Supplementary Material

Direct C-O Bond Activation Mediated by AcOH: A New Metal-free way for α-Functionalization of Ferrocene Alcohols
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Experimental Section

General

Ferrocenyl alcohols were prepared by the known method.$^{[10]}$ Other chemicals were commercially available. Melting points were recorded on an Electrothermal digital melting point apparatus and are uncorrected. IR spectra were recorded on a Varian FT-1000 spectrophotometer using KBr optics. $^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer using CDCl$_3$ or DMSO-d$_6$ as solvent and TMS as internal standard. High resolution mass spectra were obtained using Microma GCT-TOF instrument. Optical rotation was measured at 589 nm (Na D line) on an Autopol IV automatic polarimeter. The enantiomeric excesses of the product was determined by HPLC analysis on a Chiralpak AD-H column using 2-propanol/hexane as the eluent.

Typical experimental procedure of C-C bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and indole or other noleophiles (0.5 mmol) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then NaHCO$_3$ was added to remove the acetic acid, CH$_2$Cl$_2$ was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na$_2$SO$_4$, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other ferrocenyl derivatives.

Typical experimental procedure of C-N bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and aromatic amines (0.5 mmol) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then NaHCO$_3$ was added to remove the acetic acid, CH$_2$Cl$_2$ was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na$_2$SO$_4$, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other ferrocenyl derivatives.

Typical experimental procedure of C-O bond formation

A mixture of ferrocenyl alcohol (0.6 mmol) and alcohol (1 mL) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then NaHCO$_3$ was added to remove the acetic acid, CH$_2$Cl$_2$ was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na$_2$SO$_4$, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was
followed for the synthesis of other ferrocenyl derivatives.

**Typical experimental procedure of C-S bond formation**

A mixture of ferrocenyl alcohol (0.6 mmol) and naphthalene-2-thiol (0.5 mmol) in acetic acid (2 mL) was stirred at room temperature for an appropriate time. Upon completion, monitored by TLC, the mixture was poured into water, then NaHCO₃ was added to remove the acetic acid. CH₂Cl₂ was used to extract the product (15 mL×2), the organic layer was dried with anhydrous Na₂SO₄, then the solvent was evaporated under the reduced pressure. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product. This procedure was followed for the synthesis of other ferrocenyl derivatives.

**Screening the effect of volume of EtOH in C-O bond formation procedure**

![Figure 1](image)

**Characterization of compounds of α-Functionalized Ferrocene**

3-(Ferrocenylethyl)-1H-indole (3a) [a]

82% yield; δH (400 MHz, CDCl₃) 1.70 (d, J 5.2, 3H), 4.18 (s, 9H, FcH), 4.28 (s, 1H), 6.74 (s, 1H), 7.10 (d, J 2.0, 1H), 7.16 (s, 1H), 7.32 (d, J 2.8, 1H), 7.65 (d, J 6.0, 1H), 7.83 (s, 1H, NH). m/z (HRMS) 329.0881 (M⁺), calc. for C₂₀H₁₉NFe: 329.0867.

4-Methyl-3-(ferrocenylethyl)-1H-indole (3b) [a]

56% yield; δH (400 MHz, CDCl₃) 1.67 (d, J 4.4, 3H), 2.75 (s, 3H), 4.13–4.18 (m, 9H), 4.37 (q, J 6.0, 1H), 6.66 (s, 1H), 6.86 (d, J 6.4, 1H), 7.05 (t, J 7.2, 1H), 7.17 (d, J 7.6, 1H), 7.05 (s, 1H, NH). m/z (HRMS) 343.1025 (M⁺), calc. for C₂₁H₂₁NFe: 343.1023.

