Electronic Supplementary Material (ESI) for Chemical Communications.

Site-selective metallation of dicarbene precursors

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Electronic Supporting Information

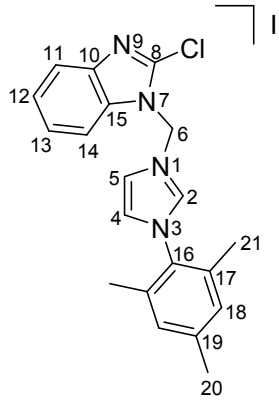
Table of Contents

1. General procedures

All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was oven dried at 120 °C. Solvents were distilled by standard procedures prior to use. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded at 300 K on Bruker AVANCE I 400, 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 mentioned otherwise. Mass spectra were obtained with an Orbitrap LTQ XL (Thermo Scientific) spectrometer. The compounds chloroiodomethane, potassium carbonate, 2-chlorobenzimidazole, Ag_2O, α,α'-dichloro-*m*-xylene, potassium hexafluorophosphate, triethyloxonium hexafluorophosphate and [Pd(PPh_3)$_4$] were used as received from commercial sources. Compounds 2,4,6-trimethylphenylimidazole, 1-(2,4,6-trimethylphenyl)-3-iodomethylimidazolium iodide and [AuCl(THT)] were synthesized according to published procedures[S1,S2,S3]. Satisfactory microanalytical data for the new compounds **4**PF_6, [**6**]$(PF_6)_2$ [**7**]PF_6 and **8**$(PF_6)_2$ could not be obtained due to the large fluorine content in the hexafluorophosphate counterions. HR-ESI mass spectroscopic data and a complete set of NMR spectra are provided instead.

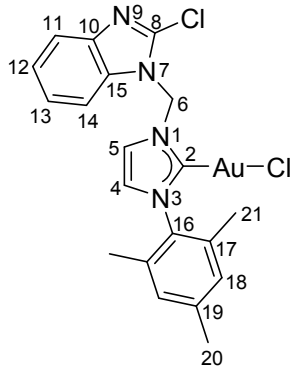
2. Experimental procedures

2.1. Synthesis of compound H-1(I)



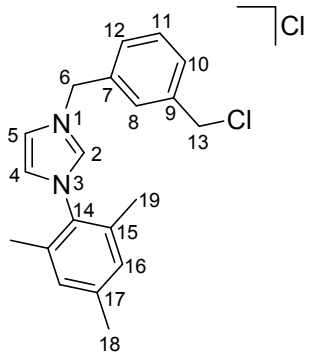
A sample of 1-(2,4,6-trimethylphenyl)-3-iodomethylimidazolium iodide (0.500 g, 1.101 mmol) was dissolved in acetonitrile (70 mL). To this was added 2-chlorobenzimidazole (0.167 g, 1.101 mmol) and potassium carbonate (0.304 g, 2.220 mmol) and the suspension was stirred at ambient temperature for 2 d. The resulting suspension was filtered and the solvent from the filtrate was removed *in vacuo* to give compound H-**1**(I) as a colorless solid. Suitable crystals for an X-ray diffraction study were obtained by slow vapor diffusion of diethyl ether into a saturated acetonitrile solution of H-**1**(I) at ambient temperature. Yield: 433 mg (0.906 mmol, 82%). ^{1}H-NMR (400 MHz, 300 K, CD_3CN): δ = 9.54 (s, 1H, H-2), 7.97 (dt, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, H-14), 7.82 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H, H-5), 7.68 (dt, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, H-11), 7.52 (t, $^{3}J_{HH}$ = 1.9 Hz, 1H, H-4), 7.44–7.40 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, H-13), 7.39–7.36 (td, $^{3}J_{HH}$ = 7.9 Hz, $^{4}J_{HH}$ = 0.9 Hz, 1H, H-12), 7.09 (s, 2H, H-18), 6.86 (s, 2H, H-6), 2.33 (s, 3H, H-20), 2.01 (s, 6H, H-21). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, CD_3CN): δ = 142.6 (C-10), 142.4 (C-19), 141.3 (C-8), 138.1 (C-2), 135.6 (C-15), 131.6 (C-16), 130.4 (C-18), 125.7 (C-4), 125.4 (C-13), 124.9 (C-12), 123.6 (C-5), 120.5 (C-11), 111.4 (C-14), 57.5 (C-6), 21.1 (C-20), 17.7 (C-21). HRMS (ESI, positive ions): *m/z* (%) = 351.1388 (calcd for [**1**]$^{+}$ 351.1376). Anal. Calcd (%) for H-**1**(I): C, 50.18; H, 4.21; N, 11.70. Found: C, 50.78; H, 4.30; N, 11.51.

2.2. Synthesis of complex [2]



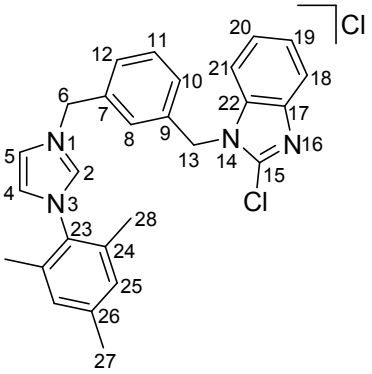
Ligand precursor H-**1**(I) (0.040 g, 0.084 mmol) and silver(I) oxide (0.048 g, 0.207 mmol) were dissolved in dichloromethane (10 mL) and stirred under exclusion of light at ambient temperature overnight. To this was added [AuCl(THT)] (0.027 g, 0.084 mmol) and the suspension was stirred at ambient temperature for another 12 h. After filtration through a pad of celite the solvent was removed from the filtrate *in vacuo* to yield complex [**2**] as a colorless solid. Suitable crystals for an X-ray diffraction study were obtained by slow evaporation of the solvent of a saturated acetonitrile solution of [**2**]. Yield: 0.037 g (0.064 mmol, 76%). ^{1}H-NMR (400 MHz, 300 K, CD_3CN): δ = 7.86–7.84 (m, 1H, H-14), 7.68–7.67 (m, 1H, H-11), 7.43 (d, $^{3}J_{HH}$ = 2.1 Hz, 1H, H-5), 7.40–7.30 (m, 2H, H-13/H-12), 7.15 (d, $^{3}J_{HH}$ = 2.1 Hz, 1H, H-4), 7.07 (s, 2H, H-18), 6.64 (s, 2H, H-6), 2.34 (s, 3H, H-20), 1.96 (s, 6H, H-21). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, CD_3CN): δ = 173.5 (C-2), 142.8 (C-10), 141.4 (C-8), 141.1 (C-19), 136.1 (C-17), 136.0 (C-16), 135.6 (C-15), 130.2 (C-18), 125.1 (C-13), 125.0 (C-4), 124.7 (C-12), 121.7 (C-5), 120.5 (C-11), 111.7 (C-14), 59.2 (C-6), 21.2 (C-20), 17.9 (C-21). HRMS (ESI, positive ions): *m/z* (%) = 897.2265 (calcd for [[**2**]$_2$ – 2Cl – Au]$^{+}$ 897.2256), 605.0550 (calcd for [[**2**] + Na]$^{+}$ 605.0544). Anal. Calcd (%) for [**2**]: C, 41.19; H, 3.28; N, 9.61. Found: C, 41.09; H, 3.32; N, 9.43.

2.3. Synthesis of compound H-3(Cl)



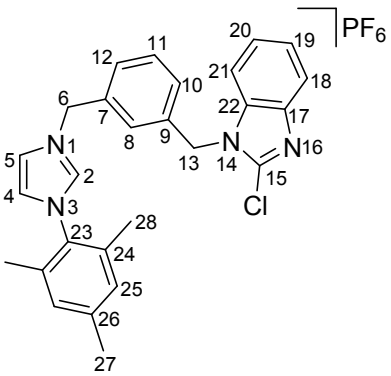
One equivalent 2,4,6-trimethylphenylimidazole (0.373 g, 2.003 mmol) and two equivalents α,α'-dichloro-*m*-xylene (0.700 g, 4.000 mmol) were dissolved in acetone (50 mL) and the resulting solution was stirred at 80 °C for 8 h. After removal of the solvent *in vacuo* the raw product was purified by column chromatography (acetone:ethanol, 6:1) to give compound H-**3**(Cl) as a colorless solid. Yield: 530 mg (1.472 mmol, 73%). ^{1}H-NMR (400 MHz, 300 K, $CDCl_3$): δ = 10.51 (s, 1H, H-2), 7.99 (s, 1H, H-5), 7.56 (s, 1H, H-8), 7.49 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H, H-12), 7.20–7.13 (m, 2H, H-10/H-11), 7.07 (s, 1H, H-4), 6.77 (s, 2H, H-16), 5.74 (s, 2H, H-6), 4.38 (s, 2H, H-13), 2.13 (s, 3H, H-18), 1.83 (s, 6H, H-19). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, $CDCl_3$): δ = 140.6 (C-17), 138.2 (C-2), 137.5 (C-9), 134.3 (C-7), 133.7 (C-15), 130.4 (C-14), 129.3 (C-16), 129.3 (C-11), 128.9 (C-12), 128.7 (C-10), 128.6 (C-8), 123.1 (C-4), 123.0 (C-5), 52.3 (C-6), 45.2 (C-13), 20.6 (C-18), 17.1 (C-19). HRMS (ESI, positive ions): *m/z* (%) = 325.1455 (calcd for [**3**]$^{+}$ 325.14725). Anal. Calcd (%) for H-**3**(Cl)·H_2O: C, 63.33; H, 6.38; N, 7.39. Found: C, 63.66; H, 6.35; N, 7.07.

2.4. Synthesis of compound H-4(Cl)



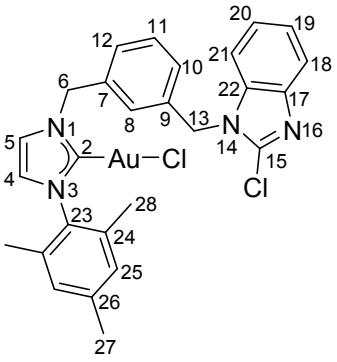
Compound H-**3**(Cl) (0.430 g, 1.194 mmol) was dissolved in acetonitrile (70 mL). To this was added 2-chlorobenzimidazole (0.181 g, 1.194 mmol) and potassium carbonate (0.329 g, 2.381 mmol) and the suspension was stirred at ambient temperature for 2 d. After filtration, the solvent was removed from the filtrate *in vacuo* to give compound H-**4**(Cl) as a colorless solid. Yield: 559 mg (1.174 mmol, 98%). ^{1}H-NMR (400 MHz, 300 K, CD_2Cl_2): δ = 11.05 (s, 1H, H-2), 7.66–7.64 (m, 1H, H-18), 7.58 (s, 1H, H-8), 7.53 (d, $^{3}J_{HH}$ = 7.7 Hz, 1H, H-12), 7.43 (s, 1H, H-5), 7.38 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, H-11), 7.37–7.33 (m, 1H, H-21), 7.27–7.20 (m, 3H, H-10/H-19/H-20), 7.10 (s, 1H, H-4), 7.04 (s, 2H, H-25), 5.89 (s, 2H, H-6), 5.44 (s, 2H, H-13), 2.35 (s, 3H, H-27), 2.04 (s, 6H, H-28). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, CD_2Cl_2): δ = 142.3 (C-17), 141.8 (C-26), 141.0 (C-15), 139.6 (C-2), 137.2 (C-9), 135.5 (C-22), 135.2 (C-7), 134.7 (C-24), 131.2 (C-23), 130.4 (C-11), 130.2 (C-25), 129.1 (C-12), 128.2 (C-10), 128.1 (C-8), 123.8 (C-4), 123.5 (C-20), 123.1 (C-5), 122.4 (C-19), 119.7 (C-18), 110.5 (C-21), 53.4 (C-6), 48.0 (C-13), 21.2 (C-27), 17.8 (C-28). HRMS (ESI, positive ions): *m/z* (%) = 441.1837 (calcd for [**4**]$^{+}$ 441.1846). Anal. Calcd (%) for H-**4**(Cl): C, 67.93; H, 5.49; N, 11.74. Found: C, 67.42; H, 5.42; N, 11.27.

2.5. Synthesis of compound H-4(PF_6)



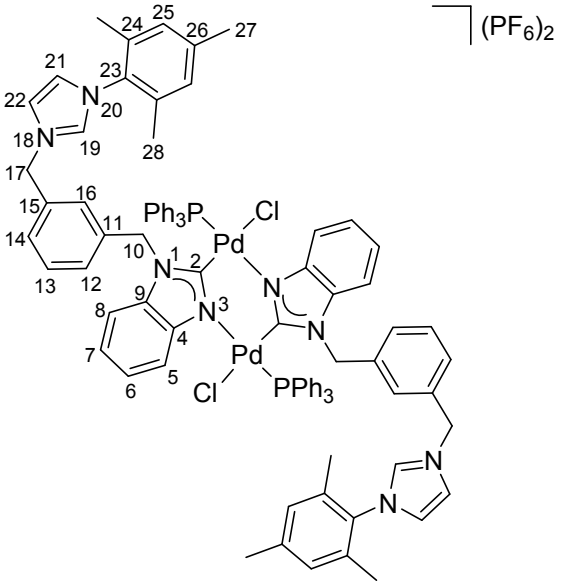
Compound H-**4**(Cl) (0.406 g, 0.853 mmol) was dissolved in methanol (2 mL). To this was added potassium hexafluorophosphate (0.313 g, 1.701 mmol) and the reaction mixture was stirred at ambient temperature for 12 h. The solvent was removed by filtration and the isolated solid was washed with methanol (2 x 2 mL) and dried *in vacuo*. Compound H-**4**(PF_6) was obtained as a colorless solid. Suitable crystals for an X-ray diffraction study were obtained by slow vapor diffusion of diethyl ether into a saturated acetonitrile solution of H-**4**(PF_6) at ambient temperature. Yield: 424 mg (0.723 mmol, 85%). ^{1}H-NMR (400 MHz, 300 K, CD_3CN): δ = 8.52 (s, 1H, H-2), 7.65–7.62 (m, 1H, H-18), 7.51 (s, 1H, H-5), 7.46 (t, $^{3}J_{HH}$ = 7.7 Hz, 1H, H-11), 7.41 (s, 1H, H-4), 7.38–7.34 (m, 3H, H-8/H-12/H-21), 7.27–7.23 (m, 3H, H-10/H-19/H-20), 7.10 (s, 2H, H-25), 5.48 (s, 2H, H-6), 5.37 (s, 2H, H-13), 2.35 (s, 3H, H-27), 1.96 (s, 6H, H-28). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, CD_3CN): δ = 142.8 (C-17), 142.4 (C-26), 141.7 (C-15), 138.4 (C-2), 137.4 (C-9), 136.3 (C-22), 135.7 (C-7), 135.3 (C-24), 131.9 (C-23), 131.0 (C-11), 130.5 (C-25), 129.4 (C-12), 129.1 (C-10), 128.0 (C-8), 125.4 (C-4), 124.3 (C-20), 124.2 (C-5), 123.8 (C-19), 120.1 (C-18), 111.3 (C-21), 54.0 (C-6), 48.3 (C-13), 21.2 (C-27), 17.5 (C-28). ^{31}P{^{1}H}-NMR (162 MHz, 300 K, CD_3CN): δ = –144.6 (sep, $^{1}J_{PF}$ = 706.4 Hz, PF_6). ^{19}F{^{1}H}-NMR (376 MHz, 300 K, CD_3CN): δ = –72.9 (d, $^{1}J_{FP}$ = 706.4 Hz, PF_6). HRMS (ESI, positive ions): *m/z* (%) = 441.1837 (calcd for [**4**]$^{+}$ 441.1846).

