Substrate-Controlled Highly Diastereoselective Synthesis of Primary and Secondary Diorganozinc Reagents by a Hydroboration/Boron–Zinc Exchange Sequence

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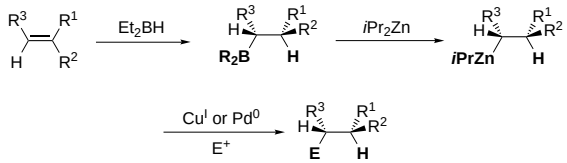
Abstract: The scope of substrate-controlled diastereoselective hydroborations can be considerably enhanced by a boron–zinc exchange reaction, providing organozinc derivatives that react with a broad range of electrophiles. Even normally unreactive boronic esters, obtained by Rh-catalyzed hydroboration with catecholborane, react readily with iPr$_2$Zn providing the corresponding zinc reagents in high diastereoselectivity.

Keywords: C–C coupling · diastereoselective synthesis · hydroboration · transmetallation · zinc organometallics

Introduction

The control of the relative stereochemistry in complex chiral molecules is an important task in organic chemistry.[1] Especially important are synthetic methods that allow this stereocontrol and at the same time lead to the formation of new C–C bonds. Some years ago, we showed that chiral organozincs possess an excellent configurational stability which is usually maintained in various transmetallations.[2, 3] This chirality has been introduced by a hydroboration/boron–zinc exchange sequence.[4] Thus, starting from a trisubstituted olefin, regioselective hydroboration with Et$_2$BH leads to an intermediate organoborane which can be transmetallated to the corresponding organozinc reagent with retention of stereochemistry.[5] This organozinc reagent can then be trapped with a broad range of electrophiles after transmetallation to Cu^I or catalyzed by Pd^0,[2c] giving the desired products in reasonable overall yield and excellent stereochemical control (Scheme 1).



Scheme 1. Synthesis and reaction of chiral diorganozinc reagents obtained by a hydroboration/boron–zinc exchange sequence.

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Substrate-controlled diastereoselective hydroboration is an important reaction in organic synthesis.[6] One major drawback of this reaction is that the resulting chiral organoboranes are usually not reactive enough to form new C–C bonds. The aim of this work was to investigate whether the boron–zinc exchange reaction can be applied to convert various organoboranes and boronic esters, obtained after substrate-controlled diastereoselective hydroborations, into the corresponding diorganozinc reagents. These diorganozinc reagents could then be easily reacted with a variety of different carbon electrophiles to form new C–C bonds.

Results and Discussion

The hydroborating reagent of choice for performing a boron–zinc exchange reaction in previous studies[2] was Et$_2$BH in Me$_2$S (ca. 7.3 M). Addition of iPr$_2$Zn to triorganoboranes, obtained after hydroboration with this hydroborating reagent, leads to a clean boron–zinc exchange reaction usually within 5 h at 25 °C. In the course of our studies on substrate controlled hydroboration on the decalin derivative **3**, which was obtained after diastereoselective Luche reduction[7] and protection of the bicyclic system **1**[8] (Scheme 2), we observed that hydroboration under our standard conditions (3 equiv Et$_2$BH in Me$_2$S, 50 °C, 16 h) gave very poor selectivities. Thus, **4** was obtained in a selectivity of 3:1 between the centers C(1) and C(2). Optimization of the conditions for the hydroboration could significantly improve this selectivity. By using CH$_2$Cl$_2$ as a cosolvent (CH$_2$Cl$_2$/Me$_2$S ≈5:1) and performing the hydroboration at 25 °C (3 equiv, 48 h) instead of 50 °C, the intermediate organoborane **4** could be obtained in an excellent selectivity of 97:3 between the centers C(1) and C(2) (Scheme 2). Subsequent boron–zinc exchange reaction

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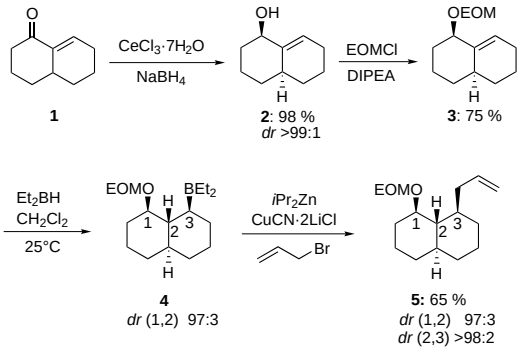
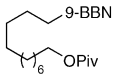
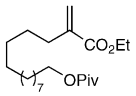
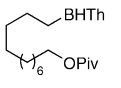
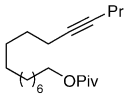
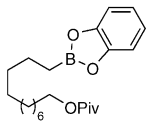
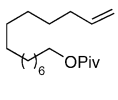
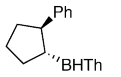
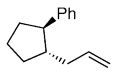
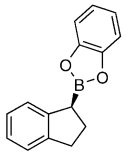
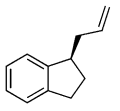
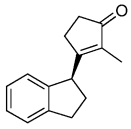
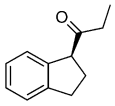


Scheme 2. Hydroboration and subsequent boron–zinc exchange reaction on the decalin derivative **3** under improved conditions for the hydroboration; EOM = $EtOCH_2$.

(*i*Pr_2Zn, 3 equiv, RT, 5 h) and Cu^I-mediated allylation of **4** ($CuCN \cdot 2\,LiCl$,[9] 0.7 equiv, −78 °C, 30 min, then allyl bromide, 3 equiv, −78 °C to RT, 14 h) gave the desired allylated product **5** in 65% overall yield and a selectivity of >98:2 between the centers C(2) and C(3), showing the configurational stability of the formed diorganozinc compound (Scheme 2).[2b]

Since Et_2BH undergoes substrate-controlled hydroboration with many chiral olefins with only low diastereoselectivities, we screened more sterically-hindered easily accessible hydroborating reagents such as $ThBH_2$,[10] 9-BBN-H and catecholborane[10] for their ability to undergo the boron–zinc exchange reaction.[11] We have found that primary organoboranes and boronic esters, obtained after hydroboration, can be directly transmetallated to the corresponding organozinc reagents by using *i*Pr_2Zn (method A). For secondary organoboranes and boronic esters, a two-step transmetallation of the organoborane/boronic ester to a diethylalkylborane, followed by a boron–zinc exchange with *i*Pr_2Zn was applied (method B). Thus, the hydroboration of 10-undecenyl pivalate with 9-BBN-H (2 equiv, RT, 12 h) provides the corresponding organoborane **6a** which, after treatment with *i*Pr_2Zn (5 equiv, RT, 4 h, method A), transmetallation with $CuCN \cdot 2\,LiCl$[9] and allylation with ethyl 2-(bromomethyl)acrylate furnishes the desired product **7a** in 66% yield (entry 1 of Table 1). Similarly, hydroboration with thexylborane[10] ($ThBH_2$) (2 equiv, −30 °C to RT, 12 h) leads to the organoborane **6b**. Reaction of **6b** with *i*Pr_2Zn (5 equiv, RT, 5 h) cleanly provides the corresponding organozinc reagent, which after transmetallation with $CuCN \cdot 2\,LiCl$ (1.5 equiv, −78 °C, 30 min) and reaction with 1-bromopentyne (5 equiv, −40 °C, 36 h) provides the desired alkyne **7b** in 52% overall yield (entry 2, Table 1). Finally, the rhodium-catalyzed hydroboration of 10-undecenyl pivalate with catecholborane (1.1 equiv, 0 °C to RT, 5 h) in the presence of $[RhCl(PPh_3)_3]$ (2 mol%)[10] gives the boronic ester **6c**. Subsequent transmetallation with *i*Pr_2Zn (10 equiv) requires 36 h at 25 °C and leads, after a copper(I)-mediated allylation, to the desired product **7c** in 58% yield (entry 3 of Table 1). These results indicate that primary functionalized organoboranes are readily converted to the corresponding organozinc species. Similar results are obtained with secondary organoboranes. Thus, the hydroboration of 1-phenylcyclopentene with thexylborane gives the corresponding organoborane **6d**. After reaction with Et_2BH (5 equiv, 50 °C, 16 h) and *i*Pr_2Zn (5 equiv, RT, 5 h) (method B), the resulting secondary diorganozinc species can be allylated with high retention of the *trans* stereochemistry (94% *trans*; entry 4 of Table 1). Benzylic zinc reagents can also be prepared. Thus, the Rh-catalyzed hydroboration of indene with catecholborane[12] leads to the boronic ester **6e**. The corresponding benzylic zinc reagent[13] is obtained after treatment with Et_2BH and *i*Pr_2Zn (method B). This organozinc reagent then undergoes copper(I)-mediated reactions with allyl bromide, 3-iodo-2-methyl-cyclopent-2-en-1-one and propionyl chloride. The expected products **7e–g** are obtained in 51–58% yield (entries 5–7 of Table 1). Although the B–Zn replacements are sometimes slow, we have not observed effects on the chemoselectivity during the residue transfer.

