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Supplementary information

Systematic evaluation of HOMO energy levels for efficient dye regeneration in dye-sensitized solar cells

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Synthesis of C^N ligands and ruthenium complexes



Synthesis of 2-(4-methylphenyl)pyridine

A mixture of 2-bromopyridine (1.00 g, 6.33 mmol), 4-methylphenylboronic acid (1.03 g, 7.59 mmol), tetrakis(triphenylphosphine)palladium(0) (Pd(PPh₃)₄) (0.219 g, 0.190 mmol) in THF (25 mL) and 1M Na₂CO₃ aqueous solution (15 mL) was heated to 70 °C for 8 h. After cooled to room temperature, the reaction mixture was extracted with CH₂Cl₂ (50 mL x 3), and dried over MgSO₄. After the filtration of the organic layer, the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography (SiO₂, CH₂Cl₂ and hexane) to give the desired compounds in 39% yield (0.417 g, 2.47 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.67 (d, *J* = 4.8 Hz, 1H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.75-7.68 (m, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 7.20 (td, *J* = 4.8, 1.6 Hz, 1H), 2.40 (s, 3H) ppm. MS (ESI-MS): *m/z* 170.0 [M+H]⁺.

Synthesis of 1a

A mixture of Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4-methylphenyl)pyridine (55.0 mg, 0.325 mmol), triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) was refluxed for 10 min by means of microwave synthesizer and allowed to cool to room temperature. The precipitated complex was collected, washed with ethanol and dried to give **1a** in 45% yield (104 mg, 0.146 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.24$ (d, J = 5.5 Hz, 1H), 8.83 (s, 2H), 8.71 (d, J = 1.7 Hz, 2H), 8.03 (d, J 8.4 Hz, 1H), 7.93-7.87 (m, 3H), 7.66 (dd, J 5.8, 1.7 Hz, 2H), 7.51 (d, J 7.9 Hz, 1H), 7.46 (t, J = 5.5 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 5.14 (s, 1H), 4.13(s, 3H), 4.13 (s, 3H), 3.95(s, 3H), 1.74(s, 3H) ppm. MS (ESI-MS): m/z 677.0 [M–Cl]⁺, 718.0 [M–Cl+MeCN]⁺.

Synthesis of 1

1a (100 mg, 0.140 mmol) in *N*,*N*-dimethylformamide (3 mL) and 1 mL of an aqueous solution of ammonium thiocyanato (10.7 mg, 0.140 mmol) were refluxed for 10 min by means of microwave synthesizer. After cooling to room temperature, 5 mL of *N*,*N*-dimethylformamide, 2 mL of triethylamine, and 1 mL of water were added, and the reaction mixture was refluxed for another 20 h to hydrolyze the ester group on the 2,2':6',2"-terpyridine ligand. The mixture was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The resulting solid was purified by column chromatography using Sephadex LH-20 as a column support and 5 mM TBA(OH) in ethanol/water (1:1, v/v) as an eluent. The solvent of collected main band was removed

by rotary evaporation. The isolated solid was dissolved in water (10 mL) and a precipitate was appeared by the addition of 1 M HCl. The precipitate was filtrated, washed with water, and dried to give **1** in 56% yield (54.6 mg, 0.0789 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 9.82 (d, *J* = 5.5 Hz, 1H), 8.78 (s, 2H), 8.62 (s, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.96 (dd, *J* = 8.1, 7.8 Hz, 1H), 7.55-7.52 (m, 6H), 6.25 (d, *J* = 8.0 Hz, 1H), 5.08 (s, 1H) ppm. MS (ESI-MS): *m/z* 316.0 [M–NCS–3H]^{2–}, 310.0 [M–NCS–CO₂H–2H+MeOH]^{2–}, 295.0 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-phenylphenyl)pyridine

2-(4-phenylphenyl)pyridine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyridine (1.00 g, 6.33 mmol), 4-biphenylboronic acid (1.50 g, 7.59 mmol), Pd(PPh₃)₄ (0.219 g, 0.190 mmol) in THF (25 mL) and 1M Na₂CO₃ aqueous solution (15 mL) to give the desired compounds in 84% yield (1.22 g, 5.29 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.71 (d, *J* = 4.6 Hz, 1H), 8.06 (d, *J* = 8.5 Hz, 2H), 7.77-7.76 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 2H), 7.65 (dd, *J* = 8.2, 1.2 Hz, 2H), 7.45 (ddd, *J* = 8.2, 6.5, 1.2 Hz, 2H), 7.37-7.33 (m, 1H), 7.25-7.22 (m, 1H) ppm. MS (ESI-MS): *m/z* 232.1 [M+H]⁺.

Synthesis of 2a

2a was prepared following the method of **1**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4-phenylphenyl)pyridine (75.2 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **2a** in 66% yield (165 mg, 0.214 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta =$ 10.30 (dd, J = 5.9, 1.0 Hz, 1H), 8.83 (s, 2H), 8.71 (d, J = 1.1 Hz, 2H), 8.11 (d, J = 8.1 Hz, 1H), 7.95 (td, J = 8.1, 1.5 Hz, 1H), 7.90 (d, J = 5.9 Hz, 2H), 7.71-7.66 (m, 3H), 7.52-7.49 (m, 1H), 7.21-7.12 (m, 3H), 7.00 (dd, J = 8.3, 1.6 Hz, 2H), 6.84 (dd, J = 8.0, 1.8 Hz, 1H), 5.59 (d, J = 1.8 Hz, 1H), 4.12 (s, 3H), 3.95 (s, 6H) ppm. MS (ESI-MS): m/z 739.0 [M–Cl]⁺, 780.0 [M–Cl+MeCN]⁺.

Synthesis of 2

2 was prepared following the method of **1**, from **2a** (100 mg, 0.129 mmol), ammonium thiocyanato (9.8 mg, 0.129 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **2** in 51% yield (49.6 mg, 0.0658 mmol). ¹H NMR (400 MHz, DMSO- d_6 - NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 9.85 (d, *J* = 5.0 Hz, 1H), 8.80 (s, 2H), 8.64 (s, 2H), 8.26 (d, *J* = 8.2 Hz, 1H), 8.01 (dd, *J* = 8.0, 6.4 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.63-7.59 (m, 3H), 7.55 (d, *J* = 5.8 Hz, 2H),

7.21 (dd, J = 7.4, 7.2 Hz, 2H), 7.12 (t, J = 7.1 Hz, 1H), 6.95 (d, J = 7.4 Hz, 2H), 6.69 (dd, J = 8.2, 1.8 Hz, 1H), 5.52 (d, J = 1.8 Hz, 1H) ppm. MS (ESI-MS): m/z 348.2 [M–NCS–3H]^{2–}, 339.8 [M–NCS–CO₂H–2H+MeOH]^{2–}, 324.9 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 3a

A mixture of Ru(Me₃tctpy)Cl₃ (1.00 g, 1.63 mmol), 2-phenylpyridine (0.252 g, 1.63 mmol), triethylamine (0.5 mL) in 3:1 (v/v) ethanol-water (200 mL) was heated to reflux for 5 h in the dark and allowed to cool to room temperature. The precipitated complex was collected, washed with ethanol and dried to give **3a** in 47% yield (0.540 g, 0.766 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.32$ (d, J = 5.5 Hz, 1H), 8.85 (s, 2H), 8.72 (d, J = 1.5 Hz, 2H), 8.09 (d, J = 8.0 Hz, 1H), 7.96 (dd, J = 8.0, 7.2 Hz, 1H), 7.90 (d, J = 5.6 Hz, 2H), 7.68 (dd, J = 5.6, 1.5 Hz, 2H), 7.63 (d, J = 7.7 Hz, 1H), 7.52 (dd, J = 7.2, 5.5 Hz, 1H), 6.63 (dd, J = 7.7, 7.2 Hz, 1H), 6.39 (dd, J = 7.2, 7.0 Hz, 1H), 5.39 (d, J = 7.0 Hz, 1H), 4.15 (s, 3H), 3.97 (s, 6H) ppm. MS (ESI-MS): m/z 663.4 [M–Cl]⁺.

Synthesis of 3

3 was prepared following the method of **1**, from **3a** (100 mg, 0.143 mmol), ammonium thiocyanato (10.9 mg, 0.143 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **2** in 37% yield (35.8 mg, 0.0529 mmol). ¹H NMR (400 MHz, DMSO-*d*₆-NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 9.88 (d, *J* = 6.0 Hz, 1H), 8.85 (s, 2H), 8.69 (s, 2H), 8.28 (d, *J* = 8.6 Hz, 1H), 8.05 (dd, *J* = 7.6, 6.0 Hz, 1H), 7.71-7.58 (m, 6H), 6.50 (dd, *J* = 8.0, 6.6 Hz, 1H), 6.27 (dd, *J* = 8.2, 6.6 Hz, 1H), 5.33 (d, *J* = 8.2 Hz, 1H) ppm. MS (ESI-MS): *m/z* 308.9 [M–NCS–3H]²⁻.



Synthesis of 5-fluoro-2-(4-methylphenyl)pyridine

5-fluoro-2-(4-methylphenyl)pyridine was prepared following the method of 2-(4methylphenyl)pyridine, from 2-bromo-5-fluoropyridine (0.500 2.84 mmol), 4g, methylphenylboronic acid (0.463 g, 3.41 mmol), Pd(PPh₃)₄ (0.0985 g, 0.0852 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 97% yield (0.518 g, 2.77 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 8.52 (d, J = 2.9 Hz, 1H), 7.85(d, J = 8.0 Hz, 2H), 7.69 (dd, J = 8.8, 4.7 Hz, 1H), 7.45 (ddd, J = 8.8, 8.0, 2.9 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2 H), 2.40 (s, 3H) ppm. MS (ESI-MS): *m/z* 188.0 [M +H]⁺.

