Efficient synthesis of ferrocifens and other ferrocenyl-substituted ethylenes via a 'sulfur approach'

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Efficient synthesis of ferrocifens and other ferrocenyl-substituted ethylenes via a 'sulfur approach'

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Stable and non-odorous alkyl ferrocenyl thioketones react with bis(4-methoxyphenyl)diazomethane according to the 'two-fold extrusion' reaction principles, and tetrasubstituted ethylenes obtained thereby can be demethylated to give (Fc,2OH)-ferrocifens in good yields. The method offers an alternative approach to this class of medically relevant compounds. A similar protocol with alkyl ferrocenyl thioketones and selected diaryldiazomethanes leads to ferrocenyl-substituted ethylenes including dibenzofulvenes. These products are of potential interest for electrochemical and photophysical studies.

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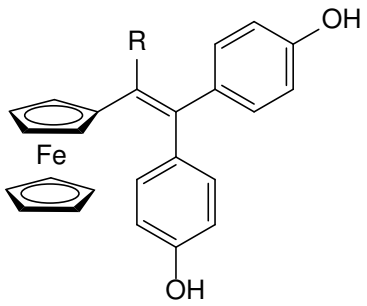
Introduction

Tetrasubstituted ethylene derivatives bearing aryl, hetaryl and ferrocenyl substituents form an important class of organic compounds with interest in materials chemistry, crystal engineering and medicinal chemistry.[1] In the latter case, aryl and ferrocenyl-substituted representatives had been studied extensively as ligands for estrogen

receptors and anticancer agents.[2] Ferrocifens with the general formula **1** containing both ferrocenyl and 4-hydroxyphenyl substituents are of special importance, and some of them are known as organometallic drugs applied for treatment of breast cancer.[2c,d]



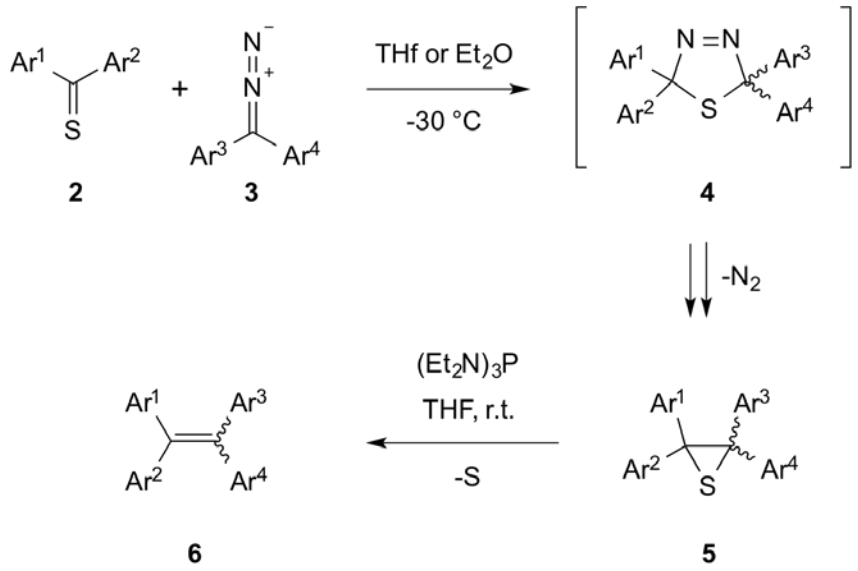
1 (R = alkyl)

Fig. 1 General structure of (Fc,2OH)-ferrocifens **1**.

Two methods for the preparation of ferrocifens **1** are known, and the first one is based on a three-step procedure starting with ethyl 2-ferrocenylbutanoate. Treatment with 4-methoxyphenyllithium, and subsequent dehydration followed by demethylation of the methoxy groups, afforded ferrocifendiphenol (Fc,2OH, **1** with R = Et) in 23% yield (over 3 steps).[3a] An alternative approach comprises the McMurray coupling of 1-ferrocenylpropanone and 4,4'-dihydroxybenzophenone.[3b] In that case, the target product was isolated in 53% yield. The disadvantage of this method are the competitive coupling reactions leading to symmetrical tetrasubstituted ethylenes.[4]

Except the McMurry coupling, reports on efficient preparations of mono-ferrocenyl ethylenes are rare. However, a recent report describing the $Rh(OAc)_4/CeCl_3$-catalyzed reaction of ferrocenecarboxaldehyde with diazoacetates in the presence of Ph_3P in dichloroethane as a method for an efficient preparation of 3-ferrocenylacrylates, is worth mentioning.[5]

One of the most efficient olefinations leading to sterically hindered ethylenes is the Barton-Kellogg reaction, also known as 'two-fold extrusion reaction'.[6] In a recent study we used this method for the preparation of diverse tetraaryl/hetarylethylenes including dibenzofulvenes[7] (Scheme 1).



Scheme 1 'Two-fold extrusion reaction' leading to tetraaryl/hetarylethylenes.

The key-step of this reaction is the [3+2]-cycloaddition of the corresponding thioketone **2** with diazocompound **3** leading to an unstable 2,5-dihydro1,3,4-thiadiazole **4**, which spontaneously eliminates N_2 to give thiirane **5** via 1,3-dipolar electrocyclization of an intermediate thiocarbonyl ylide. In some cases, spontaneous desulfurization leads to ethylene **6**, whereas in the case of stable thiiranes, removal of sulfur can be achieved by treatment with a phosphine.[6]

