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EXPERIMENTAL SECTION

General experimental details: Tetrahydrofuran (THF) was distilled from potassium and diethyl ether (Et_2O) was distilled from sodium-benzophenone. Dichloromethane (CH_2Cl_2), toluene and acetonitrile (CH_3CN) were distilled from CaH_2. Titanium tetrachloride was distilled under a nitrogen atmosphere and was stored as a stock solution in toluene (1.0 M) under an argon atmosphere. The molarities for alkylmagnesium halide reagents were established by titration with 2-butanol using 1,10-phenanthroline as an indicator. Unless otherwise noted, all reactions were carried out under an atmosphere of argon in flamed, oven-dried vessels utilizing standard syringe-septum techniques. ^{1}H NMR and ^{13}C NMR spectra were measured at 300 and 75 MHz, respectively, with a Bruker AC-300 spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts are reported as δ values in ppm relative to residual proton signals in $CDCl_3$ (δ = 7.24, 77.0) or C_6D_6 (δ = 7.15, 128.7). ^{1}H NMR coupling constants are reported in Hz and refer to apparent multiplicities located as follows: s (singlet); d (doublet); t (triplet); q (quartet); p (pentet); sx (sextet); br (broad); m (multiplet); app (apparent); dd (doublet of doublets); dt (doublet of triplets); etc. Infrared spectra were recorded on a Bruker IFS 25 IR. Electron impact mass spectra (70 eV) were obtained with a Hewlett Packard 5970 series mass selective detector. High resolution mass spectra were recorded on a VG Instruments 70E-HF spectrometer. Gas chromatographs were obtained using a Hewlett Packard 5890 Series II gas chromatograph equipped with a flame ionization detector and an Alltech Econocap SE-54 bonded phase column (15 m length, 0.54 mm id, and 0.25 m film thickness). Melting points were obtained using a Mel-Temp II apparatus equipped with a Fluke 51 digital thermometer and are uncorrected. TLC was performed on plates supplied by Alltech Associates (K42-G) and column chromatography was performed with Merck Silica Gel 60 or Aldrich Activity 1 basic alumina. Reduced pressure concentrations were performed with a Büchi rotary evaporator.

1,1-Dibromo-4-phthalimido-1-butene (5b). A solution of CBr_4 (18.7 g, 56.4 mmol) in CH_2Cl_2 (85 mL) was cooled to 0 °C and PPh_3 (29.6 g, 113 mmol) in CH_2Cl_2 (30 mL) was added dropwise over 30 min. After stirring the resulting deep orange mixture for an additional 10 min at 0° C, aldehyde **5a** (5.73 g, 28.2 mmol) was added over 30 min via a solid addition funnel. The dark burgundy mixture was stirred for 2h at 0 °C and then concentrated *in vacuo*. Trituration of the solids (EtOAc, 3 × 100 mL) followed by Celite filtration of the supernatant liquid furnished the crude product as a white solid which was subjected to chromatography on silica gel (20% EtOAc / hexane elution) to afford 8.72 g (86%) of **5b** as a white crystalline solid: mp 114.8-117.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (m, 4H, Ar*H*), 6.39 (t, J=7.2 Hz, 1H, C=C*H*), 3.73 (t, J=6.8 Hz, 2H, NCH_2), 2.44 (q, J=7.0 Hz, 2H, CH_2); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 167.92, 134.46, 133.92, 131.91, 123.19, 91.44, 35.45, 32.19; IR (KBr) 3100, 3043, 3025, 2945, 1771, 1684, 1613, 1403, 1365, 1248, 1133, 988, 872, 805, 792, 722, 713, 625 cm^{-1}; HRMS calcd for $C_{12}H_9NO_2Br_2$ 356.9000, found 356.8985.

5-Phthalimido-2-trimethylsilylmethyl-1-trimethylsilyl-2-pentene (5c). A solution of anhydrous $ZnCl_2$ (0.47M in THF, 98.0 mL, 45.9 mmol) was cooled to 0 °C and $TMSCH_2MgCl$ (1.69M in THF, 54.3 mL, 91.8 mmol) was added dropwise. The gray solution was stirred for 15 min at 0 °C and $PdCl_2(PPh_2)_2$ (1.50 g, 7 mol %, 2.14 mmol) was added in one portion. After stirring for 15 min at 25 °C, the black-brown solution was treated with **5b** (11.0 g, 30.6 mmol) in

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THF (60 mL) which was added dropwise over 40 min. Stirring was continued at 25 °C for 7h whereupon the reaction mixture was poured into cold, saturated NH_4Cl (300 mL). Both phases were decanted into a separatory funnel and the organic phase was removed. The aqueous phase was extracted with Et_2O (3 × 100 mL) and the combined organic extracts were washed with brine (2 × 200 mL), dried ($MgSO_4$) and concentrated *in vacuo*. Pentane trituration of the residue afforded crude **5c** which was purified by chromatography on silica gel (hexane - 5% EtOAc/hexane elution) to yield 11.0 g (96%) of **5c** as a white solid: mp 55.2-57.5°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (m, 4H, Ar*H*), 4.76 (t, J=7.1 Hz, 1H, C=C*H*), 3.61 (t, J=7.5 Hz, 2H, NCH_2) 2.28 (q, J=7.3 Hz, 2H, CH_2), 1.44 (s, 2H, SiCH_2), 1.36 (s, 2H, SiCH_2), -0.02 (s, 9H, (CH_3)$_3$Si), -0.12 (s, 9H (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 168.28, 138.15, 133.66, 132.34, 123.02, 114.55, 38.09, 29.61, 27.86, 23.85, -0.71, -1.28; IR (KBr) 3165, 2953, 2920, 2898, 1771, 1717, 1614, 1394, 1360, 1248, 1216, 1070, 1046, 854, 718 cm^{-1}; HRMS calcd for $C_{20}H_{31}NO_2Si_2$ 373.1893, found 373.1901.

4-Trimethylsilylmethyl-5-trimethylsilyl-3-penten-1-amine (6). To a solution of phthalimide **5c** (15.3 g, 41.0 mmol) in degassed, absolute ethanol (115 mL) was added hydrazine monohydrate (4.0 mL, 82.5 mmol). The mixture was refluxed for 8h during which time a white solid precipitated. Upon cooling to ambient temperature, the solid was collected via filtration and washed thoroughly with hexane. The solvents were evaporated *in vacuo* and the residue was triturated with hexane. Filtration of the supernatant liquid followed by solvent removal *in vacuo* gave a cloudy oil which was purified by bulb to bulb distillation to furnish 9.58 g (96%) of the title compound as a clear, colorless oil: bp 40 °C, 50 μtorr; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.71 (t, J=6.8 Hz, 1H, C=C*H*), 2.61 (t, J=6.8 Hz, 2H, NCH_2), 2.01 (q, J=6.9 Hz, 2H, CH_2), 1.44 (s, 2H, CH_2Si), 1.37 (s, 2H, CH_2Si), 1.09 (s, 2H, NH_2), -0.02 (s, 9H, (CH_3)$_3$Si), -0.05 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 136.54, 116.61, 42.70, 33.20, 29.59, 23.85, -0.70, -1.16; IR (film) 3371, 3292, 3018, 2953, 2921, 2896, 1645, 1415, 1247, 1158, 1066, 837, 698, 624 cm^{-1}; HRMS calcd for $C_{12}H_{29}NSi_2$ 243.1839, found 243.1850.

