

## Supporting Information

### Novel $\beta$ -Ketoimine-Palladium (II) Multilayers Supported on Silicon Wafer Fabricated using Layer-by-Layer Self-Assembly for Catalyzing Suzuki Cross-Coupling Reactions

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# 1. Experimental section

## 1.1 Chemicals

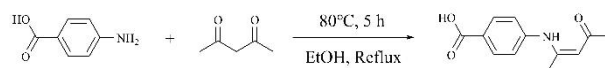
All chemical reagents are obtained from different commercial sources (Table S1) and used without further purification.

## 1.2 Characteristic instruments

X-ray diffractions (XRD) were measured on a PAN analytical X-Pert PRO instrument. Raman spectra were measured using a Thermo Scientific DXR Raman microscope with an excitation laser wavelength of 532 nm. UV spectra were recorded on UV visible photometer (ZF-6, China). X-ray photoelectron spectroscopy (XPS) was carried out with an ESCALab220i-XL electron spectrometer from VG Scientific with 300 W Al K $\alpha$  radiations. Scanning electron microscopy (SEM) images were recorded using a Hitachi S-4800 system. AFM images were measured using a SPM-8100FM (Japan) with tapping mode at ambient. The Pd content was measured by ICP-AES 6000 Series (Thermo Scientific). Cyclic voltammetry was measured by CHI-760E (Electrolyte: 0.1 M TBAHFP dichloromethane solution; Scanning rate: 10 mV/s). Water contact angles were measured on a HARKE·SPCAX1(Shanghai).

## 1.3 Synthesis of ligands (**OEABA**, **L<sub>1</sub>** and **PENDPO**, **L<sub>2</sub>**)

*Synthesis of 4-[(Z)-4-oxopent-2-en-2-yl]amino]benzoic acid (**OEABA**, **L<sub>1</sub>**)*<sup>91,92</sup>

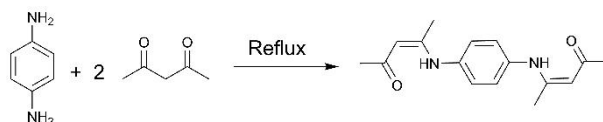


Scheme S1. Preparing route of the 4-[(Z)-4-oxopent-2-en-2-yl] amino]benzoic acid (**OEABA**, called as  **$\beta$ -Ki** (**L<sub>1</sub>**))

1.37g (10mmol) of *p*-aminobenzoic acid was added into a 50mL three-way flask, then 10 mL of anhydrous ethanol was added and stirred at 80 °C until completely dissolved to obtain *p*-aminobenzoic acid ethanol solution (denoted as solution A). 1.2

mL (12 mmol) of acetylacetone was added into a beaker with 5 mL of anhydrous ethanol, then stirred well to obtain the ethanol solution of acetylacetone (denoted as solution B). Solution B was slowly mixed with solution A. The mixture was refluxed at 80 °C for 5 h. At the end of the reaction, the most solvent was removed while it is hot until a small amount of precipitation. The solution is cooled to room temperature and filtered to obtain a bright yellow solid. After recrystallization with anhydrous ethanol, a light yellow solid was obtained. After drying at 40 °C for 12 h,  $\beta$ -ketoimine ligand 4-[(Z)-4-oxopent-2-en-2-yl]amino]benzoic acid (**OEABA**, defined as  $\beta$ -**Ki** (**L<sub>1</sub>**)) was obtained. <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  12.89 (s, 1H), 12.66 (s, 1H), 7.95 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 5.34 (s, 1H), 2.16 (s, 3H), 2.05 (s, 3H).

*Synthesis of 4,4'-[1,4-phenylenedi(nitrilo)dipenten-2-one (**PENDPO**, **L<sub>2</sub>**).*<sup>93</sup>



Scheme S2 Synthesis of the 4,4'-[1,4-phenylenedi(nitrilo)dipenten-2-one (**PDNDPO**, **L<sub>2</sub>**).

A solution of 1,4-phenylenediamine (25 mmol) was added into in ethanol (30 mL), and acetylacetone (50 mmol) was dropped. The reaction mixture was heated under reflux for 5 h and then allowed to stand at room temperature overnight. The solid compound was collected by filtration, washed with Et<sub>2</sub>O for several times and recrystallized using EtOH to give buffy plates (yield: 82%). <sup>1</sup>H NMR (400 MHz, DMSO)  $\delta$  12.47 (s, 2H), 7.20 (d, J = 8.2 Hz, 4H), 5.25 (s, 2H), 2.40 (s, 2H), 2.03 (s, 6H).

#### 1.4 General procedure for fabricating multilayers using Layer by Layer method

The wafers were hydrophilically treated by piranha solution (H<sub>2</sub>SO<sub>4</sub> : H<sub>2</sub>O<sub>2</sub> = 2 : 1) first and were functionalized with (3-aminopropyl) triethoxysilane (**3-APTES**). To a solution of 4-[(Z)-4-oxopent-2-en-2-yl]amino] benzoic acid (**L<sub>1</sub>**, 0.5 mmol), 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (**EDC·HCl**) and 4-Dimethylaminopyridine (**DMAP**) in the hot DMF, and the

functionalized wafers was then added to yield **Si@ $\beta$ -Ki**. The  $\beta$ -ketoimine-modified glass, ITO, and silicon substrates (**Si@ $\beta$ -Ki**) were immersed into a solution of  $\text{Li}_2\text{PdCl}_4/\text{methanol}$  (0.1 mM) at room temperature for 12 h, then rinsed in methanol, and dried under a stream of  $\text{N}_2$  to get **Si@[ $\beta$ -Ki-Pd]**. Subsequently, the substrates(**Si@[ $\beta$ -Ki-Pd]**) were immersed into another solution of 4,4'-[1,4-phenylenedi(nitrilo) dipenten-2-one (**L<sub>2</sub>**, 0.1 mM )/ethanol (KOH, 2mM) at room temperature for 12 h, then rinsed in ethanol, and dried under an  $\text{N}_2$  stream to give **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>]**. **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>]** was added into solution of  $\text{Li}_2\text{PdCl}_4/\text{methanol}$  (0.1 mM) at room temperature for 12 h, then the substrate was removed and rinsed in methanol, and dried under a stream of  $\text{N}_2$  to obtained **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>-Pd]**. These deposition steps were periodically operated to fabricate **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>-Pd]<sub>n</sub>** (n=0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, and 11).

### 1.5 Electrochemistry

The cyclic voltammogram (CV) for the multilayers of **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>-Pd]<sub>n</sub>** was measured by using an electrochemical analyzer (CHI-760E). A Pt wire and Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively, and the indium tin oxide (ITO) electrode supported **Si@[ $\beta$ -Ki-Pd]<sub>n</sub>** multilayers was used as the working electrode with 10 mmol/L  $\text{K}_3[\text{Fe}(\text{CN})_6]/\text{K}_4[\text{Fe}(\text{CN})_6]$  ( 1:1 ) + 0.1 mol/L KCl as the electrolyte, Scanning rate. All electrochemical measurements were done under ambient.

### 1.6 Recycling experiment

Recycling experiments were conducted under standard reaction conditions to assess the stability of the **Si@[ $\beta$ -Ki-Pd]** and **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>-Pd]<sub>n</sub>** catalyst. The catalyst was removed from reaction system and washed with ethyl acetate, ethanol, water, and acetone for three time, respectively. The treated catalyst was dried with nitrogen and used for next recycling experiment.

### 1.7 General implementation steps of Suzuki cross-coupling reactions

Suzuki cross-coupling reaction has the advantages of easy availability of raw materials, low toxicity, stable properties, mild reaction conditions, high reactivity, high selectivity, and easy separation of products. It is often used as a template reaction to explore the catalytic performance of catalysts. The general procedure for the Suzuki-Miyaura cross-coupling reaction is to add 0.10 mmol halogenated aromatics, 0.15 mmol phenylboric acid, 0.15 mmol alkali salts, 6 mL solvent, and supported catalyst (2.5cm×1cm×0.1 cm) to a flask. After the reaction, an appropriate amount of ethyl acetate was added to block the reaction, and the organic phase was extracted by ethyl acetate. Afterward, the product underwent separation through thin-layer chromatography, and the resulting yield was calculated.

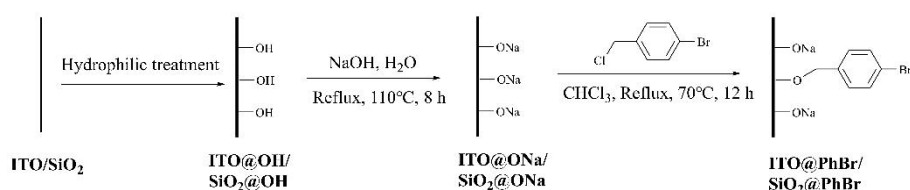
### 1.8 Surface hydrophilic treatments of silicon wafer, ITO glass, and quartz

Silicon wafer (1 cm × 1 cm) were sonicated in ethanol and in deionized water for 15 min. Subsequently, the slides were immersed in piranha solution (H<sub>2</sub>SO<sub>4</sub> /H<sub>2</sub>O<sub>2</sub> (7:3; v:v)) at 80 °C for 1 h to remove any organic residues and to create silanol groups on the surfaces. The cleaned slides were rinsed extensively with deionized water (40 mL), ethanol (40 mL), acetone (40 mL), and was sonicated in ethanol for 2 min, subsequently dried in a stream of nitrogen.

### 1.9 Three-phase experiment

The experimental procedure: In a flask, one phase (SiO<sub>2</sub>@PhBr), two phase(naphthyl boronic acid, NBA), and three phase (Si@[β-Ki-Pd][L<sub>2</sub>-Pd]<sub>11</sub>) gave a three-phase system, and there is no direct contact between one phase and three phase. If the coupled products on the surface of one phase can not be detected with UV spectra after the reaction finished, no leaching of active metals can be concluded. It is one of the evidence to distinguish a heterogeneous catalyst or not.

