Alternating Ethylene-Norbornene Co-polymerization Catalyzed by Cationic Organopalladium Complexes Bearing Hemi-labile Bidentate Ligands of α-Amino-Pyridines

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Supplementary

Experimental Section

Synthesis and Characterization.

***N*-(pyridin-2-ylmethylene)-propan-2-amine** A 30 mL solution of dichloromethane that contained 2-pyridinecarboxaldehyde (2.40 mL, 25 mmol) and isopropylamine (2.20 mL, 25 mmol) was refluxed with the presence of catalytic amounts of sulfuric acid and 4Å activated molecular sieves for 24 h. The reaction mixture was first filtrated, and the solvent was removed in *vacuo*. The product was collected as a yellow liquid by distillation. (2.58 g, 70%). ^{1}**H NMR** (300 MHz, $CDCl_3$): δ 8.56 (d, J_{HH} = 5.0 Hz, 1H, Py H-6), 8.32 (s, 1H, C*H*=N), 7.91 (d, J_{HH} = 8.3 Hz, 1H, Py H-3), 7.64 (t, J_{HH} = 7.6 Hz, 1H, Py H-4) 7.22 (t, J_{HH} = 6.8 Hz, 1H, Py H-5), 3.56 (sept, J_{HH} = 6.1 Hz, 1H, NC*H*(CH_3)$_2$), 1.21 (d, J_{HH} = 5.9 Hz, 6H, NCH(CH_3)$_2$).

^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N) (L3a) To a solution of (pyridin-2-ylmethylene)-propan-2-amine (2.58 g, 17 mmol) in methanol (50 mL) was added excess $NaBH_4$ (1.00 g, 26 mmol). The reaction was stirred overnight at 25 ^{o}C, then quenched by water and extracted into dichloromethane. After solvent was removed under reduced pressure, the residue was distilled to give a yellow liquid product **L3a** in 74% yield (1.92 g). ^{1}**H NMR** (400 MHz, $CDCl_3$): δ 8.47 (d, $J_{H\text{-}H}$ = 4.0 Hz, 1H, Py H-2), 7.55 (dt, $J_{H\text{-}H}$ = 2.0, 7.5 Hz, 1H, Py H-4), 7.20 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-5), 7.07 (t, $J_{H\text{-}H}$ = 5.9 Hz, 1H, Py H-3), 3.82 (s, 2H, Py-CH_2N), 2.79 (sept, $J_{H\text{-}H}$ = 6.1 Hz, 1H, NHC*H*(CH_3)$_2$), 1.04 (d, $J_{H\text{-}H}$ = 6.5 Hz, 6H, NCH(CH_3)$_2$). ^{13}**C NMR** (100.625 MHz, $CDCl_3$): δ 159.98 (Py C-2), 149.28 (Py C-6), 136.42 (Py C-4), 122.40 (Py C-5), 121.87 (Py C-3), 52.96 (Py-*C*H$_2$N), 48.46 (N*C*H(CH_3)$_2$), 22.94 (NCH(*C*H$_3$)$_2$).

^{t}BuHNCH$_2$(*o*-C$_6$H$_5$N) (L4a) The synthesis was carried out according to the same procedure as for **L3a**, using 2-pyridinecarboxaldehyde (2.40 mL, 25 mmol) and *tert*-butylamine (2.65 mL, 25 mmol) to give the product of condensation, 2-methyl-*N*-(pyridin-2-ylmethylene)propan-2-amine (2.87 g, 71%). ^{1}**H NMR** (300 MHz, $CDCl_3$): δ 8.54 (d, $J_{H\text{-}H}$ = 3.7 Hz, 1H, Py H-6), 8.28 (s, 1H, C*H*=N), 7.94 (d, $J_{H\text{-}H}$ = 8.1 Hz, 1H, Py H-3), 7.63 (dt, $J_{H\text{-}H}$ = 1.4, 7.7 Hz, 1H, Py H-4), 7.20 (ddd, $J_{H\text{-}H}$ = 1.4, 5.3, 6.9 Hz, 1H, Py

H-5), 1.23 (s, 9H, NC(C*H*$_3$)$_3$).

The reductive reaction of 2-methyl-*N*-(pyridin-2-ylmethylene)propan-2-amine (2.87 g, 18 mmol) gave the product **L4a** in 75% yield (2.19 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.53 (d, J_{H-H} = 4.7 Hz, 1H, Py H-6), 7.62 (dt, J_{H-H} = 1.8, 7.6 Hz, 1H, Py H-4), 7.32 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.13 (ddd, J_{H-H} = 1.0, 4.9, 7.4 Hz, 1H, Py H-5), 3.88 (s, 2H, Py-C*H*$_2$N), 1.20 (s, 9H, NC(C*H*$_3$)$_3$). **^{13}C NMR** (100.625 MHz, $CDCl_3$): δ 160.30 (Py C-2), 149.10 (Py C-6), 136.50 (Py C-4), 122.52 (Py C-5), 121.80 (Py C-3), 50.66 (N*C*(CH$_3$)$_3$), 48.47 (Py-*C*H$_2$N), 29.02 (NC(*C*H$_3$)$_3$).

PhHNCH$_2$(*o*-C$_6$H$_5$N) (L5a) A solution of 2-pyridinecarboxaldehyde (4.80 mL, 50 mmol), aniline (4.60 mL, 50 mmol), catalytic amount of sulfuric acid and activated molecular sieves 4Å in toluene (30 mL) were combined in round-bottom flask. A condensation reaction was carry out by azeotropic removal of water using Dean-Stark apparatus for 24 hr. Then the reaction mixture was filtrated, and the solvent was removed in *vacuo*. The crude product was distilled to give a yellow liquid as the product of condensation, *N*-(pyridin-2-ylmethylene)aniline (6.37 g, 70%). **^{1}H NMR** (300 MHz,$CDCl_3$): δ 8.70 (d, J_{H-H} = 4.2 Hz, 1H, Py H-6), 8.59 (s, 1H, C*H*=N), 8.19 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.77 (dt, J_{H-H} = 1.6, 7.8 Hz, 1H, Py H-4), 7.23~7.42 (m, 1H, Py H-5; m, 5H, Ar).

The successive reduction of *N*-(pyridin-2-ylmethylene)aniline (6.37 g, 35 mmol) gave a yellow liquid product **L5a** in 63% yield (5.76 g). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.60 (dd, J_{H-H} = 0.8, 4.9 Hz, 1H, Py H-6), 7.64 (dt, J_{H-H} = 1.7, 7.7 Hz, 1H, Py H-4), 7.35 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.17~7.22 (m, 1H, Py H-5; 2H, m-Ar), 6.75 (dt, J_{H-H} = 0.5, 7.4 Hz, 1H, p-Ar), 6.69 (d, J_{H-H} = 8.3 Hz, 2H, o-Ar), 4.48 (s, 2H, Py-C*H*$_2$N). **^{13}C NMR** (100.625 MHz, $CDCl_3$): δ 158.57 (Py C-2), 149.20 (Py C-6), 147.93 (ipso-Ar), 136.69 (Py C-4), 129.28 (o-Ar), 122.13 (Py C-5), 121.62 (Py C-3), 117.61 (p-Ar), 113.08 (m-Ar), 49.30 (Py-*C*H$_2$N).

(2,6-Me$_2$C$_6$H$_3$)HNCH$_2$(*o*-C$_6$H$_5$N) (L6a) The synthesis was carried out according to the same procedure as for **L5a**, using 2-pyridinecarboxaldehyde (2.40 mL, 25 mmol) and 2,6-dimethyllaniline (3.10 mL, 25 mmol) to give the product of condensation, 2,6-dimethyl-*N*-(pyridin-2-ylmethylene)aniline (3.58 g, 68%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.70 (d, $J_{H\text{-}H}$ = 5.0 Hz, 1H, Py H-6), 8.33 (s, 1H, C*H*=N), 8.23 (d, $J_{H\text{-}H}$ = 7.6 Hz, 1H, Py H-3), 7.83 (dt, $J_{H\text{-}H}$ = 1.5, 7.7 Hz, 1H, Py H-4), 7.38 (ddd, $J_{H\text{-}H}$ = 1.2, 4.9, 8.0 Hz, 1H, Py H-5), 6.90~7.15 (m, 5H, Ar), 2.17 (s, 6H, Ar-CH_3).

The reductive reaction of 2,6-dimethyl-*N*-(pyridin-2-ylmethylene)aniline (3.58 g, 17 mmol) gave the product **L6a** in 81% yield (4.24 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (ddd, $J_{H\text{-}H}$ = 0.9, 1.6, 4.8 Hz, 1H, Py H-6), 7.65 (dt, $J_{H\text{-}H}$ = 1.8, 7.6 Hz, 1H, Py H-4), 7.27 (d, $J_{H\text{-}H}$ = 7.7 Hz, 1H, Py H-3), 7.20 (ddd, $J_{H\text{-}H}$ = 0.5, 5.0, 7.4 Hz, 1H, Py H-5), 7.02 (d, $J_{H\text{-}H}$ = 7.3 Hz, 2H, m-Ar), 6.85 (t, $J_{H\text{-}H}$ = 7.5 Hz, 1H, p-Ar), 4.31 (s, 2H, Py-CH_2N), 2.35 (s, 6H, Ar-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 159.12 (Py C-2), 149.24 (Py C-6), 146.12 (ipso-Ar), 136.50 (Py C-4), 129.53 (o-Ar), 128.83 (m-Ar), 122.14 (Py C-5), 122.03 (Py C-3), 121.91 (p-Ar), 53.66 (Py-*C*H_2N), 18.69 (Ar-*C*H_3).

(2,6-^{i}Pr$_2$C$_6$H$_3$)HNCH$_2$(*o*-C$_6$H$_5$N) (L7a) The synthesis was carried out according to the same procedure as for **L5a**, using 2-pyridinecarboxaldehyde (2.40 mL, 25 mmol) and 2,6-diisopropylaniline (4.70 mL, 25 mmol) to give the product of condensation, 2,6-diisopropyl-N-(pyridin-2-ylmethylene)aniline (3.83 g, 58%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.75 (d, $J_{H\text{-}H}$ = 4.9 Hz, 1H, Py H-6), 8.35 (s, 1H, C*H*=N), 8.30 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.86 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, Py H-4), 7.43 (dd, $J_{H\text{-}H}$= 4.9, 7.4Hz, 1H, Py H-5), 7.12~7.22 (m, 2H, m-Ar; 1H, p-Ar), 3.00 (sept, $J_{H\text{-}H}$= 6.8Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.20 (d, $J_{H\text{-}H}$ = 6.9 Hz, 12H, Ar-CH(CH_3)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 162.99 (*C*H=N), 154.36 (Py C-2), 149.71 (Py-C-6), 148.40 (o-Ar), 137.27 (ipso-Ar), 136.82 (Py C-4), 123.10 (m-Ar), 125.38, 124.52, 121.38 (p-Ar, Py C-5 and Py C-3), 27.98, 27.95 (Ar-*C*H(CH_3)$_2$), 23.49 (Ar-CH(*C*H_3)$_2$).

The reductive reaction of 2,6-diisopropyl-N-(pyridin-2-ylmethylene)aniline (3.83 g, 14 mmol) gave the product **L7a** in 76% yield (2.95 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (d, $J_{H\text{-}H}$ = 4.9 Hz, 1H, Py H-6), 7.67 (dt, $J_{H\text{-}H}$ = 1.7, 7.7 Hz, 1H, Py H-4), 7.33 (d, $J_{H\text{-}H}$ = 7.8 Hz, 1H, Py H-3), 7.21 (dd, $J_{H\text{-}H}$ = 5.2, 7.2 Hz, 1H, Py H-5), 7.05~7.17 (m, 2H, m-Ar; 1H, p-Ar), 4.21 (s, 2H, Py-C*H_2*N), 3.38 (sept, $J_{H\text{-}H}$ = 6.8 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.26 (d, $J_{H\text{-}H}$ = 6.7 Hz, 12H, Ar-CH(C*H_3*)$_2$). ^{13}C NMR (100.625, $CDCl_3$): δ 159.03 (Py C-2), 149.34 (Py C-6), 143.07 (ipso-Ar), 142.72 (o-Ar), 136.50 (Py C-4), 123.91 (p-Ar), 123.59 (m-Ar), 122.16 (Py C-5), 122.04 (Py C-3), 56.81 (Py-*C*H_2N), 27.71 (Ar-*C*H(CH_3)$_2$), 24.28 (Ar-CH(*C*H_3)$_2$).

^{i}PrHNCMeH(*o*-C_6H_5N) (L3b) The synthesis was carried out according to the same procedure as for **L3a**, using 2-acetylpyridine (2.80 mL, 25 mmol) and isopropylamine (2.14 mL, 25 mmol) to give the product of condensation, *N*-(1-(pyridin-2-yl)ethylidene)propan-2-amine (3.56 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (ddd, $J_{H\text{-}H}$ = 1.0, 1.8, 4.8 Hz, 1H, Py H-6), 8.06 (dt, $J_{H\text{-}H}$ = 1.1, 8.0 Hz, 1H, Py H-3), 7.68 (dt, $J_{H\text{-}H}$ = 1.8, 7.7 Hz, 1H, Py H-4), 7.25 (ddd, $J_{H\text{-}H}$ = 1.3, 4.9, 7.4 Hz, 1H, Py H-5), 3.91 (sept, $J_{H\text{-}H}$ = 6.3 Hz, 1H, NC*H*(CH_3)$_2$), 2.36 (s, 3H, Py-C(C*H_3*)N), 1.23 (d, $J_{H\text{-}H}$ = 6.2 Hz, 6H, NCH(C*H_3*)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 163.62 (Py-*C*(CH_3)N), 158.41 (Py C-2), 148.16 (Py C-6), 136.30 (Py C-4), 123.84 (Py C-5), 121.09 (Py C-3), 51.56 (N*C*H(CH_3)$_2$), 23.42 (NCH(*C*H_3)$_2$), 13.63 (Py-C(*C*H_3)N).

The reductive reaction of *N*-(1-(pyridin-2-yl)ethylidene)propan-2-amine (3.56 g, 22 mmol) gave the product **L3b** in 73% yield (2.62 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (ddd, $J_{H\text{-}H}$ = 0.9, 1.7, 4.8 Hz, 1H, Py H-6), 7.61 (dt, $J_{H\text{-}H}$ = 1.8, 7.6 Hz, 1H, Py H-4), 7.26 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Py H-3), 7.12 (ddd, $J_{H\text{-}H}$ = 1.2, 4.8, 7.5 Hz, 1H, Py H-5), 3.96 (q, $J_{H\text{-}H}$ = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 2.59 (sept, $J_{H\text{-}H}$= 6.2 Hz, 1H, NC*H*(CH_3)$_2$), 1.35 (d, $J_{H\text{-}H}$ = 4.7 Hz, 3H, Py-CH(C*H_3*)N), 1.04, 0.98 (d, $J_{H\text{-}H}$ = 6.2, 6.3 Hz, 6H, NCH(C*H_3*)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 165.01 (Py C-2), 149.29 (Py C-6), 136.33 (Py C-4), 121.72 (Py C-5), 121.28 (Py C-3), 56.19 (Py-*C*H(CH_3)N), 45.70 (N*C*H(CH_3)$_2$), 23.24 (Py-CH(*C*H_3)N), 23.81, 22.25 (NCH(CH_3)$_2$).

^{t}BuHNCMeH(*o*-C_6H_5N) (L4b) The synthesis was carried out according to the same procedure as for **L3a**, using 2-acetylpyridine (5.60 mL, 50 mmol), *tert*-butylamine (5.30 mL, 50 mmol) to give the product **L4b** in 28% yield (2.5 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (d, $J_{H\text{-}H}$ = 4.0 Hz, 1H, Py H-6), 7.60 (dt, $J_{H\text{-}H}$ = 1.6, 7.5 Hz, 1H, Py H-4), 7.43 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.08 (dd, $J_{H\text{-}H}$ = 5.0, 7.2 Hz, 1H, Py H-5), 4.04 (q, $J_{H\text{-}H}$ = 6.8 Hz, 1H, Py-C*H*(CH_3)N), 1.33 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(C*H$_3$*)N), 1.00 (s, 9H, NC(C*H$_3$*)$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 167.69 (Py C-2), 148.67 (Py C-6), 136.30 (Py C-4), 121.36 (Py C-5), 121.03 (Py C-3), 53.75 (Py-*C*H(CH_3)N), 51.21 (N*C*(CH_3)$_3$), 29.92 (NC(*C*H$_3$)$_3$), 26.00 (Py-CH(*C*H$_3$)N).

PhHNCMeH(*o*-C_6H_5N) (L5b) The synthesis was carried out according to the same procedure as for **L5a**, using 2-acetylpyridine (11.00 mL, 98 mmol) and aniline (9.00 mL, 100 mmol) to give the product of condensation, *N*-(1-(pyridin-2-yl)ethylidene)aniline (11.65 g, 60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.66 (d, $J_{H\text{-}H}$ = 5.0 Hz, 1H, Py H-6), 8.24 (d, $J_{H\text{-}H}$ = 7.8 Hz, 1H, Py H-3), 7.77 (dt, $J_{H\text{-}H}$ = 1.3, 8.0 Hz, 1H, Py H-4), 7.33 (m, 1H, Py H-5), 7.10 (m, 2H, m-Ar), 6.82 (d, $J_{H\text{-}H}$ = 7.5 Hz, 2H, o-Ar), 6.66 (d, $J_{H\text{-}H}$ = 7.5 Hz, 1H, p-Ar), 2.33 (s, 3H, C(C*H$_3$*)=N).

The reductive reaction of *N*-(1-(pyridin-2-yl)ethylidene)aniline (11.65 g, 59 mmol) gave the product **L5b** in 85% yield (9.92 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (td, $J_{H\text{-}H}$ = 0.8, 4.8 Hz, 1H, Py H-6), 7.61 (dt, $J_{H\text{-}H}$ = 1.8, 7.7 Hz, 1H, Py H-4), 7.36 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.00~7.20 (m, 1H, Py H-5; 2H, m-Ar), 6.68 (dt, $J_{H\text{-}H}$ = 0.6, 7.3 Hz, 1H, p-Ar), 6.59 (dd, $J_{H\text{-}H}$ = 0.6, 7.7 Hz, 1H, o-Ar), 4.65 (q, $J_{H\text{-}H}$ = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 4.49 (bs, 1H, N*H*-Ar), 1.57 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(C*H$_3$*)N). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 163.92 (Py C-2), 149.31 (Py C-6), 147.14 (ipso-Ar), 136.83 (Py C-4), 129.18 (m-Ar), 121.98, 120.33, 117.41 (p-Ar, Py C-5 and Py C-3), 113.44 (o-Ar), 54.75 (Py-*C*H(CH_3)N), 23.21 (Py-CH(*C*H$_3$)N).

(2,6-$Me_2C_6H_3$)HNCMeH(*o*-C_6H_5N) (L6b) The synthesis was carried out according to the same procedure as for **L5a**, using 2-acetylpyridine (2.80 mL, 25 mmol) and 2,6-dimethylaniline (3.10 mL, 25 mmol) to give the product of condensation, 2,6-dimethyl-*N*-(1-(pyridin-2-yl)ethylidene)aniline (3.27 g, 58%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.65 (d, $J_{H\text{-}H}$ = 4.0 Hz, 1H, Py H-6), 8.35 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Py H-3), 7.79 (dt, $J_{H\text{-}H}$ = 1.9, 7.8 Hz, 1H, Py H-4), 7.36 (ddd, $J_{H\text{-}H}$ = 1.2, 4.9, 7.2 Hz, 1H, Py H-5), 7.04 (d, $J_{H\text{-}H}$ = 7.2 Hz, 2H, m-Ar), 6.92 (t, $J_{H\text{-}H}$ = 6.4 Hz, 1H, p-Ar), 2.17 (s, 3H, C(CH_3)=N), 2.02 (s, 6H, Ar-CH_3).

The reductive reaction of 2,6-dimethyl-*N*-(1-(pyridin-2-yl)ethylidene)aniline (13.27 g, 15 mmol) gave the product **L6b** in 47% yield (1.59 g). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.62 (ddd, $J_{H\text{-}H}$ = 0.9, 1.7, 4.8 Hz, 1H, Py H-6), 7.56 (dt, $J_{H\text{-}H}$ = 1.8, 7.6 Hz, 1H, Py H-4), 7.16 (ddd, $J_{H\text{-}H}$ = 1.2, 4.8, 7.5 Hz, 1H, Py H-5), 7.10 (dt, $J_{H\text{-}H}$ = 1.0, 7.7 Hz, 1H, Py H-3), 6.95 (d, $J_{H\text{-}H}$ = 7.4 Hz, 2H, m-Ar), 6.78 (t, $J_{H\text{-}H}$ = 7.4 Hz, 1H, p-Ar), 4.43 (q, $J_{H\text{-}H}$ = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 2.25 (s, 6H, Ar-CH_3), 1.49 (d, $J_{H\text{-}H}$ = 6.7 Hz, 3H, Py-CH(CH_3)N). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 163.66 (Py C-2), 149.43 (Py C-6), 144.94 (ipso-Ar), 136.39 (Py C-4), 129.28 (o-Ar), 128.76 (m-Ar), 122.09, 121.46, 121.37 (p-Ar, Py C-5 and Py C-3), 57.92 (Py-*C*H(CH_3)N), 22.58 (Py-CH(*C*H_3)N), 18.97 (Ar-*C*H_3).

