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Configurational Stability of Oxymethyllithiums as Intermediates in Intramolecular Rearrangements

Dagmar C. Kapeller, Lothar Brecker, and Friedrich Hammerschmidt*[a]

Abstract: Several homochiral oxymethyllithiums, chiral by virtue of the hydrogen isotopes protium and deuterium, were prepared. They were tested for their microscopic configurational stability in intramolecular isomerizations, such as the silyl- and germyl-[1,2]-*retro*-Brook and the sigmatropic-[2,3]-Wittig rearrangement. The influence of temperature, solvent, and migrating group on the stability of the intermediate carbanions was studied. Furthermore, the stereochemical course of these rearrangements was elucidated, resulting in highly enantioenriched alcohols (90–97% *ee*; *ee* = enantiomeric excess) up to temperatures of 0°C.

Keywords: carbanions · configurational stability · lithium · rearrangement · stereochemistry

Introduction

The synthesis of chiral, nonracemic α-heteroatom-substituted organolithiums has inspired various chemists for the last few decades.[1] Nowadays, these reagents have found their way into many organic laboratories, being versatile tools in asymmetric carbon–carbon or carbon–heteroatom bond formation. They can be trapped with a wide variety of electrophiles or act as intermediates in anionic rearrangements.[2]

Still and Sreekumar were the first to demonstrate that a heteroatom at a carbanionic centre dramatically increased its configurational stability, which is the prerequisite for their application in enantioselective syntheses. They found that α-alkoxyalkyllithiums are configurationally stable at low temperature (−78°C) and can be stereospecifically alkylated with retention of configuration.[3] This sparked a widespread interest not only amongst preparative chemists but also amongst mechanistically orientated chemists studying the methods of enantiomerization of these species and theoretically inclined chemists performing predictive calculations.

Up to now, many organolithiums have been tested for their configurational stability. This is usually done on two different time scales, not counting variable temperature NMR for half-lives less than a second due to interconversion of diastereotopic signals.[1a] There is microscopic configurational stability, which lies in the range of seconds. It refers to the stability relative to a chemical reaction and requires the rate for addition of a chiral organolithium to an electrophile to be faster than enantiomerization. Then, a species is macroscopically configurationally stable, if it retains its configuration for at least a few seconds to a few minutes. An elegant method for evaluating the configurantional stability of an alkyllithium is the Hoffmann test.[4]

Despite years of research and great effort dedicated towards this problem relatively little is known about the means of racemization. Mechanistic studies revealed three pathways for inversion of configuration, which can only be applied to a fraction of organolithium compounds. There is the classic dissociative mechanism involving a solvent separated ion pair,[5] a conducted tour mechanism with intramolecular Lewis base coordination,[6] and one predestined for sulfur and selenium compounds containing bond rotation.[7] However, the investigation of α-oxygen, α-nitrogen, and to a lesser extent α-sulfur, α-selenium, and α-halogen-substituted organolithiums gave us a good idea of their configurational stability, qualitatively speaking.

[a] D. C. Kapeller, Dr. L. Brecker, Prof. Dr. F. Hammerschmidt
University of Vienna, Institute of Organic Chemistry
Währingerstr. 38, 1090 Vienna (Austria)
Fax: (+43) 1-4277-9521
E-mail: friedrich.hammerschmidt@univie.ac.at

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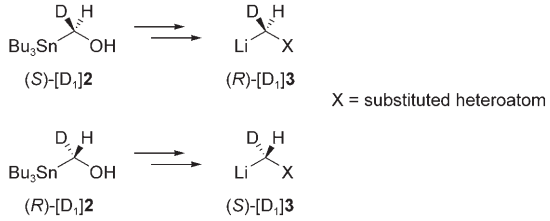
a: X = OR^1, $OC(O)NR_2$, $OC(O)C_6H_3\ iPr_3$
b: X = NR_2, $NC(O)OtBu$, NC
c: X = SR, SeR
d: X = halogen

R = Alkyl

Experimental findings led to a sequence of eroding stability: O > N > S/Se.[8] They are nicely supported by quantum chemical calculations at different levels.[9]

The most widely used heteroatom-substituted alkyllithiums are the ones α to oxygen. Among those, the carbamoyloxy group introduced by Hoppe et al. is prominent.[10] An exception in the nitrogen series are α-aminoalkyllithiums derived from Boc-protected cyclic amines, found by Beak et al.[1c,11] In both cases, configurational stability of these species ranges from −78 to about −40 °C. Their easy access in a highly enantioenriched form by metalation with (−)-sparteine/*s*BuLi makes them attractive reagents for organic synthesis. Recently, relative thermodynamic stability scales of such organolithiums were derived from measurements of tin–lithium exchange equilibria.[12]

Previous studies revealed that alkyllithiums of type **1a** differed in their macroscopic configurational stability, depending on the substitutent R and whether **1a** was a metalated ether, carbamate, or ester. For the sake of simplicity, calculations in the oxygen series concentrated on species with R = H and a hydroxy- or formyloxy-substituent, consistently neglecting alkyl and other oxygen-containing groups as substituents.[9] However, those with deuterium replacing the alkyl substituent could not be accessed until recently. These chiral methyllithiums are challenging targets of unknown configurational stability, that will play an important role in mechanistic studies in bioorganic chemistry. We have found that enantiomerically pure methyllithiums **3** with X = $OC(O)N(iPr)_2$ resist racemization at low temperature and that those with X = $OP(O)(OiPr)_2$ undergo the phosphate–phosphonate rearrangement with retention of configuration up to 0 °C (Scheme 1).[13]



Scheme 1. (*S*)- and (*R*)-tributylstannyl[D_1]methanol as precursors for α-heteroatom-substituted methyllithiums.

