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New ferrocene containing 3-(arylthio)propan-1-ones: Synthesis, spectral characterization and crystal structure of 3-[(4-chlorophenyl)thio] -1-ferrocenylpropan-1-one, 3-[(4-chlorophenyl)thio]-1-ferrocenyl -3-phenylpropan-1-one and 3-[(4-chlorophenyl)thio]-3-ferrocenyl-1-phenylpropan-1-one

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Dedicated to Professor Vukadin Leovac, good colleague, dear friend and exceptional scientist, on the happy occasion of his 70th birthday.

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ABSTRACT

Three series of ferrocene containing 3-(arylthio)propan-1-ones (each of eight examples) have been synthesized by thia-Michael addition of the corresponding thiophenols to acryloylferrocene, 1-ferrocenyl-3-phenylprop-2-en-1-one and 3-ferrocenyl-1-phenylprop-2-en-1-one promoted by the catalyst generated from a sacrificial zirconium anode. All the newly synthesized compounds (16 in total) were characterized by spectral data, whereas single crystal X-ray structure analysis was performed for 3-[(4-chlorophenyl)thio]-1-ferrocenylpropan-1-one (**1h**), 3-[(4-chlorophenyl)thio]-1-ferrocenyl-3-phenylpropan-1-one (**2h**) and 3-[(4-chlorophenyl)thio]-3-ferrocenyl-1-phenylpropan-1-one (**3h**). Molecular geometry and structural characteristics of three thiaketones (**1h**, **2h** and **3h**) were analysed and compared in detail. It was found that all three molecules do not form classical H-bonds and π···π interactions (regardless of the presence of 3 or 4 aromatic rings per a molecule). However, all three crystal structures abound in intermolecular C–H···π interactions while **2h** and **3h** in addition form intramolecular C–H···π as only evident interaction within the molecules.

1. Introduction

Several important properties of zirconium compounds caused their widespread use as catalysts of many synthetic important reactions [1–3]. First of all, metal zirconium and both classes of zirconium compounds, Zr(IV) and ZrO(II), as well as zirconium oxide, are commercially available and relatively inexpensive chemicals. Zirconium compounds are relatively insensitive to moisture, easily handled, of low toxicity and with high catalytic activity in many reactions, such as Friedel–Crafts acylations [4], Fries rearrangements [5], sodium borohydride reductions [6,7], multicomponent condensations affording dihydropyrimidinones [8] and β-aryl-β-mercaptoketones [9], esterifications of long chain aliphatic carboxylic acids and alcohols [10], Pechmann reactions [11], etc. [1–3]. The particular attention synthetics paid to application of zirconium compounds as catalysts of Michael reaction [12–18]. Recently, we reported on the suitable and simple application of anodic dissolution of a zirconium electrode for the generation of a catalyst promoting successful Ferrier rearrangement, as well as thia- and aza-Michael reactions (addition of amines and thiols to conjugated carbonyls, respectively) [19]. In continuation of our permanent interest in synthetic applications of sacrificial anode [19,20], as well as in synthesis of sulfur containing ferrocene derivatives [21–25], in this paper we describe the synthesis and spectral characterisation of three classes of ferrocene containing β-(arylthio)propan-1-ones **1–3** (Fig. 1) utilising electrochemical generated zirconium catalyst to promote addition of thiophenols to the corresponding conjugated enones.

The synthesized compounds are surely of interest to the broad auditorium of synthetics working in ferrocene chemistry, particularly to those occupied with the synthesis of derivatives of this metalocene bearing two electron-donating groups (bidentate ligands). Since β-(arylthio)propan-1-ones already contain a sulfur atom, the additional electron-donating group can be designed by diverse transformations of the carbonyl group, utilising the classical synthetic methods, such as reduction to the corresponding alcohol and successive substation of the hydroxyl group with nucleophiles,

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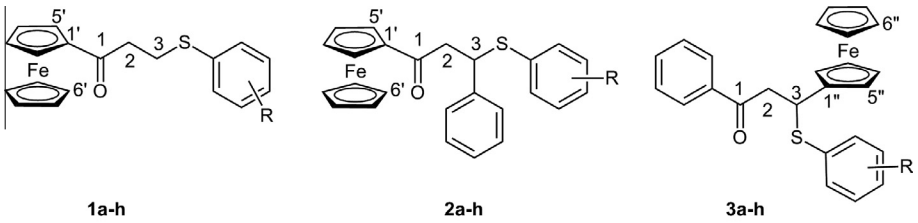


a) R = H, **b)** R = *o*-CH_3, **c)** R = *m*-CH_3, **d)** R = *p*-CH_3, **e)** R = *p*-$C(CH_3)_3$, **f)** R = *o*-Cl, **g)** *m*-Cl, **h)** *p*-Cl

Fig. 1. Synthesized β-(arylthio)propan-1-ones with the assignation of C atoms for ^{1}H NMR and ^{13}C NMR spectra description.

condensations with amines, hydroxylamine(s), hydrazine(s), etc., and further transformations of such obtained products.

2. Experimental

2.1. Materials and instruments

All chemicals were commercially available and used as received, except that the solvents were purified by distillation. The starting enones were prepared as described elsewhere in the literature [26,27]. Electrolyses were carried out in an udivided cell using an Autolab potentiostat and a Uniwatt, Beha Labor-Netzgerät (NG 394). A glass vessel provided with a spiral Zr-anode (ϕ = 15 mm, made from a ϕ = 2 mm wire) and a spiral Pt-cathode (ϕ = 8 mm, made from a ϕ = 1 mm wire) was used as the electrolytic cell. A cylindrical platinum foil (2.5 cm diameter) and a platinum spiral (1 cm diameter) were used as the working and the counter electrode, respectively. Ultrasonic cleaner Elmasonic S 10, 30 W was used for the ultrasonically supported electrolysis. Chromatographic separations were carried out using silica gel 60 (Merck, 230–400 mesh ASTM), whereas silica gel 60 on Al plates, layer thickness 0.2 mm (Merck) was used for TLC. Melting points (uncorrected) were determined on a Mel-Temp capillary melting points apparatus, model 1001. The ^{1}H and ^{13}C NMR spectra of the samples in $CDCl_3$ were recorded on a Varian Gemini (200 MHz) spectrometer. Chemical shifts are expressed in δ (ppm), relative to the residual solvent protons or $^{13}CDCl_3$ as internal standards ($CHCl_3$: 7.26 ppm for ^{1}H and 77 ppm for ^{13}C). IR measurements were carried out with a Perkin-Elmer FTIR 31725-X spectrophotometer.

