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Synthetic transformation of homopropargylic selenides to conjugated diene-substituted alcohols and amines using diisopropoxy(η^2-alkyne)titanium intermediates

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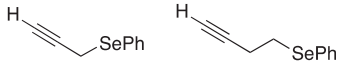
ABSTRACT

The reaction of homopropargylic selenides with the low-valent titanium reagent, derived from Ti(O-*i*-Pr)$_4$ and 2 equiv of *i*-PrMgCl, proceeded via titanium–alkyne complexes, followed by the reaction with electrophiles, such as aldehydes and imines to afford allylic alcohols and amines having a phenylseleno group in moderate to high yields with excellent regioselectivity (up to >99:1). Especially, the reaction of the silyl-substituted alkynes with imines provided the desired products in almost complete regioselectivity. The resulting products were subjected to oxidation with H_2O_2 to lead conjugated diene-substituted alcohols and amines via selenoxide elimination in high yields. In addition, the isomer ratio of products was nearly completely maintained under the oxidative deselenation conditions.

1. Introduction

Titanium–alkyne complexes are very valuable intermediates in organic synthesis.[1] In 1995, Sato and co-workers reported that the titanium complexes known as diisopropoxy(η^2-alkyne)titaniums are readily prepared from internal alkynes and the low-valent titanium reagent, generated in situ from Ti(O-*i*-Pr)$_4$ and 2 equiv of *i*-PrMgCl. These complexes can react with various electrophiles, such as aldehydes,[2] ketones,[2] imines,[3] and so on,[4] to afford a variety of di-, tri-, and tetrasubstituted alkenes. Internal alkynes are suitable substrates for this reaction, and the reports of the use of terminal alkynes are limited.[5] In addition, for a titanium complexes arising from an unsymmetrical alkyne, the reaction with ketones, unsaturated, and aromatic aldehydes indicated generally significantly high regioselectivity, which raised with increasing the steric hindrance when saturated aldehydes was used.[2]

On the other hand, organoselenium chemistry has become a very powerful tool in organic synthesis.[6] In particular, 3-phenylseleno-1-propyne **1** (propargylic selenide) and 4-phenylseleno-1-butyne **2** (homopropargylic selenide) are expected to be versatile intermediates for synthesis of polyfunctionalized compounds (Scheme 1), because several reactive moieties of them will play important roles in functional group transformations.[7,8] Those are (1) carbon–carbon bond formation via hydrometallation of a terminal triple bond, (2) formation of olefins and allylic alcohols via selenoxide elimination and [2,3]-sigmatropic rearrangement, respectively, and (3) elongation of carbon chain via abstraction of acidic protons.



1 2

Scheme 1. Terminal alkynes having a phenylseleno group.

Especially, the CH_2CH_2SePh moiety of **2** can be converted into the $CH{=}CH_2$ functional group via selenoxide elimination by oxidation, and thus is regarded as a vinylic equivalent. On the other hand, it has been reported that the reaction of conjugated enyne–titanium alkoxide complex with aldehydes gave the allenyl alcohol derivatives.[9] In this reported reaction, conjugated diene derivatives are not obtained. We herein present the efficient and facile synthetic procedure of conjugated dienes having an allylic alcohol or amine moiety, in combination with titanium–alkyne

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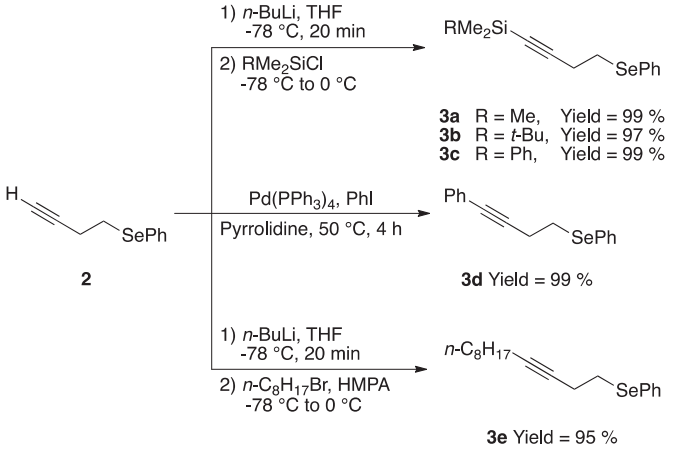
complex formation by the reaction of homopropargylic selenide derivatives with the low-valent titanium reagent and selenoxide elimination via oxidation of phenylseleno group.

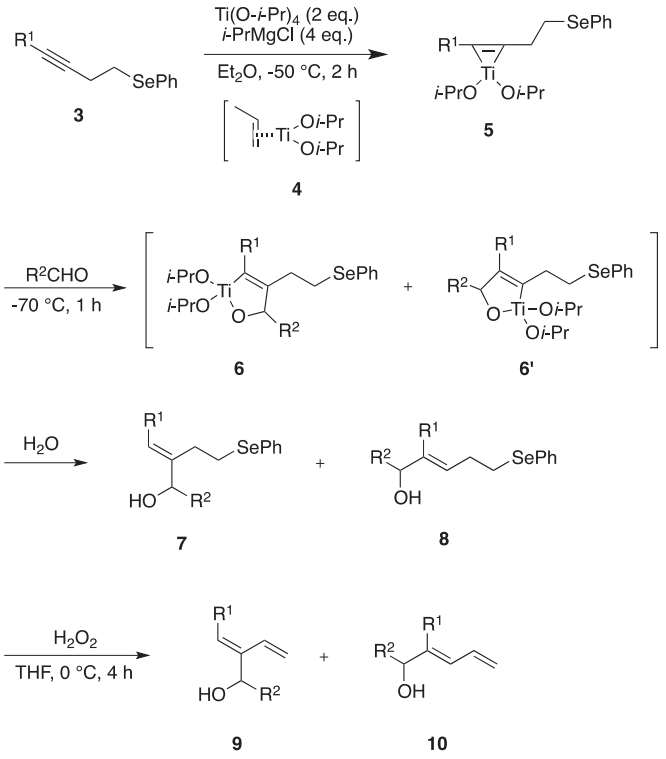
2. Results and discussion

The internal alkynes **3a**–**e** were prepared by the introduction of some groups to the terminal alkyne carbon of 4-phenylseleno-1-butyne **2** (Scheme 2). Treatment of **2** with 1.1 equiv of *n*-BuLi in THF at −78 °C generated the alkynyl anion, followed by reacting with silyl chlorides to give the corresponding silyl-substituted alkynes **3a**–**c** in excellent yields. According to Linstrumelle's procedure, the phenyl-substituted alkyne **3d** was prepared by the reaction with iodobenzene in the presence of 5 mol % of $Pd(PPh_3)_4$ in pyrrolidine at 50 °C in 99% yield.[10] The alkyl-substituted alkyne **3e** was obtained in 95% yield by abstraction of terminal acidic proton on **2** and the subsequent reaction with *n*-octyl bromide in the presence of hexamethylphosphoric triamide (HMPA).



Scheme 2. Introduction of some groups to the terminal alkyne carbon of 4-phenylseleno-1-butyne **2**.

The internal alkynes **3a**–**d** reacted with the low-valent titanium reagent **4**, generated in situ from $Ti(O\text{-}i\text{-}Pr)_4$ (2 equiv) and *i*-PrMgCl (4 equiv), in Et_2O at −50 °C for 2 h to produce titanium–alkyne complexes **5**, which were then reacted with various aldehydes at −70 °C for 1 h to give allylic alcohols **7** and **8** via oxatitanacyclopentene intermediates **6** and **6′**, respectively (Scheme 3, Table 1).[11] However, when the octyl-substituted alkyne **3e** was used as a substrate, the reaction did not proceed and the starting alkyne **3e** was completely recovered. These results are summarized in Table 1. The regioselectivity of giving products **7** and **8** was depended on both the substituent groups (R^1) of internal alkynes **3** and the steric hindrance of aldehydes. Namely, the silyl-substituted alkynes **3a**–**c** selectively underwent the addition of aldehydes at β-carbon to the silyl group to lead intermediates **6**, whereas the phenyl-substituted alkyne **3d** preferentially reacted at α-carbon to the phenyl group to give allylic alcohols **8** via intermediates **6′**, accompanying the regioisomer **7**. It was revealed that the combination of the alkynes **3a**–**c** bearing a silyl group and sterically hindered aldehydes provided allylic alcohols **7** in extremely high regioselectivity, but the selectivity decreased when primary aliphatic aldehyde was used (entries 2, 5, and 8). In the case of the alkyl-substituted alkyne **3e**, the starting alkyne was completely recovered (entries 13 and 14). This may be due to no stabilizing advantages arising from alkyl substituent influences for the complex **5**. Accordingly, the alkyne complex **5** substituted by an alkyl group was not formed from the treatment of the low-valent titanium reagent and **3e**, and the subsequent quench by H_2O afforded the starting alkyne **3e**.



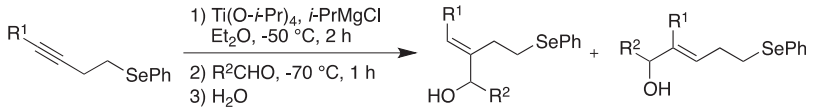
Scheme 3. Synthetic transformation to conjugated diene-substituted alcohols from **3**.

The plausible mechanism for the carbotitanation of **3** with benzaldehyde is shown in Scheme 4. The titanium–alkyne complex **5** is formed by ligand exchange of coordinated propene in the low-valent titanium reagent **4** with the internal alkyne **3** (**3a**: R^1=$SiMe_3$, **3d**: R^1=Ph). When the carbonyl group of aldehydes inserts to one of the two carbon–titanium bonds, a couple of presumable oxatitanacyclopentene intermediates **A** and **B** are possible. When the silyl-substituted alkyne **3a** was used, the addition of a carbonyl carbon to the C–Ti bond at β-position to the silyl group would selectively proceed via the intermediate **A1** to prevent forming **B1** because of steric interruption between silyl and phenyl groups, followed by the treatment with H_2O to obtain the corresponding allylic alcohol **7aa**. In contrast, the complex **5** from phenyl-substituted alkyne **3d** preferentially reacted with benzaldehyde at the carbon having the phenyl group to give the intermediate **B2**, followed by treatment with H_2O to afford mainly the allylic alcohol **8da**. This notable regioselectivity is consistent with the previous reports using unsymmetrical alkynes.[1e,2]

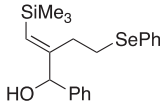
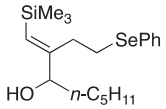
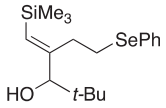
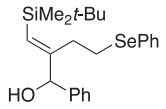
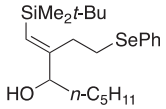
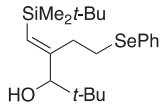
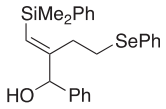
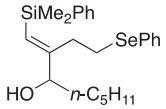
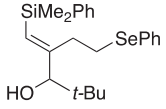
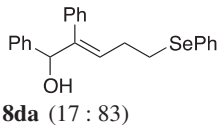
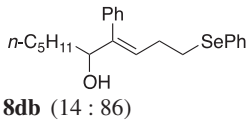
In this way, the resulting products **7** and **8** having a phenylseleno group were oxidized by H_2O_2 in THF to give conjugated diene derivatives **9** and **10** bearing an allylic alcohol moiety in high to excellent yields via *syn* elimination of the corresponding selenoxides without isomerization of alkene (Scheme 3). The results are shown in Table 2. The structure of products **9** and **10** was identified by ^{1}H NMR analysis and that ratio of the isomers (**9**, **10**) was almost completely maintained under the oxidative deselenation conditions.