(2,6-$^iPr_2C_6H_3$)HNCMeH(*o*-C_6H_5N) (L7b) The synthesis was carried out according to the same procedure as for **L5a**, using 2-acetylpyridine (2.80 mL, 25 mmol) and 2,6-diisopropyllaniline (4.70 mL, 25 mmol) to give the product of condensation, 2,6-diisopropyl-N-(1-(pyridin-2-yl)ethylidene)aniline (1.05 g, 15%). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.70 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-6), 8.38 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Py H-3), 7.83 (dt, $J_{H\text{-}H}$ = 1.7, 7.6 Hz, 1H, Py H-4), 7.40 (ddd, $J_{H\text{-}H}$ = 1.1, 4.9, 7.4 Hz, 1H, Py H-5), 7.00~7.20 (m, 2H, m-Ar; 1H, p-Ar), 2.76 (sept, $J_{H\text{-}H}$ = 6.9 Hz, 2H, Ar-C*H*(CH_3)$_2$), 2.23 (s, 3H, Py-C(CH_3)N), 1.16 (d, 12H, $J_{H\text{-}H}$ = 6.9 Hz, Ar-CH(CH_3)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 166.99 (Py-*C*(CH_3)N), 156.47 (Py C-2), 1498.59 (Py C-6), 146.40 (o-Ar), 136.51 (Py C-4), 135.81 (ipso-Ar), 123.00 (m-Ar), 124.81, 123.60, 121.34 (p-Ar, Py C-5 and Py C-3), 28.26 (Ar-*C*H(CH_3)$_2$), 22.91, 23.23

(Ar-CH(CH_3)$_2$), 17.34 (Py-C(CH_3)N).

The reductive reaction of 2,6-diisopropyl-N-(1-(pyridin-2-yl)ethylidene)aniline (1.05 g, 3.75 mmol) gave the product **L7b** in 29% yield (0.30 g). ^{1}H NMR (200 MHz, $CDCl_3$): δ 8.62 (d, J_{H-H} = 4.9 Hz, 1H, Py H-6), 7.53 (dt, J_{H-H} = 1.7, 7.5 Hz, 1H, Py H-4), 7.40 (ddd, J_{H-H} = 1.1, 4.9, 7.4 Hz, 1H, Py H-5), 7.00~7.20 (m, 1H, Py H-3; 2H, m-Ar; 1H, p-Ar), 4.17 (q, 1H, J_{H-H} = 6.7 Hz, Py-C*H*(CH_3)N), 3.21 (sept, J_{H-H} = 6.9 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.50 (d, 3H, J_{H-H} = 6.6 Hz, Py-CH(CH_3)N), 1.21, 1.04 (d, 12H, J_{H-H} = 6.7, 6.8 Hz, Ar-CH(CH_3)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$): δ 163.24 (Py C-2), 149.56 (Py C-6), 142.13 (o-Ar), 141.62 (ipso-Ar), 136.25 (Py C-4), 123.42 (m-Ar), 123.13, 122.09, 121.84 (p-Ar, Py C-5 and Py C-3), 60.94 (Py-*C*H(CH_3)N), 27.60 (Ar-*C*H(CH_3)$_2$), 24.23, 24.17 (Ar-CH(CH_3)$_2$), 21.72 (Py-CH(CH_3)N).

[^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (3a) To a solution of (COD)PdMeCl (50 mg, 0.19 mmol) in Et_2O (15 mL) was added **L3a** (28 mg, 0.19 mmol) which was dissolved in Et_2O (5 mL). The mixture was stirred for 1h at room temperature. After filtration, the resulting precipitate was washed twice with Et_2O (2×5 mL) and dried in *vacuo*. The desired air-stable complex was obtained as pale yellow powder in 96% yield (59 mg). Single crystals suitable for X-ray diffraction were grown by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution of **3a**.. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-3a**: δ 8.34 (d, J_{H-H} = 5.4 Hz, 1H, Py H-6), 7.82 (dt, J_{H-H} = 1.4, 7.7 Hz, 1H, Py H-4), 7.39 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.25~7.35 (m, 1H, Py H-5), 4.49 (dd, J_{H-H} = 6.6, 16.2 Hz, 1H, Py-C*H*'HN), 3.93 (dd, J_{H-H} = 3.1, 16.1 Hz, 1H, Py-CH'*H*N), 3.24 (bs, 1H, N*H*CH(CH_3)$_2$), 3.18 (sept, J_{H-H} = 6.9 Hz, 1H, NHC*H*(CH_3)$_2$), 0.79 (s, 3H, Pd-CH_3); ***cis*-3a**: δ 8.72 (d, J_{H-H} = 4.7 Hz, 1H, Py H-6), 7.71 (dt, J_{H-H} = 1.6, 7.7 Hz, 1H, Py H-4), 7.25~7.35 (m, 1H, Py H-3), 7.20 (t, J_{H-H} = 6.5 Hz, 1H, Py H-5), 4.75 (dd, J_{H-H} = 6.5, 16.0 Hz, 1H, Py-C*H*'HN), 4.56 (bs, 1H, N*H*CH(CH_3)$_2$), 4.05 (dd, J_{H-H} = 3.1, 16.1 Hz, 1H, Py-CH'*H*N), 3.20 (sept, J_{H-H} = 6.3 Hz, 1H, NHC*H*(CH_3)$_2$), 0.54 (s, 3H, Pd-CH_3); 1.27, 1.21, 1.25 (d, d, m, J_{H-H}= 6.2, 6.4 Hz, 12H, NHCH(CH_3)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-3a**: δ 163.99 (Py C-2), 148.08 (Py C-6), 137.96 (Py C-4), 123.78 (Py C-5), 122.37 (Py C-3), 52.43 (Py-CH_2N), 51.34 (NH*C*H(CH_3)$_2$), 22.34, 21.47 (NHCH(CH_3)$_2$), -0.09 (Pd-CH_3); ***cis*-3a**: δ 159.12 (Py C-2), 148.13 (Py C-6), 138.12 (Py C-4), 123.27 (Py C-5), 120.61 (Py C-3), 54.49 (Py-CH_2N), 53.47 (NH*C*H(CH_3)$_2$), 22.00, 21.37 (NHCH(CH_3)$_2$), -8.87 (Pd-CH_3). MS (FAB, m/z): 255.0 (M^{+1} - CH_3- Cl). Anal. Calcd for $C_{10}H_{17}N_2PdCl$: C, 39.10; H, 5.54; N, 9.12. Found: C, 38.52; H, 5.47; N, 9.29.

[$^tBuHNCH_2$(*o*-C_6H_5N)]Pd(Me)Cl (4a) The synthesis was carried out according to the same procedure as for 3a, using (COD)PdMeCl (265 mg, 1.00 mmol) and **L4a** (321 mg, 1.00 mmol) to give the pale white product **4a** (278 mg, 85%). Single crystals were grown from Et_2O/CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) for ***trans*-4a**: δ 8.37 (d, J_{H-H} = 5.5 Hz, 1H, Py H-6), 7.81 (t, J_{H-H} = 7.7 Hz, 1H, Py H-4), 7.39 (d, J_{H-H} = 7.7 Hz, 1H, Py H-3), 7.25~7.35 (m, 1H, Py H-5), 4.50 (dd, J_{H-H} = 7.0, 16.3 Hz, 1H, Py-C*H'*HN), 4.05 (d, J_{H-H} = 16.3 Hz, 1H, Py-CH'*H*N), 2.97 (d, J_{H-H} = 6.6 Hz, 1H, N*H*C(CH_3)$_3$), 1.18 (s, 9H, NHC(CH_3)$_3$), 0.89 (s, 3H, Pd-CH_3); ***cis*-4a**: δ 8.79 (d, J_{H-H} = 4.9 Hz, 1H, Py H-6), 7.73 (t, J_{H-H} = 7.7 Hz, 1H, Py H-4), 7.25~7.35 (m, 1H, Py H-3; 1H, Py H-5), 4.82 (dd, J_{H-H}= 6.4, 16.4 Hz, 1H, Py-C*H'*HN), 4.23 (d, J_{H-H} = 16.3 Hz, 1H, Py-CH'*H*N), 4.05 (1H, N*H*C(CH_3)$_3$), 1.21 (s, 9H, NHC(CH_3)$_3$), 0.67 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-4a**: δ 164.69 (Py C-2), 148.18 (Py C-6), 138.07 (Py C-4), 123.81 (Py C-5), 122.05 (Py C-3), 55.73 (NH*C*(CH_3)$_3$), 50.97 (Py-CH_2N), 29.24 (NHC(CH_3)$_3$), 0.59 (Pd-CH_3); ***cis*-4a**: δ 159.18 (Py C-2), 148.40 (Py C-6), 138.12 (Py C-4), 123.51 (Py C-5), 120.36 (Py C-3), 58.75 (NH*C*(CH_3)$_3$), 54.30 (Py-CH_2N), 29.44 (NHC(CH_3)$_3$), -10.16 (Pd-CH_3). MS (FAB, m/z): 269.0 (M^{+1} - CH_3- Cl). Anal. Calcd for $C_{11}H_{19}N_2PdCl$: C, 41.14; H, 5.92; N, 8.73. Found: C, 40.55; H, 5.72; N, 8.62.

[$PhHNCH_2$(*o*-C_6H_5N)]Pd(Me)Cl (5a) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (93 mg, 0.35 mmol) and **L5a** (64 mg, 0.35 mmol) to give the pale brown product **5a** (106 mg, 89%). Single crystals were grown from Et_2O/CH_2Cl_2. ^1H NMR (400 MHz, $CDCl_3$) for ***trans*-5a**: δ 8.34 (d, J_{H-H} = 5.6 Hz, 1H, Py H-6), 7.92 (dt, J_{H-H} = 1.5, 7.7 Hz, 1H, Py H-

4), 7.56 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.37 (t, J_{H-H} = 6.7 Hz, 1H, Py H-5), 7.10~7.21 (m, 2H, m-Ar), 7.02 (t, J_{H-H} = 7.4 Hz, 1H, p-Ar), 6.97 (d, J_{H-H} = 7.6 Hz, 2H, o-Ar), 5.87 (bs, 1H, N*H*-Ar), 0.86 (s, 3H, Pd-C*H₃*); ***cis*-5a**: δ 8.73 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.73 (dt, J_{H-H} = 1.6, 7.7 Hz, 1H, Py H-4), 7.37 (1H, Py H-3), 7.21~7.32 (m, 2H, m-Ar; 2H, o-Ar), 7.10~7.21 (m, 1H, Py H-5; 1H, p-Ar), 5.02 (dd, J_{H-H} = 6.2, 16.3 Hz, 1H, Py-C*H'*HN), 4.49 (dd, J_{H-H} = 6.7, 16.4 Hz, 1H, Py-CH'*H*N), 0.24 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-5a**: δ 163.82 (Py C-2), 148.38 (Py C-6), 146.05 (ipso-Ar), 138.46 (Py C-4), 129.19 (m-Ar), 124.07 (Py C-5), 123.89 (p-Ar), 122.38 (Py C-3), 118.61 (o-Ar), 55.50 (Py-CH_2N), -0.17 (Pd-CH_3); ***cis*-5a**: δ 158.39 (Py C-2), 147.93 (Py C-6), 147.20 (ipso-Ar), 137.83 (Py C-4), 129.19 (m-Ar), 125.79, 123.50 (Py C-5 and p-Ar), 121.85 (o-Ar), 121.59 (Py C-3), 62.86 (Py-CH_2N), -2.94 (Pd-CH_3). MS (FAB, m/z): 289.1 (M^{+1} - CH_3 - Cl). Anal. Calcd for $C_{13}H_{15}N_2PdCl$: C, 45.90; H, 4.41; N, 8.24. Found: C, 46.20; H, 4.50; N, 8.21.

[(2,6-$Me_2C_6H_3$)HNCH_2(*o*-C_6H_5N)]Pd(Me)Cl (6a) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (283 mg, 1.07 mmol) and **L6a** (227 mg, 1.07 mmol) to give the pale white product **6a** (343 mg, 87%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***cis*-6a**: δ 8.72 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.70 (dt, J_{H-H} = 1.7, 7.8 Hz, 1H, Py H-4), 7.22 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), 7.00~7.16 (m, 1H, Py H-5; 2H, m-Ar; 1H, p-Ar), 6.68 (t, J_{H-H} = 7.5 Hz, 1H, N*H*-Ar), 5.07 (dd, J_{H-H} = 7.6, 17.3 Hz, 1H, Py-C*H'*HN), 4.29 (dd, J_{H-H} = 7.3, 17.3 Hz, 1H, Py-CH'*H*N), 2.91, 2.51 (s, 6H, Ar-CH_3), 0.10 (s, 3H, Pd-CH_3); **trans-6a**: δ 8.49 (d, J_{H-H} = 6.4 Hz, 1H, Py H-6), 7.88 (dt, J_{H-H} = 1.4, 7.8 Hz, 1H, Py H-4), 7.40 (t, J_{H-H} = 7.0 Hz, 1H, Py H-5), 7.34 (d, J_{H-H} = 7.3 Hz, 1H, Py H-3), 7.00~7.16 (2H, m-Ar; 1H, p-Ar), 1.00 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***cis*-6a**: δ 158.37 (Py C-2), 147.80 (Py C-6), 143.21 (ipso-Ar), 137.58 (Py C-4), 130.82, 129.57 (o-Ar), 131.07, 123.29 (Py C-5 and p-Ar), 128.48, 125.97 (m-Ar), 120.16 (Py C-3), 59.87 (Py-CH_2N), 20.22, 18.96 (Ar-CH_3), -6.03 (Pd-CH_3); ***trans-6a***: δ 147.96 (Py C-6), 138.10 (Py C-4), 125.30, 124.04, 122.13 (Py C-5, Py C-3 and p-Ar), 62.97 (Py-CH_2N), 0.15 (Pd-CH_3). MS (FAB, m/z): 317.0 (M^{+1} - CH_3 - Cl).

[(2,6-$^iPr_2C_6H_3$)HNCH$_2$(*o*-C_6H_5N)]Pd(Me)Cl (7a) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (50 mg, 0.19 mmol) and **L7a** (51 mg, 0.19 mmol) to give the pale yellow product **7a** (59 mg, 73%). ^{1}H NMR (400 MHz, $CDCl_3$) for ***cis*-7a**: δ 8.72 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.70 (dt, J_{H-H} = 1.6, 7.8 Hz, 1H, Py H-4), 7.00~7.24 (m, 1H, Py H-3; 1H, Py H-5; 2H, m-Ar; 1H, p-Ar), 6.88 (t, J_{H-H} = 7.3 Hz, 1H, N*H*-Ar), 5.07 (dd, J_{H-H} = 7.6, 17.3 Hz, 1H, Py-C*H'*HN), 4.58, 3.46 (sept, J_{H-H} = 6.7, 6.6 Hz, 2H, Ar-C*H*(CH_3)$_2$), 4.30 (dd, J_{H-H} = 7.3, 17.3 Hz, 1H, Py-CH'*H*N), 1.43, 1.34, 1.33, 1.12 (d, J_{H-H} = 6.6, 6.4, 6.6, 6.9 Hz, 12H, Ar-CH(C*H$_3$*)$_2$), 0.12 (s, 3H, Pd-C*H$_3$*); ***trans*-7a**: δ 8.51 (d, J_{H-H} = 5.6 Hz, 1H, Py H-6), 7.89 (t, J_{H-H} = 7.8 Hz, 1H, Py H-4), 7.41 (t, J_{H-H} = 7.1 Hz, 1H, Py H-5), 7.34 (d, J_{H-H} = 8.0 Hz, 1H, Py H-3), 7.00~7.24 (m, 2H, m-Ar; 1H, p-Ar), 5.19 (bs, 1H, N*H*-Ar), 5.31, 4.24 (2H, Py-C*H'H*N), 4.78, 3.61 (sept, J_{H-H} = 6.7, 6.6 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.71, 1.29 (d, J_{H-H}= 6.6, 6.8 Hz, 6H, Ar-CH(C*H$_3$*)$_2$), 1.20~1.40 (6H, Ar-CH(C*H$_3$*)$_2$), 1.02 (s, 3H, Pd-C*H$_3$*). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***cis*-7a**: δ 157.94 (Py C-2), 148.23 (Py C-6), 142.02 (ipso-Ar), 140.39, 140.07 (o-Ar), 137.50 (Py C-4), 126.82, 126.45, 123.42, 123.21, 120.17 (Py C-5, Py C-3, p-Ar and m-Ar), 62.38 (Py-*C*H$_2$N), 28.28, 27.82 (Ar-*C*(CH_3)$_2$), 25.11, 24.62, 24.10, 23.57 (Ar-C(*C*H$_3$)$_2$), -4.12 (Pd-*C*H$_3$); ***trans*-7a**: δ 167.33 (Py C-2), 149.97 (Py C-6), 139.96, 138.83, 138.75, 138.06 (ipso-Ar, o-Ar and Py C-4), 129.07, 127.95, 124.25, 123.58, 122.21 (Py C-5, Py C-3, p-Ar and m-Ar), 58.54 (Py-*C*H$_2$N), 28.54, 27.90 (Ar-*C*(CH_3)$_2$), 24.79, 22.61 (Ar-C(*C*H$_3$)$_2$), 0.95 (Pd-*C*H$_3$). MS (FAB, m/z): 373.1 (M^{+1} - CH_3 - Cl). Anal. Calcd for $C_{19}H_{27}N_2PdCl$: C, 53.66; H, 6.35; N, 6.59. Found: C, 53.99; H, 6.43; N, 6.44.

[^{i}PrHNCMeH(*o*-C_6H_5N)]Pd(Me)Cl (3b) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (200 mg, 0.75 mmol) and **L3b** (124 mg, 0.75 mmol) to give the pale white product **3b** (214 mg, 89%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-3b**: δ 8.41 (d, J_{H-H} = 5.2 Hz, 1H, Py H-6), 7.84 (dt, J_{H-H} = 1.6, 7.7 Hz, 1H, Py H-4), 7.20~7.40 (1H, Py H-3; 1H, Py H-5), 4.14 (q, J_{H-H} = 6.8 Hz, 1H, Py-C*H*(CH_3)N), 3.05 (sept,

J_{H-H} = 6.6 Hz, 1H, NHC*H*(CH_3)$_2$), 1.89 (d, J_{H-H} = 6.8 Hz, 3H, Py-CH(C*H*$_3$)N), 1.20~1.30 (m, 6H, NHCH(C*H*$_3$)$_2$), 0.90 (s, 3H, Pd-C*H*$_3$); ***cis*-3b**: δ 8.84 (d, J_{H-H} = 5.2 Hz, 1H, Py H-6), 7.77 (dt, J_{H-H} = 1.5, 7.7 Hz, 1H, Py H-4), 7.20~7.40 (m, 1H, Py H-3; 1H, Py H-5), 4.24 (q, J_{H-H} = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 3.09 (sept, J_{H-H} = 6.5 Hz, 1H, NHC*H*(CH_3)$_2$), 1.89 (d, J_{H-H} = 6.8 Hz, 3H, Py-CH(C*H*$_3$)N), 1.20~1.30 (m, 6H, NHCH(C*H*$_3$)$_2$), 0.59 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-3b**: δ 168.41 (Py C-2), 138.42 (Py C-4), 60.00 (Py-*C*H(CH_3)N), 52.26 (NH*C*H(CH_3)$_2$), 0.17 (Pd-*C*H_3); ***cis*-3b**: δ 162.65 (Py C-2), 138.42 (Py C-4), 62.77 (Py-*C*H(CH_3)N), 55.22 (NH*C*H(CH_3)$_2$), -11.21 (Pd-*C*H_3); 148.71, 148.30 (Py C-6) 123.94, 123.70, 121.99, 120.38 (Py C-5 and Py C-3), 25.04, 24.51 (Py-CH(*C*H_3)N), 23.33, 22.97, 22.43, 22.28 (NHCH(*C*H_3)$_2$). MS (FAB, m/z): 269.0 (M^{+1} - CH_3 - Cl). Anal. Calcd for $C_{11}H_{19}N_2PdCl$: C, 41.18; H, 5.92; N, 8.73. Found: C, 40.89; H, 5.92; N, 8.53.

[^{t}BuHNCMeH(*o*-C_6H_5N)]Pd(Me)Cl (4b) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (150 mg, 0.57 mmol) and **L4b** (101 mg, 0.57 mmol) to give the pale white product **4b** (167 mg, 87%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-4b**: δ 8.38 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.83 (dt, J_{H-H} = 1.4, 7.7 Hz, 1H, Py H-4), 7.35 (d, J_{H-H} = 7.7 Hz, 1H, Py H-3), 7.25~7.35 (m, 1H, Py H-5), 4.30 (q, J_{H-H} = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 2.20 (s, 1H, N*H*C(CH_3)$_3$), 1.96 (d, J_{H-H} = 6.8 Hz, 3H, Py-CH(C*H*$_3$)N), 1.19 (s, 9H, NHC(C*H*$_3$)$_3$), 0.93 (s, 3H, Pd-C*H*$_3$); ***cis*-4b**: δ 8.80 (d, J_{H-H} = 4.5 Hz, 1H, Py H-6), 7.76 (dt, J_{H-H} = 1.6, 7.7 Hz, 1H, Py H-4), 7.25~7.35 (m, 2H, Py H-3; Py H-5), 4.39 (q, J_{H-H}= 6.7 Hz, 1H, Py-C*H*(CH_3)N), 2.93 (bs, 1H, N*H*C(CH_3)$_3$), 1.96 (d, J_{H-H} = 6.6 Hz, 3H, Py-CH(C*H*$_3$)N), 1.24 (s, 9H, NHC(C*H*$_3$)$_3$), 0.61 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-4b**: δ 169.15 (Py C-2), 148.09 (Py C-6), 138.32 (Py C-4), 123.83 (Py C-5), 121.69 (Py C-3), 57.06 (Py-*C*H(CH_3)N), 55.80 (NH*C*(CH_3)$_3$), 29.44 (NHC(*C*H_3)$_3$), 24.79 (Py-CH(*C*H_3)N), 0.65 (Pd-*C*H_3); ***cis*-4b**: δ 163.31 (Py C-2), 148.43 (Py C-6), 138.28 (Py C-4), 123.58 (Py C-5), 120.12 (Py C-3), 60.14 (Py-*C*H(CH_3)N), 58.82 (NH*C*(CH_3)$_3$), 29.70 (NHC(*C*H_3)$_3$), 25.33 (Py-CH(*C*H_3)N), -10.79 (Pd-*C*H_3). MS (FAB, m/z): 283.0 (M^{+1} - CH_3 - Cl). Anal.

Calcd for $C_{12}H_{21}N_2PdCl$: C, 43.19; H, 6.30; N, 8.40. Found: C, 42.38; H, 6.35; N, 8.57.