One phase was prepared as depicted in Scheme S3. The quartz ( $\text{SiO}_2$ ) was ultrasonically cleaned with ethanol for 5 min and put into the UV cleaner for 50 min for hydrophilic treatment to get the ITO glass or quartz ( $\text{SiO}_2$ ) with hydroxyl groups on the surface (called as  $\text{SiO}_2@\text{OH}$ ).  $\text{SiO}_2@\text{OH}$  was put into sodium hydroxide solution and reacted at reflux at 110 °C for 8 h to obtain  $\text{SiO}_2@\text{ONa}$  containing the sodium alcohol group. Using chloroform as the solvent,  $\text{SiO}_2@\text{ONa}$  was reacted with *p*-bromobenzyl chloride under reflux at 70 °C for 12 h to obtain  $\text{SiO}_2@\text{PhBr}$ .



Scheme S3 Preparing routes of the solid phase reactant  $\text{SiO}_2@\text{PhBr}$ .

$\text{SiO}_2@\text{PhBr}$  prepared above was added to naphthyl boronic acid (**NBA**) solution with  $\text{Si}@\beta\text{-Ki-Pd}[\text{L}_2\text{-Pd}]_{11}$ . Suzuki-Miyaura cross-coupling reaction can be achieved if there is leaching of the active metals from  $\text{Si}@\beta\text{-Ki-Pd}[\text{L}_2\text{-Pd}]_{11}$ .

### 1.10 Turnover Frequency (TOF)

TOF was defined as  $\text{TON h}^{-1}$ , and TON was defined as  $\text{mol-product mol}^{-1} \text{ Pd}$ .

$$\text{TOF} = \frac{N_{\text{substrate quantity}} \times \text{Yield} (\%)}{n_{\text{Pd}} \times \text{Time} (\text{h})}$$

## 2. Figure caption

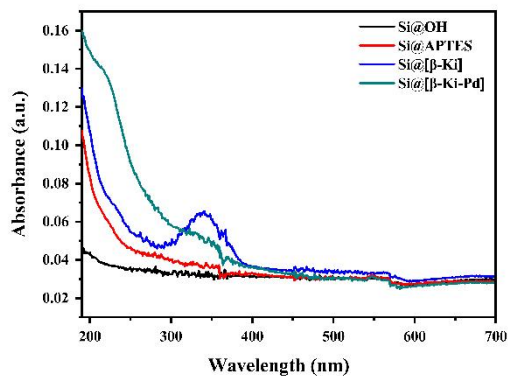


Figure S1 UV spectra of  $\text{SiO}_2@OH$  (black line),  $\text{SiO}_2@APTES$  (red line),  $\text{SiO}_2@[\beta\text{-Ki}]$  (blue line), and  $\text{SiO}_2@[\beta\text{-Ki-Pd}]$  (green line).

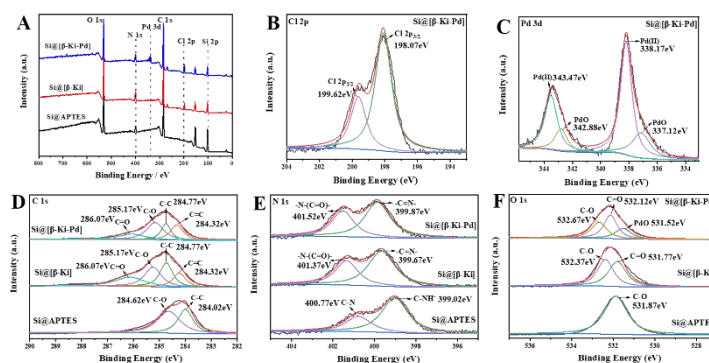


Figure S2 XPS survey spectra of self-assembly process for (A)  $\text{Si}@APTES$  (black line),  $\text{Si}@[\beta\text{-Ki}]$  (red line), and  $\text{Si}@[\beta\text{-Ki-Pd}]$  (blue line), HR-XPS of (B) Cl 2p, (C) Pd 3d, (D) C 1s, (E) N 1s, and (F) O 1s.

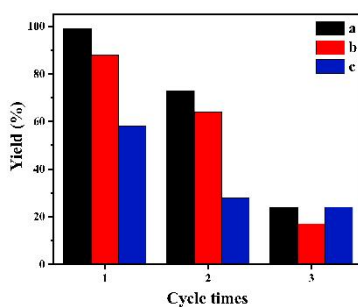


Figure S3 Recycling experiments of Suzuki cross coupling reaction of 4-bromotoluene with arylboronic acid catalyzed by  $\text{Si}@[\beta\text{-Ki-Pd}]$ . Reaction conditions: aryl halide (0.1 mmol),  $\text{PhB(OH)}_2$  (0.15 mmol),  $\text{K}_2\text{CO}_3$  (0.15 mmol), TBAB (0.15 mmol), and  $\text{EtOH}:\text{H}_2\text{O}=1:1$  (6.0 mL); a) 80 °C (black column), 12 h, b) 50 °C (red column), 12 h, c) 50 °C (blue column), 4 h.

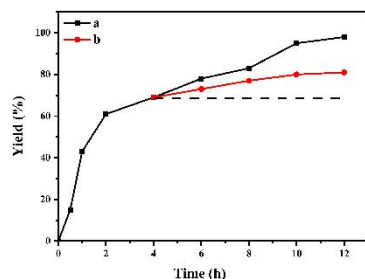


Figure S4 Hot filtration experiments in Suzuki–Miyaura cross coupling reaction catalyzed by **Si@[β-Ki-Pd]** at 1 h, 2 h, 4 h, 8 h, and 12 h.

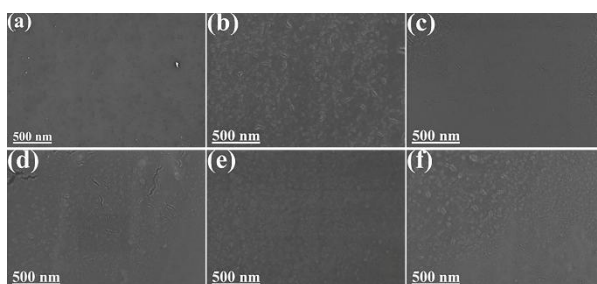


Figure S5 SEM images of Suzuki–Miyaura cross coupling reaction catalyzed by **Si@[β-Ki-Pd]**. a) 0 h, b) 1 h, c) 2 h, d) 4 h, e) 8 h, and f) 12 h without washing.

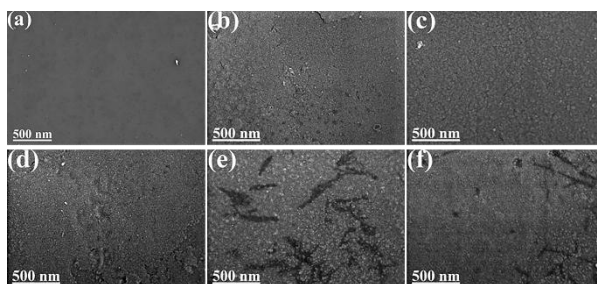


Figure S6 SEM images of Suzuki–Miyaura cross coupling reaction catalyzed by **Si@[β-Ki-Pd]**. a) 1 h, b) 2 h, c) 4 h, d) 8 h, and e) 12 h after washed with ethyl acetate, methanol, ethanol, and water three times.

The changes of HR-XPS for **Si@[β-Ki-Pd]** during catalysis were measured, and as shown in Figure S7. The binding energy (BE) peaks at 338.17 eV and 343.47 eV for Pd(II) 3d<sub>5/2</sub>, and Pd(II) 3d<sub>3/2</sub> were observed, and the BE peaks at 337.12 eV and 342.88 eV for PdO were also observed. These indicated the mainly existing of Pd(II) before catalysis. The BE peaks above shifted to low BE at 335.12 eV and 340.22 eV attributed to Pd(0) 3d<sub>5/2</sub> and Pd(0) 3d<sub>3/2</sub>, suggesting the in situ formation of Pd(0) at 1 h, and then shifted to high BE at 2 h and then to low BE at 4 h, meaning the oxidation of Pd(0) and suggesting the oxidative addition of some Pd(0) with bromobenzene.



The BE peak had almost on shifting at 8 h and at 8 h, demonstrating the reduction of Pd(II), indicating the released Pd(0) in the course of the reduction elimination. It could be described as that the electron densities of palladium existed in the range of  $0 \leq \delta \leq +2$ , showing the truly active site of Pd( $\delta^-$ ) containing Pd(0), PdO, and Pd(II).

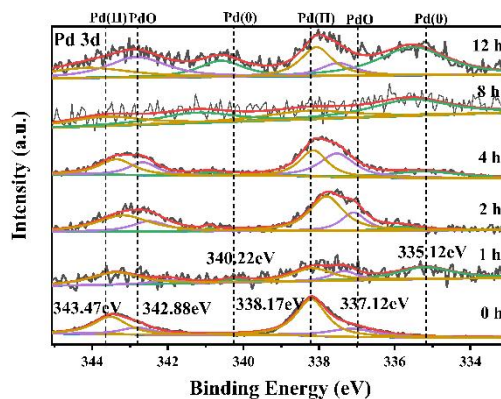


Figure S7 XPS spectra of Pd 3d in the surfaces of **Si@[ $\beta$ -Ki-Pd]** at different time (0 h, 1 h, 2 h, 4 h, 8 h, and 12 h).

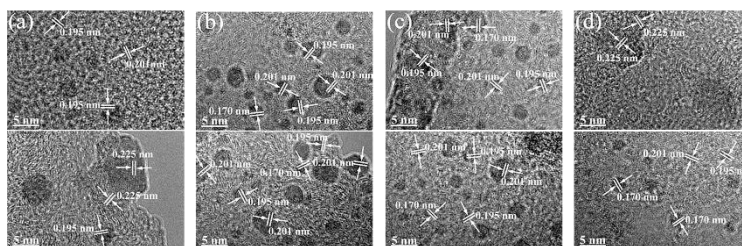


Figure S8 HR-TEM images of nanoparticles formed in Suzuki coupling reaction catalyzed by **PENDPO/Li<sub>2</sub>PdCl<sub>4</sub>** at (a) 1 h, (b) 2 h, (c) 3 h, and (d) 4 h.

