New half sandwich Ru(II) coordination compounds for anticancer activity

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Supporting Information

Syntheses of complexes **2**, **3**, **4**, **6** (PF_6 salt), **9** (PF_6 salt), **10** (PF_6 salt), **11** (Cl salt), **12** (Cl salt), **14** (PF_6 salt), **15** (PF_6 salt).

Table 1S. Crystallographic data for [Ru([9]aneN3)(dmso-S)$_2$Cl][PF_6] (**9-PF$_6$**).

Figure S1: ORTEP view, selected bond lengths and angles of [Ru([9]aneS3)(en)Cl][PF_6] (**4**).

Figure S2: The 2D homonuclear ^{1}H-^{1}H COSY and heteronuclear ^{1}H-^{13}C HSQC NMR spectra of **5** in CD_3NO_2 at 25.0 °C.

Figure S3: ^{1}H NMR spectrum of **6** in D_2O at 25.0 °C.

Figure S4: ORTEP view, selected bond lengths and angles of [Ru([9]aneN3)(dmso-S)$_2$Cl][PF_6] (**9**).

Figure S5: ^{1}H NMR spectra of complexes **9** – **12** and **14** – **16** in D_2O at 25.0 °C.

Figure S6: The 2D homonuclear ^{1}H-^{1}H COSY and heteronuclear ^{1}H-^{13}C HSQC NMR spectra of **11** in D_2O at 25.0 °C.

Figure S7: ^{1}H NMR spectra of complex **5** in absence and presence of NaCl.

Figure S8: ^{1}H NMR spectrum of **13** recorded 3 min after dissolution in D_2O at 25.0 °C.

Figure S9: Time evolution of the ^{1}H NMR spectrum of complex **12** in D_2O at 25.0 °C.

Syntheses

[Ru([9]aneS3)(dmso-S)$_2$Cl][PF$_6$] (2). A 400 mg amount of **1** (1 mmol) was suspended in 30 mL of acetone. To this mixture 1.05 eq of $AgPF_6$ (240 mg, 1.1 mmol) and 2.1 eq of DMSO (2.2 mmol, 134 μL) were added and the mixture was refluxed for 1.5 h in dark. The precipitate of AgCl was filtered off over celite and the yellow solution was rotary concentrated to dryness. Addition of ethanol induced the precipitation of **6** as yellow solid, which was collected by filtration, washed with ethanol and diethyl ether and vacuum dried (469.5 mg, 82%). Found: C, 19.5; H, 4.07%. $C_{10}H_{24}ClF_6O_2PRuS_5$ (618.11) requires: C, 19.4; H, 3.91%. Complex **2** is soluble in H_2O, methanol, acetone, partially soluble in dichloromethane, while it is insoluble in ethanol and chloroform. UV-Vis λ_{max} (H_2O)/nm 301 and 366 (ε/dm^3 mol^{-1} cm^{-1} 488 and 335). Selected IR (KBr) ν_{max}/cm^{-1} 1092s and 1080s (S=O$_{dmso-S}$), 846vs, 833vs and 557s (PF_6), 432w and 420w (Ru-S$_{dmso-S}$). δ_H (D_2O) 3.45 (6 H, s, C*H*$_3$ dmso), 3.37 (6 H, s, C*H*$_3$ dmso), 3.34 – 2.78 (12 H, m, C*H*$_2$ [9]aneS3).

[Ru([9]aneS3)(dmso)$_3$][PF$_6$]$_2$ (3). To a warm solution of **1** (300 mg, 0.69 mmol) in 20 mL of methanol 2.1 eq of $AgPF_6$ (355 mg, 1.5 mmol) and 3.5 eq of DMSO (173 μL, 2.4 mmol) were added and the mixture was refluxed for 2h in dark. The AgCl precipitate was filtered off over celite and the pale yellow filtrate was rotary evaporated to dryness to yield a yellow oil. Treatment of the oil with ca. 5 mL of ethanol afforded the product as pale yellow solid which was collected by filtration, washed with ethanol and diethyl ether and dried in vacuo (375.2 mg, 67%). Found: C, 17.9; H, 3.69%. $C_{12}H_{30}F_{12}O_3P_2RuS_6$ (805.75) requires: C, 17.9; H, 3.75%. Complex **3** is soluble in H_2O, methanol, acetone, partially soluble in dichloromethane, while it is insoluble in ethanol and chloroform. Selected IR (KBr) ν_{max}/cm^{-1} 1106m br (S=O$_{dmso-S}$), 935m br (S=O$_{dmso-O}$), 839s br and 558s (PF_6), 455w (Ru-O$_{dmso-O}$), 419w (Ru-S$_{dmso-S}$). As already reported by us,[28] in solution there is an equilibrium mixture of two linkage isomers, *i.e.* [Ru([9]aneS3)(dmso-S)$_2$(dmso-O)][PF$_6$]$_2$ (**3A**) and [Ru([9]aneS3)(dmso-S)(dmso-O)$_2$][PF$_6$]$_2$ (**3B**), the ratio between **3A** and **3B** being *ca.* 1:2.5. δ_H (CD_3NO_2) 3.43 (2.4 H, s, C*H*$_3$ dmso-S **A**), 3.40 – 2.80 (16.8 H, m, C*H*$_2$ [9]aneS3), 3.34 (2.4 H, s,

C*H*$_3$ dmso-S **A**), 3.18 (6 H, s, C*H*$_3$ dmso-S **B**), 3.04 (2.4 H, s, C*H*$_3$ dmso-O **A**), 2.96 (6 H, s, C*H*$_3$ dmso-O **B**), 2.94 (6 H, s, C*H*$_3$ dmso-O **B**).

[Ru([9]aneS3)(en)Cl][PF$_6$] (4). A 150 mg amount of **2** (0.24 mmol) was partially dissolved in 30 mL of methanol, 1,2-diaminoethane (18 μL, 0.26 mmol) was added and the reaction mixture was refluxed for 3 h under argon. During this time the precursor dissolved completely and a dark yellow solution was obtained. Rotary concentration of the solution to ca. 5 mL and saturation with diethyl ether afforded, within 24 h, compound **4** as a yellow crystalline solid. The crystals were collected by filtration, washed with cold methanol and diethyl ether and vacuum dried (64.3 mg, 51%). Found: C, 18.5; H, 3.79; N, 5.44%. $C_8H_{20}ClF_6N_2PRuS_3$ (521.94) requires: C, 18.4; H, 3.86; N, 5.37%. Complex **4** is soluble in H_2O, methanol, nitromethane, partially soluble in acetone and insoluble in ethanol, chloroform and dichloromethane. Selected IR (KBr) ν_{max}/cm^{-1} 3343m, 3216m and 3152m (NH_{en}), 838vs and 559s (PF_6). δ_H (CD_3NO_2) 3.87 (2 H, br s, N*H*$_2$ en), 3.35 (2 H, br s, N*H*$_2$ en), 3.02 – 2.90 (2 H, m, C*H*$_2$ en), 2.88 – 2.76 (2 H, m, C*H*$_2$ en), 2.73 – 2.54 (6 H, m, C*H*$_2$ [9]aneS3), 2.54 – 2.29 (6 H, m, C*H*$_2$ [9]aneS3). δ_C (CD_3NO_2) 45.7 (*C*H$_2$ en), 35.8 (*C*H$_2$ [9]aneS3), 33.0 (*C*H$_2$ [9]aneS3), 32.5 (*C*H$_2$ [9]aneS3).

