Electronic Supplementary Material (ESI) for Dalton Transactions.

Palladium pincer complexes featuring an unsymmetrical SCN indene-based ligand with an hemilabile pyridine sidearm

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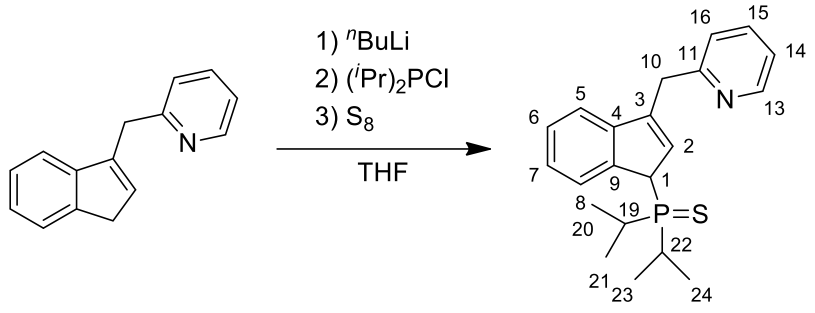
I. General remarks

All reactions and manipulations were carried out under argon atmosphere using standard Schlenk techniques. Dry oxygen–free solvents were employed using an Mbraun SPS-800 prior to use. All reagents were obtained from commercial sources. Compound **1** was synthesized following the literature procedures.[1] ^{1}H and ^{13}C spectra were recorded on Bruker Avance 300, 400 and 500 spectrometers. Chemical shifts are expressed with a positive sign, in parts per million, relative to external Me_4Si for ^{1}H NMR and to external H_3PO_4 for ^{31}P NMR. NMR spectra were recorded at 293 K.

II. Synthesis of compound 2 to 4:



1 **2**

Synthesis of pro ligand 2: In a 250 mL round-bottomed schlenk, *n*-BuLi (11.2 mL of a 1.6 M hexane solution, 0.018 mol) was added dropwise at -80°C to a solution of **1** (3.7 g, 0.018 mol) in THF (100 mL). The solution was stirred at -80°C for 30 min and then allowed to warm to room temperature and stirred for 30 min. Then, a solution of chlorodiisopropylphosphine (2.9 mL, 0.018 mol in 10 mL of THF) was added dropwise at -80°C. The reaction mixture was stirred at this temperature for 30 min and then allowed to warm to room temperature overnight. Finally, the crude was transferred *via* canula in a 250 mL round-bottomed schlenk containing elemental sulfur (1.10 g, 0.036 mmol). The reaction mixture was stirred for 2h. After the addition of 100 mL of a saturated solution of $NaHCO_3$ the organic products were extracted 3 times with 50 mL of DCM. The combined organic phases were then washed with water and dried over Na_2SO_4 and evaporated. The residue was purified by silica gel flash chromatography. The impurities were first eluted with 100% pentane and then 80:20 pentane/EtOAc. Finally, the product **2** was eluted with a gradient from 60:40 pentane/EtOAc to 100% EtOAC to afford a highly viscous brown oil in 76% yield (4.7 g).

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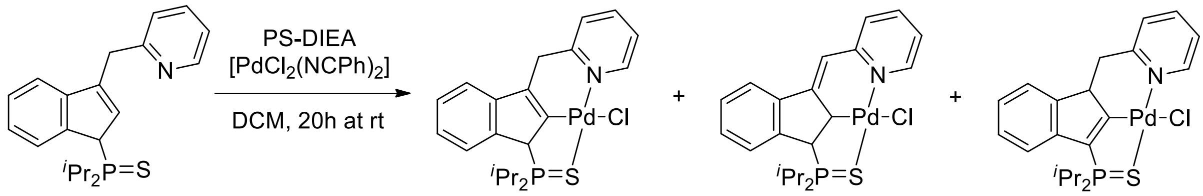
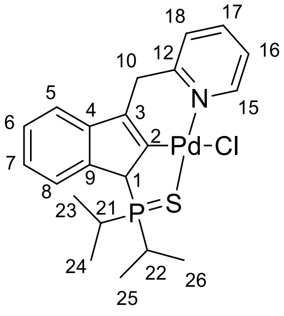
[1] V. Vreshch, J. Monot, B. Martin-Vaca and D. Bourissou, *Polyhedron*, 2018, **143**, 49.

^{31}P{^{1}H}–NMR (121 MHz, $CDCl_3$): δ *ppm* 70.2 (s). **^{1}H–NMR** (300 MHz, $CDCl_3$): δ *ppm* 8.55 (m, 1H, H13), 8.07 (m, 1H, H8), 7.60 (m, 1H, H14), 7.37 (m, 1H, H5), 7.32 (m, 1H, H7), 7.24 (m, 1H, H6), 7.21 (m, 1H, H16), 7.15 (m, 1H, H15), 6.36, (m, 1H, H2), 4.26 (dd, $^{3}J_{HH}$ = 1.8 Hz,$^{2}J_{HP}$ = 23.4 Hz, 1H, H1), 4.11 (m, 2H, H10), 2.22 (m, 1H, H22), 2.03 (m, 1H, H19), 1.19 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HP}$ = 16.8 Hz, 3H, H24), 1.07 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HP}$ = 16.8 Hz, 3H, H23), 1.03 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HP}$ = 16.8 Hz, 3H, H21), 0.90 (dd, $^{3}J_{HH}$ = 7.0 Hz, $^{3}J_{HP}$ = 16.8 Hz, 3H, H20); **^{13}C{^{1}H}–NMR** (75 MHz, $CDCl_3$): δ *ppm* 158.6 (d, $^{5}J_{CP}$ = 1.8 Hz, C11), 149.5 (s, C13), 144.5 (d, $^{2}J_{CP}$ = 3.3 Hz, C9), 143.8 (d, $^{3}J_{CP}$ = 8.5 Hz, C3), 141.0 (d, $^{3}J_{CP}$ = 3.5 Hz, C4), 136.5 (s, C14), 128.1 (d, $^{2}J_{CP}$ = 4.9 Hz, C2), 127.4 (s, C7), 125.5 (d, $^{3}J_{CP}$ = 3.3 Hz, C8), 125.4 (d, $^{5}J_{CP}$ = 2.9 Hz, C6), 123.1 (s, C16), 121.6 (s, C15), 120.2 (s, C5), 51.5 (d, $^{1}J_{CP}$ = 38.0 Hz, C1), 37.3 (d, $^{4}J_{CP}$ = 1.4 Hz, C10), 28.0 (d, $^{1}J_{CP}$ = 30.8 Hz, C22), 27.4 (d, $^{1}J_{CP}$ = 29.8 Hz, C19) 17.5 (d, $^{2}J_{CP}$ = 2.6 Hz, C21), 17.3 (d, $^{2}J_{CP}$ = 2.6 Hz, C24), 16.9 (d, $^{2}J_{CP}$ = 2.4 Hz, C23), 16.7 (d, $^{2}J_{CP}$ = 2.3 Hz, C20). **HRMS** (ESI): m/z $[M+H]^+$ Calcd: 356.1596, Found: 356.1602.



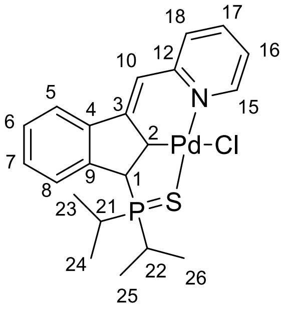
2 **3a** **3b** **3c**

Synthesis of {PdCl[($^{i}Pr_2P$=S)(CH_2Pyr)(C_9H_5)]} (3): A solution of **2** in DCM (248.8 mg, 0.7 mmol in 1 mL) was added to a solution of PS-DIEA (233.3 mg at 3 mmol/g) and $[PdCl_2(NCPh)_2]$ (268.5 mg, 0.7 mmol) in DCM (9 mL) at room temperature. The reaction mixture was stirred at room temperature for 20 hours and, then filtered over a celite pad. The products were extracted 3 times with 2 mL of DCM. The combined organic phases were evaporated and the residue was purified by silica gel flash chromatography. The products **3** were eluted with 100% DCM to afford 78.1 mg of a pale reddish powder, 103.9 mg of a yellowish powder and 84 mg of an orange powder, respectively for **3c, 3a** and **3b** (overall yield = 77 %).



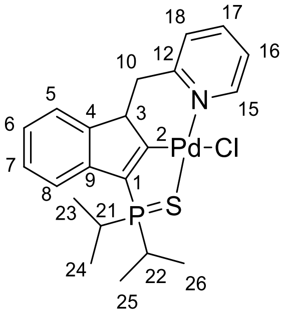
3a

Mp = 191.6°C (decomp.); **^{31}P{^{1}H}–NMR** (121 MHz, CDCl$_3$): δ *ppm* 81.9 (s); **^{1}H–NMR** (500 MHz, CDCl$_3$): δ *ppm* 9.70 (dd, $^3J_{HH}$ = 5.8 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H15), 7.75 (ddd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.3 Hz, 1H, H17), 7.45 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H18), 7.37 (m, 1H, H8) 7.36 (m, 2H, H$_{\text{AroInd}}$), 7.25 (brdd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 5.8 Hz, 1H, H16), 7.11 (m, H$_{\text{AroInd}}$), 4.78 (dd, $^2J_{HP}$ = 20.6 Hz, J_{HH} = 2.8 Hz, 1H, H1), 4.12 (brs, 2H, H10), 2.78 (m, 1H, H22), 1.83 (m, 1H, H21), 1.63 (dd, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, H26), 1.49 (dd, $^3J_{HP}$ = 17.4 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, H25), 0.97 (dd, $^3J_{HP}$ = 17.8 Hz, $^3J_{HH}$ = 7.2 Hz, 6H, H24 and H23); **^{13}C{^{1}H}–NMR** (126 MHz, CDCl$_3$): δ *ppm* 156.70 (d, $^5J_{CP}$ = 1.0 Hz, C12), 154.96 (s, C15), 153.78 (d, $^2J_{CP}$ = 1.2 Hz, C2), 145.72 (d, $^3J_{CP}$ = 3.6 Hz, C4), 140.55 (d, $^2J_{CP}$ = 1.9 Hz, C9), 138.08 (s, C18), 133.35 (d, $^3J_{CP}$ = 8.3 Hz, C3), 128.15 (d, J_{CP} = 1.5 Hz, C$_{\text{AroInd}}$), 125.13 (s, C17), 123.53 (d, J_{CP} = 2.0 Hz, C8), 123.19 (d, J_{CP} = 1.6 Hz, C$_{\text{AroInd}}$), 122.81 (s, C16), 117.90 (s, C6), 63.88 (d, $^1J_{CP}$ = 45.8 Hz, C1), 37.60 (d, $^4J_{CP}$ = 0.9 Hz, C10), 25.49 (d, $^1J_{CP}$ = 41.5 Hz, C21), 24.69 (d, $^1J_{CP}$ = 39.6 Hz, C22), 17.66 (d, $^2J_{CP}$ = 2.5 Hz, C26), 17.43 (d, $^2J_{CP}$ = 3.0 Hz, C24), 17.37 (d, $^2J_{CP}$ = 2.7 Hz, C25), 16.95 (d, $^2J_{CP}$ = 2.7 Hz, C23). **HRMS** (ESI): m/z [M-Cl]$^+$ Calcd: 460.0480, Found: 460.0481. **Elemental Anal Calcd for** $C_{21}H_{25}ClNPPdS$: C, 50.82; H, 5.08; N, 2.82. Found: C, 51.05; H, 5.35; N, 2.58.



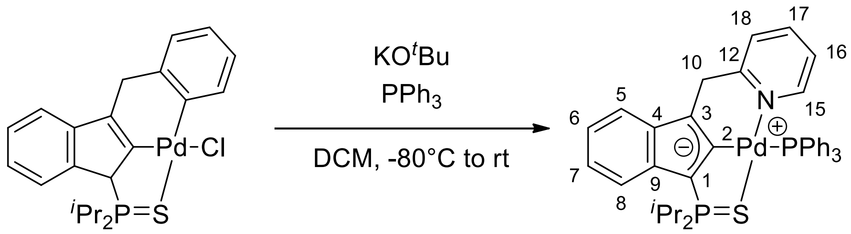
3b

Mp = 265.4°C (decomp.); **^{31}P{^{1}H}–NMR** (121 MHz, CDCl$_3$): δ *ppm* 82.5 (s); **^{1}H–NMR** (500 MHz, CDCl$_3$): δ *ppm* 9.61 (d, $^3J_{HH}$ = 5.6Hz, 1H, H15), 7.69 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H8), 7.66 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 7.7 Hz, 1H, H18), 7.39 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 7.6 Hz, 1H, H6), 7.34 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 7.6 Hz, 1H, H7), 7.27 (d, $^3J_{HH}$ = 7.7 Hz, 1H, H17), 7.24 (d, $^3J_{HH}$ = 7.6 Hz, 1H, H5), 7.17 (dd, $^3J_{HH}$ = 5.6 Hz, $^4J_{HH}$ = 7.6 Hz, 1H, H16), 6.94 (brs, 1H, H10), 5.12 ($_{\text{pseudo}}$t, $^3J_{HP}$ = 11.3 Hz, $^3J_{HH}$ = 11.3 Hz, 1H, H2), 4.63 (dd, $^2J_{HP}$ = 10.0 Hz, $^3J_{HH}$ = 11.3 Hz, 1H, H1), 2.50 (m, 1H, H22), 2.47 (m, 1H, H21), 1.56 (dd, $^3J_{HP}$ = 16.2 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, H24), 1.39 (dd, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 7.4 Hz, 3H, H26), 1.33 (dd, $^3J_{HP}$ = 16.5 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, H23), 0.84 (dd, $^3J_{HP}$ = 16.9 Hz, $^3J_{HH}$ = 7.1 Hz, 3H, H25); **^{13}C{^{1}H}–NMR** (126 MHz, CDCl$_3$): δ *ppm* 154.46 (s, C15), 154.35 (s, C9), 152.77 (s, C12), 141.76 (d, $^3J_{CP}$ = 4.2 Hz, C4), 141.33 (d, $^2J_{CP}$ = 5.4 Hz, C3), 137.83 (s, C18), 129.73 (d, $^4J_{CP}$ = 3.1 Hz, C7), 128.68 (d, $^5J_{CP}$ = 3.0 Hz, C6), 124.54 (d, $^4J_{CP}$ = 3.4 Hz, C5), 122.56 (s, C17), 122.39 (s, C16), 122.13 (d, $^3J_{CP}$ = 2.4 Hz, C8), 115.48 (d, $^4J_{CP}$ = 1.8 Hz, C10), 53.56 (d, $^1J_{CP}$ = 54.0 Hz, C1), 37.05 (d, $^2J_{CP}$ = 2.0 Hz, C2), 28.02 (d, $^{1}J_{CP}$ = 42.6 Hz, C22), 25.76 (d, $^{1}J_{CP}$ = 32.7 Hz, C21), 19.00 (d, $^{2}J_{CP}$ = 2.9 Hz, C26), 17.23 (d, $^{2}J_{CP}$ = 2.0 Hz, C24), 16.55 (d, $^{2}J_{CP}$ = 2.0 Hz, C25), 16.11 (d, $^{2}J_{CP}$ = 2.2 Hz, C23). **Elemental Anal Calcd for** $C_{21}H_{25}ClNPPdS$: C, 50.82; H, 5.08; N, 2.82. Found: C, 51.41; H, 5.38; N, 2.65.