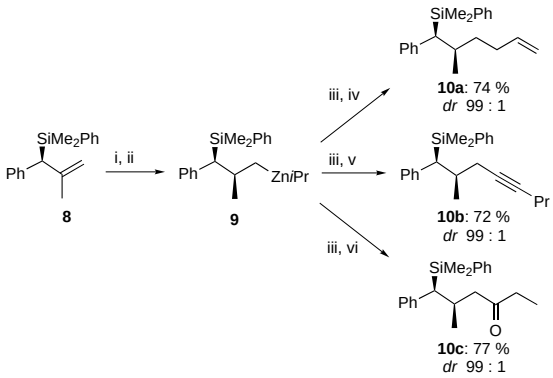
Table 1. Products obtained by copper(I) mediated reactions of diorganozinc reagents obtained by a boron–zinc exchange reaction.

Entry	Organoborane of type **6**	Method	Product of type **7**	Yield [%][a]
1	 **6a**	A	 **7a**	66
2	 **6b**	A	 **7b**	52
3	 **6c**	A	 **7c**	58
4	 **6d**	B	 **7d**	58[b]
5	 **6e**	B	 **7e**	54
6	**6e**	B	 **7f**	58
7	**6e**	B	 **7g**	51

[a] Isolated yield of analytically pure compound. Piv = pivalate; ThBH = thexylborane; 9-BBN = 9-borabicyclo[3.3.1]nonane. [b] For compound **7d**, relative configuration is shown.

Thus, we have established a method that allows us to convert various organoboranes and boronic esters into the corresponding organozinc reagents which can be used for the formation of new C–C bonds. The scope of substrate-controlled diastereoselective hydroboration already described in the literature can be considerably enhanced using the boron–zinc exchange sequence presented.

Fleming et al. have reported excellent diastereoselectivities for hydroboration of a variety of different allylsilanes using 9-BBN-H. Thus, the hydroboration of the open-chain silane **8** with 9-BBN-H,[14] generates, after direct boron–zinc exchange with iPr$_2$Zn (4 equiv, RT, 4 h), the diastereomerically pure (*dr* 99:1) primary organozinc reagent **9**. After transmetallation with CuCN·2LiCl, the organozinc reagent **9** can be quenched with electrophiles such as allyl bromide, 1-bromopentyne and propionyl chloride, leading to the expected products **10a–c** (*dr* 99:1) in 72–77% overall yield (Scheme 3).

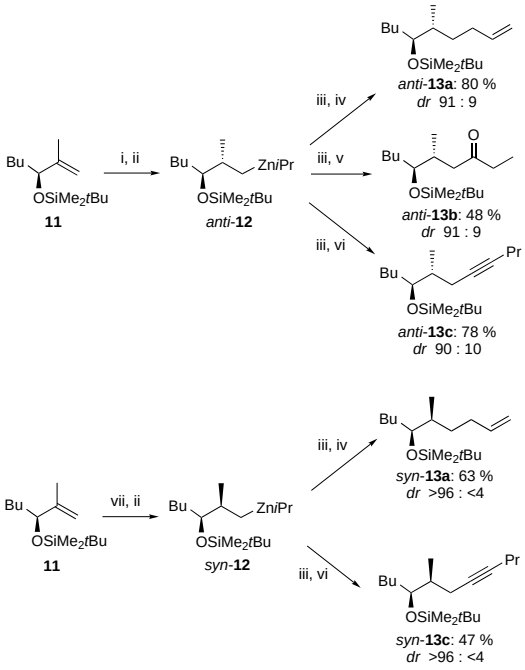


Scheme 3. Hydroborations and boron–zinc exchange reactions on the acyclic allylsilane **8**. i) 9-BBN-H (2 equiv, 25 °C, 36 h); ii) iPr$_2$Zn (4 equiv, 25 °C, 4 h); iii) CuCN·2LiCl (1.5 equiv, −78 °C, 30 min); iv) allyl bromide (3 equiv, −78 → 25 °C, 12 h); v) 1-bromo-1-pentyne (3 equiv, −40 °C, 16 h); vi) propionyl chloride (3 equiv, −78 → 25 °C, 12 h).

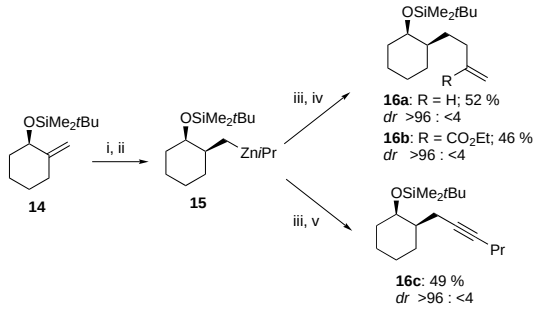
The direct hydroboration of **8** with Et$_2$BH and reaction with iPr$_2$Zn provides **9** only with a 90:10 diastereoselectivity, showing the advantage of this newly described procedure.

Still et al. showed that silylated allylic alcohols can be diastereoselectively hydroborated with 9-BBN-H.[15] Applying the reported conditions for the hydroboration with 9-BBN-H (3 equiv, 0 °C to RT, 16 h) and after a subsequent B–Zn exchange, the *anti* diastereoisomer *anti*-**12** was obtained in good diastereoselectivities (*dr* 91:9). Hydroboration of **11** with catecholborane (3 equiv, [RhCl(PPh$_3$)$_3$] (1 mol%), 0 °C to RT, 6 h) will result in the *syn* diastereoisomer as described by Evans et al.[16] After transmetallation of the resulting boronic ester with iPr$_2$Zn (16 equiv, RT, 36 h), we were able to obtain *syn*-**12** in a *syn*:*anti* ratio of 96:4. The copper(I)-mediated reactions of *syn*- and *anti*-**12** provide the desired *syn*- and *anti*-alcohol derivatives (*syn*- and *anti*-**13**), in moderate to good yields (Scheme 4).

Similarly, the protected *exo*-methylidene cyclohexyl alcohol **14** was converted, after Rh-catalyzed hydroboration,[16] directly into the corresponding Zn reagent and then allylated, yielding **16a–b** or alkynylated, affording **16c** in excellent diastereoselectivities (Scheme 5).



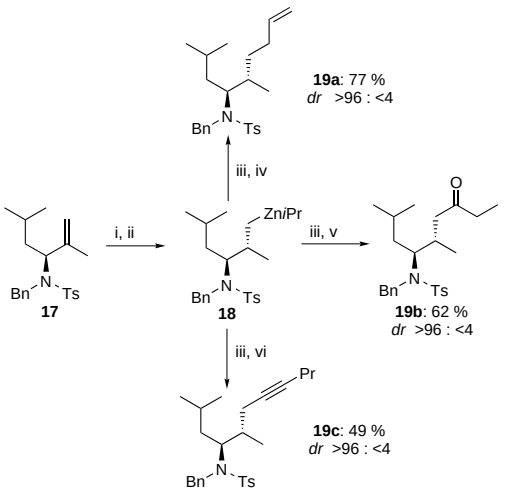
Scheme 4. Hydroborations and boron–zinc exchange reactions on the protected allylic alcohol **11**. i) 9-BBN-H (3.0 equiv, 0 → 25 °C, 16 h); ii) iPr$_2$Zn (4 equiv, 25 °C, 4 h for *anti*-**12** or 2 × 8 equiv, 25 °C, 36 h for *syn*-**12**); iii) CuCN·2LiCl (1.5 equiv, −78 °C, 30 min); iv) allyl bromide (3 equiv, −78 → 25 °C, 12 h for *anti*-**13a** or 5 equiv, −78 → 25 °C, 12 h for *syn*-**13a**); v) propionyl chloride (3 equiv, −78 → 25 °C, 12 h); vi) 1-bromo-1-pentyne (3 equiv, −40 °C, 16 h for *anti*-**13c** or 5 equiv, −40 °C, 16 h for *syn*-**13c**); vii) catecholborane (3 equiv, 0 → 25 °C, 6 h) and [RhCl(PPh$_3$)$_3$] (0.01 equiv).



Scheme 5. Hydroborations and boron–zinc exchange reactions on the protected exo-methylidene alcohol **14**. i) catecholborane (3 equiv, 0 → 25 °C, 6 h) and [RhCl(PPh$_3$)$_3$] (0.03 equiv); ii) iPr$_2$Zn, 2 × 8 equiv, 25 °C, 36 h); iii) CuCN·2LiCl (1.5 equiv, −78 °C, 30 min); iv) allylic bromide (5 equiv, −78 → 25 °C, 12 h for **16a** or 5 equiv, −40 °C, 16 h for **16b**); v) 1-bromo-1-pentyne (5 equiv, −40 °C, 16 h).

Hydroboration of **14** with Et$_2$BH and subsequent B–Zn exchange lead to only a 37:63 mixture of *syn*- and *anti*-**15**, showing again the advantage of the methodology presented herein.

Chiral amines can be hydroborated diastereoselectively as described by Burgess et al.[17] Hydroboration of the allylic amine **17** with 9-BBN-H (3 equiv, −78 °C to RT, 12 h), followed by a B–Zn exchange with iPr$_2$Zn (5 equiv, RT, 5 h) furnishes the primary organozinc reagent **18** as a 96:4 mixture of diastereoisomers. After copper(I)-mediated transformations, amines **19a–c** are obtained in 49–77% yield (Scheme 6).



