Tandem Catalysis Enabled Highly Chemoselective Deoxygenative Alkynylation and Alkylation of Tertiary Amides: A Versatile Entry to Functionalized α-Substituted Amines

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Experimental Procedures

General Methods: Melting points were determined on a Büchi M560 Automatic Melting Point apparatus and are uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques. NMR spectra were recorded on a Bruker AV 400 or AC 500 spectrometer at 25 ºC in the solvents indicated. Chemical shifts (δ) are reported in ppm and respectively referenced to internal standard Me₄Si and solvent signals (Me₄Si, 0 ppm for ¹H NMR and CDCl₃, 77.0 ppm for ¹³C NMR, some carbons are missing because of overlap). Mass spectra were recorded on a Bruker Dalton ESquire 3000 plus LC-MS apparatus (ESI direct injection). HRMS spectra were recorded on a 7.0T FT-MS apparatus. Silica gel (300-400 mesh) was used for flash column chromatography eluting (unless otherwise stated) with EtOAc/n-hexane mixture. Toluene was distilled over sodium benzophenone ketyl under N₂.
Table 1. The structures of amides used
Table 2. The structures of alkynes used

![Diagram of alkynes structures](image-url)
General procedure A: The catalytic reductive alkynylation of amides.

In a glove box charged with an atmosphere of nitrogen, IrCl(CO)(PPh₃)₂ (8 mg, 0.01 mmol, 1.0 mol%) was added to a dried 10-mL round-bottom flask equipped with a magnetic stirring bar. The flask was then removed from the glove box. A solution of a tert-amide (1.0 mmol, 1.0 equiv) in toluene (5 mL), and 1,1,3,3-tetramethyldisiloxane (0.36 mL, 2.0 mmol, 2.0 equiv or 1.2 equiv for amides without α-hydrogen) were successively added to the flask at room temperature. After being stirred for 30 min, the resulting mixture and a terminal alkyne (1.2 mmol, 1.2 equiv) were sequentially added to a suspension of CuBr (7 mg, 0.05 mmol, 5 mol %) in toluene (3 mL) in a 25-mL round-bottom flask under argon. The reaction mixture was stirred for 12 h at room temperature. The resulting mixture was concentrated under reduced pressure, and the residue was purified by flash column chromatography (FC) on silica gel to afford the corresponding propargylic amine 3.

General procedure B: the catalytic reductive alkylation of amides

To a dried 10-mL round-bottom flask containing IrCl(CO)(PPh₃)₂ (8 mg, 1.0 mol %, weighted in a glove box) were added a toluene (5 mL) solution of tert-amide (1.0 mmol) and TMDS (2.0 mmol or 1.2 mmol for amides without α-hydrogen) at room temperature. After being stirred for 10 min or 30 min (for amides without α-hydrogen), the resulting solution and an alkyne (1.2 mmol) were added to a suspension of CuBr (7 mg, 0.05 mmol, 5 mol %) in toluene (3 mL). After being stirred for 12 hours at room temperature, the mixture was filtered through Celite. The filtrate was concentrated under reduced pressure, and the residue was dissolved in MeOH (5 mL). 10% Pd/C (50 mg) was added, and the mixture was stirred under hydrogen atmosphere (1 atm) for 5 hours. The resulting mixture was filtered, the filtrate was concentrated and the residue was purified by flash chromatography on silica gel to afford the corresponding α-alkylated amine 4.
Preparation and Characterization of Alkynylated and Alkylated Products

\(N,N\)-Dibenzyl-1-phenylpent-1-yn-3-amine (1a)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1:100), propargylamine 1a (298 mg, yield: 88%) as a colorless oil. IR (film) \(\nu_{\text{max}}\): 3061, 3027, 2963, 2932, 1489, 1455, 1259, 1070, 801, 755, 701 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.99 (t, \(J = 7.4\) Hz, 3H), 1.71-1.85 (m, 2H), 3.50 (d, \(J = 13.8\) Hz, 2H), 3.51 (t, \(J = 7.6\) Hz, 1H), 3.88 (d, \(J = 13.8\) Hz, 2H), 7.19-7.50 (m, 15H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 11.2, 27.0, 54.0, 55.0, 85.2, 88.0, 123.6, 126.8, 127.0, 127.8, 128.2, 128.3, 128.6, 128.8, 129.0, 131.8, 132.0, 139.9 ppm; MS (ESI) \(m/z\) 362 (M+Na\(^+\)); HRMS (ESI) \(m/z\) calcd for \([C_{25}H_{25}NNa]^+\) (M + Na\(^+\)): 362.1879; found: 362.1881.

\(N,N\)-Dibenzyl-4-methyl-1-phenylpent-1-yn-3-amine (1b)

Following general procedure A, the reaction of tert-amide 3b (267 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1:100), propargylamine 1b (297 mg, yield: 84%) as a colorless oil. IR (film) \(\nu_{\text{max}}\): 2955, 2805, 1601, 1458, 1453, 1069, 1024, 752, 691 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 1.02 (d, \(J = 4.3\) Hz, 3H), 1.04 (d, \(J = 4.3\) Hz, 3H), 1.96-2.05 (m, 1H), 3.12 (d, \(J = 10.4\) Hz, 1H), 3.47 (d, \(J = 13.9\) Hz, 2H), 3.88 (d, \(J = 13.9\) Hz, 2H), 7.21-7.24 (m, 2H), 7.29-7.35 (m, 7H), 7.42-7.44 (m, 4H), 7.50-7.52 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 20.0, 21.0, 30.8, 55.1, 59.7, 86.0, 87.4, 123.7, 126.8, 127.8, 128.2, 128.3, 128.9, 131.8, 139.8 ppm; MS (ESI) \(m/z\) 354 (M+H\(^+\)); HRMS (ESI) \(m/z\) calcd for \([C_{26}H_{26}N]^+\) (M + H\(^+\)): 354.2216; found: 354.2215.

\(N,N\)-Dibenzyl-1,5-diphenylpent-1-yn-3-amine (1c)
Following general procedure A, the reaction of tert-amide 3c (329 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluents: EtOAc/n-hexane = 1: 100), propargylamine 1c (386 mg, yield: 93%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2832, 1600, 1489, 1453, 1070, 1028, 755, 692 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.97-2.16 (m, 2H), 2.64-2.85 (m, 2H), 3.52 (d, $J$ = 13.7 Hz, 2H), 3.67 (t, $J$ = 7.5 Hz, 1H), 3.92 (d, $J$ = 13.7 Hz, 2H), 7.05-7.07 (m, 2H), 7.12-7.25 (m, 5H), 7.29-7.34(m, 7H), 7.40-7.42 (m, 4H), 7.49-7.51 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 32.7, 35.7, 52.1, 55.2, 85.6, 87.7, 123.5, 125.7, 126.9, 127.9, 128.2, 128.3, 128.4, 128.8, 128.9, 131.8, 139.7, 141.9 ppm; MS (ESI) $m/z$ 416 (M + H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{31}$H$_{30}$N]$^+$ (M + H$^+$): 416.2373; found: 416.2381.

$N,N$-Dibenzyl-1-phenylhept-6-en-1-yn-3-amine (1d)

Following general procedure A, the reaction of tert-amide 3d (279 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluents: EtOAc/n-hexane = 1: 100), propargylamine 1d (329 mg, yield: 90%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 3061, 3027, 2938, 2832, 1599, 1489, 1453, 1119, 912, 755, 690 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.75-1.94 (m, 2H), 2.10-2.27 (m, 2H), 3.50 (d, $J$ = 13.7 Hz, 2H), 3.64 (t, $J$ = 7.6 Hz, 1H), 3.89 (d, $J$ = 13.7 Hz, 2H), 4.85-4.95 (m, 2H), 5.66-5.76 (m, 1H), 7.21-7.24 (m, 2H), 7.29-7.34 (m, 2H), 7.40-7.42 (m, 4H), 7.49-7.51 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 30.6, 33.1, 51.9, 55.1, 85.4, 87.7, 114.8, 123.5, 126.9, 127.9, 128.2, 128.3, 128.9, 131.8, 138.0, 139.7 ppm; MS (ESI) $m/z$ 366 (M + H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{27}$H$_{28}$N]$^+$ (M + H$^+$): 366.2216; found: 366.2217.

$N$-Allyl-$N$-benzyl-1-phenylpent-1-yn-3-amine (1e)
Following general procedure A, the reaction of tert-amide 3e (203 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1e (263 mg, yield: 91%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3062, 2964, 2932, 2811, 1489, 1452, 1070, 917, 691 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 1.01 (t, \( J = 7.4 \) Hz, 3H), 1.71-1.78 (m, 2H), 3.04 (dd, \( J = 14.3, 8.0 \) Hz, 1H), 3.28-3.33 (m, 1H), 3.46 (d, \( J = 14.0 \) Hz, 1H), 3.58 (t, \( J = 7.7 \) Hz, 1H), 3.91 (d, \( J = 14.0 \) Hz, 1H), 5.10-5.13 (m, 1H), 5.24-5.29 (m, 1H), 5.82-5.92 (m, 1H), 7.21-7.24 (m, 1H), 7.26-7.33 (m, 5H), 7.38-7.39 (m, 2H), 7.44-7.48 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 11.3, 27.1, 54.0, 54.9, 85.1, 88.2, 116.9, 123.6, 126.7, 127.8, 128.1, 128.2, 128.7, 131.8, 136.9, 140.1 ppm; MS (ESI) \( m/z \) 240 (M+H\(^+\)); HRMS (ESI) \( m/z \) calcd for [C\(_{21}\)H\(_{24}\)N\(^+\)]\(^{+}\) (M + H\(^+\)): 290.1903; found: 290.1904.

**N-Cinnamyl-N-methyl-1-phenylpent-1-yn-3-amine (1f)**

Following general procedure A, the reaction of tert-amide 3f (203 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 40), propargylic amine 1f (246 mg, yield: 85%) as a pale yellow oil. IR (film) \( \nu_{\text{max}} \): 2940, 2216, 1708, 1607, 1220, 1017, 759, 691 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 1.07 (t, \( J = 7.4 \) Hz, 3H), 1.72-1.80 (m, 2H), 2.33 (s, 3H), 3.23-3.28 (m, 1H), 3.33-3.38 (m, 1H), 3.58 (t, \( J = 6.8 \) Hz, 1H), 6.24-6.32 (m, 1H), 6.57 (d, \( J = 15.8 \) Hz, 1H), 7.21-7.46 (m, 10H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 11.4, 27.1, 37.7, 57.6, 58.0, 86.0, 87.3, 123.5, 126.3, 127.3, 127.8, 128.2, 128.5, 131.7, 132.4, 137.2 ppm; MS (ESI) \( m/z \) 290 (M+H\(^+\)); HRMS (ESI) \( m/z \) calcd for [C\(_{21}\)H\(_{24}\)N\(^+\)]\(^{+}\) (M + H\(^+\)): 290.1903; found: 290.1901.

**1-(1-Phenylpent-1-yn-3-yl)pyrrolidine (1g)**
Following general procedure A, the reaction of tert-amide $3g$ (127 mg, 1.0 mmol) with phenylacetylene ($2a$) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 40), propargylamine $1g$ (177 mg, yield: 83%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2964, 2933, 2873, 1488, 1360, 1136 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.09 (t, $J$ = 7.4 Hz, 3H), 1.69-1.84 (m, 6H), 2.66-2.79 (m, 4H), 3.58 (dd, $J$ = 9.2, 5.6 Hz, 1H), 7.26-7.30 (m, 3H), 7.41-7.44 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.3, 23.5, 28.2, 49.8, 56.9, 85.2, 88.2, 123.5, 127.7, 128.2, 131.7 ppm; MS (ESI) m/z 214 (M$+$H$^+$); HRMS (ESI) m/z calcd for [C$_{15}$H$_{20}$N]$^+$ (M$+$H$^+$): 214.1590; found: 214.1582.

**1-Benzyl-2-(phenylethynyl)azacyclotridecane (1h)**

Following general procedure A, the reaction of tert-amide $3h$ (287 mg, 1.0 mmol) with phenylacetylene ($2a$) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 200), propargylamine $1h$ (328 mg, yield: 88%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2965, 2854, 1489, 1070, 754, 690 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.27-1.64 (m, 19H), 1.83-1.91 (m, 1H), 2.50-2.62 (m, 2H), 3.36 (d, $J$ = 13.6 Hz, 1H), 3.92 (d, $J$ = 13.6 Hz, 1H), 3.64 (dd, d, $J$ = 3.6, 3.1 Hz, 1H), 7.20-7.32 (m, 6H), 7.37-7.39 (m, 2H), 7.43-7.46 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 24.0, 25.4, 25.5, 25.6, 26.3, 26.4, 26.6, 26.7, 33.3, 49.8, 52.0, 55.6, 84.5, 88.8, 123.7, 126.7, 127.7, 128.0, 128.2, 129.1, 131.7, 140.3 ppm; MS (ESI) m/z 374 (M + H$^+$); HRMS (ESI) m/z calcd for [C$_{27}$H$_{36}$N]$^+$ (M + H$^+$): 374.2842; found: 374.2837.

