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Brook Rearrangement

Retro-Brook Rearrangement of Ferrocene-Derived Silyl Ethers

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Abstract: An intramolecular Li–Si exchange was observed on various lithiated ferrocenylbenzyl silyl ethers. The thermodynamically more stable C-silylated isomers were isolated in good yields and fully characterized. The reaction mechanism of the [1,4] retro-Brook rearrangement was investigated by DFT calculations. Two distinct reaction routes were proposed and a possible stabilization effect of the ferrocenyl fragment on the C-silylated isomers was described. The diastereoselective rearrangement of the trimethylsilyl group to the *ortho* position of the ferrocenyl cyclopentadienyl ring was also accomplished and the absolute configuration of the product was determined.

Introduction

Functionalized organosilane derivatives are useful as reagents in organic synthesis and catalysis. However, introduction of a silyl group at a desired position in the molecule is not always routine. Therefore, the development of selective methods for the formation of C–Si bonds is highly desirable. Intramolecular substitutions involving attack of an alkoxide on a silicon atom result in the transfer of a silyl group from a carbon atom to an oxygen atom.[1] This reaction has been for the first time observed by Brook and is nowadays known as the Brook rearrangement.[2] It is usually driven by higher thermodynamic stability of an O-silylated derivative in comparison to a C-silylated compound. The typical O–Si bond dissociation energy (BDE) in simple organosiloxanes is 510–560 kJ mol^{-1}, whereas the BDE of a typical C–Si bond is considerably lower, usually around 400 kJ mol^{-1} or less.[3] The Brook rearrangement has been used in various ways in the organic synthesis. The concept of anion relay chemistry often uses a Brook rearrangement reaction as a key step.[4] Geminal bis(silanes) are also useful substrates for Brook rearrangements.[5] Highly functionalized compounds such as siloxyallenes,[6] aminocyclopropanols,[7] or silyl dienol ethers[8] can be obtained through the Brook rearrangement. Carbanions, resulting from the Brook rearrangement of α-siloxy silanes can be advantageously carboxylated with carbon dioxide, thus leading to hydroxy acid derivatives.[9] On the other hand, little is known about Brook rearrangements on organometallic compounds. Stueger and co-workers described photoinduced Brook-type rearrangement reactions on acylcyclopolysilanes.[10] Arene chromium tricarbonyl complexes are suitable substrates for the Brook rearrangement too.[11] Acylsilanes in the presence of copper alkoxides undergo [1,2]-silyl migration and afford 1-siloxy-1-alkenylcopper species.[12] Instead of lithium anions, a zinc-promoted Brook rearrangement has also recently been described by Marek and co-workers.[13] The reversed process, that is, the transfer of a silyl group from an oxygen atom to a carbon atom, is also known but much less studied.[14] Rawal and co-workers prepared silyl-substituted salen ligands with the help of a retro-Brook rearrangement.[15] Other Br–Li–Si exchanges were also described.[16] The aforementioned geminal bis(silanes) can also be formed through reversed Brook rearrangement from 3-silyl allyloxysilanes.[17] The carbanion, which is required for the retro-Brook rearrangement, can be also formed by *ortho* or lateral deprotonation of O-silylated phenols.[18] Silyloxymethyllithiums also undergo this rearrangement.[19] The reversed Brook rearrangement was described in only a few examples, possibly because of an unfavorable thermodynamic situation of this rearrangement. Transfer of the silyl group from an oxygen atom to a carbon atom can usually succeed for one of three reasons. It may be kinetically viable, that is, much faster than the reaction from a carbon atom to an oxygen atom. This type of retro-Brook rearrangement can be followed by subsequent trapping of the transient intermediate.[18a] In the retro-Brook rearrangement, stoichiometric amount of lithium base is required, therefore formation of a stable lithium alkoxide can compensate for the unfavorable change in the BDE due to a O–Si versus C–Si exchange.[20] It can also succeed if the molecule resulting from the retro-Brook rearrangement is more stable for other reasons than just a comparison of the O–Si/C–Si bond energies.

In this context, we describe herein the retro-Brook rearrangement on O-silylated ferrocenyl alcohols initiated by a Br–Li exchange as well as through diastereoselective *ortho*-lithiation of the ferrocene moiety. To the best of our knowledge, there is no report of Brook-type rearrangement reactions on ferrocene derivatives. These transformations constitute useful addition to the synthetic toolbox, which enable the preparation of silylated ferrocenyl derivatives. The resulting C-silylated

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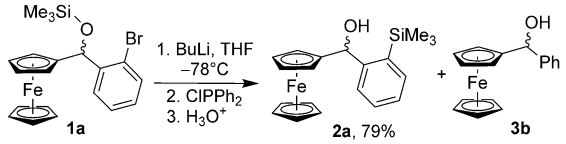
ferrocenyl alcohols are valuable starting materials for the synthesis of various ferrocenyl compounds, including chiral ligands.

Results and Discussion

Retro-Brook rearrangement initiated by Br–Li exchange

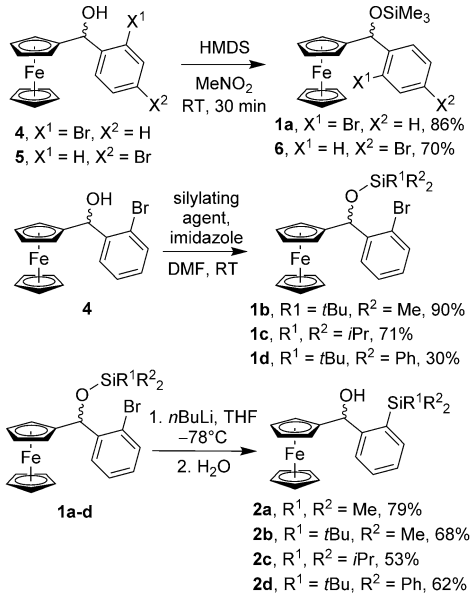
During our investigation of new ferrocenyl phosphanes we attempted to prepare phosphane alcohol from the corresponding silyl ether **1a** through lithiation and subsequent reaction with a chlorophosphane. However, no phosphane incorporation was observed. Instead, the seemingly unexpected product of a [1,4] retro-Brook rearrangement **2a** was isolated. Furthermore, compound **2a** was obtained in preparatively highly interesting 79% yield with only small amount of the debrominated alcohol **3b** (Scheme 1).



Scheme 1. Initial observation of the retro-Brook rearrangement of the silyl ether **1a**.

To explore the rearrangement of the silyl groups in more detail, a series of racemic ferrocenyl(2-bromobenzyl)silyl ethers was prepared from the corresponding alcohol *rac*-**4** following a procedure by Corey and Venkateswarlu (see the Experimental Section, Method B).[21] The silyl ether **1b** was obtained in 90% yield upon treatment of the alcohol **4** with *tert*-butyldimethylsilyl (TBDMS) chloride in DMF with imidazole as a base. Compound **1c** was obtained in a similar way in 71% yield. Instead of a silyl chloride, triisopropylsilyl (TIPS) triflate was employed. However, it is likely that the nature of the silylating agent does not influence the *O*-silylation. Introduction of the sterically more demanding *tert*-butyldiphenylsilyl (TBDPS) group, by using the corresponding TBDPS chloride led to the product **1d** in lower yield (30%) (Scheme 2). Also the 4-bromo trimethylsilyl (TMS) ether **6** was prepared by the silylation of the corresponding alcohol **5** in 70% yield (see the Experimental Section, Method A).[22] Compound **6** represents the type of substrate, which is unable to undergo an intramolecular rearrangement because of the long distance between the reacting centers.