4-Benzylxy-3-(ferrocenylethyl)-1H-indole (3c) [a]

65% yield; δH (400 MHz, CDCl₃) 1.62 (d, J 6.8, 3H), 4.01 (s, 7H), 4.15 (s, 1H), 4.21 (s, 1H), 4.57 (q, J 6.8, 1H), 5.23 (s, 2H), 6.45 (s, 1H), 6.60 (d, J 8.0, 1H), 6.93 (d, J 8.0, 1H), 7.01 (t, J 8.0, 1H), 7.34 (t, J 7.2, 1H), 7.44 (t, J 7.6, 2H), 7.57 (d, J 7.6, 2H), 7.76 (br, s, 1H, NH). m/z (HRMS) 435.1284 (M⁺), calc. for C₂₇H₂₅NOFe: 435.1286.
5-Methyl-3-(ferrocenylethyl)-1H-indole (3d)[a]
66% yield; δH (400 MHz, CDCl₃) 1.69 (d, J 7.2, 3H), 2.46 (s, 3H), 4.07–4.15 (m, 9H), 4.24 (s, 1H), 6.71 (s, 1H), 6.99 (d, J 8.4, 1H), 7.22 (d, J 8.0, 1H), 7.44 (s, 1H), 7.75 (br s, 1H, NH). m/z (HRMS) 343.1029 (M⁺), calc. for C₂₃H₂₁NFe: 343.1023.

5-Bromom-3-(ferrocenylethyl)-1H-indole (3e)[b]
61% yield; δH (400 MHz, CDCl₃) 1.67 (d, J 6.8, 3H), 4.05–4.23 (m, 9H), 4.30 (s, 1H), 6.70 (s, 1H), 7.22 (s, 1H), 7.24 (s, 1H), 7.75 (s, 1H), 7.53 (d, J 8.0, 1H), 7.73 (br s, 1H, NH). m/z (HRMS) 406.9974 (M⁺), calc. for C₂₀H₁₉NBrFe: 406.9972.

6-Methyl-3-(ferrocenylethyl)-1H-indole (3f)[a]
67% yield; δH (400 MHz, CDCl₃) 1.67 (d, J 7.2, 3H), 2.44 (s, 3H), 4.06–4.14 (m, 9H), 4.23 (s, 1H), 6.69 (s, 1H), 6.93 (d, J 8.4, 1H), 7.12 (s, 1H), 7.53 (d, J 8.0, 1H), 7.73 (br s, 1H, NH). m/z (HRMS) 343.1021 (M⁺), calc. for C₂₁H₂₁NFe: 343.1023.

7-Methyl-3-(ferrocenylethyl)-1H-indole (3g)[a]
76% yield; δH (400 MHz, CDCl₃) 1.70 (d, J 7.2, 3H), 2.45 (s, 3H), 4.07–4.16 (m, 9H), 4.26 (s, 1H), 6.76 (s, 1H), 6.97 (d, J 7.2, 1H), 7.03 (t, J 7.6, 1H), 7.51 (d, J 7.6, 1H), 7.78 (s, 1H, NH). m/z (HRMS) 343.1020 (M⁺), calc. for C₂₁H₂₁NFe: 343.1023.

2-Phenyl-3-(ferrocenylethyl)-1H-indole (3h)[a]
68% yield; δH (300 MHz, CDCl₃) 1.70 (d, J 7.2, 3H), 3.96–4.16 (m, 9H), 4.48 (q, J 7.2, 1H), 6.96 (t, J 7.5, 1H), 7.07–7.12 (m, 1H), 7.28–7.41 (m, 2H), 7.46–7.58 (m, 5H), 7.95 (br s, 1H, NH). m/z (HRMS) 405.1180 (M⁺), calc. for C₂₂H₂₁FeN: 405.1180.

3-(phenyl(ferrocenyl)methyl)-1H-indole (3i)[a]
90% yield; δH (400 MHz, CDCl₃) 3.98 (m, 9H), 5.32 (s, 1H), 6.82 (s, 1H), 6.93 (t, J 7.2, 1H), 7.10 (t, J 7.2, 1H), 7.19 (t, J 7.6, 1H), 7.25–7.30 (m, 4H), 7.35 (d, J 7.6, 2H), 7.86 (br s, 1H, NH). m/z (HRMS) 391.1021 (M⁺), calc. for C₂₂H₂₁NFe: 391.1023.

