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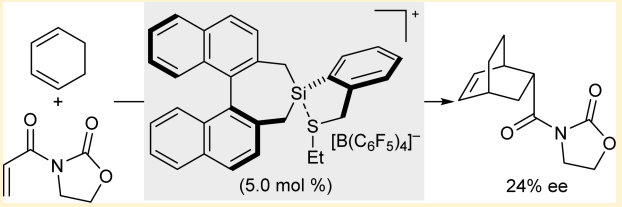
Intramolecularly Sulfur-Stabilized Silicon Cations with Chiral Binaphthyl Backbones: Synthesis of Three Different Motifs and Their Application in Enantioselective Diels–Alder Reactions

Volker H. G. Rohde,[†] Maria F. Müller,[†] and Martin Oestreich*

Institut für Chemie, Technische Universität Berlin, Straße des 17. Juni 115, 10623 Berlin, Germany

Supporting Information

ABSTRACT: The formation and ^{29}Si NMR spectroscopic characterization of silicon cations that are intramolecularly stabilized by a dialkyl thioether are described. The chemical stability of the silicon–sulfur Lewis pair and, hence, the viability of the approach, were probed with a 2-[(alkylthio)methyl]phenyl-substituted hydrosilane as a proxy before three different motifs with chiral binaphthyl backbones were prepared in multistep sequences. The degree of shielding of the silicon atom in these cations was found to depend on the substitution pattern at the silicon atom and the ring size generated by the silicon–sulfur interaction. These sulfur-stabilized silicon cations are sufficiently reactive to promote Diels–Alder reactions of cyclohexa-1,3-diene with various dienophiles; the same set of reactions with cyclopentadiene is also reported. One of the three chiral Lewis acids induces low, but promising, enantioselectivity, and 24% ee is the highest value so far obtained with a cationic tetracoordinate silicon catalyst.



INTRODUCTION

Lewis acids, including those based on silicon,[1] are widely used as catalysts in synthetic chemistry.[2] However, the number of structurally defined, chiral silicon Lewis acid catalysts is small (Figure 1). The seminal work in this field was done by Ghosez and co-workers, who accomplished an enantioselective Diels–Alder reaction with terpene-derived triflimide **1** as catalyst.[3] The methoxymethyl group in **1** in the proximity of the silicon atom was shown to be vital for achieving enantioinduction. Hatanaka and co-workers recently obtained a similar result with binaphthyl-derived triflimide **3**,[4] whereas related iodide **2** did not induce any enantioselectivity.[5] Leighton and co-workers further advanced the field by introducing fully heteroatom-substituted **4** with strain-release Lewis acidity.[6] It catalyzes Diels–Alder reactions of cyclopentadiene and selected α,β-unsaturated aldehydes with excellent enantioselectivities. These neutral tetracoordinate silicon compounds are sufficiently Lewis acidic to promote Diels–Alder reactions of reactive 1,3-dienes such as cyclopentadiene. To make, for example, less reactive cyclohexa-1,3-diene amenable to catalysis with silicon Lewis acids, the development of cationic catalysts is the logical next step, but there is little precedence for this. Jørgensen, Helmchen, and co-worker disclosed an enantioselective Diels–Alder reaction catalyzed by the acetonitrile-stabilized silicon cation or silylnitrilium ion **5**.[7] The enantiomeric excess obtained is low but still the only one reported for a cationic tetracoordinate silicon Lewis acid.[8,9]

As part of our ongoing research, we recently reported the synthesis of intramolecularly sulfur-stabilized silicon cation **6** with a planar chiral ferrocenyl substituent (Figure 2, left).[10] Its ability to act as a Lewis acid catalyst was demonstrated in the difficult Diels–Alder reaction of cyclohexa-1,3-diene and chalcone, but no asymmetric induction was seen.

Since the silicon–sulfur interaction tames this and related silicon cations **7a–7d** (see Figure 2, right) while preserving their reactivity,[10] we envisioned chiral backbones other than ferrocene. Axially chiral binaphthyl groups seemed viable alternatives as there is ample precedence for highly enantioselective Diels–Alder reactions catalyzed by binaphthol- and binaphthyl-derived Lewis acids based on aluminum and boron.[11−13] Consequently, we opted for motifs (*S*)-**8** and (*R*)-**9** with the hydrosilane unit and the pending sulfur donor attached to either the 2- and 2′- or the 2- and 3-positions of the binaphthyl backbone (Figure 3, top). Inspired by cation **5** (Figure 1, bottom right), we also targeted the axially chiral dihydrosilepine (*S*)-**10** with a 2-[(alkylthio)methyl]phenyl group installed at the silicon atom (Figure 3, bottom).

Different from our previous work,[10] we aimed to accomplish stabilization by acyclic rather than cyclic dialkyl thioethers (cf. 1,3-dithiolan-2-yl and 1,3-dithian-2-yl substituents in **6** and **7a–7d**, respectively, Figure 2). Even though Olah and co-workers had not been able to generate the intermolecular Lewis pair of the trimethyl silicon cation and dimethylsulfide,[14] we hoped that the corresponding intramolecular adducts would be chemically stable due to the formation of seven- (as in (*S*)-**8**) or five-membered rings (as in (*R*)-**9** and (*S*)-**10**). This assumption was supported by a recent study of the beneficial effect of the formation of common-sized rings to stabilize silicon cations.[15] In this article, we report the preparation and

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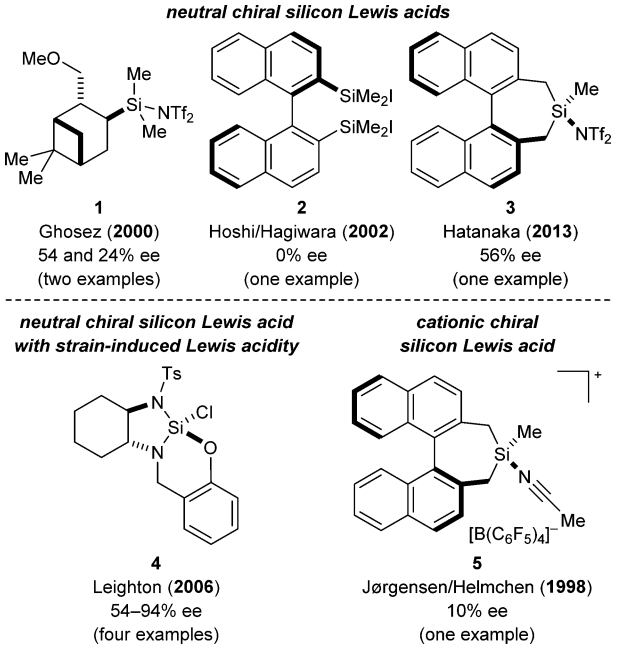


Figure 1. Reported neutral (top and bottom left) and cationic (bottom right) chiral tetracoordinate silicon Lewis acid catalysts. Enantiomeric excesses refer to the highest enantioselectivity achieved in a Diels–Alder reaction.

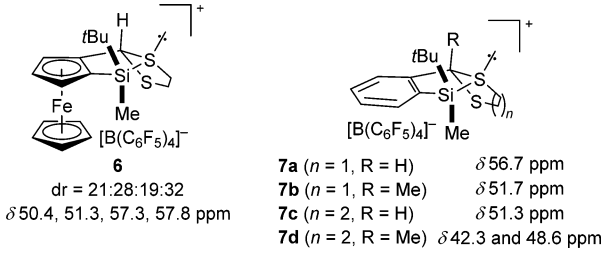


Figure 2. Intramolecularly sulfur-stabilized silicon cations based on a planar chiral ferrocene platform (left) or a benzene platform (right).

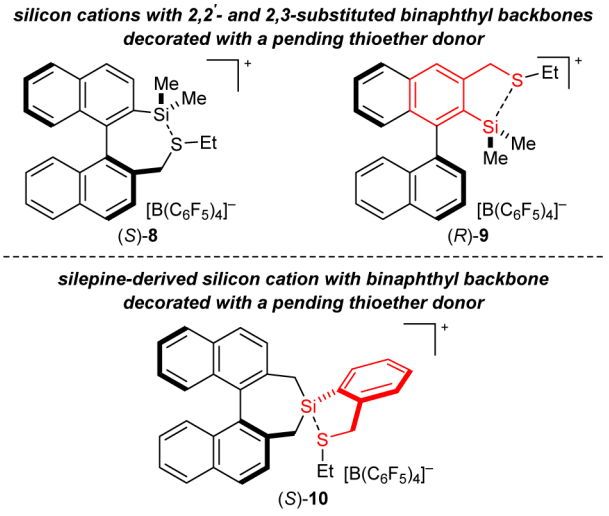


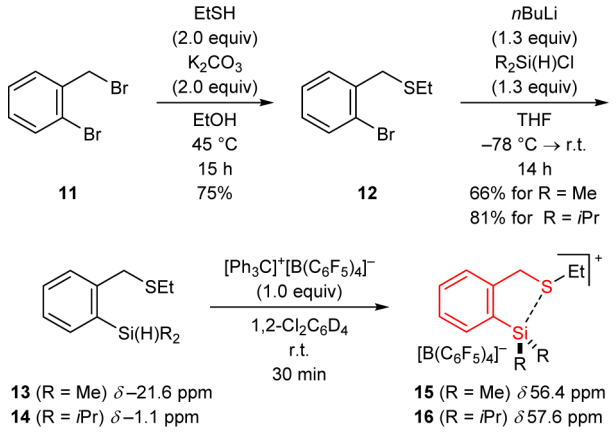
Figure 3. Sulfur-stabilized silicon cations with chiral binaphthyl backbones.

NMR-spectroscopic characterization of chiral silicon cations that are intramolecularly stabilized by a tethered thioether donor. The catalytic activity and asymmetric induction of these new silicon Lewis acids are assessed in difficult Diels–Alder reactions of cyclohexa-1,3-diene[16] and cycloadditions of more reactive cyclopentadiene.

RESULTS AND DISCUSSION

Achiral Sulfur-Stabilized Silicon Cations as Model Compounds. Before preparing the precursors for silicon cations (*S*)-**8**, (*R*)-**9**, and (*S*)-**10** in multistep sequences, we synthesized hydrosilanes **13** and **14** with the 2-[(ethylthio)-methyl]phenyl group (Scheme 1). With the thioether unit

Scheme 1. Preparation of Precursors with a Benzene Platform and Silicon Cation Generation



installed ortho to the silicon atom, we would be able to find out whether this motif lends sufficient stabilization to the electron-deficient tricoordinate silicon atom. Dimethyl-substituted **13** and diisopropyl-substituted **14** were prepared starting from 1-bromo-2-(bromomethyl)benzene (**11**). After base-mediated thioether formation (**11** → **12**), **13** and **14** were accessed in good yields by bromine–lithium exchange followed by trapping with $R_2Si(H)Cl$ (**12** → **13** for R = Me and **12** → **14** for R = *i*Pr). These substitution patterns at the silicon atom were chosen to evaluate the influence of steric bulk around the silicon atom on Lewis pair formation.

The generation of sulfur-stabilized silicon cations **15** and **16** was achieved by hydride abstraction from **13** and **14** with trityl tetrakis(pentafluorophenyl)borate, $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Scheme 1). Both were stable in 1,2-$Cl_2C_6D_4$ for weeks with little decomposition. The ^{29}Si NMR spectra showed resonance signals at δ 56.4 ppm for **15** and δ 57.6 ppm for **16**, and these are significantly shifted to higher frequencies compared to the respective hydrosilane, δ −21.6 ppm for **13** and δ −1.1 ppm for **14**.[17] The substituents at the silicon atom had no effect on the degree of deshielding of the silicon atom in **15** and **16**.[18] However, the resonance signals of the diastereotopic protons at each of the methylene groups attached to the sulfur atom show significant line broadening in the ^{1}H NMR spectra of **15** and **16**. This is more pronounced for **15** with the Me_2Si group than for **16** with the iPr_2Si group, indicating that increased steric bulk retards solvent-induced equilibration of the enantiomeric silicon–sulfur Lewis pairs with either of the lone pairs at the sulfur atom.

Synthesis of Thioether-Containing Hydrosilanes with Chiral Binaphthyl Backbones. The above model system proves that Lewis pairs composed of a silicon cation and a tethered dialkyl thioether are chemically robust. Moreover, the

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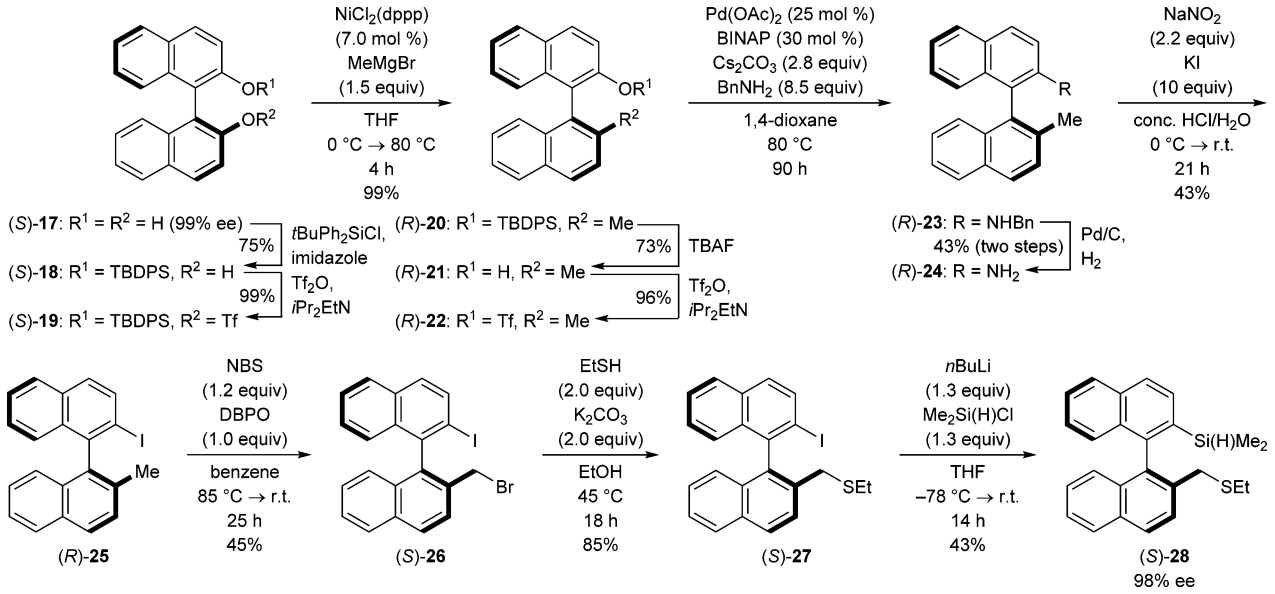
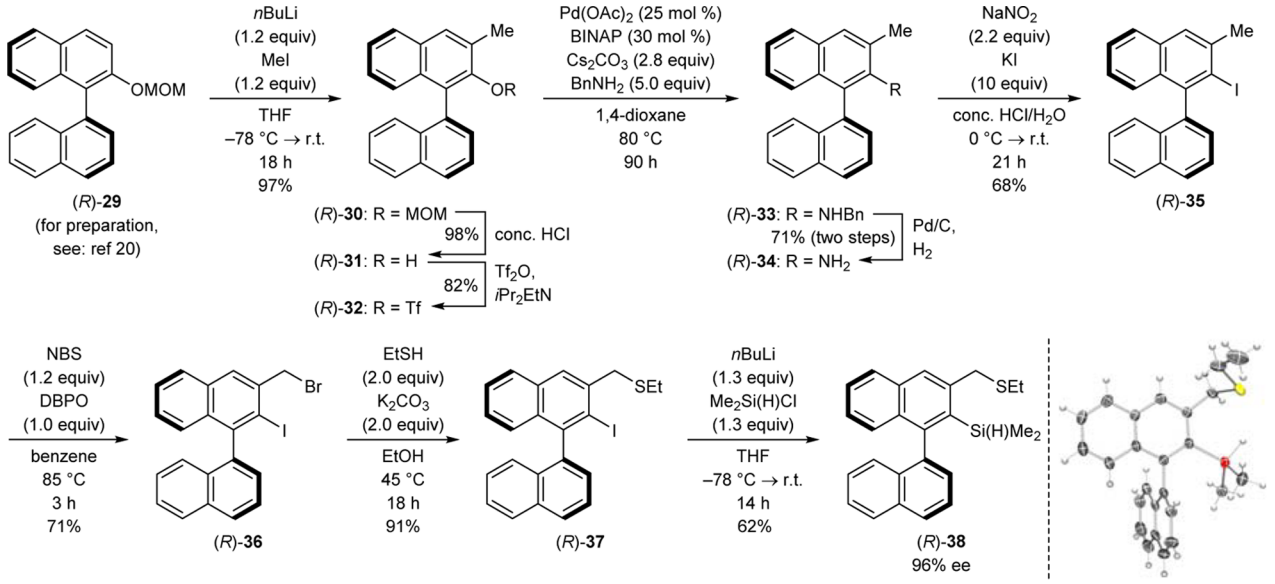
Scheme 2. Preparation of the Precursor with the 2,2′-Disubstituted Binaphthyl Backbone



Scheme 3. Preparation of the Precursor with the 2,3-Disubstituted Binaphthyl Backbone and Its Molecular Structure (ORTEP Plot Rendered with POV-Ray)



solvent rapidly scrambles the stereogenicity established at the sulfur atom with the sterically accessible Me_2Si group. Hence, we continued with the synthesis of Me_2Si-based systems with chiral binaphthyl backbones where solvent-promoted epimerization at the sulfur atom would be feasible. For this, new synthetic routes to the hydrosilanes that serve as precursors for (*S*)-**8**, (*R*)-**9**, and (*S*)-**10** depicted in Figure 3 had to be designed (Schemes 2–4).

The preparation of hydrosilane (*S*)-**28** with a 2,2′-disubstituted binaphthyl backbone commenced with five routine functional-group manipulations at (*S*)-BINOL [(*S*)-**17**, Scheme 2]: monoprotection with TBDPSCl [(*S*)-**17** → (*S*)-**18**], triflation of the remaining phenol [(*S*)-**18** → (*S*)-**19**], nickel(0)-catalyzed methylation of that triflate [(*S*)-**19** → (*R*)-**20**], deprotection of the TBDPS ether [(*R*)-**20** → (*R*)-**21**], and triflation of the liberated hydroxy group [(*R*)-**21** → (*R*)-**22**]. Intermediate (*R*)-**22** was obtained in 52% overall yield.[19]

The triflate group in (*R*)-**22** was then converted into iodide (*R*)-**25** by a three-step sequence. Buchwald–Hartwig amination with benzylamine furnished (*R*)-**23**, and reductive debenzylation afforded the free amine (*R*)-**24** [(*R*)-**22** → (*R*)-**23** → (*R*)-**24**]. Iodide (*R*)-**25** was subsequently obtained by a Sandmeyer-type reaction of amine (*R*)-**24** [(*R*)-**24** → (*R*)-**25**]. Radical bromination of the benzylic position in (*R*)-**25** yielded (*S*)-**26** that was transformed into thioether (*S*)-**27** [(*R*)-**25** → (*S*)-**26** → (*S*)-**27**]. (*S*)-**27** was then subjected to the usual iodine–lithium exchange, followed by the addition of $Me_2Si(H)Cl$ as the electrophile [(*S*)-**27** → (*S*)-**28**], affording hydrosilane (*S*)-**28** in 11 steps from (*S*)-**17** in 1.6% overall yield. The enantiomeric purity of (*S*)-**28** was 98% ee by comparison with a racemic sample.

Hydrosilane (*R*)-**38** with a 2,3-disubstituted binaphthyl backbone was prepared starting from the known MOM-protected alcohol (*R*)-**29**[20] (Scheme 3). Directed ortho

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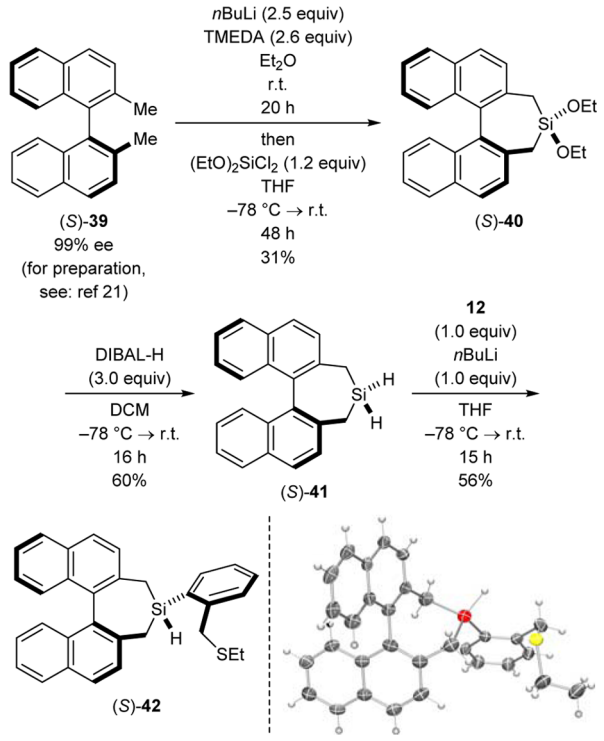
metalation of (*R*)-**29** and trapping with methyl iodide gave (*R*)-**30** [(*R*)-**29** → (*R*)-**30**]. Acid-mediated cleavage of the MOM group was followed by triflation of the unprotected phenol [(*R*)-**30** → (*R*)-**31** → (*R*)-**32**]. Advanced intermediate (*R*)-**32** was then subjected to the same sequence elaborated for the synthesis of 2,2′-disubstituted (*S*)-**28** from (*R*)-**22** (see Scheme 2). By this, hydrosilane (*R*)-**38** was obtained in nine steps from (*R*)-**29** in 15% overall yield (9.6% yield starting from (*S*)-BINOL (*S*)-**17**), and its enantiomeric purity was 96% ee by comparison with a racemic sample. The molecular structure of (*R*)-**38** was secured by X-ray diffraction and is included in Scheme 3. It is worthy of note that especially the late-stage transformations were substantially higher yielding for 2,3-disubstituted (*R*)-**38** (19% for (*R*)-**32** → (*R*)-**38**) compared to 2,2′-disubstituted (*S*)-**28** (3.0% for (*R*)-**22** → (*S*)-**28**).

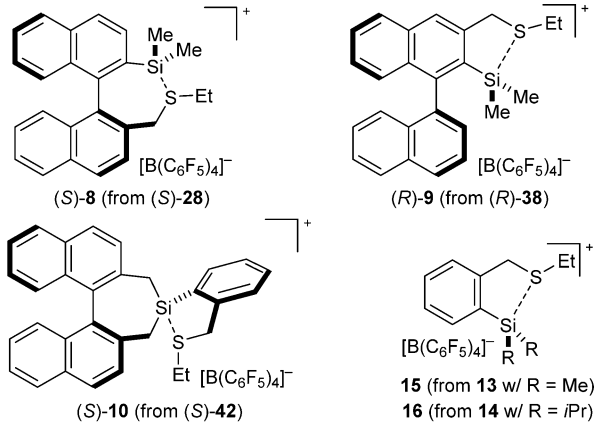
We next focused on the synthesis of dihydrosilepine (*S*)-**42** that was made from literature-known 2,2′-dimethyl-substituted (*S*)-**39**[21] (Scheme 4). From this, diethoxy-substituted (*S*)-**40**

Scheme 4. Preparation of the Dihydrosilepine Precursor with a 2-[(Ethylthio)methyl]phenyl Group Installed at the Silicon Atom and Its Molecular Structure (ORTEP Plot Rendered with POV-Ray)



was accessed by double lithiation followed by trapping of the dianionic intermediate with $(EtO)_2SiCl_2$ [(*S*)-**39** → (*S*)-**40**]. Reductive silicon−oxygen bond cleavage with DIBAL-H afforded the dihydrosilepine with two silicon−hydrogen bonds [(*S*)-**40** → (*S*)-**41**]. Treatment of (*S*)-**41** with the metalated thioether **12** (see Scheme 1) yielded desired (*S*)-**42** with the 2-[(ethylthio)methyl]phenyl group bound to the silicon atom [(*S*)-**41** → (*S*)-**42**]. Reversing the order of the last two steps resulted in lower yield of (*S*)-**42** due to disubstitution of diethoxy-substituted (*S*)-**40** with metalated **12** (not shown). The enantiomeric purity of (*S*)-**42** was not determined by comparison with a racemic sample. However, the enantiomeric excess of (*S*)-**39** was 99%, and racemization during any of the subsequent steps appears unlikely. The molecular structure of (*S*)-**42** was also assigned by X-ray diffraction and is included in Scheme 4.

Generation of Sulfur-Stabilized Silicon Cations with Chiral Binaphthyl Backbones. Silicon cations (*S*)-**8**, (*R*)-**9**, and (*S*)-**10** were again successfully generated by conventional hydride abstraction with the trityl salt $[Ph_3C]^+[B(C_6F_5)_4]^-$. Their ^{29}Si NMR shifts together with those of benzene-based **15** and **16** are collected in Figure 4.



hydrosilane	silicon cation	ring size
(*S*)-**28** δ –19.1 ppm	(*S*)-**8** δ 32.0 ppm	7
(*R*)-**38** δ –24.5 ppm	(*R*)-**9** δ 50.7 ppm	5
(*S*)-**42** δ –9.4 ppm	(*S*)-**10** δ 46.0 ppm	5
13 δ –21.6 ppm	**15** δ 56.4 ppm	5
14 δ –1.1 ppm	**16** δ 57.6 ppm	5

Figure 4. Sulfur-stabilized silicon cations prepared by hydride abstraction (cf. Scheme 1, bottom) and their ^{29}Si NMR shifts.

As previously observed for benzene-based silicon cations **15** and **16** (Scheme 1), line broadening in the ^{1}H NMR spectrum of 2,2′-disubstituted (*S*)-**8** is evidence of a dynamic equilibrium between silicon−sulfur Lewis pairs. Coordination of either of the sulfur lone pairs to the electron-deficient silicon atom produces diastereomers that cannot be resolved by NMR spectroscopy. As a result of the fast epimerization, the ^{29}Si NMR shift of δ 32.0 ppm could not be detected by a ^{29}Si DEPT experiment and had to be determined by a more sensitive ^{1}H,^{29}Si HMQC NMR measurement. For 2,3-disubstituted (*R*)-**9**, the equilibration was slower, allowing for the detection of both diastereomers in the ^{1}H NMR spectrum (dr = 67:33). However, only one resonance signal at δ 50.7 ppm was seen in the ^{29}Si NMR spectrum. ^{1}H,^{29}Si HMQC NMR spectroscopy then showed that the methyl groups of both diastereomers correlate to that signal. Attempts to determine the relative configuration by NOE experiments were unsuccessful. Likewise, the dihydrosilepine-derived silicon cation (*S*)-**10** showed two distinct diastereomers in the ^{1}H NMR spectrum (dr = 75:25). As for (*R*)-**9**, the ^{29}Si NMR spectrum of (*S*)-**10** only showed one signal at δ 46.0 ppm.

Except for 2,2′-disubstituted (*S*)-**8** (δ 32.0 ppm), the ^{29}Si NMR resonances are in the same order of those found for 1,3-dithiolan-2-yl- and 1,3-dithian-2-yl-substituted silicon cations (δ 42.3−57.8 ppm, Figure 2).[10] That difference is likely the result of the larger ring size of (*S*)-**8**, i.e., seven vs five. These findings are in good agreement with a recent study by Müller and co-workers, where it was shown that the silicon nucleus of silicon

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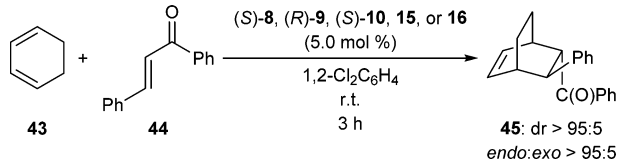
Table 1. Model Diels–Alder Reaction Catalyzed by Sulfur-Stabilized Silicon Cations[a,b]



entry	silicon cation	^{29}Si NMR (δ/ppm)	conv. (%)[c]	yield (%)[d]	ee (%)[e]
1	**15**	56.4	79	63	
2	**16**	57.6	77	52	
3	(*S*)-**8**	32.0	94	70	0
4	(*R*)-**9**	50.7	81	67	0
5	(*S*)-**10**	46.0	87	67	11

[a]All reactions were performed according to General Procedure 2 at a concentration of 0.5 M of the dienophile. [b]Diastereomeric (*trans*:*cis*) and *endo*:*exo* ratios determined by GLC analysis of the reaction mixture prior to purification. [c]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 chiral stationary phases.

cations stabilized in six-membered rings is considerably more shielded than in its five-membered counterparts.[15]

Diels–Alder Reactions Catalyzed by Sulfur-Stabilized Silicon Cations. Both achiral **15** and **16** and chiral (*S*)-**8**, (*R*)-**9**, and (*S*)-**10** were tested as catalysts in the challenging Diels–Alder reaction of cyclohexa-1,3-diene (**43**) and chalcone (**44**) to allow for comparison with known Lewis acids (Table 1).[3,4,6,7,10,16,22] All reactions were performed at room temperature and stopped after 3 h. The new sulfur-stabilized silicon cations catalyzed this cycloaddition without exception, reaching high conversion within the set time frame. Cycloadduct **45** was isolated in good yields.

Silicon cation (*S*)-**8** with the 2,2′-disubstituted binaphthyl backbone again stood out (δ 32.0 ppm), being more reactive than any of the other catalysts with less shielded silicon atoms (δ 46.0–57.6 ppm). These results emphasize once again[16c] that ^{29}Si NMR shifts are not suitable for predicting the catalytic performance of a silicon Lewis acid. It is, at best, a qualitative measure to estimate the Lewis acidity of the silicon atom.[17] The catalytic activity will also depend on the stability, i.e., strain, of the cyclic Lewis pair. Moreover, the ring size determines whether the silicon–sulfur interaction is optimal or not, and this becomes immediately visible from the ^{29}Si NMR shifts.[15] The interplay of the Lewis acidity and the ability of the sulfur donor to form the cyclic Lewis pair explains the difference between the seven-membered-ring cation (*S*)-**8** and the five-membered-ring cations (*R*)-**9**, (*S*)-**10**, **15**, and **16**.

Neither (*S*)-**8** nor (*R*)-**9** induced any enantioselectivity (Table 1, entries 3 and 4). Conversely, little, but promising, 11% ee was obtained with (*S*)-**10** where the silicon atom is part of a more rigid silepine ring (Table 1, entry 5). Repeating this experiment at −40 °C in toluene did not improve the enantiomeric excess but dramatically slowed down the reaction (14% conversion after 1 day).

Encouraged by these results, we explored the substrate scope using Lewis acid (*S*)-**10**. Difficult diene/dienophile combinations, such as **43** and α,β-unsaturated carbonyls **44** and **46** as well as particularly unreactive cyclic **47** and **48**,[16a,b,22−25] were subjected to the standard setup in 1,2-$Cl_2C_6H_4$ at room temperature (Table 2, entries 1–4). The *endo*/*exo* selectivities of cycloadducts **45** and **51**–**53** were excellent and conversions were good, but the level of enantioselection was poor. Unexpectedly,[16a,b] the yields obtained with cyclic dienophiles **47** and **48** were low, likely due to competing oligomerization. The commonly used dienophile methyl acrylate (**49**) reacted smoothly, and adduct **54** was formed in high yield and with 14% ee (Table 2, entry 5). The highest enantioselectivity was achieved with α,β-unsaturated oxazolidinone imide **50** (Table 2, entry 6). Cycloadduct **55** was isolated in 52% yield at full conversion with 24% ee. This enantiomeric excess is higher than that obtained in the same reaction with the related acetonitrile-stabilized silicon cation **5** introduced by Jørgensen, Helmchen, and co-worker (10% ee, Figure 1, bottom right).[7]

We then examined the catalyses of the same set of dienophiles with more reactive cyclopentadiene (**56**, Table 3). All reactions were completed within 1 h due to the higher reactivity of **56**. The observed trends (conversion, yield, and enantioinduction) were largely similar to those seen with cyclohexa-1,3-diene (**43**), but the *endo*/*exo* selectivities were markedly lower in the majority of the examples (Table 3, entries 2–5). The enantiomeric excess in this series was again highest for dienophile **50** (Table 3, entry 6). However, the value of 20% ee is still significantly lower than that reported by Hatanaka and co-workers for the same Diels–Alder reaction; the related triflimide **3** induced 56% ee (Figure 1, upper right).[4]

CONCLUSION

In summary, a new class of sulfur-stabilized silicon cations is introduced. A simple dialkyl thioether tether was shown to sufficiently stabilize silicon cations, and this motif was combined with chiral binaphthyl backbones having different substitution patterns. The generated silicon Lewis acids were fully characterized by NMR spectroscopy, showing distinct differences in the shielding of the cationic silicon atom in the ^{29}Si NMR spectra. As supported by Müller and co-workers' recent findings,[15] the ^{29}Si NMR shifts correlate with the ring size formed by intramolecular coordination of the sulfur atom to the silicon atom. All sulfur-stabilized silicon cations were shown to be potent Lewis acid catalysts for difficult Diels–Alder reactions. However, it was only the rigid dihydrosilepine-derived silicon cation (*S*)-**10** that induced low, but promising, levels of enantioselection. The enantiomeric excess achieved in the cycloaddition of cyclohexa-1,3-diene (**43**) and oxazolidinone imide **50** is higher than that obtained with the famous Jørgensen–Helmchen catalyst **5** (24% ee, Table 2, entry 6 vs 10% ee, Figure 1, bottom right). We consider these results a promising starting point for the development of a highly reactive and more selective silicon Lewis acid catalyst. Hence,

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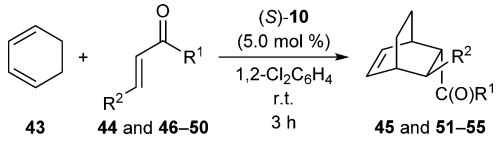
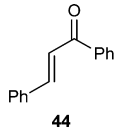
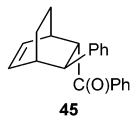
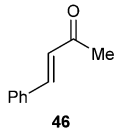
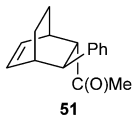
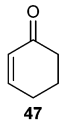
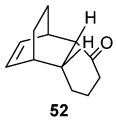
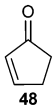
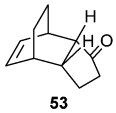
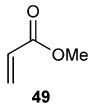
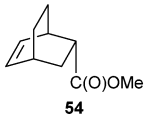
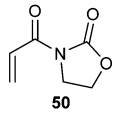
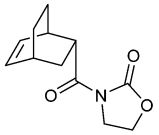
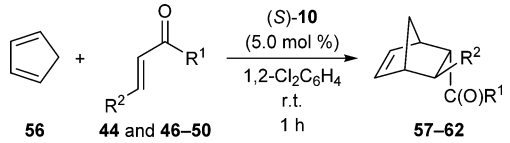
Table 2. Cyclohexa-1,3-diene (43) in Diels–Alder Reactions Catalyzed by Sulfur-Stabilized Silicon Cation (*S*)-10[a]

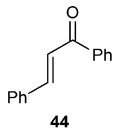
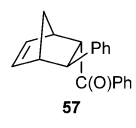
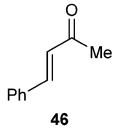
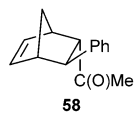
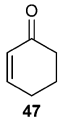
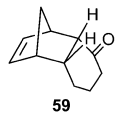
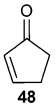
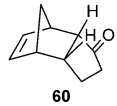
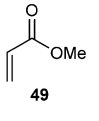
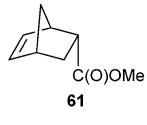
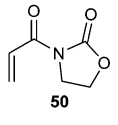
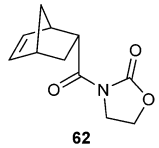


entry	dienophile	adduct	*endo*:*exo*[b] (dr)[c]	conv. (%)[d]	yield (%)[e]	ee (%)[f]
1	 **44**	 **45**	> 95:5 (> 95:5)	87	67	11
2	 **46**	 **51**	> 95:5 (> 95:5)	99	75	3
3	 **47**	 **52**	> 95:5	96	32	1
4	 **48**	 **53**	92:8	98	30	4
5	 **49**	 **54**	95:5	–[g]	83	14
6	 **50**	 **55**	95:5	97	52	24

[a]All reactions were performed according to General Procedure 2 at a concentration of 0.5 M of the dienophile. [b]Determined by GLC analysis of the reaction mixture prior to purification. [c]*trans*:*cis* ratio. [d]Determined by GLC analysis using triphenylmethane as an internal standard. [e]Analytically pure *endo*-product after flash column chromatography on silica gel. [f]Determined by HPLC or GLC analysis using chiral stationary phases. [g]Not determined as the starting material could not be detected by GLC analysis.

Table 3. Cyclopentadiene (56) in Diels–Alder Reactions Catalyzed by Sulfur-Stabilized Silicon Cation (*S*)-10[a]



entry	dienophile	adduct	*endo*:*exo*[b] (dr)[c]	conv. (%)[d]	yield (%)[e]	ee (%)[f]
1	 **44**	 **57**	> 95:5 (> 95:5)	93	80	12
2	 **46**	 **58**	74:26 (> 95:5)	99	82	7
3	 **47**	 **59**	77:23	99	59	0
4	 **48**	 **60**	64:36	99	58	3
5	 **49**	 **61**	87:13	–[g]	72	10
6	 **50**	 **62**	>95:5	99	78	20

[a]All reactions were performed according to General Procedure 2 at a concentration of 0.5 M of the dienophile. [b]Determined by GLC analysis of the reaction mixture prior to purification. [c]*trans*:*cis* ratio. [d]Determined by GLC analysis using triphenylmethane as an internal standard. [e]Analytically pure *endo*-product after flash column chromatography on silica gel. [f]Determined by HPLC or GLC analysis using chiral stationary phases. [g]Not determined as the starting material could not be detected by GLC analysis.

new sulfur-stabilized silicon cations on this basis are currently under investigation in our laboratory.

■ EXPERIMENTAL SECTION

General Remarks. All reactions were performed in flame-dried glassware using an MBraun glovebox (O_2 < 2.0 ppm, H_2O < 2.0 ppm) or conventional Schlenk techniques under a static pressure of argon or nitrogen. 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 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 (**43**) was distilled from $NaBH_4$, and cyclopentadiene (**56**) was obtained by cracking of its dimer at 180 °C prior to use. Dienophiles were distilled (for liquids) or recrystallized from ethanol and dried by azeotropic distillation with benzene (for solids) prior to use. 1-Bromo-2-(bromomethyl)benzene (**11**) was prepared according to a reported procedure.[26] Trityl tetrakis(pentafluorophenyl)borate ($[Ph_3C]^+[B(C_6F_5)_4]^-$) was prepared following a reported procedure,[27] recrystallized from CH_2Cl_2/*n*-pentane, and stored in a glovebox. Analytical thin-layer chromatography (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. ^1H, ^{11}B, ^{13}C, ^{19}F, and ^{29}Si NMR spectra were recorded in $CDCl_3$, C_6D_6, or 1,2-$Cl_2C_6D_4$ on Bruker AV500 or Bruker 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 ppm for ^1H NMR and $CDCl_3$: δ 77.16 ppm for ^{13}C NMR, C_6D_5H: δ 7.16 ppm for ^1H NMR and C_6D_6: δ 128.06 ppm for ^{13}C NMR, 1,2-$Cl_2C_6D_3H$: δ 6.94 and 7.20 ppm for ^1H and 1,2-$Cl_2C_6D_4$: δ 127.1, 130.1, and 132.5 ppm for ^{13}C NMR). Data are reported as follows: chemical shift, multiplicity (br s = broad singlet, s = singlet, br d = broad doublet,

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d = doublet, t = triplet, q = quartet, m = multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. $^1H,^{29}Si$ HMQC NMR spectra were measured with a coupling constant of 7.0 Hz for the $^3J_{H,Si}$ coupling. The peak intensities in the $^1H,^{29}Si$ HMQC NMR spectra cannot be correlated to the amount of compound. Infrared (IR) spectra were recorded on an Agilent Technologies Cary 630 FTIR spectrophotometer equipped with an ATR unit and are reported as wavenumbers [cm^{-1}] (w = weak, m = medium, s = strong, vs = very strong). 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 (m.p.) were determined with a Stuart Scientific SMP20 melting point apparatus and are not corrected. Enantiomeric excesses were determined by analytical high performance liquid chromatography (HPLC) analysis on an Agilent Technologies 1200 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OD-H or AD-H column (*n*-heptane/*i*-PrOH mixtures as solvents), and an Agilent Technologies 1290 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OJ-RH column (acetonitrile/H_2O mixtures as solvents), or by analytical gas liquid chromatography (GLC) on an Agilent Technologies 7820A gas chromatograph equipped with an IVAdex-1 capillary column (25 m × 0.25 mm, 0.25 μm film thickness) using the program indicated in the respective experiments. High-resolution mass spectrometry (HRMS) and elemental analysis were performed at the Analytical Facility of the Institut für Chemie, Technische Universität Berlin.

General Procedure for the Generation of Intramolecularly Sulfur-Stabilized Silicon Cations (*S*)-8, (*R*)-9, and (*S*)-10, 15, and 16 (GP1). 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 suspension 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 stirred for 5 min, transferred to an NMR tube, and directly subjected to NMR spectroscopic analysis.

General Procedure for Diels–Alder Reactions Catalyzed by Sulfur-Stabilized Silicon Cations (GP2). In a glovebox, a flame-dried Schlenk tube equipped with a magnetic stir bar was charged with $[Ph_3C]^+[B(C_6F_5)_4]^-$ (5.00 mol %). The Schlenk tube was transferred to a fume hood and connected to a nitrogen-vacuum manifold. After addition of 1,2-$Cl_2C_6H_4$ (0.2 mL), a solution of the corresponding silane (5.50 mol %) in 1,2-$Cl_2C_6H_4$ (0.4 mL) was added, and the resulting mixture was maintained for 30 min at room temperature. To the thus-obtained catalyst, a solution of diene (2.10 equiv) and dienophile (1.00 equiv) in 1,2-$Cl_2C_6H_4$ (0.4 mL) was added dropwise. The reaction mixture was stirred at room temperature for 1–3 h, followed by addition of saturated aqueous $NaHCO_3$ solution. The phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3×). The combined organic phases were washed with saturated aqueous NaCl solution, dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate as eluent, affording analytically pure Diels–Alder adduct.

(2-Bromobenzyl)(ethyl)sulfane (12). 1-Bromo-2-(bromomethyl)benzene (**11**, 1.0 g, 4.0 mmol, 1.0 equiv) was dissolved in ethanol (8 mL). K_2CO_3 (1.1 g, 8.0 mmol, 2.0 equiv) and ethanethiol (0.59 mL, 0.50 g, 8.0 mmol, 2.0 equiv) were added, and the resulting mixture was stirred at 45 °C for 15 h. After cooling to room temperature, the reaction was quenched by the addition of water (15 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 10 mL). The combined organic phases were washed with aqueous NaOH (2 M, 10 mL) and saturated aqueous NaCl (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane as eluent, affording thioether **12** (0.690 g, 2.99 mmol, 75%) as a colorless oil. R_f = 0.21 (cyclohexane). GLC (HP-5): t_R = 13.3 min. IR (ATR): nu(tilde) = 3056 (w), 2965 (m), 2922 (m), 2868 (w), 1918 (w), 1798 (w), 1565 (m), 1437 (s), 1374 (m), 1264 (m), 1234 (m), 1157 (w), 1109 (w), 1022 (s), 970 (w), 871 (w), 817 (w), 732 (s), 693 (m) cm^{-1}. HRMS (ESI) calculated for $C_9H_{11}BrS$ $[M]^+$: 229.9765; found: 229.9760. ^1H NMR (500 MHz, $CDCl_3$): δ 1.27 (t, *J* = 7.4 Hz, 3H), 2.52 (q, *J* = 7.5 Hz, 2H), 3.85 (s, 2H), 7.10 (m_c, 1H), 7.27 (m_c, 1H), 7.37 (dd, *J* = 7.6 Hz, *J* = 1.5 Hz, 1H), 7.56 (dd, *J* = 8.0 Hz, *J* = 1.1 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.7, 25.8, 36.3, 124.6, 127.5, 128.6, 130.8, 133.2, 138.2. Anal. Calcd for $C_9H_{11}BrS$: C, 46.77; H, 4.80; S, 13.87. Found: C, 46.65; H, 4.94; S, 14.10. The analytical and spectroscopic data are in accordance with those reported.[28]

(2-((Ethylthio)methyl)phenyl)dimethylsilane (13). To a solution of thioether **12** (0.10 g, 0.43 mmol, 1.0 equiv) in THF (5 mL) cooled to −78 °C was added *n*BuLi (3.9 M in hexane fractions, 0.15 mL, 0.56 mmol, 1.3 equiv) dropwise, and the resulting mixture was stirred for 1 h at −78 °C. $Me_2Si(H)Cl$ (63 μL, 53 mg, 0.56 mmol, 1.3 equiv) was added, and then the mixture was allowed to slowly warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of water (5 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL), the combined organic phases were washed with saturated aqueous NaCl (20 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (20/1) as eluent, affording hydrosilane **13** (60 mg, 0.29 mmol, 66%) as a colorless oil. R_f = 0.20 (cyclohexane). GLC (HP-5): t_R = 13.0 min. IR (ATR): nu(tilde) = 3055 (w), 2959 (m), 2924 (m), 2319 (w), 2120 (m), 1924 (w), 1578 (w), 1435 (m), 1248 (m), 1194 (w), 1119 (m), 1069 (w), 972 (w), 878 (vs), 835 (s), 722 (s) cm^{-1}. HRMS (ESI) calculated for $C_{11}H_{19}SSi$ $[M + H]^+$: 211.0997; found: 211.0991. ^1H NMR (500 MHz, $CDCl_3$): δ 0.40 (d, *J* = 3.8 Hz, 6H), 1.26 (t, *J* = 7.6 Hz, 3H), 2.51 (q, *J* = 7.4 Hz, 2H), 3.88 (s, 2H), 4.63 (sept, *J* = 3.8 Hz, 1H), 7.24 (m_c, 1H), 7.31–7.36 (m, 2H), 7.50 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ −2.6 (2C), 14.7, 26.0, 36.5, 126.5, 129.4, 129.5, 135.1, 137.0, 144.1. ^{29}Si DEPT (99 MHz, $CDCl_3$): δ −21.6.

(2-((Ethylthio)methyl)phenyl)diisopropylsilane (14). To a solution of thioether **12** (0.20 g, 0.87 mmol, 1.0 equiv) in THF (8.7 mL) cooled to −78 °C was added *n*BuLi (1.8 M in hexane fractions, 0.64 mL, 1.1 mmol, 1.3 equiv) dropwise, and the resulting mixture was stirred for 2 h at −78 °C. $iPr_2Si(H)Cl$ (0.19 mL, 0.17 g, 1.1 mmol, 1.3 equiv) was added, and then the mixture was allowed to slowly warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of water (10 mL), and the phases were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL), the combined organic phases were washed with saturated aqueous NaCl (20 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane as eluent, affording hydrosilane **14** (186 mg, 0.698 mmol, 81%) as a colorless oil. R_f = 0.31 (cyclohexane). GLC (HP-5): t_R = 16.4 min. IR (ATR): nu(tilde) = 3055 (w), 2937 (m), 2861 (m), 2113 (m), 1923 (w), 1811 (w), 1587 (w), 1460 (m), 1381 (w), 1261 (m), 1117 (m), 1069 (m), 1002 (s), 918 (w), 878 (m), 786 (vs), 734 (s). HRMS (ESI) calculated for $C_{15}H_{26}SSi$ $[M]^+$: 266.1524; found: 266.1526. ^1H NMR (500 MHz, $CDCl_3$): δ 0.99 (d, *J* = 7.2 Hz, 6H), 1.10 (d, *J* = 7.2 Hz, 6H), 1.23–1.30 (m, 5H), 2.50 (q, *J* = 7.4 Hz, 2H), 3.86 (s, 2H), 4.19 (t, *J* = 3.5 Hz, 1H), 7.21 (m_c, 1H), 7.31 (m_c, 1H), 7.35–7.39 (m, 1H), 7.43 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 11.5 (2C), 14.9, 19.1 (4C), 26.0, 36.9, 126.1, 129.2, 129.6, 134.3, 135.9, 144.8. ^{29}Si DEPT (99 MHz, $CDCl_3$): δ −1.1.

(2-((Ethylthio)methyl)phenyl)dimethylsilylium Tetrakis-(pentafluorophenyl)borate (15). Prepared from (2-((ethylthio)-methyl)phenyl)dimethylsilane (**13**, 11 mg, 50 μmol, 1.0 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (46 mg, 50 μmol, 1.0 equiv) according to GP1. NMR spectroscopic data for **15** are as follows. ^1H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.66 (s, 6H), 1.14 (t, *J* = 7.4 Hz, 3H), 2.41–2.68 (br s, 2H), 3.97–4.41 (br s, 2H), 7.09–7.11 (m, 1H), 7.20–7.23 (m, 1H), 7.28 (m_c, 1H), 7.35 (m_c, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ 11.5 (br s, 2C), 23.0, 31.1, 42.0, 124.8 (br m), 130.4, 133.2, 136.8 (d, *J* = 236 Hz), 138.3, 138.7 (d, *J* = 236 Hz), 139.6, 142.4, 143.3, 148.9 (d, *J* = 240 Hz). ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ −16.0. ^{19}F NMR

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(471 MHz, 1,2-$Cl_2C_6D_4$): δ −165.8, −161.9, −131.5. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 56.4 ppm.

(2-((Ethylthio)methyl)phenyl)diisopropylsilylium Tetrakis-(pentafluorophenyl)borate (16). Prepared from (2-((ethylthio)-methyl)phenyl)diisopropylsilane (**14**, 21 mg, 80 μmol, 1.0 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (74 mg, 80 μmol, 1.0 equiv) according to GP1. NMR spectroscopic data for **16** are as follows. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.82−0.91 (m, 6H), 0.96−1.08 (m, 6H), 1.24 (t, J = 7.3 Hz, 3H), 1.38 (sept, J = 7.5 Hz, 2H), 2.53−2.66 (m, 1H), 2.71−2.83 (m, 1H), 4.03−4.16 (m, 1H), 4.26−4.37 (m, 1H), 7.10−7.12 (m, 1H), 7.24−7.29 (m, 1H), 7.31−7.35 (m, 1H), 7.36−7.40 (m, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ 11.9, 13.2, 13.4, 16.9, 17.0 (br s, 2C), 17.4, 31.3, 42.8, 124.8 (br m), 126.1, 133.3, 134.0, 136.8 (d, J = 236 Hz), 138.7 (d, J = 236 Hz), 139.5, 148.9 (d, J = 240 Hz). ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ −16.0. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): δ −165.9, −162.0, −131.5. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 57.6 ppm.

(*S*)-2′-((*tert*-Butyldiphenylsilyl)oxy)-[1,1′-binaphthalen]-2-ol [(*S*)-18]. (*S*)-BINOL [(*S*)-**17**, 5.01 g, 17.5 mmol, 1.00 equiv] and imidazole (2.38 g, 34.9 mmol, 2.00 equiv) were dissolved in dry DMF (35 mL). TBDPSCl (5.14 g, 18.7 mmol, 1.07 equiv) was added, and the resulting mixture was stirred at 50 °C for 16 h. After cooling to room temperature, saturated aqueous NH_4Cl (5 mL) was added. This mixture was extracted with Et_2O (3 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl (50 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Purification by flash column chromatography on silica gel using cyclohexane/ethyl acetate (10/1) afforded (*S*)-**18** (6.87 g, 13.1 mmol, 75%) as a white solid. m.p.: 142 °C (CH_2Cl_2). R_f = 0.53 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 30.7 min. IR (ATR): nu(tilde) = 3528 (m), 3062 (w), 2922 (w), 2849 (w), 2041 (w), 1980 (w), 1902 (w), 1620 (m), 1588 (m), 1505 (m), 1459 (m), 1425 (m), 1360 (m), 1266 (m), 1208 (m), 1174 (m), 1108 (m), 1003 (m), 935 (w), 861 (w), 811 (s), 741 (s), 699 (s) cm^{-1}. HRMS (ESI) calculated for $C_{36}H_{32}O_2Si$ $[M]^+$: 524.2167; found: 524.2148. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.50 (s, 9H), 5.00 (s, 1H), 6.90 (m$_c$, 1H), 7.21 (m$_c$, 1H), 7.27−7.44 (m, 12H), 7.53 (m$_c$, 2H), 7.61 (m$_c$, 1H), 7.64 (m$_c$, 2H), 7.78 (m$_c$, 1H), 7.89 (m$_c$, 1H), 7.93 (m$_c$, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 19.1, 25.7 (3C), 115.7, 117.5, 117.6, 120.8, 123.3, 124.3, 125.1, 125.2, 126.5, 127.3, 127.8, 128.01, 128.02, 128.20, 128.23, 129.5, 129.6, 129.9, 130.0, 130.1, 130.3, 132.4, 132.8, 134.1, 134.3, 135.5, 135.6, 151.6, 152.2. The analytical and spectroscopic data are in accordance with those reported.[29]

(*S*)-2′-((*tert*-Butyldiphenylsilyl)oxy)-[1,1′-binaphthalen]-2-yl Trifluoromethanesulfonate [(*S*)-19]. To a solution of (*S*)-**18** (5.00 g, 9.53 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL) cooled to 0 °C were added *N*,*N*-diisopropylethylamine (2.2 mL, 1.6 g, 12 mmol, 1.3 equiv) and subsequently trifluoromethanesulfonic anhydride (1.8 mL, 3.0 g, 11 mmol, 1.1 equiv). The cooling bath was removed, and the mixture was stirred at room temperature for 12 h. The mixture was washed with hydrochloric acid (2 M, 15 mL), saturated aqueous $NaHCO_3$ (15 mL), and saturated aqueous NaCl (15 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. Triflate (*S*)-**19** (6.2 g, 9.4 mmol, 99%) was obtained as a white solid and used without further purification. m.p.: 109 °C (CH_2Cl_2). R_f = 0.55 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 31.3 min. IR (ATR): nu(tilde) = 3054 (w), 2931 (w), 2856 (w), 2199 (w), 1897 (w), 1590 (m), 1505 (m), 1470 (m), 1419 (m), 1338 (m), 1278 (m), 1209 (s), 1139 (s), 1111 (m), 1000 (m), 863 (w), 812 (s), 743 (m), 689 (s) cm^{-1}. HRMS (ESI) calculated for $C_{37}H_{31}F_3O_4SSi$ $[M]^+$: 656.1659; found: 656.1653. ^{1}H NMR (500 MHz, C_6D_6): δ 0.64 (s, 9H), 7.00−7.08 (m, 4H), 7.10−7.15 (m, 3H), 7.16−7.18 (m, 1H), 7.21−7.25 (m, 2H), 7.29 (m$_c$, 3H), 7.44 (m$_c$, 1H), 7.50 (m$_c$, 1H), 7.53−7.55 (m, 1H), 7.57−7.59 (m, 1H), 7.60 (m$_c$, 2H), 7.66 (m$_c$, 2H), 7.93 (m$_c$, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 19.1, 25.9 (3C), 117.7, 118.9 (q, J = 320.1 Hz), 120.0, 120.5, 124.2, 125.5, 127.0, 127.2, 127.4, 127.7, 128.2, 128.3, 128.38, 128.41, 128.46, 128.48, 129.5, 130.2, 130.47, 130.49, 130.7, 132.8, 133.0, 134.4, 134.5, 135.7, 135.8, 146.3, 151.6.

(*R*)-*tert*-Butyl((2′-methyl-[1,1′-binaphthalen]-2-yl)oxy)-diphenylsilane [(*R*)-20]. 1,3-Bis(diphenylphosphino)propane nickel(II) chloride (27 mg, 0.053 mmol, 7.0 mol %) was placed in a flame-dried Schlenk flask, and a solution of triflate (*S*)-**19** (0.50 g, 0.76 mmol, 1.0 equiv) in THF (6 mL) was added. The suspension was cooled to 0 °C, and methylmagnesium bromide (3.0 M in Et_2O, 0.38 mL, 0.11 mmol, 1.5 equiv) was added dropwise. The cooling bath was replaced by an oil bath, and the mixture heated at reflux for 4 h. The mixture was diluted with THF (3 mL), cooled to 0 °C, and carefully quenched by the addition of water (5 mL) and hydrochloric acid (2 M, 5 mL). The phases were separated, and the aqueous phase extracted with *tert*-butyl methyl ether (2 × 5 mL). The combined organic phases were washed with water (5 mL), and saturated aqueous NaCl (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (10/1) as eluent, affording (*R*)-**20** (0.39 g, 0.75 mmol, 99%) as a yellow solid. m.p.: 122 °C (CH_2Cl_2). R_f = 0.73 (cyclohexane/ethyl acetate 5/1). IR (ATR): nu(tilde) = 3048 (w), 2925 (m), 2852 (m), 2220 (w), 1950 (w), 1891 (w), 1619 (w), 1589 (m), 1502 (m), 1461 (m), 1425 (m), 1334 (m), 1247 (m), 1145 (w), 1107 (s), 996 (s), 950 (w), 863 (w), 806 (vs), 741 (s), 696 (vs) cm^{-1}. HRMS (ESI) calculated for $C_{37}H_{34}OSi$ $[M]^+$: 522.2373; found: 522.2359. ^{1}H NMR (500 MHz, C_6D_6): δ 0.60 (s, 9H), 2.25 (s, 3H), 7.03 (m$_c$, 1H), 7.08 (m$_c$, 1H), 7.10 (m$_c$, 2H), 7.12−7.15 (m, 3H), 7.18−7.21 (m, 3H), 7.23 (m$_c$, 1H), 7.30 (m$_c$, 1H), 7.34 (m$_c$, 1H), 7.44 (m$_c$, 1H), 7.49 (m$_c$, 1H), 7.53 (m$_c$, 1H), 7.69 (m$_c$, 2H), 7.77 (m$_c$, 2H), 7.79 (m$_c$, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 19.2, 20.6, 25.8 (3C), 120.8, 124.1, 124.4, 125.2, 125.6, 126.2, 126.6, 127.0, 127.9, 128.1, 128.2, 128.3, 128.4, 128.6, 129.0, 129.1, 129.8, 130.2, 133.0, 133.1, 133.6, 133.7, 134.1, 134.6, 135.3, 135.7, 135.8, 150.7. Anal. Calcd for $C_{37}H_{31}F_3O_4SSi$: C, 85.01; H, 6.56. Found: C, 84.63; H, 6.60.

(*R*)-2′-Methyl-[1,1′-binaphthalen]-2-ol [(*R*)-21]. To a solution of (*R*)-**20** (0.39 g, 0.75 mmol, 1.0 equiv) in THF (5 mL) was added TBAF (0.22 g, 0.83 mmol, 1.1 equiv). The resulting mixture was stirred at room temperature for 3.5 h and quenched by the addition of water (5 mL). The phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 5 mL). The combined organic phases were washed with saturated aqueous NaCl (5 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The free alcohol (*R*)-**21** (0.16 g, 0.55 mmol, 73%) was obtained as a mixture with the corresponding fluorosilane. The yield was determined by ^{1}H NMR spectroscopy by integration of the baseline-separated resonances of the methyl group of (*R*)-**21** and the *tert*-butyl group of the silane. The mixture of (*R*)-**21** with the fluorosilane was used without further purification. An aliquot for characterization was purified by repeated flash column chromatography on silica gel using cyclohexane as eluent. m.p.: 127 °C (CH_2Cl_2). R_f = 0.44 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 22.6 min. IR (ATR): nu(tilde) = 3489 (m), 3413 (w), 3039 (w), 2920 (w), 2104 (w), 1896 (w), 1751 (w), 1591 (m), 1505 (m), 1462 (m), 1377 (m), 1299 (m), 1268 (m), 1200 (m), 1172 (s), 1143 (s), 1025 (s), 955 (m), 860 (m), 804 (vs), 739 (vs), 663 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{16}O$ $[M]^+$: 284.1201; found: 284.1188. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.16 (s, 3H), 4.49 (br s, 1H), 6.98 (d, J = 8.7 Hz, 1H), 7.21−7.25 (m, 2H), 7.29 (m$_c$, 1H), 7.31−7.38 (m, 2H), 7.45 (m$_c$, 1H), 7.56 (d, J = 8.7 Hz, 1H), 7.88 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 8.7 Hz, 2H), 7.95 (d, J = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.3, 117.5, 117.7, 123.6, 124.7, 125.6, 125.7, 126.8, 127.0, 128.27, 128.31, 128.8, 129.15, 129.18, 129.3, 129.9, 132.7, 133.4, 133.5, 137.3, 150.9. The analytical and spectroscopic data are in accordance with those reported.[30]

(*R*)-2′-Methyl-[1,1′-binaphthalen]-2-yl Trifluoromethanesulfonate [(*R*)-22]. To a solution of alcohol (*R*)-**21** (51 wt %, 446 mg, 0.546 mmol, 1.00 equiv) in CH_2Cl_2 (4 mL) cooled to 0 °C were added *N*,*N*-diisopropylethylamine (0.24 mL, 0.18 g, 1.4 mmol, 2.5 equiv) and subsequently trifluoromethanesulfonic anhydride (0.19 mL, 0.33 g, 1.2 mmol, 2.1 equiv). The cooling bath was removed, and the mixture was stirred at room temperature for 12 h. The mixture was washed with hydrochloric acid (2 M, 5 mL), saturated aqueous $NaHCO_3$ (5 mL), and saturated aqueous NaCl (5 mL). The organic

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phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (10/1) as eluent, affording triflate (*R*)-**22** (226 mg, 0.525 mmol, 96%) as a yellow solid. m.p.: 87 °C (CH_2Cl_2). R_f = 0.50 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 22.2 min. IR (ATR): nu(tilde) = 3042 (w), 2924 (w), 2429 (w), 1908 (w), 1760 (w), 1505 (w), 1408 (m), 1204 (s), 1129 (s), 939 (m), 865 (m), 807 (m), 778 (m), 760 (m), 707 (m), 675 (m) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{15}F_3O_3S$ $[M]^+$: 416.0694; found: 416.0680. ^1H NMR (500 MHz, C_6D_6): δ 2.04 (s, 3H), 6.92 (m_o, 1H), 7.02 (m_o, 1H), 7.11−7.14 (m, 1H), 7.17−7.20 (m, 2H), 7.22 (m_o, 1H), 7.27 (m_o, 1H), 7.38 (m_o, 1H), 7.48 (m_o, 1H), 7.54 (m_o, 1H), 7.68 (m_o, 1H), 7.71 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 20.3, 118.7 (q, J = 320.0 Hz), 120.0, 125.6, 125.8, 126.91, 126.94, 127.2, 128.0, 128.4, 128.5, 128.6, 128.8, 128.9, 129.4, 130.4, 130.6, 132.6, 133.0, 133.3, 133.7, 145.4.

(*R*)-2′-Methyl-[1,1′-binaphthalen]-2-amine [(*R*)-24]. Triflate (*R*)-**22** (1.84 g, 4.41 mmol, 1.00 equiv), $Pd(OAc)_2$ (0.247 g, 1.10 mmol, 0.250 equiv), *rac*-BINAP (0.822 g, 1.32 mmol, 0.300 equiv), and Cs_2CO_3 (4.01 g, 12.3 mmol, 2.80 equiv) were dissolved in dry 1,4-dioxane (18 mL). To this suspension was added benzylamine (4.09 mL, 4.01 g, 37.4 mmol, 8.49 equiv), and the resulting mixture was degassed (three freeze−pump−thaw cycles). The mixture was stirred at 80 °C for 90 h. After cooling to room temperature, the mixture was filtered through Celite, and the solvent was removed under reduce pressure. Crude (*R*)-**23** was directly used in the next step without purification. A solution of crude (*R*)-**23** in ethyl acetate (10 mL) was added to palladium on activated charcoal (10 wt %, 0.486 g, 0.439 mmol, 10.0 mol % based on (*R*)-**22**). The atmosphere was changed to dihydrogen (1 atm), and the mixture was stirred at 40 °C. The reaction was monitored by ^1H NMR spectroscopy, and another batch of palladium on activated charcoal (10 wt %, 0.486 g, 0.439 mmol, 10.0 mol % based on (*R*)-**22**) was added after 18 h. The suspension was stirred for further 66 h. After cooling to room temperature, the mixture was filtered through Celite, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent, affording amine (*R*)-**24** (0.542 g, 1.91 mmol, 43% over two steps) as a white solid. m.p.: 111 °C (CH_2Cl_2). R_f = 0.43 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 23.5 min. IR (ATR): nu(tilde) = 3481 (w), 3387 (w), 3195 (w), 3045 (w), 1916 (w), 1826 (w), 1613 (s), 1505 (m), 1471 (m), 1430 (m), 1377 (w), 1352 (m), 1258 (w), 1145 (w), 1024 (w), 903 (w), 811 (s), 751 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{17}N$ $[M]^+$: 283.1361; found: 283.1352. ^1H NMR (500 MHz, $CDCl_3$): δ 2.15 (s, 3H), 3.51 (br s, 2H), 6.89 (m_o, 1H), 7.13 (m_o, 1H), 7.16 (m_o, 1H), 7.22 (m_o, 1H), 7.24−7.26 (m, 2H), 7.42 (m_o, 1H), 7.55 (m_o, 1H), 7.80 (m_o, 2H), 7.90 (m_o, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.1, 116.4, 118.2, 122.4, 124.1, 125.3, 125.7, 126.5, 126.7, 128.1, 128.16, 128.18, 128.3, 129.1, 129.2, 132.2, 132.8, 132.9, 133.9, 136.2, 141.7.

(*R*)-2-Iodo-2′-methyl-1,1′-binaphthalene [(*R*)-25]. To a suspension of amine (*R*)-**24** (0.30 g, 1.1 mmol, 1.0 equiv) in concentrated hydrochloric acid (37%, 1 mL) cooled to 0 °C was slowly added a solution of $NaNO_2$ (0.16 g, 2.3 mmol, 2.2 equiv) in water (3 mL). The mixture was warmed to room temperature, stirred for 2.5 h, and cooled back to 0 °C. To this mixture was added a solution of KI (1.8 g, 11 mmol, 10 equiv) in water (9 mL) dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by the addition of saturated aqueous Na_2SO_3 (5 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were washed with saturated aqueous NaCl (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (100/1) as eluent, affording iodide (*R*)-**25** (0.18 g, 0.46 mmol, 43%) as a yellow solid. m.p.: 133 °C (CH_2Cl_2). R_f = 0.24 (cyclohexane). GLC (HP-5): t_R = 23.9 min. IR (ATR): nu(tilde) = 3039 (m), 2913 (w), 2846 (w), 2047 (w), 1996 (w), 1753 (w), 1573 (w), 1497 (m), 1408 (m), 1304 (w), 1255 (w), 1201 (m), 1129 (m), 1061 (w), 942 (m), 866 (w), 806 (s), 773 (m), 742 (s), 675 (m) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{15}I$ $[M]^+$: 394.0218; found: 394.0200. ^1H NMR (500 MHz, C_6D_6): δ 2.00 (s, 3H), 6.87 (m_o, 1H), 7.02 (m_o, 1H), 7.13 (m_o, 1H), 7.17−7.20 (m, 2H), 7.26 (m_o, 1H), 7.31 (m_o, 1H), 7.56 (m_o, 1H), 7.71−7.77 (m, 3H), 7.92 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 20.1, 100.2, 125.5, 126.6, 126.9, 127.0, 127.5, 128.3, 128.4, 128.5, 128.6, 129.1, 129.4, 132.8, 132.9, 133.5, 134.0, 134.4, 136.1, 139.1, 142.7.

(*S*)-2-(Bromomethyl)-2′-iodo-1,1′-binaphthalene [(*S*)-26]. Iodide (*R*)-**25** (80 mg, 0.20 mmol, 1.0 equiv), NBS (43 mg, 0.24 mmol, 1.2 equiv), and benzoyl peroxide (49 mg, 0.20 mmol, 1.0 equiv) were dissolved in benzene (4 mL). The resulting mixture was heated at reflux for 4 h, cooled to room temperature, and stirred for further 21 h. The solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (20/1) as eluent, affording benzyl bromide (*S*)-**26** (44 mg, 92 μmol, 45%) as a white solid. m.p.: 191 °C (benzene). R_f = 0.12 (cyclohexane). GLC (HP-5): t_R = 27.1 min. IR (ATR): nu(tilde) = 3044 (w), 1753 (w), 1614 (w), 1575 (w), 1497 (m), 1433 (w), 1304 (w), 1210 (m), 1102 (m), 1053 (w), 957 (m), 871 (w), 808 (s), 784 (m), 750 (s), 690 (m) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{14}BrI$ $[M]^+$: 471.9324; found: 471.9315. ^1H NMR (500 MHz, C_6D_6): δ 4.04 (d, J = 10.4 Hz, 1H), 4.11 (d, J = 10.4 Hz, 1H), 6.88 (m_o, 1H), 6.94 (m_o, 1H), 7.10−7.15 (m, 3H), 7.17−7.19 (m, 1H), 7.24 (m_o, 1H), 7.53 (m_o, 2H), 7.62 (m_o, 1H), 7.70 (m_o, 1H), 7.86 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 31.9, 100.5, 126.5, 126.8, 126.9, 127.3, 127.5, 127.7, 128.34, 128.36, 128.4, 129.6, 130.0, 132.4, 133.3, 133.8, 133.9, 134.1, 136.0, 140.0, 140.7.

(*S*)-Ethyl((2′-iodo-[1,1′-binaphthalen]-2-yl)methyl)sulfane [(*S*)-27]. Benzyl bromide (*S*)-**26** (72 mg, 0.15 mmol, 1.0 equiv) was dissolved in ethanol (1 mL). K_2CO_3 (42 mg, 0.30 mmol, 2.0 equiv) and ethanethiol (22 μL, 19 mg, 0.30 mmol, 2.0 equiv) were added, and the resulting mixture was stirred overnight at 45 °C. After cooling to room temperature, the reaction was quenched by the addition of water (3 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 2 mL). The combined organic phases were washed with aqueous NaOH (2 M, 2 mL) and saturated aqueous NaCl (2 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Ethyl thioether (*S*)-**27** (58 mg, 0.13 mmol, 85%) was obtained as a colorless sticky oil and used without further purification. GLC (HP-5): t_R = 28.2 min. IR (ATR): nu(tilde) = 3053 (m), 2980 (m), 2921 (m), 2866 (w), 2354 (w), 2199 (w), 1914 (w), 1813 (w), 1689 (w), 1616 (w), 1577 (m), 1499 (m), 1449 (m), 1305 (w), 1260 (m), 1133 (w), 1104 (m), 1025 (w), 955 (w), 810 (s), 746 (s), 682 (w) cm^{-1}. HRMS (ESI) calculated for $C_{23}H_{20}IS$ $[M + H]^+$: 455.0330; found: 455.0319. ^1H NMR (500 MHz, $CDCl_3$): δ 0.93 (t, J = 7.0 Hz, 3H), 2.29 (m_o, 2H), 3.41 (d, J = 14.9 Hz, 1H), 3.56 (d, J = 14.9 Hz, 1H), 7.02 (m_o, 1H), 7.13 (m_o, 1H), 7.24 (m_o, 1H), 7.26−7.29 (m, 1H), 7.45 (m_o, 1H), 7.49 (m_o, 1H), 7.69 (m_o, 1H), 7.88 (m_o, 1H), 7.92 (m_o, 2H), 8.01 (m_o, 1H), 8.06 (m_o, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.5, 26.6, 34.1, 100.7, 125.9, 126.0, 126.68, 126.72, 127.1, 127.2, 127.3, 128.21, 128.23, 128.8, 129.6, 132.1, 132.9, 133.0, 134.0, 134.9, 135.8, 139.0, 141.0.

(*S*)-(2′-((Ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)-dimethylsilane [(*S*)-28]. To a solution of thioether (*S*)-**27** (43 mg, 96 μmol, 1.0 equiv) in THF (1.2 mL) cooled to −78 °C was added *n*BuLi (2.2 M in hexane fractions, 57 μL, 0.12 mmol, 1.3 equiv) dropwise, and the resulting mixture was stirred for 1 h at −78 °C. $Me_2Si(H)Cl$ (13 μL, 11 mg, 0.12 mmol, 1.3 equiv) was added, and then the mixture was allowed to slowly warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of water (3 mL), and the phases were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 3 mL), and the combined organic phases were washed with saturated aqueous NaCl (3 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10/1) as eluent, affording hydrosilane (*S*)-**28** (16 mg, 41 μmol, 43%, 98% ee) as a colorless sticky oil. R_f = 0.18 (cyclohexane/CH_2Cl_2 10/1). GLC (HP-5): t_R = 25.7 min. IR (ATR): nu(tilde) = 3047 (m), 2957 (m), 2921 (m), 2287 (w), 2111 (m), 1911 (w), 1813 (w), 1772 (w), 1590 (w), 1548 (w), 1499 (m),

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1449 (m), 1312 (m), 1245 (m), 1166 (w), 1110 (w), 1023 (m), 959 (w), 885 (s), 814 (s), 746 (s), 684 (m) cm^{-1}. HRMS (ESI) calculated for $C_{25}H_{26}SSi$ $[M]^+$: 386.1524; found: 386.1508. ^1H NMR (500 MHz, C_6D_6): δ −0.22 (d, J = 4.0 Hz, 3H), 0.05 (d, J = 4.0 Hz, 3H), 0.72 (t, J = 7.3 Hz, 3H), 2.00 (m, 2H), 3.51 (d, J = 13.3 Hz, 1H), 3.56 (d, J = 13.3 Hz, 1H), 4.12 (sept, J = 3.8 Hz, 1H), 6.95 (m_o, 1H), 6.98 (m_o, 1H), 7.16−7.19 (m, 2H), 7.22 (m_o, 1H), 7.35 (m_o, 1H), 7.68 (m_o, 1H), 7.72 (m_o, 1H), 7.76 (m_o 2H), 7.82 (m_o, 1H), 7.86 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −3.3, −3.0, 14.4, 26.6, 34.9, 125.9, 126.5, 126.6, 126.9, 127.3, 127.4, 127.5, 127.7, 128.2, 128.3, 128.6, 131.1, 133.0, 133.3, 134.3, 134.6, 135.8, 136.3, 137.3, 143.8. ^{29}Si DEPT (99 MHz, C_6D_6): δ −19.1. HPLC (Daicel Chiralcel OJ-RH, 20 °C, acetonitrile/H_2O 60/40, flow rate: 0.50 mL/min, λ = 254 nm): t_R = 41.9 min [(*R*)-(2′-((ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)dimethylsilane], t_R = 45.3 min [(*S*)-(2′-((ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)-dimethylsilane].

(*S*)-2′-Hydroxy-[1,1′-binaphthalen]-2-yl Trifluoromethanesulfonate. To a solution of (*S*)-BINOL [(*S*)-**17**, 5.00 g, 17.5 mmol, 1.00 equiv] in CH_2Cl_2 (100 mL) cooled to 0 °C were added a solution of *N*,*N*-diisopropylethylamine (3.05 mL, 2.26 g, 17.5 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) and, at the same time, a solution of trifluoromethanesulfonic anhydride (2.93 mL, 4.93 g, 17.5 mmol, 1.00 equiv) in CH_2Cl_2 (30 mL) over a period of 30 min. The cooling bath was removed, and the mixture was stirred at room temperature for 12 h. The mixture was washed with hydrochloric acid (2 M, 100 mL), saturated aqueous $NaHCO_3$ (100 mL), and saturated aqueous NaCl (100 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (1/1) as eluent, affording (*S*)-2′-hydroxy-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (6.79 g, 16.2 mmol, 93%) as a colorless sticky oil. R_f = 0.22 (cyclohexane/CH_2Cl_2 1/1). GLC (HP-5): t_R = 23.3 min. IR (ATR): nu(tilde) = 3531 (w), 3060 (w), 2923 (w), 2850 (w), 2109 (w), 1908 (w), 1818 (w), 1760 (w), 1620 (m), 1595 (m), 1506 (m), 1473 (w), 1415 (s), 1345 (m), 1204 (vs), 1132 (vs), 1066 (m), 945 (s), 810 (s), 747 (s), 675 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{13}F_3O_4S$ $[M]^+$: 418.0487; found: 418.0477. ^1H NMR (500 MHz, C_6D_6): δ 4.40 (s, 1H), 6.94 (m_o, 1H), 6.99 (m_o, 1H), 7.02 (m_o, 1H), 7.06−7.11 (m, 2H), 7.13 (m_o, 1H), 7.33 (m_o, 1H), 7.38 (m_o, 1H), 7.46 (m_o, 1H), 7.51 (m_o, 1H), 7.60 (m_o, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 112.5, 118.2, 118.8 (q, J = 320.8 Hz), 120.1, 124.0, 124.6, 126.0, 127.0, 127.4, 127.5, 128.3, 128.4, 128.6, 129.6, 131.4, 131.6, 133.2, 133.8, 133.9, 146.5, 152.4. The analytical and spectroscopic data are in accordance with those reported.[20a]

(*R*)-[1,1′-Binaphthalen]-2-ol. To a suspension of palladium on activated charcoal (10 wt %, 1.27 g, 1.19 mmol, 10.0 mol %) in MeOH (20 mL) were added *N*,*N*-diisopropylethylamine (4.15 mL, 3.08 g, 23.8 mmol, 2.00 equiv) and a solution of (*S*)-2′-hydroxy-[1,1′-binaphthalen]-2-yl trifluoromethanesulfonate (4.99 g, 11.9 mmol, 1.00 equiv) in MeOH (30 mL). The atmosphere was changed to dihydrogen (1 atm), and the mixture was stirred at room temperature for 60 h. The mixture was filtered through Celite, the residue was rinsed with ethyl acetate (20 mL), and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent, affording (*R*)-[1,1′-binaphthalen]-2-ol (2.22 g, 8.20 mmol, 69%) as a white solid. m.p.: 170 °C (CH_2Cl_2). R_f = 0.50 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 22.7 min. IR (ATR): nu(tilde) = 3522 (w), 3049 (w), 2918 (w), 1929 (w), 1813 (w), 1616 (w), 1587 (w), 1500 (w), 1465 (w), 1434 (w), 1380 (m), 1344 (w), 1267 (m), 1186 (m), 1141 (m), 1071 (w), 1012 (w), 968 (m), 935 (m), 864 (w), 777 (s), 750 (s), 677 (m) cm^{-1}. HRMS (ESI) calculated for $C_{20}H_{14}O$ $[M]^+$: 270.1039; found: 270.1042. ^1H NMR (500 MHz, $CDCl_3$): δ 4.89 (s, 1H), 7.11 (m_o 1H), 7.24 (m_o, 1H), 7.31−7.37 (m, 3H), 7.38−7.42 (m, 1H), 7.51−7.57 (m, 2H), 7.67 (m_o, 1H), 7.87 (m_o, 1H), 7.91 (m_o, 1H), 7.99 (m_o, 1H), 8.04 (m_o, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 117.6, 118.9, 123.5, 125.1, 125.9, 126.2, 126.69, 126.71, 127.0, 128.2, 128.6, 129.1, 129.4, 129.8, 130.0, 131.6, 133.0, 134.0, 134.4, 151.1. The analytical and spectroscopic data are in accordance with those reported.[31]

(*R*)-2-(Methoxymethoxy)-1,1′-binaphthalene [(*R*)-29]. To a solution of (*R*)-[1,1′-binaphthalen]-2-ol (2.02 g, 7.47 mmol, 1.00 equiv) in THF (35 mL) cooled to 0 °C was added NaH (60 wt %, 0.448 g, 11.2 mmol, 1.50 equiv) portionwise. The resulting mixture was stirred for 30 min at 0 °C. MOMBr (0.82 mL, 1.3 g, 9.0 mmol, 1.2 equiv) was added, and then the mixture was allowed to warm to room temperature, followed by stirring for 12 h. The reaction was quenched by the addition of water (25 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 35 mL). The combined organic phases were washed with saturated aqueous NaCl (30 mL), dried over $MgSO_4$, and concentrated under reduced pressure. MOM-protected alcohol (*R*)-**29** (2.32 g, 7.39 mmol, 99%) was obtained as a pale yellow solid and used without further purification. m.p.: 157 °C (benzene). GLC (HP-5): t_R = 23.6 min. IR (ATR): nu(tilde) = 3410 (w), 3037 (w), 2917 (s), 2848 (s), 2122 (w), 2050 (w), 1998 (w), 1826 (w), 1736 (w), 1685 (w), 1587 (m), 1502 (m), 1457 (m), 1367 (m), 1330 (m), 1240 (s), 1144 (s), 1028 (s), 1005 (vs), 894 (s), 781 (s), 690 (s) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{18}O_2$ $[M]^+$: 314.1307; found: 314.1297. ^1H NMR (500 MHz, C_6D_6): δ 2.87 (s, 3H), 4.68 (s, 2H), 7.00−7.08 (m, 2H), 7.16−7.19 (m, 1H), 7.24 (m_o, 1H), 7.36−7.48 (m, 3H), 7.52 (m_o, 1H), 7.56 (m_o 1H), 7.70 (m_o, 1H), 7.72−7.77 (m, 3H). ^{13}C NMR (126 MHz, C_6D_6): δ 55.6, 94.9, 117.1, 124.4, 125.3, 125.9, 126.0, 126.26, 126.27, 126.8, 126.9, 127.8, 128.0, 128.6, 128.9, 129.7, 130.3, 133.8, 134.4, 135.0, 135.4, 153.0.

(*R*)-2-(Methoxymethoxy)-3-methyl-1,1′-binaphthalene [(*R*)-30]. To a solution of MOM-protected alcohol (*R*)-**29** (1.11 g, 3.53 mmol, 1.00 equiv) in THF (39 mL) cooled to −78 °C was added *n*BuLi (1.41 M in hexane fractions, 3.00 mL, 4.24 mmol, 1.20 equiv) dropwise, and the resulting mixture was stirred for 1 h at 0 °C. Methyl iodide (0.26 mL, 0.60 g, 4.2 mmol, 1.2 equiv) was added, and then the mixture was allowed to warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of saturated aqueous NH_4Cl (15 mL) and water (15 mL). The phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (2 × 15 mL). The combined organic phases were washed with saturated aqueous NaCl (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The title compound (*R*)-**30** (1.12g, 3.41 mmol, 97%) was obtained as a pale yellow solid and used without further purification. m.p.: 89 °C (benzene). GLC (HP-5): t_R = 24.0 min. IR (ATR): nu(tilde) = 3043 (w), 2918 (s), 2851 (m), 2182 (w), 2070 (w), 1944 (w), 1588 (w), 1499 (w), 1441 (m), 1368 (m), 1331 (w), 1240 (m), 1200 (s), 1158 (s), 1094 (s), 1037 (m), 959 (vs), 926 (s), 890 (s), 796 (s), 777 (s) cm^{-1}. HRMS (ESI) calculated for $C_{23}H_{20}O_2$ $[M]^+$: 328.1463; found: 328.1452. ^1H NMR (500 MHz, C_6D_6): δ 2.50 (s, 3H), 2.70 (s, 3H), 4.45 (d, J = 5.7 Hz, 1H), 4.50 (d, J = 5.7 Hz, 1H), 6.98 (m_o, 1H), 7.04 (m_o, 1H), 7.21 (m_o 2H), 7.30−7.35 (m, 2H), 7.39 (m_o, 1H), 7.52 (m_o, 1H), 7.61 (s, 1H), 7.67−7.73 (m, 3H). ^{13}C NMR (126 MHz, C_6D_6): δ 18.0, 56.3, 99.3, 125.2, 125.7, 125.8, 126.1, 126.5, 127.1, 127.5, 128.2, 128.3, 128.4, 129.50, 129.51, 130.0, 131.6, 132.0, 133.7 (2C), 134.2, 135.3, 153.5.

(*R*)-3-Methyl-[1,1′-binaphthalen]-2-ol [(*R*)-31]. To a solution of (*R*)-**30** (2.0 g, 6.1 mmol, 1.0 equiv) in 1,4-dioxane (15 mL) was added concentrated hydrochloric acid (37%, 0.27 mL), and the resulting mixture was stirred for 72 h at 50 °C. After cooling to room temperature, the reaction was poured into water (30 mL). The phases were separated, and the aqueous phase was extracted with ethyl acetate (3 × 25 mL). The combined organic phases were washed with saturated aqueous NaCl (15 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. Alcohol (*R*)-**31** (1.7 g, 6.0 mmol, 98%) was obtained as a white solid and used without further purification. m.p.: 145 °C (CH_2Cl_2). GLC (HP-5): t_R = 23.3 min. IR (ATR): nu(tilde) = 3537 (vs), 3054 (w), 2915 (w), 2847 (w), 2732 (w), 2064 (w), 1939 (w), 1825 (w), 1621 (w), 1587 (w), 1501 (w), 1423 (w), 1383 (m), 1188 (s), 1137 (m), 1099 (m), 1061 (w), 938 (w), 853 (w), 800 (s), 749 (s), 686 (m) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{16}O$ $[M]^+$: 284.1201; found: 284.1193. ^1H NMR (500 MHz, C_6D_6): δ 2.48 (s, 3H), 4.85 (s, 1H), 7.00 (m_o 2H), 7.14 (m_o 1H), 7.17−7.27 (m, 4H), 7.49 (m_o, 1H), 7.57 (s, 1H), 7.86 (m_o, 3H). ^{13}C NMR (126 MHz, C_6D_6): δ 17.2, 118.7, 123.7, 125.3, 126.1, 126.3,

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126.4, 126.8, 126.9, 127.2, 127.7, 128.3, 129.3, 129.6, 129.9 (2C), 132.5, 133.5 (2C), 134.7, 150.8. Anal. Calcd for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.74; H, 5.68.

(*R*)-3-Methyl-[1,1′-binaphthalen]-2-yl Trifluoromethanesulfonate [(*R*)-32]. To solution of alcohol (*R*)-**31** (1.5 g, 5.3 mmol, 1.0 equiv) in CH_2Cl_2 (12 mL) cooled to 0 °C were added *N*,*N*-diisopropylethylamine (1.2 mL, 0.89 g, 6.9 mmol, 1.3 equiv) and subsequently trifluoromethanesulfonic anhydride (1.0 mL, 1.7 g, 5.8 mmol, 1.1 equiv). The cooling bath was removed, and then the mixture was stirred at room temperature for 12 h. The mixture was washed with hydrochloric acid (2 M, 15 mL), saturated aqueous $NaHCO_3$ (15 mL), and saturated aqueous NaCl (15 mL). The organic phase was dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent, affording triflate (*R*)-**32** (1.8 g, 4.4 mmol, 82%) as a white solid. m.p.: 75 °C (benzene). R_f = 0.55 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 23.1 min. IR (ATR): nu(tilde) = 3059 (w), 2219 (w), 2061 (w), 1591 (w), 1501 (w), 1326 (w), 1199 (vs), 1128 (s), 1079 (m), 936 (s), 885 (s), 818 (s), 777 (s), 749 (s), 666 (m) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{15}F_3O_3S$ $[M]^+$: 416.0694; found: 416.0676. ^1H NMR (500 MHz, C_6D_6): δ 2.47 (s, 3H), 6.90 (m_c, 1H), 7.04 (m_c, 1H), 7.17−7.18 (m, 1H), 7.20 (m_c, 1H), 7.28 (m_c, 1H), 7.31 (m_c, 1H), 7.36 (m_c, 3H), 7.52 (m_c, 1H), 7.68 (m_c, 1H), 7.73 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 18.3, 117.3, 118.6 (q, J = 320.1 Hz), 125.5, 126.1, 126.3, 126.8, 127.2, 127.4, 127.6, 128.6, 129.5, 129.6, 129.9, 131.2, 131.4, 131.8, 133.1, 133.16, 133.18, 134.2, 145.5.

(*R*)-3-Methyl-[1,1′-binaphthalen]-2-amine [(*R*)-34]. Triflate (*R*)-**32** (1.5 g, 3.6 mmol, 1.0 equiv), $Pd(OAc)_2$ (0.20 g, 0.90 mmol, 0.25 equiv), *rac*-BINAP (0.67 g, 1.1 mmol, 0.30 equiv), and Cs_2CO_3 (3.3 g, 10 mmol, 2.8 equiv) were dissolved in dry 1,4-dioxane (15 mL). To that suspension was added benzylamine (1.94 mL, 1.90 g, 18.0 mmol, 5.00 equiv), and the resulting mixture was degassed (three freeze−pump−thaw cycles). The mixture was stirred at 80 °C for 90 h. After cooling to room temperature, the mixture was filtered through Celite, and the solvent was removed under reduce pressure. The crude benzylamine (*R*)-**33** was directly used in the next step without purification. A solution of crude (*R*)-**33** in ethyl acetate (60 mL) was added to palladium on activated charcoal (10 wt %, 0.40 g, 0.38 mmol, 10 mol % based on (*R*)-**32**). The atmosphere was changed to dihydrogen (1 atm), and the mixture was stirred at 40 °C. The reaction was monitored by ^1H NMR spectroscopy, and another batch of palladium on activated charcoal (10 wt %, 0.40 g, 0.39 mmol, 10 mol % based on (*R*)-**32**) was added after 16 h. The suspension was stirred for a further 24 h. After cooling to room temperature, the mixture was filtered through Celite, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent, affording amine (*R*)-**34** (0.75 g, 2.7 mmol, 71% over two steps) as a white solid. m.p.: 228 °C (chloroform). R_f = 0.44 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 24.3 min. IR (ATR): nu(tilde) = 3375 (w), 3055 (w), 2853 (w), 1936 (w), 1625 (m), 1499 (m), 1430 (m), 1383 (m), 1275 (m), 1214 (m), 1154 (w), 1011 (m), 887 (m), 852 (w), 783 (s), 748 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{17}N$ $[M]^+$: 283.1361; found: 283.1353. ^1H NMR (500 MHz, $CDCl_3$): δ 2.45 (s, 3H), 3.58 (s, 2H), 6.95 (m_c, 1H), 7.12 (m_c, 1H), 7.21 (m_c, 1H), 7.31 (m_c, 1H), 7.39 (m_c, 1H), 7.47−7.52 (m, 2H), 7.65 (m_c, 1H), 7.69 (m_c, 1H), 7.74 (m_c, 1H), 7.98 (m_c, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.6, 117.5, 122.3, 124.5, 125.1, 125.5, 126.1, 126.3, 126.4, 126.5, 127.3, 128.0, 128.3, 128.5, 128.7, 129.2, 132.7, 133.4, 134.4, 135.3, 141.4.

(*R*)-2-Iodo-3-methyl-1,1′-binaphthalene [(*R*)-35]. To a suspension of amine (*R*)-**34** (0.30 g, 1.1 mmol, 1.0 equiv) in concentrated hydrochloric acid (37%, 1 mL) cooled to 0 °C was slowly added a solution of $NaNO_2$ (0.16 g, 2.3 mmol, 2.2 equiv) in water (3 mL). The mixture was warmed to room temperature, stirred for 2.5 h, and cooled to 0 °C. To this mixture, a solution of KI (1.8 g, 11 mmol, 10 equiv) in water (9 mL) was added dropwise. The resulting mixture was allowed to warm to room temperature and stirred overnight. The reaction was quenched by the addition of saturated aqueous Na_2SO_3 (5 mL), and the aqueous phase was extracted with CH_2Cl_2 (3 × 5 mL). The combined organic phases were washed with saturated aqueous NaCl (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (100/1) as eluent, affording iodide (*R*)-**35** (0.28 g, 0.72 mmol, 68%) as a yellow solid. m.p.: 160 °C (chloroform). R_f = 0.25 (cyclohexane). GLC (HP-5): t_R = 25.0 min. IR (ATR): nu(tilde) = 3054 (w), 2940 (w), 2915 (w), 2849 (w), 2121 (w), 2070 (w), 2024 (w), 1931 (w), 1815 (w), 1578 (m), 1502 (m), 1430 (m), 1360 (m), 1314 (m), 1254 (s), 1189 (m), 982 (m), 883 (m), 777 (s), 750 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{15}I$ $[M]^+$: 394.0218; found: 394.0209. ^1H NMR (500 MHz, $CDCl_3$): δ 2.74 (s, 3H), 7.11 (m_c, 1H), 7.16−7.21 (m, 2H), 7.30 (m_c, 1H), 7.36 (m_c, 1H), 7.44−7.51 (m, 2H), 7.64 (m_c, 1H), 7.83 (m_c, 1H), 7.86 (m_c, 1H), 7.98 (m_c, 1H), 8.01 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 30.2, 108.1, 125.8, 125.9, 126.1, 126.2, 126.4, 126.6, 127.3, 127.45, 127.51, 128.1, 128.3, 128.5, 132.0, 132.3, 133.2, 133.9, 138.5, 142.2, 143.8.

(*R*)-3-(Bromomethyl)-2-iodo-1,1′-binaphthalene [(*R*)-36]. Iodide (*R*)-**35** (0.11 g, 0.28 mmol, 1.0 equiv), NBS (60 mg, 0.34 mmol, 1.2 equiv), and benzoyl peroxide (68 mg, 0.28 mmol, 1.0 equiv) were dissolved in benzene (5 mL). The resulting mixture was heated to reflux for 3 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10/1) as eluent, affording benzyl bromide (*R*)-**36** (94 mg, 0.20 mmol, 71%) as a white solid. m.p.: 183 °C (CH_2Cl_2). R_f = 0.33 (cyclohexane/CH_2Cl_2 10/1). GLC (HP-5): t_R = 29.0 min. IR (ATR): nu(tilde) = 3054 (m), 2920 (m), 2848 (m), 2123 (w), 2021 (w), 1954 (w), 1804 (w), 1610 (w), 1572 (m), 1486 (m), 1430 (m), 1358 (m), 1281 (m), 1210 (s), 1131 (w), 1072 (w), 988 (m), 859 (w), 772 (s), 752 (s) cm^{-1}. HRMS (ESI) calculated for $C_{21}H_{14}BrI$ $[M]^+$: 471.9324; found: 471.9310. ^1H NMR (500 MHz, C_6D_6): δ 4.56 (d, J = 10.2 Hz, 1H), 4.59 (d, J = 10.2 Hz, 1H), 6.84 (m_c, 1H), 7.00 (m_c, 1H), 7.08 (m_c, 1H), 7.11−7.15 (m, 2H), 7.18−7.24 (m, 2H), 7.33 (m_c, 1H), 7.50 (m_c, 1H), 7.61 (s, 1H), 7.71 (m_c, 1H), 7.75 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 41.0, 105.5, 125.96, 126.03, 126.4, 126.9, 127.1, 127.8, 127.9, 128.2, 128.3, 128.7 (2C), 129.7, 132.4, 133.3, 133.8, 134.3, 137.6, 142.1, 145.7.

(*R*)-Ethyl((2-iodo-[1,1′-binaphthalen]-3-yl)methyl)sulfane [(*R*)-37]. Benzyl bromide (*R*)-**36** (94 mg, 0.20 mmol, 1.0 equiv) was dissolved in ethanol (1.4 mL). K_2CO_3 (55 mg, 0.40 mmol, 2.0 equiv) and ethanethiol (29 μL, 25 mg, 0.40 mmol, 2.0 equiv) were added, and the resulting mixture was stirred overnight at 45 °C. After cooling to room temperature, the reaction was quenched by the addition of water (3 mL). The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (2 × 2 mL). The combined organic phases were washed with aqueous NaOH (2 M, 2 mL) and saturated aqueous NaCl (2 mL), dried over Na_2SO_4, and concentrated under reduced pressure. Ethyl thioether (*R*)-**37** (82 mg, 0.18 mmol, 91%) was obtained as a colorless sticky oil and used without further purification. GLC (HP-5): t_R = 30.8 min. IR (ATR): nu(tilde) = 3053 (m), 2964 (m), 2920 (m), 2867 (w), 2244 (w), 2049 (w), 1929 (w), 1812 (w), 1703 (w), 1577 (m), 1490 (m), 1448 (m), 1362 (m), 1317 (w), 1256 (m), 1131 (w), 1024 (m), 987 (m), 905 (s), 774 (s), 728 (s) cm^{-1}. HRMS (ESI) calculated for $C_{23}H_{19}IS$ $[M]^+$: 454.0252; found: 454.0238. ^1H NMR (500 MHz, $CDCl_3$): δ 1.35 (t, J = 7.6 Hz, 3H), 2.65 (q, J = 7.6 Hz, 2H), 4.13 (d, J = 13.8 Hz, 1H), 4.16 (d, J = 13.8 Hz, 1H), 7.11 (m_c, 1H), 7.17 (m_c, 1H), 7.21 (m_c, 1H), 7.30 (m_c, 1H), 7.37 (m_c, 1H), 7.48 (m_c, 2H), 7.64 (m_c, 1H), 7.88 (m_c, 1H), 7.95 (s, 1H), 7.97 (m_c, 1H), 8.01 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.8, 26.2, 43.2, 106.9, 125.7, 125.9, 126.2, 126.5, 126.8, 126.9, 127.6, 127.7, 128.0, 128.1, 128.4, 128.5, 132.0, 132.8, 132.9, 133.8, 137.6, 142.1, 144.8.

(*R*)-(3-((Ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)dimethylsilane [(*R*)-38]. To a solution of ethyl thioether (*R*)-**37** (60 mg, 0.13 mmol, 1.0 equiv) in THF (1.6 mL) cooled to −78 °C was added *n*BuLi (2.2 M in hexane fractions, 80 μL, 0.17 mmol, 1.3 equiv) dropwise, and the resulting mixture was stirred for 1 h at −78 °C. $Me_2Si(H)Cl$ (19 μL, 16 mg, 0.17 mmol, 1.3 equiv) was added, and

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then the mixture was allowed to slowly warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of water (3 mL), and the phases were separated. The aqueous phase was extracted with *tert*-butyl methyl ether (3 × 3 mL), and the combined organic phases were washed with saturated aqueous NaCl (3 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (10/1) as eluent, affording hydrosilane (*R*)-**38** (39 mg, 86 μmol, 62%, 96% ee) as a white solid. Single crystals of (*R*)-**38** suitable for X-ray diffraction were obtained by slow vaporization of a cyclohexane/CH_2Cl_2 (approximately 20/1) solution. m.p.: 125 °C (CH_2Cl_2). R_f = 0.22 (cyclohexane/CH_2Cl_2 10/1). GLC (HP-5): t_R = 27.5 min. IR (ATR): nu(tilde) = 3053 (m), 2959 (m), 2920 (m), 2849 (m), 2309 (w), 2137 (m), 1998 (w), 1916 (w), 1578 (w), 1548 (w), 1502 (w), 1442 (m), 1348 (m), 1244 (m), 1184 (w), 1005 (m), 885 (s), 836 (m), 761 (s), 660 (m) cm^{-1}. HRMS (ESI) calculated for $C_{25}H_{26}SSi$ $[M]^+$: 386.1524; found: 386.1504. ^1H NMR (500 MHz, C_6D_6): δ −0.43 (d, *J* = 4.0 Hz, 3H), 0.30 (d, *J* = 4.0 Hz, 3H), 1.13 (t, *J* = 7.4 Hz, 3H), 2.65 (qd, *J* = 7.4 Hz, *J* = 1.7 Hz, 2H), 4.03 (d, *J* = 13.0 Hz, 1H), 4.24 (d, *J* = 13.0 Hz, 1H), 4.67 (sept, *J* = 3.9 Hz, 1H), 6.91 (m_c, 1H), 6.96 (m_c, 1H), 7.16−7.19 (m, 1H), 7.20−7.23 (m, 2H), 7.24−7.27 (m, 2H), 7.30 (m_c, 1H), 7.65−7.71 (m, 2H), 7.65−7.71 (m, 1H), 7.76 (s, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −2.3, −0.1, 14.8, 26.0, 38.3, 125.3, 126.22, 126.23, 126.5, 127.0, 127.37, 127.40, 127.7, 128.3, 128.4, 128.6, 129.2, 132.9, 133.8, 134.0, 134.6, 135.6, 139.4, 141.1, 148.0. ^{29}Si DEPT (99 MHz, C_6D_6): δ −24.5. HPLC (Daicel Chiralcel OJ-RH, 20 °C, acetonitrile/H_2O 60/40, flow rate: 0.50 mL/min, λ = 254 nm): t_R = 53.8 min [(*R*)-(3-((ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)dimethylsilane], t_R = 58.9 min [(*S*)-(3-((ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)-dimethylsilane].

(*S*)-[1,1′-Binaphthalene]-2,2′-diyl Bis(trifluoromethanesulfonate). To a solution of (*S*)-BINOL [(*S*)-**17**, 5.0 g, 18 mmol, 1.0 equiv] in CH_2Cl_2 (25 mL) cooled to 0 °C were added pyridine (4.2 mL, 4.2 g, 53 mmol, 3.0 equiv) and subsequently trifluoromethanesulfonic anhydride (6.5 mL, 11 g, 39 mmol, 2.2 equiv). The resulting mixture was allowed to warm to room temperature and stirred for 5 h. The reaction was quenched by the addition of water (15 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (2 × 15 mL). The combined organic phases were washed with NaCl (25 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (10/1) as eluent, affording (*S*)-[1,1′-binaphthalene]-2,2′-diyl bis(trifluoromethanesulfonate) (9.4 g, 17 mmol, 98%) as a white solid. m.p.: 84 °C (cyclohexane). R_f = 0.33 (cyclohexane/ethyl acetate 10/1). GLC (HP-5): t_R = 22.3 min. IR (ATR): nu(tilde) = 3067 (w), 2942 (w), 1906 (w), 1854 (w), 1586 (m), 1508 (m), 1401 (s), 1203 (vs), 1174 (s), 1132 (vs), 956 (s), 869 (m), 831 (vs), 751 (s), 702 (s) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{12}F_6O_6S_2$ $[M]^+$: 549.9979; found: 549.9976. ^1H NMR (500 MHz, C_6D_6): δ 6.92 (m_c, 2H), 7.10 (m_c, 2H), 7.21 (m_c, 2H), 7.37 (m_c, 2H), 7.47−7.51 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6): δ 118.8 (q, *J* = 320.7 Hz, 2C), 119.7 (2C), 124.0 (2C), 127.1 (2C), 127.4 (2C), 128.2 (2C), 128.5 (2C), 132.3 (2C), 132.7 (2C), 133.6 (2C), 145.9 (2C).

(*S*)-2,2′-Dimethyl-1,1′-binaphthalene [(*S*)-39]. 1,3-Bis(diphenylphosphino)propane nickel(II) chloride (296 mg, 0.546 mmol, 5.00 mol %) was placed in a flame-dried Schlenk flask, and a solution of (*S*)-[1,1′-binaphthalene]-2,2′-diyl bis(trifluoromethanesulfonate) (6.01 g, 10.9 mmol, 1.00 equiv) in Et_2O (55 mL) was added. The suspension was cooled to 0 °C, and methylmagnesium bromide (3.0 M in Et_2O, 11 mL, 33 mmol, 3.0 equiv) was added dropwise. The cooling bath was replaced by an oil bath, and the mixture was heated to reflux overnight. The mixture was cooled to 0 °C and was carefully quenched by the addition of hydrochloric acid (2 M, 35 mL). The phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 30 mL). The combined organic phases were washed with saturated aqueous NaCl (80 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane as eluent, affording (*S*)-**39** (3.03 g, 10.7 mmol, 98%, 99% ee) as a yellow solid. m.p.: 74 °C (cyclohexane). R_f = 0.35 (cyclohexane). GLC (HP-5): t_R = 21.6 min. IR (ATR): nu(tilde) = 3046 (w), 2913 (w), 1921 (w), 1560 (w), 1503 (m), 1438 (w), 1375 (w), 1259 (w), 1218 (w), 1142 (w), 1024 (m), 950 (w), 897 (w), 866 (m), 811 (vs), 781 (m), 744 (vs), 695 (m) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{18}$ $[M]^+$: 282.1409; found: 282.1416. ^1H NMR (500 MHz, C_6D_6): δ 1.94 (s, 6H), 7.00 (m_c, 2H), 7.21 (m_c, 2H), 7.24 (m_c, 2H), 7.33 (m_c, 2H), 7.74 (m_c, 2H), 7.76 (m_c, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 20.1 (2C), 125.4 (2C), 126.1 (2C), 126.7 (2C), 127.9 (2C), 128.4 (2C), 129.1 (2C), 132.9 (2C), 133.4 (2C), 134.5 (2C), 135.8 (2C). HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-hexane, flow rate: 0.50 mL/min, λ = 254 nm): t_R = 20.1 min [(*S*)-2,2′-dimethyl-1,1′-binaphthalene], t_R = 24.7 min [(*R*)-2,2′-dimethyl-1,1′-binaphthalene]. The analytical and spectroscopic data are in accordance with those reported.[21a]

(*S*)-4,4-Diethoxy-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]-silepine [(*S*)-40]. *n*BuLi (2.2 M in hexane fractions, 2.1 mL, 4.4 mmol, 2.5 equiv) was concentrated under reduced pressure, and the residue was dissolved in Et_2O (5 mL). To this solution were added a solution of (*S*)-**39** (0.50 g, 1.8 mmol, 1.0 equiv) in Et_2O (5 mL) and TMEDA (0.68 mL, 0.52 g, 4.5 mmol, 2.6 equiv) at room temperature. The resulting mixture was stirred for 24 h, diluted with THF (12 mL), and cooled to −78 °C. To this solution was added a solution of $(EtO)_2SiCl_2$ (0.36 mL, 0.40 g, 2.1 mmol, 1.2 equiv) in THF (8 mL), and then the mixture was allowed to slowly warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of water (20 mL), and the phases were separated. The aqueous phases was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl (40 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was rapidly purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent, affording dihydrosilepine (*S*)-**40** (0.22 g, 0.55 mmol, 31%) as a white solid. m.p.: 195 °C (cyclohexane). R_f = 0.15 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 25.9 min. IR (ATR): nu(tilde) = 3034 (br w), 2969 (m), 2919 (w), 2884 (w), 2728 (w), 2200 (w), 2118 (w), 2008 (w), 1901 (w), 1821 (w), 1723 (w), 1590 (w), 1503 (m), 1434 (w), 1386 (m), 1354 (m), 1289 (w), 1239 (w), 1145 (m), 1077 (vs), 944 (m), 864 (m), 822 (s), 772 (s), 744 (vs) cm^{-1}. HRMS (ESI) calculated for $C_{26}H_{26}O_2Si$ $[M]^+$: 398.1702; found: 398.1697. ^1H NMR (500 MHz, C_6D_6): δ 1.04 (t, *J* = 7.0 Hz, 6H), 2.11 (d, *J* = 13.7 Hz, 2H), 2.18 (d, *J* = 13.8 Hz, 2H), 3.57 (q, *J* = 7.0 Hz, 4H), 6.96 (m_c, 2H), 7.17−7.19 (m, 2H), 7.36 (m_c, 2H), 7.39 (m_c, 2H), 7.71−7.75 (m, 4H). ^{13}C NMR (126 MHz, C_6D_6): δ 18.6 (2C), 21.6 (2C), 59.0 (2C), 124.9 (2C), 126.5 (2C), 127.1 (2C), 128.3 (2C), 128.5 (2C), 128.7 (2C), 132.5 (2C), 133.4 (2C), 133.5 (2C), 135.4 (2C). ^{29}Si DEPT (99 MHz, C_6D_6): δ −6.8. Anal. Calcd for $C_{26}H_{26}O_2Si$: C, 78.35; H, 6.58. Found: C, 78.45; H, 6.52.

(*S*)-4,5-Dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*)-41]. To a solution of dihydrosilepine (*S*)-**40** (0.20 g, 0.50 mmol, 1.0 equiv) in CH_2Cl_2 (5 mL) at −78 °C was added DIBAL-H (1.2 M in toluene, 1.3 mL, 1.5 mmol, 3.0 equiv) dropwise. The mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction was cooled to 0 °C, $Na_2SO_4 \cdot 10H_2O$ (1.0 g) was added, the ice bath was removed, and the suspension was stirred for 2 h at room temperature. The suspension was filtered, the solids were extracted with CH_2Cl_2 (20 mL), and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane as eluent, affording dihydrosilepine (*S*)-**41** (94 mg, 0.30 mmol, 60%) as a white solid. m.p.: 175 °C (cyclohexane). R_f = 0.21 (cyclohexane). GLC (HP-5): t_R = 23.8 min. IR (ATR): nu(tilde) = 3039 (w), 2922 (w), 2849 (w), 2316 (w), 2127 (m), 1926 (w), 1588 (w), 1504 (m), 1408 (m), 1352 (m), 1237 (m), 1219 (w), 1143 (m), 1091 (w), 1053 (w), 1023 (w), 932 (m), 822 (vs), 736 (s), 673 (s) cm^{-1}. HRMS (ESI) calculated for $C_{22}H_{18}Si$ $[M]^+$: 310.1178; found: 310.1172. ^1H NMR (500 MHz, $CDCl_3$): δ 2.05−2.17 (m, 4H), 4.10 (tt, *J* = 5.1 Hz, *J* = 1.4 Hz, 2H), 7.09 (m_c, 2H), 7.19 (m_c, 2H), 7.38 (m_c, 2H), 7.46 (m_c, 2H), 7.88 (m_c, 4H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 17.0 (2C), 124.7 (2C), 126.1

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(2C), 126.4 (2C), 127.4 (2C), 128.2 (2C), 128.4 (2C), 132.2 (2C), 132.6 (2C), 132.8 (2C), 136.1 (2C). ^{29}Si DEPT (99 MHz, $CDCl_3$): δ −22.6. Anal. Calcd for $C_{22}H_{18}Si$: C, 85.11; H, 5.84. Found: C, 85.19; H, 5.90.

(4*RS*,11b*S*)-4-(2-((Ethylthio)methyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepine [(*S*)-42]. To a solution of thioether **12** (101 mg, 0.435 mmol, 1.00 equiv) in THF (15 mL) cooled to −78 °C was added *n*BuLi (2.2 M in hexane fractions, 0.20 mL, 0.44 mmol, 1.0 equiv) dropwise, and the resulting mixture was stirred for 1 h at −78 °C. (*S*)-**41** (135 mg, 0.435 mmol, 1.00 equiv) dissolved in THF (4 mL) was quickly added, and then the mixture was allowed to slowly warm to room temperature, followed by stirring overnight. The reaction was quenched by the addition of water (10 mL), and the phases were separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 10 mL), the combined organic phases were washed with saturated aqueous NaCl (20 mL) and dried over Na_2SO_4, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/CH_2Cl_2 (5/1) as eluent, affording hydrosilane (*S*)-**42** (112 mg, 0.243 mmol, 60%) as a white solid. Single crystals of (*S*)-**42** suitable for X-ray diffraction were obtained by slow vaporization of a cyclohexane/CH_2Cl_2 (approximately 50/1) solution. m.p.: 162 °C (benzene). R_f = 0.20 (cyclohexane/CH_2Cl_2 5/1). IR (ATR): nu(tilde) = 3042 (w), 2961 (w), 2921 (w), 2127 (m), 1917 (m), 1829 (w), 1589 (w), 1505 (m), 1423 (w), 1354 (w), 1327 (w), 1239 (m), 1147 (m), 1069 (w), 1024 (w), 961 (w), 923 (w), 850 (s), 817 (vs), 736 (vs) cm^{-1}. HRMS (ESI) calculated for $C_{31}H_{28}SSi$ $[M]^+$: 460.1681; found: 460.1676. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.21 (t, J = 7.4 Hz, 3H), 2.30−2.40 (m, 4H), 2.43 (q, J = 7.3 Hz, 2H), 3.83 (s, 2H), 4.84 (m$_c$, 1H), 7.08−7.14 (m, 3H), 7.15−7.23 (m, 3H), 7.27−7.33 (m, 3H), 7.39 (m$_c$, 2H), 7.55 (m$_c$, 1H), 7.82 (m$_c$, 1H), 7.89−7.92 (m, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 14.7, 20.87, 20.91, 26.0, 37.0, 124.6 (2C), 125.99, 126.03, 126.46, 126.50, 126.6, 127.8, 128.0, 128.19, 128.22, 128.3, 128.6, 129.7, 130.0, 132.1, 132.2, 132.7 (2C), 132.8, 132.9, 133.7, 136.0, 136.1, 136.2, 144.2. ^{29}Si DEPT (99 MHz, $CDCl_3$): δ −9.4. Anal. Calcd for $C_{31}H_{28}SSi$: C, 80.82; H, 6.13; S, 6.96. Found: C, 80.94; H, 6.37; S, 6.80.

(*S*)-(2′-((Ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)-dimethylsilylium Tetrakis(pentafluorophenyl)borate [(*S*)-8]. Prepared from (*S*)-(2′-((ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)-dimethylsilane [(*S*)-**28**, 19 mg, 50 μmol, 1.0 equiv] and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (46 mg, 50 μmol, 1.0 equiv) according to GP1. NMR spectroscopic data for (*S*)-**8** are as follows. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ −0.66 (s, 3H), 0.72 (s, 3H), 1.13 (m$_c$, 3H), 2.46−2.60 (m, 1H), 2.64−2.77 (m, 1H), 3.37−3.54 (m, 1H), 3.92−4.07 (m, 1H), 6.99 (m$_c$, 1H), 7.30 (m$_c$, 1H), 7.34 (m$_c$, 2H), 7.40 (m$_c$, 1H), 7.45−7.53 (m, 2H), 7.80 (m$_c$, 1H), 7.86 (m$_c$, 2H), 7.91 (m$_c$, 1H), 7.96 (m$_c$, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −3.8 (br s), 11.2, 30.3 (br s), 40.2 (br s), 123.3, 125.2 (br m), 126.3, 126.7, 127.5, 128.1, 128.3, 128.8, 129.4, 130.1, 131.3, 132.0, 132.2, 133.2, 134.0, 136.0, 136.7 (d, J = 239 Hz), 137.3, 138.6 (d, J = 239 Hz), 142.4, 143.2, 144.1, 144.2, 148.8 (d, J = 244 Hz). ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ −16.2. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): δ −166.0, −162.2, −131.7. ^{1}H,^{29}Si HMQC NMR (500/99 MHz, 1,2-$Cl_2C_6D_4$): δ −0.66, 0.72, 7.40/32.0 ppm.

(*R*)-(3-((Ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)dimethylsilylium Tetrakis(pentafluorophenyl)borate [(*R*)-9]. Prepared from (*R*)-(3-((ethylthio)methyl)-[1,1′-binaphthalen]-2-yl)dimethylsilane [(*R*)-**38**, 22 mg, 56 μmol, 1.0 equiv] and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (52 mg, 56 μmol, 1.0 equiv) according to GP1. The silicon cation was obtained as a mixture of diastereomers (dr = 67:33). NMR spectroscopic data for (*R*)-**9** are given for the mixture and are as follows. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ −0.64 (s, 3H), −0.11 (s, 1.5H), 0.05 (s, 1.5H), 0.65 (s, 3H), 1.10 (t, J = 7.3 Hz, 3H), 1.18 (t, J = 7.3 Hz, 1.5H), 2.44 (q, J = 7.3 Hz, 2H), 2.62 (m$_c$, 1H), 4.30−4.37 (m, 1.5H), 4.49−4.60 (m, 1.5H), 7.01 (m$_c$, 2H), 7.23−7.29 (m, 2.5H), 7.32−7.36 (m, 2.5H), 7.38−7.43 (m, 1.5H), 7.46−7.53 (m, 3.5H), 7.66−7.74 (m, 2.5H), 7.85 (m$_c$, 2.5H), 7.94 (m$_c$, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −5.5, −3.1, −1.8, 0.0, 11.1, 11.4, 30.0, 30.2, 40.7, 41.3, 124.5 (br m), 125.1, 125.38, 125.39., 125.6, 126.8, 126.9, 127.6, 127.8, 127.9, 128.4, 128.6, 129.0, 130.3, 130.4, 130.5, 130.8, 132.2, 132.6, 133.5, 134.0, 135.1, 135.3, 136.6 (d, J = 235 Hz), 137.3, 138.7 (d, J = 247 Hz), 142.4, 143.2, 148.6, 148.7 (d, J = 241 Hz). ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ −16.2. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): δ −166.0, −162.2, −131.7. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 50.7 ppm.

(4*RS*,11b*S*)-4-(2-((Ethylthio)methyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]silepinylium Tetrakis(pentafluorophenyl)borate [(*S*)-10]. Prepared from (4*RS*,11b*S*)-4-(2-((ethylthio)methyl)phenyl)-4,5-dihydro-3*H*-dinaphtho[2,1-*c*:1′,2′-*e*]-silepine [(*S*)-**42**, 15 mg, 33 μmol, 1.0 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (30 mg, 33 μmol, 1.0 equiv) according to GP1. The silicon cation was obtained as a mixture of diastereomers (dr = 75:25). NMR spectroscopic data for (*S*)-**10** are given for the major diastereomers and are as follows. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.96 (t, J = 7.1 Hz, 3H), 2.38−2.58 (m, 6H), 4.18 (d, J = 16.0 Hz, 1H), 4.55 (d, J = 12.7 Hz, 1H), 7.08−7.19 (m, 3H), 7.20−7.25 (m, 1H), 7.30−7.35 (m, 2H), 7.35−7.42 (m, 4H), 7.45−7.52 (m, 1H), 7.81−7.89 (m, 3H), 7.89−7.95 (m, 1H), 7.97−8.02 (m, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ 11.6, 19.5, 21.7, 32.1, 42.5, 124.8 (br m), 125.9, 126.0, 126.2, 126.3, 126.7, 127.1, 127.3, 127.6, 128.66, 128.68, 129.6, 129.9, 130.1, 130.4, 130.5, 132.1, 132.5, 132.6, 132.7, 133.1, 133.5, 133.8, 134.0, 134.5, 136.8 (d, J = 236 Hz), 139.6 (d, J = 236 Hz), 142.3, 143.2, 148.9 (d, J = 240 Hz). ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): δ −16.2. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): δ −166.0, −162.2, −131.7. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 46.0 ppm.

***endo*-Phenyl(−3-phenylbicyclo[2.2.2]oct-5-en-2-yl)methanone (45).** Prepared according to GP2 from chalcone (**44**, 104 mg, 0.500 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**43**, 0.10 mL, 84 mg, 1.1 mmol, 2.1 equiv) in 67% yield (96 mg, 0.33 mmol) and with *endo*:*exo* > 95:5, dr > 95:5, and 11% ee. The cycloadduct **45** was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/ethyl acetate (50/1) as eluent. R_f = 0.33 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 21.6 min (*exo*-**45**), t_R = 21.9 min (*endo*-**45**). HRMS (ESI) calculated for $C_{21}H_{21}O$ $[M + H]^+$: 289.1587; found: 289.1582. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.10−1.18 (m, 1H), 1.50 (m$_c$, 1H), 1.81−1.88 (m, 1H), 1.88−1.96 (m, 1H), 2.66−2.71 (m, 1H), 2.97−3.01 (m, 1H), 3.48−3.52 (m, 1H), 3.82 (dd, J = 6.5 Hz, J = 1.3 Hz, 1H), 6.13 (m$_c$, 1H), 6.58 (m$_c$, 1H), 7.20−7.25 (m, 1H), 7.29−7.36 (m, 4H), 7.38−7.43 (m, 2H), 7.49−7.54 (m, 1H), 7.86−7.91 (m$_c$, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.7, 26.6, 34.7, 36.6, 44.9, 51.1, 126.3, 128.2, 128.5, 128.6 (3C), 130.8, 132.8, 136.4, 136.6, 143.0, 200.9. HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 97/3, flow rate: 0.65 mL/min, λ = 254 nm): t_R = 9.7 min (major-**45**), t_R = 11.3 min (minor-**45**). The analytical and spectroscopic data are in accordance with those reported.[16b]

***endo*-1-(-3-Phenylbicyclo[2.2.2]oct-5-en-2-yl)ethan-1-one (51).** Prepared according to GP2 from 4-phenylbut-3-en-2-one (**46**, 73.1 mg, 0.500 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**43**, 0.10 mL, 84 mg, 1.1 mmol, 2.1 equiv) in 67% yield (85 mg, 0.38 mmol) and with *endo*:*exo* > 95:5, dr > 95:5, and 3% ee. The cycloadduct **51** was obtained as a sticky colorless oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.20 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 16.2 min (*exo*-**51**), t_R = 16.7 min (*endo*-**51**). HRMS (ESI) calculated for $C_{16}H_{19}O$ $[M + H]^+$: 227.1430; found: 227.1429. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.00−1.08 (m, 1H), 1.41−1.49 (m, 1H), 1.65−1.76 (m, 2H), 2.03 (s, 3H), 2.51−2.55 (m, 1H), 2.92−2.95 (m, 1H), 3.00−3.04 (m, 1H), 3.10−3.14 (m, 1H), 6.21 (m$_c$, 1H), 6.47 (m$_c$, 1H), 7.23 (m$_c$, 1H), 7.27−7.31 (m, 2H), 7.32−7.38 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 18.5, 26.1, 28.4, 32.7, 37.3, 45.6, 56.6, 126.5, 128.2, 128.6, 131.6, 136.1, 142.8, 208.9. HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 98/2, flow rate: 0.65 mL/min, λ = 254 nm): t_R = 13.2 min (major-**51**), t_R = 14.3 min (minor-**51**). The analytical and spectroscopic data are in accordance with those reported.[16b]

***endo*-Tricyclo[6.2.2.0^{2,7}]dodec-9-en-3-one (52).** Prepared according to GP2 from cyclohex-2-en-1-one (**47**, 49 μL, 48 mg, 0.50 mmol, 1.0 equiv) and cyclohexa-1,3-diene (**43**, 0.10 mL, 84 mg, 1.1 mmol, 2.1 equiv) in 32% yield (28 mg, 0.16 mmol) and with *endo*:*exo* > 95:5 and 1% ee. The cycloadduct **52** was obtained as a sticky yellow

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oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.25 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 13.1 min (*endo*-**52**). HRMS (ESI) calculated for $C_{12}H_{17}O$ $[M + H]^+$: 177.1274; found: 177.1270. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.91−0.98 (m, 1H), 1.26−1.30 (m, 2H), 1.48−1.53 (m, 1H), 1.54−1.60 (m, 1H), 1.72−1.81 (m, 3H), 2.03−2.11 (m, 1H), 2.32−2.46 (m, 3H), 2.48−2.53 (m, 1H), 3.06−3.11 (m, 1H), 6.12 (m_c, 1H), 6.26 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 20.9, 24.1, 26.1, 29.7, 31.3, 36.0, 38.9, 42.3, 53.1, 133.2, 134.6, 214.6. Chiral GLC (IVAdex-1, N_2 carrier gas, column flow: 1.74 mL min^{-1}, injection temperature: 250 °C, detector temperature: 300 °C; temperature program: isotherm 115 °C for 80 min): t_R = 56.0 min (major-**52**), t_R = 58.2 min (minor-**52**). The analytical and spectroscopic data are in accordance with those reported.[16a]

***endo*-Tricyclo[5.2.2.0^{2,6}]undec-8-en-3-one (53).** Prepared according to GP2 from cyclopent-2-en-1-one (**48**, 42 μL, 41 mg, 0.50 mmol, 1.0 equiv) and cyclohexa-1,3-diene (**43**, 0.10 mL, 84 mg, 1.1 mmol, 2.1 equiv) in 30% yield (24 mg, 0.15 mmol) and with *endo*:*exo* = 92:8 and 4% ee. The cycloadduct **53** was obtained as a slightly yellow oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.20 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 11.7 min (*endo*-**53**), t_R = 11.9 min (*exo*-**53**). HRMS (ESI) calculated for $C_{11}H_{15}O$ $[M + H]^+$: 163.1117; found: 163.1112. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.20−1.30 (m, 2H), 1.44−1.50 (m, 3H), 1.94−2.12 (m, 3H), 2.33−2.38 (m, 1H), 2.50−2.58 (m, 1H), 2.61−2.67 (m, 1H), 2.91−2.96 (m, 1H), 6.13−6.17 (m, 1H), 6.20 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.2, 24.9, 26.2, 32.6, 35.6, 38.3, 39.7, 52.5, 133.7, 133.8, 222.8. Chiral GLC (IVAdex-1, N_2 carrier gas, column flow: 1.74 mL min^{-1}, injection temperature: 250 °C, detector temperature: 300 °C; temperature program: isotherm 115 °C for 200 min): t_R = 104.3 min (major-**53**), t_R = 106.1 min (minor-**53**). The analytical and spectroscopic data are in accordance with those reported.[16a]

***endo*-Bicyclo[2.2.2]oct-5-ene-2-carboxylic Acid Methyl Ester (54).** Prepared according to GP2 from methyl acrylate (**49**, 45 μL, 43 mg, 0.50 mmol, 1.0 equiv) and cyclohexa-1,3-diene (**43**, 0.10 mL, 84 mg, 1.1 mmol, 2.1 equiv) in 83% yield (69 mg, 0.42 mmol) and with *endo*:*exo* = 95:5 and 14% ee. The cycloadduct **54** was obtained as a colorless oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (50/1) as eluent. R_f = 0.40 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 9.6 min (*exo*-**54**), t_R = 9.8 min (*endo*-**54**). HRMS (ESI) calculated for $C_{10}H_{15}O_2$ $[M + H]^+$: 167.1067; found: 167.1060. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.21−1.32 (m, 2H), 1.44−1.50 (m, 1H), 1.53−1.59 (m, 1H), 1.63−1.69 (m, 1H), 1.71−1.77 (m, 1H), 2.56−2.64 (m, 2H), 2.86−2.93 (m, 1H), 3.63 (s, 3H), 6.14 (m_c, 1H), 6.30 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.5, 25.5, 29.5, 30.0, 32.6, 42.8, 51.7, 131.5, 135.3, 176.1. Chiral GLC (IVAdex-1, 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 5 °C min^{-1}, end temperature 115 °C for 30 min): t_R = 33.3 min (minor-**54**), t_R = 33.6 min (major-**54**). The analytical and spectroscopic data are in accordance with those reported.[16a]

***endo*-3-(Bicyclo[2.2.2]oct-5-ene-2-carbonyl)oxazolidin-2-one (55).** Prepared according to GP2 from 3-acryloyloxazolidin-2-one (**50**, 70.1 mg, 0.500 mmol, 1.00 equiv) and cyclohexa-1,3-diene (**43**, 0.10 mL, 84 mg, 1.1 mmol, 2.1 equiv) in 52% yield (58 mg, 0.26 mmol) and with *endo*:*exo* = 95:5 and 24% ee. The cycloadduct **55** was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/ethyl acetate (5/1) as eluent. R_f = 0.15 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 17.4 min (*exo*-**55**), t_R = 17.5 min (*endo*-**55**). HRMS (ESI) calculated for $C_{12}H_{16}NO_3$ $[M + H]^+$: 222.1125; found: 222.1122. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.23−1.29 (m, 2H), 1.49−1.55 (m, 1H), 1.58−1.64 (m, 1H), 1.66−1.73 (m, 1H), 1.84 (ddd, J = 12.8 Hz, J = 9.9 Hz, J = 2.7 Hz, 1H), 2.58−2.63 (m, 1H), 2.80−2.84 (m, 1H), 3.74 (m_c, 1H), 3.96 (t, J = 8.3 Hz, 2H), 4.34−4.40 (m, 2H), 6.14 (m_c, 1H), 6.33 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 24.1, 25.8, 29.6, 30.3, 32.9, 42.2, 43.1, 62.0, 131.5, 135.1, 153.4, 176.1. HPLC (Daicel Chiralcel AD-H, 20 °C, *n*-heptane/*i*-PrOH 95/5, flow rate: 0.70 mL/min, λ = 254 nm): t_R = 28.4 min (major-**55**), t_R = 30.6 min (minor-**55**). The analytical and spectroscopic data are in accordance with those reported.[7a]

***endo*-Phenyl-(3-phenylbicyclo[2.2.1]hept-5-en-2-yl)methanone (57).** Prepared according to GP2 from chalcone (**44**, 104 mg, 0.500 mmol, 1.00 equiv) and cyclopentadiene (**56**, 87 μL, 69 mg, 1.1 mmol, 2.1 equiv) in 80% yield (0.11 g, 0.40 mmol) and with *endo*:*exo* > 95:5, dr > 95:5, and 12% ee. The cycloadduct **57** was obtained as a white solid after flash column chromatography on silica gel using cyclohexane/ethyl acetate (50/1) as eluent. R_f = 0.40 (cyclohexane/ethyl acetate 20/1). HRMS (ESI) calculated for $C_{20}H_{18}O$ $[M]^+$: 274.1363; found: 274.1352. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.63 (m_c, 1H), 2.01 (br d, J = 8.6 Hz, 1H), 3.09−3.13 (m,1H), 3.32 (m_c, 1H), 3.46 (dd, J = 5.0 Hz, J = 1.6 Hz, 1H), 3.89 (dd, J = 5.1 Hz, J = 3.5 Hz, 1H), 5.89 (dd, J = 5.7 Hz, J = 2.8 Hz, 1H), 6.45 (dd, J = 5.5 Hz, J = 3.4 Hz, 1H), 7.15−7.21 (m, 1H), 7.27−7.32 (m, 4H), 7.42−7.46 (m, 2H), 7.53−7.57 (m, 1H), 7.92−7.97 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 46.0, 48.1, 48.6, 48.7, 56.3, 126.1, 127.6, 128.5, 128.7 (2C), 128.7, 132.9, 133.1, 137.4, 139.3, 144.8, 200.1. HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 97/3, flow rate: 0.65 mL/min, λ = 254 nm): t_R = 9.2 min (major-**57**), t_R = 10.5 min (minor-**57**). The analytical and spectroscopic data are in accordance with those reported.[16b]

***endo*-1-(3-Phenylbicyclo[2.2.1]hept-5-en-2-yl)ethanone (58).** Prepared according to GP2 from 4-phenylbut-3-en-2-one (**46**, 73.1 mg, 0.500 mmol, 1.00 equiv) and cyclopentadiene (**56**, 87 μL, 69 mg, 1.1 mmol, 2.1 equiv) in 82% yield (87 mg, 0.41 mmol) and with *endo*:*exo* = 74:26, dr > 95:5, and 7% ee. The cycloadduct **58** was obtained as a sticky colorless oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.18 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 15.1 min (*exo*-**58**), t_R = 15.5 min (*endo*-**58**). HRMS (ESI) calculated for $C_{15}H_{17}O$ $[M + H]^+$: 213.1274; found: 213.1269. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.60 (m_c, 1H), 1.85 (br d, J = 8.6 Hz, 1H), 2.14 (s, 3H), 2.99−3.02 (m, 1H), 3.04−3.07 (m, 1H), 3.16−3.19 (m, 1H), 3.30−3.34 (m, 1H), 6.02 (dd, J = 5.7 Hz, J = 2.6 Hz, 1H), 6.39 (dd, J = 5.7 Hz, J = 3.4 Hz, 1H), 7.12−7.15 (m, 1H), 7.17−7.19 (m, 1H), 7.22−7.24 (m, 1H), 7.26−7.30 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 29.3, 45.4, 46.6, 47.7, 48.7, 61.2, 126.1, 127.6, 128.6, 133.3, 139.5, 144.6, 208.1. HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 98/2, flow rate: 0.65 mL/min, λ = 254 nm): t_R = 10.4 min (major-**58**), t_R = 12.9 min (minor-**58**). The analytical and spectroscopic data are in accordance with those reported.[16b]

***endo*-Tricyclo[5.2.1.0^{2,7}]undec-9-en-3-one (59).** Prepared according to GP2 from cyclohex-2-en-1-one (**47**, 49 μL, 48 mg, 0.50 mmol, 1.0 equiv) and cyclopentadiene (**56**, 87 μL, 69 mg, 1.1 mmol, 2.1 equiv) in 59% yield (48 mg, 0.30 mmol) in racemic form with *endo*:*exo* = 77:23. The cycloadduct **59** was obtained as a slightly yellow oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.12 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 11.4 min (*exo*-**59**), t_R = 11.5 min (*endo*-**59**). HRMS (ESI) calculated for $C_{11}H_{14}O$ $[M]^+$: 162.1045; found: 162.1039. ^{1}H NMR (500 MHz, $CDCl_3$): δ 0.76 (m_c, 1H), 1.28−1.32 (m, 1H), 1.42−1.46 (m, 1H), 1.64−1.74 (m, 1H), 1.75−1.82 (m, 1H), 1.88−1.96 (m, 2H), 2.27−2.35 (m, 1H), 2.62−2.74 (m, 2H), 2.85−2.89 (m, 1H), 3.24−3.29 (m, 1H), 6.00 (dd, J = 5.6 Hz, J = 2.9 Hz, 1H), 6.17 (dd, J = 5.9 Hz, J = 3.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 22.0, 28.1, 39.5, 41.6, 45.4, 46.7, 48.5, 51.8, 135.1, 137.8, 215.6. Chiral GLC (IVAdex-1, N_2 carrier gas, column flow: 1.74 mL min^{-1}, injection temperature: 250 °C, detector temperature: 300 °C; temperature program: isotherm 115 °C for 80 min): t_R = 52.7 min, t_R = 54.3 min. The analytical and spectroscopic data are in accordance with those reported.[16b]

***endo*-Tricyclo[5.2.1.0^{2,6}]dec-8-en-3-one (60).** Prepared according to GP2 from cyclopent-2-en-1-one (**48**, 42 μL, 41 mg, 0.50 mmol, 1.0 equiv) and cyclopentadiene (**56**, 87 μL, 69 mg, 1.1 mmol, 2.1 equiv) in 58% yield (43 mg, 0.29 mmol) and with *endo*:*exo* = 64:36 and 3% ee. The cycloadduct **60** was obtained as a slightly yellow oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent. R_f = 0.15 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 10.0 min (*exo*-**60**), t_R = 10.1 min (*endo*-**60**).

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HRMS (ESI) calculated for $C_{10}H_{12}O$ $[M]^+$: 148.0885; found: 148.0883. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.41−1.43 (m, 1H), 1.47−1.56 (m, 2H), 1.93−2.04 (m, 2H), 2.09−2.18 (m, 1H), 2.82−2.88 (m, 1H), 2.93−2.99 (m, 1H), 2.99−3.02 (m, 1H), 3.17−3.22 (m, 1H), 6.12 (dd, J = 5.5 Hz, J = 3.1 Hz, 1H), 6.21 (dd, J = 5.7 Hz, J = 2.9 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 22.8, 40.7, 41.4, 47.2, 47.6, 52.4, 54.5, 134.9, 136.3, 222.4. Chiral GLC (IVAdex-1, N_2 carrier gas, column flow: 1.74 mL min^{-1}, injection temperature: 250 °C, detector temperature: 300 °C; temperature program: isotherm 115 °C for 80 min): t_R = 29.8 min (major-**60**), t_R = 32.0 min (minor-**60**). The analytical and spectroscopic data are in accordance with those reported.[16b]

***endo*-Bicyclo[2.2.1]hept-5-ene-2-carboxylic Acid Methyl Ester (61).** Prepared according to GP2 from methyl acrylate (**49**, 45 μL, 43 mg, 0.50 mmol, 1.0 equiv) and cyclopentadiene (**56**, 87 μL, 69 mg, 1.1 mmol, 2.1 equiv) in 72% yield (55 mg, 0.36 mmol) and with *endo*:*exo* = 87:13 and 10% ee. The cycloadduct **61** was obtained as a colorless oil after flash column chromatography on silica gel using cyclohexane/ethyl acetate (50/1) as eluent. R_f = 0.25 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 7.8 min (*exo*-**61**), t_R = 7.9 min (*endo*-**61**). HRMS (ESI) calculated for $C_9H_{13}O_2$ $[M + H]^+$: 153.0910; found: 153.0907. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.25−1.29 (m, 1H), 1.39−1.44 (m, 2H), 1.90 (ddd, J = 12.4 Hz, J = 8.7 Hz, J = 3.7 Hz, 1H), 2.88−2.91 (m, 1H), 2.94 (m_c, 1H), 3.18−3.21 (m, 1H), 3.62 (s, 3H), 5.92 (dd, J = 5.8 Hz, J = 2.8 Hz, 1H), 6.18 (dd, J = 5.8 Hz, J = 3.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 29.4, 42.7, 43.3, 45.8, 49.7, 51.6, 132.5, 137.9, 175.4. Chiral GLC (IVAdex-1, 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 5 °C min^{-1}, end temperature 115 °C for 30 min): t_R = 21.8 min (minor-**61**), t_R = 22.4 min (major-**61**). The analytical and spectroscopic data are in accordance with those reported.[11c]

***endo*-3-(Bicyclo[2.2.1]hept-5-ene-2-carbonyl)oxazolidin-2-one (62).** Prepared according to GP2 from 3-acryloyloxazolidin-2-one (**50**, 70.1 mg, 0.500 mmol, 1.00 equiv) and cyclopentadiene (**56**, 87 μL, 69 mg, 1.1 mmol, 2.1 equiv) in 78% yield (81 mg, 0.39 mmol) and with *endo*:*exo* > 95:5 and 20% ee. The cycloadduct **62** was obtained as a slightly yellow solid after flash column chromatography on silica gel using cyclohexane/ethyl acetate (5/1) as eluent. R_f = 0.12 (cyclohexane/ethyl acetate 5/1). GLC (HP-5): t_R = 16.0 min (*endo*-**62**). HRMS (ESI) calculated for $C_{11}H_{13}NO_3$ $[M]^+$: 207.0897; found: 207.0890. ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.38−1.43 (m, 1H), 1.43−1.47 (m, 1H), 1.47−1.51 (m, 1H), 1.96 (ddd, J = 11.4 Hz, J = 8.1 Hz, J = 3.8 Hz, 1H), 2.92−2.96 (m, 1H), 3.29−3.33 (m, 1H), 3.92−4.02 (m, 3H), 4.37−4.42 (m, 2H), 5.92 (dd, J = 5.5 Hz, J = 2.8 Hz, 1H), 6.24 (dd, J = 5.8 Hz, J = 3.0 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 29.7, 43.0, 43.1, 43.3, 46.5, 50.3, 62.1, 131.8, 138.2, 153.5, 175.4. HPLC (Daicel Chiralcel AD-H, 20 °C, *n*-heptane/*i*-PrOH 95/5, flow rate: 0.70 mL/min, λ = 254 nm): t_R = 30.4 min (major-**62**), t_R = 39.8 min (minor-**62**). The analytical and spectroscopic data are in accordance with those reported.[32]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra of the compounds synthesized in this paper and crystallographic data. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00351.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: martin.oestreich@tu-berlin.de.

Author Contributions

†These authors contributed equally.

Notes

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