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Further Structural Modification of Sulfur-Stabilized Silicon Cations with Binaphthyl Backbones

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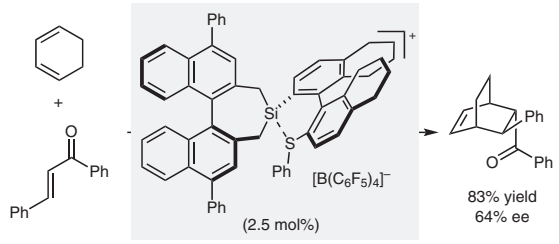

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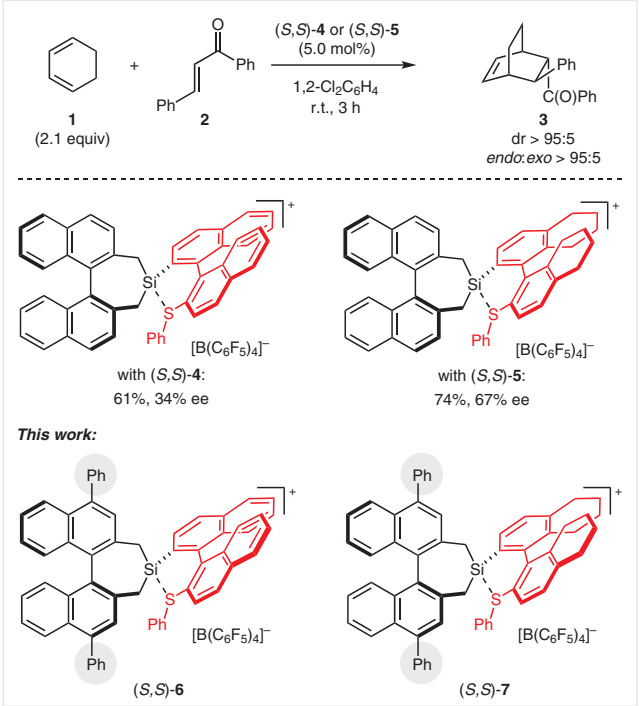
Abstract The synthesis and spectroscopic characterization of two novel cationic silicon–sulfur Lewis pairs with a chiral 4,4′-disubstituted binaphthyl silepine backbone are described. Both Lewis acids induce significant enantioselectivity in the model Diels–Alder reaction of cyclohexa-1,3-diene and chalcone but additional substitution of the binaphthyl backbone exerts a minimal effect on enantioinduction compared to previously reported Lewis acids. Another silicon cation with a chiral spirocyclic backbone induces enantioselectivity in the same range but its synthesis is laborious.

Key words asymmetric catalysis, chirality, Diels–Alder reaction, Lewis acids, silylium ions

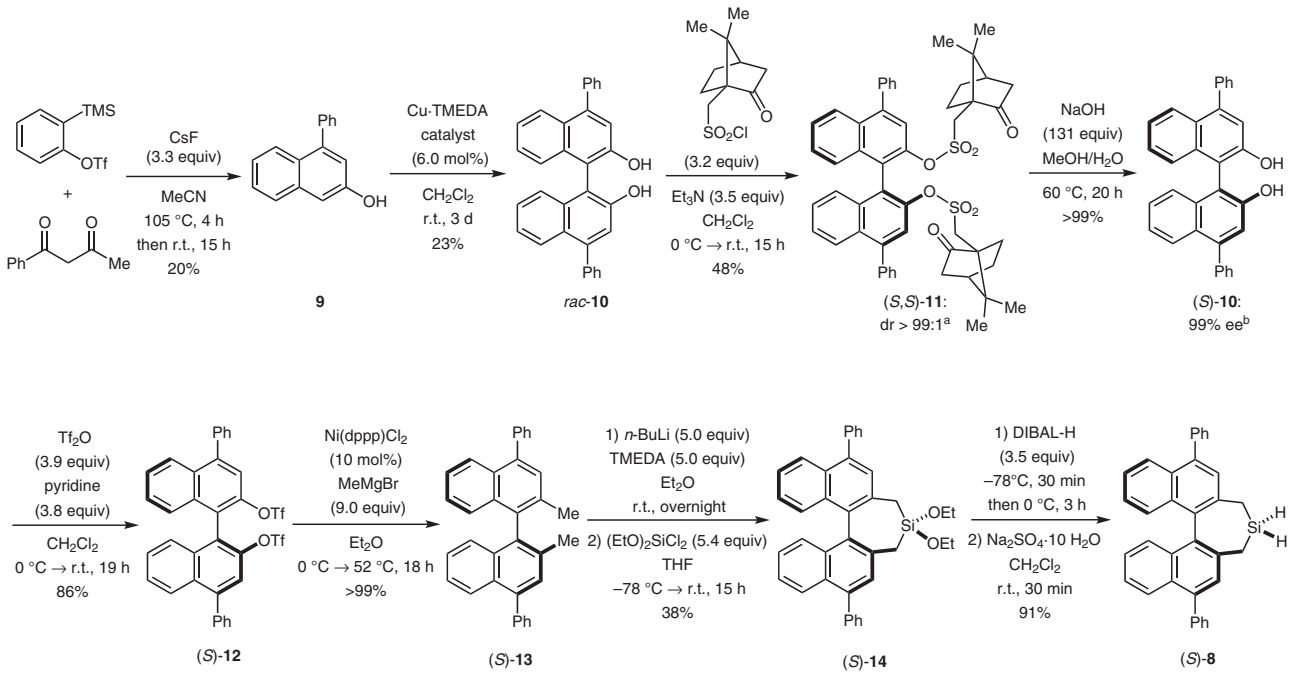
Cationic silicon Lewis acids, that is, silylium ion-like species, and chiral variants thereof have been shown to act as competent catalysts for Diels–Alder reactions.[1–3] Our laboratory recently introduced binaphthyl-based sulfur-stabilized silicon cations[4–6] (*S*,*S*)-**4** and (*S*,*S*)-**5** that induced 34% ee and 67% ee, respectively, in the challenging model reaction of cyclohexa-1,3-diene (**1**) and chalcone (**2**) (**1** + **2** → **3**, Scheme 1, top). With H_8-binaphthyl-based (*S*,*S*)-**5**, 81% ee was reached for more hindered chalcone derivatives.[4b,d] After several structural modifications of the silepine framework, including replacement of the binaphthyl by biphenyl and silaindane units,[4c] we decided to introduce phenyl groups in the 4 and 4′ positions of the binaphthyl silepine backbone in (*S*,*S*)-**4** and (*S*,*S*)-**5** (Scheme 1, bottom). Here, we describe the synthesis and spectroscopic characterization of the new Lewis acids (*S*,*S*)-**6** and (*S*,*S*)-**7** and their application in the aforementioned model Diels–Alder reaction.

Catalysts (*S*,*S*)-**6** and (*S*,*S*)-**7** are composed of an axially chiral 4,4′-disubstituted binaphthyl silepine backbone and an axially chiral thioether substituent. The dihydrosilepine



Scheme 1 Diels–Alder reaction of cyclohexa-1,3-diene (**1**) and chalcone (**2**) catalyzed by chiral sulfur-stabilized silicon cation (*S*,*S*)-**4**/(*S*,*S*)-**5** (top), and structural modifications of the catalysts [(*S*,*S*)-**6**/(*S*,*S*)-**7**, bottom]

unit (*S*)-**8** was prepared by a multistep sequence following a modified literature protocol[4a,7] (Scheme 2). Reaction of 2-(trimethylsilyl)phenyl triflate with benzoylacetone in the presence of CsF, followed by Cu·TMEDA-catalyzed oxidative coupling of resulting naphth-2-ol **9** afforded the racemic 4,4′-disubstituted BINOL *rac*-**10** [**9** → *rac*-**10**]. Enantiopure BINOL (*S*)-**10** was obtained after resolution with (*S*)-(+)-