Scheme 6. Hydroborations and boron–zinc exchange reactions on the protected amine **17**. i) 9-BBN-H (3.0 equiv, $-78\rightarrow25\,^{\circ}C$, 12 h); ii) $i Pr_2Zn$ (5 equiv, 25 °C, 5 h); iii) CuCN·2LiCl (1.5 equiv, −78 °C, 30 min); iv) allyl bromide (3.5 equiv, $-78\rightarrow25\,^{\circ}C$, 12 h); v) propionyl chloride (3.5 equiv, $-78\rightarrow25\,^{\circ}C$, 10 h); vi) 1-bromo-1-pentyne (5 equiv, −40 °C, 3 d).

Conclusion

In summary, we have shown that a substrate-controlled diastereoselective hydroboration on bicyclic chiral systems such as **3** can be carried out under our improved standard conditions. The chiral triorganoboranes obtained can be easily converted into the corresponding zinc reagents with almost no loss of stereochemistry. Furthermore, we have shown that a range of triorganoboranes and boronic esters obtained after substrate-controlled hydroboration with 9-BBN-H, thexylborane and catecholborane can be converted into the corresponding zinc-reagents and trapped with a variety of electrophiles, thus considerably broadening the scope of substrate-controlled diastereoselective hydroboration.

Experimental Section

General considerations: Unless otherwise indicated, all reactions were carried out under argon. Solvents were dried and freshly distilled. $[RhCl(PPh_3)_3]$ was purchased from Lancaster and kept under an argon atmosphere. Reactions were monitored by gas chromatography (GC and GC-MS) or thin-layer chromatography (TLC). The ratios between diastereoisomers were determined by NMR spectroscopy and/or GC-MS analysis of crude reaction mixtures; GC-MS: HP-5MS (30 m × 250 μm × 0.25 μm); method A: 3 min at 50 °C, ramp of 25 °C min^{-1} to 150 °C, ramp of 50 °C min^{-1} to 250 °C; method B: 3 min at 70 °C, ramp of 50 °C min^{-1} to 250 °C, 8 min at 250 °C.

Starting materials

Diisopropylzinc: A 1.3 M solution of isopropylmagnesium bromide in diethyl ether was prepared from 2-bromopropane (38.8 g, 0.32 mol) and magnesium (8.5 g, 0.35 mol) and transferred with a cannula to a 500 mL two-necked flask. Zinc bromide (35.5 g, 0.16 mol) was dried (120 °C, 1 mmHg, 2 h) and dissolved in diethyl ether (150 mL, ca. 30 min). This solution was carefully added to the Grignard reagent at 0 °C and the resulting biphasic mixture stirred vigorously overnight. After distilling off most of the diethyl ether at 40–50 °C (ca. 2 h), a Schlenk tube equipped with a magnetic stirring bar was connected to the distillation apparatus and cooled with liquid nitrogen. Vacuum was applied (1 mmHg) and a mixture of diisopropylzinc and diethyl ether was distilled from the remaining salts by slowly raising the temperature from 25 °C to 100 °C (ca. 2 h). After warming the condensate to 25 °C, excess diethyl ether was evaporated by slowly lowering the pressure to 20 mmHg whilst stirring over 1 h. The diisopropylzinc thus obtained (18 mL, ca. 60 %) was approximately 5 M (titration with 1 M I_2 solution in tetrahydrofurane) and was stored in the dark.

Preparation of starting materials not reported previously in the literature

1,2,3,4,4a,5,6,7-Octahydro-(1*R)-naphthalenol (2)**: 1,2,3,4,4a,5,6,7-Octahydro-1-naphthalenol (**2**) was obtained by the Luche reduction[7] of 3,4,4a,5,6,7-hexahydro-1(2*H*)-naphthalen-on[8] (**1**). The α,β-unsaturated ketone **1** (1.50 g, 10 mmol) was added to a solution of $CeCl_3\cdot7H_2O$ in MeOH (25 mL, 0.4 M). $NaBH_4$ (0.38 g, 10 mmol) was added in small portions. The reaction mixture was stirred for 30 min at 25 °C then carefully poured into a saturated aqueous NH_4Cl solution (150 mL). After extraction with Et_2O (3 × 150 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude product (1.49 g, 9.8 mmol, 98 %) used directly for the next step. IR (film): $\tilde{\nu}=3350$ (s), 2854 (vs), 1671 (w), 1447 (s), 1354 (m), 1187 (w), 1103 (m), 1059 (m), 958 (m), 852 (m), 651 (w), 540 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=5.69$ (m, 1H), 3.96 (m, 1H), 2.12–0.97 (br m, 13H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=143.0$, 115.7, 72.5, 37.2, 36.4, 34.7, 30.5, 25.2, 23.8, 21.1; MS: *m*/*z* (%): 152 (82) [M^+], 134 (37), 123 (100), 110 (82), 91 (61), 81 (65), 67 (34), 55 (20); HRMS (EI): *m*/*z*: calcd for $C_{16}H_{16}O$: 152.1201; found: 152.1202 [M^+].

(1*R)-(Ethoxymethoxy)-1,2,3,4,4a,5,6,7-octahydronaphthalene (3)**: 1-(Ethoxymethoxy)-1,2,3,4,4a,5,6,7-octahydronaphthalene (**3**) was obtained by protection[18] of the α,β-unsaturated alcohol **2**. Diisopropylethyl amine (1.53 g, 11.8 mmol, 2 equiv) and ethoxymethyl chloride (1.12 g, 11.8 mmol, 2 equiv) were added to a solution of 1,2,3,4,4a,5,6,7-Octahydro-1-naphthalenol (**2**) (0.90 g, 5.9 mmol) in CH_2Cl_2 (12 mL) at 0 °C. The solution was stirred for 12 h at 25 °C and then poured into a saturated aqueous NaCl solution (150 mL). After extraction with Et_2O (3 × 150 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude product purified by column chromatography (pentane/Et_2O 25:1). The desired protected alcohol **3** was obtained as one diastereoisomer (0.93 g, 4.4 mmol, 75 %). IR (film): $\tilde{\nu}=2927$ (s), 1447 (w), 1390 (w), 1114 (m), 1099 (s), 1046 (vs), 947 (w), 847 (w), 629 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=5.70$ (m, 1H), 4.78 (d, $J=6.9$ Hz, 1H), 4.71 (d, $J=6.9$ Hz, 1H), 3.88 (m, 1H), 3.76–3.53 (br m, 2H), 2.11–1.54 (br m, 8H), 1.51–1.00 (br m, 5H), 1.21 (t, $J=7.1$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta=140.2$, 116.5, 93.9, 63.2, 43.1, 36.6, 34.8, 34.7, 30.4, 25.2, 24.0, 21.0, 15.2; MS: *m*/*z* (%): 210 (12) [M^+], 181 (11), 164 (23), 151 (17), 136 (100), 123 (78), 110 (61), 91 (62), 59 (56); elemental analysis calcd for $C_{13}H_{22}O_2$ (210.3): C 74.24, H 10.54; found: C 74.60, H 10.84.

Preparation of the products

(1*R)-Allyl-(8*R**)-(ethoxymethoxy)decahydronaphthalene (5)**: A flame-dried 25 mL flask equipped with a magnetic stirring bar, an argon inlet and a septum was charged with 1-(ethoxymethoxy)-1,2,3,4,4a,5,6,7-octahydronaphtalene (**3**) (0.210 g, 1 mmol) in CH_2Cl_2 (2 mL). Et_2BH (0.4 mL, 7.3 M in Me_2S, 3 equiv) was slowly added and the resulting mixture was stirred for 48 h at 25 °C. After pumping off the excess volatiles (0.1 mm Hg, 25 °C, 2 h), $i Pr_2Zn$ (0.6 mL, 5 M in Et_2O, 3 equiv) was added and the mixture was stirred for 5 h at 25 °C. The boron–zinc conversion was approximately 80 % as monitored by GC analysis of oxidized aliquots (aqueous 3 M NaOH/aqueous 30 % H_2O_2). The excess volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h), the grey-black residue was diluted with THF (2.5 mL) and cooled to −78 °C. A freshly prepared solution of CuCN·2LiCl (0.7 mL, 1 M in THF, 0.7 equiv) was added over 1 h. The mixture was stirred 30 min at −78 °C. Allyl bromide (0.363 g, 3 mmol, 3 equiv) in anhydrous THF (1 mL) was slowly added (40 min). After stirring for 1 h at −78 °C, the mixture was allowed to warm up to room temperature overnight. It was then poured into a saturated aqueous NH_4Cl solution (150 mL) containing $NH_{3(aq)}$ (2 mL, 30 % in H_2O). After extraction with Et_2O (3 × 100 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude product purified by column chromatography (silica gel, pentane/Et_2O 98:2) affording **5** as a colorless oil (0.164 g, 0.65 mmol, 65 %) and as a diastereomeric mixture: *dr* (1,2) 97:3 and *dr* (2,3) >98:2 (GC-MS, method A, 10.41 min and 10.42 min). IR (film): $\tilde{\nu}=2946$ (vs), 1443 (w), 1431 (m), 1117 (m), 1080 (vs), 856 cm^{-1}(w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta=5.85$ (m, 1H), 4.99–4.92 (m, 2H), 4.78 (d, $J=6.7$ Hz, 1H),

4.71 (d, $J = 6.8$ Hz, 1H), 3.65 (m, 1H), 3.55 (m, 1H), 3.31 (m, 1H), 2.62 (m, 1H), 2.17 (m, 2H), 1.74–1.45 (br m, 5H), 1.35–1.16 (br m, 4H), 1.20 (t, $J =$ 7.1 Hz, 3H), 1.10–0.95 (br m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 138.7$, 114.9, 94.4, 82.9, 63.7, 50.8, 42.1, 41.8, 40.0, 34.3, 34.0, 33.8, 33.2, 25.8, 23.9, 15.1; MS: *m*/*z* (%): 252 (2) [M^+], 234 (3), 206 (6), 188 (14), 175 (32), 147 (29), 135 (100), 93 (65), 80 (90), 59 (71); elemental analysis calcd (%) for $C_{16}H_{28}O_2$ (252.4): C 76.14, H 11.18; found: C 76.40, H 11.32.

