Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information.

Fine-Tuning of Ferrocene Redox Potentials Towards Multiplex DNA Detection.

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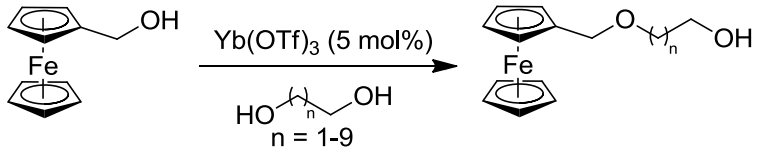
1. General.

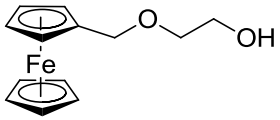
All reactions were carried out using oven dried glassware under and inert atmosphere of nitrogen unless otherwise stated. Solvents were dried prior to use using an Innovative Technology Inc. PS-400-7 solvent purification system. Reagents were used as supplied without further purification either from Sigma Aldrich Company Ltd or Alfa Aesar Ltd. Analytical thin layer chromatography was performed using commercial available aluminium backed plates coated with ALUGRAM® Xtra SIL G/UV_{254} from Macherey-Nagel Ltd. Plates were visualised under ultraviolet light (254 nm) or by chemical staining with potassium permanganate stain followed by gentle heating. Column chromatpgraphy was performed use silica gel 60Å pore size, 200-440 mesh particle size from Sigma Aldrich Company Ltd. The ^{1}H and ^{13}C NMR spectra were recored on a Brüker Avance 300 Mhz instruments. Chemical shifts are recorded in ppm and reference internally to C_6H_6 or $CHCl_3$ (as stated) at 7.16 and 7.26 ppm respectively for ^{1}H NMR and 128.1 or 77.0 ppm for ^{13}C NMR respectively. Mass spectrum analysis were recorded on a μTOF electrospray time of flight mass spectrometer (ESI-TOF). IR spectra were recorded on a Perkin Elmer 1600 FT IR spectrometer with selected absorbances quoted as υcm^{-1}. Melting points were recorded using a Buchi 535 melting point apparatus. Ferrocene methanol was synthesised *via* literature procedure.[1]

2. General Procedure A for etherification of ferrocene methanol with various diols.



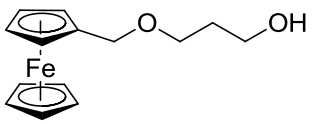
Ferrocene methanol (1 eq) was dissolved in appropriate diol (5 ml/mmo or 10 eql) and then treated with ytterbium triflate (5 mol %). The reaction was stirred at room temperature until TLC analysis showed full conversion. The reaction mixture was then diluted with ethyl acetate (20 mL) and the organics then washed with water (20 mL) and brine (sat.) (20 mL). The organic layer was then dried over $MgSO_4$, then filtered and concentrated *in vacuo*. Purification was then carried out by silica-gel chromatography eluting with hexane 1:1 ethyl acetate to give the desired product.

2-(Ferrocenyloxy)ethanol (1).



Using general procedure A with ferrocene methanol (545 mg, 2.5 mmol), ytterbium triflate (77 mg, 5 mol%) and ethylene glycol (10 mL). This gave the desired product as a yellow oil (389 mg, 59%). IR; υ_{max} (thin film) (cm^{-1}): 3431, 3100, 2903, 2856, 1464, 1396, 1234; ^1H NMR (300 MHz, C_6D_6); δ_H: 4.19–4.16 (m, 4H), 4.04 (s, 7H), 3.61 (br s, 2H), 3.38 (t, *J*=4.8 Hz, 2H), 1.99 (br s, 1H).; ^{13}C NMR (75 MHz, C_6D_6); δ_C 84.3, 71.8, 70.0, 69.9, 69.2, 69.1, 62.4. HRMS (ESI) calculated for $C_{13}H_{16}FeO_2Na$ m/z 283.0397 found 283.0372 (m/z + Na^+); Oxidation potential: 181 mV.

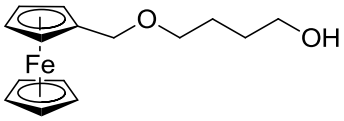
3-(Ferrocenyloxy)propan-1ol (2).[2]



Using general procedure A with ferrocene methanol (545 mg, 2.5 mmol), ytterbium triflate (77 mg, 5 mol%) and 1,3-propanediol (10 mL). This gave the desired product as an orange solid (514 mg, 75%). Mpt: 40–42 ^oC; IR; υ_{max} (thin film) (cm^{-1}): 3408, 3082, 2940, 2856, 1453, 1356, 1270, 1058; ^1H NMR (300 MHz, C_6D_6); δ_H: 4.17–4.13 (m, 4H), 4.07–4.03 (m,

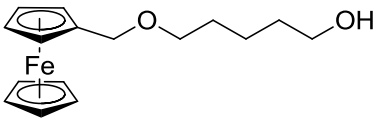
7H), 3.72 (app q, *J*=5.3, 2H), 3.48 (t, *J*=5.8, 2H), 2.19 (t, *J*=5.3, 1H), 1.87–1.52 (m, 2H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 84.7, 69.8, 69.6, 69.5, 69.2, 68.9, 62.1, 33.1; HRMS (ESI) calculated for $C_{14}H_{18}FeO_2Na$ m/z 297.0553 found 297.0560 (m/z + Na^+); Oxidation potential: 178 mV.

4-(Ferrocenyloxy)butan-1-ol (3).