Treatment of the aforementioned bromo silyl ethers **1a**–**1d** with *n*BuLi in THF at −78 °C for 2 h resulted in the clean transfer of the silyl group from the oxygen atom to the *ortho* position of the adjacent phenyl ring (Scheme 2). The corresponding *C*-silyl alcohols **2a**–**2d** were obtained in good yields (53–79%) in all of these cases. Performing the reaction on silyl ether **1a** at a concentration of 160 mM resulted in the formation of 79% of the retro-Brook rearrangement product **2a** in 2 h. However, the reaction of substrate **1a** at higher dilution ($c = 40$ mM) afforded a mixture consisting of the starting material (16%) and the rearranged product (79%) with only trace amount (5%) of the debrominated silyl ether (determined from ^{1}H NMR spectroscopy of the raw mixture). As expected, the retro-Brook rearrangement did not proceed on the substrate **6**, which carried the bromine in the *para* position of the phenyl ring. Complete conversion of the starting materials together with the presence of the debrominated silyl ethers isolated as byproducts indicates that the initial fast Br–Li exchange is followed by the slower intramolecular rearrangement step. The concentration of the reactants affects the rate of the bimolecular lithiation more significantly than the rate of the intramolecular rearrangement. The experiment on substrate **6** also suggests that the retro-Brook rearrangement on compounds **1** is an intramolecular process.



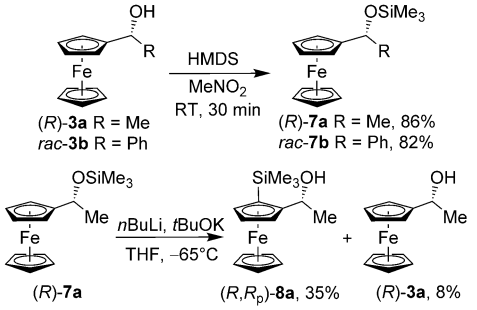
Scheme 2. Synthesis of the silyl ethers **1a**–**1d** and **6** and retro-Brook rearrangement of the silyl ethers **1a**–**1d**. HMDS = hexamethyldisilazane.

We have also attempted to perform a "classical" Brook rearrangement reaction on the product of the retro-Brook rearrangement, that is, the C-silylated alcohol **2a**. However, exposure of a solution of compound **2a** in THF to BuLi overnight led after workup only to the isolation of the starting material **2a**. Brook rearrangement of compound **2a** proceeded to a small extent (8% of the corresponding product **1a** was observed by ^{1}H NMR spectroscopy) when HMPA was used as an additive. This experiment showed that on substrates **1**, silyl transfer from an oxygen atom to a carbon atom is more preferable than the more common silyl transfer from a carbon atom to an oxygen atom.

Retro-Brook rearrangement initiated by *ortho*-lithiation

On ferrocene derivatives, a carbanion can be advantageously introduced by directed *ortho*-metalation of the cyclopentadienyl (Cp) ring. The possibility to transfer a silyl group diastereoselectively to one of the *ortho* positions of the substituted Cp ring could provide a useful method for the preparation of silyl-

protected ferrocenyl alcohols possessing the element of planar chirality. Configuration of the stereogenic plane is typically induced in the diastereoselective-directed *ortho*-metalation and is controlled by the configuration of the α-carbon chiral center. Observed rearrangement may be, therefore, used for the stereoselective protection of the preferred *ortho* position of the Cp ring. Starting from the 1-ferrocenylethanol **3a** and racemic ferrocenylbenzylalcohol **3b**, the OTMS ethers **7a** and **7b** were prepared in good yields by silylation with hexamethyldisilazane (HMDS) in nitromethane (Scheme 3).



Scheme 3. Retro-Brook rearrangement initiated by *ortho*-lithiation.

Initial attempts to perform an *ortho*-lithiation-initiated retro-Brook rearrangement by using *n*BuLi failed. We presumed that the lithiation in the *ortho* position of the substituted Cp ring requires a stronger base. However, upon treatment of the silyl ethers **7a** and **7b** with *t*BuLi the rearrangement product **8a** was observed only in traces (<5%, determined by ^{1}H NMR spectroscopy) and the corresponding phenyl analogue **8b** was isolated in 9% yield. The main products of both of these reactions were the corresponding desilylated alcohols **3a** (isolated in 70% yield) and **3b** (isolated in 32% yield), respectively. However, only one of the possible diastereoisomers was detected in both compounds **8a** and **8b**. These results show that *ortho*-lithiation of ferrocenyl silyl ethers, followed by mutual exchange of lithium for a silyl group can proceed diastereoselectively. To avoid the formation of possible byproducts due to *ortho*-lithiation of the phenyl ring in compound **7b**, we decided to optimize the reaction conditions on silyl ether **3a**.

The influence of additives on *ortho*-lithiation/retro-Brook rearrangement was explored. Various additives were described in the literature, which enhance the reactivity or stereoselectivity of *ortho*-lithiation reactions of ferrocene derivatives.[23] The addition of LiCl or *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) did not improve the yield of the desired product. On the other hand, employment of *t*BuOK as additive improved the yield of alcohol **8a** significantly. It also allowed the rearrangement of the less reactive substrates **9a** and **9b**, with bigger silyl groups. The best results were achieved by using an excess of the Schlosser base (4 mol equiv *n*BuLi/*t*BuOK 1:1) in THF at temperatures below −60 °C.[24]

The *ortho*-lithiation/rearrangement of the TMS ether **7a** proceeded regioselectively and diastereoselectively at the

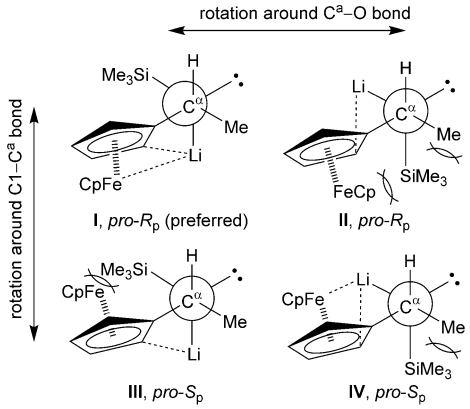
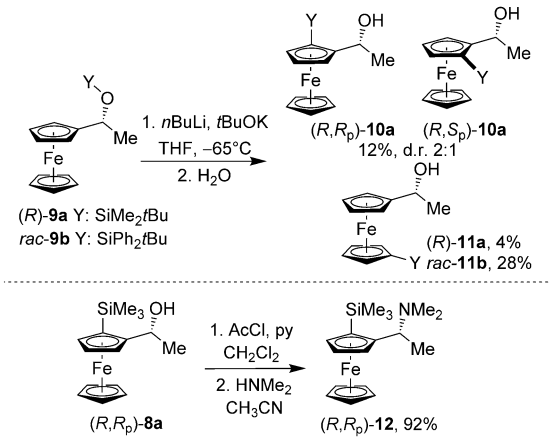


Figure 1. Tentative transition state models explaining the diastereoselectivity of the *ortho*-lithiation-initiated retro-Brook rearrangement.

ortho position of the Cp ring. However, the product **8a** was also accompanied with the desilylated alcohol **3a** (Scheme 3).

The diastereoselectivity of the *ortho*-lithiation can be explained by the tentative transition state model depicted in Figure 1. Preference for the lithiation to the *pro*-R_p position (*pro*-R_p denotes the position, from which the (R_p)-silylation product results) is probably caused by minimization of the steric repulsion between the silyl group and the α-methyl group as well as the silyl group and the ferrocenyl moiety.

Undesirable desilylation can be prevented by the use of bulkier silyl groups. The TBDMS ether **9a** was completely resistant towards desilylation side reaction. The rearrangement of the *tert*-butyldimethylsilyl group provided two diastereoisomeric *ortho*-*tert*-butyldimethylsilylated derivatives **10a** and small amount of the product of the rearrangement reaction on the non-substituted Cp ring **11a**. This alternative route was even more pronounced in the case of the TBDPS ether **9b**, where the corresponding product **11b** was obtained as the major compound (Scheme 4). It seems likely that the products **11a** and **11b** result from a long-range intramolecular



Scheme 4. *Ortho*-lithiation-initiated retro-Brook rearrangement on the sterically demanding silyl ethers **9a** and **9b**. Determination of the absolute configuration by chemical correlation (Ac = acetyl, py = pyridine).

rearrangement. The distance in space between the C(Li) of the non-substituted Cp ring and the Si atom is favorable for the reaction.

