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Supporting information belonging to publication

Chemoselective synthesis of heterobimetallic bis-NHC complexes

by
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Contents

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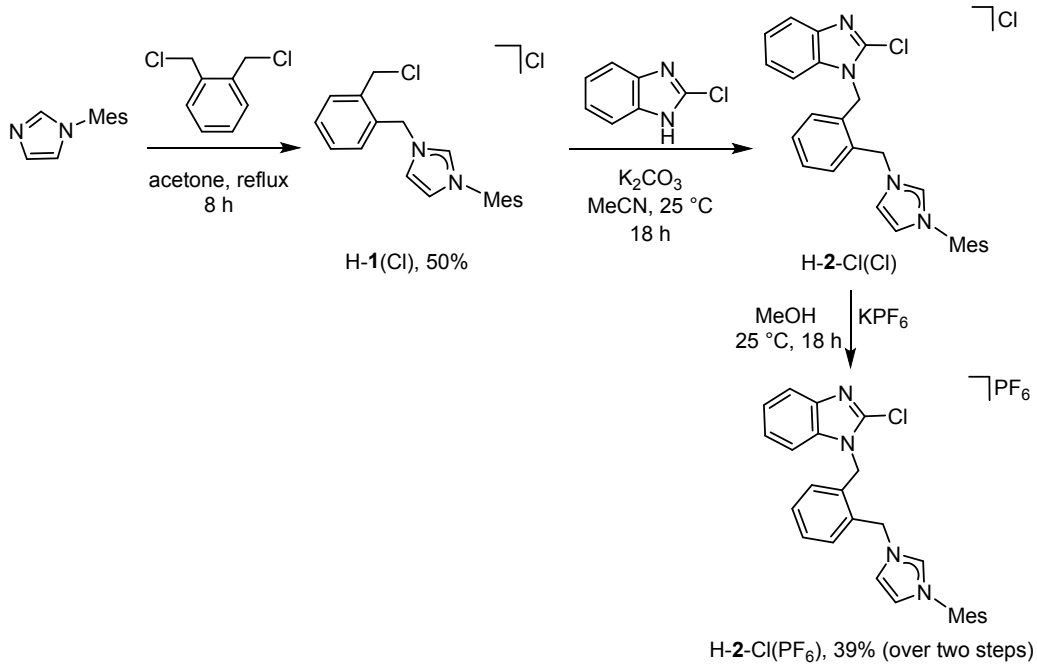
1. General Procedures

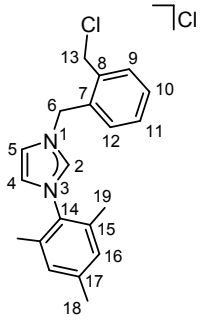
All manipulations were carried out under an argon atmosphere unless stated otherwise. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were measured on a Bruker AVANCE I 400, a Bruker AVANCE III 400 or a Bruker AVANCE Neo 500SB spectrometer. Chemical shifts (δ) are expressed in ppm relative to $SiMe_4$ using the residual protonated solvent signal as an internal standard. For the assignments of the NMR resonances see the numbering at the molecular plots. Coupling constants are expressed in Hz. Mass spectra were obtained with an Orbitrap LTQ XL spectrometer (Thermo Scientific). Compound 8-iodotheophylline[S1] was prepared as previously described.

2. Synthesis of ligand precursors H-1(Cl), H-2-Cl(Cl) and H-2-Cl(PF_6).



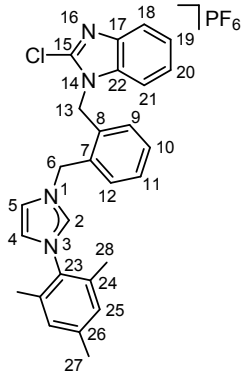
Scheme S1. Synthesis of ligand precursors H-**1**(Cl), H-**2**-Cl(Cl) and H-**2**-Cl(PF_6).

2.1. Synthesis of H-1(Cl).



Samples of *N*-mesitylimidazole (0.37 g, 1.99 mmol) and *α*,*α*‘-dichloro-*o*-xylole (0.70 g, 4.00 mmol) were suspended in acetone (50 mL) and the mixture was heated at 70 °C for 8 h. After removal of the solvent and purification by column chromatography (acetone:ethanol, 6:1), compound H-**1**(Cl) was isolated as colorless powder. Yield: 0.36 g (1.00 mmol, 50%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 10.76 (s, 1H, H2), 7.52–7.51 (m, 2H, H5, H11), 7.42–7.38 (m, 3H, H9, H10, H12), 7.09 (s, 1H, H4), 6.97 (s, 2H, H16), 6.21 (s, 2H, H6), 4.94 (2H, H13), 2.31 (s, 3H, H18), 2.05 (s, 6H, H19). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 141.2 (C17), 138.8 (C2), 137.3 (C8), 134.2 (C15), 131.8 (C7), 131.7 (C10), 131.2 (C12), 130.8 (C14), 130.3 (C11), 129.9 (C9), 129.8 (C16), 122.9 (C4), 122.5 (C5), 50.9 (C6), 44.0 (C13), 21.0 (C18), 17.7 (C19). HRMS (ESI, positive ions): *m*/*z* (%) = 325.1481 (100, calcd for [H-**1**]$^{+}$ 325.1471).

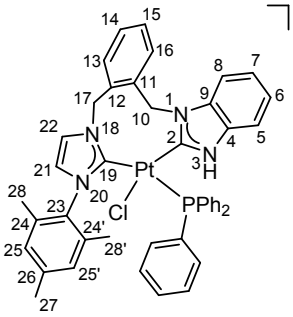
2.2. Synthesis of H-2-Cl(PF_6).



A mixture of H-**1**(Cl) (0.73 g, 2.02 mmol), 2-chlorobenzimidazole (0.31 g, 2.03 mmol) and potassium carbonate (0.56 g, 3.0 mmol) was suspended in acetonitrile (70 mL) and the suspension was stirred for 2 d at 25 °C. Filtration of the suspension and removal of the solvent from the filtrate yielded H-**2**-Cl(Cl) as a colorless powder. The chloride counterion was subsequently exchanged for a hexafluorophosphate counterion by dissolving the initially obtained chloride H-**2**-Cl(Cl) in methanol and adding of potassium hexafluorophosphate (0.56 g, 3.0 mmol). The resulting mixture was stirred for 2 d at ambient temperature. The suspension was then filtered and the solid residue was washed with a small amount of methanol (5 mL) to give H-**2**-Cl(PF_6) as a colorless powder. Yield: 46 mg (0.78 mmol, 39% over two steps). ^{1}H NMR (400 MHz, CD_3CN): δ (ppm) = 8.63 (H2), 7.69–7.68 (m, 1H, H18), 7.59 (s, 1H, H5), 7.53 (s, 1H, H4), 7.45–7.42 (m, 1H, H11), 7.37 (d, $^{3}J_{HH}$ = 6.9 Hz, 1H, H12), 7.34–7.24 (m, 4H, H10, H19, H20, H21), 7.12 (s, 2H, H25), 6.66 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, H9), 5.67 (s, 2H, H6), 5.49 (s, 2H, H13), 2.35 (s, 3H, H27), 2.06 (s, 6H, H28). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 142.9 (C17), 142.4 (C26), 141.9 (C15), 137.7 (C2), 136.5 (C22), 135.7 (C24), 135.5 (C8), 132.0 (C23), 131.3 (C7), 131.2 (C12), 131.2 (C10), 130.5 (C25), 129.9 (C11), 127.5 (C9), 125.7 (C4),

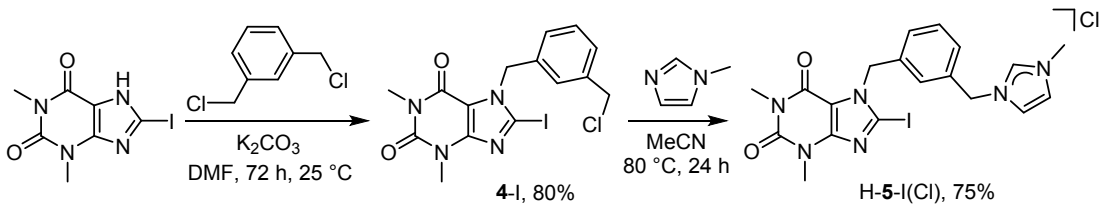
124.6 (C20), 124.5 (C5), 124.0 (C19), 120.3 (C18), 111.2 (C21), 51.8 (C6), 45.9 (C13), 21.2 (C27), 17.6 (C28). $^{31}P\{^{1}H\}$ NMR (162 MHz, CD_3CN): δ (ppm) = –144.6 (sep, $^{1}J_{PF}$ = 706.4 Hz). $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_3CN): δ (ppm) = –72.9 (d, $^{1}J_{FP}$ = 706.4 Hz). HRMS (ESI, positive ions): *m*/*z* (%) = 441.1837 (100, calcd for [H-**2**-Cl]$^{+}$ 441.1846).

3. Synthesis of complex [3](PF$_6$).



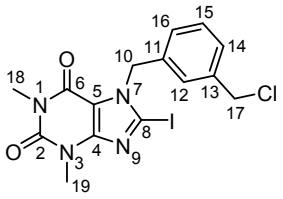
A mixture of H-**2**-Cl(PF_6) (60 mg, 0.10 mmol) and [Pt(PPh_3)$_4$] (125 mg, 0.1 mmol) was suspended in freshly distilled toluene (10 mL) and the mixture was stirred for 6 d at 120 °C. Subsequently, the solvent was removed *in vacuo* and the residue was washed with diethylether (2 × 2 mL) and *n*-hexane (2 × 2 mL) to yield [**3**]PF_6 as a colorless powder. Yield: 96 mg (0.09 mmol, 90%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 9.08 (s br, 1H, H3), 7.92–7.90 (m, 1H, H16), 7.76–7.74 (m, 1H, H13), 7.69 (d, $^{3}J_{HH}$ = 8.2 Hz, 1H, H5), 7.55–7.53 (m, 2H, H14, H15), 7.49–7.45 (m, 6H, Ph-H$_{ortho}$), 7.46 (s, 1H, H22), 7.33–7.29 (m, 4H, Ph-H$_{para}$, H6), 7.27 (m, 2H, H25 and H8), 7.26–7.22 (m, 6H, Ph-H$_{meta}$), 7.21–7.18 (m, 1H, H7), 7.11 (s, 1H, H25‘), 7.09 (d, $^{2}J_{HH}$ = 14.5 Hz, 1H, H17), 6.90 (s, 1H, H21), 6.67 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H, H10), 5.27 (d, $^{2}J_{HH}$ = 14.5 Hz, 1H, H17’), 5.02 (d, $^{2}J_{HH}$ = 14.8 Hz, 1H, H10’), 2.51 (s, 3H, H27), 2.41 (s, 3H, H28), 1.04 (s, 3H, H28‘). $^{13}C\{^{1}H\}$ NMR (101 MHz, CD_2Cl_2): δ (ppm) = 165.7 (d, $^{2}J_{CP}$ = 147.0 Hz, C19), 157.8 (d, $^{2}J_{CP}$ = 8.6 Hz, C2), 141.1 (C26), 137.1 (C24), 136.2 (C12), 134.9 (C24‘), 134.3 (d, $^{2}J_{CP}$ = 10.8 Hz, Ph-C$_{ortho}$), 134.3 (C16), 134.3 (C23), 133.7 (C9), 133.1 (C13), 133.0 (C4), 132.9 (C11), 131.6 (d, $^{4}J_{CP}$ = 2.5 Hz, Ph$_{para}$), 131.0 (C15), 130.3 (C14), 130.2 (C25), 129.6 (C25‘), 128.9 (d, $^{3}J_{CP}$ = 10.7 Hz, Ph$_{meta}$), 128.7 (d, $^{1}J_{CP}$ = 56.2 Hz, Ph$_{ipso}$), 125.2 (d, $^{4}J_{CP}$ = 4.3 Hz, C21), 124.9 (C7), 124.3 (C6), 121.1 (d, $^{4}J_{CP}$ = 4.3 Hz, C22), 112.6 (C8), 111.7 (C5), 52.8 (C17), 51.4 (C10), 21.3 (C27), 19.2 (C28), 17.5 (C28‘). $^{31}P\{^{1}H\}$NMR (162 MHz, CD_2Cl_2): δ (ppm) = 13.1 (s, Pt-satelites, $^{1}J_{PPt}$ = 2382 Hz, PPh_3), –144.3 (sep, $^{1}J_{PF}$ = 711.3 Hz, PF_6). $^{19}F\{^{1}H\}$ NMR (376 MHz, CD_2Cl_2): δ (ppm) = –72.5 (d, $^{1}J_{FP}$ = 711.3 Hz). $^{195}Pt\{^{1}H\}$ NMR (86 MHz, CD_2Cl_2): δ (ppm) = –4117 (d, $^{1}J_{PtP}$ = 2382 Hz). HRMS (ESI, positive ions): *m*/*z* (%) = 899.2402 (100, calcd for [**3**]$^{+}$ 899.2409).

4. Synthesis of ligand precursors 4-I and H-5-I(Cl).



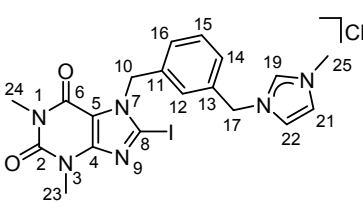
Scheme S2. Synthesis of ligand precursors **4**-I and H-**5**-I(Cl).

4.1. Synthesis of 4-I.



A mixture of 8-iodotheophylline (1.00 g, 3.27 mmol), α,α‘-dichloro-*m*-xylol (853 mg, 4.87 mmol) and potassium carbonate in (1.38 g, 10.0 mmol) in dimethylformamide (10 mL) was stirred for 3 d at 25 °C. The solvent was then removed and the residue was washed with diethylether (3 × 10 mL). Purification of the resulting solid by column chromatography (dichloromethane:methanol 95:5) yielded compound **4**-I as a white powder. Yield: 1.16 g (2.60 mmol, 80%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.36–7.32 (m, 4H, H12, H14, H15, H16), 5.53 (s, 2H, H10), 4.55 (s, 2H, H17), 3.57 (s, 3H, H19), 3.38 (s, 3H, H18). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.9 (C6), 151.3 (C2), 149.9 (C4), 138.2 (C11), 135.7 (C13), 129.3 (C15), 128.6 (C14), 127.8 (C16), 127.7 (C12), 110.2 (C5), 100.5 (C8), 51.69 (C10), 45.79 (C17), 29.9 (C18), 28.1(C19). MS (EI, 20 eV): *m*/*z* (%) = 444 (100, calcd for [**4**]$^{+}$ 444).

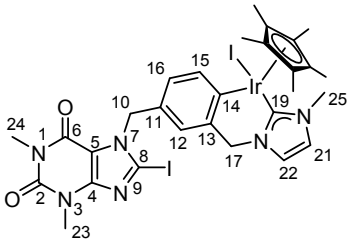
4.2. Synthesis of H-5-I(Cl).



A mixture of **4**-I (2.67 g, 6.0 mmol) and 1-methylimidazole (3.80 mL, 3.91 g, 47.6 mmol) was heated in acetonitrile (15 mL) for 24 h at 80 °C. The formed precipitate was isolated by filtration and washed with acetonitrile (3 × 10 mL) to give compound H-**5**-I(Cl) as a colorless solid. Yield: 2.39 g (4.54 mmol, 75%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.33 (s, 1H, H19), 7.78 (m, 1H, H21), 7.75 (m, 1H, H22), 7.39 (t, $^{3}J_{HH}$ = 7.6 Hz, 1H, H15), 7.33 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H14), 7.25 (s, 1H, H12), 7.13 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H16), 5.48 (s, 2H, H10),

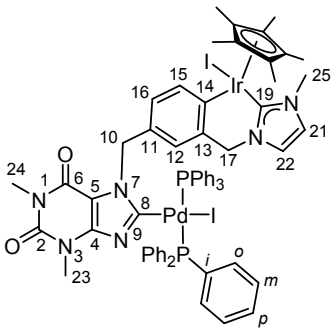
5.45 (s, 2H, H17), 3.89 (s, 3H, H25), 3.42 (s, 3H, H23), 3.19 (s, 3H, H24). $^{13}C\{^{1}H\}$ NMR (101 MHz, DMSO-d_6): δ (ppm) = 153.3 (C6), 150.7 (C2), 149.4 (C4), 136.8 (C11), 136.8 (C19) 136.7 (C13), 129.3 (C15), 127.3 (C14), 126.9 (C16), 126.5 (C12), 124.0 (C21), 122.4 (C22), 108.9 (C5), 108.2 (C8), 51.4 (C17), 50.6 (C10), 35.8 (C25), 29.4 (C24), 27.5 (C23). HRMS (ESI, positive ions): *m*/*z* (%) = 491.0686 (20, calcd for [H-**5**-I]$^+$ 491.0692).