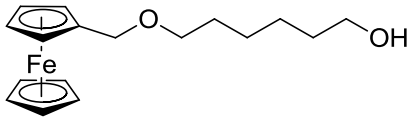
Using general procedure A with ferrocene methanol (500 mg, 2.35 mmol), ytterbium triflate (71 mg, 5 mol%) and 1,4-butanediol (10 mL). This gave the desired product as an orange oil (636 mg, 95%). IR; ν_{max} (thin film) (cm^{-1}): 3407, 3094, 2938, 2848, 1639, 1446, 1410, 1375, 1232, 1054; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.21–4.2 (m, 4H), 4.07–4.05 (m, 7H), 3.55 (br s, 2H), 3.38 (t, *J*=5.5, 2H), 2.08 (br s, 1H), 1.66–1.56 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 84.6, 70.5, 69.9, 69.7, 69.2, 68.9, 62.9, 31.1, 27.6; HRMS (ESI) calculated for $C_{15}H_{20}FeO_2Na$ m/z 311.0710 found 311.0710 (m/z + Na^+); Oxidation potential: 184 mV.

5-(Ferrocenyloxy)pentan-1-ol (4).



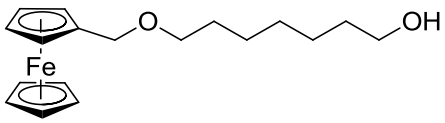
Using general procedure A with ferrocene methanol (545 mg, 2.5 mmol), ytterbium triflate (77 mg, 5 mol%) and 1,5-pentanediol (10 mL). This gave the desired product as a viscous orange oil (676 mg, 89%). IR; υ_{max} (thin film) (cm^{-1}): 3383, 3085, 2926, 1854, 1433, 1343, 1232; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4..07–4.06 (m, 4H), 3.90–3.87 (m, 7H), 3.28–3.22 (m, 4H), 1.47–1.42 (m, 2H), 1.30–1.21 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 85.0, 70.5, 69.9, 69.6, 69.2, 68.9, 62.8, 33.3, 30.3, 23.3; HRMS (ESI) calculated for $C_{16}H_{22}FeO_2Na$ m/z 325.0866 found 325.0880(m/z + Na^+); Oxidation potential: 186 mV.

6-(Ferrocenyloxyl)hexan-1-ol (5).[3]



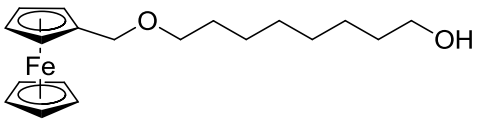
Using general procedure A with ferrocene methanol (420 mg, 1.9 mmol), ytterbium triflate (58.9 mg, 5 mol%) and 1,6-hexanediol (2.25 g, 19 mmol) with dry acetonitrile (5 cm^3) as solvent. This gave the desired product as a dark orange solid (538 mg, 89%). Mpt: 38–40 ^oC; IR; υ_{max}(thin film) (cm^{-1}): 3369, 3102, 2928, 2852, 1479, 1453, 1344, 1232, 1090 ^1H NMR (300 MHz, C_6D_6); δ_H: 4.28–4.25 (m, 4H), 4.08–4.00 (m, 7H), 3.47–3.43 (m, 4H), 1.69–1.60 (m, 2H), 1.49–1.28 (m, 6H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 85.2, 70.5, 69.9, 69.7, 69.2, 68.9, 62.9, 33.5, 30.7, 26.9, 26.3; HRMS (ESI) calculated for $C_{17}H_{24}FeO_2Na$ m/z 339.1023 found 339.1024 (m/z + Na^+); Oxidation potential: 195 mV.

7-(Ferrocenyloxy)heptan-1-ol (6).



Using general procedure A with ferrocene methanol (109 mg, 0.5 mmol), ytterbium triflate (15.5 mg, 5 mol%) and 1,7-heptanediol (2 ml). This gave the desired product as an orange oil (116 mg, 70%). IR; υ_{max}(thin film) (cm^{-1}) 3371, 3092, 2927, 2852, 2121, 1634, 1466, 1343, 1233; ^1H NMR (300 MHz, C_6D_6); δ_H: 4.29–4.26 (m, 4H), 4.09–4.06 (m, 7H), 3.49–3.41 (m, 4H), 1.71–1.62 (m, 2H), 1.54–1.28 (m, 8H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 85.2, 70.6, 69.9, 69.7, 69.2, 68.8, 63.1, 33.5, 30.6, 30.0, 27.1, 26.5; HRMS (ESI) calculated for $C_{18}H_{26}FeO_2Na$ m/z 353.1179 found 353.1191 (m/z + Na^+); Oxidation potential: 212 mV.

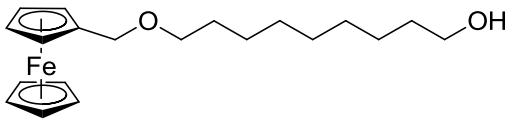
8-(Ferrocenyloxy)octan-1-ol (7).[3]



Using general procedure A with ferrocene methanol (109 mg, 0.5 mmol), ytterbium triflate (15.5 mg, 5 mol%) and 1,8-octanediol (731 mg, 5 mmol) in a minimal amount of dry 1,4-dioxane (5 ml). This gave the desired product as an orange oil (65 mg, 38%). IR; υ_{max}(thin film) (cm^{-1}): 3407, 3094, 2924, 2852, 1726, 1455, 1343, 1233, 1094; ^1H NMR (300 MHz,

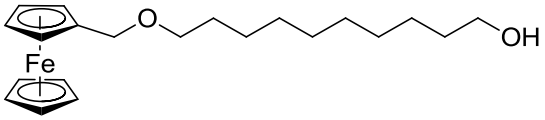
C_6D_6); δ_H: 4.30–4.26 (m, 4H), 4.09–4.06 (m, 7H), 3.51–3.42 (m, 4H), 1.73–1.64 (m, 2H), 1.45–1.30 (m, 10H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 85.2, 70.6, 69.9, 69.6, 69.2, 68.9, 63.1, 33.6, 30.7, 30.2, 30.2, 27.0, 26.5; HRMS (ESI) calculated for $C_{19}H_{28}FeO_2Na$ m/z 367.1336 found 367.1353 (m/z + Na^+). Oxidation potential: 233 mV.

