Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for:

# “Tuning the electronic properties of an N-heterocyclic carbene by charge and mesomeric effects”

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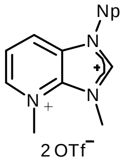
**General Considerations.** All experiments were performed with standard Schlenk techniques in a dry nitrogen atmosphere. Microwave assisted synthesis were carried out with a Cem Discover microwave. Solvents were dried and distilled under nitrogen by using standard procedures (diethyl ether and tetrahydrofuran over Na/benzophenone, dichlormethane over $CaH_2$ and n-hexane over Na). NMR spectra were measured with a Bruker Avance III – 300, Avance DRX 500 or Avance III – 600. Chemical shifts of $^1H$ and $^{13}C\{^1H\}$-NMR spectra were reported in delta (δ) units, expressed in parts per million (ppm) downfield from tetramethylsilane using the solvent as internal standard ($^1H$: chloroform-*d3* 7.26 ppm, acetone-*d6* 2.05 ppm, DMSO-*d6* 2,50 ppm, acetonitrile-*d3* 1.94 ppm; $^{13}C$: chloroform-*d3* 77.16 ppm, acetone-*d6* 29.84 ppm, DMSO-*d6* 2,50 ppm, acetonitrile-*d3* 1.32 ppm. Coupling constants are expressed in Hertz (Hz). High-resolution mass spectra (HRMS) were obtained with a Bruker Daltonics UHR-QTOF maXis 4G (ESI) and were reported as m/z. A Shimadzu IR Affinity-1 was used for IR spectroscopy. Elemental analyses were obtained with an Elementar vario Micro cube. X-ray crystal structure data were collected on a Bruker Apex Duo at 297 K. Refinement was done with SHELXL-97. Molecular structure plots were generated with Ortep3v2.

2,3-diaminopyridine, 98% [Acros Organics, Belgium (CAS: 452-58-4)] was purchased. $[PyINp_2][PF_6]$ **4**,[1] $(PyINp_2)Rh(COD)Cl$, $[Rh(COD)Cl]_2$[2] and $[Ir(COD)Cl]_2$[3] was synthesized according to literature.

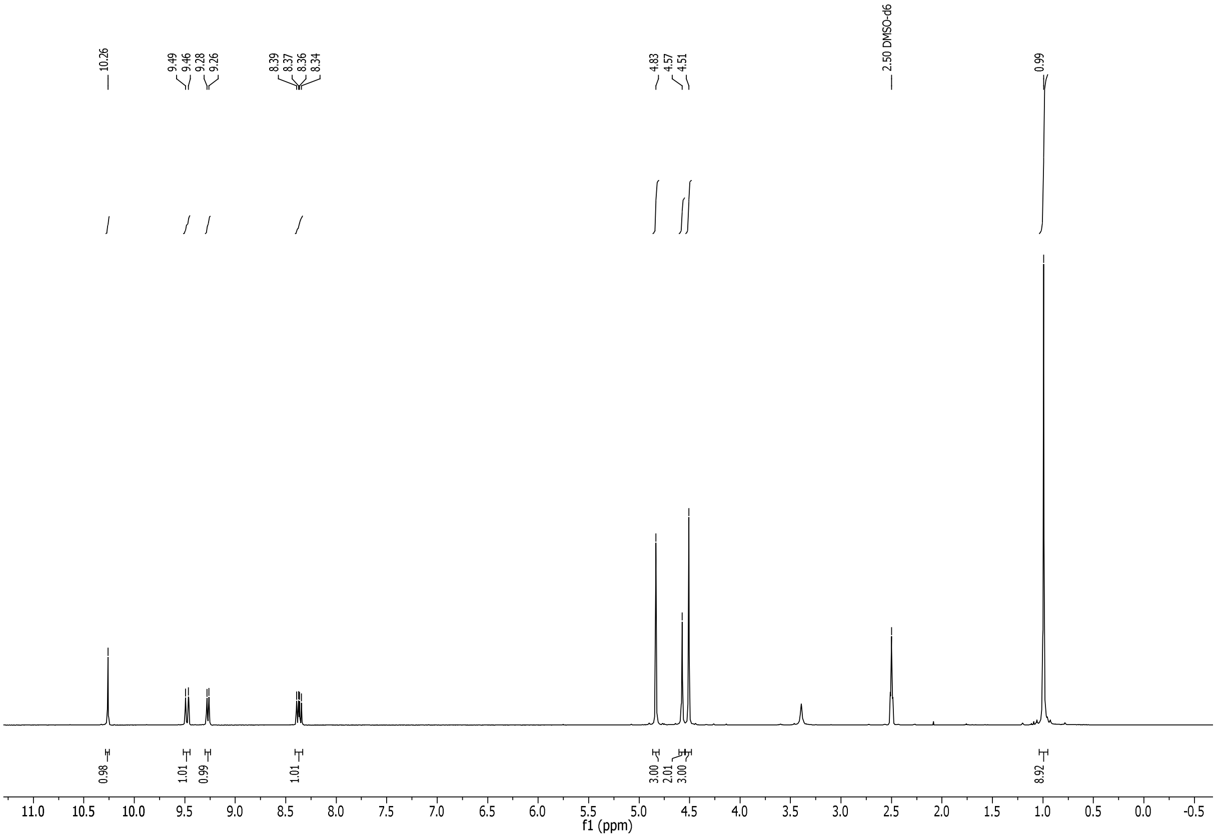
**General procedure for synthesis of the dicarbonyl complexes 10, 11 and 12:**

CO was bubbled into a solution of corresponding COD complex for 30 minutes und high stirring. During this procedure the bright orange or yellow solutions bleached, which indicates the complete conversion. To measure IR spectra the procedure was carried out in $CH_2Cl_2$. For collecting NMR data the respective deuterated solvent was taken.

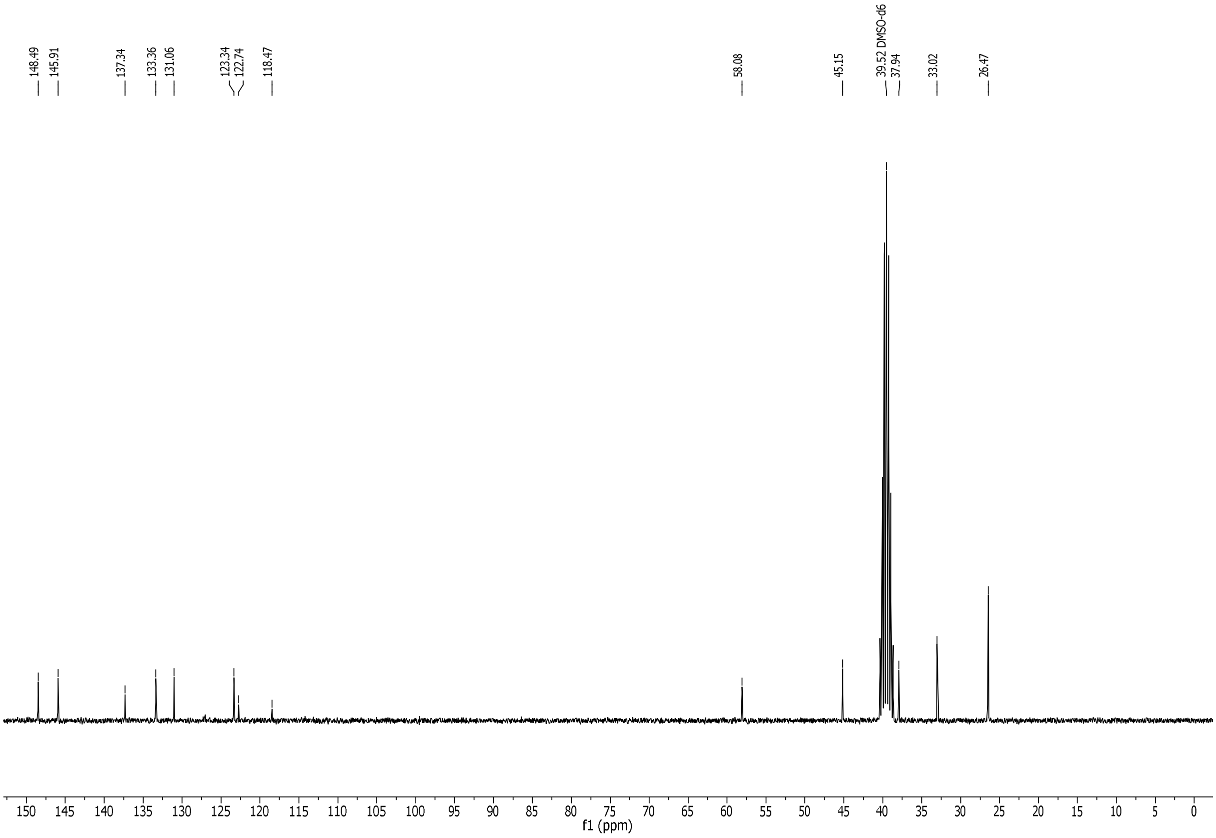


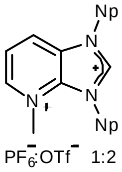
**Dicationic precursor 5a.** 4-Azabenzimidazolium hexafluorophosphate (500 mg, 1.2 mmol) was suspended in methyl trifluormethansulfonate (1.2 mL) in a 10 mL microwave tube. The suspension was stirred in the microwave oven two times for 5 minutes at 130 °C while being shaken between the passes. The resulting dark red, high viscous solution was transferred into a 250 mL Schlenkflask and mixed with 80 mL of diethyl ether. After stirring for 3 hours at ambient temperature the diethyl ether was removed by a syringe. To the red brown solid 50 mL of diethyl ether were added and the mixture was stirred again for 3 hours until a white precipitate was formed. The suspension was filtered and washed with 10 mL THF. After drying in high vacuum for several hours, the analytically pure product **5** was obtained in 91% yield (580 mg, 1.1 mmol) (**5a**). Single crystals of **5a** were grown by solvent diffusion from $Et_2O$ in a solution of **5a** in acetone. $^1$H NMR (300 MHz, DMSO-*d6*): δ 10.26 (s, 1H, C2-H), 9.48 (brd, 1H, $^3J_{HH} = 8.6$ Hz, C7-H), 9.27 (brd, 1H, $^3J_{HH} = 6.1$ Hz, C5-H), 8.37 (dd, 1H, $^3J_{HH} = 8.6$ Hz, $^3J_{HH} = 6.1$ Hz, C6-H), 4.83 (s, 3H, N4-$CH_3$), 4.57 (s, 2H, N1-$CH_2$), 4.51 (s, 3H, N3-$CH_3$), 1.00 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (75 MHz, DMSO-*d6*): δ 148.49 (s, C2), 145.91 (s, C7), 137.34 (s, $C_q$), 133.36 (s, C5), 131.06 (s, $C_q$), 123.34 (s, C6), 120.62 (q, $^1J_{CF} = 322.1$ Hz, $\underline{C}F_3$), 58.08 (s, $\underline{C}(CH_3)_3$), 45.15 (s, N4$\underline{C}H_3$), 37.94 (s, N1$\underline{C}H_2$), 35.02 (s, N3$\underline{C}H_3$), 26,47 (s, $C(\underline{C}H_3)_3$). HRMS (ESI): $[M+OH]^+$ calcd for $C_{13}H_{22}N_3O^+$: 236.17574; found: 236.17547. Anal. Calcd (%) for $C_{15}H_{21}N_3F_6O_6S_2$: C, 34.82; H, 4.09; N, 8.12; S, 12.39. Found: C, 34.68; H, 4.18; N, 8.04, S, 12.81.

$^{1}$H NMR (DMSO-*d6*)



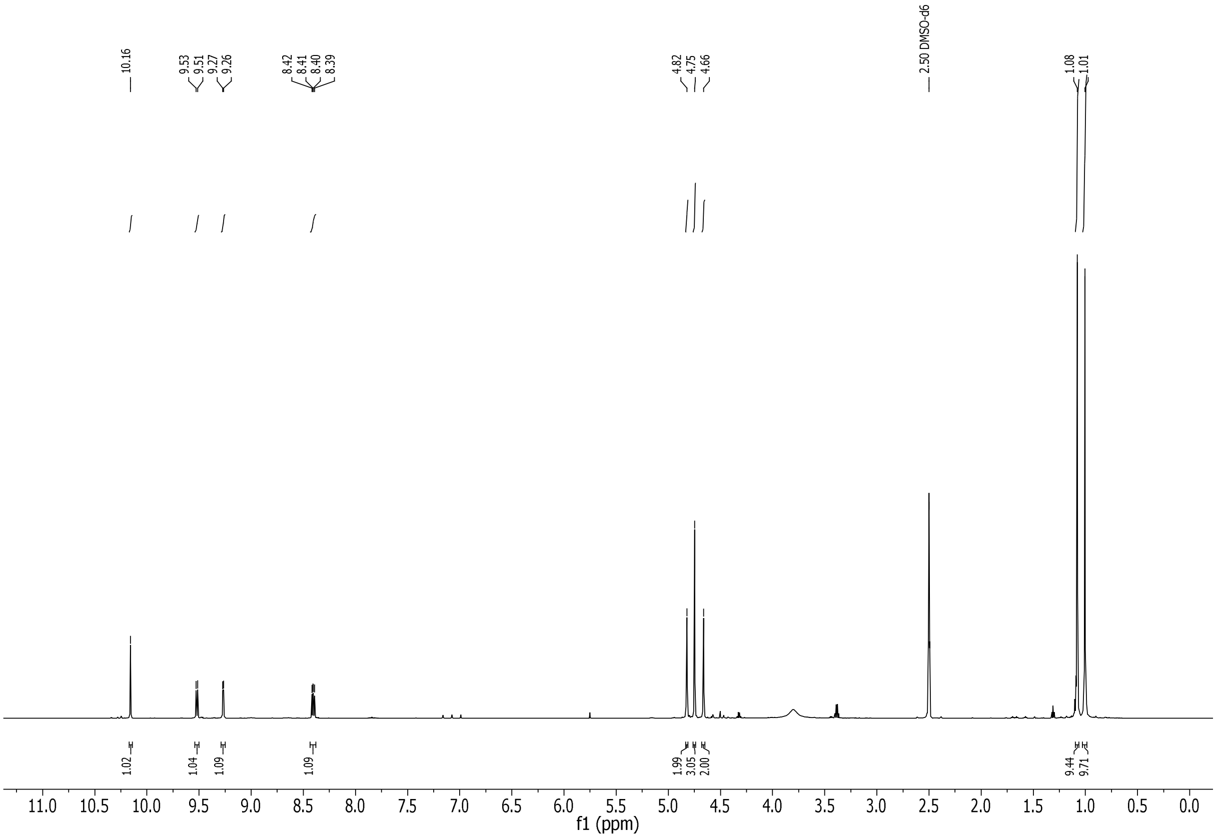
$^{13}$C{$^{1}$H} NMR (DMSO-*d6*)



