Thioamide Directed Iridium(I)-Catalyzed C-H Arylation of Ferrocenes with Aryl Boronic Acids

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1. General methods

The $^1$H NMR and $^{13}$C NMR spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer with CDCl$_3$ at room temperature. The chemical shifts in $^1$H NMR and $^{13}$C NMR spectra were determined with Si(CH$_3$)$_4$ as the internal standard ($\delta = 0.00, 77.00$ ppm). Data for $^1$H NMR are recorded as follows: chemical shift ($\delta$, ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet or unresolved, br = broad singlet, coupling constant (s) in Hz, integration). Data for $^{13}$C NMR, and $^{19}$F NMR are reported in terms of chemical shift and multiplicity where appropriate ($\delta$, ppm). The high resolution mass spectra (HRMS) were measured on a Bruker micrOTOF QII by ESI. The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. Melting points were measured on an SGW® X-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out on silica gel (300-400 mesh). Analytical TLC was performed with silica gel GF254 plates, and the products were visualized by UV detection. [IrCl(cod)]$_2$ was purchased from J&K Scientific. All Boronic Acids were purchased from Beijing Innochem science & technology Co Ltd and J&K Scientific. Catalytic reactions were carried out in Schlenk flasks under Ar atmosphere using pre-dried glassware, unless otherwise stated. All commercially available chemicals were used as received without further purification. Ferrocene carboxthioamide derivatives 1a, 1c, 1e-1g were known compounds and new compounds 1b, 1d and 1h-1m were prepared according to the literature$^{[1,2]}$.

2. General Procedure of Thioamide-Directed Ir(I)-Catalyzed C–H Arylation of Ferrocenes

![Reaction scheme]

To a 50 mL Schlenk tube was added 1 (0.1 mmol, 1 equiv.), aryl boronic acids 2 (0.3
mmol, 3equiv.), [IrCl(cod)]$_2$ (3.3 mg, 0.005 mmol, 5 mol%), Ag$_2$CO$_3$ (27.6 mg, 0.1 mmol, 1 equiv.), 2-MeTHF (1 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 °C (aluminum heat transfer block) for 24 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 500:1 to 5:1) affording the desired products 3.


3.1 Gram-Scale Synthesis

![N,S](5.3 mmol, 1.6 g) + PhB(OH)$_2$ (1.94 g, 15.9 mmol, 3 equiv.), [IrCl(cod)]$_2$ (178 mg, 0.265 mmol, 5 mol%), Ag$_2$CO$_3$ (1.46 g, 5.3 mmol, 1 equiv.), 2-MeTHF (25 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 °C (aluminum heat transfer block) for 48 h. The reaction mixture was diluted with 60 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (hexanes/ethyl acetate = 500:1 to 10:1) affording the desired product 3aa as orange solid, 1.36 g, 68% yield.

3.2 Derivations-Synthesis of 4$^{[3,4]}$:

![N,S](75.4 mg, 0.2 mmol, 1 equiv.) and THF (2 mL) were added to a 50 mL Schlenk tube, the mixture was cooled to 0 °C. LiAlH$_4$ (22.8 mg, 0.6 mmol, 3.0 equiv.) was
added slowly under the atmosphere of argon, then the tube was capped. The reaction mixture was then stirred at 70 °C for 15 h. Afterwards saturated NH₄Cl solution was slowly added to the reaction solution, followed by extraction with DCM (3*10 ml), the solvents were removed in vacuo. The crude mixture was purified by flash chromatography (petroleum ether : ethyl acetate = 2:1) affording 4 as yellow oil, Rₑ = 0.19, 66.5 mg, 96% yield.

3.3 Derivations-Synthesis of 5[^5]:

![Chemical structure of 3aa and 5](image)

3aa (75.4 mg, 0.2 mmol, 1 equiv.), H₂O₂ (51μL, 0.5 mmol, 2.5 equiv.) and EtOH (2 mL) were added to a 50 mL round-bottom flask, The reaction mixture was then stirred at 25 °C for 18 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 50:1) affording the desired product 5 as yellow solid, 22.0 mg 30% yield.

3.4 Derivations-Synthesis of 6:

![Chemical structure of 3aa and 6](image)

To a 50 mL Schlenk tube was added 3aa (0.3 mmol, 113.1 mg, 1 equiv.), allyl methyl carbonate (104.5 mg, 0.9 mmol, 3 equiv.), [Cp*Co(CO)I₂] (14.4 mg, 0.03 mmol, 10 mol%), AgNTf₂ (29.1 mg, 0.075 mmol, 25 mol%), THF (2 mL), the tube was sealed up with a cap and evacuated then refilled with Ar for three times. The reaction was kept stirring at 60 °C (aluminum heat transfer block) for 24 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silica gel (petroleum ether : ethyl acetate = 1:2) affording the desired product 6 as yellow solid, 10.7 mg 37% yield.
ethyl acetate = 50:1) affording the desired product 6 as yellow oil, $R_f = 0.62$, 81.8 mg 65% yield.


4.1 The procedure of synthesis of 1a/1a-d

To a 50 mL Schlenk tube was added 1a (0.1 mmol, 1 equiv.), CD$_3$CO$_2$D (114μL, 2 mmol, 20 equiv.), [IrCl(cod)]$_2$ (3.3 mg, 0.005 mmol, 5 mol%), Ag$_2$CO$_3$ (27.6 mg, 0.1 mmol, 1 equiv.), 2-MeTHF (0.9 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 °C (aluminum heat transfer block) for 24 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 10:1) affording the desired product 1a/1a-d.
4.2 The H/D exchange experiment of 3aa

General Procedure D: To a 50 mL Schlenk tube was added 1a (0.1 mmol), 1a-d (0.1 mmol), phenylboronic acid 2a (72 mg, 0.6 mmol, 3 equiv.), [IrCl(cod)]₂ (6.6 mg, 0.01 mmol, 5 mol%), Ag₂CO₃ (52.2 mg, 0.2 mmol, 1 equiv.), 2-MeTHF (2 mL). The air was evacuated and refilled three times with argon. Then the tube was capped. The reaction was kept stirring at 60 °C (aluminum heat transfer block) for 2 h. The reaction mixture was diluted with 40 mL DCM, the solvents were removed in vacuo. The crude mixture was purified by flash column chromatography on silicagel (petroleum ether : ethyl acetate = 100:1) affording the desired product 3aa/3aa-d. The ratio of 3aa and 3aa-d was determined by ¹H NMR to be 4.5:1.
5. Spectroscopic data

(2-phenylferrocenyl)(N,N-diethyl)methanethione (3aa)
Orange solid, 34.5 mg, 92% yield, mp: 165 ~ 166 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.57 (d, \(J = 7.6\) Hz, 2H), 7.26 (t, \(J = 7.2\) Hz, 2H), 7.20 (t, \(J = 7.0\) Hz, 1H), 4.6 (s, 1H), 4.55-4.47 (m, 2H), 4.35 (s, 1H), 4.24 (s, 5H), 3.50-3.41 (m, 1H), 3.14-3.05 (m, 1H), 2.80-2.71 (m, 1H), 1.14 (t, \(J = 7.0\) Hz, 3H), 0.59 (t, \(J = 7.0\) Hz, 3H). \(^1\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 197.3, 138.1, 128.1, 127.7, 126.5, 95.7, 82.7, 73.7, 72.7, 67.1, 64.5, 47.1, 47.0, 12.6, 10.6. HRMS (ESI) m/z: [M+H]\(^+\) calc. for C\(_{21}\)H\(_{23}\)FeNS 378.0973, found: 378.0971.