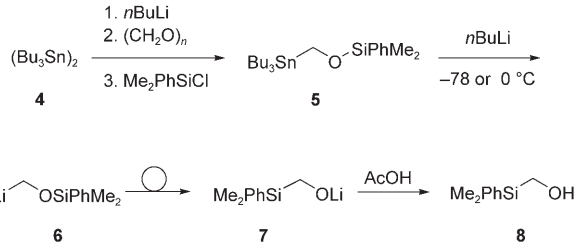
Herein, we expand our studies towards the microscopic configurational stability of chiral oxymethyllithiums and describe their role in the preparation of primary, stereospecifically labeled alcohols of known configuration. They are generated by tin–lithium exchange and accessible from enantiopure tributylstannyl[D_1]methanols ([D_1]**2**) as common precursors easily prepared in five steps (Scheme 1).[13]

We examine chiral oxymethyllithiums as short-lived intermediates in [1,2]-*retro*-Brook[14] and analogous rearrangements. The former involves the intramolecular migration of a silicon atom from an oxygen atom to a carbon atom. Thereby, silyloxyalkyllithiums **3** (for X = $OSiR_3$) rearrange via pentacoordinated intermediates to lithium alkoxides, which give α-silyl alcohols on workup. The rearrangement usually proceeds under retention of configuration in the case of aliphatic compounds[15] and under inversion with benzylic ones.[16] The reverse and thermodynamically favored process is well documented and has found numerous practical applications, such as the preparation of chiral methanol.[17] Boche et al. have determined the crystal structure of diphenyl(trimethylsilyloxy)methyllithium·3THF and found that the lithium is ligated to the oxygen atom and the benzylic carbon resembles more closely an sp^2- than sp^3-hybridized carbon atom.[9b]

Additionally, we wanted to take a look at the Wittig rearrangement. It is formally related to the Brook rearrangement, despite the two proceeding through completely different mechanisms. A direct conversion was ineligible for our purposes, as the [1,2]-Wittig rearrangement involves the formation of radicals and thus has inadequate stereocontrol. Accordingly, we decided on the [2,3] variant, which is a suprafacial six-electron pericyclic process.[2a] This sigmatropic rearrangement proceeds under inversion of configuration at the carbanionic centre. Its high synthetic value is displayed by numerous applications in natural product synthesis.[2d,18] As such it is an interesting target for our investigations.

Results and Discussion

[1,2]-*retro*-Brook rearrangement: Initially, dimethylphenylsilyl was chosen as the migrating group, as absolute configuration and enantiomeric excess (*ee*) of the expected deuterated (dimethylphenylsilyl)methanol (**8**) could be determined after transformation into the known Mosher ester.[17,19] This also allowed us to elucidate the stereochemistry of the rearrangement. Preliminary experiments performed with the nondeuterated species in a one-pot reaction proved the feasibility of our approach (Scheme 2).

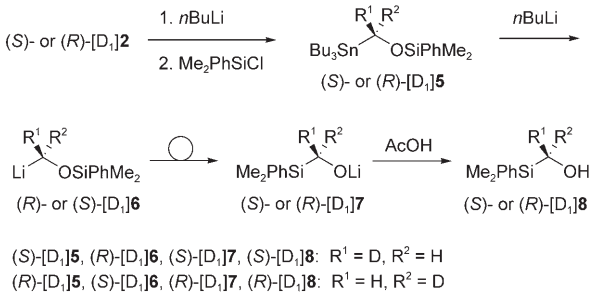


Scheme 2. Preparation and *retro*-Brook rearrangement of dimethylphenylsilyloxymethyllithium (**6**).

Hexabutyldistannane (**4**) was treated with *n*BuLi and paraformaldehyde to give lithium tributylstannylmethoxide, which was quenched with dimethylphenylsilyl chloride to yield silyl ether **5**. Further addition of *n*BuLi effected a smooth transmetalation, followed immediately by a [1,2]-*retro*-Brook rearrangement to give silylmethanol **8** after acidic workup. The overall yields of 58% (30 min, −78 °C)

and 49% (30 s, 0°C) encouraged us to continue in the labeled series (Scheme 3).

[D_1]**5** was prepared similarly to its unlabeled analogue by deprotonation of enantiopure [D_1]**2** with *n*BuLi and quenching with dimethylphenylsilyl chloride. This was followed by transmetalation, rearrangement, and acidic workup under various conditions (Table 1, entries 1–3).



Scheme 3. Preparation and *retro*-Brook rearrangement of [D_1]**6**.

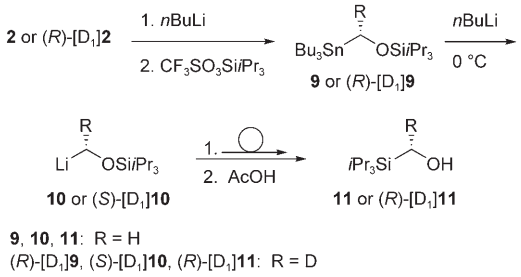
Table 1. Reaction conditions and results of rearrangements.

Entry	Substrate/product	Solvent	*t* [min][a]	*T* [°C]	Yield/*ee* [%]
1	(*S*)-[D_1]**5**/(*S*)-[D_1]**8**	THF	30	−78	81/96
2	(*S*)-[D_1]**5**/(*S*)-[D_1]**8**	THF	0.5	0	67/97
3	(*R*)-[D_1]**5**/(*R*)-[D_1]**8**	Et_2O	0.5	0	71/97
4	(*R*)-[D_1]**9**/(*R*)-[D_1]**11**	THF	0.5	0	99/95
5	(*S*)-[D_1]**12**/(*S*)-[D_1]**14**	THF	30	−78	61/90
6	(*R*)-[D_1]**12**/(*R*)-[D_1]**14**	THF	0.25	0	68/92
7	(*S*)-[D_1]**16**/(*S*)-[1-D_1]**18**	THF	5	−78	80/94
8	(*S*)-[D_1]**16**/(*S*)-[1-D_1]**18**	THF	0.5	0	71/94

[a] Reaction time for transmetalation/rearrangement.

Silylmethanols [D_1]**8** were then transformed into the diastereomeric Mosher esters to determine their *ee* values and absolute configurations. Their ^{1}H NMR spectra were in complete agreement with those reported in the literature.[17] Stannylmethanols (*S*)- and (*R*)-[D_1]**2** gave silylmethanols (*S*)- and (*R*)-[D_1]**8**, respectively. Consequently, the *retro*-Brook rearrangement proceeds with retention of configuration. Complete configurational stability of the intermediate silyloxymethyllithiums [D_1]**6** in diethyl ether as well as THF is observed from −78 to 0°C. This result nicely interlocks with the finding that the KOH-catalyzed Brook rearrangement of scalemic [D_1,T]**6** in *N*,*N*,*N*′,*N*′-tetramethylurea (plus 5% of water) gives chiral methanols with retention of configuration at room temperature, despite the experimental setting being different.[17] In the former case, the silyl group can, in principle, migrate between the carbon and oxygen atoms, even though the equilibrium lies with the lithium silylmethoxide. In the latter case, the formal silyloxymethylanion is intercepted rapidly and irreversibly by a proton.

