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Configurationally Labile Enantioenriched Lithiated 3-Arylprop-2-enyl Carbamates: Joint Experimental and Quantum Chemical Investigations on the Equilibrium of Epimers

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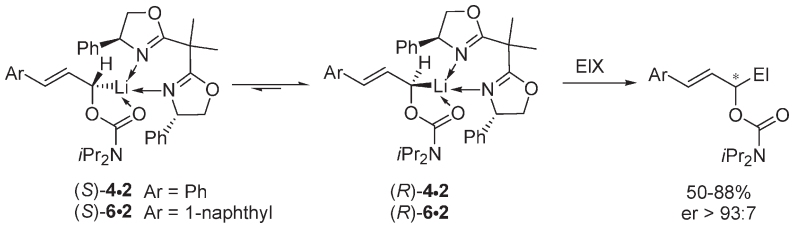

Experimental investigations as well as high-level quantum chemical calculations are performed on the two epimeric pairs of complexes **4·2** and **6·2** obtained by lithiation of cinnamyl carbamate (**1**) and 1-naphthyl derivative **5** in the presence of BOX ligands (*S*,*S*)- and (*R*,*R*)-**2**. Indeed, in the case of configurationally labile complexes and a dynamic thermodynamic resolution, which is found to take place, one of both epimers is energetically favored. The quantum chemical computations allow the prediction of the enantiomeric excess that can be expected.

Introduction

The enantioselective lithiation of prochiral allyl carbamates followed by substitution represents a valuable tool for introduction of a stereogenic center into a molecule.[1] In that context, an important challenge in the investigation of lithiated allyl carbamates is to determine the selectivity (enantioselectivity) at the stage of the deprotonation but also to solve the question of the configurational stability/lability of the lithiated species. For similar systems, quantum chemical computations allowed the prediction of the enantiomeric ratio quantitatively.[2,3]

We previously reported that the deprotonation of cinnamyl carbamate (**1**) with the chiral base pair *n*-butyllithium/(−)-sparteine led to the formation of mainly one configurationally unstable diastereoisomer.[4] Further substitution reactions with electrophiles occurred at different rates with both diastereomers, which led to a decreased enantioselectivity compared to the diastereomeric ratio of the complexes. This led to enantioenriched substitution products with er values up to 93:7. Herein, we report the joint successful experimental and quantum chemical investigations performed on lithiated "cinnamyl-type" carbamates obtained after deprotonation in the presence of chiral bisoxazoline ligands (BOX).[5]

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SCHEME 1. Deprotonation of Cinnamyl Carbamate 1

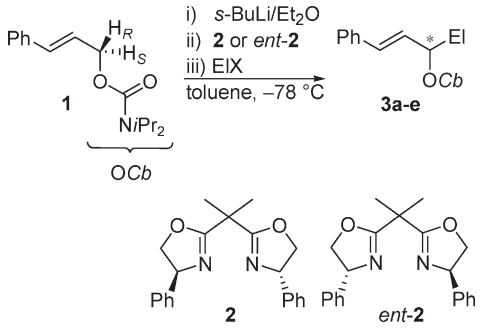


TABLE 1. Substitution of 1 with Different Electrophiles

BOX	product	EIX	yield, %	er[a]	$[\alpha]_D$
2	(*S*)-**3a**	Me_3SiCl	80	96:4	−11.4[b]
2	(*S*)-**3b**	Ph_3SnCl	50	94:6	+45.8[b]
ent-**2**	(*R*)-**3c**	Me_3SiOTf	69	94:6	+8.8[b]
ent-**2**	(*R*)-**3d**	Ph_3SiCl	88	n.d.	+0.8[b]
ent-**2**	(*R*)-**3e**	Et_3SiCl	75	97:3	−2.1[c]

[a]Determined by HPLC analysis on chiral phase. [b]*c* 0.89−1.09, CH_2Cl_2. [c]*c* 1.20, $CHCl_3$.

Results and Discussion

First, we investigated the deprotonation of cinnamyl carbamate (**1**) using *n*-butyllithium/BOX 2 (respectively *ent*-**2**) as chiral base pairs, followed by trapping lithium intermediate with reactive electrophiles (Scheme 1 and Table 1).

