SUPPLEMENTARY INFORMATION

Synthesis and anticancer activity of carbosilane metallodendrimers based on arene ruthenium (II) complexes.

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*1. Synthesis of dendritic ligands **3, 6** and **9** and NMR spectra data*

Second generation dendrimers. G_2-[NCPh(*p*-N)]$_8$ (**3**), G_2-[NCPh(*o*-N)]$_8$ (**6**) and G_2-[NCPh(*o*-OH)]$_8$ (**9**).

To a solution of G_2-[NH_2]$_8$ (240 mg, 0.14 mmol) in THF, the corresponding aldehyde, 4-pyridinecarboxaldehyde (127.3 mg, 1.19 mmol) for (**3**), 2-pyridinecarboxaldehyde (127.3 mg, 1.19 mmol) for (**6**), and salicylaldehyde (145.1 mg, 1.19 mmol) for (**9**) was added. The mixture was stirred under inert atmosphere at room temperature in the presence of anhydrous $MgSO_4$ for 24 hour. Afterwards, the solvent was rotary evaporated to give an oil that was purified by size exclusion chromatography.

G_2-[NCPh(*p*-N)]$_8$ (**3**). Yellow pale oil, yield 250 mg (72%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = -0.13 (s, 12H, -C**H**$_3$SiCH$_2$CH$_2$CH$_2$Si); -0.07 (s, 48H, -(C**H**$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 0.48 (overlapping br m, 64H, -SiC**H**$_2$CH$_2$C**H**$_2$Si, -CH$_3$SiC**H**$_2$CH$_2$C**H**$_2$Si and -(CH$_3$)$_2$SiC**H**$_2$CH$_2$CH$_2$N); 1.25 (overlapping br m, 24H, -SiCH$_2$C**H**$_2$CH$_2$Si and -CH$_3$SiCH$_2$C**H**$_2$CH$_2$Si), 1.65 (br m, 16H, -(CH$_3$)$_2$SiCH$_2$C**H**$_2$CH$_2$N); 3.59 (t, $^3J_{(H-H)}$ = 6.8 Hz, 16H, -(CH$_3$)$_2$SiCH$_2$CH$_2$C**H**$_2$N); 7.54 (m, 16H, Ar); 8.63 (m, 16H, Ar); 8.20 (s, 8H, -C**H**$_{imine}$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) = -4.8 (-(**C**H$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); -3.2 (-**C**H$_3$SiCH$_2$CH$_2$CH$_2$Si); 13.2 (-(CH$_3$)$_2$Si**C**H$_2$CH$_2$CH$_2$N); 18.6, 18.7, 18.9, 20.1 (-Si**C**H$_2$**C**H$_2$**C**H$_2$Si and -CH$_3$Si**C**H$_2$**C**H$_2$**C**H$_2$Si); 25.4 (-(CH$_3$)$_2$SiCH$_2$**C**H$_2$CH$_2$N); 65.4 (-(CH$_3$)$_2$SiCH$_2$CH$_2$**C**H$_2$N); 122.0, 143.1, 150.5 (**C**$_{Ar}$); 158.9 (-**C**H$_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = -**Si**CH$_2$CH$_2$CH$_2$Si is not observed; 0.85 (-CH$_3$**Si**CH$_2$CH$_2$CH$_2$Si); 1.88 (-(CH$_3$)$_2$**Si**CH$_2$CH$_2$CH$_2$N). ^{15}N NMR ($CDCl_3$): δ (ppm) = -64.5 (**N**$_{pyr}$); -32.2

($\mathbf{N}_{imine}$). Elemental Analysis (%): Calc. For $C_{128}H_{220}N_{16}Si_{13}$ (2348.34): C, 65.27; H, 9.44; N, 9.54; Found: C, 64.98; H, 9.33; N, 9.26.

G_2-[NCPh(*o*-N)]$_8$ (**6**). Brown oil, yield 273 mg (79%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = -0.11 (s, 12H, -C**H**$_3$SiCH$_2$CH$_2$CH$_2$Si); -0.05 (s, 48H, -(C**H**$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 0.53 (overlapping br m, 64H, -SiC**H**$_2$CH$_2$C**H**$_2$Si, -CH$_3$SiC**H**$_2$CH$_2$C**H**$_2$Si and -(CH$_3$)$_2$SiC**H**$_2$CH$_2$CH$_2$N); 1.28 (overlapping br m, 24H, -SiCH$_2$C**H**$_2$CH$_2$Si and -CH$_3$SiCH$_2$C**H**$_2$CH$_2$Si); 1.69 (br m, 16H, -(CH$_3$)$_2$SiCH$_2$C**H**$_2$CH$_2$N); 3.63 (t, $^3J_{(H-H)}$ = 7.0 Hz, 16H, -(CH$_3$)$_2$SiCH$_2$CH$_2$C**H**$_2$N); 7.28 (m, 8H, Ar); 7.71 (m, 8H, Ar); 7.97 (m, 8H, Ar); 8.62 (m, 8H, Ar); 8.35 (s, 8H, -C**H**$_{imine}$). ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) = -4.8 (-(**C**H$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); -3.2 (-**C**H$_3$SiCH$_2$CH$_2$CH$_2$Si); 13.2 (-(CH$_3$)$_2$Si**C**H$_2$CH$_2$CH$_2$N); 18.6, 18.7, 18.9, 20.2 (-Si**C**H$_2$**C**H$_2$**C**H$_2$Si$_{core}$ and -CH$_3$Si**C**H$_2$**C**H$_2$**C**H$_2$Si); 25.5 (-(CH$_3$)$_2$SiCH$_2$**C**H$_2$CH$_2$N); 65.1 (-(CH$_3$)$_2$SiCH$_2$CH$_2$**C**H$_2$N); 121.3, 124.7, 136.6, 149.5, 161.8 (C$_{Ar}$); 154.8 (-**C**H$_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = -**Si**CH$_2$CH$_2$CH$_2$Si is not observed; 0.90 (-CH$_3$**Si**CH$_2$CH$_2$CH$_2$Si); 1.90 (-(CH$_3$)$_2$**Si**CH$_2$CH$_2$CH$_2$N). ^{15}N NMR ($CDCl_3$): δ (ppm) = -67.4 ($\mathbf{N}_{pyr}$); -38.0 ($\mathbf{N}_{imine}$). Elemental Analysis (%): Calc. For $C_{128}H_{220}N_{16}Si_{13}$ (2348.34): C, 65.47; H, 9.44; N, 9.54; Found: C, 65.04; H, 8.96; N, 9.72.

G_2-[NCPh(*o*-OH)]$_8$ (**9**). Yellow oil, yield 306 g (84%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = = -0.09 (s, 12H, -C**H**$_3$SiCH$_2$CH$_2$CH$_2$Si) ; -0.04 (s, 48H, -(C**H**$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 0.54 (overlapping br m, 64H, -SiC**H**$_2$CH$_2$C**H**$_2$Si, -CH$_3$SiC**H**$_2$CH$_2$C**H**$_2$Si and -(CH$_3$)$_2$SiC**H**$_2$CH$_2$CH$_2$N); 1.27 (overlapping br m, 24H, -SiCH$_2$C**H**$_2$CH$_2$Si and -CH$_3$SiCH$_2$C**H**$_2$CH$_2$Si); 1.66 (br m, 16H, -(CH$_3$)$_2$SiCH$_2$C**H**$_2$CH$_2$N); 3.55 (t, $^3J_{(H-H)}$ = 6.5 Hz, 16H, -(CH$_3$)$_2$SiCH$_2$CH$_2$C**H**$_2$N); 6.85 (m, 8H, Ar); 6.94 (m, 8H, Ar); 7.26 (m, 16H, Ar); 8.30 (s, 8H, -C**H**$_{imine}$); -OH is not observed. ^{13}C{^{1}H}-NMR ($CDCl_3$): δ (ppm) = -4.8 (-**C**$H_3)_2SiCH_2CH_2CH_2N$); -3.2 (-**C**$H_3SiCH_2CH_2CH_2Si$); 13.0 (-$(CH_3)_2Si$**C**$H_2CH_2CH_2N$); 18.6, 18.7, 18.9, 20.1 (-Si**C**H_2**C**H_2**C**H_2Si and -CH_3Si**C**H_2**C**H_2**C**H_2Si); 25.7 (-$(CH_3)_2SiCH_2$**C**H_2CH_2N); 62.9 (-$(CH_3)_2SiCH_2CH_2$**C**H_2N); 117.2, 118.5, 118.9, 131.2, 132.2, 164.6 (**C**$_{Ar}$); 161.6 (-**C**H_{imine}). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = -**Si**$CH_2CH_2CH_2Si$ is not observed; 0.97 (-CH_3**Si**$CH_2CH_2CH_2Si$); 2.00 (-$(CH_3)_2$**Si**$CH_2CH_2CH_2N$). ^{15}N NMR ($CDCl_3$): δ (ppm) = -82.9 (**N**$_{imine}$). Elemental Analysis (%): Calc. For $C_{136}H_{228}N_8O_8Si_{13}$ (2468.43): C, 66.17; H, 9.31; N, 4.54; Found: C, 65.78; H, 9.19; N, 4.95.

2. *Synthesis and characterization of carbosilane metallodendrimers based on arene ruthenium (II) complexes* **13-15** *and* **19-21**

Neutral N- metallodendrimers. G_{0}-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_{1}$ (**13**), G_{1}-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_{4}$ (**14**) and G_{2}-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_{8}$ (**15**).

To a solution of the dendritic ligand (86.5 mg, 0.33 mmol of G_{0}-[NCPh(*p*-N)]$_{1}$; 95 mg, 0.09 mmol of G_{1}-[NCPh(*p*-N)]$_{4}$; 96.8 mg, 0.04 mmol of G_{2}-[NCPh(*p*-N)]$_{8}$) in dichlorometane was slowly added the dimer [Ru(η^6-*p*-cymene)Cl_2]$_2$ (101 mg, 0.16 mmol for G_{0}-[NCPh(*p*-N)Ru(η^6-*p*-cymene)]$_{1}$ (**13**); 114 mg, 0.19 mmol for G_{1}-[NCPh(*p*-N)Ru(η^6-*p-cymene*)]$_{4}$ (**14**) and 101 mg, 0.16 mmol for G_{2}-[NCPh(*p*-N)Ru(η^6-*p*-cymene)]$_{8}$ (**15**). The reaction was allowed to stir at room temperature for 5h. The mixture solution was concentrated, and the product, a yellow-orange solid, was precipitated with diethyl ether and dried *in vacuo*.

G_{0}-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_{1}$ (**13**). Yellow-orange solid, yield 102 mg (55%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.52 (overlapping m, 8H, -Si(C**H**$_2$CH$_3$)$_3$ and -SiC**H**$_2$CH$_2$); 0.92 (m, 9H, -Si(CH$_2$C**H**$_3$)$_3$); 1.30 (d, $^3J_{(H-H)}$ = 6.9 Hz, 6H, -(C**H**$_3$)$_2$CH$_{cye}$); 1.68 (m, 2H, -SiCH$_2$C**H**$_2$CH$_2$N); 2.09 (s, 3H, -C**H**$_{3cye}$); 2.98 (m, 1H, -(CH$_3$)$_2$C**H**$_{cye}$); 3.66 (t, $^3J_{(H-H)}$ = 6.6 Hz, 2H, -SiCH$_2$CH$_2$C**H**$_2$N); 5.22 (d, $^3J_{(H-H)}$ = 6.0 Hz, 2H, Ar$_{cye}$); 5.44 (d, $^3J_{(H-H)}$ = 6.0 Hz, 2H, Ar$_{cye}$); 7.59 (m, 2H, Ar); 9.08 (m, 2H, Ar); 8.25 (s, 1H, -C**H**$_{imine}$). ^{13}C {^{1}H}-NMR ($CDCl_3$): δ (ppm) = 3.4 (-Si(CH$_2$**C**H$_3$)$_3$); 7.6 (-Si(**C**H$_2$CH$_3$)$_3$); 9.1 (-Si**C**H$_2$CH$_2$); 18.4 (-**C**H$_{3cye}$); 22.4 (-(**C**H$_3$)$_2$CH$_{cye}$); 25.3 (-SiCH$_2$**C**H$_2$CH$_2$N); 30.8 (-(CH$_3$)$_2$**C**H$_{cye}$); 65.6 (-SiCH$_2$CH$_2$**C**H$_2$N); 82.3, 83.2 (-**C**H$_{cye}$); 97.4, 103.7 (**C**$_{cye}$); 122.6, 144.6, 155.4 (**C**Ar); 157.4 (-**C**H$_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = 7.11 (-**Si**(CH$_2$CH$_3$)$_3$). Elemental

Analysis (%): Calc. For $C_{25}H_{40}Cl_2N_2RuSi$ (568.66): C, 57.68; H, 7.71; N, 2.49; Found: C, 57.76; H, 7.42; N, 2.57.

G_1-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_4$ (**14**). Yellow-orange solid, yield 74.8 mg (55%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = -0.04 (br s, 24H, -(C**H**$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 0.54 (overlapping m, 24H, -SiC**H**$_2$CH$_2$C**H**$_2$Si and -SiC**H**$_2$CH$_2$CH$_2$N); 1.30 (overlapping br m, 32H, -(C**H**$_3$)$_2$CH$_{cye}$ and -SiCH$_2$C**H**$_2$CH$_2$Si); 1.66 (br m, 8H, -SiCH$_2$C**H**$_2$CH$_2$N); 2.07 (s, 12H, -C**H**$_{3cye}$); 2.97 (br m, 4H, -(CH$_3$)$_2$C**H**$_{cye}$); 3.63 (br m, 8H, -SiCH$_2$CH$_2$C**H**$_2$N); 5.24 (m, 8H, Ar$_{cye}$); 5.46 (m, 8H, Ar$_{cye}$); 7.55 (m, 8H, Ar); 9.04 (m, 8H, Ar); 8.20 (s, 4H, -C**H**$_{imine}$). ^{13}C {^{1}H}-NMR ($CDCl_3$): δ (ppm) = -3.1 (-(**C**H$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 13.2 (-Si**C**H$_2$CH$_2$CH$_2$N); 17.5, 18.3, 18.6 (-Si**C**H$_2$**C**H$_2$**C**H$_2$Si); 20.3 (-**C**H$_{3cye}$); 22.5 (-(**C**H$_3$)$_2$CH$_{cye}$); 25.4 (-SiCH$_2$**C**H$_2$CH$_2$N); 30.3 (-(CH$_3$)$_2$**C**H$_{cye}$); 65.4 (-SiCH$_2$CH$_2$**C**H$_2$N); 82.3, 83.3 (-**C**H$_{cye}$); 97.4, 103.6 (**C**$_{cye}$); 122.7, 144.5, 155.4 (**C**Ar); 157.6 (-**C**H$_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = 0.60 (-**Si**CH$_2$CH$_2$CH$_2$Si), 2.00 (-(CH$_3$)$_2$**Si**CH$_2$CH$_2$CH$_2$N). Elemental Analysis (%): Calc. For $C_{96}H_{148}Cl_8N_8Ru_4Si_5$ (2242.59): C, 51.42; H, 6.65; N, 5.00; Found: C, 51.35; H, 6.49; N, 4.67.

G_2-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_8$ (**15**). Yellow-orange solid, yield 89.6 mg (45%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = -0.09 (s, 12H, -C**H**$_3$SiCH$_2$CH$_2$CH$_2$Si); -0.03 (s, 48H, -(C**H**$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 0.54 (overlapping br m, 64H, -SiC**H**$_2$CH$_2$C**H**$_2$Si, -CH$_3$SiC**H**$_2$CH$_2$C**H**$_2$Si and -(CH$_3$)$_2$SiC**H**$_2$CH$_2$CH$_2$N); 1.29 (overlapping br m, 72H, -SiCH$_2$C**H**$_2$CH$_2$Si, -CH$_3$SiCH$_2$C**H**$_2$CH$_2$Si and -(C**H**$_3$)$_2$CH$_{cye}$); 1.66 (br m, 16H, -(CH$_3$)$_2$SiCH$_2$C**H**$_2$CH$_2$N); 2.06 (s, 24H, -C**H**$_{3cye}$); 2.97 (br m, 8H, -(CH$_3$)$_2$C**H**$_{cye}$); 3.63 (br m, 16H, -(CH$_3$)$_2$SiCH$_2$CH$_2$C**H**$_2$N); 5.24 (br m, 16H, Ar$_{cye}$); 5.45 (br m, 16H, Ar$_{cye}$); 7.56 (br m, 16H, Ar); 9.05 (br m, 16H, Ar); 8.22 (br s, 8H, -C**H**$_{imine}$). ^{13}C

{^{1}H}-NMR ($CDCl_3$): δ (ppm) = -4.7 (-(**C**$H_3)_2SiCH_2CH_2CH_2N$); -3.1 (-**C**$H_3SiCH_2CH_2CH_2Si$); 13.3 (-$(CH_3)_2Si$**C**$H_2CH_2CH_2N$); 18.4, 18.6, 19.0, 20.1 (-Si**C**H_2**C**H_2**C**H_2Si, -CH_3Si**C**H_2**C**H_2**C**H_2Si and -**C**H_{3cye}); 22.5 (-(**C**$H_3)_2CH_{cye}$); 25.4 (-$(CH_3)_2SiCH_2$**C**H_2CH_2N); 30.8 (-$(CH_3)_2$**C**H_{cye}); 65.4 (-$(CH_3)_2SiCH_2CH_2$**C**H_2N); 82.3, 83.3 (-**C**H_{cye}); 97.5 (**C**$_{cye}$) 122.7, 144.6, 155.4 (**C**Ar); 157.6 (-**C**H_{imine}). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = -**Si**$CH_2CH_2CH_2$Si is not observed; 0.88 (-CH_3**Si**$CH_2CH_2CH_2Si$); 2.06 (-$(CH_3)_2$**Si**$CH_2CH_2CH_2N$). Elemental Analysis (%): Calc. For $C_{208}H_{332}Cl_{16}N_{16}Ru_8Si_{13}$ (4797.89): C, 52.07; H, 6.97; N, 4.67; Found: C, 52.43; H, 7.08; N, 4.75.

Chelating N,O- neutral metallodendrimers. G_0-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_1$ (**19**), G_1-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_4$ (**20**) and G_2-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_8$ (**21**).

To a solution of *N,O*-Schiff base dendrimer (90.6 mg, 0.32 mmol of G_0-[NCPh(*o*-OH)]$_1$; 96.0 mg, 0.09 mmol of G_1-[NCPh(*o*-OH)]$_4$, 100.0 mg, 0.04 for G_2-[NCPh(*o*-OH)]$_8$) in dry ethanol, was added triethylamine (34.60 mg, 0.36 mmol for G_0-[NCPh(*o*-OH)]$_1$; 36.95 mg, 0.36 mmol for G_1-[NCPh(*o*-OH)]$_4$; 34.63 mg, 0.34 mmol for G_2-[NCPh(*o*-OH)]$_8$. The yellow suspension was stirred at room temperature for 30 mins. Immediately, [Ru(η^6-*p*-cymene)$Cl_2]_2$ (101 mg, 0.16 mmol for G_0-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_1$ (**19**); 109 mg, 0.18 mmol for G_1-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_4$ (**20**) and 99.2 mg, 0.16 mmol for G_2-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_8$ (**21**) was added to the reaction mixture and allowed to stir overnight at room temperature. The solvent was evaporated under reduced pressure and the resulting solid was purified by an extraction of CH_2Cl_2/H_2O. Then, the organic phase was dried over $MgSO_4$ and the solution was filtered and evaporated. The G_1-[NCPh(*o*-

O)Ru(η^6-*p*-cymene)Cl]$_4$ and G_2-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_8$ complexes were purified by sized exclusion chromatography.

G_0-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_1$ (**19**). Brown solid, 144 mg (81%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.56 (overlapping m, 8H, -Si(C**H**$_2$CH$_3$)$_3$ and -SiC**H**$_2$CH$_2$); 0.95 (m, 9H, -Si(CH$_2$C**H**$_3$)$_3$); 1.12 (d, $^3J_{(H\text{-}H)}$ = 6.9 Hz, 3H, -(C**H**$_3$)$_2$CH$_{cye}$); 1.23 (d, $^3J_{(H\text{-}H)}$ = 6.9 Hz, 3H, -(C**H**$_3$)$_2$CH$_{cye}$); 1.83 (br m, 1H, -SiCH$_2$C**H**$_2$CH$_2$N); 2.07 (br m, 1H, -SiCH$_2$C**H**$_2$CH$_2$N); 2.19 (s, 3H, -C**H**$_{3cye}$); 2.77 (m, 1H, -(CH$_3$)$_2$C**H**$_{cye}$); 4.00 (br m, 1H, -SiCH$_2$CH$_2$C**H**$_2$N); 4.20 (br m, 1H, -SiCH$_2$CH$_2$C**H**$_2$N); 5.01 (m, 1H, Ar$_{cye}$); 5.37 (m, 3H, Ar$_{cye}$); 6.39 (m, 1H, Ar); 6.92 (m, 2H, Ar); 7.13 (m, 1H, Ar); 7.66 (s, 1H, -C**H**$_{imine}$). ^{13}C {^{1}H}-NMR ($CDCl_3$): δ (ppm) = 3.3 (-Si(CH$_2$**C**H$_3$)$_3$); 7.6 (-Si(**C**H$_2$CH$_3$)$_3$); 9.1 (-Si**C**H$_2$CH$_2$); 18.6 (-**C**H$_{3cye}$); 21.8, 22.9 (-(**C**H$_3$)$_2$CH$_{cye}$); 26.0 (-SiCH$_2$**C**H$_2$CH$_2$N); 30.6 (-(CH$_3$)$_2$**C**H$_{cye}$); 73.1 (-SiCH$_2$CH$_2$**C**H$_2$N); 80.2, 82.1, 83.2, 85.9 (-**C**H$_{cye}$); 97.4, 101.6 (**C**$_{cye}$); 114.1, 119.3, 122.4, 134.4, 134.6, 163.4 (**C**Ar); 165.0 (-**C**H$_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = 7.10 (-**Si**(CH$_2$CH$_3$)$_3$). Elemental Analysis (%): Calc. For $C_{26}H_{40}ClNORuSi$ (547.24): C, 57.07; H, 7.37; N, 2.56; Found: C, 57.39; H, 7.20; N, 2.83.