[PhHNCMeH(*o*-C_6H_5N)]Pd(Me)Cl (5b) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (265 mg, 1.00 mmol) and **L5b** (198 mg, 1.00 mmol) to give the pale white product **5b** (322 mg, 91%). ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-5b**: δ 8.39 (d, J_{H-H} = 5.0 Hz, 1H, Py H-6), 7.95 (t, J_{H-H} = 7.7 Hz, 1H, Py H-4), 7.54 (d, J_{H-H} = 7.4 Hz, 1H, Py H-3), 7.40 (m, 1H, Py H-5), 7.19 (t, J_{H-H} = 7.8 Hz, 2H, m-Ar), 7.02 (t, J_{H-H} = 7.0 Hz, 1H, p-Ar), 6.88 (d, J_{H-H} = 7.6 Hz, 2H, o-Ar), 4.61 (m, 1H, N*H*-Ar; 1H, Py-C*H*(CH_3)N), 2.07 (d, J_{H-H} = 6.4 Hz, 3H, Py-CH(C*H*$_3$)N), 0.86 (s, 3H, Pd-C*H*$_3$); ***cis*-5b**: δ 8.83 (d, J_{H-H} = 4.8 Hz, 1H, Py H-6), 7.81 (m, J_{H-H} = 7.9 Hz, 1H, Py H-4), 7.26 (m, 1H, Py H-3; 1H, Py H-5), 7.19 (2H, o-Ar; 2H, m-Ar; 1H, p-Ar), 5.83 (d, J_{H-H} = 4.8 Hz, 1H, N*H*-Ar), 4.61 (1H, Py-C*H*(CH_3)N), 1.82 (d, J_{H-H} = 6.6 Hz, 3H, Py-CH(C*H*$_3$)N), 0.25 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-5b**: δ 167.58 (Py C-6), 148.67 (Py C-2), 145.25 (ipso-Ar), 138.79 (Py C-4), 129.30 (m-Ar), 124.33(Py C-3), 123.88 (p-Ar), 122.10(Py C-5), 118.20 (o-Ar), 61.70 (Py-*C*H(CH_3)N), 23.95 (Py-CH(*C*H$_3$)N), -0.04 (Pd-*C*H$_3$); for ***cis*-5b**: δ 161.29 (Py C-6), 148.67 (Py C-2), 146.01 (ipso-Ar), 138.24 (Py C-4),129.30 (m-Ar), 125.85 (Py C-3), 123.95 (p-Ar), 121.86 (Py C-5), 120.95 (o-Ar), 68.11 (Py-*C*H(CH_3)N), 24.05 (Py-CH(*C*H$_3$)N), -4.49 (Pd-*C*H$_3$). MS (ESI/MS, m/z): 319.3 (M^{+1} - Cl). Anal. Calcd for $C_{14}H_{17}N_2PdCl$: C, 47.34; H, 4.79; N, 7.89. Found: C, 46.97; H, 4.53; N, 7.83.

[(2,6-$Me_2C_6H_3$)HNCMeH(*o*-C_6H_5N)]Pd(Me)Cl (6b) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (265 mg, 1.00 mmol) and **L6b** (226 mg, 1.00 mmol) to give the pale white product **6b** (332 mg, 87%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***cis*-6b**: δ 9.10 (d, J_{H-H} = 4.9 Hz, 1H, Py H-6), 7.86 (dt, J_{H-H} = 1.7, 7.7 Hz, 1H, Py H-4), 7.40 (t, J_{H-H} = 7.3 Hz, 1H, Py H-5), 7.30 (d, J_{H-H} = 8.0 Hz, 1H, Py H-3), 7.15 (m, 1H, p-Ar), 7.07 (m, 2H, m-Ar), 5.50 (d, J_{H-H} = 7.9 Hz, 1H, N*H*-Ar), 4.69 (m, 1H, Py-C*H*(CH_3)N), 2.91, 2.38 (s, 6H, Ar-C*H*$_3$), 1.62 (d, J_{H-H} = 6.8 Hz, 3H, Py-CH(C*H*$_3$)N), 0.13 (s, 3H, Pd-C*H*$_3$); ***trans*-6b**: δ 8.54 (d,

$J_{H\text{-}H}$ = 5.8 Hz, 1H, Py H-6), 7.91 (dt, $J_{H\text{-}H}$ = 1.6, 7.8 Hz, 1H, Py H-4), 7.40 (1H, Py H-5), 7.34 (1H, Py H-3), 7.03 (m, 2H, m-Ar), 6.95 (m, 1H, p-Ar), 4.69 (1H, N*H*-Ar), 4.43 (m, 1H, Py-C*H*(CH_3)N), 2.51 (bs, 6H, Ar-CH_3), 1.75 (d, $J_{H\text{-}H}$ = 6.9 Hz, 3H, Py-CH(CH_3)N), 1.03 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***cis*-6b**: δ 160.39 (Py C-2), 148.79 (Py C-6), 141.10 (ipso-Ar), 138.31 (Py C-4), 131.73 (p-Ar), 130.45, 129.20 (o-Ar), 128.58, 126.16 (m-Ar), 124.07 (Py C-5), 121.04 (Py C-3), 65.17 (Py-*C*H(CH_3)N), 20.42, 18.73 (Ar-*C*H_3), 19.79 (Py-CH(*C*H_3)N), -5.18 (Pd-*C*H_3); ***trans*-6b**: δ 167.23 (Py C-2), 147.89 (Py C-6), 138.31 (Py C-4), 128.60, 128.52, 128.29, 126.55, 124.90, 124.78 (Py C-5, m-Ar, o-Ar and p-Ar), 122.64(Py C-3), 63.05 (Py-*C*H(CH_3)N), 22.75 (Py-CH(*C*H_3)N), 17.80, 17.34 (Ar-*C*H_3), 0.19 (Pd-*C*H_3). MS (ESI/MS, m/z): 331.0 (M^{+1} - CH_3 - Cl). Anal. Calcd for $C_{16}H_{21}N_2PdCl$: C, 50.15; H, 5.48; N, 7.31. Found: C, 49.50; H, 5.63; N, 7.12.

[(2,6-^{i}Pr$_2$C$_6$H$_3$)HNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)Cl (7b) The synthesis was carried out according to the same procedure as for **3a**, using (COD)PdMeCl (50 mg, 0.19 mmol) and **L7b** (54 mg, 0.19 mmol) to give the pale white product **7b** (70 mg, 84%). Single crystals were grown from Et_2O/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***cis*-7b**: δ 9.15 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.87 (dt, $J_{H\text{-}H}$ = 1.6, 7.8 Hz, 1H, Py H-4), 7.41 (ddd, $J_{H\text{-}H}$ = 0.9, 5.3, 7.5 Hz, 1H, Py H-5), 7.32 (d, $J_{H\text{-}H}$ = 8.0 Hz, 1H, Py H-3), 7.10~7.30 (m, 2H, m-Ar; 1H, p-Ar), 5.80 (d, $J_{H\text{-}H}$ = 9.3 Hz, 1H, N*H*-Ar), 4.64 (m, 1H, Py-C*H*(CH_3)N), 4.56, 2.97 (sept, $J_{H\text{-}H}$ = 6.7, 6.7 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.56 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(CH_3)N), 1.42, 1.37, 1.29, 1.21 (d, $J_{H\text{-}H}$ = 6.6, 6.6, 6.7, 6.8 Hz, 12H, Ar-CH(CH_3)$_2$), 0.26 (s, 3H, Pd-CH_3); ***trans*-7b**: δ 8.56 (d, $J_{H\text{-}H}$ = 5.4 Hz, 1H, Py H-6), 7.92 (dt, $J_{H\text{-}H}$ = 1.5, 7.7 Hz, 1H, Py H-4), 7.41 (1H, Py H-5), 7.34 (1H, Py H-3), 7.10~7.30 (m, 2H, m-Ar; 1H, p-Ar), 4.84 (d, $J_{H\text{-}H}$ = 6.5 Hz, 1H, N*H*-Ar), 4.35 (m, 1H, Py-C*H*(CH_3)N), 3.08 (sept, $J_{H\text{-}H}$ = 6.7 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.64 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(CH_3)N), 1.48, 1.09 (d, $J_{H\text{-}H}$ = 6.4, 6.8 Hz, 6H, Ar-CH(CH_3)$_2$), 1.37 (6H, Ar-CH(CH_3)$_2$), 1.01 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***cis*-7b**: δ 159.94 (Py C-2), 148.94 (Py C-6), 141.74 (ipso-Ar), 138.32 (Py C-4), 140.12, 137.66 (o-Ar), 126.97, 126.70, 124.15, 123.41, 121.21 (Py C-5, Py C-3, m-Ar and p-Ar), 66.51 (Py-*C*H(CH_3)N), 28.42, 28.39 (Ar-*C*H(CH_3)$_2$), 24.89, 24.49, 24.13, 23.57 (Ar-CH(*C*H_3)$_2$), 18.52 (Py-CH(*C*H_3)N), -3.00 (Pd-*C*H_3); ***trans*-7b**: δ 166.09 (Py C-2), 148.20 (Py C-6), 141.79, 140.64, 138.91, 138.20 (ipso-Ar, o-Ar and Py C-4), 125.99, 125.85, 123.83, 123.15, 122.75 (Py C-5, Py C-3, m-Ar and p-Ar), 63.81 (Py-*C*(CH_3)N), 28.77, 28.53 (Ar-*C*H(CH_3)$_2$), 24.28, 23.36 (Ar-CH(*C*H_3)$_2$), 20.69 (Py-CH(*C*H_3)N), -0.06 (Pd-*C*H_3). MS (FAB/MS, m/z): 387.1 (M^{+1} - CH_3 - Cl). Anal. Calcd for $C_{20}H_{29}N_2PdCl$: C, 54.69; H, 6.61; N, 6.38. Found: C, 54.48; H, 6.50; N, 6.38.

{[^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (3a') A Schlenk flask was charged with complex **3a** (120 mg, 0.39 mmol) and $AgBF_4$ (76 mg, 0.39 mmol) in a glovebox, followed with CH_2Cl_2 (15 mL) and MeCN (1 mL). The mixture was stirred at 25 ^oC for 2 h. The residue of AgCl and Pd were removed by filtering through celite. The resulting pale yellow solution was concentrated in *vacuo* and then precipitated by addition of Et_2O (20 mL). After filtration, the crude product was washed with Et_2O (2×5 mL) and dried in *vacuo*. The desired air-sensitive complex was obtained as pale white powder in 56% yield (87 mg). Alternatively, one-pot reaction with (COD)PdMeCl, $AgBF_4$, **L3a**, CH_2Cl_2 and MeCN also provided the desired product. Single crystals were grown from Et_2O/MeCN/CH_2Cl_2 solution. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-3a'**: δ 8.26 (d, $J_{H\text{-}H}$= 5.6 Hz, 1H, Py H-6), 7.91 (t, $J_{H\text{-}H}$ = 7.7 Hz, 1H, Py H-4), 7.50 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.37 (t, $J_{H\text{-}H}$ = 6.6 Hz, 1H, Py H-5), 4.51 (dd, $J_{H\text{-}H}$ = 6.3, 16.5 Hz, 1H, Py-C*H'*HN), 4.14 (bs, 1H, N*H*CH(CH_3)$_2$), 3.97 (d, $J_{H\text{-}H}$ = 16.5 Hz, 1H, Py-CH'*H*N), 2.89 (qd, $J_{H\text{-}H}$ = 6.3, 6.4 Hz, 1H, NHC*H*(CH_3)$_2$), 2.39 (s, 3H, NCC*H$_3$*), 1.22, 1.14 (d, $J_{H\text{-}H}$ = 6.3, 6.4 Hz, 6H, NHCH(C*H$_3$*)$_2$), 0.79 (s, 3H, Pd-C*H$_3$*); ***cis*-3a'**: δ 8.42 (d, $J_{H\text{-}H}$ = 4.9 Hz, 1H, Py H-6), 7.84 (t, $J_{H\text{-}H}$ = 7.8 Hz, 1H, Py H-4), 7.46 (d, $J_{H\text{-}H}$ = 6.4 Hz, 1H, Py H-3), 7.43 (t, $J_{H\text{-}H}$ = 7.6 Hz, 1H, Py H-5), 4.65 (bs, 1H, N*H*CH(CH_3)$_2$), 4.63 (dd, $J_{H\text{-}H}$ = 5.9, 16.7 Hz, 1H, Py-C*H'*HN), 4.12 (d, $J_{H\text{-}H}$= 16.6 Hz, 1H, Py-CH'*H*N), 3.03 (m, 1H, NHC*H*(CH_3)$_2$), 2.45 (s, 3H, NCC*H$_3$*), 1.17 (d, $J_{H\text{-}H}$ = 6.5 Hz, 3H, NHCH(C*H$_3$*)$_2$), 1.12~1.15 (3H, NHCH(C*H$_3$*)$_2$), 0.65 (s, 3H, Pd-C*H$_3$*). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-3a'**: δ 164.80 (Py C-2), 148.28 (Py C-6), 139.66 (Py C-4), 124.12 (Py C-5), 122.09 (Py C-3), 53.85 (Py-*C*H_2N), 52.44

(NH*C*H(CH_3)$_2$), 22.48, 21.39 (NHCH(*C*H_3)$_2$), 3.25 (NC*C*H_3), 1.82 (Pd-*C*H_3); ***cis*-3a'**: δ 158.97 (Py C-2), 148.38 (Py C-6), 139.21 (Py C-4), 124.38 (Py C-5), 121.56 (Py C-3), 56.68 (Py-*C*H_2N), 55.37 (NHCH(CH_3)$_2$), 22.41, 21.78 (NHCH(*C*H_3)$_2$), 3.18 (NC*C*H_3), -7.32 (Pd-*C*H_3). MS (FAB, m/z): 312.0 (M^{+1}), 271.0 (M^{+1} - CH_3), 254.9 (M^{+1} - CH_3- $NCCH_3$). Anal. Calcd for $C_{12}H_{20}N_3PdBF_4$: C, 36.07; H, 5.01; N, 10.52. Found: C, 35.89; H, 4.73; N, 10.52.

{[^{t}BuHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (4a') The synthesis was carried out according to the same procedure as for **3a'**, using **4a** (200 mg, 0.60 mmol) and $AgBF_4$ (116 mg, 0.60 mmol) to give the pale white product **4a'** (164 mg, 66%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-4a'**: δ 8.26 (d, $J_{H\text{-}H}$ = 5.3 Hz, 1H, Py H-6), 7.89 (dt, $J_{H\text{-}H}$ = 1.5, 7.7 Hz, 1H, Py H-4), 7.50 (d, $J_{H\text{-}H}$ = 7.8 Hz,1H, Py H-3), 7.34 (t, $J_{H\text{-}H}$ = 6.6 Hz, 1H, Py H-5), 4.52 (dd, $J_{H\text{-}H}$ = 7.2, 17.1 Hz, 1H, Py-C*H'*HN), 4.39 (d, $J_{H\text{-}H}$ = 7.1 Hz, 1H, N*H*C(CH_3)$_3$), 4.11 (d, $J_{H\text{-}H}$ = 17.1 Hz, 1H, Py-CH'*H*N), 2.42 (s, 3H, NCC*H$_3$*), 1.61 (s, 9H, NHC(C*H$_3$*)$_3$), 0.81 (s, 3H, Pd-C*H$_3$*). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-4a'**: δ 166.39 (Py C-2), 148.00 (Py C-6), 139.64 (Py C-4), 123.87 (Py C-5), 122.60 (Py C-3), 56.05 (NH*C*(CH_3)$_3$), 50.81 (Py-*C*H_2N), 28.60 (NHC(*C*H_3)$_3$), 3.38 (NC*C*H_3), 2.07 (Pd-*C*H_3). MS (FAB, m/z): 268.9 (M^{+1} - CH_3- $NCCH_3$). Anal. Calcd for $C_{13}H_{22}N_3PdBF_4$: C, 37.75; H, 5.32; N, 10.16. Found: C, 37.65; H, 5.31; N, 10.16.

{[PhHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (5a') The synthesis was carried out according to the same procedure as for **3a'**, using **5a** (150 mg, 0.44 mmol) and $AgBF_4$ (86 mg, 0.44 mmol) to give the pale white product **5a'** (100 mg, 52%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-5a'**: δ 8.27 (d, $J_{H\text{-}H}$ = 5.7 Hz, 1H, Py H-6), 8.01 (dt, $J_{H\text{-}H}$ = 1.6, 7.7 Hz, 1H, Py H-4), 7.63 (d, $J_{H\text{-}H}$ = 7.9 Hz, 1H, Py H-3), 7.43 (t, $J_{H\text{-}H}$ = 6.4 Hz, 1H, Py H-5), 7.25 (t, $J_{H\text{-}H}$ = 7.7 Hz, 2H, m-Ar), 7.08 (dt, $J_{H\text{-}H}$ = 1.1, 7.4 Hz, 1H, p-Ar), 6.93 (d, $J_{H\text{-}H}$ = 8.4 Hz, 2H, o-Ar), 6.59 (d, $J_{H\text{-}H}$ = 6.1 Hz, 1H, N*H*-Ar), 4.93 (dd, $J_{H\text{-}H}$ = 6.4, 16.7 Hz, 1H, Py-C*H'*HN), 4.36 (d, $J_{H\text{-}H}$ = 16.1 Hz, 1H, Py-CH'*H*N), 2.34 (s, 3H, NCC*H$_3$*), 0.89 (s, 3H, Pd-C*H$_3$*). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-5a'**: δ

164.65 (Py C-2), 148.35 (Py C-6), 146.14 (ipso-Ar), 139.96 (Py C-4), 129.57 (m-Ar), 124.42 (p-Ar), 124.35 (Py C-5), 122.99 (Py C-3), 118.87 (o-Ar), 57.84 (Py-*C*H_2N), 3.25 (NC*C*H_3), 2.02 (Pd-*C*H_3). MS (FAB, m/z): 305.0 (M^{+1} - CH_3). Anal. Calcd for $C_{15}H_{18}N_3PdBF_4$: C, 41.55; H, 4.15; N, 9.69. Found: C, 41.82; H, 3.86; N, 9.59.

{[(2,6-$Me_2C_6H_3$)HNCH_2(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (6a') The synthesis was carried out according to the same procedure as for **3a'**, using **6a** (200 mg, 0.54 mmol) and $AgBF_4$ (105 mg, 0.54 mmol) to give the pale white product **6a'** (207 mg, 83%). ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-6a'**: δ 8.31 (d, J_{H-H} = 5.8 Hz, 1H, Py H-6), 7.94 (dt, J_{H-H} = 1.5, 7.8 Hz, 1H, Py H-4), 7.52 (1H, Py H-3), 7.41 (1H, Py H-5), 6.95~7.15 (m, 2H, m-Ar; 1H, p-Ar), 5.89 (t, J_{H-H} = 7.6 Hz, 1H, N*H*-Ar), 4.82 (1H, Py-C*H'*HN), 4.48 (dd, J_{H-H} = 9.3, 17.1 Hz, 1H, Py-CH'*H*N), 2.76 (bs, 6H, Ar-C*H_3*), 1.85 (s, 3H, NCC*H_3*), 0.98 (s, 3H, Pd-C*H_3*); ***cis*-6a'**: δ 8.49 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.87 (dt, J_{H-H} = 1.6, 7.8 Hz, 1H, Py H-4), 7.51 (1H, Py H-5), 7.40 (1H, Py H-3), 6.95~7.15 (m, 2H, m-Ar; 1H, p-Ar), 6.48 (t, J_{H-H} = 7.7 Hz, 1H, N*H*-Ar), 4.82 (dd, J_{H-H} = 6.5, 16.9 Hz, 1H, Py-C*H'*HN), 4.40 (dd, J_{H-H} = 8.4, 16.6 Hz, 1H, Py-CH'*H*N), 2.90, 2.42 (s, 6H, Ar-C*H_3*), 2.45 (s, 3H, NCC*H_3*), 0.17 (s, 3H, Pd-C*H_3*). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-6a'**: δ 163.47 (Py C-2), 147.75 (Py C-6), 141.55 (ipso-Ar), 139.62 (Py C-4), 125.60 (p-Ar), 124.24 (Py C-5), 123.40 (Py C-3), 55.00 (Py-*C*H_2N), 2.74 (NC*C*H_3), 2.15 (Pd-*C*H_3); ***cis*-6a'**: δ 157.36 (Py C-2), 148.33 (Py C-6), 141.63 (ipso-Ar), 139.09 (Py C-4), 131.20 (p-Ar), 124.60 (Py C-5), 121.44 (Py C-3), 60.51 (Py-*C*H_2N), 3.37 (NC*C*H_3), -1.35 (Pd-*C*H_3); 130.09, 129.99, 129.91, 129.82 (o-Ar), 128.92, 126.74 (m-Ar), 20.15, 19.70, 18.06, 18.00 (Ar-*C*H_3). MS (FAB, m/z): 374.1 (M^{+1}), 317.0 (M^{+1} - CH_3 - NCCH_3). Anal. Calcd for $C_{17}H_{22}N_3PdBF_4$: C, 44.24; H, 4.77; N, 9.11. Found: C, 43.93; H, 4.85; N, 9.20.

