Supporting Information for

Synthesis of a new type of alkene metal complex using face-capping thione-alkene ligands

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General:

All reagents and solvents were purchased from commercial sources and used as supplied unless otherwise mentioned. The starting materials $[Cp^*MCl_2]_2$ (M = Ir, Rh)[1] and [trans-1,4-di-(1-methyl-imidazoium-3N)-2-butene][Br]$_2$[2] were prepared by literature method. [trans-1,4-di-(1-vinyl-imidazoium-3N)-2-butene][Br]$_2$ was synthesized as described in literature[2] by using 1-vinylimidazole instead of 1-methylimidazole. Elemental analyses were performed on an Elementar Vario EL III analyzer. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. NMR spectra were recorded on a Bruker DMX-400 Spectrometer. Proton chemical shift (δH = 7.26 ($CDCl_3$), 3.31 (CD_3OD)) and δC values (77.16 ($CDCl_3$), 49.00 (CD_3OD)) are reported relative to the solvent residual peak. ESI-MS spectra were recorded on a Micro TOF II mass spectrometer using electrospray ionization.

Ligand synthesis:

L1: In a 100 mL round-bottomed flask fitted with reflux condenser were placed. Sulfur powder (64 mg, 2 mmol), K_2CO_3 (300 mg) were added to a solution of [trans-1,4-di-(1-methyl-imidazoium-3N)-2-butene][Br]$_2$ (378 mg, 1 mmol) in CH_3OH (30 mL). The mixture was allowed to reflux for 24 h after which the methanol was removed with a rotary evaporator. The remaining solid was shaken with 2×30 mL CH_2Cl_2 which was then filtered and rotary evaporated. The product was recrystallized from CH_2Cl_2/MeOH to give colorless solid. Yield: (140 mg, 50%). Anal. Calcd for $C_{12}H_{16}N_4S_2$: C, 51.40; H, 5.75; N, 19.98; Found: C, 51.30; H, 5.76; N, 19.91. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 3.58 (s, 6H), 4.65 (m, 4H), 5.74 (m, 2H), 6.67 (d, 2H, J = 2.4 Hz), 6.70 (d, 2H, J = 2.4 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 35.3, 49.02, 116.55, 118.11, 128.45, 162.50. FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1153 (C=S).

L2: Prepared by the same procedure as described above for L_1, using sulfur powder (64 mg, 2 mmol), K_2CO_3 (300 mg) and [trans-1,4-di-(1-vinyl- imidazoium-3N)-2-butene][Br]$_2$ (402 mg, 1 mmol). **L2** was isolated as a gray solid. Yield: (183 mg, 60%). Anal. Calcd for $C_{14}H_{16}N_4S_2$: C, 55.23; H, 5.30; N, 18.40; Found: C, 55.30; H, 5.26; N, 18.41. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 4.68 (m, 4H), 4.93 (d, 2H, J = 8.8 Hz), 5.14 (d, 2H, J = 16.0 Hz), 5.76 (m, 2H), 6.77 (s, 2H), 6.98 (s, 2H), 7.53 (dd, 2H, J = 8.8, 16.0 Hz). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$, ppm): δ = 48.56, 101.11, 112.85, 118.06, 128.32, 130.39. FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1182 (C=S).

Synthesis of 1-Cl_2. **L1** (28 mg, 0.1 mmol) was added to a solution of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol) in CH_3OH (20 mL) at room temperature and stirred for 24 h. The solvent was concentrated to about 3 mL. Upon the addition of diethyl ether, a yellow solid of **1-Cl_2** was precipitated and collected, and dry in vacuum after washing with

diethyl ether. Yield: 92%. Anal. Calcd for $C_{22}H_{31}Cl_2IrN_4S_2$: C, 38.93; H, 4.60; N, 8.25; Found: C, 38.84; H, 4.52; N, 8.19. ^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.51 (d, 1H, *J* = 2.0 Hz, imidazole), 7.45 (d, 1H, *J* = 2.0 Hz, imidazole), 7.42 (d, 1H, *J* = 2.4 Hz, imidazole), 7.35 (d, 1H, *J* = 2.4 Hz, imidazole), 5.29-5.25 (m, 1H, -CH=CH-), 5.12-5.07 (m, 1H, -CH_2-), 4.96-4.92 (m, 1H, -CH_2-), 4.89-4.85 (m, 1H, -CH_2-), 3.94-3.90 (m, 1H, -CH=CH-), 3.88 (s, 3H, CH_3), 3.73 (s, 3H, CH_3), 3.57-3.50 (m, 1H, -CH_2-), 1.77 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (101 MHz, CD_3OD, ppm): δ = 8.38 (Cp*), 35.90 (CH_3), 36.36 (CH_3), 48.79 (-CH_2-), 52.06 (-CH_2-), 60.65 (-CH=CH-), 76.85 (-CH=CH-), 104.40 (Cp*), 122.58 (imidazole), 122.87 (imidazole), 123.19 (imidazole), 146.84 (C=S), 148.48 (C=S). ESI-MS: *m/z* = 607.1524 (calcd for $[M - 2Cl]^+$ 607.1533), 643.1287 (calcd for $[M - Cl]^+$ 643.1292). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1163 (C=S).

Synthesis of 1-(OTf)$_2$. AgOTf (51 mg, 0.2 mmol) was added to a solution of $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol) in CH_3OH (20 mL) at room temperature and stirred for 6 h, followed by filtration to remove AgCl. **L1** (28 mg, 0.1 mmol) was added to the filtrate. The mixture was then stirred at room temperature for 24 h. The solvent was concentrated to about 3 mL. Upon the addition of diethyl ether, a yellow solid of **1-(OTf)$_2$** was precipitated and collected, and dry in vacuum after washing with diethyl ether. Yield: 91%. Anal. Calcd for $C_{24}H_{31}F_6IrN_4O_6S_4$: C, 31.82; H, 3.45; N, 6.18; Found: C, 31.90; H, 3.47; N, 6.12. ^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.44 (d, 1H, *J* = 2.0 Hz, imidazole), 7.41 (d, 1H, *J* = 2.0 Hz, imidazole), 7.38 (d, 1H, *J* = 2.4 Hz, imidazole), 7.29 (d, 1H, *J* = 2.4 Hz, imidazole), 5.22-5.19 (m, 1H, -CH=CH-), 5.06-5.02 (m, 1H, -CH_2-), 4.92-4.91 (m, 1H, -CH_2-), 4.91-4.84 (m, 1H, -CH_2-), 3.94-3.90 (m, 1H, -CH=CH-), 3.87 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 3.55-3.48 (m, 1H, -CH_2-), 1.75 (s, 15H, Cp*). ^{13}C{^{1}H} NMR (101 MHz, CD_3OD, ppm): δ = 8.30 (Cp*), 35.86 (CH_3), 36.34 (CH_3), 48.71 (-CH_2-), 51.94 (-CH_2-), 60.49 (-CH=CH-), 76.65 (-CH=CH-), 104.43 (Cp*), 122.50 (imidazole), 122.77 (imidazole), 123.17 (imidazole), 123.21 (imidazole), 146.87 (C=S), 148.55 (C=S). ESI-MS: *m/z* = 607.1514 (calcd for $[M - 2OTf]^+$ 607.1533), 757.1126 (calcd for $[M - OTf]^+$ 757.1130). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1163 (C=S), 1256, 1029, 638 (OTf^-).

