SUPPORTING INFORMATION

Reversible Alkene Insertion into the Pd–N Bond of Pd(II)-Sulfonamidates and Implications for Catalytic Amidation Reactions

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General Experimental Considerations.

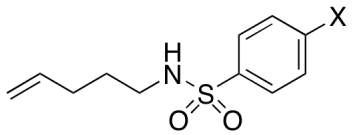
All commercially available compounds were used as received. Solvents used for synthetic reactions were dried over alumina columns prior to use; solvents for NMR spectroscopy were used as received. ^{1}H and ^{13}C NMR spectra were recorded on Bruker 300 MHz, Varian 500 MHz and Varian 600 MHz spectrometers. ^{1}H NMR chemical shifts are reported in parts per million relative to internal TMS (0.00 ppm) for $CDCl_3$ or the residual protons (2.50 ppm) for DMSO-d_6. ^{13}C NMR chemical shifts are reported in parts per million relative to the solvent peak (77.23 ppm for $CDCl_3$, 39.51 ppm for DMSO-d^6).

ESI- and EMM-MS experiments were performed on a Waters (Micromass) LCT® mass spectrometer. All exact mass measurements (EMM) for compounds containing palladium were compared against the calculated, monoistopic mass. Flash chromatography was performed using SiliaFlash® P60 (Silicycle, particle size 40-63 μm, 230-400 mesh) from Sigma Aldrich. All synthetic procedures were carried out under ambient conditions. (^{t}Bu$_2$bpy)PdCl$_2$ (**1**) was prepared according to previously reported procedures.[1]

For kinetic studies, DMSO-d_6 was used and stored under a dry nitrogen atmosphere. ^{1}H NMR spectroscopic kinetic data were recorded using Varian INOVA-500 and INOVA-600 spectrometers. Trimethyl(phenyl)silane was used as an internal standard without purification for all kinetic studies. Ethylene glycol was used for temperature calibration of the NMR spectrometer for variable temperature measurements. Under the conditions of the NMR experiments performed in this study, mass transfer of O_2 from the headspace into solution is slow. Therefore, only the dissolved O_2 concentration is relevant. In most of our experiments, we use ~3.4-3.8 atm O_2, which corresponds to a dissolved O_2 concentration of ~7-8 mM in DMSO.[2] Issues associated with O_2 solubility and mass-transfer into solution have been discussed elsewhere.[3]

General Procedure for the Synthesis of Substituted Benzenesulfonamides.

Synthesis of the substituted benzenesulfonamides from the corresponding 4-penten-1-ol was carried out according to a literature procedure.[4] The ^{1}H NMR spectrum of the compounds in DMSO-d^6 is provided for comparison with the corresponding sodium salts in the next section.



X = OMe

1.54 g, 77% yield; clear, pale yellow oil (Combiflash using hexanes/ethyl acetate; TLC conditions – 3:1 hexanes:EtOAc, R_f = 0.23). Characterization data agrees with literature report.[5]

^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 7.71 (d, J = 8.8 Hz, 2H), 7.45 (bt, J = 5.8 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 5.78-5.64 (m, 1H), 4.99-4.89 (m, 2H), 3.83 (s, 3H), 2.70 (q, J = 6.9 Hz, 2H), 1.97 (q, J = 6.9 Hz, 2H), 1.43 (pent, J = 6.6 Hz, 2H)

X = Me

Obtained from previous studies.[6] Characterization data agrees with literature report.[7]

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[1] Foley, S. R.; Shen, H.; Qadeer, U. A.; Jordan, R. F. *Organometallics* **2004,** *23*, 600-609.
[2] Battino, R. *Solubility Data Series: Oxygen and Ozone*; Pergamon Press: Oxford, U.K., 1981; Vol. 7
[3] (a) Steinhoff, B. A.; Guzei, I. A.; Stahl, S. S *J. Am. Chem. Soc.* **2004**, *126*, 11268–11278. (b) Steinhoff, B. A.; Stahl, S. S. *J. Am. Chem. Soc.* **2006**, *128*, 4348–4355.
[4] Liu, G. S.; Stahl, S.S. *J. Am. Chem. Soc.* **2007**, *129*, 6328-6335.
[5] Brenzovich, W. E.; Benitez, D.; Lackner, A. D.; Shunatona, H. P.; Tkatchouk, E.; Goddard, W. A.; Toste, F. D. *Angew. Chem. Int. Ed.* **2010,** *49*, 5519-5522.
[6] Fix, S. R.; Brice, J. L.; Stahl, S. S. *Angew. Chem. Int. Ed.* **2002,** *41*, 164-166.

