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Practical Highly Enantioselective Synthesis of Propargylamines through a Copper-Catalyzed One-Pot Three-Component Condensation Reaction

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Abstract: The one-pot three-component reaction of terminal alkynes, aldehydes and secondary amines in the presence of copper(I) bromide/quinap is reported. The reaction scope has been determined and a broad variety of all three components has been used, which afforded the corresponding propargylamines in good to excellent yields and moderate to very good enantioselectivities. The reaction showed a strong positive nonlinear effect. The transformation of a propargylamine intermediate into the alkaloid (*S*)-(+)-coniine has also been described.

Keywords: alkynes · asymmetric catalysis · C–H activation · multicomponent reactions · organocatalysis · propargylamine

Introduction

One of the most challenging tasks in organic synthesis is the efficient preparation of complex molecules starting from easily available raw materials. Especially attractive are multicomponent reactions which allow the formation of several bonds including new carbon–carbon bonds in a one-pot procedure.[1] This type of reaction plays an important role in modern organic chemistry, since it exhibits generally a high atom economy[2] and selectivity, as well as a lower level of by-products compared with classical stepwise synthesis. The Strecker reaction, developed in 1850, has been recognized as the first multicomponent reaction.[3] This three-component coupling of an amine, a carbonyl compound and hydrogen cyanide giving α-aminonitriles establishes an important route to α-amino acids. The amino group itself is one of the fundamental structures in organic chemistry. Amines and their derivatives are widespread functional groups which are found in various natural products, pharmaceuticals and fine biologically important chemicals.[4] Propargylamines are both biologically relevant and useful synthetic intermediates for the preparation of polyfunctional amino derivatives.[5] Recently, we[6] and others[7] have developed an asymmetric multicomponent one-pot copper-catalyzed preparation of propargylamines by the addition of alkynes to in situ generated iminium ions from aldehydes and secondary amines. In this paper, we disclose detailed studies on the parameters influencing the outcome of this asymmetric reaction. Furthermore, we demonstrate its broad scope and synthetic utility.

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Results and Discussion

The three-component coupling of terminal alkynes **1**, aldehydes **2** and secondary amines **3** in the presence of copper(I) bromide (5 mol%) and guinap[8] (5.5 mol%) as the catalytic system was found to be a highly efficient process. The desired propargylamines of type **4** are obtained in general high yield and moderate to excellent enantioselectivities (Scheme 1).

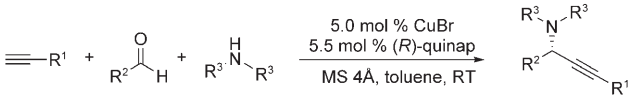
Scheme 1. Asymmetric three-component synthesis of propargylamines.

Variations in all three components were carried out and a broad substrate scope was found. Thus, various mono-substituted and protected terminal alkynes **1** were investigated, as well as various aldehydes **2**. Aliphatic as well as aromatic aldehydes were successfully used in this reaction, but aliphatic aldehydes were usually leading to higher enantioselectivities. As amine component, different types of aliphatic secondary amines **3** were successfully used in the reaction. Special at-

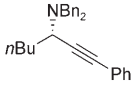
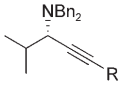
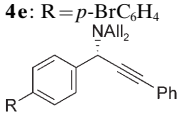
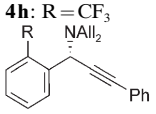
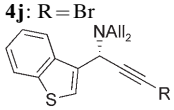
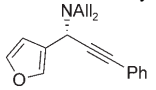
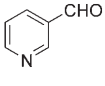
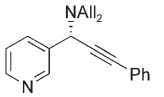
tention was paid to reactions using dibenzylamine (**3a**) and diallylamine (**3b**) as amine component, since these substituents can be removed by standard protecting group methodologies.[9] Furthermore, the sterical demand of the benzyl groups in dibenzylamine (**3a**) was found to be especially well suited for achieving high enantioselectivities. Amines derived from anilines as well as amides were found not to be suited for the formation of the desired propargylamines. A summary of the products obtained by this method is displayed in Table 1.

The conversion is usually completed within 12–48 h for the racemic reaction performed without ligand and within 1–6 d for the enantioselective reaction. Different alkynes **1a–d** bearing either a phenyl, an alkyl or an alkenyl group

Table 1. Enantioselective three-component one-pot synthesis of propargylamines **4**.



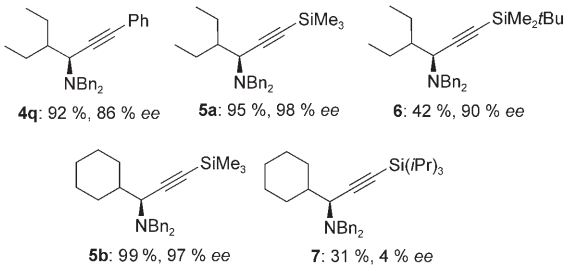
1 **2** **3** **4**

Entry	Alkyne (R^1) **1**	Aldehyde (R^2) **2**	Amine (R^3) **3**	Propargylamine **4**	Yield [%][a]	*ee* [%][b]
1	**1a**: R^1 = Ph	**2a**: R^2 = *n*Bu	**3a**: R^3 = Bn	 **4a**	85	83
2	**1a**: R^1 = Ph	**2b**: R^2 = *i*Bu	**3a**: R^3 = Bn	**4b**: R = Ph	98	86
3	**1b**: R^1 = *n*Bu	**2b**: R^2 = *i*Bu	**3a**: R^3 = Bn	**4c**: R = *n*Bu 	85	82
4	**1a**: R^1 = Ph	**2c**: R^2 = *i*Pr	**3a**: R^3 = Bn	**4d**: R = Ph	60	84
5	**1c**: R^1 = *p*-BrC_6H_4	**2c**: R^2 = *i*Pr	**3a**: R^3 = Bn	**4e**: R = *p*-BrC_6H_4 	99	83
6	**1a**: R^1 = Ph	**2d**: R^2 = Ph	**3b**: R^3 = allyl	**4f**: R = H	91	70
7	**1a**: R^1 = Ph	**2e**: R^2 = *p*-MeO-C_6H_4	**3b**: R^3 = allyl	**4g**: R = OMe	76	60
8	**1a**: R^1 = Ph	**2f**: R^2 = *p*-CF_3-C_6H_4	**3b**: R^3 = allyl	**4h**: R = CF_3 	43	63
9	**1a**: R^1 = Ph	**2g**: R^2 = *o*-CH_3-C_6H_4	**3b**: R^3 = allyl	**4i**: R = Me	84	32
10	**1a**: R^1 = Ph	**2h**: R^2 = *o*-Br-C_6H_4 	**3b**: R^3 = allyl	**4j**: R = Br 	83	25
11	**1a**: R^1 = Ph	**2i**	**3b**: R^3 = allyl	**4k**: R = Ph	80	78
12	**1d**: R^1 = *c*-hexenyl	**2i**	**3b**: R^3 = allyl	**4l**: R = *c*-hexenyl	61	74
13	**1a**: R^1 = Ph	**2j** 	**3b**: R^3 = allyl	**4m** 	55	64[c]
14	**1a**: R^1 = Ph	**2k** 	**3b**: R^3 = allyl	**4n** 	63	44
15	**1a**: R^1 = Ph	**2l**	**3b**: R^3 = allyl	**4o**: R = allyl	85	70
16	**1a**: R^1 = Ph	**2l**	**3a**: R^3 = Bn	**4p**: R = Bn	84	76

[a] Isolated yield of analytically pure product. [b] Enantiomeric excess determined by HPLC using a Chiracel OD-H column (*n*-heptane/*i*PrOH). [c] The *ee* value was determined after deprotection to give the monodeallylated derivative.

were successfully utilized. In this study, phenylacetylene (**1a**) gave the best selectivities. Branched as well as unbranched aliphatic aldehydes **2a–c** were successfully used as substrates (entries 1–5). Their reaction with dibenzylamine (**3a**) as the amine component led to high enantioselectivities (82–86% *ee*). For aromatic aldehydes, it was found that the presence of either an electron-donating or an electron-withdrawing substituent in *para*-position has only a moderate influence on the reaction enantioselectivity (compare entries 6–8, 60–70% *ee*). However, the yield of product **4h** (R = CF_3) was strongly reduced (entry 8, 43%) compared with that of **4f** (R = H) and **4g** (R = OMe) (91 and 76%, entries 6–7). A substituent in the *ortho*-position to the aldehyde function has a stronger influence on the enantioselectivity of the reaction, probably due to the steric hindrance. The use of 2-methylbenzaldehyde (**2g**) and 2-bromobenzaldehyde (**2h**) furnished products **4i–j** with dramatically decreased enantiomeric excesses (32 and 25% *ee*, respectively). Heteroaromatic aldehydes **2i–k** were also compatible and allowed the preparation of propargylamines **4k–n** with moderate to good selectivities (44–78% *ee*, entries 11–14). Herein, the use of 3-pyridinecarbaldehyde (**2k**) was leading to products with remarkably lower enantioselectivities than the five-membered heterocyclic derivatives 2-benzothienylcarbaldehyde (**2i**) and 3-furancarbaldehyde (**2j**). Furthermore, ferrocenecarbaldehyde (**2l**) was successfully reacted with phenylacetylene (**1a**) and either dibenzylamine (**3a**) or diallylamine (**3b**) leading to products **4p** and **4o** with 76 and 70% *ee*, respectively (entries 15 and 16).

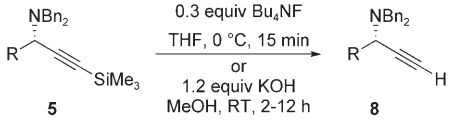
The preparation of terminal propargylamines was then investigated. The reaction with acetylene itself was investigated in previous studies in the related addition of alkynes to enamines.[10] The mono-addition product was found to be the major product. Unfortunately, it was not possible to obtain high enantioselectivities using acetylene as alkyne component. Therefore, we have examined various monoprotected alkynes in the propargylamine synthesis (Scheme 2).



Scheme 2. Alkyne protecting groups in the asymmetric propargylamine synthesis.

As can be seen from Scheme 2, the size of the alkyne substituent plays a crucial role for the enantioselectivity of the reaction. Compared with phenylacetylene as in for example in propargylamine **4q**, the introduction of a trimethylsilyl group in propargylamine **5a** led to an increase of the *ee* value (98 compared with 86% *ee*). The trimethylsilyl group as alkyne substituent was found to be optimal for the enantioselectivity of the three-component reaction. Changing from a trimethylsilyl group to a *tert*-butyldimethylsilyl group (compare **5a** vs **6** in Scheme 2) is leading to a decreased selectivity (**5a**: 98% *ee*; **6**: 90% *ee*). The use of triisopropylsilylacetylene is leading to an almost racemic mixture and proceeds very sluggishly. Trimethylsilyl-substituted propargylamine **5b** was obtained in 99% yield and 97% *ee*, whereas the triisopropylsilyl-derivative **7** was obtained with only 31% yield and 4% *ee* (Scheme 2).

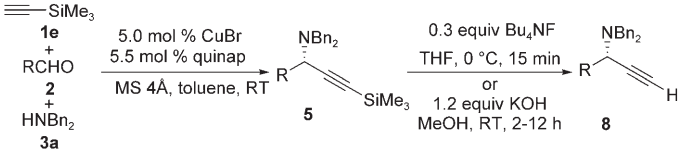
Furthermore, the trimethylsilyl group was easily removed by treatment of the silylated propargylamines **5** with Bu_4NF in THF or with KOH in MeOH (Scheme 3).

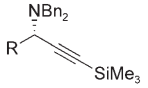
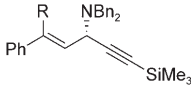
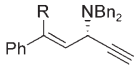
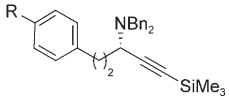
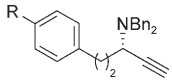
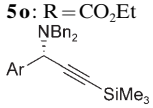


Scheme 3. Preparation of terminal propargylamines **8**.

Silylated propargylamines **5** and terminal propargylamines **8** obtained by this method are shown in Table 2. Reaction of trimethylsilylacetylene (**1e**) with dibenzylamine (**3a**) and various aldehydes **2** in the presence of CuBr and quinap led to silylated propargylamines **5** in high yields and exceptionally high enantioselectivities. Various aliphatic and aromatic aldehydes were successfully used. Unbranched aliphatic aldehydes **2a, m, n** (R = *n*Pr, *n*Bu, *n*-pent) provide the expected propargylamines **5c–e** in 88–90% *ee* and 82–99% yield. The introduction of a branch in β-position of the aldehyde (entries 4–5) is leading to an increased selectivity, giving **5f–g** in 94% *ee* and 85–94% yield. Further improvement of the selectivity was achieved using α-branched aldehydes such as **2c** und **2p**. The propargylamines **5h** and **5a** were obtained in 96 and 98% *ee*, respectively. Aldehydes bearing cyclic aliphatic substituents were also successfully used, leading to propargylamines **5i**, **5j** and **5b** with 92–97% *ee*. The selectivity increased with the size of the cycloalkyl residue. Cinnamaldehydes reacted likewise giving propargylamines **5k–l** in 82–84% *ee* and 82–96% yield. Dihydrocinnamaldehydes were also reacted successfully leading to propargylamines **5m–o**. Functional groups on the aromatic ring such as ester- and bromo-substituents were well tolerated and no decrease of the enantioselectivity was observed (entries 13–15, 87–88% *ee*, 73–96%). For aromatic aldehydes, the enantioselectivity was generally lower than for aliphatic aldehydes. The carbocyclic aldehydes **2d** and **2y** led to propargylamines **5p–q** in 68 and 54% *ee*, respectively (entries 16–17). Interestingly, thienyl- and benzothienylcarbaldehydes (**2y–2ab**) gave propargylamines **5r–u** with usually high enantioselectivities. A higher selectivity was observed for propargylamines derived from heterocycles with an aldehyde function in 2-position to sulfur (80 vs 74% *ee*, entries 18 and 19; 89 vs 82% *ee*, entries 20 and 21). Most of the silylated propargylamines **5** were transformed further to the terminal prop-

Table 2. Enantioselective three-component one-pot synthesis of silylated propargylamines **5** and desilylation to terminal propargylamines **8**.

