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Supporting Information

for

Ruthenium-Catalyzed Chemoselective *N*-Allyl Cleavage: Novel Grubbs' Carbene-Mediated Deprotection of Allylic Amines

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General Procedure for the Preparation of Tertiary Allylic Amines 1a, 1d, 1e, and 1h–k. Allyl bromide (0.29 mL, 3.375 mmol) was added dropwise to a stirred suspension of the appropriate secondary amine (1.125 mmol) and potassium carbonate (1.5 g, 11.25 mmol) in acetonitrile (25 mL), and the mixture was stirred for 24h at room temperature (compounds **1a**, **1j**, and **1k** needs 3h at reflux temperature). The solid was removed by filtration, and the filtrate was concentrated under reduced pressure. Chromatography of the residue using ethyl acetate/hexanes mixtures gave analytically pure compounds **1a**, **1d**, **1e**, and **1h–k**. Spectroscopic and analytical data for some representative pure forms follow.

Tertiary Allylic Amine 1a. From 152 mg (0.776 mmol) of 5-bromoindole, and after flash chromatography eluting with hexanes/ethyl acetate (2:1), 163 mg (89%) of the compound **1a** was obtained. Colorless oil. ^{1}H-NMR: δ 4.57 (d, 2H, *J* = 5.3 Hz), 5.07 (m, 2H), 5.87 (m, 1H), 6.35 (d, 1H, *J* = 3.1 Hz), 7.13 (m, 3H), 7.66 (d, 1H, *J* = 1.5 Hz). ^{13}C-NMR: δ 134.9, 133.1, 130.4, 129.1, 124.5, 123.5, 117.6, 112.9, 111.2, 101.1, 49.1. MS (CI), *m/z* : 237 (M^+ + 2, 100), 235 (M^+, 80). Anal. Calcd for $C_{11}H_{10}BrN$: C, 55.96; H, 4.27; N, 5.93. Found: C, 55.85; H, 4.30; N, 5.90.

Tertiary Allylic Amine 1d. From 150 mg (1.125 mmol) of 1,2,3,4-tetrahydroquinoline, and after flash chromatography eluting with hexanes/ethyl acetate (3:1), 161 mg (83%) of the compound **1d** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.89 (m, 2H), 2.69 (dd, 2H, *J* = 6.5, 6.0 Hz), 3.20 (dd, 2H, *J* = 6.0, 5.5 Hz), 3.78 (m, 2H), 5.08 (m, 2H), 5.78 (m, 1H), 6.49 and 6.91 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 145.3, 133.6, 128.9, 127.0, 122.4, 115.8, 115.7, 110.9, 53.8, 49.1, 28.1, 22.3. MS (CI), *m/z* : 174 (M^+ + 1, 100), 173 (M^+, 22). Anal. Calcd for $C_{12}H_{15}N$: C, 83.19; H, 8.73; N, 8.08. Found: C, 83.26; H, 8.70; N, 8.10.

Tertiary Allylic Amine 1e. From 300 mg (1.85 mmol) of 1-phenylpiperazine, and after flash chromatography eluting with ethyl acetate, 307 mg (82%) of the compound **1e** was obtained. Yellow oil. ^{1}H-NMR ($CDCl_3$): δ 2.62 (m, 4H), 3.07 (dt, 2H, *J* = 6.6, 1.2 Hz), 3.22 (m, 2H), 5.12 (m, 2H), 5.82 (m, 1H), 6.81 (m, 3H), 7.21 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 151.5, 135.0, 129.2, 119.8, 118.3, 116.2, 61.9, 53.2, 49.3. MS (CI), *m/z* : 203 (M^+ + 1, 100), 202 (M^+, 14). Anal. Calcd for $C_{13}H_{18}N_2$: C, 77.18; H, 8.97; N, 13.85. Found: C, 77.28; H, 8.93; N, 13.81.

Tertiary Allylic Amine 1h. From 99 mg (0.5 mmol) of dibenzylamine, 118 mg (100%) of the compound **1h** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 3.17 (d, 2H, *J* = 6.3 Hz), 3.69 (s, 4H), 5.28 (m, 2H), 6.03 (m, 1H), 7.44 (m, 10H). ^{13}C-NMR ($CDCl_3$): δ 139.7, 136.0, 128.8, 128.2, 126.8, 117.3, 57.8, 56.4. MS (CI), *m/z* : 238 (M^+ + 1, 100), 237 (M^+, 20).

Tertiary Allylic Amine 1i. From 71 mg (0.588 mmol) of *N*-benzylmethylamine, and after flash chromatography eluting with ethyl acetate, 77 mg (82%) of the compound **1i** was obtained. Pale yellow oil. ^{1}H-NMR ($CDCl_3$): δ 2.09 (s, 3H), 2.94 (dd, 2H, *J* = 6.5, 1.2 Hz), 3.40 (s, 2H), 5.09 (m, 2H), 5.81 (m, 1H), 7.17 (m, 5H). ^{13}C-NMR ($CDCl_3$): δ 139.1, 135.9, 129.2, 128.3, 127.0, 117.6, 61.8, 60.6, 42.1. MS (CI), *m/z* : 162 (M^+ + 1, 100), 161 (M^+, 12). Anal. Calcd for $C_{11}H_{15}N$: C, 81.94; H, 9.38; N, 3.69. Found: C, 81.85; H, 9.34; N, 3.67.

Tertiary Allylic Amine 1j. From 447 mg (2.44 mmol) of *N*-benzylphenylamine, and after flash chromatography eluting with hexanes/ethyl acetate (5:1), 420 mg (78%) of the compound **1j** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 3.93 (m, 2H), 4.47 (s, 2H), 5.14 (m, 2H), 5.82 (m, 1H), 6.62 (m, 4H), 7.15 (m, 6H). ^{13}C-NMR ($CDCl_3$): δ 149.1, 139.1, 133.8, 129.3, 128.8, 126.9, 126.8, 116.7, 116.5, 112.6, 54.1, 53.2. MS (CI), *m/z* : 224 (M^+ + 1, 100), 223 (M^+, 17). Anal. Calcd for $C_{16}H_{17}N$: C, 86.05; H, 7.67; N, 6.27. Found: C, 86.14; H, 7.63; N, 6.25.

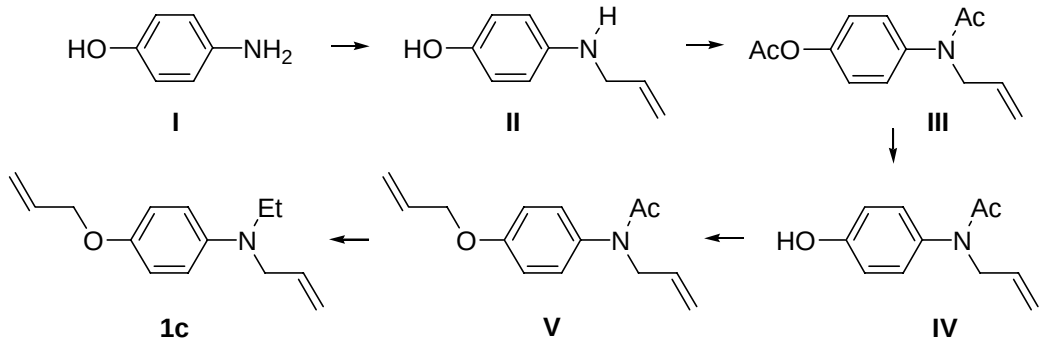
Tertiary Allylic Amine 1k. From 412 mg (2.44 mmol) of diphenylamine, and after flash chromatography eluting with hexanes/ethyl acetate (10:1), 310 mg (61%) of the compound **1k** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 4.25 (m, 2H), 5.11 (m, 2H), 5.84 (m, 1H), 6.87 (m, 5H), 7.15 (m, 5H). ^{13}C-NMR ($CDCl_3$): δ 147.8, 134.2, 129.1, 121.2,

120.7, 116.3, 54.7. MS (CI), *m/z* : 210 (M^+ + 1, 100), 209 (M^+, 15). Anal. Calcd for $C_{15}H_{15}N$: C, 86.08; H, 7.22; N, 6.69. Found: C, 86.19; H, 7.20; N, 6.67.