Synthesis of 1-(NO$_3$)$_2$. Prepared by the same procedure as described above for **1-(OTf)$_2$**, using $AgNO_3$ (34 mg, 0.2 mmol), $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol) and **L1** (28 mg, 0.1 mmol). **1-(NO$_3$)$_2$** was isolated as a yellow solid. Yield: 88%. Anal. Calcd for $C_{22}H_{31}IrN_6O_6S_2$: C, 36.10; H, 4.27; N, 11.48; Found: C, 36.15; H, 4.22; N, 11.53. ^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.46 (d, 1H, *J* = 2.0 Hz, imidazole), 7.41 (d, 1H, *J* = 2.0 Hz, imidazole), 7.39 (d, 1H, *J* = 2.4 Hz, imidazole), 7.30 (d, 1H, *J* = 2.4 Hz, imidazole), 5.23-5.20 (m, 1H, -CH=CH-), 5.08-5.03 (m, 1H, -CH_2-), 4.93-4.88 (m, 1H, -CH_2-), 4.88-4.83 (m, 1H, -CH_2-), 3.94-3.90 (m, 1H, -CH=CH-), 3.87 (s, 3H, CH_3), 3.72 (s, 3H, CH_3), 3.55-3.48 (m, 1H, -CH_2-), 1.76 (s, 15H, Cp*). ESI-MS: *m/z* = 607.1516 (calcd for $[M - 2NO_3]^+$ 607.1533). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1162 (C=S), 1384 (NO_3^-).

Synthesis of 2-Cl_2. Prepared by the same procedure as described above for **1-Cl_2**, using **L2** (30 mg, 0.1 mmol) and $[Cp^*IrCl_2]_2$ (40 mg, 0.05 mmol). **2-Cl_2** was isolated as a yellow solid. Yield: 94%. Anal. Calcd for $C_{24}H_{31}Cl_2IrN_4S_2$: C, 41.02; H, 4.45; N, 7.97; Found: C, 41.08; H, 4.43; N, 7.92. ^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.87 (d, 1H, *J* = 2.4 Hz, imidazole), 7.87 (d, 1H, *J* = 2.4 Hz, imidazole), 7.63 (d, 1H, *J* = 2.4 Hz, imidazole), 7.57 (dd, 1H, *J* = 8.8, 15.6 Hz, N-CH=), 7.46 (d, 1H, *J* = 2.0 Hz, imidazole), 7.26 (dd, 1H, *J* = 8.8, 15.6 Hz, N-CH=), 5.80 (dd, 1H, *J* = 2.4, 15.6 Hz, -CH=CH-), 5.77 (dd, *J* = 2.4, 15.6 Hz, 1H, =CH_2), 5.41 (dd, 1H, *J* = 2.4, 8.8 Hz, =CH_2), 5.34 (m, 2H, =CH_2), 5.10 (dd, 1H, -CH_2-), 5.00 (dd, 1H, *J* = 3.2, 15.6 Hz, -CH_2-), 4.93 (dd, 1H, *J* = 1.6, 15.6 Hz, -CH_2-), 4.11 (td, 1H, *J* = 2.4, 15.6 Hz, -CH=CH-), 3.59 (dd, 1H, *J* = 11.2, 15.6 Hz, -CH_2-), 1.78 (s, 15H, Cp*). ESI-MS: *m/z* = 631.1539 (calcd for $[M - 2Cl]^+$ 631.1533), 667.1292 (calcd for $[M - Cl]^+$ 667.1298). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1142 (C=S).

Complex 3-[Cp*$RhCl_3$]Cl. **L1** (6 mg, 0.02 mmol) was added to a CD_3OD (0.6 mL) solution of $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol). Complex **3-[Cp*$RhCl_3$]Cl** is stable in methanol, however, only complex **5** was obtained after removal of solvent.
^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.50 (d, 1H, *J* = 2.0 Hz, imidazole), 7.39 (d, 2H, *J* = 2.4 Hz, imidazole), 7.33 (d, 1H, *J* = 2.0 Hz, imidazole), 5.82 (d, 1H, *J* = 12.8 Hz, -CH=CH-), 5.15 (d, 1H, *J* = 16.8 Hz, -CH_2-), 4.99 (d, 1H, *J* = 15.6 Hz, -CH_2-), 4.64 (d, 1H, *J* = 16.8 Hz, -CH_2-), 3.92 (d, 1H, *J* = 12.8 Hz, -CH=CH-), 3.87 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 3.63 (dd, 1H, *J* = 11.2, 16.4 Hz, -CH_2-), 1.75 (s, 15H, Cp*), 1.64 (br, 15H, Cp*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, ppm): δ = 9.02 (Cp*), 9.41 (Cp*), 36.01 (CH_3), 36.26 (CH_3), 50.01 (-CH_2-), 51.69 (-CH_2-), 81.82 (-CH=CH-), 97.67 (-CH=CH-), 108.50 (Cp*), 122.02(imidazole), 122.49 (imidazole), 123.18(imidazole), 123.42 (imidazole), 150.54 (C=S), 151.18 (C=S). ESI-MS (solvent: methanol): *m/z* = 272.9920 (calcd for $[Cp^*RhCl]^+$ 272.9912), 517.0958 (calcd for $[M - Cp^*RhCl_4]^+$ 517.0961), 667.0570 (calcd for $[M - Cp^*RhCl_3]^+$ 667.0560), 863.0307 (calcd for $[M - Cl]^+$ 863.0306).

Complex **5**: **L1** (28 mg, 0.1 mmol) was added to a solution of $[Cp^*RhCl_2]_2$ (62 mg, 0.1 mmol) in CH_2Cl_2 at room temperature, the mixture was stirred at room temperature for 1 h. Red solids were collected after removal of solvent. Yield: 90%. Anal. Calcd for $C_{32}H_{46}Cl_4Rh_2N_4S_2$: C, 42.78; H, 5.16; N, 6.24; Found: C, 42.74; H, 5.17; N, 6.30. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.66 (s, 30H, Cp*), 3.70 (s, 6H), 4.83 (s, 4H), 5.96 (s, 2H), 6.83 (s, 2H), 6.93 (s, 2H). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1141 (C=S).

