# **Electronic Supplementary Information**

## Mechanochemically synthesized covalent organic

### frameworks as catalyst for Suzuki-Miyaura coupling reaction

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#### 1. Materials and Methods

#### 1.1 Materials

All reagents and solvents were obtained commercially and used as received without further purification. All chemicals were purchased from *Bide Pharmatech Ltd*, *Sinopharm Chemical Reagent Co. Ltd*, *Adamas-beta*, and *Aladdin*, and used directly. Solvents were purchased from *Sinopharm Chemical Reagent Co. Ltd* and used directly.

#### **1.2 General Instrumentations and Methods**

**Ball-Milling** reactions were performed in a Retsch cryomill mixer mill (Retsch GmbH, Haan, Germany), using a 5.0 mL stainless-steel jar with one 7 mm-diameter stainless-steel ball and milled at room temperature.

**Powder X-Ray Diffraction (PXRD)** data were collected using a Rigaku Ultima IV with high-intensity Microfocus rotating anode X-ray generator. All the COFs were recorded in the  $2\theta$  range between 2 to 30°. The radiation used was Cu K $\alpha$  ( $\alpha = 1.54$  Å) with a Ni filter, and the data collection was carried out using an aluminium holder at a scan speed of 10° min<sup>-1</sup> and a step size of 0.02°.

**Fourier Transform Infrared (FT-IR)** spectra were obtained using a Bruker Tensor II FTIR spectrometer with KBr pellets in the range of 4000–500 cm<sup>-1</sup>.

**Thermogravimetric Analysis (TGA)** measurements were carried out on a NETZSCH TG 209 F1 Libra analyzer over the temperature range from 30 °C to 800 °C under an N<sub>2</sub> atmosphere with a heating rate of 10 °C min<sup>-1</sup>. Before measurements, the samples were Soxhlet extracted with tetrahydrofuran (THF) for 24 h and then dried at 150 °C under vacuum.

**Scanning Electron Microscopy (SEM)** images were executed with a Genimi SEM 450 microscope. The samples were well dispersed in ethanol and ultrasonicated for 30 minutes, drop cast on a titanium wafer and dried under air, for this measurement, operating at a voltage of 2.0 kV.

**Transmission Electron Microscope (TEM)** images were obtained on a JEM-2011 instrument operated at 200 kV. The samples were well dispersed in ethanol and ultrasonicated for 30 minutes, drop cast on an ultra-thin copper mesh and dried under air.

**High-Resolution Transmission Electron Microscopy (HR-TEM)** measurements were obtained on a JEM-F200 instrument operated at 200 kV. The TEM samples were prepared for analyses by drop casting the samples (dispersed in ethanol) on copper grids

TEM window.

**Brunauer-Emmett-Teller (BET)** was measured by N<sub>2</sub> sorption and desorption using a MicroActive for ASAP 2460 Version 2.02 system. All the COFs samples were outgassed for 12 h at 150 °C under vacuum ( $10^{-5}$  bar) before analysis. The pore size distribution was calculated using the non-localized density functional theory (NLDFT) method. Before measurements, the samples were Soxhlet extracted with THF for 24 h and then dried at 150 °C under vacuum.

**X-Ray Photoelectron Spectroscopy (XPS)** measurements were performed on an X-ray photoelectron spectrometer (Thermo Scientific ESCALAB 250Xi).

**Inductively Coupled Plasma (ICP)** measurements were performed on an Optima 7300 DV inductively coupled plasma atomic emission spectrometer.

**NMR Spectra** were recorded on a Bruker Advance III HD 400 NMR spectrometer (Bruker BioSpin AG, Fällanden, Switzerland; 400 MHz for <sup>1</sup>H NMR; 101 for <sup>13</sup>C NMR) <sup>1</sup>H NMR chemical shifts were determined relative to TMS at 0.00 ppm or CDCl<sub>3</sub> at  $\delta$  7.26 ppm. Data for <sup>1</sup>H NMR are reported as follows: chemical shift ( $\delta$ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, hept = heptet, and m = multiplet).