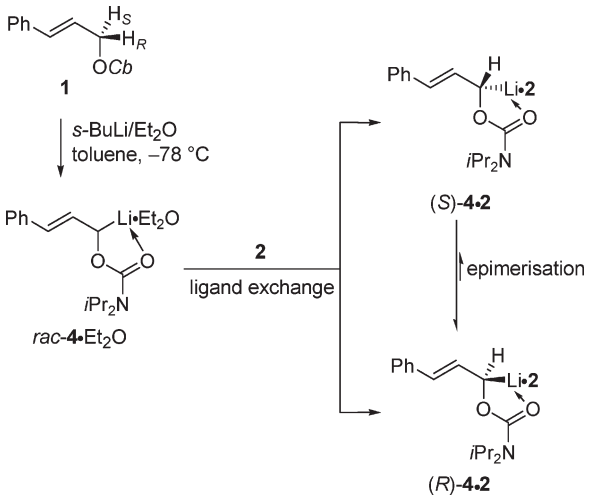
The substitution occurred exclusively in the α-position, and the enantioenriched products (**3a**−**e**) (er = 94:6−97:3) were obtained in moderate to good yield (50−88%). The configuration of the newly formed stereogenic centers was determined by comparison of the optical rotation with these of known examples, and considering an invertive substitution with tin and silyl electrophiles.[1d,4]

Carbamate **1** is smoothly deprotonated with 1.2 equiv of *s*-butyllithium/diethyl ether in toluene at −78 °C, and the addition of BOX ligand **2** induces after ligand exchange, through a dynamic thermodynamic resolution,[6] an epimerization of the stereogenic center to the almost exclusive formation of the most energetically favored complex (*R*)-**4**·**2** (Scheme 2).

In addition, the silylation of **1** with trimethylsilyl trifluoromethanesulfonate, which reacts much faster than TMSCl, led after 30 min to the formation of (*R*)-**3c** in 69% yield and er of 94:6. Those considerations minimize the possibility of a diastereotopic differentiation at the stage of the substitution (dynamic kinetic resolution[7]), and are evidence for the configurational lability of the lithium complex **4**·**2**.

Furthermore, 1-naphthyl derivative **5** was investigated in order to broaden the method developed for **1**. The deprotonation/equilibration sequence worked similarly well and **5** could be successfully silylated yielding **7** in good yield and good enantioselectivity (Scheme 3).

SCHEME 2. Nonselective Deprotonation of 1



Fortunately, suitable crystals of **7** for X-ray measurement with anomalous dispersion were obtained and the newly formed stereogenic center was determined to be (*S*)-configured (Figure 1).

The observed high enantioselectivity shows that the carbanionic pair **6**·**2** is configurationally unstable and after addition of the chiral ligand to the racemic mixture, the energetically more favorable (*R*)-configured complex is the major species in the solution.

All theses investigations suggest that the complexes **4**·**2** and **6**·**2** are configurationally labile and that a dynamic thermodynamic resolution is taking place,[6] which means that one of both epimers should be energetically favored. Thus, the diastereoisomeric ratios can be investigated by computing the equilibrium with quantum chemical methods (Scheme 4).

Previously we presented a computational scheme that allowed the prediction of the equilibria of *O*-benzyl carbamates with high accuracy.[2a,b] A slightly modified version of that procedure was applied here. Note that the maximum acceptable error of the calculated relative energies should not exceed 0.5 kcal mol^{-1}.

For a dynamic thermodynamic resolution, the observed selectivity (er = 96:4 for **3a**, measured by reaction with TMSCl, for example) reflects the ratio 96:4 of the epimeric pairs in solution ((*R*)-**4**·**2** and (*S*)-**4**·**2**) (Figure 2, eq 1). Furthermore, a determination of $\Delta\Delta G$ can be done experimentally using eq 2 in Figure 2, excluding any perturbation of the equilibrium.[9] Temperature and entropy effects are supposed to be negligible so that the calculated $\Delta\Delta E$ can be compared with the experimentally found $\Delta\Delta G$ (Figure 2, eq 3). Moreover, solvent effects and zero point vibrational energies (ZPVE) have been shown to have a minor contribution (both in the range 0.1−0.2 kcal mol^{-1}) by previous calculations on benzyl carbamates;[2b] therefore these effects are not taken into account in the following.

The alkenyl carbamates considered here have the possibility of a η^3-complexation at the lithium center in contrast to the previously investigated benzyl carbamates.[10] For this

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(8) Crystal structure data available in the Supporting Information.

(9) No precipitation was observed in the flask.