General procedure I—Reactions proceeding by hydroboration with 9-BBN-H:[14, 15, 17] A flame-dried 25 mL flask equipped with a magnetic stirring bar, an argon inlet and a septum was cooled to 0 °C and charged with the olefin (0.5 mmol, 1.0 equiv). 9-BBN-H (2 mL, 1.0 mmol, 2 equiv, 0.5 M solution in THF) was added dropwise over a period of 1 h and stirred throughout at the temperature stated. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), *i*Pr_2Zn (0.4 mL, 2.0 mmol, 4 equiv, 5.0 M in Et_2O) was added and the mixture was stirred 4 h at 25 °C. The volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h) and the grey-black residue was diluted with THF (2 mL) and cooled to −78 °C. A freshly prepared solution of CuCN·2LiCl (0.75 mL, 0.75 mmol, 1.5 equiv, 1M in THF) was slowly added over 40 min by a syringe pump and the mixture stirred for 30 min at −78 °C. A solution of the electrophile (1.5 mmol, 3 equiv) in THF (1 mL) was then slowly added over 40 min by a syringe pump. The mixture was stirred for the time indicated and at the temperature stated. The solution was then poured into a saturated aqueous NH_4Cl solution (150 mL) containing $NH_{3(aq)}$ (2 mL, 30% in H_2O). After extraction with Et_2O (3 × 100 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude products purified by column chromatography (silica gel) affording the desired products as colorless oils.

14-(2,2-Dimethyl-1-oxopropoxy)-2-methylene-ethyltetradecanoate (7a): According to GP I, 10-undecenyl pivalate[19] (0.254 g, 1.00 mmol) was reacted with 9-BBN-H (4 mL, 2.0 mmol, 2 equiv) at 25 °C for 12 h. After the addition of *i*Pr_2Zn (1.0 mL, 5 mmol, 5 equiv), transmetallation with CuCN·2LiCl (1.5 mL, 1.5 mmol, 1.5 equiv) and addition of ethyl 2-(bromomethyl)acrylate (0.072 g, 4.0 mmol, 4.0 equiv), the reaction mixture was stirred at −40 °C for 2 d. After purification by column chromatography (pentane), **7a** was obtained as a colorless oil (0.243 g, 0.66 mmol, 66%). IR (film): $\tilde{\nu} = 2928$ (s), 1728 (s), 1632 (w), 1480 (m), 1463 (m), 1285 (m), 1158 (s), 1032 (w), 941 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 6.04$ (d, $J =$ 0.9 Hz, 1H), 5.43 (d, $J = 0.9$ Hz, 1H), 4.13 (q, $J = 7.1$ Hz, 2H), 3.97 (t, $J =$ 6.6 Hz, 2H), 2.21 (m, 2H), 1.53 (m, 2H), 1.37 (m, 2H), 1.25–1.20 (m, 19H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 178.5$, 167.3, 141.1, 124.0, 64.4, 60.4, 38.7, 31.8, 29.5, 29.48, 29.4, 29.3, 29.2, 28.6, 28.4, 27.1, 25.9, 14.1; MS: *m*/*z* (%): 368 (1) [M^+], 322 (17), 266 (6), 238 (15), 220 (7), 192 (8), 152 (8), 135 (7), 123 (12), 109 (21), 95 (30), 85 (30), 69 (22), 57 (100); HRMS (CI): calcd for $C_{22}H_{41}O_4$: 369.3005; found: 369.2995 [M^++H].

General procedure II—Reactions proceeding by hydroboration with thexylborane: A flame-dried 25 mL flask equipped with a magnetic stirring bar, an argon inlet and a septum was cooled to 0 °C and charged with a solution of freshly prepared thexylborane[10] (4 mL, 2.0 mmol, 2 equiv, 0.5 M in THF). The olefin (1.0 mmol, 1.0 equiv, 1M in THF) was added dropwise over a period of 1 h. The solution was allowed to warm up to room temperature overnight. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), Et_2BH (0.69 mL, 5.0 mmol, 5 equiv, 7.3 M in Me_2S) was added and the resulting mixture was stirred for 16 h at 50 °C. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), *i*Pr_2Zn (1.0 mL, 5.0 mmol, 5 equiv, 5.0 M in Et_2O) was added and the mixture was stirred for 5 h at 25 °C. The volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h) and the grey-black residue was diluted with THF (3 mL) and cooled to −78 °C. A freshly prepared solution of CuCN·2LiCl (1.5 mL, 1.5 mmol, 1.5 equiv, 1M in THF) was added slowly over 40 min with a syringe pump and the mixture stirred for 30 min at −78 °C. A solution of the corresponding electrophile (5 mmol, 5 equiv) in THF (1 mL) was then added slowly (40 min) with a syringe pump. The solution was allowed to stir for the time indicated and the temperature stated. The reaction mixture was poured into a saturated aqueous NH_4Cl solution (150 mL) containing $NH_{3(aq)}$ (2 mL, 30% in H_2O). After extraction with Et_2O (3 × 100 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude product purified by column chromatography (silica gel) affording the desired products as colorless oils.

2,2-Dimethyl-12-hexadecynylpropanoate (7b): According to GP II, thexylborane was added to 10-undecenyl pivalate[19] (0.254 g, 1.00 mmol) at −30 °C. The reaction mixture was allowed to warm up to 25 °C overnight. For this primary diorganozinc compound, no equilibration with Et_2BH was carried out. After addition of *i*Pr_2Zn and transmetallation with CuCN·2LiCl, 1-bromopentyne (0.588 g, 4 mmol, 4 equiv) was added. The reaction mixture was stirred for 36 h at −40 °C. The desired product **7b** was obtained after purification by column chromatography (pentane) (0.168 g, 0.52 mmol, 52%) as a colorless oil. IR (film): $\tilde{\nu} = 2856$ (s), 1731 (s), 1480 (m), 1463 (m), 1284 (m), 1156 (s), 1035 (w), 771 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.97$ (t, $J = 6.6$ Hz, 2H), 2.09–2.02 (m, 4H), 1.57–1.21 (m, 20H), 1.13 (s, 9H), 0.90 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 178.6$, 80.3, 80.0, 64.4, 38.7, 29.5, 29.2, 29.15, 29.1, 28.8, 28.6, 27.2, 25.9, 22.5, 20.7, 18.7, 13.4; MS: *m*/*z* (%): 322 (<1) [M^+], 265 (1) [$M^+ - C_4H_9$], 220 (4), 191 (3), 177 (5), 163 (6), 149 (10), 135 (15), 121 (22), 109 (21), 96 (74), 82 (100), 67 (66), 57 (95); HRMS (EI): calcd for $C_{21}H_{38}O_2$: 322.2872; found: 322.2888 [M^+].

General procedure III—Reactions proceeding by Rh-catalyzed hydroborations with catecholborane

GP IIIA—Hydroboration catalysed by [RhCl(PPh$_3$)$_3$]:[16] A flame-dried 25 mL flask equipped with a magnetic stirring bar, an argon inlet and a septum was charged with catalytic amount of [RhCl(PPh$_3$)$_3$]. THF (2 mL) was added and the mixture stirred for 10 min at room temperature. The olefin (0.5 mmol, 1.0 equiv) was added and the mixture cooled to 0 °C. Catecholborane[10] (0.180 g, 1.5 mmol, 3 equiv) was added and the solution was allowed to warm up to room temperature and stirred for 6 h. After pumping off the volatiles (0.1 mm Hg, 25 °C, 3 h), *i*Pr_2Zn (1.6 mL, 8.0 mmol, 16 equiv, 5.0 M in Et_2O) was added in two portions and the mixture was stirred for 36 h at 25 °C. The volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h, coevaporation with 2 × 1 mL THF), the grey-black residue was diluted with THF (2 mL) and cooled to −78 °C. A freshly prepared solution of CuCN·2LiCl (0.75 mL, 0.75 mmol, 1.5 equiv, 1M in THF) was slowly added over 40 min with a syringe pump and the mixture stirred for 30 min at −78 °C. The electrophile (2.5 mmol, 5 equiv) in THF (1 mL) was added slowly (40 min) with a syringe pump. The mixture was stirred for the time indicated and at the temperature stated. The reaction mixture was then poured into a saturated aqueous NH_4Cl solution (150 mL) containing $NH_{3(aq)}$ (2 mL, 30% in H_2O). After extraction with Et_2O (3 × 100 mL) the combined organic phases were dried over $MgSO_4$. The solvent was removed and the crude products purified by column chromatography (silica gel) affording the desired compounds as colorless oils.

