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Zinc Salt Promoted Diastereoselective Synthesis of Chiral Propargylamines Using Chiral Piperazines and Their Enantioselective Conversion into Chiral Allenes

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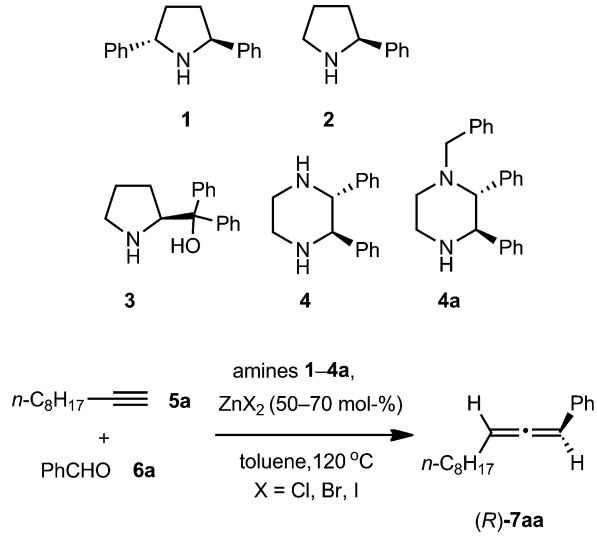
Zinc chloride catalyzed reactions of chiral piperazine derivatives **4a**–**d** with 1-alkynes and aldehydes give chiral propargylamines in 67–95 % yields with up to 99:1 *dr*. The chiral propargylamines are converted into chiral allenes by using zinc bromide in short reaction times (1–2 h) in high enantioselectivities (up to 99 % *ee*) in good yields (up to 89 %). The chiral piperazines are recovered in good yields (79–86 %) by reduction of the imine byproducts in situ by using $NaBH_4$. Unexpectedly, the chiral aryl-substituted allenes undergo facile cyclodimerization under neat conditions at 25 °C, in contrast to an earlier report that cyclodimerization takes place at 80 °C in benzene, which further illustrates the importance of the two-step procedure reported herein because the chiral propargylamine may be converted into chiral allene when required.

Introduction

Allenes are versatile building blocks and synthons for use in modern organic synthesis.[1,2] Generally, chiral allenes are synthesized from enantioenriched propargylic precursors through transfer of their stereochemical information to allenes by S_N2 type displacement reactions of chiral propargylic compounds and (3,3)-sigmatropic rearrangement of chiral propargyl alcohols.[3] There is growing interest in the synthesis of chiral allenes by using amines via chiral propargylamines.[4] Chiral propargylamines are also versatile synthetic intermediates for the synthesis of biologically active skeletons and important structural elements of natural products.[5] Methods have been reported for the enantioselective synthesis of propargylamine derivatives by using metal-based chiral ligands such as quinap,[6] pinap,[7] pybox,[8] and binam diimine[9] as well as diastereoselective synthesis of chiral propargylamines by using chiral amines and gold(III) salen complexes.[4a,4c]

Recently, we developed a "chiral amine approach" for highly enantioselective synthesis of chiral allenes by using terminal alkynes, aldehydes, and chiral amines promoted by zinc halides in a single-pot operation.[10a] Thus, the zinc halide promoted reaction of chiral secondary amines **1**–**4a**, 1-decyne **5a**, and benzaldehyde **6a** at 120 °C (Scheme 1) has been developed to access the chiral allenes in very high enantioselectivity up to 99 %*ee*.



Scheme 1. Synthesis of chiral allene **7aa** by using chiral amines **1**–**4a**.

This method has a few limitations. Whereas, the C_2-symmetric chiral amine **1** gave the chiral allene in only 18 %*ee*, the C_1 chiral pyrrolidine derivative **2** afforded the allene product in 66 %*ee*. The easily accessible and commercially available chiral amino alcohol **3** yielded chiral allene **7aa** in 98 %*ee*, and the reaction has been generalized for a variety of aldehydes and alkynes. However, the results are highly dependent on the sequential addition of the reactants and inadvertent formation of the oxazolidine intermediate **8**

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could lower the enantioselectivity of the allene to 86%*ee*.[10a]

The imine byproduct **9** could be isolated and recycled back to the chiral diphenylprolinol **3** in 75% yield by $NaBH_4/CH_3OH$-mediated reduction. However, careful analysis of the imine product mixture indicated the formation of **10** (5–10% yield) formed by condensation with the benzaldehyde present in the medium (Figure 1). The *N*-benzylpiperazine derivative **4a** gave the chiral allene in 95%*ee* without the formation of such unwanted sideproducts.[10a] Therefore, we decided to prepare different chiral *N*-benzylpiperazine derivatives for applications in this transformation, especially for the two-step conversion via the corresponding propargylamine because this would avoid the presence of aldehyde substrates that could react with the corresponding cyclic imine byproduct after the formation of the allene.[10b] A CuBr-promoted two-step protocol is available but this method requires 36 h at 25 °C for the preparation of chiral propargylamines by the reaction of 2-(dialkylamino)pyrrolidines with 1-alkynes and aldehydes in toluene, and a further 18 h at 100 °C for the CuI-promoted conversion into chiral allenes.[11] Herein, we report the synthesis of chiral piperazine derivatives **4a**–**d** (Figure 2), which enables the synthesis of chiral propargylamines in a $ZnCl_2$-promoted reaction at 100 °C in 4 h and their conversion into chiral allenes in a $ZnBr_2$ reaction at 120 °C in 1–2 h.

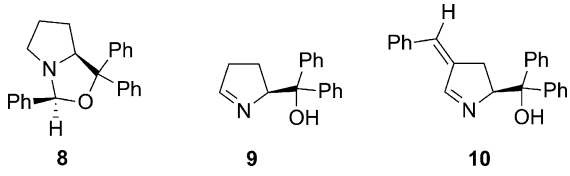


Figure 1. Structures of oxazolidine intermediate **8** and imine byproducts **9** and **10**.

