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Synthesis and reactivity of achiral and of a novel planar chiral thioferrocenoylsilanes

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Abstract

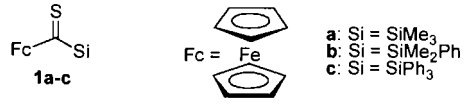
The reactions of thioferrocenoylsilanes with organolithium reagents, dienes and reducing agents which afford α-silyl sulphides, dihydrothiopyranes and α-silyl ferrocenyl thiols, respectively, have been investigated. α-Silyl sulphides were further functionalised through carbodesilylation with aldehydes. We also report the synthesis of a new planar chiral thioferrocenoylsilane that gave good diastereomeric excess in the reaction with *t*-butyllithium, lithium lutidine and 2,3-dimethylbuta-1,3-diene. The 1,1′-bis-thioferrocenoylsilane, too unstable to be isolated, was trapped in situ with dienes.

Keywords: Ferrocene; Planar chirality; Thioacylsilanes; Thiophilic addition; Diels–Alder reaction; β-Hydroxy sulphides; β-Amino sulphides

1. Introduction

Since the discovery of ferrocene in 1951 [1], its chemistry has been investigated intensively [2]. In particular the use of ferrocenyl ligands in organic catalysis still continues to grow. Among these ligands the 1,1′-bis-derivatives [2] such as 1,1′-bis(diphenylphosphino)-ferrocene (dppf) and a large variety of enantiopure 1,2-disubstituted ferrocenes with planar chirality have received considerable attention [3]. Several efficient syntheses of 1,2-disubstituted ferrocenes with planar chirality are based on the diastereoselective *ortho*-lithiation of ferrocenyl derivatives containing a chiral *ortho*-directing group such as a tertiary amine [4], an acetal [5], a sulphoxide [6] or an oxazoline [7,3c]. More recently enantioselective *ortho*-lithiation of monosubstituted ferrocenes in the presence of a tertiary chiral amine has been reported for the synthesis of enantiomerically enriched 1,2-disubstituted ferrocenes [8]. Sulphur-containing compounds such as hydroxy and amino sulphides [9], pyridine thiols [10a,b] and thioethers [10c], amino thiols [11] and imine sulphides [12] have found application as ligands in asymmetric synthesis. In connection with our ongoing interest in the chemistry of thioacylsilanes [13], a class of versatile compounds characterised by a remarkably high reactivity of the carbon–sulphur double bond, we developed the synthesis of new thioferrocenoylsilanes **1a**–**1c** [14] (Scheme 1) starting from the corresponding acylsilanes through an easy thionation with Lawesson's reagent (LR) in THF at room temperature. Compounds **1a**–**1c**, as other thioacylsilanes [13], showed a remarkable high reactivity in Diels–Alder and 1,3-dipolar cycloaddition reactions which allowed the synthesis of compounds containing the ferrocenyl substituted carbon–sulphur–silicon moiety [14].

In this paper we describe further studies on the reactivity of compounds **1a**–**1c** as well as the synthesis and the reactivity of 1,1′-disubstituted bis-thioferrocenoylsilane and of a planar chiral thioferrocenoylsilane with high potential as starting materials for the synthesis of ligands containing sulphur and the ferrocene moiety.



Scheme 1.

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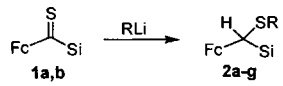
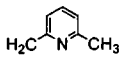
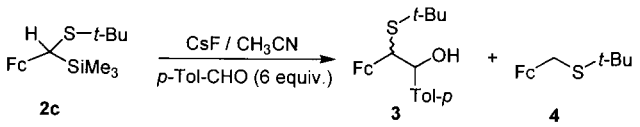
Table 1
Reaction of thioferrocenoylsilanes **1a** and **1b** with organolithium reagents



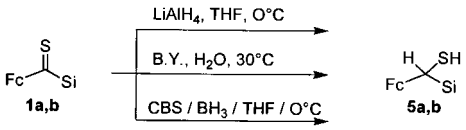
1a,b **2a-g**

Entry	Si	R	2	Yield (%)
1	$SiMe_3$	Me	**a**	41
2	$SiMe_3$	*n*-Bu	**b**	80
3	$SiMe_3$	*t*-Bu	**c**	43
4	$SiMe_3$		**d**	81
5	$SiMe_2Ph$	Me	**e**	62
6	$SiMe_2Ph$	*n*-Bu	**f**	66
7	$SiMe_2Ph$	*t*-Bu	**g**	78



2c **3** **4**

Scheme 2.



1a,b **5a,b**

Reducing agent	Si	5	Yield (%)
$LiAlH_4$	$SiMe_3$	**a**	75
$LiAlH_4$	$SiMe_2Ph$	**b**	96
B.Y.	$SiMe_3$	**a**	25
Me-CBS	$SiMe_3$	**a**	47
Me-CBS	$SiMe_2Ph$	**b**	39

Scheme 3.

2. Results and discussion

2.1. Reaction of thioferrocenoylsilanes with organolithium reagents

It is well known that thiocarbonyl compounds can undergo addition with organometallic reagents (organolithium and Grignard reagents) in high regioselective either thiophilic [15] or carbophilic [16] manner under appropriate experimental conditions. Thioacylsilanes react with organolithium reagents only at the sulphur probably because of the stabilising effect of the silyl group on the intermediate α-silyl carbanion [13]. In agreement with this behaviour thioferrocenoylsilanes **1a** and **1b** react with organolithium reagents affording α-silyl sulphides **2a**–**2g** in moderate to very good yields (Table 1).

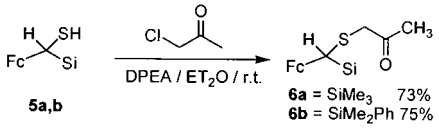
Products **2a**–**2g** exhibit a moderate stability on silica and were purified by chromatography on deactivated neutral alumina. The β-amino sulphide **2d** was obtained by reaction of **1a** with the monolithium derivative of 2,6-lutidine. It is worth to note that the same lithium derivative gave only products deriving from the carbophilic addition to other non-enethiolisable thioketones like thioadamantanone [10a] and thiofenchone [10b], the final products of these reactions being pyridine thiols.

Compound **2c** was subjected to further synthetic transformations by performing a fluorodesilylation reaction with anhydrous cesium fluoride in the presence of a carbon electrophile such as *p*-tolualdehyde. The reaction led to a diastereomeric mixture of β-hydroxy sulphides **3** in an overall yield of 52% beside a 30% yield of *tert*-butyl ferrocenylmethyl sulphide **4** (Scheme 2) arising from a competitive protiodesilylation of **2c**.

A very low d.e. value (10%) was determined by integration of the signals in the ^{1}H-NMR spectrum of the CH–OH of the major (at $\delta = 5.01$) and of the minor isomer (at $\delta = 5.18$). An higher d.e. value (42%) was obtained, though with a lower yield of the diastereoisomers **3** (30%) with a shorter reaction time (see Section 4). The relative stereochemistry of the two chiral centres has not been assigned.