2.6. Synthesis of complex [5]



Ligand precursor H-**4**(Cl) (0.040 g, 0.063 mmol) and silver(I) oxide (0.036 g, 0.158 mmol) were dissolved in dichloromethane (10 mL) and the mixture was stirred under exclusion of light at ambient temperature for 12 h. Subsequently [AuCl(THT)] (0.020 g, 0.063 mmol) was added and the suspension was stirred at ambient temperature for another 12 h. The resulting suspension was filtered through a pad of celite the solvent was removed from the filtrate *in vacuo* to give complex [**5**] as a colorless solid. Suitable crystals for an X-ray diffraction study were obtained by slow vapor evaporation of the solvent of a saturated acetonitrile solution of [**5**]. Yield: 0.041 g (0.061 mmol, 97%). ^{1}H-NMR (400 MHz, 300 K, CD_3CN): δ = 7.63–7.61 (m, 1H, H-18), 7.40–7.38 (m, 1H, H-21), 7.37 (t, $^{3}J_{HH}$ = 7.4 Hz, 1H, H-11), 7.30 (s, 1H, H-10), 7.30 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H-5), 7.29 (s, 1H, H-8), 7.27–7.25 (m, 2H, H-19/H-20), 7.21 (d, $^{3}J_{HH}$ = 7.4 Hz, 1H, H-12), 7.08 (d, $^{3}J_{HH}$ = 2.0 Hz, 1H, H-4), 7.05 (s, 2H, H-25), 5.43 (s, 2H, H-13), 5.40 (s, 2H, H-6), 2.34 (s, 3H, H-27), 1.96 (s, 6H, H-28). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, CD_3CN): δ = 172.5 (C-2), 142.8 (C-17), 141.6 (C-15), 140.8 (C-26), 138.4 (C-7), 137.8 (C-9), 136.3 (C-22), 136.2 (C-23), 136.1 (C-24), 130.6 (C-11), 130.1 (C-25), 128.2 (C-10), 128.1 (C-12), 127.4 (C-8), 124.4 (C-20), 124.0 (C-4), 123.7 (C-19), 122.7 (C-5), 120.0 (C-18), 111.4 (C-21), 55.0 (C-6), 48.5 (C-13), 21.2 (C-27), 18.0 (C-28). HRMS (ESI, positive ions): *m/z* (%) = 695.1020 (calcd for [[**5**] + Na]$^{+}$ 695.1020), 637.1431 (calcd for [[**5**] – Cl]$^{+}$ 637.1433). Anal. Calcd (%) for [**5**]: C, 48.16; H, 3.74; N, 8.32. Found: C, 48.50; H, 3.87; N, 8.64.

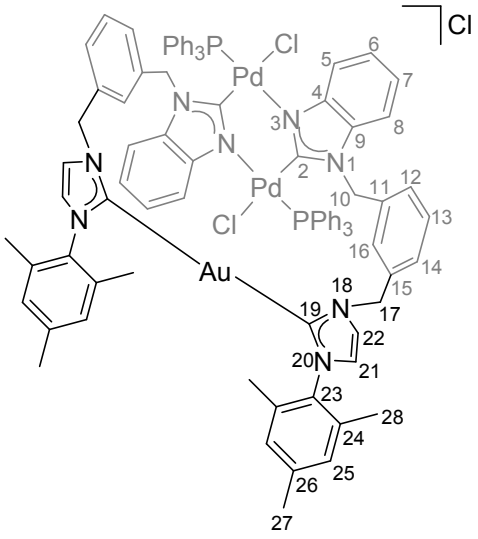
2.7. Synthesis of complex [6](PF$_6$)$_2$



Ligand precursor H-**4**(PF$_6$) (0.060 g, 0.102 mmol) and [Pd(PPh$_3$)$_4$] (0.118 g, 0.102 mmol) were suspended in toluene (10 mL) and the mixture was at 120 °C for 2 d. The solvent was then removed *in vacuo* and the solid was washed with diethyl ether (3 x 10 mL) and *n*-hexane (2 x 10 mL). The remaining solid was dissolved in dichloromethane and filtered through a pad of celite to give a clear solution. After removal of the solvent *in vacuo* complex [**6**](PF$_6$)$_2$ was obtained as a colorless solid. Yield: 0.079 g (0.041 mmol, 81%). ^{1}H-NMR (400 MHz, 300 K, CD_2Cl_2): δ = 8.30 (s, 2H, H-19), 8.04 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, H-5), 7.93 (dd, $^{3}J_{HP}$ = 11.8 Hz, 12H, P-Ph-H$_{ortho}$), 7.34 (t, $^{3}J_{HH}$ = 7.4 Hz, 6H, P-Ph-H$_{para}$), 7.21 (td, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 2.0 Hz, 12H, P-Ph-H$_{meta}$), 7.15 (s, 2H, H-21), 7.05 (s, 4H, H-25), 6.95 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, H-6), 6.93 (s, 2H, H-22), 6.87 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, H-12), 6.73 (t, $^{3}J_{HH}$ = 8.1 Hz, 2H, H-7), 6.71 (d, $^{3}J_{HH}$ = 8.0 Hz, 2H, H-14), 6.63 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, H-8), 6.61 (t, $^{3}J_{HH}$ = 8.0 Hz, 2H, H-13), 6.15 (s, 2H, H-16), 5.54 (d, $^{2}J_{HH}$ = 15.2 Hz, 2H, H-10), 4.13 (d,

$^{2}J_{HH}$ = 14.8 Hz, 2H, H-17), 4.11 (d, $^{2}J_{HH}$ = 15.2 Hz, 2H, H-10), 3.25 (d, $^{2}J_{HH}$ = 14.8 Hz, 2H, H-17), 2.35 (s, 6H, H-27), 1.97 (s, 12H, H-28). $^{13}C\{^{1}H\}$-NMR (100 MHz, 300 K, CD_2Cl_2): δ = 173.6 (d, $^{2}J_{CP}$ = 2.0 Hz, C-2), 143.4 (d, $^{3}J_{CP}$ = 2.5 Hz, C-4), 142.1 (C-26), 138.3 (C-11), 136.2 (C-19), 135.1 (d, $^{2}J_{CP}$ = 10.9 Hz, P-Ph-C$_{ortho}$), 134.7 (C-24), 134.4 (C-24), 134.3 (d, $^{4}J_{CP}$ = 3.8 Hz, C-9), 133.5 (C-15), 131.2 (d, $^{4}J_{CP}$ = 2.8 Hz, P-Ph-C$_{para}$), 130.7 (C-23), 130.6 (d, $^{1}J_{CP}$ = 52.3 Hz, P-Ph-C$_{ipso}$), 130.2 (C-25), 130.1 (C-25), 129.9 (C-13), 128.9 (d, $^{3}J_{CP}$ = 10.7 Hz, Ph-C$_{meta}$), 128.6 (C-12), 127.3 (C-14), 126.6 (C-16), 124.6 (C-21), 123.3 (C-22), 121.7 (C-6), 120.9 (C-7), 117.1 (C-5), 110.3 (C-8), 52.1 (C-17), 50.0 (C-10), 21.2 (C-27), 17.3 (C-28), 17.2 (C-28). $^{31}P\{^{1}H\}$-NMR (162 MHz, 300 K, CD_2Cl_2): δ = 24.9 (s, PPh_3), –144.4 (sep, $^{1}J_{PF}$ = 711.9 Hz, PF_6). $^{19}F\{^{1}H\}$-NMR (376 MHz, 300 K, CD_2Cl_2: δ = –72.0 (d, $^{1}J_{FP}$ = 711.9 Hz, PF_6). HRMS (ESI, positive ions): *m/z* (%) = 1765.3307 (calcd for [[**6**] – PF_6]$^{+}$ 1765.3248), 810.1826 (calcd for [[**6**] – 2PF_6]$^{2+}$ 810.1800).

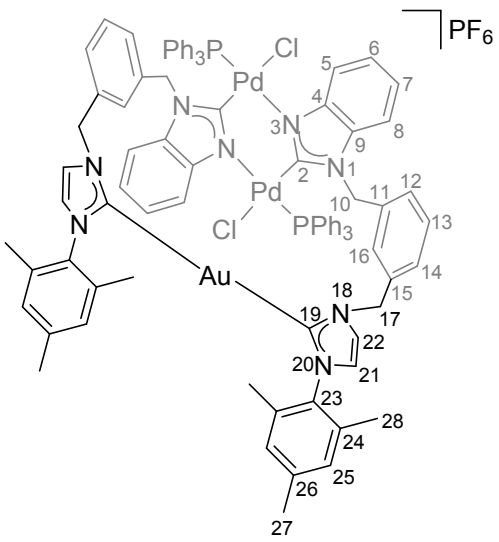
2.8. Synthesis of complex [7]Cl



Complex [**5**] (0.114 g, 0.169 mmol) and [Pd(PPh$_3$)$_4$] (0.195 g, 0.169 mmol) were suspended in toluene (10 mL) and the mixture was stirred at 120 °C for 2 d. After cooling of the reaction mixture to ambient temperature the toluene was decanted from the solid and the remaining solid was suspended in acetonitrile. The suspension was filtered through a pad of celite to give a clear solution. Addition of diethyl ether led to precipitation of a colorless solid. The solid was separated by filtration, washed with diethyl ether (2 x 10 mL) and dried *in vacuo* to give complex [**7**]Cl as a colorless solid. Yield: 0.046 g (0.025 mmol, 29%). ^{1}H-NMR (400 MHz, 300 K, CD_3CN): δ = 8.08 (d, $^{3}J_{HH}$ = 8.1 Hz, 2H, H-5), 7.95 (dd, $^{3}J_{HP}$ = 11.6 Hz, $^{3}J_{HH}$ = 7.8 Hz, 12H, P-Ph-H$_{ortho}$), 7.40 (t, $^{3}J_{HH}$ = 2.3 Hz, 6H, P-Ph-H$_{para}$), 7.24 (td, $^{3}J_{HH}$ = 10.9 Hz, $^{4}J_{HH}$ = 2.0 Hz, 12H, P-Ph-H$_{meta}$), 7.01–6.97 (m, 4H, H-6/H-22), 6.95 (s, 2H, H-21), 6.91 (s, 4H, H-25), 6.71 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, H-12), 6.62–6.57 (m, 4H, H-7/H-8), 6.24 (t, $^{3}J_{HH}$ = 7.6 Hz, 2H, H-13), 6.16 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, H-14), 6.14 (s, 2H, H-16), 5.49 (d, $^{2}J_{HH}$ = 15.0 Hz, 2H, H-10), 4.13 (d, $^{2}J_{HH}$ = 15.0 Hz, 2H, H-10), 3.93 (d, $^{2}J_{HH}$ = 16.5 Hz, 2H, H-17), 3.01 (d, $^{2}J_{HH}$ = 16.5 Hz, 2H, H-17), 2.39 (s, 6H, H-27), 1.69 (s, 6H, H-28), 1.56 (s, 6H, H-28). $^{13}C\{^{1}H\}$-NMR (100 MHz, 300 K, CD_3CN): δ = 186.0 (C-19), 173.5 (d, $^{2}J_{CP}$ = 1.7 Hz, C-2), 144.2 (d, $^{3}J_{CP}$ = 2.4 Hz, C-4), 140.4 (C-26), 138.3 (C-11), 137.8 (C-15), 135.7 (d, $^{2}J_{CP}$ = 11.1 Hz, P-Ph-C$_{ortho}$), 135.6 (C-23), 135.5 (C-24), 135.1 (d, $^{4}J_{CP}$ = 4.0 Hz, C-9), 131.9 (d, $^{4}J_{CP}$ = 2.7 Hz, P-Ph-C$_{para}$), 131.6 (d, $^{1}J_{CP}$ = 52.3 Hz, P-Ph-C$_{ipso}$), 130.0 (C-25), 129.9 (C-25), 129.4 (d, $^{3}J_{CP}$ = 10.9 Hz, P-Ph-C$_{meta}$), 129.3 (C-13), 127.8 (C-12), 126.6 (C-16), 125.4 (C-14), 123.6 (C-21), 123.6 (C-22), 122.2 (C-6), 121.4 (C-7), 117.8 (C-5), 111.3 (C-8), 53.0 (C-17), 50.0 (C-10), 21.3 (C-27), 17.7 (C-28), 17.5 (C-28). $^{31}P\{^{1}H\}$-NMR (162 MHz, 300 K, CD_3CN): δ = 25.0 (s, PPh_3). HRMS (ESI, positive ions): *m/z* (%) = 1815.3104

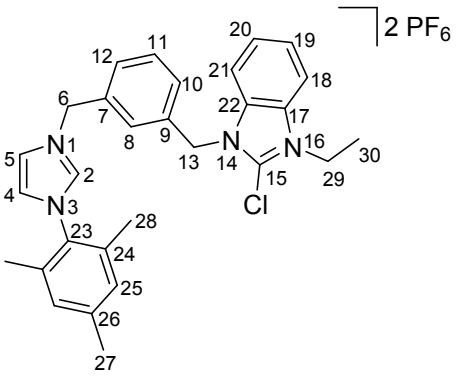
(calcd for [[**7**] – Cl]$^+$ 1817.3115). Anal. Calcd (%) for [**7**]Cl: C, 58.38; H, 4.35; N, 6.05. Found: C, 58.86; H, 4.37; N, 6.36.

2.9. Synthesis of complex [7]PF_6



Complex [**6**]$(PF_6)_2$ (0.079 g, 0.041 mmol) and silver(I) oxide (0.024 g, 0.103 mmol) were suspended in acetonitrile (10 mL) and the mixture was stirred at 70 °C for 12 h. After cooling of the reaction mixture to ambient temperature [AuCl(THT)] (0.013 g, 0.041 mmol) was added and the mixture was stirred for another 12 h. Subsequently, the volume of the suspension was reduced to 2 mL and filtered through a pad of celite to give a clear solution. Addition of diethyl ether led to precipitation of a white solid. The solid was isolated by filtration, washed with diethyl ether (2 x 10 mL) and dried *in vacuo* to give complex [**7**]PF_6 as a colorless solid. Suitable crystals for an X-ray diffraction study were obtained by slow vapor diffusion of diethyl ether into a saturated dimethylformamide solution of [**7**]PF_6 at ambient temperature. Yield: 0.045 g (0.023 mmol, 56%). ^{1}H-NMR (400 MHz, 300 K, CD_3CN): δ = 8.07 (d, $^3J_{HH}$ = 8.1 Hz, 2H, H-5), 7.94 (dd, $^3J_{HP}$ = 11.8 Hz, $^3J_{HH}$ = 8.2 Hz, 12H, P-Ph-H$_{ortho}$), 7.39 (t, $^3J_{HH}$ = 1.8 Hz, 6H, P-Ph-H$_{para}$), 7.24 (td, $^3J_{HH}$ = 8.2 Hz, $^4J_{HH}$ = 1.8 Hz, 12H, P-Ph-H$_{meta}$), 7.01–6.98 (m, 4H, H-6/H-22), 6.91 (s, 6H, H-21/H-25), 6.70 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H-12), 6.60–6.58 (m, 4H, H-7/H-8), 6.23 (t, $^3J_{HH}$ = 7.6 Hz, 2H, H-13), 6.16 (d, $^3J_{HH}$ = 7.6 Hz, 2H, H-14), 6.05 (s, 2H, H-16), 5.48 (d, $^2J_{HH}$ = 14.9 Hz, 2H, H-10), 4.12 (d, $^2J_{HH}$ = 14.9 Hz, 2H, H-10), 3.92 (d, $^2J_{HH}$ = 16.4 Hz, 2H, H-17), 3.00 (d, $^2J_{HH}$ = 16.4 Hz, 2H, H-17), 2.39 (s, 6H, H-27), 1.69 (s, 6H, H-28), 1.56 (s, 6H, H-28). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, CD_3CN): δ = 186.0 (C-19), 173.5 (d, $^2J_{CP}$ = 2.0 Hz, C-2), 144.2 (d, $^3J_{CP}$ = 2.5 Hz, C-4), 140.4 (C-26), 138.3 (C-11), 137.8 (C-15), 135.8 (d, $^2J_{CP}$ = 11.1 Hz, P-Ph-C$_{ortho}$), 135.7 (C-23), 135.6 (C-24), 135.1 (d, $^4J_{CP}$ = 4.0 Hz, C-9), 132.0 (d, $^4J_{CP}$ = 2.7 Hz, P-Ph-C$_{para}$), 131.6 (d, $^1J_{CP}$ = 52.1 Hz, P-Ph-C$_{ipso}$), 130.0 (C-25), 129.9 (C-25), 129.4 (d, $^3J_{CP}$ = 10.8 Hz, P-Ph-C$_{meta}$), 129.4 (C-13), 127.9 (C-12), 126.2 (C-16), 125.4 (C-14), 123.7 (C-21), 123.7 (C-22), 122.3 (C-6), 121.4 (C-7), 117.8 (C-5), 111.3 (C-8), 53.0 (C-17), 50.8 (C-10), 21.3 (C-27), 17.7 (C-28), 17.5 (C-28). ^{31}P{^{1}H}-NMR (162 MHz, 300 K, CD_3CN): δ = 25.0 (s, PPh_3), –144.6 (sep, $^1J_{PF}$ = 706.2 Hz, PF_6). ^{19}F{^{1}H}-NMR (376 MHz, 300 K, CD_3CN): δ = –72.9 (d, $^1J_{FP}$ = 706.2 Hz, PF_6). HRMS (ESI, positive ions): *m/z* (%) = 1815.3122 (calcd for [[**7**] – PF_6]$^+$ 1815.3115).