3c

Mp = 201.2°C (decomp.); **^{31}P{^{1}H}–NMR** (121 MHz, $CDCl_3$): δ *ppm* 81.9 (s); **^{1}H–NMR** (500 MHz, $CDCl_3$): δ *ppm* 9.93 (dd, $^{3}J_{HH}$ = 5.8 Hz, $^{4}J_{HH}$ = 1.2 Hz, 1H, H15), 7.85 (ddd, $^{3}J_{HH}$ = 7,6 Hz, J_{HH} = 7.6 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, H18), 7.49 (d, $^{3}J_{HH}$ = 7.6 Hz, 2H, H8 and H17), 7.33 (m, 1H, H16), 7.27 (dd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 7.4 Hz, 1H, H7), 7.18 (ddd, $^{3}J_{HH}$ = 7.4 Hz, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 0.8 Hz, 1H, H6), 7.16 (brd, $^{3}J_{HH}$ = 7.4 Hz, 1H, H5), 3.46 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 2.6 Hz, 1H, H10), 3.28 (dt, $^{3}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 2.6 Hz, 1H, H3), 2.74 (dd, $^{2}J_{HH}$ = 14.0 Hz, $^{3}J_{HH}$ = 14.0 Hz, 1H, H10) 2.71 (m, 1H, H22), 2.60 (m, 1H, H21), 1.46 – 1.27 (12H, H26, H25, H24 and H23); **^{13}C{^{1}H}–NMR** (126 MHz, $CDCl_3$): δ *ppm* 191.57 (d, J_{CP} = 18.6 Hz, C2), 158.87 (s, C12), 155.10 (s, C15), 143.49 (d, J_{CP} = 9.3 Hz, C4), 143.07 (d, J_{CP} = 17.9 Hz, C9), 138.50 (s, C18), 135.50 (d, J_{CP} = 92.0 Hz, C1), 127.38 (s, C7), 125.60 (s, C17), 124.01 (s, C6), 123.34 (s, C8), 122.86 (s, C16), 117.99 (d, J_{CP} = 1.0 Hz, C5), 52.64 (d, J_{CP} = 15.3 Hz, C3), 39.45 (d, J_{CP} = 0.7 Hz, C10), 27.37 (d, $^{2}J_{CP}$ = 44.9 Hz, C21), 26.06 (d, $^{2}J_{CP}$ = 44.5 Hz, C22), 17.45 (d, $^{3}J_{CP}$ = 1.9 Hz, H_3C_{iPr}), 16.95 (d, $^{3}J_{CP}$ = 2.1 Hz, H_3C_{iPr}), 16.23 (d, $^{3}J_{CP}$ = 2.1 Hz, H_3C_{iPr}), 16.03 (d, $^{3}J_{CP}$ = 2.1 Hz, H_3C_{iPr}). **HRMS** (ESI): m/z [M-Cl]$^+$ Calcd: 460.0480, Found: 460.0470.



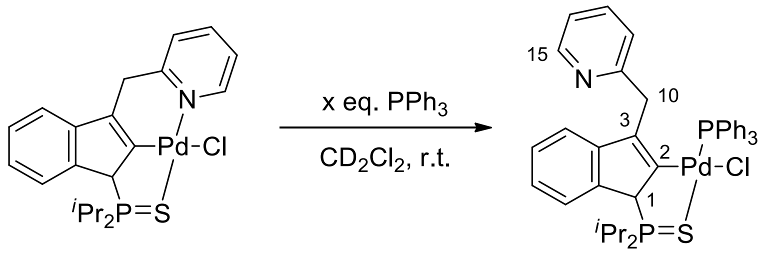
3a

4 (86%)

Synthesis of {PdPPh$_3$[(^{i}Pr$_2$P=S)(CH$_2$Pyr)(C$_9$H$_4$)]} (4): In a schlenk, potassium tert-butoxide (9 mg, 0.08 mmol) and triphenylphosphine (21 mg, 0.08 mmol) were added at -80°C to a solution of **3a** (40 mg, 0.08 mmol) in DCM (4 mL). Then the reaction mixture was allowed to warm to room temperature overnight under stirring. The mixture was filtered *via* canula and the product was extracted two times with 2 mL of DCM and precipitated with pentane. After drying under vacuum, **4** was obtained as a dark red powder in 86% yield (50 mg).

^{31}P{^{1}H}–NMR (121 MHz, C_6D_6): δ *ppm* 76.6 (d, $^3J_{PP}$ = 45.5 Hz), 17.8 (d, $^3J_{PP}$ = 45.5 Hz); **^{1}H–NMR** (500 MHz, C_6D_6): δ *ppm* 8.16 (d, $^3J_{HH}$ = 5.5 Hz, 1H, H15), 7.93 (d, J_{HH} = 7.5 Hz, 1H, H_{AroInd}), 7.70 (m, 6H, $H_{ortho\text{-}PPh3}$), 7.60 (d, J_{HH} = 7.7 Hz, 1H, H_{AroInd}), 7.42 (m, 1H, H_{AroInd}), 7.35 (m, 1H, H_{AroInd}), 6.99-6.97 (m, 9H, $H_{para\text{-}PPh3}$ and $H_{meta\text{-}PPh3}$), 6.53 (m, 1H, H18), 6.52 (m, 1H, H17), 5.71 (m, 1H, H16), 4.40 (s, 2H, H10), 2.44 (m, 2H, CH_{iPr}), 1.27 (dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, H_3C_{iPr}), 1.11 (dd, $^3J_{HP}$ = 17.6 Hz, $^3J_{HH}$ = 7.0 Hz, 3H, H_3C_{iPr}); **^{13}C{^{1}H}–NMR** (126 MHz, C_6D_6): δ *ppm* 163.25 (dd, J_{CP} = 103.9 Hz, J_{CP} = 24.5 Hz, C2), 163.06 (s, C12), 153.92 (d, $^3J_{CP}$ = 10.3 Hz, C15), 136.68 (s, C17), 134.85 (dd, $^2J_{CP}$ = 18.4 Hz, $^4J_{CP}$ = 5.0 Hz, C9), 134.55 (d, $^2J_{CP}$ = 13.3 Hz, $C_{o\text{-}PPh3}$), 132.66 (d, $^1J_{CP}$ = 28.4 Hz, $C_{i\text{-}PPh3}$), 132.26 (dd, $^3J_{CP}$ = 11.8 Hz, $^4J_{CP}$ = 10.1 Hz, C4), 129.87 (s, $C_{p\text{-}PPh3}$), 128.41 (d, $^3J_{CP}$ = 9.1 Hz, $C_{m\text{-}PPh3}$), 124.67 (s, C18), 120.10 (s, C16), 116.07 (s, C_{AroInd}), 116.06 (s, C_{AroInd}), 115.35 (s, C_{AroInd}), 102.71 (dd, $^3J_{CP}$ = 15.1 Hz, $^3J_{CP}$ = 2.7 Hz, C3), 83.87 (dd, $^1J_{CP}$ = 118.6 Hz, $^3J_{CP}$ = 4.5 Hz, C1), 38.63 (s, C10), 26.63 (d, $^1J_{CP}$ = 47.1 Hz, CH_{iPr}), 16.73 (s, H_3C_{iPr}), 16.36 (d, $^2J_{CP}$ = 2.1 Hz, H_3C_{iPr}).

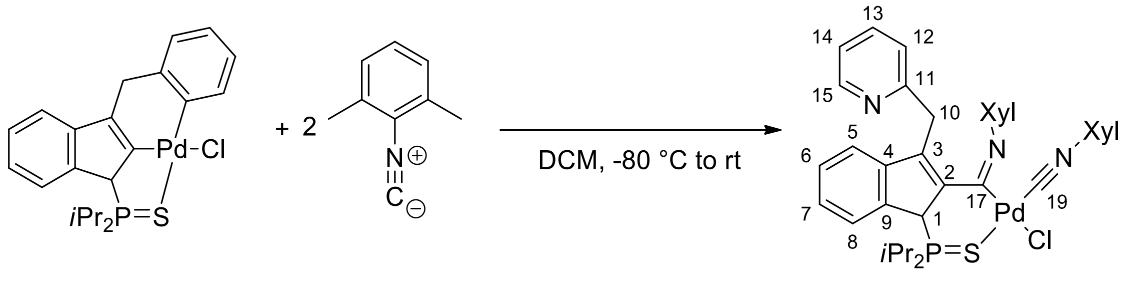
III. Lability test in presence of triphenylphosphine.



3a

In a NMR pressure tube, triphenyphosphine (5 mg, 0.02 mmol) was added to a solution of **3a** (10 mg, 0.020 mmol) in CD_2Cl_2 (0.4 mL) under argon atmosphere. Then, subsequent additions of increasing amounts of PPh_3 (up to 250 mg, 1.0 mmol) were monitored by ^{1}H and ^{31}P NMR.

IV. Lability test in presence of 2,6-dimethylisocyanide

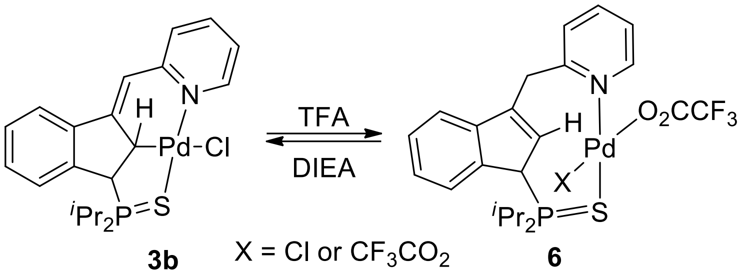


3a **5**

In a schlenk, a solution of 2,6-dimethyl isonitrile (5.2 mg, 0.04 mmol) in DCM (1 mL) was added dropwise to a solution of **3a** (10 mg, 0.02 mmol) in DCM (4 mL) cooled down at -80°C. Then the reaction mixture was allowed to warm slowly to room temperature overnight. The reaction crude was directly analysed by NMR spectroscopy to characterize **5** as the major product. Suitable crystals of **5** were grown by slow diffusion of pentane in a saturated solution in DCM at room temperature.

^{31}P{^{1}H}–NMR (162 MHz, CD_2Cl_2, 213.15 K): δ *ppm* 71.81 (s); **^{1}H–NMR** (400 MHz, CD_2Cl_2, 213.15 K): δ *ppm* 8.42 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, H15), 7.77 (d, J_{HH} = 7,6 Hz, 1H, $H_{Ind(aro)}$), 7.63 (d, J_{HH} = 7,6 Hz, 1H, $H_{Ind(aro)}$), 7.52 (m, 1H, H_{Pyr}), 7.48 (m, 1H, $H_{Ind(aro)}$), 7.42 (d, J_{HH} = 7.5 Hz, 1H H), 7.41 (d, J_{HH} = 7.5 Hz, 1H, $H_{Ind(aro)}$), 7.40 (d, J_{HH} = 7.3 Hz, 1H, H_{Pyr}), 7.23 (m, 1H, $H_{Xyl(aro)}$), 7,21 (m, 1H, $H_{Xyl(aro)}$), 7.10 (m, 1H, $H_{Pyr)}$), 7.09 (m, 1H, $H_{Xyl(aro)}$), 6.94 (t, J_{HH} = 7.5 Hz, $H_{Xyl(aro)}$), 6.64 (d, J_{HH} = 7.5 Hz, 1H, $H_{Xyl(aro)}$), 5.81 (d, $^{2}J_{HP}$ = 21.3 Hz, 1H, H1), 5.04 (d, $^{2}J_{HH}$ = 13,8 Hz, 1H, H10), 4.69 (d, $^{2}J_{HH}$ = 13.8 Hz, 1H, H10), 3.01 (m, 1H, CH_{iPr}), 2.46 (s, 3H, H_3C_{Xyl}), 2.12 (s, 6H, H_3C_{Xyl}), 1.94 (m, 1H, CH_{iPr}), 1.83 (m, 3H, H_3C_{iPr}), 1.76 (s, 3H, H_3C_{Xyl}), 1.35 (m, 3H, H_3C_{iPr}), 0.79 (m, 3H, H_3C_{iPr}), 0.50 (m, 3H, H_3C_{iPr}); **^{13}C{^{1}H}–NMR** (101 MHz, CD_2Cl_2, 213.15 K): δ *ppm* 191.88 (d, J_{CP} = 18.3 Hz, C17), 171.22 (s, C19), 158.96 (s, C11), 151.31 (s, C^{IV}_{Xyl}), 149.06 (s, C_{Pyr}), 146.77 (s, C4 or C9), 142.68 (d, $^{2}J_{CP}$ = 7.7 Hz, C2), 138.00 (s, C4 or C9), 137,54 (d, $^{3}J_{CP}$ = 6.4 Hz, C3), 136.35 (s, C_{Pyr}), 135.45 (s, C^{IV}_{Xyl}), 129.59 (s, C_{Xyl}), 129.10 (s, C^{III}_{Ind}), 128.40 (s, C^{III}_{Xyl}), 127.91 (s, C^{III}_{Xyl}), 127.39 (s, C^{III}_{Xyl}), 127.23 (s, C^{III}_{Ind}), 127.04 (s, C^{IV}_{Xyl}), 125.82 (s, C^{IV}_{Xyl}), 125.44 (s, C^{IV}_{Xyl}), 124.05 (s, C^{III}_{Ind}), 123.97 (s, C^{III}_{Ind}), 123.51 (s, C_{Pyr}), 123.19 (s, C^{III}_{Xyl}), 121.61 (s, C_{Pyr}), 57.38 (d, $^{1}J_{CP}$ = 35.6 Hz, C1), 35.24 (s, C10), 27.36 (d, $^{1}J_{CP}$ = 47.7 Hz, CH_{iPr}), 24.68 (d, $^{1}J_{CP}$ = 47.7 Hz, CH_{iPr}), 20.19 (s, H_3C_{Xyl}), 18.87 (s, H_3C_{Xyl}) 18.85 (s, H_3C_{Xyl}), 17.86 (s, H_3C_{iPr}), 16.73 (s, H_3C_{iPr}), 16.65 (s, H_3C_{iPr}), 15.99 (s, H_3C_{iPr}).

V. Test in presence of TFA and DIEA



In a J. Young NMR tube, trifluoroacetic acid (4.6 µL, 0.060 mmol) was added to a solution of complex **3b** (10 mg, 0.020 mmol) in CD_2Cl_2 (0.5 mL) under argon at room temperature. The reaction was monitored by ^1H and ^{31}P NMR and revealed the clean formation of **6**. Then, N,N-Diisopropylethylamine was added (10.4 µL, 0.060 mmol) and **3b** was recovered according to the ^1H and ^{31}P NMR.