8-(Ferrocenyloxy)nonan-1-ol (8).[3]



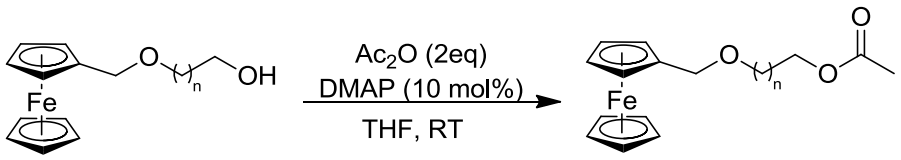
Using general procedure A with ferrocene methanol (109 mg, 0.5 mmol), ytterbium triflate (15.5 mg, 5 mol%) and 1,9-nonanediol (801 mg, 5 mmol) in a minimal amount of dry 1,4 dioxane (5 ml). This gave the desired product as an orange oil (66 mg, 37%). IR; υ_{max}(thin film) (cm^{-1}): 3407, 3093, 2925, 2852, 1725, 1434; ^1H NMR (300 MHz, C_6D_6); δ_H: δ = 4.19 (s, 2H), 4.16–4.15 (m, 2H), 4.06 (s, 7H), 3.55 (t, *J*=6.7, 2H), 3.33 (t, *J*=6.7, 2H), 1.52–1.45 (m, 4H), 1.28–1.21 (m, 10H); ^{13}C NMR (75 MHz, $CDCl_3$); δ_C 83.7, 70.1, 69.5, 69.1, 68.4, 63.0, 32.8, 29.7, 29.6, 29.4, 29.4, 26.2, 25.7; HRMS (ESI) calculated for $C_{20}H_{30}FeO_2Na$ m/z 381.1493 found 381.1561 (m/z + Na^+). Oxidation potential: 260 mV.

8-(Ferrocenyloxy)decan-1-ol (9).



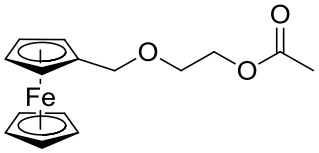
Using general procedure A with ferrocene methanol (430 mg, 2.5 mmol), ytterbium triflate (61 mg, 5 mol%) and 1,10-decanediol (3.4 g, 19.7 mmol) in a minimal amount of dry 1,4 dioxane (15 ml). This gave the desired product as an orange oil (346 mg, 47%). IR; υ_{max}(thin film) (cm^{-1}):3437, 3076, 2916, 2849, 1464, 1349; ^1H NMR (300 MHz, C_6D_6); δ_H: 4.30 (s, 2H), 4.26 (s, 2H), 4.09–4.07 (s, 7H), 3.52–3.44 (m, 4H), 1.75–1.66 (m, 2H), 1.48–1.32 (m, 14H); ^{13}C NMR (75 MHz, C_6D_6); δ_C 85.3, 70.6, 69.8, 69.7, 69.2, 68.8, 63.1, 33.6, 30.8, 30.4, 30.4, 30.3, 30.2, 27.1, 26.6; HRMS (ESI) calculated for $C_{21}H_{32}FeO_2Na$ m/z 395.1649 found 395.1637 (m/z + Na^+). Oxidation potential: 285 mV.

General Procedure B for the Acylation of ferrocene derived alcohols.



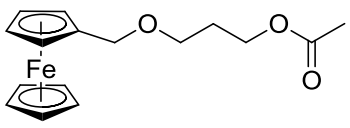
To a solution of the ferrocene alcohol (0.5 mmol) and DMAP (6 mg, 10 mol%) in dry THF (5 ml) was added acetic anhydride (90 ml, 1 mmol) dropwise over a 2 minute period. Once addition of acetic anhydride was complete the solution was allowed to stir at room temperature for 5 minutes (TLC analysis at this time shows full conversion of the starting material). The reaction was then diluted with EtOAc (20 ml) and the organics washed with water (20 ml), $NaHCO_3$ (sat) (20 ml) and brine (sat) (20 ml). The organics were then dried over $MgSO_4$, filtered and concentrated *in vacuo*, to give the desired product without need for further purification.

2-(Ferrocenyloxy)ethyl acetate (10).



Using general procedure B with 2-(ferrocenyloxy)ethanol (1) (131 mg, 0.5 mmol, 1eq). This gave the desired compound as an orange solid (132 mg, 87%). Mpt: 41–43 ^{o}C; IR; υ_{max} (thin film) (cm^{-1}): 3082, 2981, 2964, 2863, 1731, 1460; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.22–4.17 (m, 6H), 4.06–4.04 (m, 7H), 3.48–3.45 (m, 2H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.6, 84.4, 69.9, 69.7, 69.2, 68.9, 68.2, 63.9, 20.9; HRMS (ESI) calculated for $C_{15}H_{18}FeO_3Na$ m/z 325.0503 found 325.0475 (m/z + Na^+); Oxidation potential: 193 mV.

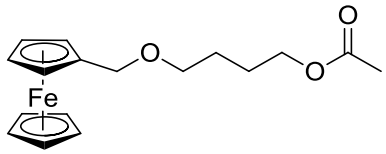
3-(Ferrocenyloxy)propyl acetate (11).



