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Supporting Information

Hydroamination of 1,1-Dimethylallene with Primary Aryl Amines Under Mild Conditions: An Atom-Economical Route to *N*-(1,1-Dimethyl-2-Propenyl)-Anilines

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General methods and instrumentation:

All manipulations involving lithium reagents were performed under an inert N_2 atmosphere using standard glove box and Schlenk techniques. Solvents were predried before use; THF and methylene chloride were passed through columns of 4Å molecular sieves and sparged with nitrogen. Pentane, diethyl ether, and toluene was passed through columns of activated alumina and 4 Å molecular sieves and sparged with nitrogen. Benzene-d_6 was dried over sodium metal, freeze-pump-thawed three times, and vacuum distilled and stored over 4 Å molecular sieves. Chloroform-d_1 was dried over calcium hydride, freeze-pump-thawed three times, and vacuum distilled and stored over 4 Å molecular sieves. Phosphorus oxychloride, *tert*-butylamine, cyclopentanone, dimethylformamide, and di-(tert-butyl)chlorophosphine were purchased commercially and used as received. Triflic acid was purchased from Acros Organics; silver triflate, *n*-butyl lithium and allylpalladium chloride dimer were purchased from Strem Chemicals, Inc.; and 3-methyl-1,2-butadiene (1,1-dimethylallene) was purchased from Sigma-Aldrich; and each was used as received. Anilines were purchased from Sigma-Aldrich or another commercial source and dried over calcium hydride, either neat (liquid anilines) or as solutions in methylene chloride (solid anilines). Liquid anilines were freeze-pump-thawed three times, and vacuum distilled. Solutions of solid anilines in methylene chloride were freeze-pump-thawed three times, filtered and the methylene chloride removed via reduced pressure. Silica gel (Porosity: 60 Å, Particle size 40-63 μm) was purchased from Sorbent Technologies and used as received. ^{1}H and ^{13}C NMR data were obtained on a 600 MHz Inova NMR or a 400 MHz VXRS NMR spectrometer at ambient temperature at 599.9 MHz for ^{1}H NMR and 150.8 MHz for ^{13}C NMR and 399.95 MHz for ^{1}H NMR and 100.56 MHz for ^{13}C NMR, respectively. All spectra were taken using C_6D_6 or $CDCl_3$ as the NMR solvent. ^{1}H NMR shifts are given relative to the

residual solvent resonances at 7.16 ppm and 7.26 ppm, respectively, and ^{13}C NMR shifts are given relative to C_6D_6 (128.1 ppm) and $CDCl_3$ (77.16 ppm). ^{31}P NMR spectra were externally referenced to 0.00 ppm with 5% H_3PO_4 in D_2O. Unless otherwise noted, all coupling constants are $^3J_{HH}$. IR samples were prepared as Nujol mulls and taken between KBr plates on a Perkin-Elmer XTL FTIR spectrophotometer. Melting points were observed on a capillary melting point (Uni-Melt) apparatus in sealed capillary tubes and are uncorrected. X-ray structure determinations were performed at The University of Notre Dame, Notre Dame, Indiana. Elemental analyses were determined by Atlantic Microlab, Inc., Norcross, GA. High resolution mass spectrometry, using electrospray ionization, was performed at the University of Illinois Mass Spectrometry Laboratory, Urbana, IL.

Catalyst Synthesis:

Compounds **1** and **2** were synthesized using existing literature methods.[1] LiP^tBu_2 was initially synthesized using a procedure analogous to that used for $LiPPh_2$;[2] however, the procedure of Schneider and coworkers was found to be superior.[3]

3IP^{tBu} (3):

A Schlenk flask was charged with **2** (0.86 g, 4.6 mmol) and 40 ml of diethyl ether was added via cannula. The reaction was cooled to 0 °C. A second Schlenk flask was charged in a nitrogen filled glove box with LiP^tBu_2 (0.741 g, 4.87 mmol). Diethyl ether (30 ml) was added, causing the white solid to completely dissolve. The LiP^tBu_2 solution was then transferred via cannula to the rapidly stirring solution of **2**. The reaction was allowed to stir for 2 hours at 0 °C, during which time a white precipitate appeared. The solvent was then removed via reduced pressure and **3** was

