SUPPORTING INFORMATION

Preparation of Tertiary Alkyl Carbinamines,
Propargylamines and α -Heteroarylamines by Ketone-
based Aminoalkylation

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Procedure for the Preparation of Benzotriazolyl Adducts 8a–i. Adduct **8a** was prepared using the literature method.^{15a} Adducts **8b–i** were prepared *in situ* by adding the corresponding enamine **7b–i** (3 mmol) to a suspension of benzotriazole (3 mmol) in dry Et₂O/THF (15 mL). After the mixture was stirred for 30 min at 20 °C, the clear solution of the benzotriazolyl adduct was used for subsequent nucleophilic replacement reactions.

General Procedure for Preparation of 9–11.

To the adduct **8** (3 mmol) prepared *in situ* in Et₂O/THF (15 mL) at 0 °C was added the corresponding nucleophile such as Grignard reagent (7 mmol), lithium phenylacetylide (3 mmol), 2-thienyl lithium (12 mmol) or 2-thiazolyl lithium (12 mmol). After the mixture was stirred at 20 °C for 8 h, aqueous work-up gave a residue which was purified by flash column chromatography using hexanes/EtOAc (10:1).

4-(1-Ethyl-1-phenylpropyl)morpholine (9b). Colorless oil; yield, 50% (0.35g); ¹H NMR δ 7.40 (d, *J* = 7.5 Hz, 2H), 7.33–7.28 (m, 2H), 7.22–7.17 (m, 1H), 3.64 (apparent t, *J* = 4.5 Hz, 4H), 2.55 (apparent t, *J* = 4.5 Hz, 4H), 1.89 (q, *J* = 7.4 Hz, 4H), 0.81 (t, *J* = 7.4 Hz, 6H); ¹³C NMR δ 143.5, 127.6, 127.6, 126.1, 68.3, 64.4, 47.3, 26.5, 8.9. Anal. Calcd for C₁₅H₂₃NO: C, 77.20; H, 9.93; N, 6.00. Found: C, 77.25; H, 10.29; N, 6.13.

4-(1-Benzyl-1-ethylpropyl)morpholine (9c). Colorless oil; yield, 60% (0.44g); ¹H NMR δ 7.30–7.16 (m, 5H), 3.65 (apparent t, *J* = 4.5 Hz, 4H), 2.74–2.68 (m, 6H), 1.52–1.42 (m, 4H), 0.82 (t, *J* = 7.5 Hz, 6H); ¹³C NMR δ 139.4, 130.5, 130.4, 128.0, 127.6, 125.6, 68.1, 60.8, 46.0, 39.7, 26.9, 8.6. Anal. Calcd for C₁₆H₂₅NO: C, 77.68; H, 10.19; N, 5.66. Found: C, 77.81; H, 10.38; N, 5.91.

4-(1-Phenyl-1-propylbutyl)morpholine (9d) Colorless oil; yield, 61% (0.48g); ¹H NMR δ 7.43–7.17 (m, 5H), 3.63 (apparent t, *J* = 4.5 Hz, 4H), 2.53 (apparent t, *J* = 4.5 Hz,

4H), 1.82–1.74 (m, 4H), 1.37–1.10 (m, 4H), 0.88 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR δ 144.1, 127.5, 127.3, 125.9, 68.2, 64.0, 47.2, 37.4, 17.6, 14.9. Anal. Calcd for $\text{C}_{17}\text{H}_{27}\text{NO}$: C, 78.11; H, 10.41; N, 5.36. Found: C, 78.51; H, 10.67; N, 5.06.

4-(1-Benzyl-1-propylbutyl)morpholine (9e). Colorless oil; yield, 47% (0.39g); ^1H NMR δ 7.30–7.17 (m, 5H), 3.64 (apparent t, $J = 4.5$ Hz, 4H), 2.70–2.67 (m, 6H), 1.45–1.15 (m, 8H), 0.86–0.81 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR δ 139.4, 130.5, 128.3, 128.2, 127.6, 125.7, 68.1, 60.8, 46.1, 40.3, 37.6, 17.3, 14.7. Anal. Calcd for $\text{C}_{18}\text{H}_{29}\text{NO}$: C, 78.49; H, 10.61; N, 5.09. Found: C, 78.80; H, 10.85; N, 5.35.