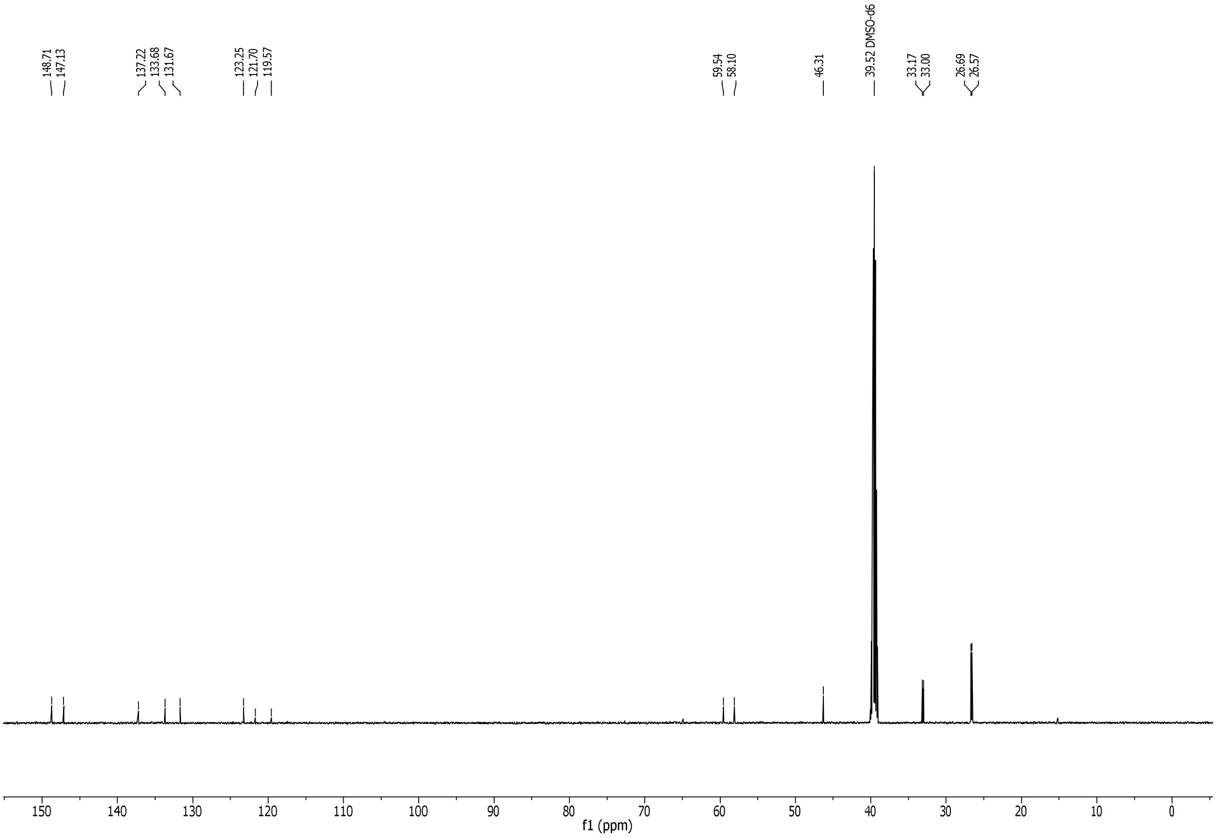


**Dicationic precursor 5b. 5b** was synthesized according to **5a** by 100 °C instead of 130 °C. The product was obtained as a white solid 74% yield (508 mg, 0,9 mmol). $^1$H NMR (600 MHz, DMSO-*d6*): δ 10.16 (s, 1H, C2-H), 9.52 (d, 1H, $^3J_{HH}$ = 8.5 Hz, C7-H), 9.27 (d, 1H, $^3J_{HH}$ = 6.1 Hz, C5-H), 8.41 (dd, 1H, $^3J_{HH}$ = 8.6vHz, $^3J_{HH}$ = 6.1 Hz, C6-H), 4.82 (s, 2H, N3-$CH_2$), 4.75 (s, 3H, N4-$CH_3$), 4.66 (s, 2H, N1-$CH_2$), 1.08 (s, 9H, N3-$C(CH_3)_3$), 1.01 (s, 9H, N1-$C(CH_3)_3$). $^{13}$C (150 MHz, DMSO-*d6*): δ 148.72 (s, C2), 147.15 (s, C5), 137.23 (s, $C_q$), 133.69 (s, C7), 131.68 (s, $C_q$), 123.26 (s, C6), 120.64 (q, $^1J_{CF}$ = 322.4 Hz, $\underline{C}F_3$), 59.54 (s, N3-$\underline{C}H_2$), 58.10 (s, N1-$\underline{C}H_2$), 46.31 (s, N4-$\underline{C}H_3$), 33.17 (s, N3-$\underline{C}(CH_3)_3$), 33.00 (s, N1-$\underline{C}(CH_3)_3$), 26.69 (s, N3-$C(\underline{C}H_3)_3$), 26.57 (s, $C(\underline{C}H_3)_3$). $^{19}$F (280 MHz, DMSO-*d6*): δ -70.16 (d, 6F, $^1J_{FP}$ = 711.2 Hz, $PF_6^-$) -77.75 (s, 6F, $CF_3$). $^{31}$P (81 MHz, DMSO-*d6*): δ -142.96 (sep, $^1J_{PF}$ = 711.2 Hz, $PF_6^-$). HRMS ESI: $[M+OH]^+$ calcd for $C_{17}H_{30}N_3O^+$: 292.23834; found 292.23866. Anal. Calcd (%) for $[C_{17}H_{29}N][(PF_6)_{1/2}(CF_3O_3S)_{3/2}]$: C, 38.57; H, 5.11; N, 7.36; S, 7.49. Found: C, 37.96; H, 5.14; N, 7.21, S, 8.01.

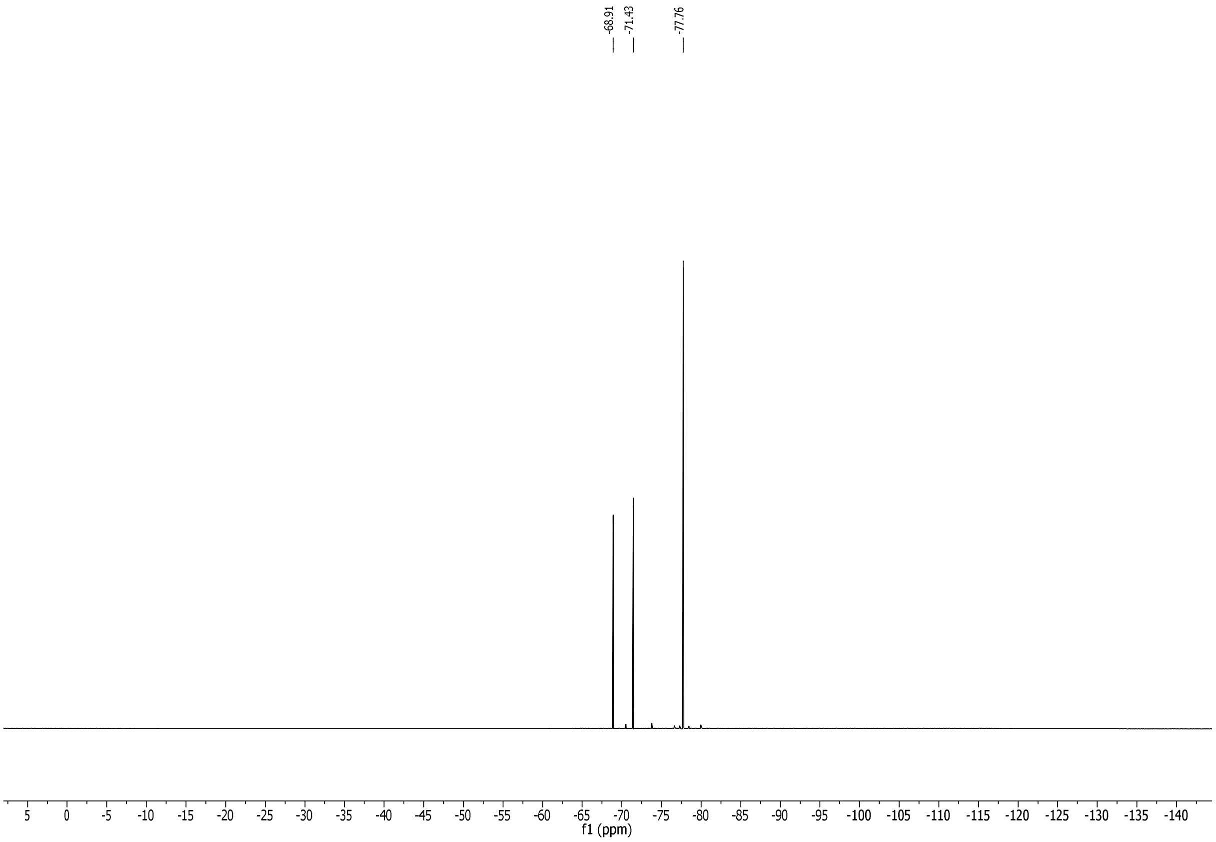
$^{1}$H NMR (DMSO-*d6*)

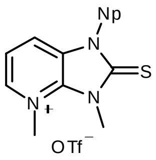


$^{13}$C{$^{1}$H} NMR (DMSO-*d6*)



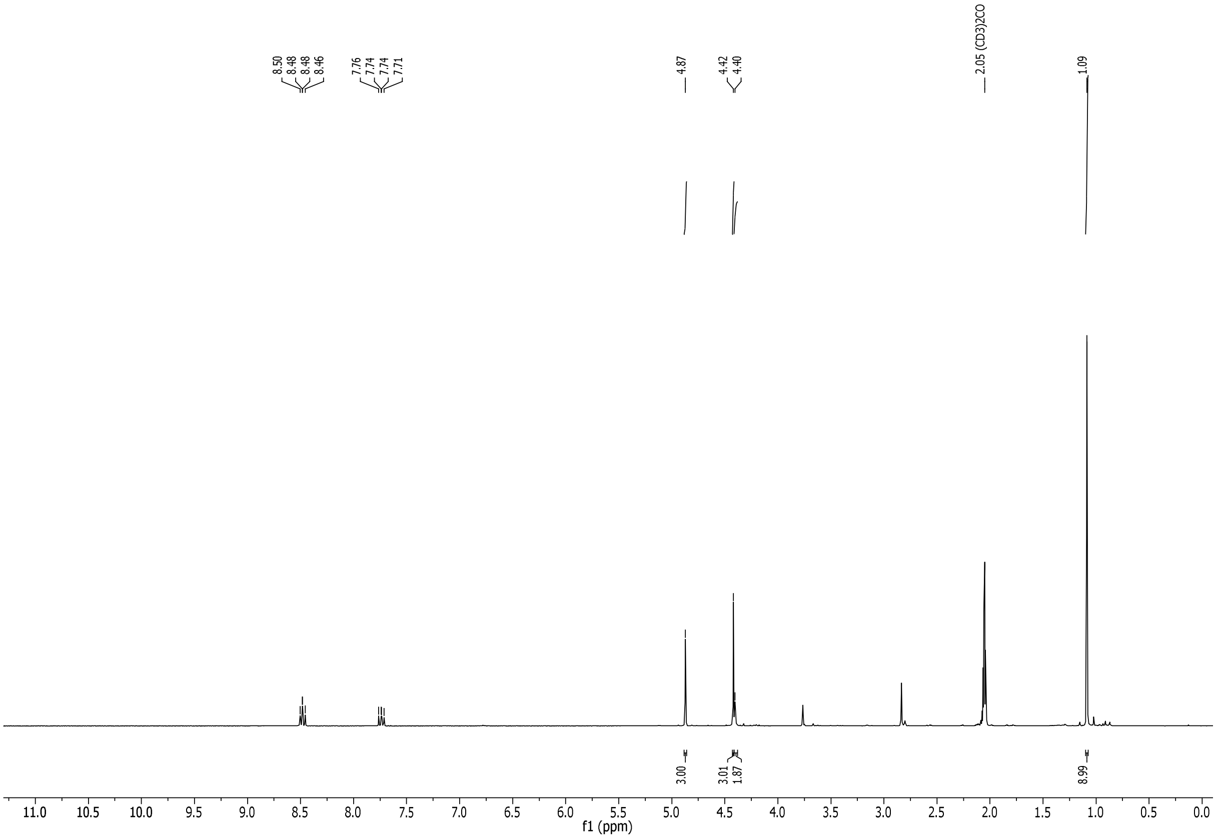
$^{19}$F NMR (DMSO-*d6*)



