Electronic Supplementary Material (ESI) for Dalton Transactions

Expanded Ring Diaminocarbene Palladium Complexes: Synthesis, Structure, and Suzuki–Miyaura Cross-Coupling of Heteroaryl Chlorides in Water

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Supporting information

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Synthesis of palladium complexes

(**4**)Pd(cinn)Cl. A solution of N-heterocyclic carbene **4** (1 eq, 0.643 g, 2.10 mmol) in 20 ml of diethyl ether was added to a suspension of Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.544 g, 1.05 mmol) in a small amount of diethyl ether. The reaction was stirred for 1 h and then filtered off, evaporated to dryness, grinded with hexane and the precipitate was filtered off and dried *in vacuo*. Yield: 0.57 g, 48%, white powder.

Anal. Calcd for $C_{30}H_{35}ClN_2Pd$: C, 63.72; H, 6.24; N, 4.95. Found: C, 63.94; H, 6.31; N, 5.03.

^{1}H NMR ($CDCl_3$, 400 MHz): δ_{ppm} 7.09-7.15 (m, 3H, Ph), 7.04-7.08 (m, 2H, Ph) 6.97 (br.s, 2H, Ar-Mes-H), 6.95 (br.s, 2H, Ar-Mes-H), 5.09 (ddd, *J* = 18.6, 12.5, 10.3 Hz, 1H, Allyl), 4.27 (d, *J* = 12.6 Hz, 1H, Allyl), 3.99 (d, *J* = 3.4 Hz, 4H, CH_2-N), 3.27 (d, *J* = 6.3 Hz, 1H, Allyl), 2.46 (s, 6H, CH_3-Mes), 2.42 (s, 6H, CH_3-Mes), 2.32 (s, 6H, CH_3-Mes), 1.93 (d, *J* = 11.7 Hz, 1H, Allyl).

^{13}C NMR (151 MHz, $CDCl_3$): δ_{ppm} 211.2 (N-C-N), 138.1 (Ar), 136.4 (Ar), 129.4 (Ar), 128.3 (Ar), 127.4 (Ar), 126.6 (Ar), 109.7 (Allyl), 90.2 (Allyl), 51.3 (CH_2-N), 46.8 (Allyl), 21.2 (CH_3-Mes), 18.64 (CH_3-Mes), 18.56 (CH_3-Mes).

(**5**)Pd(cinn)Cl. A: A solution of N-heterocyclic carbene **5** (1 eq, 0.782 g, 2.00 mmol) in 25 ml of diethyl ether was added to a suspension of Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.518 g, 1.00 mmol) in a small amount of diethyl ether. The reaction was stirred for 1 h and then filtered off, evaporated to dryness, grinded with hexane and the precipitate was filtered off and dried *in vacuo*. Yield: 0.82 g, 63%, light-yellow powder.

Anal. Calcd for $C_{36}H_{47}ClN_2Pd$: C, 66.56; H, 7.29; N, 4.31. Found: C, 67.13; H, 7.01; N, 4.24.

^{1}H NMR ($CDCl_3$, 600 MHz): δ_{ppm} 7.38 (t, *J* = 7.8 Hz, 2H, *p*-Ar-Dipp-H), 7.25 (d, *J* = 7.6 Hz, 4H, *m*-Ar-Dipp-H), 7.15-7.11 (m, 5H, Ph), 5.06 (dt, *J* = 13.1, 9.2, 1H, Allyl), 4.34 (d, *J* = 13.2 Hz, 1H, Allyl), 4.04 (s, 4H, CH_2-N), 3.45 (br.s, 4H, CH-iPr), 2.89 (br.s, 1H, Allyl), 1.58 (br. s, 1H, Allyl), 1.47 (d, *J* = 5.9 Hz, 6H, CH_3-iPr), 1.42 (d, *J* = 6.2 Hz, 6H, CH_3-iPr), 1.28 (d, *J* = 6.8 Hz, 12H, CH_3-iPr).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 212.0 (N-C-N), 147.1 (Ar), 137.6 (Ar), 136.3 (Ar), 129.0 (Ar), 128.2 (Ar), 127.2 (Ar), 126.6 (Ar), 124.1 (Ar), 109.0 (Allyl), 91.6 (Allyl), 54.0 (CH_2-N), 46.0 (Allyl), 28.5 (CH-iPr), 26.6 (CH-iPr), 23.7 (CH_3-iPr).

(**6-Mes**)Pd(cinn)Cl. A: A solution of N-heterocyclic carbene **6-Mes** (1 eq, 0.277 g, 0.86 mmol) in 10 ml of diethyl ether was added to a suspension of bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.223 g, 0.43 mmol) in a small amount of diethyl ether. The reaction was stirred for 1 h and then filtered off, evaporated to dryness, grinded with hexane and the precipitate was filtered off and

dried *in vacuo*. Yield 0.31 g, 62%, light-yellow powder.

B: In air the NHC-silver (I) complex (**6-Mes**)AgBr (1 eq, 0.877 g, 1.73 mmol) and Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.448 g, 0.87 mmol) were dissolved in 35 ml of DCM and stirred for 24 h in absence of light. The mixture was evaporated, dissolved in diethyl ether, filtered off though short pad Celite and evaporated to give the pure palladium complex. Yield: 0.88 g 88%, light-yellow powder.

Anal. Calcd for $C_{31}H_{37}ClN_2Pd$: C, 64.25; H, 6.44; N, 4.83. Found: C, 64.02; H, 6.59; N, 4.93.

^{1}H NMR(DMSO-d_6, 400 MHz): δ_{ppm} 6.99-7.09 (m, 3H, Ph), 6.95 (br.s, 2H, Ar-Mes-H), 6.87 (br.s, 2H, Ar-Mes-H), 6.68 (d, *J* = 6.4 Hz, 2H, Ph), 4.61 (ddd, *J* = 19.3, 11.8, 9.4 Hz, 1H, Allyl), 3.62 (d, *J* = 12.0 Hz, 1H, Allyl), 3.37 (s, 4H, CH_2-N), 2.39-2.43 (m, 2H, Allyl), 2.34 (br.s, 6H, CH_3-Mes), 2.28 (br.s, 12H, CH_3-Mes), 2.15-2.23 (m, 2H, CH_2) (one of the allyl protons was not observed).

