

New synthesis of propargylic amines from 2-(bromomethyl)aziridines.

Intermediacy of 3-bromoazetidinium salts

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General information

¹H NMR spectra were recorded at 270 MHz with CDCl₃ as a solvent and tetramethylsilane as an internal standard. ¹³C NMR spectra were recorded at 68 MHz with CDCl₃ as a solvent. Mass spectra were obtained with a mass spectrometer (70 eV) using a GC-MS coupling (20 m glass capillary column, i.d. 0.53 mm, He carrier gas) or were recorded using direct inlet (70 eV). Dichloromethane was distilled over calcium hydride, and diethyl ether and THF were dried by distillation over sodium benzophenone ketyl. Other solvents were used as received from the supplier.

N-Benzyl-N-(2,3-dibromopropyl)-N-((4-methylphenyl)methyl)amine 4b

Colorless oil, 54% yield, TLC Rf 0.24 (hexane/EtOAc 50/1). ¹H NMR (270 MHz, CDCl₃): δ 2.30 (3H, s), 2.83 and 3.02 (2H, 2×d×d, *J*=13.9 Hz, *J*=7.3, 6.8 Hz), 3.54 and 3.59 (2H, 2×d, *J*=12.0 Hz), 3.55 and 3.60 (2H, 2×d, *J*=12.2 Hz), 3.64 (2H, d, *J*=5.6 Hz), 3.96 (1H, quint, *J*=6.3 Hz), 7.08-7.11 and 7.13-7.33 (9H, 2×m). ¹³C NMR (67.8 MHz, CDCl₃): δ 21.7, 36.4, 51.5, 59.4, 59.6, 59.8, 127.8, 128.8, 129.5, 129.5, 135.9, 137.3, 139.2. IR (NaCl, cm⁻¹): ν _{max}= 3085, 3026, 2922, 2806, 2718, 1514, 1495, 1453. MS (70 eV): m/z (%): 409/11/13(M⁺, 3), 223(71), 121(15), 106(13), 105(100), 91(44), 77(10). Anal. Calcd for C₁₈H₂₁Br₂N: C 52.58; H 5.15; N 3.41. Found: C 52.72; H 5.26; N 3.49.

N-Benzyl-N-(2,3-dibromopropyl)-N-((4-methoxyphenyl)methyl)amine 4c

Colorless oil, 54% yield, TLC Rf 0.21 (hexane/EtOAc 20/1). ¹H NMR (270 MHz, CDCl₃): δ 2.87 and 3.07 (2H, 2×d×d, *J*=13.7 Hz, *J*=7.3, 6.6 Hz), 3.56 and 3.65 (2H, 2×d, *J*=13.9 Hz), 3.57 and 3.66 (2H, 2×d, *J*=14.5 Hz), 3.70 (2H, d, *J*=5.6 Hz), 3.80 (3H, s), 4.00 (1H, quint, *J*=6.4 Hz), 6.84-6.89 (2H, m), 7.24-7.36 (7H, m). ¹³C NMR (67.8 MHz, ref=CDCl₃): δ 35.9, 51.0, 55.2, 58.6, 59.2, 59.3, 113.7, 127.2, 128.3, 129.0, 130.2, 130.6, 138.8, 158.8. IR (NaCl,

cm^{-1}): $\tilde{\nu}_{\text{max}} = 3022, 2928, 2826, 1610, 1509, 1451, 1248, 1035$. **MS** (70 eV): m/z (%): no M^+ , 239($M^+ \text{-CH}_2\text{BrCH}_2\text{Br}$, 32), 121(100), 91(34), 83(13), 65(10). Anal. Calcd for $C_{18}\text{H}_{21}\text{Br}_2\text{NO}$: C 50.61; H 4.96; N 3.28. Found: C 50.75; H 5.09; N 3.17.