(2-(4-methylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ba)
Orange solid, 36.7 mg, 94% yield, mp: 74 ~ 77 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.38 (d, \(J = 7.6\) Hz, 2H), 7.00 (d, \(J = 7.6\) Hz, 2H), 4.55 (s, 1H), 4.48-4.42 (m, 2H), 4.25 (s, 1H), 4.17 (s, 5H), 3.45-3.36 (m, 1H), 3.09-3.00 (m, 1H), 2.72-2.66 (m, 1H), 2.25 (s, 3H), 1.08 (t, \(J = 7.0\) Hz, 3H), 0.55 (t, \(J = 7.0\) Hz, 3H). \(^1\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 197.6, 136.2, 135.1, 129.0, 127.7, 95.5, 83.1, 73.7, 72.8, 67.0, 64.6, 47.3, 47.1, 21.3, 12.7, 10.7. HRMS (ESI) m/z: [M+H]\(^+\) calc. for C\(_{22}\)H\(_{25}\)FeNS 292.1130, found: 292.1127.

(2-(4-methoxyphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ca)
Orange solid, 33.2 mg, 82% yield, mp: 137 ~ 140 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.50 (d, \(J = 8.6\) Hz, 2H), 6.83 (d, \(J = 8.6\) Hz, 2H), 4.61 (s, 1H), 4.55-4.46 (m, 2H), 4.31 (s, 1H), 4.25 (s, 5H), 3.82 (s, 3H), 3.52-3.44 (m, 1H), 3.16-3.06 (m, 1H), 2.82-3.73 (m, 1H), 1.15 (t, \(J = 4.8\) Hz, 3H), 0.63 (t, \(J = 7.1\) Hz, 3H). \(^1\)C NMR
(CDCl₃, 101 MHz) δ 179.6, 158.4, 130.3, 128.9, 113.7, 95.2, 83.1, 73.4, 72.7, 66.9, 64.6, 55.3, 47.2, 47.1, 12.7, 10.8. HRMS (ESI) m/z: [M+H]^+ calc. for C₂₂H₂₅FeNOS 408.1079, found: 408.1076.

(2-(1,1'-biphenyl)ferrocenyl)(N,N-diethyl)methanethione (3da)
Orange solid, 39.2 mg, 87% yield, mp: 166 ~ 168 °C. \(^1\)H NMR (CDCl₃, 400 MHz) δ 7.63 (t, J = 8.0 Hz, 4H), 7.53 (d, J = 8.2 Hz, 2H), 7.45 (t, J = 7.4 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 4.67 (s, 1H), 4.58-4.49 (m, 2H), 4.38 (t, J = 2.2 Hz, 1H), 4.28 (s, 5H), 3.54-3.45 (m, 1H), 3.19-3.10 (m, 1H), 2.85-2.76 (m, 1H), 1.17 (t, J = 7.0 Hz, 3H), 0.65 (t, J = 7.0 Hz, 3H). \(^{13}\)C NMR (CDCl₃, 101 MHz) δ 197.4, 140.7, 139.1, 137.4, 128.9, 128.1, 127.3, 126.8, 95.9, 82.3, 73.9, 72.9, 67.3, 64.5, 47.3, 47.2, 12.7, 10.7. HRMS (ESI) m/z: [M+H]^+ calc. for C₂₇H₂₇FeNS 454.1286, found: 454.1284.

(2-(4-vinylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ea)
Orange solid, 19.1 mg, 44% yield, mp: 136 ~ 139 °C. \(^1\)H NMR (CDCl₃, 400 MHz) δ 7.53 (d, J = 8.2 Hz, 2H), 7.32 (d, J = 8.2 Hz, 2H), 6.69 (dd, J = 17.6, 6.8 Hz, 1H), 5.75 (d, J = 17.6 Hz 1H), 5.25 (d, J = 10.8 Hz 1H), 4.65 (t, J = 1.6 Hz 1H), 4.55-4.46 (m, 2H), 4.36 (t, J = 2.4 Hz 1H), 4.25 (s, 5H), 3.54-3.45 (m, 1H), 3.16-3.09 (m, 1H), 2.82-2.73 (m, 1H), 1.17 (t, J = 7.0 Hz 3H), 0.63 (t, J = 7.0 Hz 3H). \(^{13}\)C NMR (CDCl₃, 101 MHz) δ 197.4, 138.1, 136.6, 135.7, 127.8, 126.1, 113.4, 95.9, 82.3, 74.0, 72.8, 67.3, 64.5, 47.3, 47.1, 12.7, 10.7. HRMS (ESI) m/z: [M+H]^+ calc. for C₂₃H₂₃FeNS 404.1130, found: 404.1122.

(2-(4-acetoxyphenyl)ferrocenyl)(N,N-diethyl)methanethione (3fa)
Orange solid, 28.0 mg, 64% yield, mp: 150 ~ 152 °C. \(^1\)H NMR (CDCl₃, 400 MHz) δ
7.58 (d, $J = 8.6$ Hz, 2H), 7.00 (d, $J = 8.6$ Hz, 2H), 4.64 (d, $J = 1.6$ Hz, 1H), 4.55-4.46 (m, 2H), 4.35 (t, $J = 2.4$ Hz 1H), 4.26 (s, 5H), 3.51-3.42 (m, 1H), 3.13-3.04 (m, 1H), 2.82-2.72 (m, 1H), 2.30 (s, 3H), 1.14 (t, $J = 7.0$ Hz, 3H), 0.64 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.2, 169.4, 149.3, 135.9, 128.7, 121.3, 95.9, 82.2, 73.7, 72.8, 67.2, 64.6, 47.2, 47.1, 21.3, 12.7, 10.7. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{23}$H$_{25}$FeNO$_2$S 436.1028, found: 436.1025.

(2-(4-cyclohexylphenyl)ferroceny1)(N,N-diethyl)methanethione (3ga)
Orange oil, 32.9 mg, 72% yield, R$_f$ = 0.45. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.46 (d, $J$ = 8.0 Hz, 2H), 7.10 (d, $J$ = 8.0 Hz, 2H), 4.62 (s, 1H), 4.57-4.48 (m, 2H), 4.32 (t, $J$ = 2.4 Hz, 1H), 4.25 (s, 5H), 3.48-3.40 (m, 1H), 3.12-3.03 (m, 1H), 2.79-2.70 (m, 1H), 2.47 (s, 1H), 1.86-1.73 (m, 5H), 1.46-1.24 (m, 5H), 1.12 (t, $J$ = 7.0 Hz, 3H), 0.58 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.6, 146.6, 135.3, 127.9, 126.6, 95.5, 83.3, 73.6, 72.8, 67.0, 64.6, 47.1, 47.0, 44.3, 34.6, 34.4, 27.0, 26.3, 12.5, 10.7, 1.1. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{27}$H$_{33}$FeNS 460.1756, found: 460.1752.

