Electronic Supplementary Material (ESI) for Chemical Communications

[3,3]Paracyclophanes as Planar Chiral Scaffolds for the Synthesis of New Phosphoric Acids.

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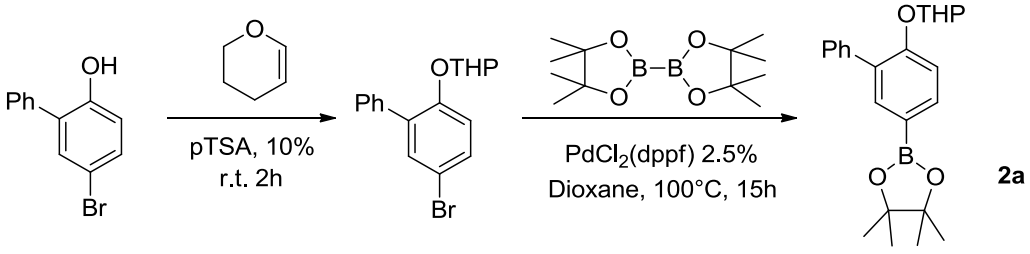
Supporting Information

I. General methods

All reactions were run under argon by using standard techniques for manipulating air-sensitive compounds. Anhydrous solvents were obtained by filtration through drying columns (THF, Et_2O, CH_2Cl_2). All reagents were of commercial quality and were used without further purification. Flash column chromatography was performed using 40-63 mesh silica. Nuclear magnetic resonance spectra (^1H, ^{13}C, ^{31}P) were recorded either on Brucker AV 500 or AV 300 spectrometers. IR spectra were recorded with a Perkin-Elmer FT-IR spectrophotometer. High resolution mass spectra (HRMS-ESI) were obtained on LCT Waters equipment. Optical rotations were determined with a JASCO P-1010 polarimeter. HPLC was performed at a column temperature of 30°C on a Waters 2695 Separations Module equipped with a diode array UV detector.

II. Synthesis of 2a.



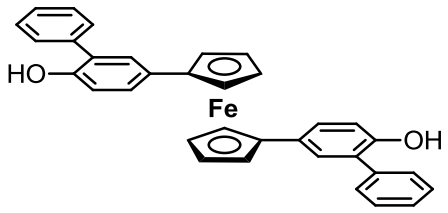
5-bromo-[1,1'-biphenyl]-2-ol was obtained by bromination of [1,1'-biphenyl]-2-ol, as reported.[1]

2-[(5-Bromobiphenyl-2-yl)oxy]tetrahydro-2*H*-pyran. In a round-bottomed flask was dissolved 5-bromobiphenyl-2-ol (12.13 g, 48.7 mmol) in 3,4-dihydro-2*H*-pyran (50 mL) and the solution was cooled to 0 °C. A catalytic amount of PTSA (10 mol%) was introduced and the mixture was allowed to warm up at room temperature for 2 h. After dilution with dichloromethane (100 mL) the organic phase was washed with a 5% (w/w) aqueous solution of NaOH (ca. 50 mL), H_2O (ca. 50 mL) and dried over $MgSO_4$. The solvents were removed under reduced pressure. After filtration on silica gel (eluent: heptane/EtOAc = 100:0 to 98:2) the title compound was isolated as a colorless syrup (16.1 g, 99%). R_f = 0.7 (heptane/EtOAc 8:2); **^{1}H NMR** (500 MHz, $CDCl_3$) : δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 2.5 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.36 (dd, *J* = 8.9, 2.5 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 1H), 7.10 (d, *J* = 8.9 Hz, 1H), 5.35 (bs, 1H), 3.73 (td, *J* = 11.0, 2.7 Hz, 1H), 3.55 (bd, *J* = 11.0 Hz, 1H), 1.77-1.70 (m, 2H), 1.66-1.62 (m, 1H), 1.57-1.50 (m, 2H), 1.31-1.27 (m, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 153.0 (C), 137.3 (C), 133.7 (C), 133.3 (CH), 131.1 (CH), 129.5 (CH), 127.9 (CH), 127.3 (CH), 117.6 (CH), 114.2 (C), 96.8 (CH), 61.8 (CH_2), 30.1 (CH_2), 25.1 (CH_2), 18.3 (CH_2).

4,4,5,5-tetramethyl-2-[6-(tetrahydro-2*H*-pyran-2-yloxy)biphenyl-3-yl)-1,3,2-dioxaborolane, 2a. 2-[(5-Bromobiphenyl-2-yl)oxy]tetrahydro-2*H*-pyran (3.33 g, 10.0 mmol), bispinacolatodiboron (3.05 g, 12.0 mmol, 1.2 eq.) and $CH_3CO_2Na\bullet 3H_2O$ (4.08 g, 30 mmol, 3.0 eq.) were introduced in a Schlenk tube and dissolved in 1,4-dioxane (25mL). The Schlenk tube was evacuated, refilled with argon (3 cycles) and $PdCl_2$(dppf) (183 mg, 0,25 mmol, 2.5 mol%) was added under a flow of argon. The mixture was refluxed for 24 h. The mixture was allowed to cool to room temperature and the solvents were removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: heptane/EtOAc = 98:2 to 90:10) gave the title compound as a white crystalline solid (2.82 g, 74%). R_f = 0.6 (heptane/EtOAc 8:2); **mp** : 81-82°C. **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.82 (d, *J* = 1.8 Hz, 1H), 7.76 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.58 (bd, *J* = 8.6 Hz, 2H), 7.39 (t, *J* = 8.6 Hz, 2H), 7.30 (t, *J* = 8.6 Hz, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 5.51 (bs, 1H), 3.78 (td, *J* = 10.8, 2.6 Hz, 1H), 3.58 (bd, *J* = 10.8 Hz, 1H), 1.79-1.47 (m, 6H), 1.34 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 156.5 (C), 138.7 (C), 137.8 (CH), 135.7 (CH), 131.1 (C), 129.8 (CH), 129.3 (C), 127.8 (CH), 126.8 (CH), 114.8 (CH), 96.3 (CH), 83.7 (C), 61.8 (CH_2), 30.3 (CH_2), 25.3 (CH_2), 25.0 (CH_3), 18.4 (CH_2). **IR** : ν_{max} = 2976, 2942, 2872, 1601, 1355, 1226, 1201, 1140, 1110, 1038, 1021, 962, 919, 871, 771, 699, 681. **HRMS** (ESI) calcd. for $C_{23}H_{30}BO_4$ $[M+H]^+$: 381.2237, found : 381.2237

III. Synthesis of the phosphoric acid 5a (Scheme 1)

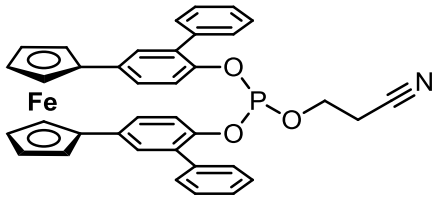
1,1'-diiodoferrocene was obtained according to the literature.[2]



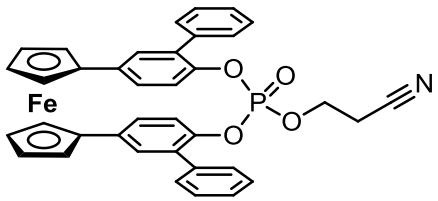
1,1'-Bis-(4-hydroxy-3-phenyl-1-phenyl)-ferrocene (3a). 1,1'-Diiodoferrecene (1.51 g 3.4 mmol), boronate **2a** (2. 9 g, 7.6 mmol, 2.2 eq) and $Ba(OH)_2\bullet 8H_2O$ (4.35 g, 13.8 mmol, 4.0 equiv.) were introduced in a Schlenk tube and dissolved in 1,4-dioxane (35 mL). The Schlenk tube was evacuated, refilled with argon (3 cycles) and the $PdCl_2$(S-Phos)$_2$ (172 mg, 0,17 mmol, 5 mol%) was added under a flow of argon. The mixture was heated at

[1] K. Hazlet, *J. Am. Chem. Soc.* **1941**, *63*, 1890
[2] M.D. Rausch, D.J. Ciappenelli, *J. Organomet. Chem.* **1967**, *10*, 127. Kovar, R.J., Rausch, M.D., Rosenber, H. *Organomet. Chem. Synth.* **1971**, *1*, 173.

100°C for 24 h. The mixture was allowed to cool to room temperature, diluted with dichloromethane (ca 30 ml), washed with a 1*M* aqueous solution of HCl (30 mL) and the aqueous phase was extracted once with dichloromethane. The organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The black residue was dissolved in MeOH (40 mL) and a catalytic amount of PTSA was added. The solution was stirred at room temperature for 2 h (monitored by TLC), then a few drops of triethylamine were added and the solvents were removed under reduced pressure. Purification by flash chromatography on silica gel (toluene/dichloromethane 1:1 mixture, then 2 % of EtOAc was added to the eluent). Compound **3a** was obtained as an orange solid (936 mg, 52%). R_f = 0.2 (heptane/EtOAc 8:2); **mp** : 109-110°C. **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.55-7.37 (m, 10H), 7.20-7.09 (m, 4H), 6.76 (m, 2H), 5.13 (bs, 2H), 4.47 (s, 4H), 4.23 (s, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 150.9 (C), 137.3 (C), 130.4 (C), 129.4 (CH), 129.2 (CH), 128.0 (CH), 127.7 (CH), 127.0 (CH), 115.9 (CH), 86.6 (C), 70.0 (CH), 67.4 (CH). **IR** : ν_{max} = 3375, 3084, 1703, 1674, 1609, 1516, 1457, 1416, 1375, 1271, 1188, 1131, 1043, 819, 771, 700. **HRMS** (ESI) calcd. for $C_{34}H_{26}FeO_2$, 522.1282, found : 522.1275.



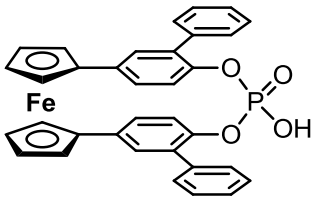
Phosphite 4a. 1,1'-Bis-(4-hydroxy-3-phenyl-1-phenyl)-ferrocene **3a** (1 eq.) and solid 1*H*-tetrazole (4 eq.) were introduced in a round-bottomed flask which was evacuated and refilled with argon. The solids were dissolved in anhydrous dichloromethane (50 mL for 1 mmol of diol) and 2-cyanoethyl *N,N,N',N'*-tetra-*iso*-propylphosphorodiamidite (1.2 eq.) was added at room temperature. The mixture was stirred at room temperature for 4 h and then quenched with a saturated aqueous solution of $NaHCO_3$. The layers were separated, the organic phase was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Purification by flash chromatography on silica gel (eluent : heptane/EtOAc 9 : 1) gave the desired macrocyclic phosphite **4a** as an orange solid in 37% yield**.** R_f = 0.7 (heptane/EtOAc 1:1); **^{31}P NMR** (200 Hz, $CDCl_3$) : δ 130 ppm. **^{1}H NMR** (500 MHz, $CDCl_3$) : δ 7.53-7.46 (m, 8H), 7.42-7.37 (m, 2H), 6.93 (bs, 1H), 6.90 (bs, 1H), 6.55 (bd, *J* = 8.2 Hz, 1H), 6.41-6.35 (m, 3H), 4.58-4.53 (br, 4H), 4.42 (s, 2H), 4.37 (s, 2H), 3.95 (dq, *J* = 10.5, 6.7 Hz, 1H), 3.79 (dq, *J* = 10.5, 6.7 Hz, 1H), 2.50 (t, *J* = 6.7 Hz, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 148.2 (C), 147.1 (d, $J_{(P-C)}$ = 5.9 Hz, C), 138.4 (d, $J_{(P-C)}$ = 3.0 Hz, C), 138.2 (C), 133.2 (d, $J_{(P-C)}$ = 3.4 Hz, C), 132.8 (C), 129.6 (CH), 129.3 (CH), 128.8 (CH), 128.4 (CH), 128.2 (C), 127.7 (CH), 127.5 (CH), 127.4 (CH), 127.2 (CH), 126.6 (CH), 125.6 (CH), 123.5 (CH), 120.0 (d, $J_{(P-C)}$ = 16.0 Hz, CH), 117.1 (CN), 86.8 (C), 86.5 (C), 69.5 (CH), 68.9 (CH), 66.6 (CH), 66.3 (CH), 65.2 (CH), 65.1 (CH), 57.6 (CH_2), 20.1 (d, $J_{(P-C)}$ = 3.6 Hz CH_2 **IR** : ν_{max} = 3055, 2926, 2854, 1600, 1511, 1457, 1412, 1260, 1213, 1134, 1035, 906, 868, 820, 765, 699. **HRMS** (ESI) calcd. for $C_{37}H_{28}FeNO_3P$ $[M]^+$: 621.1156, found : 621.1155.



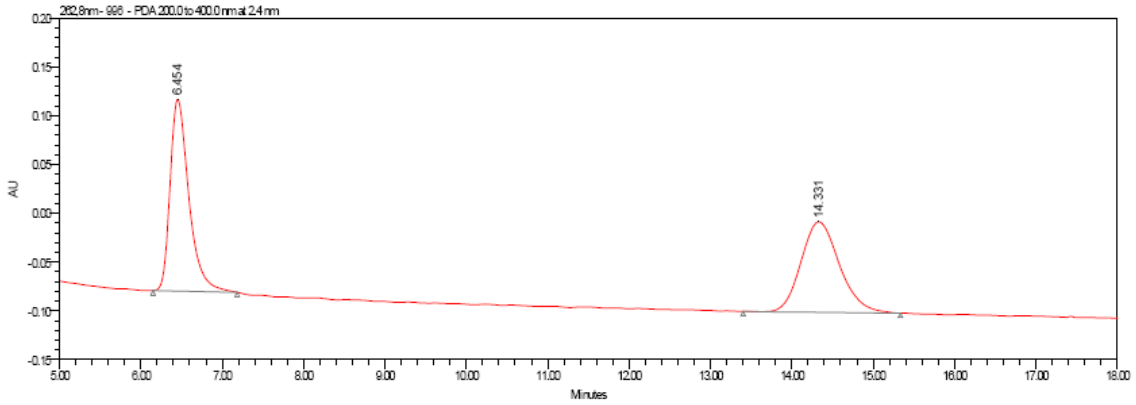
Oxidation of 4a. Phosphite **4a** (0.62 g, 1 mmol) was dissolved in DCM (1mL). TBHP (5.5*M* in decane, 0.55 mL, 3 mmol) was added to the solution at 0 °C.[3] After 15 min., the reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. The reaction was treated with saturated aqueous $Na_2S_2O_3$. The layers were separated, the organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by chromatography on silica gel (eluent: heptane/EtOAc = 70:30 to 60:40) to afford the desired phosphate. Yield 75%. Orange solid, decomposes at 150°C before melting. **^{31}P** (200 MHz, $CDCl_3$) : δ -14 ppm; **^{1}H NMR** (500 MHz, $CDCl_3$) : δ 7.56-7.48 (m, 8H), 7.46-7.40 (m, 2H), 7.04 (s,

[3] M. Sekine, O. Kurasawa, K. Shohda, K. Seio, and T. Wada, *Eur. J. Org. Chem.* **2006**, *691*, 299-308.

1H), 6.98 (s, 1H), 6.59 (d, *J* = 8.6 Hz, 1H), 6.57 (d, *J* = 8.6 Hz), 6.36 (d, *J* = 8.6 Hz), 6.30 (d, *J* = 8.4 Hz, 1H), 4.64 (s, 1H), 4.59 (s, 1H), 4.56 (s, 1H), 4.52 (s, 1H), 4.44 (s, 2H), 4.40 (s, 2H), 4.08 (m, 1H), 3.40 (m, 1H), 2.52 (dt, *J* = 17.0, 6.7 Hz, 1H), 2.30 (dt, *J* = 17.0, 6.4 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 146.6 (d, $J_{(P-C)}$ = 9.6 Hz, C), 146.2 (d, $J_{(P-C)}$ = 9.6 Hz, C), 137.7 (C), 136.8 (C), 133.0 (C), 132.8 (C), 131.3 (C), 130.9 (C), 129.5 (CH), 129.3 (CH), 129.0 (CH), 128.8 (CH), 128.1 (CH), 127.9 (CH), 127.7 (CH), 127.6 (CH), 126.2 (CH), 125.7 (CH), 122.5 (CH), 120.0 (CH), 116.4 (CN), 86.0 (C), 70.0 (CH), 69.9 (CH), 69.4 (CH), 69.3 (CH), 66.9 (CH),66.7 (CH), 65.5 (CH), 65.4 (CH), 62.5 (d, $J_{(P-C)}$ = 6.0 Hz, CH_2), 19.5 (d, $J_{(P-C)}$ = 7.9 Hz, CH_2); **IR** : ν_{max} = 3083, 2965, 1710, 1600, 1513, 1458, 1298, 1212, 1040, 954, 823, 770, 700. **HRMS** (ESI) calcd. for $C_{37}H_{28}FeNO_4P$ $[M]^+$: 637.1105, found : 637.1093

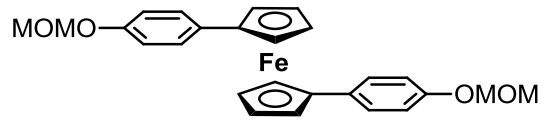


Phosphoric acid 5a. The phosphate above (0.5 mmol) was dissolved in DCM (0.5 mL) and DBU (1 mmol) was added to the solution at rt. After 30 min the reaction was diluted with DCM and hydrolyzed with saturated aqueous $NaHCO_3$. The layers were separated and the organic layer was washed twice with a 6*M* aqueous solution of HCl under vigorous stirring. The organic layer was dried over $MgSO_4$ and the solvent was removed under reduced pressure. Quantitative yield. Orange solid, decomposes at 172°C before melting. **^{31}P NMR** (121.5 MHz, $CDCl_3$) : δ -9 ppm; **H NMR** (500.2 MHz, $CDCl_3$) : δ 8.28 (br, 1H), 7.52-7.47 (m, 8H), 7.37 (bs, 2H), 7.00 (bs, 2H), 6.62 (bs, 2H), 6.23 (bs, 2H), 4.72 (bs, 2H), 4.64 (bs, 2H), 4.51 (bs, 2H), 4.47 (bs, 2H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) : δ 146.8 (d, $J_{(P-C)}$ = 5.6 Hz, C), 137.3 (C), 132.9 (d, $J_{(P-C)}$ = 4.0 Hz, C), 130.3 (C), 129.2 (CH), 128.7 (CH), 127.7 (CH),127.6 (CH), 126.0 (CH), 121.4 (CH), 87.6 (C), 70.2 (CH), 69.5 (CH), 66.9 (CH), 65.7 (CH). **IR** : ν_{max} = 3029, 2925, 2864, 1601, 1512, 1495, 1457, 1255, 1105, 1075, 1021, 955, 918, 883, 766. **HRMS** (ESI) calcd. for $C_{34}H_{24}FeO_4P$: 583.0762, found : 583.0795. Separation of enantiomers by semi-preparative HPLC: CHIRALPAK® ID column (250 x 10 mm, 5 mic), 30°C, 60% THF/40% *n*-heptane/0.3% TEA/0.5% TFA, 4.7 mL/min, UV detection at 260 nm. Retention times 6.4 min, **(+)-5a**, $[\alpha]_D^{20}$ +931 (*c* = 1, $CHCl_3$); 14.3 min, **(-)-5a** $[\alpha]_D^{20}$ -982 (*c* = 1, $CHCl_3$).