extracted from the dark red semi-solid mass with pentane (2 x 25 ml). Removal of solvent under vacuum yielded **3** as a red liquid (0.92 g, 68%). ^{1}H NMR ($CDCl_3$): δ 8.88 (d, $^{4}J_{PH}$ = 6.0 Hz, 1H), 2.87-2.84 (m, 2H), 2.68-2.66 (m, 2H), 1.85 (pseudo pent, $^{3}J_{HH}$ = 7.8 Hz, $^{3}J_{HH}$ = 7.2 Hz, 2H), 1.22 (s, 9H), 1.18 (d, $^{3}J_{PH}$ = 12.0 Hz, 18H); $^{13}C^{[4]}$ NMR ($CDCl_3$): δ 155.2 (d, $^{3}J_{PC}$ = 19.8 Hz), 155.0 (d, $^{2}J_{PC}$ = 28.4 Hz), 147.1 (d, $^{1}J_{PC}$ = 34.7 Hz), 57.4, 39.7 (d, $^{2}J_{PC}$ = 6.6 Hz), 33.0 (d, $^{3}J_{PC}$ = 5.8 Hz), 32.8 (d, $^{1}J_{PC}$ = 19.8 Hz), 30.8 (d, $^{2}J_{PC}$ = 14.0 Hz), 30.2, 23.7 (br); $^{31}P^{[4]}$ NMR ($CDCl_3$): δ 13.2; IR: 2953 (s), 2900 (s), 2848 (w), 2712 (w), 1654 (m), 1618 (m), 1560 (w), 1467 (m), 1388 (w), 1361 (m), 1330 (w), 1298 (m), 1257 (m), 1215 (m), 1173 (m), 1094 (m), 1068 (m), 1016 (m), 963 (w), 927 (w), 895 (w), 854 (w), 802 (m), 655 (w), 608 (m); $HRMS_{calc.}$: 295.2429 for $C_{18}H_{34}NP$; $HRMS_{meas.}$: 295.2416.

(3IP^{tBu})Pd(allyl)Cl (4):

A Schlenk flask was charged in a nitrogen filled glove box with **3** (0.92 g, 3.1 mmol), and dichloromethane (30 ml) was added via cannula. A second Schlenk flask was charged in a nitrogen filled glove box with $[Pd(allyl)Cl]_2$ (0.57 g, 1.6 mmol), and dichloromethane (20 ml) was added via cannula, causing the yellow solid to dissolve completely. The $[Pd(allyl)Cl]_2$ solution was then transferred via cannula to the stirring solution of **3**. The reaction was allowed to stir for 1 hour. The solvent was then removed via reduced pressure, and the solid was extracted with pentane (2 x 35 ml) yielding **4** as a light brown solid after removal of pentane under vacuum (0.93 g, 62%). ^{1}H NMR ($CDCl_3$): δ 9.36 (v. br. s., 1H), 5.38-5.31 (m, 1H), 4.60 (v. br. s., 2H), 3.60 (v. br. s., 2H), 2.99-2.96 (m, 2H), 2.79-2.76 (m, 2H), 1.91-1.88 (m, 2H), 1.41 (d, $^{3}J_{PH}$ = 14.4 Hz, 18H), 1.18 (s, 9H); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): δ 155.6 (d, $^{3}J_{PC}$ = 9.6 Hz), 153.7 (d, $^{1}J_{PC}$ = 13.7 Hz), 139.7 (v. br.), 115.4 (d, $^{2}J_{PC}$ = 18.6 Hz), 80.4 (d, $^{2}J_{PC}$ = 27.7 Hz), 58.2, 57.9

(v. br.), 40.8 (d, $^{3}J_{PC}$ = 7.2 Hz), 33.4 (d, $^{2}J_{PC}$ = 37.2 Hz), 31.0 (v. br.), 30.5 (v. br.), 29.9, 23.3 (d, $^{3}J_{PC}$ = 16.8 Hz); $^{31}P\{^{1}H\}$ NMR ($CDCl_3$): δ 42.7 (v. br.); IR: 1610 (m), 1557 (s), 1460 (s), 1366 (s), 1261 (w), 1208 (m), 1176 (m), 1062 (w), 1020 (w), 954 (w), 905 (w), 807 (m), 723 (w); $HRMS_{calc}$: 442.1855 for $C_{21}H_{39}NPPd$ $[M - Cl]^{+}$; $HRMS_{meas}$: 442.1859. Melting point: 106 °C dec.