N-Benzyl-N-((4-bromophenyl)methyl)-N-(2,3-dibromopropyl)amine 4d

Colorless oil, 52% yield, TLC Rf 0.32 (hexane/EtOAc 20/1). **$^1\text{H NMR}$** (270 MHz, CDCl_3): δ 2.87 and 3.09 (2H, $2\times\text{d}\times\text{d}$, $J=13.9$ Hz, $J=6.9, 6.6$ Hz), 3.54-3.77 (6H, m), 4.05 (1H, quint, $J=6.5$ Hz), 7.23-7.49 (9H, m). **$^{13}\text{C NMR}$** (67.8 MHz, ref= CDCl_3): δ 35.4, 50.4, 58.3, 58.8, 59.0, 127.3, 128.3, 128.8, 130.5, 131.3, 120.9, 137.5, 138.1. **IR** (NaCl, cm^{-1}): $\tilde{\nu}_{\text{max}} = 3062, 3028, 2927, 2825, 1487, 1454, 1070, 1012, 797, 742, 696$. **MS** (70 eV): m/z (%): no M^+ , 283/5($M^+ \text{-CH}_2\text{BrCH}_2\text{Br-2}\times\text{H}_2$, 71), 169/71(51), 121(18), 91(100), 90(16), 65(13). Anal. Calcd for $C_{17}\text{H}_{18}\text{Br}_3\text{N}$: C 42.89; H 3.81; N 2.94. Found: C 42.74; H 3.95; N 2.80.

N-(2,3-Dibromopropyl)-N,N-di((4-methylphenyl)methyl)amine 4e

Colorless oil, 62% yield, TLC Rf 0.50 (hexane/EtOAc 50/1). **$^1\text{H NMR}$** (270 MHz, CDCl_3): δ 2.34 (6H, s), 2.87 and 3.05 (2H, $2\times\text{d}\times\text{d}$, $J=13.9$ Hz, $J=7.6, 6.4$ Hz), 3.54 and 3.60 (4H, $2\times 2\times\text{d}$, $J=14.5$ Hz), 3.70 and 3.72 (2H, $2\times\text{d}\times\text{d}$, $J=10.9, 5.6$ Hz), 4.01 (1H, quint, $J=6.4$ Hz), 7.09-7.19 and 7.21-7.30 (8H, $2\times\text{m}$). **$^{13}\text{C NMR}$** (67.8 MHz, CDCl_3): δ 21.0, 35.8, 50.9, 58.6, 59.1, 128.8, 128.9, 135.4, 136.5. **IR** (NaCl, cm^{-1}): $\tilde{\nu}_{\text{max}} = 3047, 3021, 2922, 2819, 1514, 807$. **MS** (70 eV): m/z (%): 424/26/28(M^++1 , 7), 344/6(100), 105(17). Anal. Calcd for $C_{19}\text{H}_{23}\text{Br}_2\text{N}$: C 53.67; H 5.45; N 3.29. Found: C 53.52; H 5.57; N 3.39.

N-(2,3-Dibromopropyl)-N-((4-methoxyphenyl)methyl)-N-((4-methylphenyl)methyl)amine 4f

Colorless oil, 61% yield, TLC Rf 0.15 (hexane/EtOAc 50/1). **¹H NMR** (270 MHz, CDCl₃): δ 2.33 (3H, s), 2.85 and 3.04 (2H, 2×d×d, *J*=13.9 Hz, *J*=7.3, 6.6 Hz), 3.50-3.62 (4H, m), 3.69 (2H, d, *J*=5.6 Hz), 3.79 (3H, s), 3.99 (1H, quint, *J*=6.4 Hz), 6.84-6.87 (2H, m), 7.11-7.26 (6H, m). **¹³C NMR** (67.8 MHz, ref=CDCl₃): δ 21.0, 35.8, 50.9, 54.9, 58.2, 58.5, 58.9, 113.5, 128.7, 128.8, 129.9, 130.4, 135.4, 136.4, 158.6. **IR** (NaCl, cm⁻¹): ν_{max} = 3003, 2953, 2931, 2833, 1611, 1512, 1249. **MS** (70 eV): m/z (%): no M⁺, 253(M⁺-CH₂BrCH₂Br, 100), 121(62), 105(31). Anal. Calcd for C₁₉H₂₃Br₂NO: C 51.72; H 5.25; N 3.17. Found: C 51.86; H 5.38; N 3.11.