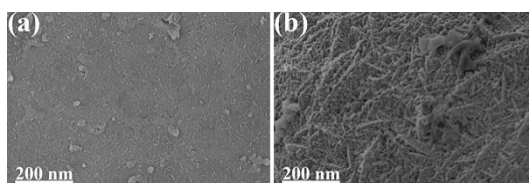


Figure S9 SEM images of **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>-Pd]<sub>11</sub>** after recycling at 80 °C, 12 h; (a) 1st and (b) 5th.

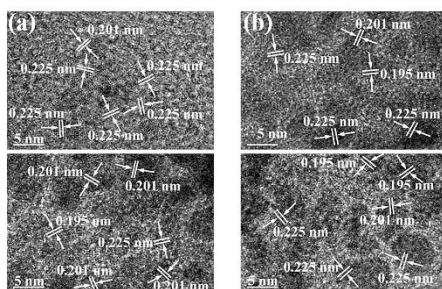


Figure S10 HR-TEM images of nanoparticles formed in Suzuki coupling reaction catalyzed by  $\text{Li}_2\text{PdCl}_4$  after recycling at  $80^\circ\text{C}$ , 12 h (a) 1st and (b) 5th.

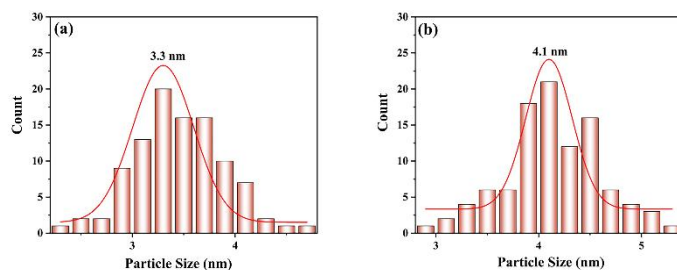


Figure S11 Particle size distribution of nanoparticles formed in Suzuki coupling reaction catalyzed by  $\text{Li}_2\text{PdCl}_4$  after recycling at  $80^\circ\text{C}$ , 12 h (a) 1st and (b) 5th.

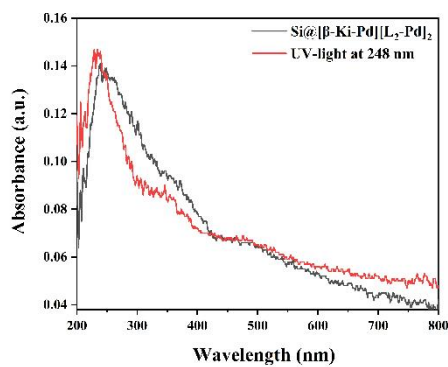
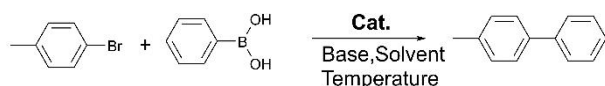


Figure S12 UV spectra of  $\text{Si}@\beta\text{-Ki-Pd}[\text{L}_2\text{-Pd}]_2$  before and after UV irradiation at 248 nm for 4 h. (UV-light were using a WFH-204B(Hangzhou Qi Wei)).

### 3. Table lists

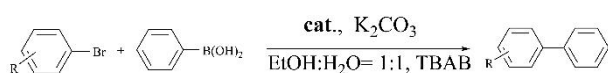
Table S1 Main experimental reagents

Reagents	Purity	Manufacturer
4-Aminobenzoic acid	99%	aladdin
Acetylacetone	99%	aladdin
4-Bromotoluene	98%	Bailingwei
2-Bromotoluene	99%	aladdin
3-Bromotoluene	98%	aladdin
4-Bromoanisole	99%	aladdin
3-Bromoanisole	97%	aladdin
2-Bromoanisole	98%	aladdin
4-Bromobenzaldehyde	99%	aladdin
3-Bromobenzaldehyde	99%	Energy Chemical
2-Bromobenzaldehyde	98%	MACKLIN
4-Bromobenzonitrile	97%	aladdin
		Shanghai Chemical
1-Bromo-4-nitrobenzene	98%	Reagent Purchasing and Supply Station
		Bailingwei
Phenylboronic acid	98%	Bailingwei
1-Naphthylboronic acid	97%	Thermo Fisher
3-Aminopropyltriethoxysilane	98%	Bailingwei
1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride	98%	aladdin
4-Dimethylaminopyridine	99%	aladdin
Ethyl acetate	99.5%	Titan
Ethanol	99.7%	Titan
DMF	99%	Bailingwei
MeOH	99.5%	Titan
Palladium chloride	59.8%	MACKLIN
Lithium chloride	99%	aladdin

Table S2 Optimization conditions for the Suzuki cross-reaction catalyzed by Si@[ $\beta$ -Ki-Pd]

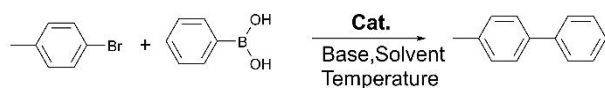
Entry	Solvent	Base	Time (h)	Temperature (°C)	Yield(%) <sup>b</sup>
1	DMF	K <sub>2</sub> CO <sub>3</sub>	12	80	7
2	DMF-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	37
3	DMF-EtOH(1:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	28
4	toluene	K <sub>2</sub> CO <sub>3</sub>	12	80	0
5	toluene-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	3
6	MeOH	K <sub>2</sub> CO <sub>3</sub>	12	80	2
7	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	12	80	54
8	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	98
9	EtOH-H <sub>2</sub> O(2:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	92
10	EtOH-H <sub>2</sub> O(3:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	82
11	EtOH-H <sub>2</sub> O(4:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	81
12	EtOH	K <sub>2</sub> CO <sub>3</sub>	12	80	77
13	EtOH-H <sub>2</sub> O(1:1)	NaHCO <sub>3</sub>	12	80	70
14	EtOH-H <sub>2</sub> O(1:1)	NaOH	12	80	77
15	EtOH-H <sub>2</sub> O(1:1)	Na <sub>2</sub> CO <sub>3</sub>	12	80	65
16	EtOH-H <sub>2</sub> O(1:1)	K <sub>3</sub> PO <sub>4</sub>	12	80	72
17	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	12	80	73
18	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	2	80	61
19	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	4	80	69
20	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	6	80	78
21	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	8	80	83
22	EtOH-H <sub>2</sub> O(1:1)	K <sub>2</sub> CO <sub>3</sub>	10	80	95

<sup>a</sup> Reaction conditions: 4-bromotoluene (0.1 mmol), PhB(OH)<sub>2</sub> (0.15 mmol), base (0.15 mmol), catalyst (2.79×10<sup>-9</sup> mol·cm<sup>-2</sup> Pd), solvent (6.0 mL), 80 °C, TBAB (0.15 mmol), silicon wafer (2.5 cm×1cm×0.1 cm). <sup>b</sup> Isolated yield.

Table S3 Suzuki reaction of arylboronic acid with aryl halides catalyzed by **Si@[ $\beta$ -Ki-Pd]**.<sup>a</sup>

Entry	Ar-Br	Ar-B(OH) <sub>2</sub>	Product	Yield (%) <sup>b</sup>
1	<i>p</i> -CH <sub>3</sub>	Ph	<i>p</i> -CH <sub>3</sub> -Ph-Ph (1a)	98
2	<i>o</i> -CH <sub>3</sub>	Ph	<i>o</i> -CH <sub>3</sub> -Ph-Ph (1b)	80
3	<i>m</i> -CH <sub>3</sub>	Ph	<i>m</i> -CH <sub>3</sub> -Ph-Ph (1c)	89
4	<i>p</i> -CH <sub>3</sub> O	Ph	<i>p</i> -CH <sub>3</sub> O-Ph-Ph (1d)	96
5	<i>o</i> -CH <sub>3</sub> O	Ph	<i>o</i> -CH <sub>3</sub> O-Ph-Ph (1e)	73
6	<i>m</i> -CH <sub>3</sub> O	Ph	<i>m</i> -CH <sub>3</sub> O-Ph-Ph (1f)	82
7	<i>p</i> -NO <sub>2</sub>	Ph	<i>p</i> -NO <sub>2</sub> -Ph-Ph (1g)	99
8	<i>p</i> -CN	Ph	<i>p</i> -CN-Ph-Ph (1j)	99
9	<i>p</i> -CHO	Ph	<i>p</i> -CHO-Ph-Ph (1l)	99
10	<i>p</i> -CH <sub>3</sub>	<i>p</i> -CH <sub>3</sub> O-Ph	<i>p</i> -CH <sub>3</sub> -Ph-Ph- <i>p</i> -CH <sub>3</sub> O (1k)	69
11	Ph-Cl	Ph	Ph-Ph (1i)	0
12	<i>p</i> -NO <sub>2</sub> -Ph-Cl	Ph	<i>p</i> -NO <sub>2</sub> -Ph-Ph (1g)	0
13	<i>p</i> -CH <sub>3</sub> -Ph-Cl	Ph	<i>p</i> -CH <sub>3</sub> -Ph-Ph (1a)	0
14	<i>p</i> -CH <sub>3</sub>	Pyridyl	<i>p</i> -CH <sub>3</sub> -Ph-Pyridine (1o)	0
15	<i>p</i> -CH <sub>3</sub>	Thienyl	<i>p</i> -CH <sub>3</sub> -Ph-Thiophene (1p)	0
16	<i>p</i> -CH <sub>3</sub>	Furanyl	<i>p</i> -CH <sub>3</sub> -Ph-Furan (1q)	0
17	<i>p</i> -CH <sub>3</sub>	Naphthyl	<i>p</i> -CH <sub>3</sub> -Ph-naphthalene (1r)	70

<sup>a</sup> Reaction conditions: aryl halide (0.1 mmol), PhB(OH)<sub>2</sub> (0.15 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15mmol), TBAB (0.15 mmol), catalyst (2.79×10<sup>-9</sup> mol·cm<sup>-2</sup> Pd) and EtOH: H<sub>2</sub>O=1:1 (6.0 mL); temperature = 80 °C, 12 h. glass wafer (2.5cm×1cm×0.1 cm). <sup>b</sup> Isolated yield.

