

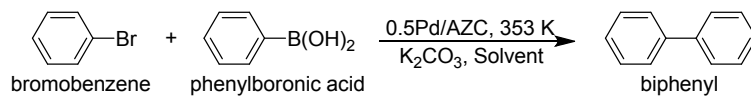
## Electronic Supplementary Information

### **Tailored Design of Palladium Species Grafted on Amino Functionalized Organozinc Coordination Polymer as Highly-Pertinent Heterogeneous Catalyst**

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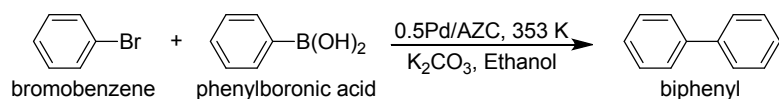
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**Table S1.** Effect of solvent on SMC reaction of bromobenzene using 0.5Pd/AZC catalyst<sup>a</sup>

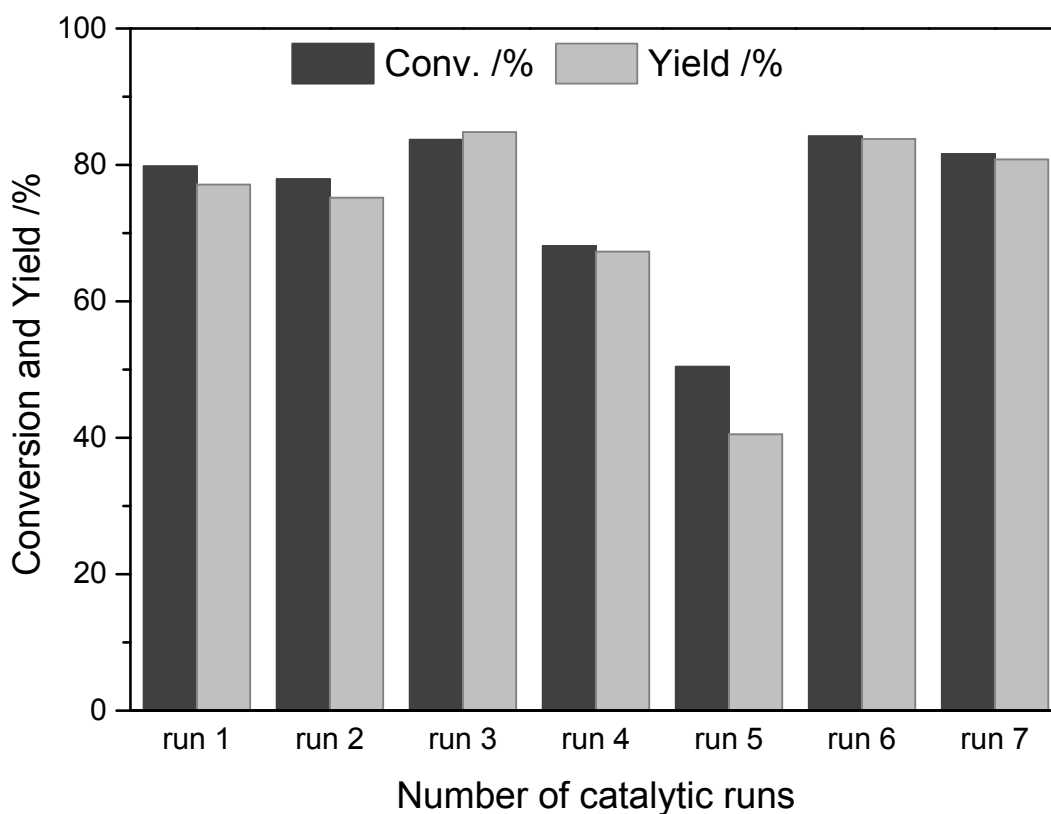
Entry	Solvent	t /h	Conv. /% <sup>b</sup>	Yield /% <sup>b</sup>
1	Ethanol	0.5	>99	>99
2 <sup>c</sup>			92.3, 91.4 <sup>d</sup>	92.7, 93.2 <sup>d</sup>
3 <sup>e</sup>			-	0.5
4 <sup>f</sup>		1	10.5	0
5 <sup>g</sup>			0	0
6	DMF	2	42.9	44.1
7	Toluene		18.2	23.8
8	Water		10.6	4.2
9	DMF:Water (4:1)		44.0	48.0
10	Ethanol:Water (4:1)	0.5	>99	>99

<sup>a</sup>Reaction conditions: Bromobenzene (2 mmol), Phenylboronic acid (3 mmol), K<sub>2</sub>CO<sub>3</sub> (4 mmol), Solvent (5 mL), 0.5Pd/AZC (30 mg), 353 K. <sup>b</sup>Determined by GC using naphthalene as internal standard on the basis of bromobenzene. <sup>c</sup>0.5Pd/AZC (5 mg). <sup>d</sup>1<sup>st</sup> reuse. <sup>e</sup>Without bromobenzene. <sup>f</sup>Without Pd loading (AZC, 5 mg). <sup>g</sup>Without catalyst.

**Table S2.** Highly efficient SMC reaction by 0.5Pd/AZC catalyst<sup>a</sup>

Entry	PhBr /mmol	Pd /nmol <sup>b</sup>	t /h	Conv. /% <sup>c</sup>	Yield /% <sup>c</sup>	TON <sup>d</sup>
1 <sup>e</sup>	2	235	1	83.7	88.8	7,576
2	4	47	6	81.6	84.2	71,501
3	15	47	14.5	86.6	85.2	271,320
4	30	47	24.5	80.7	81.3	517,104
5	75	47	40	74.7	64.5	1,029,420
6 <sup>f</sup>	10	4.7	48	94.4	>99	2,106,720

<sup>a</sup>Reaction conditions: Bromobenzene:Phenylboronic acid:K<sub>2</sub>CO<sub>3</sub> (1:1.5:2) (molar ratio), Ethanol (5 mL), 0.5Pd/AZC (1 mg), 353 K. <sup>b</sup>Estimated by the results of ICP-AES analysis of the xPd/AZC. <sup>c</sup>Determined by GC using naphthalene as an internal standard on the basis of bromobenzene. <sup>d</sup>TON was calculated based on the amount of biphenyl formed. <sup>e</sup>0.5Pd/AZC (5 mg). <sup>f</sup>0.05Pd/AZC.