***N*-((4-bromophenyl)methyl)-*N*-(2,3-dibromopropyl)-*N*-((4-methylphenyl)methyl)amine
4g**

Colorless oil, 59% yield, TLC Rf 0.45 (hexane/EtOAc 50/1). **¹H NMR** (270 MHz, CDCl₃): δ 2.33 (3H, s), 2.85 and 3.06 (2H, 2×d×d, *J*=14.1 Hz, *J*=7.0, 6.8 Hz), 3.48-3.60 (4H, m), 3.65 and 3.72 (2H, 2×d×d, *J*=10.7 Hz, *J*=6.6, 5.0 Hz), 3.99-4.06 (1H, m), 7.08-7.26 and 7.40-7.47 (8H, 2×m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 21.1, 35.5, 50.6, 58.3, 58.8, 59.1, 128.8, 129.0, 130.6, 131.3, 120.9, 135.0, 136.8, 137.7. **IR** (NaCl, cm⁻¹): ν_{max} = 3046, 3022, 2923, 2822, 1487, 806. **MS** (70 eV): m/z (%): 487/89/91(M⁺, 6), 301/3(100), 169/71(15), 105(17). Anal. Calcd for C₁₈H₂₀Br₃N: C 44.11; H 4.11; N 2.86. Found: C 44.24, H 4.24; N 2.71.

***N*-((4-bromophenyl)methyl)-*N*-(2,3-dibromopropyl)-*N*-((4-methoxyphenyl)methyl)amine
4h**

Colorless oil, 50% yield, TLC Rf 0.18 (hexane/EtOAc 50/1). **¹H NMR** (270 MHz, CDCl₃): δ 2.85 and 3.07 (2H, 2×d×d, *J*=14.1 Hz, *J*=7.1, 6.6 Hz), 3.53 and 3.60 (2H, 2×d, *J*=13.5 Hz), 3.55 and 3.61 (2H, 2×d, *J*=13.9 Hz), 3.65 and 3.73 (2H, 2×d×d, *J*=10.6 Hz, *J*=6.8, 5.0 Hz), 3.80 (3H, s), 4.04 (1H, quint, *J*=6.8), 6.84-6.89 (2H, m), 7.22-7.30 and 7.43-7.47 (6H, 2×m).

¹³C NMR (67.8 MHz, CDCl₃): δ 35.5, 50.6, 55.08, 58.2, 59.0, 113.7, 130.0, 130.5, 131.3, 120.9, 137.7, 158.7. **IR** (NaCl, cm⁻¹): ν_{max} = 2999, 2953, 2931, 2833, 1611, 1511, 1249. **MS** (70 eV): m/z (%): no M⁺, 424/6/8(M⁺-Br, 2), 317/9(100), 168/70(45), 121(90), 90(25), 78(17), 77(16). Anal. Calcd for C₁₈H₂₀Br₃NO: C 42.72; H 3.98; N 2.77. Found: C 42.84; H 4.09; N 2.68.

N-Benzyl-N-(4-chlorobenzyl)-N-(2,3-dibromopropyl)amine 4i

Colorless oil, 60% yield. **¹H NMR** (270 MHz, CDCl₃): δ 2.86 and 3.09 (2H, 2×d×d, J=14.1 Hz, J=7.1, 6.6 Hz), 3.58 and 3.64 (2H, 2×d, J=14.2 Hz), 3.60 and 3.67 (2H, 2×d, J=14.0 Hz), 3.63 and 3.73 (2H, 2×d×d, J=10.7 Hz, J=5.1, 3.6 Hz), 4.02-4.07 (1H, m), 7.25-7.41 (9H, m).