Synthesis of 3-$(OTf)_2$. Prepared by the same procedure as described above for **2-$(OTf)_2$**, using AgOTf (51 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (31 mg, 0.05 mmol) and **L1** (28 mg, 0.1 mmol). **3-$(OTf)_2$** was isolated as an orange red solid. Yield: 91%. Anal. Calcd for $C_{24}H_{31}F_6RhN_4O_6S_4$: C, 35.30; H, 3.83; N, 6.86; Found: C, 35.29; H, 3.87; N, 6.82. ^{1}H NMR (400 MHz, CD_3OD, ppm): δ = 7.45 (d, 1H, *J* = 2.4 Hz, imidazole), 7.37-7.36 (m, 2H, imidazole), 7.28 (d, 1H, *J* = 2.8 Hz, imidazole), 5.78 (d, 1H, *J* =

13.6 Hz, -CH=CH-), 5.09 (d, 1H, J = 14.8 Hz, -CH_2-), 4.95 (d, 1H, J = 8.4 Hz, -CH_2-), 4.64 (d, 1H, J = 8.4 Hz, -CH_2-), 3.94-3.88 (m, 1H, -CH=CH-), 3.86 (s, 3H, CH_3), 3.69 (s, 3H, CH_3), 3.63 (dd, 1H, J = 8.8, 16.4 Hz, -CH_2-), 1.74 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, ppm): δ = 8.96 (Cp*), 35.98 (CH_3), 36.26 (CH_3), 49.95 (-CH_2-), 51.57 (-CH_2-), 81.77 (-CH=CH-), 97.47 (-CH=CH-), 108.53 (Cp*), 121.95 (imidazole), 122.40 (imidazole), 123.17 (imidazole), 123.44 (imidazole), 150.55 (C=S), 151.22 (C=S). ESI-MS: *m/z* = 517.0975 (calcd for $[M - 2OTf]^+$ 517.0961), 667.0570 (calcd for $[M - OTf]^+$ 667.0560). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1154 (C=S), 1265, 1030, 638 (OTf^-).

Synthesis of 4-[Cp*RhCl$_3$]Cl. **L2** (6 mg, 0.02 mmol) was added to a CD_3OD (0.6 mL) solution of $[Cp^*RhCl_2]_2$ (12 mg, 0.02 mmol). Complex **4-[Cp*RhCl$_3$]Cl** is stable in methanol, however, only complex **6** was obtained after removal of solvent. ^1H NMR (400 MHz, CD_3OD, ppm): δ = 7.85 (d, 1H, J = 2.4 Hz, imidazole), 7.82 (d,1H, J = 2.4 Hz, imidazole), 7.63 (d, 1H, J = 2.4 Hz, imidazole), 7.58 (dd, 1H, J = 8.8, 15.6 Hz, N-CH=), 7.45 (d, 1H, J = 2.4 Hz, imidazole), 7.25 (dd, 1H, J = 8.8, 15.6 Hz, N-CH=), 5.91 (d, 1H, J = 13.2 Hz, -CH=CH-), 5.77 (dd, J = 2.0, 12.8 Hz, 1H, =CH_2), 5.73 (dd, 1H, J = 2.4, 13.2 Hz, =CH_2), 5.39 (dd, 1H, J = 2.4, 8.8 Hz, =CH_2), 5.31 (dd, J = 2.4, 8.8 Hz, 1H, =CH_2), 5.19 (d, 1H, J = 16.4 Hz, -CH_2-), 5.06 (d, 1H, J = 16.0 Hz, -CH_2-), 4.67 (d, 1H, J = 16.8 Hz, -CH_2-), 4.10 (t, 1H, J = 12.0 Hz, -CH=CH-), 3.68 (dd, 1H, J = 10.8, 16.4 Hz, -CH_2-), 1.77 (s, 15H, Cp*), 1.64 (s, 15H, Cp*). ESI-MS: *m/z* = 272.9919 (calcd for $[Cp^*RhCl]^+$ 272.9912), 541.0960 (calcd for $[M – Cp^*RhCl_4]^+$ 541.0961), 885.0363 (calcd for $[M - Cl]^+$ 885.0334).

Complex **6**: **L2** (30 mg, 0.1 mmol) was added to a solution of $[Cp^*RhCl_2]_2$ (62 mg, 0.1 mmol) in CH_2Cl_2 at room temperature, the mixture was stirred at room temperature for 1 h. Red solids were collected after removal of solvent. Yield: 92%. Anal. Calcd for $C_{34}H_{46}Cl_4Rh_2N_4S_2$: C, 44.27; H, 5.03; N, 6.07; Found: C, 44.28; H, 5.05; N, 6.02. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 1.65 (s, 30H), 4.81 (s, 4H), 5.00 (d, 2H, J = 8.8 Hz), 5.25 (d, 2H, J = 16.0 Hz), 5.94 (s, 2H), 7.01 (s, 2H), 7.15 (s, 2H), 7.56 (dd, 2H, J = 8.8, 16.0 Hz). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1130 (C=S).

Synthesis of 4-(OTf)$_2$. Prepared by the same procedure as described above for **3-(OTf)$_2$**, using AgOTf (51 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (31 mg, 0.05 mmol) and **L2** (30 mg, 0.1 mmol). **4-(OTf)$_2$** was isolated as an orange red solid. Yield: 90%. Anal. Calcd for $C_{26}H_{31}F_6RhN_4O_6S_4$: C, 37.14; H, 3.72; N, 6.66; Found: C, 37.12; H, 3.77; N, 6.62. ^1H NMR (400 MHz, CD_3OD, ppm): δ = 7.82 (d, 1H, J = 2.4 Hz, imidazole), 7.79 (d, 1H, J = 2.8 Hz, imidazole), 7.59 (dd, 1H, J = 8.8, 15.6 Hz, N-CH=), 7.56 (d, 1H, J = 2.8 Hz, imidazole), 7.40 (d, 1H, J = 2.4 Hz, imidazole), 7.24 (dd, 1H, J = 8.8, 15.6 Hz, N-CH=), 5.85 (d, 1H, J = 13.6 Hz, -CH=CH-), 5.76 (dd, J = 2.4, 12.8 Hz, 1H, =CH_2), 5.72 (dd, 1H, J = 2.4, 12.8 Hz, =CH_2), 5.39 (dd, 1H, J = 2.4, 8.8 Hz, =CH_2), 5.30 (dd, J = 2.4, 8.8 Hz, 1H, =CH_2), 5.11 (dd, 1H, -CH_2-), 5.00 (d, 1H, J = 16.4 Hz, -CH_2-), 4.68 (d, 1H, J = 16.4 Hz, -CH_2-), 4.12 (t, 1H, J = 11.6 Hz, -CH=CH-), 3.68 (dd,

1H, J = 10.8, 16.4 Hz, -CH_2-), 1.75 (s, 15H, Cp*). $^{13}C\{^1H\}$ NMR (101 MHz, CD_3OD, ppm): δ = 9.03 (Cp*), 49.89 (-CH_2-), 51.58 (-CH_2-), 82.15 (-CH=CH-), 97.31 (-CH=CH-), 108.29 (=CH_2), 108.62 (=CH_2), 108.97 (Cp*), 118.42 (imidazole), 118.51 (imidazole), 123.48 (imidazole), 123.82 (imidazole), 129.47 (-N-CH=), 129.65 (N-CH=), 150.77 (C=S), 151.24 (C=S). ESI-MS: *m/z* = 541.0975 (calcd for $[M - 2OTf]^+$ 541.0961), 691.0570 (calcd for $[M - OTf]^+$ 691.0560). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1158 (C=S), 1260, 1030, 637 (OTf^-).

Synthesis of 7-Cl. Prepared by the same procedure as described above for **1a**, using **L1** (28 mg, 0.1 mmol) and $PdCl_2$ (18 mg, 0.1 mmol). **7-Cl** was isolated as a red solid. Yield: 91%. Anal. Calcd for $C_{12}H_{16}Cl_2PdN_4S_2$: C, 31.49; H, 3.52; N, 12.24; Found: C, 31.42; H, 3.56; N, 12.22. ^1H NMR (400 MHz, CD_3OD, ppm): δ = 7.41 (d, 2H, J = 2.0 Hz, imidazole), 7.37 (d, 2H, J = 2.0 Hz, imidazole), 5.20 (s, 2H, -CH=CH-), 4.85 (q, 4H, J = 16.0 Hz, -CH_2-,) 3.78 (s, 6H, CH_3). ESI-MS: *m/z* = 384.9773 (calcd for $[M – 2Cl]^+$ 384.9771). FT-IR spectrum (KBr, ν, selected peaks, cm^{-1}): 1148 (C=S).