Preparation of Tertiary Allylic Amine (+)-1b. Diethyl ether (8.0 mL) was slowly added to lithium aluminum hydride (71 mg, 1.867 mmol) and aluminum(III) chloride (248 mg, 1.867 mmol), and the mixture was heated under reflux temperature for 30 min. The resulting suspension was allowed to cool to room temperature and the β-lactam (+)-(3*R*,4*S*)-1-(2-propenyl)-4-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-3-methoxy-2-azetidinone[1] (150 mg, 0.622 mmol) was added in portions. After 15 min. at room temp., the mixture was cooled to 0 ^oC and water (2 mL) was added. The reaction was allowed to warm to room temp., before being partitioned between ether and water. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give 129 mg (91%) as a colorless oil.

(+)-(2*S*, 3*R*)-2-[(*S*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-3-methoxy-1-(2-propenyl)azetidine, (+)-1b. Colorless oil. $[\alpha]_D$ = +56.3 (*c* 0.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$) δ: 1.07 and 1.03 (s, each 3H), 2.94 (m, 2H), 3.22 (s, 3H), 3.49 (m, 5H), 4.02 (m, 2H), 5.06 (m, 2H), 5.78 (m, 1H). ^{13}C-NMR ($CDCl_3$) δ: 134.5, 117.4, 73.3, 71.9, 69.6, 68.9, 68.3, 61.2, 57.2, 56.6, 22.1, 21.9. MS (ES), *m/z* : 250 (M^+ + 23, 17), 228 (M^+ + 1, 100), 227 (M^+, 14),. Anal. Calcd for $C_{12}H_{21}NO_3$: C, 63.41; H, 9.31; N, 6.16. Found: C, 63.52; H, 9.27; N, 6.18.

Preparation of Tertiary Allylic Amine 1c. Allyl-(4-allyloxyphenyl)-ethylamine was prepared as depicted in next sequence.



Preparation of Compound II. Allyl bromide (0.71 mL, 8.245 mmol) was added dropwise to a stirred solution of 4-aminophenol **I** (300 mg, 2.75 mmol) and triethylamine (1.15 mL, 8.25 mmol) in tetrahydrofuran (50 mL), and the mixture was stirred for 48h at

room temperature. The reaction mixture was concentrated under reduced pressure, and after chromatography of the residue using hexanes/ethyl acetate (4:1), 201 mg (49%) of the compound **II** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 3.63 (m, 2H), 5.15 (m, 2H), 5.88 (m, 1H), 6.49 (m, 2H), 6.61 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 148.1, 141.9, 135.6, 116.4, 116.2, 114.9. MS (CI), *m/z* : 150 (M^+ + 1, 100), 149 (M^+, 11).

Preparation of Compound III. Acetic anhydride (0.09 mL, 0.96 mmol) was added dropwise to a stirred solution of the aminophenol **II** (130 mg, 0.87 mmol), DMAP (cat.) and triethylamine (0.24 mL, 1.74 mmol) in dichloromethane (10 mL) at 0 ^{o}C, and the mixture was stirred for 48h at room temperature. Water (1 mL) was added, and the reaction was allowed to warm to room temp., before being partitioned between dichloromethane and water. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. After chromatography of the residue using ethyl acetate, 130 mg (64%) of the compound **III** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 1.79 (s, 3H), 2.24 (s, 3H), 4.20 (m, 2H), 5.02 (m, 2H), 5.80 (m, 1H), 7.08 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 169.9, 168.9, 149.8, 140.3, 132.8, 128.9, 122.5, 117.8, 51.9, 22.6, 20.9. MS (CI), *m/z* : 234 (M^+ + 1, 100), 233 (M^+, 18).

Preparation of Compound IV. Sodium methoxide (25 mg, 0.472 mmol) was added in portions to a solution of the amidoester **III** (110 mg, 0.472 mmol) in methanol (4.5 mL) at room temperature. The reaction was stirred for 1h and then water was added (1 mL). The methanol was concentrated under reduced pressure, the aqueous residue was extracted with ethyl acetate (3 x 8 mL) and the organic layer was dried ($MgSO_4$). The solvent was removed under reduced pressure, to give 57 mg (63%) of the compound **IV**. Yellow oil. ^{1}H-NMR ($CDCl_3$): δ 1.82 (s, 3H), 4.20 (m, 2H), 5.05 (m, 2H), 5.81 (m, 1H), 6.90 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 171.5, 156.3, 134.7, 132.8, 128.9, 118.1, 116.3, 52.3, 22.4. MS (CI), *m/z* : 192 (M^+ + 1, 100), 191 (M^+, 11).

Preparation of Compound V. Tetrabutyl ammonium iodide (1 mg, 0.003 mmol), 50% aqueous sodium hydroxide (2.8 mL) and allyl bromide (0.04 mL, 0.402 mmol) were sequentially added at room temperature to a solution of the phenol **IV** (48 mg, 0.251 mmol) in dichloromethane (2.8 mL). The reaction was stirred for 16 h and then water was added (1

mL), before being partitioned between dichloromethane and water. The aqueous phase was extracted with dichloromethane (3 x 5 mL), the combined organic extracts were dried ($MgSO_4$) and concentrated under reduced pressure to give 57 mg (100%) of compound **V**. Yellow oil. ^{1}H-NMR ($CDCl_3$): δ 1.77 (s, 3H), 4.18 (m, 2H), 4.48 (m, 2H), 5.05 (m, 2H), 5.32 (m, 2H), 5.95 (m, 2H), 6.85 (m, 2H), 7.00 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 170.3, 157.8, 135.7, 133.1, 132.7, 128.9, 117.8, 117.6, 115.2, 68.8, 51.9, 22.4. MS (CI), *m/z* : 232 (M^+ + 1, 100), 231 (M^+, 14).

Preparation of Compound 1c. A solution of the amide **V** (50 mg, 0.216 mmol) in diethyl ether (1.0 mL) was added dropwise to a well stirred suspension of lithium aluminum hydride (66 mg, 1.73 mmol) in the same solvent (3.5 mL) at 0 ^{o}C, and the mixture was stirred at room temperature for 30 min. Saturated aqueous ammonium chloride (1.0 mL) was added at 0 ^{o}C, and the mixture was allowed to warm to room temperature, before being extracted with diethyl ether. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with hexanes/ethyl acetate (3:1), gave 40 mg (87%) of compound **1c**. Yellow oil. ^{1}H-NMR ($CDCl_3$): δ 1.04 (t, 3H, *J* = 7.0 Hz), 3.23 (q, 2H, *J* = 7.0 Hz), 3.74 (m, 2H), 4.39 (m, 2H), 5.21 (m, 4H), 5.91 (m, 2H), 6.59 (m, 2H), 6.74 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 150.6, 143.2, 135.0, 134.1, 117.2, 116.0, 115.9, 114.7, 69.7, 53.8, 45.4, 12.2. MS (CI), *m/z* : 218 (M^+ + 1, 100), 217 (M^+, 21). Anal. Calcd for $C_{14}H_{19}NO$: C, 77.38; H, 8.81; N, 6.45. Found: C, 77.48; H, 8.79; N, 6.43.