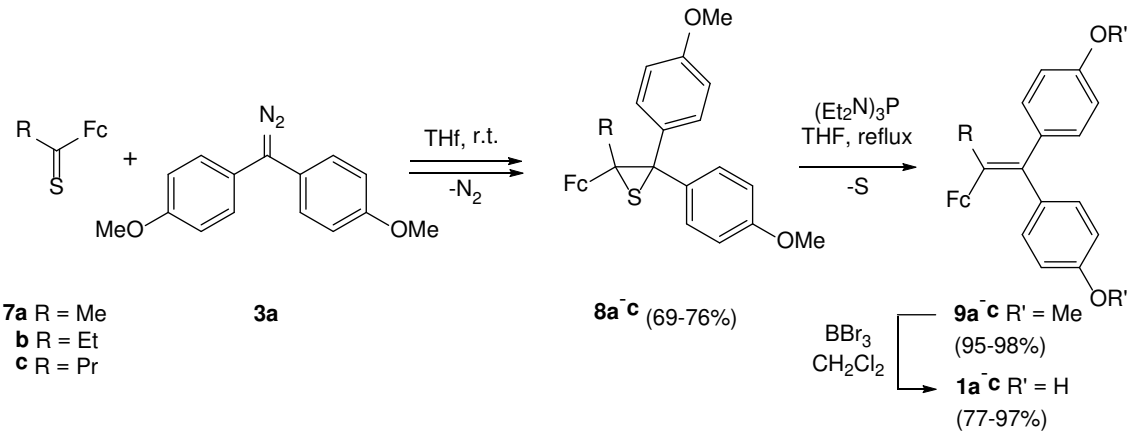
In contrast to aryl and hetaryl thioketones, ferrocenyl derivatives are rarely used as building blocks for the synthesis of more complex ferrocenyl functionalized compounds. On the other hand, in a series of recent publications, we demonstrated that ferrocenyl thioketones containing aryl, hetaryl or even alkyl groups are surprisingly stable compounds, which can be used as reactive dipolarophiles in diverse [3+2]-cycloaddition reactions, e.g. with diphenyldiazomethane,[7a] α-diazoketones,[7b] silylated thiocarbonyl ylides,[7c] and fluorinated nitrile imines.[7d]

The successful preparation of ferrocenyl-substituted thiiranes from aryl/hetaryl ferrocenyl thioketones and diphenyldiazomethane[7a] prompted us to study reactions of alkyl ferrocenyl thioketones **7** with bis(4-methoxyphenyl)diazomethane (**3a**). To date, this readily available and relatively stable diazocompound has never been explored in reactions with thioketones. The initially formed thiiranes **8** should be used as precursors of tetrasubstituted ethylenes **9**, which via demethylation will be converted into the corresponding ferrocifens **1a**–**c** (Scheme 2).

Along with **3a**, other diaryldiazomethanes such as diphenyldiazomethane (**3b**), 9-diazofluorene (**3c**), and 5-diazo-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**3d**) will also be tested in reactions with alkyl ferrocenyl thioketones **7** aimed at the preparation of corresponding ferrocifen analogues.

Results and Discussion

The surprisingly stable and non-odorous ferrocenyl thioketones **7** are easily available from the corresponding ketones by treatment with Lawesson′s reagent.[7a] To date they have practically not been applied as useful building blocks for the preparation of more complex molecules. A test experiment was performed with the propyl derivative **7c** and **3a** in THF solution at room temperature. Immediate evolution of N_2 was observed and the blue colour of **7c** disappeared. The solvent of the red-coloured reaction mixture was evaporated and the residue was identified as the expected thiirane **8c** by ^{1}H NMR spectroscopy. Two singlets of MeO groups were found at 3.69 and 3.74 ppm along with the characteristic set of signals for the ferrocenyl moiety. The *n*-propyl substituent appeared as a triplet for the Me group at 0.78 ppm and two pairs of multiplets for two CH_2 groups located at 1.46/1.80 and 1.95/2.17 ppm, respectively. Without further purification, this product was treated with an equimolar amount of tris(diethylamino)phosphine in boiling THF. After 30 min, the TLC control evidenced completion of the reaction, and after column chromatography, the desired ethylene **9c** was obtained in 79% yield. The latter product was converted into ferrocifen **1c** by treatment with BBr_3 as demethylation agent in CH_2Cl_2 according to a known procedure.[2b] Pure product was isolated after column chromatography in 67% yield.

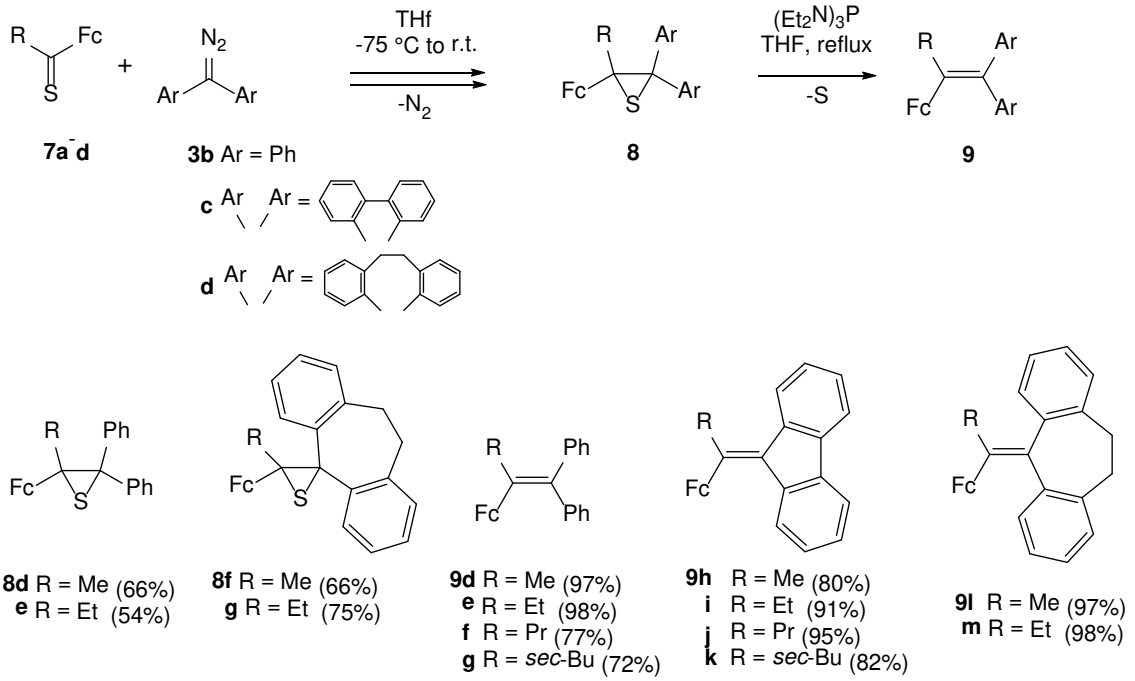


Scheme 2 Synthesis of ferrocifenes **1** via a 'sulfur approach' (Fc = ferrocenyl).

