Diastereoselective Synthesis of Tetrasubstituted Propargylamines via Hydroamination and Metalation of 1-Alkynes and Their Enantioselective Conversion to Trisubstituted Chiral Allenes

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S Supporting Information

ABSTRACT: Reaction of cyclic secondary amines with 1alkynes and copper(I) chloride at 110–120 °C gives the corresponding alkynylcopper complex, which adds to the iminium ion intermediate formed in situ by hydroamination of 1-alkynes to give the corresponding propargylamine derivatives in up to 94% yield and 99% regioselectivity. The diastereomerically pure chiral propargylamines were obtained in 23–89% yield using optically active 2-benzyl morpholine and *N*-methyl camphanyl piperazine. These chiral propargylamines are readily converted to the corresponding trisub-



stitued chiral allenes in 71–89% yields with up to 99% ee upon reaction with $ZnBr_2$ at 120 °C. The results are discussed considering mechanisms involving diastereoselective addition of alkynylcopper complex formed in situ to iminium ions formed in situ regioselectively to produce the corresponding propargylamines, which in turn give the chiral allenes with very high enantioselectivity via an intramolecular 1,5-hydrogen shift in the presence of zinc bromide.

INTRODUCTION

In recent years, there have been several reports on the hydroamination of alkynes.¹ For example, it has been reported that $Zn(OTf)_2$ promotes hydroamination of 1-alkynes using amines to give ketimine or keteminium intermediates, which upon reduction, give trisubstituted amines.² Metal salts like ZnX_2 and CuX also promote metalation of 1-alkynes to produce alkynyl metal intermediates, which could add to the keteiminium intermediates.³ Accordingly, we have envisaged the generation of iminium ions and alkynylmetal intermediates⁴ in situ for the synthesis of chiral propargylamines, which in turn could be converted to trisubstituted chiral allenes. Herein, we describe the results of detailed studies on the synthesis of tetrasubstituted chiral propargylamines and trisubstituted chiral allenes from 1-alkynes (Scheme 1).

RESULTS AND DISCUSSION

Initially, we carried out experiments using 1-decyne and morpholine for the reaction with $ZnCl_2$ or $ZnBr_2$ at 120 °C. Propargylamine 7aa was not formed under these conditions (entries 1 and 2, Table 1), but it was formed in 15% yield in 24 h (entry 3, Table 1) when ZnI_2 was used and in 27% yield when $Zn(OTf)_2$ was used (entry 4, Table 1)

Interestingly, when the reaction was carried out using $Zn(OTf)_2$ without using toluene at 120 °C, propargylamine 7aa was formed in 69% yield within 2 h (entry 5, Table 1). Further screening led to the observation that the cheaper CuCl plays the same role, affording 7aa in 83% yield (entry 8, Table

1). Propargylamine 7aa was also obtained in similar yields using other copper halides like CuBr and CuI under this reaction condition along with allene byproduct (entry 11, Table 1). The reaction temperature was also found to be crucial for this transformation. Elevating the temperature above 110 °C led to formation of more amounts of the trisubstituted allene 8a (entry 9, Table 1), whereas lowering the temperature to 100 °C resulted in lower yields of the propargylamine product 7aa (entry 12, Table 1). However, experiments carried out at different temperatures and time interval conditions to obtain the trisubstituted allene 8a as major product in a single-pot operation were not successful. The copper(II) salts CuX₂ (Cl or Br) are not effective, but Cu(OTf)₂ affords product 7aa in 92% yield within 0.5 h at 100 °C (entry 12 and 13, Table 1). Although the use $Cu(OTf)_2$ gave better results, we have explored the scope of the reaction using CuCl (Table 1, entries 6 and 8) as it is less expensive. The results are summarized in Table 2.

The reaction of morpholine and other 1-alkynes like 1octyne **2b** and 1-heptyne **2c** gave the corresponding tetrasubstituted propargylamines 7**ab** and 7**ac** in 73–79% yields. The 1-alkynes, such as 3-cyclohexyl-1-propyne (2**d**), 2cyclohexyl-1-acetylene (2**e**), and 4-phenyl-1-butyne (2**g**), furnished the corresponding products in up to 85% yield. The functionalized alkynes like 6-cyano-1-hexyne (2**j**), 1-

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Table 1. Reaction of Morpholine 1a and 1-Decyne 2a with Different Metal Salts to Produce Tetrasubstituted Propargylamine $7aa^a$



^{*a*}The reactions were carried out using morpholine 1a (1.0 mmol) and 1-decyne 2a (2.2 mmol). ^{*b*}Allene 8a was formed in 7–12% yields as determined by ¹H NMR spectral analysis of the crude reaction mixture.

methoxy-10-decyne (2k), and 1-*tert*-butyldimethylsilyloxy-5-hexyne (2l) afforded the corresponding propargylamines in 74–81% (7aj), 69–73% (7ak), and 62–69% (7al) yields, respectively.

When the reaction was carried out with phenylacetylene 2f and morpholine 1a in solvent-free conditions at 110 °C, tetrasubstituted propargylamine 7af was obtained in 29% along with some unidentified products, but the reaction in toluene solvent resulted in only a mixture of unidentified products being formed, and amine 7af was not obtained. We have also observed that the reaction of 1-decyne 2a with different cyclic amine derivatives (1b-1f) led to the corresponding tetrasubstituted propargylamines 7ba-7fa in 72-83% yields.

It was of interest to us to examine whether the hydroamination reaction under these conditions would give the corresponding chiral propargylamines with diastereoselectivity if enantiomerically pure chiral amines are used. Accordingly, we have examined the use of different readily accessible optically active chiral secondary amines 1g-11 (Figure 1).⁵

The chiral amines **1g**, **1h**, and **1k** failed to give the corresponding propargylamines under these conditions, presumably due to the sterically crowded nature of these amines. The relatively less hindered chiral amine **1i** did give the corresponding tetrasubstituted propargylamine **7ia** in 45% yield

along with the trisubstituted propargylamine 9ia in 37% yield in the reaction using CuCl in toluene at 120 °C (Scheme 2). When the reaction was carried out without using toluene, better selectivity was realized as the tetrasubstituted propargylamine 7ia was obtained in 79% yield along with the trisubstituted propargylamine 9ia (11% yield) (Scheme 2, eq-1). The reaction using the chiral morpholine derivative 1j in toluene gave the diastereomerically pure tetrasubstituted propargylamine 7ja in 76% yield, and the other diastereomer was not obtained (Scheme 2, eq-2). Slightly higher yield (87%) was realized in the experiment without using toluene. Whereas the optically active N-methyl camphanyl piperazine 11 gave an unidentified mixture of products in toluene, the diastereomerically pure chiral propargylamine 7la was obtained in 68% yield under solvent-free conditions. The presence of the other diastereomers in the product could not be detected by ¹H and ¹³C NMR spectral analysis, but in this experiment, ketone **10a** was obtained as a side product in 14% yield (Scheme 2, eq-3).

We have carried out several experiments using the chiral morpholine 1j with different alkynes, and the results are summarized in Table 3. The reactions using 1-alkyne 2b and 2c gave the corresponding propargylamines in 64–86% yield. The reaction is also applicable to substituted aliphatic 1-alkynes as illustrated by reactions using the alkynes 2d, 2e, 2g, 2h, and 2i.

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"The reactions were carried out by using amine (1.0 mmol) and 1-alkyne (2.2 mmol) in toluene (3 mL) at 120 °C for 6 h. "The reactions were carried out by using amine (1.0 mmol) and 1-alkyne (2.2 mmol) at 110 °C for 0.5 h.



Figure 1. Chiral amines (1g-1l) used in CuCl-catalyzed chiral propargylamine synthesis.

The corresponding propargylamines were obtained in 59–83% yields in these experiments. Similarly, the 1-alkynes **2***j*, **2***k*, and **2***l* also gave the corresponding diastereomerically pure propargylamines with reasonable to good yields.

The configurations at the newly formed stereogenic centers were assigned as (S) on the basis of X-ray single crystal structure analysis of propargylamine 7jf (Figure S2).

We have observed that the chiral propargylamines 7ja-7jkreact with ZnBr₂ at 120 °C to give the corresponding allenes





Table 3. Synthesis of Chiral Propargylamine 7 Using 1-Alkyne 2 and the Chiral Amine 1j Using CuCl



^{*a*}The reactions were carried out using amines (1.0 mmol) and 1-alkyne (2.2 mmol) in toluene (3 mL) at 120 °C for 6 h. ^{*b*}The reactions were carried out using amines (1.0 mmol) and 1-alkyne (2.2 mmol) at 110 °C for 0.5 h. ^{*c*}In all reactions, the propargylamine derivatives 7 were obtained in diastereomerically pure form, and the other diastereomer could not be detected by ¹H NMR or ¹³C NMR spectral data.





^{*a*}The reactions were carried out using propargylamine (1 mmol), which was obtained from chiral morpholine 1j in toluene (3 mL) with $ZnBr_2$ (0.5 mmol) at 120 °C. Yield of allenes. The ee was determined by chiral HPLC analysis.