{[(2,6-$^iPr_2C_6H_3$)HNCH_2(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (7a') The synthesis was carried out according to the same procedure as for **3a'**, using **7a** (150 mg, 0.35 mmol) and $AgBF_4$ (69 mg, 0.35 mmol) to give the pale white product **7a'** (120 mg, 66%). ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-7a'**: δ

8.33 (d, J_{H-H} = 6.1 Hz, 1H, Py H-6), 7.95 (dt, J_{H-H} = 1.5, 7.8 Hz, 1H, Py H-4), 7.55 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), 7.43 (t, J_{H-H} = 6.4 Hz, 1H, Py H-5), 7.00~7.30 (m, 2H, m-Ar; 1H, p-Ar), 5.98 (t, J_{H-H} = 8.3 Hz, 1H, N*H*-Ar), 4.88 (dd, J_{H-H} = 6.1, 16.9 Hz, 1H, Py-C*H'*HN), 4.54, 3.40 (bs, 2H, Ar-C*H*(CH_3)$_2$), 4.33 (dd, J_{H-H} = 9.5, 17.4 Hz, 1H, Py-CH'*H*N), 1.81 (s, 3H, NCC*H₃*), 1.43, 1.37, 1.31 (d, J_{H-H} = 6.6, 6.6, 6.8 Hz, 12H, Ar-CH(C*H*$_3$)$_2$), 0.97 (s, 3H, Pd-C*H*$_3$); ***cis*-7a'**: δ 8.65 (d, J_{H-H} = 5.1 Hz, 1H, Py H-6), 7.89 (t, J_{H-H} = 8.34 Hz, 1H, Py H-4), 7.65 (t, J_{H-H} = 6.5 Hz, 1H, Py H-5), 7.39 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), 7.00~7.30 (m, 2H, m-Ar; 1H, p-Ar), 6.45 (t, J_{H-H} = 7.2 Hz, 1H, N*H*-Ar), 4.71 (dd, J_{H-H} = 6.0, 16.8 Hz, 1H, Py-CH'*H*N), 4.46, 3.16 (sept, J_{H-H} = 6.8, 6.9 Hz, 2H, Ar-C*H*(CH_3)$_2$), 4.42 (dd, J_{H-H} = 6.4, 16.0 Hz, 1H, Py-CH'*H*N, 2.49 (s, 3H, NCC*H*$_3$), 1.10~1.50 (12H, Ar-CH(C*H*$_3$)$_2$), 0.29 (s, 3H, Pd-C*H*$_3$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-7a'**: δ 163.49 (Py C-2), 147.80 (Py C-6), 139.69 (Py C-4), 126.51, 124.34, 123.43, 121.26 (p-Ar, m-Ar, Py C-5 and Py C-3), 57.80 (Py-*C*H_2N), 28.00 (Ar-*C*(CH_3)$_2$), 24.98, 24.19, 23.93, 23.86 (Ar-C(*C*H_3)$_2$), 2.61 (NC*C*H_3), 2.11 (Pd-*C*H_3); ***cis*-7a'**: δ 149.02 (Py C-6), 139.20 (Py C-4), 127.68, 126.58, 125.13, 123.64 (p-Ar, m-Ar, Py C-5 and Py C-3), 63.04 (Py-*C*H_2N), 28.26 (Ar-*C*(CH_3)$_2$), 23.27, 22.59 (Ar-C(*C*H_3)$_2$), 3.43 (NC*C*H_3), 0.63 (Pd-*C*H_3); 131.38, 140.17, 138.90, 138.18 (ipso-Ar and o-Ar). MS (FAB, m/z): 430.2 (M^{+1}), 373.1 (M^{+1} - CH_3 - $NCCH_3$). Anal. Calcd for $C_{21}H_{30}N_3PdBF_4$: C, 48.89; H, 5.82; N, 8.15. Found: C, 48.59; H, 5.53; N, 7.54.

{[^{i}PrHNCMeH(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (3b') The synthesis was carried out according to the same procedure as for **3a'**, using **3b** (300 mg, 0.93 mmol) and $AgBF_4$ (182 mg, 0.93 mmol) to give the pale white product **3b'** (290 mg, 75%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-3b'**: δ 8.27 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.88 (dt, J_{H-H} = 1.4, 7.7 Hz, 1H, Py H-4), 7.46 (d, J_{H-H} = 7.8 Hz, 1H, Py H-3), 7.33 (dt, J_{H-H} = 1.2, 7.2 Hz, 1H, Py H-5), 4.22 (q, J_{H-H} = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 2.83 (qd, J_{H-H} = 6.4, 12.9 Hz, 1H, NHC*H*(CH_3)$_2$), 2.39 (s, 3H, NCC*H*$_3$), 1.87 (d, J_{H-H} = 6.5 Hz, 3H, Py-CH(C*H*$_3$)N), 1.23, 1.16 (d, J_{H-H} = 6.4, 6.5 Hz, 6H, NHCH(C*H*$_3$)$_2$), 0.81 (s, 3H, Pd-C*H*$_3$); ***cis*-3b'**: δ 8.42 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.88 (dt, J_{H-H} = 0.8, 7.7 Hz, 1H, Py H-4), 7.46 (t, J_{H-H} = 6.4 Hz, 1H, Py H-5), 7.43 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), 4.32 (q, J_{H-H} = 6.7 Hz, 1H, Py-C*H*(CH_3)N), 3.02 (qd, J_{H-H} = 6.4, 11.6 Hz, 1H, NHC*H*(CH_3)$_2$), 2.44 (s, 3H, NCCH_3), 1.82 (d, J_{H-H} = 6.7 Hz, 3H, Py-CH(CH_3)N), 1.52, 1.13 (d, J_{H-H} = 6.5, 6.5 Hz, 6H, NHCH(CH_3)$_2$), 0.66 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-3b'**: δ 168.69 (Py C-2), 148.38 (Py C-6), 139.61 (Py C-4), 124.05 (Py C-5), 122.68 (Py C-3), 60.86 (Py-*C*H(CH_3)N), 52.45 (NH*C*H(CH_3)$_2$), 23.80 (Py-CH(*C*H_3)N), 22.78, 21.50 (NHCH(*C*H_3)$_2$), 3.29 (NC*C*H_3), 1.58 (Pd-*C*H_3); ***cis*-3b'**: δ 162.99 (Py C-2), 148.55 (Py C-6), 139.61 (Py C-4), 124.54 (Py C-5), 121.52 (Py C-3), 64.08 (Py-*C*H(CH_3)N), 55.67 (NH*C*H(CH_3)$_2$), 24.68 (Py-CH(*C*H_3)N), 23.29, 22.23 (NHCH(*C*H_3)$_2$), 3.23 (NC*C*H_3), -8.20 (Pd-*C*H_3). MS (FAB, m/z): 326.0 (M^{+1}), 269.0 (M^{+1} - CH_3 - NCCH_3). Anal. Calcd for $C_{13}H_{22}N_3PdBF_4$: C, 37.83; H, 5.34; N, 10.19. Found: C, 37.54; H, 5.00; N, 9.93.

{[^{t}BuHNCMeH(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (4b') The synthesis was carried out according to the same procedure as for **3a'**, using **4b** (130 mg, 0.39 mmol) and $AgBF_4$ (76 mg, 0.39 mmol) to give the pale white product **4b'** (90 mg, 54%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (100 MHz, $CDCl_3$) for ***trans*-4b'**: δ 8.24 (d, J_{H-H}= 5.5Hz, 1H, Py H-6), 7.87 (dt, J_{H-H}= 1.3, 7.7Hz, 1H, Py H-4), 7.45 (d, J_{H-H}= 7.9Hz, 1H, Py H-3), 7.31 (dt, J_{H-H}= 1.3, 7.2Hz, 1H, Py H-5), 4.34 (q, J_{H-H}= 6.8Hz, 1H, Py-C*H*(CH_3)N), 3.92 (bs, 1H, N*H*C(CH_3)$_3$), 2.42 (s, 3H, NCCH_3), 1.91 (d, J_{H-H}= 6.8Hz, 3H, Py-CH(CH_3)N), 1.15 (s, 9H, NHC(CH_3)$_3$), 0.79 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-4b'**: δ 171.19 (Py C-3), 147.96 (Py C-6), 139.74 (Py C-4), 123.78 (Py C-5), 122.24 (Py C-3), 57.51 (Py-*C*H(CH_3)N), 56.26 (NH*C*(CH_3)$_3$), 28.70 (NHC(*C*H_3)$_3$), 24.36 (Py-CH(*C*H_3)N), 3.45 (NC*C*H_3), 2.09 (Pd-*C*H_3). MS (FAB, m/z): 340.0 (M^{+1}), 283.0 (M^{+1} - CH_3 - NCCH_3). Anal. Calcd for $C_{14}H_{24}N_3PdBF_4$: C, 39.46; H, 5.64; N, 9.86. Found: C, 39.35; H, 5.45; N, 10.32.

{[PhHNCMeH(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (5b') The synthesis was carried out according to the same procedure as for **3a'**, using **5b** (250 mg, 0.71 mmol) and $AgBF_4$ (138 mg, 0.71 mmol) to give the pale white product **5b'** (206 mg, 58%). ^{1}H NMR (400 MHz, CD_3CN) for ***trans*-5b'**: δ 8.32 (d, J_{H-H}

= 5.4 Hz, 1H, Py H-6), δ 8.11 (dt, J_{H-H} = 1.3, 7.8 Hz, 1H, Py H-4), δ 7.71 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), δ 7.51 (t, J_{H-H} = 6.2 Hz, 1H, Py H-5), δ 7.31 (t, J_{H-H} = 6.2 Hz, 2H, m-Ar), δ 7.12 (t, J_{H-H} = 7.4 Hz, 1H, p-Ar), δ 6.89 (d, J_{H-H} = 7.9 Hz, 2H, o-Ar), δ 5.78 (bs, 1H, N*H*-Ar), δ 4.79 (dq, J_{H-H} = 2.8, 6.7 Hz 1H, Py-C*H*(CH_3)N), δ 1.97 (m, 3H, NCCH_3), δ 1.77 (m, J_{H-H} = 6.4 Hz, 3H, Py-CH(CH_3)N), δ 0.91 (s, 3H, Pd-CH_3); ***cis*-5b'**: δ 8.50 (d, J_{H-H} = 4.7 Hz, 1H, Py H-6), δ 8.06 (m, 1H, Py H-4), δ 7.49 ~ 7.58 (m, 1H, Py H-3; 1H, Py H-5), δ 7.27 (m, 2H, o-Ar), δ 7.21 (t, J_{H-H} = 7.3 Hz , 1H, p-Ar), δ 7.05 (d, J_{H-H} = 7.9 Hz, 2H, m-Ar), δ 6.15 (bs, 1H, N*H*-Ar), δ 4.69 (m, 1H, Py-C*H*(CH_3)N), δ 2.16 (s, 3H, NCCH_3), δ 1.77 (m, 3H, Py-CH(CH_3)N), δ 0.56 (s, 3H, Pd-CH_3). ^{13}C NMR (100.625 MHz, D^6-acetone) for ***trans*-5b'**: δ 168.94 (Py C-2), 149.74 (Py C-6), 146.44 (ipso-Ar), 141.80 (Py C-4), 130.33 (m-Ar), 125.86 (Py C-5), 125.03 (p-Ar), 124.34 (Py C-3), 122.34 (N*C*CH_3), 119.97 (o-Ar), 62.37 (Py-*C*H(CH_3)N), 22.26 (Py-CH(*C*H_3)N), 2.77 (NC*C*H_3), 1.39 (Pd-*C*H_3); for ***cis*-5b'**: δ 163.72 (Py C-2), 149.67 (Py C-6), 147.25 (ipso-Ar), 141.18 (Py C-4), 130.49 (m-Ar), 127.10, 125.79, 123.91, 123.15 (Py C-5, p-Ar, Py C-3, o-Ar), 70.01 (Py-*C*H(CH_3)N), 22.77 (Py-CH(*C*H_3)N), 3.15 (NC*C*H_3), -4.04 (Pd-*C*H_3). Anal. Calcd for $C_{16}H_{20}BF_4N_3Pd$: C, 42.94; H, 4.50; N, 9.39. Found: C, 43.94; H, 4.85; N, 8.66.

{[(2,6-$Me_2C_6H_3$)HNCMeH(*o*-C_6H_5N)]Pd(Me)(NCMe)}(BF_4) (6b') The synthesis was carried out according to the same procedure as for **3a'**, using **6b** (100 mg, 0.26 mmol) and $AgBF_4$ (51 mg, 0.26 mmol) to give the pale white product **6b'** (60 mg, 48%). Single crystals were grown from Et_2O/MeCN/CH_2Cl_2. ^{1}H NMR (400 MHz, $CDCl_3$, 298K) for ***trans*-6b'**: δ 8.37 (d, J_{H-H} = 5.7 Hz, 1H, Py H-6), 8.04 (dt, J_{H-H} = 1.5, 7.9 Hz, 1H, Py H-4), 7.54 (d, J_{H-H} = 7.9 Hz, 1H, Py H-3), 7.47 (d, J_{H-H} = 6.6 Hz, 1H, Py H-5), 6.95~7.20 (m, 2H, m-Ar; 1H, p-Ar), 5.20 (bs, 1H, N*H*-Ar), 4.82 (qd, J_{H-H} = 6.7, 9.5 Hz, 1H, Py-C*H*(CH_3)N), 1.84 (NC*C*H_3), 0.95 (s, 3H, Pd-CH_3); ***cis*-6b'**: δ 8.62 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.95 (dt, J_{H-H} = 1.6, 8.0 Hz, 1H, Py H-4), 7.60 (dt, J_{H-H} = 1.1, 6.5 Hz, 1H, Py H-5), 7.42 (1H, J_{H-H} = 7.9 Hz, Py H-3), 6.95~7.20 (m, 2H, m-Ar; 1H, p-Ar), 5.69 (d, J_{H-H} = 9.0 Hz, 1H, Py-C*H*(CH_3)N), 4.71 (qd, J_{H-H} = 7.1, 7.4 Hz, 1H, Py-C*H*(CH_3)N), 2.85, 2.36 (s, 6H, Ar-CH_3), 2.48 (NC*C*H_3), 0.09 (s, 3H, Pd-

C*H*$_3$). 1.60 (m, 6H, Py-CH(C*H*$_3$)N). ^{1}H NMR (500 MHz, CD_2Cl_2, 253K) for ***trans*-6b'**: δ 8.37 (d, J_{H-H} = 5.7 Hz, 1H, Py H-6), 8.04 (dt, J_{H-H} = 1.5, 7.9 Hz, 1H, Py H-4), 7.52 (m, 1H, Py H-3; 1H, Py H-5), 7.20~7.20 (m, 2H, m-Ar; 1H, p-Ar), 4.90 (d, J_{H-H} = 10.8 Hz, 1H, N*H*-Ar), 4.84 (m, 1H, Py-C*H*(CH_3)N), 3.01, 2.34 (s, 6H, Ar-C*H*$_3$), 1.79 (NC*C*H$_3$), 0.92 (s, 3H, Pd-C*H*$_3$); ***cis*-6b'**: δ 8.62 (d, J_{H-H} = 5.3 Hz, 1H, Py H-6), 7.95 (dt, J_{H-H} = 1.6, 8.0 Hz, 1H, Py H-4), 7.60 (t, J_{H-H} = 6.5 Hz, 1H, Py H-5), 7.43 (1H, J_{H-H} = 8.0 Hz, Py H-3), 7.00~7.20 (m, 2H, m-Ar; 1H, p-Ar), 5.63 (d, J_{H-H} = 9.2 Hz, 1H, N*H*-Ar), 4.72 (m, 1H, Py-C*H*(CH_3)N), 2.87, 2.33 (s, 6H, Ar-C*H*$_3$), 2.45 (NC*C*H$_3$), 0.04 (s, 3H, Pd-C*H*$_3$); 1.55 (d, J_{H-H} = 6.6 Hz, 6H, Py-CH(C*H*$_3$)N). ^{13}C NMR (100.625 MHz, $CDCl_3$, 298K) for ***trans*-6b'**: δ 164.99 (Py C-2), 148.91 (Py C-6), 140.37 (ipso-Ar), 140.22 (Py C-4), 60.07 (Py-*C*H(CH_3)N), 20.13, 18.44 (Ar-*C*H$_3$), 18.32 (Py-CH(*C*H$_3$)N), 3.10 (NC*C*H$_3$), 2.00 (Pd-*C*H$_3$); ***cis*-6b'**: δ 159.71 (Py C-2), 148.32 (Py C-6), 140.02 (ipso-Ar), 139.65 (Py C-4), 66.57 (Py-*C*H(CH_3)N), 18.62, 18.44 (Ar-*C*H$_3$), 18.32 (Py-CH(*C*H$_3$)N), 3.35 (NC*C*H$_3$), -1.08 (Pd-*C*H$_3$); 131.88, 131.36, 129.32, 128.96, 126.85, 125.92 (m-Ar and p-Ar), 130.35, 130.19, 130.10, 129.90 (o-Ar), 125.35, 124.76, 123.95, 122.08 (Py C-3 and Py C-5). MS (FAB/MS, m/z): 388.1 (M^{+1}), 331.0 (M^{+1} - CH_3 - $NCCH_3$). Anal. Calcd for $C_{18}H_{24}N_3PdBF_4$: C, 45.45; H, 5.05; N, 8.84. Found: C, 45.89; H, 4.57; N, 9.74.

{[(2,6-^{i}Pr$_2$C$_6$H$_3$)HNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (7b') The synthesis was carried out according to the same procedure as for **3a'**, using **7b** (150 mg, 0.34 mmol) and $AgBF_4$ (66 mg, 0.34 mmol) to give the pale white product **7b'** (137 mg, 76%). ^{1}H NMR (400 MHz, $CDCl_3$) for ***trans*-7b'**: δ 8.40 (d, J_{H-H} = 5.6 Hz, 1H, Py H-6), 8.08 (dt, J_{H-H} = 1.5, 7.8 Hz, 1H, Py H-4), 7.56 (d, J_{H-H} = 8.0 Hz, 1H, Py H-3), 7.51 (t, J_{H-H} = 6.3 Hz, 1H, Py H-5), , 7.15~7.23 (m, 2H, m-Ar; 1H, p-Ar), 5.55 (d, J_{H-H} = 10.3 Hz, 1H, N*H*-Ar), 4.62 (m, 1H, Py-C*H*(CH_3)N), 4.55, 3.17 (sept, J_{H-H} = 6.9, 6.7 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.61 (d, J_{H-H} = 6.7 Hz, 3H, Py-CH(C*H*$_3$)N), 1.44, 1.30 (d, J_{H-H} = 6.6, 6.8 Hz, 6H, Ar-CH(C*H*$_3$)$_2$), 1.81 (s, 1H, NCC*H*$_3$), 0.96 (s, 3H, Pd-C*H*$_3$); ***cis*-7b'**: δ 8.72 (d, J_{H-H} = 4.7 Hz, 1H, Py H-6), 7.98 (dt, J_{H-H} = 1.5, 7.8 Hz, 1H, Py H-4), 7.69 (t, J_{H-H} = 6.4 Hz, 1H, Py H-5), 7.41 (d, J_{H-H} = 8.0 Hz, 1H, Py H-3), 7.15~7.23

(m, 2H, m-Ar; 1H, p-Ar), 5.79 (d, $J_{H\text{-}H}$ = 9.3 Hz, 1H, N*H*-Ar), 4.62 (m, 1H, Py-C*H*(CH_3)N), 4.30, 2.98 (sept, $J_{H\text{-}H}$ = 6.6, 6.6 Hz, 2H, Ar-C*H*(CH_3)$_2$), 1.56 (d, $J_{H\text{-}H}$ = 6.8 Hz, 3H, Py-CH(CH_3)N), 2.50 (s, 1H, NCCH_3), 0.25 (s, 3H, Pd-CH_3); 1.39, 1.36, 1.35 (d, $J_{H\text{-}H}$ = 6.7, 6.4, 6.5 Hz, 9H, Ar-CH(CH_3)$_2$), 1.23 (m, 9H, Ar-CH(CH_3)$_2$). ^{13}C NMR (100.625 MHz, $CDCl_3$) for ***trans*-7b'**: δ 164.69 (Py C-2), 148.47 (Py C-6), 140.33 (Py C-4), 62.30 (Py-*C*(CH_3)N), 29.17, 28.04 (Ar-*C*H(CH_3)$_2$), 17.34 (Py-C(*C*H_3)N), 2.92 (NC*C*H_3), 2.00 (Pd-*C*H_3); ***cis*-7b'**: δ 159.09 (Py C-2), 149.41 (Py C-6), 139.71 (Py C-4), 68.08 (Py-*C*(CH_3)N), 28.74, 28.30 (Ar-*C*H(CH_3)$_2$), 17.79 (Py-C(*C*H_3)N), 3.42 (NC*C*H_3), 1.18 (Pd-*C*H_3); 25.43, 24.86, 24.73, 24.50, 24.43, 23.89, 23.36, 22.54 (Ar-CH(*C*H_3)$_2$), 141.47, 141.22, 140.91, 140.49 (o-Ar), 136.93, 136.89 (ipso-Ar), 127.66, 126.80, 126.64, 126.16, 125.76, 124.89, 124.00, 123.81, 123.70, 121.93 (m-Ar, p-Ar, Py C-3 and Py C-5). MS (FAB, m/z): 444.2 (M^{+1}), 387.1 (M^{+1} - CH_3 - $NCCH_3$). Anal. Calcd for $C_{22}H_{31}N_3PdBF_4$: C, 49.69; H, 6.02; N, 7.91. Found: C, 48.89; H, 6.09; N, 7.53.

Determination of norbornene content and alternating percentage for copolymers

The norbornene content, X_{NB} was evluated with use of ^{13}C NMR integrations as designated in the following table according to Eq. (1) used by Kaminsky.[1]

$$X_{NB} = \frac{I(\mathrm{A})}{I(\mathrm{B}) + I(\mathrm{C}) + I(\mathrm{D}) - 1.5\, I(\mathrm{A})} \qquad (1\text{-}1)$$

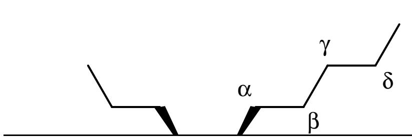


Table S1 Assignments of ethylene/norbornene copolymers in ^{13}C NMR spectra

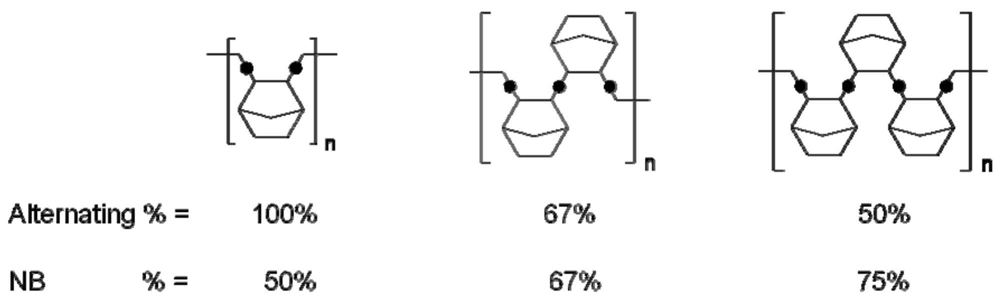
Singnal area	δ (^{13}C NMR) (ppm)	Asignments

A	51 - 45	C2, C3
B	43 - 37	C1, C4
C	37 – 32.3	C7
D	32.3 - 28	C5, C6, C_α, C_β, C_γ, C_δ

The alternating percentage in a copolymer may be calculated according to Eq. (1-2).

$$Alternating\% = 2 \times single\ NB\ mol\ \% + NB\ Diads\ mol\ \% + 2/3 \times NB\ Triads\ mol\ \% \qquad (1\text{-}2)$$

Figure S1 Examples of ethylene/norbornene copolymer and block copolymers



Determination of ethylene concentration

To obtain ethylene concentrations for our system, an experiment was conducted using a digitally monitored ethylene reservoir which provided ethylene of a specific pressure on demand to a stirred stainless reactor.[2] CH_2Cl_2 (V solution=50 mL) was injected into the reactor with a nitrogen back pressure and equilibrated at 25 °C. The solution was marginally degassed of N_2 gas without stirring by passing ethylene (100, 200, 300, 400 and 500 psi) over the headspace. To initiate the dissolution experiment, mechanical stirring was activated, and the initial pressure of the reservoir was noted. The solution was stirred for 20-30 min to ensure complete saturation, and then the final head and reservoir pressures were noted. The data collected were used to obtain the number of moles dissolved (Δn) at each pressure according to the ideal gas law: $\Delta PV = \Delta nRT$, where ΔP is the total change in reservoir pressure for a given head pressure, V is the volume of the reservoir system (50 L), R is the gas constant (1.206 L•psi/mol•K), and T is the reservoir temperature (299 K). The resuls was shown below.

