

## Supporting Information

### **Substituted Pyridazines As Ligands In Homoleptic (*fac* and *mer*) and Heteroleptic Ru(II) Complexes**

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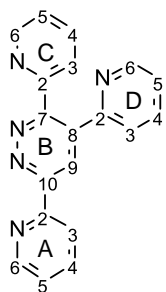
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## Experimental Details

Unless otherwise stated all reactions were carried out in air. Solvents were dried as required according to standard techniques. Flash chromatography was performed using silica gel or activated alumina (Aldrich Chemicals) as the stationary phase. All chemicals were purchased from Aldrich Chemical Co. Ltd. and were used without further purification unless otherwise stated. MALDI-TOF mass spectra were recorded on a Waters MALDI-QTOF Premier spectrometer. Nuclear magnetic resonance spectra were recorded in deuterated acetonitrile or chloroform on a Bruker Avance DPX-400 MHz, AV-400 MHz, or AV-600 MHz spectrometers, the signals referenced to a TMS standard. UV-vis absorption spectra were recorded on a Shimadzu UV-2401PC UV-Vis recording spectrometer. The emission spectra were not corrected and were recorded at room temperature on a Varian Fluorescence Cary Eclipse spectrophotometer. IR spectra were obtained using a Perkin Elmer Diffuse Reflectance spectrometer in solid form in a KBr mixture. Elemental analyses were carried out using a Carlo Erba 1006 automatic analyser. Melting points are given uncorrected and were on a Griffin melting point apparatus. Single crystal analyses were carried out on a Bruker SMART APEX CCD diffractometer using graphite monochromised Mo-K $\alpha$  ( $\lambda = 0.71073\text{\AA}$ ) radiation at the temperatures given following data. Data reduction was performed using SAINT. Intensities were corrected for Lorentz and polarization effects and for absorption by SADABS. The structures were solved by direct methods using SHELXS and refined on F<sup>2</sup> using all data by full-matrix least-squares procedures with SHELX-97. All non-hydrogen atoms were refined with anisotropic displacement parameters 1.3 times the isotropic equivalent of their carrier carbons.

Note: The following abbreviations are used to distinguish resonances in NMR analyses. Py = pyridine, ph = phenyl, pz = pyridazine, pm = pyrimidine, pr = pyrazine, bpy = bipyridine, C<sup>Q</sup> = quaternary carbon, s = singlet, d = doublet, t = triplet,  $\Psi$ t = pseudo triplet (unresolved dd).

### 3,4,6-tri (2-pyridyl) pyridazine (1a)



The reaction was carried out in air by adding a 2.5% methanolic solution of KOH (1 mL) to a THF solution (5 mL) containing bptz (0.500 g, 2.116 mmol) and 2-acetyl pyridine (400  $\mu$ L, 3.567 mmol) at 40°C. The mixture was stirred for 5 mins, allowed to cool, washed with water, and extracted into dichloromethane. The solvent was then reduced under vacuum, and the resulting mixture was run through a silica column (10% methanol in ethyl acetate) to give the product (0.530 g, 1.702 mmol). This was further purified by recrystallisation from a mixture of ethyl acetate and petroleum ether (yield 80%).

IR (KBr):  $\nu$ bar 3081m, 3066m, 3004m, 1587s, 1574s, 1560m, 1478m, 1468s, 1393s, 1095m, 993s, 788s, 769m, 748m, 619m, 584m, 537m  $\text{cm}^{-1}$ .

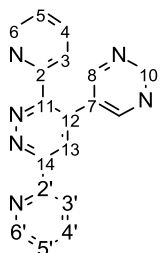
<sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>):  $\delta$  8.82 (s, 1H, H<sup>9</sup>), 8.75 (d, 1H, H<sup>3A</sup> J = 8.0 Hz), 8.69 (d, 1H, H<sup>6A</sup> J = 4.5 Hz), 8.51 (d, 1H, H<sup>6B</sup>, J = 4.5 Hz), 8.31 (d, 1H, H<sup>6C</sup>, J = 4.5 Hz), 8.13 (d, 1H, H<sup>3B</sup>, J = 8.0 Hz), 7.88 ( $\Psi$ td, 1H, H<sup>4A</sup>, J = 7.3, 1.5 Hz), 7.82 ( $\Psi$ td, 1H, H<sup>4B</sup>, J = 7.5, 1.5 Hz), 7.63 ( $\Psi$ td, 1H, H<sup>4C</sup>, J = 7.5, 1.5 Hz), 7.36 (m, 1H, H<sup>5A</sup>), 7.34 (d, 1H, H<sup>3C</sup>, J = 8.0 Hz), 7.22 ppm (m, 2H, H<sup>5B, 5C</sup>).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  157.7 (C<sup>7/10</sup>), 157.5 (C<sup>7/10</sup>), 155.3 (C<sup>2A</sup>), 155.1 (C<sup>2B</sup>), 152.8 (C<sup>2C</sup>), 149.0 (C<sup>6A, 6B</sup>), 148.1 (C<sup>6C</sup>), 138.9 (C<sup>8</sup>), 136.8 (C<sup>4A</sup>), 136.4 (C<sup>4B</sup>), 135.8 (C<sup>4C</sup>), 125.3 (C<sup>9</sup>), 124.4 (C<sup>3A</sup>), 124.2 (C<sup>5A</sup>), 123.6 (C<sup>3B</sup>), 123.0 (C<sup>5B</sup>), 122.4 (C<sup>5C</sup>), 121.4 ppm (C<sup>3C</sup>).

HRMS: (CH<sub>3</sub>CN): calculated [MH]<sup>+</sup> m/z 312.1250, found: 312.1252

Anal. Calcd. for C<sub>19</sub>H<sub>13</sub>N<sub>5</sub>: C 73.30, H 4.21; N 22.49. Found; C 72.87, H 4.32, N 22.33. m.p. 165°-166°C.

### Synthesis of 3,6 di-(2-pyridyl) 4-pyrimidyl pyridazine (2a)



The reaction was carried out in air by refluxing bptz (0.102 g, 0.433 mmol) and 5-ethynylpyrimidine (0.047 g, 0.451 mmol) in toluene (2.5 mL) for 24 hrs. The solvent was removed by rotary evaporation, and the reaction mixture purified on a silica column (ethyl acetate, 20% methanol). The product was recovered as a light yellow solid (0.087g, 0.279 mmol, 65%).

I.R. vbar 3093m, 3065m, 3039m, 3022m, 1582s, 1571s, 1555s, 1477s, 1419s, 1393s, 991s, 793s, 773s, 724m, 656m, 629m, 620m, 588w, 531w  $\text{cm}^{-1}$ .

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.21 (s, 1H,  $\text{H}^{10}$ ), 8.81 (d, 1H,  $\text{H}^3$ ,  $J = 8.0$  Hz), 8.73 (d, 1H,  $\text{H}^6$ ,  $J = 4.0$  Hz), 8.68 (s, 2H,  $\text{H}^8$ ), 8.67 (s, 1H,  $\text{H}^{13}$ ), 8.36 (d, 1H,  $\text{H}^6$ ,  $J = 4.5$  Hz), 8.32 (d, 1H,  $\text{H}^3$ ,  $J = 8.0$  Hz), 7.94 ( $\Psi$ td, 1H,  $\text{H}^4$ ,  $J = 8.0, 2.0$  Hz), 7.90 ( $\Psi$ td, 1H,  $\text{H}^4$ ,  $J = 8.0$  Hz, 1.5 Hz), 7.45 (ddd, 1H,  $\text{H}^5$ ,  $J = 7.5, 5.0, 1.0$  Hz), 7.31 ppm (ddd, 1H,  $\text{H}^5$ ,  $J = 7.5, 5.0, 1.0$  Hz).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.9 ( $\text{C}^{10}$ ), 157.7 ( $\text{C}^{14}$ ), 157.1 ( $\text{C}^{11}$ ), 156.0 ( $\text{C}^8, \text{C}^8'$ ), 154.2 ( $\text{C}^2$ ), 152.5 ( $\text{C}^2'$ ), 149.5 ( $\text{C}^6$ ), 148.7 ( $\text{C}^6'$ ), 137.3 ( $\text{C}^4$ ), 137.2 ( $\text{C}^4'$ ), 134.1 ( $\text{C}^{12}$ ), 132.0 ( $\text{C}^7$ ), 126.0 ( $\text{C}^{13}$ ), 125.2 ( $\text{C}^5$ ), 124.7 ( $\text{C}^3$ ), 124.2 ( $\text{C}^5'$ ), 121.8 ppm ( $\text{C}^3'$ ).

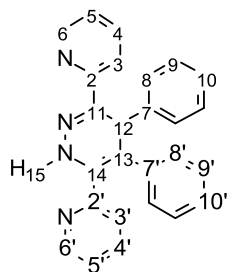
HRMS: ( $\text{CH}_3\text{CN}$ ): calculated  $[\text{MH}]^+$   $m/z$  335.1021, found: 335.1081

Anal. Calc. For  $\text{C}_{18}\text{H}_{12}\text{N}_6$ ; C, 69.22; H, 3.87; N, 26.91. Found: C, 68.93; H, 3.85; N, 26.71. m.p.  $170^\circ\text{--}172^\circ\text{C}$ .

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### 3,6-di(2-pyridyl)-4,5-diphenyl pyridazine (3a)

3,6-di(2-pyridyl) 4,5-diphenyl-1,4-dihydropyridazine



Bptz (0.600 g, 2.540 mmol) and *trans*-stilbene (0.469 g, 2.600 mmol) were refluxed in toluene (20 mL) for 24 hrs. The colour of the solution changed from dark pink to a bright yellow. The solvent was removed *in vacuo*, and the reaction mixture was run through a silica column (10% diethyl ether in dichloromethane) to furnish the product as a light yellow solid (0.9370 g, 2.210 mmol, 95%).

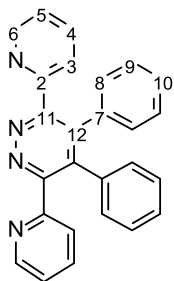
$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.43 (s, 1H,  $\text{H}^{15}$ ), 8.67 (d, 1H,  $\text{H}^6$ ,  $J = 3.8$  Hz), 8.61 (d, 1H,  $\text{H}^6'$ ,  $J = 4.4$  Hz), 8.10 (d, 1H,  $\text{H}^3$ ,  $J = 7.9$  Hz), 7.63 ( $\Psi$ td, 1H,  $\text{H}^4$ ,  $J = 7.8, 1.8$  Hz), 7.57 (d, 2H,  $\text{H}^8, \text{H}^8'$ ,  $J_{8,9} = 7.0$  Hz), 7.40 ( $\Psi$ td, 1H,  $\text{H}^4$ ,  $J = 7.8, 1.5$  Hz), 7.30-7.17 (m, 11H,  $\text{H}^3, 5, 5', 9, 10, 8', 9', 10'$ ), 5.82 ppm (s, 1H,  $\text{H}^{12}$ ).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.2 ( $\text{C}^{11}$ ), 151.6 ( $\text{C}^{14}$ ), 149.0 ( $\text{C}^6$ ), 148.3 ( $\text{C}^6'$ ), 141.9 ( $\text{C}^0$ ), 138.9 ( $\text{C}^0$ ), 136.1 ( $\text{C}^4$ ), 135.9 ( $\text{C}^4'$ ), 135.1 ( $\text{C}^0$ ), 129.9 ( $2\text{C}^0$ ), 128.5 ( $2\text{C}$ ), 128.3 ( $4\text{C}$ ), 128.3 ( $1\text{C}$ ), 127.2 ( $1\text{C}$ ), 126.7 ( $1\text{C}$ ), 125.5 ( $1\text{C}$ ), 123.0 ( $1\text{C}$ ), 122.7 ( $1\text{C}$ ), 121.5 ( $1\text{C}$ ), 108.2 ( $\text{C}^{13}$ ), 41.5 ppm ( $\text{C}^{12}$ ).

HRMS: ( $\text{CH}_3\text{CN}$ ); calculated  $[\text{MH}]^+$   $m/z$  389.1766, found: 389.1782.

Anal. Calc. For  $\text{C}_{26}\text{H}_{20}\text{N}_4$ ; C, 80.39; H, 5.19; N, 14.42. Found: C, 80.42; H, 5.26; N, 14.37

### 3,6-di(2-pyridyl)-4,5-diphenyl pyridazine



A solution of  $\text{NaNO}_2$  (6 M, 20 mL) was added dropwise to a concentrated  $\text{HCl}$  (12 mL). The gas evolved was passed through a dichloromethane solution (40 mL) of 3,6-di(2-pyridyl)-4,5-diphenyl-1,4-dihydropyridazine which was maintained at  $0^\circ\text{C}$  until all the sodium nitrite had been added. The dihydropyridazine solution was then allowed to return to room temperature, with constant  $\text{N}_2$  bubbling to remove excess nitrous gas. The solvent was removed under vacuum and the reaction mixture dissolved in water and neutralized by the addition of 10% ammonia solution. The mixture was extracted into  $\text{CH}_2\text{Cl}_2$ , dried over  $\text{MgSO}_4$  and purified using a silica column (10% methanol in ethyl acetate). The product was recovered as a white solid (0.598 g, 1.6 mmol, 74%).

I.R. vbar 3078m, 3054m, 3024m, 3003m, 1587s, 1569s, 1474s, 1377s, 1155s, 991s, 793s, 782s, 771s, 746s, 636s, 624s, 531m, 486m  $\text{cm}^{-1}$ .

$^1\text{H}$ -NMR (400 MHz,  $\text{CH}_3\text{CN}$ ):  $\delta$  8.42 (d, 2H,  $\text{H}^6$ ,  $J = 4.5$  Hz), 7.64 (m, 4H,  $\text{H}^3, 4$ ), 7.17 ( $\Psi$ td, 2H,  $\text{H}^5$ ,  $J = 6.5, 1.5$  Hz), 7.05 (m, 6H,  $\text{H}^8, \text{H}^{10}$ ), 6.87 ppm (m, 2H,  $\text{H}^9$ ).

