Supporting Information

BF_3-Mediated Additions of Organolithiums to Ketimines: X-ray Crystal Structures of BF_3-Ketimine Complexes

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I. General Procedures

All solvents were routinely distilled by vacuum transfer from blue or purple solutions containing sodium benzophenone ketyl. The hydrocarbon stills contained 1% tetraglyme to dissolve the ketyl. BF_3-Et_2O was distilled with 10 mol% Et_2O from CaH_2. The ketones and aldehydes are either commercially available or have been reported. Air and moisture sensitive materials were manipulated under argon or nitrogen using standard glove box, vacuum line, and syringe techniques.

The protocol for the BF_3-mediated addition of lithium acetylides or *n*-BuLi is described in the main text. Several other general procedures are described below and are followed by spectral data and reproductions of the spectra for the specific cases.

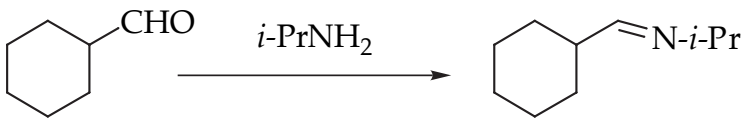
Preparation of imines. A mixture of ketone (50.0 mmol), primary amine (55.0 mmol), Et_2O (50.0 mL), and 4 Å molecular sieves (2.0 g) were stirred until the imine formation was complete as shown by GC. Imines were obtained as colorless or pale yellow oils after concentration and distillation. The assignments of the *syn* and *anti* isomers (below) are based on extensive studies reported: Liao, S.; Collum, D. B. *J. Am. Chem. Soc.* **2003**, *125*, 15114.

Preparation of crystalline imine-BF_3 complexes. To a solution of imine (10.0 mmol) in pentane (20.0 ml) was added BF_3-Et_2O (12.0 mmol) at 0 ºC. Stirring at 0 ºC for 15 min typically affords an off-white to brown precipitate. Filtration under nitrogen and recrystallization from CH_2Cl_2/pentane affords the imine-BF_3 complex as a white or off-white crystalline solid.

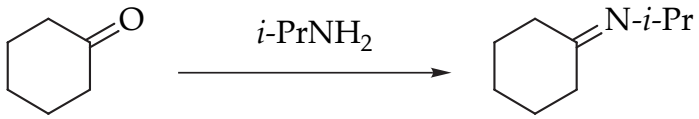
Hydrogenolysis of *N*-benzylimines. A solution of the dialkylamine (100 mg, 0.33 mmol) in 8.0 mL of EtOH/HOAc (7:1) was treated with 10% palladium on activated carbon (10 mg) in a round-bottom flask equipped with a septum. The flask was flushed with H_2 and pressurized to 40 psi. After 24 h the suspension was filtered, and the filter cake was rinsed with ether. The ether was stripped to afford the alkyl amine (RNH_2). In the case of propargylamines, the alkynyl group was also hydrogenated to the corresponding alkyl moiety.

Ammonium salt formation. A solution of the secondary amine (100 mg, 0.1 mmol) in 1.0 mL of EtOH in a 3.0 mL vial with a septum was treated with gaseous HCl. The salt was filtered, dried under vacuum, and purified by recrystallization.

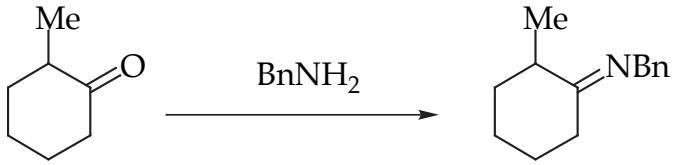
II. Spectral Data: Imines



Yield: 87%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (1H, d, J = 5.6 Hz), 3.20 (1H, m), 1.76-0.87 (17H, m). See: Rische, T.; Kitsos-Rzychon, B.; Eilbracht, P. *Tetrahedron* **1998**, *54*, 2723.

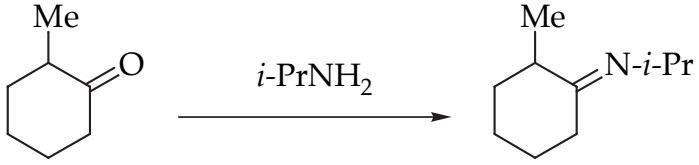


Yield: 76%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.66 (1H, m), 2.22 (4H, m), 1.18 (6H, m), 2.15-1.21 (6H, d, J = 7.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 48.7, 40.1, 28.7, 27.7, 26.8, 26.0, 23.8, 17.1. See: Hutchins, R. O.; Su, W. Y.; Sivakumar, R.; Cistone, F.; Stercho, Y. P. *J. Org. Chem.* **1983**, *48*, 3412.



5:1 *anti*/*syn*

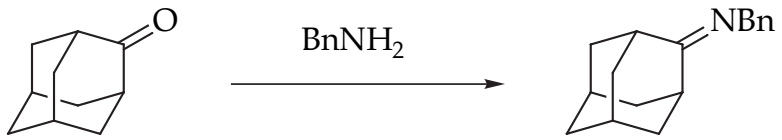
Yield: 82%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27 (5H, m), 4.68 (2H, s), 2.73 (1H, m), 2.43 (1H, m), 2.15-1.21 (7H, m), 1.25 (3H, d, J = 8.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.2, 140.7, 128.1, 127.7, 127.5, 127.1, 126.0, 53.3, 42.0, 35.9, 28.1, 27.2, 24.5, 17.1. See: Hutchins, R. O.; Su, W. Y.; Sivakumar, R.; Cistone, F.; Stercho, Y. P. *J. Org. Chem.* **1983**, *48*, 3412.