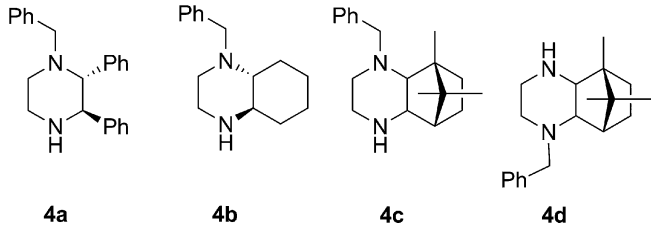
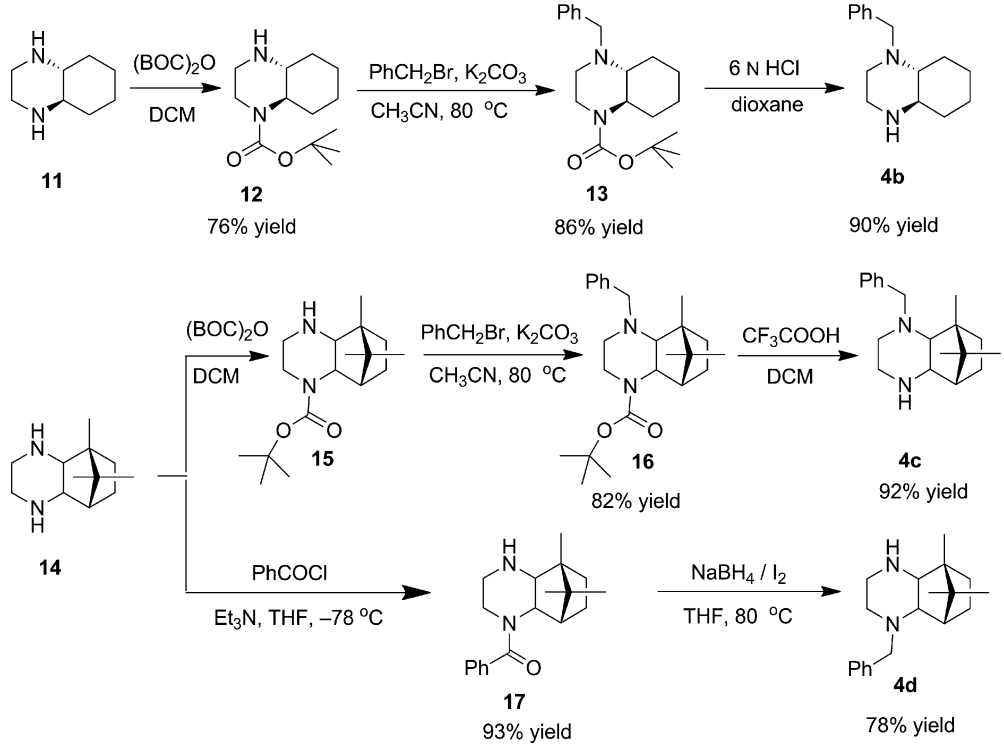


Figure 2. Chiral piperazine derivatives **4a**–**d**.

Results and Discussion

The diastereomerically pure chiral *N*-methylcamphanylpiperazine derivatives react with aldehydes and 1-alkynes in the presence of zinc halide to give both enantiomers of the corresponding chiral allene in a single-pot operation.[12] However, it is somewhat difficult to recover the chiral *N*-methylcamphanylpiperazine. Therefore, the corresponding *N*-benzylpiperazines **4b**–**d** were prepared as outlined in Scheme 2 for use in the present studies. Initial *tert*-butoxycarbonyl (BOC) protection followed by benzylation and BOC deprotection of the parent piperazines **11** and **14** gave the *N*-benzylpiperzines **4b** and **4c**, respectively, in 90–92% yields. Whereas, direct benzoylation of the camphanylpiper-

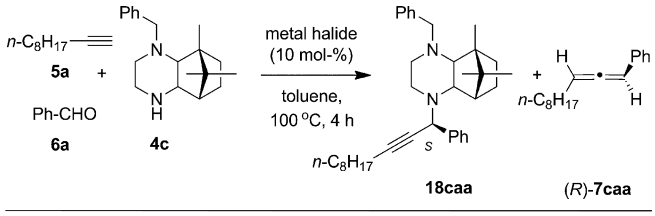


Scheme 2. Synthesis of *N*-benzylpiperazine derivatives **4b**–**d**.

azine **14** at –78 °C followed by reduction with $NaBH_4/I_2$ at 80 °C gave *N*-benzylcamphanylpiperazine **4d** in 78% yield (Scheme 2).

We then carried out detailed studies on the synthesis of chiral propargylamines and their conversion into chiral allenes. We found that chiral propargylamine **18caa** is obtained in 98% yield with 99:1 *dr* in the zinc chloride catalyzed reaction of 1-decyne **5a**, aldehyde **6a**, and chiral piperazine derivative **4c** at 100 °C (Table 1). Chiral propargylamine **18caa** was obtained in slightly lower yield by using other metal halides such as $ZnBr_2$, CuBr, and CuI under these reaction conditions (Table 1).[13]

Table 1. Synthesis of chiral propargylamine **18caa** by using 1-decyne **5a**, benzaldehyde **6a**, and the chiral *N*-benzylpiperazine **4c** with metal salts.[a]



Entry	Metal halide	mol-%	Time [h]	Yield of **18caa** [%][b]	*dr*[c]	Yield of **7caa** [%][b]	*ee* [%][d]
1	$ZnCl_2$	10	4	98	99:1	–	–
2	$ZnBr_2$	10	4	85	99:1	10	99
3	CuBr	10	4	90	98:2	8	99
4[e]	CuBr	10	24	95	99:1	–	–
5	CuI	10	4	87	97:3	15	99

[a] Reaction conditions: piperazine **4c** (1.0 mmol), 1-decyne (1.1 mmol), benzaldehyde (1.0 mmol), toluene (3 mL), 100 °C, 4 h. [b] Isolated yield. [c] *dr* ratio based on crude ^1H NMR spectroscopic analysis. [d] *ee* of allene **7caa** was determined by chiral HPLC analysis. [e] The reaction was carried out at 25 °C for 24 h.

We next investigated the synthesis of various chiral propargylamine derivatives **18** from the corresponding chiral piperazines **4a**–**c**; the results are summarized in Table 2. Arylaldehydes that have an electron-donating group such as methoxy **6f** and *para*-methyl **6g** undergo this reaction to give the corresponding propargylamines **18aag**, **18cag**, and **18caf** in 93–97% yields and up to 99:1 *dr*. Electron-deficient aryl aldehydes **6b**–**e** transformed smoothly into the desired propargylamine derivatives **18aac**, **18cad**, and **18cae** in 89–91% yields with up to 98:2 *dr*. We have also carried out the reaction with various alkynes, aldehydes, and chiral piperazine derivative **4a** under these reaction conditions. Cyano- and chloro-substituted alkynes **5b** and **5c** gave the desired propargylamines **18aba**–**aca** in 89–92% yields with up to 99:1 *dr*. Propargylamines **18ada** and **18aej** were obtained in 86 and 92% yield, respectively, with 98:2 and 99:1 *dr*. Propargylamines **18bfa**–**bdj** were obtained in 67–90% yields with up to 99:1 *dr* by using the chiral piperazine derivative **4b** (Table 2). The configuration at the newly formed stereogenic center in propargylamine **18aej** was found to be *S* by single-crystal X-ray analysis (Figure 3). Thiophene-2-carbaldehyde **6i** reacts with alkynes **5a** and **5c** to give the corresponding propargylamines **18aci** and **18cai** in reasonable yields and good selectivity. Propargylamine **18cah** was obtained in 85% yield with 98:2 *dr* within 3 h in the reaction of furfural **6h** and 1-decyne **5a** with $ZnCl_2$ at 100 °C.