4-(1,1-Dipropylpentyl)morpholine (9f). Colorless oil; yield, 48% (0.35g); ^1H NMR δ 3.62 (apparent t, $J = 4.5$ Hz, 4H), 2.63 (apparent t, $J = 4.5$ Hz, 4H), 1.36–1.22 (m, 14H), 0.92–0.85 (m, 9H); ^{13}C NMR δ 68.4, 59.4, 46.5, 37.6, 34.8, 26.5, 23.7, 17.5, 15.0, 14.2. Anal. Calcd for $\text{C}_{15}\text{H}_{31}\text{NO}$: C, 74.63; H, 12.94; N, 5.80. Found: C, 74.59; H, 13.23; N, 5.92.

4-(1,1-Dipropyl-2-propenyl)morpholine (9g) Colorless oil; yield, 51% (0.32g); ^1H NMR δ 5.68 (dd, $J = 17.7, 11.1$ Hz, 1H), 5.17 (dd, $J = 11.1, 1.5$ Hz, 1H), 4.98 (dd, $J = 17.7, 1.5$ Hz, 1H), 3.65 (apparent t, $J = 4.5$ Hz, 4H), 2.53 (apparent t, $J = 4.5$ Hz, 4H), 1.53–1.34 (m, 8H), 0.89 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR δ 140.9, 114.4, 68.0, 61.8, 46.2, 35.3, 16.7, 14.8. Anal. Calcd for $\text{C}_{13}\text{H}_{25}\text{NO}$: C, 73.88; H, 11.92; N, 6.63. Found: C, 73.63; H, 12.16; N, 6.82.

4-(1,1-Dipropyl-3-butenyl)morpholine (9h). Colorless oil; yield, 56% (0.38g); ^1H NMR δ 5.94–5.81 (m, 1H), 5.04–4.98 (m, 2H), 3.63 (apparent t, $J = 4.5$ Hz, 4H), 2.65 (apparent t, $J = 4.5$ Hz, 4H), 2.18 (d, $J = 7.2$ Hz, 2H), 1.39–1.25 (m, 8H), 0.86 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR δ 136.0, 116.2, 68.2, 59.7, 46.4, 39.7, 37.6, 17.2, 14.9. Anal. Calcd

for C₁₄H₂₇NO: C, 74.61; H, 12.07; N, 6.21. Found: C, 74.99; H, 12.46; N, 6.44.

1-[1-(2-Phenylethynyl)cyclohexyl]pyrrolidine (10b). Yellow oil; yield, 67% (0.51g); ¹H NMR δ 7.45–7.41 (m, 2H), 7.29–7.26 (m, 3H), 2.81 (d, *J* = 5.7 Hz, 4H), 2.04 (d, *J* = 11.7 Hz, 2H), 1.84–1.48 (m, 11H), 1.14–1.32 (m, 1H); ¹³C NMR δ 131.7, 128.2, 127.6, 123.7, 90.4, 86.0, 59.3, 47.0, 37.9, 25.7, 23.5, 23.1. Anal. Calcd for C₁₈H₂₃N: C, 85.32; H, 9.15; N, 5.53. Found: C, 85.47; H, 9.34; N, 5.92.

1-[1-(2-Phenylethynyl)cyclohexyl]piperidine (10c). White microcrystals (from hexane-ethyl acetate); yield, 43% (0.34g); mp 51–54 °C; ¹H NMR δ 7.46–7.43 (m, 2H), 7.33–7.28 (m, 3H), 2.67 (brs, 4H), 2.10 (d, *J* = 12 Hz, 2H), 1.76–1.45 (m, 13H), 1.27–1.22 (m, 1H); ¹³C NMR δ 131.7, 128.1, 127.6, 123.8, 90.8, 86.0, 59.2, 47.1, 35.8, 26.6, 25.7, 24.7, 23.1. Anal. Calcd for C₁₉H₂₅N: C, 85.34; H, 9.42; N, 5.24. Found: C, 85.66; H, 9.61; N, 5.03.