^{13}C NMR(DMSO-d_6, 101 MHz): δ_{ppm} 206.7 (N-C-N), 139.5 (Ar), 136.6 (Ar), 136.4 (Ar), 134.4 (Ar), 129.3 (Ar), 128.9 (Ar), 128.7 (Ar), 128.0 (Ar), 127.7 (Ar), 127.0 (Ar), 125.5 (Ar), 109.5 (Allyl), 83.7 (Allyl), 48.3 (CH_2-N), 45.9 (allyl), 31.0 (CH_2), 22.1 (CH_3-Mes), 20.6 (CH_3-Mes), 19.0 (CH_3-Mes), 17.5 (CH_3-Mes), 14.0 (CH_3-Mes).

^{13}C NMR (151 MHz, $CDCl_3$) δ_{ppm} 213.8 (N-C-N), 146.7 (Ar), 143.5 (Ar), 138.9 (Ar), 128.5 (Ar), 127.9 (Ar), 127.3 (Ar), 126.0 (Ar), 124.1 (Ar), 108.7 (allyl), 86.7 (allyl), 65.7 (N-CH_2), 49.3 (allyl), 31.5 (CH_2), 28.6 (CH_3-Mes), 26.9 (CH_3-Mes), 23.6 (CH_3-Mes), 22.6 (CH_3-Mes), 20.8 (CH_3-Mes), 15.2 (CH_3-Mes).

(**7-Mes**)Pd(cinn)Cl. B: In air the NHC-silver (I) complex (**7-Mes**)AgBr (1 eq, 0.890 g, 1.70 mmol) and Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.440 g, 0.85 mmol) were dissolved in 35 ml of DCM and stirred for 24 h in absence of light. The mixture was evaporated, dissolved in diethyl ether, filtered off though short pad Celite and evaporated to give the pure palladium complex. Yield: 0.94 g, 93%, light-yellow powder.

Anal. Calcd for $C_{32}H_{39}ClN_2Pd$: C, 64.75; H, 6.62; N, 4.72. Found: C, 64.38; H, 6.31; N, 4.83.

^{1}H NMR($CDCl_3$, 400 MHz): δ_{ppm} 7.07 (br.s, 2H, Ar-Mes-H), 6.96 (br.s, 5H, Ph), 6.75 (br.s, 2H, Ar-Mes-H), 4.63 (dd, *J* = 19.1, 11.7 Hz, 1H, Allyl), 4.09 (d, *J* = 11.0 Hz, 1H, Allyl), 3.60 - 3.90 (m, 4H, CH_2-N), 3.32 (d, *J*=5.6 Hz, 1H, Allyl), 2.02 - 2.80 (m, 22H, CH_3-Mes + CH_2CH_2), 1.54 (d, *J* = 12.3 Hz, 1H, Allyl).

^{13}C NMR($CDCl_3$, 101 MHz): δ_{ppm} 221.4 (N-C-N), 139.1 (Ar), 137.0 (Ar), 130.1 (Ar), 129.6 (Ar), 128.9 (Ar), 128.1 (Ar), 127.9 (Ar), 127.1 (Ar), 126.0 (Ar), 109.6 (Allyl), 86.0 (Allyl), 53.8 (Allyl),

48.5 (CH_2-N), 25.3 (CH_2CH_2), 20.9 (CH_3-Mes), 20.02 - 20.37 (m, CH_3-Mes), 19.55 - 20.02 (m, CH_3-Mes), 18.10 - 19.02 (m, CH_3-Mes).

(**6-Dipp**)Pd(cinn)Cl. A: A solution of N-heterocyclic carbene **6-Dipp** (1 eq, 0.269 g, 0.66 mmol) in 8 ml of diethyl ether was added to a suspension of bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.171 g, 0.33 mmol) in a small amount of diethyl ether. The reaction was stirred for 1 h and then filtered off, evaporated to dryness, grinded with hexane and the precipitate was filtered off and dried *in vacuo*. Raw product was purified by recrystallization from hexane:DCM. Yield: 0.15 g, 34%, light-yellow powder.

B: In air the NHC-silver (I) complex (**6-Dipp**)AgBr (1 eq, 1.069 g, 1.80 mmol) and Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.466 g, 0.90 mmol) were dissolved in 40 ml of DCM and stirred for 24 h in absence of light. The mixture was evaporated, dissolved in diethyl ether, filtered off though short pad Celite and evaporated to give the pure palladium complex. The pad of Celite was extracted with DCM and the filtrate was stirred 24 h, and then all process was repeated two more times. Yield: 0.85 g, 71%, light-yellow powder.

Anal. Calcd for $C_{37}H_{49}ClN_2Pd$: C, 66.96; H, 7.44; N, 4.22. Found: C, 67.19; H, 7.53; N, 4.13.

^{1}H NMR ($CDCl_3$, 400 MHz): δ_{ppm} 7.35 (t, *J* = 7.6 Hz, 2H, *p*-Ar-Dipp-H), 7.25 (d, *J* = 7.3 Hz, 4H, *m*-Ar-Dipp-H), 7.04 - 7.11 (m, 3H, Ph), 6.83 - 6.88 (m, 2H, Ph), 4.62 (dt, *J* = 12.2, 9.4 Hz, 1H, Allyl), 3.88 (d, *J* = 12.2 Hz, 1H, Allyl), 3.62 - 3.69 (t, *J* = 5.6 Hz, 4H, CH_2-N), 3.55 (dt, *J* = 13.4, 6.6 Hz, 4H, CH-iPr), 2.36 (ddd, *J* = 11.2, 6.0, 5.7 Hz, 2H, CH_2), 1.42 (d, *J* = 6.6 Hz, 12H, CH_3-iPr), 1.22 (d, *J* = 6.8 Hz, 12H, CH_3-iPr), 1.18 (d, *J* = 6.6 Hz, 1H, Allyl) (one of the allyl protons was not observed).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 213.8 (N-C-N), 146.6 (Ar), 143.5 (Ar), 138.9 (Ar), 128.5 (Ar), 127.8 (Ar), 127.3 (Ar), 126.0 (Ar), 124.1 (Ar), 108.7 (Allyl), 86.7 (Allyl), 65.7 (Allyl), 49.3 (CH_2-N), 31.5 (CH_2), 28.6 (CH-iPr), 26.9 (CH-iPr), 23.6 (CH_3-iPr), 22.5 (CH_3-iPr), 20.8 (CH_3-iPr), 15.2 (CH_3-iPr).