2.2. Synthetic procedure

The electrolytic cell was filled with 10 mL of an acetonitrile solution of $LiClO_4$ (0.1 M), 1 mmol of enone **4**–**6** and 2 mmol of the corresponding nuclephile **7a**–**h**. The cell was placed in the ultrasound bath (at a frequency of 37 kHz, with an effective ultrasonic power of 30 W and a peak of 240 W) and the constant current electrolysis (20 mA) was run 32 min (0.4 F mol^{-1}) at room temperature. After the electrolysis was finished, the reaction mixture was left 30 min in the same bath and the solvent evaporated. The residue was diluted with 20 mL of water, the obtained mixture extracted with three 20 mL portions of ethyl acetate and collected organic layers dried overnight (anhydrous sodium sulfate). After evaporation of the solvent the crude reaction product was purified by column chromatography to give the products of the reaction. The spectral data of known compounds were in complete agreement with those published elsewhere (**1a** [28], **1c** [29], **1d** [29], **1g** [29], **1h** [29], **2a** [30], **2h** [30], and **3a** [30]), whereas the data confirming structures of newly synthesized ones follow.

*2.2.1. 1-Ferrocenyl-3-(o-tolylthio)propan-1-one (**1b**)*

m.p. 62 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 1H, Ar), 7.24–7.03 (m, 3H, Ar), 4.73 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, Cp), 4.47 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, Cp), 4.14 (s, 5H, 5 × CH, Cp), 3.17 (A_2B_2, 4H, 2 × CH_2), 2.37 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 201.7, 137.4, 135.2, 130.1, 127.4, 126.4, 125.6, 78.4, 72.2, 69.7, 69.1, 38.7, 26.7, 20.2; IR: 3098, 2923, 1666.

*2.2.2. 1-Ferrocenyl-3-[(4-tert-butylphenyl)thio]propan-1-one (**1e**)*

m.p. 96 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.03 (m, 4H, Ar), 4.74 (pseudo t, *J* = 2.2 Hz, 2H, 2 × CH, Cp), 4.15 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, Cp), 4.15 (s, 5H, 5 × CH, Cp), 3.20 (A_2B_2, 4H, 2 × CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 201.3, 135.5, 133.1, 129.6, 127.8, 127.0, 126.3, 78.2, 72.3, 69.7, 69.0, 38.2, 26.2; IR: 3101, 2926, 1663.

*2.2.3. 3-[(2-Chlorophenyl)thio]-1-ferrocenylpropan-1-one (**1f**)*

m.p. 96 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.41–7.03 (m, 4H, Ar), 4.74 (pseudo t, *J* = 2.2 Hz, 2H, 2 × CH, Cp), 4.15 (pseudo t, *J* = 2.0 Hz, 2H, 2 × CH, Cp), 4.15 (s, 5H, 5 × CH, Cp), 3.20 (A_2B_2, 4H, 2 × CH_2); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 201.3, 135.5, 133.1, 129.6, 127.8, 127.0, 126.3, 78.2, 72.3, 69.7, 69.0, 38.2, 26.2; IR: 3101, 2926, 1663.

*2.2.4. 1-Ferrocenyl-3-phenyl-3-(o-tolylthio)propan-1-one (**2b**)*

m.p. 91 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.53–7.04 (m, 9H, Ar), 4.95 (dd, *J* = 8.8, 5.2 Hz, 1H, CH), 4.74–4.68 (m, 2H, 2 × CH, Cp), 4.46–4.43 (m, 2H, 2 × CH, Cp), 3.96 (s, 5H, 5 × CH, Cp), 3.42 (dd, *J* = 17.3, 8.8 Hz, 1H, CH_aH_b), 3.25 (dd, *J* = 17.3, 5.2 Hz, 1H, CH_aH_b), 2.37 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.5, 141.6, 139.8, 133.9, 132.3, 130.2, 128.4, 127.9, 127.4, 127.2, 126.3, 78.6, 72.3, 72.2, 69.7, 69.2, 69.0, 46.9, 46.1, 20.6; IR: 3112, 2923, 2852, 1659.

*2.2.5. 1-Ferrocenyl-3-phenyl-3-(m-tolylthio)propan-1-one (**2c**)*

m.p. 72 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.45–6.97 (m, 9H, Ar), 4.99 (dd, *J* = 9.0, 5.0 Hz, 1H, CH), 4.69 (brd, *J* = 6.4 Hz, 2H, 2 × CH, Cp), 4.44 (pseudo t, *J* = 1.8 Hz, 2H, 2 × CH, Cp), 3.94 (s, 5H, 5 × CH, Cp), 3.40 (dd, *J* = 17.3, 9.0 Hz, 1H, CH_aH_b), 3.22 (dd, *J* = 17.3, 5.0 Hz, 1H, CH_aH_b), 2.26 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.6, 141.6, 138.5, 134.4, 132.7, 129.0, 128.6, 128.4, 128.1, 128.0, 127.4, 78.7, 72.3, 72.2, 69.6, 69.2, 69.0, 47.5, 46.2, 21.2; IR: 3114, 2922, 2852, 1658.

*2.2.6. 1-Ferrocenyl-3-phenyl-3-(p-tolylthio)propan-1-one (**2d**)*

m.p. 80 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.44–7.39 (m, 2H, Ar), 7.33–7.13 (m, 5H, Ar), 7.06–7.02 (m, 2H, Ar), 4.92 (dd, *J* = 9.0, 5.1 Hz, 1H, CH), 4.73–4.65 (m, 2H, 2 × CH, Cp), 4.44 (pseudo t, *J* = 1.8 Hz, 2H, 2 × CH, Cp), 3.94 (s, 5H, 5 × CH, Cp), 3.39 (dd, *J* = 17.2, 9.0 Hz, 1H, CH_aH_b), 3.20 (dd, *J* = 17.2, 5.1 Hz, 1H, CH_aH_b), 2.27 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.6, 141.7, 137.5, 132.8, 130.9, 129.6, 128.4, 128.0, 127.4, 78.7, 72.3, 72.2, 69.6, 69.2, 69.0, 48.1, 46.1, 21.0; IR: 3110, 2921, 1660.

*2.2.7. 3-[(4-tert-Butylphenyl)thio]-1-ferrocenyl-3-phenylpropan-1-one (**2e**)*

m.p. 143 °C; ^{1}H NMR (200 MHz, $CDCl_3$): δ = 7.47–7.41 (m, 2H, Ar), 7.37–7.19 (m, 7H, Ar), 4.95 (dd, *J* = 9.2, 4.9 Hz, 1H, CH), 4.73–4.64 (m, 2H, 2 × CH, Cp), 4.44 (pseudo t, *J* = 1.9 Hz, 2H, 2 × CH, Cp), 3.92 (s, 5H, 5 × CH, Cp), 3.40 (dd, *J* = 17.3, 9.2 Hz, 1H, CH_aH_b),

3.22 (dd, J = 17.3, 4.9 Hz, 1H, CH_aH_b), 1.26 (s, 9H, 3 × CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.7, 150.6, 141.6, 132.2, 131.2, 128.5, 128.0, 127.4, 125.9, 78.7, 72.3, 72.2, 69.7, 69.2, 69.1, 47.9, 46.3, 34.5, 31.2; IR: 3111, 2955, 1657.