8a–8k in 68–89% yields (Table 4). The propargylamines having functionalized groups also afforded the chiral allenes **8**j and **8k** in 68–71% yields with up to 99% ee. All propargylamines are converted to the corresponding chiral allenes **8** within 1–3 h under these reaction conditions (Table 4). All of the optically active allenes obtained using chiral amines **1j** are levorotatory. Hence, the absolute configurations of the major enantiomer of the chiral allenes are assigned as *R* based on the Lowe–Brewster rule^{6a,b} and the Taff^{6c} and Runge^{6d,e} polarizabilty parameters expected for the substituents in these allenes.^{6f}

In recent years, several enantiomerically enriched chiral trisubstituted allenes were reported, but their configurations were assigned based only on reaction mechanisms without even considering the Lowe-Brewster rule. Hence, it is desirable to briefly discuss the assignment of configuration for the enantiomerically enriched trisubstituted allenes considering the Lowe-Brewster rule. The chiral allenes may be considered to have the structures with substituents A and B at one allene end and groups X and Y at the other allene end, as depicted in Figure 2. In the Lowe model,^{6a} the group with highest polarity A is placed at the top [Figure 2, structure (a)] and the other group B is also placed above the plane with the X and Y groups placed in the sides below the plane. The Lowe rule predicts the allene to be levorotatory with $(-)[\alpha]_D$ if the polarizability of the group X > Y and the allene to be dextrorotatory with $(+)[\alpha]_{D}$ if the polarizability is Y > X. For disubstitued chiral allenes, the Cahn–Ingold–Prelog (CIP) priority rules will be in the order A > B (B=H), X > Y (Y=H). Hence, the disubstitued allene with (R) configuration will have $(-)[\alpha]_{D}$, and the corresponding enantiomer will have $(+)[\alpha]_{\rm D}$ value with (*S*) configuration. This will also be the case for enantiomerically enriched trisubstituted allenes 8a-8k [A (A=Ph or alkyl) > B $(B=CH_3)$, X (X= Ph or alkyl) > Y (Y=H) reported here, where the expected Lowe-Brewster polarizability order and the CIP priority order are the same as in disubstituted allenes. Hence, the enantiomerically enriched trisubstituted allene derivatives 8a-8k with $(-)[\alpha]_{\rm D}$ values are assigned to the



Figure 2. Configuration of allenes and sign of $[\alpha]_D$ values based on Brewster–Lowe–Taft–Runge polarizability order and Cahn–Ingold–Prelog (CIP) priority rules.

(*R*) configuration. Therefore, the (*R*)-(+) configuration reported for the enantiomerically enriched chiral allene with same substituents as in 8f (Ph, CH₃ and Ph, H) but with $[\alpha]_D$ +122.4 should be corrected as (*S*)-(+).^{6h} Presumably, the (*R*)-(+) configuration was assigned erroneously in the earlier report^{6h} by comparison with incorrect drawing of the allene structure (substituents Ph, *n*-Bu and Ph, H) with $[\alpha]_D$ +251 for which the original authors did not assign the configuration.^{6g}

An interesting possibility is that a group may have higher priority as per the CIP rules but may not have the highest polarizability [Figure 2, structure (b)]. In such cases, the allene with (*R*) configuration will give $(+)[\alpha]_D$ and its (*S*) enantiomer will give $(-)[\alpha]_D$ values as per the Lowe–Brewster rule. There are several reports assigning (*R*)-(+) and (*S*)-(-) configurations for trisubstituted allenes based on reaction mechanisms,^{7a–d} but in these reports, the Lowe–Brewster and Taft– Runge polarizability and the CIP priority order for the substituents were not considered while assigning configuraScheme 3. Tentative Mechanism for the Formation of Chiral Propargylamines Using Chiral Amine 7j and Their Conversion to Chiral Allenes



tions, and the assigned configurations were also not confirmed by X-ray structure analysis or NMR spectral analysis with chiral solvating agents as was done in some other cases.^{7e,f} Such ambiguity is also expected in assigning configurations for tetrasubstituted chiral allenes.^{7g} Needless to say, because the Lowe–Brewster rule is based on the sign of optical rotation, this method of assigning configuration may not be reliable if the magnitude of the $[\alpha]_D$ value is small. In this regard, it may be of interest to note that an interesting spontaneous resolution of tetrasubstituted allenic phosphinate derivatives was reported recently, and the enantiomers were characterized by X-ray structure analysis but the samples did not have significant $[\alpha]_D$.^{7h} Presumably, the differences in polarizability of substituents are small in these cases.

The CuCl-catalyzed formation of propargylamines 7la-7lland their conversion to chiral allenes by $ZnBr_2$ -promoted transformation can be explained by the tentative mechanism and intermediates outlined in Scheme 3. Initially, chiral amine 1 would react with CuCl to form complex 15.⁸ Then, its reaction with 1-alkyne would give intermediate complex 17, which could react with the intermediate 14a formed in situ via hydroamination of alkyne through the intermediates 11, 12a, and 16 (Scheme 3).⁴ Delivery of the alkynyl group from the bottom face of the ketiminium ion species would lead to the new (*S*)stereogenic center at propargylamine product 19 (Figure S1) that could complex with $ZnBr_2$ to give intermediate 20, which after an intramolecular hydride shift and addition of H and ZnBr group across the triple bond would give intermediate **21** that after elimination of ZnBr₂ and imine **22** would afford chiral allene (*R*)-**8** (Scheme 3).^{5,9} An important aspect of this tentative mechanism for the ZnBr₂-promoted conversion of propargylamine **19** to allene (*R*)-**8** is the interaction of the morpholine oxygen with the ZnBr₂ moiety during the transformation (Scheme 3). Although there is no direct evidence for this mechanism, previously only poor selectivity was realized in the chiral disubstituted allene synthesis from enantiomerically pure propargylamines obtained using 1-alkyne, benzaldehyde, and simple chiral 2-phenyl pyrrolidine system where there is no additional oxygen or nitrogen coordination site available.^{5a}

Enantiomerically pure chiral camphanyl propargylamine derivatives of 71 are also readily prepared in 68–89% yields from the corresponding camphanyl amine 11 under solvent-free conditions (Table 5).

Unfortunately, these propargylamine derivatives 7la-7ll failed to crystallize, but the configurations of the newly formed stereocenters were assigned as (*S*) based on their conversion to the chiral (*R*) allenes as the mechanism of formation of enantiomerically enriched trisubstituted chiral allenes (Scheme 4) is expected to be same as the mechanism for conversion of tetrasubstituted morpholinyl propargylamine derivatives (Scheme 3). The chiral propargylamines 7la-7ll react with ZnBr₂ at 120 °C to give the corresponding allenes 8a-8l in 68-90% yield at 120 °C (Table 6). The propargylamines

Table 5. Synthesis of Chiral Propargylamine 7 Using 1-Alkyne 2 and the Chiral Amine 11 Using CuCl^a



^aThe reactions were carried out using amines (1.0 mmol) and 1-alkyne (2.2 mmol) at 110 $^{\circ}$ C for 0.5 h. In all reactions, the propargylamine derivatives 7 were obtained in diastereomerically pure forms, and the other diastereomer could not be detected by ¹H NMR or ¹³C NMR spectral data. ^bYield of propargylamines.

having functionalized groups also afforded the chiral allenes **8a–8l** and in 68–90% yields with up to 99% ee. It was also found that all propargylamines are converted to the corresponding chiral allenes 8 within 1–3 h under these reaction conditions (Table 6). All the optically active allenes obtained using chiral amines 11 are levorotatory from which the absolute configurations of the major enantiomers of the chiral allenes are assigned as R by the Lowe–Brewster rule considering the Taft–Runge polarizability order expected for the substituents in these allene derivatives (Figure 2).⁶

We have also found that the imine byproducts 22 and 34 could be easily reduced before workup to the starting chiral secondary amines 1j or 1l in 62-72% yields by adding sodium borohydride in methanol at -20 °C and bringing the contents to 25 °C and stirring for 2 h.

CONCLUSIONS

We have developed a convenient method for the synthesis of tetrasubstituted propargylamine derivatives via the CuClcatalyzed hydroamination of 1-alkynes using the achiral amine derivatives. In addition, we have devised a method for the diastereoselective synthesis of chiral propargylamine derivatives using chiral amines. Furthermore, we have converted these chiral propargylamine derivatives to trisubstituted chiral allenes in high enantiomeric purities using zinc bromide. Therefore, the methods described herein have considerable potential for further synthetic applications.

EXPERIMENTAL SECTION

General Procedure for the Synthesis of Tetrasubstituted Propargylamines 7 from 1-Alkyne and Amines 1 with CuCl in **Solvent Conditions.** To a stirred suspension of amines 1 (1 mmol) were added CuCl (0.020 g, 0.2 mmol) and 1-alkyne 2 (2.2 mmol) in toluene (3 mL) at 25 °C under N_2 atmosphere. The contents were stirred at 120 °C for 6 h. The reaction mixture was cooled to room temperature. Toluene was removed using reduced pressure. Water (5 mL) and DCM (15 mL) were added. The DCM layer was washed with saturated NaCl solution, dried (Na₂SO₄), and concentrated. The residue was subjected to column chromatography using hexane and ethyl acetate (90:10) as eluent to isolate propargyl amines 7.

General Procedure for the Synthesis of Tetrasubstituted Propargylamines 7 from 1-Alkyne and Amine 1 with CuCl in Solvent-Free Conditions. To a stirred suspension of amines 1 (1 mmol) were added CuCl (0.010 g, 0.1 mmol) and 1-alkyne 2 (2.2 mmol) in sealed tube at 25 °C under N₂ atmosphere. The contents were stirred at 110 °C for 0.5 h. The reaction mixture was cooled to room temperature. Water (5 mL) and DCM (15 mL) were added. The DCM layer was washed with saturated NaCl solution, dried (Na₂SO₄), and concentrated. The residue was subjected to column chromatography using hexane and ethyl acetate (90:10) as eluent to isolate propargylamines 7.

4-(9-Methylnonadec-10-yn-9-yl)morpholine (**7aa**). Using toluene as solvent (Table 2): 0.290 g, 80% yield. Under solvent-free conditions (Table 2): 0.301 g, 83% yield. Colorless oil; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 3029, 2947, 2854, 1599, 1495, 1451, 1391, 1352, 1128 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.70 (t, J = 4.0 Hz, 4H), 2.59–2.57 (m, 4H), 2.17 (t, J = 8.0 Hz, 2H), 1.48–1.39 (m, 4H), 1.38–1.23 (m, 25H), 0.87 (t, J = 8.0 Hz, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.5, 81.6, 67.4, 57.5, 47.0, 39.3, 31.8, 30.0, 29.5, 29.3, 29.2, 29.1, 29.0, 28.8, 24.0, 23.7, 22.6, 18.6, 14.0; LCMS m/z 364 [M + 1]; anal. calcd for C₂₄H₄₅NO C 79.27, H 12.47, N 3.85; found C 79.35, H 12.41, N 3.91.

