Supporting Information
for

**Free Radical-Mediated Vinyl Amination: Access to *N,N*-Dialkyl Enamines
and their β -Stannyl and β -Thio Derivatives**

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Experimental Section

Flame-dried (under vacuum) glassware was used for all non-aqueous reactions. All reagents and solvents were commercial grade and purified prior to use when necessary. Diethyl ether (Et₂O), tetrahydrofuran (THF), dichloromethane (CH₂Cl₂), and benzene (C₆H₆) were dried by passage through a column of activated alumina as described by Grubbs.¹ Benzene was additionally passed through a column containing activated Q-5 reactant. Solvents other than benzene were degassed using the freeze-pump-thaw method when necessary. All additional solvents were dried by distillation from calcium hydride when necessary. Molecular sieves (spheres, 4Å) were calcined at 400 °C and stored at room temperature in an air-tight container. AIBN was recrystallized prior to use, and tri-*n*-butyl tin hydride (*n*Bu₃SnH) was used as received from Aldrich.² Halovinyl amine substrates were generally prepared from commercially available haloalkene or haloalkyne starting materials via the Gabriel amine synthesis or azide substitution/Staudinger reduction. Satisfactory spectral data was obtained for all previously unreported intermediates. Complete experimental details and analytical data for these compounds will be reported in the full disclosure.

Thin layer chromatography (TLC) was performed using glass-backed silica gel (250 μ m) plates and flash chromatography utilized 230–400 mesh silica gel from Scientific Adsorbents. Neutral alumina was used as received from Scientific Adsorbents for chromatography of acid-sensitive intermediates or products. Products were visualized by UV light, iodine, and/or the use of ceric ammonium molybdate, potassium permanganate, ninhydrin, *p*-anisaldehyde, and potassium iodoplatinate solutions.

(1) Pangborn, A.B.; Giardello, M.A.; Grubbs, R.H.; Rosen, R.K.; Timmers, F.J. *Organometallics* **1996**, *15*, 1518–1520.

(2) Two lots (purchased six months apart) from Alfa Aesar failed to effect the radical reactions.

IR spectra were recorded on a Nicolet Avatar 360 spectrophotometer. Liquids and oils were analyzed as neat films on a salt plate (transmission), whereas solids were applied to a diamond plate (ATR). Nuclear magnetic resonance spectra (NMR) were acquired on either a Varian Inova-400 or VXR-400 instrument. Chemical shifts are measured relative to tetramethylsilane, as judged by the residual partially deuterated solvent peak. Mass spectra were obtained using a Kratos MS-80 spectrometer using the ionization technique indicated. Combustion analyses were performed by Atlantic Microlabs, GA.

Ratios of diastereomers and isomeric products were measured directly from integration of ^1H NMR absorptions of protons common to the components. Precision was checked by varying the relaxation delay for measurements on the same compound. Where possible, ratios were corroborated using GC-mass spectrometry. Ratios reported generally represent a lower limit defined by multiple runs.

General Procedure for Ketimine Condensations

A rapidly stirred benzene solution of the amine (0.5 M), ketone (0.5 M), and 4 Å MS (1:1 w/w) was stirred at 25 °C until complete conversion was achieved, as evidenced by ^1H NMR. The mixture was filtered through a pad of Celite and washed with Et₂O or benzene. The solvent was removed *in vacuo* to give the analytically pure ketimine which was used immediately.

The same procedure was used when the benzophenone ketimine was desired, except benzophenone imine³ was used in place of the ketone.⁴

***tert*-Butyl 1-(Diphenylmethyl)-5-methylenepyrrolidine-2-carboxylate (9b).** To a solution of **1** (43 mg, 100 μmol) and $^n\text{Bu}_3\text{SnH}$ (59.5 μL, 221 μmol) in hot (85 °C) benzene (9.2 mL) was added a solution of AIBN (13.2 mg, 80.4 μmol) in benzene (0.8 mL) over 4 h. Thirty minutes into the addition period, an additional amount of $^n\text{Bu}_3\text{SnH}$ (59.5 μL, 221 μmol) was added to the reaction mixture. The solution was refluxed for 1 h following complete AIBN addition, cooled to rt, and the intermediate enamine could be

(3) Pickard, P. L.; Tolbert, T. L. in "Organic Syntheses"; Wiley: NY, 1973, Collective Vol. 5, pp. 520-2.

⁴ O'Donnell, M. J.; Polt, R. L. *J. Org. Chem.* **1982**, 47, 2663.

observed by ^1H NMR spectroscopy after solvent removal. ^1H NMR (400 MHz, CDCl_3) δ 7.42-7.20 (m, 10H), 5.62 (s, 1H), 3.84 (dd, $J = 8.7, 1.3$ Hz, 1H), 3.59 (s, 1H), 3.26 (s, 1H), 2.78 (ddd, $J = 7.9, 3.7, 1.9$ Hz, 1H), 2.59 (dd, $J = 14.2, 7.1$ Hz, 1H), 1.83 (dd, $J = 12.5, 8.2$ Hz, 1H), 1.75 (s, 9H).

