# **Electronic Supplementary Information (ESI)**

# Designing a heterogeneous Pd(II)–NHC-based C–H activation catalyst on self-supported coordination polymer platform

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#### I. General methods and materials:

Reactions were performed in oven-dried glassware. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded in Bruker AVANCE III 400 MHz, 500 MHz and 700 MHz NMR spectrometers. Chemical shifts (δ) are expressed in ppm using the residual proton resonance of the solvent as an internal standard (CHCl<sub>3</sub>:  $\delta =$ 7.26 ppm for <sup>1</sup>H spectra, 77.36 ppm for <sup>13</sup>C{<sup>1</sup>H} spectra; DMSO:  $\delta = 2.50$  ppm for <sup>1</sup>H spectra, 39.52 ppm for  ${}^{13}C{}^{1}H$  spectra, CD<sub>3</sub>CN:  $\delta = 2.13$  ppm for  ${}^{1}H$  spectra, 118.260 ppm for  ${}^{13}C{}^{1}H$  spectra). All coupling constants (J) are expressed in hertz (Hz) and only given for  ${}^{1}H{}^{-1}H$  couplings. The following abbreviations were used to indicate multiplicity: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), bs (broad singlet) and bm (broad multiplet). ESI mass spectrometry was performed on a Bruker microTOF QII spectrometer. UV-Vis spectra were recorded on Agilent Technology Cary 100 UV-Vis spectrophotometer. Electrochemical experiments were done using CHI 620E Electrochemical Analyzer. Thermo Gravimetric Analyses (TGA) were carried out using Perkin Elmer TGA-6000 instrument. The morphology of the coordination polymers was examined using a Carl Zeiss (Ultra Plus) field emission scanning electron microscope (FESEM). Energy dispersive X-ray spectroscopy (EDX) was performed using Oxford Instruments X-MaxN. Inductively coupled plasma optical emission spectrometry (ICP-OES) analysis was performed in a PERKIN ELMER OPTIMA 5300 DV ICP-OES instrument in IIT Madras, India. XPS analyses were performed in PHI 5000 Versa Probe II instrument from FEI Inc. in IIT Kanpur. [Ru(para-cymene)Cl<sub>2</sub>]<sub>2</sub>, model catalyst and compound 1 were synthesized according to the reported procedures<sup>1,2,3</sup>.

#### **II.** Syntheses of relevant materials:

#### **Compound 1:**



Scheme S1. Synthesis of compound 1.

**Step-I: Compound B.** 4'-(4-(Bromomethyl) phenyl)-2,2':6',2''-terpyridine, **A** (667 mg, 1.66 mmol), imidazole (225.5 mg, 3.31 mmol) and KOH (189 mg, 3.37 mmol) were taken in 13 mL DCM and stirred for overnight. After celite filtration, the filtrate was evaporated under reduced pressure. The residue was washed with ice-cold water and diethyl ether and then dried in high vacuum. Pale yellow powder of compound **B** was obtained in 76% yield. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.71 (m, 4H), 8.66 (d, *J* = 8 Hz, 2H), 7.92-7.86 (m, 3H), 7.60 (s, 1H), 7.37-7.39 (m, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.12–7.09 (m, 1H), 6.94 (s, 1H), 5.21 (s, 1H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CDCl<sub>3</sub>): δ (ppm) = 156.2, 149.5, 149.2, 158.8, 138.8, 137.6, 137.0, 135.2,130.0, 128.1, 128.0, 124.0, 121.5, 119.5, 118.9, 50.6. HRMS (ESI, positive mode) m/z = 390.1705 [(M) – H]<sup>+</sup> (Calculated for C<sub>25</sub>H<sub>20</sub>N<sub>5</sub><sup>+</sup>: m/z = 390.1713). Anal. Calc. for C<sub>25</sub>H<sub>19</sub>N<sub>5</sub>: C, 77.10; H, 4.92; N, 17.98. Found: C, 76.97; H, 4.88; N, 17.83%.