[(3IP^{tBu})Pd(allyl)]OTf (5):

Method one: A Schlenk flask was charged in a nitrogen filled glove box with both **4** (0.52 g, 1.1 mmol) and AgOTf (0.28 g, 1.1 mmol), and on a Schlenk line, dichloromethane (30 ml) was added via cannula, causing a gray precipitate to form immediately. The reaction mixture was filtered to remove AgCl, and the filtrate was pumped down to an oily solid. Then, the solution was washed with 30 ml of pentane. Upon removal of residual pentane under vacuum a brown solid **(5)** was isolated (0.49 g, 77%). An analytically pure sample was recrystallized from a THF solution layered with pentane. **Method two:** A Schlenk flask was charged in a nitrogen filled glove box with both **3** (0.40 g, 1.4 mmol) dissolved in 15 ml of dichloromethane and $[Pd(allyl)Cl]_2$ (0.25 g, 0.68 mmol) dissolved in dichloromethane (20 ml). After swirling the Schlenk flask to ensure complete mixing, a solution of AgOTf (0.36 g, 1.4 mmol) in 20 ml of dichloromethane/toluene (3:1) was added causing a gray precipitate to form immediately. The reaction was filtered and the solvent was removed under reduced pressure. The residue was dissolved in a minimal amount of THF and layered with pentane. After cooling to –30 °C, compound **5** was isolated as a brown crystalline solid (0.51 g, 64%). ^{1}H NMR showed no difference in purity compared to that obtained after recrystallization utilizing method one.

^{1}H NMR ($CDCl_3$): δ 8.06 (d, $^{4}J_{PH}$ = 2.4 Hz, 1H), 5.61-5.54 (m, 1H), 5.26-5.23 (m, 1H), 3.99-3.94 (m, 2H), 3.09-3.04 (m, 2H), 2.91-2.89 (m, 2H), 2.62 (d, 11.4 Hz, 1H), 2.03-1.98 (m, 2H), 1.41 (d, $^{3}J_{PH}$ = 14.1 Hz, 9H), 1.40 (s, 9H), 1.24 (d, $^{3}J_{PH}$ = 14.1 Hz, 9H); ^{13}C{^{1}H} NMR ($CDCl_3$): δ 162.0 (d, $^{3}J_{PC}$ = 2.4 Hz), 156.2 (d, $^{2}J_{PC}$ = 13.6 Hz), 134.8 (d, $^{1}J_{PC}$ = 15.3 Hz), 119.1 (d, $^{2}J_{PC}$ = 5.3 Hz), 87.6 (d, $^{2}J_{PC}$ = 25.8 Hz), 65.4, 50.3, 40.1, 39.3 (d, $^{1}J_{PC}$ = 13.4 Hz), 38.2 (d, $^{2}J_{PC}$ = 10.3 Hz), 37.8 (d, $^{1}J_{PC}$ = 16.2 Hz), 30.8 (d, $^{2}J_{PC}$ = 6.4 Hz), 30.7 (d, $^{2}J_{PC}$ = 5.8 Hz), 30.4, 23.8 (d, $^{3}J_{PC}$ = 3.4 Hz);[5] ^{31}P{^{1}H} NMR ($CDCl_3$): δ 61.8; IR: 1614 (w), 1459 (s), 1372 (m), 1258 (s), 1150 (m), 1090 (m), 1025 (s), 800 (w). Anal. for $C_{22}H_{39}F_3NO_3PPdS$ (592.01 g/mol): C 44.63, H 6.64, N 2.37; found C 44.46, H 6.61, N 2.38. Melting point: 138-139 °C.

General procedure for catalytic hydroamination of 1,1-dimethylallene:

All manipulations were performed in a nitrogen filled glove box. To a solution of **[(3IP^{tBu})Pd(allyl)]OTf** (14.8 mg, 5 mol%) in 0.8 ml of benzene-d_6, an aniline (0.5 mmol) was added, followed by 1,1-dimethylallene (68 mg, 1.0 mmol). The reaction was allowed to stand for 12 to 20 hours. The conversion of anilines to the product *N*-(1,1-dimethyl-2-propenyl)-anilines was measured via ^{1}H NMR spectroscopy. In all cases, the hydroamination reaction produced only the *N*-(1,1-dimethyl-2-propenyl)-aniline derivative and no aniline-based side products were detected, inferring a close relationship between yield and conversion. The products were purified via column chromatography (silica gel; 5:1 pentane/ethyl acetate) to remove the catalyst residue and any unreacted anilines prior to the final ^{1}H and ^{13}C{^{1}H} NMR analysis, as reported herein. These purified hydroamination products were also subjected to mass spectral analysis.