The results on the reaction of alkynes **3** with various imines instead of aldehydes as electrophiles using the low-valent titanium reagent were summarized in Table 3. In this reaction, two possible allylic amine derivatives **11** and **12** were produced. Similar to the above results using aldehydes, the reaction of the silyl-substituted alkynes **3a**–**c** with imines showed excellent regioselectivity (>96:4), of which titanium–alkyne complexes underwent electrophilic addition by imines at β-carbon to the silyl group regardless of the size of imines, to give the corresponding allylic amines **11**

Table 1
Synthesis of allylic alcohol derivatives using various alkynes **3** and aldehydes

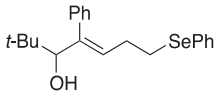


3 **7** **8**

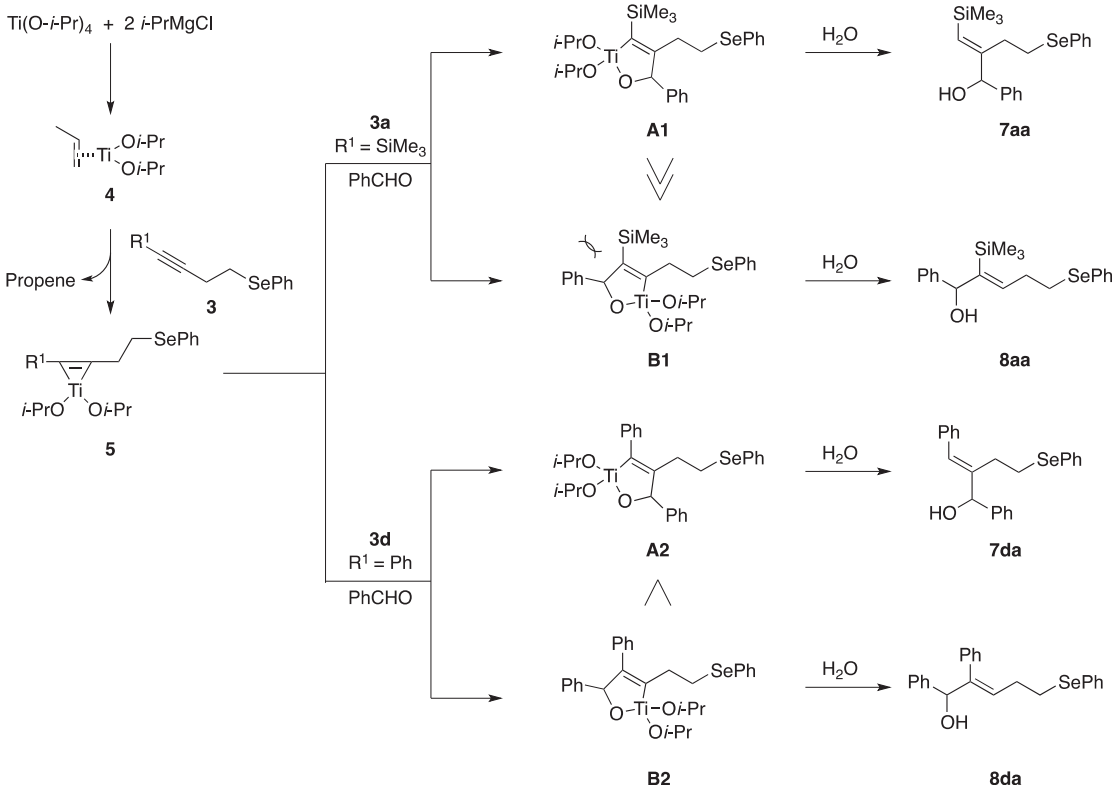
Entry	**3**	R^2	Product (Major) (**7**:**8**)[a]	Yield[b] (%)
1	**3a**	Ph	 **7aa** (>99 : 1)	66
2	**3a**	*n*-C_5H_{11}	 **7ab** (93 : 7)	62
3	**3a**	*t*-Bu	 **7ac** (>99 : 1)	48
4	**3b**	Ph	 **7ba** (>99 : 1)	89
5	**3b**	*n*-C_5H_{11}	 **7bb** (80 : 20)	87
6	**3b**	*t*-Bu	 **7bc** (>99 : 1)	47
7	**3c**	Ph	 **7ca** (>99 : 1)	78
8	**3c**	*n*-C_5H_{11}	 **7cb** (64 : 36)	61
9	**3c**	*t*-Bu	 **7cc** (>99 : 1)	43
10	**3d**	Ph	 **8da** (17 : 83)	68
11	**3d**	*n*-C_5H_{11}	 **8db** (14 : 86)	75

(*continued on next page*)

Table 1 (*continued*)

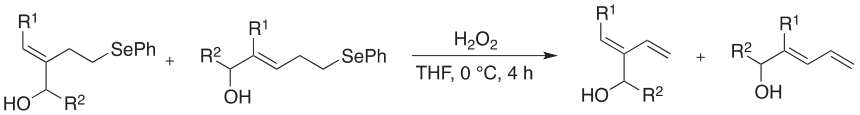
Entry	3	R^2	Product (Major) (**7**:**8**)[a]	Yield[b] (%)
12	**3d**	*t*-Bu	 **8dc** (43 : 57)	63
13	**3e**	Ph		0[c]
14	**3e**	n-C_5H_{11}		0[c]

[a] Product ratio of **7** and **8** was determined by ^{1}H NMR.
[b] Isolated yield.
[c] The starting alkyne **3e** was recovered.



Scheme 4. Plausible mechanism for carbotitanation of alkynes **3** with benzaldehyde.

Table 2
Synthesis of conjugated diene alcohols via selenoxide elimination



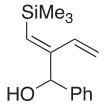
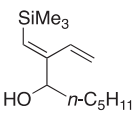
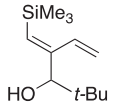
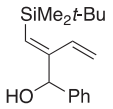
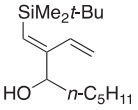
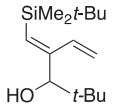
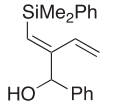
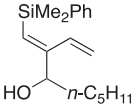
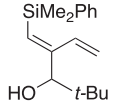
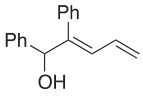
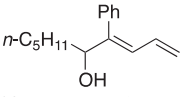
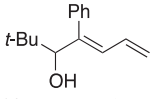
Entry	Substrate (**7**:**8**)	Product (Major) (**9**:**10**)[a]	Yield[b] (%)
1	**aa** (>99:1)	 **9aa** (>99 : 1)	98
2	**ab** (93:7)	 **9ab** (93 : 7)	75

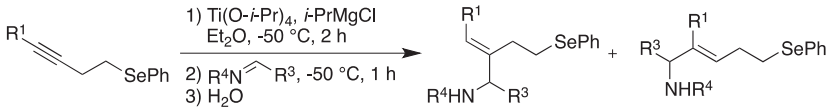
Table 2 (*continued*)

Entry	Substrate (**7**:**8**)	Product (Major) (**9**:**10**)[a]	Yield[b] (%)
3	**ac** (>99:1)	 **9ac** (>99 : 1)	69
4	**ba** (>99:1)	 **9ba** (>99 : 1)	94
5	**bb** (80:20)	 **9bb** (80 : 20)	81
6	**bc** (>99:1)	 **9bc** (>99 : 1)	92
7	**ca** (>99:1)	 **9ca** (>99 : 1)	78
8	**cb** (64:36)	 **9cb** (64 : 36)	88
9	**cc** (>99:1)	 **9cc** (>99 : 1)	76
10	**da** (17:83)	 **10da** (17 : 83)	98
11	**db** (14:86)	 **10db** (14 : 86)	99
12	**dc** (43:57)	 **10dc** (43 : 57)	99

[a] Product ratio of **9** and **10** was determined by ^{1}H NMR.
[b] Isolated yield.

in good yields (entries 1–9).[12] When the phenyl-substituted alkyne **3d** was used as the starting alkyne, isomeric allylic amines **12** were preferentially obtained in moderate yields through the addition of imines at the carbon having phenyl group in complex **5** (entries 10–12).[11] These outcomes are similar to the above results using aldehyde as an electrophile. The reaction using alkyl-substituted alkyne **3e** and imine did not proceed at all (entry 13). Subsequently, the oxidative deselenation of obtained allylic amine derivatives **11** and **12** with H_2O_2 efficiently proceeded to afford the corresponding conjugated dienes **13** and **14** having an allylic amine moiety in good to excellent yields (Table 4). The ratios of the isomers **13** and **14** were also maintained through oxidation.

Table 3
Synthesis of allylic amine derivatives using various alkynes **3** and imines



3 **11** **12**

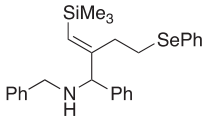
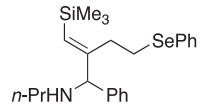
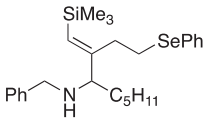
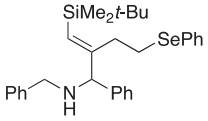
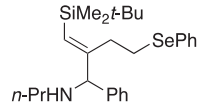
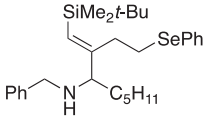
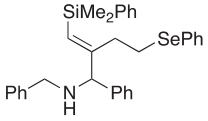
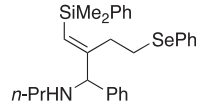
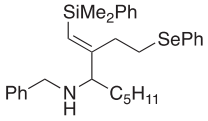
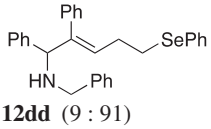
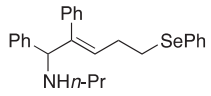
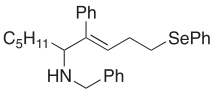
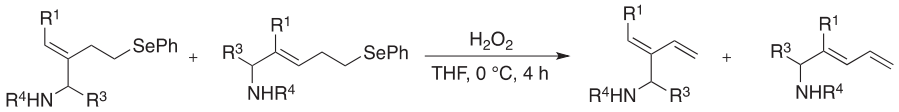
Entry	**3**	R^3	R^4	Product (Major) (**11**:**12**)[a]	Yield[b] (%)
1	**3a**	Ph	$PhCH_2$	 **11ad** (>99 : 1)	61
2	**3a**	Ph	*n*-Pr	 **11ae** (>99 : 1)	72
3	**3a**	C_5H_{11}	$PhCH_2$	 **11af** (>99 : 1)	57
4	**3b**	Ph	$PhCH_2$	 **11bd** (>99 : 1)	71
5	**3b**	Ph	*n*-Pr	 **11be** (>99 : 1)	65
6	**3b**	C_5H_{11}	$PhCH_2$	 **11bf** (96 : 4)	62
7	**3c**	Ph	$PhCH_2$	 **11cd** (>99 : 1)	56
8	**3c**	Ph	*n*-Pr	 **11ce** (>99 : 1)	69
9	**3c**	C_5H_{11}	$PhCH_2$	 **11cf** (>99 : 1)	60
10	**3d**	Ph	$PhCH_2$	 **12dd** (9 : 91)	49

Table 3 (*continued*)

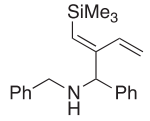
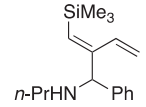
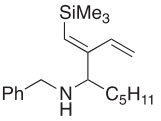
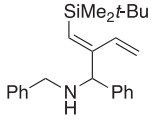
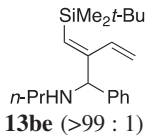
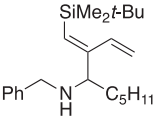
Entry	3	R^3	R^4	Product (Major) (**11**:**12**)[a]	Yield[b] (%)
11	**3d**	Ph	*n*-Pr	 **12de** (19 : 81)	43
12	**3d**	C_5H_{11}	$PhCH_2$	 **12df** (14 : 86)	32
13	**3e**	Ph	$PhCH_2$		0[c]

[a] Product ratio of **11** and **12**.
[b] Isolated yield.
[c] The starting alkyne **3e** was recovered.

Table 4
Synthesis of conjugated diene amines via selenoxide elimination

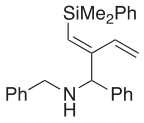
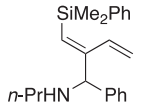
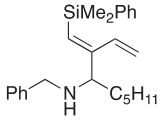
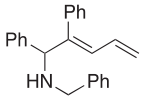
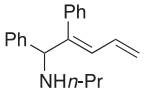
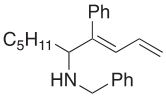


11 **12** **13** **14**

Entry	Substrate (**11**:**12**)	Product (Major) (**13**:**14**)[a]	Yield[b] (%)
1	**ad** (>99:1)	 **13ad** (>99 : 1)	85
2	**ae** (>99:1)	 **13ae** (93 : 7)	93
3	**af** (>99:1)	 **13af** (>99 : 1)	89
4	**bd** (>99:1)	 **13bd** (>99 : 1)	97
5	**be** (>99:1)	 **13be** (>99 : 1)	99
6	**bf** (96:4)	 **13bf** (96 : 4)	80

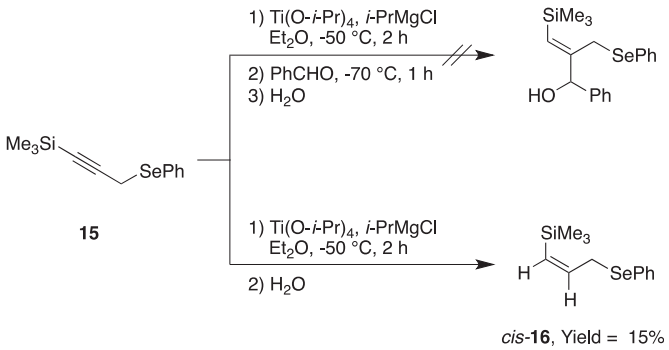
(*continued on next page*)

Table 4 (*continued*)

Entry	Substrate (**11**:**12**)	Product (Major) (**13**:**14**)[a]	Yield[b] (%)
7	**cd** (>99:1)	 **13cd** (>99 : 1)	63
8	**ce** (>99:1)	 **13ce** (>99 : 1)	99
9	**cf** (>99:1)	 **13cf** (>99 : 1)	76
10	**dd** (9:91)	 **14dd** (9 : 91)	79
11	**de** (19:81)	 **14de** (19 : 81)	68
12	**df** (14:86)	 **14df** (14 : 86)	73

[a] Product ratio of **9** and **10** was determined by ^{1}H NMR.
[b] Isolated yield.