**Step-II: Compound 1.** Compound **A** (512.5 mg, 1.27 mmol) and compound **B** (496 mg, 1.27 mmol) were taken in 15 mL of anhydrous THF and stirred for 15 h at ambient temperature to give off-white precipitate of compound **1**. The off-white precipitate was collected by filtration and was washed with diethyl ether to obtain pure compound **1** in 51% yield. <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) = 9.56 (s, 1H), 8.75 (d, *J* = 3.5 Hz, 4H), 8.74 (s, 4H), 8.65 (d, *J* = 8.0 Hz, 4H), 8.0 (m, 8H), 7.96 (d, *J* = 1.1 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 4H), 7.52 (m, 4H), 5.60 (s, 4H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  (ppm) = 155.8, 154.9, 149.3, 138.0, 137.5, 136.6, 135.9, 129.5, 127.7, 124.6, 123.1, 121.0, 118.0, 51.8. HRMS (ESI, positive mode) *m*/*z* = 711.2964 [(M) – Br]<sup>+</sup> (Calculated for C<sub>26</sub>H<sub>22</sub>N<sub>5</sub><sup>+</sup>: *m*/*z* = 711.2979). Anal. Calc. for C<sub>26</sub>H<sub>22</sub>N<sub>5</sub>Br: C, 71.30; H, 4.46; N, 14.15. Found: C, 71.37; H, 4.42; N, 14.12%.

#### <u>2-Ru-CP:</u>

Compound **1** (100 mg, 0.127 mmol) and [Ru(*para*-cymene)Cl<sub>2</sub>]<sub>2</sub> (38.7 mg, 0.063 mmol) were taken in 20 mL of methanol and the resulting mixture was refluxed for 24 h. After cooling down to ambient temperature, methanol was evaporated under reduced pressure. Water was added to the residue followed by addition of 5 eq. of ammonium hexafluorophosphate. The resulting mixture was stirred in dark for 12 h. 110 mg of dark red precipitate of **2-Ru-CP** was collected by filtration, washed with DCM and ether, and then dried under vaccum. <sup>1</sup>H NMR (700 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 9.52-7.23 (bm), 5.73 (bs). <sup>13</sup>C {<sup>1</sup>H} NMR (175 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 159.4, 155.6, 152.7, 138.6, 129.2, 125.5, 123.8, 121.6, 52.4.

# 3-Ru-CP-Pd:

**2-Ru-CP** (100.0 mg), palladium acetate (22.0 mg, 0.1 mmol) and potassium iodide (38 mg, 0.2 mmol) were taken in 4 mL of DMSO and was stirred for 12 h at 80  $^{\circ}$ C under argon atmosphere. Then, it was cooled to room temperature and 15 mL of DCM was added. 88 mg of dark red precipitate of **3-Ru-CP-Pd** was collected by filtration and was washed with DCM and ether. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 700 MHz):  $\delta$  (ppm) = 9.63-7.50 (bm), 5.85 (bs). <sup>13</sup>C {<sup>1</sup>H} NMR (175 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 172.2, 158.1, 157.7, 155.2, 138.1, 130.0, 137.8, 121.1, 118.1.

# <u>2-Zn-CP:</u>

Compound **1** (150 mg, 0.19 mmol) and  $\text{ZnCl}_2$  (26 mg, 0.19 mmol) were added in 30 mL of methanol and was refluxed for 24 h. After the reaction, methanol was evaporated under reduced pressure. Aqueous ammonium hexafluorophosphate (155 mg, 0.9 mmol) was added to the residue and was stirred for 12 h. An 101 mg off-white precipitate of **2-Zn-CP** was collected by filtration and was washed with DCM and ether. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz):  $\delta$  (ppm) = 9.63-7.50 (bm), 5.65 (bs). <sup>13</sup>C{<sup>1</sup>H} NMR (175 MHz, DMSO-d<sub>6</sub>):  $\delta$  (ppm) = 153.9, 149.9, 147.4, 141.2, 137.9, 137.2, 136.3, 129.8, 129.2, 127.9, 127.9, 123.6, 120.8, 52.2.

# 3-Zn-CP-Pd:

**2-Zn-CP** (100.0 mg), palladium acetate (20 mg, 0.09 mmol) and potassium iodide (30 mg, 0.18 mmol) were taken in 40 mL of acetonitrile and was refluxed for 24 h at 80  $^{0}$ C. After cooling the reaction mixture to room temperature, solvent was reduced under low pressure. Residue was washed several times with DCM and diethyl ether. 52 mg of white precipitate was collected by filtration and was washed with ether. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 500 MHz):  $\delta$  (ppm) = 9.65-7.75 (bm), 5.62 (bs). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO-d<sub>6</sub>, 125 MHz):  $\delta$  (ppm) = 149.4, 141.6, 140.7, 129.7, 129.1, 123.0, 120.2, 52.2.

