Supplementary Information

From ferrocene to fluorine-containing penta-substituted derivatives and all points in-between;
or, how to increase the available chemical space

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General methods

All reactions were performed under argon atmosphere using standard Schlenk techniques. THF was distilled over sodium/benzophenone. Column chromatography separations were achieved on silica gel (40-63 μm). Melting points were measured on a Kofler apparatus. IR spectra were taken on a Perkin-Elmer Spectrum 100 spectrometer. 1H, 13C and 19F Nuclear Magnetic Resonance (NMR) spectra were in general recorded on either a Bruker Avance III spectrometer at 300, 75, and 282 MHz, respectively, or a Bruker Avance III HD at 500, 126 and 470 MHz, respectively. 1H chemical shifts (δ) are given in parts per million (ppm) relative to the solvent residual peak and 13C chemical shifts are relative to the central peak of the solvent signal. Compounds 1, 2a, 2f-m, 2o-u, 3s-1, 4s-1 and 5s-I-1 were already obtained and described in our preliminary study. ZnCl2·TMEDA and 4s’-I were prepared as described previously. After opening a new bottle of 2,2,6,6-tetramethylpiperidine, KOH pellets were added and storage in a desiccator was necessary. All reagents not listed in the publication (main paper or supporting information) were obtained from commercial sources.

Crystallographic data.

CCDC 1939208 (2c), 1939209 (2t·BH3), 1939210 (3p-Br), 1939211 (3p-I), 1939212 (3s-Br), 1939213 (3u-I), 1939214 (3r-I), 1939215 (4s-Br), 1939216 (5s-I-2), 1939217 (5s-I-3), 1939218 (5s-I-4), 1939219 (5s-I-5), 1939220 (5s-I-7), 1939221 (5u-I) and 1939222 (7u-I) contain the crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

The X-ray diffraction data were collected by using a D8 VENTURE Bruker AXS diffractometer equipped with a (CMOS) PHOTON 100 detector at the temperature given in the crystal data. The samples were studied with monochromatized Mo-Kα radiation (λ = 0.71073 Å, multilayer monochromator). The structures were solved by dual-space algorithm using the SHELXT program and then refined with full-matrix least-square methods based on F2 (SHELXL). All non-hydrogen atoms were refined with anisotropic atomic displacement parameters. Except the hydrogen atom linked to O16 in the case of 5s-I-3 and the hydrogen atom linked to oxygen in the case of 5s-I-5 that were introduced in the structural model through Fourier difference maps analysis, H atoms were finally included in their calculated positions and treated as riding on their parent atom with constrained thermal parameters. The molecular diagrams were generated by ORTEP-3 (version 2.02).
Experimental procedures and analyses

General procedure 1 for the deprotolithiation-trapping sequence. To a stirred solution of the required ferrocene (1.0 equiv; unless otherwise specified in the product description, 1.0 mmol) in THF (1.0 mL mmol⁻¹) at -75 °C was added dropwise a solution of s-BuLi (about 1.1 M solution in 92:8 cyclohexane-hexane, 1.2 equiv). After 1 h at -75 °C, the required electrophile (in general 1.2 equiv; either pure or in solution, as indicated in the product description) was added. The mixture was allowed to reach room temperature before addition of water (5 mL) and extraction with Et₂O (3 x 20 mL) or AcOEt (2 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated under reduced pressure. The crude product was purified by chromatography over silica gel (the eluent is given in the product description).

1-Allyl-2-fluoroferroocene (2b, racemic mixture). The general procedure 1 starting from fluoroferrocene (1; 0.41 g, 2.0 mmol) and using allyl bromide (0.19 mL, 0.27 g, 2.2 mmol) gave 2b (eluent: petroleum ether; Rf = 0.50) in 39% yield (0.19 g) as an orange oil: IR (ATR) 661, 755, 800, 818, 915, 999, 1012, 1106, 1127, 1190, 1279, 1378, 1412, 1451, 1485, 1622, 1639, 1678, 2979, 3082 cm⁻¹; ¹H NMR (CDCl₃) δ 3.11-3.26 (m, 2H, H1’), 3.70 (d, 1H, J = 1.2 Hz, H4), 3.74 (s, 1H, H5), 4.21 (s, 5H, Cp), 4.27 (s, 1H, H3), 5.05 (d, 1H, J = 9.1 Hz, H3’), 5.09 (d, 1H, J = 16.4 Hz, H3’), 5.97 (ddt, 1H, J = 16.7, 10.0 and 6.6 Hz, H2’); ¹³C NMR (CDCl₃) δ 30.4 (d, CH₂, J = 2.6 Hz, C1’), 55.6 (d, CH, J = 15.1 Hz, C3), 59.0 (d, CH, J = 4.4 Hz, C4), 61.9 (d, CH, J = 3.0 Hz, C5), 69.9 (5CH, Cp), 74.1 (d, C, J = 13.0 Hz, C1), 115.7 (CH₂, C3’), 134.3 (d, C, J = 268.5 Hz, C2), 136.4 (CH, C2’), ¹⁹F NMR (CDCl₃) δ -192.9. MS (EI, 70 eV): 244 [M], 159, 121, 104. Anal. Calcd for C₁₃H₁₃FFe (244.09): C, 63.97; H, 5.37. Found: C, 64.14; H, 5.46.
1-(Dimethylaminomethyl)-2-fluoroferrrocene (2c, racemic mixture). The general procedure starting from fluoroferrocene (1; 0.41 g, 2.0 mmol) and using N,N-dimethylmethyleneiminium iodide (0.41 g, 2.2 mmol) gave 2c (eluent: AcOEt-petroleum ether-Et₃N 49.5:48.5:1 to 79:20:1; Rᵣ (AcOEt-petroleum ether 70:30) = 0.30) in 80% yield (0.42 g) as an orange oil: IR (ATR) 660, 758, 818, 1001, 1016, 1105, 1152, 1176, 1201, 1256, 1290, 1318, 1354, 1380, 1451, 1489, 2770, 2817, 2938, 3095 cm⁻¹; ¹H NMR (CDCl₃) δ 2.18 (s, 6H, NMe₂), 3.29 (d, 1H, J = 13.1 Hz, CH₂), 3.54 (d, 1H, J = 13.1 Hz, CH₂), 3.74 (dd, 1H, J = 3.9 and 2.5 Hz, H4), 3.86 (t, 1H, J = 1.25 Hz, H5), 4.17 (s, 5H, Cp), 4.29 (q, 1H, J = 3.95 and 2.6 Hz, H3); ¹³C NMR (CDCl₃) δ 44.7 (2CH₃), 55.3 (d, CH₂, J = 3.2 Hz), 56.0 (d, CH, J = 15.2 Hz, C3), 59.8 (d, CH, J = 4.2 Hz, C4), 63.7 (d, CH, J = 3.0 Hz, C5), 69.8 (5CH, Cp), 70.4 (d, C, J = 13.0 Hz, C1), 135.3 (d, C, J = 269.5 Hz, C2); ¹⁹F NMR (CDCl₃) δ -191.5. MS (EI, 70 eV): 261 [M], 217 [M-NMe₂], 204 [FcF]. Anal. Calcd for C₁₃H₁₆FFeN (261.06): C, 59.80; H, 6.18; N, 5.36. Found: C, 59.88; H, 6.23; N, 5.29.

