Diastereoselective Allylation and Crotylation Reactions of Aldehydes with Potassium Allyl- and Crotyltrifluoroborates under Lewis Acid Catalysis

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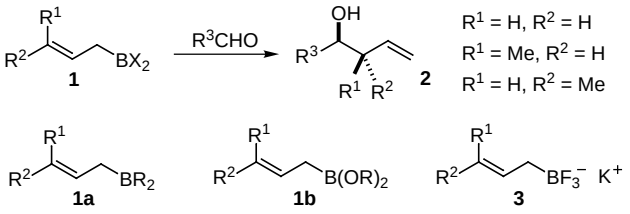
Abstract: Potassium allyl- and crotyltrifluoroborates react with aldehydes in a process catalyzed by a variety of Lewis acids, to give the corresponding homoallylic alcohols. Of the Lewis acids examined, $BF_3{\cdot}OEt_2$, used either stoichiometrically or catalytically, was found to most efficiently catalyze this reaction. The air and moisture stable potassium organotrifluoroborate salts react with a variety of alkyl, α- or β- substituted alkyl, and aryl aldehydes, and lead to the adducts in high yield and with high diastereoselectivity.

Key words: allylations, boron, alcohols, Lewis acids, catalysis

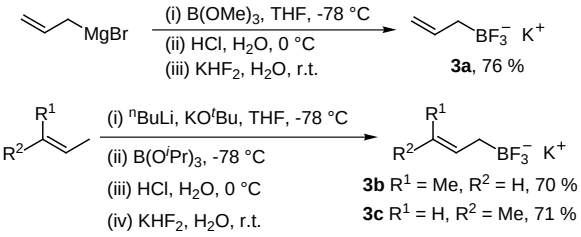
Synthetically versatile homoallylic alcohols **2** are typically prepared by the allylation and crotylation of aldehydes.[1,2] A variety of organometallic reagents have been used for these transformations, but allyl- and crotylboron compounds **1** are particularly useful because of the high yields and excellent levels of stereo control they provide (Scheme 1).[3] Of the two main classes of **1**, allyl/crotyl dialkylboranes **1a** and allyl/crotyl boronates **1b**, only one reagent, allyl pinacol boronate, is commercially available at the present time.[4] A degree of inconvenience is often associated with other allyl- and crotylboron compounds, which are usually prepared immediately prior to use due to their sensitivity to air and/or moisture, and the difficulties involved with their subsequent storage and handling. As part of our ongoing research in organoboron chemistry,[5] we recently reported a new class of allyl- and crotylboron compounds, potassium allyl- and crotyltrifluoroborates, and their $BF_3{\bullet}OEt_2$ catalyzed addition to carbonyl compounds.[6] We now report the use of other Lewis acid catalysts, and the reaction of potassium allyltrifluoroborate with aldehydes bearing α- or β-stereocentres.



Scheme 1

Organotrifluoroborate salts (RBF_3M, M = alkali metal)[5a,7] have been demonstrated to be more air and water stable than the corresponding boronic acids.[8] Vedejs and co-workers recently showed potassium aryltrifluoroborates ($ArBF_3K$) to be useful precursors for the formation of arylboron difluoride Lewis acids,[7a] and reported their preparation using aqueous KHF_2. Similarly, we reasoned that potassium allyl- and crotyltrifluoroborate **3** should be convenient precursors for the in situ formation of allylboron difluoride, a species theoretically predicted to have higher reactivity in allylation processes.[9]

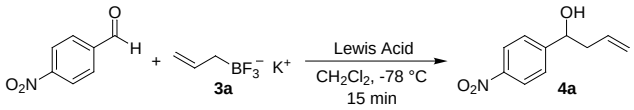
The preparation of the potassium allyl- and crotyltrifluoroborates **3** was achieved via the boronic acids in a manner analogous to that used for the synthesis of other potassium trifluoroborate salts (Scheme 2). The addition of either allylmagnesium bromide[10] or crotylpotassium[11] to trimethylborate or triisopropylborate respectively, followed by acidic hydrolysis, was used to prepare the requisite allyl- and crotylboronic acids, respectively. Conversion to the potassium allyl- or crotyltrifluoroborate **3** was then achieved by treatment with aqueous KHF_2, followed by recrystallization from acetonitrile. Particular care should be taken to avoid isomerization of (*E*)-crotylpotassium during the preparation of **3c**.[11] The salts **3** are air and water stable solids, and can be stored for extended periods of time at room temperature, in plastic bottles with no further precautions.



Scheme 2

A variety of Lewis acids were screened to evaluate their effectiveness at catalyzing the addition of allyltrifluoroborate **3a** to 4-nitrobenzaldehyde (Table 1). By conducting the allylation at −78 °C in dichloromethane, it was determined that with 2 equivalents of $BF_3{\bullet}OEt_2$, full conversion was achieved within 15 minutes, and the isolated product yield of **4a** was 93%. Other Lewis acids also promoted the reactions, but showed lower degrees of conversion under the same reaction conditions. Reaction of the salts does not occur in the absence of a Lewis acid catalyst even at elevated temperatures, presumably due to the

Table 1 Effect of Lewis acids on the Allylation of 4-Nitrobenzaldehyde with Allyltrifluoroborate **3a**

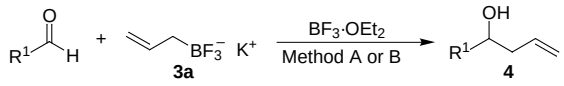


Entry	Lewis Acid	Conversion [%]	Yield [%]
1	$B(OMe)_3$	<5	–
2	$AlCl_3$	20	16
3	$Ti(O^iPr)_4$	25	20
4	TMSCl	35	28
5	$SnCl_4$	50	41
6	$BF_3{\cdot}Et_2O$	100	93

insolubility of **3** in dichloromethane. This feature distinguishes the reactivity of **3** from most allylboron compounds, which do not require prior activation.

Having established $BF_3{\bullet}OEt_2$ as the most efficient promoter for the allylation process, a variety of substituted and unsubstituted aryl and alkyl aldehydes were then allylated to give the homoallylic alcohols **4** in high isolated yields (Table 2). Two protocols were employed, using either 2 equivalents of $BF_3{\bullet}OEt_2$ with two equivalents of **3a** at −78 °C in dichloromethane over 15 minutes (Method A), or with 5 mol% of $BF_3{\bullet}OEt_2$ with 2 equivalents of **3a** at room temperature over 3−6 hours (Method B).

