Supporting Information

1,2-Disubstituted Ferrocenyl Carbohydrate Chloroquine Conjugates as Potential Antimalarial Agents

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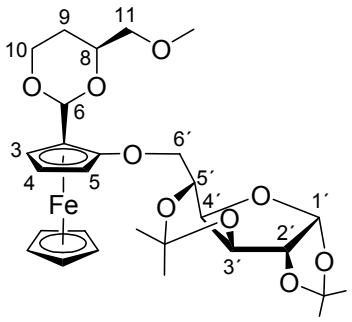
I. Experimental

(2*S*,4*S*,*Sp*)-(+)-1-[6-(1,2;3,5-Diisopropylidene)-α-D-glucofuranosidyl]-2-(4-methoxy-methyl-1,3-dioxan-2-yl)ferrocene (8)

(2*S*,4*S*,*Sp*)-1-Acetoxy-2-(4-methoxymethyl-1,3-dioxan-2-yl) ferrocene (**5**, 1020 mg, 2.72 mmol, 1 eq.) was dissolved in 100 mL dry DMF and sodium methoxide (162 mg, 3.00 mmol, 1.1 eq.) was added at room temperature. After two hours of stirring at room temperature, a solution of 6-deoxy-6-bromo-(1,2;3,5-diisopropylidene)-α-D-glucofuranose (969 mg, 3.00 mmol, 1.1 eq.) in 30 mL dry DMF was added. The resulting solution was stirred overnight. The following day, the solvent was removed in *vacuo* and the crude product was purified by column chromatography on silica with a 2 : 1 mixture of hexane/ethyl acetate as eluent (R_f = 0.21). A red waxy solid was yielded after removal of the solvent (915 mg, 1.60 mmol, 59%).



^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ [ppm] = 6.04 (d, $^3J_{HH}$ = 3.8 Hz, 1H, 1´-H); 5.36 (s, 1H, 6-H); 4.61 (d, $^3J_{HH}$ = 3.8 Hz, 1H, 2´-H); 4.41 (dd, $^3J_{HH}$ = 3.8 Hz, 6.8 Hz, 1H, 4´-H); 4.29 (dd, $^3J_{HH}$ = 5.0 Hz, $^2J_{HH}$ = 11.8 Hz, 1H, 10-H^A); 4.26 (m, 1H, 3´-H); 4.20 (s, 5H, Cp-*H*); 4.13 (m, 1H, 3-H); 4.05 (dd, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 10.2 Hz, 1H, 6´-H^A); 4.06-3.89 (m, 3H, 8-H, 10-H^B; 4-H); 3.94 (dd, $^3J_{HH}$ = 3.2 Hz, $^2J_{HH}$ = 6.8 Hz, 1H, 6´-H^B); 3.86 (dd, $^3J_{HH}$ = 3.2 Hz, 6.8 Hz, 1H, 5´-H); 3.79 (m, 1H, 5-H); 3.49 (dd, $^3J_{HH}$ = 5.4 Hz, $^2J_{HH}$ = 10.3 Hz, 1H, 12-H^A); 3.38 (dd, $^3J_{HH}$ = 5.2 Hz, $^2J_{HH}$ = 10.3 Hz, 1H, 12-H^B); 3.35 (s, 3H, -OC*H*$_3$); 1.80 (m, 1H, 9-H^A); 1.52 (m, 1H, 9-H^B); 1.50 (s, 3H, 8´-H^A); 1.41 (s, 6H, 10´-H$^{A/B}$); 1.35 (s, 3H, 8´-H^B).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ [ppm] = 124.6 (C1); 112.3 (C7´); 106.6 (C1´); 101.1 (C9´); 99.1 (C6); 84.2 (C2´); 79.7 (C4´); 76.3 (C8); 75.7 (C2); 75.6 (C3´); 75.2 (C12); 72.1 (C6´); 71.3 (C5´); 69.6 (^{Cp}C); 67.3 (C10); 61.4 (C4); 60.9 (C5); 59.4 (-O*C*H$_3$); 54.6 (C3); 28.5 (C9); 27.4 (C8´^{A}); 26.7 (C8´^{B}); 24.3 (C10´^{A}); 24.2 (C10´^{B}).

Elemental Analysis: (%) calc´d. for $C_{28}H_{38}FeO_9$ (574): C 58.54, H 6.67; found: C 58.28, H 6.67, N 0.18.

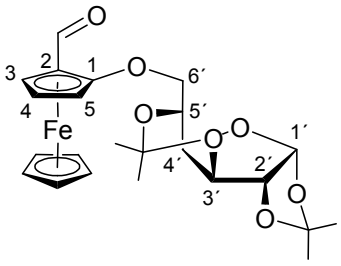
ESI+ (Acetonitrile): calc´d for $[C_{28}H_{38}FeO_9]^+$ 574.2; found: 574.3; calc´d for $[C_{28}H_{38}FeO_9 + Na]^+$ 597.2; found: 597.3.

IR (ATR): $\bar{\nu}$ [cm^{-1}] = 3096 (w), 2985 (m), 2935 (m), 2850 (m), 2121 (w), 1502 (w), 1474 (m), 1449 (m), 1373 (s), 1290 (w), 1240 (m), 1219 (s), 1165 (w), 1143 (w), 1101 (s), 1079 (m), 1000 (s), 958 (w), 916 (w), 859 (m), 816 (m), 732 (w), 526 (w), 493 (s), 469 (m).

Specific Rotation: $[\alpha]_D^{20}$ = -87.5° (0.94, chloroform).

(S_p)-(+)-1-[6-(1,2;3,5-Diisopropylidene)-α-D-glucofuranosidyl]-2-formylferrocene (9)

The protected ferrocene glucofuranoside conjugate **8** (747 mg, 1.37 mmol, 1 eq.) was dissolved in 100 mL of a 3 : 1 mixture of chloroform / water. Under stirring, *p*-toluene sulfonic acid monohydrate (519 mg, 2.73 mmol, 2 eq.) was added. The two phase mixture was vigorously stirred and heated to 90 °C under reflux. The colour of the organic phase of the solution changed from yellow to a glowing red. After 3 h, the mixture was cooled to room temperature and the organic layer separated. The aqueous phase was extracted using chloroform (3 x 50 mL each). The combined organic fractions were dried over $MgSO_4$ and, after filtration, the solvent was removed in *vacuo* to yield a red oil, which was further purified to yield the desired product by column chromatography on silica with hexane / ethyl acetate (2 : 1) as eluant. After evaporation of the solvent in *vacuo*, a red wax-like product was yielded (520 mg, 1.10 mmol, 80%).



^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ [ppm] = 10.22 (s, 1H, -C*H*O); 6.05 (d, $^3J_{HH}$ = 3.8 Hz, 1H, 1′-H); 4.63 (d, $^3J_{HH}$ = 3.8 Hz, 1H, 2′-H); 4.60, 4.35, 4.32 (each m, each 1H, 3,4,5-H); 4.40 (dd, $^3J_{HH}$ = 3.8 Hz, $^3J_{HH}$ = 7.4 Hz, 1H, 4′-H); 4.30 (s, 5H, Cp-*H*); 4.27 (d, $^3J_{HH}$ = 3.8 Hz, 1H, 3′-H); 4.15 (dd, $^3J_{HH}$ = 2.14, $^2J_{HH}$ = 10.2 Hz, 1H, 6′-H^A); 4.00 (dd, $^3J_{HH}$ = 7.1 Hz, $^2J_{HH}$ = 10.2 Hz, 1H, 6′-H^B); 3.89 (dt, $^3J_{HH}$ = 2.8 Hz, $^3J_{HH}$ = 7.1 Hz, 1H, 5′-H); 1.52, 1.41, 1.40, 1.35 (each s, each 3H, each –CH_3).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ [ppm] = 192.5 (-*C*HO); 129.5 (C1); 112.5 (-*C*$(CH_3)_2$); 106.7 (C1′); 101.4 (-*C*$(CH_3)_2$); 84.2 (C2′); 79.5 (C4′); 75.3 (C3′); 71.8 (C6′); 71.2 (C5′); 70.2 (^{Cp}C); 69.2 (C2); 66.0 (C4); 61.8 (C5); 57.2 (C3); 27.4, 26.7, 24.14, 24.06 (each –*C*H_3).

ESI+ (Acetonitrile): calc´d for $[C_{23}H_{28}FeO_7 + Na]^+$ 495.1; found: 495.2.

Elemental Analysis: (%) calc´d. for $C_{23}H_{28}FeO_7$ (472): C 58.49, H 5.98; found: C 58.35, H 5.84, N 0.03.

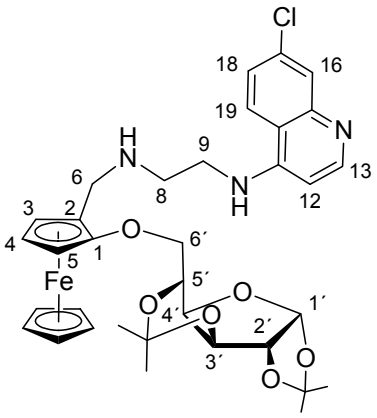
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 2987 (w), 2937 (w), 1760 (w), 1674 (vs), 1479 (m), 1454 (m), 1374 (m), 1334 (w), 1287 (w), 1216 (s), 1166 (m), 1107 (m), 1078 (s), 1025 (s), 1001 (m), 891 (w), 850 (m),774 (w).

Specific Rotation: $[\alpha]_D^{20}$ = +402° (0.94, chloroform); +404° (0.26, chloroform).

(S_p)-(-)-2-[2-(7-Chloroquinolin-4-yl-amino)ethylamino]-1-[6-(1,2;3,5-diisopropyl-idene)-α-D-glucofuranosidyl]-ferrocene (16)

The glucofuranose ferrocene **9** (90 mg, 0.19 mmol, 1 eq.) and **10** (105 mg, 0.48 mmol, 2.5 eq.) were dissolved in 15 mL dry THF. After stirring for 15 min, 101 mg of sodium triacetoxyborohydride (0.48 mmol, 2.5 eq.) were added at room temperature. The solution was

then stirred for 72 h during which time the red-coloured solution turned yellow and a white precipitate formed. The reaction was quenched by addition of 15 mL of saturated $NaHCO_3$ solution and the mixture extracted using chloroform (3 x 30 mL). The combined organic phases were dried over $CaCO_3$ and after filtration the solvent was removed in *vacuo*. Purification of the residue was performed through column chromatography on silica, using 2 : 1 :1 (ethyl acetate : hexane : triethylamine). The solvent was removed in *vacuo* and remaining impurities from the chromatography (silica gel) were removed by taking the residue up in toluene and filtering over a *Celite* pad. Removal of the solvent yielded an orange wax-like substance (62 mg, 0.09 mmol, 48 %).



^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ ^{1}H [ppm] = 8.50 (d, $^{3}J_{HH}$ = 5.3 Hz, 1H, 13-H); 7.93 (d, $^{4}J_{HH}$ = 1.8 Hz, 1H, 16-H); 7.77 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, 19-H); 7.33 (dd, $^{3}J_{HH}$ = 8.9 Hz, $^{4}J_{HH}$ = 1.8 Hz, 1H, 18-H); 6.36 (d, $^{3}J_{HH}$ = 5.3 Hz, 1H, 12-H); 6.05 (br, 1H, NH^{Ar}); 6.02 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, 1′-H); 4.61 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, 2′-H); 4.40 (dd, $^{3}J_{HH}$ = 3.7 Hz, $^{3}J_{HH}$ = 6.6 Hz, 1H, 4′-H); 4.26 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, 3′-H); 4.15 (s, 5H, *Cp*-H); 4.06 (dd, $^{3}J_{HH}$ = 3.7 Hz, $^{2}J_{HH}$ = 9.5 Hz, 1H, 6′-H^{a}); 3.99 (m, 1H, 5-H); 3.92 (dd, $^{4}J_{HH}$ = 6.6 Hz, $^{2}J_{HH}$ = 9.5 Hz, 1H, 6′-H^{b}); 3.91 (m, 1H, 3-H); 3.89 (d, $^{2}J_{HH}$ = 13.5 Hz, 1H, 6-H^{a}); 3.86 (dd, dm, $^{3}J_{HH}$ = 3.7 Hz, 1H, 5′-H); 3.78 (m, 1H, 4-H); 3.50 (d, $^{2}J_{HH}$ = 13.5 Hz, 1H, 6-H^{b}); 3.33 (m, 2H, 9-H); 3.01 (m, 2H, 8-H); 2.20 (br, NH^{Alk}); 1.50, 1.32 (each s, each 3H, $CH_3^{1'}$ and $CH_3^{2'}$); 1.37, 1.36 (each s, each 3H, $CH_3^{3'}$ and $CH_3^{5'}$).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ ^{13}C [ppm] = 152.2 (C13); 150.3 (C15); 149.3 (C11); 135.0 (C17); 128.7 (C16); 125.4 (C18); 125.3 (C1); 121.9 (C19); 117.6 (C20); 112.4 ($\underline{C}(CH_3)_2^{1'2'}$); 106.7 (C1′); 101.3 ($\underline{C}(CH_3)_2^{3'5'}$); 99.3 (C12); 84.0 (C2′); 80.2 (C4′); 75.2 (C3′); 74.9 (C2); 71.3 (C6′); 71.1 (C5′); 69.2 (*Cp*); 63.9 (C3); 60.5 (C4); 53.4 (C5); 46.5 (C8); 45.6 (C6); 41.9 (C9); 27.4, 26.7 ($\underline{C}H_3^{1'}$ and $\underline{C}H_3^{2'}$); 24.2, 24.1 ($\underline{C}H_3^{3'}$ and $\underline{C}H_3^{5'}$).

