Synthesis of Enantiopure Homoallylic Ethers by Reagent Controlled Facial Selective Allylation of Chiral Ketones

Lutz F. Tietze,* Berthold Weigand, Ludwig Völkel, Christian Wulff, and Christian Bittner[a]

Dedicated to Professor Horst Kunz on the occasion of his 60th birthday

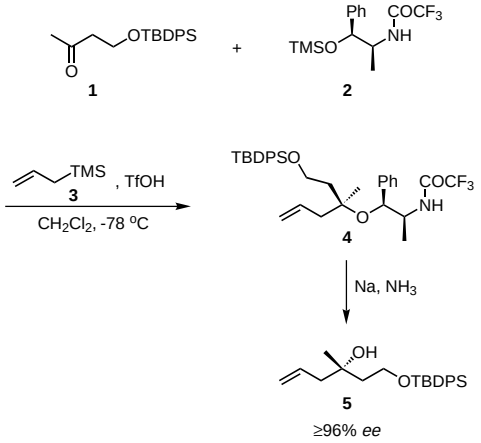
Abstract: The stereoselective allylation of chiral methyl ketones to give tertiary homoallylic ethers, which can easily be transformed into homoallylic alcohols, is described. Reaction of the enantiopure ketones **8a–d** and the racemic ketones **26a–d** with the norpseudoephedrine derivative **2** or *ent*-**2** and allylsilane in the presence of a catalytic amount of trifluoromethanesulfonic acid, led to a series of homoallylic ethers with good to excellent diastereoselectivity (85:15 to >97:3). The allylation is reagent controlled and nearly independent from the stereogenic centers in the substrates. A partial kinetic resolution was observed using the racemic ketones **26a–d**. In the reaction of the chiral ketones **8a–d** with the achiral reagents ethoxytrimethylsilane and allylsilane only a low diastereoselectivity was observed.

Keywords: amino alcohols · double stereodifferentiation · homoallylic alcohols · silanes

Introduction

The facial-selective addition of allylmetals to aldehydes or acetals to obtain enantiopure homoallylic alcohols or ethers is a widely used process in organic chemistry.[1] Typically, either an equimolar amount of a chiral allyl reagent such as allylboranes and allyltitanium compounds, or chiral acetals or chiral catalysts are employed.[2–5] However, all of these reagents, which give excellent selectivity with aldehydes, fail when applied to simple ketones.[6]

Recently we have demonstrated that reaction of aliphatic aldehydes with allylsilanes in the presence of the trimethylsilyl ether of *N*-trifluoroacetylnorpseudoephedrine (**2**) and a catalytic amount of TMSOTf leads to secondary homoallylic ethers with an asymmetric induction of >99:1.[7] Reductive cleavage using sodium in liquid ammonia provides the corresponding enantiopure homoallylic alcohols. In contrast to the other known allylation methods, this procedure can also be applied for the stereoselective synthesis of tertiary homoallylic ethers and alcohols using simple ketones as starting material;[8] allylation of for example the ketone **1** gives the homoallylic alcohol **5** in ≥96% *ee* through the ether **4** (Scheme 1). Noteworthy, the allylation of ketones and aldehydes creates the opposite absolute configuration at the newly formed stereogenic center due to different reaction mechanisms.[7, 8]



Scheme 1. Allylation of ketone **1** with **3** in presence of **2**.

Reaction of chiral substrates with chiral reagents under formation of a new stereogenic center usually leads to the formation of a "matched and a mismatched pair".[9] Rather frequently only one of the possible diastereomers can be obtained with high selectivity. It is therefore of great synthetic relevance whether a procedure allows the selective formation of the possible diastereomers independent of the configuration of the stereogenic centers in the substrate.[7] For the facial selective allylation of chiral ketones we prepared the four

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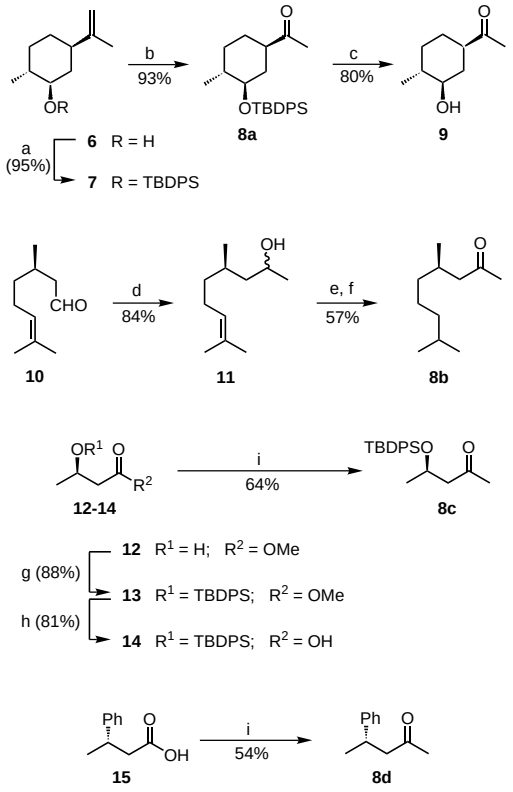
enantiopure methyl ketones **8a–d** (see Scheme 2) containing at least a stereogenic center in the α- or β-position. In addition, we also synthesized and employed the racemic ketones **26a–d** (see Scheme 5) to investigate whether a kinetic resolution is possible. Finally, we allylated the enantiopure ketones **8a–d** using achiral reagents to determine the induced diastereoselectivity in this type of transformation.

Results and Discussion

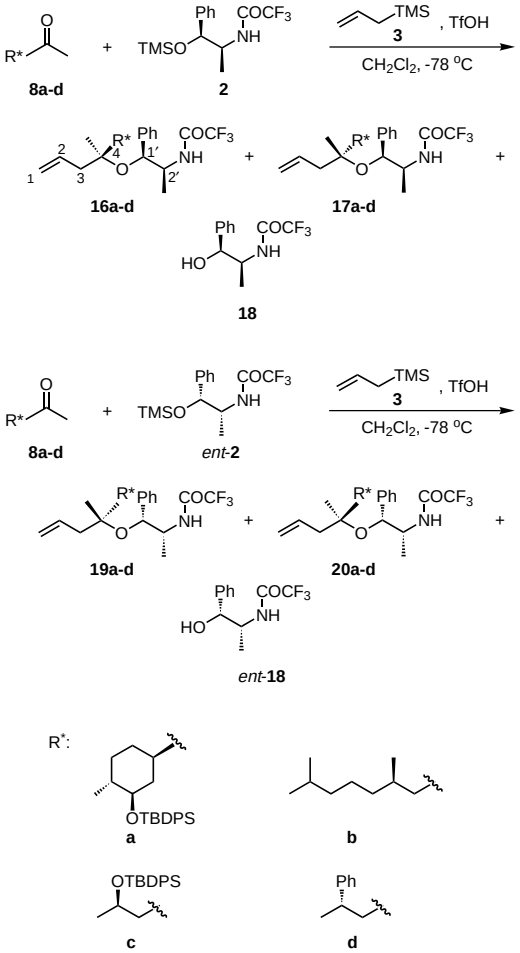
Synthesis and allylation of enantiopure aliphatic methyl ketones 8a–d: Ketone **8a** was obtained from commercially available (−)-dihydrocarveol (**6**) in an overall yield of 88% by protecting the hydroxyl group with TBDPSCl and subsequent ozonolysis of the alkenyl moiety (Scheme 2). For comparison



Scheme 2. Synthesis of enantiopure ketones **8a–d**. a) TBDPSCl, imidazole, RT; b) O_3, CH_2Cl_2/MeOH, −78 °C, PPh_3; c) TBAF, THF, RT; d) MeMgCl, THF, −78 °C; e) H_2, Pd/C, MeOH, 71%; f) Dess–Martin periodinane, CH_2Cl_2, RT, 80%; g) TBDPSCl, imidazole, THF, RT; h) NaOH, *i*PrOH/H_2O, 70 °C; i) MeLi, Et_2O, −78 °C.