5. Synthesis of complex [6].



Samples of H-**5**-I(Cl) (26.3 mg, 0.05 mmol), sodium acetate (16.4 mg, 0.20 mmol), potassium carbonate (6.2 mg, 0.05 mmol), KI (66.4 mg, 0.40 mmol) and $[IrCp^*Cl_2]_2$ (19.9 mg, 0.025 mmol) were dissolved in acetonitrile (10 mL). The yellow solution was stirred for 18 h at 86 °C. The solvent was then removed and the residue was dissolved in a small amount of ethyl acetate (2 mL). The solution was filtered through a small silica plug and the solvent was removed to give [**6**] as an orange solid. Yield: 32 mg (0.034 mmol, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.79 (d, $^{3}J_{HH}$ = 7.86 Hz, 1H, H15), 6.95 (s br, 1H, H12), 6.91 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H22), 6.90 (m, 1H, H16), 6.89 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H21), 5.47 (d, $^{2}J_{HH}$ = 14.7 Hz, 1H, H10a), 5.38 (d, $^{2}J_{HH}$ = 14.7 Hz, 1H, H10b), 4.94 (d, $^{2}J_{HH}$ = 14.4 Hz, 1H, H17a), 4.66 (d, $^{2}J_{HH}$ = 14.4 Hz, 1H, H17b), 3.80 (s, 3H, H25), 3.54 (s, 3H, H23), 3.38 (s, 3H, H24), 1.73 (s, 15H, Cp^*CH_3). $^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$): δ (ppm) = 154.0 (C19), 153.9 (C6), 151.3 (C2), 149.8 (C4), 147.4 (C15), 140.9 (C14), 138.5 (C13), 128.5 (C11), 127.1 (C16), 123.8 (C12), 121.1 (C21), 120.6 (C22), 110.2 (C5), 101.3 (C8), 90.9 (Cp*-C), 56.7 (C17), 51.8 (C10), 39.9 (C25), 29.8 (C23), 28.1 (C24), 10.0 (Cp^*-CH_3). HRMS (ESI, positive ions): *m*/*z* (%) = 817.1338 (35, calcd. for [[**6**]–I]$^+$ 817.1340).

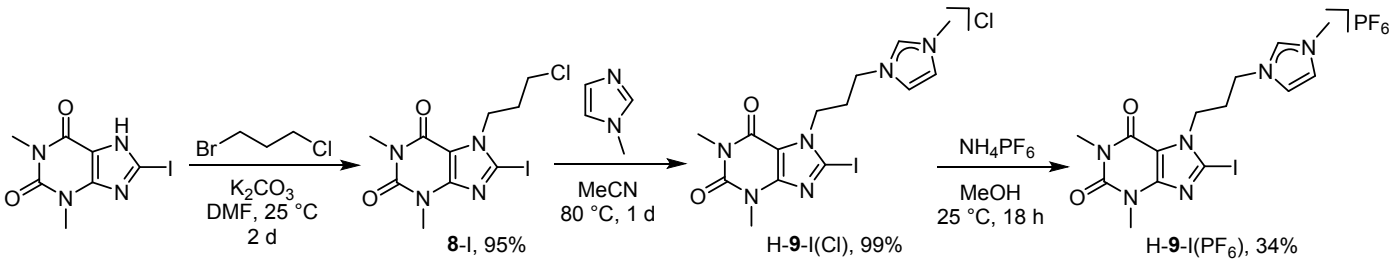
6. Synthesis of complex [7].



A mixture of [**6**] (25 mg, 0.026 mmol), $[Pd(PPh_3)]_4$ (32 mg, 0.026 mmol) and KI (34.5 mg, 0.21 mmol) was suspended in freshly distilled tetrahydrofuran (6 mL). The reaction mixture was stirred for 1 d at 25 °C. The resulting suspension was filtered under inert conditions through celite to give a clear yellow solution. After removal of the solvent, complex [**7**] was isolated as yellow solid. Yield: 24 mg

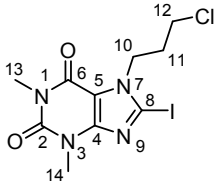
(0.015 mmol, 58%). ^{1}H NMR (400 MHz, THF-d_8): δ (ppm) = 7.71 (d, 1H, H15), 7.62–7.55 (m, 12H, Ph-H$_{ortho}$), 7.52 (s, 1H, H12), 7.49 (d, 1H, H16), 7.30–7.28 (m, 6H, Ph-H$_{para}$), 7.26 (m, 1H, H22), 7.20–7.18 (m, 12H, Ph-H$_{meta}$), 7.10 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H21), 4.86 (d, $^{2}J_{HH}$ = 13.6 Hz, 2H, H10a), 4.82 (d, $^{2}J_{HH}$ = 13.6 Hz, 2H, H10b), 4.78 (d, $^{2}J_{HH}$ = 14.0 Hz, 2H, H17a), 4.75 (d, $^{2}J_{HH}$ = 14.0 Hz, 2H, H17b), 3.80 (s, 3H, H25), 3.19 (s, 3H, H24), 3.04 (s, 3H, H23), 1.50 (s, 15H, Cp*-CH$_3$). ^{13}C{^{1}H} NMR (101 MHz, THF-d_8): δ (ppm) = 165.4 (t, $^{2}J_{CP}$ = 2.4 Hz, C8), 155.0 (C19), 154.3 (C6), 151.6 (C2), 151.5 (t, $^{4}J_{CP}$ = 1.5 Hz, C4), 148.9 (C15), 142.2 (C14), 140.4 (C13), 135.9–135.8 (Ph-C$_{ortho}$), 133.0–132.7 (Ph-C$_{ipso}$), 131.6 (C11), 130.8–130.7 (Ph-C$_{para}$), 129.2 (C16), 128.6 (vt, $^{3,5}J_{CP}$ = 5.23 Hz, Ph-C$_{meta}$), 126.1(C12), 121.9 (C21), 121.3 (C22). 109.5 8 (C5), 91 (Cp*-C), 57.7 (C17), 52.1 (C10), 39.9 (C25), 29.2 (C23), 27.5 (C24), 10.3 (Cp*-CH$_3$). ^{31}P{^{1}H} NMR (162 MHz, THF-d_8): δ (ppm) = 19.64 (s), 19.70 (s) (two doublets were expected but only two singlets were observed). HRMS (ESI, positive ions): m/z (%) = 1575.1342 (100, calcd for [[**7**]+H]$^{+}$ 1575.1334).

7. Synthesis ligand precursors H-9-I(Cl) and H-9-I(PF$_6$).



Scheme S3. Synthesis of ligand precursors **8**-I, H-**9**-I(Cl) and H-**9**-I(PF$_6$).

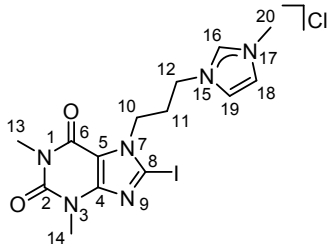
7.1. Synthesis of 8-I.



A mixture of 8-iodotheophylline (1.00 g, 3.27 mmol), and potassium carbonate (0.5 g, 3.62 mmol) was dissolved in dimethylformamide (10 mL). After stirring at ambient temperature for 1 h, 1-bromo-3-chloropropane (0.77 g, 4.89 mmol) was added. The resulting solution was stirred for 2 d at 25 °C. Subsequently, the solvent was removed and the resulting solid was extracted with chloroform (20 mL). Removal of the solvent from the extract yielded compound **8**-I as a colorless sold. Yield: 1.19 g, (3.11 mmol, 95%).

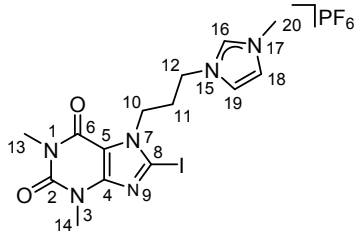
^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 4.46 (t, $^3J_{HH}$ = 7.28 Hz, 2H, H10), 3.62 (t, $^3J_{HH}$ = 6.34 Hz, 2H, H12), 3.56 (s, 3H, H14), 3.39 (s, 3H, H13), 2.31 (m, 2H, H11). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 153.9 (C6), 151.2 (C2), 150.1 (C4), 110.1 (C5), 100.2 (C8), 47.3 (C10), 41.3 (C12), 33.1 (C11), 29.9 (C14), 28.1 (C13). HRMS (ESI, positive ions): *m*/*z* (%) = 404.9586 (100, calcd for [**8**-I+Na]$^+$ 404.9591).

7.2. Synthesis of H-9-I(Cl).



A mixture of **8**-I (1.19 g, 3.11 mmol) and 1-methylimidazole (2.59 mL, 2.67 g, 32.5 mmol) was dissolved in acetonitrile (10 mL). The mixture was stirred at ambient temperature for 24 h. A white precipitate formed over this period which was isolated by filtration and washed with acetonitrile (15 mL) to give H-**9**-I(Cl) as a colorless powder Yield: 1.43 g (3.08 mmol, 99%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.23 (s, 1H, H16), 7.83 (d, $^3J_{HH}$ = 1.7 Hz, 1H, H19), 7.74 (d, $^3J_{HH}$ = 1.7 Hz, 1H, H18), 4.25 (m, 4H, H10, H12), 3.88 (s, 3H, H20), 3.39 (s, 3H, H14), 3.20 (s, 3H, H13), 2.31 (m, 2H, H11). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) = 153.2 (C6), 150.6 (C2), 149.4 (C4), 136.8 (C16), 123.5 (C18), 122.2 (C19), 108.7 (C5), 108.1 (C8), 45.8 (C12), 45.3 (C10), 35.8 (C20), 30.1 (C11), 29.4 (C14), 27.5 (C13). HRMS (ESI, positive ions): *m*/*z* (%) = 429.0526 (100, calcd for [H-**9**-I]$^+$ 429.0536).

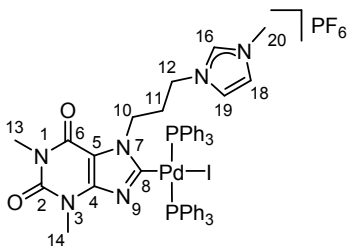
7.3. Synthesis von H-9-I(PF_6).



A sample of H-**9**-I(Cl) (0.30 g, 0.65 mmol) was suspended in methanol (10 mL) and NH_4PF_6 (1.05 g, 6.44 mmol) was added to the suspension. The reaction mixture was stirred for 18 h at ambient temperature. After filtration the solid residue was washed with a small amount of methanol (10 mL) to give H-**9**-I(PF_6) as a colorless powder. Yield: 128 mg (0.22 mmol, 34%). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 9.11 (s br, 1H, H16), 7.79 (s br, 1H, H19), 7.70 (s br, 1H, H18), 4.26 (m, 4H, H10, H12), 3.84 (s, 3H, H20), 3.40 (s, 3H, H14), 3.22 (s, 3H, H13), 2.30 (m, 2H, H11). ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ (ppm) = 153.2 (C6), 150.6 (C2), 149.3 (C4), 136.8 (C16), 123.5 (C18), 122.2 (C19), 109.0 (C5), 105.1 (C8), 45.8 (C12), 45.5 (C10), 35.7 (C20), 30.1 (C11), 29.4 (C14),

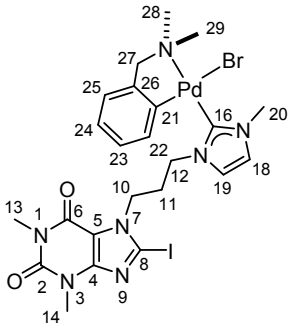
27.6 (C13). $^{19}F\{^{1}H\}$ NMR (376 MHz, DMSO-d_6): δ (ppm) = – 70.2 (d, $^{1}J_{FP}$ = 711.4 Hz). $^{31}P\{^{1}H\}$ NMR (162 MHz, DMSO-d_6): δ (ppm) = –144.2 (sep, $^{1}J_{PF}$ = 711.4 Hz). HRMS (ESI, positive ions): *m*/*z* (%) = 429.0527 (100, calcd for [H-**9**-I]$^{+}$ 429.0536).

8. Synthesis of complex [10](PF$_6$).



Samples of H-**9**-I(PF$_6$) (14 mg, 0.024 mmol) and [Pd(PPh$_3$)$_4$] (28 mg, 0.025 mmol) were dissolved in freshly distilled tetrahydrofuran and the solution was stirred at 35 °C for 1 h. Subsequently, the reaction mixture was stirred for another 18 h at 25 °C. After removal of the solvent, the residue was washed with dry diethyl ether (2 × 10 mL) and *n*-hexane (2 × 10 mL) to give complex [**10**] as colourless solid. Yield: 18 mg (0.015 mmol, 62%). ^{1}H NMR (400 MHz, CD_2Cl_2): δ (ppm) = 8.82 (s br, 1H, H16), 7.58 (m, 12H, Ph-H$_{ortho}$), 7.41 (m, 1H, H19), 7.40 (m, 6H, Ph-H$_{para}$), 7.33 (m, 12H, Ph-H$_{meta}$), 7.25 (d, $^{3}J_{HH}$ = 1.8 Hz, 1H, H18), 3.97 (t, $^{3}J_{HH}$ = 6.6 Hz, 2H, H12), 3.92 (s, 3H, H20), 3.83 (t, $^{3}J_{HH}$ = 7.5 Hz, 2H, H10), 3.21 (s, 3H, H13), 3.19 (s, 3H, H14), 1.69 (m, 2H, H11). ^{13}C NMR (101 MHz, CD_2Cl_2): δ (ppm) = 166.5 (t, $^{2}J_{CP}$ = 3.3 Hz, C8), 153.9 (C6), 151.2 (C2), 152.1 (t, $^{4}J_{CP}$ = 1.2 Hz, C4), 136.8 (C16), 135.1 (vt, $^{2,4}J_{CP}$ = 6.2 Hz, Ph-C$_{ortho}$), 131.6 (vt, $^{1,3}J_{PC}$ = 24.7 Hz, Ph-C$_{ipso}$), 131.0 (Ph-C$_{para}$), 128.5 (vt, $^{3,5}J_{CP}$ = 5.2 Hz, Ph-C$_{meta}$), 123.7 (C19), 123.1 (C18), 109.6 (C5), 45.5 (C12), 44.8 (C10), 36.9 (C20) 30.0 (C11), 29.6 (C14), 27.8 (C13). $^{31}P\{^{1}H\}$ NMR (162 Hz, CD_2Cl_2): δ (ppm) = 18.1 (s, PPh$_3$), –144.2 (sep, $^{1}J_{PF}$ = 711 Hz, PF$_6$). $^{19}F\{^{1}H\}$ NMR (376 Hz, CD_2Cl_2): δ (ppm) = –72.3 (d, $^{1}J_{FP}$ = 711 Hz). HRMS (ESI, positive ions): *m*/*z* (%) = 1059.1427 (60, calcd for [**10**]$^{+}$ 1059.1411).

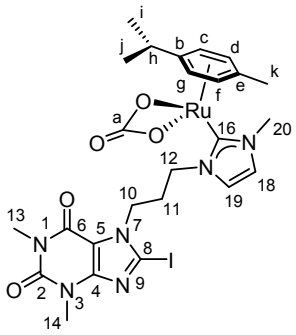
9. Synthesis of complex [11].