1-Fluoro-2-(2-pyridyl)ferrocene (2d, racemic mixture). The general procedure 1 was modified as follows: 1 h after the addition of s-BuLi onto fluoroferrocene (1; 0.41 g, 2.0 mmol) in THF at -75 °C, ZnCl₂·TMEDA (0.61 g, 2.4 mmol, 1.2 equiv) was added in one portion and the reaction mixture was allowed to warm to rt. PdCl₂ (28 mg, 0.16 mmol, 80 mequiv), dppf (89 mg, 0.16 mmol, 80 mequiv) and 2-chloropyridine (0.11 mL, 0.14 g, 1.2 mmol, 1.2 equiv) were added. The reaction mixture was heated at reflux overnight and then cooled to rt. 2d (eluent: petroleum ether-AcOEt-Et₃N 79:20:1; Rᵣ (eluent: petroleum ether-AcOEt 80:20) = 0.56) was obtained in 61% yield (0.34 g) as an orange solid: mp 60-62 °C; IR (ATR) 656, 712, 744, 783, 810, 878, 975, 1000, 1020, 1046, 1105, 1138, 1152, 1219, 1286, 1300, 1364, 1424, 1447, 1464, 1502, 1564, 1586, 3101 cm⁻¹; ¹H NMR (CDCl₃) δ 4.02 (s, 1H, H₄), 4.15 (s, 5H, Cp), 4.55 (d, 1H, J = 1.3 Hz, H₅), 4.71 (s, 1H, H₃), 7.12 (t,
1H, J = 6.0 Hz, H5’), 7.63 (t, 1H, J = 7.3 Hz, H4’), 7.73 (d, 1H, J = 7.9 Hz, H3’), 8.55 (d, 1H, J = 4.4 Hz, H6’); 13C NMR (CDCl3) δ 58.1 (d, CH, J = 15.8 Hz, C5), 61.3 (d, CH, J = 4.5 Hz, C4), 61.9 (d, CH, J = 1.8 Hz, C3), 71.0 (5CH, Cp), 71.4 (d, C, J = 8.1 Hz, C2), 121.1 (CH, C5’), 121.6 (d, CH, J = 7.7 Hz, C3’), 134.6 (d, C, J = 271 Hz, C1), 136.2 (CH, C4’), 149.6 (CH, C6’), 157.2 (d, C, J = 4.9 Hz, C2’); 19F NMR (CDCl3) δ -187.5. MS (EI, 70 eV): 281 [M], 261 [M-HF], 204 [FcF]. Anal. Calcd for C15H12FFeN (281.03): C, 64.09; H, 4.30; N, 4.98. Found: C, 64.15; H, 4.41; N, 4.87.

2-Fluoroferroceneboronic acid, pinacol boronate (2e, racemic mixture). The general procedure 1 was modified as follows: 1 h after the addition of s-BuLi onto fluoroferocene (1; 0.41 g, 2.0 mmol) in THF at -75 °C, the reaction mixture was cannulated onto a solution of triisopropylborate (1.85 mL, 1.5 g, 8.0 mmol, 4.0 equiv) in THF (3.0 mL) at -75 °C. The reaction mixture was allowed to reach 0 °C before addition of MeOH (2 mL). The reaction mixture was warmed to rt and stirred for 1 h. Pinacol (0.35 g, 3.0 mmol, 1.5 equiv) was added and volatiles were removed under vacuum. Anhydrous Et2O (15 mL) was added and the reaction mixture was stirred overnight at rt. Celite was added and volatiles were removed under vacuum. 2e (eluent: petroleum ether-AcOEt 90:10 to 80:20; Rf (eluent: petroleum ether-AcOEt 90:10) = 0.55) was obtained in 67% yield (0.45 g) as an orange solid: mp 117-119 °C; IR (ATR) 665, 687, 703, 810, 838, 857, 961, 1000, 1050, 1070, 1104, 1139, 1208, 1231, 1266, 1309, 1330, 1357, 1372, 1452, 1481, 1500, 2983 cm⁻¹; 1H NMR (CDCl3) δ 1.38 (s, 12H, 4 CH3), 4.01 (br s, 1H, H4), 4.03 (d, 1H, J = 1.1 Hz, H5), 4.26 (s, 5H, Cp), 4.50 (dd, 1H, J = 4.0 and 2.4 Hz, H3); 13C NMR (CDCl3) δ 25.0 (4 CH3), 59.5 (d, CH, J = 16.0 Hz, C3), 64.8 (d, CH, J = 3.9 Hz, C4), 66.8 (d, CH, J = 4.5 Hz, C5), 69.9 (5CH, Cp), 83.5 (2C, CMe2), 139.6 (d, C, J = 272 Hz, C2), C1 not seen due to quadrupolar coupling; 19F NMR (CDCl3) δ -181.9. 11B NMR (CDCl3) δ 32.3. MS (EI, 70 eV): 330 [M], 248, 230, 121. Crystal data for 2e. C16H20BFFeO2, M = 329.98, T = 150(2) K, monoclinic, P 2_1/n, a = 13.170(3), b = 7.7111(16), c = 15.613(4) Å, β = 105.440(10) °, V = 1528.3(6) Å³, Z = 4, d = 1.434 g cm⁻³, μ = 0.997 mm⁻¹. A final refinement on F² with 3497 unique intensities and 194 parameters converged at ωR(F²) = 0.1353 (R(F) = 0.0510) for 2883 observed reflections with I > 2σ(I). CCDC 1939208.
2-Fluoro-N-phenylferrocenecarboxamide (2n, racemic mixture). The general procedure starting from fluoroferrocene (1; 0.41 g, 2.0 mmol) and using phenyl isocyanate (0.24 mL, 0.26 g, 2.2 mmol) gave 2n (eluent: petroleum ether-AcOEt 80:20; R_f = 0.43) in 83% yield (0.54 g) as an orange powder: mp 151-153 °C; IR (ATR) 655, 690, 754, 805, 844, 892, 1003, 1013, 1076, 1182, 1241, 1274, 1319, 1368, 1437, 1451, 1464, 1498, 1534, 1599, 1645, 3333 cm⁻¹; ^1H NMR (CDCl₃) δ 4.09 (s, 1H, H4), 4.35 (s, 5H, Cp), 4.60 (s, 1H, H3), 4.67 (s, 1H, H5), 7.14 (t, 1H, J = 7.4 Hz, H4’), 7.37 (t, 2H, J = 7.8 Hz, H3’ and H5’), 7.64 (d, 2H, J = 7.9 Hz, H2’ and H6’), 7.87 and 7.88 (br s, 1H, NH); ^13C NMR (CDCl₃) δ 58.9 (d, CH, J = 16.2 Hz, C3), 62.5 (d, CH, J = 4.4 Hz, C4), 63.6 (d, C, J = 9.9 Hz, C1), 64.0 (d, CH, J = 0.7 Hz, C5), 71.4 (5CH, Cp), 120.0 (d, 2CH, J = 16.9 Hz, C2’ and C6’), 124.3 (CH, C4’), 129.1 (d, 2CH, J = 20.3 Hz, C3’ and C5’), 134.5 (d, C, J = 270 Hz, C2), 138.1 (C, C1’), 166.8 (d, C, J = 4.4 Hz, C=O); ^19F NMR (CDCl₃) δ -187.2. MS (EI, 70 eV): 323 [M], 231 [M-NHPh]. Anal. Calcd for C₁₇H₁₄FFeNO (323.15): C, 63.19; H, 4.37; N, 4.33. Found: C, 63.22; H, 4.40; N, 4.34.

1-(Diphenylphosphino)-2-fluoroferrocene, borane complex (2t·BH₃, racemic mixture). Compound 2t·BH₃ was obtained as described previously. Crystal data for 2t·BH₃, C₂₂H₂₁BFFeP, M = 402.02, T = 150(2) K, orthorhombic, P b c a, a = 12.4583(14), b = 14.7599(14), c = 20.490(2) Å, V = 3767.9(7) Å³, Z = 8, d = 1.417 g cm⁻³, μ = 0.897 mm⁻¹. A final refinement on F² with 4248 unique intensities and 236 parameters converged at wR(F²) = 0.1055 (R(F) = 0.0409) for 3453 observed reflections with I > 2σ(I). CCDC 1939209.
1-Fluoro-2-(tributylstanny)ferrocene (2v, racemic mixture). The general procedure starting from fluoroferrocene (1; 0.41 g, 2.0 mmol) and using chlorotributylstannane (0.60 mL, 0.72 g, 2.2 mmol) gave 2v after quench with methanol at -40 °C, removal of the solvent and purification (elucent: petroleum ether-Et₃N 99:1; R_f (petroleum ether) = 0.60) in 89% yield (0.88 g) as an orange oil: IR (ATR) 801, 815, 855, 968, 1000, 1018, 1106, 1146, 1332, 1410, 1432, 1464, 2853, 2871, 2923, 2956 cm⁻¹; ¹H NMR (CDCl₃) δ 0.92 (t, 9H, J = 7.3 Hz, Me), 1.00-1.18 (m, 6H, CH₂Sn), 1.37 (dq, 6H, J = 14.2 and 7.2 Hz, C₅H₅Me), 1.52-1.64 (m, 6H, C₅H₅Et), 3.59 (dt, 1H, J = 2.5 and 1.2 Hz, H₃), 3.93 (dd, 1H, J = 3.7, 2.4 and 1.4 Hz, H5); ¹³C NMR (CDCl₃) δ 10.5 (3CH₂, CH₂Sn), 13.8 (3CH₃), 27.5 (3CH₂, C₂H₅CH₃), 29.3 (3CH₂, C₂H₅CH₂CH₃), 56.9 (d, C, J = 30.8 Hz, C2), 57.3 (d, CH, J = 19.3 Hz, C5), 64.3 (d, CH, J = 2.3 Hz, C4), 66.9 (d, CH, J = 9.1 Hz, C3), 69.2 (5CH, Cp), 140.5 (d, C, J = 261 Hz, C1); ¹⁹F NMR (CDCl₃) δ -180.6. MS (EI, 70 eV): 494 [M], 437 [M-Bu], 323 [M-3Bu], 204 [M-SnBu₃+H]. Anal. Calcd for C₂₂H₃₅FFeSn (493.08): C, 53.59; H, 7.16. Found: C, 53.77; H, 7.32.

