

Supplementary Information

Swift C–C Bond Insertion by a 12-Electron Palladium(0) Surrogate

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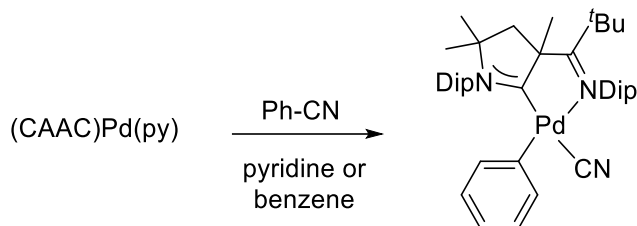
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1. General Methods

^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III 400 or a Bruker Avance III 300 instrument operating at 400.13 and 300.13 MHz for ^1H and at 100.62 and 75.47 MHz for ^{13}C , respectively, or a JEOL ECX 400 or a JEOL ECX 270 instrument operating at 400.18 and 269.71 MHz for ^1H and at 100.62 and 67.82 MHz for ^{13}C , respectively, at a probe temperature of 23 °C. The chemical shifts δ are calculated in ppm; the solvent residual signals of incomplete deuterated solvent molecules were used as internal reference for the ^1H NMR spectra and the carbon solvent signals for ^{13}C NMR spectral data. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, t = triplet, q = quartet, spt = septet, m = multiplet, br = broad signal. Coupling constants J are given in Hz. Melting points were determined using an Electrothermal IA9200 Programmable Digital Melting Point Apparatus. UV-VIS spectra were recorded on a J&M Analytik AG TIDAS 100 spectrometer and Schlenk cuvettes with a path length of 1 cm as solutions in THF. Solvents were purified using a two-column solid-state purification system (MBraun SPS 5/7 or Glass Contour System, Irvine, CA) and transferred to the glovebox without exposure to air. Pentane, hexanes and benzene were stored over a mirror of potassium, whereas all other solvents were stored over activated molecular sieves. NMR solvents were obtained dry and packaged under argon and stored over activated molecular sieves or a mirror of potassium (C_6D_6). The palladium(0) complex CAAC^{imine}-Pd(0) (**1**)¹ was synthesized as reported in the literature. Naphtho[*b*]cyclopropene was gratefully provided from Peter Chen's lab, where it was synthesized as reported in the literature.² All other reagents were obtained from commercial sources and used as is without further purification.

2. Synthesis and Crystallization of Metal Complexes

(CAAC^{imine})Pd(CN)(Ph) **2**



CAAC^{imine}-Pd(0) (1 eq., 25 mg, 40 μmol) was dissolved in benzene to give a dark-red solution. Benzonitrile (1.2 eq./5.0 μl /48 μmol) was added, and the solution turned orange-yellow within 4 hours, whereby a yellow precipitate forms. Quantitative precipitation was induced by adding *n*-pentane. The product **2** was washed with *n*-pentane and dried *in vacuo* to give it as a yellowish solid in quantitative yield. Single crystals suitable for X-ray crystallography were obtained by slow evaporation of a concentrated pyridine solution.

Note: In pyridine, quantitative conversion requires 4 days at room temperature.

¹H NMR (269.7 MHz, pyridine-*d*₅): δ = 7.47–7.56 (m, 2H, ArCH_{Dip}), 7.35–7.45 (m, 1H, ArCH_{Dip}), 7.25–7.34 (m, 3H, ArCH_{Dip}), 7.01–7.04 (m, 1H, ArH), 6.82–6.84 (m, 2H, ArH), 6.72–6.76 (m, 2H, ArH), 3.95 (spt, ³*J* = 6.8 Hz, 1H, CH(CH₃)₂), 3.34 (spt, ³*J* = 6.8 Hz, 1H, CH(CH₃)₂), 3.18 (d, ³*J* = 13.9 Hz, 1H, CH₂), 3.07 (spt, ³*J* = 6.8 Hz, 1H, CH(CH₃)₂), 2.41–2.48 (m, 1H, CH(CH₃)₂), 2.30 (d, ³*J* = 13.9 Hz, 1H, CH₂), 2.25 (s, 3H, CH₃), 2.12 (d, ³*J* = 6.2 Hz, 3H, CH(CH₃)₂), 1.99 (d, ³*J* = 6.2 Hz, 3H, CH(CH₃)₂), 1.69 (d, ³*J* = 6.2 Hz, 3H, CH(CH₃)₂), 1.46 (d, ³*J* = 6.9 Hz, 3H, CH(CH₃)₂), 1.43 (d, ³*J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.40 (s, 3H, CH₃), 1.36 (d, ³*J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.32 (s, CH₃), 1.21 (s, 9H, C(CH₃)₃), 1.10 (d, ³*J* = 6.2 Hz, 3H, CH(CH₃)₂), 0.18 (d, ³*J* = 6.2 Hz, 3H, CH(CH₃)₂) ppm.

¹³C NMR (100.6 MHz, pyridine-*d*₅): δ = 248.4 (C, carbene), 189.6 (C, imine), 147.5 (ArC_{Dip}), 146.4 (ArC_{Dip}), 146.3 (ArC_{Dip}), 145.5 (ArC_{Dip}), 140.0 (CN), 138.7 (ArC_{Dip}), 137.7 (ArC_{Dip}), 137.3 (ArCH_{Dip}), 136.5 (ArCH_{Dip}), 134.9 (ArC_{BN}), 130.4 (ArCH_{Dip}), 128.9 (ArCH_{Dip}), 126.8 (ArCH_{BN}), 126.5 (ArCH_{BN}), 126.2 (ArCH_{BN}), 124.5 (ArCH_{BN}), 122.0 (ArCH_{BN}), [Superimposed by pyridine-*d*₅: 2x ArCH_{Dip}], 82.6 (C_q), 78.1 (C_q), 45.9 (CH₂), 44.0 (C_q), 33.6 (CH₃), 31.7 (3x C(CH₃)₃), 31.3 (CH₃), 30.4 (CH(CH₃)₂), 29.8 (CH(CH₃)₂), 29.5 (CH(CH₃)₂), 29.3 (CH(CH₃)₂), 28.8 (CH(CH₃)₂), 27.5 (CH(CH₃)₂), 26.8 (CH(CH₃)₂), 25.4 (CH(CH₃)₂), 24.9 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 24.2 (CH₃), 24.1 (CH(CH₃)₂), 22.6 (CH(CH₃)₂) ppm.

M.p.: 168 °C (decomp.).

ESI-MS (in THF): *m/z* calcd. For [M+H]⁺ ([C₄₃H₆₀N₃Pd]⁺) 724.3817, found 724.3797.

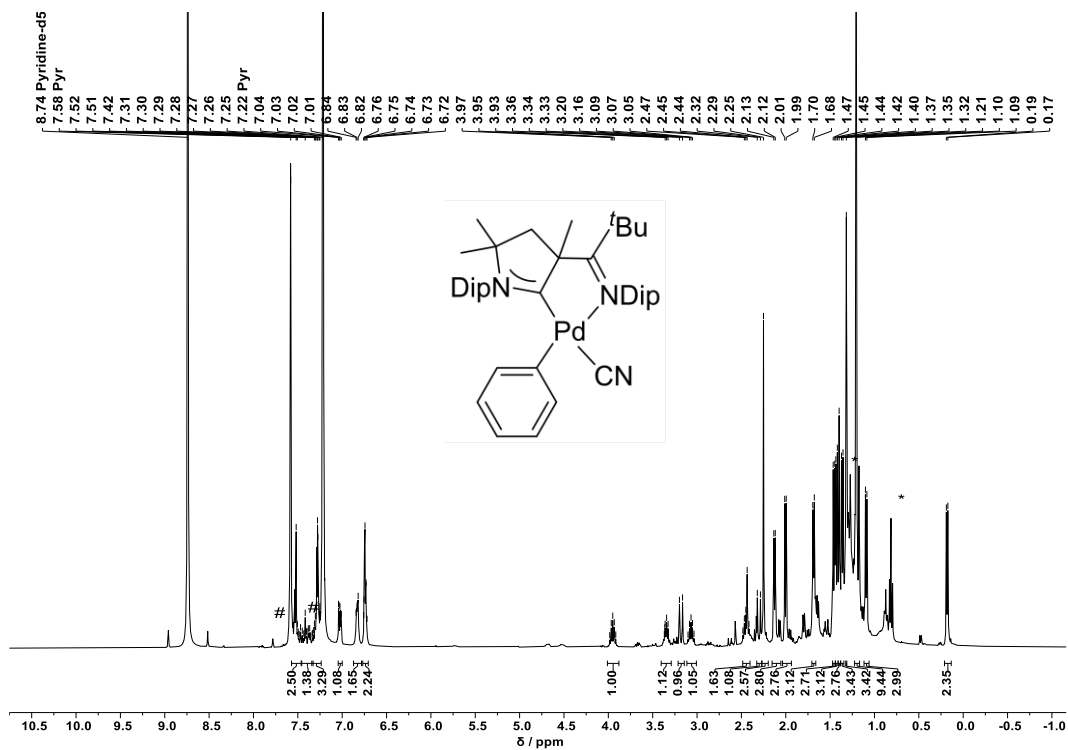


Figure S1. ^1H NMR spectrum of **2** in pyridine- d_5 (400.13 MHz). Residual solvent impurities: pentane (*), benzonitrile (#).

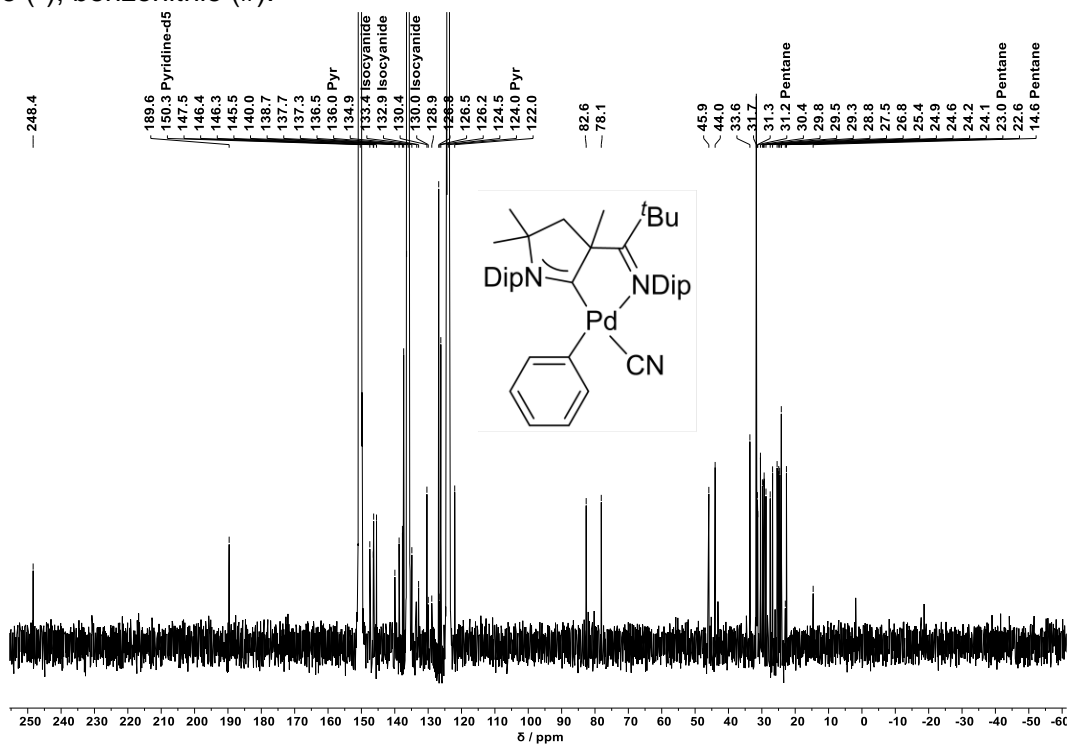


Figure S2. ^{13}C NMR spectrum of **2** in pyridine- d_5 (100.6 MHz).

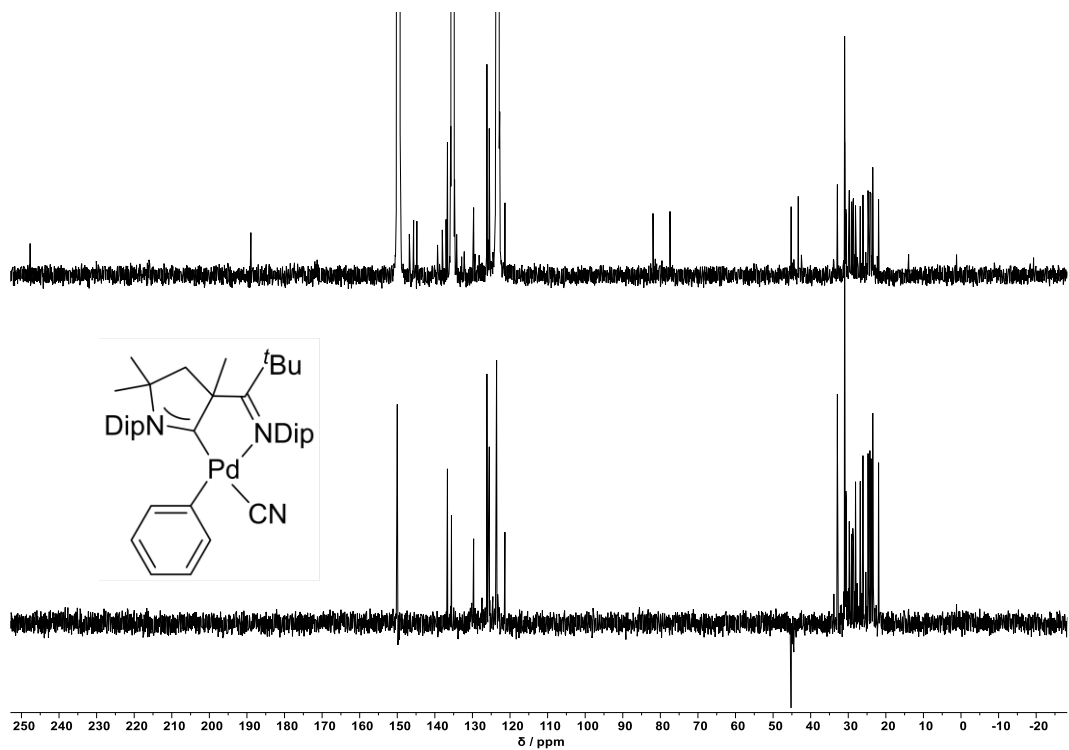


Figure S3. ^{13}C NMR spectrum of **2** in pyridine- d_5 (100.62 MHz) (top), stacked with the DEPT-135 spectrum (bottom).

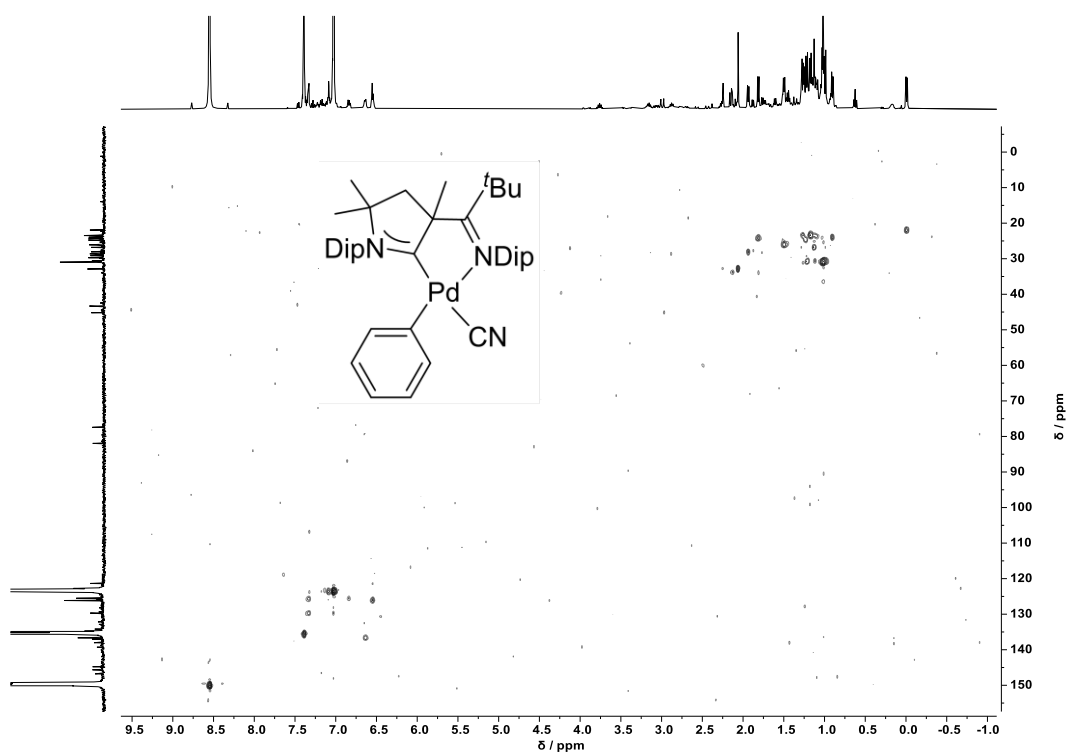


Figure S4. HSQC NMR spectrum of **2** in pyridine- d_5 (400.13 MHz, 100.62 MHz).