4-(7-Methylpentadec-8-yn-7-yl)morpholine (**7ab**). Using toluene as solvent (Table 2): 0.224 g, 73% yield. Under solvent-free conditions (Table 2): 0.230 g, 75% yield. Colorless oil; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 2953, 2916, 2845, 2820, 1435, 1118, 945,

Scheme 4. Tentative Mechanism for the Formation of Chiral Propargylamines Using Chiral Amines 71 and Their Conversion to Chiral Allenes



cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.02 (t, *J* = 8.0 Hz, 4H), 2.48 (t, *J* = 8.0 Hz, 2H), 2.22–2.15 (m, 4H), 1.66–1.55 (m, 6H), 1.39 (s, 3H), 1.26–1.17 (m, 5H), 1.09–0.98 (m, 3H), 0.90–0.88 (m, 7H), 0.79–0.77 (m, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.4, 81.5, 67.4, 57.4, 47.0, 39.3, 31.8, 31.3, 29.0, 28.5, 23.9, 23.7, 22.6, 22.5, 18.5, 14.0; LCMS *m*/*z* 307 [M + 1]; anal. calcd for C₂₀H₃₇NO C 78.11, H 12.13, N 4.55; found C 78.23, H 12.06, N 4.48.

4-(6-Methyltridec-7-yn-6-yl)morpholine (7ac). Using toluene as solvent (Table 2): 0.214 g, 77% yield. Under solvent-free conditions (Table 2): 0.220 g, 79% yield. Yellow oil; $R_f = 0.7$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 2953, 2926, 2854, 1698, 1600, 1501, 1452, 1323, 1156, 838 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.75–3.73 (m, 4H), 2.67–2.58 (m, 4H), 2.20 (t, J = 8.0 Hz, 2H), 1.61–1.28 (m, 14H), 1.27 (s, 3H), 1.00–0.83 (m, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.4, 81.5, 67.4, 57.4, 47.0, 39.3, 32.2, 31.0, 28.8, 23.7, 23.6, 22.5, 22.1, 18.5, 14.0, 13.9; LCMS m/z 280 [M + 1]; anal. calcd for C₁₈H₃₃NO C 77.36, H 11.90, N 5.01; found C 77.23, H 11.82, N 5.12.

4-(1,5-Dicyclohexyl-2-methylpent-3-yn-2-yl)morpholine (**7ad**). Using toluene as solvent (Table 2): 0.261 g, 79% yield. Under solvent-free conditions (Table 2): 0.271 g, 82% yield. Brown liquid; R_f = 0.6 (silica gel, 90:10 hexane/EtOAc); IR (neat) 2949, 2855, 2357, 2341, 1452, 1359, 1326, 1274, 1119, 1071, 1032 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.74 (t, J = 4.0 Hz, 4H), 2.66–2.61 (m, 4H), 2.22 (d, J = 4.0 Hz, 2H), 2.06–1.99 (m, 3H), 1.89–1.77 (m, 6H), 1.72–1.68 (m, 3H), 1.66–1.58 (m, 8H), 1.57–1.51 (m, 5H), 1.31 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.0, 81.8, 67.5, 57.6, 47.2, 45.2, 39.3, 36.3, 34.6, 34.4, 32.0, 25.3, 24.9, 24.5; LCMS m/z 332 [M + 1]; anal. calcd for C₂₂H₃₇NO C 79.70, H 11.2, N 4.22; found C 79.58, H 11.31, N 4.28.

4-(2,4-Dicyclohexylbut-3-yn-2-yl)morpholine (7ae). Using toluene as solvent (Table 2): 0.221 g, 73% yield. Under solvent-free conditions (Table 2): 0.239 g, 79% yield. Brown liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 2934, 2853, 2354, 2333, 1440, 1268, 1251, 1004, 792 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.72 (t, J = 4.0 Hz, 4H), 2.59 (q, J = 4.0 Hz, 2H), 2.17 (t, J = 8.0 Hz, 4H), 1.57–1.47 (m, 7H), 1.26–1.21 (m, 11H), 0.89–0.86 (m, 5H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.5, 81.5, 67.4, 57.4, 47.0, 39.3, 31.9, 30.0, 29.6, 29.3, 29.1, 28.8, 24.0, 23.7, 22.7, 18.6, 14.1; LCMS m/z 304 [M + 1]; anal. calcd for C₂₀H₃₃NO C 79.15, H 10.96, N 4.62; found C 79.23, H 10.85, N 4.56.

4-(2,4-Diphenylbut-3-yn-2-yl)morpholine (**7af**). Under solvent-free conditions (Table 2): 0.084 g, 29% yield. Brown liquid; $R_f = 0.6$ (silica gel, 95:5 hexane/EtOAc); IR (neat) 3068, 3024, 2954, 2870, 2810, 1498, 1456, 1396, 1254, 1122 1100, 1073, 1023 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.86–7.82 (m,2H), 7.62–7.59 (m,2H), 7.42–7.32 (m, 6H), 3.80–3.77 (m, 4H), 2.88–2.75 (m, 2H), 2.64–2.50 (m, 2H), 1.73 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 144.8, 131.8, 128.3, 128.2, 128.1, 127.2, 126.6, 123.1, 88.2, 67.4, 63.4, 48.0, 30.5;





^{*a*}The reactions were carried out by using propargylamine (1 mmol) which obtained from chiral amine 1l in toluene (3 mL) with $ZnBr_2$ (0.5 mmol) at 120 °C. ^{*b*}Yield of allenes. The ee was determined by chiral HPLC analysis. ^{*c*}The ee could not be determined by chiral HPLC as the AD-H, AS-H, OB-H, OD-H, and OJ-H columns available to us failed to separate the enantiomers of 8l.

LCMS m/z 292 [M + 1]; anal. calcd for C₂₀H₂₁NO C 82.44, H 7.26, N 4.81; found C 82.28, H 7.31, N 4.73.

4-(3-Methyl-1,7-diphenylhept-4-yn-3-yl)morpholine (**7ag**). Using toluene as solvent (Table 2): 0.284 g, 82% yield. Under solvent-free conditions (Table 2): 0.295 g, 85% yield. Brown liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 3084, 3057, 3030, 2958, 2931, 2860, 1715, 1649, 1600, 1490, 1452, 1260, 1128, 1013 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.18 (m, 10H), 3.74 (t, J = 4.0 Hz, 4H), 2.87 (t, J = 8.0 Hz, 2H), 2.73 (t, J = 8.0 Hz, 2H), 2.64–2.55 (m, 6H), 1.92–1.88 (m, 2H), 1.35 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 142.5, 140.7, 128.5, 128.3, 126.2, 125.7, 84.1, 82.2, 67.4, 57.4, 46.9, 41.1, 35.4, 30.5, 23.4, 20.7; LCMS m/z 349 [M + 1]; anal. calcd for C₂₄H₂₉NO C 82.95, H 8.41, N 4.03; found C 82.84, H 8.47, N 4.07.

4-(4-Methyl-1,9-diphenylnon-5-yn-4-yl)morpholine (**7ah**). Using toluene as solvent (Table 2): 0.316 g, 84% yield. Under solvent-free conditions (Table 2): 0.307 g, 82% yield. Brown liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 2944, 2845, 1733, 1623, 1485, 1435, 1271, 935, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.28 (m, SH), 7.22–7.19 (m, SH), 3.73 (t, J = 4.0 Hz 4H), 2.66–2.62 (m, 6H), 2.25 (t, J = 8.0 Hz, 2H), 1.80–1.73 (m, 3H), 1.64–1.56 (m, SH), 1.27 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 142.6, 142.4, 128.3, 128.2, 125.7, 125.6, 84.2, 81.7, 67.4, 57.4, 47.0, 39.1, 35.8, 35.3, 31.8, 30.5, 28.6, 23.8, 23.6, 18.4; LCMS m/z 376 [M + 1]; anal. calcd for C₂₆H₃₃NO C 83.15, H 8.86, N 3.73; found C 83.05, H 8.81, N 3.68.

4-(5-Methyl-1,11-diphenylundec-6-yn-5-yl)morpholine (7ai). Using toluene as solvent (Table 2): 0.326 g, 81% yield. Under solvent-free conditions (Table 2): 0.313 g, 83% yield. Brown liquid; R_f = 0.6 (silica gel, 90:10 hexane/EtOAc); IR (neat) 3057, 3024, 2926, 2854, 1484, 1441, 1380, 1326, 1254, 1123, 1024, 964 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.28 (m, 5H), 7.22–7.19 (m, 5H), 3.73 (t, *J* = 4.0 Hz, 4H), 2.67–2.57 (m, 8H), 2.25 (t, *J* = 8.0 Hz, 2H), 1.76 (q, *J* = 8.0 Hz, 4H), 1.66–1.53 (m, 6H), 1.27 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 142.6, 142.4, 128.3, 128.2, 125.7, 125.6, 84.2, 81.7, 67.4, 57.4, 47.0, 39.1, 35.8, 35.3, 31.8, 30.5, 28.6, 23.8, 23.6, 18.4; LCMS *m/z* 402 [M-1]; anal. calcd for C₂₈H₃₇NO C 83.33, H 9.24, N 3.47; found C 83.15, H 9.32, N 3.41.

7-Methyl-7-morpholinoundec-5-ynedinitrile (7aj). Using toluene as solvent (Table 2): 0.202 g, 74% yield. Under solvent-free conditions (Table 2): 0.221 g, 81% yield. Brown liquid; $R_f = 0.5$ (silica gel, 70:30

hexane/EtOAc); IR (neat) 2942, 2857, 2363, 2242, 1714, 1666, 1454, 1425, 1283, 1115 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.73–3.71 (m, 4H), 2.58–2.57 (m, 4H), 2.51–2.47 (m, 2H), 2.43–2.37 (m, 4H), 1.89–1.84 (m, 2H), 1.80–1.76 (m, 4H), 1.29 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 119.6, 119.1, 82.8, 82.2, 67.2, 60.3, 56.9, 47.0, 38.0, 24.7, 23.6, 21.0, 20.1, 17.1, 16.2, 14.1; LCMS *m*/*z* 274 [M + 1]; anal. calcd for C₁₆H₂₃N₃O C 70.30, H 8.48, N 15.37; found C 70.21, H 8.41, N 15.26.

