Regioselective C8-metalation of N-phosphine tethered adenine derivatives via C8–H activation

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Supporting Information

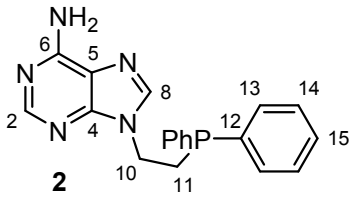
General procedures.

If not noted otherwise, all reactions were carried out under an argon atmosphere using standard Schlenk techniques or in a glove box. Glassware was oven dried at 130 °C. Solvents were dried and distilled by standard procedures prior to use. ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded on Bruker AVANCE I 400 or Bruker AVANCE III 400 spectrometers. Chemical shifts (δ) are expressed in ppm downfield from tetramethylsilane using the residual protonated solvent as an internal standard. All coupling constants are expressed in Hertz and only given for $^{1}H,^{1}H$ couplings unless noted otherwise. Mass spectra were obtained with an Orbitrap LTQ XL (Thermo Scientific, Waltham, Massachusetts) spectrometer, MicroTof (Bruker Daltonics, Bremen) or Varian MAT 212 spectrometers. Compounds $[IrCl_2Cp^*]_2$, $[RhCl_2Cp^*]_2$, $[RuClCp^*]_4$, 9-hydroxymethyladenine[1] and 9-(2-chloroethyl)adenine[2] were prepared according to published procedures. Adenine and diphenylphosphine were purchased from commercial sources and were used as received without further purification.

9-Chloromethyladenine. A sample of thionyl chloride $SOCl_2$ (7.8 mL, 12.79 g,107 mmol) was added to a solution of 9-hydroxymethyladenine[1] (2.526 g, 15.3 mmol) in CH_2Cl_2 (85 mL) and the reaction mixture was stirred at ambient temperature for 24 h. The solvent was then removed with a syringe and the solid residue was washed with CH_2Cl_2 (2 × 20 mL). The obtained solid was dried *in vacuo* to yield 9-chloromethyladenine hydrochloride as a colorless powder (3.27 g, 14.8 mmol, 97%). The hydrochloride was dissolved in a small amount of water and neutralized with a saturated aqueous solution of K_2CO_3. The resulting precipitate was isolated by filtration, washed with cold water (2 × 5 mL) and dried *in vacuo*. Compound 9-chloromethyadenine was isolated as a colorless powder. Yield: 2.11 g (11.5 mmol, 75% over two steps). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.36 (s, 1H, H8), 8.23 (s, 1H, H2), 7.42 (s, 2H, NH_2), 6.19 (s, 2H, H10). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 155.9 (C6), 153.1 (C2), 148.9 (C4), 140.5 (C8), 118.5 (C5), 50.3 (C10). MS (EI): *m*/*z* (%) = 183 (100, $[M]^+$), 148 (93, $[M–Cl]^+$). Anal. calcd for $C_6H_6N_5Cl$ (183.031): C, 39.25; H, 3.29; N, 38.15%. Found: C, 38.76; H, 3.29; N, 37.85%.

9-(Diphenylphosphinomethyl)adenine 1. A sample of diphenylphosphine (0.50 mL, 2.87 mmol) and KO*t*Bu (611 mg, 5.45 mmol) were dissolved in THF (10 mL) and stirred for 15 min at ambient temperature. The resulting red solution was added dropwise to a solution of 9-chloromethyladenine (500 mg, 2.72 mmol) in THF (20 mL) at –78 °C. The mixture was stirred for 12 h while letting it warm up to ambient temperature. From this solution compound **1** was isolated as a colorless powder after column chromatography (SiO_2, CH_2Cl_2:MeOH = 20:1). Yield: 480 mg, (1.44 mmol, 50%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.12 (s, 1H, H8), 7.73 (s, 1H, H2), 7.49 (m, 4H, H12), 7.41 (m, 6H, H13, H14), 7.18 (s, 2H, NH_2), 5.04 (d, $^2J_{H,P}$ = 5.0 Hz, 2H, H10). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ = 155.7 (C6), 152.3 (C2), 149.3 (C4), 139.9 (d, $^3J_{C,P}$ = 2.9 Hz, C8), 135.0 (d, $^1J_{C,P}$ = 14.0 Hz, C11), 132.7 (d, $^2J_{C,P}$ = 19.2 Hz, C12), 129.4 (C14), 128.7 (d, $^3J_{C,P}$ = 6.9 Hz, C13), 118.2 (C5), 41.6 (d, $^1J_{C,P}$ = 15.2 Hz, C10). ^{31}P{^{1}H} NMR (162 MHz, DMSO-d_6): δ = –15.6. MS (EI): *m*/*z* (%) = 333 (100, $[\mathbf{1}]^+$), 256 (10, $[\mathbf{1}–Ph]^+$). Anal. calcd for $C_{18}H_{16}N_5P$ (333.328): C, 64.86; H, 4.84; N, 21.01%. Found: C, 64.67; H, 4.75; N, 20.84%.

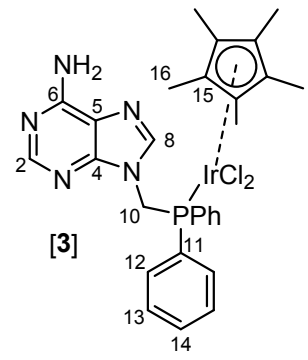
9-(2-Diphenylphosphinoethyl)adenine 2. Diphenylphosphine (1.14 mL, 1.22 g, 6.55 mmol) and KO*t*Bu (653 mg, 5.82 mmol) were dissolved in THF (10 mL) and stirred for 15 min at ambient temperature. The resulting red solution was added dropwise to a solution of 9-(2-chloroethyl)adenine[2] (1.00 g, 5.06 mmol) in THF (15 mL) at –78 °C. The mixture was stirred for 12 h while letting it warm to room temperature. Compound **2** was isolated as a colorless powder after separation from the side product 9-vinyladenine *via* column chromatography (SiO_2, CH_2Cl_2:MeOH = 20:1). Yield: 888 mg (2.56 mmol, 51%). $^1H\{^{31}P\}$ NMR (400 MHz, DMSO-d_6): δ = 8.15 (s, 1H, H2), 8.13 (s, 1H, H8), 7.47–7.42 (m, 4H, H13), 7.39–7.34 (m, 6H, H14, H15), 7.15 (s, 2H, NH_2), 4.26 (t, $^3J_{H,H}$ = 7.7 Hz, 3H, H10), 2.73 (t, $^2J_{H,H}$ = 7.7 Hz, 2H, H11). $^{13}C\{^1H\}$ NMR (101 MHz, DMSO-d_6): δ = 155.8 (C6), 152.2 (C2), 149.3 (C4), 140.4 (C8), 137.1 (d, $^1J_{C,P}$ = 12.6 Hz, C12), 132.3 (d, $^2J_{C,P}$ = 19.1 Hz, C13), 128.8 (C15), 128.5 (d, $^3J_{C,P}$ = 6.8 Hz, C14), 118.7 (C5), 40.4 (d, $^2J_{C,P}$ = 24.6 Hz, C10), 27.4 (d, $^1J_{C,P}$ = 13.4 Hz, C11). $^{31}P\{^1H\}$ NMR (162 MHz, DMSO-d_6): δ = –22.5. MS (EI): *m*/*z* (%) = 270 (98, [**2**–Ph]$^+$). MS (ESI): *m*/*z* (%) = 348.13743 (64, calcd for [**2**+H]$^+$: 348.13781). Anal. calcd for $C_{19}H_{18}N_5P$ (347.354): C, 65.69; H, 5.22; N, 20.17%. Found: C, 65.54; H, 5.01; N, 20.02%.



2

General procedure for the preparation of complexes [3]–[6]. A sample of 9-(diphenylphosphinomethyl)adenine or 9-(2-diphenylphosphinoethyl)adenine (0.075 mmol, 25.0 or 26.0 mg) and $[MCl_2Cp^*]_2$ (M = Ir, Rh) (0.038 mmol, 30.3 mg or 23.5 mg) were dissolved in toluene (10 mL) and stirred for 1 h at ambient temperature. A yellow to orange precipitate formed, which was isolated by filtration, washed with hexane (2 × 10 mL) and diethylether (2 × 10 mL) and dried *in vacuo* to give the analytically pure complexes [**3**]−[**6**].

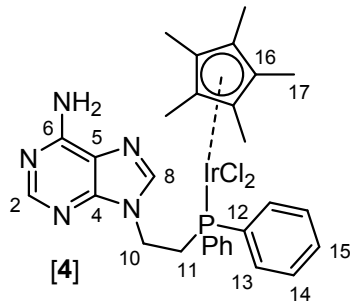
Complex [3]: Yield: 49 mg (0.067 mmol, 89%). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.96 (s, 1H, H2), 7.69 (m, 4H, H12), 7.42 (m, H14), 7.32 (m, 4H, H13), 7.18 (s, 1H, H8), 5.78 (s, 2H, H10), 5.57 (s br, 2H, NH_2), 1.38 (d, $^4J_{H,P}$ = 2.2 Hz, 15H, H16). $^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$): δ = 154.8 (C6), 152.5 (C2), 150.4 (C4), 141.0 (C8), 134.2 (d, $^2J_{C,P}$ = 9.7 Hz, C12), 131.7 (d, $^4J_{C,P}$ = 2.6 Hz, C14), 128.2 (d, $^3J_{C,P}$ = 10.3 Hz, C13), 126.3 (d, $^1J_{C,P}$ = 51.5 Hz, C11), 118.4 (C5),



[**3**]

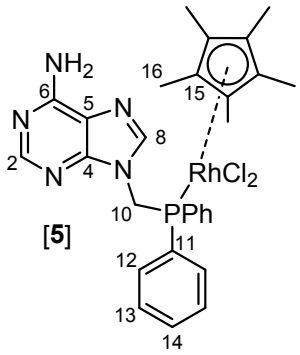
92.6 (d, $^{2}J_{C,P}$ = 3.0 Hz, C15), 42.1 (d, $^{1}J_{C,P}$ = 29.2 Hz, C10), 8.2 (C16). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 2.0. MS (MALDI-TOF): *m*/*z* (%) = 696 (100, [**3**–Cl]$^{+}$).

Complex [4]: Yield: 53 mg (0.071 mmol, 95%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.19 (s, 1H, H2), 7.88 (s, 1H, H8), 7.59 (m, 4H, H13), 7.38 (m, 2H, H15), 7.35 (m, 4H, H14), 5.72 (s, 2H, NH_2), 4.63 (dt, $^{3}J_{H,P}$ = 11.8 Hz, $^{3}J_{H,H}$ = 7.1 Hz, 2H, H10), 3.51 (dt, $^{2}J_{H,P}$ = 11.1 Hz, $^{3}J_{H,H}$ = 7.1 Hz, 2H, H11), 1.35 (d, $^{4}J_{H,P}$ = 2.2 Hz, 15H, H17). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 155.0 (C6), 152.1 (C2), 149.7 (C4), 141.7 (C8), 133.4 (d, $^{2}J_{C,P}$ = 9.8 Hz, C13), 131.0 (d, $^{4}J_{C,P}$ = 2.5 Hz, C15), 129.2 (d, $^{1}J_{C,P}$ = 51.6 Hz, C12), 128.2 (d, $^{3}J_{C,P}$ = 10.1 Hz, C14), 119.5 (C5), 92.7 (d, $^{2}J_{C,P}$ = 2.7 Hz, C16), 40.0 (C10), 29.4 (d, $^{1}J_{C,P}$ = 34.3 Hz, C11), 8.2 (C17). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = –6.6. MS (ESI): *m*/*z* (%) = 710.17829 (100, calcd for [**4**–Cl]$^{+}$ 710.17841).



