Supporting Information

for

Thiocarbonyl-enabled ferrocene C–H nitrogenation by cobalt(III) catalysis: thermal and mechanochemical

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Experimental procedures, characterization data, and NMR spectra for new compounds
Table of content

General remarks................................................................. S2
Table S1: Optimization studies for C−H nitrogenation of ferrocene........................................ S3
General procedure A: C−H nitrogenation of ferrocene with dioxazolones.............................. S4
General procedure B: mechanochemical C−H nitrogenation of ferrocene with dioxazolones .... S4
Characterization data for ferrocene amides 3 ................................................................. S5
H/D Exchange experiments ......................................................................................... S12
Intermolecular competition experiments ......................................................................... S14
Late-stage diversification ............................................................................................... S16
References .................................................................................................................... S17
$^1$H, $^{13}$C and $^{19}$F NMR spectra.................................................................................... S18
General remarks

All catalytic reactions were carried out under inert atmosphere using pre-dried 25 mL pressure tubes. Toluene was purified by an MBraun MB SPS-800 solvent purification system. DCE was distilled over CaH₂ prior to use. The following starting materials were synthesized according to previously described methods: Substituted ferrocenes 1a–e,[1] dioxazolones 2a–g,[2] [Cp*Co(CH₃CN)₃](SbF₆)₂.[3] Other chemicals were obtained from commercial sources and used without further purification. Yields refer to isolated compounds, estimated to be >95% pure as determined by ¹H NMR and GC analysis. TLC: Merck, TLC Silica gel 60 F254. Chromatographic separations were carried out on Merck Silica 60 (0.040–0.063 mm). All IR spectra were recorded on a Bruker ATR FT-IR Alpha device. In situ IR spectra were acquired using Mettler-Toledo iC IR software version 7.0.297 in the range of 650–2200 cm⁻¹ with 4 cm⁻¹ resolution. MS: EI/MS: Finnigan MAT 95, 70 eV; ESIMS: Finnigan LCQ. High-resolution mass spectrometry (HRMS): APEX IV 7T FTICR, Bruker Daltonic. Melting points (M.p.): Büchi 540 capillary melting point apparatus, values are uncorrected. NMR spectra were recorded on Varian Mercury VX 300, Inova-500, Inova-600 and Bruker Avance 300, Avance III 300, Avance III HD 400, Avance III 400, Avance III HD 500 instruments, if not otherwise specified, chemical shifts (δ) are provided in ppm. Ball mill: Retsch MM400.
Table S1: Optimization studies for C–H nitrogenation of ferrocene

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<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Ligand</th>
<th>Yield (%)&lt;sup&gt;a&lt;/sup&gt;</th>
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<td>---</td>
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<tr>
<td>2</td>
<td>DCE</td>
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<td>1-AdCO&lt;sub&gt;2&lt;/sub&gt;H</td>
<td>---&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
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</table>

<sup>a</sup>Reaction conditions: 1a (0.13 mmol), 2a (0.15 mmol), ligand (30 mol %), [Co] (5.0 mol %), solvent (1.0 mL).<sup>b</sup>Reaction performed without [Cp*Co(CH<sub>3</sub>CN)<sub>3</sub>](SbF<sub>6</sub>)<sub>2</sub>. Yields of isolated product.
General procedure A: C–H nitrogenation of ferrocene with dioxazolones

Thiocarbonylferrocene $1$ (0.25 mmol, 1.0 equiv), dioxazole $2$ (0.3 mmol, 1.2 equiv), 1-AdCO$_2$H (13.5 mg, 30 mol %) and [Cp*Co(CH$_3$CN)$_3$](SbF$_6$)$_2$ (4) (6.9 mg, 5.0 mol %) in DCE (1.0 mL) were stirred at 80 °C for 12 h under nitrogen atmosphere. At ambient temperature, the mixture was transferred into a round bottom flask with CH$_2$Cl$_2$ (15 mL) and concentrated in vacuo. Purification by column chromatography on silica gel afforded the desired products 3.