G_1-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_4$ (**20**). Brown solid, yield 136 mg (70%). ^{1}H-NMR ($CDCl_3$): δ (ppm) = 0.01 (br s, 24H, -(C**H**$_3$)$_2$SiCH$_2$CH$_2$CH$_2$N); 0.59 (overlapping m, 24H, -SiC**H**$_2$CH$_2$C**H**$_2$Si and -SiC**H**$_2$CH$_2$CH$_2$N); 1.10 (m, 12H, -(C**H**$_3$)$_2$CH$_{cye}$); 1.23 (m, 12H, -(C**H**$_3$)$_2$CH$_{cye}$); 1.28 (br m, 8H, -SiCH$_2$C**H**$_2$CH$_2$S*i*); 1.82 (br m, 4H, -SiCH$_2$C**H**$_2$CH$_2$N); 2.03 (br m, 4H, -SiCH$_2$C**H**$_2$CH$_2$N); 2.19 (s, 12H, -C**H**$_{3cye}$); 2.74 (br s, 4H, -(CH$_3$)$_2$C**H**$_{cye}$); 3.96 (br m, 4H, -SiCH$_2$CH$_2$C**H**$_2$N); 4.24 (br m, 4H, -SiCH$_2$CH$_2$C**H**$_2$N); 5.01 (m, 4H, Ar$_{cye}$); 5.38 (m, 12H, Ar$_{cye}$); 6.40 (m, 4H, Ar); 6.92 (m, 8H, Ar); 7.12 (m, 4H, Ar); 7.66 (s, 4H, -C**H**$_{imine}$). ^{13}C {^{1}H}-NMR

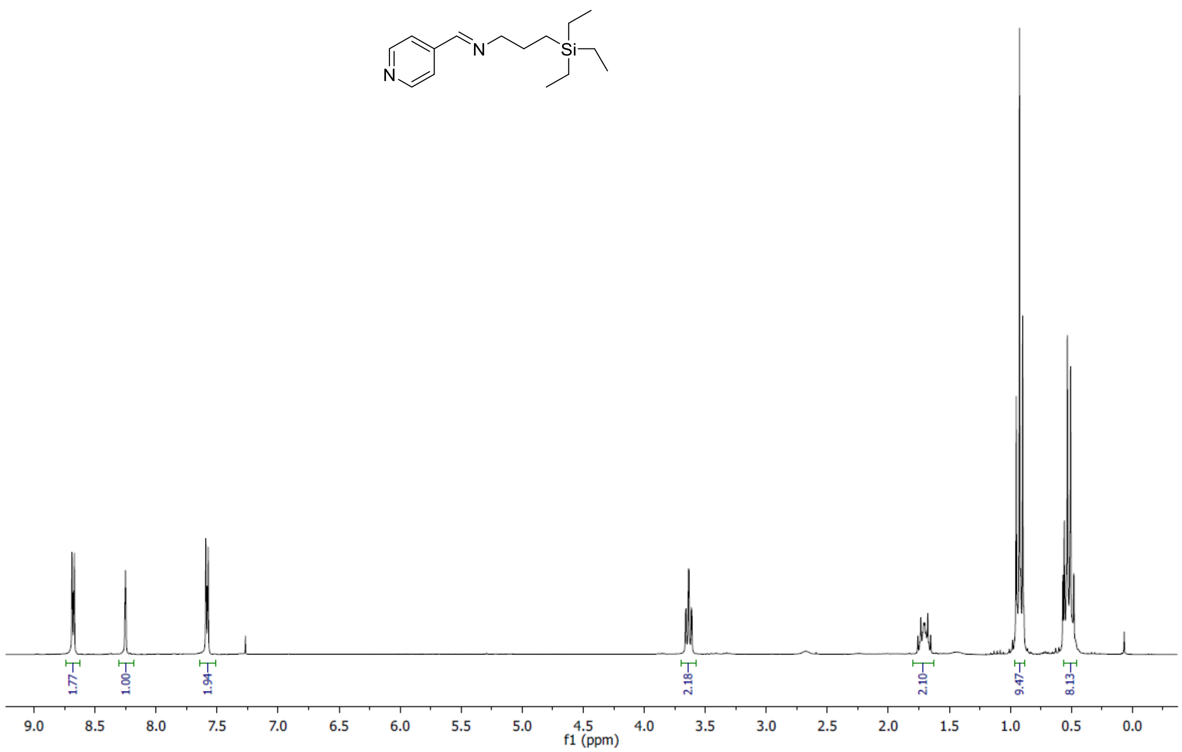
($CDCl_3$): δ (ppm) = -3.1 ($-(\mathbf{C}H_3)_2SiCH_2CH_2CH_2N$); 13.0 ($-Si\mathbf{C}H_2CH_2CH_2N$); 17.6, 18.6, 18.7 ($-Si\mathbf{C}H_2\mathbf{C}H_2\mathbf{C}H_2Si$ and $-\mathbf{C}H_{3\mathit{cye}}$); 21.7, 22.9 ($-(\mathbf{C}H_3)_2CH_{\mathit{cye}}$); 25.9 ($-SiCH_2\mathbf{C}H_2CH_2N$); 30.6 ($-(CH_3)_2\mathbf{C}H_{\mathit{cye}}$); 73.0 ($-SiCH_2CH_2\mathbf{C}H_2N$); 80.2, 82.2, 83.4, 86.1 ($-\mathbf{C}H_{\mathit{cye}}$); 97.3, 101.5 ($\mathbf{C}_{\mathit{cye}}$); 114.1, 119.3, 122.3, 134.6, 163.3 (**C**Ar); 164.9 ($-\mathbf{C}H_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = 0.60 ($-\mathbf{Si}CH_2CH_2CH_2Si$); 2.01 ($-(CH_3)_2\mathbf{Si}CH_2CH_2CH_2N$). Elemental Analysis (%): Calc. For $C_{100}H_{148}Cl_4N_4O_4Ru_4Si_5$ (2156.79): C, 55.59; H, 6.62; N, 2.70; Found: C, 55.93; H, 6.89; N, 2.58.

G_2-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_8$ (**21**). Brown-red solid, yield 126 mg (68%). ^1H-NMR ($CDCl_3$): δ (ppm) = -0.06 (br s, 48H, $-(C\mathbf{H}_3)_2SiCH_2CH_2CH_2N$); 0.02 (br s, 12H, $-C\mathbf{H}_3SiCH_2CH_2CH_2Si$); 0.57 (overlapping br m, 64H, $-SiC\mathbf{H}_2CH_2C\mathbf{H}_2Si$, $-CH_3SiC\mathbf{H}_2CH_2C\mathbf{H}_2Si$ and $-(CH_3)_2SiC\mathbf{H}_2CH_2CH_2N$); 1.10 (br m, 24H, $-(C\mathbf{H}_3)_2CH_{\mathit{cye}}$); 1.25 (overlapping br m, 72H, $-SiCH_2C\mathbf{H}_2CH_2Si$, $-CH_3SiCH_2C\mathbf{H}_2CH_2Si$ and $-(C\mathbf{H}_3)_2CH_{\mathit{cye}}$); 1.82 (br m, 8H, $-(CH_3)_2SiCH_2C\mathbf{H}_2CH_2N$); 2.03 (br m, 8H, $-(CH_3)_2SiCH_2C\mathbf{H}_2CH_2N$); 2.19 (s, 24H, $-C\mathbf{H}_{3\mathit{cye}}$); 2.75 (br s, 8H, $-(CH_3)_2C\mathbf{H}_{\mathit{cye}}$); 3.94 (br m, 8H, $-SiCH_2CH_2C\mathbf{H}_2N$); 4.23 (br m, 8H, $-SiCH_2CH_2C\mathbf{H}_2N$); 5.00 (m, 8H, Ar_{cye}); 5.38 (m, 24H, Ar_{cye}); 6.39 (br s, 8H, Ar); 6.91 (overlapping m, 16H, Ar); 7.13 (br s, 8H, Ar); 7.66 (s, 8H, $-C\mathbf{H}_{imine}$). $^{13}C\{^1H\}$-NMR ($CDCl_3$): δ (ppm) = -4.7 ($-(\mathbf{C}H_3)_2SiCH_2CH_2CH_2N$); -3.0 ($-\mathbf{C}H_3SiCH_2CH_2CH_2Si$); 13.1 ($-(CH_3)_2Si\mathbf{C}H_2CH_2CH_2N$); 17.9, 18.6, 18.8, 19.0, 19.3, 20.2, 21.8 ($-Si\mathbf{C}H_2\mathbf{C}H_2\mathbf{C}H_2Si$, $-CH_3Si\mathbf{C}H_2\mathbf{C}H_2\mathbf{C}H_2Si$ and $-\mathbf{C}H_{3\mathit{cye}}$); 23.0, 25.9 ($-(\mathbf{C}H_3)_2CH_{\mathit{cye}}$); 29.8 ($-(CH_3)_2SiCH_2\mathbf{C}H_2CH_2N$); 30.7 ($-(CH_3)_2\mathbf{C}H_{\mathit{cye}}$); 73.1 ($-(CH_3)_2SiCH_2CH_2\mathbf{C}H_2N$); 80.2, 82.3, 83.5, 86.2 ($-\mathbf{C}H_{\mathit{cye}}$); 97.3, 101.6 ($\mathbf{C}_{\mathit{cye}}$); 114.1, 119.4, 122.4, 134.6, 163.4 (**C**Ar); 165.1 ($-\mathbf{C}H_{imine}$). ^{29}Si-NMR ($CDCl_3$): δ (ppm) = -$\mathbf{Si}CH_2CH_2CH_2Si$ is not observed; 0.90 ($-(CH_3)_2\mathbf{Si}CH_2CH_2CH_2Si$); 2.16

($CH_3SiC\mathbf{H}_2CH_2CH_2N$). Elemental Analysis (%): Calc. For $C_{216}H_{332}Cl_8N_8O_8Ru_8Si_{13}$ (4626.29): C, 56.08; H, 7.23; N, 2.42; Found: C, 56.59; H, 7.66; N, 2.44.

3. *Selected ^{1}H NMR and ^{13}C NMR spectra of dendritic ligands (**1**-**9**)*

(a)



(b)

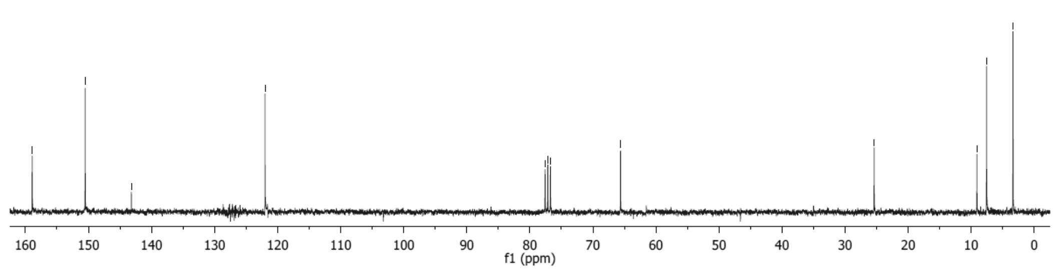
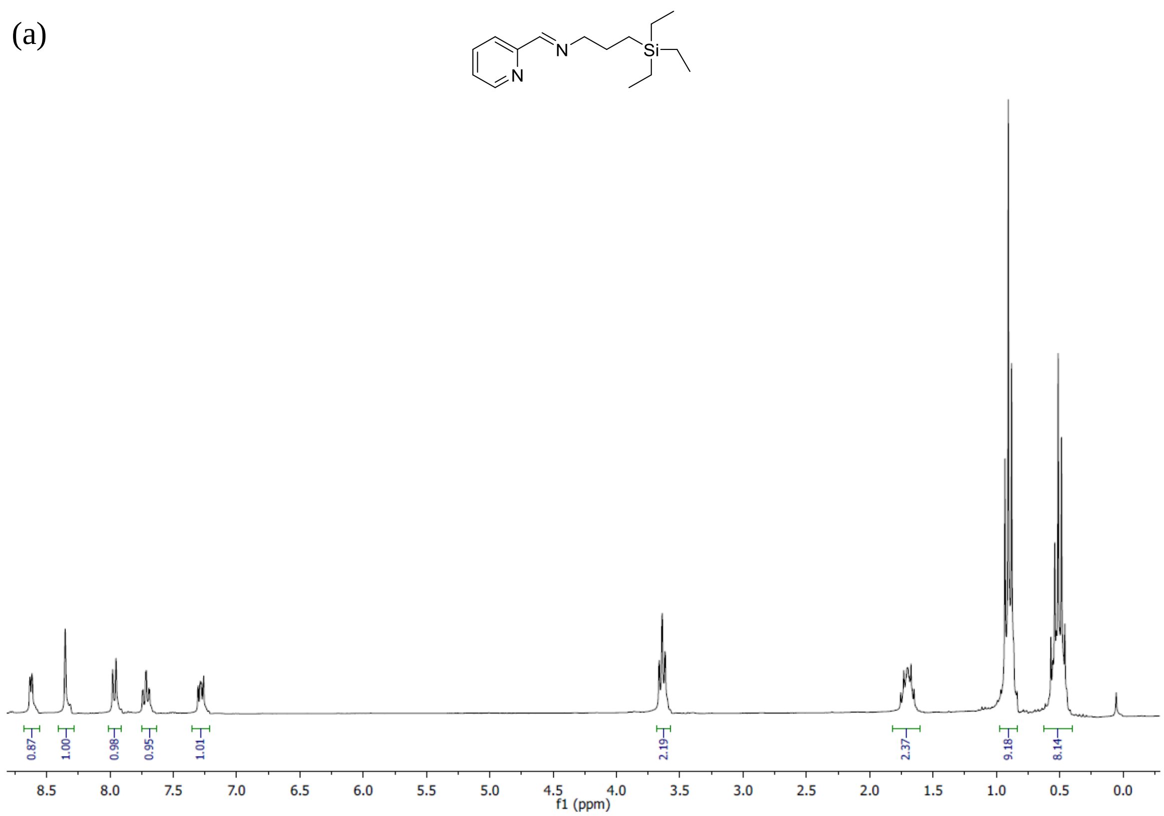


Fig. S1 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_0-[NCPh(*p*-N)]$_1$ **(1)**.

(a)



(b)

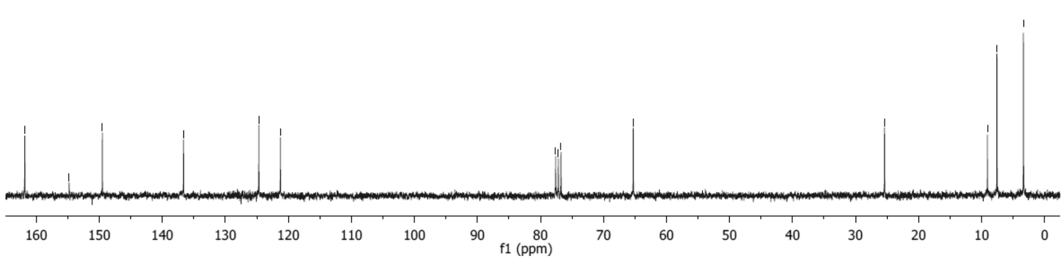
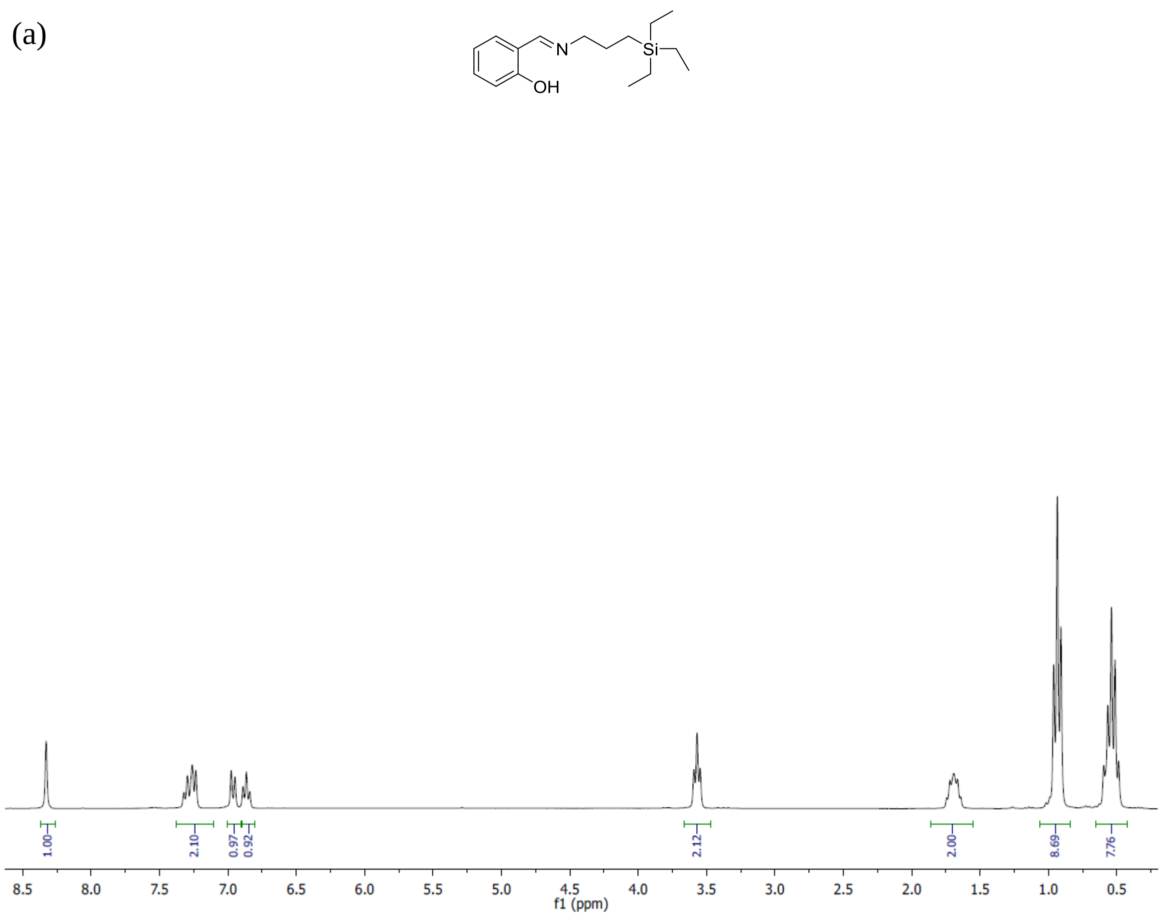


Fig. S2 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_0-[NCPh(*o*-N)]$_1$ (**4**).