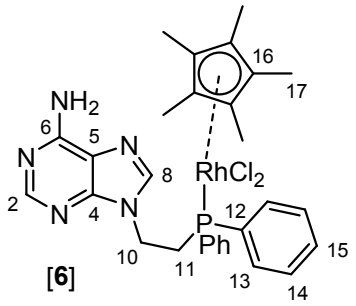
[**4**]

Complex [5]: Yield: 35 mg (0.055 mmol, 73%). ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 7.95 (s, 1H, H2), 7.77 (m, 4H, H12), 7.45 (m, 2H, H14), 7.34 (m, 4H, H13), 7.15 (s, 1H, H8), 5.72 (s, 2H, H10), 5.63 (s, 2H, NH_2), 1.39 (d, $^{4}J_{H,P}$ = 3.6 Hz, 15H, H16). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ = 154.8 (C6), 152.5 (C2), 150.3 (C4), 141.0 (C8), 134.3 (d, $^{2}J_{C,P}$ = 9.6 Hz, C12), 131.7 (C14), 128.3 (d, $^{3}J_{C,P}$ = 9.9 Hz, C13), 126.3 (d, $^{1}J_{C,P}$ = 41.3 Hz, C11), 118.4 (C5), 99.1 (dd, $^{2}J_{C,P}$ = 6.9 Hz, $^{1}J_{C,Rh}$ = 3.0 Hz, C15), 43.3 (d, $^{1}J_{C,P}$ = 22.6 Hz, C10), 8.65 (C16). $^{31}P\{^{1}H\}$ NMR (162 MHz, $CDCl_3$): δ = 33.5 (d, $^{1}J_{P,Rh}$ = 143.9 Hz). MS (MALDI-TOF): *m*/*z* (%) = 606 (100, [**5**–Cl]$^{+}$), MS (ESI): *m*/*z* (%) = 606.10874 (82, calcd for [**5**–Cl]$^{+}$ 606.10606), 642.08604 (40, calcd for [**5**+H]$^{+}$ 642.08274).

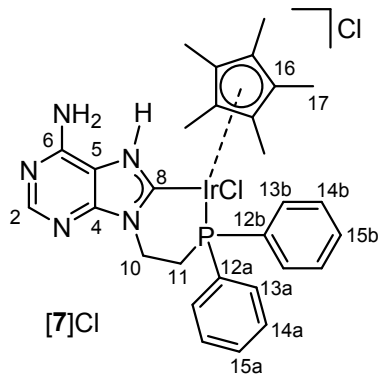


[**5**]

Complex [6]: Yield: 35 mg (0.053 mmol, 71%). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.20 (s, 1H, H2), 7.91 (s, 1H, H8), 7.74–7.65 (m, 4H, H13), 7.48–7.40 (m, 2H, H15), 7.41–7.32 (m, 4H, H14), 5.51 (s, 2H, NH_2), 4.57 (dt, $^{3}J_{H,P}$ = 11.8 Hz, $^{3}J_{H,H}$ = 6.5 Hz, 2H, H10), 3.40 (dt, $^{2}J_{H,P}$ = 11.6 Hz, $^{3}J_{H,H}$ = 6.5 Hz, 2H, H10), 1.37 (d, $^{4}J_{H,P}$ = 2.3 Hz, 15H, H17). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 154.8 (C6), 152.0 (C2), 149.8 (C4), 141.9 (C8), 133.5 (d, $^{2}J_{C,P}$ = 9.6 Hz, C13), 131.1 (d, $^{4}J_{C,P}$ = 2.5 Hz, C15), 129.4 (d, $^{1}J_{C,P}$ = 41.1 Hz, C12), 128.4 (d, $^{3}J_{C,P}$ = 9.9 Hz, C14), 119.6 (C5), 99.2 (dd, $^{2}J_{C,P}$ = 6.8 Hz, $^{1}J_{C,Rh}$ = 2.7 Hz, C16), 40.2 (C10), 30.1 (d, $^{1}J_{C,P}$ = 29.0 Hz, C11), 8.8 (d, $^{3}J_{C,P}$ = 1.1 Hz, C17). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 23.3 (d, $^{1}J_{P,Rh}$ = 144.9 Hz). MS (MALDI-TOF): *m*/*z* (%) = 620 (100, [**6**–Cl]$^{+}$). MS (ESI): *m*/*z* (%) = 620.12199 (100, calcd for [**6**–Cl]$^{+}$ 620.12171).



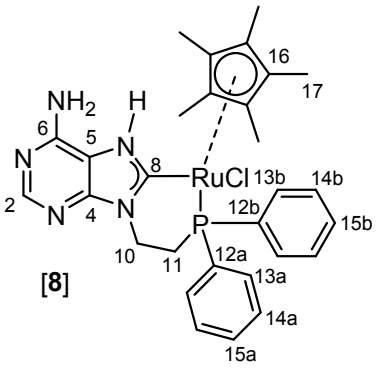
Synthesis of [7]Cl. A sample of 9-(2-diphenylphosphinoethyl)adenine (26 mg, 0.075 mmol) and $[IrCl_2Cp^*]_2$ (30 mg, 0.038 mmol) were dissolved in dry acetonitrile (10 mL) and the mixture was stirred for 3 d at 100 °C in a pressure tube. The solvent was then removed *in vacuo* and the solid residue was washed with hexane (3 ×10 mL) and Et_2O (3 ×10 mL). Drying of the solid residue under reduced pressure yields compound [**7**]Cl as a yellow solid. Crystals of [**7**]Cl·$CHCl_3$ suitable for an X-ray diffraction analysis were obtained by slow diffusion of Et_2O into a saturated solution of [**7**]Cl in a mixture of $CHCl_3$ and methanol at ambient temperature.



Yield: 28 mg (0.038 mmol, 51%). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.41 (s, 1H, NH), 8.27 (s, 1H, H2), 7.99 (s, 2H, NH_2), 7.59 (m, 3H, H14a, H15b), 7.52 (m, 2H, H13b), 7.37 (m, 1H, 15a), 7.33 (m, 2H, 14b), 7.20 (m, 2H, 13a), 5.08 (ddt, $^{3}J_{H,P}$ = 27.9 Hz, $^{3}J_{H,H}$ = 14.8, $^{3}J_{H,H}$ = 4.9 Hz, 1H, H10a), 4.20 (m, 1H, H10b), 3.30 (m, 1H, H11a), 2.86 (m, 1H, H11b), 1.58 (d, $^{4}J_{H,P}$ = 2.2 Hz, 15H, H17). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6, ppm): δ = 153.3 (C2), 151.8 (d, $^{2}J_{C,P}$ = 18.3 Hz, C8), 149.8 (C6), 149.7 (C4), 132.9 (d, $^{2}J_{C,P}$ = 9.2 Hz, C13a), 132.2 (d, $^{2}J_{C,P}$ = 9.8 Hz, C13b), 131.4 (d, $^{4}J_{C,P}$ = 2.4 Hz, C15b), 130.6 (d, $^{4}J_{C,P}$ = 2.6 Hz, C15a), 130.1 (d, $^{1}J_{C,P}$ = 54.5 Hz, C12a), 128.7 (d, $^{3}J_{C,P}$ = 10.6 Hz, C14a), 128.6 (d, $^{1}J_{C,P}$ = 58.6 Hz, C12b), 127.9 (d, $^{3}J_{C,P}$ = 10.5 Hz, C14b), 111.1 (C5), 97.3 ($^{2}J_{C,P}$ = 2.4 Hz, C16), 40.3 (C10),

23.1 (d, $^{1}J_{C,P}$ = 39.9 Hz, C11), 8.4 (C17). $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ = –7.9. MS (MALDI-TOF): *m*/*z* (%) = 710 (100, [**7**]$^+$), 674 (52, [**7**–HCl]$^+$). MS (ESI): *m*/*z* (%) = 710.17580 (100, calcd for [**7**]$^+$ 710.17841).

Synthesis of [8]. A sample of 9-(2-diphenylphosphinoethyl)adenine (30 mg, 0.086 mmol) and [RuClCp*]$_4$ (24 mg, 0.022 mmol) were dissolved in THF (10 mL) and stirred under reflux for 16 h. The solvent was then removed *in vacuo* and the residue was washed with hexane (3 × 10 mL) and THF (3 × 10 mL). Drying of the obtained solid under reduced pressure yielded compound [**8**] as a beige solid. Crystals of [**8'**]Cl·0.5CH_3CN suitable for an X-ray diffraction analysis were obtained by evaporation of the solvent from a saturated solution of [**8**] in acetonitrile under an argon atmosphere at ambient temperature. This procedure led to an exchange of the chloride ligand for an acetonitrile ligand and formation of salt [**8'**]Cl. Yield: 20 mg (0.032 mmol, 37% of [**8**]). ^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.92 (s, 1H, NH), 8.23 (s, 1H, H2), 7.91 (s, 2H, NH_2), 7.56 (m, 2H, H14a), 7.55 (m, 1H, H15a), 7.49 (m, 2H, H13a), 7.48 (2H, H14b), 7.47 (m, 1H, H15b), 7.38 (m, 2H, H13b), 5.26 (ddt, $^{3}J_{H,P}$ = 33.1 Hz, $^{3}J_{H,H}$ = 14.8 Hz, $^{3}J_{H,H}$ = 4.2 Hz, 1H, H10a), 4.19 (m, H10b), 2.77 (m, 2H, H11), 1.61 (s, 15H, H17). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ = 186.6 (d, $^{2}J_{C,P}$ = 17.6 Hz, C8), 152.3 (C2), 150.8 (C4), 148.6 (C6), 136.1 (d, $^{1}J_{C,P}$ = 39.5 Hz, C12b), 134.7 (d, $^{1}J_{C,P}$ = 43.0 Hz, C12a), 132.3 (d, $^{2}J_{C,P}$ = 10.1 Hz, C13b), 132.1 (d, $^{2}J_{C,P}$ = 10.2 Hz, C13a), 130.4 (C15a), 130.2 (C15b), 128.9 (d, $^{3}J_{C,P}$ = 9.0 Hz, C14a), 128.2 (d, $^{3}J_{C,P}$ = 9.4 Hz, C14b), 110.9 (C5), 94.5 (C16), 39.3 (C10), 23.8 (d, $^{1}J_{C,P}$ = 29.4 Hz, C11), 10.1 (C17). $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ = 35.2. MS (MALDI-TOF): *m*/*z* (%) = 619 (14, [**8**]$^+$), 584 (100, [**8**–Cl]$^+$). MS (ESI in CH_3CN): *m*/*z* (%) = 625.17850 (16, calcd for [**8**–Cl+CH_3CN]$^+$ 625.17911), 584.15190 (100, calcd for [**8**–Cl]$^+$ 584.15251). MS (ESI, in CH_3OH): *m*/*z* (%) = 616.14156 (25, calcd. for [**8**–Cl+CH_3OH]$^+$ 616.17876), 584.15135 (22, calcd for [**8**–Cl]$^+$ 584.15251).