GCOSY (300 / 300 MHz, $CDCl_3$, 300 K) δ ^{1}H / δ ^{1}H [ppm] = 8.50 / 6.36 (13-H / 12-H); 7.77 / 7.33 (19-H / 18-H); 6.05 / 3.33 (NH^{Ar} / 9-H); 6.02 / 4.61 (1′-H / 2′-H); 4.40 / 4.26, 3.86 (4′-H / 3′-H, 5′-H); 4.26 / 4.40 (3′-H / 4′-H); 4.06 / 3.92, 3.86 (6′-H^{a} / 6′-H^{b}, 5′-H); 3.99 / 3.71 (5-H / 4-H); 3.92 / 4.06, 3.86 (6′-H^{b} / 6-H^{a}, 5′-H); 3.91 / 3.78 (3-H / 4-H); 3.89 / 3.50 (6-H^{a} / 6-H^{b}); 3.86 / 4.40, 4.06, 3.92 (5′-H / 4′-H, 6′-H, 6′-H^{a}); 3.78 / 3.99, 3.91 (4-H / 5-H, 3-H); 3.50 / 3.89 (6-H^{b} / 6-H^{a}); 3.33 / 6.05, 3.01 (9-H / NH^{Ar}, 8-H); 3.01 / 3.33 (8-H / 9-H); 1.50 / 1.32 ($CH_3^{1'2'}$); 1.37 / 1.36 ($CH_3^{3'5'}$).

GHSQC (100 / 300 MHz, $CDCl_3$, 300 K) δ ^{13}C / δ ^{1}H [ppm] = 152.2 / 8.50 (C13 / 13-H); 128.7 / 7.93 (C16 / 16-H); 125.4 / 7.33 (C18 / 18-H); 121.9 / 7.77 (C19 / 19-H); 106.7 / 6.02 (C1′ / 6′-H); 99.3 / 6.36 (C12 / 12-H); 84.0 / 4.61 (C2′ / 2′-H); 80.2 / 4.40 (C4′ / 4′-H); 75.2 / 4.26 (C3′ / 3′-H); 71.3 / 4.06, 3.92 (C6′ / 6′-H^{a}, 6′-H^{b}); 71.1 / 3.86 (C5′ / 5′-H); 69.2 / 4.15 (*Cp* / *Cp*-

H); 63.9 / 3.91 (C3 / 3-H); 60.5 / 3.78 (C4 / 4-H); 53.4 / 3.99 (C5 / 5-H); 46.5 / 3.01 (C8 / 8-H); 45.6 / 3.89, 3.50 (C6 / 6-H^{a}, 6-H^{b}); 41.9 / 3.33 (C9 /9-H); 27.4 / 1.50, 26.7 / 1.32 (each $\underline{C}H_3^{1'2'}$ / $CH_3^{1'2'}$); 24.2 / 1.37, 24.1 / 1.36 (each $\underline{C}H_3^{3'5'}$ / $CH_3^{3'5'}$).

GHMBC (100 / 300 MHz, $CDCl_3$, 300 K) δ ^{13}C / δ ^{1}H [ppm] = 152.2 / 6.36 (C13 / 12-H); 150.3 / 8.50, 7.77 (C15 / 13-H, 19-H); 149.3 / 8.50, 7.93, 7.77 (C11 / 13-H, 16-H, 19-H); 135.0 / 7.93, 7.77, 7.33 (C17 / 16-H, 19-H, 18-H); 128.7 / 7.33 (C16 / 18-H); 125.4 / 7.93 (C18 / 16-H); 125.3 / 3.89, 3.50 (C1 / 6-H^{a}, 6-H^{b}); 121.9 / 6.36 (C19 / 12-H); 117.6 / 8.50, 7.93, 7.77, 7.33, 6.36 (C20 (13-H, 16-H, 19-H, 18-H, 12-H); 112.4 / 6.02, 1.50, 1.32 ($\underline{C}(CH_3)_2^{1'2'}$ / 1-H′, $CH_3^{1'2'}$, $CH_3^{1'2'}$); 106.7 / 4.61, 4.26 (C1′ / 2′-H, 3′-H); 101.3 / 4.26, 1.37, 1.36 ($\underline{C}(CH_3)_2^{3'5'}$ / 3′-H, $CH_3^{3'5'}$, $CH_3^{3'5'}$); 99.3 / 8.50 (C12 / 13-H); 84.0 / 6.02, 4.26 (C2′ / 1′-H, 3′-H); 80.2 / 6.02, 4.61, 4.26, 4.06, 3.92, 3.86 (C4′ / 1′-H, 2′-H, 3′-H, 6′-H^{a}, 6′-H^{b}, 5′-H); 75.2 / 6.02, 4.61, 4.40, 1.37 (C3′ / 1′-H, 2′-H. 4′-H, $CH_3^{3'5'}$); 74.9 / 3.99, 3.89, 3.78, 3.50 (C2 / 5-H, 6-H^{a}, 4-H, 6-H^{b}); 71.3 / 4.40(C6′ / 4′-H); 71.1 / 4.06, 3.92, 1.32 (C5′ / 6′-H^{a}, 6′-H^{b}, $CH_3^{3'5'}$); 69.2 / 4.15 (*Cp* / *Cp*-H); 63.9 / 3.99, 3.89, 3.78, 3.50 (C3 / 5-H, 6-H^{a}, 4-H, 6-H^{b}); 60.5 / 3.99, 3.89 (C4 / 5-H, 6-H^{a}); 53.4 / 3.89, 3.78 (C5 / 6-H^{a}, 4-H); 46.5 / 3.89, 3.50 (C8 / 6-H^{a}, 6-H^{b}); 45.6 / 3.01 (C6 / 8-H); 41.9 / 3.01 (C9 / 8-H); 27.4 / 1.32, 26.7 / 1.50 (each $\underline{C}H_3^{1'2'}$ / $CH_3^{1'2'}$); 24.2 / 1.36, 24.1 / 1.37 (each $\underline{C}H_3^{3'5'}$ / $CH_3^{3'5'}$).

Exact Mass (TOF MS ES+): calc′d for $[C_{34}H_{41}N_3O_6{}^{35}Cl^{56}Fe]$ 678.2033; found 678.2020.

Elemental Analysis: (%) calc′d. for $C_{34}H_{40}ClFeN_3O_6$ (678): C 60.23, H 5.95, N 6.20; found: C 60.46, H 6.42, N 6.19.

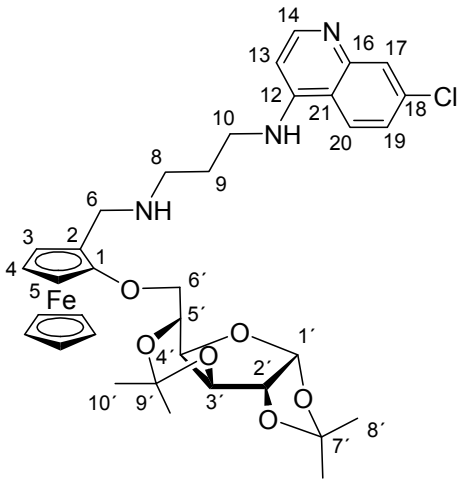
IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3307 (br), 2987 (w), 2936 (w), 1611 (w), 1581 (vs), 1533 (w), 1449 (m), 1373 (m), 1330 (w), 1276 (w), 1241 (w), 1221 (m), 1165 (m), 1138 (w), 1104 (w), 1079 (m), 1025 (m), 849 (w), 810 (w), 764 (m), 750 (m), 622 (w).

Specific Rotation: $[\alpha]_D^{20}$ = -87.3° (1.03, chloroform).

(*S*$_p$)-(-)-2-[2-(7-Chloroquinolin-4-yl-amino)propylamino]-1-[6-(1,2;3,5-diisopropyl-idene)-α-D-glucofuranosidyl]-ferrocene (17)

In an argon-purged Schlenk tube, **9** (78.4 mg, 0.17 mmol, 1 eq.) and **11** (39.0 mg,0.17 mmol, 1 eq.) were weighed in together and dissolved in 15 mL dry methanol. The solution was stirred under argon for 5 h, during which time the colour changed from red to a dark brown/black. Sodium borohydride (10.3 mg, 0.27 mmol, 1.6 eq.) was added at room temperature. The reaction mixture changed colour to a lighter brown/yellow immediately, under evolution of hydrogen gas. The mixture was then stirred at room temperature for one hour. The reaction was quenched by addition of 1 M NaOH (approximately 5 mL) and addition of 10 mL of brine. The aqueous phase was extracted using diethyl ether (3 x 50 mL). The collected organic phases were dried over $MgSO_4$, and after filtration, the solvent removed *in vacuo*. The crude product was purified by

column chromatography on silica, using a 2 : 1 : 1 mixture of ethyl acetate, hexane and triethylamine. Pure product was yielded as an orange, wax-like substance (62 mg, 53 %).



^{1}H NMR (300 MHz $CDCl_3$, 300 K): δ [ppm] = 8.46 (d, $^{3}J_{HH}$ = 5.4 Hz, 1H, 14-H); 8.09 (br, 1H, N*H*^{Ar}); 7.88 (d, $^{3}J_{HH}$ = 2.1 Hz, 1H, 17-H); 7.57 (d, $^{3}J_{HH}$ = 8.9 Hz, 1H, 20-H); 7.18 (dd, $^{3}J_{HH}$ = 8.9 Hz, $^{3}J_{HH}$ = 2.1 Hz, 1H, 19-H); 6.26 (d, $^{3}J_{HH}$ = 5.4 Hz, 1H, 13-H); 6.02 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, 1´-H); 4.60 (d, $^{3}J_{HH}$ = 3.7 Hz, 1H, 2´-H); 4.37 (dd, $^{3}J_{HH}$ = 7.0 Hz, 3.8 Hz, 1H, 4´-H); 4.24 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, 3´-H); 4.17 (s, 5H, Cp-*H*); 4.06 (dd, $^{2}J_{HH}$ = 9.8 Hz, $^{3}J_{HH}$ = 3.8 Hz, 1H, 6´–H^{A}); 4.05 (m, 1H, 3-H); 3.95 (m, 1H, 4-H); 3.94 (d, $^{2}J_{HH}$ = 12.8 Hz, 1H, 6-H^{A}); 3.88 (m, 1H, 6´-H^{B}); 3.85 (m, 1H, 5-H); 3.84 (dm, $^{3}J_{HH}$ = 3.8 Hz, 1H, 5´-H); 3.48 (d, $^{3}J_{HH}$ = 12.8 Hz, 1H, 6-H^{B}); 3.37 (br, 2H, 10-H); 2.93 (m, 2H, 8-H); 1.93 (br, 1H, N*H*^{Alk}); 1.90 (m, 2H, 9-H); 1.50 (s, 3H, 8´-H^{A}); 1.341 (s, 3H, 8´-H^{B}), 1.337 (s, 3H, 10´-H^{A}), 1.332 (s, 3H, 10´-H^{B}).

^{13}C{^{1}H} NMR ($CDCl_3$, 75 MHz, 300 K): δ [ppm] = 152.2 (C14); 150.9 (C12); 149.3 (C21); 134.6 (C18); 128.4 (C17); 125.6 (C1); 125.0 (C19); 122.9 (C20); 117.8 (C16); 112.4 (C7´); 106.7 (C1´); 101.2 (C9´); 98.2 (C13); 84.1 (C2´); 80.1 (C4´); 75.2 (C3´); 74.9 (C2); 71.4 (C6´); 71.2 (C5´); 69.2 (^{Cp}C); 63.9 (C4); 60.5 (C5); 53.5 (C3); 49.3 (C8); 46.6 (C6); 44.4 (C10); 27.4 (C8´^{A}); 27.0 (C9); 26.7 (C8´^{B}); 24.14 (C10´^{A}); 24.09 (C10´^{B}).

GCOSY (300 MHz / 300 MHz ,$CDCl_3$, 300 K): δ (^{1}H) / δ (^{1}H) [ppm] = 8.46 / 6.26 (14-H / 13-H); 8.09 / 3.37 (N*H*^{Ar} / 10-H); 7.88 / 7.18 (17-H / 19-H); 7.57 / 7.18 (20-H / 19-H); 7.18 / 7.88, 7.57 (19-H / 17-H, 20-H); 6.26 / 8.46 (13-H / 14-H); 6.02 / 4.60 (1´-H / 2´-H); 4.60 / 6.02 (2´-H / 1´-H); 4.37 / 4.24, 3.84 (4´-H / 3´-H, 5´-H); 4.24 / 4.37 (3´-H / 4´-H); 4.17 / 4.17 (Cp-*H* / Cp-*H*); 4.06 / 3.84 (6´–H^{A} / 5´-H); 4.05 / 3.85 (3-H / 5-H); 3.94 / 3.48 (6-H^{A} / 6-H^{B}); 3.85 / 4.05 (5-H / 3-H); 3.84 / 4.37, 4.06 (5´-H / 4´-H, 6´-H^{A}); 3.48 / 3.94 (6-H^{B} / 6-H^{A}); 3.37 / 1.90 (10-H / 9-H); 2.93 / 1.90 (8-H / 9-H); 1.90 / 3.37, 2.93 (9-H / 10-H, 8-H).