(2-(4-fluorophenyl)ferroceny1)(N,N-diethyl)methanethione (3ha)
Orange solid, 33.6 mg, 85% yield, mp: 167 ~ 170 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.49 (dd, $J$ = 8.2, 2.6 Hz, 2H), 6.90 (t, $J$ = 8.6 Hz, 2H), 4.55 (s, 1H), 4.47-4.40 (m, 2H), 4.27 (s, 1H), 4.18 (s, 5H), 3.45-3.37 (m, 1H), 3.05-2.96 (m, 1H), 2.75-2.66 (m, 1H), 1.07 (t, $J$ = 5.2 Hz, 3H), 0.57 (t, $J$ = 7.0 Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.3, 162.9, 160.5, 134.2 (d, $J$ = 3.3 Hz), 129.4 (d, $J$ = 7.8 Hz), 115.2 (d, $J$ = 21.4 Hz), 95.9, 82.2, 73.5, 72.8, 67.2, 64.7, 47.2, 47.1, 12.8, 10.8. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -115.8. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{21}$H$_{22}$FFeNS 396.0879, found: 396.0877.
(2-(4-chlorophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ia)
Orange solid, 32.1 mg, 78% yield, mp: 167 ~ 169 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.45 (d, $J = 8.2$ Hz, 2H), 7.17 (d, $J = 8.2$ Hz, 2H), 4.57 (s, 1H), 4.45-4.37 (m, 2H), 4.29 (s, 1H), 4.18 (s, 5H), 3.48-3.39 (m, 1H), 3.06-2.97 (m, 1H), 2.75-2.67 (m, 1H), 1.09 (t, $J = 7.0$ Hz, 3H), 0.58 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.1, 137.1, 132.2, 128.9, 128.5, 96.1, 81.6, 73.8, 72.9, 67.3, 64.5, 47.3, 47.1, 12.8, 10.8. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{21}$H$_{22}$ClFeNS 412.0584, found: 412.0583.

(2-(4-bromophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ja)
Orange solid, 34.0 mg, 75% yield, mp: 137 ~ 140 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.46 (d, $J = 8.4$ Hz, 2H), 7.39 (d, $J = 8.4$ Hz, 2H), 4.64 (t, $J = 1.8$ Hz, 1H), 4.52-4.44 (m, 2H), 4.36 (t, $J = 2.4$ Hz, 1H), 4.25 (s, 5H), 3.55-3.46 (m, 1H), 3.13-3.04 (m, 1H), 2.83-2.74 (m, 1H), 1.16 (t, $J = 7.0$ Hz, 3H), 0.65 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.1, 137.6, 131.4, 129.3, 120.2, 96.1, 81.5, 73.9, 72.9, 67.4, 64.4, 47.3, 47.1, 12.8, 10.8. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{21}$H$_{22}$BrFeNS 456.0079, found: 456.0079.

(2-(4-cyanophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ka)
Orange solid, 14.8 mg, 37% yield, mp: 171 ~ 173 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.69 (d, $J = 8.0$ Hz, 2H), 7.55 (d, $J = 8.0$ Hz, 2H), 4.72 (s, 1H), 4.53-4.43 (m, 3H), 4.26 (s, 5H), 3.58-3.49 (m, 1H), 3.11-3.01 (m, 1H), 2.84-2.75 (m, 1H), 1.17 (t, $J = 7.0$ Hz, 3H), 0.66 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 196.6, 144.6, 132.1, 127.9, 119.2, 109.5, 97.2, 80.1, 74.3, 73.1, 68.1, 64.4, 47.3, 47.1, 12.8, 10.7. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{22}$H$_{22}$FeN$_2$S 403.0926, found: 403.0924.
(2-(4-(trifluoromethyl)phenyl)ferrocenyl)(N,N-diethyl)methanethione (3la)
Orange solid, 14.6 mg, 33% yield, mp: 131 ~ 134 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$
7.70 (d, $J = 8.0$ Hz, 2H), 7.52 (d, $J = 8.2$ Hz, 2H), 4.69 (s, 1H), 4.54-4.41 (m, 3H), 4.27 (s, 5H), 3.56-3.47 (m, 1H), 3.13-3.04 (m, 1H), 2.82-2.73 (m, 1H), 1.16 (t, $J = 7.2$ Hz, 3H), 0.65 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$196.9, 142.9, 128.9, 128.5, 128.2, 127.8, 125.8, 125.2 (q, $J = 3.8$ Hz), 123.1, 96.8, 80.8, 74.2, 73.1, 67.8, 64.6, 47.3, 47.2, 12.8, 10.7. $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -62.4. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{22}$H$_{22}$F$_3$FeNS 446.0847, found: 446.0843.

(2-(3-methylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3ma)
Orange solid, 27.8 mg, 71% yield, mp: 154 ~ 157 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$
7.37 (t, $J = 7.8$ Hz, 2H), 7.16 (t, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.4$ Hz, 1H), 4.65-4.57 (m, 2H), 4.51 (s, 1H), 4.34 (t, $J = 2.2$ Hz, 1H), 4.26 (s, 5H), 3.42-3.33 (m, 1H), 3.16-3.07 (m, 1H), 2.79-2.70 (m, 1H), 2.35 (s, 3H), 1.15 (t, $J = 7.2$ Hz, 3H), 0.62 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 197.5, 138.2, 137.7, 128.4, 128.2, 127.4, 125.2, 95.7, 73.9, 72.9, 67.2, 64.6, 47.3, 47.2, 21.6, 12.7, 10.7. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{22}$H$_{25}$FeNS 392.1130, found: 392.1127.

(2-(3-methoxyphenyl)ferrocenyl)(N,N-diethyl)methanethione (3na)
Orange solid, 30.1 mg, 74% yield, mp: 119 ~ 121 °C. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$
7.21-7.13 (m, 3H), 6.77-6.75 (m, 1H), 4.62 (t, $J = 1.4$ Hz, 1H), 4.51-4.42 (m, 2H), 4.34 (t, $J = 2.4$ Hz, 1H), 4.27 (s, 5H), 3.83 (s, 3H), 3.57-3.48 (m, 1H), 3.15-3.06 (m, 1H), 2.83-2.74 (m, 1H), 1.15 (t, $J = 7.2$ Hz, 3H), 0.63 (t, $J = 7.2$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 197.5, 159.5, 139.8, 129.2, 120.4, 113.3, 112.4, 96.3, 83.0, 73.6, 72.9, 67.2, 64.6, 55.4, 47.3, 47.1, 12.7, 10.8. HRMS (ESI) m/z: [M+H]$^+$ calc. for
C_{22}H_{25}FeNOS 408.1079, found: 408.1077.

(2-(3-fluorophenyl)ferrocenyl)(N,N-diethyl) methanethione (3oa)
Orange solid, 28.1 mg, 71% yield, mp: 95 ~ 97 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) δ 7.30 (d, \(J = 7.8\) Hz, 1H), 7.22-7.14 (m, 2H), 6.86-6.81 (m, 1H), 4.59 (t, \(J = 2.2\) Hz, 1H), 4.52-4.42 (m, 2H), 4.31 (t, \(J = 2.4\) Hz, 1H), 4.19 (s, 5H), 3.44-3.35 (m, 1H), 3.08-2.99 (m, 1H), 2.76-2.67 (m, 1H), 1.10 (t, \(J = 7.0\) Hz, 3H), 0.58 (t, \(J = 7.0\) Hz, 3H). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) δ 197.1, 164.0, 161.6, 141.1 (d, \(J = 8.1\) Hz), 129.8 (d, \(J = 8.4\) Hz), 123.5 (d, \(J = 2.7\) Hz), 114.4 (d, \(J = 22.0\) Hz), 113.4 (d, \(J = 21.1\) Hz), 96.3, 81.4 (d, \(J = 2.2\) Hz), 74.0, 73.0, 67.5, 64.6, 47.3, 47.1, 12.8, 10.6. \(^{19}\)F NMR (376 MHz, CDCl\(_3\)) δ -113.5.