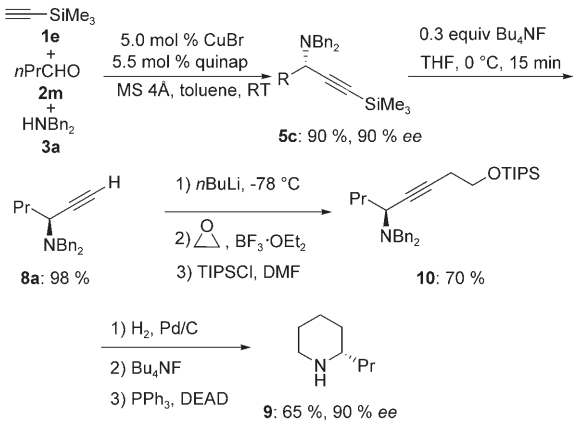


Entry	Aldehyde **2**	Propargylamine **5**	Yield [%][a]	*ee* [%][b]	Propargylamine **8**	Yield [%][a]
						
1	**2m**: *n*PrCHO	**5c**: R = *n*Pr	90	90[c]	**8a**: R = *n*Pr	98[e]
2	**2a**: *n*BuCHO	**5d**: R = *n*Bu	82	90[c]	**8b**: R = *n*Bu	92[e]
3	**2n**: *n*PentCHO	**5e**: R = *n*Pent	99	88[d]	**8c**: R = *n*Pent	96[e]
4	**2b**: *i*BuCHO	**5f**: R = *i*Bu	85	94[d]	**8d**: R = *i*Bu	99[e]
5	**2o**: *neo*-PentCHO	**5g**: R = *neo*-Pent	94	94[d]	**8e**: R = *neo*-Pent	99[e]
6	**2c**: *i*PrCHO	**5h**: R = *i*Pr	87	96[c]	**8f**: R = *i*Pr	96[e]
7	**2p**: *s*-PentCHO	**5a**: R = *s*-Pent	95	98[c]	**8g**: R = *s*-Pent	98[e]
8	**2q**: *c*-PrCHO	**5i**: R = *c*-Pr	98	92[c]	**8h**: R = *c*-Pr	99[e]
9	**2r**: *c*-PentCHO	**5j**: R = *c*-Pent	98	96	**8i**: R = *c*-Pent	99[e]
10	**2s**: *c*-HexCHO	**5b**: R = *c*-Hex	86	97[c]	**8j**: R = *c*-Hex	93[e]
						
11	**2t**: PhCH=CH-CHO	**5k**: R = H	96	82[c]	**8k**: R = H	97[f]
12	**2u**: Ph_2C=CH-CHO	**5l**: R = Ph	82	84[c]	**8l**: R = Ph	97[f]
						
13	**2v**: $Ph(CH_2)_2CHO$	**5m**: R = H	78	88[c]	**8m**: R = H	98[e]
14	**2w**: 4-Br-C_6H_4-$(CH_2)_2CHO$	**5n**: R = Br	73	88[c]	**8n**: R = Br	98[e]
15	**2x**: 4-CO_2Et-$C_6H_4(CH_2)_2CHO$	**5o**: R = CO_2Et	96	87	**8o**: R = CO_2Et	90[e]
						
16	**2d**: PhCHO	**5p**: Ar = Ph	98	68		
17	**2y**: 2-naphthyl-CHO	**5q**: Ar = 2-naphthyl	69	54		
18	**2z**: 2-thiophen-CHO	**5r**: Ar = 2-thienyl	81	80[c]	**8p**:Ar = 2-thienyl	99[f]
19	**2aa**: 3-thiophen-CHO	**5s**: Ar = 3-thienyl	85	74[c]	**8q**: Ar = 3-thienyl	99[f]
20	**2ab**: 2-benzothiophenyl-CHO	**5t**: Ar = 2-benzothienyl	42	89		
21	**2i**: 3-benzothiophenyl-CHO	**5u**:Ar = 3-benzothienyl	92	82	**8r**: Ar = 3-benzothienyl	93[f]

[a] Isolated yield of analytically pure product. [b] Enantiomeric excess determined by HPLC analysis using Chiracel OD-H column (*n*-heptane/*i*PrOH). [c] The *ee* was determined after desilylation. [d] The *ee* was determined after acylation with PhCOCl. [e] Desilylation was carried out with Bu_4NF. [f] Desilylation was carried out with KOH.

argylamines **8** by treatment with either Bu_4NF or aq. KOH. The yields were generally high (90–99%, see Table 2).

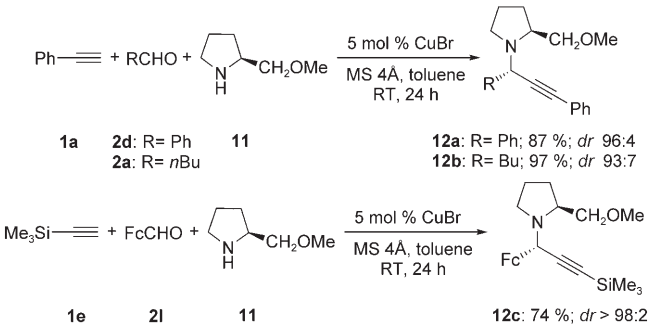
These terminal propargylamines can be further functionalized by known methods.[11] The synthetic utility of the method was shown in a short enantioselective synthesis of (*S*)-(+)-coniine (**9**).[12] Coniine is a highly toxic alkaloid inducing curare-type paralysis. It is the main alkaloid of the Schierling mushroom and used to poison Socrates 399 B.C. The synthesis is depicted in Scheme 4 and starts with the preparation of the chiral propargylamine **5c**, which was obtained in 90% yield and 90% *ee* from commercially available starting materials. After desilylation giving **8a**, the terminal propargylamine was deprotonated with *n*BuLi (1.2 equiv) and alkylated with ethylene oxide (3 equiv) in the presence of $BF_3{\cdot}OEt_2$ (1.2 equiv) under mild conditions (−78 °C, 2 h).[13] Silylation of the alcohol with TIPSCl



Scheme 4. Enantioselective synthesis of (*S*)-(+)-coniine **9**.

(1.1 equiv) in the presence of DMAP (5 mol%) and imidazole (1.5 equiv) in DMF (0°C to RT, 12 h) led to TIPS-protected derivative **10** in 70% overall yield. Hydrogenolysis of the benzyl groups and reduction of the triple bond was readily achieved by hydrogenation (1 atm) of **10** in methanol in the presence of Pd/C (10 mol%). The silyl-protected aminoalcohol was desilylated with Bu_4NF (THF, RT, 12 h) and subsequently submitted to an intramolecular Mitsunobu reaction (DEAD (1.1 equiv), PPh_3 (1.1 equiv), THF, −10°C to RT, 12 h).[14] (*S*)-(+)-coniine (**9**) was obtained in five steps with 41% overall yield and 90% *ee* (see Scheme 4).

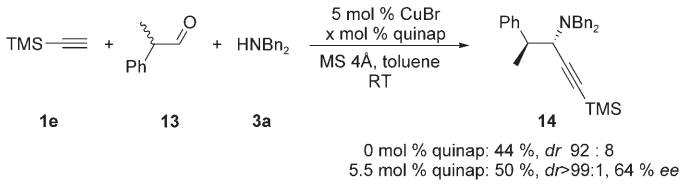
Furthermore, the propargylamine synthesis is highly diastereoselective if a chiral amine or aldehyde is used. Thus, the reaction of the proline-derived methoxymethylpyrrolidine (**11**) with benzaldehyde (**2d**) or valeraldehyde (**2a**) and phenylacetylene (**1a**) produced the corresponding propargylamines **12a** and **12b** in yields of 87 and 97% and good diastereoselectivities of 96:4 and 93:7, respectively. By reacting ferrocenecarbaldehyde (**2l**) with trimethylsilylacteylene (**1e**) and amine **11**, the corresponding propargylamine **12c** was obtained with a diastereoselectivity of >98:2 (Scheme 5).



Scheme 5. Diastereoselective propargylamine synthesis with amine **11**.

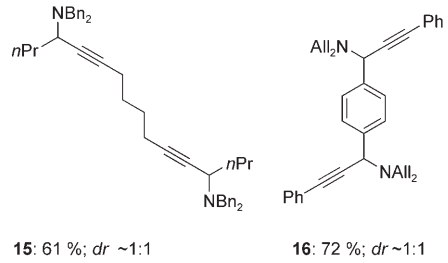
By reacting racemic hydratropaldehyde **13** with dibenzylamine (**3a**) and trimethylsilylacetylene (**1e**) without the addition of the quinap ligand, the corresponding propargylamine **14** is also obtained in good diastereoselectivity (92:8). Addition of the chiral ligand led to **14** with an increased diastereoselectivity (>99:1) and 64% *ee* (Scheme 6). The relative conformation has been determined by X-ray structure analysis.[15]

Interestingly, diines and dialdehydes can also be used in the propargylamine synthesis leading to propargyldiamines



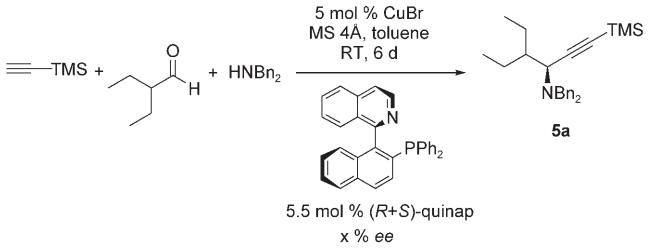
Scheme 6. Diastereoselective propargylamine synthesis with aldehyde **13**.

15 and **16** (Scheme 7). A drawback of this interesting variation of the reaction is that no diastereoselectivity was observed in the synthesis of diamines **15** and **16**.



Scheme 7. Propargyldiamines **15** and **16**.

Mechanistic investigations show that the enantioselective propargylamine synthesis displays a strong positive nonlinear effect as discussed previously.[6a] Using the quinap ligand with only 5% *ee*, the propargylamine **5a** is still obtained



with 50% *ee*. Furthermore, the reaction rate and the yield are approximately linear correlated to the enantiomeric excess of the ligand (Figure 1).

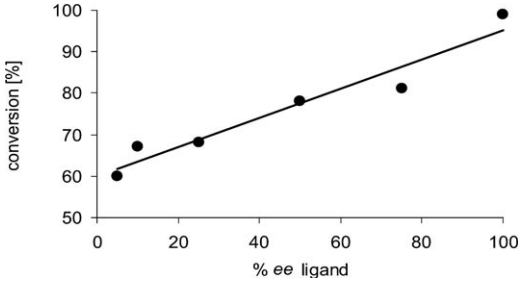


Figure 1. Influence of the enantiomeric excess on the reaction rate in the synthesis of **5a**.

As can be seen from Figure 1, the reaction rate decreases with a decreasing enantiomeric excess of the ligand. This is in accordance with the model of the reservoir effect described first by Kagan.[16] According to this model, the Cu/quinap catalyst forms dimeric species $[Cu_2quinap_2]$, which is in good agreement with the previously reported crystal structure of the $[CuBr\{(R)\text{-quinap}\}]_2$ complex.[10a] The heterochiral complex $[Cu_2Br_2\{(R)/(S)\text{-quinap}\}]$ seems to react at a much slower rate than the corresponding homochiral com-

plex [Cu_2Br_2\{(*R*)/(*R*)-quinap\}]. This explains the strong positive amplification. Since the minor enantiomer of the ligand is kept in the more stable and less reactive complex, the amount of reactive, homochiral copper/quinap complexes decreases with the % *ee* of the ligand. The reservoir model also explains the decrease in the reaction rate with the % *ee* of the ligand. Based on these and previous results, we have suggested a tentative mechanism (see ref. [6a]).

The dimeric chiral copper compound **17** forms a complex with alkyne **1**, leading to a side-on complex **18**. Aminal **19**, formed by reaction of the aldehyde **2** with the secondary amine **3**, coordinates to the copper complex **18** to give complex **20**. Deprotonation of the coordinated alkyne and elimination of H_2O led to complex **21**, an end-on copper acetylide with a coordinated iminium ion. The addition of the acetylide to the iminium ion in the coordination sphere of the chiral copper(I) complex led to chiral propargylamine **4** or **5**, respectively, and regenerates the catalyst **17**.

Conclusion

The one-pot three-component synthesis of propargylamines displays a simple and versatile method for the preparation of this interesting type of structures in asymmetric fashion with up to 98% *ee*. The mild reaction conditions and the broad scope of the reaction illustrates the good synthetic utility of this method. The reaction is a highly atom economic process producing only water as a side product. The applicability of chiral propargylamines in natural product synthesis was successfully shown in the total synthesis of the alkaloid (*S*)-(+)-coniine.

Experimental Section

General considerations: Unless otherwise indicated, all reactions were carried out under argon and with dried solvents (THF, Et_2O, toluene, dichloromethane, pentane, methanol). Reactions were monitored by gas chromatography (GC, GC-MS) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots. For all enantioselective reactions, the racemic mixtures of the products were prepared first and baseline separation of the two enantiomers were achieved by using HPLC analysis.