¹³C NMR (67.8 MHz, CDCl₃): δ 35.4, 50.5, 58.3, 58.9, 59.1, 127.3, 128.3, 128.4, 128.9, 130.2, 132.8, 137.1, 138.2. **IR** (NaCl, cm⁻¹): ν_{max} = 3084, 3062, 3028, 3028, 2930, 2826, 1490, 1089, 1015, 908, 801, 735, 699. **MS** (70 eV): m/z (%): 429/31/33/35(M⁺, 1), 350/2(4), 336/8(8), 245/7(59), 244/6(100), 210(16), 180(12), 154(15), 125/7(59), 99/101(9), 92(17), 91(48), 90(15), 89(22), 65(15). Anal. Calcd for C₁₇H₁₈Br₂ClN: C 47.31; H 4.20; N 3.25. Found: C 47.38; H 4.29; N 3.20.

N,N-Di((4-bromophenyl)methyl)-N-(2,3-dibromopropyl)amine 4j

Colorless oil, 51% yield, TLC Rf 0.23 (hexane/EtOAc 50/1). **¹H NMR** (270 MHz, CDCl₃): δ 2.84 and 3.10 (2H, 2×d×d, J=14.1 Hz, J=7.6, 5.8 Hz), 3.54 and 3.63 (2H, 2×2×d, J=13.7 Hz), 3.62 and 3.75 (2H, 2×d×d, J=10.4 Hz, J=7.9, 4.6 Hz), 4.08 (1H, m), 7.21-7.26 (4H, m), 7.44-7.47 (4H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 35.0, 50.1, 58.1, 59.0, 121.0, 150.4, 131.3, 137.2. **IR** (NaCl, cm⁻¹): ν_{max} = 3041, 3024, 2929, 2890, 2825, 1899, 1591, 1070, 1011. **MS** (70 eV): m/z (%): 551/3/5/7/9(M⁺, 5), 365/7/9(100), 169/70(51), 90(11). Anal. Calcd for C₁₇H₁₇Br₄N: C 36.79; H 3.09; N 2.52. Found: C 36.86; H 3.21; N 2.40.

N-Benzyl-N-(2-bromo-2-propenyl)-N-((4-methylphenyl)methyl)amine 6b

Colorless oil, 76% yield, Bp 135°C/0.03 mbar. **¹H NMR** (270 MHz, CDCl₃): δ 2.33 (3H, s), 3.25 (2H, s), 3.58 and 3.61 (4H, 2×s), 5.60 and 5.96 (2H, 2×s), 7.11-7.42 (9H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 21.1, 57.0, 57.2, 61.3, 118.3, 126.9, 128.2, 128.6, 128.8, 128.9, 132.2, 135.6, 136.4, 138.9. **IR** (NaCl, cm⁻¹): ν_{max} = 3026, 2922, 2801, 1629, 1454, 803. **MS** (70 eV): m/z (%): 329/31(M⁺, 3), 224(24), 121(12), 105(100), 92(20), 91(63), 77(13). Anal. Calcd for C₁₈H₂₀BrN: C 65.46; H 6.10; N 4.24. Found: C 65.34; H 5.93; N 4.33.

N-Benzyl-N-(2-bromo-2-propenyl)-N-((4-methoxyphenyl)methyl)amine 6c

Colorless oil, 80% yield, Bp 113°C/0.01 mm Hg. **¹H NMR** (270 MHz, CDCl₃): δ 3.24 (2H, s), 3.55 and 3.60 (4H, 2×s), 3.79 (3H, s), 5.60 (1H, s(broad)), 5.95 (1H, d, J=1.3 Hz), 6.84-6.91 (2H, m), 7.21-7.42 (7H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 55.1, 56.6, 57.1, 61.2, 118.4, 126.9, 113.6, 128.2, 128.6, 129.8, 130.7, 132.2, 138.9, 158.6. **IR** (NaCl, cm⁻¹): ν_{max} = 3062, 3029, 3001, 2932, 2833, 2803, 1612, 1511, 1250. **MS** (70 eV): m/z (%): 345/7(M⁺, 10), 121(100), 91(36), 77(10), 65(7). Anal. Calcd for C₁₈H₂₀BrNO: C 62.44; H 5.82; N 4.05. Found: C 62.59; H 5.95; N 3.96.

