On the Reactivity of Ferrocenoylsilanes

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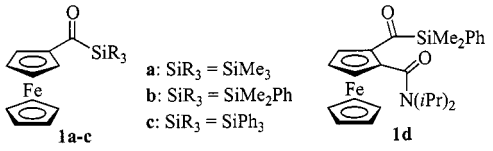
Reactions of ferrocenoylsilanes **1** with lithium aluminium hydride and organometallic reagents show unusual behaviour in that the ferrocenyl aldehydes **4** and ketones **5**–**9** are obtained instead of the expected secondary and tertiary silylated alcohols. This paper also reports on the synthesis and reactivity of the first planar chiral enantiomerically pure ferrocenoylsilane **1d** that offers the possibility of synthesizing planar chiral enantiomerically pure 1,2-disubstituted aldehyde **4b** and ketones **5b**, **6b**, **7b**, **8** and **9**. A mechanistic hypothesis is proposed for explaining the obtained results.

Introduction

Since the discovery of ferrocene in 1951,[1] its chemistry has been intensively investigated.[2] In particular, planar chiral 1,2-disubstituted ferrocenes[3] have gained increasing importance as ligands in asymmetric catalysis;[2,4] for this reason new methods for obtaining pure enantiomers of 1,2-disubstituted ferrocenes with planar chirality are of current interest. Several efficient syntheses are based on the diastereoselective lithiation of ferrocenyl derivatives containing a chiral directing group.[4a,5] More recently the enantioselective *ortho*-lithiation of monosubstituted ferrocenes in the presence of tertiary amines as chiral auxiliaries has been reported to give enantiomerically enriched 1,2-disubstituted ferrocenes.[6] Among these methods, the *n*BuLi/(−)-sparteine-induced metallation of *N*,*N*-diisopropyl ferrocenecarboxyamide reported by Snieckus[6b] provides a direct and highly enantioselective access to ferrocenes with planar chirality.

We have long been interested in the chemistry of acylsilanes,[7] due to the possibility of using these substrates as intermediates for the synthesis of silicon-free complex organic molecules via their transformation to α-hydroxysilanes by alkylation or allylation followed by desilylation.[8]

As an alternative to the method reported in the literature,[9] we recently developed a new synthetic procedure affording acylsilanes **1a**−**c** containing the ferrocene moiety in very good yields.[10]The method consisted of a nucleophilic silylation of ferrocenoyl chloride obtained from commercially available ferrocenecarboxylic acid.



Although the physical and structural properties of ferrocenoylsilanes have been studied,[11] little is known about their reactivity. In particular, no studies of the chemical behaviour of these substrates towards alkylation or reduction have been described, with the exception of a report where it was claimed that ferrocenoylsilanes do not react with lithium aluminium hydride.[9b] In the present paper we describe the synthesis of the first planar chiral enantiomerically pure ferrocenoylsilane **1d**, as well as the reactivity of **1b**−**d** towards reduction and alkylation.

Results and Discussion

Product Studies

Synthetic Strategy for (R)-2-[N,N-(Diisopropylamino)-carbonyl]ferrocenoyldimethylphenylsilane (1d)

In synthesizing **1d** we followed the Snieckus procedure.[6b] As outlined in Scheme 1, *N*,*N*-diisopropyl ferrocenecarboxyamide was lithiated in the presence of (−)-sparteine at −78 °C and the reaction was quenched with CO_2. The acid **2** ($[\alpha]_D^{20}$ = +65.4, *c* = 1.27, $CHCl_3$) was isolated in 87% yield. The enantiomeric excess of **2** was established by compar-

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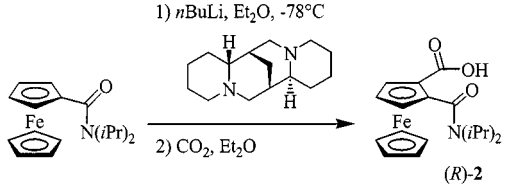
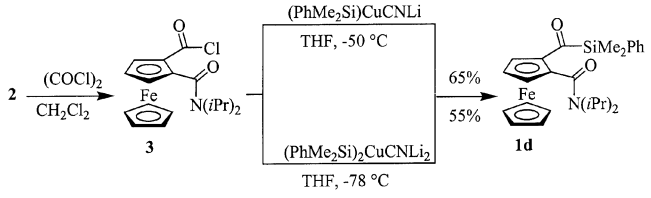
ison with the racemic product prepared by deprotonation of *N*,*N*-diisopropyl ferrocenecarboxyamide with *n*BuLi/TMEDA at −78 °C. The ^{1}H NMR spectrum of racemic **2** in $CDCl_3$ in the presence of Pirkle's alcohol {*S*(+)-1-[(9-anthryl)-2,2,2-trifluoroethanol]} showed two peaks in a 1:1 ratio at δ = 4.28 and 4.31 due to the protons of the unsubstituted cyclopentadienyl ring. The ^{1}H NMR spectrum of (+)-**2** prepared by asymmetric synthesis (see above) showed the same two signals in a 99:1 ratio (98% *ee*).



Scheme 1

The absolute configuration of **2** was established as *R* by an X-ray crystallographic analysis.[12] The acid **2** proved chemically and optically stable and could be stored for long periods without any sign of chemical degradation or racemization.

The acid (*R*)-**2** was converted in high yield (98%) to the corresponding chloride (*R*)-**3** with oxalyl chloride and then to the acylsilane (*R*)-**1d** ($[\alpha]_D^{20} = -103.1$, $c = 0.42$, $CHCl_3$, yield 65%) by nucleophilic silylation at −78 °C with (dimethylphenylsilyl)lithium cyanocuprate. It should be noted that the use of bis(dimethylphenylsilyl)lithium cyanocuprate (see Scheme 2), commonly used for the synthesis of several acylsilanes,[8f,8h,10,13] resulted in a lower yield (55%).