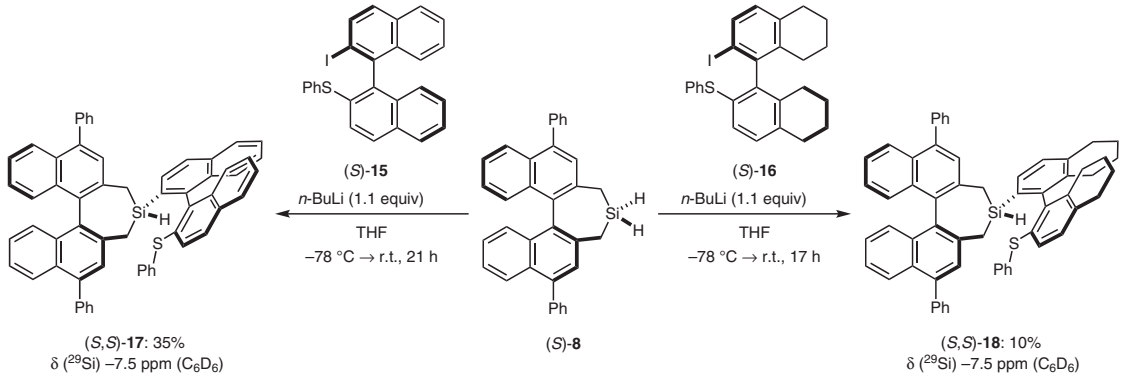


Scheme 2 Synthesis of the 4,4′-disubstituted dihydrosilepine (*S*)-**8**. [a] Separation of the diastereomers (*S*,*S*)-**11** and (*R*,*S*)-**11** (not isolated) was achieved by flash column chromatography on silica gel. Diastereomeric ratio was determined by ^{1}H NMR analysis [dr = 50:50 of crude (*SR*,*S*)-**11** before separation]. [b] Enantiomeric excess was determined by HPLC analysis (for details, see experimental section).

camphorsulfonyl chloride [*rac*-**10** → (*S*,*S*)-**11**] and removal of the chiral auxiliary [(*S*,*S*)-**11** → (*S*)-**10**]. Triflation of (*S*)-**10** [(*S*)-**10** → (*S*)-**12**], followed by nickel-catalyzed Kumada coupling furnished 2,2′-dimethyl-substituted (*S*)-**13** [(*S*)-**12** → (*S*)-**13**]. Diethoxysilepine (*S*)-**14** was then formed by double lithiation of (*S*)-**13** and trapping of the dianionic intermediate with $(EtO)_2SiCl_2$ [(*S*)-**13** → (*S*)-**14**]. Reductive silicon–oxygen bond cleavage with DIBAL-H afforded the dihydrosilepine (*S*)-**8** [(*S*)-**14** → (*S*)-**8**].

The other building blocks (*S*)-**15** and (*S*)-**16** were prepared in enantiopure form by monoselective lithiation of the literature-known diiodides,[8] followed by trapping with diphenyl disulfide (for details, see experimental section). Reaction of (*S*)-**8** with metalated thioethers (*S*)-**15** and (*S*)-**16** afforded the desired hydrosilanes (*S*,*S*)-**17** and (*S*,*S*)-**18** in moderate and low[9] yield, respectively (Scheme 3).

The sulfur-stabilized silicon cations (*S*,*S*)-**6** and (*S*,*S*)-**7** were generated in 1,2-$Cl_2C_6D_4$ from the corresponding hydrosilanes (*S*,*S*)-**17** and (*S*,*S*)-**18** following the established protocol[10] of hydride abstraction with trityl tetrakis(pentafluorophenyl)borate {$[Ph_3C]^+[B(C_6F_5)_4]^-$} (Figure 1). The ^{29}Si NMR spectra of (*S*,*S*)-**6** and (*S*,*S*)-**7** showed a single resonance signal at δ = 39.9 and 40.9, respectively. These chemical shifts fit nicely into the scale of previously reported binaphthyl-based silicon cations (*S*,*S*)-**1** (δ = 39.5) and (*S*,*S*)-**2** (δ = 41.1).



Scheme 3 Preparation of 4,4′-disubstituted hydrosilanes (*S*,*S*)-**17** and (*S*,*S*)-**18**

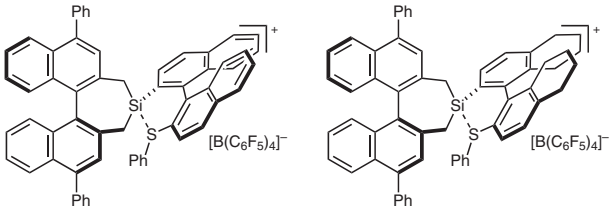
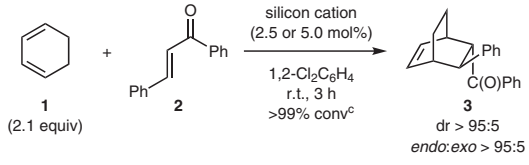


Figure 1 Sulfur-stabilized silicon cations (*S*,*S*)-**6** and (*S*,*S*)-**7** and their ^{29}Si NMR chemical shifts

We first tested the bis(binaphthyl)-based catalyst (*S*,*S*)-**6** in our model Diels–Alder reaction of cyclohexa-1,3-diene (**1**) and chalcone (**2**) (Table 1). Full conversion of **2** was observed after 3 h, and cycloadduct **3** was isolated in good yield and with enantiomeric excess of 46% (Table 1, entry 1). The direct comparison of the new Lewis acid (*S*,*S*)-**6** with the reported system (*S*,*S*)-**4** shows a slight increase in enantioselectivity (46% ee vs 34% ee, entry 1 vs entry 2). As expected, the H_8-binaphthyl silicon cation (*S*,*S*)-**7** yielded the cycloadduct **3** with enhanced enantioselectivity of 64% ee, compared to its binaphthyl analogue (*S*,*S*)-**6** (64% ee vs 46% ee, entry 3 vs entry 1). However, the 4,4′-disubstitution at the silepine backbone had no effect on enantioinduction in this case, and the achieved enantiomeric excess was similar to that found for the parent catalyst (*S*,*S*)-**5** (64% ee vs 67% ee, entry 3 vs entry 4).

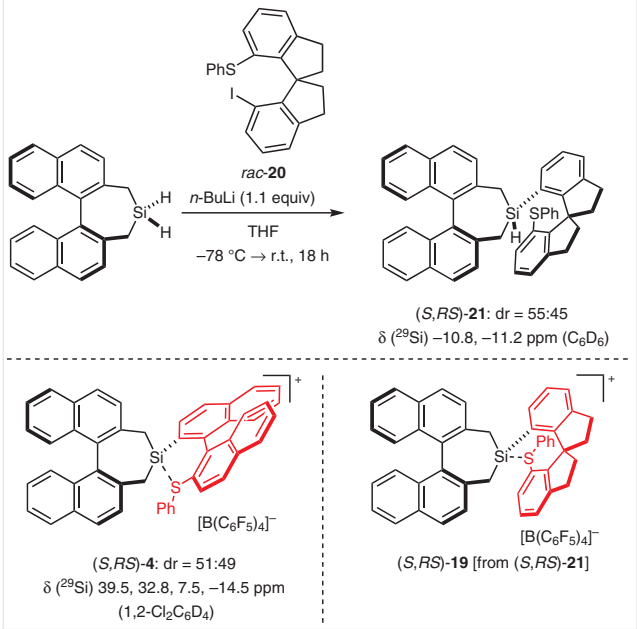
The H_8-binaphthyl backbone was again the crucial structural modification to achieve significant levels of enantioselection.[4d] We were also looking for another class of molecules with axial chirality that we could incorporate into our catalyst. The rigidity of C_2-symmetric 1,1′-spirobiindane framework attracted our attention.[11] We therefore targeted the new catalyst (*S*,*RS*)-**19** with an unsubstituted silepine and a spirocyclic thioether backbone (Scheme 4). To ease the synthetic effort, it was prepared in the form of its mixture of diastereomers as this is usually sufficient for initial testing. The synthesis of the required building block *rac*-**20** was accomplished from the literature-known diiodide according to our previously reported procedure and was subjected to the same reaction conditions elaborated for the synthesis of the 4,4′-disubstituted (*S*,*S*)-**17**/**18** (see Scheme 3). The hydrosilane (*S*,*RS*)-**21** was isolated with a diastereomeric ratio of nearly 50:50 together with an unidentified silicon compound (^{29}Si NMR: δ = 32.0). The silicon cation (*S*,*RS*)-**19** was generated by hydride abstraction with $[Ph_3C]^+[B(C_6F_5)_4]^-$ but the diastereomeric ratio and the corresponding ^{29}Si chemical shifts could not be determined due to the complexity of the ^{1}H and ^{1}H,^{29}Si HMQC NMR spectra. The ^{29}Si chemical shift of δ = 32.0 of the unknown silicon compound remained unchanged. In control experiments, we could show that this silicon species is not cata-