1,3-Dichloro-2-fluoroferrocene (3p-Cl). The general procedure 1 from 1-chloro-2-fluoroferrocene (2p; 0.24 g) and using hexachloroethane (0.28 g) in THF (3 mL) gave 3p-Cl (elucent: petroleum ether; R_f = 0.58; a second purification using petroleum ether-Et₃N-AcOEt 97.5:2:0.5 as eluent was performed) in 84% yield (0.23 g) as an orange powder: mp 65 °C; IR (ATR) 669, 801, 828, 891, 1003, 1107, 1140, 1255, 1369, 1420, 1469, 1667, 3099 cm⁻¹; ¹H NMR (CDCl₃) δ 4.09 (d, 2H, J = 0.9 Hz, H4 and H5), 4.37 (d, 5H, J = 0.75 Hz, Cp); ¹³C NMR (CDCl₃) δ 58.7 (2CH, C4 and C5), 74.1 (5CH, Cp), 79.2 (d, 2C, J = 14.4 Hz, C1 and C3), 128.1 (d, C, J = 276 Hz, C2); ¹⁹F NMR (CDCl₃) δ -197.4. Anal. Calcd for C₁₀H₇Cl₂FFe (272.91): C, 44.01; H, 2.59. Found: C, 44.16; H, 2.54.
1-Bromo-3-chloro-2-fluoroferroocene (3p-Br, racemic mixture). The general procedure 1 from 1-chloro-2-fluoroferroocene (2p; 1.2 g, 5.0 mmol) and using tetrabromomethane (2.0 g, 6.0 mmol, 1.2 equiv) in THF (5 mL) gave 3p-Br (eluuent: petroleum ether; R_f = 0.58; a second purification using petroleum ether-2361 unique intensities and 108 parameters converged at 85% yield (1.3 g) as an orange powder: mp 49-52 °C; IR (ATR) 666, 801, 826, 879, 974, 1001, 1107, 1136, 1250, 1366, 1411, 1465, 1664, 3096 cm^-1; ^1H NMR (CDCl_3) δ 4.10 (d, 1H, J = 2.8 Hz), 4.17 (d, J = 2.8 Hz, 1H), 4.35 (s, 5H, C_p); ^13C NMR (CDCl_3) δ 60.3 and 60.5 (2CH, C4 and C5), 64.4 (d, C, J = 17.1 Hz, C1), 74.3 (5CH, C_p), 79.5 (d, C, J = 14.9 Hz, C3), 129.2 (d, C, J = 274 Hz, C2); ^19F NMR (CDCl_3) δ -195.1. Crystal data for 3p-Br. C_{10}H_3BrClFe, M = 317.37, T = 150(2) K, monoclinic, P 2_1/n, a = 6.5459(10), b = 10.4479(17), c = 15.037(2) Å, β = 91.505(6)°, V = 1028.0(3) Å^3, Z = 4, d = 2.051 g cm^-3, μ = 5.579 mm^-1. A final refinement on F^2 with 2361 unique intensities and 108 parameters converged at ωR(F^2) = 0.0787 (R(F) = 0.0313) for 2060 observed reflections with I > 2σ(I). CCDC 1939210.

1-Chloro-2-fluoro-3-iodoferrocene (3p-I, racemic mixture). The general procedure 1 from 1-chloro-2-fluoroferrocene (2p; 0.24 g) and using iodine (0.30 g) in THF (3 mL) (followed by washing with 3 x 10 mL of an aqueous Na_2S_2O_3 solution) gave 3p-I (eluuent: heptane; R_f = 0.36) in 88% yield (0.32 g) as an orange powder: mp 39-41 °C; IR (ATR) 663, 710, 805, 829, 847, 872, 964, 1000, 1052, 1104, 1132, 1156, 1238, 1363, 1408, 1454, 1740, 1798, 2922, 3094 cm^-1; ^1H NMR (CDCl_3) δ 4.08 (dd, 1H, J = 2.8 and 0.9 Hz, H4), 4.27 (dd, 1H, J = 2.8 and 0.7 Hz, H5), 4.31 (s, 5H, C_p); ^13C NMR (CDCl_3) δ 26.4 (d, C, J = 19.5 Hz, C3), 63.0 (t, CH, J = 4.0 Hz, C5), 64.1 (t, CH, J = 4.2 Hz, C4), 74.7 (t, 5CH, J = 3.8 Hz, C_p), 79.6 (d, C, J = 15.8 Hz, C1), 131.6 (d, C, J = 274 Hz, C2); ^19F NMR (CDCl_3) δ -191.0. Crystal data for 3p-I. C_{10}H_3ClFeI, M = 364.36, T = 150(2) K, monoclinic, P 2_1/c, a = 6.6845(13), b = 15.913(4), c = 10.315(2) Å, β = 99.375(8)°, V = 1082.6(4) Å^3, Z = 4, d = 2.236 g cm^-3, μ = 4.459 mm^-1. A final refinement on F^2 with 2451 unique intensities and 127 parameters converged at ωR(F^2) = 0.0735 (R(F) = 0.0294) for 2244 observed reflections with I > 2σ(I). CCDC 1939211.
1-Bromo-2-fluoro-3-(trimethylsilyl)ferrocene (3s-Br, racemic mixture). The general procedure 1 from 1-fluoro-2-(trimethylsilyl)ferrocene (2s; 0.83 g, 3.0 mmol) and using tetrabromomethane (1.1 g, 3.3 mmol) in THF (4 mL) gave 3s-Br (elucent: petroleum ether; Rf = 0.57) in 61% yield (0.65 g) as an orange powder: mp 40-44 °C; IR (ATR) 663, 695, 754, 819, 835, 891, 999, 1081, 1109, 1135, 1158, 1219, 1244, 1335, 1372, 1415, 1428, 2899, 2955, 3099 cm⁻¹; ¹H NMR (CDCl₃) δ 0.29 (s, 9H, Me), 3.68 (dd, 1H, J = 2.7 and 1.7 Hz, H4), 4.24-4.28 (m, 1H, H5), 4.26 (s, 5H, Cp); ¹³C NMR (CDCl₃) δ -0.38 (3CH₃), 58.5 (d, C, J = 19.8 Hz, C3), 63.8 (d, CH, J = 5.6 Hz, C4), 66.2 (CH, C5), 67.8 (d, C, J = 19.9 Hz, C1), 72.1 (5CH, Cp), 136.5 (d, C, J = 270 Hz, C2); ¹⁹F NMR (CDCl₃) δ -186.0. Crystal data for 3s-Br. C₁₃H₁₆BrFFeSi, M = 355.11, T = 150(2) K, monoclinic, P 2₁/c, a = 17.276(4), b = 6.8553(17), c = 12.095(3) Å, β = 100.988(8) °, V = 1406.1(6) Å³, Z = 4, d = 1.677 g cm⁻³, μ = 3.986 mm⁻¹. A final refinement on F² with 3197 unique intensities and 173 parameters converged at ωR(F²) = 0.1523 (R(F) = 0.0665) for 2806 observed reflections with I > 2σ(I). CCDC 1939212.