#### 2. Synthetic Procedures of COFs

2.1 Mechanochemical **MC-Tab-Dva** COF: Synthesis of 1,4-Benzenedicarboxaldehyde (Dva) (22.3 mg, 0.12 mmol) and 1.3.5-tris(4aminophenyl)benzene (Tab) (28.0 mg, 0.08 mmol) were placed in a 5.0 mL stainless steel jar, together with one 7 mm-diameter stainless steel ball, 10 µL of 1,2dichlorobenzene (o-DCB), 10 µL of n-butanol (n-BuOH), and 5 µL of 6 M acetic acid (HOAc). The different milling time and frequency of synthesis were screened and shown in Fig. S1. In the optimized procedure, the reaction mixture was ground at 20 Hz for 30 min. The powder was Soxhlet extracted with THF and then dried at 150 °C under vacuum for 24 h to give MC-Tab-Dva COF (47.0 mg, 94% yield) as luminous yellow powder.

**2.2 Mechanochemical Synthesis of MC-Tz-Dva COF:** Dva (22.3 mg, 0.12 mmol) and 2,4,6-tris(4-aminophenyl)-1,3,5-triazine (Tz) (28.4 mg, 0.08 mmol) were placed in a 5.0 mL stainless steel jar, together with one 7 mm-diameter stainless steel ball, 10  $\mu$ L of *o*-DCB, 10  $\mu$ L of *n*-BuOH, and 10  $\mu$ L of pure HOAc. The different milling time and frequency of synthesis were screened and shown in Fig. S2. In the optimized procedure, the reaction mixture was ground at 15 Hz for 60 min. The powder was Soxhlet extracted with THF and then dried at 150 °C under vacuum for 24 h to give MC-Tz-Dva COF (45.2 mg, 89% yield) as brilliant yellow powder.



Fig. S1 PXRD patterns of MC-Tab-Dva COF under different ball-milling conditions.



Fig. S2 PXRD patterns of MC-Tz-Dva COF under different ball-milling conditions.

#### 3. Structure Modelling and Powder X-Ray Diffraction Analysis

Molecular modelling of the MC-Tab-Dva COF and MC-Tz-Dva COF was generated by using the Materials Studio 2019 suite of programs. Pawley refinement was carried out by using Reflex, a software package for crystal determination from the PXRD pattern. The unit cell dimension was set to the theoretical parameters. Pawley refinement was performed to iteratively optimize the lattice parameters until the  $R_{wp}$ and  $R_p$  value converged, and the overlay observed with refined profiles showed good consistency.



Fig. S3 PXRD patterns of the COFs and the corresponding simulated structures

**Table S1**Unit cell parameters and atomic coordinates of MC-Tab-Dva COF based onthe AA topology.

MC-Tab-Dva COF			
Space-group: P1(1)			
a = 37.5442 Å; $b = 3$	87.2924 Å; <i>c</i> = 3.5170	Å	
$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	C		
Atom name	x/a	y/b	z/c
C1	1.34740	0.72798	-0.01841
C2	1.30446	0.70951	-0.01841
C3	1.27910	0.66638	-0.01841
C4	1.29739	0.64155	-0.01841
C5	1.34029	0.65921	-0.01841
C6	1.36495	0.70248	-0.01841
C7	1.37363	0.77363	-0.01841
C8	1.35923	0.63263	-0.01841
С9	1.23378	0.64750	-0.01841
C10	1.33455	0.58931	-0.01841
C11	1.35238	0.56420	-0.01841
C12	1.39512	0.58192	-0.01841
C13	1.42001	0.62521	-0.01841
C14	1.40216	0.65029	-0.01841
C15	1.41668	0.79238	-0.01841
C16	1.44136	0.83548	-0.01841
C17	1.42344	0.86053	-0.01841
C18	1.38042	0.84198	-0.01841
C19	1.35580	0.79893	-0.01841
C20	1.21570	0.67258	-0.01841
C21	1.17299	0.65493	-0.01841

C22	1.14761	0.61194	-0.01841
C23	1.16543	0.58661	-0.01841
C24	1.20817	0.60430	-0.01841
N25	1.41241	0.55533	-0.01841
C26	1.45163	0.56901	-0.01841
C27	1.46941	0.54155	-0.01841
C28	1.44623	0.49775	-0.01841
C29	1.46707	0.47532	-0.01841
C30	1.50994	0.49495	-0.01841

