Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Construction of a transition-metal-free mesoporous organic phenanthroline-based polymeric catalyst for boosting direct activation of aromatic C-H bonds

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Experimental Section

Materials

4,7-diphenyl-1,10-phenanthroline (Phen) was purchased from Bidepharm Co., Ltd (Shanghai, China). Dichloromethane, 1, 2-dichloroethane and potassium tert-butoxide (KOtBu) were obtained from Innochem science & technology Co., Ltd (Beijing, China). Concentrated hydrochloric acid and ethanol were purchased from Titan chemical Co., Ltd (Shanghai, China). Anhydrous aluminum chloride, aromatic hydrocarbons and benzene were obtained from Aladdin chemical reagent Corp (Shanghai, China). Aryl halides were purchased from Adamas-beta reagent Co., Ltd (Shanghai, China). All the above reagents are used as received. Unless in any other case noted, all reagents were obtained from commercial suppliers and used without further purification.

Synthesis of the phenanthroline-based polymer (POP-Phen-E)

Under a N_2 atmosphere, 4, 7-diphenyl-1,10-phenanthroline (1.50 mmol, 0.50 g) was dissolved in 1, 2-dichloroethane (DCE, 15 mL) by sonication and stirring for 10 minutes, and then the catalyst ($AlCl_3$, 24.06 mmol, 3.20 g) was added at room temperature, and the reaction system connected the nitrogen package to form a relatively less air-controlled environment. The reaction system was then stirred in sequence at 0 ℃ for 4 h (ice water mixture), at 30 ℃ for 8 h, at 40 ℃ for 12 h, at 60 ℃ for 12 h, and at 80 ℃ for 24 h to obtain a porous organic phenanthroline-based polymer. The resulting precipitate was cooling down to the room temperature and quenched subsequently with $HCl\text{-}H_2O$ mixture [2:1 (v/v)], then washed thrice with water and thrice with ethanol, purified by Soxhlet extraction with ethanol for 48 h, and finally dried in a vacuum oven at 80 ℃ for 24 h. The POP-Phen-E was obtained as a darkish brown solid with a yield of 393.5% with respect to the Phen-monomers feed (Scheme 1); the observation of high yield was traditional in the solvent-knitted polymerization method. The as-prepared POP-Phen-E was stable in air and insoluble in common solvents such as water (H_2O), ethanol (EtOH), dichloromethane (DCM), dimethyl sulfoxide (DMSO) and dimethylformamide (DMF).

The yield is calculated according to the formula is as follows:

$$\text{yield}=\frac{m2}{m1}\times 100\%$$

m2: the quality of POP-Phen-X powder obtained

m1: the quality of 4,7-diphenyl-1,10-phenanthroline monomers

Synthesis of the phenanthroline-based polymer (POP-Phen-M)

This material was synthesized by using the same method of POP-Phen-E, this POP was produced by treating 4, 7-diphenyl-1, 10-phenanthroline (1.50 mmol, 0.50 g) with $AlCl_3$ (24.06 mmol, 3.20 g) in dichloromethane (15 mL). The material was obtained as a darkish brown solid (yield, 143.4%).

Characterization

Fourier Transform Infrared Spectrometer (FT-IR) spectra were recorded on an Agilent Cary

630 using the KBr disk method. Solid-state ^{13}C CP/MAS NMR spectra measurements of the sample were conducted at 14.01 T using a JNM-ECZ600R spectrometer operating at a ^{1}H resonance frequency of 599.7 MHz with a spinning rate of 12 kHz. The products of the transformation of aryl halides into biaryl compounds were characterized by Agilent Technologies 5977A MSD gas chromatography-mass spectrometry (GC-MS) analysis employing HP-5 (30 m × 0.25 mm × 0.25 μm) column and thermal conductivity detector (TCD). Yield of biaryl compounds was determined by Agilent Technologies 7820A gas chromatography (GC) analysis using HP-5 (30 m × 0.25 mm × 0.25 μm) column and flame ionization detector (FID). The products of the transformation of aryl halides into biaryl compounds were identified from ^{1}H and ^{13}C NMR spectra, which were obtained using a Bruker AVANCE III HD 400MHZ instrument and DMSO-d6 as the solvent. The N element content data was obtained by organic elemental analysis (EA) on a Vario MACRO cube/Thermo FLASH 2000/PE 2400II. X-ray diffraction (XRD) patterns were operated on a DX-3 diffractometer (Puxi) with a scan speed of 1°/min from 5° to 60° using Cu Kα (λ = 1.5418 Å) at 40 kV and 40 mA. Thermo gravimetric analysis (TGA) was performed from room temperature to 1000°C under a nitrogen atmosphere, employing a Q600 SDT Thermal analyzer with a heating rate of 10 °C min^{-1}. The specific surface area and pore size distribution were determined by autosorb iQ/AsiQwin analyzer (Quantachrome) at 77.3 K. Before the analysis, the samples were degassed at 120°C for 24 h. The specific surface areas were calculated by the multipoint BET (Brunauer-Emmett-Teller) method and the pore size distribution were obtained by the density functional theory (DFT) method. The Al contents were measured by Inductively Coupled Plasma Optical Emission Spectrometry on Agilent 5100 ICP-OES. Transmission electron microscopy (TEM) images were acquired by Talos F200x instruments with a high-resolution transmission electron microscopy-energy-dispersive. Scanning electron microscopy (SEM) images were viewed on a scan electronic microscopy (JSM-6701F) operated at 10 kV. Before measurement, the samples were dried in a vacuum oven at 80°C for 24 h and then sputter coated with platinum.

