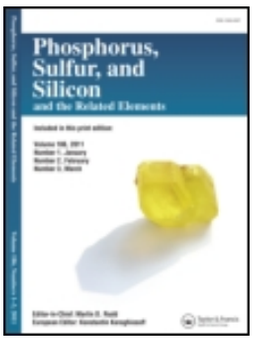

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SYNTHESIS OF FERROCENYL THIOKETONES AND THEIR REACTIONS WITH DIPHENYLDIAZOMETHANE

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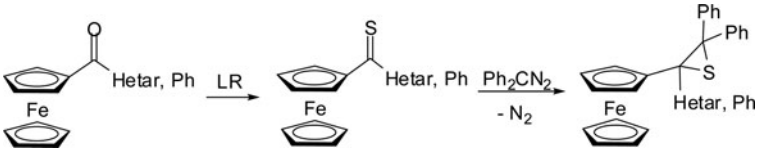
GRAPHICAL ABSTRACT



Abstract *A series of ferrocenyl ketones were obtained via the Friedel–Crafts acylation with mixed anhydrides using ferrocene as a nucleophilic agent or ferrocene carboxylic acid as a precursor of the electrophilic species. The ketones obtained thereby undergo smooth thionation (tetrahydrofuran, 65°C) with Lawesson's reagent. The ferrocenyl thioketones react with diphenyldiazomethane via N_2 elimination to afford the hitherto unknown ferrocenyl-substituted thiiranes.*

Keywords Ferrocene; thioketones; diazo compounds; thiiranes; thiophene derivatives; selenophene derivatives

INTRODUCTION

Aromatic thioketones are relatively stable compounds, which can be conveniently prepared from corresponding ketones by O/S exchange using Lawesson's reagent (LR).[1] In the last three decades, aromatic thioketones and non-enolizable aliphatic thioketones have been explored extensively as versatile building blocks for the synthesis of more complex sulfur-containing compounds. Cycloaddition reactions leading to five- and six-membered S-heterocycles are of special importance, as thioketones are recognized as superdipolarophilic[2] and superdienophilic agents.[3] Moreover, thioketones are unique substrates for the preparation of differently substituted alkenes via the so-called "two-fold extrusion reaction" with diazo compounds.[4]

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Part of the PhD thesis of Róża Hamera, University of Łódź, Łódź, Poland.
This paper is dedicated to Professor Emeritus Robert R. Holmes.
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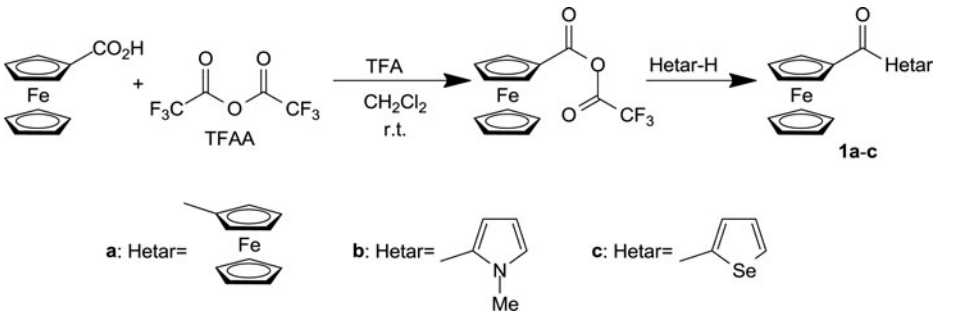
Ferrocenyl-functionalized compounds are of great importance and found applications in materials chemistry, medicinal chemistry, polymer sciences, etc.[5] In spite of growing interest in ferrocenyl-containing S-heterocycles,[6] very little is known about the ferrocenyl-substituted thioketones, which are attractive substrates for their synthesis. The synthesis of three representatives, i.e., ferrocenyl phenyl thioketone, ferrocenyl methyl thioketone, and *tert*-butyl ferrocenyl thioketones, was reported in 1978 without complete spectroscopic data.[7] In addition, diferrocenyl thioketone was described as the product of thionation of diferrocenyl ketone.[8]

In our ongoing studies on the applications of thiocarbonyl compounds for the synthesis of S-heterocycles and related compounds, we reported the synthesis of diverse aryl hetaryl and dihetaryl thioketones, which are relatively stable and can be stored without decomposition.[9] These results prompted us to elaborate a similar method for the preparation of ferrocenyl hetaryl ketones and subsequent thionation to give the corresponding thioketones.