Imine 7a. The following serves as a representative experimental procedure used for the preparation of imines **7a,b,d-g** and **11**. To a solution of amine **6** (300 mg, 1.23 mmol) in THF (3.5 mL) was added activated 4Å molecular sieves (700 mg) followed by freshly distilled isobutyraldehyde (134 μL, 1.48 mmol) and the solution was stirred for 12h at r.t. The reaction mixture was diluted with Et_2O (3 mL) and filtered through a Celite pad. Evaporation of solvents and excess aldehyde *in vacuo* afforded imine **7a** (364 mg, 99%) as a colorless oil which was used immediately in the next step: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J=5.0 Hz, 1H, N=C*H*), 4.73 (t, J=7.0 Hz, 1H, C=C*H*), 3.28 (t, J=7.4 Hz, 2H, NCH_2), 2.38 (m, 1H, C*H*(CH_3)$_2$), 2.17 (q, J=7.3 Hz, 2H, CH_2), 1.45 (s, 2H, CH_2Si), 1.36 (s, 2H, CH_2Si), 1.04 (d, J=6.9 Hz, 6H, (CH_3)$_2$CH), 0.00 (s, 9H, (CH_3)$_3$Si), -0.04 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 169.30, 135.69, 116.68, 61.84, 33.92, 30.46, 29.48, 23.91, 19.38, -0.65, -1.14; IR (film) 2956, 2894, 2829, 1669, 1646, 1464, 1247, 1156, 1064, 854, 698, 624 cm^{-1}.

Imine 7b. The above procedure was followed using amine **6** (300 mg, 1.23 mmol) and isovaleraldehyde (160 μL, 1.48 mmol) to afford 367 mg (96%) of the title imine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.58 (t, J=4.8 Hz, 1H, N=C*H*), 4.72 (t, J=7.0 Hz, 1H, C=C*H*), 3.28 (t, J=7.4 Hz, 2H, CH_2N), 2.17 (q, J=7.3 Hz, 2H, CH_2), 2.08 (t, J=6.0 Hz, 2H, N=CHCH_2), 1.85 (m, 1H,

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C*H*$(CH_3)_2$), 1.43 (s, 2H, C*H*$_2$Si), 1.34 (s, 2H, C*H*$_2$Si), 0.90 (d, J=6.8 Hz, 6H, (CH_3)$_2$CH), -0.02 (s, 9H, (CH_3)$_3$Si), -0.06 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 163.99, 135.73, 116.64, 62.01, 44.72, 30.48, 29.47, 26.31, 23.85, 22.47, -0.69, -1.18; IR (film) 2955, 2896, 2829, 1670, 1647, 1465, 1248, 1156, 1064, 854, 698, 624 cm^{-1}.

Imine 7e. Amine **6** (100 mg, 0.41 mmol) and 2-furaldehyde (41 μL, 0.49 mmol) were used following the general procedure to yield 132 mg (100%) of the title imine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (s, 1H, N=C*H*), 7.47 (s, 1H, C=C*H*O), 6.68 (d, J=3.3 Hz, 1H, *H*C=CO), 6.43 (dd, J=3.5, 1.7 Hz, 1H, *H*C=CHO), 4.76 (t, J=7.1 Hz, 1H, C=C*H*), 3.52 (t, J=7.4 Hz, 2H, C*H*$_2$N), 2.31 (q, J=7.3 Hz, 2H, C*H*$_2$), 1.46 (s, 2H, C*H*$_2$Si), 1.37 (s, 2H, C*H*$_2$Si), 0.00 (s, 9H, (CH_3)$_3$Si), -0.06 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 151.82, 149.31, 144.36, 136.25, 116.28, 113.17, 111.40, 62.35, 30.41, 29.49, 23.88, -0.70, -1.24; IR (film) 3125, 2954, 2895, 2828, 1646, 1485, 1247, 1155, 1014, 853, 744, 698, 624 cm^{-1}.

Imine 7g. The previously described procedure was followed using benzaldehyde (126 μL, 1.24 mmol) and amine **6** (250 mg, 1.03 mmol) resulting in a yield of 329 mg (96%) of the title compound obtained as a clear, colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.24 (s, 1H, N=C*H*), 7.70 (m, 2H, Ar*H*), 7.38 (m, 3H, Ar*H*), 4.80 (t, J=7.1 Hz, 1H, C=C*H*), 3.57 (dt, J=7.4, 1.0 Hz, 2H, C*H*$_2$N), 2.31 (q, J=7.3 Hz, 2H, C*H*$_2$), 1.48 (s, 2H, C*H*$_2$Si), 1.38 (s, 2H, C*H*$_2$Si), 0.02 (s, 9H, (CH_3)$_3$Si), -0.05 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 160.63, 136.50, 136.04, 130.33, 128.48, 128.06, 116.57, 62.31, 30.48, 29.53, 23.93, -0.65, -1.18; IR (film) 3063, 3026, 2953, 2895, 2832, 1647, 1450, 1310, 1156, 1063, 852, 753, 694, 624 cm^{-1}.

Imine 7d. Using *o*-anisaldehyde (118 μL, 0.98 mmol) and amine **6** (200 mg, 0.82 mmol) in the general procedure yielded 299 mg (100%) of the title imine: ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.68 (s, 1H, N=C*H*), 7.92 (dd, J=7.6, 1.6 Hz, 1H, Ar*H*), 7.33 (dt, J=8.0, 1.7 Hz, 1H, Ar*H*), 6.95 (t, J=7.5 Hz, 1H, Ar*H*), 6.86 (d, J=7.3 Hz, 1H, Ar*H*), 4.82 (t, J=7.1 Hz, 1H, C=C*H*), 3.83 (s, 3H, C*H*$_3$O), 3.57 (t, J=7.4 Hz, 2H, C*H*$_2$N), 2.30 (q, J=7.3 Hz, 2H, C*H*$_2$), 1.49 (s, 2H, C*H*$_2$Si), 1.38 (s, 2H, C*H*$_2$Si), 0.02 (s, 9H, (CH_3)$_3$Si), -0.04 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 158.65, 156.57, 135.78, 131.45, 127.34, 125.01, 120.73, 116.72, 110.93, 62.55, 55.41, 30.64, 29.48, 23.87, -0.67, -1.23; IR (film) 3085, 2998, 2953, 2893, 2836, 1639, 1601, 1487, 1465, 1439, 1373, 1298, 1286, 1248, 1159, 1047, 1029, 853, 754, 698, 624 cm^{-1}.