**Fig. S1** Reusability of 0.5Pd/AZC catalyst for the SMC reaction of bromobenzene.

*Reaction conditions:* Bromobenzene (2 mmol), phenylboronic acid (3 mmol),  $K_2CO_3$  (4 mmol), 0.5Pd/AZC (1 mg), Ethanol (5 mL), 353 K, 1 h. The reaction time was increased to 3 h for runs 6 and 7.

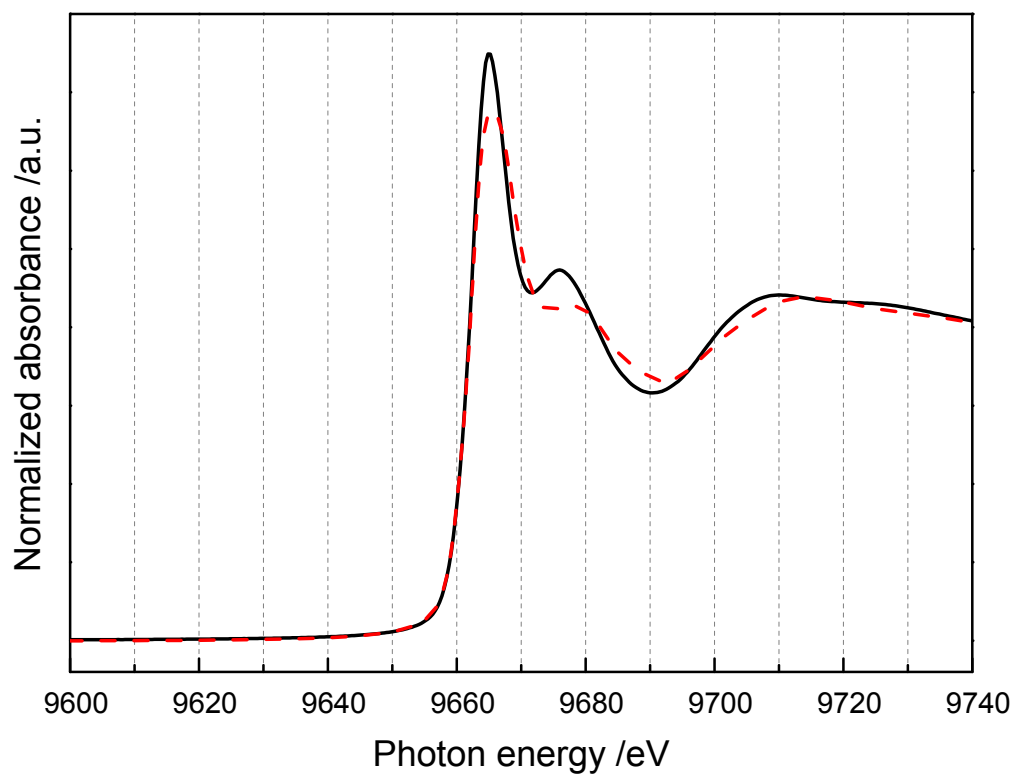
The activities of Pd/AZC showed gradual decrease from 3<sup>rd</sup> to 5<sup>th</sup> run, however, the activity could be re-achieved by increasing the reaction time as seen in 6<sup>th</sup> and 7<sup>th</sup> run. Thus, the Pd/AZC could possess its original potential even after 7<sup>th</sup> run. The observation, increase in activity with the increase in reaction time, indicated that the rate of reaction was affected during recycling runs. We supposed that the accessibility of substrates towards catalyst was compromised by increase in the base ( $K_2CO_3$ ) amount against the small quantity of Pd/AZC in five catalytic runs.

**Table S3.** Optimization of reaction parameters for maximizing biphenyl yield from chlorobenzene (CB)<sup>a</sup>

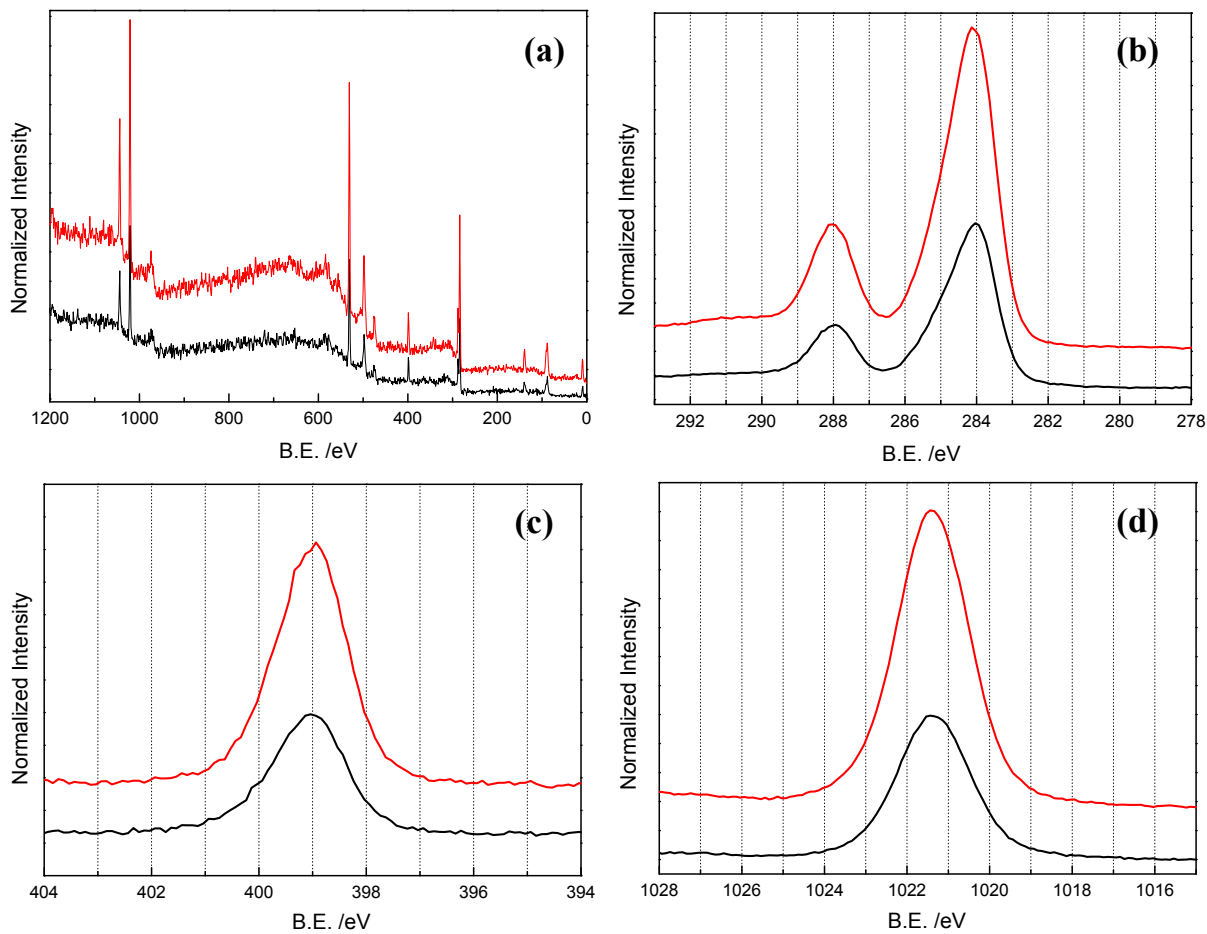
Entry	Temp. /K	Time /h	Pd / $\mu$ mol (wt%) <sup>b</sup>	Solvent	TBAB/CB ratio <sup>c</sup>	Conv. /% <sup>d</sup>	Yield /% <sup>d</sup>
1	353	2	2.4 (5)	Ethanol	0	0.6	8.5*
2				Methanol	0	3.8	7.4*
3				MIBK	0	0	0
4				DMSO	0	0	0
5				CH <sub>3</sub> CN	0	0	0
6				Acetone	0	0	0
7				1,4-Dioxane	0	0	0
8				DMA	0	0	0
9				DMA:Ethanol	0	0	0
10			14.1 (5)	Ethanol:water(4:1)	0	8.0	22.3*
11	353	4	5.6 (3)	Ethanol	1	58.4	18.4
12			0.7 (0.5)	Ethanol	0.5	49.9	7.4
13	373	6	0.2 (0.5)	Ethanol	1	39.3	3.2
14 <sup>e</sup>					1	72.0	24.8
15				DMF	1	46.8	2.0
16					0	0	0
17				H <sub>2</sub> O	1	72.0	3.0
18				Ethanol:DMF (3:2)	1	49.6	7.6
19 <sup>f</sup>			2.8 (3)	Ethanol:DMF (1:1)	1	74.5	31.2
20 <sup>e</sup>					1	58.2	34.0
21 <sup>e</sup>					0.5	46.1	30.0
22 <sup>f</sup>				Ethanol:DMF (2:3)	1	76.1	27.8
23 <sup>f</sup>				Ethanol:DMF (1:4)	1	72.5	14.1
24 <sup>f</sup>				Ethanol:DMF (4:1)	1	72.6	16.1
25 <sup>f</sup>				Ethanol:DMF (3:2)	1	73.7	23.7
26 <sup>g</sup>	353	3	1.4 (3)	Ethanol	0	>99	>99