[**8**]

X-ray Crystallography.

X-ray diffraction data were collected at *T* = 153(2) K using monochromated Mo-Kα radiation (λ = 0.71073 Å). Diffraction data were collected over the full sphere and were corrected for

absorption. Structure solutions were found with the *SHELXS-97* package[3] using direct methods and were refined with *SHELXL-97* (for [**7**]Cl·$CHCl_3$) or *SHELXL-2014* (for [**4**]·CH_2Cl_2, [**6**]·CH_2Cl_2 and [**8'**]Cl·0.5CH_3CN) against $|F^2|$ of all data using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions.

Crystallographic data for [4]·CH_2Cl_2.

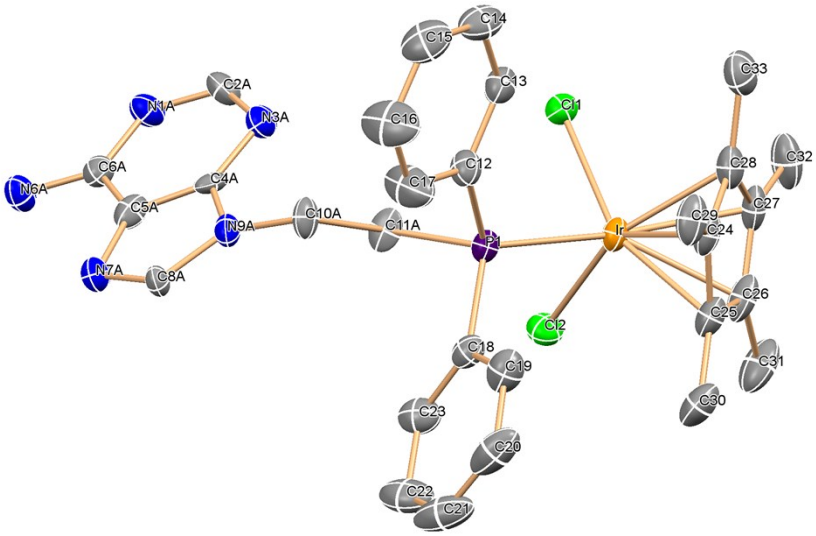


Figure S1. Molecular structure of [**4**] in [**4**]·CH_2Cl_2 (50% probability ellipsoids, hydrogen atoms have been omitted).

Crystals of [**4**]·CH_2Cl_2 were obtained by slow diffusion of diethyl ether into a saturated solution of [**4**] in $CHCl_3$. $C_{30}H_{35}N_5Cl_4PIr$, M = 830.60, orange needle, 0.35 × 0.10 × 0.08 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 8.7266(2), b = 17.0401(4), c = 20.9621(5) Å, β = 90.9520(10), V = 3116.68(13) $Å^3$, ρ_{calcd} = 1.770 $g \cdot cm^{-3}$, μ = 4.708 mm^{-1}, ω- and φ-scans, 52452 measured intensities ($4.8° \leq 2\theta \leq 59.2°$), semiempirical absorption correction ($0.5545 \leq T \leq 0.7459$), 8725 independent ($R_{int}$ = 0.0471) and 7860 observed intensities ($I \geq 2\sigma(I)$), refinement of 483 parameters against $|F^2|$ of all unique intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. R = 0.0364, wR = 0.0736, R_{all} = 0.0445, wR_{all} = 0.0753. The asymmetric unit contains one formula unit. The 9-ethyleneadenine moiety is disordered but the disorder could be resolved and all disordered atoms (SOF = 0.5) were refined with anisotropic thermal parameters.

Crystallographic data for [6]·CH_2Cl_2.

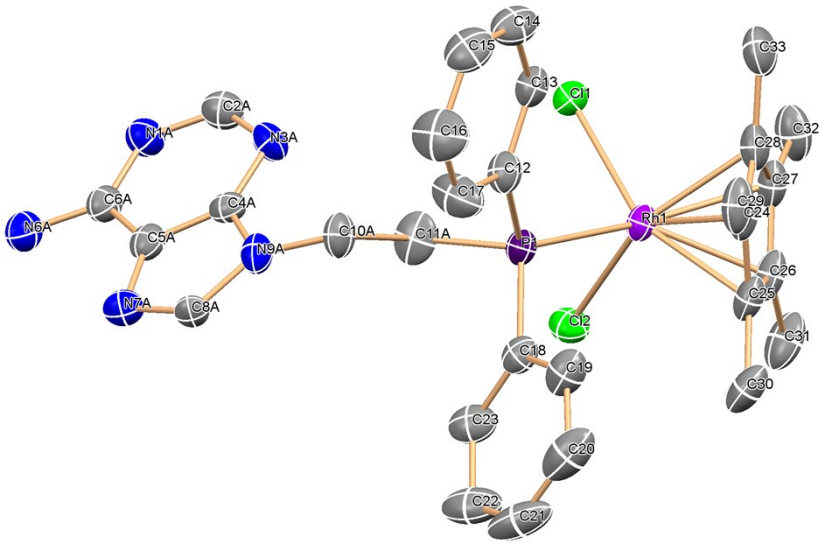


Figure S2. Molecular structure of [**6**] in [**6**]·CH_2Cl_2 (50% probability ellipsoids, hydrogen atoms have been omitted).

Crystals of [**6**]·CH_2Cl_2 were obtained by slow diffusion of diethyl ether into a saturated solution of [**6**] in dichloromethane. $C_{30}H_{35}N_5Cl_4PRh$, M = 714.31, red needle, 0.26 × 0.11 × 0.11 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 8.7068(2), b = 17.0934(2), c = 20.9150(4) Å, β = 90.8990(10), V = 3112.37(11) Å^3, ρ_{calcd} = 1.582 g·cm^{-3}, μ = 0.974 mm^{-1}, ω- and φ-scans, 34364 measured intensities (4.6° ≤ 2θ ≤ 59.2°), semiempirical absorption correction (0.5912 ≤ T ≤ 0.7459), 8699 independent (R_{int} = 0.0418) and 7758 observed intensities ($I \geq 2\sigma(I)$), refinement of 484 parameters against $|F^2|$ of all unique intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. R = 0.0558, wR = 0.1271, R_{all} = 0.0629, wR_{all} = 0.1300. The asymmetric unit contains one formula unit. The 9-ethyleneadenine moiety is disordered but the disorder could be resolved and all disordered atoms (SOF = 0.5) were refined with anisotropic thermal parameters.

Crystallographic data for [7]Cl·$CHCl_3$.

Crystals of [**7**]Cl·$CHCl_3$ were obtained by slow diffusion of diethyl ether into a saturated solution of [**7**]Cl in a mixture of trichloromethane and methanol (1:1, v:v). $C_{30}H_{34}N_5Cl_5IrP$, M = 865.04, yellow prism, 0.30 × 0.18 × 0.10 mm^3, monoclinic, space group $P2_1/n$, Z = 4, a =

13.8919(2), b = 17.5284(2), c = 14.0531(2) Å, β = 108.4630(10), V = 3245.83(8) Å^3, ρ_{calcd} = 1.770 g·cm^{-3}, μ = 4.605 mm^{-1}, ω- and φ-scans, 58315 measured intensities (7.2° ≤ 2θ ≤ 62.0°), semiempirical absorption correction (0.5667 ≤ T ≤ 0.7462), 10224 independent (R_{int} = 0.0286) and 9435 observed intensities ($I \geq 2\sigma(I)$), refinement of 392 parameters against |F^2| of all unique intensities with hydrogen atoms on calculated positions. R = 0.0178, wR = 0.0452, R_{all} = 0.0204, wR_{all} = 0.0462. The asymmetric unit contains one formula unit [**7**]Cl·$CHCl_3$.

Crystallographic data for [8']Cl·0.5CH_3CN.

Crystals of [**8a**]Cl·0.5CH_3CN were obtained by slow evaporation of the solvent from a saturated solution of [**8**] in acetonitrile The crystallization led to the exchange of a chlorido ligand for a acetonitrile ligand and formation of the salt [**8'**]Cl which co-crystallized with 0.5 equivalents of CH_3CN. $C_{32}H_{37.5}N_6ClPRu$, M = 680.67, yellow prism, 0.32 × 0.09 × 0.08 mm^3, triclinic, space group $P\bar{1}$, Z = 4, a = 10.4157(2), b = 10.7643(3), c = 29.2352(7) Å, α = 100.1770(10), β = 91.9820(10), γ = 93.9450(10), V = 3214.92(13) Å^3, ρ_{calcd} = 1.406 g·cm^{-3}, μ = 0.653 mm^{-1}, ω- and φ-scans, 53528 measured intensities (4.9° ≤ 2θ ≤ 58.6°), semiempirical absorption correction (0.7847 ≤ T ≤ 0.8612), 17380 independent (R_{int} = 0.0390) and 14135 observed intensities ($I \geq 2\sigma(I)$), refinement of 1121 parameters against |F^2| of all unique intensities with anisotropic thermal parameters for all non-hydrogen atoms and hydrogen atoms on calculated positions. R = 0.0334, wR = 0.0722, R_{all} = 0.0461, wR_{all} = 0.0777. The asymmetric unit contains two formula units of [**8'**]Cl and one free molecule of CH_3CN. One of the two molecules of [**8'**]Cl is disordered but the disorder could be resolved and all disordered atoms (SOF = 0.5) were refined with anisotropic thermal parameters.

References

S1 P. Lang, G. Magnin, G. Mathis, A. Burger and J.-F. Biellmann, *J. Org. Chem*. 2000, **65**, 7825.

S2 Q. Zhang, G. Hua, P. Bhattacharyya, A. M. Z. Slawin and J. D. Woollins, *Dalton Trans*. 2003, 3250.

S3 *SHELXS-97*, *SHELXL-97*, Sheldrick, G. M., *Acta Crystallogr., Sect. A* 2008, **64**, 112.

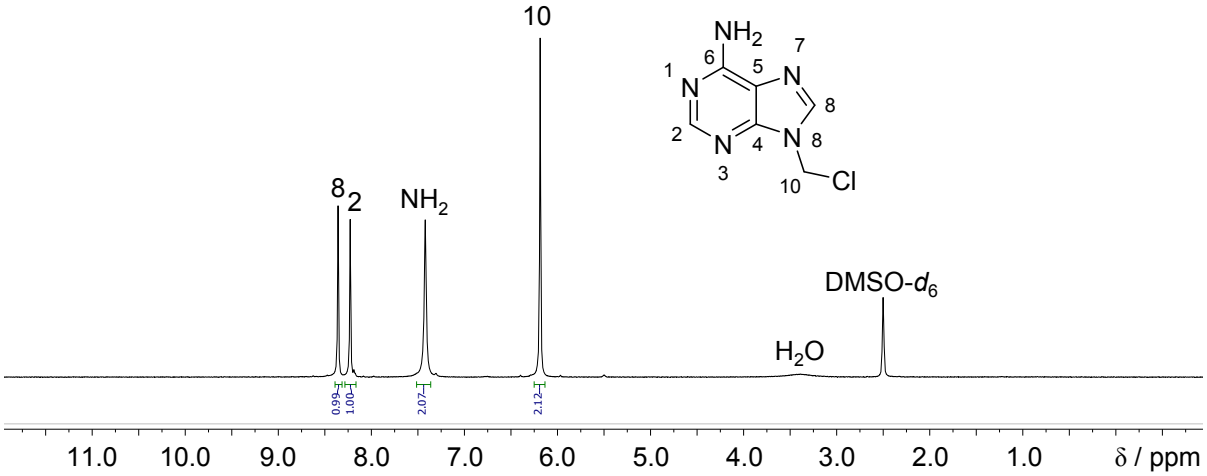


Figure S3. ^{1}H NMR spectrum of 9-chloromethyladenine (in DMSO-d_6).