**Table S2**Unit cell parameters and atomic coordinates of MC-Tz-Dva COF based onthe AA topology.

MC-Tz-Dva COF			
Space-group: P1(1)			
a = 37.1485 Å; $b = 3$	37.1342 Å; c = 3.5122	Å	
$\alpha = \beta = 90^\circ; \gamma = 120^\circ$	0		
Atom name	x/a	y/b	z/c
C1	1.29380	-0.32749	-0.00253
C2	1.31208	-0.35132	-0.00253
C3	1.35415	-0.33339	-0.00253
C4	1.37798	-0.29127	-0.00253
C5	1.36005	-0.26711	-0.00253
C6	1.31795	-0.28540	-0.00253
C7	1.24816	-0.34712	-0.00253
C8	1.38605	-0.22145	-0.00253
С9	1.37378	-0.35941	-0.00253
C10	1.34928	-0.40288	-0.00253
C11	1.36787	-0.42759	-0.00253
C12	1.41115	-0.40921	-0.00253
C13	1.43579	-0.36566	-0.00253
C14	1.41719	-0.34099	-0.00253
C15	1.22922	-0.32259	-0.00253
C16	1.18594	-0.34117	-0.00253
C17	1.16102	-0.38446	-0.00253
C18	1.17989	-0.40913	-0.00253
C19	1.22316	-0.39054	-0.00253
C20	1.42951	-0.20247	-0.00253
C21	1.45419	-0.15917	-0.00253
C22	1.43580	-0.13427	-0.00254
C23	1.39227	-0.15318	-0.00254

C24	1.36762	-0.19647	-0.00254
N25	1.42923	-0.43538	-0.00253
C26	1.46902	-0.42096	-0.00253
C27	1.48656	-0.44880	-0.00253
C28	1.45994	-0.49196	-0.00253
C29	1.47556	-0.51939	-0.00253
C30	1.51887	-0.50314	-0.00253

#### 4. Characterizations of COFs.



**Fig. S4** Full XPS spectra of (a) MC-Tab-Dva and (b) MC-Tz-Dva COFs; high-resolution XPS C 1s spectra of (c) MC-Tab-Dva and (d) MC-Tz-Dva COFs; high-resolution XPS N 1s spectra of (e) MC-Tab-Dva and (f) MC-Tz-Dva COFs.



**Fig. S5** FT-IR spectra of (a) MC-Tab-Dva and (b) MC-Tz-Dva COFs; The 13C CP-MAS NMR spectra of (c) MC-Tab-Dva and (d) MC-Tz-Dva COFs.



**Fig. S6** Nitrogen sorption isotherms at 77 K of (**a**) MC-Tab-Dva and (**d**) MC-Tz-Dva COFs; Pore size distributions of (**c**) MC-Tab-Dva and (**d**) MC-Tz-Dva COFs; TG curves of (**e**) MC-Tab-Dva and (**f**) MC-Tz-Dva COFs.



**Fig. S7** Chemical stability of (a) MC-Tab-Dva and (b) MC-Tz-Dva COFs monitored by the PXRD profiles for the COF samples treated for 2 days in different solvents compared to the as-synthesized COFs.



**Fig. S8** Chemical stability comparison of (a) MC-Tab-Dva and (b) MC-Tz-Dva COFs monitored by PXRD profiles for the COF samples treated for 24 h in acidic and alkaline conditions.



**Fig. S9** SEM images of (a) MC-Tab-Dva and (b) MC-Tz-Dva COFs; TEM images of (c) MC-Tab-Dva and (d) MC-Tz-Dva COFs; (e, f) HR-TEM images of MC-Tab-Dva COF.

**5. Mechanochemical Synthesis of MC-Tab-Pda COF:** Tab (28.0 mg, 0.08 mmol) and terephthalaldehyde (Pda) (16.1 mg, 0.08 mmol) were placed in a 5.0 mL stainless steel jar, together with one 7 mm- diameter stainless steel ball, 10  $\mu$ L of *o*-DCB, 10  $\mu$ L of *n*-BuOH, and 10  $\mu$ L HOAc. Then, the reaction mixture was ground at 20 Hz for 30 min in 39.8 mg (90% yield) as a bright yellow powder.



Fig. S10 Synthesis of MC-Tab-Pda COF under ball-milling conditions.