During the attempted measurement of the NMR spectra of **1c** in $CDCl_3$ solution, slow decomposition of this product was observed, and only replacement of the solvent by D_6-acetone allowed the measurement. Both ^1H and ^{13}C NMR data were in good agreement with the reported spectra.[2e]

The analogous three-step procedure was also applied for the conversion of thioketones **7a**, **b** into ferrocifens **1a** and **1b**, respectively. In all cases the final products were isolated in good yields. In analogy to **1c**, both products undergo decomposition during longer storage in $CDCl_3$ solution at room temperature. In our hands, all three ferrocifenes **1a–c** were obtained as orange-red solids from ethereal solutions after careful evaporation of the solvent. All attempts to crystallize these materials were unsuccessful. Remarkably, the melting points determined for products **1** differed significantly from the reported data (see Experimental).

In the next part of the study, alkyl ferrocenyl thioketones **7a–d** were reacted with diphenyldiazomethane (**3b**), 9-diazofluorene (**3c**) and 5-diazo-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**3d**, Scheme 3) and a similar procedure has been applied. The reaction mixtures of equimolar amounts of reagents in THF were prepared at –75 ºC and then slowly warmed to room temperature, whereby N_2-evolution was observed and the blue colour of the starting thioketones changed to orange-red. The initially formed thiiranes were isolated in some cases (**8d–g**) or directly converted into ethylenes (**9d–m**). The alternative procedure was applied in the cases in which partial elimination of sulfur from thiiranes was observed during workup. Complete desulfurizations were achieved by treatment with $(Et_2N)_3P$. All these two-step reactions and the products obtained therefrom are outlined in Scheme 3.



Scheme 3 Reaction of alkyl ferrocenyl thioketones **7a**-**d** with diaryldiazomethanes **3b**-**d**.

The ethylenes **9i**–**m** obtained in the reactions with **3c** form a new group of hitherto unknown ferrocenyl-substituted dibenzofulvenes.

Conclusions

The presented study shows that easily available alkyl ferrocenyl thioketones, which are stable at ambient conditions, can be explored for an alternative synthesis of ferrocifens based on the Barton-Kellogg reaction. These products are of current interest due to their unique biological activities, and their application as anti-cancer drugs has extensively been discussed.[8] In comparison with generally applied, traditional methods, e.g. McMurry coupling, the elaborated 'sulfur approach' offers comparable yields of the target products. Moreover, a long series of alkyl ferrocenyl ketones, which can be converted into the required thioketones, is accessible via an efficient acylation of ferrocene under mild conditions with the in situ generated mixed anhydrides.[7a] In contrast to alkyl aryl thioketones, the alkyl ferrocenyl representatives are remarkably stable compounds, but they have been studied only very scarcely yet.[9] The key

intermediates in the three-step procedure are 2-alkyl-2-ferrocenyl-substituted thiiranes formed via [3+2]-cycloaddition of the superdipolarophilic thioketones with bis(4-methoxyphenyl)diazomethane followed by spontaneous elimination of N_2. Subsequent desulfurization and demethylation can be performed with commercial reagents in good to high yields.

The replacement of bis(4-methoxyphenyl)diazomethane by other diaryldiazomethanes opens an convenient access to a variety of tetrasubstituted ferrocenyl-functionalized ethenes. Due to the known electrochemical and optical properties of ferrocene derivatives, these products are of potential interest for materials chemistry and optoelectronic applications.[10]

Experimental

General experimental method

All solvents were dried over appropriate drying agents and distilled before use. The ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker Avance III instrument (600 and 150 MHz, respectively), using the solvent ($CDCl_3$, residual $CHCl_3$) signal as reference. The following abbreviations are used to describe peak patterns where appropriate: b = broad, s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, dd = doublet × doublet, and td = triplet × doublet. Coupling constants (*J*) are reported in Hertz (Hz). The IR spectra (KBr pellets) were recorded on a Nexus FT-IR spectrophotometer. The elemental analyses were determined on a Vario Micro Cube. Flash column chromatography (FCC) was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). Melting points were determined in a capillary using a Stewart® SMP30 apparatus. The notation Fc in this study represents ferrocenyl. Applied ferrocenyl alkyl ketones and thioketones were obtained by known methods according to the literature protocols.[7] Bis(4-methoxyphenyl)diazomethane (**3a**),[2a] diphenyldiazomethane (**3b**),[11] 9-diazofluorene (**3c**),[11] and 5-diazo-10,11-dihydro-5*H*-dibenzo[a,d]cycloheptene (**3d**)[11] were prepared from the corresponding hydrazones by oxidation with activated manganium dioxide (MnO_2)[2a] or with yellow mercury oxide (HgO).[11] Hydrazones of bis(4-methoxyphenyl)ketone, 9*H*-fluorenone, and 10,11-dihydro-5*H*-dibenzo[a,d]cycloheptenone were efficiently prepared from the corresponding thioketones by treatment with hydrazine hydrate in ethanolic solutions; all reactions

were completed after 10–30 min at room temperature and the required hydrazones were obtained in 80–90% yield. Other reagents used were commercially available substances.