To address the influence of substituents at the silicon atom on the stereochemistry and rate of the rearrangement, the dimethylphenylsilyl group was replaced by the bulkier triisopropylsilyl one. We reasoned that the three isopropyl groups on silicon could impede the migration from the oxygen to the carbon atom and thus increase the lifetime and enantiomerization of the intermediate silyloxymethyllithium. Applying the same sequence as before, this time with triisopropylsilyl triflate, a much more powerful trapping agent than the chloride, furnished silylmethanol **11** in quantitative yield (Scheme 4).[20] When using *i*Pr_3SiCl, virtually



Scheme 4. Preparation and *retro*-Brook rearrangement of silyloxymethyllithiums **10** and (*S*)-[D_1]**10**.

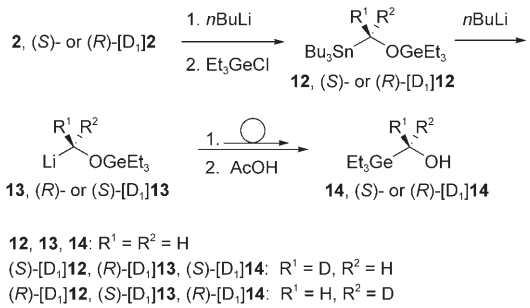
no **11** was formed under comparable conditions, which is due to its lower reactivity with the lithium stannylmethoxide. The yield was improved by performing the silylation at room temperature for extended periods of time, but still remained unsatisfactory.

When the experiment was repeated with (*R*)-[D_1]**2** at 0°C, the desired product (*R*)-[D_1]**11** of 95% *ee* was isolated (Scheme 4; Table 1, entry 4). This result proves that the stereochemical outcome of the [1,2]-*retro*-Brook rearrangement is independent of the substituents on the silicon atom. In all cases of silyl migration studied, no silyl ether was detected in the crude product by TLC.

[1,2]-*retro*-Germyl rearrangement: Wright and West found the migratory aptitude of germanium compared to silicon in [1,2]-anionic rearrangements to be very limited. The lower energy of the oxygen–germanium bond (73 kcal mol^{-1}) compared to its silicon analogue (112 kcal mol^{-1}) disfavors the [1,2]-germyl-Brook rearrangement, while promoting the reverse process.[21] One rare exception is the rearrangement of 9-triphenylgermyl-9-fluorenol.[22] The stereochemical outcome of this kind of rearrangement has not yet been unraveled, proposing an interesting challenge for us.

Accordingly, the next step in our work was to substitute silicon for germanium to see if the migrating atom had any influence on the *retro*-Brook rearrangement. For that purpose, the general experimental setup from before was applied to unlabeled alcohol **2**, with triethylgermyl chloride as the trapping reagent (Scheme 5).

Surprisingly, germyl ether **12** could not be detected in the reaction mixture by TLC, although its formation must have taken place, as triethylgermylmethanol (**14**) could be isolated in the end. Presumably, after applying a sample to the silica plate the ether hydrolyzed immediately to give the starting stannylmethanol, which could be spotted. The transmetalation/rearrangement (−78°C, 1 h) furnished rear-



Scheme 5. Preparation and rearrangement of germyloxymethyllithiums **13** and [D_1]**13**.

ranged alcohol **14** in merely 36% yield, despite the fact that it was a spot to spot transformation. This was probably due to the high volatility of the product, which was also a problem with silyl alcohol **8**. The ^{1}H NMR spectrum of its (*R*)-Mosher ester showed an AB system ($J = 12.6$ Hz) for the $GeCH_2$ group, reminiscent of the $SiCH_2$ group of the silylmethyl analogues.

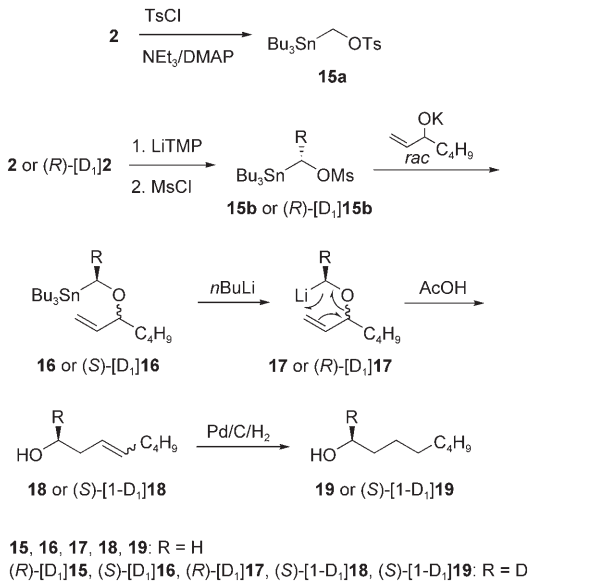
Similarly, labeled [D_1]**2** was converted to germylmethanol [D_1]**14**, performing the rearrangement at −78 and 0 °C. By taking care to minimize losses during isolation and purification (Scheme 5; Table 1, entries 5 and 6), the yields increased to 61 and 68%, respectively. We propose retention of configuration in analogy to the silyl series based on the Mosher esters. The significantly lower *ee* for [D_1]**14** (90 and 92%) compared to those of the silyl series (95–97%) likely reflects some enantiomerization (2–3%) for germyloxymethyllithium [D_1]**13**.

We also tried to convert tributylstannylmethanol to the corresponding trimethylstannyl ether, by using trimethyltin chloride for quenching. Again, the ether could not be detected by TLC. But this time the metalation/rearrangement sequence did not yield trimethylstannylmethanol. Probably, *n*BuLi exclusively attacked the trimethylstannyl group on the oxygen atom rather than the tributylstannyl one bound to the carbon atom, if the ether was formed at all.

[2,3]-Wittig rearrangement: Finally, the stereochemistry of the sigmatropic [2,3]-Wittig rearrangement employing a chiral oxymethyllithium as the intermediate was examined. According to the work of Still and Mitra, who demonstrated the feasibility of the rearrangement for such compounds, stannane **16** was chosen as the substrate.[23] Furthermore, the product could be converted easily to deuterated octanol of known configuration. Optimization of all steps was done in the unlabeled series to avoid unnecessary losses of the labeled compounds (Scheme 6).

Interestingly, the tosylate **15a** of alcohol **2**, which we wanted to use initially, gave only low yields under several standard conditions tried. It also turned out to be very labile.