General procedure B: mechanochemical C–H nitrogenation of ferrocene with dioxazolones

Thiocarbonylferrocene $1$ (0.25 mmol, 1.0 equiv), dioxazole $2$ (0.3 mmol, 1.2 equiv), 1-AdCO$_2$H (13.5 mg, 30 mol %) and [Cp*Co(CH$_3$CN)$_3$](SbF$_6$)$_2$ (4) (6.9 mg, 5.0 mol %) were milled in a 10 mL tungsten carbide milling jar with one milling ball made of the same material (10 mm in diameter). After 90 min of reaction at 30 Hz, the milling was stopped and the mixture was transferred into a round bottom flask with CH$_2$Cl$_2$ (20 mL) and concentrated in vacuo. Purification by column chromatography on silica gel afforded the desired products 3.
Characterization data for ferrocene amides 3

\[
\text{N-[}2-(2,2-\text{Dimethylpropanethioyl)}\text{ferrocenyl]}\text{benzamide (3aa)}
\]

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (49 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3aa (85 mg, 84%) as a blue foam. M. p. = 100–102 °C. \[^1\text{H NMR} \text{(400 MHz, CDCl}_3\text{): } \delta = 11.66 \text{ (brs, 1H), 8.03–7.98 (m, 2H), 7.57–7.48 (m, 3H), 6.41 (dd, } J = 3.0, 1.5 \text{ Hz, 1H), 4.81 (dd, } J = 3.0, 1.5 \text{ Hz, 1H), 4.65 (td, } J = 3.0, 0.5 \text{ Hz, 1H), 4.09 (s, 5H), 1.54 (s, 9H).} \[^{13}\text{C NMR} \text{(100 MHz, CDCl}_3\text{): } \delta = 261.9 \text{ (C}_q\text{), 166.3 \text{ (C}_q\text{), 134.8 \text{ (C}_q\text{), 131.8 (CH), 128.8 (CH), 127.5 (CH), 102.5 \text{ (C}_q\text{), 76.1 \text{ (C}_q\text{), 73.3 (CH), 68.7 (CH), 68.4 (CH), 66.4 (CH), 52.9 \text{ (C}_q\text{), 32.4 (CH}_3\text{).} } \text{IR (ATR): 2958, 2922, 1668, 1525, 1485, 1313, 700 cm}^{-1}. \text{MS (ESI) } m/z \text{ (relative intensity): 428 (90) [M+Na]^+, 406 (100) [M+H]^+, 381 (20). HR-MS (ESI) } m/z \text{ calcd for C}_{22}H_{24}FeNOS [M+H]^+ 406.0923, \text{ found 406.0917.}}
\]

\[
\text{N-[}2-(2,2-\text{Dimethylpropanethioyl)}\text{ferrocenyl]}\text{-4-methylbenzamide (3ab)}
\]

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(4-methylphenyl)-1,4,2-dioxazol-5-one (2b) (53 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 10/1) yielded 3ab (83 mg, 77%) as a blue foam. M. p. = 106–108 °C. \[^1\text{H NMR} \text{(400 MHz, CDCl}_3\text{): } \delta = 11.58 \text{ (s, 1H), 7.87 (d, } J = 8.0 \text{ Hz, 2H), 7.29 (d, } J = 8.0 \text{ Hz, 2H), 6.39 (dd, } J = 3.0, 1.5 \text{ Hz, 1H), 4.78 (dd, } J = 3.0, 1.5 \text{ Hz, 1H), 4.63 (dd, } J = 3.0, 3.0 \text{ Hz, 1H), 4.06 (s, 5H), 2.41 (s, 3H), 1.52 (s, 9H).} \[^{13}\text{C NMR} \text{(100 MHz, CDCl}_3\text{): } \delta = 261.7 \text{ (C}_q\text{), 166.2 \text{ (C}_q\text{), 142.1 \text{ (C}_q\text{), 131.9 \text{ (C}_q\text{), 129.4 (CH), 127.4 (CH), 102.5 \text{ (C}_q\text{), 75.9 \text{ (C}_q\text{), 73.1 (CH), 68.5 (CH), 68.2 (CH), 66.1 (CH), 52.7 \text{ (C}_q\text{), 32.3 (CH}_3\text{), 21.5 (CH}_3\text{).} } \text{IR (ATR): 3048, 1611, 1491, 805, 532 cm}^{-1}. \text{MS (ESI) } m/z \text{ (relative
N-[2-(2,2-Dimethylpropanethiol)ferrocenyl]-4-methoxybenzamide (3ac)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (2c) (58 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 10/1) yielded 3ac (70 mg, 64%) as a blue foam. M. p. = 105–106 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 11.57\) (brs, 1H), 7.97 (d, \(J = 8.7\) Hz, 2H), 7.01 (d, \(J = 8.7\) Hz, 2H), 6.40 (dd, \(J = 2.7, 1.4\) Hz, 1H), 4.81 (dd, \(J = 2.7, 1.4\) Hz, 1H), 4.65 (t, \(J = 2.7\) Hz, 1H), 4.09 (s, 5H), 3.89 (s, 3H), 1.54 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 261.8\) (C\(_q\)), 165.8 (C\(_q\)), 162.4 (C\(_q\)), 129.3 (CH), 127.1 (C\(_q\)), 113.9 (CH), 102.8 (C\(_q\)), 75.9 (C\(_q\)), 73.2 (CH), 68.6 (CH), 68.2 (CH), 66.1 (CH), 55.5 (CH\(_3\)), 52.8 (C\(_q\)), 32.3 (CH\(_3\)). IR (ATR): 3047, 1607, 1501, 1240, 1026, 805, 487 cm\(^{-1}\). MS (ESI) \(m/z\) (relative intensity): 474 (100), 458 (60) [M+Na]\(^+\), 436 (60) [M+H]\(^+\), 174 (20). HR-MS (ESI) \(m/z\) calcd for C\(_{23}\)H\(_{26}\)FeNO\(_2\)S [M+H]\(^+\) 436.1029, found 436.1028.