*2.2.8. 3-[(2-Chlorophenyl)thio]-1-ferrocenyl-3-phenylpropan-1-one (**2f**)*

m.p. 133 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.57–7.45 (m, 2H, Ar), 7.40–7.03 (m, 7H, Ar), 5.15 (dd, J = 9.3, 4.6 Hz, 1H, CH), 4.73–4.68 (m, 2H, 2 × CH, Cp), 4.46 (pseudo t, J = 1.8 Hz, 2H, 2 × CH, Cp), 3.94 (s, 5H, 5 × CH, Cp), 3.47 (dd, J = 17.3, 9.3 Hz, 1H, CH_aH_b), 3.24 (dd, J = 17.3, 4.6 Hz, 1H, CH_aH_b); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.2, 140.8, 135.2, 134.3, 131.6, 129.7, 128.6, 128.0, 127.7, 127.6, 127.1, 78.5, 72.4, 72.3, 69.7, 69.2, 69.0, 46.2, 46.0; IR: 3119, 2923, 1659.

*2.2.9. 3-[(3-Chlorophenyl)thio]-1-ferrocenyl-3-phenylpropan-1-one (**2g**)*

m.p. 108 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2H, Ar), 7.34–7.14 (m, 7H, Ar), 5.03 (dd, J = 8.6, 5.4 Hz, 1H, CH), 4.74–4.71 (m, 2H, 2 × CH, Cp), 4.48 (pseudo t, J = 1.8 Hz, 2H, 2 × CH, Cp), 3.98 (s, 5H, 5 × CH, Cp), 3.41 (dd, J = 17.2, 8.6 Hz, 1H, CH_aH_b), 3.26 (dd, J = 17.2, 5.4 Hz, 1H, CH_aH_b); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 200.2, 141.1, 136.8, 134.4, 131.4, 129.8, 129.6, 128.6, 128.0, 127.6, 127.2, 78.5, 72.4, 72.3, 69.7, 69.2, 69.0, 47.5, 46.1; IR: 3115, 2923, 1656.

*2.2.10. 3-Ferrocenyl-1-phenyl-3-(o-tolylthio)propan-1-one (**3b**)*

m.p. 83 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.02–7.79 (m, 2H, Ar), 7.61–7.32 (m, 4H, Ar), 7.22–6.99 (m, 3H, Ar), 4.77 (dd, J = 6.9, 5.8 Hz, 1H, CH), 4.20–3.98 (m, 8H, 8 × CH, Cp), 3.96–3.88 (m, 1H, 1 × CH, Cp), 3.61 (dd, J = 17.1, 5.8 Hz, 1H, CH_aH_b), 3.51 (dd, J = 17.1, 6.9 Hz, 1H, CH_aH_b), 2.29 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.4, 141.0, 136.9, 134.1, 133.7, 133.1, 130.2, 128.5, 128.0, 127.7, 126.2, 90.0, 68.7, 67.8, 67.7, 67.6, 66.6, 44.6, 43.4, 20.8; IR: 3087, 3058, 2919, 2898, 1682.

*2.2.11. 3-Ferrocenyl-1-phenyl-3-(m-tolylthio)propan-1-one (**3c**)*

m.p. 93 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.96–7.88 (m, 2H, Ar), 7.62–7.38 (m, 3H, Ar), 7.22–6.97 (m, 4H, Ar), 4.82 (pseudo t, J = 6.5 Hz, 1H, CH), 4.18–4.06 (m, 9H, 9 × CH, Cp), 3.54 (pseudo d, J = 6.5 Hz, 2H, CH_2), 2.24 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.6, 138.4, 136.9, 134.1, 133.8, 133.1, 130.3, 128.6, 128.5, 128.3, 128.1, 90.0, 68.7, 67.8, 67.7, 67.6, 66.9, 44.5. 43.8, 21.1; IR: 3086, 3056, 2920, 2895, 1682.

*2.2.12. 3-Ferrocenyl-1-phenyl-3-(p-tolylthio)propan-1-one (**3d**)*

m.p. 139 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.97–7.88 (m, 2H, Ar), 7.60–7.38 (m, 3H, Ar), 7.27–7.16 (m, 2H, Ar), 7.04–7.00 (m, 2H, Ar), 4.76 (pseudo t, J = 6.5 Hz, 1H, CH), 4.17–4.02 (m, 9H, 9 × CH, Cp), 3.53 (pseudo d, J = 6.5 Hz, 2H, CH_2), 2.28 (s, 3H, CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.6, 137.6, 136.9, 134.0, 133.1, 130.3, 129.4, 128.5, 128.1, 90.0, 68.7, 67.8, 67.7, 67.5, 66.8, 44.3, 44.2, 21.1; IR: 3089, 2917, 2855, 1673.

*2.2.13. 3-[(4-tert-Butylphenyl)thio]-3-ferrocenyl-1-phenylpropan-1-one (**3e**)*

m.p. 118 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.94–7.85 (m, 2H, Ar), 7.56–7.15 (m, 7H, Ar), 4.81 (pseudo t, J = 6.5 Hz, 1H, CH), 4.17–4.03 (m, 9H, 9 × CH, Cp), 3.55 (pseudo d, J = 6.5 Hz, 2H, CH_2), 1.26 (s, 3H, 3 × CH_3); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.5, 150.6, 136.9, 133.2, 133.0, 130.6, 128.4, 128.0, 125.6, 89.9, 68.7, 67.7, 67.6, 67.5, 66.9, 44.6, 43.9, 34.4, 31.1; IR: 3081, 2965, 2884, 1683.

*2.2.14. 3-[(2-Chlorophenyl)thio]-3-ferrocenyl-1-phenylpropan-1-one (**3f**)*

m.p. 94 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.95–7.87 (m, 2H, Ar), 7.60–7.30 (m, 5H, Ar), 7.17–7.08 (m, 2H, Ar), 4.99 (dd, J = 6.5, 6.2 Hz, 1H, CH), 4.23–4.06 (m, 9H, 9 × CH, Cp), 3.69 (dd, J = 17.2, 6.5 Hz, 1H, CH_aH_b), 3.51 (dd, J = 17.2, 6.2 Hz, 1H, CH_aH_b); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.3, 136.7, 136.6, 134.0, 133.6, 133.2, 129.8, 128.6, 128.2, 128.0, 127.0, 89.1, 68.8, 67.9, 67.8, 67.6, 67.3, 45.2, 42.6; IR: 3087, 3059, 2898, 1682.

*2.2.15. 3-[(3-Chlorophenyl)thio]-3-ferrocenyl-1-phenylpropan-1-one (**3g**)*

Viscous oil; ^1H NMR (200 MHz, $CDCl_3$): δ = 7.98–7.88 (m, 2H, Ar), 7.61–7.04 (m, 7H, Ar), 4.85 (dd, J = 7.2, 5.8 Hz, 1H, CH), 4.18–4.02 (m, 9H, 9 × CH, Cp), 3.61 (dd, J = 17.1, 5.8 Hz, 1H, CH_aH_b), 3.21 (dd, J = 17.1, 7.2 Hz, 1H, CH_aH_b); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.1, 136.7, 136.2, 134.0, 133.1, 132.6, 130.9, 129.6, 128.5, 127.9, 127.4, 89.4, 68.7, 67.9, 67.7, 67.6, 66.7, 44.2, 43.9; IR: 3087, 3059, 2896, 1682.