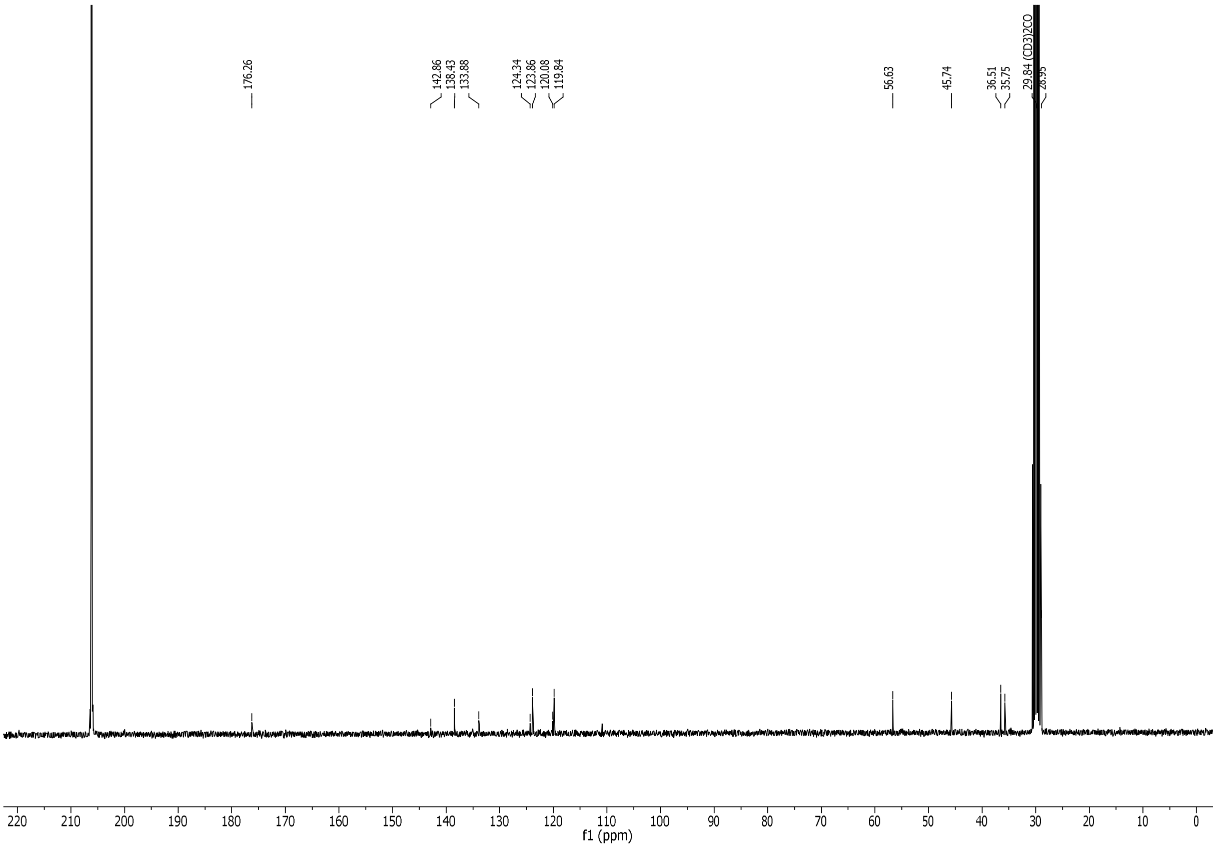


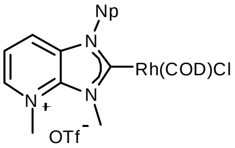
**Cationic thione 7.** A 50 mL Schlenk flask was charged with **5a** (250 mg, 483.1 $\mu$mol), sulfur (31 mg, 966.6 $\mu$mol) and potassium *tert*-butoxide (59.6 mg, 531.1 $\mu$mol). The solid mixture was cooled to -80 °C. Then 10 mL THF were added drop wise with vigorous stirring. After stirring for 20 min at -80 °C the cooling bath was removed. The red reaction mixture was warmed to ambient temperature and stirred over night. The organic phase was removed carefully with a syringe from the precipitate. Drying in high vacuum for several hours yields **7** in 41% (80.1 mg, 200.5 $\mu$mol). $^{1}$H NMR (300 MHz, acetone-*d6*): δ 8.49 (d, 1H, $^{3}J_{HH}$ = 6.4 Hz, C7-H), 8.47 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz), 7.74 (dd, 1H, $^{3}J_{HH}$ = 8.2 Hz, $^{3}J_{HH}$ = 6.5 Hz, C6-H), 4.87 (s, 3H, N3-$CH_3$), 4.42 (s, 3H, N4-CH3), 4.40 (s, 2H, N1-$CH_2$), 1.09 (s, 9H, $C(CH_3)_3$). $^{13}$C{$^{1}$H} NMR (75 MHz, acetone-*d6*): δ 176.28 (s, C2), 142.87 (s, $C_q$), 138.44 (s, C7), 133.89 (s, $C_q$), 123.87 (s, C5), 122.22 (q, $^{1}J_{CF}$ = 321.6 Hz, $\underline{C}F_3$), 119.85 (s, C6), 56.63 (s, N1-$\underline{C}H_2$), 45.74 (s, N4-$\underline{C}H_3$), 36.51 (s, $\underline{C}(CH_3)_3$), 35.75 (s, N3-<u>C</u>H$_3$), 28.95 (s, C(<u>C</u>H$_3$)$_3$). HRMS (ESI): $[M]^+$ calcd for $C_{13}H_{20}N_3S^+$: 250.13724; found: 250.13680; $[M]^-$ calcd for $CF_3O_3S^-$: 148.95257; found: 148.95271.

$^1$H NMR (acetone-*d6*)



$^{13}C\{^1H\}$ NMR (acetone-*d6*)

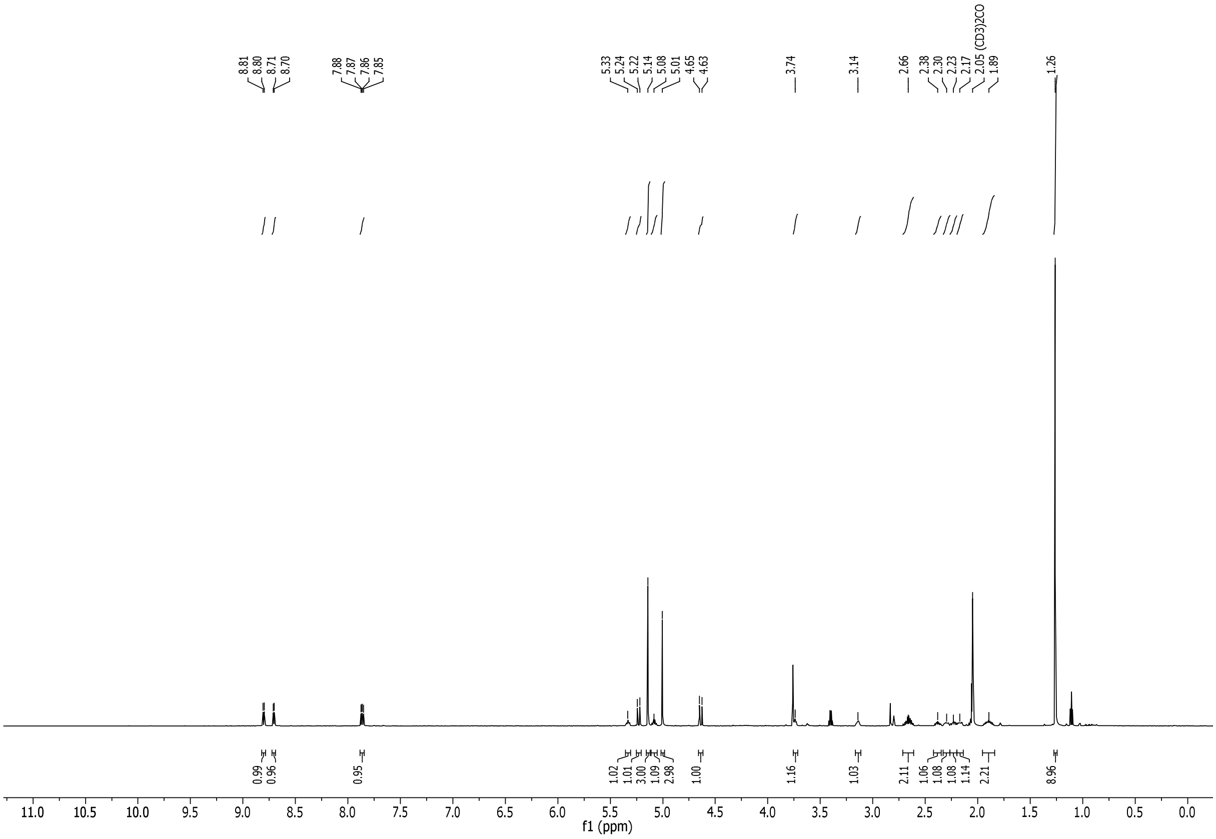




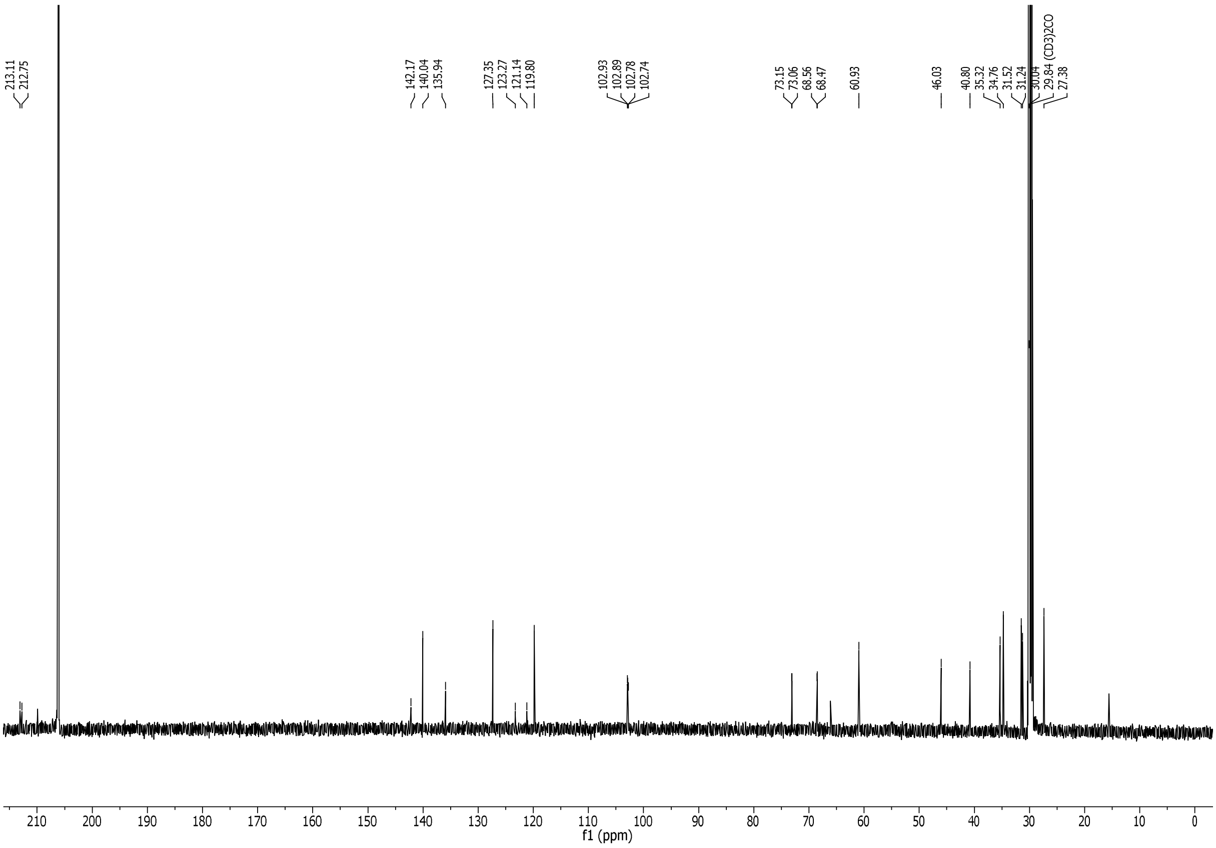
**Rhodium complex 8.** A 50 mL Schlenk flask was charged with **5a** (200 mg, 386.5 $\mu$mol), potassium *tert*-butoxide (47.7 mg, 425.2 $\mu$mol) and $[Rh(COD)Cl]_2$ (95.3 mg, 193.3 $\mu$mol). After cooling the mixture to -80 °C 15 mL THF were added drop wise with vigorous stirring. Subsequently the orange reaction mixture was stirred for 20 min at -80 °C. Then the cooling bath was removed and the mixture was warmed to ambient temperature. Stirring over night yields a yellow precipitate. Removing the organic phase carefully with a syringe and drying the remaining solid in high vacou for several hours afforded the desired compound **8** in 50% yield (118.7 mg, 193.0 $\mu$mol). $^1H$ NMR (600 MHz, acetone-*d6*): $\delta$ 8.81 (d, 1H, $^3J_{HH}$ = 8.2 Hz, C7-H), 8.71 (d, 1H, $^3J_{HH}$ = 6.2 Hz, C5-H), 7.87 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 6.2 Hz, C6-H), 5.31 – 5.35 (m, 1H, =CH), 5.23 (d, 1H, $^2J_{HH}$ = 14.2 Hz, N1-$CH_2$), 5.14 (s, 3H, N4-$CH_3$), 5.06 – 5.10 (m, 1H, =CH), 5.01 (s, 3H, N3-$CH_3$), 4.64 (d, 1H, $^2J_{HH}$ = 14.2 Hz, N1-$CH_2$), 3.73 – 3.77 (m, 1H, =CH), 3.12 – 3.16 (m, 1H,

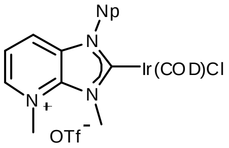
=CH), 2.62 – 2.71 (m, 2H, $CH_2$), 2.35 – 2.41 (m, 1H, $CH_2$), 2.28 – 2.32 (m, 1H, $CH_2$), 2.20 – 2.26 (m, 1H, $CH_2$), 2.20 – 2.14 ppm (m, 1H, $CH_2$), 1.85 – 1.94 (m, 2H, $CH_2$), 1.26 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (150 MHz, acetone-*d6*): δ 212.95 (d, $^1J_{CRh}$ = 53.5 Hz, C2), 142.19 (s, $C_q$), 140.06 (s, C5), 135.96 (s, $C_q$), 127.36 (s, C7), 122.22 (q, $^1J_{CF}$ = 321.5 Hz, $\underline{C}F_3$), 119.82 (s, C6), 102.92 (d, $^1J_{CRh}$ = 6.6 Hz, =$\underline{C}$H), 102.77 (d, $^1J_{CRh}$ = 6.5 Hz, =$\underline{C}$H), 73.11 (d, $^1J_{CRh}$ = 14.2 Hz, =$\underline{C}$H), 68.53 (d, $^1J_{CRh}$ = 13.7 Hz, =$\underline{C}$H), 60.93 (s, N1-$CH_2$), 46.03 (s, N3-$\underline{C}H_3$), 40.80 (s, N4-$\underline{C}H_3$), 35.32 (s, $\underline{C}H_2$), 34.76 (s, $\underline{C}(CH_3)_3$), 31.52 (s, $\underline{C}H_2$), 31.24 (s, $\underline{C}H_2$), 30.04 (s, $C(\underline{C}H_3)_3$), 27.38 (s, $\underline{C}H_2$). HRMS (ESI): $[M-Cl]^{++}$ calcd for $C_{21}H_{32}N_3Rh^{++}$: 214.58202; found: 214.58266.