8a was deprotected with TBAF·3H_2O to give **9**.[10] For the synthesis of **8b**, (*R*)-citronellal (**10**) was treated with MeMgCl to yield alcohol **11** which was first hydrogenated and then oxidized to give **8b** in 48% overall yield.[11] The β-silyloxyketone **8c** was synthesized from enantiopure β-hydroxyester **12** in 52% yield by protection of the alcohol moiety to give **13**, subsequent saponification, and treatment of carboxylic acid **14** with methyllithium.[12–14] Finally, the methyl ketone **8d** containing a phenyl group at the stereogenic center was obtained from commercially available (*R*)-3-phenylbutyric acid (**15**) by treatment with methyllithium.[15]

For the investigation of the double stereodifferentiation, the enantiopure methyl ketones **8a–d** were allylated in presence of the (*S*,*S*)- and (*R*,*R*)-norpseudoephedrine derivatives **2** and *ent*-**2**, respectively, to obtain the diastereomeric homoallylic ethers **16**/**17a–d** and **19**/**20a–d** (Scheme 3). The allylations were carried out in a domino-type reaction by mixing two equivalents of the chiral ketones **8a–d** with **2** as well as *ent*-**2** and 2.5 equivalents allylsilane **3** in dichloromethane at −78 °C, subsequent addition of a catalytic amount of TfOH and stirring for 3 d at −78 °C.[16] The reaction of



Scheme 3. Allylation of enantiopure ketones **8a–d** in the presence of **2** and *ent*-**2**.

unbranched ketones usually proceeds within a few hours, although in the case of the chiral ketones **8** the reaction is slower. For comparison of all transformations we therefore used a reasonable long reaction time. However, in the reaction of **8a** and **2** the allylation was not complete even after that time. All reactions proceeded rather well with only small amounts of the alcohols **18** and *ent*-**18** as by-products and not converted starting material **8a–d** and **2**/*ent*-**2**. We have recently found that the two-fold excess of the methyl ketones can be reduced to one equivalent by using additives, such as diisopropyl ketone without any loss in reactivity or

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selectivity;[8] this procedure, however, failed with ketones **8a–c**. In contrast, in the reactions of **8d** the yields of the homoallylic ethers **16d/17d** and **19d/20d** could be increased from 25% to 67% by addition of 10 equivalents diisopropyl ketone in presence of two equivalents of **2** and *ent*-**2**, respectively. The additive does not undergo an allylation under the reaction conditions.

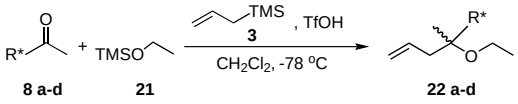
The obtained facial selectivity in the allylations of **8a–d** ranged from 85:15 for the reaction of **8d** in the presence of *ent*-**2** to >97:3 for **8c** with **2** and *ent*-**2** (Table 1). Noteworthy, in the reaction of **8a** with a stereogenic center in the α-position, no epimerization did take place. The difference in the selectivities found for the reactions of **8a–d** with **2** and *ent*-**2** was either very small or was non-existent, which clearly indicates a strong reagent control. The ratio of the formed homoallylic ethers **16a–d/17a–d** and **19a–d/20a–d** was determined by ^{13}C NMR spectroscopy of the crude products.

Table 1. Synthesis of homoallylic ethers **16a–d/17a–d** and **19a–d/20a–d** from enantiopure ketones **8a–d** (2 equiv) in the presence of **2** and *ent*-**2** (1 equiv).

Ketone	Reagent	Product	Ratio[a]	$[\alpha]_D$ [b]	Yield/%[c]
8a	**2**	**16a/17a**	97:3	+11.3	36 (91)
8a	*ent*-**2**	**19a/20a**	96:4	−29.0	64 (84)
8b	**2**	**16b/17b**	90:10	+24.3	52 (87)
8b	*ent*-**2**	**19b/20b**	89:11	−18.0	44 (73)
8c	**2**	**16c/17c**	>97:3	+11.2	41 (85)
8c	*ent*-**2**	**19c/20c**	>97:3	−20.0	44 (79)
8d	**2**	**16d/17d**	87:13	−26.6	67 (76)
8d	*ent*-**2**	**19d/20d**	85:15	+24.3	66 (80)

[a] Determination by ^{13}C NMR spectroscopy. [b] $c = 0.5$ in $CHCl_3$. [c] Yields in brackets are based on recovered starting material.

Induced diastereoselectivity of the allylation of chiral methyl ketones 8a–d with achiral reagents: For comparison we also performed the allylation of the chiral ketones **8a–d** with achiral reagents. Reaction of **8b–d** with ethoxytrimethylsilane (**21**) and allylsilane **3** led to the homoallylic ethers **22b–d** applying the same conditions as described for the transformations with **2** and *ent*-**2** (Scheme 4).



Scheme 4. Allylation of enantiopure ketones **8a–d** in the presence of achiral **21**.

Surprisingly, methyl ketone **8a** did not react under these conditions and only the starting material was recovered. In the other cases a mixture of diastereomers was formed with a rather low selectivity ranging from 1.5 to 2.1:1 (Table 2). The diastereomeric ratios were determined by gas column chromatography and ^{13}C NMR spectroscopy. A separation of the isomers by preparative chromatography was, however, not possible.

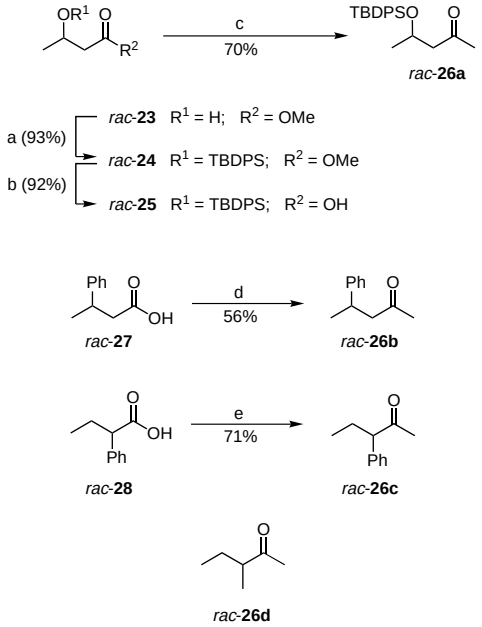
Allylation of racemic chiral ketones 26a–d in the presence of *ent*-2: A general procedure for the synthesis of enantiopure

Table 2. Allylation of enantiopure ketones **8a–d** (2 equiv) in the presence of achiral **21** (1 equiv).

Ketone	Product	Diastereomeric ratio	Yield/%
8a	**22a**	–	–[a]
8b	**22b**	2.0:1[b]	82
8c	**22c**	1.5:1[c]	89
8d	**22d**	2.1:1[b]	75

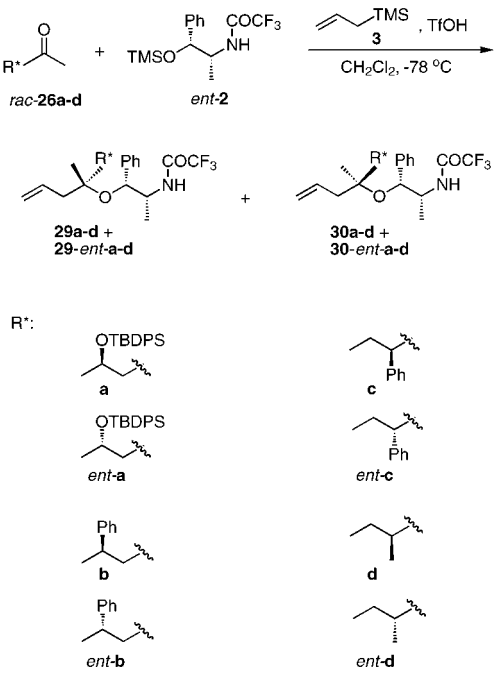
[a] No conversion. [b] Determination by GC. [c] Determination by ^{13}C NMR spectroscopy.

products is the reaction of racemic chiral substrates with enantiopure reagents or catalysts by kinetic resolution. For this purpose we prepared the racemic ketones **26a–c** and used them together with the commercially available racemic **26d** for the allylation in the presence of *ent*-**2** (Scheme 5).[12–15, 18]



Scheme 5. Synthesis of racemic ketones *rac*-**26a–d**. a) TBDPSCl, imidazole, THF, RT; b) NaOH, *i*PrOH/H_2O, 70 °C; c) MeLi, Et_2O, −78 °C; d) MeLi, Et_2O, −78 °C; e) MeLi, Et_2O, 0 °C.

In these reactions four diastereomers were formed. However, as expected the two isomers **29a–d** and **29**-*ent*-**a–d** were the major or as for the reaction of **26a** the only products; in the other cases three out of the four possible isomers could be detected by gas chromatography and ^{13}C NMR spectroscopy (Scheme 6). The ratio of the major and minor isomers **29** and **30** ranged from 89:11 to >97:3, whereas for the major isomers **29a-d**/*ent*-**a–d** a ratio of 1.4:1 to 2.1:1 was observed; this indicates that under the applied reaction conditions a partial kinetic resolution did occur (Table 3). Since the kinetic resolution usually depends on the stage of transformation we determined the ratio of the major isomers formed in the allylation of racemic **26c** after 12 h, 1 d, 3 d, and 5 d.[17] As expected, with increasing transformation a decrease of the kinetic resolution from 1.6:1 to 1.5:1 was observed.