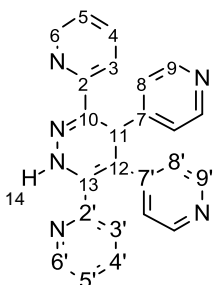
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5 ( $\text{C}^{11}$ ), 155.6 ( $\text{C}^2$ ), 148.4 ( $\text{C}^6$ ), 138.7 ( $\text{C}^{12}$ ), 135.7 ( $\text{C}^4$ ), 134.2 ( $\text{C}^7$ ), 129.7 ( $\text{C}^9$ ), 127.1 ( $\text{C}^8$ ), 126.9 ( $\text{C}^{10}$ ), 124.6 ( $\text{C}^3$ ), 122.5 ppm ( $\text{C}^5$ ).

HRMS: ( $\text{CH}_3\text{CN}$ ); calculated  $[\text{MH}]^+$   $m/z$  387.1596 found: 387.1610.

Anal. Calcd for  $\text{C}_{26}\text{H}_{18}\text{N}_4$ ; C, 80.81; H, 4.69; N, 14.50. Found: C, 79.92; H, 4.64; N, 14.26. m.p.  $189^\circ\text{--}191^\circ\text{C}$ .

### 3,6-di(2-pyridyl) 4,5-di(4-pyridyl) pyridazine (4a)

3,6-di(2-pyridyl) 4,5-di(4-pyridyl)-1,4-dihydropyridazine



Bptz (0.500 g, 2.116 mmol) and (*E*)-1,2-di(4'-pyridyl)ethene (0.410 g 2.251 mmol) were added to toluene (10 mL) and heated in a sealed tube at  $180^\circ\text{C}$  for 24 hrs. The solvent was removed *in vacuo* and the reaction mixture purified on a silica column (20% methanol in diethyl ether). The product was isolated as a bright yellow solid (0.619 g, 1.6 mmol, 75%).

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 9.50 (s, 1H, H<sup>14</sup>), 8.72 (d, 1H, H<sup>6</sup>, J = 5.0 Hz), 8.61 (d, 1H, H<sup>6</sup>, J = 6.0 Hz), 8.50 (d, 2H, H<sup>9/9'</sup>, J = 6.5 Hz), 8.41 (d, 2H, H<sup>9/9'</sup>, J = 6.0 Hz), 8.13 (d, 1H, H<sup>3</sup>, J = 8.0 Hz), 7.66 (Ψtd, 1H, H<sup>4</sup>, J = 7.8, 1.5 Hz), 7.55 (Ψtd, 1H, H<sup>4</sup>, J = 7.5, 1.5 Hz), 7.46 (d, 2H, H<sup>8/8'</sup>, J = 6.0 Hz), 7.36 (d, 1H, H<sup>3</sup>, J = 6.0 Hz), 7.32 (d, 1H, H<sup>5</sup>, J = 2.0 Hz), 7.22 (m, 1H, H<sup>5</sup>, J = 2.0 Hz), 7.06 (d, 2H, H<sup>8/8'</sup>, J = 6.0 Hz), 5.86 ppm (s, 1H, H<sup>11</sup>).

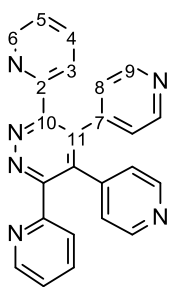
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 153.4 (C<sup>2</sup>), 150.8 (C<sup>2</sup>), 150.1 (C<sup>9/9'</sup>), 150.0 (C<sup>9/9'</sup>), 150.0 (C<sup>6</sup>), 148.4 (C<sup>6</sup>), 146.3 (C<sup>7</sup>), 140.7 (C<sup>10</sup>), 138.7 (C<sup>13</sup>), 136.5 (C<sup>4</sup>), 136.2 (C<sup>4</sup>), 125.6 (C<sup>3</sup>), 124.1 (C<sup>5</sup>), 123.9 (C<sup>8/8'</sup>), 123.3 (C<sup>5</sup>), 123.1 (C<sup>8/8'</sup>), 121.5 (C<sup>3</sup>), 102.5 (C<sup>11</sup>), 39.5 ppm (C<sup>7</sup>).

HRMS: (CH<sub>3</sub>CN); calculated for C<sub>24</sub>H<sub>19</sub>N<sub>6</sub>: [MH]<sup>+</sup> m/z 391.1671 found: 391.1667.

Anal. Calc. For C<sub>24</sub>H<sub>18</sub>N<sub>6</sub>; C: 73.83; H: 4.65; N: 21.52. Found: C: 73.85; H: 4.70; N: 20.93

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### 3,6-di(2-pyridyl)-4,5-di(4-pyridyl)pyridazine



The same procedure was used as for **3a**. Purification was carried out using column chromatography (SiO<sub>2</sub>, 50% ether, 50% methanol). The product was recovered as a white solid (0.308 g, 50 % yield).

I.R. vbar 3059m, 3039m, 3027m, 1596s, 1584s, 1568s, 1408s, 1382s, 1374s, 1218m, 991s, 813s, 808s, 796s, 786s, 750s, 648s, 624s, 538m, 489w cm<sup>-1</sup>.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 8.34 (d, 2H, H<sup>9</sup>, J = 5.5 Hz), 8.30 (d, 2H, H<sup>6</sup>, J = 4.5 Hz), 8.01 (d, 2H, H<sup>3</sup>, J = 7.6 Hz), 7.81 (Ψtd, 2H, H<sup>4</sup>, J = 7.5, 1.5 Hz), 7.23 (m, 2H, H<sup>5</sup>), 6.85 ppm (d, 2H, H<sup>8</sup>, J = 6.0 Hz).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 157.0 (C<sup>10</sup>), 154.2 (C<sup>2</sup>), 148.7 (C<sup>9</sup>), 148.3 (C<sup>6</sup>), 142.6 (C<sup>7</sup>), 136.3 (C<sup>4</sup>), 136.1 (C<sup>11</sup>), 124.5 (C<sup>3</sup>), 124.1 (C<sup>8</sup>), 123.2 ppm, (C<sup>5</sup>).

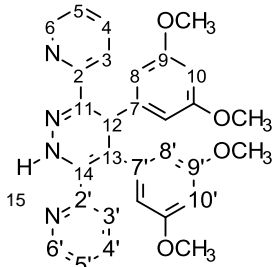
HRMS: (CH<sub>3</sub>CN); calculated: [MH]<sup>+</sup> m/z 387.1504 found: 387.1515.

Anal. Calcd. for C<sub>24</sub>H<sub>16</sub>N<sub>6</sub>: C, 74.21; H, 4.15; N, 21.64. Found: C, 75.23; H, 4.60; N, 20.88. m.p. 119 - 221

°C

### 3,6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)pyridazine (**5a**)

#### 3,6-di(2-pyridyl)-4,5-di(3,5-dimethoxyphenyl)-1,4-dihydropyridazine



The same procedure was used as for 3,6-di(2-pyridyl) 4,5-diphenyl-1,4-dihydropyridazine (above) using bptz (0.78 g, 3.29 mmol) and (E)-3,3',5,5'-tetramethoxy stilbene (0.99 g, 3.29 mmol). The product was purified using column chromatography using diethylether as eluent. The product was isolated as a yellow oil which solidified on standing (1.03 g, 2.0 mmol, 61%).

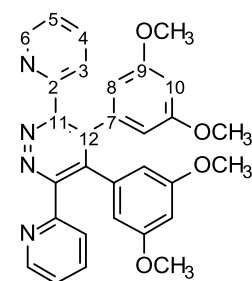
<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ 9.37 (s, 1H, H<sup>15</sup>), 8.64 (d, 1H, H<sup>6/6'</sup>, J = 5.0 Hz), 8.60 (d, 1H, H<sup>6/6'</sup>, J = 4.5 Hz), 8.16 (d, 1H, H<sup>3/3'</sup>, J = 8.0 Hz), 7.61 (Ψtd, 1H, H<sup>4/4'</sup>, J = 7.5, 1.8 Hz), 7.47 (Ψtd, 1H, H<sup>4/4'</sup>, J = 7.5, 1.5 Hz), 7.37 (d, 1H, H<sup>3/3'</sup>, J = 8.0 Hz), 7.18 (m, 2H, H<sup>5/5'</sup>), 6.80 (d, 2H, H<sup>8,8'</sup>, J = 2.0 Hz), 6.41 (d, 2H, H<sup>8/8'</sup>, J = 2.0 Hz), 6.35 (t, 1H, H<sup>10/10'</sup>, J = 2.0 Hz), 6.32 (t, 1H, H<sup>10/10'</sup>, J = 2.0 Hz), 5.75 (s, 1H, H<sup>16</sup>), 3.70 (s, 6H, -OMe), 3.61 ppm (s, 6H, -OMe).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 160.3 (C<sup>9</sup>), 159.9 (C<sup>9</sup>), 154.2 (C<sup>9</sup>), 151.5 (C<sup>9</sup>), 148.5 (C<sup>6/6'</sup>), 147.8 (C<sup>6/6'</sup>), 144.2 (C<sup>9</sup>), 140.9 (C<sup>9</sup>), 140.8 (C<sup>9</sup>), 135.5 (C<sup>4/4'</sup>), 135.5 (C<sup>4/4'</sup>), 135.4 (C<sup>9</sup>), 125.2 (C<sup>3/3'</sup>), 122.6 (C<sup>5/5'</sup>), 122.2 (C<sup>5/5'</sup>), 121.0 (C<sup>3/3'</sup>), 107.7 (C<sup>9</sup>), 107.5 (C<sup>8/8'</sup>), 106.3 (C<sup>8/8'</sup>), 99.2 (C<sup>10/10'</sup>), 98.1 (C<sup>10/10'</sup>), 54.7 (-OMe), 54.7 (-OMe), 41.1 ppm (C<sup>12</sup>).

HRMS: (CH<sub>3</sub>CN); calculated for C<sub>30</sub>H<sub>29</sub>N<sub>4</sub>O<sub>4</sub>: [MH]<sup>+</sup> m/z 509.2189 found: 509.2221.

Anal. Calc. For C<sub>30</sub>H<sub>28</sub>N<sub>4</sub>O<sub>4</sub>; C: 70.85; H: 5.55; N: 11.02. Found: C: 70.89; H: 6.00; N: 11.00.

#### 3,6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)pyridazine



The same procedure was applied as for **3a** using a dichloromethane solution (40 mL) containing 3,6-di(2-pyridyl)-4,5-di-(3,5-dimethoxyphenyl)-1,4-dihydropyridazine. The product was purified by column chromatography on silica (dichloromethane:ethanol, 5:1) and recovered as a yellow solid (0.855g, 1.68 mmol, 75 %).

I.R. (KBr) vbar 3052s, 3005s, 2941s, 2839s, 1592s, 1494s, 1462s, 1425s, 1363s, 1343s, 1204s, 1145s, 1064s, 842s, 805s, 830s, 749s, 693s cm<sup>-1</sup>.

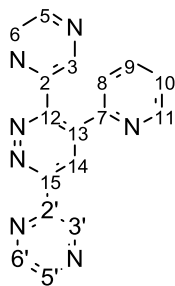
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ: 8.55 (d, 2H, H<sup>6</sup>, J = 5.0 Hz), 7.72 (Ψtd, 2H, H<sup>4</sup>, J = 7.5, 1.5 Hz), 7.61 (d, 2H, H<sup>3</sup>, J = 8.0 Hz), 7.23 (m, 2H, H<sup>5</sup>), 6.22 (t, 2H, H<sup>13</sup>, J = 2.0 Hz), 6.10 (d, 4H, H<sup>11</sup>, J = 2.0 Hz), 3.67 ppm (s, 12H, -OMe).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 160.0 (C<sup>9</sup>), 158.9 (C<sup>9</sup>), 156.1 (C<sup>9</sup>), 149.1 (C<sup>6</sup>), 138.7 (C<sup>9</sup>), 136.4 (C<sup>9</sup>), 136.2 (C<sup>4</sup>), 124.8 (C<sup>3</sup>), 123.0 (C<sup>5</sup>), 108.4 (C<sup>8</sup>), 100.4 (C<sup>10</sup>), 55.3 ppm (CH<sub>3</sub>, -OMe).

HRMS: (PhMe) calculated for [MH]<sup>+</sup> m/z: 507.2028, found: 507.2032.

Anal. Calcd. for  $C_{30}H_{26}N_4O_4$  .C 71.13, H 5.17, N 11.06. Found C 72.01, H 5.23, N 10.40. m.p. 120 – 124 °C.

### 3,6-di-(2-pyrazinyl)-4-(2-pyridyl)-pyridazine (1b)



The same procedure was used as for **1a** using bpztz (0.310 g, 1.30 mmol) and (147  $\mu$ L, 1.25 mmol) of 2-acetyl pyridine. The product was purified by column chromatography (ethyl acetate: methanol, 10:1) and isolated as an off-white solid.

I.R. vbar 3062s, 3016s, 1698m, 1586s, 1571s, 1477s, 1469s, 1387s, 1154s, 1149s, 1020, 861s, 805s, 785s, 752s, 621m, 585m, 503m, 411s  $cm^{-1}$ .

$^1H$ -NMR (400 MHz,  $CDCl_3$ ):  $\delta$  10.02 (d, 1H,  $H^{3'}$ ,  $J = 1.5$  Hz), 9.42 (d, 1H,  $H^3$ ,  $J = 1.5$  Hz), 8.81 (s, 1H,  $H^{14}$ ), 8.73 (d, 1H,  $H^{6'}$ ,  $J = 2.5$  Hz), 8.70 (d, 1H,  $H^{5'}$ ,  $J = 1.5$  Hz), 8.58 (d, 1H,  $H^{6'}$ ,  $J = 2.4$  Hz), 8.53 (d, 1H,  $H^{11}$ ,  $J = 4.7$  Hz), 8.32 (d, 1H,  $H^{5'}$ ,  $J = 1.5$  Hz), 7.75 ( $\Psi$ td, 1H,  $H^9$ ,  $J = 8.0, 1.5$  Hz), 7.45 (d, 1H,  $H^8$ ,  $J = 7.4$  Hz), 7.29 ppm (ddd, 1H,  $H^{10}$ ,  $J = 7.5, 1.5, 0.9$ Hz).