$^1$H NMR (acetone-*d6*)



$^{13}C\{^{1}H\}$ NMR (acetone-*d6*)

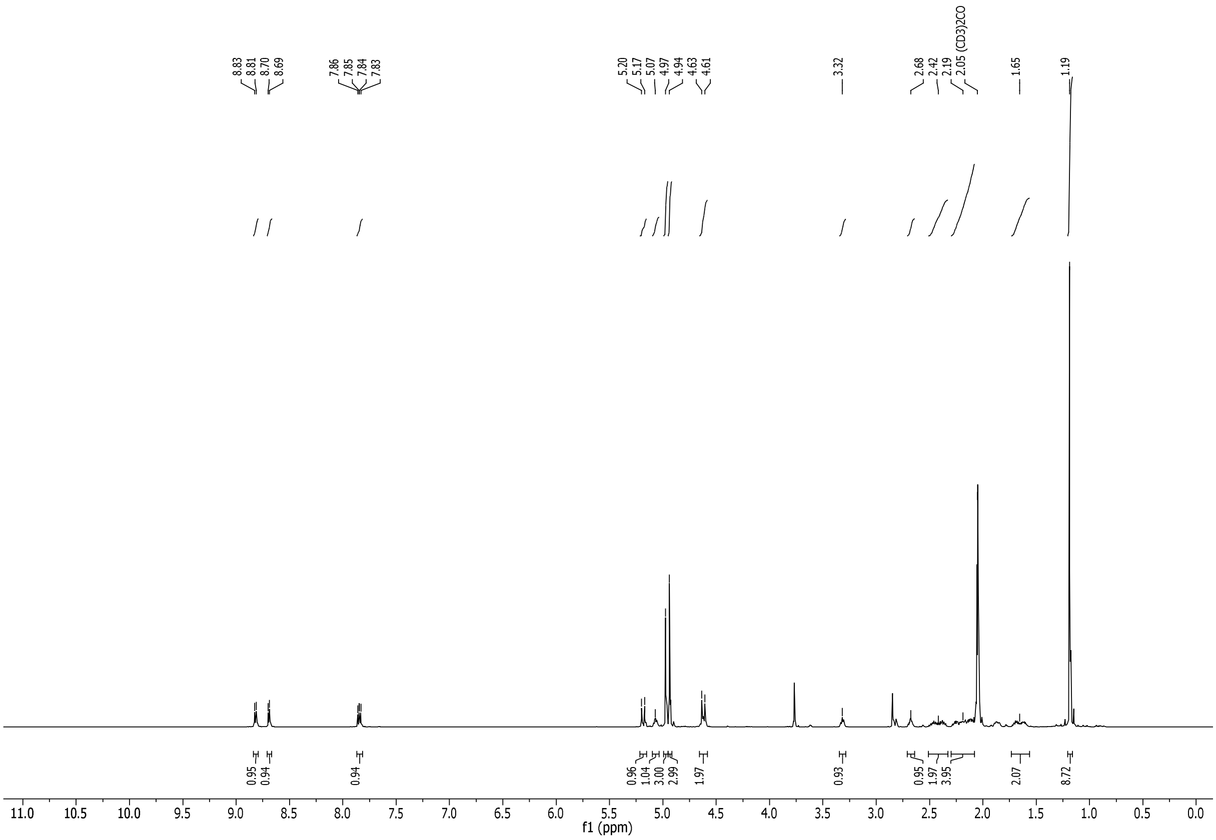




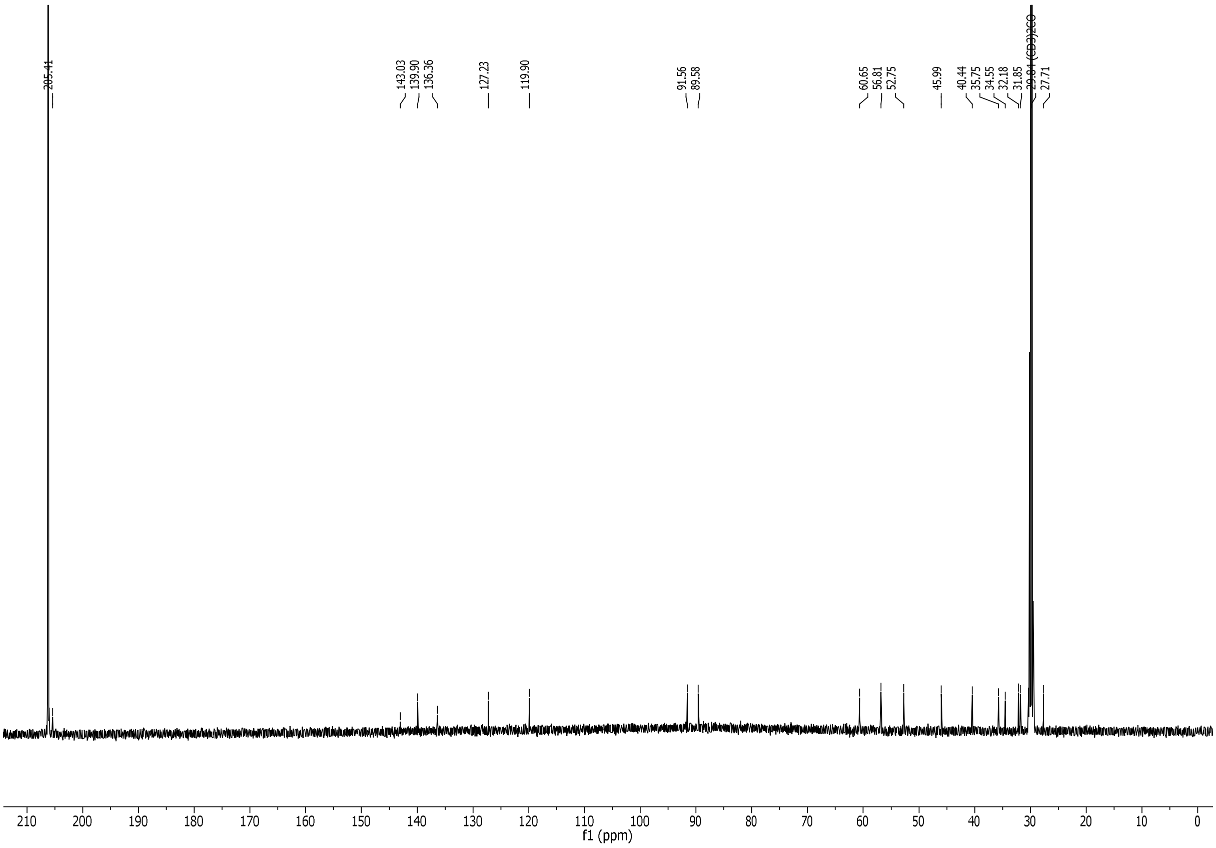
**Iridium complex 9a.** A 50 mL Schlenk flask was charged with **5a** (250 mg, 483.1 $\mu$mol), Potassium *tert*-butoxide (59.6 mg, 531.4 $\mu$mol) and $[Ir(COD)Cl]_2$ (162.3 mg, 241.6 $\mu$mol). The solids were cooled to -90 °C. Then 15 mL THF were added drop wise with vigorous stirring and the orange suspension was stirred for further 20 minutes at -85 °C. Subsequently the cooling bath was removed, the reaction mixture was warmed and stirred over night at ambient temperature. Filtration of the resulting precipitate and drying in high vacuum for several hours obtained the desired compound **9a** in 82% yield (277.3 mg, 394.3 $\mu$mol). $^{1}H$ NMR (500 MHz, acetone-*d6*): δ 8.82 (d, 1H, $^{3}J_{HH}$ = 8.3 Hz, C7-H), 8.70 (d, 1H, $^{3}J_{HH}$ = 6.2 Hz, C5-H), 7.85 (dd, 1h, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.3 Hz, C6-H), 5.19 (d, 1H, $^{2}J_{HH}$ = 14.3 Hz, N1-$CH_2$), 5.05 – 5.10 (m, 1H, =CH), 4.97 (s, 3H, N4-$CH_3$), 4.94 (s, 3H, N3-$CH_3$), 4.65 – 4.95 (m, 1H, =CH), 4.62 (d, 1H, $^{2}J_{HH}$ = 14.2 Hz, N1-$CH_2$), 3.29 – 3.34 (m, 1H, =CH), 2.64 – 2.70 (m, 1H, =CH), 2.34 – 2.51 (m, 2H, $CH_2$), 2.08 – 2.30 (m, 4H,

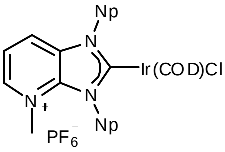
$CH_2$), 1.57 – 1.73 (m, 2H, $CH_2$), 1.19 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (125 MHz, acetone-*d6*): δ 205.43 (s, C2), 143.04 (s, $C_q$), 139.91 (s, C5), 136.38 (s, $C_q$), 127.24 (s, C7), 119.91 (s, C6), 91.57 (s, =$\underline{C}$H), 89.59 (s, =$\underline{C}$H), 60.66 (s, N1-$\underline{C}H_2$), 56.81 (s, =$\underline{C}$H), 52.76 (s, =$\underline{C}$H), 45.99 (s, $N_3$-$\underline{C}H_3$), 40.44 (s, N4-$\underline{C}H_3$), 35.75 (s, $\underline{C}H_2$), 34.55 (s, $\underline{C}H_2$), 32.18 (s, $\underline{C}H_2$), 31.84 (s, $C(\underline{C}H_3)_3$), 27.71 (s, $\underline{C}H_2$). HRMS (ESI): $[M-Cl]^{++}$ calcd for $C_{21}H_{30}IrN_3^{++}$: 258.60293; found: 258.60287.

$^1$H NMR (acetone-*d6*)



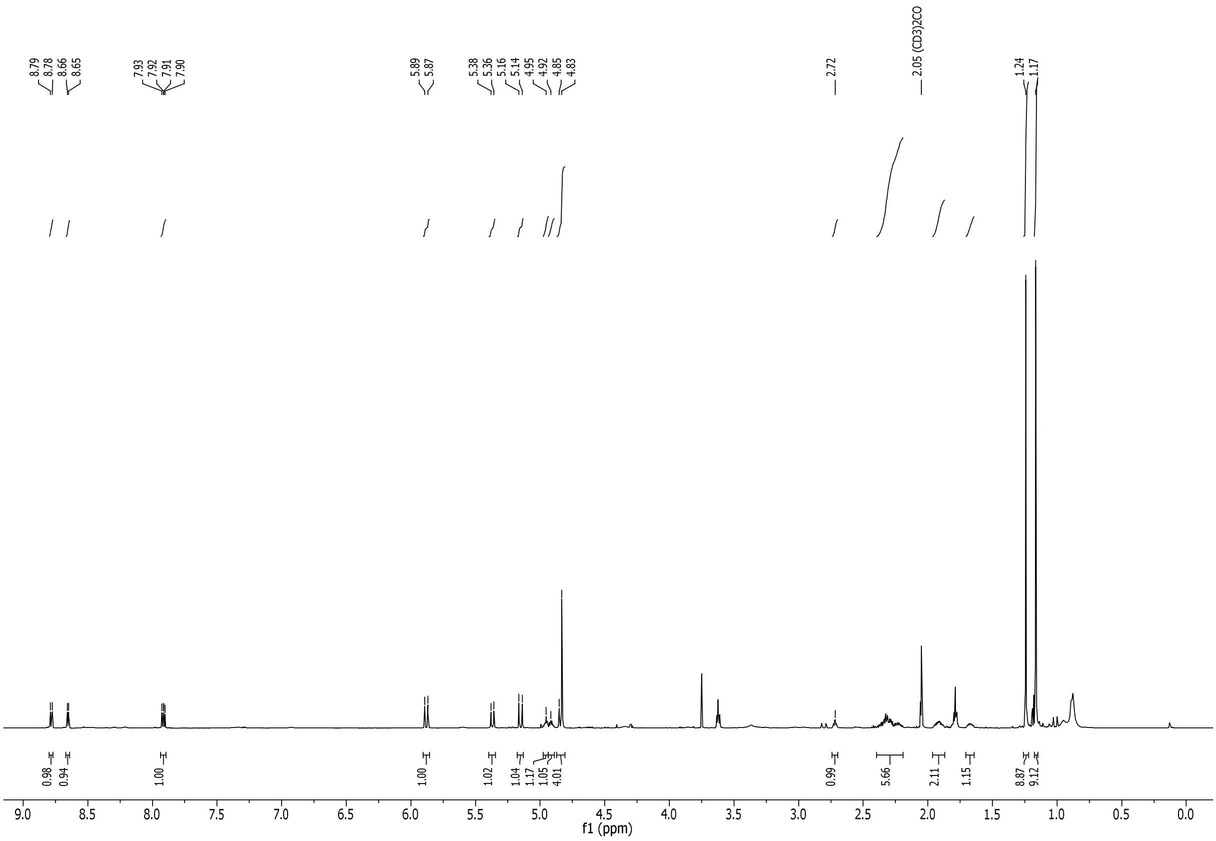
$^{13}C\{^{1}H\}$ NMR (acetone-*d6*)