1. Typical procedure for the synthesis of alkyl ferrocenyl ketones.[7a]

To a solution of the corresponding carboxylic acid (1 mmol) in dry CH_2Cl_2 (10 mL) was added trifluoroacetic anhydride (TFAA, 1 mmol, 0.15 mL). After stirring the solution for ca. 2 min at room temperature, triflic acid (TfOH, 1 mmol, 0.07 mL) and ferrocene (1 mmol, 0.19 g) were added. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, water (15 mL) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2. The combined organic extracts were dried ($MgSO_4$) and the solvent evaporated. Crude products were purified by flash chromatography (CH_2Cl_2/CH_3OH 99:1).

1.1. Ferrocenyl methyl ketone. Orange solid; yield: 203 mg (89%); m.p. 84.8–86.5 ^oC (ref.[12] 85–86 ^oC). ^1H NMR (600 MHz, $CDCl_3$): δ 2.40 (bs, 3H, CH_3), 4.21 (bs, 5H, 5 Fc-CH), 4.51 (bs, 2H, 2 Fc-CH), 4.78 (bs, 2H, 2 Fc-CH) ppm. $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 27.4 (CH_3), 69.6, 72.3 (4 CH-Fc), 69.8 (5 CH-Fc), 79.3 (C-Fc), 202.0 (C=O) ppm.

2. Typical procedure for the synthesis of alkyl ferrocenyl thioketones (7).[6a]

The solution of the corresponding ketone (1 mmol) in THF (15 mL) and Lawesson's reagent (LR, 0.6 mmol, 0.24 g) was heated to reflux. The progress of the reaction was monitored by TLC. After completion of the reaction, the mixture was concentrated and the crude product was purified by flash chromatography (hexane/CH_2Cl_2 7:3).

2.1. Ferrocenyl methyl thioketone (7a). Dark violet solid; yield: 200 mg (82%); m.p. 38.0–40.0 ^oC (ref.[9] 39.0–40.0 ^oC). ^1H NMR (600 MHz, $CDCl_3$): δ 2.88 (bs, 3H, CH_3), 4.19 (bs, 5H, 5 Fc-CH), 4.74 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 5.03 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH) ppm. $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 37.9 (CH_3), 70.2, 74.3 (4 CH-Fc), 71.5 (5 CH-Fc), 89.2 (C-Fc), 241.2 (C=S) ppm. IR (KBr): υ 3104*w,* 3085*m,* 2924*m,*

2854*w,* 1443*m,* 1376*m,* 1350*m,* 1288*s,* 1226*m,* 1158*m,* 1105*m,* 999*m,* 820*s,* 658*w,* 512*m,* 474*m* cm^{-1}. Anal. calcd. for $C_{12}H_{12}FeS$ (244.13): C 59.04, H 4.95, S 13.13; found: C 59.29, H 5.23, S 13.09.

3. Reaction of alkyl ferrocenyl thioketones 7 with diaryldiazomethanes 3; Synthesis of thiiranes

A solution of the ferrocenyl substituted thioketone **7** (1 mmol) in dry THF (5 mL) was cooled to –75 ^{o}C (dry ice/acetone). Then, a solution of an appropriate diaryldiazomethane **3** (1 mmol) in dry THF (4 mL) was added and the mixture was allowed to warm slowly to r.t. After that, the reaction was completed (TLC). The solvent was evaporated and the product was purified by flash chromatography (petroleum ether/CH_2Cl_2, 7:3). Some of the obtained thiiranes underwent spontaneous partial desulfurization during purification.

3.1. 3-Ferrocenyl-3-methyl-2,2-bis(4-methoxyphenyl)thiirane (8a). Yellow solid; yield: 324 mg (69%); m.p. 162.0–164.0 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.85 (bs, 3H, CH_3), 3.60 (bs, 1H, Fc-CH), 3.69 (bs, 3H, OCH_3), 3.77 (bs, 3H, OCH_3), 3.89 (bs, 1H, Fc-CH), 4.13 (bs, 1H, Fc-CH), 4.19 (bs, 5H, 5 Fc-CH), 4.39 (bs, 1H, Fc-CH), 6.54–6.61 (m, 2H, 2 $CH_{arom.}$), 6.7–6.82 (m, 2H, 2 $CH_{arom.}$), 6.99–7.04 (m, 2H, 2 $CH_{arom.}$), 7.36–7.38 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 26.1 (CH_3), 55.1, 55.2 (2 OCH_3), 55.7 (C_q), 67.6, 67.8, 68.9, 70.2 (4 CH-Fc), 69.0 (5 CH-Fc), 69.3 (C_q), 91.2 (C-Fc), 112.6, 113.3, 129.8, 131.0 (8 $CH_{arom.}$), 135.3, 157.8, 158.3 (3 signals for 4 $C_{arom.}$) ppm. IR (KBr): υ 2965*w*, 2917*w*, 2860*w*, 2832*w*, 1730*w*, 1605*m*, 1461*m*, 1441*m*, 1281*m*, 1244*vs*, 1173s,1105m,1028*m*, 824*m*, 566*m*, 494m cm^{-1}. Anal. calcd. for $C_{27}H_{26}FeO_2S$ (470.40): C 68.94, H 5.57, S 6.82; found: C 68.89, H 5.58, S 6.71

3.2. 3-Ethyl-3-ferrocenyl-2,2-bis(4-methoxyphenyl)thiirane (8b). Orange solid; yield: 368 mg (76%); m.p. 145.5–148.0 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.15 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.92–2.00, 2.23–2.32 (2m, 2H, CH_2), 3.47 (bs, 1H, Fc-CH), 3.71 (bs, 3H, OCH_3), 3.75 (bs, 3H, OCH_3), 3.84 (bs, 1H, Fc-CH), 4.13 (bs, 1H, Fc-CH), 4.15 (bs, 5H, 5 Fc-CH), 4.41 (bs, 1H, Fc-CH), 6.57–6.61 (m, 2H, 2 $CH_{arom.}$), 6.73–6.77 (m,