Imine 7c. The title imine was characterized via a NMR tube experiment. A flame dried NMR tube was cooled under a stream of argon and charged with amine **6** (20 mg, .082 mmol) and $CDCl_3$ (350 μL). The tube was flushed with argon, fitted with a rubber septum and the solution was cooled to 0 °C. Acetaldehyde (8 μL, 0.14 mmol) was added via a cold syringe. The resulting cloudy mixture was kept at 0 °C for 1h, allowed to reach room temperature and was immediately analyzed. The ^{1}H NMR spectrum showed the presence of a single imine (~100%): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (q, J=4.8 Hz, 1H, HC=N), 4.69 (t, J=7.0Hz, 1H, C=C*H*), 3.26 (t, J=7.4 Hz, 2H, C*H*$_2$N), 2.15 (q, J=9.5 Hz, 2H, C*H*$_2$), 1.89 (d, J=4.6 Hz, 3H, C*H*$_3$), 1.42 (s, 2H, C*H*$_2$Si), 1.34 (s, 2H, C*H*$_2$Si), -0.03 (s, 9H, (CH_3)$_3$Si), -0.06 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 160.23, 135.87, 116.49, 61.72, 30.20, 29.44, 23.85, 21.99, -0.72, -1.22.

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Imine 7f. Using *trans* - cinnamaldehyde (86μL, 0.68 mmol), amine **6** (150 mg, 0.62 mmol) and a reaction time of 24h in the above procedure, imine **7f** (101 mg, 100%) was obtained as a thick, golden oil. In this case, excess aldehyde was removed via exposure of the crude product to high vacuum (<250 μtorr, r.t., 2-3 h): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (t, J=1.2 Hz, 1H, N=C*H*), 6.89-7.47 (m, 7H, Ar*H* and ArC*H*=C*H*), 4.79 (t, J=7.1 Hz, 1H, C=C*H*), 3.48 (t, J=7.4Hz, 2H, NCH_2), 2.29 (q, J=7.3 Hz, 2H, CH_2), 1.40 (s, 2H, CH_2Si), 0.02 (s, 9H, (CH_3)$_3$Si), -0.02 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 162.35, 141.22, 136.16, 135.93, 128.96, 128.76, 128.37, 127.17, 116.37, 62.07, 30.45, 29.52, 23.92, -0.67, -1.15; IR (film) 3083, 3061, 3027, 2953, 2895, 2831, 1637, 1621, 1449, 1412, 1247, 1151, 1063, 975, 853, 748, 690 cm^{-1}.

***Trans*-*N*-tosyl-2-isopropyl-3-[(3-trimethylsilyl) isopropenyl] pyrrolidine (10a$_{trans}$).** The following represents the experimental procedure used for the preparation of pyrrolidines **8a**, **b**, **f**, and **g**. A solution of freshly prepared imine **7a** (364 mg, 1.22 mmol) in CH_2Cl_2 (8 mL) was cooled to −78 °C and treated dropwise with $TiCl_4$ (1.22 mL, 1.22 mmol of a 1.0 M toluene solution). The resulting deep orange solution was allowed to gradually warm to room temperature (2-3h) after which stirring was maintained for an additional 2h. The reaction mixture was transferred dropwise via canula into vigorously stirred, saturated aqueous $KHCO_3$ (16 mL) at 0 °C and the biphasic mixture was stirred for 30 min at r.t. The organic layer was removed and the aqueous layer was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were then dried with Na_2SO_4. The residual oil was dissolved in pentane (l0 mL), filtered through a Celite pad and concentrated to furnish pyrrolidine **8a**$_{trans}$ (272 mg, 98%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.64 (s, 1H, C=C*H*H), 4.56 (s, 1H, C=CH*H*), 3.44 (br s, 1H, N*H*), 2.94 (t, J=6.9Hz, 2H, CH_2N), 2.80 (dd, J=6.9, 6.0 Hz, 1H, C*H*N), 2.27 (q, J=7.5 Hz, 1H, C*H*RC=C), 1.92 (m, 1H, C*H*(CH$_3$)$_2$), 1.66 (m, 2H, CH_2), 1.49 (s, 2H, CH_2Si), 0.92 (d, J=7.5 Hz, 3H, CH_3CHCH$_3$), 0.90 (d, J=7.5 Hz, CH$_3$CHCH_3), -0.02 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 149.20, 107.29, 68.75, 50.12, 45.75, 33.09, 31.17, 25.73, 20.80, 18.02, −1.06; IR (film) 3312, 3077, 2955, 2896, 1629, 1467, 1418, 1383, 1365, 1248, 1161, 852 cm^{-1}; HRMS (N Tosylate) calcd for $C_{20}H_{33}NO_2SSi$ (M+) 379.2001, found 379.1986. For purposes of complete and accurate characterization as well as nOe analysis, the pyrrolidine was converted to the corresponding *N*-tosylate **10a**$_{trans}$. A solution of pyrrolidine **8a**$_{trans}$ (100 mg, 0.44 mmol) and pyridine (108 μL, 1.32 mmol), in CH_2Cl_2 (2.5 mL) was cooled to 0 °C and TsCl (105mg, 0.55 mmol) was added in one portion. The mixture was stirred at 0 °C for 2h followed by an additional 2h at r.t. Distilled H_2O (2.5mL) was added and the biphasic mixture was stirred for 1h. The organic layer was removed and the aqueous phase was then extracted with CH_2Cl_2 (3 × 1mL). The combined organic phases were then dried (Na_2SO_4). Concentration *in vacuo* and filtration of the residue through a silica gel plug (5% EtOAc / hexane) afforded the purified *N*-tosylate **10a**$_{trans}$ (142 mg, 85%) as a colorless, viscous oil: ^{1}H NMR (300 MHz, C_6D_6) δ 7.82 (d, J=8.1 Hz, 2H, Ar*H*), 6.83 (d, J=7.7 Hz, 2H, Ar*H*), 4.32 (s, 1H, C=C*H*H), 4.25 (s, 1H, C=CH*H*), 3.74 (t, J=4.4 Hz, 1H, C*H*N), 3.43 (dt, J=10.7, 6.8 Hz, 1H, NC*H*H), 3.21 (dt, J=10.7, 6.8 Hz, 1H, NCH*H*), 2.50 (m, 1H, C*H*(CH$_3$)$_2$), 2.34 (app q, J=6.4 Hz, 1H, C*H*C=C), 1.95 (s, 3H, ArCH_3), 1.46 (m, 1H, C*H*H), 1.25 (d, J=14.3 Hz, 1H, C*H*HSi), 1.19 (m, 1H, CH*H*), 1.07 (d, J=14.3 Hz, 1H, CH*H*Si), 1.00 (d, J= 7.0 Hz, 6H, (CH_3)$_2$CH), −0.07 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$; ^{1}H decoupled) δ 147.20, 142.98, 135.60, 129.33, 127.61, 107.88, 68.77, 48.72, 47.45, 33.01, 30.40, 24.75, 21.34, 19.40, 17.08, -1.29; IR (film) 3084, 3029, 2958, 2892, 2875, 1632, 1599, 1466, 1347, 1248, 1159, 1096, 1004, 853, 662 cm^{-1}; HRMS calcd for $C_{20}H_{33}NO_2SSi$