Catalytic Tests

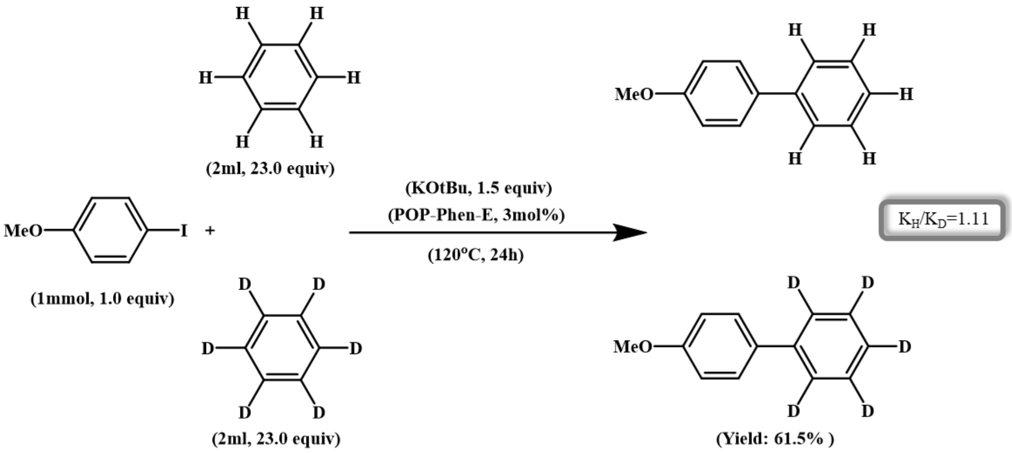
General procedure for the chemical transformation of aryl halides into biaryl compounds

Initially, we compared the catalytic performance of two porous organic polymers (POP-Phen-M and POP-Phen-E). POP-Phen-E catalyzed 4-iodoanisole to synthesize 4-methoxybiphenyl with the best yield, so we used POP-Phen-E as the catalyst in the following research (Table 2). The general procedure of the reaction is as follows, a Schlenk tube was charged with POP-Phen-E (0.03 mmol, 0.06 equiv), KOtBu (1.5 mmol, 3.0 equiv) and aryl halides (0.5 mmol) under an N_2 atmosphere at room temperature. Benzene (4.0 mL) was then added. The tube was then sealed and the resulting mixture was stirred at 120 °C for 24 h. After cooling down to room temperature, *n*-dodecane (50 µl) was added as an internal standard, and then CH_2Cl_2 (8 mL) was added. The products were analyzed by an Agilent 5977A MSD gas chromatography-mass spectrometry (GC-MS) employing HP-5 (30 m × 0.25 mm × 0.25 µm) column and thermal conductivity detector (TCD). And then the product yields were determined by Agilent Technologies 7820A gas chromatography (GC) using HP-5 (30 m × 0.25 mm × 0.25 µm) column and flame ionization detector (FID). The crude product that needs to be purified is further purified by column chromatography and was assessed using ^{1}H NMR and ^{13}C NMR spectra.

For recycling, the catalyst was separated by centrifugation, washed with THF, water and ethanol, respectively. Dried under vacuum and used directly for the next run. Reaction conditions: 4-iodoanisole (0.5 mmol), KOtBu (1.5 mmol), benzene (4.0 mL), POP-Phen-E (0.03 mmol), 120°C, 24 h.

Kinetic Isotope Effect Experiments

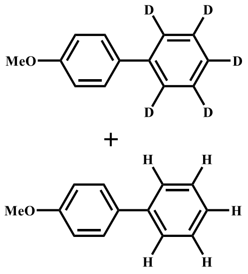
POP-Phen-E (3 mol%), 4-iodoanisole (1.0 mmol, 1.0 equiv), KOtBu (1,5 mmol, 1.5 equiv.), benzene (2.0 mL, 23.0 equiv) and benzene-d_6 (2.0 mL, 23.0 equiv) were added to Schlenk tubes under N_2 atmosphere and then the mixture was stirred in a sealed tube under a N_2 atmosphere at 120°C for 24 h. After cooled to room temperature, the reaction mixture was quenched and extracted with ethyl acetate (10 mL × 3). The organic layers were combined, dried over Na_2SO_4 and concentrated under vacuum, and then purified by silica gel chromatograph to yield the desired product. The product distribution (K_H/K_D=1.11) was analyzed by ^{1}H NMR.



Scheme S1. Kinetic isotopic effects experiment. The yield was isolated yield and K_H/K_D was calculated according to ^{1}H NMR (**Fig. S4.**)

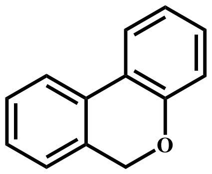
Details of product purification:

product obtained from the kinetic isotopic effects experiment.



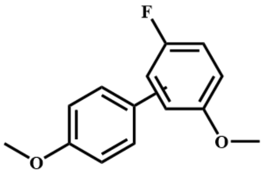
The title compound was prepared according to the general procedure described above using 4-iodoanisole with benzene and benzene-d_6, and purified by flash column chromatography as white solid (100% petroleum).