2H, 2 $CH_{arom.}$), 6.97–7.00 (m, 2H, 2 $CH_{arom.}$), 7.33–7.37 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 13.9 (CH_3), 30.6 (CH_2), 55.1, 55.2 (2 OCH_3), 60.9 (C_q), 66.9, 67.4, 69.5, 70.2 (4 CH-Fc), 69.1 (5 CH-Fc), 70.0 (C_q), 91.0 (C-Fc), 112.6, 113.2, 130.2, 131.4 (8 $CH_{arom.}$), 134.9, 135.7, 157.8, 158.2 (4 $C_{arom.}$) ppm. IR (KBr): υ 2955*m*, 2933*m*, 2832*m*, 1606*m*, 1511*vs*, 1464*m*, 1448*m*, 1378*w*, 1293*s*, 1245*vs*, 1185*s*, 995*m*, 821*vs*, 596*m*, 561*m*, 492*m* cm^{-1}. Anal. calcd. for $C_{28}H_{28}FeO_2S$ (484.43): C 69.42, H 5.83, S 6.62; found: C 69.26, H 6.11, S 6.52

3.3. 3-Ferrocenyl-3-propyl-2,2-bis(4-methoxyphenyl)thiirane (8c). Yellow solid; yield: 354 mg (71%); m.p. 107.0–109.5 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 0.78 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.42–1.51, 1.76–1.85 (2m, 2H, CH_2), 1.91–1.98, 2.14–2.21 (2m, 2H, CH_2), 3.48 (bs, 1H, Fc-CH), 3.71 (bs, 3H, OCH_3), 3.76 (bs, 3H, OCH_3), 3.84 (bs, 1H, Fc-CH), 4.12 (bs, 1H, Fc-CH), 4.15 (bs, 5H, 5 Fc-CH), 4.38 (bs, 1H, Fc-CH), 6.58–6.60 (m, 2H, 2 $CH_{arom.}$), 6.74–6.77 (m, 2H, 2 $CH_{arom.}$), 6.97–7.01 (m, 2H, 2 $CH_{arom.}$), 7.33–7.37 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 14.7 (CH_3), 22.6 (CH_2), 40.1 (CH_2), 55.1, 55.2 (2 OCH_3), 60.1 (C_q), 66.8, 67.4, 69.4, 70.4 (4 CH-Fc), 69.1 (5 CH-Fc), 69.6 (C_q), 91.4 (C-Fc), 112.6, 113.1, 130.2, 131.4 (8 $CH_{arom.}$), 134.7, 135.6, 157.8, 158.2 (4 $C_{arom.}$) ppm. IR (KBr): υ 3088*w*, 2996*w*, 2965*m*, 2930*m*, 2866*m*, 1606*s*, 1511*vs*, 1464*m*, 1222*vs*, 1179*s*, 1027*s*, 995*m*, 827*s*, 568*m*, 508*m* cm^{-1}. Anal. calcd. for $C_{29}H_{30}FeO_2S$ (498.46): C 69.88, H 6.07, S 6.43; found: C 69.85, H 6.24, S 6.49.

3.4. 3-Ethyl-3-ferrocenyl-2,2-diphenylthiirane (8e). Orange solid; yield: 229 mg (54%); m.p. 142.6–144.8 °C. ^1H NMR (600 MHz, $CDCl_3$): δ 1.91 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.91–2.00, 2.33–2.44 (2m, 2H, CH_2), 3.47 (bs, 1H, Fc-CH), 3.85 (bs, 1H, Fc-CH), 4.18 (bs, 6H, 6 Fc-CH), 4.46 (bs, 1H, Fc-CH), 7.03–7.11 (m, 3H, 3 $CH_{arom.}$), 7.12–7.20 (m, 3H, 3 $CH_{arom.}$), 7.23–7.28 (m, 2H, 2 $CH_{arom.}$), 7.49–7.53 (m, 2H, 2 $CH_{arom.}$) ppm. $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 13.8 (CH_3), 30.6 (CH_2), 60.3 (C_q), 66.7, 67.5, 69.5, 69.9 (4 CH-Fc), 69.1 (5 CH-Fc), 71.1 (C_q), 90.8 (C-Fc), 126.2, 126.7, 127.2, 127.8, 129.2, 130.4 (10 $CH_{arom.}$), 142.3, 143.0 (2 $C_{arom.}$) ppm. IR (KBr): υ 3070*w*, 3018*w*, 3053*w*, 2965*m*, 2930*m*, 2873*w*, 1597*w*, 1489*m*, 1445*m*, 1372*m*, 1103*m*, 1030*m*, 998*m*, 812*s*, 742*m*, 698*vs*, 511*m*, 482*s* cm^{-1}. Anal. calcd. for $C_{26}H_{24}FeS$ (424.38): C 73.58, H 5.70, S 7.56; found: C 73.47, H 5.69, S 7.50.

3.5. 3'-Ethyl-3'-ferrocenyl-10,11-dihydro-5*H*-spiro[dibenzo[a,d][7]annulene-5,2'-thiirane] (8g). Yellow solid; yield: 338 mg (75%); m.p. 180.0–182.0 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.39 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.47–1.57, 2.28–2.35 (2m, 2H, CH_2), 2.36–2.43, 2.83–2.92, 2.94–3.00, 3.26–3.33 (4m, 4H, 2 CH_2), 3.40 (bs, 1H, Fc-CH), 3.75 (bs, 1H, Fc-CH), 4.01 (bs, 1H, Fc-CH), 4.14 (bs, 5H, 5 Fc-CH), 4.40 (bs, 1H, Fc-CH), 6.82–6.87 (m, 1H, $CH_{arom.}$), 6.94–7.00 (m, 1H, $CH_{arom.}$), 7.04–7.16 (m, 4H, 4 $CH_{arom.}$), 7.58–7.64 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 14.2 (CH_3), 29.9 (CH_2), 30.3 (CH_2), 32.5 (CH_2), 62.3 (C_q), 67.0, 67.8, 70.2 (4 CH-Fc), 69.5 (5 CH-Fc), 72.7 (C_q), 89.7 (C-Fc), 125.6, 125.9, 127.4, 127.5, 127.7, 130.3, 130.4 (8 $CH_{arom.}$), 137.1, 138.2, 138.7, 142.1 (6 $C_{arom.}$) ppm. IR (KBr): υ 2987*w*, 2960*w*, 2933*w*, 2892*w*, 2843*w*, 1479*m*, 1453*m*, 1106*m*, 1030*m*, 994*m*, 817*s*, 772*s*, 749*vs*, 645*m*, 482*s* cm^{-1}. Anal. calcd. for $C_{28}H_{26}FeS$ (450.42): C 74.66, H 5.82, S 7.12; found: C 74.60, H 5.80, S 7.14.