4-Benzyloxy-3-(phenyl(ferrocenyl)methyl)-1H-indole (3j)[a]
69% yield; δH (400 MHz, CDCl₃) 3.80–4.28 (m, 9H), 4.97–5.16 (m, 2H), 5.77 (s, 1H), 6.43 (d, J 8.0, 1H), 6.62 (s, 1H), 6.88 (d, J 8.0, 1H), 6.98 (t, J 8.0, 1H), 7.03 (d, J 7.2, 2H), 7.11 (t, J 7.6, 3H), 7.32–7.52 (m, 5H), 7.83 (s, 1H, NH). m/z (HRMS) 497.1142 (M⁺), calc. for C₂₅H₂₃NOFe: 497.1442.

5-Bromo-3-(phenyl(ferrocenyl)methyl)-1H-indole (3k)[a]
72% yield; δH (400 MHz, CDCl₃) 4.04–4.27 (m, 9H), 5.21 (s, 1H), 6.83 (s, 1H), 7.17 (s, 2H), 7.20–7.23 (m, 1H), 7.27–7.31 (m, 4H), 7.37 (s, 1H), 7.93 (br s, 1H, NH). m/z (HRMS) 469.0132 (M⁺), calc. for C₂₃H₂₀NBrFe: 469.0129.

7-Methyl-3-(phenyl(ferrocenyl)methyl)-1H-indole (3l)[a]
80% yield; δH (400 MHz, CDCl₃) 2.45 (s, 3H), 4.05–4.29 (m, 9H), 5.28 (s, 1H), 6.85 (d, J 7.6, 1H), 6.88 (s, 1H), 6.91 (t, J 6.8, 1H), 7.11 (d, J 8.0, 1H), 7.18 (t, J 7.2, 1H), 7.29 (d, J 7.2, 2H), 7.35 (d,
J 7.6, 2H), 7.82 (s, 1H, NH). m/z (HRMS) 405.1169 (M⁺), calc. for C₂₆H₂₃NFe: 405.1180.

6-Methyl-3-(phenyl(ferrocenyl)methyl)-1H-indole (3m) [a]
94% yield; δH (400 MHz, CDCl₃) 2.40 (s, 3H), 3.96–4.21 (m, 9H), 5.30 (s, 1H), 6.75 (s, 1H), 6.79 (d, J 8.0, 1H), 7.09 (s, 1H), 7.17–7.21 (m, 1H), 7.26–7.30 (m, 2H), 7.34–7.36 (m, 2H), 7.76 (br s, 1H, NH). m/z 405.1180 (HRMS) (M⁺), calc. for C₂₆H₂₃NFe: 405.1180.

1-Phenyl-2-[phenyl(ferrocenyl)methyl]butane-1, 3-dione (3n) [b]
38% yield; δH (400 MHz, CDCl₃) 1.91 (s, 3H), 3.91–3.99 (m, 9H), 4.77 (d, J 10.8, 1H), 5.25 (d, J 10.8, 1H), 7.28–7.95 (m, 10H). m/z 436. 1138 (HRMS) (M⁺), calc. for C₂₇H₂₃O₂Fe: 436. 1126.

1, 3-diphenyl-2-[phenyl(ferrocenyl)methyl]propane-1,3-dione (3o) [b]
78% yield; δH (400 MHz, CDCl₃): δ 3.82–4.01 (m, 9H), 4.95 (d, J 10.2, 1H), 6.03 (d, J 10.2, 1H), 7.16–7.84 (m, 15H). m/z 498.1289 (HRMS) (M⁺), calc. for C₃₂H₂₆O₂Fe: 498.1282.

4-[Ferrocenyl(phenyl)methyl]benzene-1,3-diol (3p) [b]
75% yield; δH (400 MHz, CDCl₃) 3.90 (t, J 8.4, 1H), 4.00–4.20 (m, 9H), 5.20–5.21 (d, J 6.0, 1H), 5.28 (s, 1H), 6.20–6.38 (m, 2H), 6.68–7.04 (m, 1H), 7.20–7.27 (m, 5H). m/z 384.0825 (HRMS) (M⁺), calc. for C₂₃H₂₂O₂Fe: 384.0813.