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379.2001, found 379.1986.

***Cis* and *trans*-*N*-tosyl-2-phenyl-3-[(3-trimethylsilyl)isopropenyl]pyrrolidine (10g$_{cis}$, 10g$_{trans}$).** Using imine **7g** (260 mg, 0.78 mmol) in the above procedure, an inseparable mixture (1.7 : 1.0) of pyrrolidines **8g$_{cis}$** and **8g$_{trans}$** (201mg, 99%) was obtained as a colorless oil. Treatment of the mixture with TsCl as previously described furnished the purified title *N*-tosylates (1.7 : 1.0, 276 mg, 86%) as a viscous, colorless oil. A pure sample of the *cis* isomer was obtained via fractional crystallization (hexane) of the mixture and crystals suitable for X-ray analysis were recovered from recrystallization (10% Et_2O / hexane):

***Cis*-*N*-tosyl-2-phenyl-3-[(3-trimethylsilyl)isopropenyl]pyrrolidine (10g$_{cis}$).** mp 107.2-109.3 ^{1}H NMR (300 MHz, C_6D_6) δ 7.68 (d, J=8.2 Hz, 2H, SO_2ArH), 7.06 (m, 5H, Ar*H*), 6.74 (d, J=8.1 Hz, 2H, SO_2ArH), 5.15 (d, J= 7.6 Hz, 1H, NC*H*), 4.28 (s, 1H, C=C*H*H), 4.09 (s, 1H, C=CH*H*), 3.52 (app t, J= 9.0 Hz, 1H, NC*H*H), 3.31 (ddd, J= 10.6, 10.6, 6.7 Hz, 1H, NCH*H*), 2.26 (ddd, J= 13.1, 6.4, 6.4 Hz, 1H, C*H*C=C), 1.89 (s, 3H, ArCH_3), 1.74 (m, 1H, C*H*H), 1.28 (dd, J=12.1, 6.0 Hz, 1H, CH*H*), 1.18 (AB q, Δv=41.6 Hz, J=13.7 Hz, 2H, CH_2 Si), -0.18 (s, 9H, (CH_3)$_3$ Si); ^{13}C NMR (75 MHz, $CDCl_3$ ^{1}H decoupled) δ 143.08, 142.32, 139.10, 135.54, 129.37, 127.51, 127.45, 126.99, 109.70, 65.07, 51.70, 47.54, 27.18, 26.53, 21.36, -1.56; IR (film) 3086, 3063, 3031, 2953, 2889, 1636, 1599, 1495, 1454, 1346, 1248, 1160, 1097, 1015, 841, 736, 703, 666 cm^{-1}; HRMS calcd for $C_{23}H_{31}NO_2SSi$ 413.1845, found 413.1857.

***Trans*-*N*-tosyl-2-phenyl-3-[(3-trimethylsilyl)isopropenyl]pyrrolidine (10g$_{trans}$).** ^{1}H NMR (300 MHz, C_6D_6) δ 7.68 (d, J=8.1, 2H, SO_2ArH),7.31 (d, J=7.1 Hz, 2H, ArH), 7.11 (m, 3H, Ar*H*), 6.76 (d, J= 8.1 Hz, 2H, SO_2ArH), 4.80 (d, J = 6.1 Hz, 1H, NC*H*), 4.46 (s, 2H, C=CH_2), 3.70 (ddd, J=12.4, 7.3, 5.1 Hz, 1H, NC*H*H), 3.35 (ddd, J = 14.1, 7.7, 6.8 Hz, 1H, NCH*H*), 2.38 (dd, J=13.9, 6.5 Hz, 1H, C*H*C=C), 1.90 (s, 3H, ArCH_3), 1.44 (app sx, J=5.8 Hz, 1H, C*H*H), 1.29 (m, 1H, CH*H*), 1.25 (d, J=13.0 Hz, 1H, C*H*HSi), 1.04 (d, J=13.8 Hz, 1H, CH*H*Si), -0.18 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 145.44, 142.77, 139.11, 135.93, 128.24, 128.12, 127.41, 127.01, 126.42, 108.26, 67.70, 56.88, 48.69, 30.02, 25.46, 21.34, -1.45; IR (film) 3086, 3063, 3030, 2953, 2924, 2893, 1634, 1599, 1495, 1455, 1350, 1248, 1162, 1097, 1014, 851, 699, 663 cm^{-1}.

***Trans*-*N*-tosyl-2-isobutyl-3-[(3-trimethylsilyl)isopropenyl] pyrrolidine (10b$_{trans}$).** The above procedure was followed using imine **7b** (200 mg, 0.64 mmol) to furnish pyrrolidine **8b$_{trans}$** (135 mg, 88%) as a viscous oil after chromatography on silica gel (5% MeOH / CH_2Cl_2). From a crude sample of pyrrolidine **8b$_{trans}$** (108 mg, 0.45 mmol) the title *N*-tosylate was obtained as a thick, colorless oil (141 mg, 80%): ^{1}H NMR (300 MHz, C_6D_6) δ 7.80 (d, J=8.2 Hz, 2H, Ar*H*), 6.82 (d, J=8.2 Hz, 2H, Ar*H*), 4.29 (s, 1H, C=C*H*H), 4.17 (s, 1H, CH*H*), 3.76 (app p, J=4.4 Hz, 1H, C*H*N), 3.35 (dt, J=10.6, 6.4 Hz, 1H, C*H*HN), 3.22 (dt, J=10.6, 6.4 Hz, 1H, CH*H*N), 2.13 (dd, J=10.9, 6.3 Hz, 1H, C*H*C=C), 1.96 (m, 1H, C*H*H), 1.93 (s, 3H, CH_3Ar), 1.84 (m, 1H, C*H*(CH$_3$)$_2$), 1.45 (m, 2H, CH_2CH(CH$_3$)$_2$), 1.23 (d, J=14.0 Hz, 1H, C*H*HSi), 1.13 (m, 1H, CH*H*), 1.04 (d, J=6.5 Hz, 3H, CH_3CHCH$_3$), 1.00 (d, J=6.6 Hz, 3H, CH$_3$CHCH_3), 0.96 (d, J=14.6 Hz, CH*H*Si), -0.12 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, C_6D_6, ^{1}H decoupled) δ 146.89, 142.67, 137.15, 129.55, 127.66, 108.31, 62.26, 53.26, 48.05, 47.16, 29.89, 25.60, 24.74, 23.72, 22.47, 21.09, -1.25; IR (film) 3085, 3030, 2955, 2896, 2870, 1632, 1575, 1467, 1454, 1347, 1248, 1160, 1096, 1005, 847, 816, 662 cm^{-1}; HRMS calcd for $C_{21}H_{35}NO_2SSi$ 393.2158, found 393.2143.

