Synthesis of Enantiomerically Enriched Propargylamines by Copper-Catalyzed Addition of Alkynes to Enamines

Christopher Koradin, Nina Gommermann, Kurt Polborn, and Paul Knochel*[a]

Abstract: The first copper(I) bromide/Quinap-catalyzed synthesis of enantiomerically enriched propargylamines by addition of alkynes to enamines is reported. Various functionalized terminal alkynes add smoothly to N-protected enamines to afford the corresponding amines in good to high yields and moderate to good enantiomeric excesses. The influence of the metal salt, the ligand, and the protecting group on the conversion, the reaction rate, and the stereoselectivity of the reaction are investigated. The scope of the reaction and further transformations of the resulting propargylamines (deprotection, Pauson–Khand reaction) are also described.

Keywords: alkynes · amines · asymmetric catalysis · C–H activation · copper catalysis

Introduction

One of the most challenging tasks in organic synthesis is the efficient preparation of complex molecules starting from easily available raw materials. Therefore, the development of new C–C bond coupling reactions which proceed with good atom economy is of great importance.[1] The selective elaboration of stereogenic centers and the chemoselective introduction of functional groups are especially of fundamental importance.[2] Amines and their derivatives are very widespread functional groups which are found in various natural products, pharmaceuticals, and fine biologically important chemicals.[3] Propargylamines are both biologically relevant and useful synthetic intermediates for the preparation of polyfunctional amino derivatives.[4] Several diastereoselective and enantioselective syntheses of propargylamines have been reported,[5] but a metal-catalyzed enantioselective preparation has not yet been described.[6] Recently, Li[7] and our group[8] independently reported an enantioselective copper-catalyzed addition of alkynes[9] to imines and enamines, respectively.[10] In this paper we disclose detailed studies on the different parameters influencing the outcome of this asymmetric reaction. Furthermore, we demonstrate its broad scope and synthetic utility.

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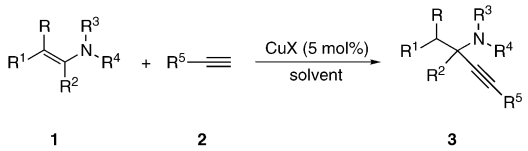
Results and Discussion

In our previous investigations we reported that only copper salts satisfactorily catalyze the addition of alkynes **2** to enamines **1** to afford propargylamines of type **3** (Scheme 1).[11]



Scheme 1. Synthesis of propargylamines of type **3** by the addition of alkynes **1** to enamines **2**.

The use of other transition metal salts, for example, AgOAc, AuI, $AuBr_3$, $Sc(OTf)_3$, $Yb(OTf)_3$, $La(OTf)_3$, $Ru(acac)_3$, $Rh(acac)_3$, Rh(acac)cod, and $Zn(OTf)_2$, gave in all cases no or inferior conversions to the desired propargylamines. Among all the copper salts tested, copper(I) and copper(II) bromide (max. 5 mol%) proved to be the most active catalysts for this transformation. The solvent of choice is toluene and its use resulted in higher conversions to the desired products compared with Et_2O, THF, *N*-methylpyrrolidinone (NMP), or others. We chose enamines with readily removable protecting groups as substrates. The substituents attached to the enamine nitrogen atom play a crucial role in the success of the reaction (Table 1). Only bisalkylated enamines (R^3, R^4 = alkyl) yielded the propargylamines **3**, whereas the replacement of one alkyl group by a trimethyl-

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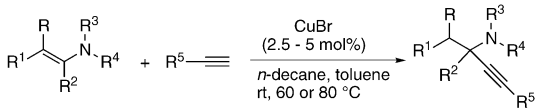
Table 1. Propargylamines of type **3** obtained by the copper(I) bromide-catalyzed addition of alkynes **2** to enamines **1**.



1a-p **2a-n** **3a-ac**

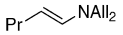
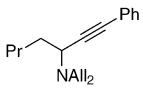
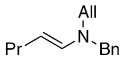
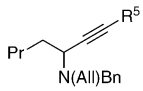
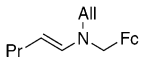
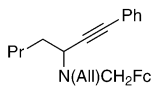
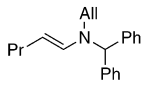
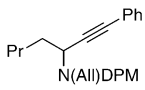
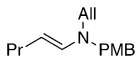
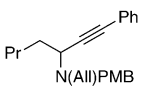
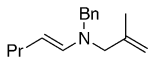
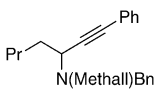
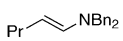
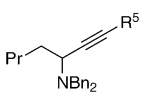
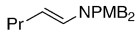
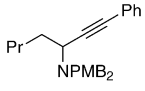
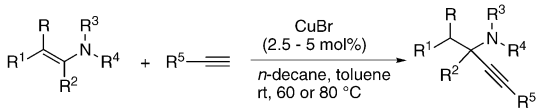
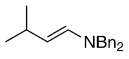
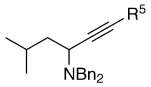
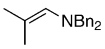
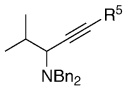
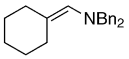
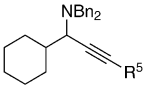
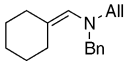
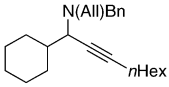
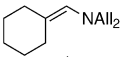
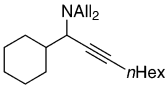
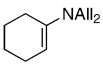
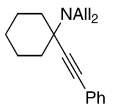
Entry	**1**	**2**	R^5	**3**	$t_{reaction}$ [h]	Yield [%][a]
						
1	**a**	**a**	Ph	**a**	16	98
						
2	**b**	**a**	Ph	**b**	16	82
3	**b**	**b**	*n*Hex	**c**	4	75
4	**b**	**c**	H	**d**	4	69
						
5	**c**	**a**	Ph	**e**	21	73
						
6	**d**	**a**	Ph	**f**	9	85
						
7	**e**	**a**	Ph	**g**	44	78
						
8	**f**	**a**	Ph	**h**	20	91
						
9	**g**	**a**	Ph	**i**	27	75
10	**g**	**d**	1-cyclohexenyl	**j**	20	77
11	**g**	**e**	$(CH_2)_3CN$	**k**	5	82[b]
12	**g**	**f**	$(CH_2)_3Cl$	**l**	67	78
13	**g**	**g**	CH_2OMe	**m**	3	84
14	**g**	**h**	$CH_2OTBDPS$	**n**	24	93
15	**g**	**i**	TMS	**o**	16	70
16	**g**	**j**	$CH(OEt)_2$	**p**	4	66
						

Table 1 (continued).



1a-p **2a-n** **3a-ac**

Entry	**1**	**2**	R^5	**3**	$t_{reaction}$ [h]	Yield [%][a]
17	**h**	**a**	Ph	**q**	5	99
						
18	**i**	**a**	Ph	**r**	18	91
19	**i**	**k**	*n*Bu	**s**	24	89
						
20	**j**	**a**	Ph	**t**	24	99
21	**j**	**l**	TIPS	**u**	7	88[b]
22	**j**	**m**	$(CH_3)_2$OTMS	**v**	20	85[b]
						
23	**k**	**a**	Ph	**w**	27	94[b]
24	**k**	**n**	*p*BrPh	**x**	18	90[b]
						
25	**l**	**b**	*n*Hex	**y**	24	80[b]
						
26	**m**	**b**	*n*Hex	**z**	15	82
						
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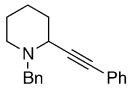
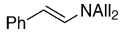
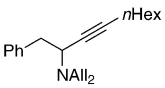
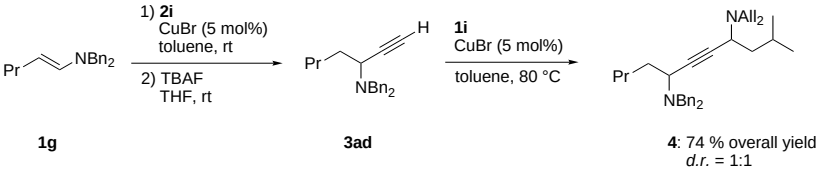
						
28	**o**	**a**	Ph	**ab**	3	86[c]
						
29	**p**	**b**	*n*Hex	**ac**	18	79[c]

[a] Isolated yield of analytically pure product. [b] The reaction was performed at 60 °C. [c] The reaction was performed at 80 °C.

silyl, acetyl, or tosyl group (R, $R^2 = H$, $R^1 = Me$ or Pr, $R^3 = Bn$, $R^4 = TMS$,[12] $C(O)CH_3$,[13] or Ts[14]) leads to no formation of **3**.

By increasing the steric hindrance of the protecting groups, the rate of the addition decreased ($(All)_2 > (All)Bn > Bn_2$). Furthermore, the substituents at the enamine double bond had a strong influence on the reaction rate. Disubstituted enamines were usually more reactive than trisubstituted ones (compare entries 9 and 20 or 23) and β,β'-trisubstituted enamines needed less activation than α,α'-trisubstituted enamines (compare entries 26 and 27). Also, electronic effects influence the outcome of the reaction. For example, the conjugated, disubstituted enamine **1p** is less reactive than the unconjugated trisubstituted enamine **1m**. As can be seen from Table 1, various functionalized alkynes undergo the addition. The reaction tolerates the presence of a double bond, different protected alcohols, a cyano, a chloride, silyl groups, and an acetal moiety. In the case of the cyclic enamine **1o**, which is in equilibrium with a dimeric structure,[15] the reaction was carried out at 80 °C (3 h; entry 28 of Table 1). Remarkably, acetylene itself (**2c**) reacted with good selectivity (>9:1) to give the monopropargylamine **3d** in good yield (entry 4, 69 %). For a second addition higher temperatures were required (Scheme 2). We were able to combine a whole

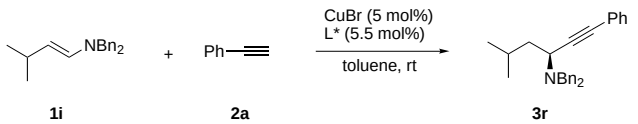


Scheme 2. Synthesis of 1,4-diamines.

range of different enamines **1** leading to 1,4-diamines like **4** as 1:1 mixtures of diastereoisomers in good to very good yields.

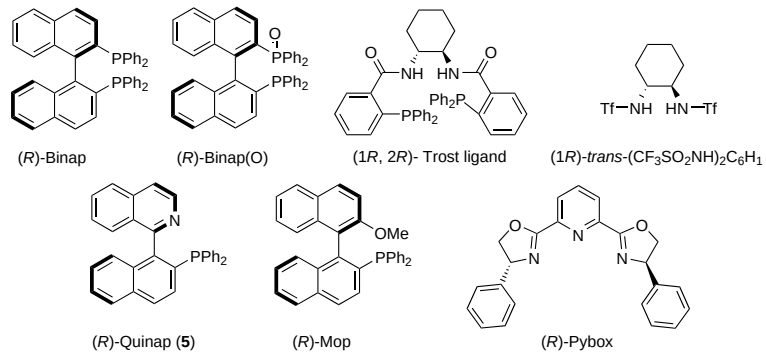
After these studies, we turned our attention to the enantioselective addition reaction. Firstly, we screened various chiral ligands, for example, diphosphanes, aminophosphanes, and diamines (Table 2, Scheme 3).

Table 2. Ligand screening for the chiral addition reaction.



Ligand	Conversion [%][a]	*ee* [%][b]
(*R*)-Binap	0	–
(*R*)-Binap(O)	0	–
(*R*)-Binap(O)[c]	40	0
(1*R*,2*R*)-Trost ligand	0	–
(*R*)-Quinap (**5**)	100	85
(1*R*)-*trans*-$(CF_3SO_2NH)_2C_6H_{10}$	100	0
(*R*)-Pybox	55	32
(R)-MOP	87	0

[a] Conversions determined by GC analysis with *n*-decane as an internal standard. [b] Enantiomeric excess determined by HPLC with a Chiracel OD column (*n*-heptane/*i*PrOH). [c] [Cu]:L* = 1:2.



Scheme 3. Ligands for the chiral addition reaction.

Generally, an added chiral ligand decreased the reactivity enormously. In most cases there was no detectable conversion to the amine **3r** at room temperature. Only (*R*)-Quinap (**5**),[16] using one equivalent relative to copper(I) bromide, was suitable to induce good enantioselectivity with very good conversion. Interestingly, with two equivalents of the catalyst **5**, conversion to the propargylamine **3r** was first achieved at 60 °C but without any enantioselectivity. We have investigated the influence of the copper salt on the selectivity and the rate of the reaction with the same enamine **1i** (Table 3).

The counterion had a dramatic effect on both parameters. The most reactive copper source (CuBr) is also the most selective one. Except for CuCl, all other tested copper salts gave poorer results. We have examined the effect of the protecting groups on the enamine nitrogen atom by using phenylacetylene (**2a**) as the alkyne under these optimized conditions (Table 4).

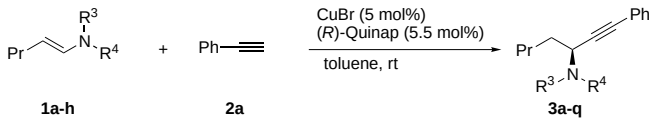
As in the case of the racemic reaction, increasing the steric bulk of the protecting group leads to a drop of reactivity. In some cases partial decomposition of the enamines **1c–e** was observed during the reaction, and the corresponding propargylamines **3c–e** could only be isolated in low yields. Initially, the enantioselectivity (% *ee*) increased with the size of the protecting group. For example, the *ee* increased from diallyl (77 % *ee*, entry 1) to allyl benzyl (82 % *ee*, entry 2) to

Table 3. Influence of the copper salt on the enantioselectivity and the reaction rate.

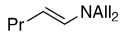
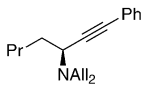
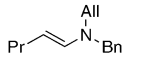
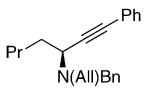
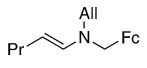
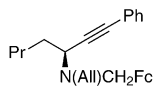
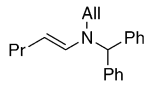
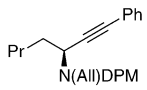
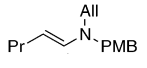
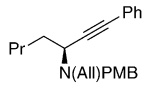
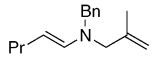
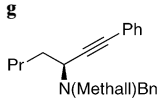
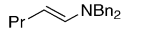
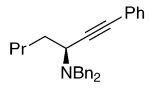
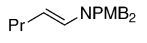
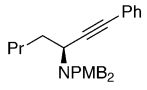
Cu salt	Conversion [%][a]	*t* [h]	*ee* [%][b]
CuCl	90	28	81
CuBr	100	18	85
CuI	75	168	62
$CuOTf \cdot 0.5\,C_6H_6$	70	168	16
$CuOTf_2$	40	120	28
CuTc[c]	50	144	40
$CuOAc_2$	40	120	12
CuCN	0	120	–
$Cu(MeCN)_4PF_6$	3	240	–

[a] Conversions determined by GC analysis with *n*-decane as an internal standard. [b] Enantiomeric excess determined by HPLC with a Chiracel OD column (*n*-heptane/*i*PrOH). [c] CuTC: copper(I) thiophene-2-carboxylate.