**Fig. S11** PXRD patterns of MC-Tab-Pda COF under different ball-milling conditions. (a) 10  $\mu$ L of HOAc milled at 15 Hz for 60 min; (b) 10  $\mu$ L of 6 M HOAc milled at 20 Hz for 30 min; (c) 5  $\mu$ L of 6 M HOAc milled at 20 Hz for 30 min; (d) 10  $\mu$ L of HOAc milled at 20 Hz for 30 min; (e) 5  $\mu$ L of HOAc milled at 20 Hz for 30 min.

6. Larger Scale Experiment: Dva (224.0 mg, 1.2 mmol) and Tab (280.0 mg, 0.8 mmol) were placed in a 10.0 mL stainless steel jar, together with one 7 mm-diameter stainless steel ball, ~100  $\mu$ L of *o*-DCB, ~100  $\mu$ L of *n*-BuOH, and ~50  $\mu$ L of 6 M HOAc, the reaction mixture was ground at 20 Hz for 90 min. Then, the high crystallinity product could be obtained in 421.2 mg (84% yield) as luminous yellow powder.



Fig. S12 Large-scale mechanosynthesis of MC-Tab-Dva COF.

#### 7. Synthetic Procedures of Pd@COFs

**7.1 Synthesis of Pd@MC-Tab-Dva COF:** Following a known literature procedure,<sup>1</sup> palladium acetate (27.2 mg) was dissolved in 4.0 mL of dichloromethane (DCM), then MC-Tab-Dva COF (100.0 mg) was added. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the powder was isolated by using Soxhlet extraction with DCM for 24 h, then dried at 120 °C under vacuum for 12 h to yield Pd@MC-Tab-Dva COF in 118.3 mg (93% yield) as a brownish yellow powder.

**7.2 Synthesis of Pd@MC-Tz-Dva COF:** Following a known literature procedure,<sup>1</sup> palladium acetate (27.2 mg) was dissolved in 4.0 mL of DCM, then MC-Tz-Dva COF (100.0 mg) was added. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the powder was isolated by using Soxhlet extraction with DCM for 24 h, then dried at 120 °C under vacuum for 12 h to yield Pd@MC-Tz-Dva COF in 115.3 mg (90% yield) as a brownish yellow powder.

**7.3 Synthesis of Pd@Tab:** A mixture of palladium acetate (0.18 mmol, 40.4 mg) and Tab (0.06 mmol, 21.1 mg) was dissolved in 4.0 mL of DCM. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the powder was isolated by using filtration, then dried at 120 °C under vacuum for 12 h to yield Pd@Tab as a brownish yellow powder.

**7.4 Synthesis of Pd@Tz:** A mixture of palladium acetate (0.18 mmol, 40.6 mg) and Tab (0.06 mmol, 21.3 mg) was dissolved in 4.0 mL of DCM. The mixture was stirred at room temperature for 24 h. After completion of the reaction, the powder was isolated by using filtration, then dried at 120 °C under vacuum for 12 h to yield Pd@Tz as a brownish yellow powder.



**Fig. S13** FT-IR spectra of (a) Pd@MC-Tab-Dva and (b) Pd@MC-Tz-Dva COFs compared to the as-synthesized COFs.





**Fig. S14** Full XPS spectra of (a) Pd@MC-Tab-Dva and (b) Pd@MC-Tz-Dva COFs, high-resolution XPS C 1s spectra of (c) Pd@MC-Tab-Dva and (d) Pd@MC-Tz-Dva COFs, high-resolution XPS N 1s spectra of (e) Pd@MC-Tab-Dva and (f) Pd@MC-Tz-Dva COFs. high-resolution XPS Pd 3d spectra of (g) Pd@MC-Tab-Dva and (h) Pd@MC-Tz-Dva COFs. high-resolution XPS Pd 3d spectra of (i) Pd@Tab and (j) Pd@Tz.



Fig. S15 PXRD patterns of (a) Pd@MC-Tab-Dva and (b) Pd@MC-Tz-Dva COFs compared to the as-synthesized COFs.



Fig. S16 TEM images of (a) Pd@MC-Tab-Dva and (b) Pd@MC-Tz-Dva COFs.