Table S2 Ethylene concentration under different pressure in CH_2Cl_2

Ethylene (psi)	**Reservoir ΔP (psi)**	**Δn (moles)**	**Observed [E] (M)**
100	16.67	0.027	0.56
200	33.33	0.055	1.11
300	50.00	0.083	1.66
400	66.67	0.111	2.22
500	83.33	0.138	2.77

Fineman-Ross plot

The copolymer compositions were determined according to the literature.[3]

$$\text{Pd-N-polymer} + \text{N} \xrightarrow{k_{NN}} \text{Pd-N-N-polymer} \quad (2\text{-}1)$$

$$\text{Pd-N-polymer} + \text{E} \xrightarrow{k_{NE}} \text{Pd-N-E-polymer} \quad (2\text{-}2)$$

$$\text{Pd-E-polymer} + \text{N} \xrightarrow{k_{EN}} \text{Pd-E-N-polymer} \quad (2\text{-}3)$$

$$\text{Pd-E-polymer} + \text{E} \xrightarrow{k_{EE}} \text{Pd-E-E-polymer} \quad (2\text{-}4)$$

Where Pd-N-polymer and Pd-E-polymer are the growing chain with norbornene and ethylene as the last inserted monomer, and the reactivity ratios are defined as $r_1 = k_{NN}/k_{NE}$ and $r_2 = k_{EE}/k_{EN}$. By using quasi-steady-state assumption for propagation, the copolymer composition equation can be derived as:

$$\left(\frac{[N]}{[E]}\right)_{polymer} = \frac{[N]}{[E]} \frac{\left(1 + r_1 \frac{[N]}{[E]}\right)}{\left(r_2 + \frac{[N]}{[E]}\right)} \quad (3)$$

where $([E]/[N])_{polymer}$ and $([E]/[N])$ are the ethylene and norbornene molar ratios in the copolymer and the bulk reaction solution. Futher replacement of $([N]/[E])_{polymer}$ and $([N]/[E])$ to f and F, the following Fineman-Ross equation can be derived as:

$$\frac{(f - 1)}{f} F = r_1 \frac{F^2}{f} - r_2 \quad (4)$$

Table S3 Fineman-Ross data of ethylene/norbornene copolymerization catalyzed by **3b'**

NB (g)	NB Conc. (M)	E Conc. (M)	*F* ([N]/[E])	NB % (^{13}C NMR)	*f* (([N]/[E])$_{polymer}$)	F^2/f	$F(f-1)/f$
0.5	0.11	1.66	0.066265	42.0	0.724138	0.006064	-0.02524
1	0.21	1.66	0.126506	42.5	0.73913	0.021652	-0.04465
3	0.64	1.66	0.385542	49.4	0.976285	0.152254	-0.00937
5	1.06	1.66	0.638554	54.0	1.173913	0.347344	0.094601
10	2.13	1.66	1.283133	52.4	1.10084	1.495611	0.117539
20	4.26	1.66	2.566265	53.3	1.141328	5.770224	0.317774
30	6.38	1.66	3.843373	59.6	1.475248	10.01291	1.238134

Correlation of T_g and norbornene content determined from ^{13}C NMR data

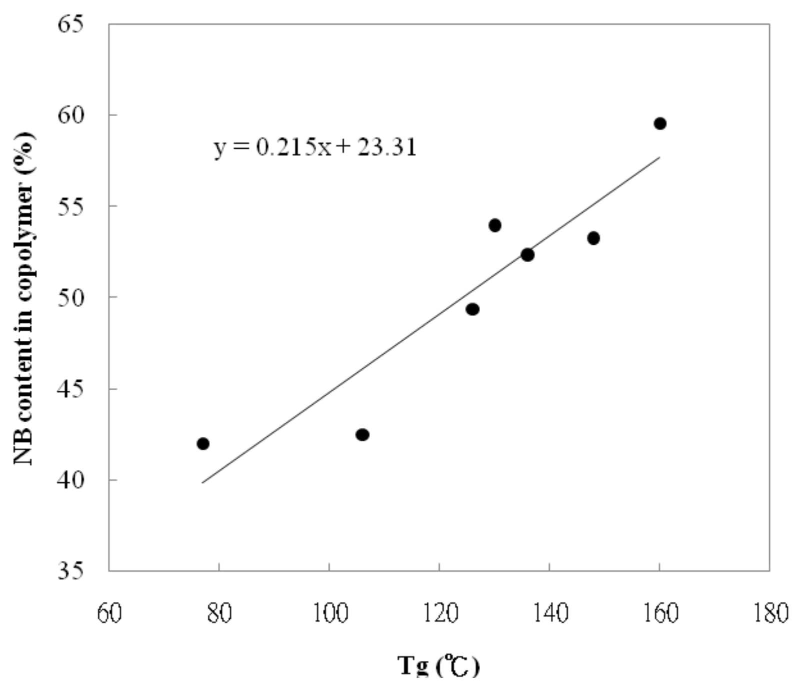


Figure S2 Norbornene content in copolymer as a function of the glass transition temperature T_g

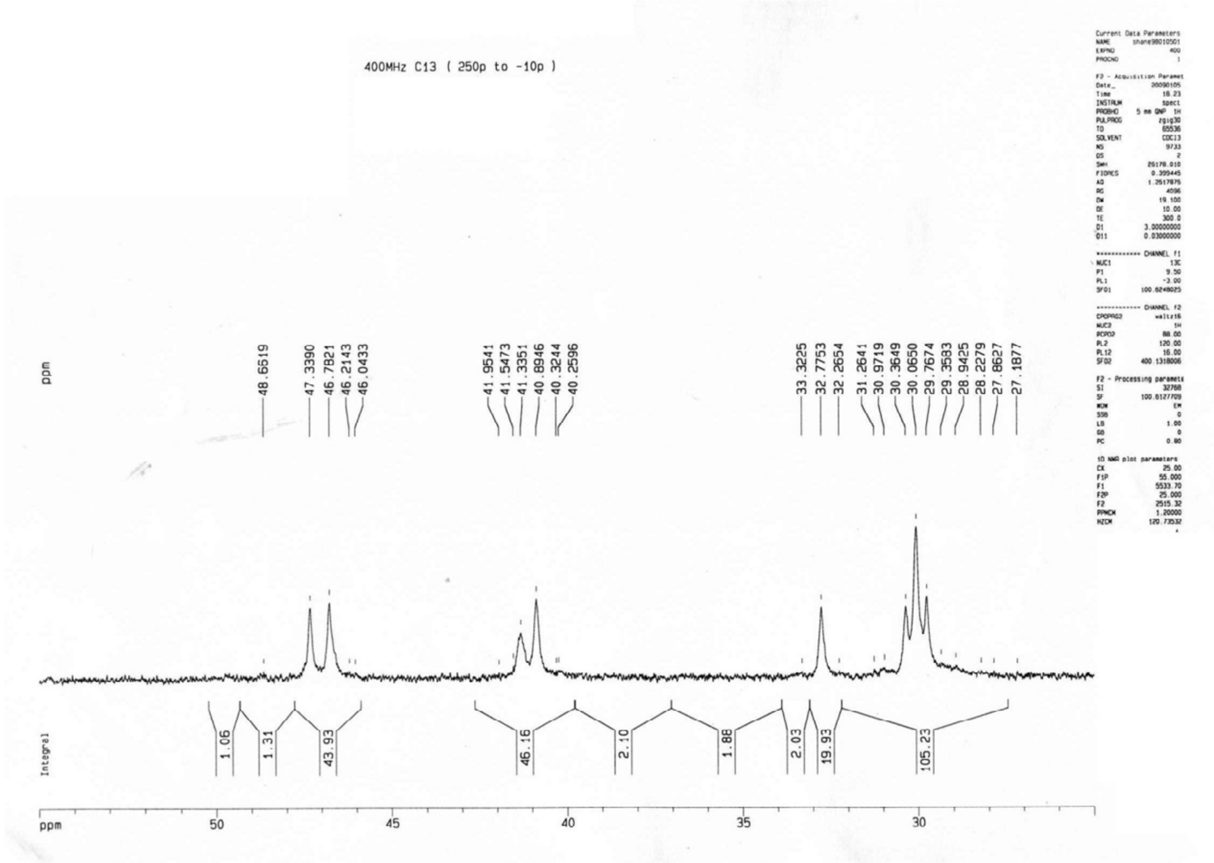


Figure S3 Ethylene/norbornen copolymer catalyzed by **3b'** with 1 g of norbornene feeding

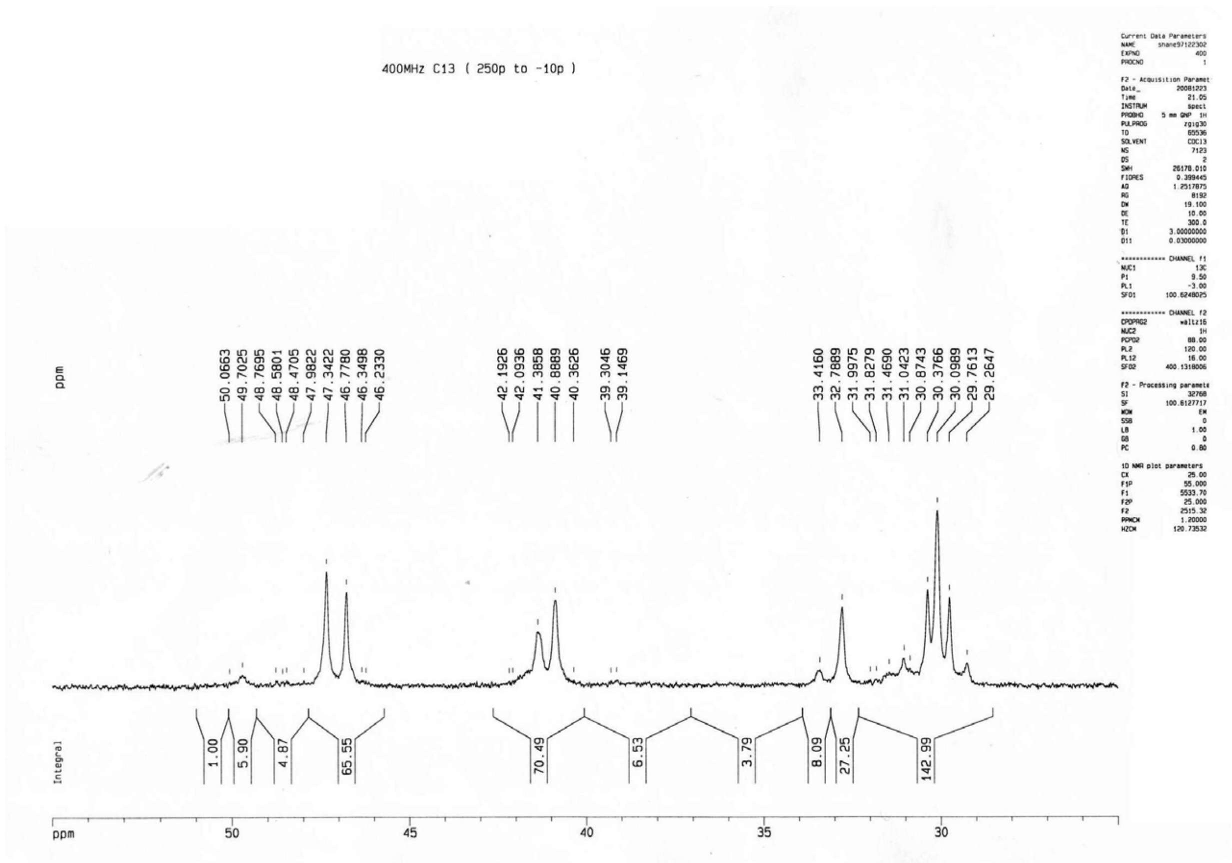


Figure S4 Ethylene/norbornen copolymer catalyzed by **3b'** with 5 g of norbornene feeding

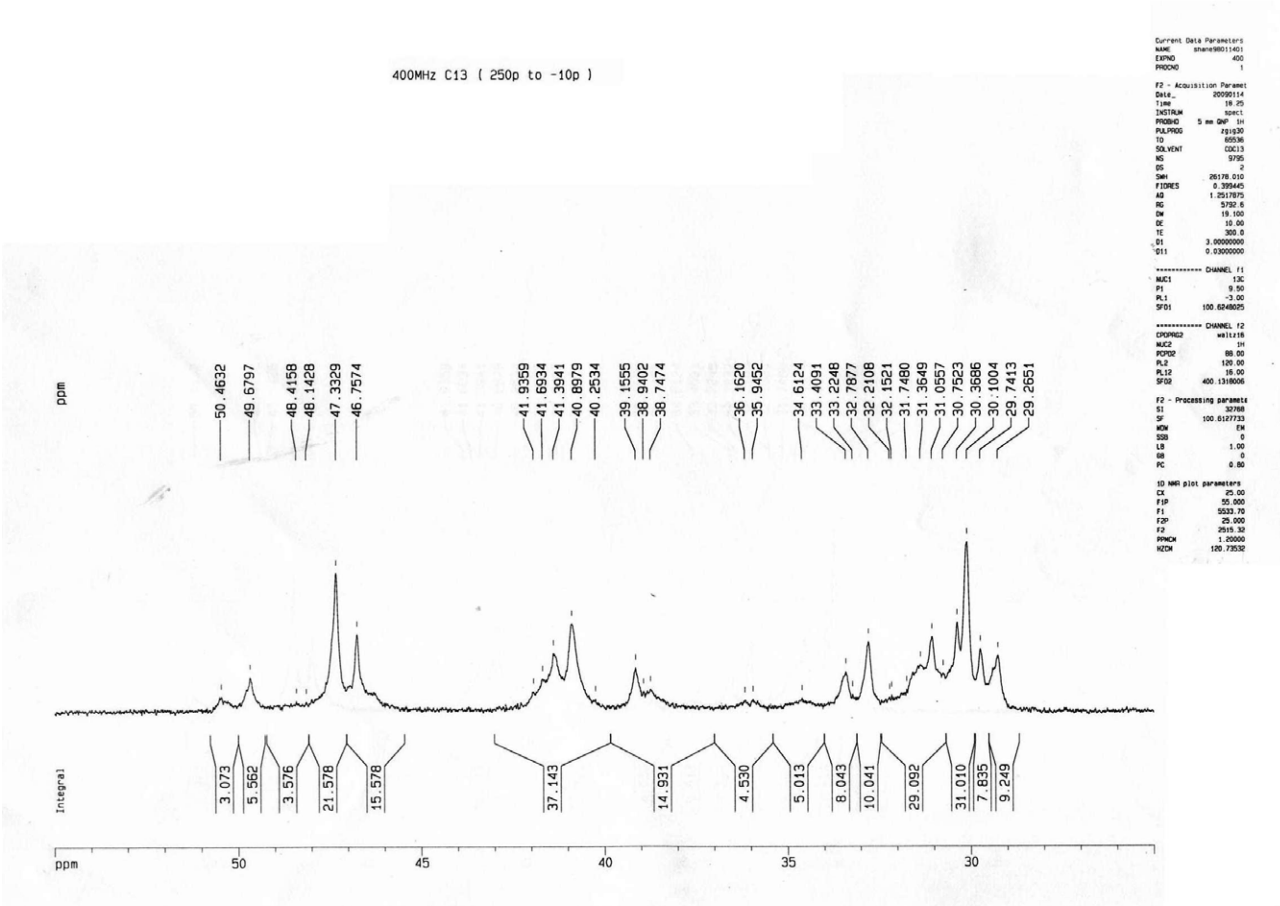


Figure S5 Ethylene/norbornen copolymer catalyzed by **3b'** with 30 g of norbornene feeding

Kinetic data and spectra of varible temperature NMR

Table S4 Kinetic data for restricted rotation

Compound (*trans* form)	(CH_3)$_2$-Ar (ppm)		Δν (Hz)	K_c (S^{-1})	$T_{coal.}$ (K)	$\Delta G^{\neq}$ (KJ/mol)
6a'	3.0113	2.3936	308.85	685.65	303	58.00
6b	2.5480	2.4020	73.00	162.06	313	61.42
6b'	3.0120	2.3363	227.85	750.03	323	58.56