Product obtained from cyclization reaction (6H-benzo[c]chromene).



The title compound was prepared according to the procedure described above and purified by flash column chromatography as colorless oil (99% petroleum ether / 1% ethyl acetate).

(18ad) Mixture of 4',5-dimethoxy-2-fluorobiphenyl, 2,4'-dimethoxy-5-fluorobiphenyl



The title compounds were prepared according to the general procedure described above using 4-fluoroanisole as solvent, and purified by flash column chromatography as light-yellow oil (98% petroleum ether / 2% ethyl acetate)

Table S1. BET Summary of POP-Phen-M and POP-Phen-E.

Samples	**BET Surface area (m^2 g^{-1})**	**Average pore Diameter (nm)**	**Pore volume (cm^3 g^{-1})**
POP-Phen-M	698	2.4	0.41
POP-Phen-E	522	4.3	0.56

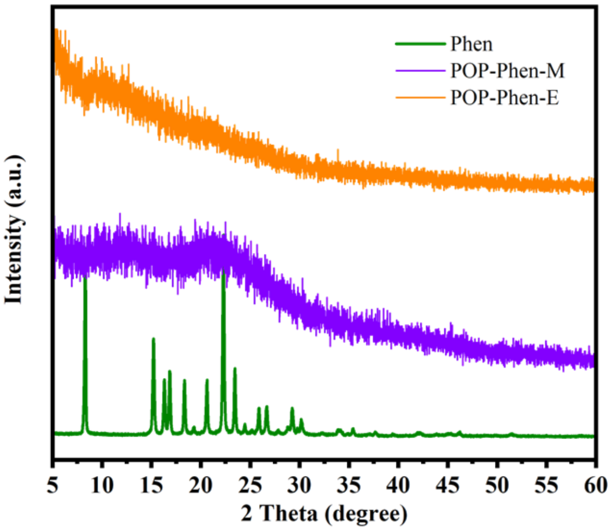


Fig. S1. XRD patterns of the Phen (green), POP-Phen-M (violet) and POP-Phen-E (orange).

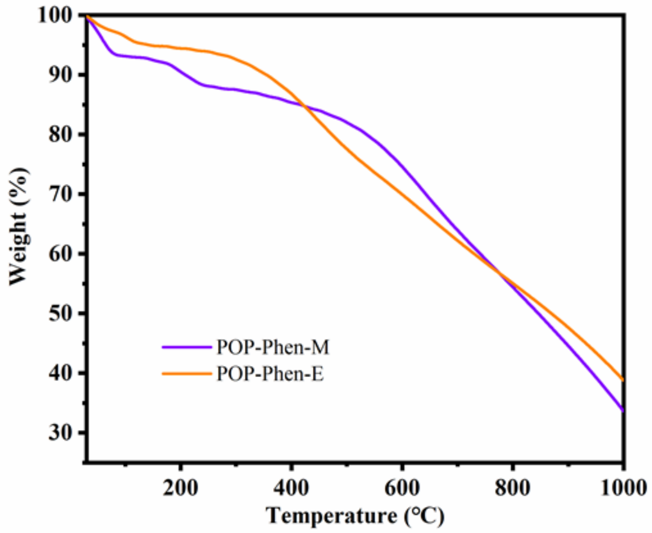


Fig. S2. TGA curves of the POP-Phen-M (violet) and POP-Phen-E (orange) performed under N_2 atmosphere.

Table S2. Inductive coupled plasma emission spectrometer of POP-Phen-M and POP-Phen-E.

Sample	**Content (wt%)**
	Al
POP-Phen-M	0.319
POP-Phen-E	0.428

Table S3. Organic element analysis of POP-Phen-M and POP-Phen-E.

Sample	**Content(wt%)**		
	C	**H**	**N**
POP-Phen-M	69.81	4.91	5.26
POP-Phen-E	77.10	6.00	1.67

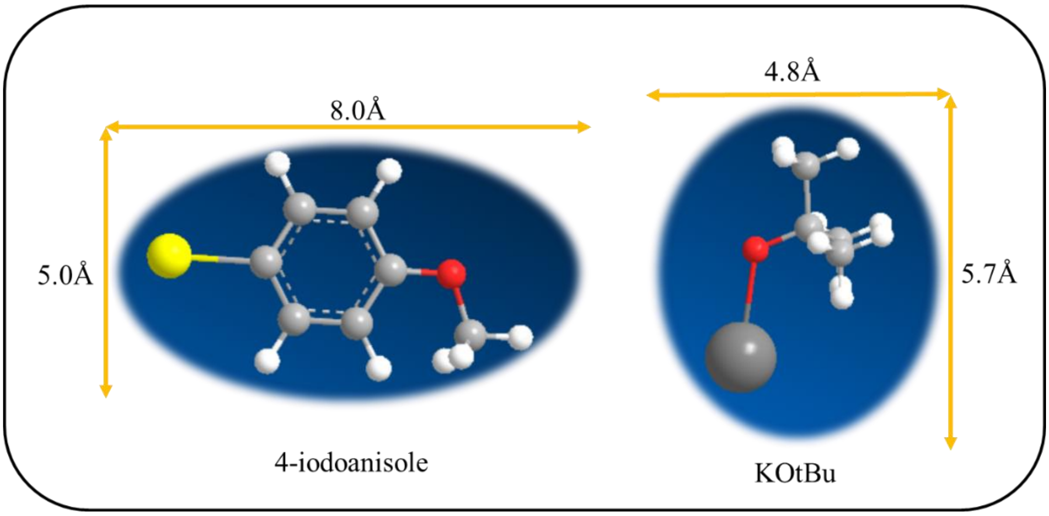


Fig. S3. The molecular size of 4-iodoanisole and KOtBu.