Table 1 Testing the Silicon Cations (*S*,*S*)-**4**–**7**, (*S*,*RS*)-**4** and (*S*,*RS*)-**19** in the Model Diels–Alder Reaction[a,b]



Entry	Silicon Cation	Yield (%)[c,d]	ee (%)[e]
1[f]	(*S*,*S*)-**6**	85	46
2[g]	(*S*,*S*)-**4**	61	34
3[f]	(*S*,*S*)-**7**	83	64
4[g]	(*S*,*S*)-**5**	74	67
5[g]	(*S*,*RS*)-**19**	86	34
6[g]	(*S*,*RS*)-**4**	53	25

[a] All reactions were performed according to the General Procedure GP 4 at a dienophile concentration of 0.14 or 0.50 M. Data are based on multiple runs.
[b] Diastereomeric ratios (*trans*:*cis* and *endo*:*exo*) were determined by GLC analysis of the crude material prior to purification.
[c] Conversion of >99% was determined by GLC analysis using triphenylmethane as an internal standard.
[d] Analytically pure cycloadduct after flash column chromatography on silica gel.
[e] Determined by HPLC analysis using a chiral stationary phase.
[f] Reactions were conducted on 0.0690 mmol scale; dienophile concentration of 0.14 M; 2.5 mol% of the catalyst.
[g] Reactions were conducted on 0.249 mmol scale; dienophile concentration of 0.50 M.; 5.0 mol% of the catalyst.



Scheme 4 Preparation of the hydrosilane (*S*,*RS*)-**21** with a spirocyclic backbone. Generation of the corresponding sulfur-stabilized silicon cation (*S*,*RS*)-**19** and its binaphthyl analogue (*S*,*RS*)-**4**. Only one diastereomer for each (*S*,*RS*)-**21**, (*S*,*RS*)-**19**, and (*S*,*RS*)-**4** is shown for a better overview. For synthetic details, see the experimental section.

lytically active. The new Lewis acid (*S*,*RS*)-**19** was tested in the reaction of cyclohexa-1,3-diene (**1**) and chalcone (**2**), giving the cycloadduct **3** in good yield and with enantioselectivity of 34% ee (Table 1, entry 5). The enantiomeric excess did not significantly exceed the value achieved with the related bis(binaphthyl) silicon cation (*S*,*RS*)-**4** in form of a diastereomeric mixture (34% ee vs 25% ee, entry 5 vs entry 6).[4b] Although both catalysts (*S*,*RS*)-**19** and (*S*,*RS*)-**4** induced similar levels of enantioselection, we had decided to pursue binaphthyl systems in the past.

To summarize, we have prepared sulfur-stabilized silicon cations (*S*,*S*)-**6** and (*S*,*S*)-**7** with 4,4′-disubstituted binaphthyl silepine backbone. With (*S*,*S*)-**6** and (*S*,*S*)-**7** enantiomeric excesses of 46% ee and 64% ee were achieved in the Diels–Alder reaction of cyclohexa-1,3-diene (**1**) and chalcone (**2**). Comparing these results with those obtained with our previously reported Lewis acids (*S*,*S*)-**4** and (*S*,*S*)-**5**, the effect of the additional 4,4′-disubstitution on enantioinduction turned out to be marginal. Silicon Lewis acid (*S*,*RS*)-**19** with spirocyclic backbone gave promising enantioselectivity in the same reaction but its preparation is more laborious.

All reactions were performed in flame-dried glassware using an MBraun glovebox or conventional Schlenk techniques under a static pressure of argon (glovebox) or N_2. Liquids and solutions were transferred with syringes. Solvents were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography were distilled prior to use. C_6D_6 and $CDCl_3$ were dried over thermally activated 4 Å molecular sieves, and 1,2-$Cl_2C_6D_4$ was dried over CaH_2, distilled, and stored under argon. Cyclohexa-1,3-diene (**1**) was distilled from CaH_2, degassed by three freeze-pump-thaw cycles, and stored in a glove box over thermally activated 4Å molecular sieves. $[Ph_3C]^+[B(C_6F_5)_4]^-$ was prepared following a reported procedure,[12] recrystallized from CH_2Cl_2/*n*-pentane, and stored in a glovebox. (*S*)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine,[4a] (*S*)-2,2′-diiodo-1,1′-binaphthalene,[8] (*S*)-2,2′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene,[8] and *rac*-7,7′-diiodo-2,2′,3,3′-tetrahydro-1,1′-spirobi[indene][13] were synthesized according to the reported procedures. The concentration of *n*-BuLi solutions was determined by titration using Suffert's reagent.[14] All other commercially available reagents and solvents were used as received. Analytical TLC was performed on silica gel 60 F254 glass plates by Merck. Flash column chromatography was performed on silica gel LC60A (40–63 µm) by Grace using the indicated solvents. ^{1}H, ^{13}C, ^{11}B, ^{19}F, and ^{29}Si NMR spectra were recorded in $CDCl_3$, C_6D_6, or 1,2-$Cl_2C_6D_4$ on Bruker AV700, AV500 or AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CHCl_3$: δ = 7.26 for ^{1}H NMR and $CDCl_3$: δ = 77.16 for ^{13}C NMR, C_6D_5H: δ = 7.16 for ^{1}H NMR and C_6D_6: δ = 128.06 for ^{13}C NMR; 1,2-$Cl_2C_6D_3H$: δ = 6.94 and 7.20 for ^{1}H NMR and 1,2-$Cl_2C_6D_4$: δ = 127.1, 130.1, and 132.5 for ^{13}C NMR). ^{11}B, ^{19}F, and ^{29}Si NMR spectra are referenced in compliance with the unified scale for NMR chemical shifts as recommended by the IUPAC stating the chemical shift relative to $BF_3{\cdot}Et_2O$, CCl_3F, and TMS, respectively.[15] Data are reported as follows: chemical shift, multiplicity (standard abbreviations; m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. ^{1}H,^{29}Si HMQC NMR spectra were measured with a coupling constant of 7.0 Hz. The peak intensities in the ^{1}H,^{29}Si HMQC NMR spectra cannot be correlated to the amount of compound. IR spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrophotometer equipped with a diamond ATR unit and are reported as wavenumbers (cm^{-1}). Gas liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph equipped with a HP-5 capillary column (30 m × 0.32 mm, 0.25 µm film thickness) using the following program: N_2 carrier gas, column flow: 1.74 mL min^{-1}, injection temperature: 250 °C, detector temperature: 300 °C; temperature program: start temperature 40 °C, heating rate 10 °C min^{-1}, end temperature 280 °C for 10 min. Melting points were determined with a Wagner & Munz Leica Galen III melting point apparatus and are not corrected. Enantiomeric excesses (ee) were determined by analytical high performance liquid chromatography (HPLC) analysis on an Agilent Technologies 1200 Infinity instrument with a Daicel Chiralcel OD-H column as the chiral stationary phase (*n*-heptane/*i*-PrOH mixtures as solvents). High-resolution mass spectrometry (HRMS) was performed at the Analytical Facility of the Institut für Chemie, Technische Universität Berlin.

Thioethers (*S*)-15, (*S*)-16, and *rac*-20; General Procedure (GP 1)

To a solution of the indicated diiodide (1.0 equiv) in THF (0.18 M) was added a hexane solution of *n*-BuLi (0.95 equiv) over a period of 1 h at –78 °C, and the reaction mixture was then maintained at this temperature for 1 h. A solution of diphenyl disulfide (1.2–1.8 equiv) in THF (0.44 M) was added over a period of 20 min, the mixture was allowed to slowly warm to r.t., followed by stirring overnight. The reaction was quenched by the addition of a sat. aq $NaHCO_3$. The aqueous phase was extracted with CH_2Cl_2 (3 ×). The combined organic phases were dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 mixtures as eluent.