Scheme 6. Allylation of ketones *rac*-**26a–d** in the presence of *ent*-**2**.

Table 3. Allylation of racemic chiral ketones **26a–d** (2 equiv) in the presence of *ent*-**2** (1 equiv) for 3 d.

Ketone	Product	Ratio **29a–d**/*ent*-**29a–d**	Ratio **29**:**30**	Yield/%[c]
26a	**29a**/**29**-*ent*-**a**	1.4:1[a]	> 97:3[a]	45 (84)
26b	**29b**/**29**-*ent*-**b**	1.5:1[a]	92:8[a]	51 (79)
26c	**29c**/**29**-*ent*-**c**	1.5:1[a, b]	91:9[a, b]	21 (85)[d]
26d	**29d**/**29**-*ent*-**d**	2.1:1[a, b]	90:10[a, b]	71

[a] Determination by ^{13}C NMR spectroscopy. [b] Determination by GC. [c] Yields are based on *ent*-**2**, in brackets are the numbers based on recovered *ent*-**2**. [d] Reaction time: 5 d.

A preparative separation of the isomers and their structure elucidation was not possible. However, in analogy to the products obtained from **8a–d** in the presence of *ent*-**2** the newly formed stereogenic center in **29a–d** and **29**-*ent*-**a–d** should have the *R* configuration.

Structure elucidation of the homoallylic ethers: The structure of the obtained homoallylic ethers **16a–d**, **17a–d**, **19a–d** and **20a–d**, as well as **22b–d**, **29a–d** and **30a–d** was determined by ^1H and ^{13}C NMR spectroscopy. The relative configuration of the stereogenic centers in the products was correlated to an X-ray crystallographic analysis obtained for **16d**.[19] As representatives for all new products the ^1H NMR spectra of **16d** and **22d** are discussed. The hydrogens at the vinyl group of **16d** resonate at $\delta = 5.02-5.12$ and $\delta = 5.68-5.82$ as multiplets; for the methyl group at the newly formed stereogenic center a singulet at $\delta = 0.81$ is observed, and the norpseudoephedrine moiety gives signals at $\delta = 4.53$ as a doublet with $J = 3.8$ Hz and a multiplet at $\delta = 3.98-4.12$. The signals for the phenyl groups are found at $\delta = 7.12-7.32$ and the signal for the NH group at $\delta = 5.97$ as a broad doublet with $J = 8.0$ Hz. The diastereotopic protons 3-H resonate at $\delta = 2.28-2.36$ and 5-H at $\delta = 1.77-2.00$. For the benzylic hydrogen 6-H a multiplet at $\delta = 2.90-3.10$ and for 7-H a doublet at $\delta = 1.05$ with $J = 6.8$ Hz is found. The ^1H NMR spectrum of **22d** is quite similar to that of **16d**, except that the signals for the ephedrine moiety are missing. Instead signals for the ethoxy group are found at $\delta = 3.24$ as a quartet with $J = 7.0$ Hz and at $\delta = 1.04$ as a triplet with $J = 7.0$ Hz for the major diastereomer.

Conclusion

The described allylation of methyl ketones using the norpseudoephedrine derivative **2** as well as *ent*-**2** and allylsilane **3** is the only method known at this time, which allows the highly stereoselective preparation of enantiopure tertiary homoallylic ethers and alcohols from simple ketones. The method shows a strong reagent control allowing a good to excellent facial selectivity up to > 97:3 independent of the stereogenic centers in the substrate. Thus, the selectivity for the "matched and mismatched pairs" is nearly identical. Using racemic mixtures of chiral methyl ketones, a partial kinetic resolution was observed, which, however, is not very pronounced.

Experimental Section

General aspects: All reactions were performed in flame-dried glassware in an atmosphere of argon unless noted otherwise. Melting points were determined on a Mettler FP61 and are uncorrected. Optical rotations were measured on a Perkin–Elmer 241 digital polarimeter in a 1 dm cell. IR spectra were recorded on a Bruker IFS 25 FT-IR instrument and ^1H NMR and ^{13}C NMR spectra with a Bruker AM-300, a Varian VXR-200 or a Varian VXR-500. Chemical shifts were reported on the δ scale relative to $CDCl_3$ as an internal standard. Mass spectra were measured at 70 eV with a Varian MAT 311A. GC analysis was carried out with hydrogen as carrier gas on a DB 1701 column (J&W Scientific, 0.25 mm × 50 m). HPLC analysis was carried out on a Chiralcel OD-R (250 mm, 0.46 cm). TLC chromatography was performed on precoated silica gel SIL G/UV_{254} aluminum plates (Macherey Nagel), and silica gel 32–63 (0.032–0.064 mm) (Macherey Nagel) was used for column chromatography. Microanalyses were carried out by the Mikroanalytisches Labor des Instituts für Organische Chemie der Universität Göttingen.

(1*R*,2*R*,5*R*)-5-Isopropenyl-2-methyl-1-(*tert*-butyldiphenylsilanyloxy)-cyclohexane (7): A solution of (−)-dihydrocarveol (**6**) (1.54 g, 10.0 mmol), TBDPSCl (3.02 g, 11.0 mmol), and imidazole (1.50 g, 22.0 mmol) in dry DMF (6 mL) was stirred for 2 h at room temperature. The mixture was poured into a mixture of CH_2Cl_2 (100 mL) and water (400 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL) and the combined organic layers were dried over Na_2SO_4. The solvent was evaporated in vacuo and the crude product was purified on silica gel (*n*-pentane/*tert*-butyl methyl ether 10:1) to give **7** (3.73 g, 9.50 mmol, 95%). $[\alpha]_D^{20} = -46.3^\circ$ ($c = 1$, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$): $\delta = 0.72-1.81$ (m, 11H), 0.97 (d, $J = 6.0$ Hz, 3H), 1.07 (s, 9H), 3.20–3.36 (m, 1H), 4.46–4.67 (m, 2H), 7.29–7.78 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.36$, 19.52, 20.91, 27.06, 30.93, 33.31, 40.43, 40.99, 43.89, 78.41, 108.1, 127.6, 127.4, 129.3, 129.4, 134.4, 135.2, 135.8, 135.8, 136.0, 149.5; IR (film): $\tilde{\nu} = 3070$, 3050, 3014, 2930, 2858, 1108, 888, 740 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 410 (100) $[M+NH_3+H]^+$, 802 (20) $[2 \times M+NH_3]^+$.

(1′*R*,3′*R*,4′*R*)-1-{4′-Methylcyclohexyl-3′-(*tert*-butyldiphenylsilanyloxy)}-ethanone (8a): Ozone was bubbled through a solution of alkene **7** (1.96 g, 5.00 mmol) in a mixture of CH_2Cl_2 (100 mL) and MeOH (20 mL) at −78 °C until a blue color remained permanent. The solution was saturated with nitrogen and PPh_3 (1.70 g, 6.47 mmol) in CH_2Cl_2 (7 mL) was added. The mixture was stirred for 10 min and then allowed to warm to room temperature. The solvent was evaporated and the residue purified on silica gel (*n*-pentane/*tert*-butyl methyl ether 9:1) to give the methyl ketone **8a** (1.83 g, 4.65 mmol, 93%). $[\alpha]_D^{20} = -73.3^\circ$ ($c = 1$, $CHCl_3$); ^1H NMR

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(200 MHz, $CDCl_3$): $\delta = 0.80-2.13$ (m, 8H), 0.98 (d, $J = 6.5$ Hz, 3H), 1.06 (s, 9H), 1.88 (s, 3H), 3.22–3.32 (m, 1H), 7.32–7.72 (m, 10H); ^{13}C-NMR (50.3 MHz, $CDCl_3$): $\delta = 19.16, 19.45, 27.06, 27.33, 27.68, 32.43, 37.38, 40.08, 50.39, 77.55, 127.4, 127.6, 129.5, 129.7, 135.7, 210.4$; IR (film): $\tilde{\nu} = 3070, 3050, 2932, 2894, 1710, 1108, 740, 704$ cm^{-1}; MS (70 eV, CI): m/z (%): 395 (100) $[M+H]^+$, 412 (20) $[M+NH_3+H]^+$, 804 (6) $[2\times M+NH_3]^+$.