The crude benzene solution was cooled to 5 °C and treated with triethylamine (140 μL , 1 mmol) and benzoyl chloride (60 μL , 500 μmol). The solution was allowed to warm to rt over 2 h. The solvent was removed and the residue subjected to flash chromatography (SiO_2 , 22% ethyl acetate in hexanes) to furnish the vinylogous amide as a white solid (31.6 mg, 69%), mp 51-53 °C; $R_f = 0.18$ (20% EtOAc/hexanes); IR (film) 3063, 1729, 1631 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (dd, $J = 7.1, 1.5$ Hz, 2H), 7.42-7.40 (m, 1H), 7.39 (d, $J = 7.9$ Hz, 2H), 7.36-7.30 (m, 6H), 7.28 (d, $J = 7.2$ Hz, 2H), 7.23 (d, $J = 7.4$ Hz, 2H), 5.95 (s, 1H), 5.68 (s, 1H), 4.11 (dd, $J = 9.3, 1.3$ Hz, 1H), 3.78 (dd, $J = 18.2, 8.7$ Hz, 1H), 3.25 (td, $J = 9.5, 9.3$ Hz, 1H), 2.35 (ddt, $J = 12.9, 11.1, 9.3$ Hz, 1H), 2.07 (dd, $J = 12.8, 8.8$ Hz, 1H), 1.29 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 188.7, 171.4, 166.5, 141.8, 139.6, 138.3, 130.7, 130.5, 130.3, 129.1, 128.9, 128.4, 128.2, 127.9, 127.8, 127.5, 92.0, 81.9, 65.7, 64.8, 32.4, 28.0; HRMS (CI, CH_4): Exact mass calcd for $\text{C}_{30}\text{H}_{31}\text{NO}_3$ $[\text{M}]^+$, 453.2304. Found 453.2288.

tert-Butyl 1-Diphenylmethyl-3-phenylcarbonyl-2-pyrroline-5-carboxylate (10b). To a solution of **2** (44 mg, 106 μmol) and $^n\text{Bu}_3\text{SnH}$ (63 μL , 234 μmol) in hot (85 °C) benzene (9.5 mL) was added a solution of AIBN (20.9 mg, 128 μmol) in benzene (1 mL) over 4 h. Thirty minutes into the addition period, an additional amount of $^n\text{Bu}_3\text{SnH}$ (63 μL , 234 μmol) was added to the reaction mixture. The solution was refluxed for 1 h following complete AIBN addition, cooled to rt, and the intermediate enamine could be observed by ^1H NMR spectroscopy after solvent removal.

The crude benzene solution was cooled to 5 °C and treated with triethylamine (150 μL , 1 mmol) and benzoyl chloride (60 μL , 500 μmol). The solution was allowed to warm to rt over 2 h. The solvent was removed and the residue subjected to flash chromatography (SiO_2 , 22% ethyl acetate in hexanes) to furnish the vinylogous amide as a pale yellow oil (24.9 mg, 54%). $R_f = 0.17$ (20% EtOAc/hexanes); IR (film) 3063, 1734, 1565 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.47 (dd, $J = 8.5, 1.5$ Hz, 2H), 7.42 (d, $J = 7.5$ Hz, 2H), 7.38

(d, $J = 7.0$ Hz, 2H), 7.35 (d, $J = 7.1$ Hz, 2H), 7.30 (d, $J = 3.9$ Hz, 2H), 7.27 (dd, $J = 6.7$, 1.6 Hz, 2H), 7.25 (dd, $J = 7.9$, 1.6 Hz, 2H), 7.24-7.22 (m, 1H), 6.82 (s, 1H), 5.80 (s, 1H), 4.30 (dd, $J = 13.2$, 7.1 Hz, 1H), 3.45 (dd, $J = 16.0$, 7.7 Hz, 1H), 3.14 (dd, $J = 15.9$, 7.0 Hz, 1H), 1.51 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) ppm 189.3, 170.8, 153.1, 141.0, 139.2, 138.5, 136.3, 130.4, 129.3, 129.2, 129.0, 128.6, 128.5, 128.2, 128.1, 128.0, 126.5, 111.7, 82.7, 65.8, 64.1, 33.7, 28.3; HRMS (EI): Exact mass calcd for $\text{C}_{29}\text{H}_{29}\text{NO}_3$ $[\text{M}]^+$, 439.2147. Found 439.2162.