GHMQC (75 MHz / 300 MHz ,$CDCl_3$, 300 K): δ (^{13}C) / δ (^{1}H) [ppm] = 152.2 / 8.46 (C14 / 14-H); 128.4 / 7.88 (C17 / 17-H); 125.0 / 7.18 (C19 / 19-H); 122.9 / 7.57 (C20 /20-H); 106.7 / 6.02 (C1´ / 1´-H); 98.2 / 6.26 (C13 / 13-H); 84.1 / 4.60 (C2´ / 2´-H); 80.1 / 4.37 (C4´ / 4´-H); 75.2 / 4.24 (C3´ / 3´-H); 71.4 / 4.06, 3.88 (C6´ / 6´-H$^{A/B}$); 71.2 / 3.84 (C5´ / 5´-H); 69.2 / 4.17 (^{Cp}C / Cp-*H*); 63.9 / 3.95 (C4 / 4-H); 60.5 / 3.85 (C5 / 5-H); 53.5 / 4.05 (C3 / 3-H); 49.3 / 2.93 (C8 / 8-H); 46.6 / 3.94, 3.48 (C6 / 6-H$^{A/B}$); 44.4 / 3.37 (C10 / 10-H); 27.4 / 1.50 (C8´^{A} / 8´-H^{A}); 27.0 / 1.90 (C9 / 9-H); 26.7 / 1.341 (C8´^{B} / 8´-H^{B}); 24.14 / 1.337 (C10´^{A} / 10´-H^{A}); 24.09 / 1.332 (C10´^{B} / 10´-H^{B}).

GHMBC (75 MHz / 300 MHz, $CDCl_3$, 300 K): δ (^{13}C) / δ (^{1}H) [ppm] = 152.2 / 6.26 (C14 / 13-H); 150.9 / 8.46, 7.57 (C12 / 14-H, 20-H); 149.3 / 8.46, 7.88, 7.57 (C21 / 14-H, 17-H, 20-H); 134.6 / 8.46, 7.88, 7.57, 7.18 (C18 / 14-H, 20-H, 19-H); 128.4 / 7.57, 7.18 (C17 / 20-H, 19-H); 125.6 / 4.05, 3.93, 3.85, 3.48 (C1 / 3-H, 6-H^A, 5-H, 6-H^B); 125.0 / 7.88 (C19 / 17-H); 122.9 / 6.26 (C20 / 13-H); 117.8 / 8.46, 7.88, 7.57, 7.18, 6.26 (C16 / 14-H, 17-H, 20-H, 19-H, 13-H); 112.4 / 6.02, 1.50, 1.341 (C7′ / 1′-H, 8′-$H^{A/B}$); 106.7 / 4.60, 4.24 (C1′ / 2′-H, 3′-H); 101.2 / 1.337, 1.332 (C9′ / 10′-$H^{A/B}$); 98.2 / 8.46 (C13 / 14-H); 84.1 / 6.02, 4.24 (C2′ / 1′-H, 3′-H); 80.1 / 6.02, 4.60, 4.24, 4.06, 3.88 (C4′ / 1′-H, 2′-H, 3′-H, 6′-$H^{A/B}$); 75.2 / 6.02, 4.60, 4.37, 4.06, 3.84 (C3′ / 1′-H, 2′-H, 4′-H. 6′-H^A, 5′-H); 74.9 / 4.05, 3.93, 3.48 (C2 / 3-H, 6-$H^{A/B}$); 71.2 / 4.37, 4.06, 3.88 (C5′ / 4′-H, 6′-$H^{A/B}$); 69.2 / 4.17 (^{Cp}C / Cp-*H*); 63.9 / 4.05, 3.93, 3.48 (C4 / 3-H, 6-$H^{A/B}$); 60.5 / 4.05, 3.95 (C5 / 3-H, 4-H); 53.5 / 3.95, 3.85 (C3 / 4-H, 5-H); 49.3 / 3.93, 3.48, 1.90 (C8 / 6-H^A, 6-H^B, 9-H); 46.6 / 2.93 (C6 / 8-H); 44.4 / 2.93, 1.90 (C10 / 8-H, 9-H); 27.4 / 1.341 (C8′^{A} / 8′-H^B); 27.0 / 3.37, 2.93 (C9 / 10-H, 8-H); 26.7 / 1.50 (C8′^{B} / 8′-H^A); 24.14 / 1.334 (C10′^{A} / 10′-H^B); 24.09 / 1.332 (C10′^{B} / 10′-H^A).

TOF MS ESI+ (MeOH): calc′d for [$C_{35}H_{42}ClFeN_3O_6$ + H^+] 692.2; found 692.4.

TOF MS ESI- (MeOH): calc′d for [$C_{35}H_{42}ClFeN_3O_6$ - H^+] 690.2; found 690.4.

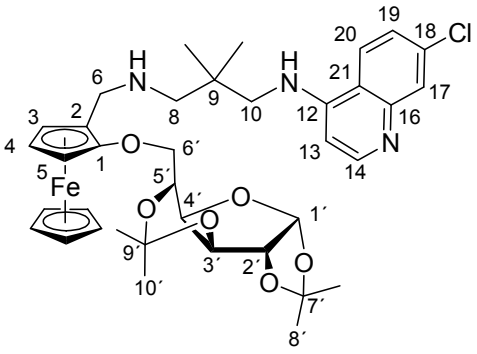
Elemental Analysis: (%) calc′d. for $C_{35}H_{42}ClFeN_3O_6$ (691): C 60.75, H 6.12, N 6.07; found: C 60.46, H 6.35, N 6.11.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3238 (w), 2987 (m), 2936 (m), 1610 (w), 1582 (s), 1538 (w), 1448 (m), 1373 (m), 1330 (w), 1284 (w), 1239 (w), 1220 (m), 1166 (w), 1139 (w), 1104 (w), 1078 (w), 1025 (m), 853 (w), 803 (w) 766 (w).

Specific Rotation: $[\alpha]_D^{20}$ = -62.2° (0.95, chloroform).

(S_p)-(-)-2-[3-(7-Chloroquinolin-4-yl-amino)-2,2-dimethylpropylamino]-1-[6-(1,2;3,5-diisopropylidene)-α-D-glucofuranosidyl]-ferrocene (18)

The glucofuranose ferrocene **9** (95.5 mg, 0.2 mmol, 1 eq.) was dissolved in 10 mL dry methanol, together **12** (53.2 mg, 0.2 mmol). After stirring for 3 h at room temperature, 13 mg (0.32 mmol) sodium borohydride were added. The solution was then stirred for 1 h during which time the red solution turned yellow. The reaction was quenched by addition of 10 mL 1 M NaOH and the mixture extracted with diethyl ether (3 x 30 mL). The combined organic phases were dried over $CaCO_3$ and after filtration the solvent was removed in vacuo. Purification of the residue was performed through column chromatography on silica, using 2 : 1 : 1 (ethyl acetate : hexane : triethylamine). After collection of the appropriate fractions, the solvent was removed in vacuo. Remaining impurities from the chromatography (silica gel) were removed by taking the residue up in toluene and filtering over a *Celite* pad. Removal of the solvent yielded an orange wax-like substance **(**64 mg, 0.09 mmol, 44 %).



^{1}H NMR (300 MHz, $CDCl_3$, 300 K): δ ^{1}H [ppm] = 8.77 (br, 1H, N$\underline{H}^{Ar}$); 8.44 (d, $^{3}J_{HH}$ = 5.4 Hz, 1H; 14-H); 7.87 (d, $^{4}J_{HH}$ = 2.1 Hz, 1H, 17-H); 7.53 (d, $^{3}J_{HH}$ = 9.0 Hz, 1H, 20-H); 7.15 (dd, $^{3}J_{HH}$ = 9.0 Hz, $^{4}J_{HH}$ = 2.1 Hz, 1H, 19-H); 6.22 (d, $^{3}J_{HH}$ = 5.4 Hz, 1H, 13-H); 6.02 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, 1´-H); 4.60 (d, $^{3}J_{HH}$ = 3.8 Hz, 1H, 2´-H); 4.36 (dd, $^{3}J_{HH}$ = 6.8, 3.7 Hz, 1H, 4´-H); 4.24 (d, $^{3}J_{HH}$ = 3.4 Hz, 1H, 3´-H); 4.16 (s, 5H, Cp-$\underline{H}$); 4.05 (m, 1H, 6´-H^{A}); 4.05 (m, 1H, 3-H); 3.95 (m, 1H, 4-H); 3.93 (d, $^{2}J_{HH}$ = 12.7 Hz, 1H, 6-H^{A}); 3.91 (m, 1H, 6´-H^{B}); 3.87 (m, 1H, 5-H); 3.82 (ddm, $^{3}J_{HH}$ = 3.6, 6.8 Hz, 1H, 5´-H); 3.44 (d, $^{2}J_{HH}$ = 12.7 Hz, 1H, 6-H^{B}); 3.12 (m, 2H, 10-H); 2.74 (m, 2H, 8-H); 1.95 (vb, 1H, -N$\underline{H}$); 1.49 (s, 3H, 8´-H^{A}); 1.33 (s, 3H, 8´-H^{B}); 1.33 (s, 3H, 10´-H^{A}); 1.32 (s, 3H, 10´-H^{B}); 1.060 (s, 3H, C^{9}C$\underline{H}_3^{A}$); 1.055 (s, 3H, C^{9}C$\underline{H}_3^{B}$).

^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$, 300 K): δ ^{13}C [ppm] = 152.2 (C14); 151.2 (C12); 149.4 (C21); 134.6 (C18); 128.4 (C17); 125.7 (C1); 124.9 (C19); 123.2 (C20); 118.0 (C16); 112.4 (C7´); 106.7 (C1´); 101.2 (C9´); 97.8 (C13); 84.1 (C2´); 80.1 (C4´); 75.2 (C3´); 74.8 (C2); 71.4 (C6´); 71.2 (C5´); 69.2 (^{Cp}C); 63.9 (C4); 61.1 (C8); 60.5 (C5); 56.1 (C10); 53.3 (C3); 47.7 (C6); 33.8 (C9); 27.4 (C8´^{A}), 26.7 (C8´^{B}); 25.6 (C$^{9}\underline{C}H_3^{A}$); 24.9 (C$^{9}\underline{C}H_3^{B}$); 24.12 (C10´^{A}); 24.09 (C10´^{B}).

GHSQC (100 / 300 MHz, $CDCl_3$, 300 K) δ ^{13}C / δ ^{1}H [ppm] = 152.2 / 8.44 (C14 / 14-H); 128.4 / 7.87 (C17 / 17-H); 124.9 / 7.15 (C19 / 19-H); 123.2 / 7.53 (C20 / 20-H); 106.7 / 6.02 (C1´ / 1´-H); 97.8 / 6.22 (C13 / 13-H); 84.1 / 4.60 (C2´ / 2´-H); 80.1 / 4.36 (C4´ / 4´-H); 75.2 / 4.24 (C3´ / 3´-H); 71.4 / 4.05, 3.91 (C6´ / 6´-H$^{A/B}$); 71.2 / 3.82 (C5´ / 5´-H); 69.2 / 4.16 (^{Cp}C / Cp-$\underline{H}$); 63.9 / 3.95 (C4 / 4-H); 61.1 / 2.74 (C8 / 8-H); 60.5 / 3.87 (C5 / 5-H); 56.1 / 3.12 (C10 / 10-H); 53.3 / 4.05 (C3 / 3-H); 47.7 / 3.93, 3.44 (C6 / 6-H$^{A/B}$); 27.4 / 1.49 (C8´^{A} / 8´-H^{A}), 26.7 / 1.33 (C8´^{B} / 8´-H^{B}); 25.6 / 1.055 (C$^{9}\underline{C}H_3^{A}$ / C^{9}C$\underline{H}_3^{A}$); 24.9 / 1.060 (C$^{9}\underline{C}H_3^{B}$ / C^{9}C$\underline{H}_3^{B}$); 24.12 / 1.33 (C10´^{A} / 10´-H^{A}); 24.09 / 1.32 (C10´^{B} / 10´-H^{B}).

GHMBC (100 / 300 MHz, $CDCl_3$, 300 K) δ ^{13}C / δ ^{1}H [ppm] = 152.2 / 6.22 (C14 / 13-H); 151.2 / 8.44, 7.53, 3.12 (C12 / 14-H, 20-H, 10-H); 149.4 / 8.44, 7.87, 7.53 (C21 / 14-H, 17-H, 20-H); 134.6 / 7.87, 7.53, 7.15 (C18 / 17-H, 20-H, 19-H); 128.4 / 7.53, 7.15 (C17 / 20-H, 19-H); 125.7 / 4.05, 3.95, 3.93, 3.87, 3.44 (C1 / 3-H, 4-H, 6-H^{A}, 5-H, 6-H^{B}); 124.9 / 7.87 (C19 / 17-H); 123.2 / 6.22 (C20 / 13-H); 118.0 / 8.44, 7.87, 7.53, 7.15, 6.22 (C16 / 14-H, 17-H, 20-H, 19-H, 13-H); 112.4 / 6.02, 1.49, 1.33 (C7´ / 1´-H, 8´-H$^{A/B}$); 106.7 / 4.60, 4.24 (C1´ / 2-H´, 3´-H); 101.2 / 4.24, 1.33, 1.32 (C9´ / 3´-H, 10´-H$^{A/B}$); 97.8 / 8.44 (C13 / 14-H); 84.1 / 6.02, 4.24 (C2´ / 1´-H, 3´-H); 80.1 / 6.02, 4.60, 4.24, 4.05, 3.91, 3.82 (C4´ / 1´-H, 2´-H, 3´-H, 6´-H^{A}, 6´-H^{B}, 5´-H); 75.2 / 6.02, 4.60, 4.36, 1.33 (C3´ / 1´-H, 2´-H, 4´-H, 10´-H^{A}); 74.8 / 4.05, 3.93, 3.87, 3.44 (C2 / 3-H, 6-H^{A}, 5-H, 6-H^{B}); 71.4 / 4.36, 3.82, 1.32 (C6´ / 4´-H, 5´-H, 10´-H^{B}); 71.2 / 4.36, 3.91 (C5´ / 4´-H, 6´-H^{B}); 69.2 / 4.16 (^{Cp}C / Cp-$\underline{H}$); 63.9 / 4.05, 3.87 (C4 / 3-H, 5-H); 61.1 / 3.44, 3.12, 1.060, 1.055 (C8 / 6-H^{B}, 10-H, C^{9}C$\underline{H}_3^{A/B}$); 60.5 / 4.05, 3.95 (C5 / 3-H, 4-H); 56.1 / 2.74, 1.060 (C10 / 8-H, C^{9}C$\underline{H}_3^{A}$); 53.3 / 3.95, 3.87 (C3 / 4-H, 5-H); 47.7 / 2.74 (C6 / 8-H); 33.8 / 3.12, 2.74, 1.060, 1.055

(C9 / 10-H, 8-H, $C^{9}C\underline{H}_{3}^{A/B}$); 27.4 / 1.33 ($C8'^{A}$ / 8′-H^{B}), 26.7 / 1.49 ($C8'^{B}$/ 8′-H^{A}); 25.6 / 3.12, 2.74, 1.060 ($C^{9}\underline{C}H_{3}^{A}$ / 10-H, 8-H, $C^{9}C\underline{H}_{3}^{B}$); 24.9 / 3.12, 2.74, 1.055 ($C^{9}\underline{C}H_{3}^{B}$ / 10-H, 8-H, $C^{9}C\underline{H}_{3}^{A}$); 24.12 / 1.32 ($C10'^{A}$ / 10′-H^{B}); 24.09 / 1.33 ($C10'^{B}$ / 10′-H^{A}).