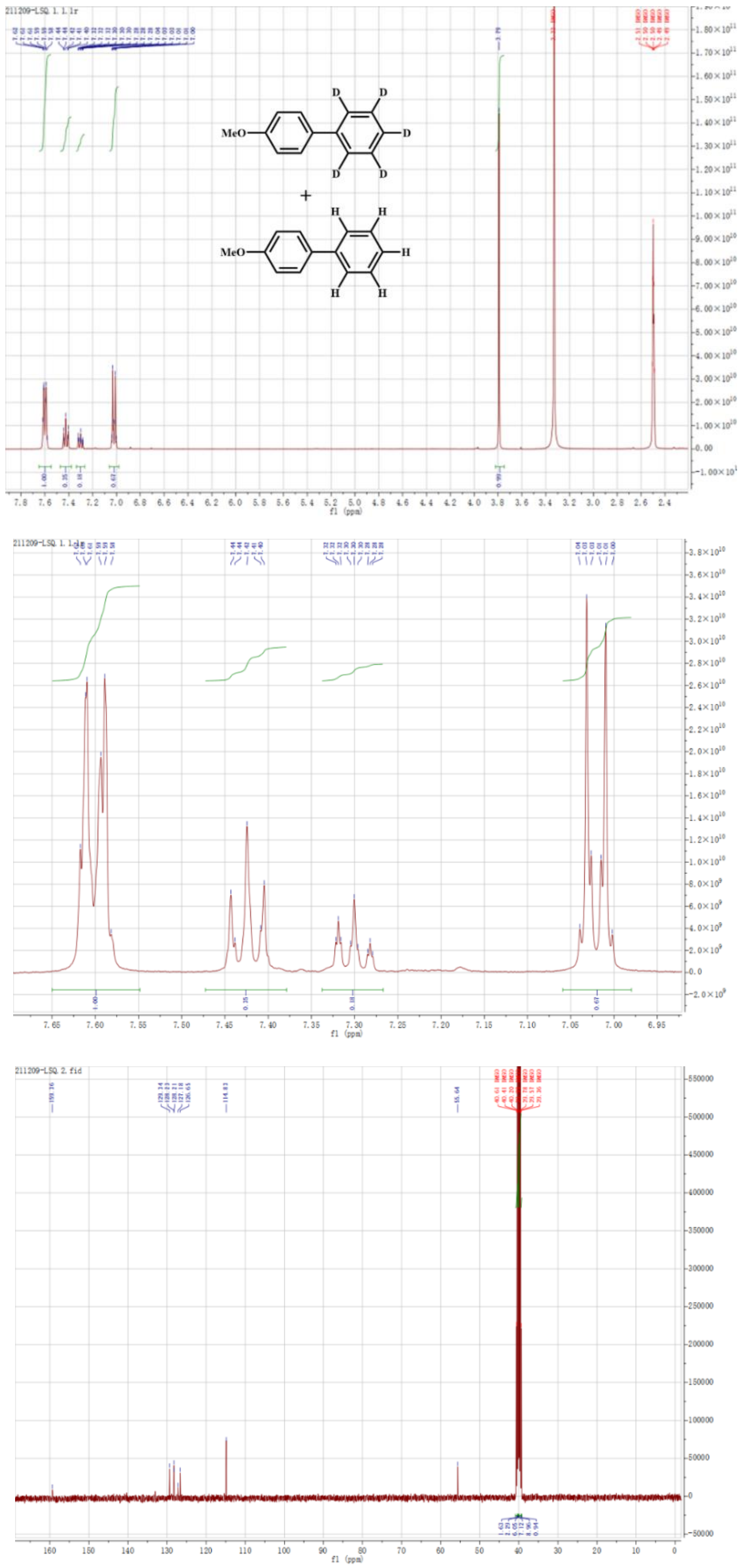
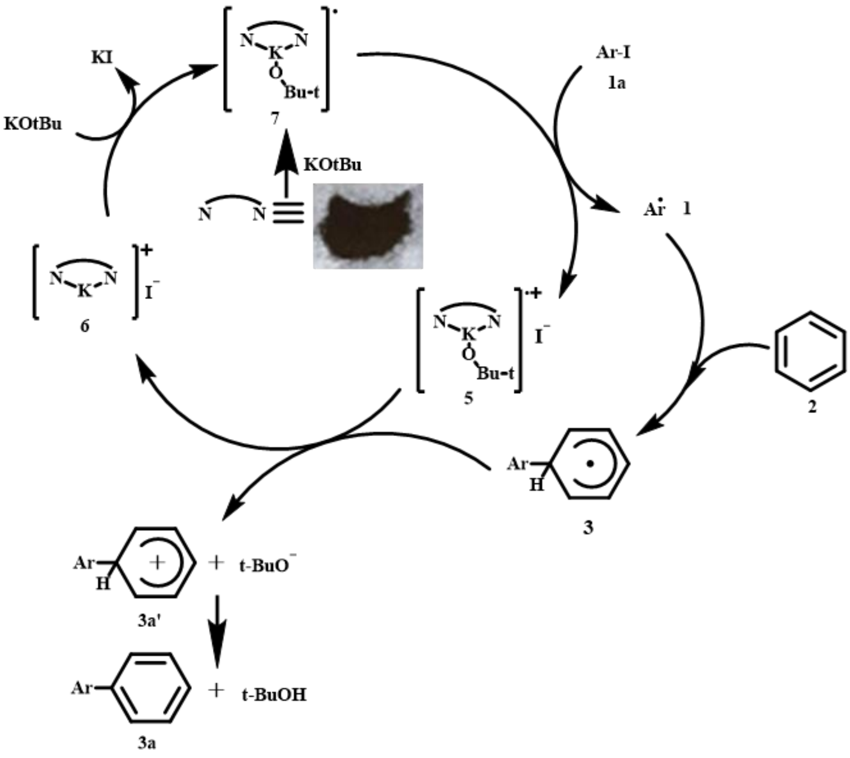