***Cis*-2-[7-Aza-7-(diphenylmethyl)bicyclo[4.3.0]non-8-ylidene]-1-**

phenylethan-1-one (*cis*-11b). Imine *cis*-3 (27.9 mg, 0.073 mmol) and $^t\text{Bu}_3\text{SnH}$ (43.0 μL , 0.16 mmol) were dissolved in C_6H_6 (7.3 ml) to make a 0.01 M solution and heated to reflux at 85°C . A solution of AIBN (10.1 mg, 0.062 mmol) in C_6H_6 (1 mL) was then added via syringe over 3 hours. After 30 m of AIBN addition, $^t\text{Bu}_3\text{SnH}$ (86.0 μL , 0.32 mmol) was added all at once. After complete addition of AIBN, the solution was allowed to reflux for an additional 1 h, after which the crude reaction mixture was cooled to 20°C and immediately treated with benzoyl chloride (8.5 μL , 0.073 mmol) and triethylamine (10.2 μL , 0.073 mmol). The solution was stirred for 2 hours, concentrated, and the residue was purified by flash chromatography (neutral alumina, 10% ethyl acetate in hexanes) to give a yellow oil (19.1 mg, 64%); $R_f = 0.52$ (20% EtOAc/hexanes); IR (film) 3060, 1628, 1529 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.1$ Hz, 2H), 7.38-7.22 (m, 13H), 5.96 (s, 1H), 5.58 (s, 1H), 3.68 (dd, $J = 17.7$, 7.5 Hz, 1H), 3.43 (dd, $J = 6.8$, 6.8 Hz, 1H), 3.14 (dd, $J = 17.4$, 11.8 Hz, 1H), 2.53-2.49 (m, 1H), 1.85-1.82 (m, 1H), 1.64-1.20 (m, 7H); ^{13}C NMR (100 MHz, CDCl_3) ppm 188.3, 166.3, 142.2, 139.7, 138.9, 130.5, 129.5 (2C), 129.0 (2C), 128.8 (2C), 128.3 (2C), 128.2, 128.1 (2C), 127.9, 127.5 (2C), 91.1, 64.9, 61.9, 36.6, 35.9, 29.2, 26.4, 23.3, 21.0; HRMS (EI) Exact mass calcd for $\text{C}_{29}\text{H}_{29}\text{NO}$ $[\text{M}]^+$, 407.2249. Found: 407.2247.

***Trans*-2-[7-Aza-7-(diphenylmethyl)bicyclo[4.3.0]non-8-ylidene]-1-phenylethan-1-one (*trans*-11b).** Imine *trans*-3 (20.6 mg, 0.054 mmol) and $^n\text{Bu}_3\text{SnH}$ (32.0 μL , 0.12 mmol) were dissolved in C_6H_6 (5.4 mL) to make a 0.01 M solution and heated to reflux at 85°C . A solution of AIBN (8.0 mg, 0.049 mmol) in C_6H_6 (1 mL) was then added via syringe over 3 hours. After 30 m of AIBN addition, $^n\text{Bu}_3\text{SnH}$ (64.0 μL , 0.24 mmol) was added all at once. After complete addition of AIBN, the solution was allowed to reflux for an additional 1 h, after which the crude reaction mixture was cooled to 20°C and immediately treated with benzoyl chloride (7.0 μL , 0.060 mmol) and triethylamine (9.0 μL , 0.065 mmol). The solution was stirred for 2 hours, treated with 1M NaOH (2 mL), and stirred an additional 30 m. Extraction with ether, drying of the organic layers, and solvent removal provided a residue that was purified by flash chromatography (neutral alumina, 15% ethyl acetate in hexanes) to give a colorless oil (12.4 mg, 57%); $R_f = 0.37$ (SiO_2 , 30% EtOAc/hexanes); IR (film) 3060, 1538 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.43-7.31 (m, 11H), 7.26-7.20 (m, 4H), 6.05 (s, 1H), 5.65 (s, 1H), 3.90 (dd, $J = 17.1, 6.4$ Hz, 1H), 3.0 (ddd, $J = 11.1, 10.7, 3.1$ Hz, 1H), 2.58 (ddd, $J = 17.1, 12.5, 1.3$ Hz, 1H), 2.05-2.00 (m, 1H), 1.88-1.84 (m, 1H), 1.77-1.73 (m, 2H), 1.36-1.26 (m, 4H), 1.24-1.19 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3) ppm 188.4, 167.4, 142.0, 138.8, 138.2, 130.6, 129.2 (2C), 129.0 (2C), 128.8 (2C), 128.4 (2C), 128.1 (2C), 127.9 (2C), 127.6 (2C), 92.3, 68.1, 63.3, 44.9, 39.0, 31.2, 29.1, 25.9, 24.9; HRMS (EI) Exact mass calcd for $\text{C}_{29}\text{H}_{29}\text{NO}$ $[\text{M}]^+$, 407.2249. Found: 407.2254.