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***Cis*-*N*-tosyl-2-(*E*-2-phenylethenyl)-3-[(3-trimethylsilyl) isopropenyl] pyrrolidine (10f$_{cis}$).** Utilizing imine **7f** (221 mg, 0.62 mmol) in the above procedure, pyrrolidines **8f**$_{cis}$ and **8f**$_{trans}$ (153 mg, 86%) were obtained as a viscous oil upon purification of the crude product by filtration through a silica gel plug (CH_2Cl_2 - 5% MeOH / CH_2Cl_2 for elution). A crude sample of the inseparable pyrrolidines (100 mg, 0.35 mmol) was converted to the corresponding, purified *N*-tosyl derivative (8.0 : 1.0, 129 mg, 84%) which was obtained as a viscous, colorless oil. The title compound was secured from the diastereomer mixture by fractional crystallization (petroleum ether): mp 113.9 - 116.4°C; ^{1}H NMR (300 MHz, C_6D_6) δ 7.83 (d, J=8.1 Hz, 2H, SO_2ArH), 7.14 (m, 5H, Ar*H*), 6.86 (d, J=15.7 Hz, 1H, ArC*H*=C), 6.79 (d, J=8.0 Hz, 2H, SO_2ArH), 5.93 (dd, J=15.6, 6.2 Hz, 1H, ArC=C*H*), 4.72 (t, J=6.6 Hz, 1H, NC*H*), 4.52 (s, 1H, C=C*H*H), 4.44 (s, 1H, C=CH*H*), 3.44 (app t, J=8.9 Hz, 1H, NC*H*H), 3.21 (dt, J=10.2, 6.8 Hz, 1H, NCH*H*), 2.13 (ddd, J=12.5, 6.1, 6.1 Hz, 1H, C*H*C=C), 1.89 (s, 3H, CH_3Ar), 1.65 (m, 1H, C*H*H), 1.42 (d, J=13.7 Hz, 1H, SiC*H*H), 1.33 (app p, J=5.9 Hz, 1H, CH*H*), 1.19 (d, J=13.7 Hz, 1H, SiCH*H*), -0.14 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 143.18, 143.00, 136.88, 135.88, 132.31, 129.53, 128.34, 127.49, 127.41, 126.59, 125.76, 109.32, 62.67, 49.80, 47.10, 26.93, 26.68, 21.36, -1.44; IR (KBr) 3084, 3025, 2952, 2873, 1631, 1598, 1495, 1341, 1335, 1246, 1163, 1097, 1044, 855, 696, 666 cm^{-1}; HRMS calcd for $C_{25}H_{33}NO_2SSi$ 439.2001, found 439.1993.

***Trans*-*N*-tosyl-2-furyl-3-[(3-trimethylsilyl) isopropenyl] pyrrolidine (10e$_{trans}$).** A solution of $TiCl_4$ (360 μL, 0.39 mmol of a 1.1 M toluene solution) in CH_2Cl_2 (3 mL) was cooled to –78 °C and imine **7e** (125 mg, 0.39 mmol) in CH_2Cl_2 (400 μL) was added dropwise over 45 min via a gas tight syringe. The resulting deep orange reaction mixture was allowed to reach ambient temperature gradually (2-3h) and stirring was continued for 24 h. The reaction mixture was quenched and the product was isolated in the manner described for **8a**$_{trans}$. Elution of the crude product through a plug of florisil (CH_2Cl_2 for elution) furnished pyrrolidine **8e**$_{trans}$ (82 mg, 84%) as a light orange oil. A crude sample of pyrrolidine **8e**$_{trans}$ (80 mg, 0.32 mmol) was converted into the title *N*-tosyl derivative (103 mg, 80%) as described above for **10a**$_{trans}$. The title compound was obtained as a viscous, colorless oil: ^{1}H NMR (300 MHz, C_6D_6) δ 7.62 (d, J=8.3 Hz, 2H, Ar*H*), 6.93 (d, J=1.7 Hz, 1H, OC*H*=C), 6.77 (d, J=8.2 Hz, 2H, Ar*H*), 6.26 (d, J=3.2 Hz, 1H, C*H*=CO), 6.00 (dd, J=3.1, 1.9 Hz, 1H, OCH=C*H*), 4.94 (d, J=5.4 Hz, 1H, NC*H*), 4.51 (s, 1H, C=C*H*H), 4.44 (s, 1H, C=CH*H*), 3.63 (ddd, J=12.9, 7.2, 5.9 Hz, 1H, NC*H*H), 3.63 (dt, J=9.8, 6.9 Hz, 1H, NCH*H*), 2.77 (app q, J=6.5 Hz, 1H, C*H*C=C), 1.91 (s, 3H, ArCH_3), 1.73 (dq, J=12.5, 6.6 Hz, H_2, 1H, C*H*H), 1.41 (dq, J=12.5, 7.2 Hz, 1H, CH*H*), 1.30 (d, J=13.7 Hz, 1H, C*H*HSi), 1.16 (d, J=13.9 Hz, 1H, CH*H*Si), -0.12 (s, 9H, (CH_3)$_3$Si); ^{13}C NMR (75 MHz, C_6D_6, ^{1}H decoupled) δ 154.96, 146.07, 142.47, 141.76, 137.67, 129.39, 127.68, 110.52, 108.38, 107.97, 61.35, 52.43, 47.98, 30.21, 25.71, 21.09, -1.42; IR (film) 3125, 3079, 3029, 2953, 2894, 1632, 1599, 1348, 1248, 1161, 1098, 1011, 852, 733, 663 cm^{-1}; HRMS calcd for $C_{21}H_{29}NO_3SSi$ 403.1637, found 403.1639.