(**7-Dipp**)Pd(cinn)Cl. A: A solution of N-heterocyclic carbene **7-Dipp** (1 eq, 0.677 g, 1.62 mmol) in 20 ml of diethyl ether was added to a suspension of bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.420 g, 0.81 mmol) in a small amount of diethyl ether. The reaction was stirred for 1 h and then filtered off, evaporated to dryness, grinded with hexane and the precipitate was filtered off and dried *in vacuo*. Raw product was purified by flash chromatography, using DCM as an eluent. Yield: 0.46 g, 42%, light-yellow powder.

B: In air the NHC-silver (I) complex (**7-Dipp**)AgBr (1 eq, 0.224 g, 0.37 mmol) and Bis(palladium(η_3-cinnamyl)chloride) (0.5 eq, 0.098 g, 0.19 mmol) were dissolved in 8 ml of DCM

and stirred for 24 h in absence of light. The mixture was evaporated, dissolved in diethyl ether, filtered off though short pad Celite and evaporated to give the pure palladium complex. The pad of Celite was extracted with DCM and the filtrate was stirred 24 h, and then all process was repeated two more times. Yield: 0.185 g, 73%, light-yellow powder.

Anal. Calcd for $C_{38}H_{51}ClN_2Pd$: C, 67.35; H, 7.59; N, 4.13. Found: C, 67.38; H, 7.35; N, 4.28.

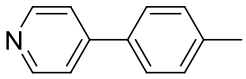
^{1}H NMR ($CDCl_3$, 600 MHz): δ_{ppm} 7.31 (t, *J* = 7.6 Hz, 2H, *p*-Ar-Dipp-H), 7.23 (d, *J* = 7.6 Hz, 4H, *m*-Ar-Dipp-H), 7.01 - 7.11 (m, 3H, Ph), 6.69 - 6.76 (m, 2H, Ph), 4.58 (dt, *J* = 21.1, 9.4 Hz, 1H, Allyl), 4.04 (br.s, 4H, CH_2-N), 3.80 (d, *J* = 12.0 Hz, 1H, Allyl), 3.61 (br.s, 4H, CH-iPr), 2.35 (br.s, 4H, CH_2CH_2), 1.45 (d, *J* = 6.7 Hz, 12H, CH_3-iPr), 1.24 (d, *J* = 6.5 Hz, 12H, CH_3-iPr) (two of the allyl protons were not observed).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 225.5 (N-C-N), 146.4 (Ar), 145.7 (Ar), 139.2 (Ar), 128.2 (Ar), 127.8 (Ar), 127.4 (Ar), 125.9 (Ar), 124.1 (Ar), 109.1 (Allyl), 85.6 (Allyl), 56.7 (Allyl), 48.3 (CH_2-N), 31.7 (CH_2CH_2), 28.9 (CH-iPr), 28.8 (CH-iPr), 27.3 (CH-iPr), 25.5(CH-iPr), 23.9 (CH_3-iPr).

Characterization of cross-coupling products

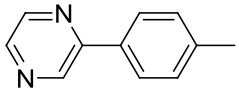
NMR data of 4-(4-Methylphenyl)pyridine,[1] 2-(4-Methylphenyl)pyrazine,[2] 2-(4-Methylphenyl)-3-nitropyridine,[3] 3,5-Bis(4-methylphenyl)pyridine,[4] 2,6-Bis(4-methylphenyl)pyridine,[4] 2-(4-Methylphenyl)thiophene,[5] 3-(4-Methylphenyl)thiophene, [6] 3-(4-Methylphenyl)pyridine,[7] 3-(4-Methylphenyl)quinoline,[8] 5-(4-Methylphenyl)pyrimidine,[9] 3,6-Bis(4-methylphenyl)pyridazine,[10] 2-(4-Methylphenyl)pyridine,[11] 2-(3-Nitrophenyl)pyridine,[12] 2-(3-(Trifluoromethyl)-phenyl)pyridine,[13] 2-(2,4,6-Trimethylphenyl)pyridine,[14] 3-(2-Pyridyl)thiophene,[15] 2-(4-Fluorophenyl)pyridine.[16] were identical to the published data.

4-(4-Methylphenyl)pyridine



1H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.59 (d, J=5.6 Hz, 2H), 7.49 (d, J=8.0 Hz, 2H), 7.44 (d, J=6.0 Hz, 2H), 7.24 (d, J=7.9 Hz, 2H), 2.37 (s, 3H).
13C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 150.1, 148.1, 139.1, 135.1, 129.7, 126.7, 121.3, 21.1.
MS (EI) m/z: 169 (M^+).

2-(4-Methylphenyl)pyrazine

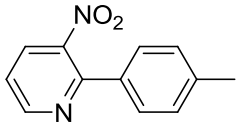


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 9.02 (d, *J*=1.5 Hz, 1H), 8.62 (dd, *J*=2.5, 1.0 Hz, 1H), 8.49 (d, *J*=2.6 Hz, 1H), 7.93 (d, *J*=8.0 Hz, 2H), 7.33 (d, *J*=8.0 Hz, 2H), 2.44 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 152.8, 144.0, 142.5, 142.0, 140.1, 133.5, 129.7, 126.8, 21.3.

MS (EI) m/z: 170 (M^+).

2-(4-Methylphenyl)-3-nitropyridine

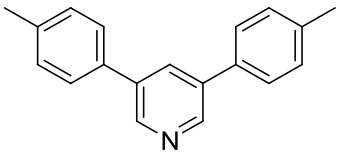


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.73 (dd, *J*=4.7, 1.5 Hz, 1H), 7.99 (dd, *J*=8.1, 1.5 Hz, 1H), 7.44 (d, *J*=8.1 Hz, 2H), 7.28-7.26 (m, 1H), 7.21 (d, *J*=7.8 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 152.3, 151.7, 145.9, 139.7, 133.2, 131.8, 129.2, 127.8, 121.9, 21.0.

MS (EI) m/z: 214 (M^+).

3,5-Bis(4-methylphenyl)pyridine

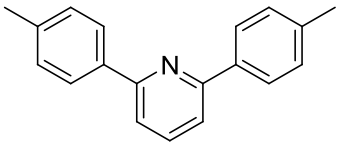


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.79 (d, *J*=2.1 Hz, 2H), 8.01 (t, *J*=2.0 Hz, 1H), 7.54 (d, *J*=8.0 Hz, 4H), 7.31 (d, *J*=7.9 Hz, 4H), 2.43 (s, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 146.6, 138.1, 136.4, 134.9, 132.4, 129.8, 127.0, 21.1.