1-Phenyl-2-[1-(phenylethyl)pyrrolidin-2-ylidene]ethan-1-one (12b). The ketimine (37.2 mg) was formed from 5-amino-2-bromo-2-pentene according to the General Procedure: oil; IR (film) 3056, 1634 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.78-7.75 (m, 2H), 7.39-7.37 (m, 3H), 5.82 (dd, $J = 6.7, 6.4$ Hz, 1H), 3.54 (t, $J = 7.0$ Hz, 2H), 2.59 (dt, $J = 7.0, 7.0$ Hz, 2H), 2.31 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 165.9, 141.4, 129.7, 128.4, 127.3, 126.8, 123.6, 51.0, 33.4, 29.1, 15.8; HRMS (EI) Exact mass calcd for $\text{C}_{13}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$, 268.0544. Found: 268.0538.

In unpurified form, the ketimine was heated (85 $^\circ\text{C}$) in benzene (14 mL) with $^n\text{Bu}_3\text{SnH}$ (87.0 μL , 0.32 mmol), after which was added a solution of AIBN (20.4 mg, 0.12 mmol) in benzene (1 mL) over 4 h via syringe pump. After 30 m of AIBN addition, $^n\text{Bu}_3\text{SnH}$ (173 μL , 0.64 mmol) was added in one portion to the reaction mixture. Following the addition period, the solution was heated for an additional 2 h. When the reaction was performed in C_6D_6 , an aliquot could be removed and analyzed by ^1H NMR spectroscopy (Figure 1, 400 MHz, C_6D_6), *partial listing*: δ 4.66 (q, $J = 7.0$ Hz, 1H), 3.83 (s, 1H), 3.75 (s, 1H), 2.83-2.74 (m, 2H), 2.38 (dd, $J = 7.9, 7.5$ Hz, 2H).

Figure 1. ^1H NMR (C_6D_6) of untreated reaction mixture.

The solution was then cooled to rt and treated immediately with benzoyl chloride (17 μL , 140 μmol) and triethylamine (20.4 μL , 150 μmol). Following a period of stirring for 2 h, the solution was concentrated and purified by flash chromatography (silica gel, 30% ethyl acetate in hexanes) to furnish the vinylogous amide as a light yellow oil (14.4 mg, 34%). $R_f = 0.1$ (30% ethyl acetate/hexanes); IR (film) 2975, 1715, 1626 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 6.3$ Hz, 2H), 7.47-7.28 (m, 8H), 5.91 (s, 1H), 5.11 (q, $J = 6.9$ Hz, 1H), 3.60-3.51 (m, 1H), 3.47-3.37 (m, 2H), 3.25-3.19 (m, 1H), 2.10-1.99 (m, 2H), 1.65

(d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 188.3, 167.3, 142.5, 140.2, 129.0, 129.0, 128.9, 128.8, 128.3, 128.3, 127.5, 127.5, 126.8, 126.8, 87.4, 53.7, 47.8, 34.4, 21.1, 17.2; HRMS (CI) Exact mass calcd for $\text{C}_{20}\text{H}_{21}\text{NO}$ $[\text{M}]^+$ 291.1623. Found 291.1622.

1-Phenyl-2-[1-(1-phenylethyl)pyrrolidin-2-ylidene]ethanone (12b) from 5-amino-2-bromo-1-pentene. The ketimine (24.3 mg) was formed from 5-amino-2-bromo-1-pentene according to the General Procedure; oil, IR (film) 3056, 1632 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.80-7.78 (m, 2H), 7.40-7.39 (m, 3H), 5.62 (s, 1H), 5.44 (s, 1H), 3.49 (t, $J = 6.7$ Hz, 2H), 2.64 (t, $J = 7.2$ Hz, 2H), 2.25 (s, 3H), 2.05 (tt, $J = 7.3$, 7.0 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) ppm 166.1, 140.0, 129.7, 128.5, 126.8, 116.9, 50.7, 39.6, 29.3, 16.0; HRMS (EI) Exact mass calcd for $\text{C}_{13}\text{H}_{17}\text{BrN}$ $[\text{M}+\text{H}]^+$ 268.0545. Found 268.0517.

In unpurified form, the ketimine was heated (85 °C) in benzene (15 mL) with $n\text{Bu}_3\text{SnH}$ (4 μL , 0.015 mmol), after which was added a solution of AIBN (20.2 mg, 0.12 mmol) and $n\text{Bu}_3\text{SnH}$ (32.0 μL , 0.12 mmol) in benzene (1 mL) over 3 h via syringe pump. The solution was then cooled to rt, and the enamine observed by ^1H NMR (Figure 2, 400 MHz, C_6D_6).