Elemental Analysis: (%) calc′d. for $C_{37}H_{46}ClFeN_3O_6$ (720): C 61.72, H 6.44, N 5.84; found: C 61.86, H 6.61, N 5.94.

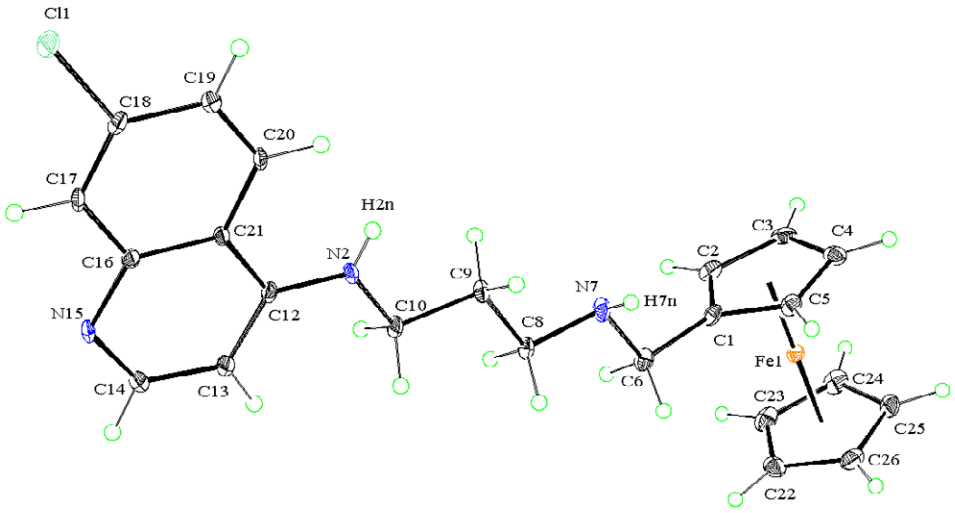
ESI+ (Acetonitrile): calc′d for $[C_{37}H_{46}N_3O_6ClFe + H]^+$ 720.3; found: 720.7; calc′d for $[C_{37}H_{46}N_3O_6ClFe + Na]^+$ 742.2; found 742.6.

Exact Mass (TOF MS ES+): calc′d for $[C_{37}H_{47}N_3O_6{}^{35}Cl^{56}Fe]^+$ 720.2503, found: 720.2487.

IR (ATR): $\tilde{\nu}$ [cm^{-1}] = 3210 (w), 2935 (br), 1609 (w), 1581 (s), 1539 (w), 1447 (m), 1382 (m), 1373 (m), 1332 (w), 1281 (w), 1241 (m), 1220 (m), 1166 (w), 1138 (w), 1079 m), 1028 (w), 902 (w), 852 (m), 805 (w), 766 (w), 669 (w), 649 (w).

Specific Rotation: $[\alpha]_D^{20}$ = -57.2° (0.91, chloroform).

II X-ray Structure Data Compound 14



Experimental

Data Collection

An orange plate crystal of $C_{23}H_{24}N_3FeCl$ having approximate dimensions of 0.03 x 0.35 x 0.45 mm was mounted on a glass fiber. All measurements were made on a *Bruker* X8 APEX II diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of -170.0 ± 0.1 °C to a maximum 2θ value of 56.1°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 20.0 second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction

The material crystallizes as a two-component twin with the two components related by a 180° rotation about the (0 0 1) reciprocal axis. Data were integrated for both twin components, including both overlapped and non-overlapped reflections. In total 37775 reflections were integrated (115458 from component one only, 10844 from component two only, 15383 overlapped). Data were collected and integrated using the *Bruker* SAINT[1] software packages. The linear absorption coefficient, μ, for Mo-Kα radiation is 9.00 cm^{-1}. Data were corrected for absorption effects using the multi-scan technique (TWINABS[2]), with minimum and maximum transmission coefficients of 0.605 and 0.973, respectively. The data were corrected for Lorentz and polarization effects.

[1] SAINT. Version 7.60A. Bruker AXS Inc., Madison, Wisconsin, USA. (1997-2009).
[2] TWINABS. Bruker Nonius scaling and absorption for twinned crystals – V2008/2, Bruker AXS Inc., Madison, Wisconsin, USA (2007).

Structure Solution and Refinement

The structure was solved by direct methods[3] using non-overlapped data from the major twin component. Subsequent refinements were carried out using an HKLF 5 format data set containing complete data from component 1 and any overlapped reflections from component 2. All non-hydrogen atoms were refined anisotropically. All N-H hydrogen atoms were located in difference maps and refined isotropically. All other hydrogen atoms were included in calculated positions but not refined. The batch scale refinement showed a roughly 55:45 ratio between the major and minor twin components. The final cycle of full-matrix least-squares refinement[4] on F^2 was based on 4847 reflections and 262 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.055$$

$$wR2 = [\Sigma (w (Fo^2 - Fc^2)^2) / \Sigma \, w(Fo^2)^2]^{1/2} = 0.089$$

The standard deviation of an observation of unit weight[5] was 1.14. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.46 and –0.47 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from *Cromer* and *Waber.*[6] Anomalous dispersion effects were included in Fcalc[7]; the values for Δf' and Δf'' were those of *Creagh* and *McAuley.*[8] The values for the mass attenuation coefficients are those of *Creagh* and *Hubbell.*[9] All refinements were performed using the SHELXTL[10] crystallographic software package of Bruker-AXS.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{23}H_{24}N_3FeCl$
Formula Weight	433.75
Crystal Colour, Habit	orange, plate
Crystal Dimensions	0.03 X 0.35 X 0.45 mm
Crystal System	monoclinic
Lattice Type	primitive
Lattice Parameters	a = 16.418(2) Å
	b = 10.201(1) Å

[3] SIR97 - Altomare A., Burla M.C., Camalli M., Cascarano G.L., Giacovazzo C. , Guagliardi A., Moliterni A.G.G., Polidori G.,Spagna R. (1999) J. Appl. Cryst. 32, 115-119.

[4] Least Squares function minimized: $\Sigma w(F_o^2-F_c^2)^2$

[5] Standard deviation of an observation of unit weight: $[\Sigma w(F_o^2 - F_c^2)^2/(N_O-N_V)]^{1/2}$

where: N_o = number of observations N_V = number of variables

[6] Cromer, D. T. & Waber, J. T.; "International Tables for X-ray Crystallography", Vol. IV, The Kynoch Press, Birmingham, England, Table 2.2 A (1974).

[7] Ibers, J. A. & Hamilton, W. C.; Acta Crystallogr., 17, 781 (1964).

[8] Creagh, D. C. & McAuley, W.J .; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.6.8, pages 219-222 (1992).

[9] Creagh, D. C. & Hubbell, J.H..; "International Tables for Crystallography", Vol C, (A.J.C. Wilson, ed.), Kluwer Academic Publishers, Boston, Table 4.2.4.3, pages 200-206 (1992).

[10] SHELXTL Version 5.1. Bruker AXS Inc., Madision, Wisconsin, USA. (1997).

	c = 12.6323(1) Å
	α = 90.0°
	β = 108.828(4)°
	γ = 90.0°
	V = 2002.4(3) Å^3
Space Group	*P* $2_1/c$ (#14)
Z value	4
D_{calc}	1.439 g/cm^3
F_{000}	904.00
μ(MoKα)	9.00 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker X8 APEX II
Radiation	MoKα (λ = 0.71073 Å)
	graphite monochromated
Data Images	1547 exposures @ 20.0 seconds
Detector Position	40.00 mm
$2\theta_{max}$	56.1°
No. of Reflections Measured	Total: 37775
	Unique: 4847, both components (R_{int} = 0.057)
Corrections	Absorption (T_{min} = 0.605, T_{max}= 0.973)
	Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w (Fo^2 – Fc^2)^2
Least Squares Weights	w=1/(σ^2(Fo^2)+(0.0170P)^2+ 2.3835P)
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00σ(I))	4847
No. Variables	262
Reflection/Parameter Ratio	18.50
Residuals (refined on F^2, all data): R1; wR2	0.055; 0.089
Goodness of Fit Indicator	1.14
No. Observations (I>2.00σ(I))	4177
Residuals (refined on F): R1; wR2	0.039; 0.080
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.46 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.47 e$^-$/Å^3

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **14**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	12924(2)	1012(3)	14885(2)	17(1)
C(2)	13572(2)	1978(3)	15343(2)	22(1)
C(3)	13558(2)	2322(3)	16421(2)	22(1)
C(4)	12905(2)	1580(3)	16650(2)	22(1)
C(5)	12512(2)	773(3)	15702(2)	19(1)
C(6)	12694(2)	429(3)	13745(2)	18(1)
C(8)	11763(2)	690(3)	11821(2)	16(1)
C(9)	11009(2)	1463(3)	11064(2)	16(1)
C(10)	10849(2)	1126(3)	9842(2)	17(1)
C(12)	9819(2)	1655(3)	8002(2)	14(1)
C(13)	10239(2)	837(3)	7467(2)	17(1)
C(14)	9957(2)	756(3)	6305(2)	17(1)
C(16)	8855(2)	2184(2)	6119(2)	14(1)
C(17)	8138(2)	2881(3)	5417(2)	15(1)
C(18)	7658(2)	3653(3)	5867(2)	16(1)
C(19)	7845(2)	3781(3)	7028(2)	16(1)
C(20)	8548(2)	3138(3)	7719(2)	14(1)
C(21)	9074(2)	2340(2)	7297(2)	12(1)
C(22)	14362(2)	-1303(3)	16039(3)	24(1)
C(23)	14981(2)	-294(3)	16417(3)	26(1)
C(24)	14988(2)	106(3)	17493(3)	26(1)
C(25)	14371(2)	-670(3)	17785(3)	24(1)
C(26)	13986(2)	-1533(3)	16888(3)	25(1)
N(2)	10089(2)	1799(2)	9126(2)	16(1)
N(7)	11965(2)	1133(2)	12976(2)	19(1)
N(15)	9301(1)	1412(2)	5615(2)	15(1)
Cl(1)	6799(1)	4535(1)	4988(1)	23(1)
Fe(1)	13800(1)	374(1)	16353(1)	15(1)

Bond lengths [A] and angles [deg] for **14**.