2.2. Reduction of thioferrocenoylsilanes

Thiols have been applied largely as nucleophiles in the conjugated addition [17] as well as in the asymmetric version of this reaction [18]. Furthermore the ring opening reaction of aziridines and epoxides [9] by thiols has also found application in recent years. The reduction of thioketones to thiols is a procedure known since many years [19], however, only recently asymmetric versions of this reaction have been reported [20]. The reduction of **1a** and **1b** (Scheme 3) was performed with a 1 M solution of $LiAlH_4$ in THF at -30 °C. After the usual work up, the thiols **5a** and **5b** were obtained in 75 and 96% yields, respectively, and were characterised fully. An asymmetric version of this reaction was attempted both with baker's yeast (BY) and with the CBS method [21]. The reaction with BY was performed on the thione **1a** in water at 30 °C. Due to the long reaction time (3 days) necessary for the disappearance of the blue colour of the thione, an extensive decomposition occurred and the thiol **5b** was isolated after chromatography in 25% yield. Following the CBS procedure at 0 °C the reactions of thiones **1a** and **1b** were completed in 40 min and the thiols **5a** and **5b** were obtained in 47 and 39% yield, respectively, after chromatography on deactivated neutral alumina. Any attempt to measure the optical rotation of both the thiols **5a** and **5b** failed, because of the very intense yellow colour of the solution. Furthermore the evaluation of



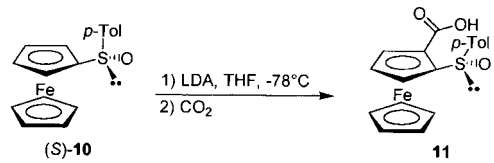
Scheme 4.

the enantiomeric excess performing the ^{1}H-NMR spectrum in the presence of Pirkle's alcohol ($S(+)$-1(antryl)-2,2,2-trifluoroethanol) was unsuccessful, since, we did not observe any splitting of signals on the racemic derivatives.

With the aim of determining the enantiomeric excess obtained during the reduction of thioacylsilanes **1a** and **1b**, we tried different derivatisations of **5a** and **5b**. Any attempt of trapping **5** with MeI and any ring opening reactions with epoxides or aziridines failed and the starting thiols were recovered, whereas the reaction with chloroacetone in dry ether in the presence of one equivalent of DPEA (diisopropylethylamine) gave the adducts **6a** and **6b** in 73 and 75% yield, respectively (Scheme 4). These products resulted rather unstable and partially decomposed during the acquisition time for the ^{13}C-NMR spectrum.

2.3. 1,1′-Bisferrocenylthioacylsilane

The 1,1′-bisferrocenylthioacylsilane (**7**) was prepared by thionation with LR at room temperature of the corresponding acylsilane **8** [22], which in turn was obtained by nucleophilic silylation with bis(dimethylphenylsilyl)lithium cyanocuprate of the corresponding ferrocenoyldichloride [22]. All the attempts to isolate the blue bis-thione **7** by chromatography failed. The blue colour of the reaction mixture disappeared on standing and a new compound was found, among other unidentified products, probably arising from an intramolecular reaction between the two thiocarbonylic functions. In fact, a peak at $m/z = 544$ corresponding to the molecular ion of the thione plus two hydrogens was detected in the mass spectrum. For this reason **7** was trapped in situ with 2,3-dimethylbuta-1,3-diene. The bis-adduct **9** was isolated in 60% yield and was characterised fully (Scheme 5).



Scheme 6.

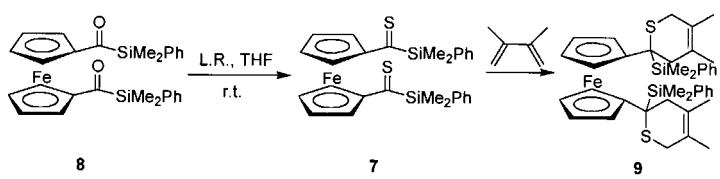
2.4. Synthesis and reactivity of a planar chiral thioferrocenoylsilane

For the synthesis of a suitable precursor for the preparation of the first planar chiral thioferrocenoylsilane we adopted the strategy reported by Kagan based on the diastereoselective *ortho*-lithiation of (*S*)-ferrocenyl *p*-tolylsulphoxide (**10**) ($[\alpha]_D = 310°$ ($c = 0.57$, $CHCl_3$), lit: $[\alpha]_D = 314°$ ($c = 0.5$)) with LDA at -78 °C [6,23]. By electrophilic quenching with CO_2, the carboxylic acid **11** was isolated as a single enantiomer in good yield (75%) and excellent diastereoselectivity (d.e. > 98%), calculated by ^{1}H-NMR (Scheme 6). The enantiomerical purity has been established by comparison of the ^{1}H-NMR spectrum of the optically active and of the racemic acid **11** (obtained with the same procedure starting from the racemic sulphoxide **10**) in the presence of Pirkle's alcohol (see Section 4).

The relative stereochemistry has been assigned (S_{Fc} and S_S) according to Kagan's results [23] obtained by quenching the lithiated sulphoxide **10** with a wide range of electrophilic reagents.

Since the conversion of product **11** into the corresponding chloride failed, **11** was deoxygenated to the sulphide **12** by reaction with Lawesson's reagent at room temperature in 50% yield (Scheme 7). This method [24] was found to be the best one among the others we tested for the reduction of **11**: SmI_2 [25] gave complete decomposition; triethylphosphite/iodine/NaI [26] gave a lower yield of **12** (12%) and the reduction with a HCl (g) saturated solution of acetonitrile [27], left **11** unreacted.

The sulphide **12** ($[\alpha]_D = -31.4°$ ($c = 0.49$, $CHCl_3$)) was found to be enantiomerically pure (e.e. > 98% within the experimental error) by comparison of its ^{1}H-NMR spectrum, in the presence of Pirkle's alcohol, with the spectrum of the same sulphide obtained starting from the sulphoxide **10** having an enantiomeric excess of only 88% ($[\alpha]_D = 280°$ ($c = 0.5$, $CHCl_3$) (see



Scheme 5.

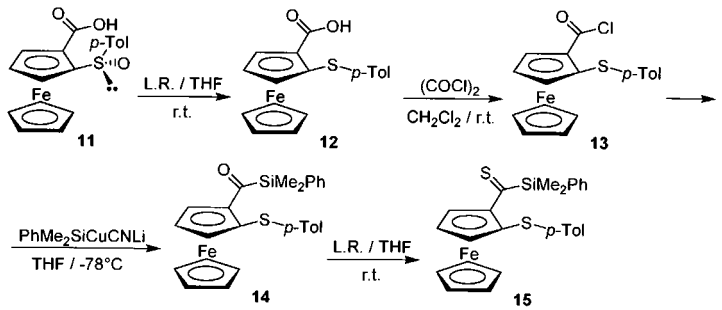
Section 4). The ^{1}H-NMR spectrum of this sulphide, in the presence of Pirkle's alcohol, showed two peaks in a 7:93 ratio at 4.34 and 4.31 ppm, respectively, the ^{1}H-NMR spectrum of the enantiomerically pure **12** showed only the signal at 4.31 ppm. Moreover the racemic sulphide **12**, obtained starting from the racemic sulphoxide **10**, gave, in the presence of Pirkle's alcohol, the two peaks in a 1:1 ratio.

Sulphide **12** was converted into the corresponding chloride **13** in quantitative yield by reaction with oxalylchloride and then into the acylsilane **14** ($[\alpha]_D = -683°$ ($c = 0.2$, $CHCl_3$) in 58% yield and e.e. > 98% by nucleophilic silylation at −78 °C with dimethylphenylsilyl lithiumcyanocuprate. Reaction of **14** with LR in THF at room temperature gave the thione **15** (Scheme 7) in 94% yield after purification by chromatography on fluorisil. The thioacylsilane **15** was characterised fully and was found to be enantiomerically pure (e.e. > 98%) but it was not possible to measure its optical rotation because of the very intense blue colour of the solution. The enantiomerical purity of compounds **14** and **15** was determined by comparison of their ^{1}H-NMR spectra with those of the corresponding compounds obtained starting from the sulphoxide **10** with e.e. = 88% in the presence of Pirkle's alcohol.