Preparation of Tertiary Allylic Amines (+)-1f and (–)-1g. A solution of the glyceraldehyde derived allyl imine (500 mg, 2.96 mmol) in acetonitrile (15 mL) was added dropwise to a stirred suspension of zinc iodide (1.038 g, 3.254 mmol) in acetonitrile (13 mL) at –20 ^{o}C. The reaction mixture was stirred at –20 ^{o}C for 15 minutes and then Danishefsky's diene (0.69 mL, 3.55 mmol) was added. After 6 h at –20 ^{o}C, saturated aqueous $NaHCO_3$ (2 mL) was added, and the mixture was extracted with ethyl acetate (3 x 25 mL). The combined organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. After chromatography of the residue eluting with ethyl acetate, 527 mg (76%) of the corresponding cycloadduct, containing *ca.* 27% of its epimer were obtained. Colorless oil.

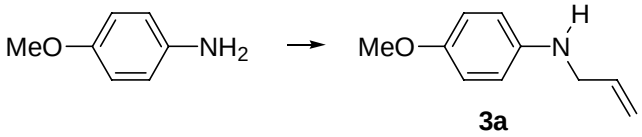
$[\alpha]_D$ = +35.0 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.17 (s, 3H), 1.23 (s, 2.1H), 1.26 (s, 0.9H), 1.87 (d, 0.7H, *J* = 16.9 Hz), 2.34 (dd, 0.3H, *J* = 16.9, 1.7 Hz), 2.68 (m, 1H), 3.39 (m, 1H), 3.84 (m, 2H), 3.85 (m, 0.3H), 4.60 (dt, 0.7H, *J* = 6.8, 6.6 Hz), 4.77 (d, 1H, *J* = 7.5 Hz), 5.16 (m, 2H), 5.65 (m, 1H), 6.85 (d, 1H, *J* = 7.5 Hz). ^{13}C-NMR ($CDCl_3$): δ 189.6 (m), 189.0 (M), 152.9 (m), 152.4 (M), 133.5 (M), 133.2 (m), 118.6 (M + m), 169.8 (M), 108.9 (m), 98.0 (m), 97.0 (M), 76.3 (m), 73.3 (M), 66.6 (M), 65.9 (m), 59.4 (M), 58.5 (M), 57.7 (m), 56.4 (m), 37.2 (M), 36.4 (m), 26.5 (M), 26.2 (m), 25.3 (M + m). A cooled solution of L-Selectride® (295 mg, 1.55 mmol) in tetrahydrofuran (1.55 mL) was added dropwise to a stirred solution of the above mixture of cycloadducts (334 mg, 1.409 mmol) in tetrahydrofuran (20 mL) at –78 ºC, and the mixture was stirred for 45 min at –78 ºC. Saturated aqueous sodium hydrogen carbonate (2 mL) was added, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. After chromatography of the residue using ethyl acetate/hexanes (2:1 containing 1% of triethylamine), 160 mg (48%) of the less polar compound (+)-**1f** and 69 mg (20%) of the more polar diastereoisomer (–)-**1g** were obtained.

Tertiary Allylic Amine (+)-1f. Pale yellow oil. $[\alpha]_D$ = +35.0 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.31 and 1.34 (s, each 3H), 2.10 (ddd, 1H, *J* = 14.6, 6.1, 0.9 Hz), 2.38 (m, 2H), 2.50 (ddd, 1H, *J* = 14.6, 5.4, 0.9 Hz), 2.86 (m, 1H), 3.17 and 3.39 (m, each 2H), 3.65 (dd, 1H, *J* = 8.1, 7.6 Hz), 3.98 (dd, 1H, *J* = 8.1, 6.3 Hz), 4.22 (m, 1H), 5.15 (m, 2H), 5.83 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 208.5, 135.3, 117.6, 109.4, 75.6, 66.3, 61.4, 56.7, 48.2, 41.0, 39.5, 26.2, 25.2. IR ($CHCl_3$, cm^{-1}): ν 1728. MS (CI), *m/z* : 240 (M^+ + 1, 100), 239 (M^+, 21). (Anal. Calcd. for $C_{13}H_{21}NO_3$: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.33; H, 8.81; N, 5.87).

Tertiary Allylic Amine (–)-1g. Yellow oil. $[\alpha]_D$ = –23.6 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.25 and 1.31 (s, each 3H), 2.37 (m, 4H), 2.91 (m, 1H), 3.11 (m, 2H), 3.34 (m, 2H), 3.61 (dd, 1H, *J* = 8.5, 7.1 Hz), 4.01 (dd, 1H, *J* = 8.5, 6.8 Hz), 4.27 (m, 1H), 5.14 (m, 2H), 5.76 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 208.6, 135.6, 118.1, 110.3, 75.4, 67.6, 61.2, 56.4, 47.9, 39.1, 38.6, 26.1, 25.3. IR ($CHCl_3$, cm^{-1}): ν 1730. MS (CI), *m/z* : 240 (M^+ + 1, 100),

239 (M^+, 17). (Anal. Calcd. for $C_{13}H_{21}NO_3$: C, 65.25; H, 8.84; N, 5.85. Found: C, 65.15; H, 8.80; N, 5.82).

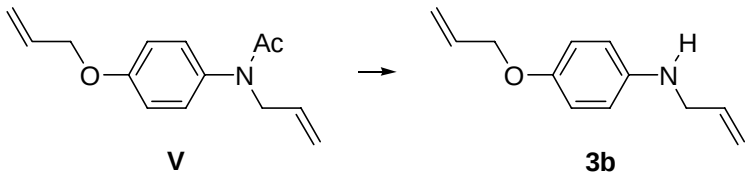
Preparation of Secondary Allylic Amine 3a. Allyl-(4-methoxyphenyl)-amine was prepared as depicted in next sequence.



3a

Allyl bromide (0.25 mL, 2.93 mmol) was added dropwise to a stirred suspension of *p*-anisidine (300 mg, 2.44 mmol) and potassium carbonate (3.3 g, 24.4 mmol) in acetonitrile (53 mL), and the mixture was stirred for 24h at room temperature. The solid was removed by filtration, and the filtrate was concentrated under reduced pressure. After chromatography of the residue using ethyl acetate/hexanes (3:1), 180 mg (45%) of compound **3a** was obtained. Colorless oil. ^{1}H-NMR ($CDCl_3$): δ 3.67 (s, 3H), 3.77 (m, 2H), 5.12 (m, 2H), 5.85 (m, 1H), 6.67 (m, 4H). ^{13}C-NMR ($CDCl_3$): δ 152.6, 142.1, 135.8, 116.5, 115.1, 114.8, 55.9, 47.9. MS (EI), *m/z* : 163 (M^+, 100). Anal. Calcd for $C_{10}H_{13}NO$: C, 73.59; H, 8.03; N, 8.58. Found: C, 73.70; H, 8.01; N, 8.60.