2.10. Synthesis of compound H-8$(PF_6)_2$



A sample of compound H-**4**(PF_6) (0.400 g, 0.682 mmol) was suspended in dichloromethane (5 mL) and cooled with ice water to 0 °C. Subsequently, triethyloxonium hexafluorophosphate (0.169 g, 0.682 mmol) dissolved in dichloromethane (5 mL) was added slowly to the suspension. The reaction mixture was stirred and allowed to warm up to ambient temperature over 12 h. The overlaying liquid was decanted off and the remaining solid was washed with dichloromethane (2 x 3 mL). Compound H-**8**$(PF_6)_2$ was obtained as a colorless solid. Yield: 0.357 g (0.470 mmol, 69%). ^{1}H-NMR (400 MHz, 300 K, $(CD_3)_2SO$): δ = 9.56 (s, 1H, H-2), 8.17 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-18), 8.02 (s, 1H, H-5), 7.99 (d, $^3J_{HH}$ = 8.2 Hz, 1H, H-21), 7.94 (s, 1H, H-4), 7.73 (t, $^3J_{HH}$ = 8.2 Hz, 1H, H-19), 7.68 (t, $^3J_{HH}$ = 8.2 Hz, 1H, H-20), 7.61 (s, 1H, H-8), 7.52–7.43 (m, 3H, H-10/H-11/H-12), 7.15 (s, 2H, H-25), 5.82 (s, 2H, H-13), 5.53 (s, 2H, H-6), 4.61 (q, $^3J_{HH}$ = 7.3Hz, 2H, H-29), 2.34 (s, 3H, H-27), 1.98 (s, 6H, H-28), 1.48 (t, $^3J_{HH}$ = 7.3 Hz, 3H, H-30). ^{13}C{^{1}H}-NMR (100 MHz, 300 K, $(CD_3)_2SO$): δ = 140.6 (C-15), 140.4 (C-26), 137.6 (C-2), 135.4 (C-7), 134.2 (C-24), 134.1 (C-9), 131.1 (C-23), 130.9 (C-22), 130.5 (C-17), 129.9 (C-11), 129.3 (C-25), 128.4 (C-12), 128.3 (C-10), 127.7 (C-8), 127.1 (C-19), 127.1 (C-20), 124.3 (C-4), 123.1 (C-5), 113.4 (C-18), 113.3 (C-21), 52.1 (C-6), 49.2 (C-13), 42.2 (C-29), 20.6 (C-27), 16.8 (C-28), 13.5 (C-30). ^{31}P{^{1}H}-NMR (162 MHz, 300 K, $(CD_3)_2SO$): δ = –144.2 (sep, $^1J_{PF}$ = 711.2 Hz, PF_6). ^{19}F{^{1}H}-NMR (376 MHz, 300 K, $(CD_3)_2SO$): δ = –70.1 (d, $^1J_{FP}$ = 711.2 Hz, PF_6). HRMS (ESI, positive ions): *m/z* (%) = 615.1910 (calcd for [[**8**] – $PF_6]^+$ 615.1879), 235.1124 (calcd for [[**8**] – $2PF_6]^{2+}$ 235.1119).

3. NMR spectra

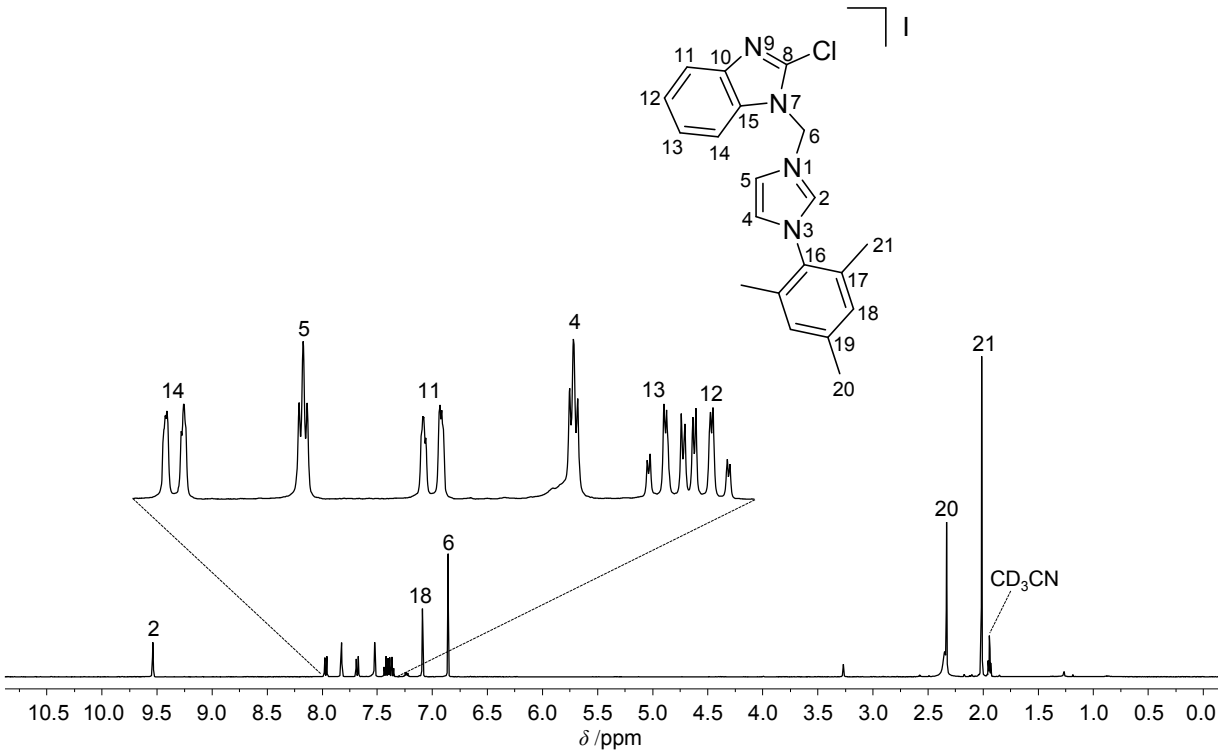


Figure S1. ^{1}H NMR spectrum of compound H-**1**(I) (400 MHz, CD_3CN).

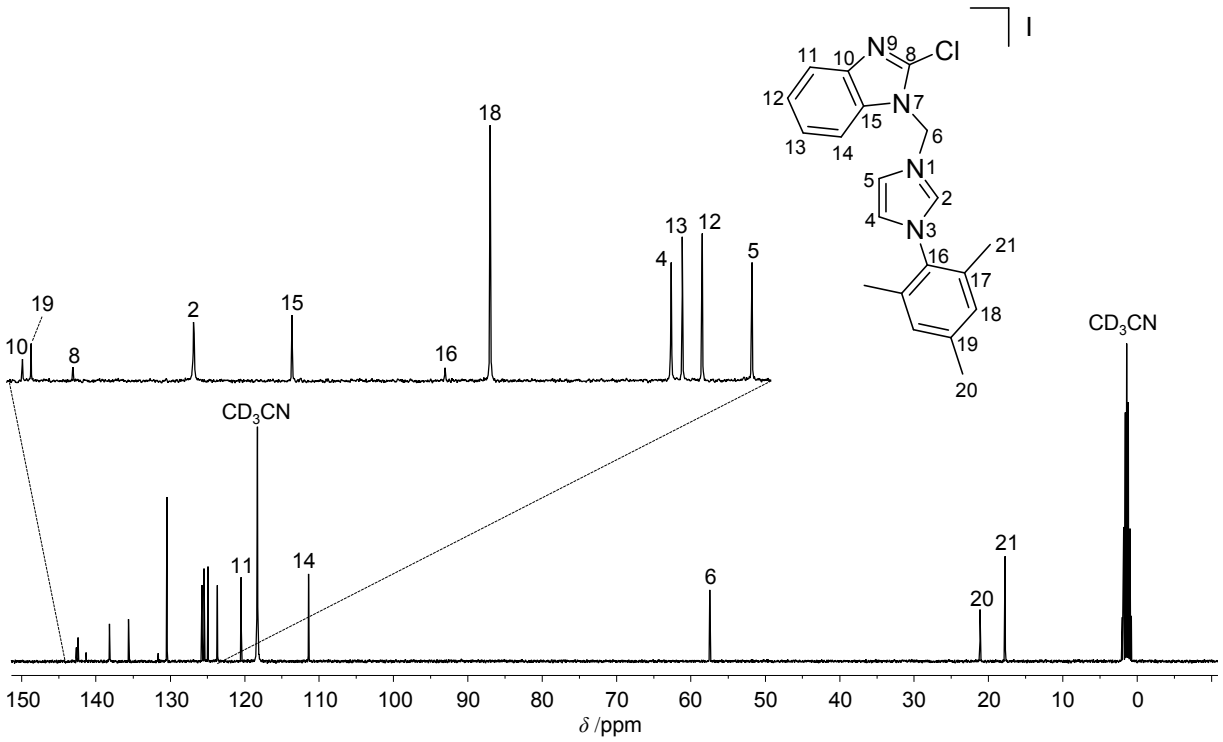


Figure S2. $^{13}C\{^{1}H\}$ NMR spectrum of compound H-**1**(I) (100 MHz, CD_3CN).

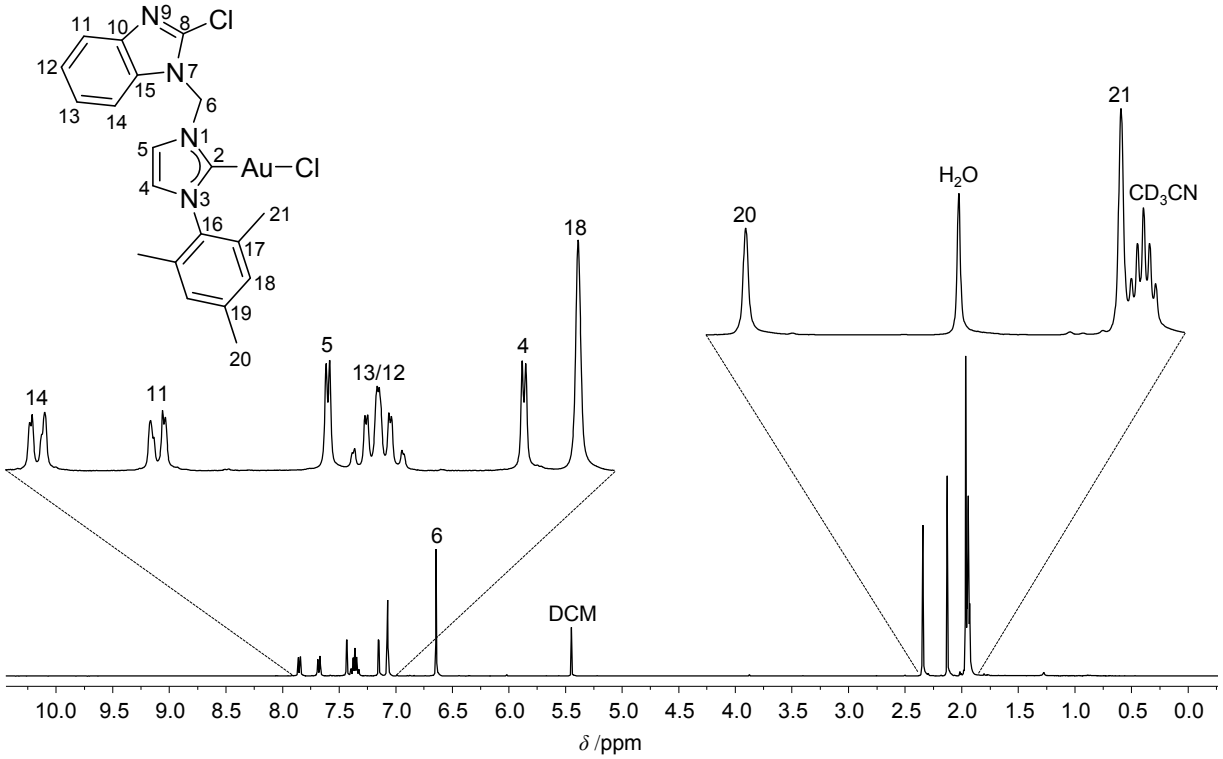


Figure S3. ^{1}H NMR spectrum of complex [**2**] (400 MHz, CD_3CN).

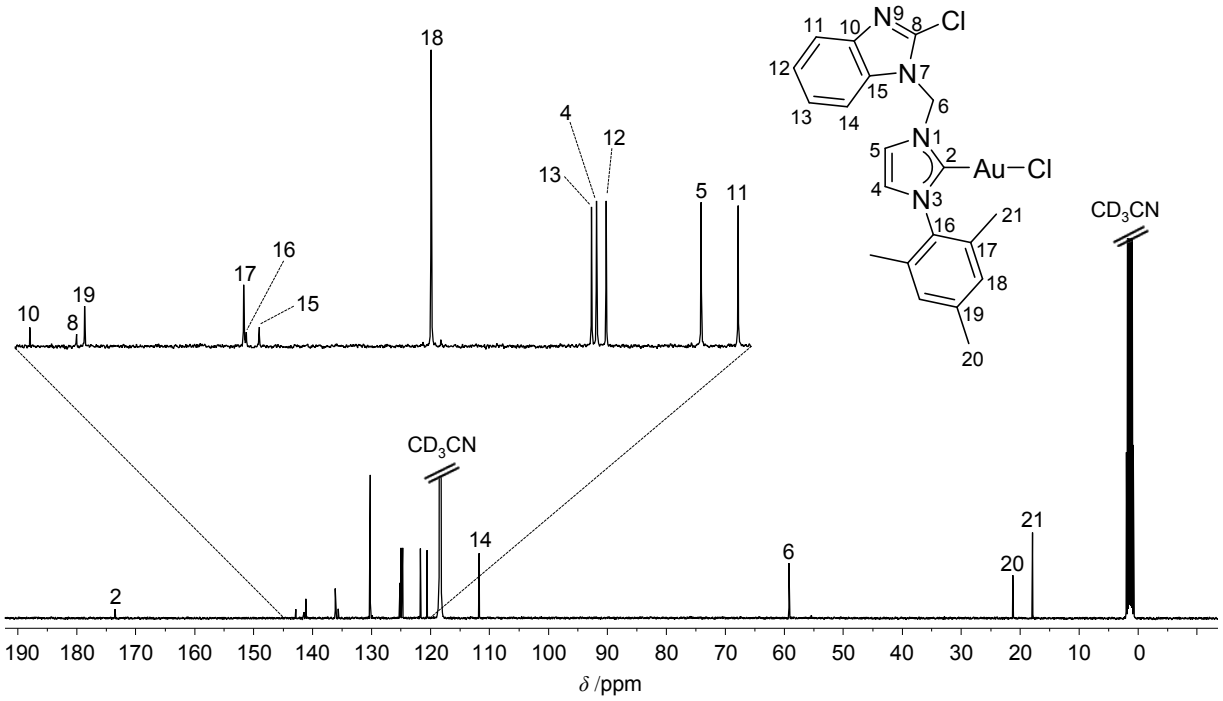


Figure S4. $^{13}C\{^{1}H\}$ NMR spectrum of complex [**2**] (100 MHz, CD_3CN).