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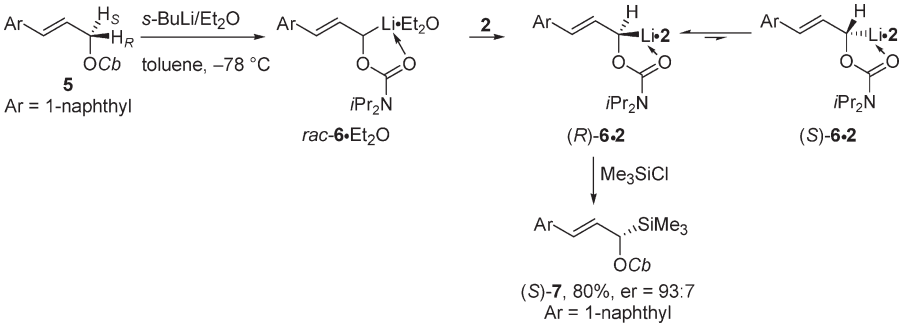
SCHEME 3. Nonselective Deprotonation of 7 Followed by Epimerization and Substitution with TMSCl



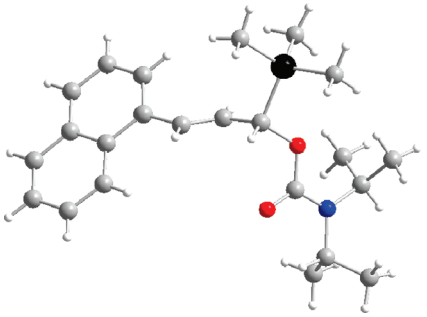


FIGURE 1. X-ray structure of **7**.[8]

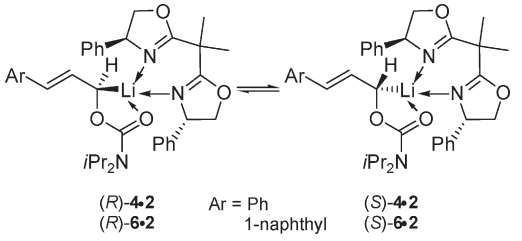
$$\frac{(S)-\mathbf{3a}}{(R)-\mathbf{3a}} = \frac{(R)-\mathbf{4 \bullet 2}}{(S)-\mathbf{4 \bullet 2}} \quad (1)$$

$$\Delta\Delta G = R_m T \ln\left(\frac{(S)-\mathbf{3a}}{(R)-\mathbf{3a}}\right) \quad (2)$$

$$\Delta\Delta E \approx \Delta\Delta H(0\,K) \approx \Delta\Delta H - T\Delta\Delta S = \Delta\Delta G \quad (3)$$

FIGURE 2. Mathematical relationships for the determination of the energy difference of epimeric complexes based on the experimental ratio within the dynamic thermodynamic resolution (eqs 1 and 2). Relationship between quantum chemically determined $\Delta\Delta E$ values and experimentally determined $\Delta\Delta G$ values.

SCHEME 4. Epimeric Complexes of 1 and 5 Investigated by High-Level Quantum Chemical Calculations



reason, the computational scheme has been modified. The geometries of the diastereomeric pairs (*R*)-**4·2** and (*S*)-**4·2** as well as of (*R*)-**6·2** and (*S*)-**6·2** were first optimized at the DFT level[11] employing the BH-LYP-D functional[12] and an

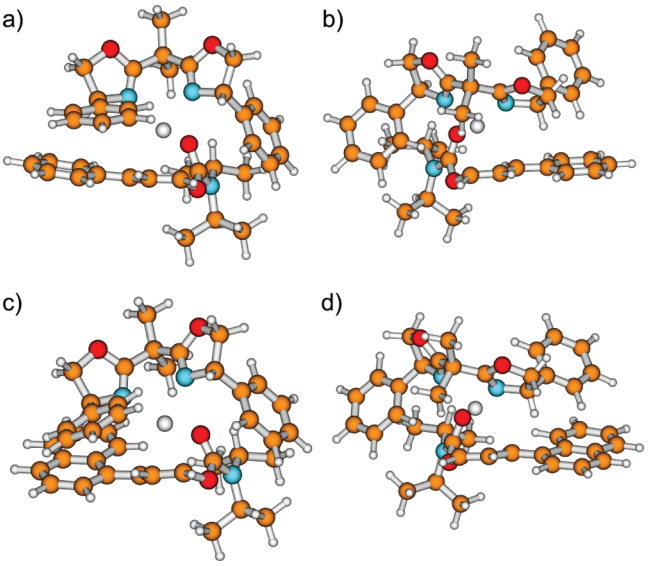


FIGURE 3. Calculated structures of complexes (*S*)-**4·2** (a), (*R*)-**4·2** (b), (*S*)-**6·2** (c), and (*R*)-**6·2** (d) (color key: white = H, orange = C, red = O, blue = N, gray = Li).