Table S4 Poisoning experiment of **Si@[ $\beta$ -Ki-Pd]**.<sup>a</sup>

No	Cat.	Poisoning additive	Yield(%) <sup>b</sup>
1	<b>Si@[<math>\beta</math>-Ki-Pd]</b>	-----	98
2	<b>Si@[<math>\beta</math>-Ki-Pd]</b>	Hg	26
3	<b>Si@[<math>\beta</math>-Ki-Pd]</b>	P(Ph) <sub>3</sub>	14
4	<b>Si@[<math>\beta</math>-Ki-Pd]</b>	Thiophene	13

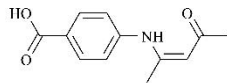
<sup>a</sup> Reaction conditions: aryl halide (0.1 mmol), PhB(OH)<sub>2</sub> (0.15 mmol), K<sub>2</sub>CO<sub>3</sub> (0.15mmol), TBAB (0.15 mmol), catalyst (2.79×10<sup>-9</sup> mol·cm<sup>-2</sup> Pd) and EtOH: H<sub>2</sub>O=1:1 (6.0 mL); at 80 °C,12 h. glass wafer (2.5cm×1cm×0.1 cm). <sup>b</sup> Isolated yield.

Table S5 Pd(0)/ Pd(II) ratio on the surface of **Si@[ $\beta$ -Ki-Pd][L<sub>2</sub>-Pd]<sub>11</sub>** during catalysis

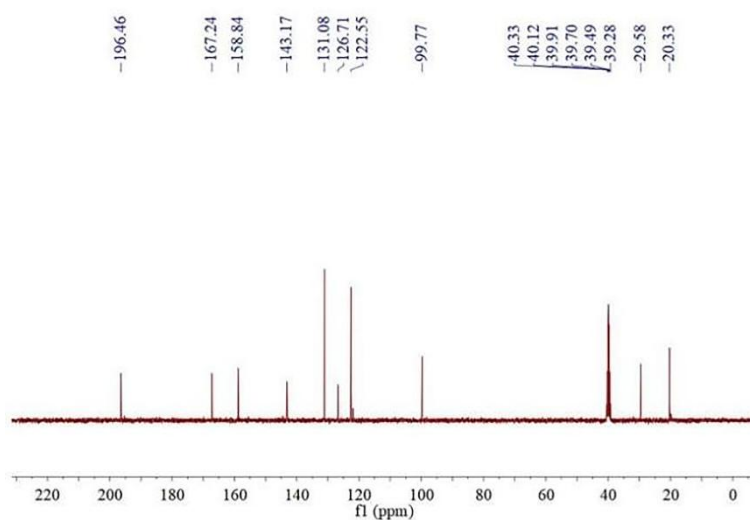
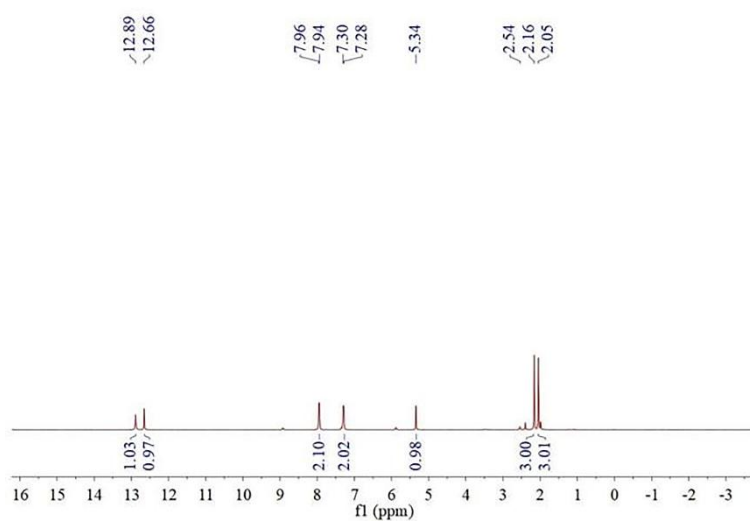
Time (h)	0.25	0.5	1	1.5	2	2.5	3	3.5	4
Pd(0)/Pd(II)	0.25	0.9	0.56	0.91	0.22	0.05	0.47	0.52	0.62

## 4. Additive

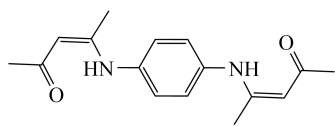
### 4-[(Z)-4-oxopent-2-en-2-yl]amino]benzoic acid (OEABA)



Pale yellow solid, 71%,  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  12.89 (s, 1H), 12.66 (s, 1H), 7.95 (d,  $J = 8.2$  Hz, 2H), 7.29 (d,  $J = 8.2$  Hz, 2H), 5.34 (s, 1H), 2.16 (s, 3H), 2.05 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  196.46, 167.24, 158.84, 143.17, 131.08, 126.71, 122.55, 99.77, 29.58, 20.33.<sup>98, 99</sup>

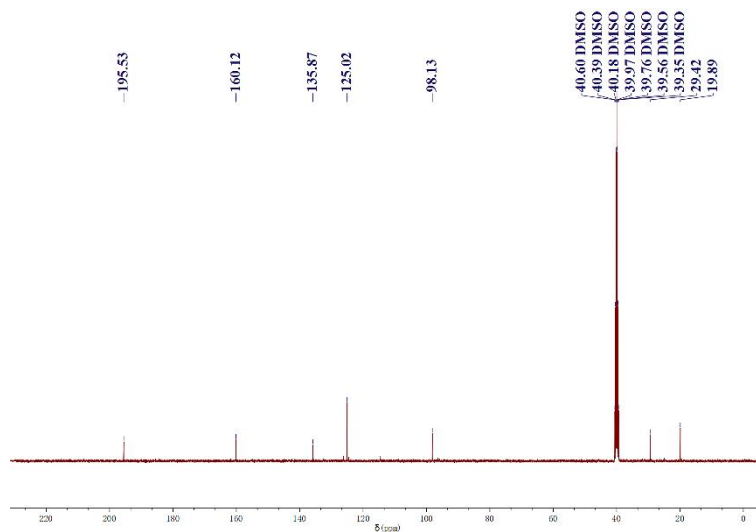
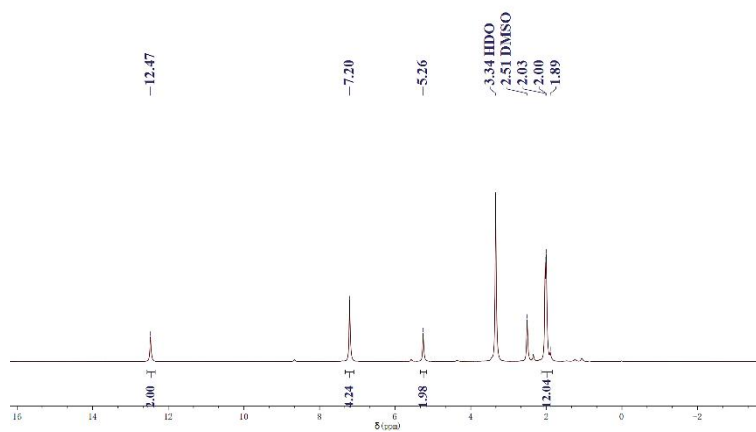


### 4,4'-[1,4-phenylenedi(nitrilo)dipenten-2-one (PENDPO)



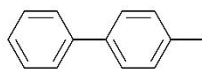
Pale yellow solid, 70%,  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$

12.47 (s, 2H), 7.20 (s, 4H), 5.25 (s, 2H), 2.03 (d,  $J = 12.1$  Hz, 12H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  195.53, 160.12, 135.87, 125.02, 98.13, 29.42, 19.89. <sup>100</sup>



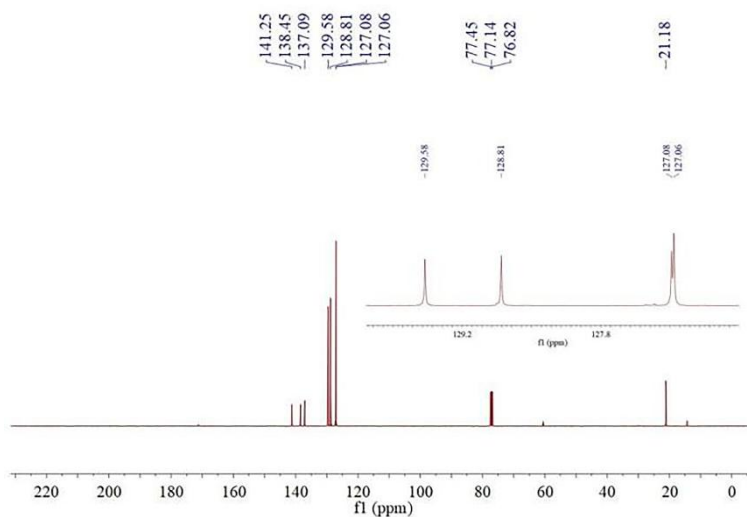
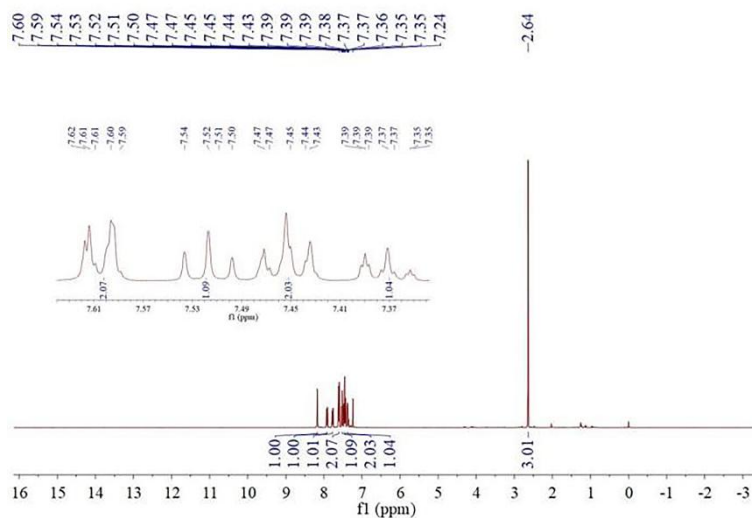