In the labeled series, mesylate (*R*)-[D_1]**15b** prepared from (*R*)-[D_1]**2** was used to alkylate the potassium salt of 1-hepten-3-ol (two steps: 60% yield) in the presence of 18-



Scheme 6. Preparation and [2,3]-Wittig rearrangement of stannylmethyllthiums **17** and (*R*)-[D_1]**17** (the configurations given with the numbers refer to the stannylmethyl part of the labeled compounds); Ms = $MeSO_2$, Ts = 4-$MeC_6H_4SO_2$.

crown-6 (Scheme 6).[24] Ether (*S*)-[D_1]**16** was then subjected to quantitative tin–lithium exchange. This led to the formation of intermediate oxymethyllithium (*R*)-[D_1]**17**, which immediately rearranged to give homoallylic alcohols (*S*)-[1-D_1]**18**, as an *E*/*Z* mixture in a ratio of 40:60. The yields of the [2,3]-Wittig rearrangement performed in THF at −78 °C (5 min) and 0 °C (30 s) were 80 and 71%, respectively (Table 1, entries 7 and 8). Catalytic hydrogenation on Pd/C furnished octanols (*S*)-[1-D_1]**19**. Their *ee*, determined by ^{1}H NMR spectroscopy of the (*R*)-Mosher esters, was 94%.

The *S* configuration of [1-D_1]**19** was inferred from the ^{1}H NMR spectrum of its Mosher ester being identical with the one from an authentic sample prepared by HLADH-catalyzed (HLADH = horse liver alcohol dehydrogenase) reduction of [*formyl*-D_1]octanal.[25] Clearly, the [2,3]-Wittig rearrangement proceeded with inversion of configuration up to 0 °C. The very small percentage of racemization (at worst 3% of enantiomerization) might have occurred during etherification or rearrangement.

Conclusion

We have found that silyloxymethyllithiums are configurationally stable at temperatures between −78 and 0 °C. They easily undergo a *retro*-Brook rearrangement following a retentive course independent of the substituents at silicon (95–97% *ee*). If silicon is exchanged for germanium, a similar isomerization takes place, although the intermediate germyloxymethyllithium [D_1]**13** is significantly less microscopically configurationally stable (90–92% *ee*). The temperature influences neither stereochemistry nor *ee*. The [2,3]-Wittig reaction proceeds with virtually complete inversion of con-

figuration. The various oxymethyllithiums generated are undoubtedly short-lived. They are microscopically configurationally stable and do not behave as carbenoids.[26]

Experimental Section

^{1}H and ^{13}C NMR spectra were measured in $CDCl_3$ at 300 K on a Bruker Avance DRX 250/DRX 400/DRX 600 at 250.13/400.13/600.13 and 100.61/150.92 MHz, respectively. Chemical shifts were referenced to residual $CHCl_3$ ($\delta_H = 7.24$) and $CDCl_3$ ($\delta_C = 77.0$). All chemical shifts (δ) are given in ppm. IR spectra were run on a silicon disc on a Perkin–Elmer 1600 FTIR spectrometer.[27] TLC was carried out on 0.25 mm thick Merck plates, silica gel 60 F_{254}. Flash chromatography was performed with Merck silica gel 60 (230–400 mesh). Spots were visualized by UV and/or dipping the plate into a solution of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (23.0 g) and of $Ce(SO_4)_2\cdot 4H_2O$ (1.0 g) in 10% aqueous H_2SO_4 (500 mL), followed by heating with a heat gun.

TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) and pyridine were refluxed over powdered CaH_2, distilled and stored over molecular sieves 4 Å. Et_2O was refluxed over $LiAlH_4$ and THF over potassium under argon. Both were distilled prior to use. CH_2Cl_2 was dried by passing through aluminum oxide 90 active neutral (0.063–0.200 mm, activity I) and stored over molecular sieves 3 Å. TMP (2,2,6,6-tetramethylpiperidine) was used as supplied.

Small quantities of reagents (μL) were measured with appropriate syringes (Hamilton).

The deuterium content of all labeled compounds lay between 97–98%, as determined by NMR spectroscopy.

Dimethylphenylsilylmethanol (8), one-pot rearrangement in the unlabeled series: Hexabutyldistannane (**4**) (580 mg, 1.0 mmol) and TMEDA (139 mg, 0.18 mL, 1.2 mmol) were dissolved in dry THF (4 mL) under argon. The flask was cooled to 0 °C and *n*BuLi (0.75 mL, 1.2 mmol, 1.6 M solution in hexane) was added, followed by paraformaldehyde (33 mg, 1.1 mmol) after 15 min. The mixture was stirred for 2 h at RT, then cooled down to the respective temperature (−78/0 °C) and quenched with dimethylphenylsilyl chloride (205 mg, 1.2 mmol) to yield intermediate tributylstannylmethyl dimethylphenylsilyl ether (**5**). Further addition of *n*BuLi (0.88 mL, 1.4 mmol, 1.6 M solution in hexane) 45 min later induced tin–lithium exchange followed by [1,2]-*retro*-Brook rearrangement. After the respective reaction time (30 min/30 s), acetic acid (210 mg, 0.20 mL, 3.5 mmol), water (10 mL), and CH_2Cl_2 (10 mL) were added. The organic phase was separated and the aqueous one extracted with CH_2Cl_2 (2×5 mL). The combined organic layers were washed with water (2×5 mL), dried ($MgSO_4$), and concentrated in vacuo. The crude product was purified by flash chromatography (hexane/EtOAc 4:1, $R_f = 0.42$) to yield (dimethylphenylsilyl)methanol ([D_1]**8**) (96 mg, 58%/82 mg, 49%) as a colorless oil. ^{1}H NMR (250.13 MHz, $CDCl_3$): $\delta = 7.57$–7.53 (m, 2 H_{arom}), 7.39–7.35 (m, 3 H_{arom}), 3.54 (t, $J = 1.9$ Hz, 1H), 0.39 (s, 1H), 0.33 ppm (s, 6H).