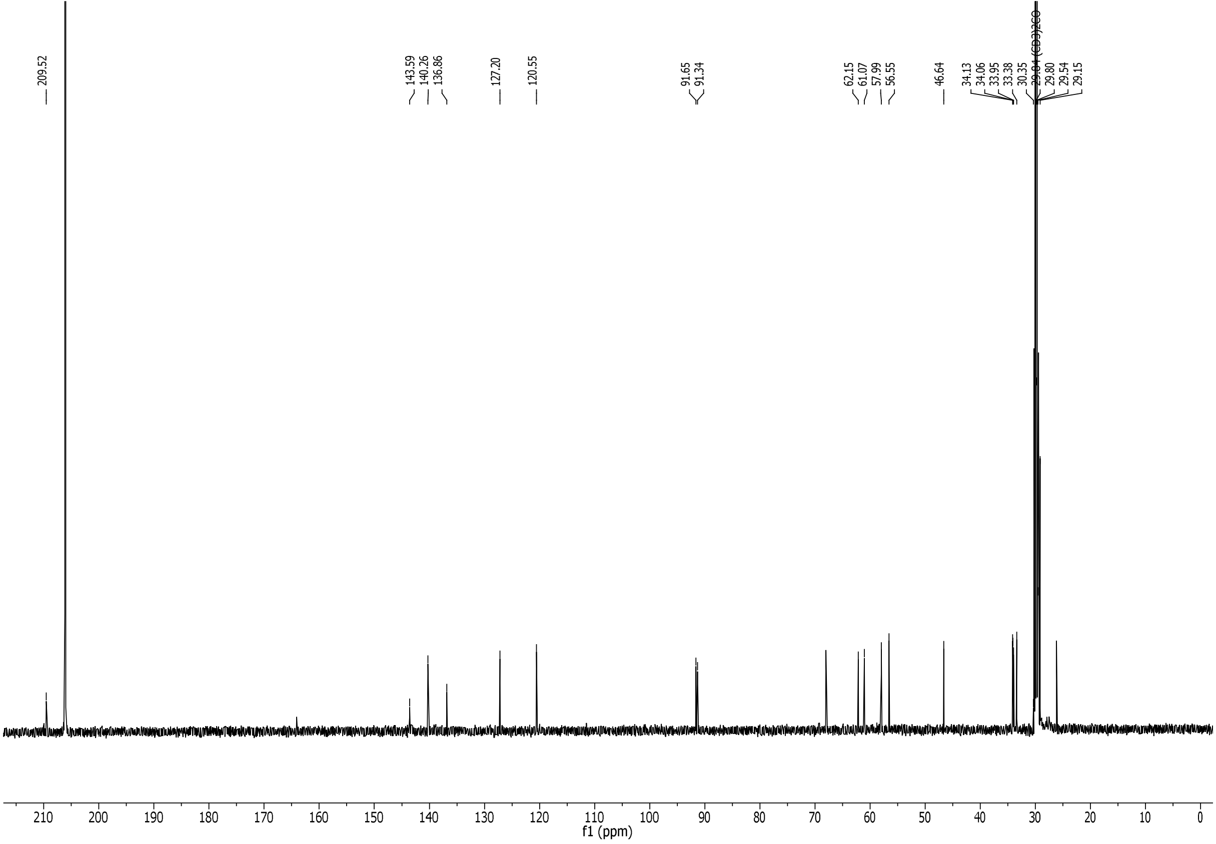


**Iridium complex 9b.** A 50 mL Schlenk flask was charged with **5b** (250 mg, 438.0 $\mu$mol), Potassium *tert*-butoxide (54.1 mg, 481.8 $\mu$mol), Potassium hexafluorophosphate (160 mg, 869.3 $\mu$mol) and $[Ir(COD)Cl]_2$ (147.1 mg, 219.0 $\mu$mol). The mixture was cooled to -90 °C and 15 mL THF were added dropwise. The suspension was stirred for 20 min at -90 °C. Then the cooling bath was removed and the mixture was stirred over night at ambient temperature. The resulting orange precipitate was filtered of. Drying for several hours in high vacuum yields **9b** in 56 % (185.2 mg, 245.3 $\mu$mol). $^{1}$H-NMR (600 MHz, acetone-*d6*): δ 8.78 (d, 1H, $^{3}J_{HH}$ = 8.2 Hz, C7-H), 8.65 (d, 1H, $^{3}J_{HH}$ = 6.3 Hz, C5-H), 7.91 (dd, 1H, $^{3}J_{HH}$ = 8.3 Hz, $^{3}J_{HH}$ = 6.3 Hz, C6-H), 5.88 (d, 1H, $^{2}J_{HH}$ = 15.2 Hz, N3-$CH_2$), 5.37 (d, 1H, $^{2}J_{HH}$ = 14.2 Hz, N1-$CH_2$), 5.15 (d, 1H, $^{2}J_{HH}$ = 15.2 Hz, N3-$CH_2$), 4.93 – 4.98 (m, 1H, =CH), 4.89 – 4.93 (m, 1H, =CH), 4.84 (d, 1H, $^{2}J_{HH}$ = 14.2 Hz, N1-$CH_2$), 4.83 (s, 3H, N4-$CH_3$), 2.69 – 2.74 (m, 1H, =CH), 2.19 – 2.39 (m, 6H, =CH, CH$_2$), 1.86 – 1.97 (m, 2H, CH$_2$), 1.64 – 1.70 (m, 1H, CH$_2$), 1.24 (s, 9H, N1-C(CH$_3$)$_3$), 1.17 (s, 9H, N3-C(CH$_3$)$_3$). $^{13}$C{$^1$H} NMR (150 MHz, acetone-*d6*): δ 209.52 (s, C2), 143.59 (s, C$_q$), 140.26 (s, C5), 136.86 (s, C$_q$), 127.20 (s, C7), 120.55 (s, C6), 91.65 (s, =$\underline{\text{C}}$H), 91.34 (s, =$\underline{\text{C}}$H), 62.15 (s, N3-$\underline{\text{C}}$H$_2$), 61.07 (s, N1-$\underline{\text{C}}$H$_2$), 57.99 (s, =$\underline{\text{C}}$H), 56.55 (s, =$\underline{\text{C}}$H), 46.64 (s, N4-$\underline{\text{C}}$H$_3$), 34.13 (s, $\underline{\text{C}}$(CH$_3$)$_3$), 34.06 (s, $\underline{\text{C}}$(CH$_3$)$_3$), 33.95 (s, $\underline{\text{C}}$H$_2$), 33.38 (s, $\underline{\text{C}}$H$_2$), 30.35 (s, $\underline{\text{C}}$H$_2$), 29.80 (s, N1-C($\underline{\text{C}}$H$_3$)$_3$), 29.54 (s, $\underline{\text{C}}$H$_2$), 29.15 (s, N3-C($\underline{\text{C}}$H$_3$)$_3$). $^{19}$F NMR (280 MHz, acetone-*d6*): δ -72.61 (d, $^1J_{FP}$ = 707.5 Hz, PF$_6^-$). ESI-MS: m/z: 287 [M-Cl]$^{++}$.

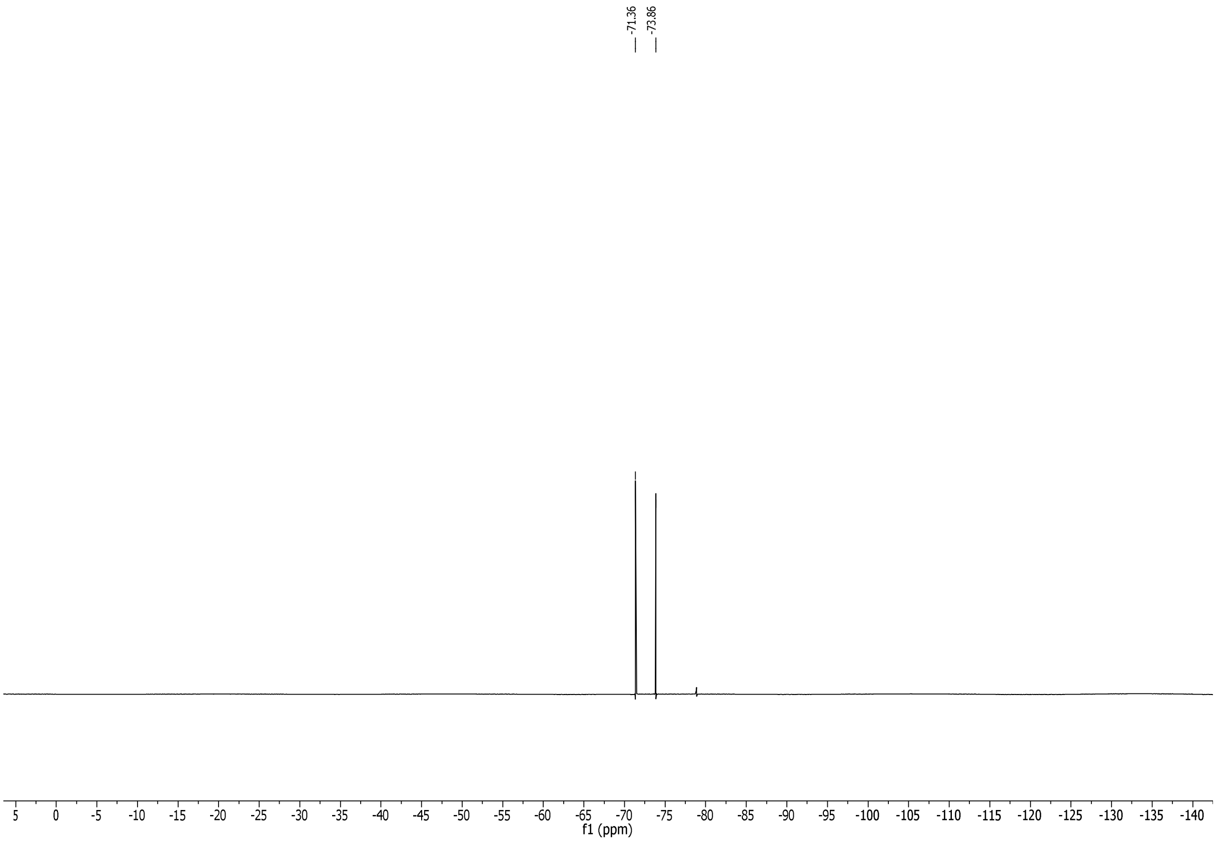
$^1$H NMR (acetone-*d6*)

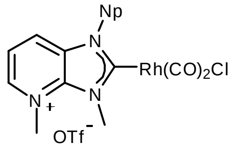


$^{13}C\{^{1}H\}$ NMR (acetone-*d6*)



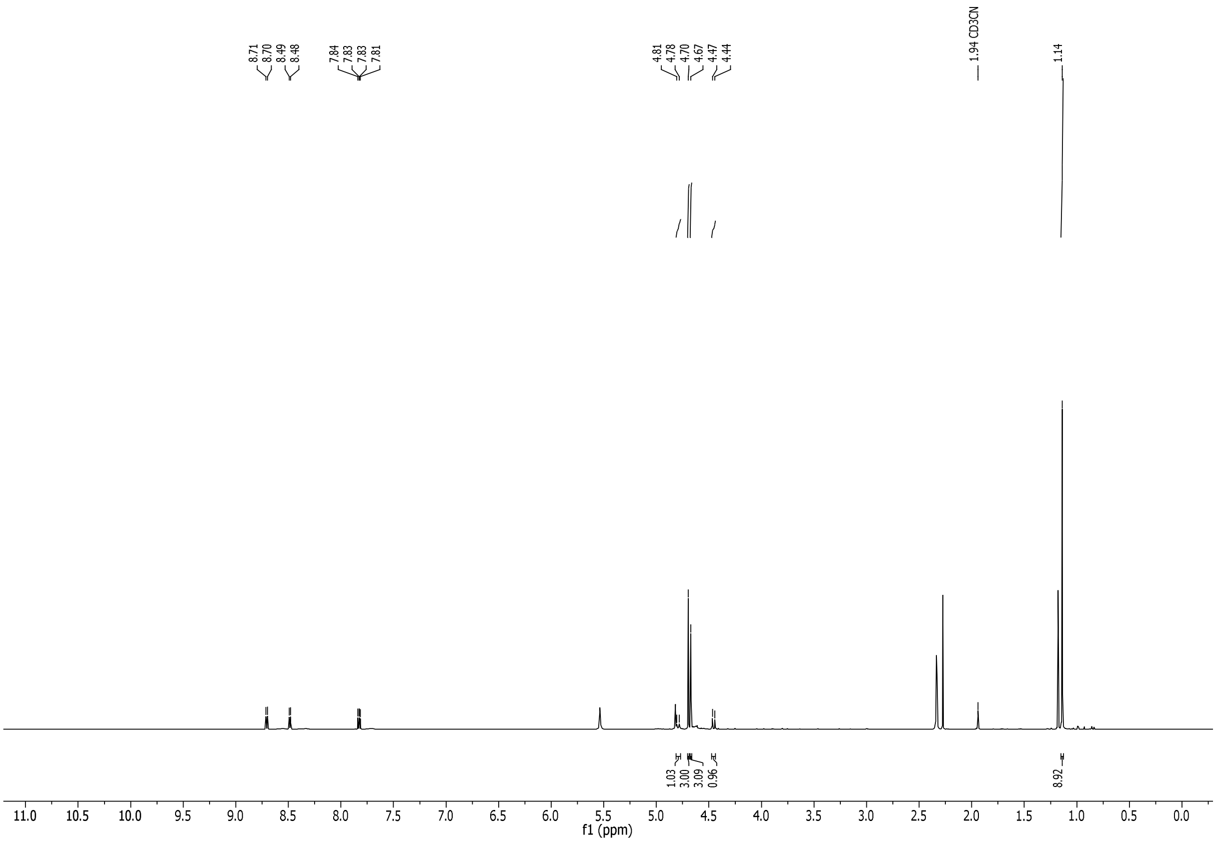
$^{19}F$ NMR (acetone-*d6*)