Table 2 Allylation of Aldehydes with Allyltrifluoroborate **3a**



Entry	R^1	Product	Yield [%] (Method A[a])	Yield [%] (Method B[b])
1	4-$O_2NC_6H_4$	**4a**	96	95
2	*n*-C_7H_{15}	**4b**	82	84
3	(*E*)-Ph-CH=CH-	**4c**	89	91
4	Ph	**4d**	93	91
5	4-$MeOC_6H_4$	**4e**	95	89
6	4-$MeSC_6H_4$	**4f**	90	93
7	4-NCC_6H_4	**4g**	95	95
8	3,4-$Cl_2C_6H_3$	**4h**	85	86
9	3-MeO-4-HOC_6H_3	**4i**	84	85

[a] $BF_3{\cdot}Et_2O$ (2.0 equiv.), **3a** (2.0 equiv.), CH_2Cl_2, –78 °C, 15 mins.
[b] $BF_3{\cdot}Et_2O$ (0.05 equiv.), **3a** (2.0 equiv.), CH_2Cl_2, rt, 3–6 h.

While requiring significantly longer reaction times, the use of catalytic $BF_3{\bullet}OEt_2$ gave comparable yields of **4**.

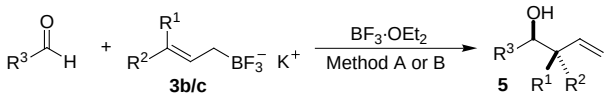
Crotylation using (*Z*)- and (*E*)-potassium crotyltrifluoroborate **3b/c** was found to work equally well using either methods A or B, leading to products **5** with excellent levels of stereocontrol and in uniformly high yields (Table 3). The (*Z*)-crotyltrifluoroborate **3b** consistently gave rise to the *syn*-diastereomer, while the (*E*)-crotyltrifluoroborate **3c** gave the expected *anti*-product. Each of these observations is consistent with addition of a tri-coordinate boron species via a Zimmerman−Traxler like transition state. The identity of the active allylation species has not been established, but allylboron difluoride, is presumably initially formed in situ under these conditions, by the Lewis acid promoted removal of fluoride from the salts **3**.

The reaction of allyl and crotyl metal reagents with aldehydes containing adjacent stereocenters is of importance in the context of acyclic stereoselective synthesis.[12] The general method employing catalytic $BF_3{\bullet}OEt_2$ (Method B) can be applied to the allylation of aldehydes with an α- or β-stereocenter. We chose to examine aldehydes **6** and **8** containing either an α- or β-*tert*-butyldimethylsilanyloxy substituent, respectively. Unfortunately, allylation of **6** and **8** with **3a** gave only modest diastereoselection, though the overall yields were generally high (Table 4, entries 1, 2 and Table 5, entries 1, 2). Prior studies by Hoffmann and co-workers in the reaction of a similar α-benzyloxy substituted aldehyde with allyl pinacol boronate also displayed only modest diastereoselectivity.[12a] In contrast, the crotylation of **6** with **3b/c** displayed greater levels of diastereoselectivity (Table 4, entries 3−6). The (*Z*)-crotyl reagent **3b** shows very good *anti* selectivity while the corresponding (*E*)-crotyl reagent **3c** displays more modest *syn* selectivity in the reaction with 2-(*tert*-butyldimethylsilanyloxy)propanal (Table 4, entries 3, 4). These results are consistent with prior studies by both Hoffmann[12b] and Roush[12c] on crotylboration of similar α-alkoxy substituted aldehydes, and have been rationalized by invoking Cornforth-like transition states.[3a, 12b,c, 13] In contrast, the reactions of both **3b** and **3c** with 2--(*tert*-butyldimethylsilanyloxy)-2-phenylacetaldehyde (Table 4, Entries 5,6) displayed good *anti* selectivity. Roush has proposed transition states to account for this type of seemingly anomolous behaviour in the context of enoloate additions to aldehydes.[13c]

Both allylation and crotylation of **8** (Table 5), on the other hand, only displayed modest diastereoselectivity presumably due to the fact that the β-stereocenter is remote from the site of the newly developing C−C bond. Roush and coworkers previously reported that the reaction of allyl pinacol boronate with a β-alkoxy substituted aldehyde also proceeded with modest diastereoselectivity.[12d]

In conclusion, we have demonstrated the viability of potassium allyl- and crotyltrifluoroborates as air and moisture stable reagents for allylation and crotylation of aldehydes. These reagents offer several advantages over existing allylboron reagents, including rapid and high

Table 3 Crotylation of Aldehydes With (*Z*)- and (*E*)-Crotyltrifluoroborates **3b/c**



Entry	R^1	R^2	R^3	Product	d.r.	Yield [%] (Method A[a])	Yield [%] (Method B[b])
1	Me	H	*n*-C_7H_{15}	**5a**	> 98 : 2	74	76
2	H	Me	*n*-C_7H_{15}	**5b**	> 98 : 2	84	85
3	Me	H	Ph	**5c**	> 98 : 2	91	92
4	H	Me	Ph	**5d**	> 98 : 2	94	93
5	Me	H	4-$MeOC_6H_4$	**5e**	96 : 4	91	93
6	H	Me	4-$MeOC_6H_4$	**5f**	97 : 3	91	95
7	Me	H	4-$O_2NC_6H_4$	**5g**	> 98 : 2	95	94
8	H	Me	4-$O_2NC_6H_4$	**5h**	> 98 : 2	96	94

[a] BF_3·Et_2O (2.0 equiv.), **3b/c** (2.0 equiv.), CH_2Cl_2, –78 °C, 15 mins.
[b] BF_3·Et_2O (0.05 equiv.), **3b/c** (2.0 equiv.), CH_2Cl_2, r.t., 3–6 h.

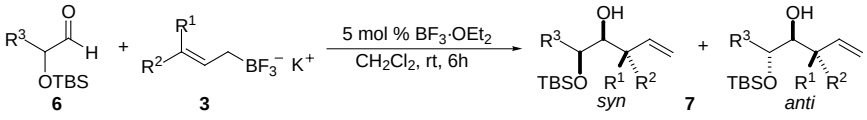
yielding additions, and excellent levels of diastereocontrol. We are currently working on extending the scope of these useful reagents and developing milder protocols for their additions.

Reagents were used as received. THF was distilled from Na metal/benzophenone ketyl under Ar. CH_2Cl_2 was distilled from CaH_2. All other solvents used were reagent grade. All manipulations were carried out under N_2 atm. Proton chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ = 7.26 ppm) or CD_3CN (δ = 1.94 ppm). Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (δ = 77.00 ppm) or CD_3CN (δ = 1.32 ppm). Boron chemical shifts were externally referenced to BF_3•OEt_2 (δ = 0.00 ppm). Fluorine chemical shifts were externally referenced to $CFCl_3$ (δ = 0.00 ppm). FT−IR spectra were recorded on a Perkin−Elmer Spectrum 1000, with samples loaded as neat films on NaCl plates or as KBr discs. Low resolution mass spectra were recorded on a Bell and Howell 21-490 spectrometer, and high resolution spectra were recorded on an AEI MS3074 spectrometer. Silica gel (60 Å, 230−400 mesh) was obtained from Whatman Company or Toronto Research Chemicals, Inc. Elemental analysis were obtained from Canadian Microanalytical Service Ltd., Delta, BC.