N,N-Dimethyl-2-fluoro-3-(phenylthio)ferrocene (3u-CONMe₂, racemic mixture). The general procedure 1 from 1-fluoro-2-(phenylthio)ferrocene (2u; 0.31 g) and using dimethylcarbamoyl chloride (0.11 mL) gave 3u-CONMe₂ (elucent: petroleum ether-AcOEt 98:2 to 90:10; Rf (petroleum ether-AcOEt 90:10) = 0.04) in 77% yield (0.30 g) as a beige powder: mp 85-86 °C; IR (ATR) 688, 707, 742, 818, 951, 1019, 1172, 1273, 1374, 1390, 1431, 1478, 1504, 1627, 2927 cm⁻¹; ¹H NMR (CDCl₃) δ 3.07 (s, 6H, 2Me), 4.27 (s, 1H), 4.43 (s, 5H, Cp), 4.48 (s, 1H), 7.09-7.23 (m, 5H, Ph); ¹³C NMR (CDCl₃) δ 35.9 (CH₃, Me), 38.6 (CH₃, Me), 65.4 (CH), 65.5 (d, C, J = 16.7 Hz), 68.2 (CH), 71.3 (d, C, J = 11.8 Hz), 73.0 (5CH, Cp), 125.9 (CH, C4'), 126.9 (2CH), 129.0 (2CH), 133.3 (d, C, J = 276 Hz, C2), 138.7 (C, C1'), 166.7 (C, C=O); ¹⁹F NMR (CDCl₃) δ -183.5. Anal. Caled for C₁₉H₁₈FFeNOS (383.26): C, 59.54; H, 4.73; N, 3.65. Found: C, 59.65; H, 4.83; N, 3.51.
2-Fluoro-1-iodo-3-(phenylthio)ferrocene (3u-I, racemic mixture). The general procedure from 1-fluoro-2-(phenylthio)ferrocene (2u; 0.31 g) and using iodine (0.30 g) in THF (3 mL) (followed by washing with 3 x 10 mL of an aqueous Na₂S₂O₃ solution) gave 3u-I (eluent: petroleum ether; Rₓ = 0.26) in a quantitative yield (0.44 g) as a yellow powder: mp 73 °C; IR (ATR) 664, 687, 736, 805, 826, 838, 877, 1001, 1024, 1082, 1108, 1132, 1226, 1411, 1440, 1479, 1584 cm⁻¹; ¹H NMR (CDCl₃) δ 4.26 (dd, 1H, J = 2.7 and 1.0 Hz, H₄), 4.32 (dd, 1H, J = 2.8 and 1.2 Hz, H₅), 4.33 (s, 5H, Cp), 7.10-7.24 (m, 5H, Ph); ¹³C NMR (CDCl₃) δ 28.5 (d, C, J = 20.5 Hz, C₁), 64.5 (d, C, J = 16.5 Hz, C₃), 68.4 (CH, C₅), 69.5 (CH, C₄), 126.1 (CH, C₄’), 127.3 (2CH), 129.0 (2CH), 136.4 (d, C, J = 274 Hz, C₂), 138.2 (C, C₁’); ¹⁹F NMR (CDCl₃) δ -186.0. Crystal data for 3u-I. C₁₆H₁₂FFeIS, M = 438.07, T = 150(2) K, triclinic, P -1, a = 7.2000(7), b = 10.0755(11), c = 11.5617(11) Å, α = 64.721(3), β = 78.205(3), γ = 84.196(4)°, V = 742.31(13) Å³, Z = 2, d = 1.960 g cm⁻³, μ = 3.232 mm⁻¹. A final refinement on F² with 3378 unique intensities and 181 parameters converged at ωR(F²) = 0.0488 (R(F) = 0.0205) for 3214 observed reflections with I > 2σ(I). CCDC 1939213.

2-Fluoro-1,3-diiodoferrocene (3r-I). To a stirred, cooled (-40 °C) solution of ZnCl₂·TMEDA (0.25 g, 1.0 mmol) and 1-fluoro-2-iodoferrocene (0.33 g, 1.0 mmol) in THF (3 mL) was added dropwise a cooled (-40 °C) solution of LiTMP (prepared at -10 °C by adding BuLi (~1.6 M in hexanes, 1.5 mmol) to a solution of 2,2,6,6-tetramethylpiperidine (0.29 mL, 1.7 mmol) in THF (3 mL) and stirring for 5 min). After 2 h at this temperature, a solution of I₂ (0.375 g, 1.5 mmol) in THF (4 mL) was added. The mixture was stirred overnight before addition of an aqueous saturated solution of Na₂S₂O₃ (10 mL) and extraction with AcOEt (3 x 20 mL). The combined organic layers were dried over MgSO₄, and concentrated under reduced pressure. The crude product was purified by chromatography over silica gel (eluent: petroleum ether; Rₓ = 0.45) to give 3r-I in a quantitative yield (0.46 g) as an orange powder: mp 61-62 °C; IR (ATR) 809, 822, 864, 976, 1001, 1107, 1410, 1436, 1458, 3096 cm⁻¹; ¹H NMR (CDCl₃) δ 4.25 (d, 2H, J = 0.8 Hz), 4.26 (s, 5H, Cp); ¹³C NMR (CDCl₃) δ
26.7 (d, 2C, J = 21.2 Hz, C1 and C3), 68.6 (2CH, C4 and C5), 75.3 (5CH, Cp), 135.1 (d, C, J = 271 Hz, C2); \(^{19}\)F NMR (CDCl\(_3\)) \(\delta\) -184.8. **Crystal data for 3r-I.** \(\text{C}_{10}\text{H}_7\text{FFeI}_2\), \(M = 455.81\), \(T = 150(2)\) K, monoclinic, \(P 2_1/c\), \(a = 12.2100(9)\), \(b = 28.6668(18)\), \(c = 6.6319(5)\) Å, \(\beta = 100.875(3)\) °, \(V = 2279.6(3)\) Å\(^3\), \(Z = 8\), \(d = 2.656\) g cm\(^{-3}\), \(\mu = 6.710\) mm\(^{-1}\). A final refinement on \(F^2\) with 5220 unique intensities and 229 parameters converged at \(\omega R(F^2) = 0.0683\) (\(R(F) = 0.0334\)) for 4893 observed reflections with \(I > 2\sigma(I)\). CCDC 1939214.

**General procedure 2.** To a stirred, cooled (0 °C) solution of 2,2,6,6-tetramethylpiperidine (0.19 mL, 1.1 mmol) in THF (2 mL) was added BuLi (−1.6 M in hexane, 1.1 mmol). The mixture was stirred for 5 min at 0 °C before introduction of the required halogenoferrocene (1.0 mmol) at -50 °C. After 2 h at -50 °C, the required electrophile (either pure or in solution, as indicated in the product description; 1.1 mmol) was added. Unless otherwise specified in the product description, the temperature was raised to room temperature before addition of water (20 mL). Extraction with AcOEt (3 x 20 mL), drying over MgSO\(_4\), concentration under reduced pressure, and purification by column chromatography over silica gel (the eluent is given in the product description) led to the expected product.

4-Bromo-1-fluoro-2-(trimethylsilyl)ferrocene (4s-Br, racemic mixture). The general procedure 2 from 1-bromo-2-fluoro-3-(trimethylsilyl)ferrocene (3s-Br; 0.355 g) and using methanol (0.5 mL) gave 4s-Br (eluent: petroleum ether; \(R_f = 0.69\)) in 63% yield (0.22 g) as a yellow ochre powder: mp 39-41 °C; IR (ATR) 667, 696, 755, 815, 838, 881, 1002, 1024, 1061, 1107, 1133, 1229, 1248, 1322, 1344, 1360, 1411, 1427, 1707, 1786, 2957, 3111 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 0.29 (s, 9H, Me), 3.97 (s, 1H, H3), 4.29 (s, 5H, Cp), 4.72 (s, 1H, H5); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) -0.28 (3CH\(_3\)), 59.7 (d, C, \(J = 21.4\) Hz, C2), 60.7 (d, C, \(J = 17.5\) Hz, C5), 67.8 (CH, C3), 72.2 (5CH, Cp), 73.7 (d, C, \(J = 3.4\) Hz, C4), 137.3 (d, C, \(J = 272\) Hz, C1); \(^{19}\)F NMR (CDCl\(_3\)) \(\delta\) -180.8. **Crystal data for 4s-Br.** \(\text{C}_{13}\text{H}_{16}\text{BrFFeSi}\), \(M = 355.11\), \(T = 295(2)\) K, monoclinic, \(P 2_1/c\), \(a = 19.502(3)\), \(b = 11.7498(14)\), \(c = 13.2300(18)\) Å, \(\beta = 107.235(5)\) °, \(V = 2895.5(7)\) Å\(^3\), \(Z = 8\), \(d = 1.629\) g cm\(^{-3}\), \(\mu = 3.871\) mm\(^{-1}\). A final
refinement on $F^2$ with 6623 unique intensities and 313 parameters converged at $oR(F^2) = 0.0767 (R(F) = 0.0352$) for 4636 observed reflections with $I > 2\sigma(I)$. CCDC 1939215.