**(6R)-N,N-Dibenzyl-6-(((3R,8R,9S,10S,13R,14S,17R)-3-((tert-butyldimethylsilyl)oxy)-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)-1-phenylhept-1-yn-3-amine (1i)**
Following general procedure A, the reaction of lithocholic acid-derived amide 3i (335 mg, 0.5 mmol) with phenylacetylene (2a) (0.065 mL, 0.6 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylic amine 1i (325 mg, yield: 86%) as an inseparable diastereomeric mixture (\(dr = 1: 1\), determined by \(^1\)H NMR). White solid; Mp: 74-76 °C; IR (film) \(\tilde{\nu}_{\text{max}}\): 2936, 2862, 1597, 1373, 1248, 1079, 867, 835, 749, 691 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), data of the two diastereomers): \(\delta\) 0.05-0.06 (m, 6H), 0.59 (d, \(J = 5.8\) Hz, 3H), 0.85-0.89 (m, 15H), 1.00-1.14 (m, 6H), 1.18-1.28 (m, 4H), 1.35-1.48 (m, 9H), 1.52-1.67 (m, 3H), 1.73-1.93 (m, 6H), 3.45-3.60 (m, 4H), 3.88 (d, \(J = 13.7\) Hz, 2H), 7.21-7.51 (m, 15H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\), data of the two diastereomers): \(\delta\) −4.6, 12.0, 18.3, 18.7, 20.8, 23.4, 24.3, 26.0, 26.5, 27.4, 28.2, 28.3, 30.5, 31.1, 32.6, 32.7, 34.6, 35.5, 35.6, 35.9, 37.0, 40.2, 40.3, 42.4, 42.6, 42.7, 52.8, 52.9, 55.0, 55.1, 56.2, 56.3, 56.4, 72.9, 85.2, 88.2, 88.3, 123.7, 126.7, 126.8, 127.8, 128.1, 128.2, 128.3, 128.7, 128.8, 131.8, 139.9, 140.0 ppm; MS (ESI) \(m/z\) 756 (M + H\(^+\)); HRMS (ESI) \(m/z\) calcd for [Cs\(_{2}\)H\(_{23}\)NOSi\(^+\)] (M + H\(^+\)): 756.5534; found: 756.5545.

1-(8-((Tert-butyldimethylsilyl)oxy)-1-phenyloct-1-yn-3-yl)pyrrolidine (1j)

Following general procedure A, the reaction of tert-amide 3j (299 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30), propargylamine 1j (350 mg, yield: 91%) as a colorless oil. IR (film) \(\tilde{\nu}_{\text{max}}\): 2965, 2857, 2807, 1488, 1254, 1101, 835, 755, 690 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.04 (s, 6H), 0.89 (s, 9H), 1.37-1.46 (m, 2H), 1.49-1.60 (m, 4H), 1.70-1.81 (m, 6H), 2.67-
2.77 (m, 4H), 3.61 (t, $J = 6.5$ Hz, 2H), 3.67 (dd, $J = 8.3, 6.5$ Hz, 1H), 7.26-7.30 (m, 3H), 7.40-7.43 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ –5.3, 18.3, 23.5, 25.6, 26.0, 26.5, 32.8, 35.1, 49.7, 55.1, 63.1, 85.2, 88.3, 123.5, 127.8, 128.2, 131.7 ppm; MS (ESI) m/z 386 (M + H$^+$); HRMS (ESI) m/z calcd for [C$_{24}$H$_{40}$NOSi]$^+$ (M + H$^+$): 386.2874; found: 386.2870.

1-(1-Phenyl-8-((tetrahydro-2$H$-pyran-2-yl)oxy)oct-1-yn-3-yl)pyrrolidine (1k)

Following general procedure A, the reaction of tert-amide 3k (269 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30), propargylamine 1k (295 mg, yield: 83%) as a colorless oil. IR (film) $\nu_{max}$: 2965, 2867, 2806, 1488, 1354, 1134, 1119, 1033, 755, 690 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.42-1.83 (m, 18H), 2.67-2.77 (m, 4H), 3.37-3.50 (m, 2H), 3.65-3.89 (m, 3H), 4.56-4.58 (m, 1H), 7.26-7.29 (m, 3H), 7.41-7.43 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 19.6, 23.5, 25.5, 26.1, 26.5, 29.7, 30.7, 35.0, 49.7, 55.0, 62.2, 67.5, 85.2, 88.3, 98.7, 98.8, 123.5, 127.8, 128.2, 131.7 ppm; MS (ESI) m/z 356 (M + H$^+$); HRMS (ESI) m/z calcd for [C$_{23}$H$_{34}$NO$_2$]$^+$ (M + H$^+$): 356.2584; found: 356.2583.

1-(8-(Methoxymethoxy)-1-phenyloct-1-yn-3-yl)pyrrolidine (1l)

Following general procedure A, the reaction of tert-amide 3l (229 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30), propargylamine 1l (252 mg, yield: 80%) as a colorless oil. IR (film) $\nu_{max}$: 2965, 2874, 2818, 1439, 1131, 1101, 994, 755, 691 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.41-1.47 (m, 2H), 1.60-1.67 (m, 4H), 1.71-1.82 (m, 6H), 2.67-2.77 (m, 4H), 3.35 (s, 3H), 3.53 (t, $J = 6.6$ Hz, 2H), 3.67 (dd, $J = 8.4, 6.3$ Hz, 1H), 4.61 (s, 2H), 7.27-7.30 (m, 3H), 7.41-7.43 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.5, 26.0, 26.5, 29.6,
1-(8-(But-2-yn-1-yloxy)-1-phenyloct-1-yn-3-yl)pyrrolidine (1m)

Following general procedure A, the reaction of tert-amide 3m (237 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30), propargylamine 1m (262 mg, yield: 81%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2936, 2856, 1639, 1485, 1440, 1351, 1251, 1136, 1095, 755, 691 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.39-1.46 (m, 2H), 1.48-1.67 (m, 4H), 1.70-1.85 (m, 9H), 2.68-2.77 (m, 4H), 3.48 (t, $J$ = 6.6 Hz, 2H), 3.67 (dd, $J$ = 8.6, 6.1 Hz, 1H), 4.07 (dd, $J$ = 4.5, 2.2 Hz, 2H), 7.27-7.30 (m, 3H), 7.41-7.43 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.5, 25.9, 26.5, 29.6, 34.9, 49.7, 55.0, 58.5, 70.0, 75.4, 82.0, 85.2, 123.4, 127.8, 128.2, 131.7 ppm; MS (ESI) m/z 324 (M + H$^+$); HRMS (ESI) m/z calcd for [C$_{22}$H$_{30}$NO]$^+$ (M + H$^+$): 324.2322; found: 324.2323.

N,N-Dibenzyl-7-chloro-1-phenylhept-1-yn-3-amine (1n)

Following general procedure A, the reaction of tert-amide 3n (315 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 90), propargylamine 1n (337 mg, yield: 84%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2942, 2832, 1598, 1489, 1322, 1070, 755, 692 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.52-1.87 (m, 6H), 3.45-3.50 (m, 4H), 3.60 (t, $J$ = 7.5 Hz, 1H), 3.88 (d, $J$ = 13.7 Hz, 2H), 7.22-7.25 (m, 2H), 7.29-7.35 (m, 7H), 7.40-7.42 (m, 4H), 7.49-7.51 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 23.7, 32.0, 33.0, 44.9, 51.9, 55.0, 85.5, 87.6, 123.4, 126.9, 127.9, 128.2, 128.3, 128.9, 131.8, 139.7 ppm; MS (ESI) m/z 402 (M + H$^+$); HRMS (ESI)
3-(Methyl(1-phenylpent-1-yn-3-yl)amino)propanenitrile (1o)

Following general procedure A, the reaction of tert-amide 3o (140 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1o (192 mg, yield: 85%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2955, 2873, 2249, 1488, 1339, 1070, 1028, 692 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 1.06 (t, $J = 7.4$ Hz, 3H), 1.69-1.77 (m, 2H), 2.35 (s, 3H), 2.52 (t, $J = 6.9$ Hz, 2H), 2.73-2.80 (m, 1H), 2.84-2.91 (m, 1H), 3.47 (t, $J = 7.6$ Hz, 1H), 7.29-7.30 (m, 3H), 7.40-7.43 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.1, 17.0, 27.2, 37.8, 50.2, 58.7, 85.8, 86.7, 118.8, 123.0, 128.0, 128.2, 131.7 ppm; MS (ESI) m/z 249 (M+Na$^+$); HRMS (ESI) m/z calcd for [C$_{15}$H$_{18}$N$_2$Na]$^+$ (M + Na$^+$): 249.1362; found: 249.1356.

Ethyl 2-(benzyl(1-phenylpent-1-yn-3-yl)amino)acetate (1q)
Following general procedure A, the reaction of tert-amide \( \mathbf{3q} \) (249 mg, 1.0 mmol) with phenylacetylene \( \mathbf{2a} \) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/\( n \)-hexane = 1: 100), propargylamine \( \mathbf{1q} \) (268 mg, yield: 80\%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 2967, 2934, 1749, 1489, 1029, 755, 692 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 1.03 (t, \( J = 7.4 \) Hz, 3H), 1.24 (t, \( J = 7.4 \) Hz, 3H), 1.67-1.82 (m, 2H), 3.32 (d, \( J = 16.8 \) Hz, 2H), 3.43 (d, \( J = 16.8 \) Hz, 2H), 3.60-3.67 (m, 2H), 3.95 (d, \( J = 13.6 \) Hz, 2H), 4.13 (dt, \( J = 7.1 \), 1.0 Hz, 2H), 7.22-7.33 (m, 6H), 7.44-7.46 (m, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 11.1, 14.2, 27.3, 52.3, 55.6, 56.4, 60.4, 85.4, 87.5, 123.3, 127.1, 127.9, 128.2, 129.0, 131.8, 139.0, 171.7 ppm; MS (ESI) \( m/z \) 358 (M+Na\(^+\)); HRMS (ESI) \( m/z \) calcd for [C\(_{22}\)H\(_{25}\)NNaO\(_2\)]\(^+\) (M + Na\(^+\)): 358.1778; found: 358.1782.

1-(1-Phenylpent-1-yn-3-yl)piperidin-4-one (\( \mathbf{1r} \))

Following general procedure A, the reaction of tert-amide \( \mathbf{3r} \) (155 mg, 1.0 mmol) with phenylacetylene \( \mathbf{2a} \) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/\( n \)-hexane = 1: 100), propargylamine \( \mathbf{1r} \) (181 mg, yield: 75\%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 2965, 2813, 1721, 1596, 1338, 1209, 757, 690 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \( \delta \) 1.10 (t, \( J = 7.4 \) Hz, 3H), 1.75-1.83 (m, 2H), 2.43-2.56 (m, 4H), 2.79-2.85 (m, 2H), 2.98-3.04 (m, 2H), 3.59 (t, \( J = 7.6 \) Hz, 1H), 7.27-7.31 (m, 3H), 7.39-7.42 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 11.3, 27.0, 41.5, 49.3, 59.0, 86.1, 86.6, 123.0, 128.0, 128.2, 131.7, 209.0 ppm; MS (ESI) \( m/z \) 264 (M+Na\(^+\)); HRMS (ESI) \( m/z \) calcd for [C\(_{16}\)H\(_{19}\)NNaO\(_2\)]\(^+\) (M + Na\(^+\)): 264.1359; found: 264.1356.

2-(3-(Dibenzylamino)-5-phenylpent-4-yn-1-yl)cyclohexanone (\( \mathbf{1s} \))
Following general procedure A, the reaction of tert-amide 3s (349 mg, 1.0 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1s (396 mg, yield: 91%) as an inseparable diastereomeric mixture ($dr = 1: 3$, determined by $^1$H NMR). A colorless oil; IR (film) $\nu_{\text{max}}$: 2927, 2853, 1601, 1460, 1050, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, data of the two diastereomers): $\delta$ 1.26-1.42 (m, 2H), 1.51-1.67 (m, 2H), 1.71-1.88 (m, 3H), 1.91-2.21 (m, 5H), 2.30-2.35 (m, 1H), 3.46 (d, $J = 13.6$ Hz, 2H), 3.56 (t, $J = 7.5$ Hz, 1H), 3.88 (d, $J = 13.6$ Hz, 2H), 7.22-7.50 (m, 15H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$, data of the two diastereomers): $\delta$ 24.9, 25.8, 26.2, 27.9, 28.1, 30.8, 31.2, 33.6, 34.3, 42.0, 42.1, 49.7, 49.8, 51.8, 51.9, 54.9, 85.4, 87.8, 123.5, 127.9, 128.2, 128.3, 128.9, 129.0, 131.8, 139.7, 139.8, 212.9, 213.0 ppm; MS (ESI) $m/z$ 436 (M + H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{31}$H$_{34}$NO]$^+$ (M + H$^+$): 436.2635; found: 436.2637.