A sample of H-**9**-I(Cl) (50 mg, 0.11 mmol) was suspended together with with potassium carbonate (55 mg, 0.40 mmol), potassium bromide (13 mg, 0.11 mmol) and [Pd(dmba)Cl]$_2$ (28 mg, 0.05 mmol) in 10 mL of acetonitrile. The reaction mixture was stirred for 18 h at 60 °C. The solvent was then removed and the residue was dissolved in a small amount of dichloromethane (5 mL). This solution was filtered through small plug of Celite. Column chromatography (dichloromethane:methanol 95:5) gave

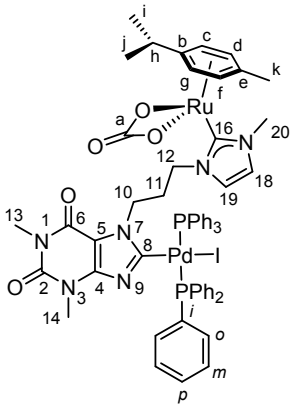
[**11**] as a yellow solid. Yield: 22 mg (0.03 mmol, 60%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.07 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H19), 6.99 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H18), 6.94 (m, 1H, H25), 6.89 (m, 1H, H24), 6.67 (dt, $^{4}J_{HH}$ = 1.7 Hz, $^{3}J_{HH}$ = 7.3 Hz, 1H, H23), 5.76 (dd, $^{4}J_{HH}$ = 1.2 Hz, $^{3}J_{HH}$ = 7.5 Hz, 1H, H22), 4.51 (m, 1H, H12a), 4.41 (m, 1H, H12b), 4.40 (m, 1H, H10a), 4.31 (m, 1H, H10b), 3.95 (d, $^{2}J_{HH}$ = 14.0 Hz, 1H, H27a), 3.89 (s, 3H, H20), 3.74 (d, $^{2}J_{HH}$ = 14.0 Hz, 1H, H27b), 3.51 (s, 3H, H14), 3.32 (s, 3H, H13), 2.97 (s, 3H, H28), 2.85 (s, 3H, H29), 2.55 (m, 1H, H11a), 2.29 (m, 1H, H11b). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 172.7 (C16), 153.7 (C6), 153.0 (C21), 151.1 (C2), 149.8 (C4), 148.6 (C26), 134.6 (C22), 125.4 (C23), 124.0 (C24), 122.7 (C18) 122.2 (C25), 120.4 (C19), 110.0 (C5), 100.5 (C8), 71.7 (C27), 52.9 (C29), 52.9 (C28), 48.4 (C12), 47.0 (C10), 38.8 (C20), 30.8 (C11), 29.8 (C14), 28.8 (C13). HRMS (ESI, positive ions): *m*/*z* (%) = 668.0464 (100, calcd for [[**11**]–Br]$^{+}$ 668.0471).

10. Synthesis of complex [12].



A mixture of H-**9**-I(Cl) (25 mg, 0.054 mmol) and silver(I)oxide (25 mg, 0.11 mmol) was suspended in dichloromethane (10 mL). The mixture was stirred for 2 h at 25 °C under exclusion of light. Subsequently, [$RuCl_2$(*p*-cymene)]$_2$ (16.5 mg, 0.027 mmol) was added and the mixture was stirred at ambient temperature for 12 h. The mixture was then filtered through celite and the solvent was removed *in vacuo* to give [**12**] as a yellow solid. Yield: 24 mg (0.033 mmol, 61%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) = 7.04 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H18), 7.00 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H19), 5.49 and 5.48 (d, 2H, H_g and H_c), 5.21 and 5.18 (d, 2H, H_f and H_d), 4.55 (m, 1H, H10a), 4.44 (m, 1H, 12a), 4.17 (m, 1H, H10b), 3.97 (m, 1H, 12b), 3.73 (s, 3H, H20), 3.53 (s, 3H, H14), 3.36 (s, 3H, H13), 2.75 (m, 1H, H_h), 2.36 (m, 1H, H11a), 2.16 (m, 1H, H11b), 2.02 (s, 3H, H_k), 1.25 (m, 3H, H_i), 1.24 (m, 3H, H_j). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ (ppm) = 178.6 (C16), 166.5 (C_a), 153.9 (C6), 151.3 (C2), 150.0 (C4), 123.6 (C18), 120.4 (C19), 110.1 (C8), 107.5 (C_b), 102.0 (C5), 96.0 (C_e), 82.5–80.7 (C_c, C_d, C_f, C_g), 47.9 (C12), 47.1 (C10), 37.8 (C20), 31.8 (C11), 31.7 (C_h), 29.8 (C14), 28.0 (C13) 22.8 (C_i), 22.6 (C_j), 18.9 (C_k).

11. Synthesis of complex [13].



A mixture of [**10**] (22 mg, 0.030 mmol) and [$Pd(PPh_3)_4$] (37 mg, 0.030 mmol) was dissolved in freshly distilled tetrahydrofuran. The mixture was stirred at ambient temperature for 3 d. Subsequently, the solvent was removed and the solid residue was washed with tetrahydrofuran (3 × 10 mL) and diethyl ether (1 × 10 mL). The residue was then dried *in vacuo* to give [**13**] as colorless solid. Yield: 23 mg (0.017 mmol, 57%). ^{1}H NMR (400 MHz, MeOH-d_4): δ (ppm) = 7.71 (m, 12H, Ph-H_{ortho}), 7.47 (m, 6H, Ph-H_{para}), 7.40 (m, 12H, Ph-H_{meta}), 7.27 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H18), 6.41 (d, $^3J_{HH}$ = 1.8 Hz, 1H, H19), 5.83 (d, $^3J_{HH}$ = 5.9 Hz, 2H, H_c and H_g), 5.54 (d, $^3J_{HH}$ = 5.9 Hz, 1H, H_d), 5.49 (d, $^3J_{HH}$ = 5.9 Hz, 1H, H_f), 4.41 (m, 1H, H10a), 4.11 (m, 1H, H12a), 3.98 (m, 1H, H12b), 3.94 (m, 1H, H10b), 3.76 (s, 3H, H20), 3.27 (s, 3H, H13), 3.16 (s, 3H, H14), 2.86 (m, 1H, H_h), 2.05 (s, 3H, H_k), 2.01 (m, 1H, H11a), 1.81 (m, 1H, H11b), 1.33 (m, 6H, H_i and H_j). ^{13}C{^{1}H} NMR (101 MHz, MeOH-d_4): δ (ppm) = 178.4 (C16), 168.8 (t, $^2J_{CP}$ = 4.5 Hz, C8), 168.5 (C_a), 154.6 (C6), 152.5 (C2), 152.5 (C4), 136.2 and 136.1 (dd, $^2J_{CP}$ = 7.2 Hz, $^4J_{CP}$ = 5.4 Hz, Ph-C_{ortho}), 132.9 and 132.5 (dd, $^1J_{CP}$ = 30.2 Hz, $^3J_{CP}$ = 19.7 Hz, Ph-C_{ipso}), 132.1 and 131.9 (Ph-C_{para}), 129.4 and 129.3 (dd, $^3J_{CP}$ = 6.3 Hz, $^5J_{CP}$ = 4.2 Hz, Ph-C_{meta}), 125.2 (C18), 121.6 (C19), 110.9 (C5), 109.5 (C_b), 98.6 (C_e), 84.9 (C_c or C_g), 83.4 (C_c or C_g), 81.6 (C_d or C_f), 81.1 (C_d or C_f), 49.2 (C12), 47.4 (C10), 38.2 (C20), 33.4 (C11), 33.1 (C_h), 30.0 (C14), 28.1 (C13), 23.4 (C_i or C_j), 22.8 (C_i or C_j), 19.1 (C_k). ^{31}P{^{1}H} NMR (162 Hz, MeOH-d_4): δ (ppm) = 19.8 and 19.7 (d, $^2J_{PP}$ = 450 Hz). HRMS (ESI, positive ions): *m*/*z* (%) = 965.1385 (5, calcd for [[**13**]–I–PPh_3]$^+$ 965.1369).

12. X-ray crystallography.

X-ray diffraction data were collected with a Bruker AXS APEXII CCD diffractometer equipped with a microsource using graphite-monochromated Mo Kα (λ = 0.71073 Å) or Cu Kα (λ = 1.154178 Å). Semiemperical multi-scan absorption corrections were applied to all data sets.[S2,S3] Structure solutions were found with SHELXT (intrinsic phasing)[S4] and were refined with SHELXL[S5] against $|F^2|$ of all data using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms have been added to the structure models on calculated positions.

*Crystal Data for [**3**]$PF_6 \cdot CH_2Cl_2$*. Single crystals were grown at ambient temperature by vapor diffusion of diethyl ether into a saturated solution of [**3**]PF_6 in CH_2Cl_2. Crystal Data for [**1**]$PF_6 \cdot CH_2Cl_2$: Formula $C_{46}H_{43}N_4Cl_3F_6P_2Pt$, M = 1129.224 g·mol^{-1}, colorless needle, 0.53 × 0.09 × 0.06 mm^3, a = 11.3321(3), b = 25.8698(6), c = 16.9685(4) Å, β = 99.1760(10)°, V = 4910.87(2) Å^3, Mo Kα radiation, ρ_{calc} = 1.525 g·cm^{-3}, μ = 3.144 mm^{-1}, monoclinic, space group $P2_1/n$, Z = 4, empirical absorption correction ($0.61 \le T \le 0.75$), T = 100(2) K, ω and φ scans, 74126 intensities collected ($4.0° \le 2\theta \le 56.1°$), 11862 unique intensities (R_{int} = 0.0733) and 9873 observed intensities ($I \ge 2\sigma(I)$), refinement of 572 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. R = 0.0430, R_w = 0.0908, R_{all} = 0.0546, $R_{w,all}$ = 0.0953. The asymmetric unit contains one formula unit [**3**]PF_6 and one molecule of CH_2Cl_2. One of the chloratoms of the dichloromethane molecule is disordered. No hydrogen positions were calculated for the disordered dichloromethane molecule.

*Crystal Data for [**6**]·2CH_3CN*. Single crystals were grown at ambient temperature from an acetonitrile solution of [**6**]. Crystal Data for [**6**]·2CH_3CN: Formula $C_{33}H_{39}N_8I_2Ir_1O_2$, M = 1025.72 g·mol^{-1}, orange block, 0.24 × 0.09 × 0.08 mm^3, a = 8.4757(2), b = 15.2789(3), c = 15.8657(3) Å, α = 116.8130(10), β = 105.4610(10), γ = 91.0970(10)°, V = 1743.98(6) Å^3, Mo Kα radiation, ρ_{calc} = 1.953 g·cm^{-3}, μ = 5.641 mm^{-1}, triclinic, space group $P\bar{1}$, Z = 2, empirical absorption correction ($0.49 \le T \le 0.75$), T = 100(2) K, ω and φ scans, 33039 intensities collected ($3.0° \le 2\theta \le 64.6°$), 11192 unique intensities (R_{int} = 0.0303) and 10273 observed intensities ($I \ge 2\sigma(I)$), refinement of 425 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. R = 0.0231, R_w = 0.0513, R_{all} = 0.0265, $R_{w,all}$ = 0.0525. The asymmetric unit contains one

formula unit [**6**] and two molecules of CH_3CN.

Crystal Data for [7]. Single crystals were grown at ambient temperature slow evaporation of the solvent from a THF solution of [**7**]. Crystal Data for [**7**]: Formula $C_{65}H_{63}N_6I_2IrO_2P_2Pd$, M = 1574.55 g·mol^{-1}, orange prism, 0.12 × 0.10 × 0.07 mm^3, a = 24.6695(6), b = 13.7796(3), c = 24.9858(6) Å, β = 110.6220(10)°, V = 7949.3(3) Å^3, Cu Kα radiation, ρ_{calc} = 1.316 g·cm^{-3}, μ = 11.789 mm^{-1}, monoclinic, space group $P2_1/n$, Z = 4, empirical absorption correction (0.39 ≤ T ≤ 0.49), T = 100(2) K, ω and φ scans, 127354 intensities collected (7.4° ≤ 2θ ≤ 133.8°), 14061 unique intensities (R_{int} = 0.1724) and 9470 observed intensities ($I \geq 2\sigma(I)$), refinement of 720 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. R = 0.0514, R_w = 0.1184, R_{all} = 0.0828, $R_{w,all}$ = 0.1334. The asymmetric unit contains one formula unit [**7**].

*Crystal Data for [**10**]$PF_6 \cdot CH_2Cl_2$*. Single crystals were grown at ambient temperature by vapor diffusion of diethyl ether into a saturated solution of [**3**]PF_6 in CH_2Cl_2. Crystal Data for [**10**]$PF_6 \cdot CH_2Cl_2$: Formula $C_{51}H_{50}N_6Cl_2F_6IO_2P_3Pd$, M = 1290.08 g·mol^{-1}, colorless prism, 0.24 × 0.16 × 0.10 mm^3, a = 14.3613(8), b = 20.3225(8), c = 18.2235(8) Å, β = 101.367(5)°, V = 5214.3(4) Å^3, ρ_{calc} = 1.643 g·cm^{-3}, μ = 1,211 mm^{-1}, monoclinic, space group $P2_1/n$, Z = 4, empirical absorption correction (0.17 ≤ T ≤ 0.21), T = 100(2) K, ω and φ scans, 97532 intensities collected (3.5° ≤ 2θ ≤ 63.2°), 16999 unique intensities (R_{int} = 0.0587) and 14188 observed intensities ($I \geq 2\sigma(I)$), refinement of 652 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. R = 0.0317, R_w = 0.0746, R_{all} = 0.0416, $R_{w,all}$ = 0.0797. The asymmetric unit contains one formula unit [**10**]PF_6 and one molecule of CH_2Cl_2. The checkcif file features an A level alert (peak of 4.73 eÅ^3 0.87 Å from I1). This peak has no physical meaning and the observation of strong residual peaks in close proximity to very heavy atoms is not uncommon. A statement regarding this situation has been added to the cif file.

*Crystal Data for [**11**]$\cdot Et_2O$*. Single crystals were grown at ambient temperature by vapor diffusion of diethyl ether into a saturated solution of [**10**] in CH_2Cl_2. Crystal Data for [**10**]$\cdot Et_2O$: Formula $C_{27}H_{39}N_7O_3Pd$, M = 822.86 g·mol^{-1}, colorless block, 0.42 × 0.21 × 0.11 mm^3, a = 9.8219(3), b = 12.6068(3), c = 25.4527(7) Å, β = 97.735(2)°, V = 3126.09(15) Å^3, ρ_{calc} = 1.748 g·cm^{-3}, μ = 2.899

mm^{-1}, monoclinic, space group $P2_1/c$, $Z = 4$, empirical absorption correction ($0.58 \leq T \leq 0.75$), $T =$ 100(2) K, ω and φ scans, 53986 intensities collected ($3.6° \leq 2\theta \leq 54.4°$), 6961 unique intensities ($R_{int} = 0.0499$) and 6111 observed intensities ($I \geq 2\sigma(I)$), refinement of 341 parameters against $|F^2|$ of all independent intensities with hydrogen atoms on calculated positions. $R = 0.0606$, $R_w = 0.1580$, $R_{all} = 0.0685$, $R_{w,all} = 0.1642$. The asymmetric unit contains one formula unit [**11**] and one molecule of diethyl ether. The positional parameters of the diethyl ether molecule were refined with isotropic thermal parameters and no hydrogen positions were calculated for the diethyl ether molecule.

CCDC 2008111 ([**3**]$PF_6 \cdot CH_2Cl_2$), 2008110 ([**6**]$\cdot 2CH_3CN$), 2008112 ([**7**]), 2008113 ([**10**]$PF_6 \cdot CH_2Cl_2$) and 2008114 ([**11**]$\cdot Et_2O$) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

11. NMR spectra of all new compounds.

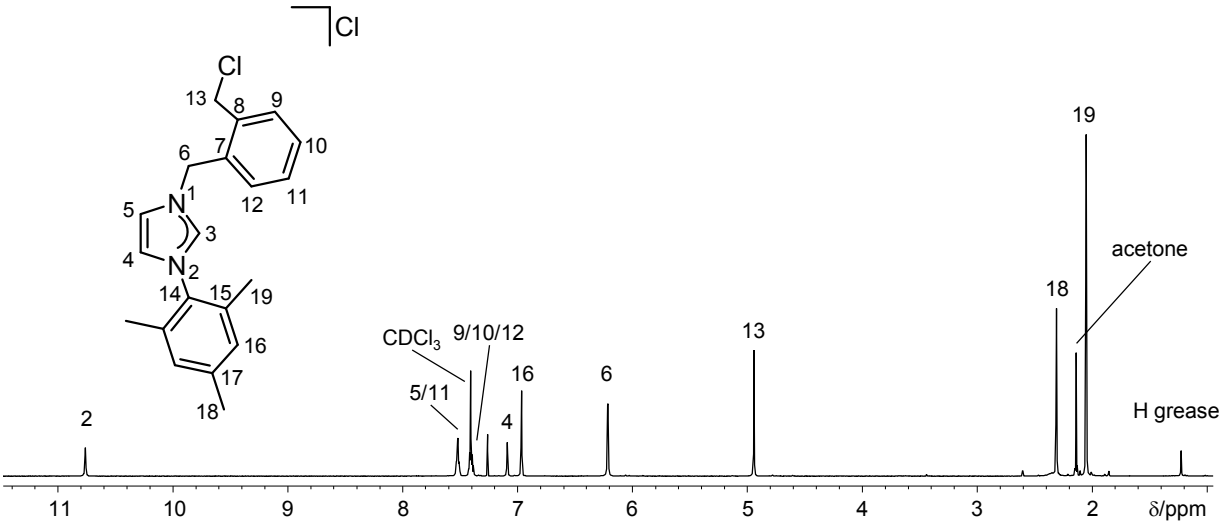


Figure S1. ^{1}H NMR spectrum of H-**1**(Cl) (400 MHz, $CDCl_3$).