On the other hand, we attempted to similar reactions by using propargylic selenide **1**. The carbotitanation of trimethylsilyl-substituted alkyne **15** with low-valent titanium reagent **4** and benzaldehyde did not proceed, resulting in the recovery of starting alkyne. To confirm the formation of titanium–alkyne complex generated from **15** and **4**, the protonolysis of that complex with H_2O was carried out and resulted in the formation of *cis* allylic selenide **16** in 15% yield and the almost recovery of starting alkyne **15** (Scheme 5).[13] This different reactivity between **1** and **2** would be due to the stabilization in the corresponding alkyne complexes.[14] In the case of the homopropargyl selenide **2**, the alkyne complex stabilized by intramolecular coordination of the selenium functional group is in situ efficiently formed. On the other hand, the complex formed from propargyl selenide **1** is difficult to coordinate with the intramolecular selenium atom because of the shortage of spatial length.



Scheme 5. Reaction of propargylic selenide **15** with low-valent titanium reagent.

3. Conclusion

In conclusion, an efficient and useful method for stereoselective syntheses of conjugated dienes having oxygen or nitrogen functionality was developed by the electrophilic addition of aldehydes or imines to titanium–alkyne complexes, generated from internal alkyne bearing a phenylseleno group and low-valent titanium reagent, followed by selenoxide elimination via oxidation.

4. Experimental section

4.1. General

^{1}H, ^{13}C, and ^{77}Se NMR spectra were recorded on JEOL JNM-FX-270 (^{1}H; 270.1 MHz and ^{13}C; 67.8 MHz) and JNM-GX-400 (^{1}H; 399.7 MHz, ^{13}C; 100.4 MHz, and ^{77}Se; 76.2 MHz, respectively) spectrometers. Chemical shifts were reported in parts per million relative to tetramethylsilane as internal standard, and were referenced to diphenyl diselenide as external standard for ^{77}Se (464.1 ppm in $CDCl_3$). IR spectra were obtained on a SHIMADZU FTIR-8300 spectrometer. Mass spectra (EI) were recorded on a JEOL JMS-700 or JMS-SX 102A mass spectrometer. Column chromatography was conducted by

using Fuji Silysia Chemical silica gel BW-127ZH. THF and Et_2O were distilled from sodium benzophenone ketyl under nitrogen. Other reagents were commercially available and used without further purification. Isopropylmagnesium chloride (2.0 M solution in Et_2O) was purchased from Sigma–Aldrich Co., Inc. and *n*-butyllithium (1.6 M solution in hexane) was purchased from Kanto Chemical Co., Inc. All reactions were performed under argon atmosphere with flame-dried glassware using a vacuum pump unless otherwise described. Propargylic selenide **1** and homopropargylic selenide **2** were synthesized according to published procedure.[7,8]

4.2. General procedure for the preparation of silyl-substituted alkynes 3a–c

To a stirred solution of 4-phenylseleno-1-butyne **2** (2.0 mmol) in THF (10 mL) was added *n*-BuLi (1.6 M solution in hexane, 2.2 mmol) dropwise at −78 °C. The reaction mixture was stirred 20 min at −78 °C, and then a silyl chloride (2.4 mmol) was slowly added. After stirring for 10 min, the mixture was warmed up to 0 °C and quenched with H_2O. The organic layer was separated and the aqueous layer was further extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel to afford alkyne **3a**–**c**.

*4.2.1. Trimethyl[4-(phenylselanyl)but-1-yn-1-yl]silane (**3a**).* Pale yellow oil, 99% yield; δ_H (400 MHz, $CDCl_3$) 0.14 (s, 9H), 2.59 (t, *J*=7.7 Hz, 2H), 3.02 (t, *J*=7.7 Hz, 2H), 7.26–7.27 (m, 3H), 7.52–7.53 (m, 2H); δ_C (100 MHz, $CDCl_3$) 0.01, 21.7, 25.8, 85.7, 105.6, 127.2, 129.1, 129.4, 133.2; δ_{Se} (76 MHz, $CDCl_3$) 317.0; ν_{max} (neat) 3071, 2959, 2897, 2176, 1578, 1477, 1250, 760, 737, 691 cm^{-1}; *m*/*z* (EI) 73 (93), 109 (47), 158 (23), 267 (15), 282 (100%, M^+). HRMS (EI): M^+, found 282.0335. $C_{13}H_{18}Si^{80}Se$ requires 282.0343.

*4.2.2. tert-Butyldimethyl[4-(phenylselanyl)but-1-yn-1-yl]silane (**3b**).* Pale yellow oil, 97% yield; δ_H (400 MHz, $CDCl_3$) 0.08 (s, 6H), 0.93 (s, 9H), 2.60 (t, *J*=7.7 Hz, 2H), 3.02 (t, *J*=7.7 Hz, 2H), 7.25–7.27 (m, 3H), 7.50–7.53 (m, 2H); δ_C (100 MHz, $CDCl_3$) −4.5, 16.5, 21.6, 26.1, 84.0, 106.1, 127.2, 129.1, 129.5, 133.2; δ_{Se} (76 MHz, $CDCl_3$) 315.8; ν_{max} (neat) 3071, 2951, 2928, 2855, 2172, 1578, 1474, 1250, 837, 775, 737, 691 cm^{-1}; *m*/*z* (EI) 109 (58), 129 (31), 239 (15), 267 (100), 324 (20%, M^+). HRMS (EI): M^+, found 324.0820. $C_{16}H_{24}Si^{80}Se$ requires 324.0812.

*4.2.3. Dimethyl(phenyl)[4-(phenylselanyl)but-1-yn-1-yl]silane (**3c**).* Pale yellow oil, 99% yield; δ_H (400 MHz, $CDCl_3$) 0.38 (s, 6H), 2.64 (t, *J*=7.8 Hz, 2H), 3.04 (t, *J*=7.8 Hz, 2H), 7.25–7.27 (m, 3H), 7.36–7.38 (m, 3H), 7.51–7.54 (m, 2H), 7.61–7.63 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.8, 21.7, 25.8, 83.8, 107.4, 127.2, 127.8, 129.1, 129.3, 133.2, 133.7, 137.2; δ_{Se} (76 MHz, $CDCl_3$) 317.0; ν_{max} (neat) 3067, 2959, 2176, 1578, 1477, 1427, 1250, 818, 733, 698 cm^{-1}; *m*/*z* (EI) 135 (81), 159 (100), 171 (74), 329 (22), 344 (97%, M^+). HRMS (EI): M^+, found 344.0495. $C_{18}H_{20}Si^{80}Se$ requires 344.0499.

4.3. General procedure for the preparation of the phenyl-substituted alkyne 3d

To a stirred solution of iodobenzene (0.071 g, 1.2 mmol) and tetrakis(triphenylphosphine)palladium (0.060 g, 0.05 mmol) in pyrrolidine (1.0 mL) was added a solution of 4-phenylseleno-1-butyne **2** (0.210 g, 1.0 mmol) in pyrrolidine (1.5 mL). After stirring at room temperature for 15 min, the mixture was hydrolyzed with a satd NH_4Cl and extracted with diethyl ether. The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel to afford phenyl(4-phenylbut-3-yn-1-yl)selane **3d** (0.282 g, 99% yield) as pale yellow oil; δ_H (400 MHz, $CDCl_3$) 2.79 (td, *J*=3.3, 7.6 Hz, 2H), 3.11 (td, *J*=3.3, 7.6 Hz, 2H), 7.27–7.28 (m, 6H), 7.37–7.39 (m, 2H), 7.55–7.57 (m, 2H); δ_C (100 MHz, $CDCl_3$) 21.2, 26.0, 81.6, 88.7, 123.5, 127.2, 127.8, 128.2, 129.1, 129.5, 131.6, 133.1; δ_{Se} (76 MHz, $CDCl_3$) 315.4; ν_{max} (neat) 3055, 2936, 1578, 1477, 1439, 1072, 1022, 756, 734, 691 cm^{-1}; *m*/*z* (EI) 77 (20), 91 (24), 128 (100), 158 (10), 171 (11), 205 (19), 286 (78%, M^+). HRMS (EI): M^+, found 286.0268. $C_{16}H_{14}^{80}Se$ requires 286.0261.

4.4. General procedure for carbotitanation of internal alkynes with low-valent titanium reagent and various aldehydes

To a stirred solution of an internal alkyne **3** (0.30 mmol) and $Ti(O\text{-}i\text{-}Pr)_4$ (0.154 g, 0.54 mmol) in Et_2O (5 mL) was added *i*-PrMgCl (2.0 M solution in Et_2O, 0.6 mL, 1.2 mmol) dropwise at −78 °C. The reaction mixture was warmed up to −50 °C over 30 min and stirred for 2 h at this temperature. Then an aldehyde (0.50 mmol) was added at −78 °C and the reaction mixture was stirred for 1 h at −70 °C. The reaction was quenched with H_2O at −70 °C. The organic layer was separated and the aqueous layer was further extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel to afford allyl alcohols **7** and **8**.

*4.4.1. (E)-1-Phenyl-4-(phenylselanyl)-2-[(trimethylsilyl)methylene]butan-1-ol (**7aa**).* Pale yellow oil, 66% yield; δ_H (400 MHz, $CDCl_3$) 0.10 (s, 9H), 2.01 (br s, 1H), 2.29–2.36 (m, 1H), 2.46–2.53 (m, 1H), 2.77–2.82 (m, 2H), 5.14 (s, 1H), 5.89 (s, 1H), 7.24–7.44 (m, 10H); δ_C (100 MHz, $CDCl_3$) 0.1, 27.2, 33.8, 78.4, 125.6, 126.8, 127.0, 127.8, 128.5, 129.0, 129.6, 133.2, 141.9, 157.5; δ_{Se} (76 MHz, $CDCl_3$) 314.8; ν_{max} (neat) 3418, 3059, 2955, 2897, 1616, 1477, 1450, 1250, 1022, 837, 737, 698 cm^{-1}; *m*/*z* (EI) 73 (100), 107 (43), 143 (40), 233 (64), 375 (9), 390 (13%, M^+). HRMS (EI): M^+, found 390.0920. $C_{20}H_{26}OSi^{80}Se$ requires 390.0918.

*4.4.2. (E)-1-(Phenylselanyl)-3-[(trimethylsilyl)methylene]nonan-4-ol (**7ab**).* Mixture of regioisomers (**7ab**:**8ab**=93:7). Pale yellow oil, 62% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.06 (s, 9H), 0.88 (t, *J*=6.8 Hz, 3H), 1.26–1.51 (m, 8H), 1.53 (br s, 1H), 2.39–2.47 (m, 1H), 2.55–2.63 (m, 1H), 2.90–3.03 (m, 2H), 4.04 (dd, *J*=4.6, 7.6 Hz, 1H), 5.56 (s, 1H), 7.23–7.29 (m, 3H), 7.50–7.55 (m, 2H); δ_C (100 MHz, $CDCl_3$) 0.1, 14.0, 22.6, 25.4, 27.5, 31.7, 33.8, 36.2, 76.4, 125.1, 127.1, 129.0, 129.7, 133.3, 159.4; δ_{Se} (76 MHz, $CDCl_3$) 313.1; ν_{max} (neat) 3402, 3071, 2955, 2858, 1612, 1578, 1477, 1439, 1250, 1022, 856, 733, 691 cm^{-1}; *m*/*z* (EI) 73 (98), 211 (53), 227 (100), 369 (16), 384 (26%, M^+). HRMS (EI): M^+, found 384.1389. $C_{19}H_{32}OSi^{80}Se$ requires 384.1388.

*4.4.3. (Z)-1-(Phenylselanyl)-4-(trimethylsilyl)dec-3-en-5-ol (**8ab**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$) 0.11 (s, 9H), 0.88 (t, *J*=6.8 Hz, 3H), 1.26–1.51 (m, 8H), 1.53 (br s, 1H), 2.39–2.47 (m, 1H), 2.55–2.63 (m, 1H), 2.90–3.03 (m, 2H), 4.12 (dd, *J*=2.6, 7.1 Hz, 1H), 6.18 (t, *J*=7.4 Hz, 1H), 7.23–7.29 (m, 3H), 7.50–7.55 (m, 2H).