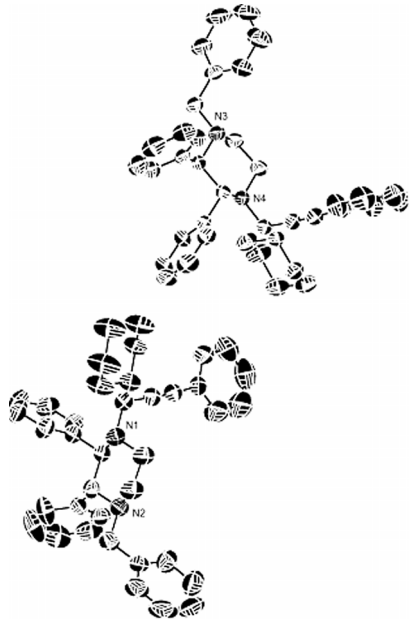


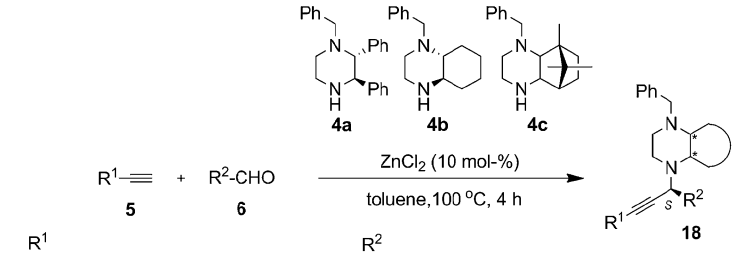
Figure 3. ORTEP representation of chiral propargylamine **18aej** (thermal ellipsoids drawn with 50% probability).

We then turned our attention to the conversion of chiral propargylamines into the corresponding chiral allenes. We have observed that the reaction of chiral propargylamine **18caa** with $ZnBr_2$ (0.5 mmol) at 120 °C gave chiral allene **7caa** in up to 89% yield with 99%*ee*. The same procedure was followed for the conversion of other diastereomerically pure propargylamines into the corresponding chiral allenes; the results are summarized in Table 3.

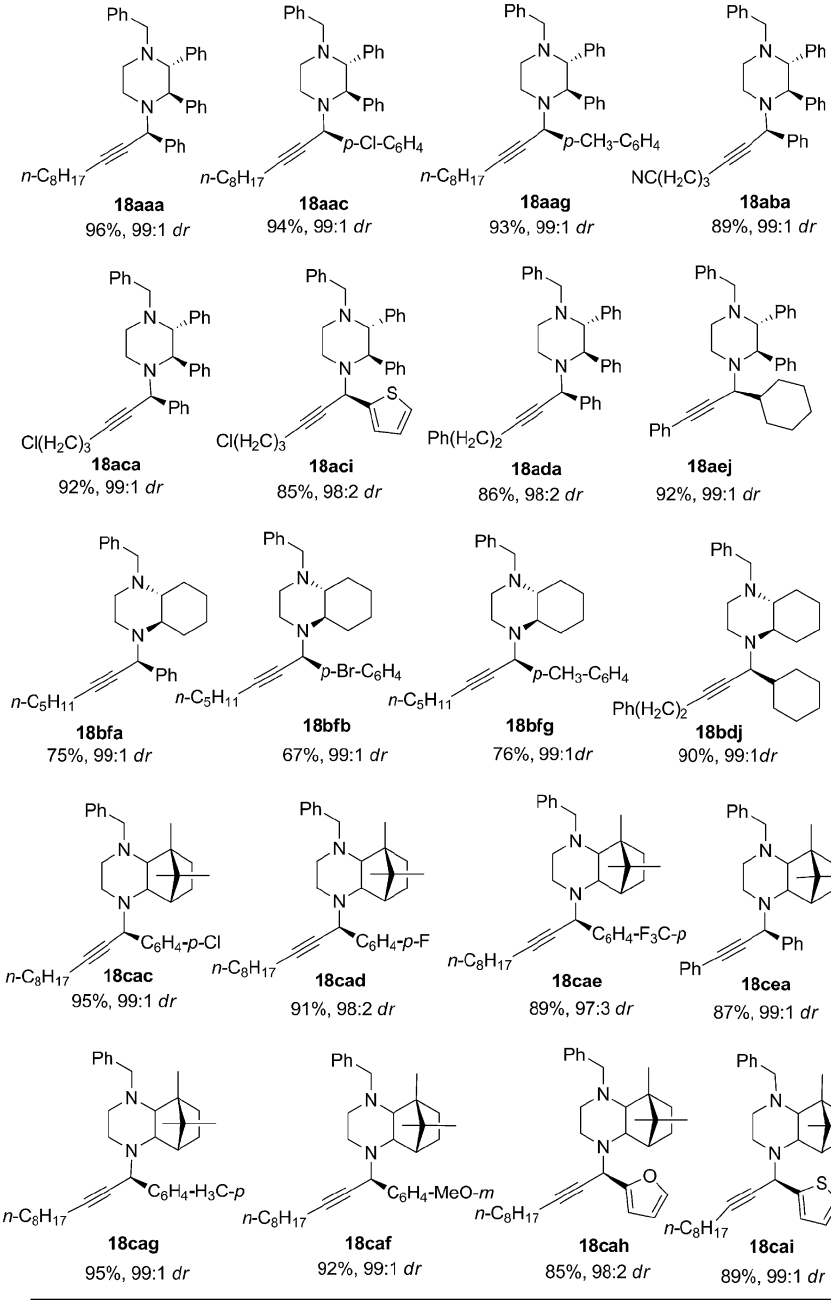
Chiral propargylamines **18aag**, **18caf**, and **18cag** substituted with methoxy and methyl groups afforded the corresponding chiral allenes **7aag**, **7caf**, and **7cag** in 72–82% yields with up to 99%*ee*. Propargylamines having chloro, fluoro, or trifluoro substituents were also compatible with the reaction conditions, affording the corresponding axially chiral aryl-substituted allenes **7aac**–**cae** in 69–71% yields and up to 99%*ee*. Propargylamines containing heteroaromatic groups **18aci**, **18cah**, and **18cai** with $ZnBr_2$ (0.5 mmol) at 120 °C gave chiral allenes **7cah**–**cai** in 69–73% yields and up to 99%*ee*. Propargylamines substituted with cyano or chloro groups afforded the corresponding chiral allenes **7aba** and **7aca** in 70–71% yields and up to 99%*ee*. Propargylamines **18ada** and **18aej** gave the corresponding chiral allenes **7ada** and **7aej** in 71–76% yields and up to 99%*ee*. Propargylamines **18bfa**–**bdj** also afforded the corresponding chiral allenes 69–89% yields with up to 99%*ee* (Table 3).