[Ru([9]aneS3)(en)(H$_2$O)]$^{2+}$ (4aq). δ_H (D_2O) 4.70 (2 H, br s, N*H*$_2$ en), 3.87 (2 H, br s, N*H*$_2$ en), 2.74 (4 H, m, C*H*$_2$ en), 2.70 – 2.53 (6 H, m, C*H*$_2$ [9]aneS3), 2.52 – 2.32 (6 H, m, C*H*$_2$ [9]aneS3).

[Ru([9]aneS3)(NH$_3$)$_3$][PF$_6$]$_2$ (6). A 50 mg amount of **3** (0.062 mmol) was suspended in 6 mL of a methanol/acetone (5:1) solution saturated with gaseous NH_3 and the mixture was heated to reflux for 1.5 h. During this time all solid dissolved, yielding a bright yellow solution. Rotary evaporation of the solvent afforded a yellow oil; addition of ethanol afforded the product as a yellow solid that was collected by filtration, washed with ethanol and diethyl ether and dried in vacuo (31.4 mg, 81%). Found: C, 11.5; H, 3.27; N, 6.69%. $C_6H_{21}F_{12}N_3P_2RuS_3$ (622.44) requires: C, 11.6; H, 3.40; N, 6.75%. Complex **6** is soluble in H_2O, methanol, acetone and nitromethane, sparingly soluble in ethanol, while it is insoluble in chloroform and dichloromethane. UV-Vis λ_{max} (H_2O)/nm 238, 294

and 354 (ε/dm^3 mol^{-1} cm^{-1} 4 783, 1 160 and 944). Selected IR (KBr) ν_{max}/cm^{-1} 3212s and 3142s (NH_{NH3}), 833vs and 555s (PF_6). δ_H (D_2O) 2.80 (9 H, br s, N*H*$_3$), 2.67 – 2.56 (6 H, m, C*H*$_2$ [9]aneS3), 2.49 - 2.37 (6 H, m, C*H*$_2$ [9]aneS3). δ_C (D_2O) 32.9 (*C*H$_2$ [9]aneS3).

[Ru([9]aneN3)(dmso-S)$_2$Cl][PF$_6$] (9). A 30 mg amount of **9** (as Cl salt, 0.06 mmol) was dissolved in 10 mL of warm ethanol and containing a slight excess of NH_4PF_6 (12 mg, 0.07 mmol, 1.1 eq) dissolved 1 mL of ethanol was added. Slow evaporation of the solvent to ca. 3 mL afforded the product as a white solid, which was collected by filtration, washed with ethanol and diethyl ether and vacuum dried (27.2 mg, 80%). Crystals of **9** (as PF_6 salt) suitable for X-Ray analysis were obtained when the above reaction was performed in methanol, upon saturation with diethyl ether. Found: C, 21.2; H, 4.97; N, 7.37%. $C_{10}H_{27}ClF_6N_3O_2PRuS_2$ (566.96) requires: C, 21.2; H, 4.80; N, 7.41%. Complex **9** is soluble in H_2O, methanol and acetone, partially soluble in nitromethane and insoluble in ethanol, chloroform, dichloromethane and toluene. UV-Vis λ_{max} (H_2O)/nm 285 and 356 (ε/dm^3 mol^{-1} cm^{-1} 600 and 287). Selected IR (KBr) ν_{max}/cm^{-1} 1084s (S=O$_{dmso-S}$), 843vs and 557s (PF_6), 423w (Ru-S$_{dmso-S}$). δ_H (D_2O) 6.35 (1 H, br s, N*H* [9]aneN3 *trans*-Cl), 6.13 (2 H, br s, 2 x N*H* [9]aneN3 *trans*-S), 3.60 – 3.52 (2 H, m, C*H*$_2$ [9]aneN3), 3.34 (6 H, s, C*H*$_3$ dmso), 3.32 (6 H, s, C*H*$_3$ dmso), 3.23 – 3.09 (4 H, m, C*H*$_2$ [9]aneN3), 3.01 – 2.85 (6 H, m, C*H*$_2$ [9]aneN3). δ_C (D_2O) 53.0 (*C*H$_2$ [9]aneN3), 50.4 (*C*H$_2$ [9]aneN3), 50.3 (*C*H$_2$ [9]aneN3), 46.0 (*C*H$_3$ dmso), 45.8 (*C*H$_3$ dmso).

[Ru([9]aneN3)(en)(dmso-S)][PF$_6$]$_2$ (10). To a warm solution of **9** (as Cl salt, 50 mg, 0.11 mmol) in 5 mL of methanol, 1,2-diaminoethane (21.9 µL, 0.32 mmol, 3 eq) was added and the mixture was refluxed for 2 h under argon. Then a 52 mg amount of $AgPF_6$ (0.22 mmol, 2.05 eq), partially dissolved in 5 mL of methanol, was added and the mixture was refluxed for additional 2 h in the dark. The precipitate of AgCl was filtered off over celite and the orange solution was rotary evaporated to ca. half volume and saturated with diethyl ether. Overnight storage at 4°C afforded the product as a dark yellow solid which was collected by filtration, washed with cold methanol and diethyl ether and vacuum dried (26.2 mg, 32%). Found: C, 18.1; H, 4.37; N, 10.71%.

$C_{10}H_{29}F_{12}N_5OP_2RuS$ (658.43) requires: C, 18.2; H, 4.44; N, 10.64%. Complex **10** is soluble in H_2O and methanol, partially soluble in ethanol, acetone and nitromethane, while it is insoluble in chloroform and dichloromethane. UV-Vis λ_{max} (H_2O)/nm 306 (ε/dm^3 mol^{-1} cm^{-1} 342). Selected IR (KBr) ν_{max}/cm^{-1} 1110m (S=$O_{dmso\text{-}S}$), 833vs and 560s (PF_6), 443w (Ru-$S_{dmso\text{-}S}$). δ_H (D_2O) 5.89 (1 H, br s, N*H* [9]aneN3 *trans*-dmso), 5.70 (2 H, br s, 2 x N*H* [9]aneN3 *trans*-en), 3.74 (4 H, s, NH_2 en), 3.33 (6 H, s, CH_3 dmso), 3.35 – 3.24 (2 H, m, CH_2 [9]aneN3), 3.14 – 2.99 (4 H, m, CH_2 [9]aneN3), 2.97 – 2.82 (4 H, m, CH_2 [9]aneN3), 2.80 – 2.69 (2 H, m, CH_2 [9]aneN3), 2.67 – 2.49 (4 H, m, CH_2 en). δ_C (D_2O) 51.3 (*C*H_2 [9]aneN3), 51.0 (*C*H_2 [9]aneN3), 48.9 (*C*H_2 [9]aneN3), 47.4 (*C*H_3 dmso), 44.5 (*C*H_2 en).