Characterization of hydroamination products:

N-(1,1-Dimethyl-2-propenyl)-aniline **(1a)**,[6] *N*-(1,1-dimethyl-2-propenyl)-3-methyl-aniline **(2a)**,[7] *N*-(1,1-dimethyl-2-propenyl)-4-methyl-aniline **(4a)**,[7] *N*-(1,1-dimethyl-2-propenyl)-3-methoxy-aniline **(7a)**,[7] *N*-(1,1-dimethyl-2-propenyl)-4-methoxy-aniline **(8a)**,[7] *N*-(1,1-dimethyl-2-propenyl)-3-chloro-aniline **(11a)**,[7] *N*-(3-methyl-2-butenyl)-3-chloro-aniline **(11b)**,[7] *N*-(1,1-dimethyl-2-propenyl)-4-chloro-aniline **(12a)**,[8] and *N*-(3-methyl-2-butenyl)-4-chloro-aniline **(12b)**[9] were identified by comparison to published NMR data.

***N*-(1,1-dimethyl-2-propenyl)-3-ethyl-aniline (3a)**

^{1}H NMR (C_6D_6): δ 7.12 (t, 7.9 Hz, 1H), 6.63 (d, 7.9 Hz, 1H), 6.58 (d, 7.9 Hz, 1H), 6.50 (s, 1H), 5.92 (dd, 14.6 Hz, 10.4 Hz, 1H), 5.12 (dd, 14.6 Hz, $^2J_{HH}$ = 1.2 Hz, 1H), 4.98 (dd, 10.4 Hz, $^2J_{HH}$ = 1.2 Hz, 1H), 3.34 (s, 1H), 2.51 (q, 7.6 Hz, 2H), 1.18 (t, 7.6 Hz, 3H), 1.15 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6): δ 147.2, 146.8, 144.9, 129.1, 117.6, 115.9, 113.6, 112.5, 54.5, 29.6, 28.3, 16.0; $HRMS_{calc}$: 190.1596 for $C_{13}H_{20}N$ $[M + H]^+$; $HRMS_{meas}$: 190.1599.

***N*-(1,1-dimethyl-2-propenyl)-3,4-dimethyl-aniline (5a)**

^{1}H NMR (C_6D_6): δ 6.91 (d, 10.5 Hz, 1H), 6.63 (dd, 10.5 Hz, $^4J_{HH}$ = 2.4 Hz, 1H), 6.56 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 5.98 (dd, 17.6 Hz, 13.5 Hz, 1H), 5.10 (dd, 17.6 Hz, $^2J_{HH}$ = 0.8 Hz, 1H), 4.98 (dd, 13.5 Hz, $^2J_{HH}$ = 0.8 Hz, 1H), 3.80 (s, 1H), 2.07 (s, 3H), 2.05 (s, 3H), 1.18 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6): δ 146.7, 144.4, 136.9, 130.4, 126.9, 119.6, 115.4, 113.0, 55.7, 28.3, 20.4, 19.1; $HRMS_{calc}$: 190.1596 for $C_{13}H_{20}N$ $[M + H]^+$; $HRMS_{meas}$: 190.1597.

_N_-(1,1-dimethyl-2-propenyl)-4-_tert_-butylaniline (6a)

^{1}H NMR (C_6D_6): δ 7.12 (d, 8.8 Hz, 2H), 6.61 (d, 8.8 Hz, 2H), 5.87 (dd, 17.2 Hz, 10.4 Hz, 1H), 5.07 (dd, 17.2 Hz, $^{2}J_{HH}$ = 1.6Hz, 1H), 4.94 (dd, 10.4 Hz, $^{2}J_{HH}$ = 1.6 Hz, 1H), 3.24 (br s, 1H), 1.22 (s, 6H), 1.10 (s, 9H); ^{13}C{^{1}H} NMR (C_6D_6): δ 147.0, 144.7, 140.2, 125.8, 116.2, 112.4, 54.6, 34.0, 31.9, 28.4; $HRMS_{calc}$: 218.1909 for $C_{15}H_{24}N$ $[M + H]^+$; $HRMS_{meas}$: 218.1907.

_N_-(1,1-dimethyl-2-propenyl)-4-methylthio-aniline (9a)

^{1}H NMR (C_6D_6): 7.20 (d, 8.7 Hz, 2H), 6.53 (d, 8.7 Hz, 2H), 5.82 (dd, 17.6 Hz, 10.8 Hz, 1H), 5.05 (dd, 17.6 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 4.95 (dd, 10.8 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 3.44 (s, 1H), 2.14 (s, 3H), 1.09 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6): δ 146.2, 131.2, 126.4, 125.3, 116.7, 112.8, 54.5, 28.2, 18.9; $HRMS_{calc}$: 208.1161 for $C_{12}H_{18}NS$ $[M + H]^+$; $HRMS_{meas}$: 208.1160.