Synthesis of 4a

A mixture of Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 5-fluoro-2-(4-methylphenyl)pyridine (60.9 mg, 0.325 mmol), triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) was refluxed for 10 min by means of microwave synthesizer and allowed to cool to room temperature. After the filtration of the mixture, the filtrate was concentrated *in vacuo*. The resulting solid was dissolved in CH₂Cl₂ (10 mL) and a precipitate was appeared by the addition of hexane (13 mL). After the filtration of the mixture, the filtrate was concentrated *in vacuo*. The resulting solid was washed with hexane and dried to give **4a** in 32% yield (75.7 mg, 0.103 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 10.27$ (dd, J = 5.8, 2.9 Hz, 1H), 8.85 (s, 2H), 8.73 (dd, J = 1.8, 0.7 Hz, 2H), 8.01 (dd, J = 9.1, 5.1 Hz, 1H), 7.88 (dd, J = 5.9, 0.7 Hz, 2H), 7.69-7.67 (m, 3H), 7.45 (d, J = 7.9 Hz, 1H), 6.44 (dd, J = 7.9, 0.7 Hz, 1H), 5.17(d, J = 0.7 Hz, 1H), 4.15 (s, 3H), 3.98 (s, 6H), 1.76 (s, 3H) ppm. MS (ESI-MS): m/z 694.8 [M–Cl]⁺.

Synthesis of 4

4 was prepared following the method of **1**, from **4a** (70.0 mg, 0.0959 mmol), ammonium thiocyanato (7.3 mg, 0.0959 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **2** in 24% yield (16.6 mg, 0.0233 mmol). ¹H NMR (600 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 10.08 (br, 1H), 8.82 (s, 2H), 8.62 (s, 2H), 8.26 (dd, *J* = 9.2, 5.5 Hz, 1H),7.96 (ddd, *J* = 9.2, 7.0, 2.6 Hz, 1H) 7.71 (d, *J* = 5.5 Hz, 2H), 7.67-7.62 (m, 3H), 6.52(d, *J* = 8.4 Hz, 1H), 5.41 (s, 1H), 1.78 (s, 3H) ppm. MS (ESI-MS): *m*/*z* 318.9 [M–NCS–CO₂H–2H+MeOH]^{2–}, 302.5 [M–NCS–CO₂H–2H]^{2–}.





A mixture of 2-(4-bromophenyl)pyridine (0.500 g, 2.14 mmol), phenylacetylene (0.262 g, 2.56 mmol), Pd(PPh₃)₄ (0.0617 g, 0.0534 mmol), CuI (0.0203 g, 0.0107 mmol) in THF (10 mL) and triethylamine (2 mL) was refluxed for 8 h. After cooled to room temperature, the reaction mixture was extracted with CH_2Cl_2 (50 mL x 3), and dried over MgSO₄. After the filtration of the organic layer, the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography

(SiO₂, CH₂Cl₂ and hexane) to give the desired compounds in 58% yield (0.317 g, 1.24 mmol). ¹H NMR (400 MHz, CD₃CN, Me₄Si): $\delta = 8.69-8.67$ (m, 1H), 8.11 (d, J = 8.6 Hz, 2H), 7.90 (d, J = 8.0 Hz, 1H), 7.85 (ddd, J = 8.0, 7.2, 1.8 Hz, 1H), 7.65 (d, J = 8.6 Hz, 2H), 7.59-7.57 (m, 2H), 7.44-7.41 (m, 3H), 7.32 (ddd, J = 7.2, 4.8, 1.4 Hz, 1H) ppm. MS (ESI-MS): m/z 256.0 [M+H]⁺.

Synthesis of 5a

5a was prepared following the method of **3a**, from Ru(Me₃tctpy)Cl₃ (500 mg, 0.813 mmol), 2-(4-(2-phenylethynyl)phenyl)pyridine (207 mg, 0.813 mmol), and triethylamine (0.25 mL) in 3:1 (v/v) ethanol-water (80 mL) to give **4** in 65% yield (423 mg, 0.530 mmol).¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.31$ (d, J = 6.4 Hz, 1H), 8.87 (s, 2H), 8.74 (d, J = 1.6 Hz, 2H), 8.11 (d, J = 8.2 Hz, 1H), 7.97 (dd, J = 8.2, 7.2 Hz, 1H), 7.86(d, J = 5.7 Hz, 2H), 7.68 (dd, J = 5.7, 1.6 Hz, 2H), 7.61 (d, J = 8.2 Hz, 1H), 7.53 (dd, J = 7.2, 6.4 Hz, 1H), 7.34-7.23 (m, 5H), 6.83 (dd, J = 8.2, 1.6 Hz, 1H), 5.57 (d, J = 1.6 Hz, 1H), 4.15 (s, 3H), 3.98 (s, 6H) ppm. MS (ESI-MS): m/z 804.4 [M–Cl+MeCN]⁺.

Synthesis of 5

5 was prepared following the method of **1**, from **5a** (200 mg, 0.251 mmol), ammonium thiocyanato (19.1 mg, 0.251 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **2** in 31% yield (60.9 mg, 0.0778 mmol). ¹H NMR (400 MHz, DMSO- d_6 -D₂O (9:1, v/v), Me₄Si): δ = 9.93 (d, *J* = 6.0, 1H), 8.86 (s, 2H), 8.70 (s, 2H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.07 (dd, *J* = 8.4, 7.2 Hz, 1H), 7.78(d, *J* = 8.0 Hz, 1H), 7.68 (dd, *J* = 7.2, 6.0 Hz, 1H), 7.36 (s, 5H), 6.69 (dd, *J* = 8.0, 1.8 Hz, 1H), 5.51 (d, *J* = 1.8 Hz, 1H) ppm. MS (ESI-MS): *m/z* 358.9 [M–NCS–3H]^{2–}.



Synthesis of 2-(4-fluorophenyl)-4-methylpyridine

2-(4-fluorophenyl)-4-methylpyridine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromo-4-picoline (1.64 g, 9.53 mmol), 4-fluorophenylboronic acid (1.60 g, 11.4 mmol), Pd(PPh₃)₄) (0.330 g, 0.286 mmol) in THF (50 mL) and 1M Na₂CO₃ aqueous solution (30 mL) to give the desired compounds in 53% yield (0.950 g, 5.08 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.52 (d, *J* = 4.6 Hz, 1H), 7.94 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.49 (s, 1H), 7.13 (t, *J* = 8.8 Hz, 2H), 7.05 (d, *J* = 4.7 Hz, 1H), 2.4 (s, 3H) ppm. MS (ESI-MS): *m/z* 188.0 [M+H]⁺.

Synthesis of 6a

6a was prepared following the method of 1a, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4-

fluorophenyl)-4-methylpyridine (60.9 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **2a** in 62% yield (147 mg, 0.202 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.07$ (d, J = 5.8 Hz, 1H), 8.83 (s, 2H), 8.71 (d, J = 1.7 Hz, 2H), 7.86 (d, J = 5.9 Hz, 2H), 7.81 (s, 1H), 7.67 (dd, J = 5.9, 1.7 Hz, 2H), 7.56 (dd, J = 8.7, 5.4 Hz, 1H), 7.32 (d, J = 5.8 Hz, 1H), 6.27 (td, J = 8.7, 2.6 Hz, 1H), 5.02 (dd, J = 9.2, 2.6 Hz, 1H), 4.13 (s, 3H), 3.96 (s, 6H), 2.68 (s, 3H) ppm. MS (ESI-MS): m/z 695.0 [M–Cl]⁺, 736.0 [M–Cl+MeCN]⁺.

Synthesis of 6

6 was prepared following the method of **1**, from **6a** (100 mg, 0.137 mmol), ammonium thiocyanato (10.4 mg, 0.137 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **6** in 54% yield (52.8 mg, 0.0744 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 9.67 (d, *J* = 5.6 Hz, 1H), 8.78 (s, 2H), 8.63 (s, 2H), 8.04 (s, 1H), 7.69-7.66 (m, 2H), 7.54 (s, 4H), 6.16(ddd, *J* = 8.2, 6.5, 2.4 Hz, 1H), 4.89 (dd, *J* = 9.9, 2.4 Hz, 1H) ppm. MS (ESI-MS): *m/z* 304.2 [M–NCS–CO₂H–2H]^{2–}, 237.2 [M–3H]^{3–}.



Synthesis of 2-(4-methylphenyl)pyrimidine

2-(4-methylphenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 4-methylphenylboronic acid (0.513 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 71% yield (0.381 g, 2.23 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 8.79 (d, *J* = 4.8 Hz, 2H), 8.33 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 7.16 (t, *J* = 4.8 Hz, 1H), 2.43 (s, 3H) ppm. MS (ESI-MS): *m/z* 171.0 [M+H]⁺.

Synthesis of 7a

7a was prepared following the method of **1a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4methylphenyl)pyrimidine (55.3 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanolwater (4 mL) to give **7a** in 45% yield (105 mg, 0.147 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 10.43 (dd, *J* = 5.5, 2.2 Hz, 1H), 8.93 (dd, *J* = 4.7, 2.2 Hz, 1H), 8.86 (s, 2H), 8.74 (d, *J* = 1.8 Hz, 2H), 7.97 (d, *J* = 7.4 Hz, 1H), 7.90 (d, *J* = 6.0 Hz, 2H), 7.69 (dd, *J* = 6.0, 1.8 Hz, 2H), 7.43 (dd, *J* = 5.5, 4.7 Hz, 1H), 6.50 (d, *J* = 7.4 Hz, 1H), 5.20 (s, 1H), 4.16 (s, 3H), 3.98 (s, 6H), 1.78 (s, 3H) ppm. MS (ESI-MS): *m/z* 678.0 [M–Cl]⁺, 719.0 [M–Cl+MeCN]⁺.