The reaction mixture was treated immediately with benzoyl chloride (9.5 μL , 82 μmol) and triethylamine (12.0 μL , 86 μmol). Following a period of stirring for 2 h, the

solution was concentrated and purified by flash chromatography (silica gel, 30% ethyl acetate in hexanes) to furnish the vinylogous amide as a light yellow oil (7.8 mg, 36%).

(1R)-11,14-Diaza-1-methyl-14-(phenylethyl)tetracyclo[6.5.1.0<2,7>.0<9,13>]tetradeca-2(7),3,5-triene-10,12-dione (13b). The amine (24.2 mg, 114 μmol), acetophenone (13.8 μL, 114 μmol), and 4Å MS were stirred in benzene (2 mL) for 3 h. The mixture was filtered and concentrated to furnish the desired imine (33 mg, 90%); IR (film) 3058, 2364, 2335, 1627 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.86 (dd, *J* = 7.4, 6.1 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.39-7.31 (m, 5H), 7.24 (dd, *J* = 7.6, 7.3 Hz, 1H), 5.90 (d, *J* = 1.5 Hz, 1H), 5.82 (d, *J* = 1.5 Hz, 1H), 4.80 (s, 2H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm 166.4, 141.2, 139.6, 133.3, 129.8, 129.4, 129.2, 128.7, 128.4, 126.9, 126.7, 121.8, 105.9, 53.3, 16.3; HRMS (EI) Exact mass calcd for C₁₇H₁₆BrN [M]⁺, 313.0466. Found 313.0454.

A 0.005 M benzene solution of the imine (30.9 mg, 0.098 mmol) and ^tBu₃SnH (79 mL, 0.29 mmol) was warmed to 80 °C and treated with a solution of AIBN (26.7 mg, 0.16 mmol) in benzene (19.6 mL) over a 3 h period using a syringe pump. The solution was cooled, concentrated, and analyzed by ¹H NMR (Figure 3). The oil was cooled to 0 °C in ether, treated with maleimide (20.8 mg, 0.21 mmol), and stored in the freezer for 12 h. The desired adduct had crystallized and could be retrieved in analytically pure form by filtration to give a white solid (10.1 mg, 31%), mp 148-152 °C; *R_f* = 0.50 (Al₂O₃, 20% EtOAc/hexanes); IR (film) 3061, 3000, 2931, 1714 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30-7.19 (m, 6H), 7.12-7.09 (m, 3H), 6.76 (s, 1H, NH), 4.40 (d, *J* = 5.5 Hz, 1H), 3.65 (dd, *J* = 8.1, 5.5 Hz, 1H), 3.44 (d, *J* = 8.2 Hz, 1H), 3.29 (q, *J* = 6.3 Hz, 1H), 1.78 (s, 3H), 1.39 (d, *J* = 6.3 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm 178.2, 177.8, 147.3, 145.9, 141.6, 128.9, 127.5, 127.4, 127.35, 127.31, 121.8, 120.5, 73.6, 65.2, 55.7, 52.7, 49.3, 24.5, 17.6; HRMS (CI, CH₄): Exact mass calcd for C₂₁H₂₀N₂O₂ [M]⁺, 332.1525. Found

332.1540.

Figure 3. ^1H NMR (400 MHz, CDCl_3) of untreated reaction mixture.

2-Methyl-1-(phenylethyl)indole (14). The aniline (109 mg, 0.52 mmol), acetophenone (124 mg, 1.0 mmol), and 4Å MS were warmed (80°C) in C₆H₆ (3 ml) overnight. The mixture was filtered through dry Celite and the solvent and excess acetophenone were removed by vacuum to leave a yellow oil (120 mg) that was used immediately in the next step. IR (film) 3059, 1634 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 8.00 (dd, *J* = 7.5, 1.5 Hz, 2H), 7.74 (d, *J* = 7.8 Hz, 1H), 7.52-7.46 (m, 3H), 7.30 (ddd, *J* = 7.5, 7.5, 1.2 Hz, 1H), 7.13 (ddd, *J* = 7.7, 7.7, 1.2 Hz, 1H), 6.73 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.52 (s, 1H), 2.41 (d, *J* = 1.3 Hz, 3H), 2.17 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm 166.7, 149.9, 139.5, 130.8, 130.0, 128.63 (2C), 128.55, 127.4, (2C), 126.8, 125.7, 123.2, 123.0, 119.0, 30.5, 18.1; HRMS (EI): Exact mass calcd for C₁₇H₁₆BrN [M]⁺, 313.0466. Found 313.0467.

