

Supporting Information

**Recyclable ionic iron substituted ceria: A precious-metal-free,  
ligand-free, and versatile catalyst for C-C coupling and *ipso*-  
hydroxylation of arylboronic acid**

Prasanna

Talent Development Centre, Indian Institute of Science Challakere Campus at Kudapura,  
Chitradurga, Karnataka 577536, India.

Email: [prasanna1@iisc.ac.in](mailto:prasanna1@iisc.ac.in)

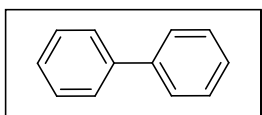
Contents	Page
1. General information	S2
2. Characterization data of the products	S2
3. References	S10
4. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra	S11

## 1 General information

The X-ray diffraction pattern of the catalyst was recorded on a Philips X'Pert Diffractometer. IR spectra are recorded in a Perkin Elmer spectrometer with a KBr pellet. NMR spectra were recorded on Bruker-AV400 spectrometer in  $\text{CDCl}_3$  and  $\text{D}_2\text{O}$ , tetramethylsilane (TMS;  $\delta = 0.00$  ppm) served as an internal standard for  $^1\text{H}$  NMR. The corresponding residual non-deuterated solvent signal ( $\text{CDCl}_3$ ;  $\delta = 77.00$  ppm) was used as an internal standard for  $^{13}\text{C}$  NMR. Column chromatography was carried out by packing glass columns with silica gel 100 – 200 mesh and thin-layer chromatography was carried out using SILICA GEL GF-254. All reagents and reactants were procured from Sigma-Aldrich and SD-Fine chemicals. Solvents used for workup and chromatographic procedures were purchased from commercial suppliers and used without further purification.

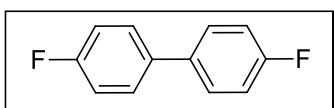
## 2 a) Characterization data for homo-coupling reaction products

### 2a Biphenyl<sup>1</sup>



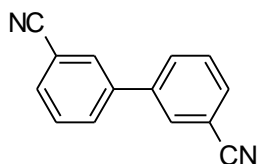
Obtained as a White solid; **Yield:** 86% (66 mg); **R<sub>f</sub>** = 0.6 (petroleum ether); **M.p:** 69 °C;  **$^1\text{H}$  NMR** ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.64 – 7.66 (d,  $J = 7.38$  Hz, 4H), 7.48 – 7.51 (t,  $J = 7.25$  Hz, 4H), 7.38 – 7.42 (t,  $J = 7.34$  Hz, 2H);  **$^{13}\text{C}$  NMR** ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 127.21, 127.29, 128.80, 141.27.

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



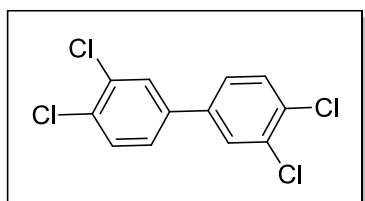
Obtained as a white solid; **Yield:** 84% (80 mg); **R<sub>f</sub>** = 0.6 (petroleum ether); **M. p** = 89 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.53 - 7.50 (dd, *J* = 8.07 Hz, 4H), 7.17 – 7.13 (t, *J* = 8.5 Hz, 4H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 163.66, 161.21, 136.42, 136.39, 128.62, 128.54, 115.81, 115.60.

### 2c 1,1'-biphenyl-3,3'-dicarbonitrile<sup>2</sup>



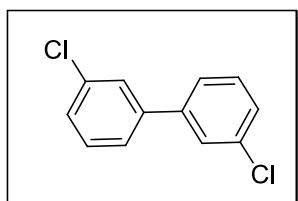
Obtained as light-yellow solid; **Yield:** 82% (83.5 mg); **R<sub>f</sub>** = 0.6 (petroleum ether); **M. p** = 170 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.86 (s, 2H), 7.83 – 7.81 (d, *J* = 8.0 Hz, 2H), 7.75 – 7.73 (d, *J* = 8.0 Hz, 2H), 7.66 – 7.62 (t, *J* = 8.0 Hz, 2H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 140.19, 131.84, 131.52, 130.68, 130.08, 118.70, 113.49.