Transformation of (*R*)- and (*S*)-tributylstannyl[D_1]methanol ([D_1]2) into (*R*)- and (*S*)-dimethylphenylsilyl[D_1]methanol ([D_1]8) as a one-pot reaction, *retro*-Brook rearrangement: Tributylstannyl[D_1]lmethanol (80 mg, 0.25 mmol) and TMEDA (35 mg, 45 μL, 0.30 mmol) were dissolved in dry solvent (2 mL, see Table 1) under argon. The flask was cooled to −78 °C and *n*BuLi (188 μL, 0.30 mmol, 1.6 M solution in hexane) was added, followed 30 min later by dimethylphenylsilyl chloride (52 mg, 0.30 mmol) to yield silyl ether **5**. After stirring for another 30 min, the temperature of the cooling bath was adjusted (see Table 1), and *n*BuLi (219 μL, 0.35 mmol, 1.6 M solution in hexane) was added. At the end of the respective reaction time, acetic acid (53 mg, 50 μL, 0.88 mmol), water (3 mL), and CH_2Cl_2 (3 mL) were added. The organic phase was separated and the aqueous one extracted with CH_2Cl_2 (2×3 mL). The combined organic layers were washed with water (2×3 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by flash chromatography (hexane/EtOAc 4:1, $R_f = 0.42$) to yield silylmethanol **8** (for yields see Table 1) as a colorless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.57$–7.53 (m, 2 H_{arom}), 7.39–7.34 (m, 3 H_{arom}), 3.57 (s, 2H), 1.13 (br s, 1H), 0.34 ppm (s, 6H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta =$ 136.8, 133.6 (2C), 129.4, 128.0 (2C), 55.5, −5.0 ppm (2C); IR (Si): $\tilde{\nu} =$ 3354, 3070, 2958, 2897, 1427, 1249, 1115 cm^{-1}.

Transformation of (tributylstannyl)methanol (2) and (*R*)-tributylstannyl[D_1]methanol ([D_1]2) into (triisopropylsilyl)methanol (11) and (*R*)-triisopropylsilyl[D_1]methanol ([D_1]11) as a one-pot reaction, *retro*-Brook rearrangement: Tributylstannylmethanol (160 mg, 0.50 mmol) and TMEDA (70 mg, 90 μL, 0.60 mmol) were dissolved in dry THF (3.5 mL) under argon. *n*BuLi (375 μL, 0.60 mmol, 1.6 M solution in hexane) was added to the mixture at −78 °C. After stirring for 15 min, triisopropylsilyl triflate (184 mg, 162 μL, 0.60 mmol) was added. Stirring was continued at −78 and 0 °C for 15 min each before addition of a second portion of *n*BuLi (438 μL, 0.70 mmol, 1.6 M solution in hexane). 30 s later 1 M acetic acid (0.7 mL) and water (3 mL) were added. The organic phase was separated and the aqueous one extracted three times with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2, $R_f = 0.43$) to quantitatively yield (triisopropylsilyl)methanol as a colorless oil, probably containing some triisopropylsilanol.

*(Triisopropylsilyl)methanol (**11**)*: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.61$ (s, 2H), 1.15–1.03 (m, 21H), 1.00 ppm (v. br s, 1H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 51.5$, 18.7 (6C), 10.1 ppm (3C); IR (Si): $\tilde{\nu} =$ 3380, 2942, 2892, 2867, 1465 cm^{-1}.

*(R)-Triisopropylsilyl[D_1]methanol ((R)-[D_1]**11**)*: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.58$ (t, $J = 1.9$ Hz, 1H), 1.15–1.01 ppm (m, 22H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 51.1$ (t, $J = 20.3$ Hz), 18.7 (6C), 10.1 ppm (3C); IR (Si): $\tilde{\nu} = 3385$, 2942, 2891, 2866, 1463, 1015 cm^{-1}.

Tributylstannylmethyl triisopropylsilyl ether (9) as reference material: Tributylstannylmethanol (300 mg, 0.93 mmol), triisopropylsilyl chloride (300 μL, 1.40 mmol), and imidazole (190 mg, 2.80 mmol) were dissolved in DMF (2 mL) and stirred for 1 h at RT. After this time, water was added (2 mL), the organic phase separated, and the aqueous one extracted two times with hexane. The combined organic layers were dried ($MgSO_4$), concentrated, and purified by flash chromatography (hexane, $R_f = 0.72$) to yield the product as a colorless oil (204 mg, 46%). ^{1}H NMR (400.13 MHz, $CDCl_3$): 3.98 (s, $J(^{117/119}Sn) = 13.4$ Hz, 2H), 1.55–1.45 (m, 6H), 1.28 (sext, $J = 7.3$ Hz, 6H), 1.11–1.01 (m, 21H), 0.90–0.85 (m, $J(^{117/119}Sn) = 50.5$, 48.5 Hz, 6H), 0.87 ppm (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 53.9$ (1C, $J(^{117/119}Sn) = 400.9$, 391.6 Hz), 29.2 (3C, $J(^{117/119}Sn) = 20.7$ Hz), 27.4 (3C, $J(^{117/119}Sn) = 52.0$ Hz), 18.3 (6C), 13.7 (3C), 11.8 (3C), 8.9 ppm (3C, $J(^{117/119}Sn) = 313.6$, 299.8 Hz); IR (Si): $\tilde{\nu} =$ 2956, 2867, 1653, 1465, 1437, 1050 cm^{-1}; elemental analysis calcd (%) for $C_{22}H_{50}OSiSn$ (477.43): C 55.35, H 10.56; found: C 55.65, H 10.31.

Transformation of (tributylstannyl)methanol (2) and (*S*)- and (*R*)-tributylstannyl[D_1]methanol ([D_1]2) into (triethylgermyl)methanol (14) and (*R*)- and (*S*)-(triethylgermyl)-[D_1]methanol ([D_1]14) as a one-pot reaction: Tributylstannylmethanol (161 mg, 0.50 mmol) was dissolved in dry solvent (3.5 mL) under argon. After addition of TMEDA (90 μL, 0.60 mmol), the flask was cooled to −78 °C and *n*BuLi (380 μL, 0.60 mmol, 1.6 M solution in hexane) was added, followed by triethylgermyl chloride (117 mg, 0.60 mmol in 0.50 mL of solvent) 15 min later. After stirring for 30 min at RT to form the intermediate tributylstannylmethyl triethylgermyl ether **12**, the reaction mixture was cooled to the respective temperature (see Table 1). *n*BuLi (440 μL, 0.70 mmol, 1.6 M solution in hexane) was added, followed by 1 M acetic acid (1.75 mL, 1 M in water), after the respective time span (see Table 1), and water (5 mL). The organic phase was separated, and the aqueous one extracted with diethyl ether (3×5 mL). The combined organic layers were washed with water (2×5 mL), dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by flash chromatography (CH_2Cl_2, $R_f = 0.28$) to yield (triethylgermyl)methanol (for yields see Table 1) as a colorless oil.