Potassium Allyltrifluoroborate (3a)

To a solution of trimethylborate (22.7 mL, 0.200 mol) in Et_2O (300 mL) cooled to −78 °C was added allylmagnesium bromide (1.0 M in Et_2O, 200 mL, 0.200 mol) slowly over approx. 30 min. The reaction mixture was stirred for 2 h at −78 °C and then poured immedi-

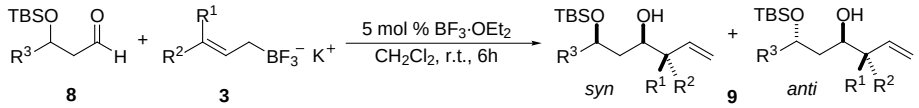
Table 4 Allylation and Crotylation of Aldehydes **6** with **3**



Entry	R^1	R^2	R^3	Product	*syn* : *anti*	Yield [%]
1	H	H	Me	**7a**	30 : 70	69
2	H	H	Ph	**7b**	35 : 65	91
3	Me	H	Me	**7c**	5 : 95[a]	73
4	H	Me	Me	**7d**	75 : 25	72
5	Me	H	Ph	**7e**	10 : 90[b]	85
6	H	Me	Ph	**7f**	10 : 90[c]	82

[a] Trace amounts of **7d**-*syn* also present in isolated adducts.
[b] Trace amounts of **7f**-*syn* also present in isolated adducts. The stereochemistry of the major diastereomer was confirmed by single crystal X-ray analysis. The authors have deposited the atomic coordinates of this compound at the Cambridge Crytallographic Data Centre.
[c] The stereochemistry was confirmed by derivatization through deprotection (TBAF) and acetalization with 2,2-dimethoxypropane. The benzylic proton of the resultant ketal appears as a doublet (J = 8.7 Hz) consistent with *cis*-orientation of the hydrogen atoms.

Table 5 Allylation and Crotylation of Aldehydes **8** with **3**



Entry	R^1	R^2	R^3	Product	*syn* : *anti*	Yield [%]
1	H	H	^{i}Pr	**9a**	35 : 65	90
2	H	H	Ph	**9b**	30 : 70	86
3	Me	H	Ph	**9c**	25 : 75[a]	84
4	H	Me	Ph	**9d**	25 : 75[a]	87

[a] The stereochemistry of these compounds were confirmed via conversion to the corresponding acetonide ((i) TBAF, (ii) 2,2-dimethoxypropane) and assigned according to Rychnovsky's protocol.[14]

ately into an Erlenmeyer flask containing 2 N HCl (300 mL). The resulting biphasic solution was vigorously stirred for 30 min. The layers were separated and the aqueous layer extracted with Et_2O (3 × 75 mL). The combined organic extracts were concentrated in vacuo to afford a pale yellow oil. KHF_2 (3.5 M in H_2O, 156 mL, 0.700 mol) was then added, the reaction mixture stirred for 30 min at r.t. and subsequently stored at 4 °C for 12 h. The white precipitate was filtered off and recrystallized from CH_3CN to afford **3a** as a white solid (22.5 g, 76%).

^{1}H NMR (CD_3CN, 500 MHz): δ = 6.00−5.89 (m, 1H), 4.75 (d, 1H, *J* = 17.0 Hz), 4.66 (d, 1H, *J* = 10.0 Hz), 1.12 (br s, 2H).

^{13}C NMR (CD_3CN, 125 MHz): δ = 142.82, 111.12, 27.20 (br).

^{11}B NMR (CD_3CN, 160 MHz): δ = 4.98 (q, *J* = 58.6 Hz).

^{19}F NMR (CD_3CN, 376 MHz): δ = −140.1 (q, *J* = 58.6 Hz).

MS (FAB): *m/z* = 257 (53), 256 (27), 109 (100).

HRMS (FAB): *m/z* calcd for $(C_3H_5BF_3)^-$ 109.0436. Found: 109.0436.

Anal. Calcd for $C_3H_5BF_3K$: C, 24.35; H, 3.41. Found: C, 24.26; H, 3.42.

(*Z*)-Potassium Crotyltrifluoroborate (3b)

To a solution of *cis*-2-butene (23.0 mL, 0.225 mol) in THF (150 mL) at −78 °C was added potassium *tert*-butoxide (22.4 g, 0.200 mol). *n*-BuLi (2.5 M in hexanes, 80.0 mL, 0.200 mol) was then added at a rate such that the internal temperature did not exceed −50 °C. After the addition was complete, the internal temperature of the reaction mixture was allowed to rise to −20 °C to −25 °C for 45 min prior to being recooled to −78 °C. Triisopropylborate was then added at a rate such that the internal temperature did not rise above −50 °C. The reaction mixture was subsequently stirred for an additional 45 min and then rapidly poured into a separatory funnel containing 1 N HCl (400 mL) saturated with NaCl. The layers were separated and the aqueous layer extracted with Et_2O (4 × 100 mL). The combined organic extracts were concentrated in vacuo to afford a clear, colorless oil, which was redissolved in MeOH (25 mL). KHF_2 (3.5 M in H_2O, 156 mL, 0.700 mol) was then added, the reaction mixture stirred for 30 min at r.t., and subsequently stored at 4 °C for 12 h. The white precipitate was filtered off and recrystallized from CH_3CN to afford **3b** as a white solid (22.7 g, 70%).

^{1}H NMR (CD_3CN, 300 MHz): δ = 5.62−5.49 (m, 1H), 5.23−5.11 (m, 1H), 1.56 (dd, 3H, *J* = 6.5, 1.0 Hz), 1.01 (br s, 2H).

^{13}C NMR (CD_3CN, 125 MHz): δ = 133.67, 120.16, 19.5 (br), 12.88.

^{11}B NMR (CD_3CN, 160 MHz): δ = 4.98 (q, *J* = 58.6 Hz).

^{19}F NMR (CD_3CN, 376 MHz): δ = −140.1 (q, *J* = 58.6 Hz).

MS (FAB): *m/z* = 287 (23), 286 (16), 285 (37), 269 (24), 125 (28), 124 (13), 123 (100), 122 (29).

HRMS (FAB): *m/z* calcd for $(C_4H_7BF_3)^-$ 123.0592. Found: 123.0587.

Anal. Calcd for $C_4H_7BF_3K$: C, 29.66; H, 4.36. Found: C, 29.23; H, 4.61.

(*E*)-Potassium Crotyltrifluoroborate (3c)

To a solution of *trans*-2-butene (23.0 mL, 0.225 mol) in THF (150 mL) at −78 °C was added potassium *tert*-butoxide (22.4 g, 0.200 mol). *n*-BuLi (2.5 M in hexanes, 80.0 mL, 0.200 mol) was then added at a rate such that the internal temperature did not exceed −60 °C. After the addition was complete, the internal temperature of the reaction mixture was allowed to rise to −50 °C. The reaction mixture was stirred for 15 min at this temperature prior to being recooled to −78 °C. Triisopropylborate was then added at a rate such that the internal temperature did not rise above −60 °C. The rest of the procedure is exactly the same as that for **3b**. The title compound was isolated as a white solid (23.0 g, 71%).