1-Fluoro-2,4-diiodoferocene (4r-I, racemic mixture). The general procedure 2, but using 2,2,6,6-tetramethylpiperidine (0.37 mL, 2.2 mmol) and butyllithium (2.2 mmol), from 2-fluoro-1,3-diiodoferrocene (3r-I; 0.46 g) and using methanol (0.5 mL) gave 4r-I (eluent: petroleum ether; $R_f$ (petroleum ether) = 0.46) in 90% yield (0.41 g) as a yellow powder: mp 95-96 °C; IR (ATR) 658, 815, 830, 861, 978, 1000, 1052, 1105, 1344, 1409, 1444, 1617, 1789, 2918, 3090, 3102 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.29 (s, 5H, Cp), 4.44 (s, 1H, H3), 4.70 (d, 1H, $J = 3.5$ Hz, H5); $^{13}$C NMR (CDCl$_3$) $\delta$ 28.6 (d, C, $J = 21.2$ Hz, C2), 33.9 (C, C4), 62.1 (d, CH, $J = 14.9$ Hz, C5), 73.3 (CH, C3), 75.5 (5CH, Cp), 134.8 (d, C, $J = 277$ Hz, C1); $^{19}$F NMR (CDCl$_3$) $\delta$ -183.8. Anal. Calcd for C$_{10}$H$_7$FFeI$_2$ (455.82): C, 26.35; H, 1.55. Found: C, 26.38; H, 1.68.

2,4-Dichloro-3-fluoroferrocenecarboxaldehyde (5p-Cl, racemic mixture). The general procedure 2 from 1,3-dichloro-2-fluoroferrocene (3p-Cl; 0.27 g) and using dimethylformamide (85 μL) gave 5p-Cl (eluent: petroleum ether-Et$_3$N 98:2 then petroleum ether-AcOEt-Et$_3$N 97:1:2) in 80% yield (0.24 g) as an unstable reddish oil: $^1$H NMR (CDCl$_3$) $\delta$ 4.46 (s, 5H, Cp), 4.89 (s, 1H, H5), 10.07 (s, 1H, CHO); $^{13}$C NMR (CDCl$_3$) $\delta$ 58.9 (CH, C5), 65.4 (C, C1, C-CHO), 75.5 (5CH, Cp), 81.4 (d, C, $J = 13.6$ Hz, C2), 82.0 (d, C, $J = 14.2$ Hz, C4), 128.6 (d, C, $J = 280$ Hz, C3), 190.9 (CH, CHO); $^{19}$F NMR (CDCl$_3$) $\delta$ -188.7.
α-(2-Methoxyphenyl)-2-fluoro-5-iodo-3-(trimethylsilyl)ferrocenemethanol (5s-I-2, mixture of stereoisomers). The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using 2-anisaldehyde (0.14 mL) gave 5s-I-2 (eluent: petroleum ether-AcOEt 90:10; R_f = 0.21) in 48% yield (0.26 g) as an orange powder: mp 130 °C; IR (ATR) 658, 700, 729, 747, 778, 817, 839, 945, 1018, 1030, 1050, 1088, 1108, 1130, 1160, 1183, 1214, 1253, 1282, 1314, 1340, 1414, 1442, 1460, 1491, 1600, 2924, 3549 cm^{-1}; ^1H NMR (CDCl_3) δ 0.30 (s, 9H, Me), 3.31 (dd, 1H, J = 7.1 and 2.1 Hz, OH), 3.87 (s, 3H, OMe), 3.99 (d, 1H, J = 1.6 Hz, H4), 4.37 (s, 5H, Cp), 5.83 (d, 1H, J = 6.9 Hz, CHO), 6.86-6.92 (m, 2H), 7.22-7.28 (m, 2H); ^13C NMR (CDCl_3) δ 0.25 (3CH_3), 40.9 (C, C5), 55.4 (d, CH_3, J = 2.4 Hz), 61.5 (d, C, J = 22.4 Hz, C3), 70.0 (CH, CHO), 71.0 (dd, CH, J = 6.8 and 2.3 Hz, C4), 73.5 (5CH, Cp), 81.2 (d, C, J = 9.9 Hz, C1), 110.8 (CH), 120.7 (CH), 128.7 (CH), 129.3 (CH), 130.3 (C, C1'), 135.3 (d, C, J = 275 Hz, C2), 157.1 (C, C2'); ^19F NMR (CDCl_3) δ -179.9. Only traces of the minor diastereoisomer were detected. Crystal data for 5s-I-2. C_{21}H_{24}FFeO_2Si, M = 538.24, T = 150(2) K, triclinic, P-1, a = 8.514(2), b = 10.875(3), c = 11.472(3) Å, α = 86.069(8), β = 84.834(9), γ = 82.271(8) °, V = 1046.7(4) Å^3, Z = 2, d = 1.708 g cm^{-3}, μ = 2.274 mm^{-1}. A final refinement on F^2 with 4783 unique intensities and 224 parameters converged at ωR(F^2) = 0.0582 (R(F) = 0.0253) for 4469 observed reflections with I > 2σ(I). CCDC 1939216.

2-Fluoro-5-iodo-α,α-diphenyl-3-(trimethylsilyl)ferrocenemethanol (5s-I-3, racemic mixture). The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using benzophenone (0.20 g) gave 5s-I-3 (eluent: petroleum ether-AcOEt-Et_3N 96:3:1; R_f (petroleum ether-Et_3O 90:10) = 0.54) in 66% yield (0.39 g) as a yellow powder: mp 147-150 °C (deg.); IR (ATR) 695, 756, 814, 840, 859, 966, 1016, 1232, 1247, 1375, 1400, 1428, 1447, 1491, 2953, 3539 cm^{-1}; ^1H NMR (CDCl_3) δ 0.26 (s, 9H, Me), 3.79 (d, 1H, J = 1.2 Hz, OH), 4.14 (d, 1H, J = 2.0 Hz, H4), 4.43 (s,
5H, Cp), 7.20-7.33 (m, 8H), 7.40-7.43 (m, 2H); ^1^H NMR (CDCl$_3$) δ -0.30 (3CH$_3$), 40.3 (C, C5), 61.7 (d, C, J = 23.6 Hz, C3), 72.4 (d, CH, J = 7.2 Hz, C4), 73.6 (5CH, Cp), 78.2 (d, C, J = 4.3 Hz), 85.9 (d, C, J = 7.7 Hz, C1), 127.3 (CH), 127.4 (2CH), 127.5 (CH), 127.9 (2CH), 128.0 (CH), 128.0 (CH), 128.3 (2CH), 135.5 (d, C, J = 278 Hz, C2), 145.1 (d, C, J = 2.3 Hz), 146.2 (C); ^1^F NMR (CDCl$_3$) δ -174.5.