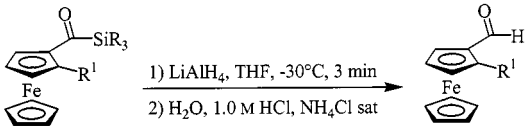


Scheme 2

The chiral acylsilane **1d** was found to be enantiomerically pure (*ee* >98%) using the same methodology applied in the case of the acid **2**, that is by comparison of the ^{1}H NMR spectra of the optically active and of the racemic acylsilane **1d** (obtained with the same procedure starting from the racemic acid **2**) in the presence of Pirkle's alcohol (see Exp. Sect.).

Reaction with Lithium Aluminium Hydride

Acylsilanes, though sensitive to light and to basic media, behave in most cases as ketones, exhibiting a similar reactivity, but this is not always the case for ferrocenoylsilanes. In particular, acylsilanes afford α-hydroxysilanes on treatment with $LiAlH_4$[14] or asymmetric reducing agents,[7c,15] whereas treatment of ferrocenoylsilanes **1b**−**d** with $LiAlH_4$ at −30 °C afforded aldehydes **4a** and **4b** (see Scheme 3).[16] Analysis of the ^{1}H NMR spectra of the optically active aldehyde **4b** and of its racemic mixture in the presence of Pirkle's alcohol showed an *ee* of greater than 98% for **4b**.



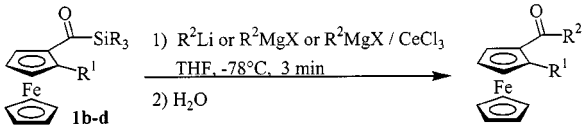
1b: $SiR_3 = SiMe_2Ph$, $R^1 = H$ **4a** 53%
1c: $SiR_3 = SiPh_3$, $R^1 = H$ **4a** 56%
1d: $SiR_3 = SiMe_2Ph$ $R^1 = CON(iPr)_2$ **4b** 52%

Scheme 3

In a similar way, the reduction of 1,1′-ferrocenedicarbonyl dimethylphenylsilane, obtained by nucleophilic silylation of 1,1′-ferrocenedicarbonyl dichloride, led again to 1,1′-ferrocenedicarboxaldehyde (yield ≤ 50%).

Reaction with Alkyllithium, Alkylcerium and Grignard Reagents

When ferrocenoylsilanes **1b**−**d** were reacted with one equivalent of organolithium reagent (MeLi, *n*BuLi) at −78 °C they led, after water quenching, to acetylferrocenes **5a**,**b** and to **6b** (Scheme 4) in an almost instantaneous reaction with the yields reported in Table 1 (entries 1, 3, 5, and 7), thus again exhibiting a behaviour at variance with that of ketones and of acylsilanes. No improvement of the yields was observed using a large excess of organolithium reagent. The fate of the silyl group has been studied in the reaction reported in entry 1. A 35% yield of dimethylphenylsilanol as well as minor amounts of diphenyltetramethyldisilane and diphenyltetramethyldisiloxane was obtained, together with a 65% yield of **5a**.



5a: $R^1 = H$ $R^2 = Me$
5b: $R^1 = CON(iPr)_2$ $R^2 = Me$
6b: $R^1 = CON(iPr)_2$ $R^2 = nBu$

Scheme 4

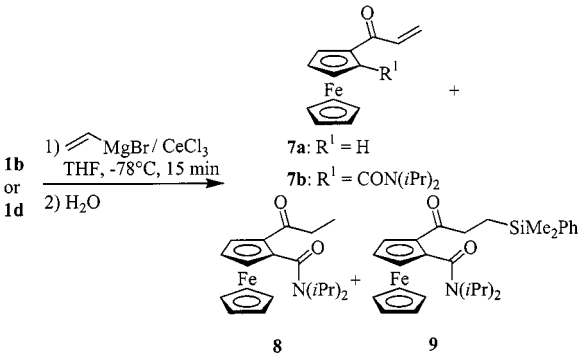
Acetylferrocene (**5a**) is also obtained, although in lower yield, by reaction of **1b** and **1c** with a large excess of methylmagnesium chloride (Table 1, entries 9 and 10). In this case a substantial amount of the starting acylsilanes was also recovered.

Analogously, in the reaction of **1b** with six equivalents of vinylmagnesium bromide the vinyl ferrocenyl ketone **7a** was obtained, again in a low yield (Table 1, entry 13 and Scheme 5).

The reactions of acylsilanes not containing the ferrocene moiety with vinylmagnesium bromide in the presence of $CeCl_3$ [17] or with organolithium/$CeCl_3$ [18] (Imamoto condi-

Table 1. Reaction of ferrocenoylsilanes with organometallic reagents

Entry	R	Si	Reagent	Equiv.	5a	5b	6b	7a	7b	8	9
1	H	$SiMe_2Ph$	MeLi	1	65						
2	H	$SiMe_2Ph$	MeLi	6	46						
3	H	$SiPh_3$	MeLi	1	60						
4	H	$SiPh_3$	MeLi	6	48						
5	$CON(iPr)_2$	$SiMe_2Ph$	MeLi	1		60					
6	$CON(iPr)_2$	$SiMe_2Ph$	MeLi	6		62					
7	$CON(iPr)_2$	$SiMe_2Ph$	*n*BuLi	1			53				
8	$CON(iPr)_2$	$SiMe_2Ph$	*n*BuLi	6			51				
9	H	$SiMe_2Ph$	MeMgCl	6	15						
10	H	$SiPh_3$	MeMgCl	6	11						
11	H	$SiMe_2Ph$	MeMgCl/ $CeCl_3$	6	30						
12	H	$SiPh_3$	MeMgCl/ $CeCl_3$	6	61						
13	H	$SiMe_2Ph$		6				14			
14	H	$SiMe_2Ph$	 / $CeCl_3$	6				49			
15	H	$SiMe_2Ph$	 / $CeCl_3$	3				32			
16	$CON(iPr)_2$	$SiMe_2Ph$	/ $CeCl_3$	6					34	28	5
17	$CON(iPr)_2$	$SiMe_2Ph$	 / $CeCl_3$	3					6		



Scheme 5

tions[19]) are currently under investigation in our laboratory, and afford α-hydroxysilanes generally in better yields than in the absence of the cerium salt.