# [**Ru**(terpy-L<sup>+</sup>)<sub>2</sub>][**PF**<sub>6</sub>]:



Scheme S2. Synthesis of the model compound  $[Ru(terpy-L^+)_2][PF_6]$ .

**Step-I: terpy-L<sup>+</sup>.** A solution of 4'-(4-(bromomethyl)phenyl)-2,2':6',2"-terpyridine, **A** (605 mg, 1.5 mmol) and 1-methyl-1H-imidazole (132  $\mu$ l, 1.65 mmol) in 22 mL of 1,4-dioxane was refluxed for 8 h. The resulting solution was cooled to room temperature to furnish a white precipitate which was collected by

filtration and washed with Et<sub>2</sub>O. The resulting white solid was recrystallized from MeOH/Et<sub>2</sub>O, washed with additional Et<sub>2</sub>O and dried under vacuum. Thus, 405 mg of **terpy-L**<sup>+</sup> was obtained (56%). <sup>1</sup>H NMR (400 MHz, DMSO-*d*6):  $\delta$  (ppm) = 9.27 (s, 1H), 8.79-8.66 (m, 6H), 8.07-8.00 (m, 4H), 7.86 (s, 1H), 7.76 (s, 1H), 7.64 (d, *J* = 8.2 Hz, 4H), 7.58-7.51 (m, 2H), 5.54 (s, 2H), 3.88 (s, 3H). HRMS (ESI, positive mode)  $m/z = 404.1890 [(M) - Br]^+$  (calcd for C<sub>26</sub>H<sub>22</sub>N<sub>5</sub><sup>+</sup>: m/z = 404.1870).

**Step-II:** [**Ru**<sup>II</sup>(**terpy-L**<sup>+</sup>)<sub>2</sub>](**PF**<sub>6</sub>)<sub>4</sub>. To 10 mL of MeOH solution of **terpy-L**<sup>+</sup> (48.3 mg, 0.1 mmol), [Ru(*para*-cymene)Cl<sub>2</sub>]<sub>2</sub> (15.4 mg, 0.025 mmol) was added. The resulting blue-colored mixture was refluxed for 18 h under N<sub>2</sub>, when a dark red solution was obtained. Solvent was removed under reduced pressure. The red residue was dissolved in minimum amount of water and saturated aqueous solution of NH<sub>4</sub>PF<sub>6</sub> (326 mg, 2 mmol) was added, followed by 2 h stirring at room temperature. The resulting dark red precipitate was collected by filtration, and was washed with water, cold MeOH and Et<sub>2</sub>O respectively to obtain 62 mg of red crystalline [**Ru**<sup>II</sup>(**terpy-L**<sup>+</sup>)<sub>2</sub>](**PF**<sub>6</sub>)<sub>4</sub> (90%). <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 9.00 (s, 4H), 8.65 (d, *J* = 8.2 Hz, 4H), 8.62 (s, 2H), 8.26 (d, *J* = 8.2 Hz, 4H), 7.95 (t, *J* = 8.4 Hz, 4H), 7.72 (d, *J* = 8.1 Hz, 4H), 7.49 (s, 2H), 7.45 (s, 2H), 7.43 (d, *J* = 5.4 Hz, 4H), 7.19 (d, *J* = 6.5 Hz, 4H), 5.52 (s, 4H), 3.90 (s, 6H). <sup>13</sup>C{<sup>1</sup>H} NMR (100 MHz, CD<sub>3</sub>CN):  $\delta$  (ppm) = 159.1, 156.5, 153.5, 148.3, 139.1, 138.6, 137.4, 137.1, 130.6, 129.6, 128.5, 125.6, 125.4, 123.5, 122.7, 53.3, 37.1. HRMS (ESI, positive mode) *m*/*z* = 600.1061 [(M) – 2PF<sub>6</sub>]<sup>2+</sup> (calcd for C<sub>52</sub>H<sub>44</sub>N<sub>10</sub>P<sub>2</sub>F<sub>12</sub>Ru<sup>2+</sup>: *m*/*z* = 600.1040), *m*/*z* = 351.7495 [(M) – 3PF<sub>6</sub>]<sup>3+</sup> (calcd for C<sub>52</sub>H<sub>44</sub>N<sub>10</sub>PF<sub>6</sub>Ru<sup>3+</sup>: *m*/*z* = 351.7478), *m*/*z* = 227.5701[(M) – 4PF<sub>6</sub>]<sup>4+</sup> (calcd for C<sub>52</sub>H<sub>44</sub>N<sub>10</sub>Ru<sup>4+</sup>: *m*/*z* = 227.5696).