(*S*)-(2′-Iodo-[1,1′-binaphthalen]-2-yl)(phenyl)sulfane [(*S*)-15]

Prepared according to GP 1 from (*S*)-2,2′-diiodo-1,1′-binaphthalene (500 mg, 0.988 mmol, 1.00 equiv) and diphenyl disulfide (259 mg, 1.19 mmol, 1.20 equiv). Desired (*S*)-**15** was obtained together with the hydrodehalogenated derivative in a ratio of 5:1 [216 mg, 188 mg (39%) of the pure thioether, determined by ^{1}H NMR analysis] as a pale yellow solid after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10:1) as eluent; R_f = 0.35 (cyclohexane/CH_2Cl_2 = 10:1).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.08 (d, *J* = 8.3 Hz, 1 H), 7.22 (d, *J* = 8.8 Hz, 1 H), 7.28–7.33 (m, 5 H),* 7.36 (d, *J* = 8.8 Hz, 1 H), 7.44–7.52 (m, 4 H), 7.72 (d, *J* = 8.8 Hz, 1 H), 7.85 (d, *J* = 9.0 Hz, 1 H), 7.89 (d, *J* = 8.2 Hz, 1 H), 7.93 (d, *J* = 8.2 Hz, 1 H), 8.10 (d, *J* = 8.7 Hz, 1 H). * Signal overlapping of the hydrodehalogenated product resonances (5 H expected).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 100.3, 125.6, 126.0, 126.6, 126.6, 127.2, 127.2, 127.3, 127.9, 128.2, 128.4, 129.1, 129.3, 129.7, 132.2, 132.5, 133.1, 133.3, 133.8, 134.5, 135.7, 135.8, 138.8, 141.0.

HRMS (APCI): *m*/*z* $[M + H]^+$ calcd for $C_{26}H_{18}IS$: 489.0168; found: 489.0168.

(*S*)-(2′-Iodo-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalen]-2-yl)(phenyl)sulfane [(*S*)-16]

Prepared according to GP 1 from (*S*)-2,2′-diiodo-5,5′,6,6′,7,7′,8,8′-octahydro-1,1′-binaphthalene (160 mg, 0.311 mmol, 1.00 equiv) and diphenyl disulfide (122 mg, 0.559 mmol, 1.80 equiv). Desired (*S*)-**16** was obtained together with the hydrodehalogenated derivative in a ratio of ~3:1 [118 mg, 89 mg (38%) of the pure thioether, determined

by ^{1}H NMR analysis] as a colorless high-viscosity oil after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10:1) as eluent and used for the next step without further purification.

rac-(7′-Iodo-2,2′,3,3′-tetrahydro-1,1′-spirobi[inden]-7-yl)(phenyl)sulfane (*rac*-20)

Prepared according to GP 1 from *rac*-7,7′-diiodo-2,2′,3,3′-tetrahydro-1,1′-spirobi[indene] (340 mg, 0.720 mmol, 1.00 equiv) and diphenyl disulfide (189 mg, 0.864 mmol, 1.20 equiv). Desired *rac*-**20** was obtained together with the hydrodehalogenated derivative in a ratio of ~1:1.1 [100 mg, 48 mg (15%) of the pure thioether, determined by ^{1}H NMR analysis] as a colorless oil after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10:1) as eluent and used for the next step without further purification.

4-Phenylnaphthalen-2-ol (9)

According to a reported procedure,[7] a stirred suspension of benzoylacetone (5.68 g, 35.0 mmol, 1.00 equiv) and anhyd CsF (17.6 g, 116 mmol, 3.30 equiv) in MeCN (350 mL) was brought to reflux. 2-(Trimethylsilyl)phenyl trifluoromethanesulfonate (11.5 g, 38.5 mmol, 1.10 equiv) was added dropwise over 30 min. The mixture was stirred for 4 h at 105 °C, then cooled to r.t., followed by stirring overnight. MeCN was evaporated under reduced pressure. The resultant residue was taken up in CH_2Cl_2 (300 mL), washed with sat. aq NH_4Cl (100 mL), H_2O (150 mL), and brine (150 mL). The organic phase was dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (1:1) → CH_2Cl_2 as eluent to afford **9** (1.33 g, 20%) as a dark orange oil; R_f = 0.21 (cyclohexane/CH_2Cl_2 1:2).

IR (ATR, diamond): 3309 (br), 3053 (w), 1619 (m), 1595 (m), 1577 (m), 1345 (m), 1161 (m), 920 (m), 866 (m), 836 (m), 779 (m), 739 (s), 698 cm^{-1} (s).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 4.92 (s, 1 H), 7.07 (d, *J* = 2.6 Hz, 1 H), 7.18 (d, *J* = 2.6 Hz, 1 H), 7.26–7.29 (m, 1 H),* 7.42–7.45 (m, 2 H), 7.46–7.51 (m, 4 H), 7.74 (d, *J* = 8.2 Hz, 1 H), 7.79 (d, *J* = 8.5 Hz, 1 H). * Signal overlapping of the $CDCl_3$ resonance (1 H expected).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 109.3, 118.8, 123.9, 126.2, 126.6, 126.9, 127.5, 127.6, 128.4, 130.1, 135.3, 140.2, 142.7, 152.8.

HRMS (APCI): *m*/*z* $[M]^{+\bullet}$ calcd for $C_{16}H_{12}O$: 220.0883; found: 220.0882.

rac-(±)-4,4′-Diphenyl-[1,1′-binaphthalene]-2,2′-diol (*rac*-10)

According to a reported procedure,[7] in a round-bottomed flask, 4-phenylnaphthalen-2-ol (**9**; 1.33 g, 6.04 mmol, 1.00 equiv) was dissolved in CH_2Cl_2 (7 mL). Then Cu·TMEDA catalyst (84 mg, 0.18 mmol, 0.03 equiv) was added, the flask was covered with a septum, and pierced with a needle to open the reaction to atmosphere. The mixture was stirred for 3 d at r.t., then filtered through a pad of Celite, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (2:1) → CH_2Cl_2 as eluent to afford *rac*-**10** (620 mg, 23%) as a yellow solid; mp 144–150 °C (*n*-pentane); R_f = 0.23 (cyclohexane/CH_2Cl_2 1:2)

HPLC: Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH (85:15), flow rate: 1.0 mL/min, λ = 250 nm; t_R = 10.8 min [(*R*)-**10**], t_R = 19.9 [(*S*)-**10**] min.

IR (ATR, diamond): 3512 (w), 3381 (br), 1587 (m), 1346 (m), 1173 (m), 1136 (s), 943 (m), 762 (s), 701 (s), 659 cm^{-1} (m).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.16 (s, 2 H), 7.31–7.39 (m, 6 H), 7.39 (s, 2 H), 7.49–7.52 (m, 2 H), 7.56 (m_c, 4 H), 7.61–7.64 (m, 4 H), 7.94–7.97 (m, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 110.6, 118.8, 124.3, 124.8, 126.9, 127.6, 127.9, 128.2, 128.6, 130.1, 134.1, 140.1, 144.1, 152.4.

HRMS (APCI): *m*/*z* $[M - H]^+$ calcd for $C_{32}H_{21}O_2$: 437.1536; found: 437.1526.

(*S*)-(−)-4,4′-Diphenyl-[1,1′-binaphthalene]-2,2′-diyl Bis[(1*S*)-camphor-10-sulfonate] [(*S*)-11]

According to a reported procedure,[7] to a solution of *rac*-**10** (1.33 g, 6.04 mmol, 1.00 equiv) and Et_3N (1.86 mL, 13.4 mmol, 3.50 equiv) in CH_2Cl_2 (30 mL) was added a solution of (1*S*)-(+)-10-camphorsulfonyl chloride (3.07 g, 12.3 mmol, 3.20 equiv) in CH_2Cl_2 (8 mL) at 0 °C over 10 min. The reaction mixture was allowed to warm to r.t., followed by stirring overnight. H_2O (10 mL) was added, the phases were separated, and the organic phase was dried (Na_2SO_4) and concentrated under reduced pressure. The crude (*SR*,*S*)-**11** (dr = 50:50) was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2/EtOAc (49:50:1) as eluent to afford the first eluting diastereomer (*S*,*S*)-**11** (805 mg, 48%, dr >99:1) as a yellow solid; mp 120 °C (*n*-pentane); R_f = 0.09 (cyclohexane/CH_2Cl_2 1:4).