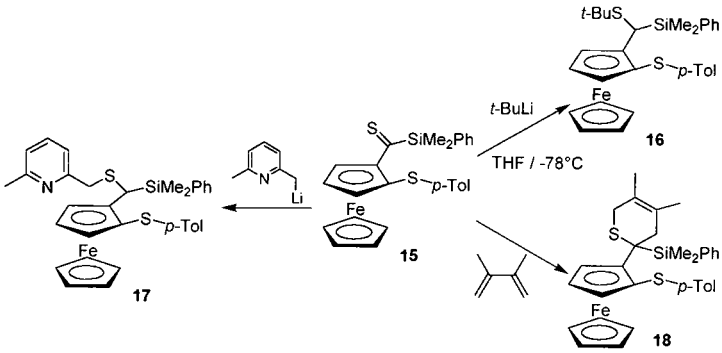
The thione **15** reacted with *t*-BuLi at −78 °C in few minutes and afforded the α-silyl sulphides **16** (Scheme 8) in 68% yield with a d.e. equal to 77% calculated from the ^{1}H-NMR of the crude reaction mixture. The major diastereoisomer of **16** could be separated by chromatography on preparative TLC and characterised fully. The reaction with the monolithium derivative of 2,6-lutidine yielded the β-ammino sulphides **17** in 53% yield with a d.e. equal to 50% (Scheme 8). The reaction of **15** with 2,3-dimethyl-buta-1,3-diene at room temperature took place in a very short reaction time and afforded two diastereomeric cycloadducts **18** in a 3.5:1 ratio (d.e. = 56%) and in 78% yield. The two diastereoisomers could be separated by chromatography and were characterised fully. The same reaction was repeated at −20 °C giving the two isomers in a 4.9:1 ratio (d.e. = 76%).

3. Conclusions

A new planar enantiomerically pure chiral thioferrocenoylsilane has been synthesised in good yield and its reactivity investigated. Dihydrothiopyrans and α-silyl sulphides were obtained in the reaction with dienes and organolithium derivatives in good yields and high diastereoselectivity. A similar chemical behaviour was observed with the achiral derivatives. Further studies are in progress for obtaining from thioferrocenoylsilanes suitable compounds to be used as ligands in asymmetric synthesis.



Scheme 7.



Scheme 8.

4. Experimental

4.1. General procedures

Melting points (uncorrected) were determined with a Büchi melting point apparatus. ^{1}H- and ^{13}C-NMR spectra were recorded using $CDCl_3$ solutions at 300 and 75.46 MHz, respectively, with a Varian Gemini 300. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ ($\delta = 7.26$ for ^{1}H and $\delta = 77.0$ for ^{13}C). J values are given in Hz. ^{13}C-NMR spectral assignments were made by DEPT experiments. IR spectra were recorded on a Perkin–Elmer model 257 grating spectrometer. Mass spectra were obtained using a VG 7070-E spectrometer at an ionising voltage of 70 eV. $[\alpha]_D^{20}$ values were determined with Perkin–Elmer Polarimeter 341. In the characterisation of the new compounds, oily products, because of the small scale used for the preparation, have been characterised by accurate mass measurements. Reactions were conducted in oven-dried (120 °C) glassware under a positive Ar atmosphere. Transfer of anhydrous solvents or mixtures was accomplished with oven-dried syringes/septum techniques. Tetrahydrofuran was distilled from sodium–benzophenone just prior to use and stored under Ar. Diethylether was distilled from P_2O_5. Dichloromethane was passed through basic alumina and distilled from CaH_2 prior to use. Other solvents were purified by standard procedures. Light petroleum ether refers to the fraction with boiling point (b.p.) 40–60 °C. The reactions were monitored by TLC performed on silica gel plates (Baker-flex IB2-F). Column chromatography was performed with Merck silica gel 60 (70–230 mesh). Preparative thick layer chromatography was carried out on glass plates using a 1 mm layer of Merck silica gel 60 Pf_{254}. All chemicals were used as obtained or purified by distillation as needed. $S(+)$-(9-anthryl)-2,2,2-trifluoroethanol was purchased by Fluka, (*S*)-2-methyl-CBS-oxazaborolidine (1 M solution in toluene) was purchased by Aldrich. Thioacylsilanes **1a** and **1b** were prepared as previously reported by us [14] and (*S*)-ferrocenyl *p*-tolyl sulphoxide **10** was prepared following the literature procedure [23].

4.2. Reaction of *1a* and *1b* with organolithium reagents. General procedure

To a stirred solution of thioacylsilane **1** (0.13 mmol) in dry THF (5 ml) under Ar at −78 °C, alkyl lithium reagent (0.15 mmol) was added dropwise. The colour of the solution rapidly changed from blue to red–yellow. The mixture was concentrated under reduced pressure and then chromatographed on deactivated neutral alumina (light petroleum–diethyl ether, 8:1) affording the α-silyl sulphide as a yellow–orange product.

4.2.1. Methyl[(ferrocenyl)(trimethylsilyl)methyl]sulphide (2a)

Following the above general procedure starting from **1a** and MeLi (1.6 M in Et_2O), **2a** was obtained in 41% yield as a solid. M.p. = 47 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.02 (s, 9H, $SiMe_3$), 2.30 (s, 3H, SMe), 2.56 (s, 1H, CH), 3.95–4.10 (4m, 4H, FcH), 4.16 (s, 5H, FcH). EIMS; m/z: 318 [M^+], 186 [Fc], 73 [$SiMe_3$]. HRMS Found: 318.0513. Calc for $C_{15}H_{22}FeSSi$: 318.0561.

4.2.2. n-Butyl[(ferrocenyl)(trimethylsilyl)methyl]sulphide (2b)

Following the above general procedure starting from **1a** and *n*-BuLi (1.6 M in hexane), **2b** was obtained in 80% yield as a pale yellow oil.^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.04 (s, 9H, $SiMe_3$), 0.93 (t, $J = 6.0$ Hz, 3H, CH_3), 1.35–1.70 (m, 4H, $2CH_2$), 2.61 (s, 1H, CH), 2.73 (t, $J = 7.0$ Hz, 2H, SCH_2), 3.90–4.10 (4m, 4H, FcH), 4.14 (s, 5H, FcH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −2.00 ($SiMe_3$), 13.81 (CH_3), 22.16 (CH_2), 31.87 (CH_2), 32.67 (CH), 34.30 (CH_2), 67.51, 67.80, 68.66, 69.46, 70.27 (FcCH), 91.78 (FcC). EIMS: m/z; 360 [M^+], 303 [$M^+ - C_4H_9$], 186 [Fc], 73 [$SiMe_3$]. HRMS Found: 360.1089. Calc. for $C_{18}H_{28}FeSSi$: 360.1030.

4.2.3. t-Butyl[(ferrocenyl)(trimethylsilyl)methyl]sulphide (2c)

Following the above general procedure starting from **1a** and *t*-BuLi (1.5 M in pentane), **2c** was obtained in 43% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 9H, $SiMe_3$), 1.37 (s, 9H,), 2.68 (s, 1H, CH), 4.04–4.12 (4m, 4H, FcH), 4.17 (s, 5H, FcH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −0.96 ($SiMe_3$), 27.49 (CH), 31.79 (CH_3), 43.62 (C), 66.54, 67.34, 68.55, 68.85, 69.42 (FcH), 95.19 (FcC). EIMS; m/z: 360 [M^+], 303 [$M^+ - C_4H_9$], 186 [Fc], 73 [$SiMe_3$]. HRMS Found: 360.1101. Calc. for $C_{18}H_{28}FeSSi$: 360.1030.