^{1}H NMR (CD_3CN, 500 MHz): δ = 5.56−5.44 (m, 1H), 5.16−5.04 (m, 1H), 1.56 (dq, 3H, *J* = 6.5, 1.5 Hz), 0.97 (br s, 2H).

^{13}C NMR (CD_3CN, 125 MHz): δ = 133.67, 120.16, 19.8 (br), 12.88.

^{11}B NMR (CD_3CN, 160 MHz): δ = 4.98 (q, *J* = 58.6 Hz).

^{19}F NMR (CD_3CN, 376 MHz): δ = −140.1 (q, *J* = 58.6 Hz).

MS (FAB): *m/z* = 287 (13), 286 (11), 285 (52), 284 (29), 283 (14), 123 (100), 122 (30).

HRMS (FAB): *m/z* calcd for $(C_4H_7BF_3)^-$ 123.0592. Found: 123.0576.

Allylation/Crotylation Reaction; Typical Procedure

Method A

To a suspension of the aldehyde (1.00 mmol) and potassium allyltrifluoroborate (296 mg, 2.00 mmol) in CH_2Cl_2 (10 mL) at −78 °C was added BF_3·OEt_2 (0.25 mL, 1.97 mmol). The reaction mixture was stirred for 15 min at −78 °C and then quenched with sat. $NaHCO_3$ (10 mL). The reaction mixture was then allowed to warm to r.t. The layers were separated and the aqueous layer extracted with CH_2Cl_2 (3 × 10 mL). The combined organic extracts were dried ($MgSO_4$), filtered and concentrated in vacuo to afford a clear, colourless oil. The homoallylic alcohol was purified by flash chromatography (silica gel), EtOAc/hexanes (2:8), to afford the compounds as clear, colourless oils.

Method B

To a suspension of the aldehyde (1.00 mmol) and potassium allyltrifluoroborate (296 mg, 2.00 mmol) in CH_2Cl_2 (10 mL) at r.t. was added BF_3•OEt_2 (60 μL, 0.05 mmol). The reaction mixture was stirred for 3−6 h. The rest of the procedure is the same as per Method A.

1-(4-Nitrophenyl)but-3-en-1-ol (4a)

IR (NaCl, thin film): ν = 3418, 3120, 2980, 2910, 1665, 1605, 1520, 1348, 1058, 922, 855, 754, 700 cm^{-1}

^1H NMR ($CDCl_3$, 400 MHz): δ = 8.17 (d, 2H, *J* = 8.5 Hz), 7.51 (d, 2H, *J* = 8.5 Hz), 5.83−5.71 (m, 1H), 5.20−5.12 (m, 2H), 4.88−4.82 (m, 1H), 2.58−2.50 (m, 1H), 2.48−2.39 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 151.11, 147.11, 133.15, 126.50, 123.54, 119.50, 72.11, 43.80.

MS (EI): *m/z* = 194 (M^+, 6), 153 (16), 152 (100), 122 (13), 106 (21), 105 (16), 94 (16), 78 (19), 77 (19).

HRMS (EI): *m/z* calcd for $C_{10}H_{12}NO_3$ 194.0817. Found: 194.0816.

Undec-1-en-4-ol (4b)[15a]

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.88−5.75 (m, 1H), 5.15−5.08 (m, 2H), 3.65−3.57 (m, 1H), 2.32−2.24 (m, 1H), 2.15−2.07 (m, 1H), 1.60 (br s, 1H), 1.48−1.18 (m, 12H), 0.86 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.91, 118.03, 70.66, 41.92, 36.80, 31.80, 29.60, 29.26, 25.66, 22.64, 14.08.

1-Phenylhexa-1,5-dien-3-ol (4c)[15b]

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.41−7.36 (m, 2H), 7.31 (t, 2H, *J* = 7.5 Hz), 7.27−7.21 (m, 1H), 6.60 (d, 1H, *J* = 16.0 Hz), 6.24 (dd, 1H, *J* = 16.0, 6.5 Hz), 5.93−5.80 (m, 1H), 5.23−5.16 (m, 2H), 4.35 (q, 1H, *J* = 6.5 Hz), 2.48−2.34 (m, 2H), 2.03 (s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 136.57, 133.98, 131.49, 130.24, 128.49, 127.57, 126.41, 118.38, 71.64, 41.92.

1-Phenylbut-3-en-1-ol (4d)[15c]

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.42−7.25 (m, 5H), 5.90−5.75 (m, 1H), 5.17 (d, 1H, *J* = 18.0 Hz), 5.15 (d, 1H, *J* = 10.0 Hz), 4.73 (t, 1H, *J* = 6.5 Hz), 2.58−2.45 (m, 2H), 2.29 (br s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.80, 134.39, 128.31, 127.44, 125.74, 118.26, 73.23, 43.72.

1-(4-Methoxyphenyl)but-3-en-1-ol (4e)[15d]

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.27 (d, 2H, *J* = 8.5 Hz), 6.87 (d, 2H, *J* = 9.0 Hz), 5.82−5.73 (m, 1H), 5.18−5.09 (m, 2H), 4.67 (t, 1H, *J* = 6.5 Hz), 3.79 (s, 3H), 2.48 (t, 2H, *J* = 7.0 Hz), 2.04 (br s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.96, 136.00, 134.58, 127.04, 118.21, 113.74, 72.93, 55.24, 43.73.

1-(4-Methylsulfanylphenyl)but-3-en-1-ol (4f)

IR (NaCl, thin film): ν = 3390, 3080, 2985, 2905, 1660, 1599, 1495, 1435, 1048, 915, 820 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.26−7.18 (m, 4H), 5.81−5.70 (m, 1H), 5.16−5.08 (m, 2H), 4.64 (t, 1H, *J* = 6.5 Hz), 2.48−2.42 (m, 5H), 2.35 (br s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.70, 137.29, 134.22, 126.47, 126.28, 118.26, 72.78, 43.57, 15.78.

MS (EI): *m/z* = 194 (M^+, 14), 154 (15), 153 (100), 110 (20), 109 (40), 79 (19), 78 (30), 77 (45).

HRMS (EI): *m/z* calcd for $C_{11}H_{14}OS$ 194.0765. Found: 194.0775.

4-(1-Hydroxybut-3-enyl)benzonitrile (4g)[15e]

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.58 (d, 2H, *J* = 8.5 Hz), 7.43 (d, 2H, *J* = 8.0 Hz), 5.79−5.68 (m, 1H), 5.14−5.08 (m, 2H), 4.76 (dd, 1H, *J* = 7.5, 5.0 Hz), 2.73 (br s, 1H), 2.52−2.36 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.22, 133.27, 132, 126.39, 119.01, 118.72, 110.72, 72.24, 43.57.