A 0.005 M benzene solution of the imine was treated with ⁿBu₃SnH (3.2 equiv) and AIBN (1.8 equiv) over a 5 h period. Concentration of the mixture and purification by flash chromatography (neutral alumina, 3% dichloromethane in hexanes) gave a white solid (15.4 mg, 64%), mp 86-89°C; R_f = 0.67 (Al₂O₃, 5% EtOAc/hexanes); IR (film) 3086, 1608 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.53 (m, 1H), 7.34-7.23 (m, 3H), 7.18 (d, *J* = 8.0 Hz, 2H), 7.13-6.96 (m, 3H), 6.31 (s, 1H), 5.78 (q, *J* = 7.3 Hz, 1H), 2.38 (s, 3H), 1.96 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) ppm 141.7, 137.0, 136.2, 128.8, 127.4, 126.5, 120.5, 120.0, 119.4, 111.2, 101.27, 101.25, 52.6, 18.9, 14.2; HRMS (EI): Exact mass calcd for C₁₇H₁₇N [M]⁺, 235.1361. Found 235.1365.

1-(Diphenylmethyl)-2-methylindole (15). The aniline (100 mg, 0.47 mmol), benzophenone imine (85.3 mg, 0.47 mmol), and 4Å MS were warmed (80°C) in C₆H₆ (3 ml) overnight. The mixture was filtered through dry Celite and the solvent was removed by vacuum. The residue could be purified by flash chromatography (neutral alumina, 3% dichloromethane in hexanes) to furnish the imine as a yellow solid (70 mg, 39%); mp 99-101 °C; R_f = 0.48 (Al₂O₃, 5% EtOAc/hexanes); IR (film) 3059, 1621 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 7.3 Hz, 2H), 7.65 (d, *J* = 7.5 Hz, 1H), 7.52 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.45 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.28-7.26 (m, 3H), 7.11-7.09 (m, 2H), 7.05

(ddd, $J = 7.7, 7.7, 1.2$ Hz, 1H), 6.97 (ddd, 7.5, 7.5, 0.8 Hz, 1H), 6.71 (s, 1H), 6.51 (d, $J = 7.8$ Hz, 1H) 2.45 (d, $J = 0.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 168.7, 150.0, 139.6, 136.5, 131.0, 129.7, 129.5, 129.4, 129.0, 128.6, 128.5, 128.1, 127.9, 126.1, 123.0, 122.8, 119.8, 30.7; HRMS (EI): Exact mass calcd for $\text{C}_{22}\text{H}_{18}\text{BrN}$ $[\text{M}]^+$, 377.0623. Found 377.0606.

The intermediate benzophenone imine was cyclized according to the General Procedure and identical to the protocol for the analogous acetophenone imine (*vide supra*) to provide the desired indole, after flash chromatography (neutral alumina, 3% dichloromethane in hexanes), as a yellow solid (8.0 mg, 53%); mp 111-113 °C; $R_f = 0.63$ (Al_2O_3 , 5% EtOAc/hexanes); IR (film) 3086, 1599 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.51 (d, $J = 7.8$ Hz, 1H), 7.34-7.28 (m, 6H), 7.15-7.13 (m, 4H), 7.00 (ddd, $J = 7.9, 7.9, 0.9$ Hz, 1H), 6.92 (s, 1H), 6.87 (ddd, $J = 8.3, 8.3, 1.2$ Hz, 1H), 6.74 (d, $J = 8.3$ Hz, 1H), 6.33 (s, 1H), 2.29 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) ppm 139.6, 137.8, 137.4, 128.81, 128.76, 128.6, 127.9, 120.7, 119.9, 119.5, 111.8, 101.9, 62.6, 14.6; HRMS (EI): Exact mass calcd for $\text{C}_{22}\text{H}_{19}\text{N}$ $[\text{M}]^+$, 297.1518. Found 297.1517.

Pent-4-ynyl-(1-phenylethylidene)amine (S1). 4-Pentynyl-1-amine (0.59 g, 6.7 mmol) was dissolved in dry benzene (15 mL), and 4Å molecular sieves (~4 g) were added to the solution. The mixture was stirred at room temperature and acetophenone (0.78 mL, 6.7 mmol) was added dropwise. The mixture was stirred until ^1H NMR spectroscopy revealed complete imine formation (~6 hr). The reaction mixture was filtered through a plug of dry Celite, and the molecular sieves were washed thoroughly with ether. The solution was concentrated *in vacuo* to afford 1.2 g (94%) of the imine as a clear oil, and was used without further purification. The imine could be stored frozen in benzene to avoid hydrolysis. IR (film) 3297, 3083, 3056, 2931, 2116, 1634, 1597, 1492, 1445, 1371, 1346, 1283, 1179, 1025, 918, 761 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.99 (s, 2H), 7.38 (s, 3H), 3.59 (t, $J = 6.2$ Hz, 2H), 2.63-2.32 (m, 2H), 2.28 (s, 3H), 2.03-1.98 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) 165.8, 141.4, 129.6, 128.4, 128.4, 126.8, 126.8, 84.7, 68.6, 50.7, 30.0, 16.6, 15.8; HRMS (CI) Exact mass calcd for $\text{C}_{13}\text{H}_{14}\text{N}$ $[\text{M}-\text{H}]^+$ 184.1126. Found 184.1129.