4.2.4. (6-Methyl-2-pyridinyl)methyl ferrocenyl(trimethylsilyl)methyl sulphide (2d)

Following the above general procedure starting from **1a** and lithium lutidine, prepared from freshly distilled lutidine (1.2 ml) in 12.5 ml of dry THF at −60 °C and *n*-BuLi (11 mmol), **2d** was obtained in 81% yield as a yellow solid. M.p. = 54 °C. ^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.10 (s, 9H, $SiMe_3$), 2.54 (s, 3H, CH_3), 2.82 (s, 1H, CH), 3.90–4.80 (11H, FcH, CH_2), 7.01 (d, $J = 7.5$ Hz, 1H, ArH), 7.19 (d, $J = 7.5$ Hz, 1H, ArH), 7.53 (t, $J = 9$ Hz, 1H, ArH). EIMS; m/z: 409 [M^+], 303 [$M^+ - C_7H_8N$], 186 [Fc], 107 [C_7H_9N]. HRMS Found: 409.0914. Calc. for $C_{21}H_{27}FeNSSi$: 409.0983.

4.2.5. Methyl {(ferrocenyl)[dimethyl(phenyl)silyl]}-methyl sulphide (**2e**)

Compound **2e** was obtained in 62% yield starting from **1b** and MeLi (1.6 M in Et_2O). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.22 (s, 3H, SiMe), 0.31 (s, 3H, SiMe), 2.13 (s, 3H, SCH_3), 2.72 (s, 1H, CH), 3.77 (m, 1H, FcH), 3.98–4.20 (3m, 3H, FcH) 4.11 (s, 5H, FcH), 7.30 (bd, $J = 8.3$ Hz, 3H, ArH), 7.42 (bd, $J = 8.3$ Hz, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −4.2, −4.0 (SiMe), 18.4 (SCH_3), 34.8 (CH), 66.4, 66.8, 67.1, 68.0, 68.6 (FcH), 91.2 (ArC), 127.2, 128.9, 134.2 (ArCH). EIMS; m/z: 380 [M^+], 365 [$M^+ - Me$], 333 [$M^+ - SMe$], 245 [$M^+ - SiMe_2Ph$], 135 [$SiMe_2Ph$]. HRMS Found: 380.0791. Calc. for $C_{20}H_{24}FeSSi$: 380.0717. IR (CCl_4, cm^{-1}): 1105 (SiPh), 1241 (SiMe), 1425 (SiPh).

4.2.6. n-Butyl {(ferrocenyl)[dimethyl(phenyl)silyl]}-methyl sulphide (**2f**)

Compound **2f** was obtained in 66% yield starting from **1b** and *n*-BuLi (1.6 M in hexane). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.21 (s, 3H, SiMe), 0.30 (s, 3H, SiMe), 0.88 (t, $J = 6.8$ Hz, 3H, CH_3), 1.35 (m, 2H, CH_2), 1.50 (m, 2H, CH_2), 2.54 (m, 2H, SCH_2), 2.78 (s, 1H, CH), 3.75–4.05 (m, 4H, Fc–H), 4.11 (s, 5H, FcH), 7.20 (m, 3H, ArH), 7.35 (bd, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −4.0, −4.4 (SiMe), 13.7 (CH_3), 22.1, 31.7 (CH_2), 32.6 (CH), 34.43 (CH_2) 66.2, 67.0, 67.4, 68.0, 68.6 (FcCH), 91.7 (FcC), 127.2, 127.4, 129.1, 134.1 (ArCH), 137.3 (ArC). EIMS; m/z: 422 [M^+], 365 [$M^+ - C_4H_9$], 286 [$M^+ - HSiMe_2Ph$], 135 [$SiMe_2Ph$]. HRMS Found: 422.1143. Calc. for $C_{23}H_{30}FeSSi$: 422.1187. IR (CCl_4, cm^{-1}): 1104 (SiPh), 1237 (SiMe), 1424 (SiPh).

4.2.7. t-Butyl {(ferrocenyl)[dimethyl(phenyl)silyl]}-methyl sulphide (**2g**)

Compound **2g** was obtained in 78% yield starting from **1b** and *t*-BuLi (1.5 M in pentane). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.32 (s, 3H, SiMe), 0.38 (s, 3H, SiMe), 1.26 (s, 9H, *t*-Bu), 2.91 (s, 1H, CH), 3.89 (m, 2H, FcH), 3.97 (m, 2H, FcH), 4.05 (s, 5H, FcH), 7.36 (m, 3H, ArH), 7.53 (m, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −2.3 (SiMe), −3.3 (SiMe), 27.4 (CH), 31.6 (CH_3), 43.8 (C), 66.2, 66.8, 68.6, 68.9, 68.7 (FcCH), 93.1 (FcC), 127.5, 129.0, 134.5 (ArCH), 138.6 (ArC). EIMS; m/z: 422 [M^+], 365 [$M^+ - C_4H_9$], 186 [Fc], 135 [$SiMe_2Ph$]. HRMS Found: 422.1201. Calc. for $C_{23}H_{30}FeSSi$: 422.1187.

4.3. Carbodesilylation of **2c**

To 0.1 g (0.66 mmol) of flame dried under high vacuum (0.1 mm Hg) cesium fluoride a solution of **2c** (79 mg, 0.22 mmol) in anhydrous CH_3CN (3 ml) and freshly distilled *p*-tolualdehyde (0.15 ml, 1.3 mmol) were added under Ar. After stirring at room temperature (r.t.) for 40 h, the reaction mixture was quenched with NH_4Cl and extracted with Et_2O. The organic phase was dried and concentrated. A ^{1}H-NMR spectrum of the reaction mixture showed a d.e. value of 41% calculated by integration of signals of the CH–OH of the major (at $\delta = 5.01$) and of the minor diastereoisomer (at $\delta = 5.18$). The crude was then purified by preparative TLC (light petroleum–diethyl ether, 10:1) to yield, as the higher R_f product, *tert*-butyl ferrocenyl methyl sulphide (**4**) in 33% yield, as the second R_f product the major diastereoisomer of **3** in 19% yield, and as the lower R_f product the minor diastereoisomer of **3** in 8% yield. The same reaction repeated using a longer reaction time (60 h) afforded the two diastereoisomers of **3** in 52% yield and with a d.e. equal to 10% beside 31% yield of **4**.

4.3.1. 2-(t-Butylsulphanyl)-2-ferrocenyl-1-(4-methylphenyl)-1-ethanol (major isomer)

Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.42 (s, 9H, *t*-Bu), 2.32 (s, 3H, CH_3), 3.41 (d, 1H, $J = 3.6$ Hz, SCH), 3.55 (m, 1H, FcH), 3.94 (m, 2H, FcH), 4.12, (m, 2H, FcH), 4.15 (s, 5H, FcH), 5.01 (dd, 1H, $J_1 = J_2 = 3.7$ Hz, CHOH), 7.06 (bs, 4H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 21.15, 31.89 (CH_3), 44.15 (C), 50.77 (CH), 66.54, 67.83, 68.34, 69.01, 69.13 (FcCH), 75.84 (CH), 86.49, (FcC), 126.64, 128.35 (ArCH), 136.75, 138.37 (ArC). EIMS; m/z: 408 [M^+], 287 [$M^+ - p$-TolCHOH], 91 [C_7H_7], 57 [C_4H_9]. HRMS Found: 408.1261. Calc. for $C_{23}H_{28}FeOS$: 408.1210. IR (CCl_4, cm^{-1}): 3450 (OH).