Using general procedure B with 2-(ferrocenyloxy)propan-1-ol (2) (138 mg, 0.5 mmol, 1eq). This gave the desired compound as an orange oil (151 mg, 95%); IR; υ_{max} (thin film) (cm^{-1}): 3094, 2980, 2856, 1734, 1365; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.24 (t, *J*=6.5, 2H), 4.20 (s,

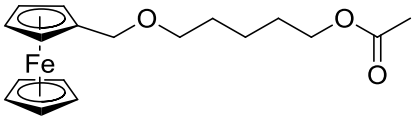
4H), 4.06–4.04 (m, 7H), 3.41 (t, *J*=6.2, 2H), 1.86–1.78 (m, 2H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.5, 84.8, 69.9, 69.7, 69.2, 68.9, 66.7, 62.1, 29.9, 20.9; HRMS (ESI) calculated for $C_{16}H_{20}FeO_3Na$ m/z 339.0659 found 339.0673 (m/z + Na^+); Oxidation potential: 200 mV.

4-(Ferrocenyloxy)butyl acetate (12).



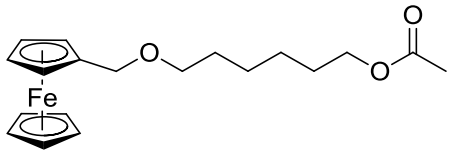
Using general procedure B with 2-(ferrocenyloxy)butan-1-ol (3) (145 mg, 0.5 mmol, 1eq). This gave the desired compound as an orange oil (144 mg, 86%); IR; υ_{max} (thin film) (cm^{-1}): 3094, 295, 2853, 1734, 1447; ^{1}H NMR (300 MHz, $CDCl_3$); δ_H: 4.22 (s, 4H), 4.08–4.06 (m, 9H), 3.35 (t, *J*=6.0, 2H), 1.75 (s, 3H), 1.69–1.56 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.5, 84.9, 69.9, 69.8, 69.6, 69.2, 68.9, 64.6, 27.0, 26.4, 20.9; HRMS (ESI) calculated for $C_{17}H_{22}FeO_3Na$ m/z 353.0816 found 353.0802 (m/z + Na^+); Oxidation potential: 212 mV.

5-(Ferrocenyloxy)pentyl acetate (13).



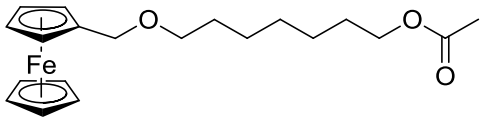
Using general procedure B with 2-(ferrocenyloxy)pentan-1-ol (4) (152 mg, 0.5 mmol, 1eq). This gave the desired compound as an orange oil (94 mg, 54%); IR; υ_{max} (thin film) (cm^{-1}): 3094, 2980, 2941, 2861, 1735, 1460; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.25–4.23 (m, 4H), 4.08–4.02 (m, 9H), 3.39 (t, *J*=6.2, 2H), 1.76 (s, 3H), 1.60–1.36 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$); δ_C: 170.5, 85.1, 70.2, 69.9, 69.6, 69.2, 68.9, 64.7, 30.2, 29.2, 23.5, 20.9. ; HRMS (ESI) calculated for $C_{18}H_{24}FeO_3Na$ m/z 367.0973 found 367.0985 (m/z + Na^+); Oxidation potential: 232 mV.

6-(Ferrocenyloxy)hexyl acetate (14).



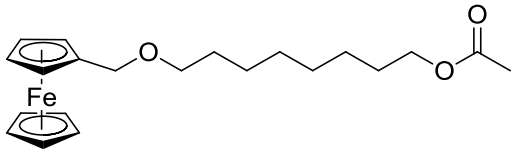
Using general procedure B with 2-(ferrocenyloxy)hexan-1-ol (5) (159 mg, 0.5 mmol, 1eq). This gave the desired compound as an orange oil (154 mg, 86%); IR; υ_{max} (thin film) (cm^{-1}): 3094, 2936, 2856, 1735, 1462; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.27 (s, 2H), 4.25 (br s, 2H), 4.09–4.01 (m, 9H), 3.42 (t, *J*=6.4, 1H), 1.77 (s, 1H), 1.64–1.44 (m, 4H), 1.38–1.21 (m, 4H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.5, 85.2, 70.3, 69.9, 69.6, 69.2, 68.9, 64.7, 30.5, 29.4, 26.7, 26.5, 20.9; HRMS (ESI) calculated for $C_{19}H_{26}FeO_3Na$ m/z 381.1129 found 381.1131 (m/z + Na^+); Oxidation potential: 257 mV.

7-(Ferrocenyloxy)heptyl acetate (15).



Using general procedure B with 2-(ferrocenyloxy)heptan-1-ol (6) (74 mg, 0.22 mmol, 1eq), acetic anhydride (40 μl, 0.44 mmol, 2 eq) and DMAP (2.7 mg, 0.02 mmol, 10 mol%). This gave the desired compound as an orange oil (80 mg, 97%); IR; υ_{max} (thin film) (cm^{-1}): 3094, 2936, 2856, 1735, 1462; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.29 (s, 2H), 4.26–4.25 (m, 2H), 4.09–4.03 (m, 9H), 3.46 (t, *J*=6.4, 2H), 1.77 (s, 3H), 1.68–1.61 (m, 2H), 1.57–1.36 (m, 5H), 1.24–1.22 (m, 3H).; ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.5, 85.2, 70.5, 69.9, 69.7, 69.2, 68.9, 64.8, 30.6, 29.7, 29.3, 26.9, 26.6, 20.9; HRMS (ESI) calculated for $C_{20}H_{28}FeO_3Na$ m/z 395.1286 found 395.1280 (m/z + Na^+); Oxidation potential: 280 mV.

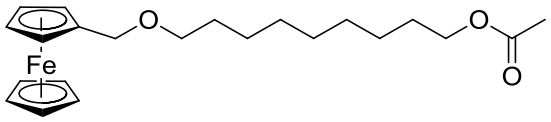
8-(Ferrocenyloxy)octyl acetate (16).