The homochiral O-silylated derivatives (*R*)-**7a** and (*R*)-**9a** were prepared by previously described procedures (see the Experimental Section, Method A for compound **7a** and Method B for compound **9a**) starting from alcohol (*R*)-**3a**, obtained by enantioselective Corey–Bakshi–Shibata (CBS) reduction of acetylferrocene.[25] Retro-Brook rearrangement was carried out by using *n*BuLi/*t*BuOK as the base and the C2-silylated products **8a** and **10a**, respectively, were characterized by specific optical rotation and CD spectroscopy.

To determine the absolute configuration of the obtained structures, alcohol **8a** was converted to the corresponding amine **12** and compared with compound (R,S_p)-**12**, described earlier by Ugi and co-workers.[26a] Alcohol **8a** was *O*-acetylated with AcCl/py and the acetoxy group was substituted on treatment with dimethylamine to yield compound **12** (Scheme 4) in excellent overall yield (92%). It has been documented that nucleophilic substitutions on the α-carbon atom in ferrocenyl compounds proceed with retention of the configuration of the stereogenic center.[27] The analysis of the ^{1}H NMR spectra revealed that our diastereoisomer **12** [$\delta = 0.29$ (TMS), 1.18 (CH_3), 2.36 (NMe_2), 3.34 ($C^{\alpha}H$), 4.12 ppm (Cp)] differs from compound (R,S_p)-**12** [$\delta = 0.26$ (TMS), 1.22 (CH_3), 2.04 (NMe_2), 3.82 ($C^{\alpha}H$), 4.07 ppm (Cp)] reported in the literature.[26b] Signs and values of the optical rotation match literature data (see the Experimental Section for details). The CD spectra also confirm that amine **12** obtained from the retro-Brook rearrangement and the one obtained by lithiation of the Ugi amine are diastereoisomers (see the Supporting information). Therefore, the absolute configuration of the product of the retro-Brook rearrangement was assigned as (R,R_p)-**8a**.

The relative configuration of the isolated diastereoisomers **10a** was determined by NOESY NMR experiments on both isomers (Figure2). For both diastereoisomers, in the most

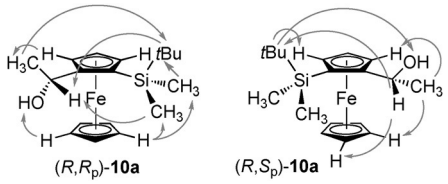


Figure 2. Determination of the relative configuration of compound **10a** by NOESY NMR spectroscopy.

preferred conformer the *tert*-butyl group is located *anti* to the Fe–Cp moiety. Repulsion of the C^{α} methyl group with the TBDMS group affects the conformation of the chiral center on the α-carbon atom resulting in a positive NOE between the C^{α} methyl group and the corresponding C5–H in both diastereoisomers. Whereas in the major isomer the OH group is *syn* oriented with respect to the Fe–Cp moiety, in the minor isomer the C^{α} methyl group as well as the C^{α} proton display interactions with the unsubstituted Cp ring. Therefore, the OH group is *anti* oriented to the Fe–Cp moiety. Starting from the homochiral TBDMS ether (*R*)-**9a** and considering the described interactions, we have determined the absolute configuration of the retro-Brook product (R,R_p)-**10a** for the major isomer and (R,S_p)-**10a** for the minor isomer.

Computational investigation of the reaction mechanism

The encouraging experimental results in the observed retro-Brook rearrangement of the ferrocenyl silyl ethers **1** prompted us to investigate the reaction mechanism by computational methods. The main question that we posed was about the possible reasons why this rearrangement works well on these compounds. In other words, what effects govern the thermodynamic viability of the reversed Brook rearrangement on this type of substrates? Therefore, we decided to compare the thermodynamic stability of the *C*-lithiated intermediate **13** with the C-silylated intermediate **14**. We also would like to locate a transition state of the rearrangement and thus find an explanation for the formation of the C–Si bond.

The first step of the reaction sequence is an electrophilic substitution of bromine with lithium upon treatment of compound **1a** with BuLi. This Br–Li exchange is fast and exothermic. The reaction produces BuBr and the *C*-lithiated intermediate **13** represented by two stable conformers, that is, *syn*-**13** and *anti*-**13** (*syn* and *anti* denote the orientation of the lithium atom with respect to the iron atom in the ferrocene moiety). Conformer *anti*-**13** is about 5 kJ mol^{-1} thermodynamically more stable than conformer *syn*-**13** (calculated at the RI-SCS-MP2 level by using def2-TZVP basis set)[38,39] (Figures 3 and 4). The modeling of the reaction mechanism showed that despite the stability of conformer *anti*-**13** its conversion to the rearrangement product *anti*-**14** through the transition state TS-1 proceeds through a higher activation barrier ($E_a = 56.8$ kJ mol^{-1}, DFT, RI-SCS-MP2/def2-TZVP). On the other hand, the less stable intermediate *syn*-**13** requires a lower activation energy ($E_a =$ 39.0 kJ mol^{-1}) to transform to the product *syn*-**14** through transition state TS-2. The conformer *syn*-**14** is calculated to be more stable than *anti*-**14** by approximately 8 kJ mol^{-1}. These calculations confirmed that the C-silylated isomer **14** is energetically more favorable than the O-silylated isomer **13**. Therefore, the equilibrium should be strongly shifted on the side of the C-silylated isomer (>99.95%). This notion is based on a Boltzmann distribution of the isomers *syn*-**13** and *syn*-**14** ($\Delta E = 18.9$ kJ mol^{-1}). Indeed, virtually no product **7a** of a Brook rearrangement was observed upon treatment of compound **2a** with *n*BuLi for several hours at room temperature. Only small amount of the product of a Brook rearrangement (8%) was observed, when HMPA was used as additive.

The energy of the C-silylated isomer **14** is lower in both conformations, although during the rearrangement, an energetically less stable bond (i.e., a C–Si bond) is formed.

The stabilizing electronic effects were studied by population analysis of all electrons condensed on the atoms (see the Supporting Information, important overlaps are highlighted). This analysis showed that the rearrangement of isomer **13** to compound **14** is accompanied with an increase of the positive

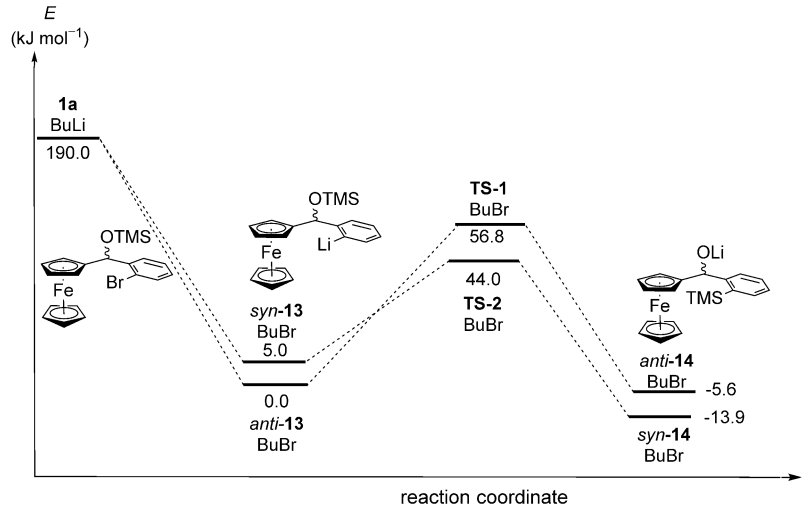


Figure 3. Reaction coordinate for the retro-Brook rearrangement reaction of compound **1a**.

Although, quantum chemical calculations suggest a stabilizing effect of ferrocene, the reaction proceeds without ferrocene too. Control experiments on two substrates also provided the corresponding retro-Brook rearrangement products. The reaction on (1-(2-bromophenyl)ethoxy)trimethylsilane proceeded cleanly, but reaction on ((2-bromophenyl)(phenyl)methoxy)trimethylsilane afforded a mixture of compounds consisting of the starting material, the retro-Brook rearrangement product, and the debrominated compound (see the Supporting Information for details).

