Supporting Information to

Use of a Fluorinated Probe to Quantitatively Monitor Amino Acid Binding Preferences of Ruthenium(II) Arene Complexes

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Preparation and characterisation of bipyridine ligands and ruthenium complexes

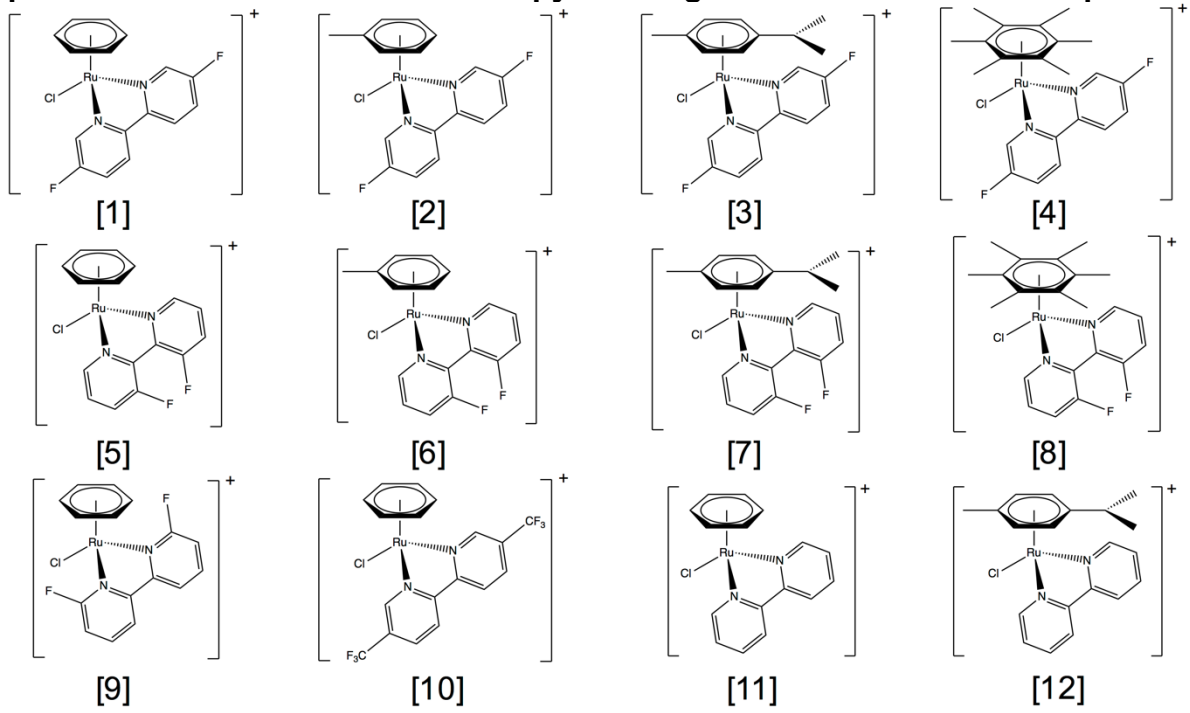


Figure S1. Structures of $Ru^{II}(\eta_6$-arene)(complexes] [1] – [12].

Synthesis of A – 3,3'-difluoro-2,2'-bipyridine

The ligand 2-bromo-3-fluoropyridine (1.00 g, 5.68 mmol), $Pd^{II}(OAc)_2$ (31.8 mg, 0.14 mmol), K_2CO_3 (0.78 g, 5.68 mmol) and poly(ethylene glycol) (Mw 4000, 5.0 g) were combined in a nitrogen purged flask. This mixture was heated to 120 °C and the temperature maintained for 48 hours with stirring. The solution was cooled to 80 °C and 15 mL of warm water was added. Once at room temperature a further 10 mL of water was added and the suspension exhaustively extracted with ethyl acetate. The combined extracts were washed with saturated aqueous $Na_2S_2O_3$ and three times with brine. The organic layer was then dried over $MgSO_4$ and the solvent removed *in vacuo*. The solid was then purified via sublimation to a white needle crystalline solid. Yield 174 mg (32%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ (ppm) 8.61 (d, $^3J_{HH}$ = 5.0 Hz, 2H, 6,6'-position), 7.54 (m, 2H, 4,4'-position,), 7.52 (m, 2H, 5,5'-position).^{13}C{^{1}H} NMR (100.57 MHz, $CDCl_3$): δ (ppm) 157.9 (dd, $^2J_{CF}$ = 265.1 Hz, $^4J_{CF}$ = 3.8 Hz, 3,3'-position), 146.1 (overlapping doublets, $^4J_{CF}$ = 2.7 Hz, $^4J_{CF}$ = Hz, 6,6'-positions), 142.3 (dd, $^2J_{CF}$ = 8.3 Hz, $^3J_{CF}$ = 2.3 Hz, 2,2'-position), 125.5 (overlapping doublets, $^3J_{CF}$ = 2.6 Hz, $^3J_{CF}$ = 2.1 Hz, 5,5'-positions), 124.2 (d, $^2J_{CF}$ = 6.7 Hz, 4,4'-position). 124.1 (d, $^2J_{CF}$ = 6.7 Hz, 4,4'-position). ^{19}F{^{1}H} NMR (376.50 MHz, $CDCl_3$): δ (ppm) -121.9 (s).

Synthesis of B – 5,5'-difluoro-2,2'-bipyridine

This product was prepared and purified in a manner similar to **A**, but using the starting pyridine 2-bromo-5-fluoropyridine instead. Yield 298 mg (55%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ (ppm) 8.50 (d, $^4J_{HH}$ = 2.8 Hz, 2H, 6,6'-position), 8.38 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HF}$ = 4.5 Hz, 2H, 3,3'-position), 7.52 (m, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.8 Hz, 2H, 4,4'-position). ^{13}C{^{1}H} NMR (100.57 MHz, $CDCl_3$): δ (ppm) 160.0 (d, $^1J_{CF}$ = 258 Hz, 5,5'-position), 151.7 (d, $^4J_{CF}$ = 4 Hz, 2,2'-position), 137.4 (d, $^2J_{CF}$ = 24 Hz, 6,6'-position), 123.8 (d, $^2J_{CF}$ = 18 Hz, 4,4'-position), 122.3 (d, $^3J_{CF}$ = 5 Hz, 3,3'-position). ^{19}F{^{1}H} NMR (376.50 MHz, $CDCl_3$): δ (ppm) -127.4 (s).

Synthesis of C – 6,6'-difluoro-2,2'-bipyridine

This product was prepared and purified in a manner similar to **A**, but using the starting pyridine 2-bromo-6-fluoropyridine instead. This product proved harder to isolate due to its low melting point. Yield 27 mg (5%).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ (ppm) 8.26 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 2.4 Hz, 2H, 3,3'-position), 7.92 (overlapping dd, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 7.8 Hz, 2H, 4,4'-position), 6.97 (dd, $^{3}J_{HH}$ = 7.8 Hz, $^{4}J_{HH}$ = 2.4 Hz, 2H, 5,5'-position). Lack of sample restricted analysis to ^{1}H and ^{19}F{^{1}H} NMR. ^{19}F{^{1}H} NMR (376.50 MHz, $CDCl_3$): δ (ppm) -67.1 (s).

Synthesis of D – 5,5'-bis(trifluoromethyl)-2,2'-bipyridine

This product was prepared and purified in a manner similar to **A**, but using the starting pyridine 2-bromo-5-(trifluoromethyl)pyridine instead. Yield 261 mg (36%).

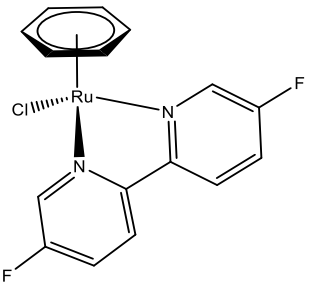
^{1}H NMR (400.13 MHz, $CDCl_3$): δ (ppm) 8.99 (d, $^{4}J_{HH}$ = 1.8 Hz, 2H, 6,6'-position), 8.65 (d, $^{3}J_{HH}$ = 8.4 Hz, 2H, 3,3'-position), 8.12 (dd, $^{3}J_{HH}$ = 8.4 Hz, $^{4}J_{HH}$ = 1.8 Hz, 2H, 4,4'-position). ^{13}C{^{1}H} NMR (100.57 MHz, $CDCl_3$): δ (ppm) 157.8 (s, 2,2'-position), 146.5 (q, $^{3}J_{CF}$ = 3.9 Hz, 6,6'-position), 134.5 (q, $^{3}J_{CF}$ = 3.9 Hz, 4,4'-position), 127.3 (q, $^{2}J_{CF}$ = 33 Hz, 5,5'-position), 123.7 (q, $^{1}J_{CF}$ = 273 Hz, $\underline{C}F_3$,), 121.4 (s, 3,3'-position). ^{19}F{^{1}H} NMR (376.50 MHz, $CDCl_3$): δ (ppm) -62.4 (s).

Synthesis of Dimeric Ruthenium Complexes

The ruthenium starting materials [Ru(η^6-benzene)Cl_2]$_2$, [Ru(η^6-tolyl)Cl_2]$_2$, [Ru(η^6-cymene)Cl_2]$_2$ and [Ru(η^6-hexamethylbenzene)Cl_2]$_2$ were prepared according to reported procedures.[1,2]

Synthesis of [1] - [Ru(η^6-benzene)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6]

[(PhH)RuCl_2]$_2$ (117 mg, 0.23 mmol) and 5,5'-difluoro-2,2'-bipyridine (90.0 mg, 0.47 mmol) were added to a nitrogen purged flask. Freshly distilled MeOH (25 mL) was added and the reaction was stirred for 24 hours at room temperature. The contents were filtered under gravity to remove excess ruthenium and the solution was reduced to approximately 5mL *in vacuo.* NH_4PF_6 (230 mg, 1.40 mmol) was added and the mixture was shaken and left at -10 °C for a further 24 hours. The suspension was washed with Et_2O (10 mL) and the product (90.7 mg, 66%) collected by gravity filtration as an orange/yellow solid. Orange prism shaped crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.

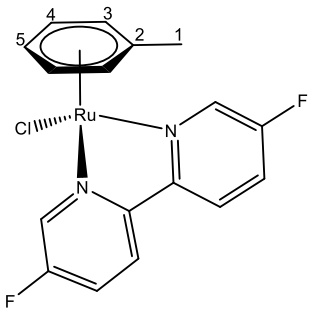


Anal. Calcd for $C_{16}H_{12}ClF_8N_2PRu$: C, 34.83; H, 2.19; N, 5.08. Found: C, 35.03; H, 2.39; N, 4.85. LRMS (ESI$^+$): *m/z* 407.01 [M – PF_6]$^+$ (m_{calc} = 406.97). ^{1}H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.78 (s, 2H, 6,6'-position), 8.71 (dd, $^{3}J_{HH}$ = 9.6 Hz, $^{3}J_{HF}$ = 4.6 Hz, 2H, 4,4'-position), 8.36 (overlapping dd, $^{3}J_{HH}$ = 9.6 Hz, $^{4}J_{HF}$ = 7.8 Hz, 2H, 3,3'-position), 6.30 (s, 6H, PhH). ^{13}C{^{1}H} NMR (100.57 MHz, d^6-DMSO): δ (ppm) 159.4 (d, $^{1}J_{CF}$ = 256 Hz, 5,5'-position),

150.7 (s, 2,2'-position), 144.7 (d, $^{2}J_{CF}$ = 33 Hz, 6,6'-position,), 127.4 (d, $^{2}J_{CF}$ = 19 Hz, 4,4'-position), 125.7 (d, $^{3}J_{CF}$ = 8.0 Hz, 3,3'-position), 87.2 (s, PhH). $^{19}F\{^{1}H\}$ NMR (376.50 MHz, d^{6}-DMSO): δ (ppm) -69.8 (d, $^{1}J_{PF}$ = 711 Hz, PF_6), -119.4 (s, 5,5'-position).

