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Intramolecularly Sulfur-Stabilized Silicon Cations as Lewis Acid Catalysts

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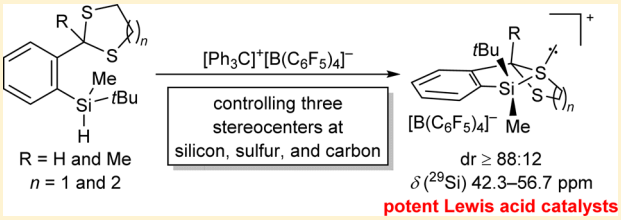
Supporting Information

ABSTRACT: The synthesis and spectroscopic characterization of previously unprecedented sulfur-stabilized silicon cations are reported. Several 1,3-dithiolan-2-yl- and 1,3-dithian-2-yl-substituted silanes were prepared and successfully transformed into the corresponding silicon cations by hydride abstraction. The silicon–sulfur interaction creates three consecutive stereocenters at three different elements. It is remarkable that the present stereocenter at the silicon atom determines the stereochemical outcome at the formerly prochiral sulfur and carbon atoms with excellent diastereoselectivity. All sulfur-stabilized silicon cations are shown to be potent catalysts in a challenging Diels–Alder reaction. Moreover, structurally related oxazoline-stabilized silicon cations were generated and characterized but found to be unreactive.



INTRODUCTION

Tetracoordinate silicon is usually weakly Lewis acidic,[1] and new strategies to boost that acidity continue to be relevant to synthetic chemistry.[2] The coordinating ability of the X group in R_3SiX influences that property, and the degree of deshielding of the silicon nucleus in the ^{29}Si NMR spectrum is a qualitative measure of its Lewis acidity (Figure 1).[3] Trends seen in the ^{29}Si NMR analysis often correlate with experimental findings.[4−6] The substituents at the silicon atom, typically alkyl and/or aryl groups, exert a minor effect on the electronic situation at the silicon atom, with $(Me_3Si)_3SiNTf_2$ being an exception,[7] but steric congestion around the silicon atom is a major parameter.[8] In addition, the Lewis acidity increases when the silicon atom is incorporated into a strained ring.[9] The electron deficiency at the silicon atom in R_3SiX further increases by interaction with another Lewis acid.[10] On the basis of seminal work by Olah and co-workers using boron Lewis acids,[11] Davis and co-workers introduced $Me_3Si[B(OTf)_4]$, which was found not to be ionized.[12] Hence, the obvious next step was to use ionized silicon Lewis acids where the silicon cation is separated from the weakly coordinating counteranion. Sterically accessible tricoordinate silicon cations (silicenium or silylium ions) are not available, as a consequence of their extreme electron deficiency.[13] However, inter- and intramolecularly stabilized systems have been developed,[2,13] and arene-stabilized $[Et_3Si(toluene)]^+[B(C_6F_5)_4]^-$[14] as well as ferrocene-stabilized $[FcSi(tBu)Me]^+[B(C_6F_5)_4]^-$, the latter reported by our laboratory,[6b,15] have been applied in Lewis acid catalysis with considerable success.[6] Again, the excellent performance of these silicon cations as catalysts is in agreement with their ^{29}Si NMR chemical shifts.[16]

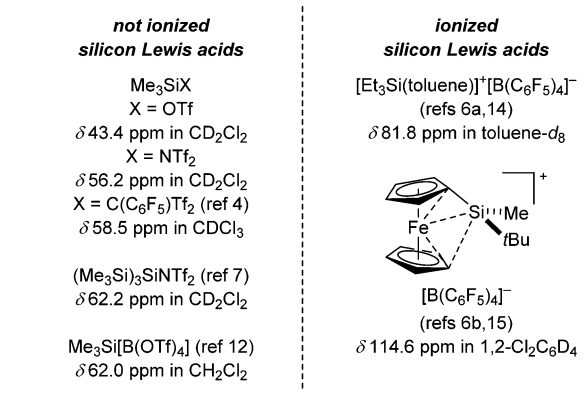


Figure 1. Silicon Lewis acids and their ^{29}Si NMR chemical shifts.

The exceptional Lewis acidity of ionized silicon acids is beneficial in one way or the other but makes these reactive intermediates seek stabilization either inter- or intramolecularly. This entails, for example, the formation of arenium ions that potentially act as proton sources and that, in turn, contains the risk of hidden proton catalysis.[6c] For us, the question was whether the pronounced and at the same time problematic Lewis acidity of reported silicon cations is really necessary for achieving high or even unprecedented catalytic activity. We therefore asked ourselves if stabilization of a tricoordinate silicon cation by a heteroatom donor would render the resulting Lewis adduct more "well behaved" while maintaining sufficient Lewis acidity. Judicious choice of the donor group would then allow us to engineer the Lewis acidity in a targeted way.

Aside from the spectroscopic and structural characterization of a few heteroatom-stabilized silicon cations, i.e., silylated

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onium ions,[13,17] the use of such adducts in Lewis acid catalysis is essentially not documented. A famous example is the chiral acetonitrile adduct introduced by Helmchen and Jørgensen, which promoted a Diels–Alder reaction with little asymmetric induction.[18,19] The ^{29}Si NMR chemical shift of δ 34.0 ppm in acetonitrile-d_3 is typical for silylnitrilium ions,[17a−c] indicating reduced Lewis acidity in comparison to conventional R_3SiX (Figure 1, left). On the basis of this precedence, one portion of the present work focuses on the preparation and characterization of oxazoline-stabilized silicon cations **1** and **2** (Figure 2, top), and we evaluate their ability to catalyze representative (enantioselective) Diels–Alder reactions.[19] The oxazoline unit is chiral, and we investigate the effect of the existing stereocenter on the stereogenicity at the silicon atom.

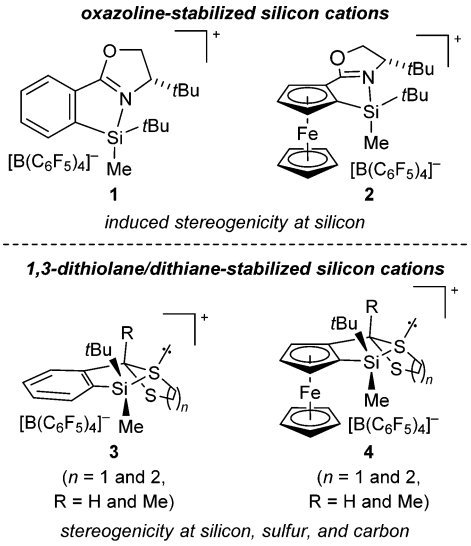


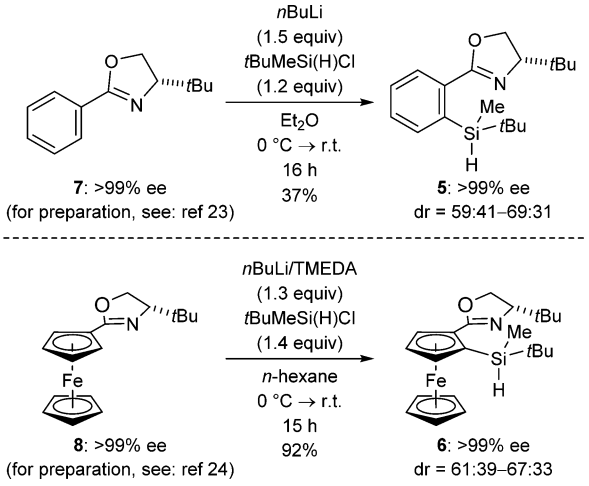
Figure 2. Heteroatom-stabilized silicon cations investigated in this work.

Another donor atom attracted our attention. Our laboratory recently disclosed the cooperative activation of Si–H bonds at the Ru–S bond of a coordinatively unsaturated ruthenium(II) thiolate complex.[20] A σ-bond metathesis splits the Si–H bond heterolytically into a ruthenium(II) hydride and sulfur-stabilized silicon cation (not shown). The $[Si–S]^+$ motif of this metallasulfonium ion is an excellent silicon electrophile that readily transfers onto various nucleophiles.[20] We were thrilled to learn that related sulfonium ions are elusive and that Olah and co-workers had only been able to prepare $[(Me_3Si)_3S]^+$ and $[(Me_3Si)_2SMe]^+$ but not $[Me_3SiSMe_2]^+$ (all with $[B(C_6F_5)_4]^-$ as counteranion).[21] It is worthy of note, though, that Jutzi and co-workers had prepared a silylium ion with two aryl substituents each equipped with a thiomethoxymethyl group in the ortho position; the dynamic coordination equilibria between tetra- and pentacoordinate cations were analyzed by NMR spectroscopy.[22] Intrigued by this fascinating insight, we decided to systematically elaborate the chemistry of sulfur-stabilized silicon cations that are expected to be rather electrophilic adducts. Disproportionation of the $[Me_3SiSMe_2]^+$ Lewis pair had thwarted its synthesis,[21] which is why we employ 1,3-dithiolanes (n = 1) and 1,3-dithianes (n = 2) as donor groups, again using benzene and ferrocene as platforms (**3** and **4**, Figure 2, bottom). The stereochemical consequence of the silicon–sulfur interaction in **3** and **4** is particularly interesting, as three consecutive stereocenters at three different elements (silicon, sulfur, and carbon) are generated in one step. The catalytic activity of this new class of silicon Lewis acids will be highlighted in Diels–Alder reactions.

RESULTS AND DISCUSSION

Oxazoline-Stabilized Silicon Cations. We anticipated that silicon cations bearing oxazolin-2-yl units would be stabilized by either the oxygen or the nitrogen atom of the heterocycle. As a result, the ferrocene backbone usually incorporated in our silicon cations[6b,c,15] (cf. Figure 1, right) would not be necessary. For that reason, the corresponding benzene-based silane **5** was synthesized in addition to the ferrocene-based silane **6** (Scheme 1). Oxazolin-2-yl phenyl silane **5** was accessible in moderate yield through ortho-directed metalation of the literature-known phenyl oxazoline **7**[23] and subsequent trapping of the anion with racemic *t*BuMeSi(H)Cl (Scheme 1, top). The silylation showed a small preference for one diastereomer with diastereomeric ratios ranging from 59:41 to 69:31. The corresponding ferrocenyl-substituted silane **6** was synthesized in high yield in a similar manner from ferrocenyl oxazoline **8**[24] (Scheme 1, bottom). The planar chirality is fully controlled by the chiral oxazolin-2-yl unit in the metalation step.[25] The diastereoselectivity seen in electrophilic substitution with *t*BuMeSi(H)Cl hence refers to the configuration at the silicon atom relative to the existing central and planar chirality of the backbone; the diastereomeric ratios obtained again ranged from 61:39 to 67:33.