(4*R*)-4,8-Dimethylnonan-2-one (8b): A solution of alkene **9** (843 mg, 4.94 mmol) in MeOH (90 mL) was hydrogenated under a pressure of 1 atm H_2 in the presence of a catalytic amount of palladium on activated carbon (300 mg, 5% Pd/C) for 1 h. After removal of the catalyst by filtration over silica gel and the solution was concentrated in vacuo. The saturated alcohol was obtained as a colorless liquid (604 mg, 3.51 mmol, 71%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.86$ (d, $J = 6.5$ Hz, 6H), 0.89 (d, $J = 6.0$ Hz, 3H), 1.08–1.58 (m, 12H), 3.84–3.94 (m, 1H).

A solution of Dess–Martin periodinane (1.25 g, 2.91 mmol) in CH_2Cl_2 was added to a solution of the alcohol (455 mg, 2.64 mmol) in CH_2Cl_2 at 0 °C and stirring was continued for 30 min. The mixture was warmed to room temperature, Et_2O (85 mL) and 1.3 M aqueous NaOH (20 mL) was added. The organic layer was separated, washed with water (25 mL), 1.3 M aqueous NaOH (20 mL), and dried over Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography (*n*-pentane/*tert*-butyl methyl ether 9:1) to give ketone **8b** (360 mg, 2.11 mmol, 80%). $[\alpha]_D^{20} = +9.5^\circ$ ($c = 1$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.77$ (d, $J = 6.0$ Hz, 6H), 0.80 (d, $J = 6.5$ Hz, 3H), 0.98–1.25 (m, 6H), 1.30–1.51 (m, 1H), 1.82–1.94 (m, 1H), 2.04 (s, 3H), 2.12 (dd, $J_1 = 8.0$ Hz, $J_2 = 16.0$ Hz, 1H), 2.32 (dd, $J_1 = 7.0$ Hz, $J_2 = 16.0$ Hz, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.82, 22.57, 22.67, 24.72, 27.93, 29.27, 30.35, 37.15, 39.08, 51.26, 208.7$.

(*R*)-4-(*tert*-Butyldiphenylsilanyloxy)-pentan-2-one (8c): A 1.6 M solution of methyllithium in Et_2O (8.00 mL, 12.8 mmol) was added dropwise within 30 min at −78 °C under stirring to a solution of **14** (2.00 g, 5.84 mmol) in anhydrous Et_2O (80 mL). Stirring was continued for 30 min, the mixture was warmed to 0 °C and then quenched by addition of saturated aqueous NH_4Cl (100 mL). The layers were separated and the aqueous layer was extracted with Et_2O (4 × 30 mL). The combined organic extracts were washed with brine and dried over Na_2SO_4, the solvent was evaporated, and the residue was purified by column chromatography (*n*-pentane/*tert*-butyl methyl ether 15:1). Ketone **8c** was obtained as a colorless oil (1.27 g, 3.73 mmol, 64%). $[\alpha]_D^{20} = -2.5^\circ$ ($c = 1$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.03$ (s, 9H), 1.09 (d, $J = 6.0$ Hz, 3H), 2.05 (s, 3H), 2.46 (dd, $J_1 = 6.0$ Hz, $J_2 = 15.0$ Hz, 1H), 2.64 (dd, $J_1 = 6.0$ Hz, $J_2 = 15.0$ Hz, 1H), 4.31 (m, 1H), 7.37–7.59 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.14, 23.61, 26.90, 30.98, 53.19, 66.46, 127.4, 127.6, 129.5, 129.7, 135.7, 207.2$; IR (film): $\tilde{\nu} = 3070, 3056, 2962, 2932, 2894, 1716$ (C=O), 1470, 1372, 1426, 1134, 1108, 1020, 740, 704 cm^{-1}.

(*S*)-4-Phenyl-2-pentanone (8d): A 1.6 M solution of methyllithium (12.6 mL, 20.1 mmol) was added dropwise at −78 °C with stirring for 30 min to a solution of (*S*)-3-phenylbutric acid (**15**, 1.50 g, 9.13 mmol) in dry Et_2O. Stirring was continued for 30 min and the mixture was allowed to warm to 0 °C. Saturated aqueous NH_4Cl solution (135 mL) was added, the organic layer separated, the aqueous layer extracted with Et_2O (4 × 50 mL), and the combined organic extracts washed with brine, dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (*n*-pentane/*tert*-butyl methyl ether 9:1) to give ketone **8d** (815 mg, 5.02 mmol, 54%) as a colorless liquid. $[\alpha]_D^{20} = +40.0^\circ$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.27$ (d, $J = 7.0$ Hz, 3H), 2.06 (s, 3H), 2.64 (dd, $J_1 = 8.0$ Hz, $J_2 = 16.5$ Hz, 1H), 2.77 (dd, $J_1 = 6.5$ Hz, $J_2 = 16.5$ Hz, 1H), 3.32 (m, 1H), 7.15–7.34 (m, 5H); ^{13}C NMR ($CDCl_3$, 50.3 MHz): $\delta = 21.99, 30.54, 35.41, 51.94, 126.2, 126.7, 128.4, 146.1, 207.8$.

(1*R*,3*R*,5*R*)-1-(3-Hydroxy-4-methylcyclohexyl)-ethanone (9): Tetrabutylammonium fluoride trihydrate (158 mg, 0.50 mmol) was added to a solution of silyl ether **8a** (100 mg, 0.25 mmol) in THF and stirring was continued for 3 h. The solvent was evaporated in vacuo and the crude product was purified by column chromatography on silica gel to give **9** (31 mg, 0.20 mmol, 80%).

(4*R*)-4,8-Dimethylnon-7-en-2-ol (11): A solution of methylmagnesium chloride (3 M, 4.80 mL, 14.6 mmol) in THF was added at −78 °C to a solution of (*R*)-citronellal (**10**). After 1 h the reaction mixture was warmed to 0 °C and an 20% aqueous solution of NH_4Cl (4 mL) was added. The organic layer was separated and the aqueous layer extracted with Et_2O (4 × 40 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by column filtration (*n*-pentane/*tert*-butyl methyl ether 9:1) to give alcohol **11** (1.73 g, 10.2 mmol, 84%). ^{1}H NMR ($CDCl_3$, 200 MHz): $\delta = 0.91$ (d, $J = 6.0$ Hz, 3H), 1.16–1.69 (m, 13H), 1.38 (s, 1H), 1.97–2.01 (m, 2H), 3.82–4.00 (m, 1H), 5.09 (m, 1H).

(*R*)-3-(*tert*-Butyldiphenylsilanyloxy)-butyric acid methyl ester (13): TBDPSCl (2.37g, 9.59 mmol) was added dropwise at 15 °C to a solution of (*R*)-3-hydroxybutyric acid methyl ester **12** (1.11 g, 9.59 mmol) and imidazole (1.65g, 23.8 mmol) in anhydrous THF (5 mL) and the reaction mixture was stirred for 2 h at room temperature. The precipating solid was filtered and washed with THF (3 × 10 mL). Water (40 mL) was added to the combined organic phases and the mixture was concentrated to 40 mL. EtOAc (40 mL) was added and the organic layer was separated, washed with water (2 × 40 mL), and dried over Na_2SO_4. The solvent was removed in vacuo and the residue was purified by flash column chromatography (*n*-pentane/*tert*-butyl methyl ether 9:1) to give silyl ether **12** (3.00 g, 8.41 mmol, 88%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.05$ (s, 9H), 1.11 (d, $J = 6.0$ Hz, 3H), 2.38 (dd, $J_1 = 6.0$ Hz, $J_2 = 15.0$ Hz, 1H), 2.58 (dd, $J_1 = 7.4$ Hz, $J_2 = 15.0$ Hz, 1H), 3.59 (s, 3H), 4.32 (m, 1H), 7.30–7.76 (m, 10H).

(*R*)-3-(*tert*-Butyldiphenylsilanyloxy)-butyric acid (14): Ester **13** (2.75 g, 7.71 mmol) and NaOH (0.62 g, 15.4 mmol) were dissolved in isopropanol (155 mL) and water (55 mL) and heated to 70 °C for 2 h with stirring. The mixture was cooled to ambient temperature and treated with 1N aqueous HCl (250 mL) and extracted with Et_2O (4 × 100 mL). The combined organic layers were dried over Na_2SO_4 and the solvent was removed in vacuo to give carboxylic acid **14** (2.16 g, 6.31 mmol, 81%) as a white solid which was used without further purification. M.p. 115 °C (pentane, *tert*-butyl methyl ether); $[\alpha]_D^{20} = +1.8^\circ$ ($c = 1$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.04$ (s, 9H), 1.14 (d, $J = 6.3$ Hz, 3H), 2.43 (dd, $J_1 = 6.0$ Hz, $J_2 = 15.0$ Hz,1H), 2.55 (dd, $J_1 = 6.0$ Hz, $J_2 = 15.0$ Hz, 1H), 4.27 (m, 1H), 7.36–7.70 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 19.14, 23.36, 26.84, 44.05, 66.64, 127.4, 127.5, 129.6, 129.7, 135.7, 176.9$.