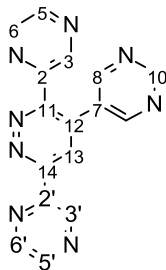
$^{13}C$ -NMR (100 MHz,  $CDCl_3$ ):  $\delta$  156.5 ( $C^{12/15}$ ), 155.9 ( $C^{12/15}$ ), 154.3 ( $C^7$ ), 150.7 ( $C^2$ ), 149.3 ( $C^{11}$ ), 147.8 ( $C^2$ ), 145.4 ( $C^{6'}$ ), 145.3 ( $C^3$ ), 144.0 ( $C^6$ ), 143.6 ( $C^5$ ), 143.4 ( $C^3$ ), 142.5 ( $C^5$ ), 139.6 ( $C^{13}$ ), 136.3 ( $C^9$ ), 125.5 ( $C^{14}$ ), 123.5 ( $C^8$ ), 123.0 ppm ( $C^{10}$ ).

HRMS: ( $CH_3CN$ ): calculated for  $[MH]^+$  m/z: 314.1154, found: 314.1158.

Anal. Calcd. for  $C_{17}H_{11}N_7$  .C 65.17, H 3.54, N 31.29. Found C 65.31, H 3.63, N 30.60. m.p. 210 - 212 °C

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### 3,6-di-(2-pyrazinyl)-4-(pyrimidyl) pyridazine (2b)



The same procedure was used as for **2a** using bpztz (0.310 g, 1.30 mmol) and 5-ethynyl pyrimidine (0.140 g, 1.39 mmol). The product was obtained after column chromatography on silica (10:1 ethyl acetate:methanol) as an off-white solid (0.214 g, 49%).

I.R. vbar 3130m, 3098m, 3033s, 1575s, 1556s, 1434s, 1380s, 1161s, 1101s, 1019s, 869s, 860s, 758m, 724s, 631s, 581m, 482m  $cm^{-1}$ .

$^1H$ -NMR (400 MHz,  $CDCl_3$ ):  $\delta$  10.02 (d, 1H,  $H^{3'}$ ,  $J = 1.4$  Hz), 9.64 (d, 1H,  $H^3$ ,  $J = 1.4$  Hz), 9.28 (s, 1H,  $H^{10}$ ), 8.79 (d, 1H,  $H^{6'}$ ,  $J = 2.2$  Hz), 8.73 (m, 3H,  $H^{8,5'}$ ), 8.66 (m, 2H,  $H^{6,13}$ ), 8.36 (d, 1H,  $H^5$ ,  $J = 2.0$  Hz).

$^{13}C$ -NMR (100 MHz,  $CDCl_3$ ):  $\delta$  158.0 ( $C^{10}$ ), 156.4 ( $C^{11}$ ), 155.4 ( $C^{8,8'}$ ), 154.9 ( $C^{14}$ ), 149.1 ( $C^2$ ), 147.2 ( $C^2$ ), 145.8 ( $C^{6'}$ ), 145.5, ( $C^3$ ), 144.80 ( $C^6$ ), 143.7 ( $C^5$ ), 143.4 ( $C^3$ ), 142.5 ( $C^5$ ), 134.6 ( $C^7$ ), 130.7 ( $C^{12}$ ), 126.09 ppm (1C,  $C^{13}$ ).

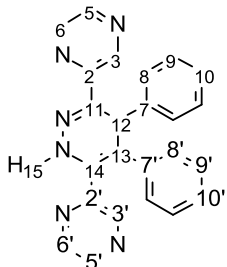
HRMS: ( $CH_3CN$ ): calculated for  $[MNa]^+$  m/z: 337.0926, found: 337.0899.

Anal. Calculated for  $C_{16}H_{10}N_8$ : C, 61.14, H, 3.21, N, 35.65. Found: C, 59.60; H, 3.17; N, 35.04. m.p. 226 – 228 °C.

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### 3,6-di-(2-pyrazinyl)-4,5-diphenylpyridazine (3b)

#### 3,6-di-(2-pyrazinyl)-4,5-diphenyl-1,4-dihydropyridazine



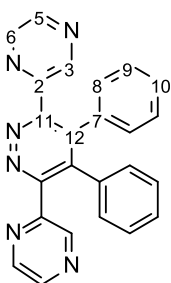
The same procedure was used as for 3,6 di-(2-pyridyl) 4,5-diphenyl-1,4-dihydropyridazine (above) using *trans*-stilbene (0.240 g, 1.33 mmol) and bpztz (0.310 g 1.30 mmol). Purification by column chromatography (dichloromethane: diethyl ether, 10:1) gave the product as a yellow solid (0.390 g, 75% yield).

$^1H$ -NMR (400 MHz,  $CDCl_3$ ):  $\delta$ : 9.50 (s, 1H,  $H^{15}$ ), 9.43 (s, 1H,  $H^{3/3'}$ ), 8.57 (d, 1H,  $H^{5/5'}$ ,  $J = 2.2$  Hz), 8.51 (d, 1H,  $H^{5/5'}$ ,  $J = 2.2$  Hz), 8.41 (m, 3H,  $H^{6,6',3/3'}$ ), 7.55 (d, 2H,  $H^{9/9'}$ ,  $J = 7.5$  Hz), 7.27 (m, 8H,  $H^{8,8',9/9',10,10'}$ ), 5.67 ppm (s, 1H,  $H^{12}$ ).

HRMS: ( $CH_3CN$ ): calculated for  $C_{24}H_{19}N_6$ :  $[MH]^+$  m/z 391.1671 found: 391.1700.

Anal. Calcd. for  $C_{24}H_{18}N_6$ : C 73.83, H 4.65, N 21.52. Found C 74.01, H 4.80, N 20.90.

#### 3,6-di-(2-pyrazinyl)-4,5-diphenylpyridazine



The same procedure was used as for **3a**, using a dichloromethane (20 mL) suspension of 3,6-di-(2-pyrazinyl)-4,5-diphenyl-1,4-dihydropyridazine. After recrystallisation from ethyl acetate/petroleum, the product was obtained as a beige solid (0.327 g, 84%).

I.R. vbar 3075s, 3049s, 2963s, 2927s, 1963m, 1737m, 1493s, 1471s, 1444s, 1371s, 1262s, 1145s, 1070s, 1064s, 1036s, 863s, 772s, 756s, 701s, 659s, 639s, 628s, 536m, 527m  $cm^{-1}$ .

$^1H$ -NMR: (400 MHz,  $CDCl_3$ ):  $\delta$  8.98 (s, 2H,  $H^3$ ), 8.51 (d, 2H,  $H^6$ ,  $J = 2.0$ Hz), 8.43 (s, 2H,  $H^5$ ), 7.11 (m, 6H,  $H^{8,10}$ ), 6.89 ppm (dd, 4H,  $H^9$ ,  $J = 6.3, 1.5$  Hz).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.3 ( $\text{C}^{11}$ ), 151.2 ( $\text{C}^2$ ), 145.4 ( $\text{C}^3$ ), 143.5 ( $\text{C}^6$ ), 143.0 ( $\text{C}^5$ ), 139.6 ( $\text{C}^{12}$ ), 133.2 ( $\text{C}^7$ ), 129.6 ( $\text{C}^8$ ), 127.5 ( $\text{C}^9, 10$ ).

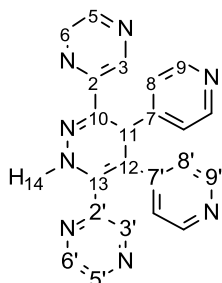
HRMS: ( $\text{CH}_3\text{CN}$ ) calculated for  $[\text{MH}]^+$   $m/z$ : 389.1515, found: 389.1515.

Anal. Calcd. for C 74.21, H 4.15, N 21.64. Found: C 73.01, H 4.35, N 20.80. m.p. 161-162 °C.

5

### 3,6-di(2-pyrazinyl)-4,5-di(4-pyridyl) pyridazine (4b)

3,6-di(2-pyrazinyl)-4,5-di(4-pyridyl)-1,4-dihydropyridazine



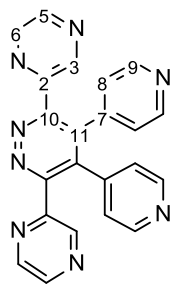
The same procedure was used as for **4a** using bpztz (0.300 g, 1.26 mmol) and (*E*)-1,2-di(4-pyridyl)ethene (0.238 g, 1.30 mmol). Purification *via* silica column chromatography (diethyl ether:methanol, 1:1) yielded the product as a bright yellow solid (0.437 g, 0.76 mmol, 60%).

$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.48 (s, 1H,  $\text{H}^{14}$ ), 9.41 (d, 1H,  $\text{H}^{3/3'}$ ,  $J = 1.0$  Hz), 8.70 (d, 1H,  $\text{H}^{3/3'}$ ,  $J = 1.4$  Hz), 8.51 (m, 8H,  $\text{H}^{5,5',6,6',9,9'}$ ), 7.44 (d, 2H,  $\text{H}^{8/8'}$ ,  $J = 5.9$  Hz), 7.04 (d, 2H,  $\text{H}^{8/8'}$ ,  $J = 5.9$  Hz), 5.68 ppm (s, 1H,  $\text{H}^{11}$ ).

HRMS: ( $\text{CH}_3\text{CN}$ ) calculated for  $[\text{MH}]^+$   $m/z$ : 393.1576, found: 393.1592

Anal. Calcd. for C 67.34, H 4.11, N 28.55. Found: C 67.53, H 4.10, N 27.80.

### 3,6-di(2-pyridyl)-4,5-di(4-pyridyl) pyridazine



The same procedure was used as for **3a** using a dichloromethane (40 mL) solution containing 3,6-di(2-pyrazinyl)-4,5-di(4-pyridyl)-1,4-dihydropyridazine. Purification was carried out by column chromatography on silica using diethyl ether: methanol (3:1) as eluent. The product was recovered as a yellow solid (0.175 g, 0.30 mmol, 40 %).

I.R. vbar 3069s, 3036s, 2987m, 1597s, 1409s, 1371s, 1154s, 1016s, 991m, 849s, 796s, 762m, 659s, 645s, 627s, 549m, 509m  $\text{cm}^{-1}$ .

$^1\text{H}$ -NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.37 (d, 2H,  $\text{H}^3$ ,  $J = 1.0$  Hz), 8.56 (d, 2H,  $\text{H}^5$ ,  $J = 2.5$  Hz), 8.40 (d, 4H,  $\text{H}^9$ ,  $J = 5.6$  Hz), 8.29 (d, 2H,  $\text{H}^6$ ,  $J = 2.0$  Hz), 6.88 (d, 4H,  $\text{H}^8$ ,  $J = 6.0$  Hz).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CDCl}_3$ ): 154.9 ( $\text{C}^{10}$ ), 149.6 ( $\text{C}^2$ ), 148.93 ( $\text{C}^9$ ), 145.4 ( $\text{C}^3$ ), 144.3 ( $\text{C}^5$ ), 142.7 ( $\text{C}^6$ ), 141.5 ( $\text{C}^{11}$ ), 137.0 ( $\text{C}^7$ ), 123.9 ( $\text{C}^8$ ).

HRMS: ( $\text{CH}_3\text{CN}$   $m/z = 391.1515$ , calculated for  $\text{C}_{22}\text{H}_{14}\text{N}_8$ :  $[\text{MH}]^+ = 391.1515$ .

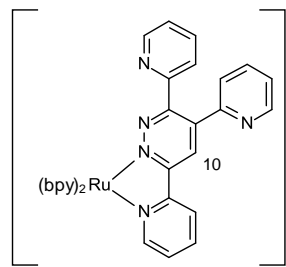
Anal. Calculated for C, 67.68; H, 3.61; N, 28.70. Found: C, 66.86, H, 3.65, N, 28.41. m.p. 216-218 °C.

### Ruthenium bis bipyridyl/ deuterated bis bipyridyl complexes

#### General Procedure:

Unless otherwise stated, ligand (**1a**, **2a**, **3a**, **4a**, **5a**, **6**) and ruthenium(II) bisbipyridine dichloride were heated for 4 hrs at 80 °C in a mixture of ethylene glycol (5 mL) and water (5 mL). The reaction mixture was then diluted with water and washed with dichloromethane to remove excess ligand. The volume of the aqueous layer was reduced under vacuum and a saturated solution of  $\text{KPF}_6$  was added. The mixture was filtered and the filtrate purified by column chromatography on silica, using the solvent systems outlined below.

#### $[\text{Ru}(\text{bpy})_2(\mathbf{1a})][\text{PF}_6]_2$



**1a** (0.100 g, 0.320 mmol) and ruthenium(II) bisbipyridine dichloride (0.156 g, 0.299 mmol). The compound was purified by column chromatography on silica (MeCN:  $\text{KNO}_3 \cdot \text{H}_2\text{O}$  10:  $\frac{1}{2}$ :1  $\frac{1}{2}$ ).

Product obtained as red solid (0.222g, 0.218 mmol, 65%).

$^1\text{H}$ -NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.99 (s, 1H,  $\text{H}^{10}$ ), 8.71 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 7.9$  Hz), 8.64 (d, 2H,  $\text{H}^{\text{Py}}$ ,  $J = 7.4$  Hz), 8.60 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 3.9$  Hz), 8.57-8.50 (m, 3H,  $\text{H}^{\text{Py}}$ ), 8.23 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 4.0$  Hz), 8.20 ( $\Psi\text{td}$ , 1H,  $\text{H}^{\text{Py}}$ ,  $J = 9.0, 1.0$  Hz), 8.17-8.08 (m, 5H,  $\text{H}^{\text{Py}}$ ), 7.99 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 4.7$  Hz), 7.98 (m, 2H,  $\text{H}^{\text{Py}}$ ), 7.92 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 5.4$  Hz), 7.82 ( $\Psi\text{td}$ , 1H,  $\text{H}^{\text{Py}}$ ,  $J = 7.5, 1.5$  Hz), 7.80 ( $\Psi\text{td}$ , 1H,  $\text{H}^{\text{Py}}$ ,  $J = 7.6, 1.6$  Hz), 7.79 (m, 1H,  $\text{H}^{\text{Py}}$ ), 7.63 (ddd, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 1.0$  Hz), 7.61-7.46 (m, 2H,  $\text{H}^{\text{Py}}$ ), 7.45 ( $\Psi\text{td}$ , 1H,  $\text{H}^{\text{Py}}$ ,  $J = 1.0$  Hz), 7.38 (m, 1H,  $\text{H}^{\text{Py}}$ ), 7.35 (d,

1H,  $\text{H}^{\text{Py}}$ ,  $J = 8.0$  Hz), 7.32 (m, 1H,  $\text{H}^{\text{Py}}$ ), 7.27 ppm (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J = 8.0$  Hz).