4.3.2. 2-(t-Butylsulphanyl)-2-ferrocenyl-1-(4-methylphenyl)-1-ethanol (minor isomer)

Yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.17 (s, 9H, *t*-Bu), 2.35 (s, 3H, CH_3), 3.40 (d, 1H, $J = 5.3$ Hz, SCH), 3.80 (d, 1H, $J = 4.7$ Hz, OH), 4.01 (m, 1H, FcH), 4.10 (m, 1H, FcH), 4.15 (m, 1H, FcH), 4.20 (s, 5H, FcH), 4.37 (m, 1H, FcH), 5.18 (dd, 1H, $J_1 = J_2 =$ 4.8 Hz, CHOH), 7.16 (d, 2H, $J = 8.0$ Hz ArH), 7.30 (d, 2H, $J = 8.0$ Hz, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 21.10, 31.61 (CH_3), 44.08 (C), 51.28 (CH), 68.00, 69.09 (FcH), 75.63 (CH), 91.94 (FcC), 126.82, 128.78 (ArCH), 137.09, 139.73 (ArC). MS; m/z: 408 [M^+], 287 [$M^+ - p$-TolCHOH], 91 [C_7H_7], 57 [C_4H_9]. HRMS Found: 408.1278. Calc. for $C_{23}H_{28}FeOS$: 408.1210. IR (CCl_4, cm^{-1}): 3450 (OH).

4.3.3. t-Butyl ferrocenyl methyl sulphide (**4**)

^{1}H-NMR (300 MHz, $CDCl_3$): δ 1.31 (s, 9H, *t*-Bu), 3.55 (s, 2H, CH_2), 4.06 (m, 2H, FcH), 4.13 (s, 5H, FcH), 4.16 (m, 2H, FcH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 28.35 (CH_2), 30.93 (*t*-Bu), 42.49 (C), 67.73, 68.62, 68.71 (FcCH), 85.32 (FcC).

4.4. Reduction of **1a** and **1b** with $LiAlH_4$

To a solution of **1a** or **1b** (0.5 mmol) in 5 ml of dry THF, under Ar atmosphere cooled to −30 °C, a 1 M solution of $LiAlH_4$ in THF was added dropwise (0.52 mmol). The colour of the solution changed immediately from blue to yellow and the reaction mixture was treated with 2 ml of EtOAc then with 2 ml of HCl (2%) and 3 ml of saturated solution of NH_4Cl. The organic layer was extracted with Et_2O, dried and concentrated under reduced pressure. Chromatography on deactivated neutral alumina gave the thiols **5a** or **5b** in yield 75 and 96%, respectively, as yellow oils.

4.4.1. Compound **5a**

^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.02 (s, 9H, $SiMe_3$). 1.83 (d, 1H, $J = 5.0$ Hz, SH), 3.08 (d, 1H, $J = 5.0$ Hz, CH), 4.03 (m, 1H, FcH), 4.06 (m, 2H, FcH), 4.09 (m, 1H, FcH), 4.21 (s, 5H, FcH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −3.08 ($SiMe_3$), 26.72 (CH), 65.96, 66.54, 67.02, 68.11, 68.52 (FcCH), 76.10 (FcC). EIMS; m/z: 304 [M^+], 271 [$M^+ - SH$], 230 [$M^+ - HSiMe_3$], 186 [Fc], 73 [$SiMe_3$]. HRMS Found: 304.0435. Calc. for $C_{14}H_{20}FeSSi$: 304.0404.

4.4.2. Compound **5b**

^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.25 (s, 3H, SiMe), 0.30 (s, 3H, SiMe),). 1.77 (bs, 1H, SH), 3.26 (bs, 1H, CH), 3.89 (bs, 1H, FcH), 4.03 (bs, 1H, FcH), 4.09 (bs, 1H, FcH), 4.14 (bs, 1H, FcH), 4.19 (s, 5H, FcH), 7.37 (m, 5H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −5.15, −4.54 (SiMe), 26.21 (CH), 66.21, 66.56, 67.00, 68.52 (FcCH), 127.61, 132.95, 134.24 (ArCH), 129.21 (ArC). EIMS; m/z: 366 [M^+], 334 [$M^+ - S$], 230 [$M^+ - HSiMe_2Ph$], 135 [$SiMe_2Ph$]. HRMS Found: 366.0515. Calc. for $C_{19}H_{22}FeSSi$: 366.0561.

4.5. Reduction of **1a** and **1b** with CBS methodology [21]

A solution of 0.15 ml of BH_3·DMS (2 M in THF, 0.294 mmol) in 6 ml of THF was slowly added at 0 °C to a solution of 0.088 ml (0.088 mmol, 1 M in toluene) of (*S*)-2-methyl-CBS-oxazaborolidine (Me–CBS) in 4 ml of THF. After few minutes a solution of 88.9 mg (0.294 mmol) of **1a** in 5 ml of THF was added. After 1 h the reaction was quenched with 1 ml of MeOH and 2 ml of saturated aqueous solution of NH_4Cl and extracted with Et_2O. Chromatography (light petroleum–Et_2O, 10:1) on deactivated neutral alumina gave the thiol **5a** in 47% yield. Through the same reaction starting from **1b**, **5b** was obtained in 39% yield.

4.6. Reduction of **1a** with baker's yeast

To a stirred suspension of 3 g of baker's yeast in 50 ml of tap water at r.t., 130 mg (0.43 mmol) of **1a** dissolved in 3 ml of *n*-hexane and 5 g of sugar were added. Stirring was continued for 3 days with further addition of 5 g of sugar dissolved in 50 ml of water. The aqueous suspension was extracted with *n*-hexane and the organic phase was dried and concentrated under reduced pressure. Chromatography (light petroleum–Et_2O, 10:1) on deactivated neutral alumina gave the thiols **5a** in 25% yield.

4.6.1. 1-{[Ferrocenyl(trimethylsilyl)methyl]sulphanyl}-acetone (**6a**) or 1-{[ferrocenyl[dimethyl(phenyl) silyl]methyl]sulphanyl}acetone (**6b**)

To a solution of **5a** or **5b** (0.25 mmol) in 10 ml of dry Et_2O under Ar, chloroacetone (2.5 mmol) and diisopropylethylamine (0.28 mmol) were added dropwise. After 3 h the starting thiol disappeared (TLC light petroleum–Et_2O, 10:1) and the mixture was concentrated in vacuo. Chromatography on deactivated neutral alumina gave the sulphide **6a** or **6b** as yellow oils in 73 and 75% yield, respectively.

4.6.2. Compound **6a**

^{1}H-NMR (300 MHz, $CDCl_3$): 0.22 (s, 9H, $SiMe_3$), 2.34 (s, 3H, CH_3), 2.75 (s, 1H, CH), 3.31 (d, 1H, $J = 9.5$ Hz, CH_2), 3.51 (d, 1H, $J = 9.5$ Hz, CH_2), 3.95–4.00 (m, 4H, FcH), 4.22 (s, 5H, FcH). EIMS; m/z: 360 [M^+], 303 [$M^+ - CH_2COCH_3$], 186 [Fc], 56 [Fe].

4.6.3. Compound **6b**

^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.20 (s, 3H, SiMe), 0.24 (s, 3H, SiMe), 2.02 (s, 3H, CH_3), 2.88 (s, 1H, CH), 3.04 (d, 1H, $J = 12.5$ Hz, CH_2), 3.29 (d, 1H, $J = 12.5$ Hz, CH_2), 3.70–4.05 (m, 4H, FcH), 4.07 (s, 5H, FcH), 7.20–7.50 (m, 5H, ArH). EIMS; m/z: 422 [M^+], 365 [$M^+ - CH_2COCH_3$], 333 [$M^+ - SCH_2COCH_3$], 230 [$M^+ - CH_2COCH_3$–$SiMe_2Ph$],186 [Fc], 135 [$SiMe_2Ph$].