4-(3,4-Dichlorophenyl)but-3-en-1-ol (4h)[15f]

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.42 (d, 1H, *J* = 2.0 Hz), 7.38 (d, 1H, *J* = 8.0 Hz), 7.13 (dd, 1H, *J* = 8.0, 2.0 Hz), 5.79−5.67 (m, 1H), 5.16−5.10 (m, 2H), 4.64 (dd, 1H, *J* = 7.5, 5.0 Hz), 2.57 (br s, 1H), 2.50−2.34 (m, 2H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.94, 133.41, 132.30, 131.10, 130.20, 127.73, 125.09, 119.09, 71.87, 43.61.

4-(1-Hydroxybut-3-enyl)-2-methoxyphenol (4i)[15g]

IR (NaCl, thin film): ν = 3422, 2936, 1640, 1604, 1517, 1465, 1431, 1374, 1270, 1235, 1153, 1124, 1034, 916, 858, 820 cm^{-1}.

^1H NMR ($CDCl_3$, 400 MHz): δ = 6.87 (d, 1H, *J* = 2.0 Hz), 6.83 (d, 1H, *J* = 8.0 Hz), 6.77 (dd, 1H, *J* = 8.0, 2.0 Hz), 5.83−5.71 (m, 2H), 5.15−5.07 (m, 2H), 4.61 (t, 1H, *J* = 6.5 Hz), 3.83 (s, 3H), 2.46 (t, 2H, *J* = 7.0 Hz), 2.33 (br s, 1H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 146.53, 144.90, 135.89, 134.57, 118.74, 118.07, 114.10, 108.32, 73.23, 55.77, 43.66.

MS (EI): *m/z* = 194 (M^+, 4), 154 (14), 153 (100), 151 (8), 125 (30), 123 (5), 110 (12), 94 (8), 93 (72), 65 (38).

HRMS (CI^-): *m/z* calcd for $C_{11}H_{13}O_3$ $(M-H)^-$ 193.0865. Found: 193.0853.

(3*R,4*R**)-3-Methylundec-1-en-4-ol (5a)[16a]**

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.83−5.73 (m, 1H), 5.12−5.03 (m, 2H), 3.50−3.44 (m, 1H), 2.31−2.21 (m, 1H), 1.51 (br s, 1H), 1.50−1.44 (m, 2H), 1.39−1.22 (m, 10H), 1.01 (d, 3H, *J* = 7.0 Hz), 0.87 (t, 3H, *J* = 6.5 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.10, 115.11, 74.65, 43.36, 33.96, 31.81, 29.63, 29.28, 26.07, 22.63, 14.07, 13.95.

(3*S,4*R**)-3-Methylundec-1-en-4-ol (5b)[16b]**

^1H NMR ($CDCl_3$, 400 MHz): δ = 5.74 (ddd, 1H, *J* = 16.5, 12.0, 8.0 Hz), 5.12−5.08 (m, 2H), 3.41−3.34 (m, 1H), 2.19 (hextet, 1H, *J* = 7.0 Hz), 1.63 (br s, 1H), 1.53−1.43 (m, 2H), 1.40−1.22 (m, 10H), 1.02 (d, 3H, *J* = 7.0 Hz), 0.87 (t, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.34, 116.14, 74.65, 44.07, 34.20, 31.82, 29.67, 29.28, 25.72, 22.63, 16.25, 14.07.

(1*S,2*R**)-2-Methyl-1-phenylbut-3-en-1-ol (5c)[16c]**

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.37−7.26 (m, 5H), 5.81−5.71 (m, 1H), 5.07−5.00 (m, 2H), 4.58 (dd, 1H, *J* = 5.5, 3.0 Hz), 2.63−2.53 (m, 1H), 2.20 (d, 1H, *J* = 3.0 Hz), 1.01 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.50, 140.21, 127.95, 127.23, 126.45, 115.40, 77.19, 44.54, 14.03.

(1*S,2*S**)-2-Methyl-1-phenylbut-3-en-1-ol (5d)[16c]**

^1H NMR ($CDCl_3$, 400 MHz): δ = 7.37−7.24 (m, 5H), 5.81 (ddd, 1H, *J* = 17.0, 10.5, 8.0 Hz), 5.23−5.16 (m, 2H), 4.34 (d, 1H, *J* = 8.0 Hz), 2.48 (sextet, 1H, *J* = 7.0 Hz), 2.29 (br s, 1H), 0.87 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 142.36, 140.57, 128.14, 127.54, 126.78, 116.69, 77.74, 46.18, 16.43.

(1*S,2*R**)-1-(4-Methoxyphenyl)-2-methylbut-3-en-1-ol (5e)[16d]**
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.21 (d, 2H, *J* = 8.5 Hz), 6.86 (d, 2H, *J* = 9.0 Hz), 5.79−5.66 (m, 1H), 5.07−5.03 (m, 1H), 5.02−4.98 (m, 1H), 4.52 (d, 1H, *J* = 6.0 Hz), 3.79 (s, 3H), 2.61−2.48 (m, 1H), 2.14 (br s,1H), 1.02 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 158.78, 140.28, 134.73, 127.6, 115.35, 113.36, 76.98, 55.18, 44.62, 14.39.

(1*S,2*S**)-1-(4-Methoxyphenyl)-2-methylbut-3-en-1-ol (5f)[15d]**
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.25 (d, 2H, *J* = 9.0 Hz), 6.88 (d, 2H, *J* = 9.0 Hz), 5.81 (ddd, 1H, *J* = 17.0, 10.5, 8.0 Hz), 5.24−5.15 (m, 2H), 4.29 (d, 1H, *J* = 8.0 Hz), 3.80 (s, 3H), 2.45 (sextet, 1H, *J* = 7.0 Hz), 2.29 (br s, 1H), 0.83 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 159.04, 140.89, 134.58, 127.92, 116.53, 113.57, 77.43, 55.18, 46.28, 16.50.

(1*S,2*R**)-2-Methyl-1-(4-Nitrophenyl)but-3-en-1-ol (5g)**
IR (NaCl, thin film): ν = 3420, 3120, 2988, 2910, 1665, 1608, 1521, 1349, 1060, 922, 855, 754, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.13 (d, 2H, *J* = 9.0 Hz), 7.45 (d, 2H, *J* = 8.5 Hz), 5.74 (ddd, 1H, *J* = 17.0, 10.5, 7.0 Hz), 5.07 (dt, 1H, *J* = 10.5, 1.5 Hz), 5.03 (dt, 1H, *J* = 17.0, 1.5 Hz), 4.73 (d, 1H, *J* = 5.0 Hz), 2.61−2.51 (m, 1H), 2.47 (br s, 1H), 0.94 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.99, 146.91, 139.25, 127.15, 123.11, 116.39, 75.97, 44.51, 13.34.

MS (EI): *m/z* = 207 (M^+, 1), 153 (20), 152 (100), 122 (20), 106 (30), 105 (24), 94 (30).