Using general procedure B with 2-(ferrocenyloxy)octan-1-ol (7) (57 mg, 0.16 mmol, 1eq), acetic anhydride (30 μl, 0.32 mmol, 2 eq) and DMAP (2 mg, 0.016 mmol, 10 mol%). This

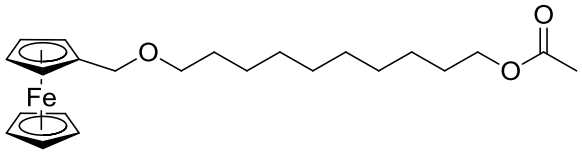
gave the desired compound as an orange oil (52 mg, 83%); IR; υ_{max} (thin film) (cm^{-1}): 3094, 2930, 2854, 1736, 1464; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.30 (s, 2H), 4.26 (s, 2H), 4.09 – 4.04 (m, 9H), 3.48 (t, *J*=6.4, 2H), 1.78 (s, 3H), 1.71–1.62 (m, 2H), 1.50–1.38 (m, 5H), 1.29–1.23 (m, 5H).; ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.5, 85.2, 70.5, 69.9, 69.7, 69.2, 68.9, 64.8, 30.7, 30.1, 29.9, 29.4, 26.9, 26.6, 20.9; HRMS (ESI) calculated for $C_{21}H_{30}FeO_3Na$ m/z 409.1442 found 409.1476 (m/z + Na^+); Oxidation potential: 302 mV.

9-(Ferrocenyloxy)nonyl acetate (17).



Using general procedure B with 2-(ferrocenyloxy)nonan-1-ol (8) (51 mg, 0.14 mmol, 1eq), acetic anhydride (28 μl, 0.28 mmol, 2 eq) and DMAP (1.7 mg, 0.014 mmol, 10 mol%). This gave the desired compound as an orange oil (43 mg, 76%); IR; υ_{max} (thin film) (cm^{-1}): 3093, 2927, 2854, 1737, 1464; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.31 (s, 2H), 4.27–4.26 (m, 2H), 4.09–4.05 (m, 9H), 3.50 (t, *J*=6.4, 2H), 1.79 (s, 3H), 1.74–1.65 (m, 2H), 1.51–1.40 (m, 5H), 1.27–1.23 (m, 7H); ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.5, 85.2, 70.6, 69.9, 69.7, 69.2, 68.9, 64.8, 30.8, 30.2, 30.2, 29.9, 29.4, 27.1, 26.6, 20.9; HRMS (ESI) calculated for $C_{22}H_{32}FeO_3Na$ m/z 423.1598 found 423.1651 (m/z + Na^+); Oxidation potential: 327 mV.

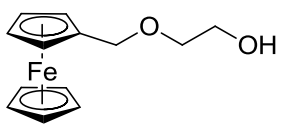
10-(Ferrocenyloxy)decyl acetate (18).



Using general procedure B with 2-(ferrocenyloxy)decan-1-ol (9) (187 mg, 0.5 mmol, 1eq),. This gave the desired compound as an orange oil (194 mg, 93%); IR; υ_{max} (thin film) (cm^{-1}): 3098, 2926, 2853, 1737, 1464; ^{1}H NMR (300 MHz, C_6D_6); δ_H: 4.30 (d, *J*=2.2, 2H), 4.27–4.26 (m, 2H), 4.09–4.06 (m, 9H), 3.50 (td, *J*=6.4, 2.7, 2H), 1.79 (s, 3H), 1.75–1.66 (m, 2H), 1.53–1.48 (m, 5H), 1.34–1.23 (m, 9H).; ^{13}C NMR (75 MHz, C_6D_6); δ_C: 170.6, 85.2, 70.6, 69.9, 69.7, 69.2, 68.9, 64.8, 30.7, 30.4, 30.3, 30.3, 30.1, 29.9, 29.4, 27.1, 26.6, 20.9; HRMS (ESI) calculated for $C_{23}H_{34}FeO_3Na$ m/z 437.1755 found 437.1785 (m/z + Na^+); Oxidation potential: 335 mV.

Oct25-2013-bm1
LAH026-1

(1)



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Owner	nmr
Site	
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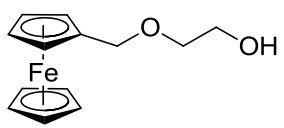
Author	
Solvent	C6D6
Temperature	294.6
Pulse Sequence	zg30
Number of Scans	32
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	9.4000
Acquisition Time	2.6542
Acquisition Date	2013-10-25T12:46:00
Modification Date	2013-10-25T11:46:16
Spectrometer Frequency	300.22
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Oct25-2013-bm1
LAH026-2

(1)



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Site	
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Author	
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Temperature	294.8
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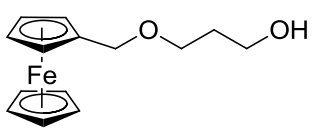
Acquisition Time	1.6122
Acquisition Date	2013-10-25T13:03:00
Modification Date	2013-10-25T12:03:58
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct25-2013-bm1
LAH029-1

(2)



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Owner	nmr
Site	
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Author	
Solvent	C6D6
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Number of Scans	32
Receiver Gain	181
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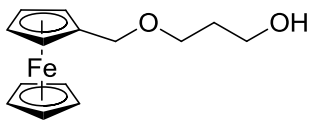
Spectrometer Frequency	300.22
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Oct25-2013-bm1
LAH029-2

(2)



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Author	
Solvent	C6D6
Temperature	294.8
Pulse Sequence	zgpg30
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Receiver Gain	9195
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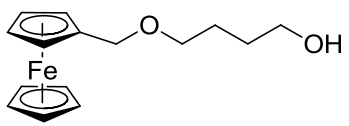
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct25-2013-bm1
LAH030-1

(3)



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Owner	nmr
Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.5
Pulse Sequence	zg30
Number of Scans	32
Receiver Gain	181
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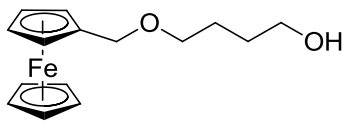
Spectrometer Frequency	300.22
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384