Table 4. Influence of the protecting group on the enantioselectivity.



1a-h **2a** **3a-q**

Entry	**1**	**3**	Yield [%][a]	*ee* [%][b]
				
1	**a**	**a**	99	77[c]
				
2	**b**	**b**	91	82[d]
				
3	**c**	**e**	10	76[e]
				
4	**d**	**f**	30	50[c]
				
5	**e**	**g**	35	68[f]
				
6	**f**	**h**	99	86[d]
				
7	**g**	**i**	78	83
				
8	**h**	**q**	99	66[g]

[a] Isolated yield of analytically pure product. [b] Enantiomeric excess determined by HPLC with a Chiracel OD-H column (*n*-heptane/*i*PrOH). [c] Enantiomeric excess determined after deprotection to **7d**. [d] Enantiomeric excess determined after deprotection to **7a**. [e] Enantiomeric excess determined after deprotection to **7b**. [f] Enantiomeric excess determined after transformation to **10**. [g] Enantiomeric excess determined after complexation with $Co_2(CO)_8$ (1.1 equiv, 90% yield).

dibenzyl (83% *ee*, entry 7). The exchange of the allyl group in **1b** by a methallyl group in **1f** furnished the highest *ee* (86% *ee*, entry 6). In contrast, the mixed enamines **1c–e** gave only moderate *ee* values, perhaps due to the degradation of these enamines.

For further investigations of the scope of the enantioselective reaction, we chose the dibenzyl group as the protecting group, because of its availability, good *ee* of the products, and the easy separation of the corresponding propargylamines by chiral HPLC analysis (Table 5).

As shown in Table 5, polyfunctional propargylamines can be prepared in 54–90% *ee* and in moderate to high yields. In general, the heteroatom-functionalized alkynes afforded lower *ee* values than the unfunctionalized alkynes. Surprisingly, both 2- and 3-pyridinylacetylene (**2o**, **2p**) yielded the amines **3ae** and **3af**, respectively, with 70% *ee* (entries 7 and 8). A second substituent at the β-carbon of the enamine (entries 11 and 12) raised the enantioselectivity further. Enamine **1k** and 1-bromo-4-ethynylbenzene (**2n**) yielded propargylamine **3x** with the highest enantioselectivity (90% *ee*, 83% yield). The absolute (*S*)-configuration of **3x** was established by X-ray analysis (Figure 1).[17]

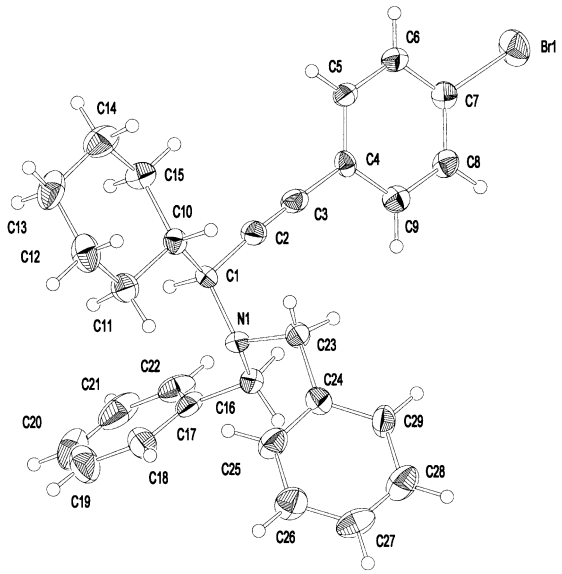
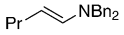
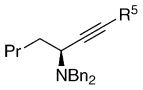
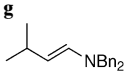
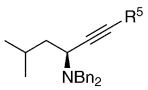
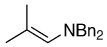
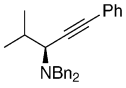
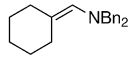
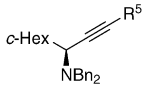


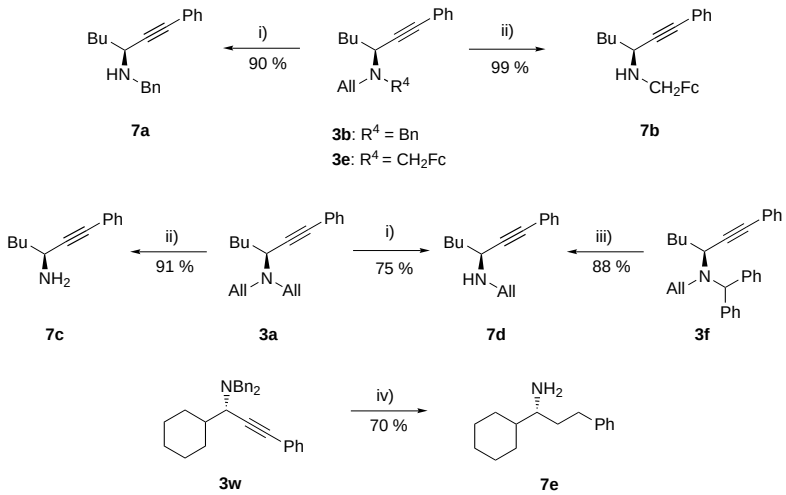
Figure 1. Structure of the propargylamine **3x** in the solid state. Selected bond lengths [Å] and angles [°]: C1–C2 1.481(4), C1–C10 1.541(4), C1–N1 1.479(4), C2–C3 1.189(5), C7–Br1 1.895(3); N1-C1-C10 113.4(3), C2-C1-C10 112.9(2), N1-C1-C2 111.6(3), C3-C2-C1 175.2(3), C2-C3-C4 178.0(4).

The propargylamines **3** obtained can be selectively deprotected by known literature methods (Scheme 4). Thus, treatment of the mixed (allyl)propargylamine **3b** with thiosalicylic acid (**6**) in the presence of a palladium(0) catalyst (5 mol% $[Pd(dba)_2]$ and 5 mol% dppb) led to the monoprotected propargylamine **7a** in 90% yield.[18] With the same catalyst, the monoallylated amine **7d** was obtained in 75% yield starting from **3a**. Treatment of **3f** with an excess of triethylsilane (5 equiv) in refluxing trifluoroacetic acid also yielded the monoallylated amine **7d** in 88% yield.[19] By using Guibé's method (5 mol% $[Pd(PPh_3)_4]$, 1,3-dimethylbarbituric acid (**8**, 3 equiv)), **3e** was converted into the monoprotected amine **7b** in 99% yield.[20] Furthermore, the absolute configuration of the propargylic amine **3a** was determined by its transformation into the amine **7c** (91%) and comparison of its optical rotation with literature data.[5e] Primary amines can be obtained by hydrogenation of dibenzyl-protected propargylamines in good yields. For example, the amine **3w** is hydrogenated to the amine **7e** in 70% yield. To demonstrate further synthetic application, the allyl-protected amines **3b** and **3g** were used in Pauson–Khand reactions (Scheme 5).[21] Treat-

Table 5. Enantioselective synthesis of propargylamines **3** by the copper(I) bromide/(*R*)-Quinap (**5**)-catalyzed addition of alkynes **2** to enamines **1**.

Entry	**1**	**2**	R^5	**3**	Yield [%][a]	*ee* [%][b]
						
1	**g**	**d**	1-cyclohexenyl	**j**	84	74
2	**g**	**e**	$(CH_2)_3CN$	**k**	50	54
3	**g**	**f**	$(CH_2)_3Cl$	**l**	58	60
4	**g**	**g**	CH_2OMe	**m**	76	55
5	**g**	**h**	$CH_2OTBDPS$	**n**	85	72
6	**g**	**i**	TMS	**o**	73	86[c]
7	**g**	**o**	2-pyr	**ae**	73	70
8	**g**	**p**	3-pyr	**af**	57	70
						
9	**i**	**a**	Ph	**r**	99	85
10	**i**	**k**	*n*Bu	**s**	56	76
						
11	**j**	**a**	Ph	**t**	64	87
						
12	**k**	**a**	Ph	**w**	79	88
13	**k**	**n**	*p*BrPh	**x**	83	90

[a] Isolated yield of analytically pure product. [b] Enantiomeric excess determined by HPLC with a Chiracel OD-H or OD column (*n*-heptane/*i*PrOH). [c] Enantiomeric excess determined after conversion to **3i** {i) TBAF; ii) PhI, Pd^0 cat., Cu^I cat.; 77% overall yield}.



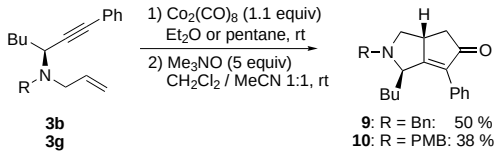
Scheme 4. Deprotection of propargylamines **3** to primary and secondary amines: i) [Pd(dba)$_2$] (5 mol%), dppb (5 mol%), **6** (1.2 equiv), THF; ii) [Pd(PPh$_3$)$_4$] (5 mol%), **8** (3 equiv per allyl group), CH_2Cl_2; iii) Et_3SiH (5 equiv), CF_3CO_2H; iv) Pd/C (10%), H_2 (1 atm), MeOH.

ment of **3b** and **3g** with $Co_2(CO)_8$ (1.1 equiv), followed by oxidation with Me_3NO (5 equiv) afforded the bicyclic compounds **9** and **10** as single diastereoisomers in 50 and 38% yield, respectively.[22]

We were able to isolate the complex [BrCu(Quinap)]$_2$ (**11**) as a yellow, air-stable solid, which was characterized by X-ray crystallography (Figure 2).[23] Complex **11** has a dimeric structure with the typical planar four-membered $Cu_2(\mu\text{-}Br)_2$ ring. The coordination spheres of both copper atoms are distorted tetrahedral, but they are not identical. The Cu1–N1 distance (2.348 Å) is much shorter than the Cu2–N2 distance (2.725 Å). In both cases the long Cu–N distances indicate the absence of direct bonding, but they are shorter than the sum of the van der Waals radii of Cu and N. Interestingly, the P and the N atoms of the two Quinap molecules are *cisoid*-orientated, in contrast to monodentate P–N complexes of CuBr.[24]

Preliminary mechanistic studies showed that the acetylenic deuterium of [D_1]phenylacetylene (**2q**) is transferred to the β-position of the enamine **1g** (>90% deuterium incorporated), leading to **12** in 91% yield (Scheme 6).

We suggest the tentative mechanism described in Scheme 7. The dimeric copper complex **11** dissociates first affording the monomeric copper species **13**, which after successive complexation of alkyne **2** and enamine **1** results in the zwitterionic



3b
3g

9: R = Bn: 50 %
10: R = PMB: 38 %

Scheme 5. Pauson–Khand reaction of propargylamines **3**.

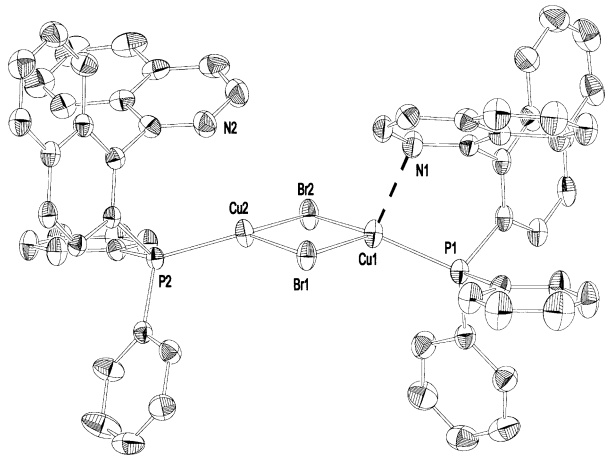
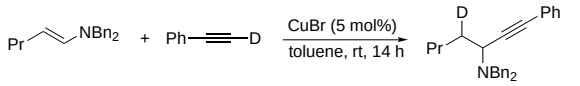
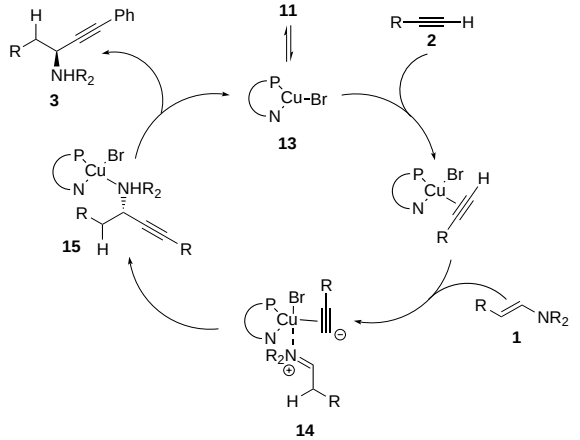


Figure 2. Structure of the complex $[BrCu(Quinap)]_2$ (**11**) in the solid state (the hydrogen atoms and crystallized solvent molecules are omitted for clarity). Selected bond lengths [Å] and angles [°]: Cu1–Br1 2.4728(8), Cu2–Br2 2.4150(8), Cu1–P1 2.199(2), Cu2–P2 2.1827(13); P2-Cu2-Br2 129.28(4), P2-Cu2-Br1 122.75(4), Br2-Cu2-Br1 104.18(3).



1g **2q** **12:** 91 %, > 90 % D

Scheme 6. Deuterium incorporation in propargylamines.



Scheme 7. Proposed mechanism.

intermediate **14**. After intramolecular transfer of the alkyne moiety to the imminium ion, the copper-complexed product **15** is formed. Decomplexation produces the free propargylic amine **3** and regenerates the catalyst **13**.

In summary, we have reported the first copper(I)/Quinap-catalyzed addition of functionalized alkynes to enamines with up to 90 % *ee* and high yields. The mild reaction conditions, the broad scope of the reaction, and the selective deprotection of the propargylamine products illustrate the good synthetic utility of this method.

Experimental Section

General methods: Unless otherwise indicated all reactions were carried out under argon and with dried solvents (THF, Et_2O, toluene, dichloromethane, pentane, acetonitrile, methanol). Reactions were monitored by gas chromatography (GC, GC-MS) or thin-layer chromatography (TLC) analysis of hydrolyzed aliquots.