<sup>a</sup>Reaction conditions: Chlorobenzene (CB, 0.5 mmol), Phenylboronic acid (0.75 mmol), K<sub>2</sub>CO<sub>3</sub> (1 mmol), Pd/AZC, Solvent (5 mL), Round bottomed flask. Abbreviation: TBAB; tetrabutylammonium bromide, MIBK; methyl isobutyl ketone, DMSO; dimethylsulfoxide, DMA; *N,N*-dimethylacetamide. DMF, *N,N*-dimethylformamide. <sup>b</sup>Determined by ICP-AES analysis. <sup>c</sup>TBAB:CB in mmol:mmol. <sup>d</sup>Determined by GC using naphthalene as internal standard on the basis of bromobenzene or chlorobenzene. <sup>e</sup>50 mL Teflon lined Autoclave. <sup>f</sup>Sealed glass tube. <sup>g</sup>*p*-Nitrochlorobenzene (0.5 mmol) was used instead of chlorobenzene.

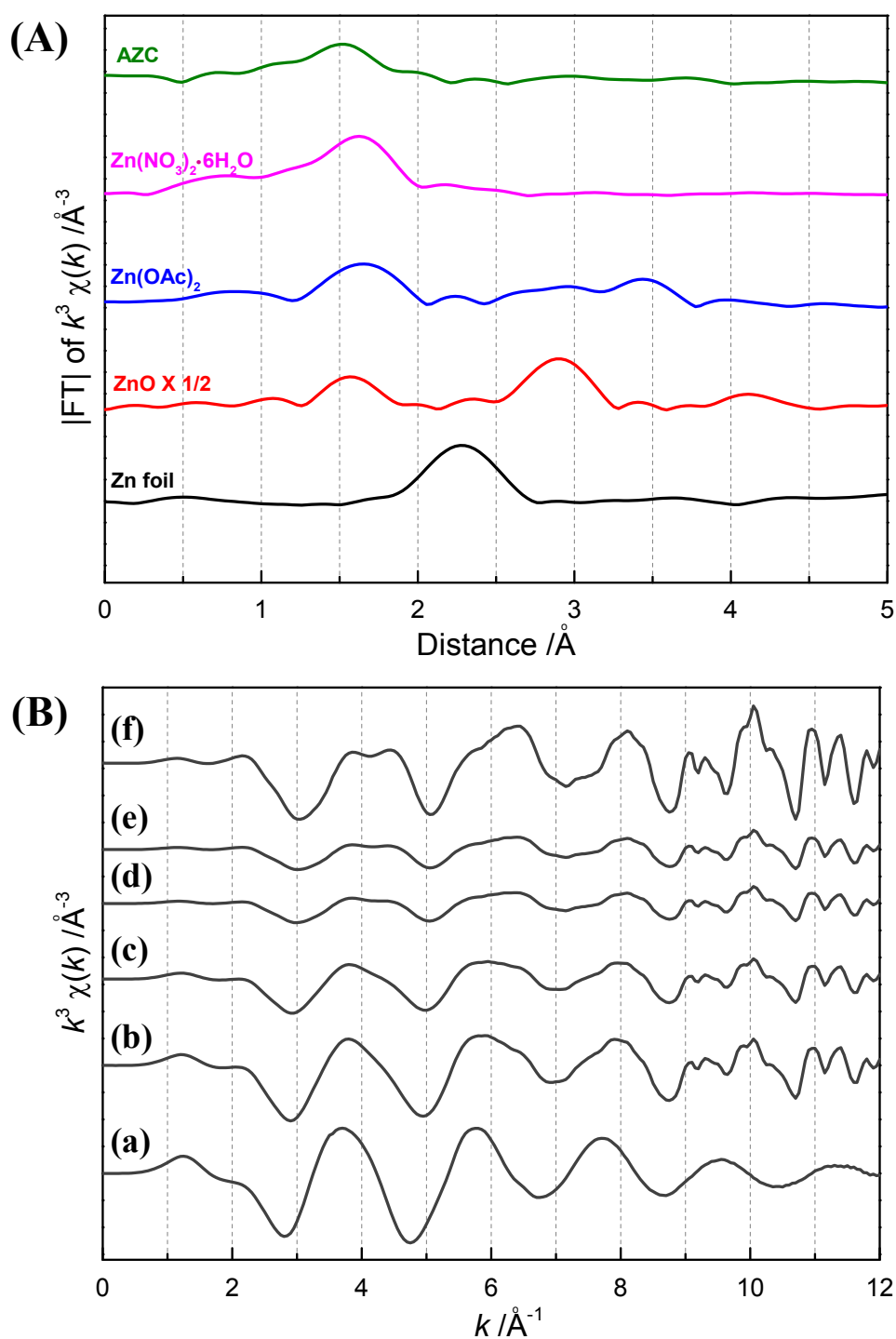
\*Note; The higher biphenyl yields than conversions in entries 1,2 and 10 are due to the homocoupling of phenylboronic acid.