Synthesis of [2] - [Ru(η^{6}-tolyl)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6]

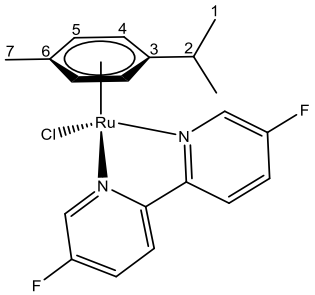
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(Tol)RuCl_2]_2$ (68.7 mg, 0.13 mmol), 5,5'-difluoro-2,2'-bipyridine (50.0 mg, 0.26 mmol) and NH_4PF_6 (150 mg, 0.92 mmol). The product (79.6 mg, 54%) was isolated as an orange powder. Orange crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.



Anal. Calcd for $C_{17}H_{14}ClF_8N_2PRu$: C, 36.09; H, 2.49; N, 4.95. Found: C, 35.75; H, 2.46; N, 4.73. LRMS (ESI^{+}): *m/z* 420.88 $[M - PF_6]^{+}$ (m_{calc} = 420.99). ^{1}H NMR (400.13 MHz, d^{6}-DMSO): δ (ppm) 9.68 (overlapping dd, $^{3}J_{HF}$ = 3.2 Hz, $^{4}J_{HH}$ = 2.5 Hz, 2H, 6,6'-bipy-position), 8.71 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HF}$ = 4.8 Hz, 2H, 3,3'-bipy-position), 8.35 (td, $^{3}J_{HH}$ = 9.0 Hz, $^{3}J_{HF}$ = 8. Hz, $^{4}J_{HH}$ = 2.5 Hz, 2H, 4,4'-bipy-position), 6.41 (t, 2H, $^{3}J_{HH}$ = 6.0 Hz, 4-Tol-position), 6.02 (d, $^{3}J_{HH}$ = 6 Hz, 2H, 3-Tol-position), 5.83 (t, $^{3}J_{HH}$ = 6.0 Hz, 1H, 5-Tol-position), 2.26 (s, 3H, 1-Tol-position). $^{13}C\{^{1}H\}$ NMR (100.57 MHz, d^{6}-DMSO): δ (ppm) 159.1 (d, $^{1}J_{CF}$ = 256 Hz, 5,5'-bipy-position), 150.7 (s, 2,2'-bipy-position) 144.6 (d, $^{2}J_{CF}$ = 33 Hz, 6,6'-bipy-position), 127.3 (d, $^{2}J_{CF}$ = 19 Hz, 4,4'-bipy-position), 125.2 (d, $^{3}J_{CF}$ = 7.0 Hz, 3,3'-bipy-position), 107.2 (s, 2-Tol-position), 90.9 (s, 4-Tol-position), 82.6 (s, 3-Tol-position), 79.9 (s, 5-Tol-position), 18.9 (s, 1-Tol-position). $^{19}F\{^{1}H\}$ NMR (376.50 MHz, d^{6}-DMSO): δ (ppm) -69.8 (d, $^{1}J_{PF}$ = 711 Hz, PF_6), -123.6 (s, 5,5'-position).

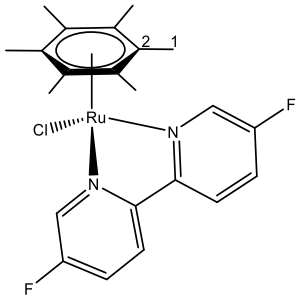
Synthesis of [3] - [Ru(η^{6}-*p*-cymene)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6]

A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(p\text{-}cym)RuCl_2]_2$ (47.8 mg, 0.08 mmol), 5,5'-difluoro-2,2'-bipyridine (30.0 mg, 0.16 mmol) and NH_4PF_6 (90.6 mg, 0.56 mmol). The product (41.1 mg, 59%) was isolated as sparkling orange crystals.



Anal. Calcd for $C_{20}H_{20}ClF_8N_2PRu$: C, 39.52; H, 3.32; N, 4.61. Found: C, 38.52; H, 3.27; N, 3.57. LRMS (ESI^+): *m/z* 462.99 $[M - PF_6]^+$ (m_{calc} = 463.03). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.66 (overlapping dd, $^3J_{HF}$ = 3.2 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, 6,6'-bipy-position), 8.72 (dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HF}$ = 4.8 Hz, 2H, 3,3'-bipy-position), 8.36 (td, $^3J_{HH}$ = 9.0 Hz, $^3J_{HF}$ = 8.0 Hz, $^4J_{HH}$ = 2.5 Hz, 2H, 4,4'-bipy-position), 6.34 (d, $^3J_{HH}$ = 6.4 Hz, 2H, 5-cym-position), 6.06 (d, $^3J_{HH}$ = 6.4 Hz, 2H, 4-cym-position), 2.60 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, 2-cym-position), 2.21 (s, 3H, 7-cym-position), 0.94 (d, $^3J_{HH}$ = 7.0 Hz, 6H, 1-cym-position). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): δ (ppm) 159.2 (d, $^1J_{CF}$ = 256 Hz, 5,5'-bipy-position), 150.6 (s, 2,2'-bipy-position), 144.5 (d, $^2J_{CF}$ = 32.5 Hz, 6,6'-bipy-position), 127.4 (d, $^2J_{CF}$ = 18.3 Hz, 4,4'-bipy-position), 124.2 (d, $^3J_{CF}$ = 8.0 Hz, 3,3'-bipy-position,), 105.1 (s, 3-cym-position), 104.5 (s, 6-cym-position), 86.8 (s, 5-cym-position), 83.5 (s, 4-cym-position), 30.4 (s, 2-cym-position), 21.8 (s, 1-cym-position), 18.4 (s, 7-cym-position). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) -69.8 d, $^1J_{PF}$ = 711 Hz PF_6), -123.1 (s, 5,5'-position).

Synthesis of [4] - [Ru(η^6-hexamethylbenzene)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6]
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(HMB)RuCl_2]_2$ (43.4 mg, 0.07 mmol), 5,5'-difluoro-2,2'-bipyridine (25.0 mg, 0.13 mmol) and NH_4PF_6 (80.1 mg, 0.49 mmol). The product (49.7 mg, 60%) was isolated as a bright orange solid. Orange crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.



Anal. Calcd for $C_{22}H_{24}ClF_8N_2PRu$: C, 41.55; H, 3.80; N, 4.41. Found: C, 40.68; H, 3.92 ; N, 4.20. LRMS (ESI^+): *m/z* 490.95 $[M - PF_6]^+$ (m_{calc} = 491.06). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 8.89 (6,6'-bipy-position, 2H, t, $^3J_{HF}$ = 3.2 Hz, $^4J_{HH}$ = 2.3 Hz), 8.72 (3,3'-bipy-position, 2H, overlapping dd, $^3J_{HH}$ = 9.0 Hz, $^4J_{HF}$ = 4.8 Hz), 8.34 (4,4'-bipy-position, 2H, td, $^3J_{HH}$ = 9.0 Hz, $^3J_{HF}$ = 8.0 Hz, $^4J_{HH}$ = 2.3 Hz), 2.06 (18H, s). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): δ (ppm) 159.5 (d, $^1J_{CF}$ = 257 Hz, 5,5'-position), 150.6 (s, 2,2'-position), 141.8 (d, $^2J_{CF}$ = 32 Hz, 6,6'-position), 127.3 (d, $^2J_{CF}$ = 19.5 Hz, 4,4'-position), 125.3 (d, $^3J_{CF}$ = 8 Hz, 3,3'-position,), 95.8 (s, 2-hmb-position) 15.0 (s, 1-hmb-position). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) -69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6), -122.7 (s, 5,5'-position).

Synthesis of [5] - [Ru(η^6-benzene)(3,3'-difluoro-2,2'-bipyridine)Cl][PF_6]
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(ben)RuCl_2]_2$ (127 mg, 0.25 mmol), 3,3'-difluoro-2,2'-bipyridine (97.6 mg, 0.50 mmol) and NH_4PF_6 (150 mg, 0.92 mmol). The product (114 mg, 41%) was isolated as an orange powder. Orange crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.
Anal. Calcd for $C_{16}H_{12}ClF_8N_2PRu$: C, 34.83; H, 2.19; N, 5.08. Found: C, 35.01; H, 2.22; N, 4.95. LRMS (ESI^+): *m/z* 407.00 $[M - PF_6]^+$ (m_{calc} = 406.97). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.64 (d, $^3J_{HH}$ = 5.3 Hz, 2H, 6,6'-position), 8.34 (dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 5.3

Hz, 2H, 5,5'-position), 7.97 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 4,4'-position), 6.29 (s, 6H, PhH). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): δ (ppm) 3,3'-bipy peak not resolvable, 153.9 (s, 6,6'-position), 141.1 (dd, $^2J_{CF}$ = 8.2 Hz, $^3J_{CF}$ = 6.4 Hz, 2,2'-position), 130.0 – 129.0 (complex m, 5,5'-position and 4,4'-position), 87.9 (s, PhH). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) 69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6), -103.9 (s, 3,3'-position)

Synthesis of [6] - [Ru(η^6-tolyl)(3,3'-difluoro-2,2'-bipyridine)Cl][PF_6]

A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(Tol)RuCl_2]_2$ (68.7 mg, 0.13 mmol), 3,3'-difluoro-2,2'-bipyridine (50.0 mg, 0.26 mmol) and NH_4PF_6 (150 mg, 0.92 mmol). The product (109.4 mg, 74%) was isolated as a dark brown powder. Orange crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.

Numbering scheme as for the analogous [Ru(η^6-tolyl)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6] complex [2].

Anal. Calcd for $C_{17}H_{14}ClF_8N_2PRu$: C, 36.09; H, 2.49; N, 4.95. Found: C, 35.86; H, 2.38; N, 4.89. LRMS (ESI$^+$): *m/z* 420.10 $[M - PF_6]^+$ (m_{calc} = 420.99). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.54 (d, $^3J_{HH}$ = 5.0 Hz, 2H, 6,6'-bipy-position), 8.32 (dd, $^3J_{HF}$ = 8.0 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, 4,4'-bipy-position), 7.95 (m, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 5.0 Hz, $^4J_{HF}$ = 3.1 Hz, 2H, 5,5'-bipy-position), 6.30 (t, $^3J_{HH}$ = 6.0 Hz, 2H, 4-Tol-position), 5.96 (d, $^3J_{HH}$ = 6.0 Hz, 2H, 3-Tol-position), 5.85 (t, $^3J_{HH}$ = 6.0 Hz, 1H, 5-Tol-position), 2.24 (s, 3H, 1-Tol-position). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): δ (ppm) 157.1 (d, $^1J_{CF}$ = 264 Hz, 1H, 3,3'-bipy-position), 153.2 (s, 6,6'-position), 140.8 (dd, $^2J_{CF}$ = 8.7 Hz, $^3J_{CF}$ = 6.4 Hz, 2,2'-position,), 129.3 (s, 5,5'-position), 129.0 (d, $^2J_{CF}$ = 12.5 Hz, 4,4'-position), 106.8 (s, 2-Tol-position), 91.2 (s, 4-Tol-position), 82.9 (s, 3-Tol-position), 80.2 (s, 5-Tol-position), 18.7 (s, 1-Tol-position). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) 69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6), -108.1 (s, 3,3'-position).