1 C. White, A. Yates and P. M. Maitlis, *Inorg. Synth*., 1992, **29**, 228.
2 S. A. Shackelford, J. L. Belletire, J. A. Boatz, S. Schneider, A. K. Wheaton, B. A. Wight, H. L. Ammon, D. V. Peryshkov and S. H. Strauss, *Org. Lett*., 2010, **12**, 2714.

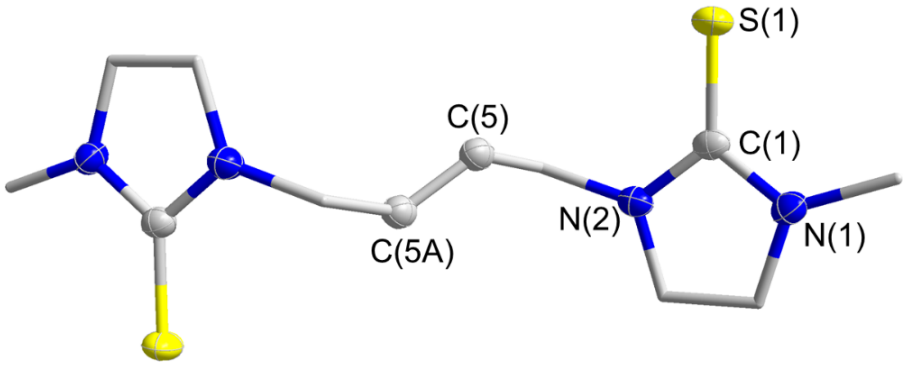

Fig. S1 Molecular structure and numbering scheme of **L1**; thermal ellipsoids shown at 50% probability. Hydrogen atoms are omitted for clarity.

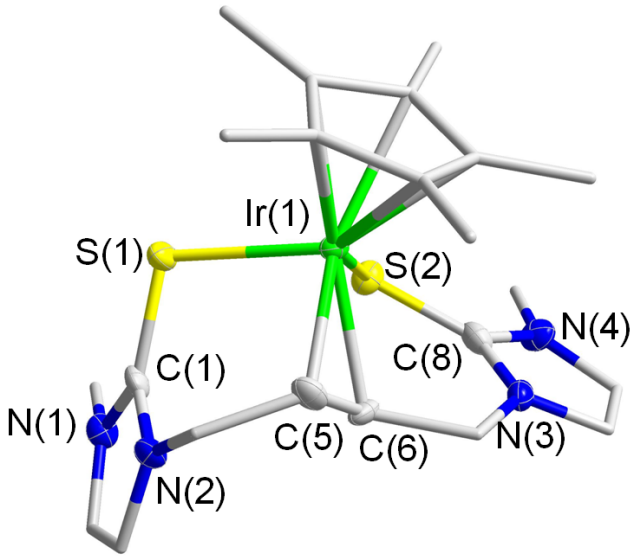

Fig. S2 Molecular structure and numbering scheme of **1-$(NO_3)_2$**; thermal ellipsoids shown at 50% probability. Hydrogen atoms, anions and solvent molecules are omitted for clarity.

Selected NMR Spectra

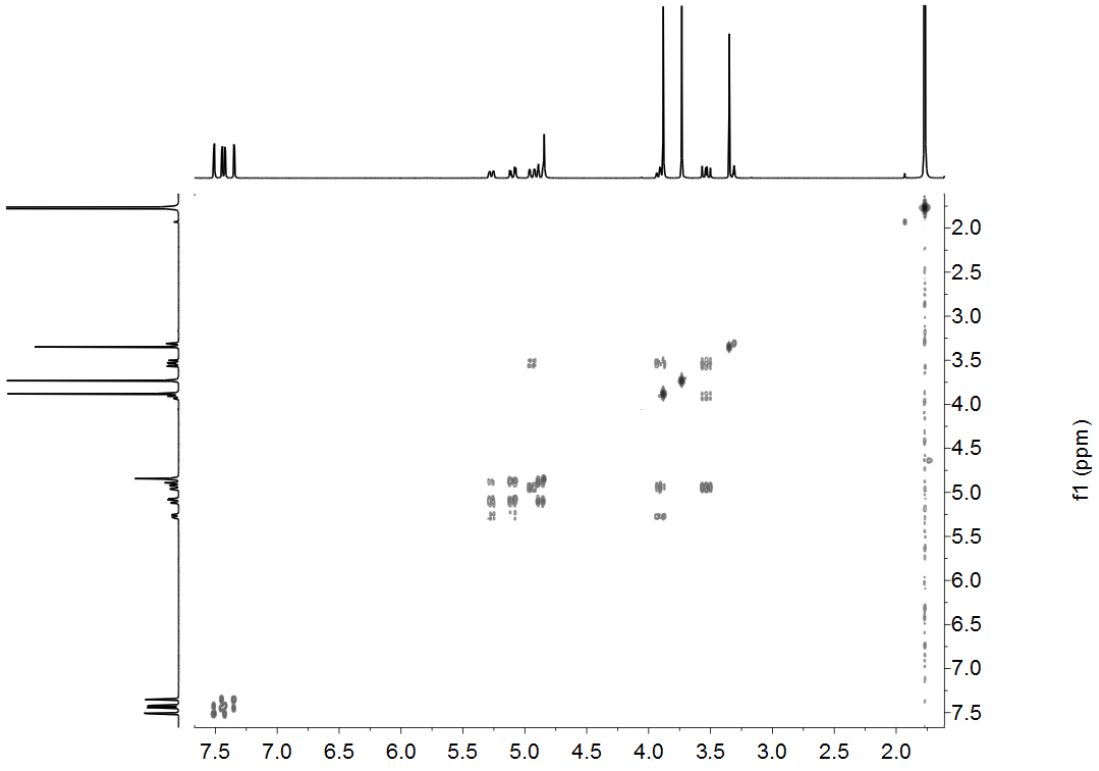

Fig. S3 ^{1}H-^{1}H COSY NMR spectrum for **1-Cl$_2$** (400 MHz, CD_3OD).