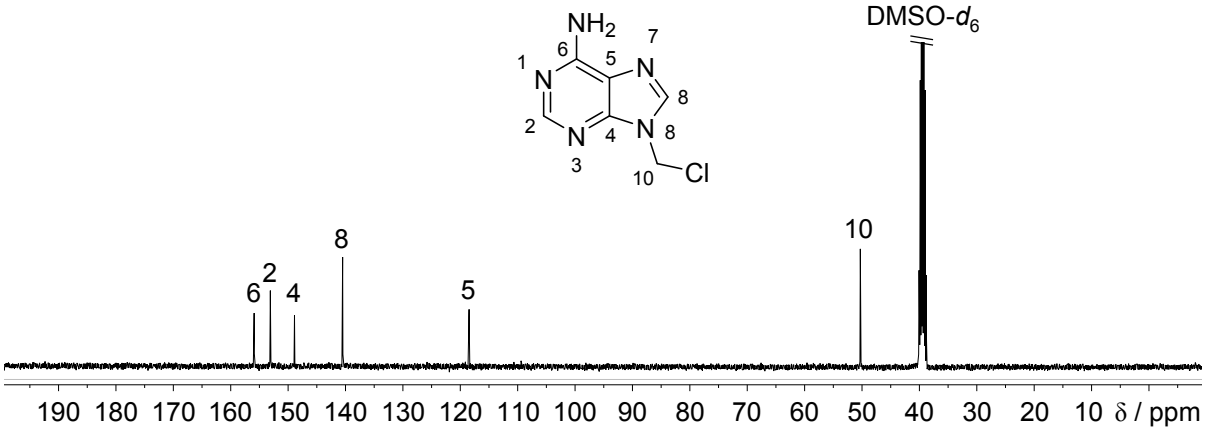


Figure S4. ^{13}C{^{1}H} NMR spectrum of 9-chloromethyladenine (in DMSO-d_6).

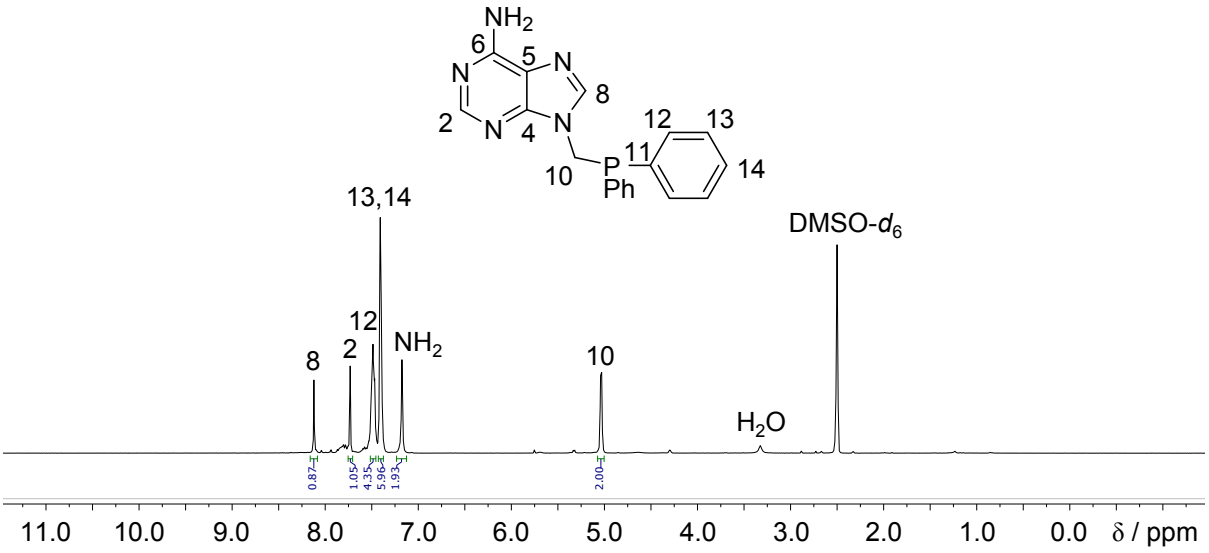


Figure S5. ^{1}H NMR spectrum of **1** (in DMSO-d_6).

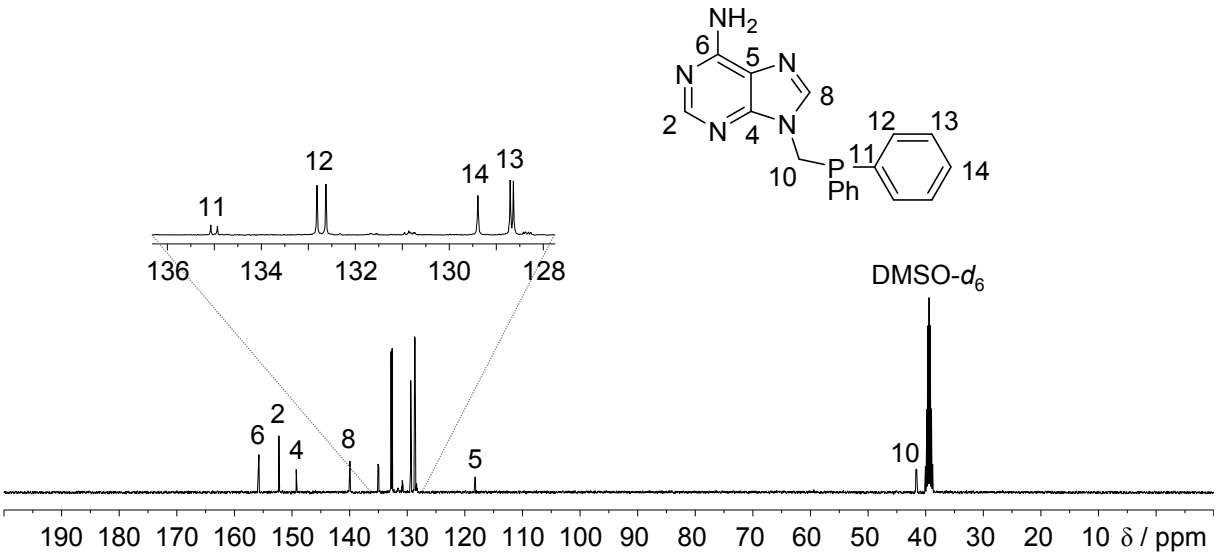


Figure S6. ^{13}C{^{1}H} NMR spectrum of **1** (in DMSO-d_6).

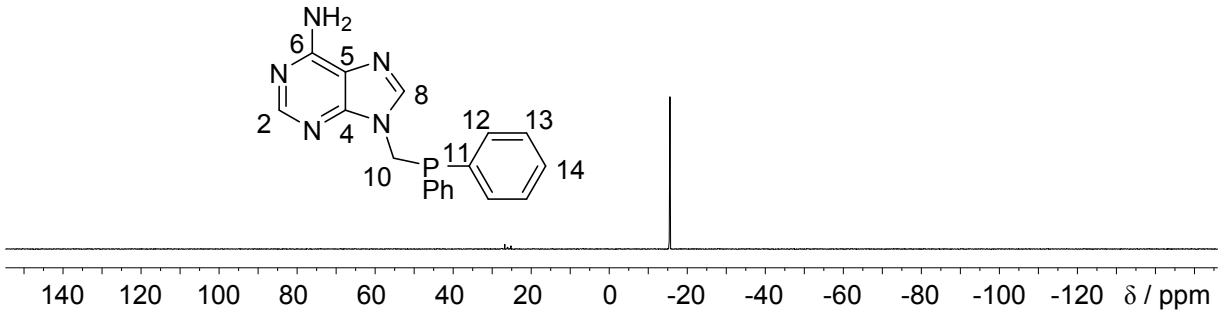


Figure S7. $^{31}P\{^{1}H\}$ NMR spectrum of **1** (in DMSO-d_6).

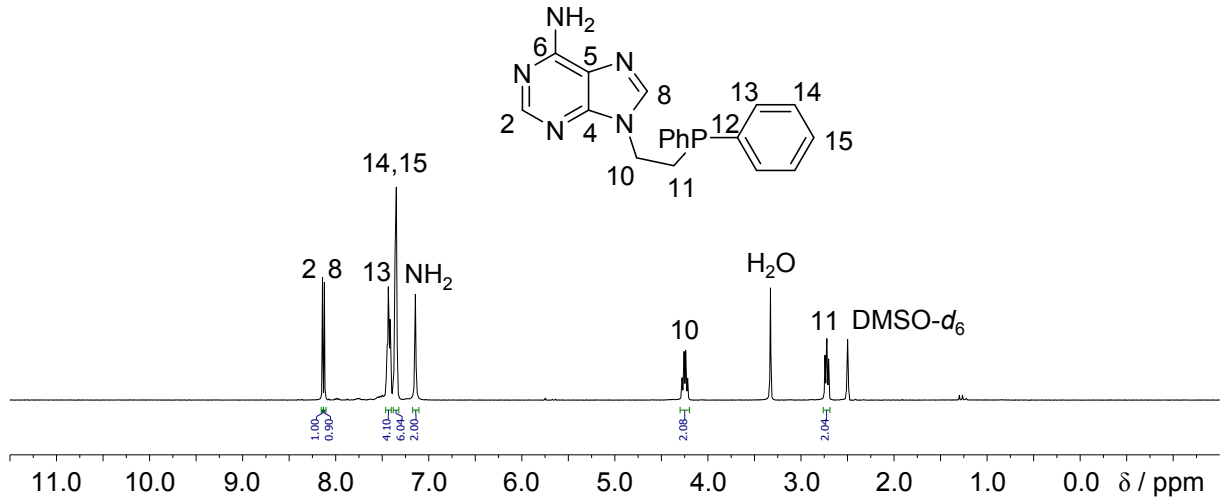


Figure S8. ^{1}H NMR spectrum of **2** (in DMSO-d_6).