1-[Phenyl(ferrocenyl)methyl]-naphthalen-2-ol (3q) [b]
75% yield; δH (400 MHz, CDCl₃) 3.98–4.30 (m, 9H), 5.48 (s, 1H), 6.18 (s, 1H), 7.06 (d, J 8.4, 1H), 7.22–7.25 (m, 1H), 7.29–7.34 (m, 3H), 7.39–7.41 (m, 2H), 7.43–7.48 (m, 1H), 7.70 (d, J 8.8, 1H), 7.77 (d, J 8.0, 1H), 8.08 (d, J 8.0, 1H). m/z 418. 1026 (HRMS) (M⁺), calc. for C₂₇H₂₀OFe: 418. 1020.

N-[(ferrocenyl)(phenyl)methyl]benzamine (5a)
94% yield; brown solid. Mp 38–40 °C. νmax(KBr)/cm⁻¹ 3411, 3056, 1605. δH (300 MHz, CDCl₃) 4.03–4.20 (m, 9H), 4.76 (s, 1H), 5.06 (s, 1H), 6.56 (d, J 7.7, 1H), 6.67 (t, J 6.9, 1H), 7.12 (t, J 7.6, 2H), 7.24 (d, J 6.1, 2H), 7.32 (t, J 7.2, 2H), 7.45 (d, J 7.4, 2H), δc (75 MHz, CDCl₃) 147.6, 143.1, 129.4, 128.6, 127.2, 126.8, 117.6, 113.5, 94.3, 68.8, 68.1, 67.9, 67.5, 66.8, 57.6. m/z 367.1010 (HRMS) (M⁺), calc. for C₂₃H₂₁FeN: 367.102.

N-[(ferrocenyl)(phenyl)methyl]-4-chlorobenzamine (5b)
96% yield; orange solid. Mp 85–86 °C. νmax(KBr)/cm⁻¹ 3411, 3025, 1597. δH (CDCl₃, 400 MHz): δ 4.07–4.28 (m, 9H), 4.74 (s, 1H), 4.98 (s, 1H), 6.41 (d, J 8.0, 2H), 7.04 (d, J 8.0, 2H), 7.24–7.42 (m, 5H), δc (75 MHz, CDCl₃) 146.3, 142.8, 129.4, 128.9, 127.6, 127.1, 122.4, 114.8, 94.1, 69.1, 68.5, 68.3, 67.7, 67.1, 57.9. m/z 401.0634 (HRMS) (M⁺), calc. for C₂₃H₂₁ClFeN: 401.0634.

N-[(ferrocenyl)(phenyl)methyl]-4-bromobenzamine (5c)
97% yield; yellow solid. Mp 78–79 °C. \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3372, 3087, 1589. \( \delta_H \) (300 MHz, CDCl\(_3\)) 4.02–4.18 (m, 9H), 4.78 (s, 1H), 5.00 (s, 1H), 6.45 (d, J 7.9, 2H), 7.18 (d, J 7.8, 2H), 7.26 (s, 1H), 7.32 (t, J 7.3, 2H), 7.41 (d, J 7.7, 2H). \( \delta_C \) (75 MHz, CDCl\(_3\)) 146.4, 142.4, 132.0, 128.7, 127.4, 126.8, 115.1, 109.2, 93.8, 68.8, 68.2, 68.0, 67.4, 66.9, 57.52. \( m/z \) 445.0115 (HRMS) (M\(^+\)), calc. for C\(_{23}\)H\(_{29}\)BrFeN: 445.0129.