N-[2-(2,2-Dimethylpropanethiol)ferrocenyl]-4-(trifluoromethyl)benzamide (3ad)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (2d) (69 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 10/1) yielded 3ad (88 mg, 79%) as blue foam. M. p. = 92–93 °C. \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 11.86\) (s, 1H), 8.13 (d, \(J = 8.1\) Hz, 2H), 7.80 (d, \(J = 8.1\) Hz, 2H), 6.42 (dd, \(J = 3.0, 1.5\) Hz, 1H), 4.87 (dd, \(J = 3.0, 1.5\) Hz, 1H), 4.71 (t, \(J = 3.0\) Hz, 1H), 4.12 (s, 5H), 1.56 (s, 9H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)): \(\delta = 262.2\) (C\(_q\)), 164.9 (C\(_q\)), 138.1 (C\(_q\)), 133.4 (q, \(^2J_{C-F} = 32.7\) Hz, C\(_q\)), 128.0 (CH), 125.9 (q, \(^3J_{C-F} = 3.7\) Hz, CH), 123.8 (q, \(^1J_{C-F} = 272.6\) Hz, C\(_q\)), 101.9 (C\(_q\)), 76.0 (C\(_q\)), 73.4 (CH), 68.9 (CH), 68.5 (CH), 66.8 (CH), 53.0 (C\(_q\)), 32.5 (CH\(_3\)). \(^{19}\)F NMR (282 MHz, CDCl\(_3\)): \(\delta = -62.89\). IR (ATR): 3029, 1616, 1559, 1448, 1125, 451 cm\(^{-1}\). MS (ESI) \(m/z\) (relative intensity): 969.
(50), 474 (100) [M+H]$^+$, 440 (10). HR-MS (ESI) $m/z$ calcd for C$_{23}$H$_{23}$F$_3$FeNOS [M+H]$^+$ 474.0798, found 474.0797.

4-Chloro-N-[2-(2,2-dimethylpropanethioyl)ferrocenyl]benzamide (3ae)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(4-chlorophenyl)-1,4,2-dioxazol-5-one (2e) (59 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3ae (85 mg, 77%) as a blue foam. 

\[ \text{M. p.} = 89–90 \degree C. \]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 11.73$ (s, 1H), 7.95 (d, $J = 8.7$ Hz, 2H), 7.50 (d, $J = 8.7$ Hz, 2H), 6.41 (dd, $J = 3.0$, 1.4 Hz, 1H), 4.85 (dd, $J = 3.0$, 1.4 Hz, 1H), 4.69 (t, $J = 3.0$ Hz, 1H), 4.11 (s, 5H), 1.56 (s, 9H).

$^{13}$C NMR (75 MHz, CDCl$_3$): $\delta =$ 261.9 (C$_q$), 165.1 (C$_q$), 138.0 (C$_q$), 133.1 (C$_q$), 129.0 (CH), 128.8 (CH), 102.1 (C$_q$), 75.9 (C$_q$), 73.2 (CH), 68.7 (CH), 68.3 (CH), 66.5 (CH), 52.8 (C$_q$), 32.4 (CH$_3$). IR (ATR): 3040, 1559, 1437, 1343, 1165, 447 cm$^{-1}$. MS (ESI) $m/z$ (relative intensity): 478 (100), 462 (40) [M+Na]$^+$, 440 (20) [M+H]$^+$. HR-MS (ESI) $m/z$ calcd for C$_{22}$H$_{23}$F$_3$ClFeNOS [M+H]$^+$ 440.0532, found 440.0533.