RESULTS AND DISCUSSION

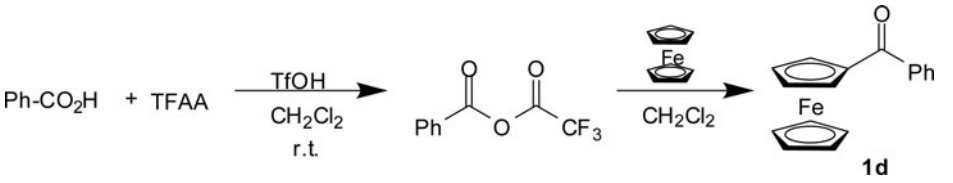
The best method for the preparation of ferrocenyl ketones **1** comprises the Friedel–Crafts acylation, and in the case of differocenyl ketone, the reported reaction was performed starting with ferrocene and ferrocenoyl chloride in the presence of $AlCl_3$ used in excess.[8] However, in our hands, this protocol turned out to be inefficient, and in the best case the desired ketone **1a** was obtained in only 25% yield. Therefore, we elaborated a new method based on acylation via the in situ-generated mixed anhydrides.[10] In the case of **1a**, ferrocenyl carboxylic acid was mixed with an equimolar amount of trifluoroacetic anhydride (TFAA) in the presence of trifluoroacetic acid (TFA) in CH_2Cl_2 solution at room temperature. Under these conditions, the added ferrocene underwent smooth acylation to give **1a** in reproducible and satisfactory yield (52%, Scheme 1). The same procedure was applied for the acylation of *N*-methylpyrrole and selenophene, leading to the desired non-symmetric ketones **1b** and **1c** (84 and 88% yield, respectively).



Scheme 1

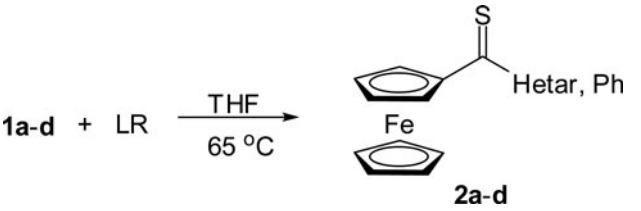
A modified procedure was applied for the preparation of ferrocenyl phenyl ketone **1d**, as the method presented above was unsuccessful. For that reason, the alternative mixed anhydride prepared from benzoic acid and TFAA in the presence of an equimolar amount of triflic acid (TfOH) in CH_2Cl_2 was prepared in situ at room temperature. Under these

conditions, the added ferrocene underwent benzoylation to afford ketone **1d** as 65% yield (Scheme 2).



Scheme 2

The transformation of ketones **1** into the corresponding thioketones **2** was smoothly achieved by their treatment with LR in tetrahydrofuran (THF) at 65°C. The crude products were purified by column chromatography and isolated as green solids in 75–85% yield (Scheme 3).

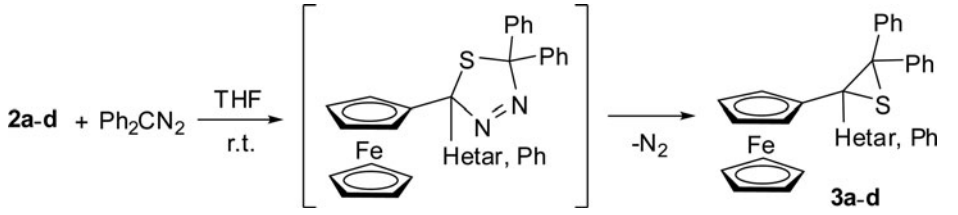


Scheme 3

Aromatic thioketones are known to react with diazomethane and its derivatives at low temperature, yielding 2,5-dihydro-1,3,4-thiadiazoles as the products of [3+2] cycloadditions.[11] Upon heating, these cycloadducts eliminate N_2 and generate in situ the reactive thiocarbonyl ylides, which, depending on the type of substituents and the reaction conditions, are converted into thiiranes, 1,4-dithianes, 1,3-dithiolanes, etc. The latter heterocycles were obtained as the sole products from the reaction of diazomethane with hetaryl thioketones.[9] However, in the series of aryl selenophenyl thioketones, the intermediate thiocarbonyl ylides unexpectedly dimerize to give 12-membered diselenaheterocycles via a postulated diradical intermediate.[12]

The test experiments with diazomethane and thioketone **2a** were performed in tetrahydrofurane (THF) solution at room temperature as well as at –60°C. In both cases, immediate disappearance of the typical color of thioketone was observed, but after a few minutes at room temperature, the solutions turned black and no defined products could be isolated. Similar course of reaction was observed in the attempted reaction of **2a** with 2-diazopropane.