### 4-methyl-1,1'-biphenyl (1a)

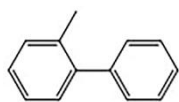


White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (t,  $J = 1.7$  Hz, 1H), 7.94 - 7.90 (m, 1H), 7.81 - 7.74 (m, 1H), 7.63 - 7.57 (m, 2H), 7.54 - 7.49 (m, 1H), 7.48 - 7.42 (m, 2H), 7.40 - 7.34 (m, 1H), 2.64 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.25, 138.45, 137.09, 129.58, 128.81, 127.08, 127.06, 21.18.<sup>6</sup>

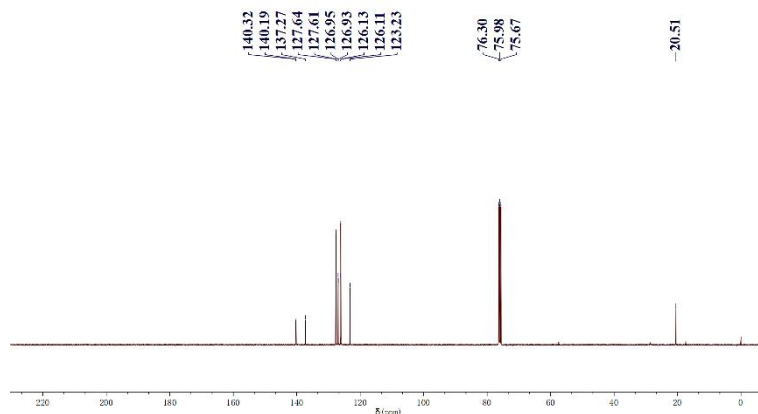
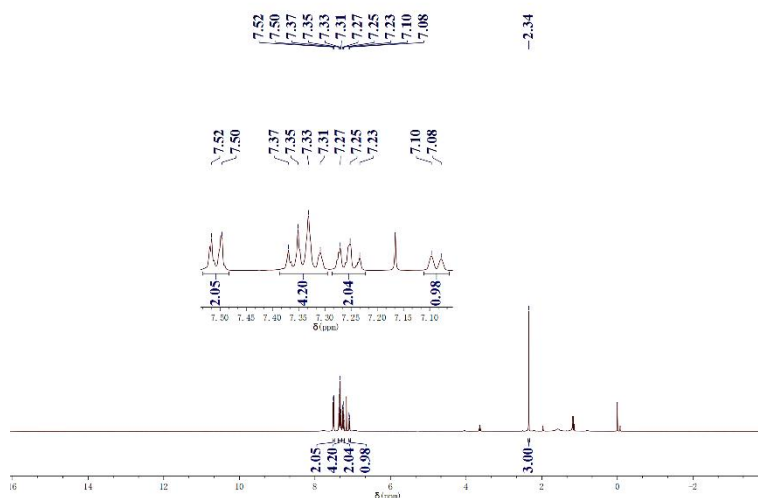


## 2-methyl-1,1'-biphenyl (1b)

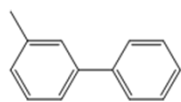


White liquid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.52-7.50(d, 2H), 7.37-7.31(m, 4H), 7.27-7.23(t, 2H), 7.10-7.08(d, 1H), 2.34(s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.32, 140.19, 137.27, 127.64, 127.61, 126.95, 126.93, 126.13, 126.11, 123.23, 20.51.<sup>6</sup>

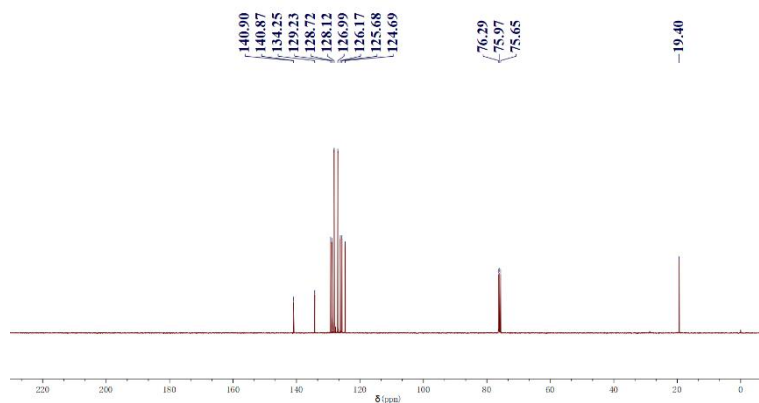
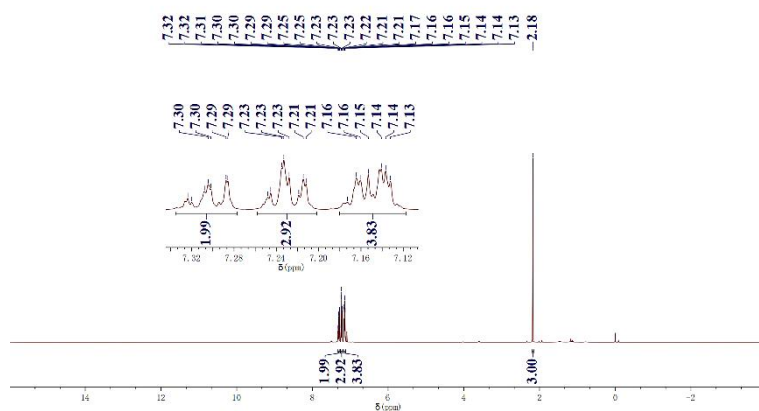


### 3-methyl-1,1'-biphenyl (1c)

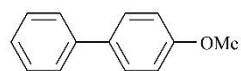


White liquid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.30-7.29(m, 2H), 7.23-7.21(m, 3H), 7.16-7.13(m, 4H), 2.18(s, 3H).

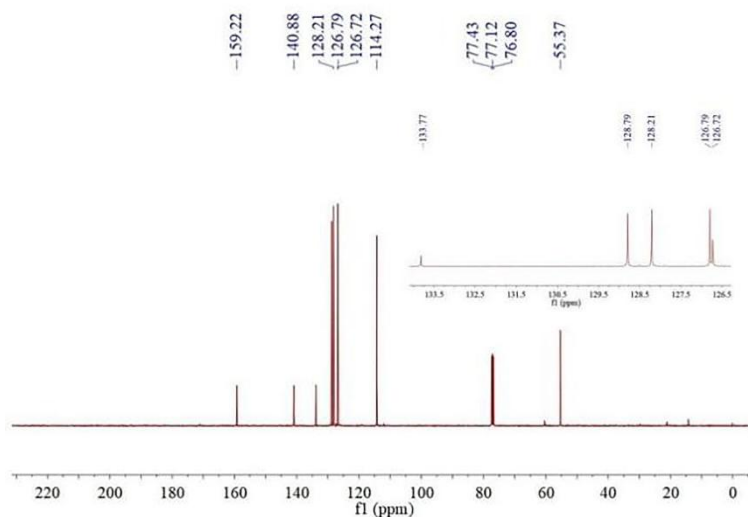
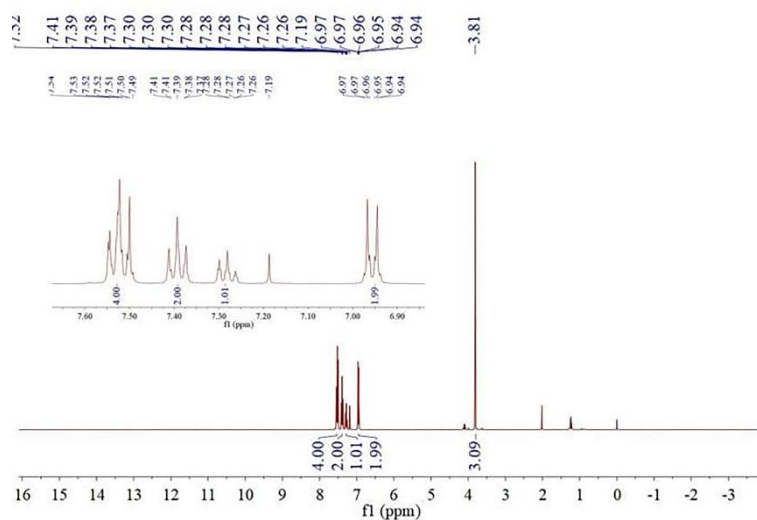
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.90, 140.87, 134.25, 129.23, 128.72, 128.12, 126.99, 126.17, 125.68, 124.69, 19.40.<sup>6</sup>



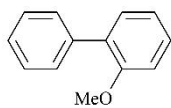
### 4-methoxy-1,1'-biphenyl (1d)



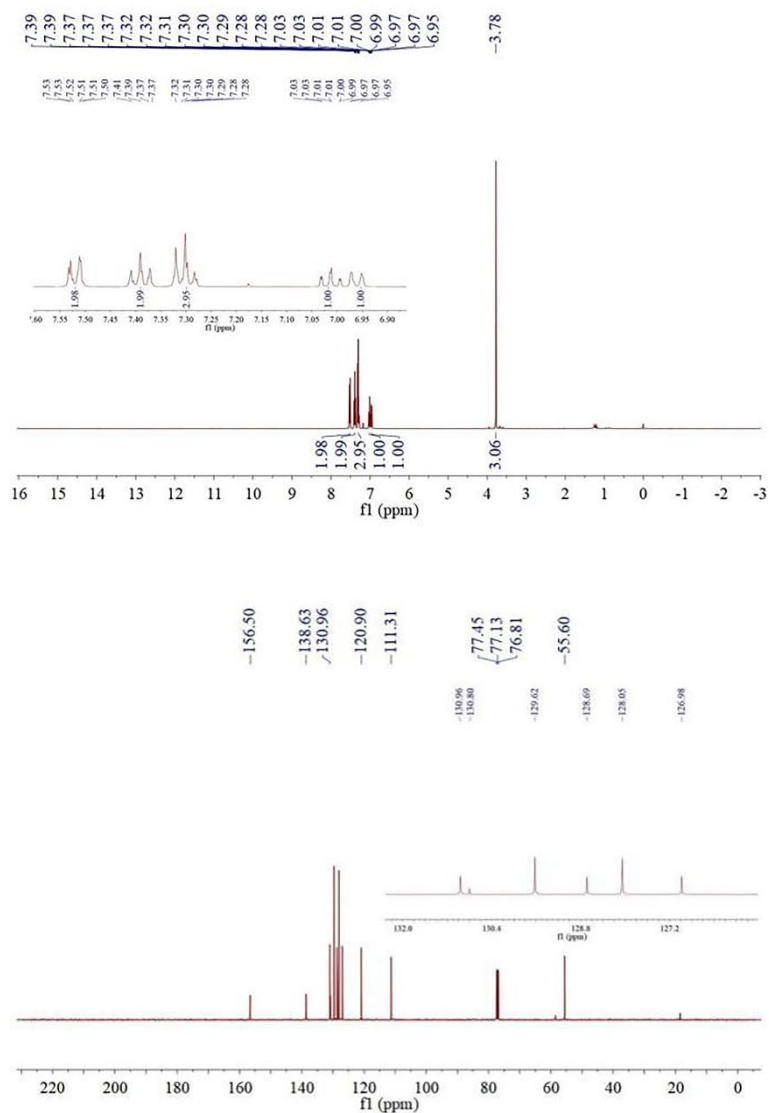
White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.58 - 7.47 (m, 4H), 7.42 - 7.35 (m, 2H), 7.31 - 7.25 (m, 1H), 6.99 - 6.92 (m, 2H), 3.81 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  159.22, 140.88, 133.77, 128.79, 128.21, 126.79, 126.72, 114.27, 55.37.<sup>6</sup>