Synthesis of [7] - [Ru(η^6-*p*-cymene)(3,3'-difluoro-2,2'-bipyridine)Cl][PF_6]

A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(p\text{-cymene})RuCl_2]_2$ (47.8 mg, 0.078 mmol), 3,3'-difluoro-2,2'-bipyridine (30.0 mg, 0.16 mmol) and NH_4PF_6 (90.6 mg, 0.56 mmol). The product (41.1 mg, 59%) was isolated as an orange crystalline solid. Orange prism shaped crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.

Numbering scheme as for the analogous [Ru(η^6-*p*-cymene)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6] complex [3].

Anal. Calcd for $C_{20}H_{20}ClF_8N_2PRu$: C, 39.52; H, 3.32; N, 4.61. Found: C, 38.50; H, 3.31; N, 4.79. LRMS (ESI$^+$): *m/z* 463.06 $[M - PF_6]^+$ (m_{calc} = 463.03). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.52 (d, $^3J_{HH}$ = 5.0 Hz, 2H, 6,6'-position), 8.34 (dd, $^3J_{HF}$ = 8.3 Hz, $^3J_{HH}$ = 5.0 Hz, 2H, 4,4'-position), 7.97 (5,5'-position, 2H, m, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 5.0 Hz, $^4J_{HF}$ = 3.1 Hz), 6.23 (d, $^3J_{HH}$ = 6.4 Hz, 2H, 5-cym-position), 6.00 (d, $^3J_{HH}$ = 6.4 Hz, 2H, 4-cym-position), 2.64 (sept, $^3J_{HH}$ = 7.0 Hz, 1H, 2-cym-position), 2.17 (s, 3H, 7-cym-position), 1.00 (d, $^3J_{HH}$ = 7.0 Hz, 6H, 1-cym-position). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): δ (ppm) 3,3'-bipy peak in baseline, 153.3 (s, 6,6'-position), 140.5 (dd, $^2J_{CF}$ = 6.8 Hz, $^3J_{CF}$ = 4.0 Hz, 2,2'-position), 129.4 (s, 5,5'-position), 128.7 (d, $^2J_{CF}$ = 12.4 Hz, 4,4'-position), 105.1 (s, 3-cym-position), 104.5 (s, 6-cym-position), 86.7 (s, 5-cym-position), 84.2 (s, 4-cym-position), 30.4 (s, 2-cym-position), 21.7 (s, 1-cym-position), 18.2 (s, 7-cym-position). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) -69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6), -103.9 (s, 3,3'-position).

Synthesis of [8] - [Ru(η^6-hexamethylbenzene)(3,3'-difluoro-2,2'-bipyridine)Cl][PF_6]

A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(HMB)RuCl_2]_2$ (86.9 mg, 0.13 mmol), 5,5'-difluoro-2,2'-bipyridine (50 mg, 0.26 mmol) and NH_4PF_6 (150 mg, 0.92 mmol). The product (90.8 mg, 55%) was isolated as a bright orange solid. Orange prism shaped crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day. Numbering scheme as for the analogous [Ru(η^6-hexamethylbenzene)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6] complex [4].
Anal. Calcd for $C_{22}H_{24}ClF_8N_2PRu$: C, 41.55; H, 3.80; N, 4.41. Found: C, 41.45; H, 3.73; N, 4.32. LRMS (ESI^+): *m/z* 490.98 $[M - PF_6]^+$ (m_{calc} = 491.06). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 8.87 (d, $^3J_{HH}$ = 5.0 Hz, 2H, 6,6'-position), 8.27 (m, $^3J_{HF}$ = 8.0 Hz $^3J_{HH}$ = 5.0 Hz, 2H, 4,4'-position), 7.94 (m, $^3J_{HH}$ = 5.0 Hz, $^3J_{HH}$ = 5.0 Hz, $^4J_{HF}$ = 3.0 Hz, 2H, 5,5'-position), 2.02 (s, 18H). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): 159.2 (d, $^1J_{CF}$ = 265 Hz, 1H, 3,3'-position), 151.1 (s, 6,6'-position), 140.6 (dd, $^2J_{CF}$ = 8.0 Hz, $^3J_{CF}$ = 6.0 Hz, 2,2'-position), 129.6 (s, 5,5'-position), 128.7 (d, $^2J_{CF}$ = 11 Hz 4,4'-position), 96.1 (s, 2-hmb-position), 15.0 (s, 1-hmb-position). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) -69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6,), -104.2 (s, 3,3'-position).

Synthesis of [9] - [Ru(benzene)(6,6'-difluoro-2,2'-bipyridine)Cl][PF_6]
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(PhH)RuCl_2]_2$ (13.0 mg, 0.026 mmol), 6,6'-difluoro-2,2'-bipyridine (10.0 mg, 0.052 mmol) and NH_4PF_6 (25.4 mg, 0.16 mmol). The product (10 mg, 35%) was isolated as an orange solid. Yellow prism like crystals were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.
Anal. Calcd for $C_{18}H_{12}ClF_{12}N_2PRu$: C, 34.83; H, 2.19; N, 5.08. Found: C, 34.61; H, 2.33; N, 4.84. LRMS (ESI^+): *m/z* 407.02 $[M - PF_6]^+$ (m_{calc} = 406.97). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 8.63 (d, $^3J_{HH}$ = 7.9 Hz, 2H, 3,3'-position), 8.52 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 7.9 Hz, 2H, 4,4'-position), 7.91 (d, $^3J_{HH}$ = 8.5 Hz, 2H, 5,5'-position), 6.32 (s, 6H, PhH). Lack of sample restricted analysis to proton and fluorine NMR. $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) 69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6), -49.7 (s, 6,6'-position)

Synthesis of [10] - Synthesis of [Ru(benzene)(5,5'-bis(trifluoromethyl)-2,2'-bipyridine)Cl][PF_6]
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(PhH)RuCl_2]_2$ (51.4 mg, 0.10 mmol), 5,5'-bis(trifluoromethyl)-2,2'-bipyridine (60.0 mg, 0.21 mmol) and NH_4PF_6 (100 mg, 0.62 mmol). The product (80.1 mg, 60%) was isolated as an orange solid. Orange prism shaped crystals for X-ray diffraction were obtained from a vapour diffusion method with diethyl ether into a concentrated acetone solution over 1 day.
Anal. Calcd for $C_{18}H_{12}ClF_8N_2PRu$: C, 33.17; H,1.86; N, 4.30. Found: C, 33.15; H, 1.80; N, 4.21. LRMS (ESI^+): *m/z* 507.00 $[M - PF_6]^+$ (m_{calc} = 506.96). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.95 (s, 2H, 6,6'-position), 9.04 (d, $^3J_{HH}$ = 8.7 Hz, 2H, 3,3'-position), 8.86 (d, $^3J_{HH}$ = 8.7 Hz, 2H 4,4'-position), 6.35 (s, 6H, PhH). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): 156.6 (s, 2,2'-position), 152.7 (q, $^3J_{CF}$ = 4.1 Hz, 6,6'-position,), 137.8 (q, $^3J_{CF}$ = 3.1 Hz , 4,4'-position,), 128.7 (q, $^2J_{CF}$ = 34 Hz, 5,5'-position,), 125.5 (s, 3,3'-position) 122.1 (q, $^1J_{CF}$ = 278 Hz , $\underline{C}F_3$,), 87.5 (s, PhH). $^{19}F\{^1H\}$ NMR (376.50 MHz, d^6-DMSO): δ (ppm) 69.8 (d, $^1J_{PF}$ = 711 Hz, PF_6,), -60.1 (s, CF_3 groups).

Synthesis of [11] - [Ru(η^6-benzene)(2,2'-bipyridine)Cl][PF_6]
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: $[(benzene)RuCl_2]_2$ (120 mg, 0.24 mmol), 2,2'-bipyridine (76.0 mg, 0.48 mmol)

and NH_4PF_6 (465 mg, 1.44 mmol). The product (159 mg, 74%) was isolated as a yellow/orange solid.
Anal. Calcd for $C_{16}H_{14}ClF_6N_2PRu$: C, 37.26; H, 2.74; N, 5.43. Found: C, 37.07; H, 2.57; N, 5.28. LRMS (ESI^+): *m/z* 371.02 $[M - PF_6]^+$ (m_{calc} = 370.99). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.63 (d, $^3J_{HH}$ = 5.6 Hz, 2H, 6,6'-position), 8.64 (d, $^3J_{HH}$ = 8.1 Hz, 2H, 3,3'-position), 8.29 (overlapping dd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 7.9 Hz, 2H, 4,4'-position), 7.79 (overlapping dd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 5.6 Hz, 2H, 5,5'-position), 6.25 (s, 6H, PhH). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): 156.0 (2,2'-position), 154.5 (6,6'-position), 140.0 (4,4'-position) 127.4 (5,5'-position), 123.7 (3,3'-position), 87.0 (PhH, s).

Synthesis of [12] - [Ru(η^6-*p*-cymene)(2,2'-bipyridine)Cl][PF_6]
A procedure entirely analogous to the synthesis of [1] was adopted, with the following masses used: [(*p*-cymene)$RuCl_2]_2$ (147 mg, 0.24 mmol), 2,2'-bipyridine (76.0 mg, 0.48 mmol) and NH_4PF_6 (465 mg, 1.44 mmol). The product (175 mg, 64%) was isolated as a yellow/orange solid.
Numbering scheme as for the analogous [Ru(η^6-*p*-cymene)(5,5'-difluoro-2,2'-bipyridine)Cl][PF_6] complex [3].
Anal. Calcd for $C_{20}H_{22}ClF_6N_2PRu$: C, 42.00; H, 3.88; N, 4.90. Found: C, 41.89; H, 3.86; N, 4.78 LRMS (ESI^+): *m/z* 427.06 $[M - PF_6]^+$ (m_{calc} = 427.05). ^1H NMR (400.13 MHz, d^6-DMSO): δ (ppm) 9.54 (d, $^3J_{HH}$ = 5.8 Hz, 2H, 6,6'-position), 8.64 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 3,3'-position), 8.29 (overlapping dd, $^3J_{HH}$ = 8.6 Hz, $^3J_{HH}$ = 8.0 Hz, 2H, 4,4'-position), 7.79 (overlapping dd, $^3J_{HH}$ = 8.0 Hz, $^3J_{HH}$ = 6.5 Hz, 2H, 5,5'-position), 6.21 (d, $^3J_{HH}$ = 6.1 Hz, 2H, 5-cym-position), 5.98 (d, $^3J_{HH}$ = 6.1 Hz, 2H, 4-cym-position), 2.57 (sept, $^3J_{HH}$ = 6.9 Hz, 1H, 2-cym-position), 2.18 (s, 3H, 7-cym-position), 0.94 (d, $^3J_{HH}$ = 6.9 Hz, 6H, 1-cym-position). $^{13}C\{^1H\}$ NMR (100.57 MHz, d^6-DMSO): 155.7 (2,2'-position), 154.3 (6,6'-position), 139.9 (4,4'-position) 127.5 (5,5'-position), 123.8 (3,3'-position), 86.7 (5-cym-position), 83.9 (4-cym-position), 30.3 (2-cym-position), 21.6 (1-cym-position), 18.3 (7-cym-position).

Crystallographic data for ruthenium complexes

Below is the crystallographic data for the fluorinated bipyridine complexes [1]-[10] and the ruthenium bipyridine with cysteine ligand, complex [13].

Table S1. Key bond lengths (Å) and angles (deg) for complexes [1] - [4] and [10].

	[1]	[2]	[3]	[4]	[10]
Bond Lengths					
Ru-Cl	2.3754(7)	2.3773(12)	2.3898(7)	2.3809(6)	2.391(2)
Ru-N	2.0827(15)	2.085(4)	2.094(2)	2.1021(19)	2.079(6)
		2.087(4)	2.087(2)	2.109(2)	2.096(6)
Ru-Arene (centroid)	1.681	1.688	1.687	1.703	1.684
Bond Angles					
N-Ru-N	77.06(8)	76.92(14)	77.02(9)	75.93(8)	77.1(2)

Table S2. X-ray crystallographic data for complexes [1] to [4].