**N-((ferrocenyl)(phenyl)methyl)-4-methylbenzenamine (5d)**

67% yield; yellow solid. Mp 46–48 °C. \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3411, 3087, 1613. \( \delta_H \) (300 MHz, CDCl\(_3\)) 2.20 (s, 3H), 4.05–4.19 (m, 9H), 4.64 (s, 1H), 5.01 (s, 1H), 6.48 (d, J 6.6, 2H), 6.59 (d, J 6.7, 2H), 7.25–7.31 (m, 3H), 7.43 (d, J 6.3, 2H). \( \delta_C \) (75 MHz, CDCl\(_3\)) 145.4, 143.4, 129.9, 128.6, 127.2, 126.8, 113.6, 94.5, 68.8, 68.1, 67.8, 67.5, 66.7, 57.9, 20.6. \( m/z \) 381.1187 (HRMS) (M\(^+\)), calc. for C\(_{24}\)H\(_{25}\)FeN: 381.1180.

**N-((ferrocenyl)(phenyl)methyl)-4-methoxybenzenamine (5e)**

66% yield; yellow solid. Mp 45–46 °C. \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3449, 3025, 1636. \( \delta_H \) (300 MHz, CDCl\(_3\)) 3.72 (s, 3H), 4.01–4.21 (m, 10H), 5.00 (s, 1H), 6.54 (d, J 9.0, 2H), 6.74 (d, J 9.0, 2H), 7.24–7.48 (m, 5H). \( \delta_C \) (75 MHz, CDCl\(_3\)) 152.2, 143.6, 142.0, 128.6, 127.2, 126.9, 115.0, 114.7, 94.6, 68.8, 68.1, 67.8, 67.5, 66.6, 58.5, 55.9. \( m/z \) 397.1127 (HRMS) (M\(^+\)), calc. for C\(_{24}\)H\(_{24}\)FeN\(_2\): 397.1129.

**N-((ferrocenyl)(phenyl)methyl)-4- nitrobenzenamine (5f)**

97% yield; yellow liquid. \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3401, 2986, 1593, 1455, 1307. \( \delta_H \) (300 MHz, CDCl\(_3\)) 3.98–4.20 (m, 9H), 5.20 (d, J 4.8, 1H), 5.52 (s, 1H), 6.50 (d, J 9.1, 2H), 7.29–7.39 (m, 5H), 8.03 (d, J 9.1, 2H). \( \delta_C \) (100 MHz, CDCl\(_3\)) 152.1, 141.0, 138.5, 128.9, 127.9, 126.8, 126.5, 112.1, 92.5, 69.0, 68.5, 68.5, 67.5, 67.3, 57.0. \( m/z \) 412.0876 (HRMS) (M\(^+\)), calc. for C\(_{23}\)H\(_{20}\)FeN\(_2\)O\(_2\): 412.0873.

**N-((Ferrocenyl)(phenyl)methyl)-2- nitro benzenamine (5g)**

95% yield; orange solid. IR (KBr) \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3381, 3091, 2840, 1617. \( \delta_H \) (300 MHz, CDCl\(_3\)) 3.80–4.28 (m, 9H), 5.33 (d, J 4.5, 1H), 6.61 (d, J 8.2, 2H), 7.26–7.42 (m, 5H), 8.23 (d, J 8.1, 1H), 9.06 (s, 1H). \( \delta_C \) (100 MHz, CDCl\(_3\)) 144.2, 142.0, 136.3, 132.4, 128.8, 127.8, 127.0, 126.8, 115.9, 115.5, 92.1, 69.2, 68.5, 68.2, 67.4, 66.2, 56.6. \( m/z \) 412.0873 (HRMS) (M\(^+\)), calc. for C\(_{23}\)H\(_{20}\)FeN\(_2\)O\(_2\): 412.0873.