*4.4.4. (E)-2,2-Dimethyl-6-(phenylselanyl)-4-[(trimethylsilyl)methylene]hexan-3-ol (**7ac**).* Yellow oil, 48% yield; δ_H (400 MHz, $CDCl_3$) 0.08 (s, 9H), 0.85 (s, 9H), 2.29–2.36 (m, 1H), 2.62–2.69 (m, 1H), 2.90–3.02 (m, 2H), 3.75 (s, 1H), 5.56 (s, 1H), 7.25–7.28 (m, 3H), 7.52–7.55 (m, 2H); δ_C (100 MHz, $CDCl_3$) 0.2, 26.1, 28.3, 35.8, 36.1, 82.4, 127.1, 127.6, 129.0, 129.8, 133.3, 158.9; δ_{Se} (76 MHz, $CDCl_3$) 308.6; ν_{max} (neat) 3476, 3059, 2955, 2870, 1609, 1477, 1439, 1250, 1007, 860, 841, 737, 691 cm^{-1}; *m*/*z* (EI) 73 (99), 213 (100), 313 (83), 355 (27), 370 (37%, M^+). HRMS (EI): M^+, found 370.1235. $C_{18}H_{30}OSi^{80}Se$ requires 370.1231.

*4.4.5. (E)-2-[(tert-Butyldimethylsilyl)methylene]-1-phenyl-4-(phenylselanyl)butan-1-ol (**7ba**).* Pale yellow oil, 89% yield; δ_H (400 MHz, $CDCl_3$) 0.037 (s, 3H), 0.042 (s, 3H), 0.88 (s, 9H), 1.97 (br s, 1H),

2.26–2.33 (m, 1H), 2.46–2.53 (m, 1H), 2.81 (t, *J*=8.6 Hz, 2H), 5.15 (s, 1H), 5.90 (s, 1H), 7.24–7.33 (m, 8H), 7.41–7.44 (m, 2H); δ_C (100 MHz, $CDCl_3$) −4.4, −4.3, 17.0, 26.5, 27.3, 33.9, 78.6, 122.6, 126.7, 127.0, 127.8, 128.5, 129.0, 129.7, 133.2, 142.0, 158.4; δ_{Se} (76 MHz, $CDCl_3$) 314.9; ν_{max} (neat) 3429, 3059, 2951, 2855, 1616, 1578, 1474, 1250, 1022, 826, 737, 698 cm^{-1}; *m*/*z* (EI) 143 (35), 187 (19), 217 (15), 375 (100), 417 (2), 432 (1%, M^+). HRMS (EI): M^+, found 432.1379. $C_{23}H_{32}OSi^{80}Se$ requires 432.1388.

*4.4.6. (E)-3-[(tert-Butyldimethylsilyl)methylene]-1-(phenylselanyl) nonan-4-ol (**7bb**).* Mixture of regioisomers (**7bb**:**8bb**=80:20). Pale yellow oil, 87% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.02 (s, 6H), 0.85 (s, 9H), 0.85–0.89 (m, 3H), 1.26–1.62 (m, 12H), 2.38–2.46 (m, 1H), 2.52–2.64 (m, 1H), 2.88–3.04 (m, 2H), 4.07 (dd, *J*=5.5, 6.9 Hz, 1H), 5.58 (s, 1H), 7.24–7.39 (m, 3H), 7.50–7.55 (m, 2H); δ_{Se} (76 MHz, $CDCl_3$) 313.3; ν_{max} (neat) 3422, 3059, 2928, 2855, 1612, 1578, 1470, 1250, 1022, 837, 737, 691 cm^{-1}; *m*/*z* (EI) 369 (100), 411 (3), 426 (2%, M^+). HRMS (EI): M^+, found 426.1861. $C_{22}H_{38}OSi^{80}Se$ requires 426.1857.

*4.4.7. (Z)-4-(tert-Butyldimethylsilyl)-1-(phenylselanyl)dec-3-en-5-ol (**8bb**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$) 0.06 (s, 3H), 0.10 (s, 3H), 0.88 (s, 9H), 0.85–0.89 (m, 3H), 1.26–1.62 (m, 12H), 2.38–2.46 (m, 1H), 2.52–2.64 (m, 1H), 2.88–3.04 (m, 2H), 4.08–4.13 (m, 1H), 6.41 (t, *J*=7.3 Hz, 1H), 7.24–7.39 (m, 3H), 7.50–7.55 (m, 2H); δ_{Se} (76 MHz, $CDCl_3$) 302.0.

*4.4.8. (E)-4-[(tert-Butyldimethylsilyl)methylene]-2,2-dimethyl-6-(phenylselanyl)hexan-3-ol (**7bc**).* Pale yellow oil, 47% yield; δ_H (400 MHz, $CDCl_3$) 0.03 (s, 3H), 0.05 (s, 3H), 0.86 (s, 9H), 0.87 (s, 9H), 1.60 (br s, 1H), 2.28–2.35 (m, 1H), 2.63–2.71 (m, 1H), 2.90–3.00 (m, 2H), 3.77 (s, 1H), 5.59 (s, 1H), 7.26–7.30 (m, 3H), 7.52–7.55 (m, 2H); δ_C (100 MHz, $CDCl_3$) −4.2, 17.0, 26.2, 26.5, 28.2, 36.0, 36.4, 82.4, 124.5, 127.1, 129.0, 129.8, 133.3, 160.1; δ_{Se} (76 MHz, $CDCl_3$) 309.6; ν_{max} (neat) 3476, 3059, 2943, 2855, 1609, 1578, 1477, 1250, 1007, 837, 737, 698 cm^{-1}; *m*/*z* (EI) 73 (65), 75 (91), 215 (11), 285 (6), 355 (100), 412 (1%, M^+). HRMS (EI): M^+, found 412.1695. $C_{21}H_{36}OSi^{80}Se$ requires 412.1701.

*4.4.9. (E)-2-[(Dimethylphenylsilyl)methylene]-1-phenyl-4-(phenylselanyl)butan-1-ol (**7ca**).* Pale yellow oil, 78% yield; δ_H (400 MHz, $CDCl_3$) 0.36 (s, 6H), 2.01 (br s, 1H), 2.18–2.25 (m, 1H), 2.37–2.44 (m, 1H), 2.53–2.66 (m, 2H), 5.13 (s, 1H), 6.06 (s, 1H), 7.17–7.35 (m, 13H), 7.49–7.52 (m, 2H); δ_C (100 MHz, $CDCl_3$) −1.09, −1.06, 26.7, 33.9, 78.4, 123.3, 126.80, 126.85, 127.88, 127.92, 128.5, 128.95, 129.01, 129.8, 132.9, 133.7, 139.1, 141.8, 159.2; δ_{Se} (76 MHz, $CDCl_3$) 315.7; ν_{max} (neat) 3425, 3067, 2955, 1612, 1578, 1477, 1250, 1111, 1022, 833, 733, 698 cm^{-1}; *m*/*z* (EI) 135 (100), 203 (41), 217 (60), 295 (30), 437 (3), 452 (2%, M^+). HRMS (EI): M^+, found 452.1077. $C_{25}H_{28}OSi^{80}Se$ requires 452.1075.

*4.4.10. (E)-3-[(Dimethylphenylsilyl)methylene]-1-(phenylselanyl) nonan-4-ol (**7cb**).* Mixture of regioisomers (**7cb**:**8cb**=64:36). Pale yellow oil, 61% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.32 (s, 6H), 0.87 (t, *J*=6.1 Hz, 3H), 1.25–1.53 (m, 8H), 1.71 (br s, 1H), 2.30–2.38 (m, 1H), 2.47–2.55 (m, 1H), 2.75–2.81 (m, 2H), 4.05 (dd, *J*=4.9, 7.3 Hz, 1H), 5.73 (d, *J*=1.0 Hz, 1H), 7.18–7.49 (m, 10H); δ_{Se} (76 MHz, $CDCl_3$) 313.5; ν_{max} (neat) 3425, 3067, 2955, 2928, 2858, 1612, 1578, 1477, 1427, 1250, 1111, 1022, 837, 733, 698 cm^{-1}; *m*/*z* (EI) 135 (99), 197 (40), 211 (98), 289 (34), 446 (12%, M^+). HRMS (EI): M^+, found 446.1553. $C_{25}H_{28}OSi^{80}Se$ requires 446.1544.

*4.4.11. (Z)-4-(Dimethylphenylsilyl)-1-(phenylselanyl)dec-3-en-5-ol (**8cb**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$) 0.37 (s, 6H), 0.87 (t, *J*=6.1 Hz, 3H), 1.25–1.53 (m, 8H), 1.71 (br s, 1H), 2.30–2.38 (m, 2H), 2.70 (t, *J*=7.4 Hz, 2H), 4.14 (dd, *J*=4.8, 7.2 Hz, 1H), 6.27 (t, *J*=7.4 Hz, 1H), 7.18–7.49 (m, 10H); δ_{Se} NMR (76 MHz, $CDCl_3$) 300.5.

*4.4.12. (E)-4-[(Dimethylphenylsilyl)methylene]-2,2-dimethyl-6-(phenylselanyl)hexan-3-ol (**7cc**).* Pale yellow oil, 43% yield; δ_H (400 MHz, $CDCl_3$) 0.35 (s, 6H), 0.86 (s, 9H), 1.61 (br s, 1H), 2.20–2.27 (m, 1H), 2.54–2.62 (m, 1H), 2.71–2.84 (m, 2H), 3.76 (s, 1H), 5.74 (s, 1H), 7.22–7.23 (m, 3H), 7.33–7.35 (m, 3H), 7.41–7.44 (m, 2H), 7.49–7.51 (m, 2H); δ_C (100 MHz, $CDCl_3$) −1.0, 26.2, 27.8, 35.9, 36.1, 82.5, 125.6, 126.9, 127.9, 129.0, 129.9, 133.0, 133.7, 139.2, 160.8; δ_{Se} (76 MHz, $CDCl_3$) 308.7; ν_{max} (neat) 3464, 3067, 2955, 2870, 1607, 1578, 1477, 1250, 1111, 1007, 833, 733, 698 cm^{-1}; *m*/*z* (EI) 75 (43), 135 (100), 197 (50), 297 (47), 417 (6), 432 (7%, M^+). HRMS (EI): M^+, found 432.1387. $C_{23}H_{32}OSi^{80}Se$ requires 432.1388.

*4.4.13. (E)-1,2-Diphenyl-5-(phenylselanyl)pent-2-en-1-ol (**8da**).* Mixture of regioisomers (**7da**:**8da**=17:83). Pale yellow oil, 68% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 1.96 (br s, 1H), 2.35 (q, *J*=7.6 Hz, 2H), 2.90 (t, *J*=7.6 Hz, 2H), 5.39 (s, 1H), 5.91 (td, *J*=1.0, 7.6 Hz, 1H), 6.87–6.89 (m, 2H), 7.18–7.39 (m, 13H); δ_{Se} (76 MHz, $CDCl_3$) 297.1; ν_{max} (neat) 3414, 3055, 3028, 2928, 2870, 1578, 1477, 1439, 1072, 1022, 733, 702 cm^{-1}; *m*/*z* (EI) 237 (100), 287 (17), 394 (26%, M^+). HRMS (EI): M^+, found 394.0839. $C_{23}H_{22}O^{80}Se$ requires 394.0836.

*4.4.14. (E)-2-Benzylidene-1-phenyl-4-(phenylselanyl)butan-1-ol (**7da**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 2.46–2.54 (m, 1H), 2.57–2.65 (m, 1H), 2.70–2.88 (m, 2H), 5.32 (s, 1H), 6.81 (s, 1H); δ_{Se} (76 MHz, $CDCl_3$) 314.8.

*4.4.15. (E)-4-Phenyl-1-(phenylselanyl)dec-3-en-5-ol (**8db**).* Mixture of regioisomers (**7db**:**8db**=14:86). Pale yellow oil, 75% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.84–0.90 (m, 3H), 1.23–1.55 (m, 8H), 1.63 (br s, 1H), 2.87 (q, *J*=7.3 Hz, 2H), 2.88 (t, *J*=7.3 Hz, 2H), 4.26 (s, 1H), 5.71 (t, *J*=7.3 Hz, 1H), 7.10–7.40 (m, 10H); δ_{Se} (76 MHz, $CDCl_3$) 297.1; ν_{max} (neat) 3418, 3055, 2955, 2858, 1578, 1439, 1022, 737, 702 cm^{-1}; *m*/*z* (EI) 231 (100), 289 (55), 388 (42%, M^+). HRMS (EI): M^+, found 388.1299. $C_{22}H_{28}O^{80}Se$ requires 388.1305.

*4.4.16. (E)-4-Benzylidene-2,2-dimethyl-6-(phenylselanyl)hexan-3-ol (**7db**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signal: 6.54 (s, 1H); δ_{Se} (76 MHz, $CDCl_3$) 314.1.