HRMS (EI): *m/z* calcd for $C_{11}H_{13}NO_3$ 207.0895. Found: 207.0882.

(1*S,2*S**)-2-Methyl-1-(4-Nitrophenyl)but-3-en-1-ol (5h)**
IR (NaCl, thin film): ν = 3419, 3120, 2988, 2910, 1665, 1609, 1520, 1350, 1059, 922, 855, 754, 700 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 8.16 (d, 2H, *J* = 9.0 Hz), 7.48 (d, 2H, *J* = 8.5 Hz), 5.72 (ddd, 1H, *J* = 17.0, 10.5, 8.0 Hz), 5.20−5.12 (m, 2H), 4.51 (d, 1H, *J* = 7.0 Hz), 2.49 (br s, 1H), 2.44 (sextet, 1H, *J* = 7.0 Hz), 0.91 (d, 3H, *J* = 7.0 Hz).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 149.83, 147.20, 139.08, 127.50, 123.27, 117.74, 76.66, 46.21, 16.17.

MS (EI): *m/z* = 207 (M^+, 1), 153 (25), 152 (100), 122 (15), 106 (24), 105 (17), 94 (17).

HRMS (EI): *m/z* calcd for $C_{11}H_{13}NO_3$ 207.0895. Found: 207.0887.

(2*S,3*S**)-2-(*tert*-Butyldimethylsilanyloxy)hex-5-en-3-ol (7a-"*syn*")[17a]**
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.92−5.80 (m, 1H), 5.12−5.05 (m, 2H), 3.72−3.66 (m, 1H), 3.40−3.33 (m, 1H), 2.40 (d, 1H, *J* = 5.5 Hz), 2.29−2.11 (m, 2H), 1.15 (d, 3H, *J* = 6.5 Hz), 0.89 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.13, 116.89, 75.11, 70.80, 38.03, 25.78, 20.10, 17.98, −4.16, −4.89.

(2*R,3*S**)-2-(*tert*-Butyldimethylsilanyloxy)hex-5-en-3-ol (7a-"*anti*")[17a]**
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.91−5.79 (m, 1H), 5.15−5.07 (m, 2H), 3.80−3.73 (m, 1H), 3.59−3.53 (m, 1H), 2.30−2.13 (m, 2H), 2.19 (d, 1H, *J* = 3.5 Hz), 1.10 (d, 3H, *J* = 6.5 Hz), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 135.03, 117.29, 74.43, 70.80, 36.72, 25.76, 17.98, 17.28, −4.46, −4.90.

MS (CI^-): *m/z* = 231 (MH^+, 8), 230 (M^+, 27), 229 ($(M-H)^-$, 100), 173 (6), 171 (9), 131 (33).

HRMS (CI^-): *m/z* calcd for $C_{12}H_{25}O_2Si$ $(M-H)^-$ 229.1624. Found: 229.1613.

IR (NaCl, thin film): ν = 3460, 3077, 2955, 2930, 2873, 2858, 1642, 1472, 1463, 1387, 1257, 1080, 1005, 968, 912, 836, 776, 668 cm^{-1}.

(1*S,2*S**)-1-(*tert*-Butyldimethylsilanyloxy)-1-phenylpent-4-en-2-ol (7b-"*syn*")[17b]**
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.35−7.25 (m, 5H), 5.90−5.79 (m, 1H), 5.08−5.01 (m, 2H), 4.45 (d, 1H, *J* = 7.0 Hz), 3.70−3.63 (m, 1H), 2.79 (d, 1H, *J* = 3.0 Hz), 2.18−2.10 (m, 1H), 2.09−2.00 (m, 1H), 0.90 (s, 9H), 0.05 (s, 3H), −0.21 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.31, 134.86, 128.13, 127.80, 127.07, 116.92, 78.49, 75.66, 36.63, 25.75, 18.08, −4.53, −5.13.

(1*R,2*S**)-1-(*tert*-Butyldimethylsilanyloxy)-1-phenylpent-4-en-2-ol (7b-"*anti*")[17b]**
IR (NaCl, thin film): ν = 3575, 3462, 3076, 3030, 2960, 2929, 2872, 2857, 1641, 1493, 1471, 1454, 1389, 1361, 1253, 1196, 1064, 1005, 913, 836, 778, 701, 674, 633 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36−7.26 (m, 5H), 5.93−5.82 (m, 1H), 5.14−5.07 (m, 2H), 4.62 (d, 1H, *J* = 5.0 Hz), 3.75 (m, 1H), 2.35−2.27 (m, 1H), 2.18−2.09 (m, 1H), 2.00 (d, 1H, *J* = 4.5 Hz), 0.93 (s, 9H), 0.08 (s, 3H), −0.14 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.13, 135.19, 127.99, 127.53, 127.01, 117.25, 77.68, 75.19, 36.34, 25.75, 18.09, −4.68, −5.11.

MS (CI^-): *m/z* = 293 (MH^+, 11), 292 (M^+, 33), 291 ($(M-H)^-$, 100), 233 (8), 159 (22), 131 (46), 119 (29).

HRMS (CI^-): *m/z* calcd for $C_{17}H_{27}O_2Si$ $(M-H)^-$ 291.1780. Found: 291.1769.

(2*R,3*S**,4*R**)-2-(*tert*-Butyldimethylsilanyloxy)-4-methylhex-5-en-3-ol (7c-"*anti*")**
IR (NaCl, thin film): ν = 3440, 2957, 2930, 2858, 1641, 1463, 1256, 1086, 1004, 969, 835, 776 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.64 (ddd, 1H, *J* = 17.5, 10.5, 8.5 Hz), 5.07−4.96 (m, 2H), 3.81 (dq, 1H, *J* = 6.0, 3.5 Hz), 3.31 (ddd, 1H, *J* = 8.5, 3.5, 2.0 Hz), 2.35 (d, 1H, *J* = 2.0 Hz), 2.30−2.14 (m, 1H), 1.08 (d, 3H, *J* = 6.5 Hz), 1.07 (d, 3H, *J* = 6.0 Hz), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.37, 114.89, 78.18, 69.51, 40.24, 25.76, 17.95, 16.74, 16.01, −4.50, −4.96.

MS (CI^-): *m/z* = 244 (M^-, 23), 243 ($(M-H)^-$, 100), 187 (45), 131 (55), 127 (24).

HRMS (CI^-): *m/z* calcd for $C_{13}H_{27}O_2Si$ $(M-H)^-$ 243.1780. Found: 243.1779.

(2*R,3*S**,4*S**)-2-(*tert*-Butyldimethylsilanyloxy)-4-methylhex-5-en-3-ol (7d-"*anti*")**
^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.90 (ddd, 1H, *J* = 17.0, 10.5, 7.5 Hz), 5.11−4.99 (m, 2H), 3.85 (dq, 1H, *J* = 6.5, 4.0 Hz), 3.31−3.26 (m, 1H), 2.27 (d, 1H, *J* = 3.5 Hz), 2.33−2.21 (m, 1H), 1.11 (d, 3H, *J* = 6.5 Hz), 0.97 (d, 3H, *J* = 7.0 Hz), 0.87 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.89, 114.67, 78.35, 69.44, 39.10, 25.75, 17.95, 16.73, 16.02, −4.42, −4.94.