4.7. Thionation of **8**

To stirred solution of acylsilane **8** [22] (48 mg, 0.094 mmol) in 3 ml of dry THF at r.t., 76 mg (0.188 mmol) of Lawesson's reagent was added. The red colour of the solution rapidly changed to deep blue. After 15 min, a TLC (light petroleum–Et_2O, 10:1) showed the disappearance of the starting acylsilane and dimethylbuta-1,3-diene (0.4 ml) was added. The mixture was reacted for 12 h. The solution was concentrated in vacuo and the residue was chromatographed on fluorisil affording **9** (42 mg) in 63% yield as a yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.55 (2s, 12H, $SiMe_2$), 1.45 (s, 12H, $4CH_3$), 3.15 (bs, 4H, $2CH_2$), 3.50 (bs, 4H, $2CH_2$), 4.45 (bs, 4H, FcH), 4.80 (bs, 4H, FcH), 7.10–7.65 (m, 10H,

ArH). EIMS; m/z: 706 [M^+], 135 [$SiMe_2Ph$]. HRMS Found: 706.2268. Calc. for $C_{40}H_{50}FeS_2Si_2$: 706.2242.

4.7.1. Ferrocenyl p-tolyl sulfoxide (10)

A solution of *m*-chloroperbenzoic acid (2.0 mmol) in CH_2Cl_2 was added dropwise to a solution of *p*-tolyl ferrocenyl sulphide [28] (0.6 g, 2.0 mmol) in CH_2Cl_2 at 0 °C. After disappearance of the starting sulphide (TLC light petroleum–EtOAc, 5:1) the organic layer was washed six times with a saturated solution of $NaHCO_3$ then dried and concentrated in vacuo. Chromatography with light petroleum–EtOAc (5:1) afforded as the first R_f fraction *p*-tolyl ferrocenyl sulphone (4% yield) and as the second R_f fraction the racemic sulphoxide **10** (74% yield).

4.7.2. ($S_{Fc}S_S$)-2-(p-Tolylsulphinyl)-ferrocenecarboxylic acid (11)

To a stirred suspension of (*S*)-ferrocenyl *p*-tolyl sulphoxide (**10**) [23] (3.0 g, 9.26 mmol) ($[\alpha]_D = 310°$ ($c = 0.57$, $CHCl_3$), lit: $[\alpha]_D = 314°$ ($c = 0.5$)) in 50 ml of dry THF at −78 °C under Ar, 10.2 mmol of freshly prepared LDA were added dropwise. The obtained red solution was stirred at −78 °C for 20 min and then was poured into a mixture of finely crushed dry ice (4 g, 92 mmol) and THF (20 ml). After warming to r.t., the reaction mixture was quenched with water (75 ml) and the organic layer was extracted with Et_2O.

The water phase was acidified with concentrated HCl. The resulting acid **11** was filtered, washed with water and dried (2.5 g, 75% yield). ($S_{Fc}S_S$)-**11** was obtained as a single diastereoisomer as was shown by the ^{1}H- and ^{13}C-NMR analysis. Yellow solid. M.p. = 175 °C (Et_2O). $[\alpha]_D = 672°$ ($c = 0.5$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 4.58 (s, 5H, FcH), 4.65 (t, 1H, $J = 2.7$ Hz, FcH), 4.85 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.6$ Hz, FcH), 5.15 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.6$ Hz, FcH), 7.24 (d, 2H, $J = 8.3$ Hz, ArH), 7.49 (d, 2H, $J = 8.3$ Hz, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 21.36 (CH_3), 72.40, 72.52, 73.25, 75.22 (FcCH), 91.46 (FcC), 124.35, 130.27 (ArCH) 139.56, 142.38 (ArC), 169.68 (CO). EIMS; m/z: 368 [M^+], 352 [$M^+ - O$]. Anal. Found: C, 58.53; H, 4.45. Calc. for $C_{18}H_{16}FeO_3S$: C, 58.69; H, 4.38%. IR (CCl_4, cm^{-1}): 1727 (COOH).

In order to establish the enantiomerical purity of **11**, a comparison of its ^{1}H-NMR spectrum with that of the racemic **11**, obtained using the same procedure starting from the racemic sulphoxide **10**, in the presence of *S*(+)-(9-anthryl)-2,2,2-trifluoroethanol as chiral solvating agent was performed. The singlet at 4.58 ppm corresponding to the 5FcH of the non-substituted ring of the racemic acid **11** was splitted in two signals at 4.484 and 4.525 ppm of the two enantiomers. The same experiment performed on the enantiomerically enriched acid **11** showed the presence of only one enantiomer (e.e. > 98%).

4.7.3. (S_{Fc})-2-(p-Tolylsulphanyl)-ferrocenecarboxylic acid (12)

To a stirred solution of ($S_{Fc}S_S$)-**11** (0.368g, 1.0 mmol) in 20 ml of dry THF at r.t., 0.44 g (1.1 mmol) of Lawesson's reagent was added. After 1 h the solution was concentrated in vacuo and the residue was chromatographed on preparative TLC affording (S_{Fc})-**12** in 50% yield (0.18 g, 0.51 mmol). Red solid. M.p. = 135–137 °C (Et_2O–*n*-hexane). $[\alpha]_D = -31.4°$ ($c = 0.49$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.30 (s, 3H, CH_3), 4.35 (s, 5H, FcH), 4.58 (t, 1H, $J = 2.7$ Hz, FcH), 4.62 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.6$ Hz, FcH), 5.11 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.6$ Hz, FcH), 7.09 (m, 4H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ 20.99 (CH_3), 71.82, 71.92, 73.02, 78.04 (FcCH), 81.49 (FcC), 128.91, 129.82 (ArCH) 133.22, 136.87 (ArC), 173.94 (CO). EIMS; m/z: 352 [M^+], 214 (FcCOH). Anal. Found: C, 61.22; H, 4.66. Calc. for $C_{18}H_{16}FeO_2S$: C, 61.36; H, 4.58%. IR (CCl_4, cm^{-1}): 1677 (COOH).

The racemic acid **12** was obtained using the same procedure starting from the racemic **11**. The singlet in the ^{1}H-NMR spectrum at 4.35 ppm corresponding to the 5FcH of the non-substituted ring of the racemic acid **12** was splitted in two signals at 4.31 and 4.34 ppm of the two enantiomers in the presence of *S*(+)-(9-anthryl)-2,2,2-trifluoroethanol as chiral solvating agent. The same experiment performed on the enantiomeric enriched acid **11** showed the presence of only one enantiomer (e.e. > 98%)

Starting from a sulphoxide **10** having an enantiomeric excess of 88% ($[\alpha]_D = 280°$ ($c = 0.5$, $CHCl_3$) and using the same procedure, the acid **12** was obtained with an e.e. = 86% that was established by analysis of its ^{1}H-NMR spectrum in the presence of Pirkle's alcohol, that showed the two peaks in a 7:93 ratio.