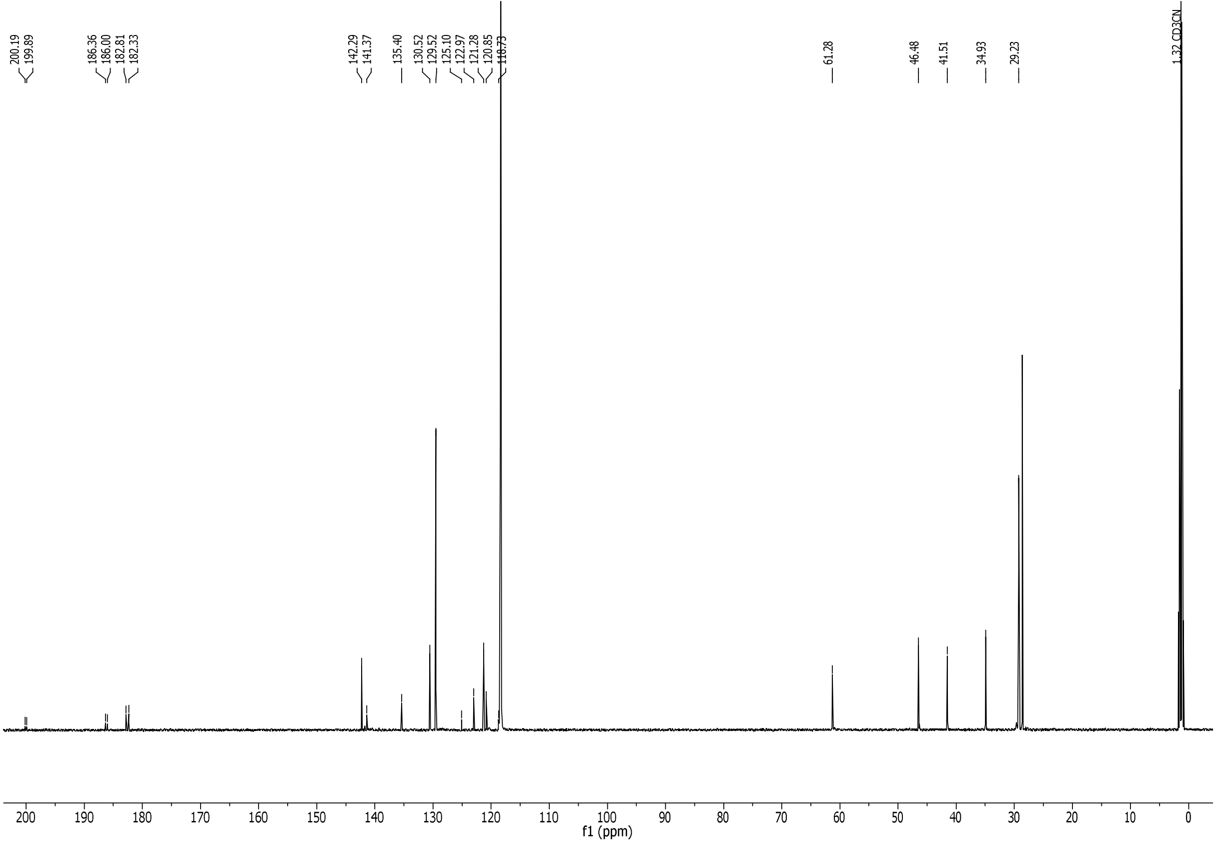


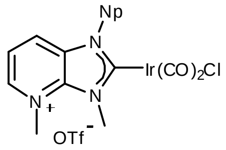
**Dicarbonylchlorido(6)rhodium(I) 10.** $^1$H-NMR (600 MHz, acetonitrile-*d3*): δ 8.71 (d, 1H, $^3J_{HH}$ = 8.4 Hz, C7-H), 8.49 (d, 1H, $^3J_{HH}$ = 6.2 Hz, C5-H), 7.83 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.2 Hz, C6-H), 4.79 (d, 1H, $^2J_{HH}$ = 14.5 Hz, N1-$CH_2$), 4.70 (s, 3H, N3-$CH_3$), 4.45 (d, 1H, $^2J_{HH}$ = 14.4 Hz, N1-$CH_2$), 1.14 (s, 9H, $C(CH_3)_3$). $^{13}$C (150 MHz, acetonitrile-*d3*): 200.04 (d, $^1J_{CRh}$ = 46.0 Hz, C2), 186.18 (d, $^1J_{CRh}$ = 55.1 Hz, $\underline{C}O$), 182.57 (d, $^1J_{CRh}$ = 73.7 Hz, $\underline{C}O$), 142.29 (s, C5), 141.37 (s, $C_q$), 135.40 (s, $C_q$), 130.52 (s, C7), 121.91 (q, $^1J_{CF}$ = 320.3 Hz, $\underline{C}F_3$), 121.28 (s, C6), 61.28 (s, N1-$\underline{C}H_2$), 46.48 (s, N3-$\underline{C}H_3$), 41.51 (s, N4-$\underline{C}H_3$), 34.93 (s, $\underline{C}(CH_3)_3$), 29.23 (s, $C(\underline{C}H_3)_3$). IR ($CH_2Cl_2$): ṽ 2095, 2022 cm$^{-1}$ (C=O).

$^1$H NMR (acetonitrile-*d3*)



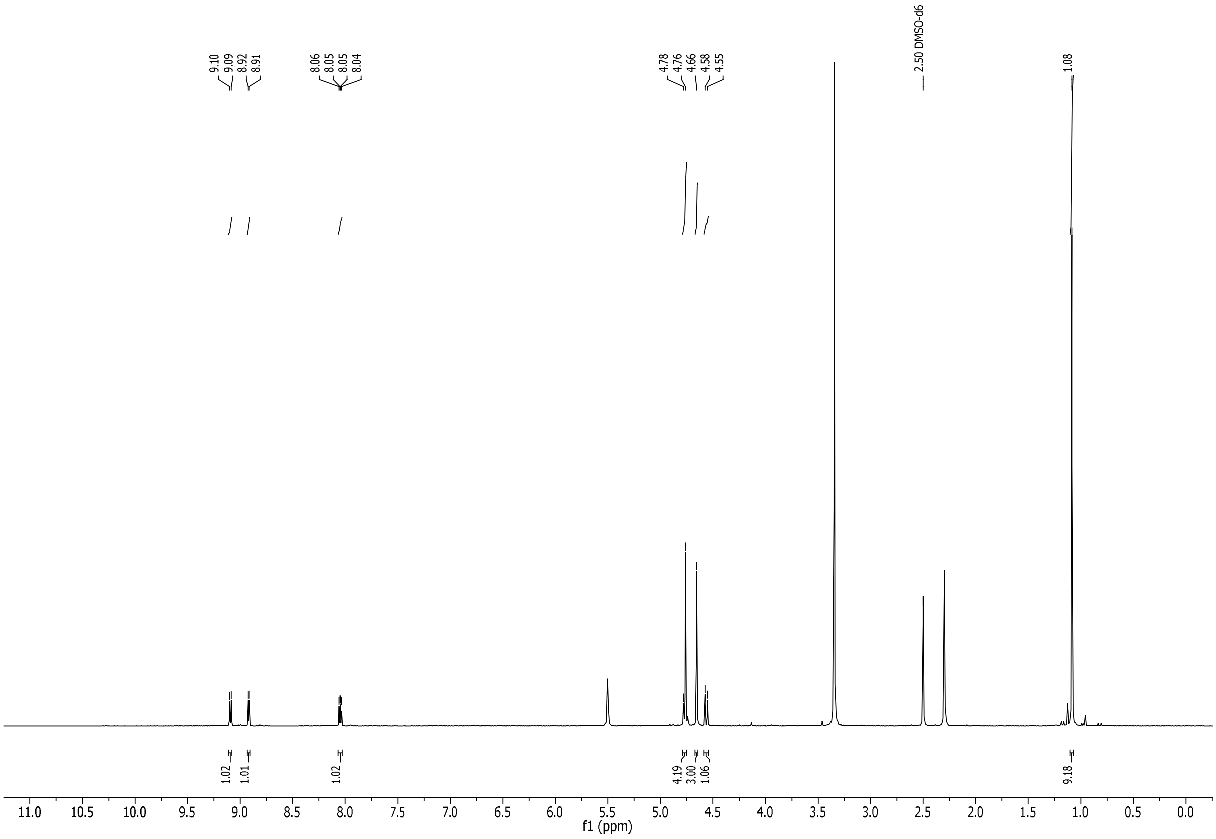
$^{13}C\{^1H\}$ NMR (acetonitrile-*d3*)



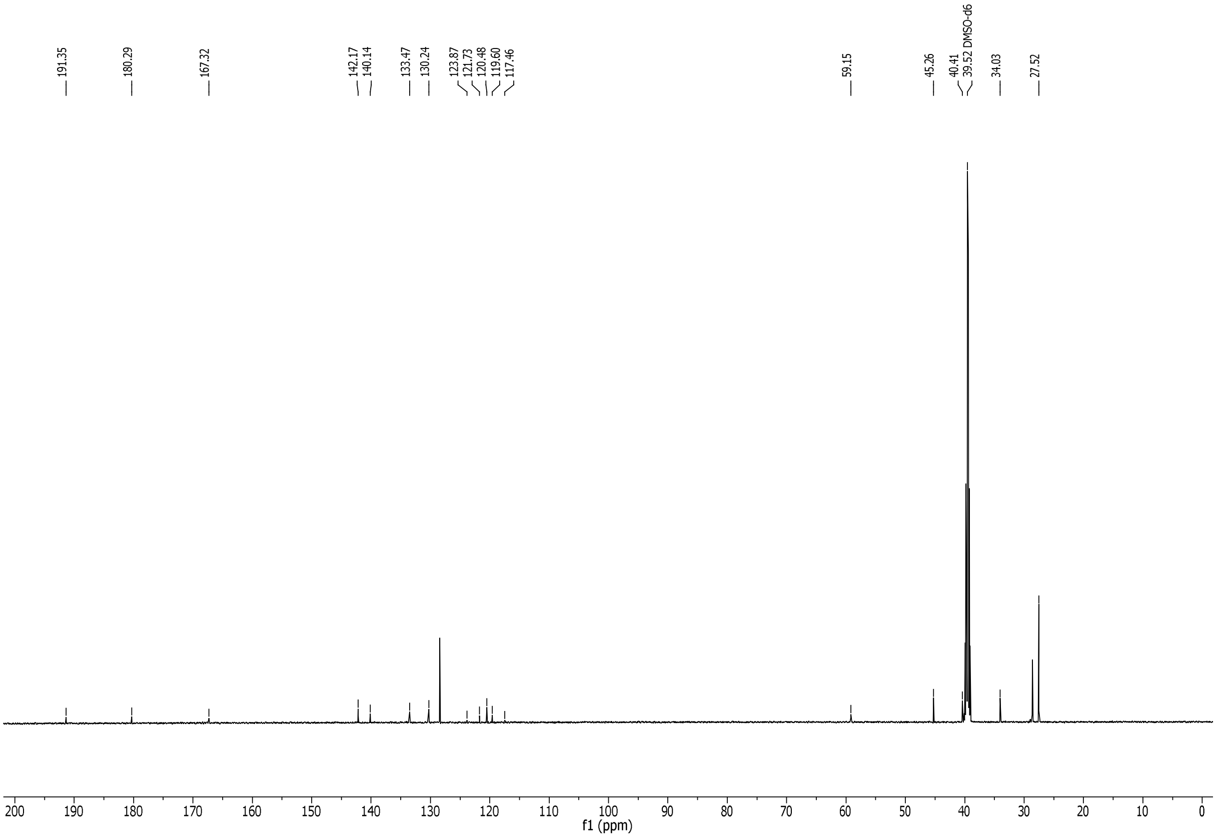


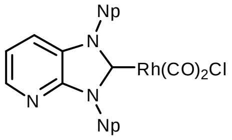
**Dicarbonylchlorido(6)iridium(I) 11.** $^1$H-NMR (600 MHz, DMSO-*d6*): δ 9.09 (d, 1H, $^3J_{HH}$ = 8.4 Hz, C7-H), 8.92 (d, 1H, $^3J_{HH}$ = 6.1 Hz, C5-H), 8.05 (dd, 1H, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 6.2 Hz, C6-H), 4.77 (d, 1H, $^2J_{HH}$ = 14.1 Hz, N1-$CH_2$), 4.76 (s, 3H, N4-$CH_3$), 4.66 (s, 3H, N3-$CH_3$), 4.56 (d, 1H, $^2J_{HH}$ = 14.2 Hz, N1-$CH_2$), 1.08 (s, 9H, $C(CH_3)_3$). $^{13}C\{^1H\}$ NMR (150 MHz, DMSO-*d6*): δ 191.35 (s, C2), 180,29 (s, $\underline{C}O$), 167.32 (s, $\underline{C}O$), 142.17 (s, C5), 140.14 (s, $C_q$), 133.47 (s, $C_q$), 130.24 (s, C7), 120.67 (q, $^1J_{CF}$ = 322.2 Hz, $\underline{C}F_3$), 120.48 (s, C6), 59.15 (s, N1-$\underline{C}H_2$), 45.26 (s, N3-$\underline{C}H_3$), 40.41 (s, N4-$\underline{C}H_3$), 34.03 (s, $\underline{C}(CH_3)_3$), 27.52 (s, $C(\underline{C}H_3)_3$). IR ($CH_2Cl_2$): $\tilde{v}$ 2082, 2004 cm$^{-1}$ (C=O).