2,2-Dimethyl-13-tetradecenylpropanoate (7c): According to GP IIIA, catecholborane (0.132 g 1.1 mmol, 1.1 equiv) was added to 10-undecenyl pivalate[19] (0.254 g, 1.0 mmol) and [RhCl(PPh$_3$)$_3$] (19 mg, 0.02 mmol, 0.02 equiv) in THF (2.6 mL) at 0 °C. The solution was allowed to warm up to 25 °C over 5 h. After pumping off the volatiles (0.1 mm Hg, 25 °C, 3 h), *i*Pr_2Zn (2 mL, 10.0 mmol, 10 equiv, 5.0 M in Et_2O) was added in two portions and the mixture was stirred for 36 h at 25 °C. The grey-black residue was diluted with THF (2.5 mL). After transmetallation with CuCN·2LiCl (1.5 mL, 1.5 mmol, 1.5 equiv), allyl bromide (0.605 g, 5 mmol, 5 equiv, 4 M in THF) was added. The reaction mixture was allowed to warm up to 25 °C overnight. The desired product **7c** was obtained after purification by column chromatography (pentane) (0.172 g, 0.58 mmol, 58%) as a colorless oil. IR (film): $\tilde{\nu} = 2855$ (s), 1732 (s), 1480 (m), 1461 (m), 1285 (m), 1157 (s), 909 (m), 734 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta =$ 5.73 (m, 1H), 4.95–4.84 (m, 2H), 3.97 (t, $J = 6.6$ Hz, 2H), 1.97 (m, 2H), 1.54 (m, 2H), 1.36–1.20 (m, 18H), 1.12 (s, 9H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 178.5$, 139.1, 114.0, 64.4, 38.7, 33.8, 29.6, 29.5, 29.45, 29.4, 29.2, 29.1, 28.9, 28.6, 27.2, 25.9; MS: *m*/*z* (%): 239 (<1) [$M^+ - C_4H_9$], 194 (6), 166 (3), 152 (3), 138 (5), 124 (9), 110 (15), 96 (38), 82 (45), 68 (30), 57 (100); HRMS (CI): calcd for $C_{19}H_{37}O_2$: 297.2794; found: 297.28121 [M^++H].

***trans*-1-Allyl-2-phenylcyclopentane[2a] (7d)**: According to GP II, thexylborane was added to 1-phenylcyclopentene[20] (0.144 g, 1.00 mmol) at 0 °C. The reaction mixture was allowed to warm up to 25 °C and stirred for 16 h. After addition of allyl bromide (0.605 g, 5 mmol, 5 equiv, 4 M in THF) the reaction mixture was allowed to warm up to 25 °C overnight. The desired product **7d** was obtained as a diastereomeric mixture of 94:6 (GC-MS, method A, 8.68 and 8.88 min) (0.108 g, 0.58 mmol, 58%; column chromatography in pentane). ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.39–7.20$ (m, 5H), 5.88–5.74 (m, 1H), 5.07–4.96 (m, 2H), 2.67–2.61 (m, 1H), 2.31–2.20 (m, 1H), 2.18–1.76 (m, 5H), 1.47–1.41 (m, 2H), 0.97–0.87 (m, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 145.5$, 137.8, 128.3 (2C), 127.6 (2C), 125.9, 115.1,

52.3, 47.7, 28.3, 35.5, 31.8, 24.1; MS: *m/z* (%): 186 (3) [M$^+$], 157 (5), 144 (100), 129 (21), 117 (26), 104 (48), 91 (72), 77 (9), 67 (20), 41 (13).

GP IIIB—Hydroborations catalyzed by [Rh(cod)$_2$]BF$_4$:[12] A flame-dried 25 mL flask equipped with a magnetic stirring bar, an argon inlet and a septum was charged with [Rh(cod)$_2$]BF$_4$ (12 mg, 0.03 mmol, 0.03 equiv) and 1,4-bis(diphenylphosphino)-butane (13 mg, 0.03 mmol, 0.03 equiv). THF (1 mL) was added and the mixture stirred for 30 min at room temperature. Indene (0.116 g, 1.0 mmol, 1.0 equiv) and catecholborane (0.144 g, 1.2 mmol, 1.2 equiv) were added and the solution was stirred at room temperature overnight. After pumping off the volatiles (0.1 mm Hg, 50 °C, 3 h), Et$_2$BH (0.69 mL, 5.0 mmol, 5 equiv, 7.3 M in Me$_2$S) was added and the resulting mixture was stirred for 16 h at 50 °C. After pumping off the volatiles (0.1 mm Hg, 25 °C, 2 h), *i*Pr$_2$Zn (1.0 mL, 5.0 mmol, 5 equiv, 5.0 M in Et$_2$O) was added and the mixture was stirred for 5 h at 25 °C. The volatiles were pumped off (0.1 mm Hg, 25 °C, 0.5 h), the grey-black residue was diluted with THF (2 mL) and cooled to −78 °C. A freshly prepared solution of CuCN·2LiCl (1.5 mL, 1.5 mmol, 1.5 equiv, 1 M in THF) was slowly added over 40 min with a syringe pump and the mixture stirred for 30 min at −78 °C. The electrophile (5 mmol, 5 equiv) in THF (1 mL) was added slowly (40 min) with a syringe pump. The mixture was stirred for the time and at the temperature stated. The reaction mixture was then poured into a saturated aqueous NH$_4$Cl solution (150 mL) containing NH$_{3(aq)}$ (2 mL, 30% in H$_2$O). After extraction with Et$_2$O (3 × 100 mL) the combined organic phases were dried over MgSO$_4$. The solvent was removed and the crude products purified by column chromatography (silica gel) affording the desired products as colorless oils.

1-Allylindane[21] **(7e)**: According to GP IIIB, allyl bromide (0.605 g, 5 mmol, 5 equiv) was added to the reaction mixture, which was then allowed to warm up to 25 °C overnight. After purification by column chromatography (pentane) the desired product **7e** was obtained as a colorless oil (0.085 g, 0.54 mmol, 54%). ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.30–7.15 (m, 4H), 6.00–5.78 (m, 1H), 5.17–5.04 (m, 2H), 3.33–3.20 (m, 1H), 3.01–2.80 (m, 2H), 2.71–2.54 (m, 1H), 2.39–2.21 (m, 2H), 1.86–1.71 (m, 1H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 146.8, 144.1, 137.1, 126.3, 126.0, 124.4, 123.6, 115.9, 44.3, 39.3, 31.5, 31.3; MS: *m/z* (%): 158 (6) [*M*$^+$], 128 (4), 117 (100), 91 (7), 65 (2), 51 (2).

3-(2,3-Dihydro-1*H*-inden-1-yl)-2-methyl-2-cyclopenten-1-one (7f): According to GP IIIB, 3-iodo-2-methyl-cyclopent-2-en-1-one (1.110 g, 5 mmol, 5 equiv) was added to the reaction mixture which was then stirred for 16 h at −20 °C. After purification by column chromatography (pentane/Et$_2$O 9:1) the desired product **7f** was obtained as a colorless oil (0.123 g, 0.58 mmol, 58%). IR (film): $\tilde{\nu}$ = 2921 (m), 1698 (vs), 1641 (s), 1477 (w), 1342 (w), 1088 (w), 759 (m), 619 cm^{-1} (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.35–7.12 (br m, 3H), 6.95 (d, *J* = 7.7 Hz, 1H), 4.51 (t, *J* = 7.4 Hz, 1H), 3.0 (m, 2H), 2.49–2.24 (br m, 5H), 2.14–2.01 (br m, 1H), 1.84 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 210.2, 174.3, 144.2, 143.4, 136.8, 127.2, 126.6, 124.7, 124.1, 46.4, 34.0, 32.2, 30.7, 25.8, 8.3; MS: *m/z* (%): 212 (95) [*M*$^+$], 197 (10), 183 (12), 169 (100), 155 (85), 141 (42), 128 (23), 115 (49); HRMS (EI): calcd for C$_{15}$H$_{16}$O [*M*$^+$]: 212.1201; found: 212.1199.

1-(2,3-Dihydro-1*H*-inden-1-yl)-1-propanone (7g): According to GP IIIB, propionyl chloride (0.463 g, 5 mmol, 5 equiv) was added to the reaction mixture which was then allowed to warm up to 25 °C overnight. After purification by column chromatography (pentane/Et$_2$O 15:1) the desired product **7g** was obtained as a colorless oil (0.089 g, 0.51 mmol, 51%). IR (film): $\tilde{\nu}$ = 2939 (s), 1737 (vs), 1458 (s), 1348 (m), 1188 (s), 1114 (m), 755 (s), 651 cm^{-1} (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.36–7.15 (m, 4H), 4.12 (t, *J* = 7.5 Hz, 1H), 3.11 (m, 1H), 2.95 (m, 1H), 2.68–2.47 (br m, 2H), 2.40–2.26 (br m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 211.4, 144.6, 141.2, 127.4, 126.4, 124.9, 124.7, 58.0, 33.6, 32.0, 28.8, 7.8; MS: *m/z* (%): 174 (8) [*M*$^+$], 117 (100), 91 (7), 57 (6); HRMS (EI): calcd for C$_{12}$H$_{14}$O: 174.1045; found: 174.1039 [*M*$^+$].

