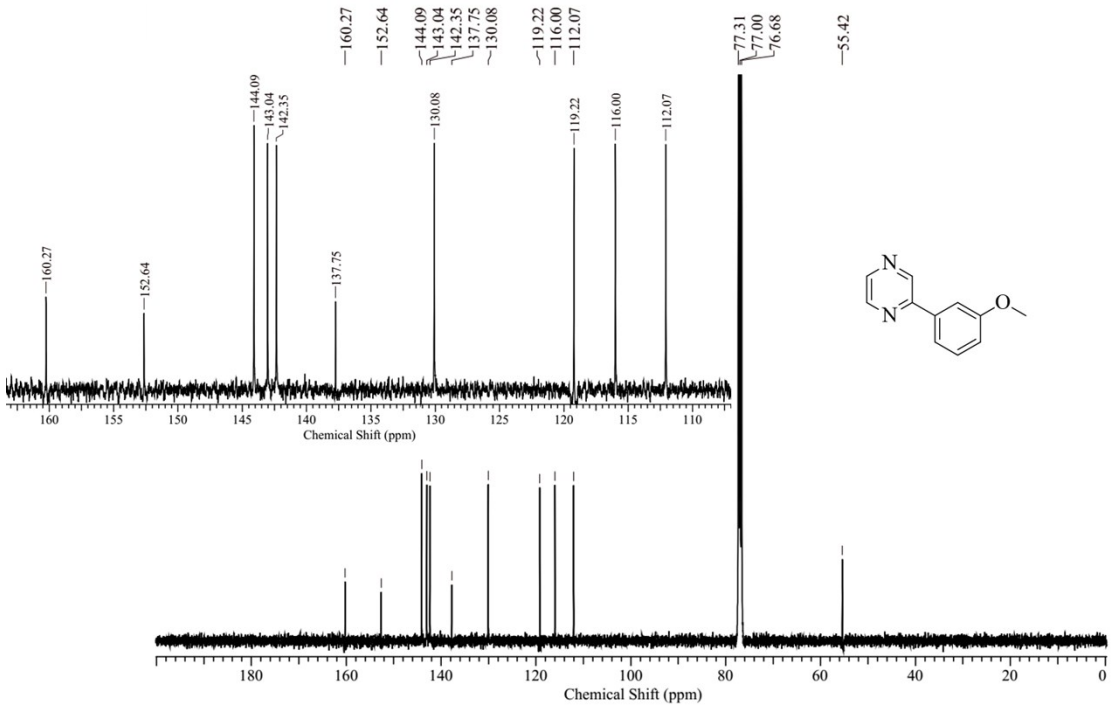



**Fig. S49** $^{13}$C NMR spectrum of 2-(3-Methoxyphenyl)-pyrazine (**4bd**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4dd** in $CDCl_3$:

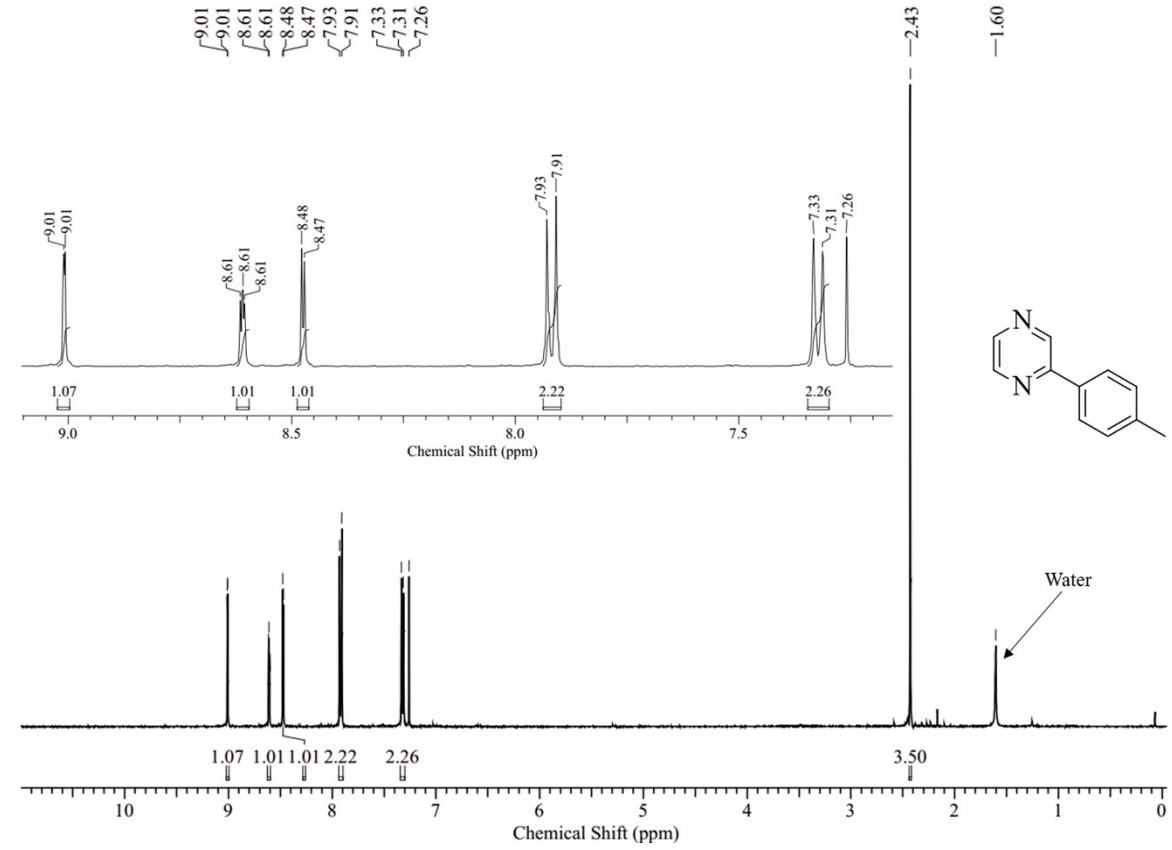



**Fig. S50** $^{1}$H NMR spectrum of 2-(p-Tolyl)-pyrazine (**4dd**) in $CDCl_3$

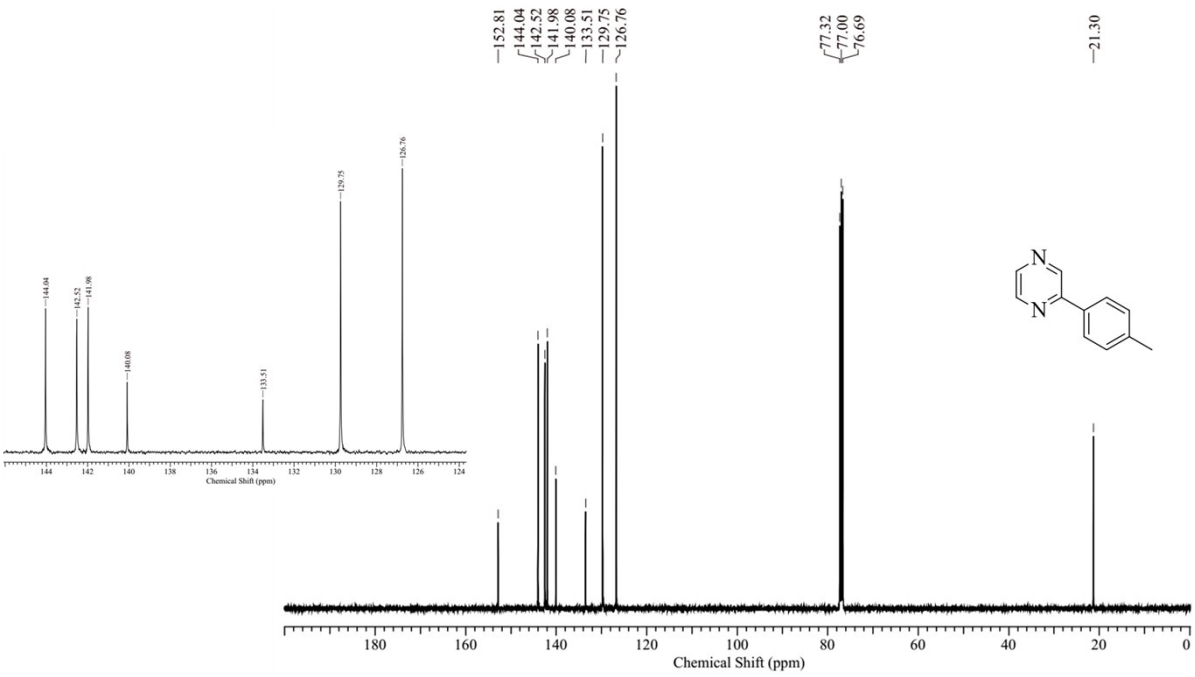



**Fig. S51** $^{13}$C NMR spectrum of 2-(p-Tolyl)-pyrazine (**4dd**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4fd** in $CDCl_3$:

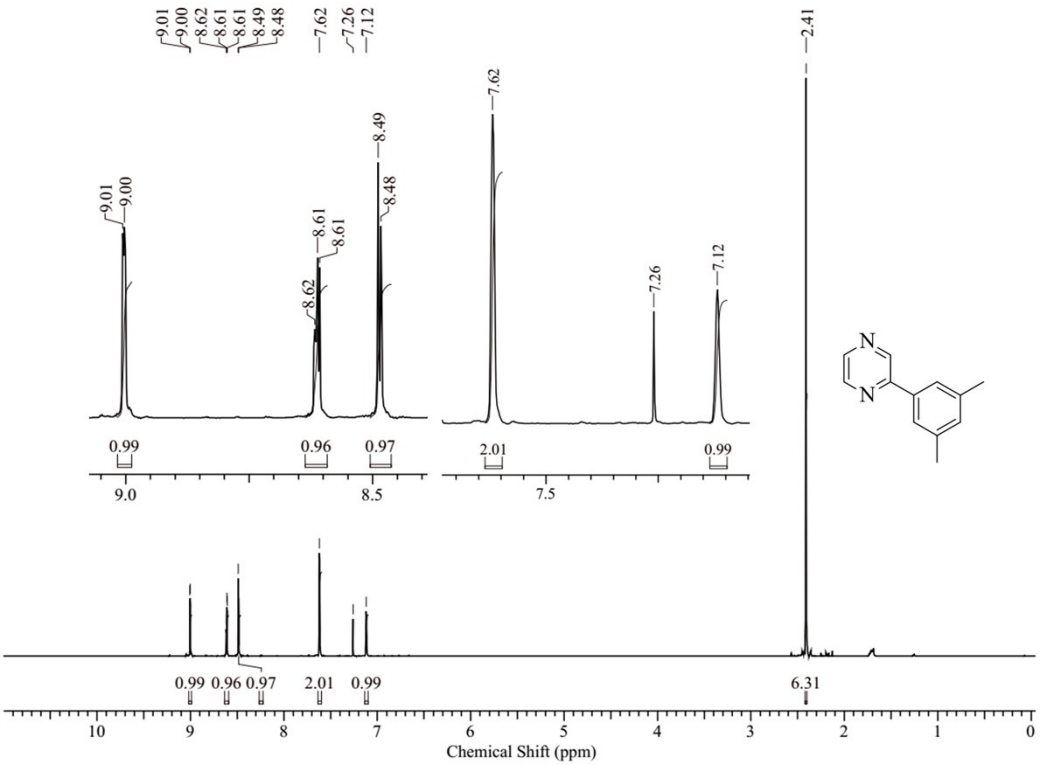



**Fig. S52** $^{1}$H NMR spectrum of 2-(3,5-Dimethylphenyl)-pyrazine (**4fd**) in $CDCl_3$

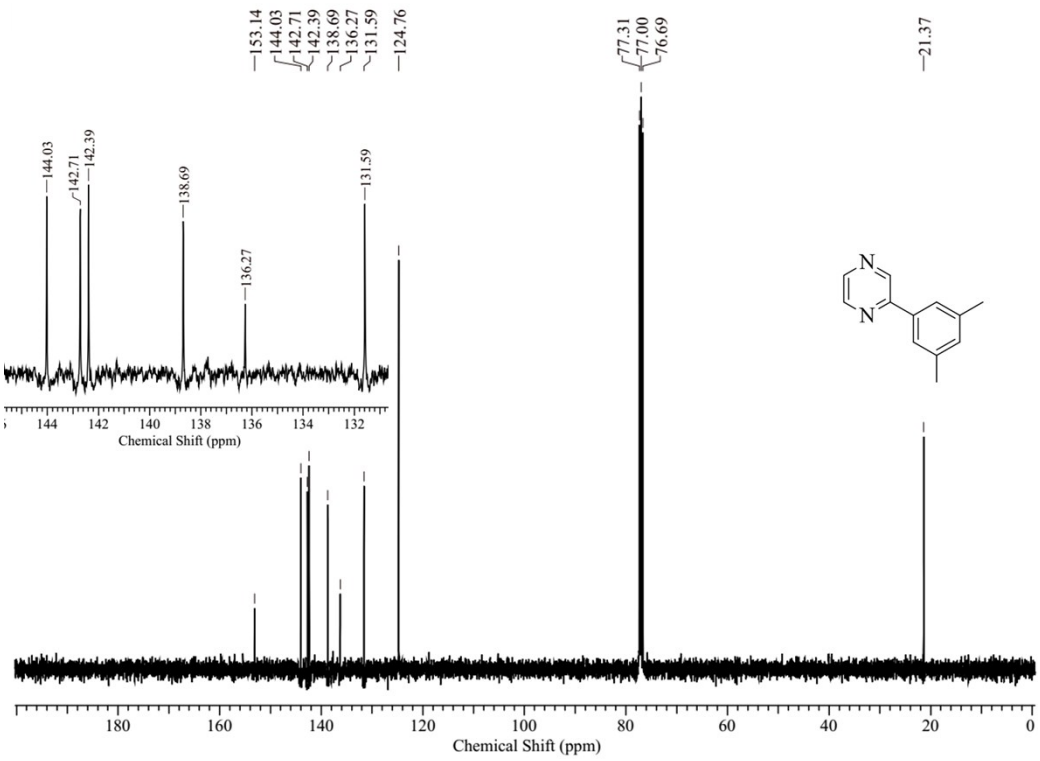



**Fig. S53** $^{13}$C NMR spectrum of 2-(3,5-Dimethylphenyl)-pyrazine (**4fd**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4gd** in $CDCl_3$:

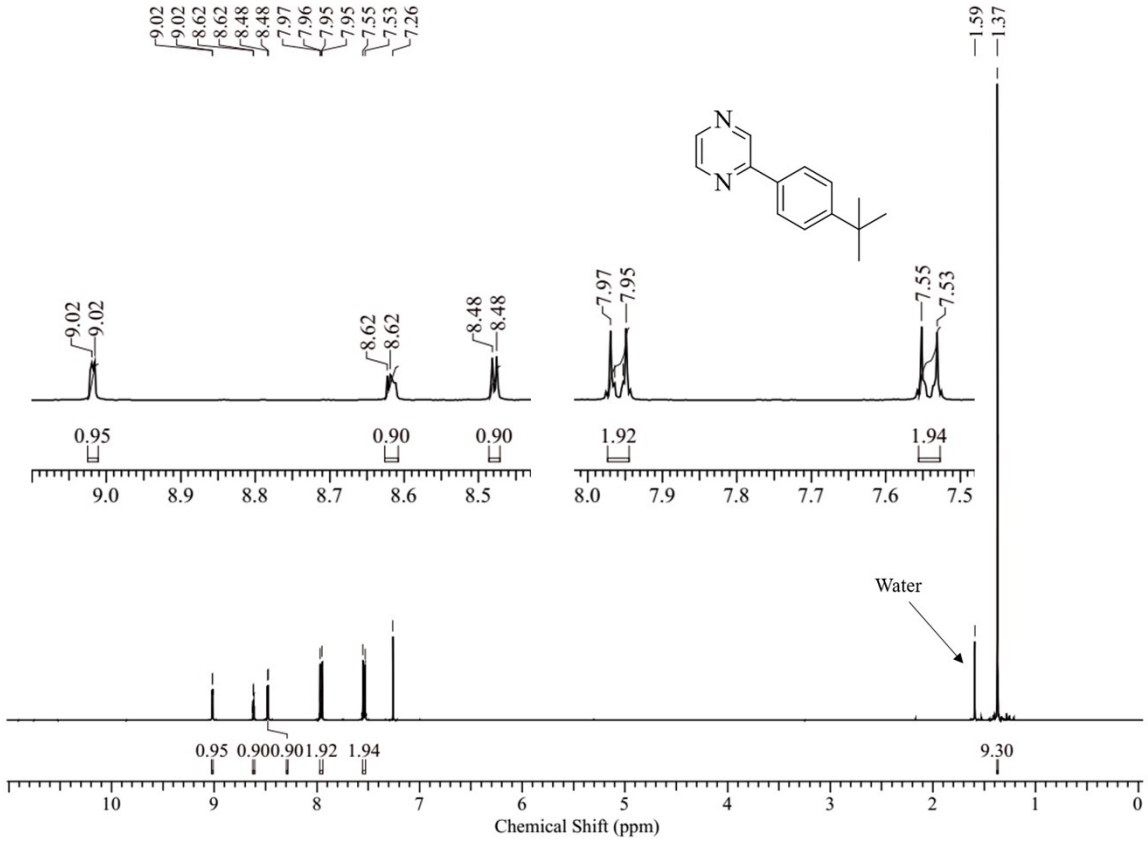



**Fig. S54** $^{1}$H NMR spectrum of 2-(4-(tert-butyl)phenyl)-pyrazine (**4gd**) in $CDCl_3$

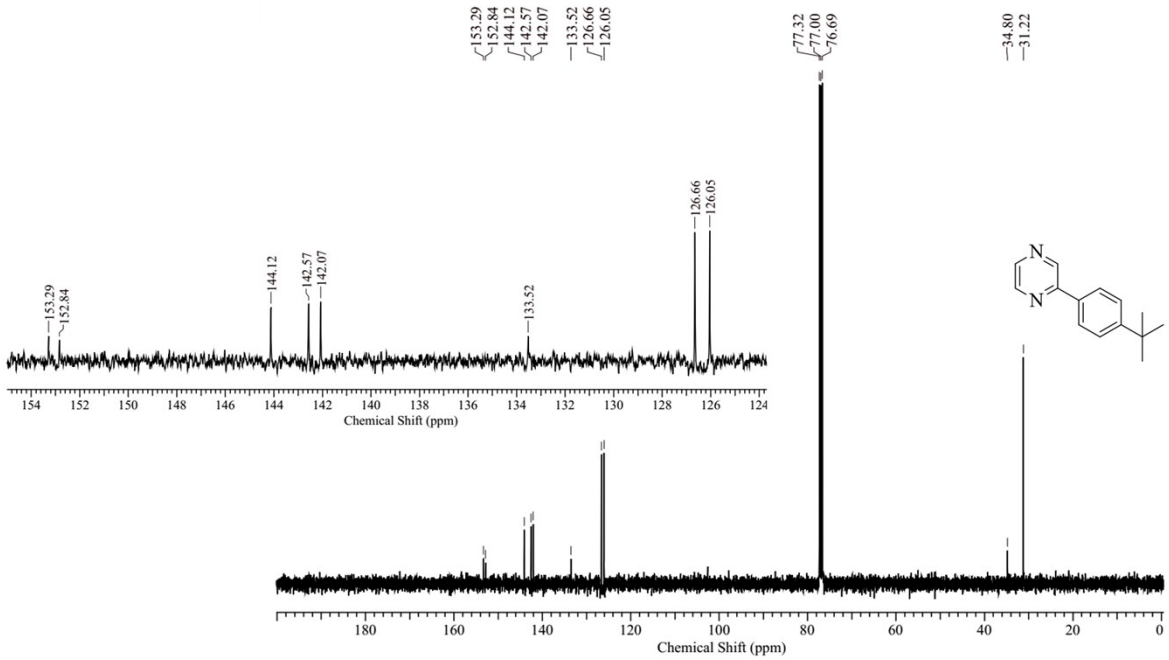



**Fig. S55** $^{13}$C NMR spectrum of 2-(4-(tert-butyl)phenyl)-pyrazine (**4gd**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4ae+4ae'** in $CDCl_3$:

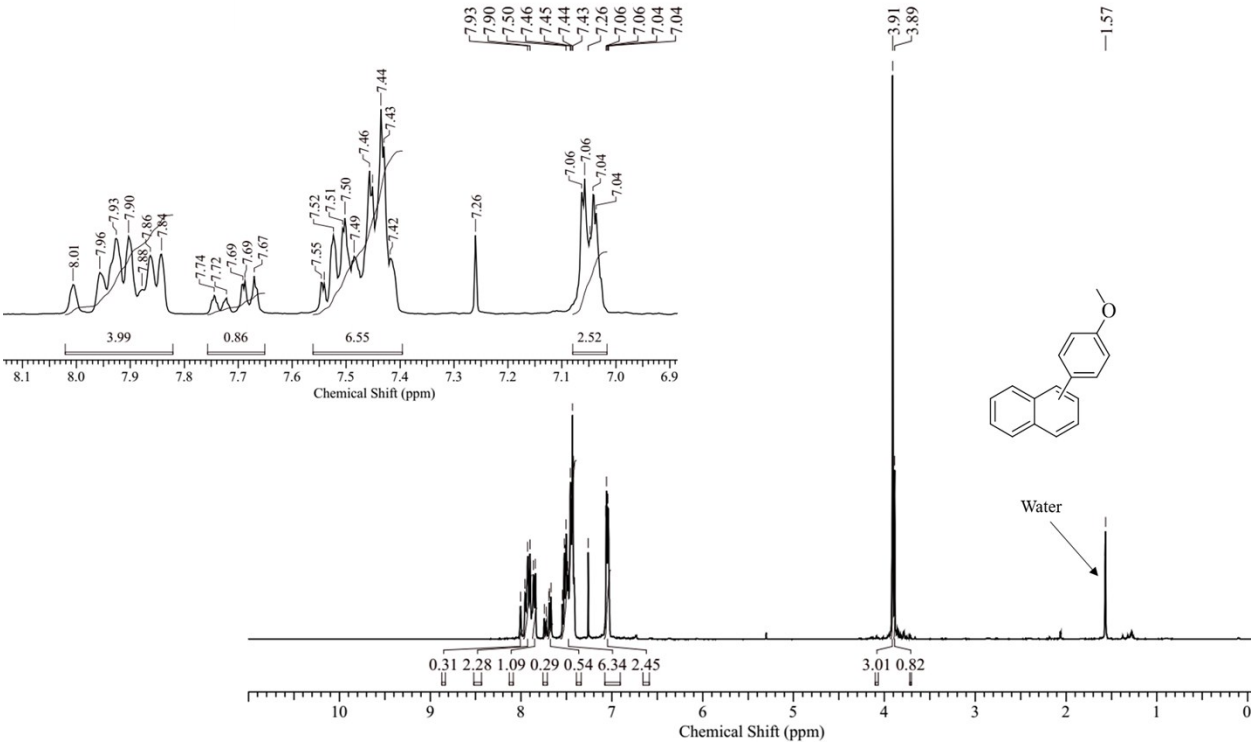



**Fig. S56** $^{1}$H NMR spectrum of mixture of 1-(4-anisyl)-naphthalene, 2-(4-anisyl)-naphthalene (**4ae+4ae'**) in $CDCl_3$

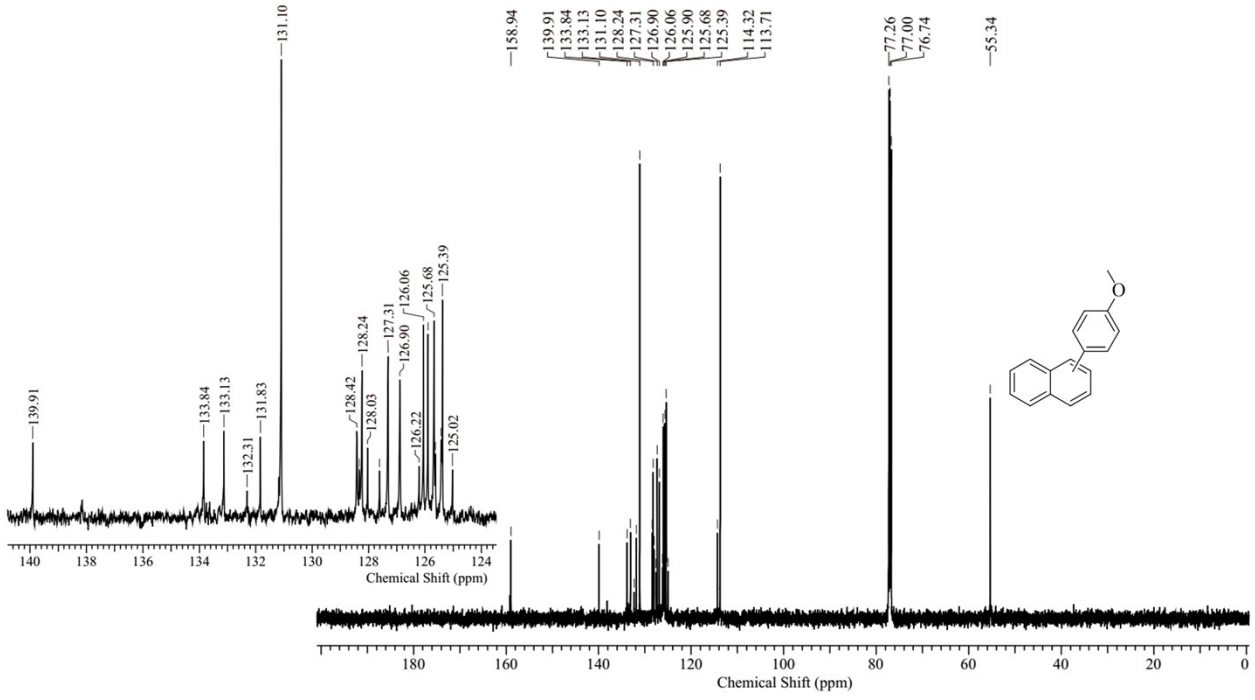



**Fig. S57** $^{13}$C NMR spectrum of mixture of 1-(4-anisyl)-naphthalene, 2-(4-anisyl)-naphthalene (**4ae+4ae'**) in $CDCl_3$

$^{1}$H NMR and $^{13}$C NMR spectra of **4td** in $CDCl_3$:

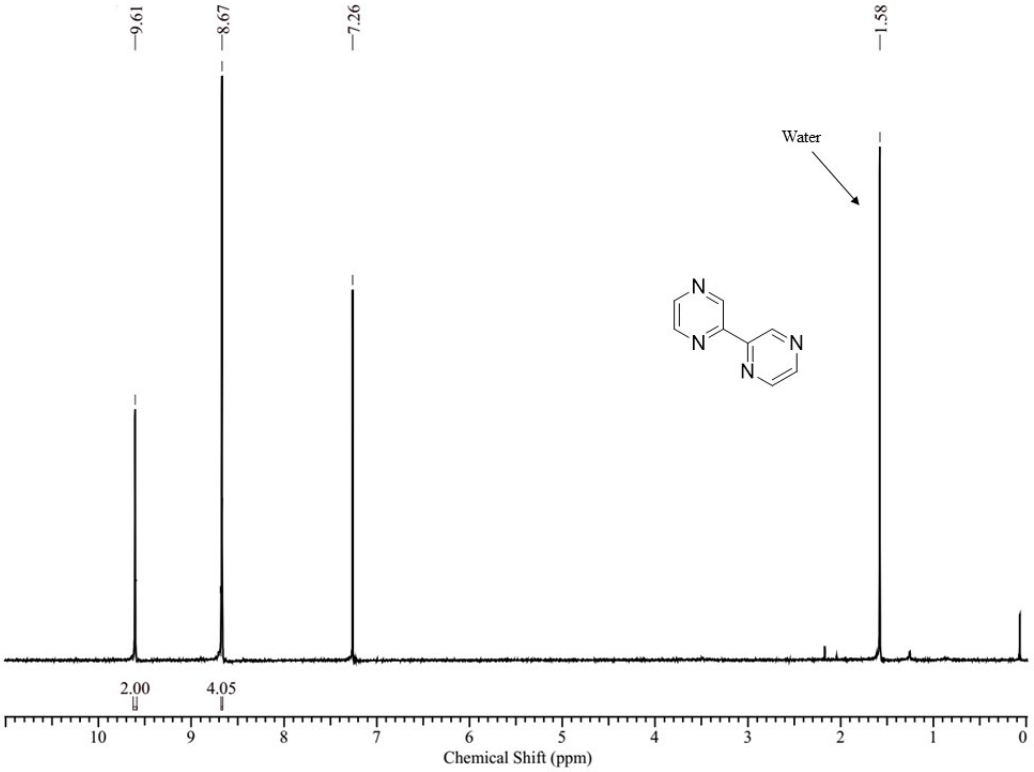



**Fig. S58** $^{1}$H NMR spectrum of 2,2'-bipyrazine (**4td**) in $CDCl_3$

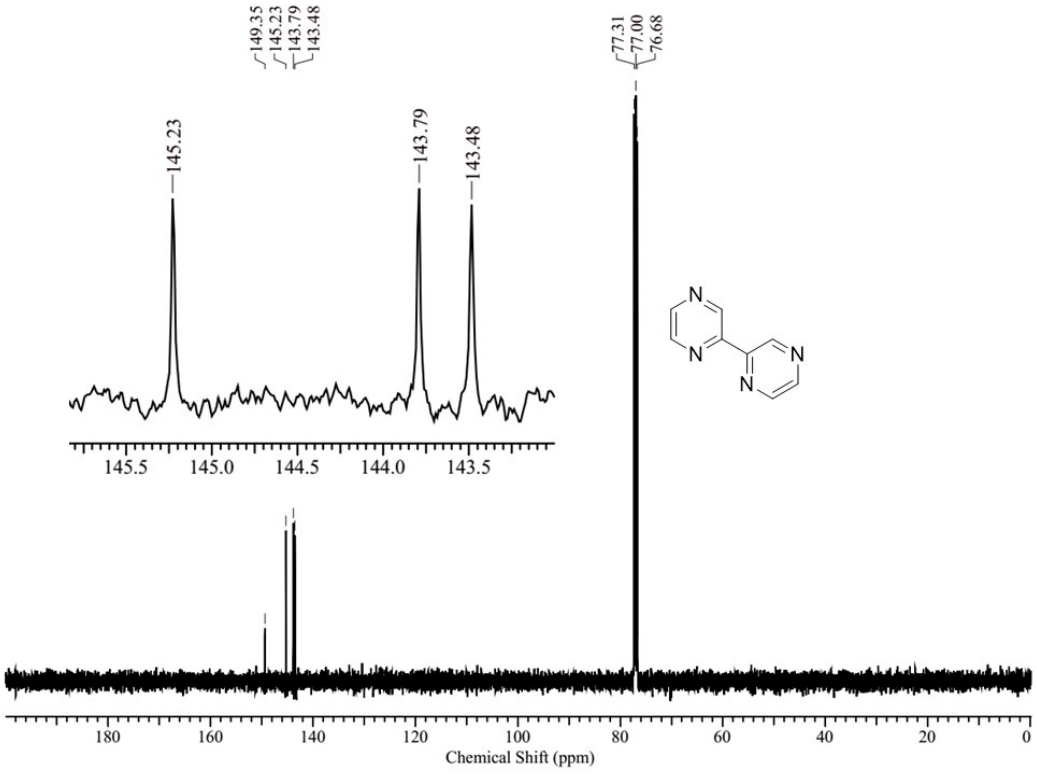



**Fig. S59** $^{13}$C NMR spectrum of 2,2'-bipyrazine (**4td**) in $CDCl_3$

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