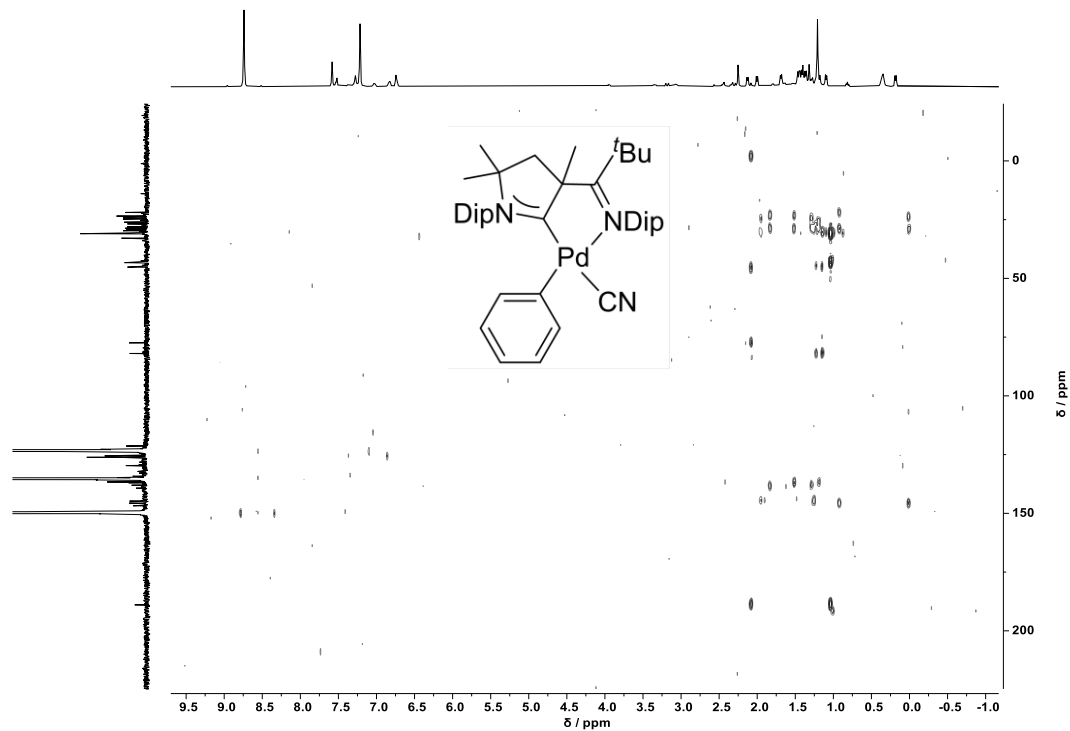


Figure S5. HMBC NMR spectrum of **2** in pyridine- d_5 (400.13 MHz, 100.62 MHz).

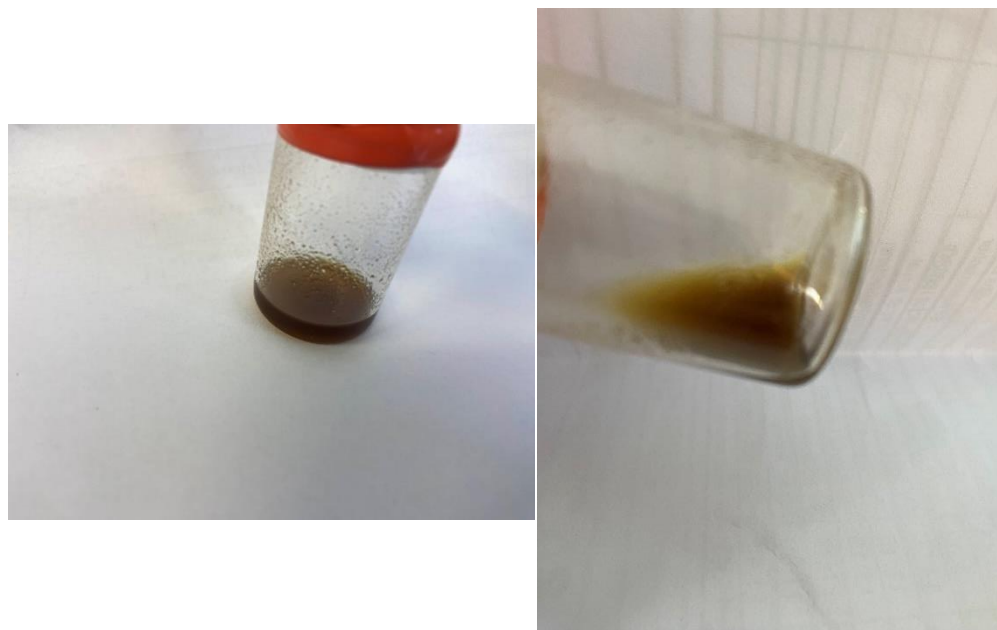


Figure S6. Precipitate of **2** in benzene- d_6 after 4 h reaction time.

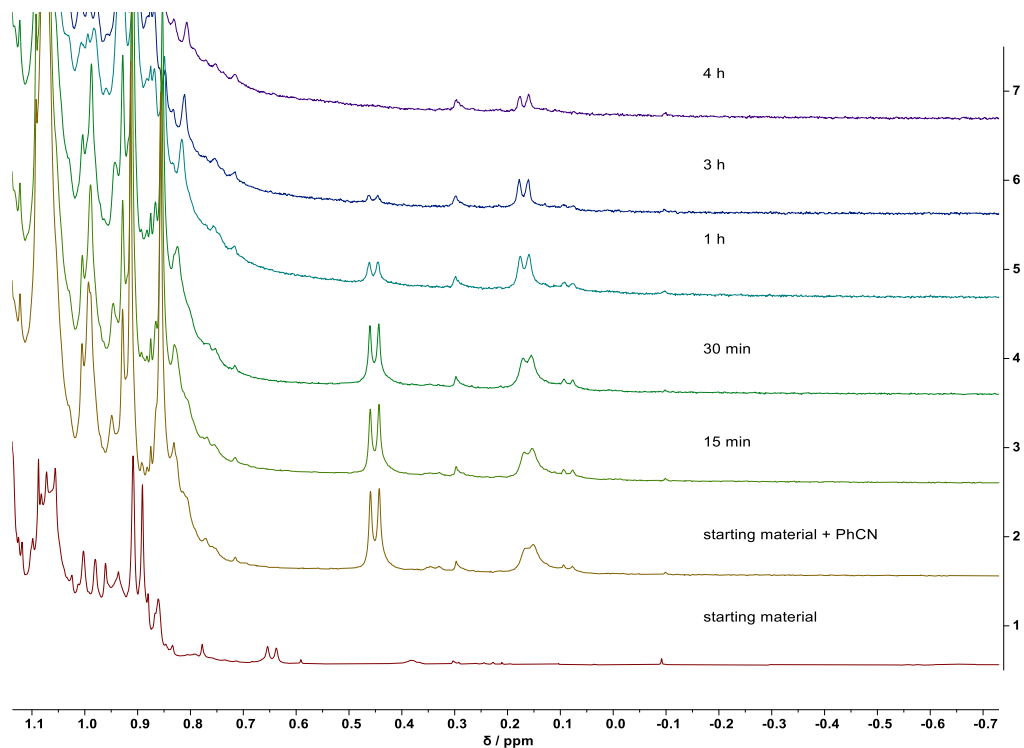
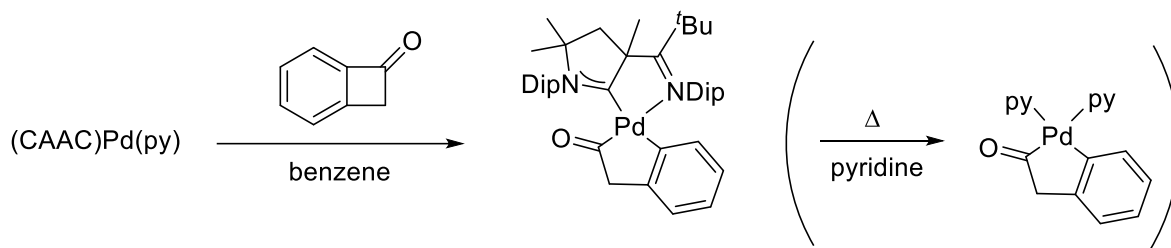


Figure S7. ¹H-NMR reaction monitoring in benzene-d₆ of the formation of **2** tentatively suggests the formation of an intermediate π -complex according to comparison with related NMR spectra in the literature.¹ Note that the starting material gives broad signals in benzene-d₆, and that precipitate is already present after 15 min reaction time.

(CAAC^{imine})Pd(benzocyclobutenone) 3



CAAC^{imine}-Pd(0) (1.0 eq., 10 mg, 14 μ mol) was dissolved in benzene to give a red solution. Benzocyclopropenone (1.2 eq., 2 mg, 17 μ mol) was added and the solution instantaneously turned yellow. Yellow crystals formed over the course of 3 h. The crystalline material was collected, washed with pentane and dried *in vacuo* to give the product as yellow solid in quantitative yield. Crystals formed this way were suitable for X-ray crystallography.

Pyridine solutions turn purple over the course of 1 week under the formation of the complex (py)₂Pd(benzocyclobutenone), quantitative conversion is obtained upon heating to 80 °C overnight.

¹H NMR (400 MHz, pyridine-*d*₅): δ = 7.53 (d, ³*J* = 7.6 Hz, 1H, ArCH), 7.49 (dd, ³*J* = 7.8, ¹*J* = 1.7 Hz, 1H, ArCH), 7.39–7.27 (m, 3H, ArCH), 7.18 (dd, ³*J* = 7.1, ¹*J* = 2.0 Hz, 1H, ArCH), 7.10 (d, ³*J* = 7.3 Hz, 1H, ArCH), 6.94 (td, ³*J* = 7.2, ¹*J* = 1.3 Hz, 1H, ArCH), 6.78 (t, ³*J* = 7.3 Hz, 1H, ArCH), 5.55 (dd, ³*J* = 7.6, ¹*J* = 1.3 Hz, 1H, ArCH), 4.46 (d, ³*J* = 15.0 Hz, 1H, CH₂C(O)Pd), 3.52 (d, ³*J* = 15.0 Hz, 1H, CH₂C(O)Pd), 3.41 (hept, ³*J* = 6.8 Hz, 1H, CH(CH₃)₂), 3.28–3.16 (m, 2H, CH(CH₃)₂), 3.13 (d, ³*J* = 13.8 Hz, 1H, CH₂ (CAAC)), 3.04 (hept, ³*J* = 6.7 Hz, 1H, CH(CH₃)₂), 2.36 (d, ³*J* = 13.7 Hz, 1H, CH₂ (CAAC)), 2.26 (s, 3H, CH₃), 1.79 (d, ³*J* = 6.6 Hz, 3H, CH(CH₃)₂), 1.49 (d, ³*J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.46 (s, 3H, CH₃), 1.41 (d, ³*J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.40 (d, ³*J* = 5.9 Hz, 3H, CH(CH₃)₂), 1.39 (s, 3H, CH₃), 1.36 (d, ³*J* = 6.8 Hz, 3H, CH(CH₃)₂), 1.34 (d, ³*J* = 6.7 Hz, 3H, CH(CH₃)₂), 1.26 (d, ³*J* = 6.9 Hz, 3H, CH(CH₃)₂), 1.20 (s, 9H, C(CH₃)₃), 0.99 (d, ³*J* = 6.7 Hz, 3H, CH(CH₃)₂).ppm.

¹³C NMR (100.6 MHz, pyridine-*d*₅): δ = 259.16 (C, carbene), 227.35 (C, carbonyl), 187.59 (C, imine), 168.88 (ArCPd), 146.85 (ArC), 146.46 (ArC), 145.55 (ArC), 138.21 (ArC), 137.47 (ArC), 136.90 (ArC), 136.52 (ArCH), 135.43 (ArC), 129.82 (ArCH), 126.01 (ArCH), 125.80 (ArCH), 125.26 (ArCH), 124.45 (ArCH), 124.24 (ArCH), 123.77 (ArCH), 123.20 (ArCH), 119.81 (ArCH), 82.04 (Cq), 77.64 (Cq), 71.65 (CH₂C(O)Pd), 46.31 (CH₂ (CAAC)), 43.91 (Cq), 35.12 (CH₃), 31.47 (CH₃), 31.42 (C(CH₃)₃), 30.29 (CH(CH₃)₂), 29.92 (CH(CH₃)₂), 29.38 (CH(CH₃)₂), 29.11 (CH(CH₃)₂), 28.46 (CH(CH₃)₂), 28.34 (CH₃), 26.58 (CH(CH₃)₂), 26.36 (CH(CH₃)₂), 24.78 (CH(CH₃)₂), 24.42 (CH(CH₃)₂), 23.78 (2 \times CH(CH₃)₂), 23.63. (CH(CH₃)₂) ppm.

M.p.: 163 °C.

ESI-MS (in THF): *m/z* calcd. For [M+H]⁺ ([C₄₄H₆₁N₂O₂pd]⁺) 739.3813, found 739.3784.

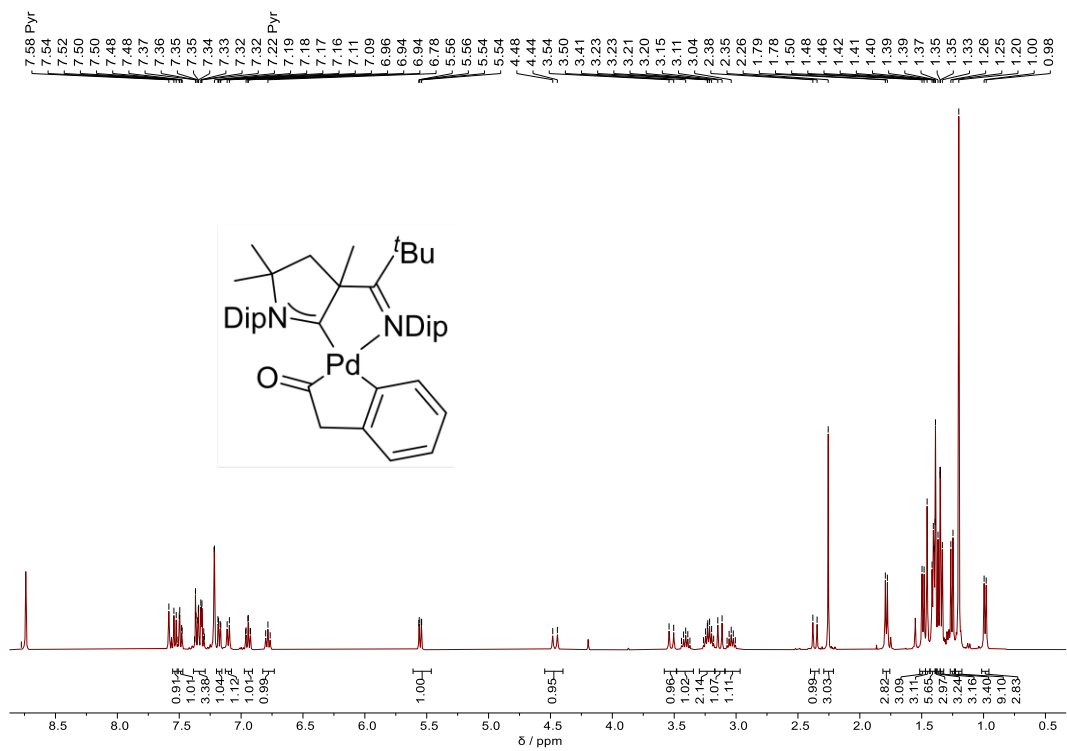


Figure S8. ¹H NMR spectrum of **3** in pyridine-d₅ (400.13 MHz).