_N_-(1,1-dimethyl-2-propenyl)-4-dimethylamino-aniline (10a)

^{1}H NMR (C_6D_6): δ 6.76 (d, 8.9 Hz, 2H), 6.63 (d, 8.9 Hz, 2H), 6.00 (dd, 17.9 Hz, 10.8 Hz, 1H), 5.11 (dd, 17.9 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 4.98 (dd, 10.8 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 2.99 (br s, 1H), 2.58 (s, 6H), 1.18 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6): δ 147.6, 145.5, 138.4, 120.5, 114.9, 112.0, 55.3, 41.7, 28.3; $HRMS_{calc}$: 205.1705 for $C_{13}H_{21}N_2$ $[M + H]^+$; $HRMS_{meas}$: 205.1703.

_N_-(1,1-dimethyl-2-propenyl)-3-fluoro-aniline (13a)

^{1}H NMR (C_6D_6): δ 6.87-6.84 (m, 1H), 6.40-6.38 (m, 1H), 5.95 (dd, 6.6 Hz, $^{3}J_{HF}$ = 2.4, 1H), 5.80 (dd, 6.6 Hz, $^{5}J_{HF}$ = 1.8 Hz, 1H), 5.42 (dd, 17.9 Hz, 10.8 Hz, 1H), 4.75 (dd, 17.9 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 4.65 (dd, 10.8 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 2.78 (s, 1H), 0.70 (s, 6H); ^{13}C{^{1}H} NMR (C_6D_6): δ 148.3 (d, $^{1}J_{CF}$ = 271.4 Hz), 144.3, 129.1 (d, $^{3}J_{CF}$ = 10.2 Hz), 111.6, 110.0 (d, $^{4}J_{CF}$ = 2.1 Hz),

107.5 (d, $^{3}J_{CF}$ = 2.4 Hz), 102.5 (d, $^{2}J_{CF}$ = 21.6 Hz), 101.9 (d, $^{2}J_{CF}$ = 25.8 Hz), 53.0, 26.5; $HRMS_{calc}$: 180.1189 for $C_{11}H_{15}FN$ $[M + H]^{+}$; $HRMS_{meas}$: 180.1190.

***N*-(1,1-dimethyl-2-propenyl)-4-fluoro-aniline (14a)**

^{1}H NMR (C_6D_6): δ 6.78 (t, 8.4 Hz, $^{3}J_{HF}$ = 8.4 Hz, 2H), 6.41 (dd, 8.4 Hz, $^{4}J_{HF}$ = 4.8 Hz, 2H), 5.80 (dd, 17.4 Hz, 10.2 Hz, 1H), 5.02 (dd, 17.4 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 4.93 (dd, 10.2 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 3.03 (s, 1H), 1.05 (s, 6H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 156.7 (d, $^{1}J_{CF}$ = 235.7 Hz), 146.4, 143.2 (d, $^{4}J_{CF}$ = 2.1 Hz), 117.6 (d, $^{3}J_{CF}$ = 7.1 Hz), 115.4 (d, $^{2}J_{CF}$ = 22.0 Hz), 112.7, 54.7, 28.1; $HRMS_{calc}$: 180.1189 for $C_{11}H_{15}FN$ $[M + H]^{+}$; $HRMS_{meas}$: 180.1189.

***N*-(1,1-dimethyl-2-propenyl)-4-bromo-3-methylaniline (15a)**

^{1}H NMR (C_6D_6): δ 7.22 (d, 8.9 Hz, 1H), 6.24 (d, $^{4}J_{HH}$ = 2.9 Hz, 1H), 6.17 (dd, 8.9 Hz, $^{4}J_{HH}$ = 2.9 Hz, 1H), 5.72 (dd, 17.4 Hz, 10.2 Hz, 1H), 4.96 (dd, 17.4 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 4.87 (dd, 10.2 Hz, $^{2}J_{HH}$ = 1.2 Hz, 1H), 3.10 (br s, 1H), 2.18 (s, 3H), 1.00 (s, 6H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 146.3, 145.9, 137.9, 132.6, 118.5, 115.1, 112.9, 112.3, 54.5, 28.1, 23.2; $HRMS_{calc}$: 254.0544 for $C_{12}H_{17}BrN$ $[M + H]^{+}$; $HRMS_{meas}$: 254.0542.