Preparation of Secondary Allylic Amine 3b. Allyl-(4-allyloxyphenyl)-amine was prepared as depicted in next sequence.

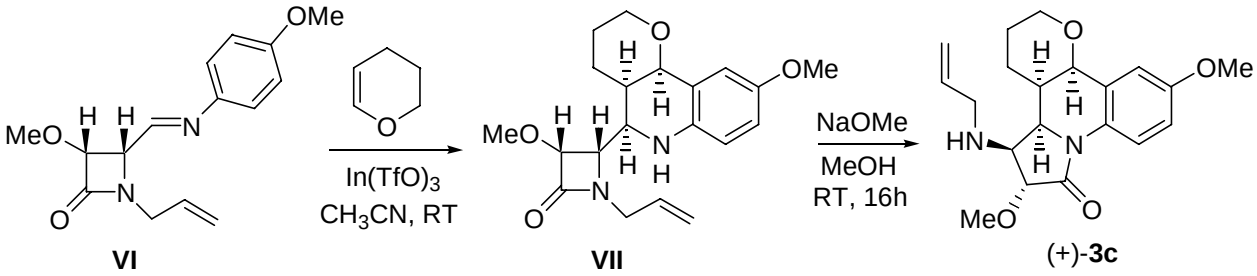


V **3b**

A suspension of the amide **V** (100 mg, 0.433 mmol) in 5 % aqueous hydrochloric acid (10 mL) was stirred at reflux temperature for 7 h. The reaction was allowed to warm to room temperature, before ammonium hydroxide was added. The mixture was extracted with ethyl acetate, the organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure to give 63 mg (77%) of compound **3b**. Yellow oil. ^{1}H-NMR ($CDCl_3$): δ 3.66 (m, 2H), 4.39 (m, 2H), 5.21 (m, 4H), 5.93 (m, 2H), 6.51 (m, 2H), 6.71 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 151.3, 142.5, 135.8, 133.9, 117.3, 116.1, 114.7, 114.4, 69.8, 47.6. MS (CI),

m/z : 190 (M^+ + 1, 100), 189 (M^+, 11). Anal. Calcd for $C_{12}H_{15}NO$: C, 76.16; H, 7.99; N, 7.40. Found: C, 76.26; H, 7.96; N, 7.37.

Preparation of Secondary Allylic Amine (+)-3c. Compound (+)-**3c** was prepared as depicted in next sequence.



Compound VI. A solution of *p*-anisidine (6.25 mmol, 0.77 g) in dichloromethane (20 mL) was added dropwise to a stirred suspension of 3-methoxy-1-(2-propenyl)-4-oxoazetidine-2-carbaldehyde (4.17 mmol, 0.70 g) and magnesium sulfate (6.25 mmol, 0.75 g) in dichloromethane (200 mL) at room temperature. After stirring 16h at room temperature, the mixture was filtered and the solvent was removed under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes (1:1 containing 1% of triethylamine) gave 1.14 g (100%) of imine **VI** as a yellow oil. $[\alpha]_D$ = +97.0 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 3.39 (s, 3H), 3.73 (s, 3H), 3.85 (m, 2H), 4.34 (dd, 1H, *J* = 6.7, 4.7 Hz), 4.66 (d, 1H, *J* = 4.7 Hz), 5.16 (m, 2H), 5.69 (m, 1H), 6.78 and 7.02 (m, each 2H), 7.78 (d, 1H, *J* = 6.7 Hz). ^{13}C-NMR ($CDCl_3$): δ 166.3, 158.9, 158.7, 143.5, 131.1, 122.1, 122.0, 119.4, 114.3, 114.2, 85.8, 61.3, 58.8, 55.4, 43.8. MS (EI), *m/z* : 274 (M^+, 100). (Anal. Calcd. for $C_{15}H_{18}N_2O_3$: C, 65.68; H, 6.61; N, 10.21. Found: C, 65.78; H, 6.66; N, 10.17).

Compound VII. Indium(III) triflate (0.365 mmol) was added in portions to a solution of the imine **VI** (1.825 mmol, 500 mg) and 3,4-dihydro-2*H*-pyran (2.19 mmol, 184 mg) in acetonitrile (13 mL) at 0 ^{o}C. After disappearance of the imine (TLC), saturated aqueous $NaHCO_3$ (2 mL) was added, and the mixture was extracted with ethyl acetate (3 x 35 mL). The combined organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes (1:1)

gave 620 mg (95%) of cycloadduct **VII** as a colorless oil. $[\alpha]_D$ = +43.5 (*c* 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.67 (m, 4H), 2.24 (m, 1H), 3.42 (m, 1H), 3.50 (s, 3H), 3.55 (m, 2H), 3.69 (s, 3H), 3.81 (m, 2H), 3.99 (m, 1H), 4.49 (d, 1H, *J* = 5.1 Hz), 4.95 (d, 1H, *J* = 5.6 Hz), 5.30 (m, 2H), 5.77 (m, 1H), 6.39 (d, 1H, *J* = 8.6 Hz), 6.61 (dd, 1H, *J* = 8.6, 2.9 Hz), 6.90 (d, 1H, *J* = 2.9 Hz). ^{13}C-NMR ($CDCl_3$): δ 168.4, 153.3, 138.4, 133.4, 121.9, 118.5, 116.4, 115.1, 111.8, 83.4, 71.8, 60.9, 60.3, 59.4, 55.8, 54.6, 44.7, 33.5, 25.2, 19.1. IR ($CHCl_3$, cm^{-1}): ν 3419, 1755. MS (CI), *m/z* : 359 (M^+ + 1, 100), 358 (M^+, 43). (Anal. Calcd. for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.11; H, 7.28; N, 7.86).

Compound (+)-3c. Sodium methoxide (30 mg, 0.154 mmol) was added in portions at 0 ^oC to a solution of the tetrahydroquinolinyl-β-lactam **VII** (0. 139 mmol, 50 mg) in methanol (3 mL). The reaction was stirred at room temperature until complete disappearance of the starting material (TLC) and then water was added (0.3 mL). The methanol was concentrated under reduced pressure, the aqueous residue was extracted with ethyl acetate (6 x 1.5 mL), the organic layer was dried over $MgSO_4$, and the solvent was removed under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes (9:1) gave 38 mg (75%) of compound (+)-**3c** as a colorless oil. $[\alpha]_D$ = +38.0 (*c* 0.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.69 (m, 4H), 2.29 (m, 1H), 3.19 (m, 1H), 3.29 (m, 2H), 3.51 (m, 2H), 3.74 and 3.76 (s, each 3H), 3.86 (m, 2H), 4.92 (d, 1H, *J* = 5.6 Hz), 5.15 (m, 2H), 5.90 (m, 1H), 6.78 (dd, 1H, *J* = 8.9, 2.9 Hz), 7.03 (d, 1H, *J* = 2.9 Hz), 7.91 (d, 1H, *J* = 8.9 Hz). ^{13}C-NMR ($CDCl_3$): δ 169.8, 157.4, 136.1, 129.4, 128.3, 122.5, 116.7, 113.9, 111.9, 83.4, 72.4, 61.1, 59.1, 58.8, 58.2, 55.5, 51.5, 33.3, 24.5, 20.3. IR ($CHCl_3$, cm^{-1}): ν 3318, 1710. MS (ES), *m/z* : 381 (M^+ + 23, 3), 359 (M^+ + 1, 100), 358 (M^+, 3). (Anal. Calcd. for $C_{20}H_{26}N_2O_4$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.10; H, 7.34; N, 7.79).