Oct25-2013-bm1
LAH030-2

(3)



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Author	
Solvent	C6D6
Temperature	294.7
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	9195
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Acquisition Time	1.6122
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Spectrometer Frequency	75.49
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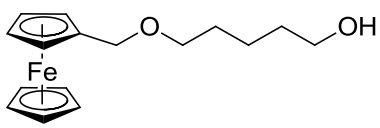
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

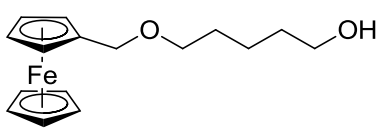
Oct25-2013-bm1
LAH028-1

(4)



Oct25-2013-bm1
LAH028-2

(4)



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Acquisition Time	1.6122
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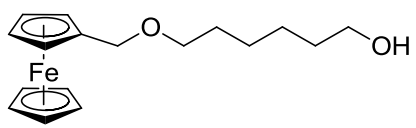
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct25-2013-bm1
LAH037-1

(5)



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Receiver Gain	181
Relaxation Delay	1.0000
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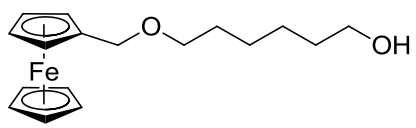
Spectrometer Frequency	300.22
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Oct25-2013-bm1
LAH037-2

(5)



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Author	
Solvent	C6D6
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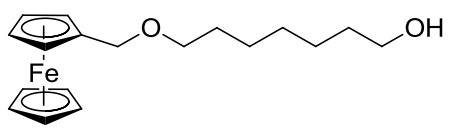
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	11585
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-10-25T16:29:00
Modification Date	2013-10-25T15:29:40
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct25-2013-bm1
LAH044-1

(6)



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Author	
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Receiver Gain	181
Relaxation Delay	1.0000
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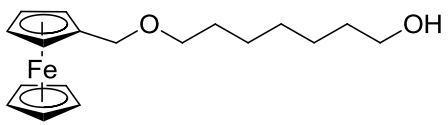
Spectrometer Frequency	300.22
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Oct25-2013-bm1
LAH044-2

(6)



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Author	
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Temperature	294.7
Pulse Sequence	zgpg30
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Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
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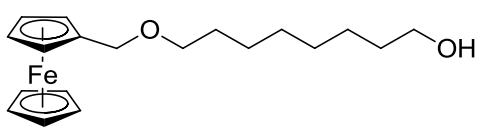
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct25-2013-bm1
LAH045-1

(7)



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Author	
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Receiver Gain	181
Relaxation Delay	1.0000
Pulse Width	9.4000
Acquisition Time	2.6543
Acquisition Date	2013-10-25T17:44:00
Modification Date	2013-10-25T16:45:02
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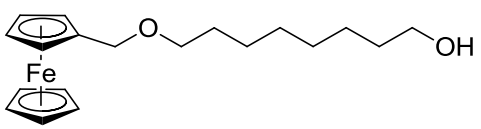
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Oct25-2013-bm1
LAH045-2

(7)



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Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.7
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	9195
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
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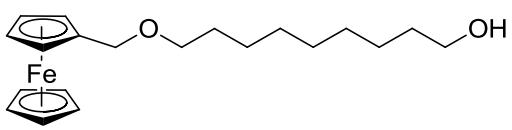
Modification Date	2013-10-25T17:02:40
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

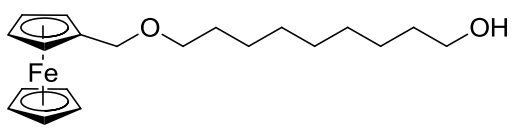
Mar16-2012-cgf
LAH046 pure

(8)



Mar16-2012-cgf
LAH046 pure

(8)



Oct25-2013-bm1
LAH034-1

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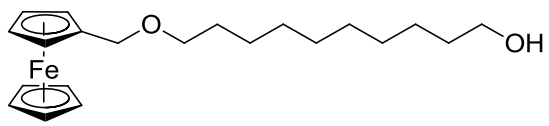
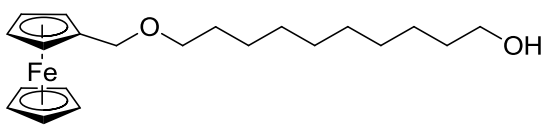


Oct25-2013-bm1
LAH034-2

(9)



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Owner	nmr
Site	
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Author	
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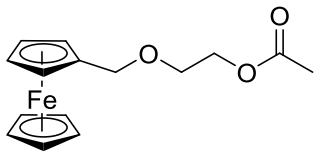
Temperature	294.7
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	9195
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-10-25T18:25:00
Modification Date	2013-10-25T17:26:04
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct28-2013-bm1
LAH048-1

(10)



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Owner	nmr
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Author	
Solvent	C6D6
Temperature	294.4
Pulse Sequence	zg30
Number of Scans	32
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	9.4000
Acquisition Time	2.6543
Acquisition Date	2013-10-28T16:35:00
Modification Date	2013-10-28T16:35:12
Spectrometer Frequency	300.22
Spectral Width	6172.8
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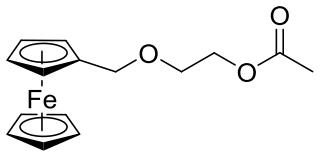
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Nov29-2013-bm1
LAH048

(10)



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Receiver Gain	9195
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-11-29T11:32:00
Modification Date	2013-11-29T11:32:18
Spectrometer Frequency	75.49
Spectral Width	20325.2
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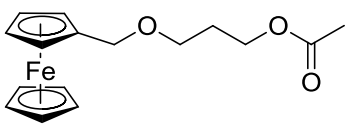
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct28-2013-bm1
LAH049-1