MS (EI) m/z: 259 (M^+).

2,6- Bis(4-methylphenyl)pyridine

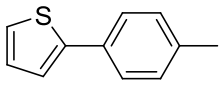


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.08 (d, *J*=8.0 Hz, 4H), 7.75-7.73 (m, 1H), 7.62 (d, *J*=7.7 Hz, 2H), 7.31 (d, *J*=3.9 Hz, 4H), 2.44 (s, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 156.6, 138.7, 137.2, 136.7, 129.3, 126.7, 117.9, 21.2.

MS (EI) m/z: 259 (M^+).

2-(4-Methylphenyl)thiophene

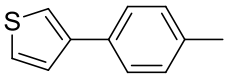


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 7.49-7.48 (m, 2H), 7.25-7.22 (m, 2H), 7.17-7.16 (m, 2H), 7.05-7.04 (m, 1H), 2.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 144.5, 137.3, 131.6, 129.5, 127.9, 125.8, 124.2, 122.5, 21.1.

MS (EI) m/z: 174 (M^+).

3-(4-Methylphenyl)thiophene

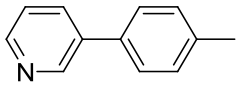


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 7.47 (d, *J*=8.0 Hz, 2H), 7.39-7.35 (m, 3H), 7.18 (d, *J*=8.4 Hz, 2H), 2.35 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 142.3, 136.9, 133.1, 129.5, 126.3, 126.0, 119.6, 21.1.

MS (EI) m/z: 174 (M^+).

3-(4-Methylphenyl)pyridine

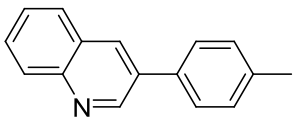


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.67 (d, *J*=1.8 Hz, 1H), 8.37 (dd, *J*=4.7, 1.2 Hz, 1H), 7.57-7.55 (m, 1H), 7.23 (d, *J*=8.0 Hz, 2H), 7.06-7.02 (m, 3H), 2.16 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 147.5, 147.4, 137.2, 135.7, 134.1, 133.2, 129.1, 126.2, 122.7, 20.4.

MS (EI) m/z: 169 (M^+).

3-(4-Methylphenyl)quinoline

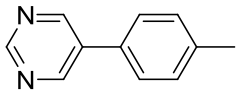


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 9.16 (d, *J*=2.2 Hz, 1H), 8.24 (d, *J*=2.0 Hz, 1H), 8.11 (d, *J*=8.5 Hz, 1H), 7.83 (d, *J*=8.0 Hz, 1H), 7.69-7.67 (m, 1H), 7.58 (d, *J*=8.0 Hz, 2H), 7.55-7.52 (m, 1H), 7.30 (d, *J*=7.9 Hz, 2H), 2.41 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 149.9, 147.2, 138.0, 134.9, 133.7, 132.7, 129.8, 129.2, 129.1, 128.0, 127.9, 127.2, 126.8, 21.1.

MS (EI) m/z: 219 (M^+).

5-(4-Methylphenyl)pyrimidine

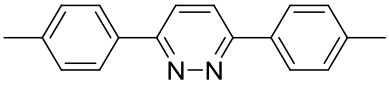


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 9.11 (s, 1H), 8.85 (s, 2H), 7.39 (d, *J*=8.0 Hz, 2H), 7.24 (d, *J*=7.8 Hz, 2H), 2.34 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 157.0, 154.5, 138.9, 134.0, 131.1, 129.9, 126.6, 21.0.

MS (EI) m/z: 170 (M^+).

3,6-Bis(4-methylphenyl)pyridazine

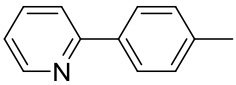


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.03 (d, *J*=8.0 Hz, 4H), 7.84 (s, 2H), 7.32 (d, *J*=8.0 Hz, 4H), 2.41 (s, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 157.3, 140.0, 134.8, 129.7, 126.7, 123.8, 21.3.

MS (EI) m/z: 169 (M^+).

2-(4-Methylphenyl)pyridine

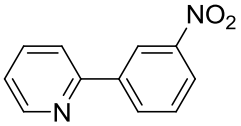


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.63-8.58 (m, 1H), 7.86 (d, *J*=8.1 Hz, 2H), 7.60-7.53 (m, 2H), 7.20 (d, *J*=7.9 Hz, 2H), 7.06 (ddd, *J*=6.7, 5.0, 1.5 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 157.0, 149.3, 138.4, 136.4, 134.9, 129.1, 126.5, 121.5, 120.0, 21.2.

MS (EI) m/z: 169 (M^+).

2-(3-Nitrophenyl)pyridine

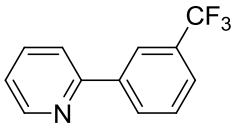


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.82 (s, 1H), 8.69 (d, *J*=4.6 Hz, 1H), 8.32 (d, *J*=7.7 Hz, 1H), 8.22 (dd, *J*=8.1, 1.2 Hz, 1H), 7.81-7.74 (m, 2H), 7.61 (t, *J*=8.0 Hz, 1H), 7.29 (ddd, *J*=6.6, 4.9, 1.6 Hz, 1H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 154.6, 150.0, 148.7, 140.9, 137.1, 132.6, 129.6, 123.5, 123.2, 121.7, 120.5.

MS (EI) m/z: 200 (M^+).

2-(3-(Trifluoromethyl)phenyl)pyridine

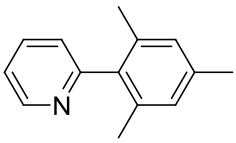


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.64 (d, *J*=4.5 Hz, 1H), 8.24 (s, 1H), 8.10 (d, *J*=7.7 Hz, 1H), 7.73-7.64 (m, 2H), 7.59 (d, *J*=7.7 Hz, 1H), 7.51 (t, *J*=7.8 Hz, 1H), 7.20 (ddd, *J*=6.9, 4.9, 1.4 Hz, 1H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 155.6, 149.7, 140.0, 136.9, 129.9, 129.0, 125.3, 124.3, 123.6, 122.7, 122.1, 120.4.