4.7.4. (S_{Fc})-2-(p-Tolylsulphanyl)-ferrocenecarboxylic acid chloride (13)

Oxalyl chloride (0.17 ml, 2.0 mmol) was added to a stirred solution of acid (S_{Fc})-**12** (0.352 g, 1.0 mmol) in dry CH_2Cl_2 (25 ml) under Ar atmosphere at r.t. After 20 min the excess of oxalyl chloride and CH_2Cl_2 were removed in vacuo and the residue was dissolved in Et_2O–pentane, filtered and concentrated in vacuo. The chloride **13** was obtained as a red oil (0.362 g, 0.98 mmol) in 98% yield. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 2.4 (s, 3H, CH_3), 4.44 (s, 5H, FcH), 4.65 (m, 2H, FcH), 5.08 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.6$ Hz, FcH), 7.08 (d, 2H, $J = 8.2$ Hz, ArH), 7.11 (d, 2H, $J = 8.2$ Hz, ArH). EIMS; m/z: 370 [M^+], 334 [$M^+ - HCl$], 214 (FcCOH) (COCl). HRMS Found: 369.9827. Calc. for $C_{18}H_{15}ClFeOS$: 369.98815, IR (CCl_4, cm^{-1}): 1750.

*4.7.5. (S_{Fc})-2-(p-Tolylsulphanyl)ferrocenoyl dimethylphenylsilane **(14)***

(S_{Fc})-**13** (0.37 g, 1.0 mmol) in dry THF (4 ml) was slowly added at −78 °C under Ar to (dimethylphenylsilyl)copper-cyanocuprate (1.2 mmol) prepared from CuCN (0.1 g, 1.2 mmol) and dimethylphenylsilyl lithium (1.2 mmol). The mixture was stirred at −50 °C for 1 h, then allowed to warm to 0 °C and further stirred for 1 h. The mixture was quenched with saturated NH_4Cl and extracted with Et_2O. The organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel column (*n*-hexane–EtOAc, 20:1) gave as the higher R_f fraction, a product arising from the silylcuprate, as the second R_f fraction the acylsilane **14** (0.72 g, 58% yield) as red oil. $[\alpha]_D = -683°$ ($c = 0.2$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.62 (s, 3H, SiMe), 0.66 (s, 3H, SiMe), 2.34 (s, 3H, CH_3), 3.96 (s, 5H, FcH), 4.18 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.4$ Hz, FcH), 4.27 (t, 1H, $J = 2.7$ Hz, FcH), 4.52 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.4$ Hz, FcH), 7.13 (d, $J = 8.0$ Hz, 2H, ArH), 7.33 (d, $J = 8.0$ Hz, 2H, ArH), 7.44 (m, 3H, ArH), 7.70 (m, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −3.245 ($SiMe_2$), 21.14 (CH_3), 70.53, 71.19, 71.68, 72.91 (FcCH), 81.53, 87.60 (FcC), 128.11, 129.76, 132.48, 134.13 (ArCH) 131.91, 135.88, 137.45 (ArC), 235.10 (COSi). EIMS; *m*/*z*: 470 [M^+], 455 [$M^+ - CH_3$], 404 [$M^+ - C_5H_6$], 347 [$M^+ - p$-Tol-S], 335 [$M^+ - SiMe_2Ph$], 135 [$SiMe_2Ph$]. HRMS Found: 470.0889. Calc. for $C_{26}H_{26}FeOSSi$: 470.0823. IR (CCl_4, cm^{-1}): 1577 (COSi).

The enantiomeric purity was established by comparison of the ^{1}H-NMR spectra in the presence of Pirkle's alcohol of this thioacylsilane with the one obtained starting from the sulphide **12** with e.e. equal to 86%. The singlet at 3.96 ppm corresponding to the 5FcH of the non-substituted ring of the latter acylsilane, was splitted in two signals at 3.917 and 3.939 of the two enantiomers in a 92.6:7.4 ratio (e.e. = 85%). On the contrary the enantiomerically pure compound showed only the signal at 3.917 (e.e. > 98%).

*4.7.6. (S_{Fc})-2-(p-Tolylsulfanyl)thioferrocenoyl dimethylphenylsilane **(15)***

To a stirred solution of (S_{Fc})-**14** (80 mg, 0.17 mmol) in 10 ml of dry THF at r.t., 100 mg (0.25 mmol) of Lawesson's reagent was added. The red colour of the solution slowly changed to deep blue. After 45 min, a TLC analysis (light petroleum–Et_2O, 10:1) showed the disappearance of the starting acylsilane. The solution was concentrated in vacuo and the residue was chromatographed on fluorisil affording **15** (78 mg) in 94% yield as a deep blue oil. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.60 (s, 3H, SiMe), 0.67 (s, 3H, SiMe), 2.35 (s, 3H, CH_3), 3.88 (s, 5H, FcH), 4.42 (t, 1H, $J = 2.7$ Hz, FcH), 4.45 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.4$ Hz, FcH), 4.61 (dd, 1H, $J_1 = 2.7$, $J_2 = 1.4$ Hz, FcH), 7.14 (d, $J = 7.8$ Hz, 2H, ArH), 7.32 (d, $J = 7.8$ Hz, 2H, ArH), 7.42 (m, 3H, ArH), 7.66 (m, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −1.05 ($SiMe_2$), 21.17 (CH_3), 70.56, 71.10, 73.16, 74.98 (FcCH), 92.50, 93.26 (FcC), 127.998, 129.50, 129.86, 132.66, 133.94 (ArCH) 132.71, 137.55 (ArC), 283.61 (COSi). HRMS Found: 486.0521. Calc. for $C_{26}H_{26}FeS_2Si$: 486.0595. EIMS; *m*/*z*: 486 [M^+], 135 [$SiMe_2Ph$]. The enantiomeric purity was established by comparison of the ^{1}H-NMR spectra in the presence of Pirkle's alcohol of this thioacylsilane with the one obtained starting from the sulphide **12** with e.e. equal to 86%. The singlet at 3.88 ppm corresponding to the 5 FcH of the non-substituted ring of the latter acylsilane, was splitted in two signals at 3.821 and 3.843 of the two enantiomers in a 8:92 ratio (e.e. = 84%). On the contrary the enantiomerically pure compound showed only the signal at 3.843 (e.e. > 98%).

*4.7.7. t-Butyl {[(2-p-tolylsulphanyl)ferrocenyl][dimethyl-(phenyl)silyl]}methyl sulphide **(16)***

To a stirred solution of thioacylsilane (S_{Fc})-**15** (70 mg, 0.14 mmol) in dry THF (5 ml) at −78 °C and under Ar, *t*-BuLi (0.15 mmol, 0.1 ml) was added dropwise. The colour of the solution rapidly changed from blue to yellow. The mixture was concentrated under reduced pressure. The ^{1}H-NMR spectrum of the mixture showed the presence of two diastereoisomers in a 7.7:1 ratio (d.e. = 77%) by integration of well-separated signals. The crude was chromatographed on deactivated neutral alumina (*n*-hexane–diethyl ether, 10:1) affording the two diastereoisomers of **16** in a 68% yield as a yellow oil. The major isomer was purified by a second chromatography on preparative TLC.

Major isomer. $[\alpha]_D = -215°$ ($c = 0.52$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.29 (s, 3H, SiMe), 0.10 (s, 3H, SiMe), 1.23 (s, 9H, *t*-Bu), 2.29 (s, 3H, CH_3), 2.99 (s, 1H, CH), 3.90 (bs, 1H, FcH), 4.26 (bt, 1H, FcH), 4.29 (s, 5H, FcH), 4.49 (bs, 1H, FcH), 7.04 (d, 2H, ArH), 7.18–7.38 (m, 7H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −4.66, −2.46 ($SiMe_2$), 21.02 (CH_3), 24.19 (CH), 31.16 (CH_3), 44.99 (C), 66.22, 67.42, 70.35, 72.45 (FcCH), 78.53, 83.03 (FcC), 127.18, 128.95, 129.15, 129.40, 134.88 (ArCH) 135.12, 135.87, 137.67 (ArC). EIMS; *m*/*z*: 544 [M^+], 487 [$M^+ - t$-Bu], 135 [$SiMe_2Ph$]. HRMS Found: 544.1343. Calc. for $C_{30}H_{36}FeS_2Si$: 544.1377.