4-Bromo-N-[2-(2,2-dimethylpropanethioyl)ferrocenyl]benzamide (3af)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(4-bromophenyl)-1,4,2-dioxazol-5-one (2f) (73 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3af (73 mg, 61%) as blue foam.

\[ \text{M. p.} = 96–97 \degree C. \]

$^1$H NMR (300 MHz, CDCl$_3$): $\delta = 11.71$ (s, 1H), 7.89 (d, $J = 7.6$ Hz, 2H), 7.67 (d, $J = 7.6$ Hz, 2H), 6.38 (dd, $J = 3.0$, 1.4 Hz, 1H), 4.83 (dd, $J = 3.0$, 1.4 Hz, 1H), 4.67 (t, $J = 3.0$ Hz, 1H), 4.09 (s, 5H), 1.54 (s, 9H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta =$ 262.3 (C$_q$), 165.2 (C$_q$), 133.6 (C$_q$), 132.0 (C$_q$), 129.0 (CH), 126.5 (CH), 102.1 (C$_q$), 75.9 (C$_q$), 73.2 (CH), 68.7 (CH), 68.3 (CH), 66.5 (CH), 52.8 (C$_q$), 32.4 (CH$_3$). IR (ATR): 3077, 1579, 1507, 1000, 488 cm$^{-1}$. MS (ESI) $m/z$ (relative intensity): 524 (100), 506 (30) [M+Na]$^+$, 484
(20) [M+H]^+, 402 (40). HR-MS (ESI) m/z calcd for C$_{22}$H$_{23}$BrFeNOS [M+H]^+ 484.0029 found 484.0030; and C$_{22}$H$_{23}$BrFeNOS [M+H]^+ 486.0008 found 486.0013.

N-[2-(2,2-Dimethylpropanethioyl)ferrocenyl]-2-methoxybenzamide (3ag)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(2-methoxyphenyl)-1,4,2-dioxazol-5-one (2g) (58 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 10/1) yielded 3ag (72 mg, 66%) as a blue foam. M. p. = 106–108 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 11.21 (s, 1H), 8.13 (dd, $J$ = 7.8, 1.8 Hz, 1H), 7.48–7.43 (m, 1H), 7.06 (dd, $J$ = 7.8 Hz, 7.8 Hz, 1H), 7.00 (d, $J$ = 7.8 Hz, 1H), 6.17 (dd, $J$ = 2.7, 1.4 Hz, 1H), 4.68 (dd, $J$ = 2.7, 1.4 Hz, 1H), 4.53 (dd, $J$ = 2.7, 2.7 Hz, 1H), 4.08 (s, 3H), 4.04 (s, 5H), 1.44 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 261.2 (C$q$), 164.5 (C$q$), 157.2 (C$q$), 132.8 (CH), 132.0 (CH), 122.7 (C$q$), 121.0 (CH), 111.2 (CH), 101.9 (C$q$), 79.3 (C$q$), 73.3 (CH), 132.8 (CH), 132.0 (CH), 122.7 (C$q$), 121.0 (CH), 111.2 (CH), 101.9 (C$q$), 79.3 (C$q$), 73.3 (CH), 69.2 (CH), 67.3 (CH), 64.2 (CH), 55.6 (CH$_3$), 52.5 (C$q$), 31.8 (CH$_3$). IR (ATR): 3048, 1611, 1491, 805, 532 cm$^{-1}$. MS (ESI) m/z (relative intensity): 474 (100), 458 (40) [M+Na]^+, 436 (50) [M+H]^+, 174 (20). HR-MS (ESI) m/z calcd for C$_{23}$H$_{26}$FeNO$_2$S [M+H]^+ 436.1029, found 436.1028.

3-Chloro-N-[2-(2,2-dimethylpropanethioyl)ferrocenyl]benzamide (3ah)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(3-chlorophenyl)-1,4,2-dioxazol-5-one (2h) (59 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3ah (80 mg, 73%) as a blue foam. M. p. = 98–100 °C. $^1$H NMR (300 MHz, CDCl$_3$): δ = 11.72 (brs, 1H), 8.00 (t, $J$ = 1.9 Hz, 1H), 7.85 (dt, $J$ = 7.8, 1.4 Hz, 1H), 7.56–7.49 (m, 1H), 7.44 (t, $J$ = 7.8 Hz, 1H), 6.38 (dd, $J$ = 3.0, 1.4 Hz, 1H), 4.83 (dd, $J$ = 3.0, 1.4 Hz, 1H), 4.67 (t, $J$ = 3.0 Hz, 1H), 4.10 (s, 5H), 1.54 (s, 9H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 262.0 (C$q$), 164.9 (C$q$), 136.6 (C$q$), 135.1 (C$q$), 131.8 (CH), 130.1 (CH), 128.0 (CH), 125.4 (CH), 102.1 (C$q$), 76.0 (C$q$), 73.3 (CH), 68.9 (CH), 68.4 (CH), 66.7 (CH), 53.0 (C$q$), 32.5 (CH$_3$). IR (ATR): 2956, 2921, 1670, 1526, 1400, 1251, 762 cm$^{-1}$. MS (ESI) m/z calcd for C$_{23}$H$_{26}$FeNO$_2$S [M+H]^+ 436.1029, found 436.1028.
739 cm\(^{-1}\). **MS** (ESI) \(m/z\) (relative intensity): 901 (30), 462 (50) [M+Na]\(^+\), 390 (80). **HR-MS** (ESI) \(m/z\) calcd for C\(_{22}\)H\(_{23}\)\(^{35}\)ClFeNOS [M+H]\(^+\) 440.0533, found 440.0538.