HRMS (ESI) m/z: [M+H]\(^+\) calc. for C\(_{21}\)H\(_{22}\)FeNS 396.0879; found: 396.0877.

(2-(3-chlorophenyl)ferrocenyl)(N,N-diethyl) methanethione (3pa)
Orange solid, 25.0 mg, 61% yield, mp: 159 ~ 161 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) δ 7.45-7.43 (m, 2H), 7.16-7.10 (m, 2H), 4.60 (t, \(J = 1.6\) Hz, 1H), 4.57-4.48 (m, 1H), 4.43 (t, \(J = 1.6\) Hz, 1H), 4.31 (t, \(J = 2.4\) Hz, 1H), 4.19 (s, 5H), 3.39-3.30 (m, 1H), 3.08-2.99 (m, 1H), 2.75-2.66 (m, 1H), 1.10 (t, \(J = 7.0\) Hz, 3H), 0.59 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) δ 197.0, 140.7, 134.2, 129.6, 127.3, 126.6, 126.1, 96.2, 81.2, 74.1, 73.0, 67.5, 64.5, 47.3, 47.2, 12.8, 10.7. HRMS (ESI) m/z: [M+H]\(^+\) calc. for C\(_{21}\)H\(_{22}\)ClFeNS 412.0584; found: 412.0582.

(2-(3-bromophenyl)ferrocenyl)(N,N-diethyl) methanethione (3qa)
Orange solid, 28.5 mg, 63% yield, mp: 163 ~ 166 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) δ 7.66 (s, 1H), 7.57 (d, \(J = 7.8\) Hz, 1H), 7.34 (dd, \(J = 8.0, 7.2\) Hz, 1H), 7.15 (t, \(J = 7.8\) Hz, 1H), 4.67 (t, \(J = 1.6\) Hz, 1H), 4.64-4.57 (m, 1H), 4.49 (q, \(J = 2.2, 0.6\) Hz, 1H),
4.38 (t, $J = 2.6$ Hz, 1H), 4.26 (s, 5H), 3.45-3.37 (m, 1H), 3.14-3.05 (m, 1H), 2.82-2.73 (m, 1H), 1.18 (t, $J = 7.0$ Hz, 3H), 0.66 (t, $J = 7.0$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 196.9, 140.9, 130.1, 129.9, 129.5, 126.5, 122.4, 96.2, 81.1, 74.1, 73.0, 67.5, 64.5, 47.3, 47.2, 12.8, 10.8. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{21}$H$_{22}$BrFeNS 456.0079, found: 456.0079.

(2-(3-nitrophenyl)ferroceny1)(N,N-diethyl)methanethione (3ra)

Brick red solid, 24.5 mg, 58% yield, mp: 95 ~ 98 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.24 (s, 1H), 8.00 (d, $J = 7.6$ Hz, 2H), 7.39 (t, $J = 7.6$ Hz, 1H), 4.63 (s, 1H), 4.53-4.38 (m, 3H), 4.21 (s, 5H), 3.45-3.39 (m, 1H), 3.08-3.01 (m, 1H), 2.79-2.70 (m, 1H), 1.08 (t, $J = 6.8$ Hz, 3H), 0.63 (t, $J = 6.8$ Hz, 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 196.3, 148.2, 140.9, 133.8, 129.1, 121.5, 121.1, 96.7, 80.1, 73.6, 72.9, 67.7, 64.8, 47.1, 12.8, 10.6. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{21}$H$_{22}$FeN$_2$O$_2$S 423.0824, found: 423.0821.

(2-(2-methylphenyl)ferrocenyl)(N,N-diethyl)methanethione (3sa)

Orange solid, 9.4 mg, 24% yield, mp: 107 ~ 110 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.96 (d, $J = 7.2$ Hz 1H), 7.12-7.04 (m, 3H), 4.62 (s, 1H), 4.40-4.31 (m, 3H), 4.23 (s, 5H), 3.35-3.26 (m, 1H), 3.01-2.93 (m, 1H), 2.69-2.60 (m, 1H), 2.22 (s, 3H), 0.91 (t, $J = 7.0$ Hz 3H), 0.51 (t, $J = 7.0$ Hz 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.4, 135.9, 135.5, 132.6, 130.2, 126.7, 125.6, 97.3, 83.9, 73.0, 72.9, 67.9, 66.6, 46.9, 46.8, 21.1, 12.7, 10.7. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{22}$H$_{25}$FeNS 392.1130, found: 392.1126.

(2-(2-chlorophenyl)ferrocenyl)(N,N-diethyl)methanethione (3ta)
Orange solid, 7.6 mg, 18% yield, mp: 120 ~ 122 °C. \( ^1H \) NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 8.15 (d, \( J = 7.8 \) Hz 1H), 7.31 (d, \( J = 8.0 \) Hz 1H), 7.25 (t, \( J = 7.6 \) Hz 1H), 7.16 (t, \( J = 7.6 \) Hz 1H), 4.75 (s, 1H), 4.68 (s, 1H), 4.48-4.41 (m, 2H), 4.31 (s, 5H), 3.42-3.34 (m, 1H), 3.18-3.10 (m, 1H), 2.82-2.73 (m, 1H), 0.97 (t, \( J = 7.0 \) Hz 3H), 0.67 (t, \( J = 7.0 \) Hz 3H). \( ^{13}C \) NMR (CDCl\textsubscript{3}, 101 MHz) \( \delta \) 196.8, 135.7, 134.1, 133.0, 129.6, 127.9, 126.4, 97.8, 81.7, 73.0, 72.4, 68.8, 66.7, 46.9, 46.7, 12.9, 10.7. HRMS (ESI) m/z: [M+H]\(^{+}\) calc. for C\textsubscript{21}H\textsubscript{22}ClFeNS 412.0584, found: 412.0582.

(2-(naphthalen-1-yl) ferrocenyl)(N,N-diethyl)methanethione (3ua)
Orange solid, 10.5 mg, 25% yield, mp: 195 ~ 197 °C. \( ^1H \) NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 8.27 (d, \( J = 7.0 \) Hz 2H), 7.85, (t, \( J = 4.0 \) Hz 1H), 7.76 (d, \( J = 8.0 \) Hz 1H), 7.50-7.42 (m, 3H), 4.79 (s, 1H), 4.70 (s, 1H), 4.50 (s, 1H), 4.41-4.33 (m, 6H), 3.33-3.25 (m, 1H), 3.09-3.00 (m, 1H), 2.56-2.50 (m, 1H), 0.84 (t, \( J = 7.0 \) Hz 3H), 0.38 (t, \( J = 7.0 \) Hz 3H). \( ^{13}C \) NMR (CDCl\textsubscript{3}, 101 MHz) \( \delta \) 197.1, 134.1, 133.7, 132.0, 130.1, 128.7, 127.3, 125.9, 125.4, 125.3, 97.9, 83.3, 73.1, 68.3, 68.8, 46.9, 46.8, 12.7, 10.6. HRMS (ESI) m/z: [M+H]\(^{+}\) calc. for C\textsubscript{25}H\textsubscript{25}FeNS 428.1130, found: 428.1128.