III. <sup>1</sup>H NMR, <sup>13</sup>C{<sup>1</sup>H} NMR, ESI-HR mass spectra:



Figure S1. <sup>1</sup>H NMR of compound B (400 MHz, CDCl<sub>3</sub>).



**Figure S2.** <sup>13</sup>C{<sup>1</sup>H} NMR of compound **B** (100 MHz, CDCl<sub>3</sub>).



Figure S3. HRMS (ESI +ve) of compound B.



Figure S4. <sup>1</sup>H NMR of compound 1 (400 MHz, DMSO-d<sub>6</sub>).



**Figure S5.** <sup>13</sup>C{<sup>1</sup>H} NMR of compound **1** (100 MHz, DMSO- $d_6$ ).



Figure S6. HRMS (ESI +ve) of compound 1.



Figure S7. <sup>1</sup>H NMR of **2-Ru-CP** (700 MHz, DMSO-d<sub>6</sub>).



**Figure S8**. <sup>13</sup>C{<sup>1</sup>H} NMR of **2-Ru-CP** (175 MHz, DMSO-d<sub>6</sub>).



Figure S9. <sup>1</sup>H NMR of 3-Ru-CP-Pd (700 MHz, DMSO-d<sub>6</sub>).



Figure S10.  $^{13}C{^{1}H}$  of 3-Ru-CP-Pd (175 MHz, DMSO-d<sub>6</sub>).



**Figure S11**. <sup>1</sup>H NMR of **2-Zn-CP** (500 MHz, DMSO- $d_6$ ).



**Figure S12**.  ${}^{13}C{}^{1}H$  NMR of **2-Zn-CP** (175 MHz, DMSO-d<sub>6</sub>).



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**Figure S13.** <sup>1</sup>H NMR of **3-Zn-CP-Pd** (500 MHz, DMSO-d<sub>6</sub>).



Figure S14.  ${}^{13}C{}^{1}H$  NMR of 3-Zn-CP-Pd (175 MHz, DMSO-d<sub>6</sub>).



**Figure S15.** <sup>1</sup>H NMR of terpy-L<sup>+</sup> (400 MHz, DMSO-d<sub>6</sub>).



**Figure S16.**  ${}^{13}C{}^{1}H$  NMR of **terpy-L**<sup>+</sup> (100 MHz, DMSO-d<sub>6</sub>).



Figure S17. <sup>1</sup>H NMR of  $[Ru(terpy-L^+)_2][PF_6]$  (400 MHz, CD<sub>3</sub>CN).



**Figure S18.**  ${}^{13}C{}^{1}H$  NMR of [**Ru**(terpy-L<sup>+</sup>)<sub>2</sub>][**PF**<sub>6</sub>] (100 MHz, CD<sub>3</sub>CN).



Figure S23. PXRD of 3-Zn-CP-Pd.

Figure S24. TGA of 3-Zn-CP-Pd.

# V. SEM images:



Figure S25. SEM image of 2-Ru-CP.



Figure S26. SEM image of 3-Ru-CP-Pd.



Figure S27. SEM image of 2-Zn-CP.



Figure S28. SEM image of 3-Zn-CP-Pd.

# VI. EDX analysis plots:



Figure S29. EDX of 2-Ru-CP.



Figure S30. EDX of 3-Ru-CP-Pd.



Figure S31. EDX of 2-Zn-CP.



Figure S32. EDX of 3-Zn-CP-Pd.

VII. XPS analysis:





Pd binding energies of 337.6 eV, and 342.8 eV confirmed Pd in +2 oxidation state.

### VIII. General procedure for directed halogenation of arenes:

Arene (1.25 mmol), NBS/NCS (0.125 mmol), and **3-Ru-CP-Pd** (1.5 mol% of Pd) were placed in a pressure tube. 1 mL of dichloroethane was added and the pressure tube was capped tightly. The resulting solution was stirred at 95  $^{\circ}$ C for 16 h. Yield was calculated by GC analysis using PhCl as internal standard.