4-(1,19-Dimethoxy-9-methylnonadec-10-yn-9-yl)morpholine (**7ak**). Using toluene as solvent (Table 2): 0.291 g, 69% yield. Under solvent-free conditions (Table 2): 0.308 g, 73% yield. Brown liquid; R_f = 0.6 (silica gel, 85:15 hexane/EtOAc); IR (neat) 2926, 2853, 2363, 1708, 1456, 1383, 1273, 1118, 964, 863, 724 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 371 (t, *J* = 4.0 Hz 4H), 3.35 (t, *J* = 8.0 Hz, 4H), 3.31 (s, 6H), 2.58–2.57 (m, 4H), 2.1 (t,*J* = 8.0 Hz, 2H), 1.59–1.53 (m, 10H), 1.38–1.29 (m, 16H), 1.23 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.4, 81.5, 72.9, 67.4, 58.5, 57.4, 47.0, 39.3, 29.9, 29.6, 29.5, 29.4, 29.1, 29.0, 28.7, 26.1, 26.0, 23.9, 23.8, 18.5; LCMS *m/z* 424 [M + 1]; anal. calcd for C₂₆H₄₉NO₃ C 73.71, H 11.66, N 3.31; found C 73.65, H 11.61, N 3.36.

4-(2,2,3,3,9,17,17,18,18-Nonamethyl-4,16-dioxa-3,17-disilanonadec-10-yn-9-yl)morpholine (**7a**l). Using toluene as solvent (Table 2): 0.316 g, 62% yield. Under solvent-free conditions (Table 2): 0.352 g, 69% yield. Brown liquid; $R_f = 0.6$ (silica gel, 95:5 hexane/EtOAc); IR (neat) 2920, 2854, 2356, 1720, 1643, 1457, 1172 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.69 (t, J = 4.0 Hz, 4H), 3.61 (t, J = 8.0 Hz, 4H), 2.60–2.56 (m, 4H), 2.19 (t, J = 8.0 Hz, 2H), 1.63–1.47 (m, 10H), 1.24 (s, 3H), 0.89 (s, 18H), 0.03 (s, 12H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.3, 81.6, 67.4, 63.0, 62.7, 57.3, 47.0, 39.1, 33.1, 32.0, 25.9, 25.6, 23.8, 20.2, 18.4, 18.3, -5.2; LCMS m/z 512 [M + 1]; anal. calcd for C₂₈H₅₇NO₃Si₂ C 65.69, H 11.22, N 2.74; found C 65.58, H 11.06, N 2.81.

1-(9-Methylnonadec-10-yn-9-yl)piperidine (**7ba**). Using toluene as solvent (Table 2): 0.277 g, 77% yield. Under solvent-free conditions (Table 2): 0.292 g, 81% yield. Yellow oil; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 3040, 2958, 2931, 2860, 1709, 1687, 1605, 1452, 1216, 1172 1024, 854 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.70–2.59 (m, 4H), 2.20 (t, J = 8.0 Hz, 2H), 1.78–1.58 (m, 6H), 1.49–1.29 (m, 29H), 0.90 (t, J = 8.0 Hz, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 83.6, 82.7, 57.8, 47.5, 39.7, 31.9, 31.8, 30.1, 29.5, 29.3,

29.2, 29.1, 29.0, 28.8, 26.6, 24.8, 24.2, 24.0, 22.6, 18.6, 14.0; LCMS m/z 362 [M + 1]; anal. calcd for C₂₅H₄₇N C 83.03, H 13.10, N 3.87; found C 82.91, H 13.15, N 3.81.

1-Methyl-4-(9-methylnonadec-10-yn-9-yl)piperazine (**7ca**). Using toluene as solvent (Table 2): 0.274 g, 73% yield. Under solvent-free conditions (Table 2): 0.300 g, 80% yield. Yellow oil; $R_f = 0.7$ (silica gel, 85:15 hexane/EtOAc); IR (neat) 3063, 2926, 2854, 2800, 2756, 1495, 1245, 1391, 1205, 1128, 1030, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 2.79–2.42 (m, 8H), 2.29 (s, 3H), 2.18 (t, J = 8.0 Hz, 3H), 1.58–1.39 (m, 9H), 1.35–1.28 (m, 19H), 0.90 (s, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 84.2, 81.9, 57.2, 55.7, 46.3, 45.9, 39.6, 31.9, 31.8, 30.0, 29.5, 29.3, 29.2, 29.1, 29.0, 28.8, 24.1, 23.9, 22.6, 18.6, 14.0; LCMS m/z 377 [M + 1]; anal. calcd for C₂₅H₄₈N₂ C 79.72, H 12.84, N 7.44; found C 79.62, H 12.76, N 7.51.

1-(9-Methylnonadec-10-yn-9-yl)-4-phenylpiperazine (**7da**). Using toluene as solvent (Table 2): 0.315 g, 72% yield. Under solvent-free conditions (Table 2): 0.337 g, 77% yield. Yellow oil; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); IR (neat) 3062, 3013, 2953, 2925, 2876, 2837, 1665, 1626, 1478, 1391, 1369, 1237, 1117, 1034, 1056 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.27 (m, 2H), 6.98–6.87 (m, 3H), 3.24 (t, J = 8.0 Hz, 4H), 2.84–2.79 (m, 4H), 2.22 (t, J = 8.0 Hz, 4H), 1.67–1.65 (m, 3H), 1.54–1.38 (m, 9H), 1.34–1.29 (m, 15H), 0.93–0.90; ¹³C{1H} NMR (100 MHz, CDCl₃) δ 151.4, 129.0, 119.4, 115.8, 84.4, 81.8, 57.3, 49.5, 46.5, 43.8, 39.6, 31.9, 31.8, 30.1, 29.6, 29.3, 29.2, 29.1, 28.8, 24.1, 24.0, 23.8, 22.6, 18.6, 14.1; LCMS *m/z* 439 [M + 1]; anal. calcd for C₃₀H₅₀N₂ C 82.13, H 11.49, N 6.39; found C 82.21, H 11.36, N 6.45.

1-Benzyl-4-(9-methylnonadec-10-yn-9-yl)piperazine (**7ea**). Using toluene as solvent (Table 2): 0.357 g, 79% yield. Under solvent-free conditions (Table 2): 0.339 g, 75% yield. Yellow oil; $R_f = 0.7$ (silica gel, 95:5 hexane/EtOAc); IR (neat) 3024, 2953, 2854, 1604, 1583, 1489, 1451, 1325, 1259, 1128, 1051, 728 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.35–7.28 (m, SH), 3.5 (s, 2H), 2.70–2.53 (m, 8H), 2.19 (t, J = 8.0 Hz, 2H), 1.58–1.52 (m, 2H), 1.51–1.49 (m, 3H), 1.43–1.41 (m, SH), 1.40–1.30 (m, 16H), 1.28 (s, 3H), 0.90 (t, J = 8.0 Hz, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 138.2, 129.2, 128.1, 126.9, 84.1, 82.2, 63.0, 57.3, 53.6, 46.4, 39.6, 31.9, 31.8, 30.0, 29.5, 29.3, 29.2, 29.1, 28.8, 24.2, 23.9, 22.6. 18.6, 14.0; LCMS m/z 451 [M – 1]; anal. calcd for C₃₁H₅₂N₂ C 82.24, H 11.58, N 6.19; found C 82.15, H 11.48, N 6.27.

1-(9-Methylnonadec-10-yn-9-yl)piperidin-3-ol (**7fa**). Using toluene as solvent (Table 2): 0.294 g, 78% yield. Under solvent-free conditions (Table 2): 0.312 g, 83% yield. Yellow oil; $R_f = 0.7$ (silica gel, 70:30 hexane/EtOAc); IR (neat) 3342, 2953, 2926, 2854, 1704, 1676, 1621, 1320, 1172, 1128, 1063, cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.81(brs, 1H), 2.73–2.35 (m, 6H), 2.16 (t, J = 8.0 Hz, 2H), 1.77–1.75 (m, 1H), 1.57–1.55 (m, 5H), 1.49–1.45 (m, 2H) 1.41–1.37 (m, 4H), 1.33–1.23 (m, 20H), 0.87 (t, J = 8.0 Hz, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 83.8, 82.3, 66.5, 57.3, 57.1, 54.0, 53.8, 47.2, 46.8, 39.8, 39.7, 32.0, 31.8, 30.0, 29.0, 28.8, 24.2, 24.0, 23.9, 22.6, 22.0, 18.5, 14.0; LCMS m/z 378 [M + 1]; anal. calcd for C₂₅H₄₇NO C 79.51, H 12.54, N 3.71; found C 79.45, H 12.48, N 3.78.

1-(((5)-1-((5)-9-methylnonadec-10-yn-9-yl)pyrrolidin-2-yl)methyl)piperidine (**7ia**). Using toluene as solvent: 0.199 g, 45% yield. Under solvent-free conditions (Table 2): 0.350 g, 79% yield. Brown oil; R_f = 0.6 (silica gel, 90:10 hexane/EtOAc); IR (neat) 2931, 2849, 2213, 1704, 1665, 1457, 1369, 1326, 1205, 1150, 1101, 1063, 991, 904, 734 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.30–3.25 (m, 2H), 2.94–2.92 (m, 2H), 2.72–2.54 (m,6H), 2.29–2.16 (m, 12H), 1.88 (d, *J* = 8.0 Hz, 2H), 1.75–1.70 (m,4H), 1.63–1.54 (m, 8H), 1.49–1.46 (m, 4H), 1.41–1.36 (m, 7H), 1.29 (s, 3H), 0.91–0.86 (m, 6H); ¹³C-{1H}NMR (100 MHz, CDCl₃) δ 82.7, 82.6, 66.6, 58.8, 56.7, 55.3, 50.0, 41.4, 31.8, 31.3, 29.7, 29.5, 29.1, 28.4, 27.1, 25.8, 24.4, 24.1, 22.6, 18.6; LCMS *m/z* 445 [M + 1]; anal. calcd for C₃₀H₅₆NO C 81.01, H 12.0, N 6.30; found C 81.12, H 12.61, N 6.21.