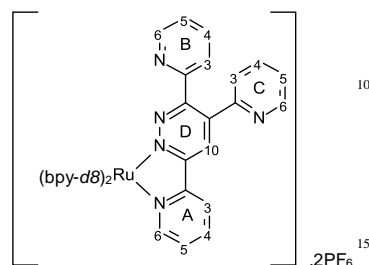
HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 362.5786$   $[\text{M}-2\text{PF}_6]^{2+}$  Calculated for  $\text{C}_{39}\text{H}_{29}\text{N}_9\text{Ru}$ : 362.5795,



Anal. Calcd.: C 46.16, H 2.88, N 12.42. Found C 46.40, H 2.99, N 12.40. m.p >280 °C

**5 [Ru(bpyd<sub>8</sub>)<sub>2</sub>(1a)]PF<sub>6</sub>]<sub>2</sub>**

**1a** (0.015 g, 0.049 mmol) and deuterated ruthenium *bis* bipyridine dichloride (0.0075 g, 0.014 mmol). The product was purified by column chromatography on silica (MeCN: KNO<sub>3</sub>:H<sub>2</sub>O 10: ½:1 ½).



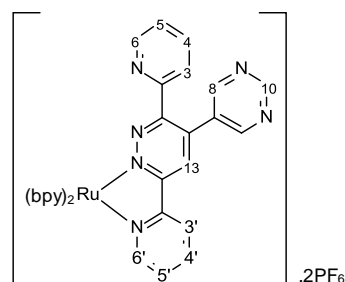
Red solid (0.0092 g, 0.009 mmol, 64%).

<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.47 (s, 1H, H<sup>D10</sup>), 8.66 (d, 1H, H<sup>A3</sup>, J = 8.0 Hz), 8.57 (d, 10 1H, H<sup>B6</sup>, J = 4.3 Hz), 8.19 (d, 1H, H<sup>C6</sup>, J = 5.5 Hz), 8.15 (d, 1H, H<sup>A4</sup>, J = 8.1 Hz), 7.94 (d, 1H, H<sup>A6</sup>, J = 5.7 Hz), 7.76 (m, 2H, H<sup>C4,B4</sup>), 7.56 (Ψtd, 1H, H<sup>A5</sup>, J = 6.8, 1.1 Hz), 7.39 (Ψtd, 1H, H<sup>B5</sup>, J = 6.2, 1.3 Hz), 7.30 (Ψtd, 1H, H<sup>C5</sup>, J = 7.6, 1.1 Hz), 7.29 (d, 1H, H<sup>B3</sup>, J = 8.1 Hz), 7.22 ppm (d, 1H, H<sup>C3</sup>, J = 7.6 Hz). m.p. > 280 °C

Anal. Calcd.: C 45.44, H 4.40, N 12.23. Found C 46.40, H 2.99, N 12.20. m.p >280 °C

**[Ru(bpy)<sub>2</sub>(2a)]PF<sub>6</sub>]<sub>2</sub>**

**2a** (0.105 g, 0.337 mmol) and ruthenium(II) *bis*bipyridine dichloride (0.157 g, 0.301 mmol). The product was purified by column chromatography on silica (MeCN: KNO<sub>3</sub>:H<sub>2</sub>O 10: ½:1 ½). Red solid (0.222 g, 0.218 mmol, 73% ).



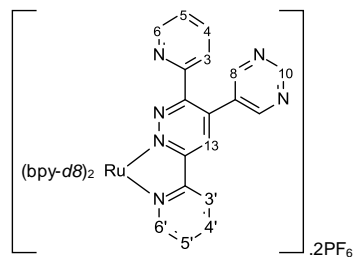
<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 9.18 (s, 1H, H<sup>10</sup>), 8.71 (m, 3H, H<sup>13, 8</sup>), 8.66-8.60 (m, 2H), 8.51 (m, 2H), 8.24 (m, 1H), 8.20-8.05 (m, 5H), 7.98 (m, 3H), 7.89 (m, 2H), 7.77-7.73 (m, 2H), 7.58-7.46 (m, 4H), 7.40-7.29 (m, 2H), 7.25 (d, 1H, H<sup>3</sup>, J = 8.0 Hz).

HRMS: (CH<sub>3</sub>CN) m/z = 363.0775 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>38</sub>H<sub>28</sub>N<sub>10</sub>Ru: 363.0771.

Anal. Calcd.: C 44.94, H 2.78, N 13.79. Found C 45.00, H 2.90, N 13.50. m.p >280 °C

**[Ru(bpyd<sub>8</sub>)<sub>2</sub>(2a)]PF<sub>6</sub>]<sub>2</sub>**

**2a** (0.009 g, 0.028 mmol) and deuterated ruthenium (II) *bis*bipyridine dichloride were reacted as for [Ru(bpy)<sub>2</sub>(1a)]PF<sub>6</sub>]<sub>2</sub>. The product was purified by chromatography on silica (MeCN: KNO<sub>3</sub>:H<sub>2</sub>O 10: ½:1 ½). Red solid (0.222 g, 0.218 mmol, 68%).



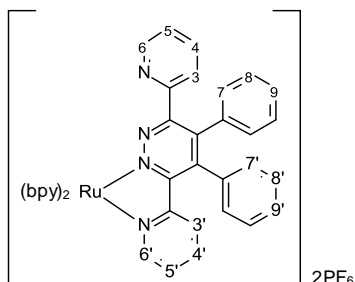
<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 9.20 (s, 1H, H<sup>10</sup>), 8.71 (s, 1H, H<sup>13</sup>), 8.69 (s, 2H, H<sup>8</sup>), 8.62 (d, 1H, H<sup>3</sup>, J = 7.9 Hz), 8.24 (d, 1H, H<sup>6</sup>, J = 4.6 Hz), 8.17 (dd, 1H, H<sup>4</sup>, J=7.9, 1.4 Hz), 7.95 (d, 35 1H, H<sup>6</sup>, J = 5.4 Hz), 7.77 (dd, 1H, H<sup>4</sup>, J = 7.5, 1.1 Hz), 7.58 (m, 1H, H<sup>5</sup>), 7.38 (Ψtd, 1H, H<sup>5</sup>, J = 4.6, 0.8 Hz), 7.23 ppm (d, 1H, H<sup>3</sup>, J = 7.9 Hz).

HRMS: (CH<sub>3</sub>CN) m/z = 371.1400 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>38</sub>H<sub>12</sub>D<sub>16</sub>N<sub>10</sub>Ru: 371.1265.

Anal. Calcd.: C 44.94, H 4.30, N 13.58. Found C 45.01, H 4.46, N 13.47. m.p >280 °C

**[Ru(bpy)<sub>2</sub>(3a)]PF<sub>6</sub>]<sub>2</sub>**

**3a** (0.100 g, 0.258 mmol) and ruthenium(II) *bis*bipyridine dichloride (0.114g, 0.222 mmol). Purification was carried out by column chromatography on silica (acetonitrile:water: sat. KNO<sub>3</sub> 10:1.5:1). (0.112 g, 0.1399 mmol, 63% yield)



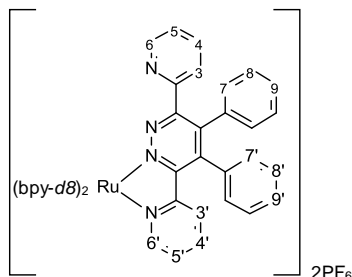
<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.60-8.52 (m, 3H), 8.44 (d, 1H, H<sup>py</sup>, J = 8.2 Hz), 8.19-8.11 (m, 5H), 7.95 (m, 2H), 7.90 (m, 2H), 7.69 (dd, 1H, H<sup>py</sup>, J = 5.5, 0.7 Hz), 7.68-7.56 (m, 4H), 7.53-7.30 (m, 7H), 7.20 (m, 1H), 7.11-7.05 (m, 5H) 6.92 ppm (1H, H<sup>py</sup>, J = 7.9 Hz).

HRMS: (CH<sub>3</sub>CN) m/z = 400.0990 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>46</sub>H<sub>34</sub>N<sub>8</sub>Ru: 400.0975.

Anal. Calcd.: C 69.07, H 4.28, N 14.01. Found C 69.00, H 4.30, N 13.90. m.p >280 °C

**[Ru(bpyd<sub>8</sub>)<sub>2</sub>(3a)][PF<sub>6</sub>]<sub>2</sub>**

**3a** (0.005g, 0.014 mmol) and deuterated ruthenium (II) *bis*bipyridine dichloride (0.007g, 0.014 mmol). Following ion exchange and filtration no further purification was required. Deep red solid (0.012 g, 0.0109 mmol, 78% yield).



<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.16 (d, 1H, H<sup>6</sup>, J = 4.7 Hz), 7.95 (d, 1H, H<sup>6'</sup>, J = 5.8 Hz), 7.66 (Ψtd, 1H, H<sup>4</sup>, J = 7.8, 0.8 Hz), 7.56 (Ψtd, 1H, H<sup>4'</sup>, J = 7.5, 0.7 Hz), 7.47-7.33 (m, 5H, H<sup>7,8,5'</sup>), 7.20 (m, 1H, H<sup>5</sup>), 7.13-7.06 (m, 6H, H<sup>8,9,3</sup>), 6.93 ppm (d, 1H, H<sup>3'</sup>, J = 8.1 Hz).

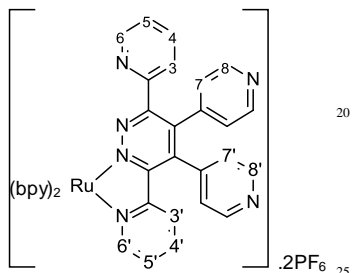
HRMS: (CH<sub>3</sub>CN) m/z = 408.1601 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>46</sub>H<sub>18</sub>D<sub>16</sub>N<sub>8</sub>Ru: 408.1601.

Anal. Calcd.: C 67.71, H 6.17, N 13.78. Found C 68.02, H 6.31, N 13.79. m.p >280 °C

10

**[Ru(bpy)<sub>2</sub>(4a)][PF<sub>6</sub>]<sub>2</sub>**

**15 4a** (0.102g, 0.264 mmol) and ruthenium(II) *bis*bipyridine dichloride (0.130g, 0.251 mmol). The product was purified by column chromatography on silica (acetone:ammonia:Sat. KNO<sub>3</sub> 20:3:0.5)



Red solid (0.144 g, 0.136 mmol, 54 %).

<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.67-8.55 (m, 4H, H<sup>4-py</sup>, H<sup>py</sup>), 8.49 (d, 1H, H<sup>py</sup>, J = 8.0 Hz), 8.41-8.08 (m, 6H), 8.04-8.00 (m, 2H), 7.92 (d, 1H, H<sup>py</sup>, J = 5.4 Hz), 7.88 (d, 1H, H<sup>py</sup>, J = 5.4 Hz), 7.71-7.67 (m, 3H), 7.59-7.52 (m, 3H), 7.46 (m, 1H), 7.43-7.35 (m, 2H), 7.25-7.14 (m, 5H), 6.82 ppm (s, 1H).

HRMS: (CH<sub>3</sub>CN) m/z = 401.0940 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>44</sub>H<sub>32</sub>N<sub>10</sub>Ru: 401.0928.

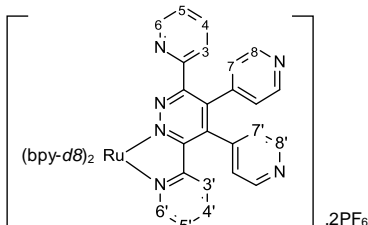
Anal. Calcd.: C 65.91, H 4.02, N 17.47. Found C 66.10, H 4.20, N 17.56. m.p >280 °C

20

.2PF<sub>6</sub> 25

**Ru(bpyd<sub>8</sub>)<sub>2</sub>(4a)[PF<sub>6</sub>]<sub>2</sub>**

**4a** (0.006 g, 0.015 mmol) and ruthenium(II) *bis*bipyridine dichloride (0.008 g, 0.015 mmol). The product was purified by chromatography on silica (acetone:ammonia:sat. KNO<sub>3</sub> 20:3:0.5).



**30** Red solid (0.012 g, 0.011 mmol, 75% yield).

<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.67 (d, 1H, H<sup>4py</sup>, J = 4.4 Hz), 8.62 (d, 1H, H<sup>4py</sup>, J = 4.7 Hz), 8.29 (m, 2H, H<sup>4py</sup>), 8.12 (d, 1H, H<sup>py</sup>, J = 3.9 Hz), 7.98 (d, 1H, H<sup>py</sup>, J = 5.5 Hz), 7.67 (m, 2H, H<sup>py</sup>), 7.40 (m, 2H, H<sup>py</sup>), 7.26 (dd, 1H, H<sup>py</sup>, J = 5.0 Hz, 1.0 Hz), 7.13 (m, 3H, H<sup>py</sup>, H<sup>4py</sup>), 6.78 ppm (m, 1H, H<sup>4py</sup>).

**35** HRMS: (CH<sub>3</sub>CN) m/z = 409.1554 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>44</sub>H<sub>16</sub>D<sub>16</sub>N<sub>10</sub>Ru: 409.1034.