TABLE 2. Experimental $\Delta\Delta G$ and Calculated $\Delta\Delta E$ for Epimeric Complexes 4·2 and 6·2

	experimental		calculated	
complex	er[a]	$\Delta\Delta G$[b] (kcal mol^{-1})	er[b]	$\Delta\Delta E$ (kcal mol^{-1})
4·2	96:4	1.2	78:22	0.5
6·2	94:6	1.0	93:7	1.0

[a]After deprotonation and substitution with TMSCl. [b]See Figure 2.

empirical dispersion correction (DFT-D),[13] using the def2-TZVP basis.[14]

In contrast to our earlier work, the GGA-type functional, previously used to compute the structures, was substituted by a hydrid functional with a large amount of Fock exchange to rule out any artificial η^3-complexation caused by so-called self-interaction (overdelocalization) errors in DFT.[15] On the optimized structures, single-point energies were computed with SCS-MP2[16] by using the

(11) For the calculations, the program Turbomole V5.10: Ahlrichs, R. et al.; University of Karlsruhe: Germany, 2008; see: http://www.turbomole.com.

(12) BH-LYP: (a) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B.* **1988**, *37*, 785. (c) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 1372.

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def2-TZVPP basis[14] and employing the resolution of identity (RI) approximation.[17]

The computed results are, despite the geometric and electronic complexity of the systems, in perfect agreement with the experimental values deduced by the deprotonation/equilibration/substitution sequence (Table 2). For both lithiated carbamates the preferred diastereomer (*R* configured intermediate, Figure 3) is predicted correctly; moreover, the enantiomeric ratio is described quantitatively (error $\ll$1 kcal mol^{-1}).

The obtained complexes show a tendency to an η^3-coordination (Figure 3), which is in agreement with the lithiated conjugated aromatic allyl systems, which have been experimentally elucidated.[10]

Conclusions

In conclusion, lithiation of 3-arylprop-2-enyl carbamates **1** and **5** in the presence of BOX ligand **2** leads to the formation of configurationally labile complexes (**4·2** and **6·2**), which undergo an efficient dynamic thermodynamic resolution and react selectively with reactive electrophiles to form enantiomerically enriched substitution products in good yields. The BOX ligands perform a larger discrimination than (−)-sparteine in the diastereomeric complexes; it leads to synthetically useful stereoselctivities. By choice of the BOX ligand, both enantiomers of the substitution products can be approached. Furthermore, the quantum chemical calculations performed on diastereoisomeric pairs (*R*)-**4·2** and (*S*)-**4·2** as well as (*R*)-**6·2** and (*S*)-**6·2** confirm the experimentally determined enantiomeric ratios.

Experimental Section

(1*S*)-(*E*)-3-Phenyl-1-trimethylsilylprop-2-enyl *N*,*N*-Diisopropylcarbamate (3a). To a solution of **1**[4] (75 mg, 0.29 mmol, 1.0 equiv) and Et_2O (0.1 mL) in toluene (2 mL) was added *s*-BuLi (1.28 M) (0.30 mL, 0.38 mmol, 1.3 equiv) slowly at −78 °C. After 1 h of deprotonation, **2** (130 mg, 0.38 mmol, 1.3 equiv), dissolved in toluene (0.5 mL), was added at −78 °C and the mixture was stirred for an additional 2 h at −78 °C. After addition of TMSCl (96 mg, 0.88 mmol, 3.0 equiv) and 2 h of reaction the mixture was quenched by the addition of 2 N HCl (5 mL) and warmed to rt before addition of Et_2O (5 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O (3 × 10 mL). The combined organic phases were neutralized with a sat. aq. $NaHCO_3$ solution (15 mL), then dried with $MgSO_4$. After evaporation of the solvent under vacuum, purification of the residue yielded **3a** (77 mg, 0.23 mmol, 80%) as a white solid: mp 65−67 °C (Et_2O); R_f 0.38 (Et_2O/PE = 1:4); $[\alpha]^{20}_D$ −11.4 (*c* 1.08, CH_2Cl_2, er = 96:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 0.06 (s, 9 H), 1.20 (s, 12 H), 3.81, 4.02 (2 br s, 2 H), 5.24 (dd, *J* = 6.1, 1.1 Hz, 1 H), 6.21 (dd, *J* = 15.9, 6.1 Hz, 1 H), 6.33 (dd, J = 15.9, 1.1 Hz, 1 H), 7.13−7.15 (m, 1 H), 7.20−7.25 (m, 4 H); ^{13}C NMR (75 MHz, $CDCl_3$) δ/ppm −3.49, 20.6, 21.4, 45.1, 46.4, 70.5, 126.1, 126.8, 128.2, 128.4, 137.5, 155.6. Chiral HPLC: ChiraGrom-2 250 × 2 mm; *i*-PrOH/*n*-hexane = 1:600; 0.3 mL min^{-1}; t_R = 9 min (main enantiomer), t_R = 12 min; the spectroscopic data are in agreement with the literature.[4]