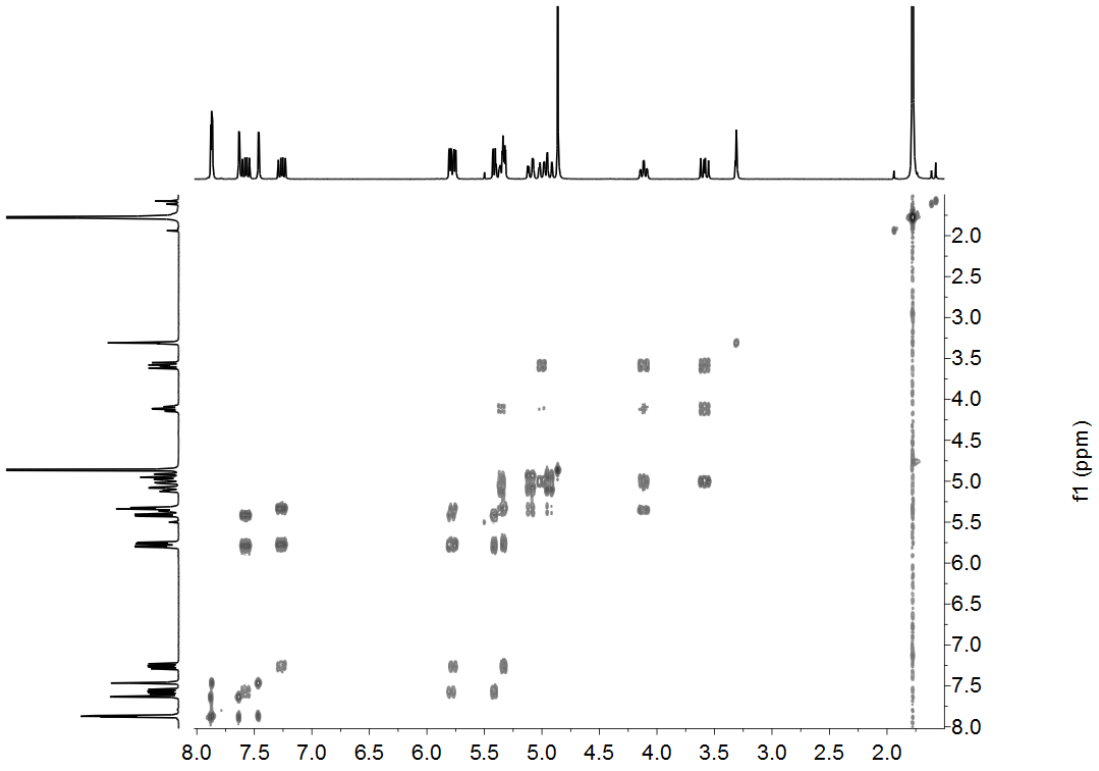

Fig. S4 ^{1}H-^{1}H COSY NMR spectrum for **2-Cl$_2$** (400 MHz, CD_3OD).

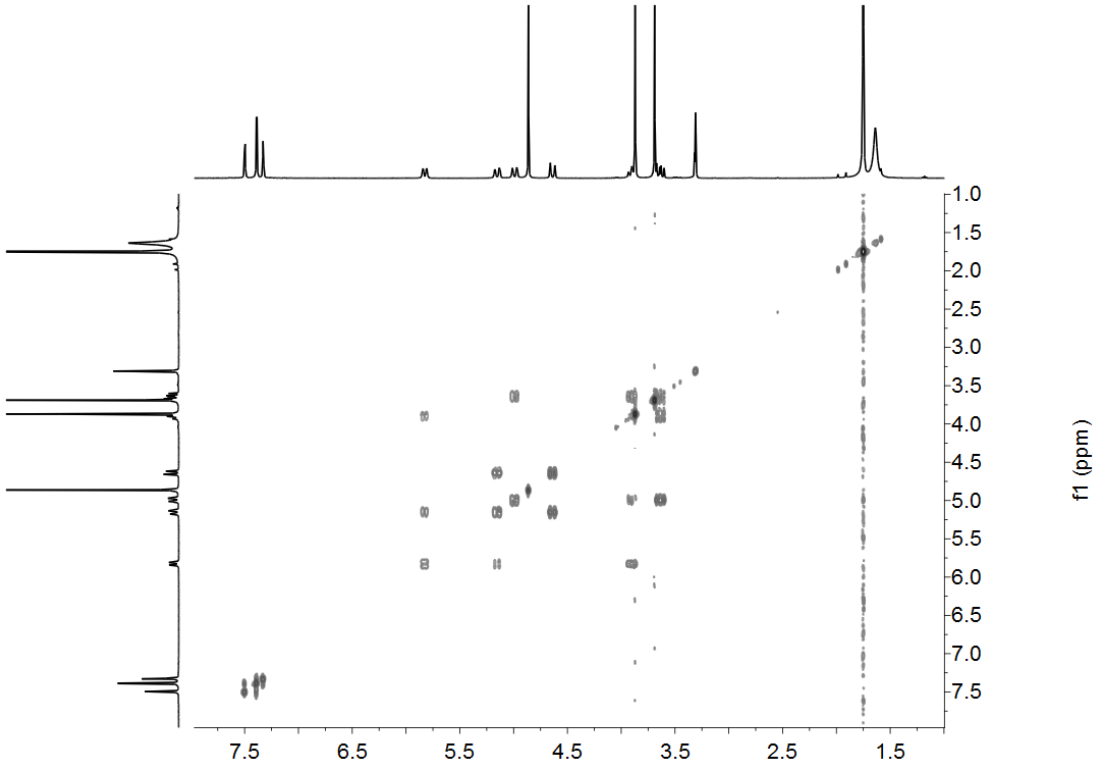

Fig. S5 ^{1}H-^{1}H COSY NMR spectrum for **3-[Cp*RhCl$_3$]Cl** (400 MHz, CD_3OD).

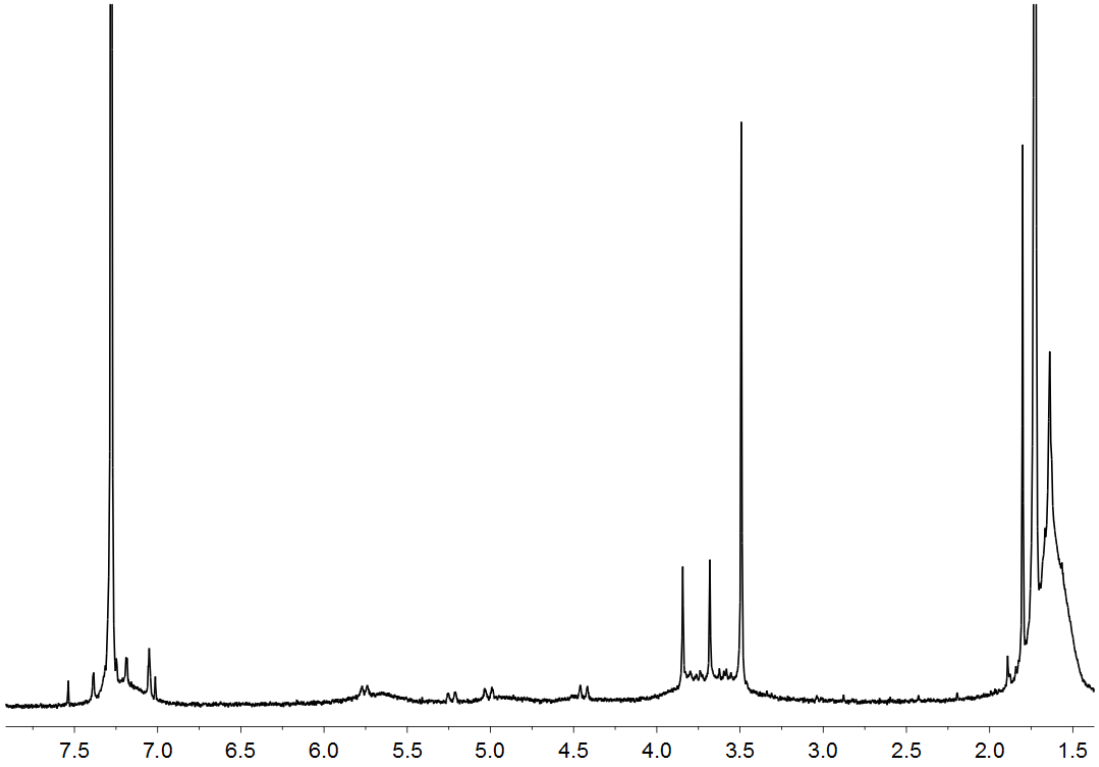

Fig. S6 ^{1}H NMR (400 MHz, $CDCl_3$) spectrum for the mixture of **3-(OTf)$_2$** and [Cp*Rh(OTf)$_2$] in 1:1 ratio (the solubility of the mixture is limited in $CDCl_3$).