N-Benzyl-N-((4-bromophenyl)methyl)-N-(2-bromo-2-propenyl)amine 6d

Colorless oil, 71% yield, Bp 145°C/0.05 mbar. **¹H NMR** (270 MHz, CDCl₃): δ 3.24 (2H, s), 3.55 and 3.60 (4H, 2×s), 5.61 and 5.92 (2H, 2×s), 7.19-7.50 (9H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 56.4, 57.1, 61.2, 118.7, 127.0, 128.2, 128.5, 130.2, 131.2, 120.6, 131.8, 137.8, 138.3. **IR** (NaCl, cm⁻¹): ν_{max} = 3062, 3027, 2924, 2802, 1629, 1487, 798. **MS** (70 eV): m/z (%): 393/5/7(M⁺, 16), 288/90(40), 224(14), 169/71(55), 105(14), 91(100), 90(17), 89(13). Anal. Calcd for C₁₇H₁₇Br₂N: C 51.67; H 4.34; N 3.54. Found: C 51.51; H 4.40; N 3.49.

N-(2-Bromo-2-propenyl)-N,N-di((4-methylphenyl)methyl)amine 6e

Colorless oil, 78% yield, Bp 144°C/0.02 mbar. **1H NMR** (270 MHz, CDCl₃): δ 2.33 (6H, s), 3.23 (2H, s), 3.56 (4H, s), 5.59 and 5.96 (2H, 2×d, J=1.3 Hz), 7.11-7.13 and 7.25-7.30 (8H, 2×m). **13C NMR** (67.8 MHz, CDCl₃): δ 21.1, 56.9, 61.3, 118.3, 128.7, 128.9, 132.3, 135.8, 136.5. **IR** (NaCl, cm⁻¹): ν_{max}= 3048, 3021, 2922, 2804, 1629, 1514, 807. **MS** (70 eV): m/z (%): 343/5(M⁺, 33), 240(30), 238(100), 124(52), 106(37), 105(90), 103(15), 91(16), 79(18), 77(20). Anal. Calcd for C₁₉H₂₂BrN: C 66.28; H 6.44; N 4.07. Found: C 66.38; H 6.55; N 3.98.

N-Benzyl-N-((4-methylphenyl)methyl)-N-(2-propynyl)amine 16b

Yellow crystals, 90% yield, TLC Rf 0.35 (hexane/EtOAc 16/1), Mp 38°C. **1H NMR** (270 MHz, CDCl₃): δ 2.27 (1H, t, J=2.3 Hz), 2.33 (3H, s), 3.25 (2H, d, J=2.3 Hz), 3.65 and 3.67 (4H, 2×s), 7.12-7.15 and 7.21-7.41 (9H, 2×m). **13C NMR** (67.8 MHz, CDCl₃): δ 21.1, 41.0, 57.1, 57.3, 73.3, 78.5, 127.1, 128.3, 129.0, 135.7, 136.6, 138.8. **IR** (NaCl, cm⁻¹): ν_{•CH}= 3299, ν_{max}= 3027, 2923, 2829, 1515, 1453, 802. **MS** (70 eV): m/z (%): 250(M⁺+1, 100), 212(55), 105(57). Anal. Calcd for C₁₈H₁₉N: C 86.70; H 7.68; N 5.62. Found: C 86.79; H 7.79; N 5.54.