MS (EI) m/z: 223 (M^+).

2-(2,4,6-Trimethylphenyl)pyridine

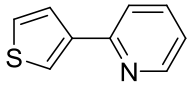


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.66 (dd, *J*=5.3, 1.9 Hz, 1H), 7.65 (td, *J*=7.6, 1.8 Hz, 1H), 7.18-7.12 (m, 2H), 6.89 (s, 2H), 2.27 (s, 3H), 1.99 (s, 6H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 159.6, 149.2, 137.4, 136.8, 135.7, 135.1, 127.8, 124.2, 121.1, 20.7, 19.7.

MS (EI) m/z: 196 (M^+).

3-(2-Pyridyl)thiophene

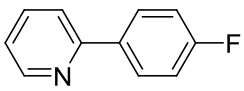


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.56-8.47 (m, 1H), 7.81 (dd, *J*=3.0, 1.2 Hz, 1H), 7.58 (dd, *J*=5.0, 1.2 Hz, 1H), 7.55-7.48 (m, 1H), 7.48-7.44 (m, 1H), 7.27 (dd, *J*=5.0, 3.0 Hz, 1H), 7.04-6.98 (m, 1H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 153.0, 149.2, 141.2, 136.3, 125.9, 125.8, 123.1, 121.4, 119.9.

MS (EI) m/z: 161 (M^+).

2-(4-Fluorophenyl)pyridine

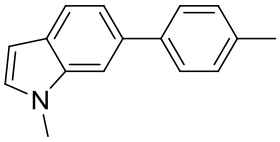


^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.60-8.53 (m, 1H), 7.91-7.84 (m, 2H), 7.61-7.55 (m, 1H), 7.55-7.51 (m, 1H), 7.11-7.07 (m, 1H), 7.06-7.02 (m, 2H).

^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 162.2 (d, J_{CF}=247.7 Hz), 156.0, 149.3, 136.5, 135.2, 128.3, 121.7, 119.8, 115.4, 115.2.

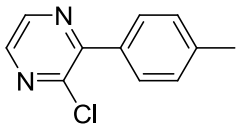
MS (EI) m/z: 173 (M^+).

1-Methyl-6-(4-methylphenyl)indole



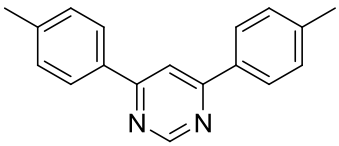
^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 7.85 (d, *J*=1.1 Hz, 1H, Ind-H), 7.58 (d, *J*=8.0 Hz, 2H, Ar-H), 7.49 (dd, *J*=8.5, 1.6 Hz, 1H, Ind-H), 7.38 (d, *J*=8.5 Hz, 1H, Ind-H), 7.27 (d, *J*=7.8 Hz, 2H, Ar-H), 7.08 (d, *J*=3.0 Hz, 1H, Ind-H), 6.54 (d, *J*=3.0 Hz, 1H, Ind-H), 3.81 (s, 3H, CH_3-N), 2.42 (s, 3H, CH_3-Ar).
^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 139.7 (C-N), 136.1 (Ar), 135.8 (Ar), 132.8 (Ar), 129.4 (CH_2-N), 129.3 (Ar), 128.9 (Ind), 127.2 (Ar), 121.3 (Ind), 119.1 (Ind), 109.3 (Ind), 101.2 (Ind), 32.9 (CH_3-N), 21.0 (CH_3-Ar).
MS (EI) m/z: 221 (M^+).

2-Chloro-3-(4-methylphenyl)pyrazine



^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 8.40-8.27 (m, 2H, Pyraz-H), 7.74 (d, *J*=8.3 Hz, 2H, Ar-H), 7.32 (d, *J*=7.9 Hz, 2H, Ar-H), 2.45 (s, 3H, CH_3).
^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 153.4 (quat. C-N), 142.2 (Cl-C-N), 141.7 (C-N), 141.6 (C-N), 139.8 (Ar), 133.3 (Ar), 129.3 (Ar), 128.9 (Ar), 21.3 (CH_3).
MS (EI) m/z: 204 (M^+).

4,6-Bis(4-methylphenyl)pyrimidine



^{1}H NMR($CDCl_3$, 600 MHz): δ_{ppm} 9.24 (s, 1H, N-CH-N), 8.04-8.00 (m, 5H, Ar-H, Pyrim-H), 7.31 (d, *J*=8.1 Hz, 4H, Ar-H), 2.42 (s, 6H, CH_3).
^{13}C NMR ($CDCl_3$, 151 MHz): δ_{ppm} 164.5 (CN), 159.1 (N-C-N), 141.3 (Ar), 134.2 (Ar), 129.7 (Ar), 127.0 (Ar), 112.1 (Pyrim-C), 21.4 (CH_3).
MS (EI) m/z: 260 (M^+).

Crystallographic data

Table S1. Selected bond lengths (Å) and angles (deg.) for the palladium complexes.

	4	(**6-Mes**)	(**7-Mes**)	(**6-Dipp**)	(**7-Dipp**)
	Pd(cinn)Cl	Pd(cinn)Cl*	Pd(cinn)Cl	Pd(cinn)Cl	Pd(cinn)Cl **
Pd–C_{carb}	2.0237(11)	2.047(3)	2.0559(11)	2.042(4)	2.054(3)
Pd–Cl	2.3609(3)	2.3924(8)	2.3658(3)	2.3351(9)	2.3580(9)
Pd–$C_{Allyl}(H_2)$	2.1131(12)	2.112(4)	2.1239(13)	2.113(4)	2.060(7)
Pd–C_{Allyl}(H)	2.1328(11)	2.140(4)	2.1358(12)	2.134(4)	2.106(4)
Pd–C_{Allyl}(PhH)	2.2131(11)	2.238(4)	2.2185(12)	2.204(4)	2.252(4)
N–C_{carb}–N	103.78(9)	117.4(3)	119.46(10)	117.1(3)	119.3(3)
C_{carb}–N–C_{Ar}	124.97(9)	120.7(3)	117.22(9)	121.2(3)	118.6(2)
	125.63(9)	118.9(3)	117.36(9)	120.2(3)	120.3(2)
C_{carb}–N–C_{ring}	111.37(9)	125.0(3)	128.74(10)	124.6(3)	128.6(2)
	111.38(9)	124.7(3)	123.31(10)	126.0(3)	123.2(2)
C_{Ar}–N–C_{ring}	123.58(9)	114.2(3)	113.95(9)	113.7(3)	112.8(2)
	122.87(9)	116.3(3)	116.92(10)	113.6(3)	114.2(2)
Pd–C_{carb}–N	129.63(7)	125.6(2)	121.91(8)	126.1(3)	123.5(2)
	126.41(7)	117.1(2)	118.60(8)	115.6(3)	117.0(2)
C_{Ar}–N…N–C_{Ar}	1.6	10.2	27.3	4.0	24.1

* - the average values for the two crystallographically independent molecules of (**6-Mes**)Pd(cinn)Cl are presented;

** - the Pd-C_{Allyl} distances are given for allyl fragment with the more occupation.

Table S2.