Experimental procedures and data of the following products have already been reported: **4b–i**, **4k–m**, **12a**,**b**;[6a] **5c**, **8a**, **9**, **10**. [6b]

Starting materials: The following starting materials were prepared according to literature procedures: 3-(4-bromophenyl)propanal (**2w**),[17] ethyl 4-(3-oxopropyl)benzoate (**2x**),[17] 2-benzothienylcarbaldehyde (**2ab**),[18] and 4-bromophenylacetylene (**1c**).[19]

***N*,*N*-Dibenzyl-5-methyl-1-phenyl-1-hexyn-3-amine (4a)**

General procedure A: A dry and argon flushed 10 mL flask, equipped with a magnetic stirrer and a septum, was charged with copper(I) bromide (3.6 mg, 0.025 mmol) and (*R*)-quinap (12.1 mg, 0.0275 mmol). Dry toluene (2 mL) was added, the mixture was stirred at RT for 30 min. 4 Å MS (0.3 g) was added, followed by phenylacetylene (**1a**) (51 mg, 0.5 mmol), valeraldehyde (**2a**) (43 mg, 0.5 mmol) and dibenzylamine (**3a**) (99 mg, 0.5 mmol). The reaction mixture was stirred for 48 h at RT. 4 Å MS was removed by filtration filtered and washed with Et_2O. The crude product was concentrated in vacuo and purified by chromatography on silica gel (pentane/Et_2O 99:1) yielding propargylamine (−)-**4a** (156 mg, 85%, 83% *ee*) as a colourless oil. $[\alpha]_D^{20} = -239$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.44$–7.10 (m, 15H), 3.80 (d, $J = 13.7$ Hz, 2H), 3.51 (t, $J = 7.4$ Hz, 1H), 3.40 (d, $J = 13.8$ Hz, 2H), 1.78–1.56 (m, 2H), 1.46–1.23 (m, 2H), 1.14 (sext, $J = 7.2$ Hz, 2H), 0.78 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 139.9$, 131.8, 128.8, 128.3, 128.2, 127.8, 126.8, 123.6, 88.1, 85.2, 55.0, 52.2, 33.6, 28.6, 22.3, 13.5; MS: *m*/*z* (%): 310 (100) [$M^+ - C_4H_9$), 218 (3), 128 (2), 115 (7), 91 (57); HRMS (EI): *m*/*z*: calcd for $C_{27}H_{33}N$: 366.2222; found: 366.2215 [$M^+ - H$]; IR (film): $\tilde{\nu}$ = 3062 (w), 3029 (w), 2955 (s), 2932 (s), 1599 (m), 1490 (s), 1454 (s), 755 (vs), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{27}H_{33}N$: C 88.24, H 7.95, N 3.81; found: C 87.85, H 7.84, N 3.73; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_R = 45.4 (+), 53.8 min (−).

***N*,*N*-Diallyl-*N*-[1-(2-bromphenyl)-3-phenyl-2-propynyl]amine (4j)**: The reaction was carried out according to GP A with phenylacetylene (**1a**) (51 mg, 0.50 mmol), 2-brombenzaldehyde (**2h**) (93 mg, 0.50 mmol) and diallylamine (**3b**) (49 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 5 d. Column chromatographic purification on silica gel (pentane/Et_2O 98:2) yielded propargylamine (−)-**4j** (151 mg, 0.42 mmol, 83%, 25% *ee*) as a colorless oil. $[\alpha]_D^{20} = -20$ ($c = 1.10$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.84$–7.80 (m, 1H), 7.59–7.50 (m, 3H), 7.36–7.25 (m, 4H), 7.16 (td, $J = 8.9$, 3.1 Hz, 1H), 5.99–5.85 (m, 2H), 5.32 (s, 1H), 5.24 (d, $J = 17.8$ Hz, 2H), 5.12 (d, $J = 9.0$ Hz, 2H), 3.40–3.33 (m, 2H), 3.08 (dd, $J = 14.9$, 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 138.0$, 136.2, 133.4, 131.8, 131.4, 129.2, 128.3, 128.2, 126.8, 124.9, 123.1, 117.2, 88.3, 85.2, 57.2, 53.9; MS (70 eV, EI): *m*/*z* (%): 366 (16) [M^+], 364 (15), 272 (21), 271 (97), 270 (20), 269 (100), 211 (13), 210 (71), 192 (12), 191 (25), 190 (20), 189 (99), 188 (14), 187 (12), 163 (10); HRMS (EI): *m*/*z*: calcd for $C_{21}H_{20}BrN$: 365.0779; found: 365.0741 [M^+]; IR (film): $\tilde{\nu}$ = 3071 (m), 2815 (m), 1642 (m), 1568 (m), 1490 (s), 1470 (s), 1441 (s), 1027 (m), 995 (m), 921 (s), 754 (vs), 690 cm^{-1} (s); elemental analysis calcd (%) for $C_{21}H_{20}BrN$: C 68.86, H 5.50, N 3.82, Br 21.81; found: C 68.83, H 5.53, N 3.79, Br 22.21; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.08 mL min^{-1}): t_R = 130.3 (+), 140.3 min (−).

***N*,*N*-Diallyl-*N*-[3-phenyl-1-(3-pyridinyl)-2-propynyl]amine (4n)**: The reaction was carried out according to GP A with phenylacteylene (**1a**) (51 mg, 0.50 mmol), 3-pyridinaldehyde (**2k**) (54 mg, 0.50 mmol) and diallylamine (**3b**) (49 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 5 d. Column chromatographic purification on silica gel (pentane/Et_2O 4:1) yielded propargylamine (−)-**4n** (91 mg, 0.32 mmol, 63%, 44% *ee*) as a yellow oil. $[\alpha]_D^{20} = -69$ ($c = 1.10$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 8.95$–8.94 (m, 1H), 8.56–8.55 (m, 1H), 8.01–7.98 (m, 1H), 7.57–7.54 (m, 2H), 7.39–7.35 (m, 3H), 7.32–7.28 (m, 1H), 5.93–5.80 (m, 2H), 5.31 (d, $J = 14.7$ Hz, 2H), 5.19–5.15 (m, 3H), 3.32–3.25 (m, 2H), 3.08 (dd, $J = 12.5$, 6.2 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 150.0$, 148.7, 136.0, 135.8, 135.0, 131.8, 128.4, 128.3, 122.9, 122.8, 117.7, 88.7, 83.7, 54.6, 53.5; MS (70 eV, EI): *m*/*z* (%): 288 (3) [M^+], 287 (11), 247 (11), 245 (17), 210 (44), 193 (44), 192 (100), 191 (25), 165 (12), 40 (17); HRMS (EI): *m*/*z*: calcd for $C_{20}H_{20}N_2$: 288.1626; found [M^+]: 288.1596; IR (film): $\tilde{\nu}$ = 3080 (m), 2819 (m), 1643 (m), 1575 (m), 1490 (s), 1444 (s), 1420 (vs), 1291 (m), 1110 (m), 1026 (m), 972 (m), 922 (s), 757 (vs), 712 (s), 691 cm^{-1} (s); elemental analysis calcd (%) for $C_{20}H_{20}N_2$: C 83.30, H 6.99, N 9.71; found: C 82.98, H 6.59, N 9.66; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_R = 41.8 (−), 46.5 min (+).

[α-(*N*,*N*-Diallylamino)-γ-phenylpropynyl]ferrocene (4o): The reaction was carried out according to GP A with phenylacetylene (**1a**) (51 mg, 0.50 mmol), ferrocenecarbaldehyde (**2l**) (107 mg, 0.50 mmol) and diallylamine (**3b**) (49 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 5 d. Column chromatographic purification on silica gel (pentane/Et_2O 9:1) yielded propargylamine (+)-**4o** (151 mg, 0.38 mmol, 76%, 70% *ee*) as a red oil. $[\alpha]_D^{20} = +240$ ($c = 1.00$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.58$–7.56 (m, 2H), 7.39–7.38 (m, 3H), 5.94–5.80 (m, 2H), 5.27 (d, $J = 17.1$ Hz, 2H), 5.17 (d, $J = 9.9$ Hz, 2H), 4.91 (s, 1H), 4.51 (s, 1H), 4.33 (s, 1H), 4.23 (s, 5H), 4.19–4.18 (m, 2H), 3.26

(dd, $J=14.2$, 5.3 Hz, 2H), 3.11 (dd, $J=14.2$, 7.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=136.7$, 132.5, 131.7, 128.3, 128.0, 117.2, 87.0, 85.8, 85.2, 69.2, 69.0, 68.9, 68.2, 67.4, 53.4, 53.3; MS (70 eV, EI): *m/z* (%): 395 (24) [M^+], 353 (11), 300 (32), 299 (100), 178 (52), 177 (18), 176 (25), 152 (17), 151 (10), 121 (23), 70 (10), 68 (11); HRMS (EI): *m/z*: calcd for $C_{25}H_{25}FeN$: 395.1336; found: 395.1370 [M^+]; IR (film): $\tilde{\nu}$ = 3080 (m), 2960 (m), 2929 (m), 2815 (m), 1728 (s), 1489 (s), 1444 (m), 1288 (s), 1106 (s), 999 (m), 920 (m), 756 (vs), 691 cm^{-1} (s); elemental analysis calcd (%) for $C_{25}H_{25}FeN$: C 75.96, H 6.37, N 3.54; found: C 75.55, H 6.70, N 3.02; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_R = 20.6 (−), 23.8 min (+).

[α-(*N*,*N*-Dibenzylamino)-γ-phenylpropynyl]ferrocene (4p): The reaction was carried out according to GP A with phenylacetylene (**1a**) (51 mg, 0.50 mmol), ferrocenecarbaldehyde (**2l**) (107 mg, 0.50 mmol) and dibenzylamine (**3a**) (99 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 9:1) yielded propargylamine (+)-**4p** (200 mg, 0.40 mmol, 81%, 76% *ee*) as a red oil. $[\alpha]_D^{20}=+43$ ($c=1.09$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.65$–7.61 (m, 2H), 7.44–7.24 (m, 13H), 4.80 (s, 1H), 4.56–4.55 (m, 1H), 4.35–4.34 (m, 1H), 4.18–4.16 (m, 2H), 4.11 (s, 5H), 3.83 (d, $J=13.7$ Hz, 2H), 3.59 (d, $J=13.7$ Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.9$, 131.8, 128.7, 128.4, 128.2, 128.0, 126.8, 123.6, 86.6, 86.3, 85.4, 69.0, 68.9, 68.8, 68.3, 67.3, 54.3, 52.9; MS (70 eV, EI): *m/z* (%): 496 (10), 495 (28) [M^+], 300 (25), 299 (100), 121 (13), 91 (29); HRMS (EI): *m/z*: calcd for $C_{33}H_{29}FeN$: 495.1649; found: 495.1629 [M^+]; IR (film): $\tilde{\nu}$ = 3084 (m), 3062 (m), 3028 (m), 2924 (m), 2833 (m), 2806 (m), 1490 (s), 1443 (vs), 1071 (s), 1027 (m), 755 (m), 698 cm^{-1} (vs); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_R = 24.2 (−), 30.0 min (+).

***N*,*N*-Dibenzyl-4-ethyl-1-phenyl-1-hexyn-3-amine (4q)**: The reaction was carried out according to GP A with phenylacetylene (**1a**) (51 mg, 0.50 mmol), 2-ethylbutyraldehyde (**2p**) (50 mg, 0.50 mmol) and dibenzylamine (**3a**) (99 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**4q** (175 mg, 0.46 mmol, 92%, 86% *ee*) as a colorless oil. $[\alpha]_D^{20}=-246$ ($c=0.53$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.59$–7.56 (m, 2H), 7.48–7.46 (m, 4H), 7.42–7.34 (m, 7H), 7.31–7.26 (m, 2H), 3.93 (d, $J=13.8$ Hz, 2H), 3.51 (d, $J=13.8$ Hz, 2H), 3.44 (d, $J=9.8$ Hz, 1H), 1.84–1.69 (m, 3H), 1.57–1.37 (m, 2H), 0.87 (t, $J=7.5$ Hz, 3H), 0.66 (t, $J=7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.7$, 131.8, 129.1, 128.3, 128.2, 127.8, 126.9, 123.8, 87.5, 86.1, 55.3, 55.2, 41.7, 22.3, 20.2, 10.6, 9.0; MS (70 eV, EI): *m/z* (%): 380 (<1) [M^+−H], 311 (22), 310 (100), 91 (23); HRMS (EI): *m/z*: calcd for $C_{28}H_{30}N$: 380.2378; found: 380.2374 [M^+−H]; IR (film): $\tilde{\nu}$ = 3030 (m), 2961 (s), 2803 (m), 1489 (m), 1454 (m), 754 (vs), 746 (vs), 698 (vs), 690 cm^{-1} (vs); elemental analysis calcd (%) for $C_{28}H_{30}N$: C 88.14, H 8.19, N 3.67; found: C 87.96, H 8.18, N 3.65; HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): t_R = 33.7 (+), 35.8 min (−).

***N*,*N*-Dibenzyl-4-ethyl-1-(trimethylsilyl)-1-hexyn-3-amine (5a)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 2-ethylbutyraldehyde (**2p**) (30 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5a** (107 mg, 0.29 mmol, 95%, 98% *ee*) as a colorless oil. $[\alpha]_D^{20}=-199$ ($c=0.41$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.43$–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); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.7$, 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 (1) [M^+−CH_3], 307 (30), 306 (100), 91 (29); HRMS (EI): *m/z*: calcd for $C_{25}H_{36}NSi$: 378.2617; found: 378.2617 [M^++H]; IR (film): $\tilde{\nu}$ = 2962 (s), 2158 (m), 1494 (m), 1454 (m), 1250 (s), 842 (vs), 747 (m), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{25}H_{36}NSi$: C 79.51, H 9.34, N 3.71; found: C 79.49, H 9.37, N 3.69. The enantiomeric excess was determined after conversion to **8g**.