[Ru([9]aneN3)(dach)(dmso-S)]Cl_2 (11). To a warm solution of **9** (as Cl salt, 50 mg, 0.11 mmol) in 15 mL of dry methanol *trans*-1,2-diaminocyclohexane (13 μL, 0.12 mmol, 1.1 eq) was added and the mixture was refluxed for 3 h. The dark yellow solution was rotary evaporated to an oil; addition of ethanol (ca. 5 mL) followed by saturation with diethyl ether led to the formation, upon standing at r.t. for 24 h, of **11** as a pale-brown solid. The product was removed by filtration, washed with acetone and diethyl ether and dried in vacuo (39 mg, 72%). Found: C, 34.2; H, 4.23; N, 14.11%. $C_{14}H_{35}Cl_2N_5ORuS$ (493.50) requires: C, 34.1; H, 7.15; N, 14.19%. Complex **11** is soluble in H_2O, methanol and ethanol, partially soluble in nitromethane, and insoluble in acetone, chloroform and dichloromethane. UV-Vis λ_{max} (H_2O)/nm 306 (ε/dm^3 mol^{-1} cm^{-1} 515). Selected IR (KBr) ν_{max}/cm^{-1} 1109m (S=$O_{dmso\text{-}S}$), 432w (Ru-$S_{dmso\text{-}S}$). δ_H (D_2O) 6.01 (1 H, br s, N*H* [9]aneN3), 5.82 (1 H, br s, N*H* [9]aneN3), 5.62 (1 H, br s, N*H* [9]aneN3), 4.35 (1 H, br d, N^1H_{eq}), 3.90 (1 H, br d, N^2H_{eq}), 3.35 (3 H, s, CH_3 dmso), 3.34 (3 H, s, CH_3 dmso), 3.35 – 2.65 (12 H, m, CH_2 [9]aneN3), 3.10 (1 H, m, N^2H_{ax}), 2.99 (1 H, m, N^1H_{ax}), 2.18 (2 H, m, C^1H/C^2H), 2.07 (2 H,m, C^3H_{ax}/C^6H_{ax}), 1.65 (2 H, m, C^4H_{ax}/C^5H_{ax}), 1.26 (2 H,m, C^3H_{eq}/C^6H_{eq}), 1.17 (2 H, m, C^4H_{eq}/C^5H_{eq}). δ_C (D_2O) 60.1/59.5 (C^1H/C^2H), 52.8 (*C*H_2 [9]aneN3), 52.7 (*C*H_2 [9]aneN3), 50.4 (*C*H_2 [9]aneN3), 50.2 (*C*H_2

[9]aneN3), 49.6 (CH_2 [9]aneN3), 47.9 (CH_2 [9]aneN3), 47.9 (CH_3 dmso), 47.7 (CH_3 dmso), 34.9/34.3 (C^3H_2/C^6H_2), 24.9/24.8 (C^4H_2/C^5H_2).

[Ru([9]aneN3)(bpy)(dmso-S)]Cl_2 (12). A 50 mg amount of **9** (as Cl salt, 0.11 mmol) was dissolved in 15 mL of an acetone/methanol (1:1) mixture and then 2,2'-bpy (34 mg, 0.22 mmol) was added. The reaction mixture was refluxed for 4 h, during which time the colour of the solution changed from yellow to red. The solvent was then removed in vacuo and replaced with acetone (ca. 2 mL) to yield the product as a yellow-brown solid. It was collected by filtration, washed thoroughly with acetone and diethyl ether and vacuum dried (40.0 mg, 69%). Crystals suitable for X-ray analysis were obtained by saturation of a methanol solution of **12** with diethyl ether. Found: C, 40.5; H, 5.54; N, 13.01%. $C_{18}H_{29}Cl_2N_5ORuS$ (535.50) requires: C, 40.4; H, 5.46; N, 13.08%. Complex **12** is soluble in H_2O, methanol and ethanol, partially soluble in nitromethane, while it is insoluble in acetone, chloroform and dichloromethane. UV-Vis λ_{max} (H_2O)/nm 241, 250, 281, 318 and 388 (ε/dm^3 mol^{-1} cm^{-1} 11 016, 10 150, 27 278, 5 459 and 4 143). Selected IR (KBr) ν_{max}/cm^{-1} 1078s ($S{=}O_{dmso\text{-}S}$), 429m ($Ru\text{-}S_{dmso\text{-}S}$). δ_H (D_2O) 8.93 (2 H, d, J = 5.4 Hz, $C^6H/C^{6'}H$), 8.48 (2 H, d, J = 8.1 Hz, $C^3H/C^{3'}H$), 8.19 (2 H, t, J = 7.9 Hz, $C^4H/C^{4'}H$), 7.73 (2 H, t, $C^5H/C^{5'}H$), 6.45 (2 H, br s, 2 × N*H* [9]aneN3), 5.65 (1 H, br s, N*H* [9]aneN3), 3.41 – 3.27 (4 H, m, CH_2 [9]aneN3), 3.07 – 2.95 (4 H, m, CH_2 [9]aneN3), 2.91 – 2.78 (4 H, m, CH_2 [9]aneN3), 2.67 (6 H, s, CH_3 dmso). δ_C (D_2O) 158.5 ($C^2/C^{2'}$), 154.1 ($C^6H/C^{6'}H$), 139.4 ($C^4H/C^{4'}H$), 128.5 ($C^5H/C^{5'}H$), 125.0 ($C^3H/C^{3'}H$), 51.1 (2 × CH_2 [9]aneN3), 50.7 (2 × CH_2 [9]aneN3), 48.8 (2 × CH_2 [9]aneN3), 44.3 (2 × CH_3 dmso).

[Ru([9]aneN3)(pic)(dmso-S)][PF_6] (14). To a warm solution of **9** (as Cl salt, 50 mg, 0.11 mmol) in 10 mL of methanol a 17.6 mg amount of K(pic) (0.11 mmol) was added and the mixture was refluxed for 6 h yielding an orange solution. After cooling, a 35 mg amount of NH_4PF_6 (0.215 mmol) was added. A yellow-orange crystalline solid formed upon standing overnight at room temperature. The product was removed by filtration, washed with ethanol and diethyl ether and vacuum dried (58.2 mg, 92%). Found: C, 29.3; H, 4.42; N, 9.89%. $C_{14}H_{25}F_6N_4O_3PRuS$ (575.47)

requires: C, 29.2; H, 4.38; N, 9.74%. Complex **14** is soluble in H_2O, acetone and nitromethane, partially soluble in methanol, while it is insoluble in ethanol, chloroform and dichloromethane. UV-Vis λ_{max} (H_2O)/nm 212, 254, 307sh and 357 (ε/dm^3 mol^{-1} cm^{-1} 5 765, 5 217, 1 296 and 1 957). Selected IR (KBr) ν_{max}/cm^{-1} 1626vs and 1596vs (COO_{asym}), 1384s and 1367s (COO_{sym}), 1096m ($S{=}O_{dmso\text{-}S}$), 838vs and 559s (PF_6), 428m (Ru-$S_{dmso\text{-}S}$). δ_H (D_2O) 8.83 (1 H, d, J = 5.4 Hz, C^6*H*), 8.11 (1 H, t, J = 7.3 Hz, C^4*H*), 8.05 (1 H, t, J = 7.2, C^3*H*) 7.73 (1 H, br t, C^5*H*), 6.17 (1 H, br s, N*H* [9]aneN3), 6.11 (2 H, br s, 2 x N*H* [9]aneN3), 3.41 – 3.13 (5 H, m, CH_2 [9]aneN3), 3.10 – 2.76 (7 H, m, CH_2 [9]aneN3), 2.92 (3 H, s, CH_3 dmso), 2.80 (3 H, s, CH_3 dmso). δ_C (D_2O) 176.5 (*C*=O), 154.9 (*C*^{6}H), 152.5 (*C*^{2}), 139.2 (*C*^{4}H), 130.2 (*C*^{5}H), 128.2 (*C*^{3}H), 54.1 (*C*H_2 [9]aneN3), 52.4 (*C*H_2 [9]aneN3), 50.0 (*C*H_2 [9]aneN3), 49.5 (*C*H_2 [9]aneN3), 47.7 (*C*H_2 [9]aneN3), 47.0 (*C*H_2 [9]aneN3), 44.3 (*C*H_3 dmso), 44.2 (*C*H_3 dmso).