(a)



(b)

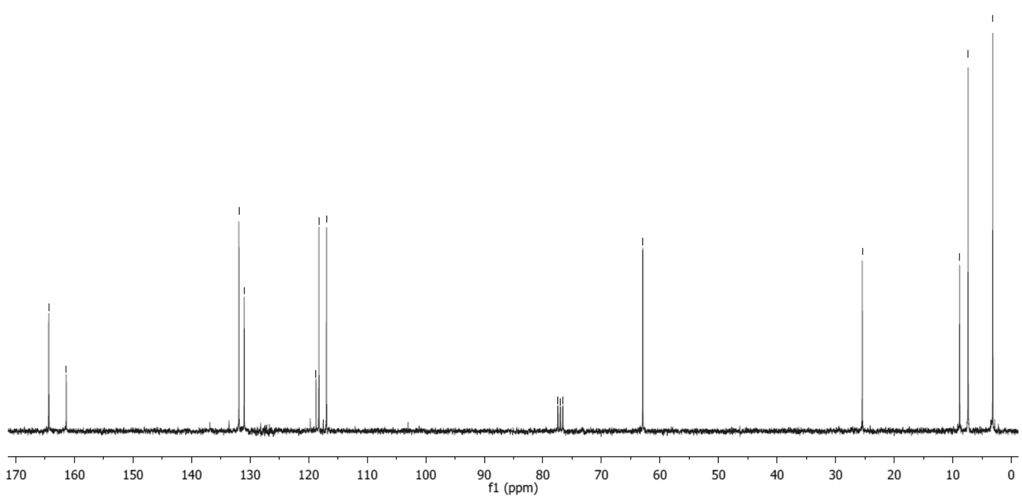
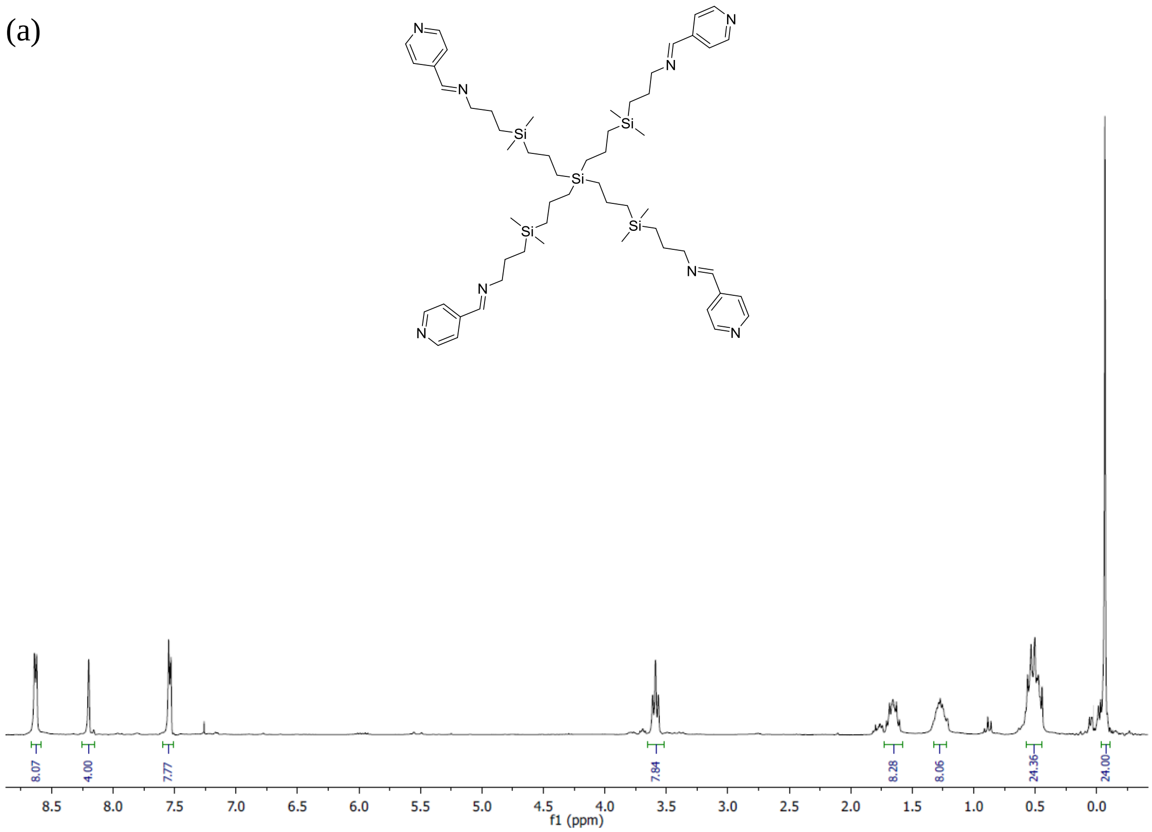


Fig. S3 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_0-[NCPh(*o*-OH)]$_1$ **(7)**.

(a)



(b)

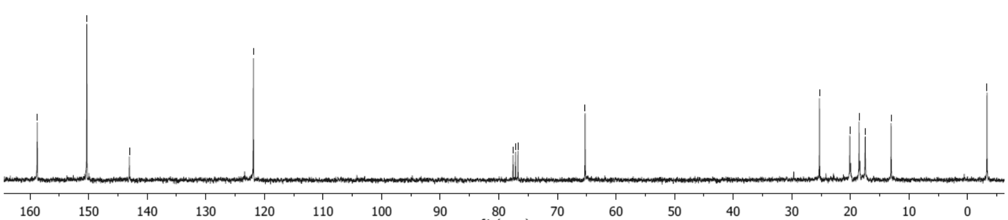
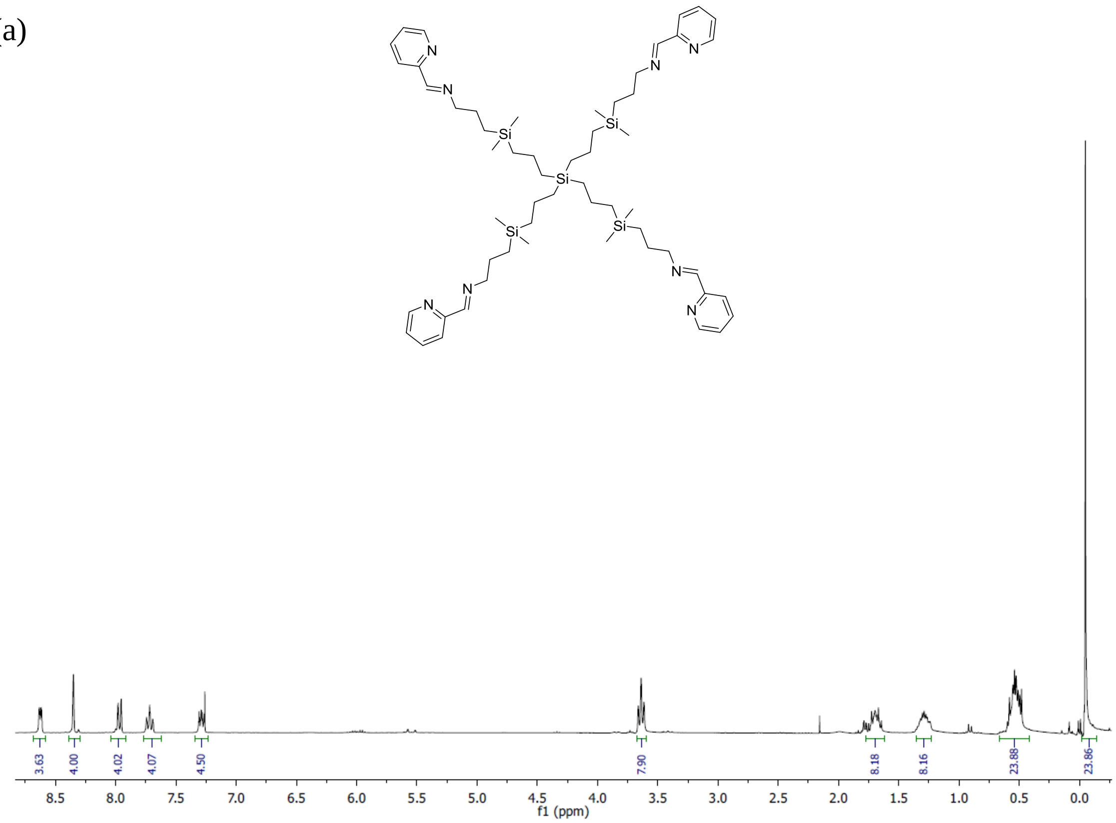


Fig. S4 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_1-[NCPh(*p*-N)]$_4$ **(2)**.

(a)



(b)

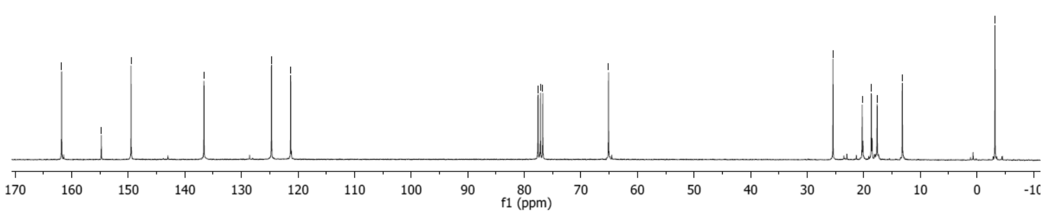
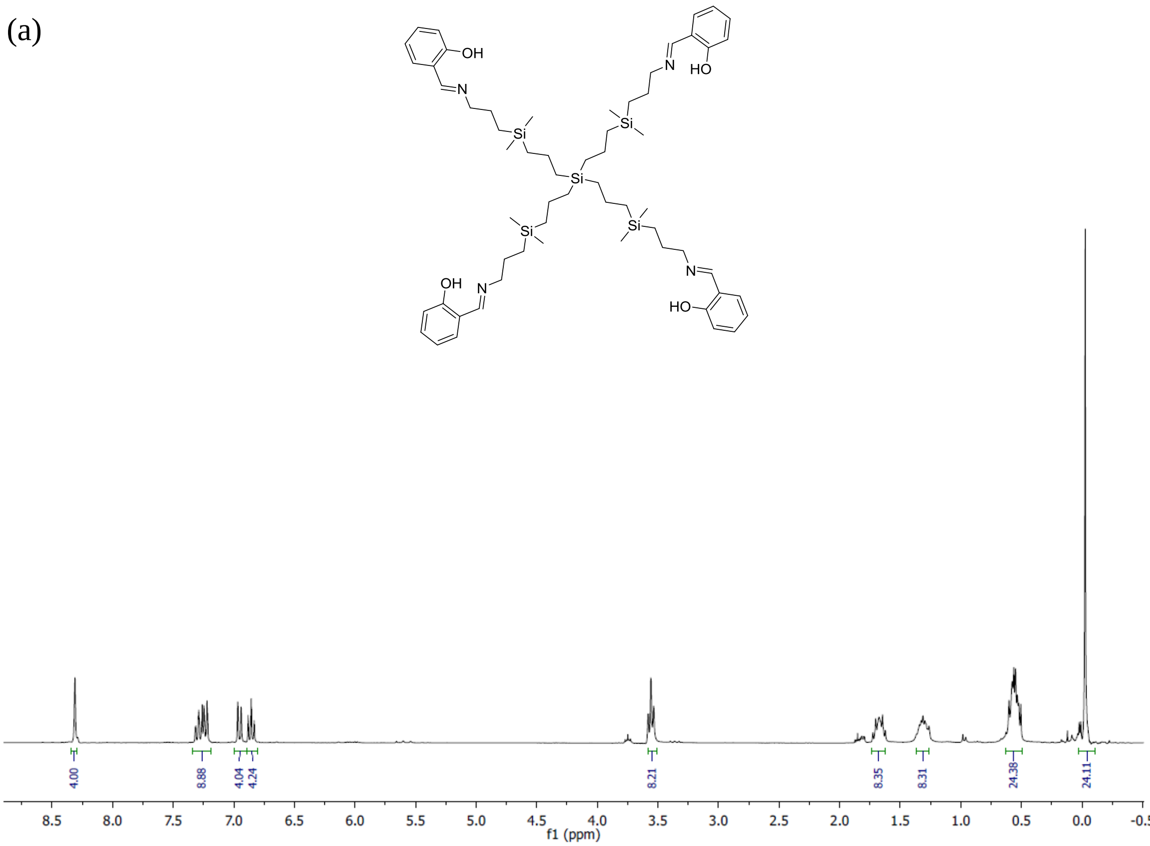


Fig. S5 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G$_{1}$-[NCPh(*o*-N)]$_{4}$ (**5**).

(a)



(b)

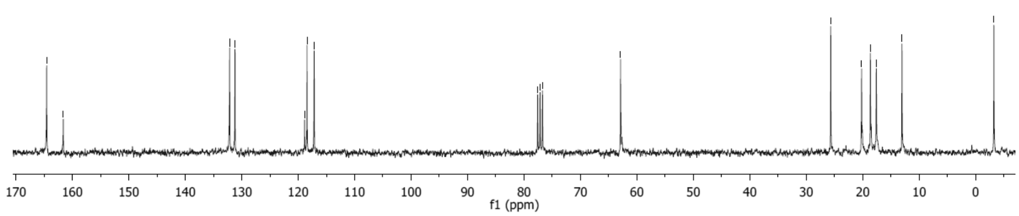
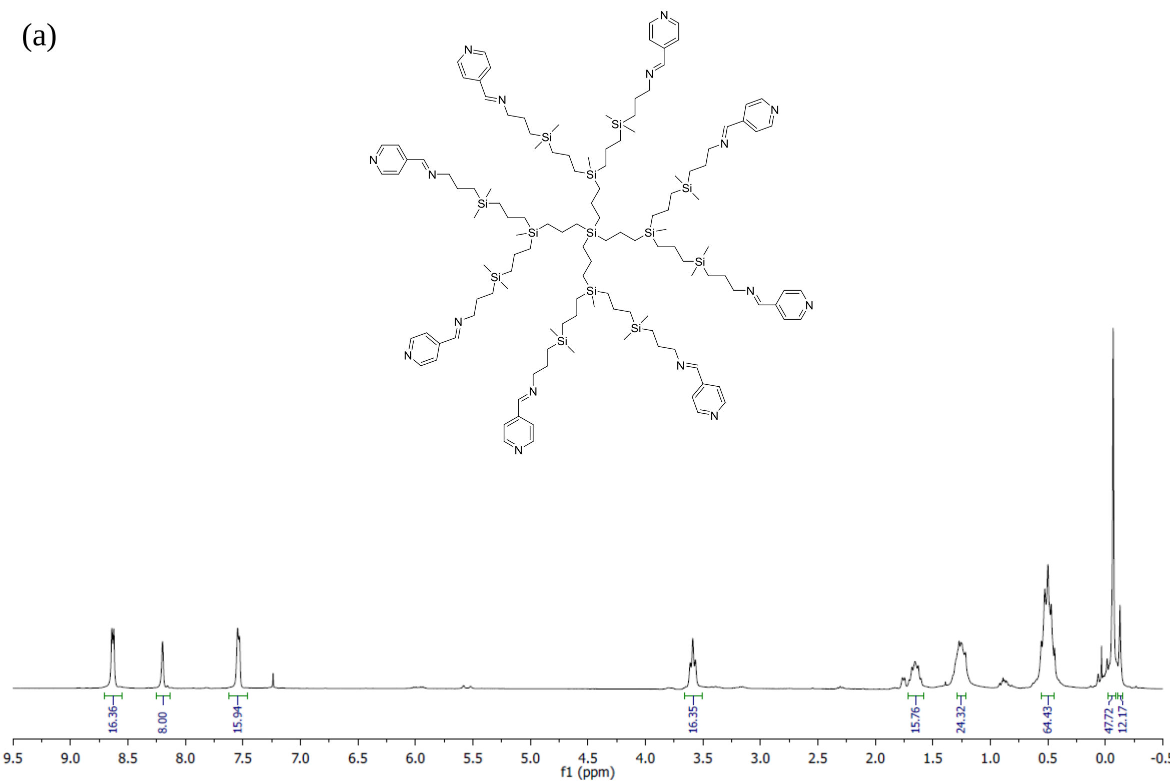


Fig. S6 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_{1}-[NCPh(*o*-OH)]$_{4}$ **(8)**.

(a)



(b)

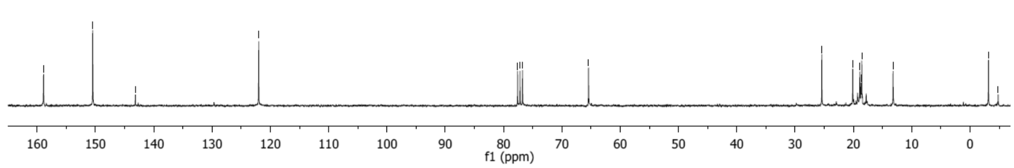
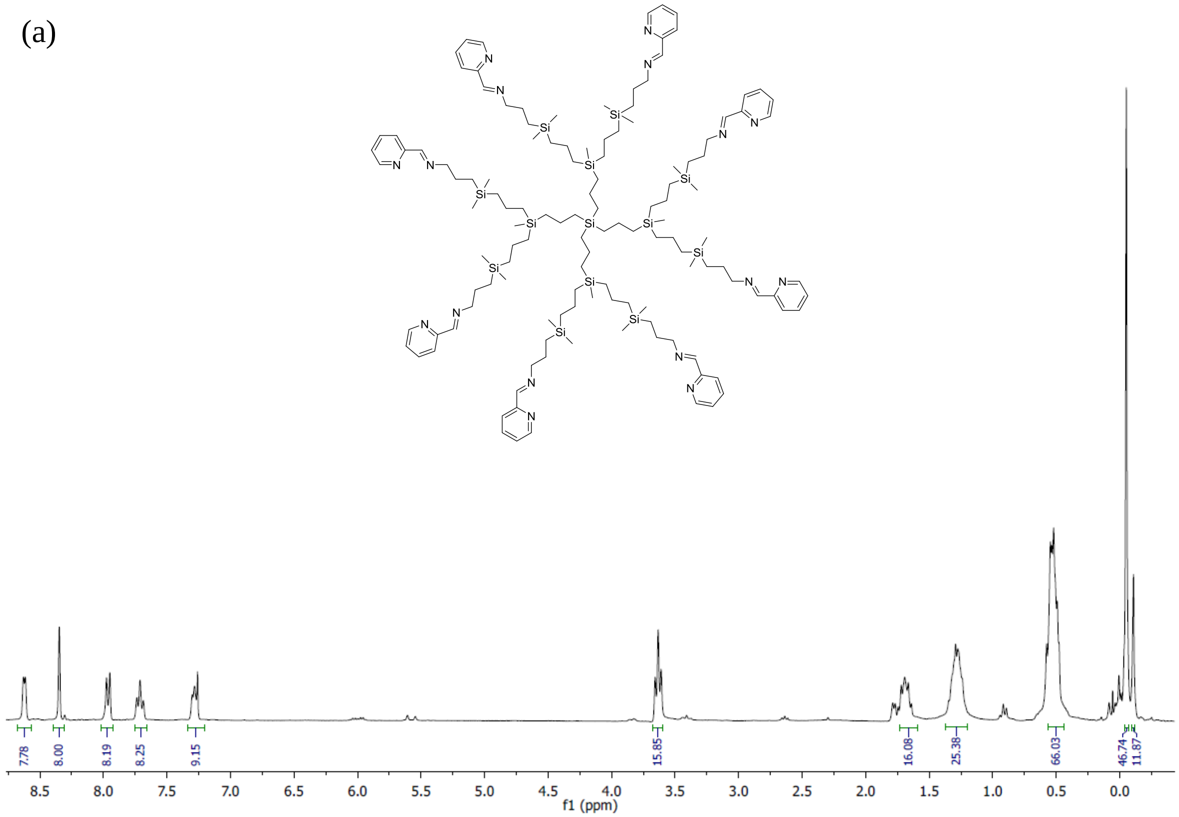


Fig. S7 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_2-[NCPh(*p*-N)]$_8$ **(3)**.

(a)



(b)

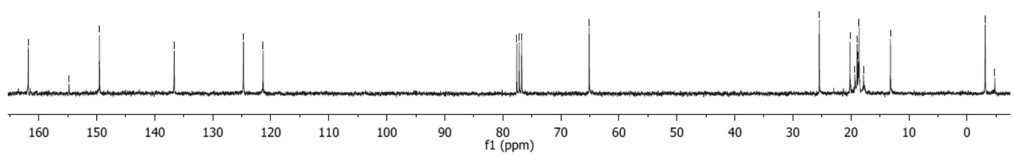
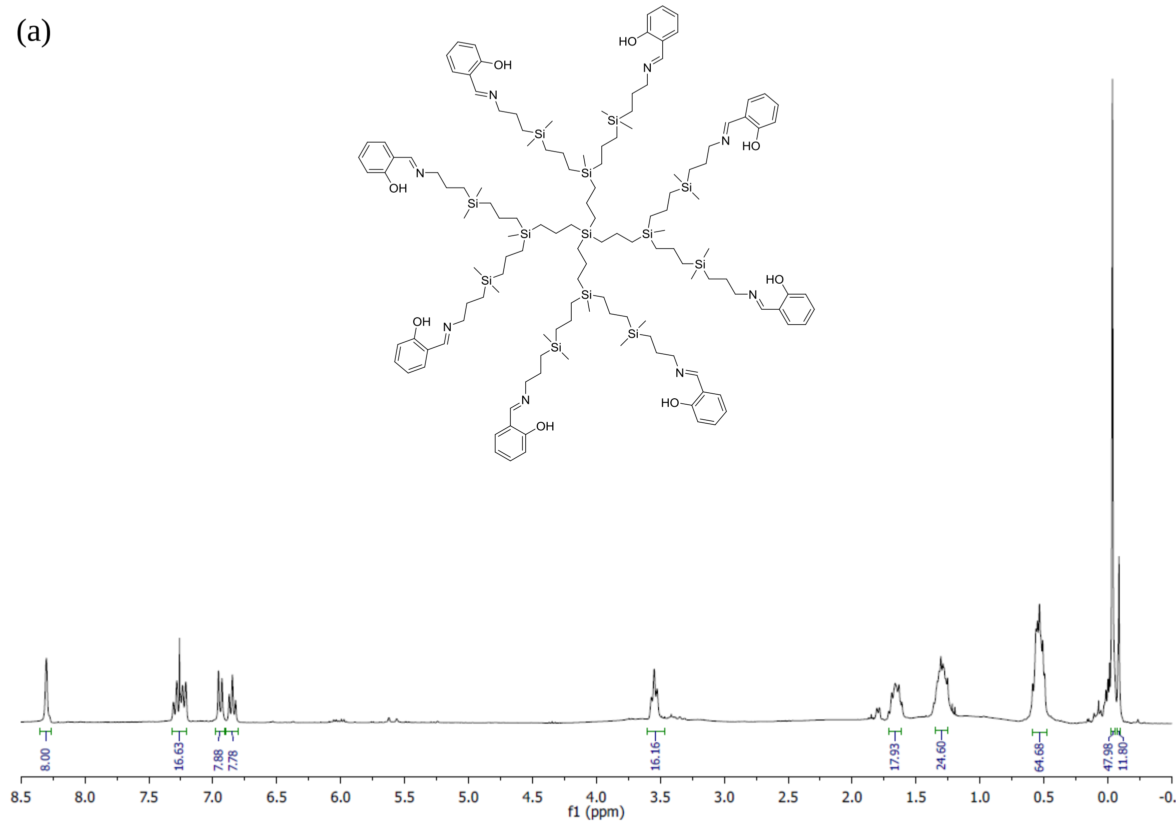


Fig. S8 a) [1]H-NMR (300 MHz, $CDCl_3$) and b) [13]C {[1]H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_2-[NCPh(*o*-N)]$_8$ **(6)**.