### 2d 3,3',4,4'-Tetrachloro-1,1'-biphenyl<sup>3</sup>



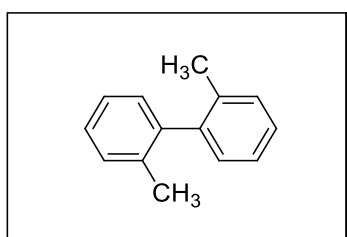
Obtained as a white solid; **Yield:** 80% (116.5 mg); **R<sub>f</sub>** = 0.6 (petroleum ether); **M. p** = 170 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.55 – 7.53 (d, *J* = 7.88 Hz, 2H), 7.58 (s, 1H), 7.56 (s, 1H), 7.43 – 7.40 (d, *J* = 8.4, 2.2 Hz, 2H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 138.72, 133.24, 132.48, 130.96, 128.80, 126.15.

### 2e 3,3'-Dichloro-1,1'-biphenyl<sup>1</sup>



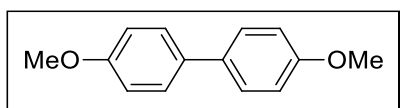
Obtained as a colorless liquid; **Yield:** 81% (90.5 mg); **R<sub>f</sub>** = 0.6 (petroleum ether); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.57 (s, 2H), 7.47 – 7.45 (m, 2H), 7.42 – 7.36 (m, 4H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 141.64, 130.13, 127.89, 127.28, 125.27.

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



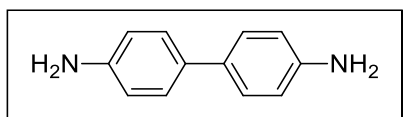
Obtained colorless liquid; **Yield:** 79% (72 mg); **R<sub>f</sub>** = 0.6 (petroleum ether); **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.42 – 7.32 (m, 6H), 7.19 – 7.17 (d, *J* = 7.38 Hz, 2H), 2.44 (s, 6H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 141.56, 136.07, 128.60, 127.99, 127.91, 124.28, 21.56.

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



Obtained as a colorless solid; **Yield:** 85% (91 mg); **R<sub>f</sub>** = 0.40 (5% ethyl acetate in petroleum ether); **M. p** = 170 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.52 - 7.50 (d, *J* = 8.28 Hz, 4H), 7.00 - 6.98 (d, *J* = 8.53 Hz, 4H), 3.87 (s, 6H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 158.69, 133.49, 127.75, 114.17, 55.37.

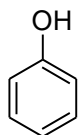
### 2h Benzidine<sup>4</sup>



Obtained as white solid; **Yield:** 86% (79 mg); **R<sub>f</sub>** = 0.36 (20% ethyl acetate in petroleum ether); **M. p** = 128 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.39 – 7.37 (d, *J* = 8.03 Hz, 4H), 6.77 – 6.75 (d, *J* = 7.78 Hz, 4H), 3.69 (br, s, 4H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 144.97, 131.84, 127.32, 115.49.

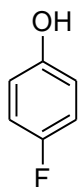
#### 4 b) Characterization data for *ipso*-hydroxylation reaction products

##### 3a Phenol<sup>5</sup>



Obtained as a white solid; **Yield:** 97% (91.2 mg); **R<sub>f</sub>** = 0.35 (10% ethyl acetate in petroleum ether); **M. p** = 41 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.31 - 7.27 (t, *J* = 7.91 Hz, 2H), 7.01 - 6.97 (t, *J* = 7.4 Hz, 1H), 6.92 – 6.90 (m, 2H), 6.58 (s, br, 1H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 155.42, 129.80, 120.88, 115.48.

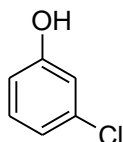
##### 3b 4-fluorophenol<sup>5</sup>



Obtained as a white solid; **Yield:** 91% (102.0 mg); **R<sub>f</sub>** = 0.29 (10% ethyl acetate in petroleum ether); **M. p** = 45 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.01 – 6.92 (m, 2H), 6.87 – 6.78

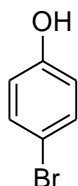
(m, 2H), 5.19 (s, br, 1H);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 158.42, 156.06, 151.52, 116.28, 115.88.

### 3c 3-chlorophenol<sup>6</sup>



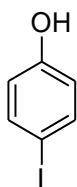
Obtained as a white solid; **Yield:** 90% (115.7 mg);  $R_f$  = 0.3 (10% ethyl acetate in petroleum ether); **M. p** = 33 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.20 – 7.16 (t,  $J$  = 8.02 Hz, 1H), 6.95 – 6.88 (m, 2H), 6.76 – 6.69 (m, 1H), 5.62 (s, br, 1H);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 156.38, 134.90, 130.47, 121.00, 115.91, 113.77.