Scheme 1. Preparation of Silicon Cation Precursors with an Oxazolin-2-yl Unit



The generation of oxazoline-stabilized silicon cations **1** and **2** was achieved by hydride abstraction from **5** and **6** with trityl tetrakis(pentafluorophenyl)borate, $[Ph_3C]^+[B(C_6F_5)_4]^-$ (Scheme 2). However, cation formation was much slower than that of non-heteroatom-bearing ferrocenyl-substituted silanes.[6b,c,15b] As a result, significantly longer reaction times were required (30 min vs 1 min). We explain this observation by competitive, yet reversible, coordination of the trityl cation to either of the heteroatoms prior to hydride abstraction. In comparison with ferrocene-stabilized $[FcSi(tBu)Me]^+[B(C_6F_5)_4]^-$ (δ 114.6 ppm),[6b,15b] the ^{29}Si NMR spectra of the pairs of diastereomers of **1** and **2** revealed pronounced upfield shifts at δ 24.2/24.7 and 25.4/26.4 ppm, respectively. We judge these chemical shifts as an indication of the heteroatom

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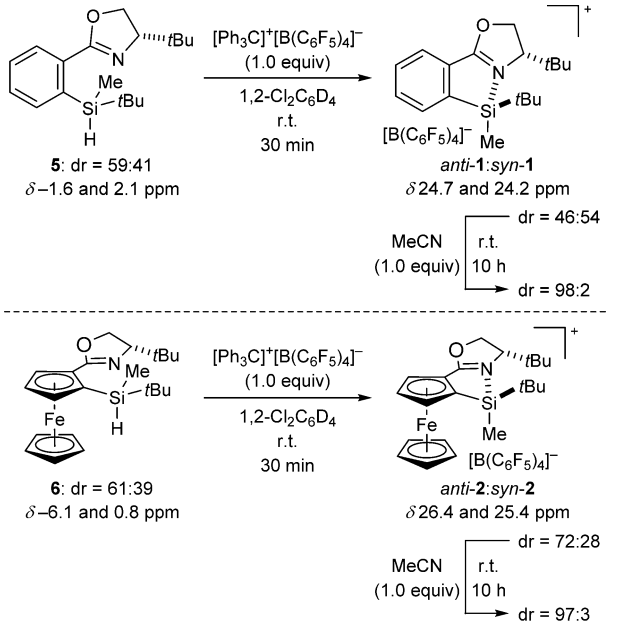
Scheme 2. Generation of Oxazoline-Stabilized Silicon Cations and Equilibration of Diastereomers



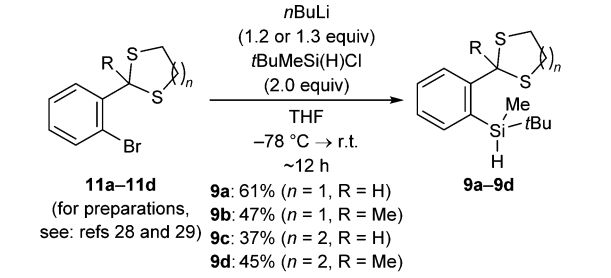
stabilization of the silicon cation by the adjacent oxazoline donor, while the ferrocenyl substituent in **2** is nothing but a spectator substituent. To distinguish between the oxygen and nitrogen atoms acting as the donor, ^{1}H,^{15}N HMQC NMR experiments of precursors **5** and **6** as well as cations **1** and **2** were performed. We observed that the ^{15}N NMR resonances of **1** and **2** were markedly shifted to lower frequencies in comparison to those of silanes **5** and **6** (^{15}N NMR $\Delta\delta \approx 80$ ppm; for details see the Supporting Information).[26] Moreover, a correlation of the nitrogen nucleus to the methyl group was detected, and that is only possible for an Si–N bond. These findings strongly indicate that it is the nitrogen donor that interacts with the empty orbital at the silicon atom.[27] This result is in agreement with previous studies where an sp^3-hybridized nitrogen atom was shown to be a better donor for a tricoordinate silicon cation than an sp^3-hybridized oxygen atom.[22]

With the nitrogen atom as the stabilizing heteroatom, the *tert*-butyl group of the oxazolin-2-yl unit is brought into close proximity of the silicon fragment. To our surprise, the diastereomeric ratio changed little during cation generation despite steric congestion: 59:41 → 54:46 for **5** → **1** and 61:39 → 72:28 for **6** → **2** (Scheme 2). Substantial amounts of the thermodynamically disfavored *syn* isomer were present. We, therefore, assume that the hydride abstraction is assisted by the nucleophilic nitrogen atom or even accompanied by simultaneous Si–N bond formation. The strength of the intramolecular Si–N adduct is demonstrated by our failed attempts to thermally enrich the thermodynamically more stable *anti* isomer (not shown). As an alternative, we anticipated that an external weak donor such as acetonitrile would promote epimerization at the silicon atom through reversible coordination. To our delight, acetonitrile (1.0 equiv) indeed transformed the *syn* into the *anti* isomer, and both **1** (dr = 98:2) and **2** (dr = 97:3) were obtained in almost diastereomerically pure form. The *anti* relative configuration was verified by NOE experiments.

On comparison of the ^{29}Si NMR chemical shifts of **1** (δ 24.7/24.2 ppm) and **2** (δ 26.4/25.4 ppm) with that of the known silicon Lewis acid Me_3SiOTf (δ 43.4 ppm), weaker Lewis acidity and, hence, lower catalytic activity are to be expected.[4b] Conversely, **1** and **2** are cationic, whereas Me_3SiOTf is neutral (not dissociated), and coordination of the weak donor acetonitrile is possible (vide supra). However, utilizing **1** and **2** as catalysts in various Diels–Alder reactions revealed that neither one is catalytically active. Even for diene/dienophile combinations with a relatively low activation barrier, poor yields were obtained after prolonged reaction times with no stereoinduction. Consequently, we must conclude that these oxazoline-stabilized silicon cations are an inappropriate choice for the development of chiral silicon Lewis acids.

1,3-Dithiolane-/1,3-Dithiane-Stabilized Silicon Cations. With the nitrogen atom being too strong of a donor, we decided to replace it with a sulfur atom (cf. Introduction).[20−22] Hence, the structurally related silanes **9a–9d** and **10** with benzene and ferrocene backbones emerged as new targets (Schemes 3 and 4). Cyclic dithioacetals were chosen not

Scheme 3. Preparation of Silicon Cation Precursors with 1,3-Dithiolan-2-yl-Substituted (n = 1) and 1,3-Dithian-2-yl-Substituted (n = 2) Phenyl Platforms and Silicon Cation Generation



		silane		silicon cation	
n = 1	R = H	**9a**	δ –7.5 ppm	**3a**	δ 56.7 ppm, dr = 98:2
n = 1	R = Me	**9b**	δ –8.2 ppm	**3b**	δ 51.7 ppm, dr = 99:1
n = 2	R = H	**9c**	δ –6.6 ppm	**3c**	δ 51.3 ppm, dr = 98:2
n = 2	R = Me	**9d**	δ –8.7 ppm	**3d**	δ 42.3 and 48.6 ppm, dr = 88:12

only because of their accessibility but also for their tolerance against harsh conditions. Several 1,3-dithiolan-2-yl- and 1,3-dithian-2-yl-substituted systems **9a–9d** were prepared by starting from the corresponding bromides **11a–11d** in moderate to good yields (Scheme 3, top). Except for **11b** (n = 1, R = Me), bromides **11a,c,d** are known compounds[28] but were synthesized according to a different procedure.[29] Variation of the ring size and the substitution pattern at C2 of the cyclic dithioacetals would allow for an evaluation of the influence of these structural features on stabilizing the silicon cation. Indeed, distinct differences in the ^{29}Si NMR chemical shifts were observed for silicon cations **3a–3d** (Scheme 3, bottom). The 1,3-dithiolan-2-yl-substituted cations **3a** (δ 56.7 ppm) and **3b** (δ 51.7 ppm) were shifted to higher frequencies in comparison to their 1,3-dithian-2-yl-substituted homologues **3c** (δ 51.3

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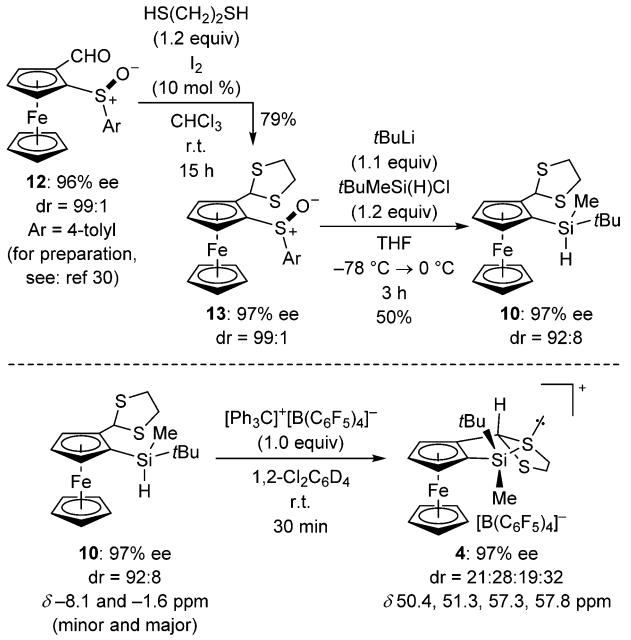
Scheme 4. Preparation of a Silicon Cation Precursor with 1,3-Dithiolan-2-yl-Substituted Ferrocenyl Platform and Silicon Cation Generation



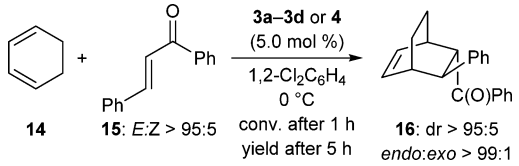
ppm) and **3d** (δ 42.3/48.6 ppm). The greater deshielding of the silicon atom in **3a,b** is likely due to a less favorable n(S) → 3p(Si) orbital overlap in the [3.3.0] bicyclic chelate as opposed to the [4.3.0] ring system in **3c,d**. The influence of the angular methyl group in these bicycles (i.e., substitution at C2 of the dithioacetals) is not fully understood but could be electronic in nature, thereby increasing the donor ability of the sulfur atom.

The stereochemical outcome of the cation formation is particularly striking. As a consequence of the Si−S interaction, additional stereogenicity is generated at the coordinating sulfur atom and at C2 of the (formerly prochiral) dithioacetal unit. We find it remarkable that the formation of one diastereomer is highly favored. The selectivity is a result of efficient diastereotopic group selection induced by the stereochemical information at the silicon atom. By this, three stereocenters at three different elements are formed with high diastereoselectivity in a single transformation. The relative configuration was assigned on the basis of NOE experiments, which indicate a *syn* relationsship of the *tert*-butyl group at the silicon atom and the R group at C2 of the dithioacetal.

On the basis of our experience with the structural design of benzene-based cations **3a−3d**, we prepared planar chiral ferrocene-based **10** starting from the literature-known aldehyde **12** (Scheme 4, top).[30] Formation of the dithiolane **13** and subsequent substitution of the adjacent sulfoxide afforded **10** in reasonable yield and with good diastereoselectivity with respect to the silicon atom. The 1,3-dithiolan-2-yl unit with R = H was used, since this ring size with no substitution at C2 had shown the highest degree of deshielding for the cations with the benzene platform (Scheme 3, bottom). The diastereomeric ratio of 92:8 did not translate into high diastereoenrichment of the corresponding cation (**10** → **4**); **4** was obtained as a mixture of four stereoisomers (Scheme 4, bottom). Attempts to accumulate one isomer in the same way as for oxazoline-stabilized silicon cations **1** and **2** were unsuccessful; addition of acetonitrile resulted in a complex mixture of compounds.