**Fig. S17** EDS elemental mapping of Pd@MC-Tab-Dva COF (a) C, (b) N, and (c) Pd. EDS elemental mapping of Pd@MC-Tz-Dva COF (d) C, (e) N, and (f) Pd.

#### 8. Catalytic Activity of COFs

#### 8.1 General Procedure

#### Suzuki-Miyaura Coupling Reaction

In our initial investigation, we selected bromobenzene and phenylboronic acid as model substrates and evaluated their reactivity under various reaction conditions in the presence of Pd@COFs (Table S3). When toluene, acetonitrile, THF and methanol were used as solvents, biphenyl was obtained in yields ranging from 13% to 95% (Table S3, entries 1–4). Gratifyingly, when *p*-xylene was employed as the solvent, the product was isolated in 99% yield (Table S3, entry 5). Other inorganic bases such as potassium hydroxide (KOH) and cesium carbonate (Cs<sub>2</sub>CO<sub>3</sub>) showed lower yields of 65% and 56%, respectively (Table S3, entries 6 and 7). When organic bases like triethylamine (Et<sub>3</sub>N) and triethylenediamine (DABCO) were used, only trace and 6% yield were obtained (Table S3, entries 8 and 9). By decreasing the amount of potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) from 2.0 equiv. to 1.0 equiv., the product yield also decreased to 87% (Table S3, entry 10). Both increasing and decreasing the amount of the catalyst resulted in lower yields (Table S3, entries 11 and 12). Changing the temperature to either 120 °C or 100 °C resulted in lower efficiency (Table S3, entries 13 and 14). When Pd@MC-Tz-Dva COF was used as a catalyst, an excellent yield of 98% could also be obtained (Table S3, entry 15).

Br +	B(OH) <sub>2</sub>	Pd@MC-Tab-Dva COF base solvent, <i>T</i> °C, 2 h	
entry	base	solvent	yield $(\%)^b$
1	$K_2CO_3$	toluene	95
2	$K_2CO_3$	acetonitrile	48
3	$K_2CO_3$	THF	13
4	$K_2CO_3$	methanol	93
5	$K_2CO_3$	<i>p</i> -xylene	99
6	KOH	<i>p</i> -xylene	65
7	$Cs_2CO_3$	<i>p</i> -xylene	56
8	Et <sub>3</sub> N	<i>p</i> -xylene	trace
9	DABCO	<i>p</i> -xylene	6
$10^{c}$	K <sub>2</sub> CO <sub>3</sub>	<i>p</i> -xylene	87
$11^{d}$	K <sub>2</sub> CO <sub>3</sub>	<i>p</i> -xylene	90
$12^e$	K <sub>2</sub> CO <sub>3</sub>	<i>p</i> -xylene	75
13 <sup>f</sup>	$K_2CO_3$	<i>p</i> -xylene	90
$14^{g}$	$K_2CO_3$	<i>p</i> -xylene	84
$15^{h}$	K <sub>2</sub> CO <sub>3</sub>	<i>n</i> -xvlene	98

Table S3 Optimization of the reaction conditions<sup>a</sup>

<sup>*a*</sup>Unless otherwise noted, all reactions were performed with bromobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), Pd@MC-Tab-Dva COF (2.0 mol%, 20.0 mg), and K<sub>2</sub>CO<sub>3</sub> (2.0 equiv.) in solvent (4.0 mL) at 150 °C for 2 h under air atmosphere. <sup>*b*</sup>Isolated yields. <sup>*c*</sup>K<sub>2</sub>CO<sub>3</sub> (1.0 equiv.). <sup>*d*</sup>Pd@MC-Tab-Dva COF (30.0 mg). <sup>*e*</sup>Pd@MC-Tab-Dva COF (10.0 mg). <sup>*f*</sup>120 °C. <sup>*g*</sup>100 °C. <sup>*h*</sup>Pd@MC-Tz-Dva COF instead of Pd@MC-Tab-Dva COF.

In a typical run of catalytic activity, bromobenzene (1.0 mmol), phenylboronic acid (1.5 equiv., 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276.0 mg, 2.0 equiv.) and Pd@MC-Tab-Dva COF or Pd@MC-Tz-Dva COF (2.0 mol%, 20.0 mg) were added to 4.0 mL of *p*-xylene. The reaction mixture was stirred at 150 °C under reflux under an ambient atmosphere. After the reaction was completed, the organic phase was then evaporated under vacuum to leave the crude products, which were further purified by column chromatography over silica gel to obtain the desired product.

