

## 2-Phenallyl as a Versatile Protecting Group for the Asymmetric One-Pot Three-Component Synthesis of Propargylamines

### Supporting Information

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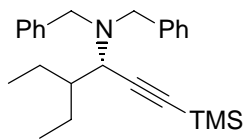
Fax: (+49)-089/2180-77680

**General** All reactions were carried out under an argon atmosphere in dried glassware. All starting materials were purchased from commercial sources and used without further purification. 2-phenyl-2-propen-1-amine<sup>1</sup> and [1-(bromomethyl)vinyl]benzene<sup>2</sup> were prepared according to literature procedures. Toluene was predried over KOH and continuously refluxed and freshly distilled from sodium. THF was continuously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. Preparative chromatography was performed on silicagel 60 (0.063-0.200 mm) from Merck. Yields refer to isolated yields of compounds estimated to be > 95% pure as determined by <sup>1</sup>H-NMR and capillary GC.

**Typical Procedure A (racemic reaction):** In a dry and argon flushed 25 mL flask, equipped with a magnetic stirrer and a septum, CuBr (0.075 mmol, 5 mol %) was suspended in dry toluene (3 mL). MS 4Å (750 mg) and *n*-decane (100 mg) were added, followed by the alkyne (1.5 mmol), the aldehyde (1.5 mmol) and bis(phenallyl)amine (1.5 mmol). The reaction mixture was stirred at rt until GC-analysis showed full conversion. MS 4Å was filtered and washed with diethyl ether. The crude product was concentrated *in vacuo* and purified by column chromatography on silica gel.

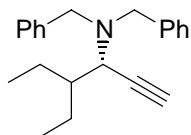
**Typical Procedure B (nonracemic reaction):** In a dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, CuBr (0.015 mmol, 5 mol %) and (*R*)-Quinap (0.017 mmol, 5.5 mol %) were suspended in dry toluene (1.5 mL) and stirred for 30 min. MS 4Å (150 mg) and *n*-decane (30 mg) were added, followed by the alkyne (0.3 mmol), the aldehyde (0.3 mmol) and bis(phenallyl)amine (0.3 mmol). The reaction mixture was stirred at rt until GC-analysis showed full conversion. MS 4Å was filtered and washed with diethyl ether. The crude product was concentrated *in vacuo* and purified by column chromatography on silica gel.

### *N,N*-Dibenzyl-4-ethyl-1-hexyn-3-amine (**1a**):



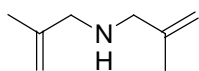
(*R*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 99 % (5 mmol scale, 1.87 g); (nonracemic): 99 % (0.3 mmol scale, 112 mg)..  $[\alpha]_{20}^D = -199$  ( $c = 0.41$ , CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.43\text{--}7.40$  (m, 4H), 7.36-7.31 (m, 4H), 7.28-7.23 (m, 2H), 3.82 (d,  $J = 13.5$  Hz, 2H), 3.37 (d,  $J = 13.5$  Hz, 2H), 3.19 (d,  $J = 10.1$  Hz, 1H), 1.75-1.27 (m, 5H), 0.81 (t,  $J = 7.9$  Hz, 3H), 0.59 (t,  $J = 7.9$  Hz, 3H), 0.29 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta = 139.7, 129.1, 128.1, 126.8, 104.0, 90.0, 55.6, 55.0, 41.4, 22.1, 20.1, 10.6, 8.9, 0.5$ . **MS** (70 eV, EI): 362 ( $M^+ - \text{Me}$ , 1), 307 (30); 306 (100), 91 (29). **HRMS** (EI): calcd. for C<sub>25</sub>H<sub>36</sub>NSi [ $M^+ + \text{H}$ ]: 378.2617, found: 378.2617. **IR** (film): 2962 (s), 2158 (m), 1494 (m), 1454 (m), 1250 (s), 842 (vs), 747 (m), 698 (s). **Anal** calcd for C<sub>25</sub>H<sub>36</sub>NSi: C: 79.51, H: 9.34, N: 3.71, found: C: 79.49, H: 9.37, N: 3.69.

### *N,N*-dibenzyl-4-ethyl-1-hexyn-3-amine (**1a-TMS**)



Amine **1a** was treated with 0.3 eq Bu<sub>4</sub>NF in THF at 0 °C for 15 min. Standard workup and column chromatographic purification (SiO<sub>2</sub>, pentane: ether = 99 : 1) gave **1a-TMS**. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 98 % (4 mmol scale, 1.20 g); (nonracemic): 95 % (0.3 mmol scale, 87 mg). **<sup>1</sup>H-NMR** (300 MHz, CDCl<sub>3</sub>):  $\delta = 7.43\text{--}7.41$  (m, 4H), 7.37-7.32 (m, 4H), 7.29-7.24 (m, 2H), 3.84 (d,  $J = 13.7$  Hz, 2H), 3.40 (d,  $J = 13.7$  Hz, 2H), 3.21 (dd,  $J = 10.1, 2.3$  Hz, 1H), 2.38 (d,  $J = 2.3$  Hz, 1H), 1.79-1.62 (m, 3H), 1.50-1.28 (m, 2H), 0.81 (t,  $J = 7.3$  Hz, 3H), 0.60 (t,  $J = 7.3$  Hz, 3H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta = 139.6, 129.0, 128.2, 126.9, 81.3, 73.3, 55.0, 54.6, 41.4, 21.9, 19.9, 10.4, 8.9$ . **MS** (70 eV, EI): 235 (20), 234 ( $M^+ - 1\text{-ethylpropyl}$ , 100), 91 (74). **HRMS** (EI): calcd. for C<sub>22</sub>H<sub>26</sub>N [ $M^+ - \text{H}$ ]: 304.2065, found: 304.2075. **IR** (film): 3302 (m), 2963 (s), 2937 (m), 1495 (m), 1454 (m), 748 (m), 698 (s). **Anal** calcd for C<sub>22</sub>H<sub>27</sub>N: C: 86.51, H: 8.91, N: 4.59, found: C: 86.45, H: 9.07, N: 4.57. **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min}) = 28.4$  (-), 31.9 (+).

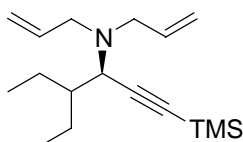
### *N,N*-bis(2-methyl-2-propenyl)amine



Prepared by reductive amination of methylacrolein (368 mg, 5.3 mmol) with methallylamine (356 mg, 5.0 mmol) and NaBH<sub>4</sub> (228 mg, 6.0 mmol) at 0 °C. Distillation in Kugelrohr (105 mbar, 120 °C) lead to the desired product (60 %, 320 mg, 2.6 mmol) as colorless oil.