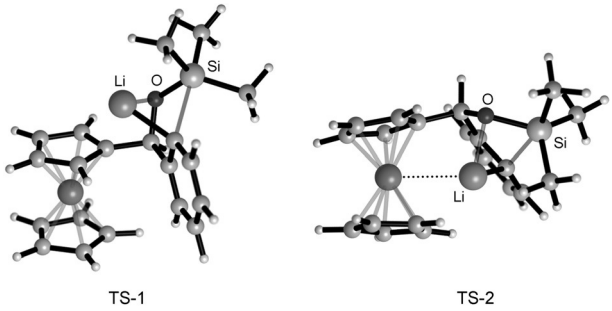
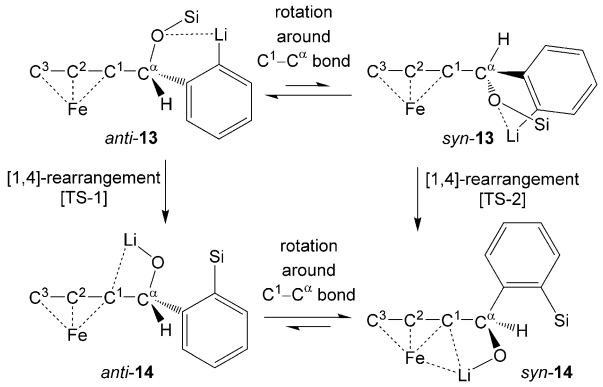


Figure 4. Calculated transition states for the retro-Brook rearrangement reaction of compound **1a**.



Scheme 5. Mechanism of the retro-Brook rearrangement reaction on ferrocenyl silyl ethers.

overlap of the oxygen-bonded Li atom with the adjacent aromatic system of the ferrocenyl moiety. Although the conformer *anti*-**13** is completely lacking this interaction, the corresponding *O*-lithiated conformer *anti*-**14** is stabilized by interaction of the lithium atom with the carbon atoms C1 and C2 of the substituted Cp ring. A different situation occurs in compounds *syn*-**13** and *syn*-**14**, where the Li is located in between the cyclopentadienyl rings. In the *C*-lithiated isomer *syn*-**13** a positive overlap is observed between the lithium atom and the nearest carbon atoms C1 and C17 of both cyclopentadienyl rings and the Fe atom. A similar Li–Fe interaction was computationally predicted in other derivatives too.[28] The shift of the Li atom to an oxygen atom results in shortening of the Li–Fe distance and thus the overlap of both atoms and the stabilizing interaction increases. The proposed mechanism of the retro-Brook rearrangement consists of two processes. The first process is the attraction of the lithium cation towards the aromatic system of ferrocene. This interaction is then followed by the transfer of the silyl group. In this step the Si–O bond is broken and a new C–Si bond is formed. It can proceed from both conformers *syn*-**13** and *anti*-**13** (Scheme 5).

Conclusion

Ferrocenylbenzylic silyl ethers undergo effective intramolecular silyl group transfer to the *ortho* position of the phenyl ring, which was initiated by a Br–Li exchange upon treatment with *n*BuLi. The influence of the adjacent ferrocenyl fragment on the course of the retro-Brook rearrangement was explained by DFT calculations and a plausible reaction mechanism was proposed. Similar rearrangement to the *ortho* position of the ferrocenyl Cp ring was also observed. This reaction was initiated by diastereoselective *ortho*-lithiation of the ferrocene moiety. In case of a TMS group, the resulting *ortho*-silylated alcohols were obtained in moderate yield (35%). Interestingly, retro-Brook rearrangement of the TMS group prefers the opposite diastereotopic site compared to classical diastereoselective *ortho*-lithiation of an Ugi amine. In the case of a TBDPS derivative, the rearrangement occurred predominantly to the unsubstituted Cp ring.

Experimental Section

Starting materials

2-Bromobenzoylferrocene,[25] 4-bromobenzoylferrocene,[28] and benzoylferrocene[29] were prepared by Friedel–Craft acylation according to literature procedures. Compound (R,S_p)-**12** was prepared according to the procedure of Ugi and co-workers.[26]

NMR spectra were recorded on Varian NMR System intruments at 23 °C at frequency 300 or 600 MHz for ^{1}H and 75 or 151 MHz for ^{13}C, respectively. Chemical shifts (δ) are given in ppm relative to tetramethylsilane as an internal standard. IR spectra were measured on Thermo Scientific Nikolet iS10 spectrometer with Smart iTR technology with diamond ATR. Elemental analyses were performed on varioMICRO cube (Elementar) instrument for simultaneous C,H,N,S analysis with options for O. High-resolution mass spectra were measured on a mass spectrometer with H-ESI Orbitrap ionization in positive mode.

General procedures

Reduction of ketones: A solution of the starting material (1.4 mmol, 1.0 equiv) in dry THF (10 mL) was added dropwise to a solution of $LiAlH_4$ (3.5 mmol, 2.5 equiv) in dry THF (10 mL) at 0 °C. The progress of the reaction was monitored by TLC (SiO_2, hexane/Et_2O 4:1). After completion the reaction was quenched with ice cold water. After filtration of the resulting mixture the organic phase was washed with water and brine, dried over Na_2SO_4, and evaporated under vacuum. The product was separated by column chromatography (SiO_2, hexane/EtOAc 8:1).

O-Silylation of alcohols: *Method A*: HMDS (1.1 mmol, 1.1 equiv) was added to a solution of the alcohol (1.0 mmol, 1.0 equiv) in $MeNO_2$ (1 mL) at RT. The progress of the reaction was monitored by TLC (SiO_2, hexane/Et_2O 4:1). After completion the reaction mixture was concentrated under vacuum. The product was separated by column chromatography (SiO_2, hexane/EtOAc 8:1).

Method B: To a mixture of the alcohol (0.67 mmol, 1.0 equiv), imidazole (1.68 mmol, 2.5 equiv), and DMF or dichloromethane (2 mL) the appropriate silyl reagent (1.68 mmol, 2.5 equiv) was added at RT. The mixture was stirred at RT overnight. The reaction mixture was concentrated in vacuum and the product was separated by column chromatography (SiO_2, hexane/EtOAc 8:1).

Lithiation and retro-Brook-rearrangement: A Solution of the silyl ether (0.32 mmol, 1 equiv) in dry THF (2 mL) was cooled to −78 °C. A solution of *n*BuLi in hexane (1.6 M, 0.38 mmol, 1.2 equiv) was added dropwise. The mixture was stirred at −78 °C for 2 h and then the temperature was allowed to rise to RT. The reaction was quenched by addition of water (1 mL). The layers were separated and the aqueous layer was extracted with Et_2O (2×5 mL). The combined organic phases were dried (Na_2SO_4) and concentrated under vacuum. The product was separated by column chromatography (SiO_2, hexane/EtOAc 8:1).

2-Bromophenyl(ferrocenyl)methanol (rac-*4)*: Yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.64 (d, J = 3.6 Hz, 1H; -OH), 4.12–4.18 (m, 2H; Fc), 4.19–4.22 (m, 1H; Fc), 4.26 (s, 5H; C_5H_5), 4.39–4.42 (m, 1H; Fc), 5.79 (d, J = 3.6 Hz, 1H; -*CH*(OH)), 7.15–7.07 (m, 1H; Ph), 7.35–7.28 (m, 1H; Ph), 7.49 (dd, J = 8.0, 1.1 Hz, 1H; Ph), 7.61 ppm (dd, J = 7.8, 1.8 Hz, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.3 (Fc), 67.6 (Fc), 67.9 (Fc), 68.2 (Fc), 68.5 (C_5H_5), 70.2 (-CH-OH), 93.7 (Fc), 122.4 (Ph), 127.5 (Ph), 127.8 (Ph), 128.9 (Ph), 132.6 (Ph), 142.4 ppm (Ph).

1-Ferrocenylethanol [(R)-3a]: Yield: 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.44 (d, J = 6.4 Hz, 3H; -CH_3), 1.88 (d, J = 4.6 Hz, 1H; -OH), 4.14–4.17 (m, 2H; Fc), 4.18–4.23 (m, 2H; Fc), 4.19 (s, 5H; C_5H_5), 4.54 ppm (dq, J = 6.4, 4.6 Hz, 1H; -*CH*(OH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 23.9 (-CH_3), 65.8 (-CH-OH), 66.3 (Fc), 66.4 (Fc), 68.1 (Fc), 68.1 (Fc), 68.5 (C_5H_5), 95.0 ppm(Fc).