*2.2.16. 3-[(4-chlorophenyl)thio]-3-ferrocenyl-1-phenylpropan-1-one (**3h**)*

m.p. 137 °C; ^1H NMR (200 MHz, $CDCl_3$): δ = 8.00–7.89 (m, 2H, Ar), 7.64–7.41 (m, 3H, Ar), 7.26–7.13 (m, 4H, Ar), 4.79 (dd, J = 7.3, 5.7 Hz, 1H, CH), 4.13–4.09 (m, 7H, 7 × CH, Cp), 4.07–4.02 (m, 2H, 2 × CH, Cp), 3.60 (dd, J = 17.3, 5.7 Hz, 1H, CH_aH_b), 3.51 (dd, J = 17.3, 7.3 Hz, 1H, CH_aH_b); ^{13}C NMR (50 MHz, $CDCl_3$): δ = 197.3, 136.8, 135.0, 133.8, 133.2, 132.5, 128.8, 128.6, 128.0, 89.7, 68.8, 68.0, 67.9, 67.8, 66.7, 44.2, 44.1; IR: 3152, 2924, 2852, 1668.

*2.3. X-ray data collection and structure refinement for compounds **1h**, **2h** and **3h***

Crystal data and experimental details for all three compounds are summarized in Table 1. Single-crystal diffraction data were collected at room temperature on an Agilent Gemini S diffractometer. Data collection for 2 and 3 h was performed using Mo Kα (0.71073 Å) radiation while the diffraction data for **1h** were collected using Cu Kα radiation (λ = 1.5418 Å). Data integration and scaling of the reflections were performed with the CRYSALIS software [31]. Numerical absorption correction based on Gaussian integration over a multifaceted crystal model was performed. The crystal structures of **1h**, **2h** and **3h** were solved by direct methods, using SIR2002 [32] and refined using SHELXL97 [33] program both incorporated in WINGX [34] program package.

All non-H atoms were refined anisotropically to convergence. All H atoms were placed at geometrically calculated positions with the C–H distances fixed to 0.93 from Csp^2 and 0.97 and 0.98 Å from methylene and methine Csp^3, respectively. The corresponding isotropic displacement parameters of the hydrogen atoms were equal to 1.2 U_{eq} and 1.5 U_{eq} of the parent Csp^2 and Csp^3, respectively. Figures were produced using ORTEP-3 [35] and MERCURY, Version 2.4 [36]. The software used for the preparation of the materials for publication: WINGX [34], PLATON [37], PARST [38].

3. Results and discussion

3.1. Synthesis

Three series of ferrocene containing 3-(arylthio)propan-1-ones were synthesized by thia-Michael addition of eight thiophenols (**7a**–**h**) to the conjugated enones acryloylferrocene (**4**), 1-ferrocenyl-3-phenylprop-2-en-1-one (**5**) and 3-ferrocenyl-1-phenylprop-2-en-1-one (**6**) in the presence electrochemically generation zirconium catalyst (Scheme 1).

Table 1
Crystallographic data for the crystal structures of **1h**, **2h** and **3h**.

	1h	2h	3h
Empirical formula	$C_{19}H_{17}ClFeOS$	$C_{25}H_{21}ClFeOS$	$C_{25}H_{21}ClFeOS$
Formula weight	384.69	460.78	460.78
Color, crystal shape	orange, prism	orange, prism	orange, prism
Crystal size (mm^3)	0.27 × 0.18 × 0.06	0.36 × 0.19 × 0.03	0.50 × 0.36 × 0.31
T (K)	293(2)	293(2)	293(2)
Wavelength (Å)	1.5418	0.71073	0.71073
Crystal system	triclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$P2_1/n$
Unit cell dimensions			
a (Å)	7.3519(5)	13.9615(5)	5.92510(10)
b (Å)	10.7781(10)	5.7503(2)	12.0161(2)
c (Å)	11.9790(8)	26.3696(12)	28.9044(5)
α (°)	101.690(7)	90	90
β (°)	104.013(6)	96.526(4)	91.7450(10)
γ (°)	107.115(7)	90	90
V ($Å^3$)	840.91(11)	2103.31(14)	2056.94(6)
Z	2	4	4
D_{calc} (Mg/m^3)	1.519	1.455	1.488
μ (mm^{-1})	9.807	0.957	0.979
θ Range for data collection (°)	3.98 to 72.42	3.16 to 28.95	3.29 to 29.04
Reflections collected	5180	16259	28507
Independent reflections, R_{int}	3222, 0.0279	4984, 0.0289	5071, 0.0213
Data/restraints/parameters	3222/0/209	4984/0/262	5071/0/262
Goodness-of-fit (GOF) on F^2	1.019	1.034	1.029
Final R_1/wR_2 indices ($I > 2\sigma_I$)	0.0355/0.0881	0.0401/0.0793	0.0268/0.0660
Final R_1/wR_2 indices (all data)	0.0442/0.0924	0.0628/0.0877	0.0326/0.0689
Largest diff. peak and hole (e $Å^{-3}$)	0.414/−0.244	0.250/−0.216	0.250/−0.270

The reaction was performed by simple constant current electrolysis (20 mA) of an acetonitrile solution of lithium perchlorate containing substrates – the corresponding enones and thiophenols (in a ratio 1:2), using a zirconium and platinum spirals as the anode and cathode, respectively [20]. Since zirconium is the most oxidizable component of the system, after establishing of an electrical circuit the oxidative dissolution of the Zr-anode took place and the formation of insoluble species was observed. Most probably these are the acting catalyst of the addition of thiophenols to the π-electronic system of the conjugated enones. The isolation and characterization of the catalyst is in progress and the results will be reported elsewhere. Reactions were performed in a 1 mmol scale and the electrolyses were carried out with 0.4 F/mol charge consumption in order to generate 0.1 mmol of zirconium(IV) species into the solution (since zirconium exchanges four electrons with the anode), i.e. to provide 10 mol% of some Zr(IV) or ZrO(II) species. In order to avoid coating of the insoluble catalyst at the anode, the electrolysis was performed placing the electrolytic cell into an ultrasound bath, providing, thus, an instantaneous removal of the coated species from the electrode surface.