4-(1-(Dibenzylamino)-3-phenylprop-2-yn-1-yl)benzaldehyde (1t)

To a dried 10 mL round-bottom flask containing IrCl(CO)(PPh$_3$)$_2$ (5.5 mg, 0.5 mol%, weighted in a glove box) were added a toluene (5 mL) solution, N,N-dibenzyl-4-formylbenzamide (3t) (460.6 mg, 1.4 mmol) and TMDS (296 µL, 1.68 mmol) at rt. After being stirred for 5 min, the resulting solution and phenylacetylene (2a) (184 µL, 1.68 mmol) were added to a suspension of CuBr (5 mol%) in toluene (3 mL). The mixture was stirred for 3 h at rt and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (EtOAc/n-hexane = 1:50) to afford the corresponding propargylic amine 1t (430.0 mg, yield: 74%) as a light yellow oil. IR (film) $\nu_{\text{max}}$: 2924, 2851, 2228, 1735, 1605, 1494, 1384, 1261, 1094, 801, 755, 698 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 10.00 (s, 1H), 7.92–7.84 (m, 4H), 7.69–7.61 (m, 2H), 7.43–7.38 (m, 7H), 7.33 (d, $J = 7.4$ Hz, 4H), 7.24 (d, $J = 6.3$ Hz, 2H), 4.96 (s, 1H), 3.77
(d, J = 13.4 Hz, 2H), 3.56 (d, J = 13.4 Hz, 2H) ppm; $^{13}$C NMR (126 MHz, CDCl$_3$) δ 191.9, 146.4, 139.0, 135.8, 132.0, 129.6, 128.9, 128.9, 128.7, 128.5, 128.5, 128.4, 128.3, 127.2, 122.8, 89.4, 83.5, 56.1, 54.9 ppm; HRMS-ESI calcd for [C$_{30}$H$_{25}$NNaO]$^+$ (M+Na$^+$): 438.1828; found: 438.1835.

$N,N$-dibenzy1-1-(thiophen-2-yl)pent-1-yn-3-amine (1u)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 2-ethynylthiophene (2b) (129.6 mg, 0.12 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1u (310 mg, yield: 90%) as a colorless oil. IR (film) $\tilde{\nu}$ max: 3027, 2964, 2932, 1493, 1453, 745, 705 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 0.98 (t, J = 7.4 Hz, 3H), 1.71-1.84 (m, 2H), 3.46 (d, J = 13.8 Hz, 2H), 3.52 (t, J = 7.7 Hz, 1H), 3.87 (d, J = 13.8 Hz, 2H), 6.97-6.99 (m, 1H), 7.21-7.24 (m, 4H), 7.29-7.32 (m, 4H), 7.40-7.42 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 11.2, 26.9, 54.3, 55.0 (2C), 78.2, 92.2, 123.6, 126.3, 126.8, 128.2, 128.8, 131.5, 139.8 ppm; MS (ESI) $m/z$ 346 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{23}$H$_{24}$NS]$^+$ (M + H$^+$): 346.1624; found: 346.1623.

$N,N$-Dibenzylnon-4-yn-3-amine (1v)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with hex-1-yne (2c) (98.5 mg, 0.14 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1v (271 mg, yield: 85%) as a colorless oil. IR (film) $\tilde{\nu}$ max: 2931, 2872, 1494, 1453, 744, 697 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): δ 0.92 (t, J = 7.5 Hz, 3H), 0.96 (t, J = 7.2 Hz, 3H), 1.45-1.72 (m, 6H), 2.28 (dt, J = 2.0, 6.8 Hz, 2H), 3.26 (tt, J = 2.0, 7.5 Hz, 1H), 3.38 (d, J = 13.8 Hz, 2H), 3.78 (d, J = 13.8 Hz, 2H), 7.18-7.40 (m, 10H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): δ 11.2, 13.6, 18.4, 22.0, 27.3, 31.4, 53.7,
N,N-dibenzyl-6-methylhept-6-en-4-yn-3-amine (1w)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 2-methylbut-1-en-3-yne (2d) (79 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1:100), propargylamine 1w (332 mg, yield: 88%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 3058, 3026, 2965, 2830, 1610, 1495, 1450, 1367, 1283, 1127, 1072, 1024, 896, 745, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.94 (t, $J = 7.4$ Hz, 3H), 1.63-1.77 (m, 2H), 1.96 (s, 3H), 3.38-3.42 (m, 3H), 3.82 (d, $J = 13.6$ Hz, 2H), 5.22 (br. s, 1H), 5.32 (br. s, 1H), 7.19-7.24 (m, 2H), 7.28-7.31 (m, 4H), 7.38-7.40 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.2, 24.1, 27.0, 54.0, 54.9, 86.5, 87.0, 120.9, 126.8, 127.0, 128.2 (4C), 128.8, 139.9 ppm; MS (ESI) $m/z$ 304 (M$^+$H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{22}$H$_{26}$N]$^+$ (M + H$^+$): 304.2060; found: 304.2059.

N,N-Dibenzyl-1-cyclopropylpent-1-yn-3-amine (1x)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with ethynylcyclopropane (2e) (79.2 mg, 0.10 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1:100), propargylamine 1x (248 mg, yield: 82%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 3026, 2963, 2932, 1494, 1453, 1027, 745, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.67-0.71 (m, 2H), 0.77-0.85 (m, 2H), 0.90 (t, $J = 7.5$ Hz, 3H), 1.26-1.34 (m, 1H), 1.53-1.70 (m, 2H), 3.22 (dt, $J = 1.4$, 7.5 Hz, 1H), 3.36 (d, $J = 13.8$ Hz, 2H), 3.77 (d, $J = 13.8$ Hz, 2H), 7.18-7.23 (m, 2H), 7.26-7.30 (m, 4H), 7.37-7.39 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ $-0.5$, 8.6, 11.2, 27.2, 53.6, 54.8, 73.1, 88.4, 126.7, 128.1, 128.8, 140.1 ppm; MS (ESI) $m/z$ 304 (M$^+$H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{22}$H$_{26}$N]$^+$ (M + H$^+$): 304.2060; found: 304.2060.
**N,N-Dibenzyl-1-(trimethylsilyl)pent-1-yn-3-amine (1y)**

Following general procedure A, the reaction of *tert*-amide 3a (253 mg, 1.0 mmol) with ethynyltrimethylsilane (2f) (117.7 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1y (268 mg, yield: 80%) as a colorless oil.

IR (film) $\nu_{\text{max}}$: 3027, 2962, 2934, 2158, 1453, 1249, 745, 697 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.23 (s, 9H), 0.92 (t, $J = 7.4$ Hz, 3H), 1.60-1.73 (m, 2H), 3.28 (t, $J = 7.7$ Hz, 1H), 3.37 (d, $J = 13.8$ Hz, 2H), 3.79 (d, $J = 13.8$ Hz, 2H), 7.21-7.23 (m, 2H), 7.27-7.31 (m, 4H), 7.37-7.39 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 0.4, 11.1, 26.8, 54.2, 54.8, 89.1, 104.5, 126.8, 128.2, 128.8, 140.0 ppm; MS (ESI) $m/z$ 336 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{22}$H$_{30}$NSi]+ (M + H$^+$): 336.2142; found: 336.2139.

**N,N-Dibenzyl-6,6-diethoxyhex-4-yn-3-amine (1z)**

Following general procedure A, the reaction of *tert*-amide 3a (253 mg, 1.0 mmol) with 3,3-diethoxyprop-1-yn (2g) (153.6 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1z (329 mg, yield: 90%) as a colorless oil.

IR (film) $\nu_{\text{max}}$: 2950, 1450, 1300, 1150, 1065, 705, 751 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.94 (t, $J = 7.3$ Hz, 3H), 1.28 (t, $J = 7.1$ Hz, 6H), 1.64-1.78 (m, 2H), 3.36 (dt, $J = 1.3$, 7.6 Hz, 1H), 3.40 (d, $J = 13.9$ Hz, 2H), 3.61-3.72 (m, 2H), 3.77-3.86 (m, 4H), 5.39 (d, $J = 1.3$ Hz, 1H), 7.20-7.39 (m, 10H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.2, 15.2, 26.7, 53.4, 54.9, 60.8, 80.5, 83.8, 91.5, 126.9, 128.2, 128.7, 139.7 ppm; MS (ESI) $m/z$ 366 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{22}$H$_{32}$NO$_2$]+ (M + H$^+$): 366.2428; found: 366.2428.

**N,N-Dibenzyl-6-((tetrahydro-2H-pyran-2-yl)oxy)hex-4-yn-3-amine (1aa)**

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Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 2-(prop-2-yn-1-yl)oxy)tetrahydro-2H-pyran (2h) (168.2 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1aa (332 mg, yield: 88%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2939, 1492, 1453, 1360, 1123, 1024, 902, 745, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.93 (t, $J =$ 7.4 Hz, 3H), 1.53-1.92 (m, 8H), 3.33 (t, $J =$ 7.6 Hz, 1H), 3.39 (d, $J =$ 13.9 Hz, 2H), 3.54-3.59 (m, 1H), 3.81 (d, $J =$ 13.9 Hz, 2H), 3.88-3.93 (m, 1H), 4.39 (t, $J =$ 3.4 Hz, 1H), 7.19-7.39 (m, 10H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.2, 19.2, 25.4, 26.9, 30.4, 53.6, 54.4, 54.9, 62.2, 80.6, 84.2, 96.5, 126.8, 128.2, 128.7, 139.9 ppm; MS (ESI) $m/z$ 378 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{25}$H$_{32}$NO$_2$]+ (M + H$^+$): 378.2428; found: 378.2427.

$N,N$-Dibenzyl-6-((tert-butyldimethylsilyl)oxy)hex-4-yn-3-amine (1ab)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with tert-butyldimethyl(prop-2-yn-1-yl)oxy)silane (2i) (204.1 mg, 0.14 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ab (362 mg, yield: 89%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2955, 2930, 2853, 1636, 1447, 1367, 1123, 1085, 838, 774, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.18 (s, 6H), 0.93 (t, $J =$ 7.4 Hz, 3H), 0.96 (s, 9H), 1.61-1.76 (m, 2H), 3.31 (t, $J =$ 7.9 Hz, 1H), 3.41 (d, $J =$ 13.9 Hz, 2H), 3.80 (d, $J =$ 13.9 Hz, 2H), 4.42 (d, $J =$ 1.7 Hz, 2H), 7.19-7.39 (m, 10H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ -4.9 (2C), 11.2, 18.3, 25.9, 26.9, 51.9, 53.5, 54.9, 83.0, 83.6, 126.8, 128.2, 128.7, 139.9 ppm; MS (ESI) $m/z$ 408 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{26}$H$_{38}$NOSi]$^+$ (M + H$^+$): 408.2717; found: 408.2715.

$N$-(4-(Dibenzylamino)hex-2-yn-1-yl)-4-methylbenzenesulfonamide (1ac)
Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 4-methyl-N-(prop-2-yn-1-yl)benzenesulfonamide (2j) (250.8 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ac (401 mg, yield: 90%) as a white solid. Mp: 86-88 °C; IR (film) $\nu_{\text{max}}$: 3276, 2965, 1601, 1453, 1325, 1159, 1069, 697, 665, 550 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.81 (t, $J$ = 7.3 Hz, 3H), 1.31-1.45 (m, 1H), 1.50-1.59 (m, 1H), 2.29 (s, 3H), 3.07 (t, $J$ = 7.5 Hz, 1H), 3.16 (d, $J$ = 13.9 Hz, 2H), 3.63 (d, $J$ = 13.9 Hz, 2H), 3.96 (dt, $J$ = 1.6, 6.0 Hz, 2H), 4.73 (br.s, 1H), 7.20-7.32 (m, 12H), 7.79-7.81 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.0, 21.4, 26.6, 33.3, 53.3, 54.7, 79.0, 83.1, 126.9, 127.3, 128.2, 128.6, 129.7, 137.0, 139.6, 143.6 ppm; MS (ESI) $m/z$ 447 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{27}$H$_{31}$N$_2$O$_2$S]$^+$ (M + H$^+$): 447.2101; found: 447.2102.