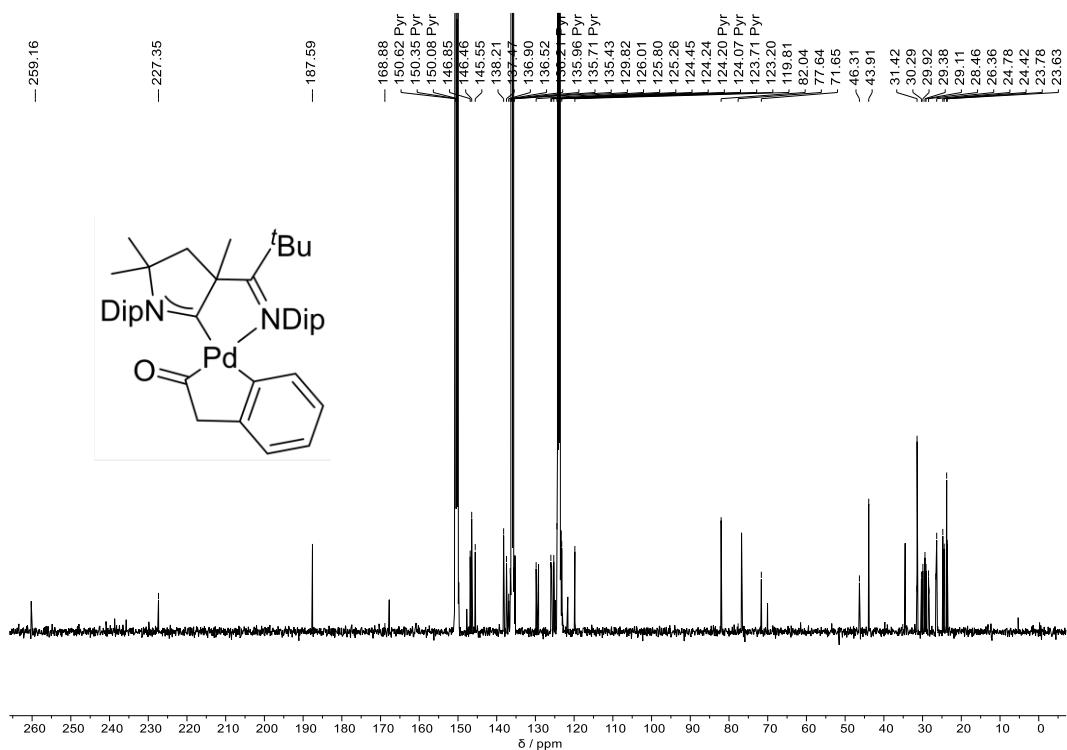


Figure S9. ¹³C NMR spectrum of **3** in pyridine-d₅ (100.6 MHz).

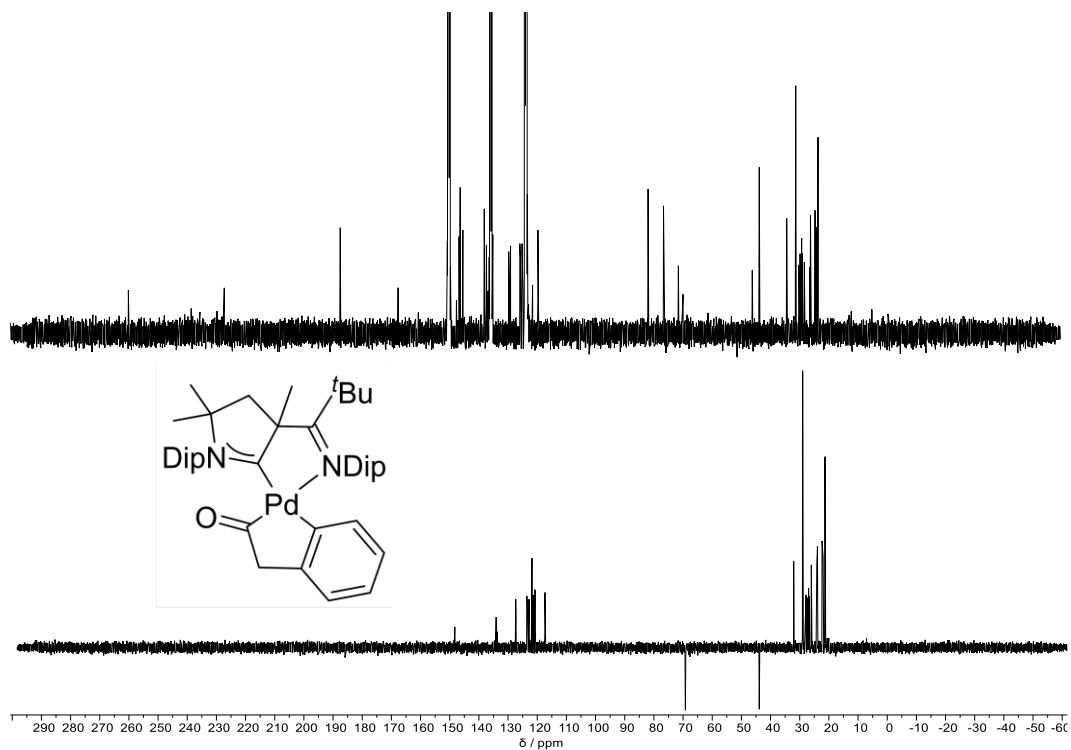


Figure S10. ^{13}C NMR spectrum of **3** in pyridine- d_5 (100.62 MHz) (top), stacked with the DEPT-135 spectrum (bottom).

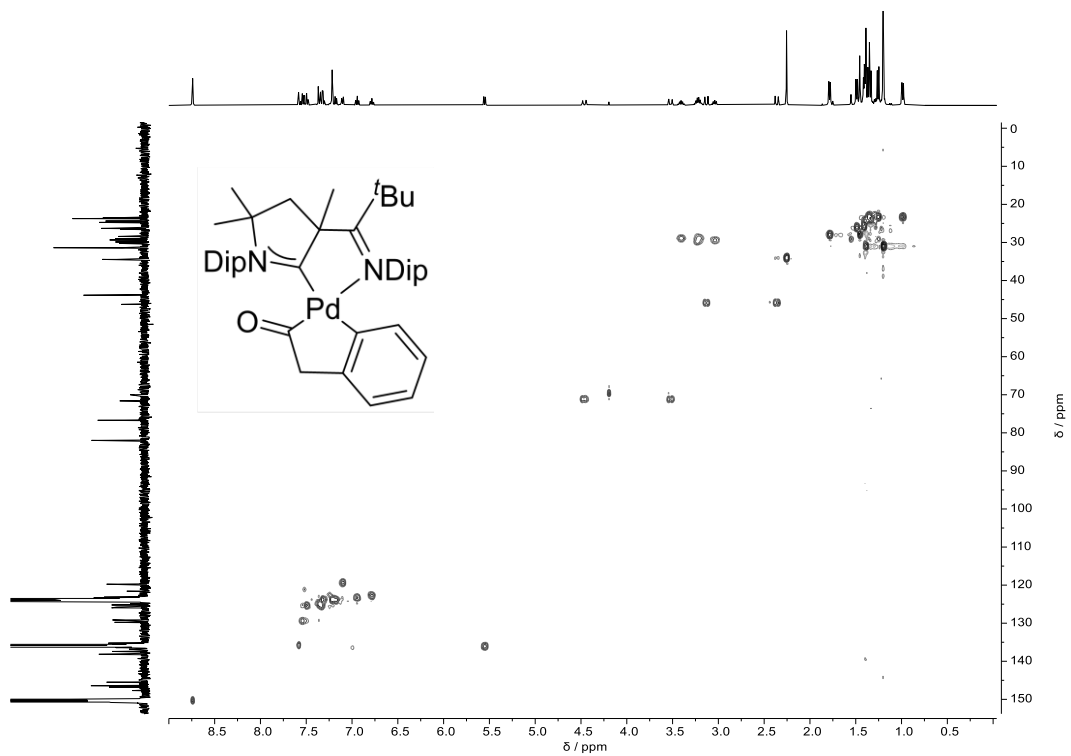


Figure S11. HSQC NMR spectrum of **3** in pyridine- d_5 (400.13 MHz, 100.62 MHz).

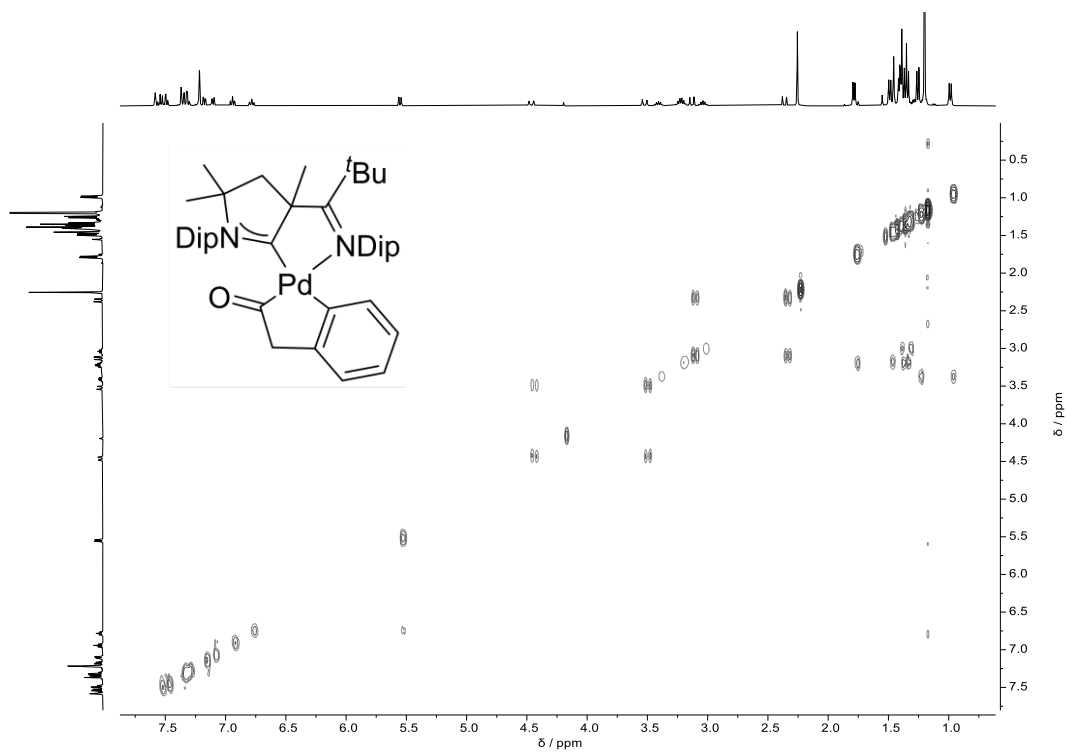


Figure S12. COSY NMR spectrum of **3** in pyridine- d_5 (400.13 MHz, 400.13 MHz).

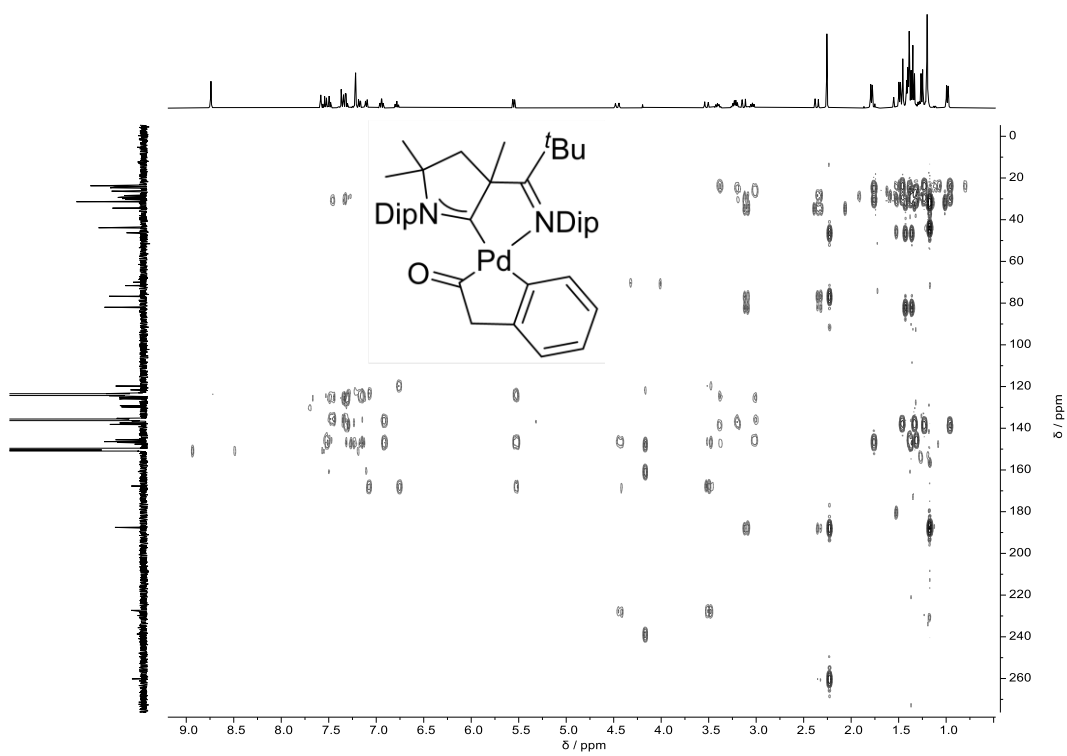


Figure S13. HMBC NMR spectrum of **3** in pyridine- d_5 (400.13 MHz, 100.62 MHz).

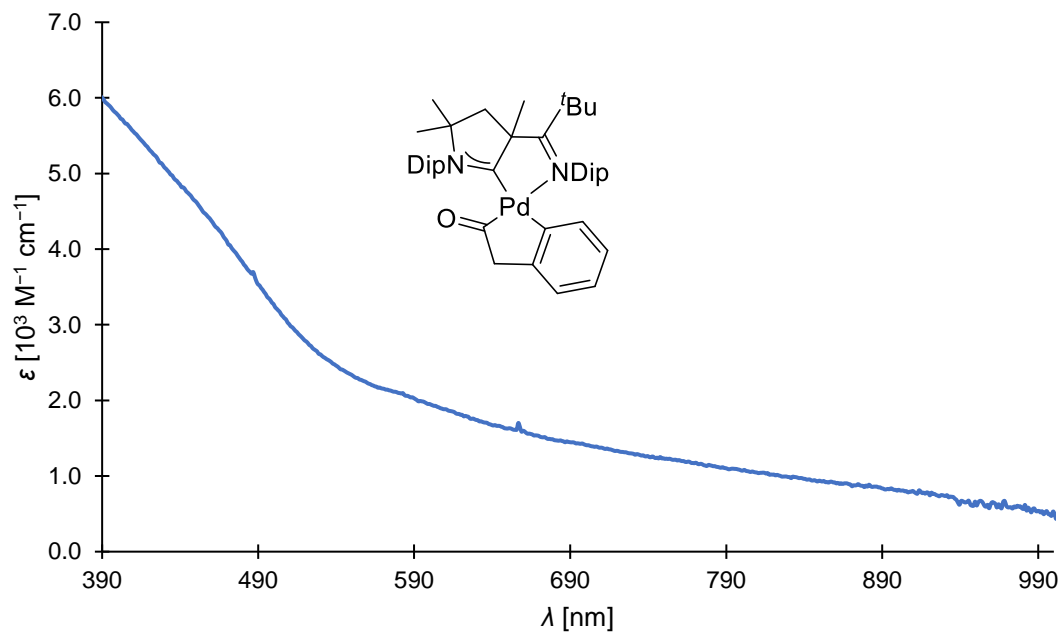
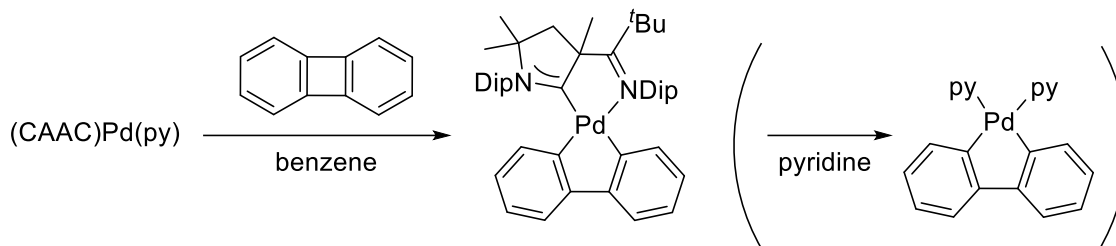


Figure S14. UV/Vis electronic absorption spectrum of **3** in THF ($c = 28 \mu\text{g/mL}$).