(2*S,3*S**,4*S**)-2-(*tert*-Butyldimethylsilanyloxy)-4-methylhex-5-en-3-ol (7d-"*syn*")**
IR (NaCl, thin film): ν = 3440, 3076, 2958, 2931, 2897, 2859, 1641, 1472, 1463, 1389, 1375, 1362, 1256, 1092, 1039 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.87 (ddd, 1H, *J* = 17.0, 10.5, 8.5 Hz), 5.06−4.96 (m, 2H), 3.74 (pentet, 1H, *J* = 6.0 Hz), 3.31 (dd, 1H,

J = 5.5, 4.5 Hz), 2.41 (d, 1H, *J* = 4.5 Hz), 2.31−2.23 (m, 1H), 1.13 (d, 3H, *J* = 6.0 Hz), 1.07 (d, 3H, *J* = 7.0 Hz), 0.88 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 140.14, 114.74, 79.02, 69.69, 40.35, 25.77, 20.09, 17.95, 17.68, −4.03, −4.92.

MS (CI^-): *m/z* = 244 (M^-, 22), 243 ($(M-H)^-$, 100), 187 (58), 131 (86), 127 (54).

HRMS (CI^-): *m/z* calcd for $C_{13}H_{27}O_2Si$ $(M-H)^-$ 243.1780. Found: 243.1778.

(1*R,2*S**,3*R**)-1-(*tert*-Butyldimethylsilanyloxy)-3-methyl-1-phenylpent-4-en-2-ol (7e-"*anti*")**

IR (NaCl, thin film): ν = 3475, 3066, 3032, 2957, 2930, 2888, 2858, 1639, 1471, 1462, 1454, 1389, 1362, 1329, 1257, 1201, 1095, 1064, 1028, 1005, 913, 837, 864, 777, 700, 666 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.40−7.25 (m, 5H), 5.88 (ddd, 1H, *J* = 17.0, 10.5, 7.5 Hz), 5.12−5.03 (m, 2H), 4.63 (d, 1H, *J* = 6.0 Hz), 3.66 (dt, 1H, *J* = 6.0, 3.0 Hz), 2.44−2.31 (m, 1H), 1.92 (d, 1H, *J* = 3.0 Hz), 1.08 (d, 3H, *J* = 7.0 Hz), 0.90 (s, 9H), 0.06 (s, 3H), −0.20 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.79, 141.11, 127.94, 127.67, 127.64, 114.75, 78.64, 75.87, 38.59, 25.78, 18.04, 14.04, −4.56, −5.16.

MS (CI^-): *m/z* = 306 (M−, 29), 305 ($(M-H)^-$, 100), 173 (10), 131 (66), 127 (20), 119 (34).

HRMS (CI^-): *m/z* calcd for $C_{18}H_{29}O_2Si$ $(M-H)^-$ 305.1937. Found: 305.1935.

(1*R,2*S**,3*S**)-1-(*tert*-Butyldimethylsilanyloxy)-3-methyl-1-phenylpent-4-en-2-ol (7f-"*anti*")**

IR (NaCl, thin film): ν = 3578, 3071, 3032, 2957, 2930, 2887, 2858, 1639, 1494, 1472, 1463, 1454, 1388, 1361, 1317, 1257, 1160, 1079, 1065, 1005, 911, 864, 837, 778, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36−7.25 (m, 5H), 5.99 (ddd, 1H, *J* = 17.5, 10.5, 7.5 Hz), 5.10 (dd, 1H, *J* = 10.5, 2.0 Hz), 4.99 (ddd, 1H, *J* = 17.5, 2.0, 1.0 Hz), 4.50 (d, 1H, *J* = 8.0 Hz), 3.53 (dt, 1H, *J* = 8.0, 2.5 Hz), 2.89 (dd, 1H, *J* = 2.0, 1.0 Hz), 2.09−1.96 (m, 1H), 1.07 (d, 3H, *J* = 7.0 Hz), 0.89 (s, 9H), 0.04 (s, 3H), −0.25 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 141.50, 139.49, 128.13, 127.81, 127.33, 115.46, 79.52, 77.24, 38.83, 25.75, 18.75, 18.07, −4.46, −5.12.

MS (CI^-): *m/z* = 306 (M^-, 33), 305 ($(M-H)^-$, 100), 119 (57).

HRMS (CI^-): *m/z* calcd for $C_{18}H_{29}O_2Si$ $(M-H)^-$ 305.1937. Found: 305.1936.

(3*S,5*S**)-3-(*tert*-Butyldimethylsilanyloxy)-2-methyloct-7-en-5-ol (9a-"*syn*")**

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.85−5.75 (m, 1H), 5.10−5.04 (m, 2H), 3.80−3.74 (m, 2H), 3.16 (d, 1H, *J* = 1.5 Hz), 2.25−2.13 (m, 2H), 1.84−1.75 (m, 1H), 1.52−1.46 (m, 2H), 0.88 (s, 9H), 0.86 (d, 3H, *J* = 6.5 Hz), 0.80 (d, 3H, *J* = 6.5 Hz), 0.08 (s, 3H), 0.06 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.87, 117.30, 77.11, 70.18, 42.05, 36.49, 33.37, 25.81, 18.16, 17.94, 15.86, −4.20, −4.73.

(3*R,5*S**)-3-(*tert*-Butyldimethylsilanyloxy)-2-methyloct-7-en-5-ol (9a-"*anti*")**

IR (NaCl, thin film): ν = 3442, 3077, 2957, 2857, 1641, 1472, 1386, 1256, 1068, 1005, 915, 835, 775, 665 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 5.85−5.76 (m, 1H), 5.11−5.04 (m, 2H), 3.96−3.87 (m, 1H), 3.66 (dt, 1H, *J* = 6.5, 3.0), 2.93 (d, 1H, *J* = 2.5 Hz), 2.23−2.16 (m, 2H), 1.87−1.77 (m, 1H), 1.60 (ddd, 1H, *J* = 14.5, 6.5, 2.5), 1.49−1.42 (m, 1H), 0.88 (d, 3H, *J* = 6.5 Hz), 0.87 (s, 9H), 0.82 (d, 3H, *J* = 6.5 Hz), 0.08 (s, 3H), 0.04 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 134.89, 117.41, 75.68, 67.64, 42.55, 38.14, 32.82, 29.86, 19.18, 17.97, 17.64, −4.46, −4.61.

MS (CI^-): *m/z* = 271 ($(M-H)^-$, 18), 157 (6), 133 (9), 132 (15), 131 (100), 91 (7).