*(Triethylgermyl)methanol (**14**)*: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.73$ (s, 2H), 1.04 (t, $J = 8.0$ Hz, 9H), 0.88 (v. br s, 1H), 0.79 ppm (m, 6H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 53.9$, 8.9 (3C), 2.9 (3C); IR (Si): $\tilde{\nu} =$

3327, 2949, 2907, 2872, 1464 cm^{-1}; elemental analysis calcd (%) for $C_7H_{18}GeO$ (190.86): C 44.05, H 9.51; found: C 44.30, H 9.30.

*(S)- and (R)-(triethylgermyl)-[D$_1$]methanol ([D$_1$]**14**)*: (*S*)- and (*R*)-[D$_1$]**14** were spectroscopically identical. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.70$ (t, $J = 1.7$ Hz, 1H), 1.04 (t, $J = 7.8$ Hz, 9H), 0.88 (brs, 1H), 0.79 ppm (m, 6H); ^{13}C NMR (161.98 MHz, $CDCl_3$): $\delta = 53.5$ (t, $J = 21.0$ Hz), 8.9 (3C), 2.9 ppm (3C); IR (Si): $\tilde{\nu} = 3339$, 2954, 2930, 2873, 2349, 1463, 1008 cm^{-1}.

Tributylstannylmethyl methanesulfonate (15b) and tributylstannyl[D$_1$]methyl methanesulfonate ([D$_1$]15b): 2,2,6,6-Tetramethylpiperidine (52 mg, 0.37 mmol) was dissolved in dry THF (1.5 mL) under argon and cooled to −10 °C. *n*BuLi (0.23 mL, 0.37 mmol, 1.6 M solution in hexane) was added and the solution stirred for 15 min, before it was cooled to −78 °C for the addition of tributylstannylmethanol (100 mg, 0.31 mmol) in dry THF (0.5 mL). Methanesulfonyl chloride (31 μL, 0.40 mmol) was added after 20 min, followed by water (2 mL) and 2 M HCl (2 mL) after 20 min. The organic layer was separated and the aqueous one extracted with EtOAc (3×2 mL). The combined organic phases were washed with a saturated solution of $NaHCO_3$ and water, dried ($MgSO_4$), and concentrated under reduced pressure. The crude product was purified by flash chromatography (hexane/EtOAc 7:1, $R_f = 0.43$) to give **15b** (80 mg, 80 %, reproducible in all cases) as a colorless oil, containing 5 % of tributylstannylmethanol.

*Tributylstannylmethyl methanesulfonate (**15b**)*: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 4.27$ (s, $J(^{117/119}Sn) = 14$ Hz, 2H), 2.93 (s, 3H), 1.55–1.46 (m, 6H), 1.29 (sext, $J = 7.3$ Hz, 6H), 1.02–0.95 (m, 6H), 0.88 ppm (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 59.6$ ($J(^{117/119}Sn) = 260.0$, 248.6 Hz), 35.7, 28.8 ($J(^{117/119}Sn) = 22$ Hz, 3C), 27.2 ($J(^{117/119}Sn) = 56$ Hz, 3C), 13.6 (3C), 9.4 ppm ($J(^{117/119}Sn) = 341.1$, 326.6 Hz, 3C); IR (Si): $\tilde{\nu} =$ 2957, 2925, 2852, 1356, 1173 cm^{-1}.

*(S)- and (R)-tributylstannyl[D$_1$]methyl methanesulfonate ([D$_1$]**15b**)*: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 4.26$ (t, $J \approx 1.0$ Hz, $J(^{117/119}Sn) = 14$ Hz, 1H), 2.92 (s, 3H), 1.54–1.45 (m, 6H), 1.28 (sext, $J = 7.3$ Hz, 6H), 1.02–0.96 (m, 6H), 0.87 ppm (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 59.3$ (t, $J = 22.2$ Hz), 35.7, 28.8 ($J(^{117/119}Sn) = 21$ Hz, 3C), 27.2 ($J(^{117/119}Sn) = 54$ Hz, 3C), 13.6 (3C), 9.3 ($J(^{117/119}Sn) = 341.1$, 325.8 Hz, 3C); IR (Si): $\tilde{\nu} = 2957$, 2926, 2872, 2853, 1357, 1176 cm^{-1}.

Tributylstannylmethyl 4-methylphenylsulfonate (15a): Tributylstannylmethanol (100 mg, 0.31 mmol) and DMAP (4 mg, 0.03 mmol) were dissolved in dry CH_2Cl_2 (1.5 mL) and cooled to 0 °C. NEt_3 (100 μL, 0.72 mmol) was added and the solution stirred for 20 min. Tosyl chloride (92 mg, 0.48 mmol) in dry CH_2Cl_2 (0.5 mL) was added and stirring was continued for 2 h. The reaction was quenched with water (2 mL), the organic layer was separated, and the aqueous one extracted with CH_2Cl_2 (3×2 mL). The combined organic phases were washed with a saturated solution of $NaHCO_3$ and water, before being dried over $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash chromatography (hexane/CH_2Cl_2 2:1, $R_f = 0.43$) to produce the pure product in 67 % yield. ^{1}H NMR (400.13 MHz, $CDCl_3$): 7.75 (d, $J = 8.1$ Hz, 2H$_{arom}$), 7.31 (d, $J = 8.1$ Hz, 2H$_{arom}$), 4.04 (s, $J(^{117/119}Sn) = 14.2$ Hz, 2H), 2.42 (s, 3H), 1.47–1.37 (m, 6H), 1.23 (sext., $J = 7.3$ Hz, 6H), 0.94–0.88 ppm (m, 6H), 0.84 (t, $J = 7.3$ Hz, 9H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 144.4$, 132.5, 129.6 (2C), 128.2, 60.2 ($J(^{117/119}Sn) = 265.4$ Hz), 28.8 ($J(^{117/119}Sn) =$ 22.2 Hz, 3C), 27.2 ($J(^{117/119}Sn) = 53.4$ Hz, 3C), 21.6, 13.6 (3C), 9.3 ppm ($J(^{117/119}Sn) = 340.4$, 325.1 Hz, 3C); IR (Si): $\tilde{\nu} = 2957$, 2926, 1363, 1187, 1175 cm^{-1}; elemental analysis calcd (%) for $C_{20}H_{36}O_3SSn$ (475.27): C 50.54, H 7.63; found: C 50.83 C, H 7.63.