Finally, the reaction of **2a** with the less reactive diphenyldiazomethane was performed in THF at room temperature. In this case, the thin layer chromatography (TLC) analysis evidenced the formation of a single product, which was identified as the symmetrical diferrocenyl-substituted thiirane **3a** on the basis of spectroscopic data (Scheme 4). Thus, in the ^{13}C NMR spectrum, the diagnostic C-signals of thiirane were found at 64.8 and 69.6 ppm. Similarly, reactions of diphenyldiazomethane with **2b–d** occurred smoothly under the same conditions leading to non-symmetrical thiiranes **3b–d**, respectively.



Scheme 4

It is worth mentioning that the ferrocenyl-substituted thiiranes **3** are stable under standard conditions and can be used for further applications aimed at the preparation of more complex ferrocenyl-containing products.

CONCLUSIONS

The method for the preparation of ferrocenyl ketones via the Friedel–Crafts acylation with trifluoroacetyl-containing mixed anhydrides opens a straightforward access to this class of compounds. These ketones can be conveniently transformed into the corresponding aryl/hetaryl ferrocenyl thioketones. Their reactions with reactive diazo compounds, such as diazomethane or 2-diazopropane, lead to decomposition. On the other hand, the less reactive diphenyldiazomethane reacts with ferrocenyl thioketones via spontaneous elimination of N_2 to give ferrocenyl-substituted thiiranes as products of 1,3-dipolar electrocyclization of the intermediate thiocarbonyl ylide.

EXPERIMENTAL

General Methods

All solvents were dried over appropriate drying agents and distilled before use. Reactions of the prepared ketones and thioketones were carried out under argon. Melting points were determined in a capillary using a Stewart® SMP30. The IR spectra (KBr pellets) were recorded on a Nexus FT-IR spectrometer. The ^{1}H- and ^{13}C NMR spectra were measured on a Bruker Avance III (600 and 150 MHz, respectively) instrument using $CHCl_3$/$CDCl_3$ signals as references. Electrospray ionization–mass spectra (ESI-MS) were recorded on a Varian 500-MS IT mass spectrometer. The elemental analyses were recorded on a Vario Micro Cube. Flash chromatography was carried out using Silica gel 60 (Sigma-Aldrich, 230–400 mesh). The notation Fc in this study represents ferrocenyl.

Synthesis of Ketones 1a–c (General Procedure)

To a solution of ferrocenecarboxylic acid (2.17 mmol, 0.5 g) in dry CH_2Cl_2 (10 mL) was added TFAA (2.17 mmol, 0.3 mL). After stirring the mixture for ca. 2 min at room temperature, TFA (2.17 mmol, 0.16 mL) and the corresponding hetarene (2.17 mmol) were added. The progress of the reaction was monitored by TLC. After the 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 was evaporated. Crude products were purified by flash chromatography (CH_2Cl_2/CH_3OH, 99:1).

Diferrocenyl Ketone (1a)

Yield: 449 mg (52%). Orange solid, m.p.: 203.1–204.3°C [lit.[13], m.p. 204°C (decomposition)]. ^{1}H NMR: δ 4.21 (s, 10H, CH-Fc), 4.53 (t, $J_{H,H}$ = 1.8 Hz, 4H, CH-Fc), 5.00 (t, $J_{H,H}$ = 1.8 Hz, 4H, CH-Fc) ppm. ^{13}C NMR: δ 70.0, 70.6, 71.4 (18C, CH-Fc), 80.5 (2C, C-Fc), 199.2 (1C, C=O) ppm. IR: υ 3123 (m), 3105 (m), 3096 (m), 3089 (m), 1772 (w), 1608 (vs, C=O), 1541 (m), 1465 (vs), 1413 (m), 1395 (m), 1377 (s), 1355 (m), 1293 (vs), 1202 (m), 1106 (s), 1064 (s), 1054 (m), 1027 (m), 1009 (m), 904 (m), 836 (s), 819 (s), 807 (vs), 771 (m), 580 (m), 510 (m), 493 (vs), 478 (vs) cm^{-1}. ESI-MS 400 (8 $[M+2]^+$), 421 (100 $[M+Na]^+$), 422 (24 $[M+Na+1]^+$).