We repeated the reactions of **1b**−**d** with Grignard reagents in the presence of $CeCl_3$ and obtained consistently higher yields of ketones (Table 1, cf. entries 9, 10 and 13 with 11, 12 and 14). We also found that lower yields were generally obtained in all the reactions using a smaller excess (three equivalents) of organometallic reagent.

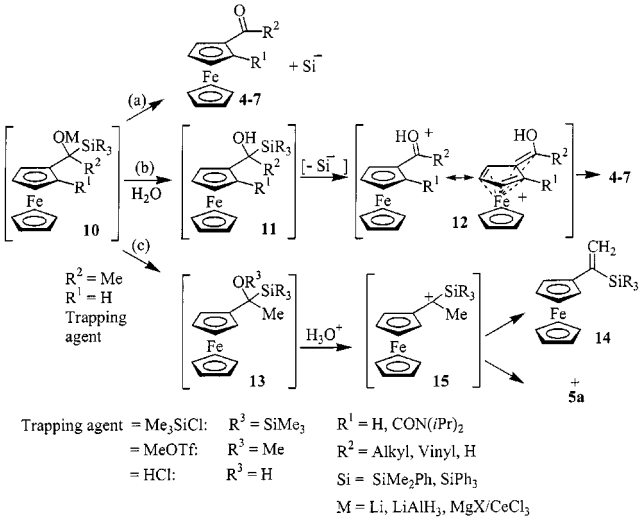
Rather surprisingly no trace of the tertiary alcohol (deriving from a further reaction of the formed ketone) was ever detected in the above reactions when using a large excess of the organometallic reagents.

The reaction of **1d** with vinylmagnesium bromide (Scheme 5), on the other hand, resulted in a more complex product distribution. Actually, the ferrocenyl vinyl ketone **7b** was obtained in 34% yield (Table 1, entry 16), and the reaction also afforded comparable amounts of (*S*)-2-[(*N*,*N*-diisopropylamino)carbonyl]ferrocenyl ethyl ketone **8** and some (*S*)-2-[(*N*,*N*-diisopropylamino)carbonyl]ferrocenyl (2-silyl)ethyl ketone **9**.The enantiomeric purity (>98%) of the starting acylsilane **1d** was maintained during its transformation into ketones **5b**, **6b**, **7b**, **8** and **9** as evidenced by comparison of the ^1H NMR spectra of the optically active and the racemic derivatives (obtained from the reaction of the racemic acylsilane **1d**) in the presence of Pirkle's alcohol (see Exp. Sect.).

A different approach to α-silyl alcohol is the treatment of aldehydes and ketones with dimethylphenylsilyllithium.[20] For this reason acetylferrocene **5a** was treated at −78 °C with one equivalent of dimethylphenylsilyllithium. The deep-red colour of the silyllithium immediately disappears on being added dropwise to the orange solution of the acetylferrocene. After quenching and chromatography of the reaction mixture we isolated 95% of acetylferrocene **5a** as well as a 73% yield of dimethylphenylsilanol and a small amount of disilane.

Discussion

The established reactivity of acylsilanes is the formation of secondary and tertiary alcohols. Ferrocenoylsilanes, however, give anomalous carbonyl-forming reactions such as ferrocenyl aldehydes with $LiAlH_4$ and alkyl ferrocenyl ketones **5a**,**b**, **6b** and **7a**,**b** with alkyllithium or Grignard reagents. Acetylferrocene is recovered in the reaction of ferrocenoylsilanes with silyllithium. No secondary or tertiary alcohols have been found in the reactions of ferrocenoylsilanes. Furthermore, the good yields of aldehydes (52−56% Scheme 3) and ketones (see Table 1) obtained in the reduction with $LiAlH_4$ and in the reaction with alkyllithium or with Grignard reagents in the presence of $CeCl_3$, compared with those obtained with Grignard reagents alone,[21] suggest that different mechanisms could be operative under different experimental conditions.



Scheme 6

The alkoxide **10**, formed by nucleophilic attack at the carbonyl carbon, might, in principle, give an unusual fragmentation with loss of the silyl anion (Scheme 6, route a) and formation of aldehydes and ketones. However, this route seems unreasonable because, in the presence of an excess of organometallic reagent, aldehydes and ketones would certainly provide the corresponding alcohols, and these are not found. Therefore it can be assumed that water quenching of **10** (Scheme 6, route b) first leads to the α-ferrocenyl-α-hydroxysilane **11**. The combined effects of the good leaving group ability of the SiR_3 moiety and the high stability of the ferrocenyl intermediate **12**[22] are the driving forces for the transformation of **11** into the carbonyl compounds **4**−**7**. The eliminated silyl anion leads to the corresponding silane that can be hydrolyzed to the silanol.[23]

The initially formed alkoxide **10** should be readily trapped by various agents (Scheme 6, route c, Table 2), such as trimethylchlorosilane (Me_3SiCl), methyl triflate (MeOTf), and 1 M hydrochloric acid. However, instead of the expected trapping products **13** a mixture of olefin **14** and **5a** was obtained (Table 2). The formation of the olefin **14** can be explained by protonation of **13** in the acid medium (1M HCl, or formed by hydrolytic quenching of the excess of Me_3SiCl, MeOTf) followed by the formation of a α-ferrocenyl-α-silylalkylcarbenium ion **15** which is stabilized by the ferrocene substituent.[22] From **15** an elimination reaction[22b] gives the olefin **14** or a competing reaction with water followed by a carbonyl-forming elimination reaction to give **7a**.