### 3d 4-bromophenol<sup>5</sup>



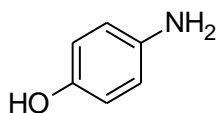
Obtained as a white solid; **Yield:** 89% (153.9 mg);  $R_f$  = 0.42 (10% ethyl acetate in petroleum ether); **M. p** = 65 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.37 – 7.34 (m, 2H), 6.77 – 6.73 (m, 2H), 5.14 (s, br, 1H);  $^{13}\text{C}$ NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 154.48, 132.55, 117.25, 113.02.

### 3e 4-iodophenol<sup>7</sup>



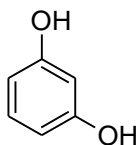
Obtained as light-yellow solid; **Yield:** 93% (204.6 mg); **R<sub>f</sub>** = 0.3 (10% ethyl acetate in petroleum ether); **M. p** = 91 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz) δ (ppm): 7.54 – 7.52 (d, *J* = 8 Hz, 2H), 6.66 – 6.64 (d, *J* = 8Hz, 2H), 5.62 (s, br, 1H); **<sup>13</sup>CNMR** (CDCl<sub>3</sub>, 100 MHz) δ (ppm): 155.14, 138.54, 117.90, 83.01.

### 3f 4-aminophenol<sup>8</sup>



Obtained as a colorless solid; **Yield:** 94% (105.2 mg); **R<sub>f</sub>** = 0.50 (60% ethyl acetate in petroleum ether); **<sup>1</sup>H NMR** (DMSO-d<sub>6</sub>, 400 MHz) δ (ppm): 8.51 (s, 1H), 6.51 – 6.43 (m, 4H), 3.68 (br, s, 2H); **<sup>13</sup>CNMR** (DMSO-d<sub>6</sub>, 100 MHz) δ (ppm): 148.70, 140.87, 115.96, 115.86.

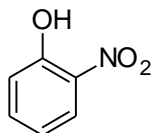
### 3g Resorcinol<sup>5</sup>



Obtained as light brown solid; **Yield:** 87% (95.8 mg); **R<sub>f</sub>** = 0.53 (30% ethyl acetate - petroleum ether); **Melting Point:** 110 °C; **<sup>1</sup>H NMR** (DMSO-d<sub>6</sub>, 400 MHz): δ 9.26 (s, 1H),

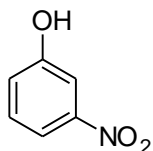
6.95-6.91 (t,  $J = 7.78$  Hz, 1H), 6.23 – 6.21 (m, 2H), 3.78 (s, br, 2H);  $^{13}\text{C}$  NMR (DMSO- $d_6$ , 100 MHz):  $\delta$  158.83, 130.29, 106.78, 102.96.

### 3h 2-nitrophenol<sup>5</sup>



Obtained as a yellow solid; **Yield:** 86% (119.6 mg);  $R_f = 0.6$  (30% ethyl acetate in petroleum ether); **M. p** = 45 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 10.60 (s, 1H), 8.13 – 8.11 (d,  $J = 8.51$  Hz, 1H), 7.62 – 7.58 (t,  $J = 7.69$ , 1H), 7.18 – 7.16 (d,  $J = 8.5$  Hz, 1H), 7.03 – 6.99 (t,  $J = 7.82$ , 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 155.12, 137.58, 125.07, 120.25, 119.98.

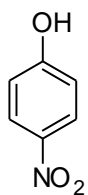
### 3i 3-nitrophenol<sup>6</sup>



Obtained as a yellow solid; **Yield:** 89% (123.7 mg);  $R_f = 0.58$  (30% ethyl acetate in petroleum ether); **M. p** = 94 - 96 °C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 400 MHz)  $\delta$  (ppm): 7.84 - 7.82 (d,  $J = 8$  Hz, 1H), 7.72 (s, 1H), 7.45 – 7.40 (t,  $J = 8.19$  Hz, 1H), 7.21 – 7.19 (m, 1H), 5.91 (s, br, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz)  $\delta$  (ppm): 156.38, 130.29, 121.93, 115.82, 110.51.