***rac*-3-(*tert*-Butyldiphenylsilanyloxy)-butyric acid ethyl ester (*rac*-24)**: Reaction of *rac*-3-hydroxybutyric acid ethyl ester (*rac*-**23**, 2.00 g, 15.1 mmol) with TBDPSCl was performed as described for **13** to give *rac*-**24** as a colorless oil (5.21 g, 14.1 mmol, 93%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 1.05$ (s, 9H), 1.12 (d, $J = 7.5$ Hz, 3H), 1.20 (t, $J = 8.0$ Hz, 3H), 2.38 (dd, $J_1 = 6.5$ Hz, $J_2 = 15.0$ Hz, 1H), 2.76 (dd, $J_1 = 7.5$ Hz, $J_2 = 15.0$ Hz, 1H), 4.06 (q, $J = 8.0$ Hz, 2H), 4.36 (m, 1H), 7.30–7.78 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 14.08, 19.12, 23.56, 26.82, 44.59, 60.15, 66.83, 127.5, 127.5, 129.5, 129.5, 135.7, 171.3$.

***rac*-3-(*tert*-Butyldiphenylsilanyloxy)-butyric acid (*rac*-25)**: A solution of *rac*-**24** (3.70 g, 10.00 mmol) and NaOH (1.13 g, 28.0 mmol) in isopropanol (200 mL) and water (60 mL) was stirred for 4 h at 60 °C. The workup was carried out as described for **14** to give carboxylic acid *rac*-**25** (3.17 g, 9.15 mmol, 92%) as a colorless solid.

***rac*-4-(*tert*-Butyldiphenylsilanyloxy)-pentan-2-one (*rac*-26a)**: Reaction of *rac*-**25** (2.00 g, 5.84 mmol) in anhydrous Et_2O (80 mL) with 1.6 M solution methyllithium (6.00 mL, 12.8 mmol) as described for **8c** gave *rac*-**26a** (1.39 g, 4.08 mmol, 70%) as a colorless solid. M.p. 42 °C (pentane, *tert*-butyl methyl ether).

***rac*-4-Phenyl-2-pentanone (*rac*-26b)**: Reaction of *rac*-3-phenylbutyric acid (*rac*-**27**, 1.64 g, 10.0 mmol) with a 1.6 M solution of methyllithium in Et_2O (13.8 mL, 22.0 mmol) as described for **8d** gave *rac*-**26b** as a colorless oil (5.61 mmol, 910 mg, 56%).

***rac*-3-Phenyl-2-pentanone (*rac*-26c)**: Reaction of *rac*-2-phenylbutyric acid (*rac*-**28**, 1.64 g, 10.0 mmol) in Et_2O (120 mL) with a 1.6 M solution methyllithium (13.3 mL, 22.2 mmol) as described for **8d** gave *rac*-**26c** (1.15 g, 7.08 mmol, 71%) after column chromatography (*n*-pentane/*tert*-butyl methyl ether 9:1) as a colorless liquid. ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.83$ (t, $J = 7.5$ Hz, 3H), 1.71 (ddq, $J_1 = 6.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 14.0$ Hz, 1H), 2.05 (s, 3H), 2.11 (ddq, $J_1 = 6.5$ Hz $J_2 = 7.5$ Hz, $J_3 = 14.0$ Hz, 1H), 3.52 (t, $J = 7.5$ Hz, 3H), 7.17–7.46 (m, 5H).

General procedure for the allylation of ketones 8 and 26: Trifluormethanesulfonic acid (0.14 mmol) was added at −78 °C with stirring to a solution of ketones **8a–d** or *rac*-**26a–d** (0.50 mmol), (*S*,*S*)- or (*R*,*R*)-2-trifluoroacetamido-1-trimethylsiloxy-1-phenyl-propane (**2** or *ent*-**2**, 0.25 mmol) or ethoxytrimethylsilane (**22**, 0.25 mmol), and allyltrimethylsilane (**3**, 0.63 mmol) and stirring was continued at −78 °C for 3 d. The reaction

was quenched by addition of triethylamine (100 µL) and the mixture poured into water (5 mL). The organic phase was separated and the aqueous phase extracted with CH_2Cl_2 (2 × 5 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated in vacuo. Purification of the residue by column chromatography (*n*-pentane/*tert*-butyl methyl ether 15:1) gave the corresponding homoallylic ethers **16a–d**, **17a–d**, **19a–d, 20a–d, 22b–d, 29a–d/29-*ent*-a–d**, and **30a–d/30-*ent*-a–d**, respectively.

(4*R*,1′*R*,2′*R*,1″*R*,3″*R*,4″*R*)-4-(2′-Trifluoroacetamido-1′-phenyl-propoxy)-4-(3″-*tert*-butyldiphenylsilanyloxy-4″-methyl-cyclohexyl)-pent-1-ene (19a): According to the general procedure, reaction of ketone **8a** (197 mg, 0.50 mmol) with *ent*-**2** (80 mg, 0.25 mmol) gave the homoallylic ether **19a** (106 mg, 0.16 mmol, 64%) as colorless needles, along with recovered *ent*-**2** (20 mg, 0.06 mmol, 20%). M.p. 181 °C (pentane); $[\alpha]_D^{20} = -29.0°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.49$ (s, 3H), 0.64–1.77 (m, 8H), 0.99 (d, $J = 6.5$ Hz, 3H), 1.03 (s, 9H), 1.09 (d, $J = 7.2$ Hz, 3H), 2.06 (dd, $J_1 = 7.0$ Hz, $J_2 = 15.0$ Hz, 1H), 2.31 (dd, $J_1 = 7.5$ Hz, $J_2 = 15.0$ Hz, 1H), 3.14–3.24 (m, 1H), 4.07 (m, 1H), 4.48 (d, $J = 3.7$ Hz, 1H), 4.86–5.01 (m, 2H), 5.45–5.61 (m, 1H), 6.26 (br d, $J = 8.0$ Hz, 1H), 7.08–7.74 (m, 15H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.41$, 19.23, 19.50, 21.70, 25.88, 27.08, 32.99, 36.69, 40.60, 40.64, 44.10, 51.59, 73.90, 78.51, 79.94, 115.8 (q, $^1J_{CF} = 289$ Hz), 117.9, 126.7, 127.3, 127.4, 127.7, 128.2, 129.3, 129.4, 133.6, 135.9, 141.1, 156.3 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3312$, 3110, 3074, 3048, 3030, 2962, 2936, 2868, 2865, 1706, 1208, 1188, 1162, 1110, 1092, 1058, 914, 758, 702 cm^{-1}; MS: (70 eV, CI): *m*/*z* (%): 683 (100) $[M+NH_3+H]^+$; $C_{39}H_{50}O_3NF_3Si$ (665.35): calcd C 70.40, H 7.57; found C 70.50, H 7.64.

(4*S*,1′*S*,2′*S*,1″*R*,3″*R*,4″*R*)-4-(2′-Trifluoroacetamido-1′-phenyl-propoxy)-4-(3″-*tert*-butyldiphenylsilanyloxy-4″-methyl-cyclohexyl)-pent-1-ene (16a): According to the general procedure, reaction of ketone **8a** (197 mg, 0.50 mmol) with **2** (80 mg, 0.25 mmol) gave the homoallylic ether **16a** (60 mg, 0.09 mmol, 36%) as a highly viscous oil, along with recovered **2** (44 mg, 0.14 mmol, 55%). ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.61$ (s, 3H), 0.64–1.70 (m, 11H), 0.99 (d, $J = 6.5$ Hz, 3H), 1.05 (s, 9H), 2.13 (m, 2H), 3.20–3.31 (m, 1H), 3.96 (m, 1H), 4.44 (d, $J = 4.0$ Hz, 1H), 4.85–4.98 (m, 2H), 5.39–5.55 (m, 1H), 6.24 (br d, $J = 8.0$ Hz, 1H), 7.04–7.71 (m, 15H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.21$, 19.34, 19.50, 21.87, 26.17, 27.02, 32.91, 36.40, 40.41, 40.56, 43.78, 51.55, 73.50, 78.72, 79.79, 115.8 (q, $^1J_{CF} = 288$ Hz), 117.9, 126.7, 127.6, 128.1, 128.2, 128.4, 129.3, 129.4, 133.6, 141.1, 156.4 (q, $^2J_{CF} = 37$ Hz); IR (film): $\tilde{\nu} = 3330$, 3134, 3072, 3030, 2972, 2934, 2894, 2860, 1722, 1210, 1166, 1112, 1078, 1028, 916, 756, 704 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 683 (100) $[M+NH_3+H]^+$.