#### **Control Experiment**

A mixture of Pd@MC-Tab-Dva COF and K<sub>2</sub>CO<sub>3</sub> was added to 4.0 mL of *p*-xylene, heated at 150  $^{\circ}$ C, and stirred for 5 h under ambient atmosphere. After the reaction was completed, the hot mixture was filtrated to remove the residue. Then, bromobenzene and phenylbornic acid were added to the filtrate. The mixture was stirred at 150  $^{\circ}$ C for 2 h. It was found that no biphenyl could be isolated.

#### Mechanism of Suzuki-Miyaura Coupling in the Presence of Pd@MC COFs

Based on the above results and prior literature,<sup>1</sup> a plausible mechanism for the Pd@MC COF-catalyzed Suzuki-Miyaura coupling reaction is proposed. The process begins with Pd@MC COFs undergoing ligand exchange and reductive elimination to generate a Pd(0) species A.<sup>1b,1d</sup> This Pd(0) species then participates in an oxidative addition with the aryl halide substrate, forming a Pd(II) intermediate **B**. Subsequent ligand exchange with K<sub>2</sub>CO<sub>3</sub> converts intermediate **B** into intermediate **C**.<sup>1b</sup> In the transmetalation step, arylboronic acid **D** reacts with intermediate **C** under basic conditions, yielding a biaryl palladium complex **E**. Finally, reductive elimination forms the biaryl product **F** while regenerating the Pd(0) species, completing the catalytic cycle.

![](_page_17_Figure_0.jpeg)

Fig. S18 Mechanism of Suzuki-Miyaura coupling in the presence of Pd@MC COFs.

**8.2 Recycling Test:** In the recycling test, bromobenzene (112  $\mu$ L, 1.0 mmol), phenylboronic acid (183.0 mg, 1.5 mmol), K<sub>2</sub>CO<sub>3</sub> (276.0 mg, 2.0 equiv.), and Pd@MC-Tab-Dva COF (30.0 mg) were added to 4.0 mL of *p*-xylene, and the reaction mixture was stirred at 150 °C for 2 h. After each cycle, the catalyst was obtained by suction filtration, washed with H<sub>2</sub>O, and dried at 100 °C for 8 h, and then used directly without other treatment.

![](_page_17_Figure_3.jpeg)

Fig. S19 Reusability of Pd@MC-Tab-Dva COF in the Suzuki-Miyaura coupling reaction.

![](_page_18_Figure_0.jpeg)

Fig. S20 FT-IR spectra of (a) Pd@MC-Tab-Dva and (b) Pd@MC-Tz-Dva COFs compared to the recycled COFs.

![](_page_18_Figure_2.jpeg)

Fig. S21 PXRD patterns of Pd@MC-Tab-Dva COF after recycling.

#### 9. NMR Data of Cross-Coupling Products

#### 1,1'-biphenyl<sup>2</sup>

Yield (153.0 mg, 99%); Prepared according to the typical procedure with bromobenzene and phenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.63–7.59 (m, 4H), 7.48–7.43 (m, 4H), 7.36 (tt, *J* = 7.4, 1.2 Hz, 2H).

#### 4-methyl-1,1'-biphenyl<sup>2</sup>

Yield (164.7 mg, 98%); Prepared according to the typical procedure with 4bromotoluene and phenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.59–7.56 (m, 2H), 7.50 (d, J = 8.4 Hz, 2H), 7.45–7.40 (m, 2H), 7.32 (tt, J = 7.4, 1.2 Hz, 1H), 7.25 (d, J = 8.0 Hz, 2H), 2.40 (s, 3H).

#### **2-methyl-1,1'-biphenyl**<sup>3</sup>

![](_page_19_Figure_4.jpeg)

Yield (127.7 mg, 76%); Prepared according to the typical procedure with 2bromotoluene and phenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.40–7.35 (m, 2H), 7.32–7.26 (m, 3H), 7.25–7.20 (m, 4H), 2.25 (s, 3H).

