Supplementary Information For:

Phenylacetylene polymerisation mediated by cationic cyclometallated palladium (II) complexes bearing benzylidene 2,6-diisopropylphenylamine and its derivatives as ligands

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Contents

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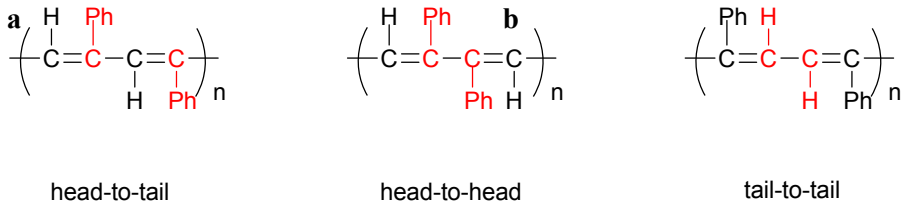
Polyphenylacetylene data and spectra



head-to-tail head-to-head tail-to-tail

Fig. S1: Regioselectivity of monomer addition.

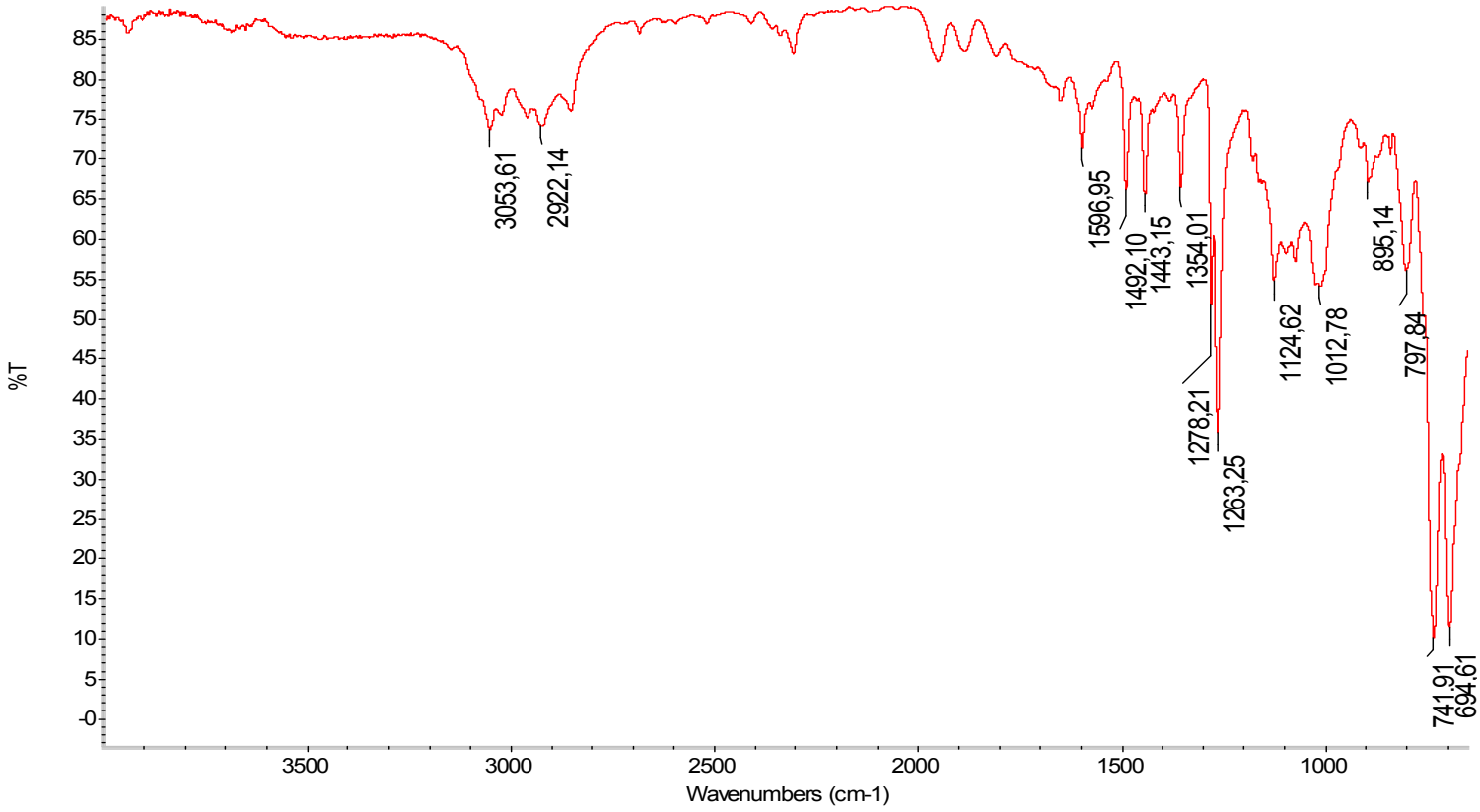


Fig. S2: IR spectrum of a polymer isolated from a catalytic reaction performed at 25 °C with a monomer to catalyst ratio of 50:1 employing catalyst **C14**.

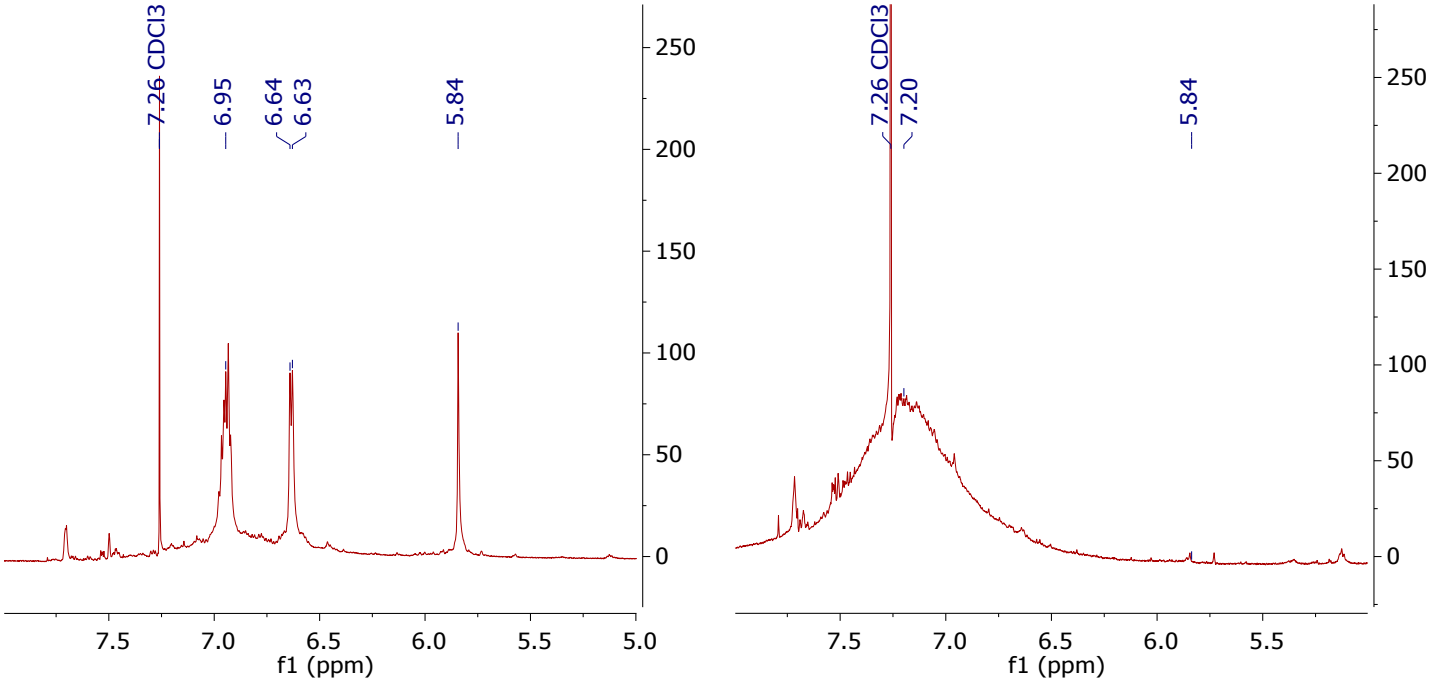


Fig. S3: ^{1}H NMR spectrum ($CDCl_3$) of PPA isolated from (**a**) a catalytic reaction performed at 25 °C (**b**) a catalytic reaction performed at 60 °C showing proton resonances in the region δ 8.00-5.00 ppm. Complex **C14** was employed as precatalyst

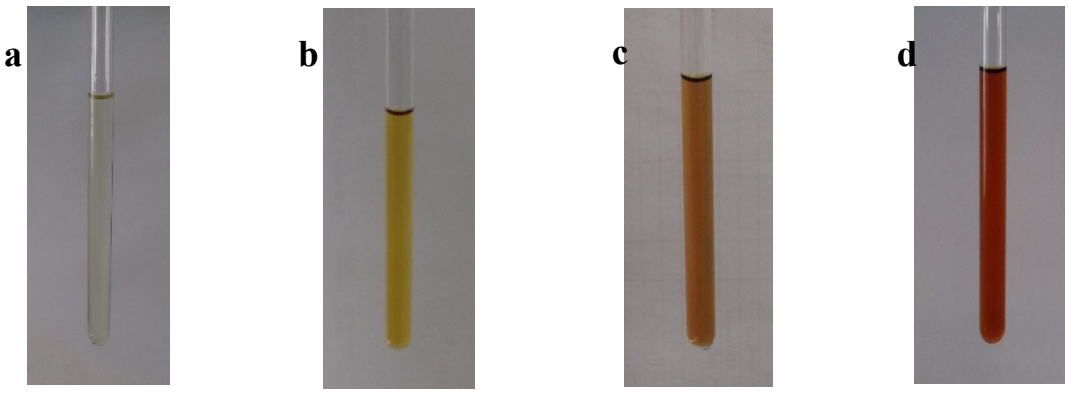


Fig. S4: Gradual colour change of the catalytic reaction at 25°C, using **C14** as precatalyst. Colour change at (**a**) before phenylacetylene addition, (**b**) 24 hours, (**c**) 48 hours and (**d**) 72 hours.

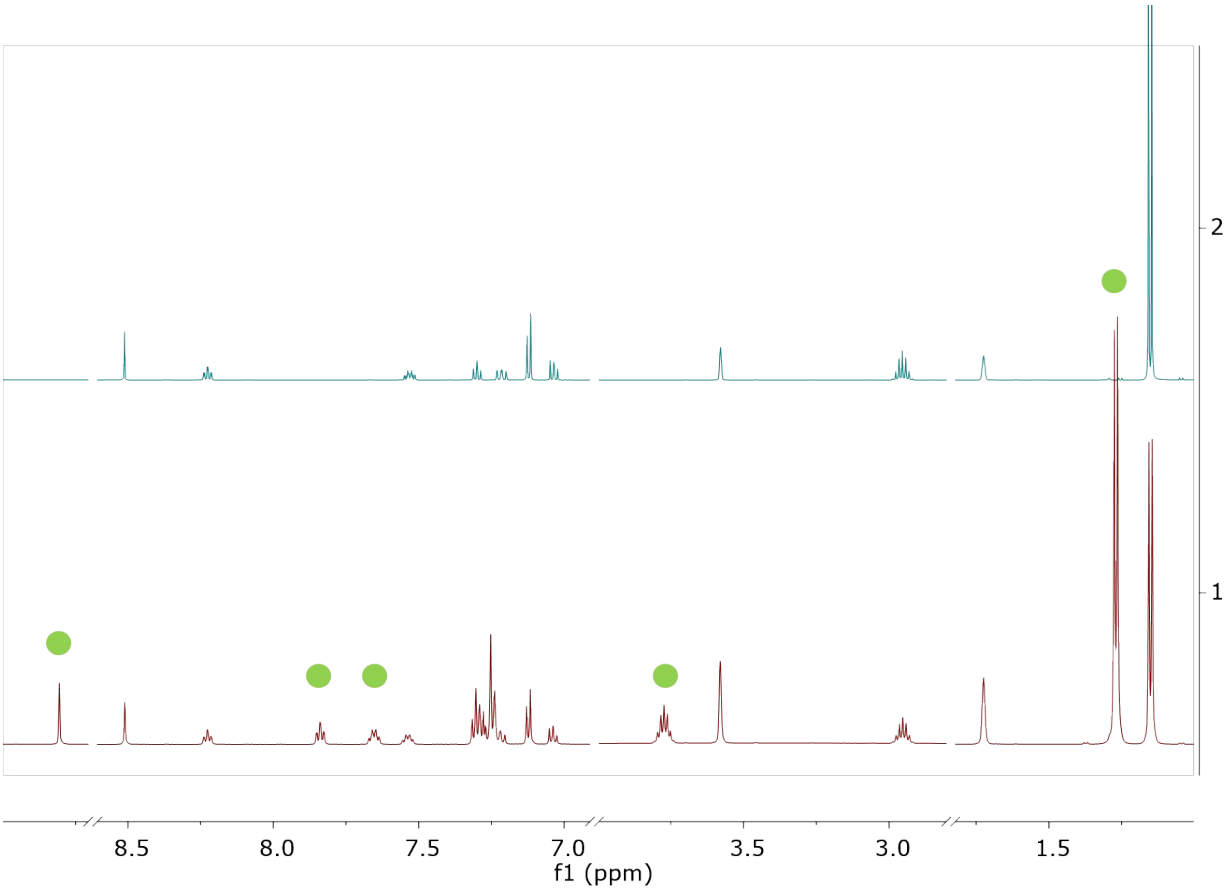


Fig. S5: Stacked ^{1}H NMR spectrum in d_8-THF for (**a**) ligand **L4** and (**b**) ligand L4 in the presence of HCl. A mixture of the free imine ligand and iminium ligand is observed when HCl is added. Confirmed resonances corresponding to the iminium ligand are indicated by ●

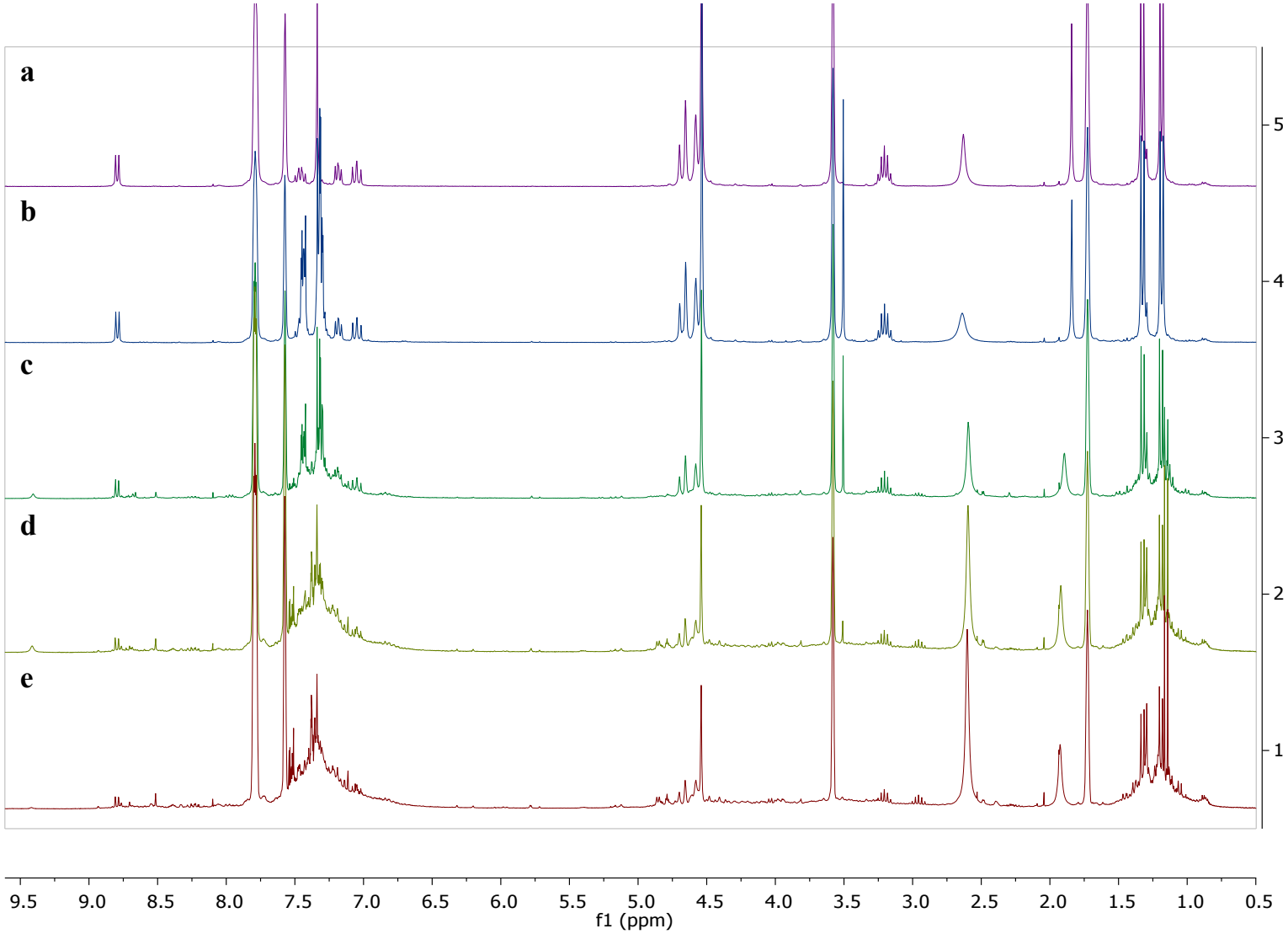


Fig. S6: Full variable time ^{1}H NMR spectrum in THF-d_8 (recorded at 25°C) of palladacycle **C14** at (a) before phenylacetylene addition; (b) after phenylacetylene addition; (c) 24 hours; (d) 48 hours and (e) 72 hours. The solvent signal in all spectra was normalized to 1

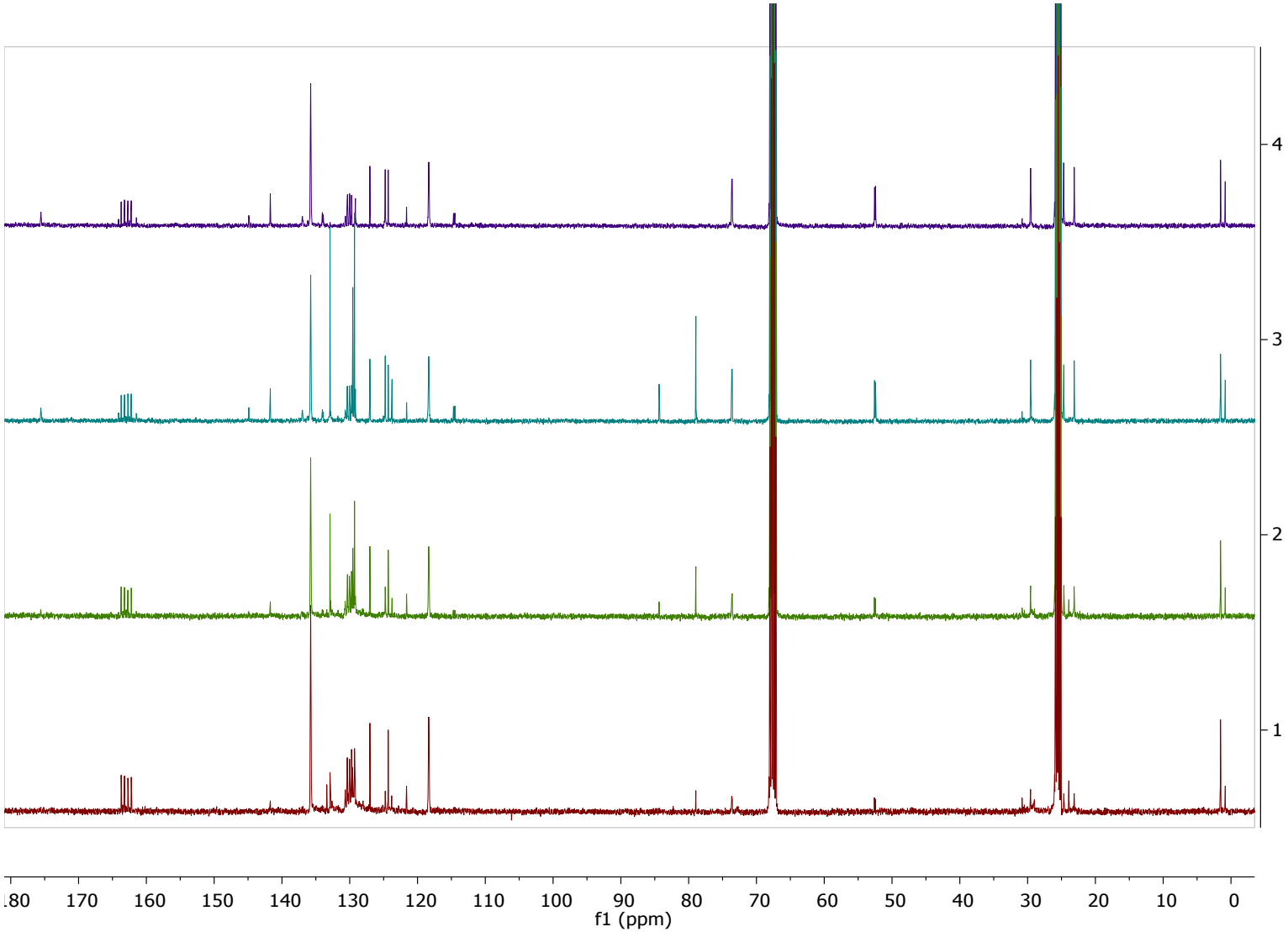


Fig. S7: Full variable time ^{13}C NMR spectrum in THF-d_8 (recorded at 25°C) of palladacycle **C14** at (a) before phenylacetylene addition; (b) 6 hours; (c) 30 hours and (d) 54 hours and (e). The solvent signal in all spectra was normalized to 1

Experimental and characterization data

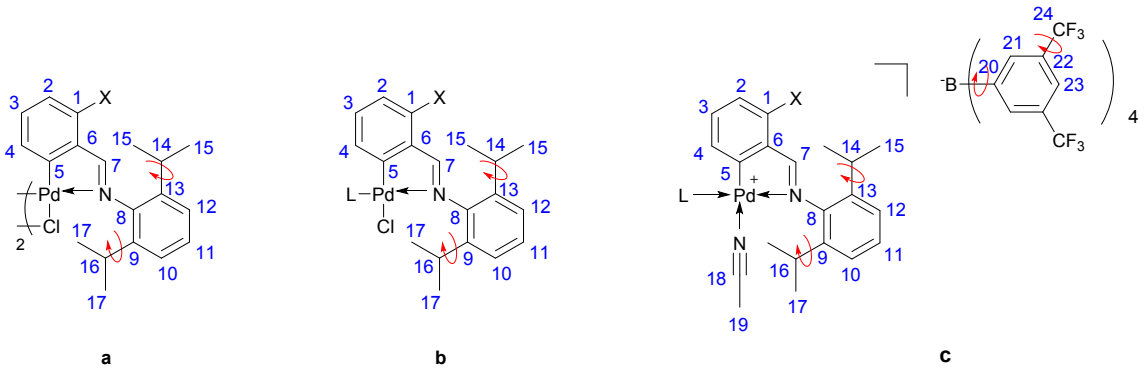


Fig. S8: (a) μ-Cl Binuclear, **(b)** neutral and **(c)** cationic palladacycle with numbering for NMR data. Free rotation about the C-C bond of the isopropyl moiety and C-C bond in the anionic counterion. X and L denotes the different substituents (X = H, Cl, Br, F, OMe) and phosphine ligands (L = PTA, PCy_3, PPh_3) respectively.

NMR abbreviations

s = singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, sept. = septet, m = multiplet (denotes complex pattern for a single proton resonance), comp. = complex (denotes complex pattern of overlapping proton resonances).

Synthesis of µ-Cl bridge palladacycles

Ligand (0.386 mmol) was added to a stirring solution of $(MeCN)_2PdCl_2$ (0.386 mmol) and sodium acetate (0.771 mmol) dissolved in dichloromethane (10 mL) and the resulting reaction mixture was stirred for 24 hours at room temperature. After the allotted time, the solvent was removed *in vacuo* and the yellow-orange solid residue was redissolved in dichloromethane (20 mL) and filtered through celite. The solvent was removed *in vacuo* from the yellow-orange filtrate and the light orange product was isolated by means of recrystallization from dichloromethane/hexane at room temperature.

[PdCl(2-F-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}]$_2$ ***(C4)***

Yield: 73 %. Melting point: 188-190 °C (decomposes without melting). FT-IR ν(C=N) 1605 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8a**): δ 8.02 (s, 2H, H^7), δ 7.37-7.28 (m, 2H, H^2), δ 7.24-7.15 (m, 4H, Ar-H), δ 7.11-7.00 (m, 2H, Ar-H), δ 6.99-6.91 (m, 2H, H^4), δ 6.73 (t, $^3J_{H\text{-}H}$ = 9.0 Hz, 2H, H^3), δ 3.56-3.40 (m, 4H, $H^{14,16}$), δ 1.39 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 12H, $H^{15,17}$), δ 1.17 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 12H, $H^{15,17}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8a**): δ 171.5 (C^7), δ 161.5 (Ar-C), δ 158.0 (Ar-C), δ 156.4 (Ar-C), δ 144.4 (Ar-C), δ 141.6 (Ar-C), δ 133.2 (Ar-C), δ 129.7 (Ar-C), δ 128.2 (Ar-C), δ 123.5 (Ar-C), δ 111.5 (d, $J_{C\text{-}F}$ = 18.9 Hz, C^1), δ 28.4 ($C^{14,16}$), δ 24.6 ($C^{15,17}$), δ 23.1 ($C^{15,17}$). ESI-MS (+.ve, m/z): 854.1 [M-Cl+MeCN]$^+$; 813.1 [M-Cl]$^+$; 429.1

[(M/2)-Cl+MeCN]$^{2+}$. *Anal. Calc.* for $C_{38}H_{42}Cl_2F_2N_2Pd_2$: C, 53.79; H, 4.99; N, 3.30. *Found:* C, 53.71; H, 5.41; N, 3.07.