Complex	[1]		[2]		[3]		[4]	
CCDC No.	1867661		1867662		1867663		1867664	
Empirical formula	$[C_{16}H_{12}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{17}H_{14}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{20}H_{20}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{22}H_{24}ClF_2N_2Ru]^+(PF_6^-)$	
Formula weight	551.77		565.79		607.87		635.92	
Temperature	180(2) K		180(2) K		180(2) K		180(2) K	
Wavelength	0.7107 Å		1.5418 Å		0.7107 Å		1.5418 Å	
Crystal system	Orthorhombic		Triclinic		Orthorhombic		Triclinic	
Space group	Pbcm		P–1		$Pca2_1$		P–1	
Unit cell dimensions	a = 8.18600(10) Å	α = 90°	a = 7.1872(3) Å	α = 99.964(2)°	a = 12.0020(2) Å	α = 90°	a = 8.4825(3) Å	α = 103.1690(11)°
	b = 12.7339(2) Å	β = 90°	b = 11.6858(4) Å	β = 97.263(2)°	b = 13.7944(2) Å	β = 90°	b = 11.8360(4) Å	β = 94.0286(11)°
	c = 17.9660(3) Å	γ = 90°	c = 11.9743(4) Å	γ = 101.058(2)°	c = 13.2815(2) Å	γ = 90°	c = 12.4837(4) Å	γ = 103.4380(10)°
Volume	1872.77(5) $Å^3$		958.79(6) $Å^3$		2198.89(6) $Å^3$		1176.89(7) $Å^3$	
Z	4		2		4		2	
Density (calculated)	1.957 mg/m^3		1.960 mg/m^3		1.836 mg/m^3		1.795 mg/m^3	
Absorption coefficient	1.147 mm^{-1}		9.488 mm^{-1}		0.986 mm^{-1}		7.808 mm^{-1}	
F(000)	1080		556		1208		636	
Crystal size	0.30 x 0.23 x 0.18 mm^3		0.04 x 0.04 x 0.03 mm^3		0.32 x 0.30 x 0.18 mm^3		0.18 x 0.12 x 0.06 mm^3	
Theta range	3.73 to 32.02°		3.80 to 66.73°		3.70 to 33.70°		3.67 to 67.18°	
Index ranges	-12<=h<=12, -17<=k<=19, -26<=l<=26		-8<=h<=8, -13<=k<=13, -14<=l<=14		-18<=h<=18, -21<=k<=21, -20<=l<=20		-10<=h<=10, -13<=k<=14, -14<=l<=14	
Reflections collected	16324		12013		24942		12913	
Independent reflections	3323 [R(int) = 0.035]		3393 [R(int) = 0.049]		8467 [R(int) = 0.031]		4156 [R(int) = 0.025]	
Completeness to θ(max)	99.3 %		99.6 %		99.8 %		98.8 %	
Data / restraints / param.	3323 / 0 / 135		3393 / 0 / 275		8467 / 1 / 301		4156 / 34 / 360	
Goodness-of-fit on F^2	1.09		1.05		1.00		1.08	
R indices [I>2sigma(I)]	R1 = 0.032	wR2 = 0.097	R1 = 0.040	wR2 = 0.091	R1 = 0.027	wR2 = 0.069	R1 = 0.024	wR2 = 0.059
R indices (all data)	R1 = 0.039	wR2 = 0.100	R1 = 0.054	wR2 = 0.096	R1 = 0.032	wR2 = 0.071	R1 = 0.025	wR2 = 0.060
Largest diff. peak and hole	0.87 and -0.78 $e.Å^{-3}$		1.38 and -0.59 $e.Å^{-3}$		0.74 and -0.83 $e.Å^{-3}$		0.66 and -0.62 $e.Å^{-3}$	
Flack parameter					-0.030(14)			

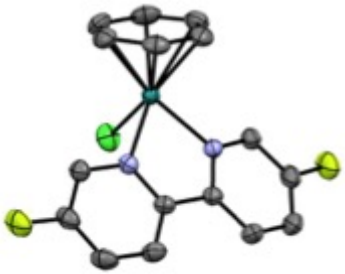
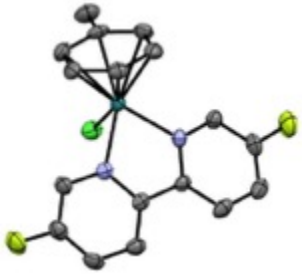
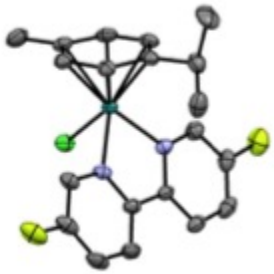
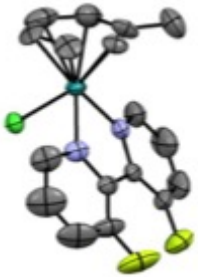
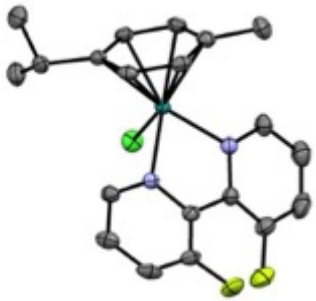
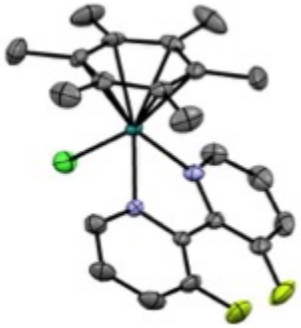
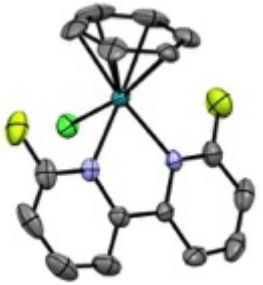
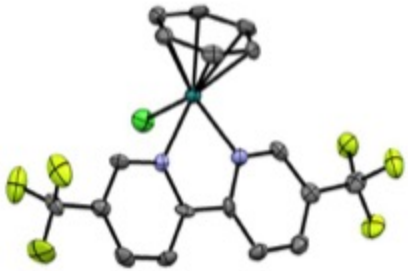
Table S3. X-ray crystallographic data for complexes [5] to [8].

Complex	[5]		[6]		[7]		[8]	
CCDC No.	1867665		1867666		1867667		1867668	
Empirical formula	$[C_{16}H_{12}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{17}H_{14}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{20}H_{20}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{22}H_{24}ClF_2N_2Ru]^+(PF_6^-)$	
Formula weight	551.77		565.79		607.87		635.92	
Temperature	180(2) K		180(2) K		180(2) K		180(2) K	
Wavelength	0.7107 Å		1.5418 Å		1.5418 Å		1.5418 Å	
Crystal system	Triclinic		Orthorhombic		Orthorhombic		Orthorhombic	
Space group	P–1		$Cmc2_1$		$Pca2_1$		$Pna2_1$	
Unit cell dimensions	a = 8.0630(5) Å	α = 104.378(3)°	a = 11.8675(3) Å	α = 90°	a = 12.3683(3) Å	α = 90°	a = 18.4489(5) Å	α = 90°
	b = 8.3719(5) Å	β = 95.336(3)°	b = 11.3437(3) Å	β = 90°	b = 13.3931(3) Å	β = 90°	b = 7.8290(2) Å	β = 90°
	c = 13.8505(11) Å	γ = 96.409(3)°	c = 14.2301(4) Å	γ = 90°	c = 13.3561(3) Å	γ = 90°	c = 16.0806(4) Å	γ = 90°
Volume	892.90(11) $Å^3$		1915.68(9) $Å^3$		2212.44(9) $Å^3$		2322.62(10) $Å^3$	
Z	2		4		4		4	
Density (calculated)	2.052 mg/m^3		1.962 mg/m^3		1.825 mg/m^3		1.819 mg/m^3	
Absorption coefficient	1.203 mm^{-1}		9.498 mm^{-1}		8.273 mm^{-1}		7.912 mm^{-1}	
F(000)	540		1112		1208		1272	
Crystal size	0.10 x 0.04 x 0.01 mm^3		0.12 x 0.10 x 0.02 mm^3		0.25 x 0.06 x 0.02 mm^3		0.40 x 0.08 x 0.03 mm^3	
Theta range	3.53 to 25.14°		5.39 to 70.42°		3.30 to 66.78°		4.79 to 66.93°	
Index ranges	-9<=h<=9, -9<=k<=9, -14<=l<=16		-14<=h<=14, -12<=k<=13, -17<=l<=17		-14<=h<=14, -15<=k<=15, -13<=l<=15		-21<=h<=21, -9<=k<=9, -19<=l<=16	
Reflections collected	7589		14279		27010		14417	
Independent reflections	3118 [R(int) = 0.105]		1909 [R(int) = 0.042]		3787 [R(int) = 0.043]		3794 [R(int) = 0.042]	
Completeness to θ(max)	97.6 %		99.9 %		99.9 %		99.5 %	
Data / restraints / param.	3118 / 0 / 262		1909 / 43 / 164		3787 / 1 / 301		3794 / 1 / 322	
Goodness-of-fit on F^2	1.10		1.03		1.05		1.04	
R indices [I>2sigma(I)]	R1 = 0.072	wR2 = 0.110	R1 = 0.033	wR2 = 0.087	R1 = 0.019	wR2 = 0.044	R1 = 0.025	wR2 = 0.054
R indices (all data)	R1= 0.124	wR2 = 0.128	R1 = 0.035	wR2 = 0.088	R1 = 0.022	wR2 = 0.045	R1 = 0.030	wR2 =0.056
Largest diff. peak and hole	0.73 and -0.76 $e.Å^{-3}$		0.71 and -0.48 $e.Å^{-3}$		0.25 and -0.31 $e.Å^{-3}$		0.45 and -0.30 $e.Å^{-3}$	
Flack parameter			0.003(17)		0.017(6)		0.017(6)	

Table S4. X-ray crystallographic data for complexes [9] to [13].