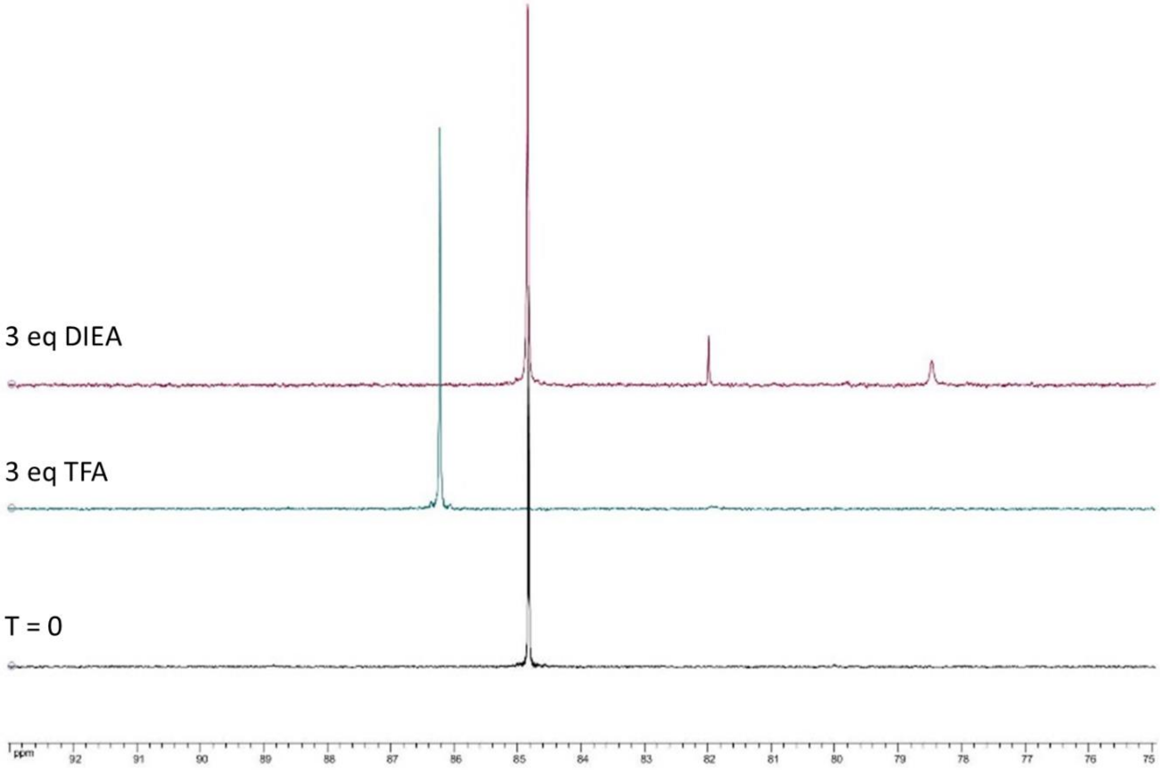
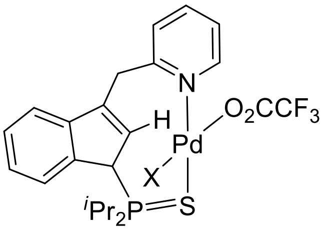


Figure S1: ^{31}P NMR monitoring of the addition of trifluoroacetic acid (3 equivalent) on **3b** and then N,N-diisopropylamine (3 equivalent).



6

X = Cl or CF$_3$CO$_2$

^{31}P{^{1}H}–NMR (162 MHz, CDCl$_3$): δ *ppm* 86.2 (s); **^{1}H–NMR** (400 MHz, CDCl$_3$): δ *ppm* 8.89 (dd, $^{3}J_{HH}$ = 5.6 Hz, $^{4}J_{HH}$ = 0.8 Hz, 1H, H15), 8.09 (m, 1H, H$_{\text{AroInd}}$), 8.03 (ddd, $^{3}J_{HH}$ = 7.6 Hz, $^{3}J_{HH}$ = 7.6 Hz, $^{4}J_{HH}$ = 1.6 Hz, 1H, H17), 7.73 (m, 2H, H$_{\text{AroInd}}$), 7.66 (d, $^{3}J_{HH}$ = 7.6 Hz, 1H, H18), 7.53 (m, , 1H, H16), 7.47 (m, 1H, H$_{\text{AroInd}}$), 6.38 (brs, 1H, H2), 5,29 (brd, $^{2}J_{HP}$ = 8 Hz, 1H, H1), 5,14 (brd, 1H, $^{2}J_{HH}$ = 20 Hz, H10), 3.89 (brd, $^{2}J_{HH}$ = 20 Hz, H10), 3.11 (m, 1H, H22), 2.71 (m, 1H, H21), 1.82 (dd, $^{3}J_{HP}$ = 19.6 Hz, $^{3}J_{HH}$ = 8.0 Hz, 3H, H$_3$C$_{iPr}$), 1.76 (dd, $^{3}J_{HP}$ = 18.0 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, H$_3$C$_{iPr}$) 1.73 (dd, $^{3}J_{HP}$ = 9.6 Hz, $^{3}J_{HH}$ = 7.2 Hz, 3H, H$_3$C$_{iPr}$), 1.27 (dd, $^{3}J_{HP}$ = 16.6 Hz, $^{3}J_{HH}$ = 7.0 Hz, 3H, H$_3$C$_{iPr}$), 1.11 (dd, $^{3}J_{HP}$ = 17.6 Hz, $^{3}J_{HH}$ = 7.0 Hz, 3H, H$_3$C$_{iPr}$); **^{13}C{^{1}H}–NMR** (100 MHz, CDCl$_3$): δ *ppm* 160.07 (q, $^{2}J_{CF}$ = 38.8 Hz, $\underline{\text{C}}$OCF$_3$), 158.55 (s, C12), 151.22 (s, C15), 143.05 (d, d, $^{2}J_{CP}$ = 3.8 Hz, C9), 141.85 (s, C17), 141.01 (d, $^{3}J_{CP}$ = 3.4 Hz, C3), 139.50 (d, $^{3}J_{CP}$ = 4.6 Hz, C4), 132.57 (d, J_{CP} = 2.3 Hz, C$_{\text{AroInd}}$), 130.92 (d, J_{CP} = 1.8 Hz, C$_{\text{AroInd}}$), 125.58 (d, J_{CP} = 3.1 Hz, C8), 125.39 (s, C16), 124.93 (s, C18), 124.74 (s, C$_{\text{AroInd}}$), 115.78 (q, $^{1}J_{CF}$ = 286.3 Hz, CF$_3$), 93.71 (d, $^{2}J_{CP}$ = 5.8 Hz, C2), 49.71 (d, $^{1}J_{CP}$ = 36.6 Hz, C1), 40.19 (s, C10), 31.04 (d, $^{1}J_{CP}$ = 35 Hz, C21), 30.37 (d, $^{1}J_{CP}$ = 37.3 Hz, C22), 20.04 (d, $^{2}J_{CP}$ = 2.9 Hz, C26), 18.74 (d, $^{2}J_{CP}$ = 2.7 Hz, C24), 18.72 (d, $^{2}J_{CP}$ = 2.0 Hz, C24), 16.05 (d, $^{2}J_{CP}$ = 2.1 Hz, C23)

VI. *In situ* infrared experiments using reactIR 15 Metler Toledo Optic silicium fiber.

To a solution of **3b** (20 mg) in DCM (2 mL) was added 202 µl (1 equivalent) solution of trifluoroacetic acid (0.1 M in DCM) at room temperature under stirring. The reaction mixture was monitored *in situ* by an infrared reactIR. Two new COO stretching bands (ν_a(COO) = 1610 and ν_s(COO) = 1375 cm^{-1}) were identified as coordinated TFA. Then subsequent addition of increasing amounst of the solution of TFA was done up to 3 equivalents to get complete conversion.

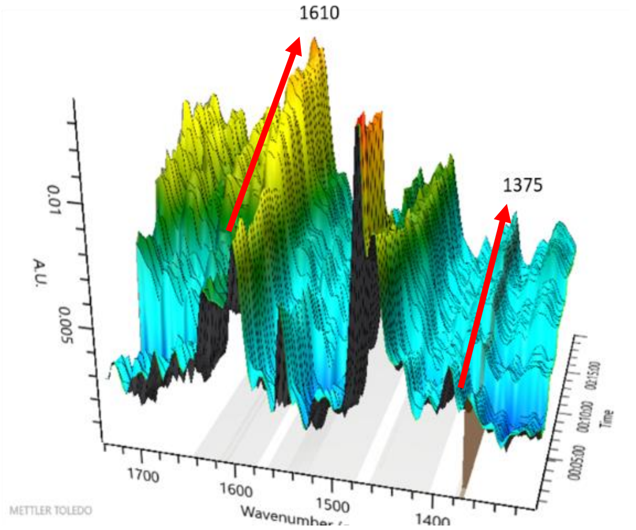
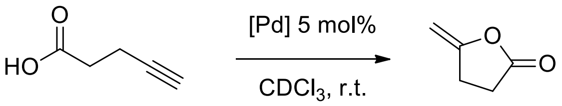
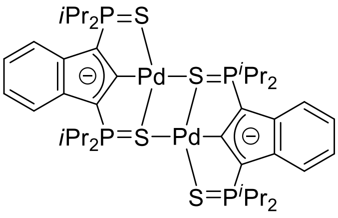


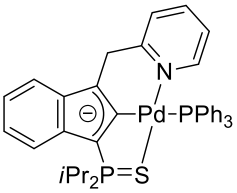
Figure S2. IR spectra of the reaction mixture between 1740 and 1300 cm^{-1}.

VII. General procedure for catalytic cycloisomerization reactions





[^{i}Pr$_2$Pd$_2$]



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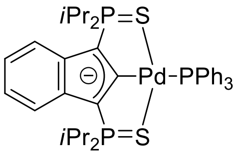
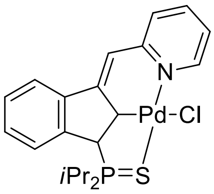


A



3b

In a NMR pressure tube, 4-pentynoic acid (0.050 mmol) and complex (5 mol% [Pd]) were dissolved in CDCl$_3$ (0.5 mL) at room temperature under argon. The reactions were monitored by ^{1}H NMR spectroscopy.

VIII. Selected crystal data

The data were collected at low temperature on a Bruker-AXS APEX II QUAZAR diffractometer (**5**) equipped with a 30W air-cooled microfocus source, and on a Bruker-AXS D8-Venture diffractometer (**3b**) equipped with a CMOS area detector, using MoKα radiation (λ = 0.71073Å). Phi- and omega- scans were used. The data were integrated with SAINT, and an empirical absorption correction with SADABS was applied.[2] The structures were solved using an intrinsic phasing method (SHELXT)[3] and refined using the least-squares method on F2.[4] All non-H atoms were refined with anisotropic displacement parameters. The H atoms were refined isotropically at calculated positions using a riding model.

CCDC-1898996 (**3b**) and CCDC-1898855 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.a-c.uk/data_request/cif.

Table S1. Crystal Data, Data Collection, and Structure Refinement for **3b** and **5**

	3b	**5**
chemical formula	$C_{21}H_{25}ClNPPdS,CH_2Cl_2$	$C_{39}H_{43}ClN_3PPdS$
*M*r	581.22	758.64
crystal system	triclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$
a [Å]	9.0650(5)	10.0673(7)
b [Å]	10.7440(6)	20.0097(13)
c [Å]	13.3785(8)	17.8258(12)
α [°]	80.298(2)	90
β [°]	75.096(2)	98.505(2)
γ [°]	78.795(2)	90
V [Å^3]	9573.8(5)	3551.4(4)
Z	2	4
ρ_{calc} [g cm^{-3}]	1.575	1.419
λ [Å]	0.71073	0.71073
T [K]	253(2)	193(2)
μ ($Mo_{K\alpha}$) [mm^{-1}]	1.245	0.734
crystal size (mm^3)	0.12 x 0.08 x 0.06	0.12 x 0.08 x 0.04
Reflections collected	21191	69386
Independent reflections	4316 [R(int) = 0.0399]	6479 [R(int) = 0.0850]
Data/Restraints/Parameters	4316 / 72 / 294	6479 / 0 / 423
GOF on F^2	1.127	1.087
R (I > 2σ(I))	0.0388	0.0402
*w*R^2 (all data)	0.0838	0.1157
Largest difference peak and hole [e Å^{-3}]	1.010 and -0.629	0.787 and -0.682

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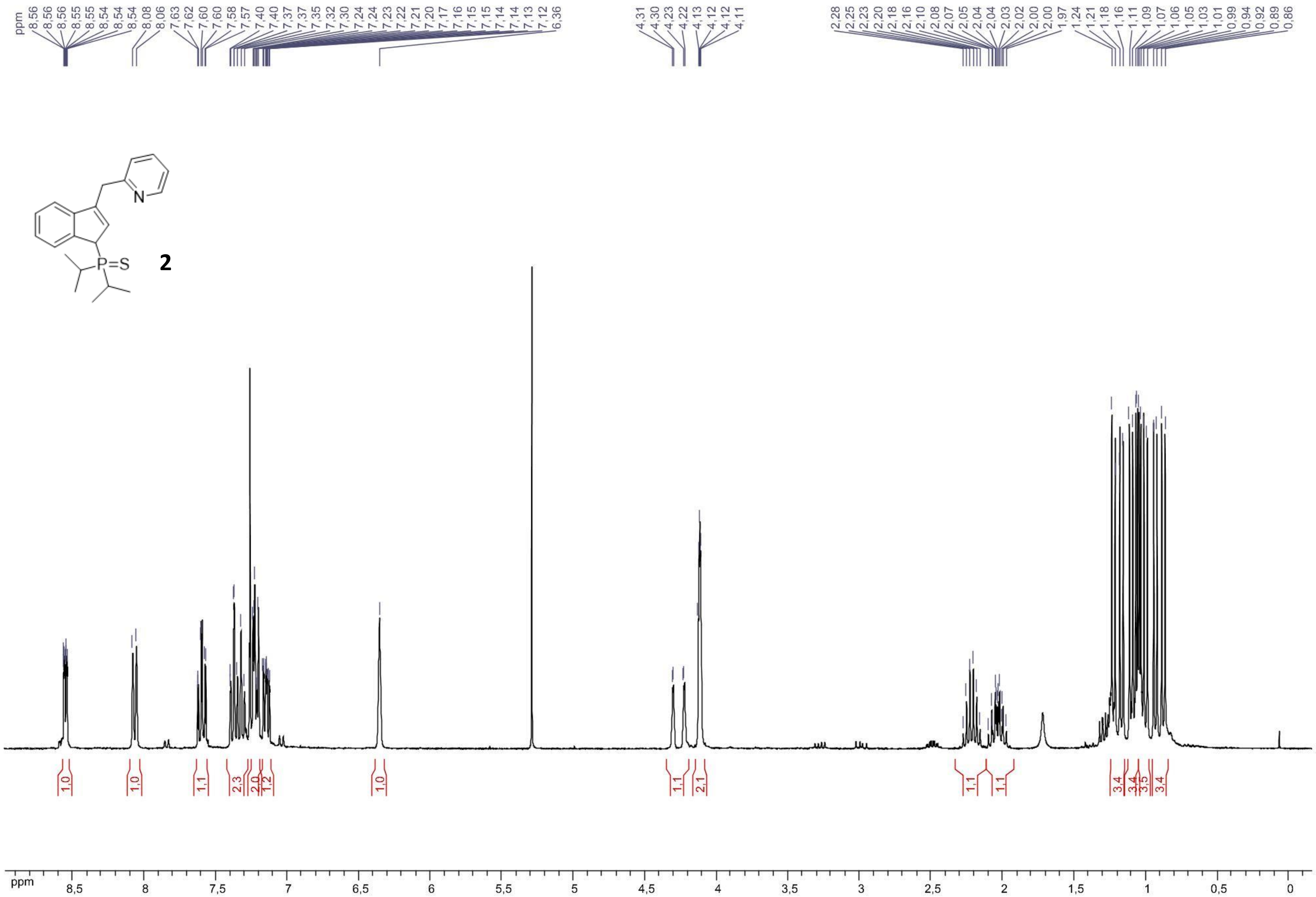
[2] SAINT, SADABS, Programs for data correction, Bruker–AXS.