3-(Tributylstannylmethoxy)hept-1-ene (16) and 3-(tributylstannyl[D$_1$]methoxy)hept-1-ene ([D$_1$]16): KO*t*Bu (263 mg, 2.34 mmol), 18-crown-6 (619 mg, 2.34 mmol), and hept-1-en-3-ol (343 mg, 3.0 mmol) were dissolved in dry THF (1.5 mL) at 0 °C under argon. After stirring for 1 h at RT, **15b** (80 mg, 0.20 mmol, dissolved in 0.5 mL of dry THF) was added and the mixture was stirred for a further 1 h at low temperature. The reaction was quenched with water (2 mL) and 2 M HCl (1 mL). The organic phase was separated and the aqueous one extracted with diethyl ether (2×2 mL). The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (hexane/CH_2Cl_2 15:1, $R_f = 0.49$) to give ether **16** (60 mg, 72 %) as a colorless oil or [D$_1$]**16** (549 mg, 77 %) starting from [D$_1$]**15b** (750 mg, 1.70 mmol).

*3-(Tributylstannylmethoxy)hept-1-ene (**16**)*: ^{1}H NMR (600.13 MHz, $CDCl_3$): $\delta = 5.66$ (ddd, $J = 17.4$, 10.6, 7.6 Hz, 1H), 5.13 (dd, $J = 10.6$, 1.9 Hz, 1H), 5.12 (dd, $J = 17.4$, 1.9 Hz, 1H), 3.76, 3.46 (d, $J = 10.2$ Hz, $J(^{117/119}Sn) = 15$ Hz, 2H), 3.35 (m, 1H), 1.56–1.36 (m, 8H), 1.33–1.21 (m, 4H), 1.28 (sext, $J = 7.6$ Hz, 6H), 0.90–0.84 (m, 9H), 0.87 ppm (t, $J =$ 7.0 Hz, 9H); ^{13}C NMR (150.92 MHz, $CDCl_3$): $\delta = 139.8$, 116.3, 85.5, 58.9, 35.1, 29.2 ($J(^{117/119}Sn) = 21$ Hz, 3C), 27.6, 27.3 ($J(^{117/119}Sn) = 51$ Hz, 3C), 22.7, 14.1, 13.7 (3C), 9.0 ppm ($J(^{117/119}Sn) = 319$ Hz, 3C); IR (Si): $\tilde{\nu} = 2957$, 2928, 2872, 1465, 1051 cm^{-1}.

*(S)-(Tributylstannyl[D$_1$]methoxy)hept-1-ene ((S)-[D$_1$]**16**)*: ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.61$ (ddd, $J = 16.9$, 10.9, 7.6 Hz 1H), 5.16–5.03 (m, 2H), 3.74, 3.44 (s, $J = 16.2$ Hz, $J(^{117/119}Sn) = 14.7$ Hz, 1H), 3.35 (m, 1H), 1.53–1.38 (m, 8H), 1.33–1.22 (m, 4H), 1.28 (sext, $J = 7.3$ Hz, 6H), 0.95–0.78 (m, 9H), 0.87 ppm (t, $J = 8.1$ Hz, 9H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 139.8$, 116.3, 85.4, 58.5 (t, $J = 19.9$ Hz), 35.1, 29.2 ($J(^{117/119}Sn) =$ 21 Hz, 3C), 27.6, 27.3 ($J(^{117/119}Sn) = 52$ Hz, 3C), 22.7, 14.1, 13.7 (3C), 8.99 ppm ($J(^{117/119}Sn) = 319.7$, 305.2 Hz, 3C); IR (Si): $\tilde{\nu} = 2957$, 2928, 2872, 2856, 1465, 1377, 1052 cm^{-1}.

Oct-3-en-1-ol (18) and [1-D$_1$]oct-3-en-1-ol ([1-D$_1$]18), [2,3]-Wittig rearrangement: *n*BuLi (0.49 mL, 0.78 mmol, 1.6 M solution in hexane) was added to a stirred solution of 3-tributylstannylmethoxy-1-heptene (**16**) (271 mg, 0.65 mmol) in dry THF (4 mL) at the respective temperature (see Table 1) under argon. The reaction was quenched with acetic acid (2.5 mL, 1 M in water) after the time given in Table 1. The organic layer was separated and the aqueous one extracted three times with diethyl ether. The combined organic layers were dried ($MgSO_4$) and concentrated under reduced pressure. The residue was purified by flash chromatography (CH_2Cl_2, $R_f = 0.29$) to yield 3-octen-1-ol (for yields see Table 1, *E*/*Z* 40:60) as a colorless liquid.

*Oct-3-en-1-ol (**18**)*: *Z* isomer (in mixture): ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.58$–5.48 (m, 1H), 5.40–5.29 (m, 1H), 3.61 (t, $J = 6.8$ Hz, 2H), 2.31 (m, 2H), 2.06 (m, 2H), 1.46 (brs, 1H), 1.37–1.22 (m, 4H), 0.874 ppm (t, $J = 7.0$ Hz, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 133.5$, 124.9, 62.3, 31.8, 30.8, 27.1, 22.3, 13.9 ppm; *E* isomer (in mixture): ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.84$–5.48 (m, 1H), 5.40–5.29 (m, 1H), 3.60 (t, $J = 6.6$ Hz, 2H), 2.23 (m, 2H), 2.00 (m, 2H), 1.46 (brs, 1H), 1.37–1.22 (m, 4H), 0.86 ppm (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 134.3$, 125.7, 62.0, 36.0, 32.3, 31.6, 22.2, 13.9 ppm; IR (Si): $\tilde{\nu} =$ 3335, 3009, 2957, 2928, 1466, 1049 cm^{-1}.

*(S)-[1-D$_1$]Oct-3-en-1-ol ((S)-[1-D$_1$]**18**)*: *Z* isomer (in mixture): ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.58$–5.48 (m, 1H), 5.40–5.29 (m, 1H), 3.59 (td, $J = 6.8$ Hz, 1.0, 1H), 2.30 (m, 2H), 2.04 (m, 2H), 1.48 (brs, 1H), 1.37–1.25 (m, 4H), 0.91–0.83 ppm (m, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta =$ 133.4, 124.9, 62.0 (t, $J = 22.2$ Hz), 31.8, 30.7, 27.1, 22.3, 13.9 ppm; *E* isomer (in mixture): ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 5.84$–5.48 (m, 1H), 5.40–5.29 (m, 1H), 3.57 (td, $J = 6.8$, 1.0 Hz, 1H), 2.23 (m, 2H), 1.99 (m, 2H), 1.48 (brs, 1H), 1.37–1.25 (m, 4H), 0.91–0.83 ppm (m, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 134.3$, 125.7, 61.7 (t, $J = 22.2$ Hz), 35.9, 32.3, 31.6, 22.2, 13.9 ppm; IR (Si): $\tilde{\nu} = 3332$, 2924, 2853, 2330, 1466, 1070 cm^{-1}.