Fig. S4. ^{1}H NMR and ^{13}C NMR spectra of product obtained from the kinetic isotopic effects experiment.



Scheme S2. A plausible mechanism of the direct C−H arylation of benzene with 4-iodoanisole catalyzed by POP-Phen-E .

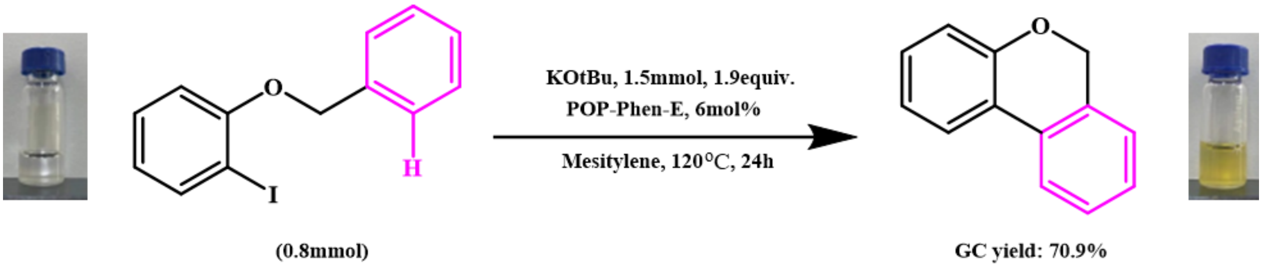


Fig. S5. Metal-free process in the intramolecular cross-coupling to prepare 6*H*-benzo[*c*]chromene. The reaction was carried out in the presence of POP-Phen-E (0.03 mmol, 4 mol%), KOtBu (1.5 mmol, 1.9 equiv.), mesitylene (3 mL) and 1-(benzyloxy)-2-bromobenzene (0.8 mmol). The reaction was stirred under a N_2 atmosphere at 120°C for 24 h.

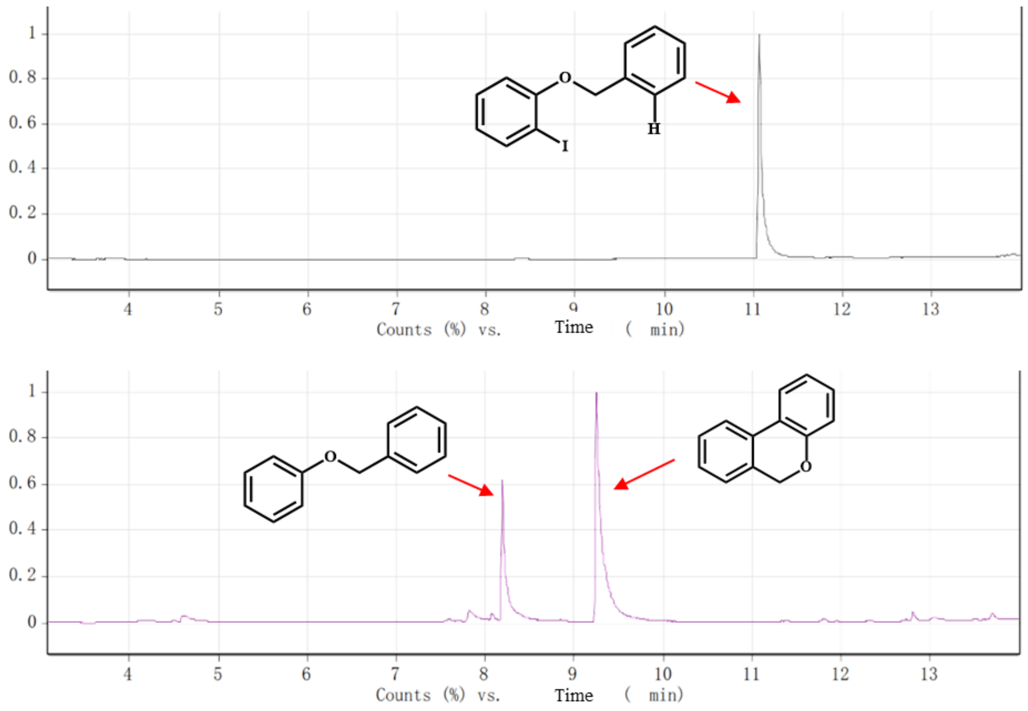


Fig. S6. GC-MS spectra before and after the cyclization reaction.