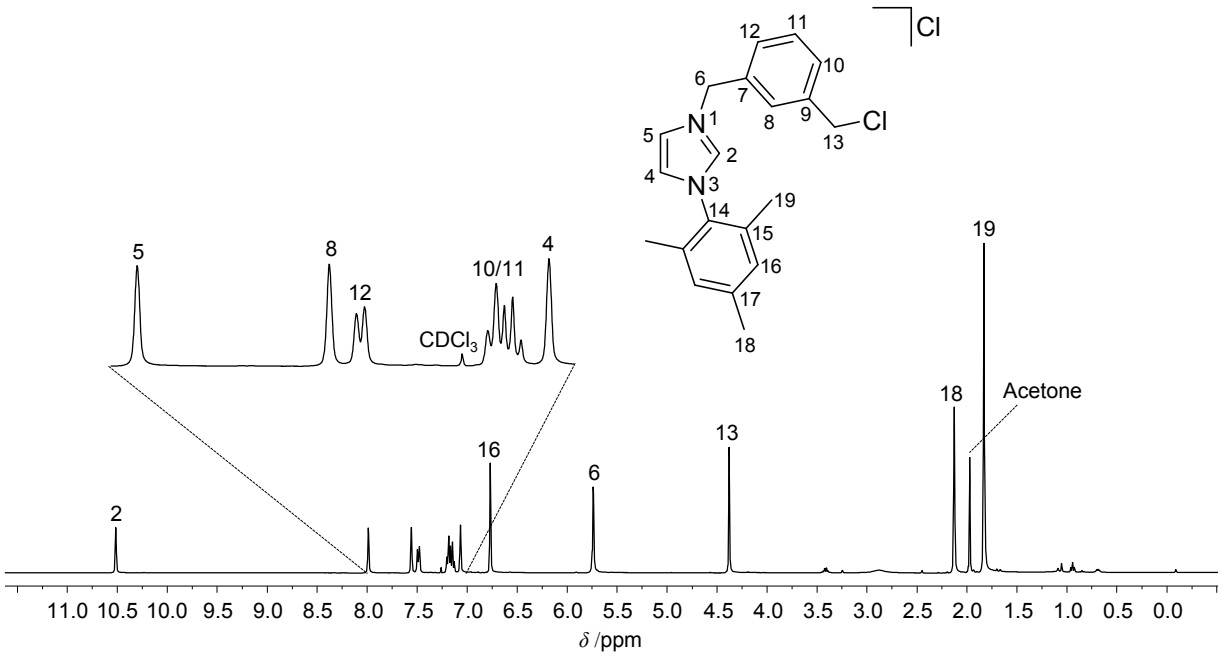


Figure S5. ^{1}H NMR spectrum of compound H-**3**(Cl) (400 MHz, $CDCl_3$).

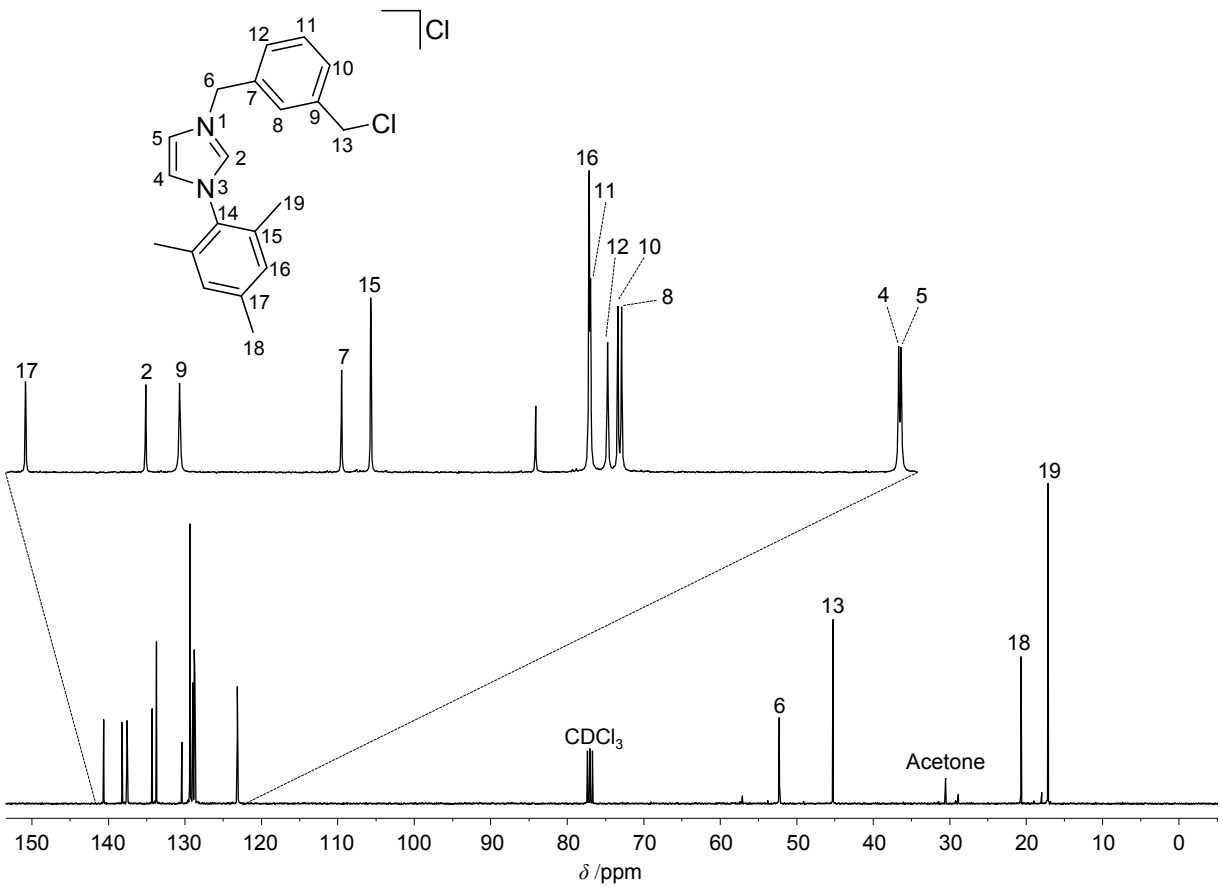


Figure S6. $^{13}C\{^{1}H\}$ NMR spectrum of compound H-**3**(Cl) (100 MHz, $CDCl_3$).

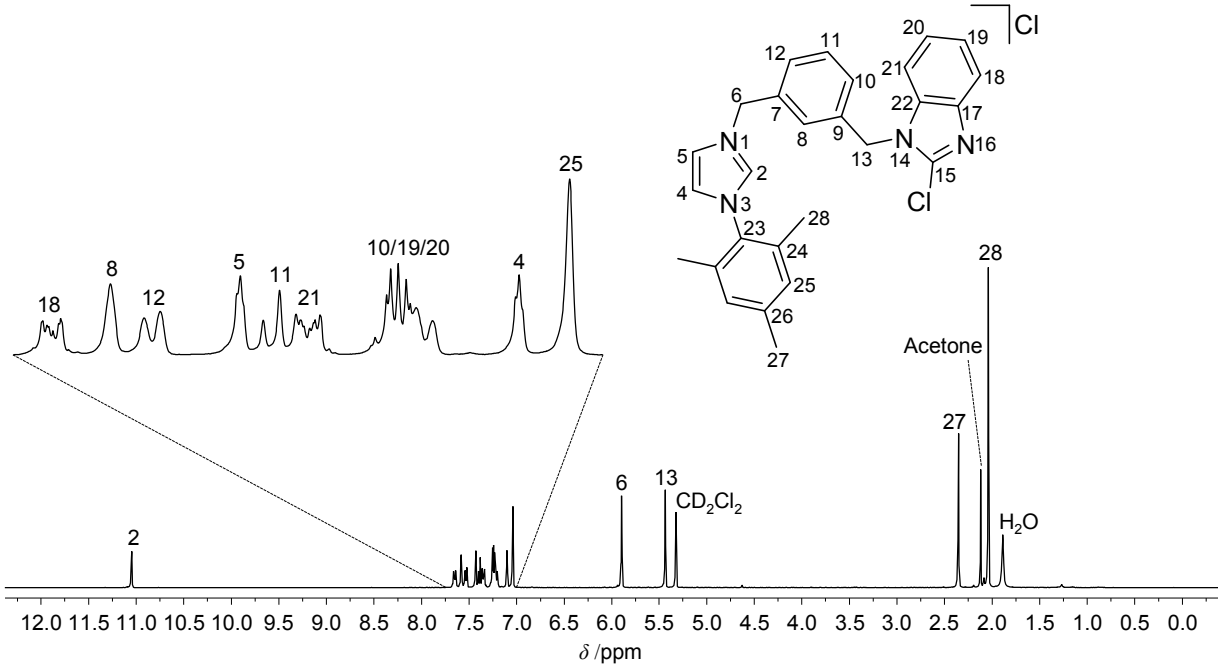


Figure S7. ^{1}H NMR spectrum of compound H-**4**(Cl) (400 MHz, CD_2Cl_2).

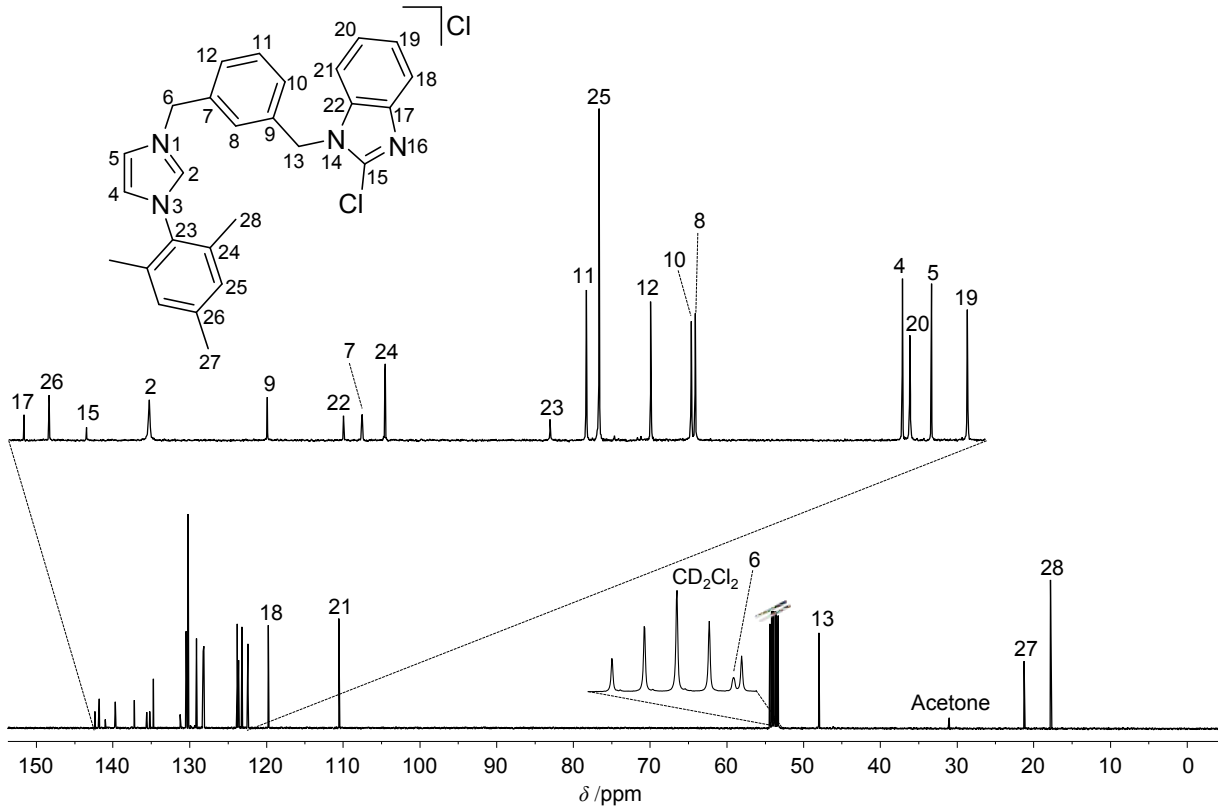


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of compound H-**4**(Cl) (100 MHz, CD_2Cl_2).

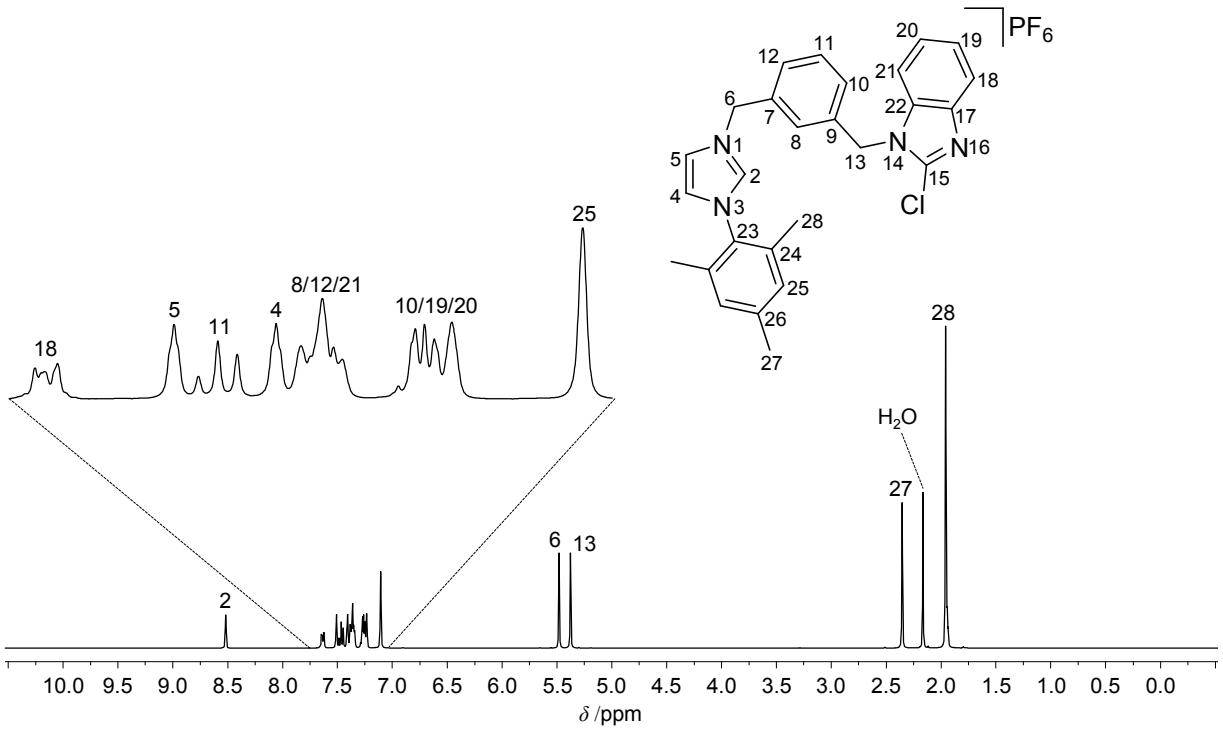


Figure S9. ^{1}H NMR spectrum of compound H-**4**(PF_6) (400 MHz, CD_3CN).

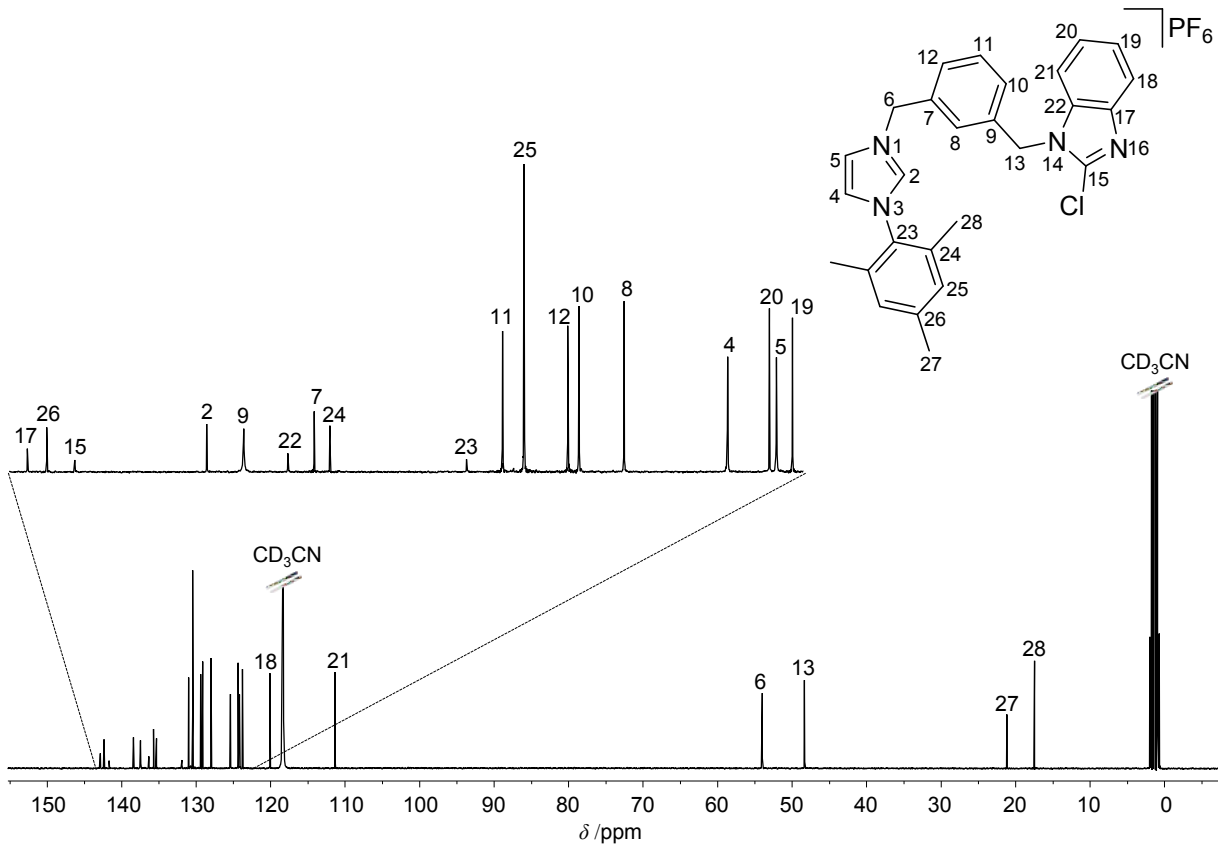


Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of compound H-**4**(PF_6) (100 MHz, CD_3CN).