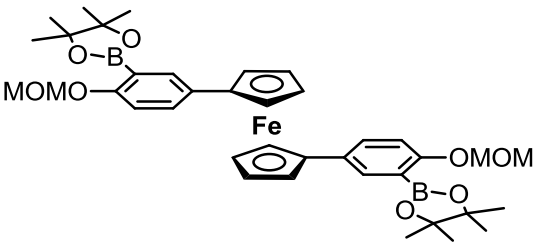


	Channel Description	RT	Area	% Area
1	PDA 200.0 to 400.0 nm at 2.4 nm	6.454	3142228	50.80
2	PDA 200.0 to 400.0 nm at 2.4 nm	14.331	3043126	49.20

IV. Synthesis of the phosphoric acid 5b (Scheme 2)

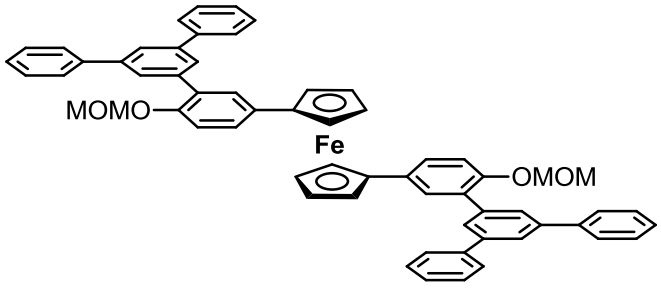


1,1'-Bis-[4-(methoxymethoxy) phenyl]ferrocene. 1,8-Diiodoferrecene (7.2 g, 16.4 mmol), [4-(methoxymethoxy)phenyl]boronic acid (**2b**)[4] (8.98 g, 49.3 mmol, 3.0 eq.) and NaOH (2.63 g, 65.8 mmol, 4.0 eq.) were introduced in a round-bottomed flask and dissolved in a mixture of DME (125 mL) and water (25 mL). The flask was evacuated and refilled with argon, then $PdCl_2$(dppf).DCM (601 mg, 0.82 mmol, 5 mol%) was added under a flow of argon. The mixture was heated at 85°C for 18 h, then allowed to cool to room temperature, diluted with EtOAc (ca 100 mL) and washed once with 100 mL of water. The aqueous phase is extracted once with EtOAc. The organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by column chromatography (eluents: toluene/heptane/EtOAc gradient from 2:8:0 to 6:4:1). The product was obtained as an orange solid (6.05 g, 80%). R_f = 0.3 (heptane/EtOAc 8:2); mp = 111-112°C. **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.22 (d, *J* = 8.8 Hz, 4H), 6.89 (d, *J* = 8.8 Hz, 4H), 5.18 (s, 4H), 4.42 (bs, 4H), 4.18 (bs, 4H), 3.52 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 155.9 (C), 131.8 (C), 127.2 (CH), 116.3 (CH), 94.8 (CH_2), 86.7 (C), 70.4 (CH), 67.7 (CH), 56.2 (CH_3). **IR** : ν_{max} = 2948, 2898, 2829, 1614, 1528, 1457, 1278, 1253, 1151, 1075, 1021, 991, 919, 826, 813. **HRMS** (ESI) calcd. for $C_{26}H_{26}FeO_4$ $[M]^+$: 458.1181, found : 458.1182.

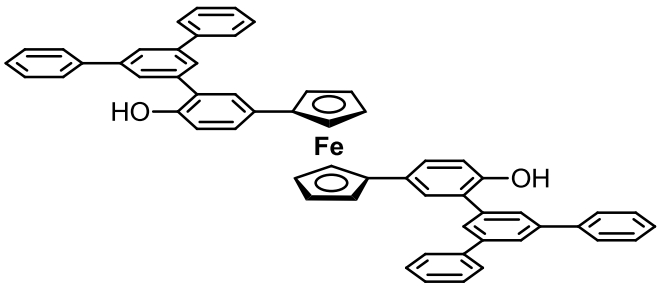


1,1'-Bis-[4-(methoxymethoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl]-ferrocene (6). In a flame dried round-bottomed flask is dissolved 1,1'-bis-[4-(methoxymethoxy)-phenyl]-ferrocene (2.3 g, 5 mmol) in anhydrous THF (45 mL). After cooling to -78 °C, *n*-BuLi (1.6*M* solution in hexane, 6.87 mL, 11.0 mmol, 2.2 eq.) was added dropwise to the orange suspension. After 5 minutes at -78°C the mixture is allowed to warm to room temperature and stirred for 4 h (the suspension turns into a clear orange solution and the dilithiated compound appears then as an orange solid). The suspension is cooled to -78 °C and 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.06 ml, 15.0 mmol, 3.0 eq.) is added dropwise. The mixture was stirred at room temperature overnight then treated with a saturated aqueous solution of NH_4Cl (ca 40 mL) and EtOAc (ca 30 mL). The phases were separated and the aqueous phase was extracted with EtOAc. The organic phases were dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: heptane/EtOAc = 9:1 to 1:1) afforded **6** as an orange solid (3.16 g, 89%). R_f = 0.1 (heptane/EtOAc 8:2); **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.70 (d, *J* = 2.2 Hz, 2H), 7.36 (dd, *J* = 8.6, 2.2 Hz, 2H), 6.92 (d, *J* = 8.6 Hz, 2H), 5.20 (s, 4H), 4.46 (bs, 4H), 4.13 (bs, 4H), 3.54 (s, 6H), 1.38 (s, 12H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 160.4 (C), 134.2 (CH), 132.1 (C), 130.4 (CH), 127.2 (C), 116.0 (CH), 95.7 (CH_2), 86.6 (C), 83.7 (C), 70.7 (CH), 67.9 (CH), 56.4 (CH_2), 25.1 (CH_3). **IR** : ν_{max} = 2978, 2932, 1738, 1605, 1579, 1506, 1418, 1348, 1235, 1142, 1062, 993, 911, 860, 822, 732. **HRMS** (ESI) calcd. for $C_{38}H_{48}B_2FeO_8$ $[M]^+$: 710.2885, found : 710.2902.

[4] (a) A. M. Selepe, S. E. Drewes, F. R. Van Heerden, *J. Nat. Prod.* **2010**, 73, 1680 – 1685. (b) M. E. Hart, K. L. Suchland, M. Miyakawa, J. R. Bunzow, D. K. Grandy, T. S. Scanlan, *J. Med. Chem.* **2006**, *49*, 1101 – 1112.

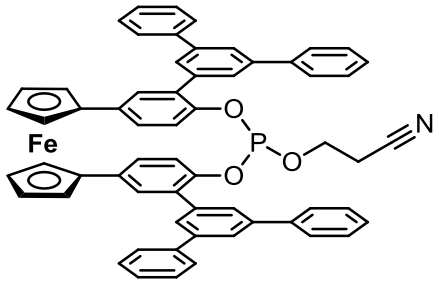


1,1'-Bis-[4-(methoxymethoxy)-3-(3',5'-diphenyl)phenyl]ferrocene. Boronate **6** (1.06 g, 1.49 mmol), 1-bromo-3,5-diphenylbenzene (1.15 g, 3.73 mmol) and $Ba(OH)_2.8H_2O$ (1.88 g, 5.96 mmol, 4 eq.), 1,4-dioxane (12 mL) and water (2.4 mL) were introduced in a round bottomed flask under argon. $Pd(PPh_3)_4$ (172 mg, 0.15 mmol) was added. The flask was then equipped with a reflux condenser and the mixture was heated at 100°C for 18 h. The mixture was diluted with EtOAc (ca 10 mL) and washed with 10 mL of water. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: heptane/EtOAc gradient from 98:2 to 90:10). The product was obtained as an orange solid (1.18 g, 86%). R_f = 0.14 (heptane/EtOAc 8:2); mp 240-242 °C (decomposition). **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.80-7.65 (m, 14H), 7.51-7.35 (m, 14H), 7.27 (dd, *J* = 8.2, 2.4 Hz, 2H), 7.04 (d, *J* = 8.2 Hz, 2H), 5.08 (s, 4H), 4.53 (bs, 4H), 4.23 (bs, 4H), 3.37 (s, 6H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 152.8 (C), 141.6 (C), 141.4 (C), 139.7 (C), 132.1 (C), 131.7 (C), 128.9 (CH), 128.6 (CH), 127.6 (CH), 127.5 (CH), 127.4 (CH), 126.7 (CH), 124.9 (CH), 116.0 (CH), 95.5 (CH_2), 86.3 (C), 70.5 (CH), 67.6 (CH), 56.3 (CH_3). **IR** : ν_{max} = 3038, 2926, 1594, 1513, 1413, 1401, 1237, 1155, 1137, 1072, 991, 878, 817, 758, 697. **HRMS** (ESI) calcd. for $C_{62}H_{51}FeO_4$ $[M+H]^+$: 915.3137, found: 915.3174.

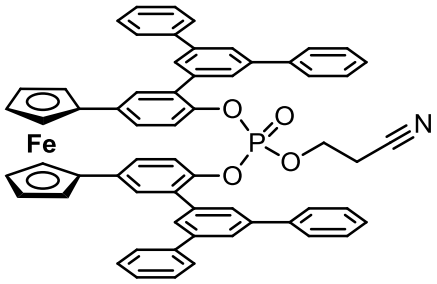


1,1'-Bis-[4-hydroxy-3-(3',5'-diphenyl)-phenyl]ferrocene (3b). To a solution of the MOM-protected diol (732 mg, 0.80 mmol) in THF/water (8:2, 30 mL), were added NaI (1.2g, 8.0 mmol) and APTS (304 mg, 1.60 mmol) at room temperature. The mixture was heated at 60°C for 18 h. The mixture was allowed to cool to room temperature and a saturated aqueous solution of $NaHCO_3$ was added, the layers were separated and the aqueous layer was extracted with EtOAc. The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. Purification by flash chromatography on silica gel (eluent: heptane/EtOAc gradient from 98:2 to 80:20). The purified product was obtained in quantitative yield, as an orange solid R_f = 0.5 (heptane/EtOAc 1:1); mp : 215-218 °C (decomposition). **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.81 (t, *J* = 1.7 Hz, 2H), 7.69-7.62 (m, 12H), 7.5-7.35 (12H), 7.24 (dd, *J* = 7.0, 2.1 Hz, 2H), 7.18 (dd, *J* = 8.1, 2.1 Hz, 2H), 6.78 (d, *J* = 8.1 Hz, 2H), 5.11 (bs, 2H), 4.51 (bs, 4H), 4.25 (bs, 4H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 151.0 (C), 142.9 (C), 140.8 (C), 138.4 (C), 130.3 (C), 129.0 (CH), 127.9 (CH), 127.5 (CH), 127.2 (CH), 126.9 (CH), 125.7 (CH), 116.0 (CH), 86.8 (C), 70.0 (CH), 67.4 (CH). **IR** : ν_{max} = 3534, 3037, 1733, 1593, 1513, 1453, 1427, 1406, 1275, 1250, 1118, 1033, 918, 879, 821, 758, 695; **HRMS** (ESI) calcd. for $C_{58}H_{43}FeO_2$ $[M+H]^+$: 827.2612, found : 827.2700.

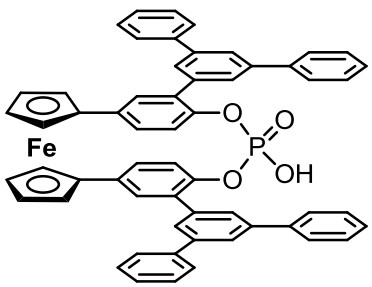
Diol 3**b** was converted into the corresponding acid **5b** by following the same procedures used for the synthesis of **5a** from **3a** (see above).



Terphenyl-substituted phosphite. The macrocyclic phosphite was obtained from 1,1'-bis-[4-hydroxy-3-phenyl-(3',5'-diphenyl)phenyl]ferrocene (**3b**) in 42% yield as an orange solid. mp 128-130 °C. **^{31}P** (200 MHz, $CDCl_3$) : δ 131 ppm. **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.85 (bs, 1H), 7.81 (bs, 1H), 7.80-7.70 (m, 12H), 7.61-7.50 (m, 8H), 7.49-7.39 (m, 4H), 7.08 (bs, 1H), 7.03 (bs, 1H), 6.69 (dd, *J* = 8.2, 1.5 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 6.44 (d, *J* = 8.2 Hz, 2H), 4.62 (s, 1H), 4.60 (s, 1H), 4.57 (s, 2H), 4.45 (s, 2H), 4.40 (s, 2H), 3.95-3.77 (m, 2H), 2.30-2.1012 (m, 2H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 148.5 (C), 147.3 (d, $J_{(P-C)}$ = 5.6 Hz, C), 142.4 (C), 142.1 (C), 141.3 (C), 141.0(C), 139.4 (d, $J_{(P-C)}$ = 2.3 Hz, C), 139.1 (C), 133.1 (d, $J_{(P-C)}$ = 3.3 Hz, C), 132.4 (C), 129.6 (C), 129.3 (CH), 129.1 (CH), 128.5 (C), 128.0 (CH), 127.7 (CH), 127.6 (CH), 127.4 (CH), 127.0 (CH), 127.0 (CH), 126.0 (CH), 125.8 (CH), 125.2 (CH), 123.6 (CH), 120.0 (CH), 119.8 (CH), 116.9 (CN), 87.0 (C), 86.8 (C), 69.7 (CH), 69.1 (CH), 66.8 (CH), 66.5 (CH), 65.4 (CH), 65.3 (CH), 57.8 (CH_2), 19.8 (d, $J_{(P-C)}$ = 3.8 Hz, CH_2). **IR** : ν_{max} = 3032, 2924, 2852, 1732, 1594, 1511, 1498, 1454, 1413, 1264, 1230, 1208, 1074, 1033, 1004, 918, 871. **HRMS** (ESI) calcd. for $C_{61}H_{45}NFeO_3P$ $[M+H]^+$: 926.2486, found : 925.2479.

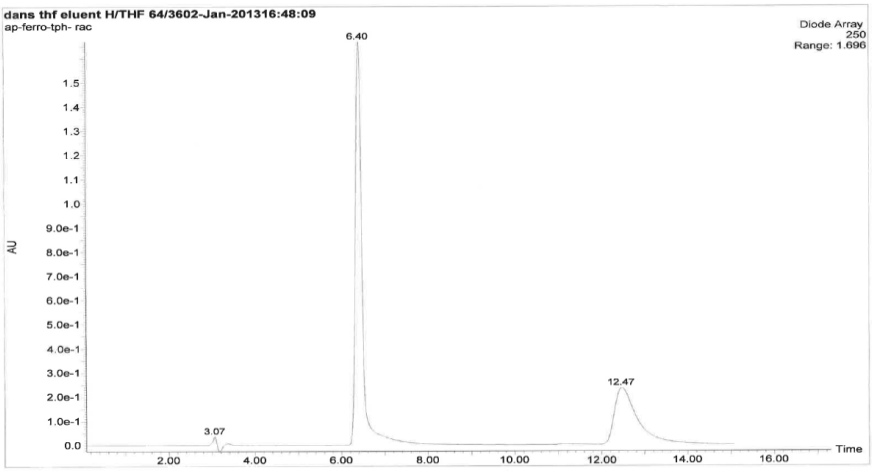


Terphenyl-substituted phosphate. The terphenyl-substituted phosphate was obtained from the corresponding phosphite in 87% yield, as an orange solid: mp 145-147 °C. **^{31}P** (200 MHz, $CDCl_3$) : δ -14 ppm. **^{1}H NMR** (300 MHz, $CDCl_3$) : δ 7.89 (bs, 1H), 7.84 (bs, 1H), 7.79-7.72 (m, 12H), 7.58-7.51 (m, 8H), 7.47 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.2 Hz, 2H), 7.16 (s, 1H), 7.12 (s, 1H), 6.73-6.70 (2H), 6.35 (1H), 6.29 (1H), 4.73-4.61 (4H), 4.51 (s, 2H), 4.47 (s, 2H), 4.11 (m, 1H), 3.49 (m, 1H), 2.44 (dt, *J* = 16.7, 6.7 Hz, 1H), 2.25 (dt, *J* = 16.7, 6.7 Hz, 1H). **^{13}C NMR** (75 MHz, $CDCl_3$) : δ 146.8 (d, $J_{(P-C)}$ = 9.9 Hz, C), 146.5 (d, $J_{(P-C)}$ = 11.0 Hz, C), 142.8 (C), 142.5 (C), 141.3 (C), 141.0 (C), 140.6 (C), 138.8 (C), 137.7 (C), 132.7 (C), 132.6 (C), 131.5 (C), 131.0 (C), 129.4 (CH), 129.1 (CH), 128.2 (C), 127.7 (CH), 127.5 (CH), 127.2 (CH), 127.1 (CH), 126.7 (CH), 126.2 (CH), 125.7 (CH), 122.7 (CH), 120.1 (CH), 116.0 (CN), 87.1 (C), 86.8 (C), 70.4 (CH), 69.7 (CH), 67.2 (CH), 65.8 (CH), 62.7 (d, $J_{(P-C)}$ = 5.8 Hz, CH_2), 19.4 (d, $J_{(P-C)}$ = 8.1 Hz, CH_2). **IR** : ν_{max} = 3078, 2925, 2852, 1728, 1595, 1578, 1512, 1455, 1414, 1296, 1266, 1207, 1075, 1039, 876, 820, 758. **HRMS** (ESI) calcd. for $C_{61}H_{45}FeNO_4P$ $[M+H]^+$: 942.2436, found : 942.2439.