Dimethyl(2-methyl-1-phenyl-5-hexenyl)phenylsilane (10a): According to GP I, dimethyl(2-methyl-1-phenyl-2-propenyl)phenylsilane[22] (**8**; 0.133 g, 0.50 mmol) was treated with 9-BBN-H at 25 °C for 36 h. After addition of allyl bromide (0.181 g, 1.5 mmol, 3.0 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product **10a** was obtained as a diastereomeric mixture of 99:1 (0.114 g, 0.37 mmol, 74%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2958 (s), 1640 (w), 1596 (w), 1427 (m), 1248 (s), 1111 (m), 908 (m), 830 (s), 700 (vs), 639 cm^{-1} (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.51–6.93 (br m, 10H), 5.71–5.53 (m, 1H), 4.90–4.75 (m, 2H), 2.15 (d, *J* = 10.3 Hz, 1H), 2.10–1.94 (m, 2H), 1.88–1.75 (m, 1H), 1.46–1.34 (m, 1H), 1.08–0.94 (m, 1H), 0.92 (d, *J* = 6.3 Hz, 3H), 0.31 (s, 3H), 0.06 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.6, 139.5, 139.2, 133.6 (2C), 128.8, 128.6, 128.0, 127.6 (2C), 124.6, 114.0, 44.1, 35.4, 34.4, 30.8, 20.2, −1.3, −3.9; MS: *m/z* (%): 308 (1) [*M*$^+$], 293 (7), 253 (4), 230 (5), 172 (5), 135 (100), 91 (6), 78 (4); HRMS (EI): *m/z*: calcd for C$_{21}$H$_{28}$Si: 308.1960; found: 308.1949 [*M*$^+$].

Dimethyl(2-methyl-1-phenyl-4-octynyl)phenylsilane (10b): According to GP I, dimethyl(2-methyl-1-phenyl-2-propenyl)phenylsilane[22] (**8**; 0.133 g, 0.50 mmol) was treated with 9-BBN-H at 25 °C for 36 h. After addition of 1-bromo-1-pentyne (0.221 g, 1.5 mmol, 3.0 equiv), the reaction mixture was stirred for 16 h at −40 °C. The desired product **10b** was obtained as a diastereomeric mixture of 99:1 (0.120 g, 0.36 mmol, 72%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2961 (s), 1596 (m), 1487 (s), 1427 (s), 1249 (s), 1111 (s), 842 (s), 701 (vs), 644 (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.50–6.98 (br m, 10H), 2.32–2.01 (br m, 5H), 1.80 (m, 1H), 1.50 (m, 2H), 1.08 (d, *J* = 6.2 Hz, 3H), 0.98 (t, *J* = 7.3 Hz, 3H), 0.30 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 143.6, 139.2, 133.9, 128.7, 128.5, 128.1 (2C), 127.6, 124.7 (2C), 81.6, 78.5, 42.6, 35.2, 26.2, 22.6, 20.8, 20.5, 13.5, −1.2, −3.9; MS: *m/z* (%): 334 (1) [*M*$^+$], 319 (2), 291 (3), 256 (3), 198 (10), 169 (5), 135 (100), 91 (4), 53 (2); HRMS (EI): calcd for C$_{23}$H$_{30}$Si: 334.2117, found: 334.2112 [*M*$^+$]; elemental analysis calcd (%) for C$_{23}$H$_{30}$Si (334.57): C 82.57, H 9.04; found: C 82.36, H 9.02.

6-[Dimethyl(phenyl)silyl]-5-methyl-6-phenyl-3-hexanone (10c): According to GP I, dimethyl(2-methyl-1-phenyl-2-propenyl)phenylsilane[22] (**8**; 0.133 g, 0.50 mmol) was treated with 9-BBN-H at 25 °C for 36 h. After addition of propionyl chloride (0.139 g, 1.5 mmol, 3.0 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product **10c** was obtained as a diastereomeric mixture of 99:1 (0.125 g, 0.39 mmol, 77%; column chromatography in pentane/Et$_2$O 9:1). IR (film): $\tilde{\nu}$ = 2971 (s), 1712 (vs), 1596 (m), 1427 (m), 1249 (s), 1111 (s), 998 (w), 831 (s), 702 (vs), 649 cm^{-1} (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 7.57–7.01 (br m, 10H), 2.68 (m, 1H), 2.41–2.04 (br m, 5H), 0.96 (m, 6H), 0.39 (s, 3H), 0.14 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 211.7, 143.2, 138.9, 133.8 (2C), 128.7, 128.6 (2C), 128.2, 127.6, 124.9, 49.6, 43.8, 36.4, 31.7, 21.3, 7.5, −1.4, −4.2; MS: *m/z* (%): 309 (1) [*M*$^+$ − CH$_3$], 206 (12), 191 (11), 177 (8), 135 (100), 118 (12), 75 (21), 58 (5); HRMS (EI): calcd for C$_{20}$H$_{25}$OSi: 309.1675; found: 309.1696 [*M*$^+$ − CH$_3$]; elemental analysis calcd for C$_{21}$H$_{28}$OSi (324.53): C 77.72, H 8.70; found: C 77.26, H 8.28.

***tert*-Butyl[(1-butyl-2-methyl-5-hexenyl)oxy]dimethylsilane (*anti*-13a)**: According to GP I, *tert*-butyl[(1-butyl-2-methyl-2-propenyl)oxy]dimethylsilane[15, 23] (**11**; 0.121 g, 0.50 mmol) was treated with 9-BBN-H (3.0 mL, 1.5 mmol, 3 equiv) at 25 °C for 16 h. After addition of allyl bromide (0.181 g, 1.5 mmol, 3.0 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product *anti*-**13a** was obtained as a diastereomeric mixture of 91:9 (quant. ^{13}C NMR, e.g. δ = 75.9 and 75.6) (0.114 g, 0.4 mmol, 80%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2957 (vs), 1641 (w), 1462 (m), 1378 (m), 1254 (s), 1117 (w), 1082 (s), 909 (m), 835 (s), 664 cm^{-1} (s); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 5.82 (m, 1H), 4.98 (m, 2H), 3.51 (m, 1H), 2.14 (m, 1H), 1.99 (m, 1H), 1.65–1.12 (br m, 10H), 0.93–0.82 (m, 14H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 139.2, 114.2, 75.9, 37.8, 31.9, 31.8, 31.7, 28.1, 25.9 (3C), 22.9, 18.2, 14.5, 14.1, −4.4 (2C); MS: *m/z* (%): 283 (1) [*M*$^+$ − H], 269 (2), 227 (51), 201 (53), 185 (3), 145 (6), 115 (7), 95 (8), 75 (100); HRMS (EI): calcd for C$_{17}$H$_{35}$OSi: 283.2457; found: 283.2472 [*M*$^+$ − H].

6-{[*tert*-Butyl(dimethyl)silyl]oxy}-5-methyl-3-decanone (*anti*-13b): According to GP I, *tert*-butyl[(1-butyl-2-methyl-2-propenyl)oxy]dimethylsilane[15, 23] (**11**; 0.121 g, 0.50 mmol) was treated with 9-BBN-H (3.0 mL, 1.5 mmol, 3 equiv) at 25 °C for 16 h. After addition of propionyl chloride (0.139 g, 1.5 mmol, 3.0 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product *anti*-**13b** was obtained as a diastereomeric mixture of 91:9 (quant. ^{13}C NMR, e.g. δ = 75.8 and 75.7) (0.072 g, 0.24 mmol, 48%; column chromatography in pentane/Et$_2$O 39:1). IR (film): $\tilde{\nu}$ = 2932 (vs), 1716 (s), 1462 (m), 1379 (m), 1255 (m), 1082 (m), 1050 (s), 937 (w), 836 (s), 774 (s), 667 cm^{-1} (w); ^{1}H NMR (CDCl$_3$, 300 MHz): δ = 3.48 (m, 1H), 2.54–2.35 (br m, 3H), 2.18 (m, 2H), 1.42–1.14 (br m, 6H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.94–0.84 (m, 15H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ = 211.7, 75.7, 44.8, 36.5, 33.7, 33.3, 27.5, 25.9 (3C), 22.9, 18.1, 16.4, 14.1, 7.9, −4.2, −4.5; MS: *m/z* (%): 299 (1) [*M*$^+$ − H], 285 (2), 243 (100), 225 (4), 201 (43), 115 (9), 95 (7), 75 (63), 57

(12); HRMS (EI): calcd for $C_{17}H_{35}O_2Si$: 299.2406; found: 299.2427 [$M^+ - H$].