Complex	[9]		[10]		[13]	
CCDC No.	1867669		1867670		1867671	
Empirical formula	$[C_{16}H_{12}ClF_2N_2Ru]^+(PF_6^-)$		$[C_{18}H_{12}ClF_{12}N_2Ru]^+(PF_6^-)$		$[C_{21}H_{22}ClN_3O_3RuS]^+(PF_6^-)(H_2O)$	
Formula weight	551.77		651.79		660.53	
Temperature	180(2) K		180(2) K		180(2) K	
Wavelength	0.7107 Å		0.7107 Å		0.7107 Å	
Crystal system	Monoclinic		Orthorhombic		Monoclinic	
Space group	$P2_1/n$		$Pca2_1$		P2	
Unit cell dimensions	a = 11.8901(4) Å	α = 90°	a = 16.0681(5) Å	α = 90°	a = 14.2643(3) Å	α = 90°
	b = 11.9766(4) Å	β = 101.146(2)°	b = 8.0666(3) Å	β = 90°	b = 8.4893(2) Å	β = 108.5325(10)°
	c = 12.8399(5) Å	γ = 90°	c = 15.9972(5) Å	γ = 90°	c = 21.3553(6) Å	γ = 90°
Volume	1793.95(11) $Å^3$		2073.48(12) $Å^3$		2451.90(10) $Å^3$	
Z	4		4		4	
Density (calculated)	2.043 mg/m^3		2.088 mg/m^3		1.789 mg/m^3	
Absorption coefficient	1.198 mm^{-1}		1.080 mm^{-1}		0.871 mm^{-1}	
F(000)	1080		1272		1328	
Crystal size	0.10 x 0.05 x 0.03 mm^3		0.10 x 0.07 x 0.05 mm^3		0.18 x 0.02 x 0.02 mm^3	
Theta range	3.66 to 27.50°		3.58 to 27.50°		3.52 to 25.03°	
Index ranges	-15<=h<=15, -15<=k<=15, -16<=l<=16		-20<=h<=16, -10<=k<=10, -20<=l<=20		-16<h<15, -9<k<10, -25<l<21	
Reflections collected	11426		8837		12840	
Independent reflections	4031 [R(int) = 0.086]		3784 [R(int) = 0.059]		7477	
Completeness to θ(max)	97.7%		97.6 %		98.3	
Data / restraints / param.	4031 / 0 / 262		3784 / 1 / 316		7477/2/673	
Goodness-of-fit on F2	1.03		1.07		1.00	
R indices [I>2sigma(I)]	R1 = 0.051	wR2 = 0.085	R1 = 0.041	wR2 = 0.074	R1 = 0.039	wR2 = 0.075
R indices (all data)	R1 = 0.105	wR2 = 0.103	R1= 0.061	wR2 = 0.082	R1 = 0.056	wR2 = 0.080
Largest diff. peak and hole	0.65 and -0.99 $e.Å^{-3}$		0.58 and -0.66 $e.Å^{-3}$		0.59 and -0.64 $e.Å^{-3}$	
Flack parameter			-0.04(4)		-0.01(3)	

Structures of complexes [1] – [10] with displacement ellipsoids at 50% probability

				
[1]	[2]	[3]	[4]	[5]
				
[6]	[7]	[8]	[9]	[10]

NMR of Ru(II) Arene complexes with amino acids and glutathione

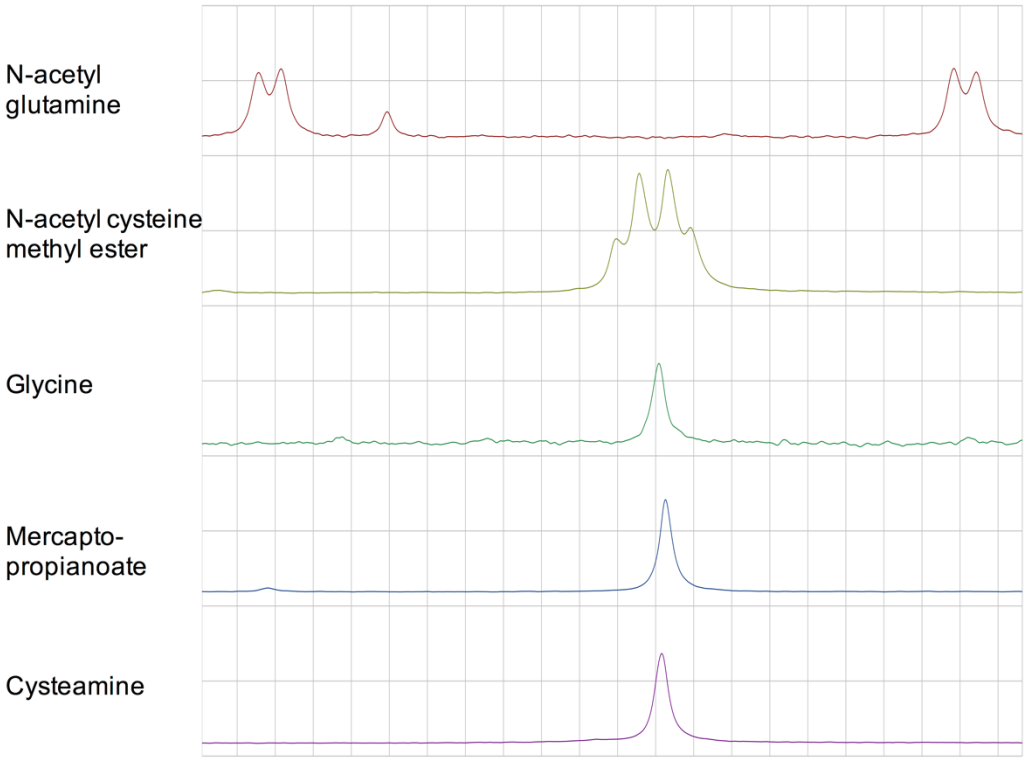


Figure S2. The $^{19}F\{^{1}H\}$ NMR peaks of [Ru(η_6-benzene)(5,5'-difluorobipyridine)()]$^{+}$ when complex [1] with both chiral amino acids and achiral small molecules (2 mM Ru, 3 eq. AA, 8 hours, 310 K). The chemical shift scale is the same for all spectra, which are aligned to the Ru-[Adduct] peak in each case.

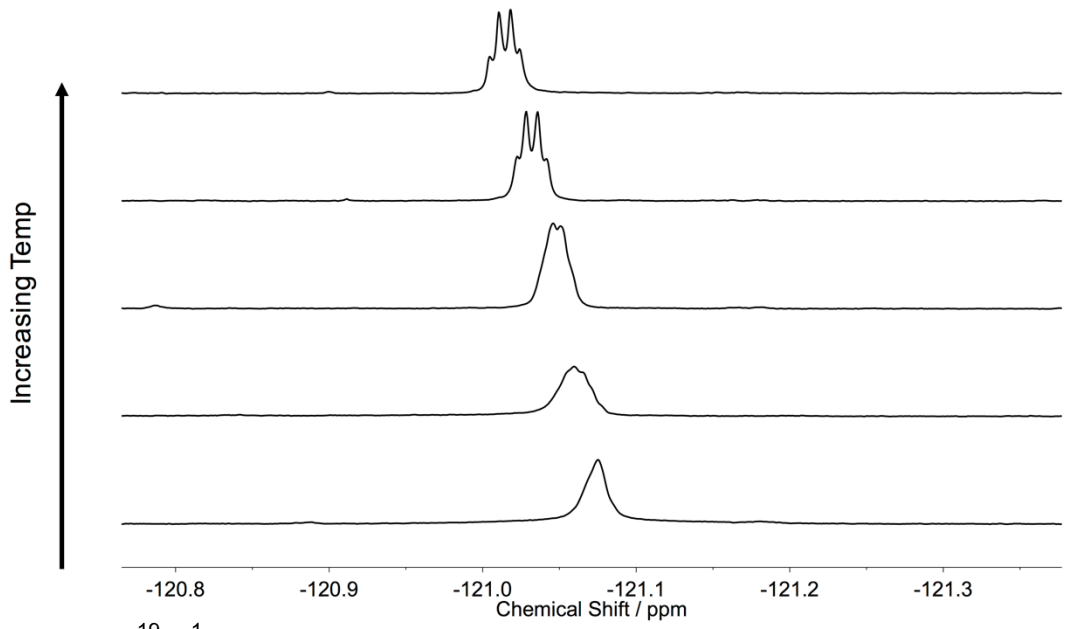


Figure S3. The $^{19}F\{^{1}H\}$ NMR peaks of [Ru(η_6-benzene)(5,5'-difluorobipyridine)(N-ac-cysteine-OMe)]$^{+}$ when complex [1] is incubated with N-acetyl cysteine methyl ester (2 mM Ru, 3 eq amino acid) at a temperature range 278 K – 328 K

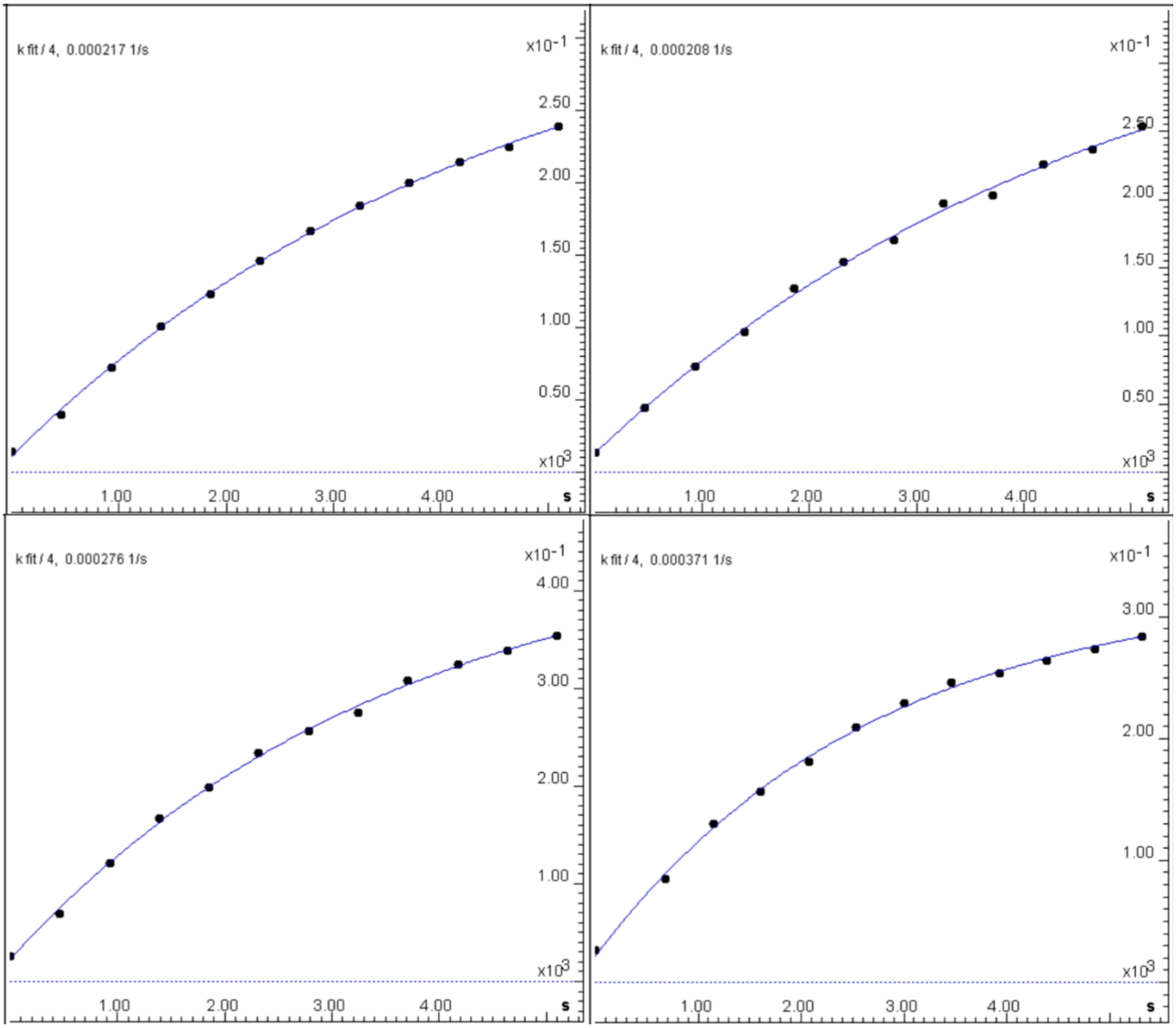


Figure S4. Plots showing the variation of the concentration of [Ru(η_6-arene)(5,5'-difluorobipyridine)(N-Ac-Cysteine-OMe)]$^+$ products with time during the reaction of complexes [1] (top left), [2] (top left), [3] (bottom left) and 4 (bottom right) (2 mM), with N-acetyl-cysteine-methyl ester (3 eq, pD 7.2, 310 K) based on the integration of Ru-cys peak. The curves in are computer-fits to first-order kinetics giving the rate constants listed in Table 2.