Table 2. Product distribution in the reaction of **1b** with different organometallic reagents and a trapping agent

Entry	Reagent	Trapping agent	**5a** (%)	**14** (%)
1	$MeLi/CeCl_3$	Me_3SiCl	41	16
2	MeLi	Me_3SiCl	38	57
3	MeLi	MeOTf	35	12
4	MeLi	HCl	25	55
5	MeMgCl	Me_3SiCl	25	60

The formation of the ketones **8** as well as the major product **7b** in the reaction of **1d** with vinylmagnesium bromide/$CeCl_3$ can be tentatively rationalized by a Brook rearrangement of the alkoxide[24] **10** (R^2 = vinyl in Scheme 6) via the corresponding homoenolate.[25] The formation of **9**, however, can be rationalized by a 1,3-rearrangement of the silyl group from **10** or an intramolecular nucleophilic substitution from the homoenolate.

Conclusion

Ferrocenoylsilanes exhibit an unusual reactivity towards reduction and alkylation, affording aldehydes and ketones instead of the expected secondary and tertiary alcohols. The good yields of enantiomerically pure aldehydes and ketones with planar chirality, obtained in the reaction with $LiAlH_4$ and with lithium reagents, make the reaction valuable for the preparation of these previously unreported interesting substrates. Their application as building blocks in asymmetric synthesis is currently underway.

Experimental Section

General Remarks: Melting points (uncorrected) were determined using a Büchi melting point apparatus. ^1H NMR and ^{13}C NMR spectra were recorded as $CDCl_3$ solutions at 300 and 75.46 MHz, respectively, with a Varian Gemini 300. Chemical shifts (δ) are reported in ppm relative to $CHCl_3$ (δ = 7.26 for ^1H and δ = 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 on a VG 7070-E spectrometer at an ionizing voltage of 70 eV. $[\alpha]_D^{20}$ values were determined using a Perkin−Elmer Polarimeter 341. CD spectra were recorded on a Jasco spectropolarimeter J-810. Because of the small scale used for the preparation, the new compounds, which formed as oily products, have been characterized by accurate mass measurements. The originality of all compounds was checked by a CAS on-line structure search. Reactions were conducted in oven-dried (120 °C) glassware under a positive Ar atmosphere. Transfer of anhydrous solvents or mixtures was accomplished by using oven-dried syringes/septum techniques. THF was distilled from sodium/benzophenone just prior to use and stored under Ar. Et_2O was distilled from phosphorus pentoxide. CH_2Cl_2 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 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*)-(+)-1-(9-Anthryl)-2,2,2-trifluoroethanol was purchased from Fluka. Ferrocenecarboxylic acid was prepared following the Reeves methodology[26] and a different method was used for the preparation of 1,1′-ferrocenedicarboxylic acid.[27] Ferrocenoylsilanes **1a**−**c** were prepared as previously described.[14]

(*R*)-2-[*N*,*N*-(Diisopropylamino)carbonyl]ferrocenecarboxylic Acid (2): *n*BuLi (13.2 mL, 21.1 mmol 1.6 M solution) was added to a stirred solution of (−)-sparteine (4.9 g, 21.1 mmol) in anhydrous Et_2O (45 mL) at −78° C under argon atmosphere and stirring was continued for 15 min at −78 °C. A solution of *N*,*N*-diisopropylferrocene carboxamide[6] (3.0 g, 9.6 mmol) in anhydrous Et_2O (15 mL) was then added and the resulting red suspension was stirred for 1 h at −78 °C. The solution was then poured onto a mixture of finely crushed dry ice (4.2 g, 96 mmol) and anhydrous Et_2O (20 mL). After warming to room temperature the reaction mixture was quenched with water (75 mL) and the organic layer was separated. The water phase was extracted twice with Et_2O and then acidified with conc. hydrochloric acid. The resulting acid **2** was filtered, washed with water and dried (3.0 g, 87% yield). Crystallization from toluene (10 mL) gave 2.5 g of **2** (73% yield): m.p. 165−168 °C (toluene). $[\alpha]_D^{20}$ = +65.4 (*c* = 1.27, $CHCl_3$). CD: λ_{max} (Δε) = 245 (−2.51), 265 (1.80) 332 (−0.05), 362 (1.14), 396 (0.20), 425 (0.33), 487 (−0.52) (*c* = 1.43 × 10^{-3} M, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.33−1.49 (3m, 12 H), 3.54 (m, 2 H), 4.28 (s, 5 H), 4.51, 4.57, 5.14 (3m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.23, 21.15 (CH_3), 47.62, 51.53 (CH), 70.49, 70.56, 72.19, 74.12 (CH),

76.74, 77.90 (C), 171.19 (CON), 172.62 (COOH). IR (CCl_4): $\tilde{\nu}$ = 1726 cm^{-1}, 1566. EI MS: *m/z* = 357 [M^+], 313, 292, 119. $C_{18}H_{23}FeNO_3$ (357.10): calcd. C 60.52, H 6.49, N 3.92; found C 60.50, H 6.48, N 3.95.

The reaction was repeated using TMEDA instead of (−)-sparteine and the racemic acid **2** was obtained in 78% yield. In the ^1H NMR spectrum of the racemic acid **2** in the presence of (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol as a chiral solvating agent, the singlet at δ = 4.28 corresponding to the five FcH protons was split into two signals corresponding to the two enantiomers at δ = 4.28 and 4.31. The same experiment performed on the enantiomerically enriched acid **2**, obtained by lithiation in the presence of (−)-sparteine, showed the presence of the two enantiomers in a 99:1 ratio (*ee* 98%).

(*R*)-2-[*N,N*-(Diisopropylamino)carbonyl]ferrocenoyl Chloride (3): Oxalyl chloride (0.97 mL, 11.2 mmol) was added to a stirred solution of acid **2** (2 g, 5.6 mmol) in dry CH_2Cl_2 (10 mL) under argon atmosphere at room temperature. After 20 min the excess of oxalyl chloride and CH_2Cl_2 were removed in vacuo and the solid residue was dissolved in Et_2O/pentane, filtered and concentrated in vacuo. The chloride **3** was obtained as a red solid in 98% yield: m.p. 213−215 °C (Et_2O/pentane). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 (2d, 6 H), 1.49 (d, 6 H), 3.45 (m, 2 H), 4.51 (s, 5 H), 4.61, 4.75, 4.91 (br. s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5, 19.7, 20.8, 20.9 (CH_3), 45.8, 50.8, 71.4, 72.2, 72.3, 72.8, 74.3 (CH), 93.3, 103.5 (C), 164.5 (CON), 168.0 (COCl). IR (CCl_4): $\tilde{\nu}$ = 1711 cm^{-1} 1639. EI MS *m/z*: 375 [M^+], 310. $C_{18}H_{22}ClFeNO_2$ (375.07): calcd. C 57.55, H 5.90, N 3.73; found C 57.59, H 5.85, N 3.78.