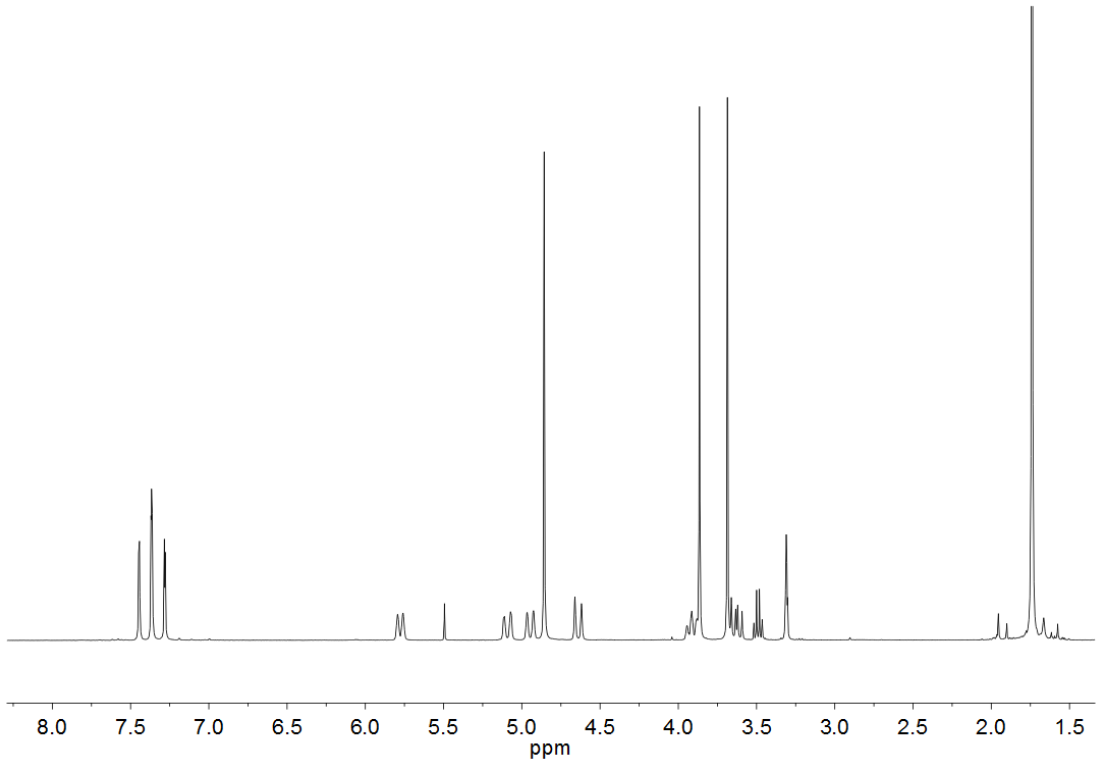

Fig. S7 ^{1}H NMR (400 MHz, CD_3OD) for **3-$(OTf)_2$**

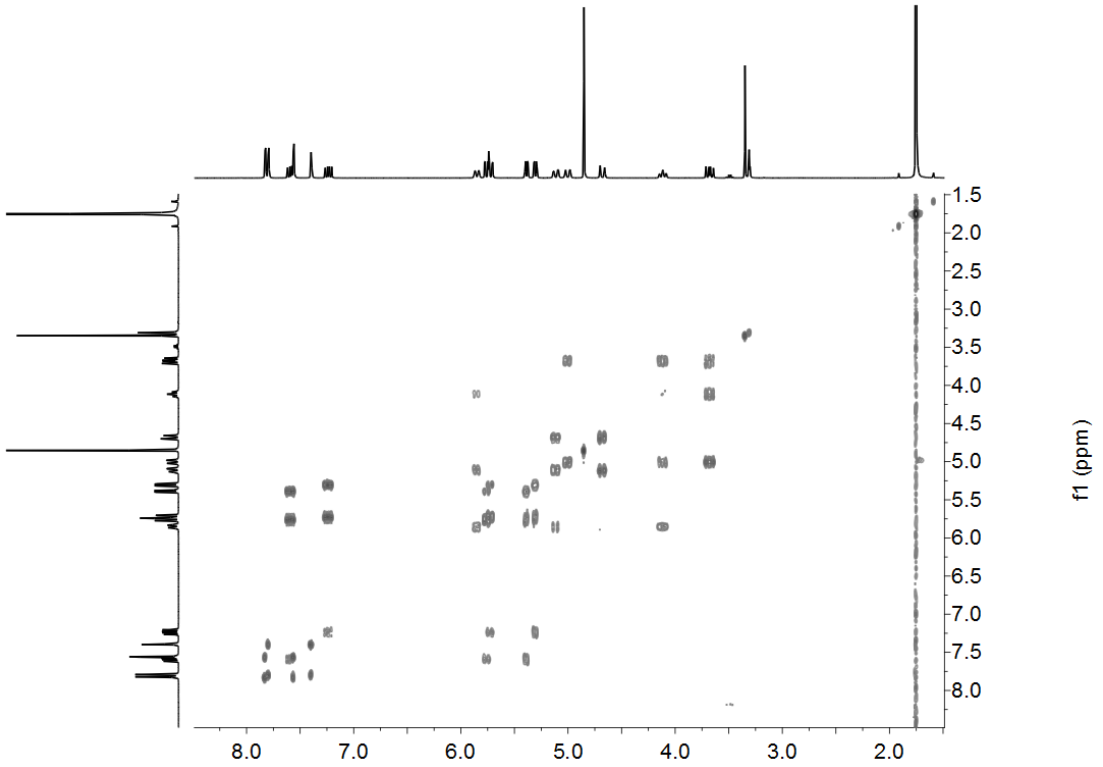

Fig. S8 ^{1}H-^{1}H COSY NMR spectrum for **4-$(OTf)_2$** (400 MHz, CD_3OD).