[Ru([9]aneN3)(acac)(dmso-S)][PF_6] (15). To a warm solution of **9** (as Cl salt, 50 mg, 0.11 mmol) in 15 mL of methanol a 15 mg amount of Na(acac) (0.12 mmol) and 20 mg of $NaPF_6$ (0.12 mmol) were added and the mixture was refluxed for 6 h, yielding an orange solution. The solvent was removed in vacuo and replaced with ethanol (ca. 1 mL) affording the product as an orange solid which was collected by filtration, washed with ethanol and diethyl ether and vacuum dried (48.0 mg, 79%). Found: C, 28.3; H, 5.23; N, 7.41%. $C_{13}H_{28}F_6N_3O_3PRuS$ (552.48) requires: C, 28.3; H, 5.11; N, 7.61%. Complex **15** is soluble in H_2O, acetone and methanol, partially soluble in nitromethane, while it is insoluble in ethanol, chloroform and dichloromethane. UV-Vis λ_{max} (H_2O)/nm 213sh, 268 and 338br (ε/dm^3 mol^{-1} cm^{-1} 3 400, 5 380 and 1 870). Selected IR (KBr) ν_{max}/cm^{-1} 1518s (CO), 1107m ($S{=}O_{dmso\text{-}S}$), 839vs and 557s (PF_6), 428m (Ru-$S_{dmso\text{-}S}$). δ_H (D_2O) 6.31 (1 H, br s, N*H* [9]aneN3 *trans*-S), 5.49 (1 H, s, C*H* acac), 5.23 (2 H, br s, 2 × N*H* [9]aneN3 *trans*-O), 3.06 (6 H, s, CH_3 dmso) 3.15 – 2.73 (12 H, m, CH_2 [9]aneN3), 1.91 (6 H, s, 2 × CH_3 acac). δ_C (D_2O) 189.4 (2 × *C*=O), 101.1 (*C*H acac), 51.2 (2 × *C*H_2 [9]aneN3), 51.0 (2 x *C*H_2 [9]aneN3), 47.8 (2 × *C*H_2 [9]aneN3), 44.9 (2 × *C*H_3 dmso), 27.5 (2 × *C*H_3 acac).

Table 1S. Crystallographic data for [Ru([9]aneN3)(dmso-S)$_2$Cl][PF$_6$] (**9-PF$_6$**).

	9-PF$_6$
Empirical formula	$C_{10}H_{27}ClF_6N_3O_2PRuS_2$
fw	566.96
Crystal system	Triclinic
Space group	$P\bar{1}$
a, Å	7.0860(9)
b, Å	10.8960(10)
c, Å	13.0630(12)
α, deg	92.552(10)
β, deg	101.365(8)
γ, deg	93.978(9)
V, Å^3	984.67(18)
Z	2
D_{calcd}, g cm^{-3}	1.912
μ(Mo-Kα), mm^{-1}	–
F(000)	572
θ range, deg	2.24 – 28.52
no. of reflns collctd	6395
no. of indep reflns	3463
*R*int	0.0275
no. of reflns $I>2\sigma(I)$	1918
no. refined params	236
goodness-of-fit (F^2)	1.133
*R*1, *wR*2 ($I>2\sigma(I)$) [a]	0.0297, 0.0793
residuals, e/Å^3	0.357, –0.614

[a] $R1 = \Sigma \; | \; |Fo| - |Fc| \; | \; / \Sigma \; |Fo|$, $wR2 = [\Sigma \, w \, (Fo^2 - Fc^2)^2 / \Sigma w \, (Fo^2)^2]^{½}$

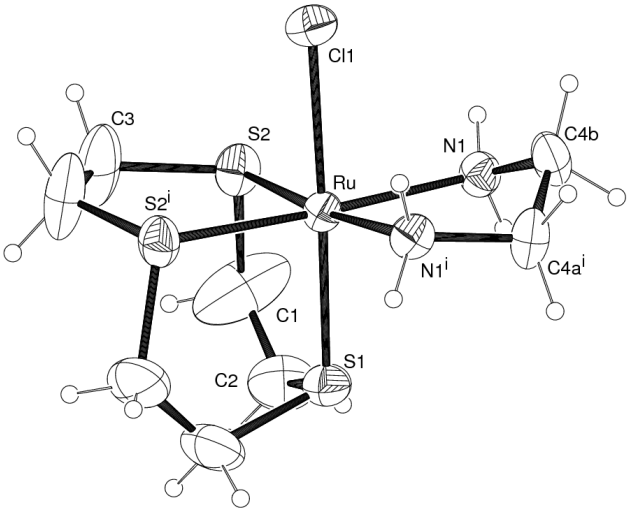

Fig. S1. ORTEP view (30% probability ellipsoids) of the cation of [Ru([9]aneS3)(en)Cl][PF_6] (**4**), which is located on a crystallographic mirror plane bisecting the chelating N–Ru–N bond angle and comprising the Cl1–Ru–S1 axis (only one conformation of the disordered en is ligand shown). Selected bond lengths (Å) and angles (°): Ru–N(1) 2.146(3), Ru–S(1) 2.2653(17), Ru–S(2) 2.2805(12), Ru–Cl(1) 2.4249(16); N(1')–Ru–N(1) 80.30(18), N(1)–Ru–S(1) 95.22(11), N(1)–Ru–S(2) 95.39(10), N(1)–Ru–S(2') 174.13(10), N(1)–Ru–Cl(1) 86.27(11), S(1)–Ru–S(2) 89.12(5), S(1)–Ru–Cl(1) 178.05(6), S(2)–Ru–S(2') 88.62(6), S(2)–Ru–Cl(1) 89.49(5) (Primed atoms at #1 x,–y+1/2,z). This structural determination confirms, as previously found by us,[19] that the Ru–S bond distance *trans* to Cl [2.2653(17) Å] is slightly shorter than those *trans* to the N atoms [2.2805(12) Å].

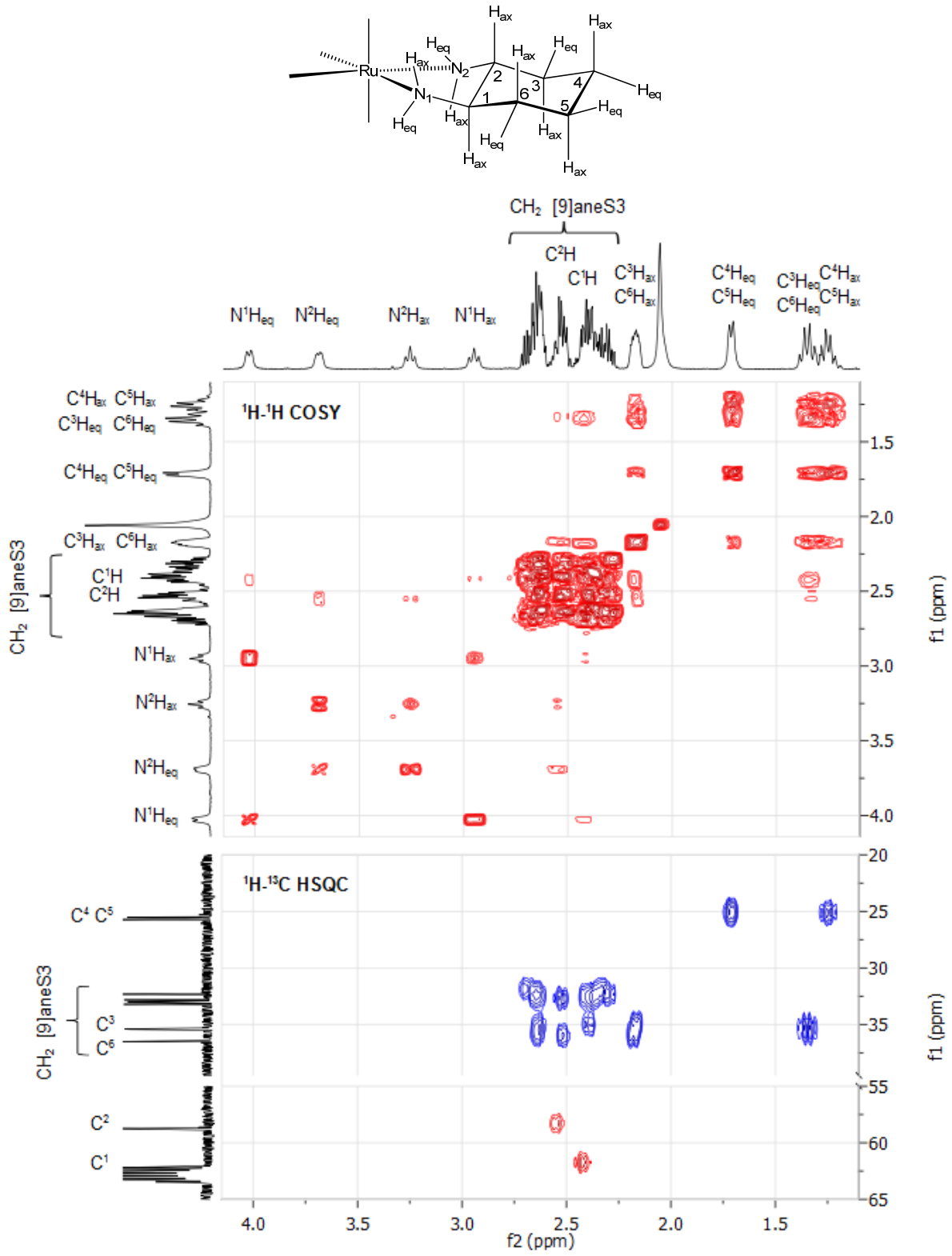

Fig. S2. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear ^{1}H-^{13}C HSQC (bottom) NMR spectra of complex [Ru([9]aneS3)(dach)Cl][PF_6] (**5**) in CD_3NO_2 at 25.0 °C. On top is the schematic representation of the chelating ligand dach in complex **5** with numbering scheme.

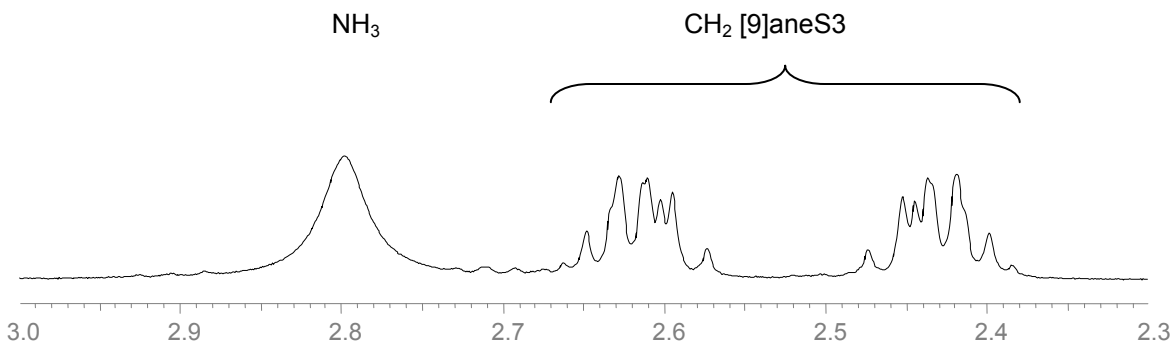

Fig. S3. The ^{1}H NMR spectrum of complex [Ru([9]aneS3)$(NH_3)_3$][PF_6]$_2$ (**6**) in D_2O at 25.0 °C.

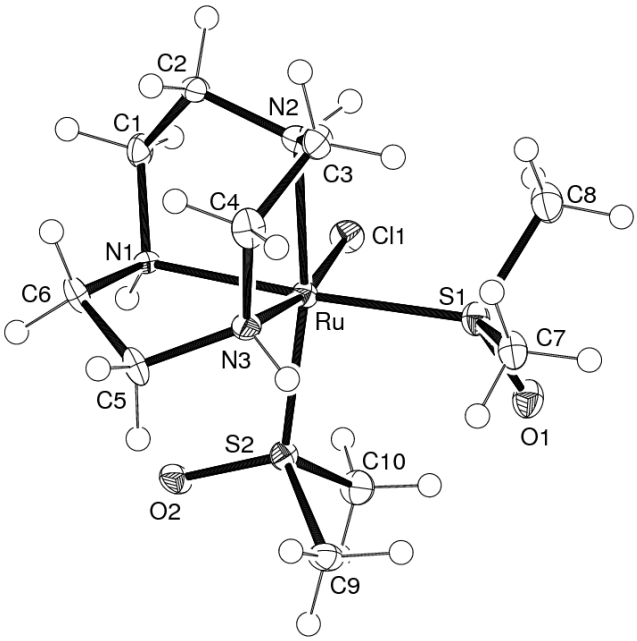

Fig. S4. ORTEP drawing (30% probability ellipsoid) of the cation of [Ru([9]aneN3)(dmso-S)$_2$Cl][PF$_6$] (**9-PF$_6$**). Selected bond lengths (Å) and angles (°): Ru–N(1) 2.123(4), Ru–N(2) 2.126(4), Ru–N(3) 2.111(4), Ru–S(1) 2.2570(14), Ru–S(2) 2.2525(13), Ru–Cl(1) 2.4177(14); N(1)–Ru–N(2) 80.20(15), N(1)–Ru–N(3) 81.00(16), N(1)–Ru–S(1) 176.39(11), N(1)–Ru–S(2) 90.73(11), N(1)–Ru–Cl(1) 90.87(12), N(2)–Ru–N(3) 80.74(16), N(2)–Ru–S(1) 96.25(11), N(2)–Ru–S(2) 170.69(11), N(2)–Ru–Cl(1) 92.05(12), N(3)–Ru–S(1) 99.13(12), N(3)–Ru–S(2) 95.90(11), N(3)–Ru–Cl(1) 169.91(12), S(1)–Ru–S(2) 92.84(5), S(1)–Ru–Cl(1) 88.62(5), S(2)–Ru–Cl(1) 90.13(5).

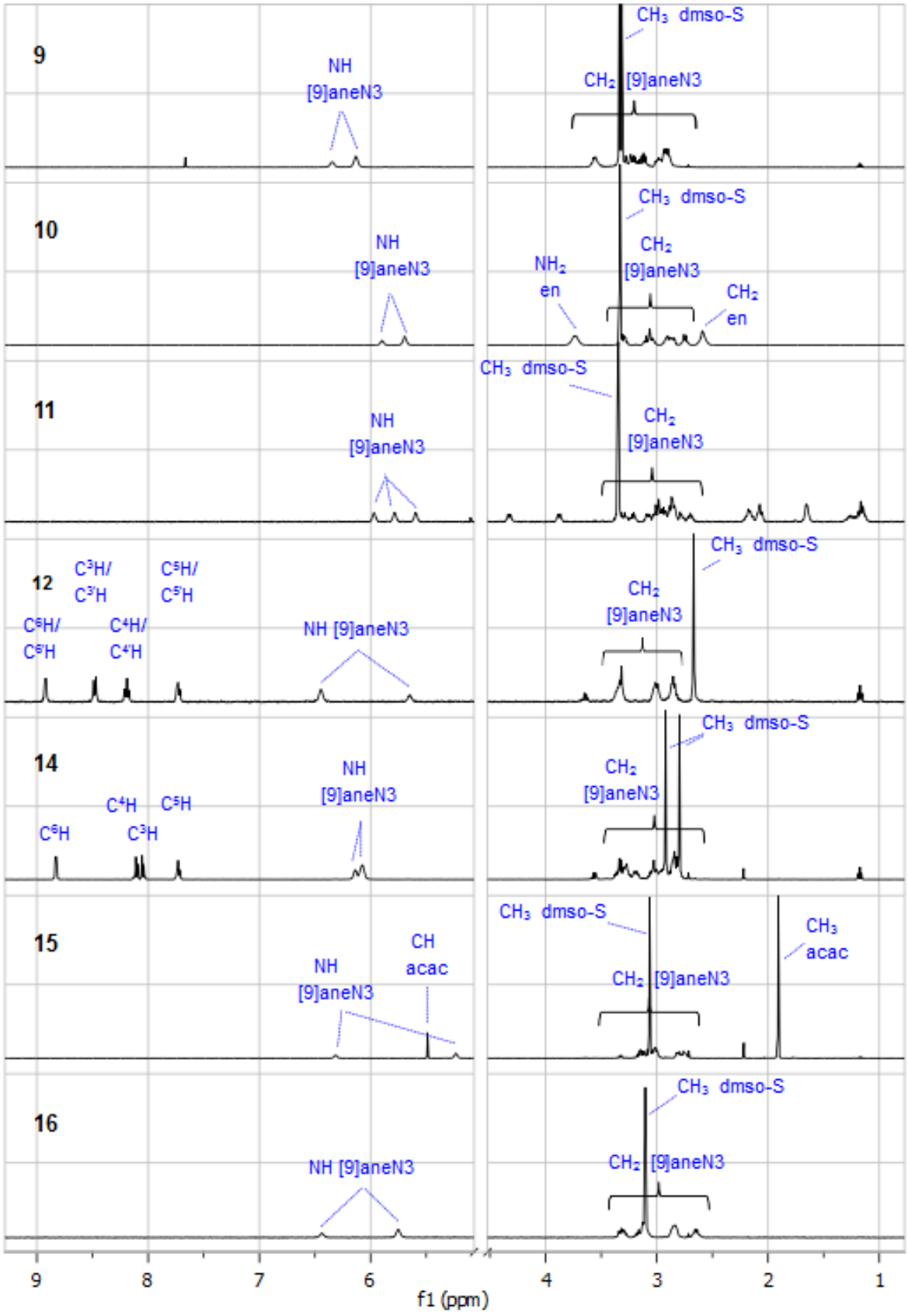

Fig. S5. The ^{1}H NMR spectra of complexes **9** – **12** and **14** – **16** in D_2O at 25.0 °C.

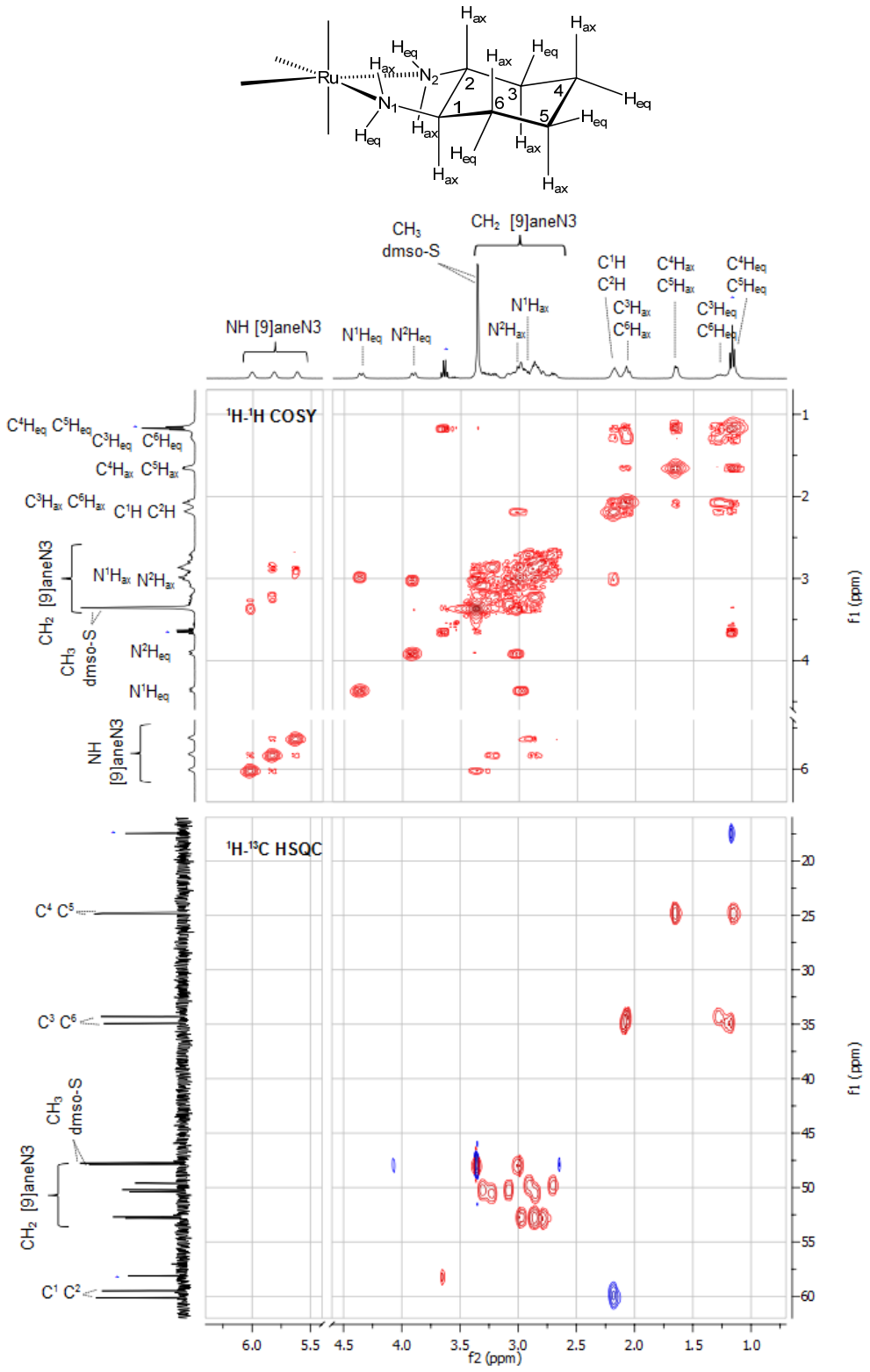

Fig. S6. The 2D homonuclear ^{1}H-^{1}H COSY (top) and heteronuclear ^{1}H-^{13}C HSQC (bottom) NMR spectra of complex cation **11** in D_2O at 25.0 °C. On top is the schematic representation of the chelating ligand dach in complex **11** with numbering scheme. The resonances of ethanol used as external reference are indicated with *.

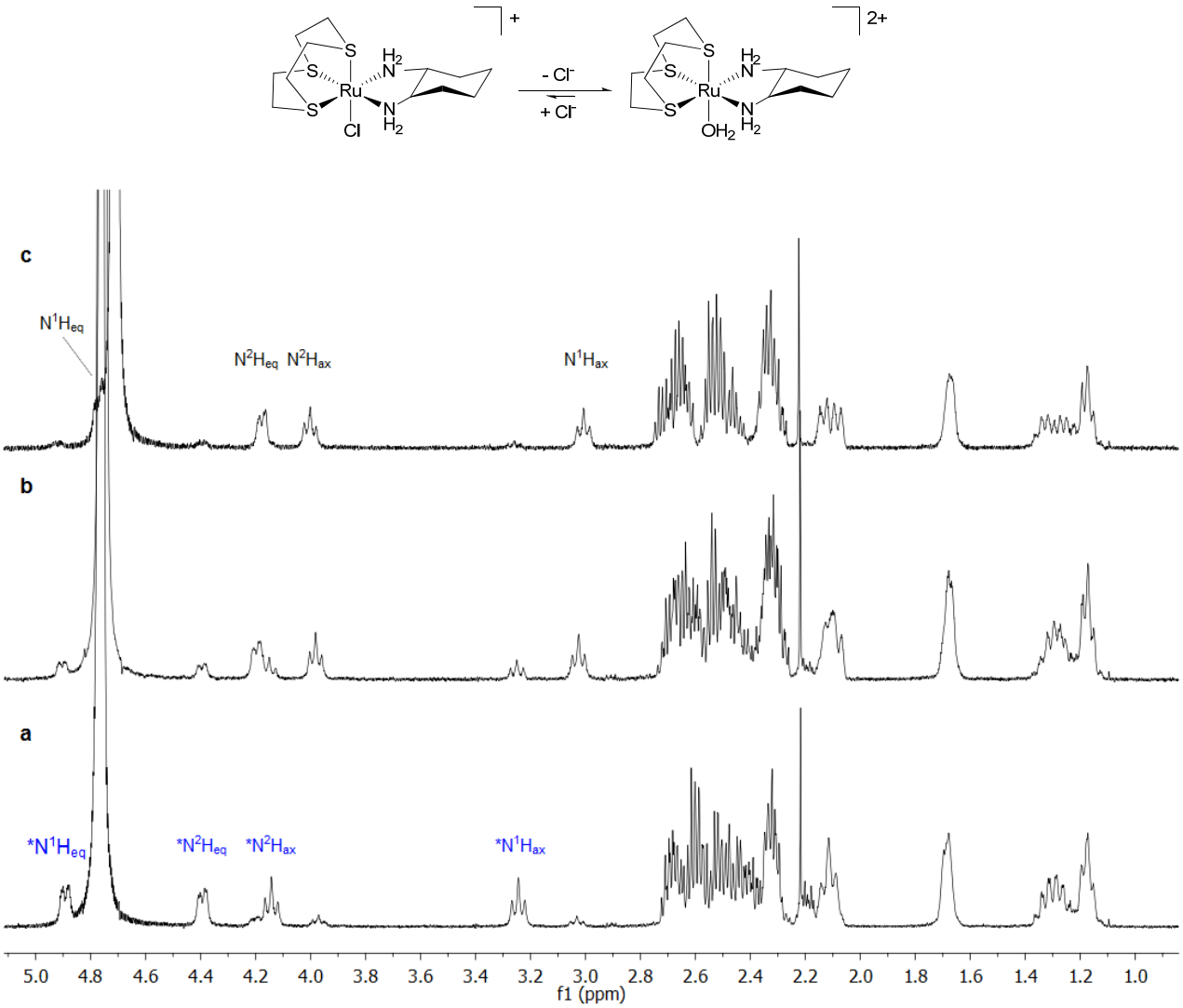

Fig. S7. The ^{1}H NMR spectra (at 25.0 °C) of a) complex **5** (3.0 mM) upon dissolution in D_2O, b) after addition of 100 mM of NaCl, and c) after addition of a large excess of NaCl. The resonances of the aqua species **5aq** are indicated with *. On top is the schematic representation of the equilibrium between complex **5** (left) and the corresponding aqua species **5aq** (right).