[PdCl(2-OMe-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}]$_2$ ***(C5)***

Yield: 75 %. Melting point: >250 °C. FT-IR ν(C=N) 1581 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per **Fig. S8a**): δ 8.05 (s, 2H, H^7), δ 7.29 (t, $^3J_{H\text{-}H}$ = 7.7 Hz, 2H, H^2), δ 7.17 (d, $^3J_{H\text{-}H}$ = 7.5 Hz, 4H, H^{10,12}), δ 6.99 (t, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, H^3), δ 6.76 (d, $^3J_{H\text{-}H}$ = 8.1 Hz, 2H, H^{11}), δ 6.51 (d, $^3J_{H\text{-}H}$ = 8.6 Hz, 2H, H^4), δ 3.76 (s, 6H, *o*-methoxy Me), δ 3.59-3.46 (m, 4H, H^{14,16}), δ 1.38 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, H^{15,17}), δ 1.15 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 12H, H^{15,17}). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, numbering as per **Fig. S 8a**): δ 173.2 (C^7), δ 158.5 (Ar-C), δ 157.5 (Ar-C), δ 145.0 (Ar-C), δ 141.9 (Ar-C), δ 134.0 (Ar-C), δ 132.9 (Ar-C), δ 127.7 (Ar-C), δ 126.5 (Ar-C), δ 123.3 (Ar-C), δ 106.9 (Ar-C), δ 55.5 (*o*-methoxy Me), δ 28.3 (C^{14,16}), δ 24.7 (C^{15,17}), δ 23.2 (C^{15,17}). ESI-MS (+.ve, m/z): 836.1 [M-Cl]$^+$; 441.1 [(M/2)-Cl+MeCN]$^{2+}$; 400.1 [(M/2)-Cl]$^{2+}$. *Anal. Calc.* for $C_{40}H_{48}Cl_2N_2O_2Pd_2$: C, 55.06; H, 5.54; N, 3.21. *Found:* C, 54.80; H, 5.96; N, 2.93.

Synthesis of neutral palladacycles

To a stirring solution of μ-Cl binuclear palladacycle complex (0.123 mmol) in dichloromethane (10 mL) was added the phosphine (0.246 mmol). The resulting light yellow solution was stirred under an inert atmosphere for 2 hours at room temperature. The solvent was removed *in vacuo* and the yellow residue was then recrystallized from dichloromethane/diethyl ether at room temperature which afforded the product as a yellow powder/crystals.

[Pd(PTA)(C_6H_4)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] ***(C6)***

Yield: 90 %. Melting point: 210-212 °C (decomposes without melting). FT-IR ν(C=N) 1606 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 7.98 (d, $^4J_{H\text{-}P}$ = 7.7 Hz, 1H, H^7), δ 7.46 (m, 1H, H^1), δ 7.35-7.14 (comp, 6H, Ar-H), δ 4.66-4.50 (comp., 12H, PTA), δ 3.29-3.13 (m, 2H, H^{14,16}), δ 1.47-0.95 (comp., 12H, H^{15,17}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 177.1 (d, $^3J_{C\text{-}P}$ = 4.1 Hz, C^7), δ 158.2 (d, $^3J_{C\text{-}P}$ = 4.3 Hz, Ar-C), δ 148.0 (Ar-C), δ 144.4 (Ar-C), δ 141.0 (Ar-C), δ 136.4 (d, $J_{C\text{-}P}$ = 9.4 Hz, Ar-C), δ 132.1 (d, $J_{C\text{-}P}$ = 4.6 Hz, Ar-C), δ 130.2 (Ar-C), δ 127.4 (Ar-C), δ 125.1 (Ar-C), δ 123.0 (Ar-C), δ 73.4 (d, $^3J_{C\text{-}P}$ = 7.1 Hz, N-CH_2-N), δ 52.6 (d, $^1J_{C\text{-}P}$ = 16.2 Hz, N-CH_2-P), δ 28.5 (C^{14,16}), δ 24.5 (C^{15,17}), δ 23.7 (C^{15,17}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -47.0 (s). ESI-MS (+ve, m/z): 568.2 [M-Cl+MeCN]$^+$; 565.1 [M+H]$^+$; 527.2 [M-Cl]$^+$. *Anal. Calc.* for $C_{25}H_{34}ClN_4PPd$: C, 53.29; H, 6.08; N, 9.94. *Found:* C, 53.40; H, 6.08; N, 9.29.

[Pd(PTA)(2-Cl-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] ***(C7)***

Yield: 79 %. Melting point: 209-211 °C (decomposes without melting). FT-IR ν(C=N) 1600 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.47 (d, $^4J_{H\text{-}P}$ = 7.6 Hz, 1H, H^7) δ 7.30-7.11 (comp, 6H, Ar-H), δ 4.64-4.47, (comp., 12H, PTA), δ 3.28-3.11 (m, 2H, H^{14,16}), δ 1.32 (d, $^3J_{H\text{-}H}$ = 6.7

Hz, 6H, $H^{15,17}$), δ 1.15 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $H^{15,17}$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 175.7 (d, $^3J_{C-P}$ = 4.1 Hz, C^7), δ 160.4 (d, $^3J_{C-P}$ = 4.0 Hz, Ar-C), δ 144.6 (Ar-C), δ 144.5 (Ar-C), δ 140.9 (Ar-C), δ 135.0 (d, J_{C-P} = 9.6 Hz, Ar-C), δ 134.6 (Ar-C), δ 133.4 (d, J_{C-P} = 4.8 Hz, Ar-C), δ 127.6 (Ar-C), δ 126.0 (Ar-C), δ 123.1 (Ar-C), δ 73.4 (d, $^3J_{C-P}$ = 7.0 Hz, N-CH_2-N), δ 52.5 (d, $^1J_{C-P}$ = 15.9 Hz, N-CH_2-P), δ 28.6 ($C^{14,16}$), δ 24.7 ($C^{15,17}$), δ 23.0 ($C^{15,17}$). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ -47.6 (s). ESI-MS (+.ve, m/z): 1161.2 $[2M-Cl]^+$; 604.1 $[M-Cl+MeCN]^+$; 599.1 $[M+H]^+$; 563.1 $[M-Cl]^+$; 447.1 $[M-Cl-PTA+MeCN]^+$; 406.0 $[M-Cl+PTA]^+$. *Anal. Calc.* for $C_{25}H_{33}Cl_2N_4PPd$: C, 50.22; H, 5.56; N, 9.37. *Found:* C, 50.00; H, 5.54; N, 9.49.

[Pd(PTA)(2-Br-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] ***(C8)***

Yield: 58 %. Melting point: 231-233 °C (decomposes without melting). FT-IR *ν*(C=N) 1597 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.47 (d, $^4J_{H-P}$ = 7.4 Hz, 1H, H^7), δ 7.31 (d, $^3J_{H-H}$ = 8.0 Hz, 1H, H^2), δ 7.26 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, H^3), δ 7.20-7.17 (comp., 3H, $H^{10,11,12}$), δ 7.09 (m, 1H, H^4), δ 4.62-4.51 (comp., 12H, PTA), δ 3.24-3.15 (m, 2H, $H^{14,16}$), δ 1.33 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, $H^{15,17}$), δ 1.16 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $H^{15,17}$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 177.7 (d, $^3J_{C-P}$ = 4.2 Hz, C^7), δ 160.5 (d, $^3J_{C-P}$ = 4.0 Hz, Ar-C), δ 146.0 (Ar-C), δ 144.5 (Ar-C), δ 140.9 (Ar-C), δ 135.6 (d, J_{C-P} = 9.3 Hz, Ar-C), δ 133.5 (d, J_{C-P} = 4.9 Hz, Ar-C), δ 129.3 (Ar-C), δ 127.6 (Ar-C), δ 123.6 (Ar-C), δ 123.1 (Ar-C), δ 73.4 (d, $^3J_{C-P}$ = 7.1 Hz, N-CH_2-N), δ 52.6 (d, $^1J_{C-P}$ = 16.1 Hz, N-CH_2-P), δ 28.6 ($C^{14,16}$), δ 24.7 ($C^{15,17}$), δ 23.0 ($C^{15,17}$). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$): δ -47.9 (s). ESI-MS (+.ve, m/z): 1249.1 $[2M-Cl]^+$; 648.09 $[M-Cl+MeCN]^+$; 643.0 $[M+H]^+$; 607.07 $[M-Cl]^+$; 491.02 $[M-Cl-PTA+MeCN]^+$; 449.9 $[M-Cl-PTA]^+$. *Anal. Calc.* for $C_{25}H_{33}BrClN_4PPd$: C, 46.75; H, 5.18; N, 8.72. *Found:* C, 46.50; H, 6.38; N, 9.14.

[Pd(PTA)(2-F-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] ***(C9)***

Yield: 89 %. Melting point: 194-197 °C (decomposes without melting). FT-IR *ν*(C=N) 1606 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.31 (d, $^4J_{H-P}$ = 7.6 Hz, 1H, H^7), δ 7.35-7.20 (comp., 2H, $H^{3,11}$), δ 7.19-7.14 (comp., 2H, $H^{10,12}$), δ 7.05 (dd, $^3J_{H-H}$ = 7.4 Hz, $^4J_{H-H}$ = 5.1 Hz 1H, H^2), δ 6.85 (m, 1H, H^4), δ 4.65-4.50 (comp., 12H, PTA), δ 3.26-3.09 (m, 2H, $H^{14,16}$), δ 1.32 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.14 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $H^{15,17}$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 171.6 (d, $^3J_{C-P}$ = 3.8 Hz, C^7), δ 163.3 (Ar-C), δ 160.4 (Ar-C), δ 159.8 (Ar-C), δ 144.5 (Ar-C), δ 141.0 (Ar-C), δ 134.4 (dd, J_{C-P} = 7.7, 4.9 Hz, Ar-C), δ 132.1 (dd, J_{C-P} = 9.2, 3.2 Hz, Ar-C), δ 127.5 (Ar-C), δ 123.1 (Ar-C) δ 112.1 (d, J_{C-P} = 19.7 Hz, Ar-C), δ 73.4 (d, $^3J_{C-P}$ = 7.0 Hz, N-CH_2-N), δ 52.7 (d, $^1J_{C-P}$ = 16.3 Hz, N-CH_2-P), δ 28.6 ($C^{14,16}$), δ 24.6 ($C^{15,17}$), δ 23.1 ($C^{15,17}$). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ -47.1 (s). ESI-MS (+.ve, m/z): 586.2 $[M-Cl+MeCN]^+$; 583.1 $[M+H]^+$; 545.1 $[M-Cl]^+$. *Anal. Calc.* for $C_{25}H_{33}ClFN_4PPd$: C, 51.65; H, 5.72; N, 9.64. *Found:* C, 51.60; H, 5.52; N, 9.65.

[Pd(PTA)(2-OMe-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] (***C10***)

Yield: 87 %. Melting point: 205-207 °C (decomposes without melting). FT-IR ν(C=N) 1597 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.40 (d, $^4J_{H\text{-}P}$ = 7.4 Hz, 1H, H^7), δ 7.30-7.12 (comp., 4H, H^{3,10,11,12}), δ 6.89-6.82 (m, 1H, H^4), δ 6.68 (d, $^3J_{H\text{-}H}$ = 8.0, 1H, H^2), δ 4.65-4.48 (comp., 12H, PTA), δ 3.80 (s, 3H, *o*-methoxy Me), δ 3.31-3.15 (m, 2H, H^{14,16}), δ 1.31 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 6H, H^{15,17}), δ 1.14 (d, $^3J_{H\text{-}H}$ = 6.5 Hz, 6H, H^{15,17}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 173.7 (C^7), δ 160.3 (Ar-C), δ 159.9 (Ar-C), δ 145.0 (Ar-C), δ 141.2 (Ar-C), δ 135.6 (Ar-C), δ 134.1 (Ar-C), δ 128.8 (d, $J_{C\text{-}P}$ = 9.4 Hz, Ar-C), δ 127.1 (Ar-C), δ 122.9 (Ar-C) δ 107.7 (Ar-C), δ 73.4 (d, $^3J_{C\text{-}P}$ = 6.8 Hz, N-CH_2-N), δ 55.7 (*o*-methoxy Me), δ 52.6 (d, $^1J_{C\text{-}P}$ = 16.0 Hz, N-CH_2-P), δ 28.4 (C^{14,16}), δ 24.7 (C^{15,17}), δ 23.1 (C^{15,17}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -48.1 (s). ESI-MS (+.ve, m/z): 598.2 [M-Cl+MeCN]$^+$; 593.1 [M+H]$^+$; 557.2 [M-Cl]$^+$; 441.1 [M-Cl-PTA+MeCN]$^+$; 400.1 [M-Cl-PTA]$^+$. *Anal. Calc.* for $C_{26}H_{36}ClN_4OPPd$: C, 52.62; H, 6.11; N, 9.44. *Found:* C, 52.5; H, 6.09; N, 9.46.

[Pd(P(Cy)$_3$)(C_6H_4)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] (***C16***)

Yield: 62 %. Melting point: 221-223 °C (decomposes without melting). FT-IR ν(C=N) 1610 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.01 (d, $^4J_{H\text{-}P}$ = 7.0 Hz, 1H, H^7), δ 7.45 (d, $^3J_{H\text{-}H}$ = 5.9 Hz, 1H, H^1), δ 7.40 (d, $^3J_{H\text{-}H}$ = 6.6 Hz, 1H, H^4), δ 7.24-7.10 (comp., 5H, H^{2,3,10,11,12}), δ 3.42-3.31 (m, 2H, H^{14,16}), δ 2.70-2.56 (comp., 3H, P(Cy)$_3$), δ 2.11-1.99 (comp., 5H, P(Cy)$_3$), δ 1.85-1.60 (comp., 16H, P(Cy)$_3$), δ 1.36-1.19 (comp., 15H, H^{15,17} & P(Cy)$_3$), δ 1.15 (d, $^3J_{H\text{-}H}$ = 6.7 Hz, 6H, H^{15,17}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 176.2 (d, $^3J_{C\text{-}P}$ = 3.8 Hz, C^7), δ 159.1 (d, $^3J_{C\text{-}P}$ = 2.5 Hz, Ar-C), δ 148.3 (Ar-C), δ 145.7 (Ar-C), δ 141.1 (Ar-C), δ 137.5 (d, $J_{C\text{-}P}$ = 5.1 Hz, Ar-C), δ 130.8 (d, $J_{C\text{-}P}$ = 3.5 Hz, Ar-C), δ 129.2 (Ar-C), δ 126.8 (Ar-C), δ 124.3 (Ar-C), δ 122.8 (Ar-C), δ 34.3 (d, $^1J_{C\text{-}P}$ = 21.7 Hz, P(Cy)$_3$), δ 30.5 (P(Cy)$_3$), δ 28.6 (P(Cy)$_3$), δ 27.8 (d, $^2J_{C\text{-}P}$ = 11.1 Hz, P(Cy)$_3$), δ 26.6 (C^{14,16}), δ 24.8 (C^{15,17}), δ 23.1 (C^{15,17}). ^{31}P {^{1}H} NMR (120 MHz, $CDCl_3$): δ 43.2 (s). ESI-MS (+.ve, m/z): 650.3 [M-Cl]$^+$. *Anal. Calc.* for $C_{37}H_{55}ClNPPd$: C, 64.72; H, 8.07; N, 2.04. *Found:* C, 64.38; H, 8.31; N, 1.60.

[Pd(P(Cy)$_3$)(2-Cl-C_6H_3)CH=N{2,6-^{i}Pr$_2$-C_6H_3}Cl] (***C17***)

Yield: 75 %. Melting point: 248-250 °C (decomposes without melting). FT-IR ν(C=N) 1606 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.54 (d, $^4J_{H\text{-}P}$ = 6.7 Hz, 1H, H^7), δ 7.31 (dd, $^3J_{H\text{-}H}$ = 7.5, $^4J_{H\text{-}H}$ = 2.9 Hz, 1H, H^2), δ 7.23 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, H^{11}), δ 7.17-7.15 (comp., 2H, H^{10,12}), δ 7.10 (t, $^3J_{H\text{-}H}$ = 7.8 Hz, 1H, H^3), δ 7.08-7.05 (m, 1H, H^4), δ 3.39-3.30 (m, 2H, H^{14,16}), δ 2.65-2.55 (comp., 3H, P(Cy)$_3$), δ 2.07-1.98 (comp., 7H, P(Cy)$_3$), δ 1.84-1.74 (comp., 7H, P(Cy)$_3$), δ 1.74-1.61 (comp., 9H, P(Cy)$_3$), δ 1.33 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H, H^{15,17}), δ 1.28-1.20 (comp., 9H, P(Cy)$_3$), δ 1.17 (d, $^3J_{H\text{-}H}$ = 7.0 Hz, 6H, H^{15,17}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 174.5 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, C^7), δ 161.6 (d, $^3J_{C\text{-}P}$ = 2.2 Hz, Ar-C), δ 145.9 (Ar-C), δ 144.8 (Ar-C), δ 141.1

(Ar-C), δ 136.0 (d, $J_{C\text{-}P}$ = 5.3 Hz, Ar-C), δ 133.5 (Ar-C), δ 132.0 (Ar-C), δ 127.0 (Ar-C), δ 125.2 (Ar-C), δ 122.8 (Ar-C), δ 34.3 (d, $^{1}J_{C\text{-}P}$ = 21.7 Hz, $P(Cy)_3$), δ 30.6 ($P(Cy)_3$), δ 28.7 ($P(Cy)_3$), δ 27.9 (d, $^{2}J_{C\text{-}P}$ = 10.9 Hz, $P(Cy)_3$), δ 26.5 ($C^{14,16}$), δ 24.9 ($C^{15,17}$), δ 23.0 ($C^{15,17}$). ^{31}P {^{1}H} NMR (120 MHz, $CDCl_3$): δ 42.8 (s). ESI-MS (+.ve, m/z): 730.2 $[M\text{-}Cl]^+$. *Anal. Calc.* for $C_{37}H_{54}Cl_2NPPd\bullet 1CH_2Cl_2$: C, 56.62; H, 7.00; N, 1.74. *Found:* C, 56.82; H, 6.63; N, 1.15.

[*Pd(P(Cy)$_3$)(2-Br-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}Cl]* (***C18***)

Yield: 81 %. Melting point: >250 °C. FT-IR *ν*(C=N) 1604 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.53 (d, $^{4}J_{H\text{-}P}$ = 6.7 Hz, 1H, H^7), δ 7.35 (dd, $^{3}J_{H\text{-}H}$ = 7.6, $^{4}J_{H\text{-}H}$ = 2.9 Hz, 1H,H^2), δ 7.27-7.20 (comp., 2H, $H^{4,11}$), δ 7.17-7.14 (comp., 2H, $H^{10,12}$), δ 7.00 (t, $^{3}J_{H\text{-}H}$ = 7.8 Hz, 1H,H^3), δ 3.38-3.29 (m, 2H, $H^{14,16}$), δ 2.64-2.53 (comp., 3H, $P(Cy)_3$), δ 2.06-1.98 (comp., 6H, $P(Cy)_3$), δ 1.82-1.74 (comp., 6H, $P(Cy)_3$), δ 1.74-1.59 (comp., 9H, $P(Cy)_3$), δ 1.36-1.13 (comp., 20H, $H^{15,17}$& $P(Cy)_3$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 176.8 (d, $^{3}J_{C\text{-}P}$ = 3.9 Hz, C^7), δ 161.8 (d, $^{3}J_{C\text{-}P}$ = 2.0 Hz, Ar-C), δ 146.0 (Ar-C), δ 145.8 (Ar-C), δ 141.1 (Ar-C), δ 136.7 (d, $J_{C\text{-}P}$ = 5.0 Hz, Ar-C), δ 132.2 (d, $J_{C\text{-}P}$ = 3.4 Hz, Ar-C), δ 128.5 (Ar-C), δ 127.0 (Ar-C), δ 122.9 (Ar-C), δ 122.6 (Ar-C), δ 34.3 (d, $^{1}J_{C\text{-}P}$ = 23.5 Hz, $P(Cy)_3$), δ 30.5 ($P(Cy)_3$), δ 28.7 ($P(Cy)_3$), δ 27.8 (d, $^{2}J_{C\text{-}P}$ = 11.4 Hz, $P(Cy)_3$), δ 26.5 ($C^{14,16}$), δ 24.9 ($C^{15,17}$), δ 23.0 ($C^{15,17}$). ^{31}P {^{1}H} NMR (120 MHz, $CDCl_3$): δ 42.6 (s). ESI-MS (+.ve, m/z): 730.2 $[M\text{-}Cl]^+$; 491.0 $[M\text{-}Cl\text{-}PCy_3\text{+}MeCN]^+$. *Anal. Calc.* for $C_{37}H_{54}BrClNPPd$: C, 58.05; H, 7.11; N, 1.83. *Found:* C, 57.60; H, 6.54; N, 2.04.

[Pd(P(Cy)$_3$)(2-F-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}Cl] (***C19***)

Yield: 74 %. Melting point: 227-230 °C (decomposes without melting). FT-IR *ν*(C=N) 1610 cm^{-1}; ^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.37 (d, $^{4}J_{H\text{-}P}$ = 6.7 Hz, 1H, H^7), δ 7.24-7.17 (comp., 3H, Ar-H), δ 7.17-7.13 (comp., 2H, Ar-H), δ 6.80-6.75 (m, 1H, H^{11}), δ 3.36-3.28 (m, 2H, $H^{14,16}$), δ 2.67-2.57 (comp., 3H, $P(Cy)_3$), δ 2.08-1.99 (comp., 5H, $P(Cy)_3$), δ 1.82-1.74 (comp., 6H, $P(Cy)_3$), δ 1.73-1.61 (comp., 10H, $P(Cy)_3$), δ 1.32 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.29-1.18 (comp., 10H, $P(Cy)_3$), δ 1.15 (d, $^{3}J_{H\text{-}H}$ = 6.9 Hz, 6H, $H^{15,17}$). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 170.7 (d, $^{3}J_{C\text{-}P}$ = 3.7 Hz, C^7), δ 162.8 (Ar-C), δ 161.6 (Ar-C), δ 159.3 (Ar-C), δ 145.8 (Ar-C), δ 141.1 (Ar-C), δ 135.3 (d, $J_{C\text{-}P}$ = 3.6 Hz, Ar-C), δ 133.1 (dq, $J_{C\text{-}P}$ = 18.3 Hz, $J_{C\text{-}P}$ = 3.6 Hz, Ar-C), δ 126.9 (Ar-C), δ 122.8 (Ar-C), δ 111.0 (Ar-C), δ 34.4 (d, $^{1}J_{C\text{-}P}$ = 21.1 Hz, $P(Cy)_3$), δ 30.5 ($P(Cy)_3$), δ 28.6 ($P(Cy)_3$), δ 27.8 (d, $^{2}J_{C\text{-}P}$ = 11.4 Hz, $P(Cy)_3$), δ 26.5 ($C^{14,16}$), δ 24.8 ($C^{15,17}$), δ 23.0 ($C^{15,17}$). ^{31}P {^{1}H} NMR (120 MHz, $CDCl_3$): δ 43.3 (s). ESI-MS (+.ve, m/z): 680.30 $[M\text{-}Cl]^+$. *Anal. Calc.* for $C_{37}H_{54}ClFNPPd\bullet 1CH_2Cl_2$: C, 57.80; H, 7.15; N, 1.77. *Found:* C, 58.18; H, 7.81; N, 1.33.

[Pd(P(Cy)$_3$)(2-OMe-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}Cl] (***C20***)

Yield: 73 %. Melting point: >250 °C. FT-IR *ν*(C=N) 1609 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.46 (d, $^{4}J_{H\text{-}P}$ = 7.4 Hz, 1H, H^7), δ 7.24-7.09 (comp., 4H, $H^{3,10,11,12}$), δ 6.99 (dd, $^{3}J_{H\text{-}H}$ = 7.8, $^{4}J_{H\text{-}H}$ = 3.0 Hz, 1H, H^2), δ 6.61 (d, $^{4}J_{H\text{-}P}$ = 7.6 Hz, 1H, H^4), δ 3.78 (s, 3H, *o*-methoxy Me),δ 3.45-

3.30 (m, 2H, $H^{14,16}$), δ 2.70-2.52 (comp., 3H, $P(Cy)_3$), δ 2.12-1.95 (comp., 6H, $P(Cy)_3$), δ 1.87-1.52 (comp., 16H, $P(Cy)_3$), δ 1.38-1.09 (comp., 20H, $P(Cy)_3$ & $H^{15,17}$). ^{13}C {^1H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 172.9 (d, $^3J_{C\text{-}P}$ = 4.2 Hz, C^7), δ 161.6 (Ar-C), δ 159.2 (Ar-C), δ 146.4 (Ar-C), δ 141.4 (Ar-C), δ 136.1 (Ar-C), δ 132.6 (Ar-C), δ 130.0 (d, $J_{C\text{-}P}$ = 4.8 Hz, Ar-C), δ 126.6 (Ar-C), δ 122.7 (Ar-C), δ 106.7 (Ar-C), δ 55.5 (*o*-methoxy Me), δ 34.3 (d, $^1J_{C\text{-}P}$ = 21.7 Hz, $P(Cy)_3$), δ 30.6 ($P(Cy)_3$), δ 28.5 ($P(Cy)_3$), δ 27.9 (d, $^2J_{C\text{-}P}$ = 10.9 Hz, $P(Cy)_3$), δ 26.6 ($C^{14,16}$), δ 24.9 ($C^{15,17}$), δ 23.1 ($C^{15,17}$). ^{31}P {^1H} NMR (120 MHz, $CDCl_3$): δ 42.2 (s). ESI-MS (+.ve, m/z): 680.3 $[M\text{-}Cl]^+$; 491.0 $[M\text{-}Cl\text{-}PCy_3\text{+}MeCN]^+$. *Anal. Calc.* for $C_{38}H_{57}ClNOPPd\bullet0.25CH_2Cl_2$: C, 62.26; H, 7.85; N, 1.90. *Found:* C, 62.13; H, 7.35; N, 2.22.

*[Pd(PPh$_3$)(2-F-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}Cl] (**C29**)*

Yield: 85 %. Melting point: 220-223 °C (decomposes without melting). FT-IR *ν*(C=N) 1608 cm^{-1}; ^1H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.47 (d, $^4J_{H\text{-}P}$ = 8.0 Hz, 1H, H^7), δ 7.76-7.71 (comp., 6H, PPh_3), δ 7.45-7.41 (comp., 3H, PPh_3), δ 7.39-7.34 (comp., 6H, PPh_3), δ 7.23-7.18 (m, 1H, H^{11}), δ 7.17-7.14 (comp., 2H, $H^{10,12}$), δ 6.73-6.69 (m, 1H, H^2), δ 6.67-6.62 (t, $^3J_{H\text{-}H}$ = 8.4 Hz, 1H, H^3), δ 6.26-6.22 (m, 1H, H^4), δ 3.47-3.39 (m, 2H, $H^{14,16}$), δ 1.38 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.24 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$). ^{13}C {^1H} NMR (151 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 171.8 (d, $^3J_{C\text{-}P}$ = 4.4 Hz, C^7), δ 162.1 (d, $J_{C\text{-}P}$ = 3.7 Hz, Ar-C), δ 161.7 (Ar-C), δ 160.0 (Ar-C), δ 145.4 (Ar-C), δ 140.9 (Ar-C), δ 135.4 (d, $J_{C\text{-}P}$ = 11.8 Hz, Ar-C), δ 133.8 (dd, $J_{C\text{-}P}$ = 10.0 Hz, $J_{C\text{-}P}$ = 3.1 Hz, Ar-C), δ 133.2 (dd, $J_{C\text{-}P}$ = 7.0 Hz, $J_{C\text{-}P}$ = 5.5 Hz, Ar-C), δ 131.3 (Ar-C), δ 130.9 (d, $J_{C\text{-}P}$ = 2.6 Hz, Ar-C), δ 128.2 (d, $J_{C\text{-}P}$ = 11.0 Hz, Ar-C), δ 127.2 (Ar-C), δ 123.0 (Ar-C), δ 111.0 (d, $J_{C\text{-}P}$ = 19.3 Hz, Ar-C), δ 28.8 ($C^{14,16}$), δ 24.7 ($C^{15,17}$), δ 23.2 ($C^{15,17}$). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ 42.2 (s). ESI-MS (+.ve, m/z): 650.16 $[M\text{-}Cl]^+$. *Anal. Calc.* for $C_{37}H_{36}ClFNPPd$: C, 64.73; H, 5.29; N, 2.04. *Found:* C, 64.29; H, 5.49; N, 1.57.