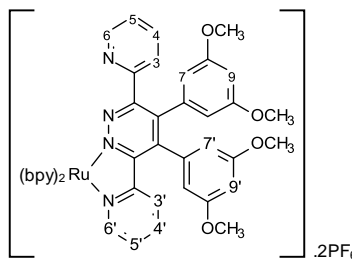
Anal. Calcd.: C 64.61, H 5.91, N 17.12. Found C 64.80, H 5.98, N 17.10. m.p >280 °C

35

.2PF<sub>6</sub>

**[Ru(bpy)<sub>2</sub>(5a)][PF<sub>6</sub>]<sub>2</sub>**

**40 5a** (0.020 g, 0.040 mmol) and ruthenium(II) *bis* bipyridine dichloride (0.021 g, 0.040 mmol) in mixture of ethylene glycol (3 mL) and water (3 mL). The product was purified by chromatography on silica (acetone:ammonia:sat. KNO<sub>3</sub> 20:2:2). Red solid (0.027 g, 0.022 mmol, 56% yield).



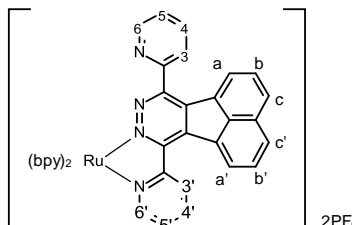
**45** <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.60 (m, 2H, H<sup>py</sup>), 8.53 (d, 1H, H<sup>py</sup>, J = 7.9 Hz), 8.43 (d, 1H, H<sup>py</sup>, J = 8.1 Hz), 8.23 (d, 1H, H<sup>py</sup>, J = 4.7, 1.0 Hz), 8.20 – 8.15 (m, 3H), 8.08 (dd, 1H, H<sup>py</sup>, J = 5.5, 0.8 Hz), 7.97 (m, 3H), 7.89 (d, 1H, H<sup>py</sup>, J = 5.0 Hz), 7.71 (m, 3H), 7.61-7.49 (m, 3H), 7.37 (Ψtd, 1H, H<sup>py</sup>, J = 5.6, 1.2 Hz), 7.22 (m, 3H), 7.10 (d, 1H, H<sup>py</sup>, J = 7.8 Hz), 6.58 (Ψt, 2H, H<sup>ph</sup>, J = 1.5 Hz), 6.34 (m, 1H, H<sup>ph</sup>), 6.24 (d, 1H, H<sup>ph</sup>, J = 2.3 Hz), 3.73 (s, 3H, H<sup>OMe</sup>), 3.71 (s, 3H, H<sup>OMe</sup>), 3.56 ppm (s, 6H, H<sup>OMe</sup>).

HRMS: (CH<sub>3</sub>CN) m/z = 460.1170 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>50</sub>H<sub>42</sub>N<sub>8</sub>O<sub>4</sub>Ru: 460.1185.

**50** Anal. Calcd.: C 65.28, H 4.60, N 12.18. Found C 66.00, H 4.70, N 12.50. m.p >280 °C

**[Ru(bpy)<sub>2</sub>(6)][PF<sub>6</sub>]<sub>2</sub>**

**6** (0.046 g, 0.128 mmol) and ruthenium(II) *bis* bipyridine dichloride (0.066 g, 0.127 mmol) were heated for 5 hrs at 80 °C in a mixture of ethylene glycol (3 mL) and water (3 mL). The reaction was allowed to cool, further diluted with water (25 mL) and an excess of NH<sub>4</sub>PF<sub>6</sub> was added. The solution was extracted into dichloromethane (30 mL) and washed with water (3 x 15 mL). The solvent





was removed *in vacuo* to yield a red solid, which was recrystallised from acetone/hexane (0.074g, 0.097 mmol, 76 %).

$^1\text{H}$  NMR (600 MHz,  $\text{CD}_3\text{CN}$ )  $\delta$ : 9.29 (d, 1H,  $\text{H}^{3'}$ ,  $J = 8.0$  Hz), 8.92 (d, 1H,  $\text{H}^{\text{a}}$ ,  $J = 7.4$  Hz), 8.87 (d, 1H,  $\text{H}^6$ ,  $J = 4.3$  Hz), 8.63 (d, 1H,  $\text{H}^{\text{a}}$ ,  $J = 7.3$  Hz), 8.48 (d, 1H,  $\text{H}^{\text{bpy}}$ ,  $J = 8.2$  Hz), 8.46 (d, 1H,  $\text{H}^{\text{bpy}}$ ,  $J = 7.6$  Hz), 8.44 (d, 1H,  $\text{H}^{\text{c}}$ ,  $J = 8.0$  Hz), 8.37 (d, 1H,  $\text{H}^{\text{c}}$ ,  $J = 8.2$  Hz), 8.25 ( $\Psi\text{td}$ , 1H,  $\text{H}^{4'}$ ,  $J = 8.0$ , 1.4 Hz), 8.16 ( $\Psi\text{td}$ , 1H,  $\text{H}^{\text{bpy}}$ ,  $J = 8.0$ , 1.4 Hz), 8.03 (m, 3H,  $2\text{H}^{\text{bpy}}$ ,  $1\text{H}^6$ ), 7.98 (m, 3H,  $2\text{H}^{\text{bpy}}$ ,  $1\text{H}^{\text{b}}$ ), 7.88 ( $\Psi\text{td}$ , 1H,  $\text{H}^4$ ,  $J = 7.8$ , 1.3 Hz), 7.84 ( $\Psi\text{t}$ , 1H,  $\text{H}^{\text{b}}$ ,  $J = 7.8$  Hz), 7.72 (d, 1H,  $\text{H}^{\text{bpy}}$ ,  $J = 5.6$  Hz), 7.62 (m, 2H,  $\text{H}^{5, 5'}$ ), 7.52 (ddd, 1H,  $\text{H}^{\text{bpy}}$ ,  $J = 7.6$ , 5.6, 1.1 Hz), 7.42 (m, 2H,  $2\text{H}^{\text{bpy}}$ ), 7.35 (ddd, 1H,  $\text{H}^{\text{bpy}}$ ,  $J = 7.5$ , 5.7, 1.3 Hz), 7.22 ppm (d, 1H,  $\text{H}^3$ ,  $J = 7.9$  Hz).

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 386.0819$  [ $\text{M}-2\text{PF}_6$ ] $^{2+}$  Calculated for  $\text{C}_{44}\text{H}_{30}\text{N}_8\text{Ru}$ : 386.0819.

Anal. Calcd.: C 68.47, H 3.92, N 14.52. Found C 69.04, H 4.00, N 14.90. m.p  $>280$  °C

## Ruthenium *tris* homoleptic complexes

### General procedure:

Unless otherwise stated, the ligand (**3a**, **4a**, **5a**) was added to ruthenium(III) chloride hydrate in ethylene glycol (5 mL). N-Ethyl morpholine (6 drops) was added and the mixture was degassed by bubbling with argon for 30 mins. The mixture was then heated at  $170^\circ\text{C}$  for 72 hrs, cooled and extracted into  $\text{CH}_2\text{Cl}_2$ . The facial and meridional isomers were isolated as described.

### [Ru(**3a**) $_3$ ][PF $_6$ ] $_2$

**3a** (0.0209g, 0.0542 mmol) was added to ruthenium(III) chloride hydrate (0.0029 g, 0.0142 mmol). The facial isomer was separated using a preparative silica TLC plate (acetone:water:sat.KNO $_3$ , 120:12:0.5) (2.70 mg, 12% yield,  $R_f = 0.35$ ). The residue remaining on the plate was collected and the meridional isomer was isolated from this mixture using a second preparative TLC plate (acetonitrile:ammonia:sat.KNO $_3$ , 20:2:4). (6.45 mg, 29% yield,  $R_f = 0.15$ ).

*Mer* isomer:

$^1\text{H}$ -NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.64 (d, 1H,  $\text{H}^{\text{py}}$ ,  $J = 5.0$  Hz), 8.40 (d, 1H,  $\text{H}^{\text{py}}$ ,  $J = 4.6$  Hz), 8.34 (d, 1H,  $\text{H}^{\text{py}}$ ,  $J = 5.1$  Hz), 8.26 (d, 2H,  $J = 4.6$  Hz), 8.18 (d, 1H,  $\text{H}^{\text{py}}$ ,  $J = 4.2$  Hz), 7.72 – 6.97 (m, 26H), 6.98 (1H,  $\text{H}^{\text{py}}$ ,  $J = 7.4$  Hz), 6.89 (1H,  $\text{H}^{\text{py}}$ ,  $J = 7.9$  Hz), 6.86 (1H,  $\text{H}^{\text{py}}$ ,  $J = 7.9$  Hz), 6.48 ppm (1H,  $\text{H}^{\text{py}}$ ,  $J = 7.4$  Hz).

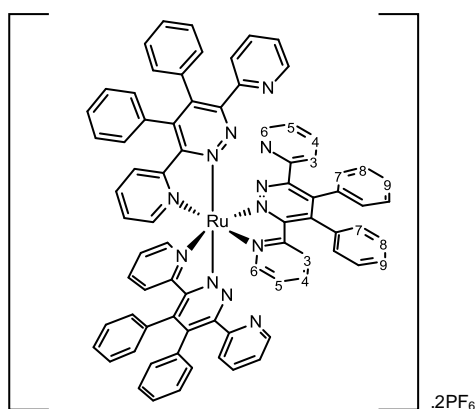
HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 630.1813$  [ $\text{M}-2\text{PF}_6$ ] $^{2+}$ . Calculated for  $\text{C}_{78}\text{H}_{54}\text{N}_{12}\text{Ru}$ : 630.1819. m.p.  $> 280$  °C

*Fac* isomer:

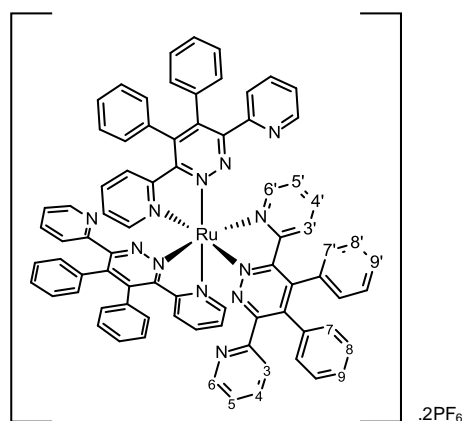
$^1\text{H}$ -NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.46 (d, 3H,  $\text{H}^6$ ,  $J = 4.0$  Hz), 8.43 (d, 3H,  $\text{H}^{6'}$ ,  $J = 6.0$  Hz), 7.72 (d, 3H,  $\text{H}^4$ ,  $J = 7.7$  Hz), 7.71 (d, 3H,  $\text{H}^{4'}$ ,  $J = 8.0$  Hz), 7.57 ( $\Psi\text{t}$ , 3H,  $\text{H}^{5'}$ ,  $J = 6.3$  Hz), 7.42 (m, 6H,  $\text{H}^{7/8/9'}$ ), 7.31 (m, 6H,  $\text{H}^{5,7/8/9'}$ ), 7.20 (d, 3H,  $\text{H}^3$ ,  $J = 7.7$  Hz), 7.09 (m, 9H,  $\text{H}^{7/8/9}$ ), 6.98 (d, 3H,  $\text{H}^{3'}$ ,  $J = 8.6$  Hz), 6.68 (m, 3H,  $\text{H}^{7/8/9'}$ ), 6.10 ppm (m, 6H,  $\text{H}^{7/8/9}$ ).

$^{13}\text{C}$ -NMR (100 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  159.4 ( $\text{C}^{\text{O}}$ ), 157.1 ( $\text{C}^{\text{O}}$ ), 155.4 ( $\text{C}^{\text{O}}$ ), 154.4 ( $\text{C}^{\text{O}}$ ), 155.8 ( $\text{C}^6$ ), 149.1 ( $\text{C}^6$ ), 143.1 ( $\text{C}^{\text{O}}$ ), 139.3 ( $\text{C}^{\text{O}}$ ), 137.4 ( $\text{C}^4$ ), 136.6 ( $\text{C}^4$ ), 133.4 ( $\text{C}^{\text{O}}$ ), 132.7 ( $\text{C}^{\text{O}}$ ), 129.4 ( $\text{C}^{7/8/9'}$ ), 129.2 ( $\text{C}^{7/8/9'}$ ), 129.2 ( $\text{C}^{7/8/9'}$ ), 129.1 ( $\text{C}^{7/8/9'}$ ), 128.5 ( $\text{C}^{7/8/9'}$ ), 128.3 ( $\text{C}^3$ ), 127.8 ( $\text{C}^{7/8/9}$ ), 127.6 ( $\text{C}^5$ ), 127.2 ( $2\text{C}^{7/8/9}$ ), 124.3 ( $\text{C}^3$ ), 123.7 ppm ( $\text{C}^5$ ).

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 630.1809$  [ $\text{M}-2\text{PF}_6$ ] $^{2+}$ . Calculated for  $\text{C}_{78}\text{H}_{54}\text{N}_{12}\text{Ru}$ : 630.1819. m.p.  $> 280$  °C



Mer



Fac

### [Ru(**4a**) $_3$ ][PF $_6$ ] $_2$

**4a** (0.0212 g, 0.0546 mmol) and ruthenium(III) chloride hydrate (0.0032 g, 0.0156 mmol). The facial isomer was separated using a TLC plate (acetone:water:sat.  $\text{KNO}_3$ , 20:5:1) (2.5 mg (10% yield,  $R_f = 0.33$ ). The residue from the previous plate was purified on a second plate (acetonitrile:ammonia:sat.  $\text{KNO}_3$ , 20:3:1) from which the meridional isomer was isolated. (3.4 mg, 14 % yield,  $R_f = 0.70$ ).