To test the catalytic activity of sulfur-stabilized silicon cations **3a−3d** and **4**, the Diels−Alder cycloaddition of cyclohexa-1,3-diene (**14**) and chalcone (**15**) to adduct **16** was chosen as a model reaction. We have already used this reaction in our previous studies, and this allows us to establish a relation between the performance of the new silicon cations and that of known Lewis acids.[6c,8b] Moreover, this rather difficult Diels−Alder reaction is catalyzed neither in the absence of any Lewis acid catalyst nor by protons.[6c,34] As was done before, a comparison of the ^{29}Si NMR shifts of **3a−3d** and **4** with Ghosez's results for Me_3SiOTf (δ 43.4 ppm) and Me_3SiNTf_2 (δ 56.2 ppm)[4b] enables a qualitative estimation of their Lewis acidity.[3] The deshielding of the sulfur-stabilized cations is more pronounced than that of Me_3SiOTf and more than that of Me_3SiNTf_2 for **3a** and two diastereomers of ferrocene-based **4**. Hence, successful catalyses were assumed at least for the latter. To our delight, these new silicon Lewis acids were all capable of catalyzing this challenging reaction[6c] even at 0 °C; **3a−3d** performed equally well (Table 1, entries 1−4). Somewhat

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



entry	Si cation	^{29}Si NMR (δ/ppm)	*n*	R	conv. (%)[c]	yield (%)[d]
1	**3a**	56.7	1	H	78	78
2	**3b**	51.7	1	Me	59	66
3	**3c**	51.3	2	H	73	62
4	**3d**	42.3/48.6	2	Me	64	65
5	**4**	50.4/51.3/57.3/57.8			59	46[e]

[a]All reactions were performed according to General Procedure 4 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 of the reaction mixture after 1 h using triphenylmethane as internal standard. [d]Yield after 5 h of analytically pure product after flash column chromatography on silica gel. [e]0% ee.

unexpectedly, **4**, with the Lewis acid attached to the ferrocene backbone, showed the lowest catalytic activity in terms of isolated yield (Table 1, entry 5). The increased steric congestion around the Lewis acid center in **4** might result in decreased accessibility. Moreover, no asymmetric induction was seen. At lower temperatures (−40 °C), reaction rates were significantly lower (<5% conversion after 22 h with **4**), still not providing any stereoinduction.

CONCLUSION

In summary, the generation of several novel heteroatom-stabilized silicon cations was accomplished. Notably, silicon Lewis acids reversibly coordinated by a sulfur donor were successfully generated and spectroscopically characterized. As a consequence of the Si−S interaction in these cations, three consecutive stereocenters at three different elements (silicon, sulfur, and carbon) were established, resulting in highly diastereomerically enriched Lewis acids. The deshielding of the silicon atom in the ^{29}Si NMR spectra is in part determined by the effectiveness of the n(S) → 3p(Si) orbital overlap that is,

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in turn, dependent on the ring size of the sulfur-donor-containing acetals. Moreover, methyl substitution at C2 of the 1,3-dithiolan-2-yl and 1,3-dithian-2-yl groups led to a shift of the ^{29}Si NMR resonance to lower frequencies. Qualitative comparison of these ^{29}Si NMR chemical shifts (δ ~50 ppm) with those of known silicon Lewis acids (cf. Figure 1) enabled us to predict substantial Lewis acidity, hence rendering sulfur-stabilized silicon cations suitable canditates for catalysis. Gratifyingly, all of them were catalytically active in a representative difficult Diels–Alder reaction at 0 °C. While no stereoinduction was seen with **4**, the present findings nevertheless pave the way for the development of chiral cationic silicon-based Lewis acids.

The structurally related oxazoline-stabilized silicon cations were also generated, but these were shown to be not sufficiently reactive to act as Lewis acid catalysts. The stabilization by the nitrogen atom results in a significantly stronger shielding of the silicon atom than in the case of the sulfur analogues.

EXPERIMENTAL SECTION

General Remarks. All reactions were performed in flame-dried glassware using an MBraun glovebox (O_2 <0.5 ppm, H_2O <0.5 ppm) or conventional Schlenk techniques under a static pressure of argon or nitrogen. Liquids and solutions were transferred with syringes. Solvents (THF, toluene, *n*-hexane, diethyl ether, acetonitrile, DMF, $CHCl_3$, CH_2Cl_2, and 1,2-$Cl_2C_6H_4$,) were dried and purified following standard procedures. Technical grade solvents for extraction or chromatography (*tert*-butyl methyl ether, CH_2Cl_2, cyclohexane, and ethyl acetate) were distilled prior to use. C_6D_6 and $CDCl_3$ (purchased from Eurisotop) were dried over 4 Å molecular sieves. 1,2-$Cl_2C_6D_4$ (purchased from Eurisotop) was dried over CaH_2, distilled, and stored under argon. Potassium *tert*-butoxide, *tert*-butyllithium (1.48–1.76 M in *n*-pentane; see respective experiment for the exact concentration), benzoyl chloride, ferrocene, ethyl chloroformate, thionyl chloride, triethylamine, trimethylaluminum (2.0 M in toluene), 2-bromobenzaldehyde, 2′-bromoacetophenone, ethane-1,2-dithiol, propane-1,3-dithiol, iodine, *n*-butyllithium (1.38–1.54 M in hexane fractions; see respective experiment for the exact concentration), 4-toluenesulfonyl chloride, tetramethylethylenediamine (TMEDA), (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate, and diisopropylamine were obtained from commercial sources and used without further purification. Cyclohexa-1,3-diene (**14**) was distilled from $NaBH_4$, and (*E*)-chalcone (**15**) was recrystallized from ethanol and dried by azeotropic distillation with benzene prior to use. (*S*)-2-Amino-3,3-dimethylbutan-1-ol[31] and *tert*-butylchloro(methyl)silane[6b] were prepared according to reported procedures. Trityl tetrakis(pentafluorophenyl)borate ($[Ph_3C]^+[B(C_6F_5)_4]^-$) was prepared following a reported procedure,[32] 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 LC60 Å (40–63 μm) by Davisil using the indicated solvents. ^{1}H, ^{13}C, ^{11}B, ^{15}N, ^{19}F, and ^{29}Si NMR spectra were recorded in $CDCl_3$, C_6D_6, or 1,2-$Cl_2C_6D_4$ on Bruker AV700, Bruker AV500, and Bruker AV400 instruments. Chemical shifts are reported in parts per million (ppm) and are calibrated to the residual solvent resonance as the internal standard ($CHCl_3$, δ 7.26 for ^{1}H NMR; $CDCl_3$, δ 77.16 for ^{13}C NMR; C_6D_5H, δ 7.16 for ^{1}H NMR; C_6D_6, δ 128.06 for ^{13}C NMR; 1,2-$Cl_2C_6D_3H$, δ 6.94 and 7.20 for ^{1}H NMR; 1,2-$Cl_2C_6D_4$, δ 127.1, 130.1, and 132.5 for ^{13}C NMR). All other nuclei (^{11}B, ^{13}C, ^{15}N, ^{19}F, and ^{29}Si) are referenced in compliance with the unified scale for NMR chemical shifts as recommended by IUPAC.[33] For ^{15}N NMR chemical shifts, liquid NH_3 was used as the standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br m = broad multiplet, m_c = centrosymmetric multiplet), coupling constants (Hz), and integration. ^{1}H,^{29}Si HMQC NMR spectra were measured with a coupling constant of 7.0 Hz for the $^3J_{H,Si}$ coupling. The peak intensities in the ^{1}H,^{29}Si HMQC NMR spectra cannot be correlated to the amount of the compound. ^{1}H,^{15}N HMQC NMR spectra were measured with a coupling constant of 3.0 Hz for the $^3J_{H,N}$ coupling. 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). Gas–liquid chromatography (GLC) was performed on an Agilent Technologies 7820A gas chromatograph equipped with an HP-5 capillary column (30 m × 0.32 mm, 0.25 μm film thickness) or on a Shimadzu GC-17A gas chromatograph equipped with a FS-SE-54 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 (mp) were determined with a Stuart Scientific SMP20 melting point apparatus and are not corrected. Optical rotations were measured on a Schmidt & Haensch Polatronic H532 polarimeter with $[\alpha]_D$ values reported in deg 10^{-1} cm^2 g^{-1}; the concentration *c* is in g 100^{-1} mL^{-1}. Enantiomeric excesses were determined by analytical high-performance liquid chromatography (HPLC) analysis on an Agilent Technologies 1290 Infinity instrument with a chiral stationary phase using a Daicel Chiralcel OD-H column (*n*-heptane/*i*-PrOH mixtures as solvents). Mass spectrometry (MS) was performed by the Analytical Facility of the Institut für Chemie, Technische Universität Berlin.

General Procedure for the Preparation of 1,3-Dithiolan-2-yl- and 1,3-Dithian-2-yl-Substituted Phenyl Bromides 11 (GP1). In analogy to a reported procedure by Firouzabadi and Iranpoor,[29] ethane-1,2-dithiol (1.2 equiv) or propane-1,3-dithiol (1.2–2.0 equiv) and iodine (0.1 equiv) were added to a solution of the corresponding carbonyl compound (1.00 equiv) in $CHCl_3$ (0.20–0.23 M), and the resulting mixture was stirred at room temperature (2–15 h). The reaction was quenched by the addition of aqueous NaOH solution (2 N), the phases are separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3×). The combined organic phases were washed with saturated aqueous NaCl solution (1×), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate mixtures as eluent or by recrystallization from ethanol, respectively.

General Procedure for the Preparation of 1,3-Dithiolan-2-yl- and 1,3-Dithian-2-yl-Substituted Phenylsilanes 9 (GP2). To a solution of the corresponding bromide **11** (1.00 equiv) in THF (0.10–0.11 M) cooled to −78 °C was added *n*BuLi (1.51–1.54 M in hexane fractions, 1.29–1.30 equiv) dropwise. After an additional 1 h at −78 °C, a solution of *tert*-butylchloro(methyl)silane (1.83–2.00 equiv) in THF (0.36–0.51 M) was added, and the resulting mixture was warmed to room temperature (2–15 h). After addition of water and dilution with *tert*-butyl methyl ether, 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 (1×), dried over Na_2SO_4, and concentrated under reduced pressure. The crude product was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate mixtures as eluent.

For the generation of the corresponding silicon cations, all silanes were azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×).

General Procedure for the Preparation of Intramolecularly Donor Stabilized Silicon Cations 1, 2, 3a–3d, and 4 (GP3). In a glovebox, a solution of the corresponding silane (1.00 equiv) in 1,2-$Cl_2C_6D_4$ (0.4 mL) was added to a suspension of $[Ph_3C]^+[B(C_6F_5)_4]^-$ (1.00–1.10 equiv) in 1,2-$Cl_2C_6D_4$ (0.2 mL) in an 8 mL vial equipped with a magnetic stir bar. The resulting mixture was stirred for 30 min, transferred to an NMR tube, and directly subjected to NMR spectroscopic analysis.