(4*R*,6*S*,1′*R*,2′*R*)-4,6,10-Trimethyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-undec-1-ene (19b): According to the general procedure, reaction of ketone **8b** (85.0 mg, 0.50 mmol) with *ent*-**2** (80 mg, 0.25 mmol) gave the homoallylic ether **19b** (49 mg, 0.11 µmol, 44%) as colorless needles, along with recovered *ent*-**2** (23 mg, 0.70 mmol, 29%). M.p. 54 °C (pentane); $[\alpha]_D^{20} = -18.0°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.79$–1.03 (m, 12H), 1.06–1.73 (m, 13H), 2.32 (m, 2H), 4.08 (m, 1H), 4.60 (d, $J = 3.5$ Hz, 1H), 5.04–5.10 (m, 2H), 5.70–5.94 (m, 1H), 6.45 (br d, $J = 8.0$ Hz, 1H), 7.20–7.42 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.22$, 22.00, 22.58, 22.73, 24.02, 24.94, 27.98, 28.66, 39.27, 39.44, 43.64, 47.48, 51.97, 74.37, 79.75, 115.7 (q, $^1J_{CF} = 288$ Hz), 118.1, 126.5, 127.7, 128.3, 134.3, 141.7, 156.4 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3306$, 3078, 3034, 2958, 2928, 2870, 1702, 1568, 1208, 1188, 1164, 914, 756, 702 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 459 (100) $[M+NH_3+H]^+$, 900 (5) $[2 \times M+NH_3+H]^+$; $C_{25}H_{38}F_3NO_2$ (441.75): calcd C 68.00, H 8.66; found: C 68.18, H 8.86.

(4*S*,6*S*,1′*S*,2′*S*)-4,6,10-Trimethyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-undec-1-ene (16b): According to the general procedure, reaction of ketone **8b** (85 mg, 0.50 mmol) with **2** (80 mg, 0.25 mmol) gave the homoallylic ether **16b** (57 mg, 0.13 mmol, 52%) as colorless needles, along with recovered **2** (28 mg, 0.09 mmol, 35%). M.p. 54 °C (pentane); $[\alpha]_D^{20} = +24.3°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.80–1.75$ (m, 25H), 2.38 (m, 2H), 4.10 (m, 1H), 4.60 (d, $J = 4.0$ Hz, 1H), 5.07–5.12 (m, 2H), 5.71–5.96 (m, 1H), 6.42 (br d, $J = 8.0$ Hz, 1H), 7.18–7.46 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.13$, 22.11, 22.56, 22.70, 24.16, 24.87, 27.97, 28.56, 39.19, 39.27, 43.86, 47.49, 51.90, 74.29, 79.74, 115.8 (q, $^1J_{CF} = 288$ Hz), 118.0, 126.6, 127.7, 128.2, 134.4, 141.5, 156.5 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3310$, 3106, 3080, 2964, 2932, 2870, 1704, 1640, 1202, 1160, 914, 756, 700 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 459 (100) $[M+NH_3+H]^+$, 900 (5) $[2 \times M+NH_3+H]^+$.

(4*R*,6*R*,1′*R*,2′*R*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-6-(*tert*-butyldiphenylsilanyloxy)-hept-1-ene (19c): According to the general procedure, reaction of ketone **8c** (170 mg, 0.50 mmol) with *ent*-**2** (80 mg, 0.25 mmol) gave the homoallylic ether **19c** (69 mg, 0.11 mmol, 44%) as colorless needles, along with recovered *ent*-**2** (30 mg, 0.09 mmol, 35%). M.p. 77 °C (pentane); $[\alpha]_D^{20} = -20.0°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.84$ (s, 3H), 1.11 (d, $J = 7.0$ Hz, 3H), 1.14 (d, $J = 7.0$ Hz, 3H), 1.19 (dd, $J_1 = 14.5$ Hz, $J_2 = 4.0$ Hz, 1H), 1.97 (dd, $J_1 = 14.5$ Hz, $J_2 = 8.5$ Hz, 1H), 2.28 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.0$ Hz, $J_3 = 13.5$ Hz, 1H), 2.36 (dd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 13.5$ Hz, 1H), 2.90 (m, 1H), 4.01 (m, 1H), 4.55 (d, $J = 4.0$ Hz, 1H), 5.02–5.12 (m, 2H), 5.67–5.81 (m, 1H), 6.30 (br d, $J = 8.0$ Hz, 1H), 7.10–7.33 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.73$, 19.09, 23.55, 25.67, 26.96, 44.47, 49.81, 51.68, 67.11, 74.27, 78.28, 115.8 (q, $^1J_{CF} = 288$ Hz), 118.2, 126.6, 127.4, 127.5, 128.6, 129.4, 129.6, 134.1, 141.1, 156.0 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3302$, 3106, 3072, 3044, 2964, 2934, 2896, 2858, 1702, 1214, 1186, 1164, 1108, 1066, 916, 760, 704 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 629 (100) $[M+NH_3+H]^+$; $C_{35}H_{44}F_3NO_3Si$ (611.82): calcd C 68.71, H 7.24; found C 68.63, H 7.41.

(4*S*,6*R*,1′*S*,2′*S*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-6-(*tert*-butyldiphenylsilanyloxy)-hept-1-ene (16c): According to the general procedure, reaction of ketone **8c** (170 mg, 0.50 mmol) with **2** (80 mg, 0.25 mmol) gave the homoallylic ether **16c** (62 mg, 0.10 mmol, 41%) as colorless needles, along with recovered **2** (35 mg, 0.11 mmol, 44%). M.p. 81 °C (pentane); $[\alpha]_D^{20} = +11.2°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.87$ (d, $J = 6.0$ Hz, 3H), 0.91 (s, 3H), 0.91 (s, 9H), 1.10 (d, $J = 6.8$ Hz, 3H), 1.53 (dd, $J_1 = 7.2$ Hz, $J_1 = 14.5$ Hz, 1H), 1.75 (dd, $J_1 = 6.0$ Hz, $J_2 = 14.4$ Hz, 1H), 2.24 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.0$ Hz, $J_3 = 14.0$ Hz, 1H), 2.36 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 14.0$ Hz, 1H), 3.84–4.12 (m, 2H), 4.44 (d, $J = 3.8$ Hz, 1H), 4.94–5.06 (m, 2H), 5.57–5.81 (m, 1H), 6.30 (br d, $J = 8.0$ Hz, 1H), 7.06–7.36 (m, 15H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 17.05$, 19.12, 24.40, 25.32, 27.00, 43.74, 49.86, 51.82, 66.89, 74.17, 78.25, 115.5 (q, $^1J_{CF} = 288$ Hz), 118.0, 126.5, 127.3, 127.6, 128.2, 129.4, 129.6, 134.2, 135.9, 141.2, 156.0 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3302$, 3106, 3072, 3044, 2964, 2934, 2896, 2858, 1702, 1214, 1186, 1164, 1108, 1066, 916, 760, 704 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 629 (100) $[M+NH_3+H]^+$; $C_{35}H_{44}F_3NO_3Si$ (611.82): calcd C 68.71, H 7.24; found C 68.49, H 7.20.

(4*R*,6*S*,1′*R*,2′*R*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-6-phenyl-hept-1-ene (19d): According to the general procedure, reaction of ketone **8d** (81 mg, 0.50 mmol) with *ent*-**2** (80 mg, 0.25 mmol) and diisopropylketone (285 mg, 2.50 mmol) gave the homoallylic ether **19d** (72 mg, 0.17 µmol, 67%) as colorless needles, along with recovered *ent*-**2** (10 mg, 30 µmol, 13%). M.p. 90 °C (pentane, *tert*-butyl methyl ether); $[\alpha]_D^{20} = +24.3°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): $\delta = 0.84$ (s, 3H), 1.11 (d, $J = 7.0$ Hz, 3H), 1.14 (d, $J = 7.0$ Hz, 3H), 1.19 (dd, $J_1 = 14.5$ Hz, $J_2 = 4.0$ Hz, 1H), 1.97 (dd, $J_1 = 14.5$ Hz, $J_2 = 8.5$ Hz, 1H), 2.28 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.0$ Hz, $J_3 = 13.5$ Hz, 1H), 2.36 (dd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 13.5$ Hz, 1H), 2.90 (m, 1H), 4.01 (m, 1H), 4.55 (d, $J = 4.0$ Hz, 1H), 5.02–5.12 (m, 2H), 5.67–5.81 (m, 1H), 6.30 (br d, $J = 8.0$ Hz, 1H), 7.10–7.33 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.91$, 24.41, 25.61, 35.87, 43.48, 47.64, 51.87, 74.44, 79.46, 115.9 (q, $^1J_{CF} = 288$ Hz), 118.2, 126.7, 127.0, 127.8, 128.3, 128.4, 134.1, 141.3, 148.7, 155.4 (q, $^2J_{CF} = 37$ Hz); IR: $\tilde{\nu} = 3310$, 3084, 3072, 3030, 2970, 2930, 2854, 1702, 1204, 1184, 1164, 1056, 918, 762, 700 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 451 (100) $[M+NH_3+H]^+$.