(11)



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Site	
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Author	
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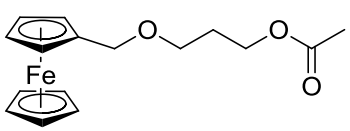
Receiver Gain	256
Relaxation Delay	1.0000
Pulse Width	9.4000
Acquisition Time	2.6543
Acquisition Date	2013-10-28T16:59:00
Modification Date	2013-10-28T16:59:38
Spectrometer Frequency	300.22
Spectral Width	6172.8
Lowest Frequency	-1234.7
Nucleus	1H
Acquired Size	16384
Spectral Size	32768

Oct28-2013-bm1
LAH049-2

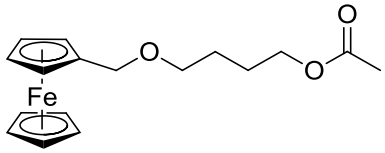
(11)

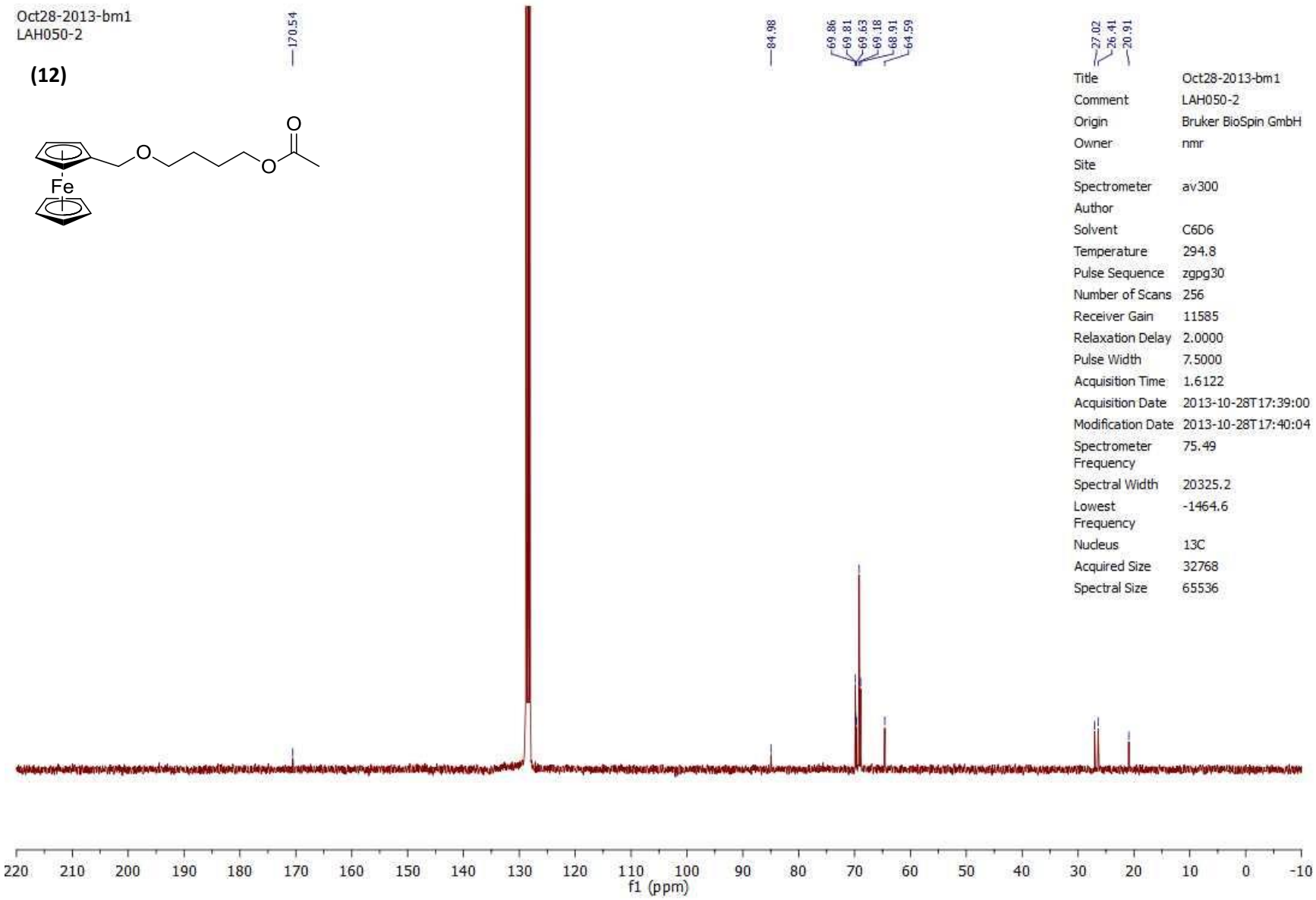


Title	Oct28-2013-bm1
Comment	LAH049-2
Origin	Bruker BioSpin GmbH
Owner	nmr
Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.8
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	11585
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-10-28T17:16:00
Modification Date	2013-10-28T17:16:36
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

Oct28-2013-bm1
LAH050-1

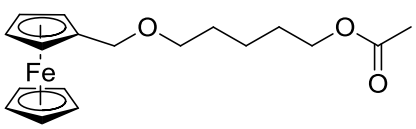
(12)




Oct28-2013-bm1
LAH050-2
(12)
Fe
O
O
O
170.54
84.98
69.86
69.81
69.63
69.18
68.91
64.59
27.02
26.41
20.91
Title Oct28-2013-bm1
Comment LAH050-2
Origin Bruker BioSpin GmbH
Owner nmr
Site
Spectrometer av300
Author
Solvent C6D6
Temperature 294.8
Pulse Sequence zgpg30
Number of Scans 256
Receiver Gain 11585
Relaxation Delay 2.0000
Pulse Width 7.5000
Acquisition Time 1.6122
Acquisition Date 2013-10-28T17:39:00
Modification Date 2013-10-28T17:40:04
Spectrometer Frequency 75.49
Spectral Width 20325.2
Lowest Frequency -1464.6
Nucleus 13C
Acquired Size 32768
Spectral Size 65536
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