*[Pd(PPh$_3$)(2-OMe-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}Cl] (**C30**)*

Yield: 89 %. Melting point: 246-248 °C (decomposes without melting). FT-IR *ν*(C=N) 1597 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 8.55 (d, $^4J_{H\text{-}P}$ = 7.9 Hz, 1H, H^7), δ 7.80-7.67 (comp., 6H, PPh_3), δ 7.47-7.29 (comp., 9H, PPh_3), δ 7.23-7.09 (comp., 3H, $H^{10,11,12}$), δ 6.67 (t, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, H^3), δ 6.46 (d, $^3J_{H\text{-}H}$ = 8.2 Hz, 1H, H^2), δ 6.07 (dd, $^3J_{H\text{-}H}$ = 7.1 Hz, $^4J_{H\text{-}P}$ = 6.0 Hz, 1H, H^4), δ 3.77 (s, 3H, *o*-methoxy Me), δ 3.55-3.40 (m, 2H, $H^{14,16}$), δ 1.37 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.22 (d, $^3J_{H\text{-}H}$ = 6.9 Hz, 6H, $H^{15,17}$). ^{13}C {^1H} NMR (101 MHz, $CDCl_3$, numbering as per **Fig. S8b**): δ 173.9 (d, $^3J_{C\text{-}P}$ = 4.8 Hz, C^7), δ 162.3 (Ar-C), δ 159.0 (Ar-C), δ 145.9 (Ar-C), δ 141.2 (Ar-C), δ 135.9 (Ar-C), δ 135.5 (d, $J_{C\text{-}P}$ = 12.1 Hz, Ar-C), δ 132.9 (d, $J_{C\text{-}P}$ = 6.2 Hz, Ar-C), δ 131.7 (Ar-C), δ 131.2 (Ar-C), δ 130.6 (Ar-C), δ 128.2 (d, $J_{C\text{-}P}$ = 10.8 Hz, Ar-C), δ 126.8 (Ar-C), δ 122.8 (Ar-C), δ 106.6 (Ar-C), δ 55.5 (*o*-methoxy Me), δ 28.7 ($C^{14,16}$), δ 24.7 ($C^{15,17}$), δ 23.2 ($C^{15,17}$). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$): δ 42.3 (s). ESI-MS (+.ve, m/z): 662.18 $[M\text{-}Cl]^+$. *Anal. Calc.* for $C_{38}H_{39}ClNOPPd$: C, 65.33; H, 5.63; N, 2.01. *Found:* C, 65.11; H, 5.70; N, 1.60.

Synthesis of cationic palladacycles

The synthesis of the cationic palladacycles were generally prepared by removal of the chloride ligand using $Na[B(Ar_f)_4]$ as chloride abstractor. The general procedure using **C11** as an example is described below.

To a stirring solution of the neutral mononuclear palladacycle complex (80 mg, 0.142 mmol) in dichloromethane (7 mL) was added 1.2 equivalence $Na[B(Ar)_4]$ (150 mg, 0.170 mmol) dissolved in acetonitrile (3 mL). The resulting off-white solution was stirred under an inert atmosphere for 1 hour at room temperature. The solvent was removed *in vacuo* leaving an off-white oily residue, which was re-dissolved in dichloromethane (10 mL). The sodium chloride precipitate, which formed, was filtered off after which the solvent was removed from the filtrate *in vacuo*. The product was isolated as an off-white powder by triturating the oily residue with *n*-hexane. Recrystallization of the palladacycle was achieved by means of slow evaporation of a dichloromethane/*n*-hexane solution of the compound at room temperature. Yield (168 mg, 83 %)

Melting point: 143 – 145 °C (decomposes without melting). FT-IR ν(C=N) 1620 cm^{-1}; $\nu([B(Ar)_4]^-)$ 1352; 1274; 1117 cm^{-1}.^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.00 (d, $^4J_{H\text{-}P}$ = 7.2 Hz, 1H, H^7), δ 7.74-7.66 (comp., 8H, $B(Ar)_4$), δ 7.56-7.49 (comp.,4H, $B(Ar)_4$), δ 7.35 (t, $^3J_{H\text{-}H}$ = 7.6 Hz, 1H, H^2), δ 7.32-7.22 (comp., 5H, $H^{1,3,10,11,12}$), δ 7.14 (m, 1H, H^4), δ 4.58-4.48 (comp., 6H, PTA), δ 4.42-4.35 (comp., 6H, PTA), δ 3.17-3.07 (m, 2H, $H^{14,16}$), δ 1.24 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.16 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.43 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 178.1 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, C^7), δ 161.8 (q, $^1J_{C\text{-}B}$ = 48.2 Hz, C^{20}), δ 152.8 (d, $J_{C\text{-}P}$ = 6.1, Ar-C), δ 147.5 (Ar-C), δ 143.0 (Ar-C), δ 140.8 (Ar-C), δ 136.2 (Ar-C), δ 136.1 (Ar-C),δ 134.9 (br, C^{21}), δ 133.7 (d, $J_{C\text{-}P}$ = 6.1, Ar-C), δ 132.0 (Ar-C), δ 129.0 (qq, $^2J_{C\text{-}F}$ = 31.5, $^3J_{C\text{-}B}$ = 3.0 Hz, C^{22}), δ 128.7 (Ar-C), δ 127.4 (Ar-C), δ 127.3 (Ar-C), δ 125.6 (Ar-C), δ 124.1 (Ar-C), δ 123.8 (Ar-C), δ 122.0 (Ar-C), δ 121.7 (C^{18}), δ 117.6 (sept., $^3J_{C\text{-}F}$ = 3.8 Hz, C^{23}), δ 73.2 (d, $^3J_{C\text{-}P}$ = 7.4 Hz, N-***C***H_2-N), δ 52.1 (d, $^3J_{C\text{-}P}$ = 14.4 Hz, N-***C***H_2-P), δ 28.6 ($C^{14,16}$), δ 24.4 ($C^{15,17}$), δ 22.8 ($C^{15,17}$), δ 0.8 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -46.9 (s). ESI-MS (+.ve, m/z): 568.18 $[M]^+$; 527.16 $[M\text{-}MeCN]^+$; 411.11 $[M\text{-}PTA]^+$; 370.08 $[M\text{-}PTA\text{-}MeCN]^+$. *Anal. Calc.* for $C_{59}H_{49}BF_{24}N_5PPd$: C, 49.48; H, 3.45; N, 4.89. *Found:* C, 49.87; H, 3.24; N, 4.43.

$[Pd(PTA)(MeCN)(2\text{-}Cl\text{-}C_6H_3)CH{=}N\{2,6\text{-}^iPr_2\text{-}C_6H_3\}]^+ [B(Ar)_4]^-$ ***(C12)***

Yield: 81 %. Melting point: 145 – 147 °C (decomposes without melting). FT-IR ν(C=N) 1611 cm^{-1}; $\nu([B(Ar)_4]^-)$ 1353; 1272; 1110 cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.46 (d, $^4J_{H\text{-}P}$ = 7.0 Hz, 1H, H^7), δ 7.73-7.65 (comp., 8H, $B(Ar)_4$), δ 7.56-7.50 (comp., 4H, $B(Ar)_4$), δ 7.37-7.20 (comp., 5H, $H^{2,3,10,11,12}$), δ 7.03-6.93 (m, 1H, H^4), δ 4.55-4.45 (comp., 6H, PTA), δ 4.40-4.30 (comp., 6H, PTA), δ 3.20-3.02 (m, 2H, $H^{14,16}$), δ 1.25 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.19 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.40 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per

Fig. S8c): δ 176.5 (d, $^{3}J_{C\text{-}P}$ = 4.2 Hz, C^{7}), δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 50.6 Hz, C^{20}), δ 150.7 (Ar-C), δ 144.6 (Ar-C), δ 143.2 (Ar-C), δ 140.8 (Ar-C), δ 136.2 (Ar-C), δ 134.9 (br, C^{21}), δ 134.5 (Ar-C), δ 131.2 (Ar-C), δ 130.1 (Ar-C), δ 129.2 (Ar-C), δ 129.0 (qq, $^{2}J_{C\text{-}F}$ = 29.9, $^{3}J_{C\text{-}B}$ = 2.7 Hz, C^{22}), δ 128.9 (Ar-C), δ 128.2 (Ar-C), δ 126.5 (Ar-C), δ 124.2 (Ar-C), δ 122.9 (Ar-C), δ 119.3 (C^{18}), δ 117.6 (sept., $^{3}J_{C\text{-}F}$ = 3.7 Hz, C^{23}), δ 73.1 (d, $^{3}J_{C\text{-}P}$ = 6.8 Hz, N-***C***H_2-N), δ 52.0 (d, $^{3}J_{C\text{-}P}$ = 14.1 Hz, N-***C***H_2-P), δ 28.6 ($C^{14,16}$), δ 24.5 ($C^{15,17}$), δ 22.7 ($C^{15,17}$), δ 0.8 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -46.9 (s). ESI-MS (+.ve, m/z): 1161.20 $[2M\text{-}2MeCN+Cl]^+$; 604.14 $[M]^+$; 563.12 $[M\text{-}MeCN]^+$; 447.07 $[M\text{-}PTA]^+$; 406.04 $[M\text{-}PTA\text{-}MeCN]^+$. *Anal. Calc.* for $C_{59}H_{48}BClF_{24}N_5PPd$: C, 48.32; H, 3.30; N, 4.78. *Found:* C, 48.66; H, 3.05; N, 4.22.

[Pd(PTA)(MeCN)(2-Br-C_6H_3)CH=N{2,6-$^{i}Pr_2$-C_6H_3}]$^+$ [B(Ar)$_4$]$^-$ ***(C13)***

Yield: 80 %. Melting point: 161 – 164 °C (decomposes without melting). FT-IR *ν*(C=N) 1612 cm^{-1}; *ν*($[B(Ar)_4]^-$) 1353; 1272; 1112 cm^{-1}.^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.47 (d, $^{4}J_{H\text{-}P}$ = 7.3 Hz, 1H, H^7), δ 7.75-7.64 (comp., 8H, $B(Ar)_4$), δ 7.56-7.49 (comp., 4H, $B(Ar)_4$), δ 7.42 (d, $^{3}J_{H\text{-}H}$ = 7.6 Hz, 1H, H^2), δ 7.37-7.23 (comp., 3H, $H^{10,11,12}$), δ 7.17 (t, $^{3}J_{H\text{-}H}$ = 8.0 Hz, 1H, H^3), δ 7.06-6.98 (m, 1H, H^4), δ 4.58-4.42 (comp., 6H, PTA), δ 4.41-4.30 (comp., 6H, PTA), δ 3.20-3.03 (m, 2H, $H^{14,16}$), δ 1.25 (d, $^{3}J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.19 (d, $^{3}J_{H\text{-}H}$ = 6.7 Hz, 6H, $H^{15,17}$), δ 1.42 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 178.9 (d, $^{3}J_{C\text{-}P}$ = 3.9 Hz, C^7), δ 161.9 (q, $^{1}J_{C\text{-}B}$ = 50.6 Hz, C^{20}), δ 154.2 (d, $J_{C\text{-}P}$ = 5.7, Ar-C), δ 145.9 (Ar-C), δ 143.2 (Ar-C), δ 140.8 (Ar-C), δ 135.2 (Ar-C), δ 135.1 (Ar-C), δ 134.9 (br, C^{21}), δ 131.5 (Ar-C), δ 129.0 (qq, $^{2}J_{C\text{-}F}$ = 31.2, $^{3}J_{C\text{-}B}$ = 2.7 Hz, C^{22}), δ 128.9 (Ar-C), δ 127.4 (Ar-C), δ 125.6 (Ar-C), δ 125.0 (Ar-C), δ 124.2 (Ar-C), δ 123.8 (Ar-C), δ 122.0 (Ar-C), δ 121.9 (C^{18}), δ 117.6 (sept., $^{3}J_{C\text{-}F}$ = 4.3 Hz, C^{23}), δ 73.2 (d, $^{3}J_{C\text{-}P}$ = 7.6 Hz, N-***C***H_2-N), δ 52.1 (d, $^{3}J_{C\text{-}P}$ = 14.5 Hz, N-***C***H_2-P), δ 28.7 ($C^{14,16}$), δ 24.5 ($C^{15,17}$), δ 22.8 ($C^{15,17}$), δ 0.8 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -47.8 (s). ESI-MS (+.ve, m/z): 1249.10 $[2M\text{-}2MeCN+Cl]^+$; 648.09 $[M]^+$; 607.07 $[M\text{-}MeCN]^+$; 491.02 $[M\text{-}PTA]^+$; 449.99 $[M\text{-}PTA\text{-}MeCN]^+$. ESI-MS (-.ve, m/z): 863.07 $[B(Ar)_4]^-$. *Anal. Calc.* for $C_{59}H_{48}BBrF_{24}N_5PPd•1CH_2Cl_2$: C, 45.15; H, 3.16; N, 4.39. *Found:* C, 45.09; H, 2.88; N, 4.59.

[Pd(PTA)(MeCN)(2-F-C6H3)CH=N{2,6-iPr2-C6H3}]+ [B(Ar)4]- ***(C14)***

Yield: 86 %. Melting point: 141 – 143 °C (decomposes without melting). FT-IR *ν*(C=N) 1611 cm^{-1}; *ν*($[B(Ar)_4]^-$) 1353; 1272; 1111 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.32 (d, $^{4}J_{H\text{-}P}$ = 7.6 Hz, 1H, H^7), δ 7.76-7.65 (comp., 8H, $B(Ar)_4$), δ 7.56-7.49 (comp., 4H, $B(Ar)_4$), δ 7.43-7.21 (comp., 4H, $H^{3,10,11,12}$), δ 7.00-6.86 (comp., 2H, $H^{2,4}$), δ 4.58-4.45 (comp., 6H, PTA), δ 4.43-4.32 (comp., 6H, PTA), δ 3.17-3.03 (m, 2H, $H^{14,16}$), δ 1.24 (d, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 6H, $H^{15,17}$), δ 1.18 (d, $^{3}J_{H\text{-}H}$ = 7.0 Hz, 6H, $H^{15,17}$), δ 1.44 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 172.8 (d, $^{3}J_{C\text{-}P}$ = 4.0 Hz, C^7), δ 163.2 (Ar-C), δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 51.1 Hz, C^{20}), δ 160.6 (Ar-C), δ 153.9 (d, $J_{C\text{-}P}$ = 6.3, Ar-C), δ 143.2 (Ar-C), δ 140.8 (Ar-C), δ 136.2 (dd, $J_{C\text{-}P}$ = 8.3, 5.7 Hz, Ar-C), δ 134.9 (br, C^{21}), δ 131.8 (dd, $J_{C\text{-}P}$ = 11.6, 3.3 Hz, Ar-C), δ 129.0 (qq, $^{2}J_{C\text{-}F}$ = 31.4, $^{3}J_{C\text{-}B}$ = 3.0

Hz, C^{22}), δ 128.8 (Ar-C), δ 128.7 (Ar-C), δ 126.1 (Ar-C), δ 124.1 (Ar-C), δ 123.3 (Ar-C), δ 121.9 (Ar-C), δ 120.0 (C^{18}), δ 117.6 (sept., $^3J_{C\text{-}F}$ = 3.8 Hz, C^{23}), δ 172.8 (d, $J_{C\text{-}P}$ = 19.3 Hz, Ar-C), δ 73.1 (d, $^3J_{C\text{-}P}$ = 7.6 Hz, N-***C***H_2-N), δ 52.2 (d, $^3J_{C\text{-}P}$ = 14.5 Hz, N-***C***H_2-P), δ 28.6 ($C^{14,16}$), δ 24.4 ($C^{15,17}$), δ 22.8 ($C^{15,17}$), δ 0.8 (C^{19}). ^{31}P {^{1}H} NMR (162 MHz, $CDCl_3$): δ -46.3 (s). ESI-MS (+.ve, m/z): 1127.25 $[2M\text{-}2MeCN+Cl]^+$; 586.17 $[M]^+$; 545.15 $[M\text{-}MeCN]^+$; 429.10 $[M\text{-}PTA]^+$; 388.07 $[M\text{-}PTA\text{-}MeCN]^+$. *Anal. Calc.* for $C_{59}H_{48}BF_{25}N_5PPd$: C, 48.86; H, 3.34; N, 4.83. *Found:* C, 49.25; H, 3.18; N, 4.34.

$[Pd(PTA)(MeCN)(2\text{-}F\text{-}C_6H_3)CH{=}N\{2,6\text{-}^iPr_2\text{-}C_6H_3\}]^+$ $[B(Ar)_4]^-$ ***(C15)***

Yield: 85 %. Melting point: 155 – 157 °C (decomposes without melting). FT-IR ν(C=N) 1605 cm^{-1}; $\nu([B(Ar)_4]^-)$ 1352; 1273; 1112 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.38 (d, $^4J_{H\text{-}P}$ = 7.7 Hz, 1H, H^7), δ 7.75-7.64 (comp., 8H, $B(Ar)_4$), δ 7.56-7.48 (comp., 4H, $B(Ar)_4$), δ 7.35-7.19 (comp., 4H, $H^{3,10,11,12}$), δ 6.75 (d, $^3J_{H\text{-}H}$ = 8.5 Hz, 1H, H^2), δ 6.68-6.63 (m, 1H, H^4), δ 4.57-4.47 (comp., 6H, PTA), δ 4.40-4.35 (comp., 6H, PTA), δ 3.82 (s, 3H, *o*-methoxy Me), δ 3.20-3.07 (m, 2H, $H^{14,16}$), δ 1.24 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.17 (d, $^3J_{H\text{-}H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.41 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 174.8 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, C^7), δ 161.8 (q, $^1J_{C\text{-}B}$ = 50.0 Hz, C^{20}), δ 160.9 (Ar-C), δ 154.7 (Ar-C), δ 143.7 (Ar-C), δ 141.2 (Ar-C), δ 135.9 (Ar-C), δ 135.1 (Ar-C), δ 134.9 (br, C^{21}), δ 130.1 (Ar-C), δ 129.0 (qq, $^2J_{C\text{-}F}$ = 31.6, $^3J_{C\text{-}B}$ = 2.9 Hz, C^{22}), δ 128.4 (Ar-C), δ 128.2 (Ar-C), δ 126.5 (Ar-C), δ 123.9 (Ar-C), δ 122.9 (Ar-C), δ 121.6 (Ar-C), δ 119.3 (C^{18}), δ 117.6 (sept., $^3J_{C\text{-}F}$ = 4.1 Hz, C^{23}), δ 109.9 (Ar-C), δ 73.2 (d, $^3J_{C\text{-}P}$ = 7.7 Hz, N-***C***H_2-N), δ 56.0 (*o*-methoxy Me), δ 52.1 (d, $^3J_{C\text{-}P}$ = 14.4 Hz, N-***C***H_2-P), δ 28.5 ($C^{14,16}$), δ 24.5 ($C^{15,17}$), δ 22.8 ($C^{15,17}$), δ 0.8 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ -48.1 (s). ^{19}F {^{1}H} NMR (282 MHz, $CDCl_3$): δ -62.6 (s). ESI-MS (+.ve, m/z): 1151.30 $[2M\text{-}2MeCN+Cl]^+$; 598.19 $[M]^+$; 557.17 $[M\text{-}MeCN]^+$; 441.12 $[M\text{-}PTA]^+$; 400.09 $[M\text{-}PTA\text{-}MeCN]^+$. *Anal. Calc.* for $C_{60}H_{51}BF_{24}N_5OPPd{\bullet}1CH_2Cl_2$: C, 47.35; H, 3.45; N, 4.53. *Found:* C, 47.62; H, 3.27; N, 4.59.

$[Pd(PCy_3)(MeCN)(C_6H_4)CH{=}N\{2,6\text{-}^iPr_2\text{-}C_6H_3\}]^+$ $[B(Ar)_4]^-$ ***(C21)***

Yield: 85 %. Melting point: 168 – 169 °C (decomposes without melting). FT-IR ν(C=N) 1615 cm^{-1}; $\nu([B(Ar)_4]^-)$ 1354; 1271; 1113 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.03 (d, $^4J_{H\text{-}P}$ = 6.6 Hz, 1H, H^7), δ 7.74-7.65 (comp., 8H, $B(Ar)_4$), δ 7.55-7.50 (comp., 4H, $B(Ar)_4$), δ 7.50-7.46 (m, 1H, H^1), δ 7.33-7.19 (comp., 6H, Ar-H), δ 3.35-3.21 (m, 2H, $H^{14,16}$), δ 2.25-2.09 (comp., 4H, $P(Cy)_3$), δ 2.02-1.90 (comp., 6H, $P(Cy)_3$), δ 1.89-1.79 (comp., 6H, $P(Cy)_3$), δ 1.78-1.68 (comp., 3H, $P(Cy)_3$), δ 1.67-1.52 (comp., 7H, $P(Cy)_3$), δ 1.31-1.08 (comp., 19H, $P(Cy)_3$ & $H^{15,17}$), δ 1.39 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 177.8 (d, $^3J_{C\text{-}P}$ = 4.0 Hz, C^7), δ 161.8 (q, $^1J_{C\text{-}B}$ = 50.6 Hz, C^{20}), δ 153.0 (Ar-C), δ 147.9 (Ar-C), δ 143.9 (Ar-C), δ 141.1 (Ar-C), δ 137.5 (d, $J_{C\text{-}P}$ = 5.7 Hz, Ar-C), δ 134.9 (br, C^{21}), δ 132.5 (d, $J_{C\text{-}P}$ = 3.8 Hz, Ar-C), δ 129.0 (qq, $^2J_{C\text{-}F}$ = 31.3, $^3J_{C\text{-}B}$ = 2.9 Hz, C^{22}), δ 128.8 (Ar-C), δ 128.5 (Ar-C), δ 126.6 (Ar-C), δ 126.1 (Ar-C), δ 124.2 (Ar-C), δ 123.3 (Ar-C), δ 120.6 (C^{18}), δ 117.6 (sept., $^3J_{C\text{-}F}$ = 3.9 Hz, C^{23}), δ 34.8 (d, $^1J_{C\text{-}P}$ = 21.2 Hz, PCy_3), δ 30.4 (PCy_3), δ 28.7 (PCy_3), δ 27.8 (d, $^2J_{C\text{-}P}$ = 10.4 Hz, PCy_3), δ 26.0 ($C^{14,16}$), δ 24.4 ($C^{15,17}$),

δ 22.7 ($C^{15,17}$), δ 0.9 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 47.7 (s). ESI-MS (+.ve, m/z): 650.3 $[M\text{-}MeCN]^+$; 411.1 $[M\text{-}P(Cy)_3]^+$. ESI-MS (-.ve, m/z): 863.07 $[B(Ar)_4]^-$. *Anal. Calc.* for $C_{71}H_{70}BF_{24}N_2PPd\bullet 0.5CH_2Cl_2$: C, 53.74; H, 4.48; N, 1.75. *Found:* C, 53.61; H, 4.82; N, 1.30.

$[Pd(PCy_3)(MeCN)(2\text{-}Cl\text{-}C_6H_3)CH{=}N\{2,6\text{-}^iPr_2\text{-}C_6H_3\}]^+ [B(Ar)_4]^-$ ***(C22)***

Yield: 85 %. Melting point: 160 – 163 °C (decomposes without melting). FT-IR *ν*(C=N) 1616 cm^{-1}; *ν*($[B(Ar)_4]^-$) 1354; 1276; 1116 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.52 (d, $^{4}J_{H\text{-}P}$ = 6.6 Hz, 1H, H^7), δ 7.74-7.65 (comp., 8H, $B(Ar)_4$), δ 7.56-7.48 (comp., 4H, $B(Ar)_4$), δ 7.36-7.24 (comp., 3H, Ar-H), δ 7.22-7.05 (comp., 3H, Ar-H), δ 3.36-3.17 (m, 2H, $H^{14,16}$), δ 2.25-2.04 (comp., 5H, $P(Cy)_3$), δ 2.02-1.47 (comp., 21H, $P(Cy)_3$), δ 1.34-1.03 (comp., 19H, $P(Cy)_3$ & $H^{15,17}$), δ 1.40 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 176.2 (d, $^{3}J_{C\text{-}P}$ = 3.9 Hz, C^7), δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 50.4 Hz, C^{20}), δ 154.6 (Ar-C), δ 144.7 (Ar-C), δ 144.1 (Ar-C), δ 141.0 (Ar-C), δ 136.0 (d, $J_{C\text{-}P}$ = 5.2 Hz, Ar-C), δ 135.3 (Ar-C), δ 134.9 (br, C^{21}), δ 133.6 (d, $J_{C\text{-}P}$ = 4.0 Hz, Ar-C), δ 130.1 (Ar-C), δ 129.0 (qq, $^{2}J_{C\text{-}F}$ = 31.5, $^{3}J_{C\text{-}B}$ = 3.3 Hz, C^{22}), δ 128.7 (Ar-C), δ 127.6 (Ar-C), δ 126.5 (Ar-C), δ 124.3 (Ar-C), δ 122.9 (Ar-C), δ 119.3 (C^{18}), δ 117.6 (sept., $^{3}J_{C\text{-}F}$ = 3.7 Hz, C^{23}), δ 34.8 (d, $^{1}J_{C\text{-}P}$ = 21.2 Hz, PCy_3), δ 30.4 (PCy_3), δ 28.8 (PCy_3), δ 27.7 (d, $^{2}J_{C\text{-}P}$ = 11.2 Hz, PCy_3), δ 26.0 ($C^{14,16}$), δ 24.5 ($C^{15,17}$), δ 22.7 ($C^{15,17}$), δ 0.9 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 47.5 (s). ESI-MS (+.ve, m/z): 684.27 $[M\text{-}MeCN]^+$. *Anal. Calc.* for $C_{71}H_{69}BClF_{24}N_2PPd\bullet 1CH_2Cl_2$: C, 51.63; H, 4.27; N, 1.67. *Found:* C, 51.29; H, 4.26; N, 1.01.