General catalytic procedure for aryl amino Claisen rearrangement:

After undergoing hydroamination for 20 hours (see above), the reaction was uncapped and triflic acid (7.5 mg, 10 mol%) was added. The reaction was then heated to 70 °C for 20 hours. The product was purified via column chromatography (silica gel; 5:1 pentane/ethyl acetate) and solvent was removed via reduced pressure.

Characterization of aryl amino Claisen rearrangement products:

2-(3-methyl-2-butenyl)-aniline **(1c)**[10] was identified by comparison to published NMR data. Compounds **(2c/d)** and **(3c/d)** were isolated as inseparable mixtures; the high resolution mass spectrometry data represent the mixtures of isomers.

2-(3-methyl-2-butenyl)-3-methyl-aniline (2c) and 2-(3-methyl-2-butenyl)-5-methyl-aniline (2d)[11]

(2c) ^{1}H NMR (C_6D_6): δ 6.96 (t, 7.2 Hz, 1H), 6.57 (d, 7.2 Hz, 1H), 6.31 (d, 7.2 Hz, 1H), 4.97 (tm, 6.6 Hz, 1H), 3.04 (d, 6.6 Hz, 2H), 2.13 (s, 3H), 1.55 (s, 3H), 1.54 (s, 3H); ^{13}C{^{1}H} NMR (C_6D_6): δ 145.2, 136.6, 132.7, 129.7, 124.7, 122.7, 119.6, 114.2, 30.8, 25.7, 20.3, 17.8. **(2d)** ^{1}H NMR (C_6D_6): δ 6.93 (d, 7.2 Hz, 1H), 6.63 (d, 7.2 Hz, 1H), 6.17 (s, 1H), 5.19 (tm, 6.6 Hz, 1H), 3.11 (d, 6.6 Hz, 2H), 2.13 (s, 3H), 1.51 (s, 3H), 1.50 (s, 3H); ^{13}C{^{1}H} NMR (C_6D_6): δ 145.5, 136.7, 132.3, 126.9, 123.1, 123.0, 121.1, 116.5, 27.0, 25.7, 20.3, 17.7; $HRMS_{calc}$: 176.1439 for $C_{12}H_{18}N$ $[M + H]^+$; $HRMS_{meas}$: 176.1439.

2-(3-methyl-2-butenyl)-3-ethyl-aniline (3c) and 2-(3-methyl-2-butenyl)-5-ethyl-aniline (3d)[12]

(3c) ^{1}H NMR (C_6D_6): δ 6.98 (t, 6.6 Hz, 1H), 6.64 (d, 6.6 Hz, 1H), 6.31 (d, 6.6 Hz, 1H), 5.00 (tm, 6.0 Hz, 1H), 3.16 (d, 6.0 Hz, 2H), 2.51 (q, 7.8 Hz, 2H), 1.55 (s, 3H), 1.51 (s, 3H), 1.08 (t, 7.8 Hz, 3H); ^{13}C{^{1}H} NMR (C_6D_6): δ 145.8, 143.2, 132.4, 127.1, 124.0, 123.4, 119.5, 114.1, 27.2, 26.5, 25.6, 17.8, 16.0. **(3d)** ^{1}H NMR (C_6D_6): δ 6.98 (d, 6.6 Hz, 1H), 6.69 (d, 6.6 Hz, 1H), 6.22 (s, 1H), 5.19 (tm, 6.0 Hz, 1H), 3.05 (d, 6.0 Hz, 2H), 2.44 (q, 7.8 Hz, 2H), 1.55 (s, 3H), 1.50 (s, 3H), 1.12

(t, 7.8 Hz, 3H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 145.2, 142.8, 132.6, 129.8, 123.2, 123.1, 118.3, 114.3, 30.8, 29.1, 25.7, 17.7, 16.2; $HRMS_{calc}$: 190.1596 for $C_{13}H_{20}N$ $[M + H]^+$; $HRMS_{meas}$: 190.1596

2-(3-methyl-2-butenyl)-4-methyl-aniline (4c)

^{1}H NMR (C_6D_6): δ 6.92 (s, 1H), 6.88 (d, 7.8 Hz, 1H), 6.40 (d, 7.8 Hz, 1H), 5.26 (tm, 6.6 Hz, 1H), 3.12 (d, 6.6 Hz, 2H), 3.00 (br s, 2H), 2.20 (s, 3H), 1.61 (s, 3H), 1.56 (s, 3H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 142.9, 132.7, 130.5 (2C), 127.4, 126.0, 123.0, 115.9, 31.2, 25.7, 20.8, 17.7; $HRMS_{calc}$: 176.1439 for $C_{12}H_{18}N$ $[M + H]^+$; $HRMS_{meas}$: 176.1436.