4-[1-(2-Phenylethynyl)cyclopentyl]morpholine (10d). White microcrystals (from hexane-ethyl acetate); yield, 47% (0.36g); mp 78–80 °C; ¹H NMR δ 7.45–7.41 (m, 2H), 7.30–7.28 (m, 3H), 3.77 (apparent t, *J* = 4.5 Hz, 4H), 2.72 (apparent t, *J* = 4.5 Hz, 4H), 2.13–2.08 (m, 2H), 1.90–1.71 (m, 6H); ¹³C NMR δ 131.6, 128.1, 127.7, 123.4, 90.4, 85.6, 67.2, 67.0, 49.5, 39.3, 23.2. Anal. Calcd for C₁₇H₂₁NO: C, 79.96; H, 8.29; N, 5.49. Found: C, 80.28; H, 8.49; N, 5.52.

4-[1-(2-Phenylethynyl)cycloheptyl]morpholine (10e). Yellow oil; yield, 52% (0.44g); ¹H NMR δ 7.44–7.40 (m, 2H), 7.29–7.27 (m, 3H), 3.76 (apparent t, *J* = 4.8 Hz, 4H), 2.70 (apparent t, *J* = 4.8 Hz, 4H), 2.01–1.86 (m, 4H), 1.68–1.60 (m, 8H); ¹³C NMR δ 131.6, 128.1, 127.7, 123.5, 91.9, 84.7, 67.5, 61.3, 47.4, 37.6, 28.2, 22.3. Anal. Calcd for C₁₉H₂₅NO: C, 80.52; H, 8.89; N, 4.94. Found: C, 80.92; H, 9.05; N, 4.82.

4-(1,1-Diethyl-3-phenyl-2-propynyl)morpholine (10f). Yellow oil; yield, 92% (0.71g); ^1H NMR δ 7.44–7.41 (m, 2H), 7.30–7.27 (m, 3H), 3.74 (apparent t, $J = 4.8$ Hz, 4H), 2.68 (apparent t, $J = 4.8$ Hz, 4H), 1.84–1.63 (m, 4H), 0.97 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR δ 131.6, 128.1, 128.1, 127.7, 123.4, 90.6, 85.3, 67.5, 61.8, 46.9, 26.8, 8.3. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.62; H, 9.21; N, 5.25.

4-(3-Phenyl-1,1-dipropyl-2-propynyl)morpholine (10g). Yellow oil; yield, 80% (0.68g); ^1H NMR δ 7.39–7.36 (m, 2H), 7.26–7.21 (m, 3H), 3.69 (apparent t, $J = 4.8$ Hz, 4H), 2.64 (apparent t, $J = 4.8$ Hz, 4H), 1.70–1.52 (m, 4H), 1.48–1.35 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 6H); ^{13}C NMR δ 131.5, 128.0, 127.6, 123.4, 90.9, 85.0, 67.4, 61.0, 46.9, 37.2, 17.1, 14.4. Anal. Calcd for $\text{C}_{19}\text{H}_{27}\text{NO}$: C, 79.95; H, 9.53; N, 4.91. Found: C, 79.96; H, 9.69; N, 4.88.

***N,N*,3-Triethyl-1-phenyl-1-pentyn-3-amine (10h).** Yellow oil; yield, 30% (0.22g); ^1H NMR δ 7.34–7.31 (m, 2H), 7.21–7.19 (m, 3H), 2.63 (q, $J = 6.9$ Hz, 4H), 1.68–1.53 (m, 4H), 1.01 (t, $J = 7.2$ Hz, 6H), 0.90 (t, $J = 7.5$ Hz, 6H); ^{13}C NMR δ 131.5, 128.1, 127.4, 124.1, 93.8, 83.6, 62.5, 43.3, 28.7, 15.6, 8.8. Anal. Calcd for $\text{C}_{17}\text{H}_{25}\text{N}$: C, 83.89; H, 10.35; N, 5.75. Found: C, 84.02; H, 10.38.