$[Pd(PCy_3)(MeCN)(2\text{-}Br\text{-}C_6H_3)CH{=}N\{2,6\text{-}^iPr_2\text{-}C_6H_3\}]^+ [B(Ar)_4]^-$ ***(C23)***

Yield: 83 %. Melting point: 168 – 170 °C (decomposes without melting). FT-IR *ν*(C=N) 1613 cm^{-1}; *ν*($[B(Ar)_4]^-$) 1353; 1275; 1115 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.53 (d, $^{4}J_{H\text{-}P}$ = 6.7 Hz, 1H, H^7), δ 7.76-7.63 (comp., 8H, $B(Ar)_4$), δ 7.57-7.48 (comp., 4H, $B(Ar)_4$), δ 7.42-7.22 (comp., 4H, Ar-H), δ 7.17-7.03 (comp., 2H, Ar-H), δ 3.36-3.16 (m, 2H, $H^{14,16}$), δ 2.23-1.46 (comp., 26H, $P(Cy)_3$), δ 1.35-1.03 (comp., 19H, $P(Cy)_3$ & $H^{15,17}$), δ 1.39 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 178.5 (d, $^{3}J_{C\text{-}P}$ = 3.6 Hz, C^7), δ 161.8 (q, $^{1}J_{C\text{-}B}$ = 52.0 Hz, C^{20}), δ 154.8 (Ar-C), δ 146.0 (Ar-C), δ 144.1 (Ar-C), δ 141.0 (Ar-C), δ 136.7 (d, $J_{C\text{-}P}$ = 5.4 Hz, Ar-C), δ 134.9 (br, C^{21}), δ 133.7 (d, $J_{C\text{-}P}$ = 4.0 Hz, Ar-C), δ 130.9 (Ar-C), δ 130.1 (Ar-C), δ 129.0 (qq, $^{2}J_{C\text{-}F}$ = 32.0, $^{3}J_{C\text{-}B}$ = 2.5 Hz, C^{22}), δ 128.8 (Ar-C), δ 126.5 (Ar-C), δ 124.3 (Ar-C), δ 124.2 (Ar-C), δ 122.9 (Ar-C), δ 119.3 (C^{18}), δ 117.6 (sept., $^{3}J_{C\text{-}F}$ = 3.8 Hz, C^{23}), δ 34.8 (d, $^{1}J_{C\text{-}P}$ = 22.1 Hz, PCy_3), δ 30.4 (PCy_3), δ 28.8 (PCy_3), δ 27.7 (d, $^{2}J_{C\text{-}P}$ = 11.3 Hz, PCy_3), δ 26.0 ($C^{14,16}$), δ 24.5 ($C^{15,17}$), δ 22.7 ($C^{15,17}$), δ 0.9 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 47.3 (s). ESI-MS (+.ve, m/z): 730.2 $[M\text{-}MeCN]^+$; 491.0 $[M\text{-}P(Cy)_3]^+$. ESI-MS (-.ve, m/z): 863.0 $[B(Ar)_4]^-$. *Anal. Calc.* for $C_{71}H_{69}BBrF_{24}N_2PPd\bullet 2CH_2Cl_2$: C, 48.60; H, 4.08; N, 1.55. *Found:* C, 48.31; H, 4.40; N, 1.35.

[Pd(PCy$_3$)(MeCN)(2-F-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}]$^+$ [B(Ar)$_4$]$^-$ ***(C24)***

Yield: 86 %. Melting point: 143 – 146 °C (decomposes without melting). FT-IR ν(C=N) 1611 cm^{-1}; ν([B(Ar)$_4$]$^-$) 1353; 1276; 1119 cm^{-1}.^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.63 (d, $^4J_{H\text{-}P}$ = 6.7 Hz, 1H, H^7), δ 7.74-7.60 (comp., 8H, B(Ar)$_4$), δ 7.54-7.46 (comp., 4H, B(Ar)$_4$), δ 7.33-7.20 (comp., 4H, Ar-H), δ 6.99-6.93 (m, 1H, Ar-H), δ 6.92-6.86 (m, 1H, H^{11}), δ 3.29-3.17 (m, 2H, H^{14,16}), δ 2.21-2.07 (comp., 4H, P(Cy)$_3$), δ 1.98-1.87 (comp., 6H, P(Cy)$_3$), δ 1.87-1.77 (comp., 6H, P(Cy)$_3$), δ 1.75-1.66 (comp., 3H, P(Cy)$_3$), δ 1.64-1.49 (comp., 6H, P(Cy)$_3$), δ 1.31-1.07 (comp., 20H, P(Cy)$_3$ & H^{15,17}), δ 1.38 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 172.5 (d, $^3J_{C\text{-}P}$ = 4.1 Hz, C^7), δ 163.3 (Ar-C), δ 161.8 (q, $^3J_{C\text{-}B}$ = 50.4 Hz, C^{20}), δ 159.8 (Ar-C), δ 154.2 (Ar-C), δ 144.1 (Ar-C), δ 141.1 (Ar-C), δ 134.9 (br, C^{21}), δ 133.2 (Ar-C), δ 130.1 (Ar-C), δ 129.0 (qq, $^2J_{C\text{-}F}$ = 31.6, $^3J_{C\text{-}B}$ =2.9 Hz, C^{22}), δ 128.7 (Ar-C), δ 126.5 (Ar-C), δ 124.2 (Ar-C), δ 122.9 (Ar-C), δ 119.3 (C^{18}), δ 117.6 (sept., $^3J_{C\text{-}F}$ = 4.0 Hz, C^{23}), δ 113.8 (Ar-C), δ 113.6 (Ar-C), δ 34.9 (d, $^1J_{C\text{-}P}$ = 22.1 Hz, PCy_3), δ 30.4 (PCy_3), δ 28.7 (PCy_3), δ 27.7 (d, $^2J_{C\text{-}P}$ = 11.4 Hz, PCy_3), δ 26.0 (C^{14,16}), δ 24.4 (C^{15,17}), δ 22.7 (C^{15,17}), δ 0.9 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 48.2 (s). ESI-MS (+.ve, m/z): 668.30 [M-MeCN]$^+$. *Anal. Calc.* for $C_{71}H_{69}BF_{25}N_2PPd$•0.5$CH_2Cl_2$: C, 53.14; H, 4.37; N, 1.73. *Found:* C, 52.83; H, 4.00; N, 1.95.

[Pd(PCy$_3$)(MeCN)(2-OMe-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}]$^+$ [B(Ar)$_4$]$^-$ ***(C25)***

Yield: 82 %. Melting point: 147 – 150 °C (decomposes without melting). FT-IR ν(C=N) 1604 cm^{-1}; ν([B(Ar)$_4$]$^-$) 1352; 1273; 1120 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.44 (d, $^4J_{H\text{-}P}$ = 6.9 Hz, 1H, H^7), δ 7.74-7.65 (comp., 8H, B(Ar)$_4$), δ 7.55-7.48 (comp., 4H, B(Ar)$_4$), δ 7.33-7.17 (comp., 4H, Ar-H), δ 6.79-6.65 (comp., 2H, Ar-H), δ 3.81 (s, 3H, *o*-methoxy Me), δ 3.29-3.21 (m, 2H, H^{14,16}), δ 2.25-2.05 (comp., 4H, P(Cy)$_3$), δ 2.02-1.46 (comp., 21H, P(Cy)$_3$), δ 1.34-1.05 (comp., 20H, P(Cy)$_3$ & H^{15,17}), δ 1.39 (s, 3H, H^{19}). ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 174.5 (d, $^3J_{C\text{-}P}$ = 3.7 Hz, C^7), δ 161.8 (q, $^3J_{C\text{-}B}$ = 50.6 Hz, C^{20}), δ 160.4 (Ar-C), δ 155.2 (Ar-C), δ 144.6 (Ar-C), δ 141.4 (Ar-C), δ 135.5 (Ar-C), δ 134.9 (br, C^{21}), δ 134.5 (d, $J_{C\text{-}P}$ = 4.2 Hz, Ar-C), δ 130.1 (Ar-C), δ 129.0 (qq, $^2J_{C\text{-}F}$ = 30.9, $^3J_{C\text{-}B}$ =2.4 Hz, C^{22}), δ 128.2 (Ar-C), δ 126.5 (Ar-C), δ 124.1 (Ar-C), δ 122.9 (Ar-C), δ 117.6 (sept., $^3J_{C\text{-}F}$ = 4.0 Hz, C^{23}), δ 109.1 (C^{18}), δ 55.9 (methoxy C), δ 34.8 (d, $^1J_{C\text{-}P}$ = 21.3 Hz, PCy_3), δ 30.4 (PCy_3), δ 28.6 (PCy_3), δ 27.7 (d, $^2J_{C\text{-}P}$ = 10.6 Hz, PCy_3), δ 26.0 (C^{14,16}), δ 24.5 (C^{15,17}), δ 22.7 (C^{15,17}), δ 0.9 (C^{19}). ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ 46.7 (s). ESI-MS (+.ve, m/z): 680.3 [M-MeCN]$^+$; 441.1 [M-P(Cy)$_3$]$^+$. ESI-MS (-.ve, m/z): 863.0 [B(Ar)$_4$]$^-$. *Anal. Calc.* for $C_{72}H_{72}BF_{24}N_2OPPd$•0.5$CH_2Cl_2$: C, 53.49; H, 4.52; N, 1.72. *Found:* C, 53.14; H, 4.71; N, 1.29.

[Pd(PPh$_3$)(MeCN)(2-F-C$_6$H$_3$)CH=N{2,6-^{i}Pr$_2$-C$_6$H$_3$}]$^+$ [B(Ar)$_4$]$^-$ ***(C34)***

Yield: 91 %. Melting point: 134 – 137 °C (decomposes without melting). FT-IR ν(C=N) 1612 cm^{-1}; ν([B(Ar)$_4$]$^-$) 1353; 1274; 1119 cm^{-1}. ^{1}H NMR (600 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.44 (d, $^4J_{H\text{-}P}$ = 7.6 Hz, 1H, H^7), δ 7.72-7.68 (comp., 8H, B(Ar)$_4$), δ 7.67-7.62 (comp., 6H, PPh_3), δ 7.53-7.48

(comp., 7H, PPh_3 & $B(Ar)_4$), δ 7.47-7.40 (comp., 6H, PPh_3), δ 7.28-7.19 (comp., 3H, $H^{10,11,12}$), δ 6.84-6.74 (comp., 2H, $H^{2,3}$), δ 6.25-6.20 (m, 1H, H^4), δ 3.36-3.27 (m, 2H, $H^{14,16}$), δ 1.29 (d, $^3J_{H-H}$ = 6.8 Hz, 6H, $H^{15,17}$), δ 1.27 (d, $^3J_{H-H}$ = 6.9 Hz, 6H, $H^{15,17}$), δ 1.05 (s, 3H, H^{19}). ^{13}C {^1H} NMR (151 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 173.2 (d, $^3J_{C-P}$ = 4.2 Hz, C^7), δ 162.2 (Ar-C), δ 161.9 (q, $^1J_{C-B}$ = 49.8 Hz, C^{20}), δ 160.4 (Ar-C), δ 155.2 (Ar-C), δ 144.2 (Ar-C), δ 140.7 (Ar-C), δ 134.9 (br, C^{21}), δ 134.8 (Ar-C), δ 134.7 (Ar-C), δ 132.6 (Ar-C), δ 129.4 (Ar-C), δ 129.2 (Ar-C), δ 129.0 (qq, $^2J_{C-F}$ = 31.6, $^3J_{C-B}$ = 2.4 Hz, C^{22}), δ 128.7 (Ar-C), δ 128.6 (Ar-C), δ 128.3 (Ar-C), δ 127.5 (Ar-C), δ 125.7 (Ar-C), δ 124.0 (Ar-C), δ 123.9 (Ar-C), δ 122.1 (Ar-C), δ 119.7 (C^{18}), δ 117.7 (sept., $^3J_{C-F}$ = 4.1 Hz, C^{23}), δ 113.7 (Ar-C), δ 113.6 (Ar-C), δ 28.9 ($C^{14,16}$), δ 24.4 ($C^{15,17}$), δ 22.9 ($C^{15,17}$), δ 0.4 (C^{19}). ^{31}P {^1H} NMR (121 MHz, $CDCl_3$): δ 41.2 (s). ESI-MS (+.ve, m/z): 650.1610 $[M\text{-}MeCN]^+$. ESI-MS (-.ve, m/z): 863.0735 $[B(Ar)_4]^-$. *Anal. Calc.* for $C_{71}H_{51}BF_{25}N_2PPd \bullet 0.5CH_2Cl_2$: C, 53.75; H, 3.28; N, 1.75. *Found:* C, 53.59; H, 3.41; N, 1.23.

*$[Pd(PPh_3)(MeCN)(2\text{-}OMe\text{-}C_6H_3)CH{=}N\{2,6\text{-}^iPr_2\text{-}C_6H_3\}]^+ [B(Ar)_4]^-$ (**C35**)*

Yield: 88 %. Melting point: 158 – 160 °C (decomposes without melting). FT-IR *ν*(C=N) 1604 cm^{-1}; *ν*($[B(Ar)_4]^-$) 1353; 1274; 1118 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 8.52 (d, $^4J_{H-P}$ = 8.0 Hz, 1H, H^7), δ 7.74-7.60 (comp., 15H, $B(Ar)_4$ & PPh_3), δ 7.54-7.47 (comp., 6H, $B(Ar)_4$), δ 7.46-7.39 (comp., 6H, PPh_3), δ 7.25-7.16 (comp., 3H, $H^{10,11,12}$), δ 6.74 (t, $^3J_{H-H}$ = 8.2 Hz, 1H, H^3), δ 6.57 (d, $^3J_{H-H}$ = 8.5 Hz, 1H, H^2), δ 6.05-5.98 (m, 1H, H^4), δ 3.79 (s, 3H, *o*-methoxy Me), δ 3.49-3.30 (m, 2H, $H^{14,16}$), δ 1.28 (d, $^3J_{H-H}$ = 6.7 Hz, 6H, $H^{15,17}$), δ 1.26 (d, $^3J_{H-H}$ = 6.6 Hz, 6H, $H^{15,17}$), δ 1.04 (s, 3H, H^{19}). ^{13}C {^1H} NMR (151 MHz, $CDCl_3$, numbering as per **Fig. S8c**): δ 175.1 (d, $^3J_{C-P}$ = 4.5 Hz, C^7), δ 161.9 (q, $^1J_{C-B}$ = 50.2 Hz, C^{20}), δ 160.2 (Ar-C), δ 156.0 (Ar-C), δ 144.6 (Ar-C), δ 140.9 (Ar-C), δ 135.6 (Ar-C), δ 134.9 (br, C^{21}), δ 134.9 (Ar-C), δ 134.8 (Ar-C), δ 134.7 (Ar-C), δ 132.3 (d, J_{C-P} = 6.6, Ar-C), δ 131.4 (Ar-C), δ 131.3 (Ar-C), δ 129.3 (Ar-C), δ 129.2 (Ar-C), δ 129.1 (Ar-C), δ 129.0 (qq, $^2J_{C-F}$ = 32.5, $^3J_{C-B}$ = 2.9 Hz, C^{22}), δ 128.8 (Ar-C), δ 128.2 (Ar-C), δ 127.4 (Ar-C), δ 125.6 (Ar-C), δ 123.8 (Ar-C), δ 123.7 (Ar-C), δ 122.0 (Ar-C), δ 119.3 (C^{18}), δ 117.6 (sept., $^3J_{C-F}$ = 3.9 Hz, C^{23}), δ 109.0 (Ar-C), δ 55.8 (*o*-methoxy Me), δ 28.7 ($C^{14,16}$), δ 24.3 ($C^{15,17}$), δ 22.8 ($C^{15,17}$), δ 0.3 (C^{19}). ^{31}P {^1H} NMR (162 MHz, $CDCl_3$): δ 41.1 (s). ESI-MS (+.ve, m/z): 662.1820 $[M\text{-}MeCN]^+$. *Anal. Calc.* for $C_{72}H_{54}BF_{24}N_2OPPd \bullet 0.5CH_2Cl_2$: C, 54.09; H, 3.44; N, 1.74. *Found:* C, 53.89; H, 3.20; N, 1.48.