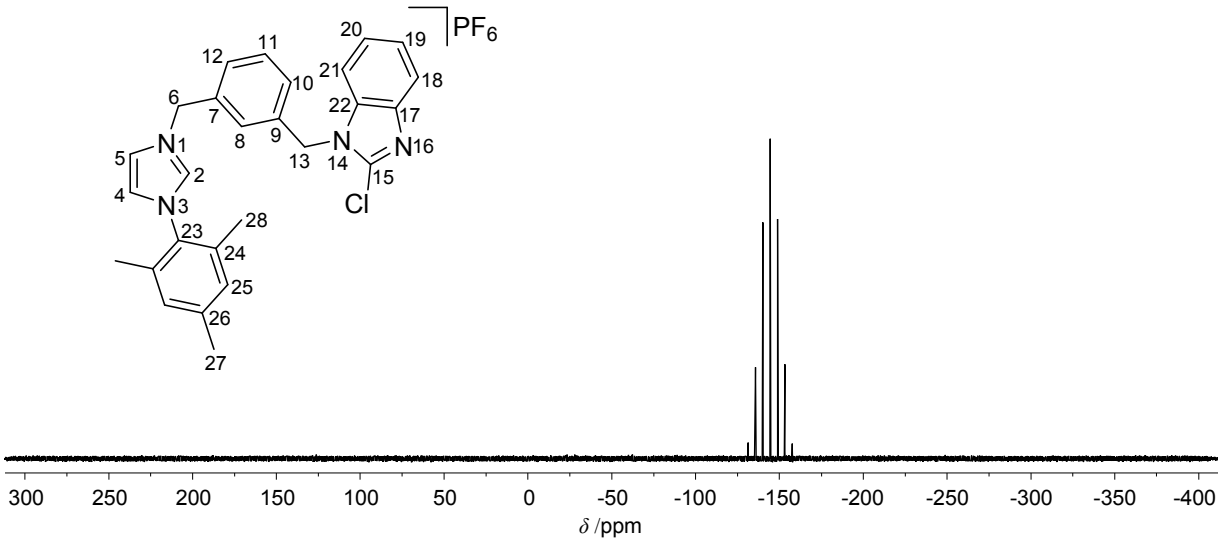


Figure S11. $^{31}P\{^{1}H\}$ NMR spectrum of compound H-**4**(PF_6) (162 MHz, CD_3CN).

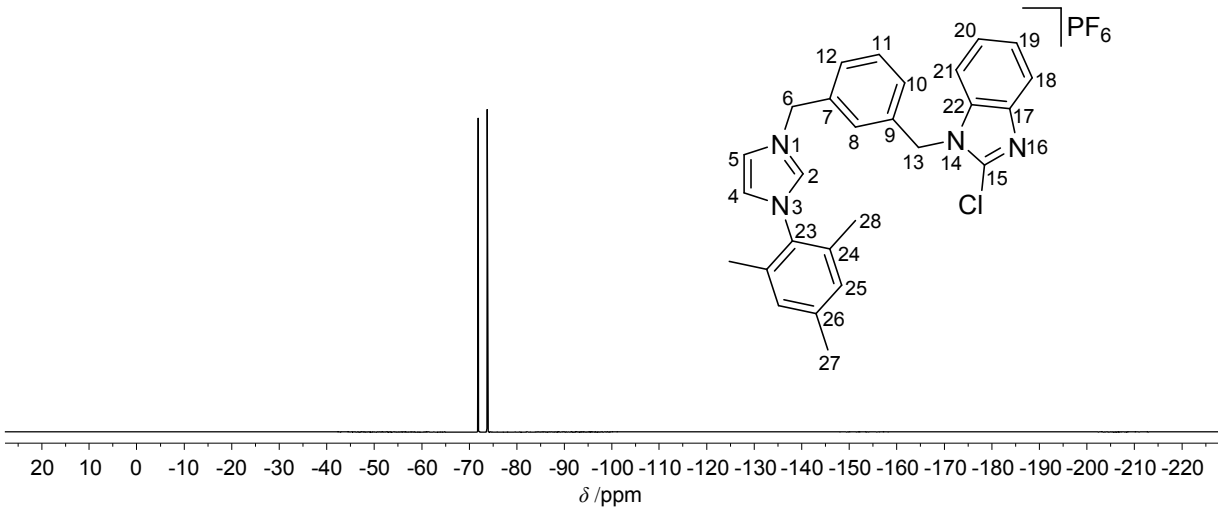


Figure S12. $^{19}F\{^{1}H\}$ NMR spectrum of compound H-**4**(PF_6) (376 MHz, CD_3CN).

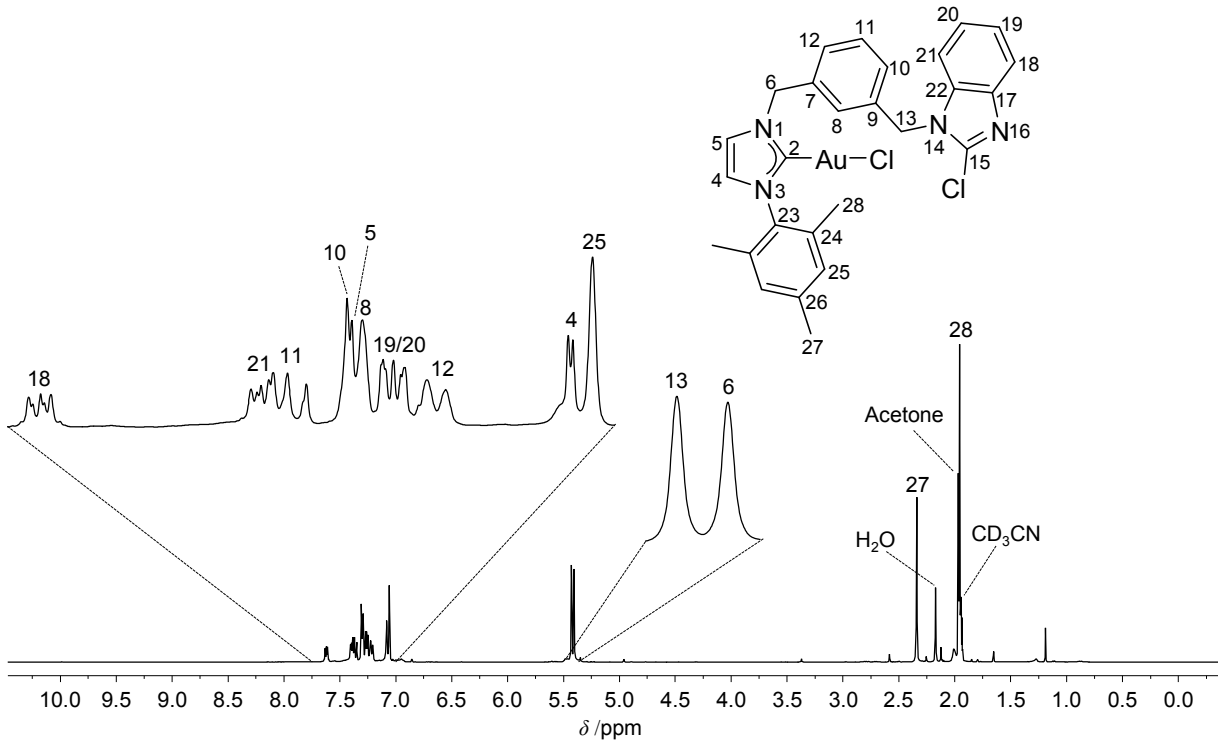


Figure S13. ^{1}H NMR spectrum of complex [**5**] (400 MHz, CD_3CN).

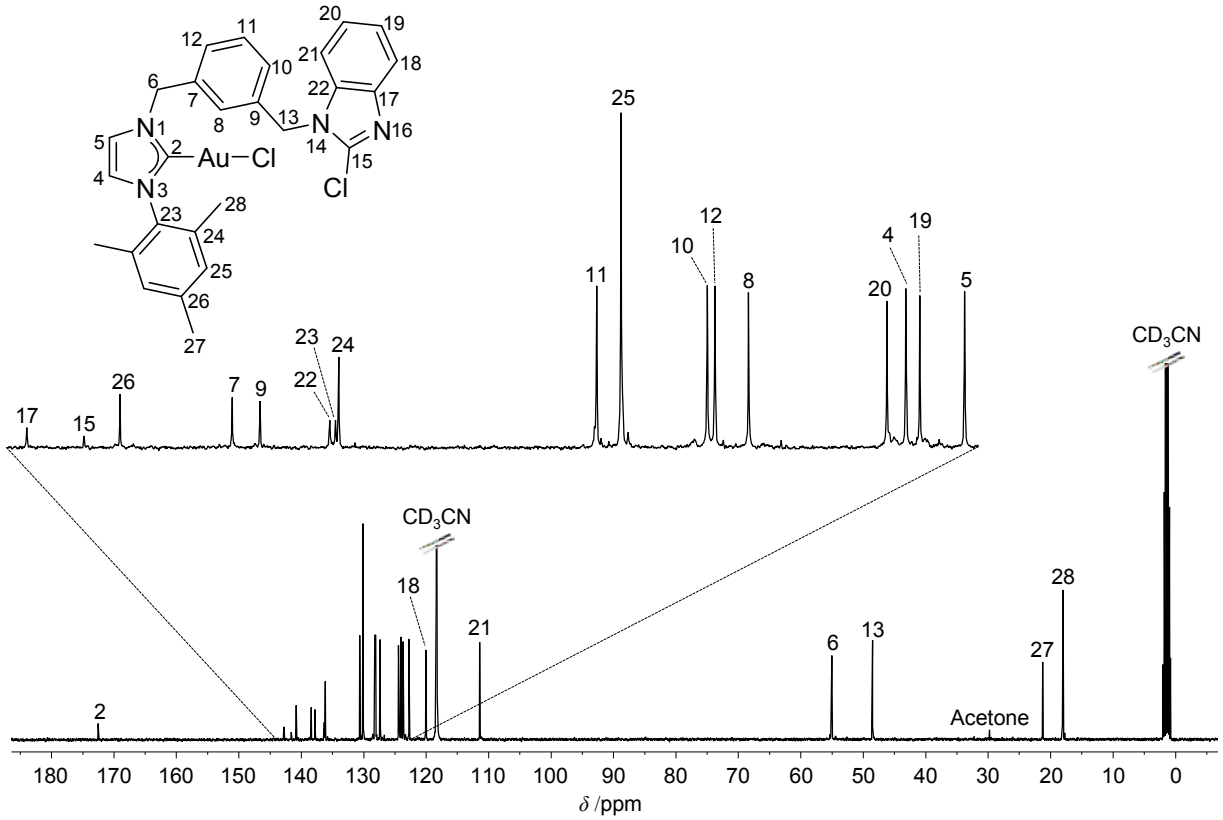


Figure S14. $^{13}C\{^{1}H\}$ NMR spectrum of complex [**5**] (100 MHz, CD_3CN).

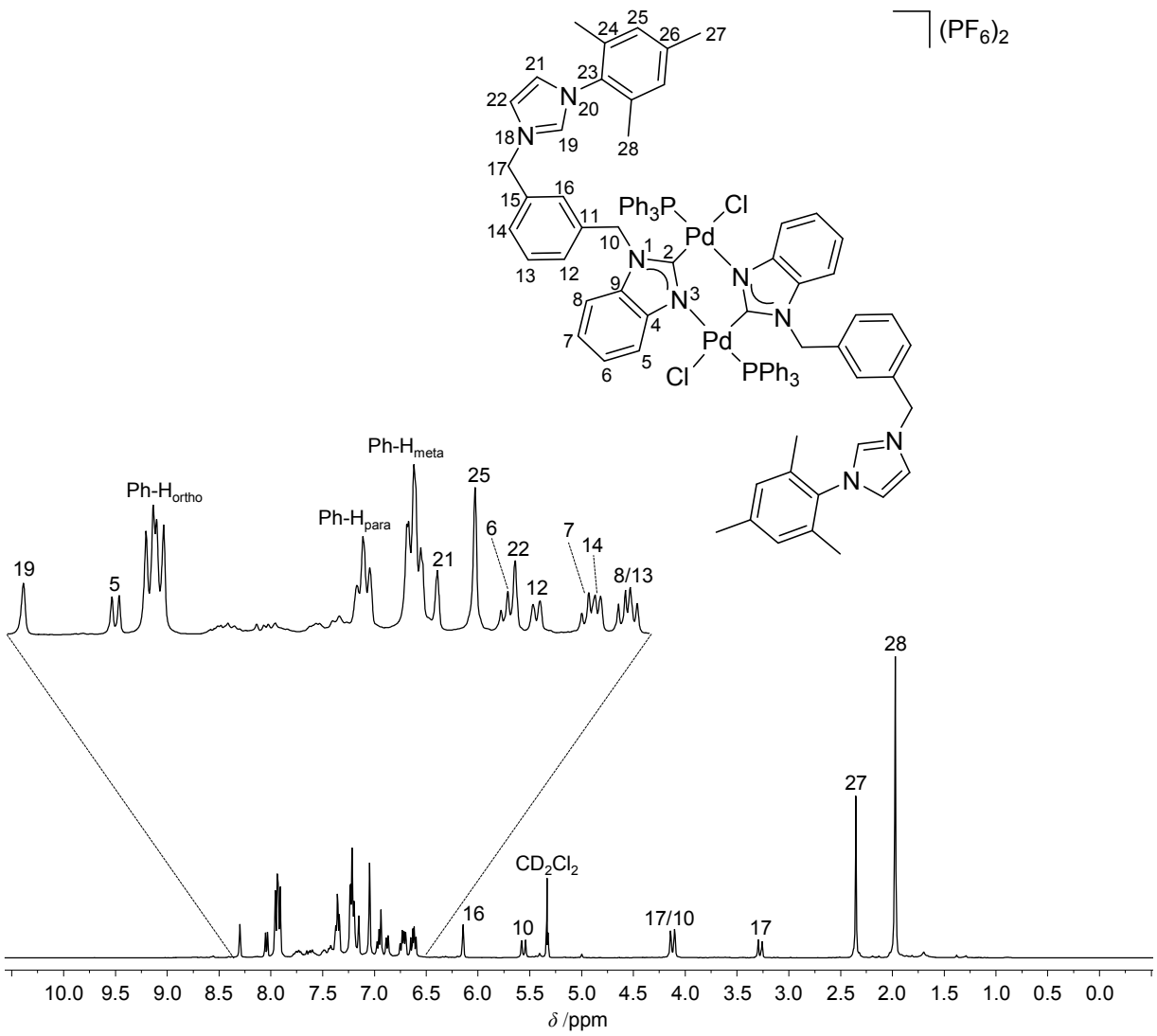


Figure S15. ^{1}H NMR spectrum of complex **[6]**$(PF_6)_2$ (400 MHz, CD_2Cl_2).