Synthesis of 7

7 was prepared following the method of 1, from 7a (80.0 mg, 0.112 mmol), ammonium thiocyanato

(8.5 mg, 0.112 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **6** in 51% yield (39.8 mg, 0.0573 mmol). ¹H NMR (600 MHz, DMSO- d_{δ} - NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 10.15 (br, 1H), 8.94 (dd, *J* = 4.8, 2.2 Hz, 1H), 8.84 (s, 2H), 8.64 (s, 2H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 5.7 Hz, 2H), 7.63 (d, *J* = 5.7 Hz, 2H), 7.59 (dd, *J* = 5.5, 4.8 Hz, 1H), 6.57 (d, *J* = 7.7 Hz, 1H), 5.50 (s, 1H), 1.81 (s, 3H) ppm. MS (ESI-MS): *m/z* 316.5 [M–NCS–3H]^{2–}, 311.3 [M–NCS–CO₂H–2H+MeOH]^{2–}, 294.6 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-chlorophenyl)pyridine

2-(4-chlorophenyl)pyridine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyridine (1.01 g, 6.40 mmol), 4-chlorophenylboronic acid (1.00 g, 6.40 mmol), Pd(PPh₃)₄ (0.222 g, 0.192 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 74% yield (0.900 g, 4.76 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.68 (d, *J* = 4.2 Hz, 1H), 7.92 (d, *J* = 8.7 Hz, 2H), 7.75 (ddd, *J* = 8.0, 7.4, 1.7 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.7 Hz, 2H), 7.26-7.22 (m, 1H) ppm. MS (ESI-MS): *m/z* 190.0 [M+H]⁺.

Synthesis of 8a

8a was prepared following the method of **3a**, from Ru(Me₃tctpy)Cl₃ (500 mg, 0.813 mmol), 2-(4chlorophenyl)pyridine (154 mg, 0.813 mmol), and triethylamine (0.25 mL) in 3:1 (v/v) ethanolwater (100 mL) to give **8a** in 46% yield (272 mg, 0.371 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.27$ (d, J = 5.9 Hz, 1H), 8.84 (s, 2H), 8.72 (s, 2H), 8.03 (dd, J = 8.3 Hz, 1H), 7.95 (d, J = 8.3, 7.2 Hz, 1H), 7.84-7.81 (m, 2H), 7.69-7.67 (m, 2H), 7.53-7.49 (m, 2H), 6.58 (d, J = 8.4 Hz, 1H), 5.32 (s, 1H), 4.14 (s, 3H), 3.97 (s, 6H) ppm. MS (ESI-MS): *m/z* 696.8 [M–Cl]⁺, 737.9 [M–Cl+MeCN]⁺. **Synthesis of 8**

ynthesis of o

8 was prepared following the method of **1**, from **8a** (200 mg, 0.273 mmol), ammonium thiocyanato (20.8 mg, 0.273 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **6** in 62% yield (87.5 mg, 0.122 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 9.90 (d, *J* = 4.9 Hz, 1H), 8.85 (s, 2H), 8.70 (d, *J* = 1.6 Hz, 2H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.06 (dd, *J* = 8.5, 6.8 Hz, 1H), 7.73 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 6.8, 4.9 Hz, 1H), 7.60 (dd, *J* = 5.8, 1.6 Hz, 2H), 7.57 (d, *J* = 5.8 Hz, 2H), 6.50 (dd, *J* = 8.3, 2.2 Hz, 1H), 5.25 (d, *J* = 2.2 Hz, 1H) ppm. MS (ESI-MS): *m*/z 325.8 [M–NCS–3H]²⁻, 320.1 [M–NCS–CO₂H–2H+MeOH]²⁻, 305.1 [M–NCS–CO₂H–2H]²⁻.



Synthesis of 5-fluoro-2-(4-methoxyphenyl)pyridine

5-fluoro-2-(4-methoxyphenyl)pyridine was prepared following the method of 2-(4methylphenyl)pyridine, from 2-bromo-5-fluoropyridine (0.500)2.84 mmol), g, 4methoxyphenylboronic acid (0.518 g, 3.41 mmol), Pd(PPh₃)₄ (0.0985 g, 0.0852 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 53% yield (0.306 g, 1.50 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 8.50 (d, J = 2.9 Hz, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.65 (dd, J = 8.6, 4.4 Hz, 1H), 7.43 (td, J = 8.6, 2.9 Hz, 1H), 6.99 (d, J = 8.8 Hz, 2H), 1.56 (s, 3H) ppm. MS (ESI-MS): *m/z* 204.0 [M+H]⁺.

Synthesis of 9a

9a was prepared following the method of **1a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 5-fluoro-2-(4-methoxyphenyl)pyridine (66.1 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **9a** in 48% yield (116 mg, 0.154 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 10.24$ (dd, J = 5.8, 2.9 Hz, 1H), 8.83 (s, 2H), 8.72 (d, J = 1.7 Hz, 2H), 7.93 (dd, J = 8.8, 5.2 Hz, 1H), 7.90 (d, J = 5.8 Hz, 2H), 7.70-7.67 (m, 3H), 7.50 (d, J = 8.7 Hz, 1H), 6.19 (dd, J = 8.7, 2.6 Hz, 1H), 4.93 (d, J = 2.6 Hz, 1H), 4.14 (s, 3H), 3.98 (s, 6H), 3.37 (s, 3H) ppm. MS (ESI-MS): m/z 711.0 [M–Cl]⁺, 752.0 [M–Cl+MeCN]⁺.

Synthesis of 9

9 was prepared following the method of **1**, from **9a** (100 mg, 0.134 mmol), ammonium thiocyanato (10.2 mg, 0.134 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **9** in 48% yield (46.7 mg, 0.0641 mmol). ¹H NMR (600 MHz, DMSO- d_6 - NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 10.06 (br, 1H), 8.81 (s, 2H), 8.62 (s, 2H), 8.19-8.17 (m, 1H), 7.95-7.92 (m, 1H), 7.73-7.68 (m, 3H), 7.63 (d, *J* = 5.9 Hz, 2H), 6.29 (d, *J* = 8.5 Hz, 1H), 5.03 (s, 1H), 3.31 (s, 3H) ppm. MS (ESI-MS): *m/z* 326.8 [M–NCS–CO₂H–2H+MeOH]^{2–}, 312.0 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-fluorophenyl)pyridine

2-(4-fluorophenyl)pyridine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyridine (1.13 g, 7.15 mmol), 4-fluorophenylboronic acid (1.00 g, 7.15 mmol), Pd(PPh₃)₄ (0.248 g, 0.214 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 81% yield (1.00 g, 5.78 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.67 (d, *J* = 4.4 Hz, 1H), 7.96 (dd, *J* = 8.8, 5.4 Hz, 2H), 7.74 (td, *J* = 7.8, 1.8 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.24-7.21 (m, 1H), 7.15 (t, *J* = 8.8 Hz, 2H) ppm. MS (ESI-MS): *m/z* 174.0 [M+H]⁺.

Synthesis of 10a

10a was prepared following the method of **3a**, from Ru(Me₃tctpy)Cl₃ (300 mg, 0.488 mmol), 2-(4-fluorophenyl)pyridine (84.5 mg, 0.488 mmol), and triethylamine (0.25 mL) in 3:1 (v/v) ethanol-water (60 mL) to give **8a** in 49% yield (172 mg, 0.240 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.26$ (d, J = 5.6 Hz, 1H), 8.84 (s, 2H), 8.73 (d, J = 1.7 Hz, 2H), 7.99 (d, J 8.2 Hz, 1H), 7.93 (ddd, J = 8.2, 7.1, 1.3 Hz, 1H), 7.87-7.83 (m, 2H), 7.70-7.67 (m, 2H), 7.58 (dd, J = 8.7, 5.4 Hz, 1H), 7.48 (ddd, J = 7.1, 5.6, 1.2 Hz, 1H), 6.29 (ddd, J = 8.7, 7.9, 2.6 Hz, 1H), 5.06 (dd, J = 9.2, 2.6 Hz, 1H), 4.14 (s, 3H), 3.96 (s, 6H) ppm. MS (ESI-MS): m/z 705.2 [M–Cl]⁺, 722.2 [M–Cl+MeCN]⁺.

Synthesis of 10

10 was prepared following the method of **1**, from **10a** (100 mg, 0.140 mmol), ammonium thiocyanato (10.6 mg, 0.140 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **10** in 49% yield (47.6 mg, 0.0683 mmol). ¹H NMR (400 MHz, DMSO- d_6 - NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 9.78$ (d, J = 5.6 Hz, 1H), 8.81 (s, 2H), 8.65 (s, 2H), 8.19 (d, J = 7.8 Hz, 1H), 8.00 (dd, J = 7.8, 6.7 Hz, 1H), 7.70 (dd, J = 8.7, 5.5 Hz, 1H), 7.60 (dd, J = 6.7, 5.6 Hz, 1H), 7.55 (s, 4H), 6.20 (ddd, J = 9.4, 8.7, 2.6 Hz, 1H), 4.93 (dd, J = 9.6, 2.6 Hz, 1H) ppm. MS (ESI-MS): m/z 318.1 [M-NCS-3H]²⁻, 311.9 [M-NCS-CO₂H-2H+MeOH]²⁻, 297.0 [M-NCS-CO₂H-2H]²⁻.



Synthesis of 2-phenylpyrimidine

2-phenylpyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2bromopyrimidine (0.500 g, 3.15 mmol), phenylboronic acid (0.460 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 69% yield (0.341 g, 2.18 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 8.81 (dd, *J* = 5.1 Hz, 2H), 8.45-8.44 (m, 2H), 7.50-7.49 (m, 3H), 7.19 (t, *J* = 5.1 Hz, 1H) ppm. MS (ESI-MS):

m/z 157.0 [M+H]+.

Synthesis of 11a

11a was prepared following the method of **1a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2phenylpyrimidine (50.8 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **11a** in 47% yield (107 mg, 0.152 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.49$ (dd, J = 5.7, 2.3 Hz, 1H), 8.97 (dd, J = 4.7, 2.3 Hz, 1H), 8.85 (s, 2H), 8.74 (d, J = 1.5 Hz, 2H), 8.09 (dd, J = 7.6, 1.2 Hz, 1H), 7.91 (d, J = 5.9 Hz, 2H), 7.70 (dd, J = 5.9, 1.5 Hz, 2H), 7.49 (dd, J = 5.7, 4.7 Hz, 1H), 6.69 (ddd, J = 7.6, 7.0, 1.2 Hz, 1H), 6.48 (td, J = 7.6, 1.4 Hz, 1H), 5.44 (dd, J = 7.0, 1.4 Hz, 1H), 4.16 (s, 3H), 3.98 (s, 6H) ppm. MS (ESI-MS): *m/z* 664.4 [M–Cl]⁺, 705.2 [M–Cl+MeCN]⁺.