***tert*-Butyl[(1-butyl-2-methyl-4-octynyl)oxy]dimethylsilane (*anti*-13c)**: According to GP I, *tert*-butyl[(1-butyl-2-methyl-2-propenyl)oxy]dimethylsilane[15, 23] (**11**; 0.121 g, 0.50 mmol) was treated with 9-BBN-H (3.0 mL, 1.5 mmol, 3 equiv) at 25 °C for 16 h. After addition of 1-bromo-1-pentyne (0.221 g, 1.5 mmol, 3.0 equiv), the reaction mixture was stirred for 16 h at −40 °C. The desired product *anti*-**13c** was obtained as a diastereomeric mixture of 90:10 (GC-MS, method A, 9.41 and 9.44 min) (0.121 g, 0.39 mmol, 78%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2932 (vs), 1463 (m), 1360 (w), 1254 (s), 1077 (s), 937 (m), 836 (s), 773 (s), 665 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.62 (m, 1H), 2.24–2.01 (m, 4H), 1.77 (m, 1H), 1.50 (m, 2H), 1.42–1.23 (m, 5H), 1.01–0.83 (br m, 19H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 80.9, 79.2, 74.7, 37.8, 32.5, 27.1, 25.9 (3C), 23.0, 22.6, 22.0, 20.8, 18.1, 15.3, 14.1, 13.5, −4.3, −4.6; MS: *m*/*z* (%): 309 (1) [$M^+ - H$], 295 (2), 253 (100), 201 (37), 177 (23), 145 (6), 115 (7), 75 (95); HRMS (EI): calcd for $C_{19}H_{37}OSi$: 309.2614; found: 309.2601 [$M^+ - H$]; elemental analysis calcd for $C_{19}H_{38}OSi$ (310.59): C 73.47, H 12.33; found: C 73.85, H 12.45.

***tert*-Butyl[(1-butyl-2-methyl-5-hexenyl)oxy]dimethylsilane (*syn*-13a)**: According to GP III-A, *tert*-butyl[(1-butyl-2-methyl-2-propenyl)oxy]dimethylsilane[15, 23] (**11**; 0.121 g, 0.50 mmol) was reacted with [RhCl(PPh$_3$)$_3$] (5 mg, 0.01 equiv, 0.005 mmol). After addition of allyl bromide (0.303 g, 2.5 mmol, 5.0 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product *syn*-**13a** was obtained as a diastereomeric mixture of >96:4 (quant. ^{13}C NMR, e.g. δ = 75.9 and 75.6) (0.091 g, 0.32 mmol, 63%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2957 (vs), 1641 (w), 1462 (m), 1380 (m), 1253 (s), 1117 (w), 1080 (s), 909 (m), 835 (s), 666 cm^{-1} (s); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.80 (m, 1H), 4.99 (m, 2H), 3.52 (m, 1H), 2.19–1.94 (br m, 2H), 1.61–1.09 (br m, 10H), 0.92–0.76 (m, 14H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.3, 114.1, 75.6, 37.1, 33.2, 31.9, 31.8, 28.2, 26.0 (3C), 22.9, 18.2, 14.1, 14.1, −4.2, −4.4; MS: *m*/*z* (%): 283 (1) [$M^+ - H$], 269 (3), 227 (81), 201 (64), 185 (5), 145 (9), 115 (8), 95 (6), 75 (100); HRMS (EI): calcd for $C_{17}H_{35}OSi$: 283.2457; found: 283.2471 [$M^+ - H$].

***tert*-Butyl[(1-butyl-2-methyl-4-octynyl)oxy]dimethylsilane (*syn*-13c)**: According to GP III-A, *tert*-butyl[(1-butyl-2-methyl-2-propenyl)oxy]dimethylsilane[15, 23] (**11**; 0.121 g, 0.50 mmol) was treated with [RhCl(PPh$_3$)$_3$] (5 mg, 0.01 equiv, 0.005 mmol). After addition of 1-bromo-1-pentyne (0.368 g, 2.5 mmol, 5.0 equiv), the reaction mixture was stirred for 16 h at −40 °C. The desired product *syn*-**13c** was obtained as a diastereomeric mixture of >96:4 (GC-MS, method A, 9.41 and 9.44 min) (0.073 g, 0.24 mmol, 47%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2931 (vs), 1463 (m), 1380 (w), 1252 (s), 1090 (s), 938 (m), 836 (s), 774 (s), 667 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.71 (m, 1H), 2.31 (t, *J* = 7.1 Hz, 1H), 2.25–1.96 (m, 3H), 1.71 (m, 1H), 1.61–1.18 (m, 7H), 1.04–0.84 (br m, 19H), 0.05 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 80.7, 79.7, 73.9, 37.5, 33.9, 27.8, 25.9 (3C), 23.0, 22.7, 22.0, 20.8, 18.2, 14.1, 13.5, 13.4, −4.3, −4.6; MS: *m*/*z* (%): 309 (1) [$M^+ - H$], 295 (2), 253 (100), 201 (28), 177 (24), 145 (5), 115 (7), 75 (98); HRMS (EI): calcd for $C_{19}H_{37}OSi$: 309.2614; found: 309.2614 [$M^+ - H$].

{[2-(3-Butenyl)cyclohexyl]oxy}(*tert*-butyl)dimethylsilane (16a): According to GP III-A, *tert*-butyl(dimethyl)[(2-methylenecyclohexyl)oxy]silane[24] (**14**; 0.113 g, 0.50 mmol) was treated with [RhCl(PPh$_3$)$_3$] (14 mg, 0.03 equiv, 0.015 mmol). After addition of allyl bromide (0.303 g, 2.5 mmol, 5.0 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product **16a** was obtained as a diastereomeric mixture of >96:4 (GC-MS, method A, 7.90 and 7.94 min) (0.070 g, 0.26 mmol, 52%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2856 (vs), 1641 (w), 1472 (w), 1253 (m), 1022 (s), 909 (m), 835 (s), 773 (m), 671 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 5.90–5.74 (br m, 1H), 5.03–4.81 (br m, 2H), 3.83 (m, 1H), 2.02 (m, 2H), 1.74–1.14 (br m, 11H), 0.90 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 139.4, 114.0, 69.8, 41.7, 33.8, 31.6, 31.3, 26.7, 25.9 (3C), 25.6, 20.6, 18.2, −4.3, −4.9; MS: *m*/*z* (%): 267 (1) [$M^+ - H$], 253 (2), 211 (78), 193 (8), 135 (7), 115 (9), 75 (100), 59 (3); HRMS (EI): calcd for $C_{16}H_{31}OSi$: 267.2144; found: 267.2147 [$M^+ - H$].

Ethyl 2-[2-(2-{[*tert*-butyl(dimethyl)silyl]oxy}cyclohexyl)ethyl]acrylate (16b): According to GP III-A, *tert*-butyl(dimethyl)[(2-methylenecyclohexyl)oxy]silane[24] (**14**; 0.113 g, 0.50 mmol) was treated with [RhCl(PPh$_3$)$_3$] (14 mg, 0.03 equiv, 0.015 mmol). After addition of ethyl 2-(bromomethyl)acrylate[25] (0.483 g, 2.5 mmol, 5.0 equiv), the reaction mixture was stirred for 16 h at −40 °C. The desired product **16b** was obtained as a diastereomeric mixture of >96:4 (GC-MS, method B, 7.79 min) (0.078 g, 0.23 mmol, 46%, column chromatography in pentane/Et$_2$O 49:1). IR (film): $\tilde{\nu}$ = 2857 (vs), 1720 (vs), 1632 (m), 1463 (m), 1369 (w), 1251 (m), 1184 (m), 1023 (s), 939 (w), 901 (w), 836 (s), 774 (m), 671 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 6.12 (m, 1H), 5.48 (m, 1H), 4.20 (q, *J* = 7.3 Hz, 2H), 3.84 (m, 1H), 2.28 (m, 2H), 1.70–1.16 (m, 11H), 1.29 (t, *J* = 7.4 Hz, 3H), 0.89 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 167.5, 141.4, 123.8, 70.0, 60.5, 41.9, 33.7, 30.8, 29.2, 26.7, 25.9 (3C), 25.4, 20.6, 18.2, 14.2, −4.3, −4.9; MS: *m*/*z* (%): 325 (2) [$M^+ - CH_3$], 295 (3), 283 (100), 237 (15), 163 (6), 143 (11), 93 (6), 75 (43), 59 (7); HRMS (EI): calcd for $C_{19}H_{35}O_3Si$: 339.2355; found: 339.2339 [$M^+ - H$].

***tert*-Butyl{[2-(2-hexynyl)cyclohexyl]oxy}dimethylsilane (16c)**: According to GP III-A, *tert*-butyl(dimethyl)[(2-methylenecyclohexyl)oxy]silane[24] (**14**; 0.113 g, 0.50 mmol) was treated with [RhCl(PPh$_3$)$_3$] (14 mg, 0.03 equiv, 0.015 mmol). After addition of 1-bromo-1-pentyne (0.368 g, 2.5 mmol, 5.0 equiv), the reaction mixture was stirred for 16 h at −40 °C. The desired product **16c** was obtained as a diastereomeric mixture of >96:4 (GC-MS, method A, 9.51 and 9.52 min) (0.072 g, 0.25 mmol, 49%; column chromatography in pentane). IR (film): $\tilde{\nu}$ = 2957 (vs), 1471 (w), 1338 (w), 1250 (m), 1113 (m), 1022 (s), 835 (s), 773 (m), 671 (w), 561 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.98 (m, 1H), 2.12 (m, 3H), 2.00 (m, 1H), 1.75–1.17 (br m, 11H), 0.97 (t, *J* = 7.1 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 3H), 0.04 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 80.6, 79.6, 68.7, 42.7, 33.7, 26.5, 25.9 (3C), 25.6, 22.6, 22.3, 20.8, 20.2, 18.2, 13.5, −4.5, −5.0; MS: *m*/*z* (%): 293 (1) [$M^+ - H$], 279 (2), 237 (51), 161 (22), 119 (4), 95 (8), 75 (100), 59 (4); HRMS (EI): calcd for $C_{18}H_{33}OSi$: 293.2301; found: 293.2274 [$M^+ - H$].