**Crystal data for 5s-I-3.** C$_{26}$H$_{26}$FFeIos, $M = 584.31$, $T = 150(2)$ K, triclinic, $P\overline{1}$, $a = 8.1302(13)$, $b = 10.5516(14)$, $c = 14.7688(19)$ Å, $α = 107.406(4)$, $β = 93.634(5)$, $γ = 98.033(5)$ °, $V = 1189.6(3)$ Å$^3$, $Z = 2$, $d = 1.631$ g cm$^{-3}$, $μ = 2.006$ mm$^{-1}$. A final refinement on $F^2$ with 5440 unique intensities and 286 parameters converged at $ωR(F^2) = 0.0556$ ($R(F) = 0.0231$) for 4916 observed reflections with $I > 2σ(I)$. CCDC 1939217.

$$
\begin{array}{c}
\text{OHC} \\
\text{1} \\
\text{2} \\
\text{3} \\
\text{4} \\
\text{SiMe$_3$} \\
\text{Fe} \\
\end{array}
$$

**2-Fluoro-5-iodo-3-(trimethylsilyl)ferrocenecarboxaldehyde (5s-I-4, racemic mixture).** The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using dimethylformamide (85 μL) gave 5s-I-4 (eluent: petroleum ether-Et$_2$O 95:5; $R_f$ (petroleum ether-Et$_2$O 90:10) = 0.37) in 60% yield (0.26 g) as a red powder: mp 72 °C; IR (ATR) 699, 752, 820, 839, 949, 1108, 1148, 1231, 1249, 1306, 1362, 1421, 1439, 1681, 2843, 2896, 2953 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 0.30 (s, 9H, Me), 4.32 (s, 5H, Cp), 4.38 (d, 1H, $J = 1.9$ Hz, H4), 10.17 (s, 1H, CHO); $^1^C$NMR (CDCl$_3$) δ -0.58 (3CH$_3$), 36.6 (C, C5), 66.1 (d, C, $J = 8.6$ Hz, C1), 67.1 (d, C, $J = 19.8$ Hz, C3), 74.1 (5CH, Cp), 75.8 (dd, CH, $J = 6.8$ and 1.7 Hz, C4), 138.0 (d, C, $J = 284$ Hz, C2), 192.3 (d, CH, $J = 3.0$ Hz, CHO); $^1^F$NMR (CDCl$_3$) δ -179.9. **Crystal data for 5s-I-4.** C$_{14}$H$_{16}$FFeIos, $M = 430.11$, $T = 150(2)$ K, monoclinic, $P 2_1/n$, $a = 6.7234(5)$, $b = 12.3647(9)$, $c = 18.5635(14)$ Å, $β = 91.338(3)$ °, $V = 1542.8(2)$ Å$^3$, $Z = 4$, $d = 1.852$ g cm$^{-3}$, $μ = 3.055$ mm$^{-1}$. A final refinement on $F^2$ with 3483 unique intensities and 167 parameters converged at $ωR(F^2) = 0.0729$ ($R(F) = 0.0382$) for 2948 observed reflections with $I > 2σ(I)$. CCDC 1939218.
2-Fluoro-5-iodo-3-(trimethylsilyl)ferrocenecarboxylic acid (5s-I-5, racemic mixture). The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using gaseous carbon dioxide (in excess) gave 5s-I-5 (eluent: petroleum ether-AcOEt-Et3N 96:3:1; Rf (AcOEt-petroleum ether 70:30) = 0.29) in 59% yield (0.53 g) as a dark orange powder: mp 168 °C (deg.); IR (ATR) 732, 818, 837, 943, 1078, 1212, 1250, 1405, 1465, 1680, 2957 cm⁻¹; ¹H NMR (CDCl₃) δ 0.32 (s, 9H, Me), 4.34 (s, 5H, Cp), 4.36 (d, 1H, J = 1.9 Hz, H₄), 10.65 (br s, 1H, OH); ¹³C NMR (CDCl₃) δ -0.54 (3CH₃), 37.5 (C, C₅), 60.6 (d, C, J = 9.4 Hz, C₁), 66.5 (d, C, J = 21.2 Hz, C₃), 74.7 (5CH, Cp), 76.1 (d, CH, J = 6.4 Hz, C₄), 137.25 (d, C, J = 283.5 Hz, C₂), 175.45 (C, C=O); ¹⁹F NMR (CDCl₃) δ -173.2. 

Crystal data for 5s-I-5. C₁₄H₁₆FFeIO₂Si, M = 446.11, T = 150(2) K, monoclinic, P 2₁/n, a = 6.7304(10), b = 13.738(3), c = 17.564(3) Å, β = 100.433(5) °, V = 1597.2(5) Å³, Z = 4, d = 1.855 g cm⁻³, μ = 2.960 mm⁻¹. A final refinement on F² with 3654 unique intensities and 164 parameters converged at ωR(F²) = 0.0799 (R(F) = 0.0322) for 3385 observed reflections with I > 2σ(I). CCDC 1939219.

2-Fluoro-5-iodo-N,N-dimethyl-3-(trimethylsilyl)ferrocenecarboxamide (5s-I-6, racemic mixture). The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using ClCONMe₂ (0.10 mL) gave 5s-I-6 (eluent: petroleum ether-Et₃N 99:1; Rf (petroleum ether-AcOEt 80:20) = 0.51) in 22% yield (0.10 g) as a yellow powder: mp 70 °C; IR (ATR) 679, 697, 756, 780, 818, 840, 880, 960, 1003, 1060, 1107, 1158, 1226, 1248, 1314, 1392, 1429, 1452, 1499, 1644, 1698, 1779, 2954 cm⁻¹; ¹H NMR (CDCl₃) δ 0.29 (s, 9H, Me), 2.85 (s, 3H, Me), 3.08 (s, 3H, Me), 4.04 (d, 1H, J = 1.4 Hz, H₄), 4.39 (s, 5H, Cp); ¹³C NMR (CDCl₃) δ -0.31 (3CH₃), 35.6 (CH₃), 38.2 (d, C, J = 1.1 Hz, C₅), 38.3 (CH₃), 60.9 (d, C, J = 21.4 Hz, C₁), 71.4 (d, CH, J = 5.3 Hz, C₄), 74.5 (5CH, Cp), 78.8 (d, C, J = 15.5 Hz, C₃), 134.9 (d, C, J = 275 Hz, C₂), 165.2 (d, C, J = 3.4 Hz, C=O); ¹⁹F NMR
(CDCl₃) δ -179.1. Anal. Calcd for C₁₆H₂₁FFeINOSi (473.18): C, 40.61; H, 4.47. Found: C, 40.73; H, 4.59.

2-(Diphenylphosphino)-3-fluoro-1-iodo-4-(trimethylsilyl)ferrocene (5s-I-7, racemic mixture). The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using chlorodiphenylphosphine (0.20 mL) gave 5s-I-7 (eluent: petroleum ether-Et₂O-Et₃N 96:3:1; Rf (petroleum ether-AcOEt 90:10) = 0.77) in 80% yield (0.47 g) as a yellow powder: mp 180 °C; IR (ATR) 693, 745, 760, 812, 840, 911, 1003, 1025, 1062, 1107, 1223, 1247, 1283, 1344, 1380, 1407, 1435, 1477, 1585, 2956, 3063 cm⁻¹; ¹H NMR (CDCl₃) δ 0.26 (s, 9H, Me), 4.11 (s, 5H, Cp), 4.27 (d, 1H, J = 1.8 Hz, H₅), 7.17-7.33 (m, 5H), 7.34-7.43 (m, 3H), 7.74 (t, 2H, J = 5.8 Hz); ¹³C NMR (CDCl₃) δ 0.28 (3CH₃), 49.1 (dd, C, J = 42.9 and 1.9 Hz), 63.9 (d, C, J = 23.4 Hz, C4), 68.3 (t, C, J = 15.9 Hz), 73.5 (5CH, Cp), 74.3 (dd, CH, J = 6.1 and 3.1 Hz, C5), 128.0 (CH), 128.1 (CH), 128.1 (CH), 128.3 (CH), 128.4 (CH), 129.5 (CH), 132.0 (CH), 132.2 (CH), 135.7 (d, C, J = 8.5 and 0.98 Hz), 136.0 (d, CH, J = 3.5 Hz), 136.3 (d, CH, J = 3.5 Hz), 138.0 (d, C, J = 8.2 Hz), 137.7 (d, C, J = 270 Hz, C3); ¹⁹F NMR (CDCl₃) δ -172.6 (d, J = 2.9 Hz); ³¹P NMR (CDCl₃) δ -11.3 (d, J = 3.3 Hz). Crystal data for the oxide of 5s-I-7. C₂₅H₂₅FFeIOPSi, M = 602.26, T = 150(2) K, triclinic, P -1, α = 8.1007(10), b = 10.7372(15), c = 14.989(2) Å, α = 108.190(5), β = 93.055(4), γ = 97.786(4) °, V = 1220.8(3) Å³, Z = 2, d = 1.638 g cm⁻³, μ = 2.020 mm⁻¹. A final refinement on F² with 5533 unique intensities and 283 parameters converged at ωR(F²) = 0.0669 (R(F) = 0.0293) for 4738 observed reflections with I > 2σ(I). CCDC 1939220.

3-Fluoro-1-iodo-2-(phenylthio)-4-(trimethylsilyl)ferrocene (5s-I-8, racemic mixture). The general procedure 2 from 2-fluoro-1-iodo-3-(trimethylsilyl)ferrocene (3s-I; 0.40 g) and using phenyl disulfide (0.24 g) gave 5s-I-8 (eluent: petroleum ether), but it proved difficult to isolate and was only
identified by NMR: $^1$H NMR (CDCl$_3$) δ 0.33 (s, 9H, Me), 4.29 (d, 1H, $J = 1.9$ Hz, H5), 4.30 (s, 5H, Cp), 7.11-7.25 (m, 5H); $^{13}$C NMR (CDCl$_3$) δ -0.39 (3CH$_3$), 49.6 (C, C1), 63.1 (d, C, $J = 21.3$ Hz, C2), 71.1 (d, C, $J = 17.2$ Hz, C4), 72.5 (d, CH, $J = 5.8$ Hz, C5), 74.2 (5CH, Cp), 126.1 (CH, C4'), 127.6 (2CH), 129.0 (2CH), 137.7 (C, C1'), 138.2 (d, C, $J = 276$ Hz, C3); $^{19}$F NMR (CDCl$_3$) δ -177.1.

**General procedure 3.** TBAF (1.0 M solution in THF, 0.70 mL, 0.70 mmol, 2.5 equiv) was added to a solution of the silane (0.27 mmol, 1.0 equiv) in THF (4.5 mL) at room temperature, and the reaction mixture was stirred for 30 min. Volatiles were removed under vacuum to give the crude product. It was purified by column chromatography on silica (the eluent is given in the product description).

1-Fluoro-3-iodoferrocene (6s-I, racemic mixture). The general procedure 3 from 1-fluoro-4-iodo-2-(trimethylsilyl)ferrocene (4s-I; 0.11 g) gave 6s-I (eluent: petroleum ether; $R_f = 0.58$) in 91% yield (80 mg) as an orange oil: IR (ATR) 811, 863, 938, 1001, 1023, 1052, 1106, 1171, 1250, 1322, 1347, 1364, 1392, 1410, 1463, 2104, 2703, 2924, 3106 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 4.11 (s, 1H, H4), 4.29 (s, 5H, Cp), 4.36 (s, 1H, H5), 4.61 (t, 1H, $J = 1.2$ Hz, H2); $^{13}$C NMR (CDCl$_3$) δ 33.6 (d, C, $J = 2.7$ Hz, C3), 57.3 (d, CH, $J = 15.7$ Hz, C5), 62.7 (d, CH, $J = 14.5$ Hz, C2), 67.6 (d, CH, $J = 3.3$ Hz, C4), 72.6 (5CH, Cp), 134.7 (d, C, $J = 274.5$ Hz, C1); $^{19}$F NMR (CDCl$_3$) δ -186.0. MS (EI, 70 eV): 330 [M]. Anal. Calcd for C$_{10}$H$_8$FFeI (329.92): C, 36.41; H, 2.44. Found: C, 36.44; H, 2.40.

1-Bromo-3-fluoroferrocene (6s-Br, racemic mixture). The general procedure 3 from 4-bromo-1-fluoro-2-(trimethylsilyl)ferrocene (4s-Br; 96 mg) gave 6s-Br (eluent: petroleum ether; $R_f = 0.51$) in 76% yield (58 mg) as a yellow powder: mp 31 °C; IR (ATR) 806, 826, 849, 869, 940, 1001, 1020, 1059, 1105, 1253, 1347, 1366, 1409, 1465, 1672, 1794, 2105, 2249, 3113 cm$^{-1}$; $^1$H NMR
(CDCl$_3$) $\delta$ 4.11 (s, 1H, H5), 4.30 (s, 1H, H4), 4.33 (s, 5H, Cp), 4.63 (s, 1H, H2); $^{13}$C NMR (CDCl$_3$) $\delta$ 55.5 (d, CH, $J = 15.7$ Hz, C4), 58.9 (d, CH, $J = 15.1$ Hz, C2), 63.3 (d, CH, $J = 2.9$ Hz, C5), 72.0 (d, C, $J = 3.6$ Hz, C1), 72.2 (5CH, Cp), 133.4 (d, C, $J = 274$ Hz, C3); $^{19}$F NMR (CDCl$_3$) $\delta$ -186.9. MS (EI, 70 eV): 282 [M]. Anal. Calcd for C$_{10}$H$_8$BrFFe (282.92): C, 42.45; H, 2.85. Found: C, 42.53; H, 2.97.

1-Chloro-3-iodoferrocene (6s'-I, racemic mixture). The general procedure 3 from 1-chloro-4-iodo-2-(trimethylsilyl)ferrocene (4s'-I; 0.11 g) gave 6s'-I (eluent: petroleum ether; $R_f = 0.53$) in a quantitative yield (94 mg) as an orange oil: IR (ATR) 823, 867, 890, 1002, 1028, 1107, 1194, 1338, 1362, 1404, 3105 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.26 (s, 5H, Cp), 4.34 (dd, 1H, $J = 2.4$ and 1.3 Hz, H4), 4.41 (dd, 1H, $J = 2.4$ and 1.3 Hz, H5), 4.67 (t, 1H, $J = 1.3$ Hz, H2); $^{13}$C NMR (CDCl$_3$) $\delta$ 37.0 (C, C3), 68.9 (CH, C5), 72.7 (CH, C4), 73.5 (5CH, Cp), 74.0 (CH, C2), 92.5 (C, C1). MS (EI, 70 eV): 346 [M]. The analyses are as described previously.[2]

2-Fluoro-4-iodo-1-(phenylthio)-3-(trimethylsilyl)ferrocene (5u-I, racemic mixture). The general procedure 2 from 2-fluoro-1-iodo-3-(phenylthio)ferrocene (3u-I; 0.44 g) and using chlorotrimethylsilane (0.14 mL) gave 5u-I (eluent: petroleum ether; $R_f$ (petroleum ether-AcOEt 95:5) = 0.70) in 45% yield (0.23 g) as a yellow powder: mp 80 $^\circ$C; IR (ATR) 690, 739, 818, 841, 923, 1026, 1105, 1246, 1345, 1383, 1402, 1439, 1478, 1580, 2896, 2955, 3103 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 4.33 (s, 5H, Cp), 4.62 (d, 1H, $J = 0.6$ Hz, H5), 7.11-7.25 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 0.45 (d, 9H, $J = 0.9$ Hz, Me), 4.33 (s, 5H, Cp), 4.62 (d, 1H, $J = 0.6$ Hz, H5), 7.11-7.25 (m, 5H); $^{13}$C NMR (CDCl$_3$) $\delta$ 0.58 (d, 3CH$_3$, $J = 2.0$ Hz), 40.7 (d, C, $J = 5.0$ Hz, C4), 64.0 (d, C, $J = 17.5$ Hz, C3), 67.8 (d, C, $J = 19.2$ Hz, C1), 74.0 (5CH, Cp), 78.0 (CH, C5), 126.2 (CH, C4'), 127.7 (2CH), 129.0 (2CH), 138.0 (C, C1'), 139.6 (d, C, $J = 277$ Hz, C2); $^{19}$F NMR (CDCl$_3$) $\delta$ -178.0. Crystal data for 5u-I. C$_{19}$H$_{20}$FFeISSi, $M = 510.25$, $T = 150(2)$ K, monoclinic, $P 2_1/c$, $a = 8.8626(14)$, $b = 11.0153(19)$, $c =
20.456(3) Å, $\beta = 98.537(5)$°, $V = 1974.8(5)$ Å$^3$, $Z = 4$, $d = 1.716$ g cm$^{-3}$, $\mu = 2.500$ mm$^{-1}$. A final refinement on $F^2$ with 4517 unique intensities and 220 parameters converged at $\omega R(F^2) = 0.0765$ ($R(F) = 0.0345$) for 4140 observed reflections with $I > 2\sigma(I)$. CCDC 1939221.

3-Fluoro-5-iodo-2-(phenylthio)-4-(trimethylsilyl)ferrocencarboxaldehyde (7u-I, racemic mixture). The general procedure 2 from 2-fluoro-4-iodo-1-(phenylthio)-3-(trimethylsilyl)ferrocene (5u-I; 0.51 g) and using dimethylformamide (85 µL) gave 7u-I (eluent: petroleum ether-AcOEt 90:10; $R_f$ (petroleum ether-AcOEt 70:30) = 0.79) in 64% yield (0.34 g) as a red powder: mp 143-145 °C; IR (ATR) 665, 692, 754, 824, 838, 854, 1005, 1028, 1065, 1109, 1249, 1261, 1302, 1366, 1377, 1400, 1440, 1474, 1689, 2749, 2853, 2924, 2952 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 0.52 (d, 9H, $J = 1.2$ Hz, Me), 4.43 (s, 5H, Cp), 7.18-7.29 (m, 5H, Ph), 10.29 (s, 1H, CHO); $^{13}$C NMR (CDCl$_3$) $\delta$ 0.65 (d, 3CH$_3$, $J = 2.3$ Hz), 41.2 (d, C, $J = 4.4$ Hz, C5), 69.9 (d, C, $J = 19.0$ Hz, C2 or C4), 70.1 (d, C, $J = 17.9$ Hz, C2 or C4), 72.3 (C, C1), 75.4 (5CH, Cp), 126.9 (CH, C4’), 128.6 (2CH, Ph), 129.2 (2CH, Ph), 136.9 (C, C1’), 141.7 (d, C, $J = 280$ Hz, C3), 194.3 (CH, CHO); $^{19}$F NMR (CDCl$_3$) $\delta$ -169.6. Crystal data for 7u-I.

$^{C_20H_{20}}$F$^2$Fe$^{11}$O$^1$Si, $M = 538.26$, $T = 150(2)$ K, triclinic, $P - 1$, $a = 7.1480(8)$, $b = 9.9469(13)$, $c = 15.3417(19)$ Å, $\alpha = 108.069(4)$, $\beta = 97.069(4)$, $\gamma = 91.763(4)$°, $V = 1026.4(2)$ Å$^3$, $Z = 2$, $d = 1.742$ g cm$^{-3}$, $\mu = 2.414$ mm$^{-1}$. A final refinement on $F^2$ with 4696 unique intensities and 248 parameters converged at $\omega R(F^2) = 0.0653$ ($R(F) = 0.0238$) for 4228 observed reflections with $I > 2\sigma(I)$. CCDC 1939222.
1- Allyl-2-fluoroferrrocene (2b, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
NOESY (300 MHz, CDCl₃)
1-(Dimethylaminomethyl)-2-fluoroferrrocene (2c, racemic mixture).

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)

COSY (500 MHz, CDCl$_3$)
HSQC (500 MHz, CDCl₃)
1-Fluoro-2-(2-pyridyl)ferrocene (2d, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
2-Fluoroferroceneboronic acid, pinacol boronate (2e, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

$^{11}$B NMR (96 MHz, CDCl$_3$)
COSY (300 MHz, CDCl₃)

HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
2-Fluoro-N-phenylferrocenecarboxamide (2n, racemic mixture).

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (471 MHz, CDCl$_3$)

COSY (500 MHz, CDCl$_3$)
HSQC (500 MHz, CDCl$_3$)
1-Fluoro-2-(tributylstanny)ferrocene (2v, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}\text{F NMR (282 MHz, CDCl}_3\text{)}$

$\text{COSY (300 MHz, CDCl}_3\text{)}$
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
1,3-Dichloro-2-fluoroferrrocene (3p-Cl).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
1-Bromo-2-fluoro-3-chloroferrocene (3p-Br, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)
1-Chloro-2-fluoro-3-iodoferrocene (3p-I, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl$_3$)

HMBC (300 MHz, CDCl$_3$)
1-Bromo-2-fluoro-3-(trimethylsilyl)ferrocene (3s-Br, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
*N,N*-Dimethyl-2-fluoro-3-(phenylthio)ferrocene (3u-CONMe₂, racemic mixture).

**\(^1\)H NMR (300 MHz, CDCl₃)**

![1H NMR spectrum](image)

**\(^{13}\)C NMR (75 MHz, CDCl₃)**

![13C NMR spectrum](image)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
2-Fluoro-1-ido-3-(phenylthio)ferrocene (3u-I, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl$_3$)

HMBC (300 MHz, CDCl$_3$)
2-Fluoro-1,3-diiodoferrocene (3r-I).

$^1$H NMR (500 MHz, CDCl$_3$)

$^{13}$C NMR (126 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
4-Bromo-1-fluoro-2-(trimethylsilyl)ferrocene (4s-Br, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl$_3$)
1-Fluoro-2,4-diiodoferrocene (4r-I, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
2,4-Dichloro-3-fluoroferrocenecarboxaldehyde (5p-Cl, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
α-(2-Methoxyphenyl)-2-fluoro-5-iodo-3-(trimethylsilyl)ferrocenemethanol (5s-I-2, mixture of stereoisomers).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
$\alpha,\alpha$-Diphenyl-2-fluoro-5-iodo-3-(trimethylsilyl)ferrocenemethanol (5s-I-3, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl$_3$)

HMBC (300 MHz, CDCl$_3$)
2-Fluoro-5-iodo-3-((trimethylsilyl)ferrocenecarboxaldehyde (5s-I-4, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
\(^{19}\text{F} \text{NMR} \ (282 \text{ MHz, CDCl}_3)\)

\(\text{COSY} \ (300 \text{ MHz, CDCl}_3)\)
**HSQC (300 MHz, CDCl₃)**

**HMBC (300 MHz, CDCl₃)**
2-Fluoro-5-iodo-3-(trimethylsilyl)ferrocenecarboxylic acid (5s-I-5, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
$N,N$-Dimethyl-2-fluoro-5-iodo-3-(trimethylsilyl)ferrocenecarboxamide (5s-I-6, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
2-(Diphenylphosphino)-3-fluoro-1-iodo-4-(trimethylsilyl)ferrocene (5s-I-7, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}F$ NMR (282 MHz, CDCl$_3$)

$^{31}P$ NMR (121 MHz, CDCl$_3$)
COSY (300 MHz, CDCl₃)

HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl$_3$)
3-Fluoro-1-iodo-2-(phenylthio)-4-(trimethylsilyl)ferrocene (5s-I-8, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}\text{F NMR (282 MHz, CDCl}_3\text{)}$

$\text{COSY (300 MHz, CDCl}_3\text{)}$
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
1-Fluoro-3-iodoferrocene (6s-I, racemic mixture).

$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100 MHz, CDCl$_3$)
$^{19}$F NMR (376 MHz, CDCl$_3$)

COSY (400 MHz, CDCl$_3$)
HSQC (400 MHz, CDCl₃)

HMBC (400 MHz, CDCl₃)
1-Bromo-3-fluoroferroocene (6s-Br, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)
1-Chloro-3-iodoferrocene (6s'-I, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^{13}$C NMR (75 MHz, CDCl$_3$)
COSY (300 MHz, CDCl₃)

HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)
2-Fluoro-4-iodo-1-(phenylthio)-3-(trimethylsilyl)ferrocene (5u-I, racemic mixture).

\(^1\)H NMR (300 MHz, CDCl\(_3\))

![1H NMR spectrum]

\(^{13}\)C NMR (75 MHz, CDCl\(_3\))

![13C NMR spectrum]
$^{19}$F NMR (282 MHz, CDCl$_3$)

COSY (300 MHz, CDCl$_3$)
HSQC (300 MHz, CDCl₃)

HMBC (300 MHz, CDCl₃)
3-Fluoro-5-iodo-2-(phenylthio)-4-(trimethylsilyl)ferrocenecarboxaldehyde (7u-I, racemic mixture).

$^1$H NMR (300 MHz, CDCl$_3$)

$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (126 MHz, CDCl$_3$)

$^{19}$F NMR (282 MHz, CDCl$_3$)
COSY (300 MHz, CDCl₃)

HSQC (300 MHz, CDCl₃)
HMBC (300 MHz, CDCl₃)

NOESY (300 MHz, CDCl₃)
References