**N-(4-(Dibenzylamino)hex-2-yn-1-yl)benzamide (1ad)**

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with N-(prop-2-yn-1-yl)benzamide (2k) (191 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30), propargylamine 1ad (356 mg, yield: 90%) as a white solid, Mp: 92-94 °C; IR (film) $\nu_{\text{max}}$: 3311, 3058, 3023, 2968, 2930, 1639, 1537, 1488, 1450, 1290, 1075, 970, 742, 694 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.94 (t, $J$ = 7.4 Hz, 3H), 1.61-1.77 (m, 2H), 3.32 (dt, $J$ = 7.7, 1.8 Hz, 1H), 3.39 (d, $J$ = 13.8 Hz, 2H), 3.80 (d, $J$ = 13.8 Hz, 2H), 4.36 (dd, $J$ = 5.1, 1.8 Hz, 2H), 6.31 (s, 1H), 7.19-7.54 (m, 13H), 7.80-7.82 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.2, 26.8, 30.2, 53.5, 54.8, 80.3, 82.1, 126.8, 127.0, 128.2, 128.6, 128.7, 131.7, 134.1, 139.7, 167.0 ppm; MS (ESI) $m/z$ 397 (M+H$^+$); HRMS (ESI) $m/z$ calcd for [C$_{27}$H$_{29}$N$_2$O]$^+$ (M + H$^+$): 397.2274; found: 397.2278.
5-(Dibenzylamino)hept-3-yn-1-yl 4-methylbenzenesulfonate (1ae)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with but-3-yn-1-yl 4-methylbenzenesulfonate (2l) (268.9 mg, 0.21 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ae (401 mg, yield: 87%) as a colorless oil; IR (film) νmax: 2965, 1597, 1492, 1364, 1175, 1095, 976, 902, 752, 694, 662, 550 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.88 (t, J = 7.4 Hz, 3H), 1.50-1.71 (m, 2H), 2.41 (s, 3H), 2.66 (dt, J = 1.8, 6.9 Hz, 2H), 3.20 (t, J = 7.6 Hz, 1H), 3.30 (d, J = 13.9 Hz, 2H), 3.73 (d, J = 13.9 Hz, 2H), 4.16 (dt, J = 1.1, 6.9 Hz, 2H), 7.20-7.37 (m, 12H), 7.81-7.83 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.1, 19.8, 21.6, 26.9, 53.5, 54.8 (2C), 68.2, 78.9, 80.6, 126.8, 127.9, 128.2, 128.7, 129.9, 133.1, 139.9, 144.9 ppm; MS (ESI) m/z 462 (M+H⁺); HRMS (ESI) m/z calcd for [C₂₈H₃₂NO₃S]⁺ (M + H⁺): 462.2097; found: 462.2098.

6-((4-(Dibenzylamino)hex-2-yn-1-yl)oxy)-1-(pyrrolidin-1-yl)hexan-1-one (1af)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 6-(prop-2-yn-1-yl)oxy)-1-(pyrrolidin-1-yl)hexan-1-one (2m) (268 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 40), propargylamine 1af (368 mg, yield: 80%) as a colorless oil; IR (film) νmax: 2936, 2869, 1642, 1428, 1348, 1095, 742, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δ 0.94 (t, J = 7.4 Hz, 3H), 1.42-1.50 (m, 2H), 1.63-1.75 (m, 6H), 1.80-1.86 (m, 2H), 1.89-1.94 (m, 2H), 2.27 (t, J = 7.6 Hz, 3H), 3.31-3.46 (m, 7H), 3.59 (t, J = 6.5 Hz, 2H), 3.81 (d, J = 13.8 Hz, 2H), 4.25 (d, J = 1.6 Hz, 2H), 7.20-7.39 (m, 10H) ppm; ¹³C NMR (100 MHz, CDCl₃): δ 11.2, 24.4, 24.7, 26.1, 26.2, 26.9,
29.5, 34.7, 45.5, 53.6, 54.9, 58.4, 69.7, 80.9, 84.3, 126.8, 128.2, 128.7, 139.8, 171.5 ppm; MS (ESI) m/z 461 (M+H⁺); HRMS (ESI) m/z calcd for [C₃₀H₄₁N₂O₂]⁺ (M + H⁺): 461.3163; found: 461.3167.

N,N-dibenzyl-6-chlorohex-4-yn-3-amine (1ag)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 3-chloroprop-1-yn (2n) (88.8 mg, 90 µL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ag (267 mg, yield: 86%) as a colorless oil; IR (film) \( \nu_{\text{max}} \): 2965, 1494, 1453, 1260, 1130, 745, 701 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 0.93 (t, \( J = 7.4 \) Hz, 3H), 1.61-1.76 (m, 2H), 3.32-3.37 (m, 1H), 3.39 (d, \( J = 13.8 \) Hz, 2H), 3.81 (d, \( J = 13.8 \) Hz, 2H), 4.25 (d, \( J = 1.9 \) Hz, 2H), 7.20-7.23 (m, 2H), 7.28-7.31 (m, 4H), 7.37-7.40 (m, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 11.2, 26.7, 30.9, 53.6, 54.9, 79.8, 85.4, 126.9, 128.4, 128.8, 139.7 ppm; MS (ESI) m/z 312 (M+H⁺); HRMS (ESI) m/z calcd for [C₂₀H₂₃ClN]⁺ (M + H⁺): 312.1514; found: 312.1512.

6-(Dibenzylamino)oct-4-ynenitrile (1ah)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with pent-4-ynenitrile (2o) (94.8 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ah (256 mg, yield: 81%) as a colorless oil; IR (film) \( \nu_{\text{max}} \): 3027, 2965, 2932, 2205, 1494, 1453, 1154, 740, 699 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃): \( \delta \) 0.93 (t, \( J = 7.4 \) Hz, 3H), 1.59-1.75 (m, 2H), 2.56-2.66 (m, 4H), 3.29 (t, \( J = 7.7 \) Hz, 1H), 3.40 (d, \( J = 13.8 \) Hz, 2H), 3.41 (d, \( J = 13.8 \) Hz, 2H), 7.19-7.23 (m, 2H), 7.28-7.31 (m, 4H), 7.38-7.40 (m, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl₃): \( \delta \) 11.2, 16.2, 18.3, 27.0, 53.5, 54.8, 80.5, 81.3, 118.5, 126.9, 128.2, 128.8, 139.9 ppm; MS (ESI) m/z 317
Methyl 4-(dibenzylamino)hex-2-ynoate (1ai)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with methyl propiolate (2p) (100.8 mg, 0.11 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ai (260 mg, yield: 81%) as a colorless oil; IR (film) \(\nu_{\text{max}}\): 3028, 2967, 2223, 1710, 1453, 1250, 1072, 748 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.96 (t, \(J = 7.4\) Hz, 3H), 1.69-1.82 (m, 2H), 3.41 (d, \(J = 13.8\) Hz, 2H), 3.43 (t, \(J = 7.8\) Hz, 1H), 3.82 (s, 3H), 3.86 (d, \(J = 13.8\) Hz, 2H), 7.21-7.25 (m, 2H), 7.29-7.32 (m, 4H), 7.37-7.39 (m, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 11.0, 26.2, 52.7, 53.4, 54.9, 77.1, 87.1, 127.1, 128.3, 128.7, 139.1, 154.1 ppm; MS (ESI) \(m/z\) 322 (M+H\(^+\)); HRMS (ESI) \(m/z\) calcd for [C\(_{21}\)H\(_{24}\)NO\(_2\)]\(^+\) (M + H\(^+\)):\(322.1802\), found: 322.1798.

2-(4-(Dibenzylamino)hex-2-yn-1-yl)isoindoline-1,3-dione (1aj)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 2-(prop-2-yn-1-yl)isoindoline-1,3-dione (2q) (222 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50), propargylamine 1aj (363 mg, yield: 86%) as a white solid. Mp: 76-79 °C; IR (film) \(\nu_{\text{max}}\): 1770, 1716, 1418, 1389, 1341, 1120, 1072, 944, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 0.89 (t, \(J = 7.3\) Hz, 3H), 1.57-1.71 (m, 2H), 3.26 (t, \(J = 7.7\) Hz, 1H), 3.35 (d, \(J = 13.8\) Hz, 2H), 3.76 (d, \(J = 13.8\) Hz, 2H), 4.06 (d, \(J = 1.8\) Hz, 2H), 7.17-7.35 (m, 10H), 7.73-7.75 (m, 2H), 7.89-7.92 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 11.1, 26.7, 27.5, 53.5, 54.8, 78.3, 81.6, 123.5, 126.7, 128.1, 128.7, 132.1, 134.1, 139.8, 167.1 ppm; MS (ESI) \(m/z\) 423 (M+H\(^+\)); HRMS (ESI) \(m/z\) calcd for [C\(_{28}\)H\(_{27}\)N\(_2\)O\(_2\)]\(^+\) (M + H\(^+\)):\(423.2067\), found: 423.2067.
5-(Dibenzylamino)hept-3-yn-2-one (1ak)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with but-3-yn-2-one (2r) (81.6 mg, 0.09 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1ak (262 mg, yield: 86%) as a pale yellow solid. Mp: 40-42 °C; IR (film) $\nu_{\text{max}}$: 3028, 2967, 2223, 1710, 1453, 1250, 1072, 741, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 0.96 (t, $J$ = 7.4 Hz, 3H), 1.68-1.82 (m, 2H), 2.41 (s, 3H), 3.40 (d, $J$ = 13.8 Hz, 2H), 3.47 (t, $J$ = 7.7 Hz, 1H), 3.85 (d, $J$ = 13.8 Hz, 2H), 7.21-7.25 (m, 2H), 7.29-7.32 (m, 4H), 7.36-7.38 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 11.1, 26.3, 33.2, 53.6, 55.0, 85.4, 91.4, 127.2, 128.4, 128.8, 139.1, 184.5 ppm; MS (ESI) $m/z$ 306 (M+H$^+$); HRMS (ESI) $m/z$ caled for [C$_{21}$H$_{24}$NO$^+$] (M + H$^+$): 306.1852; found: 306.1851.

4-(3-(Dimethylamino)-5-phenylpent-1-yn-1-yl)benzaldehyde (1al)

Following general procedure A, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with 4-ethynylbenzaldehyde (2s) (157 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 5), propargylamine 1al (241 mg, yield: 83%) as a yellow solid. Mp: 95-97°C; IR (film): 3026, 2946, 2859, 2823, 2779, 2728, 1702, 1600, 1206, 1164, 829, 700 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 2.06-1.99 (m, 2H), 2.33 (s, 6H), 2.90-2.75 (m, 2H), 3.53 (t, $J$ = 7.6 Hz, 1H), 7.25-7.17 (m, 3H), 7.31-7.27 (m, 2H), 7.58 (d, $J$ = 8.2 Hz, 2H), 7.83-7.79 (m, 2H), 9.99 (s, 1H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 32.6, 35.2, 41.4, 57.3, 85.6, 91.4, 125.9, 128.3, 128.5, 129.4, 129.6, 132.2, 135.2, 141.4, 191.3 ppm; HRMS (ESI) caled for C$_{20}$H$_{22}$NO [M+H$^+$]: 292.1696, found: 292.1697.
N,N-Bis(4-(dibenzylamino)hex-2-yn-1-yl)-4-methylbenzenesulfonamide (1am)

Following general procedure A (except that only 0.6 equiv of bisalkyne 2t was used), the reaction of tert-amide 3a (253 mg, 1.0 mmol) with 4-methyl-N,N-di(prop-2-yn-1-yl)benzenesulfonamide (2t) (148 mg, 0.6 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 150), propargylamine 1am (314 mg, yield: 87%) as an inseparable diastereomeric mixture (dr = 1: 1, determined by 1H NMR). Colorless oil; IR (film) \( \nu_{\text{max}} \): 2908, 1639, 1450, 1354, 1165, 749, 697, 659 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CD\(_2\)Cl\(_2\), data of the two diastereomers): \( \delta \) 0.77 (t, \( J = 7.3 \) Hz, 6H), 1.37-1.57 (m, 4H), 2.12 (s, 3H), 3.08 (t, \( J = 7.6 \) Hz, 2H), 3.16 (d, \( J = 13.8 \) Hz, 4H), 3.61 (d, \( J = 13.8 \) Hz, 4H), 4.29 (br.s, 4H), 7.10-7.24 (m, 22H), 7.64-7.66 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CD\(_2\)Cl\(_2\)): \( \delta \) 11.4, 21.5, 27.2, 37.0, 54.0, 55.3, 77.4, 84.7, 127.3, 128.2, 128.6, 129.1, 130.2, 135.9, 140.1, 144.4 ppm; HRMS (ESI) \( m/z \) calcd for [C\(_{47}\)H\(_{52}\)N\(_3\)O\(_2\)S]+ (M + H\(^+\)): 722.3775; found: 722.3782.