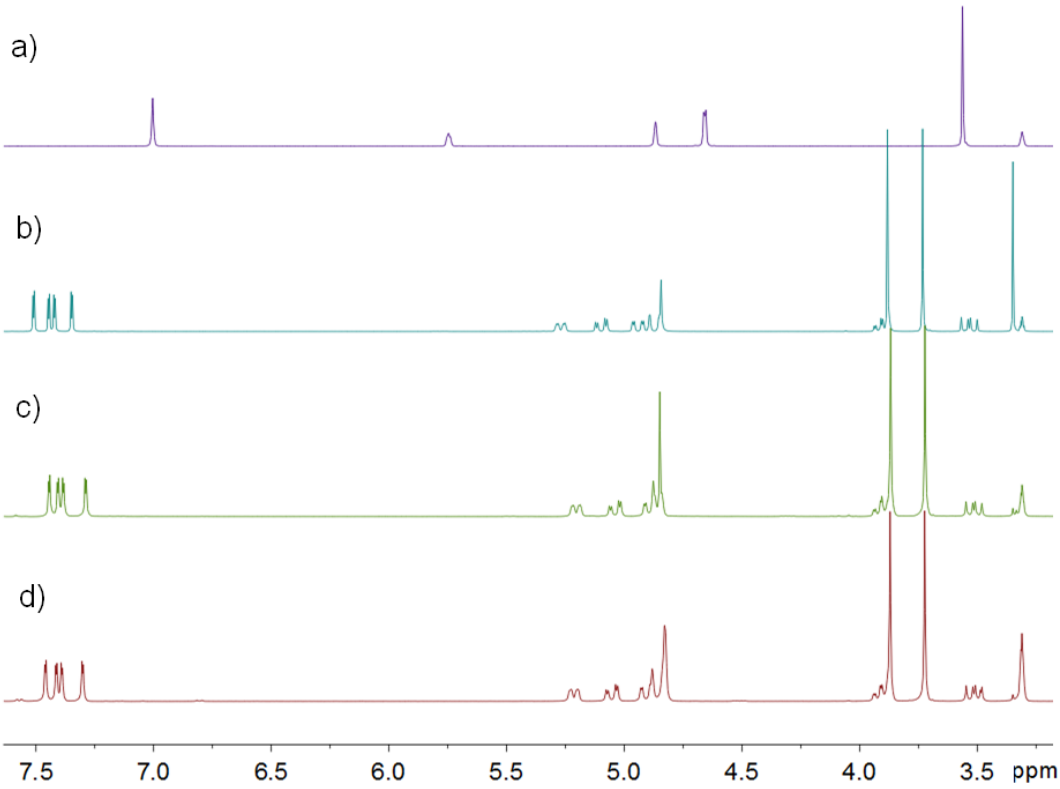

Fig. S9 Partial ^{1}H NMR (400 MHz, CD_3OD) spectra for a) **L1**, b) **1-Cl$_2$**, c) **1-(OTf)$_2$**, d) **1-(NO$_3$)$_2$**.

Table S1. Selected bond lengths (Å)

	M-S	M-C	C=C	C=S
L1			1.325(5)	1.680(3)
1-Cl_2	2.3764(9), 2.3950(8)	2.182(3), 2.190(3)	1.411(5)	1.721(3), 1.726(4)
1-$(OTf)_2$	2.378(2), 2.413(2)	2.197(8), 2.218(7)	1.407(12)	1.731(9), 1.759(10)
1-$(NO_3)_2$	2.3756(17), 2.3878(17)	2.182(6), 2.217(6)	1.392(10)	1.709(7), 1.725(7)
4-$(OTf)_2$	2.3778(13), 2.3932(13)	2.238(4), 2.239(4)	1.371(7)	1.702(5), 1.720(5)
5	2.4038(13)		1.313(10)	1.710(5)
7-Cl	2.3229(8), 2.3318(9)	2.172(3), 2.172(3)	1.385(5)	1.707(3), 1.713(3)

Table S2. Selected bond angles (°)

	S-M-S	C-M-C	C-M-S
1-Cl_2	83.09(3)	37.67(12)	81.07(9), 117.35(9), 93.80(10), 88.36(10)
1-$(OTf)_2$	84.80(9)	37.2(3)	98.6(2), 79.4(2), 114.5(2), 89.8(2)
1-$(NO_3)_2$	84.12(6)	36.9(3)	78.75(18), 97.12(18), 113.67(19), 89.03(19)
4-$(OTf)_2$	86.94(4)	35.67(17)	78.45(13), 113.05(13), 97.82(13), 91.01(12)
7-Cl	168.41(3)	37.17(13)	94.63(9), 95.63(8), 96.66(9), 94.96(9)

Table S3. Selected bond angles (°)

	Cl-M-S	C-S-M
5	94.45(4), 91.20(5)	109.04(17)
7-Cl	83.66(3), 85.03(3)	107.03(11), 108.50(11)

X-ray Crystallography Details. Single crystals of **L1** suitable for X-ray diffraction study were obtained from slow diffusion of diethyl ether into a CH_2Cl_2. Single crystals of **1-Cl$_2$**, **1-(OTf)$_2$**, **1-(NO3)$_2$**, **4-(OTf)$_2$**, **5** and **7-Cl** suitable for X-ray diffraction study were obtained from slow diffusion of diethyl ether into a CH_3OH solution at room temperature, respectively. In these data, the disordered solvent molecules which could not be restrained properly were removed using the SQUEEZE route. In asymmetric unit of **1-Cl$_2$**, there were disordered solvents (three water molecules) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit them. 2 DFIX instructions were used to restrain ligand so that there were 2 restraints in the data. Hydrogen of olefin group has been found in a difference Fourier map and others were put in calculated positions. In asymmetric unit of **1-(OTf)$_2$**, there was one disordered dichloromethane molecule which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit it. 6 ISOR and 3 DFIX instructions were used to restrain anions so that there were 39 restraints in the data. In asymmetric unit of **4-(OTf)$_2$**, one methanol molecule was disordered and it was divided into two parts (79:51). 1 ISOR and 4 DFIX instructions were used to restrain ligands and solvents so that there were 10 restraints in the data. Hydrogen of one methanol molecule could not be found. Hydrogen of another methanol and H5-6 were found in difference Fourier map and others were put in calculated positions. In asymmetric unit of **5**, 4 ISOR and 1 DFIX instructions were used to restrain ligand and Cp* fragment so that there were 25 restraints in the data. In asymmetric unit of **7-Cl**, there was disordered solvent (one methanol molecule) which could not be restrained properly. Therefore, SQUEEZE algorithm was used to omit it. 2 DFIX instructions were used to restrain O-H distance of methanol molecules so that there were 2 restraints in the data. Hydrogen of hydroxy groups in methanol molecules have been found by a difference Fourier map and others were put in calculated positions.

Table S4. Crystal data and structure refinement for **L1**.

Empirical formula	C12 H16 N4 S2	
Formula weight	280.41	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 7.0196(16) Å	α= 87.479(4)°.
	b = 7.2219(17) Å	β= 65.560(3)°.
	c = 7.4813(18) Å	γ = 78.797(3)°.
Volume	338.42(14) $Å^3$	
Z	1	
Density (calculated)	1.376 Mg/m^3	
Absorption coefficient	0.381 mm^{-1}	
F(000)	148	
Crystal size	0.180 x 0.120 x 0.080 mm^3	
Theta range for data collection	2.878 to 26.999°.	
Index ranges	-8<=h<=8, -9<=k<=8, -9<=l<=9	
Reflections collected	2370	
Independent reflections	1445 [R(int) = 0.0167]	
Completeness to theta = 25.242°	97.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.690	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	1445 / 0 / 83	
Goodness-of-fit on F^2	1.147	
Final R indices [I>2sigma(I)]	R1 = 0.0462, wR2 = 0.1533	
R indices (all data)	R1 = 0.0601, wR2 = 0.2158	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.599 and -0.453 $e.Å^{-3}$	

Table S5. Crystal data and structure refinement for **1-Cl_2**.