#### 3-methyl-1,1'-biphenyl<sup>3</sup>

![](_page_19_Figure_7.jpeg)

Yield (144.6 mg, 86%); Prepared according to the typical procedure with 3bromotoluene and phenylboronic acid. The product was collected as a yellowish solid after silica gel chromatography (petroleum ether). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.47– 7.43 (m, 2H), 7.31–7.25 (m, 4H), 7.21–7.16 (m, 2H), 7.02 (d, J = 7.6 Hz, 1H), 2.28 (s, 3H).

#### 4-methoxy-1,1'-biphenyl<sup>2</sup>

![](_page_19_Figure_10.jpeg)

Yield (147.3 mg, 80%); Prepared according to the typical procedure with 4bromoanisole and phenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether : ethyl acetate = 98:2). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.56–7.50 (m, 4H), 7.43–7.38 (m, 2H), 7.29 (tt, *J* = 7.2, 1.2 Hz, 1H), 6.99– 6.95 (m, 2H), 3.83 (s, 3H).

#### [1,1'-biphenyl]-4-carbonitrile<sup>4</sup>

![](_page_20_Picture_0.jpeg)

Yield (166.5 mg, 93%); Prepared according to the typical procedure with 4bromobenzonitrile and phenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether : ethyl acetate = 99:1).<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.74 (d, *J* = 8.6 Hz, 2H), 7.69 (d, *J* = 8.6 Hz, 2H), 7.61–7.57 (m, 2H), 7.52–7.46 (m, 2H), 7.43 (tt, *J* = 7.2, 1.2 Hz, 1H).

#### 2-phenylnaphthalene<sup>2</sup>

![](_page_20_Figure_3.jpeg)

Yield (189.8 mg, 93%); Prepared according to the typical procedure with 1bromonaphthalene and phenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether : ethyl acetate = 99:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.05 (s, 1H), 7.94–7.85 (m, 3H), 7.77–7.72 (m, 3H), 7.54–7.46 (m, 4H), 7.39 (t, *J* = 7.2 Hz, 1H).

#### 4-isopropyl-1,1'-biphenyl<sup>4</sup>

![](_page_20_Figure_6.jpeg)

Yield (190.2 mg, 97%); Prepared according to the typical procedure with bromobenzene and 4-isopropylbenzeneboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether : ethyl acetate = 99:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.58–7.54 (m, 2H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.30 (tt, *J* = 7.4, 1.2 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.65–4.55 (hept, *J* = 6.0 Hz, 1H), 1.37 (d, *J* = 6.0 Hz, 6H).

#### 4-(tert-butyl)-1,1'-biphenyl<sup>5</sup>

![](_page_20_Figure_9.jpeg)

Yield (208.0 mg, 99%); Prepared according to the typical procedure with bromobenzene and 4-tert-butylphenylboronic acid. The product was collected as a white solid after silica gel chromatography (petroleum ether : ethyl acetate = 99:1). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.61–7.57 (m, 2H), 7.55 (d, *J* = 8.0 Hz, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 2H), 7.33 (tt, *J* = 7.4, 1.2 Hz, 1H), 1.37 (s, 9H).

#### 10. References

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![](_page_22_Figure_0.jpeg)

#### 11. NMR Spectra of Cross-Coupling Products

Figure S22 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 1,1'-biphenyl

![](_page_22_Figure_3.jpeg)

Figure S23 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 4-methyl-1,1'-biphenyl

![](_page_23_Figure_0.jpeg)

Figure S24 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-methyl-1,1'-biphenyl

![](_page_23_Figure_2.jpeg)

Figure S25 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 3-methyl-1,1'-biphenyl

![](_page_24_Figure_0.jpeg)

Figure S26 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 4-methoxy-1,1'-biphenyl

![](_page_24_Figure_2.jpeg)

Figure S27<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of [1,1'-biphenyl]-4-carbonitrile

![](_page_25_Figure_0.jpeg)

Figure S28 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 2-phenylnaphthalene

![](_page_25_Figure_2.jpeg)

Figure S29 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 4-isopropyl-1,1'-biphenyl

![](_page_26_Figure_0.jpeg)

Figure S30 <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) of 4-(tert-butyl)-1,1'-biphenyl