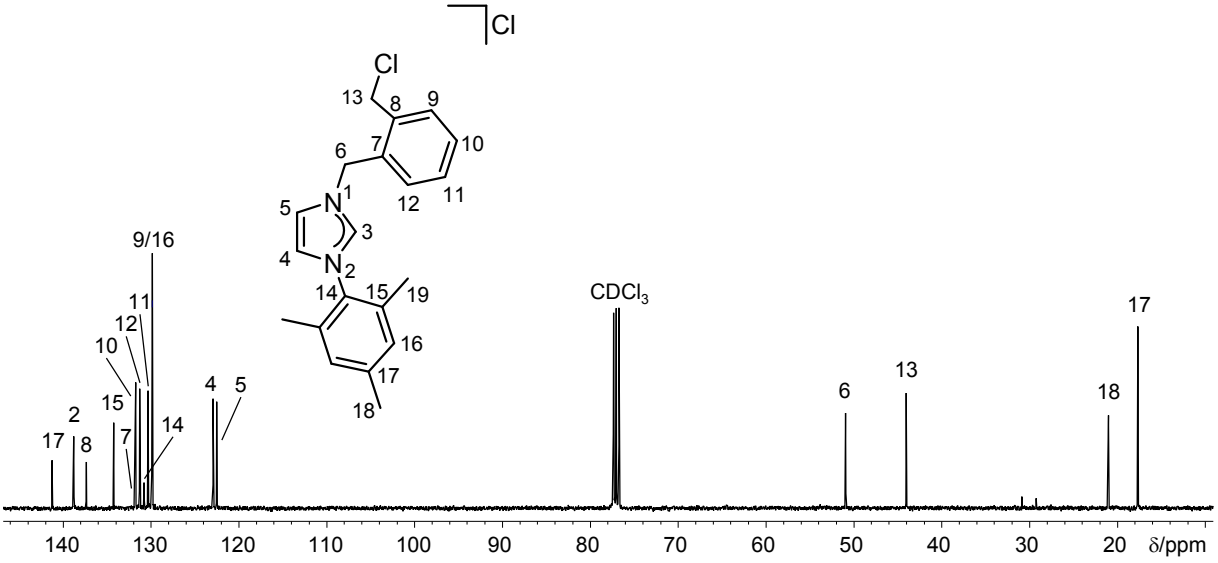


Figure S2. ^{1}H NMR spectrum of H-**1**(Cl) (101 MHz, $CDCl_3$).

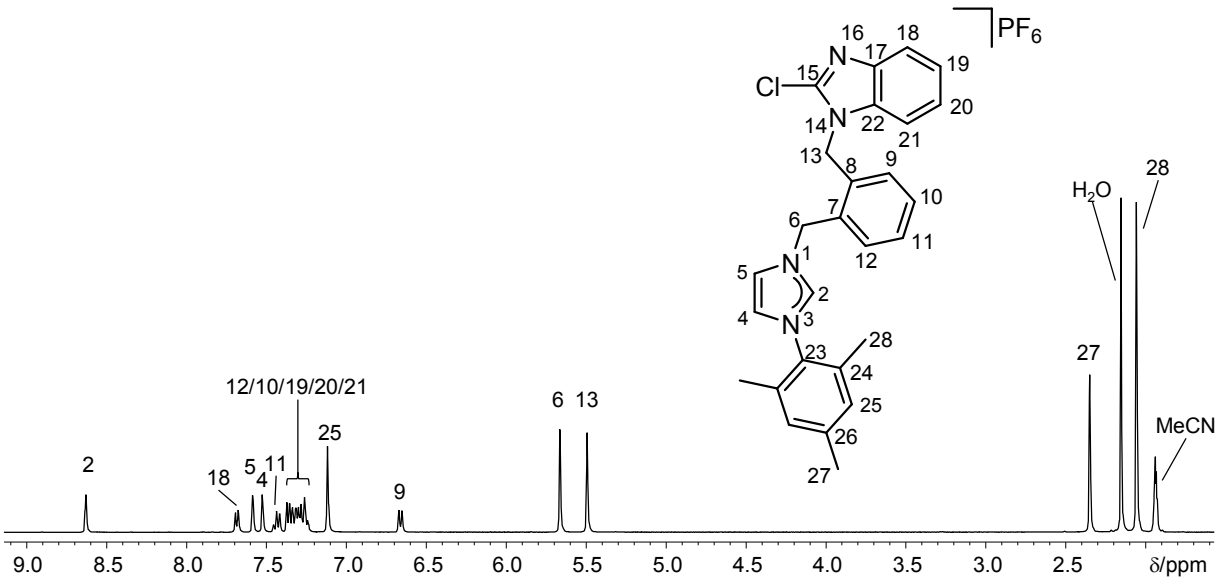


Figure S3. ^{1}H NMR spectrum of H-**2**(PF_6) (400 MHz, CD_3CN).

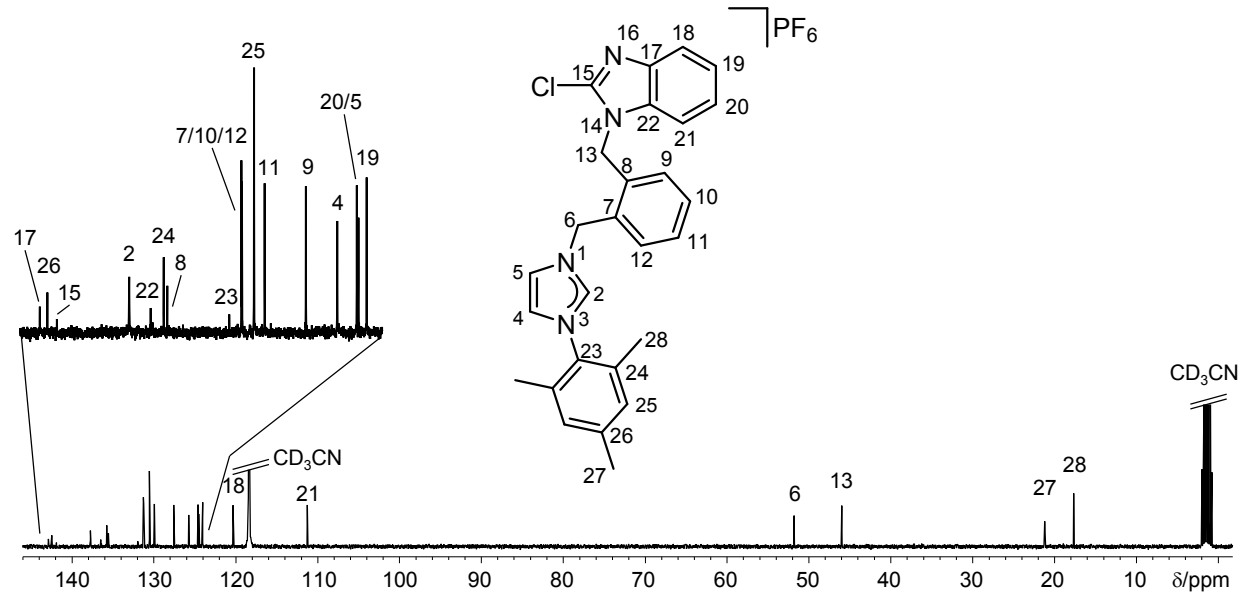


Figure S4. ^{13}C NMR spectrum of H-**2**(PF_6) (101 MHz, CD_3CN).

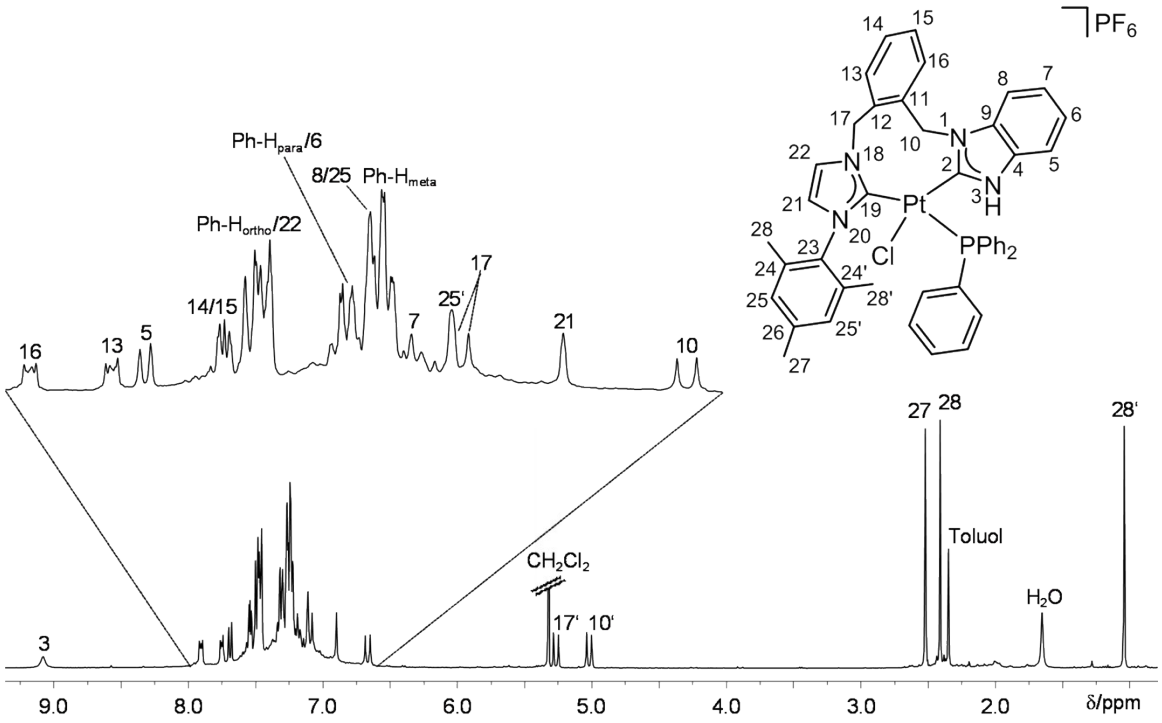


Figure S5. ^{1}H NMR spectrum of [**3**](PF_6) (400 MHz, CD_2Cl_2).

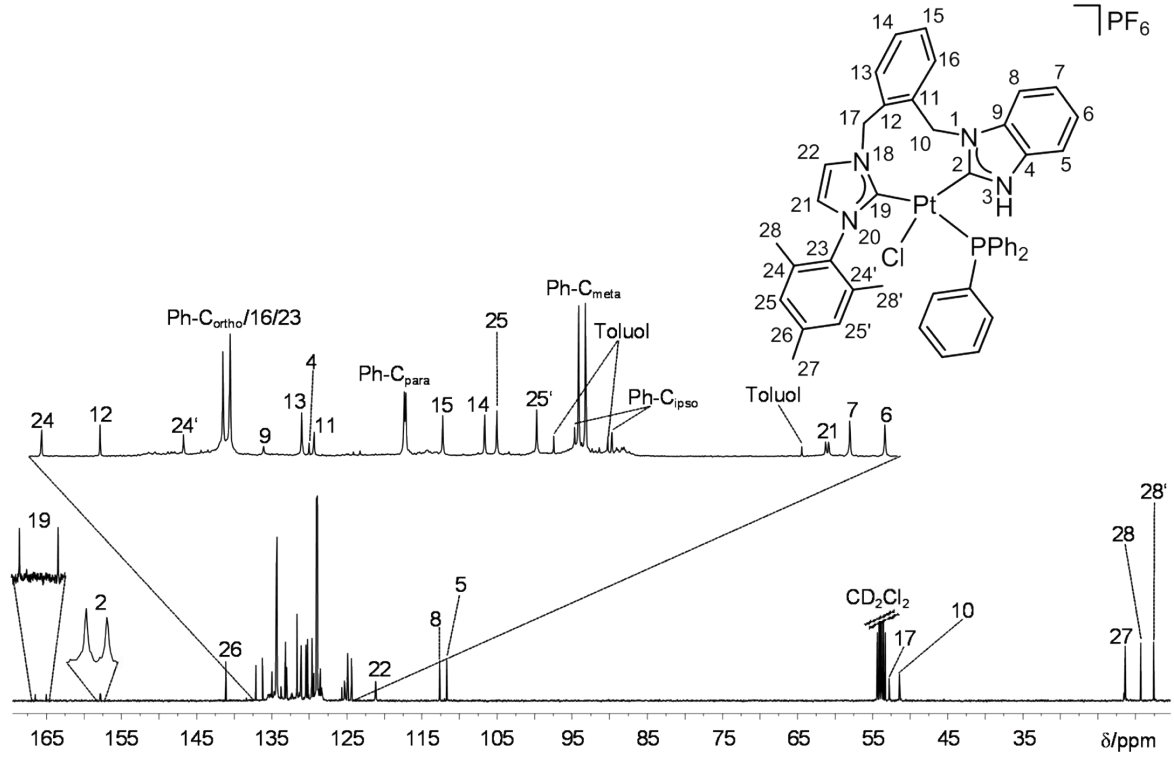


Figure S6. ^{13}C NMR spectrum of [**3**](PF_6) (101 MHz, CD_2Cl_2).

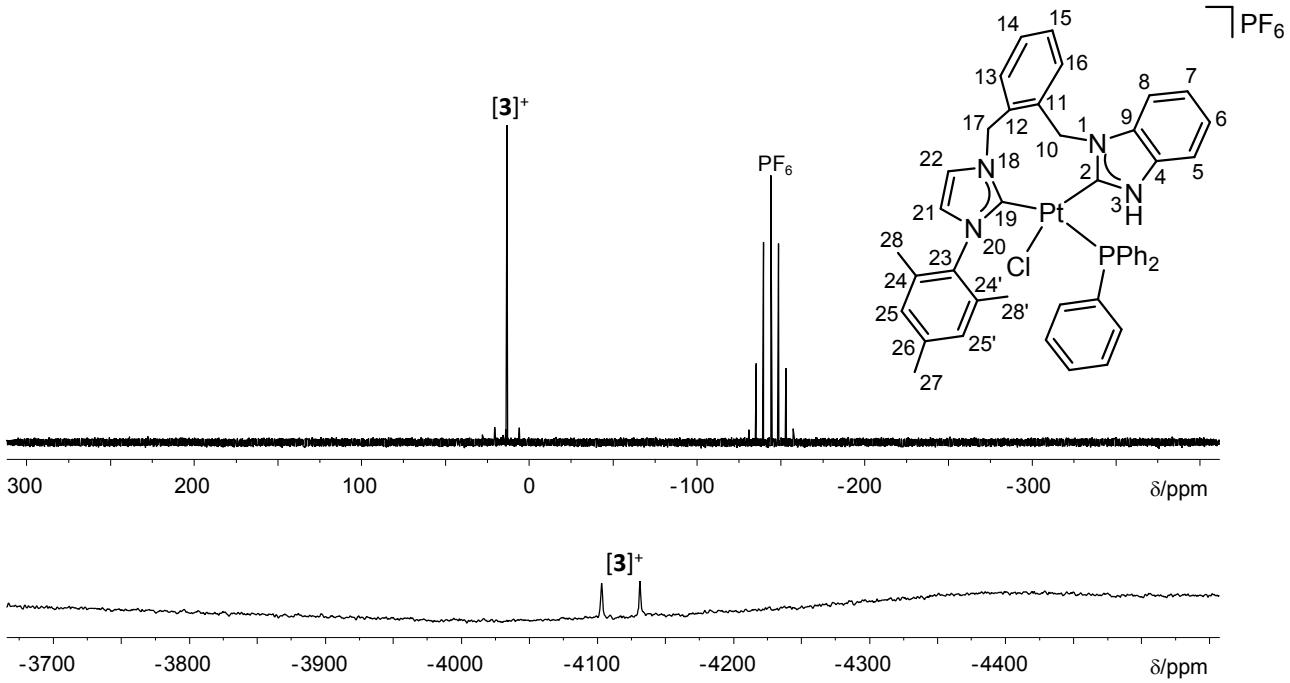


Figure S7. ^{31}P NMR spectrum (top) and ^{195}Pt NMR spectrum (bottom) of [**3**](PF_6) (162 MHz, 86 MHz, CD_2Cl_2).

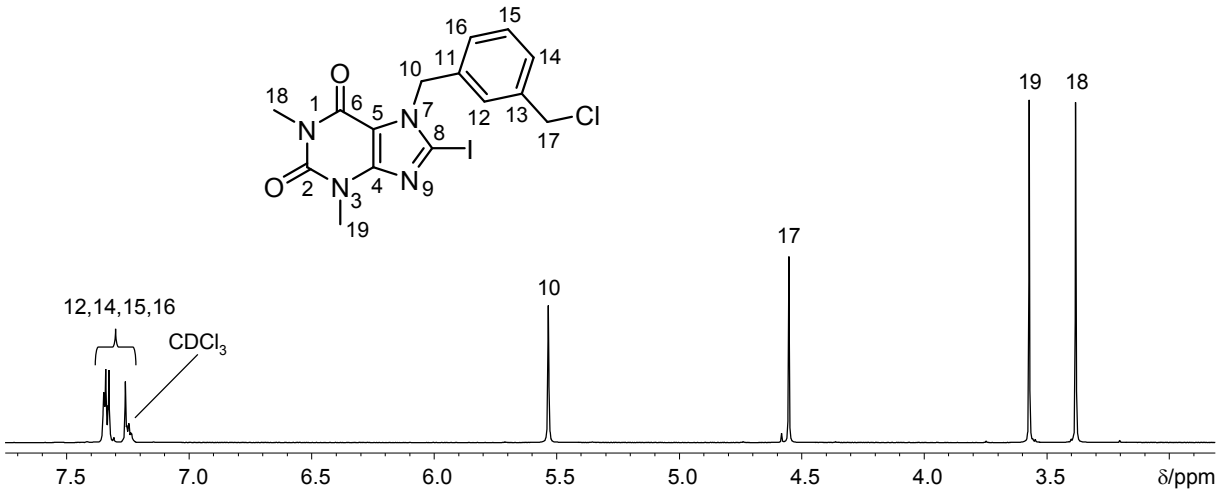


Figure S8. ^{1}H NMR spectrum of **4**-I (400 MHz, $CDCl_3$).

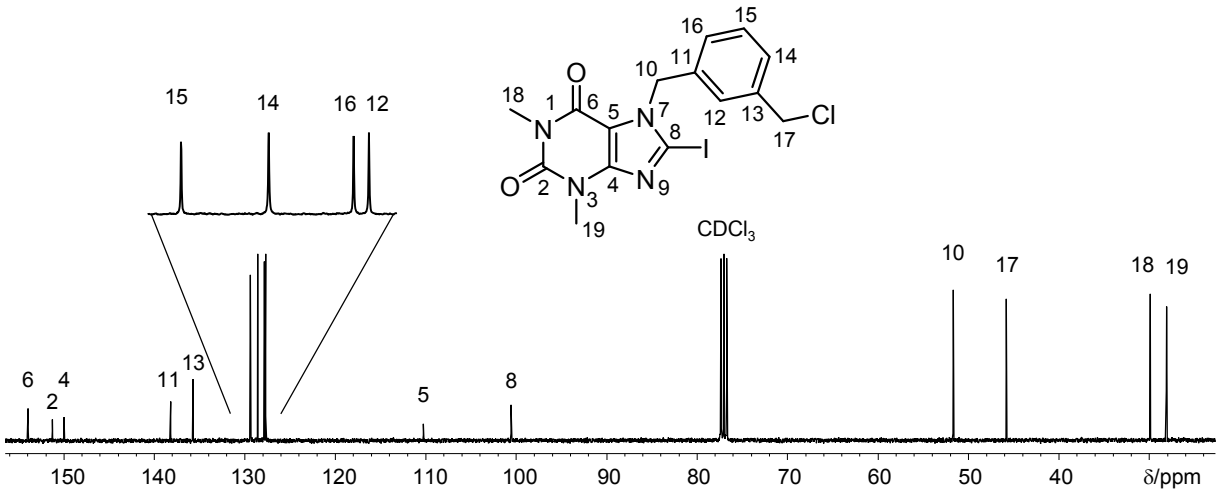


Figure S9. $^{13}C\{^{1}H\}$ NMR spectrum of **4**-I (101 MHz, $CDCl_3$).

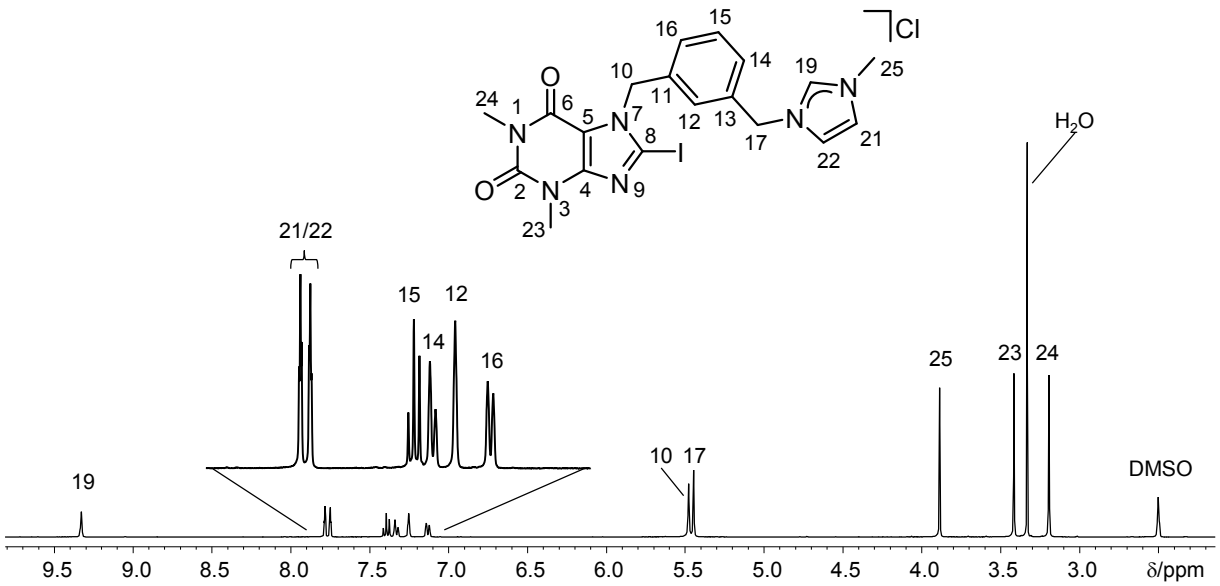


Figure S10. ^{1}H NMR spectrum of H-**5**-I(Cl) (400 MHz, DMSO-d_6).

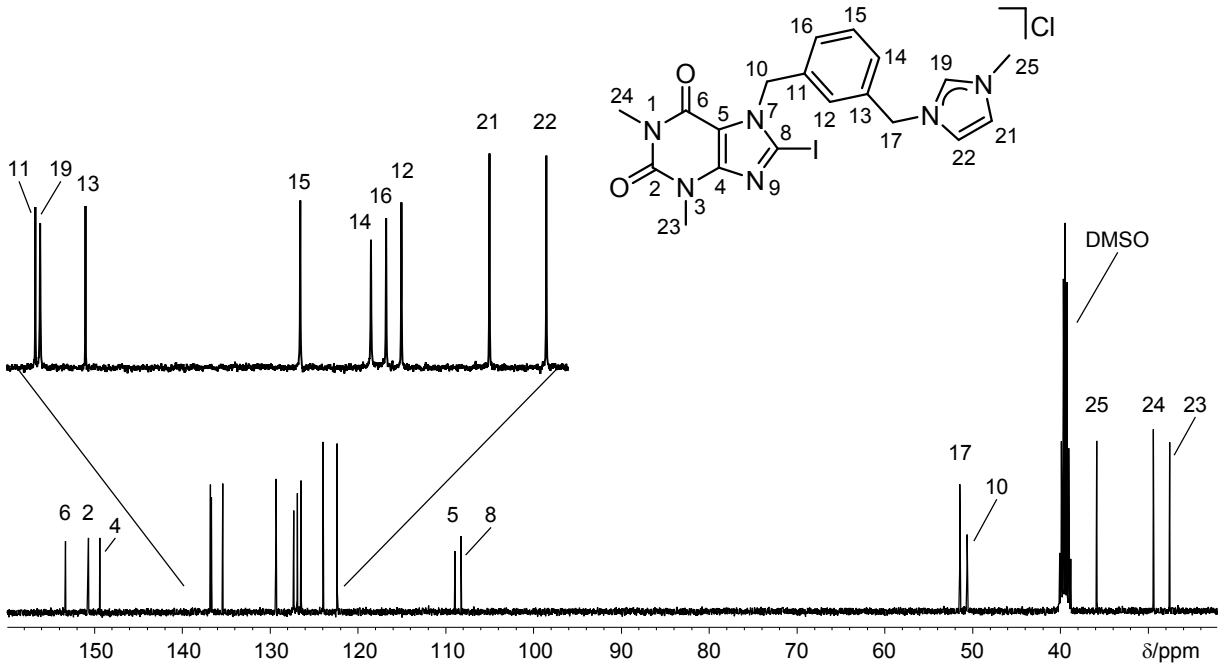


Figure S11. $^{13}C\{^{1}H\}$ NMR spectrum of H-**5**-I(Cl) (101 MHz, DMSO-d_6).

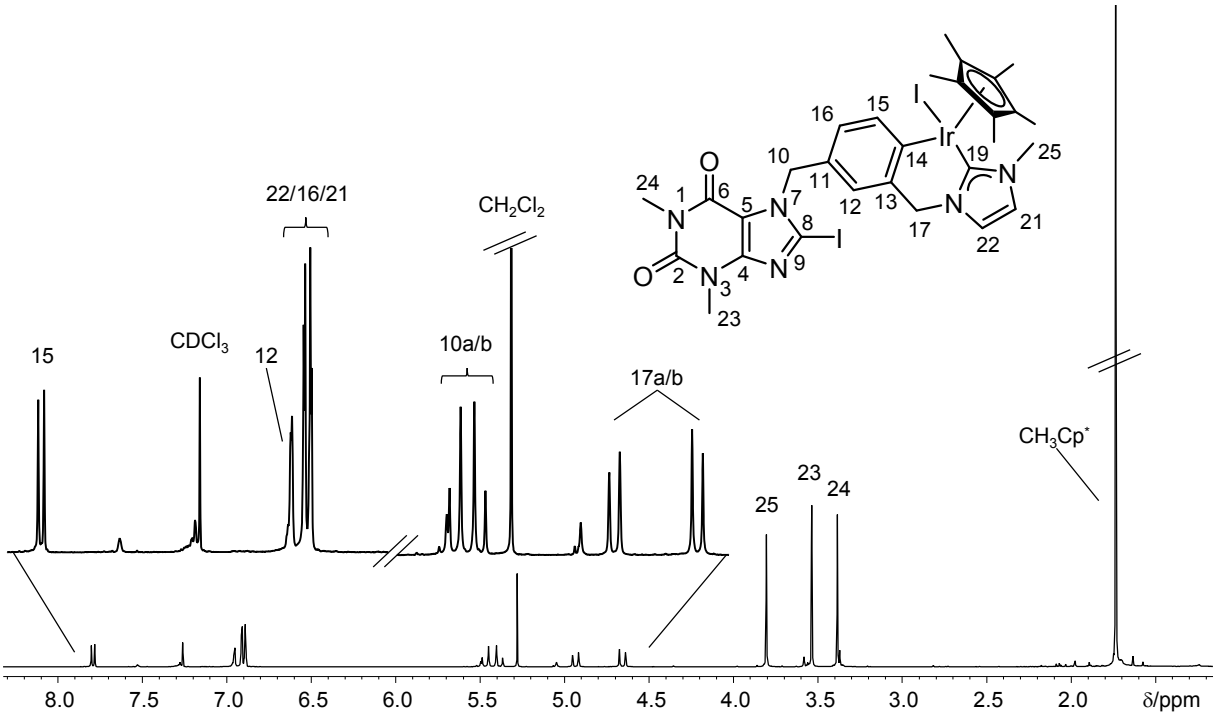


Figure S12. ^{1}H NMR spectrum of [**6**] (400 MHz, $CDCl_3$).

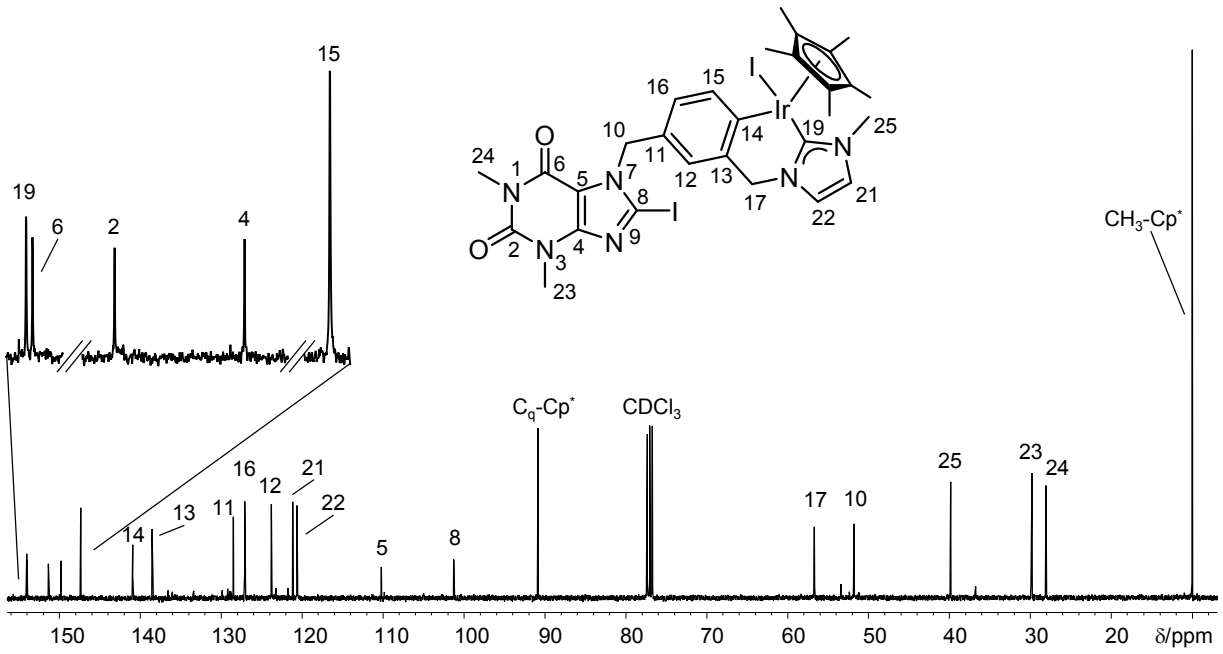


Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of [**6**] (101 MHz, $CDCl_3$).

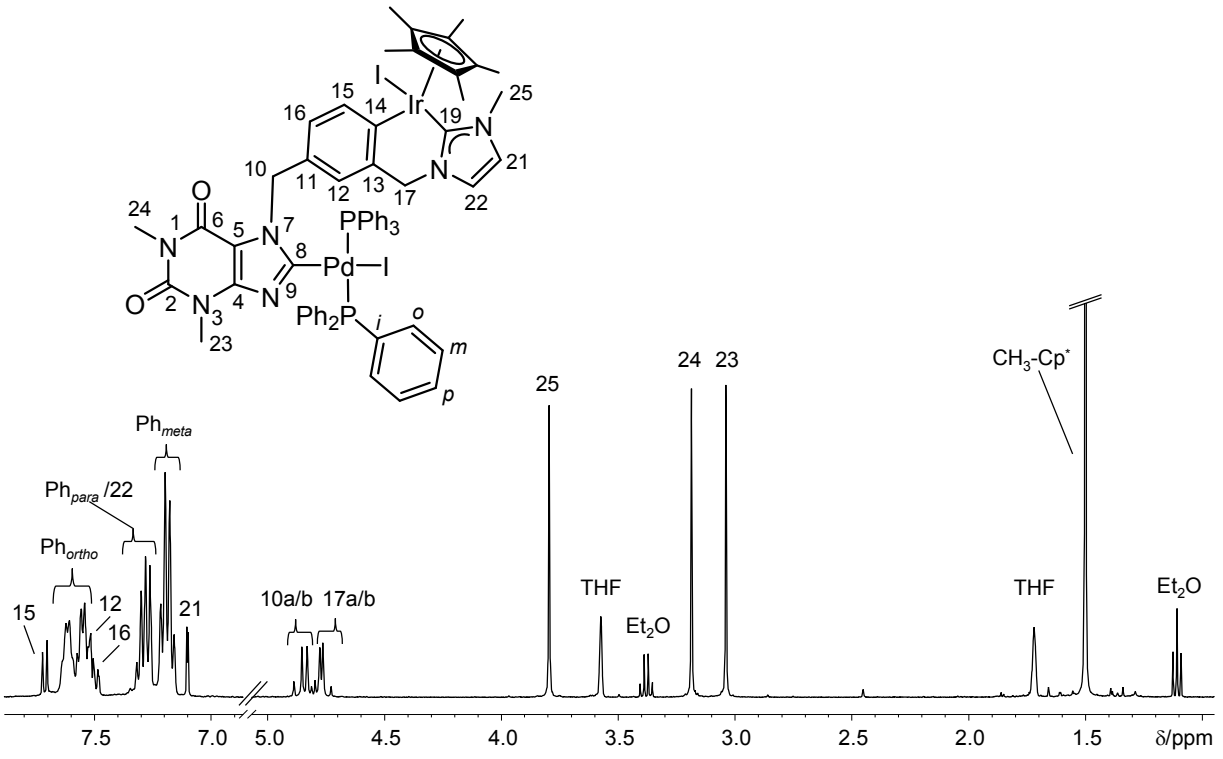


Figure S14. ^{1}H NMR spectrum of [**7**] (400 MHz, THF-d_8).

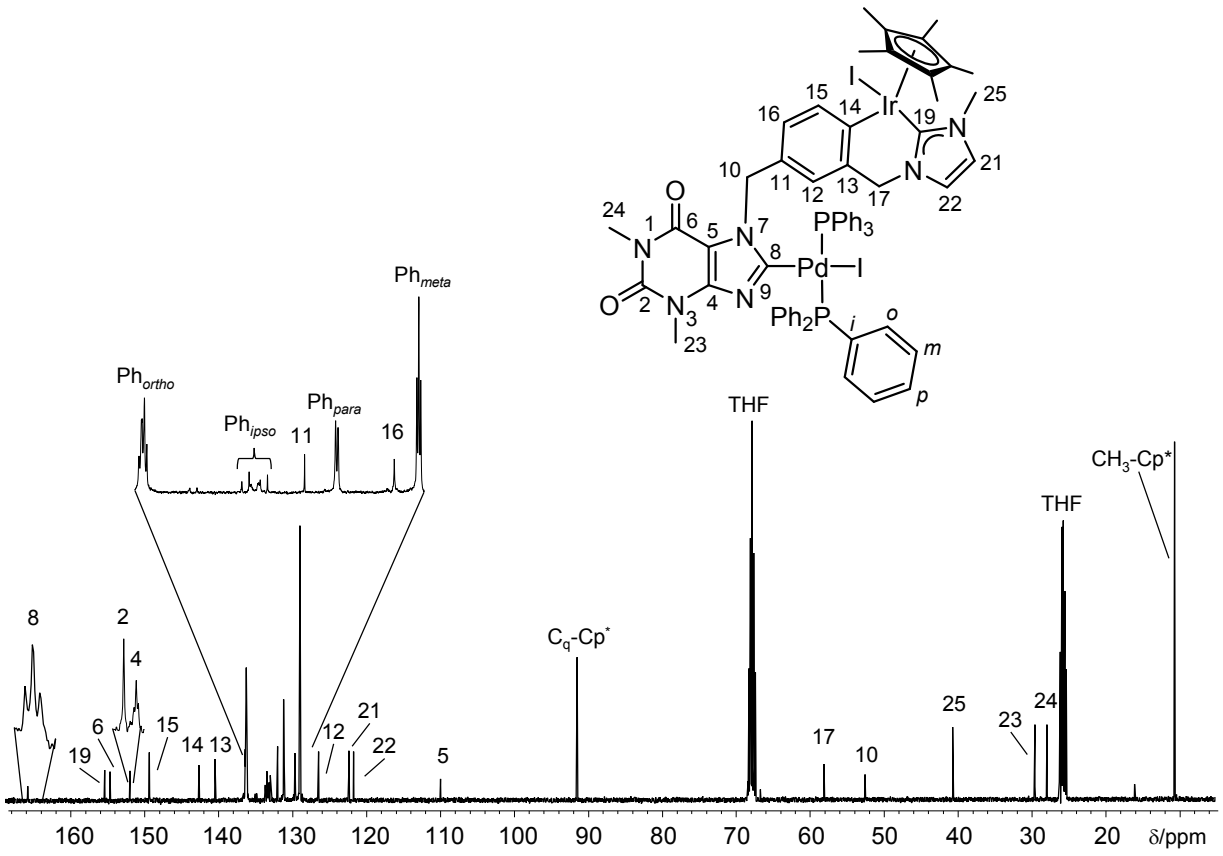


Figure S15. ^{13}C NMR spectrum of [**7**] (101 MHz, THF-d_8).

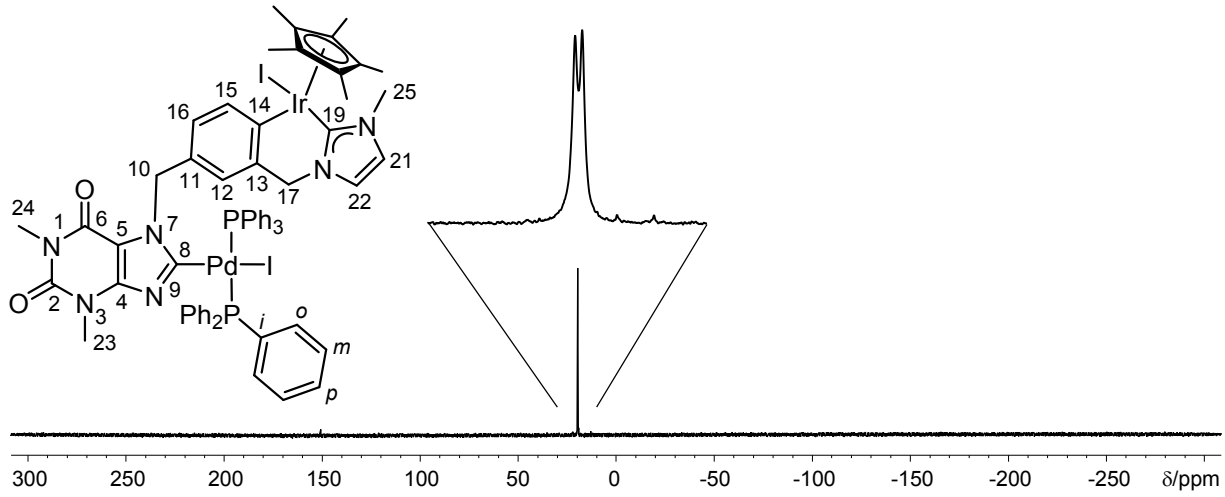


Figure S16. $^{31}P\{^1H\}$ NMR spectrum of [**7**] (162 MHz, THF-d_8).

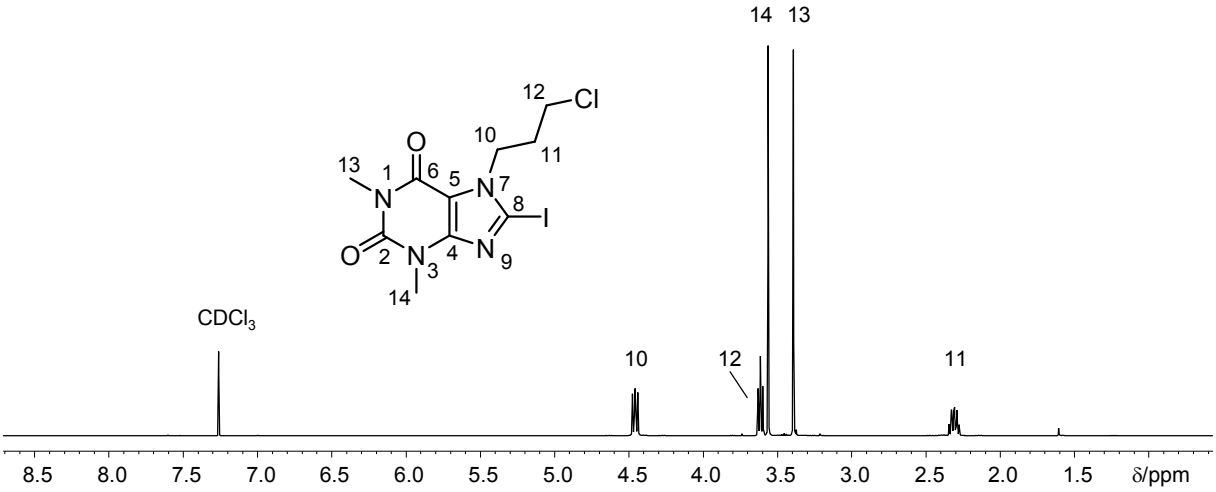


Figure S17. ^{1}H NMR spectrum of **8**-I (400 MHz, $CDCl_3$).

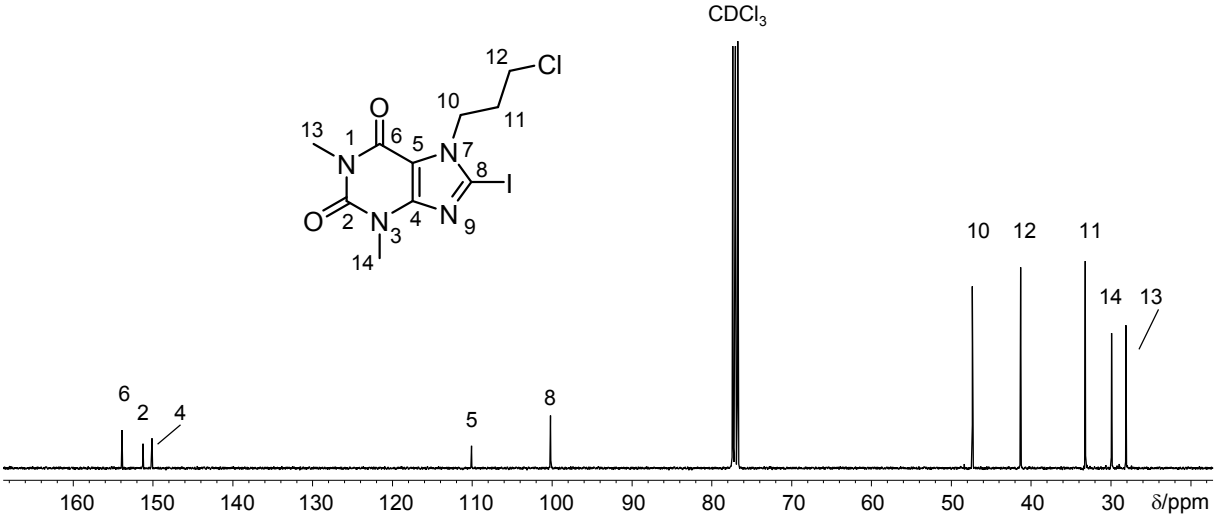


Figure S18. ^{13}C{^{1}H} NMR spectrum of **8**-I (101 MHz, $CDCl_3$).

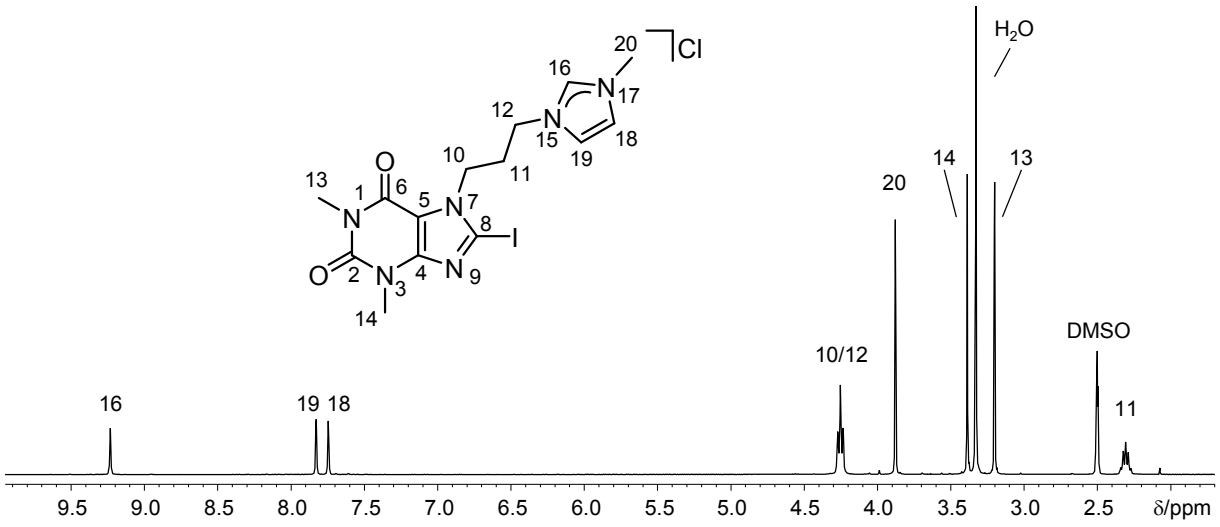


Figure S19. ^{1}H NMR spectrum of H-**9**-I(Cl) (400 MHz, DMSO-d_6).

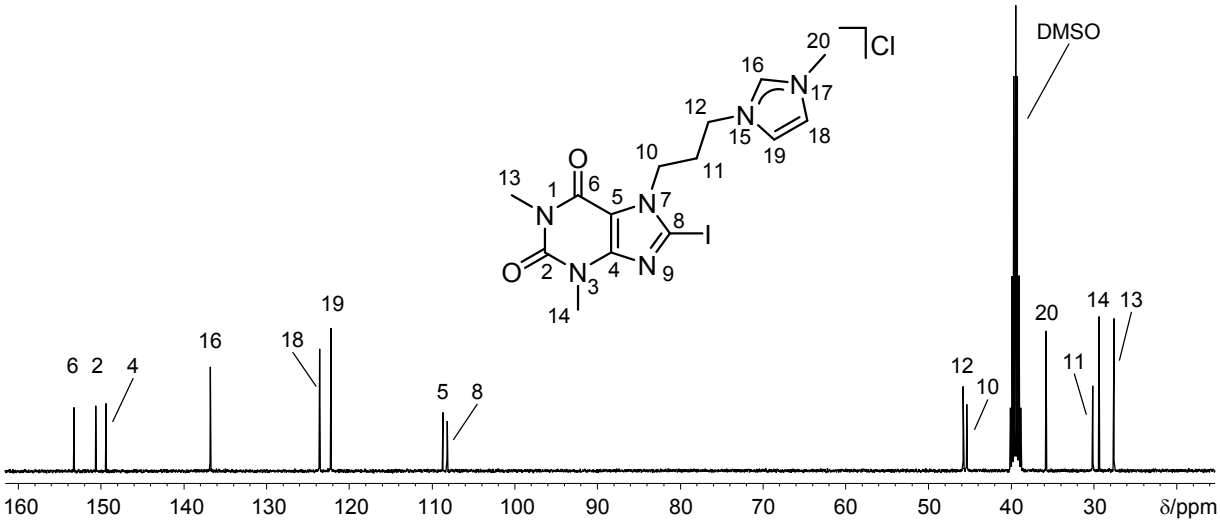


Figure S20. ^{13}C NMR spectrum of H-**9**-I(Cl) (101 MHz, DMSO-d_6).

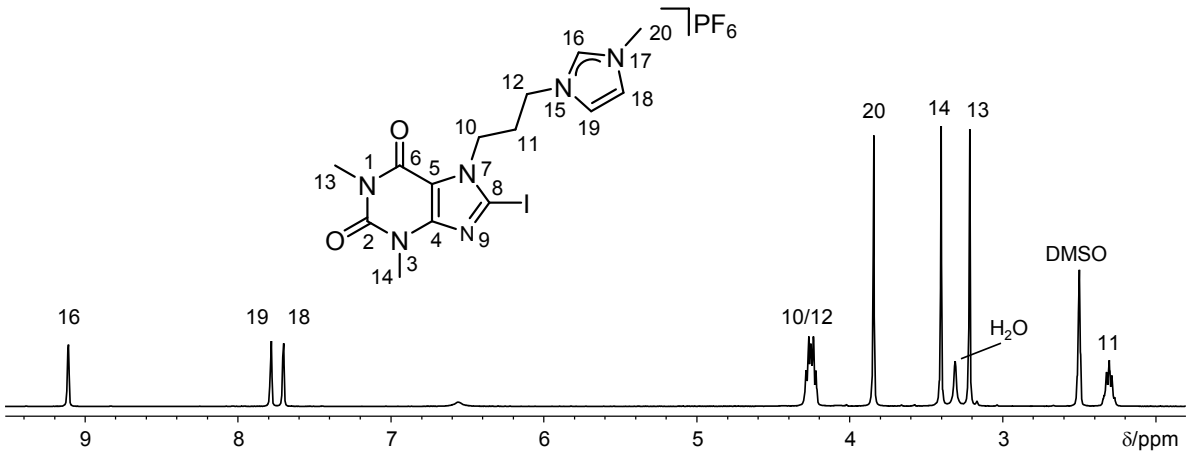


Figure S21. ^{1}H NMR spectrum of H-**9**-I(PF_6) (400 MHz, DMSO-d_6).

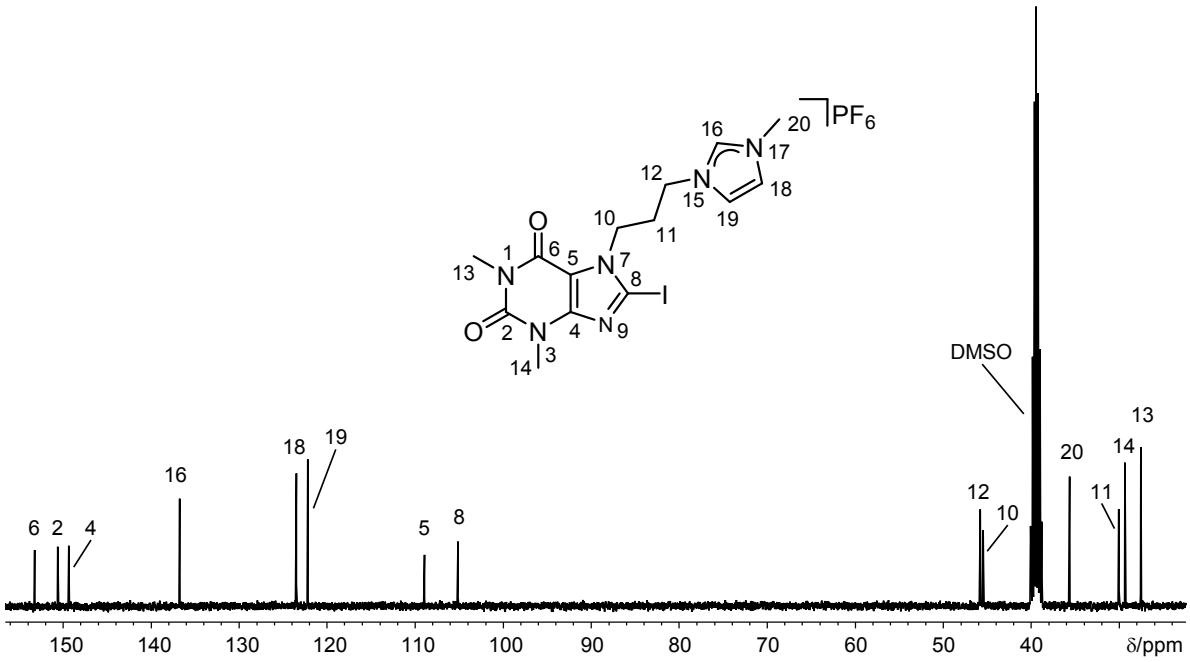


Figure S22. ^{13}C{^{1}H} NMR spectrum of H-**9**-I(PF_6) (400 MHz, DMSO-d_6).

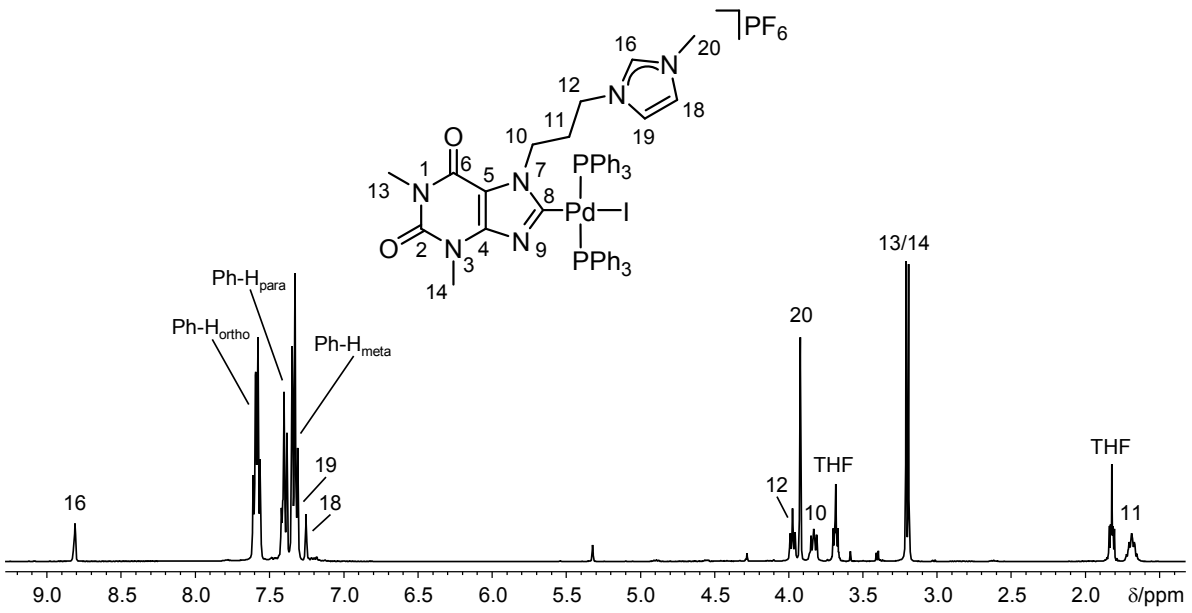


Figure S23. ^{1}H NMR spectrum of [**10**](PF_6) (400 MHz, CD_2Cl_2).

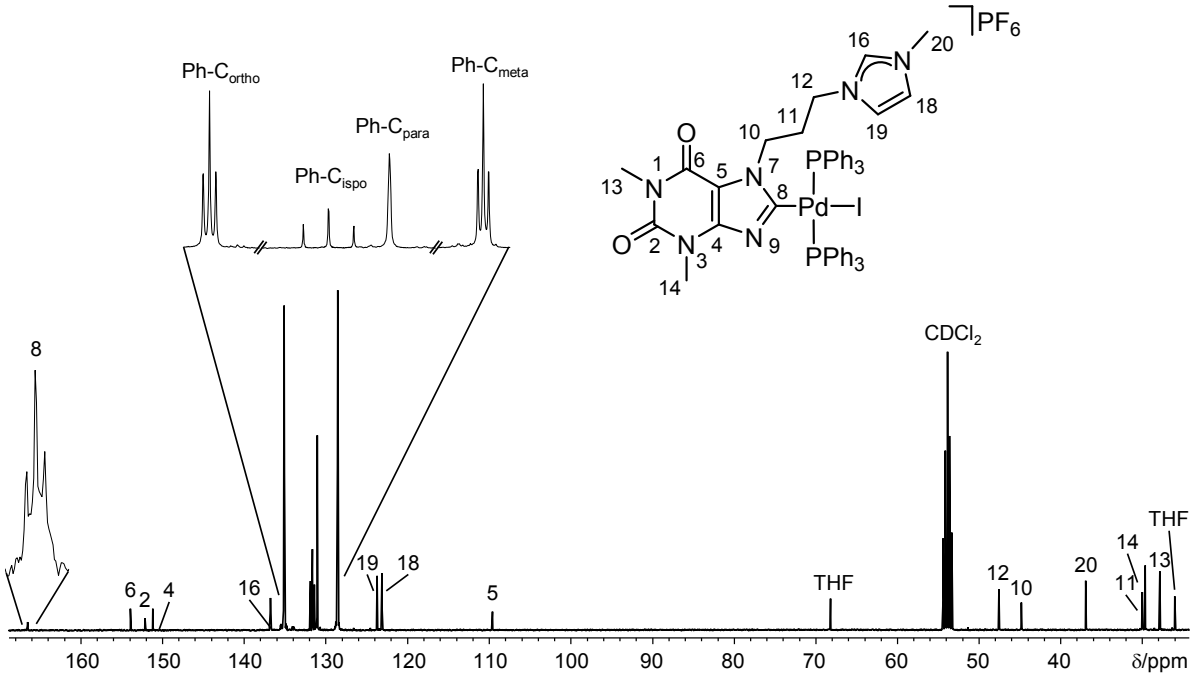


Figure S24. $^{13}C\{^{1}H\}$ NMR spectrum of [**10**](PF_6) (101 MHz, CD_2Cl_2).

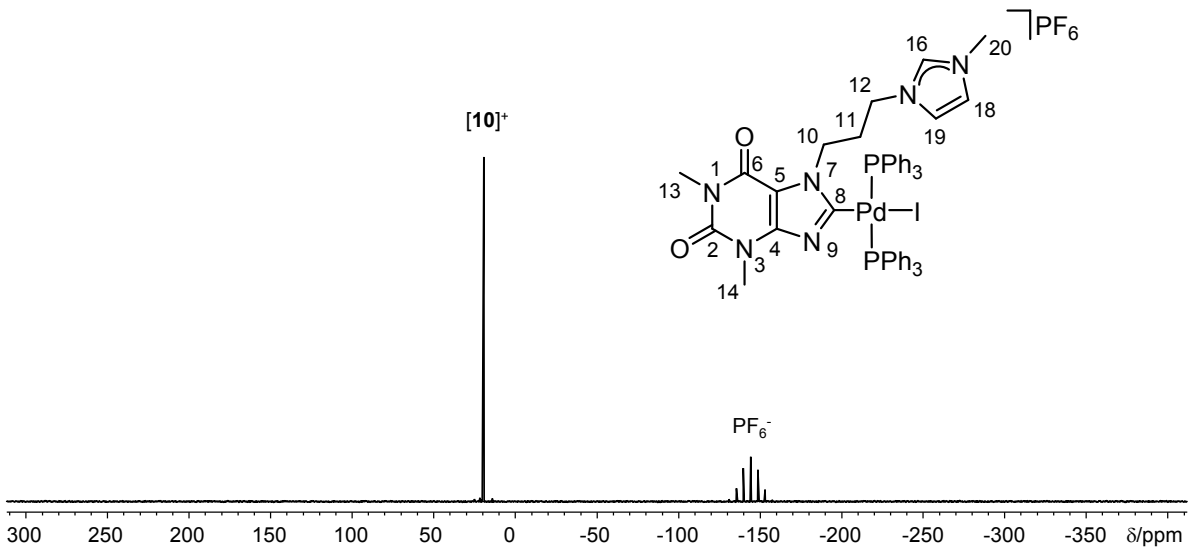


Figure S25. $^{31}P\{^{1}H\}$ NMR spectrum of [**10**](PF_6) (162 MHz, CD_2Cl_2).

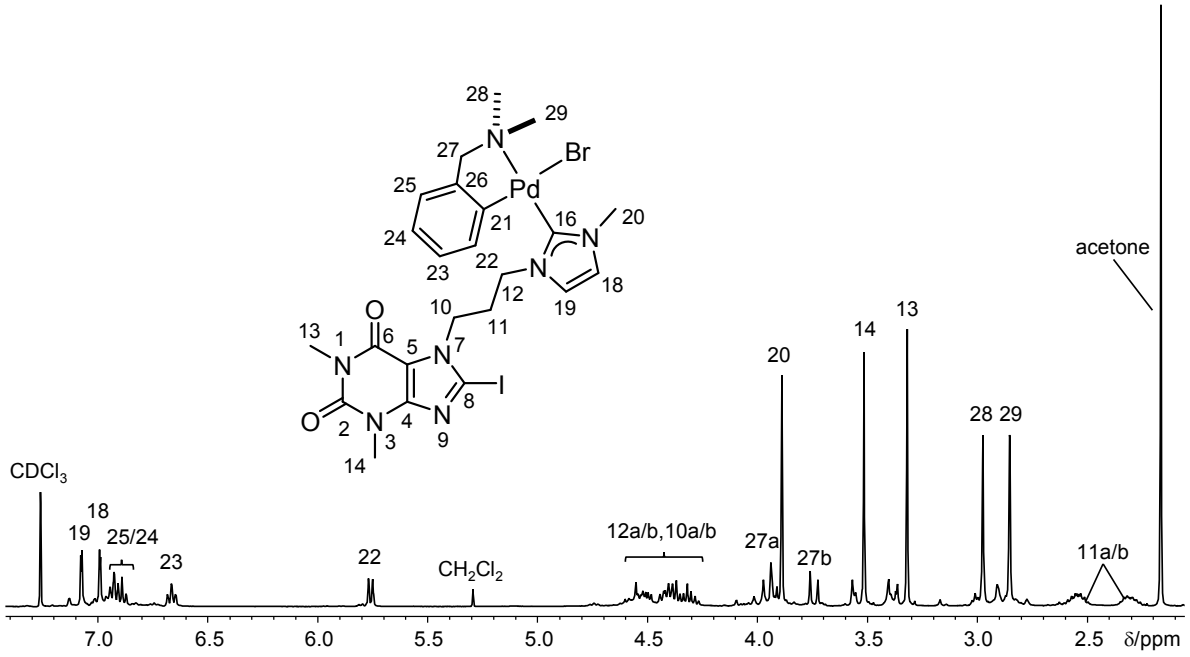


Figure S26. ^{1}H NMR spectrum of [**11**] (400 MHz, $CDCl_3$).

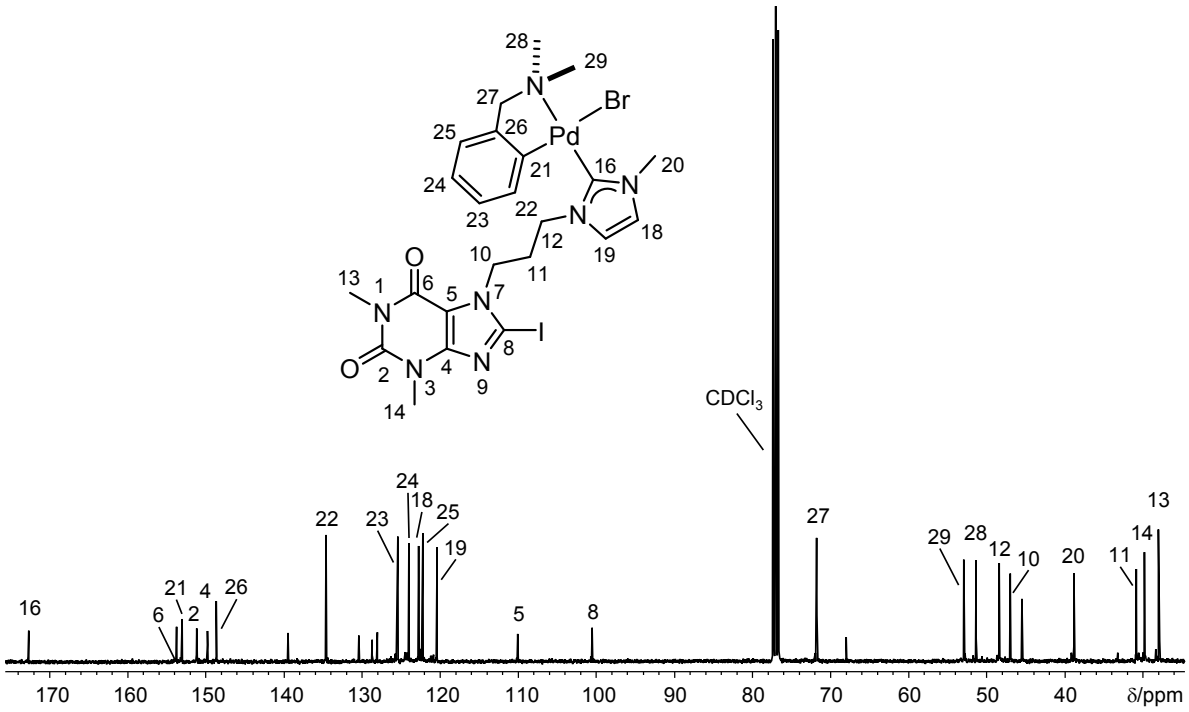


Figure S27. $^{13}C\{^{1}H\}$ NMR spectrum of [**11**] (101 MHz, $CDCl_3$).

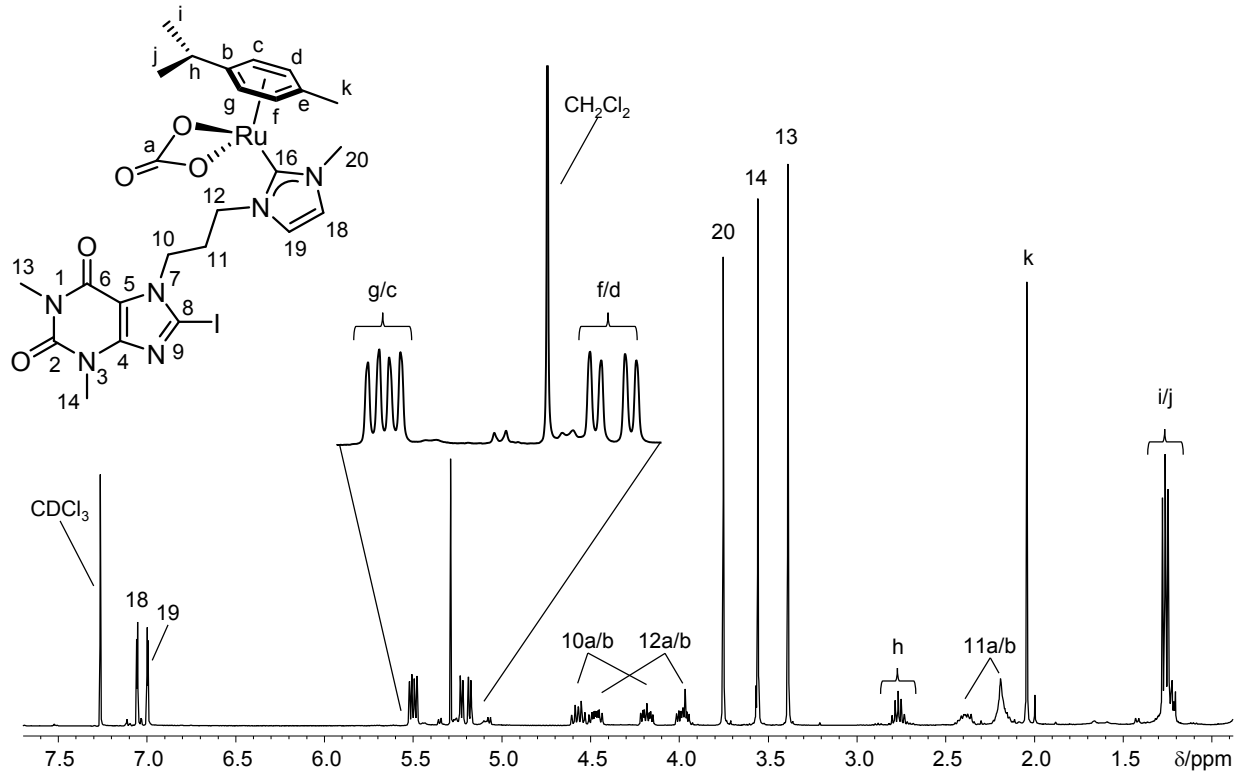


Figure S28. ^{1}H NMR spectrum of [**12**] (400 MHz, $CDCl_3$).

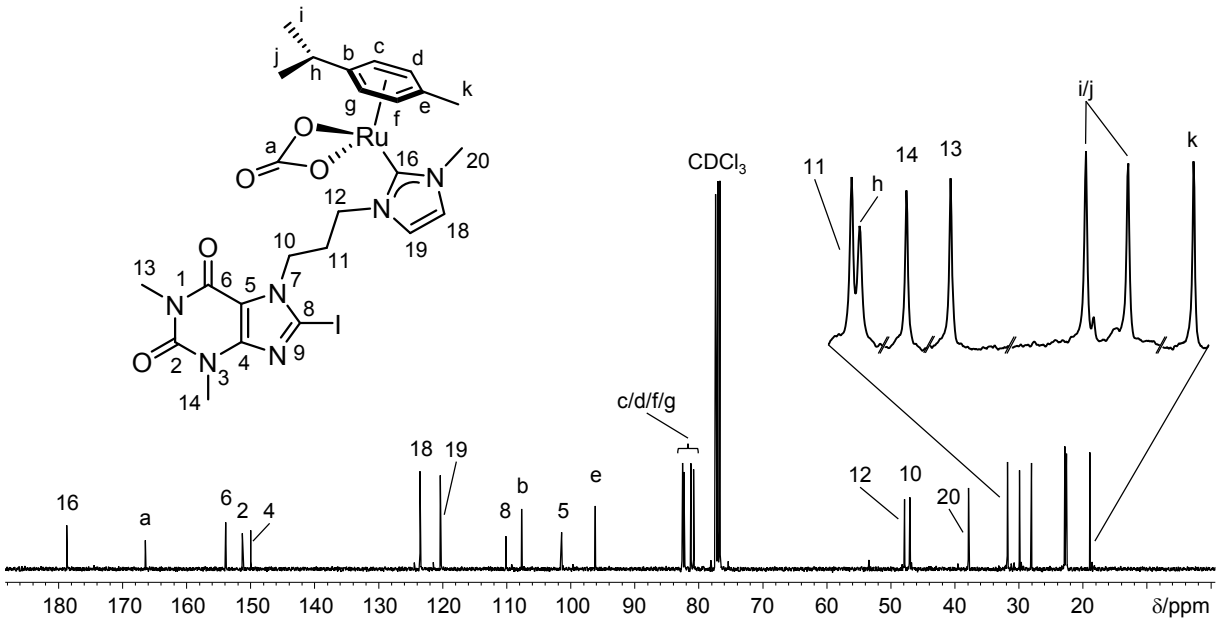


Figure S29. $^{13}C\{^{1}H\}$ NMR spectrum of [**12**] (101 MHz, $CDCl_3$).

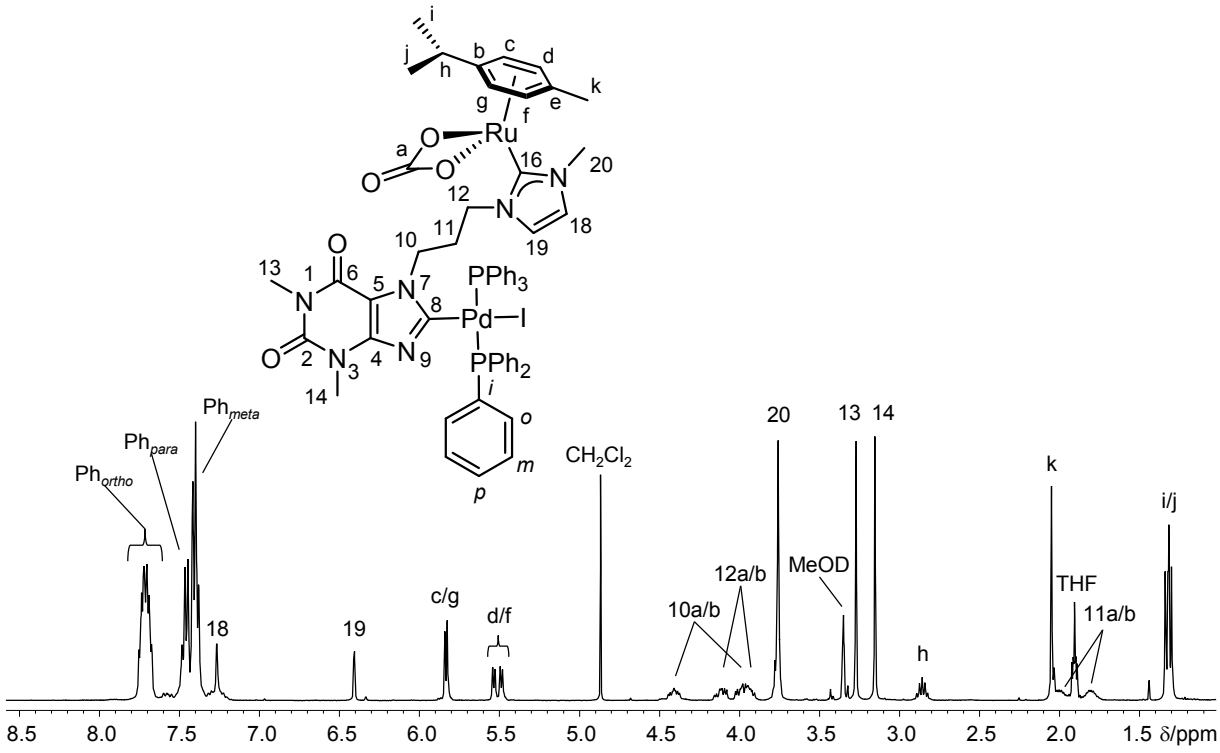


Figure S30.^{1}H NMR spectrum of [**13**] (400 MHz, MeOH-d_4).

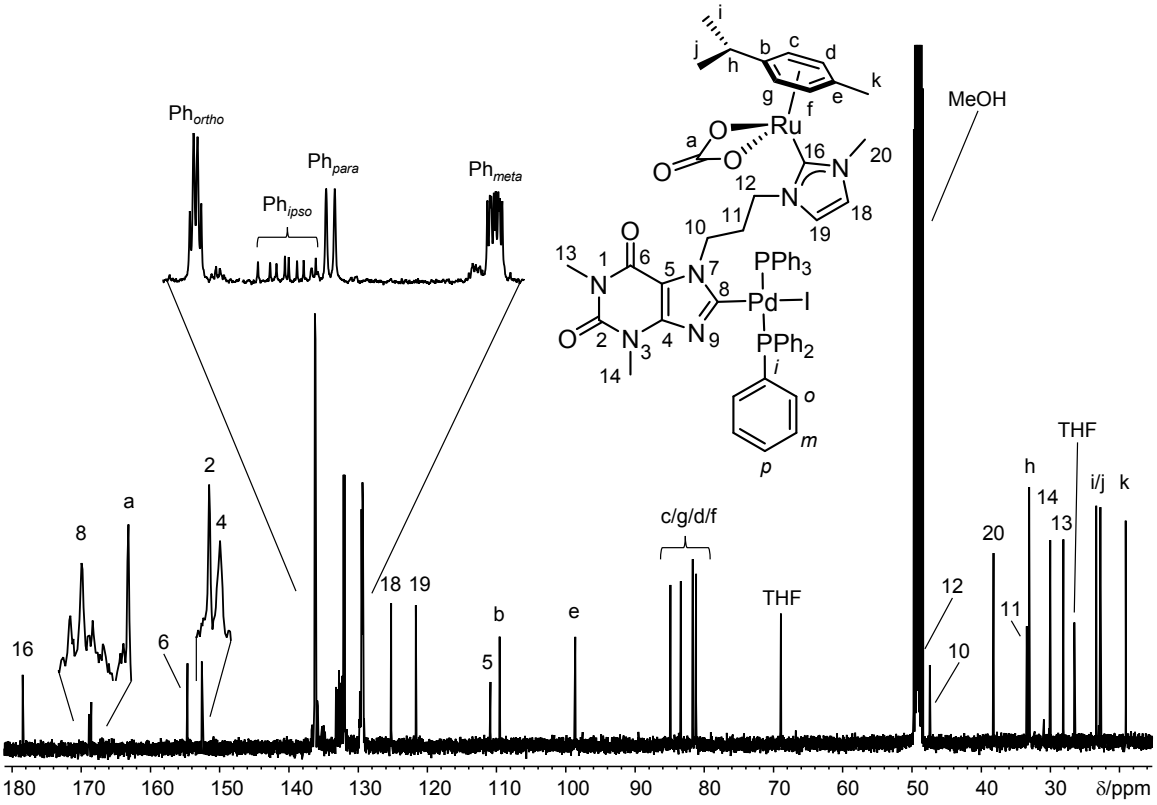


Figure S31. $^{13}C\{^{1}H\}$ NMR spectrum of [**13**] (101 MHz, MeOH-d_4).

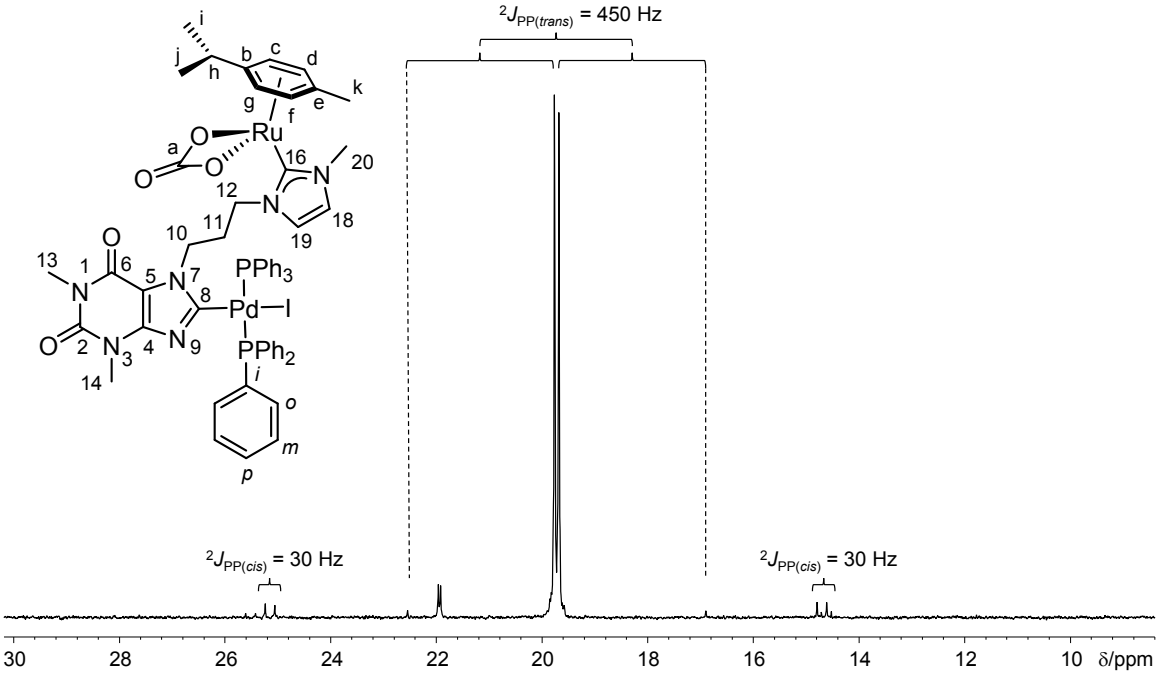


Figure S32. $^{31}P\{^{1}H\}$ NMR spectrum of [**13**] (162 MHz, MeOH-d_4).

11. References.

[S1] Mothes, W.; Gunzert, K. T. 8-Iodotheophylline. DE 1961-K42985, Feb. 24, 1961.

[S2] Krause, L.; Herbst-Irmer, R.; Sheldrick, G. M.; Stalke, D. Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *J. Appl. Crystallogr.* **2015**, *48*, 3–10.

[S3] Blessing, R. H. An Empirical Correction for Absorption Anisotropy. *Acta Cryst.* **1995**, *A51*, 33–38.

[S4] Sheldrick, G. M. *SHELXT* – Integrated space-group and crystal-structure determination. *Acta Cryst.* **2015**, *A71*, 3–8.

[S5] Sheldrick, G. M. Crystal structure refinement with *SHELXL*. *Acta Cryst.* **2015**, *C71*, 3–8.