(S)-3-Benzyl-4-((S)-9-methylnonadec-10-yn-9-yl)morpholine (**7***ja*). Using toluene as solvent (Table 3): 0.344 g, 76% yield. Under solvent-free conditions (Table 3): 0.394 g, 87% yield. Brown liquid; R_f = 0.8 (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -45.5 (c 0.62, CHCl₃); IR (neat) 3023, 2953, 2928, 2853, 2195,1601, 1495, 1455, 1366, 1274, 1120, 1079, 949, 894, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.28 (m, 3H), 7.25–7.21 (m, 2H), 3.93 (d, *J* = 8.0 Hz 2H), 3.63 (t, *J* = 8.0 Hz 2H), 3.40–3.10 (m, 2H), 2.59 (d, *J* = 12.0 Hz, 2H), 2.22–2.19 (m, 1H), 1.66–1.53 (m, 6H), 1.50 (s, 3H), 1.42–1.30 (m, 10H), 0.95–0.88 (m, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 141.0, 129.4, 128.3, 125.6, 84.9, 83.8, 68.4, 68.0, 57.0, 55.9, 41.0, 40.1, 31.9, 31.8, 30.3, 30.1, 29.6, 29.3, 29.2, 29.1, 29.0, 28.9, 27.0, 24.2, 22.6, 18.7, 14.1, 14.0; LCMS *m/z* 454 [M + 1]; anal. calcd for C₃₁H₅₁NO C 82.06, H 11.33, N 3.09; found C 82.16, H 11.26, N 3.15.

(*S*)-3-Benzyl-4-((*S*)-7-methylpentadec-8-yn-7-yl)morpholine (*7jb*). Using toluene as solvent (Table 3): 0.321 g, 81% yield. Under solvent free conditions (Table 3): 0.341 g, 86% yield. Brown liquid; $R_f = 0.8$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -41.5 (*c* 0.69, CHCl₃); IR (neat) 3020, 2953, 2927, 2853, 2033, 1606, 1495, 1364, 1276, 1120, 1077, 955, 843, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31–7.17 (m, SH), 3.95–3.37 (m, 2H), 3.23–3.10 (m, 2H), 2.65–2.42 (m, 3H), 2.22 (t, *J* = 8.0 Hz, 2H), 1.52–1.39 (m, 8H), 1.37–1.30 (m, 2H), 0.91–0.86 (m, 6H), 1.48 (s, 3H), 1.31–1.28 (m, 13H), 0.92–0.88 (m, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 140.9, 129.4, 128.4, 125.7, 84.6, 84.1, 68.5, 68.0, 56.8, 55.3, 41.7, 41.4, 31.9, 31.3, 30.0, 29.6, 29.0, 28.6, 24.5, 23.7, 22.7, 22.6, 18.7, 14.1, 14.0; LCMS *m*/*z* 398 [M – 1]; anal. calcd for C₂₇H₄₃NO C 81.55, H 10.90, N 3.52; found C 81.46, H 10.82, N 3.48.

(5)-3-Benzyl-4-((S)-6-methyltridec-7-yn-6-yl)morpholine (**7***jc*). Using toluene as solvent (Table 3): Yield: 0.287g, 78% Under solvent-free conditions (Table 3): 0.313 g, 85% yield. Brown liquid; R_f = 0.8 (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -39.5(*c* 0.36, CHCl₃); IR (neat) 3023, 2955, 2928, 2854, 2150,1601, 1455, 1366, 1273, 1120, 1079, 1029, 949, 802, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33–7.21 (m, 5H), 3.96–3.60 (m, 3H), 3.41–3.09 (m, 5H), 2.60–2.20 (m, 3H), 1.69–1.55 (m, 4H), 1.50 (s,H), 1.46–1.29 (m, 10H), 0.95–0.88 (m, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 140.9, 129.4, 128.4, 125.7, 84.7, 84.1, 68.5, 68.0, 56.8, 55.3, 41.7, 41.4, 32.1, 31.1, 30.0, 28.7, 24.5, 23.5, 22.7, 22.2, 18.7, 14.1, 14.0; LCMS *m/z* 368 [M – 1]; anal. calcd for C₂₅H₃₉NO C 81.24, H 10.64, N 3.79; found C 81.14, H 10.56, N 3.86.

(*S*)-3-Benzyl-4-((*S*)-2,4-dicyclohexylbut-3-yn-2-yl)morpholine (*Tje*). Using toluene as solvent (Table 3): 0.282 g, 72% yield. Under solvent-free conditions (Table 3): 0.310 g, 79% yield. Brown liquid; R_f = 0.8 (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -37.1 (*c* 0.56, CHCl₃); IR (neat) 2925, 2864, 1995, 1655, 1495, 1344, 1276, 1120, 1078, 1022, 974, 801, 740 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.28 (m, 2H), 7.25–7.20 (m, 3H) 3.94 (d, *J* = 8.0 Hz, 2H), 3.61 (t, *J* = 12.0 Hz, 2H), 3.42–3.13 (m, 2H), 2.60 (d, *J* = 8.0 Hz, 2H), 2.37–2.36 (m, 1H), 2.28–2.26 (m, 1H), 2.11–2.10 (m, 4H), 1.81–1.79 (m, 7H), 1.69–1.65 (m, SH), 1.53 (s, 3H), 1.29–1.26 (m, SH); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 141.2, 129.4, 128.4, 125.6, 89.3, 83.6, 68.6, 68.1, 58.6, 56.8, 45.0, 40.9, 33.1, 33.0, 29.3, 29.1, 27.4, 27.1, 26.3, 25.9, 24.8,19.4; LCMS *m*/z 394 [M + 1]; anal. calcd for C₂₇H₃₉NO C 82.39, H 9.99, N 3.56; found C 82.45, H 9.91, N 3.61.

(*S*)-*3*-*Benzyl*-*4*-((*S*)-*2*,4-*diphenylbut*-*3*-*yn*-*2*-*yl*)*morpholine* (*7jf*). Under solvent-free conditions (Table 3): Yield: 0.087g, 23%. Brown liquid; $R_f = 0.8$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25} - 35.8$ (*c* 0.74, CHCl₃); IR (neat) 3023, 2954, 2850, 2055, 1683, 1597, 1488, 1370, 1277, 1171, 1069, 975, 841, 755 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.89–7.87 (m, 3H), 7.56–7.54 (m, 2H), 7.39–7.32 (m, 10H), 3.82–3.76 (m, 2H), 3.65–3.62 (m, 2H), 3.41–3.35 (m, 2H), 2.64–2.52 (m, 1H), 2.21 (d, *J* = 8 Hz, 2H), 1.85 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 146.8, 140.6, 131.5, 129.5, 128.5, 128.3, 128.2, 128.1, 127.1, 126.3, 125.9, 123.2, 91.6, 87.9, 68.7, 67.8, 61.5, 56.8, 42.9, 30.5, 30.3; LCMS *m*/*z* 380 [M – 1]; anal. calcd for C₂₇H₂₇NO C 85.00, H 7.13, N 3.67; found C 85.12, H 7.18, N 3.75.

(S)-3-Benzyl-4-((S)-4-methyl-1,9-diphenylnon-5-yn-4-yl)morpholine (**7jh**). Using toluene as solvent (Table 3): 0.330 g, 71% yield. Under solvent-free conditions (Table 3): 0.385 g, 83% yield. Brown liquid; $R_f = 0.8$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -41.3 (c 0.59, CHCl₃); IR (neat) 3024, 2944, 2852, 1954, 1663, 1495, 1370, 1274, 1119,1080, 950, 834, 741 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.36–7.30 (m, 7H), 7.28–7.24 (m, 8H), 3.95 (d, J = 4.0 Hz 2H), 3.65 (d, J = 4.0 Hz 2H), 3.43–3.39 (m, 2H), 2.79–2.75 (m, 2H), 2.71– 2.66 (m, 2H), 2.54–2.51 (m, 2H), 2.29–2.25 (m, 3H), 1.90–1.79 (m, 6H), 1.55 (s, 3H); $^{13}C{1H}$ NMR (100 MHz, CDCl₃) δ 142.5, 141.7, 140.8, 129.4, 128.5, 128.4, 128.3, 125.8,125.7, 84.6, 84.2, 68.5, 67.9, 56.8, 55.2, 41.4, 41.1, 36.0, 34.9, 30.7, 30.1, 25.6, 24.6, 18.2; LCMS *m*/*z* 466 [M + 1]; anal. calcd for C₃₃H₃₉NO C 85.11, H 8.44, N 3.01; found C 85.03, H 8.49, N 3.18.

(S)-7-((S)-3-Benzylmorpholino)-7-methylundec-5-ynedinitrile (**7***jj*). Using toluene as solvent (Table 3): 0.250 g, 69% yield. Under solvent-free conditions (Table 3): 0.261 g, 72% yield. Brown liquid; R_f = 0.6 (silica gel, 60:40 hexane/EtOAc); $[\alpha]_D^{25}$ -37.9 (c 0.51, CHCl₃); IR (neat) 2956, 2854, 2244, 1601, 1454, 1274, 1173, 1081, 1029, 950, 866, 735 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.29 (m, 2H), 7.28-7.23 (m, 3H), 3.94 (d, *J* = 8.0 Hz 2H), 3.61 (t, *J* = 12.0 Hz, 2H), 3.25-3.21 (m, 2H), 2.55-2.50 (m, 7H), 2.19-2.11 (m, 2H), 1.94-1.87 (m, 6H), 1.43 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 140.1, 129.3, 128.5, 126.0, 119.6, 118.9, 85.2, 82.4, 68.4, 67.7, 56.7, 54.8, 41.4, 40.3, 29.9, 24.7, 24.3, 20.0, 17.9, 17.3, 16.3; LCMS *m*/*z* 364 [M + 1]; anal. calcd for C₂₃H₂₉N₃O C 76.00, H 8.04, N 11.56; found C 76.15, H 8.12, N 11.65.