N-Benzyl-N-((4-methoxyphenyl)methyl)-N-(2-propynyl)amine 16c

Yellow oil, 94% yield, TLC Rf 0.31 (hexane/EtOAc 16/1). **1H NMR** (270 MHz, CDCl₃): δ 2.27 (1H, t, J=2.3 Hz), 3.24 (2H, d, J=2.3 Hz), 3.62 and 3.66 (4H, 2×s), 3.79 (3H, s), 6.83-6.90 (2H, m), 7.20-7.41 (7H, m). **13C NMR** (67.8 MHz, CDCl₃): δ 40.9, 55.2, 56.8, 57.3, 73.3, 78.5, 113.7, 127.1, 128.3, 129.0, 130.2, 130.7, 138.9, 158.8. **IR** (NaCl, cm⁻¹): ν_{•CH}= 3291, ν_{max}= 3062, 3029, 2932, 2834, 1612, 1513, 1247. **MS** (70 eV): m/z (%): 265(M⁺, 35), 174(14), 144(11), 121(100), 92(10), 91(37). Anal. Calcd for C₁₈H₁₉NO: C 81.47; H 7.22; N 5.28. Found: C 81.42; H 7.32; N 5.15.

N-Benzyl-N-((4-bromophenyl)methyl)-N-(2-propynyl)amine 16d

Yellow oil, 91% yield, TLC Rf 0.23 (hexane/EtOAc 16/1). **¹H NMR** (270 MHz, CDCl₃): δ 2.27-2.29 (1H, m), 3.24 (2H, d, *J*=1.7 Hz), 3.62 and 3.66 (4H, 2×s), 7.17-7.49 (9H, 2×m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 41.1, 55.7, 57.4, 73.6, 78.2, 127.2, 128.3, 129.0, 130.6, 131.4, 120.9, 137.8, 138.5. **IR** (NaCl, cm⁻¹): $\bar{\nu}_{C-H}$ = 3297, $\bar{\nu}_{max}$ = 3029, 2922, 2831, 1487, 1012, 796. **MS** (70 eV): m/z (%): 313/5(M⁺, 20), 222/4(18), 169/71(44), 158(19), 144(23), 106(10), 105(20), 92(52), 91(100), 90(17), 89(15), 65(12). Anal. Calcd for C₁₇H₁₆BrN: C 64.98; H 5.13; N 4.46. Found: C 65.07; H 5.19; N 4.36.

N,N-Di((4-methylphenyl)methyl)-N-(2-propynyl)amine 16e

Yellow crystals, 92% yield, TLC Rf 0.33 (hexane/EtOAc 16/1), Mp 32°C. **¹H NMR** (270 MHz, CDCl₃): δ 2.26 (1H, t, *J*=2.3 Hz), 2.33 (6H, s), 3.24 (2H, d, *J*=2.3 Hz), 3.63 (4H, s), 7.11-7.17 and 7.24-7.29 (8H, 2×m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 21.1, 40.9, 57.1, 73.3, 78.6, 129.0, 135.7, 136.6. **IR** (NaCl, cm⁻¹): $\bar{\nu}_{C-H}$ = 3273, $\bar{\nu}_{max}$ = 3020, 2920, 2828, 1514, 1103, 808. **MS** (70 eV): m/z (%): 263(M⁺, 19), 172(11), 158(51), 106(53), 105(100), 103(11), 91(20), 79(15), 77(18). Anal. Calcd for C₁₉H₂₁N: C 86.65; H 8.04; N 5.32. Found: C 86.70; H 8.10; N 5.43.

6-[N-(4-Benzyl)-N-((4-methoxyphenyl)methyl)amino]-4-hexyn-2-ol 20b

Colorless oil, 85% yield, TLC Rf 0.11 (hexane/EtOAc 4/1). **¹H NMR** (270 MHz, CDCl₃): δ 1.32 (3H, d, *J*=6.3 Hz), 2.36-2.55 (2H, m), 3.24 (2H, t, *J*=2.2 Hz), 3.60 and 3.65 (4H, 2×s), 3.80 (3H, s), 3.96-4.03 (1H, m), 6.83-6.89 (2H, m), 7.22-7.40 (7H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 22.4, 29.3, 41.4, 55.1, 56.9, 57.4, 66.5, 77.2, 82.0, 113.6, 127.0, 128.3, 129.0, 130.2, 130.7, 138.8, 158.7. **IR** (NaCl, cm⁻¹): $\bar{\nu}_{OH}$ = 3390, $\bar{\nu}_{max}$ = 3029, 2928, 2834, 1612, 1512,

1249, 736. **MS** (70 eV): m/z (%): 324(M⁺+1, 100), 121(30). Anal. Calcd for C₂₁H₂₅NO₂: C 77.98; H 7.79; N 4.33. Found: C 77.86; H 7.88; N 4.41.