General Procedure for the Model Diels–Alder Reaction Catalyzed by Sulfur-Stabilized Silicon Cations (GP4). In a glovebox, a flame-dried Schlenk tube equipped with a magnetic stir bar

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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 stirred for 30 min at room temperature.[34] The thus obtained catalyst solution was cooled to 0 °C, and a solution of cyclohexa-1,3-diene (**14**, 2.00 equiv) and (*E*)-chalcone (**15**, 1.00 equiv) in 1,2-$Cl_2C_6H_4$ (0.4 mL) was added dropwise. The reaction mixture was stirred at 0 °C for 5 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 (50/1) as eluent, affording analytically pure Diels−Alder product **16** as a white solid.

(*S*)-4-*tert*-Butyl-2-phenyl-4,5-dihydrooxazole (7). To a solution of benzoyl chloride (1.00 g, 7.11 mmol, 1.00 equiv) in CH_2Cl_2 (20 mL) was added a solution of triethylamine (0.99 mL, 0.72 g, 7.1 mmol, 1.0 equiv) and (*S*)-*tert*-leucinol (835 mg, 7.15 mmol, 1.01 equiv, >99% ee) in CH_2Cl_2 (5 mL) dropwise at 0 °C. The resulting mixture was slowly warmed to room temperature over a period of 12 h. After removal of all volatiles under vacuum, thionyl chloride (1.55 mL, 2.54 g, 21.3 mmol, 3.00 equiv) was added, and the reaction mixture was stirred for a further 3.5 h at room temperature. The mixture was then cooled to 0 °C, diluted with *tert*-butyl methyl ether (10 mL), and carefully neutralized with aqueous NaOH solution (2 N, approximately 20 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 solution (40 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by bulb-to-bulb distillation, affording phenyl oxazoline **7** (914 mg, 4.50 mmol, 63%, >99% ee) as a colorless solid. Mp: 33.1 °C (benzene). GLC (HP-5): t_R = 13.5 min. IR (ATR): $\tilde{\nu}$ 2954 (m), 2901 (w), 2867 (w), 1648 (s), 1578 (m), 1492 (m), 1449 (m), 1355 (s), 1340 (s), 1258 (m), 1083 (m), 1053 (m), 1021 (s), 966 (s), 929 (w), 898 (m), 782 (m), 723 (m), 692 (s) cm^{-1}. HRMS (ESI): calculated for $C_{13}H_{18}NO$ $[M + H]^+$, 204.1383; found, 204.1373. ^1H NMR (500 MHz, C_6D_6): δ 0.88 (s, 9H), 3.83−3.94 (m, 3H), 7.06−7.12 (m, 3H), 8.19−8.26 (m, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 26.0, 34.0, 68.6, 76.7, 128.5, 128.7, 129.0, 131.2, 163.1. Specific rotation $[\alpha]_D^{20}$ = −9.4 (*c* = 0.26, $CHCl_3$, >99% ee). The analytical and spectroscopic data are in accordance with those reported.[23]

(^{Si}*S,*S*)-*tert*-Butyl(2-(4-*tert*-butyloxazolin-2-yl)phenyl)-methylsilane (5).** To a solution of phenyl oxazoline **7** (0.55 g, 2.7 mmol, 1.0 equiv) in diethyl ether (22 mL) was added *n*BuLi (1.51 M in hexane fractions, 2.69 mL, 4.06 mmol, 1.50 equiv) dropwise at 0 °C. After an additional 1 h at 0 °C, *tert*-butylchloro(methyl)silane (444 mg, 3.25 mmol, 1.20 equiv) was added dropwise, and the reaction mixture was warmed to room temperature (12 h). Water (10 mL) was added, 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 solution (50 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 (100/1) as eluent, affording silane **5** (0.30 g, 0.99 mmol, 37%, dr = 59:41) as a slightly yellow oil. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). R_f = 0.15 (cyclohexane/ethyl acetate 50/1). GLC (HP-5): t_R = 17.8 min (major diastereomer), t_R = 17.7 min (minor diastereomer). IR (ATR): $\tilde{\nu}$ 2954 (w), 2277 (w), 1653 (w), 1543 (m), 1471 (w), 1358 (s), 1173 (w), 1062 (s), 1023 (s), 848 (w), 735 (w), 706 (s) cm^{-1}. HRMS (ESI): calculated for $C_{18}H_{30}NOSi$ $[M + H]^+$, 304.2091; found, 304.2079. Specific rotation $[\alpha]_D^{20}$ = 41.3 (*c* = 0.96, $CHCl_3$). For NMR analysis, a diastereoenriched sample (dr = 72:28) was used, which was obtained by chromatographic separation of the diastereomers on silica gel using cyclohexane as eluent. NMR spectroscopic data for the major diastereomer are as follows. ^1H NMR (400 MHz, C_6D_6): δ 0.52 (d, *J* = 3.8 Hz, 3H), 0.88 (s, 9H), 1.12 (s, 9H), 3.80−3.92 (m, 3H), 4.63 (q, *J* = 3.7 Hz, 1H), 7.10−7.15 (m, 2H), 7.72−7.75 (m, 1H), 8.12−8.17 (m, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −4.9, 18.0, 26.2, 28.7, 33.9, 68.4, 77.1, 129.4, 129.8, 129.9, 135.0, 137.1, 137.9, 164.6. ^1H,^{15}N HMQC NMR (700/71 MHz, C_6D_6): δ 232.9. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ 2.1. NMR spectroscopic data for the minor diastereomer are as follows. ^1H NMR (400 MHz, C_6D_6): δ 0.40 (d, *J* = 3.8 Hz, 3H), 0.89 (s, 9H), 1.13 (s, 9H), 3.80−3.92 (m, 3H), 4.78 (q, *J* = 3.8 Hz, 1H), 7.10−7.15 (m, 2H), 7.64−7.68 (m, 1H), 8.12−8.17 (m, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −5.4, 18.0, 26.2, 28.6, 33.9, 68.4, 77.2, 129.2, 129.7, 130.0, 135.0, 137.1, 137.9, 164.3. ^1H,^{15}N HMQC NMR (700/71 MHz, C_6D_6): δ 234.2. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ −1.6.

Ethyl Ferrocenecarboxylate. Ferrocene (500 mg, 2.69 mmol, 1.00 equiv) and KO*t*Bu (30 mg, 0.27 mmol, 0.10 equiv) were suspended in THF (3 mL), and the suspension was cooled to −78 °C. *t*BuLi (1.76 M in *n*-pentane, 1.53 mL, 2.69 mmol, 1.00 equiv) was added dropwise, and the resulting mixture was stirred for 1 h at −78 °C and 1 h at room temperature. After the mixture was cooled to −78 °C, ethyl chloroformate (0.38 mL, 0.44 g, 4.0 mmol, 1.5 equiv) was added. The reaction mixture was warmed to room temperature and stirred overnight. After addition of saturated aqueous NH_4Cl solution (10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 50 mL). The combined organic phases were washed with saturated aqueous NaCl solution (120 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using cyclohexane/ethyl acetate (20/1) as eluent, affording ethyl ferrocenecarboxylate (554 mg, 2.15 mmol, 80%) as a brown oil. R_f = 0.57 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 16.0 min. IR (ATR): $\tilde{\nu}$ 3110 (w), 2961 (w), 1691 (s), 1455 (m), 1374 (m), 1273 (s), 1169 (w), 1129 (s), 999 (m), 915 (w), 821 (m), 778 (m) cm^{-1}. HRMS (ESI): calculated for $C_{13}H_{15}FeO_2$ $[M + H]^+$, 259.0416; found, 259.0415. ^1H NMR (400 MHz, C_6D_6): δ 1.07 (t, *J* = 7.1 Hz, 3H), 4.01 (s, 5H), 4.02 (m$_c$, 2H), 4.14 (q, *J* = 7.1 Hz, 2H), 4.88 (m$_c$, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 14.7, 60.0, 70.0, 70.6, 71.3, 72.6, 170.9. The analytical and spectroscopic data are in accordance with those reported.[24]

(*S*)-*N*-(1-Hydroxy-3,3-dimethylbutan-2-yl)ferrocenyl Carboxamide. To a solution of (*S*)-*tert*-leucinol (1.31 g, 11.2 mmol, 1.21 equiv) in toluene (25 mL) at 0 °C was added trimethylaluminum (2.00 M in toluene, 10.2 mL, 20.4 mmol, 2.20 equiv) dropwise. The cooling bath was removed, and a solution of ethyl ferrocenecarboxylate (2.40 g, 9.29 mmol, 1.00 equiv) in toluene (25 mL) was added dropwise. After complete addition, the resulting mixture was heated to reflux for 14 h. The reaction mixture was diluted with CH_2Cl_2 (30 mL) at room temperature, and an aqueous potassium sodium tartrate solution (1.3 M, 40 mL) was added. The phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic phases were washed with saturated aqueous NaCl solution (2 × 20 mL), dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by flash column chromatography on silica gel using ethyl acetate/cyclohexane (2/1) as eluent, affording (*S*)-*N*-(1-hydroxy-3,3-dimethylbutan-2-yl)-ferrocenyl carboxamide (2.28 g, 6.93 mmol, 76%) as orange needles. Mp: 174.6 °C (benzene). R_f = 0.23 (ethyl acetate/cyclohexane 2/1). GLC (HP-5): t_R = 19.4 min. IR (ATR): $\tilde{\nu}$ 3227 (br), 3083 (w), 2946 (m), 1609 (m), 1549 (s), 1465 (w), 1367 (w), 1305 (s), 1256 (w), 1183 (w), 1105 (w), 1053 (m), 999 (m), 892 (w), 806 (m), 670 (w) cm^{-1}. HRMS (ESI): calculated for $C_{17}H_{24}FeNO_2$ $[M + H]^+$, 330.1151; found, 330.1149. ^1H NMR (400 MHz, $CDCl_3$): δ 1.04 (s, 9H), 2.69 (m$_c$, 1H), 3.60−3.69 (m, 1H), 3.91−3.99 (m, 2H), 4.23 (s, 5H), 4.37 (m$_c$, 2H), 4.67 (m$_c$, 1H), 4.70 (m$_c$, 1H), 5.86 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 27.2, 33.6, 59.8, 63.7, 68.0, 68.6, 69.9, 70.66, 70.71, 76.1, 172.0. Specific rotation $[\alpha]_D^{20}$ = −21.8 (*c* = 0.80, $CHCl_3$). The analytical and spectroscopic data are in accordance with those reported.[24]

(*S*)-4-*tert*-Butyl-2-ferrocenyl-4,5-dihydrooxazole (8). To a solution of (*S*)-*N*-(1-hydroxy-3,3-dimethylbutan-2-yl)ferrocenyl car-