General Procedure for the Preparation of β-Lactam-N-allylpiperidines 5. A solution of the appropriate allylic imine (1.0 mmol), derived from allylamine and the corresponding 4-oxoazetidine-2-carbaldehyde, in acetonitrile (5 mL) was added dropwise to a stirred suspension of zinc iodide (1.10 mmol) in acetonitrile (13 mL) at –20 ^oC. The reaction mixture was stirred at –20 ^oC for 15 minutes and then Danishefsky's diene (1.20 mmol) was added. After disappearance of the imine (TLC), saturated aqueous $NaHCO_3$ (1 mL) was

added, and the mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures (containing 1% of triethylamine) gave the corresponding aza-Diels–Alder cycloadducts. A cooled solution of L-Selectride® (49 mg, 0.259 mmol) in tetrahydrofuran (0.259 mL) was added dropwise to a stirred solution of the appropriate cycloadduct (0.236 mmol) in tetrahydrofuran (3.5 mL) at –78 ºC, and the mixture was stirred for 1 h at –78 ºC. Saturated aqueous sodium hydrogen carbonate (0.5 mL) was added, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes mixtures (containing 1% of triethylamine) gave analytically pure compounds **5** .

β-Lactam-*N*-allylpiperidine (–)-5a. From 100 mg (0.456 mmol) of 3-methoxy-1-(*p*-tolyl)-4-oxoazetidine-2-carbaldehyde, after column chromatography eluting with ethyl acetate/hexanes (1:4 containing 1% of triethylamine), 49 mg (33%) of the less polar compound (–)-**5a** and 13 mg (9%) of its diastereomer **VI** [see preparation of compound (–)-**5g**] were obtained. Pale yellow oil. $[\alpha]_D$ = –91.7 (*c* 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.19 (s, 3H), 2.62 (m, 4H), 3.18 (m, 4H), 3.51 (m, 4H), 4.45 (m, 2H), 5.17 (m, 2H), 5.88 (m, 1H), 7.05 and 7.46 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 208.7, 165.6, 135.4, 134.8, 134.4, 129.6, 118.8, 118.4, 82.7, 59.8, 59.4, 58.9, 57.1, 49.0, 41.2, 39.2, 20.9. IR ($CHCl_3$, cm^{-1}): ν 1740, 1718. MS (CI), *m/z* : 329 (M^+ + 1, 100), 328 (M^+, 21). (Anal. Calcd. for $C_{19}H_{24}N_2O_3$: C, 69.49; H, 7.37; N, 8.53. Found: C, 69.40; H, 7.40; N, 8.56).

β-Lactam-*N*-allylpiperidine (+)-5b. From 100 mg (0.425 mmol) of 3-methoxy-1-(*p*-methoxyphenyl)-4-oxoazetidine-2-carbaldehyde, after column chromatography eluting with ethyl acetate (containing 1% of triethylamine), 70 mg (48%) of compound (+)-**5b** was obtained. Pale yellow oil. $[\alpha]_D$ = +103.2 (*c* 0.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.55 (m, 2H), 3.16 (m, 3H), 3.54 (m, 4H), 3.73 (s, 3H), 4.46 (m, 2H), 5.22 (m, 2H), 5.90 (m, 1H), 6.79 and 7.52 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 208.6, 165.0, 156.5, 134.5, 130.9, 119.7, 118.3, 114.1, 82.5, 59.6, 59.3, 58.7, 56.9, 55.3, 48.9, 41.0, 39.0. IR ($CHCl_3$, cm^{-1}): ν 1741, 1718.

MS (CI), *m/z* : 345 (M^+ + 1, 100), 344 (M^+, 16). (Anal. Calcd. for $C_{19}H_{24}N_2O_4$: C, 66.26; H, 7.02; N, 8.13. Found: C, 66.36; H, 7.05; N, 8.09).

Preparation of β-Lactam-*N*-allylpiperidines (+)-5c and (+)-5d. From 110 mg (0.42 mmol) of 3-allyloxy-1-(*p*-methoxyphenyl)-4-oxoazetidine-2-carbaldehyde, after column chromatography eluting with ethyl acetate/hexanes (1:1 containing 1% of triethylamine), 49 mg (35%) of the less polar compound (+)-**5c** and 35 mg (25%) of the more polar compound (+)-**5d** were obtained.

β-Lactam-*N*-allylpiperidine (+)-5c. Yellow oil. $[\alpha]_D$ = +91.1 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.48 (m, 4H), 2.89 (m, 1H), 3.09 (m, 1H), 3.24 (m, 2H), 3.56 (m, 1H), 3.72 (s, 3H), 4.27 (m, 3H), 4.69 (d, 1H, *J* = 5.2 Hz), 5.16 (m, 4H), 5.48 (m, 1H), 5.80 (m, 1H), 6.77 and 7.24 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 208.6, 165.3, 156.8, 135.0, 133.4, 130.2, 120.6, 118.0, 117.9, 114.0, 80.7, 72.3, 59.1, 58.9, 57.3, 55.4, 47.1, 39.4, 38.5. IR ($CHCl_3$, cm^{-1}): ν 1742, 1721. MS (EI), *m/z* : 393 (M^+ + 1, 15), 371 (M^+ + 1, 100), 370 (M^+, 36). (Anal. Calcd. for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 68.19; H, 7.10; N, 7.54).

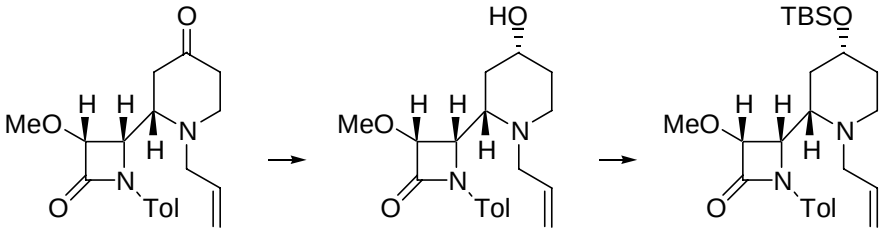
β-Lactam-*N*-allylpiperidine (+)-5d. Yellow oil. $[\alpha]_D$ = +55.43 (*c* 0.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.27 (m, 3H), 2.67 (m, 2H), 3.18 (m, 3H), 3.49 (m, 1H), 3.71 (s, 3H), 4.23 (m, 2H), 4.44 (dd, 1H, *J* = 5.5, 3.0 Hz), 4.65 (d, 1H, *J* = 5.5 Hz), 5.23 (m, 4H), 5.86 (m, 2H), 6.80 and 7.51 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 208.6, 165.3, 156.6, 134.6, 133.4, 131.1, 119.8, 118.3, 117.9, 114.2, 80.4, 72.6, 59.5, 58.9, 56.9, 55.4, 48.8, 41.1, 39.1. IR ($CHCl_3$, cm^{-1}): ν 1742, 1720. MS (EI), *m/z* : 393 (M^+ + 1, 11), 371 (M^+ + 1, 100), 370 (M^+, 27). (Anal. Calcd. for $C_{21}H_{26}N_2O_4$: C, 68.09; H, 7.07; N, 7.56. Found: C, 68.20; H, 7.04; N, 7.60).