(2-(benzo[d][1,3]dioxol-5-yl)ferrocenyl)(N,N-diethyl)methanethione (3va)
Brownish yellow solid, 29.8 mg, 71% yield, mp: 153 ~ 155 °C. \( ^1H \) NMR (CDCl\textsubscript{3}, 400 MHz) \( \delta \) 7.12 (s, 1H), 7.04 (d, \( J = 8.0 \) Hz 1H), 6.73 (d, \( J = 8.0 \) Hz 1H), 5.96 (d, \( J = 3.2 \) Hz 2H), 4.61-4.51 (m, 2H), 4.45 (s, 1H), 4.31 (s, 1H), 4.26 (s, 5H), 3.51-3.42 (m, 1H), 3.17-3.08 (m, 1H), 2.84-2.75 (m, 1H), 1.17 (t, \( J = 7.0 \) Hz 3H), 0.67 (t, \( J = 7.0 \) Hz 3H). \( ^{13}C \) NMR (CDCl\textsubscript{3}, 101 MHz) \( \delta \) 197.3, 147.4, 146.3, 132.0, 121.1, 108.4, 108.1, 100.1, 95.3, 83.1, 73.4, 72.7, 66.8, 64.6, 47.1, 47.0, 12.7, 10.6. HRMS (ESI) m/z: [M+H]\(^{+}\) calc. for C\textsubscript{22}H\textsubscript{23}FeNO\textsubscript{2}S 422.0872, found: 422.0866.
(2-(thiophen-2-yl)ferrocenyl)(N,N-diethyl)methanethione (3wa)
Orange solid, 22.1 mg, 58% yield, mp: 172 ~ 175 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 7.15 (dd, $J = 8.4$, 3.0 Hz 2H), 6.93 (t, $J = 4.2$ Hz 1H), 4.57 (s, 1H), 4.53 (s, 1H), 4.48-4.40 (m, 1H), 4.31 (s, 1H), 4.30 (s, 5H), 3.67-3.60 (m, 1H), 3.21-3.12 (m, 1H), 2.97-2.88 (m, 1H), 1.23 (t, $J = 7.2$ Hz 3H), 0.74 (t, $J = 7.2$ Hz 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 196.5, 141.0, 127.3, 124.3, 123.8, 95.3, 77.0, 73.1, 72.3, 66.9, 65.9, 47.3, 47.1, 12.8, 10.8. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{19}$H$_{21}$FeNS$_2$ 384.0538, found: 384.0534.

(2-(benzo[b]thiophen-3-yl)ferrocenyl)(N,N-diethyl)methanethione (3xa)
Brown solid, 24.4 mg, 56% yield, mp: 178 ~ 181 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.01 (d, $J = 7.8$ Hz 1H), 7.86 (d, $J = 7.8$ Hz 1H), 7.80 (s, 1H), 7.41-7.33 (m, 2H), 4.70 (s, 1H), 4.68 (s, 1H), 4.45-4.36 (m, 2H), 4.33 (s, 5H), 3.44-3.35 (m, 1H), 3.09-3.00 (m, 1H), 2.72-2.63 (m, 1H), 0.96 (t, $J = 7.0$ Hz 3H), 0.52 (t, $J = 8.8$ Hz 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 197.2, 140.3, 138.4, 132.8, 125.1, 124.3, 124.2, 123.1, 123.0, 96.6, 77.9, 72.9, 72.8, 67.1, 66.3, 47.1, 47.0, 12.8, 10.9. HRMS (ESI) m/z: [M+H]$^+$ calc. for C$_{23}$H$_{23}$FeNS$_2$ 434.0694, found: 434.0692.

(2-(6-ethoxypyridin-3-yl)ferrocenyl)(N,N-diethyl)methanethione (3ya)
Orange solid, 25.1 mg, 60% yield, mp: 116 ~ 118 °C. $^1$H NMR (CDCl$_3$, 400 MHz) δ 8.16 (d, $J = 2.0$ Hz 1H), 7.86 (dd, $J = 8.6$, 6.6 Hz 1H), 6.61 ($J = 8.6$ Hz 1H), 4.55 (s, 1H), 4.46-4.37 (m, 2H), 4.32-4.24 (m, 3H), 4.19 (s, 5H), 3.46-3.37 (m, 1H), 3.09-3.00 (m, 1H), 2.78-2.69 (m, 1H), 1.34 (t, $J = 7.0$ Hz 3H), 1.07 (t, $J = 7.0$ Hz 3H), 0.63 (t, $J = 7.0$ Hz 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) δ 196.9, 162.7, 144.7, 138.6, 126.8, 110.4, 95.4, 80.0, 73.1, 72.6, 67.1, 64.4, 61.8, 47.1, 47.0, 14.7, 12.8, 10.8. HRMS
(ESI) m/z: [M+H]^+ calc. for C_{22}H_{26}FeN_{2}OS 423.1188, found: 423.1182.

(2-phenylferrocenyl)(N,N-dipropyl)methanethione (3ab)
Orange solid, 29.3 mg, 72% yield, mp: 120 ~ 123 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.49 (d, \(J = 7.2\) Hz 2H), 7.22-7.12 (m, 3H), 4.59 (s, 1H), 4.49-4.43 (m, 2H), 4.28 (s, 1H), 4.18 (s, 5H), 3.15-3.07 (m, 1H), 3.02-2.95 (m, 1H), 2.53-2.46 (m, 1H), 1.73-1.68 (m, 1H), 1.42-1.31 (m, 1H), 1.15-1.07 (m, 1H), 0.88-0.81 (m, 1H), 0.76 (t, \(J = 7.2\) Hz 3H), 0.42 (t, \(J = 7.2\) Hz 3H). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 198.1, 138.3, 128.3, 127.9, 126.6, 96.0, 83.0, 74.4, 72.9, 67.2, 64.6, 54.7, 54.5, 20.9, 18.7, 11.6, 11.8. HRMS (ESI) m/z: [M+H]^+ calc. for C\(_{23}\)H\(_{27}\)FeNS 406.1286, found: 406.1283.

(2-phenylferrocenyl)(N,N-diisopropyl)methanethione (3ac)
Red-brown solid, 24.1 mg, 60% yield, mp: 137 ~ 139 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.67 (d, \(J = 7.2\) Hz 2H), 7.28 (t, \(J = 7.2\) Hz 2H), 7.20 (t, \(J = 7.4\) Hz 1H), 4.53 (s, 1H), 4.46 (t, \(J = 2.2\) Hz 1H), 4.32 (t, \(J = 2.4\) Hz 1H), 4.28 (s, 5H), 3.75 (s, 1H), 3.62 (s, 1H), 1.77 (s 3H), 1.62 (s, 3H), 0.83 (d, \(J = 6.8\) Hz 3H), 0.22 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 196.4, 138.3, 128.1, 128.1, 126.5, 100.6, 82.8, 72.6, 66.7, 63.6, 56.2, 50.6, 20.5, 20.3, 18.6, 17.5. HRMS (ESI) m/z: [M+H]^+ calc. for C\(_{23}\)H\(_{27}\)FeNS 406.1286, found: 406.1284.

(2-phenylferrocenyl)(N-methyl-N-phenyl)methanethione (3ad)
Orange solid, 36.4 mg, 88% yield, mp: 152 ~ 155 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.17 (t, \(J = 1.6\) Hz 3H), 7.05 (t, \(J = 3.6\) Hz 2H), 6.87 (t, \(J = 7.4\) Hz 1H), 6.77 (t, \(J = 7.8\) Hz 2H), 6.14 (d, \(J = 7.0\) Hz 2H), 4.89 (d, \(J = 1.4\) Hz 1H), 4.26 (d, \(J = 2.2\) Hz 1H), 4.17 (s, 1H), 4.15 (s, 5H), 3.70 (s, 3H). \(^{13}\)C NMR (CDCl\(_3\), 101 MHz) \(\delta\) 200.4, 145.8,
138.5, 127.9, 127.8, 126.2, 125.8, 125.4, 94.9, 83.2, 77.0, 72.9, 67.8, 65.5, 46.7.

**HRMS (ESI)** m/z: [M+H]^+ calc. for C_{24}H_{21}FeNS 412.0817, found: 412.0814.

(2-phenylferrocenyl)(N,N-dibenzyl)methanethione (3ae)

Yellow solid, 30.0 mg, 60% yield, mp: 75 ~ 78 °C. ^1^H NMR (CDCl$_3$, 400 MHz) δ 7.53 (dd, $J = 6.6$, 3.5 Hz 2H), 7.18-7.08 (m, 9H), 6.95 (dd, $J = 5.6$, 2.1 Hz 2H), 6.67 (dd, $J = 5.4$, 3.8 Hz 2H), 6.19 (d, $J = 14.6$ Hz 1H), 4.66 (t, $J = 1.6$ Hz 1H), 4.46-4.41 (m, 2H), 4.26 (t, $J = 2.4$ Hz 1H), 4.24 (s, 5H), 4.05 (d, $J = 14.6$ Hz 1H), 3.48 (d, $J = 15.4$ Hz 1H). ^13^C NMR (CDCl$_3$, 101 MHz) δ 201.1, 137.9, 135.5, 135.4, 128.7, 128.6, 128.5, 128.5, 127.7, 127.6, 127.5, 126.8, 95.8, 84.1, 74.5, 72.9, 67.6, 65.4, 54.5, 54.4. HRMS (ESI) m/z: [M+H]^+ calc. for C_{31}H_{27}FeNS 502.1286, found: 502.1281.

(2-phenylferrocenyl)(piperidin-1-yl)methanethione (3af)

Yellow solid, 23.9 mg, 61% yield, mp: 164 ~ 167 °C. ^1^H NMR (CDCl$_3$, 400 MHz) δ 7.46 (d, $J = 7.4$ Hz 2H), 7.22 (t, $J = 7.2$ Hz 2H), 7.15 (t, $J = 7.2$ Hz 1H), 4.66 (s, 1H), 4.44 (s, 1H), 3.33 (s, 1H), 4.18 (s, 5H), 4.13-3.96 (m, 2H), 2.94-2.79 (m, 2H), 1.57-1.22 (m, 4H), 0.99-0.95 (m, 1H), 0.40 (s, 1H). ^13^C NMR (CDCl$_3$, 101 MHz) δ 197.6, 138.3, 128.3, 126.7, 94.5, 83.1, 75.4, 73.0, 67.8, 64.9, 52.3, 51.7, 25.5, 25.1, 24.1. HRMS (ESI) m/z: [M+H]^+ calc. for C_{22}H_{23}FeNS 390.0973, found: 390.0967.

(2-phenylferrocenyl)(azepan-1-yl)methanethione (3ag)

Yellow solid, 26.3 mg, 65% yield, mp: 122 ~ 124 °C. ^1^H NMR (CDCl$_3$, 400 MHz) δ 7.58 (d, $J = 7.4$ Hz 2H), 7.28 (t, $J = 7.2$ Hz 2H), 7.21 (t, $J = 7.0$ Hz 1H), 4.60 (s, 1H), 4.52 (s, 1H), 4.39-4.33 (m, 2H), 4.26 (s, 5H), 3.73-3.67 (m, 1H), 3.26-3.19 (m, 1H), 2.74-2.71 (m, 1H), 2.05-1.96 (m, 1H), 1.67-1.60 (m, 1H), 1.49-1.33 (m, 2H), 1.22-1.12 (m, 4H). ^13^C NMR (CDCl$_3$, 101 MHz) δ 200.0, 138.5, 128.3, 127.7, 126.5, 96.3, 83.1,
73.7, 72.7, 67.2, 64.6, 54.1, 53.4, 27.9, 27.6, 25.9, 25.6. **HRMS (ESI)** m/z: [M+H]⁺ calc. for C_{23}H_{25}FeNS 404.1130, found: 404.1126.

(2-phenylferrocenyl)(morpholine-4-yl)methanethione (3ah)

Yellow solid, 7.2 mg, 18% yield, mp: 188 ~ 191 °C. **¹H NMR (CDCl₃, 400 MHz)** δ 7.52 (d, J = 7.2 Hz 2H), 7.32 (t, J = 7.0 Hz 2H), 7.26 (t, J = 5.8 Hz 1H), 4.77 (s, 1H), 4.52 (s, 1H), 4.45-4.40 (m, 2H), 4.25 (s, 5H), 3.98-3.92 (m, 1H), 3.73-3.65 (m, 1H), 3.41-3.36 (m, 1H), 3.14-2.99 (m, 3H), 2.27 (s, 1H). **¹³C NMR (CDCl₃, 101 MHz)** δ 199.2, 140.0, 128.5, 128.4, 127.1, 93.3, 83.2, 76.0, 73.1, 68.2, 65.8, 65.6, 65.3, 51.7, 50.6. **HRMS (ESI)** m/z: [M+H]⁺ calc. for C_{21}H_{21}FeNOS 392.0772, found: 392.0760.

(2-phenylferrocenyl)(4-methylpiperazin-1-yl)methanethione (3ai)

Yellow oil, 24.3 mg, 60% yield, Rₜ = 0.24. **¹H NMR (CDCl₃, 400 MHz)** δ 7.51 (d, J = 7.2 Hz 2H), 7.30 (t, J = 7.0 Hz 2H), 7.23 (t, J = 7.2 Hz 1H), 4.76 (s, 1H), 4.52 (s, 1H), 4.42-4.38 (m, 2H), 4.25 (s, 5H), 4.05-4.00 (m, 1H), 3.00 (s, 2H), 2.48-2.43 (m, 1H), 2.15-2.11 (m, 1H), 2.04 (s 3H), 1.94-1.87 (m, 1H), 1.05 (s, 1H). **¹³C NMR (CDCl₃, 101 MHz)** δ 198.7, 138.1, 128.4, 126.8, 93.8, 83.2, 75.7, 73.0, 68.0, 65.1, 53.7, 50.9, 50.1, 45.4. **HRMS (ESI)** m/z: [M+H]⁺ calc. for C_{22}H_{24}FeN_{2}S 405.1082, found: 405.1080.

(2-phenylferrocenyl)(4-phenylpiperazin-1-yl)methanethione (3aj)

Yellow solid, 9.4 mg, 20% yield, mp: 87 ~ 90 °C. **¹H NMR (CDCl₃, 400 MHz)** δ 7.53 (d, J = 7.4 Hz 2H), 7.28 (t, J = 7.4 Hz 2H), 7.21-7.16 (m, 3H), 6.83 (t, J = 7.2 Hz 1H), 6.68 (d, J = 8.0 Hz 2H), 4.78 (s, 1H), 4.55-4.49 (m, 2H), 4.43 (d, J = 2.2 Hz 1H), 4.25 (s, 5H), 4.17-4.11 (m, 1H), 3.27-3.13 (m, 3H), 2.92-2.87 (m, 1H), 2.68-2.63 (m, 1H),
1.87-1.84 (m, 1H). \(^{13}\text{C NMR (CDCl}_3, 101\text{ MHz})\) \(\delta\) 200.0, 150.3, 138.0, 129.2, 128.4, 128.3, 127.0, 120.4, 116.4, 93.6, 83.2, 76.0, 73.1, 68.1, 65.3, 50.8, 50.1, 48.5, 48.1.

**HRMS (ESI)** m/z: [M+H]+ calc. for C\(_{27}\)H\(_{26}\)FeN\(_2\)S 467.1239; found: 467.1237.

![Diagram](image)

**Yellow solid, 22.8 mg, 47% yield, mp: 170 ~ 173 °C.** \(^1\text{H NMR (CDCl}_3, 400\text{ MHz})\) \(\delta\) 7.49 (d, \(J = 7.2\) Hz 2H), 7.31-7.20 (m, 6H), 7.15 (d, \(J = 7.0\) Hz 2H), 4.75 (s, 1H), 4.50 (s, 1H), 4.40 (d, \(J = 2.2\) Hz 1H), 4.28-4.16 (m, 7H), 3.25 (s, 2H), 3.11-2.85 (m, 2H), 2.52-2.43 (m, 1H), 2.28-2.20 (m, 1H), 1.94-1.86 (m, 1H), 1.25-1.08 (m, 1H). \(^{13}\text{C NMR (CDCl}_3, 101\text{ MHz})\) \(\delta\) 198.4, 138.1, 137.4, 129.2, 128.4, 127.4, 126.8, 93.8, 83.2, 75.8, 73.1, 68.0, 65.1, 62.4, 51.9, 51.8, 51.1, 50.2. **HRMS (ESI)** m/z: [M+H]+ calc. for C\(_{28}\)H\(_{33}\)FeNS 481.1395, found: 481.1390.

![Diagram](image)

**3ak**

Yellow oil, 31.4 mg, 63% yield, \(R_f = 0.35\). \(^1\text{H NMR (CDCl}_3, 400\text{ MHz})\) \(\delta\) 7.51-7.48 (m, 2H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 1H), 6.96-6.90 (m, 3H), 6.85 (d, \(J = 8.0\) Hz 1H), 4.56-4.49 (m, 1H), 4.48-4.41 (m, 1H), 4.38-4.36 (m, 1.5H), 4.27 (dd, \(J = 3.6, 2.4\) Hz 0.5H), 4.22-4.17 (m, 1.5H), 4.14-4.13 (m, 0.5H), 4.10-4.08 (m, 1H), 4.02-4.00 (m, 0.5H), 3.89 (q, \(J = 7.2\) Hz 0.5H), 3.83-3.83 (m, 0.5H), 3.51 (q, \(J = 7.2\) Hz 0.5H), 3.45-3.36 (m, 1H), 3.09-2.99 (m, 1H), 2.74-2.64 (m, 1H), 2.19 (d, \(J = 6.0\) Hz 3H), 1.34 (t, \(J = 7.0\) Hz 3H), 1.08 (td, \(J = 7.0, 3.3\) Hz 3H), 0.54 (td, \(J = 7.2, 3.6\) Hz 3H). \(^{13}\text{C NMR (CDCl}_3, 101\text{ MHz})\) \(\delta\) 198.7, 144.8, 144.7, 138.2, 137.9, 135.3, 129.0, 128.3, 127.9, 127.8, 127.1, 127.0, 126.6, 96.0, 95.9, 95.9, 95.8, 82.7, 75.2, 75.1, 74.9, 74.5, 73.5, 73.2, 72.7, 69.5, 68.3, 68.2, 65.5, 47.2, 47.1, 38.5, 38.4, 22.5, 21.1, 12.7, 10.7. **HRMS (ESI)** m/z: [M+H]+ calc. for C\(_{30}\)H\(_{33}\)FeNS 496.1756, found: 496.1753.
3am
Yellow oil, 26.9 mg, 54% yield, R<sub>f</sub> = 0.45. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.49 (d, J = 7.4 Hz 2H), 7.22-7.18 (m, 2H), 7.16-7.11 (m, 1H), 6.98-6.88 (m, 2H), 6.83-6.76 (m, 2H), 4.55 (s, 0.5H), 4.49-4.41 (m, 1.5H), 4.36 (s, 1.5H), 4.25-4.14 (m, 3H), 4.03-3.94 (m, 1.5H), 3.81 (s, 0.5H), 3.53 (q, J = 14.2, 7.0 Hz 0.5H), 3.44-3.35 (m, 1H), 3.08-2.98 (m, 1H), 2.73-2.63 (m, 1H), 1.36-1.21 (m, 3H), 1.10-1.05 (m, 3H), 0.55-0.51 (m, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 197.5, 162.4, 159.9, 143.5 (d, J = 3.1 Hz), 143.3 (d, J = 3.1 Hz), 138.0, 137.7, 128.5 (t, J = 8.0 Hz), 128.3 (d, J = 3.2 Hz), 127.8 (d, J = 11.6 Hz), 126.6, 114.9 (d, J = 21.0 Hz), 96.0 (d, J = 16.5 Hz), 95.5 (d, J = 8.9 Hz), 82.7 (d, J = 1.9 Hz), 75.2, 74.9, 74.5, 73.6, 73.4, 72.9, 72.8, 69.5, 69.3, 68.3, 68.1, 65.4, 47.2, 47.1, 38.1, 37.9, 22.6, 22.5, 12.7, 10.7. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -117.7. HRMS (ESI) m/z: [M+H]<sup>+</sup> calc. for C<sub>29</sub>H<sub>30</sub>FeNS 500.1500, found: 500.1505.

1-(2-phenylferrocenyl)(N, N-diethyl)amine (4)
Yellow oil, R<sub>f</sub> = 0.19. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.69 (d, J = 7.4 Hz 2H), 7.22 (t, J = 7.4 Hz 2H), 7.14 (t, J = 7.2 Hz 1H), 4.36 (s, 1H), 4.23 (s, 1H), 4.13 (t, J = 2.4 Hz 1H), 3.97 (s, 5H), 3.64 (d, J = 12.8 Hz 1H), 3.33 (d, J = 13.0 Hz 1H), 3.33 (d, J = 13.0 Hz 1H), 2.50-2.42 (m, 2H), 2.37-2.28 (m, 2H), 0.86 (t, J = 7.1 Hz 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ 139.0, 129.7, 127.9, 126.2, 88.5, 83.0, 71.7, 70.1, 69.8, 67.0, 51.5, 46.1, 11.6. HRMS (ESI) m/z: [M+H]<sup>+</sup> calc. for C<sub>21</sub>H<sub>25</sub>FeN 348.1409, found: 348.1404.