(1*S*)-(*E*)-3-Phenyl-1-triphenylstannylprop-2-enyl *N*,*N*-Diisopropylcarbamate (3b). A solution of carbamate **1** (84 mg, 0.32 mmol, 1.0 equiv) and Et_2O (0.1 mL) in toluene (2 mL) was cooled to −78 °C; *s*-BuLi (1.22 M) (0.27 mL, 0.33 mmol, 1.2 equiv) was added slowly. After 1 h of deprotonation, a solution of **2** (125 mg, 0.37 mmol, 1.2 equiv), dissolved in toluene (0.5 mL), was added dropwise at −78 °C within 5 min. The solution was stirred for 2 h and $ClSnPh_3$ (346 mg, 0.90 mmol, 2.8 equiv) dissolved in toluene (1.0 mL) was added dropwise and reacted for 3 h. The reaction was quenched by addition of 2 N HCl (5 mL) and warmed to rt before addition of Et_2O or TBME (5 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O or TBME (3 × 10 mL). The combined organic phases were neutralized with a sat. aq. $NaHCO_3$ solution (15 mL), then dried with $MgSO_4$. After evaporation of the solvent under vacuum, the residue was purified by column chromatography (Et_2O/PE = 1:25) yielding **3b** (96 mg, 0.16 mmol, 50%) as a yellow oil: R_f 0.64 (Et_2O/PE = 1:1), $[\alpha]^{20}_D$ +45.8 (*c* 0.89, CH_2Cl_2, er = 94:6); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 1.03, 1.14 (2 s, 12 H), 3.77, 3.95 (2 br s, 2 H), 5.54 (ddd, *J* = 20.6, 6.4, 1.6 Hz, 1 H), 6.40 (dd, *J* = 15.8, 1.6 Hz, 1 H), 6.51 (dd, *J* = 15.8, 6.4 Hz, 1 H), 7.16−7.19 (m, 5 H), 7.24−7.31 (m, 9 H), 7.55−7.65 (m, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 20.3, 21.3, 45.3, 46.5, 73.2, 124.5, 126.1, 126.7, 128.2, 128.4, 128.6, 130.5, 137.4, 137.5, 140.5, 156.1; IR (ATR) ν/cm^{-1} 3063, 2971, 2933, 1660, 1495, 1479, 1428, 1369, 1351, 1305, 1287, 1212, 1156, 1136, 1072, 1045, 1022, 997, 958, 934, 727, 696. Anal. Calcd for $C_{34}H_{37}O_2NSn$ (610.37): C 66.90, H 6.11, N 2.29. Found: C 66.63, H 5.77, N 1.99. Chiral HPLC: ChiraGrom-1 250 × 2 mm; *i*-PrOH/*n*-hexane = 1:20000; 0.3 mL min^{-1}; t_{R^1} = 8 min, t_{R^2} = 14 min (main enantiomer).