[3] ShelXT, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. A*, 2015, **71**, 3.

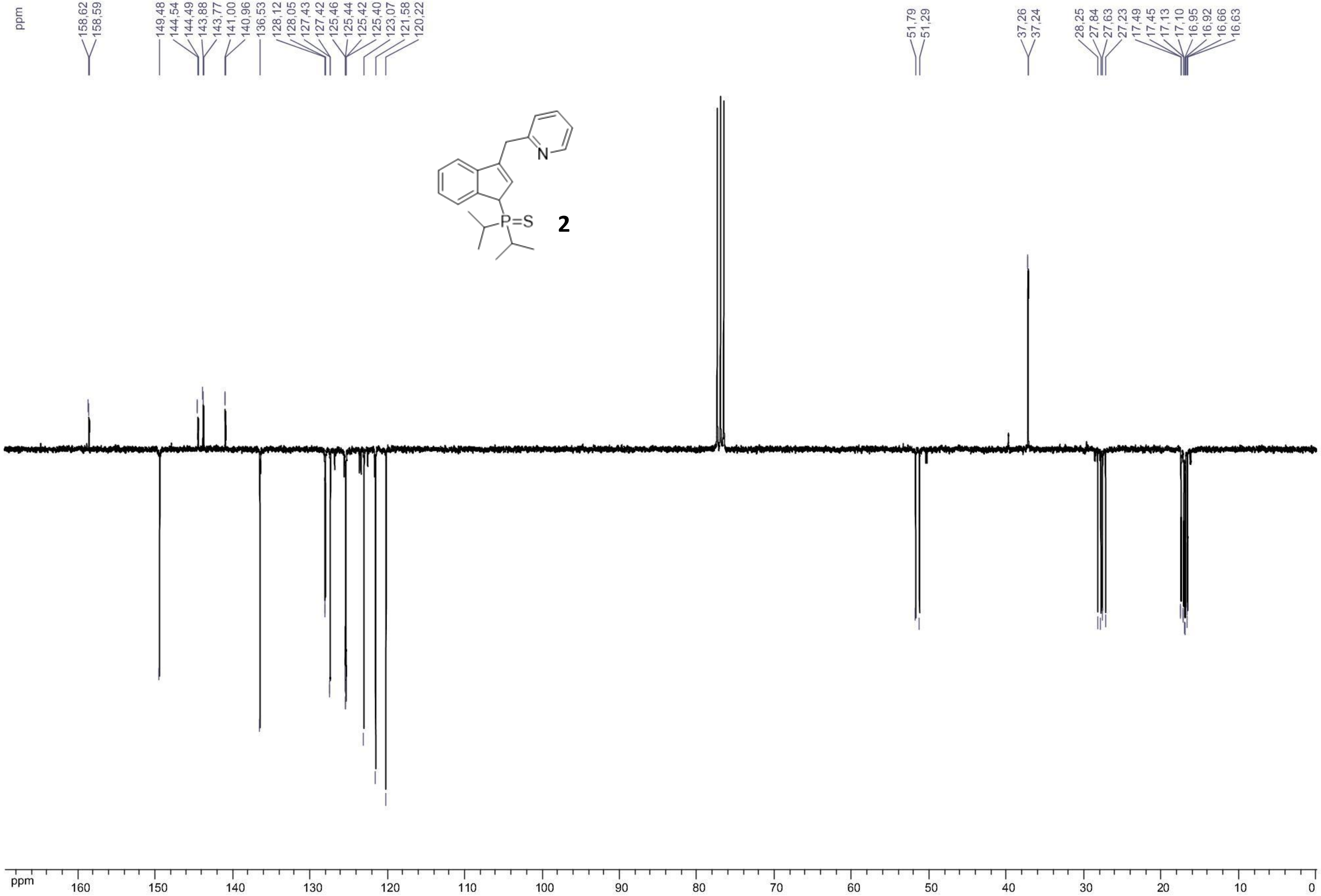
[4] ShelXL, G. M. Sheldrick, University of Göttingen, *Acta Crystallogr. Sect. C*, 2015, **71**, 3.