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boxamide (1.50 g, 4.57 mmol, 1.00 equiv) in CH_2Cl_2 (15 mL) at 0 °C were added successively tosyl chloride (1.13 g, 5.94 mmol, 1.30 equiv) and triethylamine (1.39 mL, 1.01 g, 10.0 mmol, 2.20 equiv). The cooling bath was removed, and the reaction mixture was stirred for 20 h at room temperature. After addition of saturated aqueous NH_4Cl solution (15 mL), the phases were separated, and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl solution (50 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 ferrocenyl oxazoline **8** (1.04 g, 3.34 mmol, 73%) as a brown solid. Mp: 138.7 °C (benzene). R_f = 0.06 (cyclohexane/ethyl acetate 10/1). GLC (HP-5): t_R = 19.4 min. IR (ATR): $\tilde{\nu}$ 3092 (w), 2954 (s), 1658 (s), 1473 (m), 1356 (m), 1307 (m), 1265 (m), 1195 (m), 1103 (s), 1017 (s), 967 (s), 811 (s) cm^{-1}. HRMS (ESI): calculated for $C_{17}H_{22}FeNO$ $[M + H]^+$, 312.1045; found, 312.1053. ^1H NMR (500 MHz, C_6D_6): δ 0.91 (s, 9H), 3.78 (dd, J = 10.2, 8.2 Hz, 1H), 3.85−3.93 (m, 2H), 4.02 (m_c, 2H), 4.09 (s, 5H), 4.90 (m_c, 1H), 4.94 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 26.2, 33.6, 68.2, 69.6, 69.8, 70.28, 70.35, 72.0, 76.8, 165.2. Specific rotation $[\alpha]_D^{20}$ = −183.8 (c = 0.86, $CHCl_3$). The analytical and spectroscopic data are in accordance with those reported.[24]

($^{Si}S^*,S,S_p$)-*tert*-Butyl(2-(4-*tert*-butyloxazolin-2-yl)ferrocenyl)-methylsilane (6). To a solution of ferrocenyl oxazoline **8** (141 mg, 0.452 mmol, 1.00 equiv) and TMEDA (0.89 mL, 68 mg, 0.59 mmol, 1.3 equiv) in *n*-hexane (10 mL) cooled to −78 °C was added *n*BuLi (1.4 M in hexane fractions, 0.43 mL, 0.59 mmol, 1.3 equiv) dropwise, and the resulting mixture was stirred for 2 h at −78 °C and warmed to 0 °C over a period of 1 h. *tert*-Butylchloro(methyl)silane (86.5 mg, 0.633 mmol, 1.40 equiv) was added dropwise, and the reaction mixture was warmed to room temperature over a period of 20 h. After dilution with *tert*-butyl methyl ether (15 mL) and addition of saturated aqueous sodium bicarbonate solution (20 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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/ethyl acetate (20/1) as eluent, affording silane **6** (171 mg, 0.416 mmol, 92%, dr = 61:39) as a brown oil. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). R_f = 0.17 (cyclohexane/ethyl acetate 20/1). GLC (HP-5): t_R = 22.2 min (major diastereomer), t_R = 22.1 min (minor diastereomer). IR (ATR): $\tilde{\nu}$ 3096 (w), 2951 (m), 2852 (m), 2139 (w), 1637 (m), 1547 (w), 1462 (m), 1360 (m), 1248 (m), 1139 (m), 1056 (w), 996 (m), 870 (m), 813 (s), 719 (m) cm^{-1}. HRMS (ESI): calculated for $C_{22}H_{34}FeNOSi$ $[M + H]^+$: 412.1754; found, 412.1738. Specific rotation $[\alpha]_D^{20}$ = 160.0 (c = 0.58, $CHCl_3$). NMR spectroscopic data for the major diastereomer are as follows. ^1H NMR (500 MHz, C_6D_6): δ 0.38 (d, J = 3.8 Hz, 3H), 0.92 (s, 9H), 1.13 (s, 9H), 3.71 (dd, J = 10.2, 8.2 Hz, 1H). 3.81−3.89 (m, 2H), 4.05 (m_c, 1H), 4.10 (s, 5H), 4.19−4.22 (m, 1H), 4.94 (q, J = 3.8 Hz, 1H), 5.05 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −6.5, 18.0, 26.2, 28.1, 33.5, 68.0, 68.3,[†] 70.3, 72.8, 73.7, 76.9, 77.4, 79.7, 165.2 [[†] from the HMBC experiment]. $^1H,^{15}N$ HMQC NMR (700/71 MHz, C_6D_6): δ 226.4. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ −6.1. NMR spectroscopic data for the minor diastereomer are as follows. ^1H NMR (500 MHz, C_6D_6): δ 0.78 (d, J = 3.7 Hz, 3H), 0.90 (s, 9H), 1.15 (s, 9H), 3.68 (dd, J = 9.7, 8.5 Hz, 1H), 3.75−3.83 (m, 2H), 4.14 (s, 5H), 4.19−4.22 (m, 1H), 4.31 (m_c, 1H), 4.47 (q, J = 3.6 Hz, 1H), 5.05 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −5.0, 18.0, 26.2, 28.2, 33.6, 68.0, 68.3, 70.2, 72.5, 74.1, 77.0, 77.2, 79.7, 165.2. $^1H,^{15}N$ HMQC NMR (700/71 MHz, C_6D_6): δ 224.3. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ 0.8.

($^{Si}S^*,S$)-*tert*-Butyl(2-(4-*tert*-butyloxazolin-2-yl)phenyl)-methylsilylium Tetrakis(pentafluorophenyl)borate (1). This was prepared from ($^{Si}S^*,S$)-*tert*-butyl(2-(4-*tert*-butyloxazolin-2-yl)phenyl)-methylsilane (**5**; 23.9 mg, 78.7 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (77.0 mg, 83.5 μmol, 1.06 equiv) according to GP3. NMR spectroscopic data for ($^{Si}S,S$)-**1** are as follows. ^1H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.61 (s, 3H), 0.77 (s, 9H), 0.81 (s, 9H), 4.08 (dd, J = 10.1, 7.8 Hz, 1H), 4.86 (dd, J = 10.0, 8.0 Hz, 1H), 5.00 (dd, J = 10.2, 10.4 Hz, 1H), 7.36−7.42 (m, 1H), 7.42−7.57 (m, 2H), 7.62−7.66 (m, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −5.1, 18.7, 25.28, 25.32, 33.9, 71.1, 79.1, 124.6 (br m), 126.4, 132.4, 133.5, 134.2, 136.8 (d, J = 238.1 Hz), 137.2, 138.7 (d, J = 241.8 Hz), 140.9, 148.8 (d, J = 241.8 Hz), 181.8. $^1H,^{15}N$ HMQC NMR (700/71 MHz, 1,2-$Cl_2C_6D_4$): δ 151.2. $^1H,^{29}Si$ HMQC NMR (500/99 MHz, 1,2-$Cl_2C_6D_4$): δ 24.7. NMR spectroscopic data for ($^{Si}R,S$)-**1** are as follows. ^1H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.51 (s, 3H), 0.85 (s, 9H), 0.89 (s, 9H), 4.04 (dd, J = 12.6, 9.6 Hz, 1H), 4.64 (dd, J = 12.7, 9.6 Hz, 1H), 4.92 (dd, J = 9.6, 9.6 Hz, 1H), 7.36−7.42 (m, 1H), 7.42−7.57 (m, 2H), 7.57−7.61 (m, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −8.6, 20.2, 25.97, 25.99, 32.0, 73.0, 77.7, 124.6 (br m), 125.8, 127.7, 133.5, 134.2, 136.8 (d, J = 238.1 Hz), 137.3, 138.7 (d, J = 241.8 Hz), 142.3, 148.8 (d, J = 241.8 Hz), 182.9. $^1H,^{15}N$ HMQC NMR (700/71 MHz, 1,2-$Cl_2C_6D_4$): δ 151.3. $^1H,^{29}Si$ HMQC NMR (500/99 MHz, 1,2-$Cl_2C_6D_4$): δ 24.2. ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): −16.2. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): −166.1, −162.3, −131.7.

($^{Si}S^*,S,S_p$)-*tert*-Butyl(2-(4-*tert*-butyloxazolin-2-yl)ferrocenyl)-methylsilylium Tetrakis(pentafluorophenyl)borate (2). This was prepared from ($^{Si}S^*,S,S_p$)-*tert*-butyl(2-(4-*tert*-butyloxazolin-2-yl)-ferrocenyl)methylsilane (**6**; 20.6 mg, 50.1 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (50.7 mg, 55.0 mmol, 1.10 equiv) according to GP3. The silicon cation **2** was obtained along with small amounts of unreacted silane **6**. NMR spectroscopic data for ($^{Si}S,S,S_p$)-**2** are as follows. ^1H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.71 (s, 9H), 0.79 (s, 3H), 0.81 (s, 9H), 3.79 (dd, J = 9.8, 8.1 Hz, 1H), 4.17 (s, 5H), 4.58−4.64 (m, 1H), 4.71−4.80 (m, 2H), 4.82−4.88 (m, 2H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −2.8, 18.9, 25.0, 25.5, 33.3, 66.9, 69.5, 71.8, 72.3, 74.4, 77.9, 78.8, 80.6, 124.7 (br m), 136.8 (d, 241.8 Hz), 138.7 (d, J = 239.2 Hz), 148.8 (d, J = 244.5 Hz), 188.1. $^1H,^{15}N$ HMQC NMR (700/71 MHz, 1,2-$Cl_2C_6D_4$): δ 147.7. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 26.4. NMR spectroscopic data for ($^{Si}R,S,S_p$)-**2** are as follows. ^1H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.22 (s, 3H), 0.82 (s, 9H), 1.17 (s, 9H), 3.62−3.68 (m, 1H), 4.19 (s, 5H), 4.65−4.70 (m, 1H), 4.72−4.76 (m, 1H), 4.76 (m, 1H), 4.82−4.88 (m, 2H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −4.5, 18.9, 21.0, 24.9, 26.8, 66.5, 69.5, 72.2, 72.3, 75.7, 78.2, 79.4, 80.7, 124.7 (br m), 136.8 (d, 241.8 Hz), 138.7 (d, J = 239.2 Hz), 148.8 (d, J = 244.5 Hz), 188.6. $^1H,^{15}N$ HMQC NMR (700/71 MHz, 1,2-$Cl_2C_6D_4$): δ 152.5. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 25.4. ^{11}B NMR (160 MHz, 1,2-$Cl_2C_6D_4$): −16.0. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): −165.7, −161.9, −131.4.

2-(2-Bromophenyl)-1,3-dithiolane (11a). According to GP1, ethane-1,2-dithiol (0.91 mL, 1.0 g, 11 mmol, 2.0 equiv) and iodine (0.14 g, 0.54 mmol, 0.10 equiv) were added to a solution of 2-bromobenzaldehyde (0.63 mL, 1.0 g, 5.4 mmol, 1.0 equiv) in $CHCl_3$ (23 mL), and the resulting mixture was stirred at room temperature for 15 h. After addition of aqueous NaOH solution (2 N, 20 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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 dithiolane **11a** (1.14 g, 4.36 mmol, 81%) as a colorless oil. R_f = 0.47 (cyclohexane/ethyl acetate 30/1). GLC (HP-5): t_R = 17.7 min. IR (ATR): $\tilde{\nu}$ 3053 (w), 2918 (w), 2826 (w), 1458 (m), 1435 (m), 1273 (m), 1239 (w), 1158 (w), 1111 (w), 1018 (s), 843 (m), 729 (s), 683 (m) cm^{-1}. HRMS (ESI): calculated for $C_9H_9BrS_2$ $[M]^+$, 261.9309; found, 261.9264. ^1H NMR (500 MHz, C_6D_6): δ 2.64−2.71 (m, 2H), 2.74−2.81 (m, 2H), 6.15 (s, 1H), 6.60 (m_c, 1H), 6.93 (m_c, 1H), 7.26 (m_c, 1H), 7.85 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 39.6, 55.6, 124.5, 127.7, 129.2, 129.8, 133.0, 141.0.