^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.52 (t, *J* = 5.9 Hz, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 5.81-5.67 (m, 1H), 4.93-4.81 (m, 2H), 2.68 (q, *J* = 6.6 Hz, 2H). 2.38 (s, 3H), 1.96 (q, *J* = 6.9 Hz, 2H), 1.45 (pent, *J* = 7.3 Hz, 2H)

X = Cl

1.50 g, 74% yield; clear, colorless waxy solid; mp = 30-32 °C (Combiflash using hexanes/ethyl acetate; TLC conditions – 3:1 hexanes:EtOAc, R_f = 0.49).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 8.06 (d, *J* = 8.5 Hz, 2H), 7.49 (d, *J* = 8.5 Hz, 2H), 5.75-5.67 (m, 1H), 5.00-4.96 (m, 2H), 4.63 (bt, 1H), 2.97 (q, *J* = 6.7 Hz, 2H), 2.05 (q, *J* = 7.0 Hz, 2H), 1.58 (pent, *J* = 7.0 Hz, 2H)

^{13}C NMR (CDCl3, 126 MHz) δ 139.34 δ 138.75 δ 137.25 δ 129.62 δ 128.72 δ 115.98 δ 42.87 δ 30.81 δ 28.88

^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 7.80-7.66 (m, 5H), 5.78-5.64 (m, 1H), 4.99-4.89 (m, 2H), 2.74 (q, *J* = 6.6 Hz, 2H), 1.97 (q, *J* = 7.2 Hz, 2H), 1.44 (pent, *J* = 7.3 Hz, 2H)

HRMS: m/z (ESI) calculated [M+Na]+ = 282.0326, measured 282.0319 (Δ = 2.5 ppm)

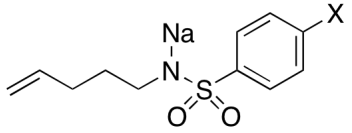
X = NO_2

1.12 g, 56% yield; yellow powder (Combiflash using hexanes/ethyl acetate; TLC conditions – 3:1 hexanes:EtOAc, R_f = 0.34). Characterization data agrees with literature report.[5]

^{1}H NMR ($(CD_3)_2SO$, 300 MHz) δ 8.42 (d, *J* = 8.7 Hz, 2H), 8.05-8.02 (m, 3H), 5.78-5.65 (m, 1H), 4.99-4.89 (m, 2H), 2.82-2.76 (m, 2H), 1.98 (q, *J* = 7.1 Hz, 2H), 1.45 (pent, *J* = 7.3 Hz, 2H)

General Procedure for the Synthesis of Na[*N*-arylsulfonyl-pent-4-enamide].

A scintillation vial, stir bar and septum were dried overnight in a 70 °C oven. The stir bar was added and the vial was capped with the septum. The vial was placed under vacuum and allowed to cool. Once the vial was cool, sodium hydride (60% by wt in a mineral oil suspension, 1 mole equivalent) was added to the vial and placed under N_2. Dry Et_2O (~3 mL/mmol NaH) was added via syringe to the vial to form a suspension of NaH. To the stirring suspension of NaH, a solution of amide (1.1 equiv) in dry diethyl ether (~6 mL/mmol NaH) was added at room temperature. Subsequently, 2 mL of dry diethyl ether was used to transfer the residual amide solution. The reaction mixture was stirred 2-3 h, after which 5 mL/mmol NaH of hexanes was added to the vial to promote precipitation. The resulting precipitate was filtered, washed with hexanes (3x5mL) and Et_2O (1x1mL) to remove the excess amide and collected.



X = OMe

56.2 mg, 65% yield; white powder.

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[7] Hegedus, L. S.; McKearin, J. M. *J. Am. Chem. Soc.* **1982,** *104*, 2444-2451.