(*R*)-2-[*N,N*-(Diisopropylamino)carbonyl]ferrocenoyldimethylphenylsilane (1d). High-Order Cuprate Methodology: Ferrocenoyl chloride **3** (1.0 g, 2.67 mmol) in anhydrous THF (5 mL) was slowly added at −78 °C under argon to bis(dimethylphenylsilyl)copper cyanocuprate[13] (2.67 mmol) prepared from CuCN (0.24 g, 2.67 mmol) and dimethylphenylsilyllithium (5.34 mmol). The mixture was stirred at −78 °C for 1 h, then allowed to warm to 0 °C and stirred for a further 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 a silica gel column (*n*-hexane/EtOAc, 3:1) gave as the higher R_f fraction a product arising from the silylcuprate and as the second R_f fraction the acylsilane **1d** (0.69 g, 55% yield) as a red solid.

Low-Order Cuprate Methodology: Ferrocenoyl chloride **3** (1 g, 2.67 mmol) in anhydrous THF (5 mL) was slowly added at −78 °C under argon to (dimethylphenylsilyl)copper cyanocuprate (2.93 mmol) prepared from CuCN (0.26 g, 2.93 mmol) and dimethylphenylsilyllithium (2.93 mmol). The mixture was stirred at −50 °C for 1 h, then allowed to warm to 0 °C and stirred for a further 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 a silica gel column (*n*-hexane/EtOAc 3:1) gave as the higher R_f fraction a product arising from the silylcuprate, and as the second R_f fraction the acylsilane **1d** (0.82 g, 65% yield) as a red solid.

1d: M.p. 68−73 °C (Et_2O). $[\alpha]_D^{20}$ = −103.1 (*c* = 0.420, $CHCl_3$). CD: λ_{max} (Δε) = 274 (3.20), 300 (−0.42), 349 (3.97), 381 (−2.40), 411 (1.88), 507 (−0.90) (*c* = 1.17 × 10^{-3} M, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.53, 0.63 (2s, 6 H), 1.45−1.47, 1.60−1.62 (2m, 6 H), 3.34 (m, 2 H), 4.18 (s, 5 H), 4.32 (m, 2 H), 4.53 (m, 1 H), 7.40−7.62 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.50, −3.26, 19.71, 19.70, 20.85, 21.00 (CH_3), 45.59, 50.45, 69.96, 70.21, 71.22, 72.27 (CH), 82.37, 90.27 (C), 127.82, 128.11, 129.79 (CH), 134.01 (C), 166.60 (CON), 233.00 (COSi). IR (CCl_4): $\tilde{\nu}$ = 1630 cm^{-1}, 1500, 1430, 1230, 1125. EI MS: *m/z* = 475 [M^+], 432, 340, 312, 135. $C_{26}H_{33}FeNO_2Si$ (475.16): calcd. C 65.68, H 7.00, N 2.95; found C 65.71, H 6.92, N 2.92.

The racemic acylsilane **1d** was obtained by the low-order cuprate methodology from the racemic acid **2** in 58% yield. The singlet in the ^1H NMR spectrum at δ = 4.18 corresponding to the five FcH protons of the unsubstituted ring of the racemic acylsilane **1d** was split into two signals corresponding to the two enantiomers at δ = 4.14 and 4.16 in the presence of (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol as the chiral solvating agent. The same experiment performed on the enantiomerically enriched acylsilane **1d** showed the presence of the two enantiomers in a 99:1 ratio (*ee* 98%).

1,1′-Ferrocenedicarbonyl Dichloride: Oxalyl chloride (1.26 mL, 14.6 mmol) and *N,N*-dimethylformamide (0.11 mL, 1.46 mmol) were added to a stirred solution of 1,1′-ferrocenedicarboxylic acid (1 g, 3.6 mmol) in dry toluene (25 mL) under argon atmosphere at room temperature. After 1 h the excess of oxalyl chloride and toluene were removed in vacuo and the solid residue was dissolved in Et_2O/pentane, filtered and concentrated in vacuo. The dichloride was obtained as a red solid in 60% yield (2.16 mmol, 0.68 g) and was used immediately after the preparation.

1,1′-Bis(dimethylphenylsilylcarbonyl)ferrocene: 1,1′-Ferrocenedicarbonyl dichloride (0.68 g, 2.16 mmol) in anhydrous THF (5 mL) was slowly added at −78 °C under argon to bis(dimethylphenylsilyl)-copper cyanocuprate[13] (4.32 mmol) prepared from CuCN (0.39 g, 4.32 mmol) and dimethylphenylsilyllithium (8.64 mmol). The mixture was stirred at −78 °C for 1 h, then allowed to warm to 0 °C and stirred for a further 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 a silica gel column (*n*-hexane/EtOAc 5:1) gave as the higher R_f fraction a product arising from the silylcuprate and as the second R_f fraction the acylsilane (0.68 g, 62% yield) as a red solid: m.p. 110 °C (pentane/Et_2O). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.55 (s, 12 H), 4.05 (m, 4 H), 4.45 (m, 4 H), 7.41 (m, 6 H), 7.59 (m, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.50 (CH_3), 69.80, 73.51, 128.20, 129.96, 134.08 (CH), 234.83 (C). IR (CCl_4): $\tilde{\nu}$ = 1095 cm^{-1}, 1230, 1430, 1540. EI MS: *m/z* = 510 [M^+], 347, 283, 135, 56. $C_{28}H_{30}FeO_2Si_2$ (510.11): calcd. C 65.87, H 5.92; found C 65.85, H 5.99.