C(1)-C(5)	1.426(4)
C(1)-C(2)	1.428(4)
C(1)-C(6)	1.490(4)
C(1)-Fe(1)	2.052(3)
C(2)-C(3)	1.414(4)
C(2)-Fe(1)	2.034(3)
C(2)-H(2)	0.9500
C(3)-C(4)	1.418(4)
C(3)-Fe(1)	2.033(3)
C(3)-H(3)	0.9500
C(4)-C(5)	1.424(4)
C(4)-Fe(1)	2.042(3)
C(4)-H(4)	0.9500
C(5)-Fe(1)	2.047(3)
C(5)-H(5)	0.9500
C(6)-N(7)	1.463(3)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(8)-N(7)	1.459(3)
C(8)-C(9)	1.518(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.519(4)
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-N(2)	1.454(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(12)-N(2)	1.353(3)
C(12)-C(13)	1.389(4)
C(12)-C(21)	1.440(3)
C(13)-C(14)	1.391(4)
C(13)-H(13)	0.9500
C(14)-N(15)	1.328(3)
C(14)-H(14)	0.9500
C(16)-N(15)	1.365(3)
C(16)-C(17)	1.415(3)
C(16)-C(21)	1.423(3)
C(17)-C(18)	1.361(4)
C(17)-H(17)	0.9500
C(18)-C(19)	1.405(4)
C(18)-Cl(1)	1.738(3)
C(19)-C(20)	1.369(4)
C(19)-H(19)	0.9500
C(20)-C(21)	1.410(4)
C(20)-H(20)	0.9500
C(22)-C(23)	1.417(4)
C(22)-C(26)	1.418(4)
C(22)-Fe(1)	2.042(3)
C(22)-H(22)	0.9500
C(23)-C(24)	1.416(5)
C(23)-Fe(1)	2.033(3)
C(23)-H(23)	0.9500
C(24)-C(25)	1.424(4)
C(24)-Fe(1)	2.034(3)
C(24)-H(24)	0.9500
C(25)-C(26)	1.413(4)
C(25)-Fe(1)	2.047(3)
C(25)-H(25)	0.9500
C(26)-Fe(1)	2.049(3)
C(26)-H(26)	0.9500
N(2)-H(2N)	0.77(3)
N(7)-H(7N)	0.79(3)
C(5)-C(1)-C(2)	106.8(3)
C(5)-C(1)-C(6)	126.9(3)
C(2)-C(1)-C(6)	126.2(3)
C(5)-C(1)-Fe(1)	69.45(15)
C(2)-C(1)-Fe(1)	68.88(15)
C(6)-C(1)-Fe(1)	129.2(2)
C(3)-C(2)-C(1)	108.7(3)
C(3)-C(2)-Fe(1)	69.63(16)
C(1)-C(2)-Fe(1)	70.21(15)
C(3)-C(2)-H(2)	125.6
C(1)-C(2)-H(2)	125.6
Fe(1)-C(2)-H(2)	126.1
C(2)-C(3)-C(4)	108.2(2)
C(2)-C(3)-Fe(1)	69.70(16)
C(4)-C(3)-Fe(1)	69.98(16)
C(2)-C(3)-H(3)	125.9
C(4)-C(3)-H(3)	125.9
Fe(1)-C(3)-H(3)	126.0
C(3)-C(4)-C(5)	107.7(3)
C(3)-C(4)-Fe(1)	69.31(16)
C(5)-C(4)-Fe(1)	69.79(16)
C(3)-C(4)-H(4)	126.2
C(5)-C(4)-H(4)	126.2
Fe(1)-C(4)-H(4)	126.3
C(4)-C(5)-C(1)	108.6(2)
C(4)-C(5)-Fe(1)	69.44(15)
C(1)-C(5)-Fe(1)	69.84(15)
C(4)-C(5)-H(5)	125.7
C(1)-C(5)-H(5)	125.7
Fe(1)-C(5)-H(5)	126.6
N(7)-C(6)-C(1)	110.1(2)
N(7)-C(6)-H(6A)	109.6
C(1)-C(6)-H(6A)	109.6
N(7)-C(6)-H(6B)	109.6
C(1)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
N(7)-C(8)-C(9)	110.2(2)
N(7)-C(8)-H(8A)	109.6
C(9)-C(8)-H(8A)	109.6
N(7)-C(8)-H(8B)	109.6
C(9)-C(8)-H(8B)	109.6
H(8A)-C(8)-H(8B)	108.1
C(8)-C(9)-C(10)	111.2(2)
C(8)-C(9)-H(9A)	109.4
C(10)-C(9)-H(9A)	109.4
C(8)-C(9)-H(9B)	109.4
C(10)-C(9)-H(9B)	109.4
H(9A)-C(9)-H(9B)	108.0
N(2)-C(10)-C(9)	111.0(2)
N(2)-C(10)-H(10A)	109.4
C(9)-C(10)-H(10A)	109.4
N(2)-C(10)-H(10B)	109.4
C(9)-C(10)-H(10B)	109.4
H(10A)-C(10)-H(10B)	108.0
N(2)-C(12)-C(13)	122.0(2)

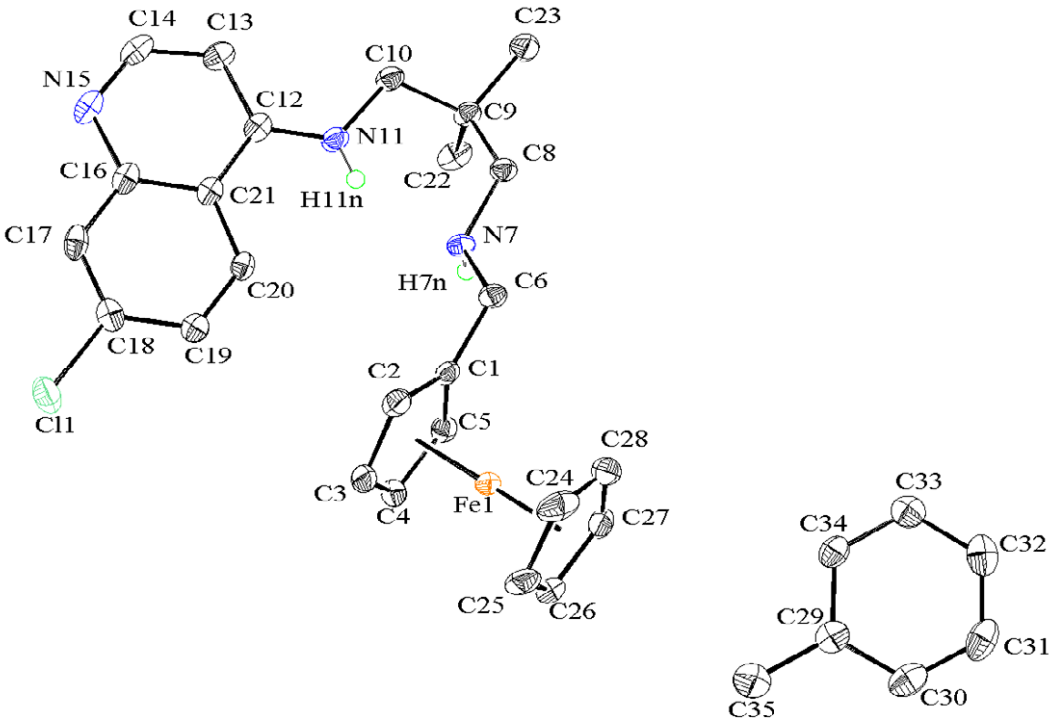
N(2)-C(12)-C(21)	121.5(2)
C(13)-C(12)-C(21)	116.6(2)
C(12)-C(13)-C(14)	120.1(2)
C(12)-C(13)-H(13)	120.0
C(14)-C(13)-H(13)	120.0
N(15)-C(14)-C(13)	125.8(3)
N(15)-C(14)-H(14)	117.1
C(13)-C(14)-H(14)	117.1
N(15)-C(16)-C(17)	117.4(2)
N(15)-C(16)-C(21)	124.0(2)
C(17)-C(16)-C(21)	118.5(2)
C(18)-C(17)-C(16)	120.3(2)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(17)-C(18)-C(19)	122.0(2)
C(17)-C(18)-Cl(1)	119.5(2)
C(19)-C(18)-Cl(1)	118.5(2)
C(20)-C(19)-C(18)	118.5(3)
C(20)-C(19)-H(19)	120.8
C(18)-C(19)-H(19)	120.8
C(19)-C(20)-C(21)	121.9(2)
C(19)-C(20)-H(20)	119.0
C(21)-C(20)-H(20)	119.0
C(20)-C(21)-C(16)	118.7(2)
C(20)-C(21)-C(12)	123.3(2)
C(16)-C(21)-C(12)	118.0(2)
C(23)-C(22)-C(26)	107.8(3)
C(23)-C(22)-Fe(1)	69.28(17)
C(26)-C(22)-Fe(1)	70.00(17)
C(23)-C(22)-H(22)	126.1
C(26)-C(22)-H(22)	126.1
Fe(1)-C(22)-H(22)	126.2
C(24)-C(23)-C(22)	108.4(3)
C(24)-C(23)-Fe(1)	69.69(18)
C(22)-C(23)-Fe(1)	70.03(17)
C(24)-C(23)-H(23)	125.8
C(22)-C(23)-H(23)	125.8
Fe(1)-C(23)-H(23)	126.0
C(23)-C(24)-C(25)	107.6(3)
C(23)-C(24)-Fe(1)	69.55(16)
C(25)-C(24)-Fe(1)	70.06(16)
C(23)-C(24)-H(24)	126.2
C(25)-C(24)-H(24)	126.2
Fe(1)-C(24)-H(24)	125.8
C(26)-C(25)-C(24)	108.0(3)
C(26)-C(25)-Fe(1)	69.91(17)
C(24)-C(25)-Fe(1)	69.10(16)
C(26)-C(25)-H(25)	126.0
C(24)-C(25)-H(25)	126.0
Fe(1)-C(25)-H(25)	126.6
C(25)-C(26)-C(22)	108.2(3)
C(25)-C(26)-Fe(1)	69.74(17)
C(22)-C(26)-Fe(1)	69.46(17)
C(25)-C(26)-H(26)	125.9
C(22)-C(26)-H(26)	125.9
Fe(1)-C(26)-H(26)	126.5
C(12)-N(2)-C(10)	121.8(2)
C(12)-N(2)-H(2N)	120(2)
C(10)-N(2)-H(2N)	118(2)
C(8)-N(7)-C(6)	112.7(2)
C(8)-N(7)-H(7N)	107(2)
C(6)-N(7)-H(7N)	109(2)
C(14)-N(15)-C(16)	115.4(2)
C(23)-Fe(1)-C(3)	121.52(13)
C(23)-Fe(1)-C(2)	105.97(12)
C(3)-Fe(1)-C(2)	40.67(12)
C(23)-Fe(1)-C(24)	40.75(13)
C(3)-Fe(1)-C(24)	104.90(12)
C(2)-Fe(1)-C(24)	119.53(12)
C(23)-Fe(1)-C(4)	158.27(13)
C(3)-Fe(1)-C(4)	40.72(12)
C(2)-Fe(1)-C(4)	68.48(12)
C(24)-Fe(1)-C(4)	122.23(12)
C(23)-Fe(1)-C(22)	40.69(13)
C(3)-Fe(1)-C(22)	158.94(13)
C(2)-Fe(1)-C(22)	123.73(13)
C(24)-Fe(1)-C(22)	68.60(13)
C(4)-Fe(1)-C(22)	159.57(13)
C(23)-Fe(1)-C(5)	158.63(13)
C(3)-Fe(1)-C(5)	68.44(11)
C(2)-Fe(1)-C(5)	68.33(11)
C(24)-Fe(1)-C(5)	160.21(13)
C(4)-Fe(1)-C(5)	40.77(11)
C(22)-Fe(1)-C(5)	124.13(12)
C(23)-Fe(1)-C(25)	68.35(13)
C(3)-Fe(1)-C(25)	120.75(12)
C(2)-Fe(1)-C(25)	155.80(12)
C(24)-Fe(1)-C(25)	40.84(12)
C(4)-Fe(1)-C(25)	107.62(12)
C(22)-Fe(1)-C(25)	68.21(12)
C(5)-Fe(1)-C(25)	125.28(12)
C(23)-Fe(1)-C(26)	68.24(12)
C(3)-Fe(1)-C(26)	157.53(13)
C(2)-Fe(1)-C(26)	161.41(12)
C(24)-Fe(1)-C(26)	68.41(12)
C(4)-Fe(1)-C(26)	123.43(12)
C(22)-Fe(1)-C(26)	40.54(12)
C(5)-Fe(1)-C(26)	110.25(12)
C(25)-Fe(1)-C(26)	40.35(12)
C(23)-Fe(1)-C(1)	121.58(12)
C(3)-Fe(1)-C(1)	68.83(11)
C(2)-Fe(1)-C(1)	40.91(11)
C(24)-Fe(1)-C(1)	156.16(12)
C(4)-Fe(1)-C(1)	68.84(11)
C(22)-Fe(1)-C(1)	108.58(12)
C(5)-Fe(1)-C(1)	40.71(11)
C(25)-Fe(1)-C(1)	162.03(12)
C(26)-Fe(1)-C(1)	125.82(12)

Symmetry transformations used to generate equivalent atoms:

Hydrogen Bonds in **14.**

Donor --- H....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(2) --H(2N) ..N(15)	[4555.01]	0.77(3)	2.42(3)	3.180(3)	168(3)

III X-ray Structure Data: Compound 15



Experimental

Data Collection

An irregular red crystal of $C_{25}H_{28}N_3FeCl$ x C_7H_8 having approximate dimensions of 0.10 x 0.25 x 0.35 mm was mounted on a glass fiber. All measurements were made on a *Bruker* APEX II diffractometer with graphite monochromated Mo-Kα radiation.

The data were collected at a temperature of -170.0 ± 0.1 °C to a maximum 2θ value of 56.1°. Data were collected in a series of ϕ and ω scans in 0.50° oscillations with 10.0-second exposures. The crystal-to-detector distance was 40.00 mm.

Data Reduction

Of the 75057 reflections that were collected, 6611 were unique (R_{int} = 0.040); equivalent reflections were merged. Data were collected and integrated using the *Bruker* SAINT1 software package. The linear absorption coefficient, μ, for Mo-Kα radiation is 6.77 cm^{-1}. Data were corrected for absorption

effects using the multi-scan technique (SADABS [11]), with minimum and maximum transmission coefficients of 0.823 and 0.935, respectively. The data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The structure was solved by direct methods.3 The material crystallizes with toluene in the lattice. All non-hydrogen atoms were refined anisotropically. All N-H hydrogen atoms were located in difference maps and refined isotropically. All other hydrogen atoms were placed in calculated positions. The final cycle of full-matrix least-squares refinement4 on F^2 was based on 6611 reflections and 345 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, ||Fo| - |Fc|| \, / \, \Sigma \, |Fo| = 0.046$$

$$wR2 = [\, \Sigma \, (\, w \, (Fo^2 - Fc^2)^2 \,) / \, \Sigma \, w(Fo^2)^2]^{1/2} = 0.096$$

The standard deviation of an observation of unit weight5 was 1.05. The weighting scheme was based on counting statistics. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.45 and –0.52 $e^-/Å^3$, respectively.

Neutral atom scattering factors were taken from *Cromer* and *Waber*.6 Anomalous dispersion effects were included in Fcalc;[7] the values for Δf' and Δf'' were those of *Creagh* and *McAuley*.8 The values for the mass attenuation coefficients are those of *Creagh* and *Hubbell*.[9] All refinements were performed using the SHELXL-97[10] via the WinGX[12] interface.