(4*S*,6*S*,1′*S*,2′*S*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-6-phenyl-hept-1-ene (16d): According to the general procedure, reaction of ketone **8d** (81 mg, 0.50 µmol) with **2** (80.0 mg, 250 µmol) and diisopropyl ketone (285 mg, 2.50 mmol) gave the homoallylic ether **16d** (72 mg, 0.17 mmol, 66%) as colorless needles along with **2** (8 mg, 0.02 mmol, 10%). M.p. 72 °C; $[\alpha]_D^{20} = -26.6°$ ($c = 0.5$, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.81$ (s, 3H, 4-CH_3), 1.05 (d, $J = 6.8$ Hz, 3H, 7-H_3), 1.24 (d, $J = 7.2$ Hz, 3H, 3′-H_2), 1.77 (dd, $J_1 = 4.0$ Hz, $J_2 = 14.5$ Hz, 1H, 5-H_a), 2.00 (dd, $J_1 = 8.7$ Hz, $J_2 = 14.5$ Hz, 1H, 5-H_b), 2.28 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.2$ Hz, $J_3 = 13.9$ Hz, 1H, 3-H_a), 2.36 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.6$ Hz, $J_3 = 13.9$ Hz, 1H, 3-H_b), 3.00 (m, 1H, 6-H), 3.98 (m, 1H, 2′-H), 4.53 (d, $J = 3.8$ Hz, 1H, 1′-H), 5.09 (m, 2H, 1-H_2), 5.68–5.82 (m, 1H, 2-H), 5.97 (br d, $J = 8.0$ Hz, 1H, N-H), 7.12–7.32 (m, 10H, phenyl-H); ^{13}C NMR (50.3 MHz, $CDCl_3$): $\delta = 16.72$, 24.36, 25.81, 35.80, 43.08, 47.57, 51.59, 74.56, 79.23, 115.7 (q, $^1J_{CF} = 288$ Hz), 118.0, 126.6, 126.9, 128.0, 128.2, 128.4, 134.0, 141.6, 148.8, 156.1 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3340$, 3080, 3028, 2968, 2930, 2872, 1704, 1454, 1206, 1178, 1158, 1108, 918, 764, 704 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 451

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(100) $[M+NH_3+H]^+$; $C_{25}H_{30}F_3NO_2$ (433.50): calcd C 69.26, H 6.98; found C 68.91, H 6.70.

(6*R*)-4,6,10-Trimethyl-4-ethoxy-undec-1-ene (22b): According to the general procedure, reaction of ketone **8b** (324 mg, 2.00 mmol) with **21** (118 mg, 1.00 mmol) gave the diastereomeric homoallylic ethers **22b** (197 mg, 0.82 mmol, 82%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 0.86$ (d, $J = 6.5$ Hz, 6H), 0.94 (d, $J = 6.5$ Hz, 3H), 1.02–1.70 (m, 16H), 2.20 (ddd, $J_1 = 1.0$ Hz, $J_2 = 6.0$ Hz, $J_3 = 13.5$ Hz, 1H), 2.31 (ddd, $J_1 = 1.0$ Hz, $J_2 = 5.0$ Hz, $J_3 = 13.0$ Hz, 1H), 3.38 (q, $J = 7.0$ Hz, 2H), 4.97 (m, 2H), 5.70–5.94 (m, 1H); ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 15.89$, 21.30, 21.49, 22.63, 22.72, 23.62, 23.91, 24.86, 25.27, 27.93, 28.00, 28.59, 38.99, 39.15, 39.26, 39.30, 43.62, 44.63, 56.00, 77.64, 117.0, 134.8, 134.9; IR (film): $\tilde{\nu} = 2956$, 2928, 2870, 1640, 1446, 1376, 1114, 1074, 1016, 846 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 258 (100) $[M+NH_3+H]^+$; $C_{16}H_{32}O$ (240.42): calcd C 79.93, H 13.43; found C 8.63, H 13.20.

(6*R*)-4-Methyl-4-ethoxy-6-(*tert*-butyldiphenylsilanyloxy)-hept-1-ene (22c): According to the general procedure, reaction of ketone **8c** (600 mg, 1.76 mmol) with **21** (104 mg, 0.88 mmol) gave the diastereomeric homoallylic ethers **22c** (320 mg, 0.77 mmol, 89%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 0.86$ (s, 3H, 4-CH_3), 0.95 (s, 9H), 0.96 (s, 9H), 1.01–1.32 (m, 6H), 1.55 (dd, $J_1 = 5.0$ Hz, $J_2 = 15.0$ Hz, 1H), 1.68 (dd, $J_1 = 7.0$ Hz, $J_2 = 15.0$ Hz, 1H), 2.01 (ddd, $J_1 = 1.0$ Hz, $J_2 = 6.0$ Hz, $J_3 = 13.5$ Hz, 1H), 2.12 (ddd, $J_1 = 1.0$ Hz, $J_2 = 5.0$ Hz, $J_3 = 13.5$ Hz, 1H), 3.20 (q, $J = 7.0$ Hz, 2H), 3.22 (q, $J = 7.0$ Hz, 2H), 4.00 (m, 1H), 4.77–5.03 (m, 2H), 5.48–5.73 (m, 1H), 7.41–7.71 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 15.75$, 19.18, 24.83, 24.97, 26.86, 68.22, 27.05, 47.15, 55.94, 59.73, 67.96, 75.19, 117.2, 127.3, 127.5, 129.5, 134.4, 136.1; IR: $\tilde{\nu} = 3070$, 3053, 2960, 2932, 2896, 2858, 1428, 1110, 1080, 1004, 914, 740, 704 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 428 (100) $[M+NH_3+H]^+$; $C_{26}H_{38}O_2Si$ (410.67): calcd C 76.04, H 9.33; found C 76.14, H 9.33.

(6*S*)-4-Methyl-4-ethoxy-6-phenyl-hept-1-ene (22d): According to the general procedure, reaction of ketone **8d** (648 mg, 4.00 mmol) with **21** (236 mg, 2.00 mmol) gave the diastereomeric homoallylic ether **22d** (350 mg, 1.50 mmol, 75%) as a colorless oil. ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 1.00$ (s, 3H), 1.04 (t, $J = 7.0$ Hz, 3H), 1.27 (d, $J = 7.0$ Hz, 3H), 1.74 (dd, $J_1 = 5.5$ Hz, $J_2 = 14.0$ Hz, 1H), 1.90 (dd, $J_1 = 6.0$ Hz, $J_2 = 14.0$ Hz, 1H), 2.16 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 13.5$ Hz, 1H), 2.22 (ddd, $J_1 = 1.0$ Hz, $J_2 = 8.0$ Hz, $J_3 = 13.5$ Hz, 1H), 2.95 (oct, $J = 7.0$ Hz, 1H), 3.19–3.40 (m, 2H), 4.93–5.05 (m, 2H), 5.63–5.84 (m, 1H), 7.11–7.32 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 15.74$, 22.16, 24.01, 24.80, 24.87, 35.42, 35.57, 43.07, 43.67, 45.63, 45.75, 56.05, 56.09, 76.42, 117.2, 125.6, 127.0, 128.3, 134.6, 149.1; IR (film): $\tilde{\nu} = 3074$, 3026, 2972, 2928, 2872, 1640, 1452, 1374, 1154, 1112, 1074, 918, 762, 700 cm^{-1}; MS (70 eV, CI) *m*/*z* (%): 250 (100) $[M+NH_3+H]^+$; $C_{16}H_{24}O$ (232.36): calcd C 82.70, H 10.41; found C 82.46, H 10.31.