Reaction of Acylsilanes with $LiAlH_4$. General Procedure: $LiAlH_4$ (1.0 M, 1.1 mmol, 1.1 mL) was added to a solution of the acylsilane (1.0 mmol) in dry THF (2 mL) cooled to −30 °C. After a few minutes EtOAc (2 mL), 1.0 M HCl (2 mL) and saturated NH_4Cl (5 mL) were added. The mixture was extracted with Et_2O (5 mL) and the organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel (*n*-hexane/EtOAc 10:1 then *n*-hexane/EtOAc 3:1) gave the aldehyde.

Ferrocenecarbaldehyde (4a): Following the above general procedure starting from **1b**, **4a** was obtained as an orange solid in 53% yield. The same reaction has been repeated in the presence of 2.0 mmol of chlorotrimethylsilane affording **4a** in 45% yield. Starting from **1c**, **4a** was obtained in 56% yield.

(*S*)-2-[*N,N*-(Diisopropylamino)carbonyl]ferrocenecarbaldehyde (4b): Starting from **1d**, **4b** was obtained as an orange oil in 52% yield. $[\alpha]_D^{20}$ = +453 (*c* = 0.14, $CHCl_3$). CD: λ_{max} (Δε) = 306 (−2.43), 349, (2.90), 371 (−1.02), 470 (2.60) (*c* = 4.4 × 10^{-3} M, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 1.00−1.20, 1.40−1.60 (2m, 6 H),

3.40−3.55, 3.75−3.95 (2m, 2 H), 4.42 (s, 5 H), 4.62, 4.72, 4.90 (3m, 3 H), 10.12 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.33, 20.80 (CH_3), 46.00, 50.66 (CH), 67.24, 71.12, 71.45, 72.70 (CH), 77.96, 90.91 (C), 165.75 (CON), 192.71 (CHO). IR (CCl_4): $\tilde{\nu}$ = 1680 cm^{-1}, 1634. EI MS: *m*/*z* = 341 [M^+], 313, 213, 186, 100. HRMS (EI): *m*/*z* calcd. for $C_{18}H_{23}FeNO_2$ 341.1078; found 341.1081.

The racemic aldehyde **4b** was obtained from the racemic acylsilane **1d** in 50% yield under the same reaction conditions. The singlet in the ^{1}H NMR spectrum at δ = 4.72 (one hydrogen of the substituted ring)was split into two signals corresponding to the two enantiomers at δ = 4.64 and 4.69 in the presence of (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol as the chiral solvating agent. The same experiment performed on the enantiomerically enriched aldehyde **4b** showed the presence of the two enantiomers in a 99:1 ratio (*ee* 98%).

1,1′-Ferrocenedicarbaldehyde: Following the general procedure starting from 1,1′-bis(dimethylphenylsilylcarbonyl)ferrocene, 1,1′-ferrocenedicarboxaldehyde was obtained as an orange oil in 48% yield: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.65, 4.91 (2m, 4 H), 9.98 (s, 1 H). IR (CCl_4): $\tilde{\nu}$ = 1680 cm^{-1}. EI MS: *m*/*z* = 242 [M^+], 186, 121, 56.

Reaction of Acylsilanes 1b−d with Alkyllithium Reagents. General Procedure: Alkyllithium (1 equiv. or 6 equiv.) was added to a solution of the acylsilane (1.0 mmol) in dry THF (2 mL) cooled to −78 °C. The red solution became immediately yellow and after one minute water (3 mL) was added. The mixture was extracted with Et_2O (5 mL) and the organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel (*n*-hexane/EtOAc 10:1 then *n*-hexane/EtOAc 4:1) gave the ketone.

Acetylferrocene (5a): Following the above general procedure starting from **1b** and MeLi (1.6 M in Et_2O), **5a** was obtained in 65% yield using 1 equiv. of MeLi and in 46% yield using 6 equiv. of MeLi (Table 1, entry 1 and 2). Starting from **1c**, the yields were 60 and 48% using 1 and 6 equiv. of MeLi respectively (Table 1, entry 3 and 4).

(*S*)-2-[*N,N*-(Diisopropylamino)carbonyl]acetylferrocene (5b): Starting from **1d** and MeLi (1.6 M in Et_2O,1 equiv.), **5b** was obtained as a yellow solid in 60% yield (Table 1, entry 5): m.p. 125−128 °C (*n*-hexane). $[\alpha]_D^{20}$ = +24.9 (*c* = 0.55, $CHCl_3$). CD: λ_{max} (Δε) = 292 (0.05), 318 (0.86), 364 (−0.47), 453 (0.75) (*c* = 1.30 × 10^{-3} M, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90−1.00 (m, 6 H), 1.45−1.58 (m, 6 H), 2.41 (s, 3 H), 3.35−3.58 (m, 2 H), 4.40 (s, 5 H), 4.40, 4.58, 4.75 (3m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.79, 19.92, 20.78, 20.99, 27.98 (CH_3), 45.77, 50.74 (CH), 68.52, 69.96, 71.60, 72.27 (CH), 77.60, 92.09 (C), 166.40 (CON), 201.16 (CO). IR (CCl_4): $\tilde{\nu}$ = 1638 cm^{-1}, 1672. EI MS: *m*/*z* = 355 [M^+], 255, 185, 100, 56, 43. $C_{19}H_{25}FeNO_2$ (355.12): calcd. C 64.24, H 7.09, N 3.94; found C 64.21, H 7.12, N 3.97.

The same reaction was tried with 6.0 mmol of MeLi and **5b** was obtained in 62% yield (Table 1, entry 6).

Racemic **5b** was obtained from the racemic acylsilane **1d** in 60% yield using the same reaction conditions. The singlet in the ^{1}H NMR spectrum at δ = 2.41 corresponding to the $COCH_3$ group of racemic **5b** was split into two signals corresponding to the two enantiomers at δ = 2.39 and 2.36 in the presence of (*S*)-(+)-1-(9-anthryl)-2,2,2-trifluoroethanol as the chiral solvating agent. The same experiment performed on enantiomerically enriched **5b** showed the presence of the two enantiomers in a 99:1 ratio (*ee* 98%).