Compound	(**4**)Pd(cinn)Cl	(**6-Mes**)Pd(cinn)Cl •½CH_2Cl_2	(**7-Mes**)Pd(cinn)Cl	(**6-Dipp**)Pd(cinn)Cl •Et_2O	(**7-Dipp**)Pd(cinn)Cl •½C_6H_{14}
empirical formula	$C_{30}H_{33}ClN_2Pd$	$C_{31.5}H_{38}Cl_2N_2Pd$	$C_{32}H_{39}ClN_2Pd$	$C_{41}H_{59}ClN_2OPd$	$C_{38}H_{58}ClN_2Pd$
fw	563.43	621.94	593.50	737.75	720.74
T, K	100(2)	120(2)	100(2)	100(2)	100(2)
crystal size, mm	0.42 x 0.31 x 0.13	0.41 x 0.22 x 0.15	0.24 x 0.16 x 0.13	0.20 x 0.15 x 0.10	0.42 x 0.25 x 0.11
crystal system	triclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
space group	P-1	$P2_1/c$	Pbca	$P2_12_12_1$	C2/c
a, Å	8.2603(4)	21.6985(17)	18.5263(13)	14.3349(8)	27.8782(17)
b, Å	10.4211(5)	16.7201(13)	9.5695(7)	15.0596(8)	15.5946(10)
c, Å	16.2545(7)	17.7371(14)	31.830(2)	17.9807(10)	19.7653(12)
α, deg.	95.6490(10)	90	90	90	90
β, deg.	90.1730(10)	112.570(2)	90	90	113.9140(10)
γ, deg.	103.6930(10)	90	90	90	90
V, $Å^3$	1352.34(11)	5942.2(8)	5643.1(7)	3881.6(4)	7655.3(8)
Z	2	8	8	4	8
d_c, g · cm^{-3}	1.384	1.390	1.397	1.262	1.213
F(000)	580	2568	2464	1560	3048
μ, mm^{-1}	0.805	0.827	0.775	0.579	0.569
$2\theta_{max}$, deg.	56	56	56	56	56
index range	$-10 \le h \le 10$ $-13 \le k \le 13$ $-21 \le l \le 21$	$-28 \le h \le 28$ $-22 \le k \le 22$ $-23 \le l \le 23$	$-28 \le h \le 28$ $-14 \le k \le 14$ $-49 \le l \le 49$	$-18 \le h \le 18$ $-19 \le k \le 19$ $-23 \le l \le 23$	$-33 \le h \le 33$ $-18 \le k \le 18$ $-23 \le l \le 23$
no. of rflns collected	15097	59982	111418	43509	33825
no. of unique rflns	6493	14317	10768	9340	6896
no. of rflns with $I > 2\sigma(I)$	6045	11534	8132	7374	4488
data/restraints/parameters	6493 / 0 / 313	14317 / 10 / 697	10768 / 0 / 331	9340 / 5 / 398	6896 / 31 / 426
*R*1; *wR*2 ($I > 2\sigma(I)$)	0.0207; 0.0521	0.0520; 0.1362	0.0310; 0.0619	0.0430; 0.0934	0.0392; 0.0782
*R*1; *wR*2 (all data)	0.0207; 0.0538	0.0664; 0.1545	0.0534; 0.0694	0.0660; 0.1022	0.0704; 0.0839
GOF on F^2	1.002	1.013	1.018	1.011	1.010
T_{min}; T_{max}	0.748; 0.923	0.730; 0.886	0.910; 0.924	0.901; 0.944	0.796; 0.940

Fig. S1.

Molecular structure of the NHC complex (**4**)Pd(cinn)Cl (all hydrogen atoms are omitted for clarity, the double lines indicate the Pd-C_{Allyl} coordination bonds).