Starting materials: The following starting materials were prepared according to literature procedures: enamines **1a**–**p**,[11–13] 4-bromophenylacetylene,[25] and *tert*-butyl(diphenyl)(2-propynyloxy)silane.[26]

***N*,*N*-Diallyl-1-phenyl-1-heptyn-3-amine (3a)**

Typical procedure A (racemic reaction): CuBr (22 mg, 0.15 mmol, 5.0 mol %) was suspended in toluene (3 mL) in a 25 mL Schlenk tube. A solution of enamine **1a** (0.645 g, 3.90 mmol, 1.3 equiv), phenylacetylene (**2a**) (0.306 g, 3.00 mmol), and *n*-decane (0.300 g, 2.11 mmol) as an internal standard in toluene (3 mL) was added at room temperature. The reaction mixture was stirred for 16 h at room temperature. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3a** as a colorless oil (0.790 g, 2.95 mmol, 98 %).

Typical procedure B (chiral reaction): CuBr (3.6 mg, 0.025 mmol, 5.0 mol %) and (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %) were suspended in toluene (2 mL) in a 10 mL Schlenk tube. After 30 min, a solution of enamine **1a** (124 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), and *n*-decane (50 mg, 0.35 mmol) as an internal standard in toluene (2 mL) was added at room temperature. After stirring for 20 h, standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3a** (133 mg, 0.50 mmol, 99 %, *ee* determined as **10**) as a colorless oil. $[\alpha]_D^{20} = -112$ ($c = 0.80$ in $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.38-7.30$ (m, 2H), 7.24–7.15 (m, 3H), 5.86–5.70 (m, 2H), 5.20–5.00 (m, 4H), 3.64 (t, $J = 7.6$ Hz, 1H), 3.31–3.22 (m, 2H), 2.91 (dd, $J = 14.3$, 7.8 Hz, 2H), 1.68–1.56 (m, 2H), 1.45–1.20 (m, 4H), 0.84 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 136.7$, 131.7, 128.2, 127.7, 123.6, 117.0, 88.4, 85.0, 54.0, 53.1, 33.6, 28.8, 22.4, 14.0 ppm; IR (film): $\tilde{\nu} = 3079$ (m), 2957 (s), 2932 (s), 2861 (m), 2815 (m), 1642 (m), 1598 (w), 1490 (s), 919 (s), 755 (vs), 691 cm^{-1} (s); MS: *m*/*z* (%): 210 (100) [$M^+ - C_4H_9$], 167 (4), 141 (6), 128 (11), 115 (22), 91 (5), 77 (2); HRMS (EI): *m*/*z*: calcd for $C_{19}H_{24}N$ [$M^+ - H$]: 266.1909; found: 266.1929; elemental analysis calcd (%) for $C_{19}H_{24}N$: C 85.34, H 9.42, N 5.24; found: C 84.89, H 9.80, N 5.17.

***N*-Allyl-*N*-benzyl-1-phenyl-1-heptyn-3-amine (3b)**: The reaction was carried out according to procedure A with enamine **1b** (0.711 g, 3.30 mmol, 1.1 equiv), phenylacetylene (**2a**) (0.306 g, 3.00 mmol), CuBr (22 mg, 0.15 mmol, 5.0 mol %), and *n*-decane (0.300 g, 2.11 mmol) in toluene (6 mL) at room temperature for 16 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3b** (0.784 g, 2.47 mmol, 82 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1b** (162 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 24 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3b** (132 mg, 0.42 mmol, 83 %, *ee* determined as **7**) as a colorless oil. $[\alpha]_D^{20} = -128$ ($c = 1.07$ in $CHCl_3$); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.42-7.34$ (m, 2H), 7.33–7.27 (m, 2H), 7.26–7.18 (m, 5H), 7.17–7.10 (m, 1H), 5.86–5.72 (m, 1H), 5.22–5.13 (m, 1H), 5.07–5.00 (m, 1H), 3.84 (d, $J = 13.9$ Hz, 1H), 3.58 (t, $J = 7.8$ Hz, 1H), 3.37 (d, $J = 13.9$ Hz, 1H), 3.30–3.18 (m, 1H), 3.00–2.90 (dd, $J = 14.1$, 7.9 Hz, 1H), 1.69–1.59 (m, 2H), 1.41–1.30 (m, 2H), 1.21 (sext, $J = 7.1$ Hz, 2H), 0.81 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.0$, 136.8, 131.8, 128.8, 128.2, 128.1, 127.8, 126.8, 123.6, 117.0, 88.4, 85.0, 54.9, 54.0, 52.7, 33.7, 28.7, 22.4, 14.0 ppm; IR (film): $\tilde{\nu} = 3082$ (w), 3030 (w), 2956 (m), 2932 (s), 1642 (w), 1599 (w), 1490 (s), 1454 (s), 918 (s), 756 (vs), 740 (s), 691 cm^{-1} (vs); MS: *m*/*z* (%): 316 (0.1) [$M^+ - H$], 260 (100), 128 (9), 115 (21), 91 (77); HRMS (EI): *m*/*z*: calcd for $C_{23}H_{26}N$ [$M^+ -$

H]: 316.2065; found: 316.2060; elemental analysis calcd (%) for $C_{23}H_{26}N$: C 87.02, H 8.57, N 4.41; found: C 87.06, H 8.13, N 4.36.

***N*-Allyl-*N*-benzyl-6-tridecyn-5-amine (3c)**: The reaction was carried out according to procedure A with enamine **1b** (0.474 g, 2.20 mmol, 1.1 equiv), 1-octyne (**2b**) (0.220 g, 2.00 mmol), CuBr (22 mg, 0.15 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 4 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3c** (0.500 g, 1.54 mmol, 74%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.30-7.14$ (m, 5H), 5.85–5.65 (m, 1H), 5.20–5.08 (m, 1H), 5.00 (d, $J = 9.8$ Hz, 1H), 3.74 (d, $J = 14.2$ Hz, 1H), 3.37–3.25 (m, 1H), 3.27 (d, $J = 13.9$ Hz, 1H), 3.19–3.06 (m, 1H), 2.85 (dd, $J = 14.1$, 8.0 Hz, 1H), 2.16 (td, $J = 6.9$, 2.0 Hz, 2H), 1.62–1.10 (m, 14H), 0.84 (t, $J = 6.7$ Hz, 3H), 0.79 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.3$, 137.1, 128.8, 128.1, 126.6, 116.6, 84.8, 78.2, 54.8, 53.9, 52.3, 33.9, 31.4, 29.2, 28.7, 28.5, 22.6, 22.4, 18.7, 14.1, 14.0 ppm; IR (film): $\tilde{\nu} = 3064$ (w), 3028 (w), 2927 (vs), 2853 (s), 1495 (w), 1450 (s), 918 (m), 738 (s), 698 cm^{-1} (s); MS: *m*/*z* (%): 268 (100) [$M^+ - C_4H_9$], 196 (1), 131 (2), 91 (36); HRMS (EI): *m*/*z*: calcd for $C_{23}H_{34}N$ [$M^+ - H$]: 324.2691; found: 324.2678; elemental analysis calcd (%) for $C_{23}H_{34}N$: C 84.86, H 10.84, N 4.30; found: C 85.16, H 10.51, N 3.96.

***N*-Allyl-*N*-benzyl-1-heptyn-3-amine (3d)**: Acetylene was bubbled through a solution of CuBr (43 mg, 0.30 mmol) in toluene (6 mL). After 5 min a solution of enamine **1b** (1.29 g, 6.00 mmol) and *n*-decane (1.00 g, 7.03 mmol) in toluene (6 mL) was added. The reaction mixture was stirred with a constant acetylene flow at room temperature for 4 h. Standard workup and purification by column chromatography (silica gel, pentane/Et_2O 98:2) afforded **3d** (1.07 g, 4.27 mmol, 69%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.30-7.10$ (m, 5H), 5.82–5.66 (m, 1H), 5.22–5.10 (m, 1H), 5.05–4.95 (m, 1H), 3.77 (d, $J = 14.0$ Hz, 1H), 3.38 (td, $J = 7.6$, 2.2 Hz, 1H), 3.27 (d, $J = 14.1$ Hz, 1H), 3.20–3.10 (m, 1H), 2.85 (dd, $J = 14.4$, 8.3 Hz, 1H), 2.17 (d, $J = 2.2$ Hz, 1H), 1.66–1.48 (m, 2H), 1.38–1.10 (m, 4H), 0.79 ppm (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 139.9$, 136.7, 128.7, 128.2, 126.8, 117.0, 82.4, 72.2, 54.7, 53.8, 51.9, 33.5, 28.5, 22.3, 14.0 ppm; IR (film): $\tilde{\nu} = 3304$ (s), 3029 (w), 2957 (vs), 2934 (vs), 2861 (s), 1643 (w), 1495 (m), 1454 (s), 920 (s), 738 (s), 698 (vs), 643 cm^{-1} (s); MS: *m*/*z* (%): 184 (100) [$M^+ - C_4H_9$], 146 (5), 131 (5), 115 (2), 91 (84); HRMS (EI): *m*/*z*: calcd for $C_{17}H_{22}N$ [$M^+ - H$]: 240.1752; found: 240.1725; elemental analysis calcd (%) for $C_{17}H_{22}N$: C 84.59, H 9.60, N 5.80; found: C 84.13, H 9.79, N 5.75.

***N*-Allyl-*N*-ferrocenylmethyl-1-phenyl-1-heptyn-3-amine (3e)**: The reaction was carried out according to procedure A with enamine **1c** (0.905 g, 2.80 mmol, 1.4 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 21 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 15:1) afforded **3e** (0.624 g, 1.47 mmol, 73%) as an orange-brown oil.

The reaction was carried out according to procedure B with enamine **1c** (242 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 72 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 15:1) yielded **3e** (20 mg, 0.05 mmol, 10%, *ee* determined as **7b**) as an orange-brown oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.48-7.45$ (m, 2H), 7.35–7.31 (m, 3H), 5.92–5.79 (m, 1H), 5.27 (dd, $J = 17.2$, 1.3 Hz, 1H), 5.14 (d, $J = 10.2$ Hz, 1H), 4.23 (d, $J = 9.7$ Hz, 2H), 4.12 (s, 7H), 3.72–3.65 (m, 2H), 3.39–3.28 (m, 2H), 2.98 (dd, $J = 14.2$, 7.9 Hz, 1H), 1.68 (q, $J = 7.1$ Hz, 2H), 1.48–1.25 (m, 4H), 0.90 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 137.0$, 131.7, 128.2, 127.7, 123.7, 116.8, 88.6, 85.11, 85.08, 70.2, 69.6, 68.5, 68.0, 67.4, 53.8, 52.7, 50.5, 33.6, 28.8, 22.4, 14.1 ppm; MS: *m*/*z* (%): 425 (21) [M^+], 200 (25), 199 (100), 170 (13), 121 (70); HRMS (EI): *m*/*z*: calcd for $C_{27}H_{31}NFe$ [M^+]: 425.1806; found: 425.1820; IR (film): $\tilde{\nu} = 2955$ (s), 2932 (s), 1490 (m), 1106 (m), 818 (m), 756 (vs), 691 (s), 484 cm^{-1} (m); elemental analysis calcd (%) for $C_{27}H_{31}NFe$: C 76.23, H 7.35, N 3.29; found: C 76.03, H 7.53, N 3.26.

***N*-Allyl-*N*-benzhydryl-1-phenyl-1-heptyn-3-amine (3f)**: The reaction was carried out according to procedure A with enamine **1d** (0.874 g, 3.00 mmol, 1.5 equiv), phenylacetylene (**2a**) (0.153 g, 1.50 mmol), CuBr (11 mg, 0.08 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 9 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 99:1) afforded **3f** (0.506 g, 1.29 mmol, 86%) as a light yellow oil.

The reaction was carried out according to procedure B with enamine **1d** (219 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 96 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 99:1) yielded **3e** (60 mg, 0.15 mmol, 30%, *ee* determined as **7d**) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.51-7.16$ (m, 15H), 6.05–5.92 (m, 1H), 5.04–4.93 (m, 2H), 5.02 (s, 1H), 3.76 (t, $J = 7.5$ Hz, 1H), 3.48 (ddt, $J = 15.9$, 6.5, 1.3 Hz, 1H), 3.24 (ddt, $J = 15.9$, 6.1, 1.3 Hz, 1H), 1.86–1.63 (m, 2H), 1.49–1.22 (m, 4H), 0.90 ppm (t, $J = 7.5$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 143.5$, 142.9, 138.6, 131.7, 128.5, 128.4, 128.3, 128.2, 128.2, 127.7, 127.0, 126.8, 123.7, 114.9, 89.6, 85.3, 72.1, 53.4, 51.8, 34.8, 28.8, 22.4, 14.0 ppm; MS: *m*/*z* (%): 393 (1) [M^+], 337 (10), 336 (35), 168 (15), 167 (100), 165 (16), 152 (10); HRMS (EI): *m*/*z*: calcd for $C_{29}H_{31}N$ [M^+]: 393.2456; found: 393.2483; IR (film): $\tilde{\nu} = 2956$ (s), 2930 (s), 2860 (m), 1490 (s), 1453 (m), 756 (vs), 705 (vs), 692 cm^{-1} (vs); elemental analysis calcd (%) for $C_{29}H_{31}N$: C 88.50, H 7.94, N 3.56; found: C 88.06, H 8.08, N 3.55.

***N*-Allyl-*N*-(4-methoxybenzyl)-1-phenyl-1-heptyn-3-amine (3g)**: The reaction was carried out according to procedure A with enamine **1e** (0.638 g, 2.60 mmol, 1.3 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 44 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 95:5) afforded **3g** (0.542 g, 1.56 mmol, 78%) as a light yellow oil.

The reaction was carried out according to procedure B with enamine **1e** (244 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 120 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 95:1) yielded **3e** (60 mg, 0.17 mmol, 35%, *ee* determined as **10**) as an light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49-7.46$ (m, 2H), 7.33–7.29 (m, 5H), 6.87 (d, $J = 8.8$ Hz, 2H), 5.95–5.81 (m, 1H), 5.27 (d, $J = 17.3$ Hz, 1H), 5.13 (d, $J = 10.2$ Hz, 1H), 3.86 (d, $J = 13.8$ Hz, 1H), 3.80 (s, 3H), 3.67 (t, $J = 7.6$ Hz, 1H), 3.40 (d, $J = 13.6$ Hz, 1H), 3.32 (ddt, $J = 14.2$, 4.4, 1.8 Hz, 1H), 3.02 (dd, $J = 14.7$, 8.0 Hz, 1H), 1.73 (qd, $J = 7.1$, 3.0 Hz, 2H), 1.50–1.40 (m, 2H), 1.31 (sext, $J = 7.8$ Hz, 2H), 0.91 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.5$, 137.0, 132.0, 131.8, 129.9, 128.2, 127.7, 123.6, 116.8, 113.6, 88.4, 84.9, 55.2, 54.3, 53.8, 52.5, 33.6, 28.7, 22.4, 14.0 ppm; MS: *m*/*z* (%): 347 (1) [M^+], 291 (12), 290 (54), 122 (10), 121 (100); HRMS (EI): *m*/*z*: calcd for $C_{24}H_{29}NO$ [M^+]: 347.2249; found: 347.2209; IR (film): $\tilde{\nu} = 2955$ (s), 2933 (s), 1612 (m), 1512 (vs), 1464 (m), 1249 (vs), 1038 (m), 756 (s), 691 cm^{-1} (m); elemental analysis calcd (%) for $C_{24}H_{29}NO$: C 82.95, H 8.41, N 4.03; found: C 82.92, H 8.38, N 4.03.