<sup>5</sup> *Mer* isomer:

<sup>1</sup>H-NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  8.73 (d, 1H,  $\text{H}^6$ ,  $J = 5.7$  Hz), 8.68 (d, 1H,  $\text{H}^6$ ,  $J = 4.5$  Hz), 8.67 (d, 1H,  $\text{H}^6$ ,  $J = 5.7$  Hz), 8.60 (d, 1H,  $\text{H}^{4\text{-pyr}}$ ,  $J = 4.5$  Hz), 8.56 (d, 1H,  $\text{H}^6$ ,  $J = 4.9$  Hz), 8.52 (d, 1H,  $\text{H}^6$ ,  $J = 5.3$  Hz), 8.41-8.26 (m, 5H), 8.17 (m, 1H), 7.81 (m, 2H,  $\text{H}^4$ ), 7.68 (m, 3H), 7.64 (m, 1H), 7.43 (m, 2H), 7.38 (m, 1H), 7.30 (m, 2H), 7.12 (m, 2H), 7.07 (d, 1H,  $\text{H}^3$ ,  $J = 8.0$ ), 6.99 (m, 2H), 6.83 (m, 2H), 6.37 ppm (d, 1H,  $\text{H}^3$ ,  $J = 4.9$ Hz).

<sup>10</sup> HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 633.17$  [ $\text{M}-2\text{PF}_6$ ]<sup>2+</sup>. Calculated for  $\text{C}_{72}\text{H}_{48}\text{N}_{18}\text{Ru}$ : 1266.3353, found: 1266.3354. m.p. > 280 °C

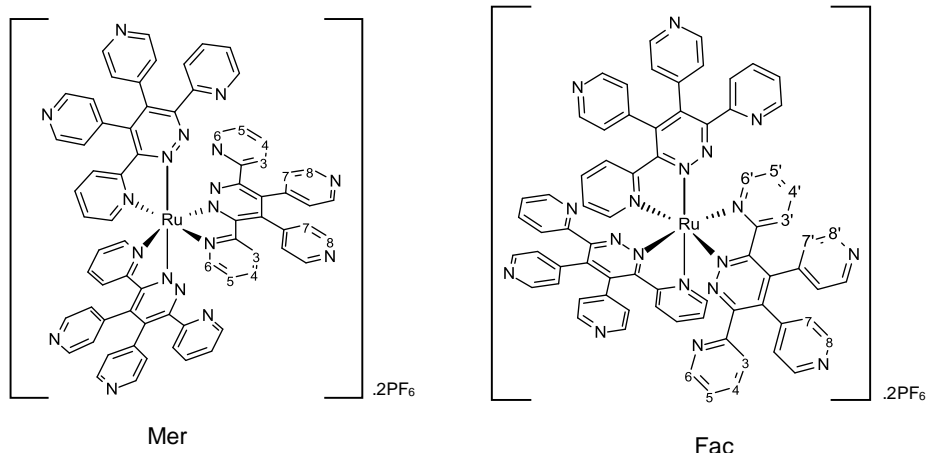
*Fac* isomer:

<sup>1</sup>H-NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.65 (d, 3H,  $\text{H}^8$ ,  $J = 4.7$  Hz), 8.53 (m, 3H,  $\text{H}^8$ ), 8.40 (m, 6H,  $\text{H}^{6'}$ ,  $J = 6$ ), 8.28 (m, 6H,  $\text{H}^8$ ), 7.81 (m, 6H,  $\text{H}^{4'}$ ,  $J = 4$ ), 7.64 ( $\Psi$ t, 3H,  $\text{H}^5$ ,  $J = 6.5$  Hz), 7.38 ( $\Psi$ td, 3H,  $\text{H}^5$ ,  $J = 4.5$ , 2.4 Hz), 7.29 (m, 6H,  $\text{H}^{3'7'}$ ), 7.20 (d, 3H,  $\text{H}^{3'}$ ,  $J = 8.5$  Hz), 6.69 (m, 3H,  $\text{H}^{7'}$ ), 6.61 ppm (m, 6H,  $\text{H}^{7'}$ ).

<sup>13</sup>C-NMR (100 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  157.7 ( $\text{C}^0$ ), 156.2 ( $\text{C}^0$ ), 154.0 ( $\text{C}^0$ ), 152.7 ( $\text{C}^0$ ), 152.4 ( $\text{C}^6$ ), 150.8 ( $\text{C}^8$ ), 150.7 ( $\text{C}^8$ ), 149.1 ( $\text{C}^6$ ), 147.0 ( $2\text{C}^8$ ), 140.5 ( $\text{C}^0$ ), 139.8 ( $\text{C}^0$ ), 138.3 ( $\text{C}^4$ ), 137.2 ( $\text{C}^4$ ), 128.6 ( $\text{C}^3$ ), 128.4 ( $\text{C}^5$ ), 124.6 ( $\text{C}^7$ ), 124.4 ( $\text{C}^7$ ), 123.9 ( $\text{C}^0$ ), 123.0 ppm ( $\text{C}^0$ ).

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 633.1663$  [ $\text{M}-2\text{PF}_6$ ]<sup>2+</sup>. Calculated for  $\text{C}_{72}\text{H}_{48}\text{N}_{18}\text{Ru}$ : 633.1677. m.p. > 280 °C

<sup>20</sup>



### [Ru(**5a**)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>

**5a** (0.100 g, 0.197 mmol) and ruthenium(III) chloride hydrate (0.0146 g, 0.0706 mmol). The facial isomer was isolated by column chromatography, (acetone:water:sat.  $\text{KNO}_3$  12:1:0.2) (0.012 g, 3% yield,  $R_f = 0.34$ ). The meridional isomer was isolated by purifying the run-off from the column on a silica TLC plate (acetonitrile:ammonia:sat.  $\text{KNO}_3$  20:1:1.5) (0.0207g, 5% yield,  $R_f = 0.12$ ).

*Mer* isomer:

<sup>1</sup>H-NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.47 (d, 1H,  $\text{H}^6$ ,  $J = 4.9$  Hz), 8.43 (d, 1H,  $\text{H}^6$ ,  $J = 3.7$ Hz), 8.27 (d, 1H,  $\text{H}^6$ ,  $J = 4.3$  Hz), 8.26 (d, 1H,  $\text{H}^6$ ,  $J = 4.6$  Hz), 8.23 (d, 1H,  $\text{H}^6$ ,  $J = 6.1$  Hz), 8.17 (d, 1H,  $\text{H}^6$ ,  $J = 5.8$  Hz), 7.81-7.62 (m, 8H), 7.38-7.11 (m, 11H), 6.60 (m, 3H,  $\text{H}^{7/9}$ ), 6.55 (m, 1H,  $\text{H}^{7/9}$ ), 6.52 (m, 1H,  $\text{H}^{7/9}$ ), 6.49 (m, 1H,  $\text{H}^{7/9}$ ), 6.40 (m, 1H,  $\text{H}^{7/9}$ ), 6.31 (m, 1H,  $\text{H}^{7/9}$ ), 6.27 (m, 4H,  $\text{H}^{7/9}$ ), 6.22 (m, 2H,  $\text{H}^{7/9}$ ), 3.75 (s, 6H,  $\text{H}^{\text{OMe}}$ ), 3.73 (s, 3H,  $\text{H}^{\text{OMe}}$ ), 3.70 (s, 3H,  $\text{H}^{\text{OMe}}$ ), 3.68 (s, 6H,  $\text{H}^{\text{OMe}}$ ), 3.55 ppm (m, 17H,  $\text{H}^{\text{OMe}}$ ).

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z = 810.2451$  [ $\text{M}-2\text{PF}_6$ ]<sup>2+</sup>. Calculated for  $\text{C}_{90}\text{H}_{78}\text{N}_{12}\text{O}_{12}\text{Ru}$ : 810.2453. m.p. > 280 °C

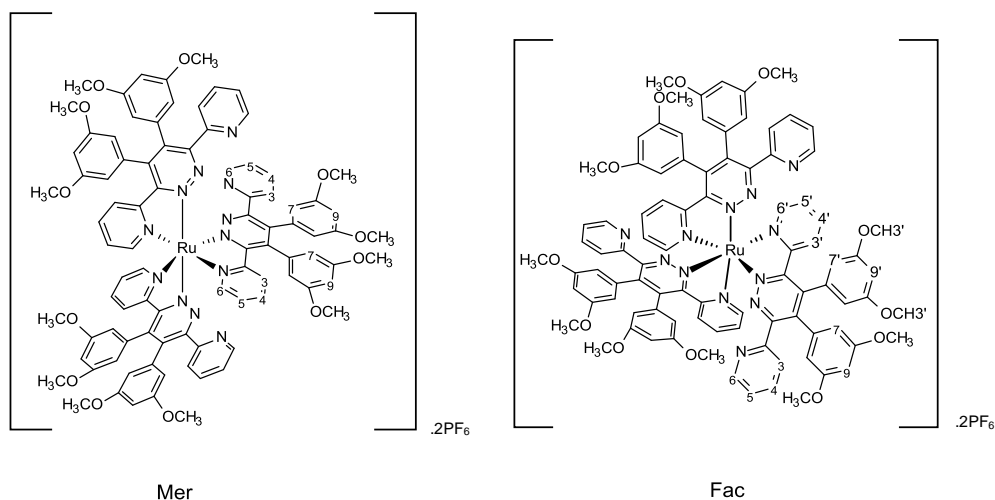
<sup>35</sup> *Fac* isomer:

<sup>1</sup>H-NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.47 (d, 3H,  $\text{H}^6$ ,  $J = 4.7$  Hz), 8.40 (d, 3H,  $\text{H}^6$ ,  $J = 5.5$  Hz), 7.81 ( $\Psi$ td, 3H,  $\text{H}^4$ ,  $J = 7.6$ , 1.5 Hz), 7.71 ( $\Psi$ td, 3H,  $\text{H}^4$ ,  $J = 7.8$ , 1.7 Hz), 7.60 (m, 3H,  $\text{H}^5$ ), 7.30 (m, 3H,  $\text{H}^5$ ), 7.27 (d, 3H,  $\text{H}^3$ ,  $J = 7.7$  Hz), 7.15 (d, 3H,  $\text{H}^3$ ,  $J = 7.7$  Hz), 6.56 (t, 4H,  $\text{H}^9$ ,  $J = 2.3$  Hz), 6.43 (d, 3H,  $\text{H}^{7'}$ ,  $J = 2.3$  Hz), 6.24 (m, 4H,  $\text{H}^9$ ), 5.94 (m, 3H,  $\text{H}^{7'}$ ), 3.70 (s, 9H,  $\text{H}^{\text{OMe}}$ ), 3.66 (s, 9H,  $\text{H}^{\text{OMe}}$ ), 3.55 (s, 18H,  $\text{H}^{\text{OMe}}$ ).

$^{13}\text{C}$ -NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  161.65 ( $\text{C}^{\text{O}}$ ), 159.82 ( $\text{C}^{\text{O}}$ ), 159.06 ( $\text{C}^{\text{O}}$ ), 156.68 ( $\text{C}^{\text{O}}$ ), 155.16 ( $\text{C}^{\text{O}}$ ), 154.26 ( $\text{C}^{\text{O}}$ ), 151.59 ( $\text{C}^6$ ), 149.09 ( $\text{C}^6$ ), 142.50 ( $\text{C}^{\text{O}}$ ), 138.60 ( $\text{C}^{\text{O}}$ ), 137.65 ( $\text{C}^4$ ), 136.46 ( $\text{C}^4$ ), 134.77 ( $\text{C}^{\text{O}}$ ), 134.42 ( $\text{C}^{\text{O}}$ ), 128.52 ( $\text{C}^3$ ), 127.66 ( $\text{C}^5$ ), 124.16 ( $\text{C}^3$ ), 123.87 ( $\text{C}^5$ ), 117.26 ( $\text{C}^7$ ), 107.64 ( $\text{C}^7$ ), 106.71 ( $\text{C}^7$ ), 100.47 ( $\text{C}^9$ ), 99.58 ( $\text{C}^9$ ), 55.39 ( $2\text{C}^{\text{OMe}}$ ), 55.16 ( $3\text{C}$ ,  $\text{C}^{\text{OMe}}$ )

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z$  = 810.25 [ $\text{M}-2\text{PF}_6$ ] $^{2+}$ . Calculated for  $\text{C}_{90}\text{H}_{78}\text{N}_{12}\text{O}_{12}\text{Ru}$ : 1620.4906, found: 1620.4956. m.p. > 280 °C

5



### Iron(II) tris homoleptic complexes – General procedure:

Unless otherwise stated, the ligand (**3a**, **4a**, **5a**) was added to a solution of acetonitrile (5 mL) containing  $\text{Fe}(\text{BF}_4)_2$ . The solution was then heated at 60°C for two hrs. The solvent was removed *in vacuo* and water was added to the reaction mixture. A saturated solution of  $\text{KPF}_6$  was added and the resulting precipitate extracted into dichloromethane and dried over  $\text{MgSO}_4$ . This was purified by silica column chromatography or on preparative TLC plates as outlined below.

#### [ $\text{Fe}(\mathbf{3a})_3$ ][ $\text{PF}_6$ ] $_2$

**3a** (0.080 g, 0.21 mmol) and  $\text{Fe}(\text{BF}_4)_2$  (0.112 g, 0.0355 mmol). Purification was by column chromatography on silica (acetone:water:sat.  $\text{KNO}_3$ , 100:10:1). Two purple products were isolated: *mer* isomer (0.069g, 24 % yield,  $R_f$  = 0.74), *fac* isomer (0.032g, 11 %,  $R_f$  = 0.26)

#### *Mer* isomer

$^1\text{H}$ -NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.58 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 4.4 Hz), 8.38 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 4.1 Hz), 8.26 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 4.1 Hz), 8.17 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 4.4 Hz), 8.10 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 3.8 Hz), 7.76 (m, 4H), 7.63-6.94 (m, 42H), 6.90 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 7.60 Hz), 6.81 (m, 2H), 6.42 (d, 1H,  $\text{H}^{\text{Py}}$ ,  $J$  = 7.60 Hz).

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z$  = 607.1972 [ $\text{M}-2\text{PF}_6$ ] $^{2+}$ . Calculated for  $\text{C}_{78}\text{H}_{54}\text{N}_{12}\text{Fe}$ : 607.1972.