(a)



(b)

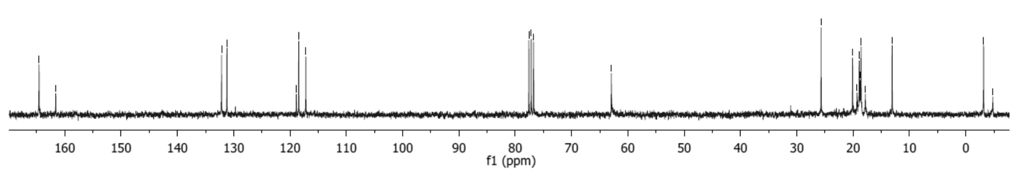
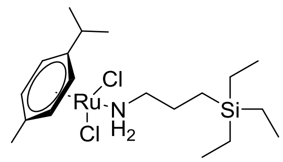
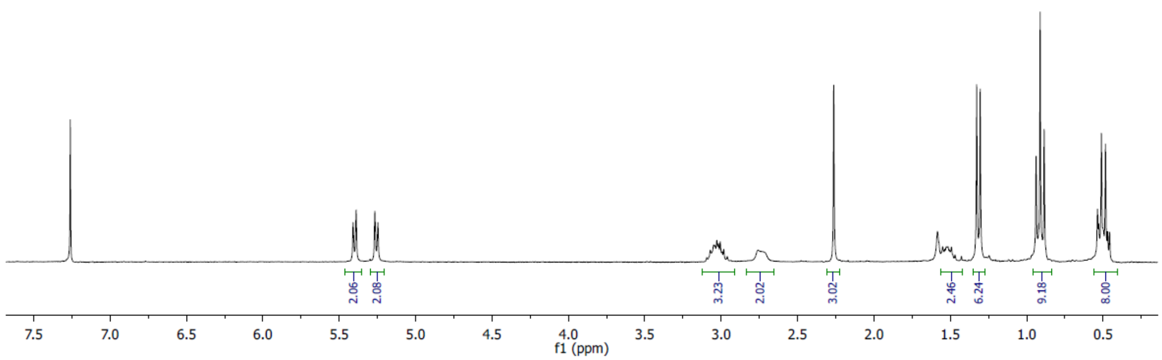


Fig. S9 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_2-[NCPh(*o*-OH)]$_8$ **(9)**.

4. *Selected ^{1}H NMR and ^{13}C NMR spectra of carbosilane metallodendrimers based on arene ruthenium (II) complexes* **(10, 11, 13-15, 17,18)**

(a)





(b)

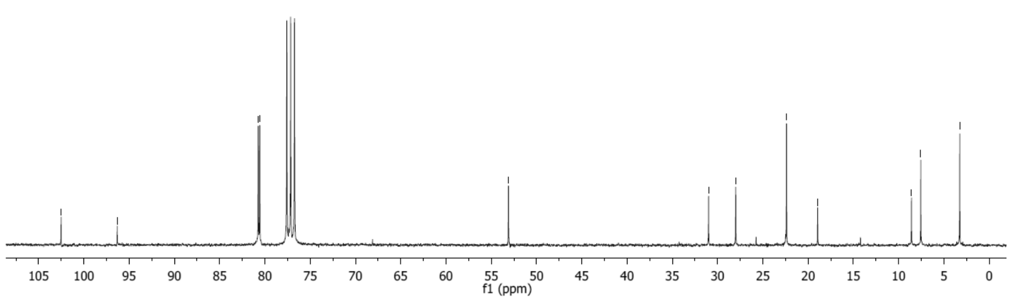
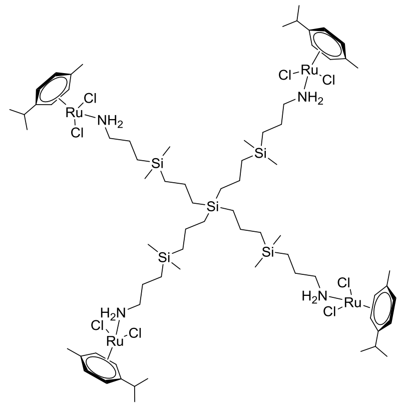
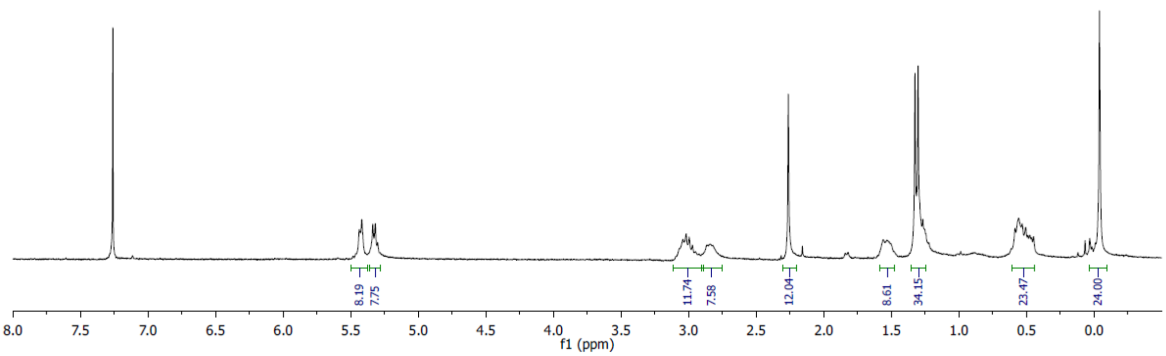


Fig. S10 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_0-[$NH_2Ru(\eta^6$-*p*-cymene)$Cl_2]_1$ **(10)**.

(a)





(b)

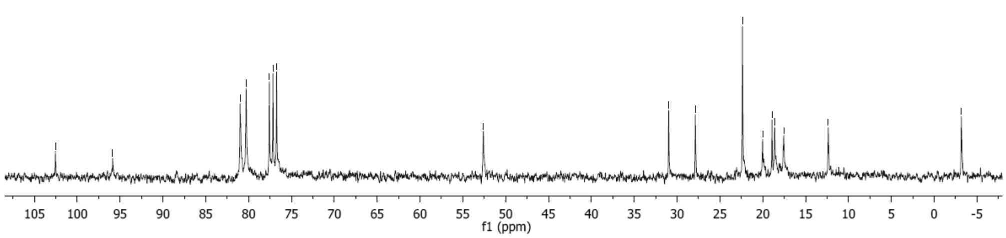
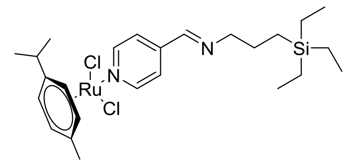
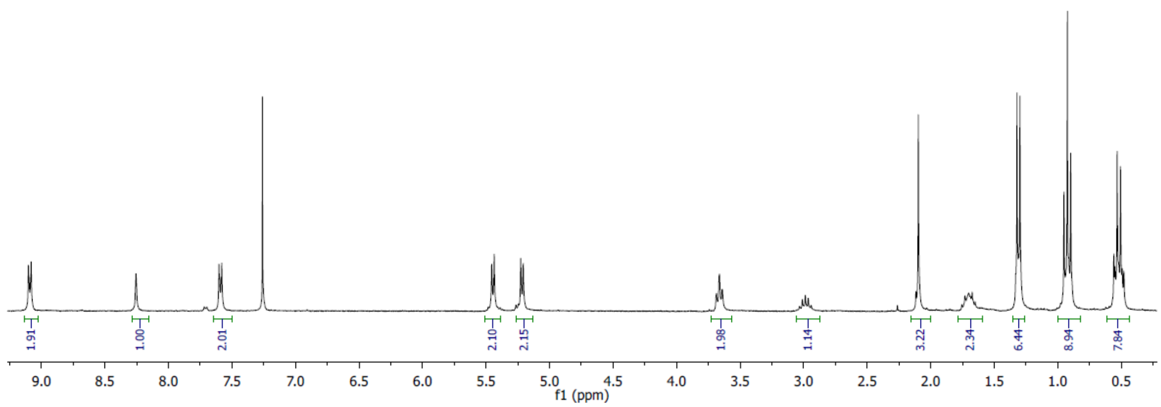


Fig. S11 a) [1]H-NMR (300 MHz, $CDCl_3$) and b) [13]C {[1]H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_1-[$NH_2Ru(\eta^6$-*p*-cymene)$Cl_2]_4$ **(11)**.

(a)





(b)

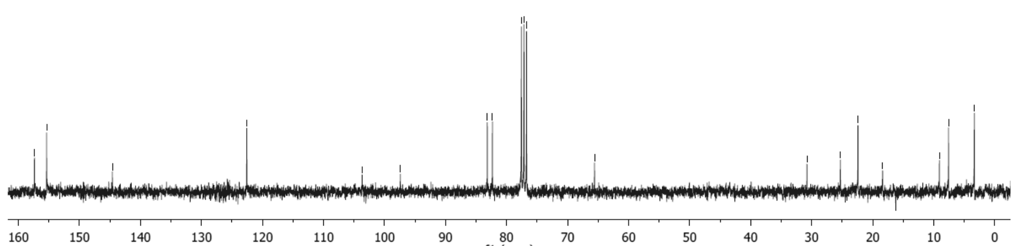


Fig. S12 a) ^{1}H-NMR and b) ^{13}C {^{1}H}-NMR spectra of compound G$_{0}$-[NCPh(*p*-N)Ru(η^{6}-*p*-cymene)Cl$_{2}$]$_{1}$ **(13)**.

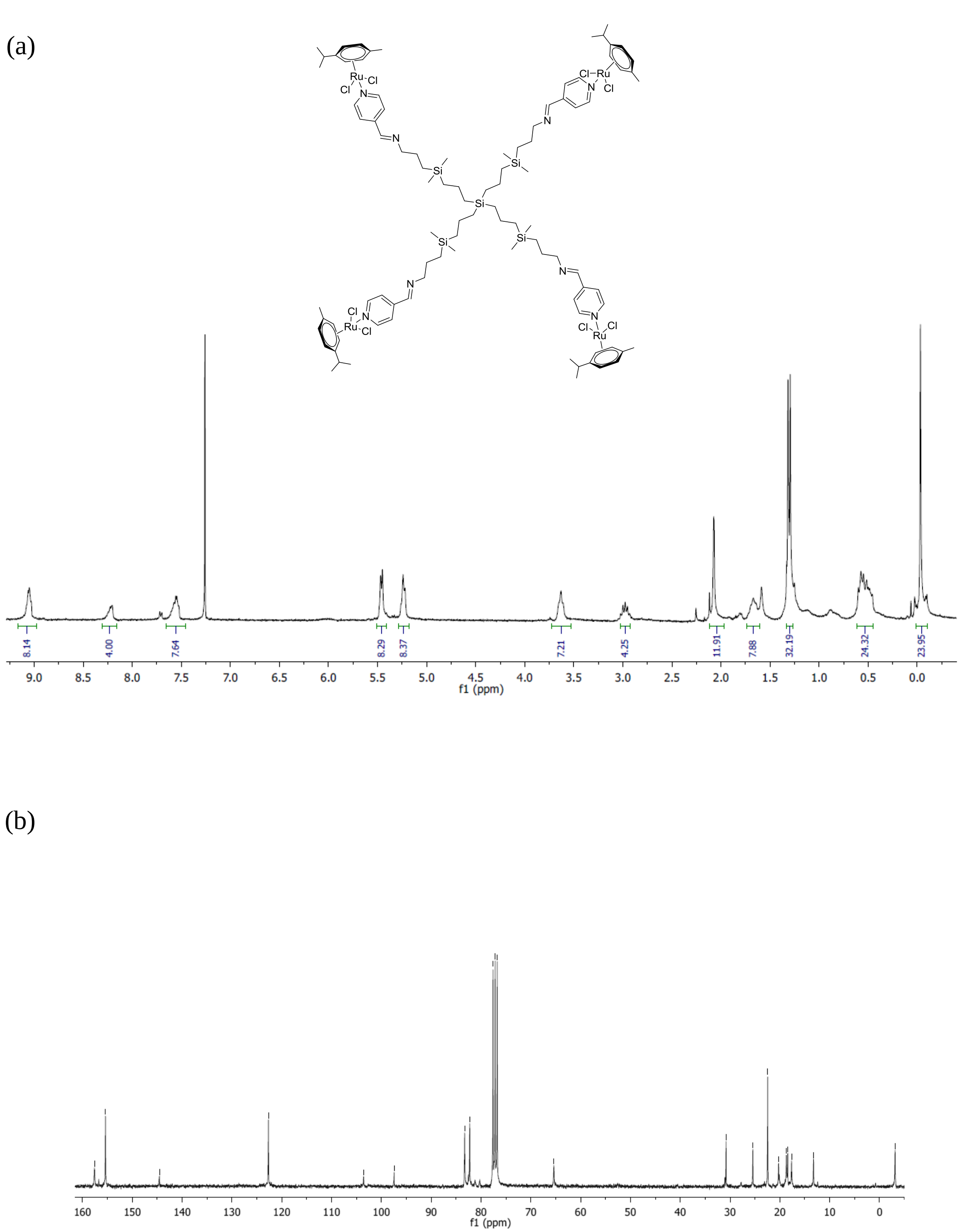
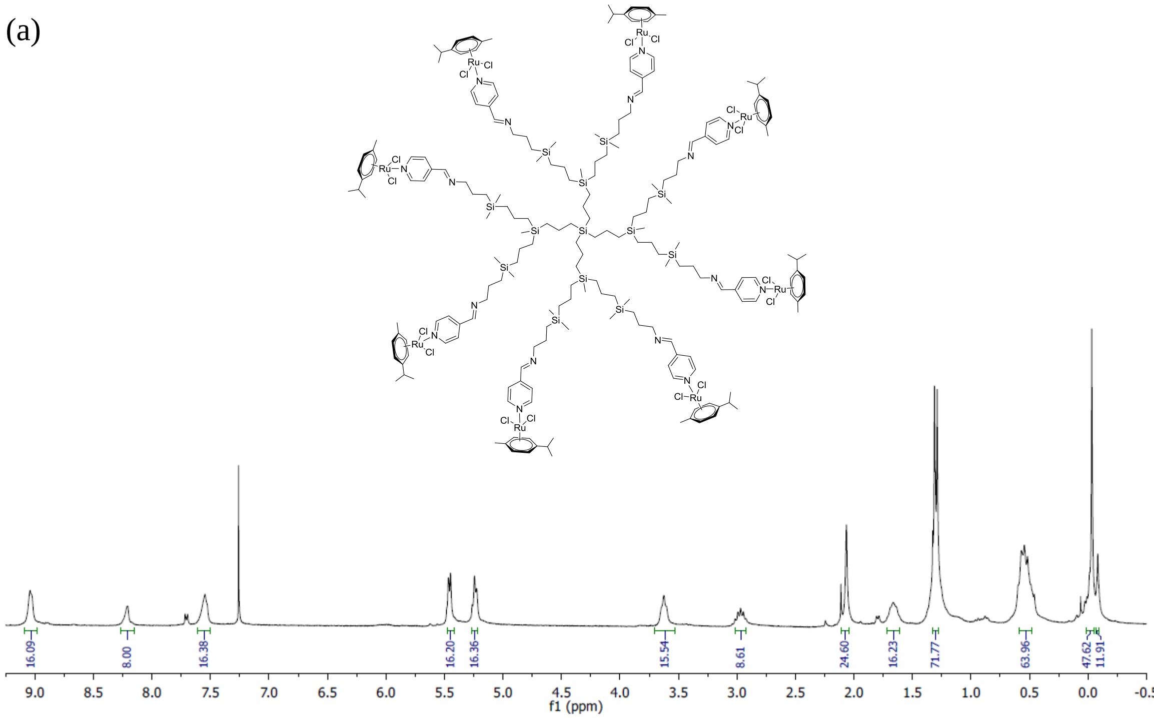


Fig. S13 a) ^{1}H-NMR and b) ^{13}C {^{1}H}-NMR spectra of compound G$_{1}$-[NCPh(*p*-N)Ru(η^{6}-*p*-cymene)Cl$_{2}$]$_{4}$ **(14)**.

(a)



(b)

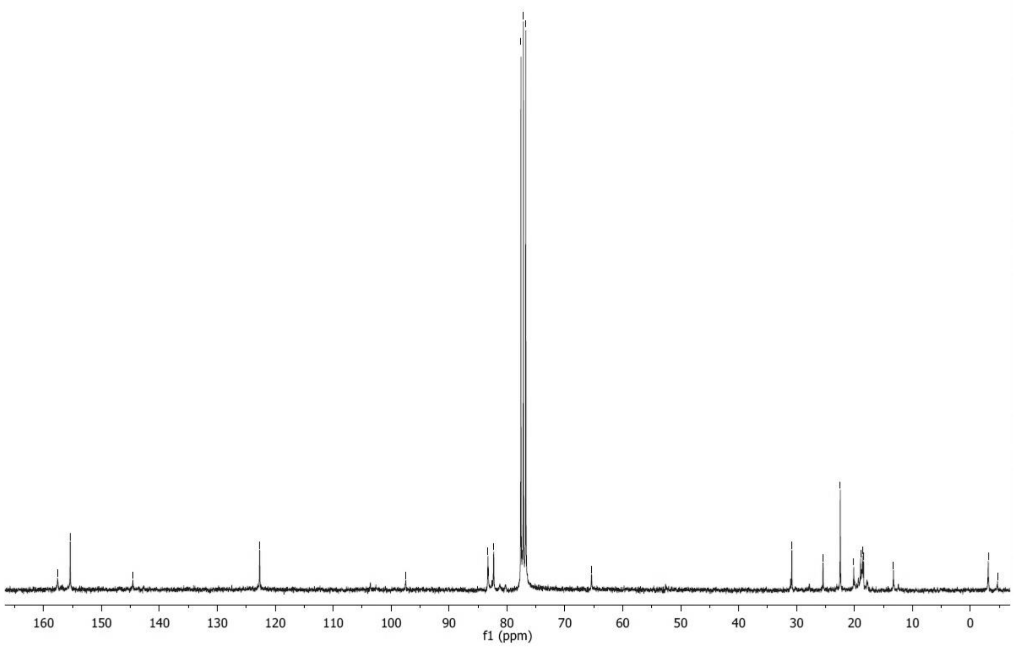
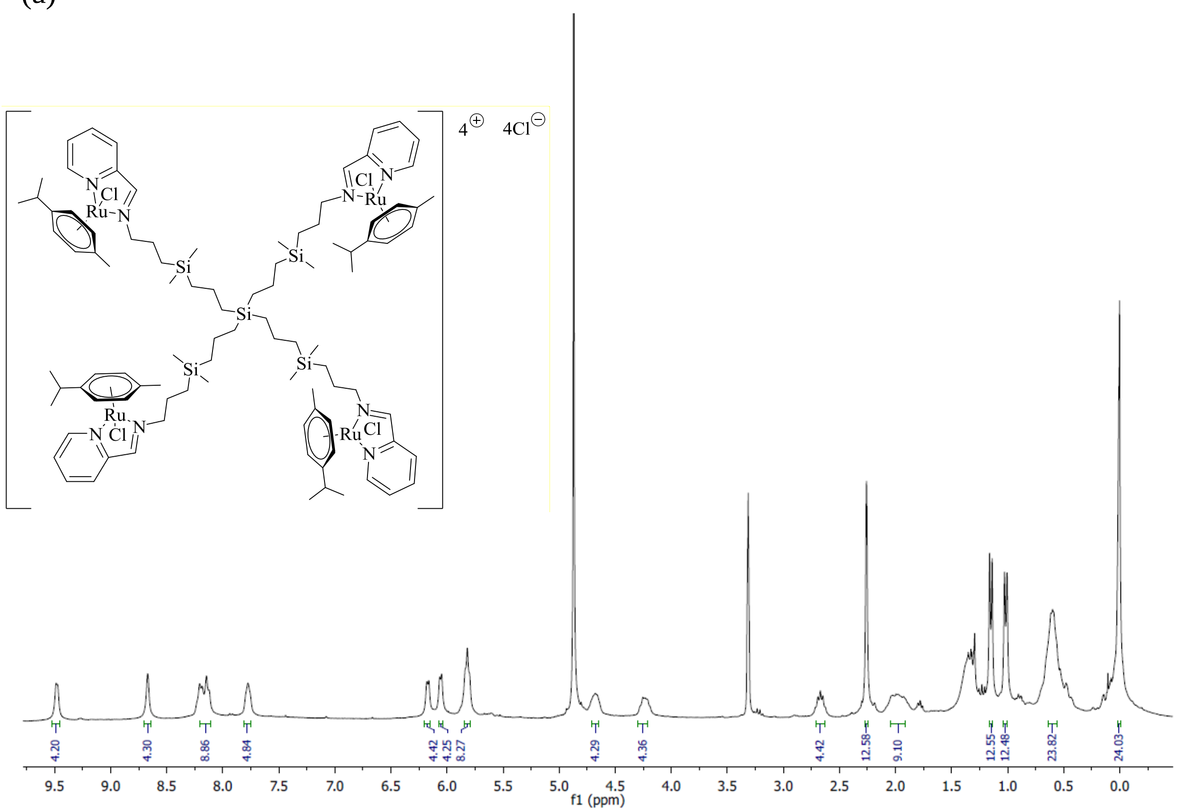


Fig. S14 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_2-[NCPh(*p*-N)Ru(η^6-*p*-cymene)Cl_2]$_8$ **(15)**.