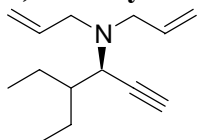
**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 4.87-4.86 (m, 2H), 4.81-4.80 (m, 2H), 3.13 (s, 4H), 1.74 (s, 6H), 1.27 (s br., 1H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 144.1, 110.5, 54.9, 20.8. . **MS** (70 eV, EI): m/z(%): 125 (M<sup>+</sup>, 1), 110 (15), 84 (31), 82 (21), 58 (31), 55 (32), 43 (100). **HRMS** (EI): calcd. for C<sub>8</sub>H<sub>15</sub>N [M<sup>+</sup>]: 125.1204, found: 125.1178. **IR** (film): 3075 (w), 2971 (s), 2920 (s), 2800 (m), 1674 (s), 1658 (s), 1446 (s), 1373 (s), 1159 (m), 1137 (m), 1045 (m), 895 (vs).

### *N,N*-diallyl-4-ethyl-1-(trimethylsilyl)-1-hexyn-3-amine (**1b**)



(*S*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 67 % (5.0 mmol scale, 934 mg); (nonracemic): 83 % (2.0 mmol scale, 459 mg). [α]<sub>20</sub><sup>D</sup> = 130 (c = 0.38, CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 5.86-5.72 (m, 2H), 5.21-5.15 (m, 2H), 5.09-5.05 (m, 2H), 3.26-3.19 (m, 3H), 2.81 (dd, *J*= 14.6, 7.9 Hz, 2H), 1.70-1.25 (m, 5H), 0.86 (t, *J*= 7.5 Hz, 3H), 0.76 (t, *J*= 7.6 Hz, 3H), 0.16 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 136.9, 116.7, 104.4, 89.3, 56.1, 53.9, 41.9, 22.2, 20.4, 10.7, 9.4, 0.3. **MS** (70 eV, EI): m/z(%): 276 (M<sup>+</sup>-H, <1), 207 (19), 206 (100). **HRMS** (EI): calcd. for C<sub>17</sub>H<sub>30</sub>NSi [M<sup>+</sup>-H]: 276.2148, found: 276.2174. **IR** (film): 2963 (s), 2937 (m), 2159 (m), 1643 (w), 1250 (s), 920 (s), 842 (vs), 760 (m).

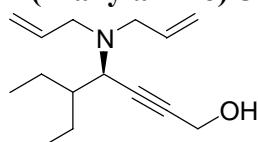
### *N,N*-diallyl-4-ethyl-1-hexyn-3-amine (**1b-TMS**)



Amine **1b** was treated with 0.3 eq Bu<sub>4</sub>NF in THF at 0 °C for 15 min. Standard workup and column chromatographic purification (SiO<sub>2</sub>, pentane: ether = 99 : 1) gave **1b-TMS**. Yield (racemic): 77 % (3.4 mmol scale, 537 mg); (nonracemic): 90 % (1.7 mmol scale, 306 mg). [α]<sub>20</sub><sup>D</sup> = 122 (c = 0.49, CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 5.85-5.72 (m, 2H), 5.22-

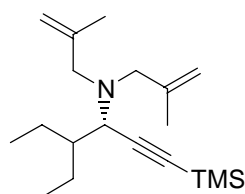
5.17 (m, 2H), 5.11-5.06 (m, 2H), 3.29-3.21 (m, 3H), 2.82 (dd,  $J= 14.2, 8.4$  Hz, 2H), 2.20 (d,  $J= 2.2$  Hz, 1H), 1.73-1.29 (m, 5H), 0.86 (t,  $J= 7.5$  Hz, 3H), 0.77 (t,  $J= 7.2$  Hz, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta= 136.7, 116.9, 81.7, 82.7, 55.1, 53.8, 41.9, 22.0, 20.2, 10.5, 9.3$ . **MS** (70 eV, EI):  $m/z(\%)$ : 205 ( $\text{M}^+$ , <1), 135 (9), 134 (100), 93 (8). **HRMS** (EI): calcd. for  $\text{C}_{14}\text{H}_{23}\text{N}$  [ $\text{M}^+$ ]: 205.1830, found: 205.1820. **IR** (film): 3307 (m), 2965 (vs), 2937 (m), 2878 (m), 2819 (m), 1644 (w), 1449 (m), 995 (m), 921 (s), 640 (m), 627 (m).

#### 4-(Diallylamino)-5-ethyl-2-heptyn-1-ol



Amine **1b-TMS** was treated with *n*-BuLi (1 eq, 1.56 M in hexane) in THF at  $-30$  °C for 15 min. Paraformaldehyde (1.1 eq) was suspended in THF and was added dropwise. The reaction mixture was allowed to warm to rt and stirred overnight. Standard workup and column chromatographic purification ( $\text{SiO}_2$ , pentane: ether = 4 : 1) gave the alcohol. Yield (racemic): 73 % (0.5 mmol scale, 86 mg); (nonracemic): 83 % (0.5 mmol scale, 97 mg).  $[\alpha]_{20}^{\text{D}} = 134$  ( $c = 0.61$ ,  $\text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta= 5.85\text{-}5.72$  (m, 2H), 5.21-5.16 (m, 2H), 5.10-5.06 (m, 2H), 4.32 (s, 2H), 3.31-3.21 (m, 3H), 2.81 (dd,  $J= 13.8, 8.2$  Hz, 2H), 1.70-1.25 (m, 6H), 0.85 (t,  $J= 7.4$  Hz, 3H), 0.77 (t,  $J= 7.1$  Hz, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta= 136.8, 116.8, 83.8, 83.3, 55.3, 53.9, 51.3, 41.9, 22.2, 20.3, 10.6, 9.3$ . **MS** (70 eV, EI):  $m/z(\%)$ : 235 ( $\text{M}^+$ , <1), 165 (12), 164 (100), 41 (17). **HRMS** (EI): calcd. for  $\text{C}_{15}\text{H}_{25}\text{NO}$  [ $\text{M}^+$ ]: 235.1936, found: 235.1919. **IR** (film): 3307 (m), 2964 (vs), 2936 (s), 2877 (s), 2818 (m), 1644 (m), 1448 (m), 1418 (m), 1107 (s), 1016 (s), 997 (s), 920 (s). **HPLC** (OD-H, 99 % *n*-heptane/ 1 % *i*-propanol, 0.2 mL/min):  $t_{\text{r}}(\text{min})= 54.2$  (+), 58.8 (-).

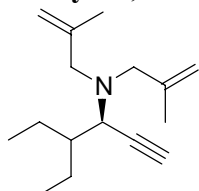
#### 4-Ethyl-*N,N*-bis(2-methyl-2-propenyl)-1-(trimethylsilyl)-1-hexyn-3-amine (1c)



(*R*)-Quinap was used. Column chromatographic purification:  $\text{SiO}_2$ , pentane: ether = 99 : 1. Yield (racemic): 77 % (1.0 mmol scale, 234 mg); (nonracemic): 84 % (0.3 mmol scale, 77 mg).  $[\alpha]_{20}^{\text{D}} = -165$  ( $c = 0.56$ ,  $\text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta= 4.93\text{-}4.90$  (m, 2H), 4.84-4.82 (m, 2H), 3.25 (d,  $J= 10.6$  Hz, 1H), 3.02 (d,  $J= 13.3$  Hz, 2H), 3.72 (d,  $J= 13.4$  Hz,

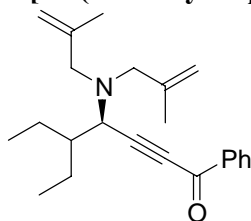
2H), 1.72 (s, 6H), 1.69-1.25 (m, 5H), 0.84 (t,  $J=7.5$  Hz, 3H), 0.76 (t,  $J=7.6$  Hz, 3H), 0.17 (s, 9H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta=143.7, 113.2, 104.1, 89.4, 57.4, 55.5, 41.4, 22.1, 20.9, 20.4, 10.3, 9.8, 0.4$ . **MS** (70 eV, EI):  $m/z(\%)$ : 304 ( $\text{M}^+-\text{H}$ , <1), 235 (19), 234 (100). **HRMS** (EI): calcd. for  $\text{C}_{19}\text{H}_{34}\text{NSi}$  [ $\text{M}^+-\text{H}$ ]: 304.2461, found: 304.2495. **IR** (film): 2964 (s), 2878 (m), 2830 (m), 2159 (m), 1649 (w), 1448 (m), 1250 (s), 898 (s), 842 (vs), 760 (m).

#### 4-ethyl-*N,N*-bis(2-methyl-2-propenyl)-1-hexyn-3-amine



Amine **1c** was treated with 0.3 eq  $\text{Bu}_4\text{NF}$  in THF at 0 °C for 15 min. Standard workup and column chromatographic purification ( $\text{SiO}_2$ , pentane: ether = 99 : 1) gave **1c-TMS**. Yield (racemic): 95 % (0.7 mmol scale, 146 mg); (nonracemic): 98 % (0.25 mmol scale, 57 mg).  $[\alpha]_{\text{D}}^{20} = -156$  ( $c = 0.52$ ,  $\text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta=4.93\text{-}4.92$  (m, 2H), 4.85-4.83 (m, 2H), 3.28 (dd,  $J=10.8, 2.2$  Hz, 1H), 3.05 (d,  $J=13.7$  Hz, 2H), 3.75 (d,  $J=13.7$  Hz, 2H), 2.25 (d,  $J=2.2$  Hz, 1H), 1.73 (s, 6H), 1.71-1.25 (m, 5H), 0.84 (t,  $J=7.5$  Hz, 3H), 0.78 (t,  $J=7.5$  Hz, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta=143.5, 113.3, 81.4, 72.8, 57.4, 54.6, 41.2, 21.9, 20.9, 20.2, 10.0, 9.8$ . **MS** (70 eV, EI):  $m/z(\%)$ : 233 ( $\text{M}^+$ , <1), 163 (11), 162 (100). **HRMS** (EI): calcd. for  $\text{C}_{16}\text{H}_{27}\text{N}$  [ $\text{M}^+$ ]: 233.2143, found: 233.2140. **IR** (film): 3308 (m), 2966 (vs), 2937 (s), 2878 (m), 2832 (m), 1648 (w), 1448 (m), 1372 (m), 1112 (m), 899 (vs), 640 (m), 625 (m).

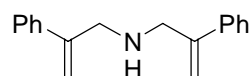
#### 4-[bis(2-methyl-2-propenyl)amino]-5-ethyl-1-phenyl-2-heptyn-1-one



Amine **1c-TMS** was treated according to the procedure of Müller<sup>3</sup> with benzoyl chloride (1.1 eq),  $\text{PdCl}_2(\text{PPh}_3)_2$  (2 mol%),  $\text{CuI}$  (2 mol%) and triethylamin (1.5 eq) in THF at rt overnight. Standard workup and column chromatographic purification ( $\text{SiO}_2$ , pentane: ether = 98 : 2) gave the desired product. Yield (racemic): 87 % (0.5 mmol scale, 140 mg); (nonracemic): 87 % (0.24 mmol scale, 70 mg).  $[\alpha]_{\text{D}}^{20} = -184$  ( $c = 0.39$ ,  $\text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta=8.19\text{-}8.15$  (m, 2H), 7.61 (tt,  $J=7.1, 1.3$  Hz, 1H), 7.49 (tt,  $J=7.5, 1.3$  Hz, 2H), 4.96-4.95 (m, 2H), 4.90-4.89 (m, 2H), 3.61 (d,  $J=10.1$  Hz, 1H), 3.18 (d,  $J=13.3$  Hz, 2H), 2.87 (d,  $J=13.3$ ,

Hz, 2H), 1.75 (s, 6H), 1.82-1.37 (m, 5H), 0.90 (t,  $J=7.3$  Hz, 3H), 0.83 (t,  $J=7.0$  Hz, 3H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta=177.9, 143.0, 137.1, 133.9, 129.5, 128.5, 113.9, 94.2, 84.4, 57.7, 55.3, 41.2, 22.1, 20.9, 20.3, 10.0, 9.7$ . **MS** (70 eV, EI):  $m/z(\%)$ : 337 ( $\text{M}^+$ , <1), 267 (20), 266 (100), 105 (26), 55 (10). **HRMS** (EI): calcd. for  $\text{C}_{23}\text{H}_{31}\text{NO}$  [ $\text{M}^+$ ]: 337.2406, found: 337.2382. **IR** (film): 2966 (s), 2938 (m), 2878 (m), 2829 (m), 2208 (m), 1646 (vs), 1598 (m), 1582 (m), 1450 (s), 1312 (m), 1259 (vs), 1174 (m), 1087 (m), 899 (s), 701 (s). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.15 mL/min):  $t_r(\text{min})=60.2$  (-), 67.7 (+).

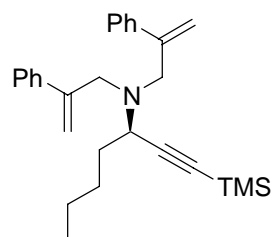
### Bis(phenallyl)amine (3)



2-phenyl-2-propen-1-amine (10.63 g, 80 mmol, 2 eq) was dissolved in THF (50 mL). [1-(bromomethyl)vinyl]benzene (7.88g, 40 mmol, 1 eq) was added *via* syringe and the resulting solution was stirred at room temperature overnight. A white precipitate formed and was collected by filtration and washed with diethyl ether. The filtrate was concentrated under reduced pressure and purified by column chromatography (Silica, pentane/diethyl ether 4/1) yielding the secondary amine (6.97 g, 28 mmol, 70 %) as a yellow oil. The collected solid being composed of the amine hydrobromide was dissolved in 2N NaOH. Extraction with dichloromethane and concentration *in vacuo* lead to recovery of the primary amine (4.46 g, 33.4 mmol, 84 %).

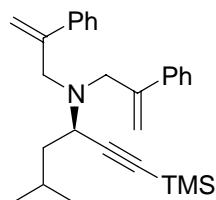
$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta=7.44-7.40$  (m, 4H), 7.37-7.28 (m, 6H), 5.44 (s, 2H), 5.28 (s, 2H), 3.71 (s, 4H), 1.70 (s, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta=146.1, 139.7, 128.4, 127.6, 126.2, 113.7, 52.5$ . **MS** (70 eV, EI):  $m/z(\%)$ : 249 ( $\text{M}^+$ , 28), 146 (100), 130 (11), 118 (21), 117 (32), 115 (25), 91 (15). **HRMS** (EI): calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}$  [ $\text{M}^+$ ]: 249.1517, found: 249.1545. **IR** (film): 3056 (w), 2920 (w), 2824 (w), 1629 (w); 1495 (m), 1444 (w), 903 (s), 778 (vs), 708 (vs).

### *N,N*-Bis(2-phenyl-2-propenyl)-1-(trimethylsilyl)-1-heptyn-3-amine (2a)



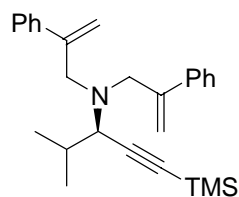
(S)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 72 % (0.7 mmol scale, 209 mg); (nonracemic): 86 % (0.3 mmol scale, 107 mg).  $[\alpha]_{20}^D = 65$  (c = 0.75, CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 7.34-7.31 (m, 4H), 7.22-7.15 (m, 6H), 5.43 (s, 2H), 5.28 (s, 2H), 3.79 (d, *J* = 13.6 Hz, 2H), 3.49 (t, *J* = 7.3 Hz, 1H), 3.17 (d, *J* = 13.6 Hz, 2H), 1.58-1.51 (m, 2H), 1.15-0.94 (m, 4H), 0.72 (t, *J* = 6.9 Hz, 3H), 0.22 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ = 145.5, 140.0, 127.9, 127.3, 126.7, 115.6, 104.5, 89.3, 55.4, 52.2, 32.3, 28.4, 22.3, 13.9, 0.4. **MS** (70 eV, EI): *m/z*(%): 415 (M<sup>+</sup>, <1), 359 (29), 358 (100). **HRMS** (EI): calcd. for C<sub>28</sub>H<sub>37</sub>NSi [M<sup>+</sup>]: 415.2695, found: 415.2670. **IR** (film): 2957 (s), 2932 (m), 2159 (m), 1496 (m), 1250 (s), 904 (s), 842 (vs), 778 (s), 695 (m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min): *t<sub>r</sub>*(min) = 28.1 (-), 32.8 (+).

#### 5-Methyl-*N,N*-bis(2-phenyl-2-propenyl)-1-(trimethylsilyl)-1-hexyn-3-amine (2b)



(S)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 83 % (1.0 mmol scale, 343 mg); (nonracemic): 67 % (0.3 mmol scale, 84 mg).  $[\alpha]_{20}^D = 74$  (c = 0.59, CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ = 7.34-7.31 (m, 4H), 7.22-7.15 (m, 6H), 5.45 (s, 2H), 5.28 (s, 2H), 3.79 (d, *J* = 13.7 Hz, 2H), 3.60 (t, *J* = 7.1 Hz, 1H), 3.17 (d, *J* = 13.7 Hz, 2H), 1.50-1.37 (m, 3H), 0.72 (d, *J* = 6.1 Hz, 3H), 0.58 (d, *J* = 6.1 Hz, 3H), 0.22 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ = 145.5, 139.9, 127.9, 127.3, 126.7, 115.7, 104.6, 89.2, 55.4, 50.4, 42.3, 24.5, 22.6, 22.1, 0.4. **MS** (70 eV, EI): *m/z*(%): 415 (M<sup>+</sup>, 2), 359 (27), 358 (100). **HRMS** (EI): calcd. for C<sub>28</sub>H<sub>37</sub>NSi [M<sup>+</sup>]: 415.2695, found: 415.2707. **IR** (film): 2957 (s), 2934 (m), 2159 (m), 1496 (m), 1250 (s), 904 (m), 842 (vs), 778 (s), 695 (m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min): *t<sub>r</sub>*(min) = 28.7 (-), 34.5 (+).

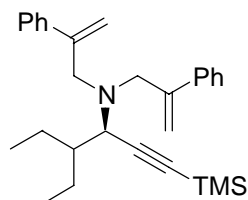
#### 4-Methyl-*N,N*-bis(2-phenyl-2-propenyl)-1-(trimethylsilyl)-1-pentyn-3-amine (2c)



(S)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 72 % (1.5 mmol scale, 434 mg); (nonracemic): 77 % (0.3 mmol scale, 93

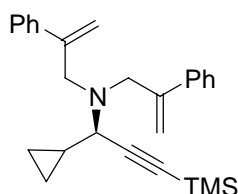
mg).  $[\alpha]_{20}^D = 65$  ( $c = 0.84$ ,  $\text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 7.33\text{-}7.29$  (m, 4H), 7.22-7.17 (m, 6H), 5.42 (s, 2H), 5.30 (s, 2H), 3.80 (d,  $J = 13.7$  Hz, 2H), 3.15 (d,  $J = 13.7$  Hz, 2H), 3.03 (d,  $J = 10.8$  Hz, 1H), 1.82-1.70 (m, 1H), 0.95 (d,  $J = 6.5$  Hz, 3H), 0.40 (d,  $J = 6.2$  Hz, 3H), 0.23 (s, 9H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 145.7$ , 140.1, 127.9, 127.3, 126.7, 115.7, 103.6, 90.3, 59.8, 55.7, 30.1, 20.9, 19.6, 0.4. **MS** (70 eV, EI):  $m/z(\%)$ : 400 ( $\text{M}^+ - \text{H}$ , <1), 359 (29), 358 (100). **HRMS** (EI): calcd. for  $\text{C}_{27}\text{H}_{34}\text{NSi}$  [ $\text{M}^+ - \text{H}$ ]: 400.2461, found: 400.2485. **IR** (film): 2958 (m), 2158 (w), 1496 (w), 1249 (m), 1022 (w), 905 (m), 842 (vs), 778 (m), 696 (m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min}) = 31.1$  (-), 37.0 (+).

#### 4-Ethyl-*N,N*-bis(2-phenyl-2-propenyl)-1-(trimethylsilyl)-1-hexyn-3-amine (2d)



(*S*)-Quinap was used. Column chromatographic purification:  $\text{SiO}_2$ , pentane: ether = 99 : 1. Yield (racemic): 83 % (1.5 mmol scale, 532 mg), (nonracemic): 67 % (0.3 mmol scale, 86 mg).  $[\alpha]_{20}^D = 66$  ( $c = 0.48$ ,  $\text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz):  $\delta = 7.32\text{-}7.29$  (m, 4H), 7.23-7.16 (m, 6H), 5.44 (s, 2H), 5.29 (s, 2H), 3.81 (d,  $J = 13.4$  Hz, 2H), 3.31 (d,  $J = 10.1$  Hz, 1H), 3.15 (d,  $J = 13.4$  Hz, 2H), 1.63-1.09 (m, 5H), 0.78 (t,  $J = 7.1$  Hz, 3H), 0.42 (d,  $J = 7.7$  Hz, 3H), 0.23 (s, 9H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta = 145.6$ , 140.1, 127.9, 127.3, 126.7, 115.9, 103.6, 90.3, 55.8, 55.6, 41.0, 22.0, 20.0, 10.0, 9.6, 0.4. **MS** (70 eV, EI):  $m/z(\%)$ : 427 ( $\text{M}^+ - 2\text{H}$ , <1), 359 (31), 358 (100), 91 (15), 73 (23). **HRMS** (EI): calcd. for  $\text{C}_{29}\text{H}_{37}\text{NSi}$  [ $\text{M}^+ - 2\text{H}$ ]: 427.2695, found: 427.2719. **IR** (film): 2961 (s), 2157 (w), 1452 (w), 1250 (m), 906 (m), 843 (vs), 778 (m), 696 (m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min}) = 25.7$  (-), 30.8 (+).

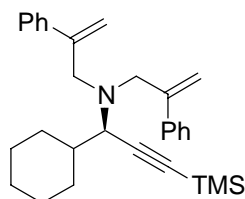
#### *N*-[1-Cyclopropyl-3-(trimethylsilyl)-2-propynyl]-2-phenyl-*N*-(2-phenyl-2-propenyl)-2-propen-1-amine (2e)





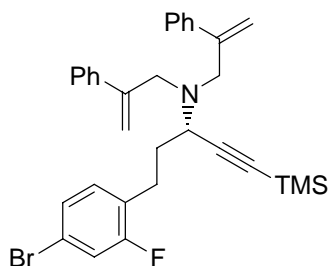
(*S*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 68 % (1.5 mmol scale, 406 mg); (nonracemic): 67 % (0.3 mmol scale, 80 mg).  $[\alpha]_{20}^D = 70$  ( $c = 0.63$ , CHCl<sub>3</sub>). **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz):  $\delta = 7.38$ -7.34 (m, 4H), 7.23-7.13 (m, 6H), 5.45 (s, 2H), 5.26 (s, 2H), 3.95 (d,  $J = 14.0$  Hz, 2H), 3.36 (t,  $J = 5.8$  Hz, 1H), 3.14 (d,  $J = 14.0$  Hz, 2H), 1.02-0.91 (m, 1H), 0.59-0.50 (m, 1H), 0.46-0.37 (m, 1H), 0.33-0.26 (m, 1H), 0.22 (s, 9H), -0.02--0.10 (m, 1H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta = 145.3$ , 139.7, 127.8, 127.3, 126.7, 115.6, 101.3, 90.4, 55.7, 50.3, 12.9, 4.0, 1.9, 0.4. **MS** (70 eV, EI):  $m/z(\%)$ : 399 (M<sup>+</sup>, 36), 358 (63), 297 (27), 296 (100), 117 (28), 115 (34), 97 (21), 91 (32), 73 (86), 59 (58). **HRMS** (EI): calcd. for C<sub>27</sub>H<sub>33</sub>NSi [M<sup>+</sup>]: 399.2382, found: 399.2353. **IR** (film): 3082 (w), 2959 (w), 2826 (w), 2159 (w), 1628 (w), 1496 (w), 1250 (m), 1026 (s), 904 (s), 843 (vs), 778 (s), 694 (m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min}) = 22.3$  (-), 27.1 (+).

***N*-[1-Cyclohexyl-3-(trimethylsilyl)-2-propynyl]-2-phenyl-*N*-(2-phenyl-2-propenyl)-2-propen-1-amine (2f)**



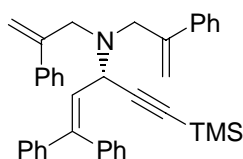
(*S*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 87 % (1.0 mmol scale, 384 mg); (nonracemic): 80 % (0.3 mmol scale, 106 mg).  $[\alpha]_{20}^D = 53$  ( $c = 0.47$ , CHCl<sub>3</sub>). **mp**: 75-76 °C **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz):  $\delta = 7.34$ -7.31 (m, 4H), 7.22-7.18 (m, 6H), 5.42 (s, 2H), 5.29 (s, 2H), 3.80 (d,  $J = 14.0$  Hz, 2H), 3.60 (t,  $J = 7.1$  Hz, 1H), 3.17-3.13 (m, 3H), 1.98 (d,  $J = 11.8$  Hz, 1H), 1.69 (d,  $J = 13.4$  Hz, 1H), 1.55-1.52 (m, 1H), 1.48-1.42 (m, 2H), 1.38-1.37 (m, 1H), 1.26-1.18 (m, 1H), 1.02-0.93 (m, 2H), 0.84-0.77 (m, 1H), 0.23 (s, 9H), 0.15-0.08 (m, 1H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta = 145.7$ , 140.2, 127.8, 127.3, 126.7, 115.7, 103.3, 90.5, 58.5, 55.7, 39.3, 31.1, 30.2, 26.6, 26.3, 25.8, 0.5. **MS** (70 eV, EI):  $m/z(\%)$ : 441 (M<sup>+</sup>, <1), 359 (28), 358 (100). **HRMS** (EI): calcd. for C<sub>30</sub>H<sub>39</sub>NSi [M<sup>+</sup>]: 441.2852, found: 441.2838. **IR** (film): 2921 (s), 2852 (m), 2162 (w), 1627 (w), 1496 (w), 1450 (w), 1250 (m), 907 (s), 854 (vs), 841 (vs), 778 (s), 705 (m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min}) = 36.3$  (-), 44.9 (+).

***N*-[1-[2-(4-Bromo-2-fluorophenyl)ethyl]-3-(trimethylsilyl)-2-propynyl]-*N,N*-bis(2-phenyl-2-propenyl)amine (2g)**



(*R*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 84 % (1.5 mmol scale, 709 mg) (nonracemic): 75 % (0.3 mmol scale, 126 mg).  $[\alpha]_D^{20} = -5$  ( $c = 0.82$ , CHCl<sub>3</sub>). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 7.35$ -7.19 (m, 10H), 7.16-7.08 (m, 2H), 6.75 (t,  $J = 8.3$  Hz, 1H), 5.46 (s, 2H), 5.31 (s, 2H), 3.85 (d,  $J = 13.7$  Hz, 2H), 3.55 (t,  $J = 7.4$  Hz, 1H), 3.23 (d,  $J = 13.7$  Hz, 2H), 2.45-2.35 (m, 1H), 2.25-2.15 (m, 1H), 1.90-1.80 (m, 2H), 0.26 (s, 9H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 160.9$  (d,  $J = 245$  Hz), 145.3, 139.7, 139.6, 131.5 (d,  $J = 6$  Hz), 128.0, 127.4, 126.9 (d,  $J = 4$  Hz), 126.6, 119.3 (d,  $J = 10$  Hz), 118.7 (d,  $J = 26$  Hz), 115.9, 103.4, 88.7, 55.5, 52.0, 32.9, 25.6, 0.3. MS (70 eV, EI):  $m/z$ (%): 559 (M<sup>+</sup>, <1), 359 (28), 358 (100). HRMS (EI): calcd. for C<sub>32</sub>H<sub>35</sub>BrFNSi [M<sup>+</sup>]: 559.1706, found: 559.1684. IR (film): 2958 (m), 2930 (m), 2159 (m), 1575 (m), 1455 (vs), 1404 (m), 1250 (s), 1124 (m), 907 (s), 843 (vs), 778 (vs), 696 (s). HPLC (OD-H, 99 % *n*-heptane/ 1 % *i*-propanol, 0.3 mL/min):  $t_r$ (min) = 42.4 (+), 48.8 (-).

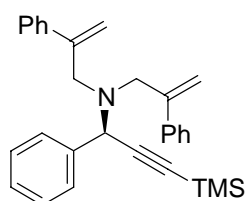
***N*-{3,3-Diphenyl-1-[(trimethylsilyl)ethynyl]-2-propenyl}-*N,N*-bis(2-phenyl-2-propenyl)amine (2h)**



(*R*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 74 % (1.5 mmol scale, 599 mg); (nonracemic): 83 % (0.3 mmol scale, 134 mg).  $[\alpha]_D^{20} = 44$  ( $c = 0.88$ , CHCl<sub>3</sub>). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta = 7.37$ -7.12 (m, 16H), 7.05-7.03 (m, 2H), 6.99-6.94 (m, 2H), 6.23 (d,  $J = 9.7$  Hz, 1H), 5.40 (s, 2H), 5.20 (s, 2H), 4.30 (d,  $J = 9.1$  Hz, 1H), 3.86 (d,  $J = 13.2$  Hz, 2H), 3.46 (d,  $J = 13.2$  Hz, 2H), 0.27 (s, 9H). <sup>13</sup>C-NMR (75 MHz, CDCl<sub>3</sub>):  $\delta = 144.7$ , 144.2, 142.6, 139.5, 138.5, 137.9, 129.9, 129.0, 128.5, 128.2, 128.1, 127.9, 127.7, 127.5, 127.2, 127.2, 126.6, 126.0, 125.3, 115.9, 103.3, 90.8,

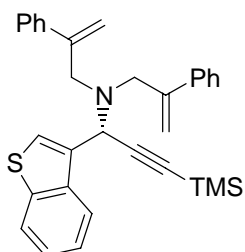
55.3, 51.7, 0.3. **MS** (70 eV, EI):  $m/z(\%)$ : 538 (14), 537 ( $M^+$ , 36), 464 (24), 370 (11), 344 (14), 290 (29), 359 (31), 289 (100), 274 (12), 117 (12), 115 (15), 97 (10), 91 (13), 73 (47). **HRMS** (EI): calcd. for  $C_{38}H_{39}NSi$  [ $M^+$ ]: 537.2852, found: 537.2854. **IR** (film): 3056 (m), 2959 (m), 2158 (m), 1495 (m), 1444 (m), 1250 (s), 998 (m), 906 (s), 844 (vs), 778 (s), 699 (vs). **HPLC** (OD-H, 99 % *n*-heptane/ 1 % *i*-propanol, 0.5 mL/min):  $t_r(\text{min})= 27.0 (+), 37.1 (-)$ .

**2-Phenyl-*N*-(2-phenyl-2-propenyl)-*N*-[1-phenyl-3-(trimethylsilyl)-2-propynyl]-2-propen-1-amine (2i)**



(*S*)-Quinap was used. Column chromatographic purification:  $SiO_2$ , pentane: ether = 99 : 1. Yield (racemic): 75 % (1.5 mmol scale, 490 mg); (nonracemic): 69 % (0.3 mmol scale, 90 mg).  $[\alpha]_{20}^D = 19$  ( $c = 0.58, CHCl_3$ ).  **$^1H$ -NMR** ( $CDCl_3$ , 300 MHz):  $\delta = 7.28-7.201$  (m, 6H), 7.17-7.08 (m, 9H), 5.50 (s, 2H), 5.34 (s, 2H), 4.83 (s, 1H), 3.76 (d,  $J = 13.3$  Hz, 2H), 3.20 (d,  $J = 13.3$  Hz, 2H), 0.35 (s, 9H).  **$^{13}C$ -NMR** (75 MHz,  $CDCl_3$ ):  $\delta = 145.3, 139.2, 138.1, 128.9, 127.8, 127.7, 127.3, 127.2, 126.8, 115.8, 100.4, 93.5, 55.9, 54.7, 0.4$ . **MS** (70 eV, EI):  $m/z(\%)$ : 435 ( $M^+$ , 21), 332 (28), 188 (17), 187 (100), 159 (49), 115 (11), 91 (11), 83 (11). **HRMS** (EI): calcd. for  $C_{30}H_{33}NSi$  [ $M^+$ ]: 435.2382, found: 435.2346. **IR** (film): 2959 (m), 2829 (m), 2162 (m), 1627 (m), 1494 (m), 1450 (m), 1250 (s), 1009 (s), 904 (s), 843 (vs), 778 (s), 758 (s), 703 (s). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min})= 36.7 (-), 45.5 (+)$ .

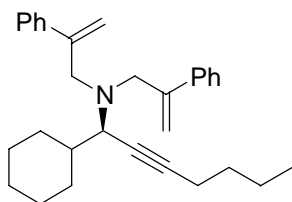
***N*-[1-(1-Benzothien-3-yl)-3-(trimethylsilyl)-2-propynyl]-2-phenyl-*N*-(2-phenyl-2-propenyl)-2-propen-1-amine (2j)**



(*R*)-Quinap was used. Column chromatographic purification:  $SiO_2$ , pentane: ether = 99 : 1. Yield (racemic): 66 % (1.5 mmol scale, 488 mg); (nonracemic): 58 % (0.3 mmol scale, 85 mg).  $[\alpha]_{20}^D = -78$  ( $c = 0.57, CHCl_3$ ). **mp.:** 89-92 °C  **$^1H$ -NMR** ( $CDCl_3$ , 300 MHz):  $\delta = 7.74$  (d,

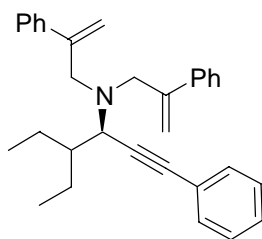
$J= 8.0$  Hz, 1H), 7.69 (dd,  $J= 10.7, 1.3$  Hz, 1H), 7.20-7.14 (m, 3H), 7.91-6.92 (m, 8H), 6.66 (tt,  $J= 8.0, 0.9$  Hz, 1H), 6.29 (d,  $J= 7.9$  Hz, 1H), 5.52 (s, 2H), 5.33 (s, 2H), 5.05 (s, 1H), 3.86 (d,  $J= 13.2$  Hz, 2H), 3.19 (d,  $J= 13.2$  Hz, 2H), 0.35 (s, 9H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta= 145.0, 140.4, 138.7, 137.5, 133.2, 127.9, 127.3, 126.8, 126.5, 124.0, 123.8, 123.5, 122.0, 116.2, 100.1, 92.6, 55.0, 52.0, 0.4$ . **MS** (70 eV, EI):  $m/z(\%)$ : 491 ( $\text{M}^+$ , 11), 248 (13), 244 (20), 243 (100), 215 (19), 203 (11), 171 (32). **HRMS** (EI): calcd. for  $\text{C}_{32}\text{H}_{33}\text{NSSi}$  [ $\text{M}^+$ ]: 491.2103, found: 491.2080. **IR** (film): 3082 (m), 3054 (m), 2959 (m), 2830 (m), 2160 (m), 1628 (m), 1495 (m), 1456 (m), 1428 (m), 1250 (s), 1106 (m), 968 (m), 903 (s), 843 (vs), 777 (vs), 759 (s), 693 (s). **HPLC** (OD-H, 99 % *n*-heptane/ 1 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min})= 35.4$  (+), 45.5 (-).

#### ***N*-(1-Cyclohexyl-2-heptynyl)-*N,N*-bis(2-phenyl-2-propenyl)amine (2k)**



(*S*)-Quinap was used. Column chromatographic purification:  $\text{SiO}_2$ , pentane: ether = 99 : 1. Yield (racemic): 62 % (1.5 mmol scale, 397 mg); (nonracemic): 81 % (0.3 mmol scale, 103 mg).  $[\alpha]_{20}^{\text{D}}$  = 30 ( $c = 0.60, \text{CHCl}_3$ ).  $^1\text{H-NMR}$  ( $\text{CDCl}_3, 300$  MHz):  $\delta= 7.32\text{-}7.31$  (m, 4H), 7.21-7.18 (m, 6H), 5.41 (s, 2H), 5.30 (s, 2H), 3.78 (d,  $J= 13.9$  Hz, 2H), 3.16 (d,  $J= 13.9$  Hz, 2H), 3.12 (d,  $J= 10.8$  Hz, 1H), 2.28 (td,  $J= 6.7, 2.1$  Hz, 2H), 1.98 (d,  $J= 12.9$  Hz, 1H), 1.70-1.67 (m, 1H), 1.58-1.32 (m, 9H), 1.26-1.17 (m, 2H), 1.01-0.95 (m, 2H), 0.96 (t,  $J= 7.4$  Hz, 3H), 0.79 (qd,  $J= 11.6, 3.3$  Hz, 1H), 0.17-0.11 (m, 1H).  $^{13}\text{C-NMR}$  (75 MHz,  $\text{CDCl}_3$ ):  $\delta= 145.9, 140.3, 127.8, 127.2, 126.7, 115.5, 86.3, 76.5, 57.8, 55.7, 39.8, 31.5, 31.3, 30.3, 26.6, 26.4, 25.9, 22.0, 18.4, 13.6$ . **MS** (70 eV, EI):  $m/z(\%)$ : 424 ( $\text{M}^+\text{-H}$ , <1), 343 (27), 342 (100). **HRMS** (EI): calcd. for  $\text{C}_{31}\text{H}_{38}\text{N}$  [ $\text{M}^+\text{-H}$ ]: 424.3004, found: 424.3012. **IR** (film): 2926 (vs), 2852 (m), 1495 (w), 1450 (m), 904 (m), 778 (m), 696(m). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min})= 31.9$  (-), 39.2 (+).

#### **4-Ethyl-1-phenyl-*N,N*-bis(2-phenyl-2-propenyl)-1-hexyn-3-amine (2l)**

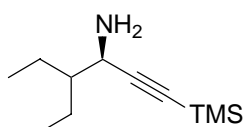


(*S*)-Quinap was used. Column chromatographic purification: SiO<sub>2</sub>, pentane: ether = 99 : 1. Yield (racemic): 85 % (1.0 mmol scale, 369 mg); (nonracemic): 73 % (0.3 mmol scale, 95 mg).  $[\alpha]_{20}^D = 84$  ( $c = 0.92$ , CHCl<sub>3</sub>). **mp**: 52-53 °C **<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz):  $\delta = 7.50$ -7.49 (m, 2H), 7.35-7.30 (m, 7H), 7.24-7.19 (m, 6H), 5.45 (s, 2H), 5.33 (s, 2H), 3.90 (d,  $J = 13.9$  Hz, 2H), 3.53 (d,  $J = 10.5$  Hz, 1H), 3.26 (d,  $J = 13.9$  Hz, 2H), 1.68-1.59 (m, 2H), 1.52-1.45 (m, 1H), 1.23-1.17 (m, 1H), 0.82 (t,  $J = 7.2$  Hz, 3H), 0.78-0.71 (m, 1H), 0.47 (t,  $J = 7.9$  Hz, 3H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>):  $\delta = 145.7$ , 140.1, 131.8, 128.2, 127.9, 127.7, 127.3, 126.7, 123.8, 116.0, 115.7, 87.1, 86.4, 55.9, 55.5, 41.4, 22.1, 20.1, 9.9, 9.7. **MS** (70 eV, EI):  $m/z(\%)$ : 432 ( $M^+ - H$ , <1), 363 (27), 362 (100), 115 (12). **HRMS** (EI): calcd. for C<sub>32</sub>H<sub>34</sub>N [ $M^+ - H$ ]: 432.2691, found: 432.2732. **IR** (film): 2963 (vs), 2934 (s), 2875 (m), 2829 (m), 1627 (w), 1490 (m), 1444 (m), 908 (s), 779 (s), 760 (s), 692(s). **HPLC** (OD-H, 100 % *n*-heptane/ 0 % *i*-propanol, 0.2 mL/min):  $t_r(\text{min}) = 53.9$  (–), 63.6 (+).

#### Typical procedure for the deprotection of the phenallyl-groups:

Pd(PPh<sub>3</sub>)<sub>4</sub> (5 mol%, 2.5 mol% per phenallyl) and 1,3-dimethylbarbituric acid (6 eq, 3 eq per phenallyl) were placed in a dried schlenk flask and evacuated for 15 min. After flushing with argon, dichloromethane (2 mL per mmol) was added. The phenallyl-protected amine was evacuated, flushed with argon and dissolved in dichloromethane (3 mL per mmol). The solution of the amine was added dropwise to the catalyst solution. Stirring was continued until TLC-analysis showed the disappearance of the starting material. The solvent was removed under reduced pressure and the slurry was taken up in diethyl ether. The organic phase was washed with sat. Na<sub>2</sub>CO<sub>3</sub> solution (2 x 25 mL) and afterwards extracted with 2M HCl (3 x 20 mL). The aqueous phase was washed with diethyl ether (20 mL) and afterwards neutralised with Na<sub>2</sub>CO<sub>3</sub> and extracted with diethyl ether (3x30 mL). The organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentration under reduced pressure yielded the desired primary amine.

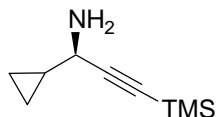
#### 1-(1-Ethylpropyl)-3-(trimethylsilyl)-2-propynylamine (6a)



The reaction was carried out on a 0.30 mmol scale (67 % yield, 39 mg).

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 3.60 (d, *J*= 5.0 Hz, 1H), 1.75 (s, 2H), 1.57-1.23 (m, 5H), 0.91 (t, *J*= 7.5 Hz, 3H), 0.90 (t, *J*= 7.1 Hz, 3H), 0.13 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 109.0, 87.1, 47.2, 46.3, 22.5, 22.0, 11.7, 11.6, 0.0. **MS** (70 eV, EI): *m/z*(%): 197 (M<sup>+</sup>, <1), 127 (13), 126 (100), 98 (18)). **IR** (film): 2962 (s), 2163 (m), 1250 (m), 842 (vs), 760 (m).

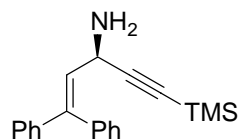
### 1-Cyclopropyl-3-(trimethylsilyl)-2-propyn-1-amine (6b)



The reaction was carried out on a 0.92 mmol scale (75 % yield, 116 mg).

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 3.48-3.44 (m, 1H), 1.70 (s, 2H), 1.08-0.99 (m, 1H), 0.48-0.30 (m, 4H), 0.12 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 107.2, 86.8, 47.2, 16.9, 3.0, 1.3, 0.0. **MS** (70 eV, EI): *m/z*(%): 166 (M<sup>+</sup>-H, 10), 139 (15), 127 (11), 126 (100), 124 (54), 98 (39), 94 (42), 86 (12), 83 (17), 74 (36), 73 (26), 59 (11) 43 (13). **HRMS** (EI): calcd. for C<sub>9</sub>H<sub>16</sub>NSi [M<sup>+</sup>-H]: 166.1052, found: 166.1024. **IR** (film): 2960 (m), 2166 (m), 1250 (s), 843 (vs), 760 (m).

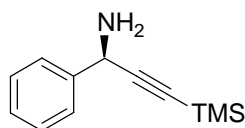
### 1,1-Diphenyl-5-(trimethylsilyl)-1-penten-4-yn-3-amine (6c)



The reaction was carried out on a 0.70 mmol scale (83 % yield, 178 mg). The acidic/basic extraction failed for this compound, therefore, the reaction was taken up in diethyl ether, washed with Na<sub>2</sub>CO<sub>3</sub> (2x 25 mL) and the organic phase was dried (Na<sub>2</sub>SO<sub>4</sub>) and concentrated *in vacuo*. The crude product was purified by column chromatography (Silica, pentane/ether 2:1 to 0:1 with 1 vol% NEt<sub>3</sub>).

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 7.44-7.33 (m, 4H), 7.31-7.27 (m, 6H), 6.08 (d, *J*= 9.4 Hz, 1H), 4.26 (d, *J*= 9.4 Hz, 1H), 1.65 (s, 2H), 0.22 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 142.3, 141.6, 138.9, 129.8, 129.2, 128.3, 128.1, 127.7, 127.6, 127.5, 107.9, 87.3, 43.2, 0.0. **MS** (70 eV, EI): *m/z*(%): 306 (24), 305 (M<sup>+</sup>, 100), 304 (32), 290 (14), 288 (13), 273 (26), 233 (20), 232 (98), 229 (11), 228 (40), 215 (23), 206 (11), 165 (12) 73 (15). **HRMS** (EI): calcd. for C<sub>20</sub>H<sub>23</sub>NSi [M<sup>+</sup>]: 305.1600, found: 305.1577. **IR** (film): 3058 (m), 2958 (m), 2167 (m), 1598 (m), 1494 (m), 1445 (m), 1250 (s), 843 (vs), 763 (s) 700 (vs).

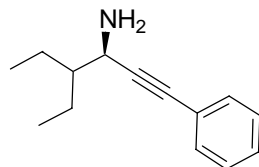
### 1-Phenyl-3-(trimethylsilyl)-2-propyn-1-amine (6d)



The reaction was carried out on a 0.90 mmol scale (77 % yield, 141 mg).

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 7.57-7.54 (m, 2H), 7.41-7.28 (m, 3H), 4.79 (s, 1H), 1.76 (s, 1H), 1.80 (s, 1H), 0.22 (s, 9H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 141.9, 128.5, 127.6, 126.8, 108.0, 88.5, 48.1, 0.0. **MS** (70 eV, EI): m/z(%): 203 (M<sup>+</sup>, 18), 202 (37), 160 (46), 159 (18), 131 (15), 130 (95), 126 (32), 125 (71), 110 (21), 98 (22), 83 (19), 77 (20), 74 (33), 73 (100). **IR** (film): 2959 (m), 2168 (m), 1602 (m), 1493 (m), 1451 (m), 1250 (s), 1011 (m), 8432 (vs), 760 (s), 698(s).

### 4-Ethyl-1-phenyl-1-hexyn-3-amine (6e)



The reaction was carried out on a 0.78 mmol scale (90 % yield, 142 mg).

**<sup>1</sup>H-NMR** (CDCl<sub>3</sub>, 300 MHz): δ= 7.44-7.39 (m, 2H), 7.32-7.28 (m, 3H), 3.88 (d, *J*= 4.5 Hz, 1H), 1.76 (s, 2H), 1.68-1.41 (m, 5H), 0.99 (t, *J*= 7.0 Hz, 3H), 0.98 (t, *J*= 7.6 Hz, 3H). **<sup>13</sup>C-NMR** (75 MHz, CDCl<sub>3</sub>): δ= 131.5, 128.2, 127.8, 123.5, 92.1, 83.2, 47.6, 46.2, 22.7, 22.1, 11.8, 11.6. **MS** (70 eV, EI): m/z(%): 200 (M<sup>+</sup>-H, <1), 131 (7), 130 (100), 103 (6). **HRMS** (EI): calcd. for C<sub>14</sub>H<sub>18</sub>N [M<sup>+</sup>-H]: 200.1439, found: 200.1433. **IR** (film): 2962 (vs), 2929 (s), 2875(s), 1598 (m), 1490 (s), 1461 (m), 756 (vs), 691(s).

### Literature:

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[2] S. F. Reed, *J. Org. Chem.* **1965**, *30*, 3258.