Synthesis of 11

11 was prepared following the method of **1**, from **11a** (100 mg, 0.143 mmol), ammonium thiocyanato (10.9 mg, 0.143 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **10** in 45% yield (43.7 mg, 0.0643 mmol). ¹H NMR (400 MHz, DMSO- d_6 -D₂O (9:1, v/v), Me₄Si): δ = 10.01 (dd, *J* = 5.6, 2.3 Hz, 1H), 8.94 (dd, *J* = 4.8, 2.3 Hz, 1H), 8.80 (s, 2H), 8.64 (d, *J* = 1.4 Hz, 2H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.67-7.61 (m, 3H), 7.55 (dd, *J* = 5.7, 1.4 Hz, 2H), 6.48 (dd, *J* = 7.5, 6.7 Hz, 1H), 6.31 (dd, *J* = 7.5, 7.1 Hz, 1H), 5.37 (d, *J* = 6.7 Hz, 1H) ppm. MS (ESI-MS): *m/z* 640.7 [M–NCS–3H+Na]⁻, 287.5 [M–NCS–CO₂H–2H+Na]²⁻, 286.5 [M–NCS–2(CO₂H)–H+Na]²⁻.



Synthesis of 5-fluoro-2-(4-phenylphenyl)pyridine

5-fluoro-2-(4-phenylphenyl)pyridine was prepared following the method of 2-(4-2.84 methylphenyl)pyridine, from 2-bromo-5-fluoropyridine (0.500 mmol), 4g, phenylphenylboronic acid (0.675 g, 3.41 mmol), Pd(PPh₃)₄ (0.0980 g, 0.0852 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 96% yield (0.682 g, 2.73 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 8.56 (d, J = 2.9 Hz, 1H), 8.02 (d, J = 8.6 Hz, 2H), 7.77 (dd, J = 8.8, 4.8 Hz, 1H), 7.71 (d, J = 8.6 Hz, 2H), 7.66 (dd, J = 7.3, 1.4 Hz, 2H), 7.50-7.45 (m, 3H), 7.37 (t, *J* = 7.5 Hz, 1H) ppm. MS (ESI-MS): *m/z* 249.9 [M+H]⁺.

Synthesis of 12a

A mixture of Ru(Me3tctpy)Cl3 (200 mg, 0.325 mmol), 5-fluoro-2-(4-phenylphenyl)pyridine (81.1

mg, 0.325 mmol), triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) was refluxed for 10 min by means of microwave synthesizer and allowed to cool to room temperature. The precipitated complex was collected, washed with ethanol and hot hexane and dried to give **4a** in 49% yield (125 mg, 0.158 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 10.32$ (m, 1H), 8.83 (s, 2H), 8.73 (d, J =1.5 Hz, 2H), 8.09 (dd, J = 9.1, 5.1 Hz, 1H), 7.91 (d, J = 5.9 Hz, 2H), 7.73-7.70 (m, 3H), 7.62 (d, J =8.2 Hz, 1H), 7.22-7.16 (m, 3H), 7.02 (d, J = 7.3 Hz, 2H), 6.86 (dd, J = 8.2, 1.7 Hz, 1H), 5.63 (d, J =1.7 Hz, 1H), 4.12 (s, 3H), 7.97 (s, 6H) ppm. MS (ESI-MS): m/z 757.2 [M–Cl]⁺, 798.2 [M–Cl+MeCN]⁺.

Synthesis of 12

12 was prepared following the method of **1**, from **12a** (100 mg, 0.126 mmol), ammonium thiocyanato (9.59 mg, 0.126 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **12** in 50% yield (48.5 mg, 0.0627 mmol). ¹H NMR (600 MHz, DMSO-*d*₆-D₂O (9:1, v/v), Me₄Si): δ = 10.16 (br, 1H), 8.84 (s, 2H), 8.64 (d, *J* = 1.4 Hz, 2H), 8.36 (dd, *J* = 9.1, 5.5 Hz, 1H), 8.03-8.00 (m, 1H), 7.85 (d, *J* = 8.4 Hz, 1H), 7.78 (d, *J* = 5.7 Hz, 2H), 7.65 (dd, *J* = 5.7, 1.4 Hz, 2H), 7.25 (t, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.04 (d, *J* = 7.3 Hz, 2H), 6.98 (dd, *J* = 8.4, 1.8 Hz, 1H), 5.82 (d, *J* = 1.8 Hz, 1H) ppm. MS (ESI-MS): *m/z* 355.8 [M–NCS–3H]^{2–}, 350.2 [M–NCS–CO₂H–2H+MeOH]^{2–}, 335.1 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-trifluorophenyl)pyridine

2-(4-trifluorophenyl)pyridine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyridine (1.00 g, 6.33 mmol), 4-trifluorophenylboronic acid (1.44 g, 7.59 mmol), Pd(PPh₃)₄ (0.219 g, 0.190 mmol) in THF (25 mL) and 1M Na₂CO₃ aqueous solution (15 mL) to give the desired compounds in 45% yield (0.633 g, 2.84 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.74-8.72 (m, 1H), 8.11 (d, *J* = 8.1 Hz, 2H), 7.82-7.76 (m, 2H), 7.73 (d, *J* = 8.1 Hz, 2H), 7.30 (ddd, *J* = 6.9, 4.8, 1.6 Hz, 1H) ppm. MS (ESI-MS): *m/z* 224.0 [M+H]⁺.

Synthesis of 13a

13a was prepared following the method of **4a**, from Ru(Me₃tctpy)Cl₃ (300 mg, 0.488 mmol), 2-(4-trifluorophenyl)pyridine (109 mg, 0.488 mmol), and triethylamine (0.25 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **13a** in 58% yield (219 mg, 0.285 mmol).¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 10.36 (dd, *J* = 5.7, 0.7 Hz, 1H), 8.87 (s, 2H), 8.74 (dd, *J* = 1.7, 0.7 Hz, 2H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.11 (dd, *J* = 8.9, 0.7 Hz, 1H), 8.01 (ddd, *J* = 8.9, 7.4, 1.5 Hz, 1H), 7.83 (dd, *J* = 5.8, 0.7 Hz, 2H)

2H), 7.69 (dd, *J* = 5.8, 1.7 Hz, 2H), 7.59 (ddd, *J* = 7.4, 5.7, 1.5 Hz, 1H), 6.86 (dd, *J* = 8.1, 1.1 Hz, 1H), 5.68 (d, *J* = 1.1 Hz, 1H), 4.16 (s, 3H), 3.98 (s, 6H) ppm. MS (ESI-MS): *m*/*z* 731.0 [M−Cl]⁺, 772.1 [M−Cl+MeCN]⁺.

Synthesis of 13

13 was prepared following the method of **1**, from **13a** (150 mg, 0.196 mmol), ammonium thiocyanato (14.9 mg, 0.196 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **13** in 52% yield (76.0 mg, 0.102 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 9.91$ (d, J = 5.8 Hz, 1H), 8.80 (s, 2H), 8.63 (s, 2H), 8.35 (d, J = 8.2 Hz, 1H), 8.05 (dd, J = 8.2, 7.4 Hz, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.68 (dd, J = 7.4, 5.8 Hz, 2H), 7.54-7.50 (m, 4H), 6.70 (d, J = 8.0 Hz, 1H), 5.62 (s, 1H) ppm. MS (ESI-MS): *m/z* 342.9 [M-NCS-3H]²⁻, 337.0 [M-NCS-CO₂H-2H+MeOH]²⁻, 321.3 [M-NCS-CO₂H-2H]²⁻.



Synthesis of 2-(4-methoxyphenyl)pyrimidine

2-(4-methoxyphenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 4-methoxyphenylboronic acid (0.574 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 62% yield (0.366 g, 1.97 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): δ = 8.75 (d, *J* = 5.0 Hz, 2H), 8.40 (d, *J* = 8.8 Hz, 2H), 7.12 (t, *J* = 5.0 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H) , 3.88 (s, 3H) ppm. MS (ESI-MS): *m/z* 187.0 [M+H]⁺.

Synthesis of 14a

14a was prepared following the method of **4a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4methoxyphenyl)pyrimidine (60.6 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanolwater (4 mL) to give **14a** in 39% yield (93.1 mg, 0.128 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 10.39$ (dd, J = 5.7, 2.2 Hz, 1H), 8.90 (dd, J = 4.7, 2.2 Hz, 1H), 8.84 (s, 2H), 8.73 (dd, J = 1.8, 0.7 Hz, 2H), 8.03 (d, J = 8.8 Hz, 1H), 7.92 (dd, J = 5.8, 0.7 Hz, 2H), 7.70 (dd, J = 5.8, 1.8 Hz, 2H), 7.39 (dd, J = 5.7, 4.7 Hz, 1H), 6.25 (dd, J = 8.8, 2.3 Hz, 1H), 4.95 (d, J = 2.3 Hz, 1H), 4.15 (s, 3H), 3.98 (s, 6H), 3.39 (s, 3H) ppm. MS (ESI-MS): *m/z* 693.9 [M–Cl]⁺, 734.9 [M–Cl+MeCN]⁺.

Synthesis of 14

14 was prepared following the method of 1, from 14a (100 mg, 0.137 mmol), ammonium thiocyanato (10.4 mg, 0.137 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give 13 in 24% yield (23.1 mg, 0.0326 mmol). ¹H NMR (600 MHz,

DMSO- $d_{6^{-}}$ NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.12-10.10$ (m, 1H), 8.90 (dd, J = 4.7, 2.2 Hz, 1H), 8.84 (s, 2H), 8.65 (d, J = 1.7 Hz, 2H), 7.94 (d, J = 8.6 Hz, 1H), 7.78 (d, J = 5.7 Hz, 2H), 7.65 (dd, J = 5.7, 1.7 Hz, 2H), 7.53 (dd, J = 5.9, 4.7 Hz, 1H), 6.36 (dd, J = 8.6, 2.5 Hz, 1H), 5.09 (d, J = 2.5 Hz, 1H), 3.34 (s, 3H) ppm. MS (ESI-MS): m/z 318.6 [M–NCS–CO₂H–2H+MeOH]^{2–}, 302.9 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-fluorophenyl)pyrimidine

2-(4-fluorophenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 4-fluorophenylboronic acid (0.440 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 97% yield (0.528 g, 3.04 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.79 (d, *J* = 4.8 Hz, 2H), 8.45 (dd, *J* = 9.0, 5.6 Hz, 2H), 7.20-7.15 (m, 3H) ppm. MS (ESI-MS): *m/z* 175.0 [M+H]⁺.