**N-(1-ferrocenylethyl)benzenamine (5h)**

61% yield; orange oil. IR (KBr) \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3409, 3092, 2971, 1602, 1504, 1313, 1105, 1000, 819, 748, 692. \( \delta_H \) (300 MHz, CDCl\(_3\)) 1.53 (d, J 6.6, 3H), 4.16–4.22 (m, 10H), 4.31–4.38 (m, 1H), 6.66–6.75 (m, 3H), 7.19–7.27 (m, 2H). \( \delta_C \) (100 MHz, CDCl\(_3\)) 147.9, 129.8, 117.6, 113.7, 94.0, 68.9, 68.2, 68.0, 67.5, 66.6, 47.5, 21.2. \( m/z \) 305.0876 (HRMS) (M\(^+\)), calc. for C\(_{18}\)H\(_{16}\)FeN: 305.0867.

**4-Chloro-N-(1-ferrocenylethyl)benzenamine (5i)**
78% yield; orange solid. Mp 96–97°C. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3403, 3086, 2972, 2870, 1595, 1500, 1398, 1308, 1132, 1028, 998, 815. δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 1.48 (d, J 6.0, 3H), 3.90 (br s, 1H), 4.18–4.23 (m, 10H), 6.56 (d, J 8.4, 2H), 7.13 (d, J 8.4, 2H). δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 146.5, 129.6, 122.0, 114.7, 93.6, 69.1, 68.9, 68.3, 68.1, 67.5, 66.5, 47.8, 21.2. m/z 339.0478 (HRMS) (M\textsuperscript{+}), calc. for C\textsubscript{18}H\textsubscript{14}ClFeN: 339.0477.

\textit{N}(1-ferrocenylyethyl)-4-methoxybenzenamine (5j)

54% yield; orange oil. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3405, 3089, 2980, 1597, 1510, 1308, 1100, 819 cm\textsuperscript{-1}. δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 1.49 (d, J 6.3, 3H), 3.76–4.27 (m, 10H), 6.23 (s, 3H), 6.23 (d, J 8.7, 2H), 6.80 (d, J 8.7, 2H), 6.80 (d, J 6.3, 2H). δ\textsubscript{C} (100 MHz, CDCl\textsubscript{3}) 152.4, 142.0, 115.4, 115.3, 93.9, 68.8, 68.1, 67.9, 67.5, 66.5, 56.2, 48.8, 21.5. m/z 335.0981 (HRMS) (M\textsuperscript{+}), calc. for C\textsubscript{18}H\textsubscript{17}FeEO: 335.0973.

\textit{N}(1-ferrocenylyethyl)-4-nitrobenzenamine (5k)

80% yield; orange solid. Mp 110–112°C. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3400, 3084, 2986, 1593, 1509, 1455, 1307, 1101, 821. δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 1.53 (d, J 6.6, 3H), 4.06–4.19 (m, 9H), 4.40–4.44 (m, 1H), 6.54 (d, J 6.0, 2H), 8.07 (d, J 6.0, 2H). δ\textsubscript{C} (75 MHz, CDCl\textsubscript{3}) δ 152.7, 137.7, 126.9, 111.5, 91.8, 68.9, 68.5, 68.2, 67.4, 66.3, 47.3, 20.7. m/z 350.0715 (HRMS) (M\textsuperscript{+}), calc. for C\textsubscript{18}H\textsubscript{18}FeNO\textsubscript{2}: 350.0718.

2-(1-Ferrocenylyethylthio)-naphthalene (7a)

85% yield; orange oil. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3087, 2971, 1656, 1581, 1364, 1221, 1002, 813. δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}) 1.67 (d, J 6.9, 3H), 4.06–4.29 (m, 10H), 7.42–7.48 (m, 3H), 7.73–7.83 (m, 4H). δ\textsubscript{C} (75 MHz, CDCl\textsubscript{3}) 134.0, 133.2, 132.8, 132.1, 130.9, 128.6, 128.1, 127.9, 126.8, 126.5, 91.2, 69.1, 68.4, 68.2, 68.1, 66.6, 44.0, 21.6. m/z 372.0635 (HRMS) (M\textsuperscript{+}), calc. for C\textsubscript{22}H\textsubscript{20}FeS: 372.0635.