*4.4.17. (E)-2,2-Dimethyl-4-phenyl-7-(phenylselanyl)hept-4-en-3-ol (**8dc**).* Mixture of regioisomers (**7dc**:**8dc**=43:57). Pale yellow oil, 63% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.79 (s, 9H), 1.64 (br s, 1H), 2.39–2.59 (m, 2H), 2.87–2.94 (m, 2H), 4.14 (s, 1H), 5.75 (t, *J*=7.4 Hz, 1H), 7.16–7.39 (m, 10H); δ_{Se} (76 MHz, $CDCl_3$) 296.8; ν_{max} (neat) 3464, 3055, 3020, 2955, 2866, 1578, 1477, 1439, 1003, 737, 702 cm^{-1}; *m*/*z* (EI) 159 (100), 317 (83), 374 (51%, M^+). HRMS (EI): M^+, found 374.1146. $C_{21}H_{26}O^{80}Se$ requires 374.1149.

*4.4.18. (E)-4-Benzylidene-2,2-dimethyl-6-(phenylselanyl)hexan-3-ol (**7dc**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$) 0.95 (s, 9H), 1.64 (br s, 1H), 2.39–2.59 (m, 2H), 2.87–2.94 (m, 2H), 3.91 (s, 1H), 6.53 (s, 1H), 7.16–7.39 (m, 10H); δ_{Se} (76 MHz, $CDCl_3$) 308.9.

4.5. General procedure for carbotitanation of internal alkynes with low-valent titanium reagent and various imines

To a solution of an internal alkynes **3** (0.30 mmol) and Ti(O-*i*-Pr)$_4$ (0.153 g, 0.54 mmol) in Et_2O (10 mL) was added *i*-PrMgCl (2.0 M solution in Et_2O, 0.6 mL, 1.2 mmol) dropwise at −78 °C. The reaction mixture was warmed up to −50 °C over 30 min and stirred for 2 h at this temperature. Then an imine (0.5 mmol) was added at −50 °C. After stirring for 1 h, the mixture was slowly warmed up to

−10 °C and quenched with H_2O. The organic layer was separated and the aqueous layer was further extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel to afford allyl amine **11** and **12**.

*4.5.1. (E)-N-Benzyl-1-phenyl-4-(phenylselanyl)-2-[(trimethylsilyl) methylene]butan-1-amine (**11ad**).* Pale yellow oil, 61% yield; δ_H (400 MHz, $CDCl_3$) 0.07 (s, 9H), 2.22–2.29 (m, 1H), 2.41–2.48 (m, 1H), 2.68–2.76 (m, 2H), 3.65 (d, *J*=5.6 Hz, 2H), 4.13 (s, 1H), 5.90 (d, *J*=1.0 Hz, 1H), 7.19–7.34 (m, 13H), 7.38–7.41 (m, 2H); δ_C (100 MHz, $CDCl_3$) 0.2, 27.3, 34.8, 51.6, 68.3, 125.4, 126.9, 127.0, 127.3, 127.7, 128.2, 128.37, 128.38, 129.0, 129.8, 133.3, 140.4, 142.1, 157.4; δ_{Se} (76 MHz, $CDCl_3$) 314.7; ν_{max} (neat) 3059, 3024, 2951, 1609, 1454, 1250, 837, 737, 698 cm^{-1}; *m*/*z* (EI) 196 (100), 322 (16), 388 (27), 406 (7), 479 (30%, M^+). HRMS (EI): M^+, found 479.1544. $C_{27}H_{33}NSi^{80}Se$ requires 479.1747.

*4.5.2. (E)-1-Phenyl-4-(phenylselanyl)-N-propyl-2-[(trimethylsilyl) methylene]butan-1-amine (**11ae**).* Pale yellow oil, 72% yield; δ_H (400 MHz, $CDCl_3$) 0.11 (s, 9H), 0.88 (t, *J*=7.7 Hz, 3H), 1.48 (sext, *J*=7.7 Hz, 2H), 2.23–2.29 (m, 1H), 2.37–2.48 (m, 3H), 2.74–2.79 (m, 2H), 4.09 (s, 1H), 5.84 (s, 1H), 7.18–7.29 (m, 8H), 7.41–7.44 (m, 2H); δ_C (100 MHz, $CDCl_3$) 0.2, 11.8, 23.2, 27.3, 34.9, 49.8, 69.3, 124.8, 126.9, 127.2, 127.7, 128.3, 129.0, 129.8, 133.2, 142.4, 157.6; δ_{Se} (76 MHz, $CDCl_3$) 314.7; ν_{max} (neat) 3058, 3024, 2955, 1612, 1582, 1477, 1454, 1250, 837, 733, 698 cm^{-1}; *m*/*z* (EI) 58 (64), 73 (26), 84 (50), 148 (100), 200 (24), 273 (17), 431 (10%, M^+). HRMS (EI): M^+, found 431.1546. $C_{23}H_{33}NSi^{80}Se$ requires 431.1547.

*4.5.3. (E)-N-Benzyl-1-(phenylselanyl)-3-[(trimethylsilyl)methylene] nonan-4-amine (**11af**).* Colorless liquid, 57% yield; δ_H (400 MHz, $CDCl_3$) 0.07 (s, 9H), 0.85 (t, *J*=7.0 Hz, 3H), 1.19–1.46 (m, 9H), 2.38 (td, *J*=5.2, 12.6 Hz, 1H), 2.53 (td, *J*=5.2, 12.6 Hz, 1H), 2.88 (td, *J*=5.2, 12.6 Hz, 1H), 2.94–3.01 (m, 3H), 3.62 (ABq, *J*=13.4 Hz, 2H), 5.53 (s, 1H), 7.23–7.30 (m, 8H), 7.48–7.50 (m, 2H); δ_C (100 MHz, $CDCl_3$) 0.2, 14.0, 22.5, 26.0, 27.5, 31.8, 34.4, 35.5, 51.4, 65.5, 126.3, 126.8, 126.9, 128.1, 128.3, 129.0, 129.9, 133.2, 140.7, 158.3; δ_{Se} (76 MHz, $CDCl_3$) 315.0; ν_{max} (neat) 3059, 3028, 2955, 2928, 2855, 1609, 1578, 1454, 1246, 853, 694 cm^{-1}; *m*/*z* (EI) 91 (94), 190 (91), 244 (100), 402 (16), 473 (2%, M^+). HRMS (EI): M^+, found 473.2022. $C_{26}H_{39}NSi^{80}Se$ requires 473.2017.

*4.5.4. (E)-N-Benzyl-2-[(tert-butyldimethylsilyl)methylene]-1-phenyl-4-(phenylselanyl)butan-1-amine (**11bd**).* Pale yellow oil, 71% yield; δ_H (400 MHz, $CDCl_3$) 0.03 (s, 3H), 0.04 (s, 3H), 0.88 (s, 9H), 2.22–2.27 (m, 1H), 2.42–2.50 (m, 1H), 2.67–2.78 (m, 2H), 3.67 (ABq, *J*=13.4 Hz, 2H), 4.14 (s, 1H), 5.98 (s, 1H), 7.19–7.34 (m, 13H), 7.39–7.41 (m, 2H); δ_C (100 MHz, $CDCl_3$) −4.3, −4.2, 17.1, 26.6, 27.3, 34.8, 51.6, 68.5, 122.4, 126.92, 126.94, 127.2, 127.7, 128.1, 128.33, 128.35, 128.9, 129.8, 133.3, 140.4, 142.3, 157.9; δ_{Se} (76 MHz, $CDCl_3$) 315.3; ν_{max} (neat) 3069, 3028, 2928, 2855, 1612, 1454, 1250, 833, 737 cm^{-1}; *m*/*z* (EI) 196 (100), 248 (44), 364 (9), 521 (12%, M^+). HRMS (EI): M^+, found 521.2012. $C_{30}H_{39}NSi^{80}Se$ requires 521.2017.

*4.5.5. (E)-2-[(tert-Butyldimethylsilyl)methylene]-1-phenyl-4-(phenylselanyl)-N-propylbutan-1-amine (**11be**).* Pale yellow oil, 65% yield; δ_H (400 MHz, $CDCl_3$) 0.02 (s, 3H), 0.03 (s, 3H), 0.88 (m, 9H), 0.88 (t, *J*=7.3 Hz, 3H), 1.48 (sextd, *J*=2.0, 7.3 Hz, 2H), 2.20–2.27 (m, 1H), 2.38–2.52 (m, 3H), 2.73–2.80 (m, 2H), 4.10 (s, 1H), 5.90 (s, 1H), 7.20–7.28 (m, 8H), 7.43–7.45 (m, 2H); δ_C (100 MHz, $CDCl_3$) −4.3, −4.2, 11.8, 17.1, 23.2, 26.6, 27.4, 35.0, 49.8, 69.6, 121.9, 126.9, 127.2, 127.6, 128.3, 129.0, 129.9, 133.2, 142.5, 158.1; δ_{Se} (76 MHz, $CDCl_3$) 315.2; ν_{max} (neat) 3059, 3024, 2955, 2928, 2855, 1612, 1458, 1250, 833, 733, 702 cm^{-1}; *m*/*z* (EI) 58 (78), 148 (100), 200 (46), 315 (20), 473 (17%, M^+). HRMS (EI): M^+, found 473.2020. $C_{26}H_{39}NSi^{80}Se$ requires 473.2017.

*4.5.6. (E)-N-Benzyl-3-[(tert-butyldimethylsilyl)methylene]-1-(phenylselanyl)nonan-4-amine (**11bf**).* Mixture of regioisomers (**11bf**:**12bf** =96:4). Pale yellow oil, 62% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.03 (s, 6H), 0.85 (t, *J*=7.2 Hz, 3H), 0.87 (s, 9H), 1.19–1.48 (m, 9H), 2.37 (td, *J*=5.6, 12.8 Hz, 1H), 2.54 (td, *J*=5.6, 12.8 Hz, 1H), 2.87–3.04 (m, 3H), 3.63 (ABq, *J*=13.2 Hz, 2H), 5.57 (s, 1H), 7.22–7.30 (m, 8H), 7.48–7.50 (m, 2H); δ_C (100 MHz, $CDCl_3$) −4.25, −4.21, 14.0, 17.0, 22.6, 26.0, 26.5, 27.5, 31.8, 34.7, 35.7, 51.4, 65.6, 123.2, 126.9, 128.2, 128.4, 129.0, 129.9, 133.2, 140.6, 158.9; δ_{Se} (76 MHz, $CDCl_3$) 315.6; ν_{max} (neat) 3063, 3028, 2951, 2855, 1609, 1462, 1250, 837, 733, 694 cm^{-1}; *m*/*z* (EI) 91 (81), 190 (62), 244 (72), 286 (100), 515 (1%, M^+). HRMS (EI): M^+, found 515.2491. $C_{29}H_{45}NSi^{80}Se$ requires 515.2486.

*4.5.7. (Z)-N-Benzyl-4-(tert-butyldimethylsilyl)-1-(phenylselanyl)dec-3-en-5-amine (**12bf**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signal: 6.44 (t, *J*=7.4 Hz, 1H).

*4.5.8. (E)-N-Benzyl-2-[(dimethylphenylsilyl)methylene]-1-phenyl-4-(phenylselanyl)butan-1-amine (**11cd**).* Pale yellow oil, 56% yield; δ_H (400 MHz, $CDCl_3$) 0.35 (s, 6H), 2.14–2.21 (m, 1H), 2.34–2.42 (m, 1H), 2.47–2.58 (m, 2H), 3.66 (ABq, *J*=13.4 Hz, 2H), 4.14 (s, 1H), 6.12 (s, 1H), 7.16–7.34 (m, 18H), 7.47–7.50 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.97, −0.89, 26.7, 35.0, 51.6, 68.4, 123.1, 126.8, 126.9, 127.3, 127.7, 127.8, 128.1, 128.35, 128.37, 128.88, 128.90, 129.9, 133.0, 133.7, 139.4, 140.3, 141.9, 159.1; δ_{Se} (76 MHz, $CDCl_3$) 316.0; ν_{max} (neat) 3063, 3024, 2951, 2847, 1609, 1578, 1454, 1250, 1111, 837, 733, 698 cm^{-1}; *m*/*z* (EI) 248 (100), 307 (14), 383 (38), 541 (3%, M^+). HRMS (EI): M^+, found 541.1706. $C_{32}H_{35}NSi^{80}Se$ requires 541.1704.