HRMS (CI^-): *m/z* calcd for $C_{15}H_{31}O_2Si$ $(M-H)^-$ = 271.2093. Found: 271.2107.

(1*S,3*S**)-1-(*tert*-Butyldimethylsilanyloxy)-1-phenylhex-5-en-3-ol (9b-"*syn*")**

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36−7.23 (m, 5H), 5.88−5.74 (m, 1H), 5.12−5.05 (m, 2H), 4.89 (dd, 1H, *J* = 10.0, 4.5 Hz), 3.91−3.80 (m, 1H), 3.48 (br s, 1H), 2.32−2.19 (m, 2H), 1.93−1.82 (m, 1H), 1.80−1.73 (m, 1H), 0.91 (s, 9H), 0.06 (s, 3H), −0.23 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.64, 134.60, 128.20, 127.37, 125.89, 117.39, 76.15, 70.29, 46.51, 41.93, 25.72, 17.89, −4.51, −5.16.

(1*R,3*S**)-1-(*tert*-Butyldimethylsilanyloxy)-1-phenylhex-5-en-3-ol (9b-"*anti*")**

IR (NaCl, thin film): ν = 3460, 2929, 2857, 1641, 1472, 1362, 1257, 1087, 1063, 914, 836, 777, 700, 666 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.36−7.20 (m, 5H), 5.87−5.72 (m, 1H), 5.11−5.07 (m, 2H), 5.05 (dd, 1H, *J* = 10.0, 4.5 Hz), 3.90−3.84 (m, 1H), 3.13 (br s, 1H), 2.26−2.18 (m, 2H), 1.81 (t, 2H, *J* = 5.0 Hz), 0.93 (s, 9H), 0.09 (s, 3H), −0.10 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.32, 134.74, 128.07, 126.95, 125.57, 117.29, 73.22, 67.23, 45.79, 42.08, 25.74, 18.04, −4.84, −5.31.

MS (CI^-): *m/z* = 306 (M^-, 8), 305 ($(M-H)^-$, 100), 173 (15).

HRMS (CI^-): *m/z* calcd for $C_{18}H_{29}O_2Si$ $(M-H)^-$ = 305.1937. Found: 305.1940.

(1*S,3*R**,4*R**)-1-(*tert*-Butyldimethylsilanyloxy)-4-methyl-1-phenylhex-5-en-3-ol (9c-"*syn*")**

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34−7.21 (m, 5H), 5.87−5.76 (m, 1H), 5.07−4.98 (m, 2H), 4.87 (dd, 1H, *J* = 7.5, 6.5 Hz), 3.70, (dd, 1H, *J* = 11.0, 5.5 Hz), 3.46 (br s, 1H), 2.32−2.18 (m, 1H), 1.90−1.70 (m, 2H), 1.04 (d, 3H, *J* = 7.0 Hz), 0.91 (s, 9H), 0.06 (s, 3H), −0.23 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.76, 140.81, 128.25, 127.43, 125.97, 114.81, 76.81, 74.54, 44.15, 43.75, 25.78, 17.94, 14.90, −4.45, −5.10.

(1*R,3*R**,4*R**)-1-(*tert*-Butyldimethylsilanyloxy)-4-methyl-1-phenylhex-5-en-3-ol (9c-"*anti*")**

IR (NaCl, thin film): ν = 3506, 3065, 3029, 2956, 2930, 2886, 2858, 1640, 1494, 1472, 1463, 1454, 1412, 1389, 1362, 1257, 1090, 1061, 1004, 914, 890, 837, 778, 701 cm^{-1}.

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.34−7.21 (m, 5H), 5.75−5.62 (m, 1H), 5.09 (dd, 1H, *J* = 6.5, 3.5 Hz), 5.06−4.97 (m, 2H), 3.65 (ddd, 1H, *J* = 6.5, 6.0, 2.0 Hz), 2.98 (br s, 1H), 2.32−2.18 (m, 1H), 1.90−1.70 (m, 2H), 1.01 (d, 3H, *J* = 7.0 Hz), 0.94 (s, 9H), 0.09 (s, 3H), −0.10 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.38, 140.92, 128.09, 126.94, 125.60, 114.86, 73.33, 71.20, 43.93, 43.41, 25.78, 18.08, 15.03, −4.78, −5.30.

MS (CI^-): *m/z* = 320 (M^-, 19), 319 ($(M-H)^-$, 62), 205 (25), 131 (35), 127 (100).

HRMS (CI^-): *m/z* calcd for $C_{19}H_{31}O_2Si$ $(M-H)^-$ 319.2093. Found: 319.2087.

(1*S, 3*R**, 4*S**)-1-(*tert*-Butyldimethylsilanyloxy)-4-methyl-1-phenylhex-5-en-3-ol (9d-"*syn*")**

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37−7.22 (m, 5H), 5.81 (ddd, 1H, *J* = 17.0, 10.5, 8.0 Hz), 5.10−5.00 (m, 2H), 4.89 (dd, 1H, *J* = 9.0, 4.5 Hz), 3.72−3.64 (m, 1H), 3.32 (br s, 1H), 2.32−2.22 (m, 1H), 1.91−1.70 (m, 2H), 1.03 (d, 3H, *J* = 7.0 Hz), 0.91 (s, 9H), 0.06 (s, 3H), −0.22 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.82, 140.30, 128.24, 127.40, 126.00, 115.17, 76.39, 74.20, 44.06, 43.70, 25.76, 17.92, 15.17, −4.50, −5.13.

(1*R,3*R**,4*S**)-1-(*tert*-Butyldimethylsilanyloxy)-4-methyl-1-phenylhex-5-en-3-ol (9d-"*anti*")**

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37−7.22 (m, 5H), 5.77 (ddd, 1H, *J* = 17.0, 10.5, 8.0 Hz), 5.11−5.00 (m, 3H), 3.70−3.62 (m, 1H), 2.85 (br s, 1H), 2.20−2.10 (m, 1H), 1.86−1.73 (m, 2H), 1.00 (d, 3H, *J* = 7.0 Hz), 0.93 (s, 9H), 0.08 (s, 3H), −0.10 (s, 3H).

^{13}C NMR ($CDCl_3$, 100 MHz): δ = 144.61, 140.48, 128.24, 126.92, 125.62, 115.35, 73.05, 71.01, 44.06, 43.79, 25.76, 18.07, 15.82, −4.82, −5.33.

MS (CI^-): *m/z* = 320 (M^-, 7), 319 ($(M-H)^-$, 27), 205 (24), 131 (100), 127 (47).

HRMS (CI−): *m/z* calcd for $C_{19}H_{31}O_2Si$ $(M-H)^-$ = 319.2093; found = 319.2077.

IR (NaCl, thin film): ν = 3506, 3065, 3029, 2956, 2929, 2886, 2858, 1640, 1473, 1462, 1454, 1413, 1389, 1362, 1257, 1090, 1060, 837, 778 cm^{-1}.

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