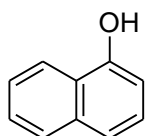
### 3j 4-nitrophenol<sup>5</sup>





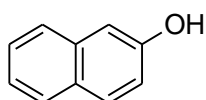
Obtained as a yellow solid; **Yield:** 91% (126.5 mg); **R<sub>f</sub>** = 0.6 (30% ethyl acetate in petroleum ether); **M. p** = 112 °C; **<sup>1</sup>H NMR** (DMSO-d<sub>6</sub>, 400 MHz) δ (ppm): 8.09 – 8.07 (d, *J* = 9.01 Hz, 2H), 6.92 – 6.89 (d, *J* = 9.01 Hz, 2H); **<sup>13</sup>C NMR** (DMSO-d<sub>6</sub>, 100 MHz) δ (ppm): 164.23, 140.01, 126.56, 116.14.

### 3k 1-naphthol<sup>5</sup>



Obtained as colourless liquid; **Yield:** 83% (119.5 mg); **R<sub>f</sub>** = 0.42 (10% ethyl acetate in petroleum ether); **M. p:** 96 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ 8.24 – 8.22 (m, 1H), 7.87 – 7.85 (m, 1H), 7.55 – 7.48 (m, 3H), 7.36 – 7.33 (t, *J* = 7.88 Hz, 1H), 6.86 – 6.84 (d, *J* = 7.38 Hz, 1H) 5.50 - 5.49 (d, br, *J*=4.88 Hz, 1H); **<sup>13</sup>C NMR** (CDCl<sub>3</sub>, 100 MHz): δ 151.39, 134.78, 127.72, 126.49, 125.88, 125.32, 121.58, 120.71, 108.65.

### 3l 2-naphthol<sup>5</sup>



Obtained as a white solid; **Yield:** 82% (118.1 mg); **R<sub>f</sub>** = 0.37 (10% ethyl acetate in petroleum ether); **M. p:** 122 °C; **<sup>1</sup>H NMR** (CDCl<sub>3</sub>, 400 MHz): δ 7.81-7.77 (t, *J* = 7.75 Hz, 2H), 7.72 –

7.70 (d,  $J = 8.25$  Hz, 1H), 7.48 – 7.44 (t,  $J = 7.44$  Hz, 1H), 7.38 – 7.34 (t,  $J = 8$  Hz, 1H), 7.18 – 7.13 (m, 2H), 5.29 (s, br, 1H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 100 MHz):  $\delta$  153.36, 134.59, 129.88, 127.79, 126.56, 126.39, 123.64, 117.77, 109.49.

### 3 References

1. Li X, Li D, Bai Y, Zhang C, Chang H, Gao W, Wei W (2016) Homocoupling reactions of terminal alkynes and arylboronic compounds catalyzed by in situ formed  $\text{Al}(\text{OH})_3$ -supported palladium nanoparticles. *Tetrahedron* 72(44):6996-7002
2. Guanjun C, Meiming L (2011) Homocoupling of Arylboronic Acids Catalyzed by  $\text{CuCl}$  in Air at Room Temperature, *Eur. J. Org. Chem.* 2519-2523.
3. Yang L, Zeng T, Shuai Q, Guo X, Li C–J (2011) Phosphine ligand triggered oxidative decarbonylative homocoupling of aromatic aldehydes: selectively generating biaryls and diaryl ketones. *Chem Commun* 47(7):2161–2163
4. Nandi D, Siwal S, Choudhary M, Mallick K (2016) Carbon nitride supported palladium nanoparticles: An active system for the reduction of aromatic nitro-compounds. *Appl Catal A* 523:31–38
5. Lingxian Liu, Zengguang Li, Changjun Chen, Huanrong Li, Lijin Xu, Zhiyong Yu, *Tetrahedron*, 2018, **74**, 2447.
6. Hong-Yan Xie, Li-Shuai Han, Shan Huang, Xiantao Lei, Yong Cheng, Wenfeng Zhao, Hongbin Sun, Xiaoan Wen, Qing-Long Xu, *J. Org. Chem.*, 2017, **82**, 5236.
7. Yuanding Fang, Rong Zhao, Yuan Yao, Yang Liu, Denghu Chang, Ming Yao, Lei Shi, *Org. Biomol. Chem.*, 2019, **17**, 7558.
8. Debkumar Nandi, Samarjeet Siwal, Meenakshi Choudhary, Kaushik Mallick, *Applied Catalysis A: General* 523 (2016) 31–38.

## 4 Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