(2-phenylferrocenyl)(N,N-diethyl) amide (5)
Yellow solid, mp: 70 ~ 72 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz) δ 7.44 (d, J = 7.4 Hz 2H), 7.17 (t, J = 6.8 Hz 2H), 7.13 (t, J = 7.0 Hz 1H), 4.47 (s, 1H), 4.44 (s, 1H), 4.23 (s, 1H), 4.20 (s, 5H), 4.65-4.57 (m, 1H), 3.13-3.04 (m, 1H), 2.89-2.81 (m, 1H), 2.71-2.62 (m, 1H), 1.02 (t, J = 7.0 Hz 3H), 0.57 (t, J = 7.0 Hz 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 101 MHz) δ
168.7, 138.1, 128.2, 127.8, 126.6, 87.2, 85.0, 71.4, 70.3, 67.2, 67.1, 65.4, 42.8, 39.5, 13.5, 12.6. **HRMS (ESI)** m/z: [M+H]+ calc. for C$_{21}$H$_{23}$FeNO 362.1202, found: 362.1200.

(2-allyl-5-phenylferrocenyl)(N,N-diethyl)methanethione (6)
Yellow oil, R$_f$ = 0.62. $^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.55 (d, $J$ = 7.4 Hz 2H), 7.18 (t, $J$ = 7.2 Hz 2H), 7.11 (t, $J$ = 7.2 Hz 1H), 5.87-5.77 (m, 1H), 5.00-4.89 (m, 2H), 4.36 (d, $J$ = 2.0 Hz 1H), 4.21 (d, $J$ = 2.0 Hz 1H), 4.18-4.11 (m, 6H), 3.66-3.58 (m, 1H), 3.35-3.22 (m, 2H), 2.95-2.86 (m, 1H), 2.74-2.66 (m, 1H), 1.05 (t, $J$ = 7.0 Hz 3H), 0.43 (t, $J$ = 7.2 Hz 3H). $^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 196.3, 138.5, 137.2, 128.2, 127.8, 126.4, 115.5, 96.0, 89.2, 82.9, 73.1, 67.4, 67.4, 62.5, 47.0, 46.5, 31.8, 12.6, 10.6. **HRMS (ESI)** m/z: [M+H]+ calc. for C$_{24}$H$_{27}$FeNS 418.1286, found: 418.1284.

### 6. References


7. Spectra.

3aa, $^1$H NMR, 400 MHz, CDCl$_3$

3aa, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ba, $^1$H NMR, 400 MHz, CDCl$_3$

3ba, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ca, $^1$H NMR, 400 MHz, CDCl$_3$

3ca, $^{13}$C NMR, 101 MHz, CDCl$_3$
3da, $^1$H NMR, 400 MHz, CDCl$_3$

3da, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ea, $^1$H NMR, 400 MHz, CDCl$_3$

3ea, $^{13}$C NMR, 101 MHz, CDCl$_3$
3fa, \(^1\)H NMR, 400 MHz, CDCl\(_3\)

3fa, \(^{13}\)C NMR, 101 MHz, CDCl\(_3\)
3ga, $^1$H NMR, 400 MHz, CDCl$_3$

3ga, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ha, $^1$H NMR, 400 MHz, CDCl$_3$

3ha, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ha, $^{19}\text{F}$ NMR, 376 MHz, CDCl$_3$
3ia, \(^1\)H NMR, 400 MHz, CDCl\(_3\)

3ia, \(^{13}\)C NMR, 101 MHz, CDCl\(_3\)
3ja, $^1$H NMR, 400 MHz, CDCl$_3$

3ja, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ka, $^1$H NMR, 400 MHz, CDCl$_3$

3ka, $^{13}$C NMR, 101 MHz, CDCl$_3$
3la, $^1$H NMR, 400 MHz, CDCl$_3$

3la, $^{13}$C NMR, 101 MHz, CDCl$_3$
3la, $^{19}\text{F NMR, 376 MHz, CDCl}_3$
3ma, $^1$H NMR, 400 MHz, CDCl$_3$

3ma, $^{13}$C NMR, 101 MHz, CDCl$_3$
3na, $^1$H NMR, 400 MHz, CDCl$_3$

3na, $^{13}$C NMR, 101 MHz, CDCl$_3$
3oa, $^1$H NMR, 400 MHz, CDCl$_3$

3oa, $^{13}$C NMR, 101 MHz, CDCl$_3$
30a, $^{19}$F NMR, 376 MHz, CDCl$_3$
3pa, $^1$H NMR, 400 MHz, CDCl$_3$

3pa, $^{13}$C NMR, 101 MHz, CDCl$_3$
3qa, $^1$H NMR, 400 MHz, CDCl$_3$

3qa, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ra, $^1$H NMR, 400 MHz, CDCl$_3$

3ra, $^{13}$C NMR, 101 MHz, CDCl$_3$
3sa, $^1$H NMR, 400 MHz, CDCl$_3$

3sa, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ta, $^1$H NMR, 400 MHz, CDCl$_3$

3ta, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ua, $^1$H NMR, 400 MHz, CDCl$_3$

3ua, $^{13}$C NMR, 101 MHz, CDCl$_3$
3va, $^1$H NMR, 400 MHz, CDCl$_3$ 

3va, $^{13}$C NMR, 101 MHz, CDCl$_3$
3wa, $^1$H NMR, 400 MHz, CDCl$_3$

3wa, $^{13}$C NMR, 101 MHz, CDCl$_3$
3xa, \(^1\)H NMR, 400 MHz, CDCl\(_3\)

3xa, \(^{13}\)C NMR, 101 MHz, CDCl\(_3\)
3ya, $^1$H NMR, 400 MHz, CDCl$_3$

3ya, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ab, $^1$H NMR, 400 MHz, CDCl$_3$

3ab, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ac, $^1$H NMR, 400 MHz, CDCl$_3$

3ac, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ad, $^1$H NMR, 400 MHz, CDCl$_3$

3ad, $^{13}$C NMR, 101 MHz, CDCl$_3$
$3ae$, $^1H$ NMR, 400 MHz, CDCl$_3$

$3ae$, $^{13}C$ NMR, 101 MHz, CDCl$_3$
3af, $^1$H NMR, 400 MHz, CDCl$_3$

3af, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ag, $^1$H NMR, 400 MHz, CDCl$_3$

3ag, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ah, $^1$H NMR, 400 MHz, CDCl$_3$

3ah, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ai, $^1$H NMR, 400 MHz, CDCl$_3$

3ai, $^{13}$C NMR, 101 MHz, CDCl$_3$
3aj, $^1$H NMR, 400 MHz, CDCl$_3$

3aj, $^{13}$C NMR, 101 MHz, CDCl$_3$
3ak, $^1$H NMR, 400 MHz, CDCl$_3$

3ak, $^{13}$C NMR, 101 MHz, CDCl$_3$
3al, $^1$H NMR, 400 MHz, CDCl$_3$
3am, $^1$H NMR, 400 MHz, CDCl$_3$

3am, $^{13}$C NMR, 101 MHz, CDCl$_3$
3am, $^{19}F$ NMR, 376 MHz, CDCl$_3$
4, $^1$H NMR, 400 MHz, CDCl$_3$

4, $^{13}$C NMR, 101 MHz, CDCl$_3$
5. $^1$H NMR, 400 MHz, CDCl$_3$

5. $^{13}$C NMR, 101 MHz, CDCl$_3$
$^{1}H$ NMR, 400 MHz, CDCl$_{3}$

$^{13}C$ NMR, 101 MHz, CDCl$_{3}$