The phosphoric acid **5b** was obtained in quantitative yield from the terphenyl-substituted phosphate above, as an orange solid. **mp** : 215-218 °C (decomposition). **^{31}P** (202.5 MHz, DMSO-d_6) : δ -12. **^{1}H NMR** (500.1 MHz, DMSO-d_6) : 7.89 (d, *J* = 7.3 Hz, 8H), 7.88 (bs, 2H), 7.54 (t, *J* = 7.3 Hz, 8H), 7.43 (t, *J* = 7.3 Hz, 4H), 7.30 (bs, 2H), 6.70 (d, *J* = 8.2 Hz, 2H), 6.49 (d, *J* = 8.2 Hz, 2H), 4.97 (s, 2H), 4.74 (s, 2H), 4.45 (s, 2H), 4.40 (s, 2H). **^{13}C NMR** (125.8 MHz, DMSO-d_6) : 147.2 (d, $J_{(P-C)}$ = 7.5 Hz, C), 140.9 (C), 140.4 (C), 138.8 (C), 131.5 (d, $J_{(P-C)}$ = 5.3 Hz, C), 129.6 (C), 129.0 (CH), 127.6 (CH), 127.3 (CH), 127.2 (CH), 126.6 (CH), 126.3 (CH), 124.3 (CH), 121.2 (CH), 86.1 (C), 69.2 (CH), 68.4 (CH), 66.8 (CH), 65.8 (CH). **IR** : ν_{max} = 3033, 2924, 1721, 1595, 1511, 1498, 1455, 1414, 1262, 1229, 1186, 1129, 1077, 1018, 927, 875. **HRMS** (ESI) calcd. for $C_{58}H_{42}FeO_4P$ $[M+H]^+$: 889.2170, found : 889.2187. Separation of

enantiomers by semi-preparative HPLC: CHIRALPAK® ID column (250 x 10 mm, 5 mic), 30°C, 36% THF/64% *n*-heptane/0.3% TEA/0.5% TFA, 4.7 mL/min, UV detection at 260 nm. Retention time 6.4 min: **(+)-5b**, $[\alpha]_D^{20}$ = +775 (*c* = 1, CH_2Cl_2); 12.4 min: **(-)-5a** $[\alpha]_D^{20}$ = -765 (*c* = 1, CH_2Cl_2).

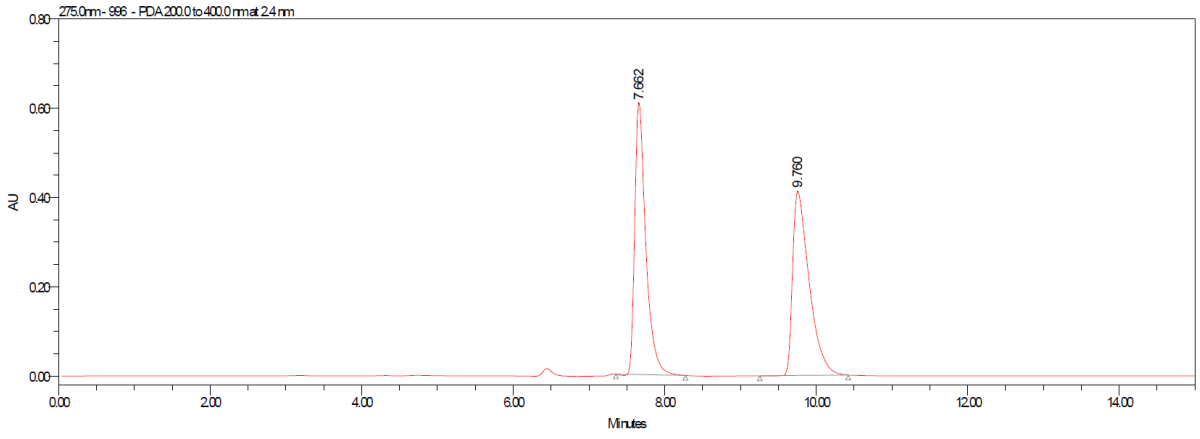


V. General procedure for the enantioselective reduction of 2-phenylquinoline.

A solution of 2-phenylquinoline (20.5 mg, 0.1 mmol), Hantzsch dihydropyridine **7** (0.24 mmol) and the acid catalyst **5** (0.01 mmol) in toluene (2 ml) was stirred at r.t. for 2h. The solvent was removed under reduced pressure and the residue was purified on silica gel with an heptane/EtOAc gradient, from 98 : 2 to 95 : 5. 2-Phenyl-1,2,3,4-tetrahydroquinoline was obtained as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) : 7.46 (d, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 1H), 7.09-7.04 (m, 2H), 6.75 (t, *J* = 7.7 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 1H), 4.63 (bs, 1H), 4.48 (dd, *J* = 9.5, 3.3 Hz, 1H), 3.01-2.94 (m, 1H), 2.80 (dt, *J* = 16.5, 4.9 Hz, 1H), 2.21-2.16 (m, 1H), 2.13-2.05 (m, 1H).

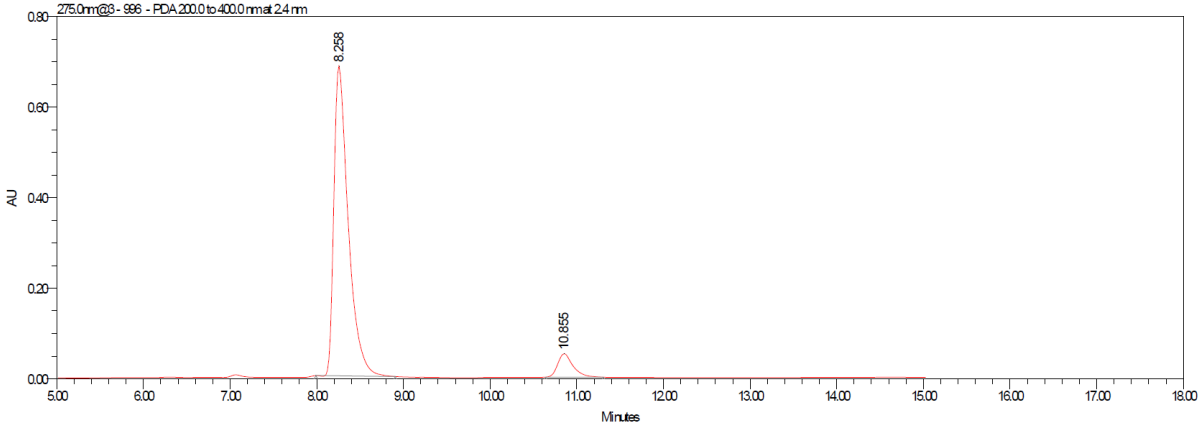
E.e.s were determined by chiral HPLC using a CHIRALPAK® IB analytical column. Eluent: *i*-PrOH/*n*-heptane, 5:95 at a flow rate of 1 mL/min [detection at 275 nm]. Retention times: 8.2 min [(-)-(S)-2-phenyl-1,2,3,4-tetrahydroquinoline] and 10.8 min.

Racemic sample:



	RT	Area	%Area
1	7.662	6191669	49.76
2	9.760	6252297	50.24

Enantioenriched sample obtained with catalyst (+)-5b and dihydropyridine 7b. ee = 85%, $[\alpha]_D^{20}$ -31 (*c* = 0.8, $CHCl_3$). {Lit.:[5] $[\alpha]_D^{20}$ -37.7 (*c* = 1, $CHCl_3$)) for (*S*)-2-Phenyl-1,2,3,4-tetrahydroquinoline at 97% ee}



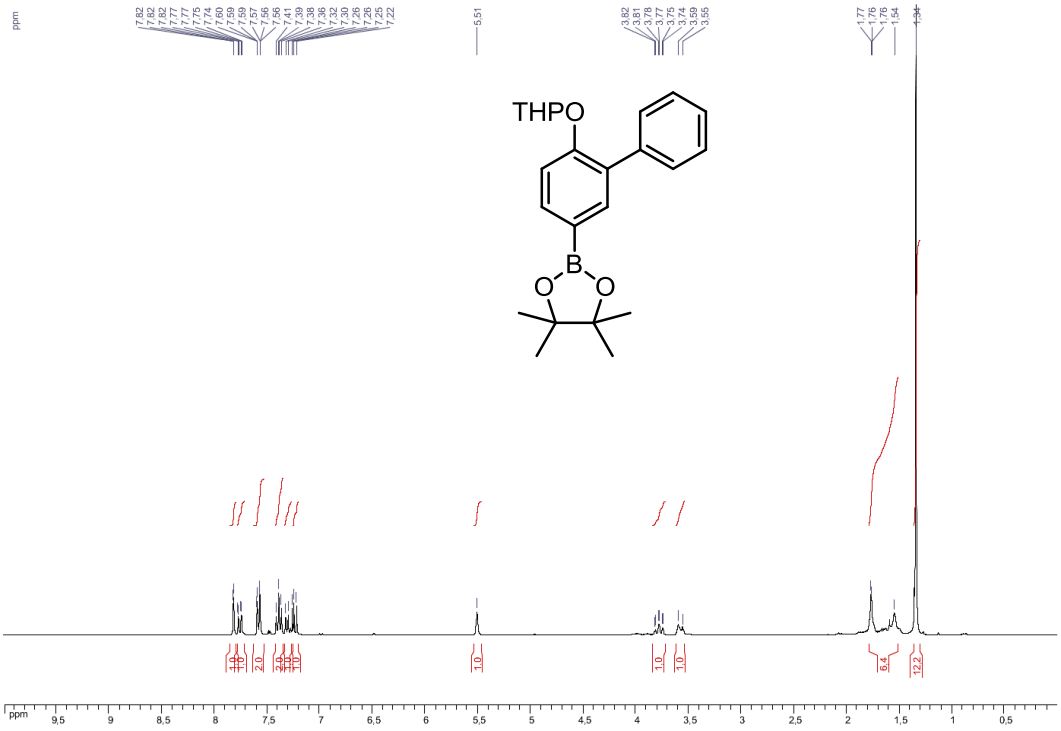
	RT	Area	%Area
1	8.258	7866568	92.59
2	10.855	629418	7.41

[5] Rueping, M.; Antonchick, A. P.; Theissmann, T. *Angew. Chem. Int. Ed.* **2006**, *45*, 3683-3686.

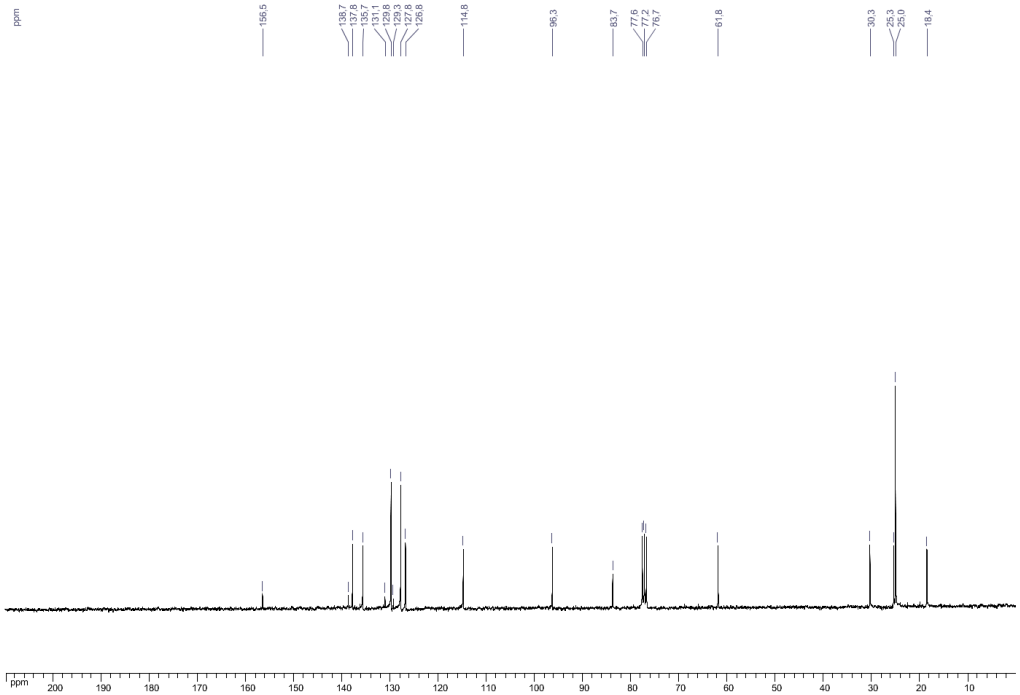
VI. NMR Spectra

4,4,5,5-tetramethyl-2-(6-(tetrahydro-2H-pyran-2-yloxy)biphenyl-3-yl)-1,3,2-dioxaborolane

^{1}H NMR (300.2 MHz, $CDCl_3$)

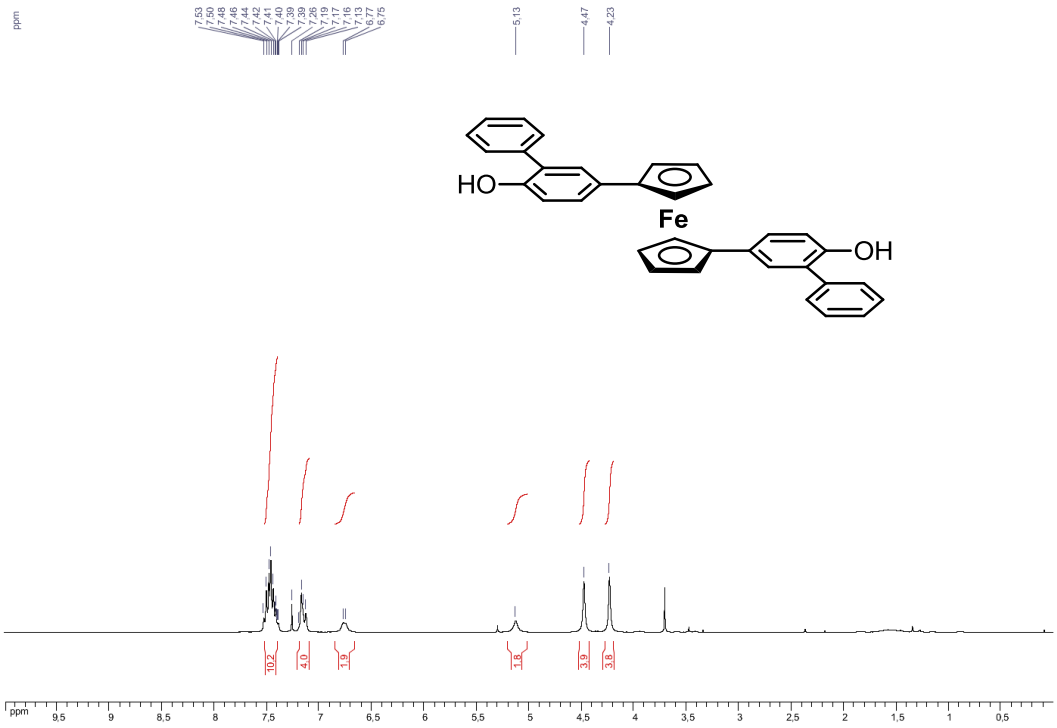


^{13}C NMR (75.5 MHz, $CDCl_3$)

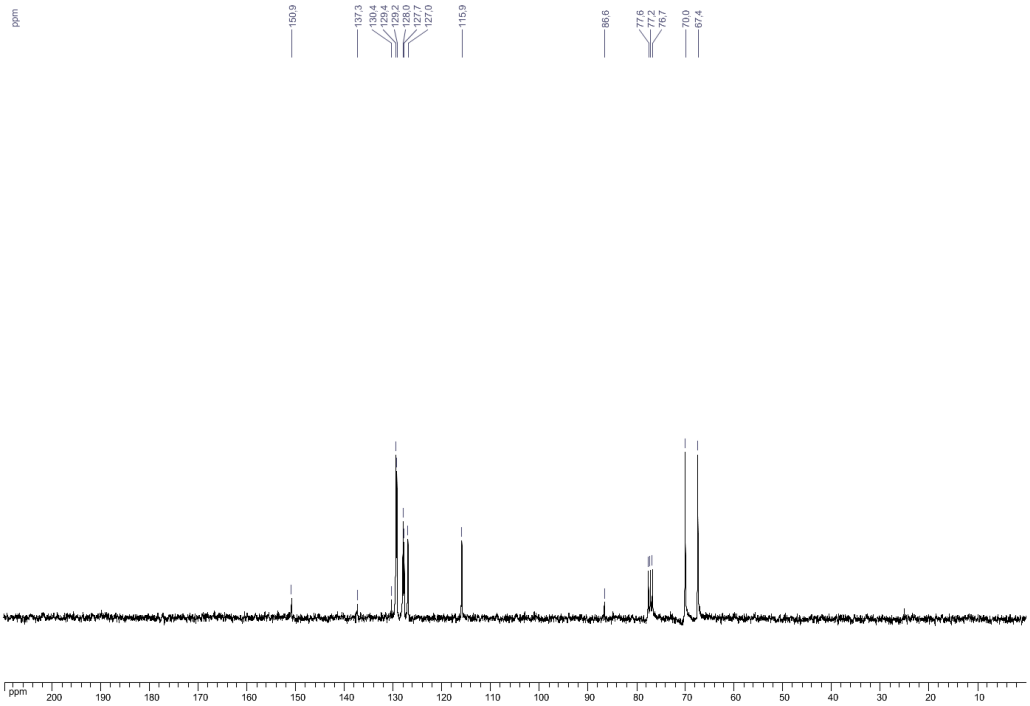


1,1'-Bis-(2-hydroxy-biphen-4-yl)-ferrocene (3a)

^{1}H NMR (300.2 MHz, $CDCl_3$)