***N*-Benzyl-*N*-(2-methyl-2-propenyl)-1-phenyl-1-heptyn-3-amine (3h)**: The reaction was carried out according to procedure A with enamine **1f** (0.642 g, 2.80 mmol, 1.4 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 20 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 99:1) afforded **3h** (0.602 g, 1.82 mmol, 91%) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1f** (172 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 72 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 99:1) yielded **3h** (164 mg, 0.49 mmol, 99%, *ee* determined as **7d**) as a colorless oil. $[\alpha]_D^{20} = -201$ ($c = 0.84$ in $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.37-7.34$ (m, 2H), 7.28–7.26 (m, 2H), 7.22–7.11 (m, 6H), 4.90 (s, 1H), 4.76 (s, 1H), 3.78 (d, $J = 14.2$ Hz, 1H), 3.50 (t, $J = 7.4$ Hz, 1H), 3.28 (d, $J = 14.0$ Hz, 1H), 3.04 (d, $J = 13.8$ Hz, 1H), 2.86 (d, $J = 13.1$ Hz, 1H), 1.65 (s, 3H), 1.64–1.55 (m, 2H), 1.39–1.27 (m, 2H), 1.17 (sext, $J = 7.2$ Hz, 2H), 0.77 ppm (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 143.7$, 140.1, 131.8, 128.8, 128.2, 128.1, 127.7, 126.8, 123.7, 113.0, 88.2, 84.9, 57.4, 54.8, 52.1, 33.5, 28.7, 22.4, 20.8, 14.0 ppm; MS: *m*/*z* (%): 331 (1) [M^+], 275 (23), 274 (100), 115 (10), 91 (39). HRMS (EI): *m*/*z*: calcd for $C_{24}H_{28}N$ [$M^+ - H$]: 330.2222; found: 330.2207;

IR (film): $\tilde{\nu}$ = 2956 (s), 2934 (s), 2860 (m), 1490 (m), 1454 (m), 1444 (m), 898 (m), 756 (vs), 741 (m), 691 cm^{-1} (m); elemental analysis calcd (%) for $C_{24}H_{28}N$: C 86.96, H 8.82, N 4.23; found: C 86.82, H 8.95, N 4.33.

***N,N*-Dibenzyl-1-phenyl-1-heptyn-3-amine (3i)**: The reaction was carried out according to procedure A with enamine **1g** (0.557 g, 2.10 mmol, 1.1 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (7.2 mg, 0.05 mmol, 2.50 mol %), and *n*-decane (0.250 g, 1.76 mmol) in toluene (4 mL) at room temperature for 24 h and at 60 °C for 3 h. Standard workup and purification by column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3i** (0.550 g, 1.50 mmol, 75 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (173 mg, 0.65 mmol, 1.3 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 24 h. Standard workup and purification by column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3i** (144 mg, 0.39 mmol, 78 %, 83 % *ee*) as a colorless oil. $[\alpha]_D^{20}$ = −239 (c = 1.00 in $CHCl_3$); HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 45.4 (+), 53.8 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 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 ppm (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 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 ppm; IR (film): $\tilde{\nu}$ = 3062 (w), 3029 (w), 2955 (s), 2932 (s), 1599 (m), 1490 (s), 1454 (s), 755 (vs), 698 cm^{-1} (vs); MS: *m*/*z* (%): 310 (100) [$M^+ - C_4H_9$], 218 (3), 128 (2), 115 (7), 91 (57); HRMS (EI): *m*/*z*: calcd for $C_{27}H_{28}N$ [M^+ − H]: 366.2222; found: 366.2215; elemental analysis calcd (%) for $C_{27}H_{28}N$: C 88.24, H 7.95, N 3.81; found: C 87.85, H 7.84, N 3.73.

***N,N*-Dibenzyl-1-(1-cyclohexen-1-yl)-1-heptyn-3-amine (3j)**: The reaction was carried out according to procedure A with enamine **1g** (0.690 g, 2.60 mmol, 1.3 equiv), 1-ethinyl-1-cyclohexene (**2d**) (0.212 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 20 h. Standard workup and purification by column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3j** (0.570 g, 1.53 mmol, 77 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (173 mg, 0.65 mmol, 1.3 equiv), 1-ethinyl-1-cyclohexene (**2d**) (53 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 44 h. Standard workup and purification by column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3j** (156 mg, 0.42 mmol, 84 %, 74 % *ee*) as a colorless oil. $[\alpha]_D^{20}$ = −172 (c = 1.03 in $CHCl_3$). HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 30.3 (+), 35.1 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.36–7.10 (m, 10H), 6.08–6.00 (m, 1H), 3.73 (d, J = 14.2 Hz, 2H), 3.39 (t, J = 7.5 Hz, 1H), 3.31 (d, J = 13.6 Hz, 2H), 2.17–1.98 (m, 4H), 1.70–1.44 (m, 6H), 1.40–1.18 (m, 2H), 1.10 (sext, J = 7.3 Hz, 2H), 0.76 ppm (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 140.1, 133.8, 128.8, 128.1, 126.7, 120.8, 86.9, 85.0, 54.9, 52.1, 33.7, 29.9, 28.6, 25.6, 22.4, 22.3, 21.6, 14.0 ppm; IR (film): $\tilde{\nu}$ = 3063 (w), 3028 (m), 2932 (vs), 1604 (w), 1494 (s), 1454 (s), 1261 (m), 1028 (m), 802 (m), 746 (s), 698 cm^{-1} (vs); MS: *m*/*z* (%): 314 (100) [$M^+ - C_4H_9$], 236 (1), 222 (2), 91 (45); HRMS (EI): *m*/*z*: calcd for $C_{25}H_{33}N$ [M^+]: 371.2613; found: 371.2589; elemental analysis calcd (%) for $C_{25}H_{33}N$: C 87.28, H 8.95, N 3.77; found: C 87.02, H 9.10, N 3.72.

7-(Dibenzylamino)-5-undecynenitrile (3k): The reaction was carried out according to procedure A with enamine **1g** (0.345 g, 1.30 mmol, 1.3 equiv), 5-hexynenitrile (**2e**) (0.093 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol %), and *n*-decane (0.100 g, 0.70 mmol) in toluene (2 mL) at 60 °C for 5 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 19:1 then 4:1) afforded **3k** (0.295 g, 0.82 mmol, 82 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (199 mg, 0.75 mmol, 1.5 equiv), 5-hexynenitrile (**2e**) (47 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 64 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 4:1) yielded **3k** (103 mg, 0.29 mmol, 51 %, 54 % *ee*) as a colorless oil. $[\alpha]_D^{20}$ = −91 (c = 1.01 in $CHCl_3$); HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.6 mL min^{-1}): t_r (min) = 17.2 (−), 21.2 (+); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.35–7.10 (m, 10H), 3.72 (d, J = 13.7 Hz, 2H), 3.26 (d, J = 13.7 Hz, 2H), 3.32–3.22 (m, 1H), 2.45 (t, J = 7.1 Hz, 2H), 2.39 (td, J = 6.8, 2.0 Hz, 2H), 1.82 (quint, J = 7.2 Hz, 2H), 1.70–1.42 (m, 2H), 1.40–1.20 (m, 2H), 1.16–1.04 (sext, J = 7.2 Hz, 2H), 0.76 ppm (t, J = 7.0 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.8, 128.7, 128.1, 126.8, 119.1, 81.8, 80.3, 54.8, 51.6, 33.7, 28.5, 25.0, 22.2, 17.9, 16.1, 13.9 ppm; IR (film): $\tilde{\nu}$ = 3062 (w), 3028 (w), 2955 (m), 2934 (m), 2248 (w), 1603 (w), 1494 (m), 1454 (s), 1122 (s), 747 (s), 699 cm^{-1} (vs); MS: *m*/*z* (%): 301 (100) [$M^+ - C_4H_9$], 181 (6), 91 (66), 65 (4); HRMS (EI): *m*/*z*: calcd for $C_{25}H_{29}N_2$ [M^+ − H]: 357.2331; found: 357.2329; elemental analysis calcd (%) for $C_{25}H_{29}N_2$: C 83.75, H 8.43, N 7.81; found: C 83.41, H 8.30, N 8.21.

***N,N*-Dibenzyl-10-chloro-6-decyn-5-amine (3l)**: The reaction was carried out according to procedure A with enamine **1g** (0.690 g, 2.60 mmol, 1.3 equiv), 5-chloro-1-pentyne (**2f**) (0.205 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 67 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3l** (0.575 g, 1.56 mmol, 78 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (173 mg, 0.65 mmol, 1.3 equiv), 5-chloro-1-pentyne (**2f**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 64 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3l** (107 mg, 0.29 mmol, 58 %, 60 % *ee*) as a colorless oil. $[\alpha]_D^{20}$ = −100 (c = 0.86 in $CHCl_3$). HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 58.2 (+), 66.3 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34–7.08 (m, 10H), 3.72 (d, J = 13.7 Hz, 2H), 3.65 (t, J = 6.4 Hz, 2H), 3.28 (d, J = 14.2 Hz, 2H), 3.29–3.20 (m, 1H), 2.40 (td, J = 6.7, 2.1 Hz, 2H), 1.93 (quint, J = 6.7 Hz, 2H), 1.68–1.41 (m, 2H), 1.40–1.10 (m, 4H), 0.76 ppm (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 140.0, 128.8, 128.1, 126.8, 82.8, 79.3, 54.9, 51.7, 43.7, 33.8, 31.9, 28.6, 22.3, 16.2, 14.0 ppm; IR (film): $\tilde{\nu}$ = 3063 (w), 3028 (w), 2956 (m), 2932 (m), 1494 (m), 1454 (s), 1028 (m), 746 (s), 698 cm^{-1} (vs); MS: *m*/*z* (%): 310 (100) [$M^+ - C_4H_9$], 196 (2), 181 (4), 91 (67); HRMS (EI): *m*/*z*: calcd for $C_{24}H_{29}ClN$ [M^+ − H]: 366.1989; found: 366.1952; elemental analysis calcd (%) for $C_{24}H_{29}ClN$: C 78.34, H 8.22, N 3.81; found: C 78.40, H 8.25, N 3.75.

***N,N*-Dibenzyl-1-methoxy-1-octyn-4-amine (3m)**: The reaction was carried out according to procedure A with enamine **1g** (0.690 g, 2.60 mmol, 1.3 equiv), 3-methoxy-1-propyne (**2g**) (0.140 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 3 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3m** (0.564 g, 1.68 mmol, 84 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (173 mg, 0.65 mmol, 1.3 equiv), 3-methoxy-1-propyne (**2g**) (35 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 20 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3m** (128 mg, 0.38 mmol, 76 %, 55 % *ee*) as a colorless oil. $[\alpha]_D^{20}$ = −98 (c = 0.98 in $CHCl_3$); HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 75.4 (+), 91.9 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.34–7.10 (m, 10H), 4.14 (d, J = 1.8 Hz, 2H), 3.75 (d, J = 13.8 Hz, 2H), 3.37 (s, 3H), 3.32 (d, J = 13.8 Hz, 2H), 3.40–3.31 (m, 1H), 1.72–1.45 (m, 2H), 1.41–1.00 (m, 4H), 0.76 ppm (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.8, 128.8, 128.2, 126.8, 84.9, 80.3, 60.1, 57.4, 54.9, 51.7, 33.5, 28.5, 22.2, 13.9 ppm; IR (film): $\tilde{\nu}$ = 3063 (w), 3029 (w), 2955 (m), 2819 (m), 1604 (w), 1494 (m), 1454 (s), 1358 (m), 1102 (vs), 747 (s), 698 cm^{-1} (vs); MS: *m*/*z* (%): 278 (100) [$M^+ - C_4H_9$], 218 (3), 196 (3), 181 (4), 91 (68); HRMS (EI): *m*/*z*: calcd for $C_{23}H_{29}NO$ [M^+]: 335.2249; found: 335.2213; elemental analysis calcd (%) for $C_{23}H_{29}NO$: C 82.34, H 8.71, N 4.18; found: C 81.74, H 8.57, N 4.11.

***N,N*-Dibenzyl-1-{[*tert*-butyl(diphenyl)silyl]oxy}-2-octyn-4-amine (3n)**: The reaction was carried out according to procedure A with enamine **1g** (0.345 g, 1.30 mmol, 1.3 equiv), *tert*-butyl(diphenyl)(2-propynyloxy)silane (**2h**) (0.294 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol %), and *n*-decane (0.300 g, 2.11 mmol) in toluene (2 mL) at room temperature for 24 h. Standard workup and column chromatographic purification (silica

gel, pentane/Et_2O 98:2) afforded **3n** (0.521 g, 0.93 mmol, 93%) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (173 mg, 0.65 mmol, 1.3 equiv), *tert*-butyl(diphenyl)(2-propynyloxy)silane (**2h**) (147 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (150 mg, 1.05 mmol) in toluene (4 mL) at room temperature for 48 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3n** as a colorless oil (238 mg, 0.43 mmol, 85%, 72% *ee*); $[\alpha]_D^{20} = -69$ ($c = 0.90$ in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_r (min) = 53.3 (−), 57.8 (+); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.74-7.64$ (m, 4H), 7.39–7.10 (m, 16H), 4.39 (d, $J = 1.8$ Hz, 2H), 3.67 (d, $J = 13.8$ Hz, 2H), 3.25 (d, $J = 13.8$ Hz, 2H), 3.30–3.20 (m, 1H), 1.64–1.20 (m, 6H), 1.02 (s, 9H), 0.75 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.0$, 135.6, 133.5, 129.8, 128.8, 128.1, 127.7, 126.8, 83.5, 83.1, 54.8, 52.9, 51.6, 33.4, 28.5, 26.7, 22.2, 19.2, 14.0 ppm; IR (film): $\tilde{\nu} = 3070$ (w), 3029 (w), 2957 (m), 2859 (m), 1494 (m), 1454 (m), 1428 (m), 1113 (vs), 1075 (s), 739 (s), 700 cm^{-1} (vs); MS: *m*/*z* (%): 559 (0.2) [M^+], 502 (90), 307 (20), 229 (10), 199 (36), 91 (100); HRMS (EI): *m*/*z*: calcd for $C_{38}H_{45}NOSi$ [M^+]: 559.3270; found: 559.3247; elemental analysis calcd (%) for $C_{38}H_{45}NOSi$: C 81.52, H 8.10, N 2.50; found: C 81.27, H 8.31, N 2.48.