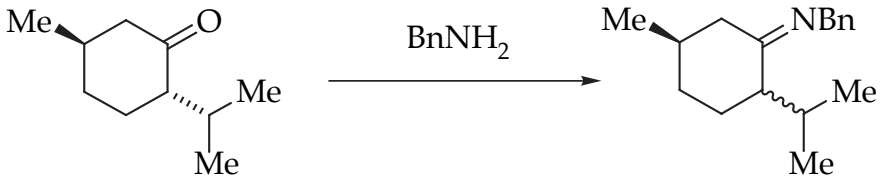
4:1 *anti*/*syn*

Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (1H, m, *anti*), 7.12 (5H, m, *syn*), 4.46 (2H, m, *syn*), 4.26 (2H, m, *anti*), 3.26 (1H, s, *syn*), 4.26 (1H, s, *anti*), 2.73 (1H, s, *anti*), 2.58 (1H, s, *syn*), 2.26 (1H, m, *syn*), 2.14 (1H, m, *anti*), 1.95-1.79 (1H, m, *anti* and *syn*), 1.61 (2H, m, *anti* and *syn*), 1.40 (1H, m, *anti* and *syn*), 1.25 (2H, m, *anti* and *syn*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.6 (*syn*), 172.3 (*anti*), 48.8 (*anti*), 46.9 (*syn*), 42.1 (*anti* and *syn*), 35.6 (*syn*), 35.3

(*anti*), 33.2 (*anti*), 31.0 (*syn*), 27.8 (*anti*), 27.7 (*syn*), 26.8 (*anti* and *syn*), 24.2 (*syn*), 24.1 (*anti* and *syn*), 24.0 (*anti*), 23.6 (*anti*), 20.4 (*syn*), 17.6 (*anti*), 17.4 (*syn*). MS (*m*/*z*): 153 (M^+), 138 (100), 125, 110, 96, 82, 54.

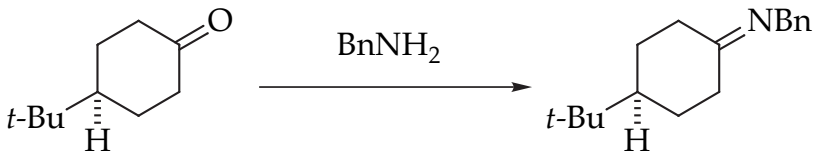


Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (5H, m), 4.55 (2H, s), 3.18 (1H, s), 2.61 (1H, s), 1.74-2.05 (12H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.4, 140.5, 128.2, 127.5, 126.2, 53.2, 43.6, 39.0, 38.1, 36.3, 33.1, 27.6. MS (*m*/*z*): 239 (M^+, 100), 162, 148, 91.

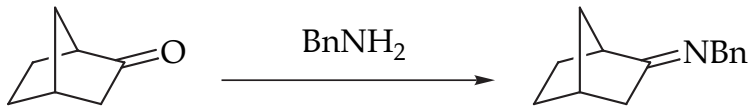


(*E*/*Z* and *cistrans* mixture)

Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.20 (2H, d, J = 8.5 Hz), 2.48 (1H, m), 2.15-1.19 (11H, m), 0.92-0.63 (12H, m). MS (*m*/*z*): 243 (M^+), 228, 201 (100), 91, 65.



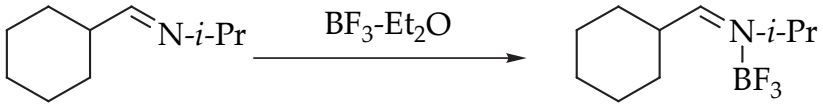
Yield: 62%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.16 (5H, m), 3.79 (2H, m), 2.76-1.25 (9H, m), 0.84 (9H, m). Hutchins, R. O.; Su, W. Y.; Sivakumar, R.; Cistone, F.; Stercho, Y. P. *J. Org. Chem.* **1983**, *48*, 3412.



5 : 1 *major*/*minor*
(unassigned)

Yield: 75%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.22 (1H, m, major), 7.12 (5H, m, minor), 4.46 (2H, m, minor), 4.26 (2H, m, major), 3.26 (1H, s,), 4.26 (1H, s, major), 2.73 (1H, s, major), 2.58 (1H, s, minor), 2.26 (1H, m, minor), 2.14 (1H, m, major), 1.95-1.79 (1H, m, major and minor), 1.61 (2H, m, major and minor), 1.40 (1H, m, major and minor), 1.25 (2H, m, major and minor); ^{13}C NMR (100 MHz, $CDCl_3$): δ 180.6 (major), 180.0 (minor), 139.7 (major and minor), 127.8 (major and minor), 127.2 (major and minor), 125.9 (major and minor), 56.7 (minor), 55.9 (major), 46.8 (major and minor), 42.3 (major), 39.4 (minor), 38.0 (minor), 37.9 (minor), 37.6 (major), 36.6 (major and minor), 35.2 (major), 34.5 (minor), 27.3 (major), 27.0 (minor), 26.0 (major), 25.3 (minor). MS (*m*/*z*): 199 (M^+), 184, 91 (100), 65, 51.