\( N^3,N^3,N'^{12},N'^{12}-\)Tetrabenzyl-1,14-diphenyltetradeca-1,13-diyne-3,12-diamine (1an)

Following general procedure A (except that double amounts of Vaska’s complex, TMDS, and alkyne 2a were used), the reaction of tert-amide 3v (280 mg, 0.5 mmol) with phenylacetylene (2a) (0.13 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 100), propargylamine 1an (344 mg, yield: 94%) as an inseparable diastereomeric mixture (dr = 1: 1, determined by \(^1\)H NMR). White solid, Mp: 91-93 °C; IR (film) \( \nu_{\text{max}} \): 3026, 2927, 2850, 1601, 1495, 1447, 1133, 1075, 752, 694 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\), data of the two diastereomers): \( \delta \) 1.06-1.09 (m, 8H), 1.29-1.40 (m, 4H), 1.57-1.76 (m, 4H), 3.39 (d, \( J = 13.7 \) Hz, 4H), 3.51 (t, \( J = 7.6 \) Hz, 2H), 3.80 (d, \( J = 13.7 \) Hz, 4H), 7.12-7.15 (m, 4H), 7.20-7.26 (m, 14H), 7.32-7.34 (m, 8H), 7.41-7.43 (m, 4H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\), data of the two diastereomers): \( \delta \) 26.3, 29.1, 29.5, 33.8, 52.1, 55.0, 85.2, 88.2, 123.6, 126.8, 127.8, 128.2, 128.3, 128.4, 131.8, 139.9 ppm; MS
(ESI) m/z 733 (M+H⁺); HRMS (ESI) m/z calcd for [C₅₄H₇₇N₂⁺]⁺ (M + H⁺): 733.4516; found: 733.4522.

N³,N³,N⁶, N⁶-Tetrabenzyloct-4-yne-3,6-diamine (1ao)

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with ethynyltrimethylsilane (2f) (1.2 mmol, 1.2 equiv) gave, a crude propargylamine, which was dissolved in dichloromethane. Then TBAF (1.2 mmol, 1.2 equiv) was added. After the reaction was complete, the reaction was quenched with a saturated aqueous solution of ammonium chloride at 0 °C and extracted with DCM (3 × 5 mL). The combined organic layers were dried over anhydrous Na₂SO₄, filtered, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel to afford the known product 2u[1] (200 mg, yield: 76%) as a colorless oil.

Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with N,N-dibenzylpent-1-yn-3-amine (2u) (315 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 150), propargylamine 1ao (425 mg, yield: 85%) as an inseparable diastereomeric mixture (dr = 1: 1, determined by ¹H NMR). White solid, Mp: 101-103 °C; IR (film) νmax: 3026, 2962, 2930, 2805, 1597, 1495, 1450, 1130, 1069, 1027, 963, 742, 694 cm⁻¹; ¹H NMR (400 MHz, CDCl₃, data of the two diastereomers): δ 1.00 (t, J = 7.4 Hz, 6H), 1.68-1.82 (m, 4H), 3.41 (t, J = 7.3 Hz, 2H), 3.49 (d, J = 13.8 Hz, 4H), 3.88 (d, J = 13.8 Hz, 4H), 7.22-7.44 (m, 20H) ppm; ¹³C NMR (100 MHz, CDCl₃, data of the two diastereomers): δ 11.3, 27.5, 53.7, 55.1, 82.6, 126.8, 128.2, 128.8, 140.0 ppm; MS (ESI) m/z 501 (M + H⁺); HRMS (ESI) m/z calcd for [C₃₆H₄₁N₂⁺]⁺ (M + H⁺): 501.3264; found: 501.3268.

6-(Dibenzylamino)-9,9-diethoxynon-7-yn-2-one (1ap)
Following general procedure A, the reaction of keto amide 3w (309 mg, 1.0 mmol) with 3,3-diethoxyprop-1-yne (2g) (153.6 mg, 0.17 mL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 5), keto propargylamine 1ap (358 mg, yield: 85%) as a colorless oil; IR (film) νmax: 2976, 2931, 2884, 1716, 1454, 1356, 1134, 1052, 749, 699 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.34 (m, 4H), 7.32-7.27 (m, 4H), 7.24-7.20 (m, 2H), 5.38 (s, 1H), 3.87-3.76 (m, 4H), 3.68-3.61 (m, 2H), 3.45 (t, J = 7.1 Hz, 1H), 3.38 (d, J = 13.6 Hz, 2H), 2.25-2.12 (m, 2H), 2.01 (s, 3H), 1.82-1.67 (m, 2H), 1.65-1.55 (m, 2H), 1.28 (dt, J = 2.1, 7.1 Hz, 6H) ppm; ¹³C-NMR (CDCl₃, 125 MHz) δ 208.3, 139.3, 128.8 (2C), 128.2 (2C), 126.9, 91.4, 83.2, 80.7, 60.7, 54.8, 50.8, 42.5, 32.5, 29.7, 20.1, 15.1 ppm; HRMS (ESI) calcd for [C₂₇H₃₆NO₃]+ (M+H)⁺: 422.2690; found: 422.2695.

(8R,9S,13S,14S,17S)-17-(3-(Dibenzylamino)pent-1-yn-1-yl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthrene-3,17-diol (1aq)
Following general procedure A, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with (8R,9S,13S,14S,17R)-17-ethynyl-3-methoxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-ol (2w) (372 mg, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 20), propargylic amine 1ar (470 mg, yield: 86%) as an inseparable diastereomeric mixture (dr = 1: 1.3, determined by $^1$H NMR), colorless foam. IR (film) $\nu_{\text{max}}$: 3420, 2927, 1626, 1455, 1194, 1136, 1075, 742, 697 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$, data of the two diastereomers): $\delta$ 0.92 (s, 3H), 0.95 (t, $J$ = 7.4 Hz, 3H), 1.34-1.54 (m, 4H), 1.61-2.12 (m, 9H), 2.23-2.27 (m, 1H), 2.31-2.42 (m, 2H), 2.85-2.94 (m, 2H), 3.35-3.39 (m, 1H), 3.41 (d, $J$ = 13.7 Hz, 2H), 3.78 (s, 3H), 3.84 (d, $J$ = 13.7 Hz, 2H), 6.64 (s, 1H), 6.71-6.74 (m, 1H), 7.20-7.31 (m, 7H), 7.36-7.38 (m, 4H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$, data of the two diastereomers): $\delta$ 11.2, 11.3, 12.8, 22.8, 26.5, 26.9, 27.0, 27.5, 29.8, 33.0, 33.1, 39.5, 39.6, 43.9, 44.0, 47.2, 49.7, 49.8, 53.5 (2C), 55.1, 55.2, 80.1 (2C), 84.2, 84.3, 88.6, 111.5, 113.8, 126.4, 126.9, 128.2, 128.7, 132.5 (2C), 137.9, 139.7, 157.5 ppm; MS (ESI) m/z 548 (M+H$^+$); HRMS (ESI) m/z calcd for [C$_{38}$H$_{46}$NO$_2$]$^+$ (M + H$^+$): 548.3523; found: 548.3528.

1-(1-Phenylpentan-3-yl)pyrrolidine (4a)
Following general procedure B, the reaction of the reaction of tert-amide 3g (127 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4a (165 mg, yield: 76%) as a colorless oil. IR (film) ν\text{max}: 2963, 2873, 2781, 1603, 1495, 1454, 1379, 745, 698 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) δ 7.32-7.24 (m, 2H), 7.23-7.15 (m, 3H), 2.83-2.69 (m, 5H), 2.67-2.57 (m, 1H), 2.42-2.32 (m, 1H), 1.95-1.80 (m, 6H), 1.77-1.68 (m, 1H), 1.67-1.56 (m, 1H), 0.98 (t, \(J = 7.5\) Hz, 3H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) δ 142.2, 128.4, 128.3, 125.9, 64.5, 51.2, 32.4, 31.8, 23.6, 23.5, 10.1 ppm; HRMS (ESI) calcd for [C\(_{15}\)H\(_{24}\)N]\(^+\) (M+H\(^+\)): 218.1903; found: 218.1874.

1-Methyl-2-phenethylpiperidine (4b)

Following general procedure B, the reaction of tert-amide 3x (113 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4b (144 mg, yield: 71%) as a colorless oil. IR (film) ν\text{max}: 2933, 2854, 2776, 1603, 1495, 1453, 1374, 1030, 770, 698 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.33-7.26 (m, 2H), 7.24-7.17 (m, 3H), 2.96-2.86 (m, 1H), 2.75 (ddd, \(J = 5.3, 11.5, 14.0\) Hz, 1H), 2.59 (ddd, \(J = 5.3, 11.5, 14.0\) Hz, 1H), 2.32 (s, 3H), 2.20-2.10 (m, 1H), 2.06-1.88 (m, 2H), 1.84-1.72 (m, 3H), 1.68-1.59 (m, 2H), 1.53-1.40 (m, 1H), 1.38-1.24 (m, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) δ 142.7, 128.4, 128.3, 125.7, 63.4, 57.1, 42.8, 34.6, 31.3, 30.4, 25.6, 24.3 ppm; HRMS (ESI) calcd for [C\(_{14}\)H\(_{22}\)N]\(^+\) (M+H\(^+\)): 204.1747; found: 204.1729.

1-(Furan-2-yl)-N,N-dimethyl-3-phenylpropan-1-amine (4c)

Following general procedure B, the reaction of tert-amide 3y (139 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (213 µL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 20) the title product 4c (188 mg, yield: 82%) as colorless oil. IR (film): 3025, 2931, 2858, 2820, 2777, 1496, 1454, 1158, 1026, 873, 789, 699, 602 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) δ 7.45-7.41 (m, 1H), 7.34-7.27 (m,
2H), 7.24-7.17 (m, 3H), 6.38 (dd, \( J = 1.8, 3.2 \) Hz, 1H), 6.19 (d, \( J = 3.2 \) Hz, 1H), 3.56 (t, \( J = 7.5 \) Hz, 1H), 2.61 (dd, \( J = 7.6, 8.3 \) Hz, 2H), 2.24 (s, 6H), 2.20-2.12 (m, 2H) ppm; \(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 153.7, 142.0, 141.7, 128.5, 128.3, 125.8, 109.7, 108.2, 61.7, 41.6, 32.9, 32.8 ppm; HRMS (ESI) calcd for [C\(_{15}\)H\(_{20}\)NO]\(^+\) (M+H\(^+\)): 230.1539; found: 230.1537.

1-(Benzo[b]thiophen-2-yl)-NN-dimethyl-3-phenylpropan-1-amine (4d)

Following general procedure B, the reaction of tert-amide 3z (205 mg, 1.0 mmol) with ethynylbenzene (2a) (131 \( \mu \)L, 1.2 mmol) and TMDS (213 \( \mu \)L, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30) the title product 4d (254 mg, yield: 86%) as a colorless oil. IR (film): 3059, 3025, 2930, 2856, 2784, 1602, 1495, 1455, 1434, 1355, 745, 726, 699 cm\(^{-1}\); \(^{1}\text{H NMR} \) (500 MHz, CDCl\(_3\)) \( \delta \) 7.82 (d, \( J = 7.7 \) Hz, 1H), 7.73 (d, \( J = 7.7 \) Hz, 1H), 7.36-7.23 (m, 4H), 7.20-7.13 (m, 3H), 7.11 (s, 1H), 3.70 (dd, \( J = 5.2, 9.2 \) Hz, 1H), 2.66-2.54 (m, 2H), 2.33-2.23 (m, 7H), 2.16-2.05 (m, 1H) ppm; \(^{13}\text{C NMR} \) (125 MHz, CDCl\(_3\)) \( \delta \) 144.4, 141.8, 139.6, 139.4, 128.5, 128.4, 125.9, 124.1, 124.0, 123.2, 122.8, 122.3, 65.2, 42.1, 36.1, 32.9 ppm; HRMS (ESI) calcd for [C\(_{19}\)H\(_{22}\)NS]\(^+\) (M+H\(^+\)): 296.1467; found: 296.1473.

1-(8-((Tert-butyldimethylsilyl)oxy)-1-phenyloctan-3-yl)pyrrolidine (4e)

Following general procedure B, the reaction of tert-amide 3j (299 mg, 1.0 mmol) with ethynylbenzene (2a) (131 \( \mu \)L, 1.2 mmol) and TMDS (355 \( \mu \)L, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4e (315 mg, yield: 81%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3025, 2930, 2856, 2784, 1602, 1495, 1461, 1386, 1360, 1254, 1101, 835, 775, 698 cm\(^{-1}\); \(^{1}\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.33-7.26 (m, 2H), 7.25-7.16 (m, 3H), 3.65 (t, \( J = 6.6 \) Hz, 2H), 2.79-2.58 (m, 6H), 2.41-2.29 (m, 1H), 1.95-1.74 (m, 6H), 1.70-1.49 (m, 4H), 1.48-1.32 (m, 4H), 0.94 (s, 9H), 0.09 (s, 6H) ppm; \(^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 142.8, 128.3 (4C), 125.7, 63.2, 62.7, 50.8, 33.3, 32.9, 31.9,
31.1, 26.3, 26.0, 25.7, 23.5, 18.4, −5.2 ppm; HRMS (ESI) calcd for $[\text{C}_{24}\text{H}_{44}\text{NOSi}]^+$ (M+H)$^+$: 390.3187; found: 390.3178.