**Fig. S2** Zn K-edge XANES spectrum of AZC (black solid line) and created spectrum using 58% Zn(OAc)<sub>2</sub> and 42% Zn(NO<sub>3</sub>)<sub>2</sub>•6H<sub>2</sub>O (red dashed line).

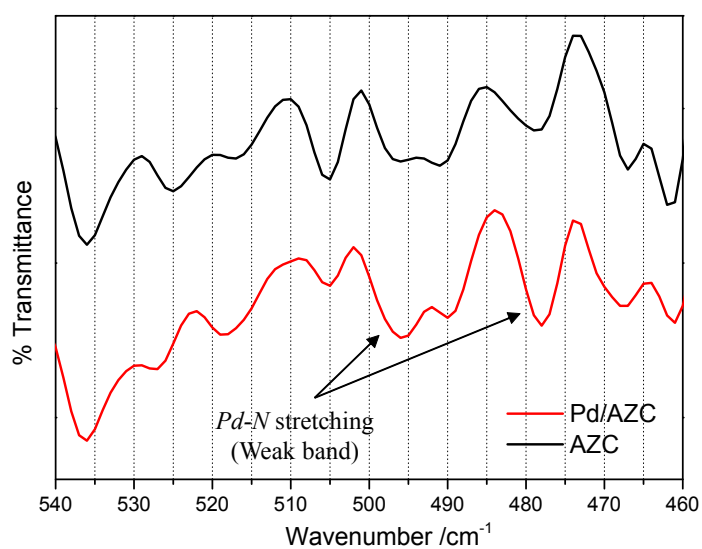
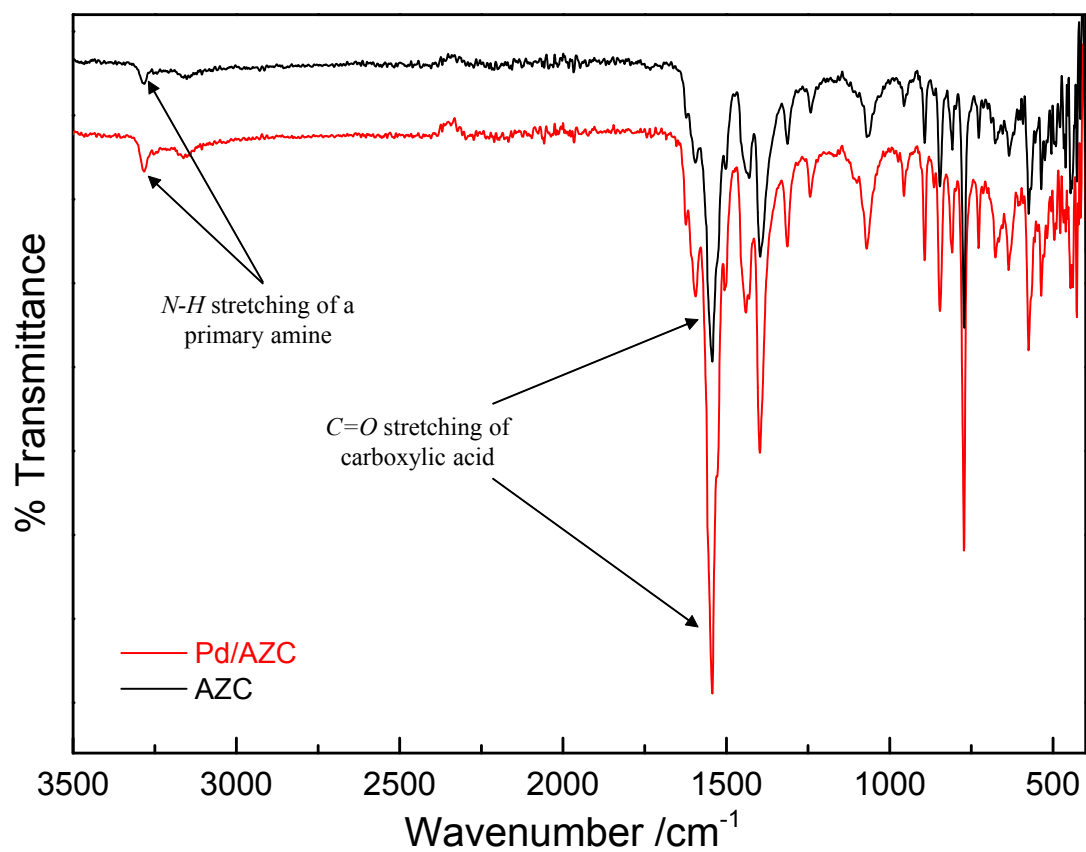