Ferrocenyl *N*-methylpyrrol-2-yl Ketone (1b)

Yield: 534 mg (84%). Red solid, m.p.: 113.9–115.4°C. ^{1}H NMR: δ 3.97 (s, 3H, CH_3), 4.22 (s, 5H, CH-Fc), 4.50 (t, $J_{H,H}$ = 1.8 Hz, 2H, CH-Fc), 4.95 (t, $J_{H,H}$ = 1.8 Hz, 2H, CH-Fc), 6.16 (dd, $J_{H,H}$ = 3.6, 2.4 Hz, 1H, $CH_{arom.}$), 6.84 (dd, $J_{H,H}$ = 2.4, 1.2 Hz, 1H, $CH_{arom.}$), 7.14 (dd, $J_{H,H}$ = 3.6, 1.2 Hz, 1H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 37.2 (1C, CH_3), 70.0, 71.0, 71.3 (9C, CH-Fc), 80.8 (1C, C-Fc), 107.6, 118.8, 129.8 (3C, $CH_{arom.}$), 131.3 (1C, $C_{arom.}$), 187.9 (1C, C=O) ppm. 70.4, 71.0, 72.2 (9 CH-Fc), 78.6 (C-Fc), 130.4, 133.4, 137.8 (3 $CH_{arom.}$), 151.4 ($C_{arom.}$), 190.5 (C=O) ppm. IR: υ 3118 (w), 3105 (m), 3082 (w), 2927 (w), 1600 (vs, C=O), 1524 (m), 1444 (vs), 1405 (vs), 1379 (s), 1320 (m), 1261 (s), 1206 (w), 1174 (w), 1066 (m), 1047 (m), 1021 (m), 940 (w), 844 (m), 836 (m), 823 (s), 745 (vs), 609 (m), 565 (m), 503 (s), 482 (s) cm^{-1}. ESI-MS 293 (20 $[M]^+$), 294 (100 $[M+1]^+$). Anal. calcd. for $C_{16}H_{15}FeNO$ (293.14): C 65.56, H 5.16, N 4.78; found: C 65.37, H 5.03, N 4.63.

Ferrocenyl Selenophen-2-yl Ketone (1c)

Yield: 655 mg (88%). Red solid, m.p.: 113.5–115.0°C. ^{1}H NMR: δ 4.24 (s, 5H, CH-Fc), 4.60 (t, $J_{H,H}$ = 1.8 Hz, 2H, CH-Fc), 5.02 (t, $J_{H,H}$ = 1.8 Hz, 2H, CH-Fc), 7.44 (dd, $J_{H,H}$ = 5.4, 3.6 Hz, 1H, $CH_{arom.}$), 8.15 (dd, $J_{H,H}$ = 3.6, 1.2 Hz, 1H, $CH_{arom.}$), 8.35 (dd, $J_{H,H}$ = 5.4, 1.2 Hz, 1H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 70.4, 71.0, 72.2 (9C, CH-Fc), 78.6 (1C, C-Fc), 130.4, 133.4, 137.8 (3C, $CH_{arom.}$), 151.4 (1C, $C_{arom.}$), 190.5 (1C, C=O) ppm. IR: υ 3096 (m), 3078 (m), 1767 (w), 1710 (w), 1594 (vs, C=O), 1557 (m), 1524 (s), 1443 (s), 1422 (vs), 1376 (s), 1290 (vs), 1152 (s), 1041 (vs), 823 (s), 769 (s), 747 (s), 710 (vs), 589 (w), 520 (m), 498 (s), 485 (s) cm^{-1}. ESI-MS 343 (45 $[M]^+$), 344 (73 $[M+1]^+$), 345 (100 $[M+2]^+$), 365 (58 $[M+Na-1]^+$). Anal. calcd. for $C_{15}H_{12}FeOSe$ (343.06): C 52.52, H 3.53; found: C 52.22, H 3.51.