β-Lactam-*N*-allylpiperidine (+)-5e. From 100 mg (0.546 mmol) of 3-methoxy-1-(3-butenyl)-4-oxoazetidine-2-carbaldehyde, after column chromatography eluting with ethyl acetate/hexanes (1:1 containing 1% of triethylamine), 65 mg (40%) of compound (+)-**5e** was obtained. Colorless oil. $[\alpha]_D$ = +58.6 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.17 (m, 4H), 2.49 (m, 2H), 3.27 (m, 6H), 3.48 (m, 4H), 3.68 (dd, 1H, *J* = 10.5, 4.9 Hz), 4.34 (d, 1H, *J* = 4.9 Hz), 5.05 (m, 4H), 5.68 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 208.7, 167.9, 135.3, 134.8, 118.1,

117.0, 82.7, 61.8, 59.8, 56.5, 55.8, 46.3, 40.6, 39.1, 37.2, 32.4. IR ($CHCl_3$, cm^{-1}): ν 1743, 1716. MS (CI), *m/z* : 293 (M^+ + 1, 100), 292 (M^+, 15). (Anal. Calcd. for $C_{16}H_{24}N_2O_3$: C, 65.73; H, 8.27; N, 9.58. Found: C, 65.80; H, 8.28; N, 9.56).

β-Lactam-*N*-allylpiperidine (+)-5f. From 80 mg (0.406 mmol) of 3-methoxy-1-(4-pentenyl)-4-oxoazetidine-2-carbaldehyde, after column chromatography eluting with ethyl acetate/hexanes (1:2 containing 1% of triethylamine), 46 mg (37%) of compound (+)-**5f** was obtained. Yellow oil. $[\alpha]_D$ = +116.9 (*c* 0.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.61 and 2.02 (m, each 2H), 2.42 and 2.57 (m, each 2H), 3.16 (m, 2H), 3.29 (m, 5H), 3.49 (s, 3H), 3.66 (dd, 1H, *J* = 10.5, 4.8 Hz), 4.35 (d, 1H, *J* = 4.8 Hz), 4.92 (m, 2H), 5.16 (m, 2H), 5.76 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 208.8, 167.9, 137.3, 135.4, 118.2, 115.3, 82.8, 61.9, 59.1, 56.4, 55.8, 46.4, 41.1, 39.2, 37.2, 31.0, 27.3. IR ($CHCl_3$, cm^{-1}): ν 1741, 1715. MS (CI), *m/z* : 307 (M^+ + 1, 100), 306 (M^+, 21). (Anal. Calcd. for $C_{17}H_{26}N_2O_3$: C, 66.64; H, 8.55; N, 9.14. Found: C, 6.72; H, 8.53; N, 9.15).

Preparation of β-Lactam-*N*-allylpiperidine (–)-5g. Compound (–)-**5g** was prepared as depicted in next sequence.



VIII **IX** **(–)-5g**

Compound VIII. For the experimental procedure, see above in preparation of compound (–)-**5a**. Pale yellow oil. $[\alpha]_D$ = +67.0 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.25 (s, 3H), 2.47 (m, 4H), 3.04 (m, 4H), 3.56 (s, 3H), 3.83 (m, 1H), 4.31 (dd, 1H, *J* = 6.9, 5.3 Hz), 4.55 (d, 1H, *J* = 5.3 Hz), 5.14 (m, 2H), 5.55 (m, 1H), 7.05 and 7.20 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 208.5, 165.3, 135.1, 134.6, 129.4, 118.7, 118.1, 83.0, 59.1, 58.4, 58.3, 57.4, 47.5, 45.4, 39.2, 38.6, 20.9. IR ($CHCl_3$, cm^{-1}): ν 1740, 1720. MS (CI), *m/z* : 329 (M^+ + 1, 100), 328 (M^+, 25). (Anal. Calcd. for $C_{19}H_{24}N_2O_3$: C, 69.49; H, 7.37; N, 8.53. Found: C, 69.59; H, 7.41; N, 8.49).

Compound IX. Sodium borohydride (74 mg, 1.92 mmol) was added in portions to a stirred solution of the piperidone **VIII** (320 mg, 0.976 mmol) in methanol (10 mL) at 0 ^{o}C, and the mixture was stirred at 0 ^{o}C for 90 min. Saturated aqueous ammonium chloride (1.5 mL) was added, and the mixture was allowed to warm to room temperature, before being extracted with ethyl acetate. The organic extract was washed with brine, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes (2:1) gave 167 mg (52%) of analytically pure hydroxypiperidine **IX** as a colorless oil. $[\alpha]_D$ = –72.2 (*c* 0.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.94 (m, 5H), 2.23 (s, 3H), 2.63 (d, 1H, *J* = 9.7 Hz), 2.86 (dd, 1H, *J* = 12.0, 8.2 Hz), 3.02 (dt, 1H, *J* = 12.0, 3.4 Hz), 3.46 (m, 5H), 4.48 (s, 2H), 5.18 (m, 2H), 5.86 (m, 1H), 6.45 and 7.54 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 165.6, 135.8, 134.8, 134.2, 129.6, 118.4, 118.0, 82.5, 68.9, 59.7, 58.5, 57.5, 56.9, 52.0, 37.2, 34.4, 21.0. IR ($CHCl_3$, cm^{-1}): ν 3340, 1738. MS (EI), *m/z* : 331 (M^+ + 1, 100), 330 (M^+, 30). (Anal. Calcd. for $C_{19}H_{26}N_2O_3$: C, 69.06; H, 7.93; N, 8.48. Found: C, 69.16; H, 7.90; N, 8.45).

β-Lactam-*N*-allylpiperidine (–)-5g. A solution of the hydroxypiperidine **VII** (167 mg, 0.505 mmol) in dimethylformamide (1.25 mL) was added dropwise to a stirred suspension of *tert*-butyldimethylsilyl chloride (126 mg, 0.833 mmol) and imidazole at 0 ^{o}C, and the mixture was stirred at room temperature for 17 h. Saturated aqueous ammonium chloride (1.0 mL) was added, and the mixture was extracted with dichloromethane. The organic extract was washed with brine, water, dried ($MgSO_4$) and concentrated under reduced pressure. Chromatography of the residue eluting with ethyl acetate/hexanes (1:5) gave 189 mg (85%) of analytically pure *tert*-butyldimethylsilyl ether (–)-**5g** as a yellow oil. $[\alpha]_D$ = –85.0 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 0.00 (s, 6H), 0.82 (s, 9H), 1.44 (m, 1H), 1.75 (m, 1H), 2.02 (m, 3H), 2.31 (s, 3H), 2.65 (d, 1H, *J* = 11.2 Hz), 3.02 (m, 2H), 3.56 (m, 5H), 4.55 (m, 2H), 5.25 (m, 2H), 5.97 (m, 1H), 7.10 and 7.66 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 165.5, 135.8, 134.8, 134.1, 129.4, 118.5, 117.8, 82.4, 70.0, 59.5, 58.4, 57.7, 56.8, 52.2, 37.4, 35.0, 25.9, 25.7, 20.9, 18.2. IR ($CHCl_3$, cm^{-1}): ν 1741. MS (EI), *m/z* : 445 (M^+ + 1, 100), 444 (M^+, 35). (Anal. Calcd. for $C_{25}H_{40}N_2O_3Si$: C, 67.52; H, 9.07; N, 6.30. Found: C, 67.63; H, 9.11; N, 6.27).