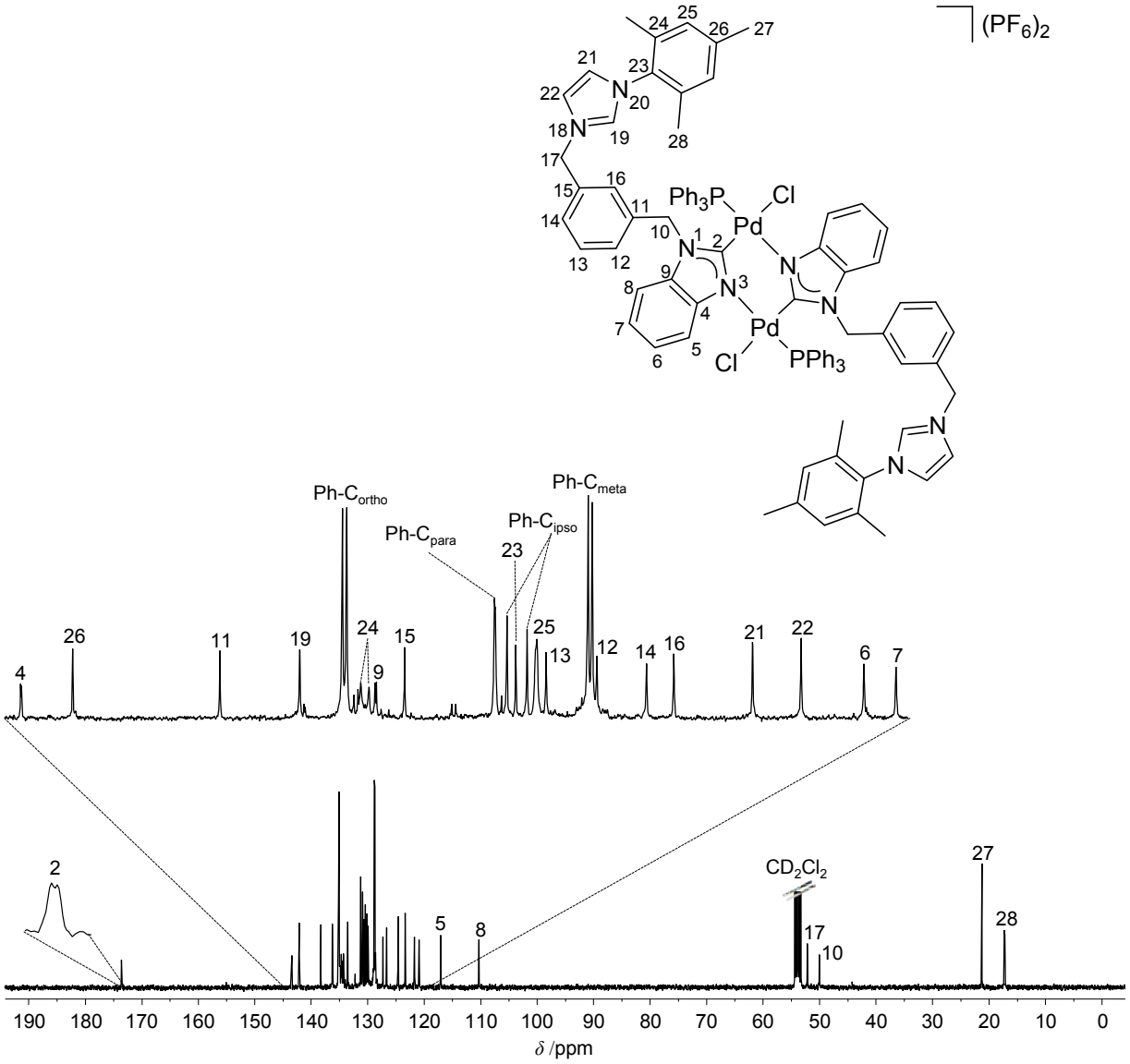


Figure S16. $^{13}C\{^{1}H\}$ NMR spectrum of complex [**6**]$(PF_6)_2$ (100 MHz, CD_2Cl_2).

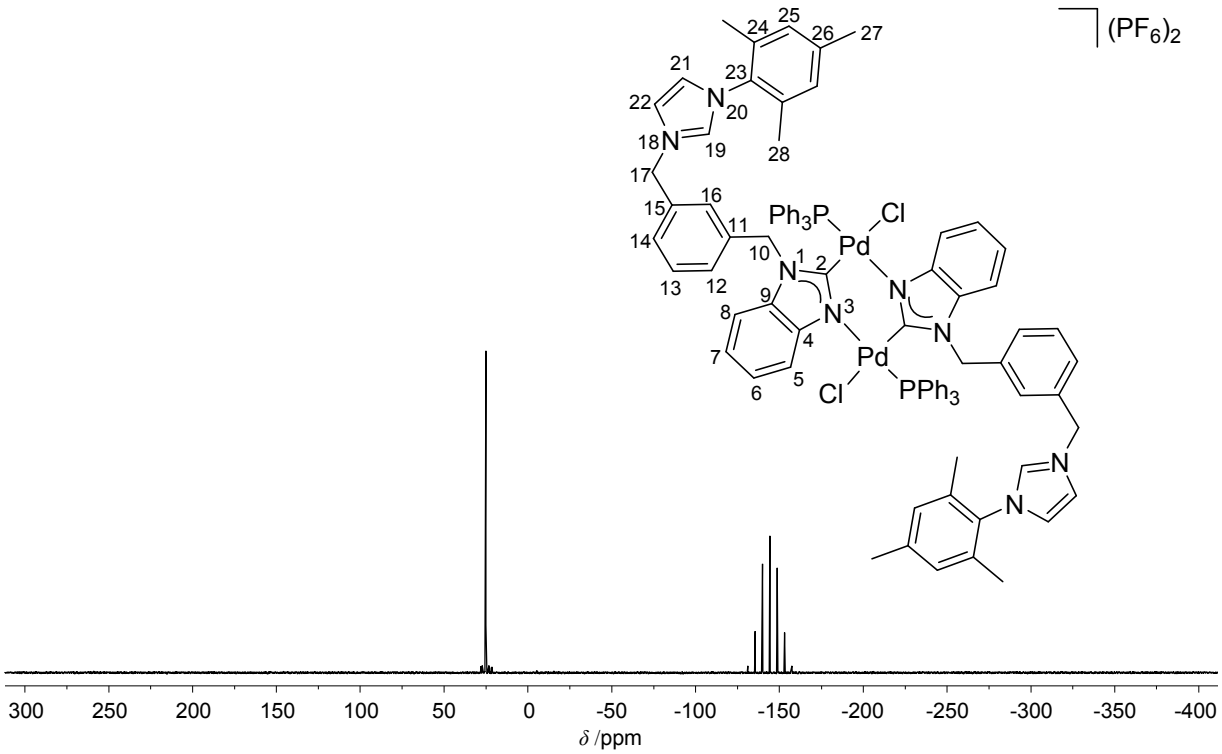


Figure S17. $^{31}P\{^{1}H\}$ NMR spectrum of complex [**6**]$(PF_6)_2$ (162 MHz, CD_2Cl_2).

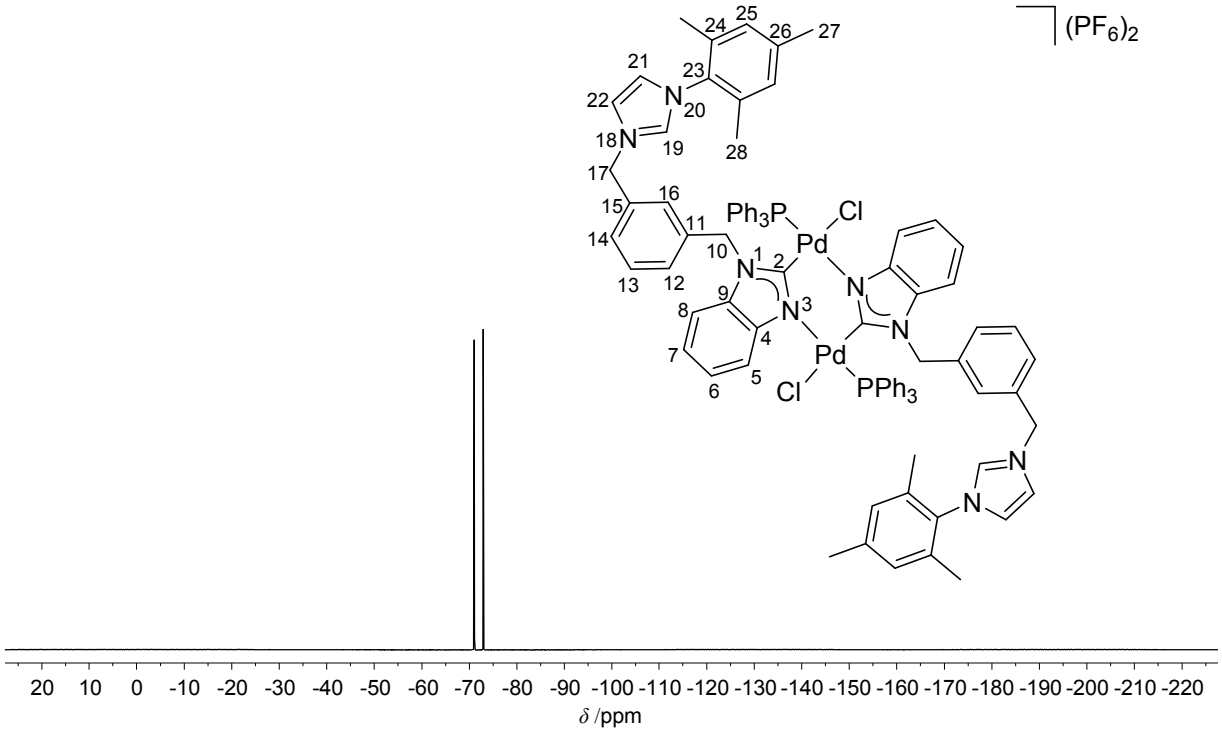


Figure S18. $^{19}F\{^{1}H\}$ NMR spectrum of complex [**6**]$(PF_6)_2$ (376 MHz, CD_2Cl_2).

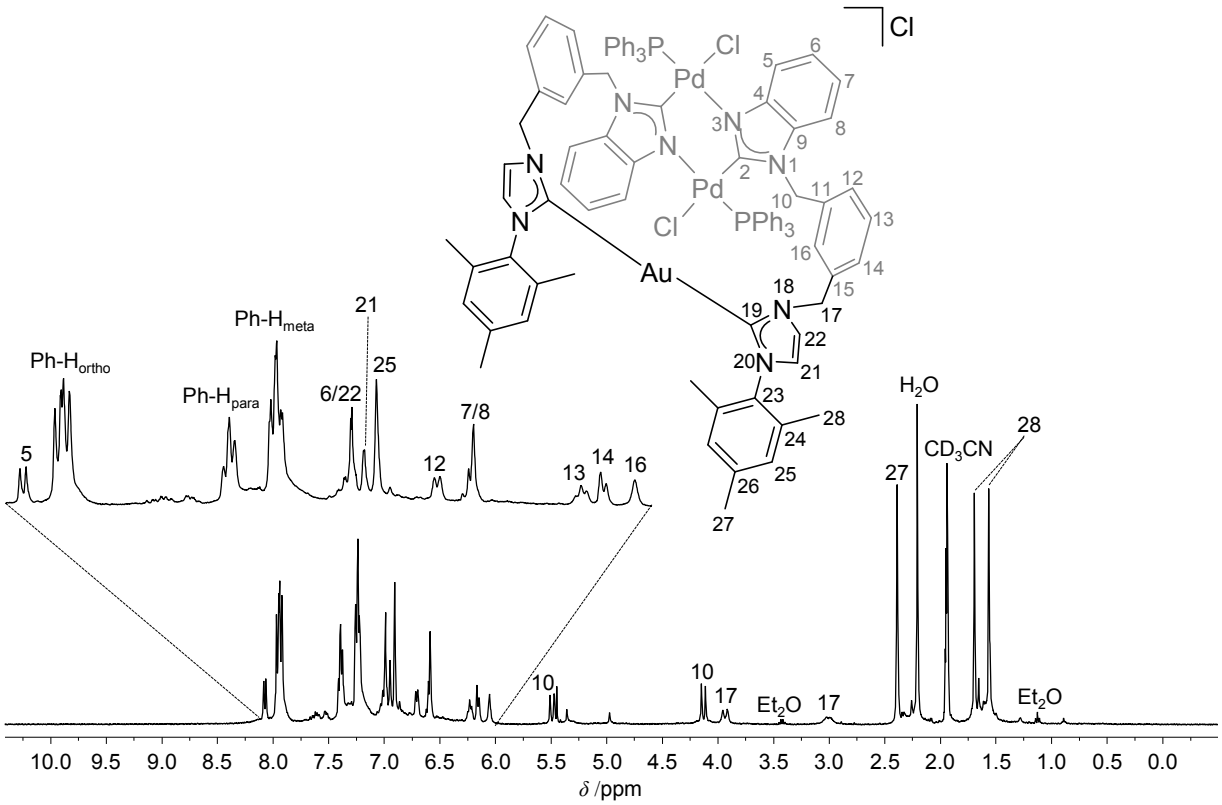


Figure S19. ^{1}H NMR spectrum of complex [**7**]Cl (400 MHz, CD_3CN).

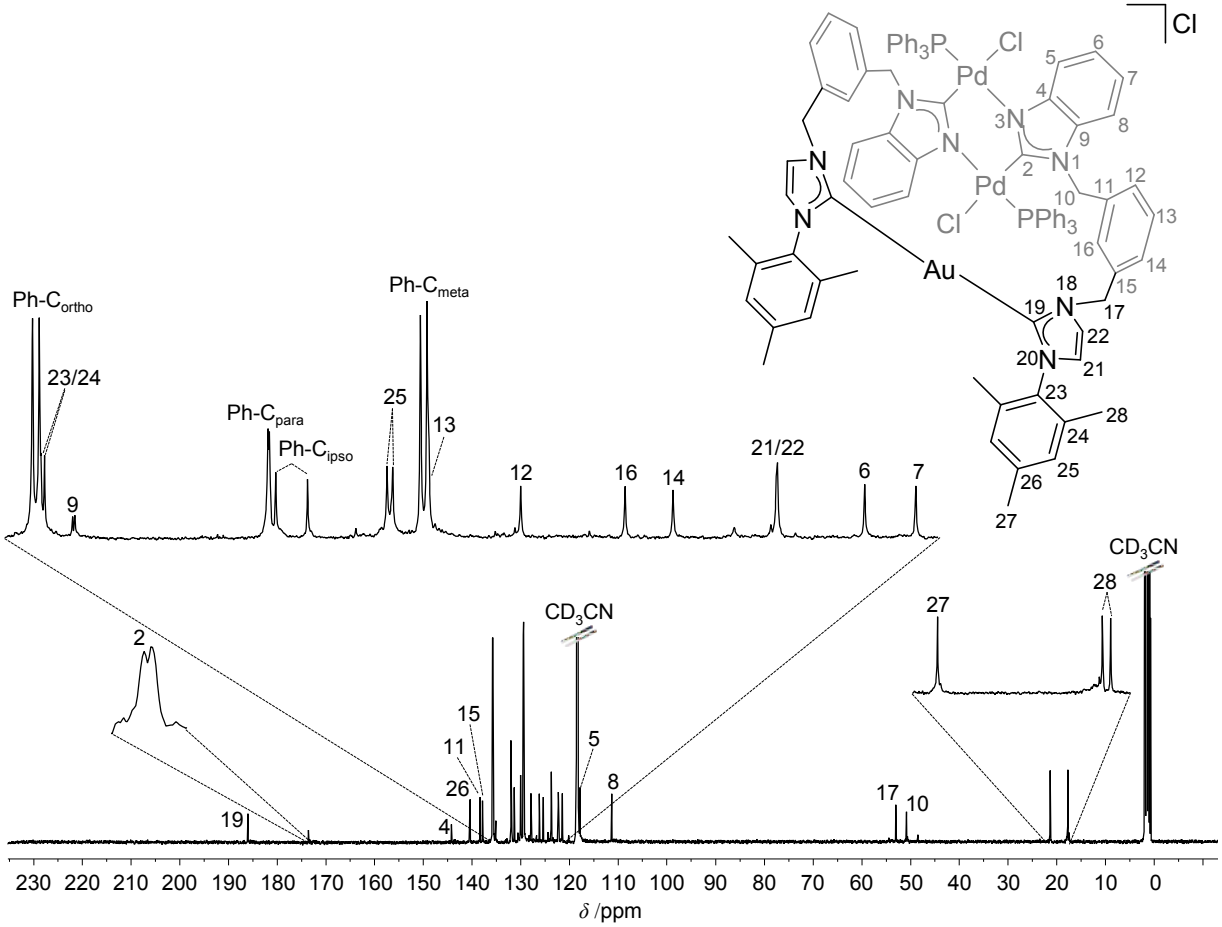


Figure S20. ^{13}C{^{1}H} NMR spectrum of complex [**7**]Cl (100 MHz, CD_3CN).