***N*,*N*-Dibenzyl-1-(trimethylsilyl)-1-heptyn-3-amine (3o)**: The reaction was carried out according to procedure A with enamine **1g** (0.345 g, 1.30 mmol, 1.3 equiv), trimethylsilylacetylene (**2i**) (0.098 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol%), and *n*-decane (0.100 g, 0.70 mmol) in toluene (2 mL) at room temperature for 16 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3o** (0.267 g, 0.73 mmol, 73%) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1g** (199 mg, 0.75 mmol, 1.5 equiv), trimethylsilylacetylene (**2i**) (49 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 24 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3o** (128 mg, 0.35 mmol, 70%, *ee* determined as **3i**) as a colorless oil. $[\alpha]_D^{20} = -164$ ($c = 0.97$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.22-7.00$ (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 ppm (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 139.5$, 128.4, 127.7, 126.4, 104.3, 88.6, 54.4, 51.9, 32.9, 28.0, 21.8, 13.5, 0.00 ppm; IR (film): $\tilde{\nu} = 3064$ (w), 3029 (w), 2958 (s), 2159 (m), 1495 (m), 1454 (m), 1250 (s), 842 (vs), 698 cm^{-1} (s); MS: *m*/*z* (%): 348 (5) [$M^+ - CH_3$], 306 (100), 214 (4), 91 (85), 73 (12); HRMS (EI): *m*/*z*: calcd for $C_{24}H_{32}NSi$ [$M^+ - H$]: 362.2304; found: 362.2333; 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.

***N*,*N*-Dibenzyl-1,1-diethoxy-2-octyn-4-amine (3p)**: The reaction was carried out according to procedure A with enamine **1g** (0.345 g, 1.30 mmol, 1.3 equiv), 3,3-diethoxy-1-propyne (**2j**) (0.128 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol%), and *n*-decane (0.130 g, 2.11 mmol) in toluene (2 mL) at room temperature for 4 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 19:1) afforded **3p** (0.260 g, 0.66 mmol, 66%) as a colorless oil. ^{1}H NMR (C_6D_6, 300 MHz): $\delta = 7.55-7.45$ (m, 4H), 7.32–7.15 (m, 6H), 5.59 (d, $J = 1.4$ Hz, 1H), 4.02 (d, $J = 12.8$ Hz, 2H), 4.10–3.90 (m, 2H), 3.77–3.64 (m, 3H), 3.64 (d, $J = 13.7$Hz, 2H), 1.88–1.62 (m, 2H), 1.42 (quint, $J = 7.5$ Hz, 2H), 1.30 (t, $J = 7.1$ Hz, 3H), 1.29 (t, $J = 7.3$ Hz, 3H), 1.16 (sext, $J = 7.5$ Hz, 2H), 0.85 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (C_6D_6, 75 MHz): $\delta = 140.1$, 129.2, 128.6, 127.3, 92.1, 83.7, 81.7, 60.8, 55.5, 52.0, 33.8, 28.8, 22.5, 15.4, 14.1 ppm; IR (film): $\tilde{\nu} = 3063$ (w), 3029 (w), 2932 (m), 2874 (m), 2236 (w), 1495 (m), 1454 (m), 1132 (s), 1053 (vs), 747 (s), 699 cm^{-1} (vs); MS: *m*/*z* (%): 348 (12) [$M^+ - C_2H_5O$], 336 (100) [$M^+ - C_4H_9$], 234 (62), 91 (85); HRMS (EI): *m*/*z*: calcd for $C_{22}H_{26}NO_2$ [$M^+ - C_4H_9$]: 336.1964; found: 336.1964; elemental analysis calcd (%) for $C_{22}H_{26}NO_2$: C 79.35, H 8.96, N 3.56; found: C 79.12, H 8.82, N 3.55.

***N*,*N*-Bis-(4-methoxybenzyl)-1-phenyl-1-heptyn-3-amine (3q)**: The reaction was carried out according to procedure A with enamine **1h** (1.300 g, 4.00 mmol, 2.0 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 5 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 4:1) afforded **3q** (0.851 g, 1.99 mmol, 99%) as a light yellow oil.

The reaction was carried out according to procedure B with enamine **1h** (244 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 96 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 4:1) yielded **3q** (212 mg, 0.49 mmol, 99%, 66% *ee*, determined by complexation with $Co_2(CO)_8$ (1.1 equiv) in pentane (room temperature, 45 min, silica gel, pentane/Et_2O 9:1, dark red oil, 90%) as a light yellow oil. $[\alpha]_D^{20} = -171$ ($c = 0.53$ in $CHCl_3$). HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.15 mL min^{-1}): $t_r = 33.1$ (−), 34.1 (+); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.53-7.50$ (m, 2H), 7.36–7.31 (m, 7H), 6.87 (d, $J = 8.7$ Hz, 4H), 3.82 (d, $J = 13.4$ Hz, 2H), 3.81 (s, 6H), 3.59 (t, $J = 7.4$ Hz, 1H), 3.40 (d, $J = 13.1$ Hz, 2H), 1.86–1.65 (m, 2H), 1.53–1.34 (m, 2H), 1.30–1.18 (m, 2H), 0.88 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 158.5$, 131.9, 131.8, 129.9, 128.2, 127.8, 123.7, 113.6, 88.3, 85.0, 55.2, 54.1, 51.9, 33.5, 28.6, 22.3, 14.0 ppm; MS: *m*/*z* (%): 425 (0.1) [$M^+ - 2H$], 371 (13), 371 (13), 370 (45), 121 (100); HRMS (EI): *m*/*z*: calcd for $C_{29}H_{33}NO_2$ [M^+]: 427.2511; found: 427.2522; IR (film): $\tilde{\nu} = 2954$ (s), 2933 (s), 2834 (m), 1612 (s), 1512 (vs), 1464 (m), 1301 (m), 1249 (s), 1171 (m), 1038 (s), 757 cm^{-1} (s); elemental analysis calcd (%) for $C_{29}H_{33}NO_2$: C 81.46, H 7.78, N 3.28; found: C 81.17, H 8.16, N 3.25.

***N*,*N*-Dibenzyl-5-methyl-1-phenyl-1-hexyn-3-amine (3r)**: The reaction was carried out according to procedure A with enamine **1i** (0.583 g, 2.20 mmol, 1.1 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 18 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3r** (0.671 g, 1.83 mmol, 91%) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1i** (199 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 19 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3r** (182 mg, 0.49 mmol, 99%, 85% *ee*) as a colorless oil. $[\alpha]_D^{20} = -237$ ($c = 1.09$ in $CHCl_3$); HPLC (OD, 99% *n*-heptane/1% isopropanol, 0.1 mL min^{-1}): t_r (min) = 94.8 (−), 112.0 (+); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.44-7.41$ (m, 2H), 7.35–7.32 (m, 4H), 7.28–7.21 (m, 7H), 7.17–7.13 (m, 2H), 3.81 (d, $J = 13.7$ Hz, 2H), 3.60 (t, $J = 7.1$ Hz, 1H), 3.40 (t, $J = 13.7$ Hz, 2H), 1.84 (sept, $J = 6.7$ Hz, 1H), 1.70–1.61 (m, 1H), 1.51–1.42 (m, 1H), 0.74 (d, $J = 6.7$ Hz, 3H), 0.62 ppm (d, $J = 6.7$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 135.8$, 131.8, 128.9, 128.3, 128.2, 127.8, 126.9, 123.6, 88.2, 85.1, 55.0, 50.2, 43.0, 24.6, 22.8, 21.9 ppm; MS: *m*/*z* (%): 365 (1) [$M^+ - 2H$], 311 (23), 310 (100), 91 (64); HRMS (EI): *m*/*z*: calcd for $C_{27}H_{29}N$ [$M^+ - H$]: 366.2222; found: 366.2224; IR (film): $\tilde{\nu} = 2954$ (s), 2932 (m), 1490 (s), 1454 (s), 755 (vs), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{27}H_{29}N$: C 88.24, H 7.95, N 3.81; found: C 88.03, H 8.33, N 3.81.

***N*,*N*-Dibenzyl-2-methyl-5-decyn-4-amine (3s)**: The reaction was carried out according to procedure A with enamine **1i** (0.583 g, 2.20 mmol, 1.1 equiv), 1-hexyne (**2k**) (0.164 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 24 h and at 60 °C for 1 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3s** (0.618 g, 1.78 mmol, 89%) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1i** (80 mg, 0.30 mmol, 1.2 equiv), 1-hexyne (**2k**) (21 mg, 0.25 mmol), CuBr (1.8 mg, 0.0125 mmol, 5.0 mol%), (*R*)-Quinap (6.0 mg, 0.01375, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (3 mL) at room temperature for 120 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3s** (47 mg, 0.14 mmol, 56%, 76% *ee*) as a colorless oil. $[\alpha]_D^{20} = -124$ ($c = 1.03$ in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.1 mL min^{-1}): t_r (min) = 47.2 (−), 50.6 (+); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.40-7.38$ (m, 4H), 7.33–7.20 (m, 6H), 3.80 (d, $J = 13.7$ Hz, 2H), 3.44 (tt, $J = 7.8$, 2.2 Hz, 1H), 3.37 (d, $J = 13.7$ Hz, 2H), 2.30 (td, $J = 7.2$, 2.3 Hz, 2H), 1.86 (sept, $J = 6.6$ Hz, 1H), 1.67–1.36 (m, 6H), 0.98 (t, $J = 7.0$ Hz, 3H), 0.78 (d, $J = 6.6$ Hz, 3H), 0.66 ppm (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.1$, 128.9,

128.1, 126.7, 84.8, 78.1, 54.8, 49.7, 43.3, 31.4, 24.6, 22.8, 22.0, 21.9, 18.4, 13.6 ppm; MS: *m/z* (%): 291 (22) [$M^+ - C_4H_9$], 290 (100), 91 (61); HRMS (EI): *m/z*:calcd for $C_{25}H_{32}N$ [$M^+ - H$]: 346.2583; found: 346.2543; IR (film): $\tilde{\nu} = 2956$ (vs), 2932 (vs), 2869 (m), 1494 (m), 1454 (s), 745 (s), 698 cm^{-1} (vs); elemental analysis calcd (%) for $C_{25}H_{32}N$: C 86.40, H 9.57, N 4.03; found: C 86.18, H 9.70, N 4.00.

***N,N*-Dibenzyl-4-methyl-1-phenyl-1-pentyn-3-amine (3t)**:[27] The reaction was carried out according to procedure A with enamine **1j** (0.653 g, 2.60 mmol, 1.3 equiv), phenylacetylene (**2a**) (0.204 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 12 h and at 60 °C for 1 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 99:1) afforded **3t** (0.702 g, 1.99 mmol, 99 %) as a colorless oil.

The reaction was carried out according to procedure B with enamine **1j** (189 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 120 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 99:1) yielded **3t** (113 mg, 0.32 mmol, 64 %, 87 % *ee*) as a colorless oil. $[\alpha]_D^{20} = -303$ ($c = 0.58$ in $CHCl_3$); HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 21.2 (−), 22.9 (+); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.48 - 7.15$ (m, 15H), 3.84 (d, $J = 13.7$ Hz, 2H), 3.42 (d, $J = 13.6$ Hz, 2H), 3.07 (d, $J = 10.1$ Hz, 1H), 2.01 – 1.87 (m, 1H), 0.97 (d, $J = 6.1$ Hz, 3H), 0.96 ppm (d, $J = 6.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.8$, 131.8, 128.9, 128.3, 128.2, 127.8, 126.8, 123.7, 87.4, 86.0, 59.7, 55.1, 30.8, 21.0, 20.0 ppm; MS: *m/z* (%): 353 (1) [M^+], 311 (25), 310 (100), 91 (48).

***N,N*-Dibenzyl-4-methyl-1-(triisopropylsilyl)-1-pentyn-3-amine (3u)**: The reaction was carried out according to procedure A with enamine **1j** (1.510 g, 6.00 mmol, 1.5 equiv), triisopropylacetylene (**2l**) (0.720 g, 4.00 mmol), CuBr (28 mg, 0.20 mmol, 5.0 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 14 h and at 60 °C for 7 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3u** (1.530 g, 3.52 mmol, 88 %) as a colorless oil which slowly crystallized. M.p. 43 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.33 - 7.30$ (m, 4H), 7.25 – 7.12 (m, 6H), 3.75 (d, $J = 13.7$ Hz, 2H), 3.34 (d, $J = 13.7$ Hz, 2H), 2.85 (d, $J = 10.1$ Hz, 1H), 1.90 – 1.77 (m, 1H), 1.22 – 1.18 (m, 3H), 1.08 (s, 18H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.92 ppm (d, $J = 6.6$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.8$, 128.8, 128.2, 126.8, 105.5, 85.4, 59.9, 55.1, 30.2, 20.9, 19.9, 18.8, 11.4 ppm; MS: *m/z* (%): 433 (1) [M^+], 391 (33), 390 (100), 91 (26); HRMS (EI): *m/z*: calcd for $C_{29}H_{42}NSi$ [$M^+ - H$]: 432.3087; found: 432.3054; IR (KBr): $\tilde{\nu} = 2942$ (vs), 2865 (vs), 2157 (m), 1494 (m), 1454 (s), 1383 (m), 1365 (m), 1070 (m), 1017 (s), 883 (m), 746 (s), 697 (vs), 676 (s), 659 cm^{-1} (m); elemental analysis calcd (%) for $C_{29}H_{42}NSi$: C 80.30, H 9.99, N 3.23; found: C 80.47, H 9.80, N 3.05.

***N,N*-Dibenzyl-2,6-dimethyl-6-[(trimethylsilyl)oxy]-4-heptyn-3-amine (3v)**: The reaction was carried out according to procedure A with enamine **1j** (0.754 g, 3.00 mmol, 1.5 equiv), [(1,1-dimethyl-2-propynyl)oxy](trimethyl)-silane (**2m**) (0.313 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at room temperature for 14 h and at 60 °C for 20 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 97:3) afforded **3v** (0.691 g, 1.70 mmol, 85 %) as a colorless oil which slowly crystallized. M.p. 59 °C; ^1H NMR (300 MHz, $CDCl_3$): $\delta = 7.33 - 7.30$ (m, 4H), 7.25 – 7.12 (m, 6H), 3.74 (d, $J = 13.7$ Hz, 2H), 3.30 (d, $J = 13.8$ Hz, 2H), 2.83 (d, $J = 10.7$ Hz, 1H), 1.91 – 1.71 (m, 1H), 1.51 (d, $J = 2.0$ Hz, 6H), 0.93 (d, $J = 6.6$ Hz, 3H), 0.89 (d, $J = 6.7$ Hz, 3H), 0.17 ppm (s, 9H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 139.8$, 128.8, 128.2, 126.8, 91.2, 80.4, 66.7, 59.1, 55.1, 33.9, 30.6, 20.9, 19.9, 2.1 ppm; MS: *m/z* (%): 407 (1) [M^+], 365 (29), 364 (100), 91 (39); HRMS (EI): *m/z*: calcd for $C_{26}H_{35}NOSi$ [$M^+ - H$]: 406.2566; found: 406.2561; IR (KBr): $\tilde{\nu} = 2981$ (s), 2959 (s), 1454 (m), 1248 (s), 1161 (s), 1033 (vs), 842 (vs), 746 (s), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{26}H_{35}NOSi$: C 76.60, H 9.15, N 3.44; found: C 76.33, H 9.21, N 3.39.