$^{1}$H NMR (DMSO-*d6*)



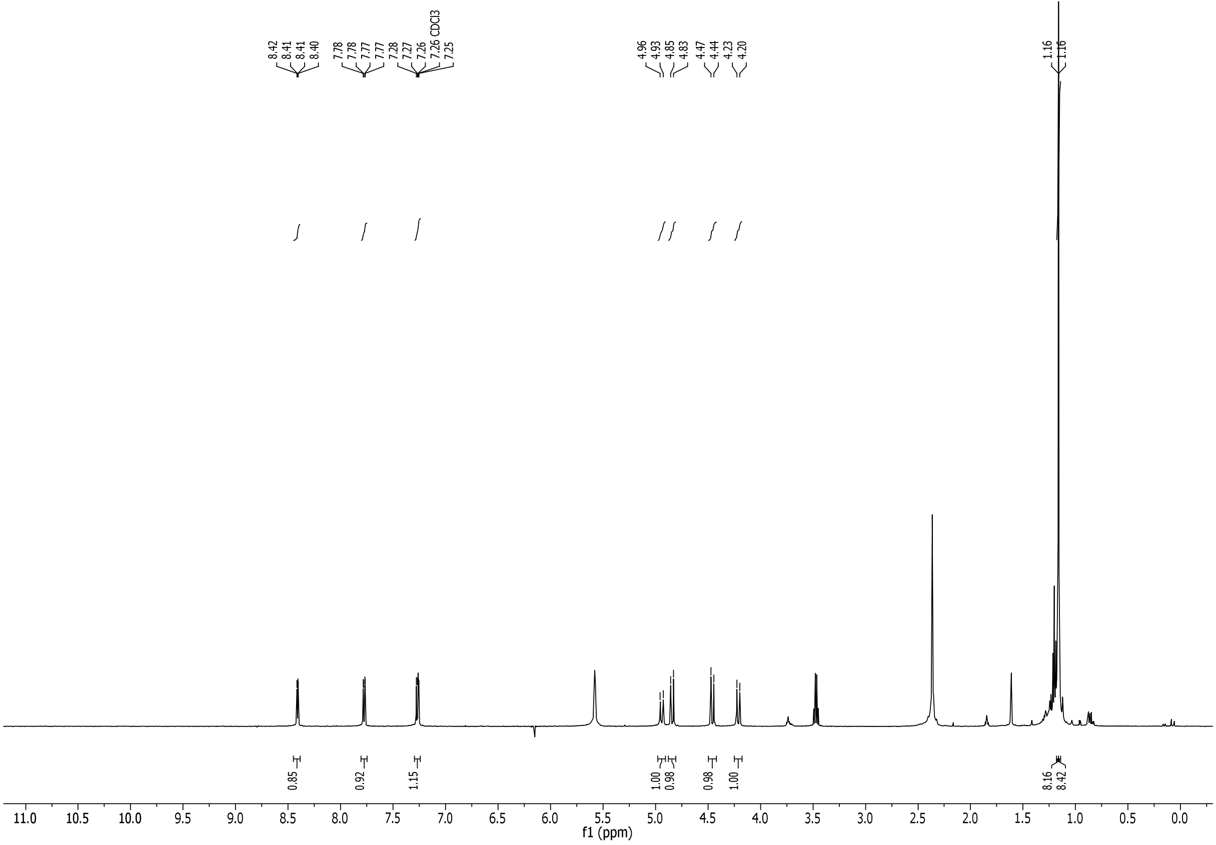
$^{13}$C{$^{1}$H} NMR (DMSO-*d6*)



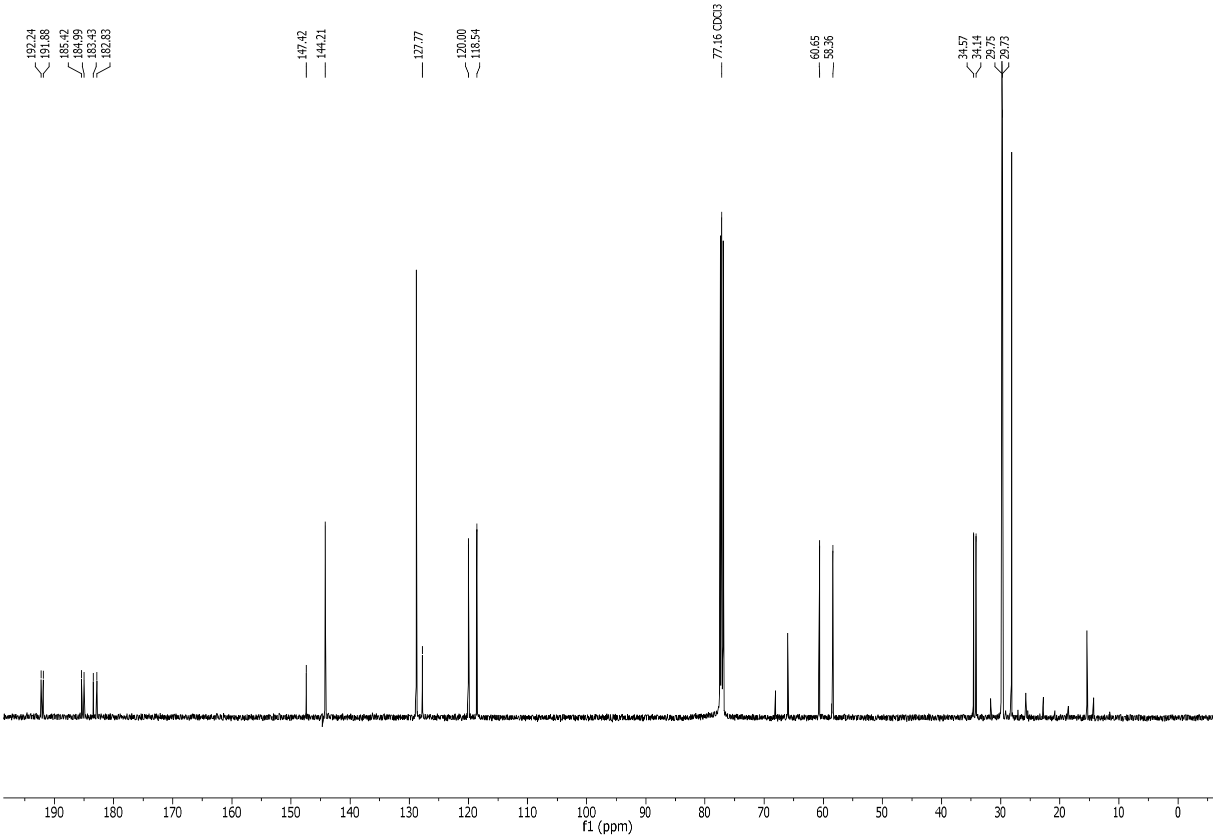


**Dicarbonylchlorido(PyINp$_2$)rhodium(I) 12.** $^1$H-NMR (500 MHz, chloroform-*d3*): δ 8.41 (dd, 1H, $^3J_{HH}$ = 4.7 Hz, $^4J_{HH}$ = 1.4 Hz, C5-H), 7.78 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.4 Hz, C7-H), 7.27 (dd, 1H, $^3J_{HH}$ = 8.2 Hz, $^3J_{HH}$ = 4.7 Hz, C6-H), 4.95 (d, 1H, $^2J_{HH}$ = 14.1 Hz, N-CH$_2$), 4.84 (d, 1H, $^2J_{HH}$ = 13.7 Hz, N-CH$_2$), 4.46 (d, 1H, $^2J_{HH}$ = 13.7 Hz, N-CH$_2$), 4.22 (d, 1H, $^2J_{HH}$ = 14.1 Hz, N-CH$_2$), 1.16 (s, 9H, C(CH$_3$)$_3$), 1.16 (s, 9H, C(CH$_3$)$_3$). $^{13}$C{$^1$H} NMR (125 MHz, chloroform-*d3*): δ 192.06 (d, $^1J_{CRh}$ = 45.29 Hz, C2), 185.20 (d, $^1J_{CRh}$ = 54.2 Hz, $\underline{C}$O), 183.13 (d, $^1J_{CRh}$ = 74.9 Hz, $\underline{C}$O), 147.42 (s, C$_q$), 144.21 (s, C5), 127.77 (s, C$_q$), 120.00 (s, C7), 118.54 (s, C6), 60.65 (s, N-$\underline{C}$H$_2$), 58.36 (N-$\underline{C}$H$_2$), 34.57 (s, $\underline{C}$(CH$_3$)$_3$), 34.14 (s, $\underline{C}$(CH$_3$)$_3$), 29.75 (s, C($\underline{C}$H$_3$)$_3$), 29.73 (s, C($\underline{C}$H$_3$)$_3$). IR (CH$_2$Cl$_2$): ṽ 2084, 2003 cm$^{-1}$ (C=O)

$^1$H NMR (chloroform-*d3*)

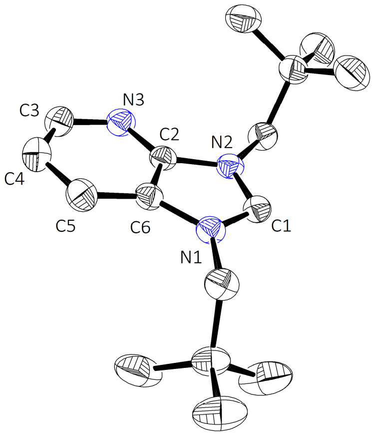


$^{13}$C{$^{1}$H} NMR (chloroform-*d3*)



## X-ray Details

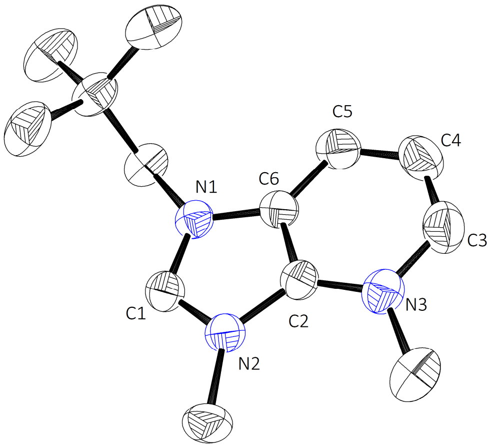
## Details of the X-ray diffraction study of compound 4



| | |
|---|---|
| CCDC refcode | 932700 |
| Empirical formula | C16 H26 F6 N3 P |
| Formular weight | 405.37 |
| Temperature | 296 |
| Wavelength (Å) | 0.71073 |
| Crystal system | monoclinic |
| Space group | P $2_1$/c (no. 14) |
| Unit cell dimensions (Å) | a = 10.098(2) |
| | b = 19.944(5) |
| | c = 10.579(2) |
| | $\beta$ = 103.041(5) |
| Volume ($^3$) | 2075.7(8) |
| Z | 4 |
| F (000) | 848 |
| Density (calculated, Mg/m$^3$) | 1.297 |
| Absorption coefficient (mm$^{-1}$) | 0.188 |
| Crystal size (mm$^3$) | 0.5 x 0.1 x 0.1 |
| Theta range | 2.23 – 23.70 |
| Index ranges | $-12 \leq h \leq 12$ |
| | $-23 \leq k \leq 23$ |
| | $-12 \leq l \leq 12$ |
| Reflections collected | 18698 |
| Independent reflections | 3758 [$R_{int}$ = 0.0397] |
| Completeness to theta = 25.25 | 1.00 |
| Observed reflections (I>2sigma(I)) | 2979 |
| Data / restraints / parameters | 3758 / 0 / 242 |

| | |
|---|---|
| GooF | 1.183 |
| Final R Inices (I>2sigma(I)) | *R1* = 0.0691 |
| | *wR2* = 0.1403 |
| R indices (all data) | *R1* = 0.825 |
| | *wR2* = 0.1450 |
| Largest diff. peak and hole (eÅ$^{-3}$) | 0.499 and -0.368 |

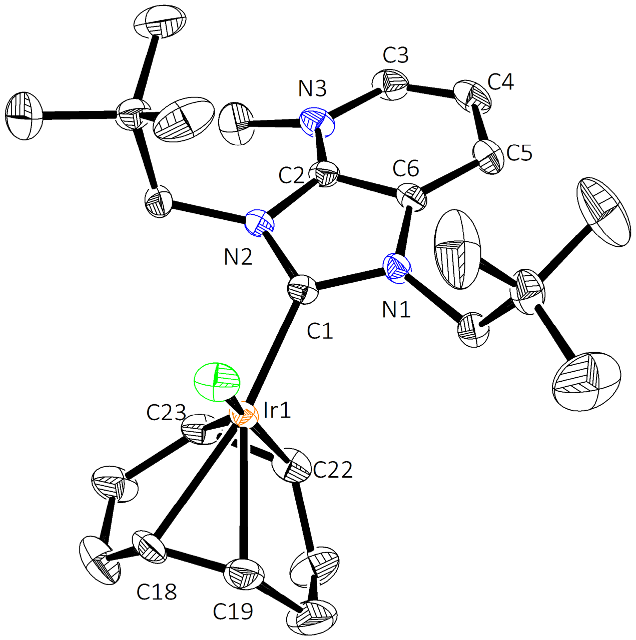
## Details of the X-ray diffraction study of compound 5a



| | |
|---|---|
| CCDC refcode | 932701 |
| Empirical formula | C15 H21 F6 N3 O6 S2 |
| Formular weight | 517.47 |
| Temperature (K) | 293 |
| Wavelength (Å) | 0.71073 |
| Crystal System | triclinic |
| Space group | P-1 (no. 2) |
| Unit cell dimensions (Å) | a = 6.6711(11) |
| | b = 12.796(2) |
| | c = 14.462(2) |
| | $\alpha$ = 102.692(11) |
| | $\beta$ = 92.911(11) |
| | $\gamma$ = 104.750(11) |
| Volume (Å$^3$) | 1157.2(3) |
| Z | 2 |
| F (000) | 532 |
| Density (calculated, Mg/m$^3$) | 1.485 |

| | |
|---|---|
| Absorption coefficient (mm$^{-1}$) | 0.313 |
| Crystal size (mm$^{3}$) | 0.5 x 0.1 x 0.1 |
| Theta range | 2.49 – 24.24 |
| Index ranges | $-7 \leq h \leq 7$ |
| | $-15 \leq k \leq 15$ |
| | $-17 \leq l \leq 17$ |
| Reflections collected | 10200 |
| Independent reflections | 4063 [$R_{int}$ = 0.0264] |
| Completenes to theta = 25.00 | 0.999 |
| Observed reflections (I>2sigma(I)) | 2641 |
| Data / restraints / parameters | 4063 / 0 / 294 |
| GooF | 1.121 |
| Final R Indices (I>2sigma(I)) | $R1$ = 0.0679 |
| | $wR2$ = 0.1939 |
| R indices (all data) | $R1$ = 0.0999 |
| | $wR2$ = 0.2067 |
| Largest diff. peak and hole (Åe$^{-3}$) | 0.365 and -0.357 |