**Fig. S3** XPS of AZC (black) and Pd/AZC (red) for (a) survey, (b) C 1s, (c) N 1s, and (d) Zn 2p<sub>3/2</sub>.

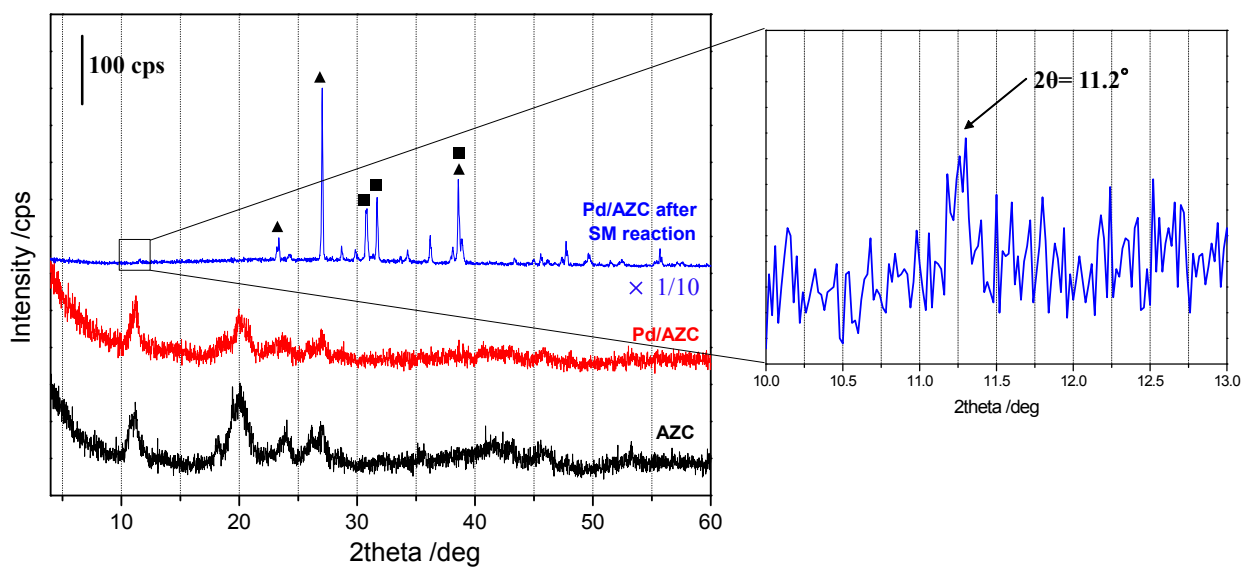


**Fig. S4** (A) Fourier transform (FT) of  $k^3$ -weighted Zn K-edge EXAFS spectrum of references and AZC. (B) Calculated Zn K-edge EXAFS spectrum of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Zn}(\text{OAc})_2$  in different ratio. The ratio of  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to  $\text{Zn}(\text{OAc})_2$  are (a) 100:0, (b) 50:50, (c) 25:75, (d) 20:80, (e) 10:90, (f) 0:100. The merged spectra with higher content of  $\text{Zn}(\text{OAc})_2$  (above 80%) demonstrated good correlation to the obtained features of AZC (the humped peak).