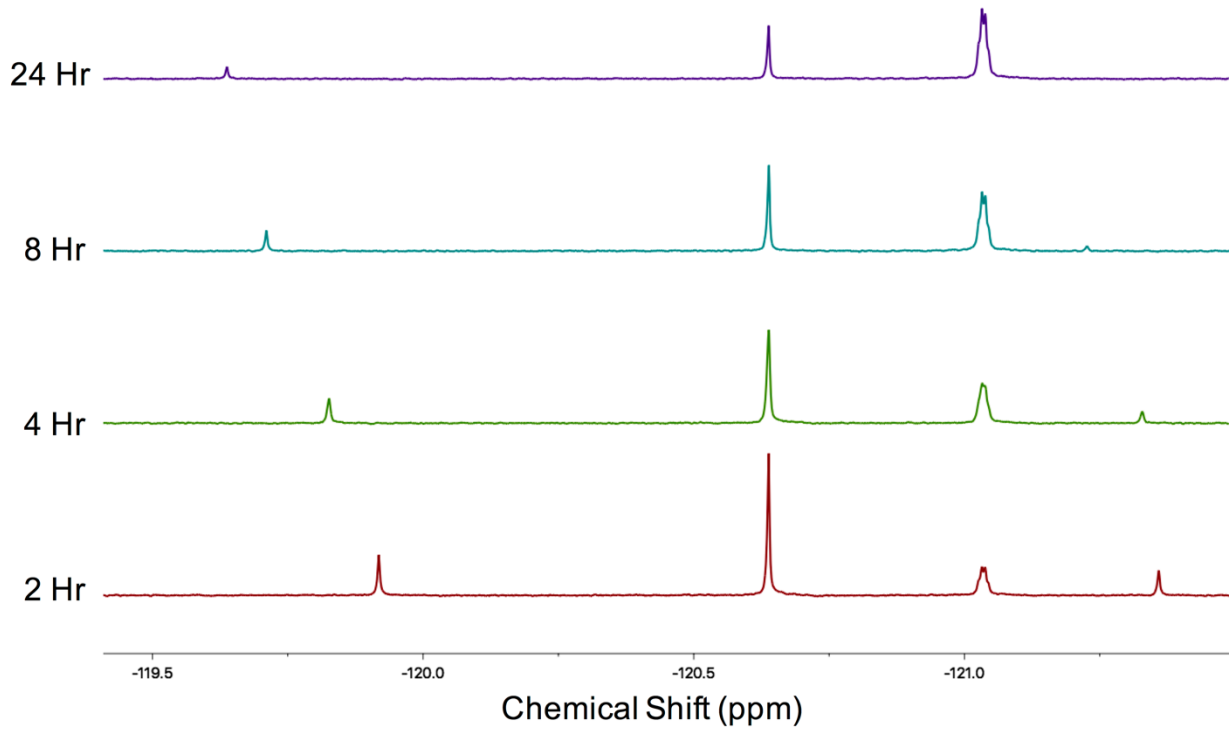


Figure S5. A time series of $^{19}F\{^{1}H\}$ NMR spectra when complex [1] is incubated with N-Ac-Cys-OMe (2 mM Ru, 3 eq. amino acid, 310 K).

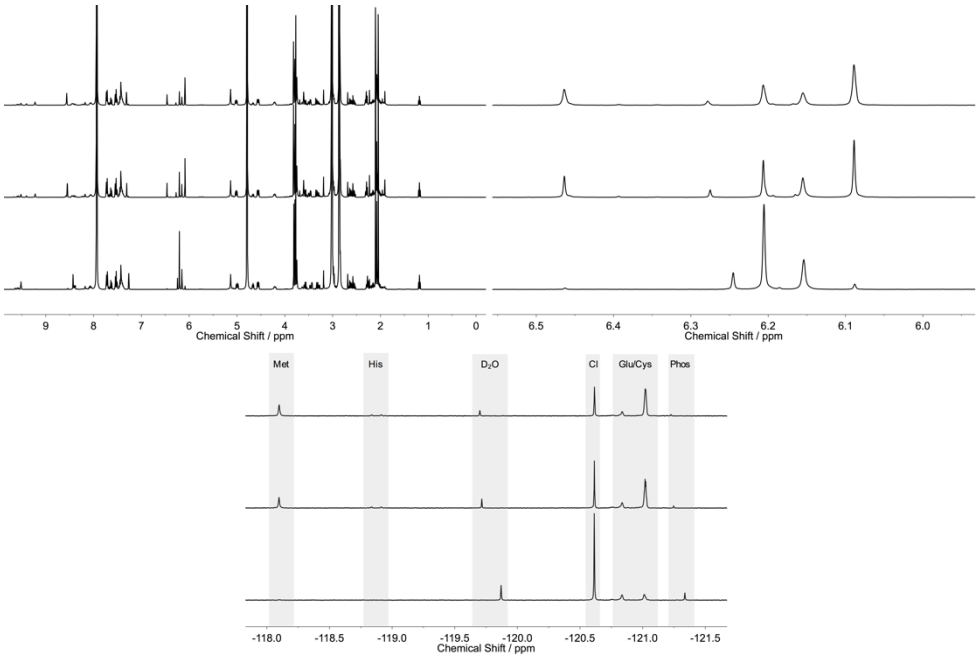


Figure S6. A comparison of $^{19}F\{^{1}H\}$ NMR (bottom) and ^{1}H spectra (top) when complex [1] is incubated with a mixture protected amino acids, N-Ac-Cys-OMe, N-Z-Glu-OMe, N-Bz-His-OMe, N-Ac-Met-OMe, and a mixture of all amino acids together, (4 mM Ru, 1.5 eq. each amino acid, 310 K).

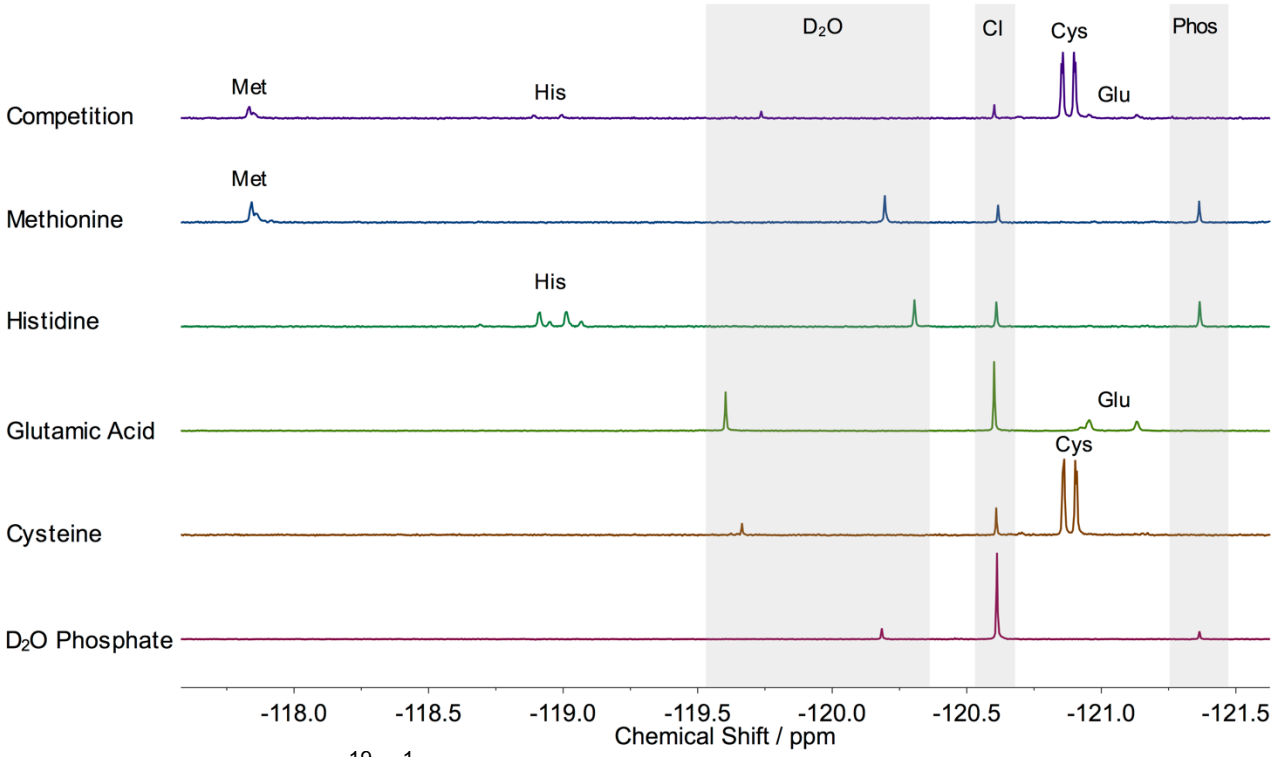


Figure S7. A series of $^{19}F\{^{1}H\}$ NMR spectra when complex [2] is incubated with the protected amino acids, N-Ac-Cys-OMe, N-Z-Glu-OMe, N-Bz-His-OMe, N-Ac-Met-OMe, and a mixture of all amino acids together, (2 mM Ru, 3 eq. amino acid, 24 hr, 310 K).

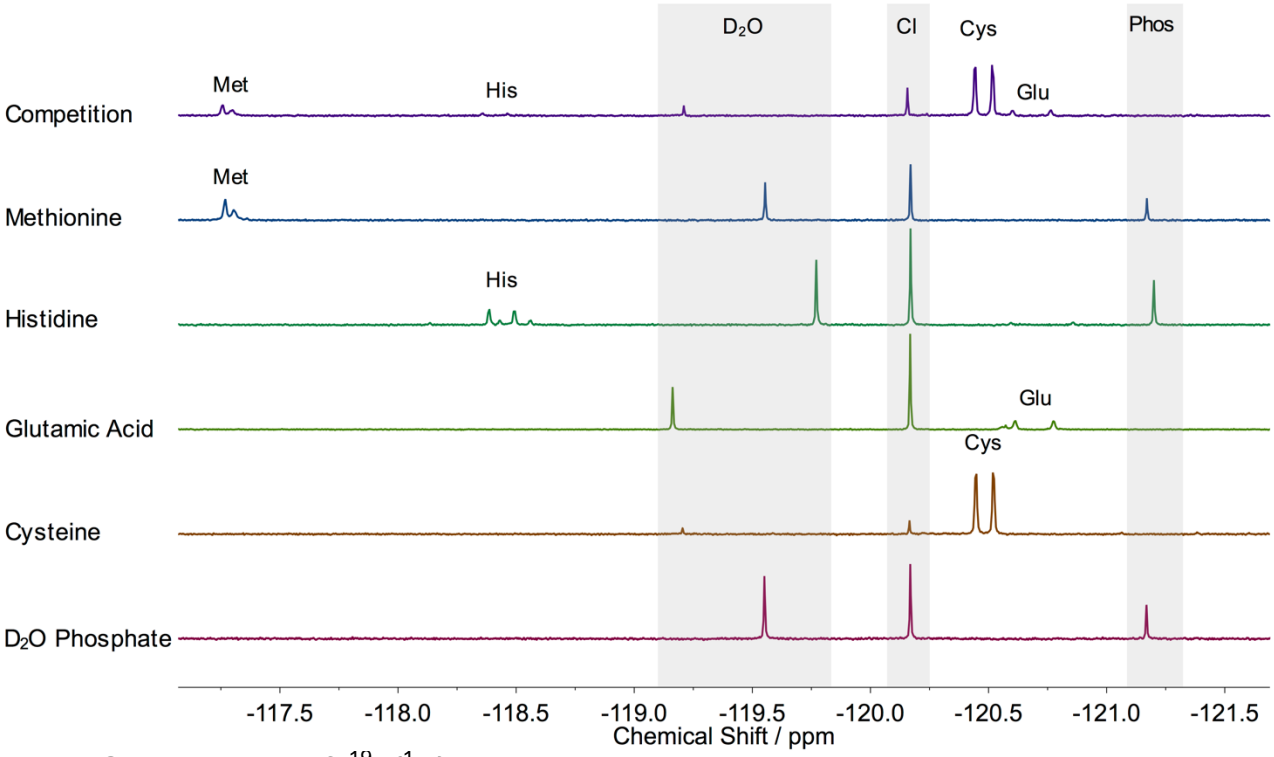


Figure S8. A series of $^{19}F\{^{1}H\}$ NMR spectra when complex [3] is incubated with the protected amino acids, N-Ac-Cys-OMe, N-Z-Glu-OMe, N-Bz-His-OMe, N-Ac-Met-OMe, and a mixture of all amino acids together, (2 mM Ru, 3 eq. amino acid, 24 hr, 310 K).