NMR (^{1}H, ^{13}C, ^{31}P) and mass spectra

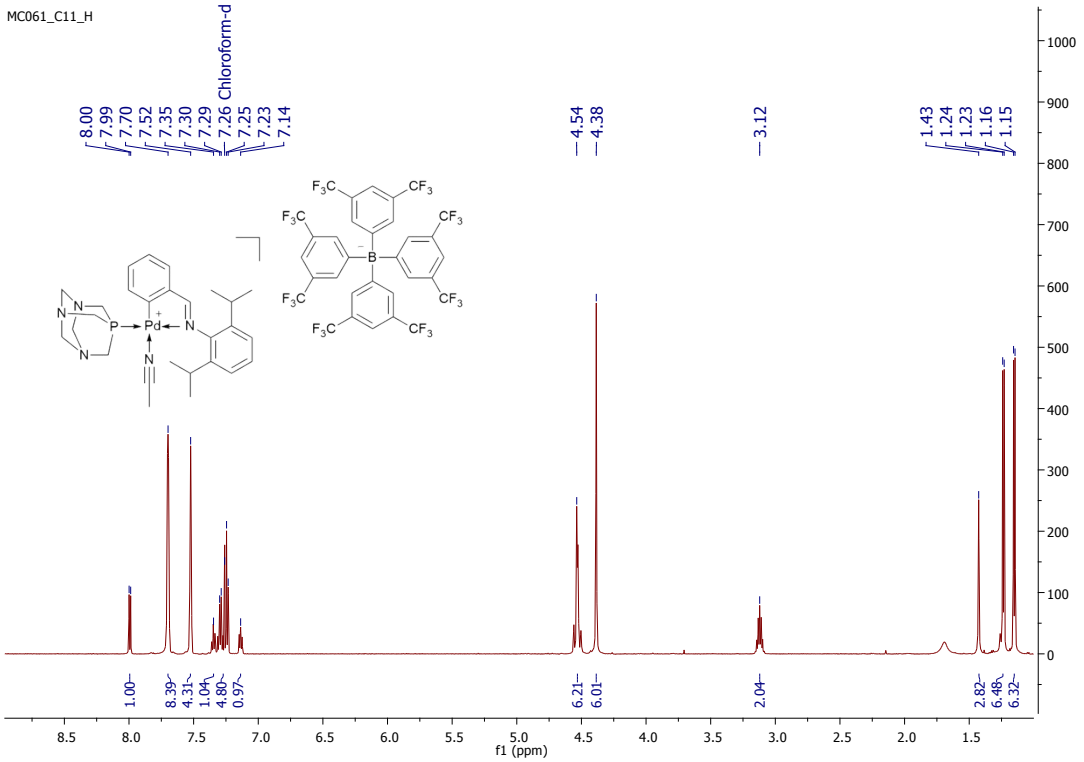


Fig. S9: ^{1}H NMR spectrum of **C11** in *d*-chloroform**.**

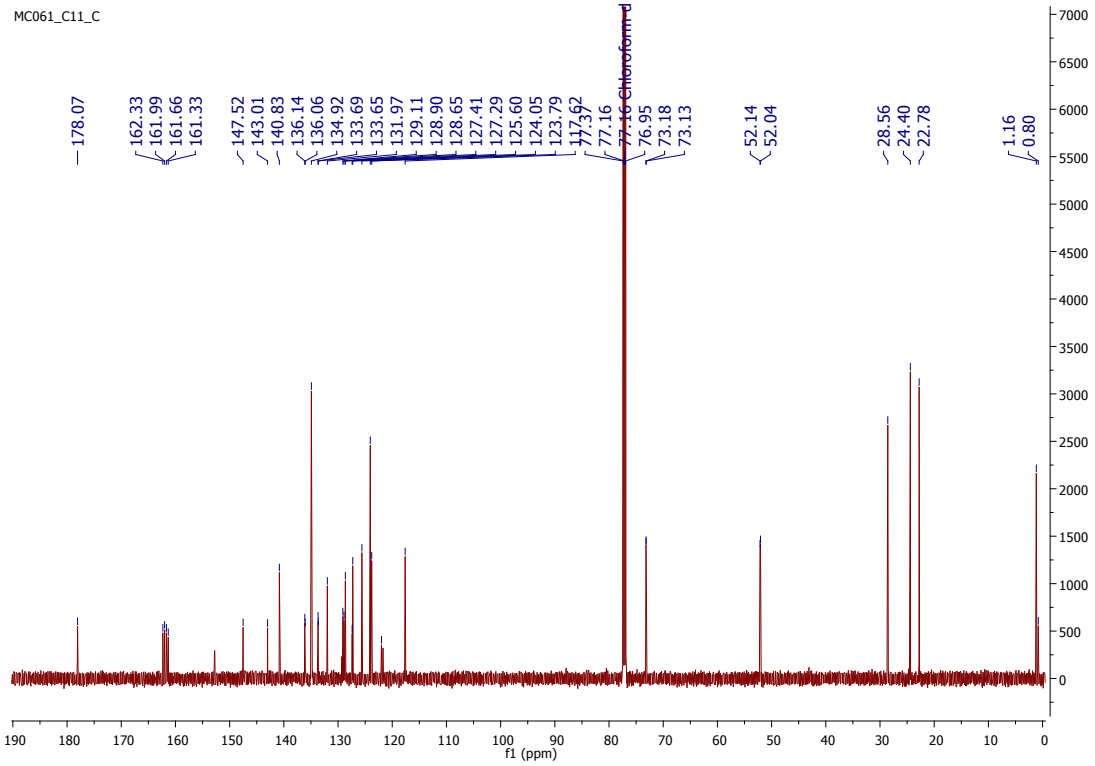


Fig. S10: ^{13}C NMR spectrum of **C11** in *d*-chloroform**.**

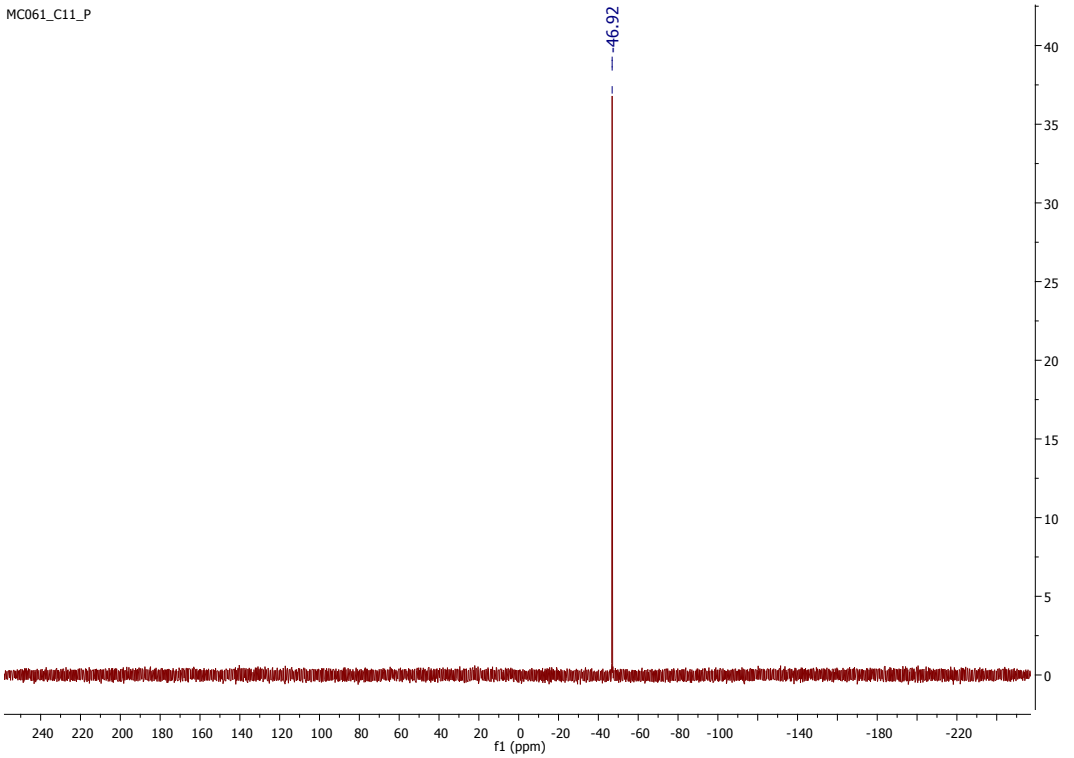


Fig. S11: ^{31}P NMR spectrum of **C11** in *d*-chloroform**.**

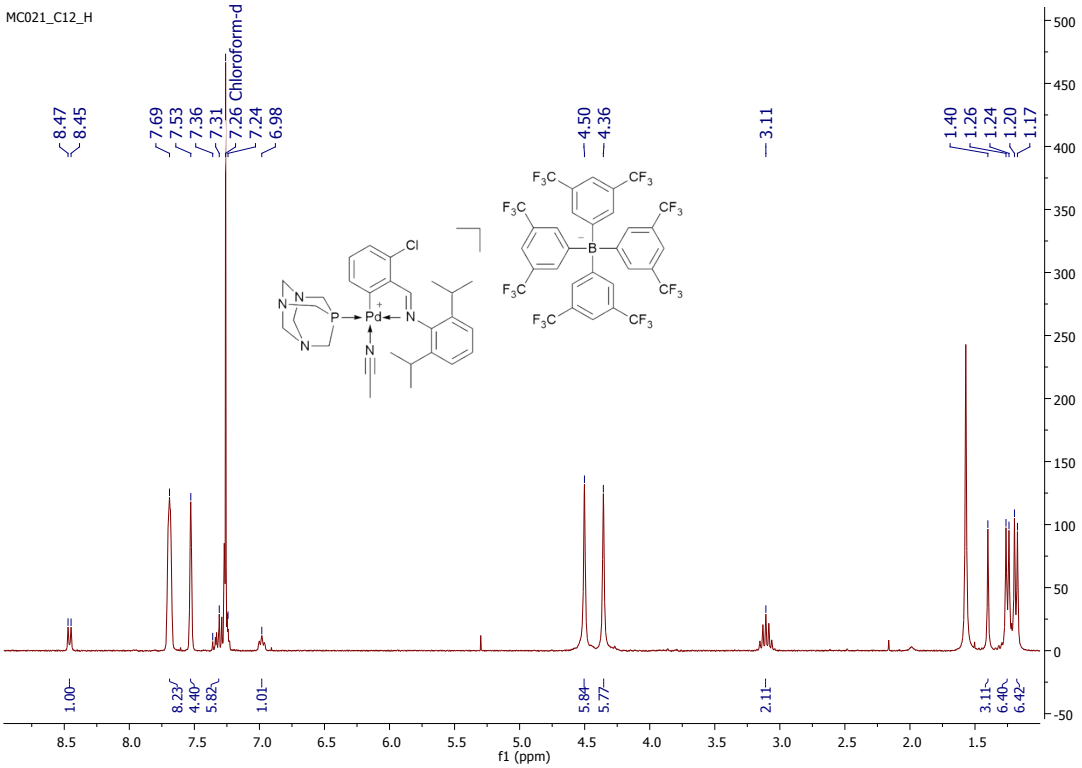


Fig. S12: ^{1}H NMR spectrum of **C12** in *d*-chloroform**.**

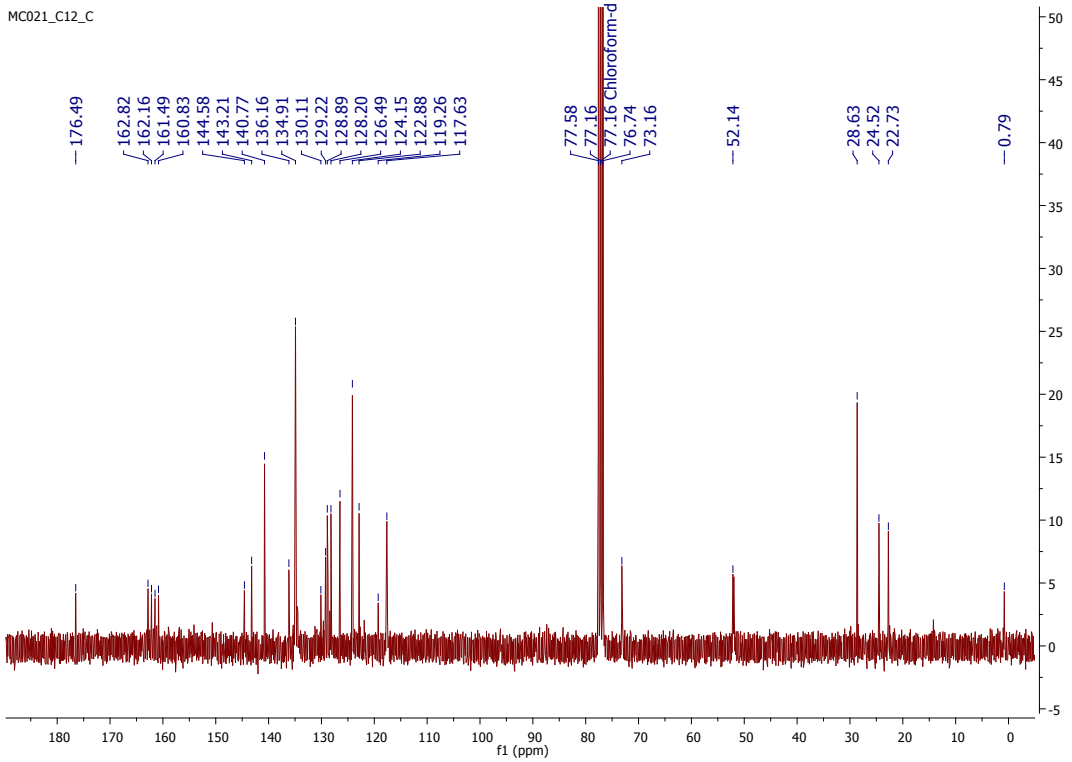


Fig. S13: ^{13}C NMR spectrum of **C12** in *d*-chloroform**.**

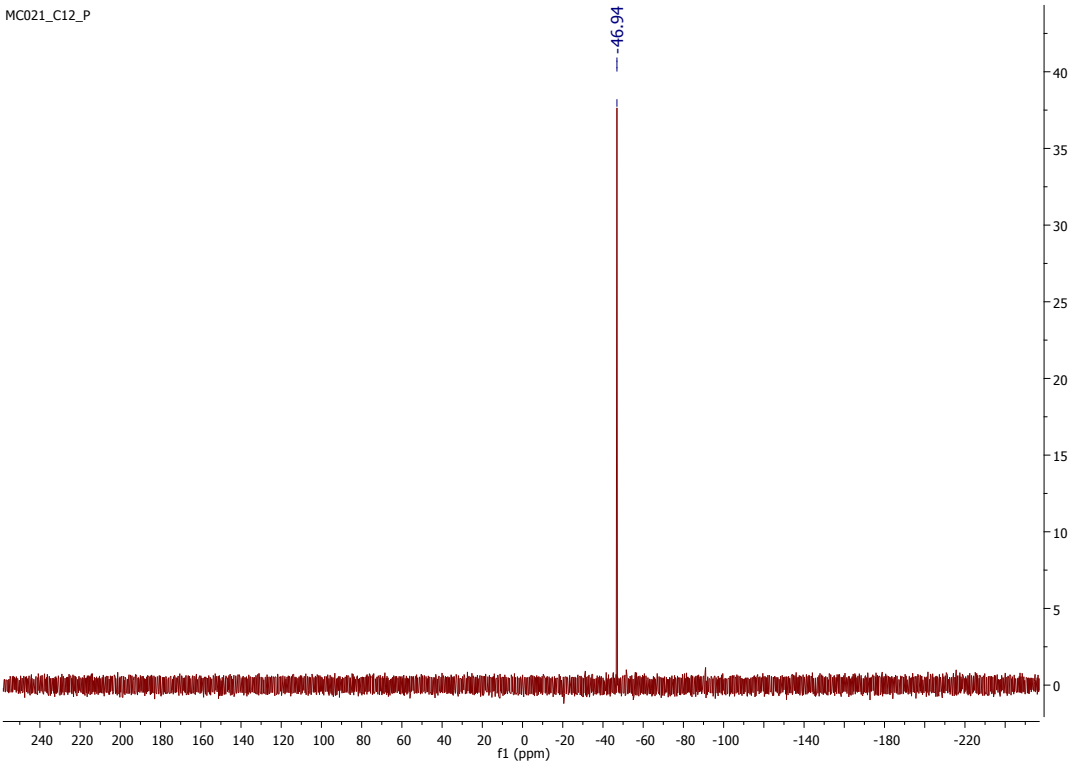


Fig. S14: ^{31}P NMR spectrum of **C12** in *d*-chloroform**.**

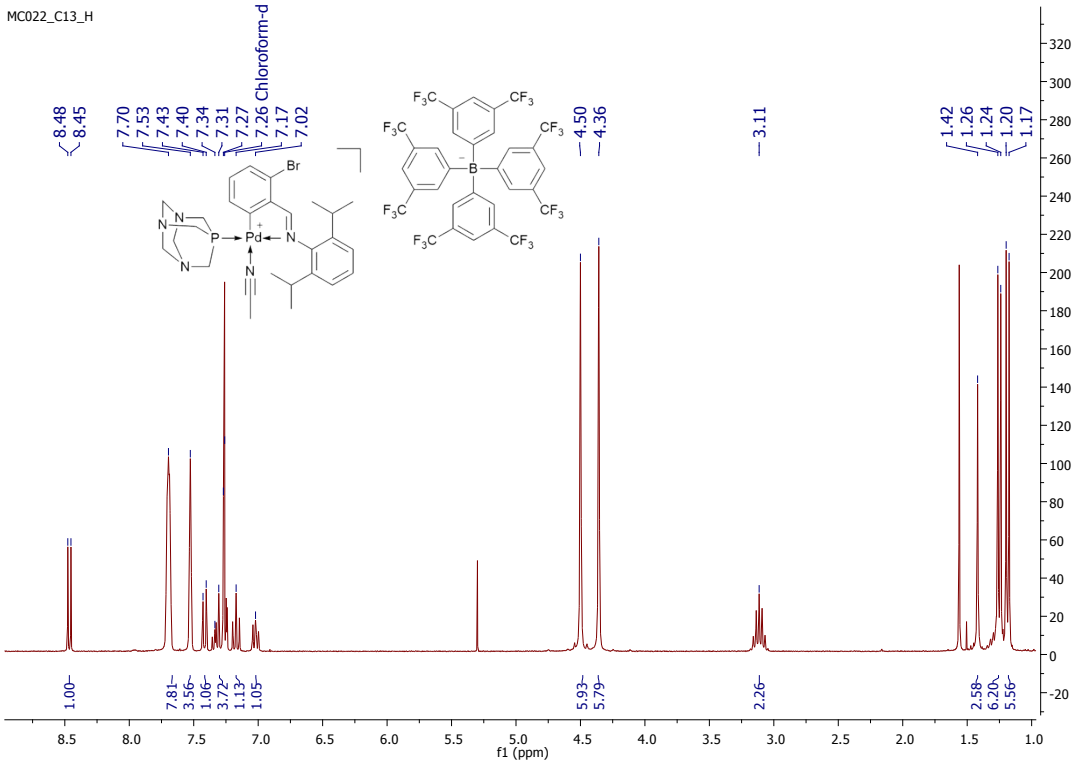


Fig. S15: [1]H NMR spectrum of **C13** in *d*-chloroform**.**

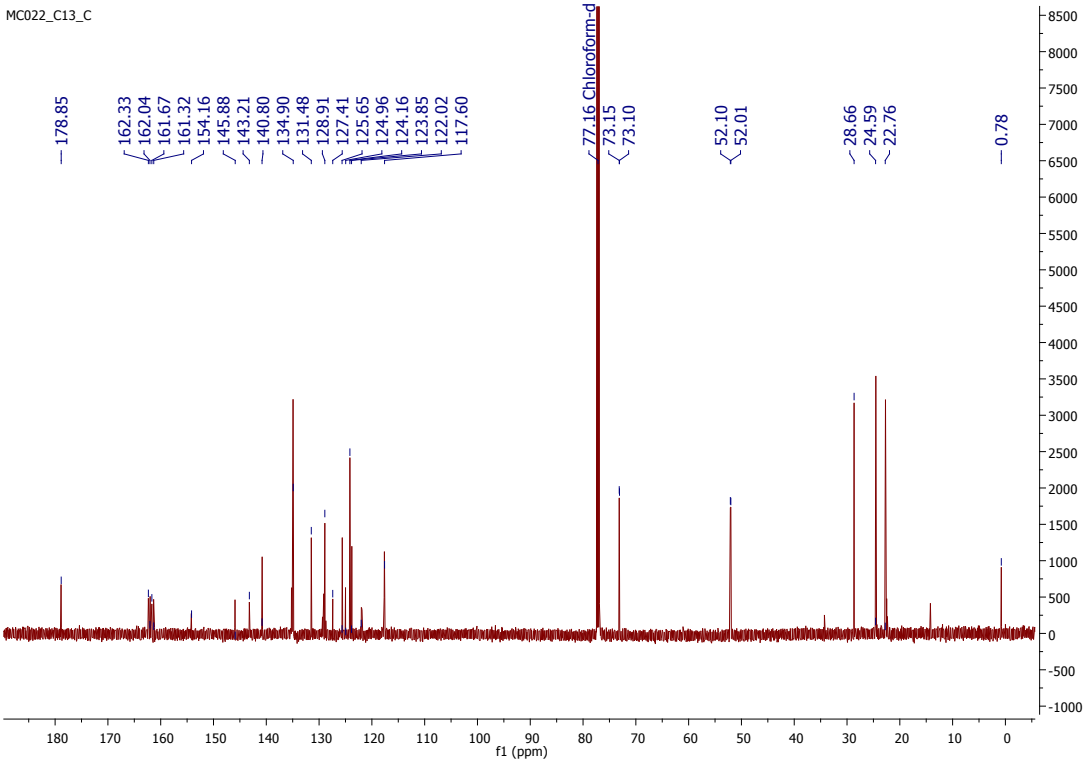


Fig. S16: [13]C NMR spectrum of **C13** in *d*-chloroform**.**

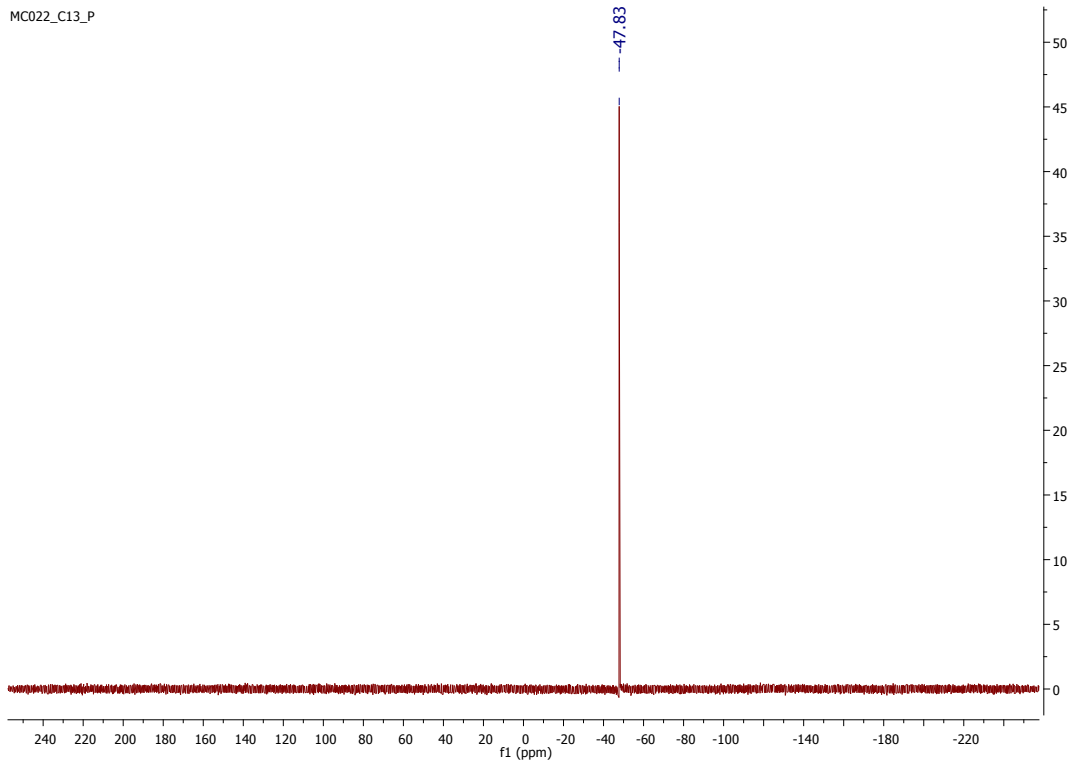


Fig. S17: ^{31}P NMR spectrum of **C13** in *d*-chloroform**.**

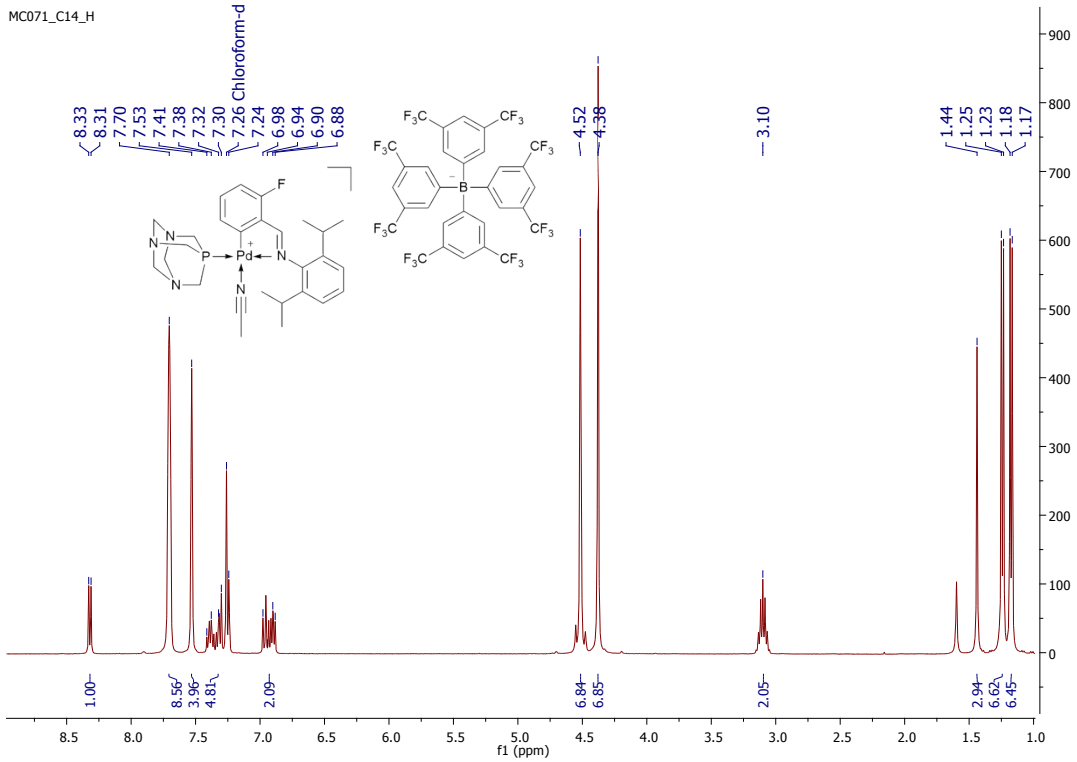


Fig. S18: ^{1}H NMR spectrum of **C14** in *d*-chloroform**.**

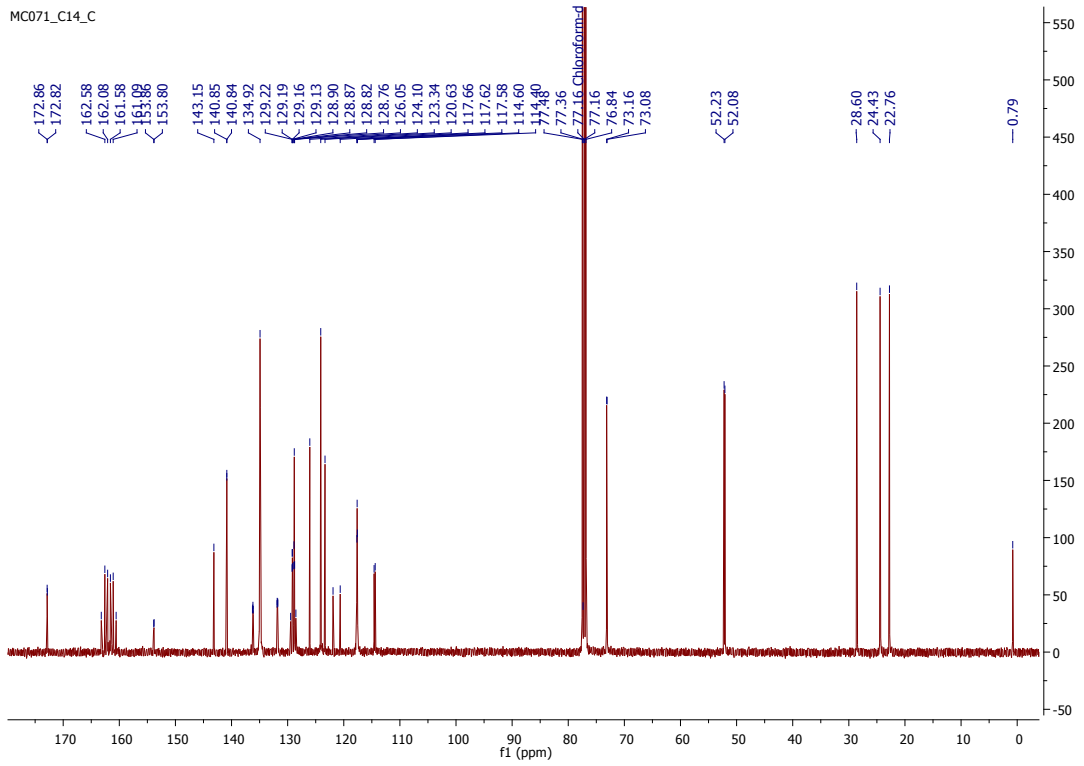