We also carried out the allene synthesis by using chiral propargylamine **18daa**, with *R* configuration at the prop-

Table 2. $ZnCl_2$-promoted synthesis of chiral propargylamines **18** by using 1-alkynes **5**, aldehydes **6**, and chiral piperazine derivatives **4a**–**c**.[a,b,c]

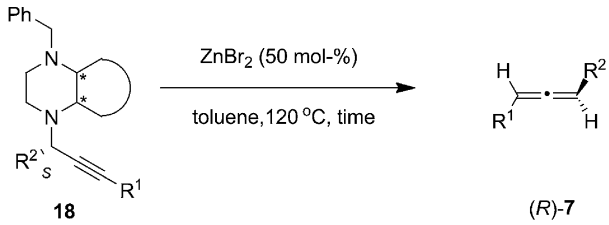


R^1	R^2			
5a n-C_8H_{17}	**5d** $PhCH_2CH_2$	**6a** Ph	**6d** C_6H_4-p-F	**6g** C_6H_4-p-CH_3
5b $NCCH_2CH_2CH_2$	**5e** Ph	**6b** C_6H_4-p-Br	**6e** C_6H_4-p-CF_3	**6h** fur-2-yl
5c $ClCH_2CH_2CH_2$	**5f** n-C_5H_{11}	**6c** C_6H_4-p-Cl	**6f** C_6H_4-m-OCH_3	**6i** thiophen-2-yl
				6j cHexyl



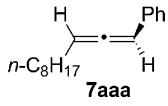
[a] Reaction conditions: chiral piperazine (1.0 mmol), 1-alkyne (1.1 mmol), aldehyde (1.0 mmol), toluene (3 mL), 100 °C, 4 h. [b] *dr* ratio based on crude ^1H NMR spectroscopic analysis. [c] Isolated yield.

Table 3. $ZnBr_2$-promoted synthesis of chiral allenes from chiral propargylamines **18**.[a,b,c]

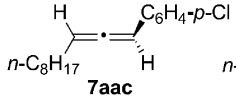


18 (*R*)-**7**

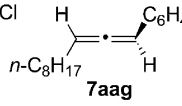
18aaa (R^1 = *n*-C_8H_{17}, R^2 = Ph)
18aac (R^1 = *n*-C_8H_{17},R^2 = C_6H_4-*p*-Cl)
18aag (R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-CH_3)
18aba (R^1 = $NC(CH_2)_3$-, R^2 = Ph)
18aca (R^1 = $Cl(CH_2)_3$-, R^2 = Ph)
18aci (R^1 = $Cl(CH_2)_3$-, R^2 = thiophen-2-yl)
18ada (R^1 =$PhCH_2CH_2$, R^2 = Ph)
18aej (R^1 =Ph, R^2 = *c*Hexyl)
18bfa (R^1 = *n*-C_5H_{11}, R^2 = Ph)
18bfb (R^1 = *n*-C_5H_{11} R^2 = C_6H_4-*p*-Br)
18bfg (R^1 = *n*-C_5H_{11}, R^2 = C_6H_4-*p*-CH_3)
18bdj (R^1 =$PhCH_2CH_2$, R^2 = *c*Hexyl)
18cac (R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-Cl)
18cad (R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-F)
18cae (R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-CF_3)
18cea (R^1 = Ph, R^2 = Ph)
18cag (R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*p*-CH_3)
18caf (R^1 = *n*-C_8H_{17}, R^2 = C_6H_4-*m*-OCH_3)
18cah (R^1 = *n*-C_8H_{17}, R^2 = fur-2-yl)
18cai (R^1 = *n*-C_8H_{17}, R^2 = thiophen-2-yl)