***Trans*-*N*-tosyl-2-(2-methoxyphenyl)-[(3-trimethylsilyl)isopropenyl]pyrrolidine (10d$_{trans}$).** Using the procedure described for the preparation of **8e**$_{trans}$, imine **7d** (216 mg, 0.60 mmol) was converted into 182 mg (100%) of a mixture (ca. 1.5 : 1.0) of the corresponding pyrrolidine and the monoprotodesilylated isomer. Direct treatment of the crude mixture with TsCl in the manner previously described yielded 164 mg (62% overall from amine **6**) of the title *N*-tosylpyrrolidine as

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a viscous, colorless oil. A portion of this sample was crystallized from 10% Et_2O / hexane to furnish colorless crystals: mp 85.5 - 88.4 °C; ^{1}H NMR (300 MHz, C_6D_6) δ 7.75 (d, J=8.0 Hz, 2H, SO_2ArH), 7.46 (d, J=7.3 Hz, 1H, Ar*H*), 7.07 (t, J=7.6 Hz, 1H, Ar*H*), 6.86 (t, J=7.5 Hz, 1H, Ar*H*), 6.78 (d, J=8.1 Hz, 2H, SO_2ArH), 6.49 (d, J=8.1 Hz, 1H, Ar*H*), 5.38 (d, J=3.3 Hz, 1H, C*H*N), 4.35 (s, 1H, C=C*H*H), 4.33 (s, 1H, C=CH*H*), 3.56 (app t, J=5.8 Hz, 2H, NCH_2), 3.30 (s, 3H, $ArOCH_3$), 2.45 (ddd, J=3.1, 6.2, 3.1 Hz, 1H, C*H*C=C), 1.92 (s, 3H, SO_2ArCH_3), 1.70 (dq, J=12.6, 7.2 Hz, 1H, C*H*H), 1.59 (d, J=13.6 Hz, 1H, C*H*HSi), 1.41 (dq, J=12.0, 5.3 Hz, 1H, CH*H*), 1.18 (d, J=13.7 Hz, 1H, CH*H*Si), −0.12 (s, 9H, $(CH_3)_3Si$); ^{13}C NMR (75 MHz, C_6D_6, ^{1}H decoupled) δ 156.47, 146.56, 142.36, 137.57, 132.11, 129.27, 128.54, 128.32, 128.05, 120.79, 110.64, 107.48, 63.33, 54.83, 54.04, 48.18, 28.80, 25.58, 21.10, −1.43; IR (film) 3098, 3080, 3030, 2998, 2973, 2948, 2890, 2845, 1630, 1598, 1489, 1344, 1247, 1159, 1096, 1023, 853, 763, 665 cm^{-1}; HRMS calcd for $C_{24}H_{33}NO_3SSi$ 443.1950, found 443.1930.

***Trans*-*N*-tosyl-2-methyl-[(3-trimethylsilyl)isopropenyl] pyrrolidine (10c$_{trans}$).** A solution of amine **6** (200 mg, 0.82 mmol) in CH_2Cl_2 (4 mL) containing 4Å molecular sieves (400 mg) was cooled to −10 °C and acetaldehyde (50 μL, 0.90 mmol, *freshly distilled*) was added dropwise. The mixture was stirred at −10 °C for 1h and quickly filtered through a Celite pad. The resulting solution of imine **7c** was diluted with CH_2Cl_2 (2 mL), cooled to −78 °C without delay and $TiCl_4$ (820 μL, 0.82 mmol of a 1.0 M toluene stock solution) was added dropwise. The resulting deep orange solution was gradually warmed to r.t. (~2-3h) and stirred for an additional 2h. Reaction quench and product isolation was carried out as described for **8a$_{trans}$** to afford pyrrolidine **8c$_{trans}$** (106 mg, 65%) as a colorless oil after purification of the crude product via filtration through a plug of florisil (CH_2Cl_2 - 5% MeOH / CH_2Cl_2 elution). A sample of crude **8c$_{trans}$** (100 mg, 0.51 mmol) was treated with TsCl as described previously to furnish the purified title compound (147 mg, 82%) as a viscous, colorless oil: ^{1}H NMR (300 MHz, C_6D_6) δ 7.75 (d, J=8.2 Hz, 2H, Ar*H*), 6.84 (d, J=8.2 Hz, 2H, Ar*H*), 4.38 (d, J=0.9 Hz, 1H, C=C*H*H), 4.29 (s, 1H, C=CH*H*), 3.51. (t, J=6.4 Hz, 1H, NC*H*), 3.42 (ddd, J=14.9, 8.7, 6.2 Hz, 1H, NC*H*H), 3.19 (ddd, J=11.3, 7.5, 3.1 Hz, 1H, NCH*H*), 1.97 (app q, J=6.8 Hz, 1H, C*H*C=C), 1.93 (s, 3H, CH_3Ar), 1.46 (d, J=6.2 Hz, 3H, CH_3), 1.34 (m, 1H, C*H*H), 1.12 (d, J=13.8 Hz, 1H, SiC*H*H), 0.97 (m, 1H, CH*H*), 0.91 (d, J=13.9 Hz, 1H, SiCH*H*), -0.14 (s, 9H, $(CH_3)_3Si$); ^{13}C NMR (75 MHz, C_6D_6, ^{1}H decoupled) δ 146.11, 142.75, 136.79, 129.60, 127.81, 108.62, 59.90, 55.79, 48.48, 30.20, 24.32, 22.33, 21.10, -1.27; IR (film) 3080, 3029, 2955, 2928, 2895, 1632, 1598, 1452, 1346, 1248, 1163, 1093, 854, 816, 737, 658 cm^{-1}; HRMS calcd for $C_{18}H_{29}NO_2SSi$ 351.1688, found 351.1670.