Fig. S19: ^{13}C NMR spectrum of **C14** in *d*-chloroform**.**

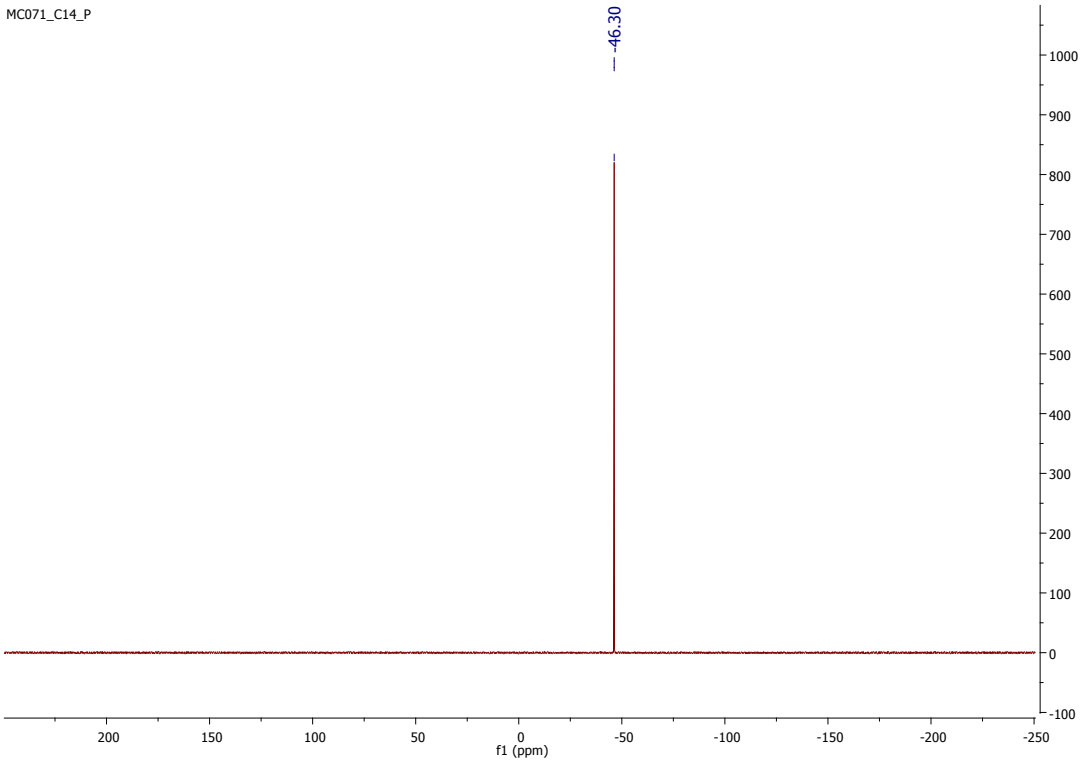


Fig. S20: ^{31}P NMR spectrum of **C14** in *d*-chloroform**.**

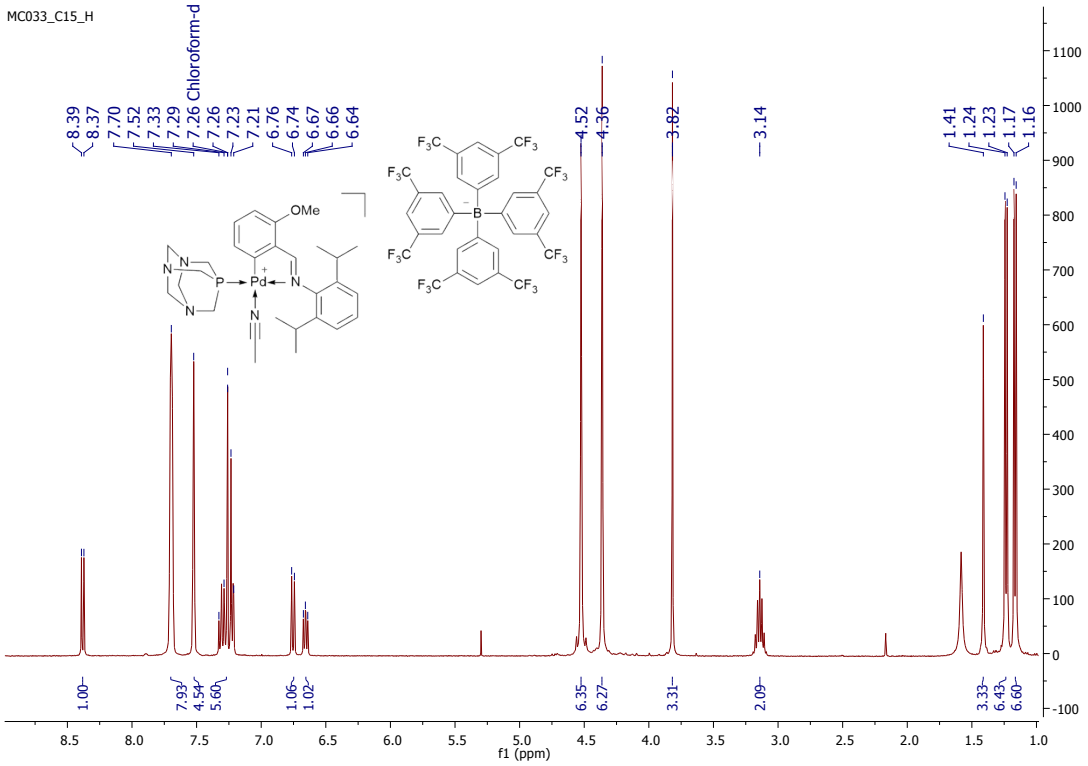


Fig. S21: [1]H NMR spectrum of **C15** in *d*-chloroform**.**

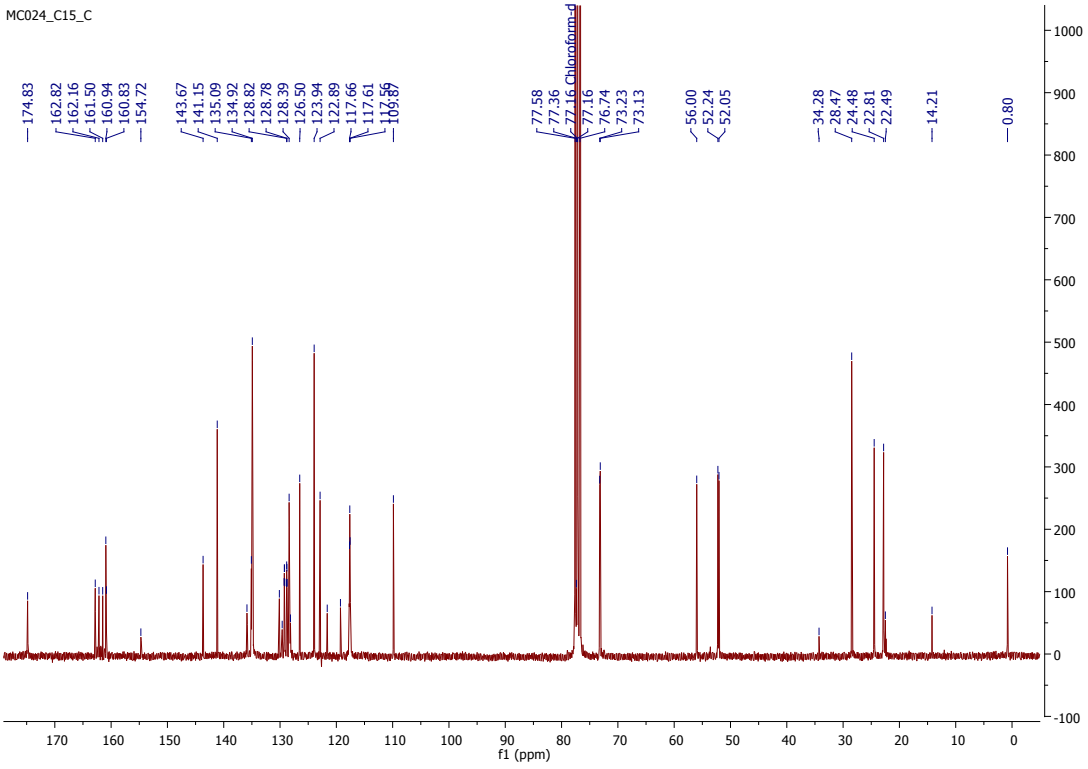


Fig. S22: [13]C NMR spectrum of **C15** in *d*-chloroform**.**

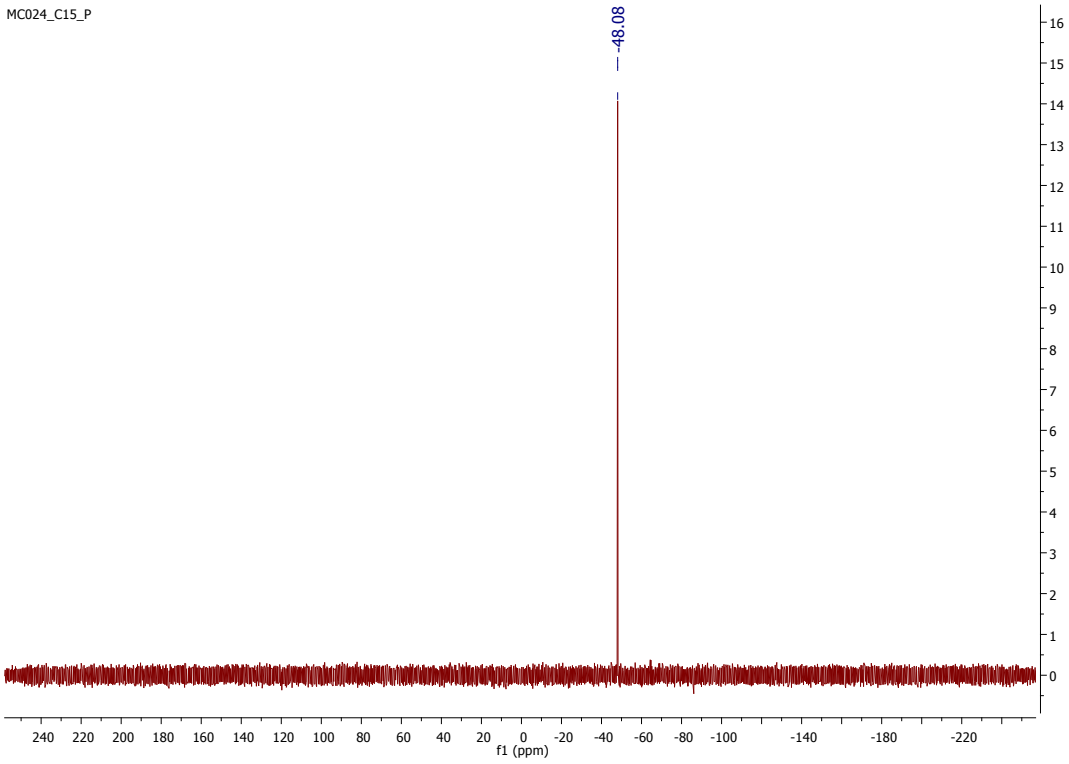


Fig. S23: ^{13}P NMR spectrum of **C15** in *d*-chloroform**.**

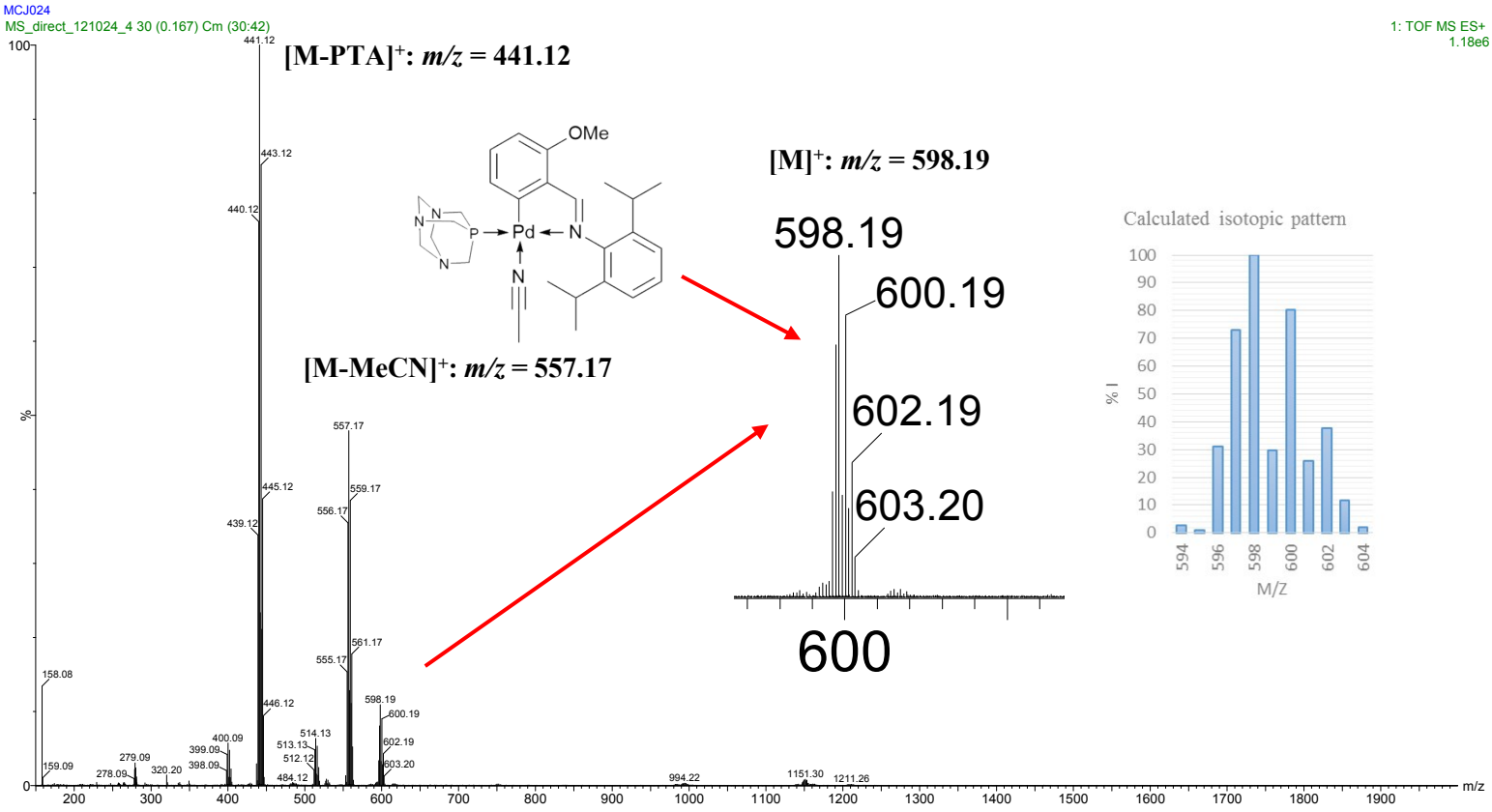


Fig. S24: ESI-MS spectrum of **C15** recorded in the positive. Clusters of peaks centred at 441.1 *m/z*, 557.2 *m/z* and 598.2 *m/z* correspond to the $[M\text{-}PTA]^+$, $[M\text{-}MeCN]^+$ and $[M]^+$ fragments respectively. Inset shows experimental and calculated isotopic pattern for the $[M]^+$ fragment.

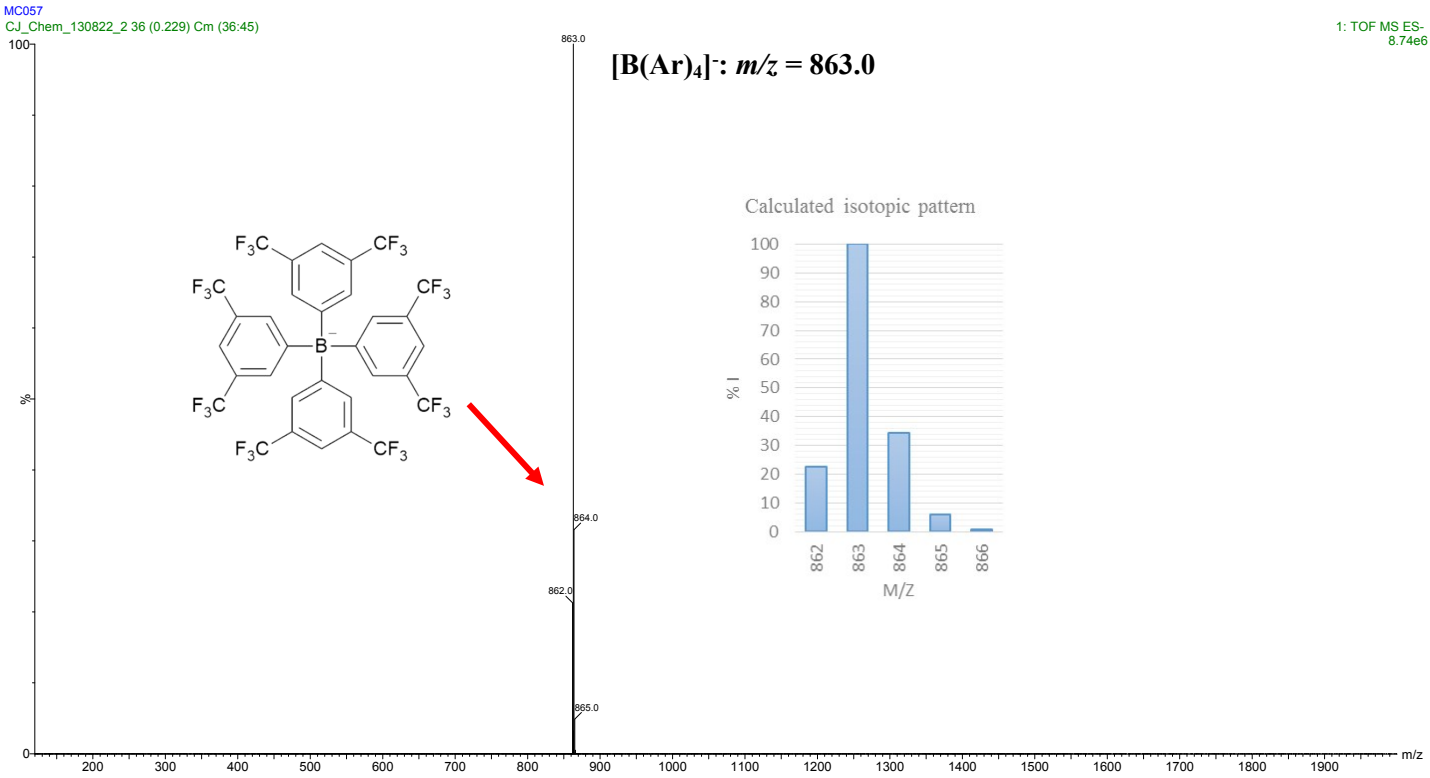


Fig. S25: ESI-MS spectrum of **C15** recorded in the negative mode. Cluster of peaks centred at 863.0 *m/z* correspond to the $[B(Ar)_4]^-$ counterion fragment. Inset shows calculated isotopic pattern for a specific fragmentation.