^{1}H NMR ($(CD_3)_2SO$, 500MHz) δ 7.51 (d, *J* = 8.6 Hz, 2H), 6.84 (d, *J* = 8.6 Hz, 2H), 5.78-5.70 (m, 1H), 4.92-4.88 (m, 1H), 4.85-4.82 (m, 1H), 3.75 (s, 3H), 2.55 (t, *J* = 7.0 Hz, 2H), 1.94 (q, *J* = 7.5 Hz, 2H), 1.30 (m, *J* = 7.3 Hz, 2H)

^{13}C NMR ($(CD_3)_2SO$, 126 MHz) δ 159.07 δ 140.73 δ 139.67 δ 127.88 δ 113.83 δ 112.65 δ 55.09 δ 45.44 δ 32.04 δ 31.49

X = Me

821.8 mg, 83% yield; white powder.

^{1}H NMR ($(CD_3)_2SO$, 500MHz) δ 7.51 (d, *J* = 7.9 Hz, 2H), 7.14 (d, *J* = 7.9 Hz, 2H), 5.77-5.69 (m, 1H), 4.92-4.88 (m, 1H), 4.85-4.83 (m, 1H), 2.59 (t, *J* = 7.1 Hz, 2H). 2.29 (s, 3H), 1.94 (q, *J* = 7.7 Hz, 2H), 1.35 (m, *J* = 7.6 Hz, 2H)

^{13}C NMR ($(CD_3)_2SO$, 126 MHz) δ 144.48 δ 139.40 δ 138.02 δ 128.22 δ 126.36 δ 114.01 δ 44.90 δ 31.51 δ 31.30 δ 20.79

X = Cl

61.9 mg, 90% yield; white powder.

^{1}H NMR ($(CD_3)_2SO$, 500MHz) δ 7.57 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.4 Hz, 2H), 5.77-5.69 (m, 1H), 4.91-4.88 (m, 1H), 4.85-4.83 (m, 1H), 2.58 (t, *J* = 7.0 Hz, 2H), 1.94 (q, *J* = 7.5 Hz, 2H), 1.32 (m, *J* = 7.4 Hz, 2H)

^{13}C NMR ($(CD_3)_2SO$, 126 MHz) δ 147.74 δ 139.56 δ 132.42 δ 128.05 δ 127.49 δ 113.88 δ 45.40 δ 31.96 δ 31.40

X = NO_2

57 mg, 58% yield; yellow powder.

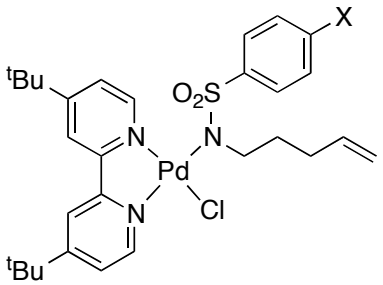
^{1}H NMR ($(CD_3)_2SO$, 300MHz) δ 8.21 (d, *J* = 8.8 Hz, 2H), 7.76 (bd, *J* = 8.8 Hz, 2H), 5.76-5.68 (m, 1H), 4.91-4.83 (m, 2H), 2.67 (t, *J* = 7.1 Hz, 2H), 1.94 (q, *J* = 7.7 Hz, 2H), 1.35 (m, *J* = 7.4 Hz, 2H)

^{13}C NMR ($(CD_3)_2SO$, 126 MHz) δ 153.91 δ 147.26 δ 139.14 δ 127.25 δ 123.42 δ 114.18 δ 44.73 δ 31.26 δ 31.11

General Procedure for the Synthesis of (^{t}Bu$_2$bpy)Pd(*N*-arylsulfonamidate)(Cl), 3a-d.

Minimal amounts of CH_2Cl_2 were added to ^{t}Bu$_2$bpyPdCl$_2$ (**1**, 1 equiv) in a scintillation vial to form a clear, yellow solution. This solution was added to another vial containing the sodium salt of the desired amide (1.1 equiv) and stir bar. Residual amounts of **1** were transferred to the reaction vial with minimal amounts of CH_2Cl_2. The reaction vial was capped with a teflon cap and the reaction mixture was stirred for 2-3 h at room temperature. Subsequently, the reaction mixture was filtered through a Celite pad to remove sodium salts and washed with CH_2Cl_2 to remove any palladium-amidate complex left on the Celite. The filtrate was collected into a round-bottom flask and the solvent was removed, either by rotovap or by blowing N_2 over the solution. Minimal amounts of benzene were added to the resulting glassy Pd-amidate complex and the solution was dripped slowly into a stirring round-bottom flask of hexanes (≥10 mL hexanes/1 mL benzene used to dissolve the Pd-amidate). Yellow, fluffy precipitate formed and was allowed to stir for 20 minutes. [note*:* If hard, globular, orange precipitate is observed, either the benzene solution was too concentrated or not enough CH_2Cl_2 was removed. In either case, the precipitation step must be repeated.] The precipitate was