Ferrocenyl(phenyl)methanol (rac-*3b)*: Yield: 87%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.49 (d, J = 3.2 Hz, 1H; -OH), 4.13–4.23 (m, 4H; Fc), 4.21 (s, 5H; C_5H_5), 5.45 (d, J = 3.1 Hz, 1H; -*CH*(OH)), 7.20–7.27 (m, 1H; Ph), 7.27–7.35 (m, 2H; Ph), 7.35–7.41 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 66.0 (Fc), 67.4 (Fc), 68.1 (Fc), 68.1 (Fc), 68.5 (C_5H_5), 72.0 (-CH-OH), 94.2 (Fc), 126.2 (2 × Ph), 127.4 (Ph), 128.2 (2× Ph), 143.2 ppm (Ph).

4-Bromophenyl(ferrocenyl)methanol (rac-*5)*: Yield: 67%;^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.47 (d, J = 2.9 Hz, 1H; -OH), 4.14–4.25 (m, 4H; Fc), 4.22 (s, 5H; C_5H_5), 5.40 (d, J = 2.9 Hz, 1H; -*CH*(OH)), 7.22–7.28 (m, 2H; Ph), 7.40–7.47 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 65.7 (Fc), 67.4 (Fc), 68.3 (Fc), 68.3 (Fc), 68.5 (C_5H_5), 71.3 (-CH-OH), 94.0 (Fc), 121.2 (Ph), 127.9 (2×Ph), 131.2 (2×Ph), 142.2 ppm (Ph).

(α-Ferrocenyl-2-bromobenzyloxy)trimethylsilane (rac-*1a)*: Yield: 86%; m.p. 58–60 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.09 (s, 9H; -$Si(CH_3)_3$), 4.03–4.09 (m, 2H; Fc), 4.13 (s, 5H; C_5H_5), 4.15–4.18 (m, 2H; Fc), 5.97 (s, 1H; -CH-OTMS), 7.04–7.12 (m, 1H; Ph), 7.26–7.32 (m, 1H; Ph), 7.48 (dd, J = 8.0, 1.2 Hz, 1H; Ph), 7.6 ppm (dd, J = 7.8, 1.8 Hz, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.20 (-$Si(CH_3)_3$), 66.1 (Fc), 67.0 (Fc), 67.1 (Fc), 67.7 (Fc), 68.7 (C_5H_5), 71.5 (-CH-OTMS), 93.3 (Fc), 121.6 (Ph), 127.5 (Ph), 128.6 (Ph), 129.2 (Ph), 132.1 (Ph), 144.4 ppm (Ph); IR (neat): $\tilde{\nu}$ = 818, 841, 878, 1019, 1080, 1117, 1250, 2899, 2960, 3053, 3101 cm^{-1}; elemental analysis calcd for $C_{20}H_{23}BrFeOSi$: C 54.2, H 5.23; found: C 54.06, H 5.25.

tert-*Butyl(α-ferrocenyl-2-bromobenzyloxy)dimethylsilane* (rac-*1b)*: Yield: 90%; m.p. 75–77 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = −0.18 (s, 3H; -$SiCH_3$), 0.16 (s, 3H; -$SiCH_3$), 0.96 (s, 9H; -$SiC(CH_3)_3$), 4.01–4.10 (m, 3H; Fc), 4.14 (s, 5H; C_5H_5), 4.11–4.16 (m, 1H; Fc), 5.98 (s, 1H; -CH-OTBDMS), 7.06–7.13 (m, 1H; Ph), 7.27–7.34 (m, 1H; Ph), 7.49 (dd, J = 8.0, 1.2 Hz, 1H; Ph), 7.60 ppm (dd, J = 7.8, 1.5 Hz, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.9 (-$SiCH_3$), −4.7 (-$SiCH_3$), 18.1 (-$SiC(CH_3)_3$), 25.8 (-$SiC(CH_3)_3$), 65.6 (Fc), 66.7 (Fc), 67.3 (Fc), 67.7 (Fc), 68.6 (C_5H_5), 71.4 [-CH(OTBDMS)], 93.6 (Fc), 121.6 (Ph), 127.4 (Ph), 128.6 (Ph), 129.2 (Ph), 132.0 (Ph), 144.4 ppm (Ph); IR (neat): $\tilde{\nu}$ = 810, 870, 1022, 1105, 1260, 1463, 1712, 2854, 2924, 2949, 3093 cm^{-1}; elemental analysis calcd for $C_{23}H_{29}BrFeOSi$: C 56.92, H 6.02; found: C 57.22, H 6.07.

(α-Ferrocenyl-2-bromobenzyloxy)triisopropylsilane (rac-*1c)*: Yield: 71%; m.p. 59–63 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.99 (d, J = 6.2 Hz, 9H; -$SiCH(CH_3)_2$), 1.01–1.07 (m, 12H; -$SiCH(CH_3)_2$), 3.94–4.00 (m, 1H; Fc), 4.01–4.06 (m, 1H; Fc), 4.04 (s, 5H; C_5H_5), 4.08–4.12 (m, 1H; Fc), 4.15–4.20 (m, 1H; Fc), 6.04 (s, 1H; -CH-OTIPS), 7.10–7.18 (m, 1H; Ph), 7.33–7.41 (m, 1H; Ph), 7.52 (dd, J = 8.0, 1.2 Hz, 1H; Ph), 7.77 ppm (dd, J = 7.8, 1.5 Hz, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 11.4, 16.9, 17.0, 65.0 (Fc), 65.7 (Fc), 66.4 (Fc), 67.4 (Fc), 67.6 (C_5H_5), 70.4(-CH-OTIPS), 92.8 (Fc), 121.0 (Ph), 126.2 (Ph), 127.6 (Ph), 128.4 (Ph), 130.9 (Ph), 143.8 ppm (Ph); IR (neat): $\tilde{\nu}$ = 812, 882, 1020, 1037, 1052, 1084, 1105, 1260, 1462, 2861, 2938, 3094 cm^{-1}; elemental analysis calcd for $C_{26}H_{35}BrFeOSi$: C 59.21, H 6.69; found: C 59.14, H 6.83.

tert-*Butyl(α-ferrocenyl-2-bromobenzyloxy)diphenylsilane* (rac-*1d)*: Yield: 30%; m.p. 102–106 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.05 (s, 9H; -$SiC(CH_3)_3$), 3.91–3.97 (m, 1H; Fc), 3.94 (s, 5H; C_5H_5), 3.98–4.02 (m, 2H; Fc), 4.06–4.02 (m, 1H; Fc), 6.05 (s, 1H; -CH-OTBDPS), 7.03–7.12 (m, 1H; Ph), 7.18–7.26 (m, 2H; Ph), 7.28–7.49 (m, 8H; Ph), 7.67–7.74 (m, 2H; Ph), 7.78 ppm (dd, J = 7.8, 1.6 Hz, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.4 (-$SiC(CH_3)_3$), 27.0 (-$SiC(CH_3)_3$), 66.2 (Fc), 66.9 (Fc), 67.8 (Fc), 68.7 (Fc), 68.9 (C_5H_5), 72.4 (-CH-OTBDPS),

93.1 (Fc), 122.1 (Ph), 127.2 (Ph), 127.4 (2 × Ph), 127.5 (2×Ph), 128.5 (Ph), 129.5 (2×Ph), 129.6 (Ph), 131.8 (Ph), 133.3 (Ph), 133.8 (Ph), 136.0 (2×Ph), 136.0 (2×Ph), 144.1 ppm (Ph); IR (neat): $\tilde{\nu}$ = 819, 1020, 1064, 1105, 1260, 1469, 2856, 2928, 2963, 3064 cm^{-1}; elemental analysis calcd for $C_{33}H_{33}BrFeOSi$: C 65.03, H 5.46; found: C 64.73, H 5.78.