2-(2-Bromophenyl)-2-methyl-1,3-dithiolane (11b). According to GP1, ethane-1,2-dithiol (0.17 mL, 0.19 g, 2.0 mmol, 2.0 equiv) and iodine (25.6 mg, 0.101 mmol, 0.101 equiv) were added to a solution of 2′-bromoacetophenone (0.14 mL, 0.20 g, 1.0 mmol, 1.0 equiv) in $CHCl_3$ (4.3 mL), and the resulting mixture was stirred at room temperature for 5 h. After addition of aqueous NaOH solution (2 N,

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10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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/ethyl acetate (20/1) as eluent, affording dithiolane **11b** (208 mg, 0.755 mmol, 75%) as a colorless oil. R_f = 0.45 (cyclohexane/ethyl acetate 10/1). GLC (HP-5): t_R = 17.9 min. IR (ATR): $\tilde{\nu}$ 3054 (w), 2965 (m), 2917 (m), 2854 (m), 2719 (w), 2368 (w), 2281 (w), 2097 (w), 1922 (w), 1804 (w), 1454 (s), 1418 (s), 1369 (m), 1274 (m), 1184 (m), 1123 (w), 1051 (m), 1016 (s), 947 (m), 848 (m), 804 (w), 756 (s), 730 (s), 663 (s) cm^{-1}. HRMS (ESI): calculated for $C_{10}H_{12}BrS_2$ $[M + H]^+$, 276.9538; found, 276.9538. ^1H NMR (500 MHz, C_6D_6): δ 2.34 (s, 3H), 2.60−2.67 (m, 2H), 2.76−2.83 (m, 2H), 6.63 (m_o, 1H), 6.91 (m_o, 1H), 7.44 (dd, J = 7.9, 1.4 Hz, 1H), 8.21 (dd, J = 8.0, 1.7 Hz, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 31.3, 40.0, 70.4, 123.8, 127.2, 128.7, 136.0, 144.8.

2-(2-Bromophenyl)-1,3-dithiane (11c). According to GP1, propane-1,3-dithiol (1.1 mL, 1.2 g, 11 mmol, 2.0 equiv) and iodine (0.14 g, 0.54 mmol, 0.10 equiv) were added to a solution of 2-bromobenzaldehyde (0.63 mL, 1.0 g, 5.4 mmol, 1.0 equiv) in $CHCl_3$ (23 mL), and the resulting mixture was stirred at room temperature for 15 h. After addition of aqueous NaOH solution (2 N, 20 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl solution (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by recrystallization from EtOH, affording dithiane **11c** (1.18 g, 4.29 mmol, 79%) as a colorless solid. Mp: 98.3 °C (benzene). GLC (HP-5): t_R = 18.5 min. IR (ATR): $\tilde{\nu}$ 3071 (w), 2929 (m), 2896 (m), 2831 (m), 1465 (m), 1417 (s), 1274 (s), 1175 (s), 1111 (w), 910 (m), 875 (m), 741 (s), 667 (s) cm^{-1}. HRMS (ESI): calculated for $C_{10}H_{11}BrS_2$ $[M]^+$, 275.9465; found, 275.9600. ^1H NMR (500 MHz, C_6D_6): δ 1.31−1.39 (m, 1H), 1.60 (m_o, 1H), 2.26−2.33 (m, 2H), 2.51−2.60 (m, 2H), 5.81 (s, 1H), 6.56 (m_o, 1H), 6.84 (m_o, 1H), 7.26 (m_o, 1H), 7.91 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 25.2, 32.1, 51.3, 123.4, 128.3, 129.9, 130.4, 133.2, 139.2. The analytical and spectroscopic data are in accordance with those reported.[28b]

2-(2-Bromophenyl)-2-methyl-1,3-dithiane (11d). According to GP1, propane-1,3-dithiol (0.18 mL, 0.20 g, 1.8 mmol, 1.2 equiv) and iodine (38.3 mg, 0.151 mmol, 0.100 equiv) were added to a solution of 2′-bromoacetophenone (0.20 mL, 0.30 g, 1.5 mmol, 1.0 equiv) in $CHCl_3$ (7.5 mL), and the resulting mixture was stirred at room temperature for 2 h. After addition of aqueous NaOH solution (2 N, 10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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/ethyl acetate (10/1) as eluent, affording dithiane **11d** (252 mg, 0.871 mmol, 49%) as a colorless oil. R_f = 0.50 (cyclohexane/ethyl acetate 10/1). GLC (FS-SE-54): t_R = 19.0 min. IR (ATR): $\tilde{\nu}$ 3055 (w), 2899 (m), 2231 (w), 2087 (w), 1922 (w), 1811 (w), 1579 (w), 1419 (s), 1259 (m), 1181 (m), 1120 (m), 1056 (m), 1015 (s), 907 (m), 735 (s), 662 (s) cm^{-1}. HRMS (ESI): calculated for $C_{11}H_{13}BrS_2$ $[M]^+$, 289.9622; found, 289.9572. ^1H NMR (500 MHz, C_6D_6): δ 1.25−1.32 (m, 1H), 1.55−1.65 (m, 1H), 2.11 (s, 3H), 2.15−2.22 (m, 2H), 2.31−2.40 (m, 2H), 6.67 (m_o, 1H), 6.98 (m_o, 1H), 7.54 (m_o, 1H), 8.24 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ 24.4, 28.7, 29.1, 54.1, 123.3, 127.0, 128.8, 132.6, 137.3, 141.4.

***tert*-Butyl(2-(1,3-dithiolan-2-yl)phenyl)methylsilane (9a).** According to GP2, *n*BuLi (1.5 M in hexane fractions, 0.66 mL, 1.0 mmol, 1.3 equiv) was added dropwise to a solution of bromide **11a** (0.20 g, 0.77 mmol, 1.0 equiv) in THF (7 mL) at −78 °C. After an additional 1 h at −78 °C, a solution of *tert*-butylchloro(methyl)silane (209 mg, 1.53 mmol, 1.99 equiv) in THF (3 mL) was added, and the resulting mixture was warmed to room temperature over a period of 2 h. After addition of water (10 mL) and dilution with *tert*-butyl methyl ether (10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 7 mL). The combined organic phases were washed with saturated aqueous NaCl solution (20 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 (50/1) as eluent, affording silane **9a** (132 mg, 0.467 mmol, 61%) as a slightly yellow oil. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). R_f = 0.35 (cyclohexane/ethyl acetate 50/1). GLC (HP-5): t_R = 19.0 min. IR (ATR): $\tilde{\nu}$ 3051 (w), 2923 (s), 2852 (s), 2111 (s), 1587 (w), 1463 (m), 1427 (m), 1360 (w), 1253 (m), 1119 (m), 1067 (w), 1007 (m), 887 (s), 822 (s), 725 (s) cm^{-1}. HRMS (ESI): calculated for $C_{14}H_{22}S_2Si$ $[M]^+$, 283.0966; found, 283.1010. ^1H NMR (500 MHz, $CDCl_3$): δ 0.39 (d, J = 3.8 Hz, 3H), 0.98 (s, 9H), 3.33−3.41 (m, 2H), 3.51−3.61 (m, 2H), 4.44 (q, J = 3.7 Hz, 1H), 5.98 (s, 1H), 7.23 (m_o, 1H), 7.37−7.43 (m, 2H), 7.94 (m_o, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ −7.1, 17.2, 27.5, 40.7, 40.8, 56.5, 127.1, 128.9, 130.2, 134.5, 135.3, 146.3. ^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ −7.5.

***tert*-Butylmethyl(2-(2-methyl-1,3-dithiolan-2-yl)phenyl)-silane (9b).** According to GP2, *n*BuLi (1.5 M in hexane fractions, 0.92 mL, 1.4 mmol, 1.3 equiv) was added dropwise to a solution of bromide **11b** (0.30 g, 1.1 mmol, 1.0 equiv) in THF (10 mL) at −78 °C. After an additional 1 h at −78 °C, a solution of *tert*-butylchloro(methyl)-silane (298 mg, 2.18 mmol, 1.98 equiv) in THF (5 mL) was added, and the resulting mixture was warmed to room temperature over a period of 15 h. After addition of water (20 mL) and dilution with *tert*-butyl methyl ether (15 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl solution (35 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 (50/1) as eluent, affording silane **9b** (153 mg, 0.516 mmol, 47%) as a slightly red oil. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). R_f = 0.45 (cyclohexane/ethyl acetate 50/1). GLC (FS-SE-54): t_R = 19.5 min. IR (ATR): $\tilde{\nu}$ 3048 (w), 2923 (s), 2852 (s), 2146 (s), 1927 (w), 1580 (w), 1458 (s), 1440 (m), 1361 (m), 1247 (s), 1089 (m), 1065 (m), 1008 (m), 842 (s), 716 (s) cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{24}S_2Si$ $[M]^+$: 297.1122; found, 297.1162. ^1H NMR (500 MHz, C_6D_6): δ 0.41 (d, J = 3.6 Hz, 3H), 1.08 (s, 9H), 2.32 (s, 3H), 259−2.69 (m, 2H), 2.75−2.87 (m, 2H), 5.15 (q, J = 3.5 Hz, 1H), 7.04 (m_o, 1H), 7.12 (m_o, 1H), 7.58 (m_o, 1H), 8.28 (m_o, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −5.5, 18.1, 28.9, 34.5, 38.5, 39.5, 72.2, 125.9, 126.7, 128.4, 136.50, 136.51, 153.2. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ −8.2.

***tert*-Butyl(2-(1,3-dithian-2-yl)phenyl)methylsilane (9c).** According to GP2, *n*BuLi (1.5 M in hexane fractions, 0.63 mL, 0.95 mmol, 1.3 equiv) was added dropwise to a solution of bromide **11c** (0.20 g, 0.73 mmol, 1.0 equiv) in THF (7 mL) at −78 °C. After an additional 1 h at −78 °C, a solution of *tert*-butylchloro(methyl)silane (199 mg, 1.45 mmol, 1.99 equiv) in THF (3 mL) was added, and the resulting mixture was warmed to room temperature over a period of 15 h. After addition of water (10 mL) and dilution with *tert*-butyl methyl ether (10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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 (30/1) as eluent, affording silane **9c** (80.7 mg, 0.272 mmol, 37%) as a colorless oil. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). R_f = 0.30 (cyclohexane/ethyl acetate 50/1). GLC (HP-5): t_R = 19.8 min. IR (ATR): $\tilde{\nu}$ 3053 (w), 2925 (m), 2891 (m), 2852 (m), 2109 (s), 1586 (w), 1465 (m), 1421 (m), 1273 (m), 1170 (w), 1121 (m), 1066 (w), 1006 (w), 885 (s), 820 (s), 730 (s), 674 (m) cm^{-1}. HRMS (ESI): calculated for $C_{15}H_{24}S_2Si$ $[M]^+$, 297.1122; found, 297.1169. ^1H NMR (500 MHz, $CDCl_3$): δ 0.41 (d, J = 3.8 Hz, 3H), 1.00 (s, 9H), 1.95 (m_o, 1H), 2.14−2.21 (m, 1H), 2.86−2.95 (m, 2H), 3.03 (m_o, 2H), 4.38 (q, J = 3.6 Hz, 1H), 5.36 (s, 1H),

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7.24−7.29 (m, 1H), 7.40 (m_c, 1H), 7.45 (m_c, 1H), 7.69 (m_c, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ −7.2, 17.3, 25.3, 27.4, 32.5, 32.8, 52.7, 127.5, 128.3, 130.2, 133.8, 136.1, 145.1. ^{29}Si DEPT NMR (99 MHz, $CDCl_3$): δ −6.6.