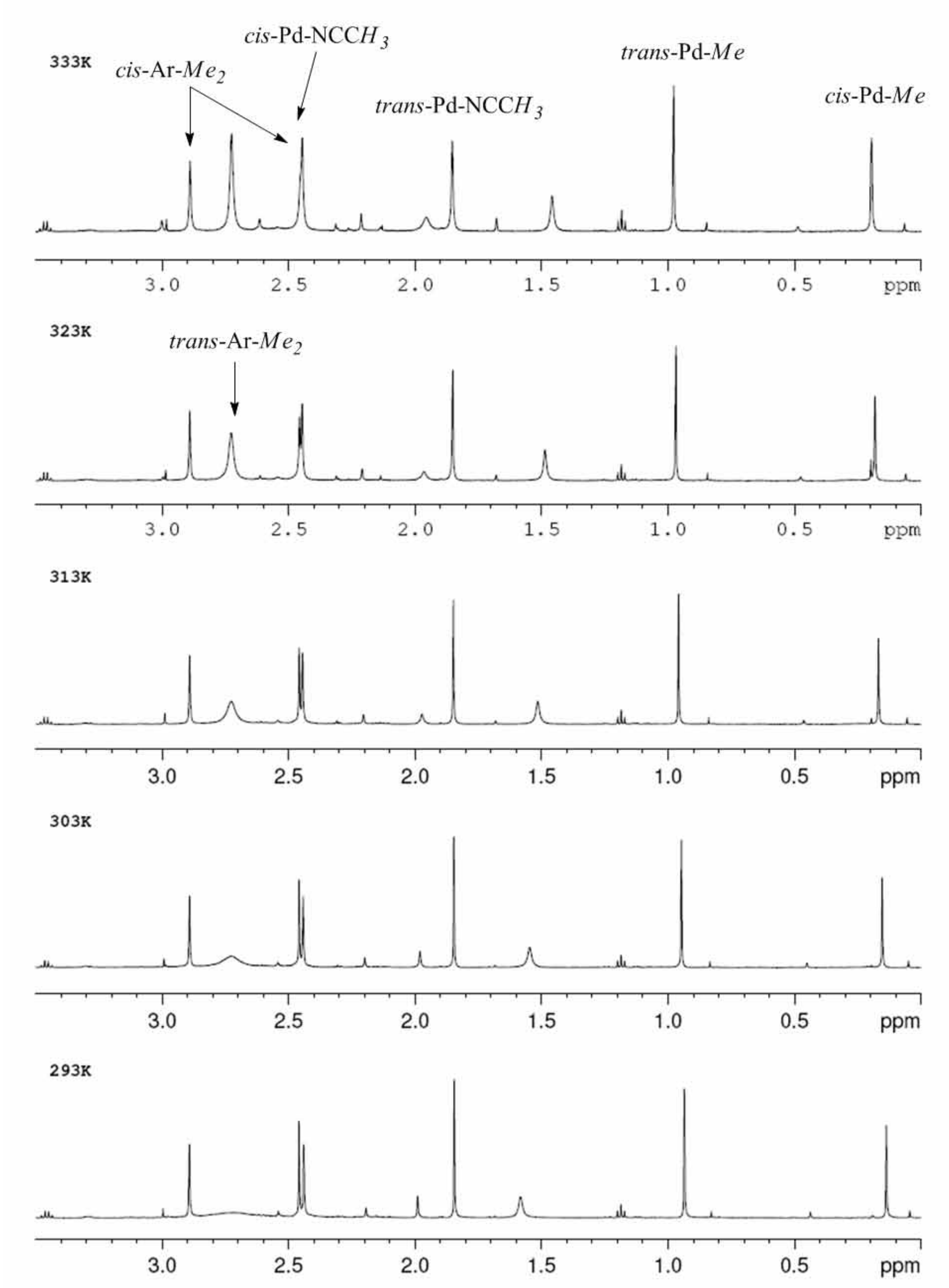
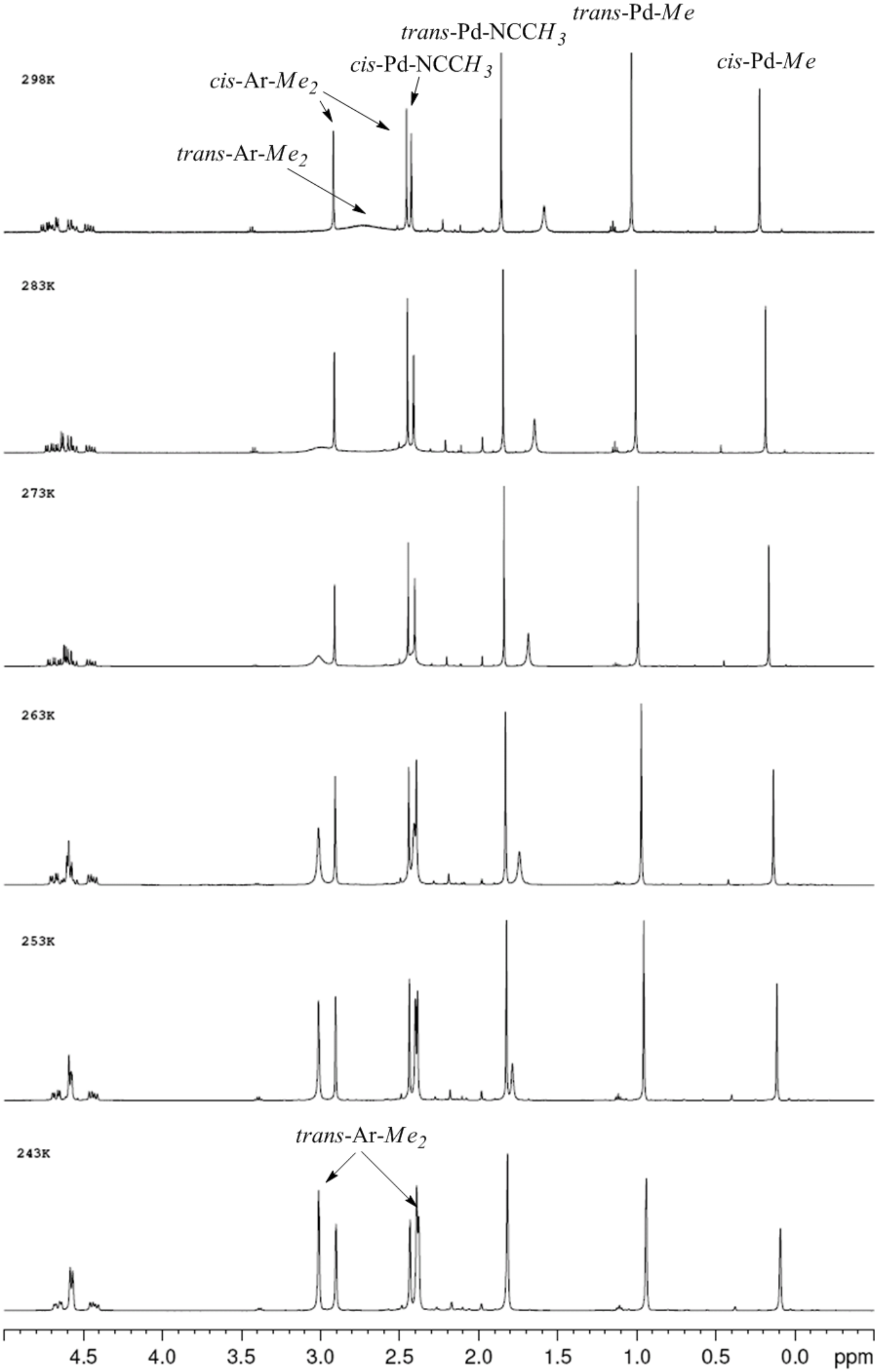
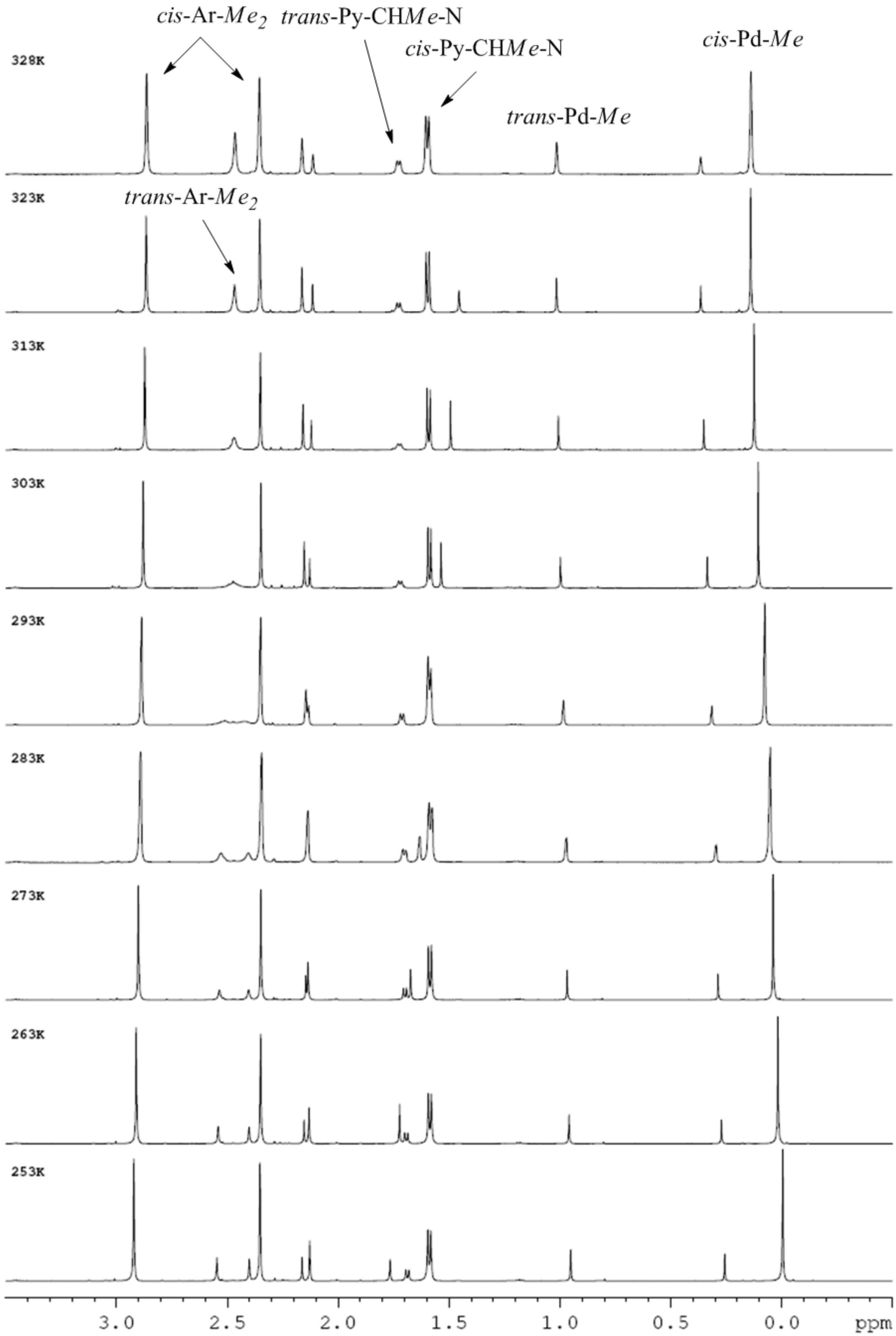

333K
cis-Ar-Me2
cis-Pd-NCCH3
trans-Pd-NCCH3
trans-Pd-Me
cis-Pd-Me
3.0
2.5
2.0
1.5
1.0
0.5
ppm
323K
trans-Ar-Me2
313K
303K
293K

Figure S6 ^{1}H NMR spectra of **6a'** in CD_2Cl_2 from 293 K to 333K



trans-Pd-Me
trans-Pd-NCCH3
cis-Pd-NCCH3
cis-Pd-Me
cis-Ar-Me2
trans-Ar-Me2
298K
283K
273K
263K
253K
243K
trans-Ar-Me2
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Figure S7 ^{1}H NMR spectra of **6a'** in CD_2Cl_2 from 243 K to 298K



cis-Ar-Me2
trans-Py-CHMe-N
cis-Py-CHMe-N
cis-Pd-Me
trans-Pd-Me
trans-Ar-Me2
328K
323K
313K
303K
293K
283K
273K
263K
253K
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Figure S8 ^{1}H NMR spectra of **6b** in $CDCl_3$ from 253 K to 328K

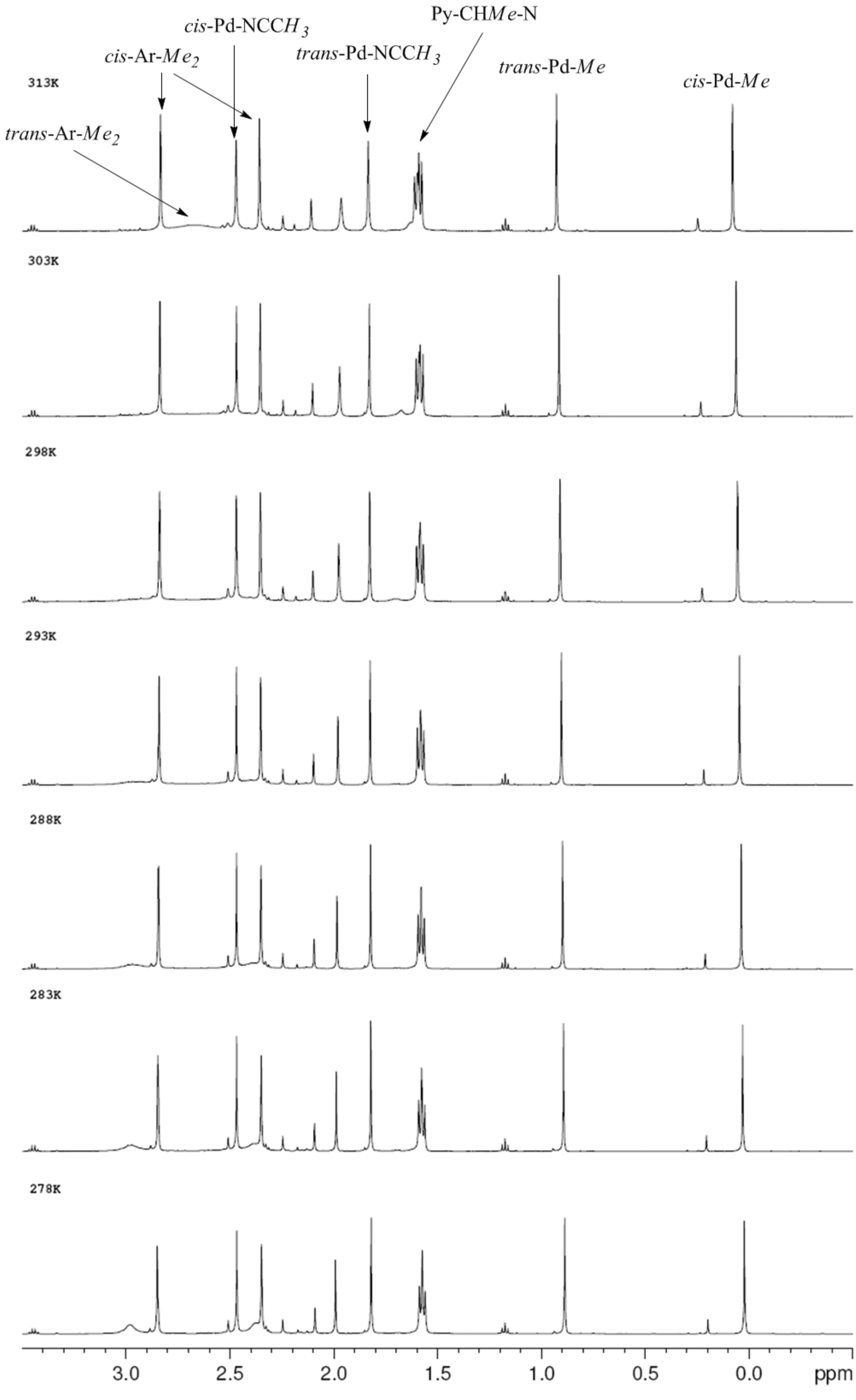

cis-Pd-NCCH3
Py-CHMe-N
cis-Ar-Me2
trans-Pd-NCCH3
trans-Pd-Me
cis-Pd-Me
trans-Ar-Me2
313K
303K
298K
293K
288K
283K
278K
3.0
2.5
2.0
1.5
1.0
0.5
0.0
ppm

Figure S9 ^{1}H NMR spectra of **6b'** in CD_2Cl_2 from 278 K to 313K

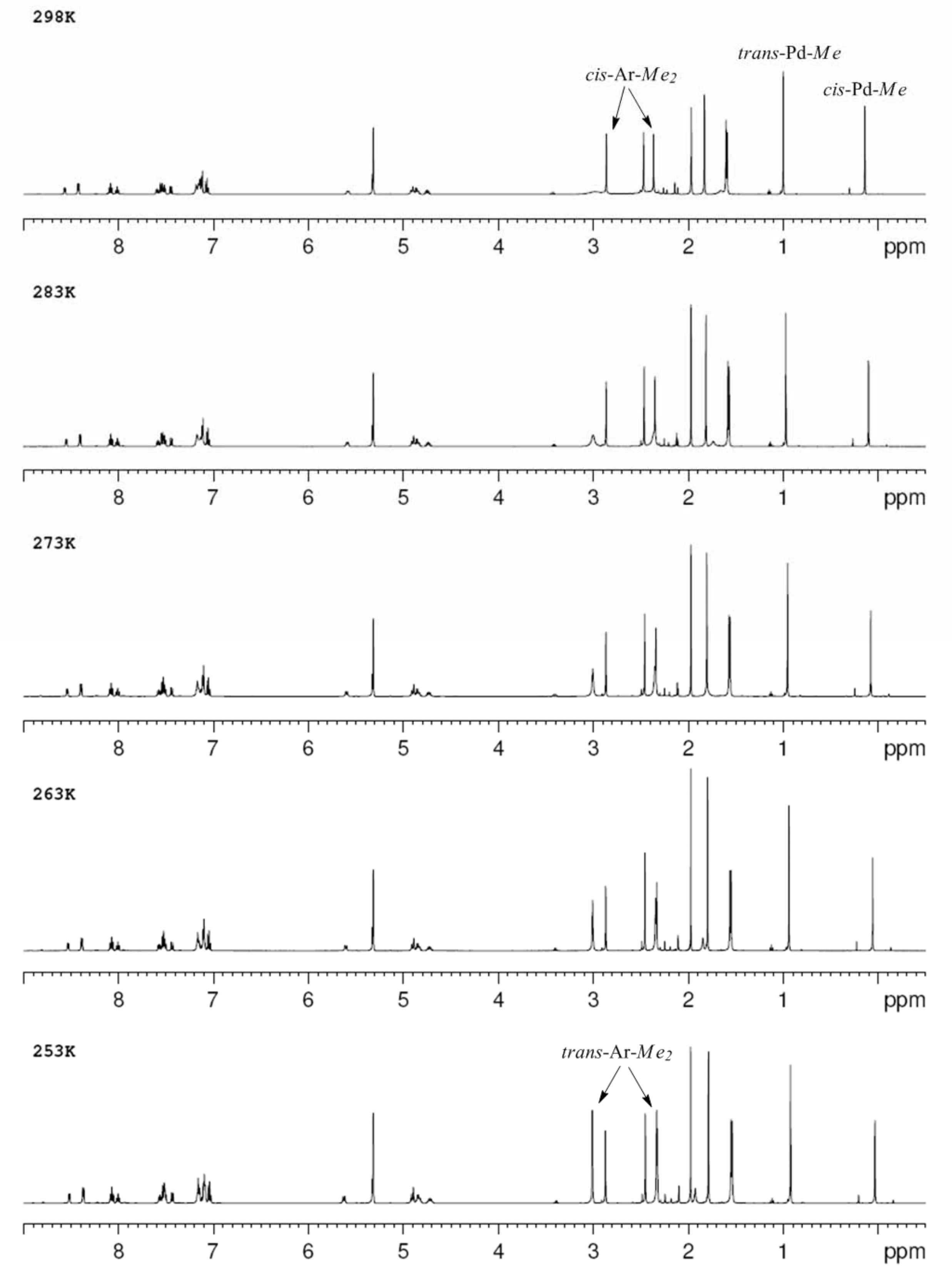


Figure S10 ^{1}H NMR spectra of **6b'** in CD_2Cl_2 from 253 K to 298K

Table S5 X-ray crystal parameters and data collection

Compound	*trans*-**4a**	*trans*-**5a**	*cis*-**6a**	*cis*-**4b**	*cis*-**6b**
Formula	$C_{11}H_{19}ClN_2Pd$	$C_{13}H_{15}ClN_2Pd$	$C_{15}H_{19}ClN_2Pd$	$C_{12}H_{21}ClN_2Pd$	$C_{16}H_{21}ClN_2Pd$
Formular wt	321.13	341.12	369.17	335.16	383.20
Crystal size / mm	0.25×0.20×0.15	0.25×0.25×0.20	0.30×0.25×0.20	0.30×0.25×0.20	0.30×0.25×0.20
Crystal system	Monoclinic	Triclinic	Triclinic	Orthorhombic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_12_12_1$	$P\bar{1}$
a / Å	9.1813(2)	8.2253(2)	8.4240(3)	9.1900(1)	8.3247(1)
b / Å	7.0402(1)	9.1194(2)	9.6334(3)	10.1268(1)	9.6563(1)
c / Å	20.5243(3)	10.6977(2)	10.8944(4)	15.3491(2)	10.8820(1)
α / °	90	93.887(1)	110.517(2)	90	108.680(1)
β / °	95.1410(9)	110.902(1)	105.171(2)	90	101.983(1)
γ / °	90	113.454(1)	98.641(2)	90	93.616(1)
V / Å^3	1321.32(4)	666.77(3)	770.00(5)	1428.47(3)	802.66(2)
Z	4	2	2	4	2
ρ_{calcd} / Mg·m^{-3}	1.614	1.699	1.592	1.558	1.586
$F(000)$	648	340	372	680	388
T / K	295(2)	295(2)	295(2)	295(2)	295(2)
μ / mm^{-1}	1.579	1.571	1.367	1.464	1.314
Transmission	0.732-0.792	0.654-0.731	0.520-0.767	0.732-0.804	0.651-0.773
θ range / °	1.99~27.50	2.10~27.45	3.63~27.46	2.41~27.46	2.84~27.50
h, k, l	±11, ±9, ±26	±10, ±11, ±13	±10, ±12, -13~14	±11, ±13, -16~19	±10, ±12, ±14
Reflections collected	10638	5239	5884	9298	6809
Indepent reflections	3021	3008	3469	3239	3657
R_{int}	0.0270	0.0207	0.0463	0.0226	0.0183
Data / restraints	3021/0	3008/0	3469/0	3239/0	3657/0
Parameters	141	159	177	146	186
R_1 [I>2 σ (I)]	0.0226	0.0278	0.0393	0.0156	0.0209
wR_2 [I>2 σ (I)]	0.0517	0.0668	0.0970	0.0419	0.0603
R_1 (all data)	0.0293	0.0325	0.0484	0.0185	0.0219
wR_2 (all data)	0.0548	0.0697	0.1034	0.0466	0.0614
Goodness of fit on F^2	1.049	1.038	1.010	1.094	0.941
Largest diff. peak and hole, eÅ^{-3}	0.369 and -0.366	0.392 and -0.442	0.656 and -0.869	0.498 and -0.617	0.404 and -0.457

Compound	*cis*-**7b**	*cis*-**3a'**	*trans*-**4a'**	*trans*-**5a'**	*trans*-**4b'**
Formula	$C_{20}H_{29}ClN_2Pd$	$C_{12}H_{20}BF_4N_3Pd$	$C_{13}H_{22}BF_4N_3Pd$	$C_{15}H_{18}BF_4N_3Pd$	$C_{14}H_{24}BF_4N_3Pd$
Formular wt	439.30	399.52	413.55	433.53	427.57
Crystal size / mm	0.20×0.20×0.15	0.25×0.20×0.10	0.30×0.25×0.20	0.25×0.20×0.20	0.20×0.20×0.15
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$C2/c$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a / Å	24.5827(4)	7.5470(2)	7.6329(1)	9.9543(2)	11.6589(2)
b / Å	9.6041(2)	11.2769(2)	12.1420(3)	9.4463(2)	7.3818(2)
c / Å	17.4202(3)	11.2845(2)	20.1943(5)	18.9653(3)	22.3551(6)
α / °	90	62.790(1)	90	90	90
β / °	93.369(1)	78.055(1)	99.206(1)	102.237(1)	100.554(1)
γ / °	90	78.412(1)	90	90	90
V / Å^3	4105.7(1)	829.36(3)	1847.47(7)	1742.81(6)	1891.41(8)
Z	8	2	4	4	4
ρ_{calcd} / Mg·m^{-3}	1.421	1.600	1.487	1.652	1.502
$F(000)$	1808	400	832	864	864
T / K	295(2)	295(2)	295(2)	295(2)	295(2)
μ / mm^{-1}	1.038	1.153	1.038	1.105	1.017
Transmission	0.821-0.857	0.722-0.892	0.723-0.812	0.720-0.784	0.795-0.864
θ range / °	1.66~27.48	2.05~27.44	1.96~27.47	2.09~27.47	1.78~27.47
h, k, l	±31, ±12, -21~22	±9, -13~14, ±14	±9, ±15, ±26	±12, ±12, -22~24	±15, ±9, -28~29
Reflections collected	12879	6276	10140	10796	13190
Indepent reflections	4667	3711	4044	3966	4270
R_{int}	0.0273	0.0289	0.0249	0.0285	0.0411
Data / restraints	4667/0	3711/0	4404/0	3966/0	4270/0

Parameters	222	191	204	222	209
R_1 [I>2 σ (I)]	0.0313	0.0605	0.0456	0.0299	0.0553
wR_2 [I>2 σ (I)]	0.0715	0.1658	0.1305	0.0646	0.1530
R_1 (all data)	0.0506	0.0702	0.0556	0.0478	0.0841
wR_2 (all data)	0.0798	0.1804	0.1441	0.0724	0.1829
Goodness of fit on F^2	1.019	1.123	1.101	1.028	1.054
Largest diff. peak and hole, eÅ^{-3}	0.493 and -0.491	1.115 and -0.677	1.287 and -0.804	0.574 and -0.461	0.995 and -0.562

Table S6 Selected bond distances (Å) and angles (^{o})