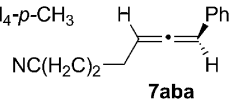
7aaa
2 h, 75%, >99% *ee*



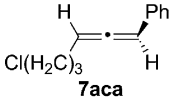
7aac
2 h, 75%, >99% *ee*



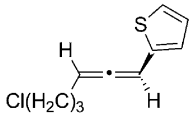
7aag
2 h, 72%, >99% *ee*



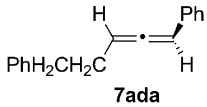
7aba
2 h, 70%, >99% *ee*



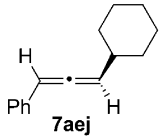
7aca
2 h, 71%, 99% *ee*



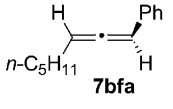
7aci
2 h, 69%, 98% *ee*



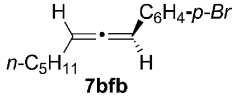
7ada
2 h, 71%, 96% *ee*



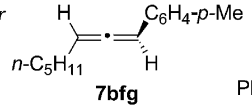
7aej
2 h, 76%, >99% *ee*



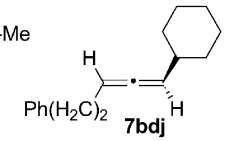
7bfa
2 h, 75%, 94% *ee*



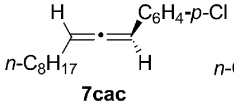
7bfb
2 h, 69%, 99% *ee*



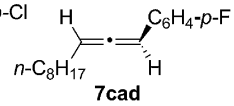
7bfg
2 h, 73%, 92% *ee*



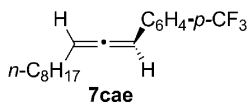
7bdj
2 h, 89%, 98% *ee*



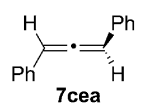
7cac
1 h, 76%, 99% *ee*



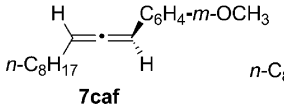
7cad
1 h, 69%, 99% *ee*



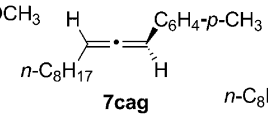
7cae
1 h, 71%, 99% *ee*



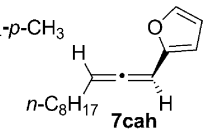
7cea
1 h, 71%, 93% *ee*



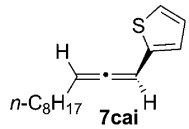
7caf
1.5 h, 82%, 99% *ee*



7cag
1.5 h, 75%, 99% *ee*



7cah
1 h, 69%, 99% *ee*

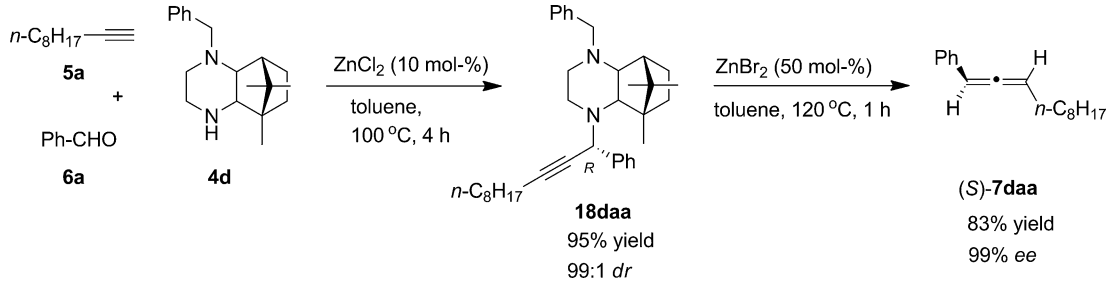


7cai
1 h, 73%, 99% *ee*

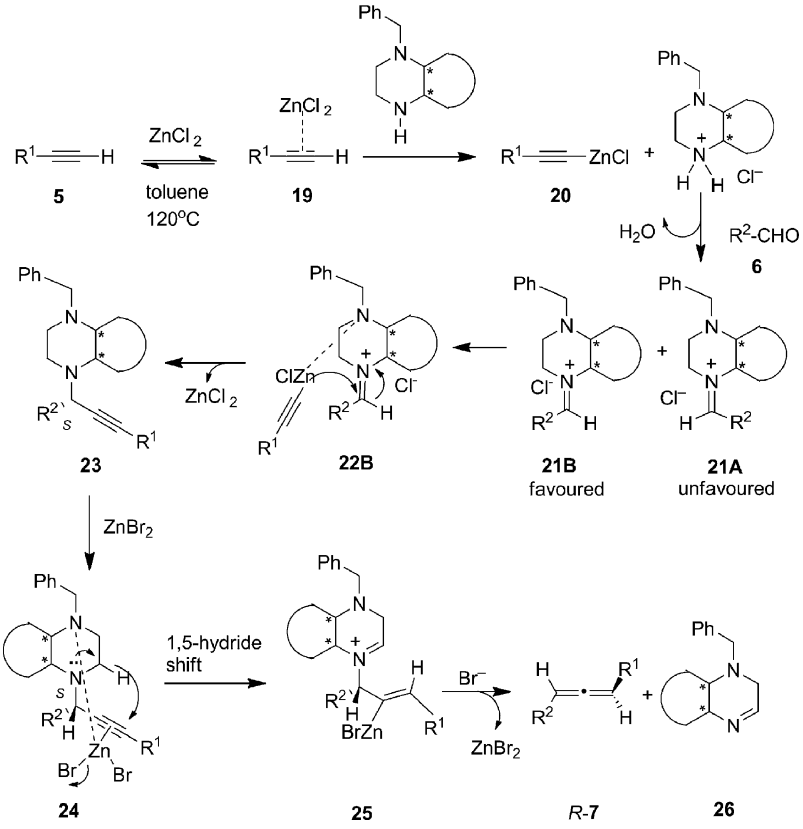
[a] Reaction conditions: propargylamine **18** (1 mmol), toluene (3 mL), $ZnBr_2$ (0.5 mmol). [b] Isolated yield. [c] *ee* determined by using chiral HPLC analysis.

argylic stereogenic center. As expected, the *S* chiral allene **7daa** was obtained in 83% yield and 99%*ee* under these conditions (Scheme 3).

The formation of chiral propargylamines and their conversion into chiral allenes can be rationalized by the mechanism outlined in Scheme 4. The initially formed alkynylzinc



Scheme 3. Synthesis of chiral allene (*S*)-**7daa** by using propargylamine **18daa**.



Scheme 4. Mechanism for formation of (*R*)-allene by using chiral piperazines **4a**–**c**.

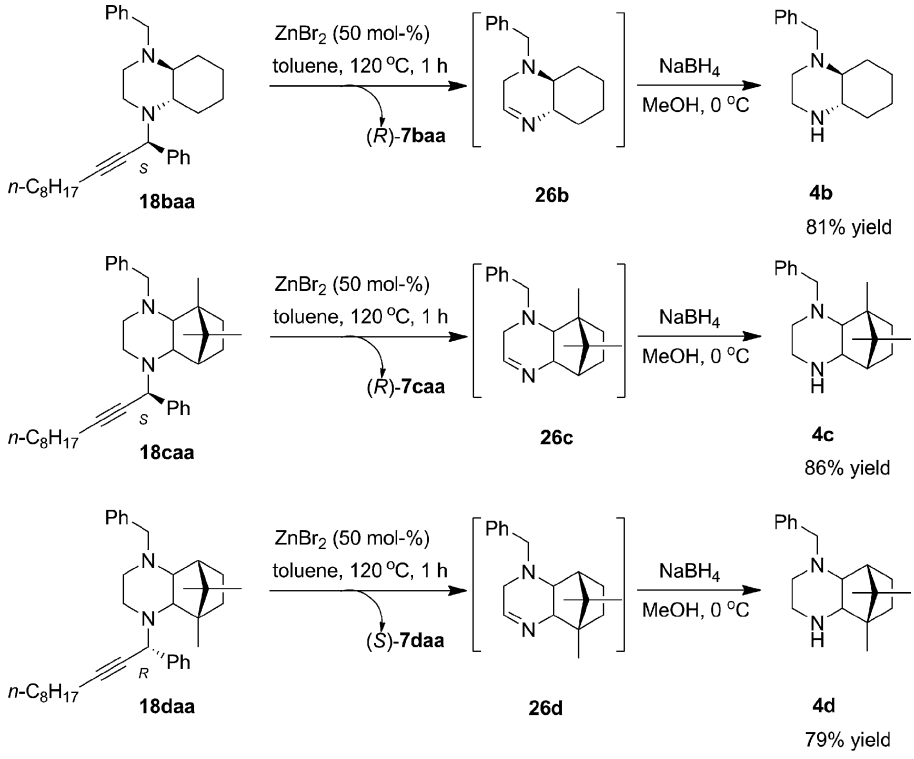
intermediate[14] **20** would react with the favored conformer **21B** of the iminium ion derived from aldehyde **6** and chiral piperazine to give selectively the corresponding propargylamine **23**.

The corresponding zinc bromide complex of **24** would then undergo intramolecular hydride shift from the piperazine skeleton to the acetylinic moiety, leading to the formation of alkenylzinc intermediate **25**. Subsequently, cleavage of the C–N bond in intermediate **25** releases the chiral allenes **7** and the imine byproduct **26**.

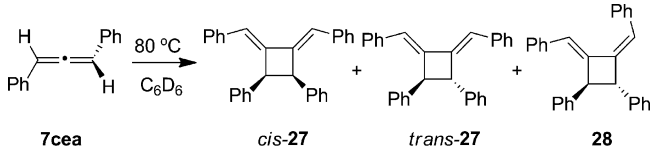
All the optically active allenes obtained by using chiral piperazine derivatives **4a**–**c** were levorotatory, from which the absolute configurations of the major enantiomer was assigned as *R* (Table 3), whereas the optically active allene **7daa** obtained with chiral *N*-benzylcamphanylpiperazine **4d** was dextrorotatory, from which the absolute configuration of the major enantiomer was assigned as *S* by the Lowe–Brewster rule and also by comparison with reported $[\alpha]_D^{25}$ values.[15] We have also found that imine byproducts **26b**–**d** could be easily converted in situ into the corresponding chiral piperazines **4b**–**d** in 79–86% yield by simple sodium borohydride mediated reduction (Scheme 5).

We have observed that the chiral allenes containing aryl substituents were not stable, and that they readily undergo cyclodimerization under neat ambient conditions. Previously, it was reported that the 1,3-diphenyl allene **7cea** undergoes dimerization at 80 °C in [D_6]benzene (Scheme 6).[16]

Surprisingly, we have observed that under neat conditions, 1,3-diphenyl allene **7cea** undergoes cyclodimerization even at 25 °C in 24 h. Thus, whereas the freshly prepared pure chiral allene **7cea** sample exhibits an $[\alpha]_D^{25}$ = –830 (*c* = 0.53, $CHCl_3$), the value becomes zero when the product was kept at 25 °C for 72 h. The ^{13}C NMR spectrum of the prod-



Scheme 5. In situ reduction of imine byproducts **26b**–**d**.