***N*-Benzyl-*N*-(1-isobutyl-2-methyl-5-hexenyl)-4-methylbenzene sulfonamide (19a)**: Following GP I, 9-BBN-H (3.0 mL, 1.5 mmol, 3 equiv) was added to *N*-benzyl-*N*-(1-isobutyl-2-methyl-2-propenyl)-4-methylbenzenesulfonamide[17] (**17**; 0.186 g, 0.50 mmol) in THF (1.9 mL) at −78 °C. The reaction mixture was allowed to warm up to 25 °C overnight. After addition of *i*Pr$_2$Zn (0.5 mL, 2.5 mmol, 5 equiv), the reaction mixture was stirred for 5 h at 25 °C. After transmetallation with CuCN·2LiCl (0.75 mL, 0.75 mmol, 1.5 equiv) and addition of allyl bromide (0.212 g, 1.75 mmol, 3.5 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product **19a** was obtained as a diastereomeric mixture of >96:4 (quant. ^{13}C NMR, e.g. δ = 129.3 and 129.2) (0.159 g, 0.39 mmol, 77%; column chromatography in pentane/Et$_2$O 30:1). IR (film): $\tilde{\nu}$ = 2956 (s), 1599 (w), 1456 (m), 1338 (s), 1155 (s), 1092 (s), 1028 (m), 912 (m), 857 (m), 724 (m), 658 (s), 546 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.56 (d, *J* = 8.5 Hz, 2H), 7.26–7.13 (m, 7H), 5.60 (m, 1H), 4.78–4.89 (m, 2H), 4.37 (d, *J* = 15.9 Hz, 1H), 4.12 (d, *J* = 15.9 Hz, 1H), 3.60 (m, 1H), 2.32 (s, 3H), 1.95 (m, 1H), 1.79 (m, 1H), 1.47–1.31 (m, 3H), 1.27–0.91 (m, 3H), 0.72 (d, *J* = 6.0 Hz, 3H), 0.61 (d, *J* = 7.0 Hz, 3H), 0.51 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 142.7, 138.6, 138.5, 138.0, 129.2, 128.5, 128.2, 127.4, 127.3, 114.5, 61.7, 48.2, 39.3, 35.9, 32.9, 31.1, 24.2, 23.1, 21.6, 21.4, 17.1; MS: *m*/*z* (%): 412 (<1) [M^+], 356 (1), 330 (100), 155 (2), 132 (2), 91 (96), 65 (3), 55 (2); elemental analysis calcd for $C_{25}H_{35}NO_2S$ (413.6): C 72.60, H 8.53, N 3.39, S 7.75; found: C 72.58, H 8.61, N 3.55, S 7.75.

***N*-Benzyl-*N*-(1-isobutyl-2-methyl-4-oxohexyl)-4-methylbenzene sulfonamide (19b)**: Following GP I, 9-BBN-H (3.0 mL, 1.5 mmol, 3 equiv) was added to *N*-benzyl-*N*-(1-isobutyl-2-methyl-2-propenyl)-4-methylbenzenesulfonamide[17] (**17**; 0.186 g, 0.50 mmol) in THF (1.9 mL) at −78 °C. The reaction mixture was allowed to warm up to 25 °C overnight. After addition of *i*Pr$_2$Zn (0.5 mL, 2.5 mmol, 5 equiv), the reaction mixture was stirred for 5 h at 25 °C. After transmetallation with CuCN·2LiCl (0.75 mL, 0.75 mmol, 1.5 equiv) and addition of propionyl chloride (0.162 g, 1.75 mmol, 3.5 equiv), the reaction mixture was allowed to warm up to 25 °C overnight. The desired product **19b** was obtained as a diastereomeric mixture of >96:4 (quant. ^{13}C NMR, e.g. δ = 138.3 and 138.2) (0.133 g, 0.31 mmol, 62%; column chromatography in pentane/Et$_2$O 6:1). IR (film): $\tilde{\nu}$ = 2957 (s), 1714 (s), 1599 (w), 1456 (m), 1337 (s), 1158 (s), 1092 (s), 859 (w), 816 (w), 725 (m), 659 (m), 550 cm^{-1} (m); ^{1}H NMR ($CDCl_3$, 300 MHz): δ = 7.55 (d, *J* = 8.3 Hz, 2H), 7.29–7.16 (m, 7H), 4.32 (d, *J* = 16.3 Hz, 1H), 4.18 (d, *J* = 16.3 Hz, 1H), 3.72 (m, 1H), 2.52 (dd, *J* = 17 and 5 Hz, 1H), 2.33 (s, 3H), 2.31–1.99 (m, 4H), 1.33 (m, 1H), 1.16 (m, 1H), 0.95 (t, *J* = 7.3 Hz, 3H), 0.91–0.81 (m, 1H), 0.70 (d, *J* = 6.0 Hz, 3H), 0.59 (d, *J* = 6.7 Hz, 3H), 0.53 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 210.5, 143.0, 138.2, 137.8, 129.4, 128.3, 128.2, 127.5, 127.3, 60.0, 48.3, 46.5, 38.8, 36.2, 31.1,

24.4, 22.5, 22.4, 21.4, 16.5, 7.7; MS: m/z (%): 429 (<1) [M^+], 372 (1) [$M^+ - C_4H_9$], 330 (100), 274 (2), 216 (1), 174 (1), 160 (2), 155 (2), 132 (2), 91 (85), 65 (3), 57 (4); HRMS (CI): calcd for $C_{25}H_{36}NO_3S$: 430.2416; found 430.2393 [M^++H]; elemental analysis calcd for $C_{25}H_{35}NO_3S$ (429.6): C 69.89, H 8.21, N 3.26, S 7.46; found: C 69.86, H 8.22, N 3.23, S 7.20.

***N*-Benzyl-*N*-(1-isobutyl-2-methyl-4-octynyl)-4-methylbenzene sulfonamide (19c)**: Following GP I, 9-BBN-H (3.0 mL, 1.5 mmol, 3 equiv) was added to *N*-benzyl-*N*-(1-isobutyl-2-methyl-2-propenyl)-4-methylbenzenesulfonamide[17] (**17**; 0.186 g, 0.50 mmol) in THF (1.9 mL) at −78 °C. The reaction mixture was allowed to warm up to 25 °C overnight. After addition of iPr$_2$Zn (0.5 mL, 2.5 mmol, 5 equiv), the reaction mixture was stirred for 5 h at 25 °C. After transmetallation wit CuCN·2 LiCl (0.75 mL, 0.75 mmol, 1.5 equiv) and addition of 1-bromo-1-pentyne (0.367 g, 2.5 mmol, 5.0 equiv), the reaction mixture was stirred for 3 d at −40 °C. The desired product **19c** was obtained as a diastereomeric mixture of >96:4 (quant. ^{13}C NMR, e.g. $\delta = 138.7$ and 138.6) (0.108 g, 0.25 mmol, 49%; column chromatography in pentane/Et$_2$O 30:1). IR (film): $\tilde{\nu} = 2959$ (s), 1456 (m), 1338 (s), 1158 (s), 1092 (m), 857 (w), 815 (w), 727 (w), 658 (m), 559 cm^{-1} (w); ^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 7.59$ (d, $J = 8.7$ Hz, 2H), 7.25–7.16 (m, 7H), 4.40 (d, $J = 15.4$ Hz, 1H), 4.08 (d, $J = 15.4$ Hz, 1H), 3.80 (m, 1H), 2.34 (s, 3H), 2.06 (m, 4H), 1.61 (m, 1H), 1.49–1.39 (m, 3H), 1.15–1.04 (m, 2H), 0.92 (t, $J = 7.4$ Hz, 3H), 0.75 (d, $J = 6.1$ Hz, 3H), 0.69 (d, $J = 6.6$ Hz, 3H), 0.51 (d, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 142.8$, 138.7, 137.8, 129.2, 128.8, 128.3, 127.53, 127.5, 82.4, 76.9, 60.9, 40.0, 35.7, 24.2, 24.0, 23.3, 22.5, 21.6, 21.5, 20.8, 17.7, 13.6; MS: m/z (%): 382 (1) [$M^+ - C_4H_9$], 330 (79), 284 (5), 254 (1), 226 (1), 207 (9), 155 (2), 139 (1), 132 (1), 117 (1), 105 (1), 91 (100), 79 (2), 65 (3), 55 (2); HRMS (CI): calcd for $C_{27}H_{38}NO_2S$: 440.2623; found 440.2641 [M^++H]; elemental analysis calcd for $C_{27}H_{37}NO_2S$ (439.6): C 73.76, H 8.48, N 3.19; found: C 73.57, H 8.38, N 3.32.

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