***N,N*-Dibenzyl-1-cyclohexyl-3-phenyl-2-propyn-1-amine (3w)**: The reaction was carried out according to procedure A with enamine **1k** (1.049 g, 3.60 mmol, 1.2 equiv), phenylacetylene (**2a**) (0.306 g, 3.00 mmol), CuBr (22 mg, 0.15 mmol, 5.0 mol %), and *n*-decane (0.300 g, 2.11 mmol) in toluene (6 mL) at room temperature for 24 h and at 60 °C for 3 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3w** (1.115 g, 2.83 mmol, 94 %) as a white solid.

The reaction was carried out according to procedure B with enamine **1k** (219 mg, 0.75 mmol, 1.5 equiv), phenylacetylene (**2a**) (51 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 96 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3w** (155 mg, 0.39 mmol, 79 %, 88 % *ee*) as a white solid. $[\alpha]_D^{20} = -231$ ($c = 0.50$ in $CHCl_3$); HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 41.3 (+), 46.2 (−); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.46 - 7.11$ (m, 15H), 3.80 (d, $J = 13.7$ Hz, 2H), 3.39 (d, $J = 13.8$ Hz, 2H), 3.17 (d, $J = 10.3$ Hz, 1H), 2.25 (d, $J = 12.9$ Hz, 1H), 1.99 (d, $J = 12.80$ Hz, 1H), 1.68 – 1.45 (m, 4H), 1.23 – 0.55 ppm (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 139.8$, 131.8, 128.9, 128.3, 128.2, 127.8, 126.8, 123.7, 87.1, 86.2, 58.4, 55.1, 39.8, 31.4, 30.3, 26.6, 26.2, 26.0 ppm; IR (KBr): $\tilde{\nu} = 3061$ (w), 3030 (w), 2928 (vs), 2850 (s), 1598 (w), 1489 (m), 1450 (m), 756 (s), 747 (s), 698 (s), 692 cm^{-1} (s); MS: *m/z* (%): 310 (100) [$M^+ - C_6H_{11}$], 218 (3), 191 (2), 115 (5), 91 (51); HRMS (EI): *m/z*: calcd for $C_{29}H_{30}N$ [$M^+ - H$]: 392.2378; found: 392.2349.

***N,N*-Dibenzyl-3-(4-bromophenyl)-1-cyclohexyl-2-propyn-1-amine (3x)**: The reaction was carried out according to procedure A with enamine **1k** (0.758 g, 2.60 mmol, 1.3 equiv), 4-bromophenylacetylene (**2n**) (0.362 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol %), and *n*-decane (0.360 g, 2.53 mmol) in toluene (4 mL) at room temperature for 14 h and at 60 °C for 4 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3x** (0.855 g, 1.81 mmol, 90 %) as a white solid.

The reaction was carried out according to procedure B with enamine **1k** (219 mg, 0.75 mmol, 1.5 equiv), 4-bromophenylacetylene (**2n**) (91 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol %), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol %), and *n*-decane (100 mg, 0.70 mmol) in toluene (4 mL) at room temperature for 44 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) yielded **3x** (197 mg, 0.42 mmol, 83 %, 90 % *ee*) as a white solid. $[\alpha]_D^{20} = -239$ ($c = 0.80$ in $CHCl_3$); HPLC (OD-H, 99 % *n*-heptane/1 % isopropanol, 0.2 mL min^{-1}): t_r (min) = 21.1 (−), 22.9 (+); ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.41 - 7.11$ (m, 14H), 3.80 (d, $J = 13.7$ Hz, 2H), 3.36 (d, $J = 14.1$ Hz, 2H), 3.15 (d, $J = 10.4$ Hz, 1H), 2.30 – 2.16 (m, 1H), 2.10 – 1.88 (m, 1H), 1.68 – 1.48 (m, 4H), 1.25 – 0.91 (m, 3H), 0.88 – 0.60 ppm (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 139.7$, 133.3, 131.5, 128.8, 128.2, 126.9, 122.6, 121.9, 88.5, 85.2, 58.4, 55.1, 39.7, 31.3, 30.3, 26.6, 26.1, 26.9 ppm; IR (KBr): $\tilde{\nu} = 3062$ (w), 3028 (w), 2932 (vs), 2850 (m), 1603 (w), 1485 (vs), 1452 (m), 1070 (m), 827 (s), 747 (s), 698 cm^{-1} (vs); MS: *m/z* (%): 310 (100) [$M^+ - C_6H_{11}$], 218 (3), 191 (2), 115 (5), 91 (51); HRMS (EI): *m/z*: calcd for $C_{29}H_{29}BrN$ [$M^+ - H$]: 470.1483; found: 470.1495; elemental analysis calcd (%) for $C_{29}H_{29}BrN$: C 73.72, H 6.40, N 2.96; found: C 73.52, H 6.55, N 2.94.

***N*-Allyl-*N*-benzyl-1-cyclohexyl-2-nonyn-1-amine (3y)**: The reaction was carried out according to procedure A with enamine **1l** (0.531 g, 2.60 mmol, 1.3 equiv), 1-octyne (**2b**) (0.220 g, 2.00 mmol), CuBr (7 mg, 0.05 mmol, 2.5 mol %), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at 60 °C for 24 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3y** (0.570 g, 1.62 mmol, 80 %) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.32 - 7.10$ (m, 5H), 5.82 – 5.64 (m, 1H), 5.19 – 5.09 (m, 1H), 5.04 – 4.95 (m, 1H), 3.74 (d, $J = 13.8$ Hz, 1H), 3.25 (d, $J = 13.7$ Hz, 1H), 3.17 – 3.05 (m, 1H), 2.97 (dt, $J = 10.1$, 2.3 Hz, 1H), 2.81 (dd, $J = 14.5$, 8.1 Hz, 1H), 2.17 (td, $J = 6.8$, 2.0 Hz, 2H), 2.15 – 2.05 (m, 1H), 1.98 – 1.85 (m, 1H), 1.68 – 0.66 (m, 17H), 0.84 ppm (t, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.4$, 137.3, 128.7, 128.1, 126.6, 116.5, 85.6, 77.1, 58.2, 54.9, 53.7, 40.2, 31.4, 31.3, 30.4, 29.3, 28.5, 26.7, 26.2, 26.0, 22.6, 18.7, 14.1 ppm; IR (film): $\tilde{\nu} = 3065$ (w), 3029 (w), 2957 (s), 2932 (vs), 2859 (m), 1494 (w), 1455 (m),918 (m), 737 (m), 698 cm^{-1} (m); MS: *m/z* (%): 268 (100) [$M^+ - C_6H_{11}$], 196 (2), 146 (2), 131 (2), 91 (45); HRMS (EI): *m/z*: calcd for $C_{23}H_{33}N$ [$M^+ - C_2H_4$]: 323.2613; found: 323.2598.

***N,N*-Diallyl-1-cyclohexyl-2-nonyn-1-amine (3z)**: The reaction was carried out according to procedure A with enamine **1m** (0.631 g, 3.30 mmol, 1.1 equiv), 1-octyne (**2b**) (0.331 g, 3.00 mmol), CuBr (22 mg, 0.15 mmol, 5.0 mol %), and *n*-decane (0.300 g, 2.11 mmol) in toluene (4 mL) at room temperature for 15 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3z** (0.754 g, 2.50 mmol, 82 %) as a colorless oil. ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 5.86 - 5.72$ (m, 2H), 5.23 – 5.20 (m, 1H), 5.17 – 5.14 (m, 1H), 5.10 – 5.07 (m, 1H), 5.06 – 5.03 (m, 1H), 3.60 – 3.14 (m, 2H), 3.09 (dt, $J = 10.1$, 2.0 Hz, 1H), 2.83 (dd, $J = 14.4$, 8.1 Hz, 2H), 2.21 (td, $J = 6.9$, 2.2 Hz, 2H), 2.10 – 1.90 (m, 2H),

1.77–1.02 (m, 16H), 0.98–0.74 (m, 1H), 0.88 ppm (t, $J=6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=137.3, 116.4, 85.4, 77.2, 58.3, 53.9, 40.3, 31.3, 31.2, 30.4, 29.2, 28.5, 26.7, 26.2, 26.0, 22.6, 18.7, 14.0$ ppm; IR (film): $\tilde{\nu}=3079$ (w), 2925 (vs), 2853 (s), 1839 (w), 1643 (m), 1448 (s),918 cm^{-1} (s); MS: m/z (%): 300 (1) $[M^+-H]$, 218 (100), 192 (3), 162 (6), 146 (2), 120 (8), 106 (7), 91 (8); HRMS (EI): m/z: calcd for $C_{21}H_{36}N$ $[M^++H]$: 302.2848; found: 302.2860; elemental analysis calcd (%) for $C_{21}H_{36}N$: C 83.65, H 11.70, N 4.65; found: C 83.72, H 11.93, N 4.67.

***N,N*-Diallyl-1-(phenylethynyl)cyclohexanamine (3aa)**: The reaction was carried out according to procedure A with enamine **1n** (0.585 g, 3.30 mmol, 1.1 equiv), phenylacetylene (**2a**) (0.306 g, 3.00 mmol), CuBr (22 mg, 0.15 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (6 mL) at 60 °C for 24 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3aa** (0.626 g, 2.24 mmol, 75%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=$ 7.37–7.30 (m, 2H), 7.25–7.17 (m, 3H), 5.90 (m, 2H), 5.07 (dd, $J=1.8$, 17.3 Hz, 2H), 4.98 (dd, $J=1.8$, 10.2 Hz, 2H), 3.29 (d, $J=6.3$ Hz, 4H), 2.04–1.92 (m, 2H), 1.68–1.40 (m, 7H), 1.22–0.80 ppm (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=137.7, 131.5, 128.2, 127.6, 123.8, 115.7, 92.5, 85.4, 59.1, 51.8, 37.3, 25.6, 23.1$ ppm; IR (film): $\tilde{\nu}=3077$ (w), 2933 (vs), 2856 (m), 1642 (w), 1598 (w), 1490 (m), 1444 (m), 915 (s), 755 (vs), 690 cm^{-1} (m); MS: m/z (%): 278 (100) $[M^+-H]$, 264 (48), 250 (62), 236 (55), 222 (24), 208 (72), 115 (48), 91 (19); HRMS (EI): m/z: calcd for $C_{20}H_{24}N$ $[M^+-H]$: 278.1909; found: 278.1902; elemental analysis calcd (%) for $C_{20}H_{24}N$: C 85.97, H 9.02, N 5.01; found: C 85.83, H 8.96, N 5.02.

1-Benzyl-2-(phenylethynyl)piperidine (3ab): The reaction was carried out according to procedure A with enamine **1o** (0.347 g, 2.00 mmol), phenylacetylene (**2a**) (0.225 g, 2.20 mmol, 1.1 equiv), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at 80 °C for 3 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 9:1) afforded **3ab** (0.476 g, 1.73 mmol, 86%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=7.43-7.11$ (m, 10H), 3.64 (d, $J=13.3$ Hz, 1H), 3.64–3.55 (m, 1H), 3.56 (d, $J=13.4$ Hz, 1H), 2.60–2.49 (m, 1H), 2.48–2.34 (m, 1H), 1.80–1.38 ppm (m, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=138.6, 131.7, 129.2, 128.2, 128.1, 127.8, 126.9, 123.6, 87.5, 86.7, 60.5, 51.7, 49.2, 31.4, 25.8, 20.8$ ppm; IR (film): $\tilde{\nu}=3063$ (w), 3028 (w), 2955 (m), 2934 (m), 2248 (m), 1603 (w), 1494 (s), 1454 (s), 1028 (m), 747 (s), 699 cm^{-1} (vs); MS: m/z (%): 275 (82) $[M^+]$, 246 (37), 184 (100), 156 (19), 128 (52), 115 (39), 91 (87); HRMS (EI): m/z: calcd for $C_{20}H_{21}N$ $[M^+]$: 275.1674; found: 275.1663. elemental analysis calcd (%) for $C_{20}H_{21}N$: C 87.23, H 7.69, N 5.09; found: C 87.28, H 7.97, N 5.08.

***N,N*-Diallyl-1-phenyl-3-decyn-2-amine (3ac)**: The reaction was carried out according to procedure A with enamine **1p** (0.518 g, 2.60 mmol, 1.3 equiv), 1-octyne (**2b**) (0.220 g, 2.00 mmol), CuBr (14 mg, 0.10 mmol, 5.0 mol%), and *n*-decane (0.200 g, 1.41 mmol) in toluene (4 mL) at 60 °C for 20 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3ac** (0.489 g, 1.58 mmol, 79%) as a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.37-7.23$ (m, 5H), 5.93–5.79 (m, 2H), 5.28–5.25 (m, 1H), 5.22–5.20 (m, 1H), 5.18–5.16 (m, 1H), 5.15–5.12 (m, 1H), 3.84–3.76 (m, 1H), 3.42–3.33 (m, 2H), 3.10–2.86 (m, 4H), 2.25 (td, $J=6.9$, 2.3 Hz, 2H), 1.60–1.28 (m, 8H), 0.98 ppm (t, $J=6.9$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.1, 136.6, 129.4, 127.9, 126.1, 116.9, 86.0, 77.4, 54.7, 53.9, 40.6, 31.3, 29.0, 28.5, 22.2, 18.6, 14.0$ ppm; MS: m/z (%): 218 (100) $[M^+-C_7H_8]$, 162 (3), 146 (3), 128 (3), 106 (3), 91 (13); HRMS (EI): m/z: calcd for $C_{22}H_{32}N$ $[M^++H]$: 310.2535; found: 310.2557; IR (film): $\tilde{\nu}=$ 3079 (w), 2956 (vs), 2930 (s), 2858 (m), 1642 (w), 1496 (w), 1454 (m), 919 (s), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{22}H_{32}N$: C 85.38, H 10.10, N 4.53; found: C 85.22, H 10.45, N 4.51.