4. Desulfurization of thiiranes 8 to give ethylenes 9

To a solution of the corresponding thiirane (pure compound or crude material; 1 mmol) in THF (4 mL), hexaethyl phosphorous triamide ($[(C_2H_5)_2N]_3P$, 1.2 mmol, 296 mg, 0.32 mL) was added. Then, the mixture was heated to reflux, and the progress of the reaction was monitored by TLC. After the completion of the reaction, the solvent was evaporated and the crude product was purified by FCC (petroleum ether/CH_2Cl_2, 7:3).

4.1. 2-Ferrocenyl-1,1-bis(4-methoxyphenyl)prop-1-ene (9a). Orange solid; yield: 456 mg (97%); m.p. 126.0–128.0 °C; desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.12 (bs, 3H, CH_3), 3.78 (bs, 3H, OCH_3), 3.82 (bs, 3H, OCH_3), 3.96 (bs, 2H, 2 Fc-CH), 4.11 (bs, 2H, 2 Fc-CH), 4.16 (bs, 5H, 5 Fc-CH), 6.72–6.75 (m, 2H, 2 $CH_{arom.}$), 6.84–6.89 (m, 2H, 2 $CH_{arom.}$), 6.91–6.95 (m, 2H, 2 $CH_{arom.}$), 7.08–7.10 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 22.0 (CH_3), 55.1, 55.2 (2 OCH_3), 67.9, 69.2 (4 CH-Fc), 69.0 (5 CH-Fc), 88.1 (C-Fc), 113.3, 113.4, 131.0, 131.5 (8 $CH_{arom.}$), 129.7, 137.1, 137.2, 137.4, 157.9, 158.0 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 2984*w*, 2949*w*, 2825*w*, 1604m, 1505*s*, 1461*m*,1432*m*, 1290*m*, 1280*m*, 1242*vs*, 1171*m*, 1106*m*, 1038*m*, 992*m*, 910*w*, 835*m*, 817*m*, 485*m* cm^{-1}. Anal. calcd. for $C_{27}H_{26}FeO_2$ (438.34): C 73.98, H 5.98; found: C 73.82, H 5.85.

4.2. 2-Ferrocenyl-1,1-bis(4-methoxyphenyl)but-1-ene (9b).[13] Thick orange oil; yield: 431 mg (95%); desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.02 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 2.51 (q, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 3.79 (bs, 3H, OCH_3), 3.82 (bs, 3H, OCH_3), 4.02 (bs, 2H, 2 Fc-CH), 4.12–4.21 (m, 7H, 7 Fc-CH), 6.76–6.80 (m, 2H, 2 $CH_{arom.}$), 6.85–6.89 (m, 2H, 2 $CH_{arom.}$), 6.97–7.00 (m, 2H, 2 $CH_{arom.}$), 7.09–7.12 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 15.4 (CH_3), 27.9 (CH_2), 55.1, 55.2 (2 OCH_3), 68.0, 69.3 (4 CH-Fc), 69.2 (5 CH-Fc), 87.3 (C-Fc), 113.5, 113.6, 130.4, 131.0 (8 $CH_{arom.}$), 136.6, 137.3, 137.5, 157.8, 157.9 (C=C, 4 $C_{arom.}$) ppm.

4.3. 2-Ferrocenyl-1,1-bis(4-methoxyphenyl)pent-1-ene (9c). Yellow solid; yield: 457 mg (98%); m.p. 103.0–106.0 ^{o}C; desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 0.83 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.45–1.51 (m, 2H, CH_2), 2.50–2.57 (m, 2H, CH_2), 3.79 (bs, 3H, OCH_3), 3.83 (bs, 3H, OCH_3), 3.96 (bs, 2H, 2 Fc-CH), 4.12 (bs, 2H, 2 Fc-CH), 4.15 (bs, 5H, 5 Fc-CH), 6.75–6.78 (m, 2H, 2 $CH_{arom.}$), 6.85–6.88 (m, 2H, 2 $CH_{arom.}$), 6.96–6.99 (m, 2H, 2 $CH_{arom.}$), 7.09–7.12 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 14.4 (CH_3), 23.9 (CH_2), 37.1 (CH_2), 55.1, 55.2 (2 OCH_3), 68.4, 69.5 (4 CH-Fc), 69.6 (5 CH-Fc), 88.6 (C-Fc), 113.4, 113.5, 130.6, 131.2 (8 $CH_{arom.}$), 135.0, 137.3, 137.6, 138.0, 157.9, 158.0 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 3031*w*, 3006*w*, 2955*w*, 2873*w*, 2832*w*, 1603*m*, 1507*m*, 1458*m*, 1439*m*, 124*vs*, 1181*m*, 1169*m*, 1103*m*, 1035*m*, 838*m*, 755*m*, 584*m* cm^{-1}. Anal. calcd. for $C_{29}H_{30}FeO_2$ (466.39): C 74.68, H 6.48; found: C 74.56, H 6.50.