EXPERIMENTAL DETAILS

A. Crystal Data

Empirical Formula	$C_{32}H_{36}N_3FeCl$
Formula Weight	553.94
Crystal Colour, Habit	red, irregular
Crystal Dimensions	0.10 X 0.25 X 0.35 mm
Crystal System	orthorhombic
Lattice Type	primitive
Lattice Parameters	a = 13.1852(5) Å
	b = 18.4105(7) Å
	c = 22.4888(9) Å
	α = 90°
	β = 90°
	γ = 90°
	V = 5459.1(4) $Å^3$

[11] SADABS. Bruker Nonius area detector scaling and absorption correction - V2008/1, Bruker AXS Inc., Madison, Wisconsin, USA (2008).
[12] WinGX – V1.70 – Farrugia, L.J.; J. Appl. Cryst., 32, 837 (1999).

Space Group	*P bca* (#61)
Z value	8
D_{calc}	1.348 g/cm^3
F_{000}	2336.00
μ(MoKα)	6.77 cm^{-1}

B. Intensity Measurements

Diffractometer	Bruker X8 APEX II
Radiation	MoKα (λ = 0.71073 Å) graphite monochromated
Data Images	1413 exposures @ 10.0 seconds
Detector Position	40.00 mm
$2\theta_{max}$	56.1°
No. of Reflections Measured	Total: 75057 Unique: 6611(R_{int} = 0.040)
Corrections	Absorption (T_{min} = 0.823, T_{max}= 0.935) Lorentz-polarization

C. Structure Solution and Refinement

Structure Solution	Direct Methods (SIR97)
Refinement	Full-matrix least-squares on F^2
Function Minimized	Σ w ($Fo^2 - Fc^2$)^2
Least Squares Weights	w=1/($\sigma^2(Fo^2)$+(0.0473P)^2+ 3.4742P)
Anomalous Dispersion	All non-hydrogen atoms
No. Observations (I>0.00σ(I))	6611
No. Variables	345
Reflection/Parameter Ratio	19.16
Residuals (refined on F^2, all data):	R1; wR2 0.046; 0.096
Goodness of Fit Indicator	1.05
No. Observations (I>2.00σ(I))	5423
Residuals (refined on F): R1; wR2	0.033; 0.087
Max Shift/Error in Final Cycle	0.00
Maximum peak in Final Diff. Map	0.45 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.52 e$^-$/Å^3

Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **15**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	7737(1)	711(1)	4265(1)	19(1)
C(2)	7302(1)	1163(1)	4715(1)	23(1)
C(3)	6274(1)	953(1)	4797(1)	24(1)
C(4)	6061(1)	378(1)	4394(1)	23(1)
C(5)	6960(1)	227(1)	4067(1)	20(1)
C(6)	8799(1)	750(1)	4029(1)	20(1)
C(8)	9827(1)	1000(1)	3153(1)	20(1)
C(9)	9874(1)	1296(1)	2514(1)	21(1)
C(10)	9650(1)	2117(1)	2494(1)	22(1)
C(12)	8239(1)	2940(1)	2781(1)	20(1)
C(13)	8546(1)	3515(1)	2416(1)	24(1)
C(14)	7990(1)	4162(1)	2419(1)	27(1)
C(16)	6864(1)	3750(1)	3105(1)	21(1)
C(17)	6000(1)	3877(1)	3461(1)	24(1)
C(18)	5691(1)	3369(1)	3865(1)	23(1)
C(19)	6207(1)	2707(1)	3939(1)	22(1)
C(20)	7030(1)	2567(1)	3587(1)	19(1)
C(21)	7374(1)	3072(1)	3157(1)	19(1)
C(22)	9134(2)	891(1)	2108(1)	28(1)
C(23)	10956(1)	1183(1)	2286(1)	31(1)
C(24)	7952(2)	-33(1)	5751(1)	35(1)
C(25)	6922(2)	-249(1)	5803(1)	29(1)
C(26)	6749(1)	-819(1)	5390(1)	26(1)
C(27)	7670(1)	-951(1)	5080(1)	30(1)
C(28)	8412(1)	-464(1)	5304(1)	35(1)
C(29)	8713(1)	-2724(1)	6117(1)	28(1)
C(30)	8963(2)	-3359(1)	6424(1)	33(1)
C(31)	9884(2)	-3699(1)	6339(1)	33(1)
C(32)	10581(2)	-3417(1)	5943(1)	32(1)
C(33)	10349(1)	-2788(1)	5632(1)	28(1)
C(34)	9419(1)	-2447(1)	5716(1)	25(1)
C(35)	7717(2)	-2349(1)	6220(1)	42(1)
N(7)	8794(1)	956(1)	3396(1)	19(1)
N(11)	8701(1)	2289(1)	2792(1)	22(1)
N(15)	7171(1)	4300(1)	2736(1)	26(1)
Cl(1)	4637(1)	3544(1)	4310(1)	33(1)
Fe(1)	7212(1)	95(1)	4956(1)	18(1)

Bond lengths [A] and angles [deg] for **15**.

C(1)-C(5)	1.428(2)
C(1)-C(2)	1.431(2)
C(1)-C(6)	1.499(2)
C(1)-Fe(1)	2.0451(15)
C(2)-C(3)	1.422(2)
C(2)-Fe(1)	2.0436(16)
C(2)-H(2)	0.9500
C(3)-C(4)	1.422(2)
C(3)-Fe(1)	2.0388(17)
C(3)-H(3)	0.9500
C(4)-C(5)	1.422(2)
C(4)-Fe(1)	2.0418(17)
C(4)-H(4)	0.9500
C(5)-Fe(1)	2.0401(16)
C(5)-H(5)	0.9500
C(6)-N(7)	1.474(2)
C(6)-H(6A)	0.9900
C(6)-H(6B)	0.9900
C(8)-N(7)	1.470(2)
C(8)-C(9)	1.539(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(23)	1.529(2)
C(9)-C(22)	1.530(2)
C(9)-C(10)	1.541(2)
C(10)-N(11)	1.455(2)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(12)-N(11)	1.345(2)
C(12)-C(13)	1.399(2)
C(12)-C(21)	1.440(2)
C(13)-C(14)	1.399(2)
C(13)-H(13)	0.9500
C(14)-N(15)	1.319(2)
C(14)-H(14)	0.9500
C(16)-N(15)	1.371(2)
C(16)-C(17)	1.412(2)
C(16)-C(21)	1.423(2)
C(17)-C(18)	1.365(2)
C(17)-H(17)	0.9500
C(18)-C(19)	1.406(2)
C(18)-Cl(1)	1.7436(18)
C(19)-C(20)	1.369(2)
C(19)-H(19)	0.9500
C(20)-C(21)	1.415(2)
C(20)-H(20)	0.9500
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-C(28)	1.417(3)
C(24)-C(25)	1.420(3)
C(24)-Fe(1)	2.0498(19)
C(24)-H(24)	0.9500
C(25)-C(26)	1.420(3)
C(25)-Fe(1)	2.0443(17)
C(25)-H(25)	0.9500
C(26)-C(27)	1.422(2)
C(26)-Fe(1)	2.0387(16)
C(26)-H(26)	0.9500
C(27)-C(28)	1.419(3)
C(27)-Fe(1)	2.0368(18)
C(27)-H(27)	0.9500
C(28)-Fe(1)	2.0420(18)
C(28)-H(28)	0.9500
C(29)-C(34)	1.393(2)
C(29)-C(30)	1.397(3)
C(29)-C(35)	1.502(3)
C(30)-C(31)	1.379(3)
C(30)-H(30)	0.9500
C(31)-C(32)	1.382(3)
C(31)-H(31)	0.9500
C(32)-C(33)	1.387(3)
C(32)-H(32)	0.9500
C(33)-C(34)	1.391(3)
C(33)-H(33)	0.9500
C(34)-H(34)	0.9500
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
N(7)-H(7N)	0.85(2)
N(11)-H(11N)	0.79(2)
C(5)-C(1)-C(2)	107.20(14)
C(5)-C(1)-C(6)	126.16(14)

C(2)-C(1)-C(6)	126.62(15)
C(5)-C(1)-Fe(1)	69.35(9)
C(2)-C(1)-Fe(1)	69.46(9)
C(6)-C(1)-Fe(1)	127.70(11)
C(3)-C(2)-C(1)	108.39(15)
C(3)-C(2)-Fe(1)	69.44(9)
C(1)-C(2)-Fe(1)	69.57(9)
C(3)-C(2)-H(2)	125.8
C(1)-C(2)-H(2)	125.8
Fe(1)-C(2)-H(2)	126.8
C(2)-C(3)-C(4)	107.96(15)
C(2)-C(3)-Fe(1)	69.80(9)
C(4)-C(3)-Fe(1)	69.72(9)
C(2)-C(3)-H(3)	126.0
C(4)-C(3)-H(3)	126.0
Fe(1)-C(3)-H(3)	126.0
C(5)-C(4)-C(3)	108.05(15)
C(5)-C(4)-Fe(1)	69.55(9)
C(3)-C(4)-Fe(1)	69.49(10)
C(5)-C(4)-H(4)	126.0
C(3)-C(4)-H(4)	126.0
Fe(1)-C(4)-H(4)	126.6
C(4)-C(5)-C(1)	108.39(14)
C(4)-C(5)-Fe(1)	69.68(9)
C(1)-C(5)-Fe(1)	69.72(9)
C(4)-C(5)-H(5)	125.8
C(1)-C(5)-H(5)	125.8
Fe(1)-C(5)-H(5)	126.4
N(7)-C(6)-C(1)	110.46(13)
N(7)-C(6)-H(6A)	109.6
C(1)-C(6)-H(6A)	109.6
N(7)-C(6)-H(6B)	109.6
C(1)-C(6)-H(6B)	109.6
H(6A)-C(6)-H(6B)	108.1
N(7)-C(8)-C(9)	113.77(13)
N(7)-C(8)-H(8A)	108.8
C(9)-C(8)-H(8A)	108.8
N(7)-C(8)-H(8B)	108.8
C(9)-C(8)-H(8B)	108.8
H(8A)-C(8)-H(8B)	107.7
C(23)-C(9)-C(22)	109.22(14)
C(23)-C(9)-C(8)	107.57(14)
C(22)-C(9)-C(8)	111.08(13)
C(23)-C(9)-C(10)	107.59(13)
C(22)-C(9)-C(10)	109.76(14)
C(8)-C(9)-C(10)	111.52(13)
N(11)-C(10)-C(9)	111.41(13)
N(11)-C(10)-H(10A)	109.3
C(9)-C(10)-H(10A)	109.3
N(11)-C(10)-H(10B)	109.3
C(9)-C(10)-H(10B)	109.3
H(10A)-C(10)-H(10B)	108.0
N(11)-C(12)-C(13)	123.67(16)
N(11)-C(12)-C(21)	119.83(14)
C(13)-C(12)-C(21)	116.50(15)
C(12)-C(13)-C(14)	119.31(16)
C(12)-C(13)-H(13)	120.3
C(14)-C(13)-H(13)	120.3
N(15)-C(14)-C(13)	126.63(16)
N(15)-C(14)-H(14)	116.7
C(13)-C(14)-H(14)	116.7
N(15)-C(16)-C(17)	117.30(15)
N(15)-C(16)-C(21)	123.98(16)
C(17)-C(16)-C(21)	118.71(15)
C(18)-C(17)-C(16)	120.25(15)
C(18)-C(17)-H(17)	119.9
C(16)-C(17)-H(17)	119.9
C(17)-C(18)-C(19)	121.98(16)
C(17)-C(18)-Cl(1)	119.52(13)
C(19)-C(18)-Cl(1)	118.50(13)
C(20)-C(19)-C(18)	118.45(16)
C(20)-C(19)-H(19)	120.8
C(18)-C(19)-H(19)	120.8
C(19)-C(20)-C(21)	121.81(15)
C(19)-C(20)-H(20)	119.1
C(21)-C(20)-H(20)	119.1
C(20)-C(21)-C(16)	118.71(15)
C(20)-C(21)-C(12)	122.97(14)
C(16)-C(21)-C(12)	118.29(14)
C(9)-C(22)-H(22A)	109.5
C(9)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(9)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5
C(9)-C(23)-H(23A)	109.5
C(9)-C(23)-H(23B)	109.5
H(23A)-C(23)-H(23B)	109.5
C(9)-C(23)-H(23C)	109.5
H(23A)-C(23)-H(23C)	109.5
H(23B)-C(23)-H(23C)	109.5
C(28)-C(24)-C(25)	108.11(18)
C(28)-C(24)-Fe(1)	69.44(11)
C(25)-C(24)-Fe(1)	69.50(10)
C(28)-C(24)-H(24)	125.9
C(25)-C(24)-H(24)	125.9
Fe(1)-C(24)-H(24)	126.7
C(24)-C(25)-C(26)	107.88(17)
C(24)-C(25)-Fe(1)	69.92(10)
C(26)-C(25)-Fe(1)	69.44(10)
C(24)-C(25)-H(25)	126.1
C(26)-C(25)-H(25)	126.1
Fe(1)-C(25)-H(25)	126.1
C(25)-C(26)-C(27)	108.05(17)
C(25)-C(26)-Fe(1)	69.86(10)
C(27)-C(26)-Fe(1)	69.51(10)
C(25)-C(26)-H(26)	126.0
C(27)-C(26)-H(26)	126.0
Fe(1)-C(26)-H(26)	126.2
C(28)-C(27)-C(26)	107.85(17)
C(28)-C(27)-Fe(1)	69.84(11)
C(26)-C(27)-Fe(1)	69.65(10)
C(28)-C(27)-H(27)	126.1
C(26)-C(27)-H(27)	126.1
Fe(1)-C(27)-H(27)	126.0
C(24)-C(28)-C(27)	108.11(16)
C(24)-C(28)-Fe(1)	70.03(11)
C(27)-C(28)-Fe(1)	69.45(10)
C(24)-C(28)-H(28)	125.9
C(27)-C(28)-H(28)	125.9
Fe(1)-C(28)-H(28)	126.2
C(34)-C(29)-C(30)	117.98(17)
C(34)-C(29)-C(35)	121.04(17)
C(30)-C(29)-C(35)	120.98(18)
C(31)-C(30)-C(29)	121.26(18)
C(31)-C(30)-H(30)	119.4
C(29)-C(30)-H(30)	119.4
C(30)-C(31)-C(32)	120.28(18)
C(30)-C(31)-H(31)	119.9
C(32)-C(31)-H(31)	119.9
C(31)-C(32)-C(33)	119.54(18)
C(31)-C(32)-H(32)	120.2
C(33)-C(32)-H(32)	120.2
C(32)-C(33)-C(34)	120.13(18)
C(32)-C(33)-H(33)	119.9
C(34)-C(33)-H(33)	119.9
C(33)-C(34)-C(29)	120.80(17)
C(33)-C(34)-H(34)	119.6