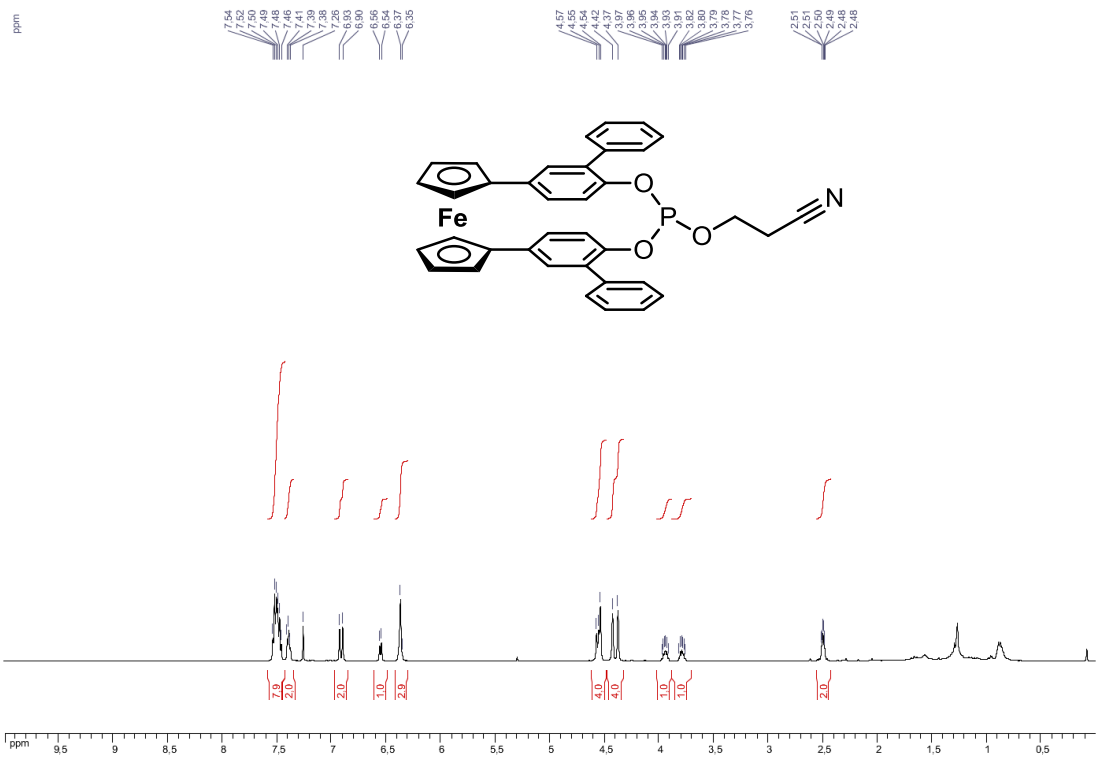


^{13}C NMR (75.5 MHz, $CDCl_3$)

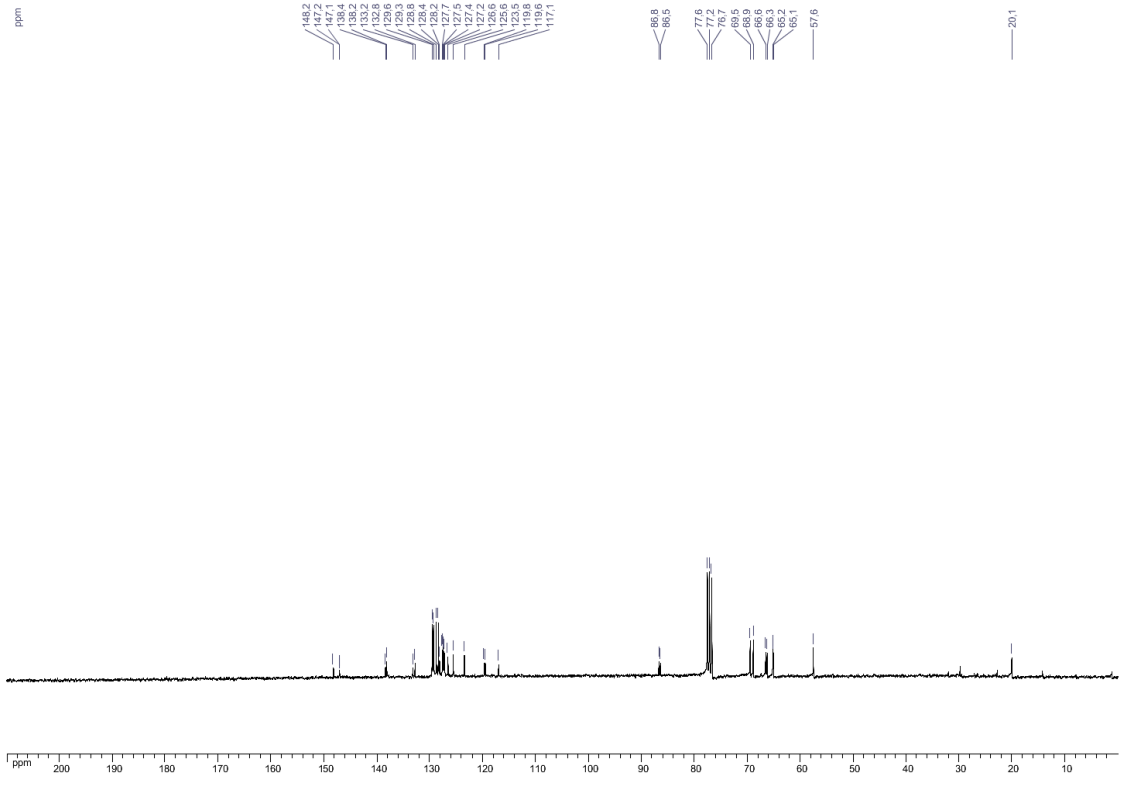


Phosphite 4a

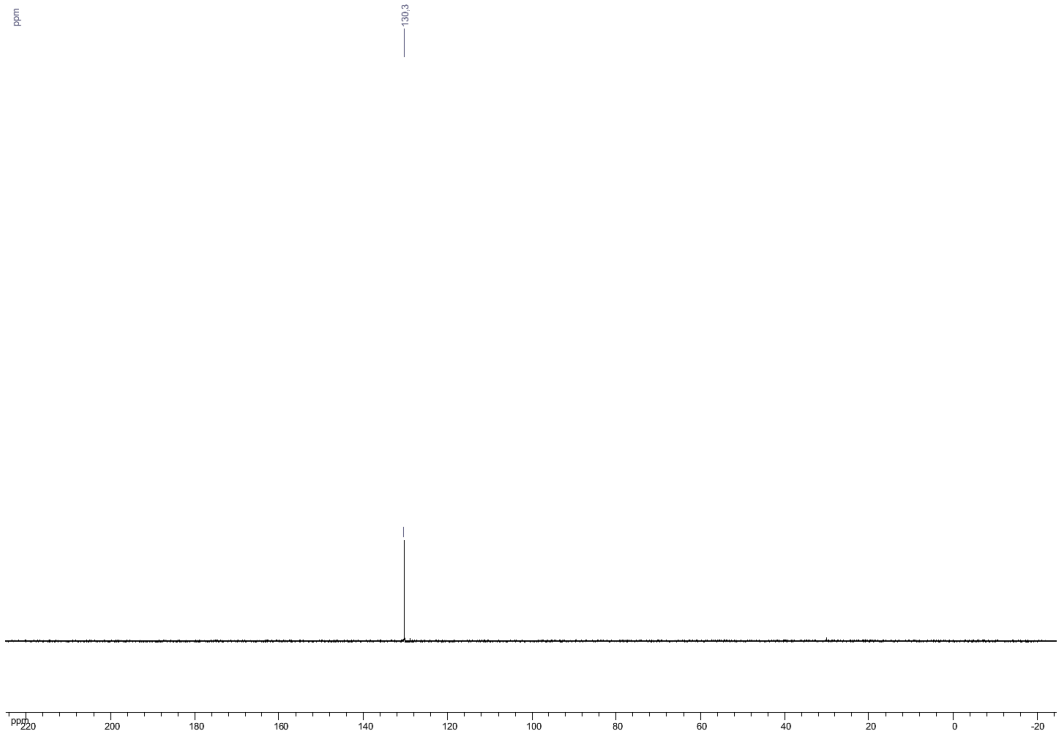
^{1}H NMR (500.2 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

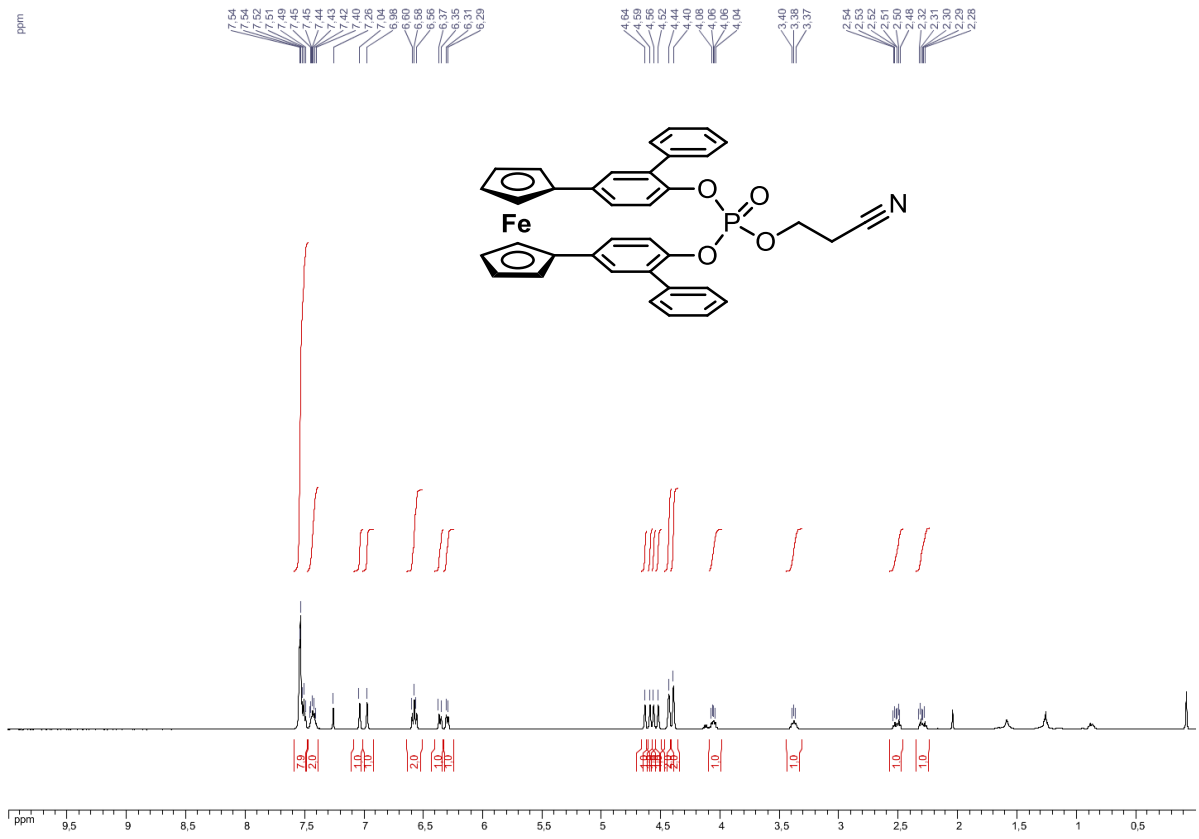


^{31}P NMR (202.5 MHz, $CDCl_3$)

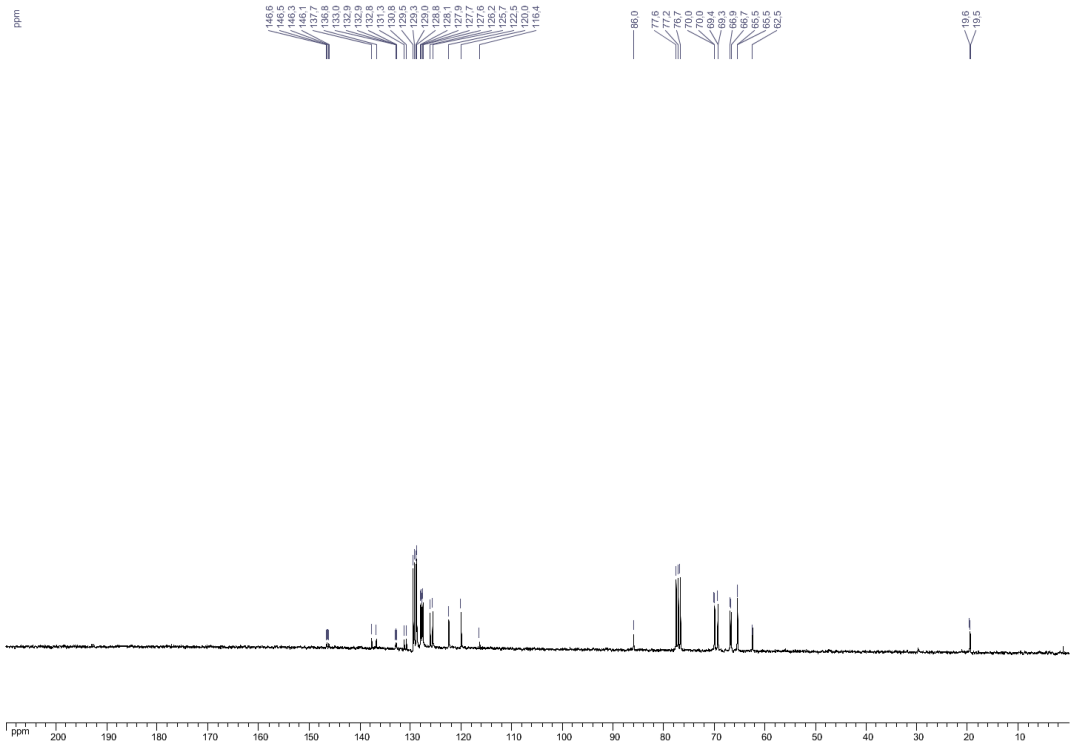


Phosphate

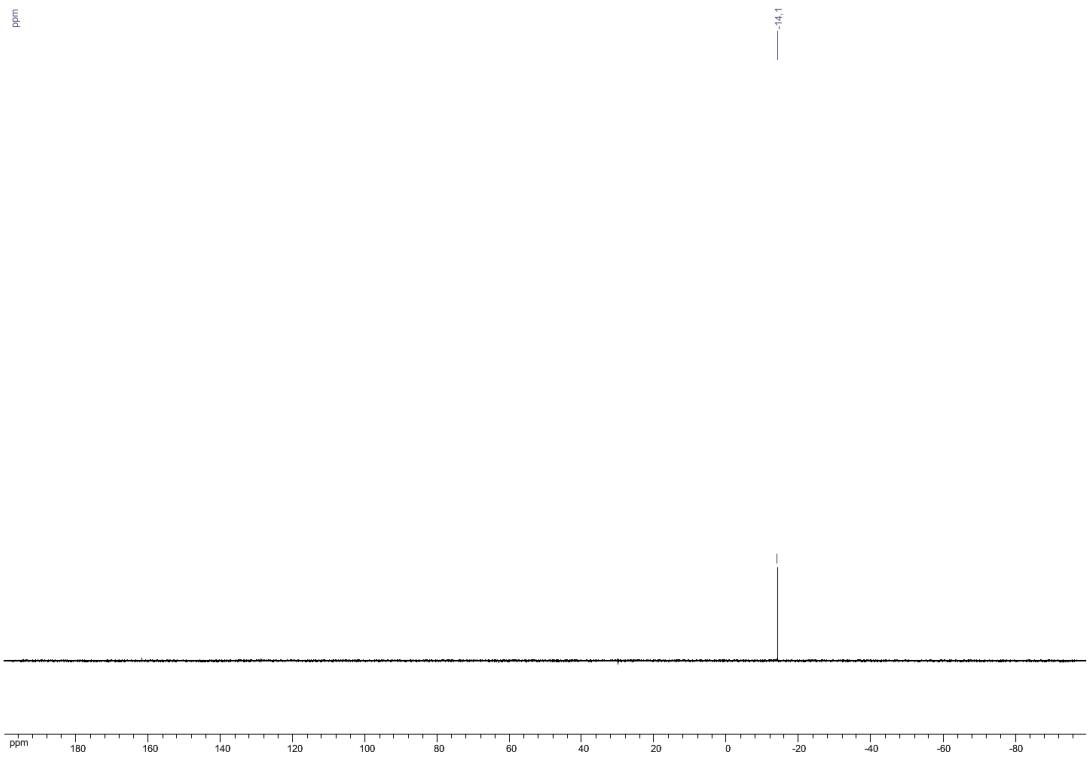
^{1}H NMR (500.2 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

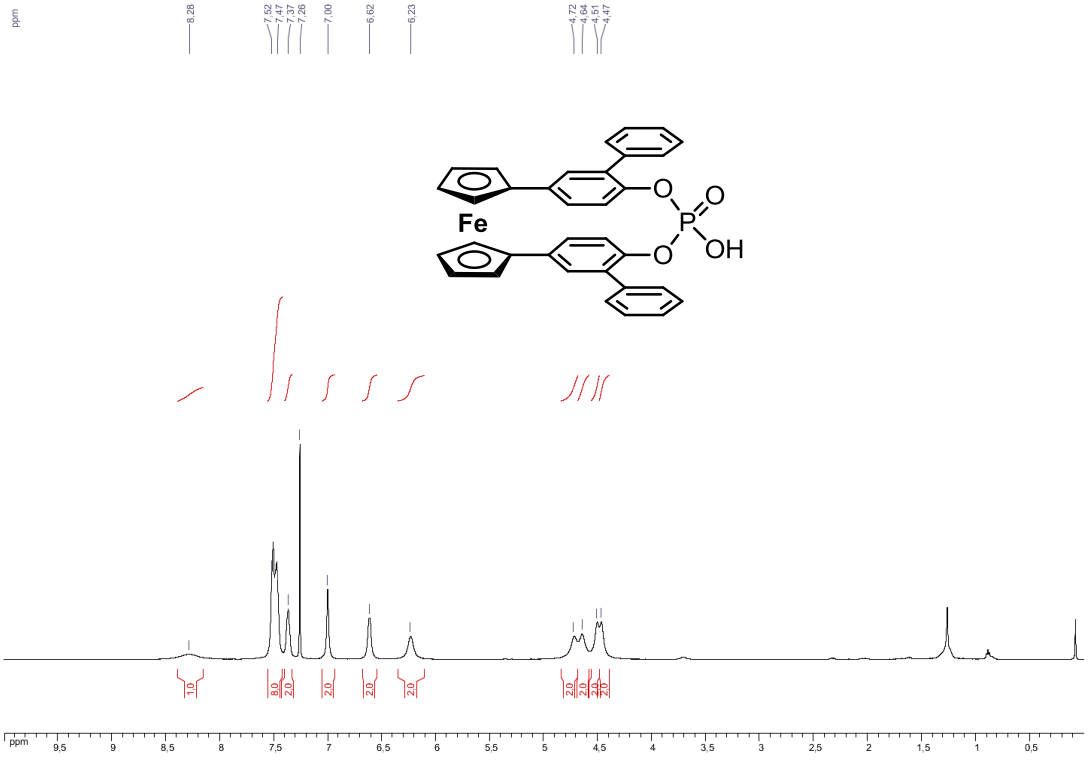


^{31}P NMR (202.5 MHz, $CDCl_3$)