Synthesis of 15a

15a was prepared following the method of **3a**, from Ru(Me₃tctpy)Cl₃ (500 mg, 0.813 mmol), 2-(4-fluorophenyl)pyrimidine (142 mg, 0.813 mmol), and triethylamine (0.25 mL) in 3:1 (v/v) ethanol-water (100 mL) to give **15a** in 59% yield (341 mg, 0.480 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.44$ (dd, J = 5.7, 2.3 Hz, 1H), 8.95 (dd, J = 4.8, 2.3 Hz, 1H), 8.87 (s, 2H), 8.75 (d, J = 1.4 Hz, 2H), 8.08 (dd, J = 8.8, 5.8 Hz, 1H), 7.88 (d, J = 5.8 Hz, 2H), 7.72 (dd, J = 5.8, 1.4 Hz, 2H), 7.47 (dd, J = 5.7, 4.8 Hz, 1H), 6.37 (td, J = 8.8, 2.5 Hz, 1H), 5.13 (dd, J = 9.1, 2.1 Hz, 1H), 4.16 (s, 3H), 3.99 (s, 6H) ppm. MS (ESI-MS): m/z 682.3 [M–Cl]⁺, 723.3 [M–Cl+MeCN]⁺.

Synthesis of 15

15 was prepared following the method of 1, from 15a (150 mg, 0.209 mmol), ammonium thiocyanato (15.9 mg, 0.209 mmol), triethylamine (2 mL) and water (2 mL) in N,Ndimethylformamide (8 mL) to give 15 in 53% yield (77.3 mg, 0.111 mmol). ¹H NMR (400 MHz, DMSO- d_6 - NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 9.97$ (dd, J = 5.4, 2.2 Hz, 1H), 8.93 (dd, J =4.9, 2.2 Hz, 1H), 8.81(s, 2H), 8.65 (s, 2H), 7.92 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.66 (dd, *J* = 5.4, 4.9 Hz, 1H), 7.61 (d, J = 5.7 Hz, 2H), 7.56 (d, J = 5.7 Hz, 2H), 6.25 (td, J = 8.7, 2.5 Hz, 1H), 5.02 (dd, J = 5.7 Hz, 2H), 6.25 (td, J = 8.7, 2.5 Hz, 1H), 5.02 (dd, J = 5.7 Hz, 2H), 6.25 (td, J = 8.7, 2.5 Hz, 1H), 5.02 (dd, J = 5.7 Hz, 2H), 6.25 (td, J = 8.7, 2.5 Hz, 1H), 5.02 (dd, J = 5.7 Hz, 2H), 6.25 (td, J = 8.7, 2.5 Hz, 1H), 5.02 (dd, J = 5.7 Hz, 2H), 6.25 (td, J = 8.7, 2.5 Hz, 2H), 6.25 (td, J = 8.7, 2H), 7.5 318.1 [M-NCS-3H]²⁻ 9.5, MS (ESI-MS): 2.5 Hz, 1H) ppm. m/z312.5 [M-NCS-CO₂H-2H+MeOH]²⁻ 297.4 [M-NCS-CO₂H-2H]²⁻.



Synthesis of 5-fluoro-2-(4-trifluorophenyl)pyridine

5-fluoro-2-(4-trifluorophenyl)pyridine was prepared following method 2-(4the of 2-bromo-5-fluoropyridine 2.84 methylphenyl)pyridine, from (0.500)mmol). 4g, trifluorophenylboronic acid (0.647 g, 3.41 mmol), Pd(PPh₃)₄ (0.0985 g, 0.0852 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 88% yield (0.602 g, 2.50 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 8.58$ (d, J = 2.9 Hz, 1H), 8.06 (d, J = 8.2 Hz, 2H), 7.77 (dd, *J* = 8.8, 3.7 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 2H), 7.52 (ddd, *J* = 8.8, 7.7, 2.9 Hz, 1H) ppm. MS (ESI-MS): *m/z* 242.1 [M+H]+.

Synthesis of 16a

16a was prepared following the method of **4a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 5-fluoro-2-(4-trifluorophenyl)pyridine (78.5 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **16a** in 27% yield (70.0 mg, 0.0892 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 10.36$ (s, 1H), 8.87 (s, 2H), 8.74 (s, 2H), 8.14-8.12 (m, 1H), 7.82 (d, J = 5.9 Hz, 2H), 7.77-7.74 (m, 1H), 7.70 (d, J = 5.9 Hz, 2H), 7.63 (d, J = 7.9 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 5.70 (s, 1H), 4.17 (s, 3H), 3.98 (s, 6H) ppm. MS (ESI-MS): m/z 748.9 [M–Cl]⁺, 789.9 [M–Cl+MeCN]⁺.

Synthesis of 16

16 was prepared following the method of **1**, from **16a** (60.0 mg, 0.0765 mmol), ammonium thiocyanato (5.8 mg, 0.0765 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **16** in 33% yield (19.5 mg, 0.0255 mmol). ¹H NMR (400 MHz, DMSO- d_6^- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 9.89$ (m, 1H), 8.81 (s, 2H), 8.64 (s, 2H), 8.40 (dd, J = 9.6, 5.4 Hz, 1H), 7.97 (td, J = 8.3, 3.0 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.57-7.53 (m, 4H), 6.72 (dd, J = 8.2, 1.3 Hz, 1H), 5.63 (d, J = 1.3 Hz, 1H) ppm. MS (ESI-MS): *m/z* 351.9 [M–NCS–3H]^{2–}, 345.9 [M–NCS–CO₂H–2H+MeOH]^{2–}, 329.8 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-chlorophenyl)pyrimidine

2-(4-chlorophenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 4-chlorophenylboronic acid (0.639 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.0944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 89% yield (0.532 g, 2.79 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 8.80$ (d, J = 4.8 Hz, 2H), 8.40 (d, J = 9.0 Hz, 2H), 7.46 (d, J = 9.0 Hz, 2H), 7.2 (t, J = 4.8 Hz, 1H) ppm. MS (ESI-MS): m/z 190.9 [M+H]⁺.

Synthesis of 17a

17a was prepared following the method of **1a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4-chlorophenyl)pyrimidine (62.0 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanolwater (4 mL) to give **17a** in 46% yield (111 mg, 0.154 mmol). ¹H NMR (600 MHz, CDCl₃, Me₄Si): $\delta = 10.43$ (d, J = 5.5, 2.2 Hz, 1H), 8.95 (dd, J = 5.0, 2.2 Hz, 1H), 8.87 (s, 2H), 8.75 (d, J = 1.5 Hz, 2H), 8.00 (d, J = 8.3 Hz, 1H), 7.85 (d, J = 5.9 Hz, 2H), 7.71 (dd, J = 5.9, 1.5 Hz, 2H), 7.48 (dd, J =5.5, 5.0 Hz, 1H), 6.67 (dd, J = 8.3, 1.7 Hz, 1H), 5.41 (d, J = 1.7 Hz, 1H) ppm. MS (ESI-MS): *m/z* 698.1 [M–Cl]⁺, 739.2 [M–Cl+MeCN]⁺.

Synthesis of 17

17 was prepared following the method of **1**, from **17a** (100 mg, 0.136 mmol), ammonium thiocyanato (10.4 mg, 0.136 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **18** in 27% yield (26.6 mg, 0.0373 mmol). ¹H NMR (600 MHz, DMSO- d_6 - NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 10.16 (d, *J* = 4.8 Hz, 1H), 9.01 (dd, *J* = 4.8, 2.2 Hz, 1H), 8.91 (s, 2H), 8.71 (s, 2H), 7.99 (d, *J* = 8.4 Hz, 1H), 7.81 (d, *J* = 5.5 Hz, 2H), 7.69-7.67 (m, 3H), 6.82 (d, *J* = 8.4 Hz, 1H), 5.58 (s, 1H) ppm. MS (ESI-MS): *m*/*z* 325.2 [M–NCS–2H]^{2–}, 304.6 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(4-trifluorophenyl)pyrimidine

2-(4-trifluorophenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 4-trifluorophenylboronic acid (0.717 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.0944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 83% yield (0.588 g, 2.63 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 8.85$ (d, J = 4.8 Hz, 2H), 8.57 (d, J = 8.1 Hz, 2H), 7.75 (d, J = 8.1 Hz, 2H), 7.26 (t, J = 4.8 Hz, 1H) ppm. MS (ESI-MS): m/z 242.0 [M+H]⁺.

Synthesis of 18a

18a was prepared following the method of **1a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(4-trifluoromethylphenyl)pyrimidine (72.9 mg, 0.325 mmol), and triethylamine (0.1 mL) in 3:1 (v/v) ethanol-water (4 mL) to give **18a** in 45% yield (113 mg, 0.146 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 10.52$ (dd, J = 5.7, 2.3 Hz, 1H), 9.01 (dd, J = 4.8, 2.3 Hz, 1H), 8.88 (s, 2H), 8.76 (d, J = 1.4 Hz, 2H), 8.17 (d, J = 8.3 Hz, 1H), 7.84 (d, J = 5.8 Hz, 2H), 7.71 (dd, J = 5.8, 1.4 Hz, 2H), 7.54 (dd, J = 5.7, 4.8 Hz, 1H), 6.91 (d, J = 8.3 Hz, 1H), 5.74 (s, 1H), 4.17 (s, 3H), 3.99 (s, 6H) ppm. MS (ESI-MS): m/z 731.9 [M–Cl]⁺, 772.9 [M–Cl+MeCN]⁺.