Spectroscopic and analytical data for some representative pure forms of deallylated amines **2**, **4**, and **6** follow.

Secondary Amine 2a. From 163 mg (0.691 mmol) of *N*-allyl-5-bromoindole **1a**, and after flash chromatography eluting with hexanes/ethyl acetate (4:1), 110 mg (81%) of the commercially available 5-bromoindole **2a** was obtained. Anal. Calcd for C_8H_6BrN: C, 49.01; H, 3.08; N, 7.14. Found: C, 49.10; H, 3.05; N, 7.17.

Secondary Amine 2d. From 70 mg (0.404 mmol) of *N*-allyl-1,2,3,4-tetrahydroquinoline **1d**, and after flash chromatography eluting with hexanes/ethyl acetate (10:1), 41 mg (77%) of the commercially available 1,2,3,4-tetrahydroquinoline **2d** was obtained. Anal. Calcd for $C_9H_{11}N$: C, 81.16; H, 8.32; N, 10.52. Found: C, 81.27; H, 8.30; N, 10.48.

Secondary Amine 2e. From 50 mg (0.247 mmol) of *N*-allyl-1-phenylpiperazine **1e**, and after flash chromatography eluting with ethyl acetate/ethyl alcohol (10:1), 30 mg (75%) of the commercially available 1-phenylpiperazine **2e** was obtained. Anal. Calcd for $C_{10}H_{14}N_2$: C, 74.03; H, 8.70; N, 17.27. Found: C, 74.10; H, 8.73; N, 17.32.

Secondary Amine (–)-2g. From 70 mg (0.293 mmol) of tertiary allylamine (–)-**1g**, and after flash chromatography eluting with ethyl acetate, 40 mg (69%) of *NH*-piperidine (–)-**2g** was obtained. Colorless oil. $[\alpha]_D$ = –17.8 (*c* 0.5, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.29 and 1.37 (s, each 3H), 1.68 (brs, 1H), 2.18 (m, 1H), 2.41 (m, 3H), 2.92 (m, 2H), 3.37 (m, 1H), 3.85 and 3.96 (dd, each 1H, *J* = 7.9, 6.5 Hz), 4.05 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 208.5, 109.5, 77.9, 65.5, 58.6, 45.4, 44.2, 42.8, 26.3, 24.9. IR ($CHCl_3$, cm^{-1}): ν 3344, 1716. MS (CI), *m/z* : 200 (M^+ + 1, 100), 199 (M^+, 14). (Anal. Calcd. for $C_{10}H_{17}NO_3$: C, 60.28; H, 8.60; N, 7.03. Found: C, 60.17; H, 8.64; N, 7.06).

Secondary Amine 2h. From 118 mg (0.5 mmol) of *N*-allyl-dibenzylamine **1h**, and after flash chromatography eluting with ethyl acetate, 83 mg (77%) of the commercially available N-benzylmethylamine **2h** was obtained. Anal. Calcd for $C_{14}H_{15}N$: C, 85.24; H, 7.66; N, 7.10. Found: C, 85.34; H, 7.70; N, 7.07.

Secondary Amine 2i. From 30 mg (0.184 mmol) of *N*-allyl-N-benzylmethylamine **1i**, and after flash chromatography eluting with ethyl acetate, 19 mg (78%) of the commercially

available N-benzylmethylamine **2i** was obtained. Anal. Calcd for $C_8H_{11}N$: C, 79.29; H, 9.15; N, 11.56. Found: C, 79.40; H, 9.18; N, 11.60.

Secondary Amine 2j. From 140 mg (0.627 mmol) of *N*-allyl-*N*-benzylphenylamine **1j**, and after flash chromatography eluting with hexanes, 81 mg (71%) of the commercially available N-benzylphenylamine **2j** was obtained. Anal. Calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64. Found: C, 85.33; H, 7.17; N, 7.60.

Secondary Amine 2k. From 120 mg (0.574 mmol) of *N*-allyl-diphenylamine **1k**, and after flash chromatography eluting with hexanes, 60 mg (62%) of the commercially available diphenylamine **2k** was obtained. Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.15; N, 8.28. Found: C, 85.29; H, 6.17; N, 8.31.

Primary Amine 4a. From 100 mg (0.613 mmol) of allyl-(4-methoxyphenyl)-amine **3a**, and after flash chromatography eluting with ethyl acetate/hexanes (1:4), 60 mg (81%) of the commercially available 4-methoxyphenylamine **4a** was obtained. Anal. Calcd for C_7H_9NO: C, 68.27; H, 7.37; N, 11.37. Found: C, 68.37; H, 7.40; N, 11.33.

β-Lactam-*NH*-piperidine (+)-6b. From 30 mg (0.087 mmol) of *N*-allylpiperidine (+)-**5b**, and after flash chromatography eluting with ethyl acetate (containing 1% of triethylamine), 19 mg (73%) of the *NH*-piperidine (+)-**6b** was obtained. Colorless oil. $[\alpha]_D$ = +12.2 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.18 (s, 1H), 2.32 (m, 4H), 2.76 (m, 1H), 3.37 (m, 2H), 3.63 (s, 3H), 3.73 (s, 3H), 4.15 (m, 1H), 4.63 (d, 1H, *J* = 5.9 Hz), 6.81 and 7.31 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 206.8, 164.7, 156.9, 130.2, 119.8, 114.5, 83.0, 59.6, 57.2, 55.5, 54.9, 45.9, 45.7, 42.8. IR ($CHCl_3$, cm^{-1}): ν 3355, 1741, 1715. MS (ES), *m/z* : 305 (M^+ + 1, 100), 304 (M^+, 15). (Anal. Calcd. for $C_{16}H_{20}N_2O_4$: C, 63.14; H, 6.62; N, 9.20. Found: C, 63.23; H, 6.65; N, 9.17).

β-Lactam-*NH*-piperidine (+)-6d. From 70 mg (0.180 mmol) of *N*-allylpiperidine (+)-**5d**, and after flash chromatography eluting with ethyl acetate (containing 1% of triethylamine), 36 mg (58%) of the *NH*-piperidine (+)-**6d** was obtained. Colorless oil. $[\alpha]_D$ = +47.0 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.30 (m, 4H), 2.74 (m, 1H), 3.37 (m, 2H), 3.72 (s, 3H), 4.16 (m, 2H), 4.41 (dd, 1H, *J* = 12.8, 5.4 Hz), 4.77 (d, 1H, *J* = 5.4 Hz), 5.24 (m, 2H), 5.90 (m, 1H), 6.79 and 7.32 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 207.8, 164.6, 156.7, 133.1,

130.2, 119.6, 118.2, 114.2, 80.7, 72.3, 60.1, 57.2, 55.4, 45.7, 45.6, 42.9. IR ($CHCl_3$, cm^{-1}): ν 3344, 1742, 1718. MS (ES), *m/z* : 331 (M^+ + 1, 100), 330 (M^+, 7). (Anal. Calcd. for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.55; H, 6.68; N, 8.44).