Scheme 6. Cyclodimerization of 1,3-diphenyl allene **7cea**.

uct mixture indicates the presence of the cyclodimerized products.[16e] We have also found that when freshly prepared pure chiral 1,3-diphenylallene **7cea** was stored in $CDCl_3$ solution, new signals corresponding to the cyclodimerized products started appearing in the ^{13}C NMR spectrum in 24 h at 25 °C.[17]

We have also observed that the aryl-alkyl-substituted allenes also undergo slow cyclodimerization to give a complex mixture of products under neat conditions at 25 °C within a week, as indicated by ^{13}C NMR spectroscopic analysis. Periodic analysis of optical rotations of chiral aryl-substituted allenes indicated that in 14 days the optical rotation values of the samples became zero. However, when the aryl-substituted allenes **7caa** or **7cac** were stored in hexane or $CDCl_3$ solutions, there was no change in the optical rotation values or ^{13}C NMR signals, even after 14 days. The mechanism of the facile cyclodimerization of aryl-substituted allenes under ambient conditions is not clearly understood at this stage. Previously, cyclodimerizations with some loss in optical activity were reported for chiral allenes at temperatures of more than 100 °C, and the reaction has been reported to go through a stepwise mechanism.[18]

Conclusions

We have developed a simple, practical, and very inexpensive method for the diastereoselective preparation of chiral propargylamines by using chiral piperazines **4a**–**d** and their enantioselective conversion into chiral allenes upon reaction with $ZnBr_2$. The surprisingly facile cyclodimerization reactions observed with aryl-substituted allenes illustrates the hidden difficulties in handling and storing of allenes.

Experimental Section

Synthesis of Chiral Amines 4b–d

***tert*-Butyl Octahydroquinoxaline-1-carboxylate (12):** To a solution of decahydroquinoxaline (1.40 g, 10.0 mmol) in CH_2Cl_2 (10 mL), di-*tert*-butyldicarbonate (2.2 mL, 10 mmol) was added at 0 °C slowly by using a syringe under an N_2 atmosphere. The reaction mixture was brought to room temperature slowly and further stirred for 6 h. Upon completion of the reaction (which was monitored by TLC), the solvent was evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel (100–200 mesh; hexane/EtOAc, 50:50) afforded **12** (1.82 g, 76%) as a colorless viscous liquid; R_f = 0.3 (silica gel; hexane/EtOAc, 50:50); $[a]_D^{25}$ = –74.29 (c = 0.52, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 3.51–3.47 (m, 2 H), 3.08–2.99 (m, 2 H), 2.98–2.93 (m, 1 H), 2.60 (dt, J = 10.8, 3.6 Hz, 1 H), 2.23–2.19 (d, J = 12.8 Hz, 1 H), 1.82–1.79 (d, J = 12.8 Hz, 1 H), 1.73–1.68 (t, J = 18.4 Hz, 2 H), 1.59–1.46 (m, 2 H), 1.43 (s, 9 H), 1.33–1.08 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.5, 79.4, 63.7, 56.2, 44.8, 41.2, 33.2, 30.3, 28.5, 25.3, 25.1 ppm. IR (neat): $\tilde{\nu}$ = 3320, 2969, 2931, 2854, 1693, 1457, 1413, 1369, 1249, 1150, 1095, 1013, 767 cm^{-1}.

HRMS (ESI): *m*/*z* calcd. for $C_{13}H_{24}N_2O_2$ [M + H^+] 240.1838; found 241.1917.

***tert*-Butyl 4-Benzyl-octahydroquinoxaline-1-carboxylate (13):** To a solution of **12** (1.50 g, 6.25 mmol) in acetonitrile (30 mL) was added benzyl bromide (0.83 mL,7 mmol), K_2CO_3 (1.79 g,13 mmol), and KI (0.498), and the mixture was stirred and heated to reflux for 12 h. After cooling to room temperature, the mixture was filtered to remove K_2CO_3 and the solvent was evaporated under reduced pressure. The residue was extracted with CH_2Cl_2 (2× 40 mL) and water (20 mL) and the combined organic extract was washed with brine (20 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (100–200 mesh; hexane/EtOAc, 50:50) to afford **13** (1.78 g, 86%) as a colorless liquid. We proceeded to next step without further purification of this product. R_f = 0.6 (silica gel; hexane/EtOAc, 50:50); $[\alpha]_D^{25}$ = –71.07 (*c* = 0.45, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.29–7.28 (d, *J* = 4.4 Hz, 4 H), 7.23–7.21 (m, 1 H), 4.01–3.98 (d, *J* = 13.2 Hz, 1 H), 3.63–3.57 (m, 1 H), 2.82–2.76 (m, 1 H), 2.45–2.40 (m, 1 H), 2.34–2.28 (m, 1 H), 2.21 (s, 2 H), 1.77–1.75 (d, *J* = 8.8 Hz, 3 H), 1.45 (s, 9 H), 1.32–1.27 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2, 139.4, 128.7, 128.1, 126.7, 79.2, 62.2, 61.9, 56.7, 51.8, 42.9, 30.7, 30.5, 28.5, 25.6, 25.2 ppm. IR (neat): $\tilde{\nu}$ = 3084, 3068, 3030, 2975, 2931, 2854, 2794, 1693, 1446, 1402, 1353, 1282, 1249, 1161, 1013, 849, 734, 695 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $C_{20}H_{30}N_2O_2$ [M + Na^+] 330.2307; found 353.2206.

1-Benzyl-decahydroquinoxaline (4b): To **13** (5.5 mmol 1.83 g) in 1,4-dioxane (20 mL), 6 M HCl (5 mL) was added slowly by using a syringe over 15 min under an N_2 atmosphere. The resulting mixture was stirred for 12 h at room temperature, then the solvent was evaporated and the residue was neutralized with 6 N NaOH solution and the organic layer was extracted with CH_2Cl_2. The combined organic extract was washed with brine (20 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by chromatography on basic alumina (100–200 mesh; hexane/EtOAc, 50:50) to obtain **4b** (1.16 g, 90%) as a colorless solid; R_f = 0.2 (silica gel; hexane/EtOAc, 50:50); m.p. 95–96 °C; $[\alpha]_D^{25}$ = –109.81 (*c* = 0.52, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.31–7.30 (d, *J* = 4.4 Hz, 4 H), 7.26 (s, 1 H), 4.13–4.10 (d, *J* = 13.2 Hz, 1 H), 3.16–3.12 (d, *J* = 13.2 Hz, 1 H), 2.94–2.84 (m, 2 H), 2.73–2.70 (d, *J* = 11.6 Hz, 1 H), 2.48–2.42 (m, 1 H), 2.27–2.23 (d, *J* = 13.2 Hz, 1 H), 2.12 (dt, *J* = 11.2, 4 Hz, 1 H), 1.87–1.78 (m, 2 H), 1.72–1.70 (d, *J* = 7.2 Hz, 2 H), 1.38–1.13 (m, 5 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.0, 129.1, 128.1, 126.7, 67.0, 60.4, 57.3, 53.7, 46.0, 32.8, 29.0, 25.2, 24.9 ppm. IR (KBr): $\tilde{\nu}$ = 3254, 3046, 3030, 2980, 2904, 2854, 2794, 1605, 1512, 1446, 1347, 1309, 1254, 1150, 1128, 1084, 1073, 1052, 1002, 827, 756 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $C_{15}H_{22}N_2$ [M + H^+] 230.1783; found 231.1861.