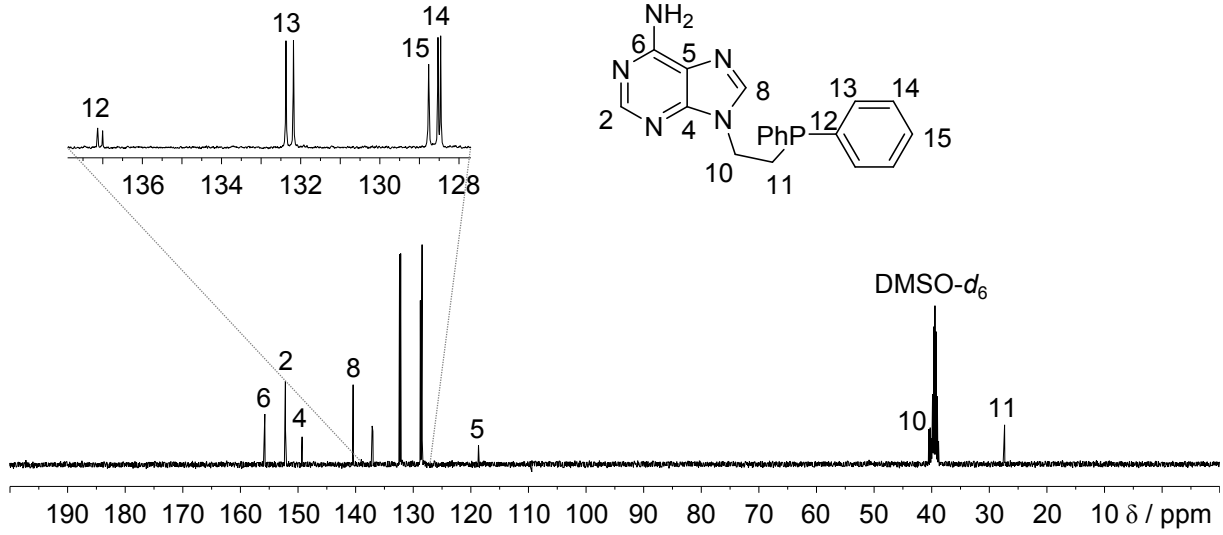


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **2** (in DMSO-d_6).

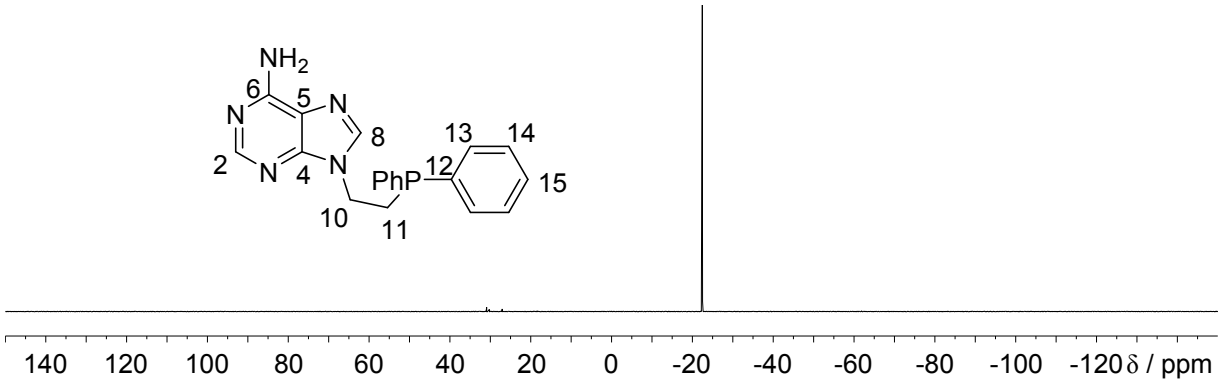


Figure S10. $^{31}P\{^{1}H\}$ NMR spectrum of **2** (in DMSO-d_6).

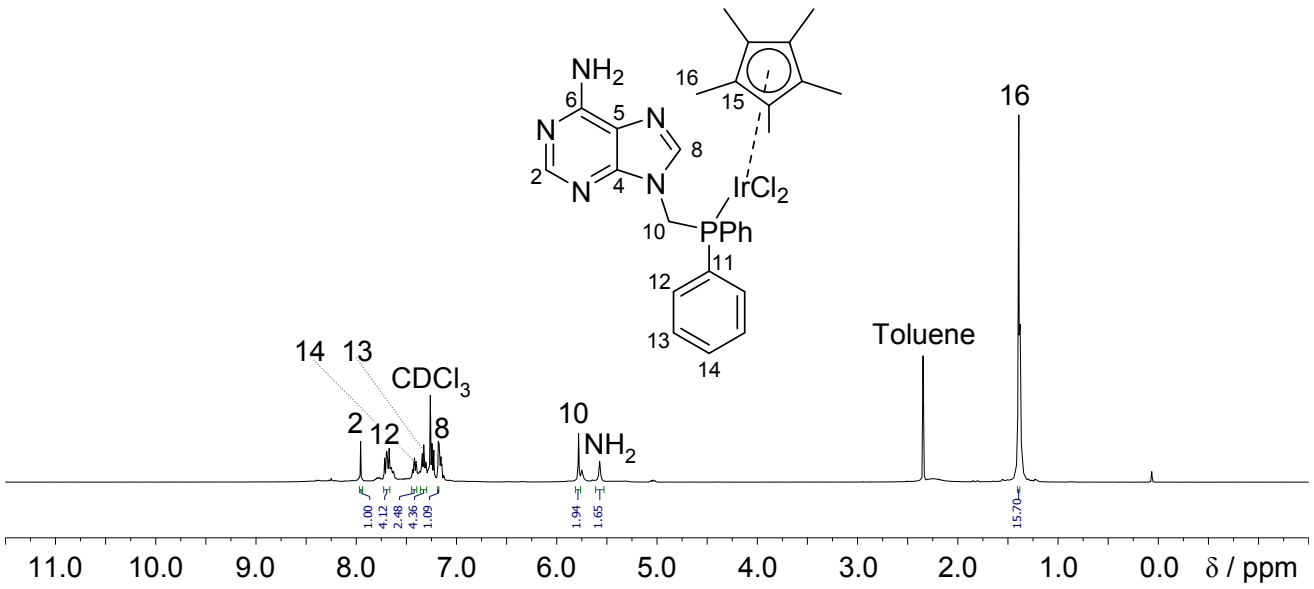


Figure S11. ^{1}H NMR spectrum of [**3**] (in $CDCl_3$).

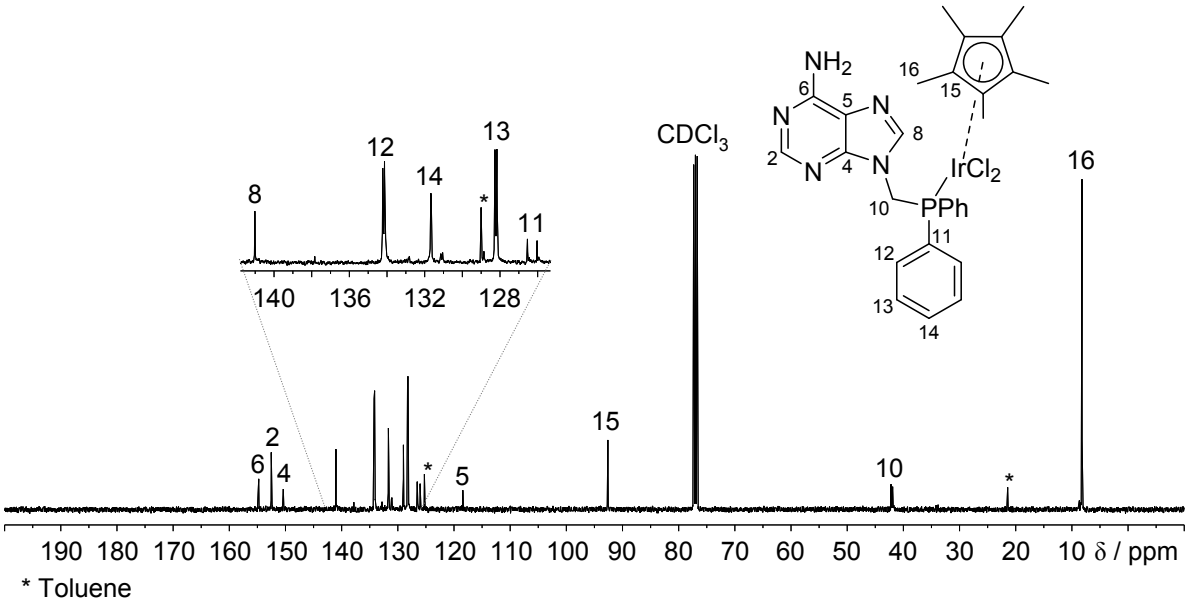


Figure S12. $^{13}C\{^{1}H\}$ NMR spectrum of [**3**] (in $CDCl_3$).

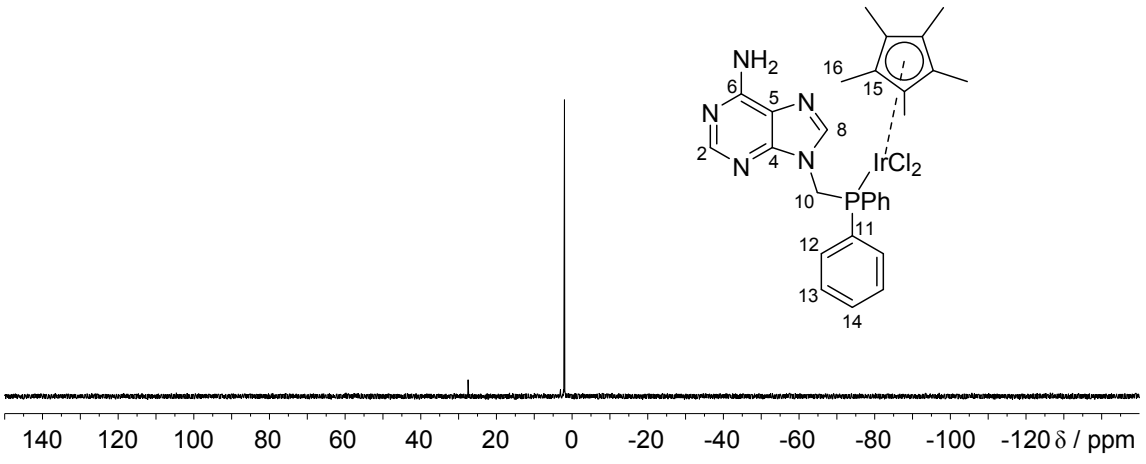


Figure S13. $^{31}P\{^{1}H\}$ NMR spectrum of [**3**] (in $CDCl_3$).