1-{2-[*N,N*-(Diisopropylamino)carbonyl]ferrocenyl}-1-pentanone (6b): Following the above general procedure starting from **1d** and *n*BuLi (1.6 M in hexane, 1 equiv.), **6b** was obtained as a yellow solid in 53% yield (Table 1, entry 7). m.p. 135−138 °C. $[\alpha]_D^{20}$ = +18.8 (*c* = 0.61, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.94 (t, 3 H), 1.31−1.46 (m, 2 H), 1.47−1.57 (m, 6 H), 1.61−1.74 (m, 2 H), 2.55−2.70 (m, 1 H), 2.77−2.92 (m, 1 H), 3.33−3.56 (2m, 2 H), 4.38 (s, 5 H), 4.45, 4.53, 4.72 (m, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.97, 19.84, 19.90, 20.78 (CH_3), 20.99, 22.56, 26.34 (CH_2), 39.75, 45.72, 68.33, 69.74, 71.43, 72.08 (CH), 71.45, 91.80 (C), 166.53 (CON), 203.61 (CO). IR (CCl_4): $\tilde{\nu}$ = 1638 cm^{-1}, 1672. EI MS: *m*/*z* = 397 [M^+], 297, 270, 121, 56, 43. $C_{22}H_{31}FeNO_2$ (397.17): calcd. C 66.50, H 7.86, N 3.53; found C 66.45, H 7.89, N 3.50. The same reaction repeated using 6 equiv. of *n*BuLi afforded **6b** in 51% yield (Table 1, entry 8)

Reaction of Ferrocenoylsilanes 1b,c with Grignard Reagents. General Procedure: The Grignard reagent [6.0 mmol of MeMgCl (3.0 M in THF) or vinylmagnesium bromide (1.0 M in THF)] was added to a solution of the acylsilane (1.0 mmol) in dry THF (2 mL) cooled to −78 °C. After 2 h water (3 mL) was added. The mixture was extracted with Et_2O (5 mL) and the organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel (*n*-hexane/EtOAc, 10:1, then *n*-hexane/EtOAc, 4:1) gave as the higher R_f fraction the unchanged acylsilane and as the second R_f fraction the ketone.

Acetylferrocene (5a): Starting from **1b** and MeMgCl, **5a** was obtained in 15% yield (Table 1, entry 9). Starting from **1c**, **5a** was obtained in 11% yield (Table 1, entry 10).

Ferrocenyl Vinyl Ketone (7a): Starting from **1b** and vinylmagnesium bromide, **7a** was obtained as a red solid in 14% yield (Table 1, entry 13): m.p. 208 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.20 (s, 5 H), 4.58, 4.82 (2bs, 2 H), 5.60−5.80, 6.40−6.80, 6.70−6.90 (3m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 70.08, 72.84, 76.58, 77.00, 79.66 (CH), 126.30 (CH_2), 132.96 (CH), 193.06 (CO). IR (CCl_4): $\tilde{\nu}$ = 1664 cm^{-1}. EI MS: *m*/*z* = 240 [M^+], 212, 185. $C_{13}H_{12}FeO$ (240.02): calcd. C 65.04, H 5.04; found C 65.10, H 4.99.

Preparation of the Organocerium Reagents: Cerium chloride ($CeCl_3 \cdot 7H_2O$) (2.2 g, 6.0 mmol), was dried in vacuo (10^{-3} Torr) at 130 °C for 5 h and then cooled to 0 °C. Dry THF (20 mL) was added under Ar and stirring was continued overnight at room temperature. The suspension was then cooled to −78 °C and MeMgCl (3.0 M in THF 6 mmol) or vinylmagnesium bromide (1.0 M in THF, 6.0 mmol) was added. The resulting solution was then stirred for an additional hour at −78 °C.

Reaction of Acylsilanes 1b−d with Organocerium Reagents. General Procedure: A red solution of the acylsilane (1.0 mmol) in THF (5 mL) was added to the organocerium reagent prepared as described above. The red colour immediately disappeared and the reaction mixture was quenched with water and extracted with Et_2O. The organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel (*n*-hexane/EtOAc, 5:1) gave the ketone.

Acetylferrocene (5a): Following the above general procedure starting from **1b** and MeMgCl/$CeCl_3$, **5a** was obtained in 30% yield (Table 1, entry 11). Starting from **1c** and MeMgCl/$CeCl_3$, **5a** was obtained in 61% yield (Table 1, entry 12).

Ferrocenyl Vinyl Ketone (7a): Starting from **1b** and vinylmagnesium bromide/$CeCl_3$, **7a** was obtained in 49% yield (Table 1, entry 14). The same reaction was performed using only 3 equivalents of the

organocerium regent and **7a** was obtained in 32% yield (Table 1, entry 15).

(*S*)-2-[*N,N*-(Diisopropylamino)carbonyl]ferrocenyl Vinyl Ketone (7b): Chromatography on silica gel (*n*-hexane/EtOAc 4:1) of the reaction mixture obtained starting from **1d** and vinylmagnesium bromide/$CeCl_3$, gave disilane and disiloxane as the higher R_f fraction, as the second R_f fraction the β-silylethyl ketone **9** as an orange oil, as the third R_f fraction the ethyl ketone **8** as a yellow solid, and as the lower R_f fraction the vinyl ketone **7b** as a red solid. The ratio between the three ketones **7b**, **8** and **9** depended on the reaction time: a 20 min reaction gave **7b** (34%), **8** (28%) and **9** (5%) (Table 1, entry 16), a 1 h reaction gave **7b** (3%), **8** (25%) and **9** (25%).