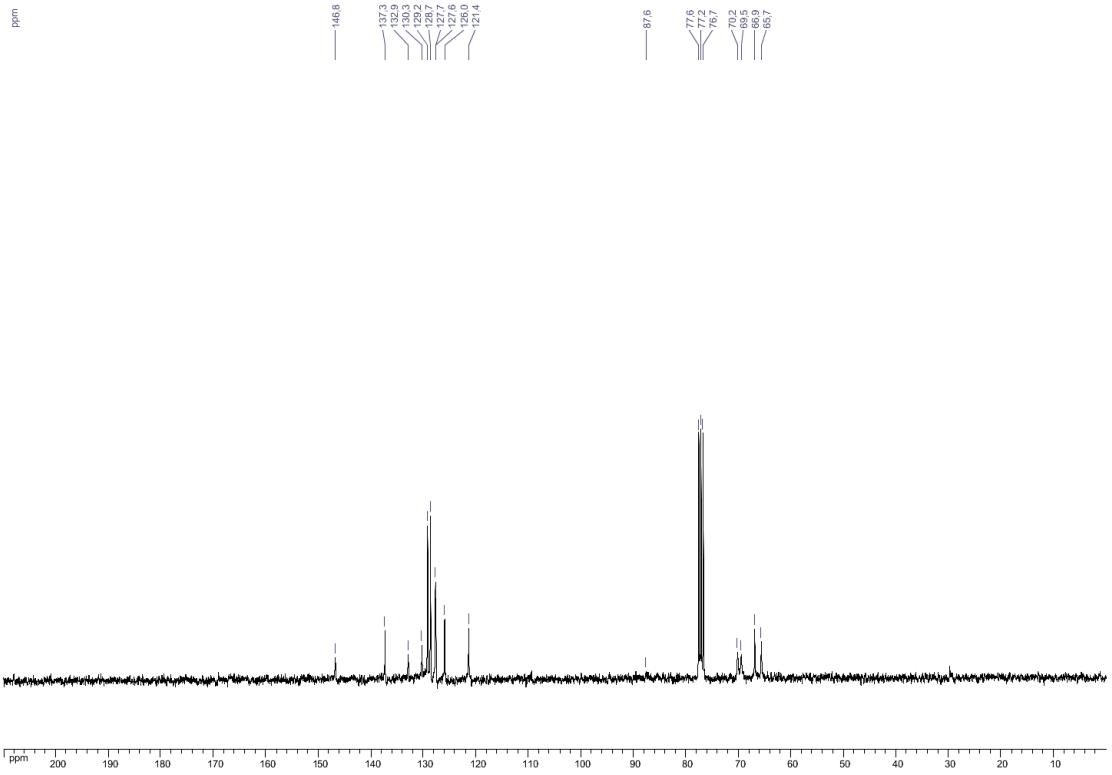


Phosphoric acid 5a

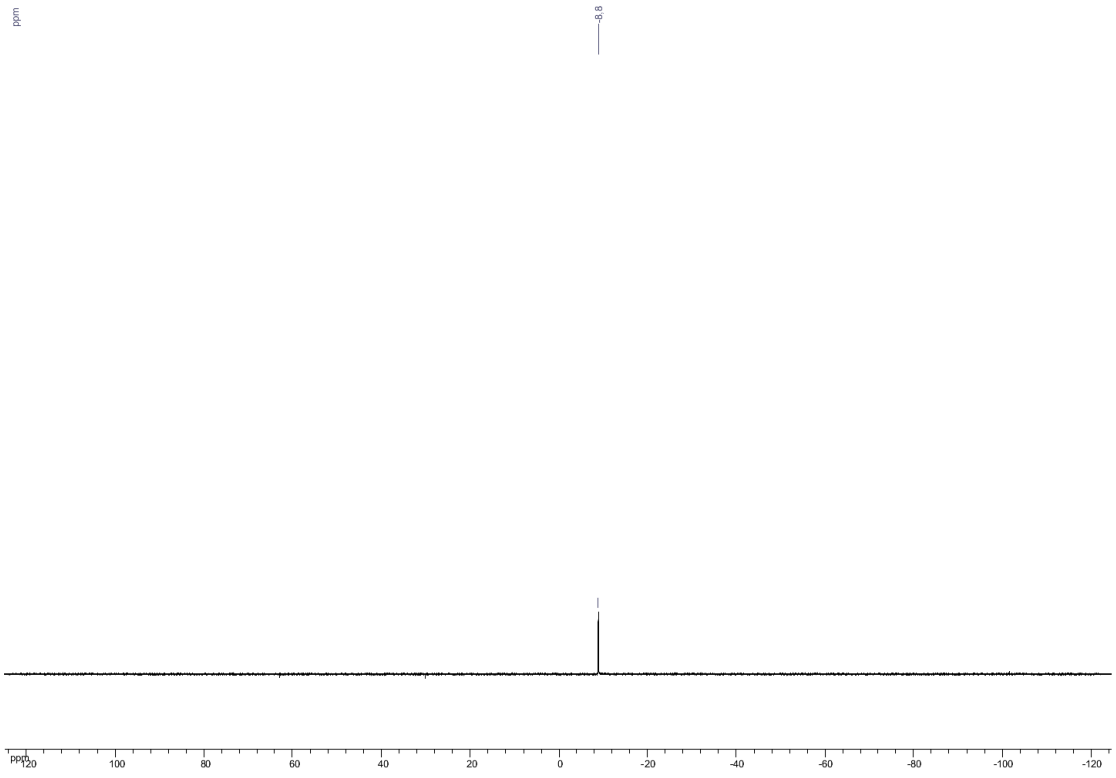
^{1}H NMR (500.2 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

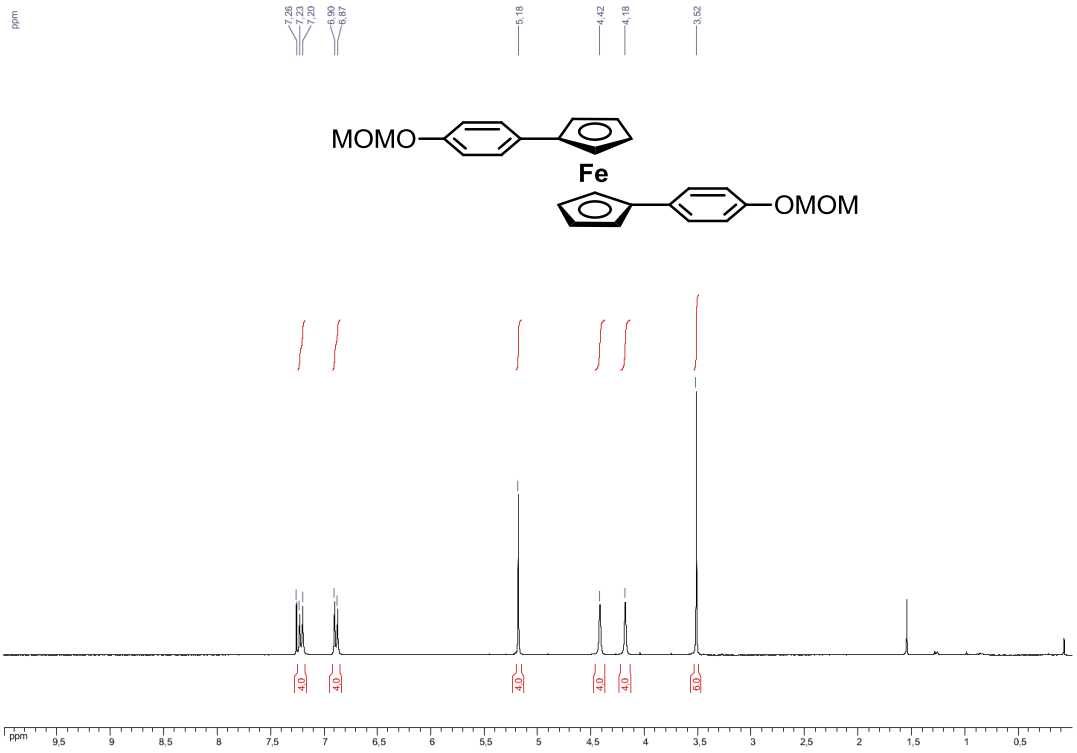


^{31}P NMR (202.5 MHz, $CDCl_3$)

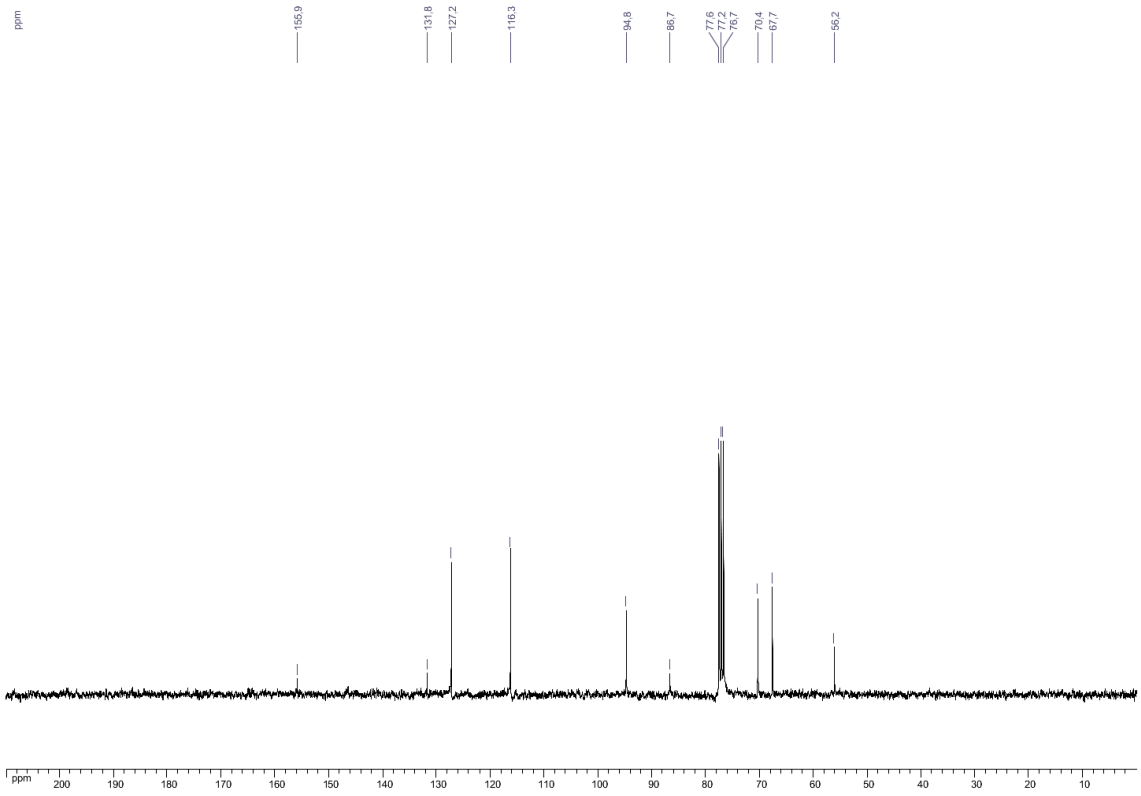


1,1'-Bis-[4-(methoxymethoxy)-1-phenyl]-ferrocene.

^{1}H NMR (300.2 MHz, $CDCl_3$)

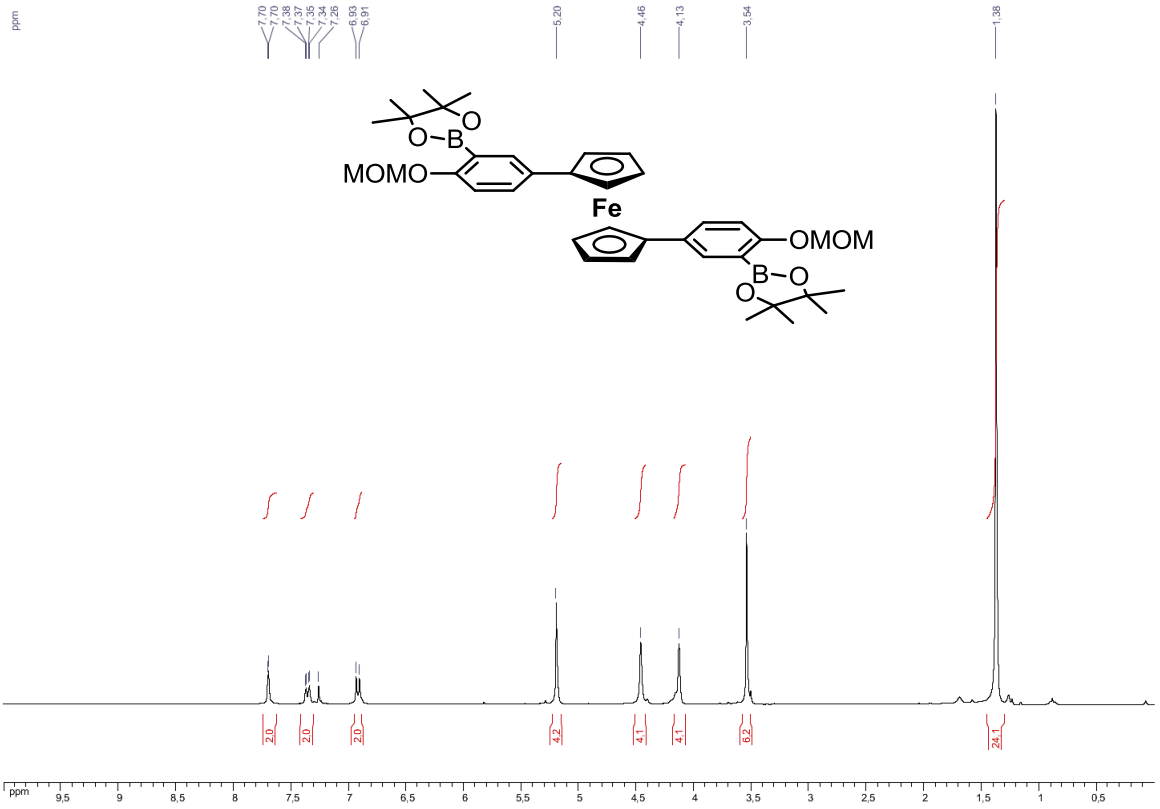


^{13}C NMR (75.5 MHz, $CDCl_3$)

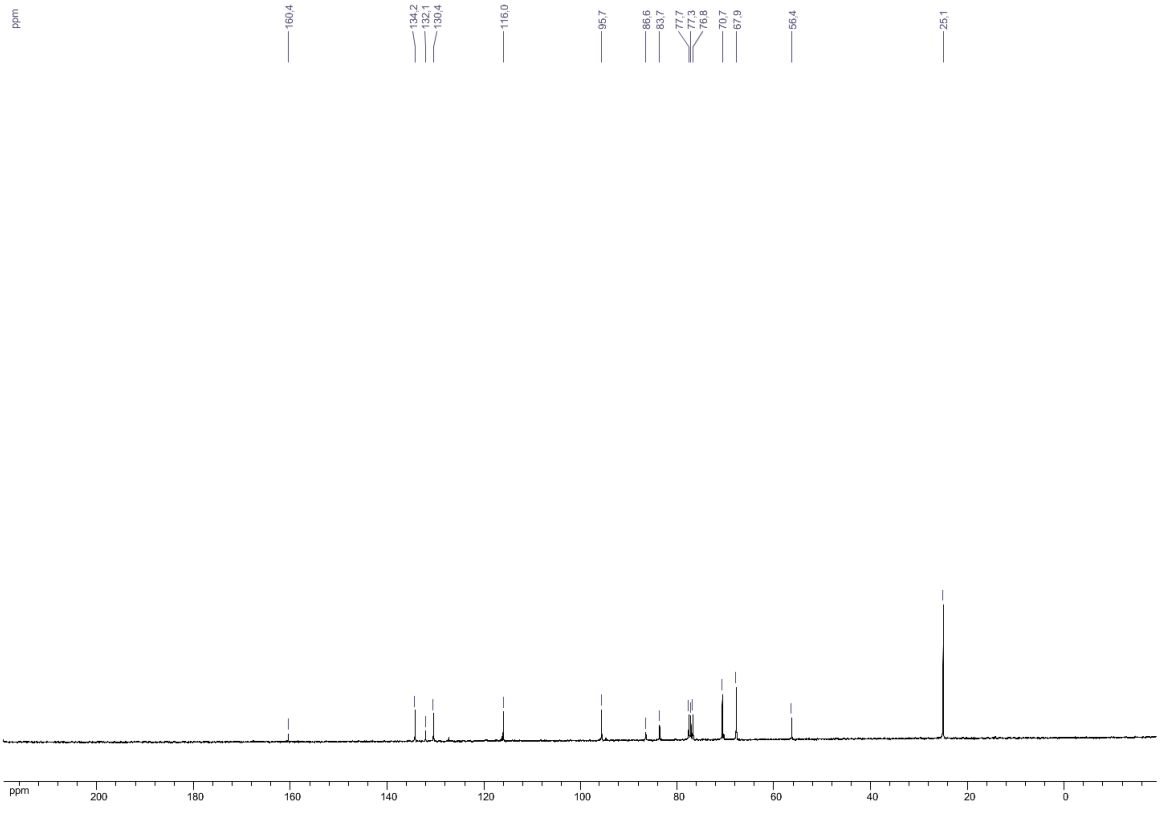


1,1'-Bis-[4-(methoxymethoxy)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-phenyl]ferrocene (6)

^{1}H NMR (300.2 MHz, $CDCl_3$)