Synthesis of 18

18 was prepared following the method of **1**, from **18a** (150 mg, 0.196 mmol), ammonium thiocyanato (14.9 mg, 0.196 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (8 mL) to give **18** in 52% yield (76.0 mg, 0.102 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.07$ (dd, J = 5.5, 2.2 Hz, 1H), 9.01 (dd, J = 4.9, 2.2 Hz, 1H), 8.80 (s, 2H), 8.63 (d, J = 1.5 Hz, 2H), 8.03 (d, J = 8.0 Hz, 2H), 7.75 (dd, J = 5.5, 4.9 Hz, 1H), 7.58 (d, J = 5.8 Hz, 2H), 7.54 (dd, J = 5.8, 1.5 Hz, 2H), 6.75 (s, 1H), 5.72 (s, 1H) ppm. MS (ESI-MS): m/z 710.3 [M–NCS–3H+Na]⁻, 321.5 [M–NCS–CO₂H–2H+Na]^{2–}, 299.4 [M–NCS–2(CO₂H)–H+Na]^{2–}.



Synthesis of 2-(2-trifluorophenyl)pyrimidine

2-(2-trifluorophenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 2-trifluorophenylboronic acid (0.717 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.0944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 84% yield (0.594 g, 2.65 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): $\delta = 8.86$ (d, J = 5.0 Hz, 1H), 7.80 (d, J = 7.7 Hz, 1H), 7.72 (d, J = 7.7 Hz, 1H), 7.65 (t, J = 7.7 Hz, 1H), 7.58 (t, J = 7.7 Hz, 1H), 7.31 (t, J = 5.0 Hz, 1H) ppm. MS (ESI-MS): m/z 225.0 [M+H]⁺.

Synthesis of 19a

A mixture of Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(2-trifluorophenyl)pyrimidine (0.365 g, 1.63 mmol), triethylamine (0.2 mL) in 3:1 (v/v) *N*,*N*-dimethylformamide-water (4 mL) was refluxed for 1 h by means of microwave synthesizer. The mixture was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The resulting solid was washed with hexane to remove unreacted 2-(2-trifluorophenyl)pyrimidine. Then, the solid was purified by column chromatography using Sephadex LH-20 as a column support and 5 mM TBA(OH) in ethanol/water (1:1, v/v) as an eluent. The solvent of collected main band was removed by rotary evaporation. The isolated solid was dissolved in water (10 mL) and a precipitate was appeared by the addition of 1 M HCl. The precipitate was filtrated, washed with water, and dried to give **19a** in 35% yield (82.1 mg, 0.113 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.17$ (dd, *J* = 5.5, 2.2 Hz, 1H), 8.96 (dd, *J* = 5.1, 2.2 Hz, 1H), 8.82 (s, 2H), 8.64 (s, 2H), 7.67 (dd, *J* = 5.5, 5.1 Hz, 1H), 7.55-7.51 (m, 4H), 6.86 (d, *J* = 7.7 Hz, 1H), 6.42 (t, *J* = 7.7 Hz, 1H), 5.69 (t, *J* = 7.7 Hz, 1H) ppm. MS (ESI-MS): *m/z* 337.7 [M-Cl-CO₂H-2H+MeOH]²⁻, 322.3 [M-Cl-CO₂H-2H]²⁻.

Synthesis of 19

19a (40.5 mg, 0.0559 mmol) in *N*,*N*-dimethylformamide (4 mL) and 1 mL of an aqueous solution of ammonium thiocyanato (8.5 mg, 0.112 mmol) were refluxed for 10 min by means of microwave synthesizer. The mixture was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The product was purified by column chromatography using Sephadex LH-20 as a column support and 5 mM TBA(OH) in ethanol/water (1:1, v/v) as an eluent. The solvent of collected main band was removed by rotary evaporation. The isolated solid was dissolved in water (10 mL) and a precipitate was appeared by the addition of 0.5 M HCl. The precipitate was filtrated,

washed with water, and dried to give **19** in 72% yield (30.2 mg, 0.0404 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 10.17-10.15 (m, 1H), 8.97-8.95 (m, 1H), 8.81 (s, 2H), 8.64 (s, 2H), 7.67(dd, *J* = 5.5, 4.8 Hz, 1H), 7.55-7.51 (m, 4H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.42 (t, *J* = 7.6 Hz, 1H), 5.69 (d, *J* = 7.6 Hz, 1H) ppm. MS (ESI-MS): *m/z* 343.5 [M–NCS–3H]^{2–}, 338.5 [M–NCS–CO₂H–2H+MeOH]^{2–}, 322.3 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 2-(3-trifluorophenyl)pyrimidine

2-(3-trifluorophenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 3-trifluorophenylboronic acid (0.717 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.0944 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 78% yield (0.552 g, 2.47 mmol). ¹H NMR (500 MHz, CDCl₃, Me₄Si): $\delta = 8.84$ (d, J = 4.9 Hz, 2H), 8.76 (s, 1H), 8.65 (d, J = 7.8 Hz, 1H), 7.74 (d, J = 7.8 Hz, 1H), 7.62 (t, J = 7.8 Hz, 1H), 7.25 (t, J = 4.9 Hz, 1H) ppm. MS (ESI-MS): m/z 242.0 [M+H]⁺.

Synthesis of 20a

20a was prepared following the method of **19a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 2-(2-trifluoromethylphenyl)pyrimidine (365 mg, 1.63 mmol), and triethylamine (0.6 mL) in 3:1 (v/v) *N*,*N*-dimethylformamide-water (4 mL) to give **20a** in 28% yield (65.6 mg, 0.0905 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.03$ (dd, J = 5.7, 2.2 Hz, 1H), 8.99 (dd, J = 4.8, 2.2 Hz, 1H), 8.80 (s, 2H), 8.64 (d, J = 1.2 Hz, 2H), 8.07 (d, J = 1.8 Hz, 2H), 7.74 (dd, J = 5.7, 4.8 Hz, 1H), 7.58 (d, J = 5.8 Hz, 2H), 7.55 (dd, J = 5.8, 1.2 Hz, 2H), 6.58 (dd, J = 8.0, 1.8 Hz, 1H), 5.70 (d, J = 8.0 Hz, 1H) ppm. MS (ESI-MS): *m/z* 343.5 [M-Cl-3H]²⁻, 337.5 [M-Cl-CO₂H-2H+MeOH]²⁻, 322.5 [M-Cl-CO₂H-2H]²⁻, 299.9 [M-Cl-2CO₂H-H]²⁻.

Synthesis of 20

20a (39.4 mg, 0.0544 mmol) in *N*,*N*-dimethylformamide (4 mL) and 1 mL of an aqueous solution of ammonium thiocyanato (41.4 mg, 0.544 mmol) were refluxed for 10 min by means of microwave synthesizer. The mixture was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The product was purified by column chromatography using Sephadex LH-20 as a column support and 5 mM TBA(OH) in ethanol/water (1:1, v/v) as an eluent. The solvent of collected main band was removed by rotary evaporation. The isolated solid was dissolved in water (10 mL) and a precipitate was appeared by the addition of 0.5 M HCl. The precipitate was filtrated, washed with water, and dried to give **20** in 80% yield (33.1 mg, 0.0442 mmol). ¹H NMR (400 MHz,

DMSO- $d_{6^{-}}$ NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.05$ (dd, J = 5.7 Hz, 1H), 8.99 (dd, J = 4.8 Hz, 1H), 8.79 (s, 2H), 8.63 (s, 2H), 8.07 (s, 1H), 7.74 (dd, J = 5.7, 4.8 Hz, 1H), 7.58-7.53 (m, 4H), 6.57 (dd, J = 8.0, 1.7 Hz, 1H), 5.70 (d, J = 8.0 Hz, 1H) ppm. MS (ESI-MS): m/z 343.4 [M–NCS–3H]^{2–}, 337.4 [M–NCS–CO₂H–2H+MeOH]^{2–}, 322.4 [M–NCS–CO₂H–2H]^{2–}, 299.7 [M–NCS–2CO₂H–H]^{2–}.



Synthesis of 2-(2,4-bistrifluoromethylphenyl)pyrimidine

2-(2,4-bistrifluoromethylphenyl)pyrimidine was prepared following the method of 2-(4methylphenyl)pyridine, from 2-bromopyrimidine (2.00 g, 12.6 mmol), 2,4bistrifluoromethylphenylboronic acid (3.89 g, 15.1 mmol), Pd(PPh₃)₄ (0.436 g, 0.377 mmol) in THF (30 mL) and 1M Na₂CO₃ aqueous solution (20 mL) to give the desired compounds in 61% yield (2.24 g, 7.66 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.89 (d, *J* = 4.9 Hz, 1H), 8.07 (s, 1H), 7.94-7.89 (m, 2H), 7.38 (t, *J* = 4.9 Hz, 1H) ppm. MS (ESI-MS): *m/z* 292.9 [M +H]⁺.

Synthesis of 21a

21a was prepared following the method of **19a**, from Ru(Me₃tctpy)Cl₃ (300 mg, 0.488 mmol), 2-(2,4-bistrifluoromethylphenyl)pyrimidine (0.713 g, 2.44 mmol), triethylamine (0.3 mL) in 3:1 (v/v) *N*,*N*-dimethylformamide-water (4 mL) to give **21a** in 38% yield (147 mg, 0.185 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.16$ (dd, J = 5.7, 2.3 Hz, 1H), 9.03 (dd, J = 4.8, 2.3 Hz, 1H), 8.85 (s, 2H), 8.66 (d, J = 1.2 Hz, 2H), 7.77 (dd, J = 5.7, 4.8 Hz, 1H), 7.56 (dd, J = J 5.7, 1.2 Hz, 2H), 7.53 (d, J = 5.7 Hz, 2H), 7.04 (s, 1H), 6.04 (s, 1H) ppm. MS (ESI-MS): *m/z* 777.3 [M-Cl-3H+Na]⁻, 355.4 [M-Cl-CO₂H-3H+Na]²⁻, 333.4 [M-Cl-2(CO₂H)-H+Na]²⁻. **Synthesis of 21**

21 was prepared following the method of **20**, from **21a** (60.0 mg, 0.0757 mmol) and ammonium thiocyanato (57.6 mg, 0.757 mmol) in 4:1 (v/v) *N*,*N*-dimethylformamide-water (5 mL) to give **21** in 66% yield (40.5 mg, 0.0500 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.21$ (dd, J = 5.6, 2.3 Hz, 1H), 9.03 (dd, J = 4.7, 2.3 Hz, 1H), 8.83 (s, 2H), 8.64 (d, J = 1.5 Hz, 2H), 7.77 (dd, J = 5.6, 4.7 Hz, 1H), 7.55 (dd, J = 5.7, 1.5 Hz, 2H), 7.50 (d, J = 5.7 Hz, 2H), 7.02 (s, 1H), 6.03 (s, 1H) ppm. MS (ESI-MS): *m*/z 777.8 [M–NCS–3H+Na]⁻, 355.5 [M–NCS–CO₂H–2H+Na]²⁻, 333.4 [M–NCS–2(CO₂H)–H+Na]²⁻.