(1*R*)-(*E*)-3-Phenyl-1-triphenylsilylprop-2-enyl *N*,*N*-Diisopropylcarbamate (3d). A solution of carbamate **1** (85 mg, 0.32 mmol, 1.0 equiv) and Et_2O (0.1 mL) in toluene (2 mL) was cooled to −78 °C; *s*-BuLi (1.22 M) (0.27 mL, 0.33 mmol, 1.0 equiv) was added slowly. After 1 h of deprotonation, a solution of *ent*-**2** (123 mg, 0.37 mmol, 1.1 equiv), dissolved in toluene (0.5 mL), was added dropwise at −78 °C within 5 min. The solution was stirred for 2 h and $ClSiPh_3$ (263 mg, 0.89 mmol, 2.8 equiv) dissolved in toluene (1 mL) was added slowly. After 3 h the reaction was quenched by addition of 2 N HCl (5 mL) and warmed to rt before addition of Et_2O or TBME (5 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O or TBME (3 × 10 mL). The combined organic phases were neutralized with a sat. aq. $NaHCO_3$ solution (15 mL), then dried with $MgSO_4$. After evaporation of the solvent under vacuum, the residue was purified by column chromatography (toluene) yielding **3d** as a colorless solid (155 mg, 0.249 mmol, 88%); mp: 72−74 °C (Et_2O); R_f 0.35 (toluene); $[\alpha]^{20}_D$ +0.8 (*c* 1.04, CH_2Cl_2); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 0.94, 1.18 (2 br s, 12 H), 3.82 (br s, 2 H), 6.24−6.25 (m, 1 H), 6.27−6.30 (m, 2 H), 7.13−7.63 (m, 20 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 20.9, 45.7, 46.2, 67.9, 126.2, 127.6, 127.9, 128.3, 128.8, 130.0, 132.4, 135.0, 135.2, 136.1, 154.9; IR (ATR) ν/cm^{-1} 3069, 2969, 2934, 1680, 1485, 1427, 1369, 1328, 1285, 1215, 1156, 1112, 1045, 962, 856, 739, 696; HR-MS (ESI) (*m*/*z*) calcd $[C_{34}H_{37}NO_2Si + Na]^+$ = 542.2486, found $[C_{34}H_{37}NO_2Si + Na]^+$ = 542.2479. The enantiomeric excess could not be determined, neither by HPLC on chiral stationary phase, nor by GC on chiral stationary phase or by ^{1}H NMR shift experiments.

(1*R*)-(*E*)-3-Phenyl-1-triethylsilylprop-2-enyl *N*,*N*-Diisopropylcarbamate (3e). A solution of carbamate **1** (85 mg 0.32 mmol, 1.0 equiv) and Et_2O (0.1 mL) in toluene (2 mL) was cooled to −78 °C; *s*-BuLi (1.22 M) (0.27 mL, 0.33 mmol, 1.1 equiv) was added slowly. After 1 h of deprotonation, a solution of *ent*-**2** (129 mg, 0.38 mmol, 1.2 equiv), dissolved in toluene (0.5 mL), was added dropwise at −78 °C within 5 min. The solution was stirred for 2 h, then TESCl (139 mg, 0.92 mmol, 2.8 equiv) was added slowly. After 3 h the reaction was quenched by addition of 2 N HCl (5 mL) and warmed to rt before addition of Et_2O or TBME (5 mL). The organic phase was separated and the aqueous layer was extracted with Et_2O or TBME (3 × 10 mL). The combined organic phases were neutralized with a sat. aq. $NaHCO_3$ solution (15 mL), then dried with $MgSO_4$. After evaporation of the solvent under vacuum, the residue was

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purified by column chromatography (Et_2O/PE = 1:10), yielding **3e** (90 mg, 0.24 mmol, 75%) as a colorless oil: R_f 0.51 (Et_2O/PE = 1:4), $[\alpha]^{20}_D$ −2.1 (*c* 1.20, $CHCl_3$, er = 97:3); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 0.68 (q, *J* = 8.1 Hz, 6 H), 1.01 (t, *J* = 8.1 Hz, 9 H), 1.27 (d, *J* = 6.6 Hz, 12 H), 3.98 (br s, 2 H), 5.48 (dd, *J* = 6.1, 1.2 Hz, 1 H), 6.29 (dd, *J* = 15.9, 6.1 Hz, 1 H), 6.38 (dd, *J* = 15.9, 1.2 Hz, 1 H), 7.14−7.22 (m, 1 H), 7.23−7.61 (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 2.1, 7.4, 20.8, 21.3, 45.9, 68.5, 126.1, 126.3, 126.8, 128.4, 128.8, 137.6, 155.2; IR (ATR) ν/cm^{-1} 3058, 2961, 29376, 1693, 1454, 1426, 1377, 1367, 1333, 1290, 1219, 1158, 1135, 1063, 1045, 1010, 972, 732, 793. Anal. Calcd for $C_{22}H_{37}NO_2Si$ (375.62): C 70.35, H 9.93, N 3.73. Found: C 70.16, H 9.97, N 3.70. Chiral HPLC: ChiraGrom-2 250 × 2 mm; *i*-PrOH/*n*-hexane = 1:600; 0.3 mL min^{-1}; t_{R^1} = 9 min, t_{R^2} = 15 min (main enantiomer).