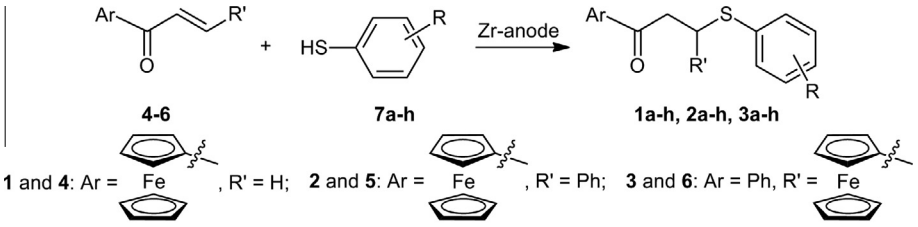
Acryloylferrocene (**4**) was the first substrate we submitted to the described reaction conditions and results obtained are summarised in Table 2. As data listed therein show, the desired 3-(arylthio)-1-ferrocenylpropan-1-ones (**1a**–**h**) were obtained in high yields (76–91%).

The addition of thiophenols **7a**–**h** to 1-ferrocenyl-3-phenylprop-2-en-1-one (**5**) proceeded in a similar manner (see Table 3). The only remarkable discrepancy was occurred in the case of *o*-thiocresol (**7b**), which gave the corresponding saturated ketone **2b** in lower yield (50%).

However, the addition of thiophenols **7a**–**h** to 3-ferrocenyl-1-phenylprop-2-en-1-one (**6**) was considerably different regarding the yields of the saturated ketones **3a**–**h** (see Table 4). Although the addition of three chlorothiophenols (**7f**–**h**) was as successful as in the case of enones **4** and **5**, yields obtained by reacting **6** with thiophenol (**7a**) and three thiocresols (**7b**–**d**) were remarkable lower (38–58%). It is not easy to rationale this phenomenon. Steric effects should be rejected, since thiophenol **7e** (containing a voluminous *tert*-buthyl group) gave under the same conditions the corresponding product **3e** in the considerable higher yield (91%) than *p*-thiocresol (58%).

3.2. Spectral characterisation

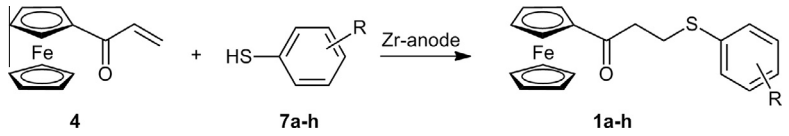
All synthesized ferrocene-containing β-(arylthio)propanones were characterized by IR, ^1H and ^{13}C NMR spectral data. In IR spectra of the synthesized compounds the most recognizable band appears in the carbonyl group region 1660–1666, 1656–1663 and 1668–1683 cm^{-1} (for **1a**–**h**, **2a**–**h** and **3a**–**h**, respectively).

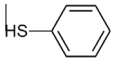
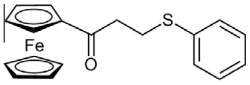
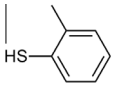
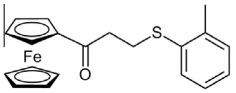
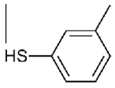
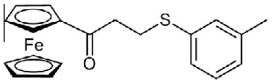
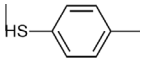
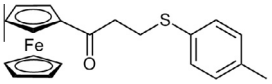
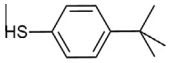
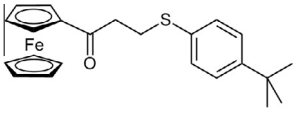
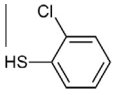
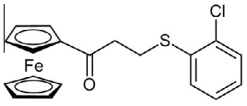
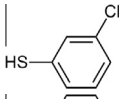
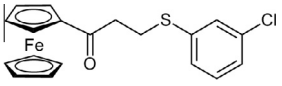
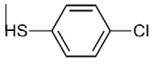
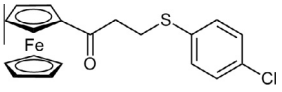


1, **2**, **3** and **7**: **a)** R = H, **b)** R = *o*-CH_3, **c)** R = *m*-CH_3, **d)** R = *p*-CH_3, **e)** R = *p*-$C(CH_3)_3$, **f)** R = *o*-Cl, **g)** *m*-Cl, **h)** *p*-Cl

Scheme 1. Synthesis ferrocene containing 3-(arylthio)propan-1-ones.

Table 2
Synthesis of 3-(arylthio)-1-ferrocenylpropan-1-ones **1a–h.**



Entry	Thiophenol **7**		Product **1**		Yield[a] (%)
1		**7a**		**1a**	82
2		**7b**		**1b**	78
3		**7c**		**1c**	84
4		**7d**		**1d**	90
5		**7e**		**1e**	86
6		**7f**		**1f**	76
7		**7g**		**1g**	91
8		**7h**		**1h**	78

[a] Isolated yields based on the starting enone **4**.

Three sets of signals could be recognized in ^{1}H NMR spectra of each of three series of β-(arylthio)propanones: the first belonging to protons of aliphatic parts of these molecules, the second to protons of ferrocene units and the third one to aromatic protons. The chemical shifts and shapes of signals corresponding to the given protons in spectra of three series are, however, different. Thus, signals of all four methylene protons of compounds **1a–h** (–COC**H**$_2$– and –C**H**$_2$S–) appear at similar chemical shifts (at 2.98–3.07 and 3.25–3.32 ppm) as broad triplets (**1a** and **1e**) or A_2B_2 multiplets (**1b–d** and **1f–h**). Signals of –COC**H**$_2$– protons of compounds **2a–h** and **3a–h** are of the similar chemical shift as those of **1a–h**, whereas their shapes are different. Due to germinal couplings, these protons exhibit doublets of doublets (**2a–h**, **3a**,**b**,**f–h**) and pseudo-doublets (**3c–e**) in their spectra. Protons from methine groups in these compounds (–C**H**Ph–S– and –C**H**Fc–S–, where Fc = ferrocenyl) differ dramatically. Their signals appear as doublets of doublets (**2a–h**, **3a**,**b**,**f–h**) and pseudo-triplets (**3c–e**) at 4.76–5.15 ppm. However, the methine protons next to phenyl groups in the series **2a–h** had values of their chemical shifts shifted downfield by a relatively constant value of 0.14–0.18 ppm when compared to the corresponding protons in compounds **3a–h**. This could be interpreted as the result of the differing diamagnetic ring currents of the phenyl and ferrocenyl groups. Such a trend is in general agreement with the difference in chemical shifts of the methyl groups in toluene and methylferrocene (*ca.* 0.3 ppm in $CDCl_3$).

Signals of the unsubstituted ring's protons from the ferrocene unit of compounds **1a–h**, **2a–h** (C6′–10′, Fig. 1) and **3a–h** (C6″–10″, Fig. 1) appear as singlets at 3.92–4.17, as it could be expected for acylferrocenes. However, chemical shifts, and particularly the shape of signals, of substituted ring's protons are different from each other. Signals of both kinds of the substituted ring's protons of compounds **1a–h** (at C3″/C4″ and C2″/C5″, respectively, Fig. 1) appear as pseudo-triplets, at 4.44–4.50 and 4.70–4.75 ppm. The substituted ring's protons of compound **2a–h** have chemical shifts very similar to those of **1a–h**, but protons of C2′/C5′ (Fig. 1) have the signals in the shape of multiplets. The signals of both kinds of protons of compounds **3a–h** (C3″/C4″ and C2″/C5″, Fig. 1) represent complex multiplets at 3.91–4.23 ppm.