(4*R*,6*R*,1′*R*,2′*R*)- and (4*R*,6*S*,1′*R*,2′*R*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-6-(*tert*-butyldiphenylsilanyloxy)-hept-1-ene (29a and 29-*ent*-a): According to the general procedure, reaction of ketone *rac*-**26a** (170 mg, 0.50 mmol) with *ent*-**2** (80.0 mg, 0.25 mmol) gave a diastereomeric mixture of homoallylic ethers **29a** and **29**-*ent*-**a** (68.0 mg, 112 μmol, 45%) as colorless needles, along with recovered *ent*-**2** (31 mg, 0.10 mmol, 39%). ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 0.77$ (s, 3H), 0.94 (s, 3H), 0.92 (d, $J = 6.5$ Hz, 3H), 0.99 (s, 9H), 1.01 (s, 9H), 1.11 (d, $J = 7.0$ Hz, 3H), 1.13 (d, $J = 7.0$ Hz, 3H), 1.57–1.75 (m, 2H), 2.18–2.46 (m, 2H), 3.96–4.08 (m, 2H), 4.47 (d, $J = 3.0$ Hz, 1H), 4.49 (d, $J = 3.0$ Hz, 1H), 4.94–5.14 (m, 2H), 5.63–5.80 (m, 1H), 6.32 (br d, $J = 8.0$ Hz, 1H), 7.08–7.76 (m, 15H); ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 16.74$, 17.06, 19.13, 23.56, 24.40, 25.31, 25.68, 26.97, 43.73, 44.74, 49.65, 49.81, 51.67, 51.81, 66.87, 67.11, 74.14, 74.25, 78.22, 78.26, 115.5 (q, $^1J_{CF} = 288$ Hz), 117.9, 118.1, 127.3, 127.5, 127.7, 128.2, 134.9, 135.8, 135.9, 141.2, 156.3 (q, $^2J_{CF} = 37$ Hz); IR (film): $\tilde{\nu} = 3314$, 3070, 3050, 2968, 2934, 2894, 1722, 1704, 1208, 1184, 1164, 1110, 1068 1056, 918, 756, 702 cm^{-1}; MS: (70 eV, CI): *m*/*z* (%): 629 (100) $[M+NH_3+H]^+$.

(4*R*,6*R*,1′*R*,2′*R*)- and (4*R*,6*S*,1′*R*,2′*R*)-4-Methyl-4-(2′-trifluoracetamido-1′-phenyl-propoxy)-6-phenyl-hept-1-ene (29b and 29-*ent*-b): According to the general procedure, reaction of ketone *rac*-**26b** (324 mg, 2.00 mmol) with *ent*-**2** (320 mg, 1.00 mmol) and diisopropyl ketone (1.14 g, 10 mmol) gave a diastereomeric mixture of homoallylic ethers **29b** and **29**-*ent*-**b** (221 mg, 512 μmol, 51%) as colorless needles, along with recovered *ent*-**2** (72 mg, 0.07 mmol, 28%). M.p. 73 °C; ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 0.83$ (s, 1H), 0.88 (s, 1H), 1.06–1.40 (m, 7H), 1.61–2.12 (m, 2H), 2.29 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 13.5$ Hz, 1H), 2.38 (ddd, $J_1 = 1.0$ Hz, $J_2 = 7.5$ Hz, $J_3 = 13.5$ Hz, 1H), 2.78–3.10 (m, 1H), 4.00 (m, 1H), 4.52 (d, $J = 4.0$ Hz, 1H), 4.55 (d, $J = 4.2$ Hz, 1H), 4.95–5.20 (m, 2H), 5.60–5.87 (m, 1H), 5.96 (br d, $J = 8.0$ Hz), 6.30 (br d, $J = 8.0$ Hz), 7.08–7.59 (m, 10H); ^{13}C NMR (125.7 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 16.87$, 16.91, 24.41, 24.54, 25.60, 25.96, 35.86, 35.97, 43.18, 43.46, 47.63, 47.69, 51.66, 74.20, 74.42, 74.64, 79.40, 79.46, 115.8 (q, $^1J_{CF} = 288$ Hz), 117.9, 118.2, 118.3, 125.8, 125.9, 126.5, 126.7, 127.0, 127.7, 127.8, 128.2, 128.3, 128.4, 134.1, 141.3, 141.6, 148.7, 148.9, 156.5 (q, $^2J_{CF} = 37$ Hz); IR (KBr): $\tilde{\nu} = 3340$, 3078, 3031, 2965, 2930, 2872, 1704, 1454, 1206, 1178, 1158, 1107, 921, 767, 701 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 451 (100) $[M+NH_3+H]^+$; $C_{25}H_{30}F_3NO_2$ (433.50): calcd C 69.26, H 6.98; found C 68.91, H 6.70.

(4*R*,5*R*,1′*R*,2′*R*)- and (4*R*,5*S*,1′*R*,2′*R*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-5-phenyl-hept-1-ene (29c and 29-*ent*-c): According to the general procedure, reaction of ketone *rac*-**26c** (81 mg, 0.50 mmol) with *ent*-**2** (80 mg, 0.25 mmol) gave after a reaction time of 5 d a diastereomeric mixture of homoallylic ethers **29c** and **29**-*ent*-**c** (23 mg, 0.05 mmol, 21%) as colorless needles, along with recovered *ent*-**2** (51 mg, 0.16 mmol, 64%). M.p. 103 °C (pentane); ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 0.57$ (t, $J = 7.0$ Hz, 3H, 7-H_3), 0.87 (s, 3H, 4-CH_3), 1.30 (d, $J = 7.5$ Hz, 3H, 3′-H_3), 1.15–1.28 (m, 2H, 6-H_2), 2.38 (m, 2H, 3-H_2), 2.53–2.67 (m, 1H, 5-H), 4.25 (m, 1H), 4.76 (d, $J = 4.0$ Hz, 1H), 4.78 (d, $J = 4.0$ Hz, 1H), 5.08–5.20 (m, 2H), 5.88–6.02 (m, 1H), 6.36 (br d, $J = 7.5$ Hz, 1H), 7.08–7.41 (m, 10H); ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 12.56$, 12.78, 13.50, 16.99, 17.13, 21.66, 21.94, 22.13, 23.65, 40.75, 41.32, 42.37, 51.51, 51.89, 55.56, 74.65, 80.77, 115.9 (q, $^1J_{CF} = 288$ Hz), 117.9, 118.4, 126.4, 126.6, 127.7, 127.8, 128.1, 128.1, 133.9, 134.0, 141.2, 141.4, 156.4 (*q*, $^2J_{CF} = 36$ Hz); IR: $\tilde{\nu} = 3320$, 3086, 3062, 3030, 2968, 2936, 2904, 2882, 1698, 1204, 1182, 1164, 1076, 1062, 1026, 918, 762, 702 cm^{-1}; MS: (70 eV, CI): *m*/*z* (%): 451 (100) $[M+NH_3+H]^+$; $C_{20}H_{28}NO_2F_3$ (371.44): calcd C 69.26, H 6.98; found C 69.36, H 7.20.

(4*R*,5*R*,1′*R*,2′*R*)- and (4*R*,5*S*,1′*R*,2′*R*)-4-Methyl-4-(2′-trifluoroacetamido-1′-phenyl-propoxy)-5-methyl-hept-1-ene (29d and 29-*ent*-d): According to the general procedure, reaction of ketone *rac*-**26d** (50 mg, 0.50 mmol) with *ent*-**2** (80 mg, 0.25 mmol) gave a diastereomeric mixture of homoallylic ethers **29d** and **29**-*ent*-**d** (66 mg, 0.18 mmol, 71%) as colorless needles. M.p. 50 °C (pentane); ^{1}H NMR (200 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 0.64$ (t, $J = 7.5$ Hz, 3H), 0.80–0.99 (m, 9H), 0.91 (s, 3H), 1.16 (d, $J = 7.0$ Hz, 3H), 1.18 (d, $J = 7.0$ Hz, 3H), 2.37 (m, 2H), 3.60 (d, $J = 3.5$ Hz, 1H), 4.09 (m, 1H), 3.56 (d, $J = 3.5$ Hz, 1H), 5.05–5.16 (m, 2H), 5.74–5.97 (m, 1H), 6.40 (s, 1H), 7.20–7.40 (m, 5H); ^{13}C NMR (50.3 MHz, $CDCl_3$, mixture of diastereomers): $\delta = 12.47$, 12.94, 13.50, 13.61, 16.60, 16.78, 21.62, 21.84, 23.74 23.81, 40.48, 40.57, 42.05, 42.37, 42.57, 51.93, 51.99, 74.38, 81.56, 116.0 (q, $^1J_{CF} = 288$ Hz), 117.7, 117.8, 117.9, 125.9, 127.1, 128.4, 134.4, 134.6, 141.5, 156.6 (q, $^2J_{CF} = 36$ Hz); IR (KBr): $\tilde{\nu} = 3070$, 3030, 2970, 2938, 2882, 1726, 1704, 1564, 1210, 1186, 1164, 1088, 916, 760, 702 cm^{-1}; MS (70 eV, CI): *m*/*z* (%): 389 (100) $[M+NH_3+H]^+$; $C_{20}H_{28}NO_2F_3$ (371.44): calcd C 64.67, H 7.60; found C 64.88, H 6.79.

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