Synthesis of 4-trifluoromethyl-2-(4-(trifluoromethyl)phenyl)pyrimidine

4-trifluoromethyl-2-(4-(trifluoromethyl)phenyl)pyrimidine was prepared following the method of 2-(4-methylphenyl)pyridine, from 2-chloro-4-trifluoromethylpyrimidine (0.500 g, 2.74 mmol), 4trifluoromethylphenylboronic acid (0.624 g, 3.29 mmol), Pd(PPh₃)₄ (0.0950 g, 0.0822 mmol) in THF (20 mL) and 1M Na₂CO₃ aqueous solution (10 mL) to give the desired compounds in 92% yield (0.738 g, 2.52 mmol). ¹H NMR (500 MHz, CDCl₃, Me₄Si): δ = 9.09 (d, *J* = 5.0 Hz, 1H), 8.64 (d, *J* = 8.9 Hz, 2H), 7.77 (d, *J* = 8.9 Hz, 2H), 7.59 (d, *J* = 5.0 Hz, 2H) ppm. MS (ESI-MS): *m/z* 291.0 [M–H]⁺, 323.0 [M–H+MeOH]⁺.

Synthesis of 22a

22a was prepared following the method of **19a**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), 4-(trifluoromethyl)-2-(4-(trifluoromethyl)phenyl)pyrimidine (0.475 g, 3.25 mmol), triethylamine (0.2 mL) in 3:1 (v/v) *N*,*N*-dimethylformamide-water (4 mL) to give **22a** in 15% yield (39.8 mg, 0.0502 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.36$ (d, *J* = 6.0 Hz, 1H), 8.83 (s, 2H), 8.65 (d, *J* = 1.6 Hz, 2H), 8.12 (d, *J* = 6.0 Hz, 1H), 8.07 (d, *J* = 8.3 Hz, 1H), 7.63 (d, *J* = 5.7 Hz, 2H), 7.53 (dd, *J* = 5.7, 1.6 Hz, 2H), 6.82 (d, *J* = 8.3 Hz, 1H), 5.86 (s, 1H) ppm. MS (ESI-MS): *m/z* 377.6 [M-Cl-2H]²⁻, 355.3 [M-Cl-CO₂H-2H]²⁻.

Synthesis of 22

22 was prepared following the method of 20, from 21a (35.2 mg, 0.0444 mmol) and ammonium thiocyanato (33.8 mg, 0.444 mmol) in 4:1 (v/v) N,N-dimethylformamide-water (5 mL) to give 22 in 74% yield (26.8 mg, 0.0329 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me_4Si): $\delta = 10.34$ (d, J = 5.8 Hz, 1H), 8.83 (s, 2H), 8.65 (d, J = 1.3 Hz, 2H), 8.12 (d, J = 5.8 Hz, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.63 (d, J = 5.8 Hz, 2H), 7.53 (dd, J = 5.8, 1.3 Hz, 2H), 6.82 (d, J = 8.1 Hz, 377.7 [M-NCS-3H]²⁻ 1H), 5.87 (s, 1H) ppm. MS (ESI-MS): m/z370.5 [M-NCS-CO₂H-2H+MeOH]²⁻ 355.5 [M-NCS-CO₂H-2H]²⁻.



Synthesis of 2-(3,5-bistrifluoromethylphenyl)pyrimidine

2-(3,5-bistrifluoromethylphenyl)pyrimidine was prepared following the method of 2-(4methylphenyl)pyridine, from 2-bromopyrimidine (0.500 g, 3.15 mmol), 2,4bistrifluoromethylphenylboronic acid (0.973 g, 3.77 mmol), Pd(PPh₃)₄ (0.109 g, 0.0944 mmol) in THF (10 mL) and 1M Na₂CO₃ aqueous solution (6 mL) to give the desired compounds in 73% yield (0.67 g, 2.30 mmol). ¹H NMR (400 MHz, CDCl₃, Me₄Si): δ = 8.95 (2H, s), 8.86 (d, *J* = 4.8 Hz, 2H), 7.98 (s, 1H), 7.31 (t, *J* = 4.8 Hz, 1H) ppm. MS (ESI-MS): *m/z* 292.9 [M+H]⁺, 334.0 [M+H+MeCN]⁺.

Synthesis of 23a

23a was prepared following the method of **19a**, from Ru(Me₃tctpy)Cl₃ (300 mg, 0.488 mmol), 2-(3,5-bistrifluoromethylphenyl)pyrimidine (0.713 g, 2.44 mmol), triethylamine (0.9 mL) in 3:1 (v/v) *N*,*N*-dimethylformamide-water (4 mL) to give **23a** in 22% yield (83.2 mg, 0.105 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): δ = 9.98 (dd, *J* = 5.7, 2.2 Hz, 1H), 9.06 (dd, *J* = 4.7, 2.2 Hz, 1H), 8.70 (s, 2H), 8.58 (s, 3H), 7.68 (dd, *J* = 5.7, 4.8 Hz, 1H), 7.44 (dd, *J* = 5.7, 1.7 Hz, 2H), 7.35 (d, *J* = 5.7 Hz, 2H), 7.11 (d, *J* = 1.5 Hz, 1H) ppm. MS (ESI-MS): *m/z* 377.4 [M-Cl-3H]²⁻, 371.3 [M-Cl-CO₂H-2H+MeOH]²⁻, 356.6 [M-Cl-CO₂H-2H]²⁻.

Synthesis of 23

23 was prepared following the method of **20**, from **23a** (62.7 mg, 0.0791 mmol) and ammonium thiocyanato (60.2 mg, 0.791 mmol) in 4:1 (v/v) *N*,*N*-dimethylformamide-water (5 mL) to give **23** in 51% yield (32.8 mg, 0.0402 mmol). ¹H NMR (400 MHz, DMSO-*d*₆- NaOH saturated D₂O (9:1, v/v), Me₄Si): $\delta = 10.00$ (dd, J = 5.7, 2.2 Hz, 1H), 9.05 (dd, J = 4.7, 2.2 Hz, 1H), 8.70 (s, 2H), 8.57 (s, 3H), 7.68 (dd, J = 5.7, 4.7 Hz, 1H), 7.43 (dd, J = 5.8, 1.4 Hz, 2H), 7.33 (d, J = 5.8 Hz, 2H), 7.11 (s, 1H) ppm. MS (ESI-MS): *m/z* 377.7 [M–NCS–3H]^{2–}, 370.0 [M–NCS–CO₂H–2H+MeOH]^{2–}, 355.3 [M–NCS–CO₂H–2H]^{2–}.



Synthesis of 24

Ru(Me₃tctpy)(4-imidazolecarboxylato)Cl was prepared by the addition of 4-imidazolecarboxylic acid (54.7 mg, 0.488 mmol), LiCl (212 mg, 4.88 mmol) and 0.3 mL of triethylamine to a solution of Ru(Me₃tctpy)Cl₃ (300 mg, 0.488 mmol) in 60 mL ethanol. The reaction mixture was refluxed for 5 h, and the solution was concentrated to 20 mL with a rotary evaporator. The precipitated complex was collected, washed with ethanol and dried to give the desired compounds in 70 % yield (225 mg, The synthesis of **24** then proceeded as follows: 0.342 mmol). Ru(Me₃tctpy)(4imidazolecarboxylato)Cl (100 mg, 0.153 mmol) in 5 mL of N,N-dimethylformamide and 1 mL of an aqueous solution of ammonium thiocyanato (11.6 mg, 0.153 mmol) were refluxed for 5 h. After cooling to room temperature, 2 mL of triethylamine and 1 mL of water were added, and the reaction mixture was refluxed for another 20 h to hydrolyze the ester group on the 2,2':6',2"-terpyridine ligand. The mixture was allowed to cool to room temperature, and the solvent was removed by rotary evaporation. The mixture was purified by column chromatography using Sephadex LH-20 as a column support and 5 mM TBA(OH) in ethanol/water (1:1, v/v) as an eluent. The solvent of collected main band was removed by rotary evaporation. The isolated solid was dissolved in minimal amount of water and was purified by column chromatography using Sephadex LH-20 as a column support and 5 mM TBA(OH) in water as an eluent. The solvent of collected band was removed by rotary evaporation. The isolated solid was dissolved in water (10 mL) and a precipitate was appeared by the addition of 0.1 M HCl. The precipitate was filtrated and dried to give 24 in 10% yield (9.4 mg, 0.0147 mmol). ¹H NMR (400 MHz, D₂O, 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt): $\delta = 8.83$ (s, 2H), 8.74 (d, J = 1.6 Hz, 2H), 8.33 (s, 1H), 7.11 (d, J = 5.7 Hz, 2H), 7.87 (s, 1H), 7.81 (dd, J = 5.7, 1.6 Hz, 2H) ppm. MS (ESI-MS): m/z 210.8 [M-3H]³⁻.