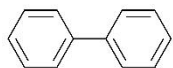
## 2-methoxy-1,1'-biphenyl (1e)



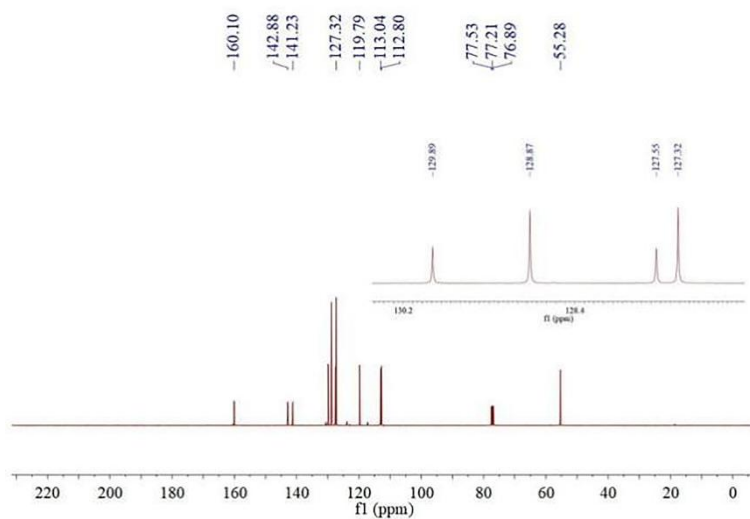
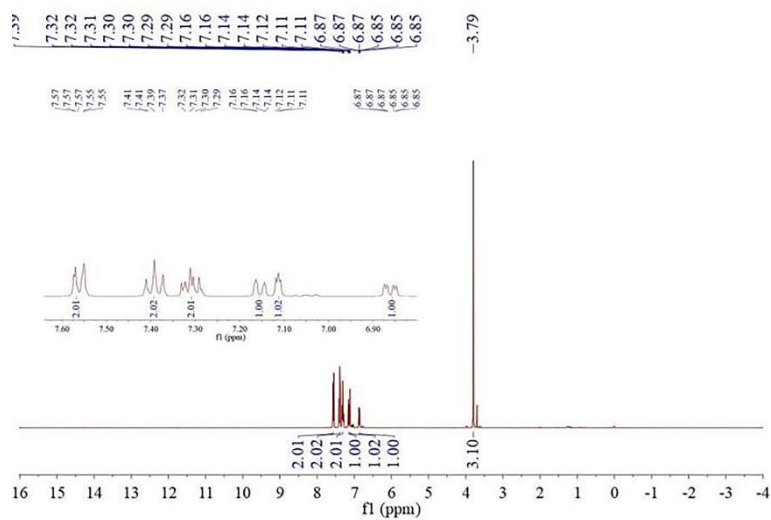
White solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 - 7.47 (m, 2H), 7.43 - 7.34 (m, 2H), 7.34 - 7.25 (m, 3H), 7.01 (td, J = 7.5, 1.1 Hz, 1H), 6.98 - 6.94 (m, 1H), 3.78 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 156.50, 138.63, 130.96, 130.80, 129.62, 128.69, 128.05, 126.98, 120.90, 111.31, 55.60.<sup>6</sup>



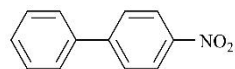
### 3-methoxy-1,1'-biphenyl (1f)



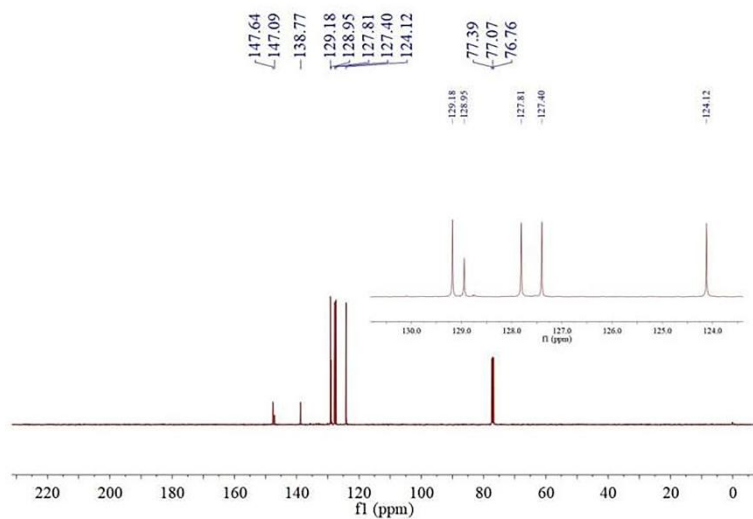
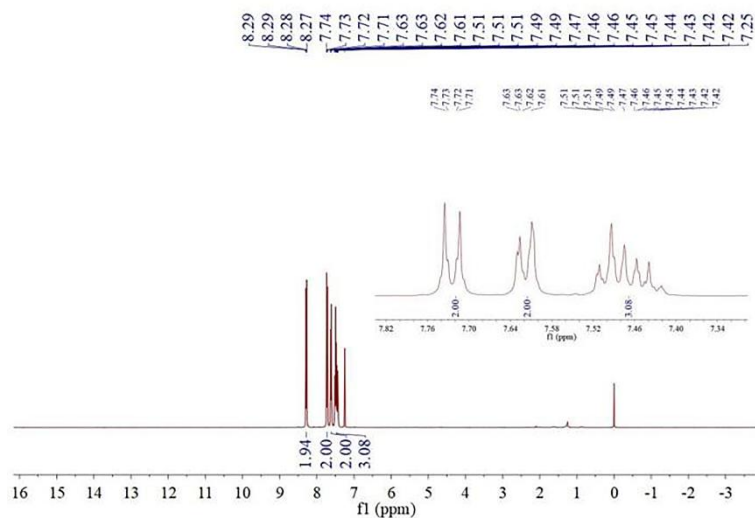
OMe White solid, <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.59 - 7.53 (m, 2H), 7.42 - 7.36 (m, 2H), 7.34 - 7.27 (m, 2H), 7.15 (dd, J = 7.6, 0.9 Hz, 1H), 7.12 - 7.11 (m, 1H), 6.88 - 6.83 (m, 1H), 3.79 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 160.10, 142.88, 141.23, 129.89, 128.87, 127.55, 127.32, 119.79, 113.04, 112.80, 77.53, 77.21, 76.89, 55.28.<sup>7</sup>



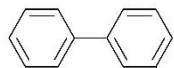
### 4-nitro-1,1'-biphenyl (1g)



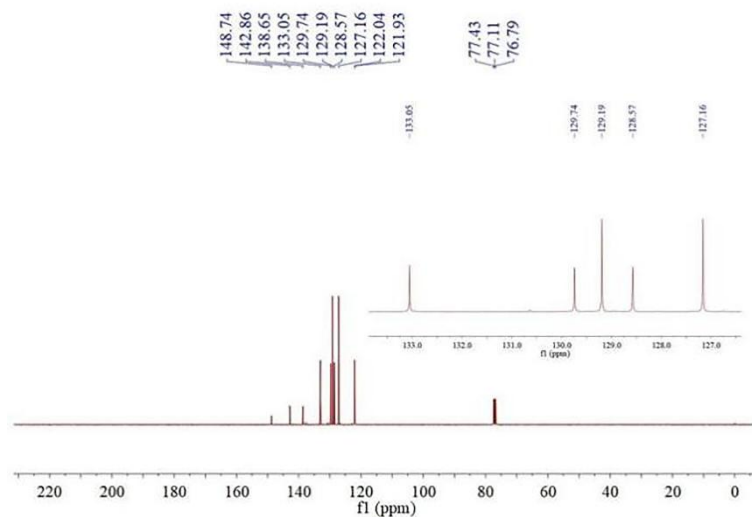
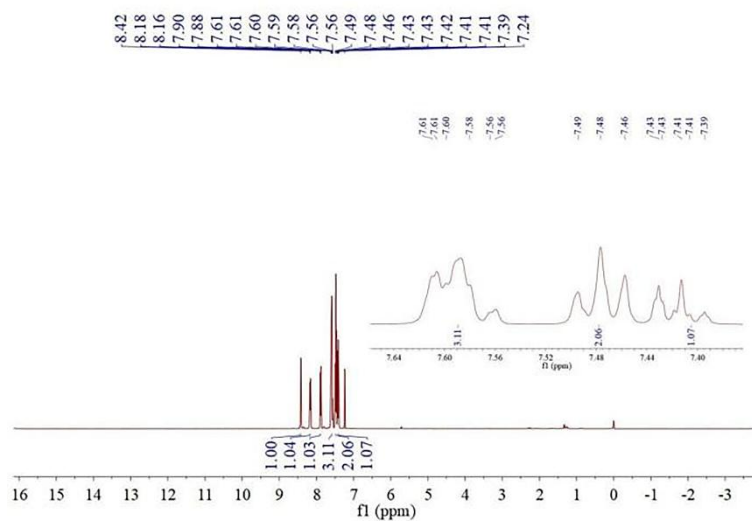
White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 - 8.26 (m, 2H), 7.75 - 7.69 (m, 2H), 7.66 - 7.57 (m, 2H), 7.53 - 7.40 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  147.64, 147.09, 138.77, 129.18, 128.95, 127.81, 127.40, 124.12.<sup>10</sup>