III. Spectral Data: Imine-BF_3 Complexes



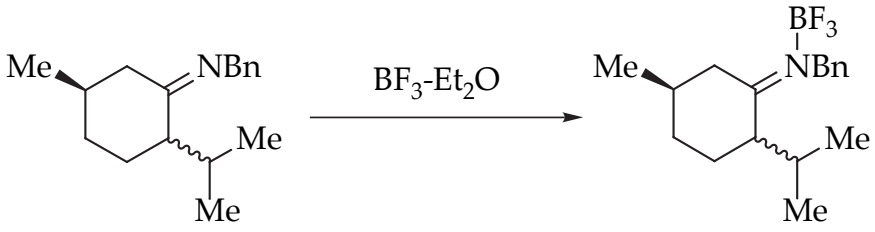
24

(7:1 *E*/*Z*)

Yield: 86%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (1H, d, *J* = 18, 7.2 Hz), 7.43 (1H, s, *E*), 4.08 (2H, m, *E* and *Z*), 3.19 (1H, m, *E*), 2.87 (1H, m, *Z*), 1.82-1.62 (18H, m, *E* and *Z*), 1.49-1.30 (12H, *E* and *Z*), 1.27 (6H, s, *E* and *Z*), 1.15 (12H, m, *E* and *Z*); ^{13}C NMR (100 MHz, $CDCl_3$): δ 182.0 (*Z*), 178.6 (*E*), 57.5 (*Z*), 56.6 (*E*), 42.6 (*Z*), 40.6 (*E*), 28.5, 27.9 (*Z*), 25.2 (*E*), 24.9 (*Z*), 24.3 (*E*), 24.1 (*Z*), 22.2 (*E*), 21.1 (*Z*). IR: 1698 cm^{-1} (*E*) and 1671 cm^{-1} (*Z*). ^{1}H,^{1}H-NOESY, ^{1}H,^{1}H-COSY, and ^{1}H,^{13}C-HMBC, and ^{1}H,^{13}C-HMQC were recorded and are archived below. A crystal structure of the *Z*-isomer is also reported below.

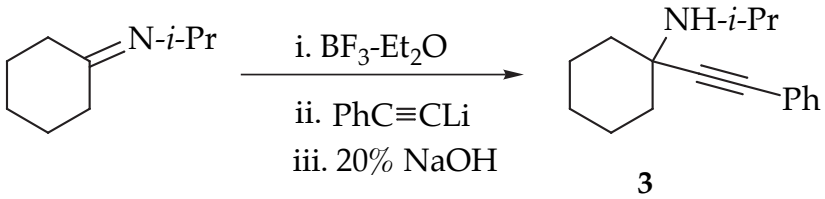
25

Yield: 78%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.32 (1H, m), 3.00 (1H, m), 2.77 (2H, m), 2.01-1.67 (10H, m), 1.42 (3H, d, *J* = 8.0 Hz), 1.39 (3H, d, *J* = 8.0 Hz), 1.29 (3H , t, *J* = 1.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.8, 51.0, 40.6, 34.6, 29.0, 27.7, 21.1, 20.9, 16.5. A crystal structure is reported below.



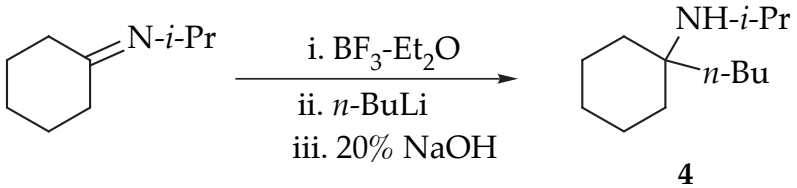
Yield: 50%. Complex spectra suggest an *E*/*Z* and diastereomeric mixture as drawn. A crystal structure of the *E*/*trans*-diaxial isomer drawn is reported below.

IV. Spectral Data: Amines



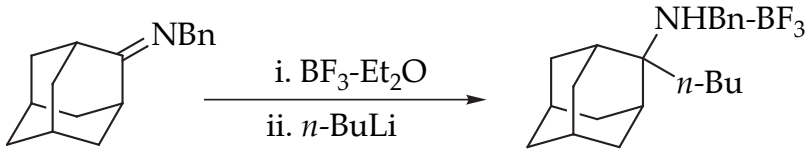
3

Flash chromatography (15% EtOAc/hexane) afforded **3** in 63% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (2H, m), 7.21 (3H, m), 3.22 (1H, m), 1.86 (2H, m), 1.61 (4H, m), 1.36 (2H, m), 1.19 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.5, 128.2, 127.6, 123.8, 94.2, 84.0, 55.1, 44.4, 39.2, 25.9, 25.8, 23.1. MS (*m*/*z*): 241 (M^+), 226, 198 (100), 156, 128, 91, 77.



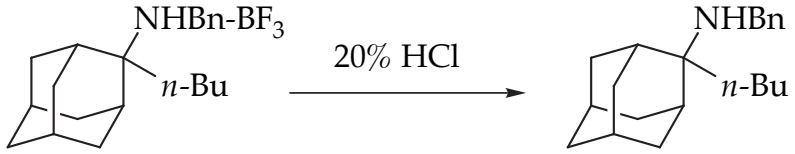
4

Flash chromatography (10% EtOAc/hexane) afforded **4** in 60% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.85 (1H, m), 1.36-1.14 (16H, m), 0.97 (6H, d, J = 4.0 Hz), 0.86 (3H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 54.3, 41.3, 36.4, 26.3, 26.14, 24.9, 23.4, 22.1, 14.2. MS (*m*/*z*): 197, 140 (100), 98, 54. **4**-HCl salt: Anal. Calcd for $C_{13}H_{28}NCl$ C, 66.78; N, 5.99; H, 12.07. Found C, 66.63; N, 5.73; H, 11.87.