***N,N*-Dibenzyl-1-heptyn-3-amine (3ad)**: The reaction was carried out according to procedure A with enamine **1g** (1.274 g, 4.80 mmol, 1.2 equiv), trimethylsilylacetylenene (**2i**) (0.392 g, 4.00 mmol), CuBr (28 mg, 0.20 mmol, 5.0 mol%), and *n*-decane (0.400 g, 2.81 mmol) in toluene (8 mL) at room temperature for 20 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **3o** (1.142 g, 3.14 mmol, 79%) as a colorless oil. Propargylamine **3o** (0.909 g, 2.5 mmol) was dissolved in THF (10 mL) and TBAF (1M in THF, 2.75 mL, 2.75 mmol, 1.1 equiv) was added dropwise at room temperature. The reaction mixture was stirred for 30 min, hydrolyzed, and extracted with Et_2O. The combined organic layers were dried over $MgSO_4$ and the crude product purified by column chromatography (silica gel, pentane/Et_2O 98:2) to afford **3ad** (0.694 g, 2.40 mmol, 95%) as a light yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta=7.32-7.30$ (m, 4H), 7.25–7.12 (m, 6H), 3.75 (d, $J=$ 13.7 Hz, 2H), 3.34–3.28 (m, 3H), 2.23 (d, $J=2.2$ Hz, 1H), 1.72–1.49 (m, 2H), 1.39–1.22 (m, 2H), 1.17–1.05 (m, 2H), 0.76 ppm (d, $J=7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta=139.7, 128.8, 128.2, 126.9, 82.2, 72.4, 54.7, 51.4, 33.4, 28.4, 22.2, 13.9$ ppm; MS: m/z (%): 290 (1) $[M^+-H]$, 235 (22), 234 (98), 181 (11), 92 (100), 65 (10); HRMS (EI): m/z: calcd for $C_{21}H_{24}N$ $[M^+-H]$: 290.1909; found: 290.1885; 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 $C_{21}H_{24}N$: C 86.55, H 8.65, N 4.81; found: C 86.84, H 8.80, N 4.97.

***N,N*-Dibenzyl-1-(2-pyridinyl)-1-heptyn-3-amine (3ae)**: The reaction was carried out according to procedure A with enamine **1g** (0.318 g, 1.20 mmol, 1.2 equiv), 2-pyridinylacetylene (**2o**) (0.103 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol%), and *n*-decane (0.100 g, 0.70 mmol) in toluene (2 mL) at 60 °C for 48 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 9:1, then pentane/Et_2O 1:1) afforded **3ae** (0.173 g, 0.47 mmol, 47%) as a yellow oil.

The reaction was carried out according to procedure B with enamine **1g** (199 mg, 0.75 mmol, 1.5 equiv), 2-pyridinylacetylene (**2o**) (52 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 76 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 9:1 then 1:1) yielded **3ae** (135 mg, 0.37 mmol, 73%, 70% *ee*) as a yellow oil. $[\alpha]_D^{20}=-174$ ($c=$ 0.98 in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.5 mL min^{-1}): t_r (min) = 17.3 (−), 18.8 (+); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.54-8.50$ (m, 1H), 7.55 (td, $J=7.7$, 1.8 Hz, 1H), 7.42–7.30 (m, 4H), 7.25–7.19 (m, 4H), 7.17–7.09 (m, 4H), 3.83 (d, $J=13.6$ Hz, 2H), 3.56 (t, $J=$ 7.6 Hz, 1H), 3.50 (d, $J=13.6$ Hz, 2H), 1.81–1.60 (m, 2H), 1.42–1.22 (m, 2H), 1.12 (sext, $J=7.4$ Hz, 2H), 0.76 ppm (t, $J=7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=149.9, 143.6, 139.7, 136.0, 128.8, 128.1, 127.4, 126.8, 122.5, 88.6, 84.8, 54.9, 52.0, 33.3, 28.4, 22.2, 13.9$ ppm; IR (film): $\tilde{\nu}=3062$ (m), 3029 (m), 2955 (s), 2932 (s), 2860 (m), 2214 (w), 1582 (vs), 1463 (vs), 1427 (s), 779 (s), 740 (s), 690 cm^{-1} (vs); MS: m/z (%): 311 (100) $[M^+-C_4H_9]$, 219 (6), 194 (9), 130 (5), 91 (65); HRMS (EI): m/z: calcd for $C_{22}H_{19}N_2$ $[M^+-C_4H_9]$: 311.1548; found: 311.1522; elemental analysis calcd (%) for $C_{22}H_{19}N_2$: C 84.74, H 7.66, N 7.60; found: C 84.28, H 7.61, N 7.43.

***N,N*-Dibenzyl-1-(3-pyridinyl)-1-heptyn-3-amine (3af)**: The reaction was carried out according to procedure A with enamine **1g** (0.318 g, 1.20 mmol, 1.2 equiv), 3-pyridinylacetylene (**2p**) (0.103 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol%), and *n*-decane (0.100 g, 0.70 mmol) in toluene (2 mL) at 60 °C for 48 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 9:1, then pentane/Et_2O 1:1) afforded **3af** (0.215 g, 0.58 mmol, 58%) as a yellow oil.

The reaction was carried out according to procedure B with enamine **1g** (199 mg, 0.75 mmol, 1.5 equiv), 3-pyridinylacetylene (**2p**) (52 mg, 0.50 mmol), CuBr (3.6 mg, 0.025 mmol, 5.0 mol%), (*R*)-(+)-Quinap (12.1 mg, 0.0275 mmol, 5.5 mol%), and *n*-decane (50 mg, 0.35 mmol) in toluene (4 mL) at room temperature for 48 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 9:1 then 1:1) yielded **3af** (104 mg, 0.28 mmol, 57%, 70% *ee*) as a yellow oil. $[\alpha]_D^{20}=-190$ ($c=$ 0.91 in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.5 mL min^{-1}): t_r (min) = 17.3 (+), 18.5 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=8.65$ (br s, 1H), 8.43 (d, $J=4.0$ Hz, 1H), 7.66 (dt, $J=7.8$, 2.0 Hz, 1H), 7.36–7.10 (m, 11H), 3.81 (d, $J=13.7$ Hz, 2H), 3.54 (t, $J=7.7$ Hz, 1H), 3.38 (d, $J=13.7$ Hz, 2H), 1.80–1.56 (m, 2H), 1.46–1.22 (m, 2H), 1.13 (sext, $J=$ 7.3 Hz, 2H), 0.78 ppm (t, $J=7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=$ 152.5, 148.2, 139.6, 138.6, 128.7, 128.2, 127.1, 126.9, 122.9, 91.8, 81.9, 54.9, 52.2, 33.3, 28.4, 22.2, 13.9 ppm; IR (film): $\tilde{\nu}=3062$ (w), 3028 (m), 2955 (m), 2932 (m), 2228 (vw), 1604 (w), 1494 (s), 1454 (s), 804 (m), 747 (s), 699 cm^{-1} (vs); MS: m/z (%): 311 (100) $[M^+-C_4H_9]$, 219 (3), 194 (4), 116 (3), 91 (67); HRMS (EI): m/z: calcd for $C_{22}H_{19}N_2$ $[M^+-C_4H_9]$: 311.1548; found: 311.1558.

***N*^{4},*N*^{4}-Diallyl,*N*^{7},*N*^{7}-dibenzyl-2-methyl-5-undecyne-4,7-diamine (4)**: The reaction was carried out according to procedure A with enamine **1i** (0.149 g, 0.90 mmol, 1.2 equiv), *N,N*-dibenzyl-1-heptyn-3-amine (**3ad**) (0.219 g, 0.75 mmol), CuBr (5.4 mg, 0.0375 mmol, 5.0 mol%), and *n*-decane (0.100 g, 0.70 mmol) in toluene (2 mL) at 60 °C for 19 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 93:7) afforded **4** (0.342 g, 0.74 mmol, 99%, diastereomeric ratio 1:1) as a

colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.32-7.30$ (m, 4H), 7.23 (t, $J = 8.0$ Hz, 4H), 7.17–7.13 (m, 2H), 5.85–5.75 (m, 2H), 5.18 (d, $J = 17.0$ Hz, 2H), 5.06 (d, $J = 10.0$ Hz, 2H), 3.75 (d, $J = 13.7$ Hz, 2H), 3.63 (t, $J = 7.6$ Hz, 1H), 3.33 (d, $J = 13.7$ Hz, 2H), 3.34–3.24 (m, 3H), 2.90 (dd, $J = 14.0$, 6.1 Hz, 2H), 1.82 (sept, $J = 6.8$ Hz, 1H), 1.67–1.51 (m, 2H), 1.48 (t, $J = 7.1$ Hz, 2H), 1.40–1.24 (m, 2H), 1.18–1.08 (m, 2H), 0.89 (d, $J = 6.7$ Hz, 3H), 0.86 (d, $J = 6.8$ Hz, 3H), 0.78 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.0$, 136.9, 128.8, 128.2, 126.8, 116.9, 82.9, 82.5, 55.0, 54.2, 51.8, 50.8, 43.4, 33.9, 28.6, 25.2, 22.8, 22.5, 22.3, 14.0 ppm; MS: m/z (%): 400 (19) [$M^+ - C_4H_9$], 399 (62), 266 (10), 234 (27), 166 (10), 134 (22), 91 (100); HRMS (EI): m/z: calcd for $C_{32}H_{45}N$ [M^++H]: 457.3583; found: 457.3607; IR (film): $\tilde{\nu} = 2955$ (vs), 2932 (vs), 2870 (m), 2812 (m), 1454 (m), 919 (m), 698 cm^{-1} (s); elemental analysis calcd (%) for $C_{32}H_{45}N$: C 84.16, H 9.71, N 6.11; found: C 84.09, H 10.09, N 6.03.

***N*-Benzyl-1-phenyl-1-heptyn-3-amine (7a)**

Typical procedure C: $Pd(dba)_2$ (29 mg, 0.05 mmol, 5 mol%) and dppb (21 mg, 0.05 mmol, 5 mol%) were dissolved in THF (1 mL) and the reaction mixture was stirred at room temperature for 15 min. In a second flask, thiosalicylic acid (**6**) (0.170 g, 1.10 mmol, 1.1 equiv) was dissolved in THF (2 mL), propargylamine **3b** (0.317 g, 1.00 mmol) was added and the reaction mixture stirred for 15 min. The catalyst solution was then added dropwise to the amine solution and stirred at room temperature for 5 h. After dilution with Et_2O, extraction with saturated Na_2CO_3 solution, and drying over $MgSO_4$, the crude product was purified by column chromatography (silica gel, pentane/Et_2O 4:1) to afford **7a** (0.249 g, 0.90 mmol, 90%) as a colorless oil.

The chiral reaction was similarly performed with $Pd(dba)_2$ (12 mg, 0.021 mmol, 5 mol%), dppb (9 mg, 0.021 mmol, 5 mol%), **6** (96 mg, 0.62 mmol, 1.5 equiv), and **3b** (132 mg, 0.42 mmol) at room temperature for 2 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 4:1) yielded **7a** (105 mg, 0.38 mmol, 91%, 82% *ee*) as a colorless oil. $[\alpha]_D^{20} = -66$ ($c = 0.38$ in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.9 mL min^{-1}): t_r (min) = 30.6 (+), 41.8 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.40-7.10$ (m, 10H), 4.00 (d, $J = 12.8$ Hz, 1H), 3.80 (d, $J = 12.9$ Hz, 1H), 3.50 (t, $J = 6.8$ Hz, 1H), 1.73–1.55 (m, 2H), 1.50–1.35 (m, 3H), 1.28 (sext, $J = 7.2$ Hz, 2H), 0.83 ppm (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 140.1$, 131.6, 128.34, 128.32, 128.2, 127.8, 126.9, 123.4, 91.1, 83.9, 51.5, 50.0, 35.8, 28.3, 22.5, 13.9 ppm; IR (film): $\tilde{\nu} =$ 3083 (w), 3029 (w), 2956 (s), 2931 (s), 2205 (vw), 1622 (w), 1599 (w), 1490 (s), 1454 (s), 756 (vs), 692 cm^{-1} (vs); MS: m/z (%): 277 (1) [M^+], 220 (100), 128 (3), 115 (7), 91 (39); HRMS (EI): m/z: calcd for $C_{20}H_{24}N$ [M^++H]: 278.1909; found: 278.1895; elemental analysis calcd (%) for $C_{20}H_{24}N$: C 86.59, H 8.36, N 5.05; found: C 86.27, H 8.26, N 5.10.

***N*-Ferrocenylmethyl-1-phenyl-1-heptyn-3-amine (7b)**

Typical procedure D: $Pd(PPh_3)_4$ (17 mg, 0.015 mmol, 5 mol%) and **8** (140 mg, 0.90 mmol, 3 equiv) were dissolved in CH_2Cl_2 (2.5 mL). A solution of **3e** (0.128 g, 0.30 mmol) in CH_2Cl_2 (2.5 mL) was added at room temperature and the reaction mixture was stirred for 2 h. After evaporation of CH_2Cl_2 in vacuo, the residue was dissolved in Et_2O. The organic phase was extracted with saturated K_2CO_3 solution and dried over $MgSO_4$. Column chromatographic purification (silica gel, pentane/Et_2O 2:1) afforded **7b** (0.116 g, 0.30 mmol, 99%) as an orange-brown oil.

The chiral reaction was similarly performed with $[Pd(PPh_3)_4]$ (3.0 mg, 0.0025 mmol, 5 mol%), **8** (23 mg, 0.15 mmol, 3 equiv) and **3e** (21 mg, 0.05 mmol) in CH_2Cl_2 (2 mL). Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 2:1) yielded **7b** (15 mg, 0.04 mmol, 78%, 76% *ee*) as an orange-brown oil. $[\alpha]_D^{20} = +32$ ($c = 0.55$ in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.2 mL min^{-1}): t_r (min) = 61.8 (−), 66.2 (+); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.49-7.46$ (m, 2H), 7.35–7.30 (m, 3H), 4.27–4.24 (m, 2H), 4.15 (s, 5H), 4.12–4.11 (m, 2H), 3.81 (d, $J = 13.0$ Hz, 1H), 3.65 (t, $J = 6.8$ Hz, 1H), 3.60 (t, $J = 12.8$ Hz, 1H), 1.77–1.68 (m, 2H), 1.58–1.35 (m, 5H), 0.94 ppm (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 131.6$, 128.3, 127.9, 123.5, 91.3, 86.9, 83.3, 68.6, 68.4, 68.0, 67.7, 67.6, 50.3, 46.4, 35.8, 28.3, 22.5, 14.0 ppm; MS: m/z (%): 385 (20) [M^+], 353 (19), 352 (91), 288 (16), 287 (100), 200 (15), 199 (38), 173 (18), 145 (22), 121 (24); HRMS (EI): m/z: calcd for $C_{24}H_{27}FeN$ [M^+]: 385.1493; found: 385.1521; IR (film): $\tilde{\nu} = 2956$ (s), 2931 (s), 2859 (m), 1490 (m), 1443 (m), 1105 (m), 818 (m), 756 (vs), 691 (vs), 484 cm^{-1} (m).