***tert*-Butylmethyl(2-(2-methyl-1,3-dithian-2-yl)phenyl)silane (9d).** According to GP2, *n*BuLi (1.54 M in hexane fractions, 1.17 mL, 1.80 mmol, 1.30 equiv) was added dropwise to a solution of bromide **11d** (0.40 g, 1.4 mmol, 1.0 equiv) in THF (13 mL) at −78 °C. After an additional 1 h at −78 °C, a solution of tert-butylchloro(methyl)-silane (345 mg, 2.53 mmol, 1.80 equiv) in THF (7 mL) was added, and the resulting mixture was warmed to room temperature over a period of 15 h. After addition of water (15 mL) and dilution with *tert*-butyl methyl ether (10 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 20 mL). The combined organic phases were washed with saturated aqueous NaCl solution (30 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 (50/1) as eluent, affording silane **9d** (193 mg, 0.621 mmol, 45%) as a white solid. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). Mp: 75.9 °C (cyclohexane/ethyl acetate). R_f = 0.45 (cyclohexane/ethyl acetate 20/1). GLC (FS-SE-54): t_R = 20.5 min. IR (ATR): $\tilde{\nu}$ 2930 (s), 2851 (s), 2197 (s), 2111 (w), 1582 (w), 1449 (m), 1244 (m), 1125 (w), 1058 (s), 1003 (w), 818 (s), 713 (s) cm^{-1}. HRMS (ESI): calculated for $C_{16}H_{26}S_2Si$ $[M]^+$, 311.1279; found, 311.1320. ^{1}H NMR (500 MHz, C_6D_6): δ 0.37 (d, *J* = 3.5 Hz, 3H), 1.10 (s, 9H), 1.34−1.41 (m, 1H), 1.61 (m_c, 1H), 2.09 (s, 3H), 2.15−2.30 (m, 3H), 2.41 (m_c, 1H), 5.35 (q, *J* = 3.4 Hz, 1H), 7.07 (m_c, 1H), 7.14−7.19 (m, 1H), 7.68 (m_c, 1H), 8.19 (m_c, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −5.2, 18.5, 24.3, 28.3, 28.8, 29.1, 32.4, 55.9, 125.9, 128.5, 129.3, 137.1, 137.8, 150.3. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ −8.7.

***tert*-Butyl(2-(1,3-dithiolan-2-yl)phenyl)methylsilylium Tetrakis(pentafluorophenyl)borate (3a).** This was prepared from *tert*-butyl(2-(1,3-dithiolan-2-yl)phenyl)methylsilane (**9a**; 14.1 mg, 49.9 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (50.7 mg, 55.0 μmol, 1.10 equiv) according to GP3. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.67 (s, 3H), 0.81 (s, 9H), 2.39 (ddd, *J* = 13.3, 10.1, 5.7 Hz, 1H), 3.20 (ddd, *J* = 13.3, 5.2, 3.1 Hz, 1H), 3.44 (ddd, *J* = 11.9, 10.2, 5.2 Hz, 1H), 3.49 (ddd, *J* = 11.9, 5.7, 3.1 Hz, 1H), 6.20 (s, 1H), 7.18−7.22 (m, 1H), 7.25 (m_c, 1H), 7.31−7.35 (m, 1H), 7.39 (m_c, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −6.2, 20.0, 24.7, 36.8, 46.1, 71.8, 124.7 (br m), 127.2, 128.1, 131.8, 133.8, 136.8 (d, *J* = 240.2 Hz), 138.7 (d, *J* = 243.1 Hz), 142.5, 143.0, 148.8 (d, *J* = 243.1 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, −162.1, −131.8. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 56.7.

***tert*-Butylmethyl(2-(2-methyl-1,3-dithiolan-2-yl)phenyl)-silylium Tetrakis(pentafluorophenyl)borate (3b).** This was prepared from *tert*-butylmethyl(2-(2-methyl-1,3-dithiolan-2-yl)-phenyl)silane (**9b**; 23.7 mg, 79.9 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv) according to GP3. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.62 (s, 3H), 0.85 (s, 9H), 2.04 (s, 3H), 2.36 (ddd, *J* = 13.5, 11.6, 4.8 Hz, 1H), 3.18 (ddd, *J* = 13.5, 5.0, 1.6 Hz, 1H), 3.49 (ddd, *J* = 12.0, 3.6, 1.4 Hz, 1H), 3.63 (ddd, *J* = 11.8, 5.0, 5.0 Hz, 1H), 7.18−7.20 (m, 1H), 7.25 (m_c, 1H), 7.31−7.35 (m, 1H), 7.41 (m_c, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −6.1, 19.6, 25.1, 29.1, 38.5, 48.4, 92.6, 124.5 (br m), 125.8, 128.1, 131.6, 134.0, 136.8 (d, *J* = 248.9 Hz), 138.7 (d, *J* = 240.2 Hz), 142.5, 148.8 (d, *J* = 243.1 Hz), 149.6. ^{11}B NMR (225 MHz, 1,2-$Cl_2C_6D_4$): δ −16.0. ^{19}F NMR (471 MHz, 1,2-$Cl_2C_6D_4$): δ −166.1, −162.1, −132.0. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 51.7.

***tert*-Butyl(2-(1,3-dithian-2-yl)phenyl)methylsilylium Tetrakis(pentafluorophenyl)borate (3c).** This was prepared from *tert*-butyl(2-(1,3-dithian-2-yl)phenyl)methylsilane (**9c**; 14.9 mg, 50.2 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (51.0 mg, 55.3 μmol, 1.10 equiv) according to GP3. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.53 (s, 3H), 0.81 (s, 9H), 1.79−1.87 (m, 2H), 2.19−2.32 (m, 2H), 2.42−2.50 (m, 1H), 2.67 (m_c, 1H), 5.44 (s, 1H), 7.30−7.34 (m, 1H), 7.37−7.40 (m, 1H), 7.50 (m_c, 1H), 7.60 (m_c, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −9.1, 21.0, 22.7, 22.9, 24.9, 31.5, 59.3, 124.7 (br m), 128.1, 130.1, 134.1, 134.8, 136.8 (d, *J* = 243.1 Hz), 138.7 (d, *J* = 240.2 Hz), 140.2, 142.5, 148.8 (d, *J* = 240.2 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 −166.0, −162.2, −131.7. ^{29}Si DEPT NMR (99 MHz, 1,2-$Cl_2C_6D_4$): δ 51.3.

***tert*-Butylmethyl(2-(2-methyl-1,3-dithian-2-yl)phenyl)-silylium Tetrakis(pentafluorophenyl)borate (3d).** This was prepared from *tert*-butylmethyl(2-(2-methyl-1,3-dithian-2-yl)phenyl)-silane (**9d**; 24.9 mg, 80.2 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv) according to GP3. ^{1}H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.59 (s, 3H), 0.92 (s, 9H), 1.56−1.63 (m, 1H), 1.70−179 (m, 1H), 1.76 (s, 3H), 2.27 (ddd, *J* = 13.7, 8.1, 4.8 Hz, 1H), 2.35−2.43 (m, 1H), 2.64 (ddd, *J* = 12.7, 10.0, 2.7 Hz, 1H), 3.00 (ddd, *J* = 11.9, 7.6, 2.4 Hz, 1H), 7.26−7.31 (m, 1H), 7.31−7.34 (m, 1H), 7.42−7.48 (m, 2H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −6.1, 19.7, 20.1, 25.2, 26.3, 33.6, 34.9, 73.8, 125.0 (br m), 126.0, 128.1, 130.3, 134.0, 134.2, 136.8 (d, *J* = 246.0 Hz), 138.7 (d, *J* = 237.4 Hz), 147.7, 148.8 (d, *J* = 240.2 Hz). ^{11}B NMR (225 MHz, 1,2-$Cl_2C_6D_4$): δ −16.0. ^{19}F NMR (659 MHz, 1,2-$Cl_2C_6D_4$): δ −165.7, −161.9, −131.5. ^{29}Si DEPT NMR (139 MHz, 1,2-$Cl_2C_6D_4$): δ 42.3, 48.6.

(^{S}*S*)-Ferrocenyl *p*-Tolyl Sulfoxide. Ferrocene (0.50 g, 2.7 mmol, 1.0 equiv) and KO*t*Bu (30 mg, 0.27 mmol, 0.10 equiv) were suspended in THF (8 mL), and the suspension was cooled to −78 °C. *t*BuLi (1.48 M in *n*-pentane, 1.73 mL, 2.55 mmol, 0.944 equiv) was added dropwise. The resulting mixture was stirred for 30 min at −78 °C and 30 min at room temperature and then added dropwise to a solution of (1*R*,2*S*,5*R*)-(−)-menthyl (*S*)-*p*-toluenesulfinate (0.791 g, 2.69 mmol, 1.00 equiv) in THF (8 mL) at −78 °C. The reaction mixture was warmed to room temperature and stirred for a further 16 h. After addition of water (15 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 10 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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 (2/1) as eluent, affording (^{S}*S*)-ferrocenyl *p*-tolyl sulfoxide (585 mg, 1.80 mmol, 67%, 93% ee) as an orange solid. Mp: 141.8 °C (cyclohexane/ethyl acetate). R_f = 0.40 (cyclohexane/ethyl acetate 1/1). GLC (FS-SE-54): t_R = 24.1 min. IR (ATR): $\tilde{\nu}$ 3075 (m), 3029 (w), 2915 (w), 2161 (w), 2074 (w), 1918 (w), 1653 (w), 1595 (w), 1491 (m), 1446 (w), 1402 (m), 1159 (m), 1083 (m), 1043 (s), 890 (w), 808 (s), 704 (m) cm^{-1}. HRMS (ESI): calculated for $C_{17}H_{17}FeOS$ $[M + H]^+$, 325.0305; found, 325.0341. ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H), 4.32 (m_c, 1H), 4.36 (m_c, 2H), 4.37 (s, 5H), 4.61 (m_c, 1H), 7.25 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.5, 65.4, 68.0, 70.0, 70.1, 124.5, 129.8, 141.1, 143.1† (the dagger (†) denotes a signal from the HMBC experiment). HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 90/10, flow rate 0.70 mL/min, λ = 230 nm): t_R = 18.7 min [(^{S}*R*)-ferrocenyl(*p*-tolyl)sulfoxide], t_R = 22.1 min [(^{S}*S*)-ferrocenyl(*p*-tolyl)sulfoxide]. Specific rotation $[\alpha]_D^{20}$ = 284.4 (*c* = 0.93, $CHCl_3$). The analytical and spectroscopic data are in accordance with those reported.[30a]