(CAAC^{imine})Pd(biphenylene) 4 and (py)₂Pd(biphenylene) 6



CAAC^{imine}-Pd(0) (1 eq., 25 mg, 40 μmol) was dissolved in benzene to give a red solution. Biphenylene (1.1 eq., 7 mg, 44 μmol) was added and the solution turned instantaneously yellow-orange. According to NMR data, the conversion was completed within 5 min. The product was then precipitated with an excess of *n*-pentane. It was washed with *n*-pentane and dried *in vacuo* to obtain **4** as a pale-yellow solid in quantitative yield. Single crystals suitable for X-ray crystallography were obtained by vapor diffusion of pentane into a concentrated pyridine solution at -30 °C.

Solutions of **4** in pyridine turn colorless within 2 hours, thereby forming colorless needles, which are not only insoluble in pyridine, but also DMSO, benzene and chloroform. Single crystals of this product suitable for X-ray crystallography were obtained through layering a solution of crude **4** in pyridine with pentane at room temperature. SC-XRD (*vide infra*) identified this precipitate as compound **6**.

¹H NMR (400.1 MHz, benzene-*d*₆): δ = 7.46 (d, ³J = 7.5 Hz, 1H, ArCH_{bp}), 7.42 (d, ³J = 7.5 Hz, 1H, ArCH_{bp}), 7.13-7.22 (m, 3H, ArCH) [*superimposed by benzene*], 7.05-7.10 (m, 2H ArCH), 7.00-7.03 (m, 2H, ArCH/ ArCH_{bp}), 6.91-6.96 (m, 1H, ArCH_{bp}), 6.74 (t, ³J = 7.4 Hz, 1H, ArCH_{bp}), 6.36 (t, ³J = 7.3 Hz, 1H, ArCH_{bp}), 6.29 (d, ³J = 7.6 Hz, 1H, ArCH_{bp}), 5.41 (d, ³J = 7.6 Hz, 1H, ArCH_{bp}), 4.11 (spt, ³J = 6.8 Hz, 1H, CH(CH₃)₂), 3.69 (spt, ³J = 6.6 Hz, 1H, CH(CH₃)₂), 2.92 (spt, ³J = 6.9 Hz, 1H, CH(CH₃)₂), 2.59-2.67 (m, 2H, CH(CH₃)₂/CH₂), 1.81 (s, 3H, CH₃), 1.59 (d, ³J = 6.8 Hz, 3H, CH(CH₃)₂), 1.51 (d, ³J = 6.6 Hz, 3H, CH(CH₃)₂), 1.45 (d, ³J = 6.6 Hz, 3H, CH(CH₃)₂), 1.40 (s, 1H, CH₂), 1.30 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 1.23 (d, ³J = 6.7 Hz, 3H, CH(CH₃)₂), 1.19 (d, ³J = 6.9 Hz, 3H, CH(CH₃)₂), 1.13 (d, ³J = 6.8 Hz, 6H, CH(CH₃)₂ and CH₃), 0.94 (d, ³J = 6.8 Hz, 6H, CH(CH₃)₂ and CH₃), 0.93 (s, 9H, C(CH₃)₃ ppm.

¹³C NMR (100.6 MHz, benzene-*d*₆): δ = 265.0 (C, carbene), 185.7 (C, imine), 172.0 (ArC), 161.7 (ArC), 158.7 (ArC), 157.4 (ArC), 146.6, (ArC), 146.3 (ArC), 145.6 (ArC), 140.9 (ArCH_{bp}), 140.0 (ArC), 136.6 (ArC), 135.8 (ArC), 134.7 (ArCH_{bp}), 129.8 (ArCH_{Dip}), 127.4 (ArCH_{bp} or ArCH_{Dip}), 126.3 (ArCH_{Dip}), 125.6 (ArCH_{Dip}), 124.4 (ArCH_{Dip}), 123.9 (ArCH_{bp} or ArCH_{Dip}), 123.5 (ArCH_{bp}), 123.4 (ArCH_{bp}), 122.7 (ArCH_{Dip}), 122.6 (ArCH_{bp}), 119.5 (ArCH_p), 118.7 (ArCH_{bp}), 80.9 (Cq), 76.4 (Cq), 44.9 (CH₂), 43.1 (Cq/C(CH₃)₃), 34.5 (CH₃), 32.3 (CH₃), 31.5 (3x C(CH₃)₃), 29.7 (CH(CH₃)₂), 29.5 (CH(CH₃)₂), 29.1 (2x CH(CH₃)₂), 26.6 (CH(CH₃)₂), 26.4 (CH(CH₃)₂), 25.1 (2x CH(CH₃)₂), 24.9 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 23.3 (CH(CH₃)₂), 22.7 (CH₃), 22.1 (CH(CH₃)₂) ppm.

m.p.: 198 °C (decomp.).

ESI-MS (in THF): m/z calcd. For $[M+H]^+$ ($[C_{48}H_{63}N_2Pd]^+$) 773.4020, found 773.4080.

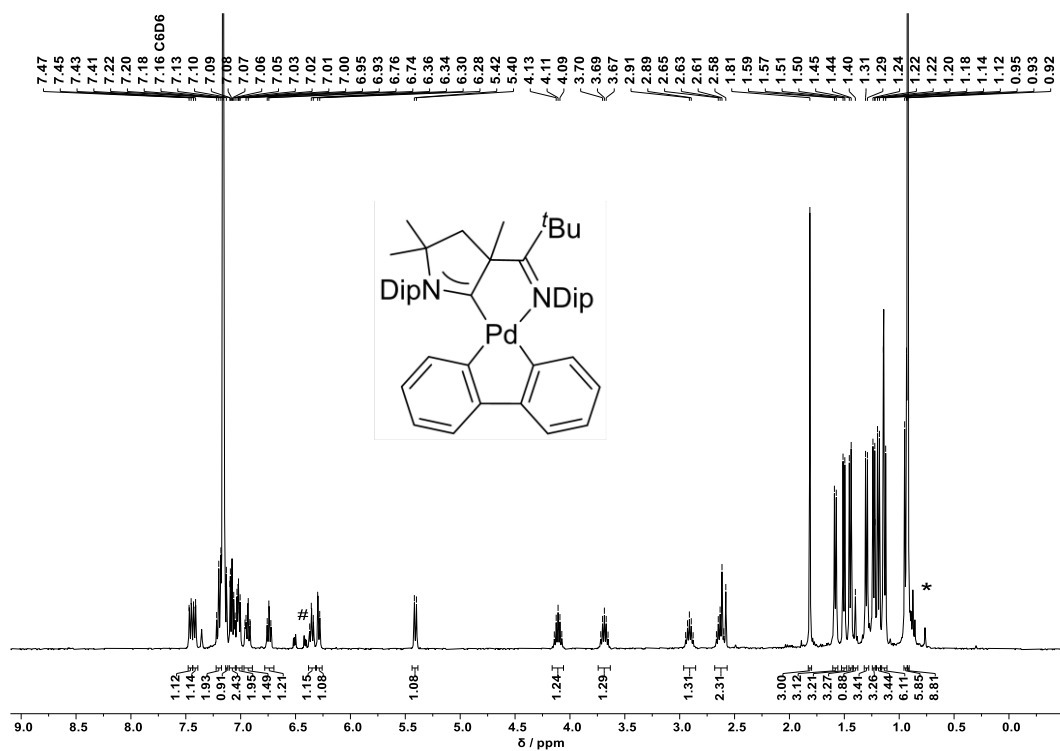


Figure S15. 1H NMR spectrum of **4** in benzene- d_6 (400.13 MHz). Impurities are labeled with # (biphenylene) and * (pentane).

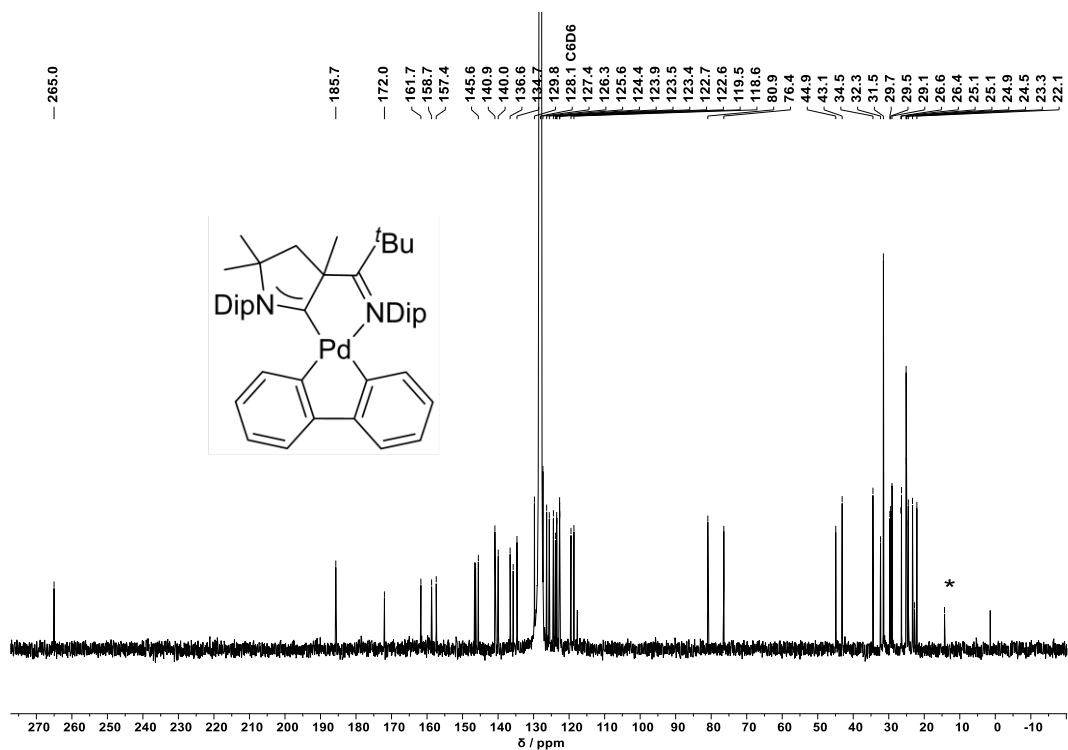


Figure S16. ^{13}C NMR spectrum of **4** in benzene- d_6 (100.62 MHz). Pentane impurity is labeled with *.

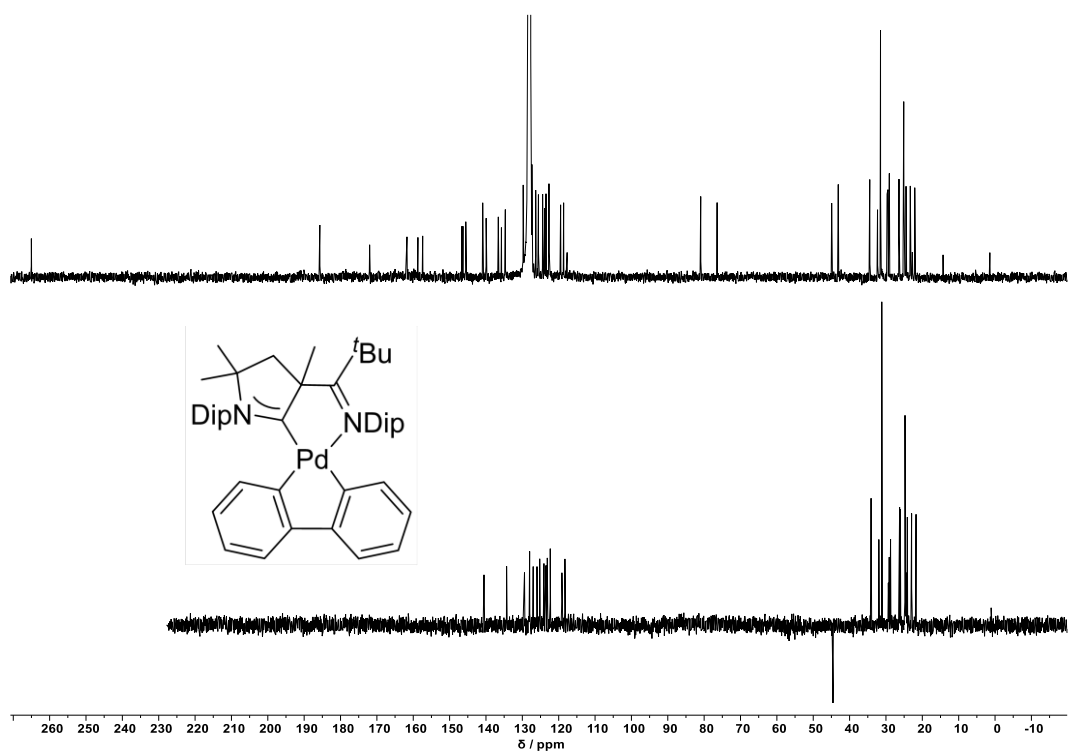


Figure S17. ^{13}C NMR spectrum of **4** in benzene- d_6 (100.62 MHz). (top), stacked with the DEPT-135 spectrum (bottom).

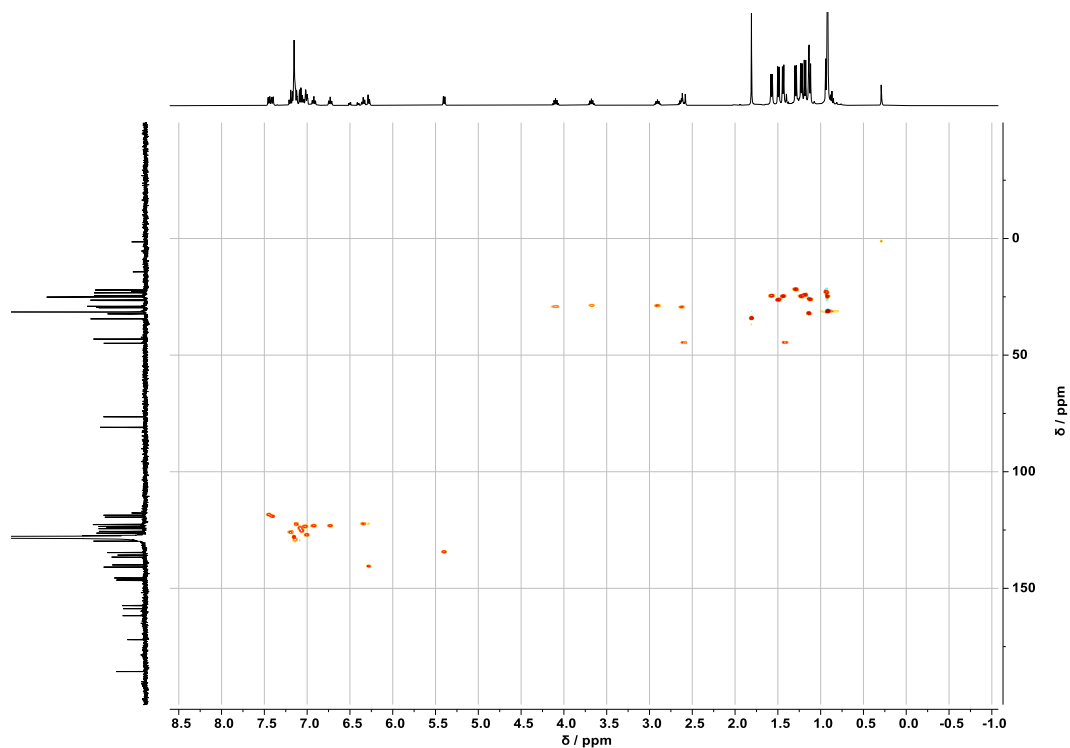


Figure S18. HSQC NMR spectrum of **4** in benzene- d_6 (400.13 MHz, 100.62 MHz).