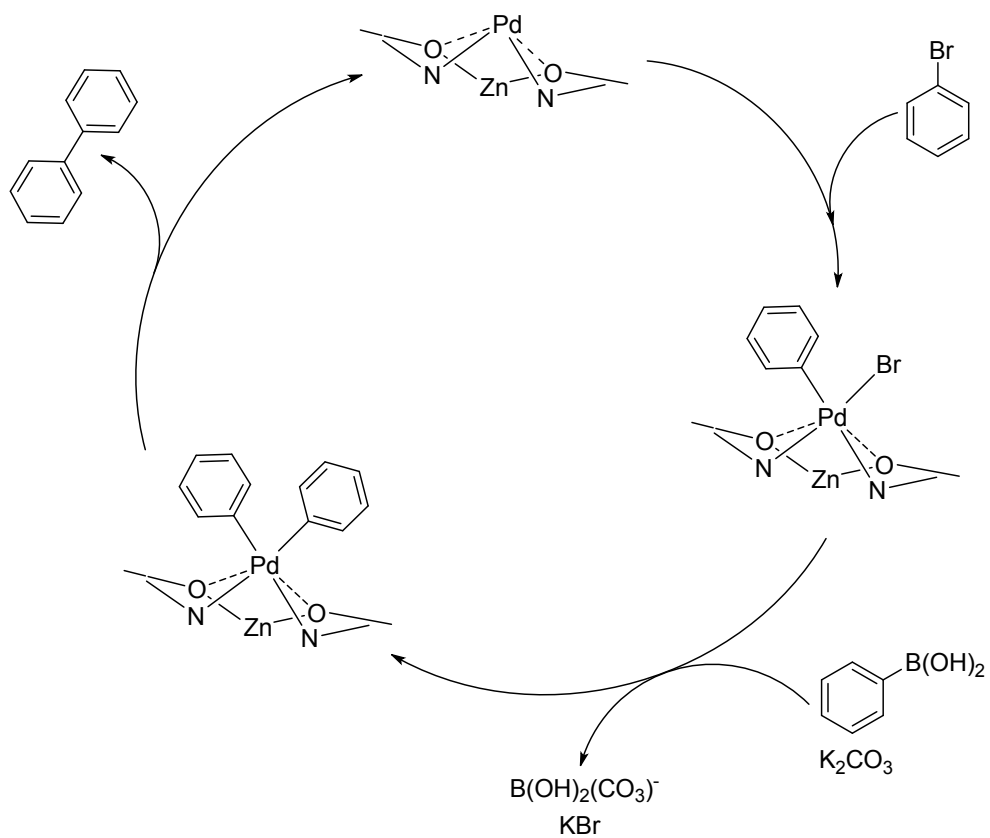




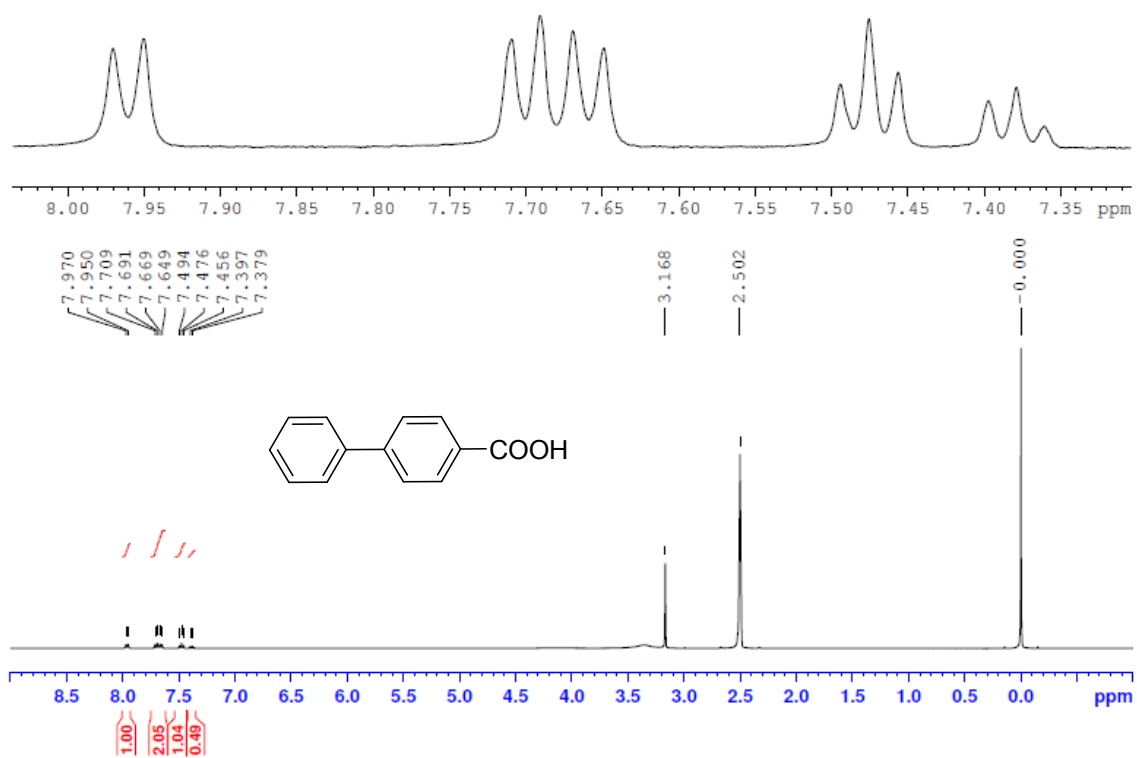
**Fig. S5** Infrared (IR) spectra of AZC and Pd/AZC. The weak band of Pd-N is also shown.



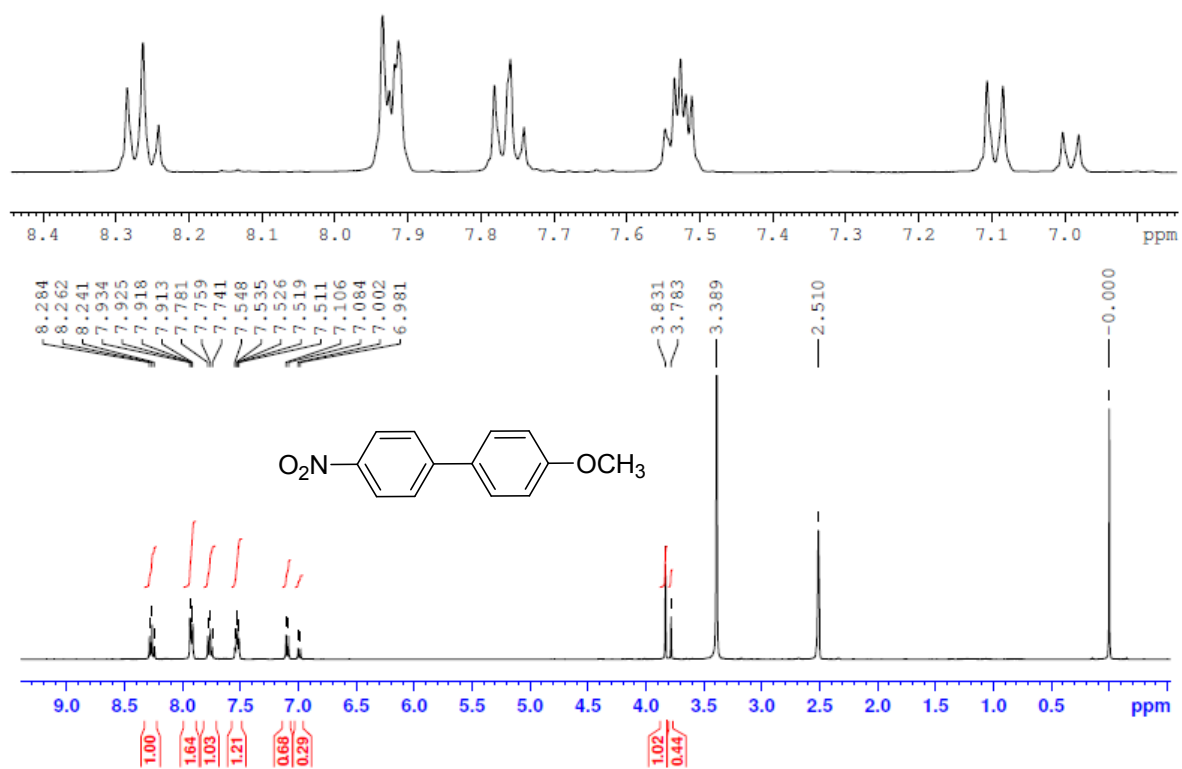
**Fig. S6** XRD patterns of various organozinc coordination polymer. A part of the XRD pattern was magnified to demonstrate the reflection of material after reaction. The catalyst was found to possess structural resemblance after the SMC reaction. The catalyst amount was low and thus was measured along with KBr ( $\blacktriangle$ ) formed in the reaction and  $\text{K}_2\text{CO}_3$  ( $\blacksquare$ ). The arrow indicates one of the main reflection from the material at  $11.2^\circ$  in the Pd/AZC after the SMC reaction.



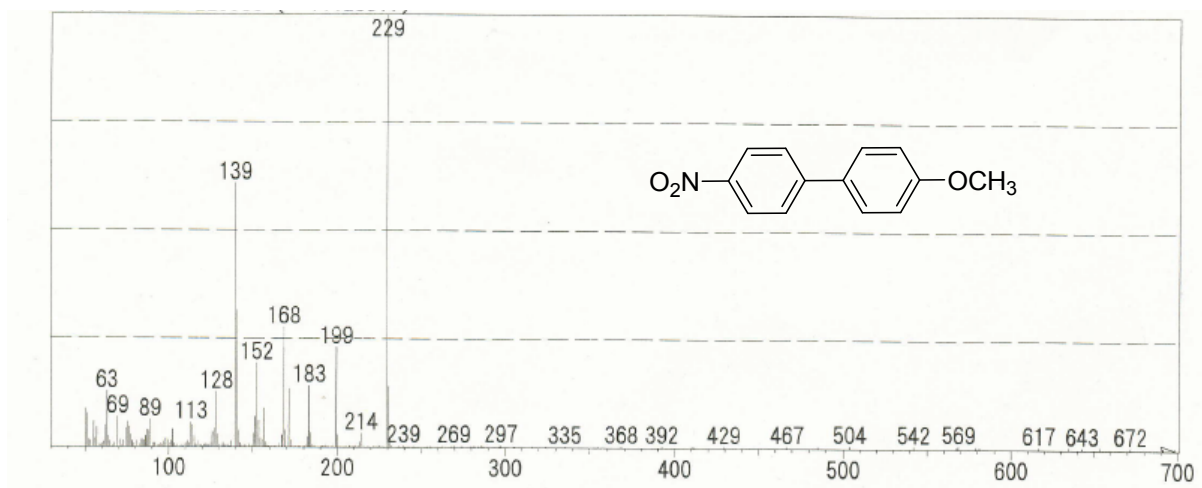
**Scheme S1** An illustrative sketch of proposed mechanism of the SMC reaction of bromobenzene in the presence of Pd/AZC catalyst. Hydrogen atoms on nitrogen atoms are not shown for simplicity.