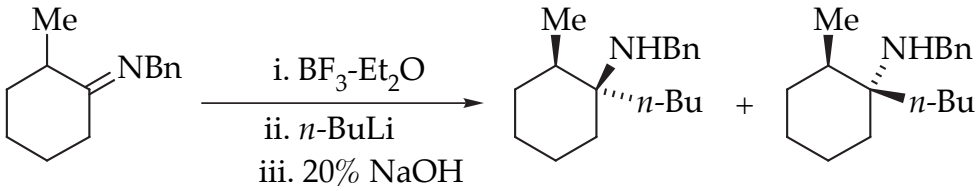
23

Yield: 80%. **23**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28 -7.16 (5H, m), 3.68 (2H, m), 1.73-1.47 (9H, m), 1.40-1.30 (6H, m), 0.99 (3H, t, J = 3.2 Hz), 0.95 (3H, d, J = 4.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.2, 128.4, 128.3, 128.2, 128.1, 126.6, 55.5, 44.9, 36.7, 36.1, 31.4, 29.78, 25.8, 24.7, 23.7, 21.9, 14.7, 14.2. MS (*m*/*z*): 364 (M^+-1, 100), 365 (M^+), 250, 191, 135, 91.



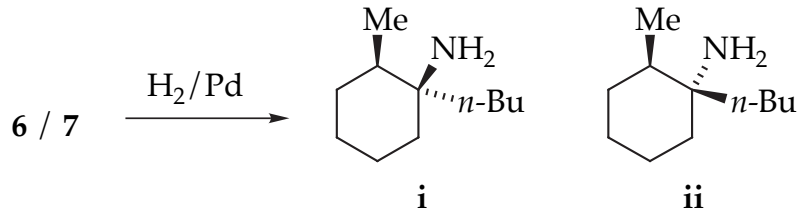
23 **5**

Complex **18** (1.0 mmol) in 20% HCl (5.0 mL) was stirred overnight and then extracted with ether (3 x 5.0 mL) work up as usual to afford compound **5** 92% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.30 (5H, m), 3.57 (2H, s), 2.24 (2H, m), 2.01 (2H, m), 2.22 (1H, s), 2.00-0.76 (14H, m), 0.98 (3H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.9, 128.5, 126.0, 57.2, 44.4, 39.1, 34.1, 33.6, 32.7, 31.2, 27.9, 27.8, 24.0, 23.4, 14.4. MS (*m*/*z*): 296 (M-1), 281, 241, 240 (100), 91. **5**-HBr salt: Anal. Calcd for $C_{21}H_{33}NBr$: C, 66.48; N, 3.69; H, 8.77. Found C, 66.65; N, 3.56; H, 8.50.

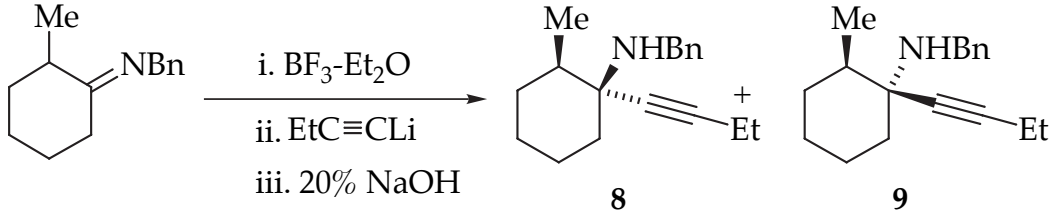


6 **7**

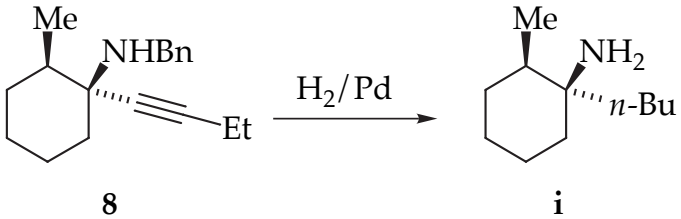
Amines **6** and **7** were prepared as an inseparable 1:3 mixture in 69% combined yield after flash chromatography (5% EtOAc/hexane). The hydrogenolysis products were separated as described below. Also, a sample of pure **6** could be prepared in 51% yield by reacting the *N*-benzylimine without $BF_3 \cdot Et_2O$ in neat toluene (0.5 h) or 10% yield in neat THF (0.5 h). **6**: ^{1}H NMR (100 MHz, $CDCl_3$): δ 7.44 -7.28 (5H, m), 3.67 (2H, m), 1.85-1.24 (14H, m), 0.97 (3H, t, J = 2.5 Hz), 0.94 (3H, d, J = 5.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.1, 128.4, 128.3, 128.2, 128.1, 126.6, 55.5, 44.9, 36.7, 36.1, 31.4, 29.8, 25.8, 24.7, 23.7, 21.9, 14.7, 14.3. MS (*m*/*z*): 259 (M+), 202, 196, 147, 91 (100), 65. **6**-HBr salt: Anal. Calcd for $C_{18}H_{30}NBr$: C, 63.55; N, 4.12; H, 8.87. Found C, 63.58; N, 3.97; H, 8.75. From the mixture of **6** and **7**, the data for **7** was determined as follows: ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.33 -7.7.15 (5H, m), 3.54 (1H, m), 1.84-1.08 (14H, m), 0.87 (3H, t, J = 5.0 Hz), 0.81 (3H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 128.3, 128.2, 128.2, 126.6, 56.2, 45.2, 35.8, 32.8, 31.1, 29.7, 25.8, 24.3, 23.6, 23.4, 22.3, 14.6. MS (*m*/*z*): 259, 202, 147, 91 (100), 65.