Pyrrolizidine 12a. Applying the method outlined above for the preparation of imine **7a**, condensation of amine **6** (4.02 g, 16.5 mmol) and ethyl levulinate (2.58 mL, 18.1 mmol) over a 24h period afforded imine **11** (6.15 g, 100%) as a clear oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.76 (t, J=7.1 Hz, 1H, C=C*H*), 4.07 (q, J=7.3 Hz, 2H, CH_3CH_2), 3.14 (t, J=7.6 Hz, 2H, NCH_2), 2.51 (s, 4H, CH_2CH_2C=O), 2.14 (q, J=7.3 Hz, 2H, CH_2C=C), 1.77 (s, 3H, CH_3), 1.44 (s, 2H, $SiCH_2$), 1.35 (s, 2H, $SiCH_2$), 1.20 (t, J=7.2 Hz, 3H, CH_3CH_2), -0.02 (s, 9H, $(CH_3)_3Si$), -0.06 (s, 9H, $(CH_3)_3Si$); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 173.51, 166.33, 135.28, 117.29, 60.07, 51.89, 36.37, 30.52, 30.37, 29.43, 23.81, 17.69, 14.21, -0.71, -1.20. Imine **11** was immediately subjected to the previously described cyclization conditions used for the preparation of **8a$_{trans}$** to yield pyrrolizidine **12a** (3.31 g, 80%) as a crystalline solid upon purification by silica gel

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chromatography (90% EtOAc / hexane): mp 74.2 - 75.9°C; ^{1}H NMR (300 MHz,C_6D_6) δ 4.56 (s, 1H, C=C*H*H), 4.38 (s, 1H, C=CH*H*), 3.82 (ddd, J=13.5, 8.4, 5.3 Hz, 1H, NC*H*H), 2.65 (ddd, J=11.9, 8.0, 7.0 Hz, 1H, NCH*H*), 2.41 (dt, J=16.3, 9.9 Hz, 1H, O=CC*H*H), 2.19 (ddd, J=16.3, 9.8, 2.4 Hz, 1H, O=CCH*H*), 1.99 (app t, J=6.4 Hz, 1H, C*H*C=C), 1.83 (dt, J=12.4, 10.1 Hz, 1H, O=CCH$_2$C*H*H), 1.61 (m, 2H, C*H*$_2$CHC=C), 1.43 (d, J=13.4 Hz, 1H, SiC*H*H), 1.26 (app tt, J=9.2, 2.2 Hz, 1H, O=CCH$_2$CH*H*), 1.08 (d, J=13.4 Hz, 1H, SiCH*H*), -0.06 (s, 9H, (C*H*$_3$)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 174.38, 147.61, 107.70, 69.99, 53.20, 39.83, 33.47, 31.77, 29.36, 29.16, 28.10, -1.54; IR (film) 3082, 2956, 2926, 2855, 1696, 1630, 1457, 1402, 1248, 1170, 856 cm^{-1}; HRMS calcd for $C_{14}H_{25}NOSi$ 251.1705, found 251.1708.

Thiolactam 12b. To a vigorously stirred solution of lactam **12a** (2.09 g, 8.31 mmol) and diisopropylethyl amine (362 μL, 2.08 mmol) in toluene (8 mL) was added Lawesson's reagent (1.85 g, 4.57 mmol) in one portion. Vigorous stirring was maintained for 1h after which the reaction mixture was concentrated *in vacuo*. The residue was triturated with 20% EtOAc / hexane (3 × 10 mL) and the resulting solution was filtered through a silica gel pad (20% EtOAc / hexane elution) to afford thiolactam **12b** (2.07 g, 93%) as a white crystalline solid upon evaporation of solvents *in vacuo*: mp 86.0 - 88.3 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.63 (s, 1H, C=C*H*H), 4.33 (s, 1H, C=CH*H*), 3.85 (dt, J=14.0, 8.2 Hz, 1H, NC*H*H), 3.22 (m, 2H, S=CC*H*$_2$), 2.95 (dd, J=17.3, 9.1 Hz, 1H, C=CC*H*), 2.44 (m, 1H, NC*H*H), 2.29 (dd, J=7.9, 2.1 Hz, C*H*H), 2.10 (m, 2H, C*H*$_2$), 1.70 (dd, J=12.3, 8.0 CH*H*), 1.58 (d, J=13.3 Hz, 1H, SiC*H*H), 1.34 (s, 3H, C*H*$_3$), 1.14 (d, J=13.3 Hz, 1H, SiCH*H*), -0.05 (s, 9H, (C*H*$_3$)$_3$Si); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.77, 147.35, 108.28, 77.98, 52.47, 47.00, 43.37, 31.67, 31.17, 29.35, 26.10, -1.51; IR (film) 3081, 2961, 2914, 2887, 1632, 1498, 1475, 1322, 1245, 1169, 1119, 1080, 845 cm^{-1}; HRMS calcd for $C_{14}H_{25}NSSi$ 267.1477, found 267.1466.

Tricyclic pyrrolizidine 13. A solution of thiolactam **12b** (200 mg, 0.748 mmol) in CH_3CN (3 mL) was cooled to 0 °C and treated dropwise with triethyloxonium tetrafluoroborate (700μL, 0.868 mmol of a 1.24M CH_2Cl_2 solution). The reaction mixture was stirred for 2h at 0 °C, diluted with CH_3CN (3mL) and allowed to reach ambient temperature. Stirring was continued for 8h after which the reaction mixture was poured into cold aqueous LiOH (10mL, 2M). After the biphasic mixture was stirred for 30 min at r.t., the organic layer was removed and the aqueous phase was extracted with Et_2O (3 × 4 mL). The combined organic phases were washed with brine (2 × 10mL) and dried over $MgSO_4$. Filtration and evaporation of solvents followed by elution of the resulting oil through a column of basic alumina (20% Et_2O / pentane) furnished tricyclic pyrrolizidine **13** as a clear oil (152 mg, 90%): ^{1}H NMR (300 MHz, C_6D_6) δ 4.48 (d, J=1.9 Hz, 2H, C=C*H*$_2$), 3.28 (ddd, J=13.8, 9.1, 5.4 Hz, 1H, NC*H*H), 2.73 (ddd, J=14.3, 9.5, 4.3 Hz, 1H, NCH*H*), 2.71 (dq, J=12.3, 7.6 Hz, 1H, SC*H*HCH$_3$), 2.48 (dq, J=12.5, 7.5, 1H, SCH*H*CH$_3$), 2.16 (m, 2H, SCC*H*$_2$), 2.14 (d, J=13.9 Hz, 1H, C*H*HC=C), 1.95 (d, J=14.1 Hz, 1H, CH*H*C=C), 1.77 (m, 2H, C*H*$_2$), 1.66 (dq, J=11.5, 2.6 Hz, 1H, CHC*H*H), 1.36 (m, 2H, C*H* and CHCH*H*), 1.18 (t, J=7.5 Hz, 3H, C*H*$_3$CH$_2$S), 0.96 (s, 3H, C*H*$_3$); ^{13}C NMR (75 MHz, C_6D_6, ^{1}H decoupled) δ 149.54, 106.24, 77.44, 71.44, 53.44, 42.59, 40.69, 36.46, 31.65, 31.19, 23.92, 21.01, 15.48; IR (film) 3070, 2964, 1648, 1459, 1372, 1257, 1227, 1121, 1103, 1024, 981, 932, 885, 743 cm^{-1}; HRMS calcd for $C_{13}H_{21}NS$ 223.1395, found 223.1393.