Minor isomer. ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.62 (s, 3H, SiMe), 0.65 (s, 3H, SiMe), 0.78 (s, 9H, *t*-Bu), 2.26 (s, 3H, CH_3), 3.18 (s, 1H, CH), 4.0 (s, 5H, FcH), 4.42 (m, 2H, FcH), 4.52 (m, 1H, FcH), 7.0–7.4 (m, 9H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −1.50, −0.36 ($SiMe_2$), 20.92 (CH_3), 25.51 (CH), 30.49 (CH_3), 44.1 (C), 66.50, 70.26, 71.33, 72.91 (FcCH), 127.58, 128.39, 128.82, 129.38, 134.40 (ArCH). EIMS; *m*/*z*: 568 [M^+], 135 [$SiMe_2Ph$].

4.8. (6-Methyl-2-pyridinyl)methyl{[(2-p-tolylsulfanyl)-ferrocenyl][(dimethyl(phenyl)silyl]}methyl sulphide (17)

To a stirred solution of thioacylsilane under Ar (S_{Fc})-**15** (70 mg, 0.14 mmol) in dry THF (5 ml) at −78 °C, lithium lutidine (0.16 mmol) prepared from freshly distilled lutidine (1.2 ml) in 12.5 ml of dry THF at −60 °C and *n*-BuLi (11 mmol), was added dropwise. The colour of the solution rapidly changed from blue to yellow. The ^{1}H-NMR spectrum of the mixture showed the presence of two diastereoisomers in a 3:1 ratio (d.e. = 50%) by integration of well-separated signals. The mixture was concentrated under reduced pressure and then chromatographed on deactivated neutral alumina (light petroleum–diethyl ether, 8:1) affording the two diastereoisomers of **17** as a yellow oil. A further attempt of separation of the two diastereoisomers on silica preparative TLC failed.

^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.315 (s, 3H, SiMe major isomer), 0.00 (s, 3H, SiMe major isomer), 0.359 (s, 3H, SiMe minor isomer), 0.411 (s, 3H, SiMe minor isomer), 2.24 (s, 3H, CH_3 minor isomer), 2.28 (s, 3H, CH_3 major isomer), 2.48 (s, 3H, CH_3 minor isomer), 255 (s, 3H, CH_3 major isomer), 3.44 (s, 2H, CH_2 minor isomer), 3.48 (s, 2H, CH_2 major isomer), 3.73 (s, 1H, CH minor isomer), 3.77 (s, 1H, CH major isomer), 3.94 (s, 5H, FcH minor isomer), 4.01 (m, 1H, FcH major isomer), 4.13 (m, 1H, FcH minor isomer), 4.23 (m, 1H, FcH minor isomer), 4.27 (s, 5H, FcH major isomer), 4.31 (m, 1H, FcH major isomer), 4.48 (m, 1H, FcH minor isomer), 4.50 (m, 1H, FcH major isomer), 6.85-7.74 (10 m, 24H, ArH major and minor isomer), ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −4.97, −3.21 (SiMe major isomer), −2.94, −2.05 (SiMe minor isomer), 20.86, 20.97 (CH major and minor isomer), 27.21, 29.69, 30.31, 30.40, (CH_3 major and minor isom), 40.77 (CH_2, major isomer), 41.27 (CH_2, minor isomer) 66.79, 67.71, 67.81, 70.38, 70.49, 70.988, 71.329, 73.07, (FcCH major and minor isomer), 120.10, 120.32, 121.12, 121.31, 126.52, 127.18, 127.26, 127.75, 128.43, 128.83, 129.16, 129.30, 134.30, 134.38, 136.40 (ArCH major and minor isomer). EIMS; *m*/*z*: 593 [M^+], 487 [$M^+ - CH_2C_5H_3NCH_3$], 352 [487 − $SiMe_2Ph$], 319 [352 − SH], 135 [$SiMe_2Ph$]. HRMS Found: 593.1366. Calc. for $C_{33}H_{35}FeNS_2Si$: 593.1330.

4.9. [4,5-Dimethyl-2-(2-p-tolylsulphanylferrocenyl)-2-dimethyl(phenyl)silyl]3,6-dihydro-2H-thiopyrane (18)

To a stirred solution of thioacylsilane (S_{Fc})-**15** (70 mg, 0.14 mmol) in dry Et_2O (1 ml) at r.t. and under Ar, 2,3-dimethylbuta-1,3-diene (1 ml) was added. After 1 h the blue colour disappeared and the mixture was concentrated under reduced pressure and analysed by ^{1}H-NMR. A 3.5:1 ratio (d.e. = 56%) between the two diasteromeric cycloadducts was determined by integration of well-separated signals. The mixture was then chromatographed on preparative TLC (*n*-hexane–Et_2O, 40:1) affording as the first R_f fraction the major diastereoisomer and as the second R_f fraction the minor one in an overall yield of 78%. The same reaction has been performed at −20 °C and afforded in 24 h the two diastereoisomers in 76% yield in a 4.9:1 ratio (d.e. = 76%).

Major isomer. $[\alpha]_D = -236°$ ($c = 0.547$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ −0.05 (s, 3H, SiMe), 0.16 (s, 3H, SiMe), 1.34 (s, 3H, CH_3), 1.68 (s, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.71 (dd, $J_1 = J_2 = 16.8$ Hz, 2H, CH_2), 3.25 (dd, $J_1 = J_2 = 16.8$ Hz, 2H, CH_2), 4.18–4.23 (m, 2H, FcH), 4.27 (m, 1H, FcH), 4.28 (s, 5H, FcH), 7.10 (d, 2H, ArH), 7.20 (m, 5H, ArH), 7.4 (d, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −3.43, −2.62 ($SiMe_2$), 19.03, 21.03, 21.10 (CH_3), 31.64, 40.84 (CH_2), 66.86, 68.54, 70.67, 73.87 (FcCH), 81.49, 87.28 (FcC), 126.85, 128.68, 129.45, 129.52, 134.27 (ArCH) 132.91, 135.25, 137.12 (ArC). EIMS; *m*/*z*: 568 [M^+], 135 [$SiMe_2Ph$]. HRMS Found: 568.1348. Calc. for $C_{32}H_{36}FeS_2Si$: 568.1377.

Minor isomer. $[\alpha]_D = -309°$ ($c = 0.336$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): δ 0.09 (s, 3H, SiMe), 0.34 (s, 3H, SiMe), 1.46 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 2.45 (d, $J = 17.1$ Hz, 1H, H_a–CH_2), 2.96 (m, 3H, H_b–$CH_2 + CH_2$), 3.90 (bdd, 1H, FcH), 4.04 (bt, 1H, FcH), 4.11, 3.90 (bdd, 1H, FcH), 4.25 (s, 5H, FcH), 7.10 (d, 2H, ArH), 7.20 (m, 5H, ArH), 7.4 (m, 2H, ArH). ^{13}C-NMR (75.46 MHz, $CDCl_3$): δ −2.92, −2.46 ($SiMe_2$), 19.09, 20.74, 21.05 (CH_3), 31.83, 41.45 (CH_2), 66.05, 68.28, 70.64, 72.58 (FcCH), 82.25, 86.23 (FcC), 126.96, 128.72, 129.45, 130.05, 134.24 (ArCH) 134.91, 136.02, 138.25 (ArC). EIMS; *m*/*z*: 568 [M^+], 135 [$SiMe_2Ph$]. HRMS Found: 568.1352. Calc. for $C_{32}H_{36}FeS_2Si$: 568.1377.

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