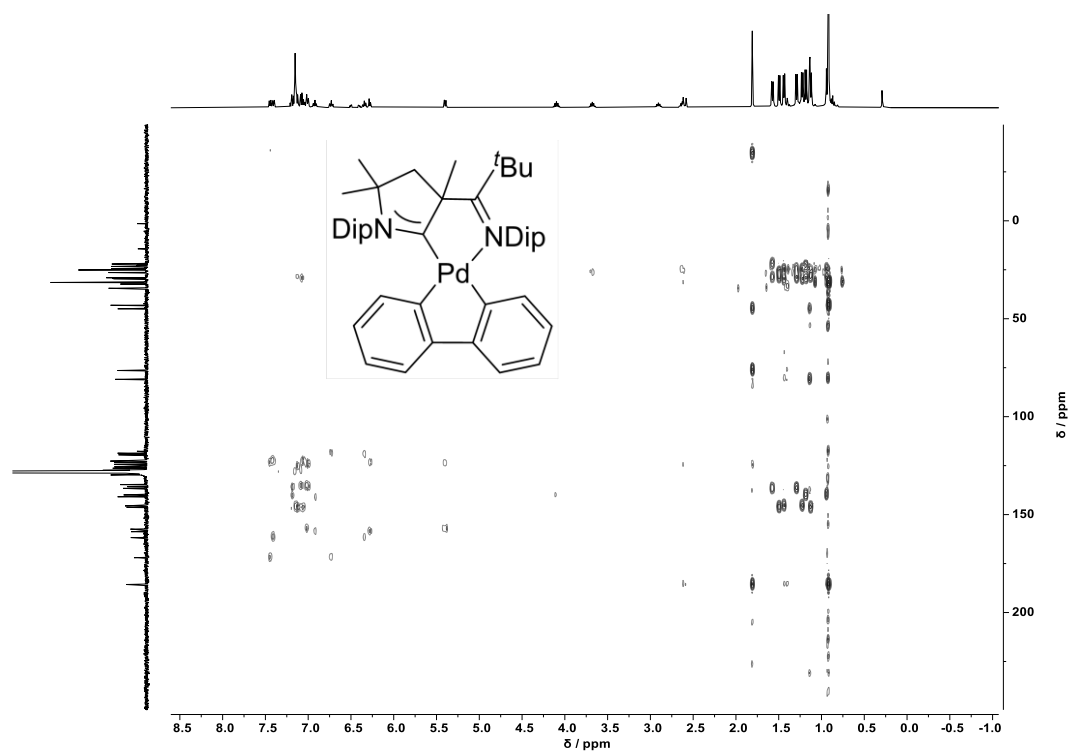


Figure S19. HMBC NMR spectrum of **4** in benzene- d_6 (400.13 MHz, 100.62 MHz).

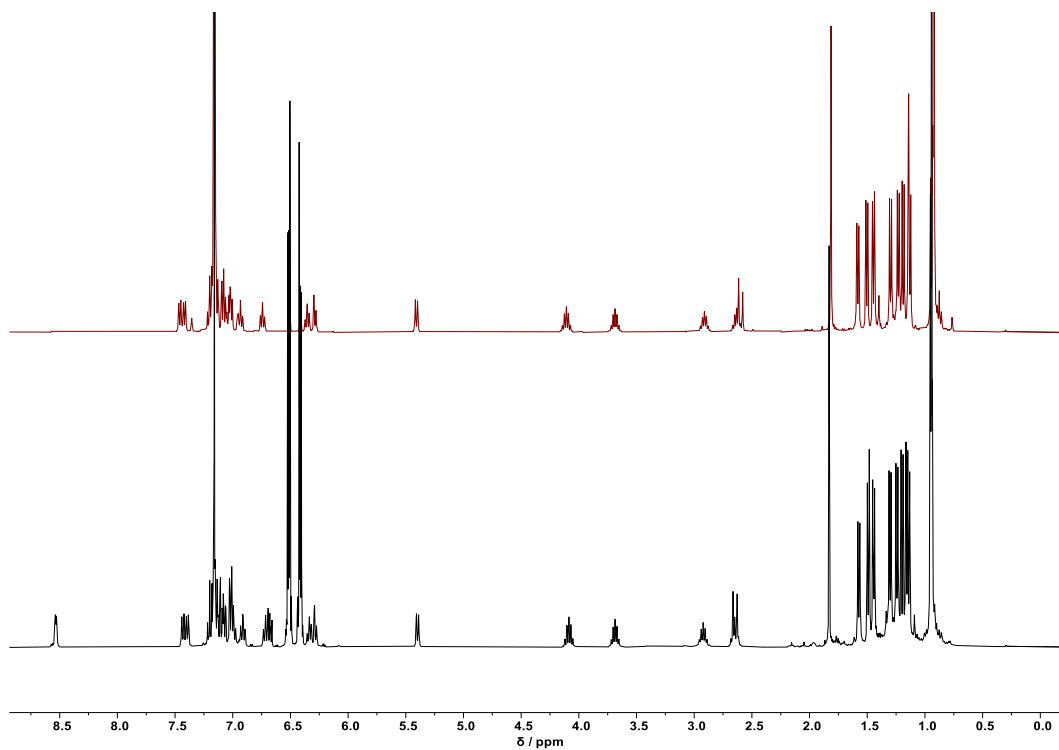
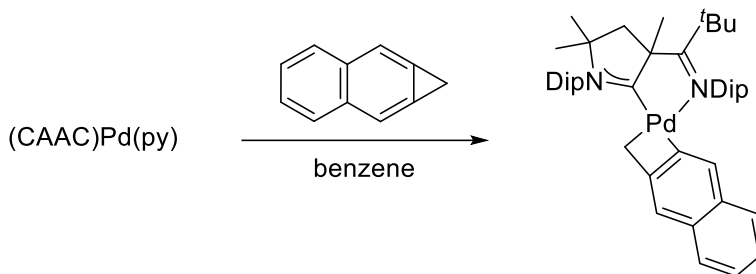


Figure S20. The *in-situ* ^1H NMR (C_6D_6 , 400 MHz) spectrum after 5 min (black, bottom), stacked with the spectrum of isolated **4** (red, top), confirms quantitative conversion within <5 min.

(CAAC^{imine})Pd(naphthocyclopropene) **5**



CAAC^{imine}-Pd(0) (1 eq., 20 mg, 29 μ mol) was dissolved in benzene to give a red solution. Naphtho[*b*]cyclopropene (2 eq., 8 mg, 58 μ mol) was added and the solution immediately turned pale yellow and precipitate formed over the course of 3 h. The precipitate was collected, washed with pentane and dried *in vacuo* to give CAAC^{imine}-Pd(naphtho[*b*]cyclopropene) **5** as beige-yellow solid in quantitative yield, which co-crystallizes with about 0.8 eq. benzene according to the ¹H NMR spectroscopic analysis. Crystallization attempts through vapor diffusion of hydrocarbon solvents or diethyl ether into a THF solution of **5** only led to the formation of fine powder. Single crystals suitable for X-ray crystallography were obtained through layering of a solution of **1** in benzene with a solution of naphtho[*b*]cyclopropene in pentane at room temperature.

¹H NMR (400 MHz, pyridine-*d*₅): δ = 7.60 (d, ³*J* = 7.7 Hz, 1H, ArCH), 7.54 (d, ³*J* = 7.6 Hz, 1H, ArCH), 7.50 (d, ³*J* = 7.7 Hz, 1H, ArCH), 7.46 (d, ³*J* = 7.7 Hz, 1H, ArCH), 7.45 – 7.37 (m, 2H, ArCH), 7.37 (s, 5H, benzene), 7.36 – 7.31 (m, 2H, ArCH), 7.26 – 7.22 (m, 1H, ArCH), 7.14 (ddd, ³*J* = 8.1, ³*J* = 6.7, ⁴*J* = 1.4 Hz, 1H, ArCH), 6.81 (s, 1H, ArCH), 6.22 (s, 1H, ArCH), 3.58 (hept, ³*J* = 6.8 Hz, 1H, CH(CH₃)₂), 3.31 (hept, ³*J* = 6.9 Hz, 1H, CH(CH₃)₂), 3.19 (hept, ³*J* = 6.8 Hz, 1H, CH(CH₃)₂), 3.13 (hept, ³*J* = 6.9 Hz, 1H, CH(CH₃)₂), 3.02 (d, ³*J* = 13.1 Hz, 1H, CH₂ (CAAC)), 2.62 (d, ³*J* = 13.0 Hz, 1H, CH₂ (CAAC)), 2.21 (s, 3H, CH₃), 1.79 (d, ³*J* = 6.6 Hz, 3H, CH(CH₃)₂), 1.58 – 1.53 (m, 6H, CH(CH₃)₂), 1.47 – 1.44 (m, 6H, CH(CH₃)₂), 1.39 – 1.33 (m, 4H, CH(CH₃)₂) and PdCH₂), 1.32 (d, ³*J* = 6.9 Hz, 3H, CH(CH₃)₂), 1.30 (s, 3H, CH₃), 1.28 (s, 3H, CH₃), 1.28 – 1.22 (m, 12H, C(CH₃)₃ and CH(CH₃)₂), 0.52 (d, ³*J* = 11.4, 1H, PdCH₂) ppm.

¹³C NMR (100.6 MHz, pyridine-*d*₅): δ = 256.97 (C, carbene), 187.03 (C, imine), 162.58 (ArC), 148.18 (ArC), 146.53 (ArC), 146.04 (ArC), 145.40 (ArC), 137.57 (ArC), 137.48 (ArC), 136.46 (ArC), 133.78 (ArC), 133.27 (ArC), 130.00 (ArCH), 129.20 (benzene), 128.57 (ArCH), 128.39 (ArCH), 127.66 (ArCH), 125.92 (ArCH), 125.78 (ArCH), 125.52 (ArCH), 124.79 (ArCH), 124.33 (ArCH), 122.62 (ArCH), 122.57 (ArCH), 118.54 (ArCH), 80.22 (Cq), 76.40 (Cq), 46.34 (CH₂), 43.56 (Cq), 31.45 (C(CH₃)₃), 31.23 (CH(CH₃)₂), 30.24 (CH(CH₃)₂), 30.17 (CH₃), 29.62 (CH(CH₃)₂), 29.46 (CH(CH₃)₂), 29.05 (CH(CH₃)₂), 28.40 (CH(CH₃)₂), 27.39 (CH(CH₃)₂), 26.35 (CH(CH₃)₂), 25.54 (CH(CH₃)₂), 24.89 (CH(CH₃)₂), 24.82 (CH(CH₃)₂), 24.48 (CH₃), 24.35 (CH₃), 23.37 (CH(CH₃)₂), –8.96 (PdCH₂) ppm.

M.p.: 193 °C.

ESI-MS (in pyridine): m/z calcd. For $[M+H]^+$ ($[C_{47}H_{63}N_2Pd]^+$) 761.4021, found 761.4097.

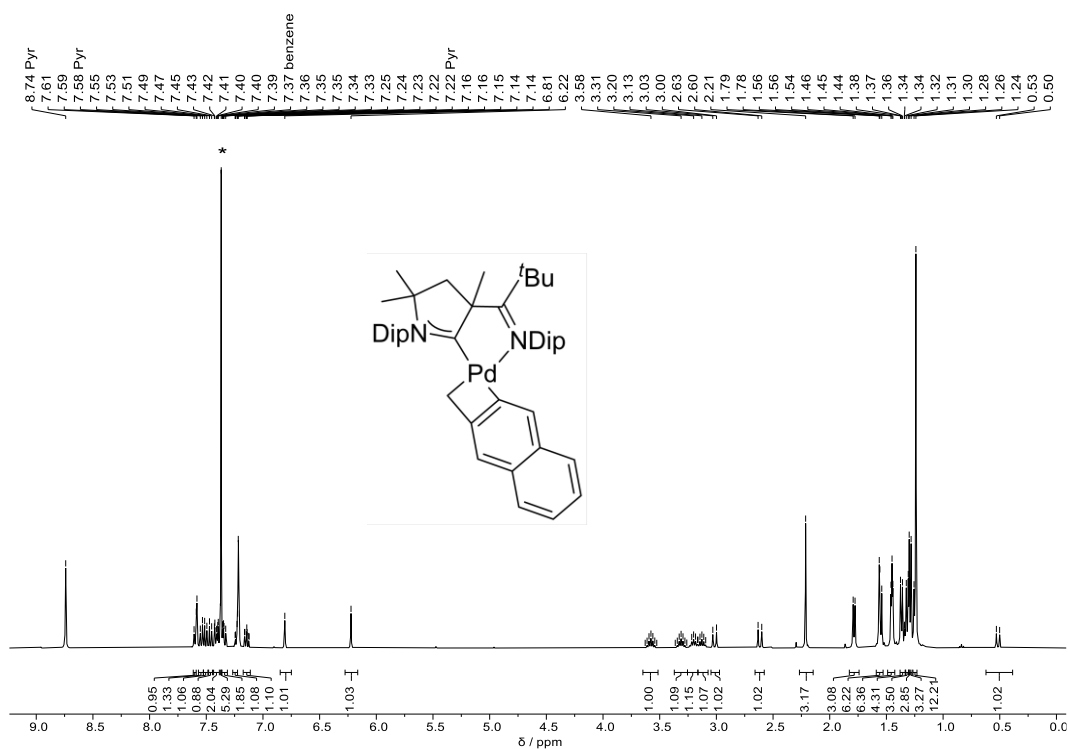


Figure S21. 1H NMR spectrum of **5** in pyridine- d_5 (400.13 MHz). Note that benzene (*) co-crystallizes with the product.

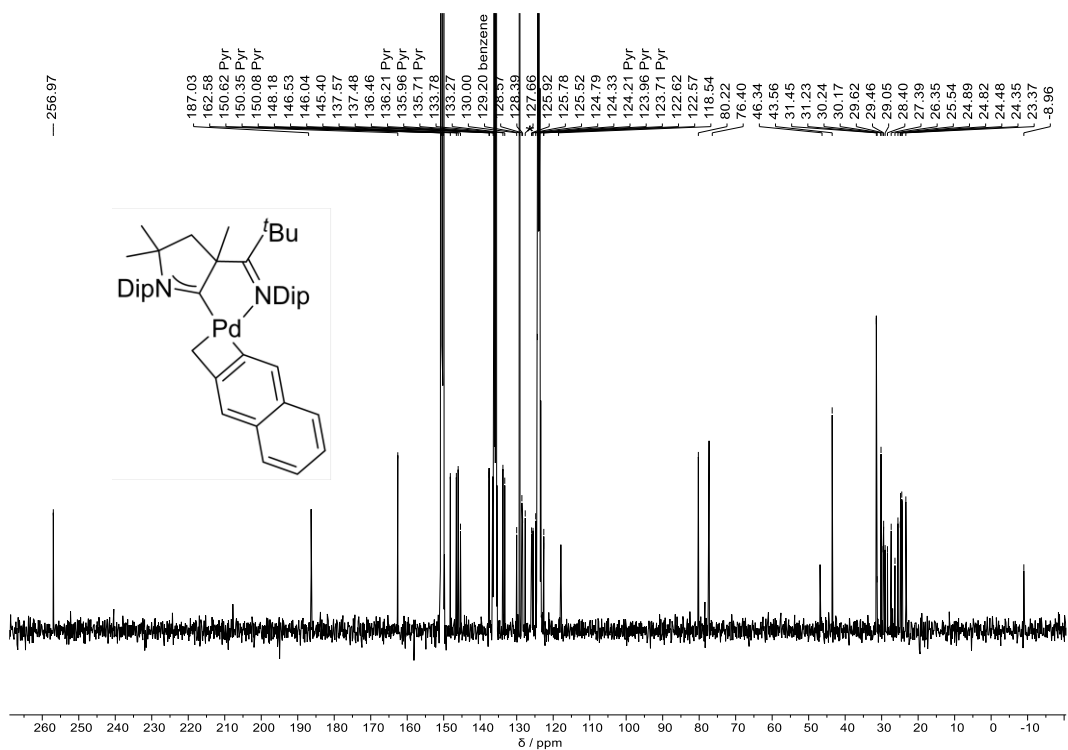


Figure S22. ^{13}C NMR spectrum of **5** in pyridine- d_5 (100.62 MHz). Note that benzene (*) co-crystallizes with the product.