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\text{N-[2-(2,2-Dimethylpropanethioyl)ferrocenyl]-4-nitrobenzamide (3ai)}
\]

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol) and 3-(4-nitrophenyl)-1,4,2-dioxazol-5-one (2i) (62 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3ai (90 mg, 80%) as a blue foam. **M. p.** = 90–92 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 11.96\) (brs, 1H), 8.37 (d, \(J = 8.8\) Hz, 2H), 8.15 (d, \(J = 8.8\) Hz, 2H), 6.39 (dd, \(J = 3.0, 1.4\) Hz, 1H), 4.87 (dd, \(J = 3.0, 1.4\) Hz, 1H), 4.71 (t, \(J = 3.0\) Hz, 1H), 4.12 (s, 5H), 1.55 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 262.3\) (C\(_q\)), 164.1 (C\(_q\)), 149.8 (C\(_q\)), 140.3 (C\(_q\)), 128.6 (CH), 124.1 (CH), 101.6 (C\(_q\)), 76.0 (C\(_q\)), 73.4 (CH), 69.1 (CH), 68.5 (CH), 67.0 (CH), 53.1 (C\(_q\)), 32.5 (CH\(_3\)). **IR** (ATR): 2957, 2921, 1672, 1527, 1313, 1065, 753 cm\(^{-1}\). **MS** (ESI) \(m/z\) (relative intensity): 923 (30), 473 (50) [M+Na]\(^+\), 451 (100) [M+H]\(^+\), 381 (80). **HR-MS** (ESI) \(m/z\) calcd for C\(_{22}\)H\(_{23}\)FeN\(_2\)O\(_3\)S [M+H]\(^+\) 451.0774, found 451.0774.

\[
\text{N-\{2-(2,2-Dimethylpropanethioyl)-4'-methyl-[1,1'-ferrocenylphenyl]-3-yl\}benzamidine (3ba)}
\]

The general procedure A was followed using 2,2-dimethyl-1-(4'-methyl-[1,1'-ferrocenophenyl]-2-yl)propane-1-thione (1b) (94 mg, 0.25 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (49 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3ba (66 mg, 53%) as a red foam. **M. p.** = 108–110 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)): 7.73–7.65 (m, 2H), 7.58 (brs, 1H), 7.55–7.43 (m, 3H), 7.37 (d, \(J = 8.1\) Hz, 2H), 7.13–7.03 (m, 2H), 5.45 (d, \(J = 2.6\) Hz, 1H), 4.64 (d, \(J = 2.6\) Hz, 1H), 4.15 (s, 5H), 2.33 (s, 3H), 1.03 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl\(_3\)): \(\delta = 272.2\) (C\(_q\)), 165.6 (C\(_q\)), 136.6 (C\(_q\)), 136.2 (C\(_q\)), 134.3 (C\(_q\)), 132.0 (CH), 129.1 (CH), 129.0 (CH), 128.3 (CH), 126.9
(CH), 98.0 (Cq), 96.9 (Cq), 80.6 (Cq), 73.7 (CH), 65.0 (CH), 62.3 (CH), 56.0 (Cq), 32.1 (CH), 21.3 (CH₃). **IR** (ATR): 2956, 2921, 1675, 1520, 1482, 818 cm⁻¹. **MS** (ESI) m/z (relative intensity): 518 (100) [M+Na]⁺, 496 (40) [M+H]⁺, 398 (20). **HR-MS** (ESI) m/z calcd for C₂₀H₃₀FeNOS [M+H]⁺ 496.1392, found 496.1387.