N-Butyl-4-(N,N-dibenzylamino)butynamide 21

Orange crystals, 45% yield, TLC Rf 0.22 (hexane/EtOAc 4/1), Mp 60-64°C. **¹H NMR** (270 MHz, CDCl₃): δ 0.94 (3H, t, J=7.3 Hz), 1.37 (2H, sext, J=7.3 Hz), 1.53 (2H, quint, J=7.3 Hz), 2.71 (2H, q, J=7.3 Hz), 3.36 (2H, s), 3.70 (4H, s), 5.87 (1H, s(broad)), 7.22-77.41 (10H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 13.7, 20.0, 31.3, 39.6, 41.3, 57.7, 80.5, 81.1, 127.2, 128.3, 129.0, 138.4, 153.1. **IR** (NaCl, cm⁻¹): ν NH=3246, ν C=O=1624, ν max= 3062, 3030, 2955, 2929, 2861, 1553. **MS** (70 eV): m/z (%): 335(M⁺+1, 100). Anal. Calcd for C₂₂H₂₆N₂O: C 79.00; H 7.84; N 8.38. Found: C 79.12; H 7.77; N 8.33.

Methyl 4-(dibenzylamino)-2-butynoate 22

Yellow liquid, 68% yield, TLC Rf 0.25 (hexane/EtOAc 9/1). **¹H NMR** (270 MHz, CDCl₃): δ 3.28 (2H, s), 3.64 (4H, s), 3.71 (3H, s), 7.16-7.35 (10H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 41.0, 52.5, 57.6, 77.8, 83.6, 127.3, 128.4, 128.9, 138.2, 153.7. **IR** (NaCl, cm⁻¹): ν C=O=1718, ν max= 3063, 3029, 2953, 2826, 2227, 1251, 750, 699. **MS** (70 eV): m/z (%): 294(M⁺+1, 100). Anal. Calcd for C₁₉H₁₉NO₂: C 77.79; H 6.53; N 4.77. Found: C 77.92; H 6.62; N 4.72.

1,7-Bis(N,N-dibenzylamino)-4-isopropyl-2,5-heptadiyne-4-ol 23

Yellow oil, 55% yield, TLC Rf 0.12 (hexane/EtOAc 9/1). **¹H NMR** (270 MHz, CDCl₃): δ 1.27 (6H, d, J=6.6 Hz), 2.17 (1H, sept, J=6.8 Hz), 3.34 (4H, s), 3.72 (8H, s), 7.16-7.42 (20H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 17.9, 40.0, 41.3, 57.7, 68.1, 78.8, 85.9, 127.1, 128.3, 129.0, 138.6. **IR** (NaCl, cm⁻¹): ν OH= 3427, ν C=C= 2248, ν max= 3086, 3063, 3029, 2966, 2925,

2825, 1495, 1454. **MS** (70 eV): m/z (%): 541(M⁺+1, 100). Anal. Calcd for C₃₈H₄₀N₂O: C 84.40; H 7.46; N 5.18. Found: C 84.52; H 7.57; N 5.30.