(*S*)-3-Benzyl-4-((*S*)-1,19-dimethoxy-9-methylnonadec-10-yn-9yl)morpholine (**7**jk). Using toluene as solvent (Table 3): 0.425 g, 83% yield. Under solvent-free conditions (Table 3): 0.456 g, 89% yield. Brown liquid; $R_f = 0.8$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -29.3 (*c* 0.47, CHCl₃); IR (neat) 2925, 2852, 2201, 1718, 1658, 1455, 1356, 1274, 1173, 1029, 973, 843, 741 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.17 (m, 5H), 3.92 (d, *J* = 4.0 Hz, 2H), 3.59 (t, *J* = 8.0, 2H), 3.38–3.35 (m, 2H), 3.33 (s, 3H), 3.32 (s, 3H), 3.21–3.05 (m, 4H), 2.55 (d, *J* = 12.0 Hz, 2H), 2.43–2.39 (m, 1H), 2.18 (t, *J* = 8.0, 2H), 1.58–1.50 (m, 10H), 1.46 (s, 3H), 1.30–1.27 (m, 16H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 140.9, 129.3, 128.3, 125.7, 84.6, 84.1, 72.9, 72.8, 68.5, 68.0, 58.5, 56.8, 55.2, 43.7, 41.7, 41.3, 29.9, 29.8, 29.6, 29.5, 29.4, 29.3, 29.2, 29.0, 28.9, 28.8, 26.1, 26.0, 24.5, 23.8, 18.6; LCMS *m*/ *z* 514 [M + 1]; anal. calcd for C₃₃H₅₅NO₃ C 77.14, H 10.79, N 2.73; found C 77.26, H 10.72, N 2.71.

(4aS,5R,8S,8aR)-4,5,9,9-Tetramethyl-1-((S)-9-methylnonadec-10yn-9-yl)decahydro-5,8-methanoquinoxaline (7la). Under solventfree conditions (Table 5): 0.329 g, 68% yield. Yellow liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -32.1 (c 0.42, CHCl₃); IR (neat) 2953, 2925, 2854, 2794, 1462, 1385, 1259, 1150, 1084, 1023, 855, 799, 710 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.09–2.95 (m, 2H), 2.49–2.40 (m, 4H), 2.27–2.21 (m, 4H), 2.14 (s, 3H), 1.64–1.51 (m, 8H), 1.31–1.24 (m, 20H), 1.19 (s, 3H), 0.99 (s, 3H), 0.90–0.87 (m, 10H), 0.79 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 85.2, 81.1, 62.1, 60.1, 55.4, 55.1, 49.2, 49.0, 46.3, 44.1, 41.4, 36.9, 31.9, 31.8, 30.0, 29.6, 29.3, 29.1, 28.8, 27.2, 25.7, 23.8, 22.6, 22.0, 20.3, 18.6, 14.4, 14.1; LCMS m/z 486 [M + 2]; anal. calcd for C₃₃H₆₀N₂ C 81.75, H 12.47, N 5.78; found C 81.62, H 12.36, N 5.71.

(4aS,5R,8S,8aR)-4,5,9,9-Tetramethyl-1-((S)-7-methylpentadec-8-yn-7-yl)decahydro-5,8-methanoquinoxaline (**7lb**). Under solvent-free conditions (Table 5): 0.273 g, 64% yield. Yellow liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -48.8 (c 0.13, CHCl₃); IR (neat) 2964, 2926, 2854, 2810, 1457, 1375, 1271, 1128, 958, 931, 860, 830, 750, 706 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.08–2.99 (m, 2H), 2.52–2.47 (d, J = 4.0 Hz, 1H), 2.25–2.16 (m, 7H), 1.73–1.49 (m, 8H), 1.30–1.26 (m, 17H), 1.17 (s, 3H), 1.12–1.07 (m, 1H), 0.99 (s, 3H), 0.90–0.88 (m, 7H), 0.78 (s, 3H); ¹³C{1H}NMR (100 MHz, CDCl₃) δ 85.2, 81.1, 77.3, 62.1, 60.2, 55.4, 55.1, 49.2, 49.0, 46.3, 44.1, 41.4, 36.9, 31.8, 31.4, 29.6, 29.0, 28.5, 27.2, 25.7, 23.7, 22.6, 22.1, 20.3, 18.7, 14.4, 14.1; LCMS m/z 428 [M+]; anal. calcd for C₂₉H₅₂N₂ C 81.24, H 12.22, N 6.53; found C 81.06, H 12.15, N 6.45.

(4aS,5R,8S,8aR)-1-((S)-1,5-Dicyclohexyl-2-methylpent-3-yn-2-yl)-4,5,9,9-tetramethyldecahydro-5,8-methanoquinoxaline (7ld). Under solvent-free conditions (Table 5): 0.275 g, 61% yield. Yellow liquid; R_f = 0.6 (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -42.3 (*c* 0.39, CHCl₃); IR (neat) 2914, 2844, 2363, 1669, 1432, 1368, 1277, 1258, 1156, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.45 (t, *J* = 8.0 Hz, 1H), 2.89–2.82 (m, 2H), 2.75–2.70 (m, 1H), 2.58–2.53 (m, 1H), 2.26 (s, 3H), 2.12–2.08 (m, 5H), 1.80–1.64 (m, 15H), 1.54–1.40 (m, 5H), 1.25 (s, 3H), 1.18–1.04 (m, 10H), 0.99 (s, 3H), 0.77 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 82.9, 80.1, 78.7, 64.8, 54.7, 53.9, 50.0, 48.3, 47.4, 47.1, 41.8, 37.7, 37.4, 37.3, 34.2, 33.4, 33.2, 32.6, 31.2, 26.7, 26.5, 26.3, 26.2, 25.9, 22.1, 20.8, 14.6; LCMS m/z 452 [M + 2]; anal. calcd for $C_{31}H_{52}N_2$ C 82.24, H 11.58, N 6.19; found C 82.15, H 11.51, N 6.23.

(4aS, 5R,8S,8aR)-1-((S)-2,4-Dicyclohexylbut-3-yn-2-yl)-4,5,9,9-tetramethyldecahydro-5,8-methanoquinoxaline (**7le**). Under solvent-free conditions (Table 5): 0.250 g, 59% yield. Yellow liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ –39.3 (c 0.52, CHCl₃); IR (neat) 2922, 2850, 1447, 1388, 1366, 1341, 1314, 1259, 1117, 1021, 965, 889, 804, 766 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.04–3.00 (m, 2H), 2.20 (s, 5H), 2.12 (s, 1H), 1.92–1.86 (m, 3H), 1.80–1.64 (m, 2H), 1.59–1.55 (m, 2H), 1.48–1.42 (m, 6H), 1.16 (s, 4H), 1.11 (s, 5H), 1.09 (s, 2H), 0.97 (s, 3H), 0.76 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 85.6, 84.4, 77.4, 63.9, 61.8, 55.5, 55.2, 51.4, 49.2, 49.1, 46.3, 45.8, 43.7, 37.0, 33.2, 32.5, 29.6, 28.9, 28.4, 27.4, 27.1, 26.4, 26.0, 25.5, 24.7, 22.3, 22.0, 20.3, 14.4; LCMS m/z 425 [M + 1]; anal. calcd for C₂₉H₄₈N₂ C 82.01, H 11.39, N 6.60; found C 82.15, H 11.31, N 6.73.

(4aS,5R,8S,8aR)-4,5,9,9-Tetramethyl-1-((S)-3-methyl-1,7-diphenylhept-4-yn-3-yl)decahydro-5,8-methanoquinoxaline (7lg). Under solvent-free conditions (Table 5): 0.355 g, 76% yield. Yellow liquid; R_f = 0.6 (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -35.1 (c 0.39, CHCl₃); IR (neat) 3024, 2950, 2931, 2849, 1457, 1265, 1213, 1117, 1050, 915, 739, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.28 (m, 6H), 7.24–7.19 (m, 4H), 3.16–3.10 (t, J = 8.0 Hz, 3H), 3.06–2.91 (m, 2H), 2.88–2.77 (m, 2H), 2.74–2.61 (m, 2H), 2.56–2.46 (m, 3H), 2.27–2.18 (m, 4H), 2.14–1.76 (m, 4H),1.65–1.58 (m, 2H), 1.39 (s, 3H), 1.24 (s, 3H), 1.19–1.09 (m, 2H) 1.03 (s, 3H), 0.82 (m, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 143.0, 140.8, 128.5, 128.4, 128.3, 126.2, 125.5, 85.5, 80.7, 62.0, 60.1, 55.4, 55.0, 49.3, 49.0, 46.4, 44.1, 43.4, 36.9, 35.4, 30.4, 29.3, 27.1, 25.6, 22.0, 20.7, 20.4, 14.4; LCMS m/z 469 [M + 1]; anal. calcd for C₃₃H₄₄N₂ C 84.56, H 9.46, N 5.98; found C 84.48, H 9.36, N 5.91.

(4*aS*,*SR*,8*S*,8*aR*)-4,5,9,9-Tetramethyl-1-((S)-4-methyl-1,9-diphenylnon-5-yn-4-yl)decahydro-5,8-methanoquinoxaline (7*lh*). Under solvent-free conditions (Table 5): 0.372 g, 75% yield. Yellow liquid; *R*_f = 0.6 (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -41.8 (*c* 0.53, CHCl₃); IR (neat) 3057, 3018, 2953, 2962, 2832, 1665, 1621, 1473, 1445, 1385, 1232, 1160, 760 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.27 (m, SH), 7.24–7.19 (m, SH), 2.90–2.88 (m, 3H), 2.77 (t, *J* = 8.0 Hz, 2H), 2.62 (t, *J* = 8.0 Hz, 2H), 2.29–2.16 (m, 6H), 1.85–1.46 (m, 13H), 1.29 (s, 3H), 1.03 (s, 3H), 0.93 (s, 3H), 0.81 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 142.6, 141.8, 128.5, 128.5, 128.3, 128.2, 125.8, 125.6, 85.5, 80.8, 77.2, 62.1, 60.1, 55.3, 55.1, 49.2, 49.0, 46.3, 44.1, 40.9, 36.9, 36.1, 34.8, 30.7, 27.2, 25.7, 25.5, 22.0, 20.3, 18.1, 14.4; LCMS *m*/*z* 498 [M + 2]; anal. calcd for C₃₅H₄₈N₂ C 84.62, H 9.74, N 5.64; found C 84.56, H 9.71, N 5.58.