C(29)-C(34)-H(34)	119.6
C(29)-C(35)-H(35A)	109.5
C(29)-C(35)-H(35B)	109.5
H(35A)-C(35)-H(35B)	109.5
C(29)-C(35)-H(35C)	109.5
H(35A)-C(35)-H(35C)	109.5
H(35B)-C(35)-H(35C)	109.5
C(8)-N(7)-C(6)	111.59(13)
C(8)-N(7)-H(7N)	110.3(14)
C(6)-N(7)-H(7N)	106.8(14)
C(12)-N(11)-C(10)	125.10(14)
C(12)-N(11)-H(11N)	120.5(15)
C(10)-N(11)-H(11N)	113.2(15)
C(14)-N(15)-C(16)	115.20(14)
C(27)-Fe(1)-C(26)	40.84(7)
C(27)-Fe(1)-C(3)	159.54(8)
C(26)-Fe(1)-C(3)	122.82(7)
C(27)-Fe(1)-C(5)	107.20(7)
C(26)-Fe(1)-C(5)	121.28(7)
C(3)-Fe(1)-C(5)	68.71(7)
C(27)-Fe(1)-C(4)	123.12(8)
C(26)-Fe(1)-C(4)	106.52(7)
C(3)-Fe(1)-C(4)	40.80(7)
C(5)-Fe(1)-C(4)	40.77(6)
C(27)-Fe(1)-C(28)	40.71(8)
C(26)-Fe(1)-C(28)	68.48(7)
C(3)-Fe(1)-C(28)	158.01(8)
C(5)-Fe(1)-C(28)	124.16(8)
C(4)-Fe(1)-C(28)	160.22(8)
C(27)-Fe(1)-C(2)	158.23(7)
C(26)-Fe(1)-C(2)	159.79(7)
C(3)-Fe(1)-C(2)	40.76(7)
C(5)-Fe(1)-C(2)	68.60(7)
C(4)-Fe(1)-C(2)	68.53(7)
C(28)-Fe(1)-C(2)	122.73(8)
C(27)-Fe(1)-C(25)	68.59(7)
C(26)-Fe(1)-C(25)	40.69(7)
C(3)-Fe(1)-C(25)	106.86(7)
C(5)-Fe(1)-C(25)	156.88(7)
C(4)-Fe(1)-C(25)	121.12(7)
C(28)-Fe(1)-C(25)	68.40(8)
C(2)-Fe(1)-C(25)	123.76(7)
C(27)-Fe(1)-C(1)	121.89(7)
C(26)-Fe(1)-C(1)	157.43(7)
C(3)-Fe(1)-C(1)	69.01(6)
C(5)-Fe(1)-C(1)	40.93(6)
C(4)-Fe(1)-C(1)	68.89(6)
C(28)-Fe(1)-C(1)	107.96(7)
C(2)-Fe(1)-C(1)	40.97(6)
C(25)-Fe(1)-C(1)	160.66(7)
C(27)-Fe(1)-C(24)	68.37(8)
C(26)-Fe(1)-C(24)	68.31(8)
C(3)-Fe(1)-C(24)	122.00(8)
C(5)-Fe(1)-C(24)	160.95(8)
C(4)-Fe(1)-C(24)	157.25(8)
C(28)-Fe(1)-C(24)	40.53(9)
C(2)-Fe(1)-C(24)	108.24(8)
C(25)-Fe(1)-C(24)	40.58(7)
C(1)-Fe(1)-C(24)	124.41(7)

Symmetry transformations used to generate equivalent atoms

Hydrogen Bonds for **15**.

Donor --- H....Acceptor	[ARU]	D - H	H...A	D...A	D - H...A
N(11) --H(11N) ..N(7)	[ ]	0.79(2)	2.11(2)	2.807(2)	148(2)

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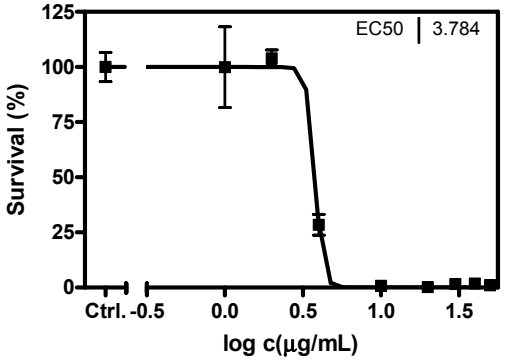
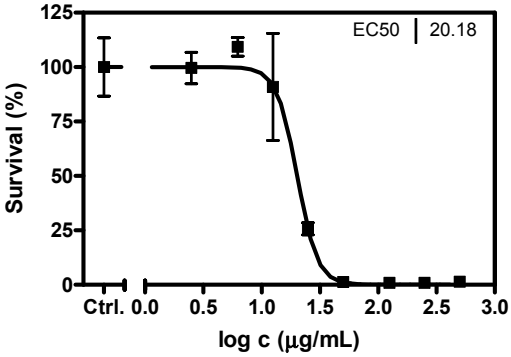
IV. Biological Activity Studies

MDA-MB-435S

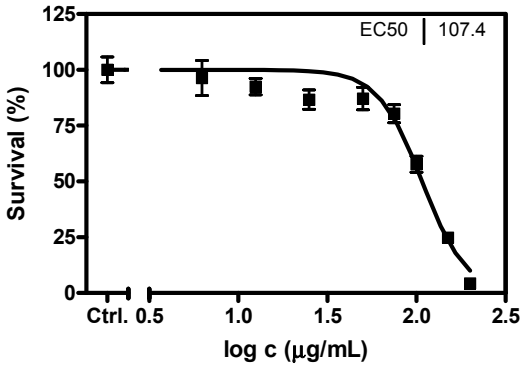
FQ vs. MDA-MB435S



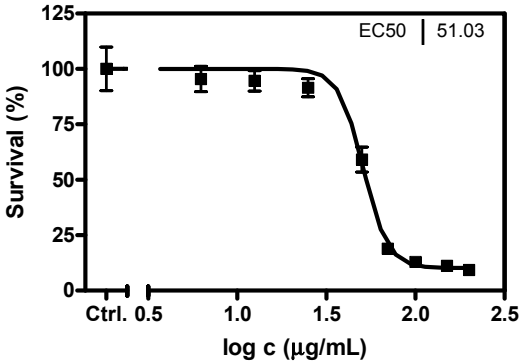
CQ vs. MDA-MB-435S



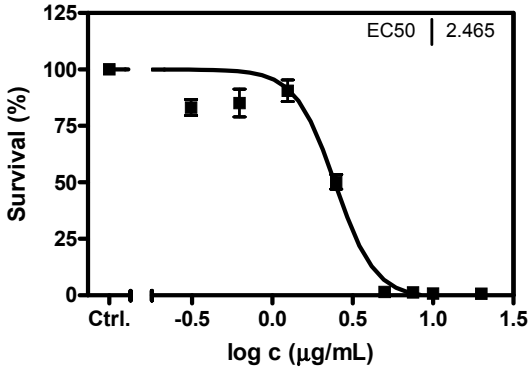
Compound 8 vs. MDA-MB-435S



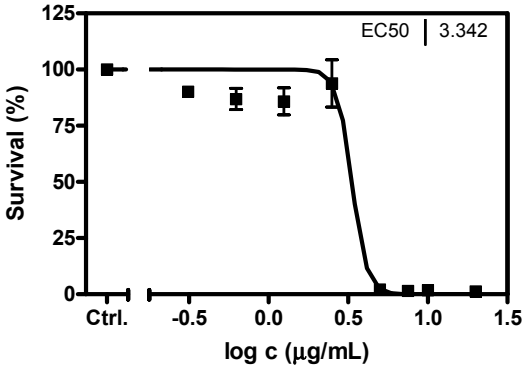
Compound 9 vs. MDA-MB-435S

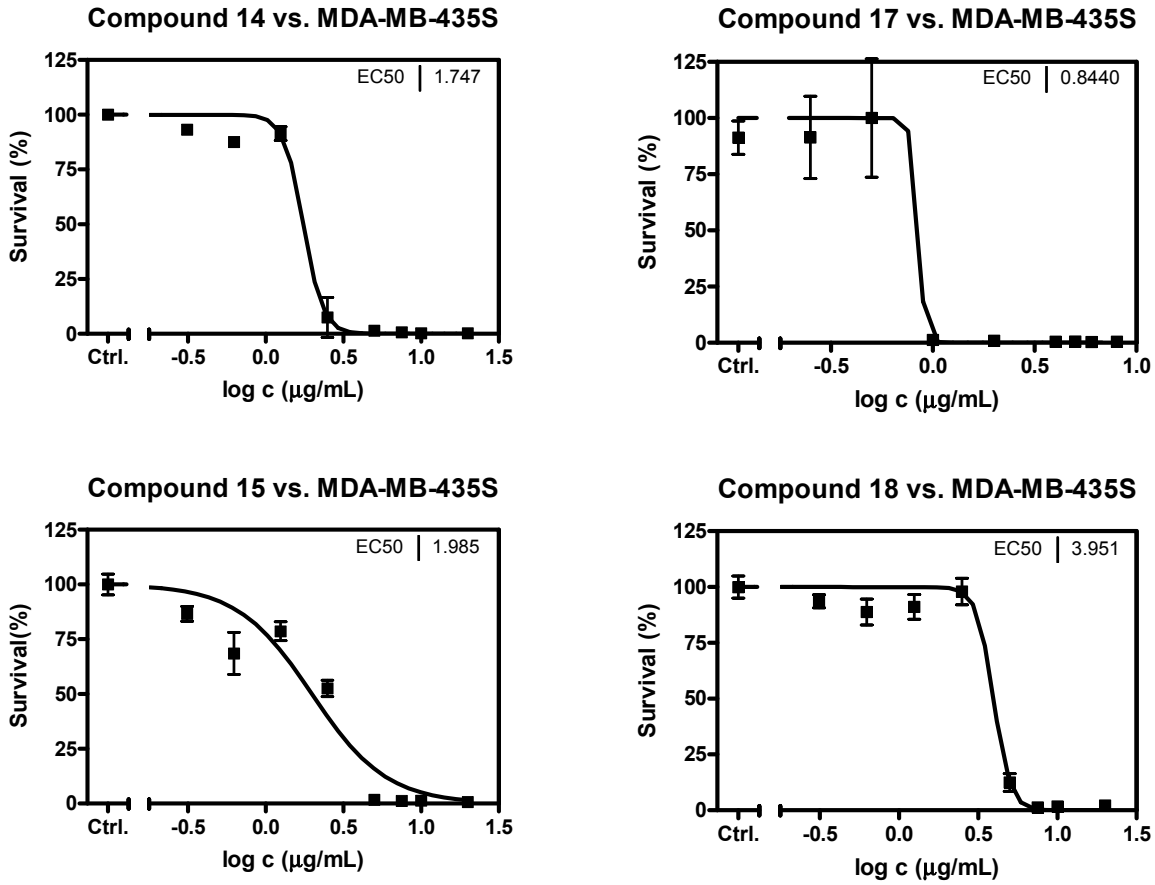


Compound 13 vs. MDA-MB-435S



Compound 16 vs. MDA-MB-435S

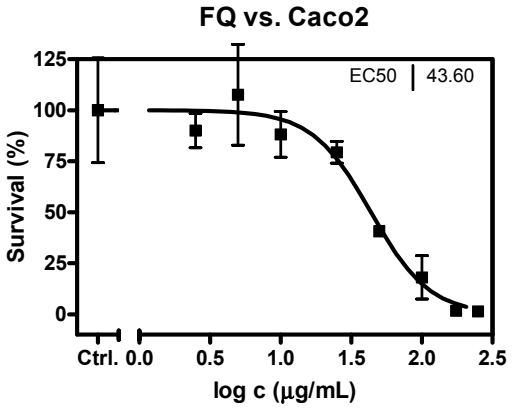


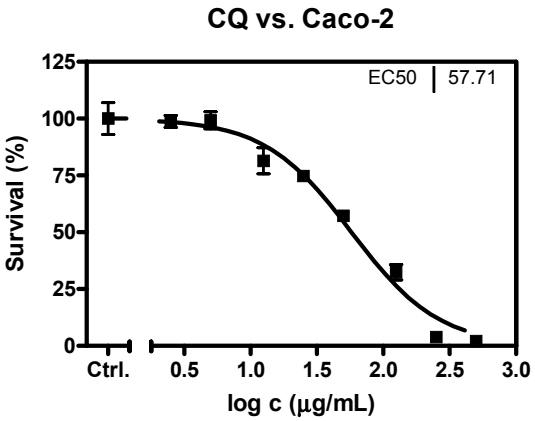


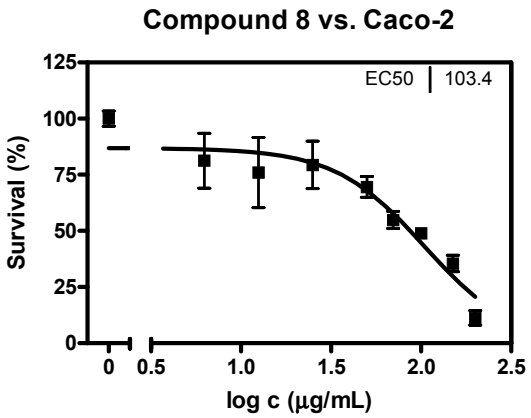
8, **9**, **13, 14, 15** tested as hexuplicates. The incubator was run without CO_2. Condensation in the 96 well-plates was a recurring problem, leading to varying read-out for equi-concentrated wells. The problem occured mostly on the outmost wells, even though a protective well-barrier with water was placed around the 6 x 10 grid.