***tert*-Butyl 4-Benzyl-5,9,9-trimethyl-octahydro-5,8-methanoquinazoline-1-carboxylate (16):** To a solution of chiral camphanylpiperazine **14** (1.940 g, 10 mmol) in CH_2Cl_2 (100 mL), di-*tert*-butyldicarbonate (2.2 mL, 10 mmol) was added at 0 °C slowly (for 10 min) by using a syringe under an N_2 atmosphere. The reaction mixture was brought to room temperature slowly and further stirred for 6 h. Upon completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure. Purification of the residue by column chromatography on silica gel (100–200 mesh; hexane/EtOAc, 50:50) afforded *tert*-butyl 5,9,9-trimethyl-octahydro-5,8-methanoquinzoline-1-carboxylate **15** (2.941 g, 10 mmol) as a colorless viscous liquid. To a solution of **15** (2.941 g, 10 mmol) in anhydrous acetonitrile (30 mL) was added benzyl bromide (0.83 mL, 7 mmol), K_2CO_3 (1.79 g, 13 mmol), and KI (0.498 g), and the mixture was stirred and heated to reflux for 12 h. After cooling to room temperature, the mixture was filtered to remove K_2CO_3 and the solvent was evaporated under reduced pressure. The residue was extracted with CH_2Cl_2 (80 mL) and water (20 mL), and the combined organic extract was washed with brine (20 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography, to afforded **16** (3.148 g, 82%) as a colorless liquid; R_f = 0.7 (silica gel; hexane/EtOAc, 95:5); $[\alpha]_D^{25}$ = 21.61 (*c* = 0.70, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.39–7.25 (m, 5 H), 4.18–4.14 (d, *J* = 16.0 Hz, 1 H), 3.71–3.65 (m, 1 H), 3.32–3.25 (m, 2 H), 2.90–2.86 (d, *J* = 16.0 Hz, 1 H), 2.72–2.60 (m, 2 H), 2.05–2.03 (m, 1 H), 1.70 (s, 2 H), 1.48–1.45 (s, 9 H), 1.30 (s, 3 H), 1.16 (s, 2 H), 1.07 (s, 3 H), 0.84 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 156.5, 139.5, 128.3, 127.9, 126.8, 79.5, 72.4, 71.9, 63.2, 59.2, 53.6, 50.6, 50.0, 45.8, 43.1, 36.0, 28.5, 26.8, 22.3, 20.5, 20.2, 14.5 ppm. IR (neat): $\tilde{\nu}$ = 2953, 2887, 2814, 2781, 1691, 1602, 1477, 1452, 1371, 1294, 1232, 1174, 1143, 1109, 1080, 1032, 987 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $C_{24}H_{36}N_2O_2$ [M + H^+] 384.2777; found 385.2854.

1-Benzyl-5,9,9-trimethyl-decahydro-5,8-methanoquinazoline (4c): To a solution of **16** (3.072 g, 8.0 mmol) in 1,4-dioxane (20 mL), 6 M HCl (5 mL) was added slowly by using a syringe over 15 min under an N_2 atmosphere. The resulting mixture was stirred at room temperature for 12 h, then the solvent was evaporated and the residue was neutralized with 6 N NaOH solution. The organic layer was extracted with CH_2Cl_2 and the combined organic extract was washed with brine (20 mL) and dried with anhydrous Na_2SO_4. The solvent was evaporated and the residue was purified by column chromatography to afford the **4c** (2.090 g, 92%) as a yellow liquid; R_f = 0.4 (silica gel; hexane/EtOAc, 50:50); $[\alpha]_D^{25}$ = 11.15 (*c* = 0.44, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.36–7.23 (m, 3 H), 4.34–4.30 (d, *J* = 16.0 Hz, 1 H), 2.94–2.91 (m, 2 H), 2.80–2.74 (m, 2 H), 2.64–2.60 (m, 1 H), 2.25–2.23 (d, *J* = 8.0 Hz, 1 H), 1.82–1.78 (m, 2 H), 1.71–1.70 (d, *J* = 4.0 Hz, 1 H), 1.56 (s, 3 H), 1.46–1.44 (m, 1 H), 1.23–1.18 (m, 2 H), 1.09 (s, 3 H), 0.86 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 140.2, 128.4, 128.2, 128.1, 126.6, 76.2, 61.1, 61.0, 50.9, 50.4, 50.1, 47.4, 41.6, 37.0, 27.1, 22.3, 21.1, 15.5 ppm. IR (neat): $\tilde{\nu}$ = 3281, 3076, 2934, 1554, 1485, 1415, 1379, 1147, 1055, 808, 692 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{28}N_2$ [M + H^+] 284.2252; found 285.2329.

Phenyl-(5,9,9-trimethyl-octahydro-5,8-methanoquinazolin-1-yl)methanone (17): To a solution of chiral piperazine **14** (1.940 g, 10 mmol) and trimethylamine (1.36 mL, 10.0 mmol) in CH_2Cl_2 (100 mL), benzoyl chloride (1.270 mL, 10 mmol) was added at –78 °C slowly (for 30 min) by using a syringe under an N_2 atmosphere. The reaction mixture was brought to room temperature slowly and further stirred for 12 h. Upon completion of the reaction (monitored by TLC), the solvent was evaporated under reduced pressure and the residue was washed with $NaHCO_3$. Purification of the residue by column chromatography afforded **17** (2.771 g, 93%) as a brown solid. R_f = 0.6 (silica gel; hexane/EtOAc, 60:40); $[\alpha]_D^{25}$ = 38.67 (*c* = 0.60, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.38–7.28 (m, 5 H), 4.02–3.98 (q, *J* = 16.0 Hz, 1 H), 3.80–3.78 (d, *J* = 12.0 Hz, 1 H), 3.50–3.45 (t, *J* = 20.0 Hz, 1 H), 3.08–3.06 (d, *J* = 8.0 Hz, 2 H), 2.82–2.79 (d, *J* = 12.0 Hz, 1 H), 2.57–2.48 (m, 2 H),1.92 (s, 1 H), 1.47–1.45 (t, *J* = 12.0 Hz, 1 H), 1.20 (s, 4 H), 1.10–1.04 (m, 2 H), 0.84 (s, 3 H), 0.74 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 173.0, 137.2, 131.7, 129.6, 128.2, 127.9, 127.1, 66.2, 60.2, 58.4, 51.2, 48.6, 48.0, 45.8, 42.9, 35.4, 26.5, 21.8, 20.8, 14.1, 11.4 ppm. IR (KBr): $\tilde{\nu}$ = 3314, 3079, 3062, 3024, 2947, 2887, 2739, 1610, 1577, 1445, 1402, 1237, 1160, 1122, 1023, 793 cm^{-1}. HRMS (ESI): *m*/*z* calcd. for $C_{19}H_{26}N_2O$ [M + H^+] 298.2045; found 299.2123.