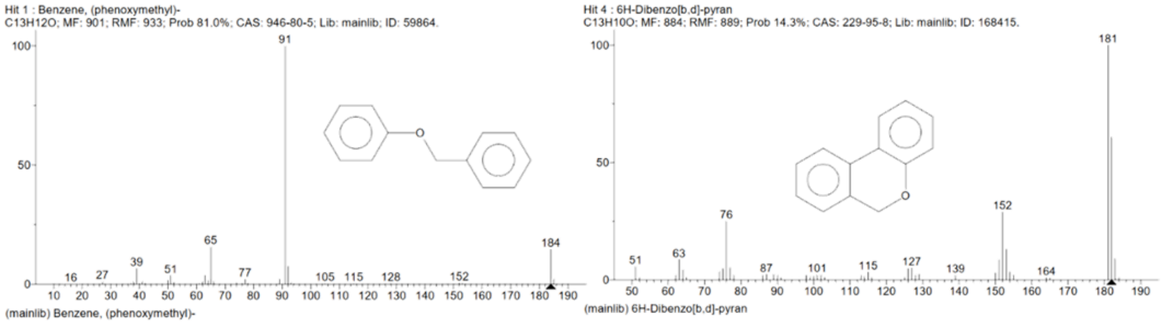


Fig. S7. GC-MS of the products of cyclization reaction.

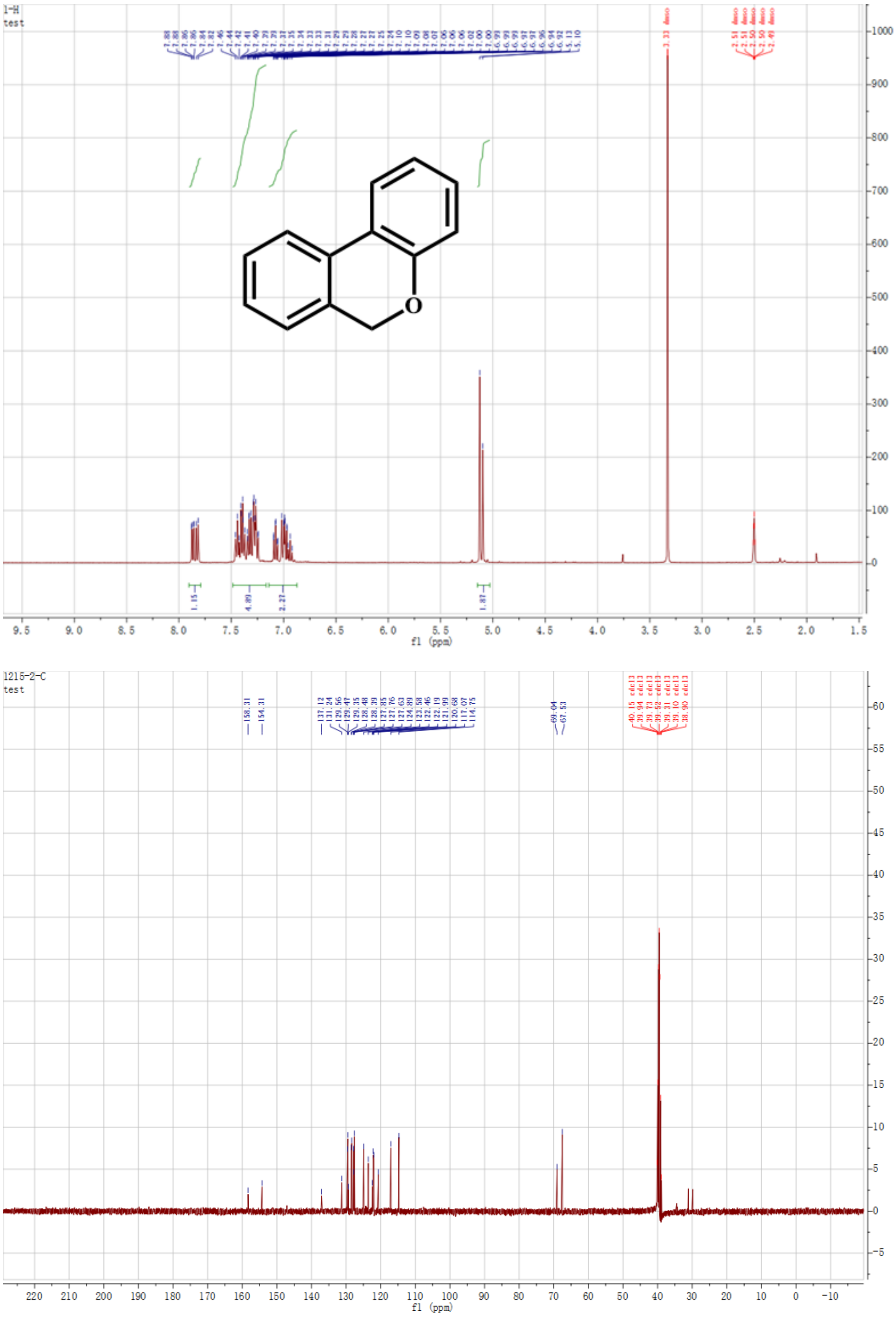


Fig. S8. ^{1}H NMR and ^{13}C NMR spectra of the products of cyclization reaction.