The compounds **24** and **25** were prepared in accordance with a procedure adopted from the literature.^{73,74} – General procedure for the preparation of propargylamines **24** and **25**: To a solution of a *N,N*-di(aryl methyl)-*N*-(2-propynyl)amine **16** (2 mmol) in THF (20 ml) and Et₃N (6 ml) was added under nitrogen atmosphere tetrakis(triphenylphosphine) palladium (0.05 equivalents), CuI (0.1 equivalents), BuNH₂ (3.0 equivalents) and the halogenated compound (1.05 equivalents), and the resulting solution was stirred for 15 hours. Quenching of the reaction mixture with saturated NH₄Cl (20 ml), extraction with diethyl ether (3×20 ml), drying (MgSO₄), filtration of the drying agent and removal of the solvent in vacuo afforded propargylamines **24** and **25**. Compound **24** was purified by column chromatography (SiO₂). Purity of compound **25** > 95% (GC).

N*-[3-((4-methoxyphenyl)methyl)-2-propynyl]-*N,N*-di[((4-methylphenyl)methyl)amine **24*

Colorless crystals, 67% yield, TLC Rf 0.25 (hexane/EtOAc 15/1), Mp 140-145°C. **¹H NMR** (270 MHz, CDCl₃): δ 2.34 (6H, s), 3.43 (2H, s), 3.69 (4H, s), 3.82 (3H, s), 6.85-6.89 (2H, m), 7.12-7.32 (8H, m), 7.41-7.45 (2H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 21.1, 41.9, 55.2, 57.3, 83.0, 85.5, 113.9, 128.9, 129.0, 133.1, 135.9, 136.5, 115.6, 135.6, 136.7, 159.3. **IR** (NaCl, cm⁻¹): ̳_{max} = 3049, 3022, 3007, 2922, 2854, 2820, 1486, 1245. **MS** (70 eV): m/z (%): 370(M⁺+1, 100), 266(72), 264(32), 105(27), 91(14). Anal. Calcd for C₂₆H₂₇NO: C 84.51; H 7.37; N 3.79. Found: C 84.59; H 7.48; N 3.79.

N,N,N',N'-Tetrabenzylhexa-2,4-diyne-1,6-diamine **25**

Yellow crystals, 93% yield, Mp 87-95°C. **¹H NMR** (270 MHz, CDCl₃): δ 3.37 (4H, s), 3.73 (8H, s), 7.12-7.49 (20H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 41.9, 57.6, 70.1, 73.6, 127.2, 128.3, 129.0, 139.0. **IR** (NaCl, cm⁻¹): ν_{max} = 3083, 3062, 3027, 2916, 2805, 1949, 1871, 1811, 1601, 1494, 1452, 1367, 1314. **MS** (70 eV): m/z (%): 272(M⁺-N(CH₂C₆H₅)₂, 32), 260(91), 91(100), 77(12). Anal. Calcd for C₃₄H₃₂N₂: C 87.14; H 6.88; N 5.98. Found: C 87.20; H 6.93; N 5.86.

(4Z)-6-[Di(phenylmethyl)amino]-5-phenyl-4-hexen-2-ol 27

Colorless oil, 24% yield, TLC Rf 0.35 (hexane/EtOAc 4/1). **¹H NMR** (270 MHz, CDCl₃): δ 1.22 (3H, d, *J*=6.3 Hz), 2.28 and 2.29 (2H, 2×d, *J*=7.7 Hz, *J*=6.3 Hz), 3.36 and 3.51 (4H, 2×d, *J*=12.9 Hz), 3.42-3.71 (2H, m), 3.80-3.91 (1H, m), 5.90 (1H, t, *J*=7.7 Hz), 7.09-7.78 (15H, m). **¹³C NMR** (67.8 MHz, CDCl₃): δ 23.3, 38.2, 52.1, 58.4, 67.3, 126.8, 127.0, 128.1, 128.3, 129.4, 129.5, 126.9, 138.9, 140.5, 142.9. **IR** (NaCl, cm⁻¹): ν_{OH} = 3385, ν_{max} = 3083, 3061, 3028, 2965, 2926, 2832, 1602. **MS** (70 eV): m/z (%): 372(M⁺+1, 100). Anal. Calcd for C₂₆H₂₉NO: C 84.06; H 7.87; N 3.77. Found: C 84.14; H 7.98; N 3.72.