(α-Ferrocenyl-4-bromobenzyloxy)trimethylsilane (rac-*6*): Yield: 70%; m.p. 84–85 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 9H; -Si(CH_3)$_3$), 3.86–3.90 (m 1H; Fc), 4.05–4.11 (m, 2H; Fc), 4.08 (s, 5H; C_5H_5) 4.12–4.16 (m, 1H; Fc), 5.50 (s, 1H; -CH-OTMS), 7.26–7.32 (m, 2H; Ph), 7.41–7.50 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.3 (-Si(CH_3)$_3$), 66.5 (Fc), 67.3 (Fc), 67.7 (Fc), 67.8 (Fc), 68.7 (C_5H_5), 72.9 (-CH-OTMS), 93.1 (Fc), 120.9 (Ph), 128.3 (2×Ph), 131.1 (2×Ph), 143.5 ppm (Ph); IR (neat): $\tilde{\nu}$ = 815, 839, 883, 1010, 1086, 1103, 1249, 1486, 2889, 2957, 3093 cm^{-1}; elemental analysis calcd for $C_{20}H_{23}BrFeOSi$: C 54.2, H 5.23; found: C 54.4, H 5.18.

*1-Ferrocenylethyloxytrimethylsilane [(*R*)-7a]*:[30] Yield: 86%; $[\alpha]_D^{20}$ = −10.6 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.13 (s, 9H; -Si(CH_3)$_3$), 1.50 (d, *J* = 6.4 Hz, 3H; -CH*C*H_3), 4.08–4.17 (m, 3H; Fc), 4.14 (s, 5H; C_5H_5), 4.18–4.22 (m, 1H; Fc), 4.72 ppm (q, *J* = 6.4 Hz, 1H; -CH-OTMS); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.5 (-Si(CH_3)$_3$), 23.9 (-CHCH_3), 65.7(Fc), 66.5 (-CH-OTMS), 67.5 (2×Fc), 67.8 (Fc), 68.5 (C_5H_5), 93.1 ppm (Fc).

α-Ferrocenylbenzyloxytrimethylsilane (rac-*7b*): Yield: 82%; m.p. 58–59 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.06 (s, 9H; -Si(CH_3)$_3$), 3.90–3.94 (m, 1H; Fc), 4.03–4.10 (m, 2H; Fc), 4.07 (s, 5H; C_5H_5), 4.17–4.20 (m, 1H; Fc), 5.54 (s, 1H; -CH-OTMS), 7.20–7.28 (m, 1H; Ph), 7.28–7.36 (m, 2H; Ph), 7.37–7.44 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ 0.3 (-Si(CH_3)$_3$), 66.7 (Fc), 67.4 (Fc), 67.5 (Fc), 67.7 (Fc), 68.6 (C_5H_5), 73.5 (-CH-OTMS), 93.6 (Fc), 126.6 (2×Ph), 127.1 (Ph), 127.9 (2×Ph), 144.4 ppm (Ph);IR (neat): $\tilde{\nu}$ = 813, 838, 883, 1069, 1102, 1248, 2886, 2955, 3081 cm^{-1}; elemental analysis calcd for $C_{20}H_{24}FeOSi$: C 65.93, H 6.64; found: C 65.77, H 6.63.

Ferrocenyl(2-(trimethylsilyl)phenyl)methanol (rac-*2a*): Yield: 79%; m.p. 97–101 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.37 (s, 9H; -Si(CH_3)$_3$), 2.40 (d, *J* = 3.7 Hz, 1H; -OH), 4.14–4.22 (m, 4H; Fc), 4.26 (s, 5H; C_5H_5), 5.73 (d, *J* = 3.7 Hz, 1H; -C*H*(OH)), 7.20–7.28 (m, 1H; Ph), 7.30–7.38 (m, 1H; Ph), 7.43–7.52 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 0.9 (-Si(CH_3)$_3$), 67.0 (Fc), 67.3 (Fc), 67.4 (Fc), 68.6 (C_5H_5), 71.1 (-CH(OH)), 94.5 (Fc), 126.7 (Ph), 127.0 (Ph), 129.4 (Ph), 134.3 (Ph), 137.9 (Ph), 148.7 ppm (Ph); IR (neat): $\tilde{\nu}$ = 836, 999, 1122, 1250, 2926, 2958, 3045, 3089, 3534, 3585 cm^{-1}; elemental analysis calcd for $C_{20}H_{24}FeOSi$: C 65.93, H 6.64; found: C 65.72, H 6.65.

*2-(*tert*-Butyldimethylsilyl)phenyl(ferrocenyl)methanol* (rac-*2b*): Yield: 68%; m.p. 122–124 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.32 (s, 3H; -SiCH_3), 0.43 (s, 3H; -SiCH_3), 0.94 (s, 9H; -SiC(CH_3)$_3$), 2.35 (d, *J* = 4.0 Hz, 1H; -OH), 4.14–4.22 (m, 4H; Fc), 4.24 (s, 5H; C_5H_5), 5.70 (d, *J* = 4.0 Hz, 1H; -C*H*-OH), 7.19–7.26 (m, 1H; Ph), 7.29–7.37 (m, 1H; Ph), 7.44–7.52 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.0 (-SiCH_3), −2.3 (-SiCH_3), 17.6 (-Si*C*(CH_3)$_3$), 27.0 (-SiC(*C*H_3)$_3$), 66.8 (Fc), 67.2 (Fc), 67.5 (Fc), 68.5 (*C*$_5$H$_5$), 68.6 (Fc), 71.5 (-CH(OH)), 94.6 (Fc), 126.6 (Ph), 126.9 (Ph), 129.2 (Ph), 135.4 (Ph), 135.9 (Ph), 149.2 ppm (Ph); IR (neat): $\tilde{\nu}$ = 820, 1005, 1294, 1359, 2853, 2922, 2947, 3550 cm^{-1}; elemental analysis calcd for $C_{23}H_{30}FeOSi$: C 67.97, H 7.44; found: C 67.99, H 7.53.

Ferrocenyl(2-triisopropylsilylphenyl)methanol (rac-*2c*): Yield: 53%; m.p. 74–78 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.11 (d, *J* = 7.5 Hz, 9H; 3×-SiCHCH_3), 1.17 (d, *J* = 7.5 Hz, 9H; 3×-SiCHCH_3), 1.49 (sp, *J* = 7.5, 3H; 3×-C*H*(CH_3)$_2$), 2.40 (d, *J* = 4.1, 1H; -OH), 4.14–4.20 (m, 3H; Fc), 4.21–4.25 (m, 1H; Fc), 4.27 (s, 5H; C_5H_5), 5.57 (d, *J* = 4.1 Hz, 1H; -C*H*(OH)), 7.19–7.28 (m, 1H; Ph), 7.29–7.38 (m, 1H; Ph), 7.52 (dd, *J* = 7.5, 1.2 Hz, 1H; Ph), 7.58 ppm (dd, *J* = 7.8, 1.1 Hz, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.1, 19.2, 19.3, 66. 9 (Fc), 67.2 (Fc), 67.8 (Fc), 68.5 (C_5H_5), 68.6 (Fc), 71.2 (-CH(OH)), 94.9 (Fc), 126.8 (Ph), 127.6 (Ph), 129.0 (Ph), 134.2 (Ph), 136.1 (Ph), 149.5 ppm (Ph); IR (neat): $\tilde{\nu}$ = 803, 881, 1011, 1104, 1260, 1462, 2864, 2947, 3553 cm^{-1}; elemental analysis calcd for $C_{26}H_{36}FeOSi$: C 69.63, H 8.09; found: C 69.58, H 8.17.