β-Lactam-*NH*-piperidine (+)-6f. From 50 mg (0.171 mmol) of *N*-allylpiperidine (+)-**5f**, and after flash chromatography eluting with ethyl acetate/hexanes (1:1 containing 1% of triethylamine), 22 mg (51%) of the *NH*-piperidine (+)-**6f** was obtained. Colorless oil. $[\alpha]_D$ = +107.5 (*c* 0.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 1.64 (m, 2H), 2.01 (m, 2H), 2.33 (m, 4H), 2.86 (m, 1H), 3.03 (m, 2H), 3.39 (m, 1H), 3.53 (s, 3H), 3.67 (dd, 1H, *J* = 5.2, 4.8 Hz), 4.43 (d, 1H, *J* = 4.8 Hz), 4.96 (m, 2H), 5.74 (m, 1H). ^{13}C-NMR ($CDCl_3$): δ 207.6, 167.6, 137.1, 115.6, 83.3, 59.5, 59.4, 59.3, 57.5, 45.7, 42.9, 41.1, 31.0, 26.7. IR ($CHCl_3$, cm^{-1}): ν 3348, 1741, 1711. MS (ES), *m/z* : 267 (M^+ + 1, 100), 266 (M^+, 6). (Anal. Calcd. for $C_{14}H_{22}N_2O_3$: C, 63.13; H, 8.33; N, 10.52. Found: C, 63.23; H, 8.30; N, 10.48).

β-Lactam-*NH*-piperidine (–)-6g. From 190 mg (0.425 mmol) of *N*-allylpiperidine (–)-**5g**, and after flash chromatography eluting with ethyl acetate/hexanes (2:1 containing 1% of triethylamine), 136 mg (78%) of the *NH*-piperidine (–)-**6g** was obtained. Red oil. $[\alpha]_D$ = –32.5 (*c* 0.6, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 0.00 (s, 6H), 0.79 (s, 9H), 1.27 (m, 2H), 1.80 (m, 2H), 2.29 (s, 3H), 2.55 (td, 1H, *J* = 12.4, 2.2 Hz), 3.16 (m, 2H), 3.56 (m, 1H), 3.65 (s, 3H), 4.16 (dd, 1H, *J* = 5.9, 5.4 Hz), 4.60 (d, 1H, *J* = 5.4 Hz), 6.99 (s, 1H), 7.10 (m, 2H), 7.31 (m, 2H). ^{13}C-NMR ($CDCl_3$): δ 165.2, 134.6, 134.3, 129.4, 118.4, 82.7, 69.7, 60.5, 59.3, 55.5, 44.5, 39.7, 36.1, 25.6, 20.7, 17.9. IR ($CHCl_3$, cm^{-1}): ν 3438, 1743. MS (CI), *m/z* : 405 (M^+ + 1, 100), 404 (M^+, 17). (Anal. Calcd. for $C_{22}H_{36}N_2O_3Si$: C, 65.30; H, 8.97; N, 6.92. Found: C, 65.42; H, 9.00; N, 6.89).

Spectroscopic and analytical data for some representative pure forms of indolizidines **7** follow.

Indolizidine (+)-7c. From 30 mg (0.087 mmol) of the *NH*-piperidine-β-lactam (+)-**6d**, 26 mg (87%) of compound (+)-**7c** was obtained. Orange oil. $[\alpha]_D$ = +18.2 (*c* 0.4, $CHCl_3$). ^{1}H-NMR ($CDCl_3$): δ 2.41 (m, 3H), 2.69 (dd, 1H, *J* = 13.7, 3.2 Hz), 2.97 (m, 1H), 3.53 (m, 1H), 3.69 (m, 4H), 3.92 (d, 1H, *J* = 5.9 Hz), 4.21 (dd, 1H, *J* = 12.6, 5.9 Hz), 4.43 (m, 2H), 5.19 (m, 2H), 5.86 (m, 1H), 6.60 and 6.74 (m, each 2H). ^{13}C-NMR ($CDCl_3$): δ 205.1, 170.6,

139.9, 136.0, 133.8, 118.0, 115.8, 114.9, 81.0, 71.9, 61.7, 55.6, 47.1, 39.7, 37.9, 29.6. IR ($CHCl_3$, cm^{-1}): ν 3446, 1724, 1710. MS (ES), *m/z* : 331 (M^+ + 1, 100), 330 (M^+, 11). (Anal. Calcd. for $C_{18}H_{22}N_2O_4$: C, 65.44; H, 6.71; N, 8.48. Found: C, 65.54; H, 6.74; N, 8.44).

Indolizidine (–)-7e. From 45 mg (0.107 mmol) of the *NH*-piperidine-β-lactam (–)-**6g**, 45 mg (100%) of compound (–)-**7e** was obtained as a colorless oil. $[\alpha]_D$ = –12.5 (*c* 0.9, $CHCl_3$). ^{1}H-NMR (CD_3OD): δ 0.04 (s, 3H), 0.06 (s, 3H), 0.86 (s, 9H), 1.30 (m, 4H), 1.88 and 2.14 (m, each 1H), 2.19 (s, 3H), 2.74 (td, 1H, *J* = 13.2, 2.2 Hz), 3.24 (m, 2H), 3.52 (s, 3H), 3.69 (dd, 1H, *J* = 6.6, 6.1 Hz), 3.83 (dd, 1H, *J* = 6.1, 1.2 Hz), 4.06 (ddd, 1H, *J* = 13.4, 5.1, 1.7 Hz), 6.66 (m, 2H), 6.95 (m, 2H). ^{13}C-NMR (CD_3OD): δ 172.0, 146.7, 130.9, 128.6, 115.6, 85.7, 70.0, 62.8, 60.1, 59.6, 42.8, 38.7, 35.2, 26.4, 20.8, 19.0. IR ($CHCl_3$, cm^{-1}): ν 3335, 1722. MS (CI), *m/z* : 405 (M^+ + 1, 100), 404 (M^+, 18). (Anal. Calcd. for $C_{22}H_{36}N_2O_3Si$: C, 65.30; H, 8.97; N, 6.92. Found: C, 65.19; H, 8.93; N, 6.89).

Spectroscopic data for some representative forms of enamines **10** follow.

Enamine 10d. ^{1}H-NMR ($CDCl_3$): δ 1.72 (d, 1.5H, *J* = 8.8 Hz), 1.73 (d, 1.5H, *J* = 7.6 Hz), 1.98 (m, 2H), 2.66 (m, 2H), 3.27 (m, 2H), 5.50 (m, 1H), 6.04 (d, 0.5H, *J* = 15.5 Hz), 6.12 (d, 0.5H, *J* = 11.5 Hz), 6.60 (m, 4H).

Enamine 10h. ^{1}H-NMR (CD_3COCD_3): δ 1.67 (d, 1.5H, *J* = 8.0 Hz), 1.69 (d, 1.5H, *J* = 7.8 Hz), 3.55 (s, 4H), 5.11 (m, 1H), 5.75 (d, 0.5H, *J* = 11.0 Hz), 5.81 (d, 0.5H, *J* = 15.0 Hz), 7.09 (m, 5H).

Enamine 10j. ^{1}H-NMR ($CDCl_3$): δ 1.91 (m, 3H), 4.68 (m, 2H), 5.59 (m, 1H), 6.27 (m, 1H), 6.66 (m, 4H), 7.23 (m, 6H).