4.4. 2-Ferrocenyl-1,1-diphenylbut-1-ene (9e). Orange solid; yield: 384 mg (98%); m.p. 114.7–116.5 ^{o}C; desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.07 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 2.61 (q, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 3.91 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.09 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.14 (bs, 5H, 5 Fc-CH), 7.10–7.13 (m, 2H, 2 $CH_{arom.}$), 7.16–7.19 (m, 1H, $CH_{arom.}$), 7.22–7.26 (m, 5H, 5 $CH_{arom.}$), 7.32–7.36 (m, 2H, 2 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 15.5 (CH_3), 27.8 (CH_2), 68.1, 69.3 (4 CH-Fc), 69.2 (5 CH-Fc), 86.5 (C-Fc), 126.2, 128.1, 128.2, 129.3, 129.8 (10 $CH_{arom.}$), 137.4, 138.0, 144.6, 144.7 (C=C, 2 $C_{arom.}$) ppm. IR (KBr): υ 3079*w*, 3044*w*, 2974*m*, 2961*m*, 2933*w*, 2870*w*, 1597*m*, 1489*m*, 1442*m*, 1109m, 1074*m*, 1049*m*, 1024*m*, 1005*m*, 821*m*, 805*m*, 774*m*, 704*vs*, 523*m*, 489*s* cm^{-1}. Anal. calcd. for $C_{26}H_{24}Fe$ (392.31): C 79.60, H 6.17; found: C 79.64, H 6.20.

4.5. 9-(1-Ferrocenylethylidene)-9*H*-fluorene (9h). Orange solid; yield: 301 mg (80%); m.p. >215 °C (decomposition); spontaneous desulfurization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.91 (bs, 3H, CH_3), 4.27 (bs, 5H, 5 Fc-CH), 4.47 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.54 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 6.97–7.01 (m, 1H, $CH_{arom.}$), 7.18–7.23 (m, 1H, $CH_{arom.}$), 7.31–7.34 (m, 1H, $CH_{arom.}$), 7.35–7.38 (m, 2H, 2 $CH_{arom.}$), 7.69–7.71 (m, 1H, $CH_{arom.}$), 7.78–7.81 (m, 1H, $CH_{arom.}$), 7.98–8.01 (m, 1H, $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 26.5 (CH_3), 68.9, 71.0 (4 CH-Fc), 69.5 (5 CH-Fc), 90.0 (C-Fc), 119.0, 119.5, 124.8, 125.0, 125.9, 126.4, 126.6, 126.7 (8 $CH_{arom.}$), 134.4, 138.5, 139.4, 139.5, 139.7, 140.5 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 3098*w*, 3060*w*, 3047*w*, 2961*w*, 1613*m*, 1591*s*, 1445*s*, 1432*m*, 1340*m*, 1106*m*, 1005*m*, 995*m*, 780*s*, 736*vs*, 644*m*, 482*m* cm^{-1}. Anal. calcd. for $C_{25}H_{20}Fe$ (376.27): C 79.80, H 5.36; found: C 79.87, H 5.45.

4.6. 9-(1-Ferrocenylpropylidene)-9*H*-fluorene (9i). Yellow solid; yield: 355 mg (91%); m.p. >166 °C (decomposition); spontaneous desulfurization. ^{1}H NMR (600 MHz, $CDCl_3$): δ 1.45 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 3.44 (q, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 4.24 (bs, 5H, 5 Fc-CH), 4.45 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 4.50 (t, 2H, $J_{H,H}$ = 1.8 Hz, 2 Fc-CH), 6.94–6.98 (m, 1H, $CH_{arom.}$), 7.11–7.16 (m, 1H, $CH_{arom.}$), 7.17–7.20 (m, 1H, $CH_{arom.}$), 7.34–7.38 (m, 2H, 2 $CH_{arom.}$), 7.66–7.70 (m, 1H, $CH_{arom.}$), 7.76–7.80 (m, 1H, $CH_{arom.}$), 7.92–7.96 (m, 1H, $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 15.1 (CH_3), 32.4 (CH_2), 68.6, 70.8 (4 CH-Fc), 69.5 (5 CH-Fc), 91.8 (C-Fc), 118.8, 119.4, 124.8, 125.5, 125.8, 126.4, 126.7, 126.9 (8 $CH_{arom.}$), 133.9, 138.6, 138.9, 139.5, 139.9, 146.9 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 3094*w*, 2984*w*, 2958*w*, 2927*w*, 2870*w*, 1613*m*, 1591*m*, 1473*m*, 1448*s*, 1337*w*, 1277*w*, 1109*m*, 1024*m*, 1002*m*, 941*w*, 821*s*, 768*m*, 694*w*, 732*vs*, 694*w*, 485*s* cm^{-1}. Anal. calcd. for $C_{26}H_{22}Fe$ (390.30): C 80.01, H 5.68; found: C 80.06, H 5.70.

4.7. 5-(1-Ferrocenylethylidene)-10,11-dihydro-5*H*-dibenzo[a,d][7]annulene (9l). Orange solid; yield: 392 mg (97%); m.p. 143.0–145.0 °C; desulfurization of thiirane. ^{1}H NMR (600 MHz, $CDCl_3$): δ 2.14 (bs, 3H, CH_3), 2.83–2.98 (m, 2H, CH_2), 3.43–3.57 (m, 3H, Fc-CH, CH_2), 4.02 (bs, 1H, Fc-CH), 4.14 (bs, 5H, 5 Fc-CH), 4.25 (bs, 1H, Fc-CH), 4.40 (bs, 1H, Fc-CH), 6.94–6.98 (m, 1H, $CH_{arom.}$), 6.99–7.03 (m, 1H, $CH_{arom.}$), 7.12–7.20 (m, 6H, 6 $CH_{arom.}$) ppm. ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 20.3 (CH_3), 32.3 (2

CH_2), 68.2, 68.5, 69.2, 69.5 (4 CH-*Fc*), 69.3 (5 CH-Fc), 87.1 (C-Fc), 125.3, 126.0, 126.7, 126.8, 128.6, 129.0, 129.1, 129.2 (8 $CH_{arom.}$), 136.2, 137.3, 137.5, 142.6, 142.8 (C=C, 4 $C_{arom.}$) ppm. IR (KBr): υ 3063*w*, 3006*w*, 2939*w*, 2909*m*, 2828*w*, 1594*w*, 1481*m*, 1440*m*, 1396*m*, 1255*m*, 1104*m*, 1006*m*, 907*m*, 821*vs*, 775*s*, 756*vs*, 745*m*, 622*m*, 509*m* cm^{-1}. Anal. calcd. for $C_{27}H_{24}Fe$ (404.32): C 80.21, H 5.98; found: C 80.24, H 5.91.