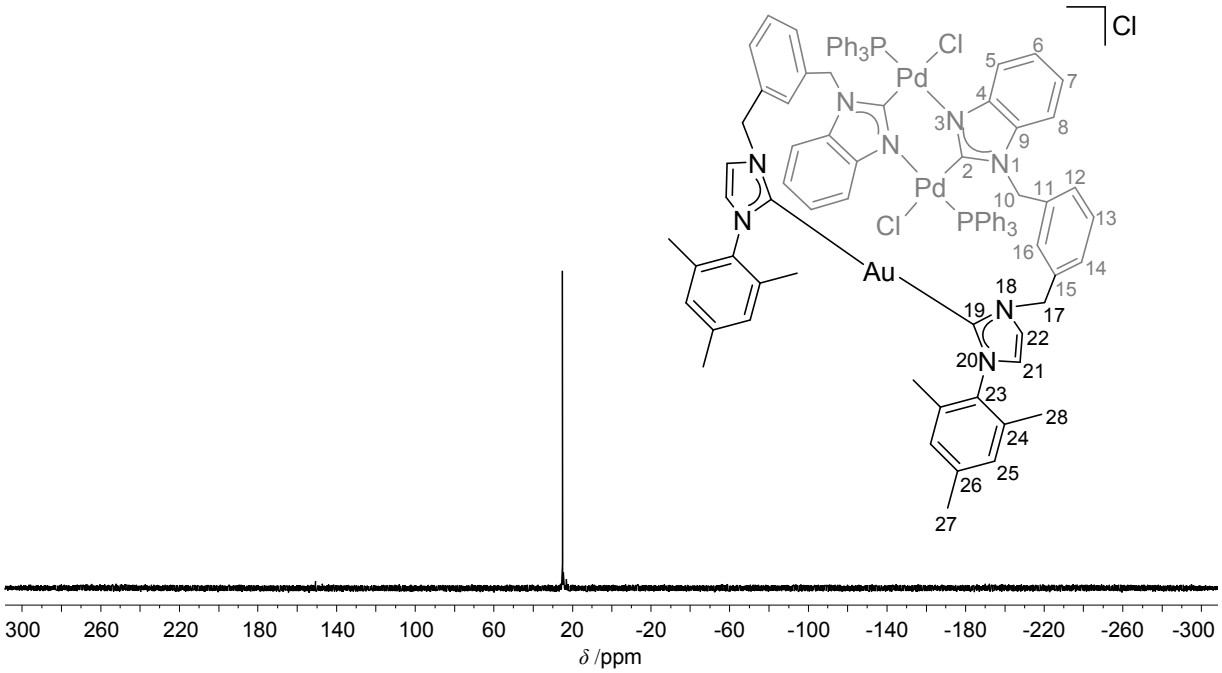


Figure S21. $^{31}P\{^{1}H\}$ NMR spectrum of complex [**7**]Cl (162 MHz, CD_3CN).

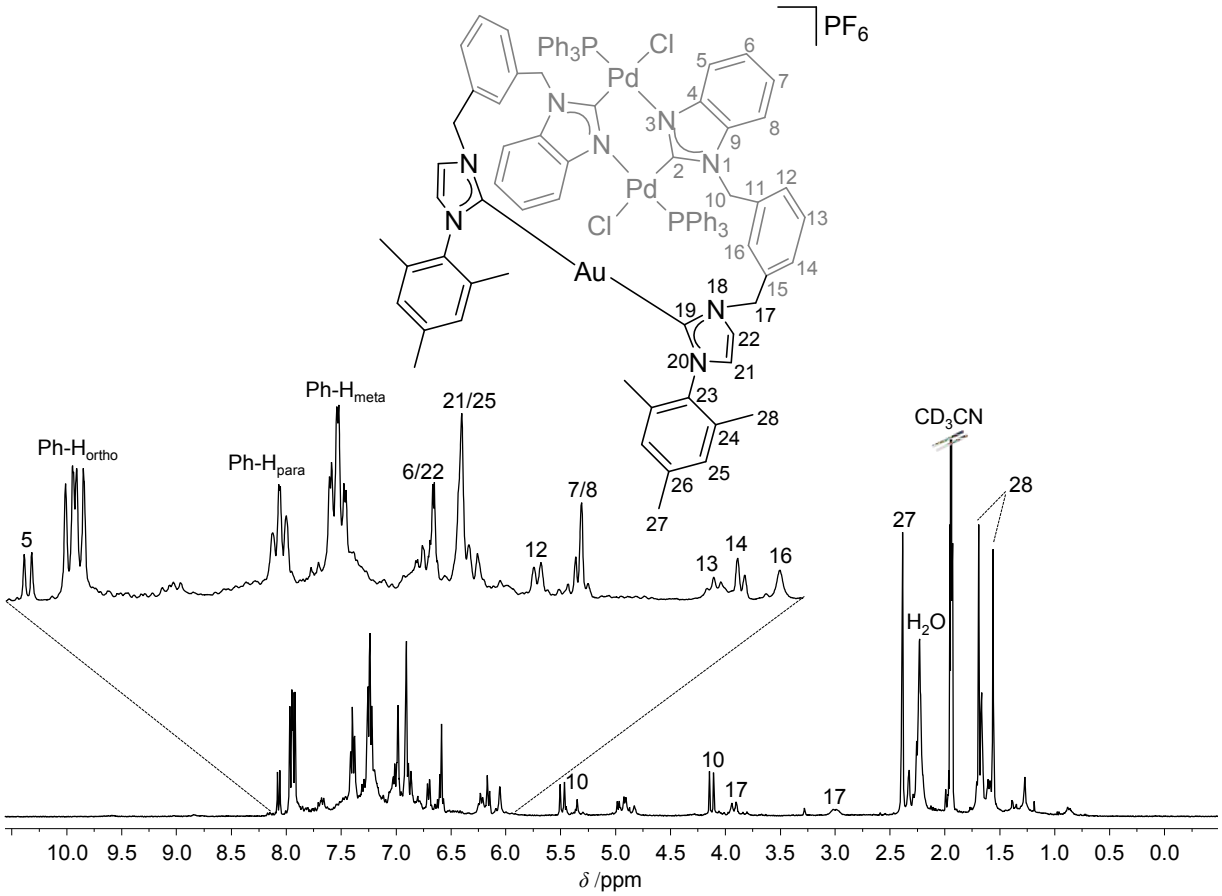


Figure S22. ^{1}H NMR spectrum of complex [**7**]PF_6 (400 MHz, CD_3CN).

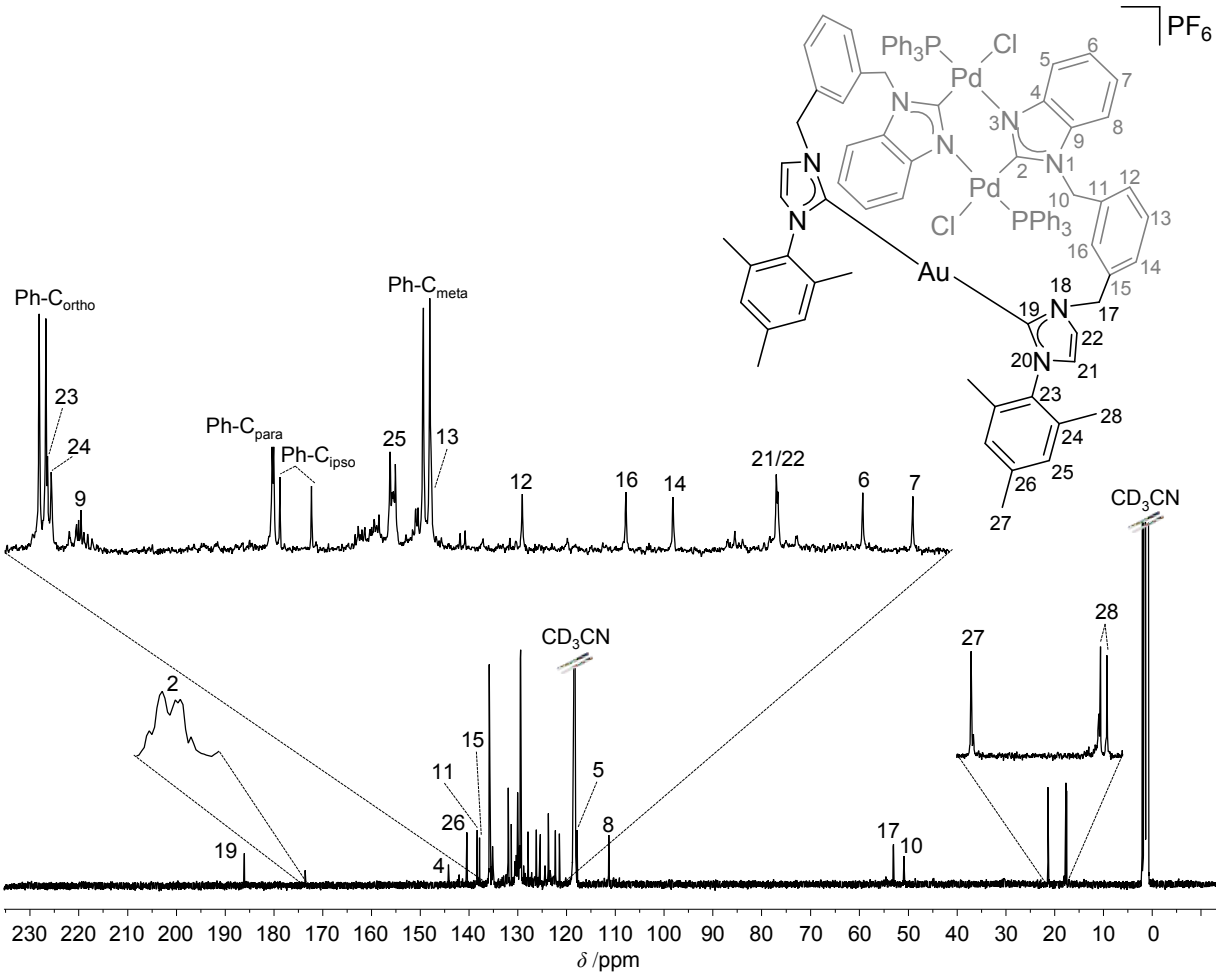


Figure S23. $^{13}C\{^{1}H\}$ NMR spectrum of complex [**7**]PF_6 (100 MHz, CD_3CN).

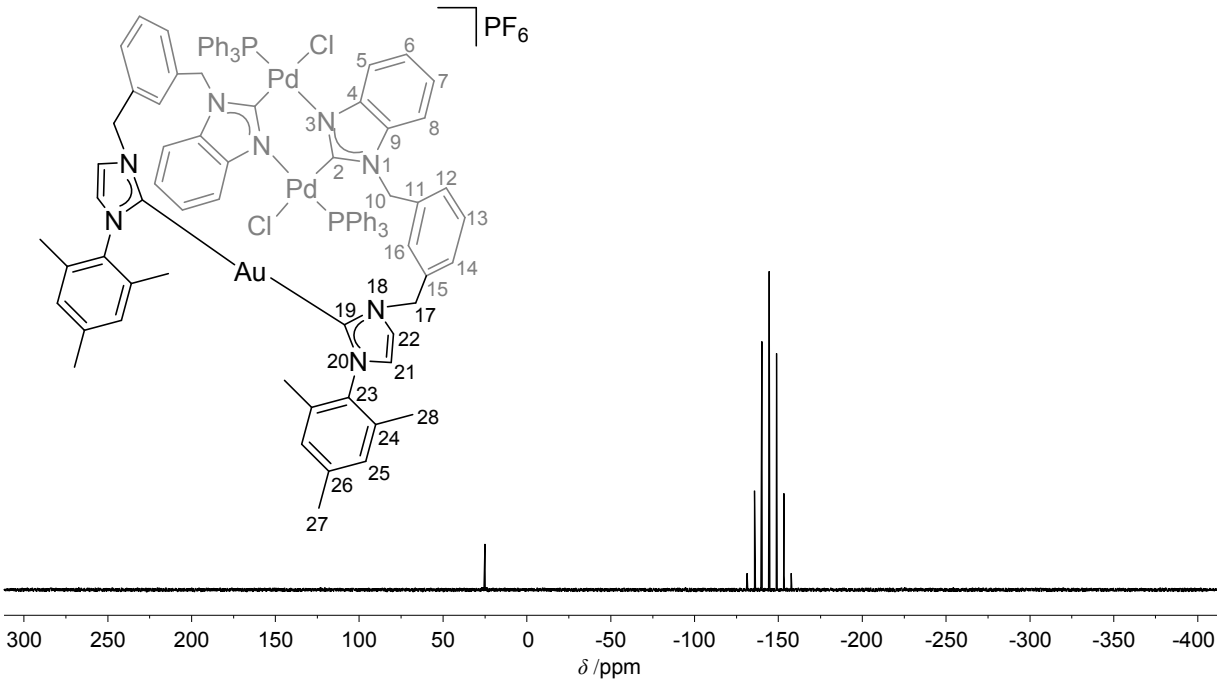


Figure S24. $^{31}P\{^{1}H\}$ NMR spectrum of complex [**7**]PF_6 (162 MHz, CD_3CN).

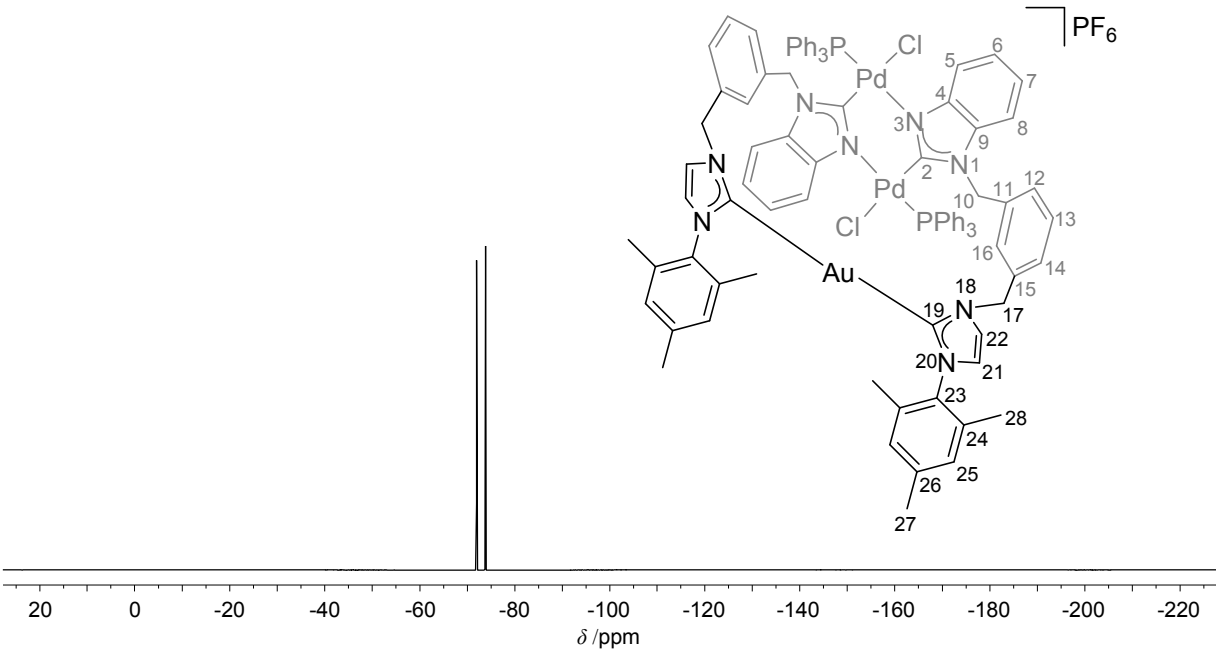


Figure S25. $^{19}F\{^{1}H\}$ NMR spectrum of complex [**7**]PF_6 (376 MHz, CD_3CN).