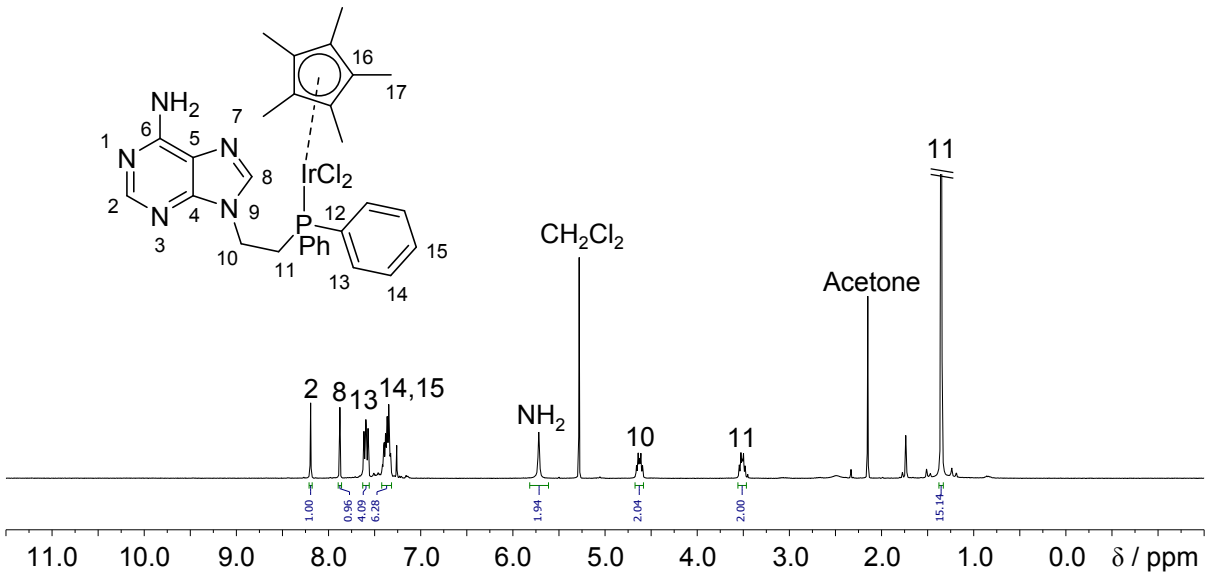


Figure S14. ^{1}H NMR spectrum of [**4**] (in $CDCl_3$).

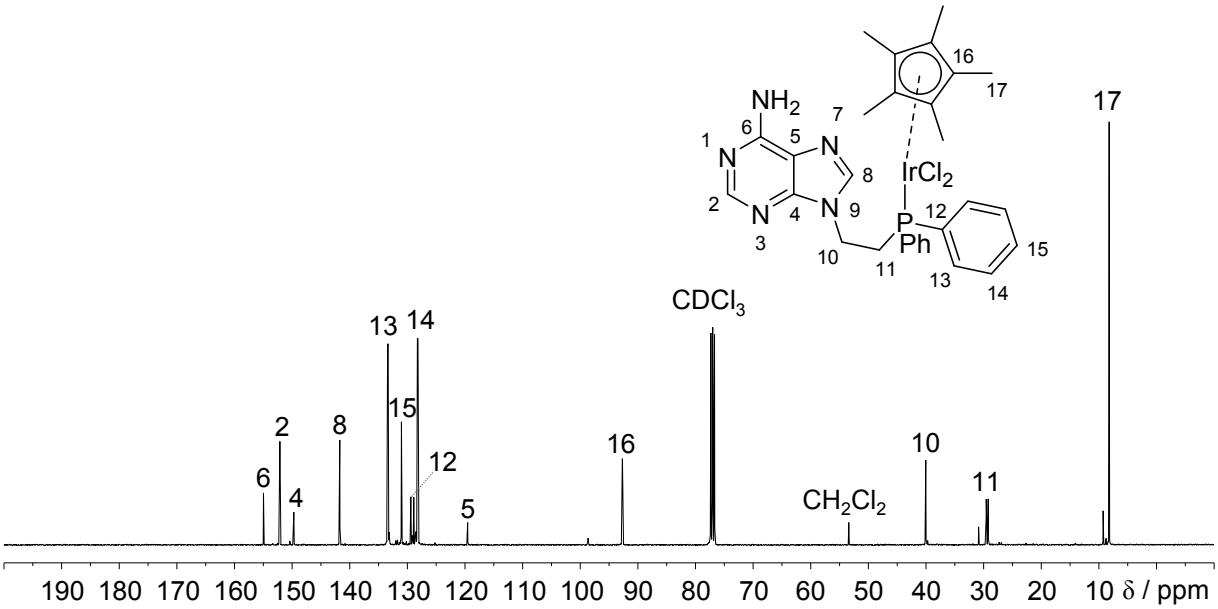


Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of [**4**] (in $CDCl_3$).

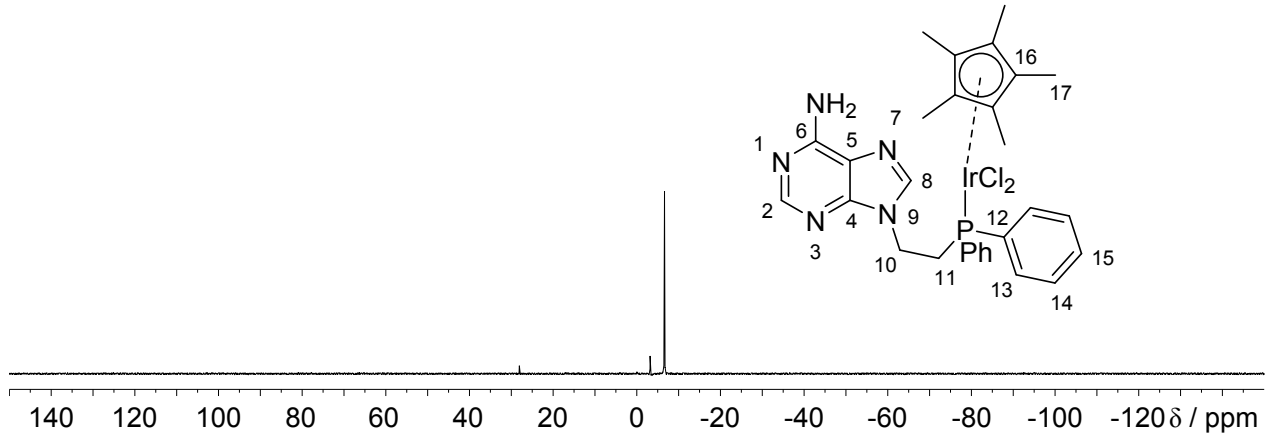


Figure S16. $^{31}P\{^{1}H\}$ NMR spectrum of [**4**] (in $CDCl_3$).

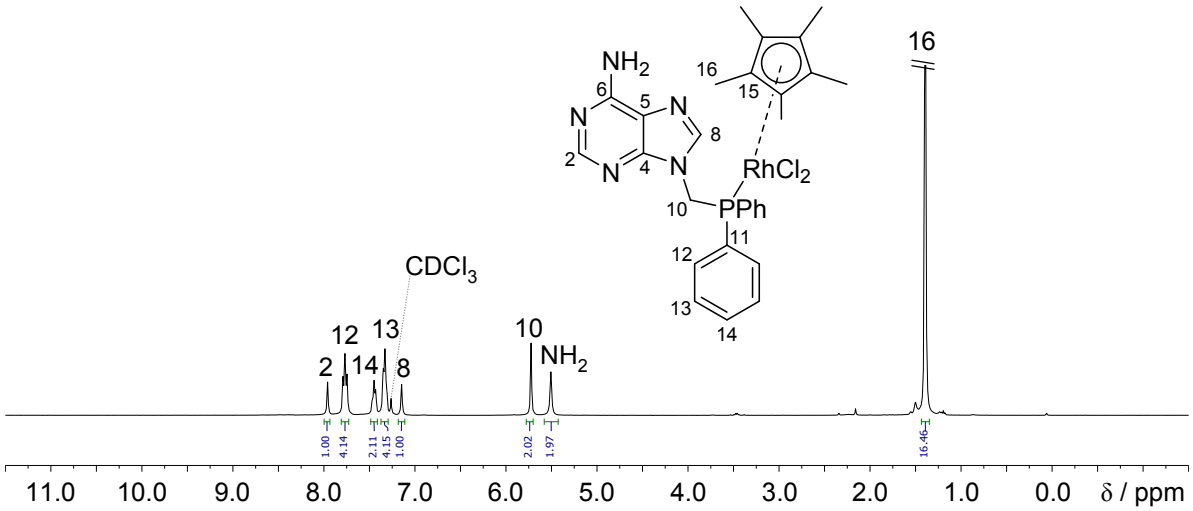


Figure S17. ^{1}H NMR spectrum of [**5**] (in $CDCl_3$).

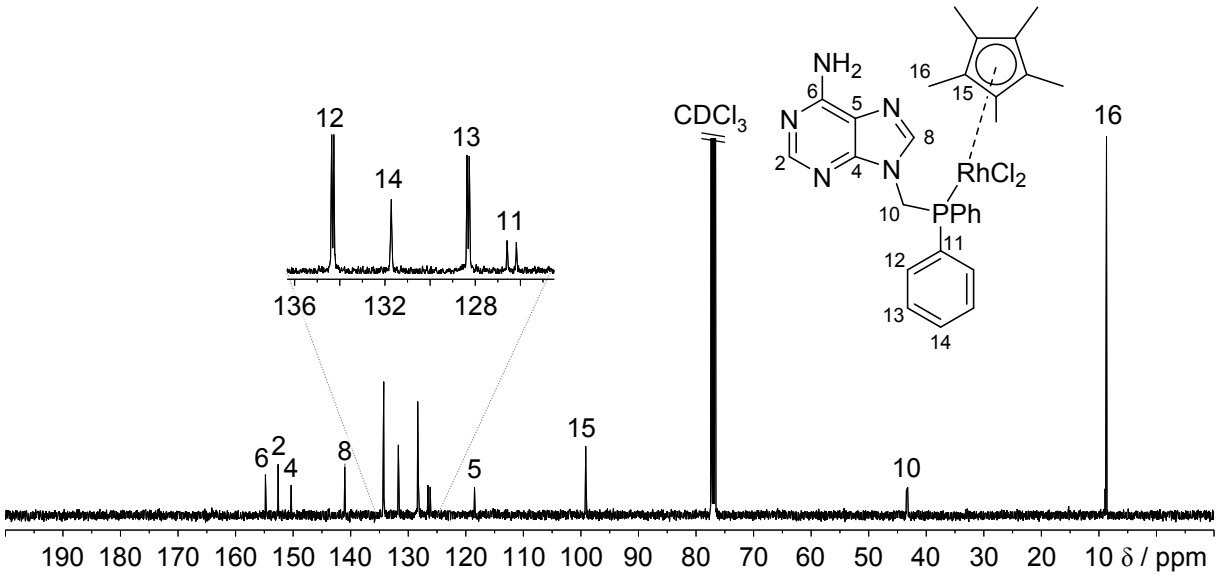


Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of [**5**] (in $CDCl_3$).