2-((Ferrocenylyl)(phenyl)methylthio)-naphthalene (7b)

83% yield; orange solid. Mp 140–141°C. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3051, 2922, 1581, 1494, 1194, 1028, 815, 742. δ\textsubscript{H} (300 MHz, CDCl\textsubscript{3}): δ 4.11–4.19 (m, 9H), 5.25 (s, 1H), 7.18–7.23 (m, 2H), 7.28–7.32 (m, 2H), 7.40–7.43 (m, 4H), 7.63–7.68 (m, 3H), 7.72–7.76 (m, 1H). δ\textsubscript{C} (75 MHz, CDCl\textsubscript{3}) 142.4, 133.9, 133.6, 132.6, 131.5, 130.2, 128.8, 128.6, 128.4, 128.0, 127.9, 127.7, 126.7, 126.4, 90.0, 69.4, 69.0, 68.6, 68.2, 68.1, 54.7. m/z 343.0792 (HRMS) (M\textsuperscript{+}), calc. for C\textsubscript{27}H\textsubscript{22}FeS: 343.0792.

\textit{Ferrocenyl (phenyl) (methoxyl)methane (8a)\textsuperscript{[c]}}

40% yield; orange solid. Mp 112–113°C. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3091, 2981, 2870, 1494, 1453, 1397, 1194. δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 3.28 (s, 3H), 3.98–4.30 (m, 9H), 4.98 (s, 1H), 7.30–7.42 (m, 5H). m/z 306.0707 (HRMS) (M\textsuperscript{+}), calc. for C\textsubscript{18}H\textsubscript{18}FeO: 306.0707.

\textit{Ferrocenyl (phenyl) (ethoxyl)methane (8b)}

75% yield; orange solid. Mp 54–55°C. v\textsubscript{max}(KBr)/cm\textsuperscript{-1} 3085, 3027, 2869, 2840, 1491, 1452, 1014. δ\textsubscript{H} (400 MHz, CDCl\textsubscript{3}) 1.19 (s, 3H), 3.42 (d, J 3.6, 2H), 4.00–4.32 (m, 9H), 5.08 (s, 1H), 7.29–7.41 (m, 5H). δ\textsubscript{C} (100 MHz, DMSO-\textsubscript{d}\textsubscript{6}): δ 148.0, 133.7, 132.9, 132.5, 96.3, 85.2, 74.2, 73.0, 73.0, 72.8, 72.4, 69.2, 21.0. m/z (HRMS) 320.0864 (M\textsuperscript{+}), calc. for C\textsubscript{18}H\textsubscript{20}FeO: 320.0864.

\textit{Ferrocenyl (phenyl) (isopropoxy)methan (8c)}
40% yield; orange solid. Mp 67–68°C. \( v_{\text{max}}(\text{KBr})/\text{cm}^{-1} \) 3084, 2965, 2925, 2872, 1490, 1453, 1103, 1062, 809, 726, 701. \( \delta_H \) (400 MHz, CDCl\(_3\)) 1.09 (d, \( J = 6.0 \), 3H), 1.21 (d, \( J = 6.0 \), 3H), 3.51–3.60 (m, 1H), 3.94–4.25 (m, 9H), 5.22 (s, 1H), 7.27–7.44 (m, 5H). \( \delta_C \) (100 MHz, DMSO-\( d_6 \)) 148.7, 133.6, 132.6, 97.0, 82.1, 74.2, 73.8, 72.9, 72.8, 72.7, 72.3, 28.8, 27.1. \( m/z \) (HRMS) 334.1018 (M\(^+\)), calc. for C\(_{20}\)H\(_{22}\)FeO: 334.1020.