*4.5.9. (E)-2-[(Dimethylphenylsilyl)methylene]-1-phenyl-4-(phenylselanyl)-N-propylbutan-1-amine (**11ce**).* Pale yellow oil, 69% yield; δ_H (400 MHz, $CDCl_3$) 0.34 (s, 6H), 0.87 (t, *J*=7.4 Hz, 3H), 1.41 (br s, 1H), 1.42–1.52 (m, 2H), 2.14–2.21 (m, 1H), 2.34–2.42 (m, 2H), 2.44–2.64 (m, 3H), 4.09 (s, 1H), 6.04 (d, *J*=1.0 Hz, 1H), 7.17–7.33 (m, 13H), 7.48–7.50 (m, 2H); δ_C (100 MHz, $CDCl_3$) −1.0, −0.9, 11.8, 23.2, 26.7, 35.0, 49.8, 69.4, 122.4, 126.7, 127.2, 127.6, 127.7, 128.3, 128.8, 128.9, 129.9, 132.8, 132.9, 133.7, 139.5, 142.3, 159.6; δ_{Se} (76 MHz, $CDCl_3$) 316.0; ν_{max} (neat) 3067, 2955, 2932, 1609, 1477, 1454, 1250, 1111, 833, 733, 698 cm^{-1}; *m*/*z* (EI) 135 (54), 148 (100), 200 (99), 306 (68), 335 (34), 493 (10%, M^+). HRMS (EI): M^+, found 493.1705. $C_{28}H_{35}NSi^{80}Se$ requires 493.1704.

*4.5.10. (E)-N-Benzyl-3-[(dimethylphenylsilyl)methylene]-1-(phenylselanyl)nonan-4-amine (**11cf**).* Pale yellow oil, 60% yield; δ_H (400 MHz, $CDCl_3$) 0.34 (s, 6H), 0.86 (t, *J*=7.1 Hz, 3H), 1.21–1.44 (m, 9H), 2.31 (td, *J*=5.6, 12.4 Hz, 1H), 2.47 (td, *J*=5.6, 12.4 Hz, 1H), 2.75 (td, *J*=5.6, 12.4 Hz, 2H), 3.03 (t, *J*=7.1 Hz, 1H), 3.64 (ABq, *J*=13.2 Hz, 2H), 5.72 (s, 1H), 7.17–7.38 (m, 13H), 7.50–7.52 (m, 2H); δ_C (100 MHz, $CDCl_3$) −1.0, −0.9, 14.0, 22.6, 26.0, 26.9, 31.8, 34.6, 35.5, 51.5, 65.5, 124.0, 126.7, 126.8, 127.8, 128.1, 128.3, 128.86, 128.93, 130.0, 132.76, 132.81, 132.9, 133.7, 129.6, 140.7, 160.4; δ_{Se} (76 MHz, $CDCl_3$) 315.7; ν_{max} (neat) 3067, 3024, 2955, 2928, 2855, 1609, 1578, 1454, 1427, 1250, 1111, 837, 698 cm^{-1}; *m*/*z* (EI) 91 (98), 190 (100), 306 (99), 535 (1%, M^+). HRMS (EI): M^+, found 535.2179. $C_{31}H_{41}NSi^{80}Se$ requires 535.2173.

*4.5.11. (E)-N-Benzyl-1,2-diphenyl-5-(phenylselanyl)pent-2-en-1-amine (**12dd**).* Mixture of regioisomers (**11dd**:**12dd**=9:91). Pale yellow oil, 49% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 2.34 (q, *J*=7.4 Hz, 2H), 2.89 (t, *J*=7.4 Hz, 2H), 3.71–3.86 (m, 2H), 4.43 (s, 1H), 5.89 (t, *J*=7.4 Hz, 1H), 6.79–6.81 (m, 2H), 7.16–7.34 (m, 18H); δ_{Se} (76 MHz, $CDCl_3$) 295.7; ν_{max} (neat) 3059, 3024, 2928, 1578, 1493, 1477, 1454, 1119, 1072, 1026, 737, 698 cm^{-1}; *m*/*z* (EI) 91 (99), 196

(100), 326 (28), 483 (7%, M^+). HRMS (EI): M^+, found 483.1460. $C_{30}H_{29}N^{80}Se$ requires 483.1465.

*4.5.12. (E)-N-Benzyl-2-benzylidene-1-phenyl-4-(phenylselanyl)butan-1-amine (**11dd**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 4.31 (s, 1H), 6.88 (s, 1H); δ_{Se} (76 MHz, $CDCl_3$) 316.6.

*4.5.13. (E)-1,2-Diphenyl-5-(phenylselanyl)-N-propylpent-2-en-1-amine (**12de**).* Mixture of regioisomers (**11de**:**12de**=19:81). Pale yellow oil, 43% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.90 (t, J=7.4 Hz, 3H), 1.40 (br s, 1H), 1.48–1.54 (m, 2H), 2.31 (q, J=7.4 Hz, 2H), 2.47–2.68 (m, 2H), 2.88 (t, J=7.4 Hz, 2H), 4.37 (s, 1H), 5.84 (t, J=7.4 Hz, 1H), 6.78–6.79 (m, 2H), 7.16–7.33 (m, 13H); δ_{Se} (76 MHz, $CDCl_3$) 296.3; ν_{max} (neat) 3055, 3024, 2959, 2928, 2870, 1578, 1477, 1454, 1072, 1022, 737, 702 cm^{-1}; m/z (EI) 91 (58), 148 (100), 250 (49), 278 (48), 435 (33%, M^+). HRMS (EI): M^+, found 435.1475. $C_{26}H_{29}N^{80}Se$ requires 435.1465.

*4.5.14. (E)-2-Benzylidene-1-phenyl-4-(phenylselanyl)-N-propylbutan-1-amine (**11de**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 4.25 (s, 1H), 6.83 (s, 1H); δ_{Se} (76 MHz, $CDCl_3$) 316.6.

*4.5.15. (E)-N-Benzyl-4-phenyl-1-(phenylselanyl)dec-3-en-5-amine (**12df**).* Mixture of regioisomers (**11df**:**12df**=14:86). Pale yellow oil 32% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.85 (t, J=7.0 Hz, 3H), 1.24–1.53 (m, 9H), 2.33 (q, J=7.5 Hz, 2H), 2.86–2.94 (m, 3H), 3.86 (ABq, J=13.2 Hz, 2H), 5.59 (t, J=7.5 Hz, 1H), 7.07–7.41 (m, 15H); δ_{Se} (76 MHz, $CDCl_3$) 295.1; ν_{max} (neat) 3059, 3024, 2928, 2855, 1578, 1492, 1454, 1072, 1022, 733, 698 cm^{-1}; m/z (EI) 91 (75), 190 (55), 248 (87), 320 (13), 406 (100), 477 (2%, M^+). HRMS (EI): M^+, found 477.1937. $C_{26}H_{29}N^{80}Se$ requires 477.1935.

*4.5.16. (E)-N-Benzyl-3-benzylidene-1-(phenylselanyl)nonan-4-amine (**11df**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 3.72 (ABq, J=13.2 Hz, 1H), 6.48 (s, 1H); δ_{Se} (76 MHz, $CDCl_3$) 318.4.

4.6. General procedure for oxidative deselenation of allylic selenides

To a solution of allylic selenides (0.15 mmol) in THF (2 mL) was added 10 equiv of H_2O_2 (30% in H_2O) at 0 °C. After stirring for 4 h at this temperature, the reaction was quenched with satd $NaHCO_3$ and extracted with ether. The combined organic layers were washed with brine, dried over $MgSO_4$, concentrated, and purified by column chromatography on silica gel to afford conjugated dienes.

*4.6.1. (E)-1-Phenyl-2-[(trimethylsilyl)methylene]but-3-en-1-ol (**9aa**).* Pale yellow oil, 98% yield; δ_H (400 MHz, $CDCl_3$) 0.20 (s, 9H), 1.98 (br s, 1H), 5.10 (d, J=11.2 Hz, 1H), 5.15 (d, J=17.6 Hz, 1H), 5.51 (s, 1H), 6.12 (s, 1H), 6.56 (dd, J=11.2, 17.6 Hz, 1H), 7.28–7.38 (m, 5H); δ_C (100 MHz, $CDCl_3$) 0.2, 74.9, 116.4, 127.0, 127.8, 128.5, 130.4, 135.4, 142.4, 153.9; ν_{max} (neat) 3356, 3090, 3063, 3028, 2955, 2897, 1566, 1454, 1250, 988, 837, 768, 698 cm^{-1}; m/z (EI) 73 (100), 107 (63), 216 (9), 232 (17%, M^+). HRMS (EI): M^+, found 232.1280. $C_{14}H_{20}OSi$ requires 232.1283.

*4.6.2. (E)-3-[(Trimethylsilyl)methylene]non-1-en-4-ol (**9ab**).* Mixture of regioisomers (**9ab**:**10ab**=93:7). Colorless liquid, 75% yield; Minor regioisomer (**10ab**) was not isolated by column chromatography on silica gel; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.15 (s, 9H), 0.89 (t, J=7.6 Hz, 3H), 1.25–1.51 (m, 7H), 1.63–1.70 (m, 2H), 4.46 (dd, J=3.9, 7.6 Hz, 1H), 5.16 (d, J=11.2 Hz, 1H), 5.30 (d, J=17.8 Hz, 1H), 5.85 (s, 1H), 6.57 (dd, J=11.2, 17.8 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 0.01, 14.0, 22.6, 25.6, 31.7, 37.0, 72.2, 114.8, 128.1, 135.9, 156.5; ν_{max} (neat) 3348, 3090, 2955, 2932, 2858, 1566, 1250, 906, 852, 768, 691 cm^{-1}; m/z (EI) 73 (79), 139 (12), 156 (70), 226 (4%, M^+). HRMS (EI): M^+, found 226.1757. $C_{13}H_{26}OSi$ requires 226.1753.

*4.6.3. (E)-2,2-Dimethyl-6-(phenylselanyl)-4-[(trimethylsilyl)methylene]hexan-3-ol (**9ac**).* Pale yellow oil, 69% yield; δ_H (400 MHz, $CDCl_3$) 0.16 (s, 9H), 0.90 (s, 9H), 1.55 (br s, 1H), 4.31 (s, 1H), 5.14 (d, J=11.2 Hz, 1H), 5.32 (d, J=17.6 Hz, 1H), 5.79 (s, 1H), 6.60 (dd, J=11.2, 17.6 Hz, 1H); δ_C (100 MHz, $CDCl_3$) 0.3, 26.4, 35.5, 77.7, 115.2, 131.0, 138.0, 155.3; ν_{max} (neat) 3472, 2955, 2905, 1558, 1477, 1362, 1250, 991, 841, 756, 691 cm^{-1}; m/z (EI) 75 (100), 140 (23), 156 (3), 212 (5%, M^+). HRMS (EI): M^+, found 212.1599. $C_{12}H_{24}OSi$ requires 212.1596.

*4.6.4. (E)-2-[(tert-Butyldimethylsilyl)methylene]-1-phenylbut-3-en-1-ol (**9ba**).* Pale yellow oil, 94% yield; δ_H (270 MHz, $CDCl_3$) 0.18 (s, 3H), 0.19 (s, 3H), 0.94 (s, 9H), 2.00 (br s, 1H), 5.10 (d, J=13.5 Hz, 1H), 5.18 (d, J=16.2 Hz, 1H), 5.55 (d, J=2.7 Hz, 1H), 6.14 (s, 1H), 6.58 (dd, J=13.5, 16.2 Hz, 1H), 7.26–7.39 (m, 5H); δ_C (68 MHz, $CDCl_3$) −4.0, −3.9, 17.3, 26.5, 75.0, 116.3, 127.0, 127.7, 128.0, 128.5, 135.7, 142.5, 154.7; ν_{max} (neat) 3402, 3063, 3028, 2951, 2855, 1566, 1470, 1250, 906, 779, 698 cm^{-1}; m/z (EI) 107 (52), 145 (46), 173 (98), 218 (100), 259 (4), 274 (3%, M^+). HRMS (EI): M^+, found 274.1757. $C_{17}H_{26}OSi$ requires 274.1753.

*4.6.5. (E)-3-[(tert-Butyldimethylsilyl)methylene]non-1-en-4-ol (**9bb**).* Mixture of regioisomers (**9bb**:**10bb**=80:20). Pale yellow oil, 81% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.13 (d, J=7.1 Hz, 6H), 0.89 (t, J=7.1 Hz, 3H), 0.91 (s, 9H), 1.26–1.72 (m, 9H), 4.51 (dd, J=4.1, 7.6 Hz, 1H), 5.16 (dt, J=1.1, 11.4 Hz, 1H), 5.30 (d, J=17.9 Hz, 1H), 5.88 (s, 1H), 6.58 (dd, J=11.4, 17.9 Hz, 1H); ν_{max} (neat) 3356, 3090, 2955, 2928, 2858, 1566, 1466, 1250, 907, 833, 779, 687 cm^{-1}; m/z (EI) 141 (97), 194 (95), 211 (75), 268 (10%, M^+). HRMS (EI): M^+, found 268.2220. $C_{16}H_{32}OSi$ requires 268.2222.