IR (ATR, diamond): 2955 (w), 2924 (w), 2850 (w), 1744 (m), 1360 (m), 1162 (m), 1141 (m), 992 (m), 944 (m), 805 (m), 766 (s), 701 cm^{-1} (s).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 0.53 (s, 6 H), 0.79 (s, 6 H), 1.22–1.37 (m, 4 H), 1.79 (d, *J* = 18.4 Hz, 2 H), 1.82–1.88 (m, 2 H), 1.95 (t, *J* = 4.4 Hz, 2 H), 2.03–2.10 (m, 2 H), 2.22 (dt, *J* = 4.3, 18.6 Hz, 2 H), 2.54 (d, *J* = 14.9 Hz, 2 H), 2.96 (d, *J* = 14.9 Hz, 2 H), 7.39–7.52 (m, 8 H), 7.54–7.58 (m, 4 H), 7.62–7.64 (m, 4 H), 7.75 (s, 2 H), 8.03–8.05 (m, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 19.5, 19.6, 25.0, 26.9, 42.4, 42.9, 47.7, 49.2, 57.8, 122.4, 122.6, 126.6, 126.7, 127.2, 127.7, 128.1, 128.7, 130.3, 134.0, 139.2, 143.4, 145.4, 213.3.

HRMS (APCI): *m*/*z* $[M + H]^+$ calcd for $C_{52}H_{51}O_8S_2$: 867.3020; found: 867.2996.

(*S*)-(−)-4,4′-Diphenyl-[1,1′-binaphthalene]-2,2′-diol [(*S*)-10]

According to a reported procedure,[7] to a solution of (*S*)-**11** (805 mg, 0.928 mmol, 1.00 equiv) in MeOH (17 mL) was added a solution of NaOH (4.86 g, 122 mmol, 131 equiv) in H_2O (13 mL). The reaction mixture was stirred at 60 °C overnight and then cooled to r.t. The reaction was quenched by the addition of aq 1 M HCl (10 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL), the combined organic phases were dried (Na_2SO_4), and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/EtOAc (2:1) as eluent to afford (*S*)-**10** (408 mg, >99%, 99% ee) as a yellow solid.

HPLC: Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH (85:15), flow rate: 1.0 mL/min, λ = 250 nm; t_R = 10.9 min (minor-**10**), t_R = 19.8 min (major-**10**).

(*S*)-4,4′-Diphenyl-[1,1′-binaphthalene]-2,2′-diyl Bis(trifluoromethanesulfonate) [(*S*)-12]

According to a reported procedure,[7] to a solution of (*S*)-**10** (408 mg, 0.930 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) was added pyridine (0.29 mL, 3.5 mmol, 3.8 equiv) and Tf_2O (0.61 mL, 3.6 mmol, 3.9 mmol) dropwise at 0 °C. The reaction mixture was allowed to warm to r.t., followed by stirring overnight. The reaction was quenched by the addition of H_2O (10 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography on

silica gel using cyclohexane/CH_2Cl_2 (5:1) as eluent to afford (*S*)-**12** (563 mg, 86%) as a yellow solid; mp 72–75 °C (*n*-pentane); R_f = 0.33 (cyclohexane/CH_2Cl_2 5:1).

IR (ATR, diamond): 3059 (w), 1584 (w), 1416 (m), 1204 (s), 1134 (s), 983 (m), 943 (s), 822 (s), 764 (s), 700 (s), 658 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 7.43–7.47 (m, 4 H), 7.52–7.56 (m, 4 H), 7.58–7.63 (m, 10 H), 8.05 (d, *J* = 8.6 Hz, 2 H).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 118.3 (q, *J* = 319 Hz), 120.2, 122.7, 126.9, 127.4, 128.0, 128.5, 128.8 (2 C), 130.2, 131.0, 133.9, 138.8, 145.0, 145.0.

^{19}F NMR (470 MHz, $CDCl_3$): δ = –74.5 (s).

HRMS (APCI): *m*/*z* $[M + H]^+$ calcd for $C_{34}H_{21}F_6O_6S_2$: 703.0678; found: 703.0671.

(*S*)-2,2′-Dimethyl-4,4′-diphenyl-1,1′-binaphthalene [(*S*)-13]

According to a reported procedure,[7] to a suspension of (*S*)-**12** (563 mg, 0.801 mmol, 1.00 equiv) and Ni(dppp)Cl_2 (43 mg, 0.080 mmol, 0.10 equiv) in Et_2O (12 mL) was added MeMgBr (3 M in Et_2O, 2.4 mL, 7.2 mmol, 9.0 equiv) dropwise at 0 °C and the reaction mixture was stirred under reflux overnight. The reaction was quenched by the addition of ice cold aq 1 M HCl (10 mL), and the phases were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane as eluent to afford (*S*)-**13** (345 mg, 99%) as a yellow solid; mp 112–116 °C (*n*-pentane); R_f = 0.30 (cyclohexane).

IR (ATR, diamond): 3055 (w), 2917 (w), 2852 (w), 1590 (w), 1490 (w), 1440 (w), 1341 (w), 1029 (w), 884 (w), 764 (s), 699 (s), 679 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 2.12 (s, 6 H), 7.21–7.27 (m, 4 H),* 7.36 (m_c, 2 H), 7.46–7.49 (m, 4 H), 7.56 (m_c, 4 H), 7.63–7.65 (m, 4 H), 7.97 (d, *J* = 8.4 Hz, 2 H). * Signal overlapping of the $CDCl_3$ resonance (4 H expected).

^{13}C NMR (101 MHz, $CDCl_3$): δ = 20.3, 125.1, 126.1, 126.2, 126.2, 127.4, 128.4, 130.0, 130.4, 130.5, 133.3, 134.1, 134.9, 139.8, 141.1.

HRMS (APCI): *m*/*z* $[M]^{\bullet+}$ calcd for $C_{34}H_{26}$: 434.2029; found: 434.2037.

(*S*)-4,4-Diethoxy-1,7-diphenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*)-14]

To solution of (*S*)-**13** (348 mg, 0.801 mmol, 1.00 equiv) in Et_2O (6 mL) was added a hexane solution of *n*-BuLi (2.80 M, 1.43 mL, 4.01 mmol, 5.00 equiv) dropwise at 0 °C followed by TMEDA (0.60 mL, 4.0 mmol, 5.0 equiv). The reaction mixture was allowed to warm to r.t., stirred for 19 h, then diluted with THF (4 mL), and cooled to –78 °C. To this solution was added a solution of $(EtO)_2SiCl_2$ (0.725 mL, 4.33 mmol, 5.40 equiv) in THF (2 mL), and then the mixture was allowed to slowly warm to r.t., followed by stirring overnight. The reaction was quenched by the addition of H_2O (10 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (2:1 → 1:1) as eluent to afford the silepine (*S*)-**13** (169 mg, 38%) as a white solid; mp 105–110 °C (*n*-pentane); R_f = 0.29 (cyclohexane/CH_2Cl_2 1:1).

IR (ATR, diamond): 3055 (w), 2969 (w), 2878 w), 1588 (w), 1490 (w), 1339 (w), 1152 (m), 1101 (m), 1070 (s), 933 (m), 765 (s), 700 (s) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.18 (t, *J* = 7.0 Hz, 6 H), 2.22 (m_c, 4 H), 3.73–3.82 (m, 4 H), 7.19–7.24 (m, 4 H), 7.32 (m_c, 2 H), 7.44 (s, 2 H), 7.45–7.49 (m, 2 H), 7.55 (m_c, 4 H), 7.60–7.62 (m, 4 H), 7.94 (d, *J* = 8.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.6, 21.0, 59.2, 124.7, 125.9, 126.3, 127.1, 127.4, 128.4, 129.4, 130.2, 130.3, 132.5, 133.3, 134.6, 140.4, 141.0.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –6.4.