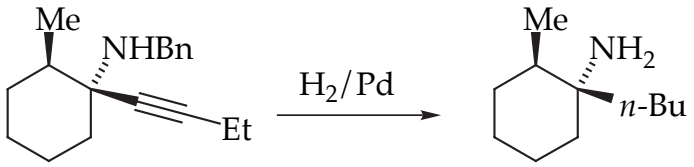
Isomers **i** and **ii** were formed in a 1:10 ratio, separated by flash chromatography (30% EtOAc/hexane), and isolated in 94% combined yield. **i** (86% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.68-1.15 (15H, m), 0.81 (3H, d, *J* = 6.4 Hz), 0.91 (3H, t, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.5, 42.0, 38.0, 37.1, 30.5, 26.0, 25.5, 23.5, 21.9, 15.1, 14.2. MS (*m*/*z*): 169 (M^+), 140, 126, 112 (100), 95, 84, 57. **ii** (8% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.76-0.98 (15H, m), 0.86 (3H, d, *J* = 6.4 Hz), 0.91 (3H, t, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 52.9, 43.0, 37.3, 32.7, 30.9, 25.2, 24.7, 23.6, 23.0, 15.1, 14.2. MS (*m*/*z*): 169 (M^+), 140, 126, 112 (100), 95, 84, 57.



Amines **8** and **9** are formed as an 8:1 mixture, separated by flash chromatography (20% EtOAc/hexane), and isolated in 92% combined yield. **8**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 -7.16 (5H, m), 3.70 (2H, q, *J* = 8.0 Hz), 2.20 (1H, q, *J* = 7.6 Hz), 1.89-1.72 (2H, m), 1.57-1.23 (7H, m), 1.10 (3H, t, *J* = 7.6 Hz), 0.92 (3H, d, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 128.4, 128.2, 126.6, 84.6, 84.5, 56.1, 47.5, 39.6, 35.0, 29.2, 24.1, 21.5, 15.1, 14.6, 12.4. MS (*m*/*z*): 255 (M^+), 226, 212, 198 (100), 91, 77. Anal.Calcd for $C_{18}H_{25}N$: C, 84.65; N, 5.48; H, 9.87. Found: 84.55; N, 5.58; H, 9.92. **9**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36-7.17 (5H, m), 3.85 (1H, d, *J* = 1.2 Hz), 3.69 (1H, d, *J* = 1.2 Hz), 2.20 (1H, q, *J* = 8.0 Hz), 2.00 (1H, m), 1.57-1.30 (9H, m), 1.19 (3H, t, *J* = 8.0 Hz), 0.88 (3H, d, *J* = 6.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 128.4, 128.4, 126.7, 87.5, 80.4, 59.4, 47.8, 41.1, 37.0, 32.0, 25.8, 23.5, 16.5, 14.8, 12.5. MS (*m*/*z*): 255 (M^+), 240, 226, 212, 198 (100), 91 (100), 77. Anal.Calcd for $C_{18}H_{25}N$: C, 84.65; N, 5.48; H, 9.87. Found: 84.85; N, 5.31; H, 9.97.

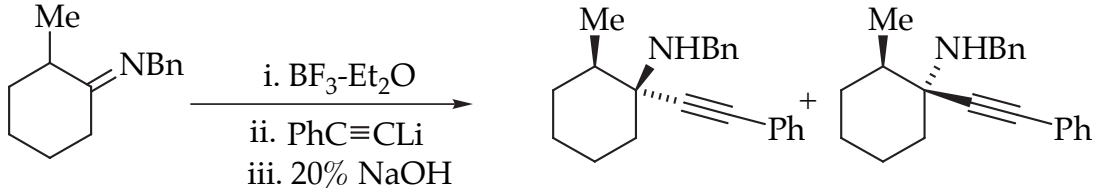


Amine **8** was hydrogenated to provide **i** in 99% yield after flash chromatography (30% EtOAc/hexane). Amine **i** displayed spectral properties as described above.



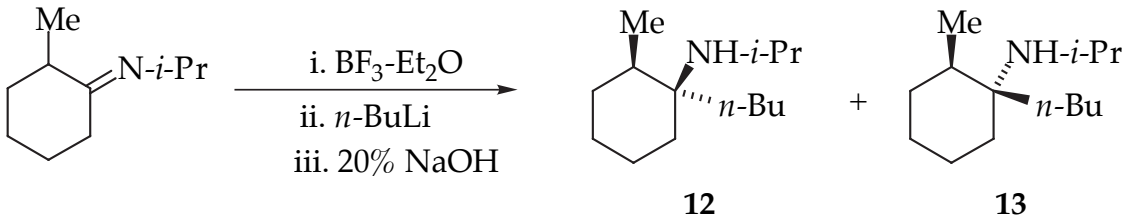
9 **ii**

Amine **9** was hydrogenated to provide **ii** in 97% yield after flash chromatography (30% EtOAc/hexane) and displayed spectral properties as described above.