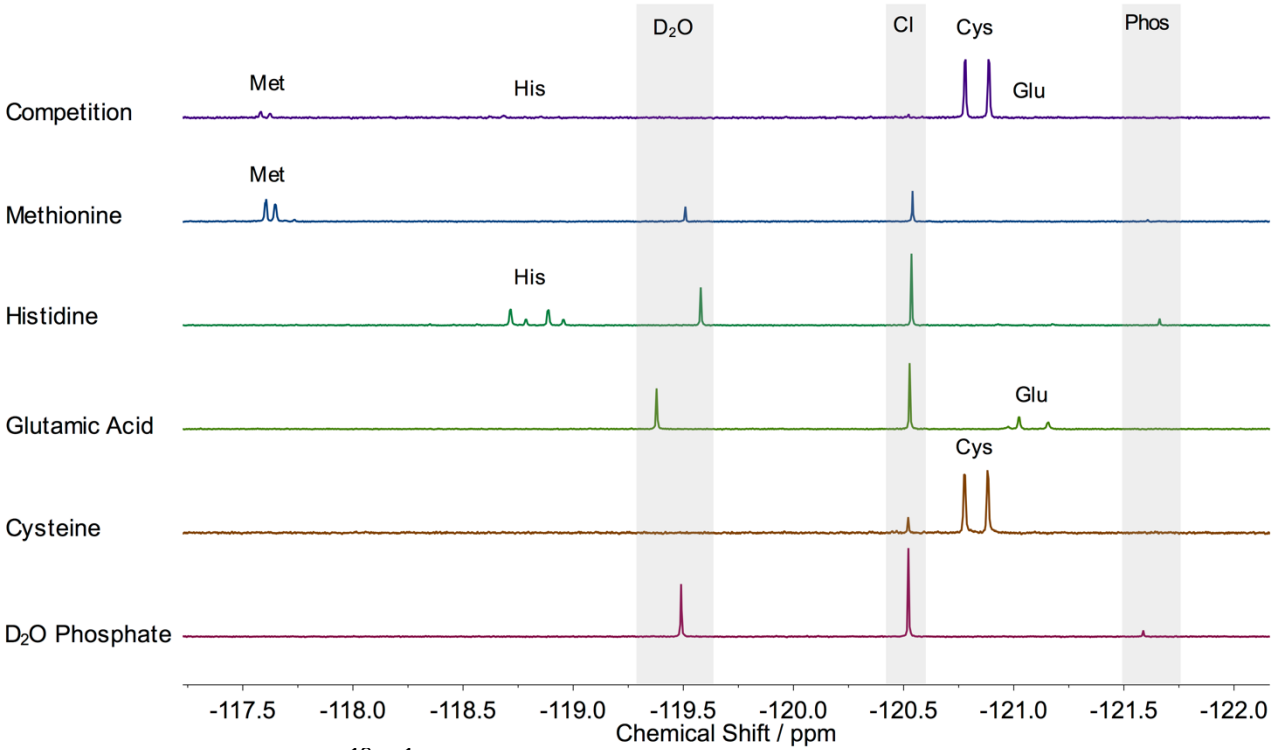


Figure S9. A series of $^{19}F\{^{1}H\}$ NMR spectra when complex [4] is incubated with the protected amino acids, N-Ac-Cys-OMe, N-Z-Glu-OMe, N-Bz-His-OMe, N-Ac-Met-OMe, and a mixture of all amino acids together, (2 mM Ru, 3 eq. amino acid, 24 hr, 310 K).

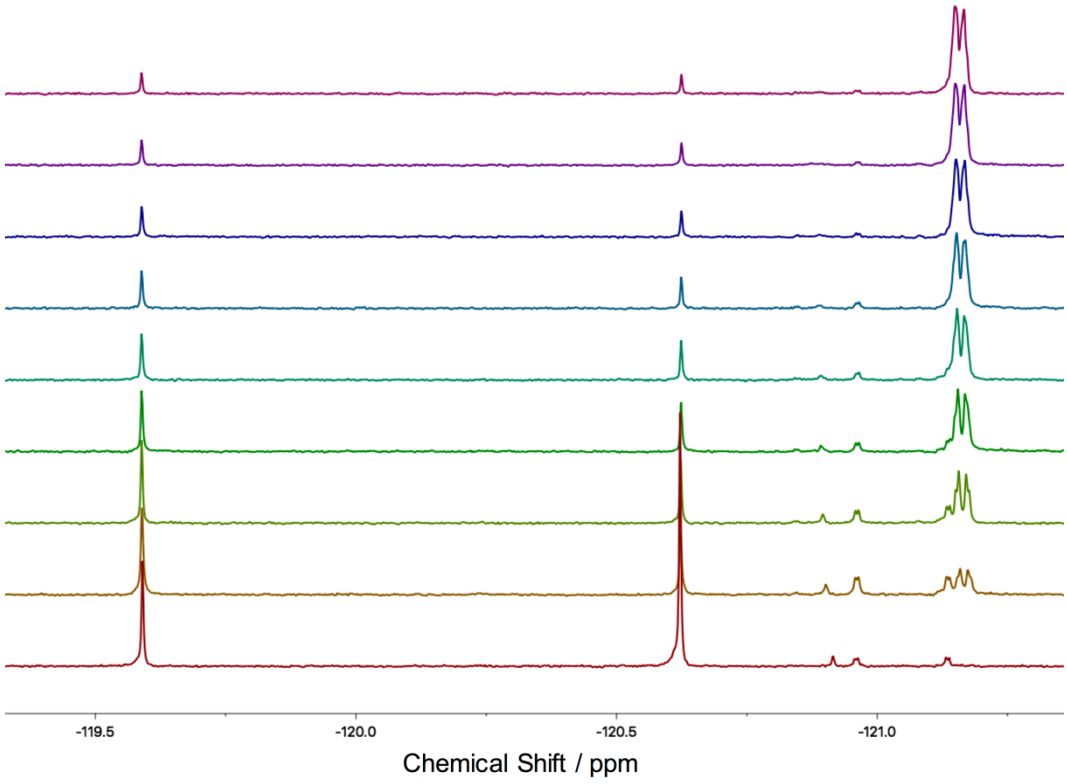


Figure S10. A time series of $^{19}F\{^{1}H\}$ NMR spectra when complex [1] is incubated with N-Ac-Cys-OOH (2 mM Ru, 3 eq. amino acid, 310 K, 0 – 24 hr).

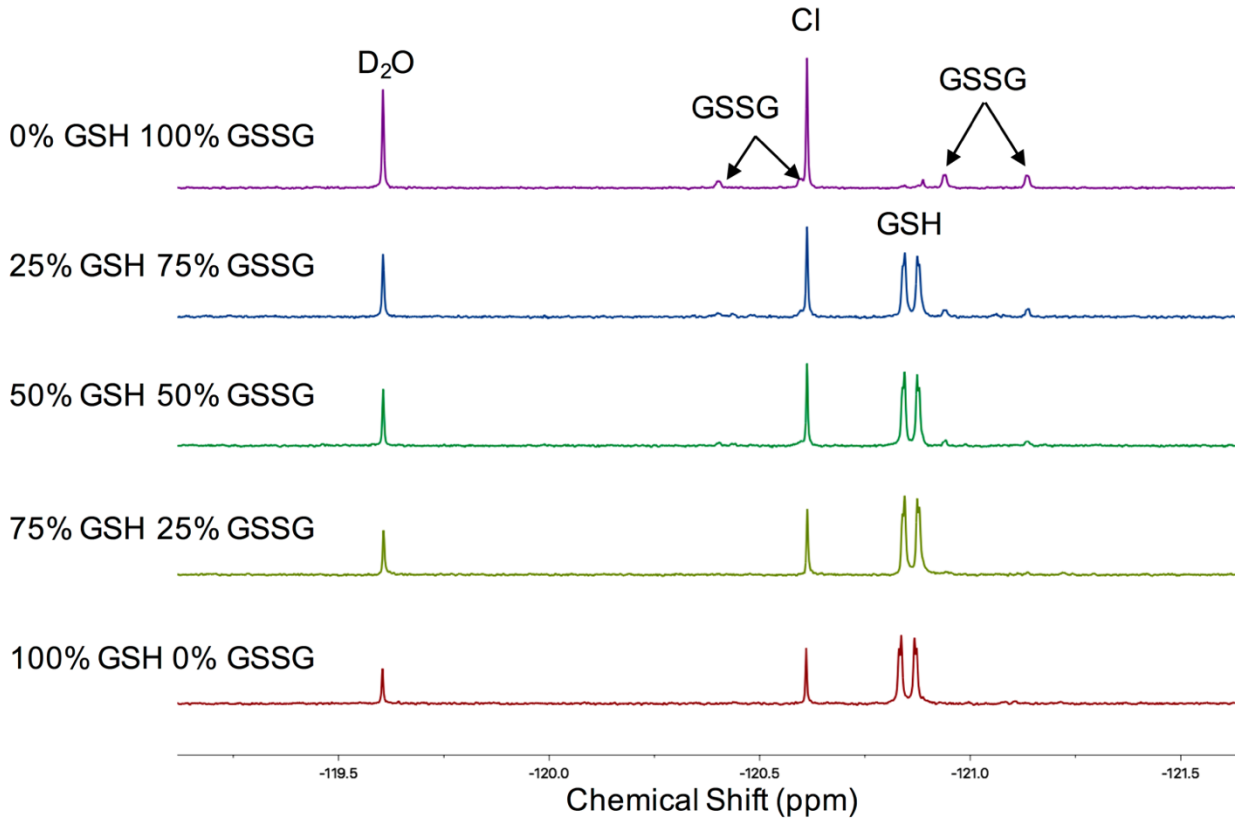


Figure S11. A series of $^{19}F\{^{1}H\}$ NMR spectra when complex [2] is incubated with defined mixtures of reduced and oxidised glutathione (2 mM Ru, 3 eq. glutathione, 24 hr, 310 K).