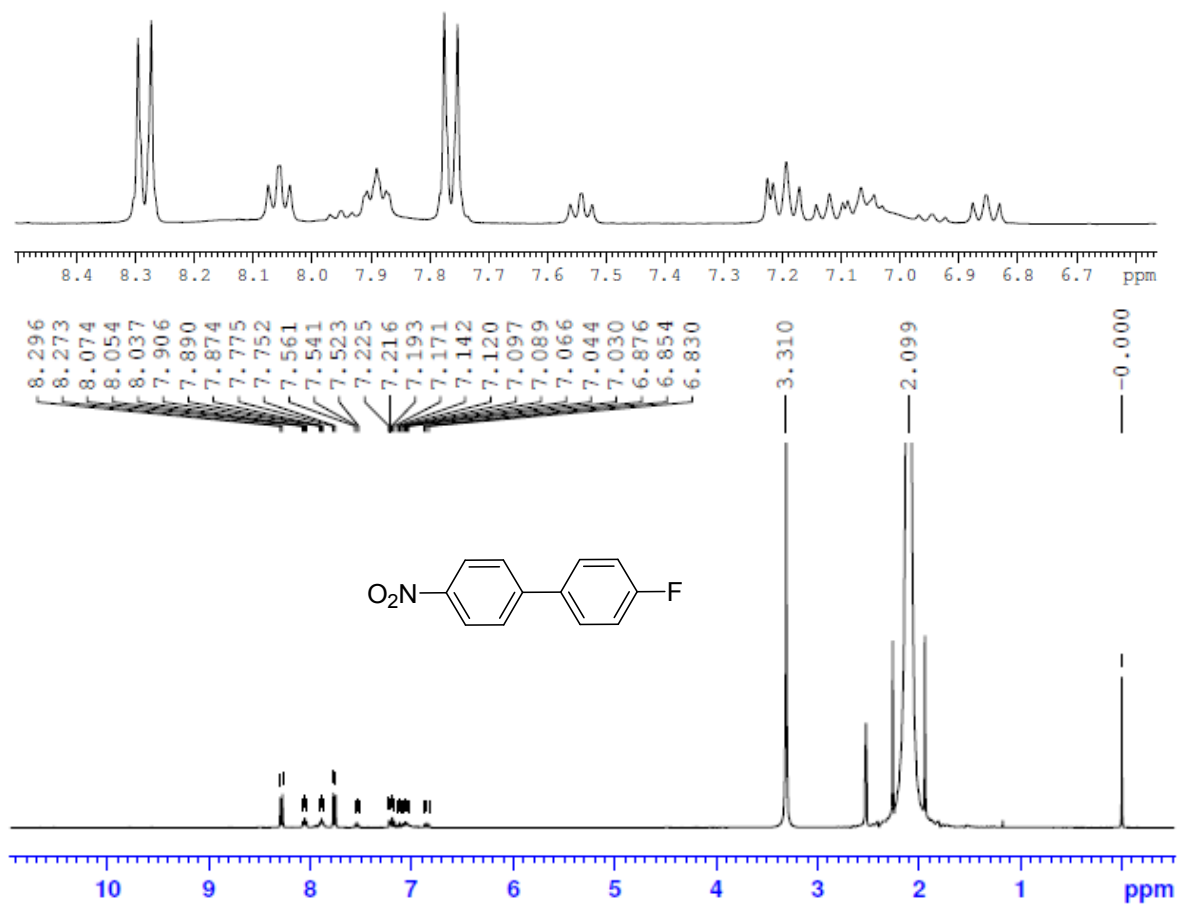
**Fig. S7**  $^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) of isolated 4-phenylbenzoic acid (Table 2, entry 4) obtained as colorless crystals.



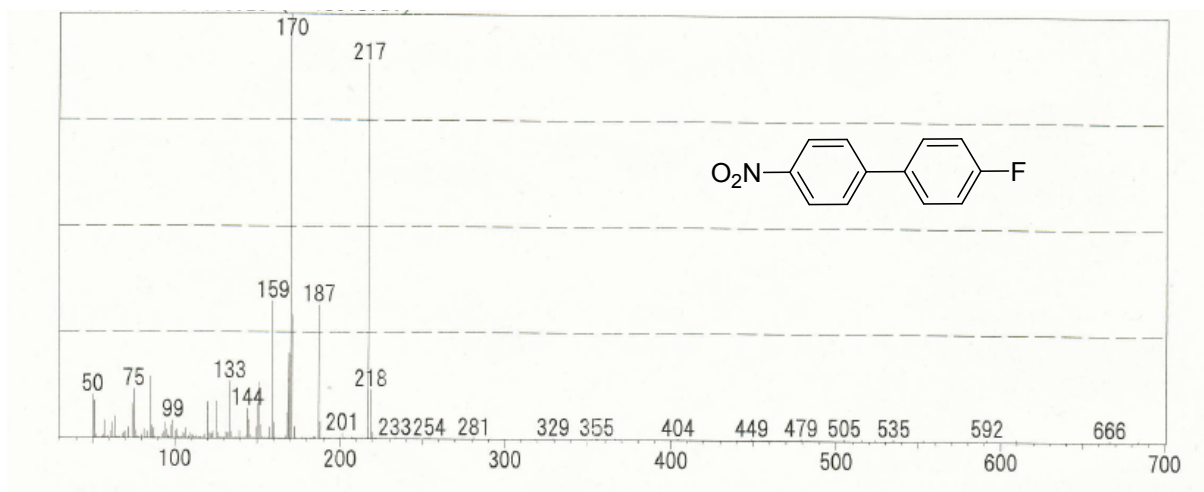
**Fig. S8** <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>) of 4-methoxy-4'-nitro-1,1'-biphenyl (Table 2, entry 6) obtained as yellow solid. An impurity of 4-methoxyphenylboronic acid was also recorded at δ 3.783, 6.9915, 7.9225 ppm.