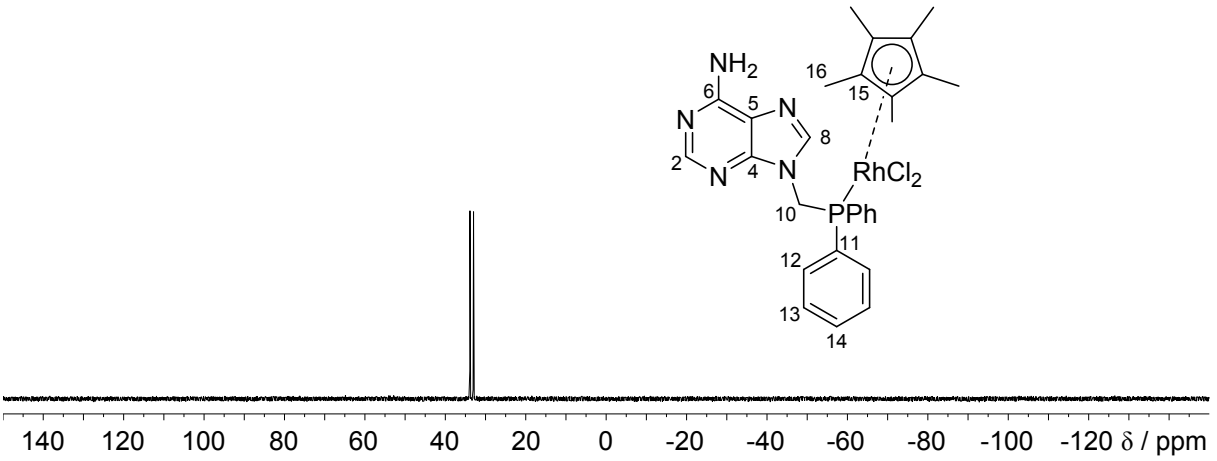


Figure S19. $^{31}P\{^{1}H\}$ NMR spectrum of [**5**] (in $CDCl_3$).

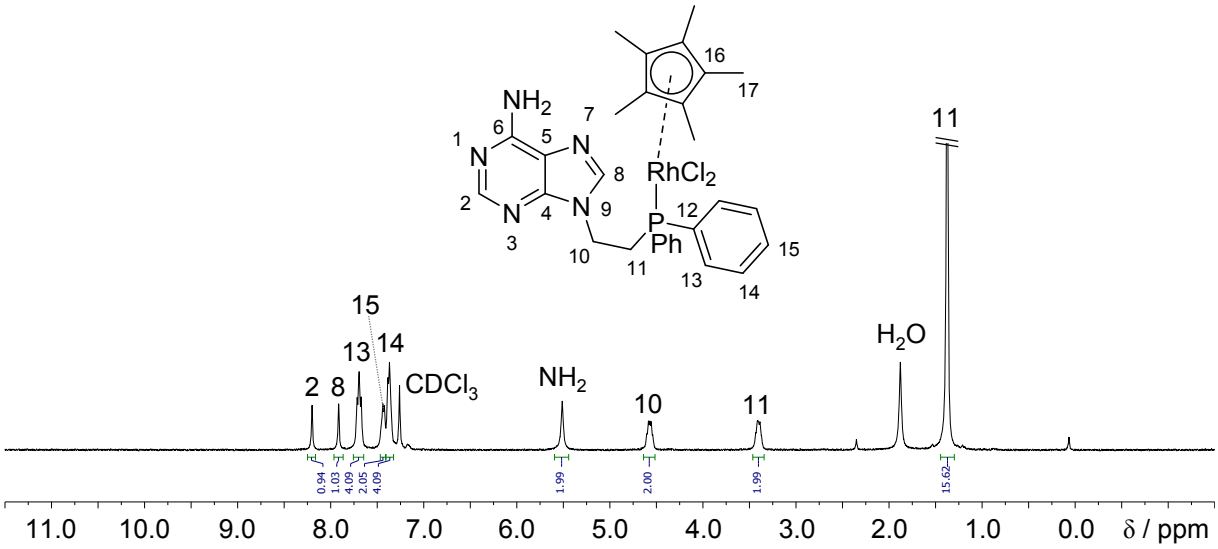


Figure S20. ^{1}H NMR spectrum of [**6**] (in $CDCl_3$).

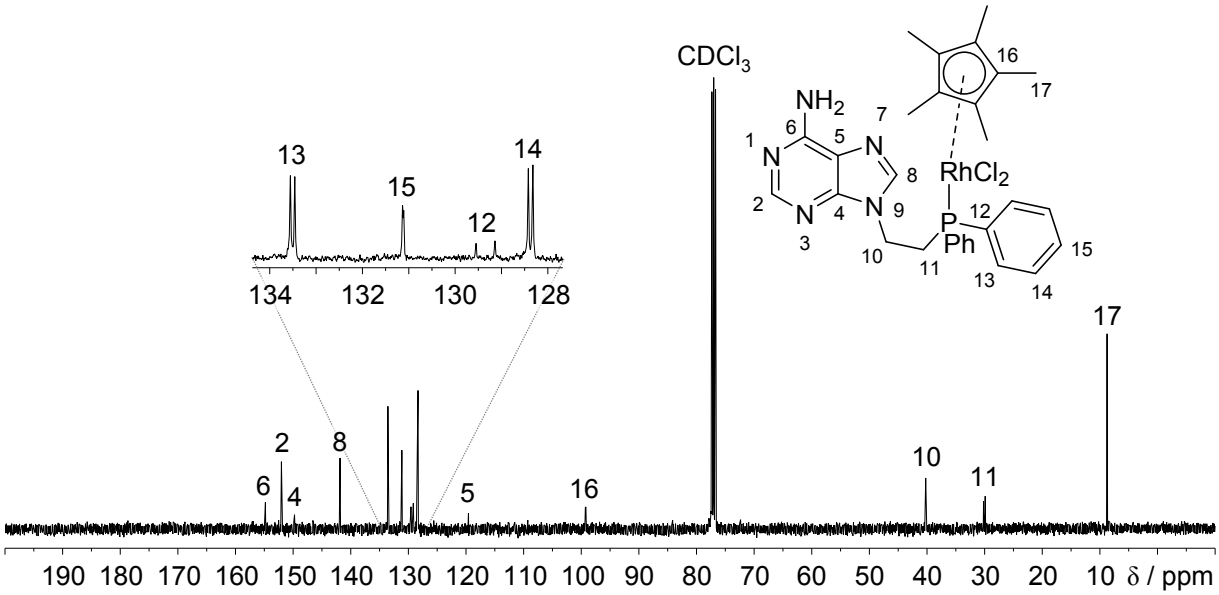


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of [**6**] (in $CDCl_3$).

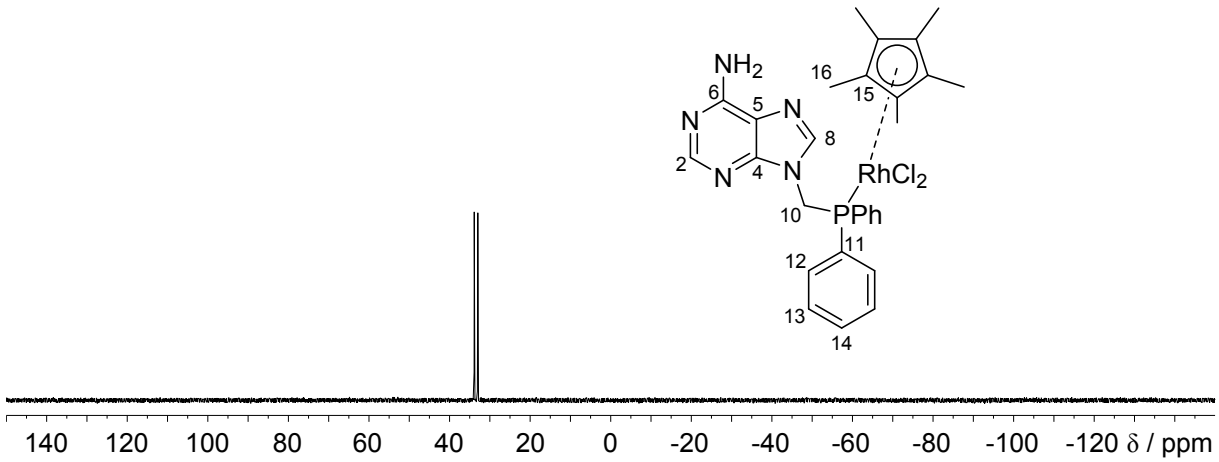


Figure S22. $^{31}P\{^{1}H\}$ NMR spectrum of [**6**] (in $CDCl_3$).

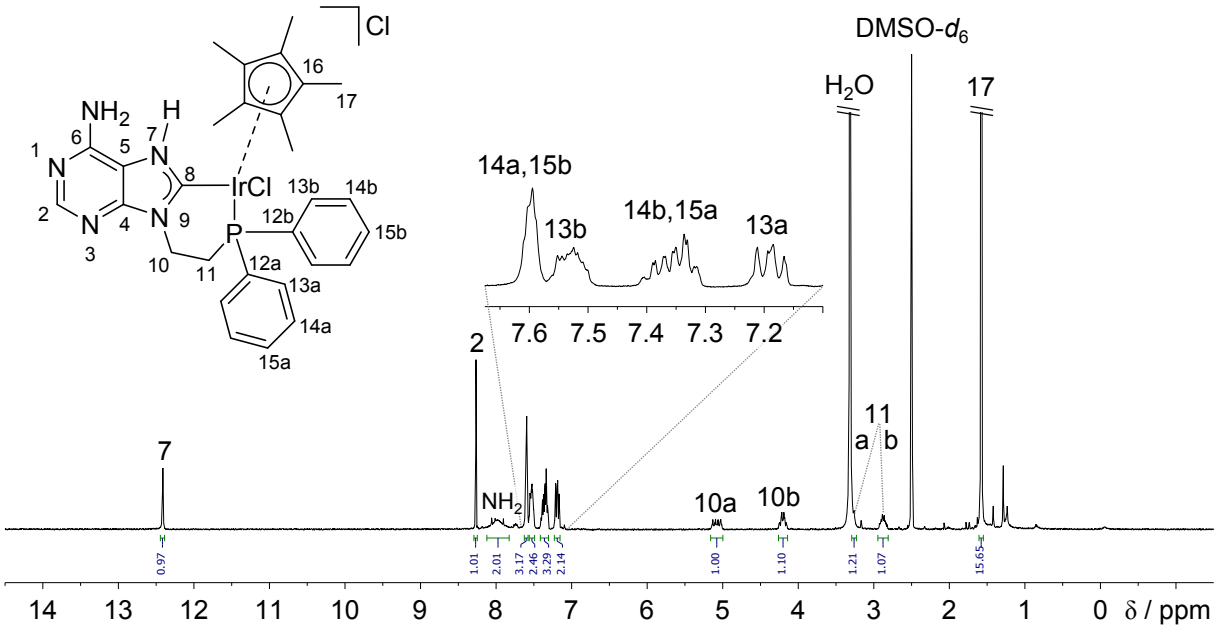


Figure S23. ^{1}H NMR spectrum of [**7**]Cl (in DMSO-d_6).