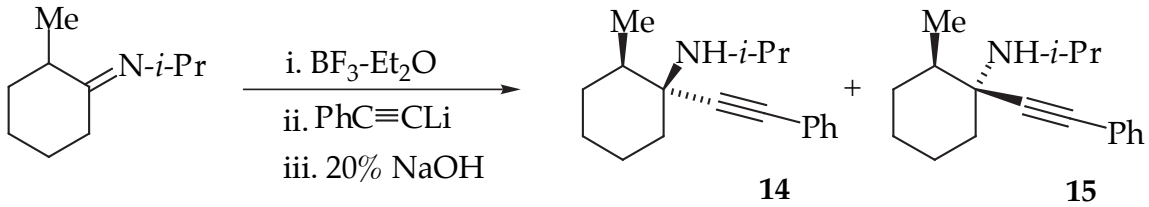
10 **11**

Amines **10** and **11** are formed in a 5:1 ratio. Flash chromatography (20% EtOAc/hexane) afforded **10** and **11** as separate isomers in a combined 81% yield. The isomers were assigned by analogy to the EtCCLi adducts as follows: **10** (58% yield)**:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.7 (10H, m), 3.90 (2H, q, *J* = 7.6 Hz), 2.14 (2H, m), 1.65-1.59 (6H, m), 1.34 (1H, m), 1.09 (1H, d, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 131.7, 128.5, 128.4, 128.2, 127.6, 126.8, 123.8, 94.9, 83.5, 56.8, 47.7, 39.5, 34.7, 29.2, 24.0, 21.5, 15.2. MS (*m*/*z*): 303 (M^+), 288 (100), 266 (100), 246 (100), 232, 212, 128, 91. Anal.Calcd for $C_{22}H_{25}N$: C, 87.09; N, 4.61; H, 8.30. Found: 87.10; N, 4.45; H, 8.51. **11** (11% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.17 (10H, m), 3.95 (1H, d, *J* = 12.0 Hz), 3.79 (1H, d, *J* = 12.0 Hz), 1.65-1.20 (9H, m), 0.98 (1H, d, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 131.7, 128.4, 128.2, 127.7, 126.9, 123.7, 91.2, 86.3, 59.8, 48.0, 41.4, 36.9, 32.1, 25.8, 23.5, 16.6. MS (*m*/*z*): 303 (M^+), 288, 266, 246 (100), 232, 212, 180, 128, 91. Anal.Calcd for $C_{22}H_{25}N$: C, 87.09; N, 4.61; H,8.30. Found: 86.61; N, 4.35; H, 8.37.



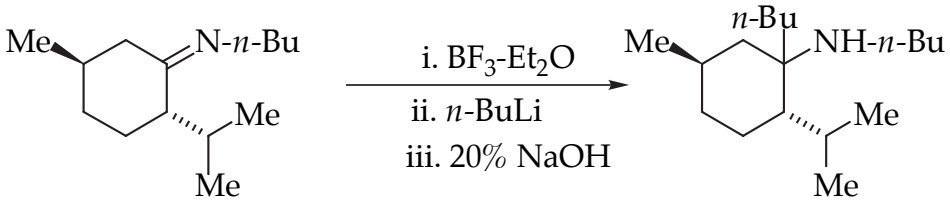
12 **13**

Flash chromatography (5% EtOAc/hexane) afforded **12** and **13** as an inseparable mixture. Combined yield: 40%. **12**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.91 (1H, sept, *J* = 3.0 Hz), 1.63-1.24 (15H, m), 1.03 (6H, d, *J* = 8.0 Hz), 0.91 (3H, t, *J* = 5.0 Hz), 0.83 (3H , d, *J* = 8.5 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 56.6, 41.4, 37.6, 37.0, 32.4, 30.2, 27.1, 26.6, 26.3, 25.2, 23.9, 22.4, 15.1, 14.5. MS (*m*/*z*): 211 (M^+), 182, 168, 154 (100), 112, 99, 84, 67. **12**-HCl salt: Anal. Calcd for $C_{14}H_{30}NCl$: C, 67.84; N, 5.65; H, 12.20. Found C, 66.61; N, 5.09; H, 11.68. **13**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.80 (1H, sept, *J* = 3.0 Hz), 1.66-1.13 (15H, m), 1.05 (6H, m), 0.91 (3H, t, *J* = 4.4.0 Hz), 0.84 (3H , t, *J* = 6.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.1, 40.8, 36.6, 32.7, 31.6, 30.7, 26.8, 26.2, 23.6, 22.9, 22.6, 15.5, 14.3, 14.1. MS (*m*/*z*): 211 (M^+), 181, 168, 154 (100), 112, 99, 84, 67.