1-(1-Phenylethyl)-2-(tributylstannylmethylene)pyrrolidine

(17). Imine **S1** (0.171 g, 0.922 mmol) was dissolved in benzene (30 mL, 0.03 M)⁵ and heated to reflux in an oil bath at 85 °C. The AIBN (60.5 mg,

0.368 mmol) and tri-*n*-butyltinhydride (0.297 mL, 1.10 mmol) were dissolved in a minimal amount of benzene (~2 mL) and drawn into a Hamilton Gastight syringe. This solution was added dropwise over 3 hr *via* syringe pump to the refluxing solution of imine **S1**. After complete addition of AIBN and tri-*n*-butyltin hydride, the mixture was allowed to reflux for an additional 3 hr. Once alkyne consumption was complete, as determined by ¹H NMR, the reaction mixture was cooled to room temperature, and the solvent was removed *in vacuo*. The crude product, a light yellow oil, was then dissolved in benzene and frozen.

General procedure for Acylation Reactions: The crude β-stannyl enamine **17** was dissolved in tetrahydrofuran and cooled to 0 °C. To this 0.1 M solution, an acid chloride (1 equiv) was added dropwise. After 30 minutes, the solvent was removed to afford the acylated enamine product. The crude mixture was then taken into diethyl ether and stirred at room temperature while a saturated solution of KF was added. The mixture was allowed to stir for 4-6 hrs. The organic layer was separated and the aqueous layer was extracted with diethyl ether. The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo* to afford the crude product, which was purified by flash column chromatography on silica gel.

1-Phenyl-2-[1-(1-phenylethyl)pyrrolidin-2-ylidene]ethanone (18a) from 17.

Following the general procedure, to β-stannyl enamine **17** (0.556 g, 1.17 mmol) in cold THF (0 °C) was added benzoyl chloride (0.183 g, 1.17 mmol) to give the vinylogous amide in 60% yield as a yellow oil. *R*_f = 0.1 (30% ethyl acetate/hexanes); IR (film) 2975, 1715, 1626, 1532 cm⁻¹; ¹H

NMR (400 MHz, CDCl₃) δ 7.83 (d, *J* = 6.3 Hz, 2H), 7.47-7.28 (m, 8H), 5.91 (s, 1H), 5.11 (q, *J* = 6.9 Hz, 1H), 3.60-3.51 (m, 1H), 3.47-3.37 (m, 2H), 3.25-3.19 (m, 1H), 2.10-1.99 (m, 2H), 1.65 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) 188.3, 167.3, 142.5, 140.2, 129.0, 129.0, 128.9, 128.8, 128.3, 128.3, 127.5, 127.5, 126.8, 126.8, 87.4, 53.7, 47.8, 34.4, 21.1, 17.2; HRMS (CI) Exact mass calcd for C₂₀H₂₁NO [M]⁺ 291.1623. Found 291.1622.

(5) It is essential to use this Molarity for optimal cyclization.

1-[1-(Phenylethyl)pyrrolidin-2-ylidene]propan-2-one (18b). Following the

general procedure, to β -stannyl enamine **17** (0.563 g, 1.18 mmol) in cold THF (0°C) was added acetyl chloride (92.8 mg, 1.18 mmol) to give the vinylogous amide in 51% yield as a clear oil. $R_f = 0.37$ (20% acetone/ CH_2Cl_2); IR (film) 3060, 1713, 1638, 1541 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.23 (m, 5H), 5.28 (s, 1H), 4.97 (q, $J = 6.9$ Hz, 1H), 3.46-3.26 (m, 2H), 3.21 (ddd, $J = 16.9, 7.9, 7.9$ Hz, 1H), 3.09 (ddd, $J = 8.4, 8.4, 5.2$ Hz, 1H), 2.07, (s, 3H), 1.99-1.81 (m, 2H), 1.58 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 194.8, 165.4, 140.3, 128.9, 127.8, 126.8, 90.2, 53.2, 47.2, 33.9, 31.0, 21.0, 16.9; HRMS (CI) Exact mass calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ $[\text{M}]^+$ 229.1467. Found 229.1456.

[1-(1-Phenylethyl)pyrrolidin-2-ylidene]acetic acid phenyl ester (18c).