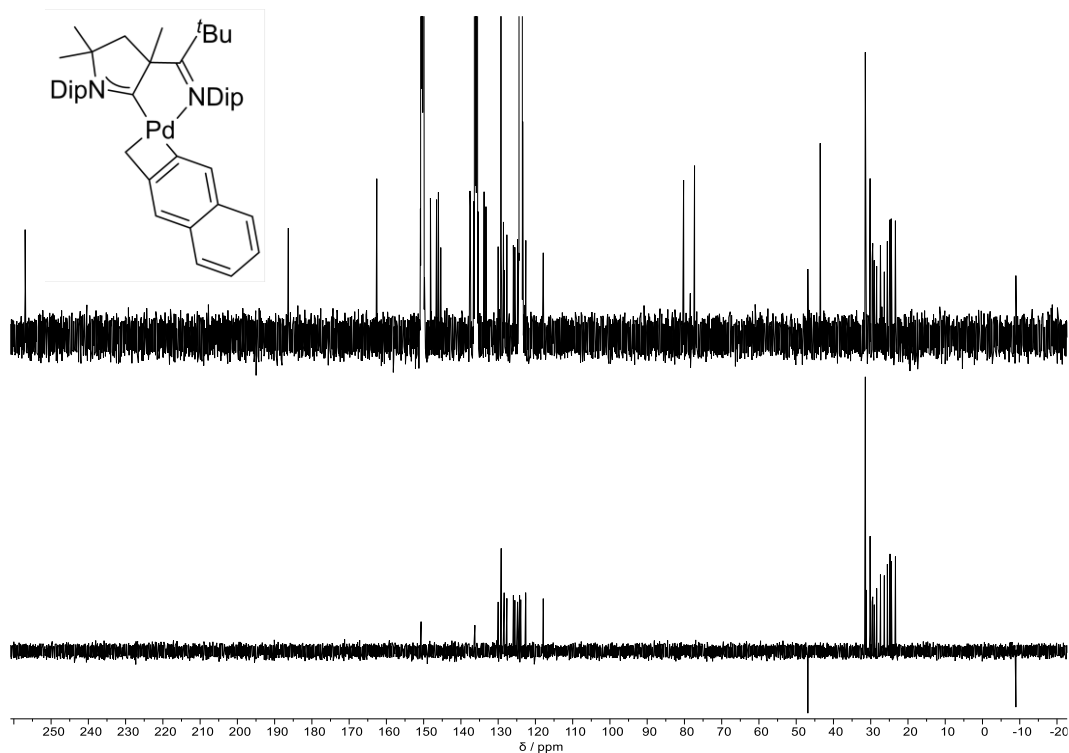


Figure S23. ^{13}C NMR spectrum of **5** in pyridine- d_5 (100.62 MHz) (top), stacked with the DEPT-135 spectrum (bottom).

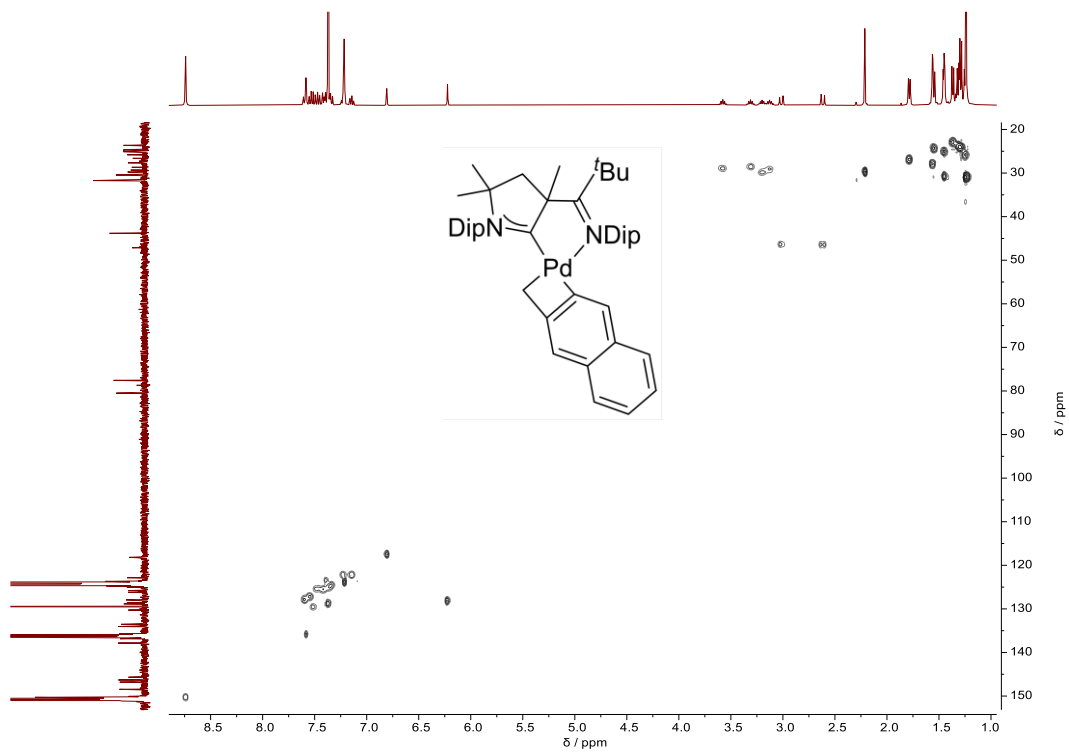


Figure S24. HSQC NMR spectrum of **5** in pyridine- d_5 (400.13 MHz, 100.62 MHz).

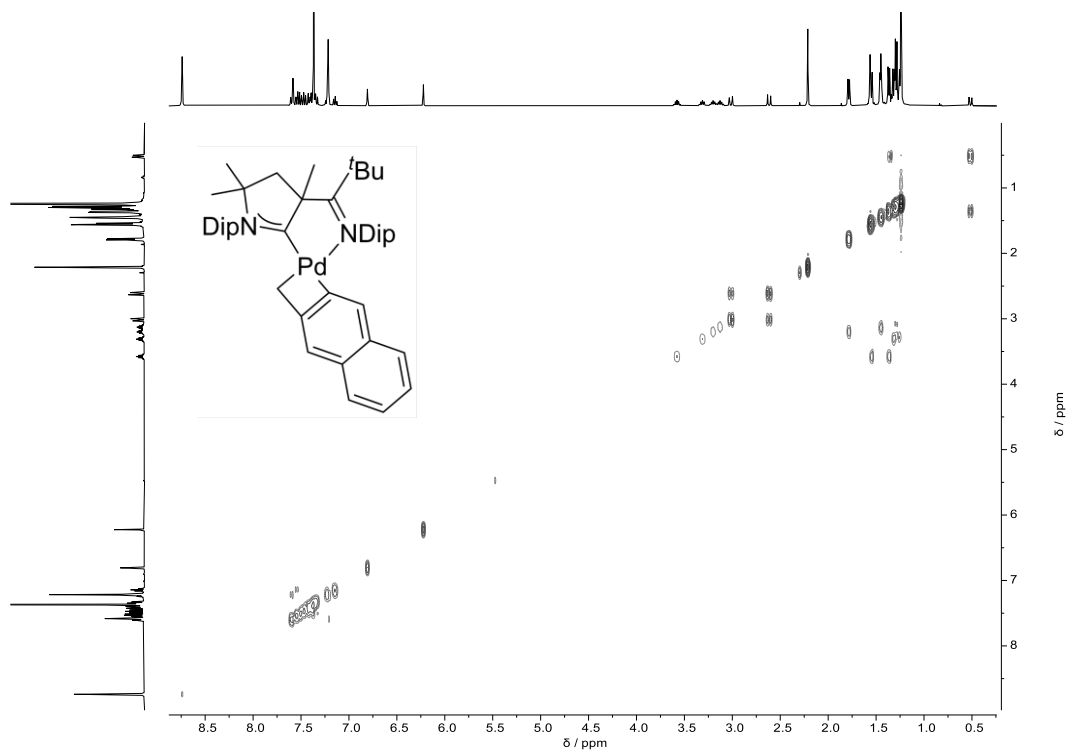


Figure S25. COSY NMR spectrum of **5** in pyridine- d_5 (400.13 MHz, 400.13 MHz).

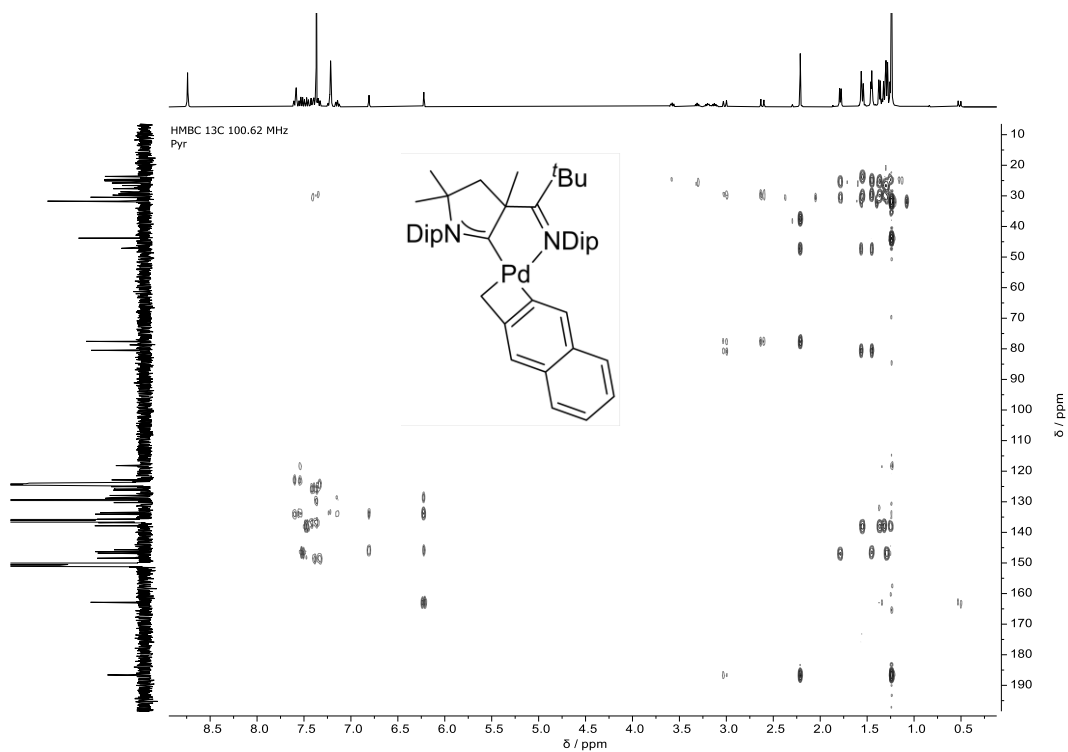


Figure S26. HMBC NMR spectrum of **5** in pyridine- d_5 (400.13 MHz, 100.62 MHz).

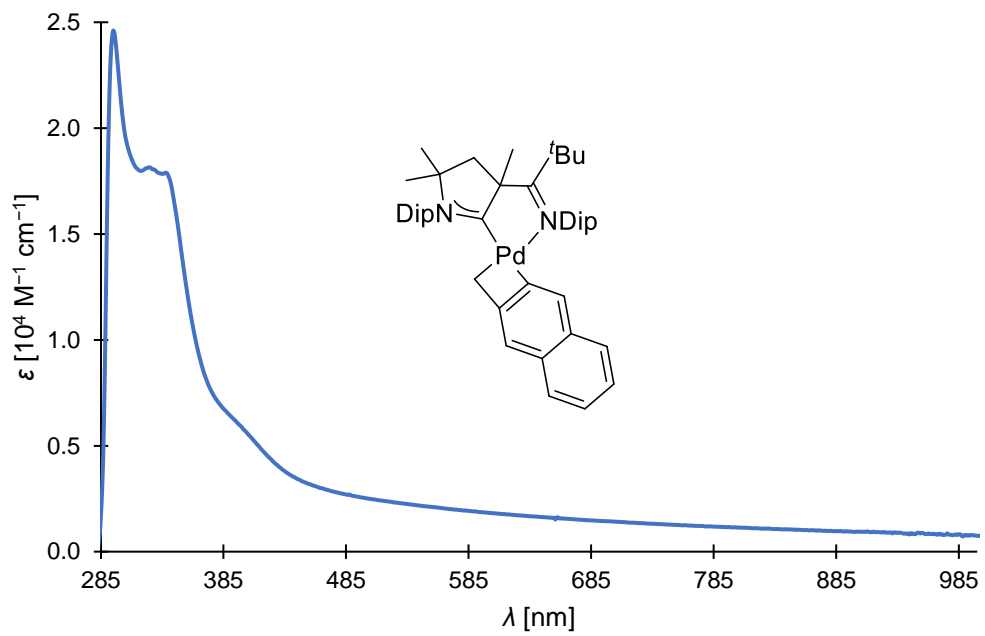


Figure S27. UV/Vis electronic absorption spectrum of **5** in THF ($c = 36 \mu\text{g/mL}$).

3. Single Crystal Structure Elucidation and Refinement (SC-XRD)

X-ray Structure Determination: X-ray quality crystals were selected in Fomblin YR-1800 perfluoroether (Alfa Aesar) at ambient temperature. The samples were cooled to 100(2) K (compounds **2**, **4**, **6**) or 150(2) K (compounds **3** and **5**) during measurement. The data were collected on a Bruker Kappa $I\mu S$ Duo Photon II CPAD diffractometer (compounds **2** and **6**) or Bruker APEX-II CCD diffractometer (**3**, **4**, and **5**) using monochromated MoK α ($\lambda = 0.71073 \text{ \AA}$) radiation. The structures were solved by intrinsic phasing (SHELXT)³ and refined by full matrix least squares procedures (SHELXL)⁴ within the OLEX2⁵ platform. Semi-empirical absorption corrections (multiscan and additional spherical absorption correction) were applied to the recorded diffraction data using the SADABS application within the APEX2 or APEX3 platform.⁶ All non-hydrogen atoms were refined anisotropically, hydrogen atoms were included in the refinement at calculated positions using a riding model. The isotropic displacement parameters of all hydrogen atoms were tied to those of their corresponding carrier atoms by a factor of 1.2 or 1.5. All special refinement details (if required) for disordered structures as well as molecular structure representations are summarized down below. A summary on standard crystallographic parameters as well as the CSD entry numbers within the Cambridge Crystallographic Data Centre (CCDC) is subsequently provided in Tables S1 and S2.

Special Refinement Details:

Compound 2: The structure shows no signs of disordered atom positions and all atoms except hydrogen atoms were refined anisotropically with high precision.

Compound 3: One of the Dip groups was found to be disordered which is why a disorder model was described for tilting of the whole fragment containing C27, C28, C29, C27A, C28A and C29A. Two respective split positions have been refined according to the free variable 2 (FVAR2) which refined into occupancies of 0.82 and 0.18. To fix the refinement, soft DELU and ISOR restraints were embedded to the refinement reaching more reasonable displacement.

Compound 4: The compound crystallized with two independent halves of a pyridine solvent molecule, both of which were located on crystallographic twofold axes (Wyckoff position 4e). These solvent molecules were disordered with regard to the position of the pyridine's nitrogen atom. Accordingly, equal coordinate (EXYZ) and equal anisotropic displacement parameter (EADP) constraints were applied for the affected atoms.

Compound 5·2C₆H₆: The structure was solved based on comparably poor diffraction data, due to poor scattering behavior. Recrystallization from various solvents turned out to be unsuccessful. The best choice of single crystal was obtained from benzene solutions, which led to the incorporation of solvent molecules. The crystals were thin, colorless needles, which further complicated the data collection. We are aware of the high value of R_{int} and provided the only and hence best data where a structure solution was possible. The high R_{int} is caused by the poor scattering of the crystal as evident from checking the reciprocal space in all three directions of the unit cell. The reciprocal space revealed no twinning, modulation, or other ambiguity. The Pd-complex is nicely ordered whereas the benzene molecules show slight rotational disorder, yet no description of a disorder model is necessary here.

Compound 6·C₅H₅N: The structure of the Pd-complex shows no signs of disordered atom positions and all atoms except hydrogen atoms were refined anisotropically with high precision. It is notable that the solvent molecule is slightly tilting, yet the description of a disorder model was not performed.

Molecular Structure Representations: All molecular structure representations in the ESI as well as the main article have been prepared with the Diamond software package⁷ or OLEX2⁵ in combination with POV-Ray 3.7.⁸ A mixed representation of ellipsoid plots as well as wires/sticks was chosen for clarity. All ellipsoids are represented at the 50% probability level.

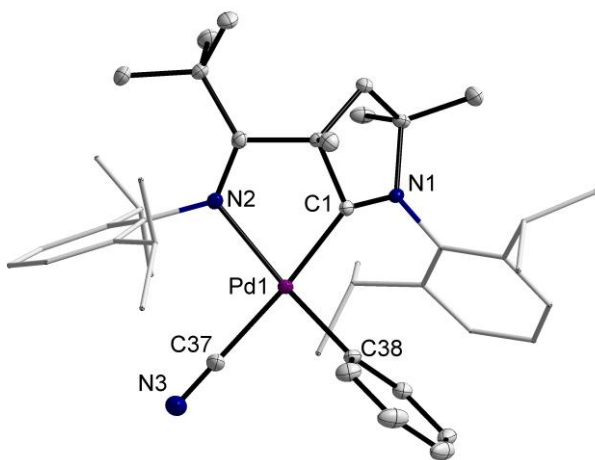


Figure S28. Molecular structure representation of **2** in the crystal with ellipsoids set to a 50% probability level. Hydrogen atoms are omitted, and Dip-groups rendered as wireframes for clarity. Selected atom distances [Å] and angles [°] for **2**: Pd1–C1 1.9847(17), Pd1–N2 2.1846(14), Pd1–C37 2.0182(18), Pd1–C38 2.0107(17), N1–C1 1.298(2), N3–C37 1.149(2), Pd1–C37–N3 176.33(19), C1–Pd1–N2 76.49(6), C1–Pd1–C38 101.24(7), N2–Pd1–C37 97.91(6), C38–Pd1–C37 86.45(7).