1-(1-Phenyl-8-((tetrahydro-2H-pyran-2-yl)oxy)octan-3-yl)pyrrolidine (4f)

Following general procedure B, the reaction of tert-amide 3k (269 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30) the title product 4f (305 mg, yield: 85%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2937, 2866, 2786, 1673, 1454, 1352, 1200, 1135, 1077, 1037, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.29-7.23 (m, 2H), 7.21-7.13 (m, 3H), 4.59-4.54 (m, 1H), 3.90-3.82 (m, 1H), 3.78-3.70 (m, 1H), 3.52-3.45 (m, 1H), 3.42-3.35 (m, 1H), 3.73-3.56 (m, 6H), 3.36-3.28 (m, 1H), 1.90-1.30 (m, 22H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.7, 128.3, 125.7, 98.8, 67.6, 62.6, 62.3, 50.8, 33.2, 31.9, 31.0, 30.8, 29.7, 26.7, 25.7, 25.5, 23.5, 19.7 ppm; HRMS (ESI) calcd for $[\text{C}_{23}\text{H}_{38}\text{NO}_2]^+$ (M+H)$^+$: 360.2897; found: 360.2904.

Tert-butyl 4-(1,3-diphenylpropyl)piperazine-1-carboxylate (4g)

Following general procedure B, the reaction of tert-amide 3aa (290 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (213 µL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 5) the title product 4g (277 mg, yield: 73%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2974, 2930, 2859, 2811, 1697, 1453, 1421, 1365, 1246, 1172, 1130, 764, 701 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.24 (t, $J = 7.4$ Hz, 2H), 7.19-7.10 (m, 5H), 7.06 (t, $J = 7.4$ Hz, 1H), 7.01 (d, $J = 7.3$ Hz, 1H), 3.35-3.23 (m, 5H), 2.43-2.36 (m, 2H), 2.30-2.10 (m, 5H), 2.00-1.90 (m, 1H), 1.32 (s, 9H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 154.7, 142.2, 139.4, 128.7, 128.4, 128.3, 128.2, 127.3, 125.8, 79.4, 69.1, 49.9, 34.2, 32.6, 28.5 ppm; HRMS (ESI) calcd for $[\text{C}_{24}\text{H}_{32}\text{N}_2\text{O}_2\text{Na}]^+$ (M+Na)$^+$: 403.2356; found: 403.2363.
**Tert-butyl (1-(1,3-diphenylpropyl)piperidin-4-yl)carbamate (4h)**

Following general procedure B, the reaction of tert-amide 3ab (304 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (213 µL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 5) the title product 4h (272 mg, yield: 69%) as a white solid. Mp: 147~149 °C; IR (film) \( \nu_{\text{max}} \) : 3347, 3025, 2974, 2930, 2800, 2753, 1712, 1495, 1452, 1389, 1365, 1286, 1235, 1172, 1045, 701 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.42-7.13 (m, 10H), 4.52 (br. s, 1H), 3.48-3.31 (m, 2H), 2.88 (d, d, \( J = 10.7 \) Hz,1H), 2.80 (d, \( J = 11.5 \) Hz,1H), 2.59-2.45 (m, 2H), 2.33-2.20 (m, 1H), 2.18-2.05 (m, 2H), 2.02-1.83 (m, 3H), 1.47 (s, 9H), 1.41-1.35 (m, 1H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 155.2, 142.3, 139.6, 128.7, 128.4, 128.3, 128.1, 127.2, 125.8, 79.1, 69.0, 50.2, 48.0, 47.7, 34.5, 33.1, 33.0, 32.7, 28.5 ppm; HRMS (ESI) calcd for \([C_{25}H_{35}N_2O_2]^+\) (M+H\(^+\))\(^-\): 395.2693; found: 395.2697.

**1-(1-Phenylpentan-3-yl)piperidine-4-carbonitrile (4i)**

Following general procedure B, the reaction of tert-amide 3p (166 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30) the title product 4i (205 mg, yield: 80%) as a colorless oil. IR (film) \( \nu_{\text{max}} \) : 2927, 2873, 2806, 2238, 1602, 1494, 1450, 752, 701 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.22-7.12 ( m, 5H), 2.77-2.59 (m, 4H), 2.41-2.37 (m, 1H), 2.13-2.09 (m, 1H), 1.96-1.76 (m, 4H), 1.74-1.65 (m, 2H), 1.64-1.46 (m, 2H), 1.31-1.24 (m, 2H), 0.86 (t, \( J = 7.3 \) Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \( \delta \) 142.7, 128.3 (2C), 128.2 (2C), 125.6, 122.0, 65.3, 46.7, 46.4, 33.2, 31.6, 29.4 (2C), 26.8, 22.1, 11.8 ppm; HRMS (ESI) calcd for \([C_{17}H_{23}N_2]^+\) (M+H\(^+\))\(^-\): 257.2012; found: 257.2014.

**3-(Methyl(1-phenylpentan-3-yl)amino)propanenitrile (4j)**
Following general procedure B, the reaction of tert-amide 3o (140 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 10) the title product 4j (202 mg, yield: 88%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2930, 2859, 2801, 2247, 1602, 1454, 1364, 1029, 749, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.26 (t, $J$ = 7.5 Hz, 2H), 7.21-7.13 (m, 3H), 2.76-2.58 (m, 4H), 2.40-2.27 (m, 3H), 2.23 (s, 3H), 1.70-1.56 (m, 2H), 1.51-1.41 (m, 1H), 1.35-1.25 (m, 1H), 0.89 (t, $J$ = 7.4 Hz, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.7, 128.5, 128.4, 125.7, 119.3, 64.7, 49.8, 36.1, 33.3, 32.1, 22.6, 17.7, 11.9 ppm; HRMS (ESI) calcd for [C$_{15}$H$_{23}$N$_2$] $^+$ (M+H)$^+$: 231.1856; found: 231.1857.

5-(Dimethylamino)-1-(4-fluorophenyl)-7-phenylheptan-1-one (4k)

Following general procedure B, the reaction of tert-amide 3ac (237 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4k (212 mg, yield: 65%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 3062, 3025, 2928, 2857, 2819, 2774, 1686, 1598, 1505, 1454, 1230, 1155, 835, 699 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.06-7.93 (m, 2H), 7.32-7.10 (m, 5H), 2.95 (t, $J$ = 7.1 Hz, 2H), 2.67 (t, $J$ = 8.0 Hz, 2H), 2.48-2.39 (m, 1H), 2.27 (s, 6H), 1.88-1.73 (m, 3H), 1.66-1.54 (m, 2H), 1.47-1.37 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 198.5, 166.8, 164.3, 142.6, 133.4 (d, $J_{C-F}$ = 2.9 Hz), 130.5 (d, $J_{C-F}$ = 9.3 Hz), 128.3 (d, $J_{C-F}$ = 7.1 Hz), 125.6, 115.5 (d, $J_{C-F}$ = 21.6 Hz), 62.9, 40.2, 38.4, 33.2, 31.2, 28.6, 21.8 ppm; HRMS (ESI) calcd for [C$_{21}$H$_{26}$FNNaO]$^+$ (M+Na)$^+$: 350.1891; found: 350.1897.

Methyl ((R)-1-(4-cyanophenyl)-3-phenylpropyl)-L-prolinate (4l)
Following general procedure B, the reaction of tert-amide 3ad (361.0 mg, 1.4 mmol) with ethynylbenzene (2a) (172 µL, 1.2 mmol) and TMDS (296 µL, 1.2 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 5) the title product 4l (381.0 mg, yield: 78%, dr = 14: 1) as a light yellow oil. $[^\alpha]_{25}D = -80.5$ (c 1.0, CHCl$_3$); IR (film) $\nu_{\text{max}}$: 2956, 2924, 2852, 2228, 1734, 1653, 1456, 1383, 1196, 1091, 801, 701 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.66-7.61 (m, 2H), 7.45 (d, $J = 8.2$ Hz, 2H), 7.24 (d, $J = 7.6$ Hz, 2H), 7.19-7.16 (m, 1H), 7.06-7.00 (m, 2H), 3.67-3.63 (m, 1H), 3.52 (dd, $J = 9.2$, 3.0 Hz, 1H), 3.48 (s, 3H), 3.08-3.01 (m, 1H), 2.54-2.46 (m, 1H), 2.37-2.21 (m, 3H), 2.09-1.99 (m, 2H), 1.95-1.78 (m, 3H) ppm; $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 175.1, 147.7, 141.3, 132.0, 129.5, 128.4, 126.0, 118.8, 111.2, 66.9, 62.9, 51.4 (2C), 35.9, 32.1, 30.0, 23.3 ppm; HRMS-ESI calcd for [C$_{22}$H$_{24}$N$_2$NaO$_2$]$^+$ (M+Na$^+$): 371.1730; found: 371.1721.

Methyl ((S)-1-phenylpentan-3-yl)-L-prolinate (4m)

Following general procedure B, the reaction of tert-amide 3ae (185 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30) the title product 4m (206 mg, yield: 75%, dr = 10.7: 1, determined by $^1$H NMR) as a colorless oil. $[^\alpha]_{25}D = -39.8$ (c 1.0, CHCl$_3$); IR (film) $\nu_{\text{max}}$: 2950, 2872, 1732, 1495, 1454, 1434, 1276, 1193, 1167, 747, 699 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.33-7.27 (m, 2H), 7.23-7.17 (m, 3H), 3.69 (s, 3H), 3.56 (dd, $J = 8.5$, 3.7 Hz, 1H), 3.07-3.17 (m, 3H), 2.75-2.56 (m, 4H), 2.08-1.91 (m, 3H), 1.84-1.63 (m, 3H), 1.59-1.48 (m, 2H), 0.96 (t, $J = 7.4$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 176.0, 142.8, 128.3 (4C), 125.6, 61.7, 60.9, 51.5, 48.1, 32.9, 32.3, 30.1, 24.5, 24.0, 10.9 ppm; HRMS (ESI) calcd for [C$_{17}$H$_{24}$N$_2$NaO$_2$]$^+$ (M+Na$^+$): 371.1730; found: 371.1721.

$N,N$-Dimethyl-1,5-diphenylpentan-3-amine (4n)
Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (elucent: EtOAc/n-hexane = 1: 50) the title product 4n (245 mg, yield: 92%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3025, 2930, 2857, 2816, 2773, 1602, 1495, 1453, 748, 697 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \) 7.19-7.13 (m, 4H), 7.10-7.03 (m, 6H), 2.52 (t, \( J = 8.0 \) Hz, 4H), 2.32-2.24 (m, 1H), 2.13 (s, 6H), 1.75-1.65 (m, 2H), 1.53-1.43 (m, 2H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \) 142.7, 128.3, 128.2, 125.6, 62.4, 40.2, 33.3, 31.2 ppm; HRMS (ESI) caled for [C\(_{19}\)H\(_{26}\)N\(_2\)]\(^+\) (M+H\(^+\)): 268.2060, found: 268.2060.

1-(2-Methoxyphenyl)-N,N-dimethyl-5-phenylpentan-3-amine (4o)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with 1-ethynyl-2-methoxybenzene (2x) (158 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (elucent: EtOAc/n-hexane = 1: 50) the title product 4o (261 mg, yield: 88%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 2928, 2855, 2773, 1601, 1493, 1454, 1241, 1048, 751, 698 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CD\(_3\)CN) \( \delta \) 7.36-7.17 (m, 7H), 6.99-6.86 (m, 2H), 3.84 (s, 3H), 3.04-2.94 (m, 1H), 2.86-2.69 (m, 4H), 2.60 (s, 6H), 2.16-1.97 (m, 2H), 1.93-1.76 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 158.3, 142.1, 130.9, 129.9, 129.4 (2C), 129.3 (2C), 128.6, 127.0, 121.4, 111.5, 65.5, 55.9, 40.0 (2C), 32.9, 31.8, 29.7, 28.1 ppm; HRMS (ESI) caled for [C\(_{20}\)H\(_{28}\)NO\(_2\)]\(^+\) (M+H\(^+\)): 298.2165; found: 298.2163.