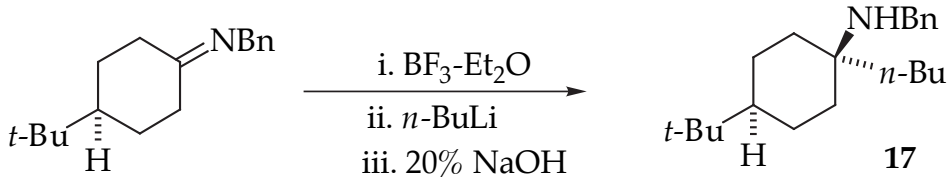
14 **15**

Isomers **14** and **15** were separated by flash chromatography (20% EtOAc/hexane). **14** (17% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.34 (2H, m), 7.25-7.19 (3H, m), 3.16 (2H, m), 1.60-1.57 (3H, m), 1.50-1.18 (6H, m), 1.10 (3H, d, *J* = 6.4 Hz), 1.04 (3H, d, *J* = 6.4 Hz), 0.97 (3H, d, *J* = 6.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.8, 128.4, 127.8, 124.1, 92.1, 85.7, 59.8, 44.5, 41.9, 38.7, 32.3, 26.7, 26.1, 25.6, 23.7, 16.9. MS (*m*/*z*): 255 (M^+), 240, 226, 212, 198 (100), 184, 170, 128, 102, 77. Anal.Calcd for $C_{18}H_{25}N$: C, 84.65; N, 5.48; H, 9.87. Found: 84.80; N, 5.27; H, 9.92. **15** (53% yield): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.31 (2H, m), 7.22-7.19 (3H, m), 3.11 (1H, sept, *J* = 6.4 Hz), 1.91-1.80 (2H, m), 1.60-1.20 (8H, m), 1.09 (3H, d, *J* = 6.0 Hz), 1.05 (3H, d, *J* = 6.0 Hz), 0.97 (3H, d, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.7, 128.4, 128.4, 127.7, 124.3, 96.4, 82.8, 56.7, 44.7, 40.5, 36.0, 29.4, 26.1, 25.5, 24.3, 21.8, 15.7. MS (*m*/*z*): 255 (M^+), 240 (100), 226, 212, 198, 184, 170, 156, 128, 102, 77. Anal.Calcd for $C_{18}H_{25}N$: C, 84.65; N, 5.48; H, 9.87. Found: 84.36; N,5.34; H,10.06.



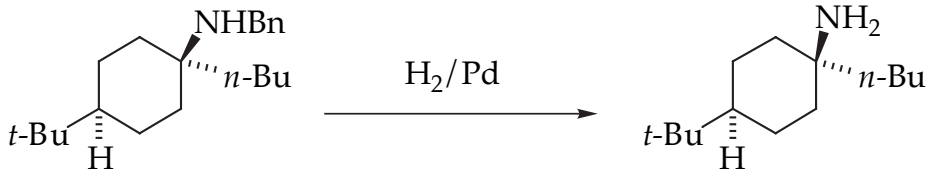
16

Flash chromatography (5% EtOAc/hexane) gave **16** as pale yellow oil in 39% yield as a single (undetermined) stereoisomer. ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.43 (1H, m), 2.32 (1H, m), 2.20 (1H, m), 1.72-1.10 (16H, m), 0.94 (6H, d, *J* = 1.6 Hz), 0.90 (6H, m), 0.86 (3H, d, *J* = 5.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ 57.3, 44.9, 40.6, 40.5, 34.6, 33.2, 32.0, 27.8, 26.1, 25.2, 24.8, 23.4, 22.8, 21.7, 21.6, 20.7, 14.3, 14.1. MS (*m*/*z*): 267 (M^+), 252, 210, 182 (100), 140, 98, 72.



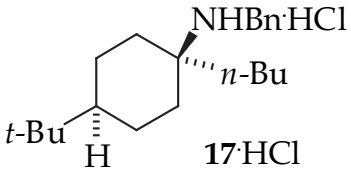
17

Flash chromatography (5% EtOAc/hexane) afforded **17** in 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44-7.15 (5H, m), 3.47 (2H, s), 1.71 (2H, d, *J* = 11.6 Hz), 1.42 (2H, d, *J* = 11.6 Hz), 1.30-1.05 (11H, m), 0.85 (3H, t, *J* = 7.2 Hz), 0.79 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.0, 128.3, 128.2, 126.6, 52.7, 48.2, 45.4, 39.7, 35.6, 32.4, 27.6, 25.0, 23.5, 22.0, 14.3. MS (*m*/*z*): 301 (M^+), 286, 245, 244 (100), 202, 91.



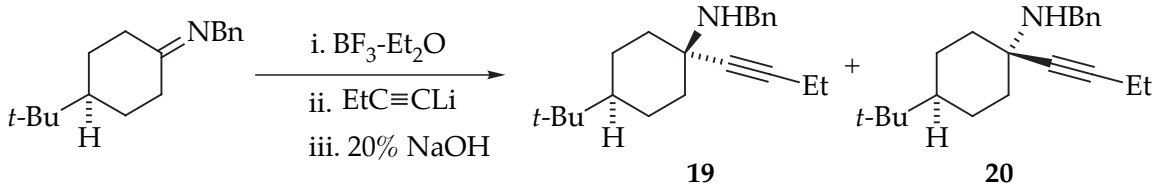
17 **iii**

Flash chromatography (20% EtOAc/hexane) afforded **iii** (described above) in 97% yield.