^{1}H NMR in CDCl$_3$

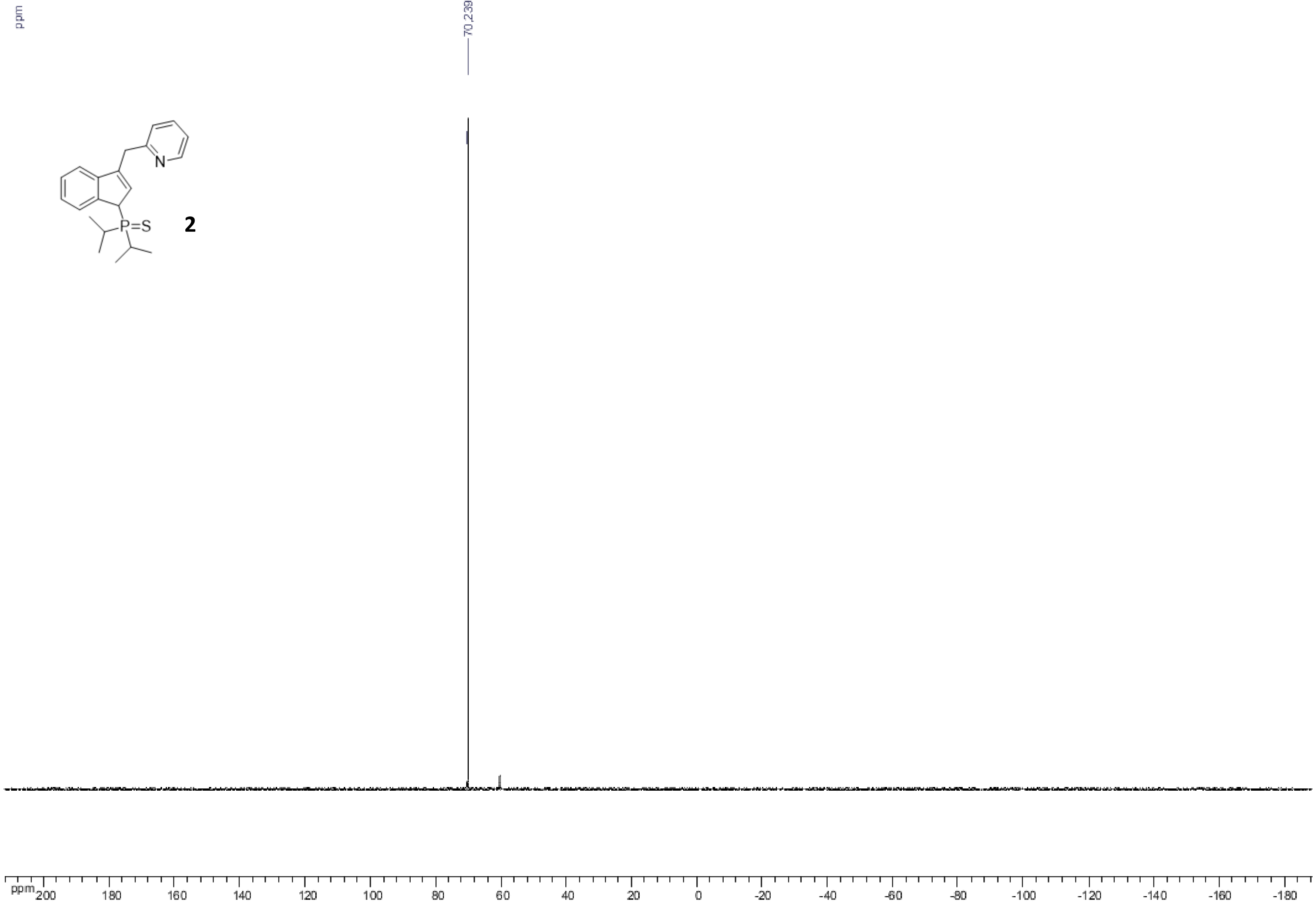
2



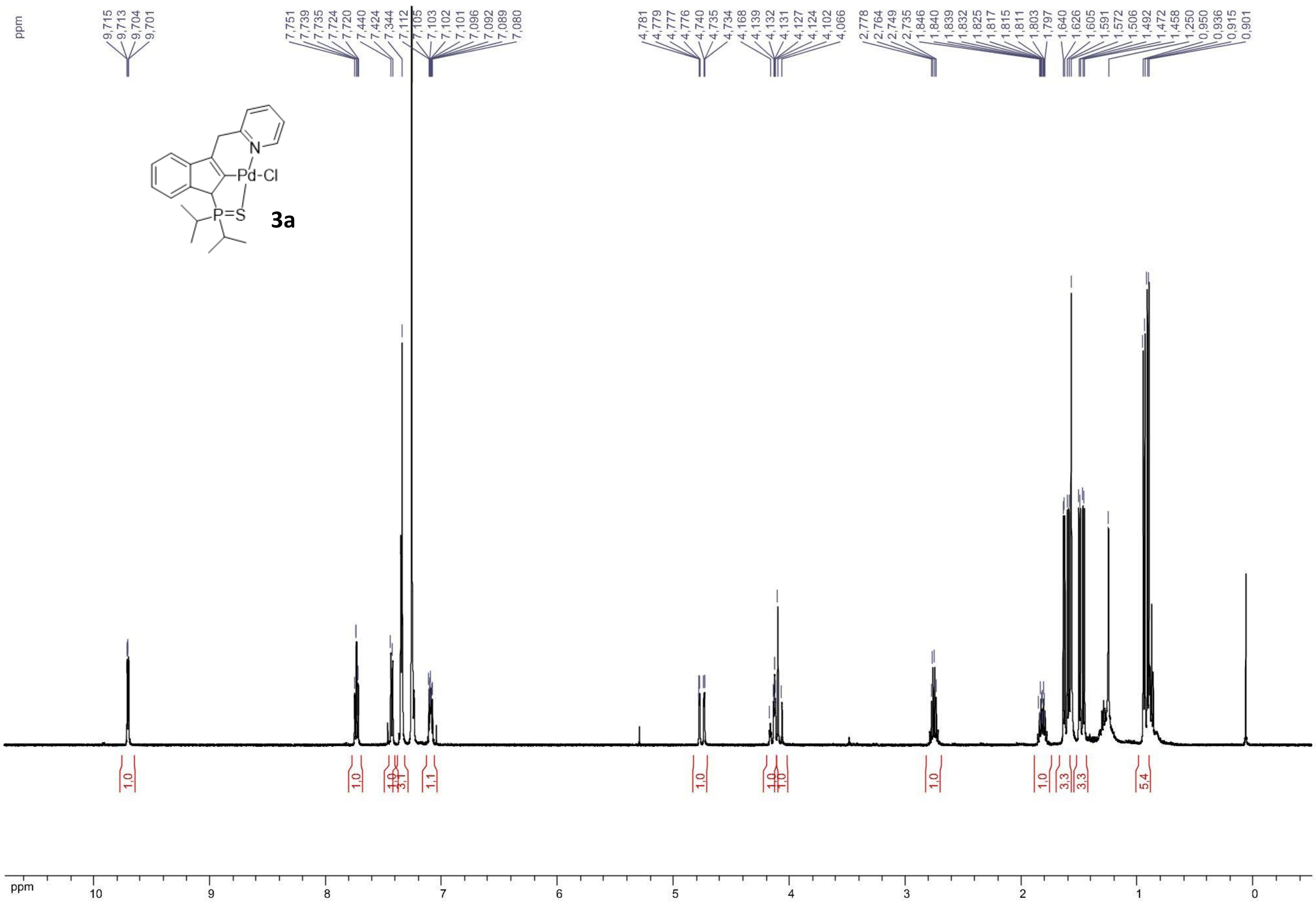
^{13}C NMR in $CDCl_3$



^{31}P NMR in CDCl$_3$

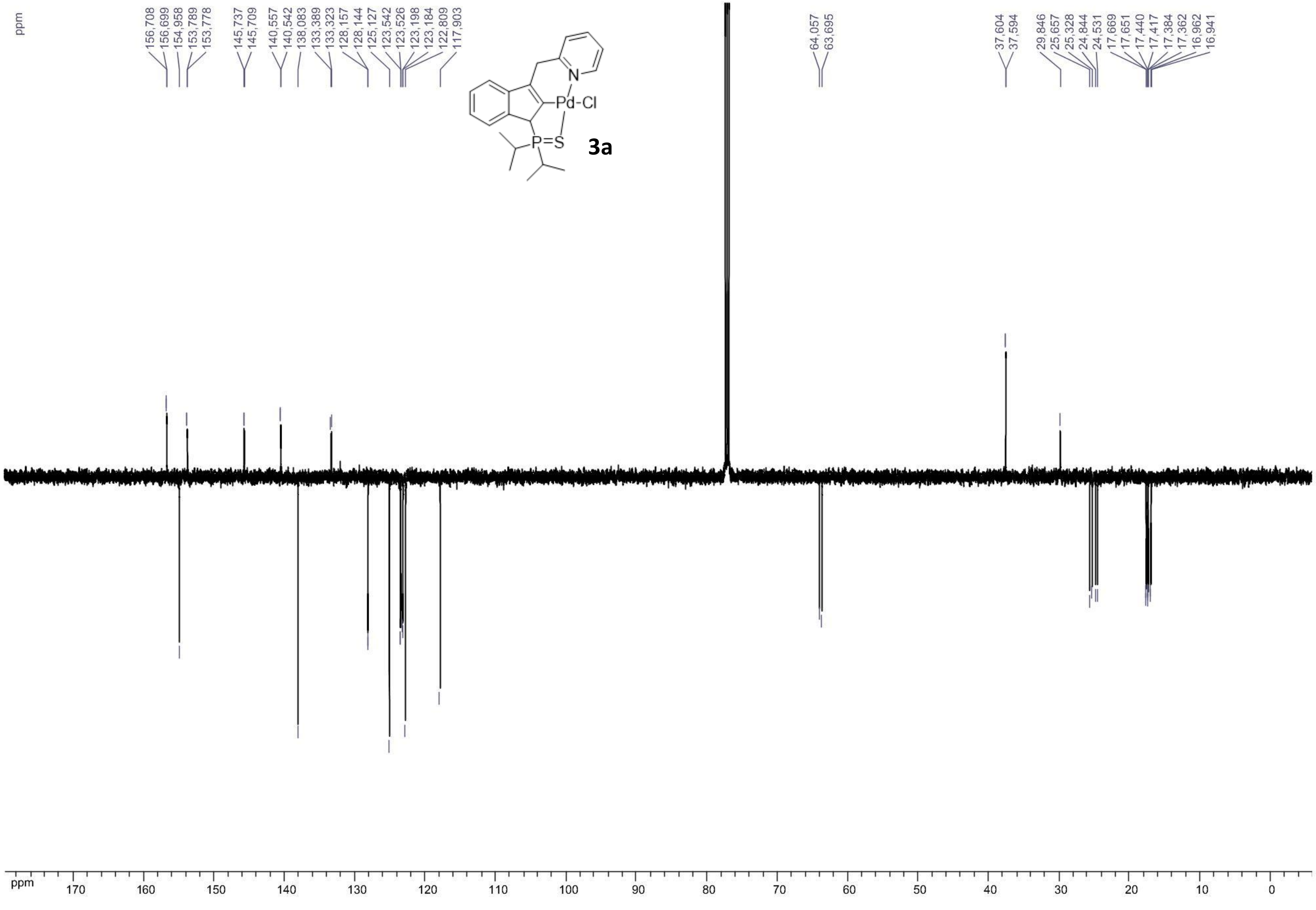


^{1}H NMR in $CDCl_3$



3a

^{13}C NMR in CDCl$_3$



3a

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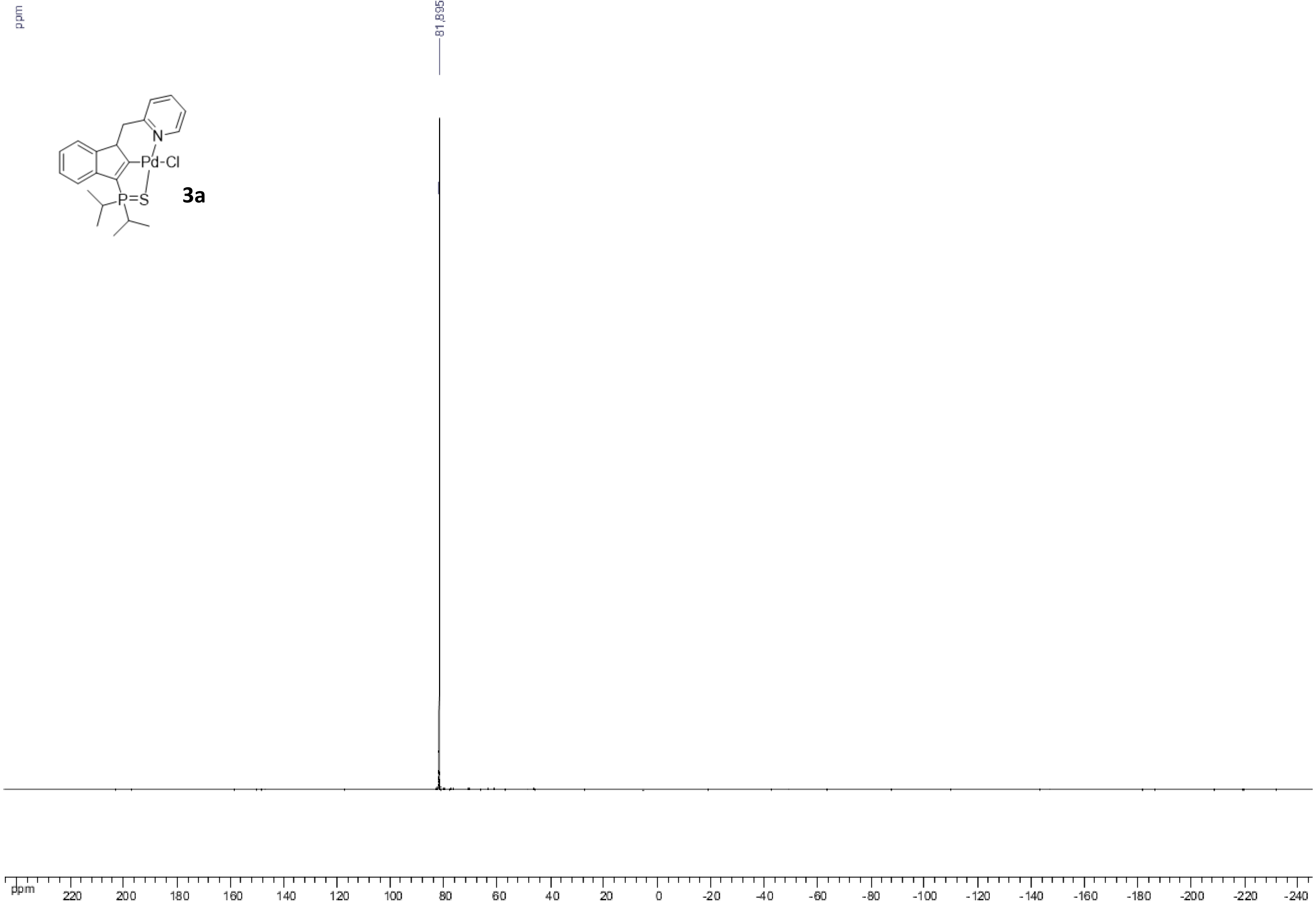
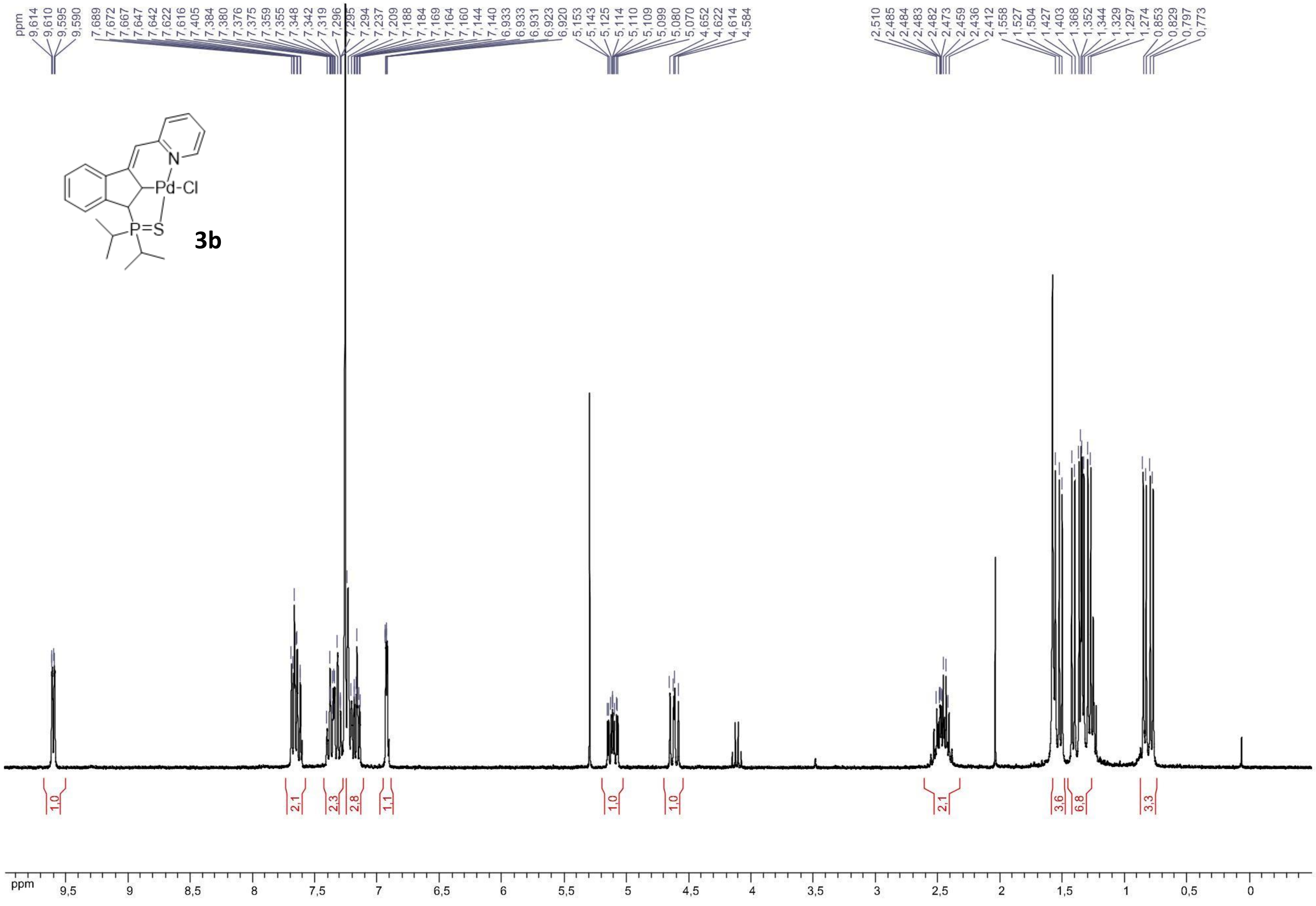


^{1}H NMR in CDCl$_3$



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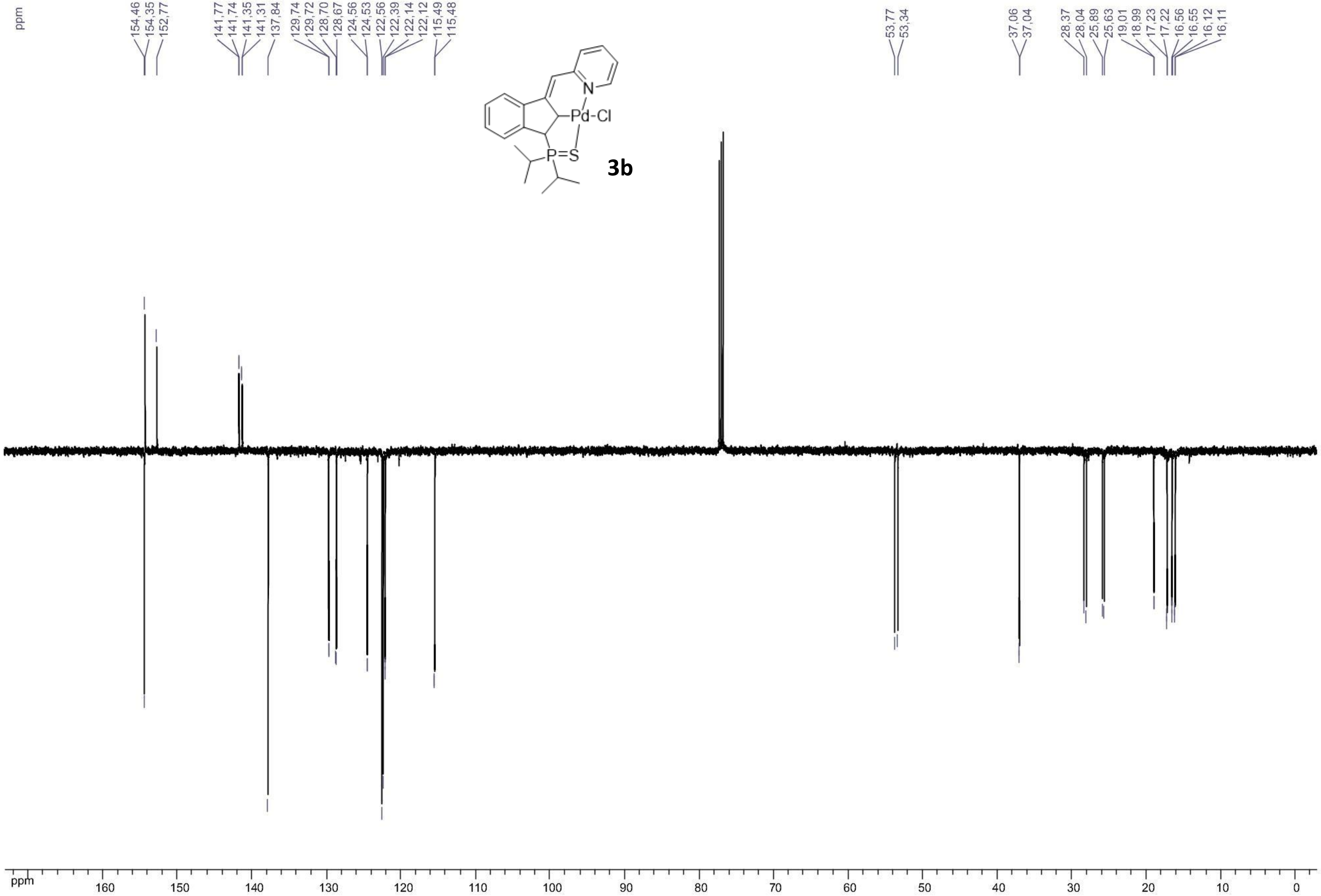