2-(3-methyl-2-butenyl)-4-*tert*-butylaniline (6c)

^{1}H NMR (C_6D_6): δ 7.19 (d, $^{4}J_{HH}$ = 2.0 Hz, 1H), 7.12 (dd, 8.0 Hz, $^{4}J_{HH}$ = 2.0 Hz, 1H), 6.44 (d, 8.0 Hz, 1H), 5.26-5.23 (m, 1H), 3.16 (d, 6.0 Hz, 2H), 3.04 (s, 2H), 1.59 (s, 3H), 1.57 (s, 3H), 1.32 (s, 9H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 143.0, 141.2, 132.7, 126.8, 125.6, 124.2, 123.3, 115.7, 34.1, 31.9, 31.8, 25.7, 17.8; $HRMS_{calc}$: 218.1909 for $C_{15}H_{24}N$ $[M + H]^+$; $HRMS_{meas}$: 218.1902.

2-(3-methyl-2-butenyl)-4-(methylthio)aniline (9c)

^{1}H NMR (C_6D_6): 7.26 (d, $^{4}J_{HH}$ = 2.5 Hz, 1H), 7.17 (dd, 7.9 Hz, $^{4}J_{HH}$ = 2.5 Hz, 1H), 6.28 (d, 7.9 Hz, 1H), 5.15 (tm, 7.2 Hz, 1H), 3.03 (s, 2H), 2.99 (d, 7.2 Hz, 2H), 2.17 (s, 3H), 1.57 (s, 3H), 1.49 (s, 3H); $^{13}C\{^{1}H\}$ NMR (C_6D_6): δ 144.2, 133.4, 132.2, 131.9, 129.5, 122.2, 116.3, 113.7, 30.9, 25.7, 18.9, 17.6; $HRMS_{calc}$: 208.1160 for $C_{12}H_{18}NS$ $[M + H]^+$; $HRMS_{meas}$: 208.1157.

2-(3-methyl-2-butenyl)-3-fluoroaniline (13c)

^{1}H NMR (C_6D_6): δ 6.85 (dd, 8.3 Hz, $^{5}J_{FH}$ = 2.3 Hz, 1H), 6.73 (td, 8.3 Hz, $^{4}J_{FH}$ = 3.0 Hz, 1H), 6.13 (dd, 8.3 Hz, $^{3}J_{FH}$ = 4.8 Hz, 1H), 5.09 (tm, 7.2 Hz, 1H), 2.90 (d, 7.2 Hz, 2H), 2.83 (br s, 2H), 1.56 (s, 3H), 1.45 (s, 3H); ^{13}C{^{1}H} NMR (C_6D_6): δ 157.0 (d, $^{1}J_{FC}$ = 234.9 Hz), 141.2 (d, $^{3}J_{FC}$ = 2.0 Hz), 133.9, 126.6 (d, $^{4}J_{FC}$ = 6.6 Hz), 121.6, 116.2 (d, $^{3}J_{FC}$ = 7.4 Hz), 116.0 (d, $^{2}J_{FC}$ = 22.4 Hz), 113.4 (d, $^{2}J_{FC}$ = 32.0 Hz), 30.7, 25.6, 17.2; $HRMS_{calc}$: 180.1189 for $C_{11}H_{15}FN$ $[M + H]^{+}$; $HRMS_{meas}$: 180.1188.

Table S1. Selected bond distances (Å) and angles (deg) in **5**

Pd1-N1	2.134(2)
Pd1-P1	2.3356(8)
N1-C1	1.273(3)
C1-C2	1.467(4)
C2-C3	1.345(4)
P1-C3	1.842(3)
P1-C7	1.895(3)
Pd1-C20	2.109(3)
Pd1-C21	2.182(3)
Pd1-C22	2.262(3)
N1-Pd1-P1	92.52(6)
C1-N1-Pd1	123.3(2)
C3-P1-Pd1	101.23(9)
C7-P1-Pd1	115.1(1)
N1-C1-C2	126.9(2)