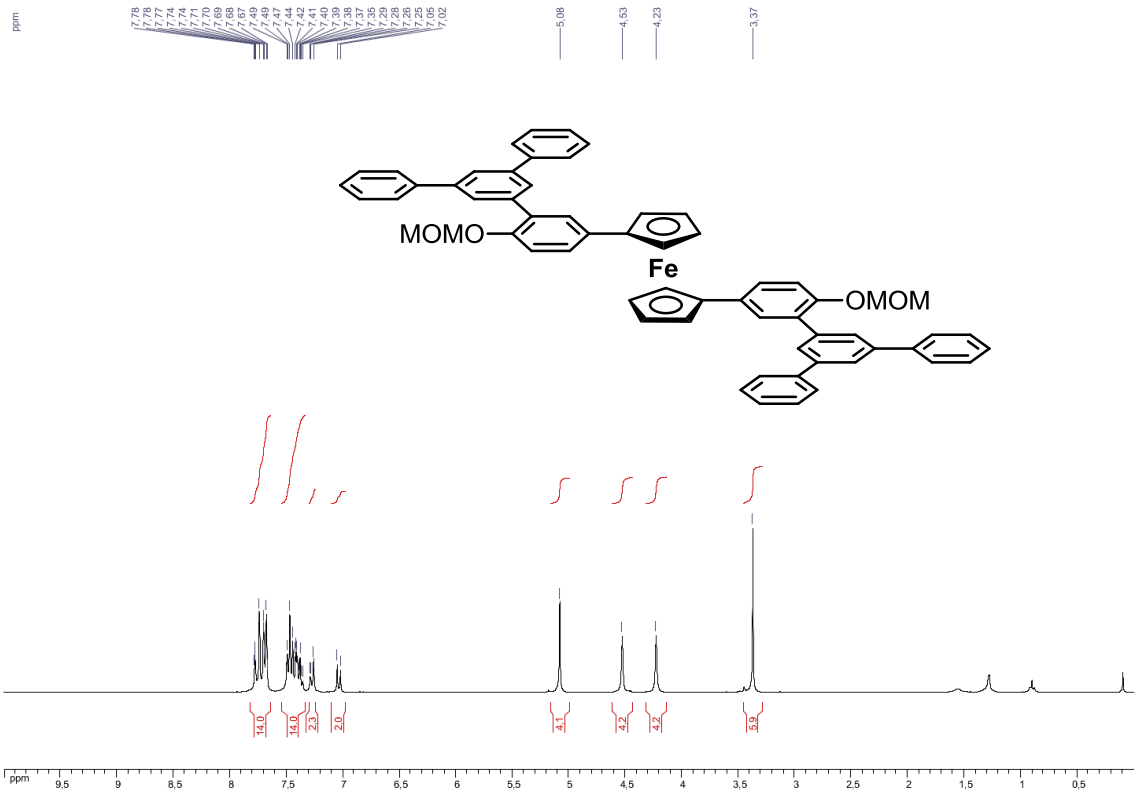


^{13}C NMR (75.5 MHz, $CDCl_3$)

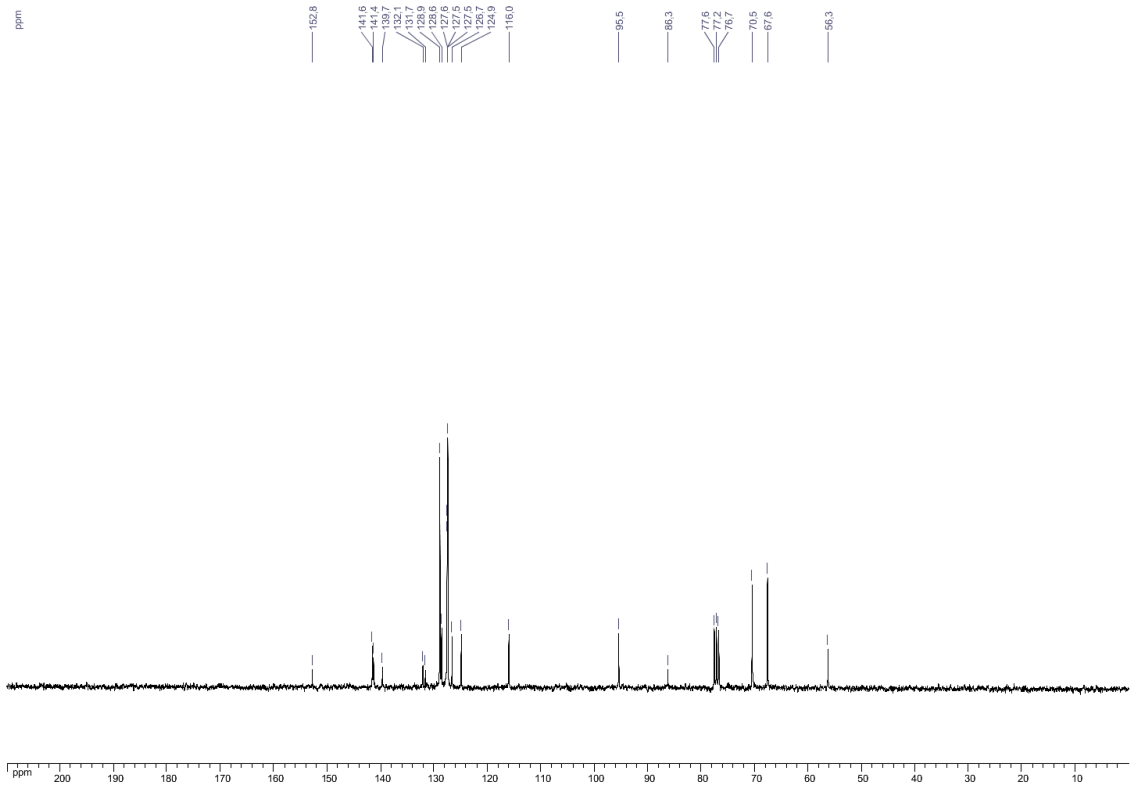


1,1'-Bis-[4-(methoxymethoxy)-3-(3',5'-diphenyl)phenyl]ferrocene.

^{1}H NMR (300.2 MHz, $CDCl_3$)

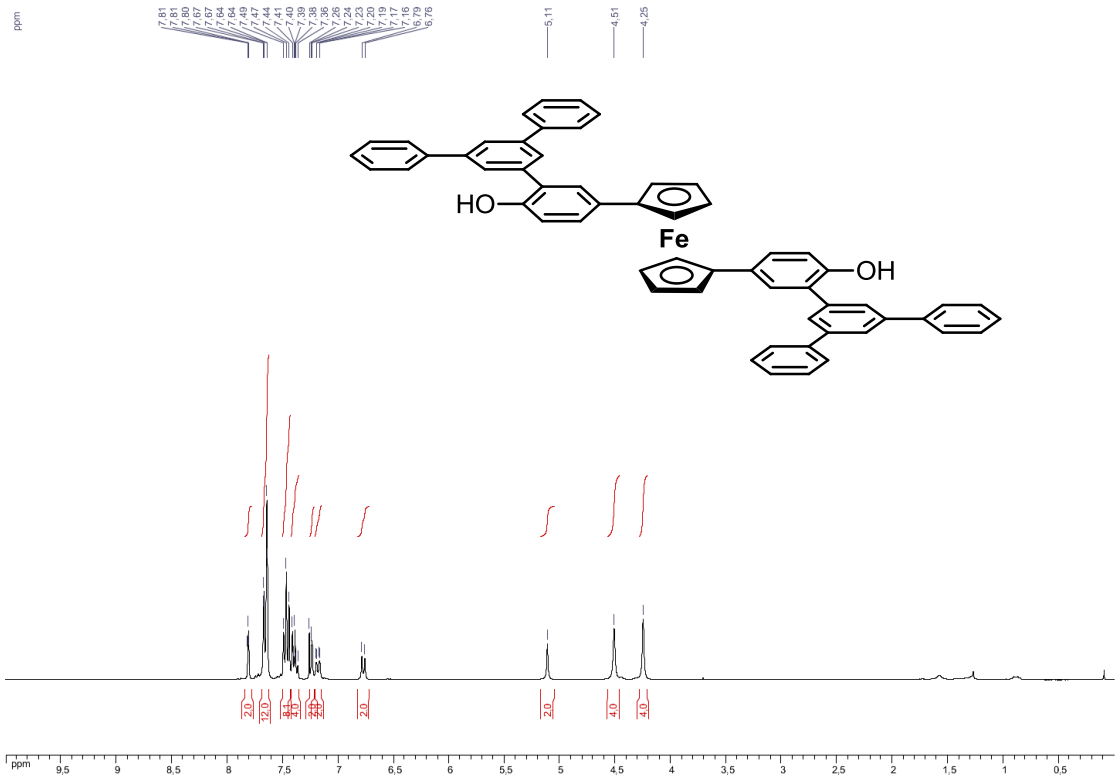


^{13}C NMR (75.5 MHz, $CDCl_3$)

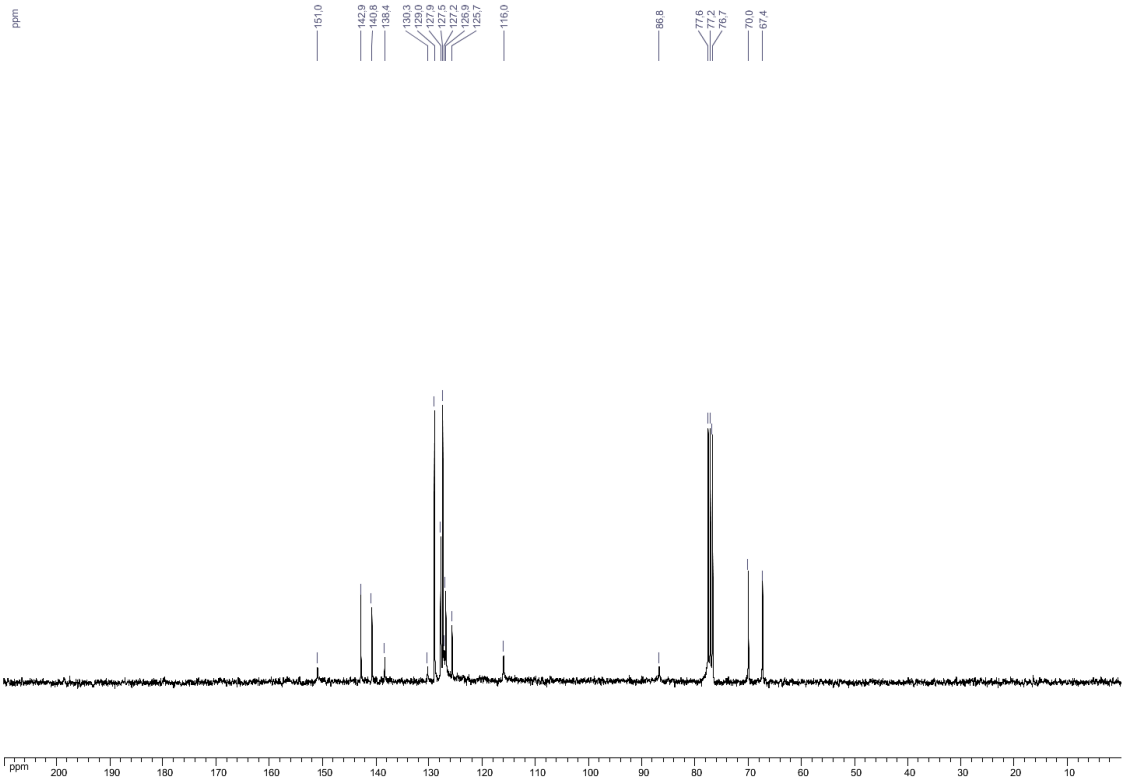


1,1'-Bis-[4-(hydroxy)-3-(3',5'-diphenyl)phenyl]ferrocene (3b).

^{1}H NMR (300.2 MHz, $CDCl_3$)

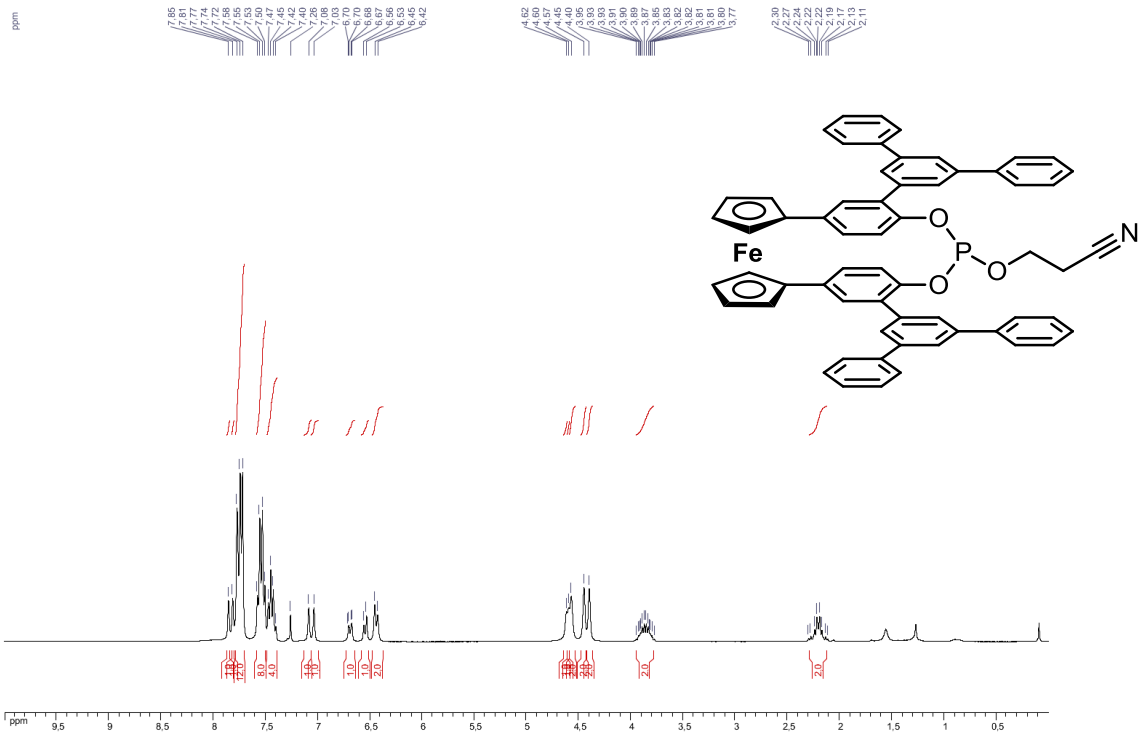


^{13}C NMR (75.5 MHz, $CDCl_3$)

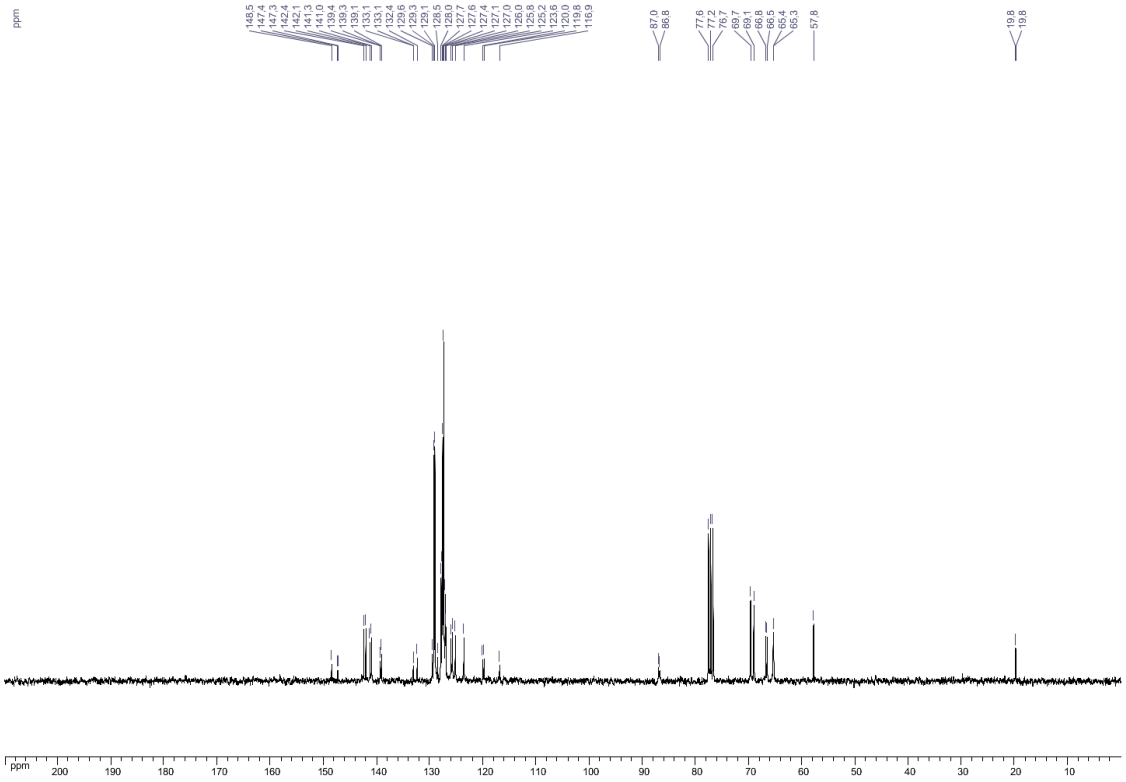


Terphenyl-substituted phosphite

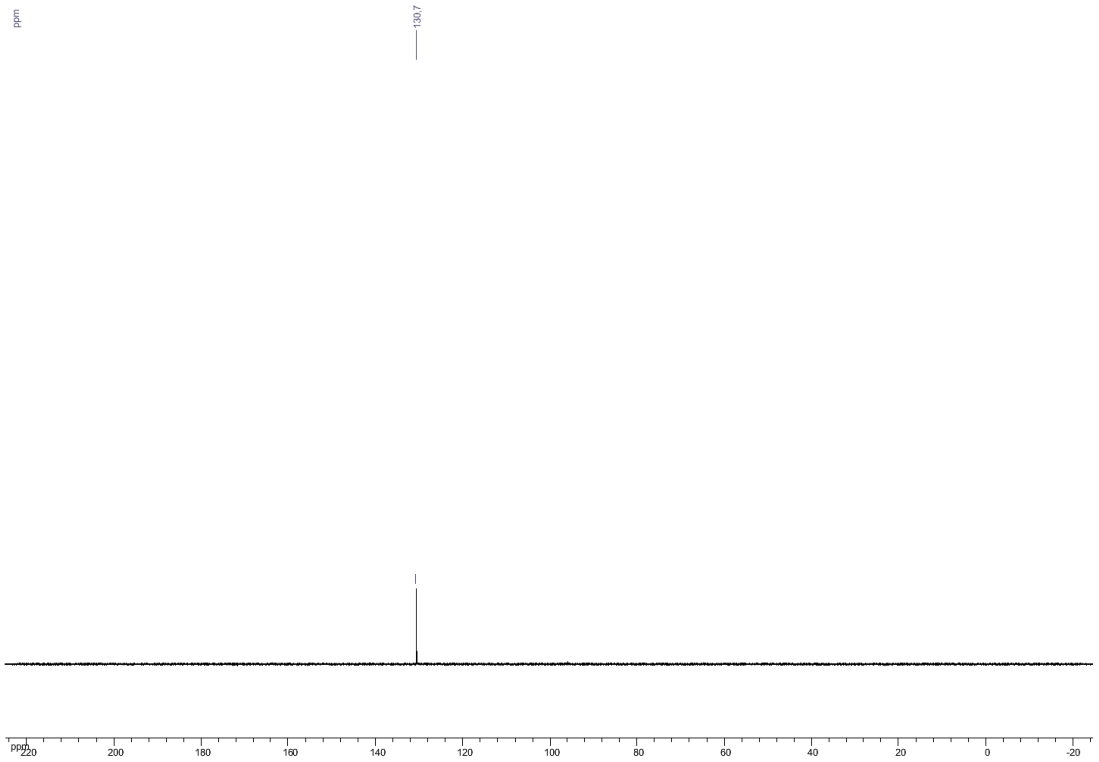
^{1}H NMR (300.2 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