[1-D$_1$]Octan-1-ol ([1-D$_1$]19), hydrogenation of [1-D$_1$]18: Pd/C (12 mg, 10 %) was prehydrogenated in dry EtOAc (2 mL) before the addition of [1-D$_1$]**18** (55 mg, 0.43 mmol) dissolved in EtOAc (0.5 mL). The mixture was stirred for 1 h under hydrogen at 1 atm, before being directly purified by flash chromatography (CH_2Cl_2/diethyl ether 30:1; TLC: hexane/EtOAc 3:1, $R_f = 0.29$) to yield the alcohol [1-D$_1$]**19** (18 mg, 33 %, low yield due to loss at chromatography) as a colorless oil. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 3.59$ (tt, $J = 6.8$, 1.5 Hz, 1H), 1.53 (q, $J = 6.8$ Hz, 2H), 1.51 (v. brs, 1H), 1.36–1.21 (m, 10H), 0.86 ppm (t, $J = 6.8$ Hz, 3H); ^{13}C NMR (100.61 MHz, $CDCl_3$): $\delta = 62.7$ (t, $J = 21.4$ Hz), 32.7, 31.8, 29.4, 29.3, 25.7, 22.6, 14.1 ppm; IR (Si): $\tilde{\nu} = 3338$, 2956, 2927, 2856, 2145, 1467 cm^{-1}.

Esterification of alcohols with (*S*)-Mosher acid chloride ((*S*)-MTPACl): A solution of the alcohol (0.06 mmol), dry pyridine (0.17 mL), and (*S*)-MTPACl (0.18 mL, 0.09 mmol, 0.5 M solution in dry CH_2Cl_2) in dry CH_2Cl_2 (1.40 mL) was left overnight at RT. CH_2Cl_2 (10 mL) and 1 M HCl

(3 mL) were added, the organic layer was separated and washed with a saturated aqueous solution of $NaHCO_3$ (5 mL). The organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash chromatography to yield the (*R*)-Mosher ester as a colorless oil in virtually quantitative yield.

(*R*)-Mosher ester of (dimethylphenylsilyl)methanol (8·MTPA-(*R*)): Chromatography: hexane/EtOAc 10:1, $R_f = 0.48$; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.49$–7.45 (m, $2H_{arom}$), 7.44–7.30 (m, $8H_{arom}$), 4.18 (AB system, $J_{AB} = 14.1$ Hz, 2H); 3.44 (q, $J = 1.0$ Hz, 3H); 0.34 ppm (s, 6H); (*S*)-[D_1]**8**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$): spectrum was identical to that of **8**·MTPA-(*R*) except for the signal at $\delta = 4.12$ ppm (t, $J = 1.3$ Hz, 1H); (*R*)-[D_1]**8**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$): spectrum was identical to that of **8**·MTPA-(*R*) except for the signal at $\delta = 4.20$ ppm (t, $J = 1.3$ Hz, 1H).

(*R*)-Mosher ester of (triisopropylsilyl)methanol (11·MTPA-(*R*)): Chromatography: hexane/CH_2Cl_2 3:1, $R_f = 0.29$; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.50$–7.44 (m, $2H_{arom}$), 7.38–7.32 (m, $3H_{arom}$), 4.09 (AB system, $J_{AB} = 14.7$ Hz, 2H), 3.51 (q, $J = 1.0$ Hz, 3H), 1.08–0.94 (m, 21H); (*R*)-[D_1]**11**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$) spectrum was identical to that of **11**·MTPA-(*R*) except for the signal at $\delta = 4.14$ (t, $J \approx 1.0$ Hz, 1H). Furthermore, a very weak signal was found at $\delta = 3.99$ (t, $J \approx 1.0$ Hz), which we attributed to (*S*)-[D_1]**11**·MTPA-(*R*).

(*R*)-Mosher ester of (triethylgermyl)methanol (14·MTPA-(*R*)): Chromatography: hexane/CH_2Cl_2 4:1, $R_f = 0.28$; ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.51$–7.46 (m, $2H_{arom}$), 7.39–7.35 (m, $3H_{arom}$), 4.26 (AB system, $J_{AB} = 12.6$ Hz, 2H), 3.51 (q, $J = 1.0$ Hz, 3H), 0.98 (t, $J = 7.8$ Hz, 9H), 0.77 ppm (m, 6H); (*S*)-[D_1]**14**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$): spectrum was identical to that of **14**·MTPA-(*R*) except for the signal at $\delta = 4.18$ ppm (t, $J = 1.4$ Hz, 1H); (*R*)-[D_1]**14**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$): spectrum was identical to that of **14**·MTPA-(*R*) except for the signal at $\delta = 4.31$ ppm (t, $J = 1.3$ Hz, 1H).

(*R*)-Mosher ester of 1-octanol (19·MTPA-(*R*)): Chromatography: hexane/CH_2Cl_2 4:1, $R_f = 0.27$. ^{1}H NMR (400.13 MHz, $CDCl_3$): $\delta = 7.53$–7.48 (m, $2H_{arom}$), 7.41–7.32 (m, $3H_{arom}$), 4.29 (t, AB system, $J_{AB} = 10.9$, $J = 6.7$ Hz, 2H), 3.54 (q, $J = 0.8$ Hz, 3H), 1.67 (quin, $J = 6.9$ Hz, 2H), 1.39–1.18 (m, 10H), 0.86 (t, $J = 6.9$ Hz, 3H); (*S*)-[1-D_1]**19**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$): spectrum was identical to that of **19**·MTPA-(*R*) except for the signal at $\delta = 4.30$ (br t, $J = 6.6$ Hz, 1H); when irradiated at 1.67 ppm it collapsed to a br s; (*R*)-[1-D_1]**19**·MTPA-(*R*): ^{1}H NMR (400.13 MHz, $CDCl_3$) spectrum was identical to that of **19**·MTPA-(*R*) except for the signal at $\delta = 4.26$ (br t, $J = 6.6$ Hz, 1H); when irradiated at 1.67 ppm it collapsed to a br s.

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