Synthesis of Ketone 1d

A solution of benzoic acid (2.69 mmol, 0.33 g) and TFAA (2.69 mmol, 0.37 mL) in dry CH_2Cl_2 (10 mL) was stirred for ca. 2 min at room temperature. Then, TfOH (2.69 mmol, 0.16 mL) and ferrocene (2.69 mmol, 0.5 g) were added. The progress of the reaction was monitored by TLC. The subsequent work-up procedure was analogous to the one described for ketones **1a–c**.

Ferrocenyl Phenyl Ketone (1d)

Yield: 507 mg (65%). Red solid, m.p.: 106.5°C [lit.[14], m.p. 106–107°C]. ^{1}H NMR: δ 4.20 (s, 5H, CH-Fc), 4.58 (t, $J_{H,H} = 1.8$ Hz, 2H, CH-Fc), 4.90 (t, $J_{H,H} = 1.8$ Hz, 2H, CH-Fc), 7.46 (t, $J_{H,H} = 7.7$ Hz, 2H, $CH_{arom.}$), 7.54 (t, $J_{H,H} = 7.3$ Hz, 1H, $CH_{arom.}$), 7.89 (d, $J_{H,H} = 7.3$ Hz, 2H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 70.2, 71.5, 72.5 (9C, CH-Fc), 78.2 (1C, C-Fc), 128.0, 128.2, 131.4 (5C, $CH_{arom.}$), 139.9 (1C, $C_{arom.}$), 199.0 (1C, C=O) ppm. IR: υ 3113 (w), 3091 (w), 3065 (w), 1626 (vs, C=O), 1597 (s), 1577 (s), 1450 (s), 1440 (s), 1375 (s), 1289 (vs), 1166 (m), 1057 (m), 1025 (s), 1003 (m), 952 (m), 826 (s), 724 (vs), 696 (s), 676 (m), 564 (m) cm^{-1}. ESI-MS 290 (31 $[M]^+$), 291 (100 $[M+1]^+$), 313 (54 $[M+Na]^+$). Anal. calcd. for $C_{17}H_{14}FeO$ (290.14): C 70.37, H 4.86; found: C 70.41, H 4.83.

Synthesis of Thioketones 2a–d (General Procedure)

The solution of the corresponding ketone **1** (1 mmol) in THF or benzene (5 mL) was heated to 65°C, and next LR (0.6 mmol, 0.24 g) was added. After the complete reaction (TLC), the mixture was concentrated and the crude product was purified by flash chromatography (hexane/CH_2Cl_2, 7:3).

Diferrocenyl Thioketone (2a)

Yield: 311 mg (75%). Violet solid, m.p.: >135°C (decomposition) [lit.[8], m.p. 135°C (decomposition)]. ^{1}H NMR: δ 4.20 (s, 10H, CH-Fc), 4.68 (s, 4H, CH-Fc), 5.22 (s, 4H, CH-Fc) ppm. ^{13}C NMR: δ 71.3, 72.5, 72.6 (18C, CH-Fc), 90.4 (2C, C-Fc), 237.1 (1C, C=S) ppm. IR: υ 3120 (w), 3096 (m), 3084 (m), 2958 (w), 2922 (m), 2851 (w), 1677 (m), 1654 (m), 1623 (m), 1594 (m), 1443 (vs), 1430 (s), 1400 (m), 1378 (m), 1352 (m), 1334 (m), 1286 (s), 1249 (vs), 1206 (m), 1190 (m), 1105 (m), 1073 (s), 1045 (s), 1004 (s), 945 (m), 887 (m), 873 (m), 847 (m), 830 (s), 817 (vs), 767 (m), 696 (m), 546 (m), 516 (s), 484 (vs), 474 (vs), 444 (m) cm^{-1}. ESI-MS 414 (4 $[M]^+$), 415 (100 $[M+1]^+$), 416 (26 $[M+2]^+$).