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\text{Ar = 4-MeOC₆H₄}
\]

**N-\{2-(2,2-Dimethylpropanethiolyl)-4'-(methoxy)-[1,1'-ferrocenephenyl]-3-yl\}benzamide (3ca)**

The general procedure A was followed using 2,2-dimethyl-1-\{4'-(methoxy)-[1,1'-ferrocenephenyl]-2-yl\}propane-1-thione (1c) (98 mg, 0.25 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (49 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3ca (77 mg, 60%) as a red foam. **M. p.** = 105–107 °C. **¹H NMR** (400 MHz, CDCl₃): δ = 7.80–7.65 (m, 2H), 7.61–7.35 (m, 6H), 6.82 (d, J = 8.7 Hz, 2H), 5.43 (d, J = 2.6 Hz, 1H), 4.61 (d, J = 2.6 Hz, 1H), 4.16 (s, 5H), 3.82 (s, 3H), 1.02 (s, 9H). **¹³C NMR** (100 MHz, CDCl₃): δ = 272.2 (Cq), 165.7 (Cq), 158.7 (Cq), 134.3 (Cq), 132.0 (Cq), 131.3 (CH), 129.5 (CH), 129.0 (CH), 126.9 (CH), 113.9 (CH), 97.8 (Cq), 96.7 (Cq), 73.6 (CH), 72.2 (Cq), 64.9 (CH), 62.4 (CH), 56.0 (Cq), 55.4 (CH₃), 32.0 (CH₃). **IR** (ATR): 2956, 2921, 1675, 1520, 1463, 1247, 1177, 755 cm⁻¹. **MS** (ESI) m/z (relative intensity): 534 (100) [M+Na]⁺, 512 (80) [M+H]⁺. **HR-MS** (ESI) m/z calcd for C₂₀H₃₀FeNO₂S [M+H]⁺ 512.1342, found 512.1347.

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\text{Ar = 4-F₃CC₆H₄}
\]

**N-\{2-(2,2-Dimethylpropanethiolyl)-4'-(trifluoromethyl)-[1,1'-ferrocenephenyl]-3-yl\}benzamide (3da)**

The general procedure A was followed using 2,2-dimethyl-1-\{4'-(trifluoromethyl)-[1,1'-ferrocenephenyl]-2-yl\}propane-1-thione (1d) (108 mg, 0.25 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (49 mg, 0.3 mmol). Purification by column chromatography (n-
hexane/EtOAc: 19/1) yielded 3da (70 mg, 51%) as a blue foam. M. p. = 102–104 °C. 

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.73–7.67 (m, 2H), 7.62–7.43 (m, 8H), 5.55 (d, J = 2.7 Hz, 1H), 4.68 (d, J = 2.7 Hz, 1H), 4.16 (s, 5H), 1.04 (s, 9H), Z. 13C NMR (100 MHz, CDCl$_3$): δ = 271.2 (C$_q$), 165.6 (C$_q$), 144.0 (C$_q$), 134.1 (C$_q$), 132.2 (CH), 129.2 (q, $^2$J$_{C-F}$ = 32.6 Hz, C$_q$), 129.1 (CH), 128.6 (CH), 128.9 (CH), 126.9 (CH), 125.7 (q, $^1$J$_{C-F}$ = 273.6 Hz, C$_q$), 125.4 (q, $^3$J$_{C-F}$ = 3.8 Hz, CH), 98.5 (C$_q$), 97.3 (C$_q$), 73.9 (C$_q$), 65.6 (CH), 62.2 (CH), 56.3 (C$_q$), 32.0 (CH$_3$). 19F NMR (282 MHz, CDCl$_3$) δ = −62.47. IR (ATR): 2951, 2925, 1670, 1530, 1400, 1050, 732 cm$^{-1}$. MS (ESI) m/z (relative intensity): 572 (100) [M+Na]$^+$, 550 (40) [M+H]$^+$, 452 (30), 381 (20). HR-MS (ESI) m/z calcd for C$_{29}$H$_{27}$FeNOSF$_3$, [M+H]$^+$ 550.1110, found 550.1116.

N-[2-(2,2-Dimethylbutanethioyl)ferrocenyl]benzamide (3ea)