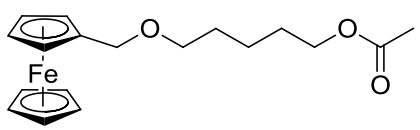
Oct29-2013-bm1
LAH047-1

(13)



Oct30-2013-bm1
LAH047-3

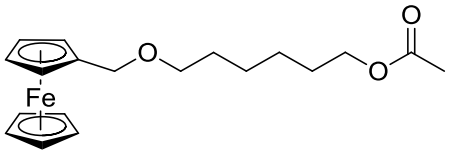
(13)



Title	Oct30-2013-bm1
Comment	LAH047-3
Origin	Bruker BioSpin GmbH
Owner	nmr
Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.8
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	9195
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-10-30T09:01:00
Modification Date	2013-10-30T09:01:48
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

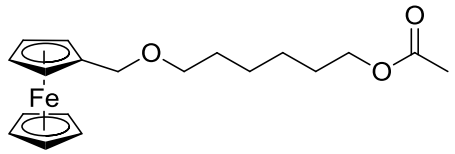
Oct29-2013-bm1
LAH052-1

(14)



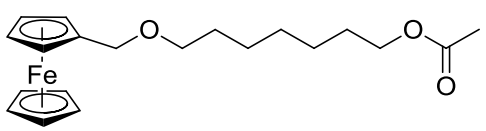
Oct29-2013-bm1
LAH052-2

(14)



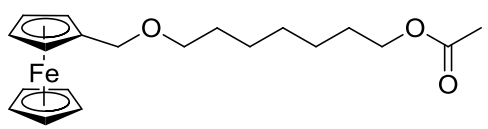
Oct29-2013-bm1
LAH055-1

(15)



Oct29-2013-bm1
LAH055-2

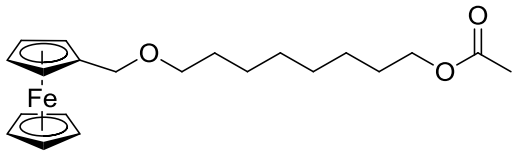
(15)



Title	Oct29-2013-bm1
Comment	LAH055-2
Origin	Bruker BioSpin GmbH
Owner	nmr
Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.7
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	11585
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-10-29T15:53:00
Modification Date	2013-10-29T15:53:52
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

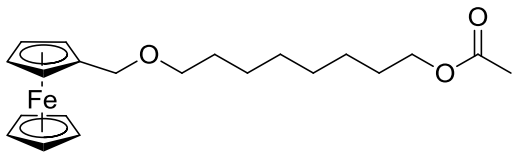
Oct30-2013-bm1
LAH056-1

(16)



Oct30-2013-bm1
LAH056-2

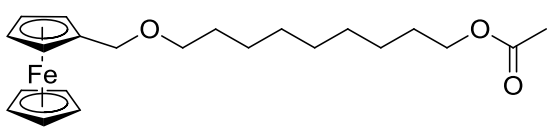
(16)



Title	Oct30-2013-bm1
Comment	LAH056-2
Origin	Bruker BioSpin GmbH
Owner	nmr
Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.3
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	9195
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-10-30T09:48:00
Modification Date	2013-10-30T09:49:04
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

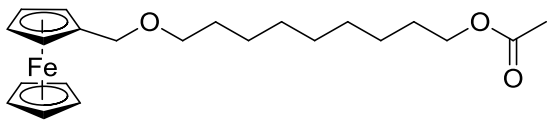
Oct30-2013-bm1
LAH057-1

(17)



Nov19-2013-bm1
LAH057-3

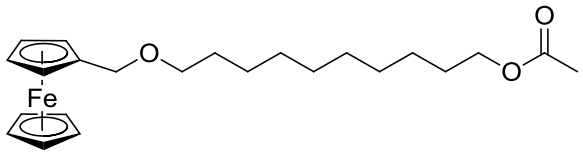
(17)



Title	Nov19-2013-bm1
Comment	LAH057-3
Origin	Bruker BioSpin GmbH
Owner	nmr
Site	
Spectrometer	av300
Author	
Solvent	C6D6
Temperature	294.4
Pulse Sequence	zgpg30
Number of Scans	256
Receiver Gain	11585
Relaxation Delay	2.0000
Pulse Width	7.5000
Acquisition Time	1.6122
Acquisition Date	2013-11-19T21:36:00
Modification Date	2013-11-19T21:36:30
Spectrometer Frequency	75.49
Spectral Width	20325.2
Lowest Frequency	-1464.6
Nucleus	13C
Acquired Size	32768
Spectral Size	65536

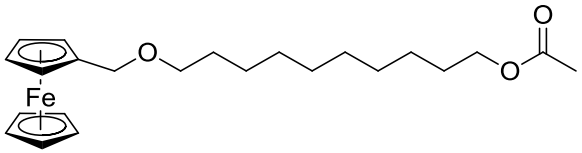
Oct30-2013-bm1
LAH053-1

(18)



Oct30-2013-bm1
LAH053-2

(18)



4. References.

1. B.Floris, P. Gallon, R. Seraglia, P. Tagliatesta., *J*. Organometallic *Chem*, **2003**, *679*, 202–207.

2 C. Bunte, L. Hussein, G. A. Urban., *J. Power Sources*, **2014**, *247*, 579–586.

3 Y. Suzaki, H. Endo, K. Kojima, K. Osakada., *Dalton Trans*, **2013**, *42*, 16222–16230.