# IX. Hot filtration test for chlorination of 2-phenyl pyridine:

*Experiment I*: 2-phenylpyridine (0.18 mL, 1.25 mmol), NCS (16.6 mg, 0.125 mmol) and **3-Ru-CP-Pd** (5 mg, 1.5 mol% Pd) were taken in 1 mL of mixed solvent EtOAc/CH<sub>3</sub>CN (3/2). The mixture was stirred at 95  $^{\circ}$ C in a Schlenk tube under Ar. Similar set-up was maintained for another reaction. The progress of both the reactions was monitored at regular interval by GC, using chlorobenzene as internal standard. After 5 h, one of the reactions was stopped and the reaction mixture was filtered under hot condition. The filtrate was further kept at 95  $^{\circ}$ C with stirring in a Schlenk tube and progress of the reaction was monitored by GC. The other reaction was allowed to proceed without hot filtration and its progress was also monitored by GC at regular intervals.

*Experiment II*: 2-phenylpyridine (0.18 mL, 1.25 mmol), NCS (16.6 mg, 0.125 mmol) and **3-Ru-CP-Pd** (5 mg, 1.5 mol% Pd) were taken in 1 mL of 1,2-dichloroethane. The mixture was stirred at 95  $^{\circ}$ C in a Schlenk tube under Ar. Similar set-up was maintained for another reaction. The progress of both the reactions was monitored at regular interval by GC, using chlorobenzene as internal standard. After 5 h, one of the reactions was stopped and the reaction mixture was filtered under hot condition. The filtrate was further kept at 95  $^{\circ}$ C with stirring in a Schlenk tube and the progress of the reaction was monitored by GC. The other reaction was allowed to proceed without hot filtration and its progress was also monitored by GC at regular intervals.

### X. Reusability test:

2-phenylpyridine (0.9 mL, 6.25 mmol), NCS (83 mg, 0.625 mmol) and **3-Ru-CP-Pd** (25 mg, 1.5 mol% Pd) were taken in 5 mL of mixed solvent EtOAc/CH<sub>3</sub>CN (3/2). The mixture was stirred at 95  $^{\circ}$ C in a sealed tube for 16 h. After cooling to room temperature, the yield of the reaction was calculated by GC using chlorobenzene as internal standard. **3-Ru-CP-Pd** was separated from the reaction mixture by centrifugation and washed with 3×3 mL of mixed solvent EtOAc/CH<sub>3</sub>CN (3/2) by sonication. **3-Ru-CP-Pd** was then re-used for the next set of reaction.

### XI. Characterization of the recovered catalyst:

After reusing the catalyst 5 times for a typical set-up as described in section **IX**, the catalyst **3-Ru-CP-Pd** was separated from the reaction mixture by centrifugation and washed with 3×3 mL of mixed solvent EtOAc/CH<sub>3</sub>CN (3/2) by sonication followed by diethyl ether. Colorless washing solution was decanted and the red solid thus obtained was dried in vacuum. This recovered catalyst was dissolved in DMF and UV-Vis spectrum was recorded, and compared with the original UV-Vis spectrum of **3-Ru-CP-Pd** in DMF. In both the cases approximately 0.1 mg of **3-Ru-CP-Pd** was dissolved in 1 mL of DMF. SEM image and EDX were also taken for the recovered **3-Ru-CP-Pd**. From another typical reaction, the recovered catalyst was analyzed by XPS also for verifying the nature of Pd oxidation state.



Figure S34. UV-Vis spectrum of 3-Ru-CP-Pd before and after chlorination.



Figure S35. SEM image of recovered 3-Ru-CP-Pd after chlorination.



Figure S36. EDX of recovered 3-Ru-CP-Pd after chlorination.



**Figure S37.** XPS spectrum of palladium for the **3-Ru-CP-Pd** catalyst recovered from the reaction mixture for a typical chlorination reaction of 2-phenyl pyridine after 40% yield. Pd binding energies of 338.0 eV, and 343.4 eV confirmed Pd in +2 oxidation state.

# XII. GCMS data for brominated and chlorinated products:







Figure S38. GCMS for the chlorination of 2-phenylpyridine.







Figure S39. GCMS for the bromination of 2-phenylpyridine.





Figure S40. GCMS for the chlorination of 1-phenylpyrazole.





Figure S41. GCMS for the bromination of 1-phenylpyrazole.







Figure S42. GCMS for the bromination of 2-phenylthiophene.









Figure S43. GCMS for the chlorination of 2-phenylthiophene.





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Figure S44. GCMS for the bromination of acetophenone.







Figure S45. GCMS for the chlorination of acetophenone.





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Figure S46. GCMS for the bromination of N-benzylidene aniline.







Figure S47. GCMS for the chlorination of N-benzylidene aniline.

# XIII. References:

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