### 3-nitro-1,1'-biphenyl (1h)

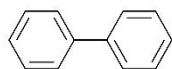


White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (s, 1H), 8.17 (d,  $J = 8.2$  Hz, 1H), 7.89 (d,  $J = 7.7$  Hz, 1H), 7.63 - 7.55 (m, 3H), 7.48 (t,  $J = 7.4$  Hz, 2H), 7.44 - 7.37 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  148.74, 142.86, 138.65, 133.05, 129.74, 129.19, 128.57, 127.16, 122.04, 121.93.<sup>10</sup>



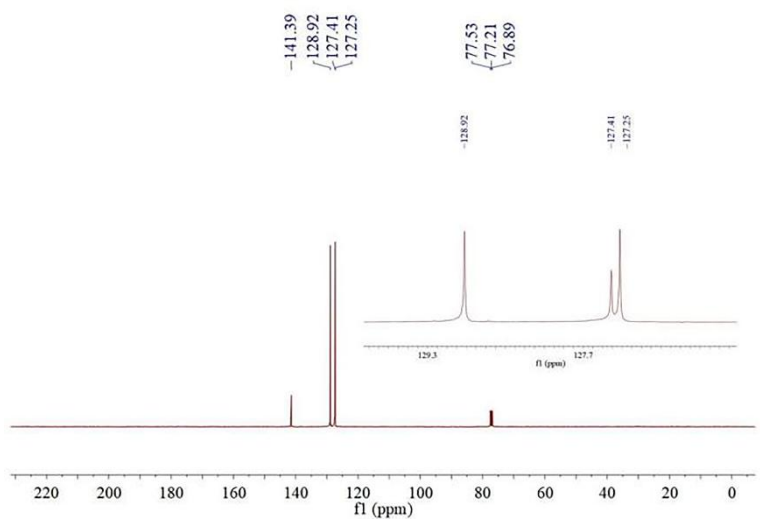
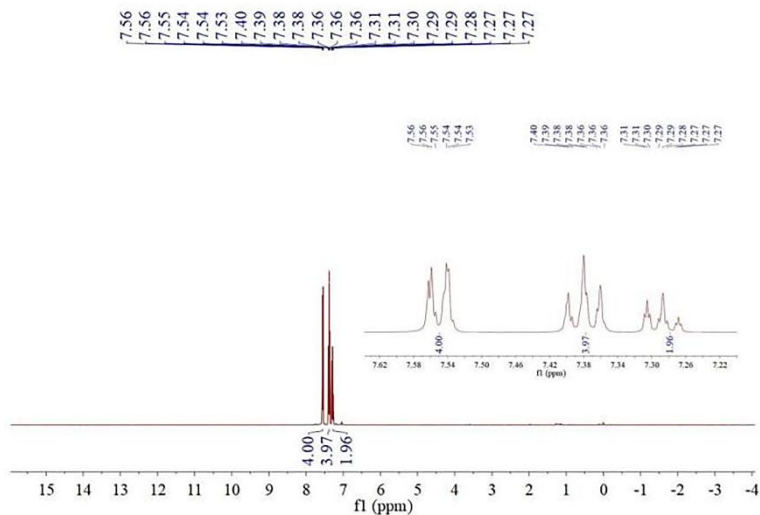


### 1,1'-biphenyl (1i)

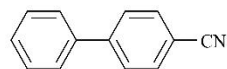


White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.57 - 7.53 (m, 4H), 7.41 - 7.34 (m, 4H), 7.32 - 7.25 (m, 2H).

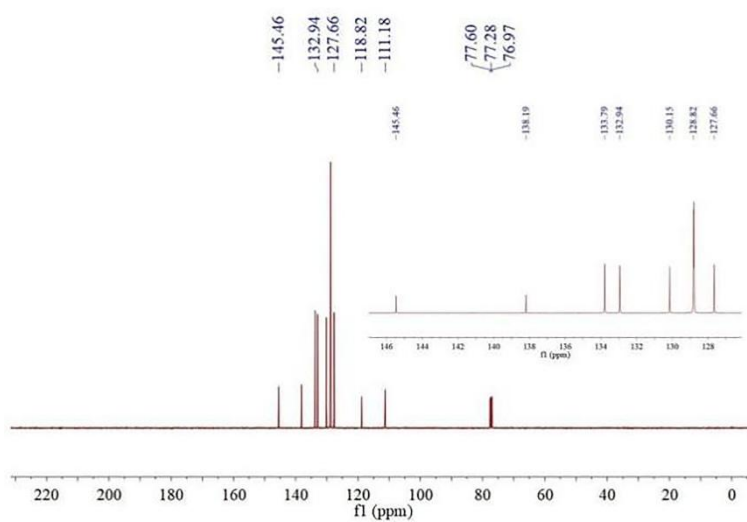
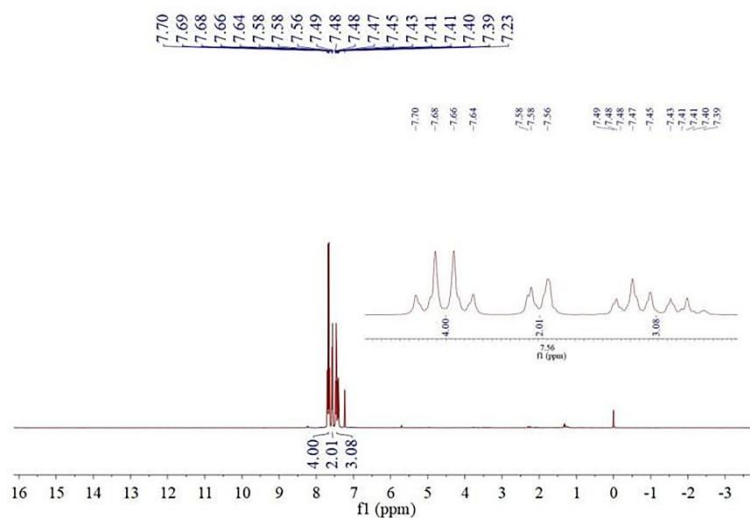
$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  141.39, 128.92, 127.41, 127.25.<sup>6</sup>



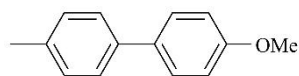
### [1,1'-biphenyl]-4-carbonitrile (1j)



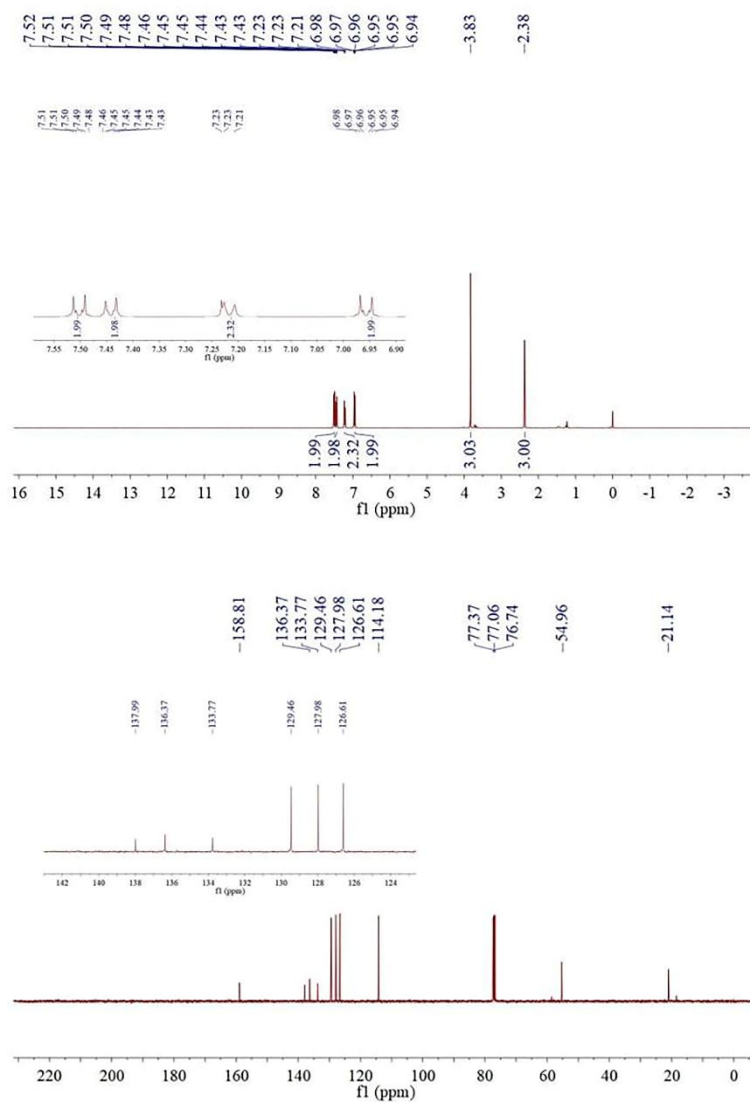
White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 - 7.63 (m, 4H), 7.59 - 7.54 (m, 2H), 7.50 - 7.37 (m, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  145.46, 138.19, 133.79, 132.94, 130.15, 128.82, 127.66, 118.82, 111.18.<sup>6</sup>



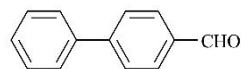
### 4-methoxy-4'-methyl-1,1'-biphenyl (1k)