[^{t}BuHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*trans*-**4a**)							
Pd-N1	2.038 (2)	Pd-N2	2.202 (2)	Pd-C1	2.032 (2)	Pd-Cl1	2.3150 (6)
N1-C6	1.348 (3)	N2-C7	1.470 (3)	C6-C7	1.503 (3)	N2-C8	1.510 (3)
N1-Pd-N2	80.52 (7)	C1-Pd-Cl1	88.37 (8)	Pd-N1-C6	114.3 (1)	Pd-N2-C7	101.8 (1)
N1-C6-C7	115.8 (2)	N2-C7-C6	111.8 (2)	C8-N2-Pd	123.5 (1)	C8-N2-C7	115.6 (2)
[PhHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*trans*-**5a**)							
Pd-N1	2.055 (2)	Pd-N2	2.212 (2)	Pd-C1	2.015 (3)	Pd-Cl1	2.3065 (7)
N1-C6	1.349 (4)	N2-C7	1.468 (4)	C6-C7	1.510 (4)	N2-C8	1.438 (4)
N1-Pd-N2	80.56 (9)	C1-Pd-Cl1	88.57 (9)	Pd-N1-C6	114.1 (2)	Pd-N2-C7	103.0 (2)
N1-C6-C7	116.8 (2)	N2-C7-C6	112.2 (2)	C8-N2-Pd	111.1 (2)	C8-N2-C7	117.6 (2)
[(2,6-Me$_2$C$_6$H$_3$)HNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*cis*-**6a**)							
Pd-N1	2.138 (3)	Pd-N2	2.109 (3)	Pd-C1	2.021 (4)	Pd-Cl1	2.3152 (9)
N1-C6	1.340 (5)	N2-C7	1.490 (5)	C6-C7	1.504 (5)	N2-C8	1.455 (5)
N1-Pd-N2	81.0 (1)	C1-Pd-Cl1	88.7 (1)	Pd-N1-C6	114.3 (2)	Pd-N2-C7	111.8 (2)
N1-C6-C7	118.2 (3)	N2-C7-C6	114.2 (3)	C8-N2-Pd	117.5 (3)	C8-N2-C7	113.7 (3)
[^{t}BuHNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*cis*-**4b**)							
Pd-N1	2.143 (2)	Pd-N2	2.105 (2)	Pd-C1	2.021 (2)	Pd-Cl1	2.3172 (5)
N1-C6	1.335 (3)	N2-C7	1.492 (2)	C6-C7	1.511 (3)	N2-C9	1.527 (3)
N1-Pd-N2	79.75 (7)	C1-Pd-Cl1	90.21 (7)	Pd-N1-C6	111.7 (1)	Pd-N2-C7	103.8 (1)
N1-C6-C7	115.7 (2)	N2-C7-C6	110.2 (2)	C9-N2-Pd	116.4 (1)	C9-N2-C7	116.0 (2)
[(2,6-Me$_2$C$_6$H$_3$)HNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*cis*-**6b**)							
Pd-N1	2.132 (2)	Pd-N2	2.101 (2)	Pd-C1	2.034 (2)	Pd-Cl1	2.3140 (5)
N1-C6	1.341 (3)	N2-C7	1.503 (3)	C6-C7	1.512 (3)	N2-C9	1.457 (2)
N1-Pd-N2	80.62 (6)	C1-Pd-Cl1	89.04 (7)	Pd-N1-C6	114.6 (1)	Pd-N2-C7	112.3 (1)
N1-C6-C7	117.7 (2)	N2-C7-C6	111.9 (2)	C9-N2-Pd	117.6 (1)	C9-N2-C7	111.7 (2)
[(2,6-^{i}Pr$_2$C$_6$H$_3$)HNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)Cl (*cis*-**7b**)							
Pd-N1	2.115 (2)	Pd-N2	2.098 (2)	Pd-C1	2.075 (2)	Pd-Cl1	2.3124 (7)
N1-C6	1.346 (3)	N2-C7	1.511 (3)	C6-C7	1.519 (3)	N2-C9	1.462 (3)
N1-Pd-N2	80.77 (8)	C1-Pd-Cl1	89.23 (7)	Pd-N1-C6	115.5 (2)	Pd-N2-C7	113.0 (2)
N1-C6-C7	117.8 (2)	N2-C7-C6	111.8 (2)	C9-N2-Pd	116.7 (2)	C9-N2-C7	113.0 (2)
{[^{i}PrHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (*cis*-**3a**')							
Pd-N1	2.125 (4)	Pd-N2	2.042 (4)	Pd-C1	2.031 (6)	Pd-N3	2.008 (5)
N1-C6	1.326 (7)	N2-C7	1.470 (8)	C6-C7	1.517 (7)	N2-C8	1.548 (8)
N1-Pd-N2	81.7 (2)	C1-Pd-N3	89.9 (3)	Pd-N1-C6	112.7 (3)	Pd-N2-C7	109.0 (3)
N1-C6-C7	116.1 (4)	N2-C7-C6	112.8 (4)	C8-N2-Pd	109.7 (4)	C8-N2-C7	118.0 (5)
{[^{t}BuHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (*trans*-**4a'**)							
Pd-N1	2.034 (3)	Pd-N2	2.201 (3)	Pd-C1	2.022 (4)	Pd-N3	1.994 (4)
N1-C6	1.368 (5)	N2-C7	1.500 (5)	C6-C7	1.506 (6)	N2-C8	1.542 (6)
N1-Pd-N2	81.1 (1)	C1-Pd-N3	87.9 (2)	Pd-N1-C6	114.6 (2)	Pd-N2-C7	103.8 (2)
N1-C6-C7	117.1 (3)	N2-C7-C6	111.5 (3)	C8-N2-Pd	116.2 (3)	C8-N2-C7	117.5 (3)
{[PhHNCH$_2$(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (*trans*-**5a'**)							
Pd-N1	2.024 (2)	Pd-N2	2.185 (2)	Pd-C1	2.007 (3)	Pd-N3	1.993 (2)
N1-C6	1.355 (3)	N2-C7	1.470 (3)	C6-C7	1.495 (4)	N2-C8	1.434 (3)
N1-Pd-N2	80.80 (9)	C1-Pd-N3	88.3 (1)	Pd-N1-C6	114.6 (2)	Pd-N2-C7	104.2 (2)
N1-C6-C7	116.9 (2)	N2-C7-C6	112.2 (2)	C8-N2-Pd	110.9 (2)	C8-N2-C7	117.2 (2)
{[^{t}BuHNCMeH(*o*-C$_6$H$_5$N)]Pd(Me)(NCMe)}(BF$_4$) (*trans*-**4b'**)							
Pd-N1	2.032 (4)	Pd-N2	2.184 (4)	Pd-C1	2.020 (6)	Pd-N3	1.996 (5)
N1-C6	1.332 (6)	N2-C7	1.487 (6)	C6-C7	1.524 (7)	N2-C9	1.513 (7)
N1-Pd-N2	80.5 (2)	C1-Pd-N3	88.3 (2)	Pd-N1-C6	113.7 (3)	Pd-N2-C7	102.6 (3)
N1-C6-C7	117.6 (4)	N2-C7-C6	109.5 (4)	C9-N2-Pd	118.8 (3)	C9-N2-C7	115.9 (4)

Figure S11 ORTEP drawing of *trans*-**4a**, all hydrogen atoms are omitted for clarity.

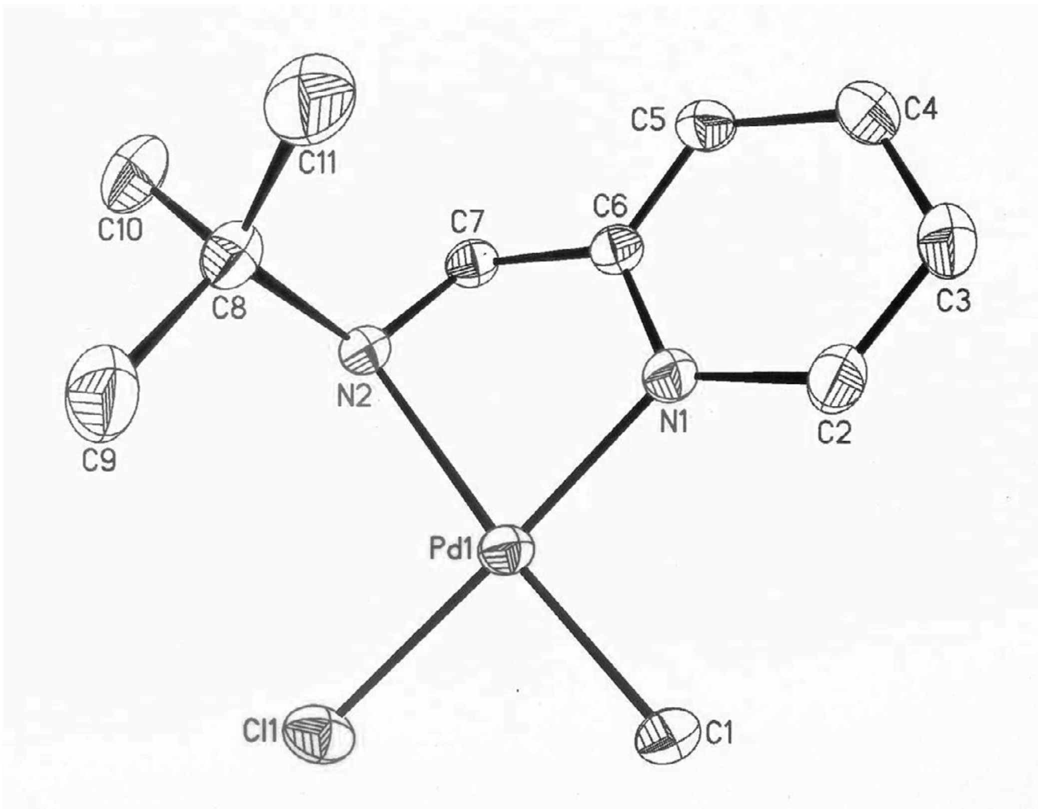


Figure S12 ORTEP drawing of *trans*-**5a**, all hydrogen atoms are omitted for larity.

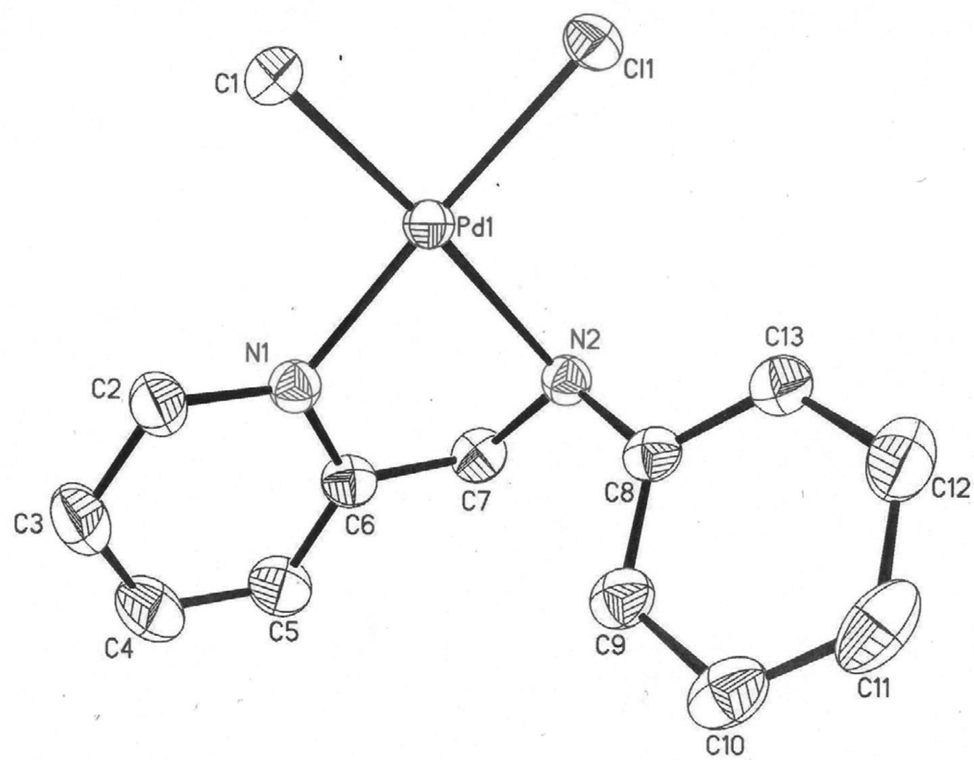


Figure S13 ORTEP drawing of *cis*-**6a**, all hydrogen atoms are omitted for clarity.

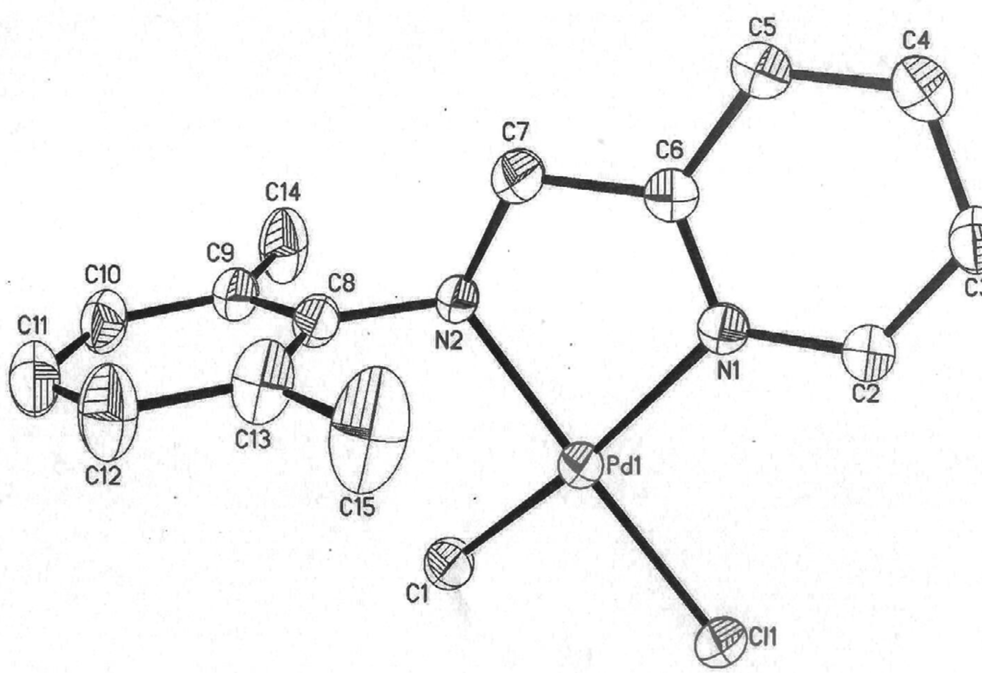


Figure S14 ORTEP drawing of *cis*-**4b**, all hydrogen atoms are omitted for clarity.

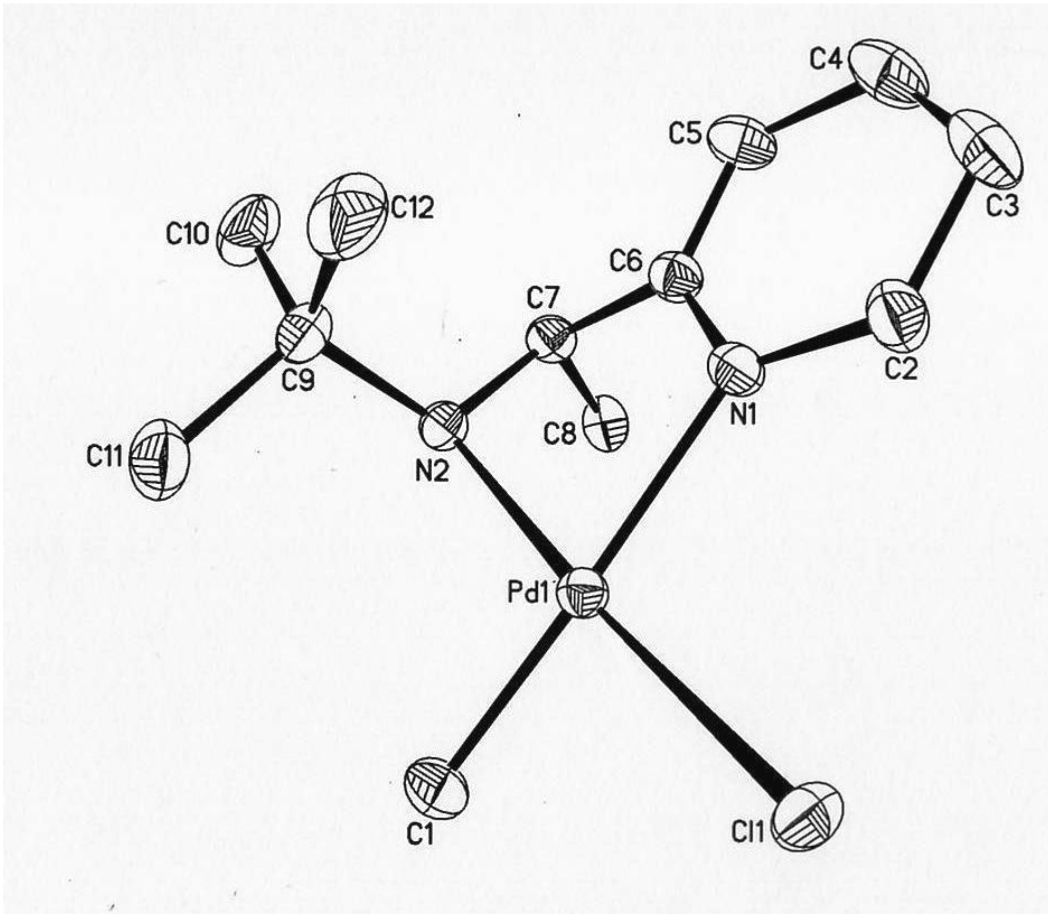


Figure S15 ORTEP drawing of *cis*-**6b**, all hydrogen atoms are omitted for clarity.

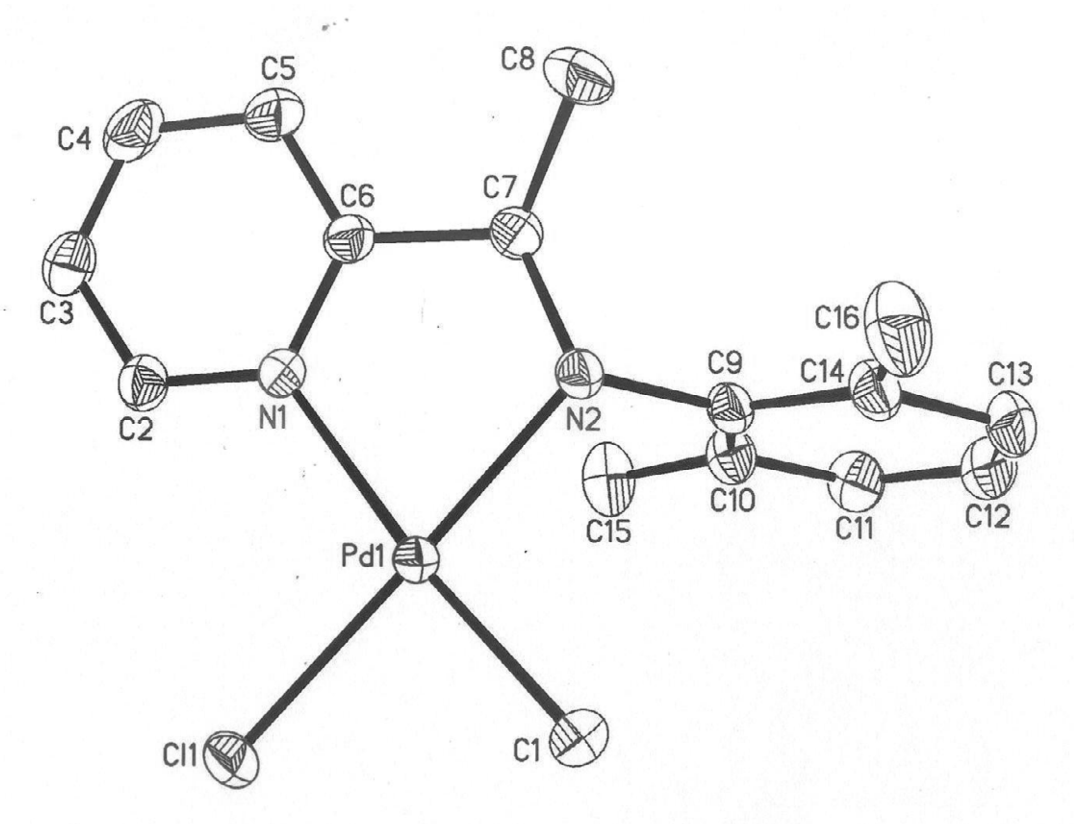


Figure S16 ORTEP drawing of *cis*-**7b**, all hydrogen atoms are omitted for clarity.

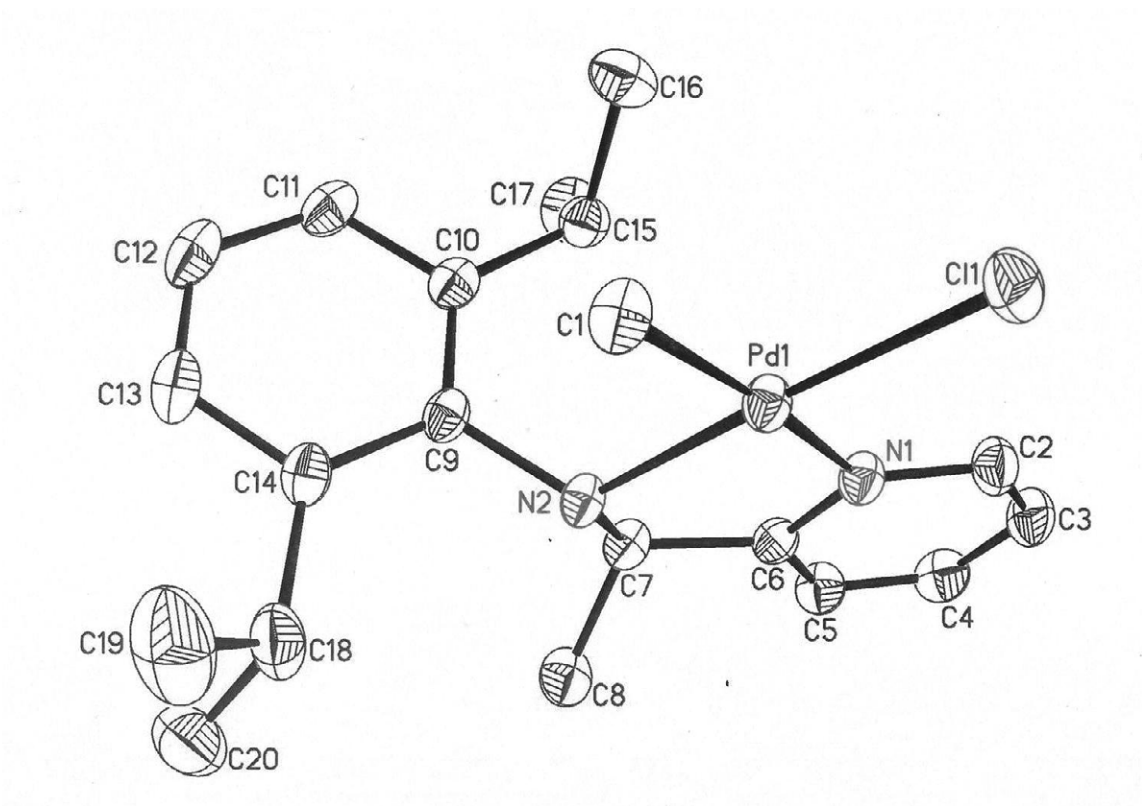


Figure S17 ORTEP drawing of *cis*-**3a'**, all hydrogen atoms are omitted for clarity.