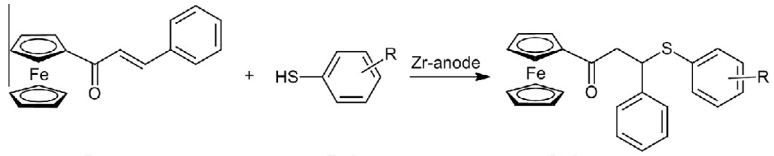
Signals of the aromatic ring's protons are located in expected region of ^{1}H NMR spectra, and the only fact worth of comment is the shape of the signal of these protons in **1e**. Namely, only one singlet for aromatic protons of this compound appears in the corresponding region, apparently due to these protons are accidentally isochronous.

Signals belonging to the corresponding carbon atoms of the synthesized compounds appear in the expected regions of their ^{13}C NMR spectra.

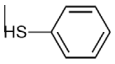
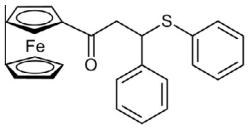
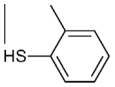
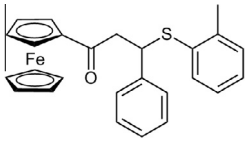
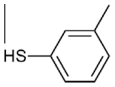
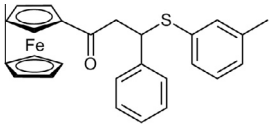
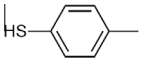
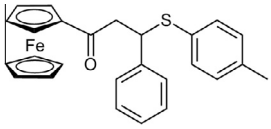
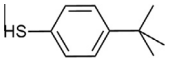
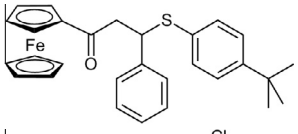
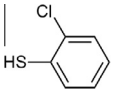
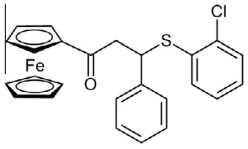
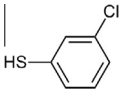
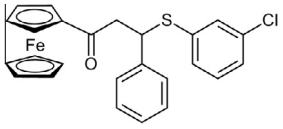
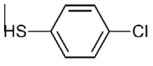
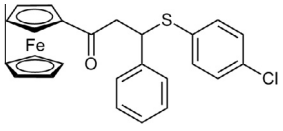
3.3. Crystal structure discussion of *1h*, *2h* and *3h*

Three compounds are characterized by single-crystal X-ray structure analysis. Two of them, **2h** and **3h**, crystallize in the same $P2_1/n$ space group while **1h** crystallizes in triclinic crystal system ($P\bar{1}$). All three molecules contain as a common structural part the

Table 3
Synthesis of 3-(arylthio)-1-ferrocenyl-3-phenylpropan-1-ones **2a–h**.



5 **7a-h** **2a-h**

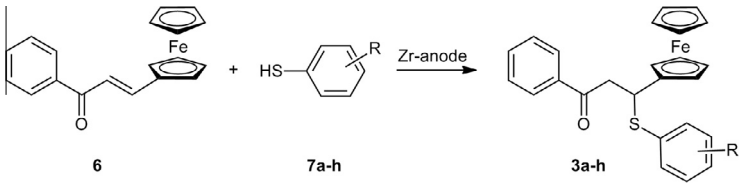
Entry	Thiophenol **7**		Product **2**		Yield[a] (%)
1		**7a**		**2a**	86
2		**7b**		**2b**	50
3		**7c**		**2c**	72
4		**7d**		**2d**	80
5		**7e**		**2e**	88
6		**7f**		**2f**	93
7		**7g**		**2g**	98
8		**7h**		**2h**	97

[a] Isolated yields based on the starting enone **5**.

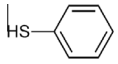
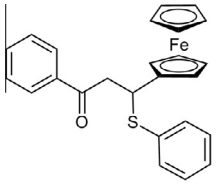
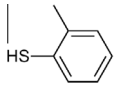
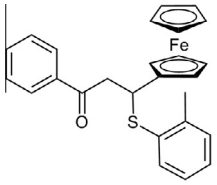
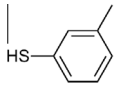
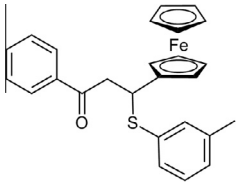
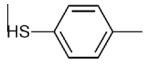
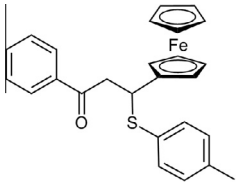
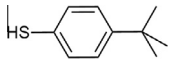
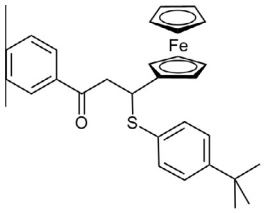
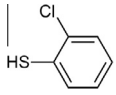
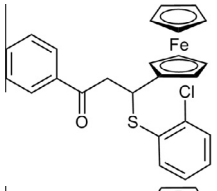
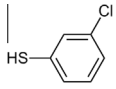
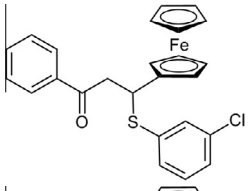
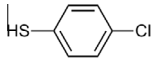
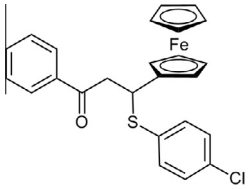
O1–C11–C12–C13–S1 aliphatic fragment and the C14–C19 phenyl ring with Cl1 chlorine atom substituted in *para* position. In Fig. 2 the molecules of **1h**, **2h** and **3h** are placed approximately in the same projection regarding the above common fragment (the position of O1–C11–C12 is used as a primary criterion for the orientation of molecules).