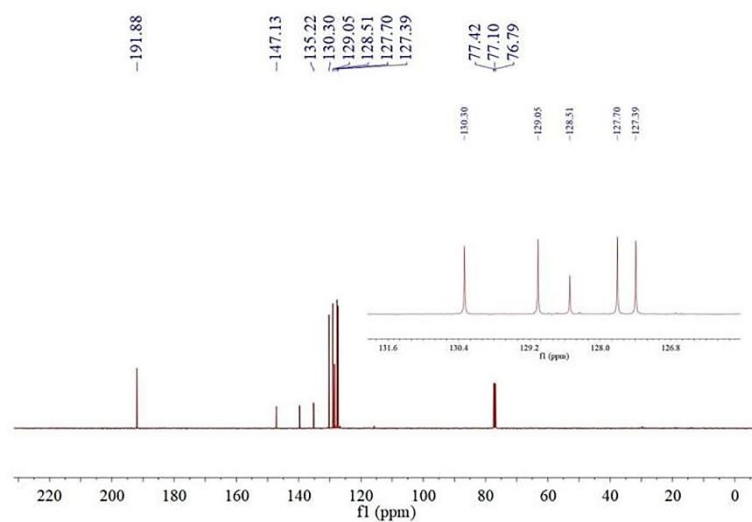
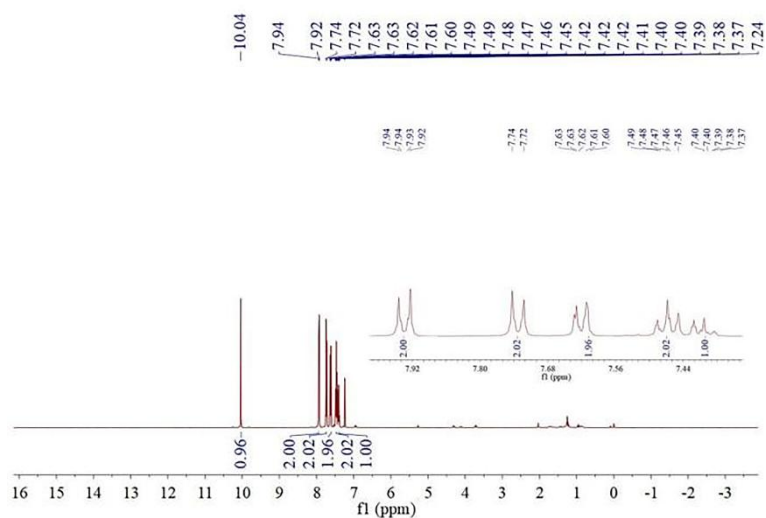
White solid,  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.54 - 7.47 (m, 2H), 7.47 - 7.41 (m, 2H), 7.24 - 7.19 (m, 2H), 6.99 - 6.93 (m, 2H), 3.83 (s, 3H), 2.38 (s, 3H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  158.81, 137.99, 136.37, 133.77, 129.46, 127.98, 126.61, 114.18, 54.96, 21.14.<sup>11</sup>



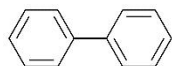
### [1,1'-biphenyl]-4-carbaldehyde (1)



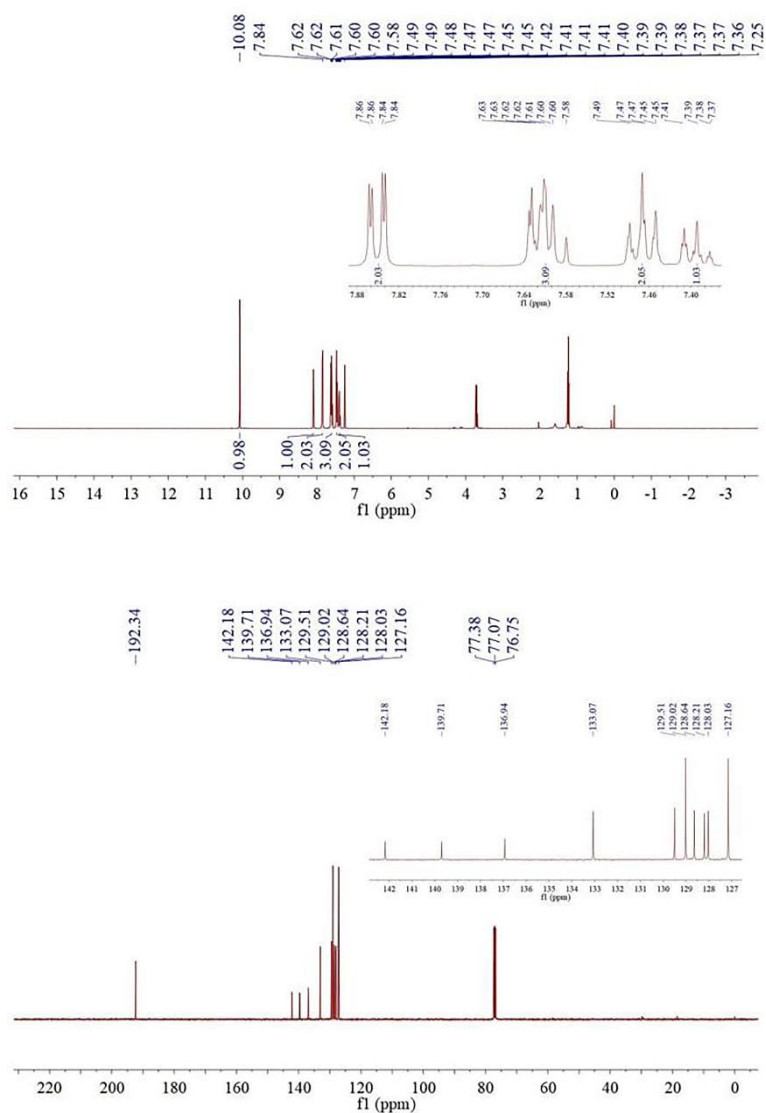
White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.04 (s, 1H), 7.96 - 7.91 (m, 2H), 7.73 (d,  $J = 8.3$  Hz, 2H), 7.64 - 7.58 (m, 2H), 7.51 - 7.44 (m, 2H), 7.44 - 7.37 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  191.88, 147.13, 139.72, 135.22, 130.30, 129.05, 128.51, 127.70, 127.39.<sup>11</sup>



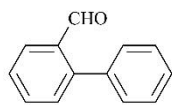
### [1,1'-biphenyl]-3-carbaldehyde (1m)



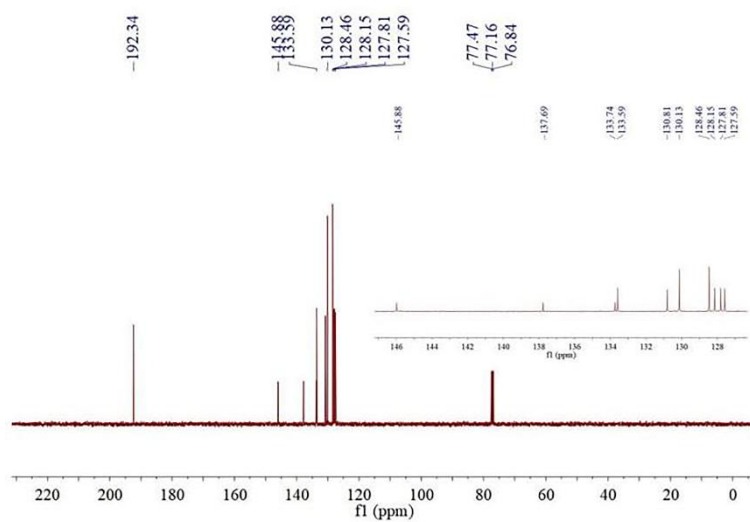
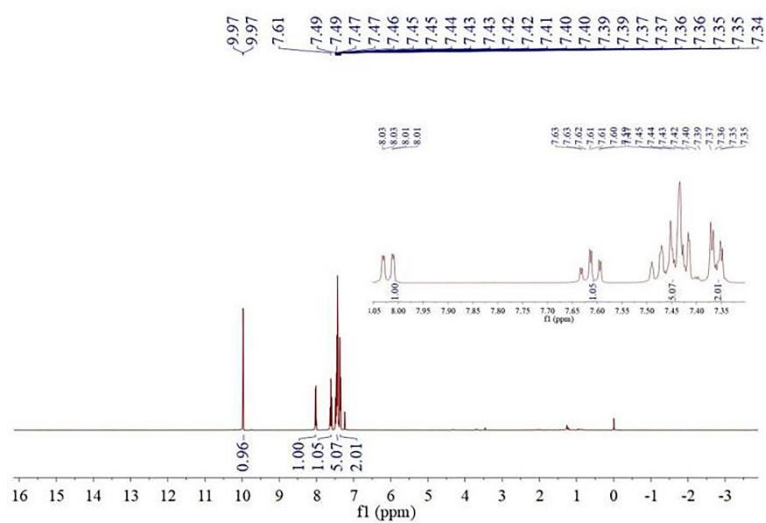
White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  10.08 (s, 1H), 8.09 (t,  $J = 1.6$  Hz, 1H), 7.85 (dd,  $J = 7.7, 1.8$  Hz, 2H), 7.65 - 7.56 (m, 3H), 7.50 - 7.44 (m, 2H), 7.43 - 7.36 (m, 1H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.34, 142.18, 139.71, 136.94, 133.07, 129.51, 129.02, 128.64, 128.21, 128.03, 127.16.<sup>15</sup>



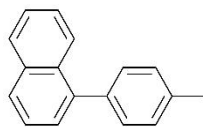
## [1,1'-biphenyl]-2-carbaldehyde (1n)



White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  9.97 (d,  $J = 0.7$  Hz, 1H), 8.02 (dd,  $J = 7.8, 1.3$  Hz, 1H), 7.64 - 7.59 (m, 1H), 7.50 - 7.39 (m, 5H), 7.39 - 7.32 (m, 2H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  192.34, 145.88, 137.69, 133.74, 133.59, 130.81, 130.13, 128.46, 128.15, 127.81, 127.59.<sup>14</sup>



## 1-(*p*-tolyl)naphthalene (1r)



White solid,  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.91 (d,  $J = 8.4$  Hz, 1H), 7.84 (d,  $J = 7.8$  Hz, 1H), 7.81 - 7.76 (m, 1H), 7.49 - 7.40 (m, 2H), 7.40 - 7.34 (m, 4H), 7.25 (d,  $J = 7.8$  Hz, 2H), 2.40 (s, 3H).  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  140.43, 138.01, 137.04, 134.02, 131.92, 130.14, 129.16, 128.44, 127.63, 127.07, 126.28, 126.10, 125.88, 125.58, 21.41.<sup>9</sup>