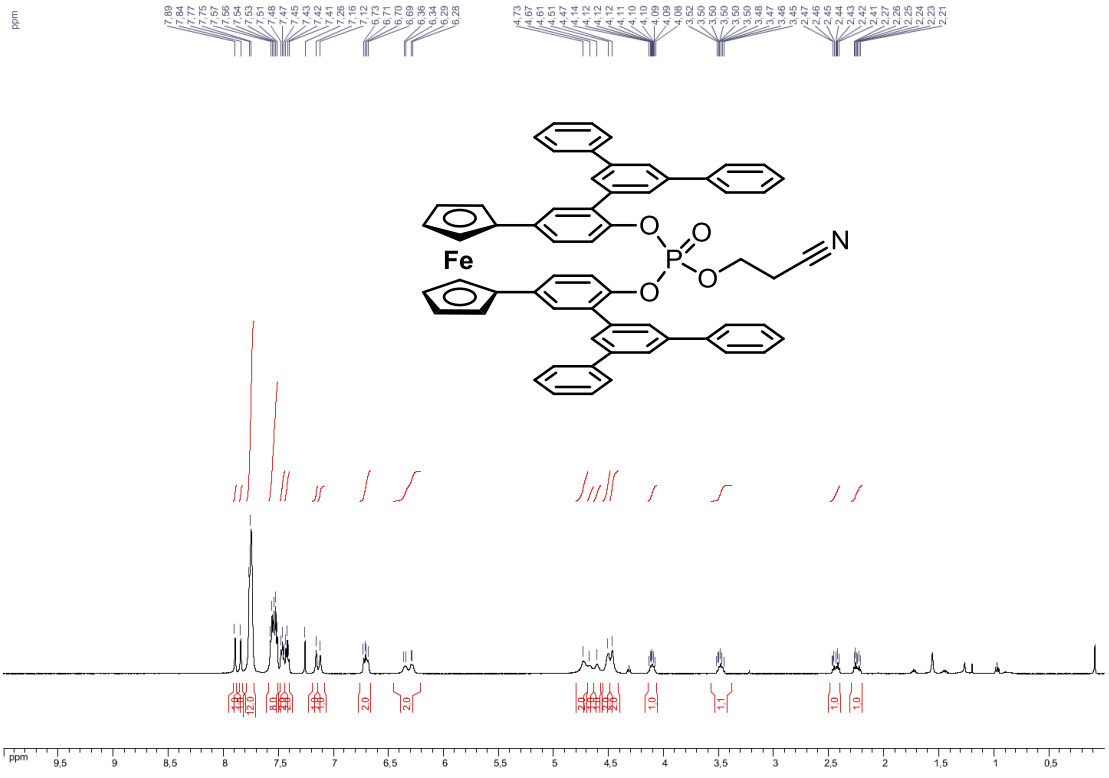


^{31}P NMR (202.5 MHz, $CDCl_3$)

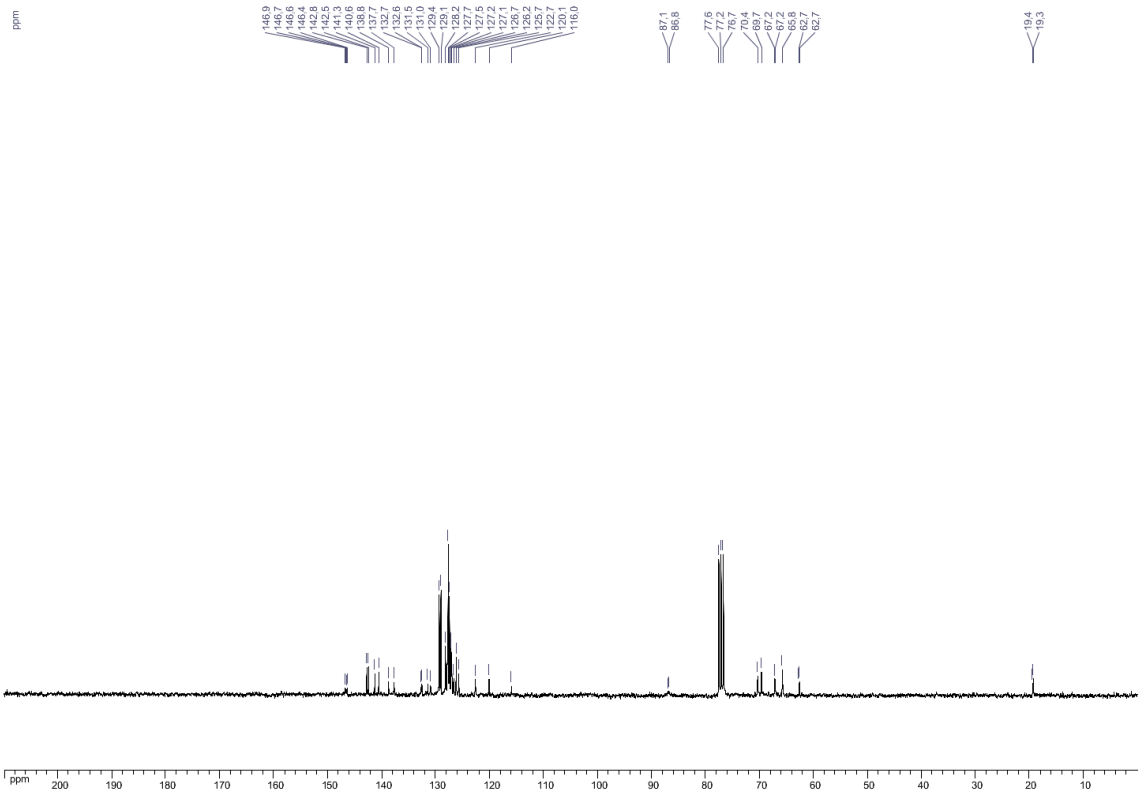


Terphenyl-substituted phosphate

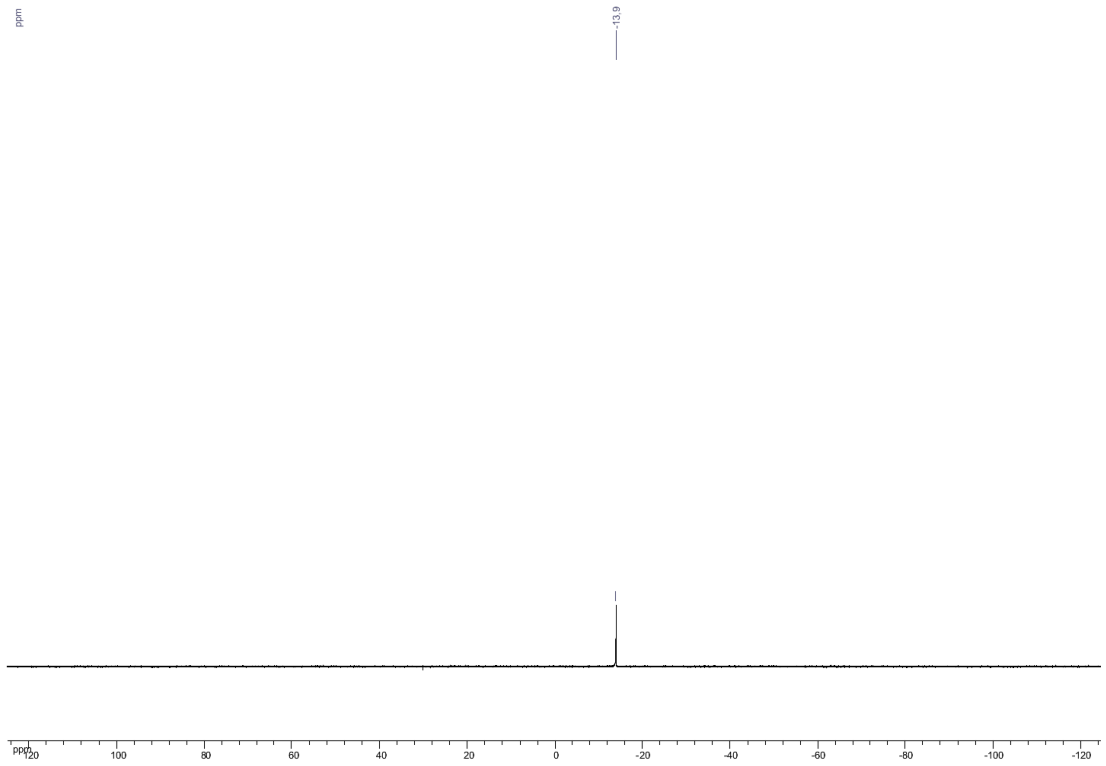
^{1}H NMR (500.2 MHz, $CDCl_3$)



^{13}C NMR (75.5 MHz, $CDCl_3$)

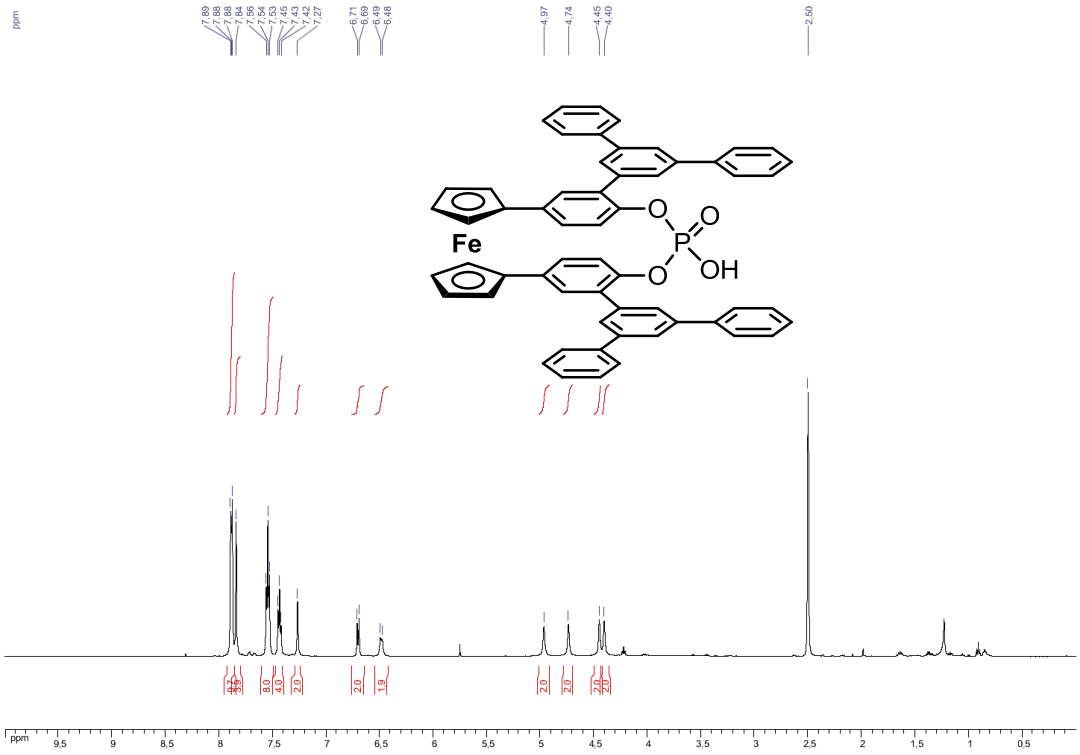


^{31}P NMR (202.5 MHz, $CDCl_3$)

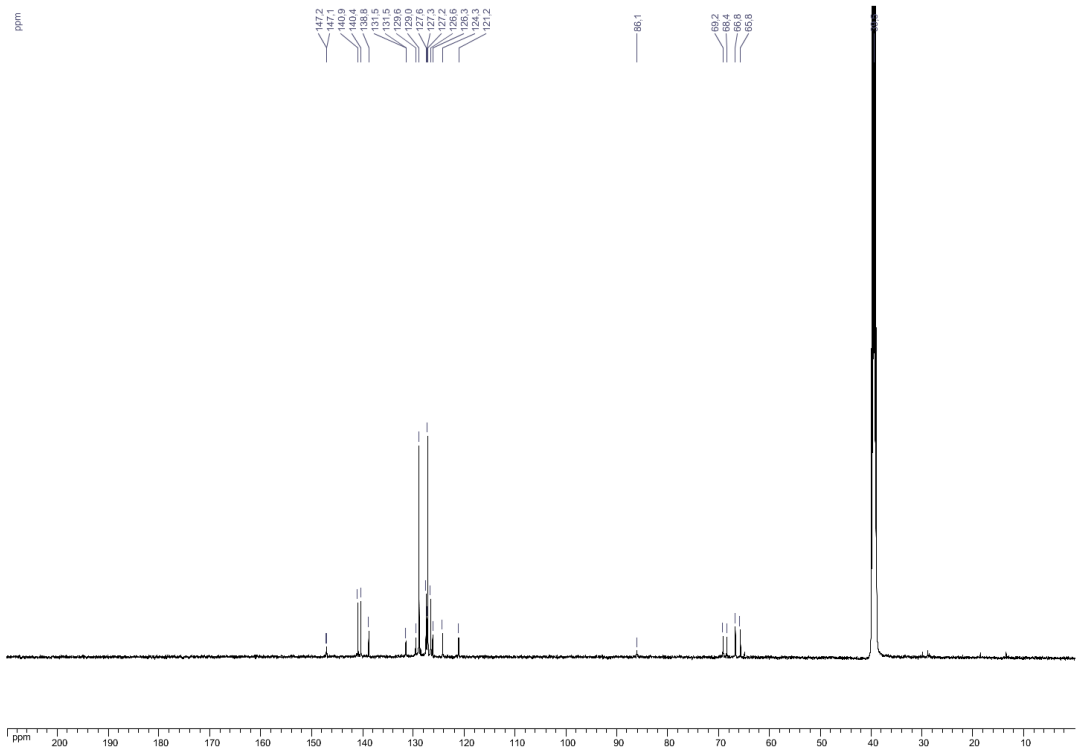


Phosphoric acid 5b

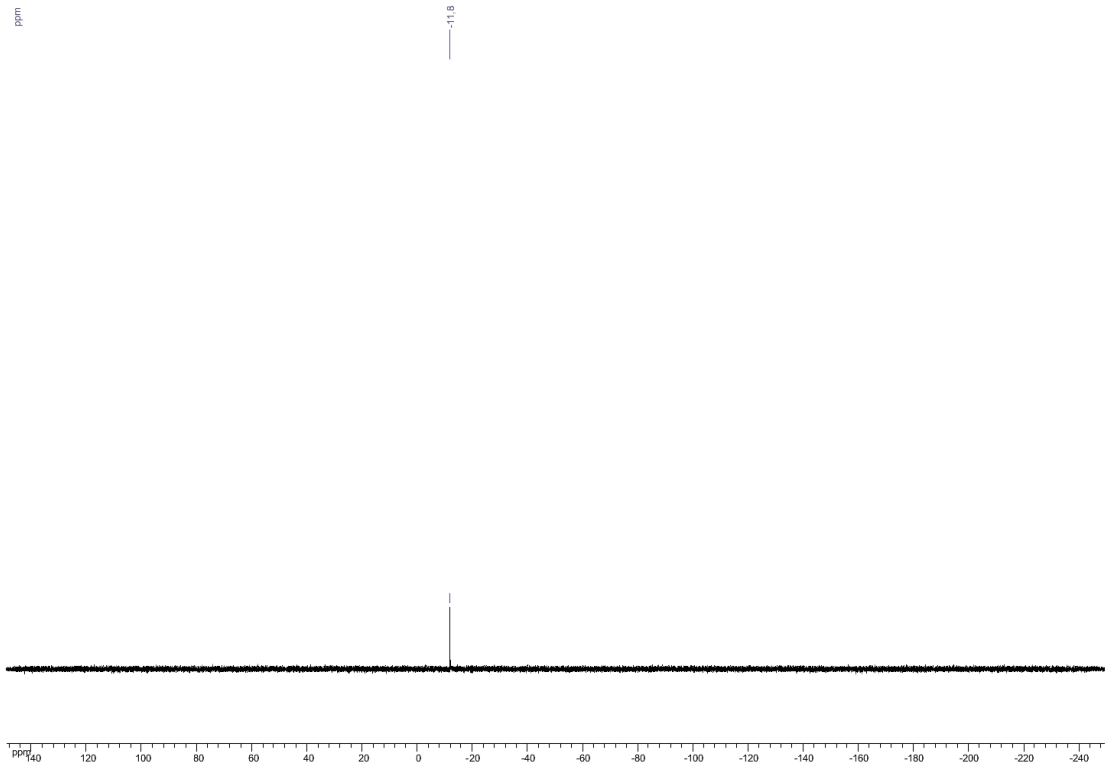
^{1}H NMR (500.1 MHz, DMSO-d_6)



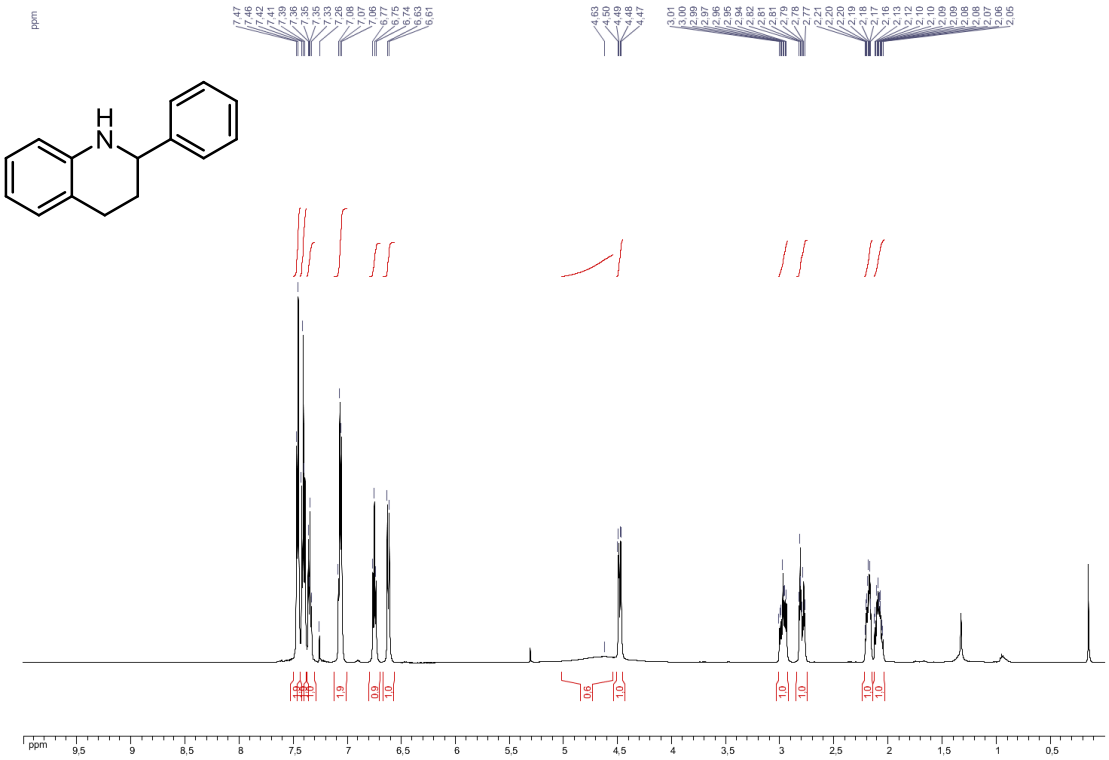
^{13}C NMR (500.1 MHz, DMSO-d_6)



^{31}P NMR (202.5 MHz, DMSO-d_6)



2-phenyl-1,2,3,4-tetrahydroquinoline.