***N*,*N*-Dibenzyl-1-cyclohexyl-3-(trimethylsilyl)-2-propyn-1-amine (5b)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), cyclohexylcarbaldehyde (**2s**) (34 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 4 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5b** (100 mg, 0.26 mmol, 86%, 97% *ee*) as a colorless solid. M.p. 81–82 °C; $[\alpha]_D^{20}=-185$ ($c=0.89$, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=$ 7.44–7.42 (m, 4H), 7.37–7.32 (m, 4H), 7.28–7.23 (m, 2H), 3.83 (d, $J=$ 13.6 Hz, 2H), 3.39 (d, $J=13.6$ Hz, 2H), 3.06 (d, $J=10.9$ Hz, 1H), 2.32–2.28 (m, 1H), 2.04–2.00 (m, 1H), 1.73–1.55 (m, 4H), 1.28–1.07 (m, 3H), 0.89–0.67 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.8$, 128.8, 128.2, 126.8, 103.5, 90.1, 58.6, 54.9, 39.5, 31.2, 30.3, 26.6, 26.2, 25.9, 0.5; MS (70 eV, EI): 307 (27) [M^+−*c*Hex], 306 (100), 91 (34); HRMS (EI): *m/z*: calcd for $C_{26}H_{35}NSi$: 389.2539; found: 389.2506 [M^+]; IR (KBr): $\tilde{\nu}$ = 2924 (s), 2852 (m), 2160 (m), 1494 (m), 1451 (m), 1248 (s), 1006 (m), 844 (vs), 737 (s), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{26}H_{35}NSi$: C 80.14, H 9.05, N 3.59; found: C 79.90, H 9.07, N 3.54. The enantiomeric excess was determined after conversion to **8j**.

***N*,*N*-Dibenzyl-1-(trimethylsilyl)-1-heptyn-3-amine (5d)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), valeraldehyde (**2a**) (26 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 5 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5d** (89 mg, 0.25 mmol, 82%, 90% *ee*) as a colorless oil. $[\alpha]_D^{20}=-186$ ($c=0.69$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.22$–7.00 (m, 10H), 3.62 (d, $J=13.7$ Hz, 2H), 3.19 (d, $J=13.7$ Hz, 2H), 3.21–3.15 (m, 1H), 1.59–1.35 (m, 2H), 1.30–1.10 (m, 2H), 1.10–0.94 (sext, $J=7.3$ Hz, 2H), 0.66 (t, $J=7.3$ Hz, 3H), 0.07 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.5$, 128.4, 127.7, 126.4, 104.3, 88.6, 54.4, 51.9, 32.9, 28.0, 21.8, 13.5, 0.4; MS (70 eV, EI): *m/z* (%): 348 (5) [M^+−CH_3], 306 (100), 214 (4), 91 (85), 73 (12); HRMS (EI): *m/z*: calcd for $C_{24}H_{32}NSi$: 362.2304; found: 362.2333 [M^+−H]; IR (film): $\tilde{\nu}$ = 3064 (w), 3029 (w), 2958 (s), 2159 (m), 1495 (m), 1454 (m), 1250 (s), 842 (vs), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{24}H_{32}NSi$: C 79.28, H 9.15, N 3.85; found: C 79.19, H 9.15, N 3.83. The enantiomeric excess was determined after conversion to **8b**.

***N*,*N*-Dibenzyl-1-(trimethylsilyl)-1-octyn-3-amine (5e)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), hexanal (**2n**) (30 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 3 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5e** (113 mg, 0.29 mmol, 99%, 88% *ee*) as a colorless oil. $[\alpha]_D^{20}=-152$ ($c=0.45$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.43$–7.40 (m, 4H), 7.36–7.22 (m, 6H), 3.83 (d, $J=$ 13.8 Hz, 2H), 3.43–3.37 (m, 3H), 1.77–1.56 (m, 2H), 1.48–1.11 (m, 6H), 0.87 (t, $J=7.7$ Hz, 3H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=$ 139.9, 128.8, 128.2, 126.8, 104.7, 89.0, 54.8, 52.3, 33.5, 31.3, 25.9, 22.5, 14.0, 0.4; MS (70 eV, EI): m/z (%): 377 (<1) [M^+], 307 (25), 306 (100), 91 (45); HRMS (EI): *m/z*: calcd for $C_{25}H_{34}NSi$: 376.2461; found: 376.2448 [M^+−H]; IR (film): $\tilde{\nu}$ = 2957 (s), 2933 (s), 2159 (m), 1494 (m), 1454 (m), 1250 (s), 842 (vs), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{25}H_{34}NSi$: C 79.51, H 9.34, N 3.71; found: C 79.39, H 9.40, N 3.64. The enantiomeric excess was determined after conversion to **8c** and acylation with valeroylchloride: HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_R = 22.9 (−), 26.0 min (−).

***N*,*N*-Dibenzyl-5-methyl-1-(trimethylsilyl)-1-hexyn-3-amine (5f)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), isovaleraldehyde (**2b**) (22 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5f** (93 mg,

0.26 mmol, 85%, 94 *ee*) as a colorless oil. $[\alpha]_D^{20} = -185$ ($c = 0.31$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.43–7.41$ (m, 4H), 7.36–7.33 (m, 4H), 7.29–7.25 (m, 2H), 3.83 (d, $J = 14.0$ Hz, 2H), 3.49 (dd, $J = 8.5$, 7.0 Hz, 1H), 3.39 (d, $J = 14.0$ Hz, 2H), 1.93–1.86 (m, 1H), 1.71–1.66 (m, 1H), 1.47–1.42 (m, 1H), 0.83 (d, $J = 6.4$ Hz, 3H), 0.68 (d, $J = 6.4$ Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.8$, 128.9, 128.1, 126.8, 104.8, 88.9, 54.8, 50.3, 42.7, 24.5, 22.9, 21.7, 0.4; MS (70 eV, EI): m/z (%): 363 (<1) [M^+], 307 (26), 306 (100), 91 (78); HRMS (EI): *m/z*: calcd for $C_{24}H_{33}NSi$: 363.2382,; found: 363.2363 [M^+]; IR (film): $\tilde{\nu}$ = 3029 (m), 2957 (s), 2159 (m), 1494 (m), 1454 (s), 1250 (s), 989 (m), 842 (vs), 747 (s), 698 cm^{-1} (vs). The enantiomeric excess was determined after conversion to **8d** and acylation with benzoylchloride: HPLC (OD-H, 98% *n*-heptane/2% isopropanol, 0.5 mL min^{-1}): $t_R = 9.2$ (−), 10.4 min (+).

***N,N*-Dibenzyl-5,5-dimethyl-1-(trimethylsilyl)-1-hexyn-3-amine (5g)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 3,3-dimethylbutyraldehyde (**2o**) (26 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5g** (106 mg, 0.28 mmol, 94%, 94% *ee*) as a colorless oil. $[\alpha]_D^{20} = -182$ ($c = 0.47$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.44–7.40$ (m, 4H), 7.36–7.23 (m, 6H), 3.81 (d, $J = 13.7$ Hz, 2H), 3.47 (dd, $J = 8.1$, 4.0 Hz, 1H), 3.40 (d, $J = 13.8$ Hz, 2H), 1.78–1.62 (m, 2H), 0.84 (s, 9H), 0.26 (s, 9H); ^3C NMR (75 MHz, $CDCl_3$): $\delta = 139.7$, 128.9, 128.1, 126.8, 105.8, 88.9, 54.9, 48.9, 48.6, 30.6, 29.7, 0.3; MS (70 eV, EI): m/z (%): 377 (<1) [M^+], 307 (23), 306 (100), 91 (43); HRMS (EI): *m/z*: calcd for $C_{25}H_{34}NSi$: 376.2461; found: 376.2491 [M^+−H]; IR (film): $\tilde{\nu}$ = 2957 (s), 2158 (m), 1454 (m), 1367 (m), 1250 (s), 842 (vs), 745 cm^{-1} (s). The enantiomeric excess was determined after conversion to **8e** and acylation with benzoylchloride: HPLC (OD-H, 98% *n*-heptane/2% isopropanol, 0.3 mL min^{-1}): $t_R = 14.2$ (−), 15.7 min (+).

***N,N*-Dibenzyl-4-methyl-1-(trimethylsilyl)-1-pentyn-3-amine (5h)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), isobutyraldehyde (**2c**) (22 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 3 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5h** (91 mg, 0.26 mmol, 87%, 96% *ee*) as a colorless oil. $[\alpha]_D^{20} = -275$ ($c = 0.44$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.45–7.42$ (m, 4H), 7.37–7.36 (m, 6H), 3.84 (d, $J = 13.6$ Hz, 2H), 3.39 (d, $J = 13.6$ Hz, 2H), 2.94 (d, $J = 10.5$ Hz, 1H), 1.96–1.86 (m, 1H), 1.03 (d, $J = 6.3$ Hz, 3H), 1.00 (d, $J = 6.2$ Hz, 3H), 0.29 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.8$, 128.9, 128.2, 126.8, 103.6, 89.9, 59.9, 55.0, 30.5, 20.8, 19.9, 0.4; MS (70 eV, EI): *m/z*: 307 (27) [M^+−*i*Pr], 306 (100), 91 (34); HRMS (EI): *m/z*: calcd for $C_{23}H_{30}NSi$: 348.2148; found: 348.2166 [M^+−H]; IR (film): $\tilde{\nu}$ = 2959 (s), 2158 (m), 1494 (m), 1454 (s), 1249 (vs), 1019 (s), 842 (vs), 746 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{23}H_{30}NSi$: C 79.02, H 8.94, N 4.01; found: C 79.10, H 9.17, N 3.83. The enantiomeric excess was determined after conversion to **8f**.

***N,N*-Dibenzyl-1-cyclopropyl-3-(trimethylsilyl)-2-propyn-1-amine (5i)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), cyclopropylcarbaldehyde (**2q**) (21 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5i** (102 mg, 0.29 mmol, 98%, 92% *ee*) as a colorless oil. $[\alpha]_D^{20} = -163$ ($c = 0.42$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.47–7.42$ (m, 4H), 7.37–7.23 (m, 6H), 3.98 (d, $J = 13.8$ Hz, 2H), 3.45–3.39 (m, 3H), 1.14–1.04 (m, 1H), 0.59–0.37 (m, 3H), 0.28–0.26 (m, 1H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.1$, 128.8, 128.1, 126.8, 101.4, 90.1, 55.8, 55.0, 13.3, 3.6, 1.7, 0.4; MS (70 eV, EI): *m/z*: 347 (3) [M^+], 307 (27), 306 (100), 91 (56), 73 (10); HRMS (EI): *m/z*: calcd for $C_{23}H_{29}NSi$: 347.2069; found: 347.2034 [M^+]; IR (film): $\tilde{\nu}$ = 2959 (m), 2160 (m), 1494 (m), 1454 (m), 1250 (s), 1026 (m), 842 (vs), 747 (m), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{23}H_{29}NSi$: C 79.48, H 8.41, N 4.03; found: C 79.32, H 8.75, N 4.04. The enantiomeric excess was determined after conversion to **8h**.

***N,N*-Dibenzyl-1-cyclopentyl-3-(trimethylsilyl)-2-propyn-1-amine (5j)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), cyclopentylcarbaldehyde (**2r**) (29 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5j** (110 mg, 0.29 mmol, 98%, 96% *ee*) as a colorless oil. $[\alpha]_D^{20} = -178$ ($c = 0.5$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.44$ (d, $J = 7.8$ Hz, 4H), 7.34 (t, $J = 7.8$ Hz, 4H), 7.29–7.25 (m, 2H), 3.87 (d, $J = 13.7$ Hz, 2H), 3.38 (d, $J = 13.8$ Hz, 2H), 3.06 (d, $J = 10.6$ Hz, 1H), 2.28–2.22 (m, 1H), 1.90–1.82 (m, 2H), 1.54–1.36 (m, 5H), 1.31–1.25 (m, 1H), 0.29 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.9$, 128.9, 128.1, 126.8, 104.3, 89.0, 57.7, 54.9, 42.6, 30.9, 30.2, 25.0, 24.9, 0.4; MS (70 eV, EI): *m/z*: 375 (<1) [M^+], 307 (26), 306 (100), 91 (53); HRMS (EI): *m/z*: calcd for $C_{25}H_{32}NSi$: 374.2304; found: 374.2289 [M^+−H]; IR (film): $\tilde{\nu}$ = 2957 (s), 2868 (m), 2158 (m), 1494 (m), 1454 (m), 1250 (s), 842 (vs), 747 (m), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{25}H_{32}NSi$: C 79.51, H 9.34, N 3.71; found: C 80.05, H 9.38, N 3.76; HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): $t_R = 22.1$ (−), 25.0 min (+).