**Fig. S9** MS of 4-methoxy-4'-nitro-1,1'-biphenyl ( $C_{13}H_{11}NO_3$ ; Calcd. Mol. Mass  $229.23 \text{ g mol}^{-1}$ ) (Table 2, entry 6) obtained as yellow solid.

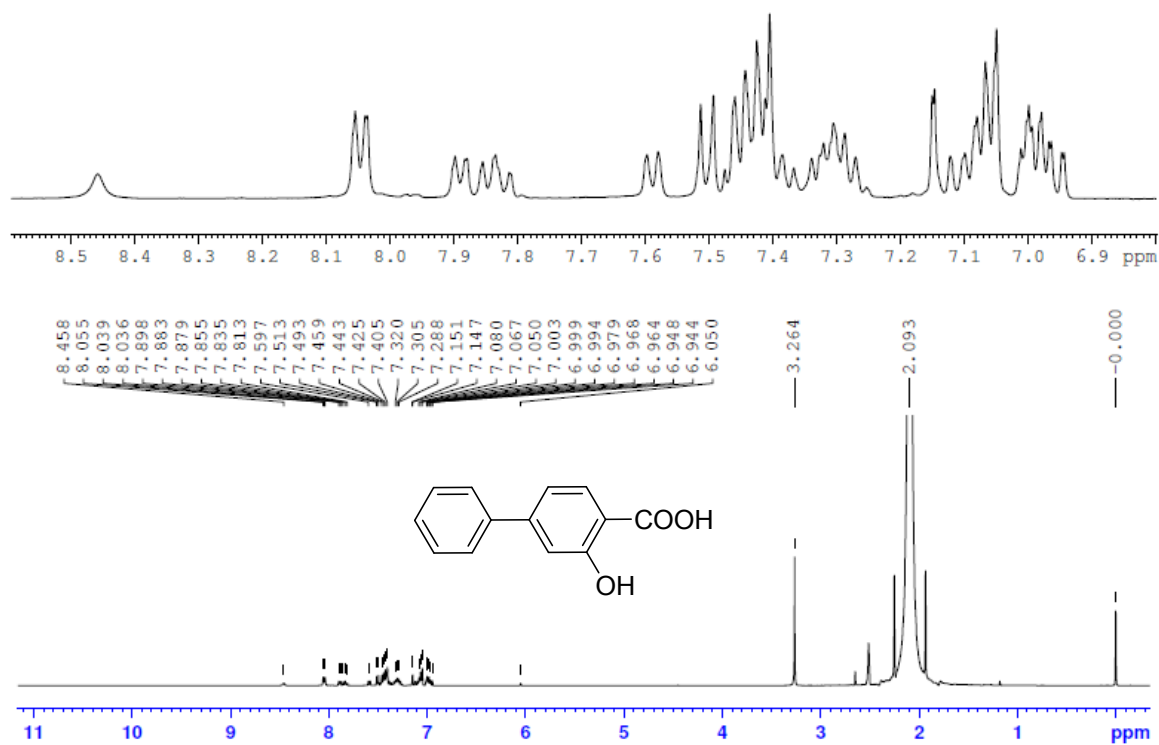


**Fig. S10**  $^1\text{H}$  NMR (400MHz,  $\text{DMSO-d}_6$ ) of 4-fluoro-4'-nitro-1,1'-biphenyl (Table 2, entry 7) obtained as dirty yellow to light brown solid. The spectrum was recorded for the reaction mixture.

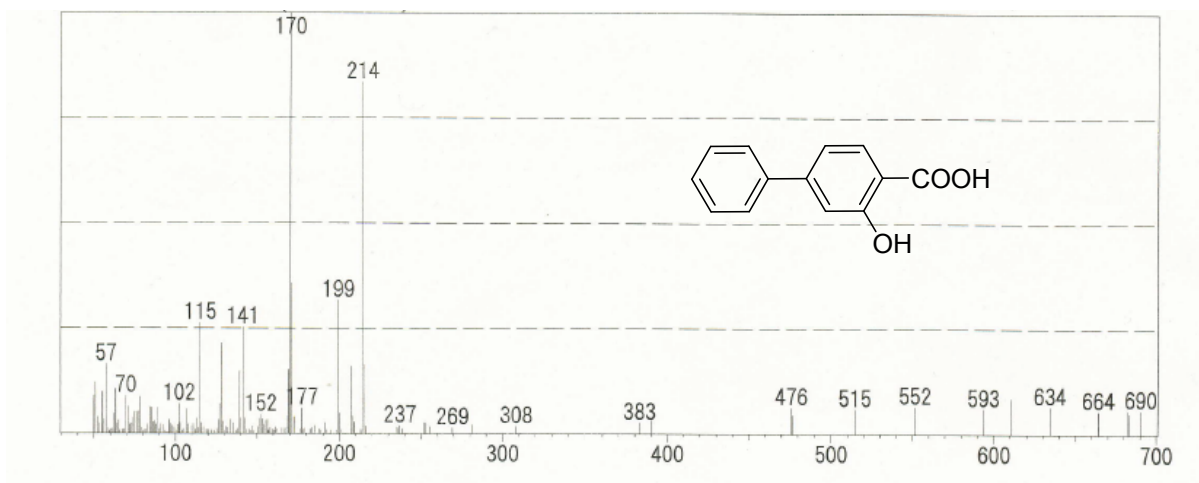


**Fig. S11** MS of 4-fluoro-4'-nitro-1,1'-biphenyl ( $C_{12}H_8FNO_2$ ; Calcd. Mol. Mass  $217.20 \text{ g mol}^{-1}$ ) (Table 2, entry 7) obtained as dirty yellow to light brown solid.





**Fig. S12** <sup>1</sup>H NMR of (400MHz, DMSO-d<sub>6</sub>) 3-hydroxy-[1,1'-biphenyl]-4-carboxylic acid (Table 2, entry 11) obtained as light pink solid. The spectrum was recorded for the reaction mixture.



**Fig. S13** MS of 3-hydroxy-[1,1'-biphenyl]-4-carboxylic acid ( $C_{13}H_{10}O_3$ ; Calcd. Mol. Mass 214.22  $g\ mol^{-1}$ ) (Table 2, entry 11) obtained as light pink solid.