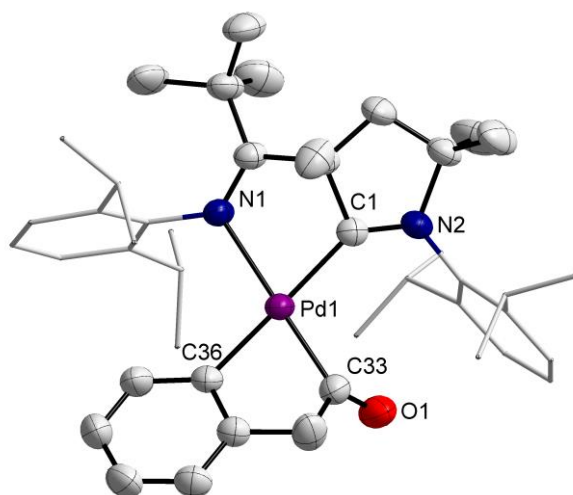


Figure S29. Molecular structure representation of **3** in the crystal with ellipsoids set to a 50% probability level. Hydrogen atoms are omitted, and Dip-groups rendered as wireframes for clarity. Selected atom distances [Å] and angles [°] for **3**: Pd1–N1, 2.2460(15); Pd1–C1 2.0565(18), Pd1–C33 1.970(2), Pd1–C36 2.0859(19), C1–N2 1.303(2), C33–O1 1.190(2), C1–Pd1–N1 76.25(6), C1–Pd1–C33 102.86(8), N1–Pd1–C36 104.23(7), C33–Pd1–C36 77.21(8).

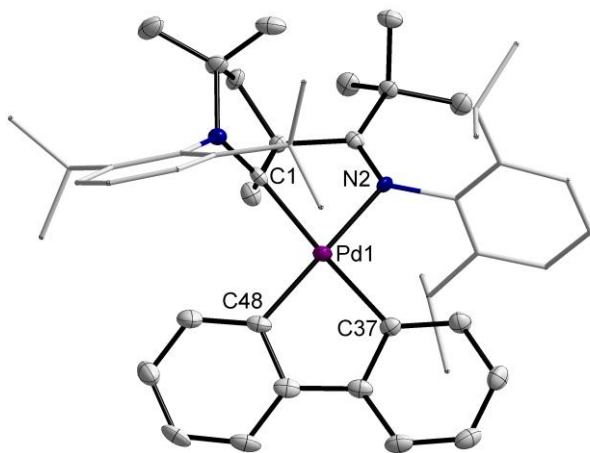


Figure S30. Molecular structure representation of **4** in the crystal with ellipsoids set to a 50% probability level. Hydrogen atoms and co-crystalline pyridine molecules are omitted, and Dip-groups rendered as wireframes for clarity. Selected atom distances [Å] and angles [°] for **4**: Pd1–C1 2.044(4), Pd1–N2 2.210(4), Pd1–C37 2.085(4), Pd1–C48 1.990(4), C1–Pd1–N2 75.85(14), C1–Pd1–C48 101.92(17), N2–Pd1–C37 103.44(14), C37–Pd1–C48 80.10(17).

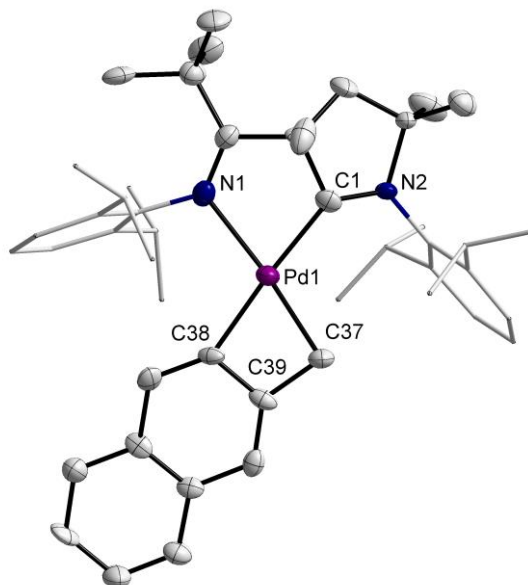


Figure S31. Molecular structure representation of **5** in the crystal with ellipsoids set to a 50% probability level. Hydrogen atoms and co-crystalline benzene molecules are omitted, and Dip-groups rendered as wireframes for clarity. Selected atom distances [Å] and angles [°] for **5**: Pd1–N1 2.175(6), Pd1–C1 2.012(7), Pd1–C37 2.063(7), Pd1–C38 2.050(6), C1–N2 1.296(8), C1–Pd1–N1 76.8(2), C1–Pd1–C37 108.1(3), N1–Pd1–C36 106.8(2), C37–Pd1–C38 67.9(2), C37–C39–C38 104.1(5).

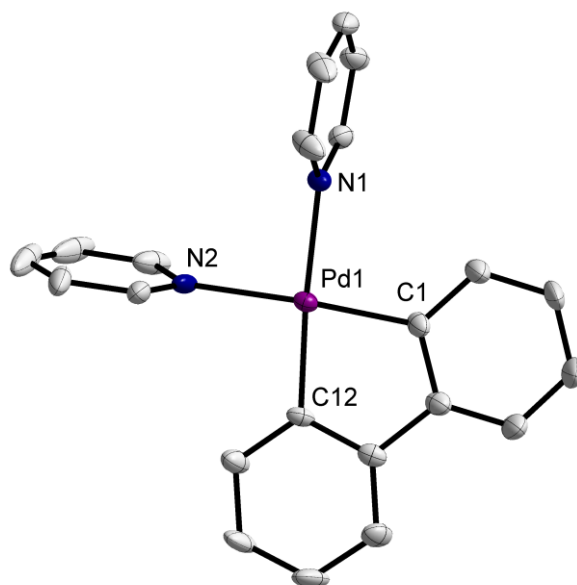


Figure S32. Molecular structure representation of **6** in the crystal with ellipsoids set to a 50% probability level. Hydrogen atoms and co-crystalline pyridine molecules are omitted, and Dip-groups rendered as wireframes for clarity. Selected atom distances [Å] and angles [°] for **6**: Pd1–C1 2.002(3), Pd1–C12 2.002(3), Pd1–N1 2.127(3), Pd1–N2 2.128(3), C1–Pd1–C12 81.41(13), C1–Pd1–N1 94.66(12), C12–Pd1–N2 95.57(12), N1–Pd1–N2 88.36(10).

Table S1. Crystallographic details for 2–5.

Compound	2	3	4·C ₅ H ₅ N	5·2C ₆ H ₆
Empirical formula	C ₄₃ H ₅₉ N ₃ Pd	C ₄₄ H ₆₀ N ₂ OPd	C ₅₃ H ₆₇ N ₃ Pd	C ₅₉ H ₇₄ N ₂ Pd
Formula weight	724.33	739.34	852.49	917.60
Temperature/K	100(2)	150(2)	100(2)	150(2)
Crystal system	triclinic	monoclinic	monoclinic	orthorhombic
Space group	<i>P</i> -1	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>Pbca</i>
<i>a</i> /Å	9.9410(5)	12.9417(8)	21.1187(8)	17.2411(12)
<i>b</i> /Å	13.2345(6)	17.4620(11)	13.1872(6)	18.2386(11)
<i>c</i> /Å	14.5821(7)	18.3894(11)	32.3582(13)	32.1839(18)
α /°	79.083(1)	90	90	90
β /°	86.088(2)	105.537(2)	103.994(2)	90
γ /°	85.104(2)	90	90	90
Volume/Å ³	1874.2(2)	4003.9(4)	8744.2(6)	10120.3(11)
<i>Z</i>	2	4	8	8
ρ_{calc} /cm ³	1.283	1.226	1.295	1.204
μ /mm ⁻¹	0.528	0.497	0.464	0.405
<i>F</i> (000)	768.0	1568.0	3616.0	3904.0
Crystal size/mm ³	0.18 × 0.12 × 0.025	0.24 × 0.22 × 0.2	0.32 × 0.16 × 0.12	0.3 × 0.07 × 0.04
Radiation	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.832 to 59.188	3.266 to 54.266	4.188 to 54.204	2.53 to 49**
Index ranges	-13 ≤ <i>h</i> ≤ 13, -18 ≤ <i>k</i> ≤ 18, -14 ≤ <i>l</i> ≤ 20	-15 ≤ <i>h</i> ≤ 16, -22 ≤ <i>k</i> ≤ 22, -23 ≤ <i>l</i> ≤ 23	-27 ≤ <i>h</i> ≤ 27, -16 ≤ <i>k</i> ≤ 16, -41 ≤ <i>l</i> ≤ 40	-20 ≤ <i>h</i> ≤ 9, -21 ≤ <i>k</i> ≤ 16, -32 ≤ <i>l</i> ≤ 37
Reflections collected	76300	57235	71739	37672
Independent reflections	10514 [<i>R</i> _{int} = 0.0584, <i>R</i> _{sigma} = 0.0369]	8860 [<i>R</i> _{int} = 0.0304, <i>R</i> _{sigma} = 0.0218]	9630 [<i>R</i> _{int} = 0.0242, <i>R</i> _{sigma} = 0.0207]	8384 [<i>R</i> _{int} = 0.2177, <i>R</i> _{sigma} = 0.2252]**
Data/restraints/parameters	10514/0/438	8860/43/477	9630/0/528	8384/0/549
Goodness-of-fit on <i>F</i> ²	1.060	1.038	1.474	0.880
Final <i>R</i> indexes [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0324, <i>wR</i> ₂ = 0.0607	<i>R</i> ₁ = 0.0282, <i>wR</i> ₂ = 0.0688	<i>R</i> ₁ = 0.0660, <i>wR</i> ₂ = 0.1356	<i>R</i> ₁ = 0.0711, <i>wR</i> ₂ = 0.1181
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0409, <i>wR</i> ₂ = 0.0636	<i>R</i> ₁ = 0.0383, <i>wR</i> ₂ = 0.0735	<i>R</i> ₁ = 0.0689, <i>wR</i> ₂ = 0.1364	<i>R</i> ₁ = 0.2131, <i>wR</i> ₂ = 0.1494**
Largest diff. peak/hole / e Å ⁻³	0.62/-0.95	0.36/-0.36	0.82/-1.78	0.97/-0.68
Absolute structure parameter	-	-	-	-
CCDC #	2288559	2288557	2288560	2288556

* Restraints used to fix disorder. ** Please see special refinement details for further information (*vide infra*).

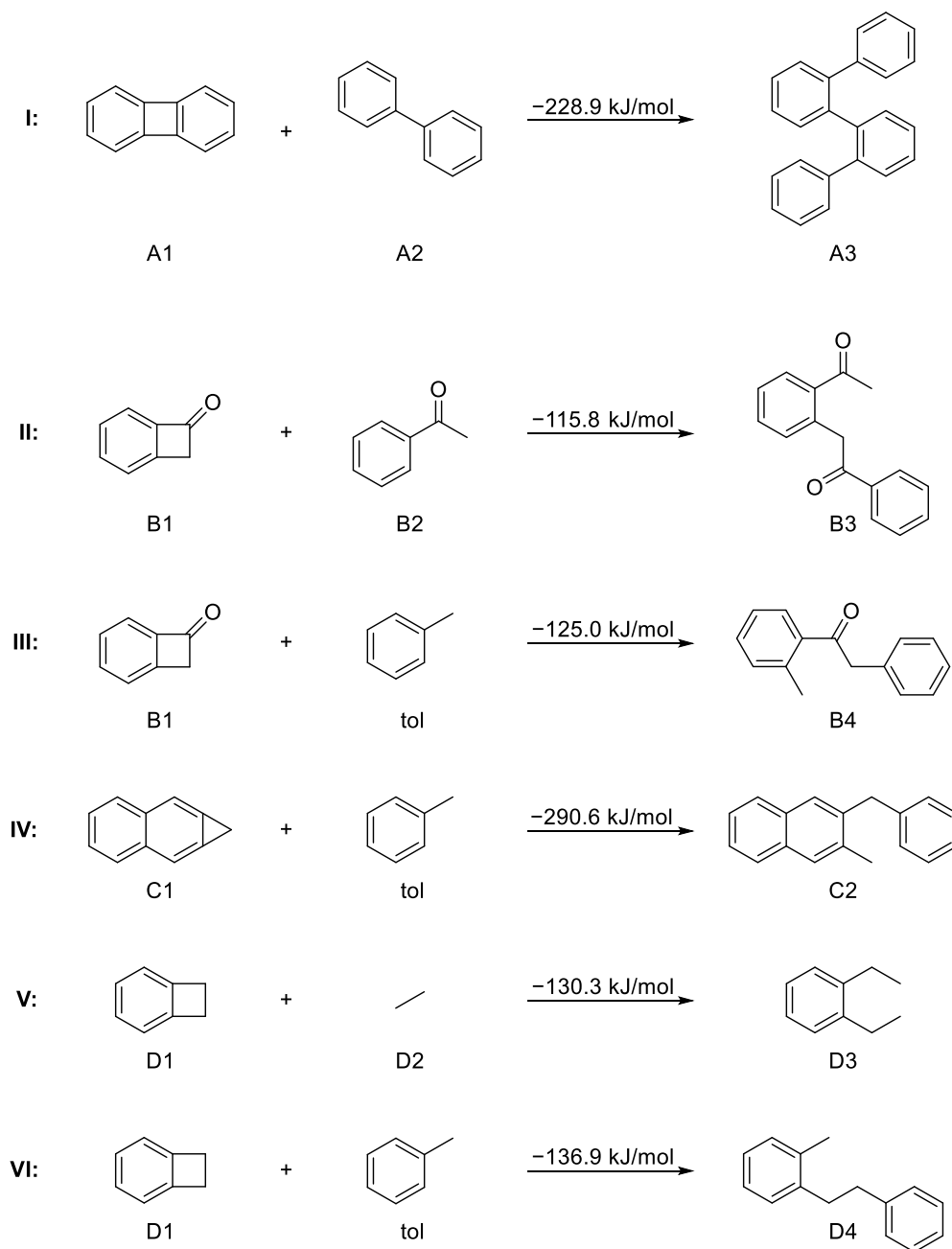
Table S2. Crystallographic details for **6**.

Compound	6 ·C ₅ H ₅ N
Empirical formula	C ₂₇ H ₂₃ N ₃ Pd
Formula weight	495.88
Temperature/K	100(2)
Crystal system	triclinic
Space group	<i>P</i> -1
<i>a</i> /Å	9.6158(6)
<i>b</i> /Å	10.0704(7)
<i>c</i> /Å	12.4686(8)
α /°	80.144(2)
β /°	75.837(2)
γ /°	67.448(2)
Volume/Å ³	1077.1(2)
<i>Z</i>	2
ρ_{calc} /cm ³	1.529
μ /mm ⁻¹	0.881
<i>F</i> (000)	504.0
Crystal size/mm ³	0.19 × 0.04 × 0.03
Radiation	MoK α (λ = 0.71073)
2 θ range for data collection/°	3.382 to 59.224
Index ranges	-13 ≤ <i>h</i> ≤ 13, -9 ≤ <i>k</i> ≤ 13, -17 ≤ <i>l</i> ≤ 17
Reflections collected	19699
Independent reflections	6011 [<i>R</i> _{int} = 0.0531, <i>R</i> _{sigma} = 0.0600]
Data/restraints/parameters	6011/0/280
Goodness-of-fit on <i>F</i> ²	1.066
Final <i>R</i> indexes [<i>I</i> ≥ 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0442, <i>wR</i> ₂ = 0.0853
Final <i>R</i> indexes [all data]	<i>R</i> ₁ = 0.0614, <i>wR</i> ₂ = 0.0931
Largest diff. peak/hole / e Å ⁻³	1.28/-1.43
Absolute structure parameter	-
CCDC #	2288558

3. Computational Details

All computations were carried out with ORCA 5.0.3.⁹ The structural parameters were optimized without constraints and tighter-than-default convergence settings (*tightopt*) using the r²SCAN-3c composite method.¹⁰ The optimized structural parameters were verified as true minima by the absence of negative eigenvalues in the harmonic vibrational frequency analysis.

Ring strains were computed as the reaction enthalpies of the following homodesmotic equations:



Scheme S1. Homodesmotic equations for the computation of ring strains.

Table S6. Energies of computed compounds.