4-(1-Isopropyl-1-methyl-3-phenyl-2-propynyl)morpholine (10i). Yellow oil; yield, 31% (0.24g); ^1H NMR δ 7.44–7.41 (m, 2H), 7.29–7.27 (m, 3H), 3.75 (apparent t, $J = 4.8$ Hz, 4H), 2.74–2.60 (m, 4H), 2.12–2.07 (m, 1H), 1.23 (s, 3H), 1.11 (d, $J = 6.9$ Hz, 3H), 0.94 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR δ 131.7, 128.2, 127.8, 123.5, 90.9, 85.3, 67.6, 61.7, 47.1, 32.8, 18.9, 17.8, 16.0. Anal. Calcd for $\text{C}_{17}\text{H}_{23}\text{NO}$: C, 79.33; H, 9.01; N, 5.44. Found: C, 79.33; H, 9.33; N, 5.59.

1-[1-(2-Thienyl)cyclohexyl]pyrrolidine (11b). White microcrystals (from hexane-ethyl acetate); yield, 47% (0.33g); mp 37–39 °C (lit.²⁷ mp 44.5–45 °C); ¹H NMR δ 7.21 (dd, J = 5.1, 1.2 Hz, 1H), 7.03 (dd, J = 5.1, 3.6 Hz, 1H), 6.86 (dd, J = 3.6, 1.2 Hz, 1H), 2.56–2.52 (m, 4H), 2.13–2.08 (m, 2H), 1.98–1.91 (m, 2H), 1.69–1.59 (m, 6H), 1.45–1.36 (m, 4H); ¹³C NMR δ 144.6, 126.0, 124.6, 123.0, 59.1, 44.8, 37.5, 25.8, 23.3, 22.5. Anal. Calcd for C₁₄H₂₁NS: C, 71.44; H, 8.99; N, 5.95. Found: C, 71.61; H, 9.29; N, 5.92.

1-[1-(2-Thienyl)cyclohexyl]piperidine (11c)²⁷. Red oil, yield, 35% (0.26g); ¹H NMR δ 7.19 (d, J = 5.1 Hz, 1H), 7.00 (dd, J = 5.1, 3.6 Hz, 1H), 6.82 (d, J = 3.6 Hz, 1H), 2.33 (br s, 4H), 2.04–2.02 (m, 4H), 1.75–1.72 (m, 2H), 1.57–1.30 (m, 10H); ¹³C NMR δ 146.6, 125.9, 123.9, 122.7, 60.1, 46.3, 36.1, 27.0, 26.0, 24.9, 22.2. Anal. Calcd for C₁₅H₂₃NS: C, 72.23; H, 9.29; N, 5.62. Found: C, 71.91; H, 9.43; N, 5.55.

4-[1-(2-Thienyl)cycloheptyl]morpholine (11d). Yellow oil; yield, 55% (0.44g); ¹H NMR δ 7.18 (dd, J = 5.1, 1.1 Hz, 1H), 6.92 (dd, J = 5.1, 3.6 Hz, 1H), 6.87 (dd, J = 3.6, 1.1 Hz, 1H), 3.65 (apparent t, J = 4.8 Hz, 4H), 2.46 (apparent t, J = 4.5 Hz, 4H), 2.18 (dd, J = 14.7, 8.7 Hz, 2H), 2.02–1.92 (m, 2H), 1.75–1.67 (m, 2H), 1.62–1.45 (m, 6H); ¹³C NMR δ 152.3, 125.6, 123.7, 123.7, 67.8, 64.4, 46.9, 43.8, 37.2, 30.4, 29.7, 24.3, 23.1; Anal. Calcd for C₁₅H₂₃NOS: C, 67.88; H, 8.73; N, 5.28. Found: C, 67.87; H, 8.99; N, 5.47.

4-[1-Ethyl-1-(2-thienyl)propyl]morpholine (11e). Yellow oil; yield, 73% (0.52g); ¹H NMR δ 7.18 (dd, J = 5.1, 0.5 Hz, 1H), 6.96 (dd, J = 5.1, 3.6 Hz, 1H), 6.81 (dd, J = 3.6, 0.5 Hz, 1H), 3.66 (apparent t, J = 4.5 Hz, 4H), 2.53 (apparent t, J = 4.5 Hz, 4H), 1.99–1.80 (m, 4H), 0.86 (t, J = 7.2 Hz, 6H); ¹³C NMR δ 148.9, 126.0, 124.2, 123.4, 68.0, 63.6, 46.8, 27.3, 8.5. Anal. Calcd for C₁₃H₂₁NOS: C, 65.23; H, 8.84; N, 5.85. Found: C,

65.16; H, 9.15; N, 6.07.