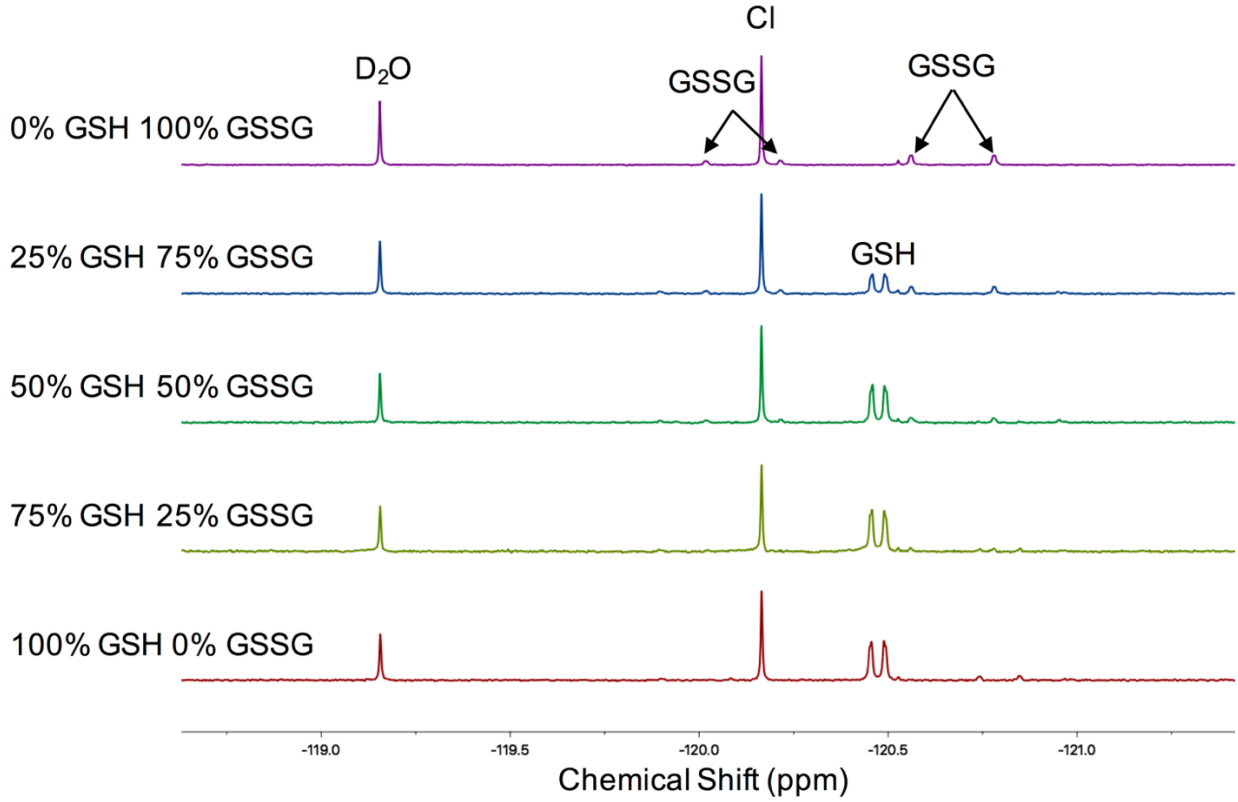


Figure S12. A series of $^{19}F\{^{1}H\}$ NMR spectra when complex [3] is incubated with defined mixtures of reduced and oxidised glutathione (2 mM Ru, 3 eq. glutathione, 24 hr, 310 K).

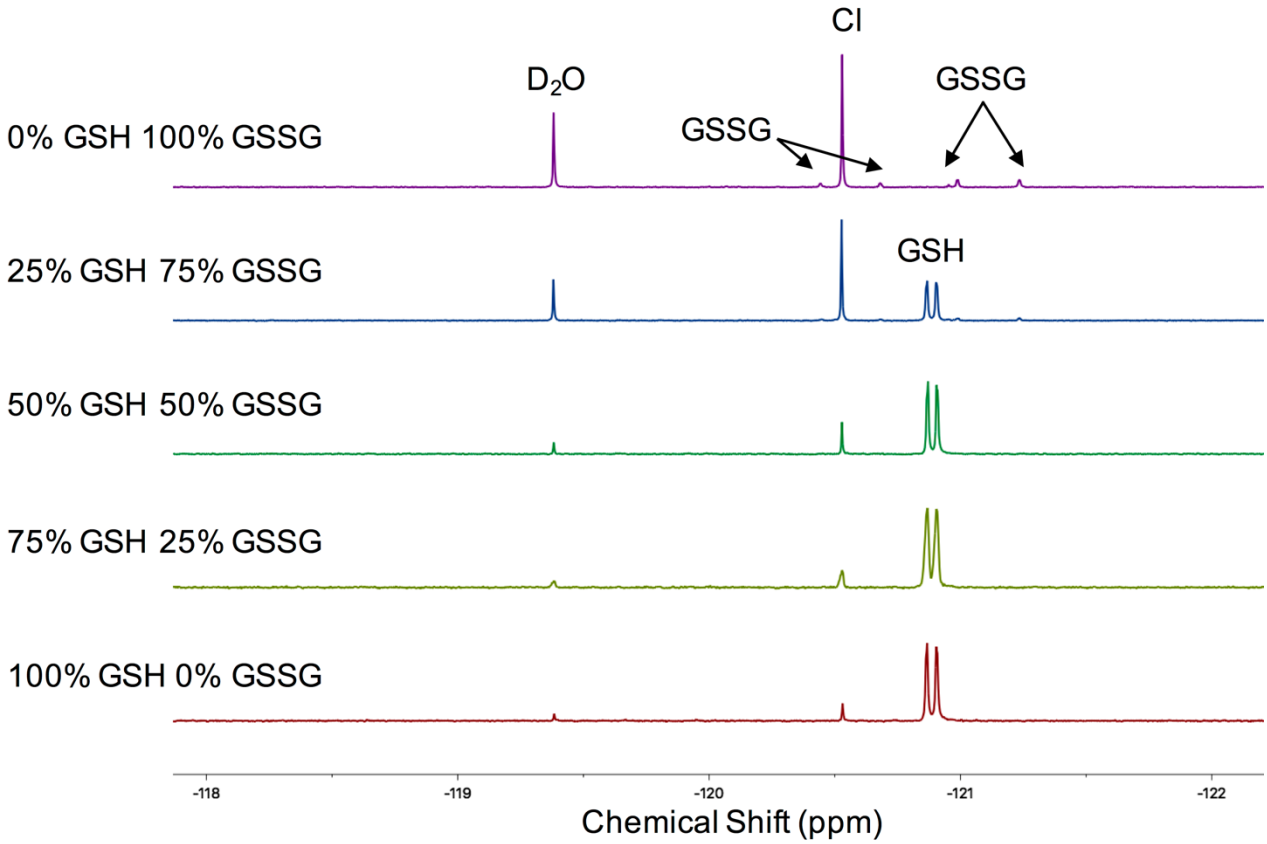


Figure S13. A series of $^{19}F\{^{1}H\}$ NMR spectra when complex [4] is incubated with defined mixtures of reduced and oxidised glutathione (2 mM Ru, 3 eq. glutathione, 24 hr, 310 K).

Table S5. $^{19}F\{^{1}H\}$ NMR chemical shift values of complexes [1], [2], [3], [4], [5] and [7] incubated with N-acetyl cysteine methyl ester (2 mM Ru, 3 eq. amino acid, 24 hr, 310 K).

	Chemical Shift / ppm			
	D_2O	Cl	Cys	Phos
Complex [1]	-119.63	-120.64	-121.04	-121.82
Complex [2]	-119.60	-120.60	-120.86, -120.90	-121.51
Complex [3]	/	-120.15	-120.43, -120.50	/
Complex [4]	/	-120.52	-120.77, -120.88	/
Complex [5]	/	-104.42	-104.16	/
Complex [7]	/	-104.86	-104.72	/

ESI-MS of Ru(II) arene complexes in phosphate buffer

Table S6. ESI-MS data from the incubations of complexes [1] – [4] in deuterated phosphate, focussed on the presence of a phosphate bound ruthenium adduct. Sample diluted into acetonitrile:water 1:1.

Assignment	Molecular Formula	Observed m/z	Theoretical m/z
[1]			
Ru-Cl	$C_{16}H_{12}ClF_2N_2Ru$	406.82	406.97
Ru-Phosphate	$C_{16}H_{14}F_2N_2O_4PRu$	468.77	468.97
[2]			
Ru-Cl	$C_{17}H_{14}ClF_2N_2Ru$	420.83	420.99
Ru-Phosphate	$C_{17}H_{16}F_2N_2O_4PRu$	482.84	482.99
[3]			
Ru-Cl	$C_{20}H_{20}ClF_2N_2Ru$	462.85	463.03
Ru-Phosphate	$C_{20}H_{22}F_2N_2O_4PRu$	524.87	525.03
[4]			
Ru-Cl	$C_{22}H_{24}ClF_2N_2Ru$	490.93	491.06
Ru-Phosphate	$C_{22}H_{26}F_2N_2O_4PRu$	552.96	553.06

ESI-MS of Ru(II) arene complexes with amino acids and glutathione

Table S7. ESI-MS data from the incubations of complexes [1] – [4] with the protected amino acids, N-Ac-Cys-OMe, N-Z-Glu-OMe, N-Bz-His-OMe, N-Ac-Met-OMe and reduced glutathione (2 mM Ru, 3 eq. amino acid, 24 hr, 310 K). Samples are diluted in D_2O, therefore the titratable groups present remain deuterated.

Assignment	Molecular Formula	Observed m/z	Theoretical m/z
[1] with Amino Acids and Glutathione			
Ru-Cl	$C_{16}H_{12}ClF_2N_2Ru$	407.06	406.97
Ru-Cys	$C_{22}H_{21}DF_2N_3O_3RuS$	549.09	549.05
Ru-Glu	$C_{30}H_{27}DF_2N_3O_6Ru$	667.15	667.11
Ru-His	$C_{30}H_{25}D_2F_2N_5O_3Ru$	323.68	323.33
Ru-Met	$C_{24}H_{26}DF_2N_3O_3RuS$	289.10	288.82
Ru-GSH	$C_{26}H_{23}D_5F_2N_5O_6RuS$	683.13	683.11
[2] with Amino Acids and Glutathione			
Ru-Cl	$C_{17}H_{14}ClF_2N_2Ru$	421.18	420.83
Ru-Cys	$C_{23}H_{23}DF_2N_3O_3RuS$	563.01	562.60
Ru-Glu	$C_{31}H_{29}DF_2N_3O_6Ru$	681.07	681.12
Ru-His	$C_{31}H_{27}D_2F_2N_5O_3Ru$	330.79	330.34
Ru-Met	$C_{25}H_{28}DF_2N_3O_3RuS$	296.14	295.83
Ru-GSH	$C_{27}H_{25}D_5F_2N_5O_6RuS$	697.08	697.12
[3] with Amino Acids and Glutathione			
Ru-Cl	$C_{20}H_{20}ClF_2N_2Ru$	462.98	463.03
Ru-Cys	$C_{26}H_{29}DF_2N_3O_3RuS$	605.00	605.11
Ru-Glu	$C_{34}H_{35}DF_2N_3O_6Ru$	722.96	723.17
Ru-His	$C_{34}H_{33}D_2F_2N_5O_3Ru$	350.39	351.60
Ru-Met	$C_{28}H_{34}DF_2N_3O_3RuS$	318.30	317.08
Ru-GSH	$C_{30}H_{31}D_5F_2N_5O_6RuS$	740.31	739.17
[4] with Amino Acids and Glutathione			
Ru-Cl	$C_{22}H_{24}ClF_2N_2Ru$	491.16	491.06
Ru-Cys	$C_{28}H_{33}DF_2N_3O_3RuS$	633.16	633.14
Ru-Glu	$C_{36}H_{39}DF_2N_3O_6Ru$	751.16	751.20
Ru-His	$C_{36}H_{37}D_2F_2N_5O_3Ru$	365.71	365.61
Ru-Met	$C_{30}H_{38}DF_2N_3O_3RuS$	331.28	331.09
Ru-GSH	$C_{32}H_{35}D_5F_2N_5O_6RuS$	768.24	767.20

References

1 M. A. Bennett and A. K. Smith, *J. Chem. Soc. Dalt. Trans.*, 1974, **0**, 233.
2 R. Lalrempuia and M. Rao Kollipara, *Polyhedron*, 2003, **22**, 3155–3160.