Ferrocenyl *N*-methylpyrrol-2-yl Thioketone (2b)

Yield: 263 mg (85%). Violet solid, m.p.: 102.0–102.8°C. ^{1}H NMR: δ 3.97 (s, 3H, CH_3), 4.18 (s, 5H, CH-Fc), 4.68 (t, $J_{H,H} = 1.8$ Hz, 2H, CH-Fc), 5.11 (t, $J_{H,H} = 1.8$ Hz, 2H, CH-Fc), 6.14 (dd, $J_{H,H} = 4.2$, 2.4 Hz, 1C, $CH_{arom.}$), 6.85 (dd, $J_{H,H} = 4.2$, 1.8 Hz, 1C, $CH_{arom.}$), 7.72 (dd, $J_{H,H} = 2.4$, 1.8 Hz, 1C, $CH_{arom.}$) ppm. ^{13}C NMR: δ 37.4 (CH_3), 71.6, 72.8, 72.9 (9C, CH-Fc), 91.1 (1C, C-Fc), 107.6, 117.1, 132.9 (3C, $CH_{arom.}$), 142.4 (1C, $C_{arom.}$), 218.0 (1C, C=S) ppm. IR: υ 3105 (m), 2948 (w), 1636 (w), 1518 (m), 1454 (s), 1432 (vs), 1401 (vs), 1271 (vs), 1242 (m), 1188 (m), 1068 (s), 1048 (s), 1020 (s), 1002 (m), 830 (m), 821 (m), 784 (s), 742 (vs), 702 (m), 604 (m), 493 (s) cm^{-1}. ESI-MS 309 (54 $[M]^+$), 310 (100 $[M+1]^+$). Anal. calcd. for $C_{16}H_{15}FeNS$ (309.21): C 62.15, H 4.89, N 4.53, S 10.37; found: C 62.36, H 4.94, N 4.53, S 10.75.

Ferrocenyl Selenophen-2-yl Thioketone (2c)

Yield: 298 mg (83%). Green solid, m.p.: 83.5–85.0°C. ^{1}H NMR: δ 4.22 (s, 5H, CH-Fc), 4.78 (s, 2H, CH-Fc), 5.15 (s, 2H, CH-Fc), 7.45 (brs/m, 1H, $CH_{arom.}$), 7.94 (brs/m, 1H, $CH_{arom.}$), 8.35 (brs/m, 1H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 72.2, 73.0, 73.8 (9C, CH-Fc), 88.5

(1C, C-Fc), 129.3, 131.2, 141.4 (3C, $CH_{arom.}$), 162.0 (1C, $C_{arom.}$), 224.9 (1C, C=S) ppm. IR: υ 3083 (m), 1503 (m), 1432 (vs), 1410 (vs), 1379 (s), 1332 (vs), 1285 (v), 1274 (s), 1228 (vs), 1214 (s), 1171 (m), 1107 (m), 1058 (s), 1042 (s), 1001 (m), 977 (m), 860 (s), 830 (s), 808 (s), 716 (vs), 681 (m), 641 (m), 588 (m), 506 (s), 483 (s) cm^{-1}. ESI-MS 359 (48 $[M]^+$), 361 (100 $[M+2]^+$). Anal. calcd. for $C_{15}H_{12}FeSSe$ (359.13): C 50.17, H 3.37, S 8.93; found: C 50.25, H 3.42, S 8.97.

Ferrocenyl Phenyl Thioketone (2d)[7]

Yield: 254 mg (83%). Violet solid, m.p.: 71.2–72.5°C. ^1H NMR: δ 4.17 (s, 5H, CH-Fc), 4.82 (s, 2H, CH-Fc), 5.05 (s, 2H, CH-Fc), 7.37 (brs/m, 2H, $CH_{arom.}$), 7.47 (brs/m, 1H, $CH_{arom.}$), 7.67 (d, $J_{H,H} = 6.0$ Hz, 2H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 72.1, 72.6, 74.8 (9C, CH-Fc), 89.4 (1C, C-Fc), 126.9, 127.6, 130.1 (5C, $CH_{arom.}$), 149.0 (1C, $C_{arom.}$), 238.7 (1C, C=S) ppm. IR: υ 3108 (w), 3095 (w), 3073 (w), 3058 (w), 2925 (w), 2852 (w), 1592 (m), 1444 (s), 1431 (vs), 1398 (m), 1374 (s), 1294 (s), 1280 (vs), 1242 (vs), 1175 (m), 1108 (m), 1087 (m), 1065 (s), 1007 (vs), 932 (m), 827 (vs), 768 (vs), 701 (vs), 684 (s), 635 (m), 506 (vs), 483 (vs) cm^{-1}. ESI-MS 230 (24 $[M–Ph+1]^+$), 307 (100 $[M+1]^+$), 308 (25 $[M+2]^+$). Anal. calcd. for $C_{17}H_{14}FeS$ (306.20): C 66.68, H 4.61, S 10.47; found: C 66.82, H 4.73, S 10.42.