1-Phenyl-1-heptyn-3-amine (7c): The reaction was carried out according to procedure D with $Pd(PPh_3)_4$ (58 mg, 0.005 mmol, 5 mol%), **8** (0.937 g, 6.00 mmol, 6 equiv), and **3a** (0.267 g, 1.00 mmol) in CH_2Cl_2 (3 mL) at room temperature for 90 min. Purification of the crude product (solution in Et_2O) was achieved by extraction with HCl solution (2 M), then treatment with saturated K_2CO_3 solution (pH > 8), extraction of the aqueous layers with CH_2Cl_2 and drying over $MgSO_4$ to yield **7c** (0.170 g, 0.91 mmol, 91%) as a yellow oil.

The chiral reaction was similarly performed with $[Pd(PPh_3)_4]$ (11 mg, 0.009 mmol, 5 mol%), **8** (175 mg, 1.12 mmol, 6 equiv), and **3a** (50 mg, 0.19 mmol) in CH_2Cl_2 (2 mL) at room temperature for 90 min and yielded **7c** (28 mg, 0.15 mmol, 80%) as a yellow oil. $[\alpha]_D^{20} = +5$ ($c = 1.02$ in $CHCl_3$); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.35-7.28$ (m, 2H), 7.23–7.15 (m, 3H), 3.68 (t, $J = 6.5$ Hz, 1H), 1.70–1.10 (m, 6H), 0.86 ppm (t, $J = 7.2$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 131.5$, 128.2, 127.8, 123.3, 93.1, 82.4, 44.0, 38.0, 28.2, 22.4, 14.0 ppm; IR (film): $\tilde{\nu} = 3370$ (w), 3057 (w), 2931 (s), 2957 (vs), 2859 (m), 1682 (w), 1598 (m), 1490 (s), 756 (vs), 692 cm^{-1} (vs); MS: m/z (%): 186 (1) [$M^+ - H$], 130 (100), 115 (3), 103 (11), 77 (7); HRMS (EI): m/z: calcd for $C_{13}H_{16}N$ [$M^+ - H$]: 186.1283; found: 186.1281.

***N*-Allyl-1-phenyl-1-heptyn-3-amine (7d)**

Starting from 3a: The reaction was carried out according to procedure C with $Pd(dba)_2$ (29 mg, 0.05 mmol, 5 mol%), dppb (21 mg, 0.05 mmol, 5 mol%), **6** (0.185 g, 1.2 mmol, 1.2 equiv), and **3a** (0.267 g, 1.00 mmol) in THF (3 mL) at 0 °C for 2 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 1:1) yielded **7d** (0.170 g, 0.75 mmol, 75%) as a colorless oil. The chiral reaction was similarly performed with $[Pd(dba)_2]$ (5.4 mg, 0.009 mmol, 5 mol%), dppb (4.0 mg, 0.009 mmol, 5 mol%), **6** (35 mg, 0.22 mmol, 1.2 equiv), and **3a** (50 mg, 0.19 mmol) in THF (3 mL) at 0 °C for 2 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 1:1) yielded **7d** (25 mg, 0.11 mmol, 62%, 77% *ee*) as a colorless oil. $[\alpha]_D^{20} = -46$ ($c = 0.75$ in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.6 mL min^{-1}): t_r (min) = 8.6 (+), 11.2 (−); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.38-7.30$ (m, 2H), 7.25–7.15 (m, 3H), 5.95–5.80 (m, 1H), 5.22–5.02 (m, 2H), 3.56–3.44 (m, 2H), 3.33–3.22 (m, 1H), 1.72–1.54 (m, 2H), 1.52–1.11 (m, 4H), 0.86 ppm (t, $J =$ 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 136.5$, 131.6, 128.2, 127.9, 123.4, 116.2, 91.0, 83.8, 51.5, 50.2, 35.9, 28.3, 22.5, 14.0 ppm; IR (film): $\tilde{\nu} =$ 3316 (m), 3080 (w), 2957 (s), 2931 (s), 1598 (w), 1490 (m), 918 (m), 756 (vs), 691 cm^{-1} (s); MS: m/z (%): 226 (1) [$M^+ - H$], 170 (100), 128 (18), 115 (11), 91 (3), 77 (2); HRMS (EI): m/z: calcd for $C_{16}H_{22}N$ [M^++H]: 228.1752; found: 228.1759; elemental analysis calcd (%) for $C_{16}H_{22}N$: C 84.53, H 9.31, N 6.16; found: C 84.76, H 9.74, N 6.09.

Starting from 3f: Propargylamine **3f** (78 mg, 0.20 mmol) was dissolved in CF_3CO_2H (3 mL). Et_3SiH (116 mg, 1.00 mmol, 5 equiv) was added at room temperature and then the reaction mixture was heated to 80 °C for 2 h. After cooling to room temperature, the mixture was diluted with CH_2Cl_2, hydrolyzed and neutralized with saturated K_2CO_3 solution. The organic layer was separated, washed with saturated K_2CO_3 solution and dried over $MgSO_4$. Column chromatographic purification (silica gel, pentane/Et_2O 4:1 then 1:1) afforded **7d** (40 mg, 0.18 mmol, 88%) as a colorless oil. The chiral reaction was similarly performed with **3f** (60 mg, 0.15 mmol), CF_3CO_2H (2.5 mL), and Et_3SiH (87 mg, 0.75 mmol, 5 equiv) and yielded **7d** (17 mg, 0.075 mmol, 50%, 50% *ee*). $[\alpha]_D^{20} = -25$ ($c = 0.50$ in $CHCl_3$); HPLC (OD-H, 99% *n*-heptane/1% isopropanol, 0.3 mL min^{-1}): t_r (min) = 18.8 (+), 23.7 (−).

1-Cyclohexyl-3-phenyl-propyl-1-amine (7e): Palladium on charcoal (10%, 0.550 g) was suspended in methanol (5 mL) under a hydrogen atmosphere (1 atm). A solution of **3w** (0.550 g, 1.40 mmol) in methanol (5 mL) was added at room temperature and the reaction mixture was stirred for 14 h. After filtration over Celite and evaporation of the solvent in vacuo, the crude product was purified by bulb-to-bulb destillation in vacuo to yield **7e** (0.213 g, 0.98 mmol, 70%) as a colorless oil which slowly crystallized. M.p. < 25 °C; ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.28-7.09$ (m, 5H), 2.79–2.65 (m, 1H), 2.59–2.40 (m, 2H), 1.80–1.40 (m, 7H), 1.24–0.82 ppm (m, 8H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 142.6$, 128.32, 128.30, 125.6, 55.7, 44.0, 36.7, 33.0, 29.6, 27.8, 26.63, 26.55, 26.42 ppm; IR (film): $\tilde{\nu} = 3083$ (w), 3029 (w), 2956 (s), 2931 (s), 2205 (vw), 1622 (w), 1599 (w), 1490 (s), 1454 (s), 756 (vs), 692 cm^{-1} (vs); MS: m/z (%): 218 (2) [M^++H], 134 (100), 117 (28), 104 (4), 91 (62); HRMS (EI): m/z: calcd for $C_{15}H_{24}N$ [M^++H]: 218.1909; found: 218.1893; elemental analysis calcd (%) for $C_{15}H_{24}N$: C 82.89, H 10.67, N 6.44; found: C 82.46, H 10.77, N 6.08.

2-Benzyl-1-butyl-6-phenyl-2,3,3a,4-tetrahydrocyclopenta[*c*]-pyrrol-5(1*H*)-one (9)

Typical procedure E: $Co_2(CO)_8$ (135 mg, 0.40 mmol, 1.2 equiv) was dissolved in Et_2O (3.5 mL). A solution of **3b** (105 mg, 0.33 mmol) in Et_2O (1.5 mL) was added at room temperature (CO evolution observed) and stirred for 1 h. After filtration over Celite, the solvent was evaporated and the residue was dissolved in CH_2Cl_2 (5 mL). This solution was added to a suspension of Me_3NO (183 mg, 1.65 mmol, 5.0 equiv) in MeCN (5 mL) and the reaction mixture was stirred for 14 h. Evaporation of the solvents in vacuo and column chromatographic purification (silica gel, pentane/Et_2O 1:1) afforded **9** (57 mg, 0.16 mmol, 50%, diastereomeric ratio = > 99:1) as a yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.40-7.16$ (m, 10H), 3.95 (d, $J = 13.1$ Hz, 1H), 3.68–3.60 (m, 1H), 3.48–3.40 (m, 1H), 3.40 (d. $J = 14.0$ Hz, 1H), 3.26 (t, $J = 7.5$ Hz, 1H), 3.20–3.06 (m, 1H), 2.63 (dd, $J = 17.9$, 6.4 Hz, 1H), 2.15 (dd, $J = 18.0$, 3.7 Hz, 1H), 1.88 (dd, $J = 10.5$, 8.4 Hz, 1H), 1.75–1.58 (m, 2H), 1.54–1.40 (m, 1H), 1.25–1.15 (m, 2H), 0.78 ppm (t, $J = 7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 207.6$, 182.7, 138.9, 135.1, 131.6, 128.7, 128.4, 128.32, 128.30, 127.9, 127.1, 63.7, 59.3, 57.9, 42.6, 40.0, 33.6, 27.4, 22.9, 14.0 ppm; IR (film): $\tilde{\nu} = 3060$ (m), 3029 (m), 2958 (s), 2930 (s), 1713 (vs), 1601 (m), 1495 (s), 1454 (s), 1137 (s), 756 (m), 698 cm^{-1} (s); MS: *m*/*z* (%): 345 (7) [M^+], 288 (100), 168 (3), 141 (3), 115 (3), 91 (52); HRMS (EI): *m*/*z*: calcd for $C_{24}H_{27}NO$ [M^+]: 345.2093; found: 345.2063.

1-Butyl-2-(4-methoxybenzyl)-6-phenyl-2,3,3a,4-tetrahydrocyclo-penta[*c*]-pyrrol-5(1*H*)-one (10): The reaction was carried out according to procedure E with $Co_2(CO)_8$ (113 mg, 0.33 mmol, 1.1 equiv) and **3g** (104 mg, 0.30 mmol) in pentane (4 mL) at room temperature for 45 min. The oxidation was performed with Me_3NO (167 mg, 1.50 mmol, 5.0 equiv) in CH_2Cl_2/MeCN (1:1, 10 mL) at room temperature for 5 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 1:1) afforded **10** (43 mg, 0.11 mmol, 38%, diastereomeric ratio > 99:1) as a yellow oil.

The chiral reaction was similarly performed with $Co_2(CO)_8$ (64 mg, 0.19 mmol, 1.1 equiv), **3g** (60 mg, 0.19 mmol), and Me_3NO (94 mg, 0.85 mmol, 5.0 equiv) to yield **10** (20 mg, 0.05 mmol, 31%, 68% *ee*). $[\alpha]_D^{20} = -21$ ($c = 0.55$ in $CHCl_3$); HPLC (OD-H, 98% *n*-heptane/2% isopropanol, 0.6 mL min^{-1}): t_r (min) = 46.4 (+), 51.1 (−); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 7.38-7.22$ (m, 5H), 7.17 (d, $J = 8.9$ Hz, 2H), 6.79 (d, $J = 8.7$ Hz, 2H), 3.88 (d, $J = 13.3$ Hz, 1H), 3.74 (s, 3H), 3.61 (t, $J = 3.5$ Hz, 1H), 3.37 (d, $J = 13.0$ Hz, 1H), 3.24 (t, $J = 7.5$ Hz, 1H), 3.18–3.08 (m, 1H), 2.64 (dd, $J = 17.7$, 6.7 Hz, 1H), 2.15 (dd, $J = 18.0$, 3.3 Hz, 1H), 1.87 (dd, $J = 10.6$, 7.8 Hz, 1H), 1.74–1.59 (m, 2H), 1.54–1.40 (m, 2H), 1.27–1.11 (m, 2H), 0.78 ppm (t, $J = 7.4$ Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 207.7$, 182.8, 158.8, 135.0, 131.6, 130.9, 129.8, 128.4, 128.3, 127.9, 113.7, 63.5, 58.6, 57.8, 55.3, 42.5, 40.1, 33.7, 27.4, 22.9, 14.0 ppm; MS: *m*/*z* (%): 375 (6) [M^+], 318 (26), 121 (100); HRMS (EI): *m*/*z*: calcd for $C_{25}H_{29}NO_2$ [M^+]: 375.2198; found: 375.2177; IR (film): $\tilde{\nu} = 2956$ (s), 2931 (s), 2858 (m), 1706 (vs), 1612 (m), 1512 (vs), 1465 (m), 1300 (m), 1249 (vs), 1175 (m), 1136 (m), 1035 (m), 697 cm^{-1} (m).

***N*,*N*-Dibenzyl-1-phenyl-1-heptyn-3-amine (12)**: The reaction was carried out according to procedure A with enamine **1g** (0.345 g, 1.30 mmol, 1.3 equiv), phenylacetylene-*d* (**2q**) (0.102 g, 1.00 mmol), CuBr (7 mg, 0.05 mmol, 5.0 mol%), and *n*-decane (0.100 g, 0.70 mmol) in toluene (2 mL) at room temperature for 14 h. Standard workup and column chromatographic purification (silica gel, pentane/Et_2O 98:2) afforded **12** (0.334 g, 0.91 mmol, 91%, >90% deuterium incorporation) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.46-7.10$ (m, 15H), 3.82 (d, $J = 13.7$ Hz, 2H), 3.56–3.48 (m, 1H), 3.42 (d, $J = 13.7$ Hz, 2H), 1.80–1.60 (m, 1H), 1.42–1.24 (m, 2H), 1.15 (sext, $J = 7.2$ Hz, 2H), 0.79 ppm (t, $J = 7.3$ 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, 52.1 (t, $J = 5.0$ Hz), 33.6, 33.2 (t, $J = 19.3$ Hz), 28.5 (t, $J = 7.3$ Hz), 22.3 (t, $J = 2.0$ Hz), 13.5 ppm; IR (film): $\tilde{\nu} = 3024$ (m), 2924 (m), 2858 (w), 1639 (m), 1606 (s), 1488 (m), 1443 (m), 994 (s), 913 (vs), 790 (m), 702 cm^{-1} (vs); MS: *m*/*z* (%): 310 (100) [$M^+ - C_4H_8D$], 218 (2), 191 (2), 115 (5), 91 (56); HRMS (EI): *m*/*z*: calcd for $C_{27}H_{26}DN$ [$M^+ - 2H$]: 365.2127; found: 365.2098.

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hydrogen atoms were refined anisotropically. $R1 = 0.0374$, $\omega R2 = 0.0834$ for all data with $I > 2\sigma(I)$. CCDC 182716 contains the supplementary crystallographic data (excluding structure factors) and can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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