Synthesis of 25

 $Ru(Me_3tctpy)$ (4-methoxypyridinecarboxylato)Cl was prepared following the method of **24**, from $Ru(Me_3tctpy)Cl_3$ (300 mg, 0.488 mmol), 4-methoxypicolinic acid (74.7 mg, 0.488 mmol), LiCl (212 mg, 4.88 mmol), and triethylamine (0.3 mL) in ethanol (60 mL) to give the desired compounds in 76% yield (258 mg, 0.371 mmol). **25** was prepared from $Ru(Me_3tctpy)$ (4-methoxypyridinecarboxylato)Cl (200 mg, 0.287 mmol), ammonium thiocyanato (21.9 mg, 0.287

mmol), triethylamine (4 mL) and water (2 mL) in *N*,*N*-dimethylformamide (10 mL) to give **25** in 16% yield (40.4 mg, 0.0459 mmol). ¹H NMR (400 MHz, D₂O, 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt): $\delta = 9.32$ (d, J = 6.3 Hz, 1H), 8.87 (s, 2H), 8.78 (d, J = 1.5 Hz, 2H), 8.09 (d, J = 5.7 Hz, 2H), 7.83 (d, J = 2.9 Hz, 1H), 7.78 (dd, J = 5.7, 1.5 Hz, 2H), 7.67 (dd, J = 6.3, 2.9 Hz, 1H), 4.14 (s, 3H) ppm. MS (ESI-MS): m/z 224.6 [M-3H]³⁻, 235.2 [M-3H+MeOH]³⁻.



Synthesis of 26

Ru(Me₃tctpy)(3-isoquinolinecarboxylato)Cl was prepared following the method of **24**, from Ru(Me₃tctpy)Cl₃ (100 mg, 0.163 mmol), 3-isoquinolinecarboxylic acid (28.2 mg, 0.163 mmol), LiCl (70.6 mg, 1.63 mmol), and triethylamine (0.1 mL) in ethanol (15 mL) to give the desired compounds in 64% yield (74.1 mg, 0.103 mmol). **26** was prepared from Ru(Me₃tctpy)(3-isoquinolinecarboxylato)Cl (74.1 mg, 0.103 mmol), ammonium thiocyanato (7.88 mg, 0.103 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (3 mL) to give **26** in 39% yield (35.8 mg, 0.0405 mmol). ¹H NMR (400 MHz, D₂O, 3-(trimethylsilyl)propionic-2,2,3,3-*d*₄ acid sodium salt): $\delta = 10.12$ (s, 1H), 8.90 (s, 2H), 8.75 (d, *J* = 1.6 Hz, 2H), 8.71 (s, 1H), 8.37 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.0 Hz, 1H), 8.05-7.94 (m, 5H), 7.64 (dd, *J* = 5.7 Hz, 2H) ppm. MS (ESI-MS): *m/z* 231.3 [M–3H]^{3–}, 242.0 [M–3H+MeOH]^{3–}.



Synthesis of 27

Ru(Me₃tctpy)(3-methylpyridinecarboxylato)Cl was prepared following the method of 24, from Ru(Me₃tctpy)Cl₃ (300 mg, 0.488 mmol), 4-methoxypicolinic acid (66.9 mg, 0.488 mmol), LiCl (212 mg, 4.88 mmol), and triethylamine (0.3 mL) in ethanol (60 mL) to give the desired compounds in 86% vield (283 mg, 0.418 mmol). 27 was prepared from Ru(Me₃tctpy)(3methylpyridinecarboxylato)Cl (250 mg, 0.368 mmol), ammonium thiocyanato (28.0 mg, 0.368 mmol), triethylamine (4 mL) and water (2 mL) in N,N-dimethylformamide (10 mL) to give 27 in 11% yield (27.2 mg, 0.0391 mmol). ¹H NMR (400 MHz, D₂O, 3-(trimethylsilyl)propionic-2,2,3,3- d_4 acid sodium salt): $\delta = 9.45$ (d, J = 4.9 Hz, 1H), 8.87 (s, 2H), 8.77 (d, J = 1.5 Hz, 2H), 8.09 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 5.7 Hz, 2H), 7.95 (dd, J = 7.6, 4.9 Hz, 1H), 7.76 (dd, J = 5.7, 1.5 Hz, 2H), 2.76 (s, 3H) ppm. MS (ESI-MS): m/z 219.2 [M-3H]³⁻, 229.9 [M-3H+MeOH]³⁻.



Synthesis of 28

Ru(Me₃tctpy)(2-quinolinecarboxylato)Cl was prepared following the method of **24**, from Ru(Me₃tctpy)Cl₃ (500 mg, 0.813 mmol), 2-quinolinecarboxylic acid (141 mg, 0.813 mmol), LiCl (345 mg, 8.13 mmol), and triethylamine (0.4 mL) in ethanol (75 mL) to give the desired compounds in 45% yield (261 mg, 0.364 mmol). **28** was prepared from Ru(Me₃tctpy)(2-quinolinecarboxylato)Cl (200 mg, 0.279 mmol), ammonium thiocyanato (21.3 mg, 0.279 mmol), triethylamine (4 mL) and water (4 mL) in *N*,*N*-dimethylformamide (5 mL) to give **28** in 22% yield (42.8 mg, 0.0613 mmol). ¹H NMR (400 MHz, DMSO-*d*₆, Me₄Si): δ = 9.34 (d, *J* = 7.2 Hz, 1H), 9.14 (s, 2H), 9.05 (s, 2H), 8.86 (d, *J* = 8.0 Hz, 1H), 8.41-8.39 (m, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.97-7.95 (m, 2H), 7.90 (d, *J* = 6.0 Hz, 2H) ppm. MS (ESI-MS): *m/z* 231.4 [M–3H]^{3–}.



Synthesis of 29 and 30

Ru(Me₃tctpy)(2-pyridinecarboxylato)Cl was prepared following the method of **30**, from Ru(Me₃tctpy)Cl₃ (200 mg, 0.325 mmol), picolinic acid (40.0 mg, 0.325 mmol), LiCl (138 mg, 3.25 mmol), and triethylamine (0.15 mL) in ethanol (30 mL) to give the desired compounds in 81% yield (176 mg, 0.265 mmol). **29** and **30** were prepared rom Ru(Me₃tctpy)(2-pyridinecarboxylato)Cl (100 mg, 0.150 mmol), ammonium thiocyanato (11.2 mg, 0.150 mmol), triethylamine (2 mL) and water (2 mL) in *N*,*N*-dimethylformamide (5 mL) to give **29** in 9% yield (8.8 mg, 0.0136 mmol) and **30** in 32% yield (30.4 mg, 0.0471 mmol). Data of **29** is as follows: ¹H NMR (400 MHz, DMSO-*d*₆, Me₄Si): δ = 9.37 (dd, *J* = 5.4, 1.6 Hz, 1H), 9.22 (s, 2H), 9.14 (d, *J* = 1.4 Hz, 2H), 8.34 (ddd, *J* = 7.8, 7.6, 1.6 Hz, 1H), 8.23 (ddd, *J* = 7.6, 5.4, 1.6 Hz, 1H), 8.13 (dd, *J* = 7.8, 1.6 Hz, 1H), 8.08 (d, *J* = 5.8 Hz, 2H), 7.96 (dd, *J* = 5.8, 1.4 Hz, 2H) ppm. MS (ESI-MS): *m/z* 214.7 [M- 3H]³⁻. Data of **30** is as

follows: ¹H NMR (400 MHz, DMSO-*d*₆, Me₄Si): $\delta = 9.16$ (s, 2H), 9.07 (s, 2H), 8.51 (d, J = 5.7 Hz, 2H), 8.04 (d, J = 5.7 Hz, 2H), 7.88 (d, J = 7.8 Hz, 1H), 7.65 (dd, J = 7.8, 7.4 Hz, 1H), 6.96 (dd, J = 7.4, 5.4 Hz, 1H), 6.74 (d, J = 5.4 Hz, 1H) ppm. MS (ESI-MS): *m*/*z* 214.6 [M–3H]^{3–}, 225.2 [M–3H+MeOH]^{3–}.



Fig. S1 Normarized differential pulse voltammograms of ruthenium complexes.









Fig. S2 Absorption spectra of (a) 1-6, (b) 7-12, (c) 13-18, (d) 19-24, (e) 25-30, (f) N719 and N749. Table S1 Electrochemical data of ruthenium complexes

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Complexes	E_{HOMO} /V vs. SCE	$E_{0-0} a/eV$	E_{LUMO} b/V vs. SCE
1	0.33	1.32	-0.99
2	0.33	1.36	-1.03
3	0.37	1.41	-1.04
4	0.37	1.27	-1.04
5	0.38	1.44	-0.90
6	0.39	1.36	-1.06
7	0.39	1.39	-0.97
8	0.40	1.44	-1.00
9	0.40	1.32	-0.92
10	0.42	1.43	-1.01
11	0.42	1.35	-0.93
12	0.42	1.29	-0.87

13	0.43	1.41	-0.98
14	0.43	1.41	-0.98
15	0.48	1.44	-0.96
16	0.48	1.48	-1.00
17	0.48	1.32	-0.84
18	0.49	1.46	-0.97
19	0.49	1.44	-0.95
20	0.51	1.46	-0.95
21	0.52	1.49	-0.97
22	0.55	1.51	-0.96
23	0.56	1.61	-1.05
24	0.61	1.60	-0.99
25	0.65	1.55	-0.90
26	0.68	1.65	-0.97
27	0.69	1.59	-0.90
28	0.71	1.59	-0.88
29	0.73	1.68	-0.95
30	0.77	1.65	-0.88
N719	0.85	1.91	-1.06
N749	0.66	1.61	-0.95

^{*a*} Excitation energies were estimated using the absorption thresholds^[A-C]. ^b E_{LUMO} was calculated from the equality $E_{LUMO} = E_{HOMO} - E_{0-0}$. E_{LUMO} of these complexes are higher than the conduction band edge of TiO₂ (-0.7 V vs. SCE).





(d)

S28



Fig. S3 Photocurrent action spectra of DSSCs sensitized with (a) 1-6, (b) 7-12, (c) 13-18, (d) 19-24, (e) 25-30, (f) N719 and N749.



Fig. S4 Maximum of IPCE values of DSSCs as a function of E_{HOMO} of complexes **1-23**. Introduction of electron donating group (\blacksquare), electron withdrawing group(s) (\blacklozenge), and H or both groups (\circ).

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