then filtered through a medium-fritted funnel, washed with hexanes (2x2 mL) and Et_2O (2x1mL) and allowed to dry. [note: Small amounts of product are lost in the ether wash, but this step is necessary to fully remove sulfonamide from the Pd-amidate complex.] The dried palladium complex was then transferred to a vial and stored in a glovebox.



3a: X = Me

248.3 mg, 77% yield; fine yellow powder.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.32 (d, *J* = 6.2 Hz, 1H), 9.17 (d, *J* = 6.2 Hz, 1H), 7.96 (d, *J* = 8.1 Hz, 2H), 7.86 (s, 1H), 7.85 (s, 1H), 7.67 (dd, *J* = 2.2, 6.3 Hz, 1H), 7.44 (dd, *J* = 2.3, 6.0 Hz), 7.24 (d, *J* = 8.1 Hz, 2H), 5.86-5.78 (m, 1H), 4.96 (dm, *J* = 16.9 Hz, 1H), 4.87 (dm, *J* = 10.3 Hz, 1H), 2.87-2.76 (m, 2H), 2.38 (s, 3H), 2.30-2.22 (m, 1H), 2.12 (q, *J* = 8.1 Hz, 2H), 1.94-1.87 (m, 1H), 1.45 (s, 9H), 1.42 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.08 δ 164.74 δ 156.28 δ 155.59 δ 151.33 δ 151.15 δ 140.70 δ 139.95 δ 139.15 δ 128.66 δ 128.39 δ 124.03 δ 123.56 δ 118.43 δ 118.31 δ 114.44 δ 49.92 δ 35.88 δ 32.42 δ 31.95 δ 30.51 δ 21.69

HRMS: m/z (ESI) calculated $[M\text{-}Cl]^+$ = 610.1876, measured 610.1890 (Δ = 2.3 ppm)

3b: X = OMe

83 mg, 75% yield; fine yellow powder.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.32 (d, *J* = 6.1 Hz, 1H), 9.18 (d, *J* = 6.1 Hz, 1H), 8.02 (d, *J* = 8.9 Hz, 2H), 7.86 (s, 1H), 7.85 (s, 1H), 7.68 (dd, *J* = 1.9, 6.6 Hz, 1H), 7.45 (dd, *J* = 2.1, 6.6 Hz), 6.93 (d, *J* = 8.9 Hz, 2H), 5.86-5.78 (m, 1H), 4.96 (dm, *J* = 17.4 Hz, 1H), 4.88 (dm, *J* = 11.3 Hz, 1H), 3.84 (s, 3H), 2.88-2.74 (m, 2H), 2.30-2.22 (m, 1H), 2.13 (q, *J* = 7.1 Hz, 2H), 1.95-1.86 (m, 1H), 1.45 (s, 9H), 1.42 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.08 δ 164.74 δ 161.37 δ 156.28 δ 155.59 δ 151.30 δ 151.30 δ 139.15 δ 135.12 δ 130.27 δ 124.05 δ 123.58 δ 118.44 δ 118.32 δ 114.43 δ 113.16 δ 55.47 δ 49.89 δ 35.88 δ 32.36 δ 31.95 δ 30.51 δ 30.49

HRMS: m/z (ESI) calculated $[M\text{-}Cl]^+$ = 628.1815, measured 628.1846 (Δ = 5.0 ppm)

3c: X = Cl

116.9 mg, 83% yield; fine yellow powder.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.26 (d, *J* = 6.1 Hz, 1H), 9.16 (d, *J* = 5.7 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 2H), 7.87 (bs, 2H), 7.67 (bd, *J* = 5.6 Hz, 1H), 7.47 (bd, *J* = 6.4 Hz), 7.39 (d, *J* = 8.8 Hz, 2H), 5.86-5.78 (m, 1H), 4.97 (bd, *J* = 17.3 Hz, 1H), 4.89 (bd, *J* = 10.1 Hz, 1H), 2.88-2.78 (m, 2H), 2.31-2.22 (m, 1H), 2.13 (bq, *J* = 7.1 Hz, 2H), 1.94-1.86 (m, 1H), 1.45 (s, 9H), 1.42 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.25 δ 164.94 δ 156.28 δ 155.64 δ 151.32 δ 151.03 δ 141.44 δ 138.97 δ 136.67 δ 129.86 δ 128.23 δ 124.10 δ 123.69 δ 118.52 δ 118.42 δ 114.58 δ 49.91 δ 35.91 δ 32.35 δ 31.88 δ 30.51 δ 30.49