*2-(*tert*-Butyldiphenylsilyl)phenyl(ferrocenyl)methanol* (rac-*2d*): Yield: 62%; m.p. 50–58 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.19 (s, 9H; -SiC(CH_3)$_3$), 1.25 (d, *J* = 3.2 Hz, 1H; -OH), 3.19–3.25 (m, 1H; Fc), 3.80 (s, 5H; C_5H_5), 3.83–3.88 (m, 1H; Fc), 3.95–4.00 (m, 1H; Fc), 4.25–4.30 (m, 1H; Fc), 5.41 (d, *J* = 3.2 Hz, 1H; -C*H*-OH), 7.51–7.27 (m, 9H; Ph), 7.71–7.77 (m, 2H; Ph), 7.78–7.84 (m, 2H; Ph), 7.92–7.99 ppm (m, 1H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.8 (-Si*C*(CH_3)$_3$), 28.3 (-SiC(CH_3)$_3$), 66.3 (Fc), 66.5 (Fc), 66.6 (Fc), 67.9 (Fc), 68.5 (C_5H_5), 71.0 (-CH(OH)), 92.2 (Fc), 126.4 (Ph), 127.9 (Ph), 128.1 (Ph), 129.1 (Ph), 129.4 (Ph), 129.7 (Ph), 130.4 (Ph), 132.7 (Ph), 135.6 (Ph), 135.8 (Ph), 136.2 (Ph), 136.5 (Ph), 151.3 ppm (Ph); IR (neat): $\tilde{\nu}$ = 817, 1007, 1103, 1427, 1588, 2857, 2927, 3069, 3564 cm^{-1}; elemental analysis calcd for $C_{33}H_{34}BrFeOSi$: C 74.71, H 6.46; found: C 74.8, H 6.77.

Phenyl(2-trimethylsilylferrocenyl)methanol (rac-*8b*):[31] Yield: 9%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.34 (s, 9H; -Si(CH_3)$_3$), 1.97 (d, 1H; *J* = 3.8 Hz, 1H; -CH-O*H*), 3.92–3.95 (m, 1H; Fc), 4.03 (s, 5H; C_5H_5), 4.13–4.16 (m, 1H; Fc), 4.24–4.27 (m, 1H; Fc), 5.69 (d, *J* = 3.8 Hz, 1H; -C*H*-OH), 7.28–7.36 (m, 1H; Ph), 7.36–7.44 (m, 2H; Ph), 7.46–7.52 ppm (m, 2H; Ph).

*1-Ferrocenylethyloxy(tert-butyl)dimethylsilane [(*R*)-9a]*: Yield: 68%; $[\alpha]_D^{20}$ = +15.6 (*c* = 0.50, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.07 (s, 3H; -SiCH_3), 0.09 (s, 3H; -SiCH_3), 0.93 (s, 9H; -SiC(CH_3)$_3$), 1.46 (d, *J* = 6.3 Hz, 3H; -CHCH_3), 4.05–4.08 (m, 1H; Fc), 4.09–4.12 (m, 2H; Fc), 4.14–4.18 (m, 1H; Fc), 4.15 (m, 6H; Fc, C_5H_5), 4.67 ppm (q, *J* = 6.3 Hz, 1H; -C*H*CH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = −4.6 (-SiCH_3), −4.2 (-SiCH_3), 18.1 (-Si*C*(CH_3)$_3$), 24.1 (-CH*C*H$_3$), 25.9 (-SiC(*C*H_3)$_3$), 65.7, 66.1, 67.2, 67.3, 67.4, 68.5 (C_5H_5), 94.3 ppm (Fc); HRMS calcd for $C_{18}H_{28}FeOSi$: 367.115652 [*M*+Na]$^+$; found: 367.11473.

1-Ferrocenylethyloxy(tert-butyl)diphenylsilane (rac-*9b*): Yield: 98%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (s, 9H; -SiC(CH_3)$_3$), 1.40 (d, *J* = 6.3 Hz, 3H; -CHCH_3), 3.87–3.93 (m, 1H; Fc), 3.98–4.03 (m, 1H; Fc), 4.06–4.11 (m, 1H; Fc), 4.08 (s, 5H; C_5H_5), 4.21–4.25 (m, 1H; Fc), 4.71 (q, *J* = 6.3 Hz, 1H; -C*H*CH$_3$), 7.30–7.48 (m, 6H; Ph), 7.62–7.69 (m, 2H; Ph), 7.69–7.76 ppm (m, 2H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.3 (-Si*C*(CH_3)$_3$), 23.8 (-CHCH_3), 27.1 (-SiC(*C*H_3)$_3$), 65.6, 67.2, 67.4, 67.5, 67.8, 68.5 (C_5H_5), 93.6 (Fc), 127.4 (Ph), 129.5 (Ph), 134.1 (Ph), 134.7 (Ph), 136.0 ppm (Ph); HRMS calcd for $C_{28}H_{32}FeOSi$: 468.157182 [*M*]$^+$; found: 468.15648.

Lithiation and retro-Brook rearrangement to the *ortho* position of the ferrocenyl Cp ring: *n*BuLi (1.6 M solution in hexane, 4.0 equiv) was added dropwise to a solution of 1-ferrocenylethoxysilane (1.0 equiv) and *t*BuOK (4.0 equiv) in anhydrous THF (6 mL per mmol of substrate) at −65 °C. The mixture was stirred at −65 °C for 24 h. A saturated aqueous solution of NH_4Cl (2 mL) was added and the mixture was stirred until the temperature increased to RT. The layers were separated and the aqueous part was extracted with Et_2O (3×5 mL). The combined organic parts were dried over Na_2SO_4 and evaporated. The products were isolated by column chromatography (SiO_2, hexane/EtOAc 8:1 + 1% Et_3N).

*1-(2-Trimethylsilylferrocenyl)ethanol [(*R,R$_p$*)-8a]*: Yield: 35% and 8% of the desilylated alcohol **3a**; $[\alpha]_D^{20}$ = −44.7 (*c* = 0.83, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.27 (s, 9H; -Si(CH_3)$_3$), 1.32 (d, *J* = 6.3 Hz, 3H; -CHCH_3), 2.06 (s, 1H; -OH), 4.08–4.12 (dd, *J* = 2.3, 1.3 Hz, 1H; Fc), 4.20 (s, 5H; C_5H_5), 4.29–4.33 (m, 1H; Fc), 4.44–4.49 (m, 1H; Fc), 4.58 ppm [dq, *J* = 6.3, 1.2 Hz, 1H; -C*H*(OH)]; ^{13}C NMR (75 MHz,

$CDCl_3$): $\delta = 1.0$ (-Si(CH_3)$_3$), 25.0 ($CHCH_3$), 65.4 (-*C*H-OH), 67.2 (Fc), 68.3 (C_5H_5), 70.0 (Fc), 70.5 (C^{Fc}-Si), 74.0 (Fc), 101.4 ppm (Fc); HRMS calcd for $C_{15}H_{22}FeOSi$: 302.078932 $[M]^+$; found: 302.07789.

N,N-*Dimethyl-1-(2-trimethylsilylferrocenyl)ethan-1-amine [(*R,R$_p$*)-12]*: Acetylchloride (0.22 mmol, 5.0 equiv) was added to a solution of compound (*R*,*R*$_p$)-**8a** (0.044 mmol, 1.0 equiv) and pyridine (0.27 mmol, 6.0 equiv) in dry dichloromethane (1 mL) and the mixture was stirred at RT for 15 h. The volatile parts were evaporated under reduced pressure and the rest was dissolved in CH_3CN (1 mL). An aqueous solution of $HNMe_2$ (40%, 2.2 mmol, 50 equiv) was added and the mixture was stirred at 38 °C for three days. The mixture was diluted with water (5 mL) and extracted with Et_2O (3× 5 mL), dried over Na_2SO_4 and evaporated under vacuum. The product was separated by column chromatography (SiO_2, hexane/EtOAc 3:1 + 1% Et_3N). Yield: 92%; $[\alpha]_D^{20} = +46.0$ (*c* = 1.32, $CHCl_3$); +45.0 (*c* = 1.0, EtOH); lit.:[26] +42.2 (*c* = 0.6, EtOH). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.29$ (s, 9H; -Si(CH_3)$_3$), 1.18 (d, *J* = 6.9 Hz, 3H; -CHC*H*$_3$), 2.36 (s, 6H; -N(CH_3)$_2$), 3.34 (q, *J* = 6.9 Hz, 3H; -C*H*-OH), 4.00–4.03 (m, 1H; Fc), 4.12 (s, 5H; C_5H_5), 4.26–4.28 (m, 1H; Fc), 4.32–4.34 ppm (m, 1H; Fc); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 1.0$ (-Si(CH_3)$_3$), 18.5 ($CHCH_3$), 43.0 (-N(CH_3)$_2$), 59.2 (-CH(OH)), 65.9 (Fc), 68.9 (Fc), 69.1 (C_5H_5), 70.8 (Fc), 73.5 (Fc), 99.8 ppm (Fc); HRMS calcd for $C_{15}H_{22}FeOSi$: 285.076192 $[M-N(CH_3)_2]^+$; found: 285.07527.