5. Typical procedure for the demethylation of compounds 9a–c.

The solution of the corresponding ethylene **9a–c** (1 mmol) in dichloromethane (4 mL) was cooled to –78 °C (acetone/dry ice) and then 2 mL (2 mmol) of a solution of BBr_3 (1M in CH_2Cl_2) was added in one portion. The cooling bath was removed and the solution was stirred for 1.5 h. Then, the mixture was again cooled to 0 °C in ice bath, 3 mL of methanol were added, and the solvent was evaporated. The crude product was purified by CC (SiO_2, petroleum ether/ethyl acetate 8:2). In all cases, viscous materials were obtained, which after dissolution in diethylether and careful evaporation of the solvent converted into foam-like solids.

5.1. 2-Ferrocenyl-1,1-bis(4-hydroxyphenyl)prop-1-ene (1a).[14] Purified chromatographically, orange-red solid; yield: 316 mg (77%); m.p. 59−63°C (ref.[14] 94.0–95.0 °C (from pentane/diethylether)). ^{1}H NMR (600 MHz, acetone-d_6): δ 2.15 (bs, 3H, CH_3), 3.94 (bs, 2H, 2 Fc-CH), 4.06 (bs, 2H, 2 Fc-CH), 4.14 (bs, 5H, 5 Fc-CH), 6.67–6.70 (m, 2H, 2 $CH_{arom.}$), 6.79–6.84 (m, 4H, 4 $CH_{arom.}$), 7.01–7.04 (m, 2H, 2 $CH_{arom.}$), 8.13 (bs, 1H, OH), 8.20 (bs, 1H, OH) ppm. ^{13}C{^{1}H}NMR (150 MHz, acetone-d_6): δ 22.3 (CH_3), 68.6, 69.9 (4 CH-Fc), 69.8 (5 CH-Fc), 89.1 (C-Fc), 115.6, 115.7, 131.9, 132.3 (8 $CH_{arom.}$), 129.9, 137.0, 137.1, 138.8, 156.6, 156.7 (C=C, 4 $C_{arom.}$) ppm.

5.2. 2-Ferrocenyl-1,1-bis(4-hydroxyphenyl)but-1-ene (1b).[3b] Purified chromatographically, orange-red solid; yield: 316 mg (90%); m.p. 81−83 °C (ref.[3b] m.p. 219 °C (no solvent used for crystallization reported)). ^{1}H NMR (600 MHz, acetone-d_6): δ 1.03 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 2.62 (q, 2H, $J_{H,H}$ = 7.2 Hz, CH_2), 3.92 (bs, 2H, 2 Fc-CH), 4.06 (bs, 2H, 2 Fc-CH), 4.11 (bs, 5H, 5 Fc-CH), 6.69–6.72 (m, 2H, 2 $CH_{arom.}$), 6.80–6.83 (m, 2H, 2 $CH_{arom.}$), 6.86–6.89 (m, 2H, 2 $CH_{arom.}$), 7.05–7.08 (m, 2H, 2 $CH_{arom.}$), 8.16 (bs, 2H, 2 OH) ppm. ^{13}C{^{1}H}NMR (150 MHz, acetone-d_6): δ 15.0 (CH_3),

27.6 (CH_2), 67.7, 69.1 (4 CH-Fc), 69.0 (5 CH-Fc), 87.1 (C-Fc), 114.9, 115.0, 130.3, 130.8 (8 $CH_{arom.}$), 136.0, 136.3, 136.6, 137.9, 155.7, 155.8 (C=C, 4 $C_{arom.}$) ppm.

5.3. 2-Ferrocenyl-1,1-bis(4-hydroxyphenyl)pent-1-ene (1c).[2e] Purified chromatographically, orange-red solid; yield: 425 mg (97%); m.p. 59−62 °C (ref.[2e] m.p. 186.0 °C (no solvent used for crystallization reported)). ^{1}H NMR (600 MHz, acetone-d_6): δ 0.82 (t, 3H, $J_{H,H}$ = 7.2 Hz, CH_3), 1.46–1.63 (m, 2H, CH_2), 2.57–2.64 (m, 2H, CH_2), 3.92 (bs, 2H, 2 Fc-CH), 4.05 (bs, 2H, 2 Fc-CH), 4.12 (bs, 5H, 5 *Fc*-CH), 6.69–6.72 (m, 2H, 2 $CH_{arom.}$), 6.79–6.83 (m, 2H, 2 $CH_{arom.}$), 6.85–6.88 (m, 2H, 2 $CH_{arom.}$), 7.03–7.07 (m, 2H, 2 $CH_{arom.}$), 8.15 (bs, 2H, 2 OH) ppm. ^{13}C{^{1}H}NMR (150 MHz, acetone-d_6): δ 14.7 (CH_3), 24.7 (CH_2), 37.7 (CH_2), 68.7, 70.1 (4 CH-Fc), 69.9 (5 CH-Fc), 88.7 (C-Fc), 115.8, 115.9, 131.4, 131.8 (8 $CH_{arom.}$), 135.3, 137.4, 137.6, 139.3, 156.6, 156.7 (C=C, 4 $C_{arom.}$) ppm.

Conflicts of interest

There are no conflicts of interest to declare.

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Graphical abstract: