Supporting Information

for

Ferrocenyl-substituted tetrahydrothiophenes via formal [3 + 2]-cycloaddition reactions of ferrocenyl thio ketones with donor–acceptor cyclopropanes

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Experimental data for selected compounds 9, details of the crystal structure determination, and the original $^1$H and $^{13}$C NMR spectra for all products
1. Experimental

1.1. Experimental data for thio ketone 8c

Ferrocenyl (2-naphthyl) meth anthione (8c): Yield: 1.09 g (92%). Deep blue crystals; mp 127-128°C; $^1$H-NMR (600 MHz, CDCl3): $\delta$ 4.19 (s, 5HC(Fc)); 4.85 (s, 2HC(Fc)); 5.07 (s, 2HC(Fc)); 7.36-7.43 (m, 3 arom. HC); 7.47-7.54 (m, 2 arom. HC); 7.66-7.73 (m, 2 arom. HC); $^{13}$C-NMR (151 MHz, CDCl3): $\delta$ 72.3, 72.9, 74.9 (for 9HC(Fc)), 89.6 (C(Fc)), 125.6, 126.0, 126.7, 127.3, 127.4, 127.7, 129.1 (7 arom. HC), 132.3, 134.2, 146.2 (3 arom. C), 238.1 (C=S); Anal. calcd for C21H16SFe: C 70.80; H 4.53; S 9.00; found C 70.67; H 4.69; S 9.02.

1.2. Experimental data for tetrahydrothiophenes 9e–k, m–n

Dimethyl 2-ferrocenyl-5-phenyl-2-(n-propyl)tetrahydrothiophene-3,3-dicarboxylate (9e): Yield: 147 mg (97%); isolated chromatographically as a 52:48 mixture of isomers. The major component was isolated as a less polar fraction by repeated preparative thin layer chromatography on silica. Yellow crystals; mp 109-110°C; $^1$H-NMR (600 MHz, CDCl3) (major isomer): $\delta$ 1.12 (t, $J$ = 7.2 Hz, 3H, CH3(n-Pr)), 1.29 (t, $J$ = 7.1 Hz, 2H, CH2(n-Pr)), 2.75 (dd, $J$ = 13.9, $J$ = 11.1 Hz, 1H, HC(4)) 3.00 (dd, $J$ = 13.9, $J$ = 6.8 Hz, 1H, HC(4)) 3.41 (s, 3H, OCH3), 3.67 (s, 3H, OCH3), 4.15 (q, $J$ = 14.3, $J$ = 7.1 Hz, CH2(n-Pr)), 4.18 (s, 6HC(Fc)), 4.20 (s, 1HC(Fc)), 4.38 (s, 1HC(Fc)), 4.57 (s, 1HC(Fc)), 5.43 (dd, $J$ = 11.0, 6.8 Hz, 1H, HC(5)), 7.36-7.40 (m, 2 arom. HC), 7.53-7.56 (m, 2 arom. HC); $^{13}$C-NMR (151 MHz, CDCl3) (major isomer): $\delta$ 15.1 (CH3), 20.2 (CH2CH2CH3), 44.2 (CH2CH2CH3), 47.3 (C(4)) 48.9 (HC(5)), 52.2, 52.5 (2OCH3), 65.5, 71.7 (C(2) and C(3)), 67.1, 68.1, 68.2, 69.3, 69.4 (for 9HC(Fc)), 91.5 (C(Fc)), 127.3, 127.7, 128.7 (for 5 arom. HC), 142.1 (1 arom. C), 169.2, 170.1 (2C=O); IR: v 1731 brs (2C=O), 1449m, 1431m, 1241s, 1209s, 1105m, 1051m, 818s, 762m, 697vs, 482vs cm$^{-1}$; HRMS–El (m/z): [M]+ calcd. for [C27H30O4SFe]+, 506.1214; found, 506.1211.

Dimethyl 2-ferrocenyl-5-(2-naphthyl)-2-phenyltetrahydrothiophene-3,3-dicarboxylate (cis-9f): Yellow crystals, 22 mg (30%); mp 178-180°C. $^1$H-NMR (600 MHz, CDCl3): $\delta$ 2.73 (dd, $J$ = 13.9, $J$ = 4.3 Hz, 1H, HC(4)), 3.46 (s, 3H, OCH3), 3.49 (s, 3H, OCH3), 3.59-3.61 (m, 1HC(Fc)), 3.69 (dd, $J$ = 13.7, $J$ = 12.9 Hz, 1H, HC(4)), 4.02-4.04 (m, 1HC(Fc)), 4.07 (s, 5HC(Fc)), 4.30-4.31 (m, 1HC(Fc)), 4.73-4.75 (m, 1HC(Fc)), 5.00 (dd, $J$ = 12.6, $J$ = 4.3 Hz, 1H, HC), 7.33-7.39 (m, 1 arom. HC), 7.41-7.46 (m, 2 arom. HC), 7.51-7.56 (m, 2 arom. HC), 7.81-
7.86 (m, 1 arom. HC), 7.89-7.91 (m, 2 arom. HC), 7.94-7.96 (m, 1 arom. HC), 8.00 (s, 1 arom. HC), 8.24-8.27 (m, 2 arom. HC); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ 48.0 (C(4)), 48.2 (C(5)), 52.5, 52.6 (OCH$_3$), 67.8, 68.7, 69.1, 69.9, 71.1 (for 9HC(Fc)), 73.7 (for C(2) and C(3)), 96.9 (C(Fc)), 125.7, 126.1, 126.3, 126.6, 126.9, 127.1, 127.7, 127.8, 128.5, 128.8 (for 12 arom. HC), 133.1, 133.4, 136.1, 144.2 (4 arom. C), 168.9, 170.3 (2C=O); IR: v 1744 vs (2C=O), 1444m, 1427m, 1258m, 1239vs, 1187m, 1168m, 1051m, 814m, 723m, 698m, 480vs cm$^{-1}$; Anal calcd for C$_{34}$H$_{30}$FeO$_4$S (590.51): C 68.92 H 5.44, S 5.43; found: C 68.85, H 5.44, S 5.47.

**Dimethyl 2,5-di(2-naphthyl)-2-ferrocenyltetrahydrothiophene-3,3-dicarboxylate (9g):**
Yield: 25 mg (31%); mp = 220°C (dec.). $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 2.78 (dd, $J$ = 13.8, $J$ = 4.3 Hz, 1H, HC(4)), 3.44 (s, 3H, OCH$_3$), 3.51 (s, 3H, OCH$_3$), 3.56-3.58 (m, 1HC(Fc)), 3.76 (dd, $J$ = 13.7, $J$ = 12.9 Hz, 1H, HC(4)), 4.00-4.02 (m, 1HC(Fc)), 4.07 (s, 5HC(Fc)), 4.31-4.33 (m, 1HC(Fc)), 4.78-4.80 (m, 1HC(Fc)), 5.05 (dd, $J$ = 12.6, $J$ = 4.3 Hz, 1H, HC(5)), 7.52-7.58 (m, 4 arom. HC), 7.85-7.94 (m, 5 arom. HC), 7.96-8.01 (m, 2 arom. HC), 8.04 (s, 1 arom. HC), 8.38-8.41 (m, 1 arom. HC), 8.77-8.78 (m, 1 arom. HC); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ 48.1 (C(4)), 48.3 (C(5)), 52.5, 52.6 (2OCH$_3$), 67.8, 68.7, 69.2, 69.9, 71.2 (for 9HC(Fc)), 71.2, 73.5 (C(2) and C(3)), 97.3 (C(Fc)), 125.7, 125.8, 125.9, 126.1, 126.2, 126.3, 126.9, 127.3, 127.4, 127.7, 127.9, 128.0, 128.6, 128.7 (14 arom. HC), 132.1, 132.8, 133.1, 133.4, 136.1, 141.8 (6 arom. C), 168.9, 170.4 (2C=O); IR: v 1723 vs (2C=O), 1433m, 1299m, 1246s, 1217m, 1172m, 814s, 751s, 497m, 473 vs cm$^{-1}$; Anal. calcd for C$_{38}$H$_{32}$FeO$_4$S (640.57): C 71.25 H 5.04, S 5.01; found: C 71.21, H 5.25, S 5.01.

**Dimethyl 2-ferrocenyl-2-phenyl-5-(4-(methyl)phenyl)tetrahydrothiophene-3,3-dicarboxylate (9h):**
Yield: 133 mg (85.1%). Yellow crystals; mp 146-148°C; $^1$H-NMR (600 MHz, CDCl$_3$): $\delta$ 2.41 (s, 3H, CH$_3$), 2.62 (dd, $J$ = 13.9, $J$ = 4.3 Hz, 1H, HC(4)), 3.44 (s, 3H, OCH$_3$), 3.46 (s, 3H, OCH$_3$), 3.53-3.57 (dd, $J$ = 13.6, $J$ = 12.9 Hz, 1H, HC(4)), 3.57-3.58 (m, 1HC(Fc)), 4.00-4.02 (m, 1HC(Fc)), 4.06 (s, 5HC(Fc)), 4.27-4.29 (m, 1HC(Fc)), 4.68-4.70 (m, 1HC(Fc)), 4.78 (dd, $J$ = 12.6, $J$ = 4.3 Hz, 1H, HC(5)), 7.25, 7.52 (AB system, $J$ = 8.0 Hz, 4 arom. HC), 7.33-7.34 (m, 1 arom. HC), 7.39-7.43 (m, 2 arom. HC), 8.21-8.24 (m, 2 arom. HC); $^{13}$C-NMR (151 MHz, CDCl$_3$): $\delta$ = 21.2 (CH$_3$), 47.8 (C(5)), 48.4 (C(4)), 52.4 (2OCH$_3$), 67.8, 68.7, 69.2, 69.9, 71.0 (for 9HC(Fc)), 70.9, 73.7 (C(2) and C(3)), 97.0 (C(Fc)), 126.6, 127.1, 127.9, 128.8, 129.5 (for 9 arom. HC), 135.8, 137.6, 144.3 (3 arom. C), 168.9, 170.4 (2C=O); IR: v 1729brvs (2C=O), 1703s (2C=O).
1429\text{m}, 1254\text{s}, 1162\text{s}, 1023\text{m}, 935\text{m}, 814\text{vs}, 721\text{s}, 700\text{s}, 484\text{m} \text{cm}^{-1}; \text{Anal. calcd for C}_{31}\text{H}_{30}\text{FeO}_{4}\text{S (554.48): C 67.15, H 5.45, S 5.78; found: C 67.13, H 5.61, S 5.73.}

**Dimethyl 2-ferrocenyl-2-phenyl-5-(4-(methoxy)phenyl)tetrahydrothiophene-3,3-dicarboxylate (9i):** Yield: 128 mg (79%). Yellow crystals; mp 138-140°C. $^1\text{H-NMR}$ (600 MHz, CDCl$_3$): $\delta$ 2.61 (dd, $J = 13.9$, $J = 4.4$ Hz, 1H, HC(4)), 3.44 (s, 3H, OCH$_3$), 3.45 (s, 3H, OCH$_3$), 3.54 (dd, $J = 13.6$, $J = 12.9$ Hz, 1H, HC(4)), 3.57-3.59 (m, 1HC(Fc)), 3.87 (s, 3H, OCH$_3$), 4.00-4.02 (m, 1HC(Fc)), 4.06 (s, 1HC(Fc)), 4.27-4.29 (m, 1HC(Fc)), 4.68-4.70 (m, 1HC(Fc)), 4.77 (dd, $J = 12.6$, $J = 4.3$ Hz, 1H, HC(5)), 6.98, 7.56 (AB system, $J = 8.6$ Hz, 4 arom. HC), 7.31-7.35 (m, 1 arom. HC), 7.39-7.44 (m, 2 arom. HC), 8.21-8.24 (m, 2 arom. HC); $^{13}\text{C-NMR}$ (151 MHz, CDCl$_3$): $\delta$ 47.5 (C(5)), 48.5 (C(4)), 52.4, 55.3 (for 3OCH$_3$), 67.8, 68.7, 69.2, 69.9, 71.0 (for 9HC(Fc)), 70.8, 73.6 (C(2) and C(3)), 96.9 (C(Fc)), 114.2, 126.5, 127.0, 128.8, 129.1, (for 9 arom. HC), 130.6, 144.3, 159.2 (3 arom. C), 168.9, 170.3 (2C=O); $\text{IR: } \nu 1731\text{b}rs$ (2C=O), 1515\text{m}, 1431\text{m}, 1250\text{vs}, 1157\text{s}, 1039\text{m}, 935\text{m}, 833\text{m}, 818\text{m}, 721\text{m}, 700\text{m}, 486\text{s} \text{cm}^{-1}; \text{Anal. calcd for C}_{31}\text{H}_{30}\text{FeO}_{5}\text{S (570.48): C 65.27, H 5.30, S 5.62; found: C 65.35, H 5.42, S 5.61.}

**Dimethyl 2-ferrocenyl-2-phenyl-5-(4-(bromo)phenyl)tetrahydrothiophene-3,3-dicarboxylate (9j):** Yield: 128 mg (92.5%). Yellow crystals; mp 182-184°C. $^1\text{H-NMR}$ (600 MHz, CDCl$_3$): $\delta$ 2.63 (dd, $J = 13.9$, $J = 4.4$ Hz, 1H, HC(4)), 3.44 (s, 3H, OCH$_3$), 3.45 (s, 3H, OCH$_3$), 3.49 (dd, $J = 13.9$, $J = 12.7$ Hz, 1H, HC(4)), 3.57-3.59 (m, 1HC(Fc)), 4.00-4.02 (m, 1HC(Fc)), 4.06 (s, 5HC(Fc)), 4.27-4.29 (m, 1HC(Fc)), 4.61-4.63 (m, 1HC(Fc)), 4.76 (dd, $J = 12.6$, $J = 4.3$ Hz, 1H, HC(5)), 7.31-7.35 (m, 1 arom. HC), 7.39-7.43 (m, 2 arom. HC), 7.50, 7.56 (AB system, $J = 8.4$ Hz, 4 arom. HC), 8.20-8.22 (m, 2 arom. HC); $^{13}\text{C-NMR}$ (151 MHz, CDCl$_3$): $\delta$ 47.4 (C(5)), 48.2 (C(4)), 52.4, 52.5 (2OCH$_3$), 67.8, 68.8, 69.2, 69.7, 71.1 (for 9HC(Fc)), 71.2, 73.5 (C(2) and C(3)), 96.7 (C(Fc)), 126.6, 127.1, 128.7, 129.7, 131.9 (for 9 arom. HC), 121.6, 138.0, 144.0 (3 arom. C), 168.7, 170.2 (2C=O); $\text{IR: } \nu 1729\text{b}rs$ (2C=O), 1490\text{m}, 1440\text{m}, 1256\text{s}, 1162\text{s}, 1073\text{m}, 814\text{s}, 721\text{m}, 700\text{m}, 486\text{s} \text{cm}^{-1}; \text{Anal. calcd for C}_{30}\text{H}_{27}\text{BrFeO}_{4}\text{S (619.35): C 58.18, H 4.39, S 5.18; found: C 58.11, H 4.41, S 5.13.}

**Dimethyl 2-ferrocenyl-2-phenyl-5-(3,3,3-trifluoromethyl)phenyl)tetrahydro-thiophene-3,3-dicarboxylate (9k):** Yield: 134 mg (95.1%). Yellow crystals; mp 168-170°C. $^1\text{H-NMR}$ (600 MHz, CDCl$_3$): $\delta$ 2.68 (dd, $J = 13.9$, $J = 4.4$ Hz, 1H, HC(4)), 3.45 (s, 3H, OCH$_3$), 3.47 (s, 3H, OCH$_3$), 3.53 (dd, $J = 13.8$, $J = 12.7$ Hz, 1H, HC(4)), 3.59-3.61 (m, 1HC(Fc)), 4.02-4.04 (m, 1HC(Fc)), 7.35 (m, 4 arom. HC), 7.53 (m, 1 arom. HC), 7.70-7.72 (m, 2 arom. HC), 8.13 (d, 2H, 2C=O); $\text{IR: } \nu 1709\text{b}rs$ (2C=O), 1525\text{m}, 1429\text{m}, 1250\text{vs}, 1156\text{s}, 1038\text{m}, 935\text{m}, 833\text{m}, 818\text{m}, 721\text{m}, 682\text{m}, 486\text{s} \text{cm}^{-1}; \text{Anal. calcd for C}_{30}\text{H}_{27}\text{FeF}_{3}\text{O}_{4}\text{S (635.40): C 58.18, H 4.39, S 5.18; found: C 58.11, H 4.41, S 5.13.}
4.07 (s, 5HC(Fc)), 4.29-4.31 (m, 1HC(Fc)), 4.61-4.63 (m, 1HC(Fc)), 4.86 (dd, J = 12.6, J = 4.4 Hz, 1H, HC(5)), 7.33-7.37 (m, 1 arom. HC), 7.41-7.45 (m, 2 arom. HC), 7.70, 7.75 (AB system, J = 8.2 Hz, 4 arom. HC) 8.20-8.23 (m, 2 arom. HC); ^13^C-NMR (151 MHz, CDCl$_3$): δ 47.5 (C(5)), 48.2 (C(4)), 52.5, 52.6 (2OCH$_3$), 67.8, 68.8, 69.2, 69.7, 71.7 (for 9HC(Fc)), 71.3, 73.6 (C(2) and C(3)), 96.6 (C(Fc)), 125.7, 125.8, 126.7, 127.1, 128.4, 128.7 (for 9 arom. HC), 129.7, 129.9, 130.2, 130.4 (CF$_3$), 143.2, 143.9 (2 arom. C), 168.6, 170.1 (2C=O); IR: ν 1731 brs (2C=O), 1429 m, 1328 m, 1258 m, 1162 s, 1116 s, 1067 s, 936 m, 820 m, 723 m, 700 m, 486 m cm$^{-1}$; Anal. calcd for C$_{31}$H$_{27}$F$_3$FeO$_4$S (608.45): C 61.19, H 4.47, S 5.27; found: C 61.26, H 4.48, S 5.17.

**Dimethyl 2-ferrocenyl-2-(2-furanyl)-5-phenyltetrahydrothiophene-3,3-dicarboxylate (9m):** Yield: 152 mg (96%). Isolated chromatographically as a 60:40 mixture of isomers. Yellow crystals; mp 124-126°C. Major isomer (based on the registered spectrum of the mixture): ^1^H-NMR: δ 3.04 (dd, J = 13.8, J = 6.4 Hz, 1H, HC(4)), 3.40 (dd, J = 11.2, J = 3.2 Hz, 1H, HC(4)), 3.49 (s, 3H, OCH$_3$), 3.59 (s, 3H, OCH$_3$), 5.24 (dd, J = 11.2, J = 6.4 Hz, 1H, HC(5)); Remaining signals registered for the mixture: ^1^H-NMR δ 4.09 (s, 4HC(Fc)), 4.10-4.11 (s, 1HC(Fc)), 4.12 (s, 6HC(Fc)), 4.23-4.26 (m, 4HC(Fc)), 4.55-4.57 (m, 1HC(Fc)), 4.69-4.71 (m, 1HC(Fc)), 4.55-4.57 (m, 1HC(Fc)), 6.48-6.50 (m, 2 arom. HC), 6.84 (d, J = 3 Hz, 1 arom. HC), 7.16 (d, J = 3.1 Hz, 1 arom. HC), 7.34-7.38 (m, 3 arom. HC), 7.40-7.45 (m, 2 arom. HC), 7.47-7.49 (m, 1 arom. HC), 7.49-7.51 (m, 1 arom. HC), 7.52-7.55 (m, 3 arom. HC), 7.59-7.62 (m, 2 arom. HC); ^13^C-NMR (registered for the mixture): δ 46.2, 47.7 (2C(4)); 48.1, 49.5 (2HC(5)); 52.3, 52.4, 52.6, 52.8 (4OCH$_3$); 64.0, 64.2 (2C(2), 71.8, 72.0 (2C(3)); 66.8, 68.1, 68.4, 68.9, 69.3, 69.5, 69.9, 70.1, 70.4 71.9 (for 18HC(Fc)); 86.0, 92.5 (2C(Fc)); 108.1, 109.2, 110.5, 110.6, 140.5, 140.8 (6 arom. HC); 127.4, 127.8, 128.0, 128.1, 128.6, 128.7 (for 10 arom. HC), 138.9, 141.3, 156.3, 157.9 (4 arom. C), 168.4, 168.8, 169.0, 169.4 (4C=O); IR (registered for the mixture): ν 1731 vs (2C=O), 1492 m, 1429 m, 1248 s, 1146 m, 816 m, 732 m, 698 vs, 598 m, 490 vs cm$^{-1}$; HRMS–EI (m/z): [M]$^+$ calcd for [C$_{28}$H$_{26}$FeO$_5$S]$^+$, 530.0850; found 530.0856.

**Dimethyl 2-ferrocenyl-5-(phtalimid-1-yl)-2-phenyltetrahydrothiophene-3,3-dicarboxylate (9n):** Yield: 48 mg (34.1%). Isolated chromatographically as a 60:40 mixture of isomers. Yellow crystals; mp ca. 170°C (dec.); Major isomer (based on the registered spectrum of the mixture):
\[ ^1 \text{H-NMR: } \delta 2.47 (dd, J = 13.7, J = 5.1 \text{ Hz}, 1H, HC(4)), 3.44 (s, 3H, OCH}_3, 3.46 (s, 3H, OCH}_3), 4.66 \text{ (pseudo-dd, } J = 13.5, J = 12.3 \text{ Hz}, 1H, HC(4)), 6.31 (dd, J = 12.1, J = 5.1 \text{ Hz}, 1H, HC(5)); \]

Minor isomer (based on the registered spectrum of the mixture): \[ ^1 \text{H-NMR: } \delta 3.22 (dd, J = 14.5, J = 7.7 \text{ Hz}, 1H, HC(4)), 3.49 (s, 3H, OCH}_3, 3.56 (s, 3H, OCH}_3), 4.23 \text{ (pseudo-dd, } J = 14.5 \text{ Hz}, J = 7.5, H, HC(4)), 6.43 \text{ (pseudo-dd, } J = 8.0, J = 7.4 \text{ Hz}, 1H, HC(5)); \]

Remaining signals registered for the mixture: \[ \delta 3.54 \text{ (s, } 1\text{HC(Fc)}), 3.90 \text{ (s, } 1\text{HC(Fc)}), 3.99 \text{ (s, } 1\text{HC(Fc)}), 4.05 \text{ (s, } 5\text{HC(Fc)}), 4.08 \text{ (s, } 6\text{HC(Fc)}), 4.18 \text{ (s, } 1\text{HC(Fc)}), 4.25-4.26 \text{ (m, } 1\text{HC(Fc)}), 4.37 \text{ (s, } 1\text{HC(Fc)}), 5.45 \text{ (s, } 1\text{HC(Fc)}), 7.30-7.35 \text{ (m, } 2\text{ arom. } HC), 7.37-7.44 \text{ (m, } 3\text{ arom. } HC), 7.71-7.75 \text{ (m, } 2\text{ arom. } HC), 7.79-7.83 \text{ (m, } 2\text{ arom. } HC), 7.84-7.86 \text{ (m, } 2\text{ arom. } HC), 7.94-7.98 \text{ (m, } 2\text{ arom. } HC), 8.18-8.24 \text{ (m, } 2\text{ arom. } HC); \]

\[ ^13 \text{C-NMR (registered for the mixture): } \delta 39.2, 40.2 \text{ (2C(4))}, 52.3, 52.5, 52.6, 52.7 \text{ (4OCH}_3), 53.1, 55.7 \text{ (2HC(5))}, 70.9, 71.7, 72.5 \text{ (for } 2\text{C(2) and } 2\text{C(3)}), 67.6, 69.1, 69.4, 69.5, 70.1, 71.4 \text{ (for } 18\text{HC(Fc)}), 97.1 \text{ (for } 2\text{C(Fc))}, 123.4, 123.6, 126.7, 126.8, 127.0, 127.1, 128.8, 129.1, 134.2, 134.4 \text{ (for } 18\text{ arom. } HC), 131.8, 131.9, 143.9 \text{ (for } 6\text{ arom. } C), 167.5, 167.7, 168.1, 168.9, 169.2, 170.1 \text{ (for } 8\text{C}=\text{O}); \]

\[ \text{IR: } 1736 \text{m}, 1716 \text{vs (2C}=\text{O), 1431m, 1354m, 1241s, 1172m, 1107m, 967m, 818m, 713vs, 501s, 486s cm}^{-1}; \]

\[ \text{Anal. calcd for } C_{32}H_{27}FeNO}_6S (609.47): \text{ C 63.06, H 4.47, N 2.30, S 5.26; found: C 63.06, H 4.45, N 2.56, S 5.19.} \]

2. Crystal structure determinations

Crystals were mounted in inert oil on nylon loops and transferred to the cold gas stream of the diffractometer (trans-9c: Oxford Diffraction Nova A using mirror-focussed Cu Kα radiation; cis-9d: Rigaku/Oxford XtaLAB Synergy using mirror-focussed MoKα radiation). Absorption corrections were implemented on the basis of multi-scans. The structures were refined anisotropically on \( F^2 \) using the program SHELXL-2017 [S1]. Hydrogen atoms were included using rigid methyl groups or a riding model starting from calculated positions. Crystallographic data are summarized in Table S1. Additionally, complete data have been deposited with the Cambridge Crystallographic Data Centre under the numbers CCDC 1992864 & 1992865. Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/data_request/cif.
Table S1: Crystallographic data and structure refinement details for compounds trans-9c and cis-9d.

| Compound | trans-9c | cis-9d |
|----------|----------|--------|
| CCDC number | 1992864 | 1992865 |
| Formula | C_{25}H_{26}FeO_{4}\text{S} | C_{34}H_{38}FeO_{4}\text{S} |
| \(M_r\) | 478.37 | 590.59 |
| Crystal size (mm) | 0.2 x 0.03 x 0.01 | 0.15 x 0.1 x 0.05 |
| Crystal system | monoclinic | triclinic |
| Space group | \(P2_1/c\) | \(P(-1)\) |
| Temperature (°C) | -173 | -170 |
| \(a\) (Å) | 13.1715(5) | 9.6177(2) |
| \(b\) (Å) | 17.8170(5) | 11.0241(3) |
| \(c\) (Å) | 9.6616(4) | 14.8441(3) |
| \(\alpha\) (°) | 90 | 71.105(2) |
| \(\beta\) (°) | 106.781(4) | 77.475(2) |
| \(\gamma\) (°) | 90 | 65.076(3) |
| \(V\) (Å³) | 2170.80 | 1344.43 |
| \(Z\) | 4 | 2 |
| \(D_x\) (Mg m⁻³) | 1.464 | 1.459 |
| \(\lambda\) (Å) | 1.54184 | 0.71073 |
| \(\mu\) (mm⁻¹) | 6.7 | 0.68 |
| Transmissions | 0.638 – 1.000 | 0.929 – 1.000 |
| \(F(000)\) | 1000 | 616 |
| \(2\theta_{\text{max}}\) | 154.8 | 70.3 |
| Refl. measured | 46122 | 97549 |
| Refl. indep. | 4568 | 11091 |
| \(R_{\text{int}}\) | 0.055 | 0.037 |
| Parameters | 283 | 363 |
| \(wR(F^2, \text{all refl.})\) | 0.095 | 0.080 |
| \(R(F, >4\sigma(F))\) | 0.037 | 0.029 |
| \(S\) | 1.04 | 1.06 |
| Max. \(\Delta p\) (e Å⁻³) | 0.38, -0.51 | 0.57, -0.40 |
3. \( ^1H \) and \( ^{13}C \) NMR spectra

3. 1. \( ^1H \) and \( ^{13}C \) NMR spectra for ferrocenyl (naphth-2-yl) thioketone (8c)

Figure S1: \( ^1H \) NMR spectrum for thioketone 8c.

Figure S2: \( ^{13}C \) NMR spectrum for thioketone 8c.
3.2. Collection of spectra for isolated tetrahydrothiophenes 9a–n

**Figure S3:** $^1$H NMR spectrum for 9a.

**Figure S4:** $^{13}$C NMR spectrum for 9a.

**Figure S5:** IR spectrum for 9a.
Figure S6: $^1$H NMR spectrum for 9b.

Figure S7: $^{13}$C NMR spectrum for 9b.
Figure S8: $^1$H NMR spectrum for 9c.

Figure S9: $^{13}$C NMR spectrum for 9c.
Figure S10: $^1$H NMR spectrum for 9d (isomer cis).

Figure S11: $^{13}$C NMR spectrum for 9d (isomer cis).

Figure S12: $^1$H NMR spectrum for 9d (isomer trans).
Figure S13: $^{13}$C NMR spectrum for 9d (isomer trans).

Figure S14: $^1$H NMR spectrum for 9e (crude mixture).

Figure S15: $^1$H NMR spectrum for 9e (isomer trans).
Figure S16: $^{13}$C NMR spectrum for 9e (isomer trans).

Figure S17: $^1$H NMR spectrum for 9f.

Figure S18: $^{13}$C NMR spectrum for 9f.
Figure S19: $^1$H NMR spectrum for 9g.

Figure S20: $^{13}$C NMR spectrum for 9g.

Figure S21: $^1$H NMR spectrum for 9h.
Figure S22: $^{13}$C NMR spectrum for 9h.

Figure S23: $^1$H NMR spectrum for 9i.

Figure S24: $^{13}$C NMR spectrum for 9i.
Figure S25: $^1$H NMR spectrum for 9j.

Figure S26: $^{13}$C NMR spectrum for 9j.

Figure S27: $^1$H NMR spectrum for 9k.
Figure S28: $^{13}$C NMR spectrum for 9k.

Figure S29: $^1$H NMR spectrum for 9l.

Figure S30: $^{13}$C NMR spectrum for 9l.
Figure S31: $^1$H NMR spectrum for 9m.

Figure S32: $^{13}$C NMR spectrum for 9m.

Figure S33: $^1$H NMR spectrum for 9n.
Figure S34: $^{13}$C NMR spectrum for 9n.

References

[S1] G. M. Sheldrick, Acta Cryst. C71, 3–8 (2015).