VII. X-ray data for (**5a**)$_2$Ca

Single orange crystals of (**5a**)$_2$.Ca suitable to X-ray diffraction were grown by slow evaporation of methanol solutions. A platelet-like crystal was mounted in paratone-N oil on a nylon loop. X-ray diffraction data were recorded on a Rigaku RAPID II (IP area detector system) at 203K using mm007HF rotating anode Cu**K**α radiation. They were then indexed, integrated and scaled with *FS_Process* from the *CrystalClear*[6] software suite. The collected data were also corrected for polarization, Lorentz and absorption, the last one using a multi-scan method as implemented with *FS_Abscor*. Analyses of the reduced data done by *XPrep* [7] confirmed what was visually obvious from the diffraction images, namely the crystal was a poor diffractor, and the retained dataset was only truncated at the resolution of 2θ of 95° (1.05Å) for which R(sigma) = Σ [σ($\boldsymbol{F}_o^2$)] / Σ [$\boldsymbol{F}_o^2$] and R(int) = Σ|$\boldsymbol{F}_o^2$ - $\boldsymbol{F}_o^2$(mean)|/Σ[$\boldsymbol{F}_o^2$] are 0.24 and 0.20, respectively, despite mean $I/\sigma(I)$ below 2 beyond 2θ=72° (1.3Å). The structure was nevertheless solved by direct methods using the *SIR2004*[8] program and refined to an acceptable structural model with full-matrix least-squares technique on $\boldsymbol{F}^2$ using the *SHELXL-97*[9] program. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were set on calculated positions and refined with a riding model on their parent atoms using constrained isotropic temperature factors as follows U_H = 1.2 $U_{parent\ atom}$ (or U_H = 1.5 U_C in the case of methyl or hydroxyl groups) and the following distances C_{aryl}–H 0.94 Å; C_{methyl}–H 0.97 Å, $O_{hydroxyle}$–H, 0.83 Å. Phenyl rings were refined as rigid bodies (AFIX 66, C–C distance of 1.39 Å and bond angles of 120°) and restraints were used for the anisotropic displacement parameters (DELU, SIMU). Figures were produced using the program MERCURY.[10] The crystal structure of (**5a**)$_2$.Ca was found to consist of a dimeric complex centred around a hexacoordinated calcium atom occupying an inversion centre of the crystal, which belongs to the monoclinic spacegroup, C 2/c. The calcium atom is octahedrally coordinated by four methanol molecules and two phosphate O atoms in trans. Two additional methanol molecules are associated with the dimer, each making a hydrogen bond with a phosphate O atom (distance O–H…O=P 1.97Å).

Crystal data for (**5a**)$_2$.Ca: C_{72} H_{60} Ca Fe_2 O_{12} P_2, 2(C H_4 O), **M**r = 1395.00, monoclinic, space group **C** 2/c, **a** = 27.866(11), **b** = 7.426(3), **c** = 33.582(14) Å, β = 102.66(2)°, **V** = 12451(4) Å^3, **T** = 203(2) K, λ = 1.54187 Å, **Z** = 4, ρ_{calc} = 1.367 g cm^{-3}, μ = 5.074 mm^{-1}, 3078 unique reflections [12605 measured (**R**int = 0.203)] and 1424 observed with **I** > 2**σ**(**I**), 2.70º ≤ θ ≤ 47.5º, **R** = 0.133 (0.198 for all data), **wR** = 0.304 (0.345 for all data) with 397 parameters and 272 restraints, the final Fourier-difference map showed maximum and minimum height peaks of 0.38 and -0.44 e Å^{-3}.

Crystallographic data (including structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 916122. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail:deposit@ccdc.cam.ac.uk).

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[7] Bruker (2005). *XPREP*. Bruker AXS Inc., Madison, Wisconsin, USA.
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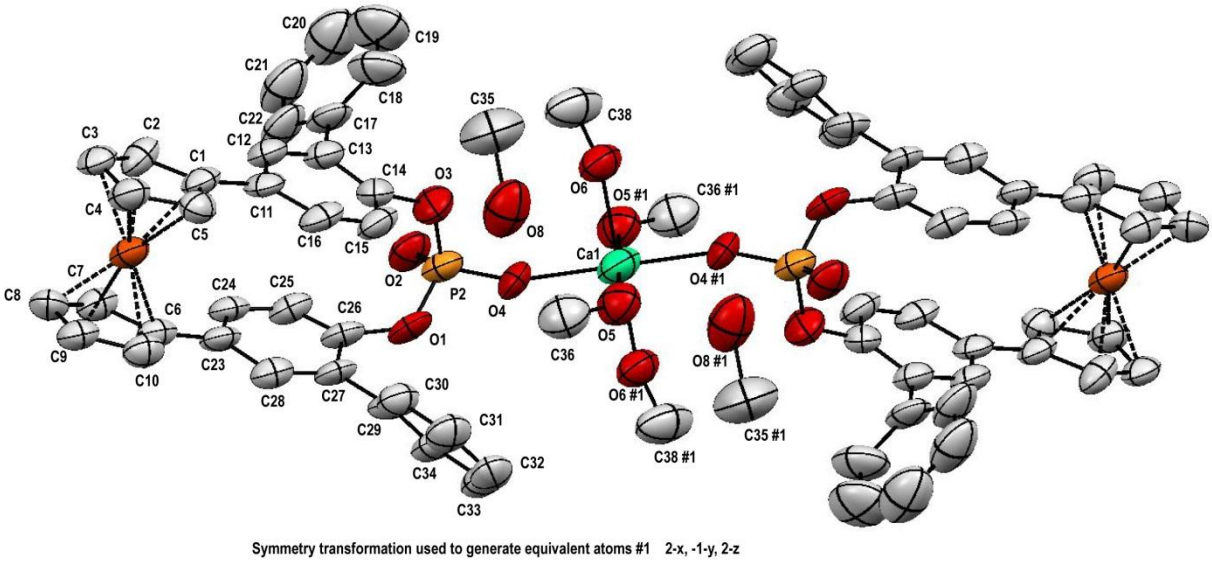
[10] Macrae, C. F., Edgington, P. R., McCabe, P., Pidcock, E., Shields, G. P., Taylor, R., Towler, M. & van de Streek, J. (2006). Mercury: visualization and analysis of crystal structures. *J.Appl. Cryst.* **39**, 453-457



Symmetry transformation used to generate equivalent atoms #1 2-x, -1-y, 2-z

Table 1. Bond lengths [Å] and angles [°] for **(5a)$_2$.**Ca.

Fe(1)-C(4)	1.997(14)	C(1)-C(11)	1.500(16)
Fe(1)-C(10)	2.019(12)	C(2)-C(3)	1.399(15)
Fe(1)-C(2)	2.027(13)	C(3)-C(4)	1.425(16)
Fe(1)-C(8)	2.039(14)	C(4)-C(5)	1.444(15)
Fe(1)-C(9)	2.040(13)	C(6)-C(10)	1.401(14)
Fe(1)-C(1)	2.046(14)	C(6)-C(7)	1.434(16)
Fe(1)-C(3)	2.056(12)	C(6)-C(23)	1.474(16)
Fe(1)-C(7)	2.063(13)	C(7)-C(8)	1.408(15)
Fe(1)-C(6)	2.068(12)	C(8)-C(9)	1.419(15)
Fe(1)-C(5)	2.074(14)	C(9)-C(10)	1.417(15)
P(2)-O(2)	1.455(9)	C(11)-C(12)	1.395(16)
P(2)-O(4)	1.480(8)	C(11)-C(16)	1.401(16)
P(2)-O(1)	1.579(9)	C(12)-C(13)	1.409(15)
P(2)-O(3)	1.614(9)	C(13)-C(14)	1.369(17)
Ca(1)-O(4)#1	2.186(9)	C(13)-C(17)	1.453(15)
Ca(1)-O(4)	2.186(9)	C(14)-C(15)	1.413(17)
Ca(1)-O(5)#1	2.236(10)	C(15)-C(16)	1.376(15)
Ca(1)-O(5)	2.236(10)	C(23)-C(24)	1.345(14)
Ca(1)-O(6)#1	2.297(9)	C(23)-C(28)	1.394(16)
Ca(1)-O(6)	2.297(9)	C(24)-C(25)	1.371(14)
O(1)-C(26)	1.427(15)	C(25)-C(26)	1.347(17)
O(3)-C(14)	1.420(13)	C(26)-C(27)	1.406(16)
O(5)-C(36)	1.387(14)	C(27)-C(28)	1.413(15)
O(6)-C(38)	1.407(15)	C(27)-C(29)	1.483(14)
C(1)-C(2)	1.387(17)	C(35)-O(8)	1.58(2)
C(1)-C(5)	1.453(15)		

C(4)-Fe(1)-C(10)	120.7(5)	P(2)-O(4)-Ca(1)	157.8(6)
C(4)-Fe(1)-C(2)	69.4(5)	C(36)-O(5)-Ca(1)	127.0(9)
C(10)-Fe(1)-C(2)	162.5(6)	C(38)-O(6)-Ca(1)	127.8(10)

C(4)-Fe(1)-C(8)	123.7(6)	C(2)-C(1)-C(5)	111.6(14)
C(10)-Fe(1)-C(8)	67.9(5)	C(2)-C(1)-C(11)	128.6(14)
C(2)-Fe(1)-C(8)	120.3(6)	C(5)-C(1)-C(11)	119.8(13)
C(4)-Fe(1)-C(9)	105.9(5)	C(2)-C(1)-Fe(1)	69.3(8)
C(10)-Fe(1)-C(9)	40.9(4)	C(5)-C(1)-Fe(1)	70.4(8)
C(2)-Fe(1)-C(9)	155.0(5)	C(11)-C(1)-Fe(1)	126.8(8)
C(8)-Fe(1)-C(9)	40.7(4)	C(1)-C(2)-C(3)	107.3(13)
C(4)-Fe(1)-C(1)	68.2(6)	C(1)-C(2)-Fe(1)	70.8(8)
C(10)-Fe(1)-C(1)	127.2(5)	C(3)-C(2)-Fe(1)	71.1(8)
C(2)-Fe(1)-C(1)	39.8(5)	C(2)-C(3)-C(4)	108.3(12)
C(8)-Fe(1)-C(1)	155.9(5)	C(2)-C(3)-Fe(1)	68.8(7)
C(9)-Fe(1)-C(1)	162.9(6)	C(4)-C(3)-Fe(1)	67.2(7)
C(4)-Fe(1)-C(3)	41.1(5)	C(3)-C(4)-C(5)	109.4(13)
C(10)-Fe(1)-C(3)	156.4(5)	C(3)-C(4)-Fe(1)	71.6(8)
C(2)-Fe(1)-C(3)	40.1(4)	C(5)-C(4)-Fe(1)	72.1(8)
C(8)-Fe(1)-C(3)	107.5(5)	C(4)-C(5)-C(1)	102.9(14)
C(9)-Fe(1)-C(3)	120.5(5)	C(4)-C(5)-Fe(1)	66.4(8)
C(1)-Fe(1)-C(3)	66.3(5)	C(1)-C(5)-Fe(1)	68.3(8)
C(4)-Fe(1)-C(7)	161.0(6)	C(10)-C(6)-C(7)	106.0(13)
C(10)-Fe(1)-C(7)	67.3(5)	C(10)-C(6)-C(23)	128.1(14)
C(2)-Fe(1)-C(7)	108.0(6)	C(7)-C(6)-C(23)	125.9(12)
C(8)-Fe(1)-C(7)	40.1(4)	C(10)-C(6)-Fe(1)	68.1(7)
C(9)-Fe(1)-C(7)	68.1(5)	C(7)-C(6)-Fe(1)	69.5(7)
C(1)-Fe(1)-C(7)	122.6(5)	C(23)-C(6)-Fe(1)	124.9(8)
C(3)-Fe(1)-C(7)	125.0(5)	C(8)-C(7)-C(6)	108.5(12)
C(4)-Fe(1)-C(6)	155.9(6)	C(8)-C(7)-Fe(1)	69.0(7)
C(10)-Fe(1)-C(6)	40.1(4)	C(6)-C(7)-Fe(1)	69.9(8)
C(2)-Fe(1)-C(6)	125.5(5)	C(7)-C(8)-C(9)	108.6(12)
C(8)-Fe(1)-C(6)	68.4(5)	C(7)-C(8)-Fe(1)	70.9(7)
C(9)-Fe(1)-C(6)	68.7(5)	C(9)-C(8)-Fe(1)	69.7(8)
C(1)-Fe(1)-C(6)	109.8(5)	C(10)-C(9)-C(8)	106.2(13)
C(3)-Fe(1)-C(6)	161.9(5)	C(10)-C(9)-Fe(1)	68.8(7)
C(7)-Fe(1)-C(6)	40.6(4)	C(8)-C(9)-Fe(1)	69.6(7)
C(4)-Fe(1)-C(5)	41.5(4)	C(6)-C(10)-C(9)	110.7(15)
C(10)-Fe(1)-C(5)	107.3(5)	C(6)-C(10)-Fe(1)	71.8(7)
C(2)-Fe(1)-C(5)	69.9(6)	C(9)-C(10)-Fe(1)	70.4(8)
C(8)-Fe(1)-C(5)	161.0(5)	C(12)-C(11)-C(16)	118.6(14)
C(9)-Fe(1)-C(5)	123.7(5)	C(12)-C(11)-C(1)	117.8(14)
C(1)-Fe(1)-C(5)	41.3(4)	C(16)-C(11)-C(1)	123.6(14)
C(3)-Fe(1)-C(5)	69.1(5)	C(11)-C(12)-C(13)	122.2(14)
C(7)-Fe(1)-C(5)	156.8(5)	C(14)-C(13)-C(12)	115.4(14)
C(6)-Fe(1)-C(5)	120.7(5)	C(14)-C(13)-C(17)	122.5(14)
O(2)-P(2)-O(4)	118.6(6)	C(12)-C(13)-C(17)	122.2(13)
O(2)-P(2)-O(1)	112.1(6)	C(13)-C(14)-C(15)	125.6(15)
O(4)-P(2)-O(1)	105.4(5)	C(13)-C(14)-O(3)	122.4(14)
O(2)-P(2)-O(3)	109.1(5)	C(15)-C(14)-O(3)	112.0(14)
O(4)-P(2)-O(3)	105.3(6)	C(16)-C(15)-C(14)	115.9(14)
O(1)-P(2)-O(3)	105.3(5)	C(15)-C(16)-C(11)	122.0(14)
O(4)#1-Ca(1)-O(4)	180.00(6)	C(18)-C(17)-C(13)	119.3(10)
O(4)#1-Ca(1)-O(5)#1	98.1(4)	C(22)-C(17)-C(13)	120.4(11)

O(4)-Ca(1)-O(5)#1	81.9(4)	C(24)-C(23)-C(28)	118.7(14)
O(4)#1-Ca(1)-O(5)	81.9(4)	C(24)-C(23)-C(6)	122.2(14)
O(4)-Ca(1)-O(5)	98.1(4)	C(28)-C(23)-C(6)	119.0(13)
O(5)#1-Ca(1)-O(5)	180.0(3)	C(23)-C(24)-C(25)	121.8(15)
O(4)#1-Ca(1)-O(6)#1	92.3(3)	C(26)-C(25)-C(24)	120.0(14)
O(4)-Ca(1)-O(6)#1	87.7(3)	C(25)-C(26)-C(27)	121.4(15)
O(5)#1-Ca(1)-O(6)#1	86.8(4)	C(25)-C(26)-O(1)	125.4(13)
O(5)-Ca(1)-O(6)#1	93.2(4)	C(27)-C(26)-O(1)	113.2(14)
O(4)#1-Ca(1)-O(6)	87.7(3)	C(26)-C(27)-C(28)	116.2(13)
O(4)-Ca(1)-O(6)	92.3(3)	C(26)-C(27)-C(29)	125.1(13)
O(5)#1-Ca(1)-O(6)	93.2(4)	C(28)-C(27)-C(29)	118.4(12)
O(5)-Ca(1)-O(6)	86.8(4)	C(23)-C(28)-C(27)	121.1(13)
O(6)#1-Ca(1)-O(6)	180.000(3)	C(30)-C(29)-C(27)	121.6(8)
C(26)-O(1)-P(2)	127.6(7)	C(34)-C(29)-C(27)	118.4(8)
C(14)-O(3)-P(2)	124.7(8)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+2,-y-1,-z+2