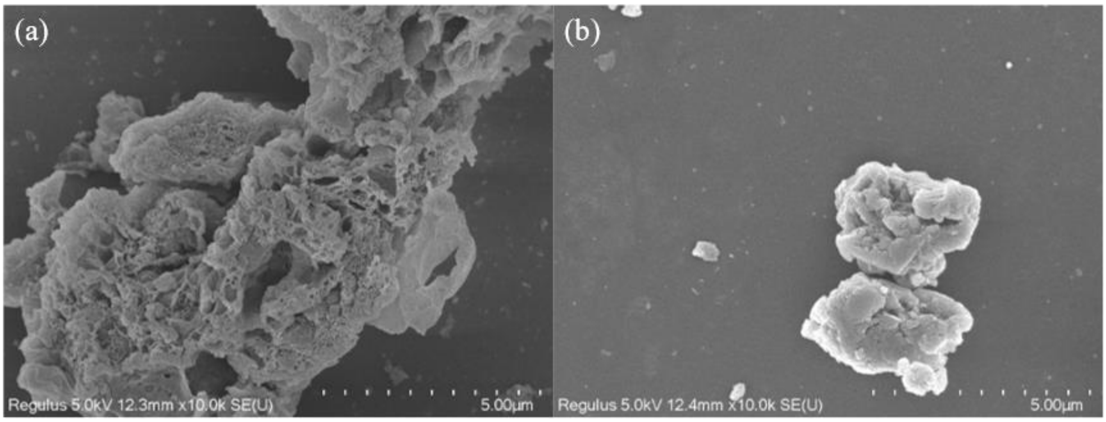


Fig. S9. SEM images of the POP-Phen-E fresh (**a**) and after 9 cycles (**b**)

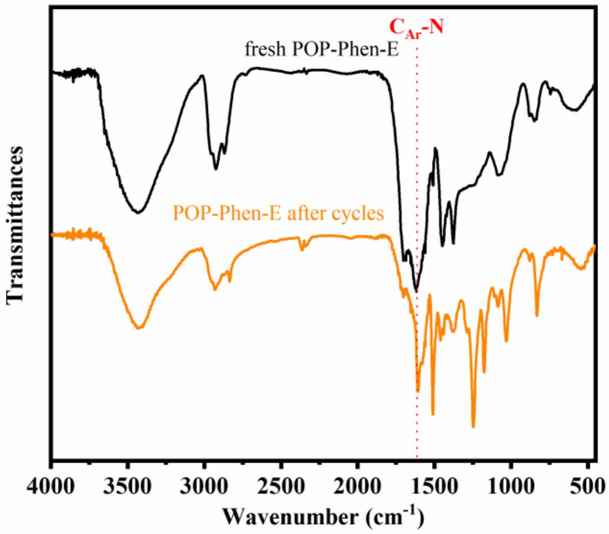
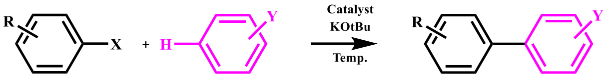
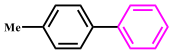
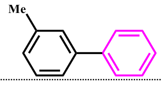
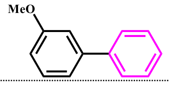
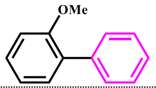
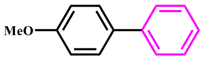
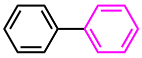
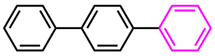
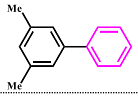
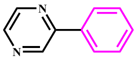
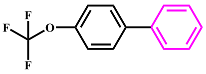
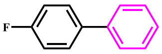
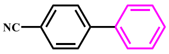
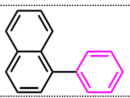
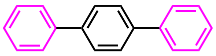
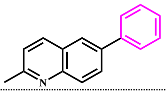
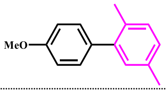
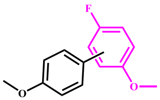


Fig. S10. FT-IR spectra of the POP-Phen-E fresh and after 9 cycles

Table S4. Cross-coupling of various aryl iodides/bromides with arenes in the presence of a catalytic amount of POP-Phen-E.[a]



1 2 3

Entry	X	Product	Yield [%]
1a	I		80.1
1b	Br		66.3
2a	I		78.8
2b	Br		50.5
3a	I		82.6
3b	Br		81.3
4a	I		70.3
4b	Br		68.8
5a	I		87.2
5b	Br		80.6
6a	I		86.8
6b	Br		58.2
7a	I		97.7
7b	Br		67.8
8a	I		88.5
8b	Br		59.3
9a	I		92.3
9b	Br		90.4
10a	I		82.2
10b	Br		59.8
11a	I		92.3
11b	Br		90.0
12a	I		80.1
12b	Br		81.2
13a	I		82.4
13b	Br		72.1
14a[b]	I		73.9
14b[b]	Br		57.2
15a	Br		54.8
16a	I		74.5
17a	I		56.4 (2-F/5-F=1/3.1)

[a] Reaction conditions: **1** (0.5 mmol), **2** (4 mL), KOtBu (1.5 mmol), POP-Phen-E (6 mol%, 0.03mmol), 120°C, 24 h. The reaction was carried out under a nitrogen atmosphere. The products structure was characterized GC-MS. Yields determined by GC analysis. [b] R is *p*-I.