HRMS (APCI): *m*/*z* $[M]^{\bullet+}$ calcd for $C_{38}H_{34}O_2Si$: 550.2323; found: 550.2315.

(*S*)-1,7-Diphenyl-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*)-8]

To a solution of (*S*)-**14** (164 mg, 0.298 mmol, 1.00 equiv) in CH_2Cl_2 (3 mL) was added a *n*-pentane solution of DIBAL-H (2.0 M, 0.52 mL, 1.0 mmol, 3.5 equiv) dropwise at –78 °C over a period of 10 min, and the reaction mixture was then maintained at this temperature for 30 min. The mixture was then warmed to 0 °C, and stirred at this temperature for 3 h. $Na_2SO_4{\cdot}10H_2O$ (820 mg) was added, the ice bath was removed, and the suspension was stirred for 30 min at r.t. The suspension was filtered, the filter cake washed with CH_2Cl_2 (50 mL), and the solvent removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (9:1) as eluent to afford the silepine (*S*)-**8** (125 mg, 91%) as a white solid; mp >230 °C (*n*-pentane); R_f = 0.59 (cyclohexane/CH_2Cl_2 2:1).

IR (ATR, diamond): 3061 (w), 2904 (w), 2122 (s), 1586 (w), 1153 (m), 932 (s), 845 (s), 771 (s), 758 (s), 698 (s), 681 cm^{-1} (m).

^1H NMR (400 MHz, $CDCl_3$): δ = 2.18–2.25 (m, 4 H), 4.14–4.15 (m, 2 H), 7.20–7.27 (m, 4 H),* 7.32–7.37 (m, 2 H), 7.44 (s, 2 H), 7.46–7.50 (m, 2 H), 7.55 (m_c, 4 H), 7.63–7.65 (m, 4 H), 7.98 (d, *J* = 8.5 Hz, 2 H). * Signal overlapping of the $CDCl_3$ resonance (4 H expected).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 17.1, 124.8, 125.9, 126.3, 126.9, 127.5, 128.5, 128.6, 130.4, 130.4, 132.2, 133.3, 135.8, 140.6, 141.0.

^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ = –22.5.

HRMS (APCI): *m*/*z* $[M]^{\bullet+}$ calcd for $C_{34}H_{26}Si$: 462.1798; found: 462.1792.

Hydrosilanes (*S*,*S*)-17, (*S*,*S*)-18, and (*S*,*RS*)-21; General Procedure 2 (GP 2)

To a solution of the indicated thioether (1.00 equiv) in THF (0.03 M) cooled to –78 °C was added a solution of *n*-BuLi in *n*-hexane (1.10 equiv) dropwise, and the resulting mixture was maintained at –78 °C for 1 h. Indicated dihydrosilane (*S*)-**8** or (*S*)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine (1.00 equiv) dissolved in THF (0.11 M) was precooled to –78 °C and quickly added, and the mixture was subsequently allowed to warm to r.t., followed by stirring overnight. The reaction was quenched by the addition of H_2O. The aqueous phase was extracted with CH_2Cl_2 (3 ×), and the combined organic phases were dried (Na_2SO_4). The solvents were removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using *n*-pentane/CH_2Cl_2 mixtures as eluent to afford the respective hydrosilanes.

(4*S*,11b*S*)-1,7-Diphenyl-4-{2′-(phenylthio)-[1,1′-binaphthalen]-2-yl}-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*,*S*)-17]

Prepared according to GP 2 from contaminated thioether (*S*)-**15** (66 mg, mixture of the thioether and the hydrodehalogenated derivative in a ratio of ~5:1) and dihydrosilane (*S*)-**8** (54 mg, 0.116 mmol) in 35% yield (34 mg, calculated with the mass of the pure thioether). The

hydrosilane (*S*,*S*)-**17** was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10:1) as eluent; mp 176–182 °C (*n*-pentane); R_f = 0.21 (cyclohexane/CH_2Cl_2 5:1).

IR (ATR, diamond): 3051 (w), 2917 (w), 2129 (w), 1583 (w), 1338 (w), 1151 (m), 811 (s), 766 (s), 744 (s), 700 cm^{-1} (s).

^{1}H NMR (400 MHz, C_6D_6): δ = 1.94 (dd, *J* = 13.3, 1.5 Hz, 1 H), 2.33 (dd, *J* = 2.7, 13.5 Hz, 1 H), 2.49 (dd, *J* = 13.5, 7.3 Hz, 1 H), 2.63 (d, *J* = 13.6 Hz, 1 H), 4.40–4.43 (m, 1 H), 6.83–6.89 (m, 4 H), 6.94–7.05 (m, 5 H), 7.09–7.29 (m, 12 H),* 7.32 (d, *J* = 8.8 Hz, 1 H), 7.36–7.43 (m, 3 H), 7.47–7.56 (m, 5 H), 7.63–7.65 (m, 2 H), 7.69–7.75 (m, 3 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 8.21 (d, *J* = 8.2 Hz, 1 H). * Signal overlapping of the C_6D_6 resonance (12 H expected).

The following of the expected 60 ^{13}C NMR resonances were detected:

^{13}C NMR (101 MHz, C_6D_6): δ = 20.4, 20.7, 125.1, 125.2, 125.9, 126.3, 126.4, 126.7, 126.7, 126.8, 126.9, 127.1, 127.4, 127.4, 127.5, 128.5, 128.6, 128.7, 129.0, 129.0, 129.2, 129.5, 130.2, 130.6, 130.6, 130.9, 130.9, 131.4, 132.1, 132.9, 133.0, 133.0, 133.1, 133.4, 133.8, 133.8, 134.6, 135.1, 136.1, 136.2, 136.4, 136.7, 140.6, 140.9, 141.2, 141.5, 144.4.

^{29}Si DEPT NMR (99 MHz, C_6D_6): δ = –7.5.

HRMS (APCI): *m*/*z* [M – H]$^+$ calcd for $C_{60}H_{41}SSi$: 821.2693; found: 821.2691.

(4*S*,11b*S*)-1,7-Diphenyl-4-{2′-(phenylthio)-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalen]-2-yl}-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*,*S*)-18]

Prepared according to GP 2 from contaminated thioether (*S*)-**16** (82 mg, mixture of the thioether and the hydrodehalogenated derivative in a ratio of ~3:1) and dihydrosilane (*S*)-**8** (56 mg, 0.121 mmol) in 10% yield (9.5 mg, calculated with the mass of the pure thioether). The hydrosilane (*S*,*S*)-**18** was obtained as a white solid after flash column chromatography on silica gel (3 runs) using cyclohexane/CH_2Cl_2 (10:1) as eluent; mp 135–140 °C (*n*-pentane); R_f = 0.27 (cyclohexane/CH_2Cl_2 5:1)

IR (ATR, diamond): 2919 (w), 2851 (w), 2114 (w), 1580 (w), 1338 (w), 1150 (w), 835 (m), 765 (m), 748 (m), 700 cm^{-1} (s).

^{1}H NMR (700 MHz, C_6D_6): δ = 1.23–1.41 (m, 4 H),* 1.51–1.62 (m, 4 H), 2.12 (d, *J* = 13.2 Hz, 1 H), 2.14–2.21 (m, 2 H), 2.30–2.35 (m, 2 H), 2.41–2.48 (m, 3 H), 2.57 (d, *J* = 13.7 Hz, 1 H), 2.63–2.67 (m, 3 H), 4.63–4.65 (m, 1 H), 6.74 (d, *J* = 8.3 Hz, 1 H), 6.89–6.93 (m, 3 H), 7.00–7.03 (m, 4 H), 7.12–7.15 (m, 3 H), 7.20–7.23 (m, 3 H), 7.24–7.27 (m, 3 H), 7.39–7.40 (m, 2 H), 7.51 (s, 1 H), 7.53–7.54 (m, 2 H), 7.57 (d, *J* = 8.6 Hz, 1 H), 7.59–7.60 (m, 2 H), 7.61 (d, *J* = 8.6 Hz, 1 H), 7.78 (s, 1 H), 8.11 (d, *J* = 8.3 Hz, 1 H), 8.16 (d, *J* = 8.3 Hz, 1 H). * Signal overlapping of the *n*-pentane and H grease resonances (4 H expected).