Synthesis of Thiiranes 3a–d (General Procedure)

To a solution of the appropriate thioketone **2** (1 mmol) in dry THF (4 mL) was added a solution of diphenyldiazomethane (1 mmol, 0.19g) in dry THF (2 mL). After stirring overnight, the reaction was completed (according to TLC). The solvent was evaporated and the product was purified by flash chromatography (hexane/CH_2Cl_2, 7:3).

3,3-Diferrocenyl-2,2-diphenylthiirane (3a)

Yield: 320 mg (55%). Orange solid, m.p.: >183°C (decomposition). ^1H NMR: δ 3.95–3.97 (m, 2H, CH-Fc), 4.04 (s, 10H, CH-Fc), 4.09–4.10 (m, 2H, CH-Fc), 4.11–4.12 (m, 2H, CH-Fc), 4.13–4.14 (m, 2H, CH-Fc), 7.09–7.13 (m, 2H, $CH_{arom.}$), 7.15–7.19 (m, 4H, $CH_{arom.}$), 7.42 (brs, 4H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 59.1, 72.3 (2C, Cq), 66.4, 67.4, 69.5, 70.7, 70.8 (18C, CH-Fc), 92.6 (2C, C-Fc), 126.5, 127.6, 130.1 (10C, $CH_{arom.}$), 143.9 (2C, $C_{arom.}$) ppm. IR: υ 3091 (m), 3082 (m), 3053 (w), 3026 (w), 1595 (m), 1487 (m), 1444 (m), 1412 (m), 1273 (m), 1199 (m), 1158 (m), 1106 (m), 1063 (m), 1025 (m), 1000 (m), 817 (s), 807 (s), 780 (m), 745 (m), 704 (vs), 689 (s), 633 (m), 605 (m), 571 (m), 529 (m), 490 (vs) cm^{-1}. ESI-MS 548 (100 $[M–S]^+$), 549 (49 $[M–S+1]^+$), 580 (79 $[M]^+$), 581 (40 $[M+1]^+$). Anal. calcd. for $C_{34}H_{28}Fe_2S$ (580.34): C 70.37, H 4.86, S 5.53; found: C 70.62, H 4.63, S 5.59.

3-Ferrocenyl-2,2-diphenyl-3-(*N*-methylpyrrol-2-yl)thiirane (3b)

Yield: 252 mg (53%). Yellow solid, m.p.: >73°C (decomposition). ^1H NMR: δ 3.11 (s, 3H, CH_3), 3.40–3.41 (m, 1H, CH-Fc), 3.81–3.82 (m, 1H, CH-Fc), 3.84–3.85 (m, 1H, CH-Fc), 4.00–4.01 (m, 1H, CH-Fc), 4.13 (s, 5H, CH-Fc), 6.11 (dd, $J_{H,H} = 3.6$, 3.0 Hz, 1H, $CH_{arom.}$), 6.25 (t, $J_{H,H} = 1.8$ Hz, 1H, $CH_{arom.}$), 6.60 (dd, $J_{H,H} = 3.6$, 2.4 Hz, 1H, $CH_{arom.}$), 6.96–7.0 (m, 2H, $CH_{arom.}$), 7.02–7.08 (m, 3H, $CH_{arom.}$), 7.21–7.26 (m, 5H, $CH_{arom.}$) ppm.