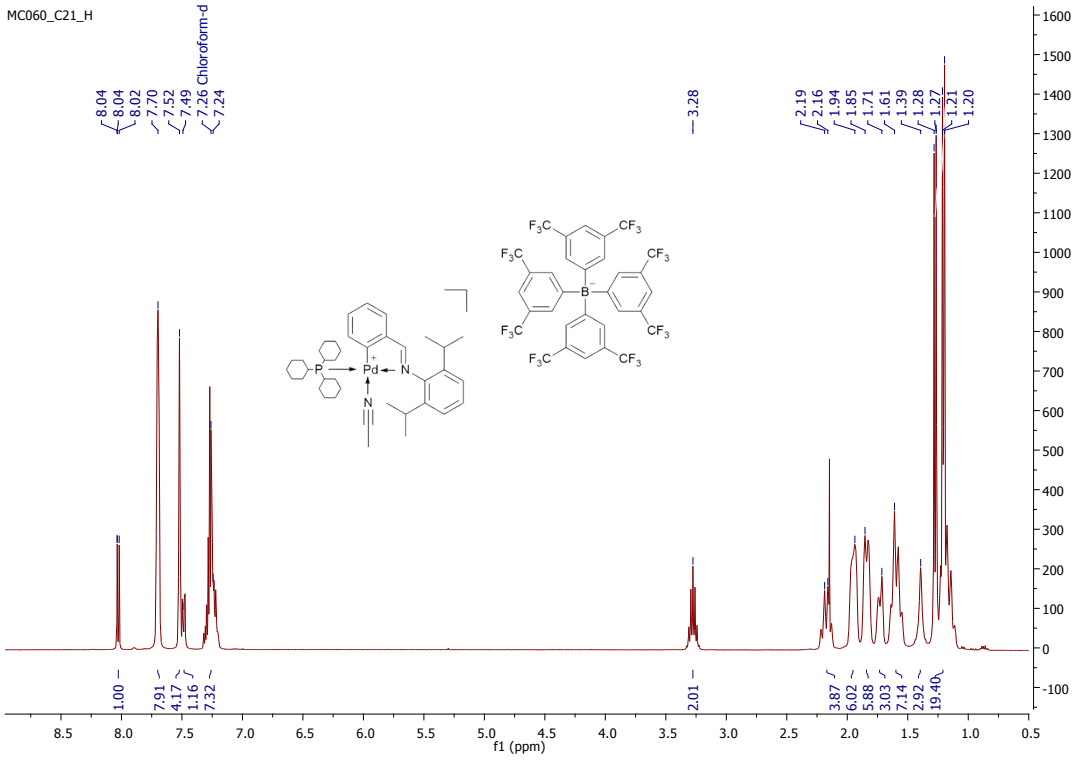


Fig. S26: ^{1}H NMR spectrum of **C21** in *d*-chloroform**.**

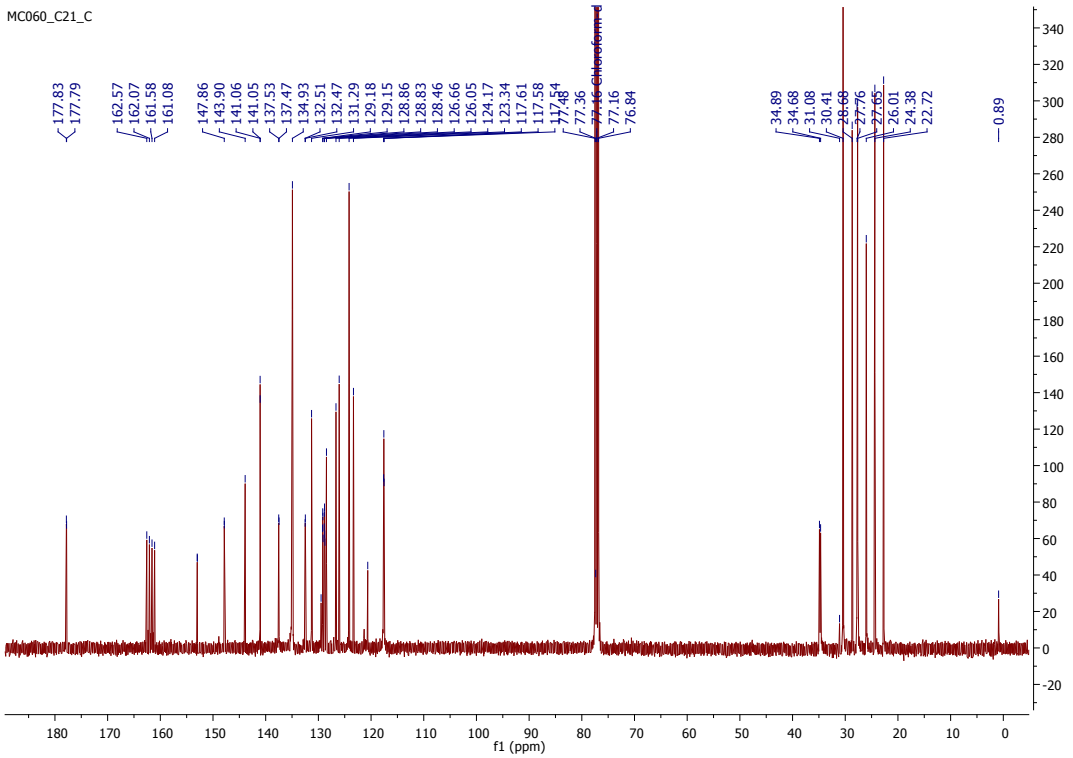


Fig. S27: ^{13}C NMR spectrum of **C21** in *d*-chloroform**.**

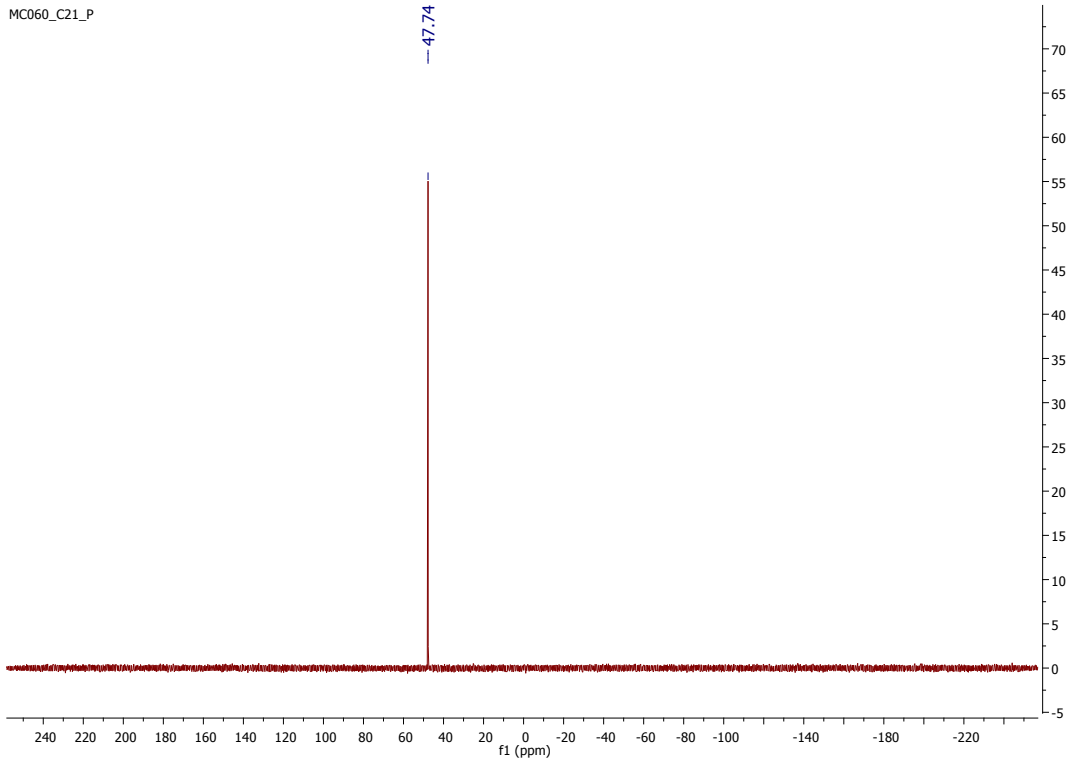


Fig. S28: ^{31}P NMR spectrum of **C21** in *d*-chloroform**.**

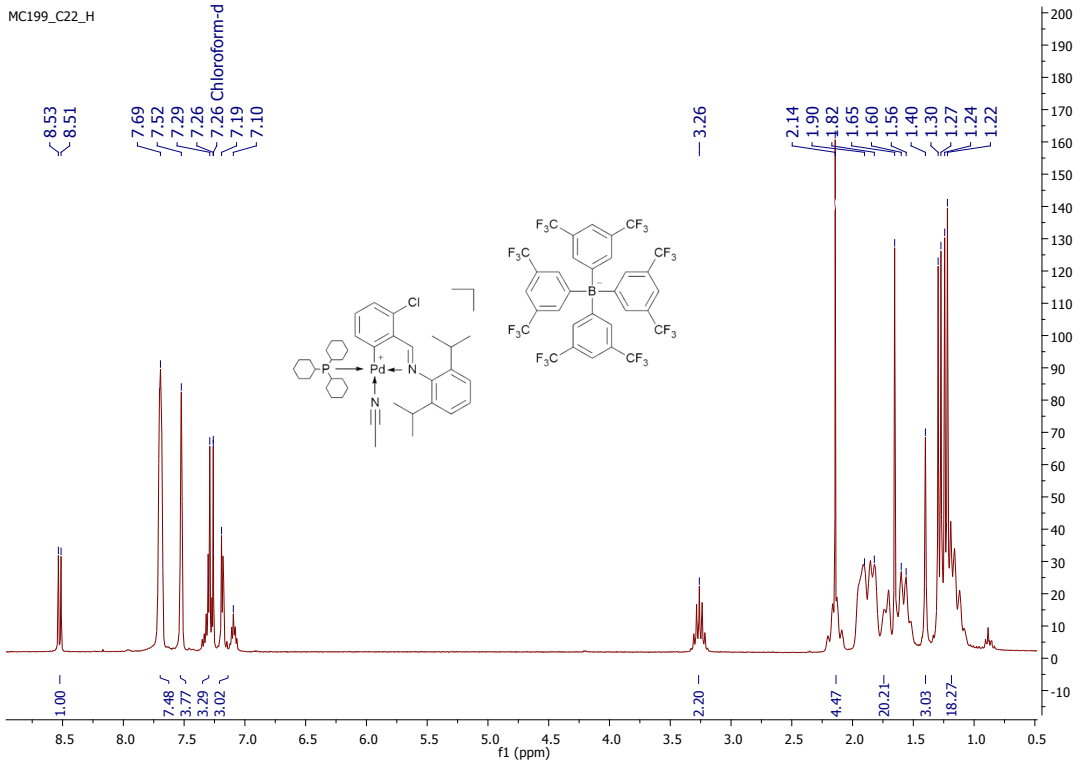


Fig. S29: [1]H NMR spectrum of **C22** in *d*-chloroform**.**

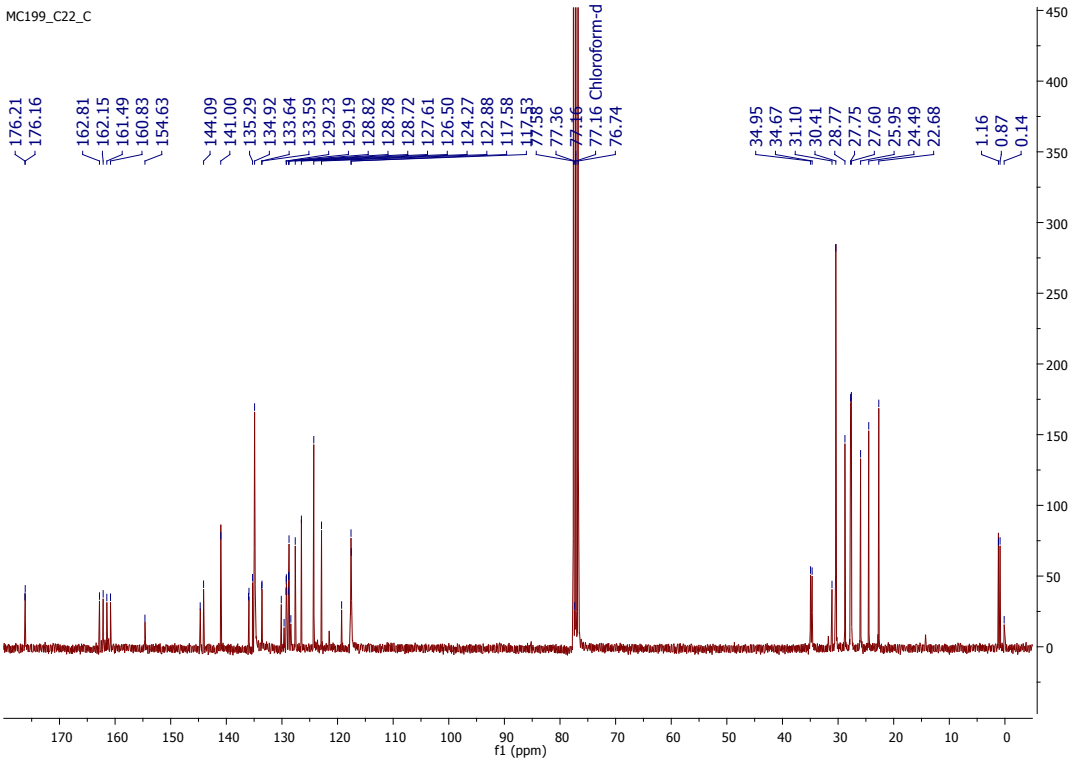


Fig. S30: [13]C NMR spectrum of **C22** in *d*-chloroform**.**

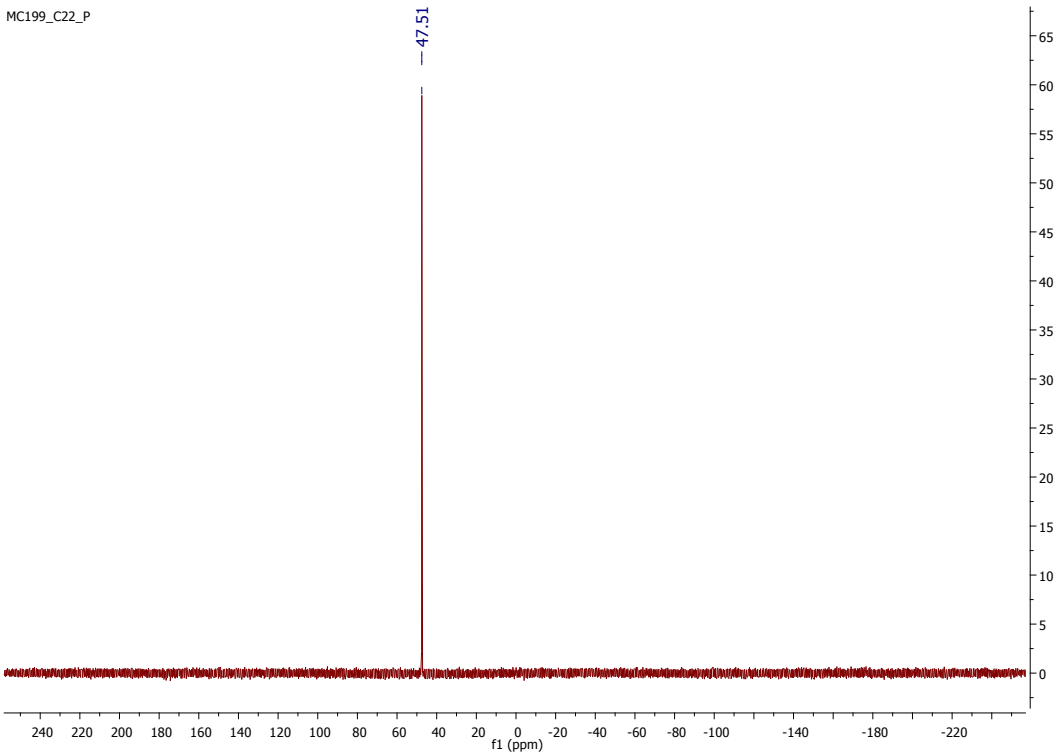


Fig. S31: ^{31}P NMR spectrum of **C22** in *d*-chloroform**.**

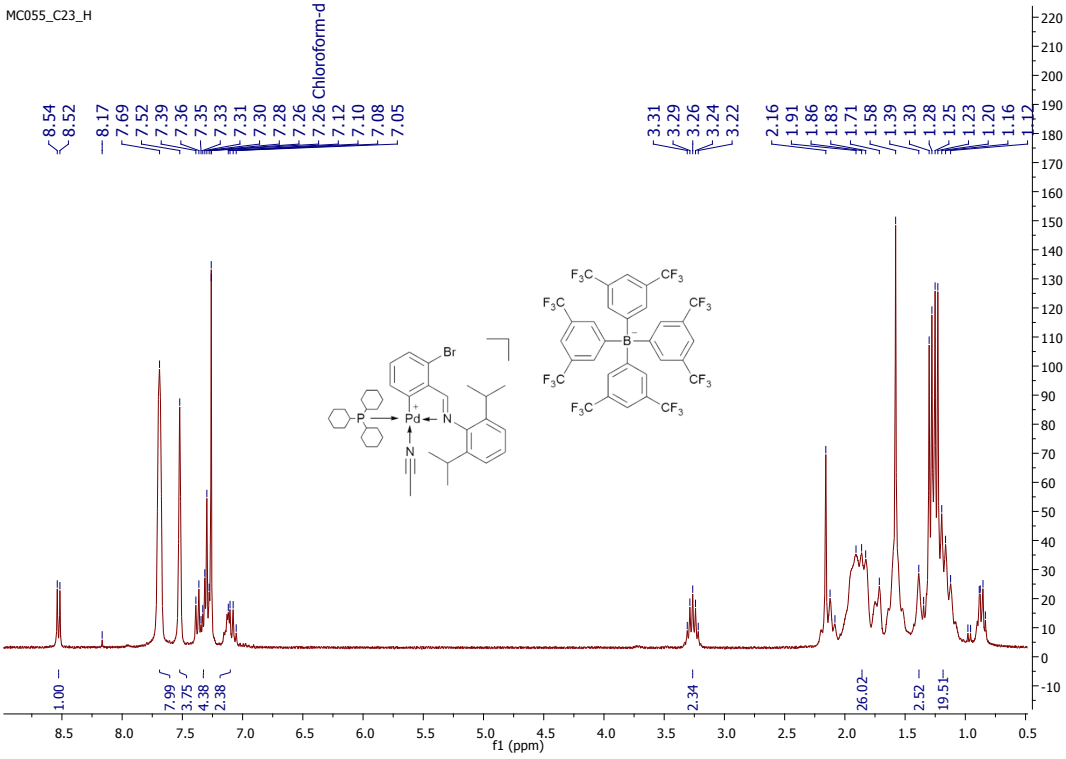


Fig. S32: ^{1}H NMR spectrum of **C23** in *d*-chloroform**.**

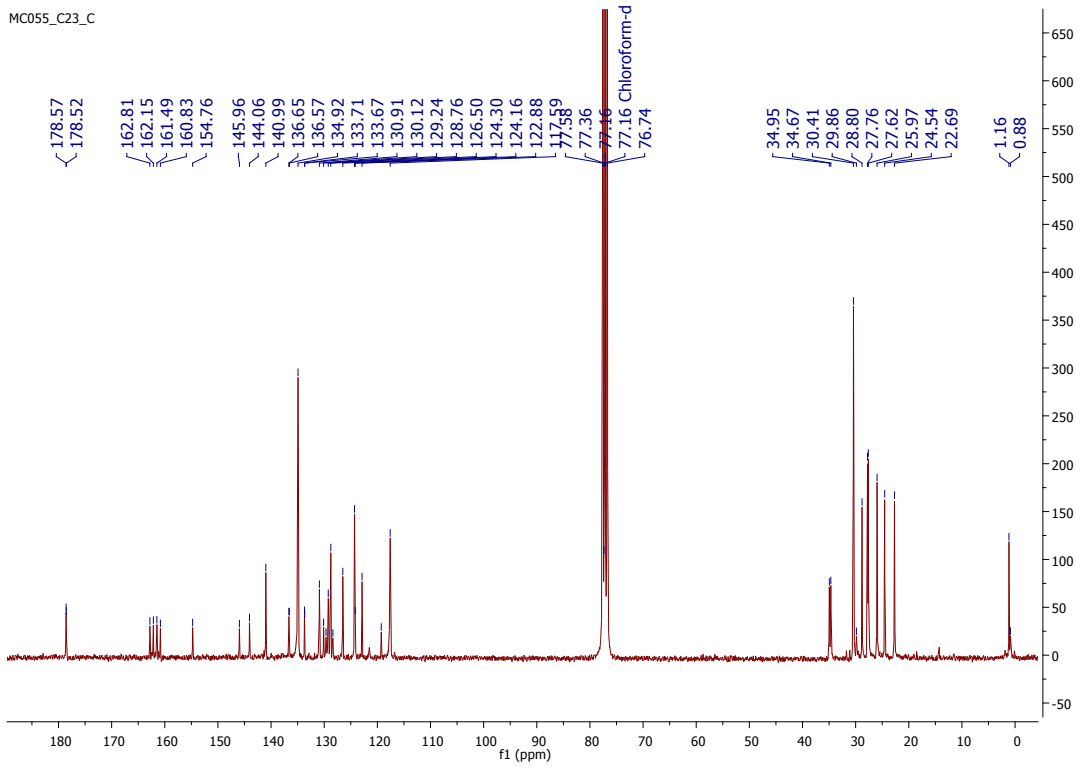


Fig. S33: ^{13}C NMR spectrum of **C23** in *d*-chloroform**.**

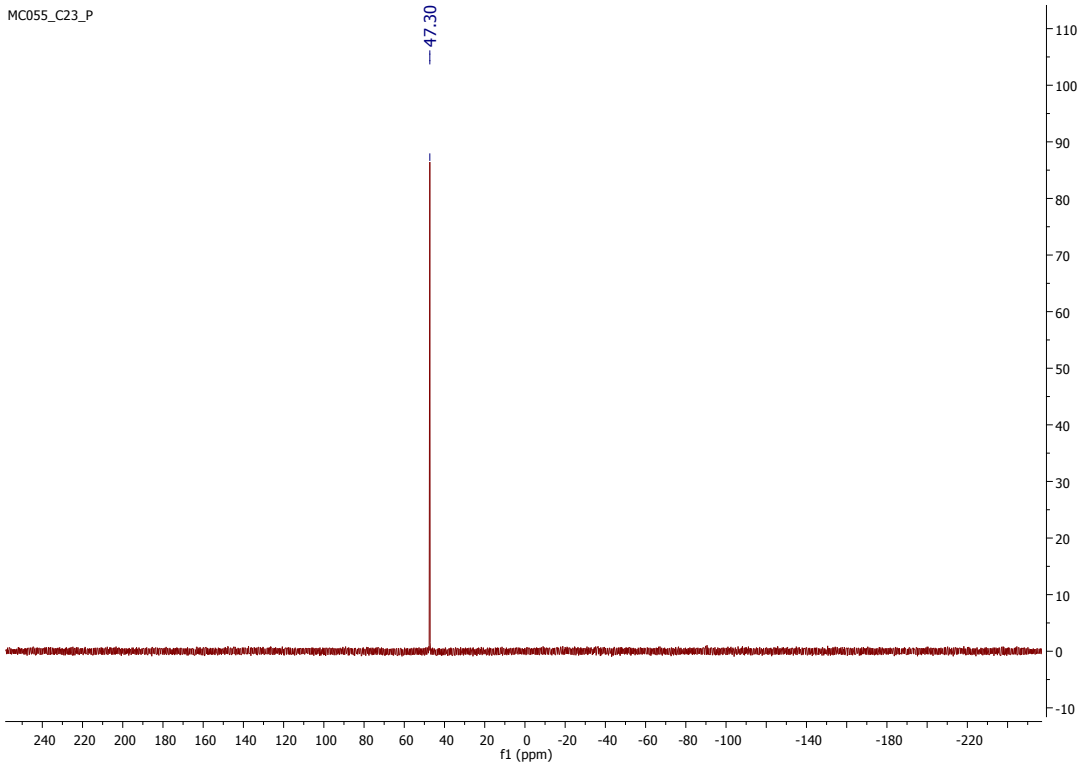


Fig. S34: ^{31}P NMR spectrum of **C23** in *d*-chloroform**.**

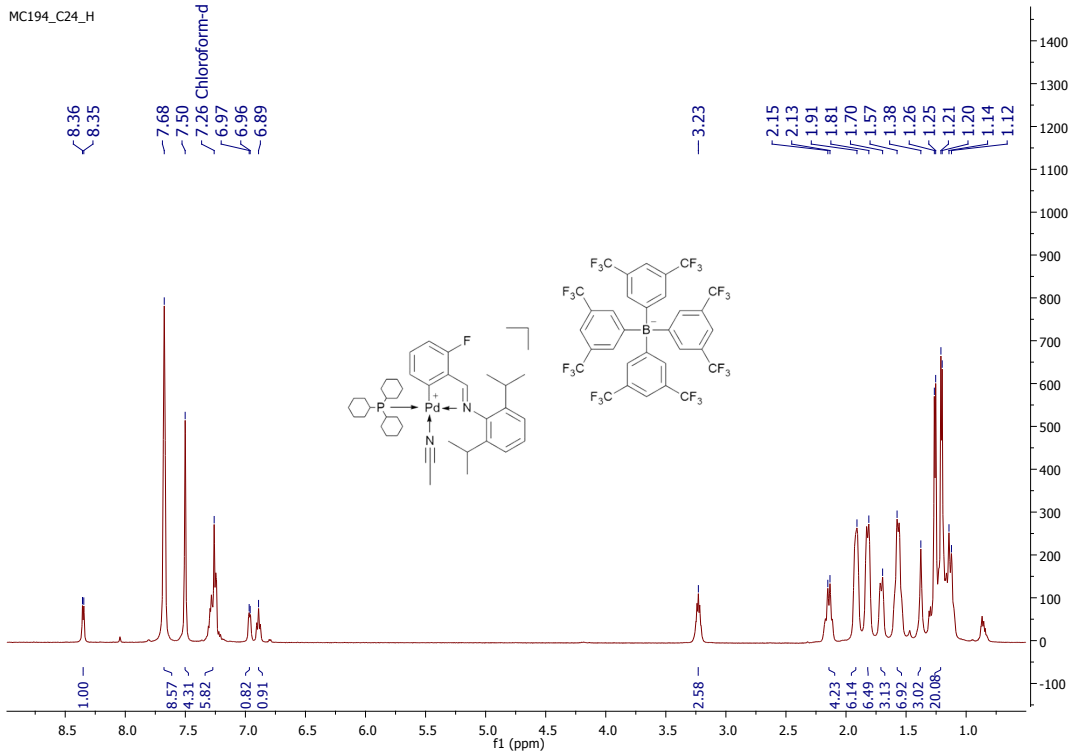


Fig. S35: ^{1}H NMR spectrum of **C24** in *d*-chloroform**.**

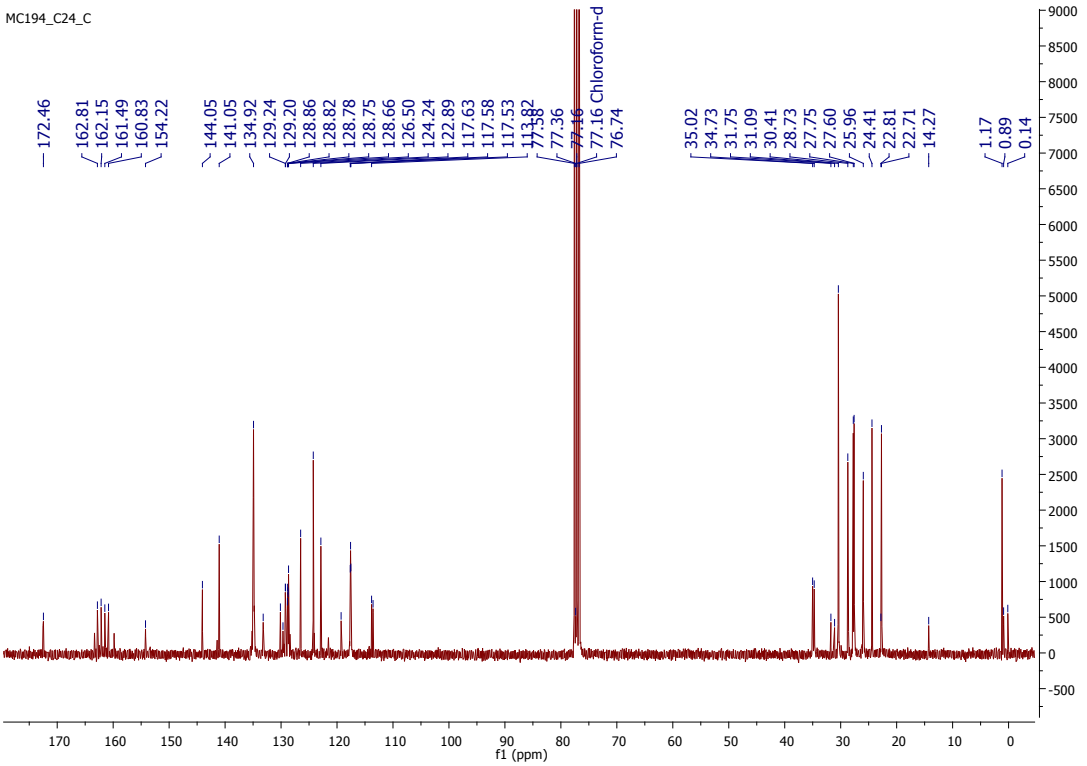


Fig. S36: ^{13}C NMR spectrum of **C24** in *d*-chloroform**.**

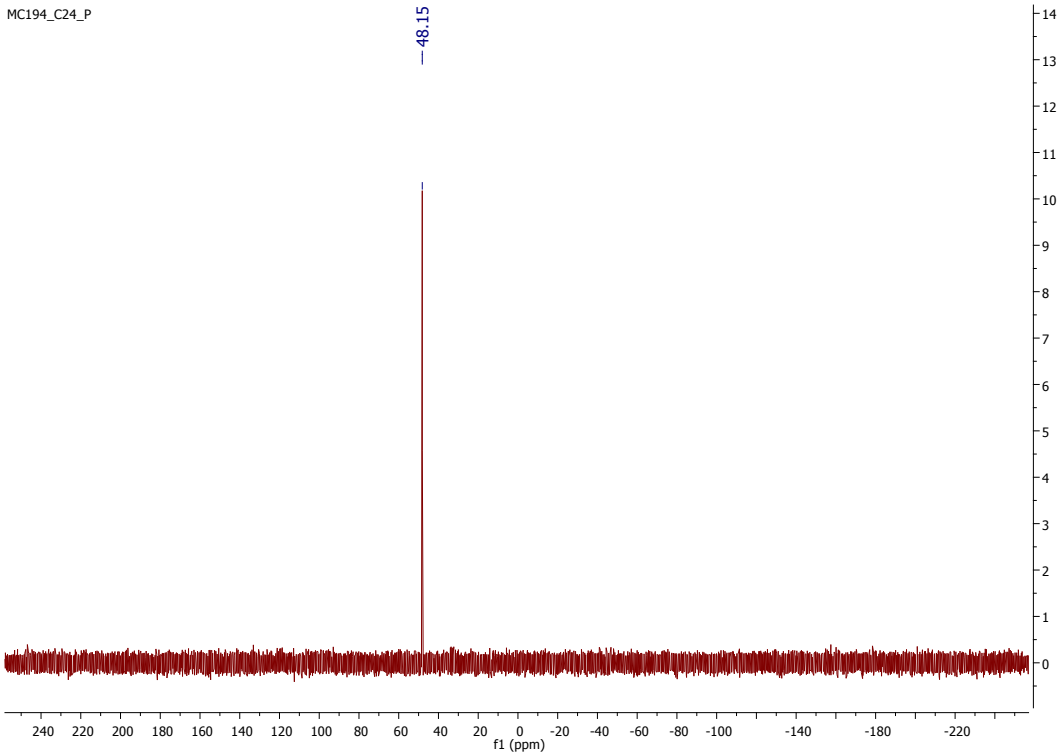


Fig. S37: [1]P NMR spectrum of **C24** in *d*-chloroform**.**

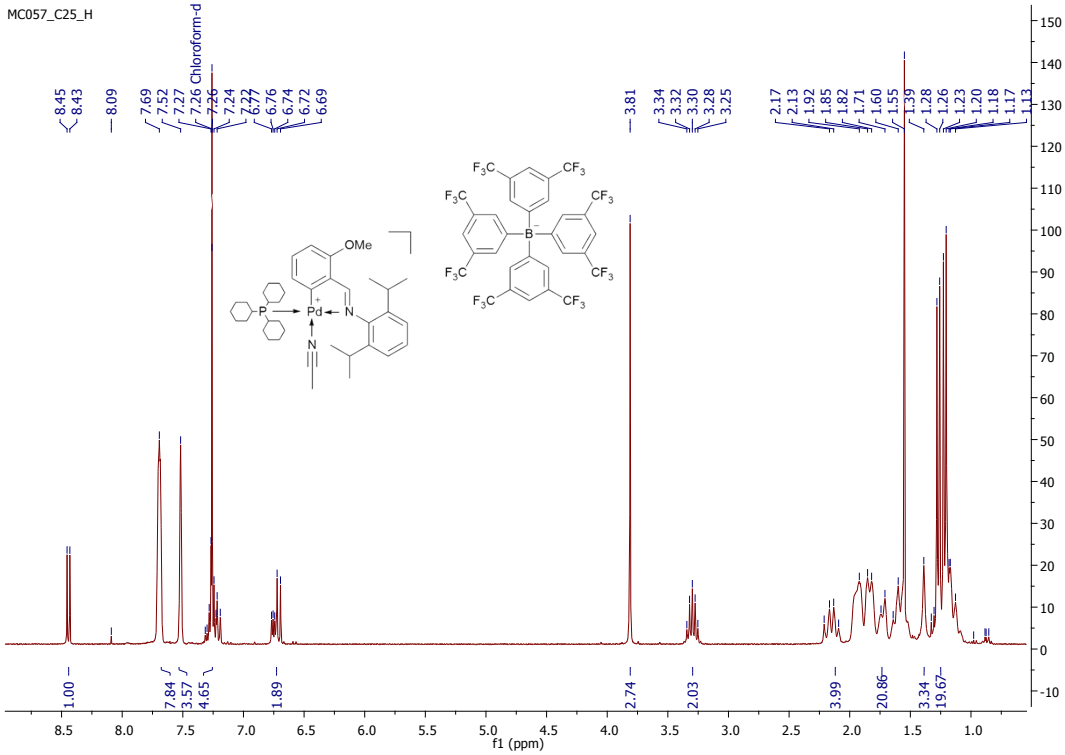


Fig. S38: [1]H NMR spectrum of **C25** in *d*-chloroform**.**

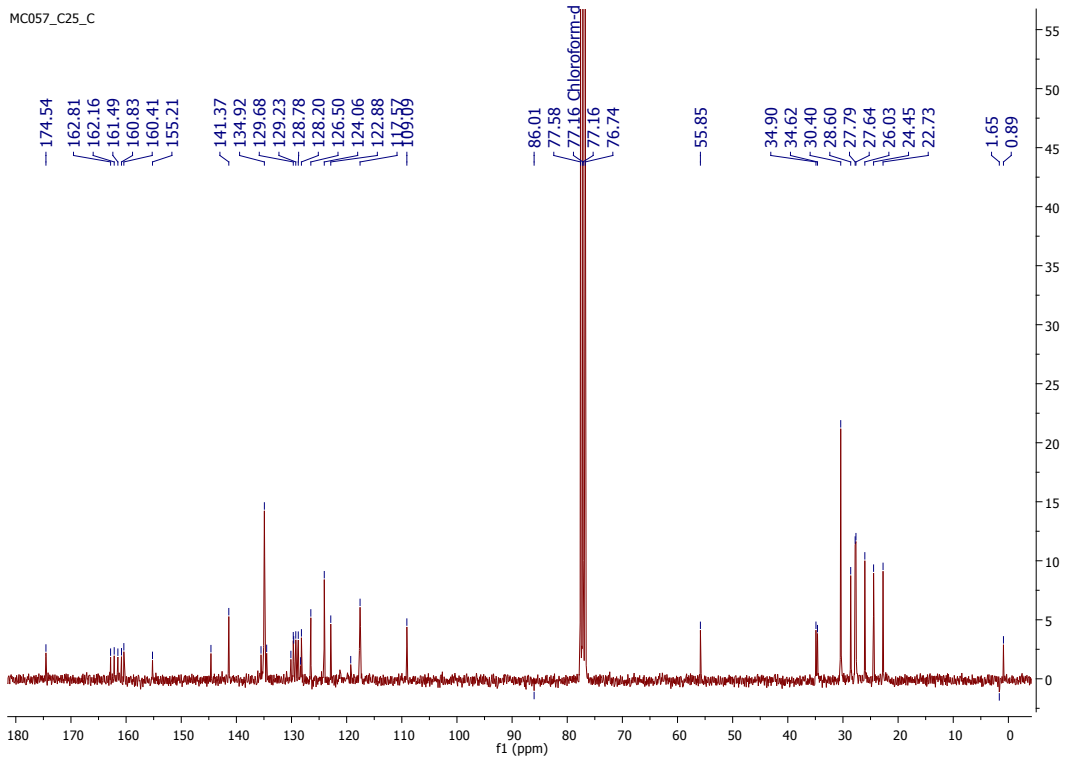


Fig. S39: ^{13}C NMR spectrum of **C25** in *d*-chloroform**.**

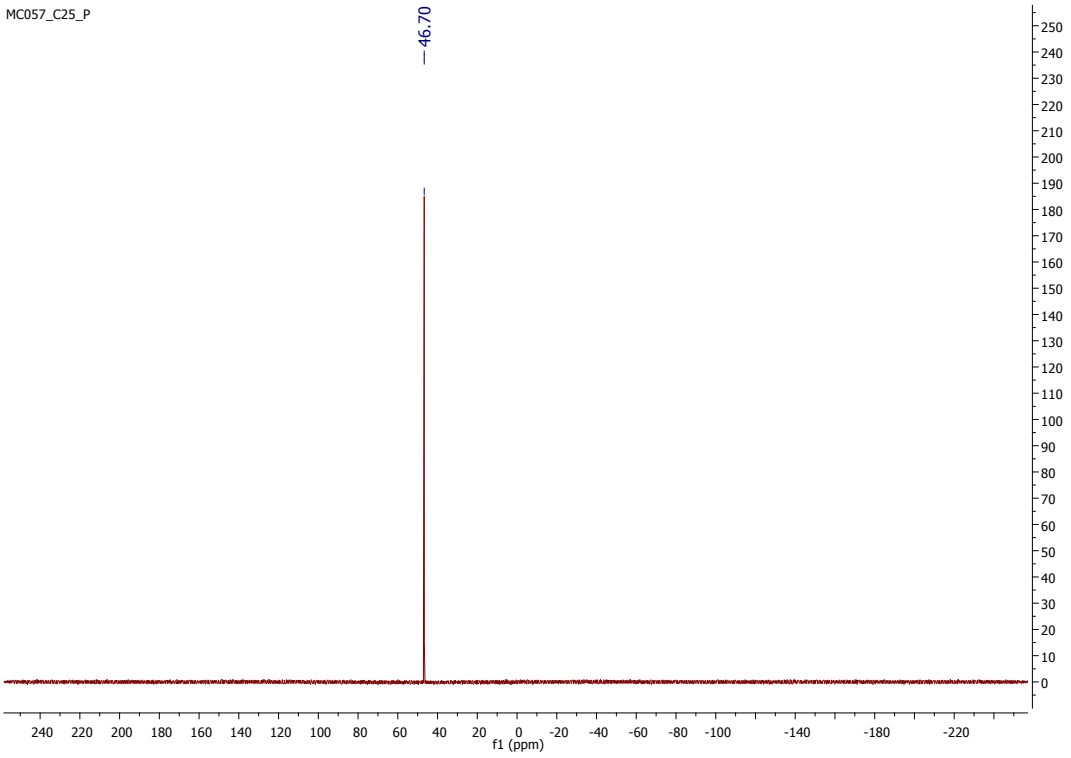


Fig. S40: ^{31}P NMR spectrum of **C25** in *d*-chloroform**.**

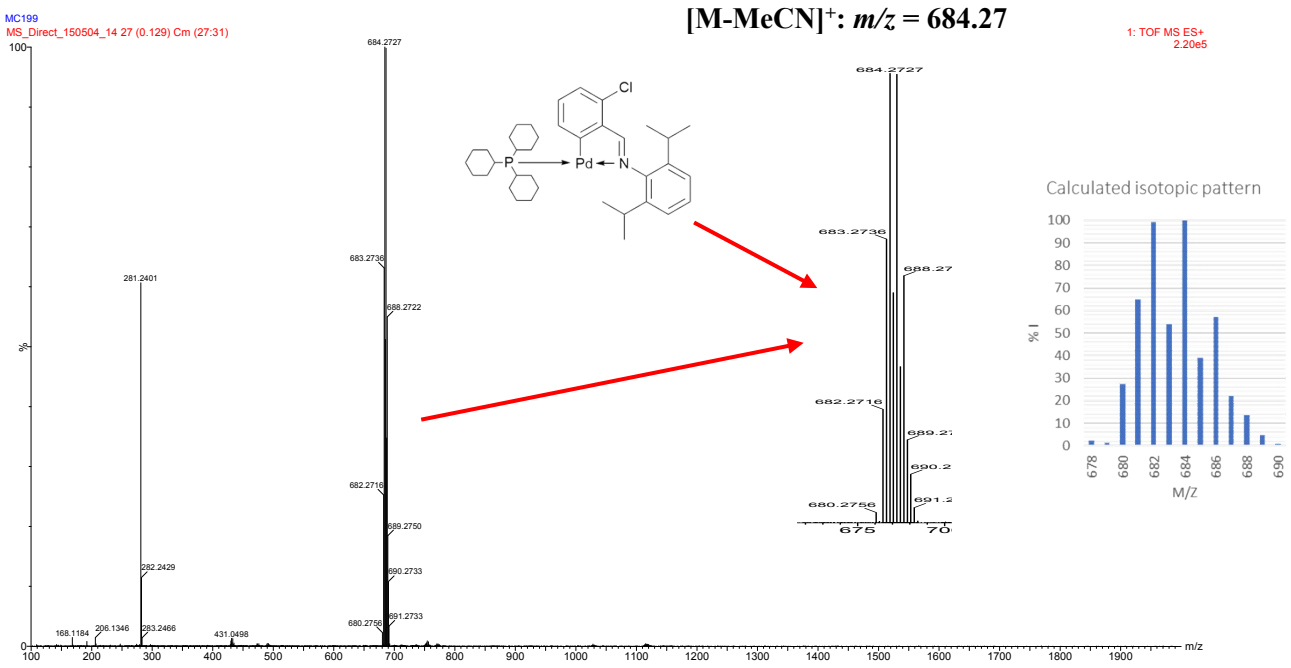


Fig. S41: ESI-MS spectrum of **C22** recorded in the positive. Clusters of peaks centred at 684.27 *m/z* correspond to the [M-MeCN]$^+$ fragment. Inset shows experimental and calculated isotopic pattern for the [M-MeCN]$^+$ fragment.

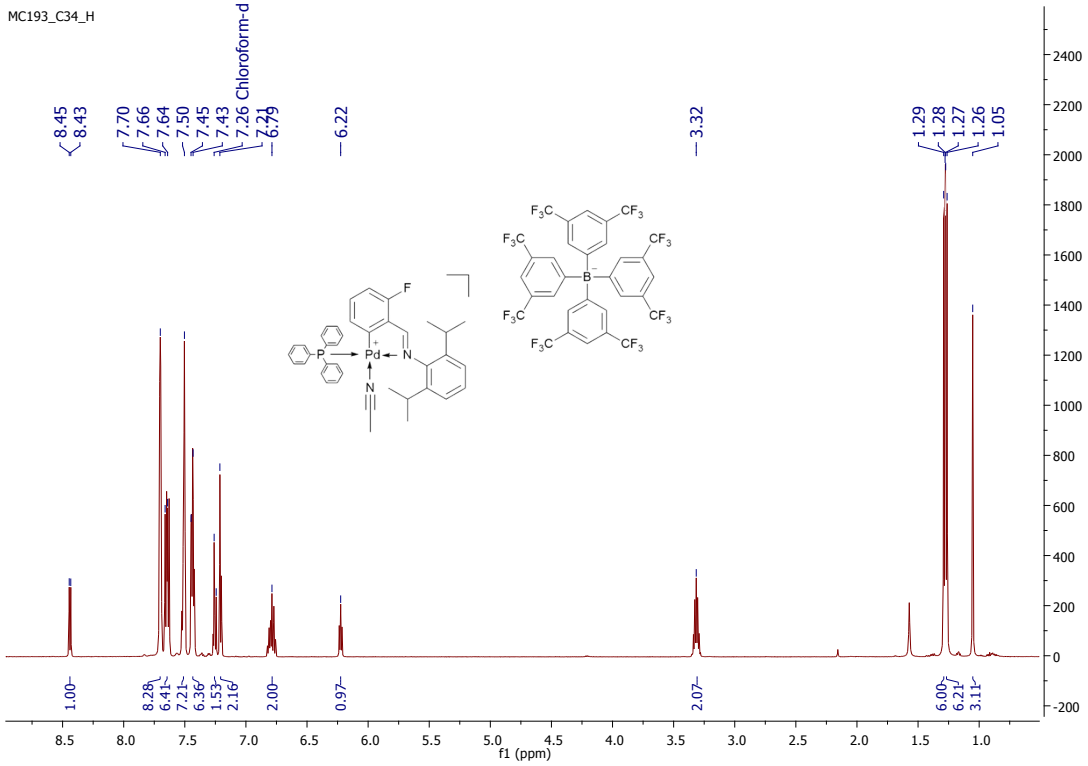


Fig. S42: ^{1}H NMR spectrum of **C34** in *d*-chloroform**.**

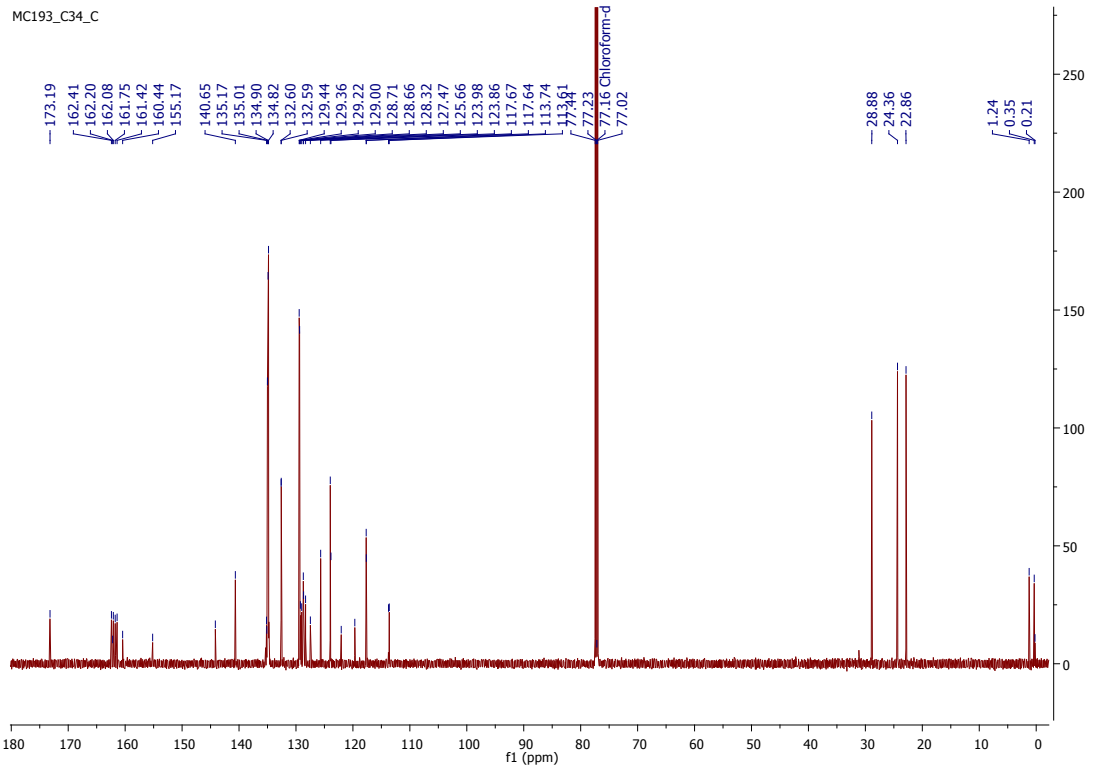


Fig. S43: ^{13}C NMR spectrum of **C34** in *d*-chloroform**.**

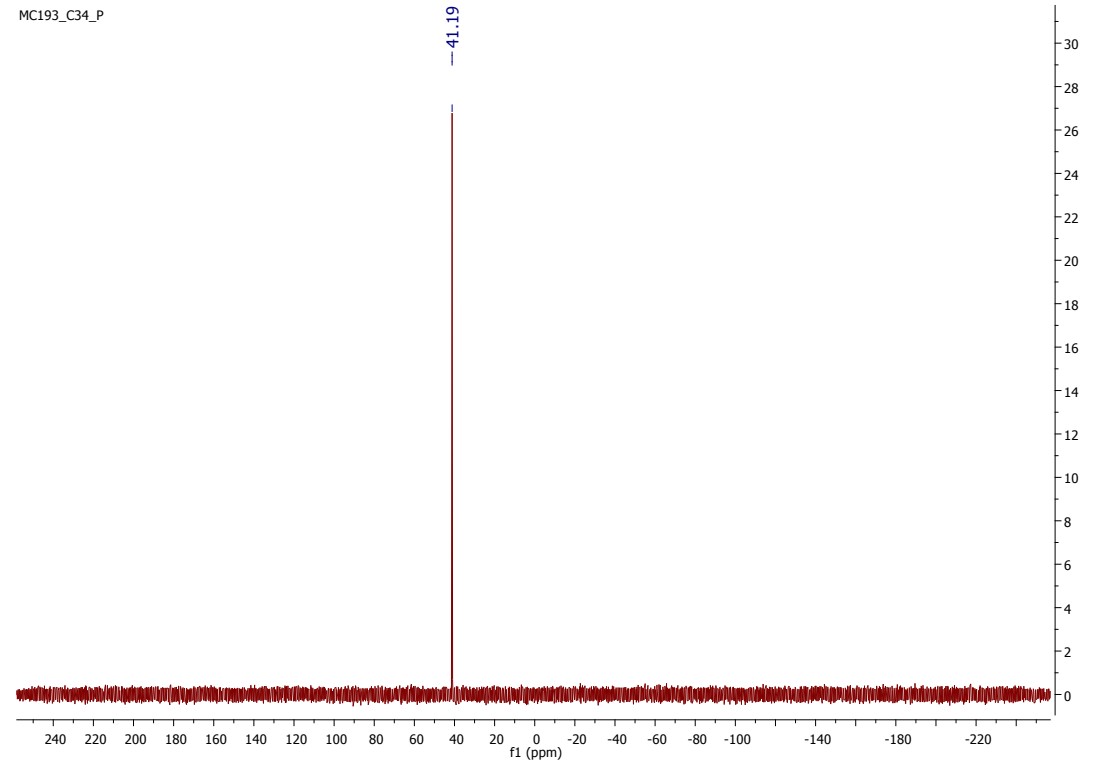


Fig. S44: ^{31}P NMR spectrum of **C34** in *d*-chloroform**.**

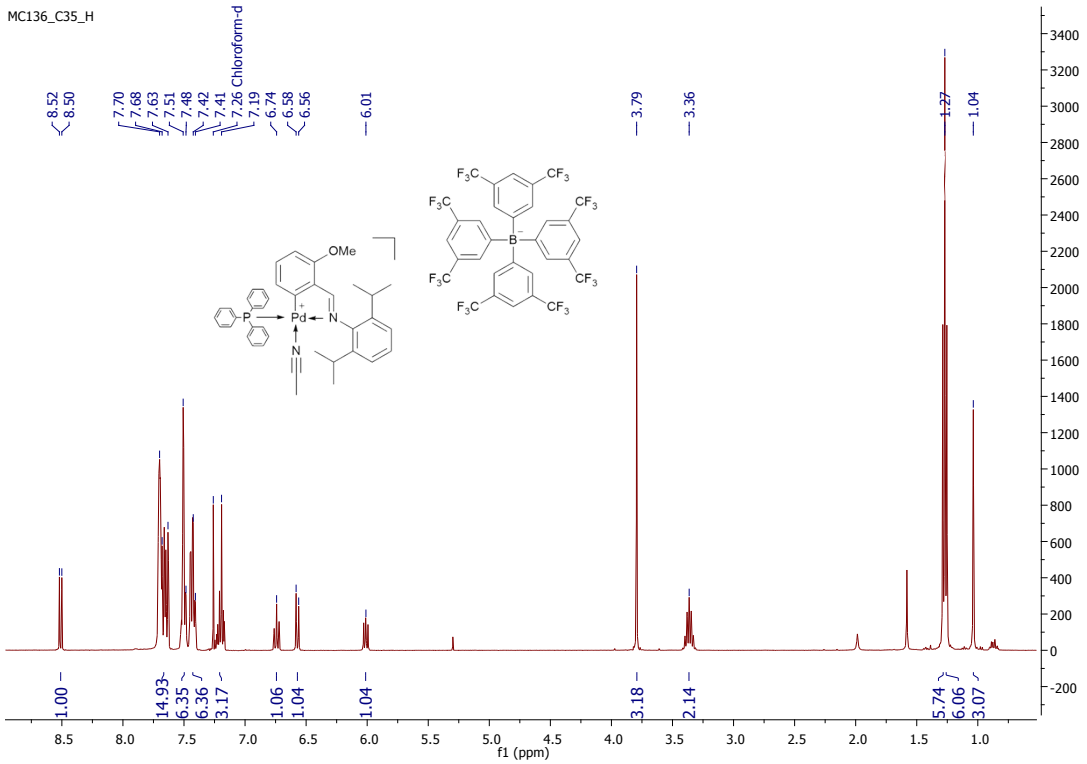


Fig. S45: [1]H NMR spectrum of **C35** in *d*-chloroform**.**

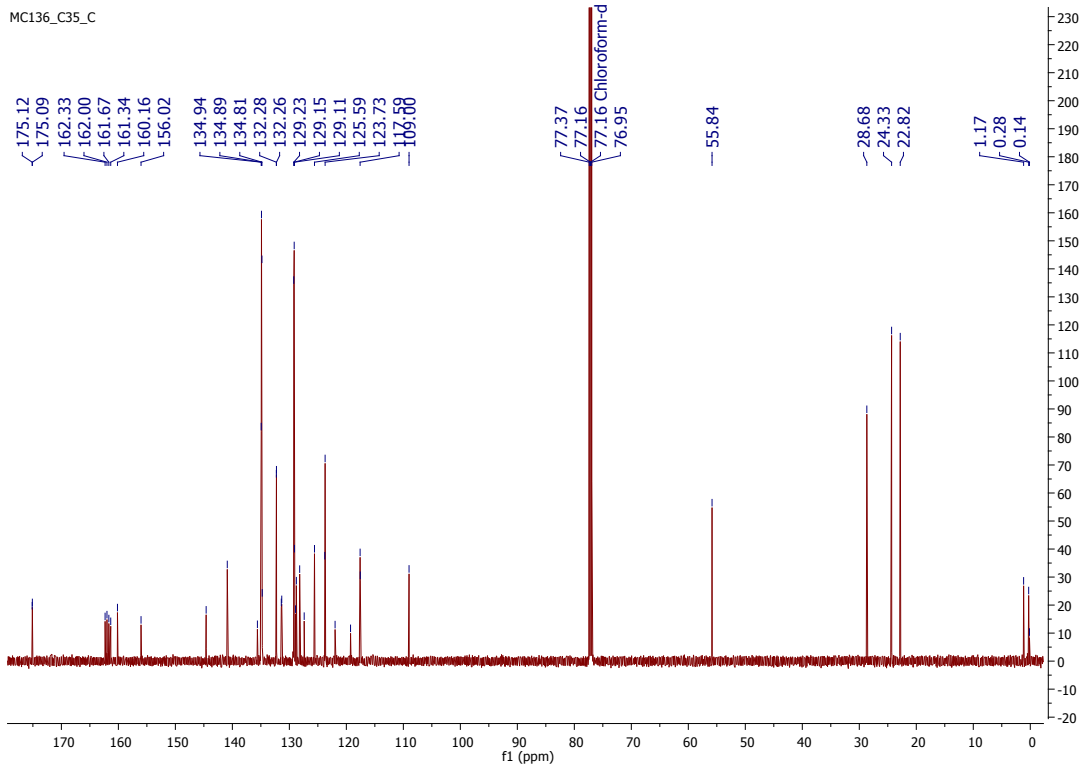


Fig. S46: [13]C NMR spectrum of **C35** in *d*-chloroform**.**

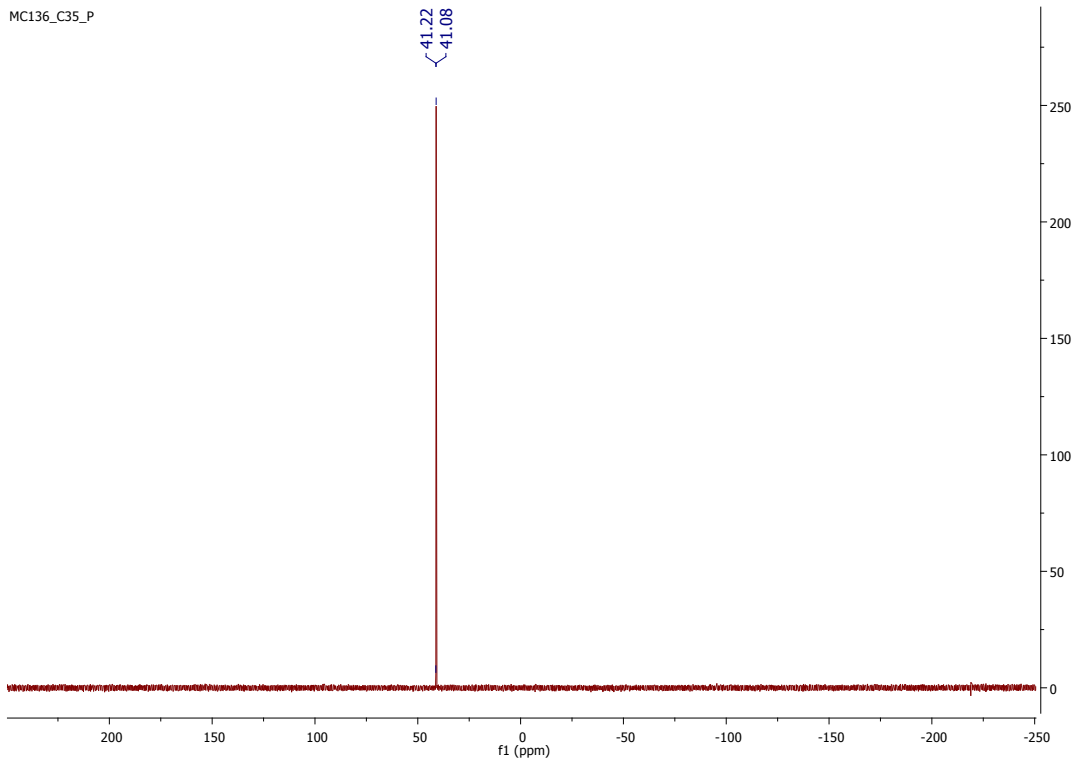


Fig. S47: ^{31}P NMR spectrum of **C35** in *d*-chloroform**.**

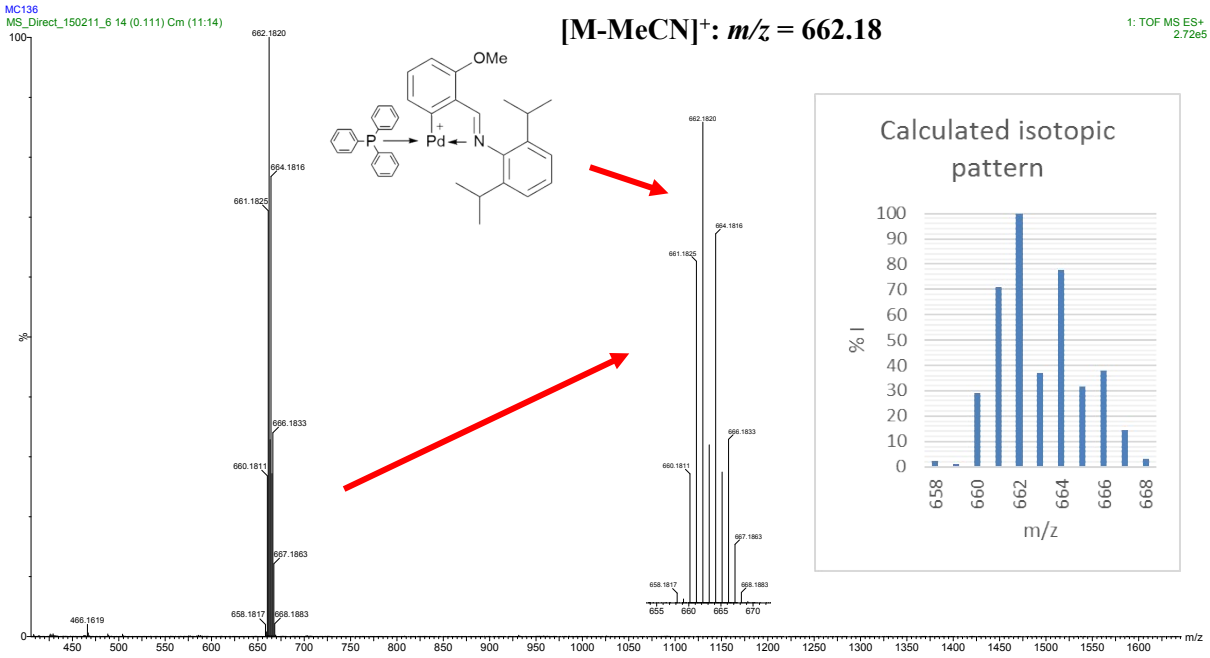


Fig. S48: ESI-MS spectrum of **C35** recorded in the positive. Clusters of peaks centred at 662.18 *m/z* correspond to the [M-MeCN]$^+$ fragment. Inset shows experimental and calculated isotopic pattern for the [M-MeCN]$^+$ fragment.

Crystallography

Single crystals suitable for X-ray diffraction analysis of complexes **C15** and **C25** were isolated by slow diffusion of hexane into a dichloromethane solution at room temperature which resulted in the formation of colourless crystals. Single X-ray diffraction intensity data were collected on a Bruker SMART Apex 2 diffractometer equipped with a CCD area detector[1] using graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). Data collection, reduction and refinement were performed using SMART and SAINT software.[2] Absorption corrections[3] and other systematic errors were accounted for using SADABS.[4] All structures were solved by Direct Methods using SHELXS-2013[5] and refined using SHELXL-2016.[6] The program X-Seed[7] was used as a graphical interface for the SHELX program. All non-hydrogen atoms were refined anisotropically. High resolution molecular diagrams were produced using the program POV-Ray.[8] CCDC 1568394 for complex **C15** and CCDC 1568393 for complex **C25** contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

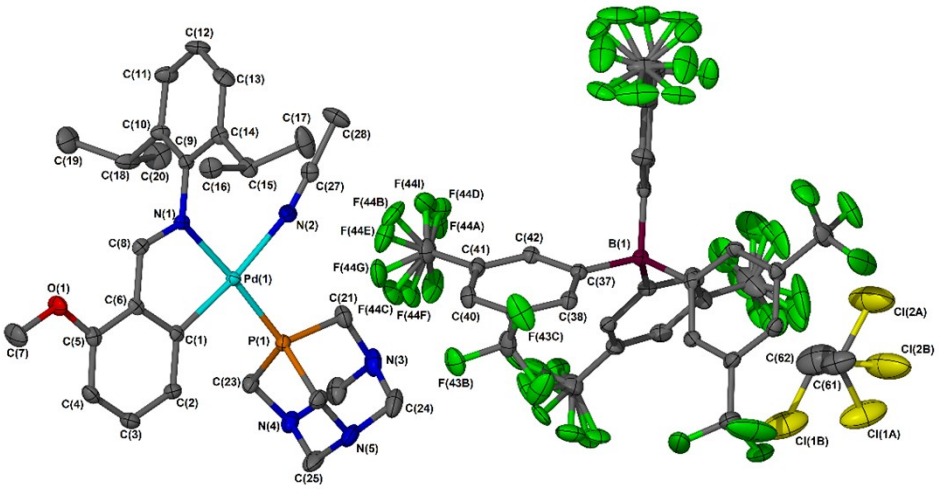


Fig. S49: Molecular structure of solvated complex **C15** with atomic numbering, drawn at 50% probability ellipsoids. All hydrogen atoms are omitted for clarity. Some of the trifluoromethyl substituents are disordered due to fluxional motion the fluoride atoms. Dichloromethane solvent is also disordered over two positions.

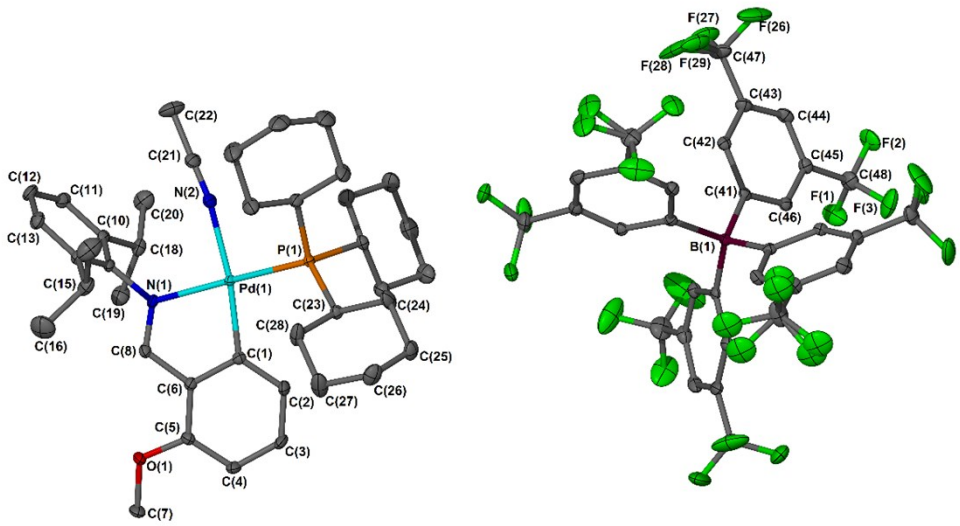


Fig. S50: Molecular structure of complex **C25** with atomic numbering, drawn at 50% probability ellipsoids. All hydrogen atoms are omitted for clarity.

Table S1: Crystallographic data and structure refinement parameters for cationic palladacycles **C15** and **C25**.

Parameter	Complex	
	C15	**C25**
Empirical formula	$C_{61}H_{53}BCl_2F_{24}N_5OPPd$	$C_{72}H_{72}BF_{24}N_2OPPd$
Mr (g/mol)	1547.16	1585.50
Crystal system	Orthorhombic	Triclinic
Space group	P2(1)2(1)2(1)	P-1
***a* (Å)**	13.9241(13)	10.0762(10)
***b* (Å)**	18.1629(17)	18.3919(19)
***c* (Å)**	25.815(2)	19.844(2)
***α* (deg)**	90	101.149(1)
***β* (deg)**	90	92.522(1)
***γ* (deg)**	90	92.592(1)
Crystal dimension (mm)	0.33 × 0.34 × 0.40	0.15 × 0.19 × 0.22
Volume (Å^3)	6528.7(11)	3599.1(6)
Z	4	2
D_{calc} (g/cm^3)	1.574	1.463
F(000)	3112.0	1616
λ (MoK$_\alpha$) (Å)	0.71073	0.71073
Temperature (K)	100	100
2*θ* max (deg)	28.272	28.482
absorption corrections applied (mm^{-1})	0.504	0.387
Goodness-of-fit on F^2	1.019	1.039
Final R_1 indices [I>2σ(I)]	0.0331	0.0383
***wR*$_2$ (all reflections)**	0.0767	0.0941
Flack x parameter	0.084(8)	-

Table S2: Selected bond lengths (Å), bond angles (°) and torsion angle (°) as determined for cationic palladacycles **C15** and **C25**. [a]

	Complex	
	C15	**C25**
Bond lengths		
Pd-C1	2.008(3)	2.001(2)
Pd-N1	2.095(3)	2.0995(17)
Pd-N2	2.090(3)	2.1078(18)
Pd-P1	2.2421(10)	2.3086(7)
N1-C8	1.283(4)	1.283(3)
N1-C9	1.442(4)	1.437(3)
C6-C8	1.432(5)	1.440(3)
O1-C5	1.358(4)	1.358(3)
Bond angles		
N1-Pd-N2	90.03(11)	89.62(7)
N1-Pd-C1	81.76(11)	80.75(7)
C1-Pd-P1	94.58(9)	98.58(6)
P1-Pd-N2	93.72(8)	92.59(5)
Torsion angles		
C8-N1-C9-C10	-88.0(4)	-108.2(2)

[a] Atoms are labelled as per numbering given in **Fig. S49** and **Fig. S50**.

References

1. *Apex2 Data Collection Software,* Bruker AXS, 2010.
2. *SAINT Data Reduction Software*, Version 6.45; Bruker AXS Inc.: Madison, WI, 2003.
3. R. H. Blessing, *Acta Cryst., Sect. A.,* 1995, **51**, 33.
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5. G. M. Sheldrick, Acta Cryst., 2008, **A64**, 112.
6. G. M. Sheldrick, Acta Cryst., 2015, **C71**, 3.
7. L. J. Barbour, J. Supramol. Chem., 2001, **1**, 189.
8. POV-Ray, Version 3.6, Williamstown, Australia, Persistence of vision ray.