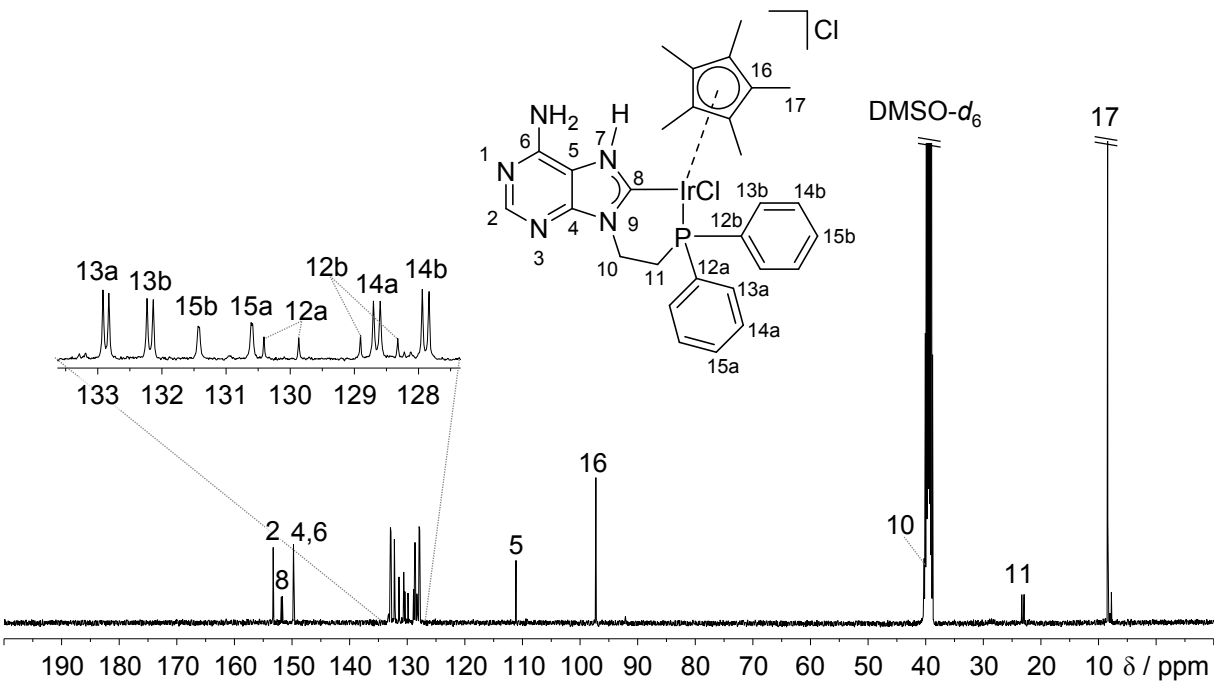


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of [**7**]Cl (in DMSO-d_6).

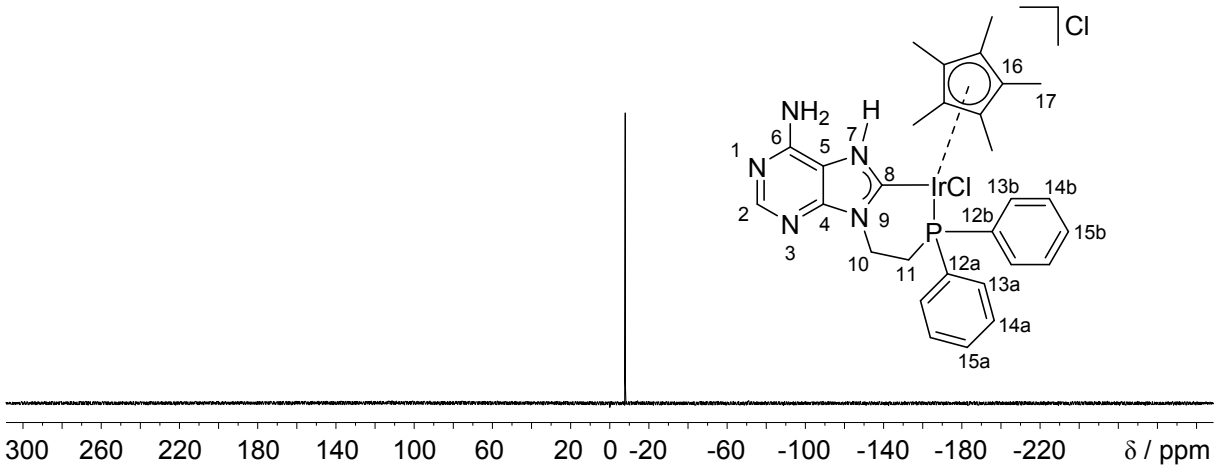


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of [**7**]Cl (in DMSO-d_6).

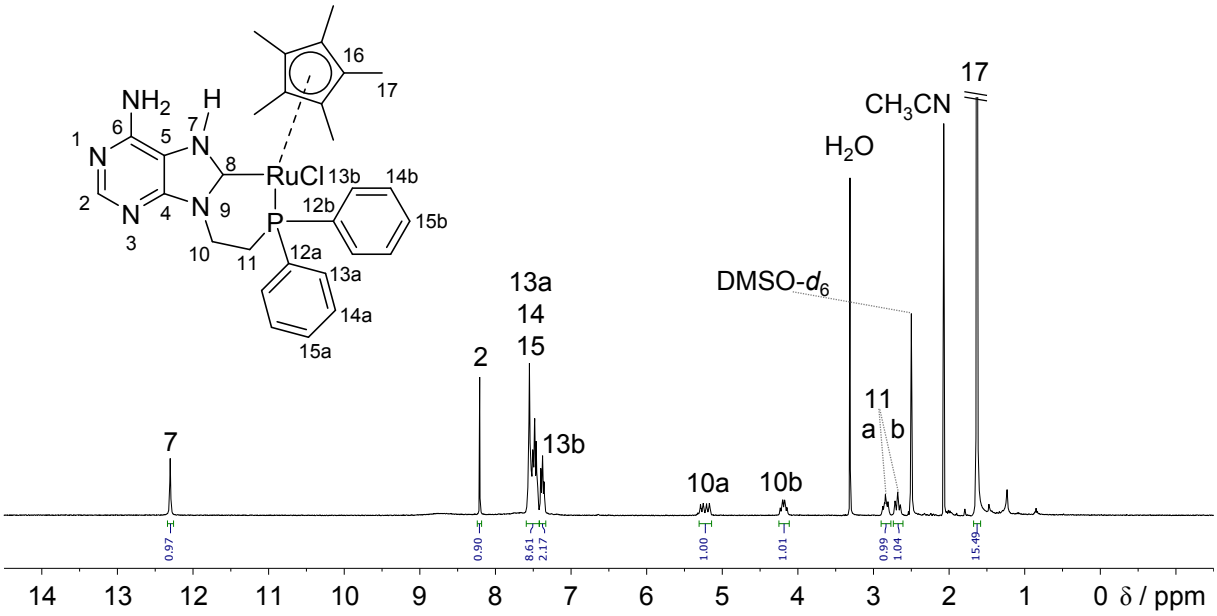


Figure S26. ^{1}H NMR spectrum of [**8**] (in DMSO-d_6).

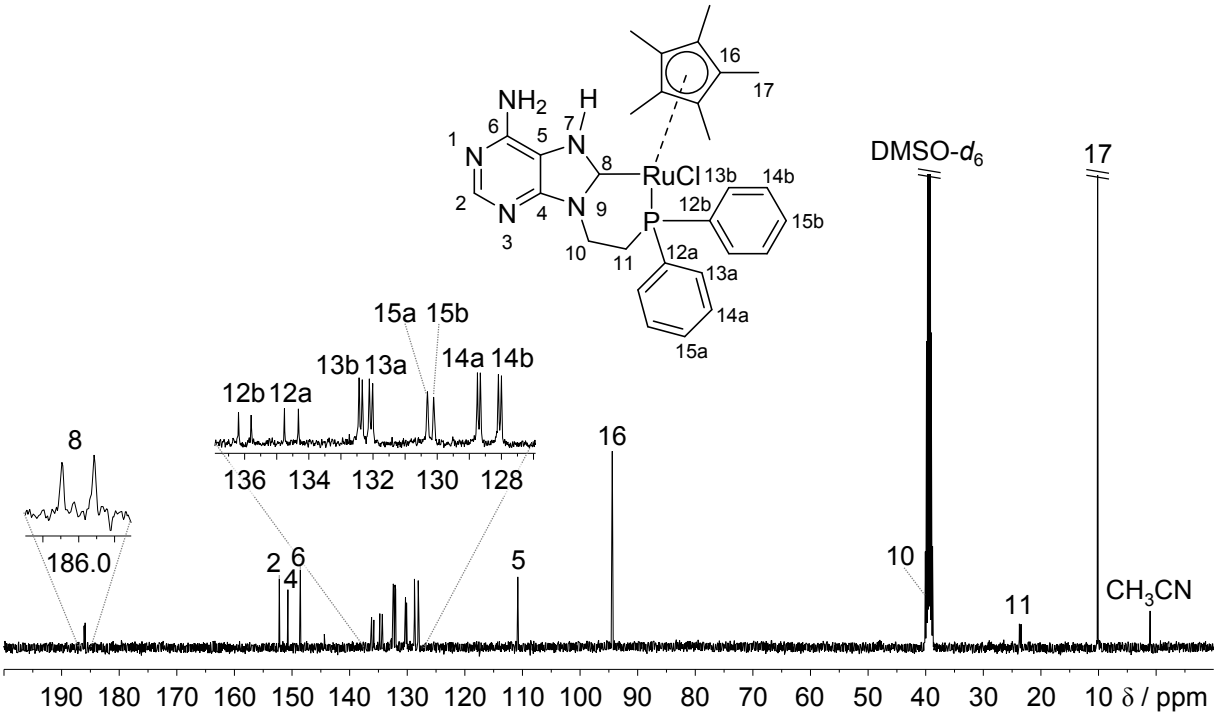


Figure S27. ^{13}C{^{1}H} NMR spectrum of [**8**] (in DMSO-d_6).

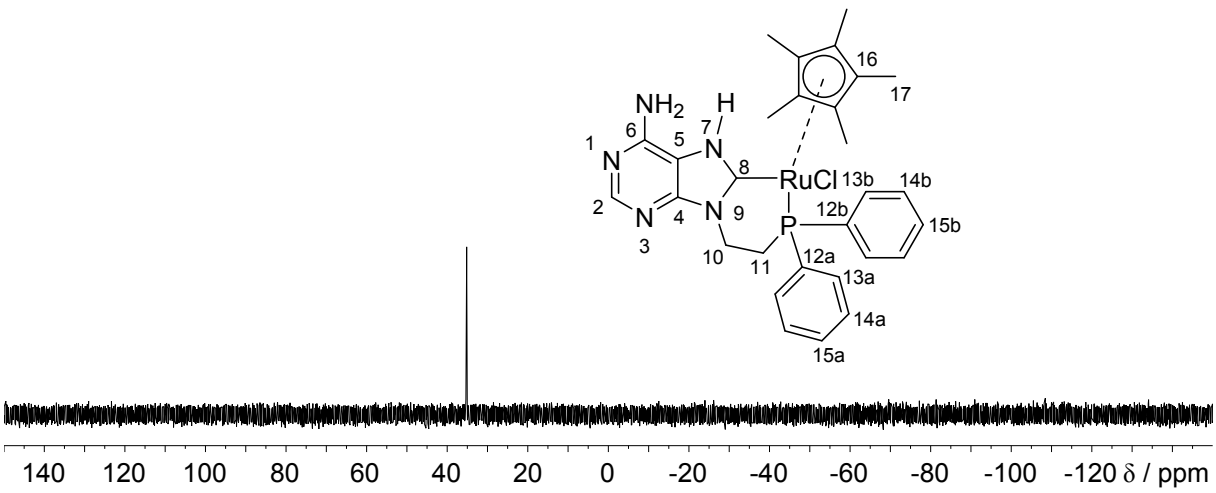


Figure S28. $^{31}P\{^{1}H\}$ NMR spectrum of [**8**] (in DMSO-d_6).