Compound	<i>E</i> [Eh]	<i>H</i> [Eh]	<i>G</i> [Eh]
A1	-461.914384	-461.7480412	-461.7904238
A2	-463.185817	-462.9952266	-463.0391533
A3	-925.191208	-924.8304634	-924.8935492
B1	-383.563361	-383.4407686	-383.4794766
B2	-384.806909	-384.6610113	-384.7021590
B3	-768.417742	-768.1458822	-768.2046178
B4	-655.101693	-654.8411785	-654.8960081
C1	-423.795523	-423.6362752	-423.6774918
C2	-695.397897	-695.0997380	-695.1559291
D1	-309.543457	-309.4027422	-309.4396362
D2	-79.791850	-79.7130830	-79.7389365
D3	-389.388731	-389.1654580	-389.2108667
D4	-581.086557	-580.8076858	-580.8612312
tol	-271.487210	-271.3527965	-271.3900431

Table S7. Computed ring strains with comparison to literature values, if available.

Compound	Equation	ΔH_{comp} [kJ mol ⁻¹]	ΔH_{lit} [kJ mol ⁻¹]
A1	I	-228.9	-222 ¹¹
B1	II	-115.8	-
	III	-125.0	
C1	IV	-290.6	-
D1	V	-130.3	-136 ¹²
	VI	-136.9	

XYZ Coordinates

20				C	-4.644244	1.168717	-1.920550
A1				C	-3.743266	0.980278	-2.989762
C	-8.093258	1.998268	0.626542	C	-4.554431	2.338205	-1.156511
C	-6.859714	2.550816	1.048823	C	-3.618049	3.323545	-1.440219
C	-5.736115	1.946771	0.549950	C	-2.740166	3.146482	-2.504011
C	-5.799152	0.837133	-0.333347	C	-2.806071	1.984870	-3.261249
C	-6.987492	0.294676	-0.745141	H	-2.096278	1.827079	-4.068661
C	-8.154735	0.913999	-0.235499	H	-5.261295	2.480825	-0.342982
H	-7.056023	-0.554553	-1.418214	H	-1.996717	3.903385	-2.736575
H	-9.126677	0.527460	-0.528185	H	-3.578024	4.225028	-0.835790
H	-9.018736	2.436283	0.989027	C	-6.816974	0.232119	-3.828236
H	-6.831739	3.399148	1.725943	C	-3.736985	-0.236021	-3.833974
C	-4.235080	1.902767	0.498412	C	-3.791222	-1.517404	-3.273619
C	-4.297815	0.793089	-0.384858	C	-3.651435	-0.116924	-5.225781
C	-3.046688	2.443968	0.911868	C	-3.631775	-1.245149	-6.035943
C	-1.879408	1.824998	0.402219	C	-3.695826	-2.514355	-5.469140
C	-1.940708	0.741768	-0.461139	C	-3.772722	-2.645239	-4.084899
C	-3.174249	0.189634	-0.984379	H	-3.843359	-1.237609	-2.194770
H	-3.201731	-0.658346	-1.561939	H	-3.684469	-3.397416	-6.101746
H	-2.978648	3.292632	1.585725	H	-3.811748	-3.632171	-3.632456
H	-1.015411	0.303764	-0.824093	H	-3.645417	0.872282	-5.675640
H	-0.907302	2.210595	0.695605	H	-3.583301	-1.131197	-7.115211
				C	-6.750625	1.596828	-4.131524
				C	-7.025133	-0.676612	-4.872184
22				C	-7.153140	-0.236186	-6.183337
A2				C	-6.878376	2.036301	-5.443560
C	-7.838700	2.048820	0.929573	C	-7.077232	1.122209	-6.475141
C	-6.452960	1.948311	0.957593	H	-7.040578	-1.741108	-4.654532
C	-5.762809	1.271800	-0.056089	H	-7.295845	-0.958849	-6.981788
C	-6.502704	0.699856	-1.098698	H	-6.602974	2.316346	-3.331984
C	-7.888384	0.801722	-1.126279	H	-6.828714	3.099752	-5.660100
C	-8.562587	1.476268	-0.112428	H	-7.173510	1.467994	-7.500458
H	-8.444023	0.360245	-1.948779				
H	-5.981588	0.196453	-1.908437	15			
H	-9.645524	1.555301	-0.134249	B1			
H	-8.356854	2.568685	1.730423	C	-11.615122	0.222821	1.682844
H	-5.897011	2.373249	1.788876	C	-11.949278	0.701938	0.408003
C	-4.289188	1.163955	-0.025789	C	-10.293489	0.192409	2.126181
C	-3.649494	-0.026132	-0.394787	C	-9.347502	0.664270	1.225915
C	-3.498782	2.249031	0.373474	C	-9.676973	1.143071	-0.046408
C	-2.113136	2.146930	0.402325	C	-10.986474	1.175020	-0.490504
C	-1.489435	0.958321	0.033757	H	-12.409156	-0.130963	2.334076
C	-2.263830	-0.127515	-0.364649	H	-12.994775	0.703818	0.111499
H	-1.786534	-1.062425	-0.644440	H	-10.031901	-0.177879	3.112685
H	-4.248113	-0.887152	-0.679458	H	-11.272686	1.540623	-1.472283
H	-3.976686	3.189081	0.635519	C	-8.244785	1.467848	-0.446583
H	-0.406566	0.878774	0.056926	C	-7.895720	0.925062	0.988482
H	-1.516741	3.002960	0.705106	H	-8.006592	2.526612	-0.597860
				H	-7.819464	0.878894	-1.266842
42				O	-6.871343	0.792932	1.599801
A3							
C	-6.604854	-1.257526	0.190381	17			
C	-5.677884	-0.318206	-0.241627	B2			
C	-5.695423	0.183706	-1.548309	C	-11.666905	0.174504	1.729872
C	-6.696487	-0.260992	-2.437472	C	-12.253955	0.696743	0.577969
C	-7.622655	-1.208533	-1.984266	C	-10.289018	0.203435	1.881893
C	-7.582043	-1.708870	-0.689997	C	-9.477735	0.755387	0.883387
H	-8.408024	-1.531396	-2.662158	C	-10.074480	1.277508	-0.269489
H	-8.319372	-2.438310	-0.367635	C	-11.456451	1.247834	-0.420355
H	-6.560311	-1.636624	1.207175	C	-12.289423	-0.255456	2.509178
H	-4.894333	0.018990	0.432307				

H	-13.333575	0.673781	0.459342	O	2.485000	-0.395031	0.247074
H	-9.809991	-0.197159	2.769901	C	4.453035	1.576822	0.272975
H	-11.911893	1.655196	-1.318158	C	5.164227	0.790138	1.180619
C	-7.996659	0.762493	1.093461	C	5.095639	2.016425	-0.884106
O	-7.510789	0.298381	2.110607	C	6.424416	1.682584	-1.129819
H	-9.464690	1.710456	-1.056414	C	7.125814	0.900763	-0.218223
C	-7.114679	1.356764	0.017141	C	6.490736	0.454740	0.938024
H	-7.251987	0.829327	-0.933514	H	4.669015	0.430294	2.078579
H	-6.073621	1.276774	0.331171	H	4.551362	2.627555	-1.600694
H	-7.365404	2.409693	-0.154149	H	6.911716	2.035483	-2.034291
				H	8.163155	0.639810	-0.406733
				H	7.031122	-0.159134	1.652993
32				C	3.013815	1.925531	0.522109
B3				H	2.882042	2.261761	1.561247
C	-10.674445	-0.006605	-0.078188	H	2.703852	2.762713	-0.113292
C	-11.385551	1.168667	-0.296201				
C	-9.344056	-0.080359	-0.465052				
C	-8.700290	1.014285	-1.050913	19			
C	-9.425933	2.190118	-1.313766	C1			
C	-10.766200	2.242489	-0.923735	C	-5.785052	1.062825	-0.280495
H	-11.152748	-0.860428	0.392099	C	-5.681462	0.079959	-1.282114
H	-12.425479	1.246224	0.007601	C	-4.446735	-0.394829	-1.659632
H	-8.770098	-0.988611	-0.307612	C	-4.652021	1.553570	0.325981
H	-11.338845	3.145388	-1.126287	H	-6.579381	-0.303795	-1.757633
C	-7.230989	0.828682	-1.326230	H	-6.762537	1.434017	0.013388
O	-6.837505	-0.207287	-1.828898	C	-3.365759	1.092140	-0.033270
C	-6.261398	1.891398	-0.860923	H	-4.732277	2.313248	1.099963
H	-6.653088	2.457524	-0.010544	C	-3.259381	0.083420	-1.061318
H	-6.055381	2.590921	-1.678920	H	-4.367428	-1.154258	-2.433976
H	-5.322340	1.401720	-0.593511	C	-2.194131	1.615518	0.609762
C	-8.834176	3.352507	-2.080121	C	-1.031470	1.081676	0.162417
C	-8.184243	2.980504	-3.417895	C	-0.931095	0.129105	-0.808597
H	-8.067464	3.879270	-1.503594	C	-1.979099	-0.422578	-1.467577
H	-9.627999	4.082512	-2.287024	H	-2.289743	2.374337	1.383046
O	-7.049436	3.354113	-3.664404	H	-1.914204	-1.182755	-2.242657
C	-8.947064	2.168359	-4.405114	C	0.339522	0.614688	-0.195881
C	-10.340425	2.050259	-4.369609	H	0.879732	-0.034331	0.496825
C	-8.229135	1.525231	-5.420541	H	0.992291	1.272783	-0.773532
C	-8.892816	0.771101	-6.375847				
C	-11.004458	1.310108	-5.339924	34			
C	-10.282125	0.664501	-6.339198	C2			
H	-7.148554	1.624831	-5.433460	C	-11.548219	-0.030135	1.652842
H	-10.913417	2.539596	-3.589800	C	-11.893756	0.590893	0.433519
H	-12.087130	1.231201	-5.312492	C	-10.234184	-0.095412	2.049898
H	-8.328712	0.261878	-7.151550	C	-9.208767	0.456588	1.246280
H	-10.801813	0.075445	-7.089595	C	-9.558367	1.084571	0.014334
				C	-10.919678	1.136413	-0.367871
				H	-12.327379	-0.457500	2.277399
				H	-12.935827	0.635855	0.130346
				H	-9.963967	-0.573326	2.988504
30				H	-11.183891	1.615317	-1.307805
B4				C	-8.524245	1.632846	-0.779394
C	-2.130555	1.653586	0.073060	C	-7.845956	0.405989	1.622353
C	-1.652405	0.451398	-0.433289	C	-6.855641	0.944488	0.834919
C	-1.248163	2.564676	0.641899	C	-7.203148	1.576585	-0.400467
C	0.103424	2.258679	0.686450	C	-6.136471	2.171709	-1.277595
C	0.597565	1.041389	0.194357	H	-8.791624	2.112382	-1.719279
C	-0.299366	0.108123	-0.378565	H	-7.586066	-0.074933	2.561794
H	-3.191955	1.878956	0.018923	C	-5.394301	0.890556	1.242069
H	-2.348446	-0.250498	-0.885576	H	-5.564818	2.945598	-0.751326
H	-1.607961	3.507293	1.042802	H	-6.575286	2.625728	-2.169340
H	0.784947	2.976671	1.130386	H	-5.414798	1.413984	-1.605936
C	0.126138	-1.216252	-0.947871	C	-5.121014	0.167817	2.533467
H	0.985808	-1.116146	-1.615732	H	-4.820256	0.414970	0.434777
H	-0.703820	-1.667094	-1.499434				
H	0.441233	-1.903006	-0.157143				
C	2.055829	0.741990	0.307338				

H	-5.008911	1.917434	1.312710	H	-9.498389	4.651299	-1.740214
C	-4.920706	-1.213951	2.543813	H	-8.568351	5.207574	-3.142810
C	-5.098700	0.856768	3.747088	H	-7.790885	5.069946	-1.561943
C	-4.880476	0.181923	4.944369	H	-10.428258	3.986246	-3.748305
C	-4.681121	-1.195496	4.943177	H	-9.347457	-0.695650	-4.862003
C	-4.702251	-1.892488	3.738290	H	-11.912285	2.710400	-5.233221
H	-4.943482	-1.762101	1.604500	H	-11.367232	0.347127	-5.795292
H	-5.259244	1.932602	3.752395				
H	-4.863257	0.733602	5.880086	31			
H	-4.507758	-1.723136	5.876525	D4			
H	-4.545272	-2.967396	3.728308	C	-7.393198	-1.689392	-3.528999
				C	-7.249063	-0.163540	-3.479619
16				C	-8.491059	0.638210	-3.791334
D1				H	-6.445745	0.130015	-4.171272
C	-8.991308	-2.014100	-6.494926	H	-6.878572	0.115646	-2.482361
C	-9.276398	-0.648209	-6.585542	C	-9.704872	0.029942	-4.112930
C	-8.187972	-2.533423	-5.471967	C	-8.424601	2.046237	-3.757128
C	-7.698188	-1.612550	-4.562987	C	-9.568983	2.788606	-4.044776
C	-7.982096	-0.253399	-4.653037	C	-10.773819	2.169891	-4.364306
C	-8.773920	0.273050	-5.658071	C	-10.840467	0.784157	-4.398029
H	-9.004310	1.331937	-5.741589	C	-7.139079	2.749123	-3.414989
H	-7.975186	-3.597722	-5.414513	H	-9.513125	3.874378	-4.017309
H	-9.406123	-2.687153	-7.240257	H	-9.776106	-1.052613	-4.144273
H	-9.905065	-0.296581	-7.399026	H	-11.652227	2.769575	-4.584619
C	-6.848302	-1.448047	-3.315961	H	-11.772608	0.284358	-4.645407
C	-7.170929	0.093903	-3.418059	H	-6.337272	2.489519	-4.116642
H	-5.788832	-1.699973	-3.430409	H	-6.782507	2.475480	-2.414645
H	-7.233652	-1.935564	-2.414352	H	-7.269395	3.833846	-3.439989
H	-6.297589	0.731521	-3.590726	C	-6.087547	-2.364364	-3.197082
H	-7.743033	0.496391	-2.575575	H	-7.723903	-1.997363	-4.528705
				H	-8.164784	-2.010334	-2.818246
8				C	-5.156835	-2.650122	-4.198387
D2				C	-5.758600	-2.669186	-1.874477
C	-6.856469	-1.423659	-3.321344	C	-3.928834	-3.225463	-3.887434
C	-7.167924	0.068006	-3.420342	C	-3.612160	-3.524412	-2.565597
H	-6.181132	-1.743020	-4.121640	C	-4.531833	-3.244634	-1.559059
H	-7.767401	-2.026128	-3.397395	H	-6.475402	-2.456362	-1.083963
H	-6.377478	-1.667636	-2.367623	H	-5.400628	-2.422248	-5.234061
H	-7.646914	0.311983	-4.374063	H	-3.219094	-3.445398	-4.680064
H	-6.256992	0.670474	-3.344291	H	-2.655445	-3.976908	-2.321563
H	-7.843261	0.387367	-2.620045	H	-4.295175	-3.479788	-0.525137
24				15			
D3				tol			
C	-7.210565	-1.044800	-3.583354	C	-5.842334	0.958494	-0.231352
C	-7.473335	0.404421	-3.186952	C	-5.622267	0.018715	-1.232781
H	-7.092589	-1.152237	-4.666680	C	-4.327523	-0.250335	-1.667901
H	-8.023219	-1.705136	-3.263028	C	-4.757490	1.625425	0.331770
H	-6.289281	-1.400762	-3.112479	H	-6.460840	-0.511028	-1.676116
C	-8.718101	1.042263	-3.764248	H	-6.851423	1.167756	0.111402
H	-6.602453	1.013397	-3.469232	C	-3.465931	1.353486	-0.105590
H	-7.520526	0.469825	-2.090285	H	-4.917864	2.358042	1.117912
C	-9.572963	0.335114	-4.608669	C	-3.231724	0.413776	-1.113548
C	-9.027749	2.383537	-3.444945	H	-4.164297	-0.988863	-2.449419
C	-10.178182	2.957141	-3.984843	H	-2.623561	1.876627	0.341899
C	-11.022458	2.237831	-4.827079	C	-1.833600	0.145919	-1.601244
C	-10.718839	0.921890	-5.140088	H	-1.121196	0.119221	-0.770645
C	-8.111007	3.165030	-2.529405	H	-1.502377	0.933301	-2.289608
C	-8.520532	4.603549	-2.230747	H	-1.772808	-0.806817	-2.134793
H	-8.013056	2.618984	-1.580088				
H	-7.099678	3.165678	-2.961230				

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