4-[1-Propyl-1-(2-thienyl)butyl]morpholine (11f). White microcrystals (from hexane-ethyl acetate); yield, 66% (0.53g); mp 62–63 °C; ^1H NMR δ 7.17 (d, J = 5.1 Hz, 1H), 6.95 (dd, J = 5.1, 3.6 Hz, 1H), 6.81 (d, J = 3.6 Hz, 1H), 3.65 (apparent t, J = 4.5 Hz, 4H), 2.52 (apparent t, J = 4.5 Hz, 4H), 1.89–1.70 (m, 4H), 1.47–1.30 (m, 2H), 1.26–1.12 (m, 2H), 0.91 (t, J = 7.2 Hz, 6H); ^{13}C NMR δ 149.5, 126.0, 123.9, 123.3, 68.0, 63.3, 46.8, 38.1, 17.3, 14.7. Anal. Calcd for $\text{C}_{15}\text{H}_{25}\text{NOS}$: C, 67.37; H, 9.42; N, 5.24. Found: C, 67.22; H, 9.74; N, 5.16.

4-[1-(1,3-Thiazol-2-yl)cycloheptyl]morpholine (11i). Dark red needles (from hexane-ethyl acetate); yield, 38% (0.30g); mp 52–53 °C; ^1H NMR δ 7.68 (d, J = 3.3 Hz, 1H), 7.26 (d, J = 3.3 Hz, 1H), 3.67 (apparent t, J = 4.5 Hz, 4H), 2.54 (apparent t, J = 4.5 Hz, 4H), 2.21–2.03 (m, 4H), 1.74–1.59 (m, 8H); ^{13}C NMR δ 178.9, 141.2, 118.8, 67.7, 66.8, 47.2, 36.5, 29.8, 23.2. Anal. Calcd for $\text{C}_{14}\text{H}_{22}\text{N}_2\text{OS}$: C, 63.12; H, 8.32; N, 10.52. Found: C, 62.86; H, 8.34; N, 10.73.

4-[1-Ethyl-1-(1,3-thiazol-2-yl)propyl]morpholine (11j). Dark red oil; yield, 72% (0.52g); ^1H NMR δ 7.72 (d, J = 3.3 Hz, 1H), 7.25 (d, J = 3.3 Hz, 1H), 3.68 (apparent t, J = 4.5 Hz, 4H), 2.64 (apparent t, J = 4.5 Hz, 4H), 2.12–1.93 (m, 4H), 0.87 (t, J = 7.5 Hz, 6H); ^{13}C NMR δ 176.4, 141.6, 118.5, 67.8, 66.0, 47.2, 26.8, 8.3. Anal. Calcd for $\text{C}_{12}\text{H}_{20}\text{N}_2\text{OS}$: C, 59.96; H, 8.39; N, 11.65. Found: C, 59.86; H, 8.41; N, 12.04.

4-[1-Propyl-1-(1,3-thiazol-2-yl)butyl]morpholine (11k). Orange oil; yield, 80% (0.64g); ^1H NMR δ 7.71 (d, J = 3.6 Hz, 1H), 7.25 (d, J = 3.6 Hz, 1H), 3.68 (apparent t, J = 4.8 Hz, 4H), 2.64 (apparent t, J = 4.8 Hz, 4H), 1.97–1.88 (m, 4H), 1.42–1.14 (m, 4H), 0.91 (t, J = 7.5 Hz, 6H); ^{13}C NMR δ 177.3, 141.7, 118.7, 67.9, 65.8, 47.3, 37.4, 17.3,

14.6. Anal. Calcd for $C_{14}H_{24}N_2OS$: C, 62.65; H, 9.01; N, 10.44. Found: C, 63.04; H, 9.16; N, 10.65.