*4.6.6. (Z)-4-(tert-Butyldimethylsilyl)deca-1,3-dien-5-ol (**10bb**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 0.15 (s, 3H), 0.23 (s, 3H), 0.93 (s, 9H), 4.25 (d, J=8.3 Hz, 1H), 7.00 (d, J=11.2 Hz, 1H).

*4.6.7. (E)-4-[(tert-Butyldimethylsilyl)methylene]-2,2-dimethylhex-5-en-3-ol (**9bc**).* Pale yellow oil, 92% yield; δ_H (400 MHz, $CDCl_3$) 0.12 (s, 3H), 0.16 (s, 3H), 0.91 (s, 18H), 1.58 (br s, 1H), 4.37 (s, 1H), 5.14 (d, J=11.6 Hz, 1H), 5.33 (d, J=17.6 Hz, 1H), 5.84 (s, 1H), 6.63 (dd, J=11.6, 17.6 Hz, 1H); δ_C (100 MHz, $CDCl_3$) −4.0, −3.8, 17.2, 26.47, 26.50, 35.7, 77.5, 115.0, 128.5, 138.3, 156.2; ν_{max} (neat) 3472, 2955, 2858, 1558, 1466, 1362, 1254, 826 cm^{-1}; m/z (EI) 180 (60), 197 (46), 254 (1%, M^+). HRMS (EI): M^+, found 254.2070. $C_{15}H_{30}OSi$ requires 254.2066.

*4.6.8. (E)-2-[(Dimethylphenylsilyl)methylene]-1-phenylbut-3-en-1-ol (**9ca**).* Pale yellow oil, 78% yield; δ_H (400 MHz, $CDCl_3$) 0.45 (s, 6H), 2.02 (br s, 1H), 5.02 (d, J=11.5 Hz, 1H), 5.14 (d, J=17.8 Hz, 1H), 5.54 (s, 1H), 6.28 (s, 1H), 6.48 (dd, J=11.5, 17.8 Hz, 1H), 7.25–7.39 (m, 8H), 7.55–7.57 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.68, −0.72, 74.9, 116.9, 127.0, 127.7, 127.9, 128.6, 129.0, 133.8, 135.4, 139.1, 142.3, 155.3; ν_{max} (neat) 3383, 3024, 2955, 2897, 1562, 1427, 1250, 1111, 910, 826, 729, 698 cm^{-1}; m/z (EI) 75 (100), 135 (100), 203 (62), 278 (3), 294 (2%, M^+). HRMS (EI): M^+, found 294.1438. $C_{19}H_{22}OSi$ requires 294.1440.

*4.6.9. (E)-3-[(Dimethylphenylsilyl)methylene]non-1-en-4-ol (**9cb**).* Mixture of regioisomers (**9cb**:**10cb**=64:36). Pale yellow oil, 88% yield; δ_H (400 MHz, $CDCl_3$) 0.40 (s, 3H), 0.41 (s, 3H), 0.89 (t, J=7.0 Hz, 3H), 1.27–1.75 (m, 9H), 4.52 (dd, J=3.8, 7.7 Hz, 1H), 5.09 (d, J=11.5 Hz, 1H), 5.28 (d, J=17.8 Hz, 1H), 6.00 (s, 1H), 6.49 (dd, J=11.5, 17.8 Hz, 1H), 7.34–7.36 (m, 3H), 7.52–7.54 (m, 2H); ν_{max} (neat) 3360, 3051, 2955, 2932, 2858, 1562, 1427, 1250, 1111, 818,

775, 729, 702 cm^{-1}; *m*/*z* (EI) 135 (100), 217 (25), 288 (46%, M^+). HRMS (EI): M^+, found 288.1906. $C_{18}H_{28}OSi$ requires 288.1909.

*4.6.10. (Z)-4-(Dimethylphenylsilyl)deca-1,3-dien-5-ol (**10cb**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$) 0.46 (s, 6H), 0.87 (t, *J*=7.0 Hz, 3H), 1.27–1.75 (m, 9H), 4.29 (dd, *J*=3.9, 7.8 Hz, 1H), 5.10 (d, *J*=10.0 Hz, 1H), 5.22 (dd, *J*=1.7, 16.6 Hz, 1H), 6.48 (ddd, *J*=10.0, 11.2, 16.6 Hz, 1H), 6.90 (d, *J*=11.2 Hz, 1H), 7.34–7.36 (m, 3H), 7.52–7.54 (m, 2H).

*4.6.11. (E)-4-[(Dimethylphenylsilyl)methylene]-2,2-dimethylhex-5-en-3-ol (**9cc**).* Pale yellow oil, 70% yield; δ_H (400 MHz, $CDCl_3$) 0.41 (s, 3H), 0.42 (s, 3H), 0.93 (s, 9H), 1.58 (br s, 1H), 4.35 (s, 1H), 5.06 (d, *J*=11.2 Hz, 1H), 5.31 (d, *J*=17.6 Hz, 1H), 5.95 (s, 1H), 6.52 (dd, *J*=11.2, 17.6 Hz, 1H), 7.34–7.36 (m, 3H), 7.52–7.55 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.8, −0.6, 26.5, 35.7, 77.8, 115.7, 127.8, 128.4, 128.9, 133.7, 138.0, 139.3, 156.9; ν_{max} (neat) 3472, 3051, 2955, 2905, 2870, 1728, 1558, 1427, 1362, 1250, 1111, 991, 814, 779, 702 cm^{-1}; *m*/*z* (EI) 135 (99), 140 (98), 203 (62), 217 (100), 274 (1%, M^+). HRMS (EI): M^+, found 274.1749. $C_{17}H_{26}OSi$ requires 274.1745.

*4.6.12. (E)-1,2-Diphenylpenta-2,4-dien-1-ol (**10da**).* Mixture of regioisomers (**9da**:**10da**=17:83). Pale yellow oil, 98% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 2.09 (br s, 1H), 5.09 (dd, *J*=1.8, 10.8 Hz, 1H), 5.33 (dd, *J*=1.8, 17.0 Hz, 1H), 5.51 (s, 1H), 6.26 (dt, *J*=10.8, 17.0 Hz, 1H), 6.52 (d, *J*=10.8 Hz, 1H), 6.99–7.01 (m, 2H), 7.24–7.32 (m, 8H); ν_{max} (neat) 3371, 3082, 3055, 3020, 2932, 2858, 1713, 1466, 999, 906, 702 cm^{-1}; *m*/*z* (EI) 105 (100), 129 (50), 236 (99%, M^+). HRMS (EI): M^+, found 236.1209. $C_{17}H_{16}O$ requires 236.1201.

*4.6.13. (E)-2-Benzylidene-1-phenylbut-3-en-1-ol (**9da**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 5.15 (d, *J*=11.5 Hz, 1H), 5.29 (d, *J*=17.6 Hz, 1H), 5.67 (s, 1H), 6.71 (dd, *J*=11.5, 17.6 Hz, 1H).

*4.6.14. (E)-4-Phenyldeca-1,3-dien-5-ol (**10db**).* Mixture of regioisomers (**9db**:**10db**=14:86). Pale yellow oil, 99% yield; Minor regioisomer (**9db**) was not isolated by column chromatography on silica gel; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.85 (t, *J*=7.0 Hz, 3H), 1.19–1.51 (m, 8H), 1.62 (br s, 1H), 4.39 (t, *J*=5.4 Hz, 1H), 5.05 (dd, *J*=2.0, 11.1, 1H), 5.29 (dd, *J*=2.0, 16.5 Hz, 1H), 6.27 (dd, *J*=11.1, 16.5 Hz, 1H), 6.35 (d, *J*=11.1 Hz, 1H), 7.19–7.38 (m, 5H); ν_{max} (neat) 3371, 3082, 3055, 3020, 2932, 2858, 1713, 1466, 999, 907, 702 cm^{-1}; *m*/*z* (EI) 99 (100), 129 (76), 159 (57), 230 (16%, M^+). HRMS (EI): M^+, found 230.1676. $C_{16}H_{22}O$ requires 230.1671.

*4.6.15. (E)-2,2-Dimethyl-4-phenylhepta-4,6-dien-3-ol (**10dc**).* Mixture of regioisomers (**9dc**:**10dc**=43:57). Pale yellow oil, 99% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.82 (s, 9H), 4.28 (s, 1H), 5.08 (d, *J*=8.8, 1H), 5.32 (dd, *J*=1.8, 16.0 Hz, 1H), 6.36–6.42 (m, 2H), 7.25–7.35 (m, 5H); ν_{max} (neat) 3456, 3082, 3055, 3024, 2955, 2905, 2870, 1477, 1366, 1072, 1003, 910, 732 cm^{-1}; *m*/*z* (EI) 58 (100), 159 (59), 216 (10%, M^+). HRMS (EI): M^+, found 216.1513. $C_{15}H_{20}O$ requires 216.1514.

*4.6.16. (E)-4-Benzylidene-2,2-dimethylhex-5-en-3-ol (**9dc**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 0.99 (s, 9H), 4.48 (s, 1H), 5.19 (d, *J*=11.5 Hz, 1H), 5.43 (d, *J*=17.9 Hz, 1H), 6.78 (dd, *J*=11.5, 17.9 Hz, 1H).

*4.6.17. (E)-N-Benzyl-1-phenyl-2-[(trimethylsilyl)methylene]but-3-en-1-amine (**13ad**).* Pale yellow oil, 85% yield; δ_H (400 MHz, $CDCl_3$) 0.10 (s, 9H), 1.55 (br s, 1H), 3.63 (ABq, *J*=13.1 Hz, 2H), 4.51 (s, 1H), 4.98 (d, *J*=11.2 Hz, 1H), 5.13 (d, *J*=17.6 Hz, 1H), 6.04 (s, 1H), 6.48 (dd, *J*=11.2, 17.6 Hz, 1H), 7.15–7.28 (m, 10H); δ_C (100 MHz, $CDCl_3$) 0.4, 51.9, 64.2, 115.4, 126.9, 127.0, 127.7, 128.29, 128.33, 130.7, 136.6, 140.5, 142.7, 153.5; ν_{max} (neat) 3063, 3028, 2955, 1562, 1493, 1454, 1250, 907, 748, 698 cm^{-1}; *m*/*z* (EI) 91 (30), 196 (100), 321 (14%, M^+). HRMS (EI): M^+, found 321.1915. $C_{21}H_{27}NSi$ requires 321.1913.

*4.6.18. (E)-1-Phenyl-N-propyl-2-[(trimethylsilyl)methylene]but-3-en-1-amine (**13ae**).* Mixture of regioisomers (**13ae**:**14ae**=97:3). Pale yellow oil, 93% yield; Minor regioisomer (**14ae**) was not isolated by column chromatography on silica gel; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.17 (s, 9H), 0.90 (t, *J*=7.4 Hz, 3H), 1.50 (sextd, *J*=2.6, 7.4 Hz, 2H), 2.43–2.56 (m, 2H), 4.53 (s, 1H), 5.06 (d, *J*=11.2 Hz, 1H), 5.25 (d, *J*=17.6 Hz, 1H), 6.04 (s, 1H), 6.54 (dd, *J*=11.2, 17.6 Hz, 1H), 7.22–7.33 (m, 5H); δ_C (100 MHz, $CDCl_3$) 0.3, 11.9, 23.3, 50.1, 65.0, 115.2, 126.9, 127.6, 128.3, 130.2, 136.8, 142.9, 153.8; ν_{max} (neat) 3059, 3024, 2955, 1562, 1454, 1250, 907, 841, 752, 698 cm^{-1}; *m*/*z* (EI) 73 (18), 106 (29), 148 (100), 273 (13%, M^+). HRMS (EI): M^+, found 273.1915. $C_{17}H_{27}NSi$ requires 273.1913.

*4.6.19. (E)-N-Benzyl-3-[(trimethylsilyl)methylene]non-1-en-4-amine (**13af**).* Pale yellow oil, 89% yield; δ_H (400 MHz, $CDCl_3$) 0.17 (s, 9H), 0.85 (t, *J*=7.1 Hz, 3H), 1.19–1.57 (m, 9H), 3.43 (t, *J*=7.1 Hz, 1H), 3.62 (ABq, *J*=12.9 Hz, 2H), 5.12 (d, *J*=11.2 Hz, 2H), 5.31 (d, *J*=17.8 Hz, 1H), 5.77 (s, 1H), 6.61 (dd, *J*=11.2, 17.8 Hz, 1H), 7.20–7.33 (m, 5H); δ_C (100 MHz, $CDCl_3$) 0.4, 14.0, 22.5, 26.0, 31.8, 36.0, 51.3, 60.6, 114.6, 126.7, 128.3, 137.3, 140.9, 155.5; ν_{max} (neat) 3028, 2955, 2928, 2855, 1558, 1454, 1250, 853, 737, 698 cm^{-1}; *m*/*z* (EI) 91 (48), 190 (100), 244 (65), 315 (13%, M^+). HRMS (EI): M^+, found 315.2378. $C_{20}H_{33}NSi$ requires 315.2382.