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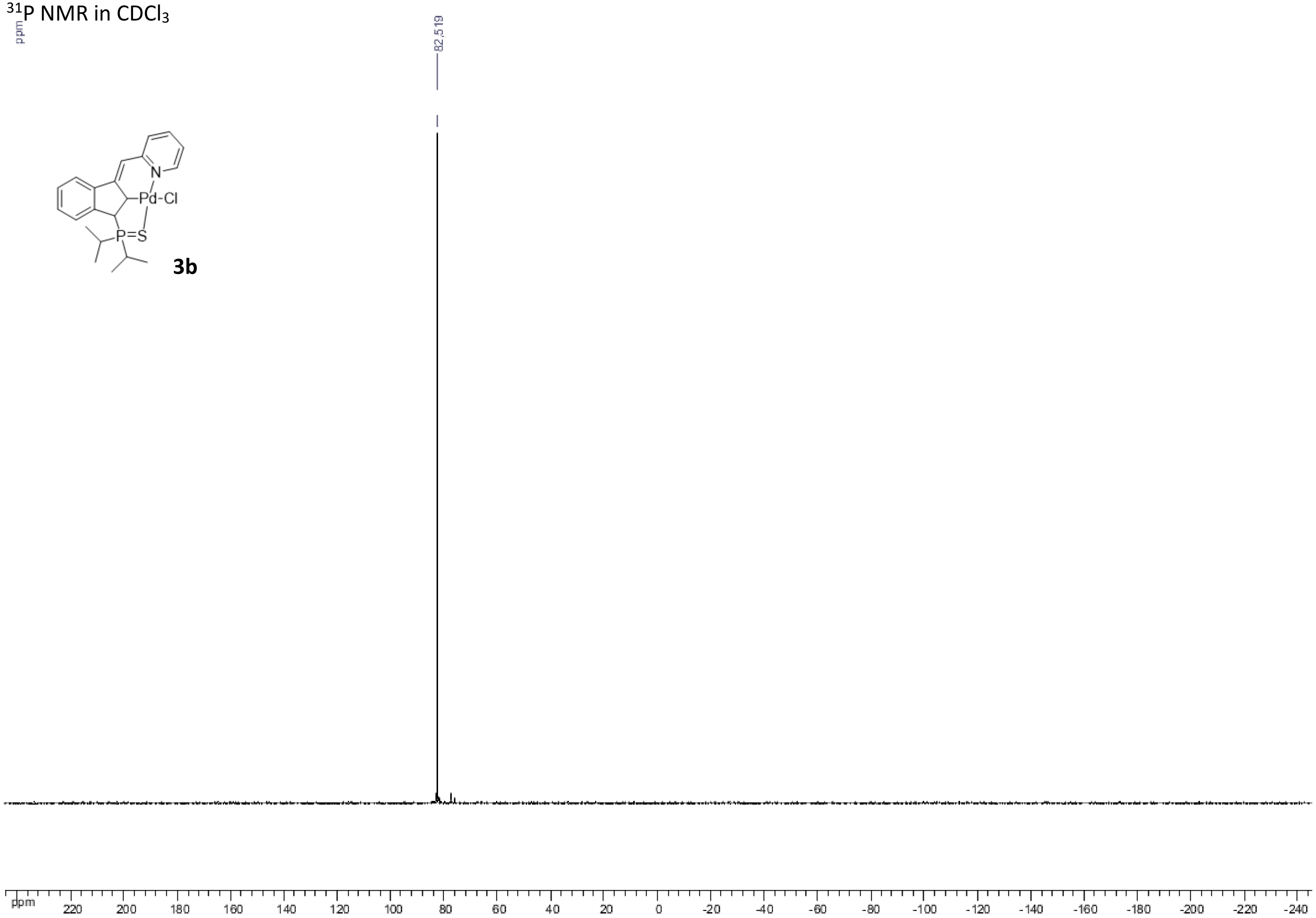
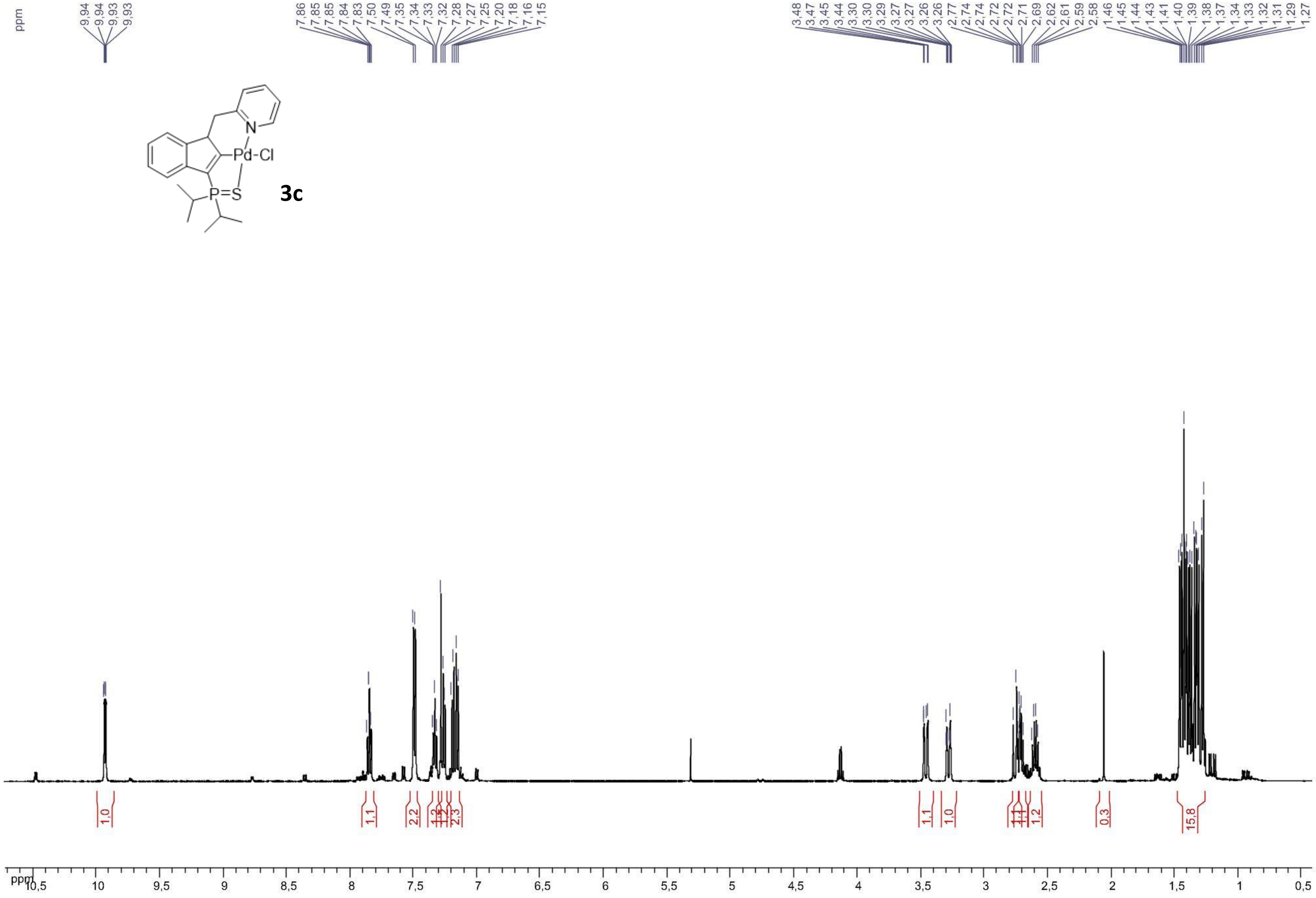
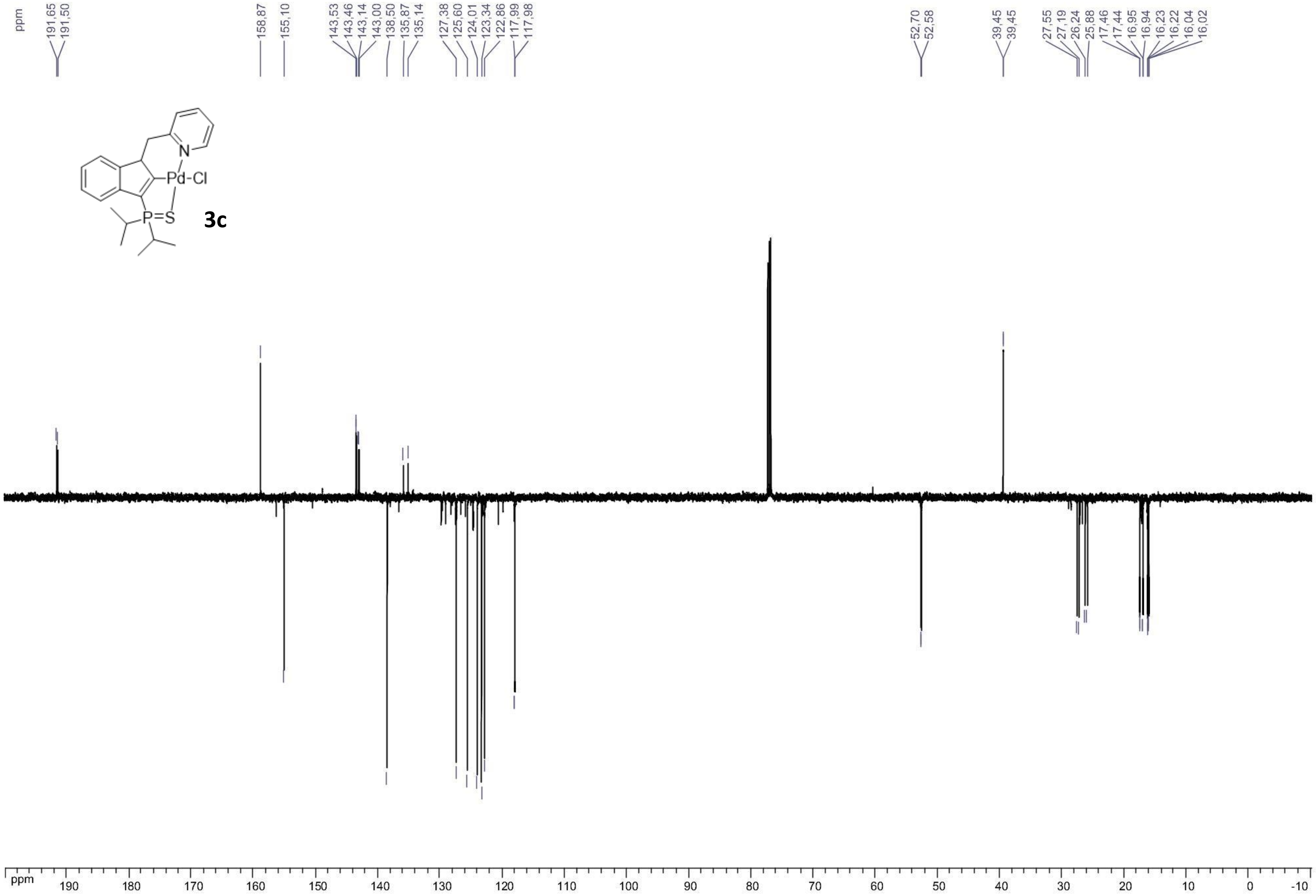


^1H NMR in $CDCl_3$


3c

^{13}C NMR in $CDCl_3$



3c

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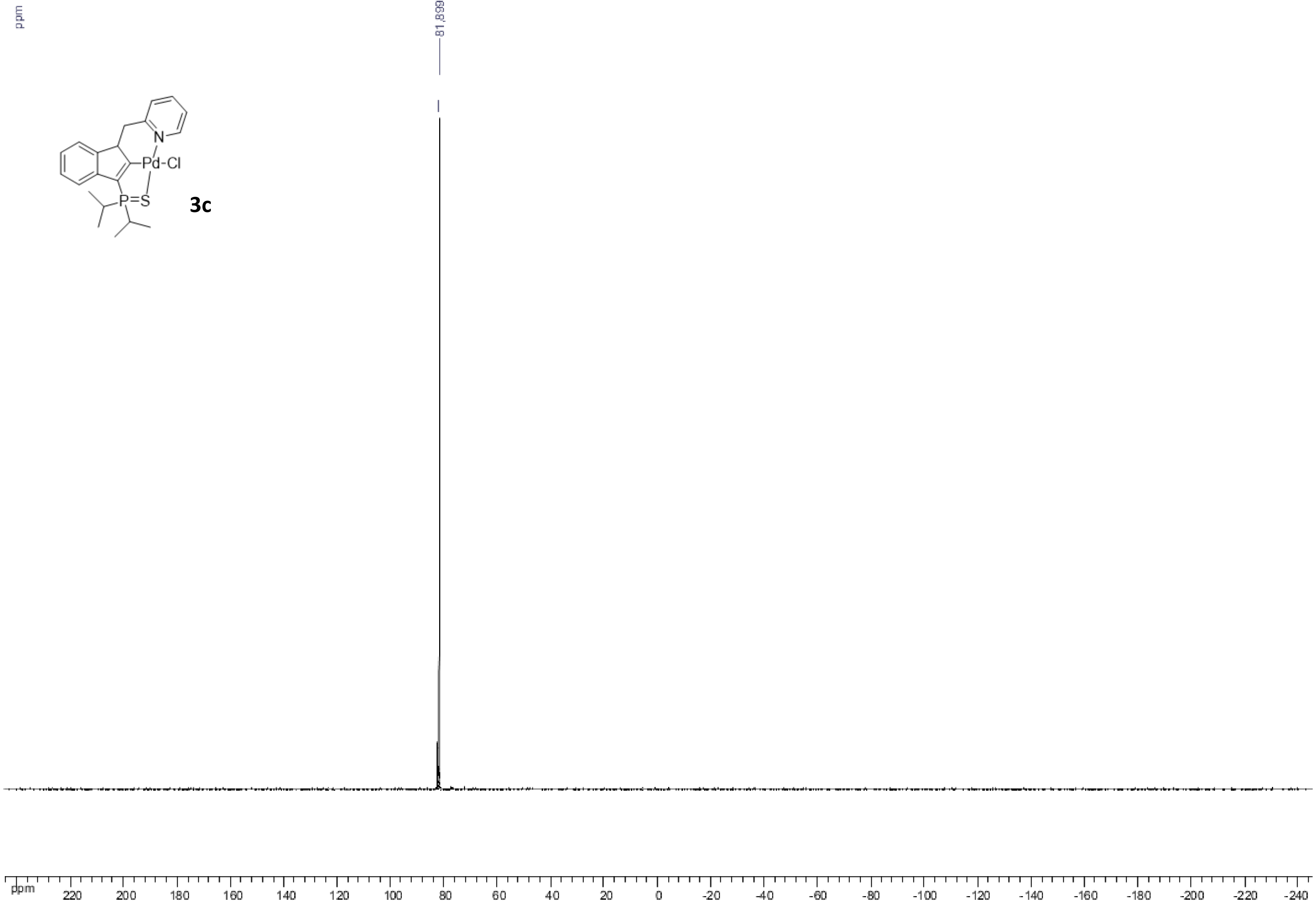