(1*S*)-(*E*)-3-(1-Naphthyl)-1-trimethylsilylprop-2-enyl *N*,*N*-Diisopropylcarbamate (7). A solution of carbamate **5** (93 mg, 0.30 mmol, 1.0 equiv) and Et_2O (0.1 mL) in toluene (2 mL) was cooled to −78 °C; *s*-BuLi (1.22 M) (0.27 mL, 0.33 mmol, 1.2 equiv) was added slowly. After 1 h of deprotonation, a solution of **2** (128 mg, 0.38 mmol, 1.3 equiv) in toluene (0.5 mL) was added dropwise at −78 °C within 5 min. The solution was stirred for 2 h and TMSCl (103 mg, 0.93 mmol, 3.1 equiv) was added dropwise and reacted for 1 h. After quenching with MeOH (0.3 mL) at −78 °C and warming to rt, 2 N HCl (0.03 mL) and Et_2O (10 mL) were added and the organic phase was dried with $MgSO_4$. The solvent was evaporate under reduced pressure and the crude product was purified by column chromatography (Et_2O/PE = 1:10), yielding **7** (92 mg, 0.27 mmol, 80%) as a colorless solid: mp 51−56 °C (Et_2O); R_f 0.64 (Et_2O/PE = 1:1); $[\alpha]^{20}_D$ +18.4 (*c* 1.01, $CHCl_3$, er = 93:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ/ppm 0.18 (s, 9 H), 1.29 (br s, 12 H), 3.95, 4.09 (2 br s, 2 H), 5.42 (dd, *J* = 6.3, 1.9 Hz, 1 H), 6.31 (dd, *J* = 15.7, 6.3 Hz, 1 H), 7.11 (dd, *J* = 15.7, 1.9 Hz, 1 H), 7.42−7.48 (m, 4 H), 7.73 (d, 1 H), 7.83 (m, 1 H), 8.05−8.07 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ/ppm 3.4, 20.9, 46.2, 70.8, 123.5, 123.9, 124.0, 125.6, 125.8, 127.3, 128.4, 131.3, 131.6, 133.6, 135.6, 155.6; IR (ATR) ν/cm^{-1} = 3058, 2963, 2930, 1688, 1472, 1435, 1368, 1314, 1281, 1247, 1213, 1157, 1125, 1065, 1045, 960, 934, 839, 792, 775. Anal. Calcd for $C_{23}H_{33}NO_2Si$ (383.60): C 72.01, H 8.67, N 3.65. Found: C 72.38, H 8.75, N 3.41. Chiral HPLC: Chiracel OD-H; *i*-PrOH/*n*-hexane = 1:75; 1.0 mL min^{-1}; t_{R^1} = 5 min (main enantiomer), t_{R^2} = 12 min.

Computational Details. All DFT and SCS-MP2[16] computations have been performed with a modified version of Turbomole[11] 5.10. The structures were optimized with DFT employing the BH-LYP[12] functional and an empirical dispersion correction (DFT-D, $s6_{BH\text{-}LYP} = 0.9$).[13] An Ahlrichs' triple ξ basis set (def2-TZVP) was used for all geometry optimizations. The final energies were calculated with SCS-MP2 and an Ahlrichs' triple ξ basis with additional polarization functions (def2-TZVPP).[14] The resolution of the identity (RI) approximation[17] with auxiliary basis sets from the Turmobole library was used for both the DFT and MP2 steps. For the numerical integration a large multiple grid (grid 'm4'[18] option in Turbomole) was used. Both the structure optimizations as well as the energy calculations were performed with a convergence criterion of 10^{-7} hartree.

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Supporting Information Available: Experimental procedures, spectroscopic data of all new compounds, X-ray crystal analyze of compound **7**, ^{1}H and ^{13}C NMR spectra, and SCS-MP2 total energies. This material is available free of charge via the Internet at http://pubs.acs.org.

(18) Numerical quadrature multiple grid ('grid m4' option in Turbomole): Treutler, O.; Ahlrichs, R. *J. Chem. Phys.* **1995**, *102*, 346.