(a)



(b)

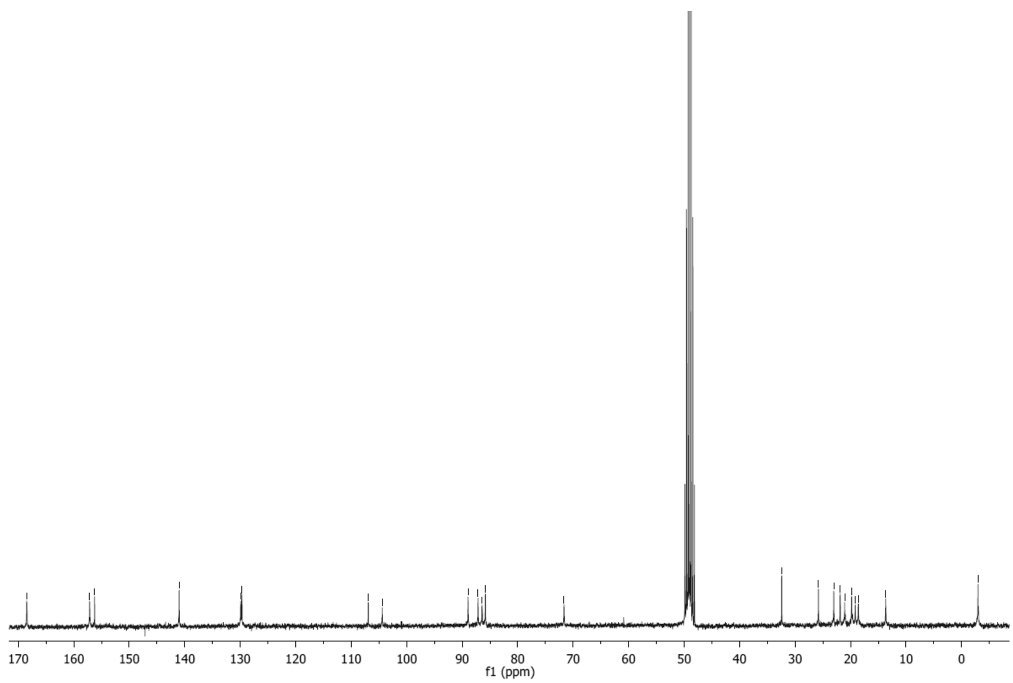


Fig. S15 a) ^{1}H-NMR (300 MHz, CD_3OD) and b) ^{13}C {^{1}H}-NMR (300 MHz, CD_3OD) spectra of compound G$_{1}$-[[NCPh(*o*-N)Ru(η^6-*p*-cymene)Cl]*Cl*]$_4$ **(17)**.

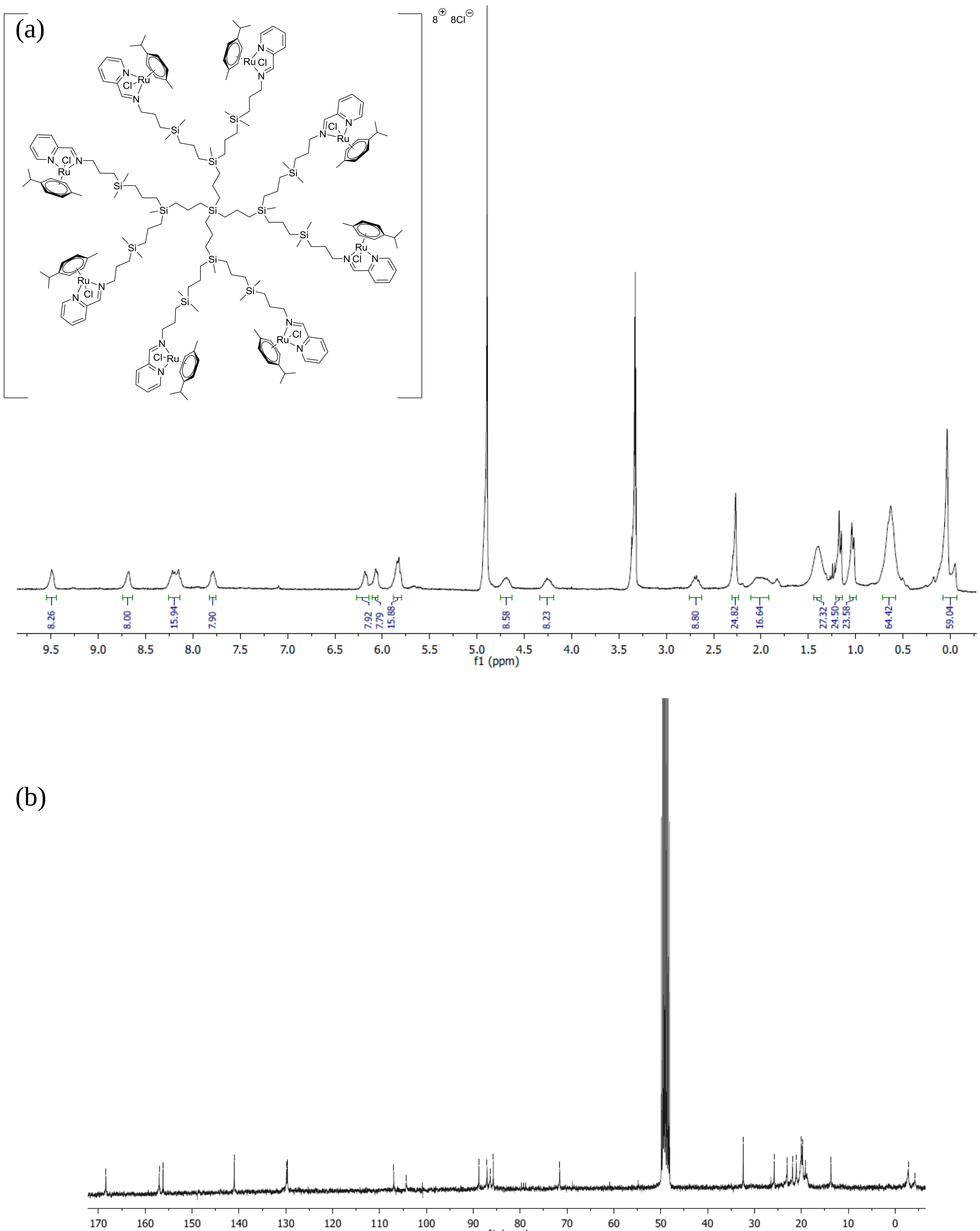
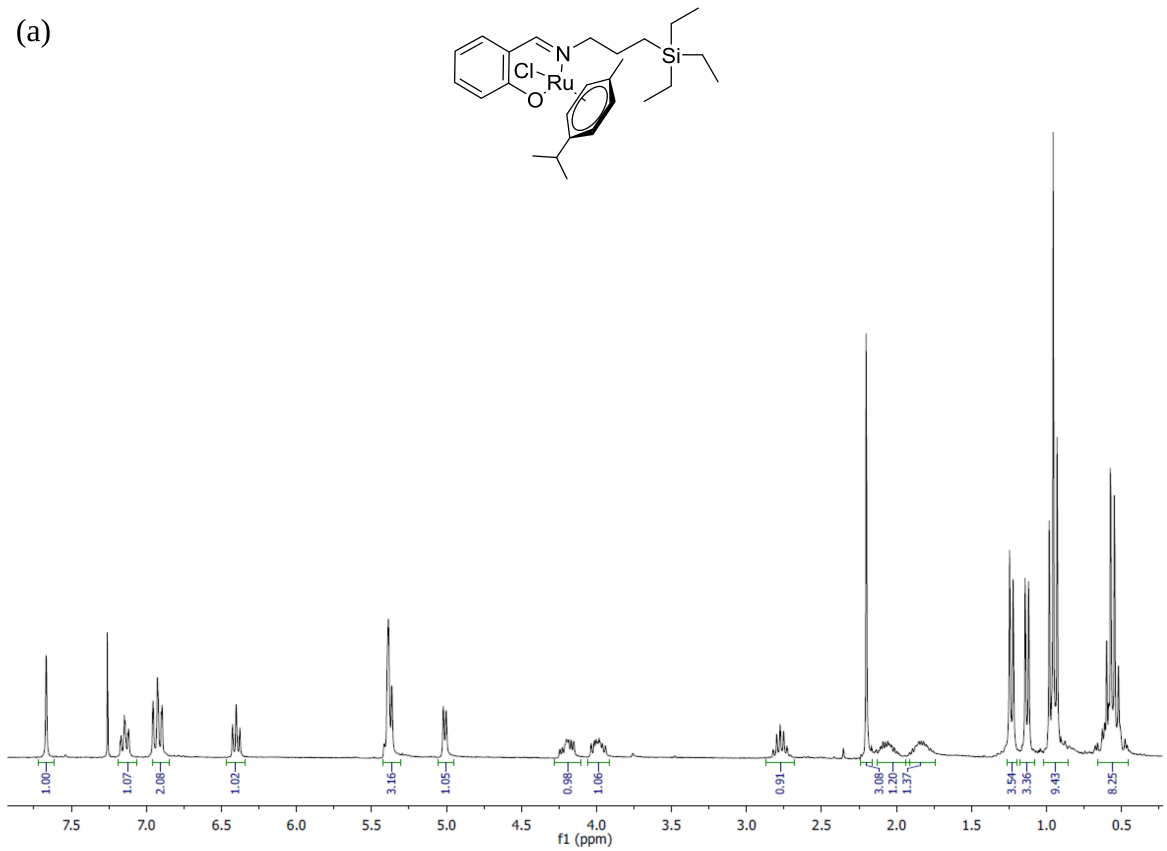


Fig. S16 a) [1]H-NMR (300 MHz, CD_3OD) and b) [13]C {[1]H}-NMR (300 MHz, CD_3OD) spectra of compound G_2-[[NCPh(*o*-N)Ru(η^6-*p*-cymene)Cl]*Cl*]$_8$ **(18)**.

(a)



(b)

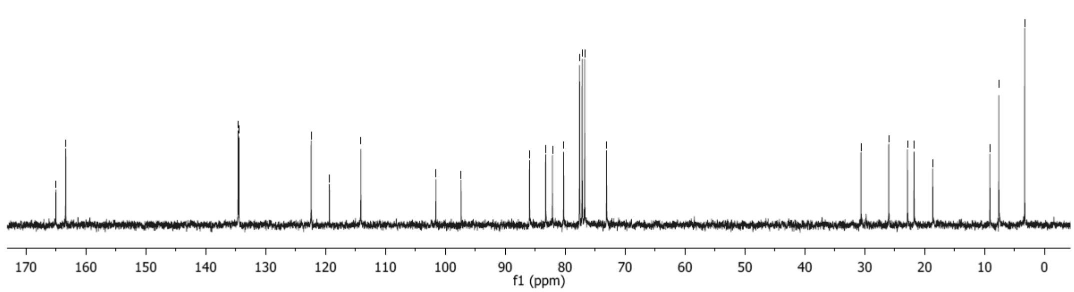
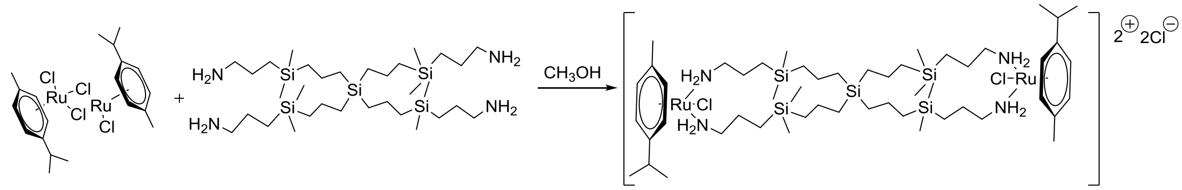


Fig. S17 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of compound G_0-[NCPh(*o*-O)Ru(η^6-*p*-cymene)Cl]$_1$ **(19)**.

5. ^{1}H *and ESI-TOF mass spectra of the reaction S1*



Scheme S1 1 equivalent of ruthenium with 1 equivalent of the G_1-$[NH_2]_4$ (**II**).

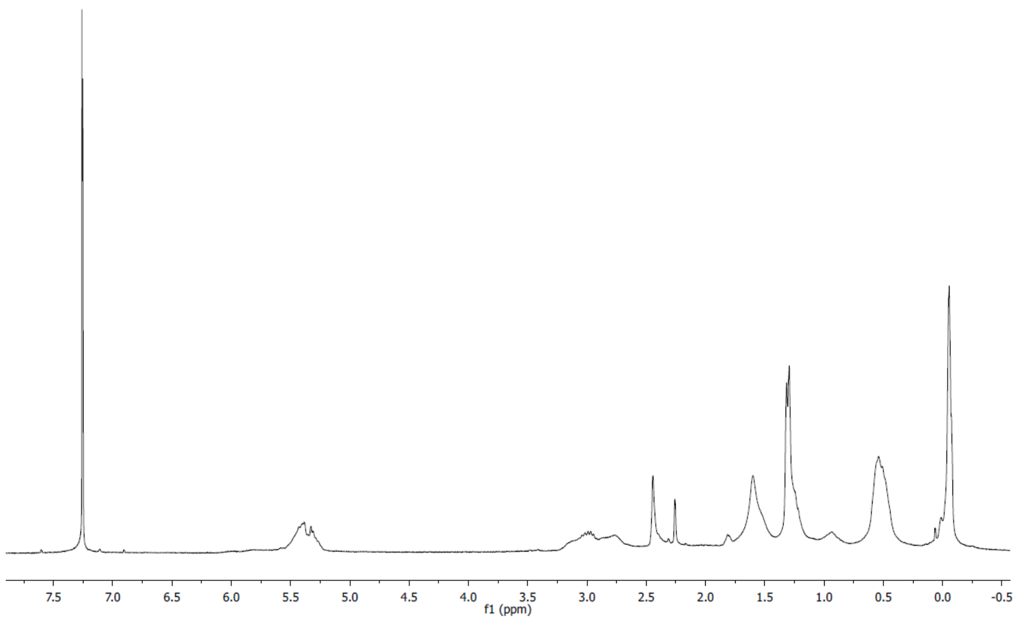


Fig. S18 ^{1}H-NMR (300 MHz, $CDCl_3$) spectra of reaction S1.

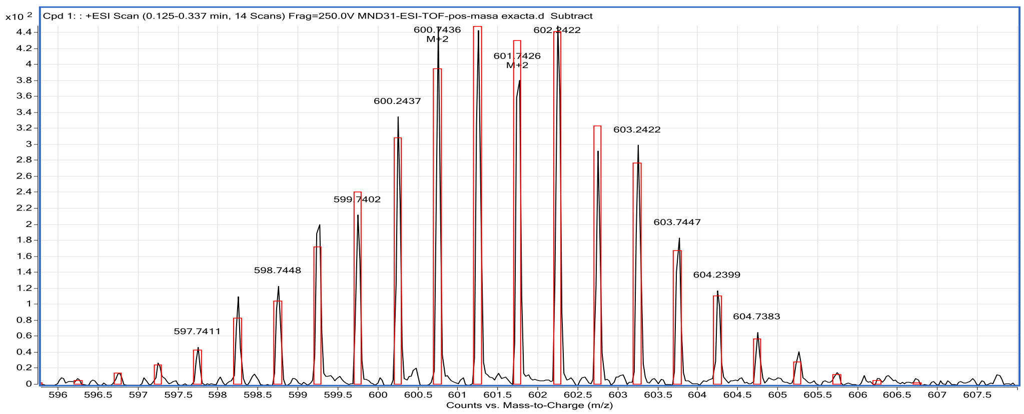
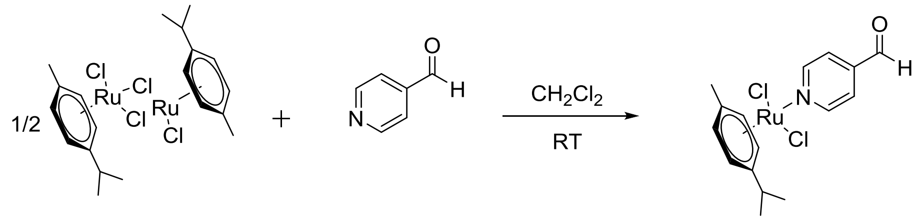


Fig. S19 ESI-TOF mass spectra of reaction S1.

6. *[1]H and [13]C-NMR spectra of the reaction S2*



Scheme S2 ½ equivalent of [Ru] with 1 equivalent of the commercial 4-pyridinecarboxaldehyde.

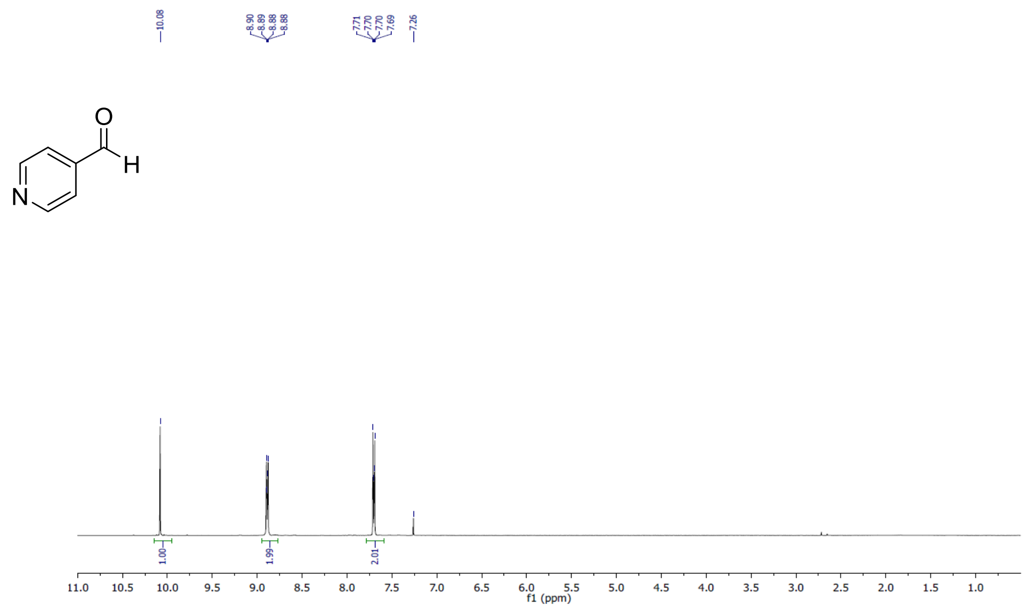
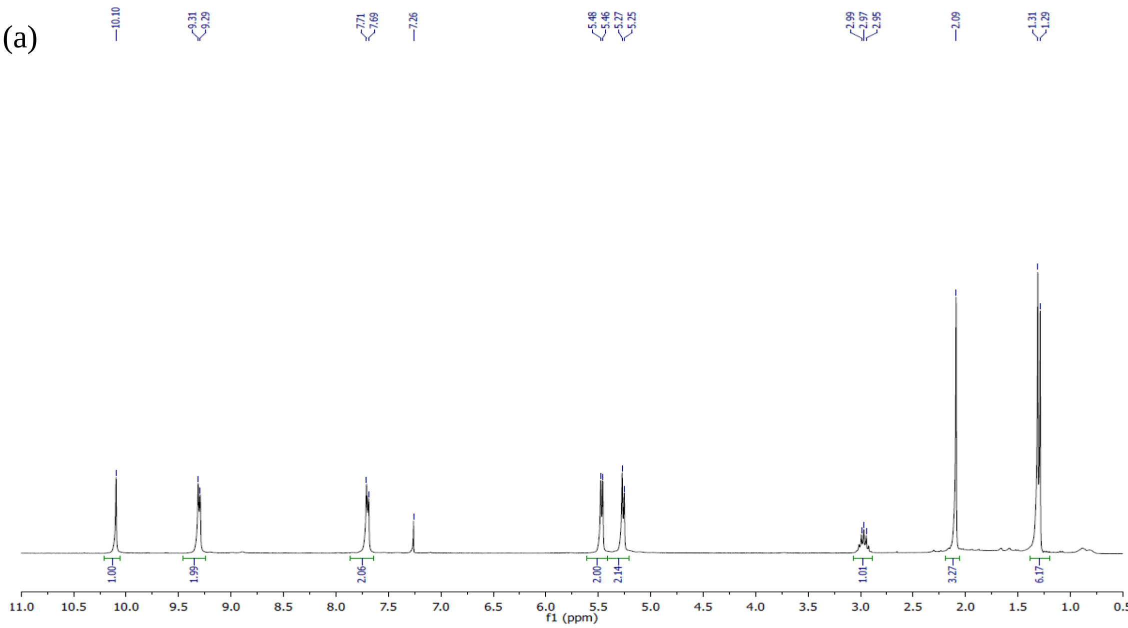


Fig. S20 ^{1}H-NMR spectra of commercial 4-pyridinecarboxaldehyde.