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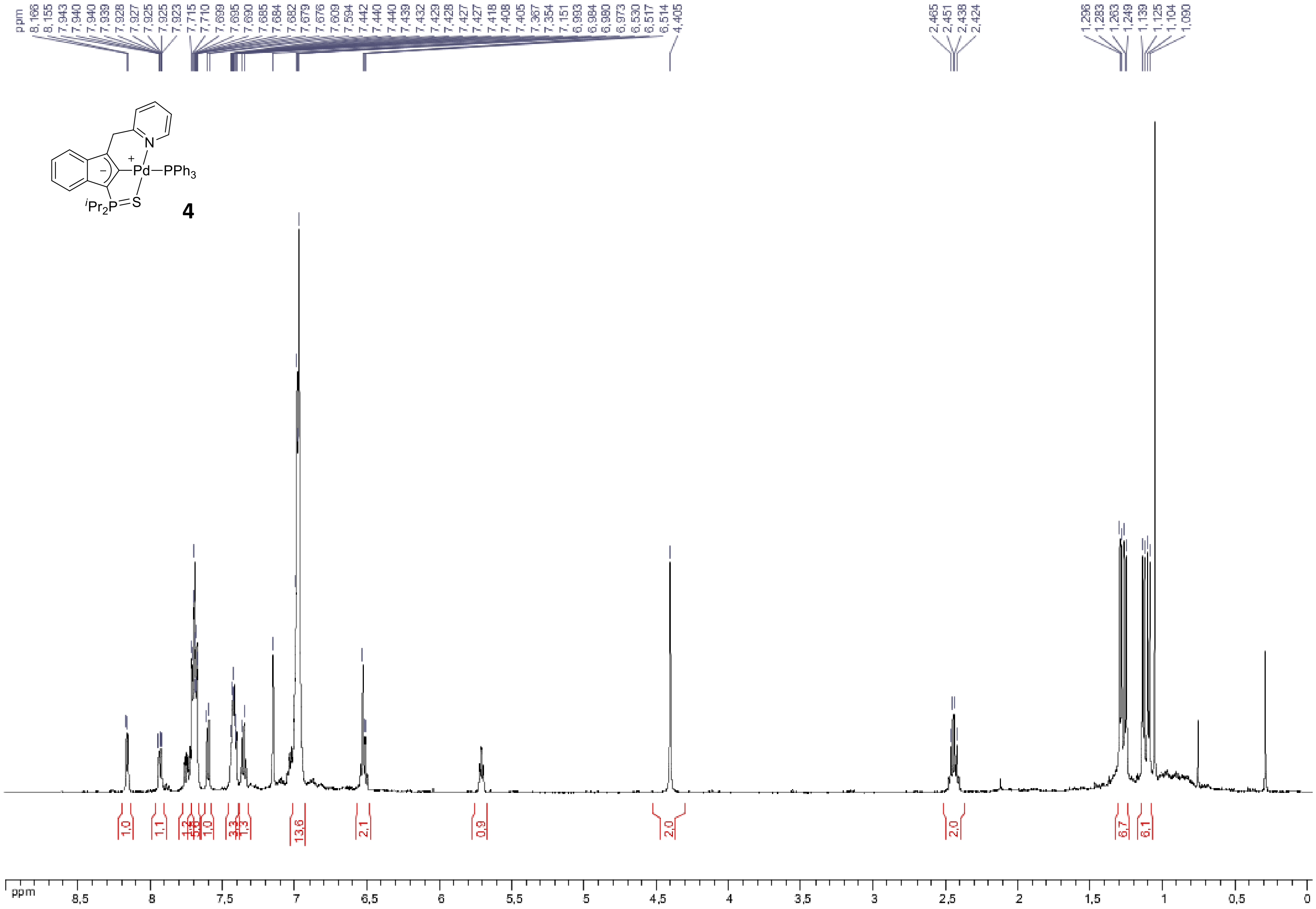
^{1}H NMR in C_6D_6



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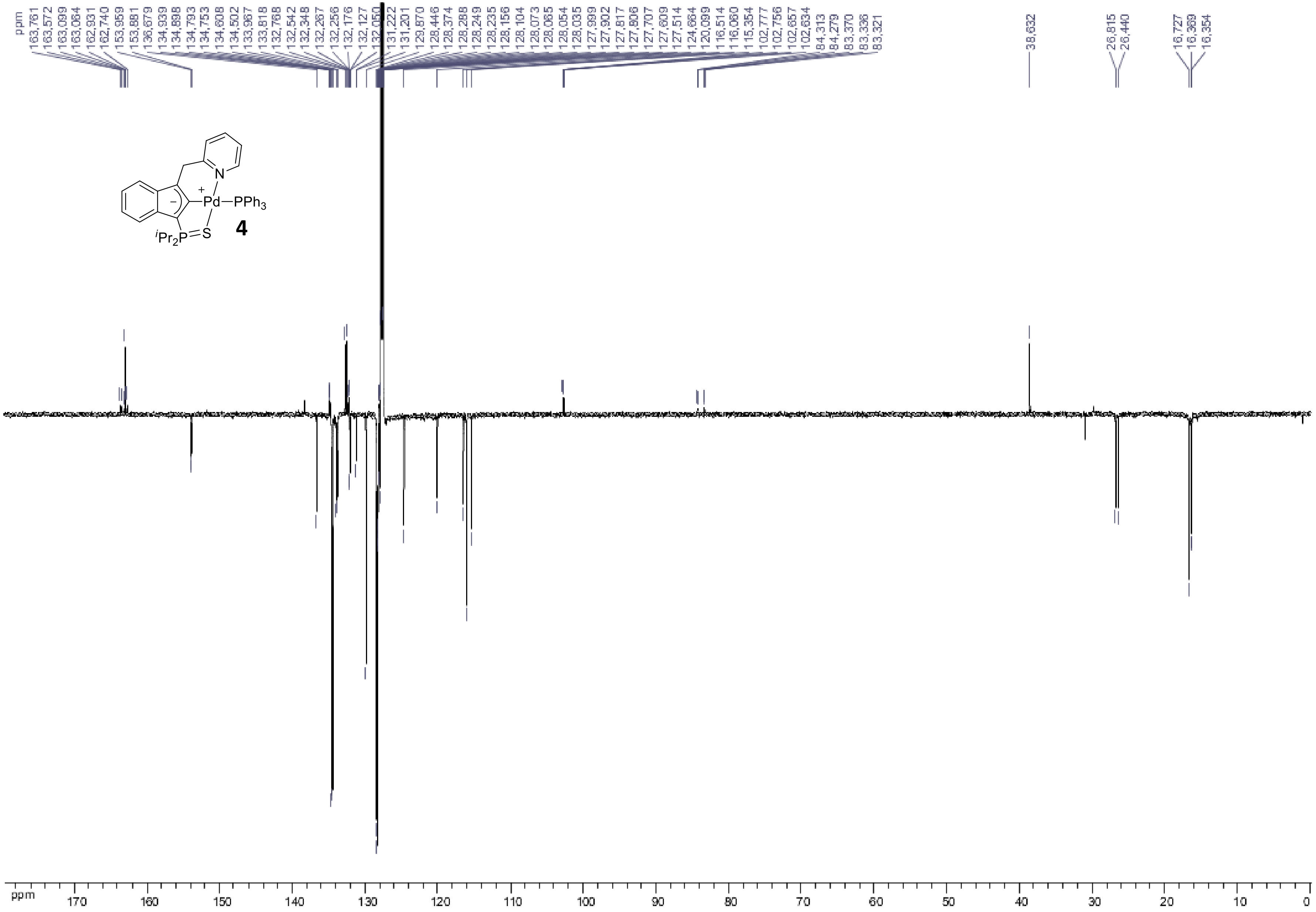
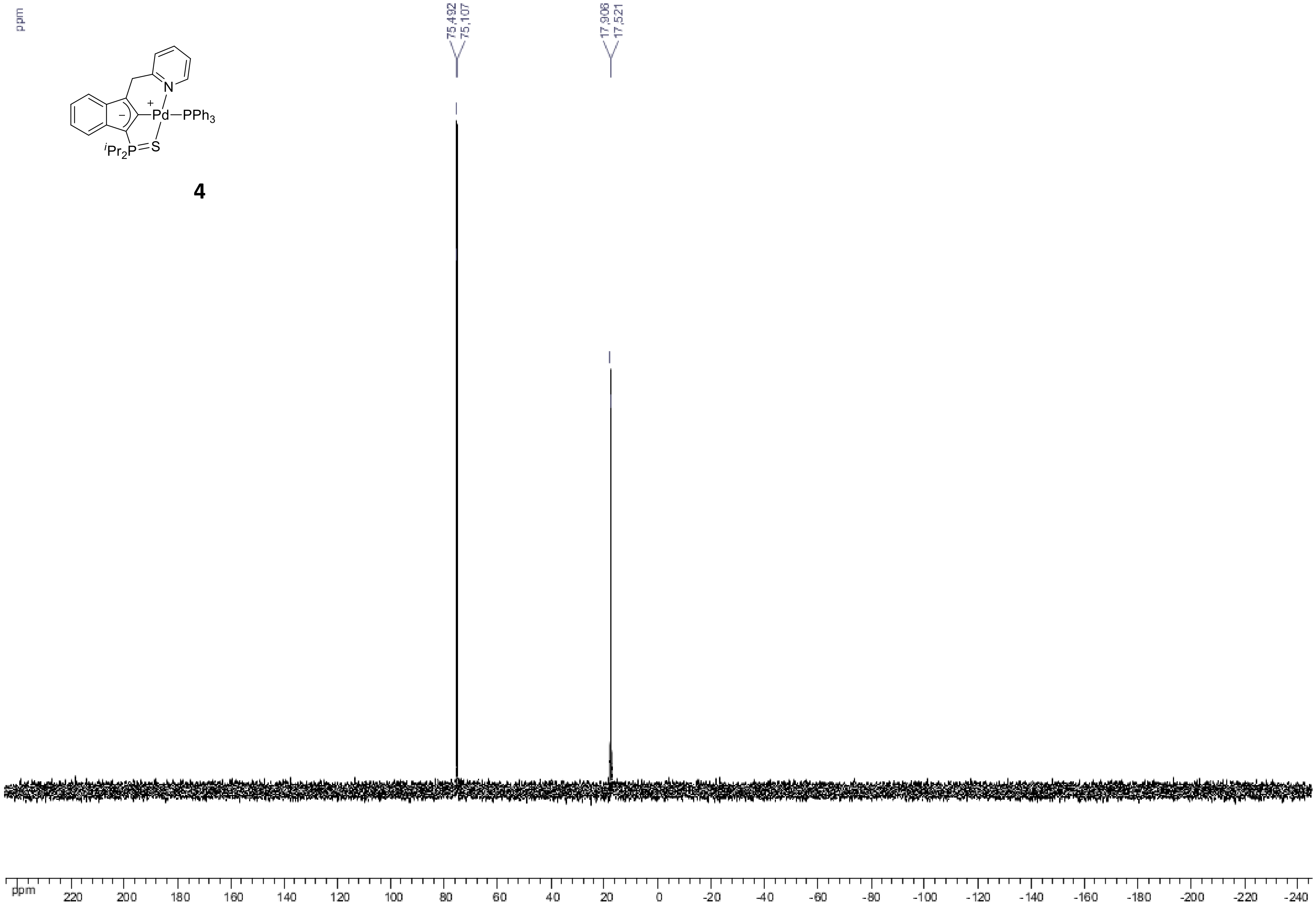
^{13}C NMR in C_6D_6