Table S2. Crystallographic data for **5**

Compound	**[(3IP^{tBu})Pd(allyl)]OTf (5)**
Formula	$C_{22}H_{39}F_3NO_3PPdS$
Formula weight	591.97
Space group	$P2_1/c$
Temperature (K)	153
a (Å)	11.227(2)
b (Å)	8.450(2)
c (Å)	27.587(6)
α (°)	90.00
β (°)	91.82(3)
γ (°)	90.00
V (Å^3)	2615.9(9)
Z	4
Density$_{calc}$ (g/cm^3)	1.503
Diffractometer	Bruker APEX-II
Radiation	Mo-K$_\alpha$ (λ = 0.71073 Å)
Monochromator	Graphite
Detector	CCD detector
Scan type, width	ω, 0.3°
Scan speed (s)	10
Reflections measured	Hemisphere
2θ range (°)	3.62 - 52.74
Crystal dimensions	0.120 x 0.134 x 0.206
Reflections measured	30828
Unique reflections	5334
Observations (I >	4490
R_{int}	0.0430
Parameters	289
R, R_w, R_{all}	0.0328,0.0817, 0.0421
GoF	1.069

Crystallography. A summary of crystal data and collection parameters for the crystal structure of **[(3IP^{tBu})Pd(allyl)]OTf** is provided in Table S2. A detailed description of data collection, as well as data solution, is provided below. The ORTEP diagram was generated with the ORTEP-3 software package.[13] A suitable crystal was mounted on a glass fiber using Paratone-N hydrocarbon oil. The crystal was transferred to a Bruker APEX-II diffractometer with a CCD detector,[14] centered in the X-ray beam, and cooled to 153 K using a nitrogen-flow low-temperature apparatus that had been previously calibrated by a thermocouple placed at the same position as the crystal. An arbitrary hemisphere of data was collected using 0.3° ω scans, and the data were integrated by the program SAINT.[15] The final unit cell parameters were determined by a least-squares refinement of the reflections with $I > 2\sigma(I)$. Data analysis using Siemens XPREP[16] and the successful solution and refinement of the structure determined the space group. Empirical absorption corrections were applied using the program SADABS.[17]

References

[1] A. R. Shaffer, J. A. R. Schmidt, *Organometallics* **2008**, *27*, 1259-1266.
[2] K. M. Zhu, P. D. Achord, X. W. Zhang, K. Krogh-Jespersen, A. S. Goldman, *J. Am. Chem. Soc.* **2004**, *126*, 13044-13053.
[3] J. Meiners, A. Friedrich, E. Herdtweck, S. Schneider, *Organometallics* **2009**, *28*, 6331-6338.
[4] S. L. G. Ayala, E. Stashenko, A. Palma, A. Bahsas, J. M. Amaro-Luis, *Synlett* **2006**, 2275-2277.
[5] The triflate carbon was not observed in the ^{13}C spectrum.
[6] T. Ohshima, Y. Miyamoto, J. Ipposhi, Y. Nakahara, M. Utsunomiya, K. Mashima, *J. Am. Chem. Soc.* **2009**, *131*, 14317-14328.
[7] B. Plietker, *Angew. Chem. Int. Edit.* **2006**, *45*, 6053-6056.
[8] S. Jolidon, H. J. Hansen, *Helv. Chim. Acta* **1976**, *30*, 21-23.
[9] C. D. Xu, S. M. Lu, X. Huang, *Heteroatom Chem.* **1994**, *5*, 7-8.
[10] M. A. Cooper, M. A. Lucas, J. M. Taylor, A. D. Ward, N. M. Williamson, *Synthesis* **2001**, 621-625.
[11] A broad resonance corresponding to the NH protons of **2c** and **2d** was observed at 3.03 ppm overlapping with the methylene protons of the 3-methyl-2-butenyl group.

[12] Peaks corresponding to the NH protons of **3c** and **3d** were observed at 3.08 and 3.05 ppm, but could not be assigned to the individual compounds.
[13] L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
[14] *APEX-II: Area-Detector Software Package, v.* 2.1, Bruker Analytical X-ray Systems, Inc., Madison, WI, 2006.
[15] *SAINT: SAX Area-Detector Integration Program, v.* 6.22, Bruker AXS, Inc., Madison, WI, 1997-2001.
[16] *XPREP: Reciprocal Space Exploration Program, v.* 6.12, Bruker AXS, Inc., Madison, WI, 2001.
[17] *SADABS: Bruker/Siemens Area Detector Absorption Program, v.* 2.03, Bruker AXS, Inc., Madison, WI, 2001.