## Details of the X-ray diffraction study of compound 9b



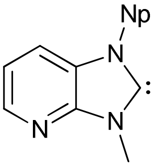
| | |
|---|---|
| CCDC refcode | 932702 |
| Empirical formula | C25 H40 Cl F6 Ir N3 P |
| Formular weight | 755.22 |
| Temperature (K) | 296 |
| Wavelength (Å) | 0.71073 |
| Crystal system | orthorhombic |
| Space group | P $2_1$ $2_1$ $2_1$ (no. 19) |
| Unit cell dimensions (Å) | a = 11.8317(19) |
| | b = 11.9035(19) |
| | c = 20.770(3) |
| Volume (Å$^3$) | 2925.2(8) |
| Z | 4 |
| F (000) | 1496 |
| Density (calculated, Mg/m$^3$) | 1.715 |

| | |
|---|---|
| Absorption coefficient ($mm^{-1}$) | 4.768 |
| Crystal size ($mm^3$) | 0.65 x 0.25 x 0.25 |
| Theta range | 2.427 - 25.027 |
| Index ranges | $-14 \leq h \leq 14$ |
| | $-14 \leq k \leq 13$ |
| | $-24 \leq l \leq 23$ |
| Reflections collected | 20212 |
| Independent reflections | 5066 |
| Completeness to theta = 25.080 | 0.996 |
| Observed reflections (I>2sigma(I)) | 4861 |
| Data / restraints / parameters | 5066 / 6 / 341 |
| GooF | 0.991 |
| Final R Indices (I>2sigma(I)) | $R1$ = 0.0184 |
| | $wR2$ = 0.0401 |
| R indices (all data) | $R1$ = 0.0200 |
| | $wR2$ = 0.0405 |
| Largest diff. peak and hole (Å$^3$) | 0.507 and -0.275 |

## Computational Details

The geometries of all molecules were optimized using the B3LYP[4] functional with the *Gaussian03* program package.[5] Ahlrichs' def2-TZVP[6] basis set was used. Harmonic frequency calculations verified the nature of the ground states or excited states, having no imaginary frequencies, respectively. All relative energies include zero-point corrections.

**Cartesian coordinates of the optimized geometries for the calculation of the singlet-triplet gap of [PyINpMe]:** B3LYP/def2-TZVP



### singlet-[PyINpMe]

**SCF-Energy = -631704116 a.u. Zeropoint = 0.274143 a.u.**

**Orbital energies: $E_{HOMO}$ = -6.12 eV; $E_{LUMO}$ = -1.20 eV; $\Delta_{HOMO-LUMO}$ = 4.93 eV**

| atoms | X | Y | Z |
|---|---|---|---|
| C | -1.88236900 | 0.28008100 | 0.00479000 |
| C | -0.76368100 | -0.50809700 | -0.31231700 |
| C | -0.91140100 | -1.88451300 | -0.33342400 |
| C | -2.18034300 | -2.37246400 | -0.02450100 |
| C | -3.21929100 | -1.49376100 | 0.28506300 |
| C | -0.14588800 | 1.68974400 | -0.43836900 |
| H | -0.09643000 | -2.55424700 | -0.57172900 |
| H | -2.36803100 | -3.43770200 | -0.02164900 |
| H | -4.20251900 | -1.88043000 | 0.52741000 |
| N | -3.08950400 | -0.16214500 | 0.30300700 |
| N | 0.26744700 | 0.38829700 | -0.56075500 |
| N | -1.45664500 | 1.59531800 | -0.07805300 |
| C | 1.61832900 | 0.02986000 | -0.97987200 |
| H | 1.55516600 | -0.91344300 | -1.52822400 |
| H | 1.93776100 | 0.79899200 | -1.68277600 |
| C | -2.31464500 | 2.74097900 | 0.16251200 |
| H | -1.71594500 | 3.63468800 | 0.01219400 |
| H | -3.15899700 | 2.73714900 | -0.52763900 |
| H | -2.70281100 | 2.71935800 | 1.18141400 |
| C | 2.68242000 | -0.10035600 | 0.13761000 |
| C | 3.98454300 | -0.54295900 | -0.54883600 |
| H | 4.79036400 | -0.63614300 | 0.18186300 |
| H | 3.86825100 | -1.51214800 | -1.04105500 |
| H | 4.30235200 | 0.18155900 | -1.30252100 |
| C | 2.90838800 | 1.24967700 | 0.83135200 |
| H | 3.22617900 | 2.01184800 | 0.11713000 |
| H | 1.99943900 | 1.61447300 | 1.30924300 |
| H | 3.68382400 | 1.15430700 | 1.59522900 |
| C | 2.27394800 | -1.15406500 | 1.17624500 |
| H | 2.13331000 | -2.13624800 | 0.71762700 |
| H | 3.05070900 | -1.25553900 | 1.93731400 |

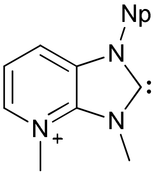
| | | | |
|---|---|---|---|
| H | 1.34821800 | -0.88151800 | 1.68525700 |

## triplet-[PyINpMe]

**SCF-Energy = -631.589446 a.u. Zeropoint = 0.270848 a.u.**

| atoms | X | Y | Z |
|---|---|---|---|
| C | -1.93475300 | 0.29024300 | -0.03245900 |
| C | -0.78958800 | -0.52564700 | -0.21358900 |
| C | -0.94345100 | -1.90005600 | -0.19123000 |
| C | -2.26343200 | -2.36819600 | 0.00985600 |
| C | -3.30383800 | -1.48295100 | 0.19001400 |
| C | -0.15693900 | 1.61461200 | -0.27594800 |
| H | -0.11473100 | -2.58306400 | -0.31028900 |
| H | -2.45847000 | -3.43194100 | 0.03430000 |
| H | -4.31137700 | -1.84622300 | 0.35237300 |
| N | -3.16203900 | -0.13032400 | 0.17898100 |
| N | 0.30310200 | 0.31315200 | -0.39584600 |
| N | -1.52705800 | 1.61259500 | -0.11527600 |
| C | 1.60143600 | -0.06399700 | -0.92347400 |
| H | 1.48937800 | -1.05391300 | -1.37144900 |
| H | 1.84979700 | 0.63328900 | -1.73047700 |
| C | -2.35783400 | 2.76485900 | 0.14417100 |
| H | -2.26546000 | 3.49126000 | -0.66530000 |
| H | -3.38739500 | 2.42105700 | 0.20716900 |
| H | -2.07888300 | 3.24553500 | 1.08601900 |
| C | 2.76574100 | -0.09086600 | 0.09629700 |
| C | 4.01680600 | -0.55905600 | -0.66226300 |
| H | 4.87959400 | -0.59351400 | 0.00569100 |
| H | 3.87917300 | -1.55998000 | -1.07892500 |
| H | 4.26102500 | 0.11753700 | -1.48508700 |
| C | 3.00756900 | 1.31369800 | 0.66508800 |
| H | 3.25105200 | 2.02549800 | -0.12794800 |
| H | 2.12955200 | 1.68749800 | 1.19526300 |
| H | 3.84256800 | 1.30148800 | 1.36923900 |
| C | 2.45617600 | -1.06963900 | 1.23617500 |
| H | 2.31467700 | -2.08576100 | 0.86012600 |
| H | 3.28078700 | -1.09314500 | 1.95171800 |
| H | 1.55332300 | -0.78161400 | 1.77673600 |

**Cartesian coordinates of the optimized geometries for the calculation of the singlet-triplet gap of 6a:** B3LYP/def2-TZVP



## singlet-6a

**SCF-Energy = -671.355752 a.u. Zeropoint = 0.315457 a.u.**

**Orbital energies: $E_{HOMO}$ = -9.99 eV; $E_{LUMO}$ = -6.26 eV; $\Delta_{HOMO-LUMO}$ = 3.73 eV**

| atoms | X | Y | Z |
|---|---|---|---|
| C | -1.57572000 | 0.20877700 | -0.09874400 |
| C | -0.41851200 | -0.55395600 | -0.37582600 |
| C | -0.46952900 | -1.93173700 | -0.39773800 |
| C | -1.70162200 | -2.52969800 | -0.12872100 |
| C | -2.80504400 | -1.75943200 | 0.14932800 |
| C | 0.13340500 | 1.64205500 | -0.50825300 |
| H | 0.40333900 | -2.53164000 | -0.61075200 |
| H | -1.80829800 | -3.60447000 | -0.13211700 |
| H | -3.76835500 | -2.19324000 | 0.36729600 |
| N | 0.58326500 | 0.36820700 | -0.60379200 |
| N | -1.21009200 | 1.52174600 | -0.17869600 |
| N | -2.75460100 | -0.39919300 | 0.16725600 |
| C | -2.01841800 | 2.73347700 | -0.01217000 |
| H | -1.32847000 | 3.56582100 | -0.10753200 |
| H | -2.77462700 | 2.81153600 | -0.79161400 |
| H | -2.48240300 | 2.76628600 | 0.97135600 |
| C | 1.97573900 | 0.04978400 | -0.96890900 |
| H | 1.96071500 | -0.89412600 | -1.51689100 |
| H | 2.28143900 | 0.83063600 | -1.66260500 |
| C | -3.98486700 | 0.35196500 | 0.49795300 |
| H | -3.86191400 | 0.86480600 | 1.44884500 |
| H | -4.21064400 | 1.06443000 | -0.28928200 |
| H | -4.80209500 | -0.35708200 | 0.57843900 |
| C | 2.98888400 | -0.03176800 | 0.19669100 |
| C | 3.11141900 | 1.32071900 | 0.91100600 |
| H | 2.17780500 | 1.61884900 | 1.38963500 |
| H | 3.87840000 | 1.26272300 | 1.68500700 |
| H | 3.39247500 | 2.11392600 | 0.21643500 |
| C | 2.59658400 | -1.12082700 | 1.20506600 |
| H | 2.53830900 | -2.10589700 | 0.73406900 |

| | | | |
|---|---|---|---|
| H | 3.34503200 | -1.18743300 | 1.99584400 |
| H | 1.64026300 | -0.90799700 | 1.68863200 |
| C | 4.33885000 | -0.39490900 | -0.44489500 |
| H | 4.65024900 | 0.35823200 | -1.17160800 |
| H | 5.11458400 | -0.45673800 | 0.31922500 |
| H | 4.29716900 | -1.36064800 | -0.95448500 |

## triplet-6a

**SCF-Energy = -671.271737 a.u. Zeropoint = 0.311391 a.u.**

| atoms | X | Y | Z |
|---|---|---|---|
| C | 1.58387000 | 0.21489100 | -0.04300900 |
| C | 0.62344700 | -0.79625700 | -0.15383900 |
| C | 0.96268600 | -2.15506000 | -0.13919900 |
| C | 2.34057100 | -2.41737700 | 0.01495900 |
| C | 3.26476800 | -1.42431000 | 0.12889900 |
| C | -0.38604000 | 1.15615300 | -0.25315900 |
| H | 0.23762300 | -2.94491100 | -0.24586300 |
| H | 2.69315100 | -3.43868000 | 0.04408500 |
| H | 4.31860400 | -1.61696000 | 0.24558300 |
| N | -0.60761000 | -0.16021700 | -0.27738800 |
| N | 0.92596700 | 1.42735400 | -0.10877200 |
| N | 2.91445200 | -0.06522300 | 0.10759200 |
| C | 1.42418100 | 2.80433900 | 0.00265800 |
| H | 0.58633200 | 3.46931900 | -0.18705700 |
| H | 1.80576200 | 2.99124700 | 1.00395900 |
| H | 2.19566900 | 2.99135700 | -0.73859900 |
| C | -1.89963700 | -0.83688200 | -0.48640600 |
| H | -2.02103700 | -0.99913900 | -1.56014100 |
| H | -1.81885100 | -1.81093400 | -0.00592600 |
| C | 3.96646900 | 0.94810200 | 0.12072000 |
| H | 4.05338100 | 1.44424800 | -0.84779900 |
| H | 3.79448800 | 1.68713700 | 0.90131200 |
| H | 4.90873700 | 0.45209800 | 0.33365200 |
| C | -3.10885200 | -0.07159900 | 0.08384600 |
| C | -3.00444200 | 0.04424100 | 1.61131200 |
| H | -2.13131000 | 0.62160900 | 1.92295100 |
| H | -3.88611500 | 0.54572000 | 2.01219700 |
| H | -2.94262100 | -0.94049200 | 2.07870700 |
| C | -3.20055900 | 1.31441200 | -0.55650900 |
| H | -3.33541800 | 1.26365100 | -1.63819000 |
| H | -4.01238800 | 1.90212200 | -0.12492100 |
| H | -2.27353200 | 1.89821900 | -0.36893800 |
| C | -4.35962200 | -0.88912400 | -0.28776000 |
| H | -4.32271100 | -1.88790800 | 0.15171300 |

| | | | |
|---|---|---|---|
| H | -5.25642900 | -0.39537900 | 0.08742600 |
| H | -4.46403900 | -0.99488900 | -1.36926100 |

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