The general procedure A was followed using 2,2-dimethyl-1-ferrocenylbutane-1-thione (1e) (75 mg, 0.25 mmol) and 3-phenyl-1,4,2-dioxazol-5-one (2a) (49 mg, 0.3 mmol). Purification by column chromatography (n-hexane/EtOAc: 19/1) yielded 3ea (85 mg, 81%) as blue foam. M. p. = 95–97 °C. $^1$H NMR (400 MHz, CDCl$_3$): δ = 11.51 (brs, 1H), 8.16–7.91 (m, 2H), 7.67–7.27 (m, 3H), 6.38 (dd, J = 2.9, 1.5 Hz, 1H), 4.80 (dd, J = 2.9, 1.5 Hz, 1H), 4.62 (dt, J = 2.9 Hz, 1H), 4.09 (s, 5H), 2.10 (dd, J = 13.9, 7.4 Hz, 1H), 1.84 (dd, J = 13.9, 7.4 Hz, 1H), 1.56 (s, 3H), 1.41 (s, 3H), 0.78 (t, J = 7.5 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 262.2 (C$_q$), 166.2 (C$_q$), 134.8 (C$_q$), 131.8 (CH), 128.8 (CH), 127.5 (CH), 102.5 (C$_q$), 77.4 (C$_q$), 73.3 (CH), 68.4 (CH), 68.3 (CH), 65.2 (CH), 56.7 (C$_q$), 36.1 (CH$_2$), 30.3 (CH$_3$), 30.3 (CH$_3$), 9.3 (CH$_3$). IR (ATR): 2964, 2924, 1669, 1523, 1488, 1399, 1249, 650 cm$^{-1}$. MS (ESI) m/z (relative intensity): 442 (100) [M+Na]$^+$, 420 (80) [M+H]$^+$. HR-MS (ESI) m/z calcd for C$_{23}$H$_{26}$FeNOS [M+H]$^+$ 420.1079, found 420.1077.
**H/D Exchange experiment**

Thiocarbonylferrocene 1a (71 mg, 0.25 mmol), 1-AdCO₂H (13.5 mg 30 mol %), [Cp*Co(CH₃CN)₃][SbF₆]₂ (6.9 mg, 5.0 mol %), DCE (0.9 mL) and CD₃OD (0.1 mL) were placed in a 25 mL Schlenk tube under N₂ and the mixture was stirred at 80 °C for 12 h. At ambient temperature, the mixture was transferred into a round bottom flask with CH₂Cl₂ (5 mL) and concentrated in vacuo. Purification by column chromatography on silica gel (n-hexane) yielded the product [D]ₙ-1a (65 mg, 92%) with 85% deuterium incorporation.
Thiocarbonylferrocene $1a$ (71 mg, 0.25 mmol), dioxazolone $2a$ (49 mg, 0.3 mmol, 1.2 equiv), 1-AdCO$_2$H (13.5 mg 30 mol %), [Cp*Co(CH$_3$CN)$_3$](SbF$_6$)$_2$ (6.9 mg, 5.0 mol %), DCE (0.9 mL) and CD$_3$OD (0.1 mL) were placed in a 25 mL Schlenk tube under N$_2$ and the mixture was stirred at 80 °C for 3 h. At ambient temperature, the mixture was transferred into a round bottom flask with CH$_2$Cl$_2$ (15 mL) and concentrated in vacuo. Purification by column chromatography on silica gel (n-hexane/EtOAc: 19/1) yielded the product [D]$_{n}$-$1a$ (65 mg, 60%) with 12% deuterium incorporation and [D]$_{n}$-$3aa$ (34 mg, 34%) with 13% deuterium incorporation in ortho-ferrocene and 8% deuterium incorporation in amide, respectively.
Intermolecular competition experiment

A suspension of 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol), 2,2-dimethyl-1-{4'-(methoxy)-[1,1'-ferrocenephenyl]-2-yl}propane-1-thione (1c) (91 mg, 0.25 mmol), 3-phenyl-1,4,2-dioxazol-5-one (2a) (49 mg, 0.3 mmol), 1-AdCO₂H (13.5 mg, 0.3 mol %) and [Cp*Co(CH₃CN)₃][SbF₆]₂ (6.9 mg, 5.0 mol %) in DCE (1.0 mL) was stirred at 80 °C for 1 h under N₂ atmosphere. At ambient temperature, the mixture was transferred into a round-bottom flask with CH₂Cl₂ (15 mL) and concentrated in vacuo. Purification by column chromatography (n-hexane/EtOAc: 19/1) on silica gel afforded the products 3aa (15 mg, 15%) and 3ca (27 mg, 21%).
A suspension of 2,2-dimethyl-1-ferrocenylpropane-1-thione (1a) (71 mg, 0.25 mmol), 3-(4-methoxyphenyl)-1,4,2-dioxazol-5-one (2b) (48 mg, 0.25 mmol), 3-[4-(trifluoromethyl)phenyl]-1,4,2-dioxazol-5-one (2e) (58 mg, 0.25 mmol), 1-AdCO₂H (13.5 mg, 30 mol %) and [Cp*Co(CH₃CN)₃][SbF₆]₂ (6.9 mg, 5.0 mol %) in DCE (1.0 mL) was stirred at 80 ºC for 1 h under N₂ atmosphere. After cooling to ambient temperature, the mixture was transferred into a round-bottom flask with CH₂Cl₂ (15 mL) and concentrated in vacuo. Purification by column chromatography (n-hexane/EtOAc: 19/1) on silica gel afforded the products 3ab (64 mg, 59%) and 3ae (35 mg, 30%).
Late-stage diversification