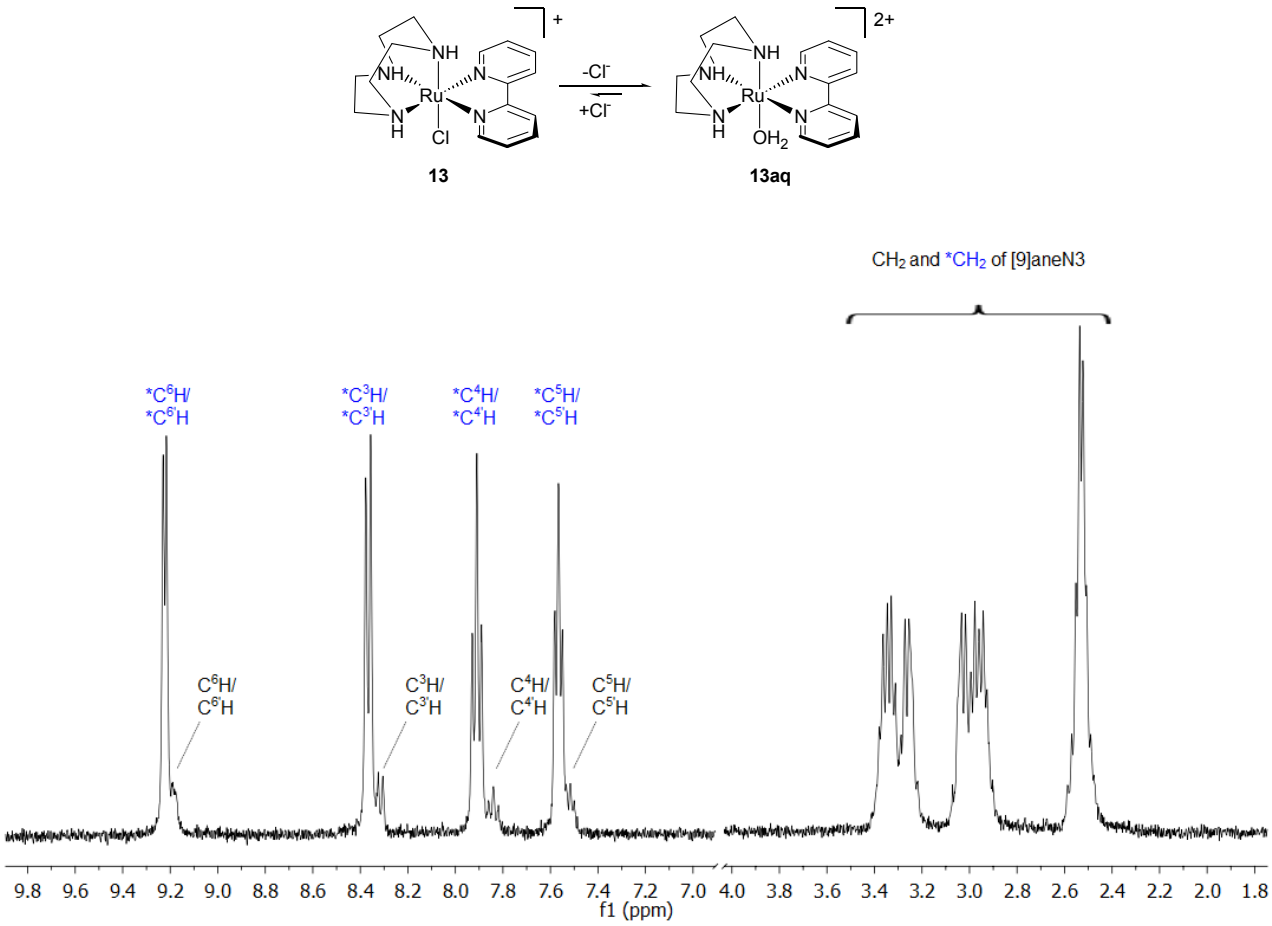

Fig. S8. The ^{1}H NMR spectrum of complex **13** (ca. 3.0 mM) recorded 3 min after dissolution in D_2O at 25.0 °C. The resonances of the aqua species **13aq** are indicated with *. On top is the schematic representation of the equilibrium between complex **13** and the corresponding aqua species **13aq**.

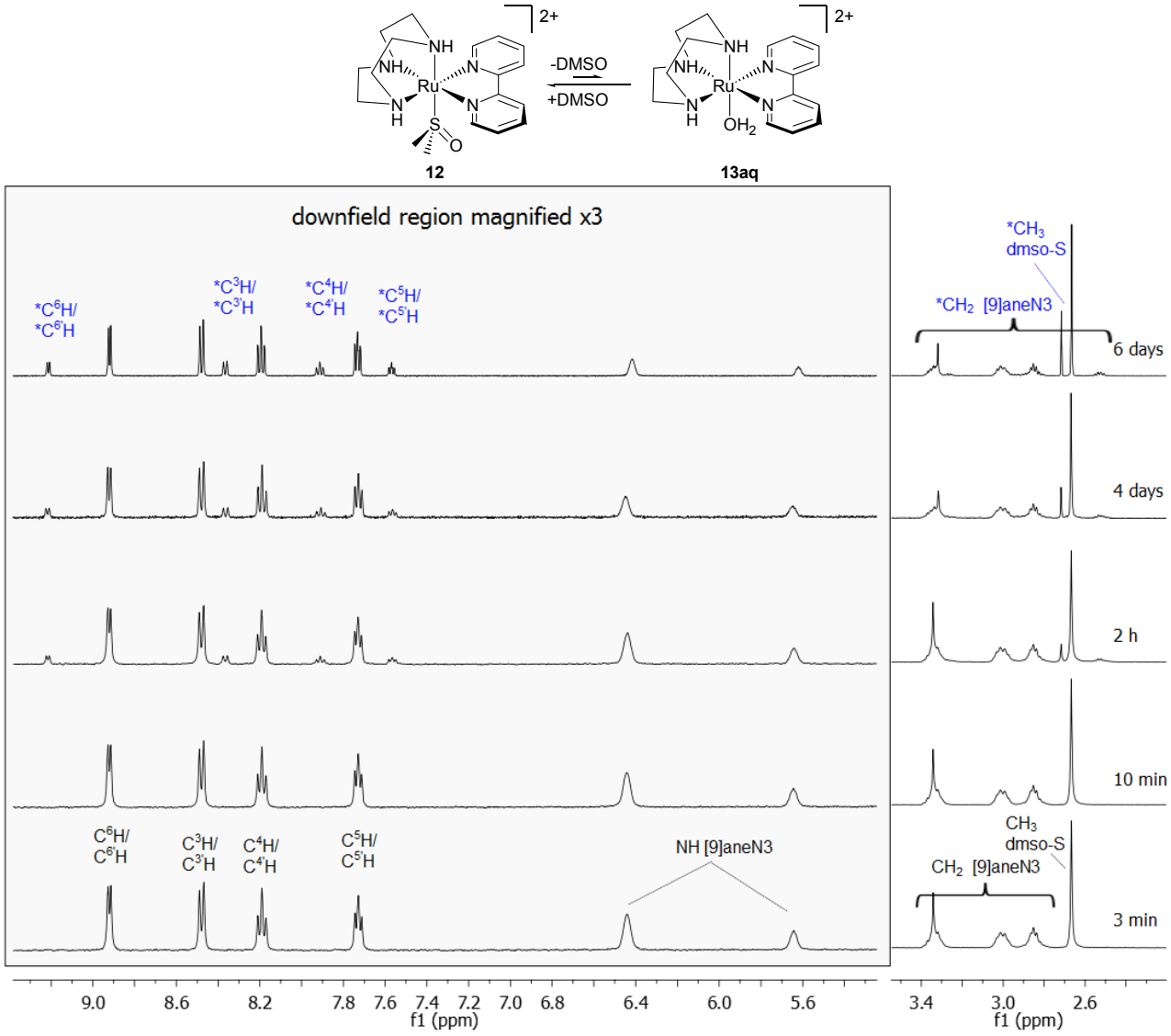

Fig. S9. Time evolution of the ^{1}H NMR spectrum of complex **12** (ca. 3.0 mM) upon dissolution in D_2O at 25.0 °C. The resonances of the aqua species **13aq** are indicated with *. In the grey frame the downfield region of each spectrum is magnified 3 times compared to the upfield region. On top is the schematic representation of the equilibrium between complex **12** and the corresponding aqua species **13aq**.