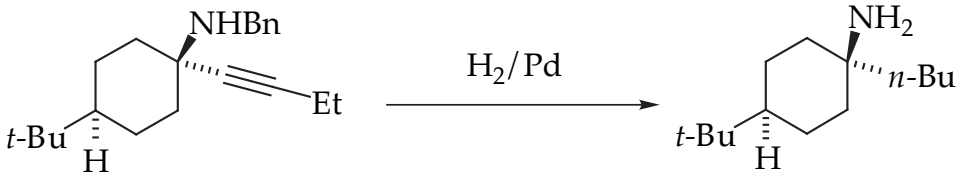


17·HCl

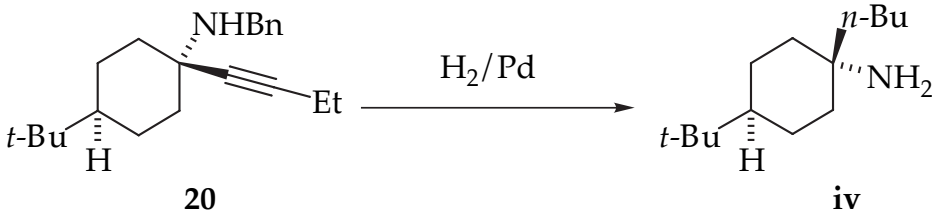
17·HCl**:** (98% yield) ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.13 (2H, s), 7.77 (2H, d, *J* = 5.6 Hz), 7.35-7.26 (3H, m), 3.14 (2H, s), 2.68 (2H, d, *J* = 11.2 Hz), 1.69 (2H, m), 1.60-1.20 (11H, m), 0.85-0.73 (11H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 132.3, 130.5, 129.1, 128.9, 62.7, 47.9, 45.9, 37.0, 32.7, 32.4, 27.8, 25.6, 23.0, 21.7, 13.9. COSY, NOESY and *J* HMO were recorded as depicted below. Anal. Calcd for $C_{21}H_{35}NCl$: C, 74.85; N, 4.16; H, 10.47. Found C, 73.95; N, 4.04; H, 10.04.



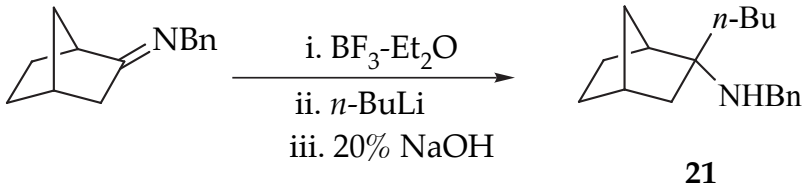
Amines **19** and **20** are formed in a 1:1 ratio. Flash chromatography (15% EtOAc/hexane) afforded **19** and **20** as separate isomers in a combined 87% yield. **19**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40 -7.21 (5H, m), 3.70 (2H, s), 2.16 (H, q, *J* = 1.2 Hz), 1.90-1.86 (2H, m), 1.52-1.35 (5H, m), 1.10 (3H, t, *J* = 2.8 Hz), 0.92 (1H, m), 0.93 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.6, 128.5, 128.3, 126.7, 85.5, 83.2, 51.6, 47.8, 47.6, 37.7, 27.6, 21.6, 14.6, 12.5. MS (*m*/*z*): 297 (M^+), 240, 212, 198 (100), 156, 91, 57. Anal.Calcd for $C_{21}H_{31}N$: C,84.80; N,4.71; H,10.50. Found: 84.79; N, 4.65; H,10.50. **20**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34 -7.16 (5H, m), 3.83 (2H, s), 2.20 (H, q, *J* = 7.6 Hz), 1.84 (2H, m), 1.60 (2H, m), 1.34 (4H, m), 1.12 (3H, t, *J* = 7.6 Hz), 0.87 (1H, m), 0.80 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 128.4, 128.3, 126.7, 86.7, 82.6, 55.2, 48.1, 47.6, 38.8, 32.3, 27.6, 24.0, 14.7, 12.5. MS (*m*/*z*): 297 (M^+), 240, 212, 198 (100), 156, 91, 57. Anal.Calcd for $C_{21}H_{31}N$: C,84.80; N,4.71; H,10.50. Found: 84.65; N, 4.46; H,10.76.



Flash chromatography (20% EtOAc/hexane) afforded **iii** in 98% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.59 (2H, d, *J* = 13.6 Hz), 1.52 (2H, m), 1.36-1.21 (11H, m), 0.97-0.864 (11H, m). ^{13}C NMR (100 MHz, $CDCl_3$): δ 49.8, 48.2, 45.5, 38.4, 32.3, 27.5, 25.3, 23.5, 22.5, 14.1. MS (*m*/*z*): 211 (M^+), 154 (100), 112 (100), 95, 81, 57.



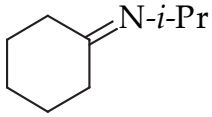
Flash chromatography (20% EtOAc/hexane) afforded **iv** in 95% yield: ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.74 (2H, d, *J* = 12.8 Hz), 1.60 (2H, d, *J* = 10.4 Hz), 1.41 (2H, m), 1.28 (7H, m), 1.059 (3H, m), 0.9 (3H, t, *J* = 6.8 Hz) 0.82 (9H, s). ^{13}C NMR (100 MHz, $CDCl_3$): δ 50.8, 47.6, 39.8, 36.1, 32.3, 30.3, 27.6, 27.6, 25.0, 23.7, 23.4, 14.2. MS (*m*/*z*): 211 (M^+), 154, 112 (100), 95, 69, 57.



21

Flash chromatography (5% EtOAc/hexane) afforded **21** in 60% yield. **21**: ^{1}H NMR (MHz, $CDCl_3$): δ 7.39 (5H, m), 3.66 (1H, d, J = 12.5 Hz), 3.53 (1H, d, J = 12.5 Hz), 2.21 (1H, m), 1.95 (1H, m), 1.66 (1H, m) 1.64 (2H, m), 1.37 (10H, m), 1.02 (3H, t, J = 7.5.0 Hz.) ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.4, 128.3, 128.1, 126.7, 62.6, 47.9, 45.2, 45.0, 38.1, 36.9, 36.0, 28.9, 25.0, 23.3, 23.1, 14.3. MS (*m*/*z*): 257 (M^+), 228, 200, 147, 91 (100), 65.

IV. Spectra



^{1}H and ^{13}C NMR Spectra
(see p S3)