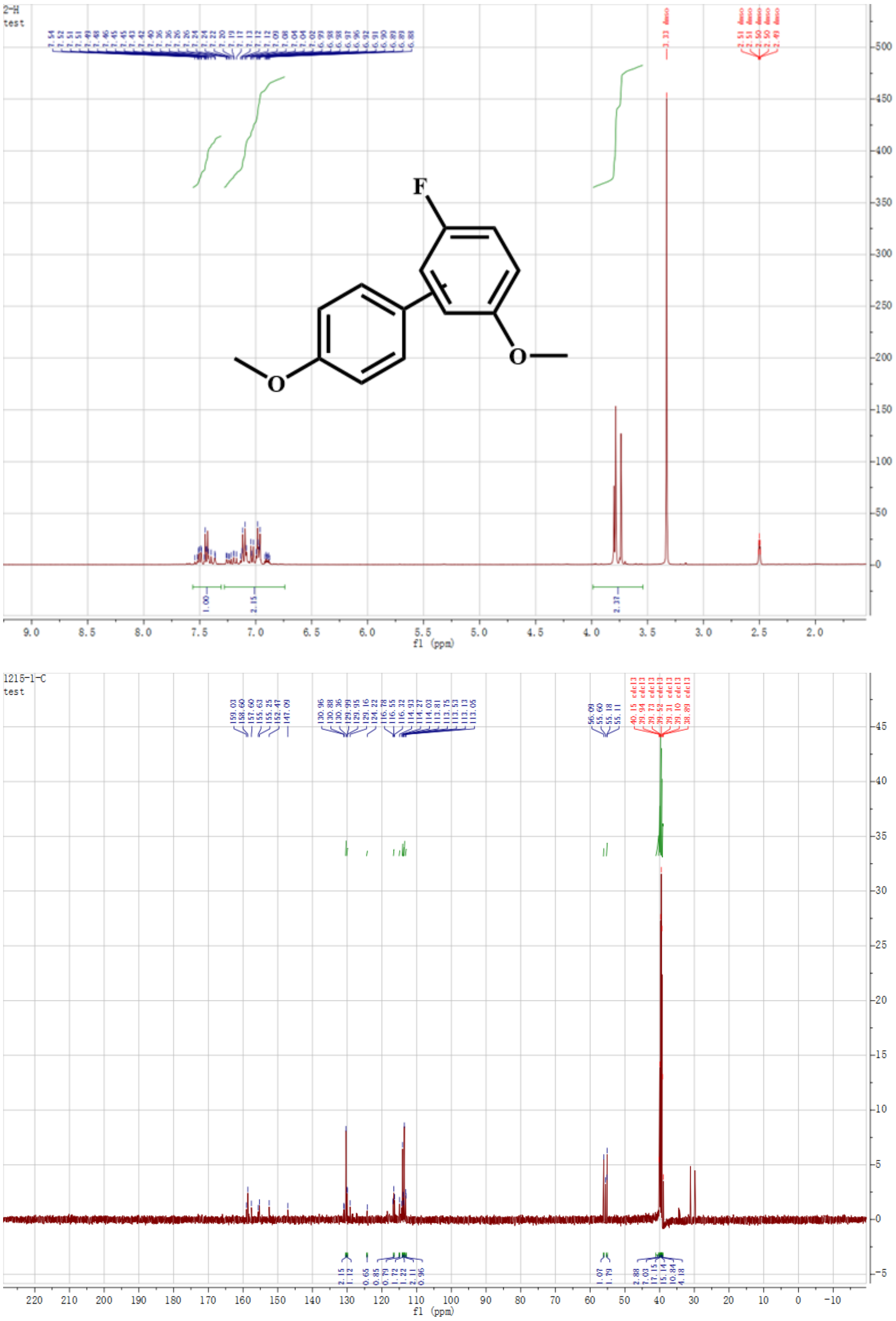


Fig. S11. ^{1}H NMR and ^{13}C NMR spectrum of **18a** separated from the reaction filtrate.

Table S5. Performance of representative catalytic systems in the literature.

Catalyst	T (˚C)	t (h)	Catalyst (mol%)	Type	Yield (%)	Ref.
DMEDA	80	48	30	Homogeneous	79	1
DMEDA	80	4	20	Homogeneous	84	2
bathophenanthroline	80	20	10	Homogeneous	93	3
1,10-phenanthroline	120	24	40	Homogeneous	83	4
1,10-phenanthroline	155	6	10	Homogeneous	82	5
Proline	150	24	20	Homogeneous	87	6
MOF-253	100	24	30	Heterogeneous	96	7
amino-NHC	80	4	20	Homogeneous	75	8
ROH	80	12	40	Homogeneous	83	9
1,10-phenanthroline	--	24	50	Homogeneous	89	10
GO	120	24	10(mg)	Heterogeneous	87.6	11
Phen polymer	120	24	40	Heterogeneous	84.3	12
POP-Phen-E	120	24	6	Heterogeneous	87.2	**This Work**

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