The following of the expected 60 ^{13}C NMR resonances were detected:

^{13}C NMR (176 MHz, C_6D_6): δ = 20.5, 20.6, 23.0, 23.1, 23.6, 23.8, 27.6, 28.5, 29.9, 30.5, 125.1, 125.1, 126.0, 126.3, 126.3, 126.8, 126.8, 127.4, 127.4, 127.5, 128.6, 128.6, 128.6, 129.1, 129.3, 129.5, 129.7, 130.1, 130.3, 130.6, 130.7, 130.8, 131.0, 132.9, 133.0, 133.5, 133.5, 133.8, 133.9, 133.9, 134.8, 135.0, 135.4, 135.6, 136.2, 136.6, 136.7, 140.1, 140.3, 140.5, 140.9, 141.5, 141.5, 145.9.

^{29}Si DEPT NMR (99 MHz, C_6D_6): δ = –7.5.

HRMS (APCI): *m*/*z* [M – H]$^+$ calcd for $C_{60}H_{49}SSi$: 829.3319; found: 829.3311.

(4*S*,11b*S*)-4-{7′-(Phenylthio)-2,2′,3,3′-tetrahydro-1,1′-spirobi[inden]-7-yl}-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*,*RS*)-21]

Prepared according to GP 2 from contaminated thioether *rac*-**20** (36 mg, mixture of the thioether and the hydrodehalogenated derivative in a ratio of ~1:1.1) and (*S*)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine (15 mg, 0.048 mmol). The hydrosilane (*S*,*RS*)-**21** (dr = 55:45) was obtained together with an unidentified silicon compound (^{29}Si NMR: δ = 32.0) as a white solid after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10:1) as eluent; R_f = 0.14 (cyclohexane/CH_2Cl_2 5:1).

^{1}H NMR (700 MHz, C_6D_6): δ = 1.99 (dd, *J* = 1.6, 13.4 Hz, 1 H), 2.02 (d, *J* = 14.0 Hz, 1 H), 2.05–2.12 (m, 3 H), 2.18–2.22 (m, 2 H), 2.23–2.26 (m, 1 H), 2.28 (d, *J* = 13.2 Hz, 1 H), 2.31–2.36 (m, 2 H), 2.45–2.48 (m, 2 H), 2.51 (dd, *J* = 7.5, 13.2 Hz, 1 H), 2.76–2.92 (m, 10 H), 4.11–4.13 (m, 1 H), 4.33–4.34 (m, 1 H), 6.69–6.72 (m, 1 H), 6.77–6.78 (m, 1 H), 6.82 (d, *J* = 8.3 Hz, 1 H), 6.83–6.84 (m, 2 H), 6.86–7.01 (m, 11 H), 7.02–7.05 (m, 1 H), 7.09–7.21 (m, 11 H),* 7.24 (d, *J* = 8.3 Hz, 1 H), 7.27–7.29 (m, 2 H), 7.30 (d, *J* = 8.5 Hz, 1 H), 7.39 (m_c, 2 H), 7.42–7.46 (m, 3 H), 7.60 (d, *J* = 8.1 Hz, 1 H), 7.66–7.68 (m, 3 H), 7.76–7.82 (m, 5 H). * Signal overlapping of C_6D_6 resonance (11 H expected).

The following of the expected 90 ^{13}C NMR resonances were detected:

^{13}C NMR (176 MHz, C_6D_6): δ = 20.8, 20.8, 21.4, 22.6, 31.4, 31.4, 31.4, 31.4, 37.5, 37.5, 40.6, 40.8, 63.8, 63.8, 122.9, 123.1, 124.7, 124.8, 124.9, 126.3, 126.3, 126.4, 126.4, 126.6, 126.7, 126.8, 126.8, 126.9, 126.9, 127.0, 127.1, 127.5, 127.5, 128.5, 128.5, 128.5, 128.6, 128.7, 128.7, 128.7, 128.9, 128.9, 129.2, 129.3, 129.3, 129.4, 129.5, 131.1, 132.6, 132.7, 132.7, 132.7, 132.9, 133.0, 133.1, 133.2, 133.3, 133.3, 133.4, 133.4, 133.4, 133.5, 133.5, 133.7, 134.7, 135.2, 135.7, 136.0, 136.2, 136.8, 136.8, 136.8, 137.1, 143.5, 143.5, 145.5, 145.6, 149.3, 149.5, 156.1, 156.6.

^{29}Si DEPT NMR (99 MHz, C_6D_6): δ = –10.8, –11.2.

HRMS (APCI): *m*/*z* [M – H]$^+$ calcd for $C_{45}H_{35}SSi$: 635.2223; found: 635.2229.

Generation of Intramolecularly Sulfur-Stabilized Silicon Cations; General Procedure 3 (GP 3)

In a glovebox, a solution of the indicated hydrosilane (1.00 equiv) in 1,2-$Cl_2C_6D_4$ (0.4 mL) was added to a solution of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (1.00 equiv) in 1,2-$Cl_2C_6D_4$ (0.2 mL) in an 8 mL vial. The resulting mixture is transferred to a Young NMR tube, and directly subjected to NMR spectroscopic analysis.

(4*S*,11b*S*)-1,7-Diphenyl-4-{2′-(phenylthio)-[1,1′-binaphthalen]-2-yl}-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepinylium Tetrakis(pentafluorophenyl)borate [(*S*,*S*)-6]

Prepared according to GP 3 from (*S*,*S*)-**17** (7.8 mg, 9.4 µmol, 1.0 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (8.7 mg, 9.4 µmol, 1.0 equiv).

^{1}H NMR (700 MHz, 1,2-$Cl_2C_6D_4$): δ = 1.44 (d, *J* = 15.4 Hz, 1 H), 2.34 (d, *J* = 15.4 Hz, 1 H), 3.05 (d, *J* = 14.5 Hz, 1 H), 3.13 (d, *J* = 14.5 Hz, 1 H), 6.50 (d, *J* = 7.5 Hz, 2 H), 6.66 (m_c, 2 H), 6.76–6.79 (m, 1 H), 6.98–7.53 (m, 11 H),* 7.55–7.62 (m, 6 H), 7.65–7.71 (m, 7 H), 7.77–7.81 (m, 4 H), 7.98 (d, *J* = 8.4 Hz, 1 H), 8.08–8.13 (m, 3 H). * Signal overlapping of 1,2-$Cl_2C_6D_4$, benzene, Ph_3CH and remaining $[Ph_3C]^+[B(C_6F_5)_4]^-$ resonances (11 H expected).

The following of the expected 84 ^{13}C NMR resonances were detected:

^{13}C NMR (176 MHz, 1,2-$Cl_2C_6D_4$): δ = 19.4, 20.2, 113.9, 120.3, 122.5, 124.8 (br m, *ipso*-C-$[B(C_6F_5)_4]^-$), 125.8, 126.0, 126.2, 126.7, 126.7, 126.9, 126.9, 128.0, 128.2, 128.4, 128.9, 129.0, 129.1, 129.2, 129.3,

130.6, 131.0, 131.2, 131.5, 131.6, 131.7, 133.1, 133.6, 133.7, 136.8 (d, $^1J_{C,F}$ = 251 Hz, *m*-*C*F-[$B(C_6F_5)_4]^-$), 136.9, 138.7 (d, $^1J_{C,F}$ = 243 Hz, *p*-*C*F-[$B(C_6F_5)_4]^-$), 139.8, 140.1, 140.7, 141.2, 142.9, 143.1, 148.9 (d, $^1J_{C,F}$ = 243 Hz, *o*-*C*F-[$B(C_6F_5)_4]^-$).

^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ = –16.4 (s).

^{19}F NMR (470 MHz, 1,2-$Cl_2C_6D_4$): δ = –166.1 (m_c), –162.3 (m_c), –131.7 (m_c).