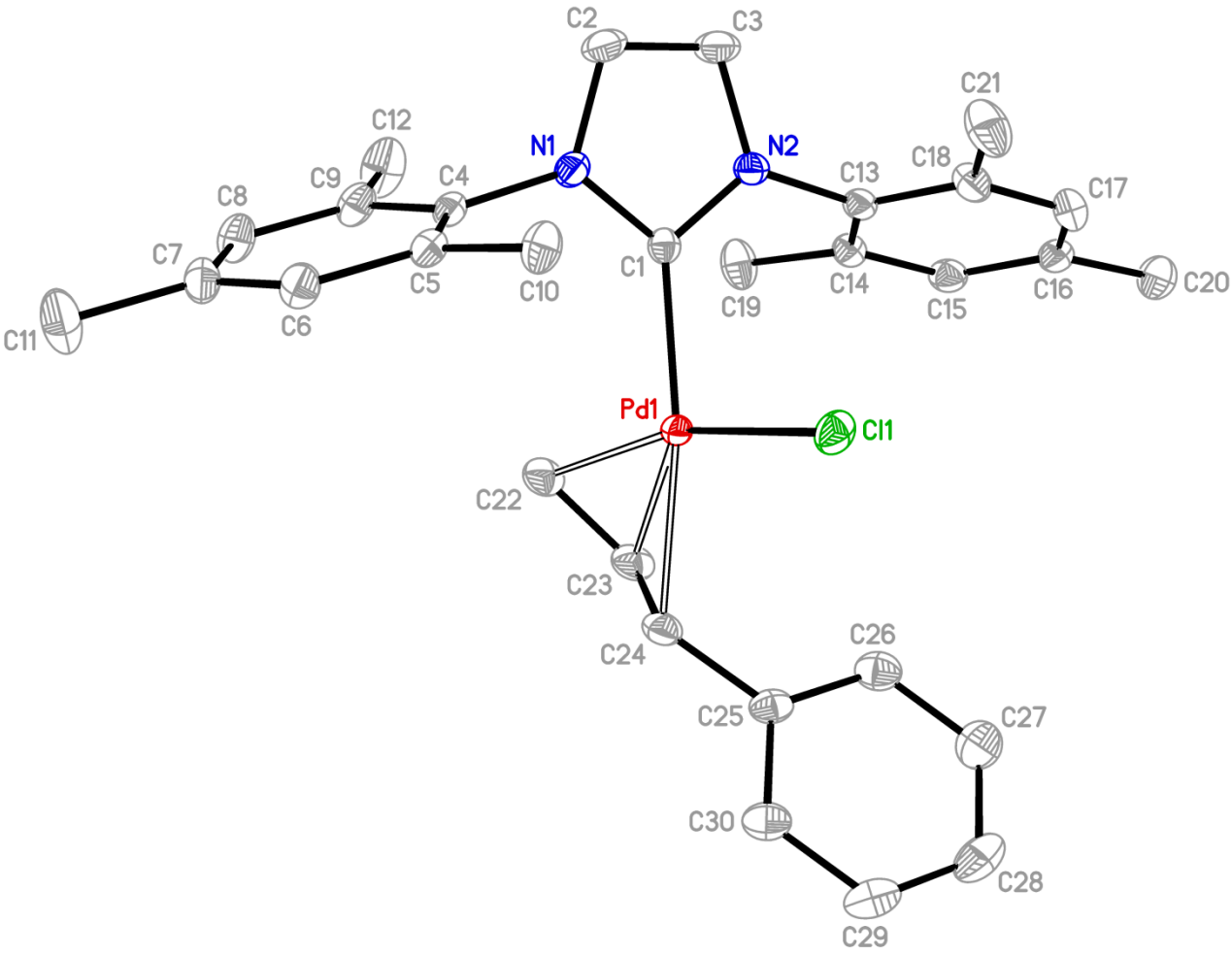


Fig. S2.

Molecular structure of the NHC complex (**6-Mes**)Pd(cinn)Cl (all hydrogen atoms are omitted for clarity, the solvate methylene chloride molecule is not shown, the double lines indicate the Pd-C_{Allyl} coordination bonds, the alternative position of the disordered fragment of carbene ligand is depicted by dashed lines).

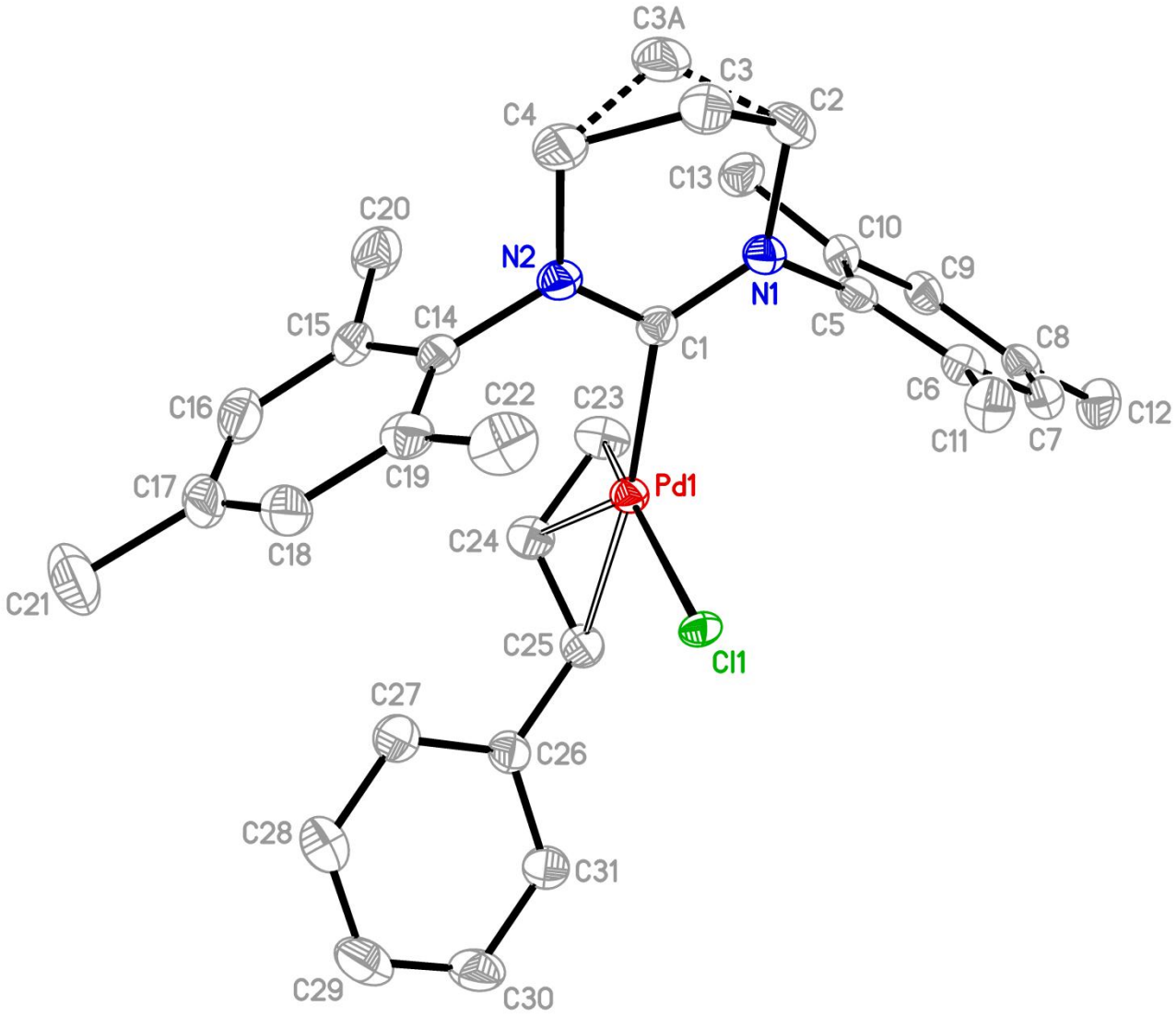
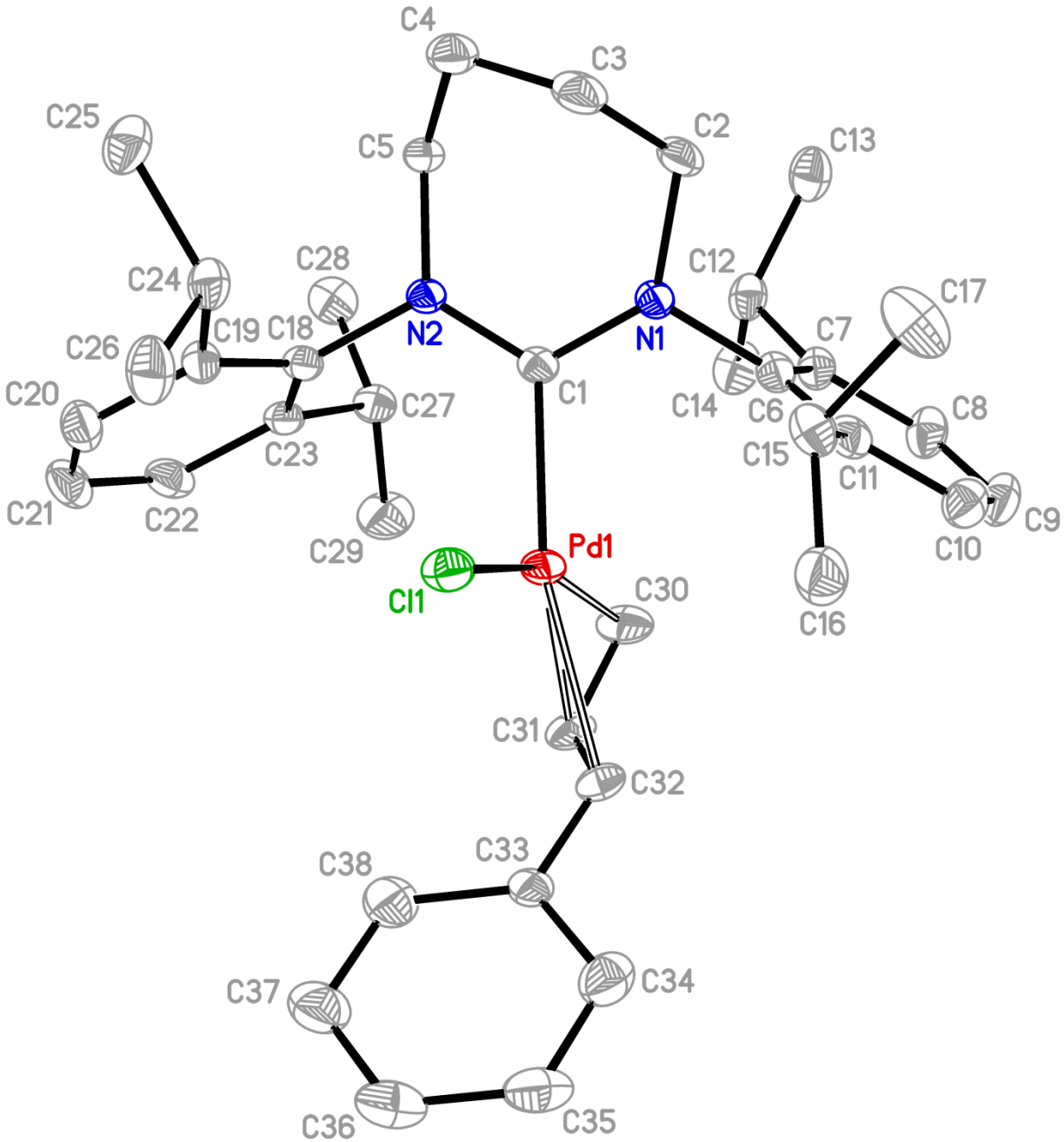