HRMS: m/z (ESI) calculated $[M\text{-}Cl]^+$ = 628.1346, measured 628.1373 (Δ = 4.3 ppm)

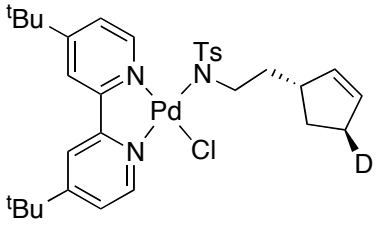
3d: X = NO_2

84 mg, 79% yield; fine yellow powder.

^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.20 (d, *J* = 6.2 Hz, 1H), 9.11 (d, *J* = 6.2 Hz, 1H), 8.27 (d, *J* = 9.1 Hz, 2H), 8.21 (d, *J* = 9.1 Hz, 2H), 7.90-7.88 (m, 2H), 7.69 (dd, *J* = 2.1, 6.1 Hz, 1H), 7.48 (dd, *J* = 1.9, 6.1 Hz), 5.86-5.77 (m, 1H), 4.98 (bdd, *J* = 1.5 Hz, 17.1 Hz, 1H), 4.90 (bdd, *J* = 1.3 Hz, 10.1 Hz, 1H), 2.94-2.84 (m, 2H), 2.33-2.24 (m, 1H), 2.15 (bq, *J* = 7.3 Hz, 2H), 1.95-1.86 (m, 1H), 1.46 (s, 9H), 1.43 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.47 δ 165.21 δ 156.28 δ 155.71 δ 151.32 δ 150.87 δ 148.90 δ 138.74 δ 129.37 δ 124.16 δ 123.84 δ 123.44 δ 118.66 δ 118.59 δ 114.77 δ 50.04 δ 35.97 δ 35.94 δ 32.33 δ 31.83 δ 30.43 δ 30.41

HRMS: m/z (ESI) calculated $[M\text{-}Cl]^+$ = 641.1571, measured 641.1600 (Δ = 4.5 ppm)



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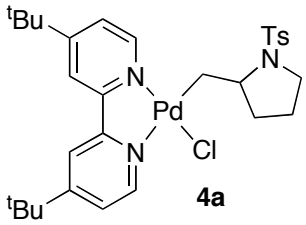
40.7 mg, 90% yield; fine yellow powder

^{1}H NMR ($CDCl_3$, 500 MHz) δ 9.31 (dd, *J* = 1.8, 6.2 Hz, 1H), 9.18 (d, *J* = 6.2 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 2H), 7.85 (m, 2H), 7.66 (dd, *J* = 1.8, 6.1 Hz, 1H), 7.43 (bd, *J* = 6.1 Hz, 1H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.72-5.63 (m, 1H), 2.91 (m, 2H), 2.72 (m, 1H), 2.43-2.35 (m, 1H, diast.), 2.38 (s, 3H) 2.32-2.26 (m, 1H), 2.23-2.16 (m, 1H, diast.), 2.05-1.98 (m, 1H), 1.96-1.89 (m, 1H, diast.), 1.77-1.69 (m, 1H, diast.), 1.49 (m, 1H), 1.44 (s, 9H), 1.42 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 165.03 δ 164.68 δ 156.30 δ 155.59 δ 151.39 δ 151.17 δ 140.69 δ 140.03 δ 135.71 δ 135.65 δ 130.14 δ 128.68 δ 128.40 δ 124.06 δ 123.55 δ 118.40 δ 118.29 δ 48.97 δ 48.91 δ 43.88 δ 43.85 δ 39.46 δ 35.87 δ 31.86 (1:1:1 triplet) δ 30.53 δ 30.51 δ 29.99 δ 29.88 δ 21.71

HRMS: m/z (ESI) calculated $[M\text{-}Cl]^+$ = 635.2112, measured 635.2120 (Δ = 1.3 ppm)

Synthesis of Alkyl-Palladium(II) Complex 4a.