Anal. Calculated for  $\text{C}_{78}\text{H}_{54}\text{F}_{12}\text{N}_{12}\text{P}_2\text{Fe}$ : C, 62.24; H, 3.62; N, 11.17. Found: C, 61.46, H, 4.61, N, 9.36. m.p. > 280 °C

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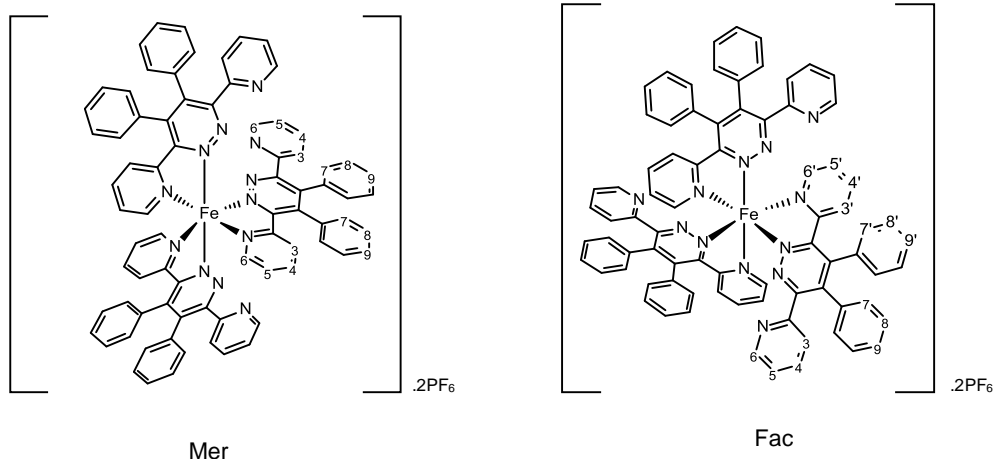
#### *Fac* isomer

$^1\text{H}$ -NMR (600 MHz,  $\text{CD}_3\text{CN}$ ):  $\delta$  8.45 (d, 3H,  $\text{H}^{\text{Py}}$ ,  $J$  = 5.0 Hz), 8.16 (d, 3H,  $\text{H}^{\text{Py}}$ ,  $J$  = 5.6 Hz), 7.74 (m, 6H, 2  $\text{H}^{\text{Py}}$ ), 7.57 (m, 3H,  $\text{H}^{\text{Py}}$ ), 7.43 (m, 6H,  $\text{H}^{\text{ph}}$ ), 7.33 (m, 6H,  $\text{H}^{\text{ph},5}$ ), 7.21 (d, 3H,  $\text{H}^{\text{Py}}$ ,  $J$  = 7.5 Hz), 7.01 (m, 12H,  $\text{H}^{\text{ph}}$ ), 6.94 (d, 3H,  $\text{H}^{\text{Py}}$ ,  $J$  = 8.1 Hz), 6.65 (m, 3H,  $\text{H}^{\text{ph}}$ ), 6.08 (s, 3H,  $\text{H}^{\text{ph}}$ ).

HRMS: ( $\text{CH}_3\text{CN}$ )  $m/z$  = 607.1969 [ $\text{M}-2\text{PF}_6$ ] $^{2+}$ . Calculated for  $\text{C}_{78}\text{H}_{54}\text{N}_{12}\text{Fe}$ : 607.1969.

Anal. Calculated for  $\text{C}_{78}\text{H}_{54}\text{P}_2\text{F}_{12}\text{N}_{12}\text{Fe}$ : C, 62.24; H, 3.62; N, 11.17. Found: C, 59.74, H, 3.55, N, 10.17. m.p. > 280 °C

30



**[Fe(4a)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>**

**4a** (0.0201 g, 0.0515 mmol) and Fe(BF<sub>4</sub>)<sub>2</sub> (0.0138 g, 0.06 mmol). The mixture was separated on a silica preparative TLC plate (acetone:ammonia:sat. KNO<sub>3</sub>, 20:4:4). *Mer* isomer (3.35 mg, 16% yield, R<sub>f</sub> = 0.77), *fac* isomer (8.80 mg, 42% yield, R<sub>f</sub> = 0.63).

*Mer* isomer

<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.75 (d, 1H, H<sup>4py</sup>, J = 5.3 Hz), 8.69 (d, 1H, H<sup>4py</sup>, J = 4.5 Hz), 8.66 (d, 1H, H<sup>4py</sup>, J = 5.0 Hz), 8.58 (d, 1H, H<sup>4py</sup>, J = 5.0 Hz), 8.50 (d, 1H, H<sup>py</sup>, J = 5.0 Hz), 8.47 (d, 1H, H<sup>4py</sup>, J = 5.2 Hz), 8.43 (d, 1H, H<sup>4py</sup>, J = 5.2 Hz), 8.33 (m, 6H, H<sup>py</sup>), 8.16 (d, 1H, H<sup>py</sup>, J = 4.8 Hz), 8.03 (d, 1H, H<sup>py</sup>, J = 6.0 Hz), 7.87 (Ψt, 1H, H<sup>py</sup>, J = 7.6 Hz), 7.80 (Ψt, 1H, H<sup>py</sup>, J = 7.9 Hz), 7.76 (d, 1H, H<sup>py</sup>, J = 5.9 Hz), 7.67 (m, 4H), 7.63 (Ψt, 1H, H<sup>py</sup>, J = 6.9 Hz), 7.46 (d, 1H, H<sup>4py</sup>, J = 4.8 Hz), 7.39 (m, 3H), 7.30 (m, 2H), 7.26 (d, 1H, H<sup>py</sup>, J = 5.0 Hz), 7.19 (d, 1H, H<sup>4py</sup>), 7.12 (m, 2H), 7.06 (d, 1H, H<sup>py</sup>, J = 7.6 Hz), 6.99 (m, 3H), 6.88 (d, 1H, H<sup>py</sup>, J = 5.1 Hz), 6.35 (d, 1H, H<sup>py</sup>, J = 4.5 Hz).

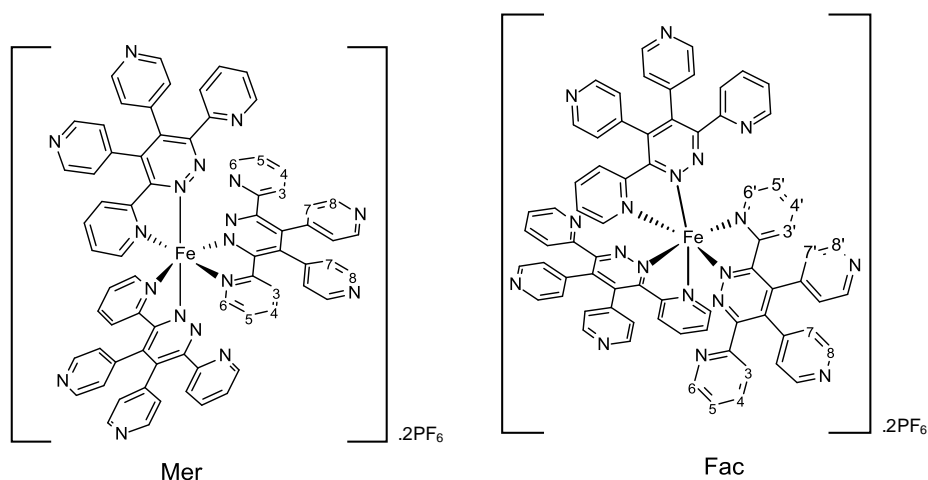
HRMS: (CH<sub>3</sub>CN) m/z = 610.1832 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>72</sub>H<sub>48</sub>N<sub>18</sub>Fe: 610.1830. m.p. > 280 °C

15

*Fac* isomer

<sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.67 (d, 3H, H<sup>8'</sup>, J = 5.2 Hz), 8.55 (d, 3H, H<sup>8'</sup>, J = 4.6 Hz), 8.40 (d, 3H, H<sup>6</sup>, J = 4.3 Hz), 8.27 (br. s, 6H, H<sup>8</sup>), 8.12 (d, 3H, H<sup>8'</sup>, J = 5.2 Hz), 7.88 (Ψtd, 3H, H<sup>4</sup>, J = 8.2, 1.2 Hz), 7.82 (Ψtd, 3H, H<sup>4</sup>, J = 7.4, 1.3 Hz), 7.63 (Ψt, 3H, H<sup>5</sup>, J = 6.4 Hz), 7.38 (m, 3H, H<sup>5</sup>), 7.31 (dd, 3H, H<sup>7</sup>), 7.26 (d, 3H, H<sup>3</sup>, J = 7.9 Hz), 7.21 (d, 3H, H<sup>3</sup>, J = 7.6 Hz), 6.67 (m, 3H, H<sup>7</sup>), 6.15 (s, 6H, H<sup>7</sup>). m.p. > 280 °C

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**[Fe(5a)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub>**

**5a** (0.0916 g, 0.181 mmol) and Fe(BF<sub>4</sub>)<sub>2</sub> (0.0674 g, 0.201 mmol). The meridional and facial isomers were separated by column chromatography on silica (1:1:0.1 of methanol:water:sat. KNO<sub>3</sub>). *Mer* isomer (0.039g, 37% yield, R<sub>f</sub> = 0.51), *fac* isomer (0.021 g, 20% yield, R<sub>f</sub> = 0.14).

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*Mer* isomer

<sup>5</sup> <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.42 (d, 1H, H<sup>Py</sup>, J = 4.2 Hz), 8.37 (d, 1H, H<sup>Py</sup>, J = 5.6 Hz), 8.30 (d, 1H, H<sup>Py</sup>, J = 4.4 Hz), 8.26 (d, 1H, H<sup>Py</sup>, J = 4.2 Hz), 7.89 (d, 1H, H<sup>Py</sup>, J = 5.0 Hz), 7.86 (Ψtd, 1H, H<sup>Py</sup>, J = 9.2, 1.5 Hz), 7.75 (m, 2H), 7.65 (m, 5H), 7.40 (d, 1H, H<sup>Py</sup>, J = 8.3 Hz), 7.36 (d, 1H, H<sup>Py</sup>, J = 8.0 Hz), 7.35 (m, 3H), 7.31 (m, 2H), 7.26 (d, 1H, H<sup>Py</sup>, J = 8.3 Hz), 7.15 (d, 1H, H<sup>Py</sup>, J = 7.9 Hz), 7.10 (d, 1H, H<sup>Py</sup>, J = 7.8 Hz), 7.06 (d, 1H, H<sup>Py</sup>, J = 8.4 Hz), 6.64 (m, 3H), 6.55 (d, 1H, H<sup>Ph</sup>, J = 1.2 Hz), 6.53 (d, 1H, H<sup>Ph</sup>, J = 2.0 Hz), 6.50 (d, 1H, H<sup>Ph</sup>, J = 1.2 Hz), 6.37 (d, 1H, H<sup>Ph</sup>, J = 2.2 Hz), 6.29 (m, 3H, H<sup>Ph</sup>), 6.26 (m, 2H, H<sup>Ph</sup>), 6.23 (m, 2H, H<sup>Ph</sup>), 5.75  
10 (m, 1H, H<sup>Ph</sup>), 3.76 (m, 5H, H<sup>OMe</sup>), 3.71 (s, 3H H<sup>OMe</sup>), 3.67 (s, 3H, H<sup>OMe</sup>), 3.64 (m, 4H, H<sup>OMe</sup>), 3.57 (s, 7H, H<sup>OMe</sup>), 3.54 (s, 7H, H<sup>OMe</sup>).

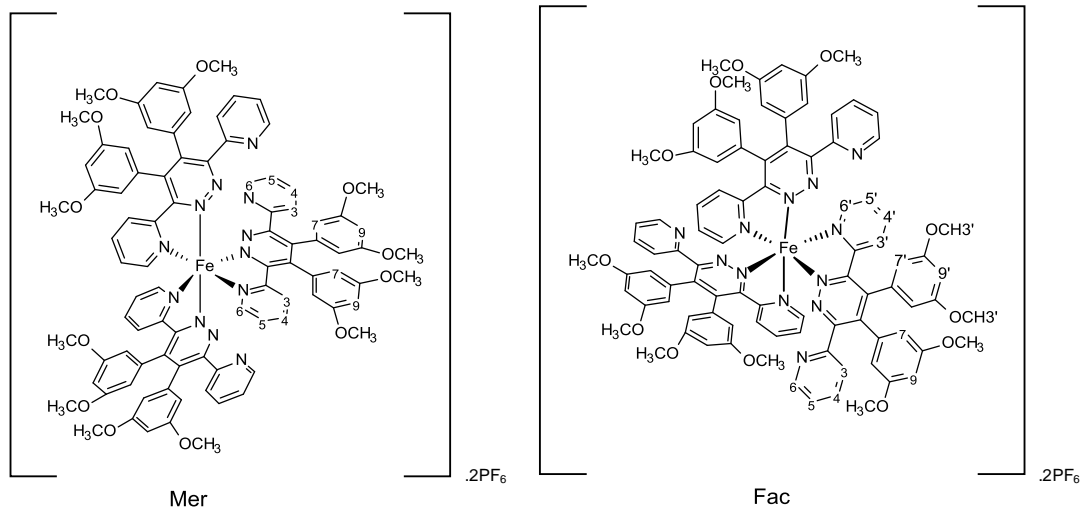
HRMS: (CH<sub>3</sub>CN) m/z = 787.2571 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>90</sub>H<sub>78</sub>N<sub>12</sub>O<sub>12</sub>Fe: 787.2606. m.p. > 280 °C

*Fac* isomer

<sup>15</sup> <sup>1</sup>H-NMR (600 MHz, CD<sub>3</sub>CN): δ 8.46 (d, 3H, H<sup>6</sup>, J = 4.2 Hz), 8.12 (d, 3H, H<sup>6</sup>, J = 5.6 Hz), 7.87 (Ψtd, 3H, H<sup>4</sup>, J = 7.0, 1.7 Hz), 7.73 (d, 3H, H<sup>4</sup>, J = 8.1, 1.4 Hz), 7.60 (d, 3H, H<sup>5</sup>, J = 1.5 Hz), 7.31 (d, 3H, H<sup>5</sup>, J = 1.3 Hz), 7.25 (d, 3H, H<sup>3</sup>, J = 8.1 Hz), 7.17 (d, 3H, H<sup>3</sup>, J = 7.8 Hz), 6.58 (s, 3H, H<sup>7</sup>), 6.46 (s, 3H, H<sup>9</sup>), 6.24 (s, 3H, H<sup>7</sup>), 5.90 (s, 3H, H<sup>9</sup>), 3.72 (s, 2H, H<sup>OMe</sup>'), 3.66 (s, 2H, H<sup>OMe</sup>'), 3.55 (s, 5H, H<sup>OMe</sup>).