Following the general procedure, to β -stannyl enamine **17** (0.566 g, 1.18 mmol) in cold THF (0°C) was added phenyl chloroformate (0.167 g, 1.18 mmol) to give the vinylogous amide in 49% yield as a yellow solid, mp 97-99.5 °C. $R_f = 0.28$ (40% Et_2O / hexanes); IR (film) 3060, 1702, 1574 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.27 (m, 7H), 7.18-7.10 (m, 3H), 4.99 (q, $J = 6.9$ Hz, 1H), 4.92 (s, 1H), 3.42-3.30 (m, 2H), 3.23-3.14 (m, 2H), 2.03-1.84 (m, 2H), 1.62 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 168.2, 166.9, 152.0, 140.3, 129.3, 129.0, 127.9, 126.9, 124.7, 122.5, 77.2, 53.3, 47.7, 33.3, 21.0 17.0; HRMS (EI) Exact mass calcd for $\text{C}_{20}\text{H}_{21}\text{NO}_2$ $[\text{M}]^+$ 307.1572. Found 307.1578.

3,3-Dimethyl-1-[1-(1-phenylethyl)pyrrolidin-2-ylidene]butan-2-one (18d).

Following the general procedure, to β -stannyl enamine **17** (0.366 g, 0.769 mmol) in cold THF (0°C) was added pivaloyl chloride (92.8 mg, 0.769 mmol) to give the vinylogous amide in 53% yield as a yellow oil. $R_f = 0.12$ (30% ethyl acetate/hexanes); IR (film) 2963, 1637, 1541 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.37-7.24 (m, 5H), 5.37 (s, 1H), 4.93 (q, $J = 6.9$ Hz, 1H), 3.40-3.30 (m, 2H), 3.25-3.15 (m, 2H), 1.98-1.82 (m, 2H), 1.60 (d, $J = 6.9$ Hz, 3H), 1.11 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) 203.6, 165.9, 140.9, 128.9, 127.7, 126.7, 86.2, 53.6, 47.6, 42.6, 33.9, 28.2, 28.2, 28.2, 21.2, 17.3; HRMS (CI) Exact mass calcd for $\text{C}_{18}\text{H}_{25}\text{NO}$ $[\text{M}]^+$ 271.1936. Found 271.1925.

1-(1-Phenylethyl)-2-phenylsulfanylmethylenepyrrolidine (18e). Imine **S1** (0.11 g, 0.62 mmol) and diphenyldisulfide (0.20 g, 0.93 mmol) were heated to reflux (85 °C) in benzene. AIBN (80.0 mg, 0.49 mmol) and tributyltin hydride (0.25 mL, 0.93 mmol) were dissolved in a minimal amount of benzene (~1 mL) and drawn into a Hamilton Gastight syringe. This solution was added dropwise *via* syringe pump to the refluxing solution (0.03 M) of **S1** and diphenyldisulfide. After complete addition of AIBN and stannane, the mixture was allowed to reflux for an additional 1 hr. Upon completion, as determined by ^1H NMR, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. Flash chromatography on silica gel (4%-25% ether/hexanes) gave a colorless oil (69.5 mg, 38%). IR (film) 3056, 1580 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.36 (dd, $J = 8.3, 8.3$ Hz, 2H), 7.31- 7.27 (m, 3H), 7.16 (dd, $J = 8.1, 8.1$ Hz, 2H), 7.07 (d, $J = 8.1$ Hz, 2H), 7.00 (dd, $J = 7.3, 7.3$ Hz, 1H), 4.84 (q, $J = 6.9$ Hz, 1H), 4.42 (s, 1H), 3.36 (dddd, $J = 7.1, 7.1, 7.1, 5.2$ Hz, 2H), 2.77 (dd, $J = 15.4, 15.4$ Hz, 2H), 1.83-1.81 (m, 2H), 1.59 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) 160.1, 142.7, 142.3, 128.8, 128.6, 128.5, 126.7, 124.4, 123.7, 70.8, 53.5, 48.6, 31.5, 21.3, 17.9; HRMS (CI) Exact mass calcd for $\text{C}_{19}\text{H}_{21}\text{NS}$ $[\text{M}]^+$ 295.1395. Found 295.1407.

1-[1-(Phenylethyl)pyrrolidin-2-ylidene]propan-2-one by Acyl radical addition (18f). Imine **S1** (0.13 g, 0.69 mmol) and phenyl acylselenoate (27.7 mg, 0.14 mmol) were dissolved in benzene and heated to reflux at 85 °C. AIBN (11.4 mg, 69.7 μ mol) and tri-*n*-butyltinhydride (56.0 μ L, 0.21 mmol) were dissolved in a minimal amount of benzene (~1 mL) and drawn into a Hamilton Gastight syringe. This solution was added dropwise *via* syringe pump to the refluxing solution (0.03 M) of **S1** and phenyl acylselenoate. After complete addition of AIBN and tri-*n*-butyltinhydride, the mixture was allowed to reflux for an additional 30 min. Upon completion, as determined by ^1H NMR, the reaction mixture was cooled to room temperature and concentrated *in vacuo*. Flash chromatography on silica gel (*vide supra*) provided the vinylogous amide **18f** (**18b**) as a colorless oil (9.4 mg, 29%).