(a)



(b)

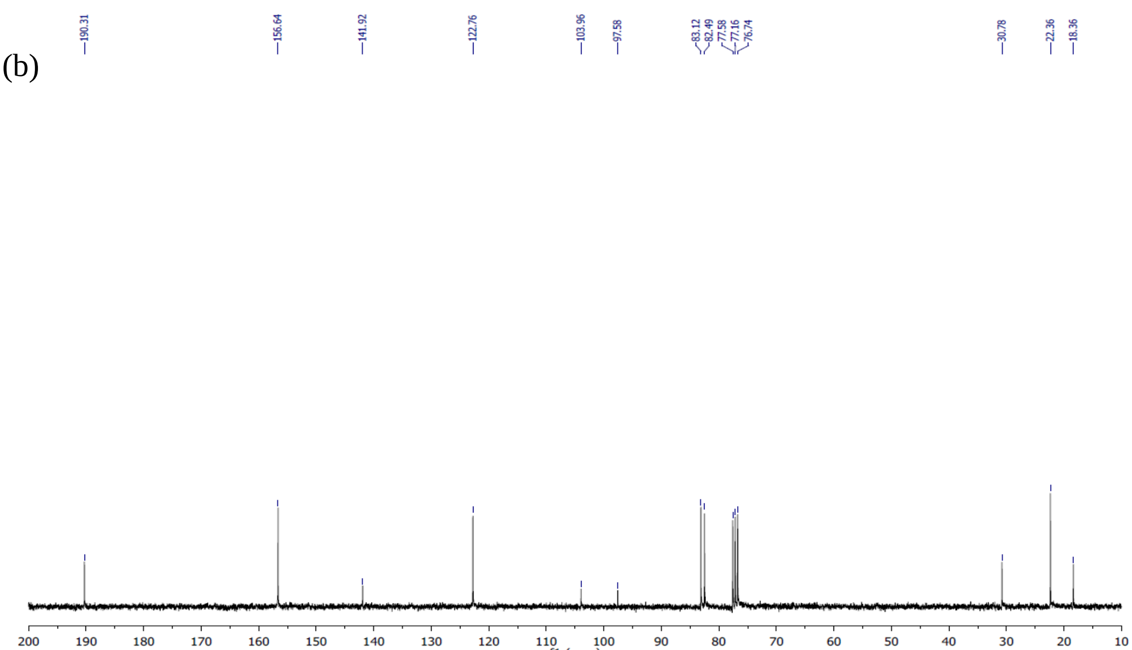
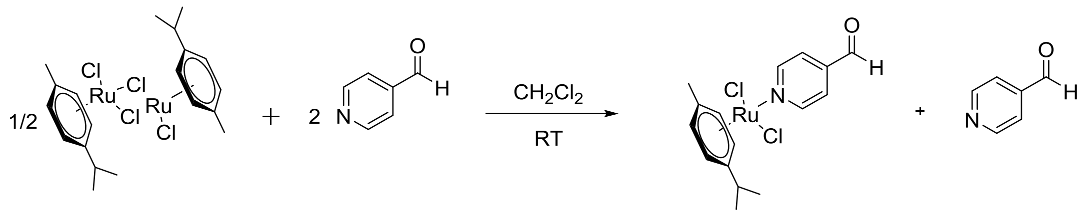


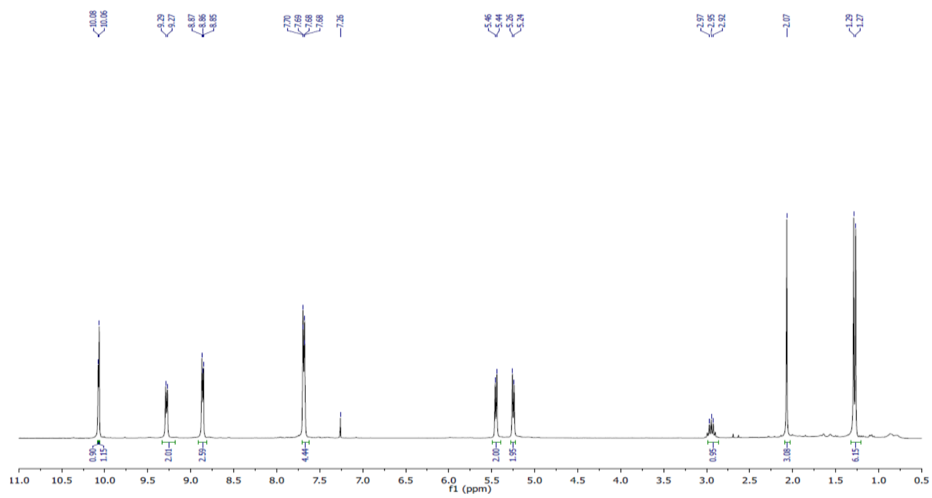
Fig. S21 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of reaction S2.

7. *[1]H and [13]C-NMR spectra of the reaction S3*



Scheme S3 ½ equivalent of [Ru] with 2 equivalents of the commercial 4-pyridinecarboxaldehyde.

(a)



(b)

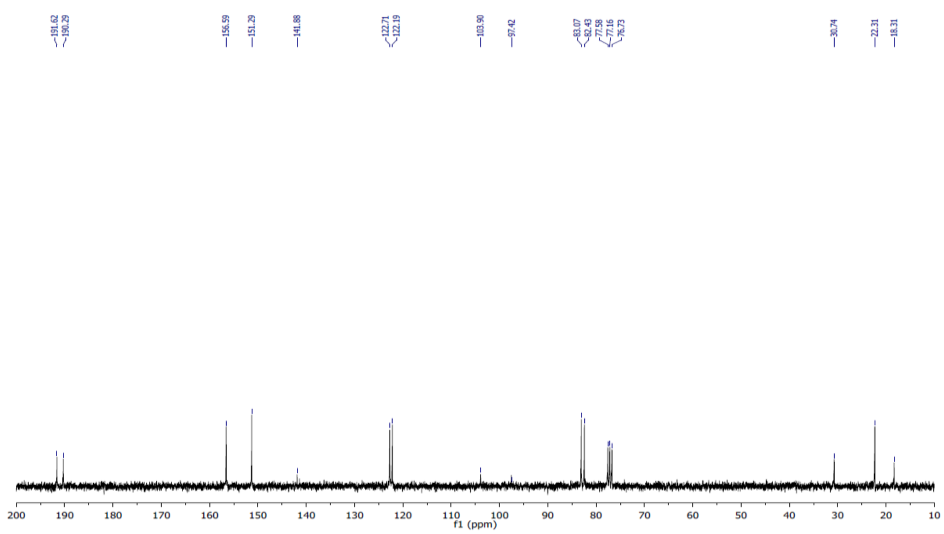


Fig. S22 a) ^{1}H-NMR (300 MHz, $CDCl_3$) and b) ^{13}C {^{1}H}-NMR (300 MHz, $CDCl_3$) spectra of reaction S3.

8. **Stability tests**

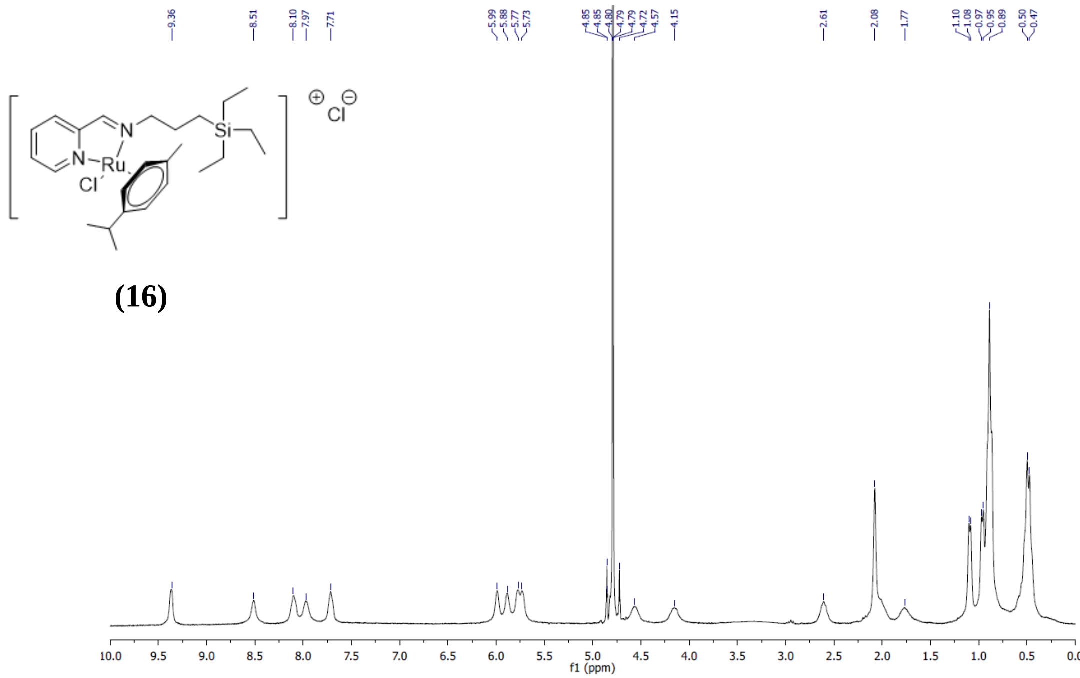


Fig. S23 ^{1}H-NMR (300 MHz, D_2O) of complex **16**.

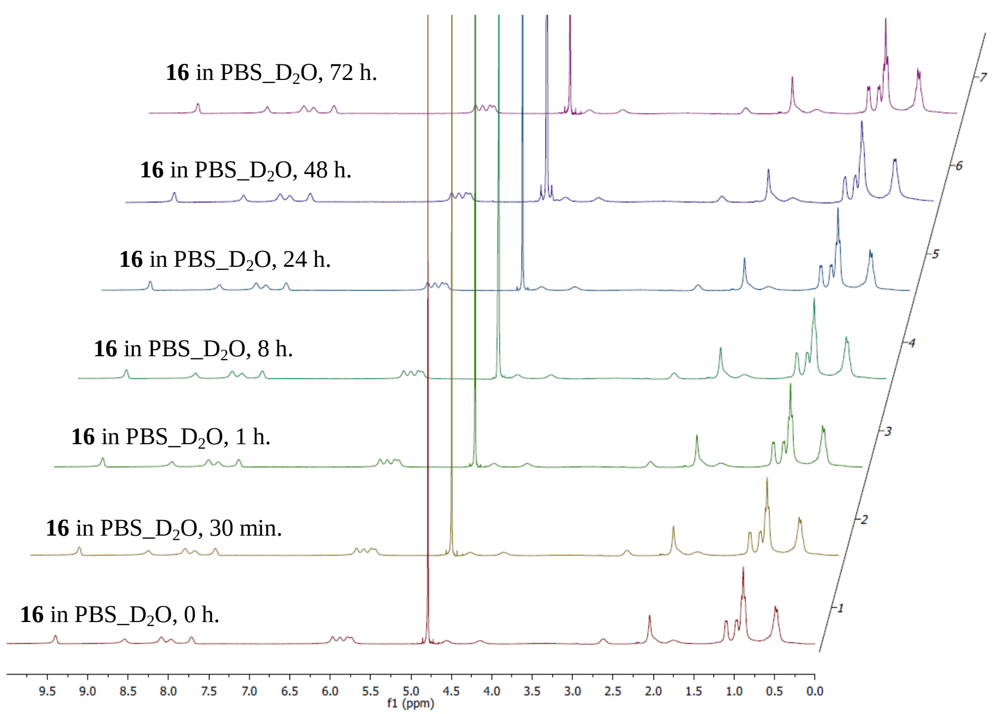


Fig. S24 Time dependent ^{1}H-NMR (300 MHz, PBS_D_2O) of complex **16** (pH = 7.4).

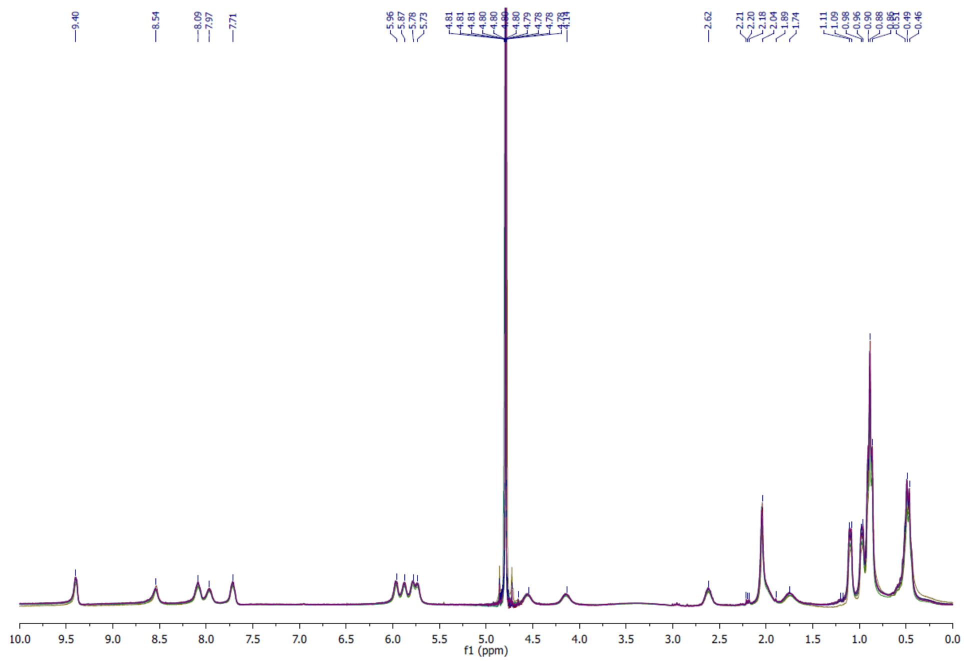


Fig. S25 Time dependent (from 0 to 72h) overlap ^{1}H-NMR (300 MHz, PBS_D_2O) of complex **16** (pH = 7.4).

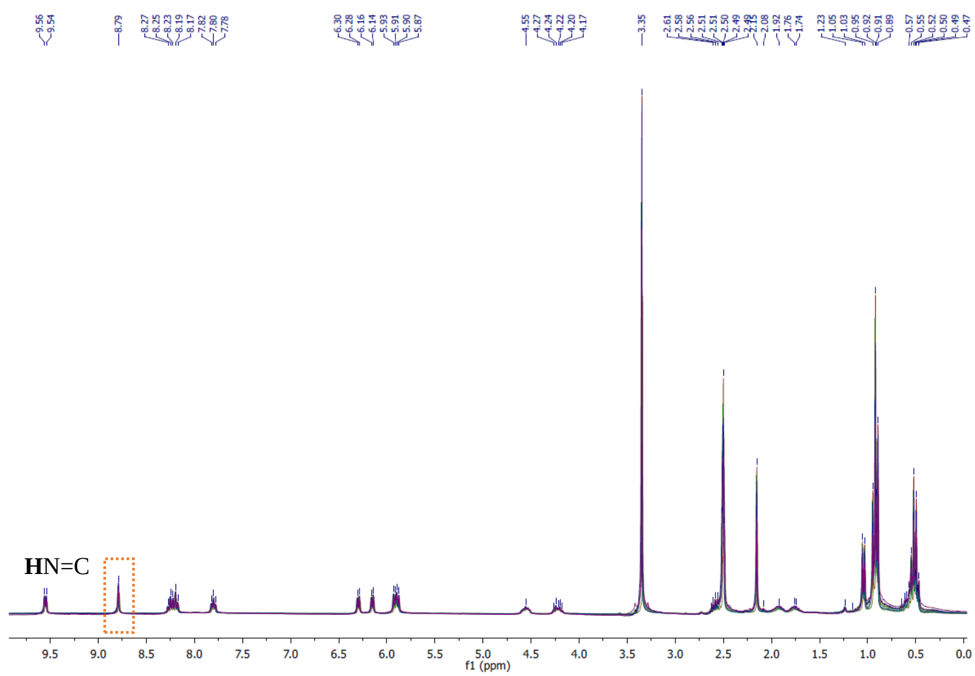


Fig. S26 Time dependent (from 0 to 72h) overlap ^{1}H-NMR (300 MHz, DMSO_d_6) of complex **16**.

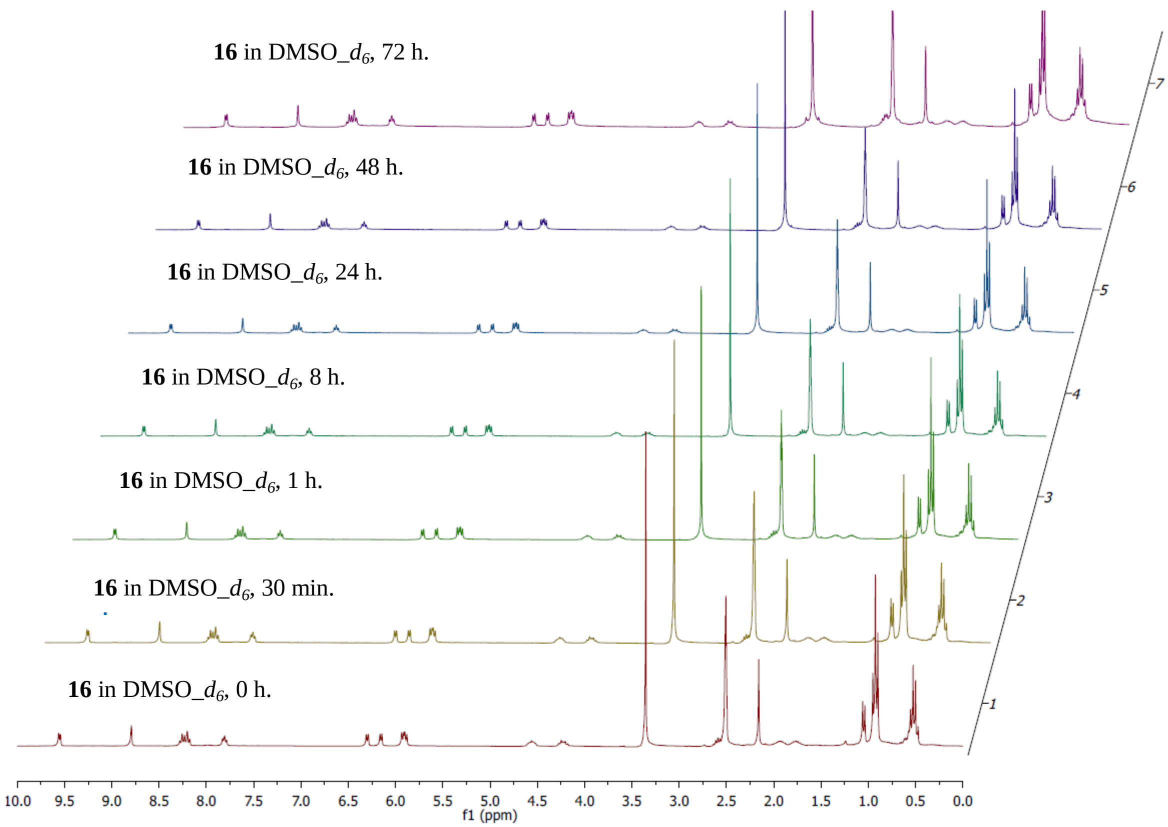


Fig. S27 Time dependent ^{1}H-NMR (300 MHz, DMSO_d_6) of complex **16.**

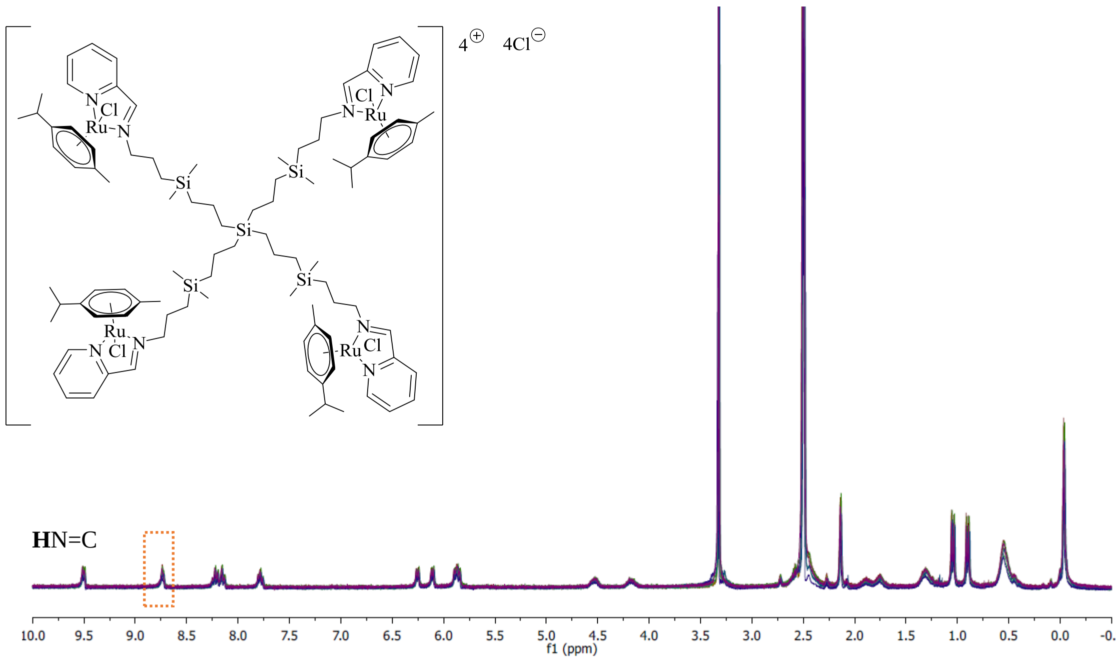


Fig. S28 Time dependent (from 0 to 72h) overlap ^{1}H-NMR (300 MHz, DMSO_d_6) of complex **17**.

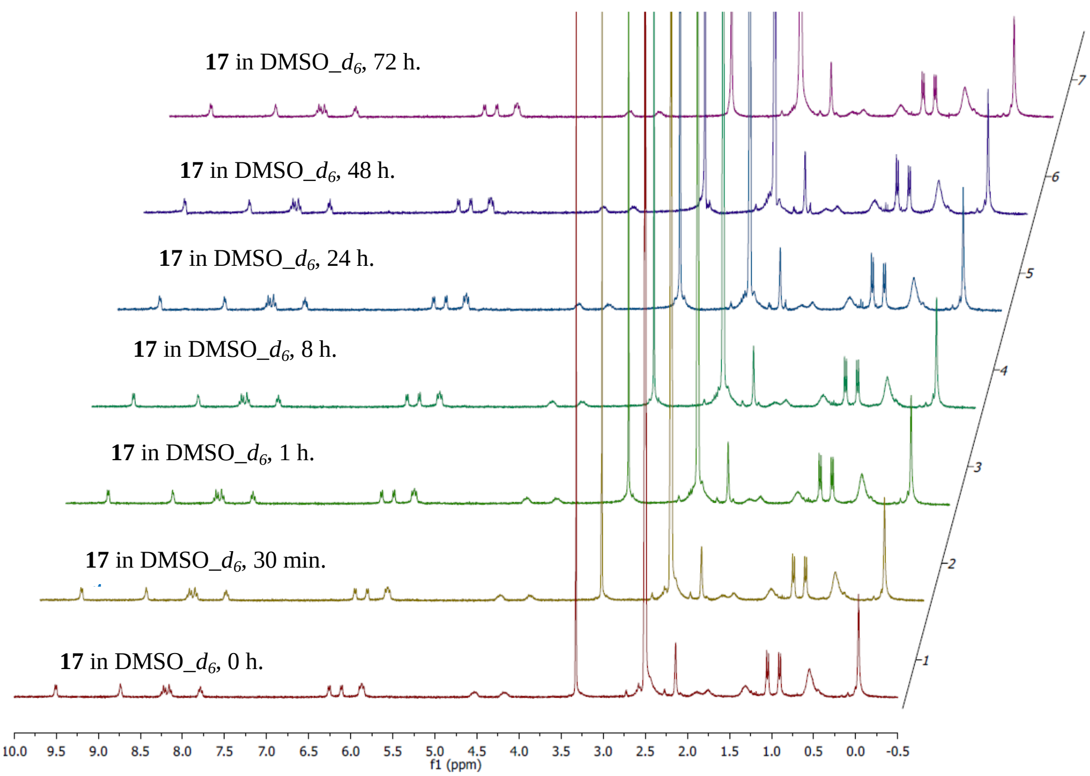


Fig. S29 Time dependent ^{1}H-NMR (300 MHz, DMSO_d_6) of complex **17.**

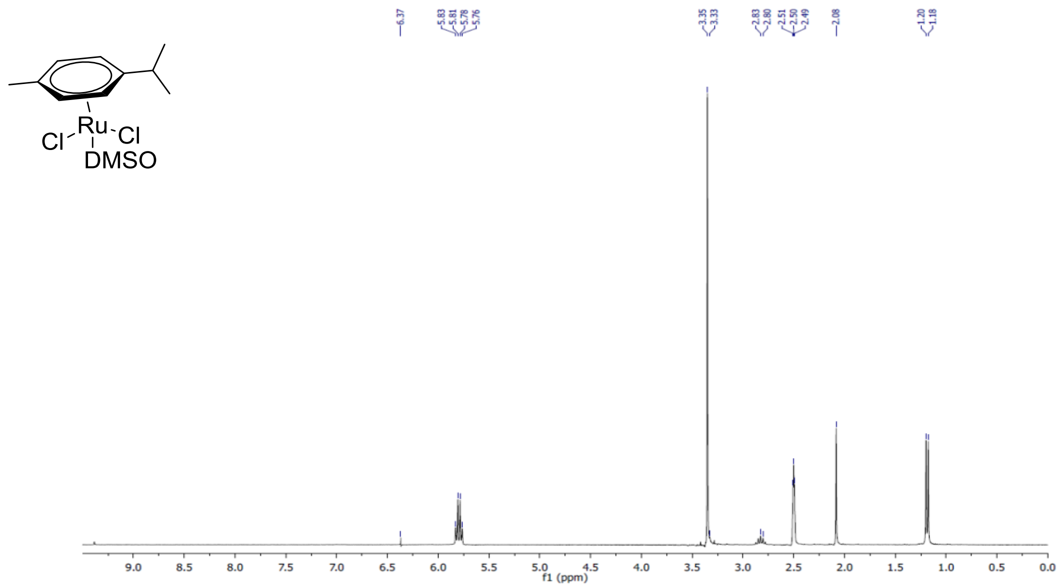


Fig. S30 [1]H-NMR (300 MHz, DMSO_d_6) of complex **[Ru(η^6-*p*-cymene)Cl_2(DMSO)]**.

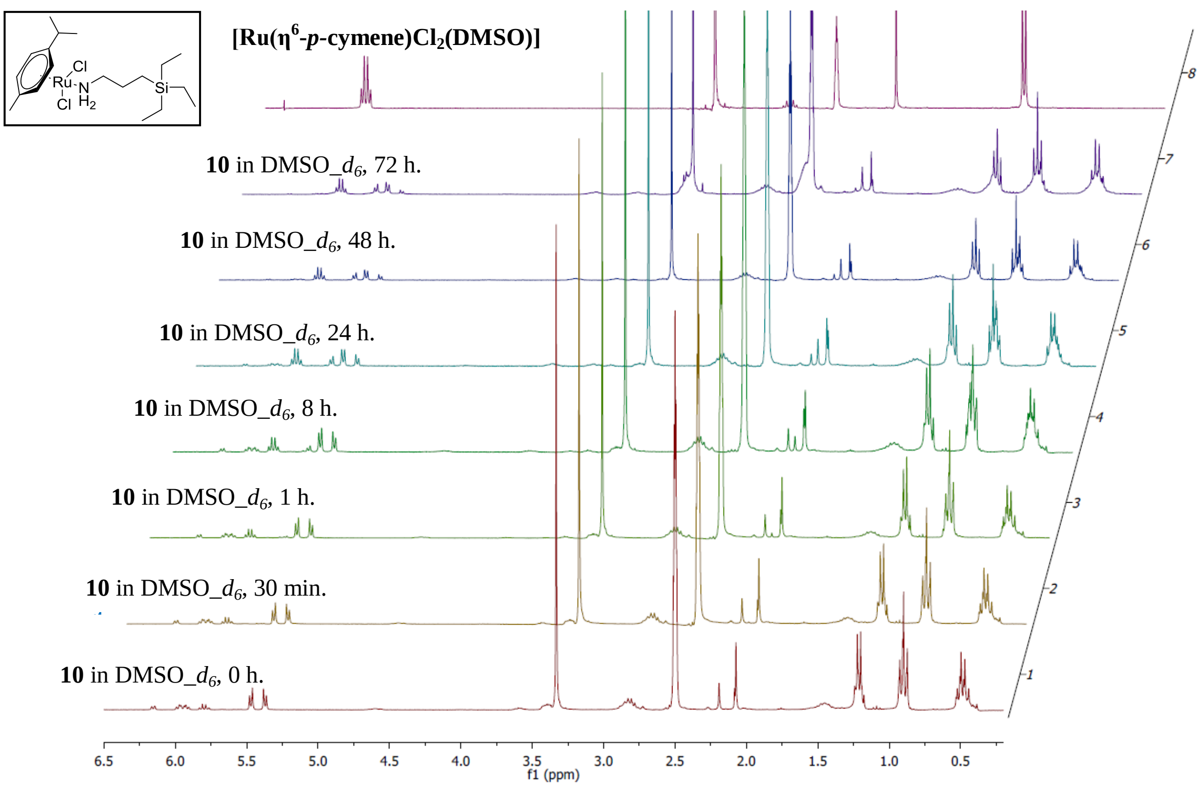


Fig. S31 Time dependent [1]H-NMR (300 MHz, DMSO_d_6) of complex **10.**

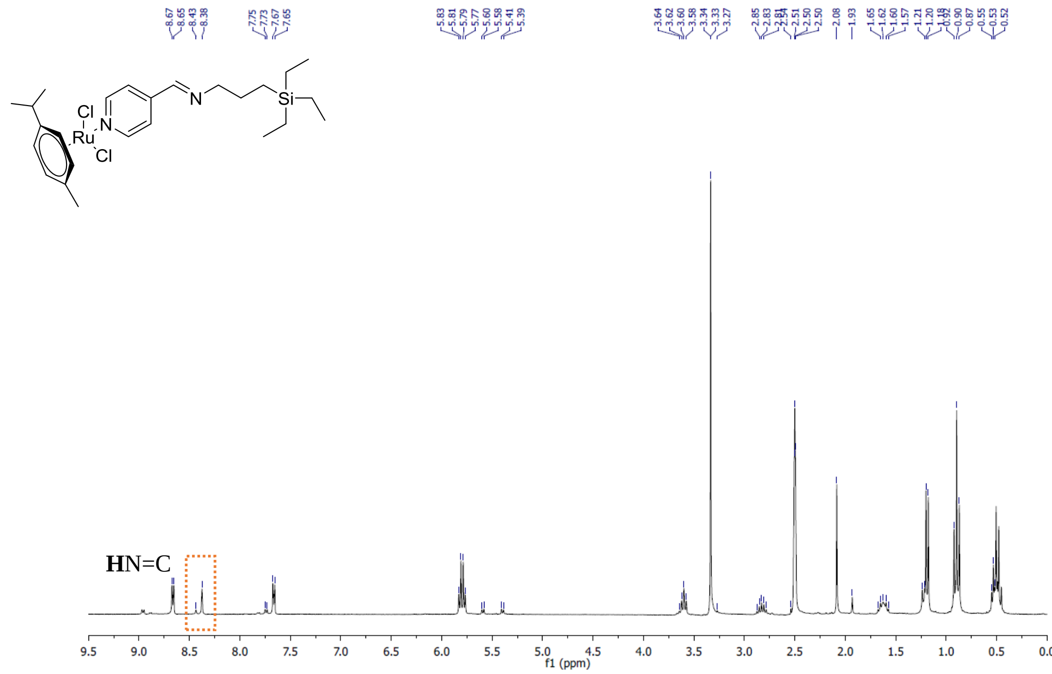
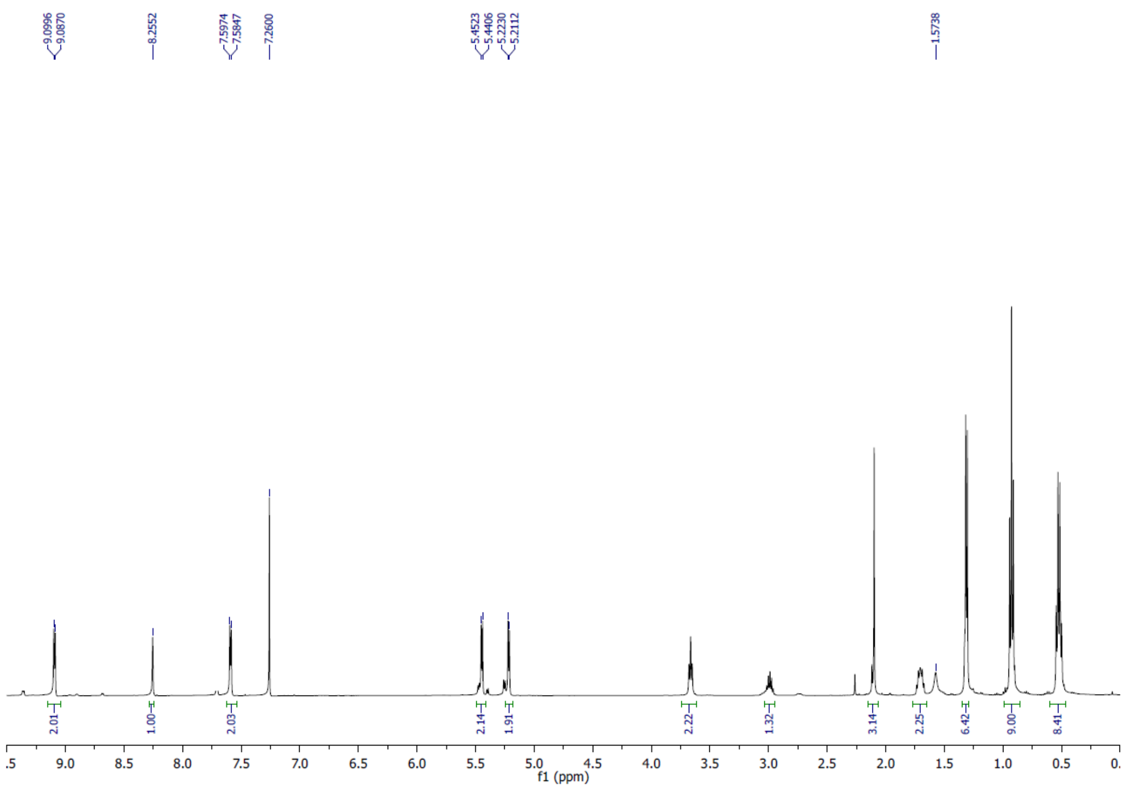


Fig. S32 ^{1}H-NMR (300 MHz, DMSO_d_6) of complex **13**.



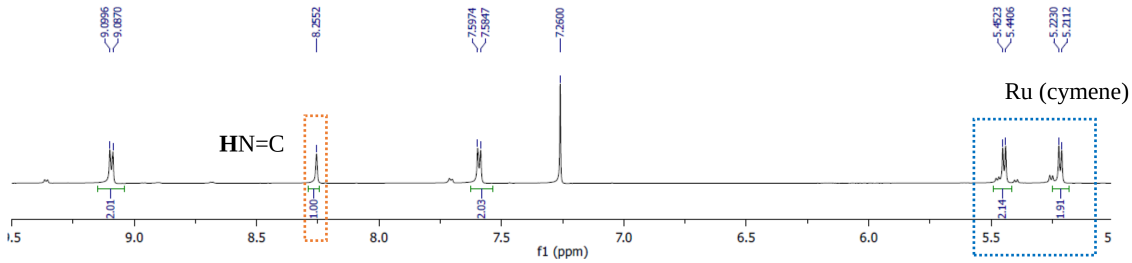


Fig. S33 ^{1}H-NMR (300 MHz, $CDCl_3$) of complex **13.**

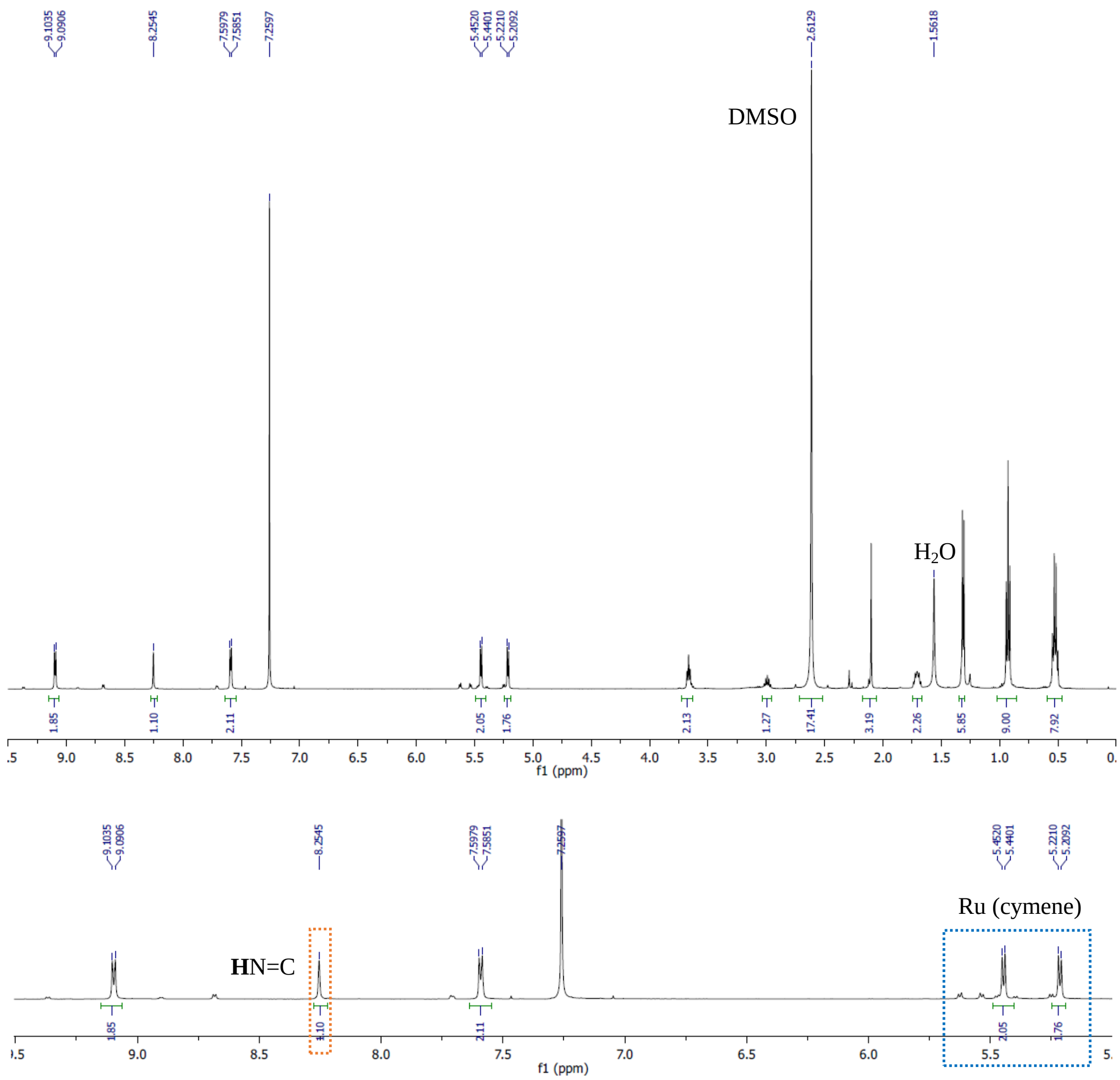


Fig. S34 ^{1}H-NMR (300 MHz, $CDCl_3$/DMSO (1:4)) of complex **13.**

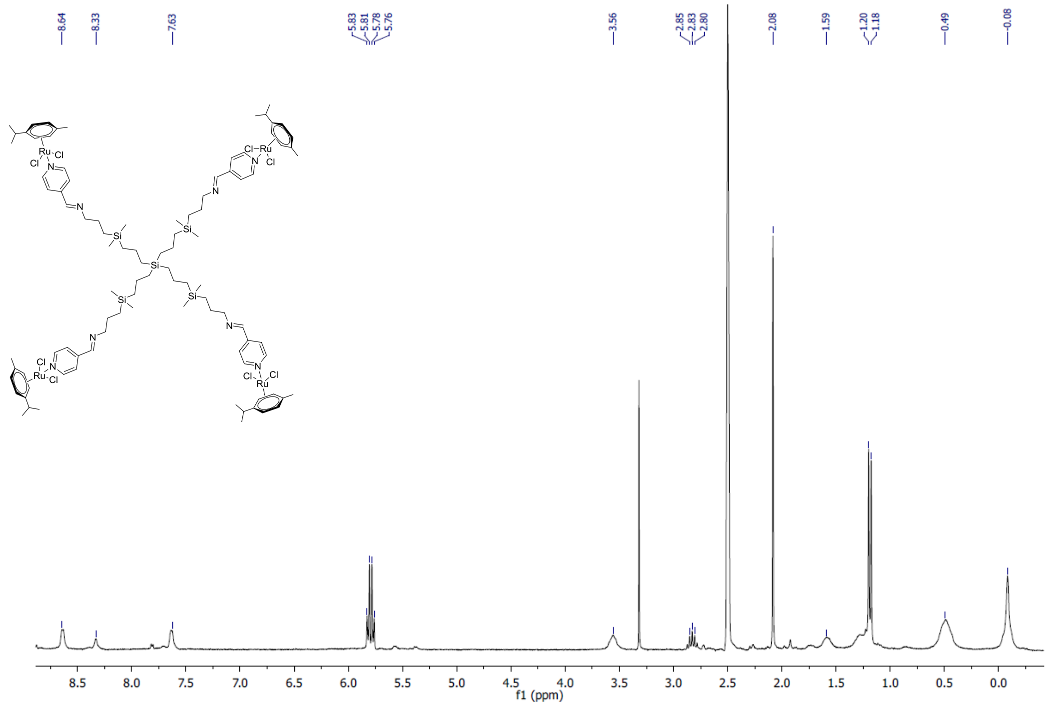


Fig. S35 ^{1}H-NMR (300 MHz, DMSO_d_6) of complex **14**.