References


The \(^1H\) NMR and \(^{13}C\) NMR charts for compounds

of \( \alpha \)-Functionalized Ferrocene 3-(ferrocenylethyl)-1H-indole (3a)

4-methyl-3-(ferrocenylethyl)-1H-indole (3b)
4-benzylOxy-3-(ferrocenylethyl)-1H-indole (3c)

5-methyl-3-(ferrocenylethyl)-1H-indole (3d)
5-bromol-3-(ferrocenylethyl)-1H-indole (3e)

6-methyl-3-(ferrocenylethyl)-1H-indole (3f)
7-methyl-3-(ferrocenylethyl)-1H-indole (3g)

2-phenyl-3-(ferrocenylethyl)-1H-indole (3h)
3-(phenyl(ferrocenyl)methyl)-1H-indole (3i)
4-benzyloxy-3-(phenyl(ferrocenyl)methyl)-1H-indole (3j)

5-bromo-3-(phenyl(ferrocenyl)methyl)-1H-indole (3k)

7-methyl-3-(phenyl(ferrocenyl)methyl)-1H-indole (3l)
6-methyl-3-(phenyl(ferrocenyl)methyl)-1H-indole (3m)

1-phenyl-2-[phenyl(ferrocenyl)methyl]butane-1, 3-dione (3n)
1, 3-diphenyl-2-[phenyl(ferrocenyl)methyl]propane-1,3-dione (3o)
4-[ferrocenyl(phenyl)methyl]benzene-1, 3-diol (3p)
1- phenyl(ferroceny)methyl-naphthalen-2-ol (3q)

N-((Ferrocenyl)(phenyl)methyl)benzenamine (5a)
$N-((\text{Ferrocenyl})(\text{phenyl})\text{methyl})-4$-chlorobenzenamine (5b)
$N$-((Ferrocenyl)(phenyl)methyl)-4-bromobenzenamine (5c)
$N-((\text{Ferrocenyl})(\text{phenyl})\text{methyl})-4\text{-methylbenzenamine (5d)}$
N-((Ferrocenyl)(phenyl)methyl)-4-methoxybenzenamine (5e)
$N$-((Ferrocenyl)(phenyl)methyl)-4- nitrobenzenamine (5f)
$N$-((Ferrocenyl)(phenyl)methyl)-2-nitro benzenamine (5g)
$N$-(1-ferrocenylethyl)benzenamine (5h)
$^1\text{H NMR}$
4-chloro-N-(1-ferrocenylethyl)benzenamine (5i)
$^1$H NMR
$^{13}$C NMR

$N$-$(1$-ferrocenylethyl)$-4$-methoxybenzamine $(5j)$

$^1$H NMR

$^{13}$C NMR
**N-(1-ferrocenylethyl)-4-nitrobenzenamine (5k)**

**$^1$H NMR**

**$^{13}$C NMR**
2-(1-ferrocenylethylthio)-naphthalene (7a)

2-((ferrocenyl)(phenyl)methylthio)-naphthalene (7b)
Ferrocenyl (phenyl) (methoxyl)methane (8a)

Ferrocenyl (phenyl) (ethoxyl)methane (8b)
Ferrocenyl (phenyl) (isopropoxyl)methan (8c)
Information of HPLC analysis of (R)-5b'

HPLC analysis of (R)-5b'

[α]₀ = -50.0 (c 0.1, THF)
HPLC analysis AD-H: flux 1mL/m (hexane: i-PrOH) 99:1. tm: “10.29 min”, TM: “12.76 min”, ce 98.5%.

Copies of HPLC analysis of race-2ad and (R)-5b’

race-5b
Spectrum Index Plot

Peaks:

- Peak 1: 11.564 nm
- Peak 2: 13.224 nm

Measured Values:

- Peak 1:
  - Height: 255.2
  - Width: 308.4

- Peak 2:
  - Height: 255.2
  - Width: 308.4

AU vs Minutes:

- Minimum AU: 0.00
- Maximum AU: 0.55

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18:15:02 PRC

(R)-5b'
**Sample Information**

- **Sample Name:** L-AcOH
- **Sample Type:** Unknown
- **Vial:** 1
- **Injection #:** 3
- **Injection Volume:** 5.00 µl
- **Run Time:** 16.0 Minutes
- **Date Acquired:** 2010-3-18 18:13:04 CST
- **Date Processed:** 2010-3-18 18:34:28 CST

**Auto-Scaled Chromatogram**

**Peak Results**

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