(^{S}*S*,*S*$_p$)-1-Formyl-2-((4-methylphenyl)sulfinyl)ferrocene (12). To a solution of (^{S}*S*)-ferrocenyl(*p*-tolyl)sulfoxide (0.50 g, 1.5 mmol, 1.0 equiv, 93% ee) in THF (7.7 mL) cooled to −78 °C was added freshly prepared lithium diisopropylamide (0.88 M in THF, 2.3 mL, 2.0 mmol, 1.3 equiv), and the resulting mixture was stirred for 30 min at −78 °C. DMF (0.30 mL, 0.28 g, 3.9 mmol, 2.5 equiv) was added, and the reaction mixture was stirred for an additional 30 min at −78 °C and 1.5 h at 0 °C. After addition of aqueous NaOH solution (2 N, 15 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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 (1/1) as eluent, affording aldehyde **12** (305 mg, 0.865 mmol, 56%, 96% ee) as a dark brown solid. Mp: 147.9 °C (cyclohexane/ethyl acetate). R_f = 0.20 (cyclohexane/ethyl acetate 1/1). IR (ATR): $\tilde{\nu}$ 3320 (w), 3092 (w), 2818 (w), 2320 (w), 1667 (s), 1594 (w), 1434 (m), 1225 (m), 1162 (m), 1029 (s), 814 (s), 752 (s)

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cm^{-1}. HRMS (ESI): calculated for $C_{18}H_{17}FeOS$ $[M + H]^+$, 353.0254; found, 353.0294. ^1H NMR (500 MHz, $CDCl_3$): δ 2.37 (s, 3H), 4.49 (s, 5H), 4.71 (m_o, 1H), 4.76 (m_o, 1H), 5.02 (m_o, 1H), 7.25 (d, J = 6.6 Hz, 2H), 7.50 (d, J = 7.5 Hz, 2H), 10.49 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 21.5, 70.7, 71.8, 73.1, 74.2, 78.7, 97.4, 124.3, 130.0, 141.4, 142.4, 192.9. HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 80/20, flow rate 0.70 mL/min, λ = 210 nm): t_R = 21.4 min [(^{S}*S*,*S*$_p$)-**12**], t_R = 28.8 min [(^{S}*R*,*R*$_p$)-**12**]. Specific rotation $[\alpha]_D^{20}$ = 223.5 (c = 0.74, $CHCl_3$). The analytical and spectroscopic data are in accordance with those reported.[30c]

(^{S}*S*,*S*$_p$)-1-(1,3-Dithiolan-2-yl)-2-((4-methylphenyl)sulfinyl)-ferrocene (13). Ethane-1,2-dithiol (75 μL, 80 mg, 0.85 mmol, 1.2 equiv) and iodine (18 mg, 0.071 mmol, 0.10 equiv) were added to a solution of aldehyde **12** (0.25 g, 0.71 mmol, 1.0 equiv, 96% ee) in $CHCl_3$ (3.5 mL), and the resulting mixture was stirred at room temperature for 3.5 h. After addition of aqueous NaOH solution (2 N, 8 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 8 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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/ethyl acetate (2/1) as eluent, affording dithiolane **13** (241 mg, 0.563 mmol, 79%, 97% ee) as an orange solid. Mp: 143.5 °C (cyclohexane/ethyl acetate). R_f = 0.50 (cyclohexane/ethyl acetate 1/1). GLC (FS-SE-54): t_R = 32.1 min. IR (ATR): $\tilde{\nu}$ 3037 (w), 2919 (w), 2299 (w), 2064 (w), 1893 (w), 1717 (w), 1491 (m), 1408 (m), 1276 (w), 1229 (m), 1180 (w), 1083 (m), 1034 (s), 804 (s), 701 (m) cm^{-1}. HRMS (ESI): calculated for $C_{20}H_{20}FeOS_3$ $[M]^+$, 429.0059; found, 429.0095. ^1H NMR (500 MHz, C_6D_6): δ 1.98 (s, 3H), 2.50–2.57 (m, 1H), 2.64 (m_o, 2H), 2.73–2.80 (m, 1H), 3.95 (m_o, 1H), 4.24 (m_o, 1H), 4.44 (s, 5H), 4.53 (m_o, 1H), 6.70 (s, 1H), 6.96 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 8.3 Hz, 2H). ^{13}C NMR (126 MHz, C_6D_6): δ 21.2, 39.4, 40.0, 49.6, 69.3, 70.1, 70.6, 71.6, 90.0, 92.1, 124.9, 129.8, 140.1, 143.9. HPLC (Daicel Chiralcel OD-H, 20 °C, *n*-heptane/*i*-PrOH 80/20, flow rate 0.70 mL/min, λ = 254 nm): t_R = 19.3 min [(^{S}*S*,*S*$_p$)-**13**], 50.9 min [(^{S}*R*,*R*$_p$)-**13**]. Specific rotation $[\alpha]_D^{20}$ = 455.1 (c = 0.89, $CHCl_3$).

(^{Si}*S,*S*$_p$)-*tert*-Butyl(2-(1,3-dithiolan-2-yl)ferrocenyl)-methylsilane (10).** To a solution of dithiolane **13** (0.25 g, 0.58 mmol, 1.0 equiv, 97% ee) in THF (3 mL) cooled to −78 °C was added *t*BuLi (1.5 M in *n*-pentane, 0.43 mL, 0.64 mmol, 1.1 equiv) dropwise, and the resulting mixture was stirred for an additional 30 min at −78 °C. A solution of *tert*-butylchloro(methyl)silane (95.7 mg, 0.700 mmol, 1.21 equiv) in THF (4 mL) was added, and the reaction mixture was warmed to room temperature over a period of 20 h. After addition of aqueous NaOH solution (2 N, 20 mL), the phases were separated, and the aqueous phase was extracted with *tert*-butyl methyl ether (3 × 15 mL). The combined organic phases were washed with saturated aqueous NaCl solution (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/CH_2Cl_2 (10/1) as eluent, affording silane **10** (114 mg, 0.291 mmol, 50%, 97% ee, dr = 92:8) as a brown oil. For the generation of the corresponding silicon cation, the silane was azeotropically dried by addition and subsequent evaporation of dry benzene under vacuum (3×). R_f = 0.30 (cyclohexane/CH_2Cl_2 10/1). GLC (FS-SE-54): t_R = 24.3 min (major diastereomer), t_R = 24.6 min (minor diastereomer). IR (ATR): $\tilde{\nu}$ 3090 (w), 2922 (m), 2850 (m), 2366 (w), 2098 (m), 1462 (m), 1418 (w), 1390 (w), 1248 (m), 1145 (m), 1037 (m), 1000 (m), 873 (m), 814 (s), 723 (s) cm^{-1}. HRMS (ESI): calculated for $C_{18}H_{26}FeS_2Si$ $[M]^+$, 390.0595; found, 390.0591. Specific rotation $[\alpha]_D^{20}$ = 199.2 (c = 0.76, $CHCl_3$). NMR spectroscopic data for the major diastereomer are as follows. ^1H NMR (500 MHz, C_6D_6): δ 0.49 (d, J = 3.9 Hz, 3H), 1.09 (s, 9H), 2.69–2.77 (m, 2H), 2.84–2.92 (m, 2H), 4.08 (m_o, 1H), 4.19 (s, 5H), 4.24 (m_o, 1H), 4.32 (q, J = 3.9 Hz, 1H), 4.82 (m_o, 1H), 5.76 (s, 1H). ^{13}C NMR (126 MHz, C_6D_6): δ −6.5, 17.5, 27.7, 39.9, 40.3, 54.0, 65.8, 70.1, 71.0, 72.2, 76.4, 94.6. ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ −1.6. NMR spectroscopic data for the minor diastereomer are as follows. ^1H NMR (500 MHz, C_6D_6): δ 0.29 (d, J = 3.7 Hz, 3H), 1.07 (s, 9H), 2.69–2.77 (m, 2H), 2.84–2.92 (m, 2H), 3.86 (m_o, 1H), 4.17 (s, 5H), 4.24 (m_o, 1H), 4.49 (q, J = 3.4 Hz, 1H), 4.84 (m_o, 1H), 5.89 (s, 1H). ^{29}Si DEPT NMR (99 MHz, C_6D_6): δ −8.1.

(*S*$_p$)-*tert*-Butyl(2-(1,3-dithiolan-2-yl)ferrocenyl)-methylsilylium Tetrakis(pentafluorophenyl)borate (4). This was prepared from (*S*$_p$)-*tert*-butyl(2-(1,3-dithiolan-2-yl)ferrocenyl)-methylsilane (**10**; 31.2 mg, 79.9 μmol, 1.00 equiv) and $[Ph_3C]^+[B(C_6F_5)_4]^-$ (73.8 mg, 80.0 μmol, 1.00 equiv) according to GP3. ^1H NMR (500 MHz, 1,2-$Cl_2C_6D_4$): δ 0.53 (s, 2H, SiMe), 0.54 (s, 3H, SiMe), 0.80 (s, 6H, Si*t*Bu), 0.86 (s, 9H, Si*t*Bu), 0.87 (s, 2H, SiMe), 0.90, (s, 3H, SiMe), 0.98 (s, 6H, Si*t*Bu), 1.09 (s, 10H, Si*t*Bu), 2.98–2.95 (m_o, 3H), 3.14–3.21 (m_o, 1H), 3.23–3.33 (m, 3H), 3.34–3.43 (m, 2H), 3.45–3.48 (m, 1H), 3.48–3.51 (m, 2H), 3.51–3.59 (m, 5H), 3.59–3.65 (2H), 4.03–4.04 (m 1H), 4.05 (s, 5H), 4.06 (s, 5H), 4.10–4.11 (m, 1H), 4.14 (s, 3H), 4.17 (s, 1H), 4.34–4.41 (m, 3H), 4.47–4.51 (m, 3H), 4.52–4.55 (m, 2H), 5.66 (s, 1H), 6.00 (s, 1H), 6.07 (s, 1H). ^{13}C NMR (126 MHz, 1,2-$Cl_2C_6D_4$): δ −3.0, −2.2, −0.62, −0.60, 19.9, 20.3, 21.3, 22.8, 24.9, 26.01, 26.03, 26.2, 26.4, 26.5, 37.3, 41.4, 42.0, 42.4, 42.7, 42.9, 43.1, 44.4, 63.6, 64.6, 68.6, 69.3, 69.6, 70.8, 70.9, 71.11, 71.14, 71.3, 71.5, 71.8, 74.1, 76.7, 77.5, 78.2, 78.5, 78.7, 80.0, 85.1, 85.8, 87.8, 96.7, 124.6 (br m), 136.7 (d, J = 243.1 Hz), 138.6 (d, J = 243.1 Hz), 148.7 (d, J = 237.4 Hz). ^{11}B NMR (225 MHz, 1,2-$Cl_2C_6D_4$): δ −16.4. ^{19}F NMR (659 MHz, 1,2-$Cl_2C_6D_4$): δ −166.1, −162.2, −131.9. ^1H,^{29}Si HMQC NMR (500/99 MHz, 1,2-$Cl_2C_6D_4$): δ 50.4, 51.3, 57.3, 57.8.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving NMR spectra of the compounds synthesized in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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