^{13}C NMR: δ 34.4 (1C, CH_3), 57.3, 69.0 (2C, Cq), 67.3, 67.4, 69.4, 69.9, 70.8 (9C, CH-Fc), 92.1 (1C, C-Fc), 106.7, 114.3, 120.9, 126.6, 126.8, 127.0, 129.0, 132.3 (13C, $CH_{arom.}$), 131.6, 139.6, 140.3 (3C, $C_{arom.}$) ppm. IR: υ 3085 (w), 3057 (w), 2953 (w), 2926 (w), 1491 (m), 1444 (m), 1307 (m), 1106 (m), 1078 (w), 1055 (w), 1030 (w), 1002 (m), 818 (m), 783 (m), 753 (m), 736 (m), 699 (s), 609 (w), 498 (m) cm^{-1}. ESI-MS 443 (28 $[M–S]^+$), 475 (100 $[M]^+$), 476 (40 $[M+1]^+$). Anal. calcd. for $C_{29}H_{25}FeNS$ (475.43): C 73.26, H 5.30, N 2.95, S 6.74; found: C 73.32 H 5.41, N 3.04, S 6.69

3-Ferrocenyl-2,2-diphenyl-3-(selenophen-2-yl)thiirane (3c)

Yield: 298 mg (57%). Yellow solid, m.p.: 125.0–126.7°C. ^{1}H NMR: δ 3.66 (s, 1H, CH-Fc), 3.87 (s, 1H, CH-Fc), 4.07 (s, 5H, CH-Fc), 4.09 (s, 1H, CH-Fc), 4.39 (s, 1H, CH-Fc), 6.98–7.08 (m, 4H, $CH_{arom.}$), 7.13 (brs, 3H, $CH_{arom.}$), 7.19–7.27 (m, 3H, $CH_{arom.}$), 7.30 (d, $J_{H,H} = 6.6$ Hz, 2H, $CH_{arom.}$), 7.76 (d, $J_{H,H} = 4.8$ Hz, 1H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 60.7, 72.2 (2C, Cq), 67.6, 68.2, 69.2, 70.5, 71.1 (9C, CH-Fc), 90.2 (1C, C-Fc), 126.5, 126.7, 127.2, 128.2, 129.4, 130.4, 131.1, 131.2 (13C, $CH_{arom.}$), 140.4, 141.2, 151.9 (3C, $C_{arom.}$) ppm. IR: υ 3082 (m), 3055 (m), 3026 (m), 2922 (m), 2850 (m), 1598 (m), 1490 (m), 1444 (m), 1227 (m), 1106 (m), 1079 (m), 1032 (m), 1001 (m), 818 (m), 777 (m), 750 (m), 696 (s), 658 (m), 604 (m), 491 (m) cm^{-1}. ESI-MS 524 (50 $[M–1]^+$), 526 (100 $[M+1]^+$), 527 (28 $[M+2]^+$). Anal. calcd. for $C_{28}H_{22}FeSSe$ (525.34): C 64.02, H 4.22, S 6.10; found: C 64.09, H 4.31, S 6.11.

3-Ferrocenyl-2,2,3-triphenyl Thiirane (3d)

Yield: 240 mg (51%). Yellow solid, m.p.: 150.2–152.2°C. ^{1}H NMR: δ 3.61 (s, 1H, CH-Fc), 3.87 (s, 2H, CH-Fc), 4.02 (s, 6H, CH-Fc), 6.90–6.93 (m, 3H, $CH_{arom.}$), 7.05–7.09 (m, 1H, $CH_{arom.}$), 7.12–7.20 (m, 6H, $CH_{arom.}$), 7.23–7.29 (m, 2H, $CH_{arom.}$), 7.38 (brs, 2H, $CH_{arom.}$) ppm. ^{13}C NMR: δ 64.8, 69.6 (2C, Cq), 67.8, 68.2, 68.9, 70.0, 71.2 (9C, CH-Fc), 91.8 (1C, C-Fc), 126.2, 126.6, 126.7, 126.8, 127.0, 127.1, 129.2, 131.5, 131.7 (15C, $CH_{arom.}$), 138.9, 140.1, 140.9 (3C, $C_{arom.}$) ppm. IR: υ 3081 (w), 3052 (m), 3025 (m), 2923 (w), 2850 (w), 1597 (w), 1491 (m), 1444 (m), 1107 (m), 1078 (m), 1028 (m), 1002 (m), 816 (m), 780 (m), 751 (m), 723 (m), 698 (s), 660 (m), 601 (m), 512 (m), 484 (m) cm^{-1}. ESI-MS 439 (24 $[M–S+1]^+$), 472 (100 $[M]^+$), 473 (55 $[M+1]^+$). Anal. calcd. for $C_{30}H_{24}FeS$ (472.42): C 76.27, H 5.12, S 6.79; found: C 76.26, H 4.97, S 7.18.

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