(1*E*)-*N,N*-Dibenzyl-1-phenyl-5-(trimethylsilyl)-1-penten-4-yn-3-amine (5k): The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), cinnamaldehyde (**2t**) (40 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 5 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5k** (118 mg, 0.29 mmol, 96%, 82% *ee*) as a colorless oil. $[\alpha]_D^{20} = -13$ ($c = 0.70$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.46–7.24$ (m, 15H), 6.91 (dd, $J = 16.1$, 2.0 Hz, 1H), 6.24 (dd, $J = 16.1$, 4.0 Hz, 1H), 4.34 (dd, $J = 4.0$, 2.0 Hz, 1H), 3.88 (d, $J = 13.6$ Hz, 2H), 3.50 (d, $J = 13.6$ Hz, 2H), 0.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.6$, 136.8, 132.6, 128.8, 128.5, 128.3, 128.2, 127.5, 126.9, 126.6, 101.2, 92.6, 54.8, 54.5, 0.4; MS (70 eV, EI): *m/z*: 409 (8) [M^+], 408 (10), 336 (12), 319 (25), 318 (85), 306 (19), 213 (31), 97 (18), 92 (11), 91 (100), 73 (32); HRMS (EI): *m/z*: calcd for $C_{28}H_{31}NSi$: 409.2226; found: 409.2251 [M^+]; IR (film): $\tilde{\nu}$ = 3028 (m), 2959 (m), 2160 (m), 1494 (s), 1454 (m), 1250 (s), 968 (m), 842 (s), 866 (vs), 746 (s), 697 cm^{-1} (vs); elemental analysis calcd (%) for $C_{28}H_{31}NSi$: C 82.10, H 7.63, N 3.42; found: C 82.23, H 8.14, N 3.43. The enantiomeric excess was determined after conversion to **8k**.

***N,N*-Dibenzyl-1,1-diphenyl-5-(trimethylsilyl)-1-penten-4-yn-3-amine (5l)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), β-phenylcinnamaldehyde (**2u**) (62 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 3 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**5l** (119 mg, 0.25 mmol, 82%, 84% *ee*) as a colorless oil. $[\alpha]_D^{20} = +46$ ($c = 0.43$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.31–7.13$ (m, 20H), 6.17 (d, $J = 9.3$ Hz, 1H), 4.26 (d, $J = 9.3$ Hz, 1H), 3.86 (d, $J = 13.6$ Hz, 2H), 3.60 (d, $J = 13.7$ Hz, 2H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 144.3$, 142.3, 139.4, 138.7, 129.7, 128.9, 128.1, 128.0, 127.9, 127.7, 127.5, 127.2, 126.7, 125.8, 103.6, 90.3, 55.1, 51.9, 0.3; MS (70 eV, EI): *m/z*: 485 (16) [M^+], 413 (14), 412 (26), 408 (11), 395 (19), 394 (56), 318 (12), 306 (15), 298 (15), 290 (19), 289 (68), 215 (14), 167 (16), 92 (12), 91 (100), 73 (60); HRMS (EI): *m/z*: calcd for $C_{34}H_{35}NSi$: 485.2539; found: 485.2500 [M^+]; IR (film): $\tilde{\nu}$ = 3029 (m), 2959 (m), 2158 (m), 1494 (s), 1445 (m), 1250 (s), 843 (vs), 748 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{34}H_{35}NSi$: C 84.07, H 7.20, N 2.88; found: C 84.08, H 7.78, N 2.82. The enantiomeric excess was determined after conversion to **8l**.

***N,N*-Dibenzyl-5-phenyl-1-(trimethylsilyl)-1-pentyn-3-amine (5m)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), dihydrocinnamaldehyde (**2v**) (40 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 3 d. Column chromatographic

purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5m** (96 mg, 0.23 mmol, 78%, 88% *ee*) as a colorless oil. $[\alpha]_D^{20}=-114$ ($c=0.38$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.44$–7.14 (m, 13H), 7.09–7.06 (m, 2H), 3.88 (d, $J=13.6$ Hz, 2H), 3.50 (d, $J=7.6$ Hz, 1H), 3.45 (d, $J=13.6$ Hz, 2H), 2.85–2.75 (m, 1H), 2.69–2.59 (m, 1H), 2.12–1.88 (m, 2H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=141.9$, 139.7, 128.9, 128.4, 128.3, 128.2, 126.9, 125.7, 104.2, 89.6, 55.0, 52.2, 35.6, 32.6, 0.4; MS (70 eV, EI): *m/z*: 411 (<1) [M^+], 307 (25), 306 (100), 91 (60); HRMS (EI): *m/z*: calcd for $C_{28}H_{33}NSi$: 411.2382; found: 411.2406 [M^+]; IR (film): $\tilde{\nu}$ = 3027 (m), 2956 (m), 2158 (m), 1495 (s), 1454 (s), 1250 (s), 842 (vs), 746 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{28}H_{33}NSi$: C 81.69, H 8.08, N 3.40; found: C 81.92, H 8.56, N 3.37. The enantiomeric excess was determined after conversion to **8m**.

***N,N*-Dibenzyl-5-(4-bromphenyl)-1-(trimethylsilyl)-1-pentyn-3-amine (5n)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 3-(4-bromophenyl)propanal (**2w**) (64 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 2 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5n** (107 mg, 0.22 mmol, 73%, 88% *ee*) as a colorless oil. $[\alpha]_D^{20}=-76$ ($c=0.28$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.41$–7.25 (m, 12H), 6.88 (d, $J=8.3$ Hz, 2H), 3.85 (d, $J=13.8$ Hz, 2H), 3.44 (dd, $J=7.1$, 1.0 Hz, 1H), 3.42 (d, $J=13.8$ Hz, 2H), 2.76–2.53 (m, 2H), 2.06–1.83 (m, 2H), 0.27 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=140.7$, 139.6, 131.2, 130.2, 128.9, 128.2, 126.9, 119.4, 103.9, 89.7, 55.0, 51.7, 35.3, 31.8, 0.4; MS (70 eV, EI): *m/z*: 489 (<1) [M^+], 307 (26), 306 (100), 91 (54); HRMS (EI): *m/z*: calcd for $C_{28}H_{32}BrNSi$: 489.1487; found: 489.1441 [M^+]; IR (film): $\tilde{\nu}$ = 2956 (m), 2158 (m), 1488 (s), 1454 (m), 1250 (s), 1072 (m), 1012 (m), 843 (vs), 747 (m), 698 cm^{-1} (s). The enantiomeric excess was determined after conversion to **8n**.

Ethyl 4-[3-(dibenzylamino)-5-(trimethylsilyl)-4-pentynyl]-benzoate (5o): The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), ethyl 4-(3-oxopropyl)benzoate (**2x**) (62 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 2 d. Column chromatographic purification on silica gel (pentane/Et_2O 9:1) yielded propargylamine (−)-**5o** (140 mg, 0.29 mmol, 96%, 87% *ee*) as a colorless oil. $[\alpha]_D^{20}=-72$ ($c=0.72$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.89$ (d, $J=8.4$ Hz, 2H), 7.42–7.22 (m, 10H), 7.09 (d, $J=8.0$ Hz, 2H), 4.39 (q, $J=6.9$ Hz, 2H), 3.86 (d, $J=13.6$ Hz, 2H), 3.45 (d, $J=7.3$ Hz, 1H), 3.43 (d, $J=13.7$ Hz, 2H), 2.88–2.78 (m, 1H), 2.72–2.62 (m, 1H), 2.10–1.87 (m, 2H), 1.42 (t, $J=6.9$ Hz, 3H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=166.6$, 147.2, 139.5, 129.6, 128.9, 128.3, 128.2, 128.0, 126.9, 103.8, 89.8, 60.7, 55.0, 51.9, 35.1, 32.6, 14.4, 0.4; MS (70 eV, EI): *m/z*: 483 (<1) [M^+], 307 (26), 306 (100), 91 (45); HRMS (EI): *m/z*: calcd for $C_{31}H_{37}NO_2Si$: 483.2594; found: 483.2627 [M^+]; IR (film): $\tilde{\nu}$ = 2957 (m), 2158 (m), 1719 (vs), 1454 (m), 1276 (vs), 1250 (s), 1178 (m), 1107 (s), 843 (s), 748 (s), 699 cm^{-1} (s); elemental analysis calcd (%) for $C_{31}H_{37}NO_2Si$: C 76.97, H 7.71, N 2.90; found: C 76.66, H 7.73, N 2.77; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.3 mL min^{-1}): $t_R=16.9$ (−), 26.8 min (+).

***N,N*-Dibenzyl-1-(2-naphthyl)-3-(trimethylsilyl)-2-propyn-1-amine (5q)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 2-naphthaldehyde (**2y**) (47 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*S*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 7 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**5q** (45 mg, 0.11 mmol, 35%, 54% *ee*) as a colorless solid. M.p. 98–99 °C; $[\alpha]_D^{20}=+2$ ($c=0.25$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=8.17$ (s, 1H), 7.91–7.84 (m, 3H), 7.74 (dd, $J=8.8$, 1.8 Hz, 1H), 7.51–7.44 (m, 6H), 7.35 (t, $J=8.0$ Hz, 4H), 7.29–7.24 (m, 2H), 4.89 (s, 1H), 3.79 (d, $J=13.3$ Hz, 2H), 3.50 (d, $J=13.3$ Hz, 2H), 0.42 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.5$, 136.4, 133.0, 132.9, 128.9, 128.3, 128.1, 127.8, 127.5, 127.2, 127.0, 126.4, 125.9, 125.8, 100.9, 93.5, 56.4, 54.5, 0.4; MS (70 eV, EI): *m/z* (%): 434 (11), 433 (31) [M^+], 360 (13), 343 (11), 342 (33), 307 (16), 306 (62), 238 (40), 237 (100), 223 (11), 209 (50), 197 (35), 196 (49), 195 (11), 91 (61), 83 (11), 73 (13); HRMS (EI): *m/z*: calcd for $C_{30}H_{31}NSi$: 433.2226; found: 433.2240 [M^+]; IR (KBr): $\tilde{\nu}$ = 3436 (m br), 3063 (m), 3029 (m), 2960 (m), 2834 (m), 2808 (m), 2164 (w), 1495 (m), 1454 (m), 1250 (s), 1121 (m), 1007 (m), 843 (vs), 816 (m), 762 (m), 744 (s), 697 cm^{-1} (s); HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): t_R =34.2 (−), 38.7 min (+).

***N,N*-Dibenzyl-1-(2-thienyl)-3-(trimethylsilyl)-2-propyn-1-amine (5r)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 2-thiophencarbaldehyde (**2z**) (34 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*S*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 7 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**5r** (95 mg, 0.24 mmol, 81%, 80% *ee*) as a colorless solid. M.p. 90–91 °C; $[\alpha]_D^{20}=+84$ ($c=0.33$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.52$–7.49 (m, 4H), 7.35 (t, $J=7.5$ Hz, 4H), 7.29–7.24 (m, 4H), 6.96 (dd, $J=5.3$, 3.6 Hz, 1H), 4.86 (s, 1H), 3.86 (d, $J=13.6$ Hz, 2H), 3.47 (d, $J=13.6$ Hz, 2H), 0.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=144.4$, 139.2, 128.7, 128.2, 127.1, 126.2, 126.0, 125.4, 100.3, 91.8, 54.4, 52.9, 0.3; MS (70 eV, EI): *m/z* (%): 389 (30) [M^+], 298 (27), 194 (17), 193 (100), 165 (50), 91 (50); HRMS (EI): *m/z*: calcd for $C_{24}H_{27}NSSi$: 389.1633; found: 389.1625 [M^+]; IR (KBr): $\tilde{\nu}$ = 3436 (m br), 3028 (w), 2957 (w), 2835 (w), 2167 (w), 1495 (w), 1454 (w), 1249 (m), 987 (m), 854 (s), 752 (m), 698 cm^{-1} (vs). The enantiomeric excess was determined after conversion to **8p**.

***N,N*-Dibenzyl-1-(3-thienyl)-3-(trimethylsilyl)-2-propyn-1-amine (5s)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 3-thiophencarbaldehyde (**2aa**) (34 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*S*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 7 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**5s** (99 mg, 0.26 mmol, 85%, 74% *ee*) as a colorless solid. M.p. 75–76 °C; $[\alpha]_D^{20}=+69$ ($c=0.60$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.45$–7.42 (m, 5H), 7.37–7.24 (m, 8H), 4.69 (s, 1H), 3.78 (d, $J=13.6$ Hz, 2H), 3.45 (d, $J=13.6$ Hz, 2H), 0.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=140.8$, 139.5, 128.8, 128.2, 127.4, 127.0, 125.6, 123.2, 101.4, 91.4, 54.5, 52.8, 0.4; MS (70 eV, EI): *m/z* (%): 389 (47) [M^+], 316 (15), 306 (21), 299 (15), 298 (59), 196 (53), 195 (12), 194 (33), 193 (92), 179 (12), 166 (13), 165 (88), 153 (11), 92 (11), 91 (100); HRMS (EI): *m/z*: calcd for $C_{24}H_{27}NSSi$: 389.1633; found: 389.1624 [M^+]; IR (KBr): $\tilde{\nu}$ = 3436 (m), 2834 (w), 2168 (w), 1495 (w), 1454 (w), 1249 (m), 844 (vs), 757 (s), 700 cm^{-1} (s). The enantiomeric excess was determined after conversion to **8q**.

***N*-[1-(1-Benzothien-2-yl)-3-(trimethylsilyl)-2-propynyl]-*N,N*-dibenzylamine (5t)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 2-benzothiophencarbaldehyde (**2ab**) (49 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 7 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5t** (55 mg, 0.13 mmol, 42%, 89% *ee*) as a yellow solid. M.p. 112–113 °C; $[\alpha]_D^{20}=-14$ ($c=0.29$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta=7.80$–7.77 (m, 1H), 7.71–7.68 (m, 1H), 7.51–7.49 (m, 4H), 7.45–7.44 (m, 1H), 7.36–7.21 (m, 8H), 4.90 (d, $J=1.4$ Hz, 1H), 3.87 (d, $J=13.7$ Hz, 2H), 3.45 (d, $J=13.7$ Hz, 2H), 0.35 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=145.5$, 140.3, 139.3, 139.0, 128.8, 128.3, 128.2, 127.1, 124.0, 123.3, 122.7, 122.3, 99.6, 92.5, 54.5, 53.4, 0.3; MS (70 eV, EI): m/z (%): 439 (12) [M^+], 281 (13), 244 (29), 243 (100), 215 (21), 207 (39), 203 (19), 91 (49); HRMS (EI): *m/z*: calcd for $C_{28}H_{29}NSSi$: 439.1790; found: 439.1816 [M^+]; IR (KBr): $\tilde{\nu}$ = 3027 (w), 2835 (w), 2165 (w), 1494 (m), 1454 (m), 1249 (s), 990 (m), 981 (m), 854 (vs), 749 (s), 698 cm^{-1} (s); HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): $t_R=29.2$ (−), 31.3 min (+).

***N*-[1-(1-Benzothien-3-yl)-3-(trimethylsilyl)-2-propynyl]-*N,N*-dibenzylamine (5u)**: The reaction was carried out according to GP A with trimethylsilylacetylene (**1e**) (29 mg, 0.30 mmol), 3-benzothiophencarbaldehyde (**2i**) (49 mg, 0.30 mmol) and dibenzylamine (**3a**) (59 mg, 0.30 mmol) in

the presence of CuBr (2.2 mg, 15.0 μmol) and (*R*)-quinap (7.3 mg, 16.5 μmol) and MS 4 Å (150 mg) in toluene (2 mL) at RT for 7 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**5u** (121 mg, 0.28 mmol, 92%, 82% *ee*) as a yellow solid. M.p. 132–133 °C; $[\alpha]_D^{20} = -128$ ($c = 0.77$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.81$ (s, 1H), 7.70 (s, 1H), 7.23–7.14 (m, 12H), 7.10 (d, $J = 7.2$ Hz, 1H), 4.89 (s, 1H), 3.70 (d, $J = 12.3$ Hz, 2H), 3.35 (d, $J = 12.3$ Hz, 2H), 0.28 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.5$, 138.7, 137.2, 133.2, 129.1, 127.8, 126.8, 125.9, 123.9, 123.2, 123.1, 122.2, 100.2, 92.0, 54.5, 51.9, 0.0; MS (70 eV, EI): *m/z* (%): 439 (18), 348 (10), 244 (28), 243 (100), 215 (25), 203 (13), 196 (17 [M^+]), 91 (51); HRMS (EI): *m/z*: calcd for $C_{28}H_{29}NSSi$: 439.1790; found: 439.1787 [M^+]; IR (KBr): $\tilde{\nu}$ = 3027 (m), 2955 (m), 2838 (m), 2164 (w), 1495 (m), 1454 (m), 1248 (s), 1106 (m), 1054 (m), 981 (m), 954 (m), 845 (vs), 751 (s), 738 (s), 700 cm^{-1} (s); HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): $t_R = 31.7$ (−), 39.7 min (+).

***N,N*-Dibenzyl-1-(*tert*-butyldimethylsilyl)-4-ethyl-1-hexyn-3-amine (6)**: The reaction was carried out according to GP A with *tert*-butyldimethylsilylacetylene (70 mg, 0.50 mmol), 2-ethylbutyraldehyde (**2p**) (50 mg, 0.50 mmol) and dibenzylamine (**3a**) (99 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 7 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**6** (88 mg, 0.21 mmol, 42%, 90% *ee*) as a colorless oil. $[\alpha]_D^{20} = -192$ ($c = 0.26$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.43$–7.19 (m, 10H), 3.83 (d, $J = 13.8$ Hz, 2H), 3.40 (d, $J = 13.8$ Hz, 2H), 3.20 (d, $J = 10.3$ Hz, 1H), 1.76–1.59 (m, 3H), 1.47–1.28 (m, 2H), 1.06 (s, 9H), 0.81 (t, $J = 7.5$ Hz, 3H), 0.61 (t, $J = 7.5$ Hz, 3H), 0.22 (s, 3H), 0.21 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.7$, 129.1, 128.1, 126.8, 104.5, 88.0, 55.6, 55.1, 41.6, 26.2, 26.0, 22.1, 20.2, 16.6, 10.6, 9.0, −4.2, −4.9; MS (70 eV, EI): *m/z* (%): 419 (<1) [M^+], 350 (12), 349 (49), 348 (94), 97 (13), 92 (15), 91 (100), 83 (13), 73 (21), 59 (12), 57 (11), 42 (13); HRMS (EI): *m/z*: calcd for $C_{28}H_{41}NSi$: 419.3008; found: 419.3038 [M^+]; IR (film): $\tilde{\nu}$ = 2957 (vs), 2930 (vs), 2857 (s), 2158 (m), 1495 (m), 1470 (m), 1454 (s), 1249 (s), 834 (s), 826 (s), 747 (s), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{28}H_{41}NSi$: C 80.13, H 9.85, N 3.34; found: C 79.63, H 10.22, N 3.17. The enantiomeric excess was determined after conversion to **8g**.

***N,N*-Dibenzyl-1-cyclohexyl-3-[tri-*tert*-butylsilyl]-2-propyn-1-amine (7)**: The reaction was carried out according to GP A with triisopropylsilylacetylene (91 mg, 0.50 mmol), 2-ethylbutyraldehyde (**2p**) (50 mg, 0.50 mmol) and dibenzylamine (**3a**) (99 mg, 0.50 mmol) in the presence of CuBr (3.6 mg, 25.0 μmol) and (*R*)-quinap (12.1 mg, 27.5 μmol) and MS 4 Å (250 mg) in toluene (2 mL) at RT for 6 d. Column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**7** (73 mg, 0.15 mmol, 31%, 4% *ee*) as a colorless oil. $[\alpha]_D^{20} = -8$ ($c = 0.40$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.43$–7.19 (m, 10H), 3.86 (d, $J = 13.7$ Hz, 2H), 3.46 (d, $J = 13.6$ Hz, 2H), 3.10 (d, $J = 10.4$ Hz, 1H), 2.31 (d, $J = 13.3$ Hz, 1H), 2.07 (d, $J = 13.3$ Hz, 1H), 1.74–1.59 (m, 4H), 1.35–1.27 (m, 3H), 1.18 (s, 21H), 0.87–0.74 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.9$, 128.8, 128.2, 126.8, 105.2, 85.7, 58.6, 55.0, 39.7, 31.3, 30.3, 29.7, 29.4, 26.6, 25.9, 18.8, 18.5, 11.4; MS (70 eV, EI): *m/z* (%): 472 (<1) [M^+−H], 319 (24), 390 (100), 91 (28); HRMS (EI): *m/z*: calcd for $C_{32}H_{46}NSi$: 472.3400; found: 472.3418 [M^+−H]; IR (film): $\tilde{\nu}$ = 2940 (vs), 2864 (s), 2156 (w), 1452 (m), 1003 (m), 883 (m), 746 (m), 698 (s), 676 cm^{-1} (m); elemental analysis calcd (%) for $C_{32}H_{46}NSi$: C 81.12, H 10.00, N 2.96; found: C 80.75, H 9.84; N 2.73. The enantiomeric excess was determined after conversion to **8j**.

***N,N*-Dibenzyl-1-heptyn-3-amine (8b)**

General procedure B: Propargylamine (−)-**5d** (89 mg, 0.25 mmol) was dissolved in dry THF (3 mL) and cooled to 0 °C. Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) was added dropwise and the reaction was stirred for 15 min. The reaction mixture was quenched with water (25 mL) and extracted with Et_2O (3×20 mL). After evaporation of the solvent and column chromatographic purification on silica gel (pentane/Et_2O 99:1), propargylamine (−)-**8b** (69 mg, 0.24 mmol, 95%) was obtained as a colorless oil. $[\alpha]_D^{20} = -190$ ($c = 0.87$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.41$ (d, $J = 7.7$ Hz, 4H), 7.33 (t, $J = 7.3$ Hz, 4H), 7.25 (t, $J = 7.3$ Hz, 2H), 3.85 (d,= 13.8 Hz, 2H), 3.46–3.40 (m, 3H), 2.33 (d, $J = 1.3$ Hz, 1H), 1.83–1.73 (m, 1H), 1.71–1.63 (m, 1H), 1.50–1.33 (m, 2H), 1.25–1.17 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.7$, 128.8, 128.2, 126.9, 82.2, 72.4, 54.7, 51.5, 33.4, 28.4, 22.2, 13.9; MS (70 eV, EI): *m/z* (%):290 (1) [M^+−H], 235 (22), 234 (98), 181 (11), 92 (100), 65 (10); HRMS (EI): *m/z*: calcd for $C_{21}H_{25}N$: 290.1909; found: 290.1885 [M^+−H]; IR (film): $\tilde{\nu}$ = 3302 (m), 2956 (s), 2934 (s), 2860 (m), 1494 (m), 1454 (s), 746 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{21}H_{25}N$: C 86.55, H 8.65, N 4.81; found: C 86.84, H 8.80, N 4.97; HPLC (OD-H, 100% *n*-heptane, 0.8 mL min^{-1}): $t_R = 11.3$ (+), 12.9 min (−).

***N,N*-Dibenzyl-1-octyn-3-amine (8c)**: The reaction was carried out according to GP B with propargylamine (−)-**5e** (113 mg, 0.29 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8c** (84 mg, 0.28 mmol, 95%) as a colorless oil. $[\alpha]_D^{20} = -115$ ($c = 0.41$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.44$ (d, $J = 7.2$ Hz, 4H), 7.35 (t, $J = 7.2$ Hz, 4H), 7.29–7.26 (m, 2H), 3.87 (d, $J = 13.7$ Hz, 2H), 3.44 (d, $J = 13.7$ Hz, 2H), 3.44–3.43 (m, 1H), 2.35 (d, $J = 2.3$ Hz, 1H), 1.80–1.74 (m, 1H), 1.70–1.64 (m, 1H), 1.49–1.37 (m, 2H), 1.30 (sext, $J = 7.2$ Hz, 2H), 1.20–1.15 (m, 2H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.7$, 128.8, 128.2, 126.9, 82.2, 72.4, 54.7, 51.4, 33.6, 31.3, 25.9, 22.5, 14.0; MS (70 eV, EI): *m/z* (%): 305 (<1) [M^+], 235 (18), 234 (93), 91 (100); HRMS (EI): *m/z*: calcd for $C_{22}H_{27}N$: 305.2143; found: 305.2165 [M^+]; IR (film): $\tilde{\nu}$ = 3304 (m), 2954 (s), 2933 (s), 1495 (m), 1454 (s), 746 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{22}H_{27}N$: C 86.51, H 8.91, N 4.59; found: C 86.31, H 8.99, N 4.55.

***N,N*-Dibenzyl-5-methyl-1-hexyn-3-amine (8d)**: The reaction was carried out according to GP B with propargylamine (−)-**5f** (93 mg, 0.26 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8d** (75 mg, 0.26 mmol, 99%) as a colorless oil. $[\alpha]_D^{20} = -165$ ($c = 0.45$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.43$ (d, $J = 7.3$ Hz, 4H), 7.35 (t, $J = 7.3$ Hz, 4H), 7.29–7.26 (m, 2H), 3.86 (d, $J = 13.8$ Hz, 2H), 3.51 (td, $J = 7.7$, 2.5 Hz, 1H), 3.42 (d, $J = 13.8$ Hz, 2H), 2.35 (d, $J = 2.2$ Hz, 1H), 1.91–1.87 (m, 1H), 1.72–1.68 (m, 1H), 1.52–1.48 (m, 1H), 0.83 (d, $J = 6.3$ Hz, 3H), 0.70 (d, $J = 6.3$ Hz, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.7$, 128.9, 128.2, 126.9, 82.3, 72.3, 54.8, 49.4, 42.8, 24.5, 22.7, 21.8; MS (70 eV, EI): *m/z* (%): 291 (<1) [M^+], 235 (18), 234 (100), 91 (89); HRMS (EI): *m/z*: calcd for $C_{21}H_{24}N$: 290.1909; found: 290.1885 [M^+−H]; IR (film): $\tilde{\nu}$ = 3302 (m), 2955 (s), 2934 (s), 1495 (m), 1454 (s), 746 (s), 698 cm^{-1} (vs).

***N,N*-Dibenzyl-5,5-dimethyl-1-hexyn-3-amine (8e)**: The reaction was carried out according to GP B with propargylamine (−)-**5g** (106 mg, 0.28 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8e** (85 mg, 0.28 mmol, 99%) as a colorless oil. $[\alpha]_D^{20} = -175$ ($c = 0.65$, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): $\delta = 7.43$–7.40 (m, 4H), 7.33–7.30 (m, 4H), 7.26–7.22 (m, 2H), 3.81 (d, $J = 13.8$ Hz, 2H), 3.48–3.44 (m, 1H), 3.40 (d, $J = 13.8$ Hz, 2H), 2.34 (d, $J = 2.3$ Hz, 1H), 1.76 (dd, $J = 13.6$, 7.7 Hz, 1H), 1.67 (dd, $J = 13.5$, 4.0 Hz, 1H), 0.82 (s, 9H); ^{13}C NMR (150 MHz, $CDCl_3$): $\delta = 139.6$, 128.9, 128.2, 126.9, 83.3, 72.4, 54.8, 48.7, 48.1, 30.7, 29.6; MS (70 eV, EI): *m/z* (%): 305 (<1) [M^+], 235 (12), 234 (71), 91 (100), 58 (12), 44 (36); HRMS (EI): *m/z*: calcd for $C_{22}H_{26}N$: 304.2065; found: 304.2076 [M^+−H]; IR (film): $\tilde{\nu}$ = 3304 (m), 2956 (s), 1495 (m), 1454 (s), 1368 (m), 746 (s), 698 cm^{-1} (vs).

***N,N*-Dibenzyl-4-methyl-1-pentyn-3-amine (8f)**: The reaction was carried out according to GP B with propargylamine (−)-**5h** (91 mg, 0.26 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8f** (71 mg, 0.25 mmol, 98%) as a colorless oil. $[\alpha]_D^{20} = -231$ ($c = 0.76$, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.46$–7.24 (m, 10H), 3.87 (d, $J = 13.7$ Hz, 2H), 3.42 (d, $J = 13.7$ Hz, 2H), 2.95 (d, $J = 10.8$ Hz, 1H), 2.38 (s, 1H), 2.02–1.90 (m, 1H), 1.04 (t, $J = 6.7$ Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.6$, 128.8, 128.2, 126.9, 81.2, 73.2, 58.9, 54.9, 30.5, 20.8, 19.8; MS (70 eV, EI): *m/z*: 235 (18), 234 (100) [M^+−*i*Pr], 91 (16); HRMS (EI): *m/z*: calcd for

$C_{20}H_{22}N$: 276.1752; found: 276.1720 [M^+−H]; IR (film): $\tilde{\nu}$ = 2959 (m), 1495 (m), 1454 (m), 746 (m), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{20}H_{22}N$: C 86.59, H 8.36, N 5.05; found: C 86.25, H 8.20, N 4.98; HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): t_R = 29.7 (−), 34.9 min (+).

***N,N*-Dibenzyl-4-ethyl-1-hexyn-3-amine (8g)**: The reaction was carried out according to GP B with propargylamine (−)-**5a** (107 mg, 0.29 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8g** (87 mg, 0.28 mmol, 98%) as a colorless oil. $[\alpha]_D^{20}$ = −252 (*c* = 0.47, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.41 (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); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 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): *m*/*z*: 235 (20), 234 (100) [M^+ −H−ethylpropyl], 91 (74); HRMS (EI): *m*/*z*: calcd for $C_{22}H_{26}N$: 304.2065; found: 304.2075 [M^+−H]; IR (film): $\tilde{\nu}$ = 3302 (m), 2963 (s), 2937 (m), 1495 (m), 1454 (m), 748 (m), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{22}H_{26}N$: 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, 0.2 mL min^{-1}): t_R = 28.4 (−), 31.9 min (+).

***N,N*-Dibenzyl-1-cyclopropyl-2-propyn-1-amine (8h)**: The reaction was carried out according to GP B with propargylamine (−)-**5i** (102 mg, 0.29 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8h** (80 mg, 0.29 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ = −138 (*c* = 0.40, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.33 (d, *J* = 7.1 Hz, 4H), 7.23 (t, *J* = 7.8 Hz, 4H), 7.18–7.13 (m, 2H), 3.89 (d, *J* = 13.8 Hz, 2H), 3.34 (d, *J* = 13.8 Hz, 2H), 3.24 (dd, *J* = 5.7, 2.1 Hz, 1H), 2.21 (d, *J* = 2.1 Hz, 1H), 1.06–0.98 (m, 1H), 0.49–0.30 (m, 3H), 0.19–0.13 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.9, 128.7, 128.2, 126.8, 79.4, 73.2, 55.1, 55.0, 13.5, 3.7, 2.0; MS (70 eV, EI): *m*/*z*: 275 (2) [M^+], 234 (37), 91 (100), 77 (13), 65 (11); HRMS (EI): *m*/*z*: calcd for $C_{20}H_{21}N$: 275.1674; found: 275.1655 [M^+]; IR (film): $\tilde{\nu}$ = 3299 (m), 3027 (m), 1495 (m), 1454 (m), 1027 (m), 746 (s), 698 cm^{-1} (vs); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_R = 20.5 (−), 22.9 min (+).

***N,N*-Dibenzyl-1-cyclopentyl-2-propyn-1-amine (8i)**: The reaction was carried out according to GP B with propargylamine (−)-**5j** (110 mg, 0.29 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8i** (87 mg, 0.29 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ = −138 (*c* = 0.57, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.42 (m, 4H), 7.37–7.24 (m, 6H), 3.89 (d, *J* = 13.8 Hz, 2H), 3.40 (d, *J* = 13.8 Hz, 2H), 3.09 (dd, *J* = 10.6, 2.3 Hz, 1H), 2.34 (d, *J* = 2.3 Hz, 1H), 2.36–2.20 (m, 1H), 1.93–1.81 (m, 2H), 1.56–1.22 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 128.9, 128.2, 126.9, 81.8, 72.4, 56.9, 54.9, 42.6, 30.8, 30.2, 24.9, 24.8; MS (70 eV, EI): *m*/*z*: 303 (<1) [M^+], 235 (15), 234 (82), 91 (100), 43 (25); HRMS (EI): *m*/*z*: calcd for $C_{22}H_{25}N$: 303.1987; found: 303.2011 [M^+]; IR (film): $\tilde{\nu}$ = 3301 (m), 2955 (s), 1495 (m), 1453 (m), 747 (s), 698 cm^{-1} (vs).

***N,N*-Dibenzyl-1-cyclohexyl-2-propyn-1-amine (8j)**: The reaction was carried out according to GP B with propargylamine (−)-**5b** (100 mg, 0.26 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8j** (78 mg, 0.25 mmol, 95%) as a colorless solid. M.p. 75–76 °C; $[\alpha]_D^{20}$ = −157 (*c* = 0.35, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.41 (m, 4H), 7.36–7.31 (m, 4H), 7.27–7.23 (m, 2H), 3.85 (d, *J* = 13.7 Hz, 2H), 3.41 (d, *J* = 13.7 Hz, 2H), 3.07 (dd, *J* = 10.6, 2.2 Hz, 1H), 2.37 (d, *J* = 2.2 Hz, 1H), 2.35–2.28 (m, 1H), 2.06–2.00 (m, 1H), 1.72–1.59 (m, 4H), 1.31–1.07 (m, 3H), 0.91–0.72 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.7, 128.8, 128.2, 126.8, 81.0, 73.4, 57.6, 54.8, 39.5, 31.2, 30.2, 26.5, 26.1, 25.9; MS (70 eV, EI): *m*/*z*: 235 (21), 234 (100) [M^+−*c*-Hex], 91 (88); HRMS (EI): *m*/*z*: calcd for $C_{23}H_{27}N$: 317.2143; found: 317.2139 [M^+]; IR (KBr): $\tilde{\nu}$ = 3302 (s), 2926 (vs), 2851 (s), 1495 (m), 1448 (m), 746 (s), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{23}H_{27}N$: C 87.02, H 8.57, N 4.41; found: C 86.74, H 8.37, N 4.32; HPLC (OD-H, 100% *n*-heptane, 0.2 mL min^{-1}): t_R = 31.7 (−), 36.0 min (+).

(1*E*)-*N,N*-Dibenzyl-1-phenyl-1-penten-4-yn-3-amine (8k)

General procedure C: Propargylamine (+)-**5k** (118 mg, 0.29 mmol) was dissolved in MeOH (5 mL). KOH (0.4 mL, 1.0 m in MeOH, 0.40 mmol) was added and the reaction mixture was stirred at RT for 12 h. The reaction mixture was quenched with water (25 mL) and extracted with Et_2O (3 × 20 mL). After evaporation of the solvent and column chromatographic purification on silica gel (pentane/Et_2O 99:1), propargylamine (+)-**8k** (93 mg, 0.28 mmol, 95%) was obtained as a colorless oil. $[\alpha]_D^{20}$ = +41 (*c* = 0.77, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.47–7.25 (m, 15H), 6.95 (dd, *J* = 15.9, 1.7 Hz, 1H), 6.26 (dd, *J* = 15.9, 4.4 Hz, 1H), 4.37–3.36 (m, 1H), 3.91 (d, *J* = 13.9 Hz, 2H), 3.52 (d, *J* = 13.9 Hz, 2H), 2.63 (d, *J* = 2.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 139.5, 136.6, 132.7, 128.8, 128.5, 128.3, 128.0, 127.6, 127.0, 126.6, 79.0, 75.6, 54.7, 53.6; MS (70 eV, EI): *m*/*z*: 337 (12) [M^+], 336 (24), 246 (44), 142 (16), 141 (68), 115 (31), 92 (11), 91 (100), 65 (11); HRMS (EI): *m*/*z*: calcd for $C_{25}H_{23}N$: 337.1830; found: 337.1853 [M^+]; IR (film): $\tilde{\nu}$ = 3291 (s), 3281 (s), 3024 (m), 2839 (m), 1494 (m), 1453 (m), 967 (s), 745 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{25}H_{23}N$: C 88.98, H 6.87, N 4.15; found: C 88.64, H 7.12, N 4.08; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.15 mL min^{-1}): t_R = 35.0 (−), 46.3 min (+).

***N,N*-Dibenzyl-1,1-diphenyl-1-penten-4-yn-3-amine (8l)**: The reaction was carried out according to GP C with propargylamine (+)-**5l** (119 mg, 0.25 mmol) and KOH (0.40 mL, 0.40 mmol) in MeOH (3 mL) at RT for 12 h. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**8l** (101 mg, 0.25 mmol, 98%) as a colorless oil. $[\alpha]_D^{20}$ = +47 (*c* = 0.27, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.11 (m, 20H), 6.20 (d, *J* = 9.3 Hz, 1H), 4.29 (dd, *J* = 9.3, 2.2 Hz, 1H), 3.89 (d, *J* = 13.8 Hz, 2H), 3.62 (d, *J* = 13.8 Hz, 2H), 2.46 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.6, 142.2, 139.3, 138.6, 129.6, 128.8, 128.1, 128.0, 127.7, 127.6, 127.3, 126.8, 125.3, 112.3, 81.6, 73.5, 55.1, 50.9; MS (70 eV, EI): *m*/*z*: 413 (16) [M^+], 412 (20), 323 (23), 322 (86), 218 (20), 217 (83), 218 (18), 215 (39), 202 (45), 139 (28), 91 (100); HRMS (EI): *m*/*z*: calcd for $C_{31}H_{37}N$: 413.2143; found: 413.2103 [M^+]; IR (film): $\tilde{\nu}$ = 3292 (m), 3028 (m), 1494 (m), 1454 (m), 1444 (m), 748 (m), 697 cm^{-1} (vs); elemental analysis calcd (%) for $C_{31}H_{37}N$: C 90.03, H 6.58, N 3.39; found: C 90.34, H 6.65, N 3.23; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.15 mL min^{-1}): t_R = 37.4 (−), 40.5 min (+).

***N,N*-Dibenzyl-5-phenyl-1-pentyn-3-amine (8m)**: The reaction was carried out according to GP B with propargylamine (−)-**5m** (96 mg, 0.23 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8m** (75 mg, 0.22 mmol, 97%) as a colorless oil. $[\alpha]_D^{20}$ = −83 (*c* = 0.46, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.45–7.15 (m, 13H), 7.09–7.07 (m, 2H), 3.91 (d, *J* = 13.8 Hz, 2H), 3.52 (dd, *J* = 8.0, 2.2 Hz, 1H), 3.48 (d, *J* = 13.8 Hz, 2H), 2.87–2.77 (m, 1H), 2.72–2.62 (m, 1H), 2.39 (d, *J* = 2.2 Hz, 1H), 2.16–1.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 141.7, 139.5, 128.9, 128.3, 128.3, 128.2, 126.9, 125.7, 81.7, 72.9, 54.9, 51.2, 35.5, 32.5; MS (70 eV, EI): *m*/*z*: 339 (1) [M^+], 235 (18), 234 (100), 91 (94); HRMS (EI): *m*/*z*: calcd for $C_{25}H_{25}N$: 339.1987; found: 339.1975 [M^+]; IR (film): $\tilde{\nu}$ = 3295 (m), 3027 (m), 1495 (s), 1454 (s), 746 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{25}H_{25}N$: C 88.45, H 7.42, N 4.13; found: C 88.30, H 7.47, N 4.01; HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.15 mL min^{-1}): t_R = 38.6 (+), 42.5 min (−).

***N,N*-Dibenzyl-5-(4-bromphenyl)-1-pentyn-3-amine (8n)**: The reaction was carried out according to GP B with propargylamine (−)-**5n** (107 mg, 0.22 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8n** (92 mg, 0.22 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ = −54 (*c* = 0.41, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.41–7.25 (m, 12H),6.89 (d, *J* = 8.2 Hz, 2H), 3.87 (d, *J* = 14.0 Hz, 2H), 3.45 (d, *J* = 14.0 Hz, 2H), 3.43 (dd, *J* = 7.4, 2.1 Hz, 1H), 2.77–2.56 (m, 2H), 2.38 (d, *J* = 2.2 Hz, 1H), 2.09–1.87 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5, 139.4, 131.3, 130.1, 128.9,

128.3, 127.0, 119.5, 81.5, 73.0, 55.0, 50.8, 35.3, 31.8; MS (70 eV, EI): *m/z*: 417 (<1) [M^+], 235 (19), 234 (100), 91 (79); HRMS (EI): *m/z*: calcd for $C_{25}H_{24}BrN$: 417.1092; found: 417.1044 [M^+]; IR (film): $\tilde{\nu}$ = 3296 (m), 3028 (m), 2931 (m), 2835 (m), 1488 (vs), 1454 (s), 1072 (s), 1012(s), 747 (s), 698 cm^{-1} (vs); HPLC (OD-H, 100% *n*-heptane, 0.5 mL min^{-1}): t_R = 47.8 (−), 67.2 min (+).

Ethyl 4-[3-(dibenzylamino)-4-pentynyl]benzoate (8o): The reaction was carried out according to GP B with propargylamine (−)-**5o** (140 mg, 0.29 mmol) and Bu_4NF (0.10 mL, 0.10 mmol) in THF (3 mL) at 0 °C for 15 min. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 9:1) yielded propargylamine (−)-**8o** (108 mg, 0.26 mmol, 91%) as a colorless oil. $[\alpha]_D^{20}$ = −83 (*c* = 0.81, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.89 (d, *J* = 8.2 Hz, 2H), 7.42–7.24 (m, 10H), 7.09 (d, *J* = 8.5 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 3.88 (d, *J* = 13.6 Hz, 2H), 3.50–3.46 (m, 1H), 3.45 (d, *J* = 13.6 Hz, 2H), 2.88–2.78 (m, 1H), 2.74–2.63 (m, 1H), 2.39 (d, *J* = 2.2 Hz, 1H), 2.13–1.90 (m, 2H), 1.42 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6, 147.0, 139.4, 129.6, 128.9, 128.3, 128.1, 127.0, 88.6, 81.5, 73.1, 60.7, 55.0, 51.0, 35.1, 32.5, 14.4; MS (70 eV, EI): *m/z*: 411 (2) [M^+], 235 (19), 234 (100), 91 (83); HRMS (EI): *m/z*: calcd for $C_{28}H_{29}NO_2$: 411.2198; found: 411.2233 [M^+]; IR (film): $\tilde{\nu}$ = 3295 (m), 2936 (m), 1716 (vs), 1611 (m), 1454 (m), 1367 (m), 1277 (vs), 1178 (m), 1107 (s), 747 (m), 699 cm^{-1} (s); elemental analysis calcd (%) for $C_{28}H_{29}NO_2$: C 81.72, H 7.10, N 3.40; found: C 81.60, H 7.19, N 3.29.

***N*,*N*-Dibenzyl-1-(2-thienyl)-2-propyn-1-amine (8p)**: The reaction was carried out according to GP C with propargylamine (+)-**5r** (95 mg, 0.24 mmol) and KOH (0.40 mL, 0.40 mmol) in MeOH (3 mL) at RT for 12 h. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**8p** (76 mg, 0.24 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ = +32 (*c* = 0.50, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.53–7.51 (m, 4H), 7.37 (t, *J* = 7.5 Hz, 4H), 7.30–7.25 (m, 4H), 6.97 (dd, *J* = 4.8, 3.6 Hz, 1H), 4.90 (s br, 1H), 3.90 (d, *J* = 13.8 Hz, 2H), 3.51 (d, *J* = 13.8 Hz, 2H), 2.64 (d, *J* = 2.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.0, 139.0, 128.7, 128.3, 127.1, 126.2, 126.1, 125.5, 78.4, 74.8, 54.4, 52.1; MS (70 eV, EI): *m/z* (%): 317 (22) [M^+], 226 (32), 121 (100); HRMS (EI): *m/z*: calcd for $C_{21}H_{19}NS$: 317.1238; found: 317.1255 [M^+]; IR (film): $\tilde{\nu}$ = 3294 (m), 3028 (m), 2834 (m), 2810 (m), 1495 (m), 1454 (m), 1232 (m), 1116 (m), 745 (m), 698 (vs), 665 cm^{-1} (m); HPLC (OD-H, 98% *n*-heptane/2% isopropanol, 0.2 mL min^{-1}): t_R = 21.0 (−), 23.0 min (+).

***N*,*N*-Dibenzyl-1-(3-thienyl)-2-propyn-1-amine (8q)**: The reaction was carried out according to GP C with propargylamine (+)-**5s** (99 mg, 0.26 mmol) and KOH (0.40 mL, 0.40 mmol) in MeOH (3 mL) at RT for 12 h. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (+)-**8q** (74 mg, 0.26 mmol, 99%) as a colorless oil. $[\alpha]_D^{20}$ = +22 (*c* = 0.52, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 7.43–7.37 (m, 5H), 7.32–7.18 (m, 8H), 4.67 (s br, 1H), 3.75 (d, *J* = 13.6 Hz, 2H), 3.42 (d, *J* = 13.6 Hz, 2H), 2.55 (d, *J* = 2.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.5, 139.4, 128.8, 128.3, 127.4, 127.0, 125.7, 123.2, 79.3, 74.5, 54.4, 52.0; MS (70 eV, EI): *m/z* (%): 317 (22) [M^+], 226 (31), 196 (48), 122 (20), 120 (100), 92 (12), 91 (84); HRMS (EI): *m/z*: calcd for $C_{21}H_{19}NS$: 317.1238; found: 317.1232 [M^+]; IR (film): $\tilde{\nu}$ = 3294 (s), 3028 (m), 2809 (m), 1494 (s), 1454 (s), 1284 (m), 1116 (m), 1074 (m), 842 (m), 790 (s), 753 (s), 741 (s), 698 (vs), 660 cm^{-1} (m); HPLC (OD-H, 98% *n*-heptane/2% isopropanol, 0.2 mL min^{-1}): t_R = 20.6 (−), 23.5 min (+).

***N*-[1-(1-Benzothien-3-yl)-2-propynyl]-*N*,*N*-dibenzylamine (8r)**: The reaction was carried out according to GP C with propargylamine (−)-**5u** (121 mg, 0.28 mmol) and KOH (0.40 mL, 0.40 mmol) in MeOH (3 mL) at RT for 12 h. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) yielded propargylamine (−)-**8r** (95 mg, 0.26 mmol, 92%) as a yellow oil. $[\alpha]_D^{20}$ = −119 (*c* = 0.82, $CHCl_3$); ^1H NMR (600 MHz, $CDCl_3$): δ = 7.70 (m, 1H), 7.67 (m, 1H), 7.63 (s, 1H), 7.24–7.20 (m, 10H), 7.16–7.14 (m, 2H), 4.92 (s, 1H), 3.73 (d, *J* = 13.1 Hz, 2H), 3.37 (d, *J* = 13.1 Hz, 2H), 2.61 (s, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ = 141.3, 139.4, 137.9, 133.7, 129.9, 128.6, 127.6, 126.7, 124.8, 124.1, 123.8, 123.0, 79.0, 75.8, 55.2, 51.8; MS (70 eV, EI): *m/z* (%): 367 (10) [M^+], 196 (16), 172 (19), 171 (100), 91 (33); HRMS (EI): *m/z*: calcd for $C_{25}H_{21}NS$: 367.1395; found: 367.1382 [M^+]; IR (film): $\tilde{\nu}$ = 3274 (vs), 3026 (m), 2836 (m), 1453 (m), 1428 (m), 1368 (m), 1099 (m), 755 (s), 737 (s), 701 (s), 674 (m), 658 cm^{-1} (m).

***(R)*-1-Ferrocenyl-1-[(*S*)-2-methoxymethyl-1-pyrrolidinyl]-3-trimethylsilyl-2-propyne (12c)**: Prepared according to GP A from trimethylsilylacetylene (**1e**) (982 mg, 10.0 mmol), ferrocenecarbaldehyde (**2l**) (2.14 g, 10.0 mmol), (2*S*)-2-(methoxymethyl)pyrrolidine (1.15 g, 10.0 mmol), CuBr (72 mg, 0.50 mmol), MS 4 Å (5.0 g) in toluene (20 mL) at RT for 5 d. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 9:1) afforded **12c** as a red oil (3.03 g, 7.40 mmol, 74%). $[\alpha]_D^{20}$ = +181.9 (*c* = 1.56, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ = 4.72 (s, 1H), 4.43 (s, 1H), 4.20 (s, 1H), 4.16 (s, 5H), 4.08 (s, 2H), 3.39 (s, 3H), 3.38 (dd, *J* = 9.2 Hz, 5.9 Hz, 1H), 3.28 (dd, *J* = 9.2 Hz, 6.3 Hz, 1H), 3.11–3.07 (m, 1H), 2.66–2.61 (m, 2H), 1.86–1.80 (m, 1H), 1.67–1.56 (m, 3H), 0.24 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 103.0, 88.8, 86.1, 76.6, 76.2, 68.6, 68.3, 67.8, 67.1, 59.5, 58.7, 53.9, 48.1, 26.3, 22.5, 0.12; MS (EI, 70 eV): *m/z* (%): 410 (10) [M^+−H], 409 (31), 296 (33), 295 (100); HRMS: *m/z*: calcd for $C_{22}H_{31}FeNOSi$: 409.1524; found: 409.1544; IR (KBr): $\tilde{\nu}$ = 3096 (m), 2960 (s), 2873 (s), 2825 (m), 2161 (m), 1449 (m), 1249 (s), 1106 (vs), 999 (s), 842 cm^{-1} (vs).

***N*,*N*-Dibenzyl-4-phenyl-1-pentyn-3-amine (14)**: Prepared according to GP A from trimethylsilylacetylene (**1e**) (196 mg, 2.00 mmol), phenyl propionaldehyde (268 mg, 2.00 mmol), dibenzylamine (**3a**) (394 mg, 2.00 mmol), CuBr (14.2 mg, 0.10 mmol) and MS 4 Å (1.0 g) in toluene (4 mL) at RT for 4 d. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) afforded **14** as a white solid (363 mg, 0.88 mmol, 44%). The *dr* 92:8 was determined by ^1H NMR analysis. M.p. 79–81 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.31–7.28 (m, 3H), 7.23–7.19 (m, 6H), 7.00–6.91 (m, 6H), 3.77 (d, *J* = 13.6 Hz, 2H), 3.53 (d, *J* = 11.3 Hz, 1H), 3.32 (d, *J* = 13.6 Hz, 2H), 3.14–3.02 (m, 1H), 1.34 (d, *J* = 6.8 Hz, 3H), 0.33 (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 144.1, 139.2, 129.0, 128.9, 128.2, 128.0, 127.9, 126.7, 126.1, 103.3, 90.6, 58.5, 54.5, 42.7, 21.2, 0.4; MS (70 eV, EI): *m/z* (%): 396 (1) [M^+−CH_3], 307 (28), 306 (100), 91 (32); HRMS (EI): *m/z*: calcd for $C_{28}H_{32}NSi$: 410.2304; found: 410.2329 [M^+−H]; IR (KBr): $\tilde{\nu}$ = 2958 (w), 2806 (w), 2158 (w), 1495 (w), 1453 (w), 1247 (m), 1005 (m), 838 (s), 748 (s), 698 cm^{-1} (vs); elemental analysis calcd for $C_{28}H_{33}NSi$: C 81.69, H 8.08, N 3.40; found: C 81.99, H 7.87, N 3.32.

***N*^{4},*N*^{4},*N*^{13},*N*^{13}-Tetrabenzyl-5,11-hexadecadiyne-4,13-diamine (15)**: Prepared according to GP A from 1,7-octadiyne (106 mg, 1.00 mmol), butyraldehyde (**2m**) (144 mg, 2.00 mmol), dibenzylamine (**3a**) (394 mg, 2.00 mmol), CuBr (14.2 mg, 0.10 mmol) and MS 4 Å (1.0 g) in toluene (4 mL) at RT for 7 d. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 99:1) afforded **15** (372 mg, 0.61 mmol, 61%)as a colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.37 (m, 8H), 7.31–7.18 (m, 12H), 3.81 (d, *J* = 14.0 Hz, 4H), 3.40 (d, *J* = 14.0 Hz, 4H), 3.39–3.36 (m, 2H), 2.39–2.37 (m, 2H), 1.81–1.37 (m, 12H), 0.78 (t, *J* = 7.2 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 140.1, 128.8, 128.1, 126.7, 84.4, 78.5, 54.9, 51.5, 36.4, 28.4, 19.6, 18.3, 13.7; MS (70 eV, EI): *m/z* (%): 608 (<1) [M^+], 566 (13), 565 (29), 370 (12), 92 (12), 91 (100); HRMS (EI): *m/z*: calcd for $C_{44}H_{52}N_2$: 608.4130; found: 608.4106 [M^+]; IR (KBr): $\tilde{\nu}$ = 3028 (m), 2956 (s), 2935 (s), 2871 (m), 1494 (s), 1454 (s), 747 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{44}H_{52}N_2$: C 86.79, H 8.61, N 4.60; found: C 87.04, H 8.59, N 4.52.

***N*,*N*-Diallyl-*N*-(1-{4-[1-(diallylamino)-3-phenyl-2-propynyl]-phenyl}-3-phenyl-2-propynyl)amine (16)**: Prepared according to GP A from phenylacetylene (**1a**) (408 mg, 4.00 mmol), terephthalaldehyde (268 mg, 2.00 mmol), diallylamine (**3b**) (388 mg, 4.00 mmol), CuBr (28.7 mg, 0.20 mmol) and MS 4 Å (2.0 g) in toluene (6 mL) at RT for 1 d and at 60 °C for 18 h. Standard workup and column chromatographic purification on silica gel (pentane/Et_2O 24:1) afforded **16** (718 mg, 1.45 mmol, 72%)as a yellow solid. M.p. 73 °C; ^1H NMR (300 MHz, $CDCl_3$): δ = 7.68–7.47 (m, 4H), 7.56–7.52 (m, 4H), 7.37–7.32 (m, 6H), 5.94–5.81 (m, 4H), 5.31–5.26 (m, 4H), 5.16–5.13 (m, 4H), 5.11 (s, 2H), 3.33–3.27 (m, 4H), 3.10–3.03 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 138.5, 136.5, 131.8, 128.3, 128.1, 128.0, 123.3, 117.3, 87.8, 85.5, 56.4, 53.6; MS (70 eV, EI): *m/z* (%): 496 (10) [M^+], 455 (13), 401 (29), 400 (100), 399 (11), 358 (12), 318 (11), 305 (25), 304 (50), 210 (26), 41 (28); HRMS (EI): *m/z*: calcd for

$C_{36}H_{36}N_2$: 496.2878; found: 496.2878 [M^+]; IR (KBr): $\tilde{\nu}$ = 3079 (m), 2817 (m), 1643 (m), 1490 (s), 1443 (m), 1417 (m), 995 (m), 972 (m), 920 (s), 755 (vs), 690 cm^{-1} (s); elemental analysis calcd (%) for $C_{36}H_{36}N_2$: C 87.05, H 7.31, N 5.64; found: C 87.01, H 7.43, N 5.51.

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