A suspension of $N$-[2-(2,2-dimethylpropanethioyl)ferrocenyl]benzamide (3aa) (101 mg, 0.25 mmol) and $\text{Ag}_2\text{CO}_3$ (69 mg, 0.25 mmol) in $\text{CH}_2\text{Cl}_2$ (1.0 mL) was stirred at 23 °C for 6 h under air. Then, the mixture was transferred into a round bottom flask and concentrated in vacuo. Purification by column chromatography on silica gel ($n$-hexane/EtOAc: 19/1) afforded the product 4aa as a yellow oil (97%). $^1\text{H NMR}$ (300 MHz, CDCl$_3$): $\delta$ = 10.68 (s, 1H), 8.19–7.92 (m, 2H), 7.52–7.32 (m, 3H), 6.01 (s, 1H), 4.65 (dd, $J$ = 2.8, 1.5 Hz, 1H), 4.44 (t, $J$ = 2.8 Hz, 1H), 4.18 (s, 5H), 1.42 (s, 9H). $^{13}\text{C NMR}$ (100 MHz, CDCl$_3$): $\delta$ = 217.4 (C$_q$), 165.7 (C$_q$), 134.5 (C$_q$), 131.8 (CH), 128.8 (CH), 127.2 (CH), 100.4 (C$_q$), 71.1 (CH), 68.4 (CH), 66.6 (CH), 65.0 (CH), 63.7 (C$_q$), 45.5 (C$_q$), 28.6 (CH$_3$). IR (ATR): 2957, 2921, 1671, 1530, 701 cm$^{-1}$. MS (ESI) $m/z$ (relative intensity): 412 (100) [M+Na]$^+$, 406 (40), 390 (30), 381 (20). HR-MS (ESI) $m/z$ calcd for C$_{22}$H$_{24}$FeNO$_2$ [M+H]$^+$ 390.1151, found 390.1151.
References


$^1$H, $^{13}$C and $^{19}$F NMR spectra

[Diagram of 3aa (400 MHz, CDCl$_3$)]

[Diagram of 3aa (100 MHz, CDCl$_3$)]
3ab
(400 MHz, CDCl₃)

3ab
(100 MHz, CDCl₃)
3ac
(300 MHz, CDCl₃)

3ac
(75 MHz, CDCl₃)
3ad
(300 MHz, CDCl₃)

3ad
(75 MHz, CDCl₃)
3ad
(282 MHz, CDCl₃)

3ae
(300 MHz, CDCl₃)
3ae
(75 MHz, CDCl₃)

3af
(300 MHz, CDCl₃)
3af
(75 MHz, CDCl₃)

3ag
(400 MHz, CDCl₃)
3ag
(100 MHz, CICH3)

3ah
(300 MHz, CICH3)
3ah
(100 MHz, CDCl₃)

3ai
(400 MHz, CDCl₃)
3ai
(100 MHz, CDCl₃)

3ba
(400 MHz, CDCl₃)

Ar = 4-MeC₆H₄
Ar \quad t-Bu

Fe \quad NH\text{Bz}

Ar = 4-\text{MeC}_6\text{H}_4

3ba
(100 MHz, CDCl$_3$)

Ar \quad t-Bu

Fe \quad NH\text{Bz}

Ar = 4-\text{MeOC}_6\text{H}_4

3ca
(400 MHz, CDCl$_3$)
Ar = 4-MeOC₆H₄

3ca
(100 MHz, CDCl₃)

Ar = 4-F₃CC₆H₄

3da
(400 MHz, CDCl₃)
Ar \quad t{-}Bu
\begin{array}{c}
\text{Fe} \\
\text{NHBz}
\end{array}

Ar = 4{-}F_3CC_6H_4

3da
(100 \text{ MHz, CDCl}_3)

Ar \quad t{-}Bu
\begin{array}{c}
\text{Fe} \\
\text{NHBz}
\end{array}

Ar = 4{-}F_3CC_6H_4

3da
(283 \text{ MHz, CDCl}_3)
3ea
(400 MHz, CDCl₃)

3ea
(100 MHz, CDCl₃)
4aa
(300 MHz, CDCl₃)

4aa
(100 MHz, CDCl₃)