7b: $[\alpha]_D^{20} = +16.8$ ($c = 0.59$, $CHCl_3$). m.p. 88−90 °C (hexane). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (m, 6 H), 1.50 (m, 6 H), 3.40, 3.48 (2m, 2 H), 4.38 (s, 5 H), 4.55, 4.62, 4.78 (3m, 3 H), 5.68 (dd, 1 H), 6.44 (dd, 1 H), 6.95 (dd, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.68, 19.81, 20.72, 20.97 (CH_3), 33.0 (CH_2), 45.86, 50.89, 67.99, 70.56, 71.45, 71.79, 73.28 (CH), 78.04, 92.37 (C), 126.53, 133.73, 166.54 (CON), 192.36 (CO). = IR (CCl_4): $\tilde{\nu} = 1634\ cm^{-1}$, 1659. EI MS: *m/z* = 367 [M^+], 268, 240, 185, 100, 56. $C_{20}H_{25}FeNO_2$ (367.12): calcd. C 65.41, H 6.86, N 3.81; found C 65.47, H 6.81, N 3.78.

8: M.p. 90 °C (pentane). $[\alpha]_D^{20} = +14.9$ ($c = 0.52$, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (m, 6 H), 1.15 (t, 3 H), 1.50, (m, 6 H), 2.70, 2.85 (4m, 4 H), 3.40 (m 2 H), 4.38 (s, 5 H), 4.48, 4.55, 4.75 (3m, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.21, 19.84, 19.89, 20.75, 20.97 (CH_3), 32.99 (CH_2), 45.71, 50.66, 68.23, 69.71, 71.40, 71.77, 72.02 (CH), 77.29, 91.79 (C), 166.52 (CON), 203.99 (COEt). IR (CCl_4): $\tilde{\nu} = 1637\ cm^{-1}$, 1675. EI MS: *m/z* = 369 [M^+], 242, 185, 100, 85. $C_{20}H_{27}FeNO_2$ (369.14): calcd. C 65.05, H 7.37, N 3.79; found C 65.00, H 7.41, N 3.75.

9: $[\alpha]_D^{20} = +14.2$ ($c = 0.356$, $CHCl_3$). ^1H NMR (300 MHz, $CDCl_3$): δ = 0.32 (s, 6 H), 0.9 (m, 6 H), 1.10−1.35 (m, 2 H), 1.50 (m, 6 H) 2.55−2.70 (m, 1 H), 2.75−2.88 (m, 1 H), 3.30−3.50 (m, 2 H), 4.30 (s, 5 H), 4.40, 4.52, 4.60 (3m, 3 H), 7.20−7.60 (m, 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −3.22, −2.94 (CH_3), 9.62 (CH_2), 19.95, 20.00, 20.73, 20.95 (CH_3), 34.16 (CH_2), 45.70, 50.61, 68.36, 69.68, 71.40, 72.05 (CH), 77.52, 91.73 (C), 133.54, 129.02, 127.84 (CH), 138.46 (C), 166.37 (CON), 204.00 (CO). IR (CCl_4): $\tilde{\nu} = 1637\ cm^{-1}$, 1672. EI MS: *m/z* = 503 [M^+], 185, 135. HRMS (EI): *m/z* calcd. for $C_{28}H_{37}FeNO_2Si$ 503.1943; found 503.1949.

Trapping Experiments. General Procedure: The reaction of **1b** (1.0 mmol) with the organometallic reagent (6.0 mmol) was quenched with the trapping agent (10 mmol) reported in Table 2. After the usual work up the mixture was separated by preparative TLC on silica gel (*n*-hexane/EtOAc 10:1 then *n*-hexane/EtOAc 4:1) and gave as the higher R_f fraction the olefin **14**: ^1H NMR (300 MHz, $CDCl_3$): δ = 0.45 (s, 6 H), 3.91 (s, 5 H), 4.10, 4.22 (m, 2 H), 5.52, 6.19 (m, 1 H), 7.35−7.58 (m 5 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = −1.87 (CH_3), 67.27, 67.97, 69.44 (CH), 103.61 (C), 125.13 (CH_2), 127.76, 129.03, 134.02 (CH), 138.70, 146.02 (C). IR (CCl_4): $\tilde{\nu} = 1429\ cm^{-1}$, 1250, 1107. EI MS: *m/z* = 346 [M^+], 281, 135, 56. HRMS (EI): *m/z* calcd. for $C_{20}H_{22}FeSi$ 346.0840; found 346.0835, and as the second R_f fraction **5a** (see Table 2).

2-{2-[*N,N*-(Diisopropylamino)carbonyl]}ferrocenyl-2-propanol: MeLi (1.6 M in Et_2O, 2.5 mmol, 1.6 mL) was added to a solution of **5b** (0.15 g, 0.42 mmol) in dry THF (2 mL) cooled to −78 °C. After 30 min H_2O (3 mL) was added. The mixture was extracted with Et_2O (5 mL) and the organic layer was dried and concentrated under reduced pressure. Chromatography on silica gel (*n*-hexane/EtOAc 3:1) gave as the higher R_f fraction the alcohol (0.16 mmol, 0.06 g, 38% yield): ^1H NMR (300 MHz, $CDCl_3$): δ = 1.05 (m, 3 H), 1.20 (m, 3 H), 1.30 (s, 3 H), 1.50 (m, 6 H), 1.58 (s, 3 H), 3.45 (m, 1 H), 4.08, 4.22, 4.27 (3m, 3 H), 4.34 (s, 5 H), 4.35 (m, 1 H), 6.31 (s,1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.91 (br, CH_3), 29.22, 32.94 (CH_3), 46.42, 50.82, 64.93, 66.24 (CH), 68.16 (C), 68.26, 70.56 (CH), 80.61, 102.54, 171.89 (C). IR (CCl_4): $\tilde{\nu} = 3338\ cm^{-1}$ (OH), 1602. EI MS: *m/z* = 371 [M^+], 353, 306, 288, 56, 43. HRMS (EI): *m/z* calcd. for $C_{20}H_{29}FeNO_2$ 371.1548; found 371.1541. The second R_f fraction contained the starting material (12% yield).

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