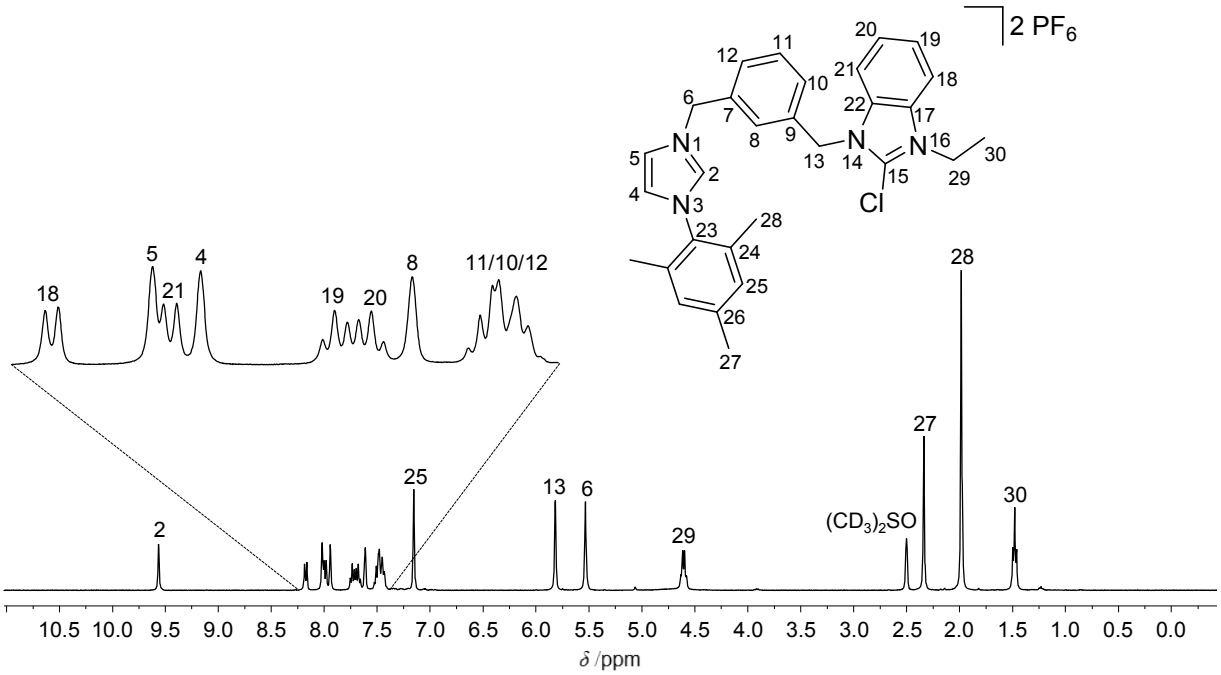


Figure S26. ^{1}H NMR spectrum of compound H-**8**$(PF_6)_2$ (400 MHz, $(CD_3)_2SO$).

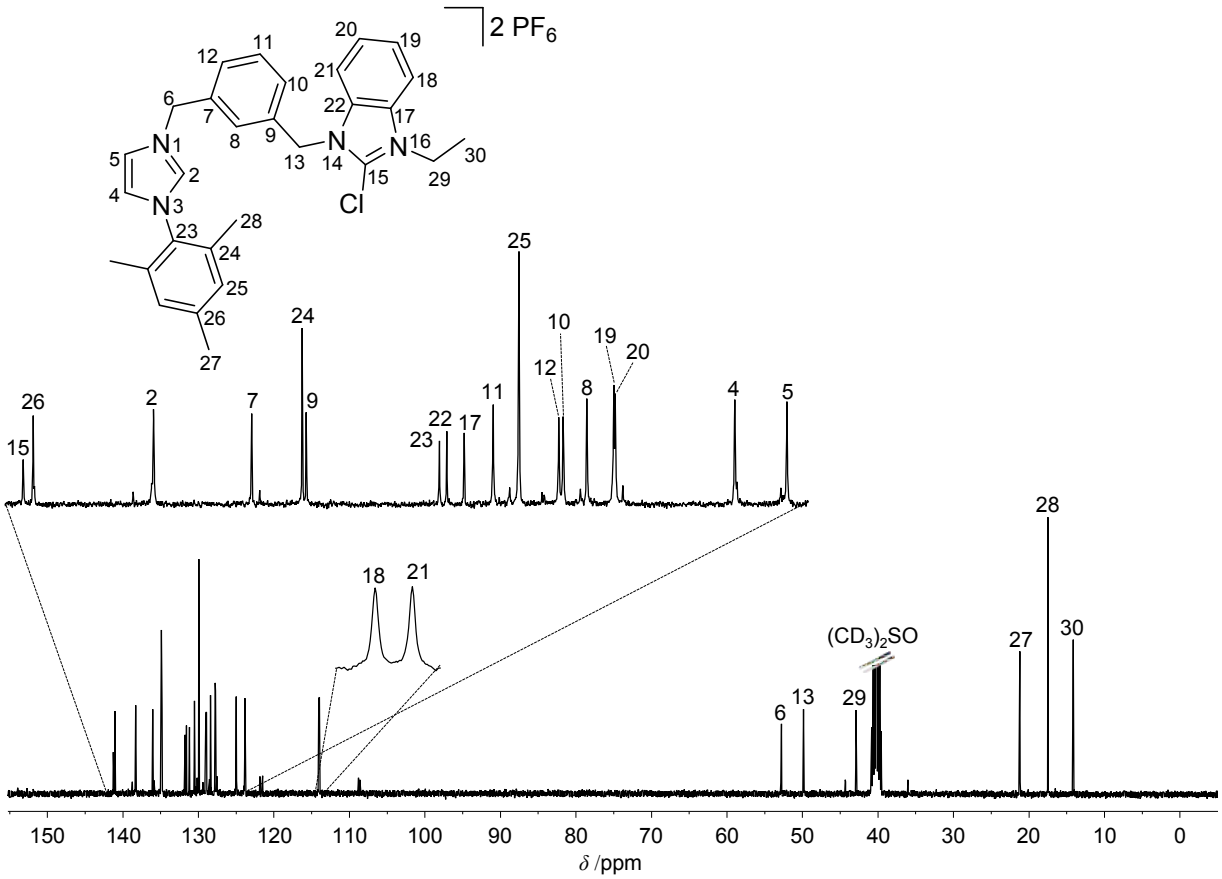


Figure S27. $^{13}C\{^1H\}$ NMR spectrum of compound H-**8**$(PF_6)_2$ (100 MHz, $(CD_3)_2SO$).

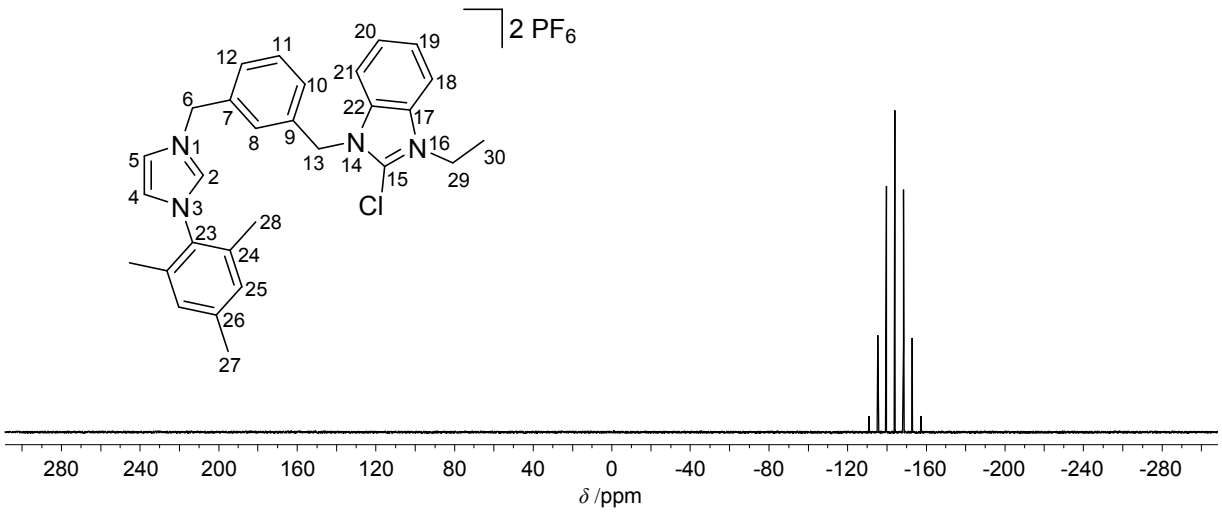


Figure S28. $^{31}P\{^1H\}$ NMR spectrum of compound H-**8**$(PF_6)_2$ (162 MHz, $(CD_3)_2SO$).

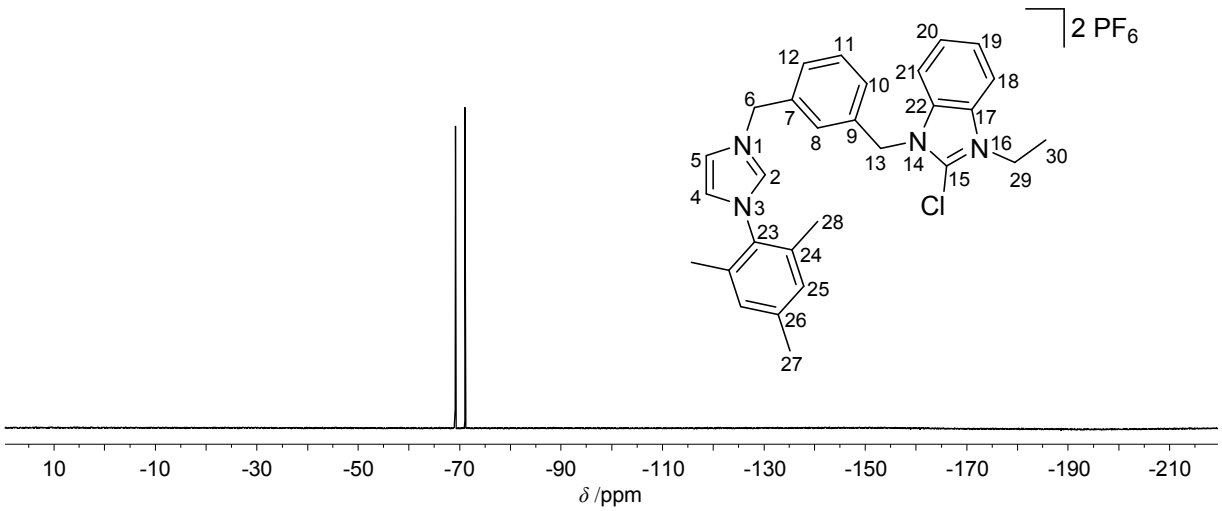


Figure S29. $^{19}F\{^{1}H\}$ NMR spectrum of compound H**8**$(PF_6)_2$ (376 MHz, $(CD_3)_2SO$).

4. X-ray crystallography

X-ray diffraction data for the compounds H-**1**(I), [**2**], H-**4**(PF_6), [**5**] and [**7**]PF_6 were recorded with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at T = 100(2) K (H-**1**(I), [**2**], [**5**] and [**7**]PF_6) and at T = 153(2) K (for H-**4**(PF_6)). Diffraction data were collected over the full sphere and were corrected for absorption. Structure solutions were found with the SHELXS[S4] package using direct methods and were refined with SHELXL[S4] against $|F^2|$ using first isotropic and later anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added to the structure models on calculated positions and refined as riding atoms.

*Crystal data and structure refinement details for H-**1(I):*** $C_{20}H_{20}N_4ClI$, M = 478.75, colorless block, 0.39 × 0.09 × 0.08 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 14.0786(2) Å, b = 11.8861(2) Å, c = 11.9437(2) Å, β = 96.7670(10)°, V = 1984.73(6) Å^3, ρ_{calcd} = 1.602 g cm^{-3}, μ = 1.759 mm^{-1}, ω and φ scans, 22242 measured intensities (6.8° ≤ 2θ ≤ 62.0°), semiempirical absorption correction (0.693 ≤ T ≤ 0.796), 6250 independent (R_{int} = 0.0373) and 5105 observed intensities ($I \geq 2\sigma(I)$), refinement of 238 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0278, R_w = 0.0567, R_{all} = 0.0380, $R_{w,all}$ = 0.0616. The asymmetric unit contains one formula unit of H-**1**(I).

*Crystal data and structure refinement details for [**2**]:* $C_{20}H_{19}N_4AuCl_2$, M = 583.26, colorless cube, 0.44 × 0.41 × 0.03 mm^3, monoclinic, space group $C2/c$, Z = 8, a = 29.8651(5) Å, b = 9.3064(2) Å, c = 16.4107(3) Å, β = 120.9910(10)°, V = 3910.02(13) Å^3, ρ_{calcd} = 1.982 g cm^{-3}, μ = 7.811 mm^{-1}, ω and φ scans, 35917 measured intensities (6.8° ≤ 2θ ≤ 64.6°), semiempirical absorption correction (0.226 ≤ T ≤ 0.746), 6480 independent (R_{int} = 0.0534) and 5974 observed intensities ($I \geq 2\sigma(I)$), refinement of 248 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0292, R_w = 0.0728, R_{all} = 0.0323, $R_{w,all}$ = 0.0742. The asymmetric unit contains one formula unit of [**2**].

*Crystal data and structure refinement details for H-**4**(PF_6)*: $C_{27}H_{26}N_4ClF_6P$, M = 586.94, colorless prism, 0.50 × 0.49 × 0.32 mm^3, triclinic, space group P-1, Z = 2, a = 9.95650(10) Å, b = 10.01450(10) Å, c = 15.3242(2) Å, α = 96.9790(10)°, β = 112.4490(10)°, γ = 112.4490(10)°, V = 1311.90(3) Å^3, ρ_{calcd} = 1.486 g cm^{-3}, μ = 0.275 mm^{-1}, ω and φ scans, 20599 measured intensities (4.6° ≤ 2θ ≤ 56.6°), semiempirical absorption correction (0.921 ≤ T ≤ 1.000), 6500 independent (R_{int} = 0.0177) and 5919 observed intensities ($I \geq 2\sigma(I)$), refinement of 355 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0459, $\underline{R}_w$ = 0.1223, R_{all} = 0.0497, $R_{w,all}$ = 0.1261. The asymmetric unit contains one formula unit of H-**4**(PF_6).

*Crystal data and structure refinement details for [**5**]:* $C_{27}H_{25}N_4AuCl_2$, M = 673.38, colorless block, 0.25 × 0.21 × 0.19 mm^3, monoclinic, space group $P2_1/n$, Z = 4, a = 10.70450(10) Å, b = 14.7865(2) Å, c = 15.7768(2) Å, β = 90.9040(10)°, V = 2496.87(5) Å^3, ρ_{calcd} = 1.791 g cm^{-3}, μ = 6.129 mm^{-1}, ω and φ scans, 45118 measured intensities (6.1° ≤ 2θ ≤ 61.0°), semiempirical absorption correction (0.490 ≤ T ≤ 0.615), 8065 independent (R_{int} = 0.0283) and 6882 observed intensities ($I \geq 2\sigma(I)$), refinement of 310

parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0188, R_w = 0.0419, R_{all} = 0.0254, $R_{w,all}$ = 0.0442. The asymmetric unit contains one formula unit of [**5**].

*Crystal data and structur refinement details for [**7**]PF_6:* $C_{90}H_{80}N_8AuCl_2F_6P_3Pd_2$, M = 1961.19, colorless block, 0.13 × 0.11 × 0.09 mm^3, monoclinic, space group $C2/c$, Z = 8, a = 38.160(2) Å, b = 19.3493(11) Å, c = 28.080(2) Å, β = 112.666(3)°, V = 19132(2) Å^3, ρ_{calcd} = 1.362 g cm^{-3}, μ = 2.064 mm^{-1}, ω and φ scans, 85693 measured intensities (3.1° ≤ 2θ ≤ 52.7°), semiempirical absorption correction (0.631 ≤ T ≤ 0.746), 19560 independent (R_{int} = 0.0553) and 14984 observed intensities ($I \geq 2\sigma(I)$), refinement of 1033 parameters against $|F^2|$ of all measured intensities with hydrogen atoms on calculated positions. R = 0.0331, R_w = 0.0828, R_{all} = 0.0503, $R_{w,all}$ = 0.0907. The asymmetric unit contains one formula unit of [**7**]PF_6. The co-crystallized solvent molecule was severely disordered. Therefore, the electron density of the solvent molecule was removed from the least-squares calculations by means of the SQUEEZE function of the PLATON program.

5. References

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