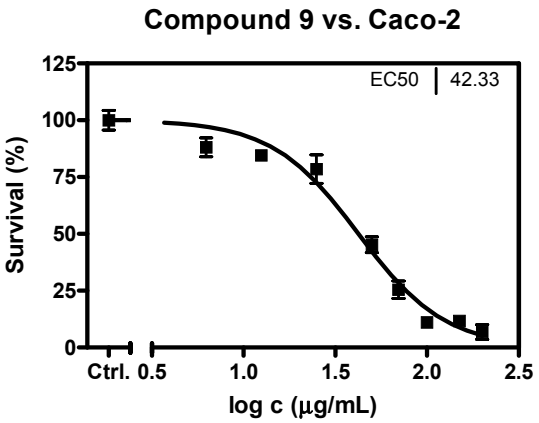
IC_{50} derived from a sigmoidal curve fit (variable slope) with top and bottom constrained to 100 % and 0 %, respectively. Bottom constraint was not used for compound **9**. Data points are the mean value, error bars are displayed as standard deviation (SD). Software used: GraphPad Prism 4.0.

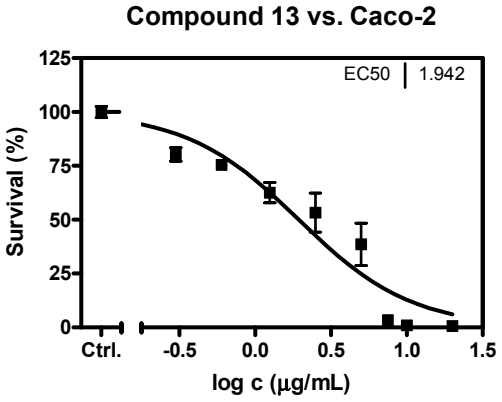
Caco-2

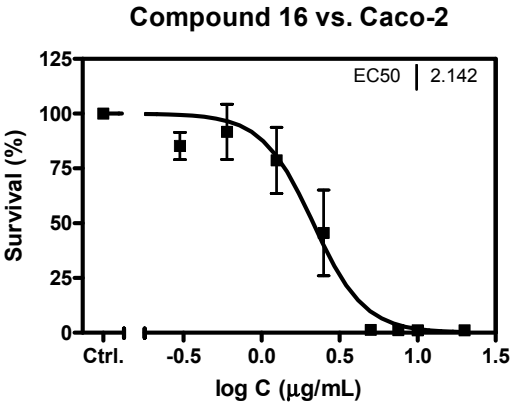


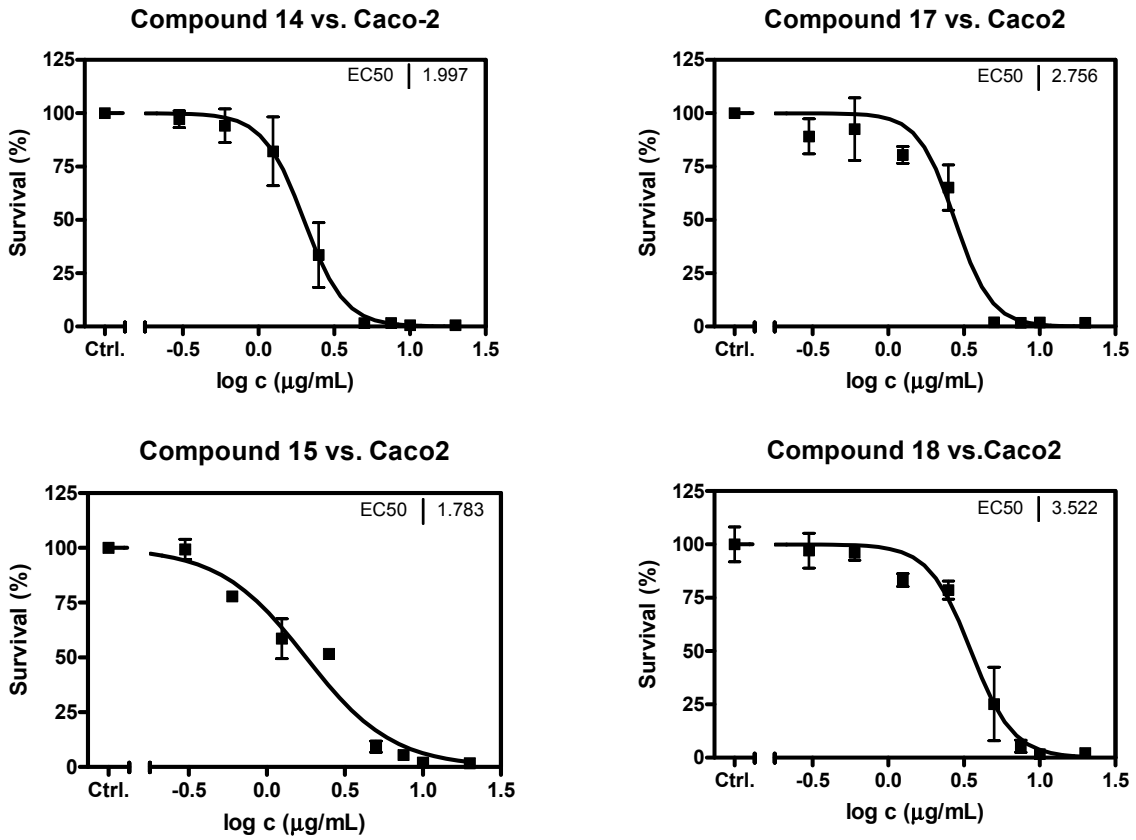








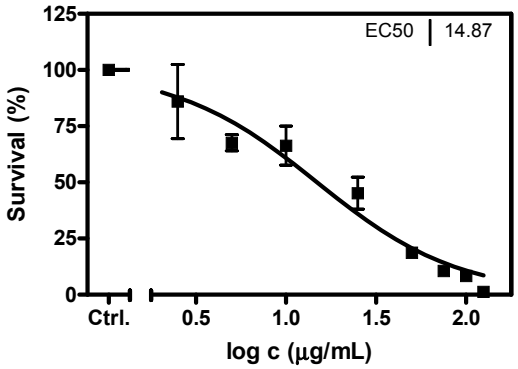




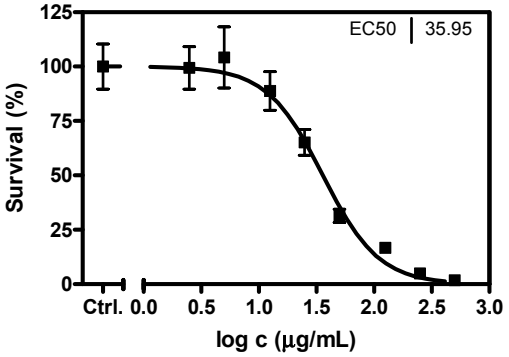
IC_{50} derived from a sigmoidal curve fit (variable slope) with top and bottom constrained to 100 % and 0 %, respectively. Data points are the mean value, error bars are displayed as standard deviation (SD). Software used: GraphPad Prism 4.0.

MCF-10A

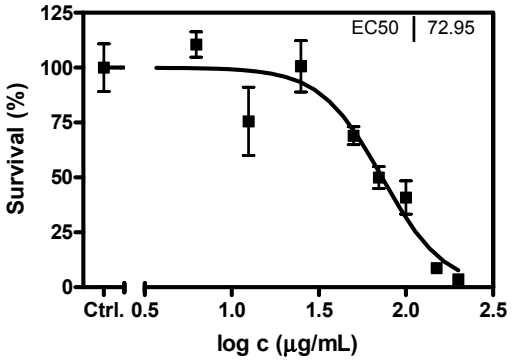
FQ vs. MCF-10A



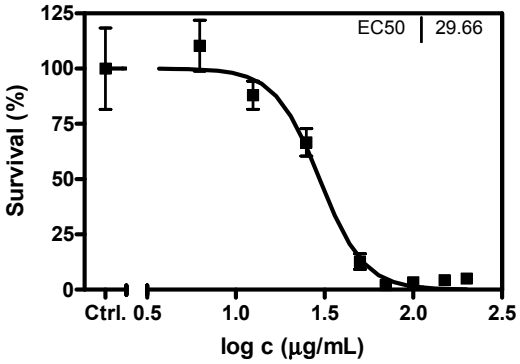
Chloroquine vs. MCF-10A



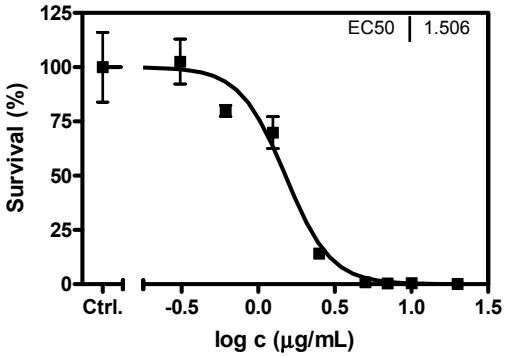
Compound 8 vs. MCF-10A



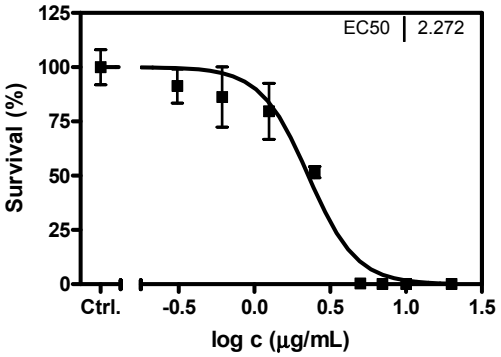
Compound 9 vs. MCF-10A

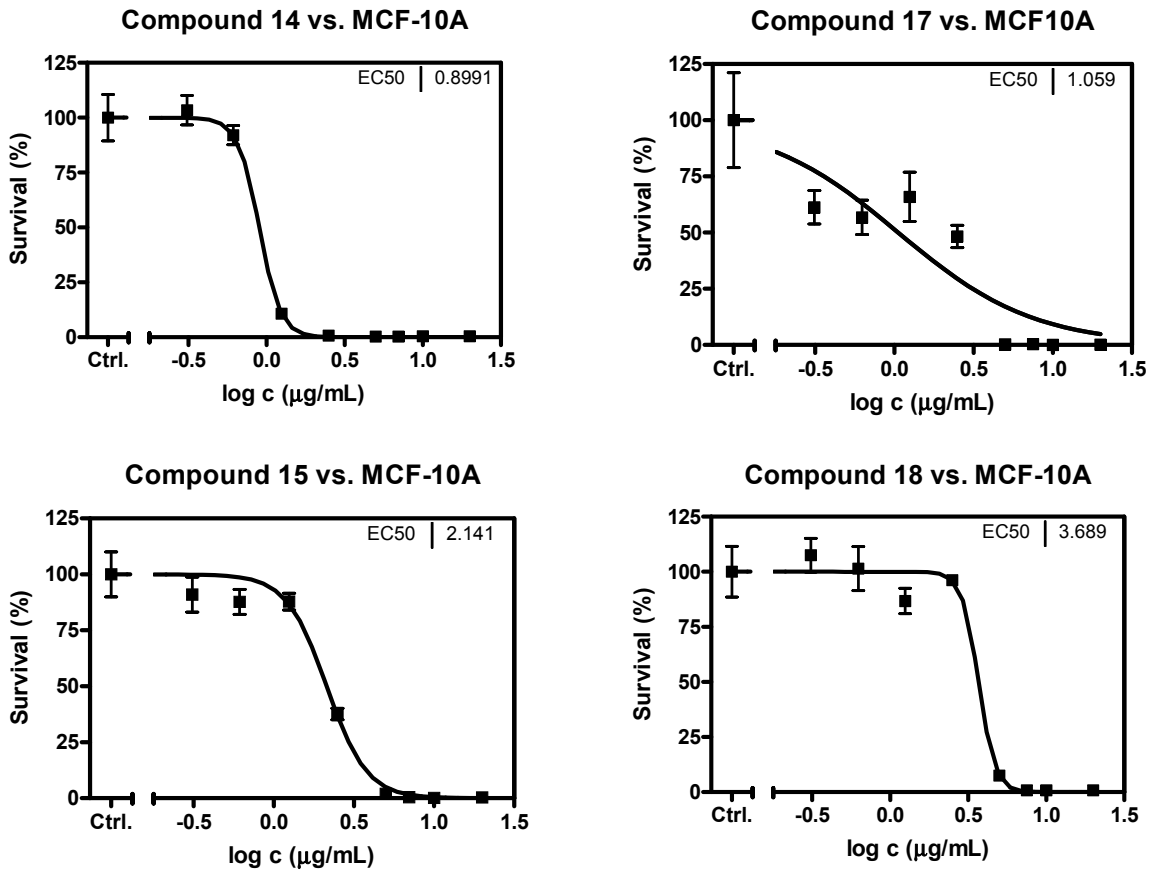


Compound 13 vs. MCF-10A



Compound 16 vs. MCF-10A





IC_{50} derived from a sigmoidal curve fit (variable slope) with top and bottom constrained to 100 % and 0 %, respectively. Data points are the mean value, error bars are displayed as standard deviation (SD). Software used: GraphPad Prism 4.0.