N,N-*Dimethyl-1-(2-trimethylsilylferrocenyl)ethan-1-amine [(*R,S$_p$*)-12]*: ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.24$ (s, -Si(CH_3)$_3$), 1.21 (d, *J* = 6.8 Hz, 3H; -CHC*H*$_3$), 2.03 (s, 6H; -N(CH_3)$_2$), 3.80 (q, *J* = 6.8 Hz, 1H; -C*H*CH_3), 4.04–4.05 (m, 1H; Fc), 4.06 (s, 5H; C_5H_5), 4.22–4.24 (m, 1H; Fc), 4.26–4.28 ppm (m, 1H; Fc); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = 0.2$ (-Si(CH_3)$_3$), 9.4 (-CHCH_3), 39.6 (-N(CH_3)$_2$), 58.0 (-*C*HCH_3), 68.6 (Fc), 68.9 (C_5H_5), 70.0 (Fc), 72.1 (Fc), 74.6 (Fc), 96.6 ppm (Fc); $[\alpha]_D^{20} = +13.9$ (*c* = 1.46, dichloromethane); +17.3 (*c* = 1.7, EtOH); lit.:[26] +15.5 (*c* = 1.5, EtOH).

1-(2-tert-Butyldimethylsilylferrocenyl)ethanol (10a): Yield: 12% mixture of diastereoisomers (*R*,*R*$_p$)-**10a** and (*R*,*S*$_p$)-**10a** 2:1.

Major isomer (*R*,*R*$_p$)-10a: $[\alpha]_D^{20} = -11.2$ (*c* = 1.13, $CHCl_3$). ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.28$ (s, 3H; -SiCH_3), 0.36 (s, 3H; -SiCH_3), 0.83 (s, 9H; -SiC(CH_3)$_3$), 1.33 (d, *J* = 6.3 Hz, 3H; -CHC*H*$_3$), 2.18 (br s, 1H; -OH), 4.07–4.10 (m, 1H; Fc), 4.20 (s, 5H; C_5H_5), 4.36–4.38 (m, 1H; Fc), 4.47 (dq, *J* = 6.3, 1.2 Hz, -C*H*-OH), 4.49–4.51 ppm (m, 1H; Fc); ^{13}C NMR (151 MHz, $CDCl_3$): $\delta = -3.9$ (2×SiCH_3), 17.6 (-Si*C*(CH_3)$_3$), 24.6 ($CHCH_3$), 26.8 (-SiC(CH_3)$_3$), 64.5 (-CH(OH)), 67.3 (Fc), 68.5 (C_5H_5), 68.9 (Fc), 70.6 (Fc), 74.7 (Fc), 103.1 ppm (Fc); HRMS calcd for $C_{18}H_{28}FeOSi$: 344.125882 $[M]^+$; found: 344.12516.

Minor isomer (*R*,*S*$_p$)-10a: $[\alpha]_D^{20} = -10.5$ (*c* = 0.16, $CHCl_3$); ^{1}H NMR (600 MHz, $CDCl_3$): $\delta = 0.29$ (s, 3H; -SiCH_3), 0.41 (s, 3H; -SiCH_3), 0.87 (s, 9H; -SiC(CH_3)$_3$), 1.60 (d, *J* = 6.3 Hz, 3H; -CHC*H*$_3$), 4.05–4.08 (m, 1H; Fc), 4.10 (s, 5H; C_5H_5), 4.35–4.38 (m, 1H; Fc), 4.46–4.49 (m, 1H; Fc), 4.71 ppm (dq, *J* = 6.3, 4.7 Hz, 1H; -C*H*-OH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -4.1$ (-SiCH_3), −3.6 (-SiCH_3), 17.6 (-Si*C*(CH_3)$_3$), 23.3 (-CHCH_3), 27.1 (-SiC(CH_3)$_3$), 66.2 (-*C*HCH_3), 68.5 (Fc), 68.6 (Fc), 69.2 (C_5H_5), 70.7 (Fc), 75.7 (Fc), 96.9 ppm (Fc); HRMS calcd for $C_{18}H_{28}FeOSi$: 344.125882 $[M]^+$; found: 344.12506.

*1-(1′-*tert*-Butyldimethylsilylferrocenyl)ethanol (R)-11a*: Yield: 4%; $[\alpha]_D^{20} = -10.0$ (*c* = 0.71, $CHCl_3$). ^{1}H NMR (300 MHz, [D$_6$]acetone): $\delta =$ 0.29 (s, 6H; -Si(CH_3)$_2$), 0.80 (s, 9H; -SiC(CH_3)$_3$), 1.40 (d, *J* = 6.7 Hz, 3H; -CHC*H*$_3$), 3.51 (d, *J* = 5.0 Hz, 1H; -OH), 4.05–4.13 (m, 4H; Fc), 4.16–4.19 (m, 1H; Fc), 4.19–4.23 (m, 1H; Fc), 4.35–4.41 (m, 2H; Fc), 4.62 ppm (dq, *J* = 6.7, 5.0 Hz, 1H; -CHC*H*$_3$); ^{13}C NMR (75 MHz, [D$_6$]acetone): $\delta = -5.4$ (-Si(CH_3)$_2$), 17.6 (-Si*C*(CH_3)$_3$), 24.5 (-CHCH_3), 26.8 (-SiC(CH_3)$_3$), 65.8, 66.5, 67.7, 68.5, 68.6, 69.9, 72.3, 72.4, 74.7, 74.8, 95.4 ppm (Fc); HRMS calcd for $C_{18}H_{28}FeOSi$: 344.125882 $[M]^+$; found: 344.12481.

1-(1′-tert-Butyldiphenylsilylferrocenyl)ethanol (rac-*11b*): Yield: 28%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.07$ (s, 9H; -SiC(CH_3)$_3$), 1.28 (d, *J* = 6.4 Hz, 3H; -CHC*H*$_3$), 3.80–3.88 (m, 2H; Fc), 3.93–3.97 (m, 1H; Fc), 3.98–4.03 (m, 1H; Fc), 4.14–4.19 (m, 2H; Fc), 4.26 (q, *J* = 6.4 Hz, 1H; -C*H*CH_3), 4.37–4.44 (m, 2H; Fc), 7.35–7.49 (m, 6H; Ph), 7.70–7.80 ppm (m, 4H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 18.7$ (-Si*C*(CH_3)$_3$), 23.7 (-CHCH_3), 28.2 (-SiC(CH_3)$_3$), 65.5, 66.1, 66.4, 67.5, 68.3, 69.0, 69.0, 71.2, 75.4, 75.7, 94.5, 127.4 (Ph), 129.1 (Ph),135.5 (Ph), 136.4 ppm (Ph): HRMS calcd for $C_{28}H_{32}FeOSi$: 468.157182 $[M]^+$; found: 468.15619.

Computational details

The molecules were drawn in Spartan[32] and firstly optimized by the semi-empirical method PM3.[33] The prepared molecules were later optimized at the RI-DFT level[34] by using the BP-86 functional[35] in the Turbomole package.[36] The def-SVP basis set[37] was used for pre-optimization and then the def-TZVP basis set[38] was used for optimization of the structures. Transition states were calculated by using the PES (potential energy scan) by prolonging of the C_{Ar}–Si bond of the product (from 2.1993 to 3.0962 Å) at the RI-DFT level by using the BP-86 functional and the def-SVP base. The vibration spectra of all resulted conformers were calculated. The conformer with the highest imaginary frequency was then used for searching of the transition states following the imaginary frequencies by using def-TZVP basis set. The resulted transition states were confirmed by one negative imaginary vibration (C_{Ar}–Si vibration). The energy of the molecules and transition states were calculated on the RI-SCS-MP2 level[39] (C(OS) = 1.20 and C(SS) = 0.3333) by using the def2-TZVP basis set[38] in the Turbomole package.

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