*4.6.20. (E)-N-Benzyl-2-[(tert-butyldimethylsilyl)methylene]-1-phenylbut-3-en-1-amine (**13bd**).* Pale yellow oil, 99% yield; δ_H (400 MHz, $CDCl_3$) 0.16 (s, 6H), 0.93 (s, 9H), 3.73 (ABq, *J*=13.2 Hz, 2H), 4.62 (s, 1H), 5.03 (d, *J*=11.2 Hz, 1H), 5.17 (d, *J*=17.3 Hz, 1H), 6.21 (s, 1H), 6.56 (dd, *J*=11.2, 17.3 Hz, 1H), 7.19–7.38 (m, 10H); δ_C (100 MHz, $CDCl_3$) −3.88, −3.86, 17.4, 26.6, 52.0, 64.3, 115.2, 126.9, 127.0, 127.6, 128.26, 128.35, 137.0, 140.5, 142.8, 154.0; ν_{max} (neat) 3063, 3028, 2951, 2855, 1562, 1493, 1454, 1250, 907, 833, 737, 698 cm^{-1}; *m*/*z* (EI) 91 (80), 196 (100), 363 (21%, M^+). HRMS (EI): M^+, found 363.2379. $C_{24}H_{33}NSi$ requires 363.2382.

*4.6.21. (E)-2-[(tert-Butyldimethylsilyl)methylene]-1-phenyl-N-propylbut-3-en-1-amine (**13be**).* Pale yellow oil, 99% yield; δ_H (400 MHz, $CDCl_3$) 0.15 (s, 6H), 0.88 (t, *J*=5.4 Hz, 3H), 0.91 (s, 9H), 1.51 (sextd, *J*=1.5, 7.6 Hz, 2H), 2.46–2.58 (m, 2H), 4.59 (s, 1H), 5.05 (d, *J*=11.5 Hz, 1H), 5.25 (d, *J*=17.8 Hz, 1H), 6.12 (s, 1H), 6.56 (dd, *J*=11.5, 17.8 Hz, 1H), 7.22–7.36 (m, 5H); δ_C (100 MHz, $CDCl_3$) −3.90, −3.87, 11.9, 17.4, 23.3, 26.6, 50.2, 65.1, 115.0, 126.9, 127.6, 127.9, 128.3, 137.2, 143.1, 154.2; ν_{max} (neat) 3063, 3024, 2955, 2928, 2855, 1562, 1462, 1250, 907, 833, 779, 698 cm^{-1}; *m*/*z* (EI) 148 (100), 200 (62), 286 (68), 315 (74%, M^+). HRMS (EI): M^+, found 315.2390. $C_{20}H_{33}NSi$ requires 315.2382.

*4.6.22. (E)-N-Benzyl-3-[(tert-butyldimethylsilyl)methylene]non-1-en-4-amine (**13bf**).* Mixture of regioisomers (**13bf**:**14bf**=96:4). Pale yellow oil, 80% yield; Minor regioisomer (**14bf**) was not isolated by column chromatography on silica gel; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.15 (s, 6H), 0.85 (t, *J*=7.1 Hz, 3H), 0.92 (s, 9H), 1.21–1.56 (m, 9H), 3.49 (t, *J*=6.0 Hz, 1H), 3.62 (ABq, *J*=12.7 Hz, 2H), 5.10 (d, *J*=11.2 Hz, 1H), 5.32 (d, *J*=17.6 Hz, 1H), 5.83 (s, 1H), 6.63 (dd, *J*=11.2, 17.6 Hz, 1H), 7.12–7.30 (m, 5H); δ_C (100 MHz, $CDCl_3$) −3.83, −3.80, 14.0, 17.3, 22.6, 26.6, 31.9, 36.3, 51.4, 60.4, 114.3, 126.4, 126.8, 128.27, 128.30, 137.7, 140.9, 156.1; ν_{max} (neat) 3063, 3028, 2955, 2928, 2855, 1562, 1462, 1250, 906, 829, 694 cm^{-1}; *m*/*z* (EI) 91 (22), 190 (100), 286 (47), 357 (12%, M^+). HRMS (EI): M^+, found 357.2845. $C_{23}H_{39}NSi$ requires 357.2852.

*4.6.23. (E)-N-Benzyl-2-[(dimethylphenylsilyl)methylene]-1-phenylbut-3-en-1-amine (**13cd**).* Pale yellow oil, 63% yield; δ_H (400 MHz, $CDCl_3$) 0.10 (s, 6H), 1.67 (br s, 1H), 3.73 (ABq, *J*=13.1 Hz, 2H), 4.63 (s, 1H), 4.97

(d, *J*=11.2 Hz, 1H), 5.19 (d, *J*=17.6 Hz, 1H), 6.31 (s, 1H), 6.48 (dd, *J*=11.2, 17.6 Hz, 1H), 7.21–7.39 (m, 13H), 7.52–7.55 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.57, −0.54, 51.9, 64.2, 115.9, 127.0, 127.1, 127.7, 127.8, 128.1, 128.3, 128.4, 128.8, 133.8, 136.6, 139.4, 140.2, 142.5, 154.9; ν_{max} (neat) 3063, 3024, 2955, 1562, 1493, 1454, 1427, 1250, 1111, 837, 729, 698 cm^{-1}; *m*/*z* (EI) 91 (42), 135 (17), 196 (100), 383 (11%, M^+). HRMS (EI): M^+, found 383.2075. $C_{26}H_{29}NSi$ requires 383.2069.

*4.6.24. (E)-2-[(Dimethylphenylsilyl)methylene]-1-phenyl-N-propylbut-3-en-1-amine (**13ce**).* Pale yellow oil, 99% yield; δ_H (400 MHz, $CDCl_3$) 0.42 (s, 3H), 0.43 (s, 3H), 0.95 (t, *J*=7.4 Hz, 3H), 1.51 (sextd, *J*=1.2, 7.6 Hz, 2H), 2.51–2.65 (m, 2H), 4.57 (s, 1H), 5.03 (d, *J*=11.2 Hz, 1H), 5.30 (d, *J*=17.8 Hz, 1H), 6.23 (s, 1H), 6.52 (dd, *J*=11.2, 17.8 Hz, 1H), 7.20–7.36 (m, 8H), 7.52–7.54 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.57, −0.54, 11.8, 23.3, 50.2, 65.2, 115.7, 127.0, 127.4, 127.6, 127.8, 128.3, 128.8, 133.8, 136.8, 139.5, 142.9, 155.4; ν_{max} (neat) 3067, 3024, 2959, 1562, 1454, 1427, 1250, 1111, 907, 833, 729, 698 cm^{-1}; *m*/*z* (EI) 135 (37), 148 (100), 335 (14%, M^+). HRMS (EI): M^+, found 335.2067. $C_{22}H_{29}NSi$ requires 335.2069.

*4.6.25. (E)-N-Benzyl-3-[(dimethylphenylsilyl)methylene]non-1-en-4-amine (**13cf**).* Pale yellow oil, 76% yield; δ_H (400 MHz, $CDCl_3$) 0.42 (s, 6H), 0.86 (t, *J*=7.0 Hz, 3H), 1.22–1.58 (m, 9H), 3.50 (t, *J*=6.5 Hz, 1H), 3.65 (ABq, *J*=12.9 Hz, 2H), 5.04 (d, *J*=11.2 Hz, 1H), 5.31 (d, *J*=16.8 Hz, 1H), 5.95 (s, 1H), 6.54 (dd, *J*=11.2, 16.8 Hz, 1H), 7.22–7.35 (m, 8H), 7.54–7.56 (m, 2H); δ_C (100 MHz, $CDCl_3$) −0.6, −0.5, 14.0, 22.6, 26.0, 31.8, 36.2, 51.4, 60.5, 115.1, 126.4, 126.8, 127.8, 128.3, 128.8, 133.8, 137.2, 139.7, 140.8, 157.1; ν_{max} (neat) 3067, 3024, 2955, 2928, 2855, 1562, 1454, 1250, 1111, 841, 729, 698 cm^{-1}; *m*/*z* (EI) 91 (70), 190 (100), 306 (55), 377 (25%, M^+). HRMS (EI): M^+, found 377.2542. $C_{25}H_{35}NSi$ requires 377.2539.

*4.6.26. (E)-N-Benzyl-1,2-diphenylpenta-2,4-dien-1-amine (**14dd**).* Mixture of regioisomers (**13dd**:**14dd**=9:91). Pale yellow oil, 79% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 3.81 (ABq, *J*=13.4 Hz, 2H), 4.52 (s, 1H), 5.03 (dd, *J*=1.8, 10.1 Hz, 1H), 5.30 (dd, *J*=1.8, 17.0 Hz, 1H), 6.27 (dt, *J*=10.1, 17.0 Hz, 1H), 6.53 (d, *J*=10.1 Hz, 1H), 7.21–7.36 (m, 5H); ν_{max} (neat) 3082, 3059, 3024, 2831, 1701, 1601, 1493, 1454, 910, 702 cm^{-1}; *m*/*z* (EI) 91 (78), 196 (100), 234 (30), 325 (86%, M^+). HRMS (EI): M^+, found 325.1828. $C_{24}H_{23}N$ requires 325.1830.

*4.6.27. (E)-N-Benzyl-2-benzylidene-1-phenylbut-3-en-1-amine (**13dd**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 4.73 (s, 1H), 5.10 (d, *J*=11.2 Hz, 1H), 6.72 (dd, *J*=11.2, 17.8 Hz, 1H), 6.99 (s, 1H).

*4.6.28. (E)-1,2-Diphenyl-N-propylpenta-2,4-dien-1-amine (**14de**).* Mixture of regioisomers (**13de**:**14de**=19:81). Pale yellow oil, 68% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.91 (t, *J*=7.3 Hz, 3H), 1.48 (br s, 1H), 1.50–1.57 (m, 2H), 2.50–2.68 (m, 2H), 4.47 (s, 1H), 5.02 (dd, *J*=2.0, 10.0, 1H), 5.29 (dd, *J*=2.0, 17.0 Hz, 1H), 6.22 (dt, *J*=10.0, 17.0 Hz, 1H), 6.49 (d, *J*=10.0 Hz, 1H), 6.90–6.93 (m, 2H), 7.18–7.34 (m, 8H); ν_{max} (neat) 3059, 3024, 2957, 2870, 1601, 1493, 1450, 907, 745, 702 cm^{-1}; *m*/*z* (EI) 148 (82), 277 (100%, M^+). HRMS (EI): M^+, found 277.1829. $C_{20}H_{23}N$ requires 277.1830.

*4.6.29. (E)-2-Benzylidene-1-phenyl-N-propylbut-3-en-1-amine (**13de**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 4.67 (s, 1H), 5.11 (d, *J*=11.5 Hz, 1H), 5.36 (d, *J*=17.8 Hz, 1H), 6.71 (dd, *J*=11.5, 17.8 Hz, 1H), 6.99 (s, 1H).

*4.6.30. (E)-N-Benzyl-4-phenyldeca-1,3-dien-5-amine (**14df**).* Mixture of regioisomers (**13df**:**14df**=14:86). Pale yellow oil, 73% yield; Major regioisomer; δ_H (400 MHz, $CDCl_3$) 0.86 (t, *J*=7.0 Hz, 3H), 1.18–1.40 (m, 8H), 1.53 (br s, 1H), 3.57 (t, *J*=6.5 Hz, 1H), 3.74 (ABq, *J*=13.2 Hz, 2H), 5.17 (d, *J*=11.5 Hz, 1H), 5.45 (d, *J*=18.1 Hz, 1H), 6.23–6.28 (m, 1H), 6.76 (dd, *J*=11.5, 18.1 Hz, 1H), 7.16–7.36 (m, 10H); ν_{max} (neat) 3059, 3028, 2928, 2855, 1600, 1493, 1454, 907, 698 cm^{-1}; *m*/*z* (EI) 91 (100), 190 (29), 248 (79), 319 (6%, M^+). HRMS (EI): M^+, found 319.2306. $C_{23}H_{29}N$ requires 319.2300.

*4.6.31. (E)-N-Benzyl-4-phenyldeca-1,3-dien-5-amine (**13df**).* Minor regioisomer; δ_H (400 MHz, $CDCl_3$), characteristic signals: 3.32 (t, *J*=6.2 Hz, 1H), 3.84 (ABq, *J*=13.3 Hz, 1H), 4.99–5.02 (m, 1H), 5.21–5.26 (m, 1H), 6.74 (s, 1H).

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