4a

Pd(II)-amidate complex **3a** (122 mg) was dissolved in 2 mL of $CDCl_3$ that had been passed through oven-dried K_2CO_3. The solution was capped and stored in a dark cabinet at room temperature. A small amount of the solution was used for periodic examination by ^{1}H NMR spectroscopy to the monitor reaction progress. After 9 d, **4a** had reached its maximum quantity (~85% yield) and began decomposing via β-hydride elimination into heterocyclic products **8a-a"** and byproducts **1** and **9**. The solvent was removed and crystals of **4a**, **1** and **3a** were obtained by vapor diffusion of pentanes into C_6H_6. The yellow crystals of **4a** were manually separated from the orange crystals of **3a**. Efforts to remove **1** from **4a** via recrystallization or filtration were unsuccessful. Consequently, **4a** contains 8.5 mol % **1** by ^{1}H NMR spectroscopy. Overall yield post-recrystallization for **4a** was 47% yield.

^{1}H NMR ($CDCl_3$, 500MHz) δ 9.24 (d, *J* = 6.1 Hz, 1H), 9.07 (d, *J* = 5.7 Hz, 1H), 8.02 (bd, *J* = 1.9 Hz, 2H), 7.95 (bd, *J* = 1.4 1H), 7.73 (d, *J* = 8.3 Hz, 2H), 7.70 (dd, *J* = 2.0, 6.1 Hz, 1H), 7.49 (dd, *J* = 1.5, 5.7 Hz, 1H), 7.36 (C_6H_6), 7.24 (d, *J* = 8.3 Hz, 2H), 4.11-4.06 (m, 1H), 3.37-3.33 (m, 1H), 3.19-3.14 (m, 1H), 2.50 (bdd, *J* = 8.5, 12.0 Hz, 1H), 2.47-2.42 (m, 1H), 2.40 (s, 3H), 2.11-2.02 (m, 1H), 1.98 (bdd, *J* = 3.2, 8.2 Hz, 1H), 1.82-1.75 (m, 1H), 1.61-1.55 (m, 1H), 1.47 (s, 9H), 1.42 (s, 9H).

^{13}C NMR ($CDCl_3$, 126 MHz) δ 163.43 δ 163.39 δ 156.73 δ 153.38 δ 150.71 δ 149.09 δ 142.89 δ 136.74 δ 129.66 δ 127.41 δ 124.44 δ 123.57 δ 123.57 δ 118.97 δ 117.79 δ 62.81 δ 48.57 δ 35.74 δ 35.65 δ 33.68 δ 30.61 δ 30.53 δ 25.21 δ 23.76 δ 21.65

HRMS: m/z (ESI) calculated $[M\text{-}Cl]^+$ = 610.1876, measured 610.1876 (Δ = 0.0 ppm)

General Procedure for Kinetic Studies by ^{1}H NMR Spectroscopy under Aerobic and Anaerobic Conditions.

Aerobic

A pre-weighed amount of a Pd-amidate or Pd-alkyl complex along with a J-Young tube were brought into a purge-box containing a dry nitrogen atmosphere. The Pd complex was dissolved in 500 μL of a DMSO-d_6 stock solution containing phenyl trimethylsilane as an internal standard and transferred to the J-Young tube that was subsequently sealed and placed inside a dry ice/acetone bath to freeze the sample. The J-Young tube was connected to a gas manifold and its headspace was evacuated and refilled with 1 atm O_2. This step was repeated twice. After the last evacuation step, the NMR tube was backfilled with 3.4-3.8 atm O_2 by condensing O_2 into the tube using liquid nitrogen and monitoring the amount of O_2 using a manometer in a sealed vacuum line. For every tube, enough O_2 was condensed in order to have at least a 1:1 molar ratio of dissolved O_2:Pd-complex. *Warning: Pressurizing the tube beyond the standard limits, based on tube diameter and wall thickness, or warming a pressurized tube too rapidly can cause the tube to explode.* The NMR tube was left in an acetone/dry ice bath until it was warmed and inserted in the preheated NMR spectrometer.

Anaerobic

The procedure was identical to the aerobic procedure except that the evacuation of the headspace and backfilling with O_2 were omitted.

Kinetic Profile for Reaction of 3a at 50 °C.

