

## Supporting Information

### **Mono-*N*-protected Amino Acid Palladium Complexes: Experimental Validation of the Ligand Cooperation Model in C-H Activation**

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## 1. Experimental details

### 1.1- General considerations.

$^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and  $^{19}\text{F}$  NMR spectra were recorded on Bruker AV-400 or Agilent MR-500 spectrometers at the Laboratorio de Técnicas Instrumentales (LTI) of the UVa. Chemical shifts (in  $\delta$  units, ppm) were referenced to  $\text{SiMe}_4$  ( $^1\text{H}$  and  $^{13}\text{C}$ ) and  $\text{CFCl}_3$  ( $^{19}\text{F}$ ). The spectral data were recorded at 293 K unless otherwise noted. For the NMR spectra registered in non-deuterated solvents, a coaxial tube containing  $\text{DMSO-}d_6$  was used to maintain the lock to the  $^2\text{H}$  signal. Homonuclear ( $^1\text{H-COSY}$ ) and heteronuclear ( $^1\text{H-}^{19}\text{F}$  HOESY,  $^1\text{H-}^{13}\text{C}$  HSQC,  $^1\text{H-}^{13}\text{C}$  HMBC,  $^{19}\text{F-}^{13}\text{C}$  HSQC) experiments were used to help with the signal assignments. HRMS analyses (ESI-TOF) were carried out on a Bruker Maxis Impact mass spectrometer at the Laboratorio de Técnicas Instrumentales (LTI) of the UVa. Elemental analyses were carried out in a Carlo Erba 1108 microanalyser at the Burgos University, Spain. Infrared spectra were recorded in the range 4000-200  $\text{cm}^{-1}$  on a Perkin-Elmer FT-IR Spectrum Frontier with an ATR diamond accessory. Solvents were dried using a solvent purification system SPS PS-MD-5 (diethyl ether and THF) or distilled from appropriate drying agents under nitrogen prior to use and stored over 3 Å or 4 Å molecular sieves (acetone, acetonitrile, pyridine, toluene, *N,N*-dimethylacetamide and ethyl benzoate). Tetrabutylammonium bromide, silver carbonate, *N*-acetylglycine, *N*-methylglycine (sarcosine) and *N*-acetylvaline are commercially available and were purchased from Sigma-Aldrich, Alfa Aesar or Fluorochem. All commercial reagents and solvents were used as received unless otherwise noted.  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$ ,<sup>1</sup>  $(\text{NBu}_4)_2[\text{Pd}_2(\mu\text{-Br})_2(\text{C}_6\text{F}_5)_4]$ ,<sup>2</sup>  $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{py}_2]$  (**5**),<sup>3</sup> and  $[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})_2]$  (**6**)<sup>4</sup> were prepared according to the procedures in the literature.

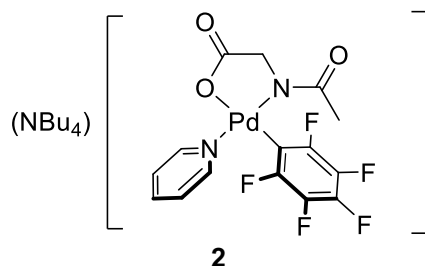
### 1.2- Synthesis of Palladium complexes

$(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (**1**). The synthesis of this complex has been reported before but the NMR characterization was not included.<sup>1</sup>  $^1\text{H}$  NMR (499.73 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 9.14 (m, 2H,  $\text{H}_{\text{ortho}}^{\text{py}}$ ), 7.87 (m, 1H,  $\text{H}_{\text{para}}^{\text{py}}$ ), 7.40 (m, 2H,  $\text{H}_{\text{meta}}^{\text{py}}$ ), 3.43 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 1.82 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 1.44 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 0.97 (t,  $J = 7.22$  Hz, 12 H,  $\text{CH}_3^{\text{Bu}}$ ).  $^{19}\text{F}$  NMR (470.17 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): -116.95 (m, 2F,  $\text{F}_{\text{ortho}}$ ), -167.51 (t,  $J = 19.5$  Hz, 1F,  $\text{F}_{\text{para}}$ ), -169.13 (m, 2F,  $\text{F}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 152.7 ( $\text{C}_{\text{ortho}}^{\text{py}}$ ), 147.3 (m,  $^1\text{J}_{\text{C-F}} = 245$  Hz,  $\text{C}_{\text{ortho}}^{\text{Pfl}}$ ), 137.3 ( $\text{C}_{\text{para}}^{\text{py}}$ ), 135.7 (m,  $^1\text{J}_{\text{C-F}} = 247$  Hz,  $\text{C}_{\text{para}}^{\text{Pfl}}$ ), 134.6 (m,  $^1\text{J}_{\text{C-F}} = 252$  Hz,  $\text{C}_{\text{meta}}^{\text{Pfl}}$ ), 123.9 ( $\text{C}_{\text{meta}}^{\text{py}}$ ), 58.5 ( $\text{CH}_2^{\text{Bu}}$ ), 23.5 ( $\text{CH}_2^{\text{Bu}}$ ), 19.5 ( $\text{CH}_2^{\text{Bu}}$ ), 13.0 ( $\text{CH}_3^{\text{Bu}}$ ). \* Anal. Calcd. for  $\text{C}_{27}\text{H}_{41}\text{F}_5\text{Br}_2\text{N}_2\text{Pd}$ : C, 42.96%; H, 5.47%; N, 3.71 %.; Found: C, 42.98 %; H, 5.56 %; N, 3.6 %.

\*The chemical shifts of the  $\text{C}_6\text{F}_5$  carbon resonances were assigned with the help of a  $^{19}\text{F-}^{13}\text{C}$  HSQC experiment.

Crystals suitable for X-Ray diffraction analysis were obtained by slow diffusion of *n*-heptane in a solution of the compound in acetone (Figure S13).

**(NBu<sub>4</sub>)[Pd(κ<sup>2</sup>-*N,O*-AcN-Gly-O)(C<sub>6</sub>F<sub>5</sub>)py] (2).** *N*-acetylglycine (AcNH-Gly-OH, 0.027 g, 0.23 mmol), silver carbonate (0.127 g, 0.46 mmol) and dry THF (5 mL) were introduced in a Schlenk flask in a nitrogen atmosphere. After stirring for one hour (NBu<sub>4</sub>)[PdBr<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)py] (0.174 g, 0.23 mmol) was added. The mixture was stirred at room temperature for 4 hours. Then, the reaction mixture was filtered through kiesselghur to remove the silver salts. The solvent was evaporated to dryness and the residue was triturated and washed with dry diethylether (3 x 5 mL) and vacuum dried. The complex was isolated as a pale-yellow solid (98 mg, 60 % yield).



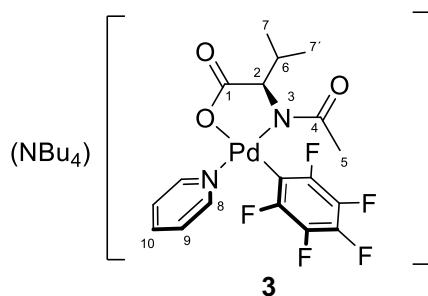
<sup>1</sup>H NMR (499.73 MHz, δ, (CD<sub>3</sub>)<sub>2</sub>CO): 8.48 (m, 2H, H<sub>ortho</sub><sup>py</sup>), 7.93 (m, 1H, H<sub>para</sub><sup>py</sup>), 7.42 (m, 2H, H<sub>meta</sub><sup>py</sup>), 4.18 (s, 2H, CH<sub>2</sub><sup>aa</sup>), 3.44 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.81 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.44 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.26 (s, 3H, CH<sub>3</sub><sup>aa</sup>), 0.98 (t, J = 7.4 Hz, 12 H, CH<sub>3</sub><sup>Bu</sup>). <sup>19</sup>F NMR (470.17 MHz, δ, (CD<sub>3</sub>)<sub>2</sub>CO): -117.62 (m, 2F, F<sub>ortho</sub>), -164.50 (t, J = 19.5 Hz, 1F, F<sub>para</sub>), -165.86 (m, 2F, F<sub>meta</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100.56 MHz, δ, (CD<sub>3</sub>)<sub>2</sub>CO): 181.0 (OCO), 173.2 (NCO), 152.1 (C<sub>ortho</sub><sup>py</sup>), 147.9 (C<sub>ortho</sub><sup>Pf</sup>), 138.3 (C<sub>para</sub><sup>py</sup>), 136.7 (C<sub>para</sub><sup>Pf</sup>), 135.4 (C<sub>meta</sub><sup>Pf</sup>), 125.1 (C<sub>meta</sub><sup>py</sup>), 58.4 (CH<sub>2</sub><sup>Bu</sup>), 57.5 (CH<sub>2</sub><sup>aa</sup>), 25.3 (CH<sub>3</sub><sup>aa</sup>), 23.5 (CH<sub>2</sub><sup>Bu</sup>), 19.5 (CH<sub>2</sub><sup>Bu</sup>), 13.0 (CH<sub>3</sub><sup>Bu</sup>). \* IR (neat, cm<sup>-1</sup>): 1614 (ν-COO) 1452 (ν-C(O)-N) 965 (δ-C-H py). HRMS ESI-TOF(-): m/z calc. for [2]<sup>-</sup> (C<sub>15</sub>H<sub>10</sub>F<sub>5</sub>N<sub>2</sub>O<sub>3</sub>Pd) 466.9658, found 466.9652. Anal. Calcd. for C<sub>31</sub>H<sub>46</sub>F<sub>5</sub>N<sub>3</sub>O<sub>3</sub>Pd: C, 52.43%; H, 6.53%; N, 5.92 %.; Found: C, 52.34 %; H, 6.67 %; N, 5.80 %.

\*The chemical shifts of the C<sub>6</sub>F<sub>5</sub> carbon resonances were determined by <sup>19</sup>F-<sup>13</sup>C HSQC.

The stereochemistry of the complex (cis Pf-N(acyl) groups; Pf = C<sub>6</sub>F<sub>5</sub>) has been determined by <sup>1</sup>H-<sup>19</sup>F HOESY (a cross peak between the methyl and F<sub>ortho</sub> groups can be detected).

**(NBu<sub>4</sub>)[Pd(κ<sup>2</sup>-*N,O*-AcN-Val-O)(C<sub>6</sub>F<sub>5</sub>)py] (3).** *N*-acetylvaline (AcNH-Val-OH, 0.012 g, 0.077 mmol) and silver carbonate (0.073 g, 0.015 mmol) were introduced in a Schlenk flask in a nitrogen atmosphere and dry THF (5 mL) was added. After stirring for one hour, (NBu<sub>4</sub>)[PdBr<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)py] (0.059 g, 0.077 mmol) was added to the reaction mixture. After 6 hours, the mixture was filtered through kiesselghur to remove the silver salts. The solvent was evaporated in vacuo and the

residue was washed with dry diethylether (3 x 5 mL) and vacuum dried. The complex was isolated as a yellow solid (32 mg, 57 % yield).



<sup>1</sup>H NMR (499.73 MHz,  $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO): 8.46 (m, 2H, H<sup>8</sup>), 7.91 (m, 1H, H<sup>10</sup>), 7.41 (m, 2H, H<sup>9</sup>), 4.54 (d, *J* = 6.7 Hz, 1H, H<sup>2</sup>), 3.45 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 2.52 (m, 1H, H<sup>6</sup>), 1.81 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.46 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.36 (s, 3H, H<sup>5</sup>), 1.26 (d, *J* = 6.7 Hz, 3H, H<sup>7</sup>), 1.20 (d, *J* = 6.7 Hz, 3H, H<sup>7'</sup>), 0.99 (t, *J* = 7.2 Hz, 12 H, CH<sub>3</sub><sup>Bu</sup>). <sup>19</sup>F NMR (470.17 MHz,  $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO): -115.95 (br, 1F, F<sub>ortho</sub>), -117.94 (br, 1F, F<sub>ortho</sub>), -164.70 (t, *J* = 19.8 Hz, 1F, F<sub>para</sub>), -165.99 (m, 2F, F<sub>meta</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (125.67 MHz,  $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO): 182.4 (C<sup>1</sup>), 172.5 (C<sup>4</sup>), 152.1 (C<sup>8</sup>), 148.0 (C<sub>ortho</sub><sup>Pf</sup>), 138.1 (C<sup>10</sup>), 136.6 (C<sub>para</sub><sup>Pf</sup>), 135.4 (C<sub>meta</sub><sup>Pf</sup>), 125.0 (C<sup>9</sup>), 72.0 (C<sup>2</sup>), 58.5 (CH<sub>2</sub><sup>Bu</sup>), 34.2 (C<sup>6</sup>), 26.0 (C<sup>5</sup>), 23.6 (CH<sub>2</sub><sup>Bu</sup>), 20.2 (C<sup>7,7'</sup>), 19.5 (CH<sub>2</sub><sup>Bu</sup>), 13.0 (CH<sub>3</sub><sup>Bu</sup>). Anal. Calcd. for C<sub>34</sub>H<sub>52</sub>F<sub>5</sub>N<sub>3</sub>O<sub>3</sub>Pd: C, 54.29 %; H, 6.97 %; N, 5.59 %.; found: C, 54.35 %; H, 7.02 %; N, 5.35 %.

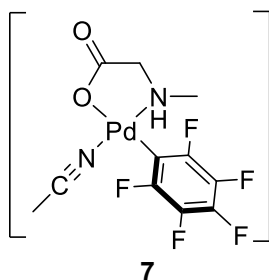
\*The chemical shifts of the C<sub>6</sub>F<sub>5</sub> carbon resonances were determined by <sup>19</sup>F-<sup>13</sup>C HSQC.

\*The stereochemistry of the complex (cis Pf-N(acyl) groups; Pf = C<sub>6</sub>F<sub>5</sub>) has been determined by <sup>1</sup>H-<sup>19</sup>F HOESY.

(NBu<sub>4</sub>)<sub>2</sub>[Pd( $\kappa^2$ -*N,O*-AcN-Gly-O)<sub>2</sub>] (**4**). The complex was isolated as white crystals when attempting the crystallization of complex **2** by slow diffusion of hexane into a solution of the compound in dichloromethane. Those crystals were suitable for X-Ray diffraction analysis (Figure S14).

<sup>1</sup>H NMR (499.73 MHz,  $\delta$ , CDCl<sub>3</sub>): 4.02 (s, 2H, CH<sub>2</sub><sup>aa</sup>), 3.26 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 2.00 (s, 3H, CH<sub>3</sub><sup>aa</sup>), 1.66 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.49 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 1.04 (t, *J* = 7.2 Hz, CH<sub>3</sub><sup>Bu</sup>).

[Pd( $\kappa^2$ -*N,O*-MeNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)(NCMe)] (**7**). *N*-methyl glycine (MeNH-Gly-OH, 24 mg, 0.269 mmol) was added to a solution of complex [Pd<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(CH<sub>3</sub>CN)<sub>2</sub>( $\mu$ -OAc)<sub>2</sub>] (100 mg, 0.134 mmol) in CH<sub>3</sub>CN (10 mL). The initial suspension turned into a solution and it was stirred at room temperature for 6 h. During this time the yellow solution became lighter. The solvent was evaporated to dryness and the white solid obtained was washed with diethylether (2 x 3 mL) and vacuum dried. Yield: 62 mg (56 %).

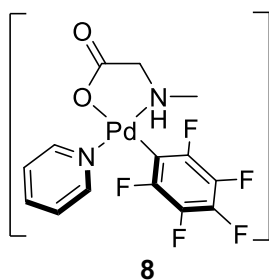


$^1\text{H}$  NMR (499.73 MHz,  $\delta$ ,  $\text{CD}_3\text{CN}$ ): 4.35 (br, 1H, NH), 3.72 (dd,  $J = 15.9, 6.1$  Hz, 1H,  $\text{CHH}^{\text{aa}}$ ), 3.13 (dd,  $J = 15.9, 4.3$  Hz, 1H,  $\text{CHH}^{\text{aa}}$ ), 2.35 (d,  $J = 6.0$  Hz, 3H,  $\text{CH}_3^{\text{aa}}$ ), 1.99 (s, NCM*e*).  $^{19}\text{F}$  NMR (470.17 MHz,  $\delta$ ,  $\text{CD}_3\text{CN}$ ): -122.04 (m, 2F,  $\text{F}_{\text{ortho}}$ ), -161.95 (t,  $J = 19.1$  Hz, 1F,  $\text{F}_{\text{para}}$ ), -165.27 (m, 2F,  $\text{F}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz,  $\delta$ ,  $\text{CD}_3\text{CN}$ ): 177.2 (OCO), 148.18 ( $\text{C}_{\text{ortho}}^{\text{Pf}}$ ), 137.9 ( $\text{C}_{\text{para}}^{\text{Pf}}$ ), 135.8 ( $\text{C}_{\text{meta}}^{\text{Pf}}$ ), 118.3 (NCMe), 59.6 ( $\text{CH}_2^{\text{aa}}$ ), 42.1 ( $\text{CH}_3^{\text{aa}}$ ). Anal. Calcd. for  $\text{C}_{11}\text{H}_9\text{F}_5\text{N}_2\text{O}_2\text{Pd}$ : C, 32.82%; H, 2.25%; N, 6.96 %.; Found: C, 33.03 %; H, 2.43 %; N, 6.75%.

\*The chemical shifts of the  $\text{C}_6\text{F}_5$  carbon resonances were determined by  $^{19}\text{F}$ - $^{13}\text{C}$  HSQC.

Crystals suitable for X-Ray diffraction analysis were obtained by slow evaporation of a  $\text{CH}_3\text{CN}$  solution of the compound (Figure S16).

**[Pd( $\kappa^2$ -*N,O*-MeNH-Gly-O)( $\text{C}_6\text{F}_5$ )py] (8).** To a solution of complex [Pd( $\kappa^2$ -*N,O*-MeNH-Gly-O)( $\text{C}_6\text{F}_5$ )(NCMe)] (7, 50 mg, 0.124 mmol) in acetone (10 mL) was added py (10  $\mu\text{L}$ , 0.124 mmol). The mixture was stirred at room temperature for 2h. The colorless solution was evaporated to dryness and the white solid obtained was filtered, washed with diethylether ( $2 \times 3$  mL) and vacuum dried. Yield: 45 mg (82%).

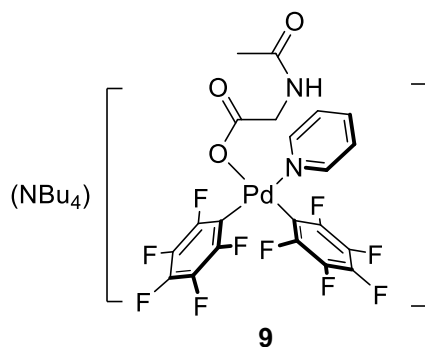


$^1\text{H}$  NMR (499.73 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 8.44 (m, 2H,  $\text{H}_{\text{ortho}}^{\text{py}}$ ), 8.03 (m, 1H,  $\text{H}_{\text{para}}^{\text{py}}$ ), 7.52 (m, 2H,  $\text{H}_{\text{meta}}^{\text{py}}$ ), 5.07 (s, 1H, NH), 3.87 (dd,  $J = 15.7, 6.0$  Hz, 1H,  $\text{CHH}^{\text{aa}}$ ), 3.32 (dd,  $J = 15.7, 4.4$  Hz, 1H,  $\text{CHH}^{\text{aa}}$ ), 2.52 (d,  $J = 6.0$  Hz, 3H,  $\text{CH}_3^{\text{aa}}$ ).  $^{19}\text{F}$  NMR (470.17 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): -120.25 (br, 2F,  $\text{F}_{\text{ortho}}$ ), -161.99 (t,  $J = 19.4$  Hz, 1F,  $\text{F}_{\text{para}}$ ), -164.45 (m, 2F,  $\text{F}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 176.2 (OCO), 152.2 ( $\text{C}_{\text{ortho}}^{\text{py}}$ ), 148.1 ( $\text{C}_{\text{ortho}}^{\text{Pf}}$ ), 139.5 ( $\text{C}_{\text{para}}^{\text{py}}$ ), 138.0 ( $\text{C}_{\text{para}}^{\text{Pf}}$ ), 135.9 ( $\text{C}_{\text{meta}}^{\text{Pf}}$ ), 125.8 ( $\text{C}_{\text{meta}}^{\text{py}}$ ), 60.5 ( $\text{CH}_2^{\text{aa}}$ ), 41.9 ( $\text{CH}_3^{\text{aa}}$ ). Anal. Calcd. for  $\text{C}_{14}\text{H}_{11}\text{F}_5\text{N}_2\text{O}_2\text{Pd}$ : C, 38.16 %; H, 2.52 %; N, 6.36 %.; Found: C, 38.14 %; H, 2.69 %; N, 6.27 %.

\*The chemical shifts of the  $\text{C}_6\text{F}_5$  carbon resonances were determined by  $^{19}\text{F}$ - $^{13}\text{C}$  HSQC.

Crystals suitable for X-Ray diffraction analysis were obtained by slow diffusion of *n*-heptane in a solution of the compound in acetone (Figure S17).

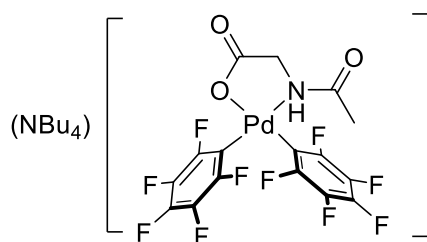
**(NBu<sub>4</sub>)[Pd( $\kappa^1$ -*O*-AcNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>py] (9)**. To a solution of complex (NBu<sub>4</sub>)[Pd( $\kappa^2$ -*N,O*-AcNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (**10**, 15 mg, 0.018 mmol) in acetone (3 mL) was added py (1.5  $\mu$ L, 0.018 mmol). The mixture was stirred at room temperature for 1 h. The colorless solution was evaporated to dryness and the off white solid obtained was washed with diethylether (2  $\times$  3 mL) and vacuum dried. Yield: 8 mg (74%).



<sup>1</sup>H NMR (399.86 MHz,  $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO): 8.65 (m, 2H, H<sub>ortho</sub><sup>py</sup>), 7.86 (m, 1H, H<sub>para</sub><sup>py</sup>), 7.39 (m, 2H, H<sub>meta</sub><sup>py</sup>), 6.48 (s, 1H, NH), 3.45 (m, 10H, CH<sub>2</sub><sup>aa</sup> + CH<sub>2</sub><sup>Bu</sup>), 1.82 (m, 11H, CH<sub>3</sub><sup>aa</sup> + CH<sub>2</sub><sup>Bu</sup>), 1.42 (m, 8H, CH<sub>2</sub><sup>Bu</sup>), 0.97 (t, J = 7.2 Hz, 12 H, CH<sub>3</sub><sup>Bu</sup>). <sup>19</sup>F NMR (376.19 MHz,  $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO): -115.13 (m, 4F, F<sub>ortho</sub>), -165.40 (t, J = 19.6 Hz, 1F, F<sub>para</sub>), -166.53 (t, J = 19.7 Hz, 1F, F<sub>para</sub>), -166.79 (m, 2F, F<sub>meta</sub>), -169.91 (m, 2F, F<sub>meta</sub>). <sup>19</sup>F NMR (470.17 MHz,  $\delta$ , toluene/DMA (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -114.68 (m, 4F, F<sub>ortho</sub>), -164.79 (t, J = 21.6 Hz, 1F, F<sub>para</sub>), -166.01 (t, J = 20.1 Hz, 1F, F<sub>para</sub>), -166.14 (m, 2F, F<sub>meta</sub>), -167.34 (m, 2F, F<sub>meta</sub>). <sup>13</sup>C {<sup>1</sup>H} NMR (100.56 MHz,  $\delta$ , (CD<sub>3</sub>)<sub>2</sub>CO): 171.8 (OCO), 167.8 (NCO), 151.5 (C<sub>ortho</sub><sup>py</sup>), 147.9 (C<sub>ortho</sub><sup>Pf</sup>), 137.5 (C<sub>para</sub><sup>py</sup>), 136.0 (C<sub>para</sub><sup>Pf</sup>), 135.9 (C<sub>para</sub><sup>Pf</sup>), 135.2 (C<sub>meta</sub><sup>Pf</sup>), 134.8 (C<sub>meta</sub><sup>Pf</sup>), 124.7 (C<sub>meta</sub><sup>py</sup>), 58.3 (CH<sub>2</sub><sup>Bu</sup>), 43.7 (CH<sub>2</sub><sup>aa</sup>), 23.3 (CH<sub>2</sub><sup>Bu</sup>), 21.9 (CH<sub>3</sub><sup>aa</sup>), 19.5 (CH<sub>2</sub><sup>Bu</sup>), 12.9 (CH<sub>3</sub><sup>Bu</sup>).\*

\*The chemical shifts of the C<sub>6</sub>F<sub>5</sub> carbon resonances were determined by <sup>19</sup>F-<sup>13</sup>C HSQC.

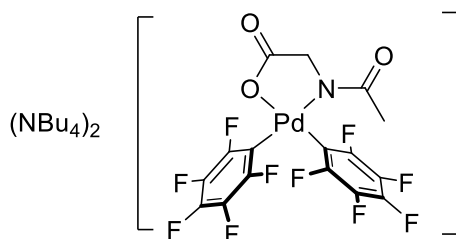
**(NBu<sub>4</sub>)[Pd( $\kappa^2$ -*N,O*-AcNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (10)**. *N*-acetylglycine (AcNH-Gly-OH, 0.033 g, 0.28 mmol), silver carbonate (0.077 g, 0.28 mmol) and dry THF (5 mL) were placed in a Schlenk flask in a nitrogen atmosphere. After stirring this mixture for one hour (NBu<sub>4</sub>)<sub>2</sub>[Pd<sub>2</sub>( $\mu$ -Br)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.213 g, 0.14 mmol) was added. The mixture was stirred at room temperature for 4 hours. Then, the suspension was filtered through kieselghur to remove the silver salts. The solvent was evaporated to dryness and the residue was triturated and washed with dry diethylether (3  $\times$  5 mL) and vacuum dried. The complex was isolated as a white solid (112 mg, 50 % yield).



**10**

$^1\text{H}$  NMR (499.73 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 6.58 (s, 1H, NH), 3.57 (br, 2H,  $\text{CH}_2^{\text{aa}}$ ) 3.46 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 1.85 (br, 3H,  $\text{CH}_3^{\text{aa}}$ ), 1.82 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 1.43 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 0.98 (t,  $J = 7.22$  Hz, 12 H,  $\text{CH}_3^{\text{Bu}}$ ).  $^{19}\text{F}$  NMR (470.17 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): -116.05 (br, 4F,  $\text{F}_{\text{ortho}}$ ), -165.40 (br, 2F,  $\text{F}_{\text{para}}$ ), -167.47 (br, 4F,  $\text{F}_{\text{meta}}$ ). HRMS ESI-TOF(-):  $m/z$  calc. for  $[\mathbf{10}]^-$  ( $\text{C}_{16}\text{H}_6\text{F}_{10}\text{NO}_3\text{Pd}$ ) 555.9224, found 555.9168 (see Figure S12).

**(NBu<sub>4</sub>)<sub>2</sub>[Pd( $\kappa^2$ -N,O-AcN-Gly-O)(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>] (11)**. *N*-acetylglycine (AcNH-Gly-OH, 0.02 g, 0.17 mmol), silver carbonate (0.095 g, 0.34 mmol) and dry THF (5 mL) were introduced in a Schlenk flask in a nitrogen atmosphere. After stirring for one hour (NBu<sub>4</sub>)<sub>2</sub>[Pd<sub>2</sub>( $\mu$ -Br)<sub>2</sub>(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] (0.132 g, 0.08 mmol) and NBu<sub>4</sub>Br (0.056 g, 0.17 mmol) were added. The mixture was stirred at room temperature for 4 hours. Then, the reaction mixture was filtered through kielselghur to remove the silver salts. The solvent was evaporated in vacuo and the residue was triturated and washed with dry diethylether (3 x 5 mL) and vacuum dried. The complex was isolated as a yellow oil (96 mg, 53 % yield).



**11**

$^1\text{H}$  NMR (499.73 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 3.99 (s, 2H,  $\text{CH}_2^{\text{aa}}$ ), 3.43 (m, 16H,  $\text{CH}_2^{\text{Bu}}$ ), 1.80 (m, 16H,  $\text{CH}_2^{\text{Bu}}$ ), 1.42 (m, 16H,  $\text{CH}_2^{\text{Bu}}$ ), 1.20 (s, 3H,  $\text{CH}_3^{\text{aa}}$ ) 0.97 (t,  $J = 7.2$  Hz, 12 H,  $\text{CH}_3^{\text{Bu}}$ ).  $^{19}\text{F}$  NMR (470.17 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): -113.35 (m, 2F,  $\text{F}_{\text{ortho}}$ ), -113.99 (m, 2F,  $\text{F}_{\text{ortho}}$ ), -167.62 (t,  $J = 19.8$  Hz, 1F,  $\text{F}_{\text{para}}$ ), -167.98 (m, 2F,  $\text{F}_{\text{meta}}$ ), -168.39(m, 3F,  $\text{F}_{\text{para}} + \text{F}_{\text{meta}}$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 183.6 (OCO), 172.6 (NCO), 148.1 ( $\text{C}_{\text{ortho}}^{\text{Pf}}$ ), 147.6 ( $\text{C}_{\text{ortho}}^{\text{Pf}}$ ), 134.9 ( $\text{C}_{\text{para}}^{\text{Pf}}$ ,  $\text{C}_{\text{meta}}^{\text{Pf}}$ ), 58.4 ( $\text{CH}_2^{\text{Bu}}$ ), 55.2 ( $\text{CH}_2^{\text{aa}}$ ), 25.3 ( $\text{CH}_3^{\text{aa}}$ ), 23.6 ( $\text{CH}_2^{\text{Bu}}$ ), 19.5 ( $\text{CH}_2^{\text{Bu}}$ ), 13.0 ( $\text{CH}_3^{\text{Bu}}$ ).\*

\*The chemical shifts of the C<sub>6</sub>F<sub>5</sub> carbon resonances were determined by  $^{19}\text{F}$ - $^{13}\text{C}$  HSQC.

### 1.3- Attempt at isolating acetylglycine complex **2** from $[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})_2]$ (**6**).

The use of the acetato dimeric complex **6** as starting material to obtain *N*-acetylglycine derivatives was also tested, but the formation of a mixture of complexes was observed which makes this route synthetically less useful.

For these experiments  $(\text{NBu}_4)(\text{NH-acetylglycine})$  was prepared as follows.

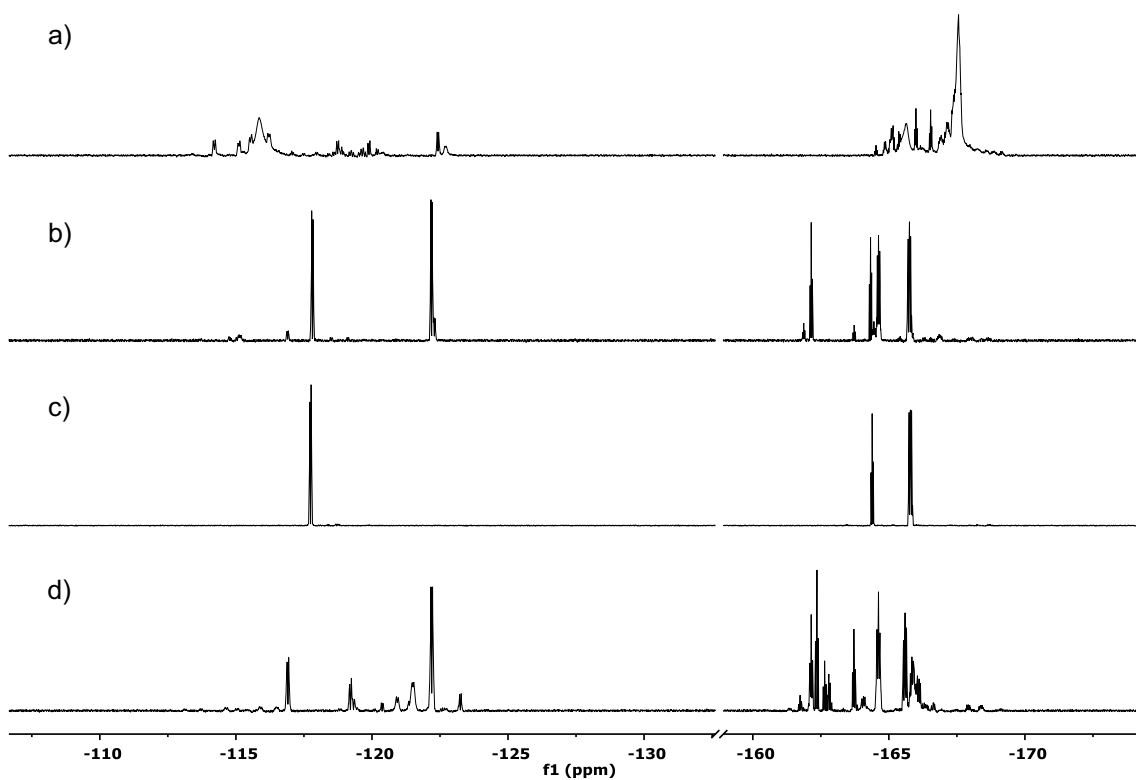
**(NBu<sub>4</sub>)(NH-acetyl glycine).** *N*-acetylglycine (1.5 g, 12.8 mmol) and a  $\text{NBu}_4\text{OH}$  solution in methanol (1.0 M, 12.8 mL) were introduced in a Schlenk flask in a nitrogen atmosphere. After stirring for 30 minutes the solution was evaporated to dryness and the residue washed with dry diethylether (3 x 5 mL) and vacuum dried.

$^1\text{H}$  NMR (399.86 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 6.85 (s, 1H, NH), 3.48 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 3.39 (s, 2H,  $\text{CH}_2^{\text{aa}}$ ), 1.84 (s, 3H,  $\text{CH}_3^{\text{aa}}$ ), 1.80 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 1.41 (m, 8H,  $\text{CH}_2^{\text{Bu}}$ ), 0.97 (t,  $J = 7.2$  Hz, 12 H,  $\text{CH}_3^{\text{Bu}}$ ).  
 $^{13}\text{C}\{^1\text{H}\}$  NMR (100.56 MHz,  $\delta$ ,  $(\text{CD}_3)_2\text{CO}$ ): 170.1 (OCO), 167.6 (NCO), 58.4 ( $\text{CH}_2^{\text{Bu}}$ ), 44.6 ( $\text{CH}_2^{\text{aa}}$ ), 23.6 ( $\text{CH}_2^{\text{Bu}}$ ), 22.3 ( $\text{CH}_2^{\text{aa}}$ ), 19.5 ( $\text{CH}_2^{\text{Bu}}$ ), 13.0 ( $\text{CH}_3^{\text{Bu}}$ ).

$(\text{NBu}_4)\text{AcNH-Gly-O}$  (60 mg, 0.16 mmol) was suspended in 15 mL of dry acetone in a Schlenk flask in a nitrogen atmosphere. This mixture was cooled to 200 K in an isopropanol bath. Then,  $[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})_2]$  (**6**, 63 mg, 0.08 mmol) was added and the suspension gradually turns into a clear solution. After stirring for one hour at low temperature the solvent was evaporated in vacuo and the residue was washed with dry diethylether (3 x 5 mL) and vacuum dried. The complex was isolated as a yellow solid.

A portion of the yellow solid (4.8 mg) was dissolved in acetone- $d_6$  and the  $^{19}\text{F}$  NMR spectrum showed a mixture of species and broad signals which are a sign of a fluxional behavior (Figure S1, a)). Pyridine (2  $\mu\text{L}$ ) was added to his sample and two organometallic species were formed (see Figure S1, b)). One of them corresponds to  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**2**) (cf. Figure S1, c)) and the other compound does not contain a coordinated amino acid since it is also formed upon addition of pyridine to  $[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})_2]$  (see Figure S1, d)).





**Figure S1.**  $^{19}\text{F}$  NMR (470.17 MHz) spectra in acetone- $d_6$  at 298 K of: a) Yellow solid obtained from the reaction of  $(\text{NBu}_4)\text{AcNH-Gly-O}$  and  $\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})_2$ ; b) the sample shown in a) upon addition of pyridine; c) Complex **2**; d)  $[\text{Pd}_2(\text{C}_6\text{F}_5)_2(\text{CH}_3\text{CN})_2(\mu\text{-OAc})_2]$  and pyridine (Pd:py = 1:1 mol ratio).

### 1.4- Decomposition reactions of the MPAA palladium complexes in the presence of arenes

The palladium complex (0.01 mmol) and the corresponding arene (0.5 mL) or arene/DMA mixture (0.5 mL, 1:1 volume ratio) were added into an NMR tube along with a sealed glass capillary filled with (CD<sub>3</sub>)<sub>2</sub>SO as NMR lock signal. The mixture was heated at 130 °C for the specified time. The reaction was monitored by <sup>19</sup>F NMR and Tables S1-S2 collect the relative amount of the species formed. The <sup>19</sup>F NMR data of the species formed in solution are specified below.

**Table S1.** Decomposition of complexes **2** and **9** were heated in the presence of an arene.<sup>a</sup>

Complex	Solvent	Pd-MPAA <sup>b</sup> (%)	Pf-Arene % (o:m:p ratio)	PfH (%)	“PdPf <sub>2</sub> ” <sup>b</sup> (%) <sup>b</sup>	Other (%) <sup>c</sup>
<b>2</b>	Toluene	18 ( <b>2</b> )	Pf-Tol, 53 (1:4:2)	17	–	12
<b>2</b>	Toluene/DMA (1:1)	–	Pf-Tol, 67 (0:2:1)	11	22 ( <b>9</b> )	–
<b>2<sup>d</sup></b>	Toluene/HFIP (1:1)	–	Pf-Tol, 28 (0:2.5:1)	26	10 (Pf-Pf)	36
<b>2</b>	PhCOOEt	–	Pf-C <sub>6</sub> H <sub>4</sub> COOEt, 83 (0:2.5:1)	17	–	–
<b>2</b>	pyridine	90 ( <b>2</b> )	Pf-py, 4 (0:1:0)	–	6 ([PdPf <sub>2</sub> py <sub>2</sub> ])	–
<b>9</b>	Toluene/DMA (1:1)	73 ( <b>9</b> )	Pf-Tol, 10 (0:2:1)	17	–	–

a) Reaction conditions T = 130 °C, 30 min. Pf = C<sub>6</sub>F<sub>5</sub>. The percentages shown were determined by integration of <sup>19</sup>F NMR signals and they reflect the fluorinated aryl distribution in the mixture (not molar ratio of compounds). b) Species in parenthesis. c) Unidentified species. d) Reaction temperature: 90 °C due to the low boiling point of HFIP.

**Table S2.** Decomposition of palladium complexes **2**, **3**, **8** and **9** when heated in the presence of toluene.<sup>a</sup>

Complex	Solvent <sup>b</sup>	Pf-Tol (%) (o:m:p ratio)	Pd-MPAA <sup>c</sup> (%)	PfH (%)	[PdPf <sub>2</sub> py <sub>2</sub> ] (%)
<b>2</b>	Toluene/DMA	79 (0:2:1)	–	21	–
<b>9</b>	Toluene/DMA	16 (0:2:1)	58 ( <b>9</b> )	26	–
<b>3</b>	Toluene/DMA	77 (1:8:4)	–	23	–
<b>8</b>	Toluene/DMA	6 (0:1:1)	62 ( <b>8</b> )	3	29

a) Reaction conditions T = 130 °C, 60 min. Pf = C<sub>6</sub>F<sub>5</sub>. The percentages shown were determined by integration of <sup>19</sup>F NMR signals and they reflect the fluorinated aryl distribution in the mixture (not molar ratio of compounds). b) Ratio Toluene:DMA = 1:1 (v/v). c) Palladium species in parenthesis.

Decomposition in the arene as solvent:

**C<sub>6</sub>F<sub>5</sub>H**: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/(CD<sub>3</sub>)<sub>2</sub>SO capillary): -139.71 (m, 2F, F<sub>ortho</sub>), -154.65 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -162.96 (m, 2F, F<sub>meta</sub>).

**C<sub>6</sub>F<sub>5</sub>-Tol**: mixture of three isomers (o:m:p = 1:4:2 mol ratio). Ortho isomer: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.52 (m, 2F, F<sub>ortho</sub>), -155.22 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -162.54 (m, 2F, F<sub>meta</sub>); MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>]. Meta isomer:<sup>5</sup> <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.29 (m, 2F, F<sub>ortho</sub>), -157.05 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -163.44 (m, 2F, F<sub>meta</sub>); MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>]. Para isomer:<sup>5</sup> <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/(CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.68 (m, 2F, F<sub>ortho</sub>), -157.34 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -163.32 (m, 2F, F<sub>meta</sub>); MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>].

**C<sub>6</sub>F<sub>5</sub>-BzOEt**:<sup>6,7</sup> <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, ethyl benzoate/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.24 (m, 2F, F<sub>ortho</sub>), -155.95 (t, J = 19.8 Hz, 1F, F<sub>para</sub>), -163.39 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z (%) 316 (100) [M<sup>+</sup>]. <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, ethyl benzoate/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.57 (m, 2F, F<sub>ortho</sub>), -156.32 (t, J = 20.6 Hz, 1F, F<sub>para</sub>), -163.14 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z, 316 [M<sup>+</sup>].

**m-C<sub>6</sub>F<sub>5</sub>-py**:<sup>8</sup> <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, pyridine/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.05 (m, 2F, F<sub>ortho</sub>), -155.95 (t, J = 19.8 Hz, 1F, F<sub>para</sub>), -163.39 (m, 2F, F<sub>meta</sub>); MS (EI, 70 eV): m/z, 245 [M<sup>+</sup>]. **[Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>py<sub>2</sub>]**: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, pyridine/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -116.54 (m, 2F, F<sub>ortho</sub>), -161.93 (t, J = 19.8 Hz, 1F, F<sub>para</sub>), -162.62 (m, 2F, F<sub>meta</sub>).

Decomposition in toluene/DMA:

**C<sub>6</sub>F<sub>5</sub>H**: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/DMA (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -139.83 (m, 2F, F<sub>ortho</sub>), -156.01 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -163.74 (m, 2F, F<sub>meta</sub>).

**C<sub>6</sub>F<sub>5</sub>-Tol**: mixture of two isomers (m:p = 2:1). Meta isomer: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/DMA (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.34 (m, 2F, F<sub>ortho</sub>), -157.90 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -164.18 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>]. Para isomer: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/DMA (1:1)/(CD<sub>3</sub>)<sub>2</sub>SO capillary): -144.60 (m, 2F, F<sub>ortho</sub>), -158.15 (t, J = 20.7 Hz, 1F, F<sub>para</sub>), -164.11 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>].

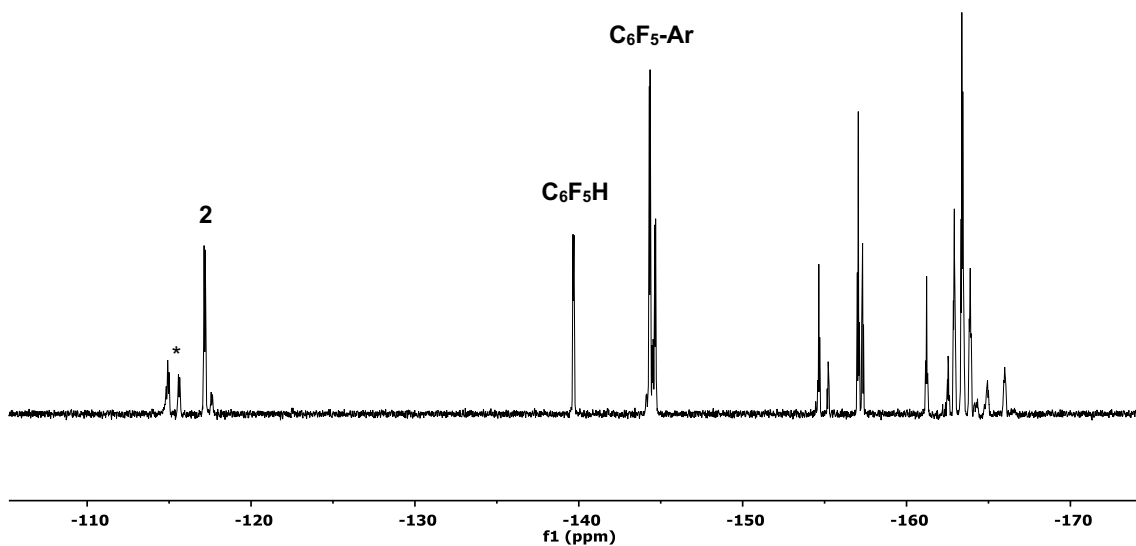
**[Pd(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>py<sub>2</sub>]**: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/DMA (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -116.37 (m, 2F, F<sub>ortho</sub>), -163.02 (t, J = 19.8 Hz, 1F, F<sub>para</sub>), -165.16 (m, 2F, F<sub>meta</sub>).

Decomposition in toluene/HFIP:

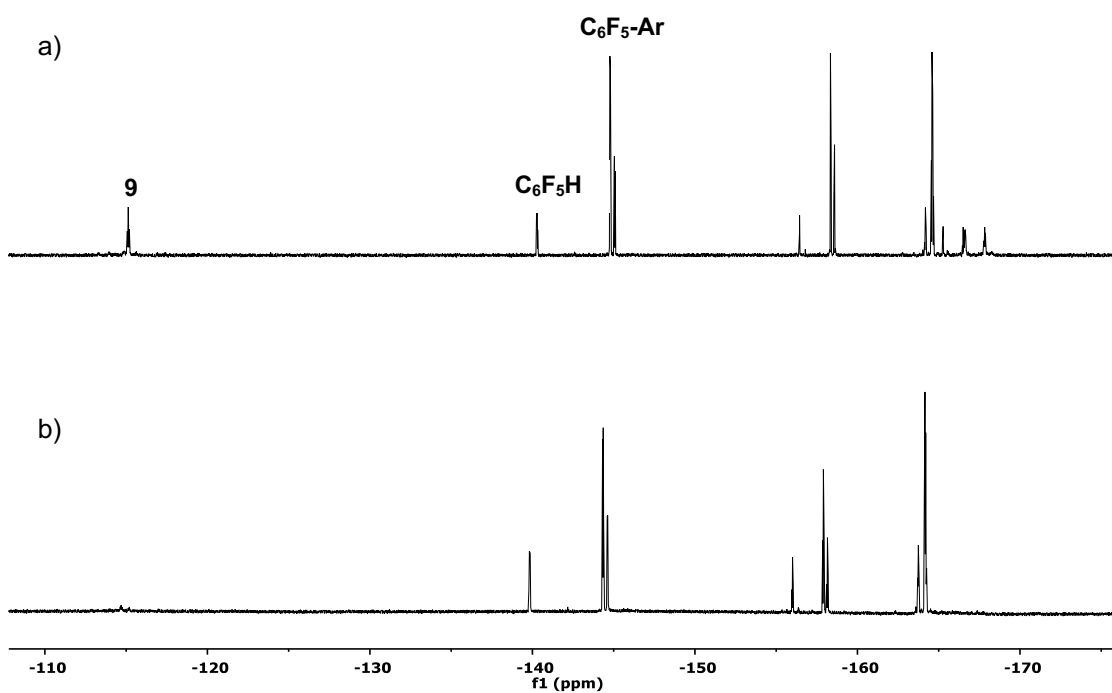
**C<sub>6</sub>F<sub>5</sub>H**: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/HFIP (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -141.20 (m, 2F, F<sub>ortho</sub>), -156.81 (t, J = 19 Hz, 1F, F<sub>para</sub>), -165.04 (m, 2F, F<sub>meta</sub>).

**C<sub>6</sub>F<sub>5</sub>-Tol**: mixture of two isomers (m:p = 2.5:1). Meta isomer: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/HFIP (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -145.62 (m, 2F, F<sub>ortho</sub>), -159.01 (t, J = 19.8 Hz, 1F, F<sub>para</sub>), -165.35 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>]. Para isomer: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/HFIP (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -145.92 (m, 2F, F<sub>ortho</sub>), -159.23 (t, J = 19.8 Hz, 1F, F<sub>para</sub>), -165.35 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z, 258 [M<sup>+</sup>].

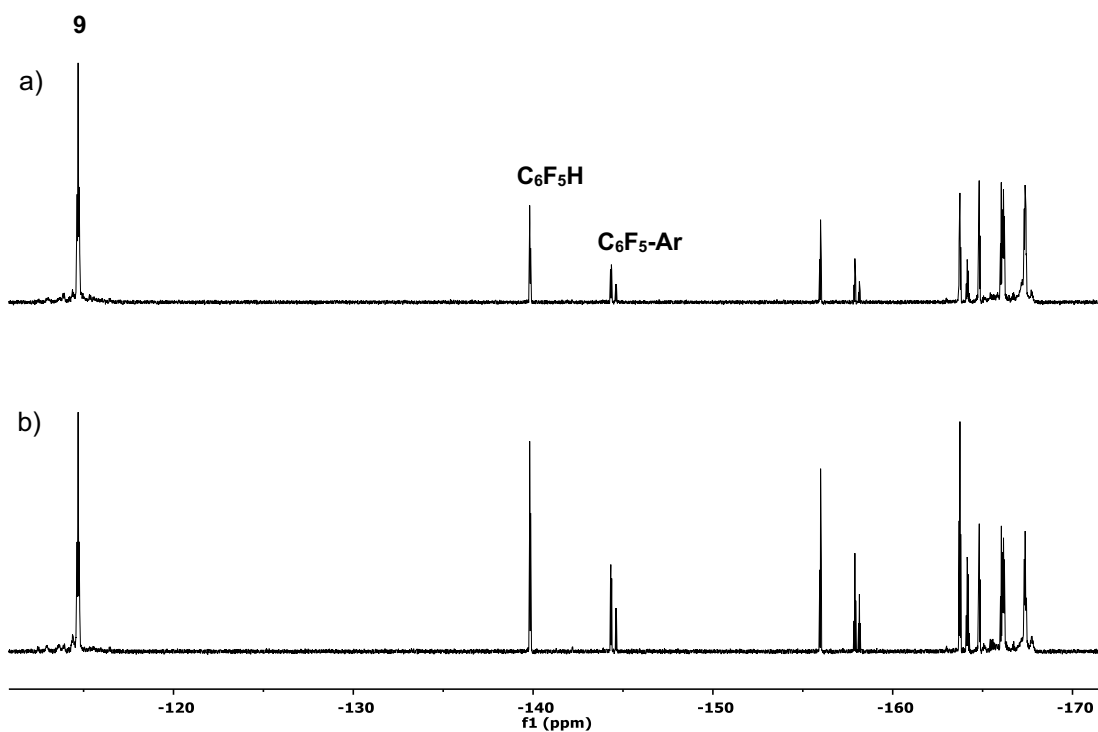
**C<sub>6</sub>F<sub>5</sub>-C<sub>6</sub>F<sub>5</sub>**: <sup>19</sup>F NMR (470.17 MHz, 298 K, δ, toluene/HFIP (1:1)/ (CD<sub>3</sub>)<sub>2</sub>SO capillary): -140.27 (m, 2F, F<sub>ortho</sub>), -152.67 (t, J = 20 Hz, 1F, F<sub>para</sub>), -163.43 (m, 2F, F<sub>meta</sub>). MS (EI, 70 eV): m/z, 334 [M<sup>+</sup>].



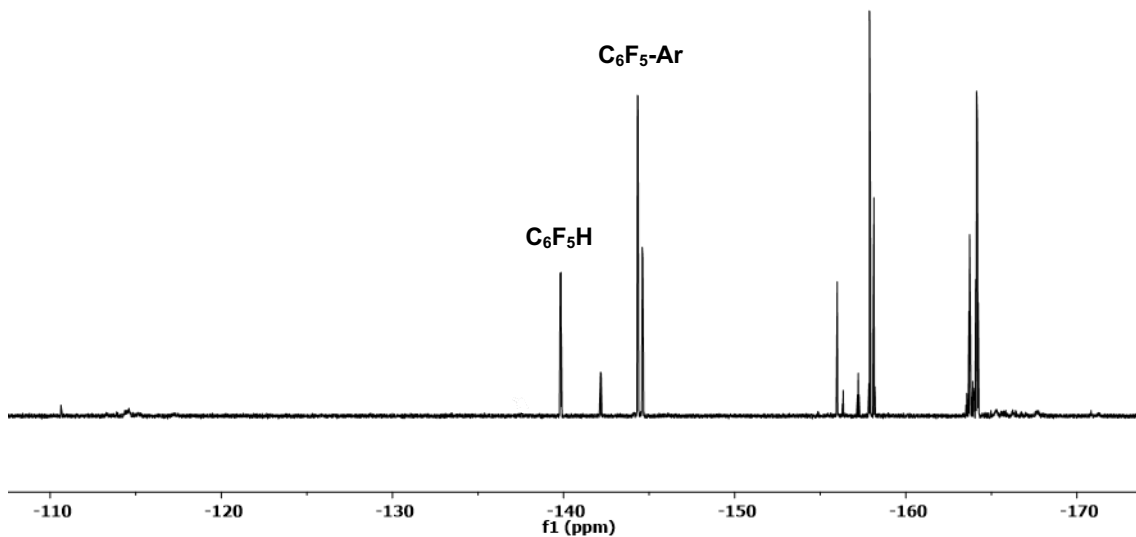
**Figure S2.** <sup>19</sup>F NMR (470.17 MHz) spectrum in toluene as solvent (DMSO-*d*<sub>6</sub> capillary) after heating complex **2** for 30 min at 130 °C. \* Unknown species. (C<sub>6</sub>F<sub>5</sub>-Ar is a mixture of three isomers). Only the <sup>19</sup>F ortho region is labeled for clarity (Ar = Toly).



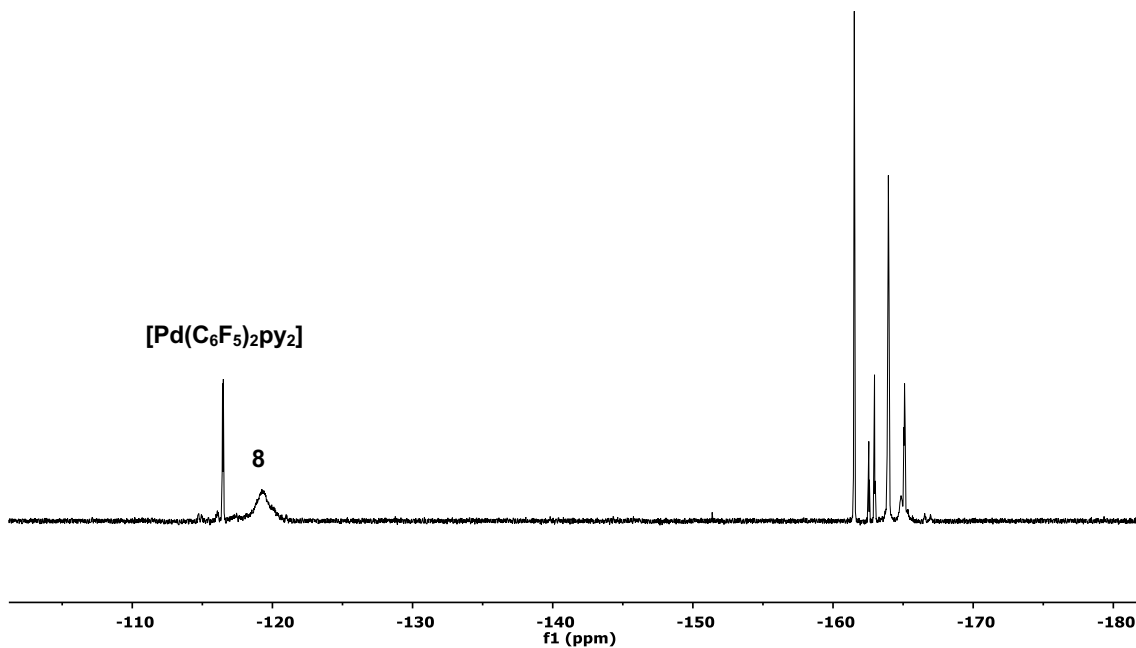
**Figure S3.**  $^{19}\text{F}$  NMR (470.17 MHz) spectra in toluene/DMA as solvent (DMSO- $d_6$  capillary): a) after heating complex **2** for 30 min at 130 °C. ( $\text{C}_6\text{F}_5\text{-Ar}$  is a mixture of two isomers); b) after heating complex **2** for 1 h at 130 °C. Only the  $^{19}\text{F}$  ortho region is labeled for clarity (Ar = Toly).l).



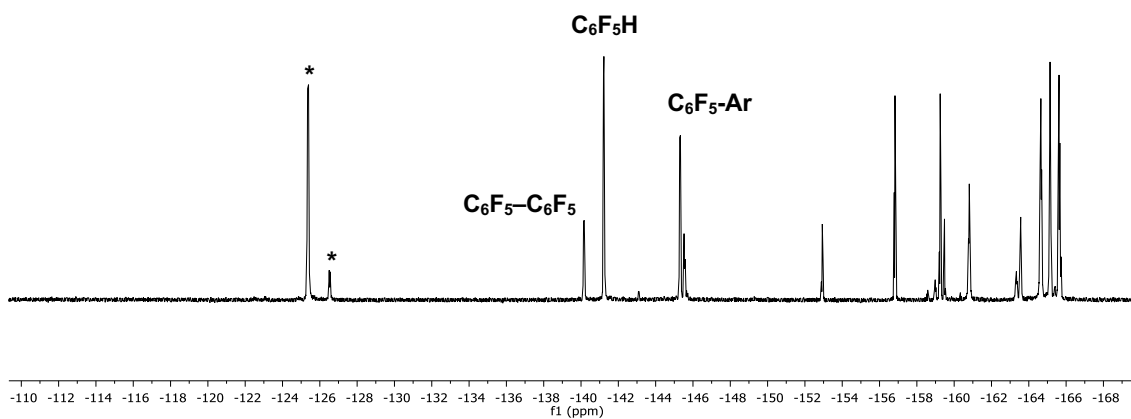
**Figure S4.**  $^{19}\text{F}$  NMR (470.17 MHz) spectra in toluene/DMA as solvent (DMSO- $d_6$  capillary): a) after heating complex **9** for 30 min at 130 °C ( $\text{C}_6\text{F}_5\text{-Ar}$  is a mixture of two isomers); b) after heating complex **9** for 1 h at 130 °C. Only the  $^{19}\text{F}$  ortho region is labeled for clarity (Ar = Toly).l).



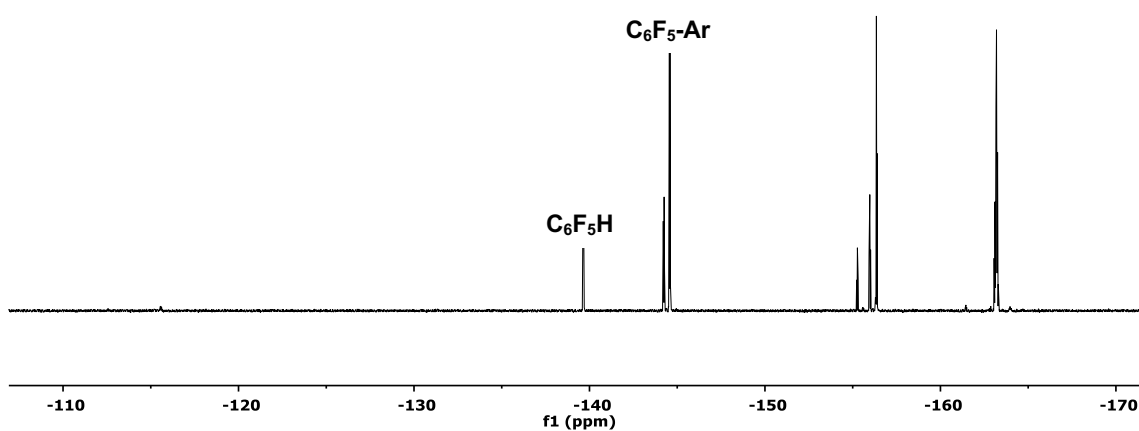
**Figure S5.**  $^{19}\text{F}$  NMR (470.17 MHz) spectrum in toluene/DMA as solvent (DMSO- $d_6$  capillary) after heating the valine complex **3** for 1 h at 130 °C ( $\text{C}_6\text{F}_5\text{-Ar}$  is a mixture of three isomers). Only the  $^{19}\text{F}$  ortho region is labeled for clarity (Ar = Toly).



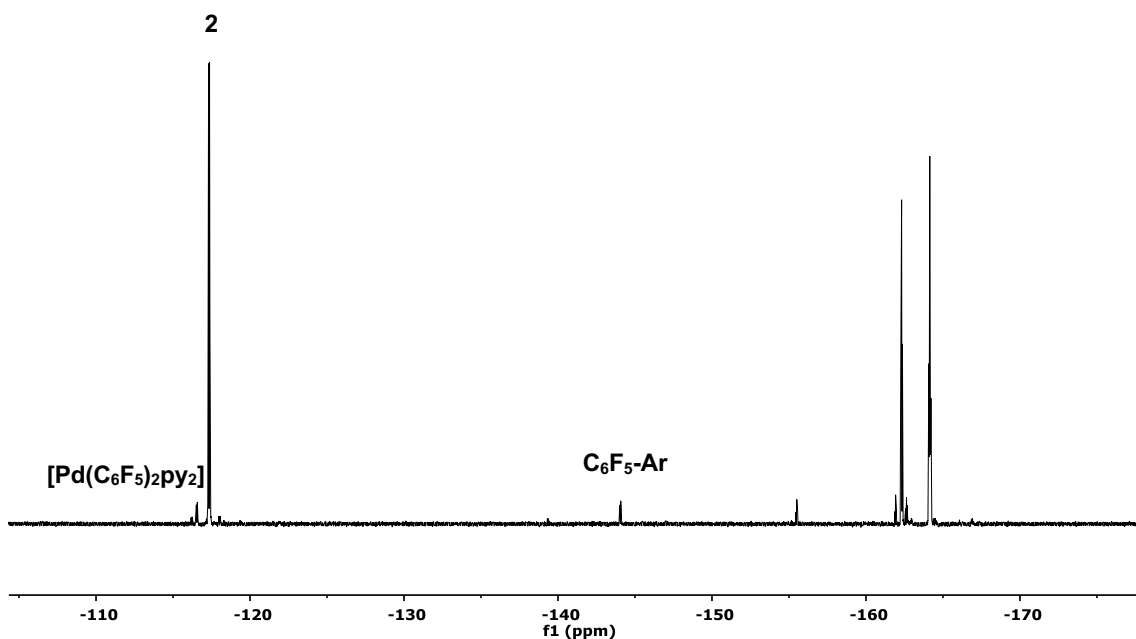
**Figure S6.**  $^{19}\text{F}$  NMR (470.17 MHz) spectrum in toluene/DMA as solvent (DMSO- $d_6$  capillary) after heating the *N*-methylglycine complex **8** for 30 min at 130 °C. Only the  $^{19}\text{F}_{\text{ortho}}$  region is labeled for clarity.



**Figure S7.**  $^{19}\text{F}$  NMR (470.17 MHz) spectrum in toluene/HFIP as solvent (DMSO- $d_6$  capillary) after heating complex **2** for 1 h at 90 °C ( $\text{C}_6\text{F}_5\text{-Ar}$  is a mixture of two isomers). Only the  $^{19}\text{F}_{\text{ortho}}$  region is labeled for clarity. \* Unidentified Pd-complexes.



**Figure S8.**  $^{19}\text{F}$  NMR (470.17 MHz) spectrum in ethyl benzoate as solvent (DMSO- $d_6$  capillary) after heating complex **2** for 30 min at 130 °C. Only the  $^{19}\text{F}_{\text{ortho}}$  region is labeled for clarity. (Ar =  $\text{C}_6\text{H}_4\text{COOEt}$ ).



**Figure S9.**  $^{19}\text{F}$  NMR (470.17 MHz) spectrum in pyridine as solvent (DMSO- $d_6$  capillary) after heating complex **2** for 30 min at 130 °C. Only the  $^{19}\text{F}$  ortho region is labeled for clarity. (Ar = pyridyl).

## 1.5- Kinetic experiments

### 1.5.1 Monitoring the decomposition reaction of complex **2** in the presence of toluene.

A mixture of toluene/DMA (0.5 mL, 1:1 v/v) was added to an NMR tube containing  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**2**, 10 mg, 0.014 mmol,  $[\mathbf{2}]_0 = 0.028\text{ M}$ ). A sealed glass capillary filled with  $(\text{CD}_3)_2\text{SO}$  as NMR lock signal and reference was introduced and the NMR tube was closed and shaken just before its introduction in the NMR probe previously thermostated at 90 °C. The reaction was monitored by  $^{19}\text{F}$  NMR for 15 h with data collected every 5 minutes. The course of the reaction is shown in Figure 3 (main text).

### 1.5.2 Determination of the KIE.

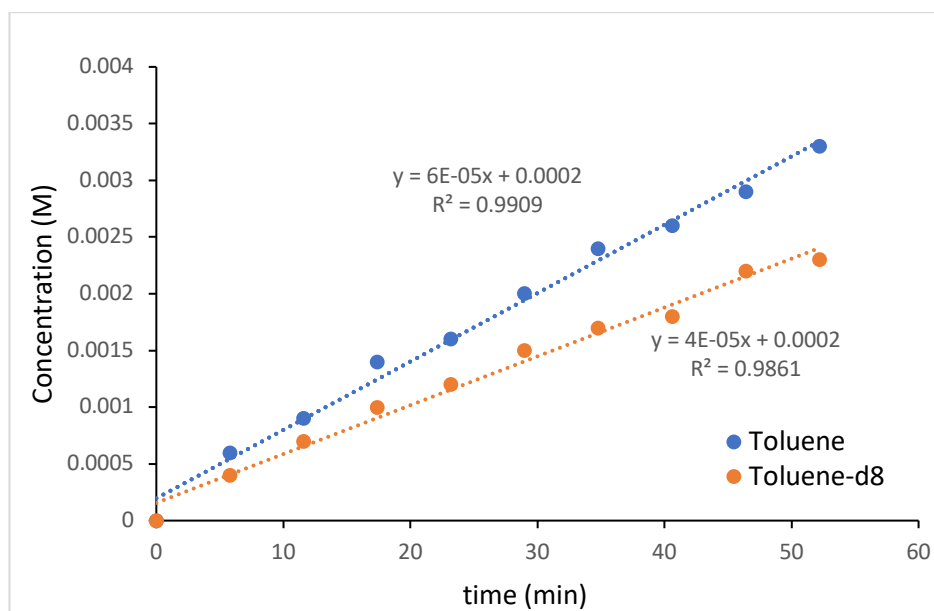
Two NMR tubes were prepared containing complex **2** (10 mg, 0.014 mmol) in DMA (0.2 mL) and a sealed glass capillary filled with  $(\text{CD}_3)_2\text{SO}$  as NMR lock signal and reference. Then, toluene- $d_8$  (0.2 mL) was added to one NMR tube and toluene (0.2 mL) to the other. The reactions were followed by  $^{19}\text{F}$  NMR at 90 °C and the concentration of the product was determined by integration of the ortho fluorine signals of the C-C coupling products.



The KIE ( $k_{\text{obs}(\text{toluene})}/k_{\text{obs}(\text{toluene-}d_8)}$ ) was determined by comparing the initial rates for the reactions of toluene and toluene- $d_8$  in the independent experiments described above (Figure S10). The ratio of initial reaction rate constants gives the KIE value:  $k_{\text{H}} = 6.0 \pm 0.2 \times 10^{-5}$ ;  $k_{\text{D}} = 4.30 \pm 0.18 \times 10^{-5}$ .  
<sup>5</sup>.  $\text{KIE} = k_{\text{H}}/k_{\text{D}} = 1.4 \pm 0.1$ .

**Table S3.** Time and product concentration data for the KIE determining experiments.

	<b>Toluene</b>	<b>Toluene-<math>d_8</math></b>
<b>Time (min)</b>	<b>[C<sub>6</sub>F<sub>5</sub>-Tol] (M)</b>	<b>[C<sub>6</sub>F<sub>5</sub>-Tol-<math>d_8</math>] (M)</b>
0	0	0
5.8	0.0006	0.0004
11.6	0.0009	0.0007
17.4	0.0014	0.001
23.2	0.0016	0.0012
29	0.002	0.0015
34.8	0.0024	0.0017
40.6	0.0026	0.0018
46.4	0.0029	0.0022
52.2	0.0033	0.0023



**Figure S10.** Concentration-time plots of the C-H activation reaction of toluene and toluene- $d_8$ .

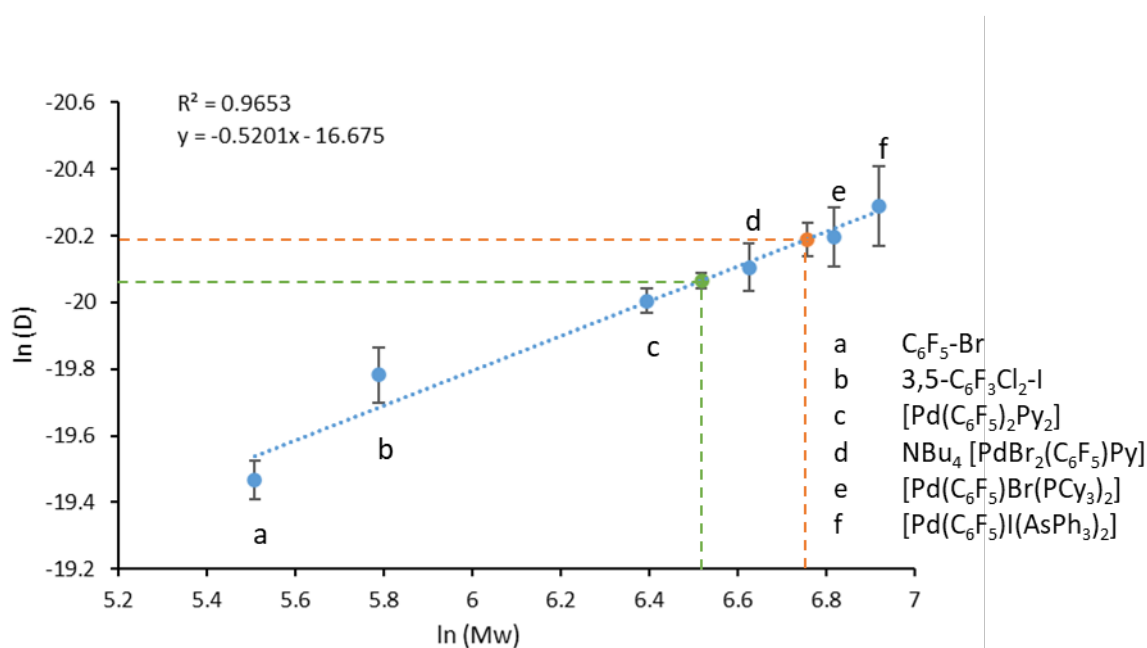
## 1.6- Diffusion experiments: NMR DOSY

$^{19}\text{F}$  NMR experiments were recorded using an Agilent MR-500 spectrometer (500 MHz). All spectra were acquired at 298.15 K in 5 mm NMR tubes.

DOSY experiments were performed using DOSY Bipolar Pulse Pair Simulated Echo with convection compensation (dbppste\_cc) pulse sequence. The total diffusion-encoding pulse duration  $\delta$  and the diffusion delay  $\Delta$  were optimized in order to obtain a 1-5% residual signal with the maximum gradient strength. Typically, in each NMR experiment “dbppste\_cc” using 20 spectra on 16 K data points were collected, the value of  $\delta$  was of 1.0 ms duration, the diffusion delay ( $\Delta$ ) was set to 25 ms in all experiments and relaxation time ( $t_1$ ) between acquisitions was set to 2 s. The experiments were performed without sample spinning.

For the calibration line, different tubes were charged with similar quantities of the standard substances (0.02 mmol) in acetone- $d_6$  (0.5 mL). The sample solutions were placed into the NMR probe. An empirical relation between diffusion coefficient and molecular weight was established and its expressed as:  $D = K \cdot M_w \cdot \alpha$  where  $K$  is a molecule-dependent constant and  $\alpha$  is a parameter that depends highly on the particle shape.<sup>9</sup> This equation was transformed into a linear equation in order to obtain the parameter  $\alpha$ .

$$\ln D = \ln K + \alpha \cdot \ln M_w$$



**Figure S11.** Plot of  $\ln(D)$  versus  $\ln(M_w)$ . Blue dots represent experimental values obtained for known complexes and resulting calibration line. The orange dot corresponds to complex **9** and the green dot to complex **2**.

**Table S4.** Results of diffusion experiments of different compounds in acetone-*d*<sub>6</sub> at 298 K for the calibration line.

Name	Compound	M <sub>w</sub> (calc) / g mol <sup>-1</sup>	D (m <sup>2</sup> s <sup>-1</sup> )
a	C <sub>6</sub> F <sub>5</sub> Br	246.9	35.2 ± 1.01E-10
b	3,5-C <sub>6</sub> F <sub>3</sub> Cl <sub>2</sub> I	326.9	25.6 ± 1.06E-10
c	[Pd(C <sub>6</sub> F <sub>5</sub> ) <sub>2</sub> py <sub>2</sub> ]	598.8	20.5 ± 0.38E-10
d	NBu <sub>4</sub> [PdBr <sub>2</sub> (C <sub>6</sub> F <sub>5</sub> )py]	754.7	18.5 ± 0.67E-10
e	[Pd(C <sub>6</sub> F <sub>5</sub> )Br(PCy <sub>3</sub> ) <sub>2</sub> ]	914.3	16.9 ± 0.76E-10
f	[Pd(C <sub>6</sub> F <sub>5</sub> )I(AsPh <sub>3</sub> ) <sub>2</sub> ]	1012.9	15.5 ± 0.93E-10
	<b>9</b>		17.0 ± 0.20E-10
	<b>2</b>		19.3 ± 0.49E-10

Using the linear equation resulting from the plot shown in Figure S11 the molecular weight of the target compounds can be determined from <sup>19</sup>F diffusion coefficient NMR spectroscopy.

$$\ln M_w = (\ln D + b)/m$$

$$\ln M_w = (\ln D + 16.675)/(-0.520)$$

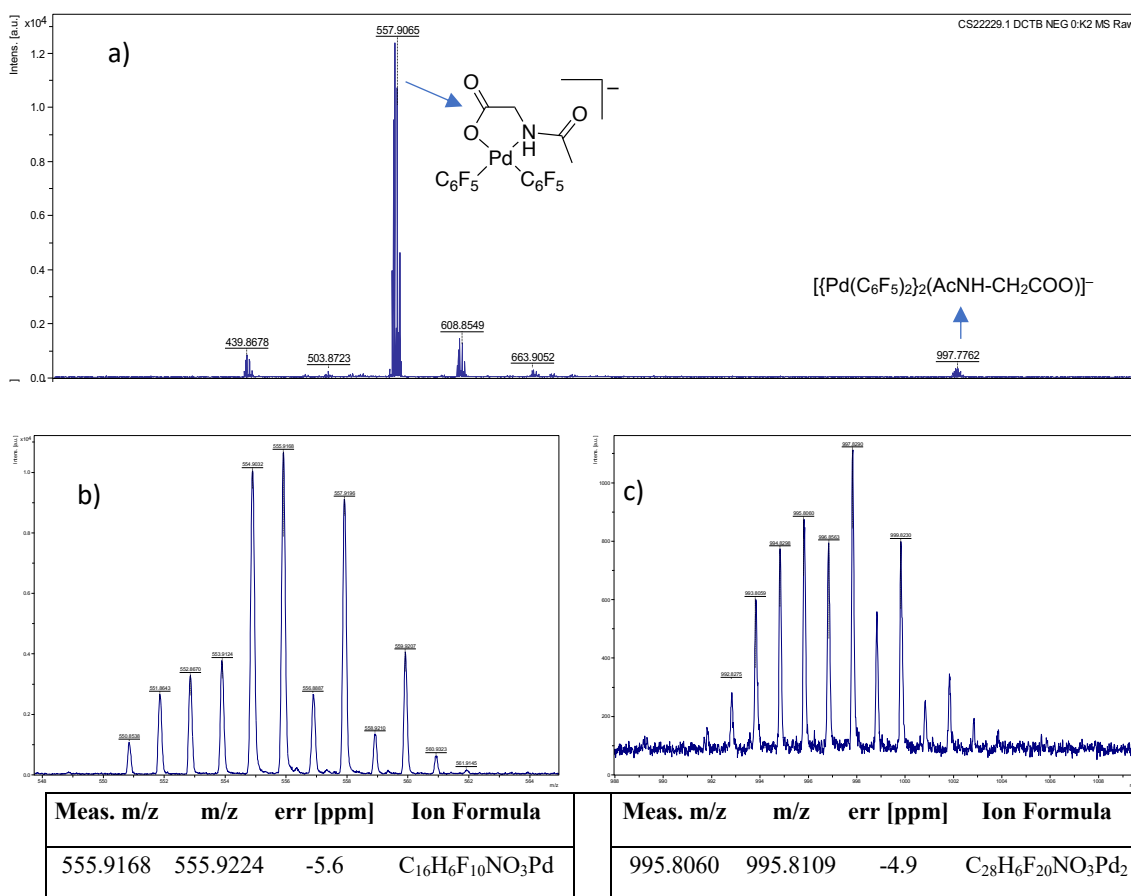
The resulting values of M<sub>w</sub> are:

**9**: 862±20 (M<sub>w</sub> calc = 878.21)

**2**: 679±33 (M<sub>w</sub> calc = 710.14)

The DOSY experiments are consistent with monomeric species in solution for complexes **2** and **9**. The observed M<sub>w</sub> in both cases is too low to accommodate a dinuclear complex.

## 1.7- Mass spectrum of complex 10.



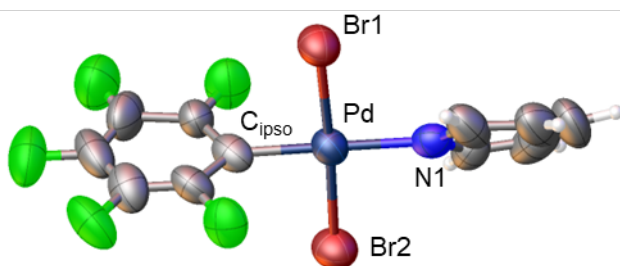
**Figure S12.** HRMS spectrum of complex 10 (DCTB, negative mode): a) Complete fragment distribution; b) major monomeric species; c) minor dimeric fragment.

## 2. Data for X-Ray molecular structure determinations

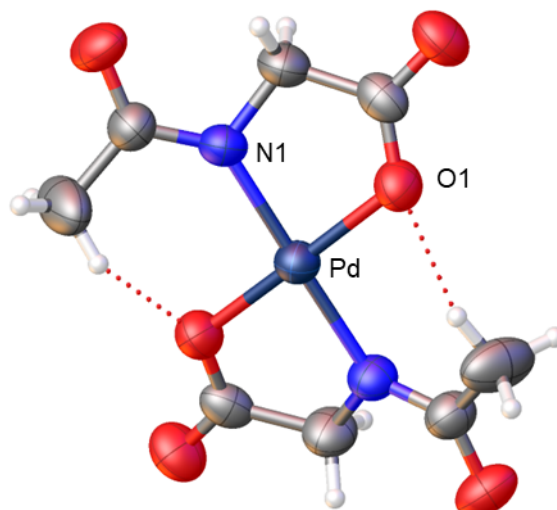
Crystals suitable for X-ray analyses were obtained as described in the synthesis of each palladium complex. Complex **5** was crystallized, along with complex **4**, when attempting the crystallization of complex **2** by slow diffusion of hexane in a solution of the compound in dichloromethane at  $-28\text{ }^{\circ}\text{C}$ .

Each crystal was attached to a glass fiber and transferred to an Agilent Supernova diffractometer with an Atlas CCD area detector. Data collection was performed with Mo-K $\alpha$  radiation ( $\lambda = 0.71073\text{ \AA}$ ) or with Cu K $\alpha$  ( $\lambda = 1.54184$ ). Data integration, scaling and empirical absorption correction were carried out using the CrysAlisPro program package.<sup>10</sup> The crystal was kept at 294 K or 220 K during data collection. Using Olex2,<sup>11</sup> the structure was solved with the ShelxT,<sup>12</sup> and refined with the Shelx program.<sup>13</sup> The non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed at idealized positions and refined using the riding model. Refinement proceeded smoothly to give the residuals shown in Tables S5-S6.

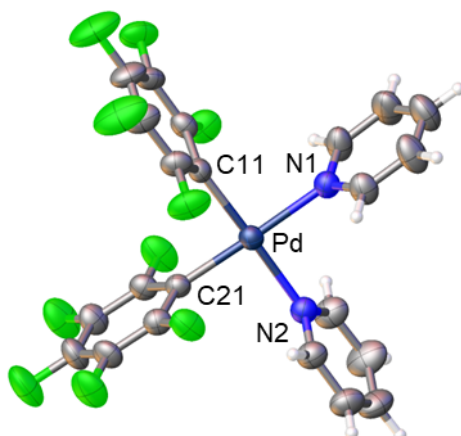
CCDC deposition numbers 2255463 (for **1**), 2255464 (for **4**), 2255465 (for **5**), 2255468 (for **7**), and 2255469 (for **8**) contains the supporting crystallographic data for this paper. These data can be obtained free of charge at [www.ccdc.cam.ac.uk/conts/retrieving.html](http://www.ccdc.cam.ac.uk/conts/retrieving.html) (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)). Figures S13-S17 show the molecular structures obtained.



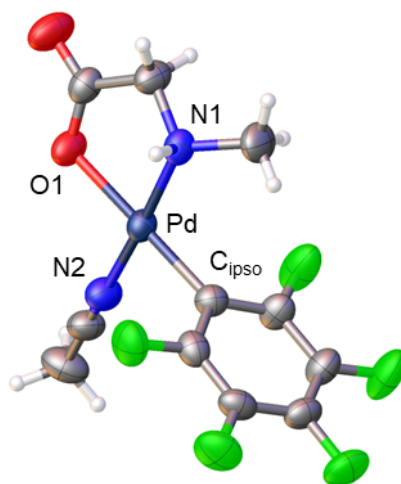
**Figure S13.** X-ray molecular structure of  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (**1**) (ORTEP 40% probability ellipsoids).  $\text{NBu}_4^+$  is omitted for clarity. Selected bond lengths ( $\text{\AA}$ ): Pd–C<sub>ipso</sub> = 1.983(7); Pd–N(1) = 2.106(5); Pd–Br(1) = 2.4366(10); Pd–Br(2) = 2.4301(10).



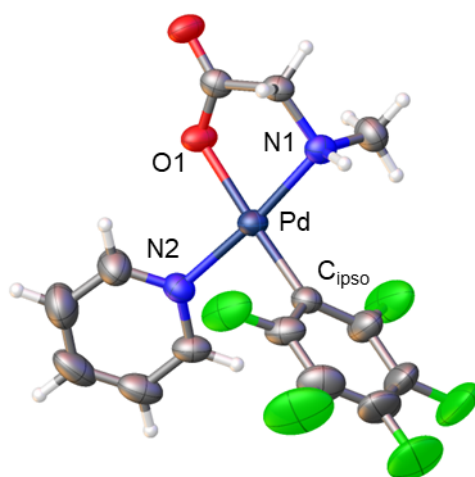
**Figure S14.** X-ray molecular structure of  $(\text{NBu}_4)_2[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})_2]$  (**4**) (ORTEP 40% probability ellipsoids).  $\text{NBu}_4^+$  is omitted for clarity. Selected bond lengths ( $\text{\AA}$ ): Pd–N(1)= 2.018(3); Pd–O(1) = 2.002(3).



**Figure S15.** X-ray molecular structure of  $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{py}_2]$  (**5**) (ORTEP 40% probability ellipsoids). Selected bond lengths ( $\text{\AA}$ ): Pd–N(1)= 2.104(3); Pd–N(2)= 2.104(3); Pd–C(11)= 1.994(3); Pd–C(21)= 1.994(3). Only one of the two slightly different molecules of  $[\text{Pd}(\text{C}_6\text{F}_5)_2\text{py}_2]$  that constitute the asymmetric unit is shown.



**Figure S16.** X-ray structure of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)(\text{NCMe})]$  (**7**) (ORTEP 40% probability ellipsoids). Selected bond lengths (Å): Pd–O(1)= 2.055(2); Pd–N(1) = 2.024(3); Pd–N(2)= 2.001(4); Pd–C<sub>ipso</sub>= 1.999(3).



**Figure S17.** X-ray structure of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**8**) (ORTEP 40% probability ellipsoids). Selected bond lengths (Å): Pd–O(1)= 2.065(3); Pd–N(1) = 2.045(3); Pd–N(2)= 2.039(3); Pd–C<sub>ipso</sub>= 1.995(5). Only one of the two slightly different complex of **8** that constitute the asymmetric unit is shown.

**Table S5.** Crystal data and structure refinements for complexes **1**, **4** and **5**.

	<b>1</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>27</sub> H <sub>41</sub> Br <sub>2</sub> F <sub>3</sub> N <sub>2</sub> Pd	C <sub>40</sub> H <sub>82</sub> N <sub>4</sub> O <sub>6</sub> Pd	C <sub>22</sub> H <sub>10</sub> F <sub>10</sub> N <sub>2</sub> Pd
Formula weight	754.84	821.49	684.25
Temperature/K	298	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic
Space group	P-1	C2/c	P2 <sub>1</sub> /c
a/Å	9.8832(12)	18.3972(5)	9.8649(3)
b/Å	10.4913(12)	12.8302(4)	34.9214(14)
c/Å	16.8579(14)	19.2798(5)	13.1305(5)
α/°	75.651(9)	90	90
β/°	87.092(8)	92.492(2)	109.505(4)
γ/°	71.514(10)	90	90
Volume/Å <sup>3</sup>	1605.3(3)	4546.5(2)	4263.8(3)
Z	2	4	7
ρ <sub>calc</sub> /cm <sup>3</sup>	1.562	1.2	1.865
μ/mm <sup>-1</sup>	7.985	0.453	0.971
F(000)	756	1776	2336
Crystal size/mm <sup>3</sup>	0.232 × 0.206 × 0.163	0.311 × 0.275 × 0.268	0.307 × 0.269 × 0.105
Radiation	Cu Kα (λ = 1.54184)	Mo Kα (λ = 0.71073)	Mo Kα (λ = 0.71073)
2θ range for data collection/°	9.166 to 150.38	6.694 to 59.236	6.578 to 59.526
Index ranges	-7 ≤ h ≤ 12, -10 ≤ k ≤ 13, -19 ≤ l ≤ 20	-23 ≤ h ≤ 22, -17 ≤ k ≤ 11, -26 ≤ l ≤ 19	-9 ≤ h ≤ 13, -24 ≤ k ≤ 45, -16 ≤ l ≤ 17
Reflections collected	9382	12298	18369
Independent reflections	6236 [R <sub>int</sub> = 0.0646, R <sub>sigma</sub> = 0.0671]	5396 [R <sub>int</sub> = 0.0251, R <sub>sigma</sub> = 0.0336]	9904 [R <sub>int</sub> = 0.0285, R <sub>sigma</sub> = 0.0530]
Data/restraints/parameters	6236/0/339	5396/0/246	9904/0/631
Goodness-of-fit on F <sup>2</sup>	1.024	1.056	1.027
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0626, wR <sub>2</sub> = 0.1674	R <sub>1</sub> = 0.0440, wR <sub>2</sub> = 0.1167	R <sub>1</sub> = 0.0394, wR <sub>2</sub> = 0.0778
Final R indexes [all data]	R <sub>1</sub> = 0.0833, wR <sub>2</sub> = 0.2009	R <sub>1</sub> = 0.0561, wR <sub>2</sub> = 0.1284	R <sub>1</sub> = 0.0689, wR <sub>2</sub> = 0.0971
Largest diff. peak/hole / eÅ <sup>-3</sup>	0.90/-0.96	0.48/-0.33	0.49/-0.48



**Table S6.** Crystal data and structure refinements for complexes **7** and **8**.

	<b>7</b>	<b>8</b>
Empirical formula	C <sub>11</sub> H <sub>9</sub> F <sub>5</sub> N <sub>2</sub> O <sub>2</sub> Pd	C <sub>14</sub> H <sub>10</sub> N <sub>2</sub> O <sub>2</sub> F <sub>5</sub> Pd
Formula weight	402.6	439.64
Temperature/K	293(2)	293(2)
Crystal system	orthorhombic	triclinic
Space group	Pbca	P-1
a/Å	10.3513(4)	10.0930(7)
b/Å	9.1559(3)	11.7688(8)
c/Å	28.7456(8)	14.7684(9)
α/°	90	107.490(6)
β/°	90	107.025(6)
γ/°	90	100.307(6)
Volume/Å <sup>3</sup>	2724.38(16)	1529.75(19)
Z	8	4
ρ <sub>calc</sub> /cm <sup>3</sup>	1.963	1.909
μ/mm <sup>-1</sup>	1.425	1.278
F(000)	1568	860
Crystal size/mm <sup>3</sup>	0.604 × 0.332 × 0.261	0.371 × 0.075 × 0.073
Radiation	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)
2θ range for data collection/°	6.582 to 59.102	7.044 to 59.192
Index ranges	-10 ≤ h ≤ 14, -12 ≤ k ≤ 7, -38 ≤ l ≤ 37	-12 ≤ h ≤ 11, -11 ≤ k ≤ 16, -20 ≤ l ≤ 17
Reflections collected	9235	10727
Independent reflections	3325 [R <sub>int</sub> = 0.0361, R <sub>sigma</sub> = 0.0477]	7020 [R <sub>int</sub> = 0.0332, R <sub>sigma</sub> = 0.0675]
Data/restraints/parameters	3325/0/192	7020/0/435
Goodness-of-fit on F <sup>2</sup>	1.079	1.039
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0384, wR <sub>2</sub> = 0.0716	R <sub>1</sub> = 0.0434, wR <sub>2</sub> = 0.0829
Final R indexes [all data]	R <sub>1</sub> = 0.0694, wR <sub>2</sub> = 0.0869	R <sub>1</sub> = 0.0718, wR <sub>2</sub> = 0.1029
Largest diff. peak/hole / eÅ <sup>-3</sup>	0.34/-0.85	0.67/-0.75

### 3. Selected NMR spectra

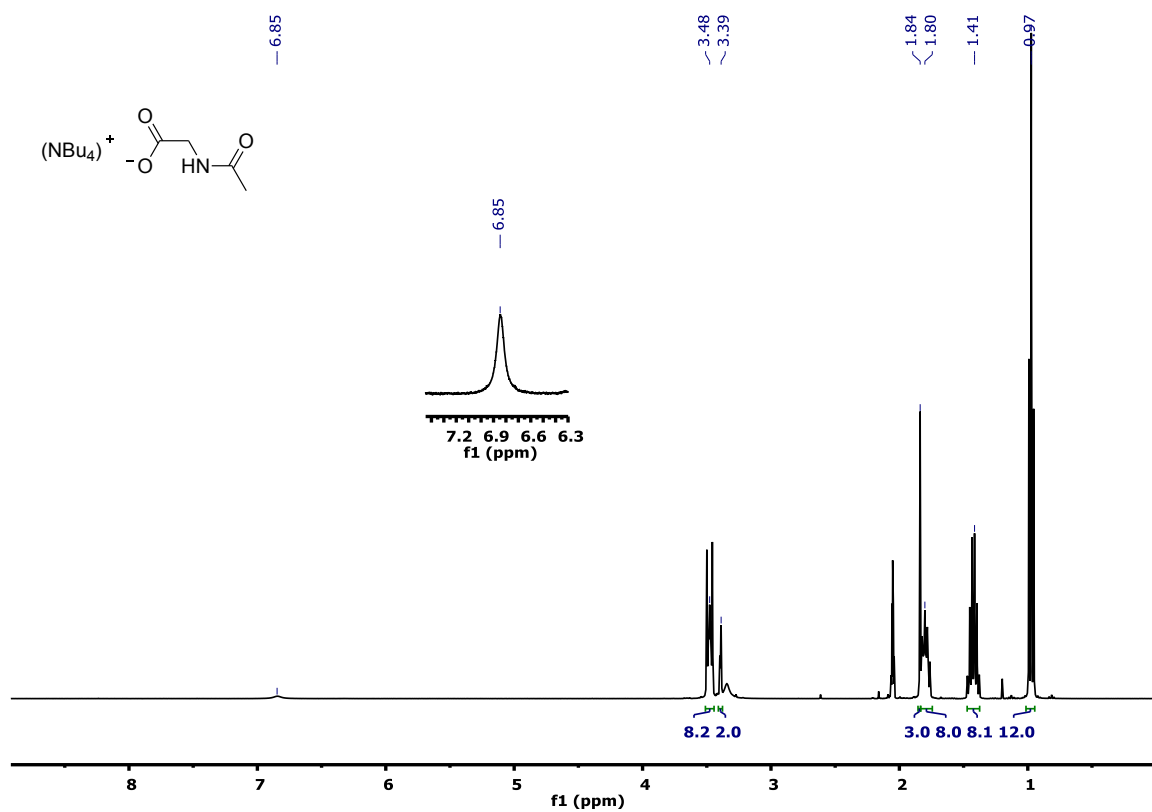


Figure S18.  $^1\text{H}$  NMR (399.86 MHz,  $\text{acetone-}d_6$ , 298 K) of  $(\text{NBu}_4)(\text{NH-acetyl})\text{glycine}$ .

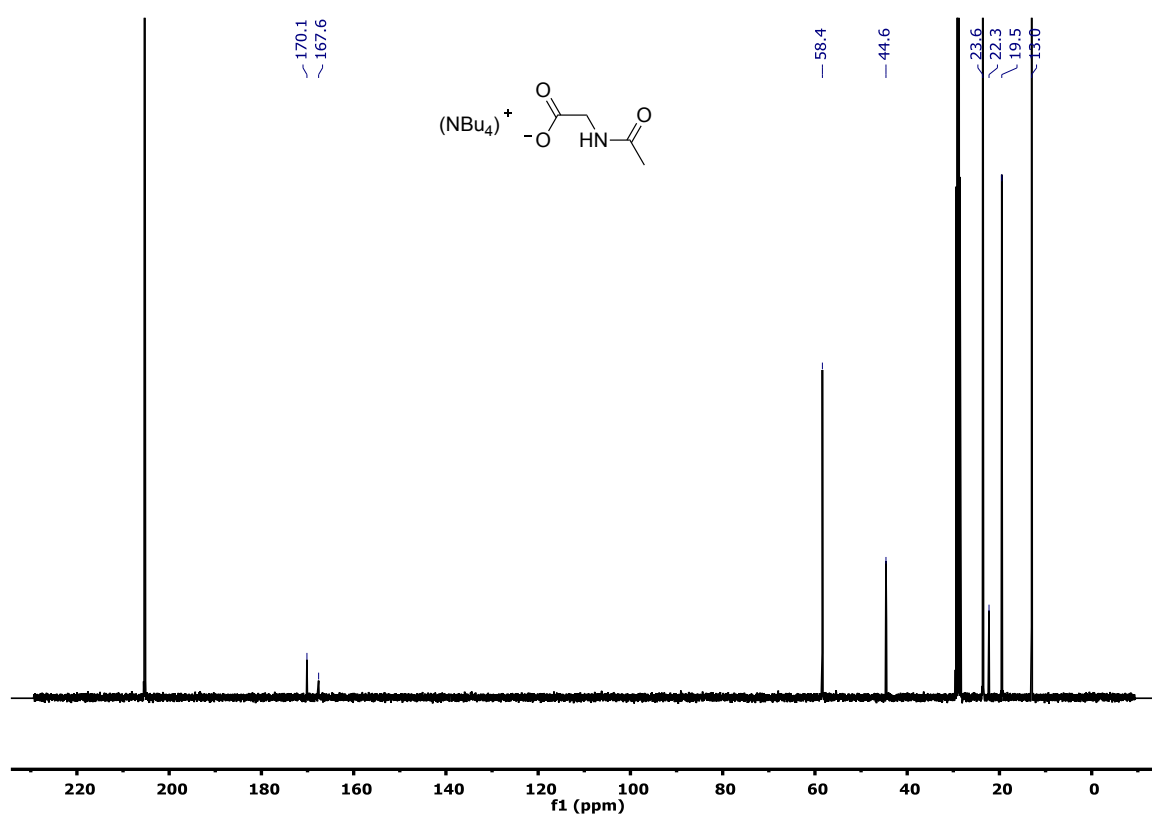


Figure S19.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.56 MHz,  $\text{acetone-}d_6$ , 298 K) of  $(\text{NBu}_4)(\text{NH-acetyl})\text{glycine}$ .

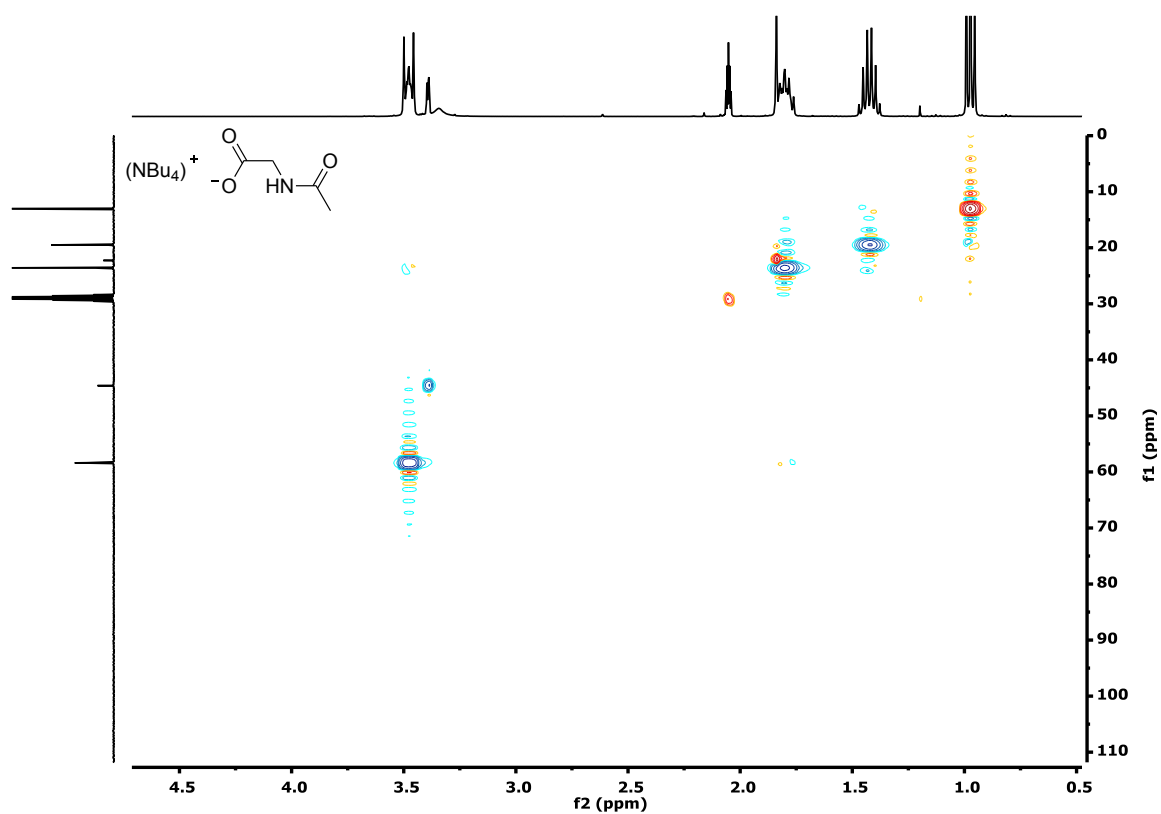


Figure S20.  $^1\text{H}$ - $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)(\text{NH-acetylglycine})$  in acetone- $d_6$  at 298 K.

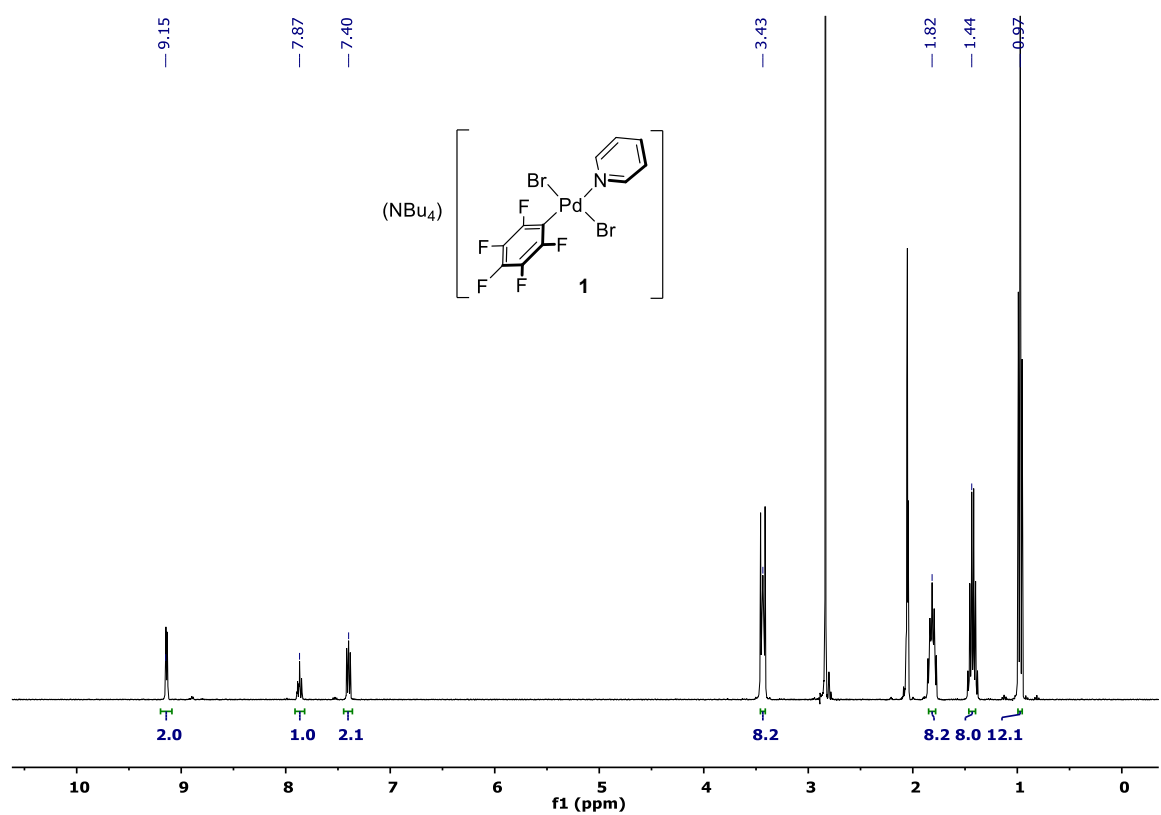


Figure S21.  $^1\text{H}$  NMR (499.73 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (**1**).

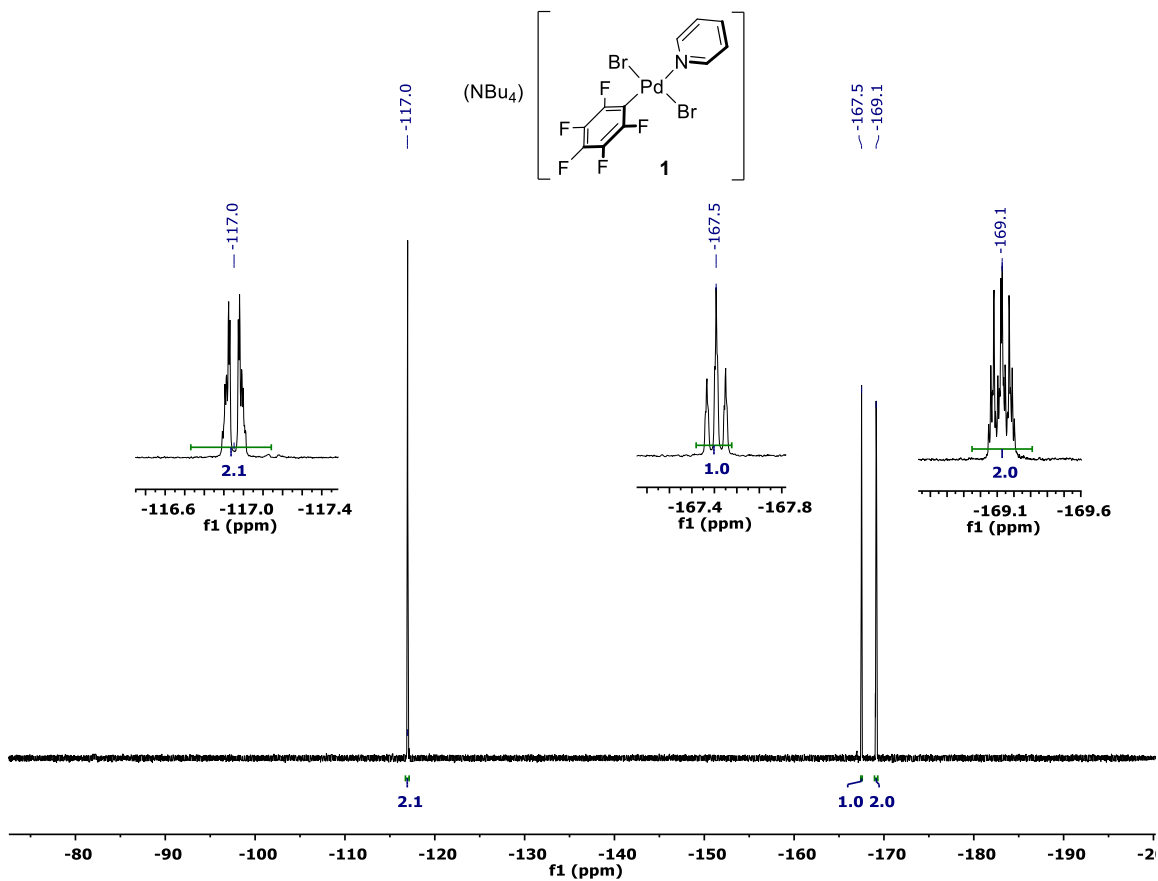


Figure S22.  $^{19}\text{F}$  NMR (470.17 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (**1**).

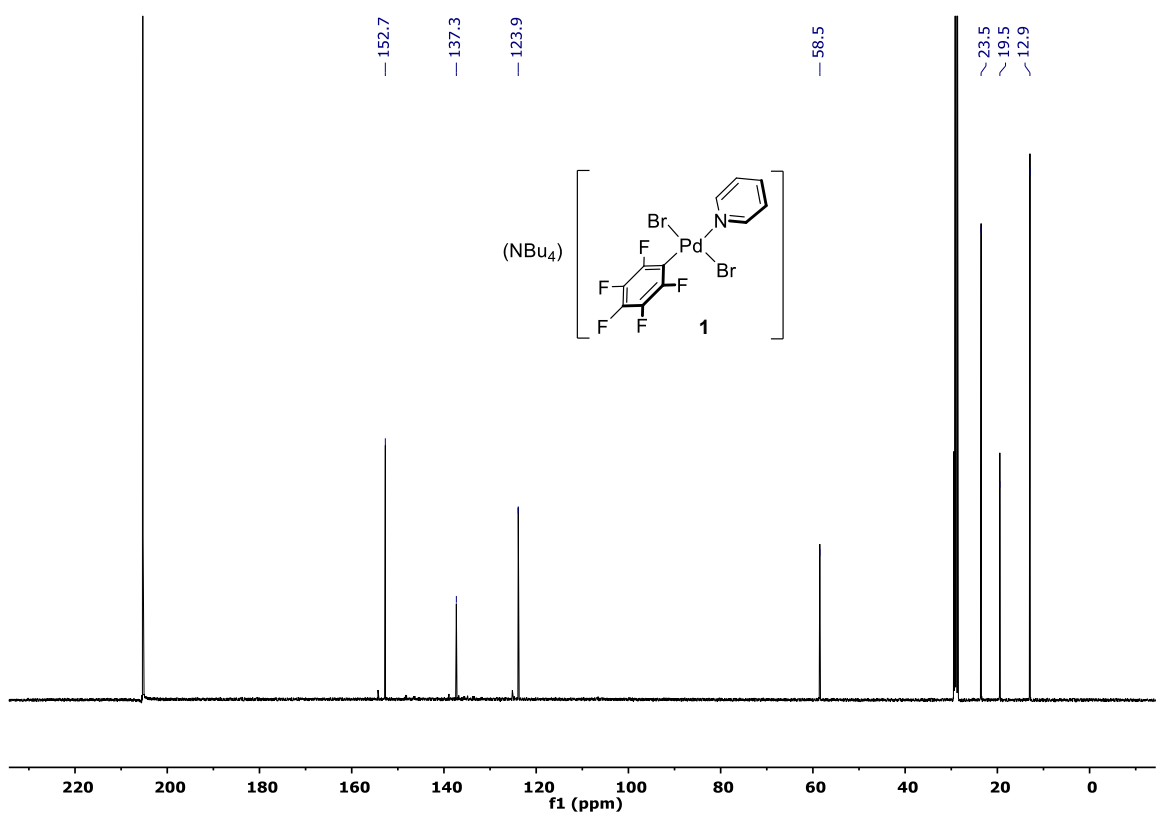


Figure S23.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (**1**).

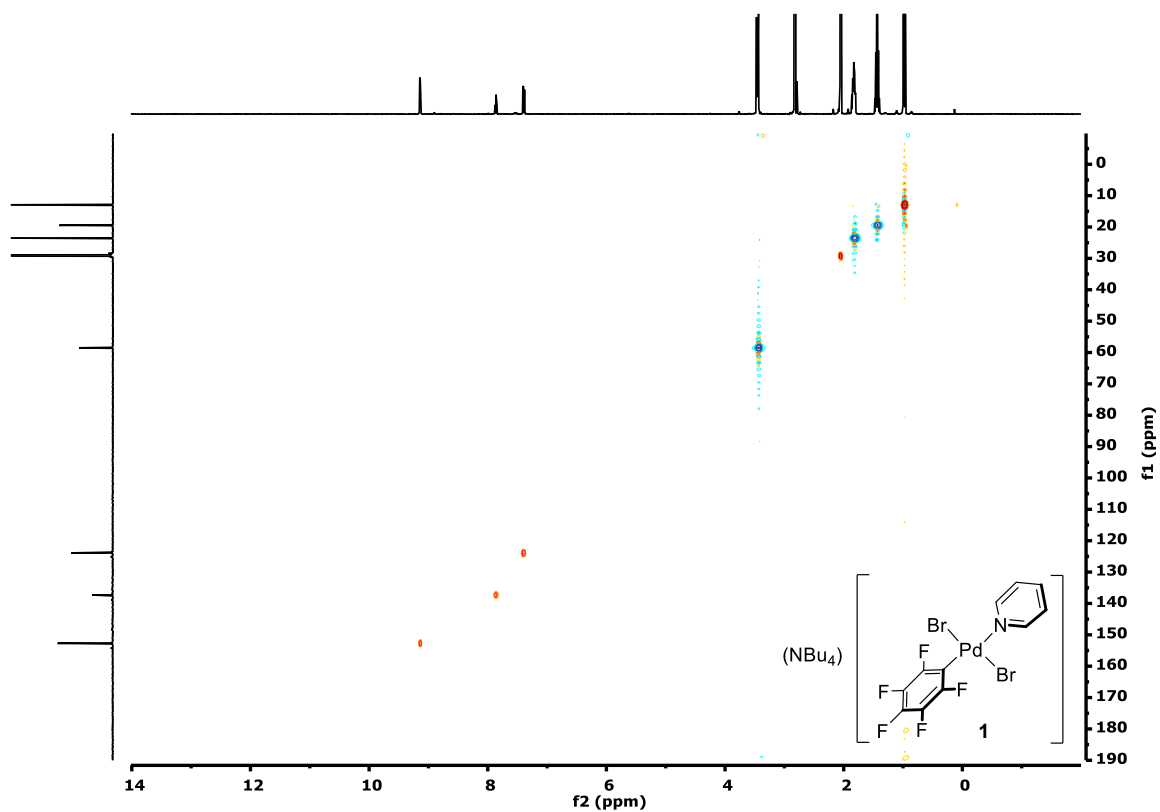


Figure S24.  $^1\text{H}$ - $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (1) in  $\text{acetone-}d_6$  at 298 K.

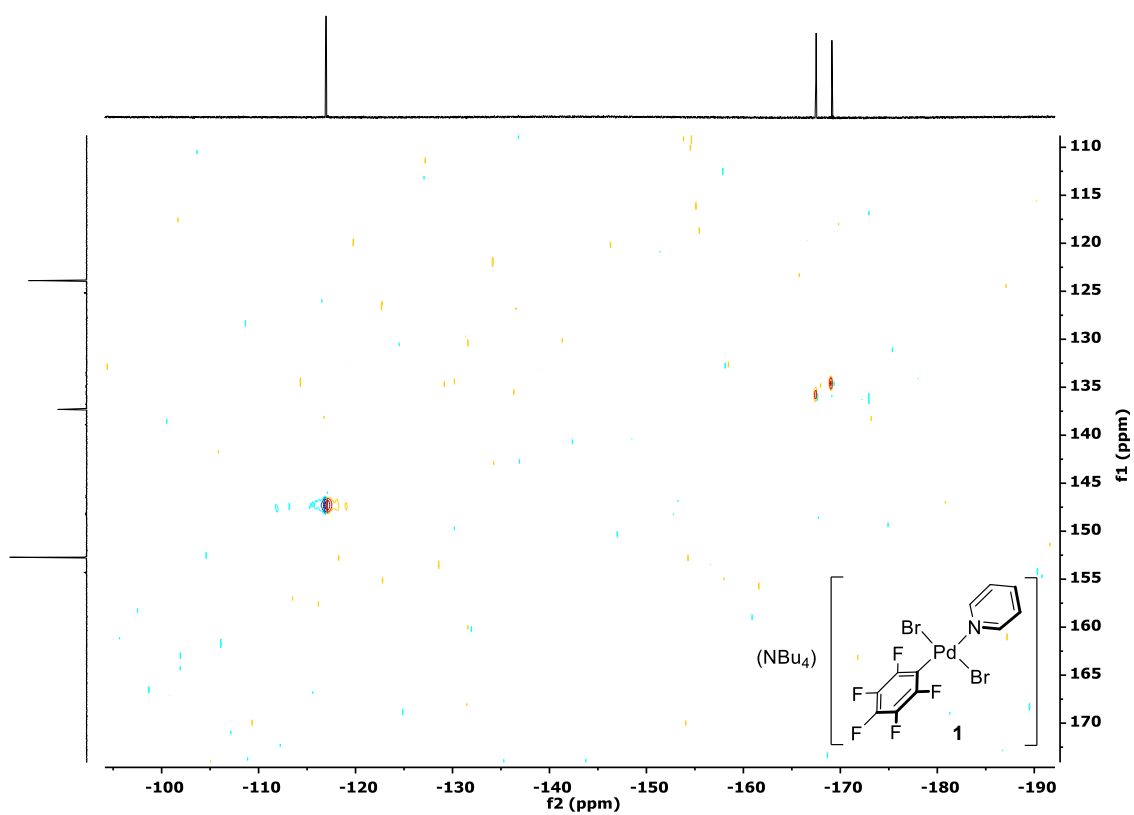


Figure S25.  $^{19}\text{F}$ - $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)[\text{PdBr}_2(\text{C}_6\text{F}_5)\text{py}]$  (1) in  $\text{acetone-}d_6$  at 298 K.

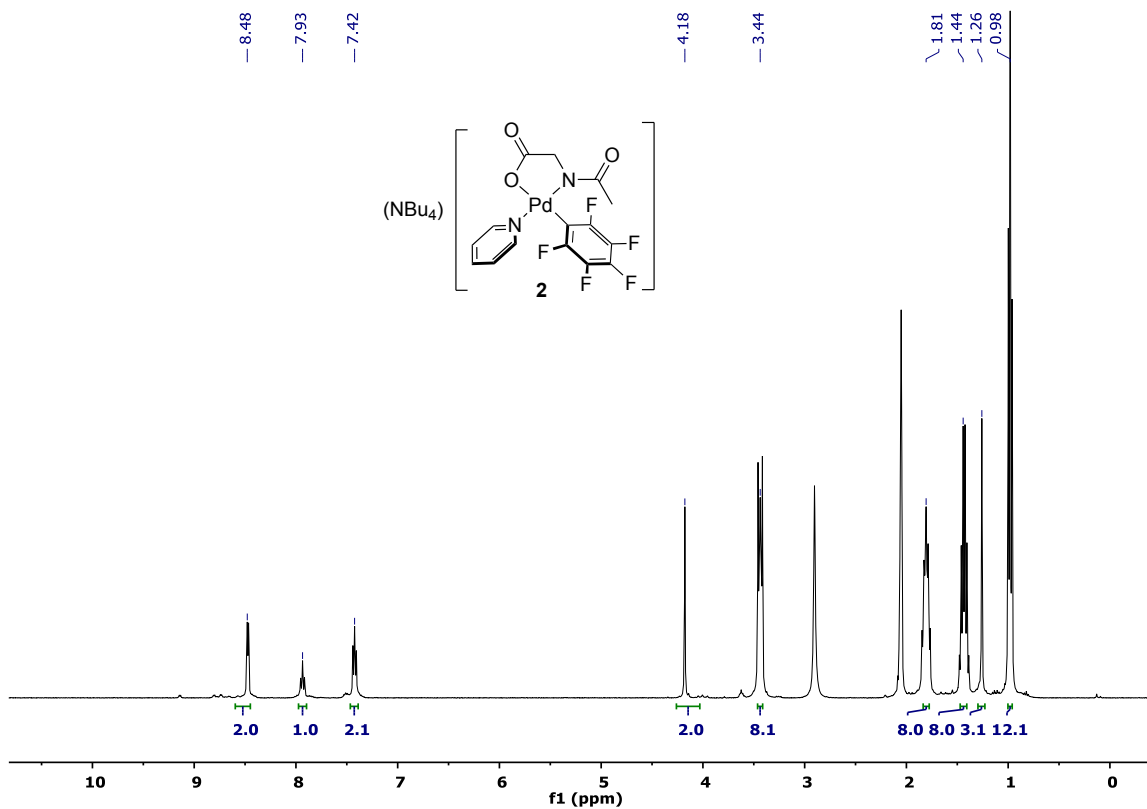


Figure S26.  $^1\text{H}$  NMR (499.73 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (2).

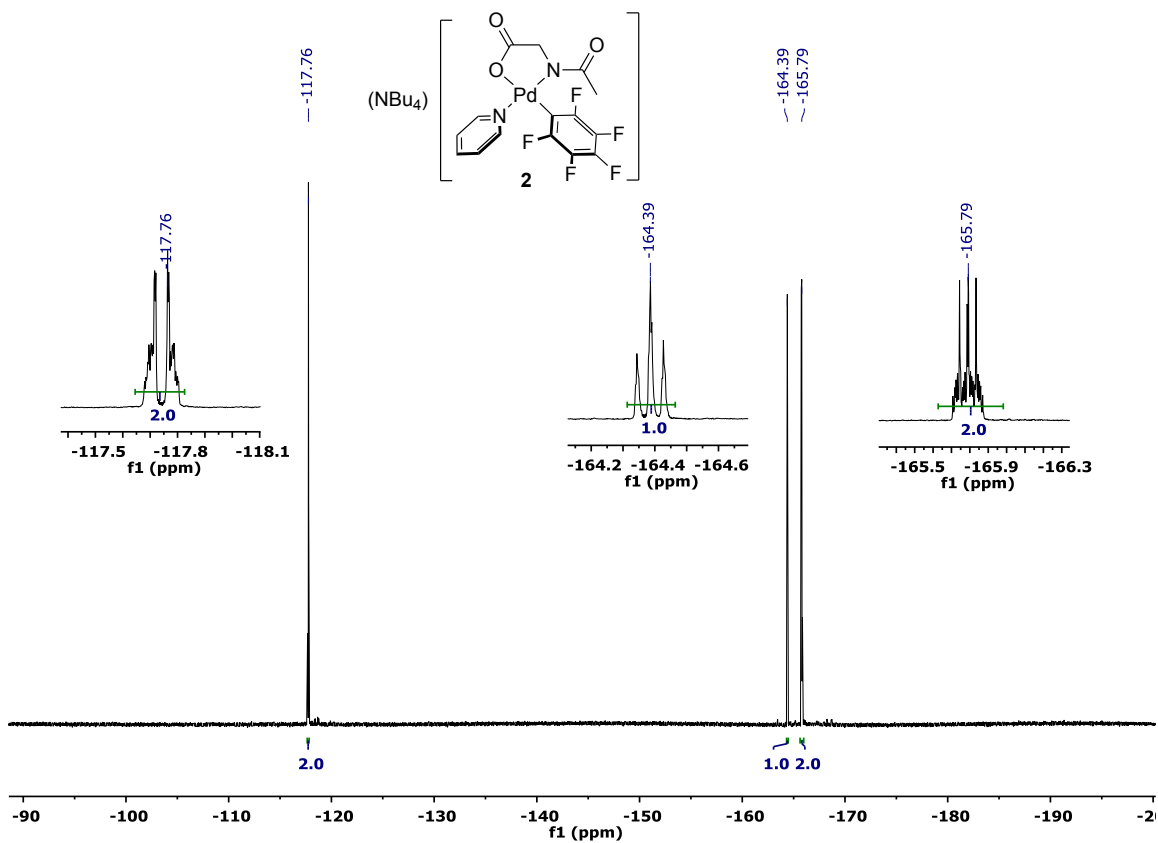


Figure S27.  $^{19}\text{F}$  NMR (470.17 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (2).

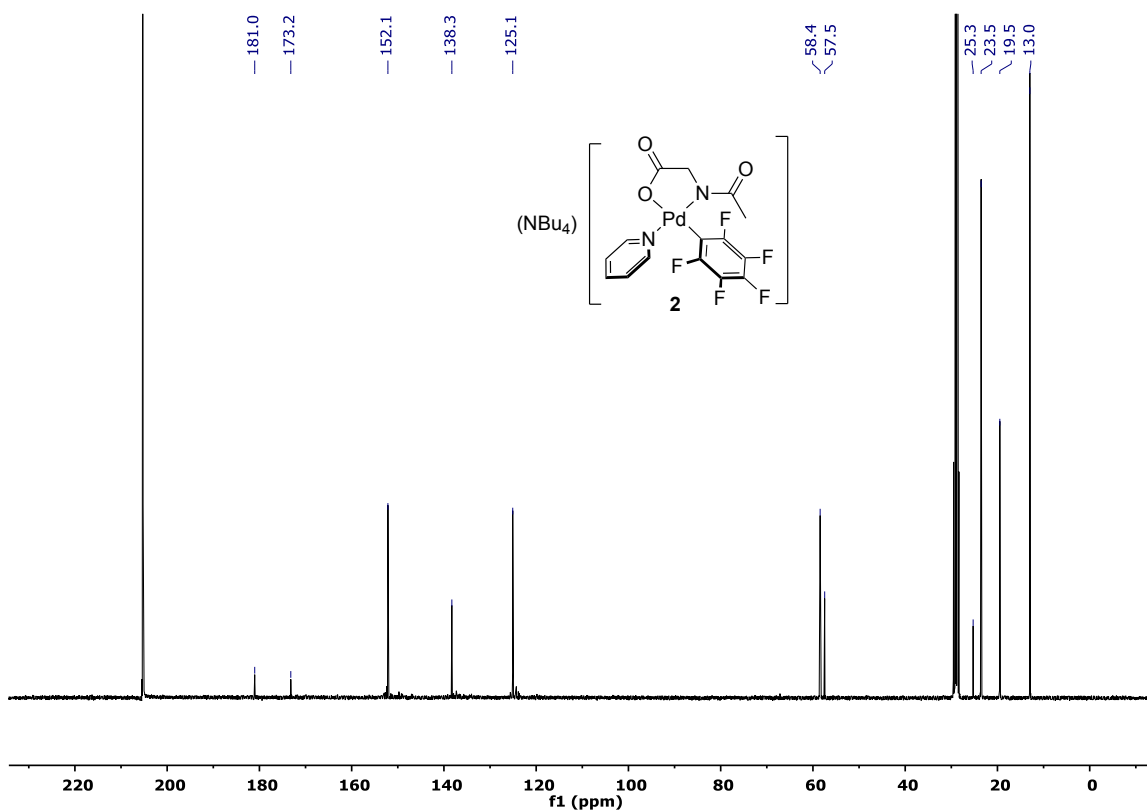


Figure S28.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.56 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**2**).

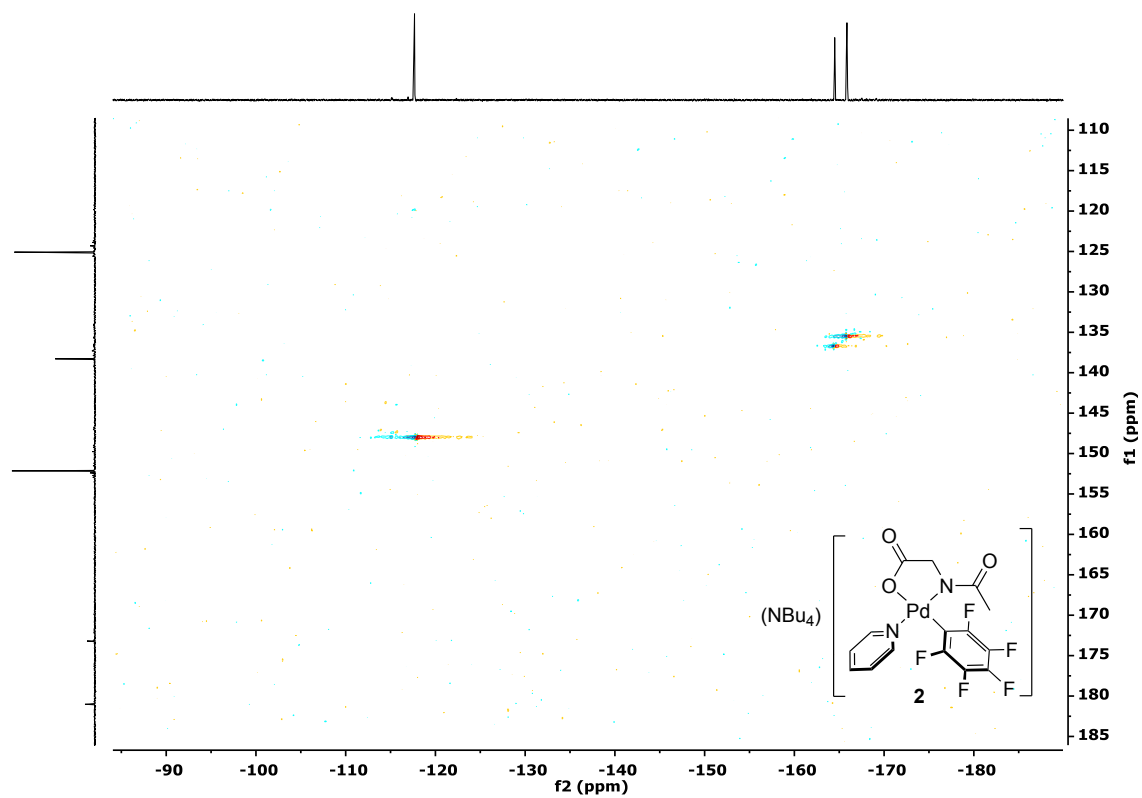


Figure S29.  $^{19}\text{F}$  -  $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  in acetone- $d_6$  at 298 K (**2**).

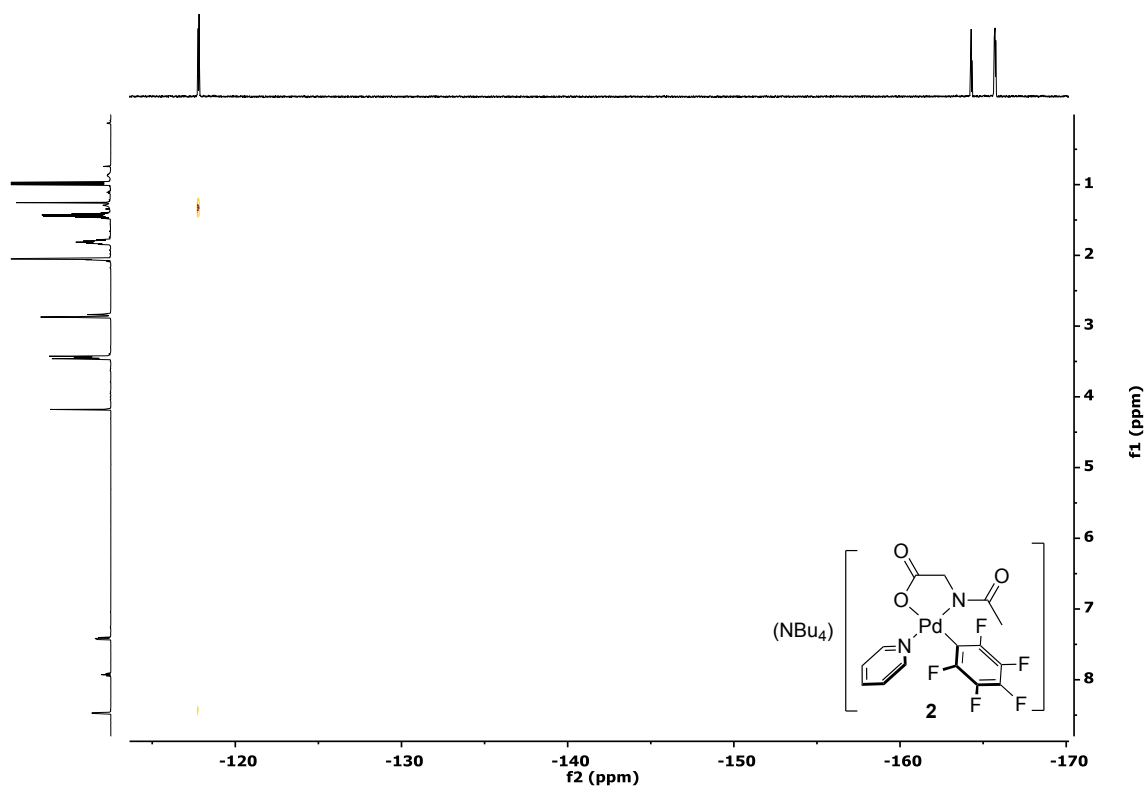


Figure S30.  $^1\text{H} - ^{19}\text{F}$  HOESY of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  in acetone- $d_6$  at 298 K (2).

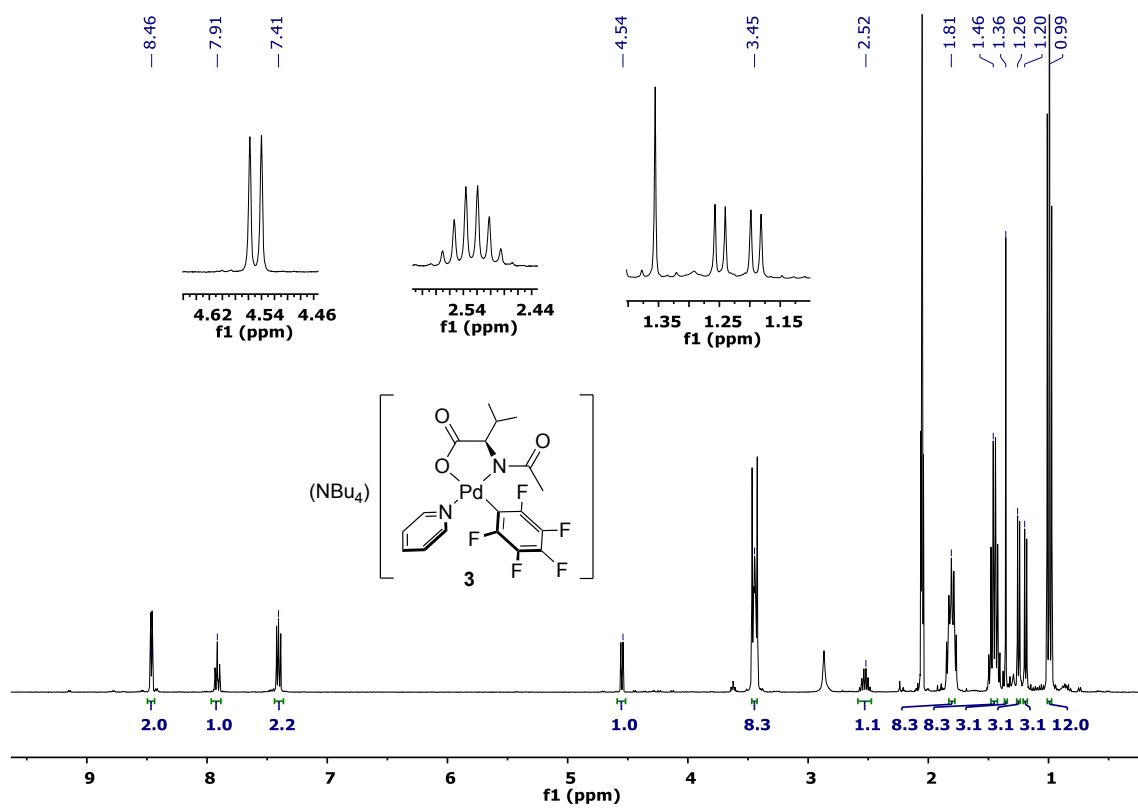


Figure S31.  $^1\text{H}$  NMR (499.73 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Val-O})(\text{C}_6\text{F}_5)\text{py}]$  (3).



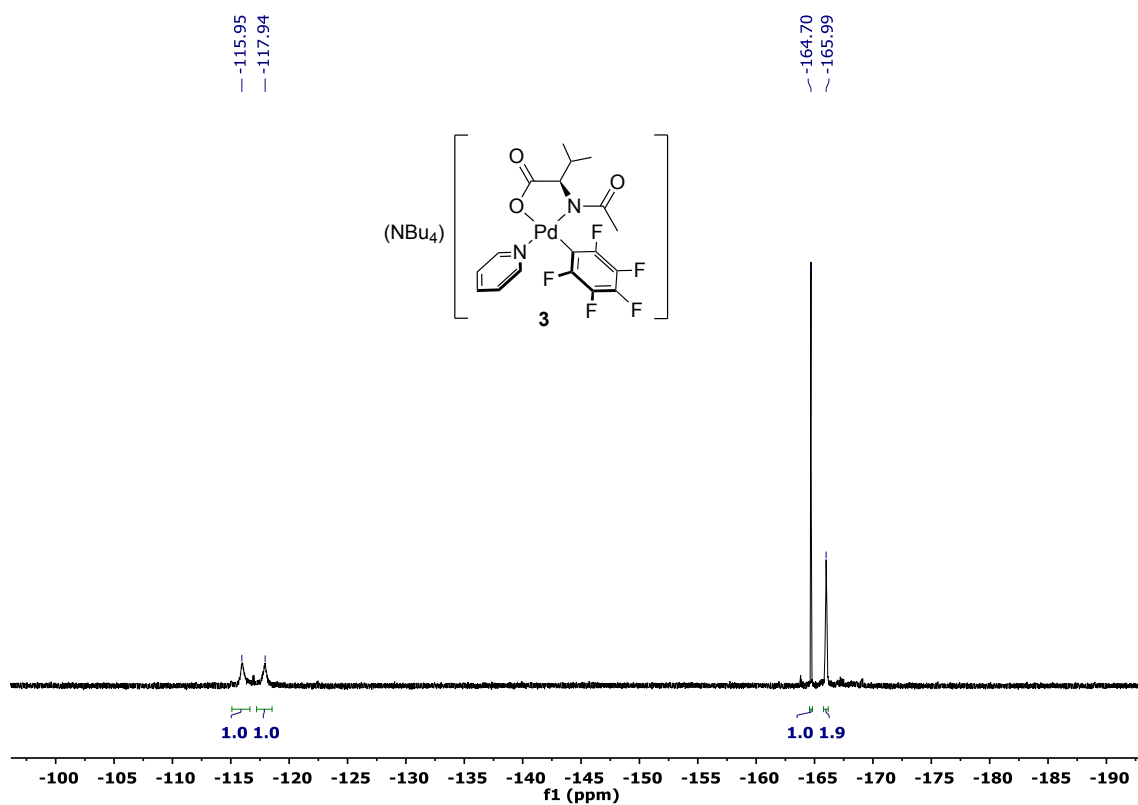


Figure S32.  $^{19}F$  NMR (470.17 MHz, acetone- $d_6$ , 298 K) of  $(NBu_4)[Pd((\kappa^2-N,O\text{-AcN-Val-O})(C_6F_5)py)]$  (**3**).

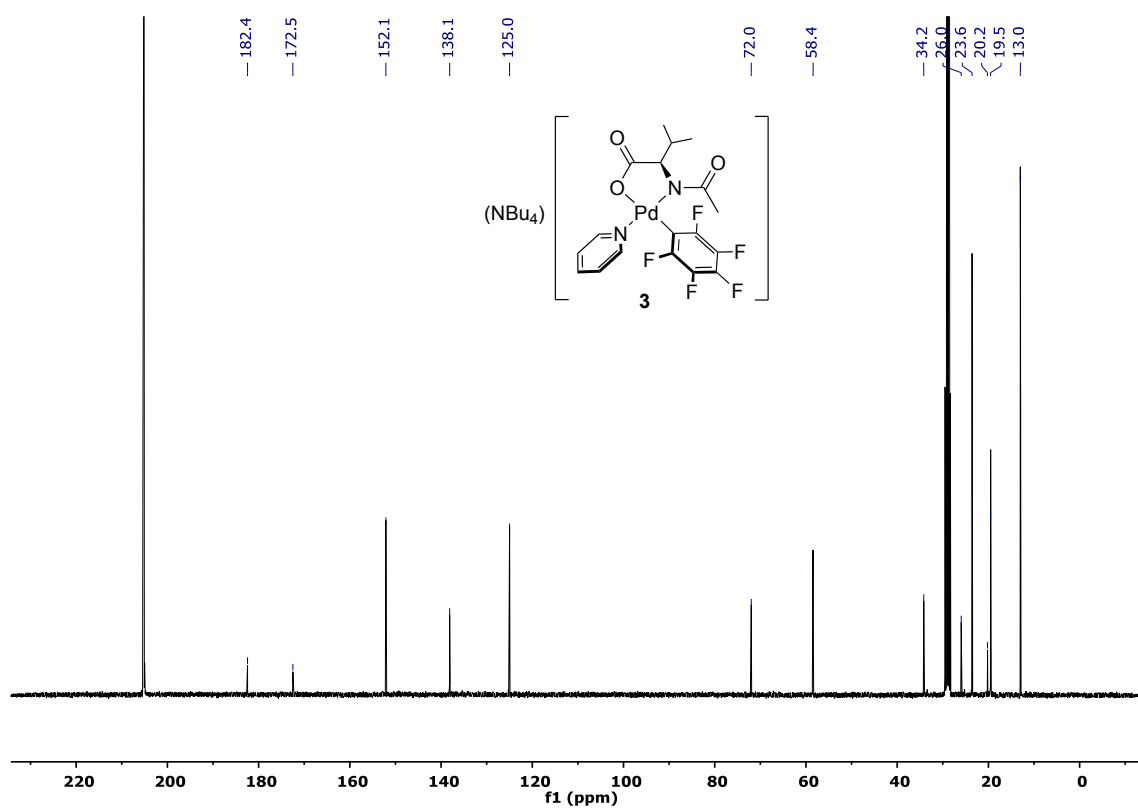


Figure S33.  $^{13}C\{^1H\}$  NMR (125.67 MHz, acetone- $d_6$ , 298 K) of  $(NBu_4)[Pd((\kappa^2-N,O\text{-AcN-Val-O})(C_6F_5)py)]$  (**3**).

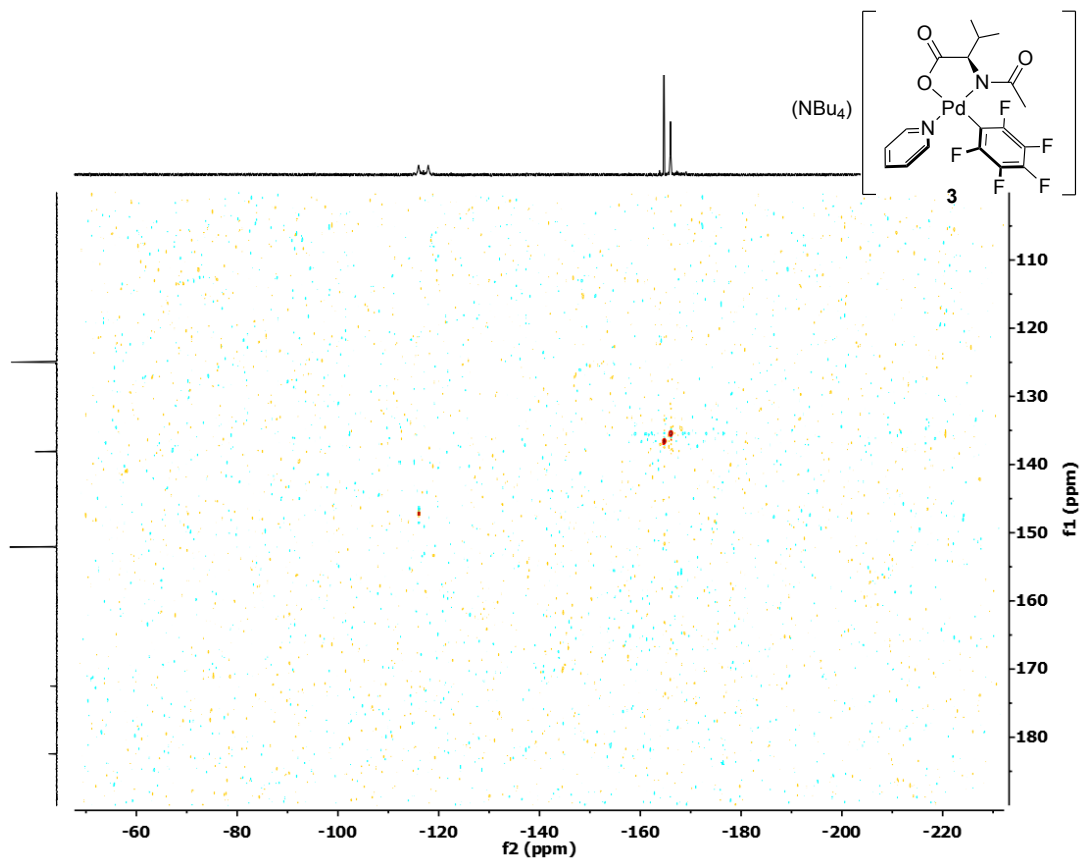


Figure S34.  $^{19}\text{F}$  -  $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)[\text{Pd}((\kappa^2\text{-}N,O\text{-AcN-Val-O})(\text{C}_6\text{F}_5)\text{py})]$  (**3**), in acetone- $d_6$  at 298 K.

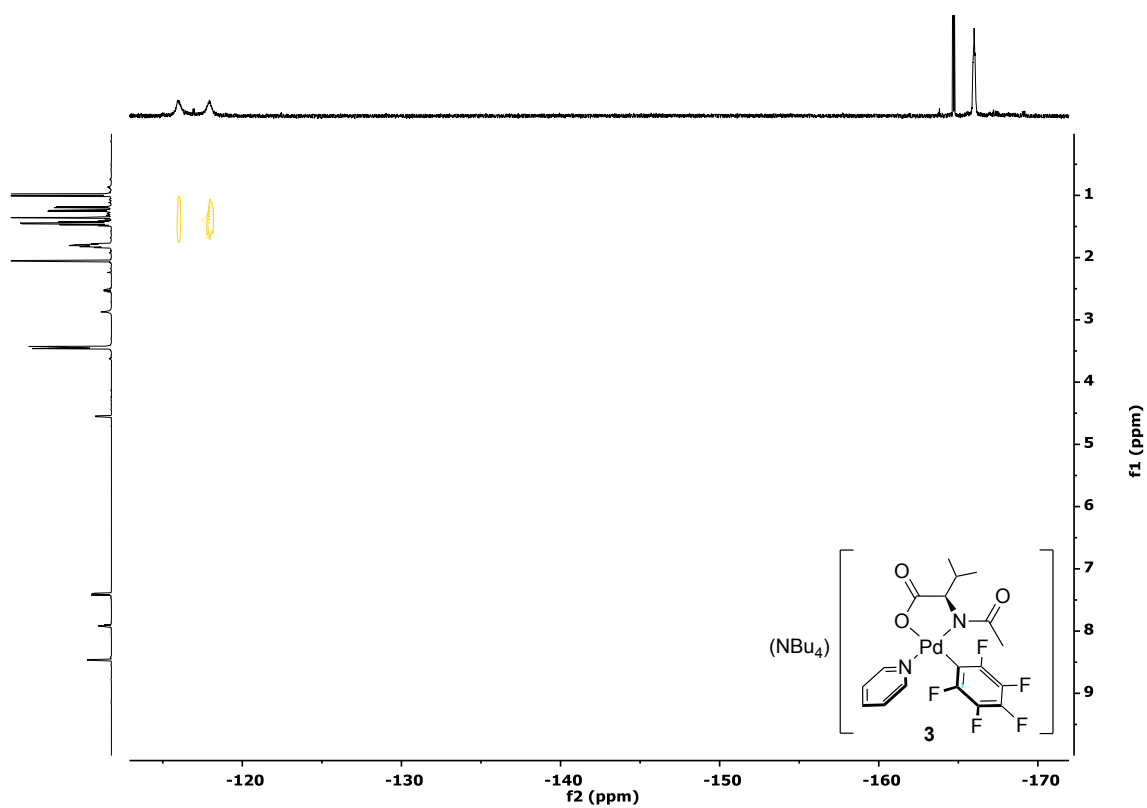


Figure S35.  $^1\text{H}$  -  $^{19}\text{F}$  HOESY of  $(\text{NBu}_4)[\text{Pd}((\kappa^2\text{-}N,O\text{-AcN-Val-O})(\text{C}_6\text{F}_5)\text{py})]$  (**3**) in acetone- $d_6$  at 298 K.

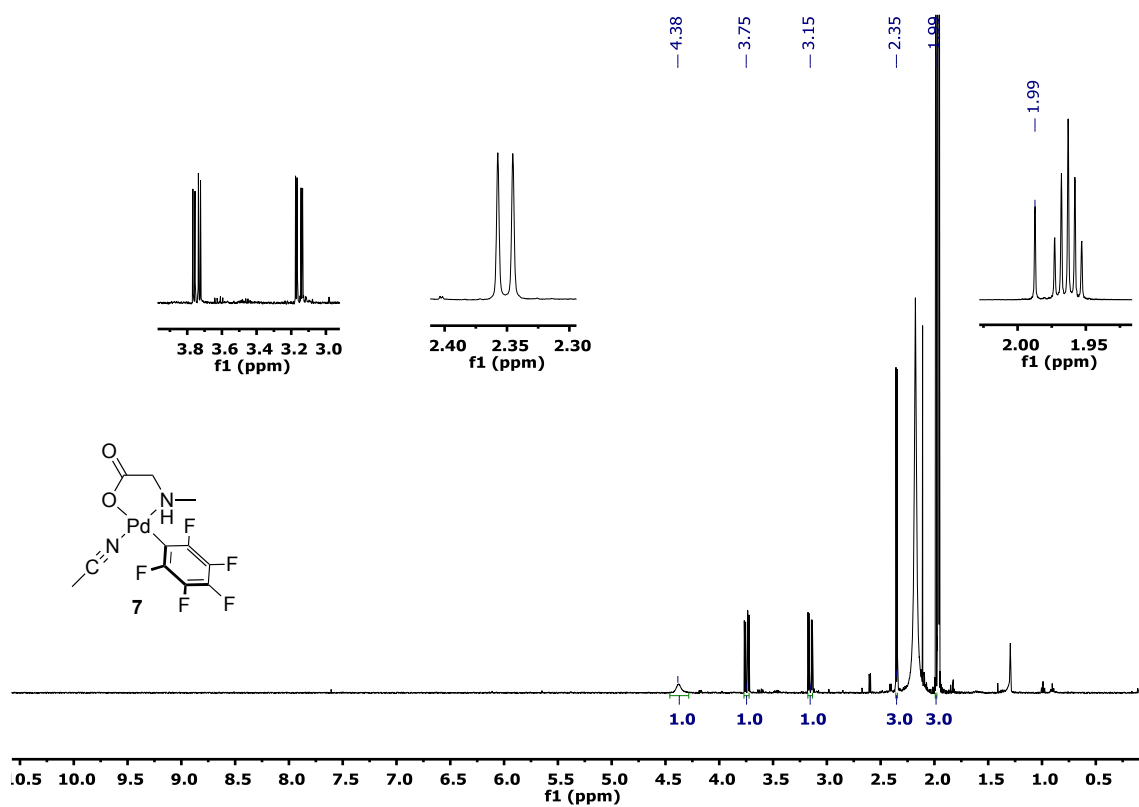


Figure S36. <sup>1</sup>H NMR (499.73 MHz, CD<sub>3</sub>CN, 298 K) of [Pd(κ<sup>2</sup>-N,O-MeNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)(NCMe)] (7).

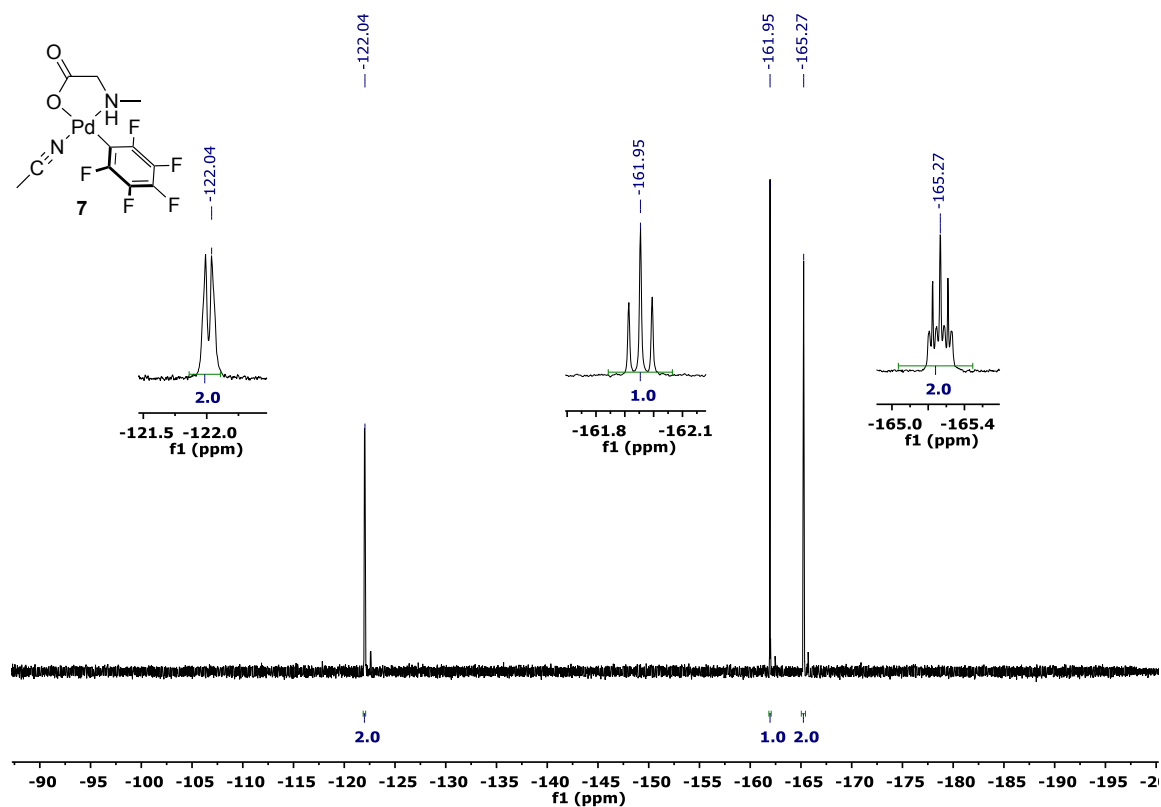


Figure S37. <sup>19</sup>F NMR (470.17 MHz, CD<sub>3</sub>CN, 298 K) of [Pd(κ<sup>2</sup>-N,O-MeNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)(NCMe)] (7).

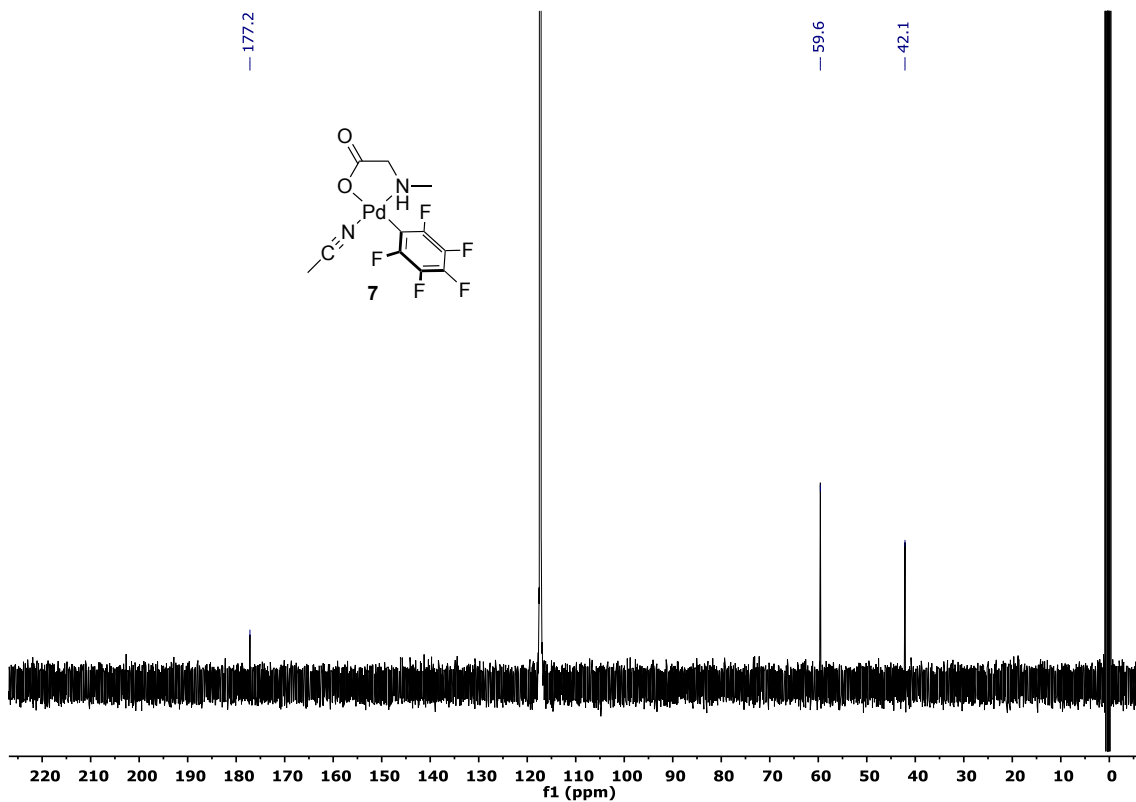


Figure S38.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz,  $\text{CD}_3\text{CN}$ , 298 K) of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)(\text{NCMe})]$  (7).

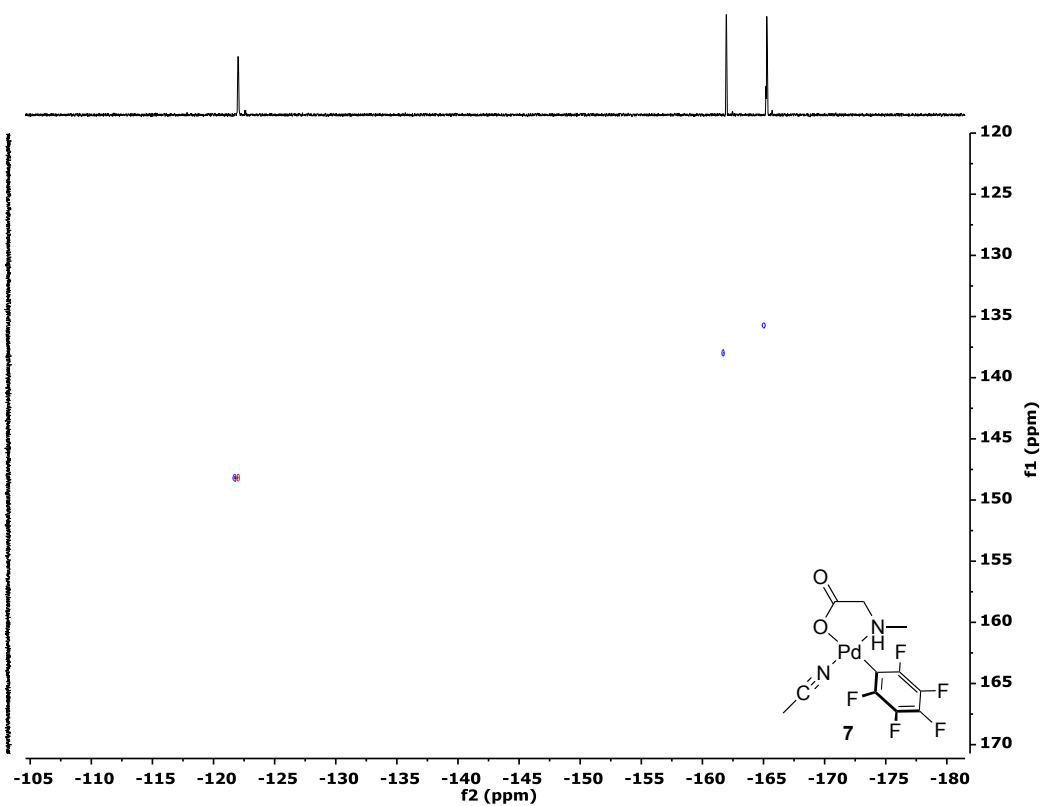


Figure S39.  $^{19}\text{F} - ^{13}\text{C}$  HSQC of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)(\text{NCMe})]$  (7) in  $\text{CD}_3\text{CN}$  at 298 K.

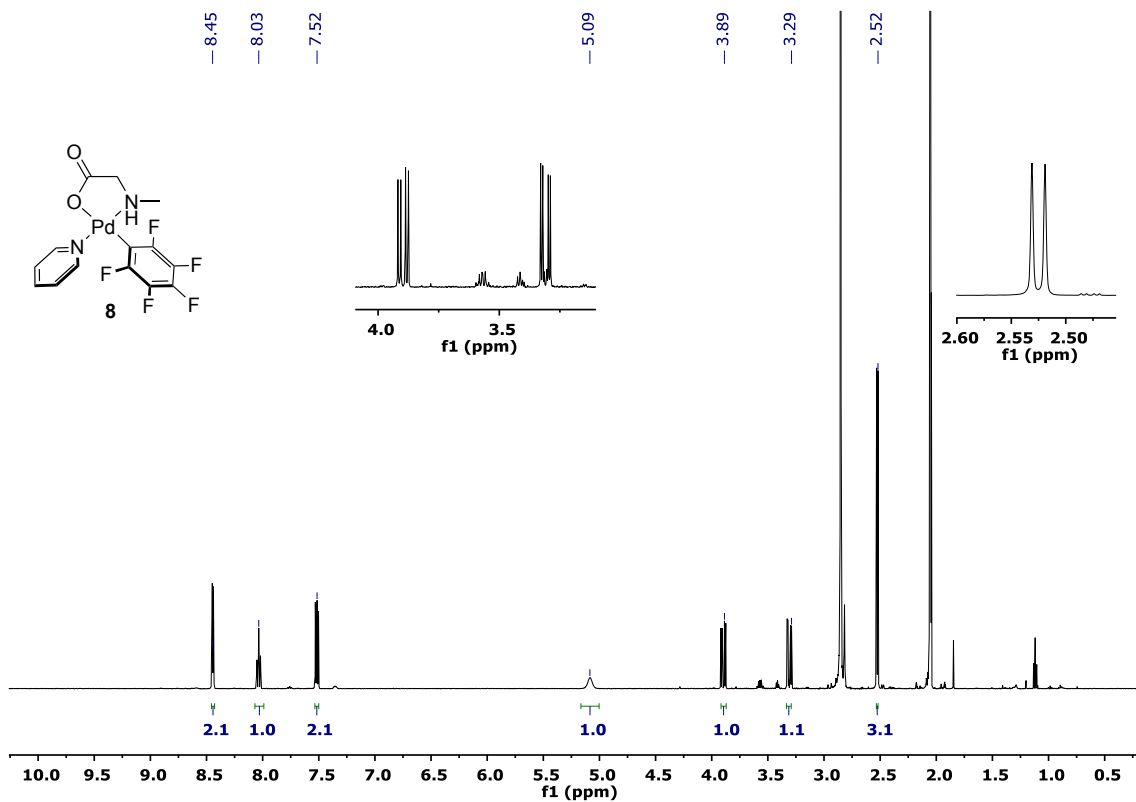


Figure S40. <sup>1</sup>H NMR (499.73 MHz, acetone-*d*<sub>6</sub>, 298 K) of [Pd( $\kappa^2$ -*N,O*-MeNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)py] (**8**).

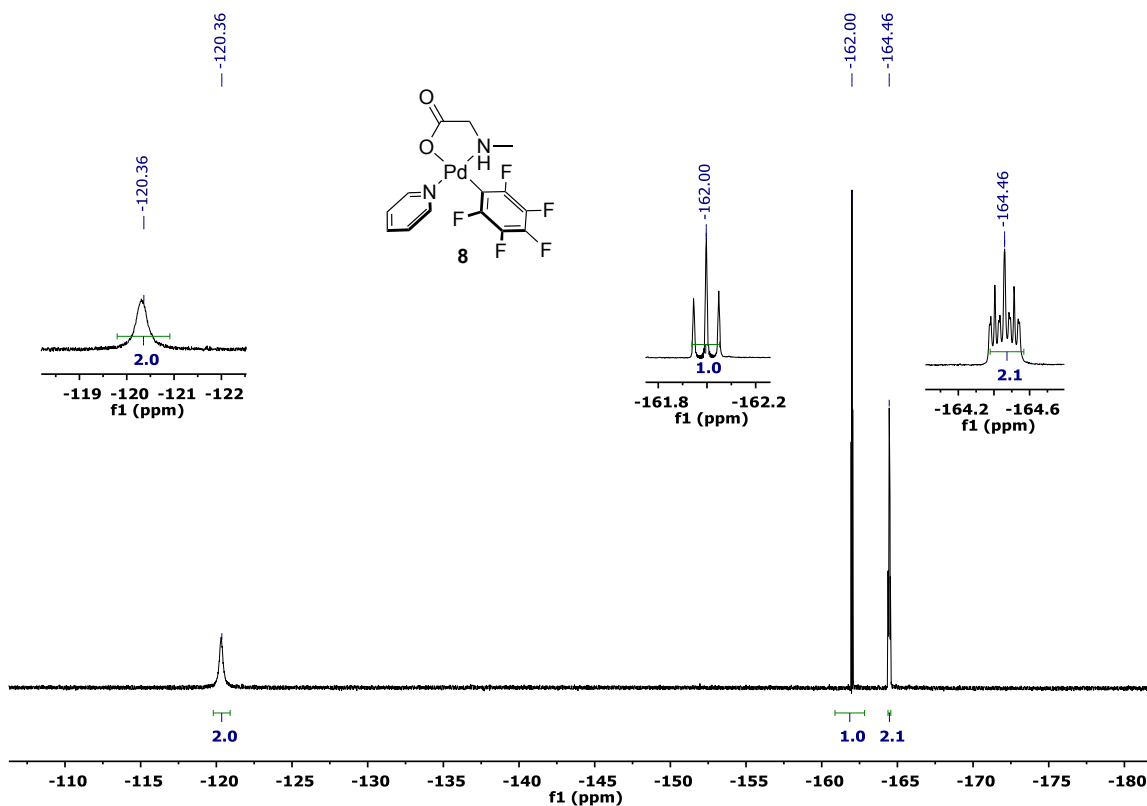


Figure S41. <sup>19</sup>F NMR (470.17 MHz, acetone-*d*<sub>6</sub>, 298 K) of [Pd( $\kappa^2$ -*N,O*-MeNH-Gly-O)(C<sub>6</sub>F<sub>5</sub>)py] (**8**).

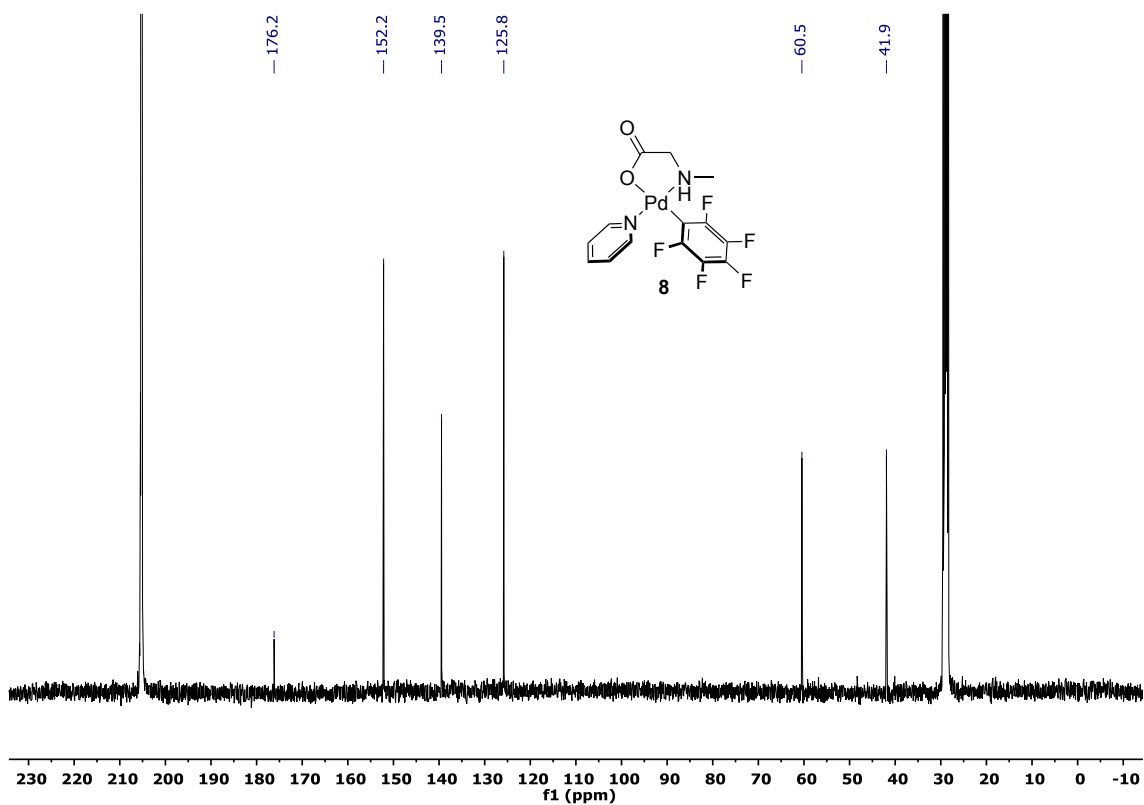


Figure S42.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz, acetone- $d_6$ , 298 K) of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**8**).

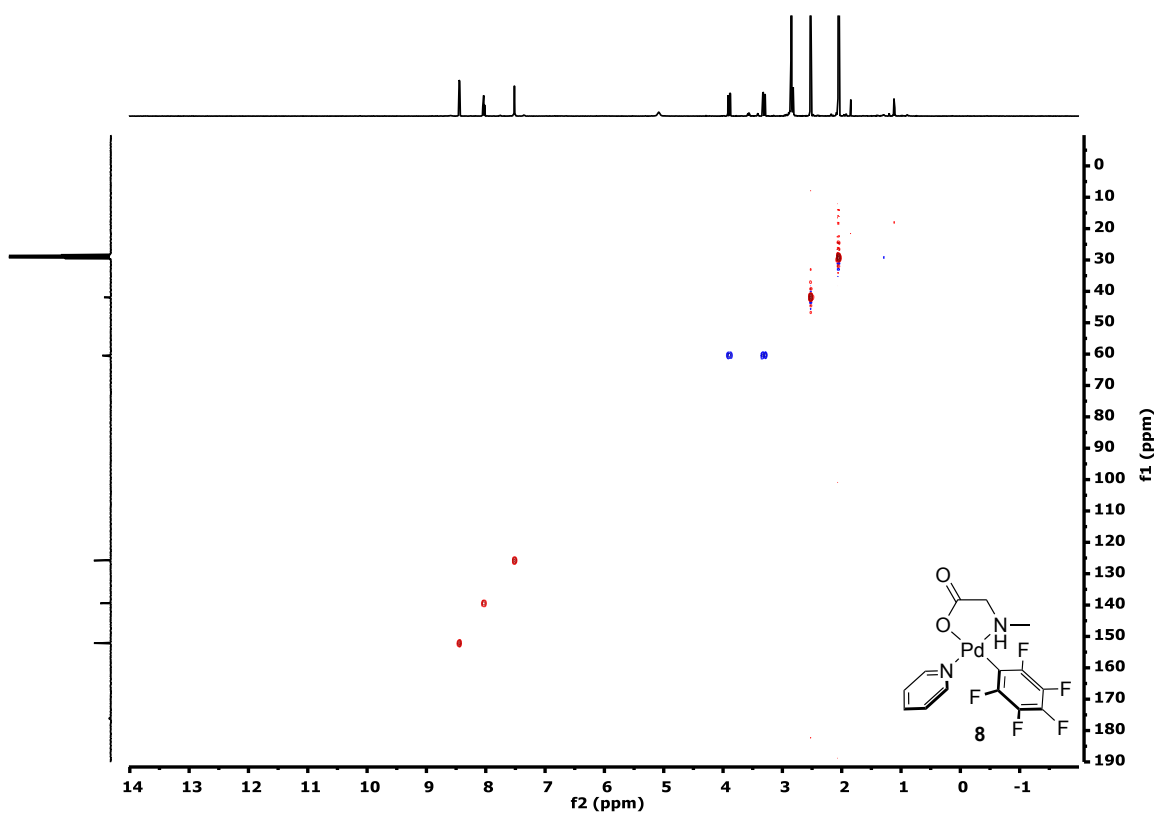


Figure S43.  $^1\text{H}\text{-}^{13}\text{C}$  HSQC of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**8**) in acetone- $d_6$  at 298 K.

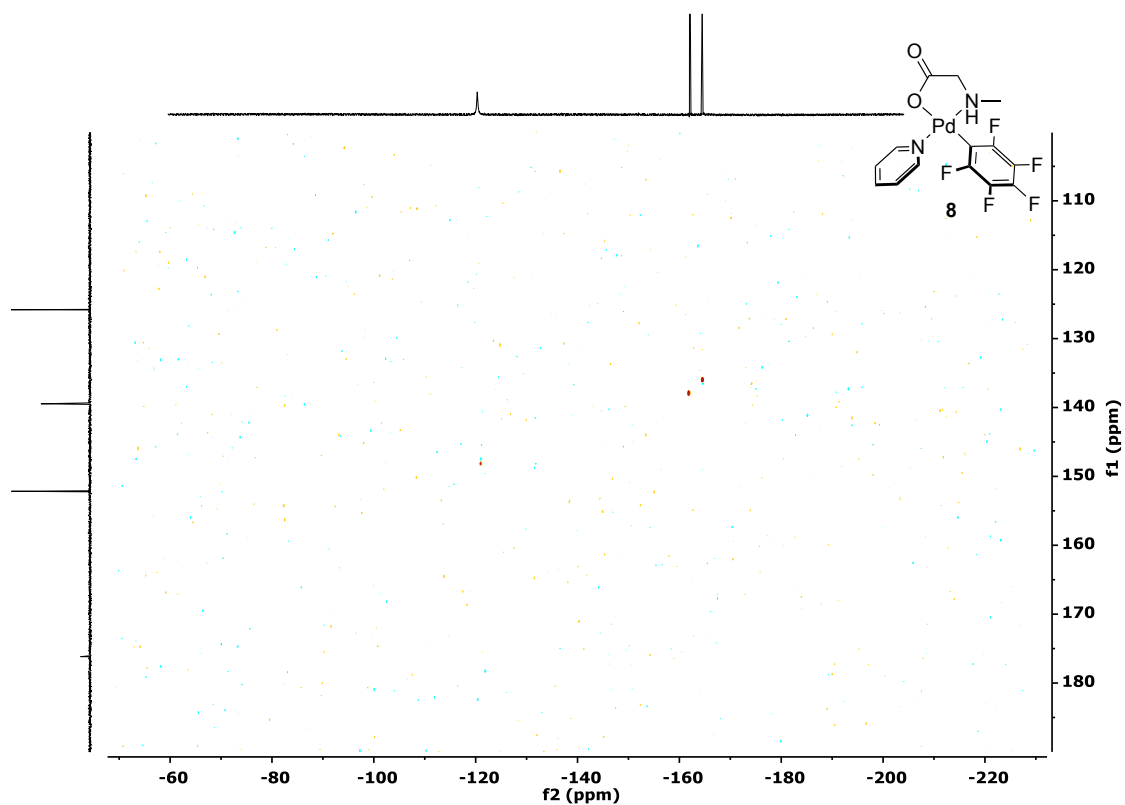


Figure S44.  $^{19}\text{F}$  -  $^{13}\text{C}$  HSQC of  $[\text{Pd}(\kappa^2\text{-}N,O\text{-MeNH-Gly-O})(\text{C}_6\text{F}_5)\text{py}]$  (**8**) in acetone- $d_6$  at 298 K.

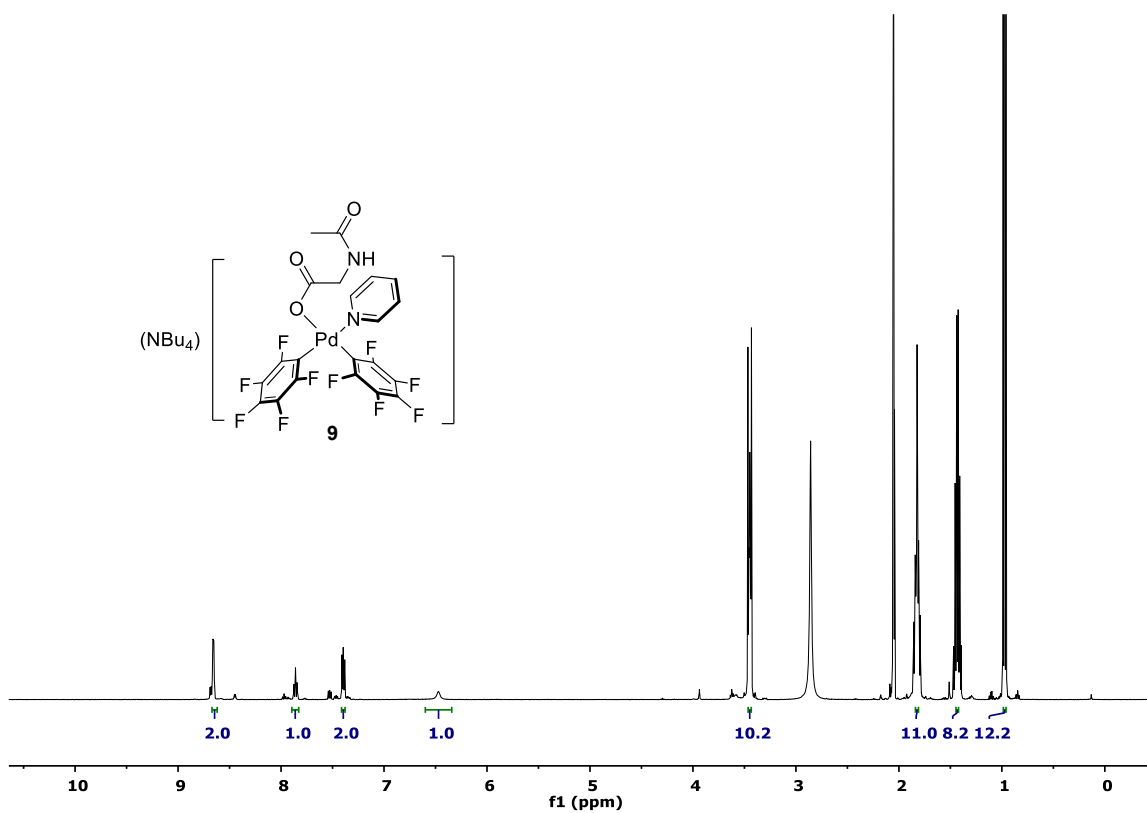


Figure S45.  $^1\text{H}$  NMR (399.86 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^1\text{-}O\text{-AcNH-Gly-O})(\text{C}_6\text{F}_5)_2\text{py}]$  (**9**).

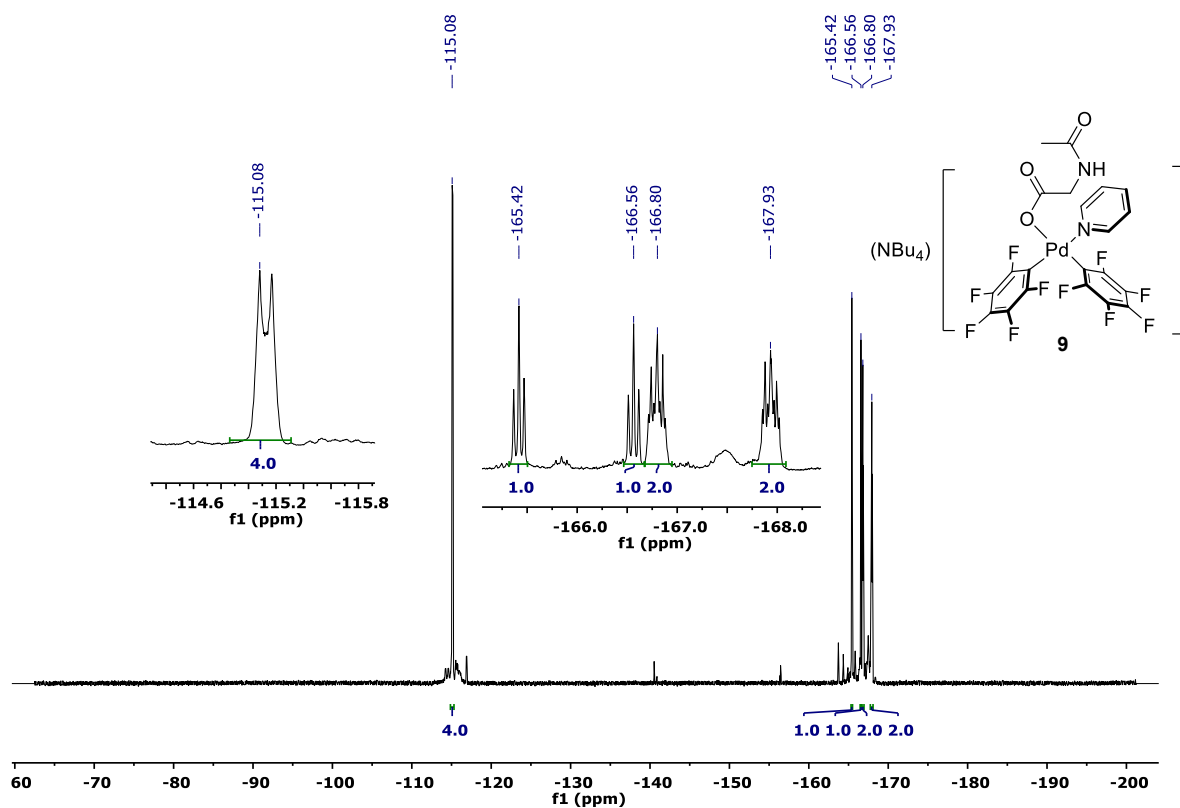


Figure S46.  $^{19}\text{F}$  NMR (376.19 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^1\text{-O-AcNH-Gly-O})(\text{C}_6\text{F}_5)_2\text{py}]$  (**9**).

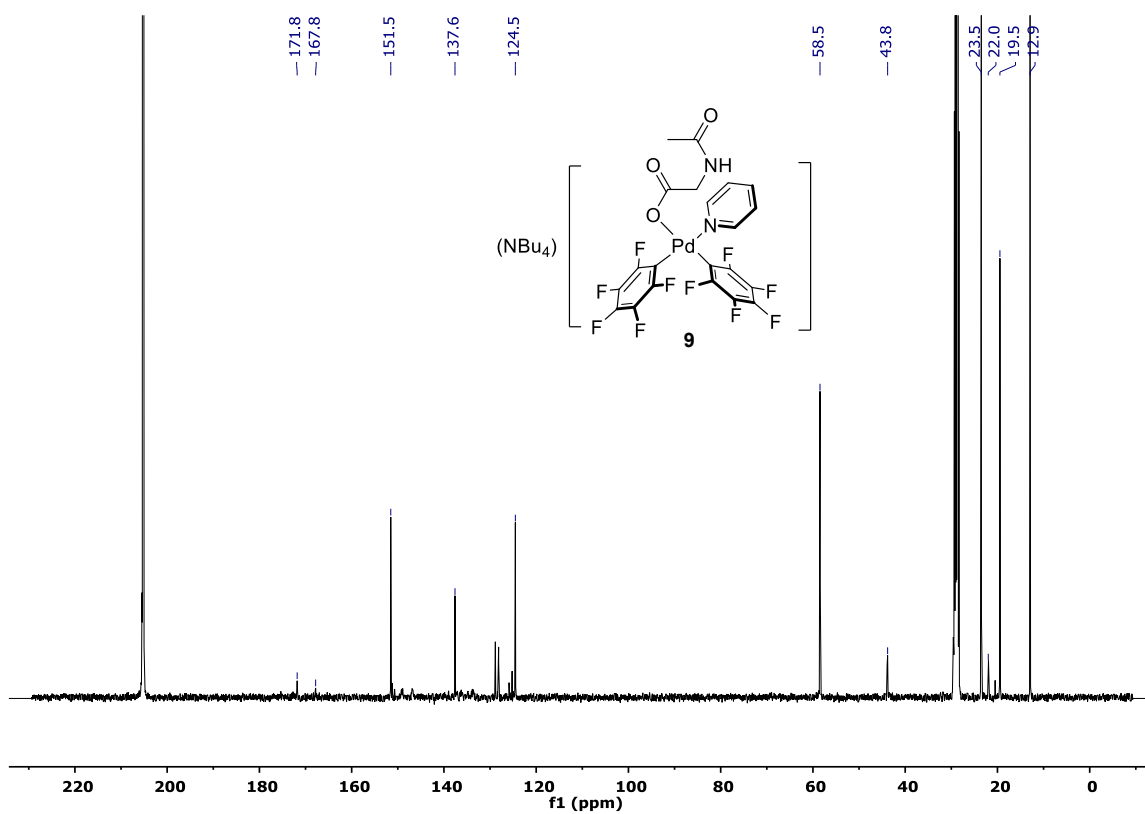


Figure S47.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.56 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^1\text{-O-AcNH-Gly-O})(\text{C}_6\text{F}_5)_2\text{py}]$  (**9**).



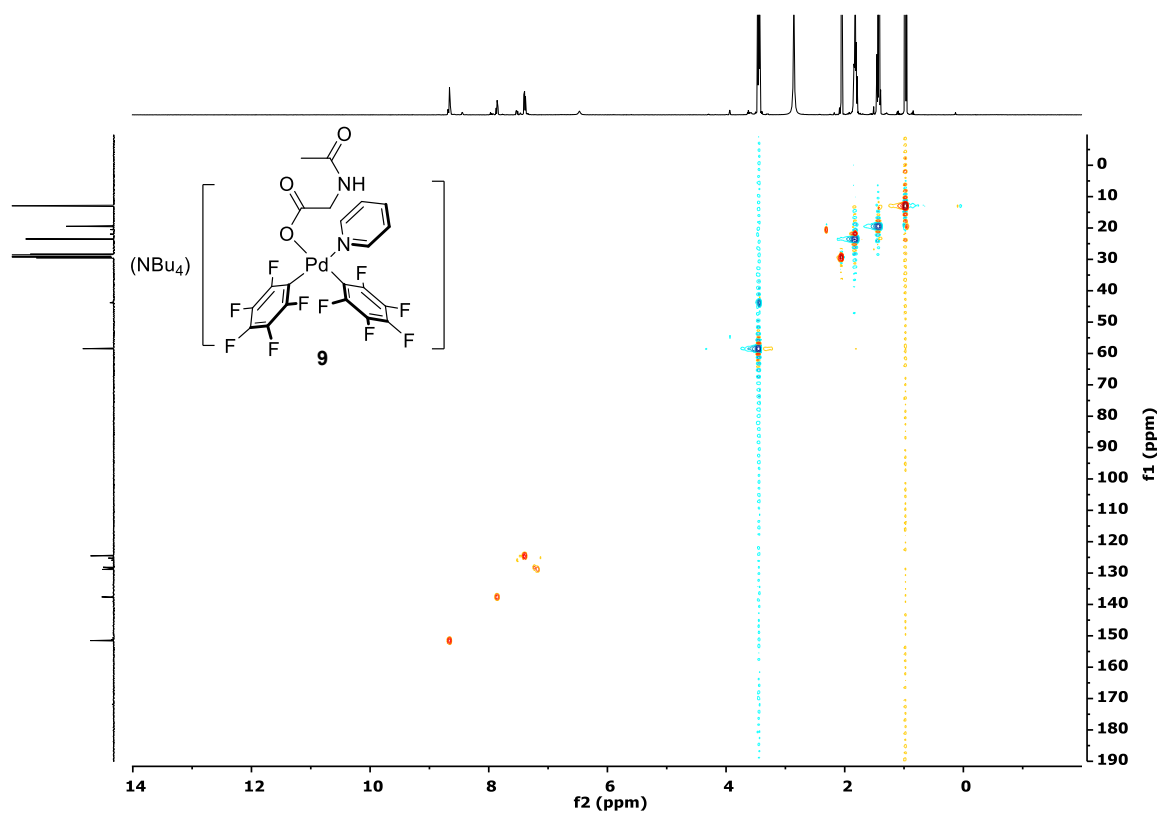


Figure S48.  $^1\text{H}$ - $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)[\text{Pd}(\kappa^1\text{-O-AcNH-Gly-O})(\text{C}_6\text{F}_5)_2\text{py}]$  (**9**) in acetone- $d_6$  at 298 K.

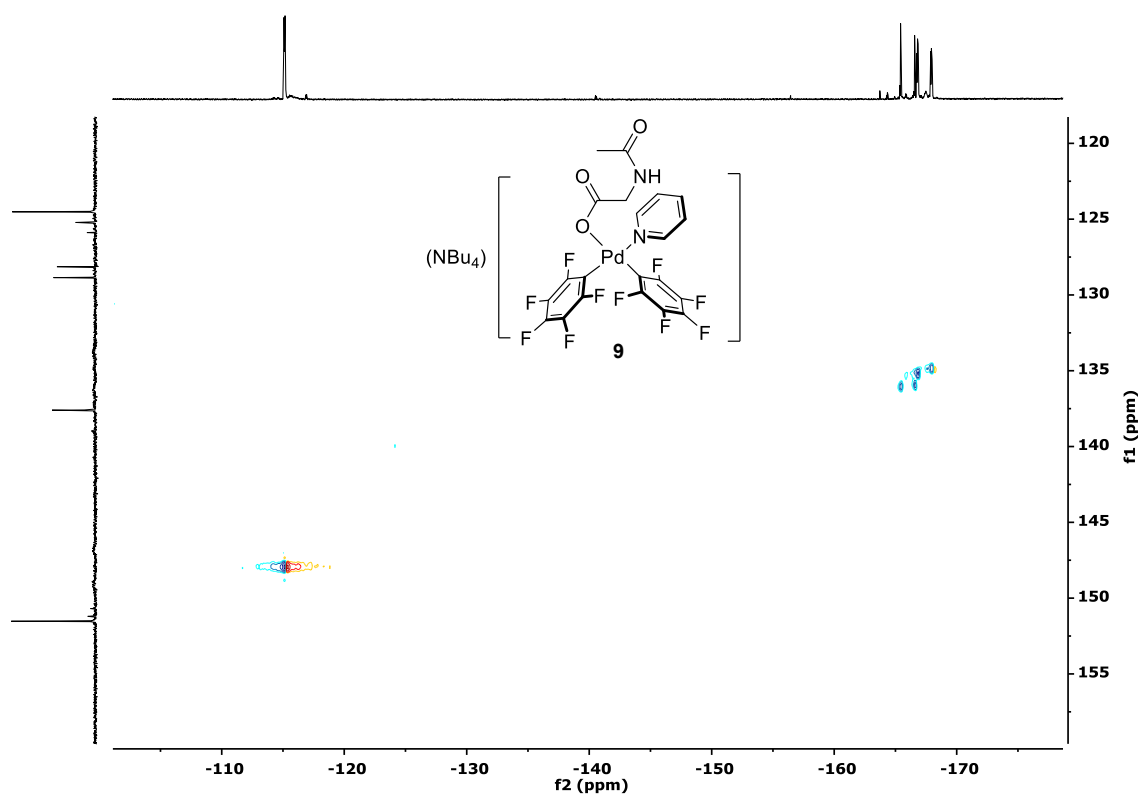
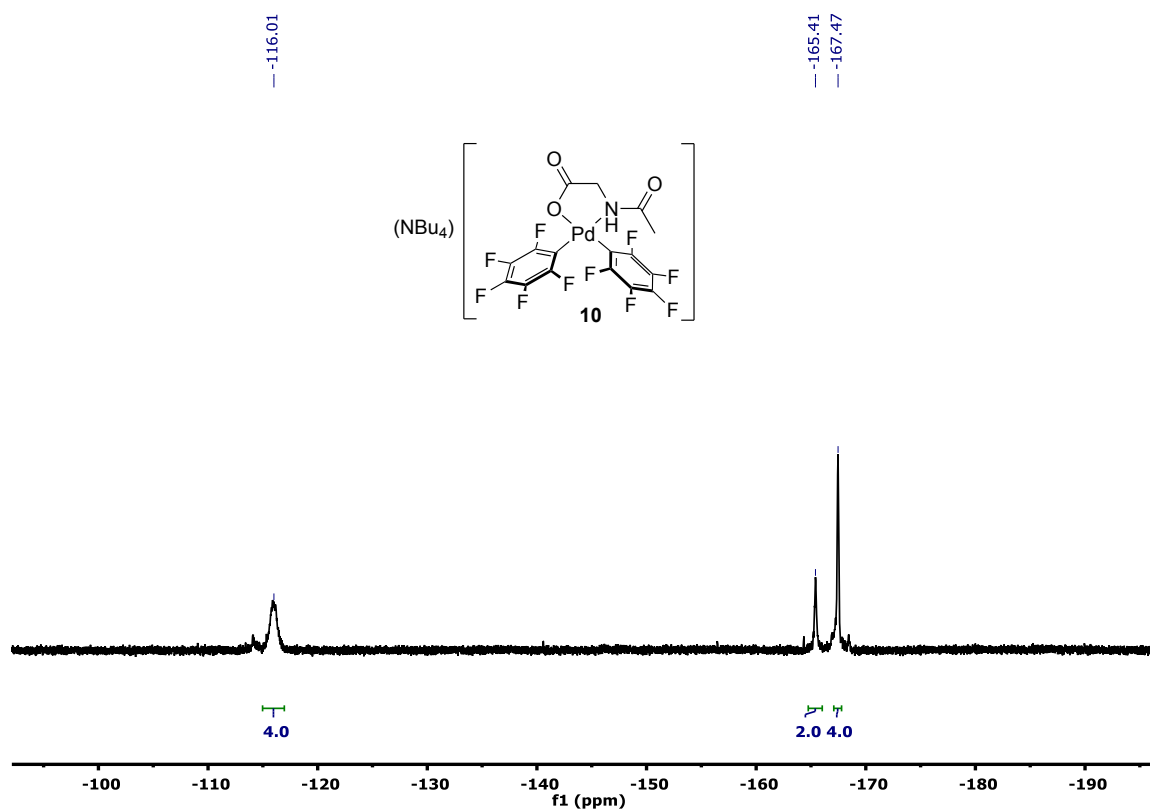
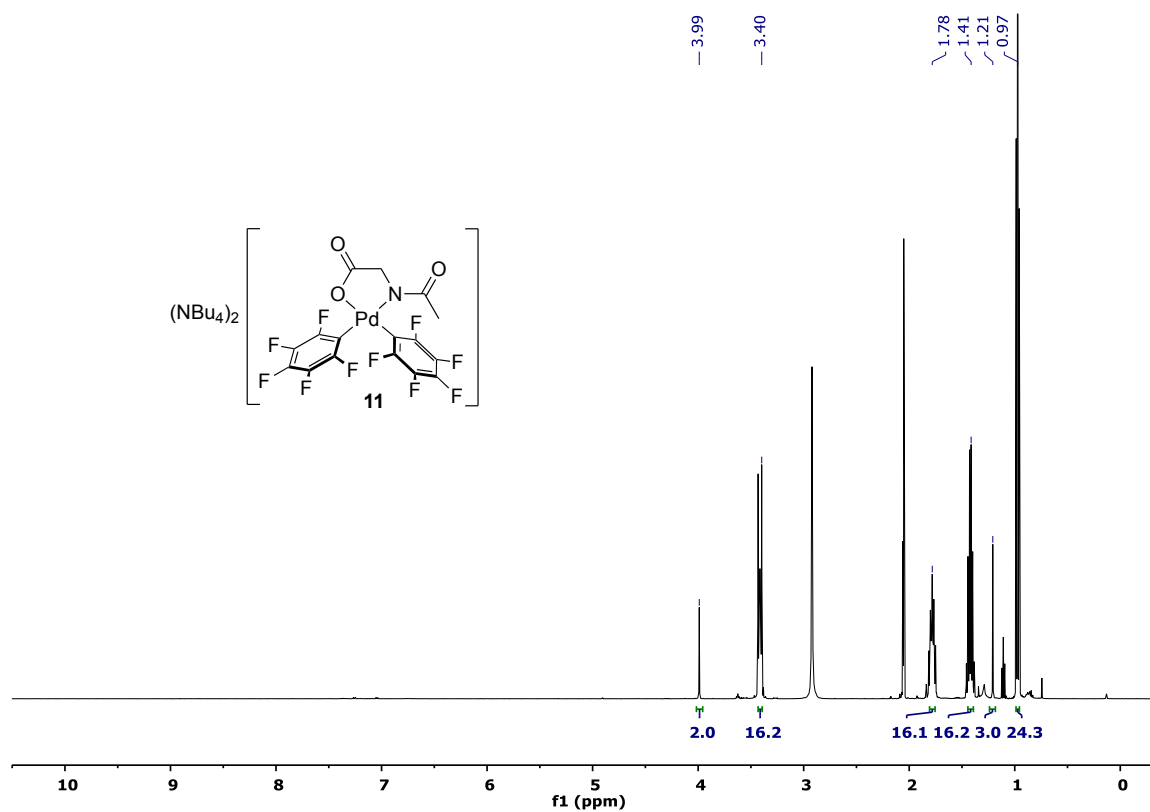


Figure S49.  $^{19}\text{F}$ - $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)[\text{Pd}(\kappa^1\text{-O-AcNH-Gly-O})(\text{C}_6\text{F}_5)_2\text{py}]$  (**9**) in acetone- $d_6$  at 298 K.



**Figure S50.**  $^{19}\text{F}$  NMR (470.17 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)[\text{Pd}(\kappa^2\text{-}N,O\text{-AcNH-Gly-O})(\text{C}_6\text{F}_5)_2]$  (**10**).



**Figure S51.**  $^1\text{H}$  NMR (499.73 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)_2[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)_2]$  (**11**).

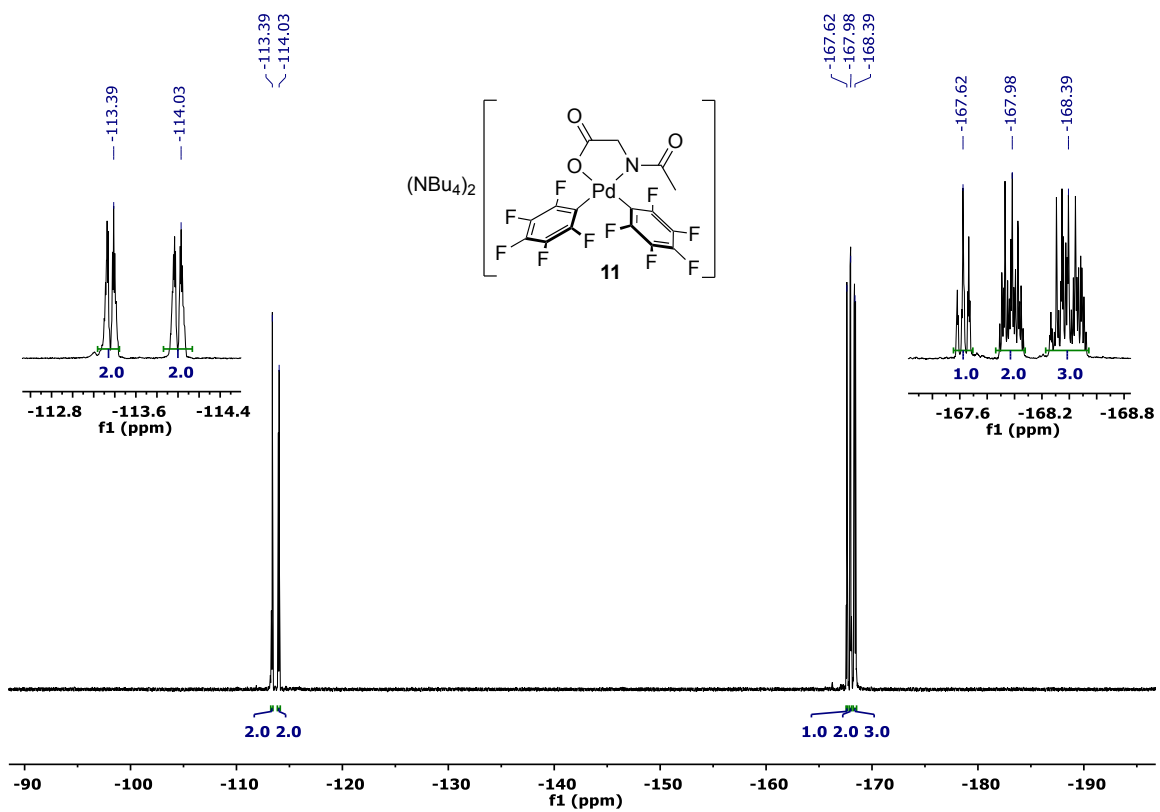


Figure S52.  $^{19}\text{F}$  NMR (470.17 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)_2[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)_2]$  (**11**).

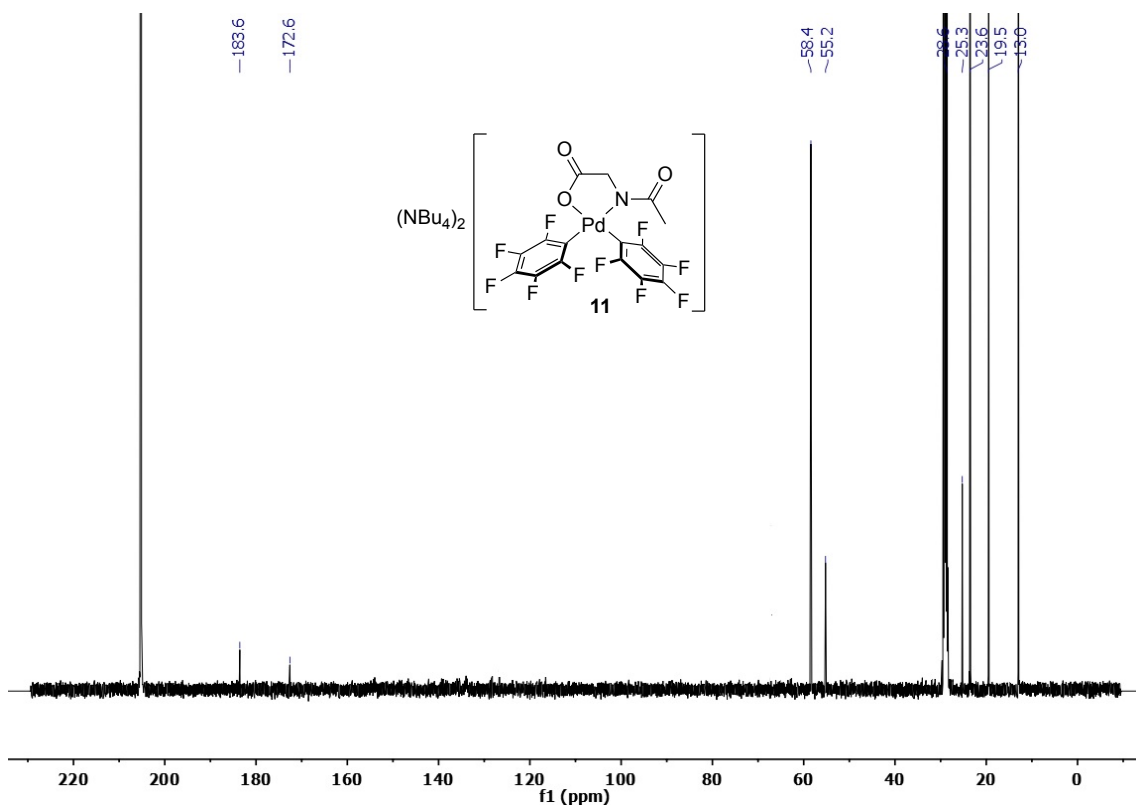
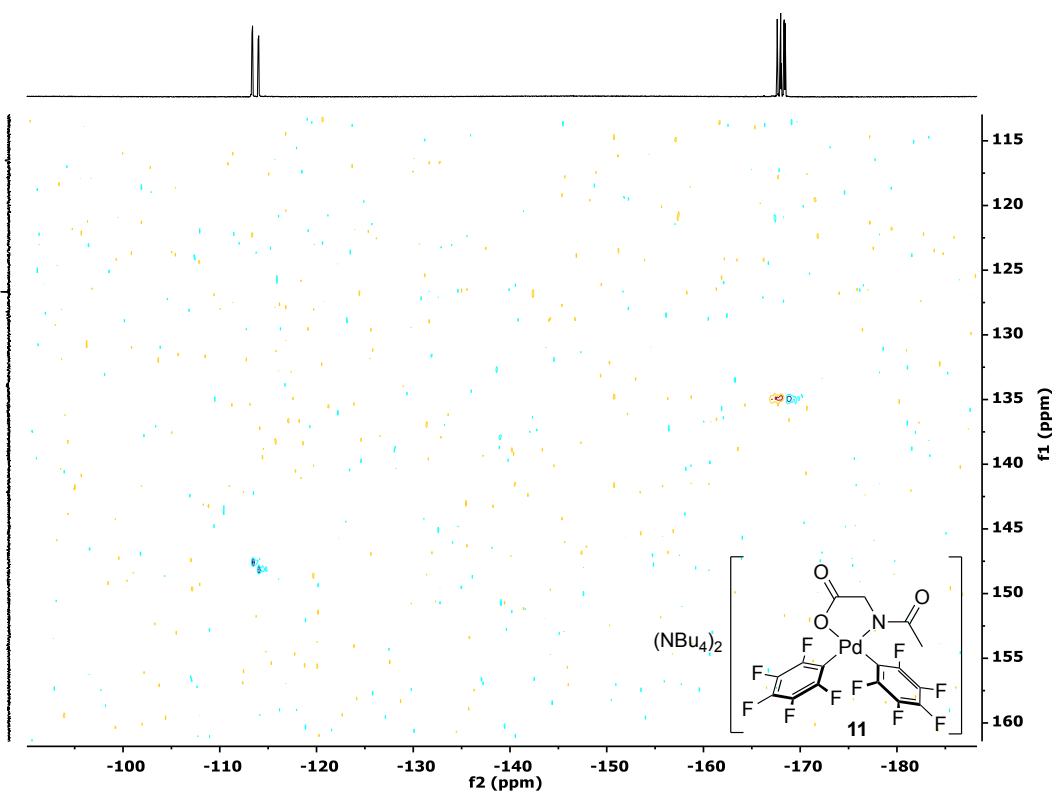


Figure S53.  $^{13}\text{C}\{^1\text{H}\}$  NMR (125.67 MHz, acetone- $d_6$ , 298 K) of  $(\text{NBu}_4)_2[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)_2]$  (**11**).



**Figure S54.**  $^{19}\text{F}$ - $^{13}\text{C}$  HSQC of  $(\text{NBu}_4)_2[\text{Pd}(\kappa^2\text{-}N,O\text{-AcN-Gly-O})(\text{C}_6\text{F}_5)_2]$  (**11**) in acetone- $d_6$  at 298 K.

## 4. Computational Details

### 4.1 Computational methods.

The DFT studies have been performed with the M06 functional, as implemented in the Gaussian09 program package.<sup>14</sup> C and H atoms were described using the double- $\zeta$  basis set 6-31G(d,p), whereas the same basis set plus diffuse functions was employed to describe the more electronegative O, Cl and F atoms and LANL2TZ,<sup>15</sup> including f-polarization functions for Pd (exponent: 1.472).<sup>16</sup> Solvent effects have been considered through the continuum model SMD for the experimental solvent, toluene ( $\epsilon = 2.3741$  at 25 °C),<sup>17</sup> which was introduced in all the optimizations, frequency calculations and potential energy refinement. All structure optimizations were carried out in solvent phase with no symmetry restrictions. Free energy corrections were calculated at 403.15 K (the experimental temperature). Vibrational frequency calculations were performed in order to confirm that the stationary points were minima (without imaginary frequencies) or transition states (with one imaginary frequency). Connectivity of the transition state structures was confirmed by relaxing the transition state geometry towards both the reactant and the product.

### 4.2 Isomers of complex 2.

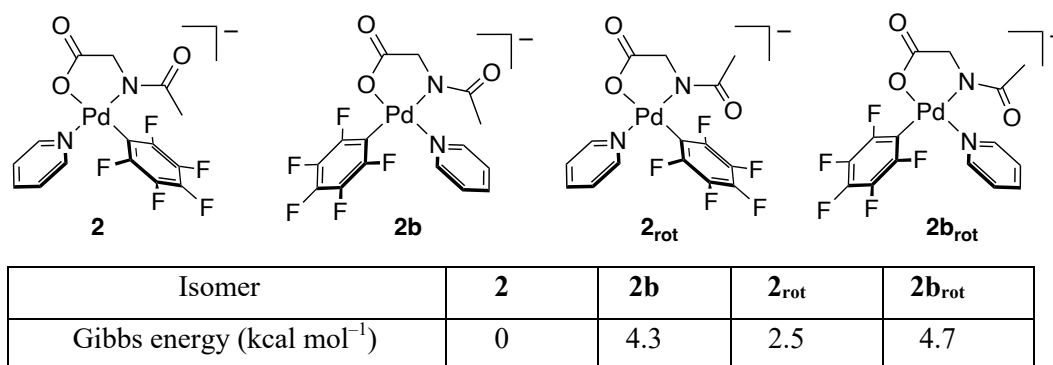


Figure S55. Possible isomers of complex 2 and their relative energies.

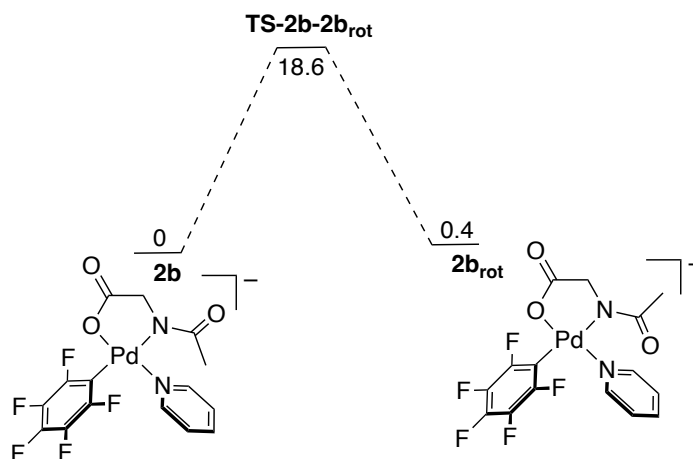
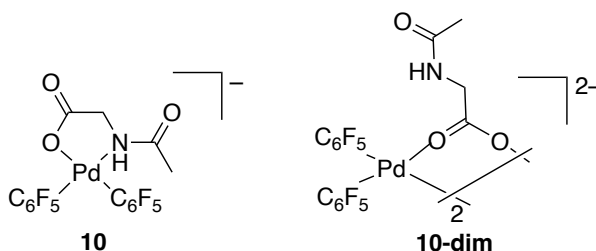


Figure S56. Gibbs energy profile for the rotation of the acyl group (energies in kcal mol<sup>-1</sup>).

### 4.3 Dimeric vs monomeric isomeric species of complex 10.



Complex	10	10-dim
Gibbs energy (kcal mol <sup>-1</sup> )	0	2.7

Figure S57. Relative energies of the monomeric and dimeric isomers of complex 10.

### 4.4 Cartesian Coordinates and Calculated Potential Energies (atomic units)

The sum of SCF energy and free energy correction energies provides the final free energy of each compound.

<b>2</b>	C	-2.366366000	-2.582026000	0.421258000
	H	-2.215255000	-2.792547000	1.494617000
	H	-2.712209000	-3.523244000	-0.024311000
SCF Energy = -1538.08786697	C	0.978841000	-0.013788000	0.068562000
Thermal Correction to Gibbs Free Energy = 0.148724	N	-1.267346000	1.972120000	0.126306000
	C	-1.759349000	4.700181000	0.230533000
	H	-1.950961000	5.769895000	0.268295000
	F	1.042832000	-1.071858000	2.194309000
	F	1.146156000	1.069730000	-2.032757000
	F	3.833811000	1.174662000	-1.895001000
	F	3.721408000	-0.959309000	2.299625000
	F	5.135341000	0.154494000	0.263474000
	C	-0.383600000	-3.078558000	-0.832611000
	C	-3.474206000	-1.541687000	0.317864000
	C	-0.317498000	2.820455000	0.553896000
	C	-0.527140000	4.189351000	0.620997000
	C	-2.743969000	3.820611000	-0.202001000
	C	-2.467712000	2.461539000	-0.237658000
	N	-1.137552000	-2.139465000	-0.222384000
	Pd	-1.037020000	-0.129644000	-0.048372000
	H	-3.205185000	1.716383000	-0.529109000
	H	-3.724409000	4.172975000	-0.508497000
	H	0.269611000	4.836920000	0.974840000
	H	0.629463000	2.374527000	0.846281000
	C	1.744842000	0.555996000	-0.935864000
	C	1.685580000	-0.510165000	1.152785000
	C	3.073087000	-0.470520000	1.234860000
	C	3.800294000	0.097016000	0.198829000
	C	3.130951000	0.619237000	-0.898827000
	O	-4.627215000	-1.845290000	0.600914000
	O	-3.100348000	-0.353273000	-0.055472000
	O	-0.636268000	-4.289626000	-0.776010000
	C	0.807611000	-2.613375000	-1.643559000
	H	0.632583000	-1.656179000	-2.143542000
	H	1.696040000	-2.509846000	-1.007511000
	H	1.024033000	-3.383400000	-2.390087000
	C	-2.366366000	-2.582026000	0.421258000
	H	-2.215255000	-2.792547000	1.494617000
	H	-2.712209000	-3.523244000	-0.024311000
	C	0.978841000	-0.013788000	0.068562000
	N	-1.267346000	1.972120000	0.126306000
	C	-1.759349000	4.700181000	0.230533000
	H	-1.950961000	5.769895000	0.268295000
	F	1.042832000	-1.071858000	2.194309000
	F	1.146156000	1.069730000	-2.032757000
	F	3.833811000	1.174662000	-1.895001000
	F	3.721408000	-0.959309000	2.299625000
	F	5.135341000	0.154494000	0.263474000
	C	-0.187043000	-2.937899000	-0.647855000
	C	-3.538999000	-1.500096000	0.136613000
	C	-0.243338000	2.832450000	0.565231000
	C	-0.421832000	4.204946000	0.650170000
	C	-2.669741000	3.890354000	-0.108225000
	C	-2.423300000	2.526286000	-0.164700000
	N	-1.149969000	-2.105218000	-0.199585000
	O	0.920367000	-2.582917000	-1.057284000
	Pd	-1.043673000	-0.097255000	-0.015213000
	H	-3.183375000	1.800212000	-0.446466000
	C	-0.187043000	-2.937899000	-0.647855000
	C	-3.538999000	-1.500096000	0.136613000
	C	-0.243338000	2.832450000	0.565231000
	C	-0.421832000	4.204946000	0.650170000
	C	-2.669741000	3.890354000	-0.108225000
	C	-2.423300000	2.526286000	-0.164700000
	N	-1.149969000	-2.105218000	-0.199585000
	O	0.920367000	-2.582917000	-1.057284000
	Pd	-1.043673000	-0.097255000	-0.015213000
	H	-3.183375000	1.800212000	-0.446466000

H	-3.650808000	4.266365000	-0.383111000
H	0.399520000	4.832328000	0.983678000
H	0.702859000	2.362250000	0.820908000
C	1.697391000	0.519209000	-0.999151000
C	1.704342000	-0.485444000	1.120668000
C	3.091985000	-0.454580000	1.154340000
C	3.787587000	0.074842000	0.077819000
C	3.083753000	0.571780000	-1.009246000
O	-4.713564000	-1.822289000	0.279345000
O	-3.119349000	-0.290040000	-0.046785000
C	-0.519581000	-4.427297000	-0.651128000
H	-0.899746000	-4.776907000	0.316247000
H	-1.280428000	-4.665239000	-1.405436000
H	0.393860000	-4.973335000	-0.897639000
C	-2.463937000	-2.582789000	0.198333000
H	-2.473077000	-2.971323000	1.233737000
H	-2.820781000	-3.407852000	-0.435603000
N	-1.224216000	2.007878000	0.161699000
C	0.966615000	-0.015611000	0.047826000
C	-1.654416000	4.745105000	0.303239000
H	-1.822328000	5.818172000	0.356942000
F	1.089997000	-1.030849000	2.191414000
F	3.773989000	-0.920413000	2.211679000
F	5.126844000	0.126341000	0.097251000
F	3.756242000	1.099541000	-2.043414000
F	1.064707000	1.021476000	-2.081828000

### c1

SCF Energy = -1561.32386999

Thermal Correction to Gibbs Free Energy = 0.185332

C	3.998790000	0.912513000	0.233333000
C	2.604884000	-2.453049000	-0.617489000
C	-0.923715000	-0.535306000	-0.001510000
C	-1.554050000	-0.992908000	1.141265000
C	-2.916935000	-1.251534000	1.203555000
C	-3.694218000	-1.062042000	0.069800000
C	-3.093131000	-0.630128000	-1.102593000
C	-1.724311000	-0.392100000	-1.118666000
N	3.159425000	-0.097881000	-0.047597000
O	3.636765000	2.051884000	0.568633000
Pd	1.071006000	-0.133715000	0.000506000
C	-0.375969000	2.569866000	-0.944999000
C	0.722839000	1.952567000	1.138650000
C	-1.654374000	2.390327000	1.083598000
H	-0.318463000	2.773258000	-2.013757000
H	1.657182000	1.846800000	1.686221000
H	-2.617245000	2.452052000	1.591919000
C	0.793544000	2.233366000	-0.240079000
H	1.779397000	2.332918000	-0.688266000
O	1.366800000	-2.087723000	-0.448159000
O	2.928772000	-3.594143000	-0.915883000
C	5.493316000	0.634591000	0.131617000
H	5.809571000	-0.139413000	0.842306000
H	5.780204000	0.285575000	-0.868277000
H	6.030201000	1.559445000	0.354366000

C	3.679286000	-1.393760000	-0.434700000
H	4.386478000	-1.808557000	0.303582000
H	4.234245000	-1.362369000	-1.389199000
C	-1.600917000	2.641256000	-0.302537000
C	-0.522295000	2.046643000	1.793255000
H	-0.584089000	1.851764000	2.861794000
C	-2.846233000	2.938272000	-1.083129000
H	-2.978099000	2.206734000	-1.891799000
H	-3.740988000	2.903802000	-0.451617000
H	-2.804790000	3.928475000	-1.554457000
F	-0.857025000	-1.157544000	2.284513000
F	-3.498453000	-1.668004000	2.337093000
F	-5.011342000	-1.298319000	0.106379000
F	-3.845236000	-0.430443000	-2.195623000
F	-1.209457000	0.042531000	-2.288568000

### TS-c1-c2

SCF Energy = -1561.30094913

Thermal Correction to Gibbs Free Energy = 0.179332

C	3.738787000	1.159952000	0.196648000
C	2.961740000	-2.409551000	-0.539725000
C	-0.874655000	-0.707896000	-0.039597000
C	-1.524727000	-1.164650000	1.092706000
C	-2.885957000	-1.437174000	1.131714000
C	-3.645195000	-1.254841000	-0.014555000
C	-3.031530000	-0.803320000	-1.173081000
C	-1.665980000	-0.549471000	-1.162548000
N	3.163858000	0.002817000	-0.022538000
O	3.064494000	2.214540000	0.437711000
Pd	1.116921000	-0.264838000	-0.018242000
C	-0.208477000	2.358660000	-0.611092000
C	-0.122072000	1.859950000	1.740996000
C	-2.018993000	3.012421000	0.809684000
H	0.240096000	2.311353000	-1.605679000
H	0.385897000	1.417388000	2.597801000
H	-2.995347000	3.480346000	0.941843000
C	0.470738000	1.765424000	0.467033000
H	1.790027000	1.886885000	0.433188000
O	1.686985000	-2.197232000	-0.475616000
O	3.475315000	-3.495007000	-0.781992000
C	5.238218000	1.287237000	0.172251000
H	5.696473000	0.627322000	0.918551000
H	5.636799000	0.993715000	-0.806243000
H	5.525895000	2.319343000	0.381309000
C	3.891383000	-1.217201000	-0.295336000
H	4.556165000	-1.499101000	0.537654000
H	4.534856000	-1.128608000	-1.186086000
C	-1.456135000	2.966117000	-0.468386000
C	-1.353125000	2.478823000	1.912582000
H	-1.809101000	2.537851000	2.899554000
C	-2.190410000	3.495631000	-1.663794000
H	-2.999970000	4.177401000	-1.379191000
H	-1.517897000	4.032300000	-2.343478000
H	-2.639570000	2.676631000	-2.242652000
F	-0.843299000	-1.338971000	2.245722000

F	-3.482167000	-1.867723000	2.253472000
F	-4.960235000	-1.510466000	-0.002179000
F	-3.768055000	-0.616728000	-2.279340000
F	-1.133543000	-0.098233000	-2.320284000

**c2**

SCF Energy = -1561.32713582

Thermal Correction to Gibbs Free Energy = 0.182438

C	3.775474000	0.189223000	-0.282698000
C	2.178647000	-3.107937000	-0.133240000
C	-1.260940000	-0.550537000	-0.021390000
C	-1.997516000	-0.696071000	1.141161000
C	-3.384919000	-0.750102000	1.158451000
C	-4.081763000	-0.646594000	-0.036433000
C	-3.381902000	-0.489785000	-1.223326000
C	-1.994295000	-0.442473000	-1.189383000
N	2.895088000	-0.707516000	-0.021107000
O	3.433088000	1.442386000	-0.544524000
Pd	0.758541000	-0.543421000	-0.011932000
C	0.183601000	2.359446000	-0.598455000
C	0.891286000	1.904523000	1.650969000
C	0.474183000	4.179138000	0.947069000
H	-0.088837000	2.016817000	-1.599471000
H	1.195155000	1.204607000	2.429830000
H	0.443947000	5.245803000	1.170817000
C	0.566302000	1.422609000	0.370517000
H	2.457230000	1.524479000	-0.461672000
O	1.001905000	-2.647735000	-0.324277000
O	2.527576000	-4.286304000	-0.175571000
C	5.251093000	-0.038576000	-0.338934000
H	5.603901000	-0.534479000	0.571231000
H	5.506912000	-0.685398000	-1.186180000
H	5.771948000	0.913602000	-0.456138000
C	3.279747000	-2.092675000	0.223243000
H	3.505269000	-2.230577000	1.292112000
H	4.181662000	-2.379115000	-0.334230000
C	0.137674000	3.734950000	-0.330439000
C	0.844413000	3.265695000	1.932774000
H	1.103312000	3.621799000	2.929591000
C	-0.278347000	4.695751000	-1.405130000
H	-1.322276000	4.533041000	-1.703631000
H	-0.185741000	5.737228000	-1.076390000
H	0.329827000	4.574050000	-2.310480000
F	-1.373769000	-0.787554000	2.334984000
F	-4.065754000	-0.896284000	2.304486000
F	-5.420553000	-0.693874000	-0.043206000
F	-4.058190000	-0.382661000	-2.376547000
F	-1.368154000	-0.270537000	-2.375531000

**TS-c2-c3**

SCF Energy = -1561.296667

Thermal Correction to Gibbs Free Energy = 0.179482

C	-3.773568000	0.075088000	0.268844000
C	-2.179389000	-3.194373000	-0.484010000
N	-2.928243000	-0.845128000	0.004175000
O	-3.359696000	1.306273000	0.571910000
H	-2.379009000	1.283317000	0.552243000
O	-0.997131000	-2.743261000	-0.392034000
O	-2.527355000	-4.358205000	-0.709112000
C	-5.257708000	-0.078824000	0.292509000
H	-5.604797000	-0.587872000	-0.613137000
H	-5.558323000	-0.698311000	1.146252000
H	-5.748689000	0.893294000	0.375422000
C	-3.345024000	-2.199658000	-0.304931000
H	-3.931717000	-2.226910000	-1.237447000
H	-3.998747000	-2.609358000	0.481519000
Pd	-0.703463000	-0.568711000	-0.008831000
C	1.253172000	0.037530000	0.082420000
C	1.996101000	-0.356358000	1.217867000
C	2.014974000	-0.007726000	-1.106656000
C	3.337226000	-0.689463000	1.195340000
C	3.356244000	-0.336386000	-1.162026000
C	4.038253000	-0.671562000	-0.001551000
C	0.081538000	1.343653000	0.273867000
C	-0.104445000	1.887187000	1.568372000
C	-0.121220000	2.223281000	-0.819408000
C	-0.478374000	3.214350000	1.740520000
H	0.039178000	1.256971000	2.439121000
C	-0.491776000	3.554472000	-0.649926000
H	0.012093000	1.846712000	-1.829439000
C	-0.670988000	4.050682000	0.645927000
H	-0.633128000	3.596459000	2.748576000
H	-0.965754000	5.090187000	0.789550000
F	1.427700000	0.258616000	-2.291994000
F	4.006789000	-0.358794000	-2.333058000
F	5.338883000	-0.984965000	-0.037364000
F	3.969890000	-1.055334000	2.318157000
F	1.390006000	-0.447601000	2.420535000
C	-0.696725000	4.449334000	-1.836467000
H	-0.656172000	3.887519000	-2.775758000
H	-1.666687000	4.960566000	-1.792564000
H	0.073050000	5.230920000	-1.884082000

**c3**

SCF Energy = -1561.31330233

Thermal Correction to Gibbs Free Energy = 0.183226

C	-3.720017000	-0.071362000	-0.333885000
C	-2.008539000	-3.378501000	-0.130125000
N	-2.840555000	-0.989127000	-0.219441000
O	-3.364464000	1.215565000	-0.315310000
H	-2.380085000	1.218985000	-0.208517000
O	-0.847307000	-2.901869000	-0.082675000
O	-2.368180000	-4.570267000	-0.113156000
C	-5.192078000	-0.282008000	-0.486397000
H	-5.398296000	-0.936564000	-1.341680000
H	-5.597403000	-0.781263000	0.402356000
H	-5.711689000	0.668541000	-0.627914000



C	-3.199108000	-2.392317000	-0.230839000
H	-3.746566000	-2.656364000	-1.152060000
H	-3.879320000	-2.631803000	0.603791000
Pd	-0.663661000	-0.473791000	0.011369000
C	1.341495000	0.371380000	0.142973000
C	2.136051000	-0.335396000	1.134455000
C	2.015628000	0.362748000	-1.144226000
C	3.416044000	-0.759723000	0.930275000
C	3.297819000	-0.060043000	-1.338017000
C	4.056326000	-0.633489000	-0.309589000
C	0.367638000	1.433472000	0.504124000
C	-0.027783000	1.667658000	1.864563000
C	-0.020767000	2.452301000	-0.432948000
C	-0.796097000	2.763492000	2.211260000
H	0.278925000	0.961646000	2.628415000
C	-0.789961000	3.545933000	-0.072377000
H	0.282652000	2.347325000	-1.471278000
C	-1.197453000	3.711647000	1.263509000
H	-1.088538000	2.889286000	3.254672000
H	-1.810442000	4.567650000	1.547003000
F	1.288745000	0.632816000	-2.280332000
F	3.842943000	-0.007217000	-2.586306000
F	5.435091000	-0.526684000	-0.348687000
F	4.082262000	-1.406089000	1.928218000
F	1.520120000	-0.782269000	2.278147000
C	-1.235023000	4.529678000	-1.116751000
H	-0.653763000	4.429081000	-2.041049000
H	-2.292230000	4.379625000	-1.379682000
H	-1.138849000	5.566842000	-0.767213000

**2b**

SCF Energy = -1538.08085186

Thermal Correction to Gibbs Free Energy = 0.144464

C	3.503353000	-1.579496000	-0.109473000
C	2.038443000	1.717065000	0.377555000
C	-1.511008000	-0.257649000	-0.351645000
C	-2.011849000	0.258726000	-1.536018000
C	-3.362909000	0.511985000	-1.743363000
C	-4.266812000	0.242324000	-0.725666000
C	-3.808058000	-0.278027000	0.475710000
C	-2.447695000	-0.515273000	0.635469000
N	2.543097000	-0.683683000	0.172549000
Pd	0.492589000	-0.589882000	-0.103429000
C	0.447841000	-3.206140000	1.261876000
C	-0.458922000	-3.353342000	-0.858568000
C	-0.681923000	-4.714388000	-0.712966000
C	-0.323094000	-5.330265000	0.480027000
C	0.247608000	-4.559689000	1.486125000
H	0.909114000	-2.562476000	2.007960000
H	-0.723026000	-2.823317000	-1.771826000
H	-1.133852000	-5.274082000	-1.528029000
H	-0.486614000	-6.396586000	0.624047000
H	0.543898000	-4.994915000	2.437130000
N	0.105204000	-2.614039000	0.107515000
O	2.365539000	2.876907000	0.590615000

O	0.884034000	1.386730000	-0.137994000
O	4.696442000	-1.454205000	0.207877000
C	3.083481000	-2.817481000	-0.885394000
H	2.815220000	-3.640805000	-0.207078000
H	2.234007000	-2.631284000	-1.553104000
H	3.942680000	-3.153500000	-1.477708000
C	2.987086000	0.577537000	0.727908000
H	3.993404000	0.836530000	0.368339000
H	3.068185000	0.546876000	1.830781000
F	-5.568901000	0.473398000	-0.904288000
F	-3.810561000	0.999860000	-2.903721000
F	-4.681443000	-0.543928000	1.451842000
F	-2.066804000	-1.026957000	1.822230000
F	-1.189037000	0.522857000	-2.564220000

**TS-2b-2b<sub>rot</sub>**

SCF Energy = -1538.049842

Thermal Correction to Gibbs Free Energy = 0.147190

C	3.584246000	-0.059321000	0.387068000
C	1.715759000	-3.103692000	-0.576910000
C	-1.331014000	-0.263748000	-0.099797000
C	-2.077511000	-0.861287000	0.900445000
C	-3.460059000	-0.753996000	0.986365000
C	-4.141679000	-0.012699000	0.032453000
C	-3.432116000	0.607734000	-0.984728000
C	-2.050484000	0.469522000	-1.024537000
N	2.746429000	-0.856509000	-0.394463000
O	3.460124000	0.140172000	1.587494000
Pd	0.714259000	-0.486797000	-0.181465000
C	1.315422000	2.351472000	-0.843896000
C	0.830153000	2.043362000	1.407049000
C	1.043541000	3.387425000	1.674937000
C	1.408848000	4.230999000	0.632111000
C	1.546683000	3.704962000	-0.647563000
H	1.409459000	1.879425000	-1.819012000
H	0.551780000	1.333811000	2.181945000
H	0.927566000	3.757184000	2.689198000
H	1.585037000	5.288259000	0.814815000
H	1.829287000	4.329084000	-1.490026000
N	0.966543000	1.541762000	0.169427000
O	1.826407000	-4.293095000	-0.845651000
O	0.577619000	-2.472580000	-0.544608000
C	4.701520000	0.598860000	-0.390331000
H	5.263999000	-0.163546000	-0.944309000
H	4.271442000	1.268380000	-1.145635000
H	5.373919000	1.162153000	0.264681000
C	2.938739000	-2.287341000	-0.183517000
H	3.116141000	-2.532983000	0.884582000
H	3.807301000	-2.680513000	-0.739951000
F	-1.472739000	-1.579456000	1.868832000
F	-1.415279000	1.107841000	-2.036475000
F	-4.149395000	-1.340783000	1.976194000
F	-4.093927000	1.329179000	-1.902768000
F	-5.474009000	0.110460000	0.097944000

**2b<sub>rot</sub>**

SCF Energy = -1538.07979641

Thermal Correction to Gibbs Free Energy = 0.148104

C	3.376596000	-1.677401000	0.147603000
C	2.072774000	1.824935000	0.079014000
C	-1.508879000	-0.242248000	-0.247074000
C	-2.050959000	0.276147000	-1.411614000
C	-3.410287000	0.516469000	-1.575505000
C	-4.279678000	0.228079000	-0.533302000
C	-3.778444000	-0.297913000	0.648990000
C	-2.411318000	-0.521004000	0.765185000
N	2.569865000	-0.604284000	0.141927000
O	2.988773000	-2.851646000	0.056647000
Pd	0.502022000	-0.540902000	-0.052970000
C	0.362128000	-3.276544000	1.087958000
C	-0.264398000	-3.205698000	-1.132689000
C	-0.443250000	-4.580346000	-1.170175000
C	-0.219600000	-5.315720000	-0.012823000
C	0.180767000	-4.648993000	1.138012000
H	0.708486000	-2.711841000	1.949958000
H	-0.438499000	-2.581216000	-2.007090000
H	-0.758067000	-5.056270000	-2.095603000
H	-0.355579000	-6.395762000	-0.008199000
H	0.371175000	-5.181976000	2.066145000
N	0.134843000	-2.568872000	-0.025176000
O	2.425050000	2.997104000	0.118184000
O	0.838774000	1.448356000	-0.076892000
C	4.877048000	-1.423494000	0.269936000
H	5.268073000	-0.887340000	-0.606525000
H	5.130060000	-0.816981000	1.150750000
H	5.386574000	-2.389412000	0.343851000
C	3.122795000	0.728716000	0.220388000
H	3.875867000	0.928620000	-0.563214000
H	3.638336000	0.923926000	1.179208000
F	-3.898132000	1.008356000	-2.718321000
F	-1.262482000	0.553601000	-2.463700000
F	-1.986541000	-1.039489000	1.933367000
F	-4.618174000	-0.581354000	1.649766000
F	-5.589586000	0.446666000	-0.670561000

**10**

SCF Energy = -2018.06724

Thermal Correction to Gibbs Free Energy = 0.145468

C	2.62798900	-2.20735600	-1.05954200
C	0.52853100	-3.88005000	0.76318400
C	-1.53021500	-0.25316100	0.13366600
C	-2.08322200	0.45900900	1.18291700
C	-3.37572800	0.96511900	1.14831000
C	-4.15489000	0.76020900	0.02001700
C	-3.63202300	0.05457600	-1.05315900
C	-2.33604300	-0.43681100	-0.97657600
Pd	0.30660100	-1.04425300	0.19520700
C	0.91813800	1.59298800	-1.11648800
C	1.66559500	1.43301100	1.10173300

C	2.13377900	3.41699000	-0.15149000
C	1.00036100	0.83917100	0.04213600
O	-0.36006000	-3.02731100	0.38796800
O	0.31925400	-5.06681600	0.99800800
C	1.94784200	-3.35872400	1.00770700
H	2.04658700	-3.16178300	2.08103500
H	2.66178400	-4.14271200	0.73353500
C	1.47160200	2.86054300	-1.23552700
C	2.23511600	2.69691800	1.02902000
F	-1.36863400	0.69026700	2.30347900
F	-3.88127700	1.64437700	2.18469800
F	-5.40138700	1.23851300	-0.03298200
F	-4.38331600	-0.13999000	-2.14330100
F	-1.87730500	-1.11281500	-2.04859400
F	0.30434300	1.09669900	-2.21148500
F	1.37953100	3.55297300	-2.37682700
F	2.67177600	4.63628200	-0.24484300
F	2.87621800	3.23060800	2.07524800
F	1.80564200	0.77204000	2.27209300
N	2.27187600	-2.10325400	0.30717400
H	2.84735200	-1.45422300	0.84078800
O	2.38061200	-3.21778200	-1.68273100
C	3.28923700	-1.00058300	-1.65468500
H	4.18280600	-1.32559000	-2.19680800
H	2.60686100	-0.55041500	-2.38453800
H	3.56264400	-0.24329500	-0.91444200

**10-dim**

SCF Energy = -4036.158202

Thermal Correction to Gibbs Free Energy = 0.318967

C	0.70517700	0.15761500	3.55629900
C	-0.03403400	1.56485100	0.17569800
C	4.10061400	1.46285600	-0.09039700
C	4.87945900	1.40561900	1.05213400
C	5.88808900	2.32098300	1.32563500
C	6.14364400	3.34006600	0.42254900
C	5.38675400	3.42965800	-0.73560900
C	4.38616000	2.49696100	-0.96902300
Pd	2.56728400	0.25087900	-0.50312600
C	4.64432300	-1.18623000	-2.05682100
C	4.16400200	-2.21595600	0.00068600
C	5.76721200	-3.21840700	-1.47218400
C	3.91836700	-1.17085900	-0.87637100
O	1.15814200	1.89633100	-0.07559800
O	-0.97186200	1.62699000	-0.66006500
C	-0.37877300	1.14466900	1.59799900
H	-0.94104100	1.97863700	2.04585800
H	-1.07690400	0.29356600	1.58654200
C	5.55618500	-2.18467200	-2.37076500
C	5.06596400	-3.23507400	-0.27716500
F	4.68251700	0.43643000	1.96996500
F	6.61415600	2.23328900	2.44595300
F	7.10899800	4.23049200	0.66648000
F	5.63266300	4.41283200	-1.60892500
F	3.68233800	2.64056900	-2.10876300
F	4.48713300	-0.20472200	-2.96723100
F	6.23382500	-2.16384000	-3.52395500
F	6.63877000	-4.19005900	-1.75586100
F	5.26991000	-4.23063000	0.59272100

F	3.52268000	-2.29193800	1.18424700	C	0.42308200	-2.18491100	0.77501600
N	0.79351900	0.80772800	2.36581400	H	0.94548200	-3.10285700	0.46020700
H	1.69371600	1.00813900	1.94223100	H	1.17049400	-1.57355900	1.29859800
O	-0.37474100	-0.05632500	4.10084000	C	-5.72450500	3.10609300	-1.33392100
C	2.00952900	-0.33149700	4.11856600	C	-5.04061900	3.38676200	0.94185700
H	2.04429700	-0.13966100	5.19512300	F	-4.36847600	-0.92057300	1.75021800
H	2.02928400	-1.41964800	3.97095800	F	-6.20326900	-2.88035000	1.81146000
H	2.88505800	0.11201400	3.63461600	F	-6.96211900	-4.12657900	-0.48654500
C	-0.54548000	-2.91173200	2.90634800	F	-5.83462300	-3.40958500	-2.85248500
C	-0.02830100	-1.45125300	-0.47509900	F	-3.96930400	-1.48006700	-2.94225900
C	-4.11633000	-1.10205300	-0.60313900	F	-4.74766700	1.46371700	-2.66103900
C	-4.71276800	-1.50111200	0.58068300	F	-6.49459400	3.47503700	-2.36410200
C	-5.66120900	-2.51321900	0.64439900	F	-6.71448300	4.77043100	0.01557200
C	-6.04589100	-3.15476100	-0.52248400	F	-5.15082400	4.02482900	2.11264800
C	-5.46850200	-2.78414000	-1.72758800	F	-3.39025700	2.02261400	1.84926200
C	-4.51604600	-1.77390200	-1.74622100	N	-0.70016100	-2.46564200	1.63483000
Pd	-2.62101100	0.22028500	-0.62298300	H	-1.61565200	-2.25410000	1.25288300
C	-4.81028500	2.06849500	-1.45852700	O	0.55516200	-3.20388200	3.36770800
C	-4.13808500	2.34500100	0.77509400	C	-1.80692500	-2.98307500	3.72040800
C	-5.84059000	3.76958500	-0.12292300	H	-1.82333800	-2.09286700	4.36030000
C	-3.98992800	1.65910200	-0.41975200	H	-2.71800100	-2.99401100	3.11366100
O	-1.25716500	-1.50180000	-0.75773300				
O	0.83894000	-0.86833200	-1.17341000				

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