(4aS, 5*R*,8S,8aR)-*i*,5,9,9-Tetramethyl-1-((S)-4-methyl-1,10-diphenyldec-5-yn-4-yl)decahydro-5,8-methanoquinoxaline (**7li**). Under solvent-free conditions (Table 5): 0.413 g, 79% yield. Yellow liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -47.6 (*c* 0.56, CHCl₃); IR (neat) 3056, 3016, 2956, 2849, 1664, 1625, 1473, 1384, 1236, 1150, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32–7.21 (m, 10H), 2.92–2.81 (m, 4H), 2.66–2.52 (m, 5H), 2.34–2.26 (m, 8H), 1.79–1.70 (m, 7H), 1.36–1.29 (m, 12H), 1.04 (s, 3H), 0.81 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 142.4, 128.4, 128.3, 125.7, 84.8, 78.2, 75.1, 65.3, 54.5, 50.1, 47.7, 47.5, 47.1, 46.5, 43.5, 37.3, 35.4, 30.4, 29.7, 28.6, 26.3, 22.2, 20.5, 18.5, 14.9; LCMS *m*/*z* 525 [M + 1]; anal. calcd for C₃₇H₅₂N₂ C 84.68, H 9.99, N 5.34; found C 84.49, H 9.91, N 5.26.

(4aS, 5R, 8S, 8aR)-1-((S)-1, 19-Dimethoxy-9-methylnonadec-10-yn-9-yl)-4,5,9,9-tetramethyldecahydro-5,8-methanoquinoxaline (7lk). Under solvent-free conditions (Table 5): 0.424 g, 78% yield. Yellow liquid; $R_f = 0.6$ (silica gel, 90:10 hexane/EtOAc); $[\alpha]_D^{25}$ -48.6 (c 0.61, CHCl₃); IR (neat) 2925, 2951, 2854, 1451, 1391, 1265, 1122, 1030, 910, 854, 730, 701 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.39–3.36 (m, 4H), 3.34 (s, 6H), 3.08–3.00 (m, 3H), 2.23 (s, 4H), 2.20–2.15 (m, 3H), 1.59–1.55 (m, 7H), 1.51–1.46 (m, 4H), 1.34–1.27 (m, 22H), 1.18 (s, 3H), 1.12–1.08 (m, 2H), 0.99 (s, 3H), 0.79 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 85.2, 81.0, 77.1, 72.9, 62.1, 60.1,

58.5, 55.4, 55.1, 49.2, 49.0, 46.3, 44.1, 41.3, 36.9, 29.9, 29.6, 29.5, 29.4, 29.3, 29.1, 29.0, 28.8, 27.2, 26.1, 25.6, 23.7, 22.0, 20.3, 18.6, 14.4; LCMS m/z 546 [M + 2]; anal. calcd for $C_{35}H_{64}N_2O_2$ C 77.15, H 11.84, N 5.14; found C 77.31, H 11.76, N 5.23.

(4a5,5R,85,8aR)-4,5,9,9-Tetramethyl-1-((S)-2,2,3,3,9,17,17,18,18nonamethyl-4,16-dioxa-3,17-disilanonadec-10-yn-9-yl)decahydro-5,8-methanoquinoxaline (**7II**). Under solvent-free conditions (Table 5): 0.391 g, 62% yield. Yellow liquid; $R_f = 0.6$ (silica gel, 85:15 hexane/ EtOAc); $[\alpha]_D^{25}$ -31.9 (*c* 0.73, CHCl₃) IR (neat) 2947, 2931, 2851, 2859, 2788, 1467, 1396, 1254, 1106, 832, 782 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.64–3.61 (m, 4H), 3.08–2.96 (m, 2H), 2.53–2.45 (m, 1H), 2.23–2.14 (m, 6H), 1.73–1.46 (m, 11H), 1.43–1.34 (m, 2H), 1.28 (s, 5H), 1.18 (s, 3H), 1.12–1.07 (m, 2H), 0.99 (s, 3H), 0.90 (s, 18H), 0.78 (s, 3H), 0.06 (s, 12H); ¹³C{1H}NMR (100 MHz, CDCl₃) δ 85.2, 81.0, 63.3, 62.7, 62.1, 60.1, 55.4, 55.1, 49.2, 49.0, 46.3, 44.0, 41.3, 36.9, 33.2, 32.0, 29.6, 27.2, 25.9, 25.6, 25.5, 22.0, 20.3, 20.2, 18.5, 18.3, 14.4, -5.2; LCMS *m*/*z* 634 [M + 2]; anal. calcd for C₃₇H₇₂N₂O₂Si₂ C 70.09, H 11.46, N 4.42; found C 70.27, H 11.37, N 4.36.

General Procedure for the Preparation of Chiral Allenes from Propargylamines. The chiral propargylamines 7 (1 mmol) were added to a stirred suspension of $ZnBr_2$ (0.113 g, 50 mol %) in dry toluene (3 mL), and the contents were refluxed for 1–3 h at 120 °C under a nitrogen atmosphere. Toluene was removed under reduced pressure, and the crude product was purified with silica gel (100–200 mesh) column chromatography using hexane/ethyl acetate as eluent to isolate the chiral allenes 8.

(*R*)-9-Methylnonadeca-9,10-diene (**8a**). From chiral propargylamine 7ja: 0.239 g, 86% yield, 96% ee; $[\alpha]_D^{25}$ –99.9 (*c* 0.51, CHCl₃). From chiral propargylamine 7la: 0.247 g, 89% yield, 97% ee; $[\alpha]_D^{25}$ –101.5 (*c* 0.72, CHCl₃). Colorless liquid, R_f = 0.8 (silica gel, 100:0 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel Phenomenex cellulose-1, 100:0 hexanes/ i-PrOH; flow rate, 1.5 mL/min, 190 nm; retention times, 2.3 min (minor) and 3.5 min (major); IR (neat) 2958, 2926, 2854, 1961, 1468, 1380, 723 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.00 (s, 1H), 2.36 (s, 1H), 1.95–1.92 (m, 4H), 1.67–1.66 (t, *J* = 4.0 Hz, 3H), 1.40- 1.36 (m, 21H), 0.90–0.89 (m, 8H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 201.1, 99.1, 90.0, 34.1, 31.8, 31.7, 29.4, 29.3, 29.0, 28.8, 27.5, 22.7, 19.3, 14.1; LCMS *m*/*z* 279 [M + 1]; anal. calcd for C₂₀H₃₈ C 86.25, H 13.75; found C 86.42, H 13.71.

(-)-7-Methylpentadeca-7,8-diene (**8b**). From chiral propargylamine 7jb: 0.197 g, 89% yield, 90% ee; $[\alpha]_D^{25}$ –98.8 (c 0.42, CHCl₃). From chiral propargylamine 7lb: 0.200 g, 90% yield, 96% ee; $[\alpha]_D^{25}$ –121.8 (c 0.56, CHCl₃). Colorless liquid, R_f = 0.8 (silica gel, 100:1 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel OB-H, 90:10 hexanes/i-PrOH; flow rate, 0.3 mL/min, 190 nm; retention times, 10.3 min (major) and 13.3 min (minor); IR (neat) 2958, 2926, 2854, 1961, 1498, 1380, 723 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.00–4.97 (m, 1H), 1.99–1.91 (m, 4H), 1.68–1.58 (m, 3H), 1.44–1.31 (m, 16H), 0.93–0.89 (m, 6H); ¹³C{1H}NMR (100 MHz, CDCl₃) δ 201.1, 99.1, 90.0, 34.1, 31.8, 31.7, 29.7, 29.4, 29.3, 29.0, 28.8, 27.5, 22.7, 19.3, 14.1; LCMS *m*/*z* 223 [M + 1]; anal. calcd for C₁₆H₃₀ C 86.40, H 13.60; found C 86.28, H 13.51.

(*R*)-(2-Methylpenta-2,3-diene-1,5-diyl)dicyclohexane (**8**d). From chiral propargylamine 7ld: 0.209 g, 85% yield, 99% ee; $[\alpha]_D^{25}$ -91.1 (*c* 0.39, CHCl₃). Colorless liquid, $R_f = 0.9$ (silica gel, 100:0 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel OJ-H, 95:5 hexanes/i-PrOH; flow rate, 0.5 mL/min, 190 nm; retention times, 6.4 min (minor) and 8.1 min (major); IR (neat) 3059, 3030, 2923, 2853, 1965, 1605, 1495, 1454, 1263, 1074, 1019 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.90 (s, 1H), 1.86–1.80 (m, 3H), 1.71–1.63 (m, 10H), 1.4–1.18 (m, 10H), 0.89 (m, 6H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 202.3, 96.5, 87.6, 42.3, 38.1, 37.5, 35.7, 33.4, 33.3, 33.1, 26.6, 26.3, 19.4; LCMS *m/z* 247 [M + 1]; anal. calcd for C₁₈H₃₀ C 87.73, H 12.27; found C 87.63, H 12.21.