Empirical formula	C22 H37 Cl2 Ir N4 O3 S2	
Formula weight	732.77	
Temperature	203(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C 2/c	
Unit cell dimensions	a = 12.2789(8) Å	α= 90°.
	b = 23.1197(16) Å	β= 90.0720(10)°.
	c = 19.1348(13) Å	γ = 90°.
Volume	5432.1(6) $Å^3$	
Z	8	
Density (calculated)	1.792 Mg/m^3	
Absorption coefficient	5.298 mm^{-1}	
F(000)	2912	
Crystal size	0.380 x 0.360 x 0.340 mm^3	
Theta range for data collection	1.878 to 27.362°.	
Index ranges	-15<=h<=15, -29<=k<=29, -20<=l<=24	
Reflections collected	19418	
Independent reflections	6117 [R(int) = 0.0273]	
Completeness to theta = 25.242°	99.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.612	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6117 / 2 / 295	
Goodness-of-fit on F^2	1.114	
Final R indices [I>2sigma(I)]	R1 = 0.0210, wR2 = 0.0598	
R indices (all data)	R1 = 0.0275, wR2 = 0.0620	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.012 and -1.483 e.$Å^{-3}$	

Table S6. Crystal data and structure refinement for **1-(OTf)$_2$**.

Empirical formula	C25 H33 Cl2 F6 Ir N4 O6 S4	
Formula weight	990.89	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.944(3) Å	α= 106.941(3)°.
	b = 12.599(3) Å	β= 91.963(3)°.
	c = 12.787(3) Å	γ = 93.828(3)°.
Volume	1833.7(8) Å^3	
Z	2	
Density (calculated)	1.795 Mg/m^3	
Absorption coefficient	4.087 mm^{-1}	
F(000)	976	
Crystal size	0.120 x 0.100 x 0.080 mm^3	
Theta range for data collection	1.667 to 25.008°.	
Index ranges	-12<=h<=14, -14<=k<=10, -15<=l<=14	
Reflections collected	8325	
Independent reflections	6182 [R(int) = 0.0290]	
Completeness to theta = 25.242°	93.1 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.638	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6182 / 39 / 413	
Goodness-of-fit on F^2	1.025	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.1168	
R indices (all data)	R1 = 0.0698, wR2 = 0.1255	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.621 and -1.072 e.Å^{-3}	

Table S7. Crystal data and structure refinement for **1-$(NO_3)_2$**.

Empirical formula	C44 H62 Ir2 N12 O12 S4	
Formula weight	1463.69	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 10.7834(7) Å	α= 70.6920(10)°.
	b = 11.3480(7) Å	β= 75.0870(10)°.
	c = 11.3793(7) Å	γ = 82.5810(10)°.
Volume	1268.42(14) $Å^3$	
Z	1	
Density (calculated)	1.916 Mg/m^3	
Absorption coefficient	5.479 mm^{-1}	
F(000)	724	
Crystal size	0.240 x 0.200 x 0.180 mm^3	
Theta range for data collection	1.948 to 25.599°.	
Index ranges	-12<=h<=13, -13<=k<=13, -11<=l<=13	
Reflections collected	6333	
Independent reflections	4668 [R(int) = 0.0123]	
Completeness to theta = 25.242°	97.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.622	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4668 / 0 / 341	
Goodness-of-fit on F^2	1.229	
Final R indices [I>2sigma(I)]	R1 = 0.0254, wR2 = 0.0674	
R indices (all data)	R1 = 0.0297, wR2 = 0.1049	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.895 and -1.311 $e.Å^{-3}$	

Table S8. Crystal data and structure refinement for **4-(OTf)$_2$**.

Empirical formula	C28 H39 F6 N4 O8 Rh S4	
Formula weight	904.78	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 11.3390(15) Å	α= 105.937(3)°.
	b = 13.3112(18) Å	β= 107.966(3)°.
	c = 14.488(3) Å	γ = 106.131(2)°.
Volume	1836.4(5) Å^3	
Z	2	
Density (calculated)	1.636 Mg/m^3	
Absorption coefficient	0.775 mm^{-1}	
F(000)	924	
Crystal size	0.240 x 0.060 x 0.040 mm^3	
Theta range for data collection	1.608 to 27.483°.	
Index ranges	-14<=h<=14, -17<=k<=17, -17<=l<=18	
Reflections collected	13482	
Independent reflections	8262 [R(int) = 0.0335]	
Completeness to theta = 25.242°	98.2 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.687	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	8262 / 10 / 477	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0459, wR2 = 0.1057	
R indices (all data)	R1 = 0.0731, wR2 = 0.1420	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.748 and -0.572 e.Å^{-3}	

Table S9. Crystal data and structure refinement for **5**.

Empirical formula	C32 H46 Cl4 N4 Rh2 S2	
Formula weight	898.47	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 8.7048(16) Å	α= 72.896(3)°.
	b = 8.8755(16) Å	β= 82.099(3)°.
	c = 14.672(3) Å	γ = 74.103(3)°.
Volume	1039.9(3) $Å^3$	
Z	1	
Density (calculated)	1.435 Mg/m^3	
Absorption coefficient	1.176 mm^{-1}	
F(000)	456	
Crystal size	0.300 x 0.150 x 0.060 mm^3	
Theta range for data collection	2.437 to 27.502°.	
Index ranges	-11<=h<=11, -11<=k<=11, -19<=l<=15	
Reflections collected	7495	
Independent reflections	4692 [R(int) = 0.0246]	
Completeness to theta = 25.242°	98.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.621	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4692 / 25 / 205	
Goodness-of-fit on F^2	1.062	
Final R indices [I>2sigma(I)]	R1 = 0.0491, wR2 = 0.1551	
R indices (all data)	R1 = 0.0625, wR2 = 0.1660	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.847 and -0.963 $e.Å^{-3}$	

Table S10. Crystal data and structure refinement for **7-Cl**.

Empirical formula	C15 H28 Cl2 N4 O3 Pd S2	
Formula weight	553.83	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.409(2) Å	α= 90°.
	b = 7.4204(10) Å	β= 100.341(2)°.
	c = 20.302(3) Å	γ = 90°.
Volume	2283.6(5) $Å^3$	
Z	4	
Density (calculated)	1.611 Mg/m^3	
Absorption coefficient	1.252 mm^{-1}	
F(000)	1128	
Crystal size	0.250 x 0.200 x 0.180 mm^3	
Theta range for data collection	2.232 to 27.442°.	
Index ranges	-19<=h<=18, -9<=k<=9, -23<=l<=26	
Reflections collected	15757	
Independent reflections	5176 [R(int) = 0.0345]	
Completeness to theta = 25.242°	99.3 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.746 and 0.584	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5176 / 2 / 238	
Goodness-of-fit on F^2	1.066	
Final R indices [I>2sigma(I)]	R1 = 0.0350, wR2 = 0.0925	
R indices (all data)	R1 = 0.0427, wR2 = 0.0998	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.651 and -0.717 $e.Å^{-3}$	