Fig. S3.

Molecular structure of the NHC complex (**7-Dipp**)Pd(cinn)Cl (all hydrogen atoms are omitted for clarity, the solvate hexane molecule is not shown, the double lines indicate the Pd-C_{Allyl} coordination bonds, the alternative position of the disordered allyl ligand is not presented).



References

1. M. Li and R. Hua, *Tetrahedron Lett.*, **2009**, *50*, 1478.
2. D. H. Huh, H. Ryu and Y. G. Kim, *Tetrahedron*, **2004**, *60*, 9857.
3. F.-A. Kang, Z. Sui and W. V. Murray, *J. Am. Chem. Soc.*, **2008**, *130*, 11300.
4. S. M. Spinella, Z.-H. Guan, J. Chen and X. Zhang, *Synthesis*, **2009**, *2009*, 3094.
5. H. Zhao, G. Zheng, W. Hao and M. Cai, *Appl. Organomet. Chem.*, **2010**, *24*, 92.
6. T. Hatakeyama, S. Hashimoto, K. Ishizuka and M. Nakamura, *J. Am. Chem. Soc.*, **2009**, *131*, 11949.
7. Á. Gordillo, E. de Jesús and C. López-Mardomingo, *Org. Lett.*, **2006**, *8*, 3517.
8. K. M. Dawood and M. M. El-Deftar, *ARKIVOC*, **2010**, *IX*, 319.
9. C. Liu and W. Yang, *Chem. Commun.*, **2009**, 6267.
10. J. Nakayama, T. Konishi, A. Ishii and M. Hoshino, *Bull. Chem. Soc. Jpn.*, **1989**, *62*, 2608.
11. A. Núñez, A. Sánchez, C. Burgos and J. Alvarez-Builla, *Tetrahedron*, **2004**, *60*, 6217.
12. J. Wen, S. Qin, L.-F. Ma, L. Dong, J. Zhang, S.-S. Liu, Y.-S. Duan, S.-Y. Chen, C.-W. Hu and X.-Q. Yu, *Org. Lett.*, **2010**, *12*, 2694.
13. K. L. Billingsley and S. L. Buchwald, *Angew. Chem., Int. Ed.*, **2008**, *47*, 4695.
14. Y. Zhang, J. Feng and C.-J. Li, *J. Am. Chem. Soc.*, **2008**, *130*, 2900.
15. B. Bhayana, B. P. Fors and S. L. Buchwald, *Organic Letters*, **2009**, *11*, 3954.
16. C. Gosmini, C. Bassene-Ernst and M. Durandetti, *Tetrahedron*, **2009**, *65*, 6141.