The O1–C11–C12–C13–S1 chain adopts different conformation in crystal structure of **1h**, **2h** and **3h**. Thus in **1h** all non-hydrogen atoms in this aliphatic fragment are practically coplanar (root-mean-square deviation from a mean plane of fitted atoms is only 0.044 Å). For **2h** and **3h** rms deviation is 0.128 and 0.299 Å respectively. However the difference in the conformation of the O1–C11–C12–C13–S1 fragment could be illustrated in the best way by comparison of the O1–C11–C12–C13 torsion angle [3.4(4), 22.5(3) and 37.8(2)° in **1h**, **2h** and **3h** respectively]. The C11–C12–C13–S1 torsion angle also displays the largest deviation from coplanar position for **3h** structure [172.9(2), −171.8(2) and −146.1(1)° in **1h**, **2h** and **3h** respectively]. Obviously the O1–C11–C12–C13–S1 chain is the most puckered in the crystal structure of **3h**. Bond lengths in the chain are very similar (Table 5) with an exception for the value of C13–S1 bond which is for about 0.04 Å shorter in **1h** than in **2h** and **3h**. Of course an explanation for this structural difference could be found in the fact that the C13 bind different number of hydrogen atoms in **1h** versus **2h** and **3h**. Another structural difference can be found for the C13–S1–C14 angle which is for about 4° smaller in **2h** than in **1h** and **3h** (Table 5). The S1–C14–C15 and S1–C14–C15 bond angles are very similar in **2h** but significantly different in **1h** and **3h** (Table 5). Geometrical parameters within

Table 4
Synthesis of 3-(arylthio)-3-ferrocenyl-1-phenylpropan-1-ones **3a**–**h**.



6 **7a-h** **3a-h**

Entry	Thiophenol **6**		Product **3**		Yield[a] (%)
1		**7a**		**3a**	50
2		**7b**		**3b**	38
3		**7c**		**3c**	45
4		**7d**		**3d**	58
5		**7e**		**3e**	91
6		**7f**		**3f**	79
7		**7g**		**3g**	97
8		**7h**		**3h**	98

[a] Isolated yields based on the starting enone **6**.

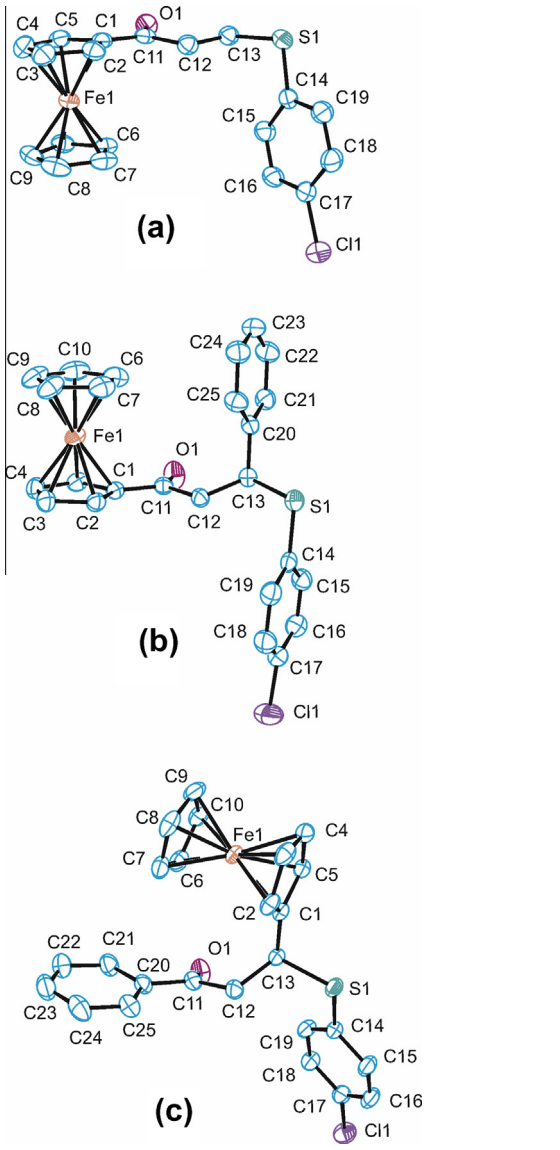


Fig. 2. Crystal structure and atom-numbering scheme of compounds **1h** (a), **2h** (b) and **3h** (c). Displacement ellipsoids are drawn at the 40% probability level. H atoms have been omitted for clarity.

Table 5
Selected bond lengths (Å) and bond angles (°) in crystal structures of **1h**, **2h** and **3h**.

	1h	2h	3h
Cl1–C17	1.743(3)	1.737(2)	1.7467(15)
S1–C14	1.766(3)	1.770(2)	1.7668(15)
S1–C13	1.801(2)	1.842(2)	1.8369(13)
O1–C11	1.214(3)	1.214(2)	1.2152(18)
C11–C12	1.513(3)	1.518(3)	1.515(2)
C12–C13	1.515(4)	1.523(3)	1.5336(19)
C14–C15	1.384(3)	1.387(3)	1.396(2)
C14–C19	1.392(4)	1.382(3)	1.387(2)
C15–C16	1.380(4)	1.377(3)	1.377(2)
C16–C17	1.375(4)	1.376(3)	1.375(2)
C17–C18	1.369(4)	1.372(4)	1.374(2)
C18–C19	1.381(4)	1.378(3)	1.385(2)
C14–S1–C13	104.2(1)	100.76(9)	104.75(7)
O1–C11–C1	121.9(2)	121.76(18)	120.09(13)
O1–C11–C12	122.0(2)	121.62(18)	119.96(13)
C15–C14–S1	124.9(2)	121.69(17)	116.41(11)
C19–C14–S1	116.3(2)	119.77(18)	125.10(11)
C18–C17–Cl1	118.9(2)	119.45(19)	119.41(13)
C16–C17–Cl1	120.2(2)	119.6(2)	119.62(12)

the C14–C19 phenyl ring as well as the Cl1–C17 and S1–C14 bond lengths are very similar for all three crystal structures.

The structures of **1h**, **2h** and **3h** comprise a ferrocenyl group substituted on one cyclopentadiene (Cp) ring. In **1h** and **2h** the Cp rings adopt nearly eclipsed geometry. The C1–Cg1–Cg2–C10 torsion angle is −6.19° and 6.09° in **1h** and **2h** respectively (Cg1 and Cg2 are centroids of the corresponding Cp rings). In **3h** the Cp rings are somewhat less eclipsed with the C1–Cg1–Cg2–C10 torsion angle of −17.19°. As expected, in all three structures the Cp rings are almost ideally parallel with a dihedral angle of 0.73(16)°, 1.17(10)° and 3.30(9)° for **1h**, **2h** and **3h** respectively. Also a distance of the Fe1 atom from a mean plane of the substituted Cp ring is somewhat shorter than a distance to the unsubstituted ring (1.645/1.652, 1.649/1.655 and 1.648/1.656 Å for **1h**, **2h** and **3h** respectively). In **1h** and **2h** the ferrocene unit (Fc) is connected to the O1–C11–C12–C13–S1 aliphatic fragment via the same C1–C11 bond but spatial directionality of the Fc and the C14–C19 phenyl ring relating to the fragment is completely different (Fig. 2). In molecule **3h** the Fc unit is connected to the O1–S1 fragment via the C1–C13 bond with bond distance [1.5033(18) Å] slightly longer than for corresponding C1–C11 bond in **1h** [1.471(4) Å] and **2h** [1.465(3) Å].