1-Benzyl-5,9,9-trimethyl-decahydro-5,8-methanoquinazoline (4d): To a suspension of $NaBH_4$ (1.9 g, 50 mmol) in THF (50 mL) was added a solution of I_2 (6.32 g, 25 mmol) in THF (40 mL) at 0 °C under an N_2 atmosphere over 30 min. Imide **17** (2.98 g, 10 mmol) was added to the generated diborane and the mixture was heated to reflux for 24–36 h. The reaction was brought to room temperature and quenched with methanol. The solvents were evaporated and the residue was heated to reflux with 10 N KOH for 6 h. The mixture was extracted with CH_2Cl_2 (2 × 30 mL) and the combined organic extract was evaporated to obtain decahydroquinazoline **4d**. The crude amine **4d** was purified by chromatography to give **4d** (2.215 g, 78%) as a yellow liquid; R_f = 0.4 (silica gel; hexane/EtOAc, 50:50); $[\alpha]_D^{25}$ = 18.94 (c = 0.46, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.31–7.24 (m, 3 H), 4.19–4.16 (d, J = 12.0 Hz, 1 H), 3.03–3.01 (m, 1 H), 2.91–2.88 (d, J = 12.0 Hz, 1 H), 2.69–2.63 (m, 2 H), 2.11–2.06 (m, 2 H), 1.76 (m, 1 H), 1.64–1.58 (m, 1 H), 1.54 (s, 3 H), 1.26 (s, 2 H), 0.95 (s, 3 H), 0.85 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 139.2, 128.8, 128.1, 126.8, 97.0, 59.2, 48.8, 48.1, 47.1, 46.6, 41.6, 36.4, 29.7, 26.5, 22.6, 20.7, 12.1 ppm. IR (neat): $\tilde{\nu}$ = 3377, 3030, 2955, 2879, 2802, 2752, 2687, 2310, 1653, 1604, 1483, 1452, 1388, 1265, 1143, 1109, 1072, 1010, 895 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{19}H_{28}N_2$ [M + H$^+$] 284.2252; found 285.2331.

General Procedure for the Preparation of Chiral Propargylamines: To a 25 mL reaction flask was added $ZnCl_2$ (0.014 g, 10 mol-%), chiral piperazine **4a–d** (1 mmol), 1-alkyne **5** (1.1 mmol), and aldehyde **6** (1 mmol) in toluene (3 mL), and the mixture was heated to 100 °C for the given time. The reaction mixture was the brought to room temperature and, after evaporation of the toluene, the residue was purified by chromatography on silica gel (100–200 mesh; hexane/ethyl acetate) to obtain the chiral propargylamines **18**.

1-Benzyl-2,3-diphenyl-4-(1-phenylundec-2-ynyl)piperazine (18aaa): Yield: 0.532 g (96%); colorless liquid; R_f = 0.9 (silica gel; hexane/EtOAc, 99:1); $[\alpha]_D^{25}$ = –22.28 (c = 0.40, $CHCl_3$). ^{1}H NMR(400 MHz, $CDCl_3$): δ = 7.83 (s, 1 H), 7.59–7.57 (d, J = 7.4 Hz, 2 H), 7.37–7.21 (m, 10 H), 7.15–7.11 (m, 5 H), 6.92 (s, 1 H), 6.52 (s, 1 H), 4.52 (s, 1 H), 3.77–3.72 (m, 2 H), 3.44–3.41 (d, J = 9.0 Hz, 1 H), 2.90–2.86 (d, J = 13.4 Hz, 2 H), 2.78–2.73 (t, J = 23.1 Hz, 1 H), 2.45–2.38 (m, 3 H), 2.32–2.26 (t, J = 22.7 Hz, 1 H), 1.69–1.58 (m, 4 H), 1.40–1.35 (m, 8 H), 0.91–0.94 (t, J = 13.1 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 144.2, 140.4, 129.4, 129.1, 128.4, 128.1, 127.9, 126.4, 125.4, 124.8, 122.9, 88.5, 75.1, 73.0, 65.8, 63.5, 57.9, 50.6, 50.2, 48.2, 47.2, 42.9, 36.4, 34.6, 31.8, 31.6, 29.3, 29.1, 29.0, 28.9, 26.2, 25.2, 22.2, 21.0, 18.7, 14.1, 13.8 ppm. IR (neat): $\tilde{\nu}$ = 3084, 3062, 3029, 2953, 2925, 2854, 2799, 1604, 1489, 1451, 1330, 1270, 1111, 1073, 1029, 914, 859, 766 cm^{-1}. HRMS (ESI): m/z calcd. for $C_{40}H_{46}N_2$ [M + H$^+$] 554.3661; found 555.3740. The data for the propargylamine derivatives are given in the Supporting Information.

General Procedure for the Synthesis of Chiral Allenes from Chiral Propargylamines 18: Chiral propargylamine (1 mmol) was added to a stirred suspension of $ZnBr_2$ (0.113 g, 0.5 mmol) in anhydrous toluene (3 mL) and the mixture was heated for 1–2 h at 120 °C under a nitrogen atmosphere. The mixture was brought to room temperature and toluene was removed under reduced pressure. The crude product was purified on silica gel (100–200 mesh; hexane) to isolate the chiral allenes **7**. The spectroscopic data (see the Supporting Information) are consistent with reported data.[10a] The optical rotation values reported are for freshly prepared samples (see the Supporting Information). Details on the variation of optical rotation values for aryl-substituted allenes and the NMR spectroscopic data for mixtures of cyclodimerized products formed from aryl-substituted allenes are given in the Supporting Information (Tables SI-1 to SI-3).

X-ray Crystallography: X-ray reflections (for **18aej**) were collected with an Oxford CCD X-ray diffractometer (Yarnton, Oxford, UK) equipped with a Cu-K_α radiation (λ = 1.5406 Å) source. Data reduction was performed using the CrysAlisPro 171.33.55 software. The crystal structure was solved and refined by using Olex2-1.0 with anisotropic displacement parameters for non-H atoms. Hydrogen atoms were experimentally located through the Fourier difference electron density map. All C–H atoms were geometrically fixed by using the HFIX command in the SHELX-TL program of Bruker-AXS. A check of the final CIF file by using PLATON did not show any missed symmetry. CCDC-1008592 (for **18aej**), contains the crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Chiral HPLC analysis data, ^{1}H and ^{13}C NMR spectra for all new compounds.

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