^{1}H,^{29}Si HMQC NMR (500/99 MHz, 1,2-$Cl_2C_6D_4$): δ = 1.44, 2.35, 3.05, 3.13/39.9.

(4*S*,11b*S*)-1,7-Diphenyl-4-{2′-(phenylthio)-5,5′,6,6′,7,7′,8,8′-octahydro-[1,1′-binaphthalen]-2-yl}-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepinylium Tetrakis(pentafluorophenyl)borate [(*S*,*S*)-7]

Prepared according to GP 3 from (*S*,*S*)-**18** (4.4 mg, 5.3 µmol, 1.0 equiv] and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (4.9 mg, 5.3 µmol, 1.0 equiv).

^{1}H NMR (700 MHz, 1,2-$Cl_2C_6D_4$): δ = 1.09–1.68 (m, 7 H),* 1.74–1.78 (m, 1 H), 2.01–2.05 (m, 1 H), 2.35–2.41 (m, 2 H), 2.49–2.55 (m, 3 H), 2.66–2.73 (m, 2 H), 2.74–2.80 (m, 2 H), 2.98 (d, *J* = 14.6 Hz, 1 H), 3.01 (d, *J* = 14.6 Hz, 1 H), 6.56 (d, *J* = 7.9 Hz, 2 H), 6.79 (d, *J* = 7.6 Hz, 1 H), 7.03–7.39 (m, 9 H),** 7.47–7.48 (m, 3 H), 7.52–7.56 (m, 4 H), 7.62–7.65 (m, 5 H), 7.72 (d, *J* = 8.2 Hz, 1 H), 7.75 (d, *J* = 6.4 Hz, 2 H), 8.05 (d, *J* = 8.5 Hz, 1 H), 8.10 (d, *J* = 8.5 Hz, 1 H). * Signal overlapping of *n*-pentane, H grease and unidentified impurities resonances [7 H expected, including the signal of the silepine methylene proton at δ = 1.46 (d, *J* = 15.1 Hz, 1 H)]; ** Signal overlapping of 1,2-$Cl_2C_6D_4$, benzene, Ph_3CH, remaining $[Ph_3C]^+[B(C_6F_5)_4]^-$ and unidentified impurities resonances (9 H expected).

The following of the expected 84 ^{13}C NMR resonances were detected:

^{13}C NMR (176 MHz, 1,2-$Cl_2C_6D_4$): δ = 19.8, 20.5, 21.7, 22.0, 22.0, 22.2, 27.5, 28.5, 29.8, 30.1, 114.1, 120.2, 122.6, 124.7 (br m, *ipso*-*C*-[$B(C_6F_5)_4]^-$), 126.8, 127.0, 128.9, 129.0, 129.1, 131.2, 131.5, 131.7, 131.9, 133.5, 133.6, 133.6, 136.8 (d, $^1J_{C,F}$ = 247 Hz, *m*-*C*F-[$B(C_6F_5)_4]^-$), 138.6, 138.7 (d, $^1J_{C,F}$ = 249 Hz, *p*-*C*F-[$B(C_6F_5)_4]^-$), 139.4, 139.9, 140.1, 140.8, 141.2, 142.7, 142.9, 143.4, 145.6, 148.4, 148.8 (d, $^1J_{C,F}$ = 242 Hz, *o*-*C*F-[$B(C_6F_5)_4]^-$).

^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ = –16.5 (s).

^{19}F NMR (470 MHz, 1,2-$Cl_2C_6D_4$): δ = –166.0 (m_c), –162.2 (m_c), –131.6 (m_c).

^{1}H,^{29}Si HMQC NMR (500/99 MHz, 1,2-$Cl_2C_6D_4$): δ = 1.46, 2.49–2.55, 2.98, 3.01/40.9.

(4*S*,11b*S*)-4-{7′-(Phenylthio)-2,2′,3,3′-tetrahydro-1,1′-spirobi[inden]-7-yl}-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepinylium Tetrakis(pentafluorophenyl)borate [(*S*,*RS*)-19]

Prepared according to GP 3 from (*S*,*RS*)-**21** (10.0 mg, 1.0 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (14.5 mg, 15.7 µmol, 1.0 equiv).

Selected NMR spectroscopic data for (*S*,*RS*)-**19**

^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ = – 16.1 (s).

^{19}F NMR (470 MHz, 1,2-$Cl_2C_6D_4$): δ = –166.0 (m_c), –162.3 (m_c), –131.6 (m_c).

Diels–Alder Reaction of Cyclohexa-1,3-diene (1) and Chalcone (2) Catalyzed by Sulfur-Stabilized Silicon Cations; General Procedure 4 (GP 4)

In a glovebox, a GC vial equipped with a magnetic stir bar was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (2.50 or 5.00 mol%). After addition of 1,2-$Cl_2C_6H_4$ (0.034 or 0.12 M), a solution of the indicated hydrosilane (3.00 or 5.50 mol%) in 1,2-$Cl_2C_6H_4$ (0.021 or 0.070 M) was added, and the resulting mixture was stirred for 30 min at r.t. Then, a solution of cyclohexa-1,3-diene (**1**; 2.10 equiv) and chalcone (**2**; 1.00 equiv) in 1,2-$Cl_2C_6H_4$ (0.20 or 0.83 M) was added dropwise and the reaction mixture was stirred at r.t. for 3 h. The crude mixture was purified by flash column chromatography on silica gel to afford the Diels–Alder cycloadduct **3**.

***endo*-Phenyl(3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (3)**

Prepared according to GP 4 from chalcone (**2**; 14.4 mg, 0.069 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**; 11.6 mg, 0.145 mmol, 2.10 equiv) in 1,2-$Cl_2C_6H_4$ (0.50 mL) with silicon cation (*S*,*S*)-**6** (2.50 mol%). The cycloadduct **3** [17 mg (85%), *endo*:*exo* >95:5, dr >95:5, 46% ee] was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (4:1) as eluent.

Prepared according to GP 4 from chalcone (**2**; 14.4 mg, 0.069 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**; 11.6 mg, 0.145 mmol, 2.10 equiv) in 1,2-$Cl_2C_6H_4$ (0.50 mL) with silicon cation (*S*,*S*)-**7** (2.50 mol%). The cycloadduct **3** [16.5 mg (83%), *endo*:*exo* >95:5, dr >95:5, 64% ee] was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (4:1) as eluent.

Prepared according to GP 4 from chalcone (**2**; 51.9 mg, 0.249 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**1**; 50.0 µL, 0.523 mmol, 2.10 equiv) in 1,2-$Cl_2C_6H_4$ (0.50 mL) with silicon cation (*S*,*RS*)-**19** (5.00 mol%). The cycloadduct **3** [62 mg (86%), *endo*:*exo* >95:5, dr >95:5, 34% ee] was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (4:1) as eluent.

Mp 120–122 °C (cyclohexane); R_f = 0.33 (cyclohexane/EtOAc 20:1)

HPLC: Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH (97:3), flow rate: 0.65 mL/min, λ = 250 nm; t_R = 9.9 min (major-**3**), t_R = 11.6 min (minor-**3**).

^{1}H NMR (500 MHz, $CDCl_3$): δ = 1.11–1.16 (m, 1 H), 1.49 (m_c, 1 H), 1.81–1.87 (m, 1 H), 1.88–1.94 (m, 1 H), 2.67–2.69 (m, 1 H), 2.98–2.99 (m, 1 H), 3.49–3.50 (m, 1 H), 3.81–3.82 (m, 1 H), 6.13 (m_c, 1 H), 6.58 (m_c, 1 H), 7.20–7.23 (m, 1 H), 7.29–7.34 (m, 4 H), 7.38–7.41 (m, 2 H), 7.49–7.52 (m, 1 H), 7.88 (d, *J* = 7.4 Hz, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$): δ = 18.7, 26.6, 34.7, 36.6, 44.9, 51.1, 126.3, 128.2, 128.6 (2C), 128.6, 130.8, 132.8, 136.4, 136.6, 143.0, 200.9.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{21}H_{21}O$: 289.1587; found: 289.1582.

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Supporting Information

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