Figure 3b in the manuscript show the approach to equilibrium **3** ⇆ **4**, starting from the various Pd-amidate complexes, **3a–d**. At temperatures suitable for monitoring this reaction, the β-hydride elimination step is quite slow. In order to monitor full conversion to the oxidative amination products, one of these reactions was carried out and monitored at 50 °C. Complex **3a** was dissolved in DMSO-d_6 and monitored by ^{1}H NMR spectroscopy at 50 °C for seven hours, revealing the equilibrium formation of **4a** and subsequent complete formation of **8a-8a"**. The kinetic profile of this reaction is shown below (every third data point is shown for clarity).

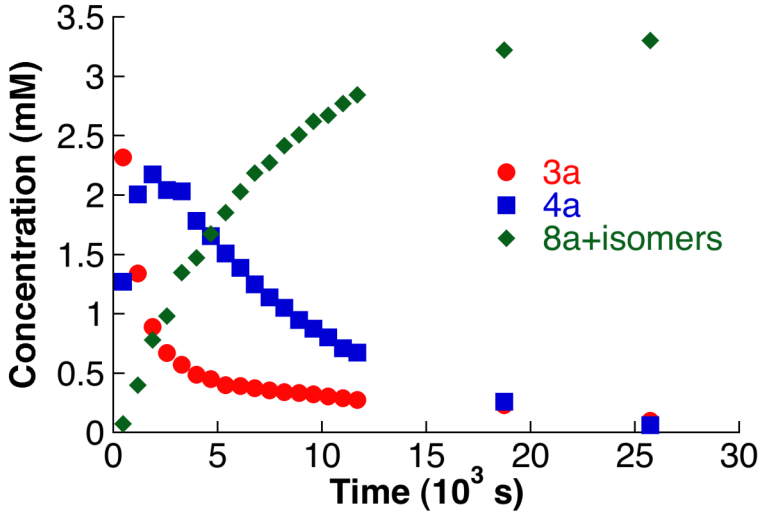
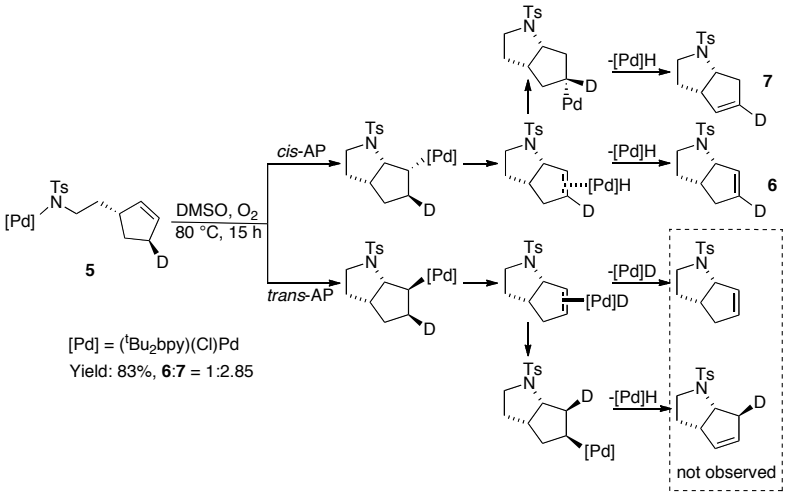


Figure S1. Kinetic profile for the reaction of **3a** at 50 °C in DMSO-d_6.

Stereochemical Analysis of the Amidopalladation Step.



Sample preparation was identical to the experiments performed above for acyclic Pd-alkenylamidates. A ^{1}H NMR acquisition array was set-up at 80 °C in DMSO-d_6 and data was collected every four minutes for fifteen hours. Once the reaction was complete, the ratio of products were analyzed and quantified relative to trimethyl(phenyl)silane (PhTMS) as an the internal standard. The identities of the products were identified by comparing the ^{1}H NMR spectrum to the spectrum of a mixture of the known non-

deuterated compounds (Figure S2). See ref. 4 for further details of product analysis and identification.