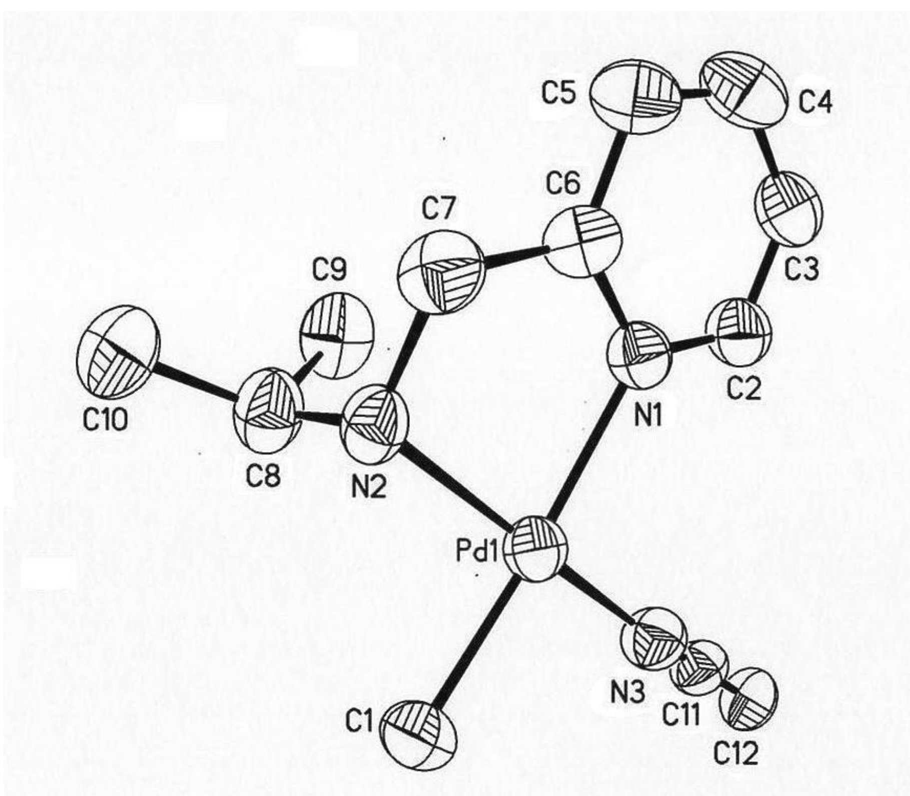


Figure S18 ORTEP drawing of *trans*-**4a'**, all hydrogen atoms are omitted for clarity.

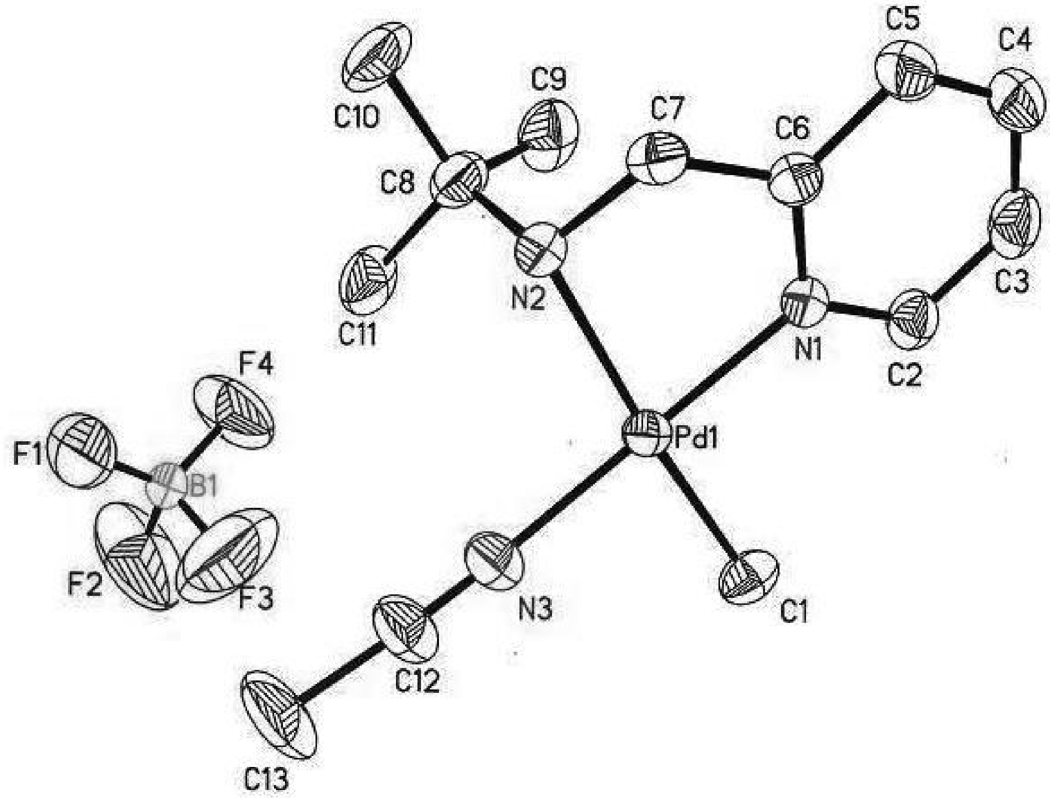


Figure S19 ORTEP drawing of *trans*-**5a'**, all hydrogen atoms are omitted for clarity.

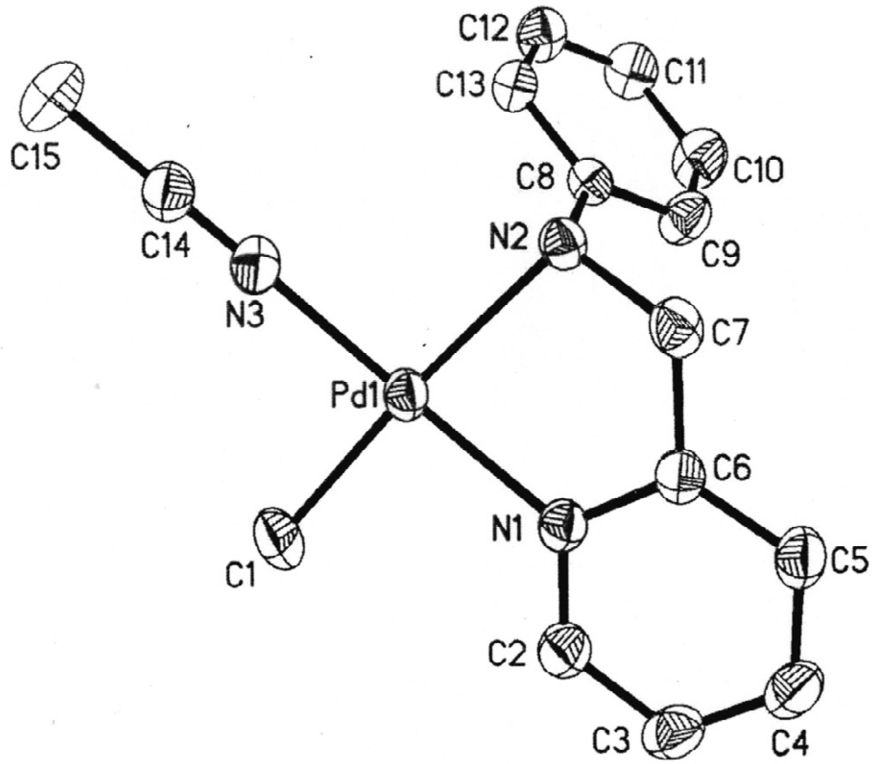


Figure S20 ORTEP drawing of *trans*-**4b'**, all hydrogen atoms are omitted for clarity.

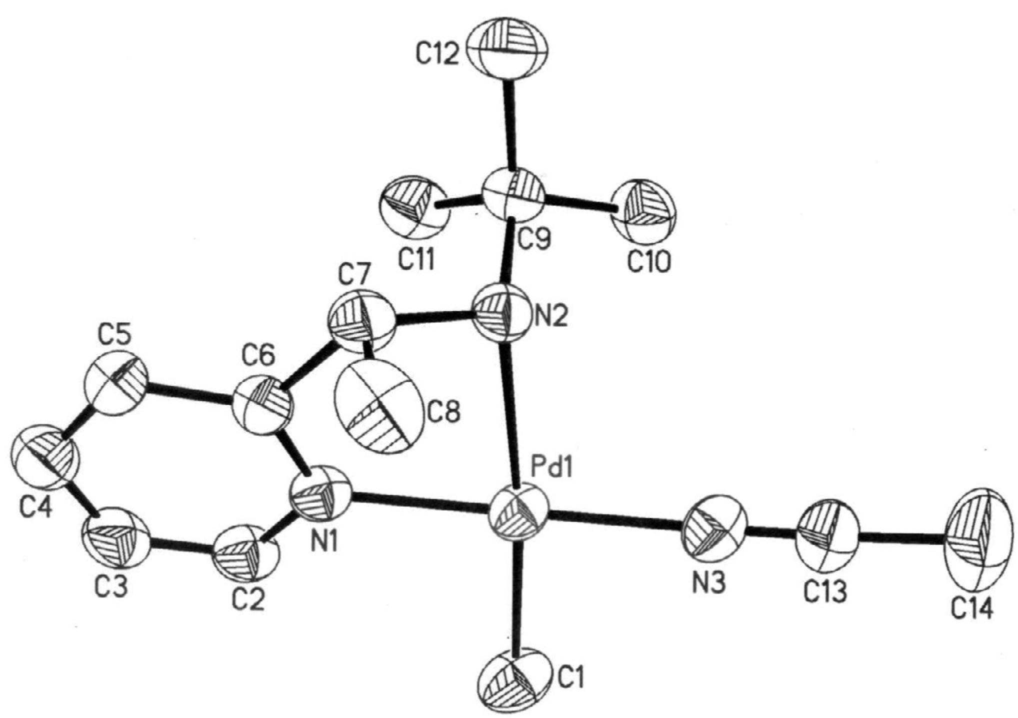


Figure S21 2D-NOSEY spectrum for **3b** in $CDCl_3$

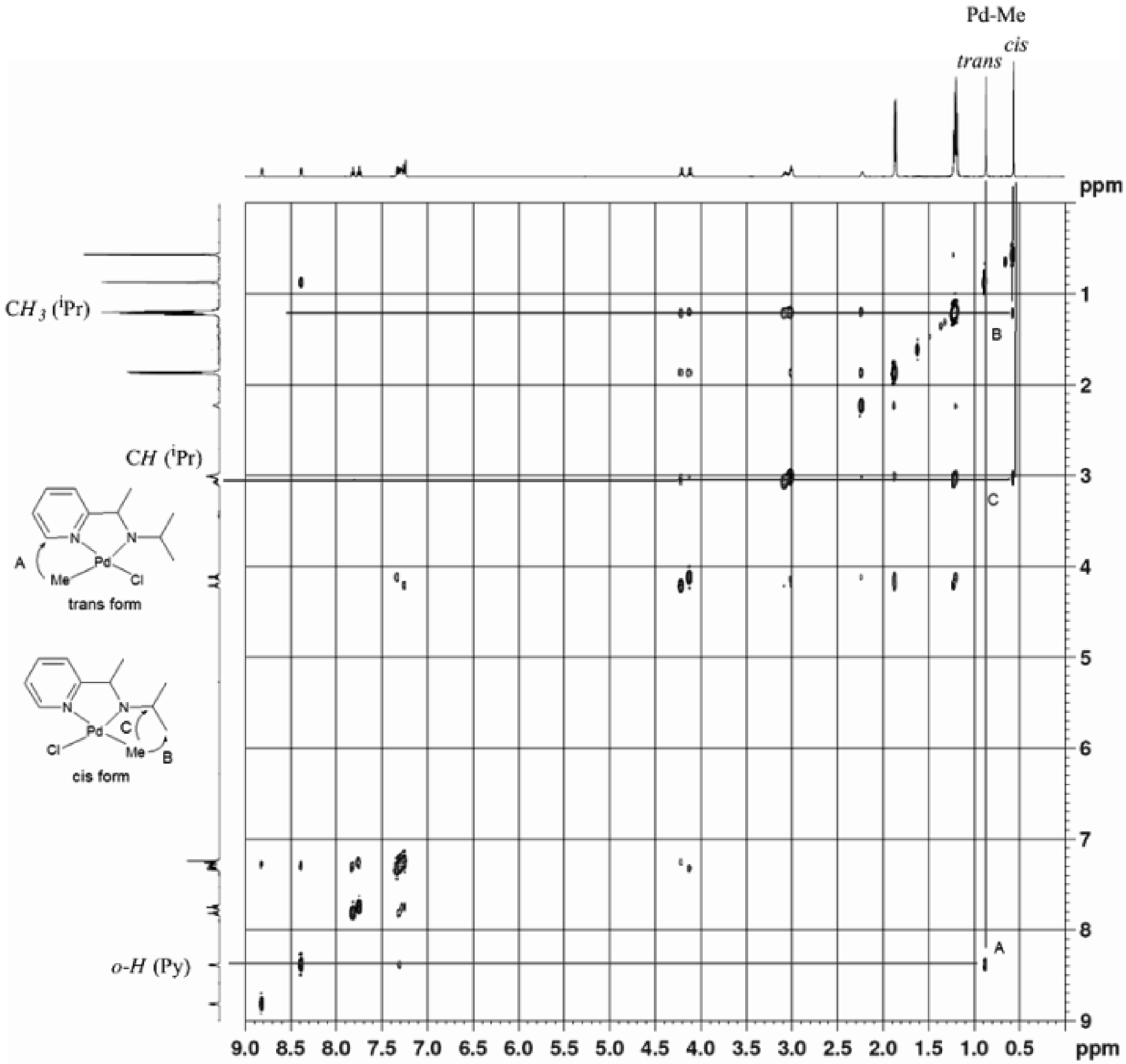
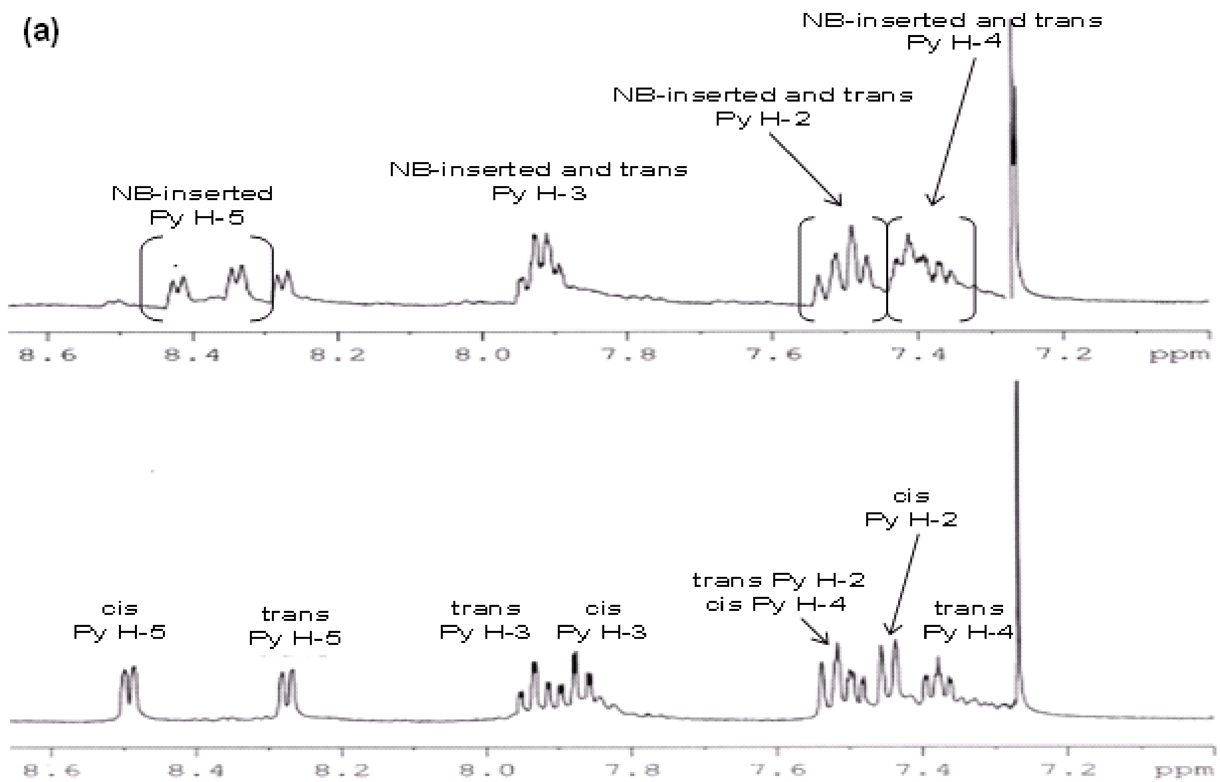
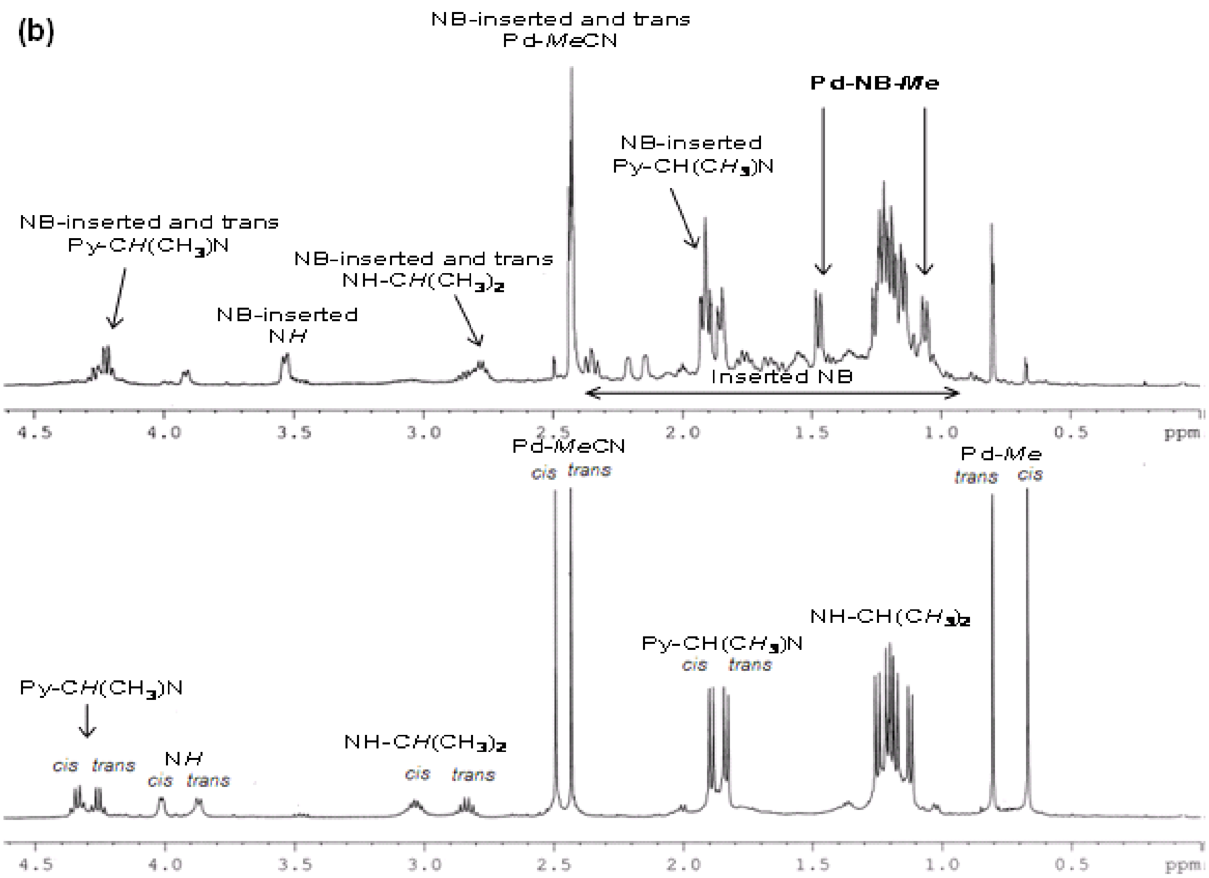


Figure S22 Comparative [1]H NMR spectrum of norbornene insertion into **3b’** in the regions of (a) 8.7 ~ 7 ppm and (b) 4.6 ~ 0 ppm.





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2. A. L. McKnight and R. M. Waymouth, *Macromolecules*, 1999, **32**, 2816-2825.
3. (a) M. Fineman and S. D. Ross, J. Polym. Sci., 1950, 5, 259-265; (b) M. P. Stevens, *Polymer Chemistry: An Introduction*, 3rd Edition, Oxford University Press, New York, 1999, p194.