HRMS: (CH<sub>3</sub>CN) m/z = 787.26 [M-2PF<sub>6</sub>]<sup>2+</sup>. Calculated for C<sub>90</sub>H<sub>78</sub>N<sub>12</sub>O<sub>12</sub>Fe: 787.2606. m.p. > 280 °C

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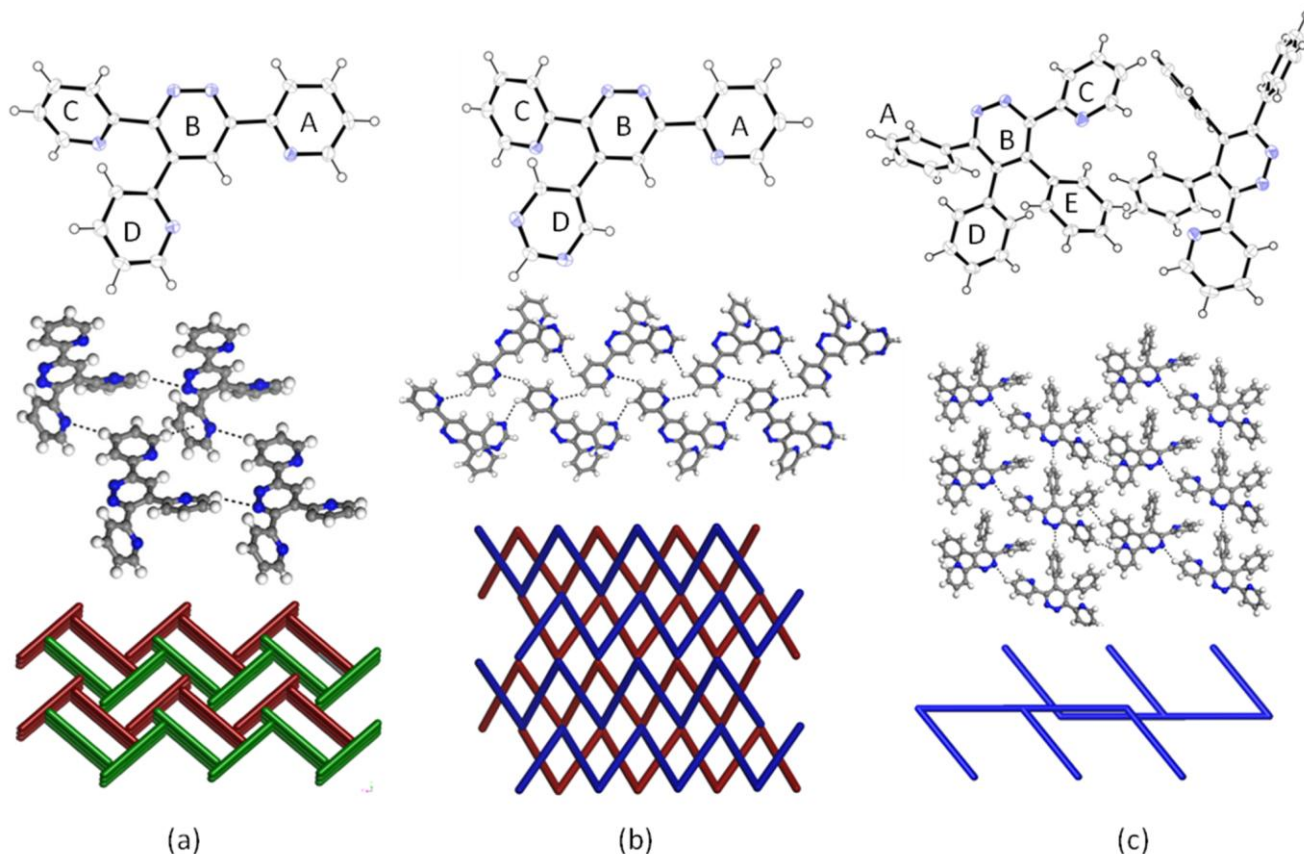


## Crystallographic Structural Data and Discussion

**Table S1:** Data for compounds **1a**, **2a**, **3a**, **6**

Compound reference	1a	2a	3a	6
Chemical formula	C <sub>18</sub> H <sub>12</sub> N <sub>6</sub>	C <sub>19</sub> H <sub>13</sub> N <sub>5</sub>	C <sub>26</sub> H <sub>18</sub> N <sub>4</sub>	C <sub>24</sub> H <sub>14</sub> N <sub>4</sub>
Formula Mass	312.34	311.34	386.44	358.39
Crystal system	Orthorhombic	Monoclinic	Triclinic	Orthorhombic
<i>a</i> /Å	11.061(2)	9.484(9)	10.4655(5)	21.426(2)
<i>b</i> /Å	18.238(4)	11.136(2)	12.1742(6)	10.013(1)
<i>c</i> /Å	7.349(5)	14.432(3)	15.8820(8)	7.9162(8)
$\alpha$ /°	90.00	90.00	93.674(1)	90.00
$\beta$ /°	90.00	90.87(3)	91.256(1)	90.00
$\gamma$ /°	90.00	90.00	101.750(1)	90.00
Unit cell volume/Å <sup>3</sup>	1482.6(5)	1524.1(5)	1975.8(7)	1698.3(3)
Temperature/K	153(2)	153(2)	153(2)	153(2)
Space group	<i>Pca</i> 2(1)	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> 1	<i>Pbcn</i>
No. of formula units per unit cell, <i>Z</i>	4	4	4	4
No. of reflections measured	14602	15793	25705	9267
No. of independent reflections	2914	2691	9068	1757
<i>R</i> <sub>int</sub>	0.0200	0.0180	0.0330	0.0586
Final <i>R</i> <sub><i>I</i></sub> values ( <i>I</i> > 2σ( <i>I</i> ))	0.0282	0.0321	0.0459	0.0489
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values ( <i>I</i> > 2σ( <i>I</i> ))	0.0771	0.0821	0.1069	0.1065
Final <i>R</i> <sub><i>I</i></sub> values (all data)	0.0291	0.0344	0.0713	0.0769
Final <i>wR</i> ( <i>F</i> <sup>2</sup> ) values (all data)	0.0780	0.0845	0.1189	0.1178



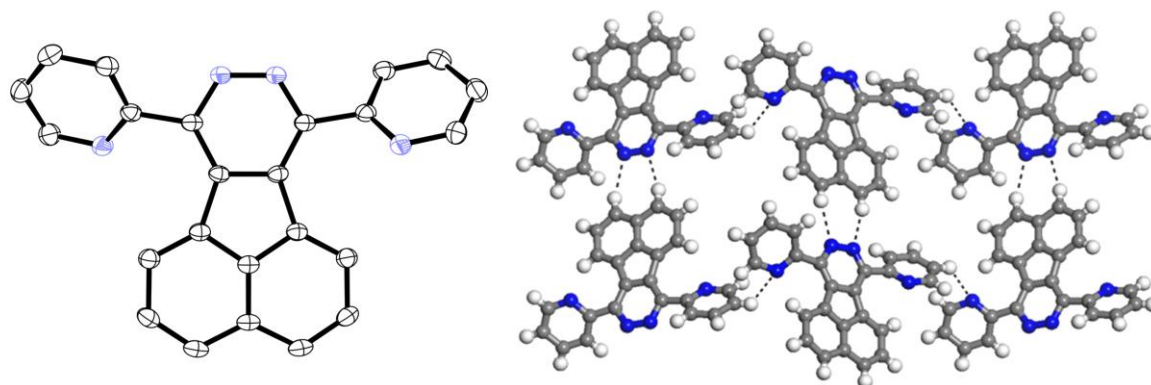


**Fig. S1** Asymmetric units (top) and representations of the lattice interactions in ligands **1a**, **2a** and **3a** in molecular structure (centre) and schematic (bottom) forms.

Single crystals of **1a** were grown from dichloromethane and had a  $P2_1/n$  centrosymmetric space group. One molecule is found in the asymmetric unit, as shown in Figure S1 (a). Rings A and B are almost coplanar, with a dihedral angle of  $7.13^\circ$  between them. The angle between the central pyridazine ring (B) and ring C is  $55.04^\circ$ , with an angle of  $29.05^\circ$  between rings B and D. The collective interactions of the pyridazine and the 2-pyridyl units leads to the formation of infinite chains giving a herringbone arrangement which is represented schematically in Figure S1 (a). In the three-dimensional arrangement, these chains are held by  $C-H \cdots \pi$  ( $H \cdots \pi$ ,  $2.83 \text{ \AA}$ ) interactions.

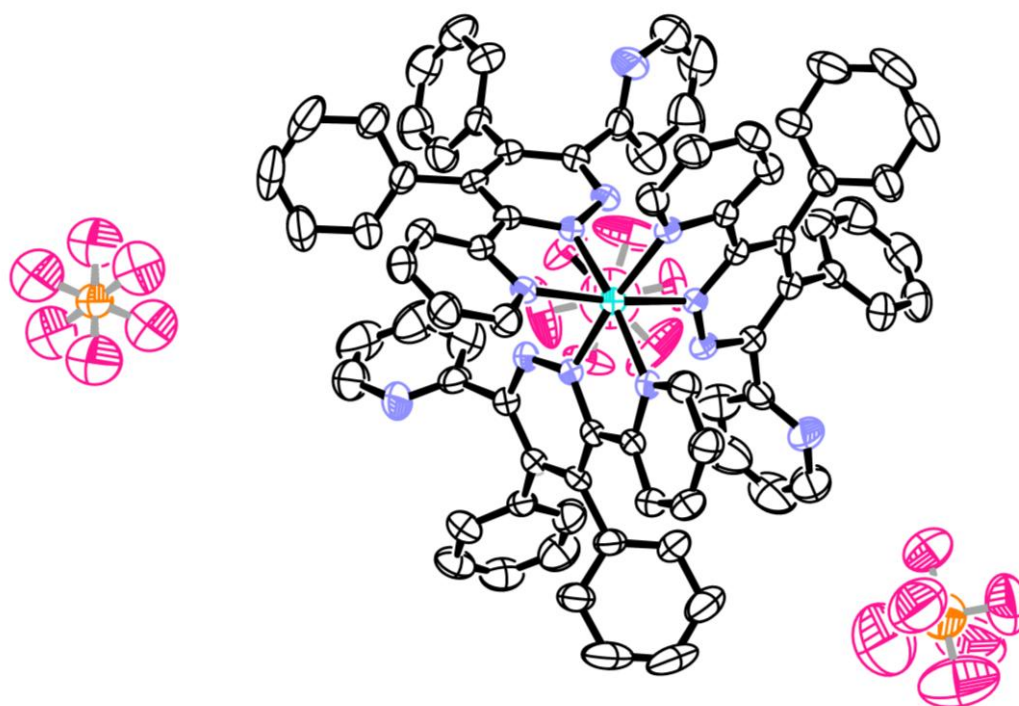
Colourless rod-like crystals of **2a** were obtained from a dichloromethane-hexane solution. Single crystal X-ray analysis revealed that the compound crystallises in an orthorhombic crystal system with one molecule of **2a** in the asymmetric unit. There is a small dihedral angle between the rings labelled A and B of  $5.02^\circ$ . The angles between B and C, and C and D, are  $31.47^\circ$  and  $48.18^\circ$  respectively. In the crystal lattice, the molecules are stabilised by  $C-H \cdots N$  hydrogen bonds involving both pyridyl units ( $H \cdots N$ ,  $2.64 \text{ \AA}$ ) as well as the pyrimidyl ring ( $H \cdots N$ ,  $2.68 \text{ \AA}$ ). This interaction leads to the formation of an undulated layer as shown in Figure S1 (b) (bottom). Unlike **2a**, the pyridazine ring plays no significant role in the hydrogen bond formation or stabilisation of the molecular assembly. The layers form an ABAB pattern and a zig-zag architecture.

Crystals of **3a** were grown from a dichloromethane solution. The asymmetric unit (containing two independent molecules) and representations of the lattice packing are shown in Figure S1 (c). The dihedral angle between the central ring (B) and the two 2-pyridyl rings (A and C) is  $45.19^\circ$  and  $43.06^\circ$  respectively. The torsion angles between ring B and the two phenyl rings D and E are  $55.60^\circ$  and  $68.01^\circ$ . The molecules interact with each other through  $C-H \cdots N$  Hydrogen bonds ( $2.5-2.6 \text{ \AA}$ ) and  $C-H \cdots \pi$  interactions ( $3.0-3.2 \text{ \AA}$ ) to form linear chains with branches on one side. This interaction can be viewed pictorially as two interlocking branched chains as is represented in Figure S1 (c).



**Fig. S2** *Left*: Molecular structure of the **6** (Black: carbon, blue: nitrogen). *Right*: Lattice arrangement of **6**, showing N...H interactions both between and within layers.

Crystals of **6** were obtained from a saturated dichloromethane solution. The compound crystallised in the orthorhombic *Pbcn* space group, the asymmetric unit consisting of half a molecule of **6** owing to the crystallographically imposed two-fold symmetry. The pyridazine ring forms intermolecular non-centrosymmetric hydrogen bonds (C-H...N, 3.466 Å) with the fluoranthene moiety, as shown in Figure S2. This, along with C-H...N interactions between neighbouring pyridyl rings (3.490 Å), results in the corrugated sheet structure observed in the lattice.



**Fig. S3** ORTEP representation of *fac*-[Ru(**3a**)<sub>3</sub>][PF<sub>6</sub>]<sub>2</sub> (ellipsoids shown at 50% probability). Fluorine: pink, phosphorus: orange, carbon: black, nitrogen: purple, ruthenium: grey. P-F bonds have been shaded a lighter colour for clarity. See article for discussion.