

## Supporting Information

### Synthesis and characterisation of **L**<sup>1</sup>:

To a mixture of (bis(2-pyridylmethyl)amino)acetic acid (0.384 g, 1.494 mmol), 1,3-dicyclohexylcarbodiimide (0.338 g, 1.640 mmol), N-hydroxysuccinimide (0.189 g, 1.640 mmol), and dimethylaminopyridine (0.020 g, 0.163 mmol) was added DMF (15 mL) at 0° C. The mixture was warmed to room temperature after 1 hr and then filtered after 6 hrs. To the resulting solution glucosamine·HCl (0.353 g, 1.640 mmol) and triethylamine (0.327 g, 3.232 mmol) were added as a solution in DMF/H<sub>2</sub>O (2 mL/1 mL). The reaction was evacuated after a further 24 hrs and the residue purified by silica gel chromatography (7:3 EtOAc: MeOH eluent) to afford the product as a light yellow solid (0.542 g, 87%).

<sup>1</sup>H NMR (MeOH-*d*<sub>4</sub>, 400.13 MHz): δ 8.54 (d, <sup>3</sup>*J*<sub>13,14</sub> = 4.0 Hz, 2H; H-14), 7.80 (m, 2H; H-12), 7.53 (d, <sup>3</sup>*J*<sub>11,12</sub> = 8.0 Hz, 1.4H; H-11α), 7.49 (d, <sup>3</sup>*J*<sub>11,12</sub> = 8.0 Hz, 0.6H; H-11β), 7.32 (m, 2H; H-13), 5.13 (d, <sup>3</sup>*J*<sub>1',2'</sub> = 2.0 Hz, 0.7H; H-1α), 4.74 (d, <sup>3</sup>*J*<sub>1,2</sub> = 8.0 Hz, 0.3H; H-1β), 3.93 (d, <sup>2</sup>*J*<sub>9a,9b/9'a,9'b</sub> = 15.0 Hz, 2H; H-9a, H-9'a), 3.90 (d, <sup>2</sup>*J*<sub>9a,9b/9'a,9'b</sub> = 15.0 Hz, 2H; H-9'a, H-9'b), 3.85 (m, 2.1H, H-2α, H-3α, H-4α), 3.71 (m, 1.9H; H-2β, H-6αα, H-6bβ, H-3β or H-4β), 3.45 (m, 0.7H; H-5α), 3.32 (m, 2.9H; H-6aβ, H-6bβ, H-8a, H-8b, H-5β, H-3β or H-4β). <sup>13</sup>C{<sup>1</sup>H} NMR (MeOH-*d*<sub>4</sub>, 100.62 MHz): δ 174.41 (C7β), 173.67 (C7α), 159.12 (C10α), 159.07 (C10β), 150.04 (C14β), 150.01 (C14α), 138.68 (C12α), 138.68 (C12β), 125.28 (C11β), 125.11 (C11α), 124.00 (C13α and β), 97.01 (C1β), 92.56 (C1α), 77.98, 75.82 (C3β/C4β), 73.13, 72.83 (C3α/C4α), 72.19 (C5α), 72.04 (C5β), 61.04 (C9), 60.79 (C6α), 59.13 (C6β), 58.92 (C8), 58.46 (C2β), 55.68 (C2α). IR (cm<sup>-1</sup>, thin film, AgBr plate): 3311 (br) (ν(OH)); 2965 (m) (ν(CH)); 1653 (m) (ν(amide I)). +ES-MS *m/z* (relative intensity) = 441 ([M + Na]<sup>+</sup>, 100). Found: C, 53.82; H, 6.30; N, 12.61. Calc. for C<sub>20</sub>H<sub>26</sub>N<sub>4</sub>O<sub>6</sub>·1.5H<sub>2</sub>O: C, 53.92; H, 6.56; N, 12.58.

### Characterisation data for [Re(**L**<sup>1</sup>)(CO)<sub>3</sub>]Br:

<sup>1</sup>H NMR (MeOH-*d*<sub>4</sub>, 400.13 MHz): δ 8.90 (d, <sup>3</sup>*J*<sub>13,14</sub> = 5.7 Hz, 2H; H-14), 7.98 (m, 2H; H-12), 7.59 (m, 2H; H-11), 7.42 (m, 2H; H-13), 5.38 (d, <sup>2</sup>*J*<sub>9a,9b</sub> = 15.6 Hz, 1H; H-9a), 5.28

(d,  $^2J_{9'a,9'b} = 17.4$  Hz, 1H; H-9'a) 5.26 (d,  $^3J_{1',2'} = 3.3$  Hz, 0.7H; H-1 $\alpha$ ), 5.02 (m, 2H; H-9b, H-9'b), 4.73 (m, 2H; H-8a, H-8b), 4.66 (d,  $^3J_{1,2} = 7.6$  Hz, 0.3H; H-1 $\beta$ ), 3.85 (dd,  $^3J_{1',2'} = 3.3$  Hz,  $^3J_{2',3'} = 10.5$  Hz, 0.7H; H-2 $\alpha$ ), 3.92 (dd,  $^3J_{5',6a'} = 2.1$  Hz,  $^2J_{6a',6b'} = 12.0$  Hz, 0.7H; H-6 $\alpha$ ), 3.80 (m, 3H; H-6b $\alpha$ , H-6a $\beta$ , H-6b $\beta$ , H-2 $\beta$ , H-3 $\alpha$ , H-4 $\alpha$ ), 3.35 (m, 0.9H; H-3 $\beta$ , H-4 $\beta$ , H-5 $\beta$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (MeOH- $d_4$ , 100.62 MHz):  $\delta$  196.81, 196.73, 196.19 (*fac*-Re(CO) $_3$ ), 169.70 (C7 $\beta$ ), 169.45 (C7 $\alpha$ ), 162.71, 162.35, 162.33, 162.07 (C10), 153.19, 153.08 (C14), 141.73 (C12), 126.97, 126.93, 126.79 (C11), 124.82, 124.75, 124.54 (C13), 96.89 (C1 $\beta$ ), 92.58 (C1 $\alpha$ ), 78.08, 75.94 (C3 $\beta$ /C4 $\beta$ ), 73.12, 72.80, 72.43 (C3 $\alpha$ /C4 $\alpha$ /C5 $\alpha$ ), 72.08 (C5 $\beta$ ), 70.44, 69.98, 69.60, 69.50 (C8 $\alpha$ , C8 $\beta$ , C9, C9'), 62.74, 62.70 (C6 $\alpha$ /C6 $\beta$ ), 58.36 (C2 $\beta$ ), 55.64 (C2 $\alpha$ ). IR (cm $^{-1}$ , thin film, AgBr plate). 3390 (br) ( $\nu$ (OH)); 2960 (m) ( $\nu$ (CH)); 2030 (vs), 1922 (vs) ( $\nu$ (*fac*-Re(CO) $_3$ )); 1665 (w) ( $\nu$ (amide I)). +ES-MS  $m/z$  (relative intensity) = 689, 687 ([M] $^+$ , 100).  $\Lambda_M = 145$   $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$  (1:1 electrolyte). Found: C, 35.34; H, 3.61; N, 7.09. Calc. for [C $_{23}$ H $_{26}$ N $_4$ O $_9$ Re]Br·H $_2$ O: C, 35.12; H, 3.59; N, 7.12.