9. *Fluorescence titration curve of HSA with compound* ***10-11, 13-15, 17-18***

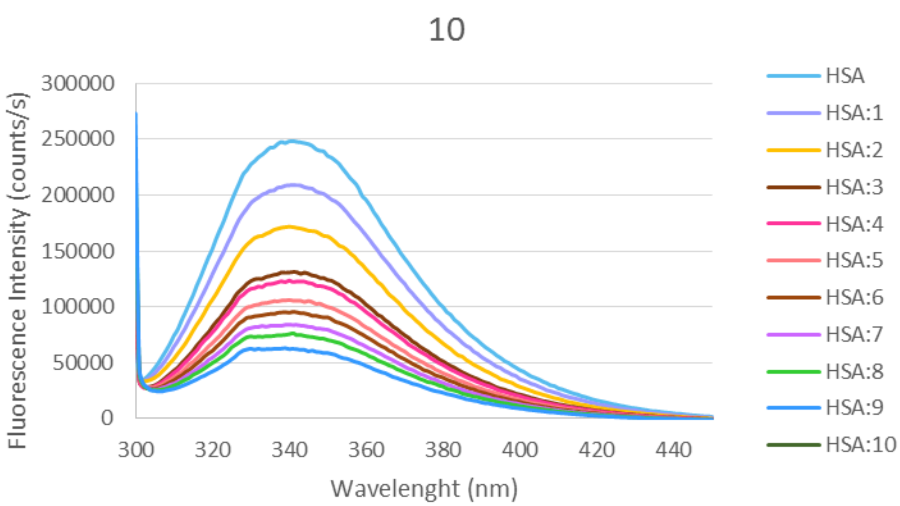


Fig. S36 Fluorescence titration curve of HSA with compound **10**.

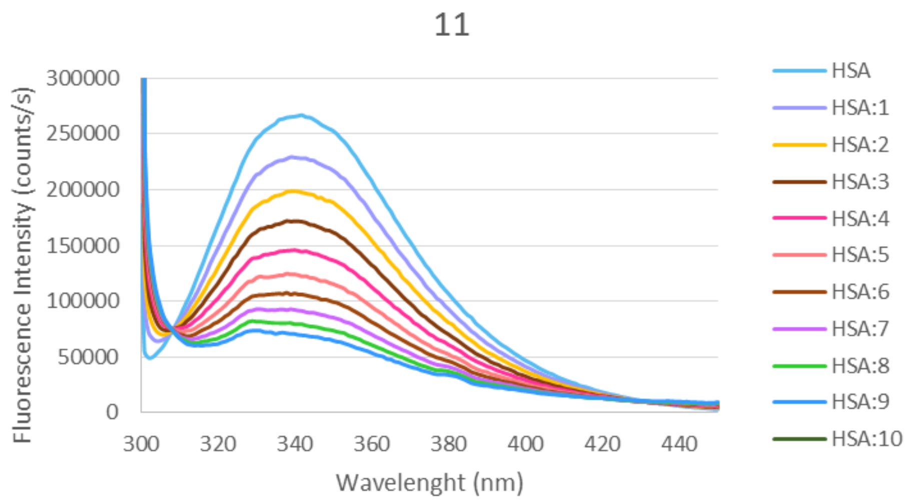


Fig. S37 Fluorescence titration curve of HSA with compound **11**.

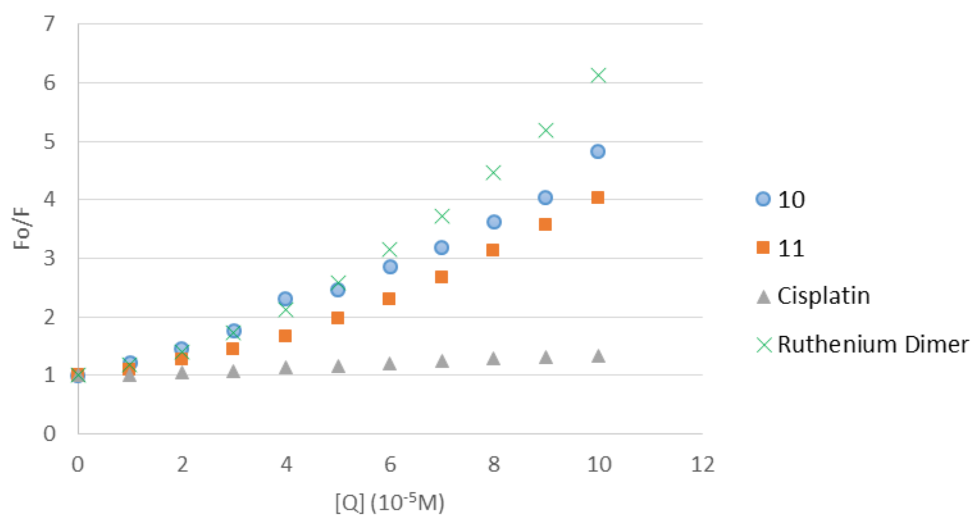


Fig. S38 Stern-Volmer plot for HSA fluorescence quenching observed with compound **10, 11,** the ruthenium dimer [Ru(η^6-*p*-cymene)Cl_2]$_2$ and cisplatin.

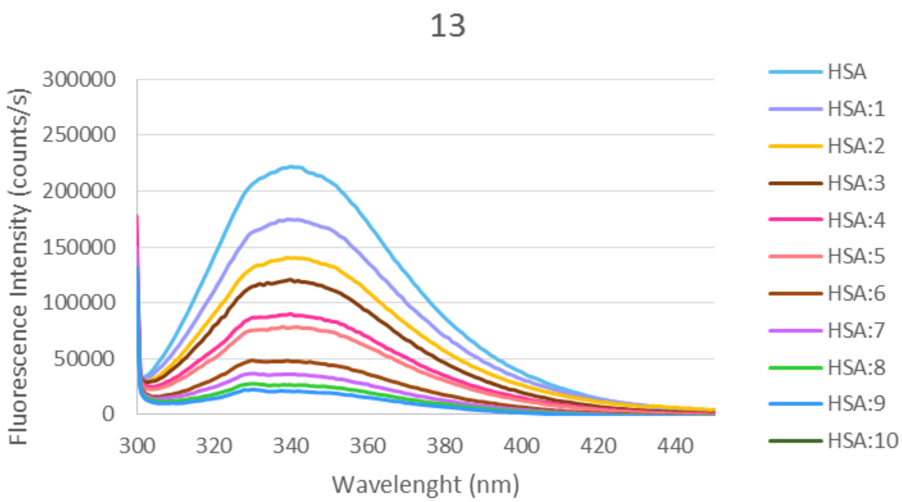


Fig. S39 Fluorescence titration curve of HSA with compound **13**.

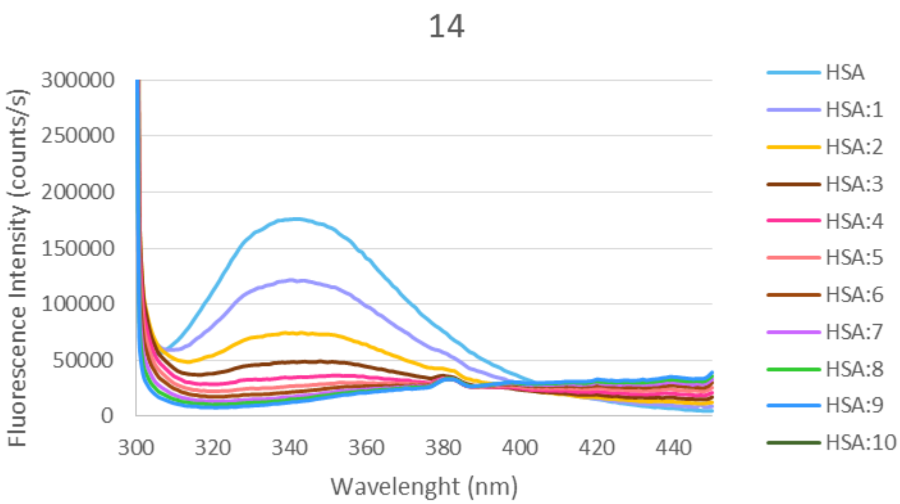


Fig. S40 Fluorescence titration curve of HSA with compound **14**.

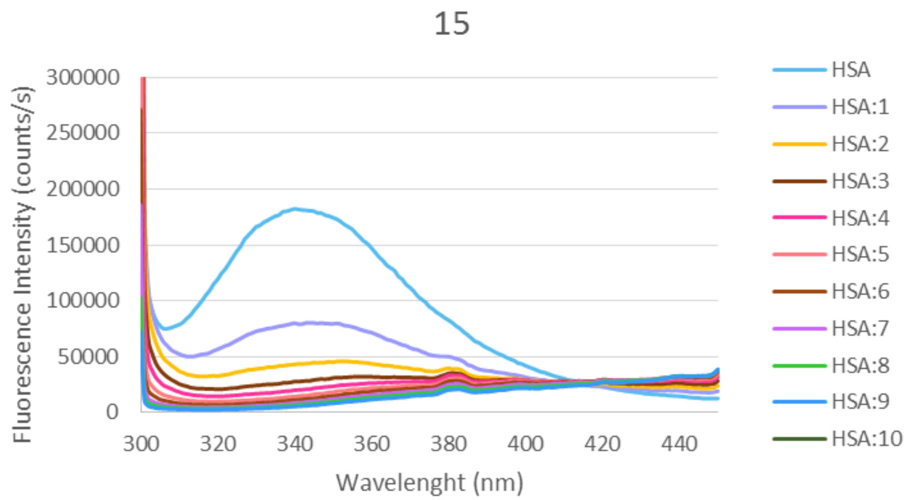


Fig. S41 Fluorescence titration curve of HSA with compound **15**.

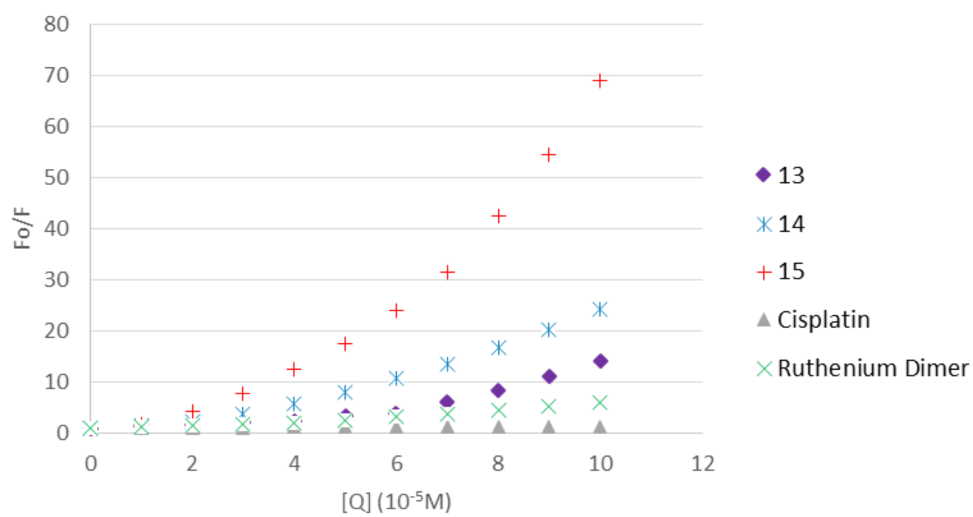


Fig. S42 Stern-Volmer plot for HSA fluorescence quenching observed with compound **13, 14, 15,** the ruthenium dimer [Ru(η^6-*p*-cymene)Cl_2]$_2$ and cisplatin.

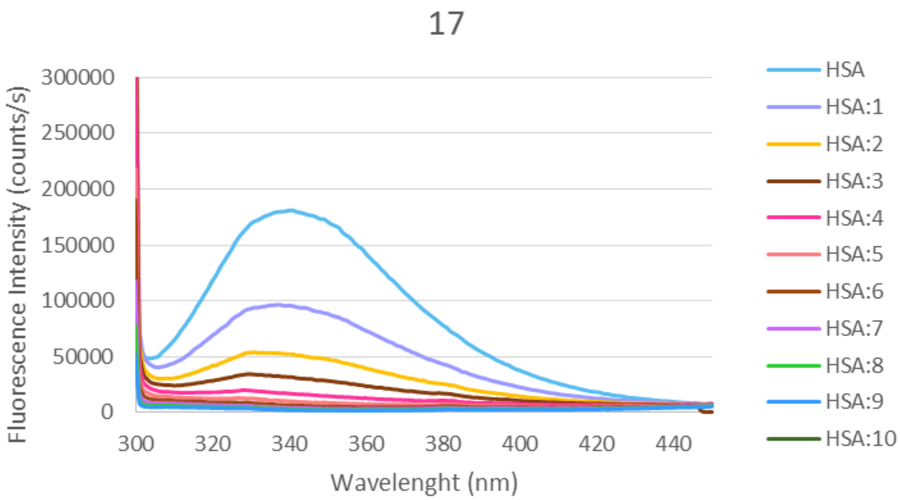


Fig. S43 Fluorescence titration curve of HSA with compound **17**.

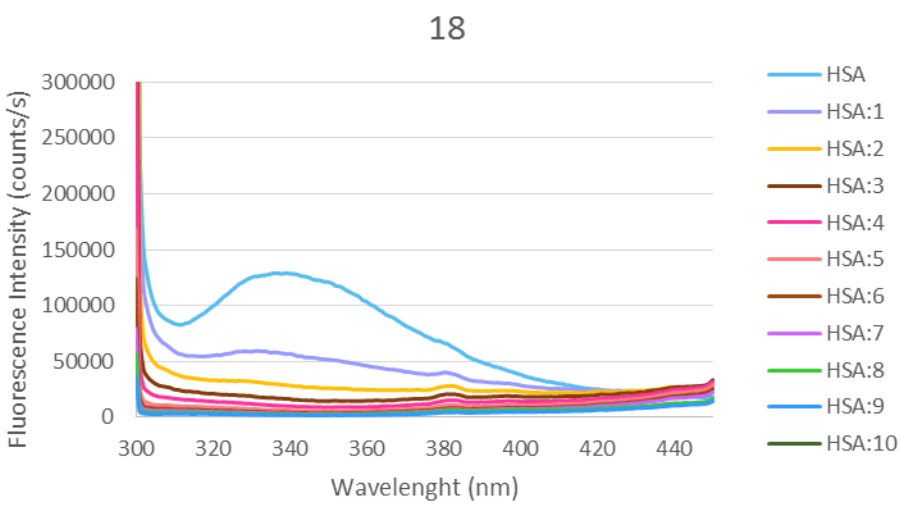


Fig. S44 Fluorescence titration curve of HSA with compound **18**.

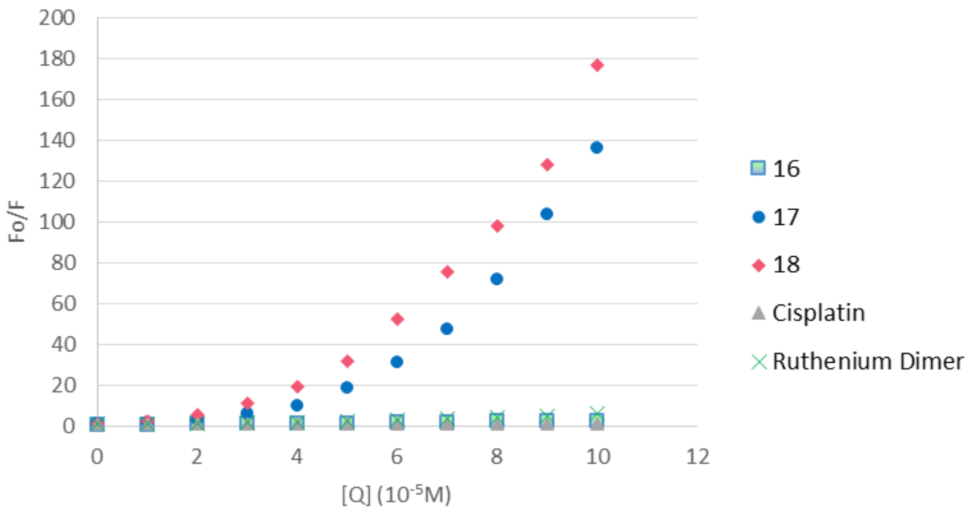


Fig. S45 Stern-Volmer plot for HSA fluorescence quenching observed with compound **16, 17, 18,** the ruthenium dimer [Ru(η^6-*p*-cymene)Cl_2]$_2$ and cisplatin.

10. Crystal and structure refinement data for compound **10**

Table S1 Crystal and structure refinement data for compound **10.**

Empirical formula	$C_{19}H_{37}Cl_2NRuSi$
Formula weight	479.57
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	
A	7.2564(5) Å
B	11.7148(10) Å
C	13.8168(14) Å
α	78.098(8)°

β	82.292(5)º
γ	85.667(6)º
Volume, ^ Å 3	1137.50(17) - Å 3
Z, Cal.density Mg/m^3	2,1.400
Absorption coefficient mm^{-1}	0.979
F(000)	500
Crystal size, mm	0.30 x 0.26 x 0.2
θ range for data collection	3.04º to 27.50º
Limiting indices	-9<=h<=9, -15<=k<=15, -17<=l<=17
Reflections collected /unique	9855 / 5217 [R(int) = 0.0858]
Completeness to θ	θ =27.50; 99.8 %
Absorption correction	Multi-scan
Max. and min. transmission	0.864 and 0.649
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5217 / 0 / 217
Goodness-of-fit on F^2	0.755
Final R indices [I>2σ(I)]	R1 = 0.0487, wR2 = 0.1049
R indices (all data)	R1 = 0.980, wR2 = 0.1253
Largest diff. peak and hole e.$^{-3}$ Å	0.712 and -0.637

Table S2 Selected bond lengths (Å) and angles (º) for compound **10**.

Selected bond lengths (Å) for compound 10.			
Ru(1)-Cl(1)	2.4246 (12)	Ru (1)-C(4)	2.203 (5)
Ru(1)-Cl(2)	2.4126 (12)	Ru (1)-C(1)	2.208 (5)
Ru(1)-N(1)	2.135 (4)	N(1)-C(11)	1.475 (6)
Ru(1)-Cent	1.668	Si(1)-C(18)	1.861 (5)
Ru(1)-C(5)	2.163 (5)	Si(1)-C(16)	1.864 (6)
Ru(1)-C(3)	2.165 (4)	Si(1)-C(14)	1.877 (6)
Ru(1)-C(2)	2.184 (4)	Si(1)-C(13)	1.878 (5)
Ru(1)-C(6)	2.192 (5)		
Selected bond angles (º) for compound 10.			
N(1)-Ru(1)-Cl(2)	80.51 (11)	C(18)-Si(1)-C(16)	108.7 (3)
N(1)-Ru(1)-Cl(1)	80.89 (11)	C(18)-Si(1)-C(14)	109.0 (3)
Cl(2)-Ru(1)-Cl(1)	87.79 (5)	C(16)-Si(1)-C(14)	110.2 (3)
Cent*-Ru(1)-Cl(1)	128.24	C(18)-Si(1)-C(13)	109.4 (2)
Cent*-Ru(1)-Cl(1)	128.63	C(16)-Si(1)-C(13)	107.6 (2)
Cent*-Ru(1)-Cl(1)	133.35	C(14)-Si(1)-C(13)	111.9 (3)
C(11)-N(1)-Ru(1)	120.2 (3)		
*Cent is the centroid of C1 C2 C3 C4 C5 C6.			