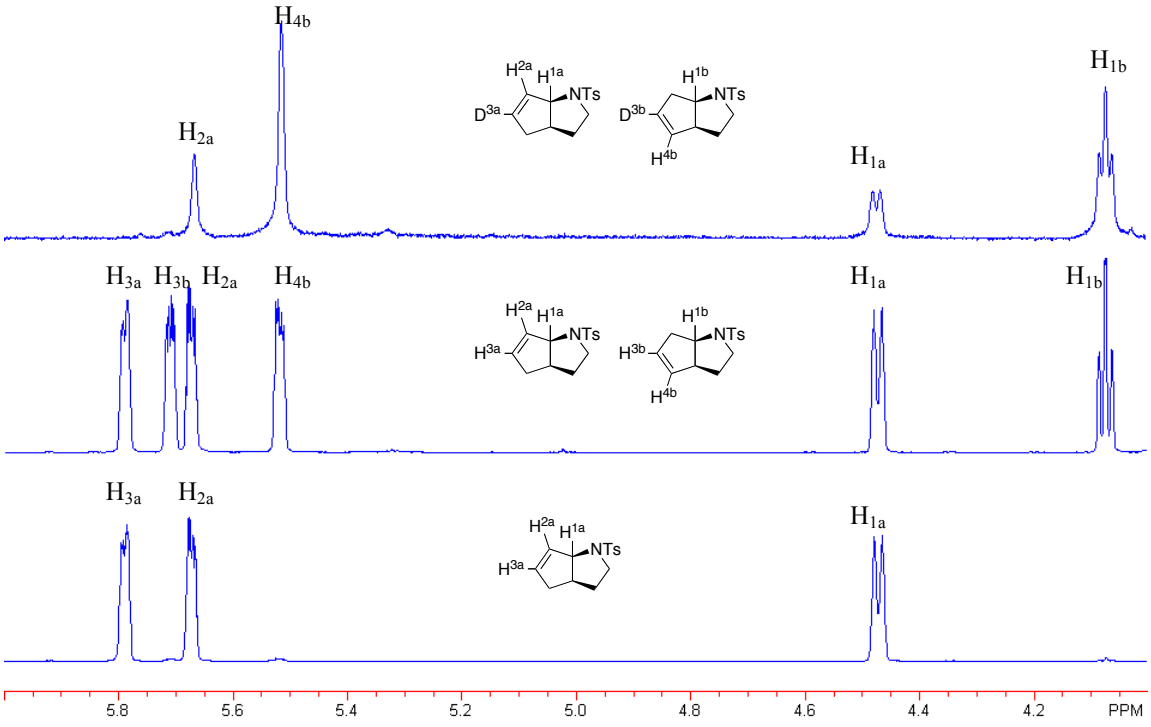
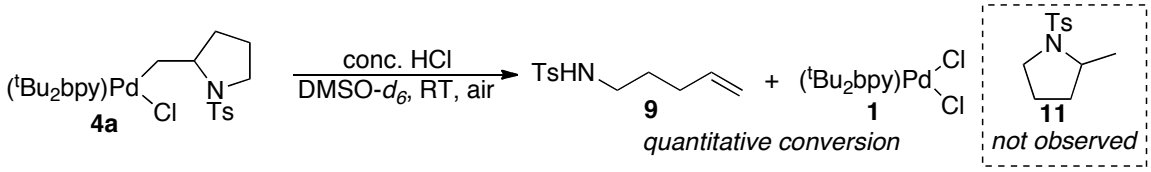


Figure S2. ^{1}H NMR spectra of the products of the reaction of Pd(II)-amidate complex **5** and reference compounds in DMSO-d_6.

Addition of HCl to the Alkyl-Pd(II) Complex 4a.



A solution of **4a** (2.70 mg, 4.16 μmol) and 1,3,5-trimethoxybenzene as an internal standard (0.44 mg, 2.62 μmol) in 600 μL of DMSO-d_6 was added to a standard 5 mm NMR tube. A ^{1}H NMR spectrum of the sample was obtained, and then a drop of concentrated HCl (~8 μL, 277 μmol HCl, ~60 equiv) was added to the side of the tube. The sample was mixed by pipetting the sample over the drop of HCl several times. Shortly after mixing, a white cloudy precipitate began to form. A ^{1}H NMR spectrum was obtained of the sample after addition of the acid. The conversion of **4a** to **9** was quantitative and proceeded with good mass balance for the aliphatic fragments (i.e. "pyrrolidine" to amide). Only 66% yield of **1** was observed by ^{1}H NMR, suggesting that some of the Pd was present in the precipitate or formed tetrachloropalladate in situ.