(*R*)-Buta-1,2-diene-1,3-diyldicyclohexane (**8e**). From chiral propargylamine 7je: 0.189 g, 87% yield, 99% ee; $[\alpha]_D^{25}$ -77.9 (*c* 0.42, CHCl₃). From chiral propargylamine 7le: 0.187 g, 85% yield, 99% ee; $[\alpha]_D^{25}$ -76.8 (*c* 0.59, CHCl₃). Colorless liquid, $R_f = 0.8$ (silica gel,

100:0 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel OJ-H, 95:5 hexanes/i-PrOH; flow rate, 0.5 mL/min, 190 nm; retention times, 6.4 min (major) and 8.2 min (minor); IR (neat) 2936, 2841, 2239, 1964, 1448, 1416, 1280, 1232, 840 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.02 (s, 1H), 1.90–1.67 (m, 12H), 1.26–1.22 (m, 9H), 1.14–1.00 (m, 4H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 199.2, 105.3, 96.9, 41.6, 37.7, 33.3, 32.1, 32.0, 26.5, 26.4, 26.3, 26.1, 17.8; LCMS *m*/*z* 219 [M + 1]; anal. calcd for C₁₆H₂₆ C 88.00, H 12.0; found C 87.91, H 12.06.

(*R*)-Buta-1,2-diene-1,3-diyldibenzene (**8**f). From chiral propargylamine 7jf: 0.146 g, 71% yield, 94% ee; $[\alpha]_D^{25}$ -962.3 (c 0.47, CHCl₃). Colorless liquid, R_f = 0.6 (silica gel, 97:3 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel OB-H, 98:2 hexanes/i-PrOH; flow rate, 1.0 mL/min, 220 nm; retention times, 6.15 min (minor) and 7.05 min (major); IR (neat) 3060, 3027, 2955, 1936, 1597, 1493, 1452, 758 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.59–7.55 (m, 2H), 7.44–7.33 (m, 8H), 6.57 (s, 1H), 2.32 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 206.8, 136.3, 134.5, 128.7, 128.4, 127.0, 126.9, 125.8, 104.5, 96.5, 16.7. The ¹³C NMR data showed 1:1 correspondence with the reported data.

(*R*)-(3-Methylhepta-3,4-diene-1,7-diyl)dibenzene (**8***g*). From chiral propargylamine 7lg: 0.233 g, 89% yield, 99% ee; $[\alpha]_D^{25}$ -109.3 (c 0.45, CHCl₃). Colorless liquid, $R_f = 0.9$ (silica gel, 100:0 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel chiralcel OJ-H, 100:0 hexanes/i-PrOH; flow rate, 0.5 mL/min, 214 nm; retention times, 11.8 min (major) and 16.1 min (minor); IR (neat) 3084, 3068, 3024, 2854, 1961, 1600, 1495, 1452, 1265, 1035, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (t, *J* = 8.0 Hz, 5H), 7.21 (d, *J* = 4.0 Hz, 5H), 5.14–5.10 (m, 1H), 2.69 (t, *J* = 8.0 Hz, 4H), 2.31–2.22 (m, 4H), 1.70 (s, 3H); ¹³C{1H}NMR (100 MHz, CDCl₃) δ 201.4, 142.2, 142.0, 128.4, 128.3, 128.1, 125.6, 99.4, 90.2, 35.6, 35.4, 33.8, 30.8, 19.3; LCMS *m*/*z* 263 [M + 1]; anal. calcd for C₂₀H₂₂ C 91.55, H 8.45; found C 91.45, H 8.53.

(*R*)-(4-Methylnona-4,5-diene-1,9-diyl)dibenzene(8h). From chiral propargylamine 7jh: 0.243 g, 84% yield, 99% ee; $[\alpha]_D^{25}$ -85.9 (*c* 0.46, CHCl₃). From chiral propargylamine 7lh: 0.251 g, 86% yield, 99% ee; $[\alpha]_D^{25}$ -85.5 (*c* 0.63, CHCl₃). Colorless liquid, $R_f = 0.6$ (silica gel, 100:0 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel Phenomenex amylose-2, 100:0 hexanes/i-PrOH; flow rate, 0.5 mL/min, 190 nm; retention times, 8.1 min (major) and 11.7 min (minor); IR (neat) 2958, 2849, 1960, 1447, 1347, 1258, 986, 962, 889, 842 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34–7.29 (m, 5H), 7.24–7.20 (m, 5H), 5.10 (s, 1H), 2.74 (t, *J* = 8.0 Hz, 2H), 2.68–2.64 (m, 3H), 2.23 (d of t J_1 = 8.0 Hz, J_2 = 2.6 Hz, 2H), 2.08–1.99 (m, 4H), 1.80–1.72 (m, 4H), 1.28 (t, *J* = 8.0 Hz, 1H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 201.3, 142.6, 128.4, 128.2, 125.6, 99.1, 90.1, 35.4, 35.3, 33.5, 31.0, 29.3, 28.8, 19.4; LCMS *m*/*z* 291 [M + 1]; anal. calcd for C₂₂H₂₆ C 90.98, H 9.02; found C 90.82, H 9.08.

(*R*)-(5-Methylundeca-5,6-diene-1,11-diyl)dibenzene(**8**i). From chiral propargylamine 7li: 0.263 g, 83% yield, 94% ee; $[\alpha]_D^{25}$ –97.2 (c 0.49, CHCl₃). Colorless liquid, $R_f = 0.9$ (silica gel, 100:0 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel Phenomenex amylose-2, 100:0 hexanes/i-PrOH; flow rate, 1.0 mL/min, 190 nm; retention times, 3.7 min (major) and 5.2 min (minor); IR (neat) 2923, 2850, 1962, 1727, 1599, 1489, 1448, 1089, 1019, 810 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.30–7.27 (m, SH), 7.26–7.18 (m, SH), 5.06–4.96 (m, 1H), 2.65–2.58 (m, SH), 2.23–2.19 (m, 2H), 1.97 (t, *J* = 8.0 Hz, 4H), 1.66–1.63 (m, 4H), 1.46 (s, 3H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 201.2, 142.8, 128.4, 128.2, 125.6, 99.1, 90.0, 35.8, 33.9, 31.1, 29.2, 29.0, 28.8, 27.2, 19.3; LCMS *m*/*z* 319 [M + 1]; anal. calcd for C₂₄H₃₀ C 90.51, H 9.49; found C 90.65, H 9.39.

(*R*)-5-Methylundeca-5,6-dienedinitrile(**8***j*). From chiral propargylamine 7jj: 0.133 g, 71% yield, 99% ee; $[\alpha]_D^{25}$ –56.2 (*c* 0.35, CHCl₃). Colorless liquid, $R_f = 0.6$ (silica gel, 95:5 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel AS-H, 100:0 hexanes/i-PrOH; flow rate, 0.3 mL/min, 190 nm; retention times, 13.0 min (minor) and 17.2 min (major); IR (neat) 3298, 2931, 2854, 2246, 1956, 1446, 1424, 1375, 1238 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.04 (m, 1H), 2.37 (q, J = 8.0 Hz, 4H), 2.14–2.06 (m, 4H), 1.80–1.72 (m, 4H), 1.68 (s, 3H); $^{13}C{1H}$ NMR (100 MHz, CDCl₃) δ 201.5, 119.5, 98.6, 89.2, 32.5, 27.9, 24.7, 23.2, 19.1, 16.5, 16.4; LCMS m/z 188 [M + 1]; anal. calcd for $C_{12}H_{16}N_2$ C 76.55, H 8.57, N 14.88; found C 76.63, H 8.51, N 14.72.

(*R*)-1, 19-Dimethoxy-9-methylnonadeca-9, 10-diene(**8**k). From chiral propargylamine 7jk: 0.229 g, 68% yield, 99% ee; $[\alpha]_D^{25}$ –92.3 (c 0.55, CHCl₃). From chiral propargylamine 7lk: 0.246 g, 73% yield, 90% ee; $[\alpha]_D^{25}$ –79.1 (c 0.62, CHCl₃). Yellow oil, R_f = 0.7 (silica gel, 98:2 hexane/EtOAc). The enantioselectivity was determined by HPLC using chiral column, chiralcel OD-H, 100:0 hexanes/i-PrOH; flow rate, 1.0 mL/min, 190 nm; retention times, 6.0 min (major) and 9.2 min (minor); IR (neat) 2920, 2860, 1967, 1714, 1457, 1368, 1261, 1172, 745 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.97 (s, 1H), 3.41–3.32 (m, 10H), 1.95–1.88 (m, 3H), 1.65–1.64 (m, 3H), 1.61–1.52 (m, 4H), 1.42–1.30 (m, 20H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 201.1, 99.1, 90.0, 72.9, 58.5, 34.1, 29.6, 29.5, 29.3, 29.2, 29.0, 27.5, 26.1, 19.3; LCMS *m*/z 339 [M + 1]; anal. calcd for C₂₂H₄₂O₂ C 78.05, H 12.5; found C 78.23, H 12.41.

(*R*)-2,2,3,3,13,25,25,26,26-Nonamethyl-4,24-dioxa-3,25-disilaheptacosa-13,14-diene (**8**). From chiral propargylamine 7**l**!: 0.289 g, 68% yield; $[\alpha]_{\rm D}^{25}$ -66.3 (*c* 0.41, CHCl₃). Colorless liquid, *R*_f = 0.6 (silica gel, 97:3 hexane/EtOAc); IR (neat) 2958, 2936, 2806, 1715, 1473, 1260, 1095 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.0 (*s*, 1H), 3.63–3.59 (m, 4H), 2.21 (*s*, 3H), 1.98–1.95 (m, 4H), 1.66–1.52 (m, 4H), 1.46–1.26 (m, 4H), 0.89 (*s*, 18H), 0.05 (*s*, 12H); ¹³C{1H} NMR (100 MHz, CDCl₃) δ 201.2, 99.2, 90.1, 84.5, 68.2, 63.1, 62.5, 33.8, 32.4, 32.3, 31.8, 31.5, 29.1, 25.9, 25.5, 24.9, 23.8,19.2, 18.3, 18.2, -5.20; LCMS *m*/*z* 427 [M + 1]; anal. calcd for C₂₄H₅₀O₂Si₂ C 67.54, H 11.81; found C 67.41, H 11.76.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b02554.

Copies of the ¹H and ¹³C NMR spectra of the products, HPLC analysis profiles, X-ray data, and ORTEP diagram (PDF)

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Notes

The authors declare no competing financial interest.

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