1-(4-Methoxyphenyl)-N,N-dimethyl-5-phenylpentan-3-amine (4p)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with 1-ethynyl-4-methoxybenzene (2y) (158 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol)
gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4p (252 mg, yield: 85%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3025, 2930, 2856, 2773, 1611, 1511, 1454, 1299, 1245, 1176, 1038, 822, 699 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.35-7.28 (m, 2H), 7.25-7.18 (m, 3H), 7.15-7.07 (m, 2H), 6.90-6.82 (m, 2H), 3.82 (s, 3H), 2.67 (t, \( J = 8.0 \) Hz, 2H), 2.64-2.56 (m, 2H), 2.48-2.40 (m, 1H), 2.29 (s, 3H), 1.91-1.77 (m, 2H), 1.69-1.55 (m, 2H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 157.7, 142.6, 134.6, 129.2 (2C), 128.4 (2C), 128.3 (2C), 125.7, 113.7, 62.5, 55.2, 40.2 (2C), 33.3, 32.3, 31.4, 31.3 ppm; HRMS (ESI) calcd for [C\(_{20}\)H\(_{28}\)NO]\(^+\) (M+H): 298.2165; found: 298.2163.

\( N,N \)-Dimethyl-1-phenyl-5-(thiophen-2-yl)pentan-3-amine (4q)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with 2-ethynylthiophene (2b) (130 mg, 1.2 mmol) and TMDS (355 \( \mu \)L, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4q (248 mg, yield: 91%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3025, 2928, 2856, 2818, 2773, 1452, 696 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.29-7.23 (m, 2H), 7.19-7.13 (m, 3H), 7.11-7.07 (m, 1H), 6.90 (dd, \( J = 5.0, 3.5 \) Hz, 1H), 6.77-6.73 (m, 1H), 2.85 (t, \( J = 7.8 \) Hz, 2H), 2.67-2.56 (m, 2H), 2.45-2.37 (m, 1H), 2.24 (s, 6H), 1.90-1.76 (m, 2H), 1.72-1.62 (m, 1H), 1.60-1.49 (m, 1H) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 145.6, 142.7, 128.4, 128.2, 126.6, 125.7, 124.0, 122.8, 62.2, 40.2, 33.3, 31.6, 30.9, 27.3 ppm; HRMS (ESI) calcd for [C\(_{17}\)H\(_{24}\)NS]\(^+\) (M+H): 274.1624; found: 274.1622.

\( N,N \)-dimethyl-1-phenyl-5-(pyridin-2-yl)pentan-3-amine (4r)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with 2-ethynlypyridine (2z) (124 mg, 1.2 mmol) and TMDS (355 \( \mu \)L, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4r (222 mg, yield: 83%) as a
colorless oil. IR (film) $\nu_{\text{max}}$: 2927, 2856, 2774, 1678, 1568, 1495, 1454, 1152, 1048, 749, 699 cm$^{-1}$; $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 8.51 (d, $J = 4.68$ Hz, 1H), 7.66 (t, $J = 7.62$ Hz, 1H), 7.33-7.27 (m, 2H), 7.26-7.15 (m, 5H), 2.95-2.80 (m, 2H), 2.77-2.63 (m, 3H), 2.40 (s, 6H), 2.10-1.81 (m, 3H), 1.77-1.65 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.9, 150.4, 143.6, 137.9, 129.8 (2C), 129.7 (2C), 127.2, 124.4, 122.6, 64.7, 40.6 (2C), 36.2, 33.9, 32.1, 30.0 ppm; HRMS (ESI) calcd for [C$_{16}$H$_{24}$N$_2$Na]$^+$ (M+Na)$^+$: 291.1832; found: 291.1839.

$N,N$-Dimethyl-1-phenylnonan-3-amine (4s)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with hex-1-yne (2c) (98 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30) the title product 4s (212 mg, yield: 86%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 3084, 2926, 2855, 2818, 1495, 1454, 1377, 1044, 749, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CD$_3$CN) $\delta$ 7.34-7.26 (m, 4H), 7.24-7.19 (m, 1H), 2.82-2.71 (m, 3H), 2.48 (s, 6H), 2.01-1.91 (m, 1H), 1.79-1.64 (m, 2H), 1.52-1.27 (m, 10H), 0.92 (t, $J = 6.6$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.3, 131.8 (2C), 131.7 (2C), 129.3, 67.6, 42.5 (2C), 35.9, 34.7, 34.6, 32.3, 31.9, 29.8, 25.7, 16.7 ppm; HRMS (ESI) calcd for [C$_{17}$H$_{30}$N]$^+$ (M+H)$^+$: 248.2373; found: 248.2378.

$N,N$-dimethyl-1-phenyldodecan-3-amine (4t)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with non-1-yne (2aa) (149 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4t (240 mg, yield: 83%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2925, 2854, 2817, 2775, 1495, 1454, 698 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.37-7.29 (m, 2H), 7.28-7.19 (m, 3H), 2.78-2.63 (m, 2H), 2.44-2.35 (m, 1H), 2.29 (s, 6H), 1.87-1.74 (m, 1H), 1.69-1.49 (m, 2H), 1.39-1.28 (m, 15H), 0.95 (t, $J = 6.9$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 142.9, 128.3 (2C), 128.2 (2C), 125.5,
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63.4, 40.4 (2C), 33.3, 31.9, 31.8, 30.0, 29.6 (2C), 29.3, 28.9, 27.2, 22.7, 14.1 ppm; HRMS (ESI) calcd for [C₂₀H₃₆N]⁺ (M+H)⁺: 290.2842; found: 290.2844.

**N,N-Dimethyl-1-phenyltridecan-3-amine (4u)**

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with dec-1-yne (2ab) (165 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4u (254 mg, yield: 84%) as a colorless oil. IR (film) \( \tilde{\nu} \) max: 3026, 2925, 2854, 1454, 1030, 698 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.35-7.29 (m, 2H), 7.27-7.19 (m, 3H), 2.75-2.63 (m, 2H), 2.43-2.34 (m, 1H), 2.29 (s, 6H), 1.86-1.73 (m, 1H), 1.68-1.58 (m, 1H), 1.42-1.22 (m, 1H), 0.94 (t, J = 6.8 Hz, 3H) ppm; \(^1\)C NMR (100 MHz, CDCl₃) \( \delta \) 142.9, 128.3 (2C), 128.2 (2C), 125.6, 63.4, 40.4 (2C), 33.4, 31.9, 31.8, 30.0, 29.6 (3C), 29.3, 28.9, 27.2, 22.7, 14.1 ppm; HRMS (ESI) calcd for [C₂₁H₃₈N]⁺ (M+H)⁺: 304.2999; found: 304.3003.

**N,N-dimethyl-1-phenylpentadecan-3-amine (4v)**

Following the general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with dodec-1-yne (2ac) (199 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4v (291 mg, yield: 88%) as a colorless oil. IR (film) \( \tilde{\nu} \) max: 2924, 2853, 2775, 1682, 1604, 1495, 1376, 1259, 1030, 698 cm⁻¹; \(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.34-7.28 (m, 2H), 7.25-7.19 (m, 3H), 2.75-2.63 (m, 2H), 2.43-2.32 (m, 1H), 2.28 (s, 6H), 1.84-1.72 (m, 1H), 1.66-1.58 (m, 1H), 1.34-1.27 (m, 1H), 0.92 (t, J = 6.8 Hz, 3H) ppm; \(^1\)C NMR (100 MHz, CDCl₃) \( \delta \) 142.9, 128.3 (2C), 125.6, 63.5, 40.4 (2C), 33.4, 31.9, 31.8, 30.0, 29.7 (5C), 29.3, 29.0, 27.2, 22.7, 14.1 ppm; HRMS (ESI) calcd for [C₂₃H₄₂N]⁺ (M+H)⁺: 332.3312; found: 332.3310.

**7-((Tert-butyldiphenylsilyl)oxy)-N,N-dimethyl-1-phenylheptan-3-amine (4w)**
Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with (but-3-yn-1-yloxy)(tert-butyldiphenylsilane (3ad) (370 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4w (421 mg, yield: 89%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3069, 2930, 2857, 2818, 2773, 1427, 1111, 822, 739, 700 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.71-7.63 (m, 4H), 7.42-7.32 (m, 6H), 7.28-7.22 (m, 2H), 7.20-7.12 (m, 3H), 3.67 (t, \( J = 6.4 \) Hz, 2H), 2.72-2.58 (m, 2H), 2.41-2.32 (m, 1H), 2.24 (s, 6H), 1.80-1.70 (m, 1H), 1.63-1.47 (m, 4H), 1.45-1.32 (m, 2H), 1.30-1.21 (m, 1H), 1.06 (s, 9H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 142.8, 135.7, 134.2, 129.6, 128.5, 128.4, 127.7, 125.8, 63.9, 63.5, 40.4, 33.4, 32.9, 31.9, 28.8, 27.0, 23.5, 19.3 ppm; HRMS (ESI) calcd for [C\(_{31}\)H\(_{44}\)NOS] \(^+\) (M+H) \(^+\): 474.3187; found: 474.3186.

\( \text{7-(Dimethylamino)-9-phenylnonanenitrile (4x)} \)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with hex-5-ynenitrile (2ae) (111 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 50) the title product 4x (219 mg, yield: 85%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 2931, 2857, 2818, 2773, 1427, 1111, 822, 739, 700 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.31-7.26 (m, 2H), 7.22-7.16 (m, 3H), 2.74-2.62 (m, 2H), 2.36 (s, 6H), 2.33 (t, \( J = 7.0 \) Hz, 2H), 1.93-1.80 (m, 1H), 1.70-1.55 (m, 4H), 1.49-1.33 (m, 5H) ppm; \(^13\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 141.7, 128.3, 128.2, 125.9, 119.6, 63.5, 40.0, 33.0, 31.0, 29.0, 28.6, 26.0, 25.0, 16.9 ppm; HRMS (ESI) calcd for [C\(_{17}\)H\(_{27}\)N\(_2\)] \(^+\) (M+H) \(^+\): 259.2169, found: 259.2170.

\( \text{Methyl 4-(dimethylamino)-6-phenylhexanoate (4y)} \)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with methyl propiolate (2p) (100 mg, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after
FC (eluent: EtOAc/n-hexane = 1: 20) the title product 4y (189 mg, yield: 76%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3025, 2934, 2858, 2821, 2776, 1737, 1453, 1275, 748 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.27 (t, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 7.20-7.15 (m, 3\text{H}), 3.65 (s, 3\text{H}), 2.72-2.57 (m, 2\text{H}), 2.47-2.40 (m, 1\text{H}), 2.37 (t, \( J = 7.6 \text{ Hz}, 2\text{H} \)), 2.26 (s, 6\text{H}), 1.88-1.77 (m, 2\text{H}), 1.75-1.67 (m, 1\text{H}), 1.56-1.47 (m, 1\text{H}) ppm; \(^{13}\)C NMR (125 MHz, CDCl\(_3\)) \( \delta \): 174.2, 142.1, 128.3, 128.2, 125.8, 62.8, 51.4, 40.0, 33.2, 31.4, 30.5, 24.9 ppm; HRMS (ESI) calcd for [C\(_{15}\)H\(_{24}\)NO\(_2\)]\(^{+}\) (M+H\(^+\))\(^\ddagger\): 250.1802; found: 250.1801.

\( N,N\)-dimethyl-1-phenyl-5-(trimethylsilyl)pentan-3-amine (4z)

![Chemical structure image]

Following general procedure B, the reaction of \textit{tert}-amide 3af (177 mg, 1.0 mmol) with ethynyltrimethylsilane (2f) (118 mg, 1.2 mmol) and TMDS (355 \( \mu\)L, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 30) the title product 4z (171 mg, yield: 65%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3026, 2951, 2923, 2857, 2776, 1495, 1454, 1247, 862, 836, 698 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \): 7.34-7.29 (m, 2\text{H}), 7.26-7.18 (m, 3\text{H}), 2.73-2.62 (m, 2\text{H}), 2.29 (s, 6\text{H}), 1.84-1.72 (m, 1\text{H}), 1.70-1.59 (m, 1\text{H}), 1.59-1.47 (m, 1\text{H}), 1.37-1.27 (m, 2\text{H}), 0.55-0.47 (m, 2\text{H}), 0.02 (s, 9\text{H}) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \): 143.0, 128.3 (4\text{C}), 125.6, 66.2, 40.5 (2\text{C}), 33.5, 31.1, 22.9, 13.5, -1.9 (3\text{C}) ppm; HRMS (ESI) calcd for [C\(_{16}\)H\(_{30}\)NSi\(^+\)]\(^{+}\) (M+H\(^+\))\(^\ddagger\): 264.2142; found: 264.2144.