Isotropane 3a. To a heterogeneous mixture of pyrrolidine **8a**$_{trans}$ (203 mg, 0.90 mmol) in 3:1

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Isotropane 3a. To a heterogeneous mixture of pyrrolidine **8a**$_{trans}$ (203 mg, 0.90 mmol) in 3:1 H_2O / THF (4.5 mL) was added aqueous CH_2O (146 µL, 1.80 mmol, 37% in H_2O) and the resulting cloudy mixture was stirred vigorously for 1.5h. Upon cooling the reaction mixture to 0 °C, TFA (73 µL, 0.94 mmol) was added dropwise and the resulting homogeneous solution was stirred for 10 min at 0 °C followed by 2h at room temperature. Aqueous NaOH (2 mL, 2N) was added dropwise and stirring was continued for an additional 30 min. The mixture was diluted with H_2O (2 mL) and was extracted with Et_2O (3 × 4mL). The extracts were washed with brine (2 × 4mL), dried over $MgSO_4$, filtered and concentrated. Silica gel chromatography (10% IPA / EtOAc) of the residue afforded isotropane **3a** (115 mg, 77%) as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.51 (t, J=2.2 Hz, 1H, C=C*H*H), 4.24 (t, J=2.2 Hz, 1H, C=CH*H*), 2.92 (dt, J=13.1, 7.1 Hz, 2H, NCH_2), 2.78 (d, J=6.2, 1H, C*H*), 2.75 (dt, J=13.0, 7.0Hz, 2H, NCH_2), 2.28 (m, 1H, C*H*HC=C), 2.19 (d, J=10.3 Hz, 1H, NC*H*), 1.92 (dd, J=14.8, 5.1 Hz, 1H, CHC*H*H), 1.80 (m, 1H, CH*H*C=C), 1.56 (ddd, J=13.5, 8.9, 5.1 Hz, 1H, CHCH*H*), 1.33 (m, 1H, C*H*$(CH_3)_2$), 0.92 (d, J=6.5 Hz, 3H, CH_3CHCH$_3$), 0.86 (d, J=6.6 Hz, 3H, CH$_3$CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 152.64, 103.02, 80.00, 57.17, 48.99, 45.76, 30.23, 28.45, 27.68, 20.17, 19.95; IR (film) 3070, 2956, 2873, 1644, 1469, 1457, 1090, 1078, 1030, 1013, 920, 879 cm^{-1}; HRMS calcd for $C_{11}H_{19}N$ 165.1517, found 165.1516.

Isotropane 3b. Using the procedure described for the preparation of **3a** pyrrolidine **8b**$_{trans}$ (174 mg, 0.73 mmol) was converted into isotropane **3b** (97 mg, 74%) which was obtained as a colorless oil: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.48 (t, J=2.2 Hz, 1H, C=C*H*H), 4.41 (t, J=2.2 Hz, 1H, C=CH*H*), 2.69 - 3.01 (m, 5H, NCH_2 × 2 and NC*H*), 2.52 (d, J=6.4 Hz, 1H, CH), 2.26 (m, 1H, C=CC*H*H), 1.89 (dd, J=14.9, 5.0 Hz, 1H, CHC*H*H), 1.85 (m, 1H, C=CCH*H*), 1.60 (m, 1H, $(CH_3)_2$C*H*), 1.56 (ddd, J=13.5, 8.9, 5.0 Hz, 1H, CHCH*H*), 1.45 (dt, J=13.8, 7.1 Hz, 1H, C*H*HCH$(CH_3)_2$), 0.98 (dt, J=13.7, 7.4 Hz, 1H, CH*H*CH$(CH_3)_2$); 0.87 (d, J=2.3 Hz, 3H, CH_3CHCH$_3$), 0.85 (d, J=2.4 Hz, 3H, CH$_3$CHCH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ^{1}H decoupled) δ 152.44, 103.01, 70.92, 57.00, 49.05, 47.84, 40.50, 30.07, 28.30, 25.41, 22.94, 22.57; IR (film) 3071, 2954, 2871, 1652, 1456, 1095, 1080, 1028, 922, 879, 743, 734 cm^{-1}; HRMS calcd for $C_{12}H_{21}N$ 179.1674, found 179.1681.

Isotropane 3c (TFA derivative). A solution of amine **6** (300 mg, 1.23 mmol) in CH_3CN (6 mL) was treated dropwise with aqueous CH_2O (400 mL, 4.92 mmol, 37% in H_2O). The resulting cloudy mixture was stirred for 2h after which TFA (95 µl, 1.23 mmol) was added dropwise. The resulting homogeneous solution was stirred for 8h, basified with NaOH (3mL, 2M) and partitioned with brine (6 mL). The organic phase was removed, washed with brine (3 mL), dried ($MgSO_4$) and filtered. The resulting solution of the crude, volatile isotropane (97% G.C.) was cooled to 0 °C and TFA (95 µL, 1.23 mmol) was added dropwise. After stirring for 1h at 0 °C, the reaction mixture was concentrated *in vacuo* and the resulting viscous oil was washed with hexane (3 × 5 mL). The residue was dissolved in Et_2O and filtered through a Celite plug to furnish the title compound (257 mg, 88%) as a colorless, viscous oil which solidified upon cold storage: ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.98 (br s, 1H, $^+$N*H*), 4.89 (d, J=2.1 Hz, 1H, C=C*H*H), 4.82 (d, J=2.0 Hz, 1H, C=CH*H*), 3.72 (ddd, J=13.4, 7.4, 5.2 Hz, 1H, $^+$NHC*H*H), 3.40 (br t, J=10.6 Hz, 3H, $^+$NHCH_2 and $^+$NHC*H*H), 3.29 (dq, J=13.4, 5.5 Hz, 1H, $^+$NHCH*H*), 3.17 (unresolved, 1H, $^+$NHCH*H*), 3.15 (dd, J = 10.7, 4.4 Hz, 1H, C*H*), 2.67 (m, 1H, C=CC*H*H), 2.47 (dd, J = 16.0, 5.4 Hz, 1H, CHC*H*H), 2.32 (m, 1H, C=CCH*H*), 1.97 (dddd, J = 14.4, 6.9, 5.2,

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1.7Hz, 1H, CHCH*H*); ^{13}C NMR (75 MHz, $CDCl_3$, ^1H decoupled) δ 162.02, 142.57, 119.05, 110.55, 58.96, 52.68, 49.78, 42.22, 28.23, 25.15; IR (film) 3414, 3072, 2993, 1680, 1654, 1470, 1173, 1012, 911, 798, cm^{-1}; HRMS (–HO_2CCF_3) calcd for $C_8H_{13}N$, 123.1048, found 123.1047.