There is no any classical H-bond in all three crystal structures. Reason could be found in the fact that the molecules of **1h**, **2h** and **3h** do not possess any significant H-bond donor as O–H, N–H or similar donor group. The C11–O1 carbonyl group may be accepted as the best H-bond acceptor in all three compounds but in **1h** the O1 atom does not form any C–H···O weak hydrogen bond with H···O distance shorter than 2.60 Å. However, there are three C–H···O1 interactions in **1h** with H···O distances between 2.63 and 2.70 Å and the C–H···O1 angles larger than 150° (Table 6). Although weak, these intermolecular C–H···O interactions probably stabilize the crystal packing of **1h**. Using the C25–H···O1 weak H-bond (Table 6) the molecules in crystal structure of **2h** form a chain along the *b* unit cell axis (for illustration see Supplementary material file, Fig. S1) while the molecules of **3h** form a chain along the *a* axis (Fig. S2) but using the C2–H···O1 hydrogen bond (Table 6).

The Cl1 atom in all there crystal structures does not form any C–H···Cl interaction with H···Cl distance shorter than 2.90 Å. In **1h** and **2h** there are two intermolecular contacts with H···Cl distances of 2.95 and 2.94 Å but could not be taken as important since that corresponding bond angles [C5–H5···Cl1^{i} and C23–H23···Cl1^{ii} for **1h** and **2h** respectively; symmetry codes: (i) $x-1,y,z-1$, (ii) $x+1,y,z$] are rather small (105° and 128°). It is known from the charge density studies [39,40] that sulfur atom is able to act as a good acceptor of C–H groups even at the H···S distance of 3.10 Å. In **1h** and **3h** there are two C–H···S intermolecular interactions, the C16–H···S1 and C10–H···S1 in **1h** and **3h** respectively (Table 6).

Regardless of the lack of classical H-bonds the present crystal structures form numerous C–H···π interactions where all π systems, Cp and phenyl rings, act as π acceptors. In **1h** the molecules form a chain along the *a* unit cell axis using the C12–H···π intermolecular interaction (Table 6) with π system from unsubstituted Cp ring. Formation of this chain is supplemented by above mentioned the C16–H···S1 interaction (Fig. S3). In **2h** the C14–C19 phenyl ring participates in C4–H···π interactions (Table 6, Fig. S4) while in crystal structures of **3h** both Cp rings and both phenyl rings act as π acceptors in the C9–H···π, C12–H···π, C16–H···π and C23–H···π intermolecular interactions (Table 6, Fig. S5). The most interesting is that the C–H···π interactions form only evident intramolecular interactions in crystal structures of **2h** and **3h**

Table 6
Geometrical parameters for intra- and intermolecular C–H···O, C–H···S and C–H···π interactions in crystal structures of **1h**, **2h** and **3h**. (Cg1, Cg2, Cg3 and Cg4 are midpoints of the C6–C10, C14–C19, C20–C25 and C1–C5 rings respectively). Criteria for C–H···O interactions: the H···O distance shorter than 2.65 Å and the C–H···O angle larger than 130°. Criteria for C–H···π interactions: perpendicular distance of H atom on the corresponding ring shorter than 3.0 Å and the C–H···Cg angle larger than 130°.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)	Symmetry codes:
1h					
C15–H15···O1	0.93	2.63	3.574(4)	167.3	$-x+1, y-2, -z+1$
C16–H16···S1	0.93	3.08	3.859(7)	157.6	$x-1, y, z$
C12–H12b···Cg1	0.97	2.85	3.594(3)	133.7	$x-1, y, z$
2h					
C25–H25···O1	0.93	2.55	3.478(3)	172.0	$x, y+1, z$
C4–H4···Cg2	0.93	3.09	3.994(2)	165.4	$-x, -y, -z+1$
C6–H6···Cg3	0.93	3.04	3.890(3)	152.6	x, y, z
3h					
C2–H2···O1	0.93	2.50	3.428(2)	173.9	$x-1, y, z$
C10–H10···S1	0.93	2.99	3.804(2)	146.6	$-x+1.5, y+0.5, -z+1.5$
C7–H7···Cg3	0.93	3.03	3.819(2)	143.5	x, y, z
C9–H9···Cg4	0.93	2.92	3.591(2)	130.6	$-x+0.5, y+0.5, -z+1.5$
C12–H12a···Cg3	0.97	3.07	4.150(7)	139.3	$-x+1, -y, -z+1$
C23–H23···Cg2	0.93	2.85	3.635(2)	143.2	$-x+1, -y, -z+1$

(Fig. S6) and in that way it play certain influence to the present conformation of the molecules. Namely in both molecules the unsubstituted Cp ring act as C–H donor while the C20–C25 phenyl ring participate as π acceptor (Table 6, C6–H···π and C7–H···π for **2h** and **3h** respectively). Moreover these two rings (Cp and phenyl) form almost ideally the most favorable orthogonal orientation (dihedral angle between mean planes of the C6–C10 and C20–C25 rings is 86.86(9)° and 82.79(5)° for **2h** and **3h** respectively). It is worth mentioning that regardless of this conformational similarity in two molecules, the C20–C25 ring has very different orientation relating to other C14–C19 phenyl ring (dihedral angle between two phenyl rings is 5.47 (11) and 69.10(4)° for **2h** and **3h** respectively).

4. Conclusion

In conclusion, we described herein the thia-Michael reaction of thiophenols with ferrocene containing conjugated enones in the presence of an electrochemically generated zirconium catalyst. It was shown that this procedure represent a versatile method for the synthesis of ferrocene containing 3-arylthiopropan-1-ones, compounds that can serve as good precursors for the synthesis of bidentate ligands, since their carbonyl groups can be transformed in a plethora of other functionalities. 24 ferrocene derivatives were synthesised (16 being new ones) and described by spectral data. Single crystal X-ray analysis revealed that three compounds (**1h**, **2h** and **3h**) although similar in composition exhibit different conformational characteristics. Thus: (i) the O1–C11–C12–C13–S1 aliphatic fragment is the most puckered in the crystal structure of **3h**; (ii) the C13–S1–C14 angle is for about 4° smaller in **2h** than in **1h** and **3h**; (iii) the C13–S1 bond is for about 0.04 Å shorter in **1h** than in **2h** and **3h**; (iv) spatial directionality of the Fc unit and the C14–C19 phenyl ring relating to the aliphatic fragment in **1h** and **2h** is opposite; (v) crystal structures of **2h** and **3h**, dislike to **1h**, form intramolecular C–H···π interactions; (vi) dihedral angle between two phenyl rings in **2h** and **3h** is very different (5.5° and 69.1° respectively). However, regardless of quoted structural differences all three compounds form numerous intermolecular C–H···π interactions and weak C–H···O interactions while none of them form π···π interactions.

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Appendix A. Supplementary data

CCDC 970342, 970343 and 970344 contain the supplementary crystallographic data for compounds **1h**, **2h** and **3h** respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk. Additional data concerning single crystal X-ray structural analysis (Figs. S1–S6) are available in the Supplementary material file. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2013.12.012.

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