\( (4-(3-(\text{Dimethylamino})-5-phenylpentyl)phenyl)methanol (4aa) \)

![Chemical structure image]

Following general procedure B, the reaction of \textit{tert}-amide 3af (177 mg, 1.0 mmol) with 4-ethynylbenzaldehyde (2s) (156 mg, 1.2 mmol) and TMDS (355 \( \mu\)L, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 10) the title product 4aa (226 mg, yield: 74%) as a colorless oil. IR (film) \( \nu_{\text{max}} \): 3388, 3022, 2929, 2857, 2351, 1453, 1030, 749, 699 cm\(^{-1}\); \(^1\)H NMR (500 MHz, CDCl\(_3\)) \( \delta \): 7.29-7.20 (m, 4\text{H}), 7.19-7.08 (m, 5\text{H}), 4.59 (s, 2\text{H}), 3.91-3.19 (s, br, 1\text{H}), 2.66-2.54 (m, 4\text{H}), 2.44-2.34 (m, 1\text{H}), 2.22 (s, 6\text{H}), 1.86-1.74 (m,
2H), 1.64-1.53 (m, 2H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$ 142.3, 141.6, 138.6, 128.3, 128.2, 128.1, 127.0, 125.6, 64.7, 62.6, 40.1, 33.1, 32.8, 31.3, 31.2; HRMS (ESI) calcd for [C$_{20}$H$_{28}$NO]$^+$ (M+H)$^+$: 298.2165; found: 298.2163.

6,6-Diethoxy-$N,N$-dimethyl-1-phenylhexan-3-amine (4ab)

Following general procedure B, the reaction of tert-amide 3af (177 mg, 1.0 mmol) with 3,3-diethoxyprop-1-yne 2g (153.6 mg, 0.17 mL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 10) the title product 4ab (249 mg, yield: 85%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 2972, 2930, 2868, 1454, 1373, 1129, 1064, 699 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.17-7.11 (m, 2H), 7.10-7.00 (m, 3H), 4.34 (t, $J$ = 5.5 Hz, 1H), 3.57-3.46 (m, 2H), 3.40-3.31 (m, 2H), 2.52 (t, $J$ = 8.1 Hz, 2H), 2.27-2.18 (m, 1H), 2.11 (S, 6H), 1.71-1.59 (m, 1H), 1.57-1.37 (m, 4H), 1.28-1.19 (m, 1H), 1.08 (t, $J$ = 7.2 Hz, 6H) ppm; $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ 142.7, 128.2 (2C), 128.1 (2C), 125.5, 102.9, 62.9, 60.8, 60.7, 40.2 (2C), 33.2, 31.4, 30.9, 23.8, 15.2 (2C) ppm; HRMS (ESI) calcd for [C$_{18}$H$_{32}$NO$_2$]$^+$ (M+H)$^+$: 294.2428; found: 294.2421.

1-phenylpentan-3-amine (4ac)

Following general procedure B, the reaction of tert-amide 3a (253 mg, 1.0 mmol) with ethynylbenzene (2a) (131 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: MeOH/CH$_2$Cl$_2$ = 1: 20) the title product 4ac (142 mg, yield: 87%) as a colorless oil. IR (film) $\nu_{\text{max}}$: 3429, 2955, 2927, 1569, 1456, 697 cm$^{-1}$; $^1$H NMR (500 MHz, CDCl$_3$) $\delta$ 7.30-7.24 (m, 2H), 7.22-7.14 (m, 3H), 2.78-2.70 (m, 1H), 2.69-2.58 (m, 2H), 1.81-1.69 (m, 1H), 1.61-1.45 (m, 2H), 1.37 (br s, 2H), 1.34-1.26 (m, 1H), 0.92 (t, $J$ = 7.4 Hz, 3H) ppm; $^{13}$C-NMR (CDCl$_3$, 125 MHz) $\delta$ 142.4, 128.3 (4C), 125.6, 52.2, 39.3, 32.6, 30.7, 10.2 ppm; HRMS (ESI) calcd for [C$_{11}$H$_{18}$N]$^+$ (M+H)$^+$: 164.1434; found: 164.1425.
5-Isobutylpyrrolidin-2-one (6)

Following general procedure B, the reaction of tert-amide 3u (281 mg, 1.0 mmol) with methyl propiolate (2p) (107 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: EtOAc/n-hexane = 1: 5) the title product 6 (103 mg, yield: 73%) as a white solid. Mp: 70–72 °C (lit.[2] 65–66 °C); IR (film) ν max: 3189, 2957, 2355, 1699, 1461, 1288, 1074, 782 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.64 (s, 1H), 3.72-3.68 (m, 2H), 2.33-2.20 (m, 3H), 1.70-1.59 (m, 2H), 1.49-1.40 (m, 1H), 1.34-1.25 (m, 1H), 0.91 (d, J = 6.5 Hz, 6H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 178.3, 52.7, 45.9, 30.2, 27.8, 25.2, 22.9, 22.4 ppm; HRMS (ESI) calcd for [C₈H₁₆NO]⁺ (M+H)⁺: 142.1226; found: 142.1221.

Isosolenopsin (8)

Following general procedure B, the reaction of tert-amide 3w (309 mg, 1.0 mmol) with non-1-yne (2aa) (197 µL, 1.2 mmol) and TMDS (355 µL, 2.0 mmol) gave, after FC (eluent: MeOH/CH₂Cl₂ = 1: 10) isosolenopsin (8) (153 mg, yield: 68%) as a colorless oil, which was converted to isosolenopsin hydrochloride salt as a white solid. Analytical data are in full agreement with those previously published.[3] Mp: 172–173 °C (lit.[3a] 174-175 °C); IR (film) ν max: 3429, 2931, 2849, 2525, 1464, 1132, 1076 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.44 (br s, 1H), 9.06 (br s, 1H), 3.13-2.96 (m, 1H), 2.96-2.90 (m, 1H), 2.22-2.09 (m, 1H), 2.00-1.79 (m, 5H), 1.65-1.55 (m, 3H), 1.43-1.21 (m, 16H), 0.88 (t, J = 6.7 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 58.6, 54.5, 53.2, 31.8, 30.7, 29.5, 29.4, 29.3, 29.2, 27.4, 25.6, 22.9, 22.6, 19.4, 14.0 ppm; HRMS (ESI) calcd for [C₁₅H₃₂N]⁺ (M+H)⁺: 226.2529; found: 226.2523.
Reference:


$^1$H and $^{13}$C NMR Spectra of the Alkynylated and Alkylated Products

$^1$H NMR and $^{13}$C NMR spectra of compound 1a
$^1$H NMR and $^{13}$C NMR spectra of compound 1b
$^1$H NMR and $^{13}$C NMR spectra of compound 1c
$^1$H NMR and $^{13}$C NMR spectra of compound 1d
$^1$H NMR and $^{13}$C NMR spectra of compound 1e
$^1$H NMR and $^{13}$C NMR spectra of compound 1f
$^1$H NMR and $^{13}$C NMR spectra of compound 1g
$^1$H NMR and $^{13}$C NMR spectra of compound 1h
$^1$H NMR and $^{13}$C NMR spectra of compound 1i
$^1$H NMR and $^{13}$C NMR spectra of compound 1j
$^{1}H$ NMR and $^{13}C$ NMR spectra of compound $1k$
$^1\text{H NMR}$ and $^{13}\text{C NMR}$ spectra of compound 11
$^1$H NMR and $^{13}$C NMR spectra of compound 1m
$^1$H NMR and $^{13}$C NMR spectra of compound 1n
$^1$H NMR and $^{13}$C NMR spectra of compound 1o
$^1$H NMR and $^{13}$C NMR spectra of compound 1p
$^1$H NMR and $^{13}$C NMR spectra of compound 1q
$^1$H NMR and $^{13}$C NMR spectra of compound 1r
$^1$H NMR and $^{13}$C NMR spectra of compound 1s
$^1$H NMR and $^{13}$C NMR spectra of compound 1t
$^1$H NMR and $^{13}$C NMR spectra of compound 1u
$^1$H NMR and $^{13}$C NMR spectra of compound 1v
$^1$H NMR and $^{13}$C NMR spectra of compound 1w
$^1$H NMR and $^{13}$C NMR spectra of compound $1x$
$^1$H NMR and $^{13}$C NMR spectra of compound 1y
$^1$H NMR and $^{13}$C NMR spectra of compound 1z
$^1$H NMR and $^{13}$C NMR spectra of compound 1aa
$^1$H NMR and $^{13}$C NMR spectra of compound 1ab
$^1$H NMR and $^{13}$C NMR spectra of compound 1ac
$^1$H NMR and $^{13}$C NMR spectra of compound 1ad
$^1$H NMR and $^{13}$C NMR spectra of compound 1ae
$^1$H NMR and $^{13}$C NMR spectra of compound 1af
$^1$H NMR and $^{13}$C NMR spectra of compound 1ag
$^1$H NMR and $^{13}$C NMR spectra of compound 1ah
$^1$H NMR and $^{13}$C NMR spectra of compound 1ai
$^1$H NMR and $^{13}$C NMR spectra of compound 1aj
$^1$H NMR and $^{13}$C NMR spectra of compound 1ak
$^1$H NMR and $^{13}$C NMR spectra of compound 1al
$^1$H NMR and $^{13}$C NMR spectra of compound 1am

82
\(^1\)H NMR and \(^{13}\)C NMR spectra of compound 1an
$^1$H NMR and $^{13}$C NMR spectra of compound 1ao
$^1$H NMR and $^{13}$C NMR spectra of compound 1ap
\(^1\text{H} \text{NMR and } ^{13}\text{C} \text{NMR spectra of compound 1aq}\)
$^1$H NMR and $^{13}$C NMR spectra of compound 1ar
$^1$H and $^{13}$C NMR Spectra of Compound 4a
$^1$H and $^{13}$C NMR Spectra of Compound 4b
$^1$H and $^{13}$C NMR Spectra of Compound 4c
$^1$H and $^{13}$C NMR Spectra of Compound 4d
$^1$H and $^{13}$C NMR Spectra of Compound 4e

$^1$H NMR Spectra:

$^{13}$C NMR Spectra:
$^1$H and $^{13}$C NMR Spectra of Compound 4f
$^1$H and $^{13}$C NMR Spectra of Compound 4g
$^1$H and $^{13}$C NMR Spectra of Compound 4h
\(^1\)H and \(^{13}\)C NMR Spectra of Compound 4i
$^1$H and $^{13}$C NMR Spectra of Compound 4j

**$^1$H NMR Spectra**

- Phenyl group: 7.55 - 7.20 ppm
- Methine: 4.27 ppm
- Methine: 4.18 ppm
- Methine: 3.57 ppm
- Methine: 2.78 ppm
- Methine: 1.34 ppm
- Methine: 1.25 ppm

**$^{13}$C NMR Spectra**

- Phenyl group: 138.2 ppm
- Methine: 75.9 ppm
- Methine: 71.8 ppm
- Methine: 70.6 ppm
- Methine: 61.5 ppm
- Methine: 21.8 ppm
$^1$H and $^{13}$C NMR Spectra of Compound 4k
$^1$H and $^{13}$C NMR Spectra of Compound 41
$^1$H and $^{13}$C NMR Spectra of Compound 4m
$^1$H and $^{13}$C NMR Spectra of Compound 4n
$^1$H and $^{13}$C NMR Spectra of Compound 4o
$^1$H and $^{13}$C NMR Spectra of Compound 4p
$^1$H and $^{13}$C NMR Spectra of Compound 4q
$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 4r
$^1$H and $^{13}$C NMR Spectra of Compound 4s

1H NMR, CD3CN
200 MHz, 08-22
$^1$H and $^{13}$C NMR Spectra of Compound 4t
$^1$H and $^{13}$C NMR Spectra of Compound 4u
$^1\text{H}$ and $^{13}\text{C}$ NMR Spectra of Compound 4v
$^{1}$H and $^{13}$C NMR Spectra of Compound 4w
$^1$H and $^{13}$C NMR Spectra of Compound 4x
$^{1} \text{H}$ and $^{13} \text{C}$ NMR Spectra of Compound 4z

NMR-δ-135
PROTON
CDCl₃
400 MHz
2020.07.11

[Chemical structure and NMR spectrum image]

NMR-δ-135
PROTON
CDCl₃, 101 MHz
2020.07.11

[Chemical structure and NMR spectrum image]
$^1$H and $^{13}$C NMR Spectra of Compound 4aa

$^1$H NMR
- Solvent: CDCl$_3$
- Temperature: 298 K
- Measured at 500 MHz
- Date: 2017-01-4

$^{13}$C NMR
- Solvent: CDCl$_3$
- Temperature: 298 K
- Measured at 125 MHz
- Date: 2017-01-4
$^1$H and $^{13}$C NMR Spectra of Compound 4ab
$^1$H and $^{13}$C NMR Spectra of Compound (±)-6
$^1$H and $^{13}$C NMR Spectra of Compound (±)-isosolenopsin (8)