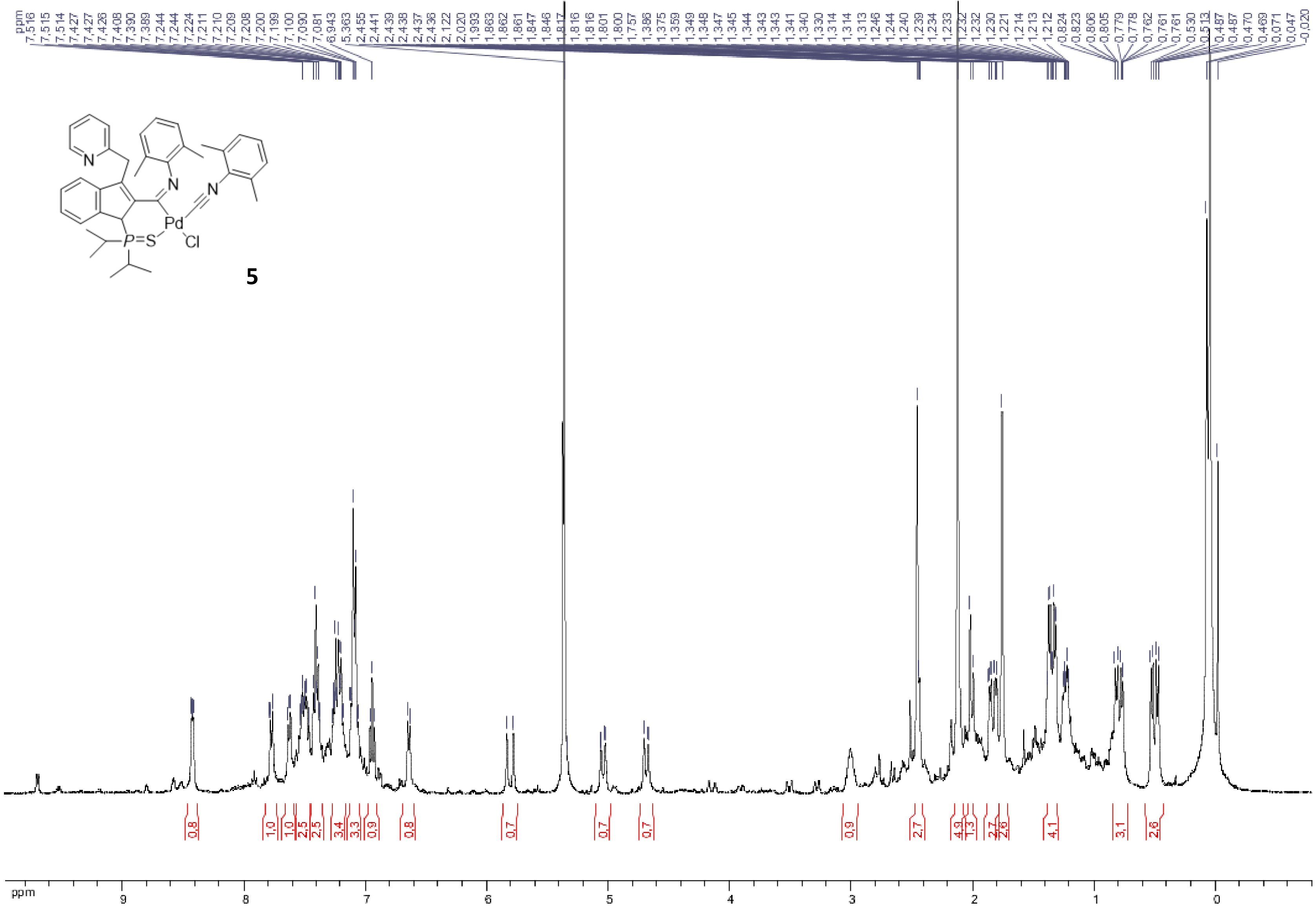


^{31}P NMR in C_6D_6



4

^1H NMR CD_2Cl_2



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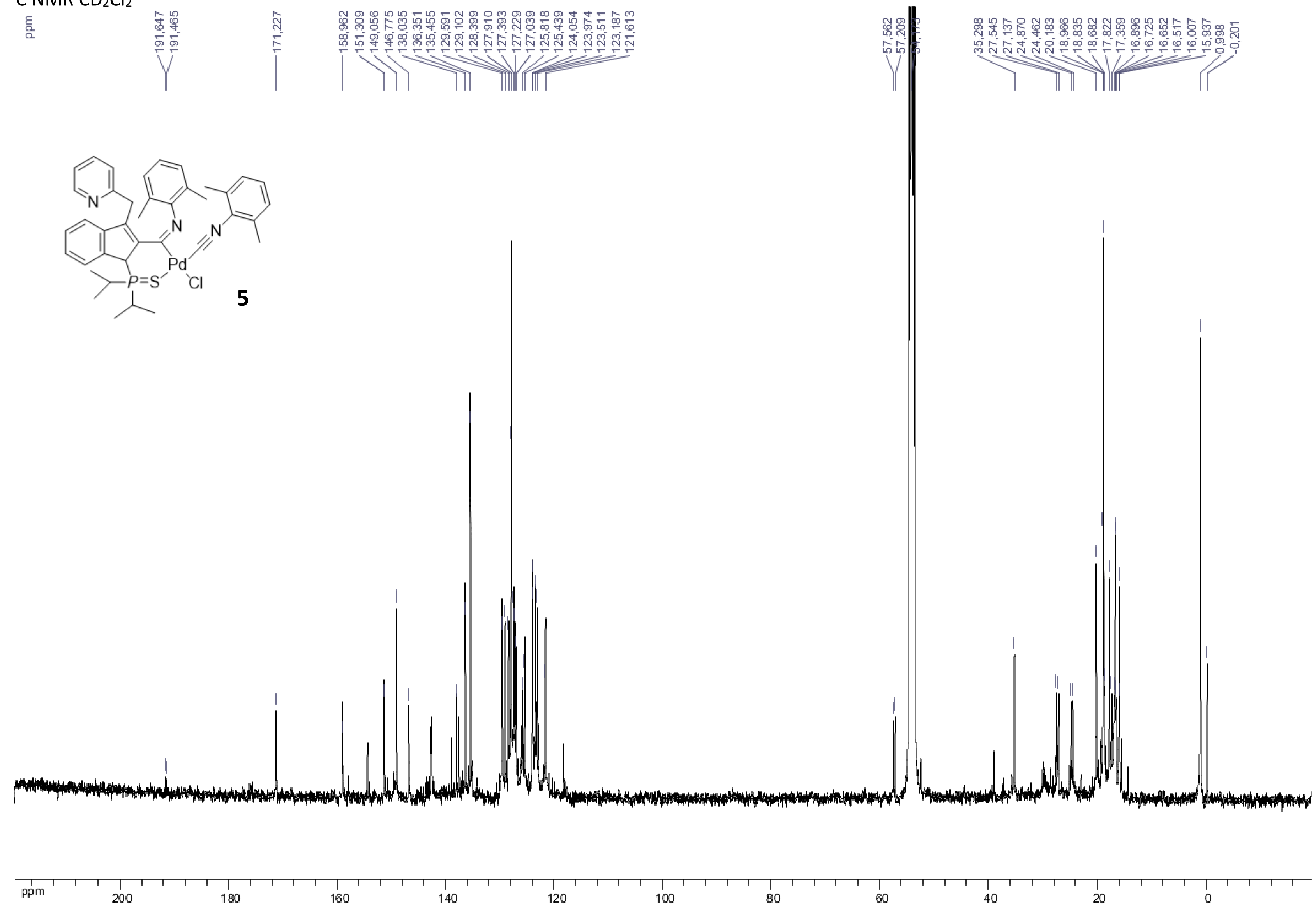
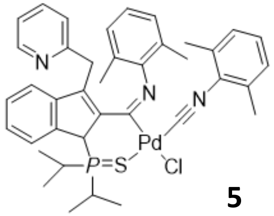


5

$^{31}P\{^1H\}$ NMR CD_2Cl_2



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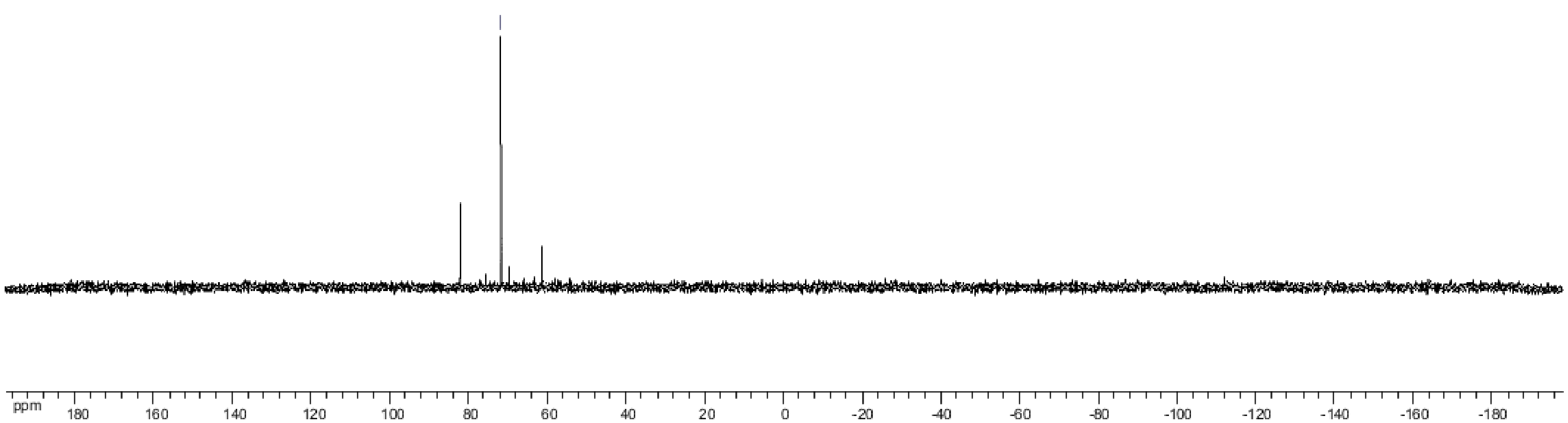
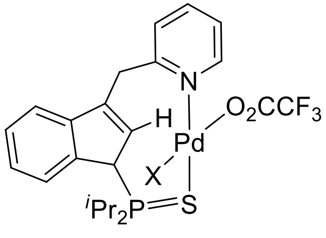
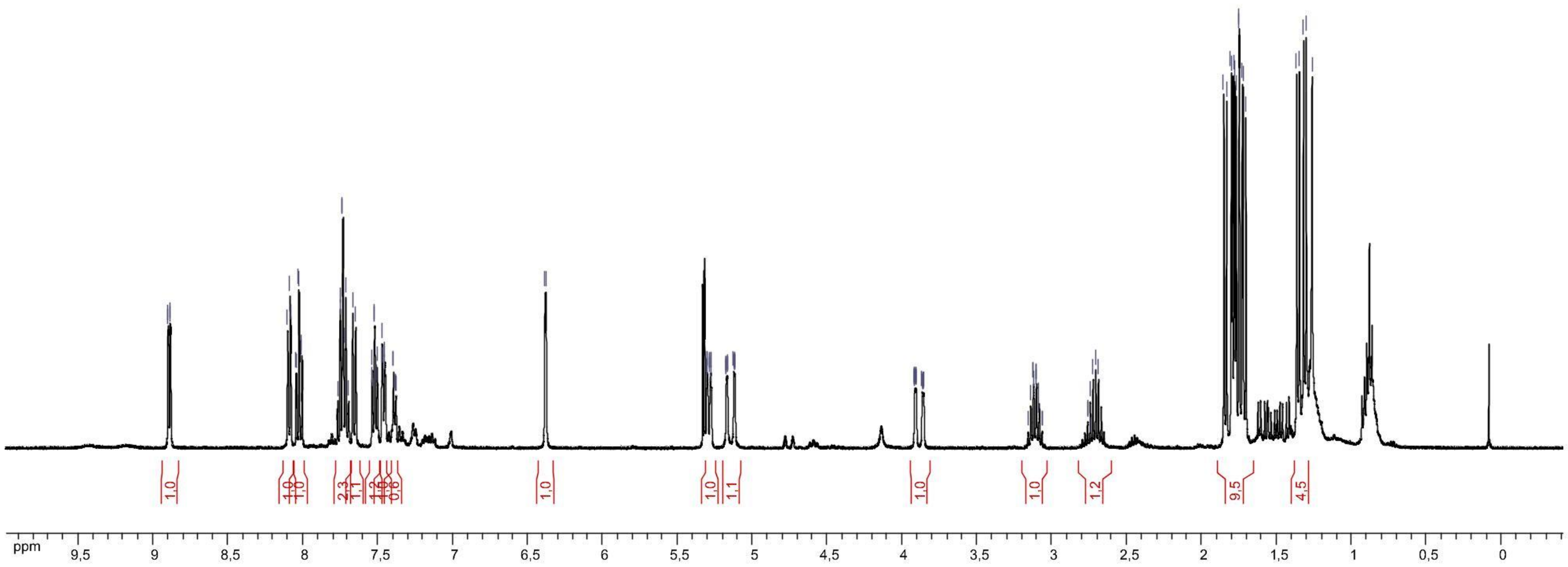


^{1}H NMR in CD_2Cl_2

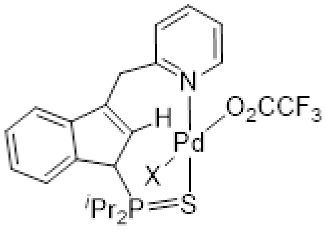


6

X = Cl or CF_3CO_2



^{31}P NMR in CD_2Cl_2



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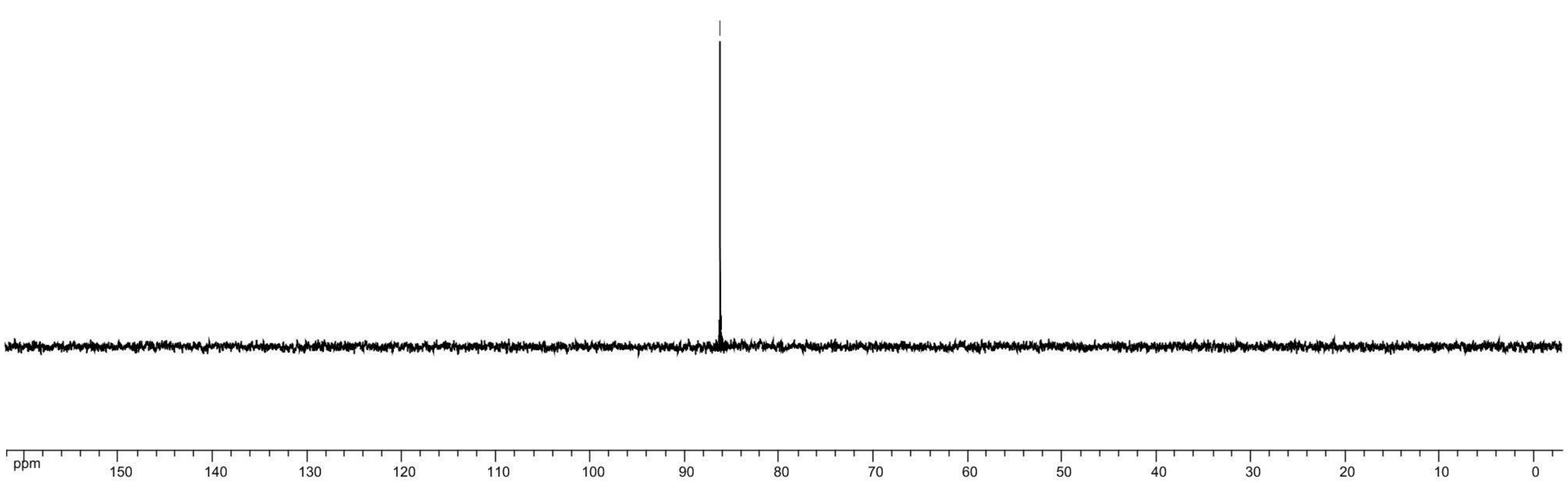
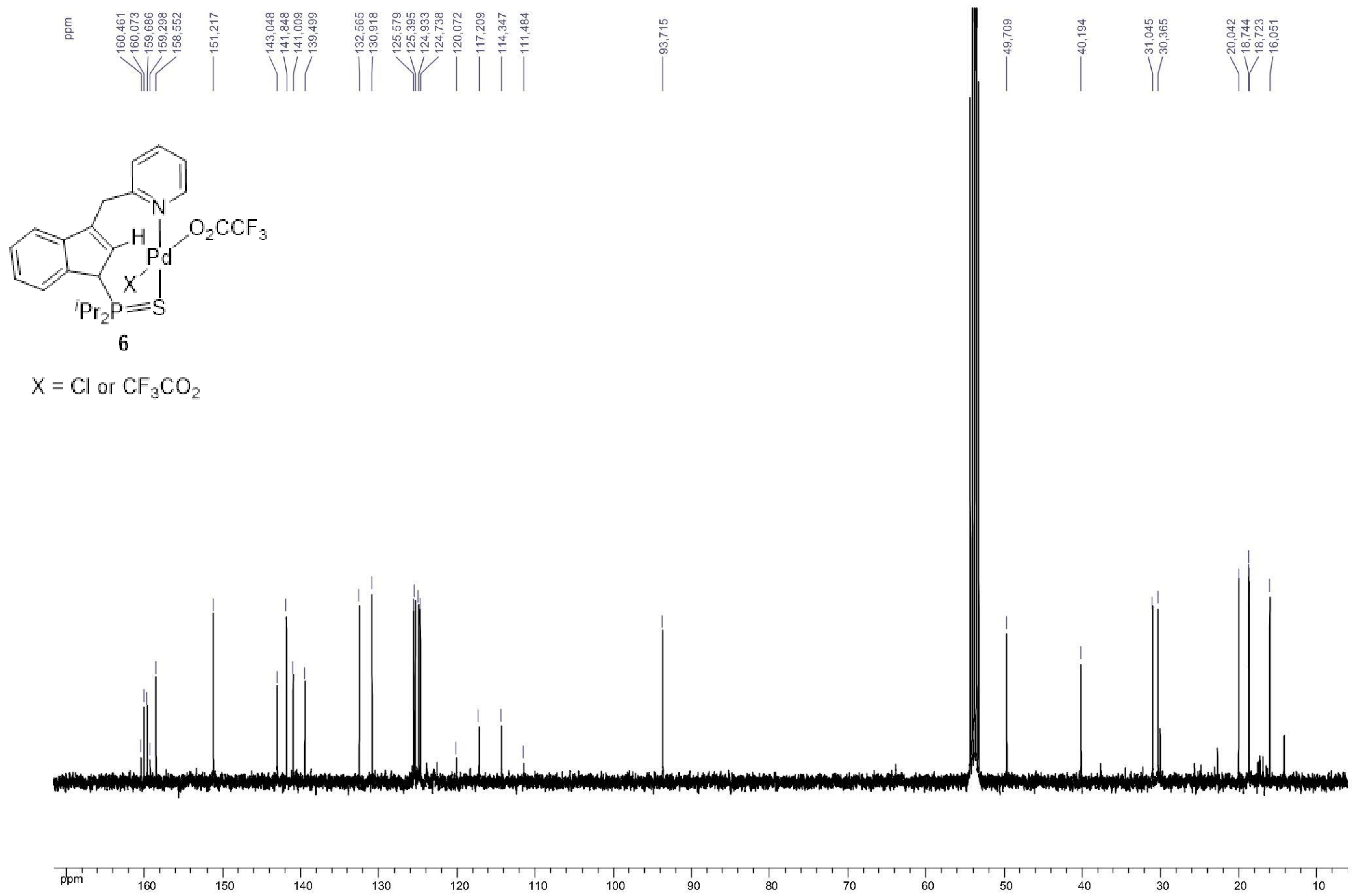
X = Cl or CF_3CO_2



^{13}C NMR in CD_2Cl_2



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X = Cl or CF_3CO_2