

SUPPORTING INFORMATION

Development of chiral phosphoric acids based on ferrocene-bridged paracyclophane frameworks

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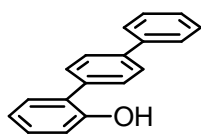
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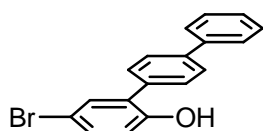
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Experimental Procedures

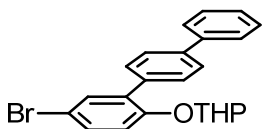
Synthesis of diol 3c.



2-([1,1'-Biphenyl]-4-yl)phenol. 2-Bromophenol (6.48 g, 37.5 mmol), [1,1'-biphenyl]-4-ylboronic acid (8.90 g, 50.0 mmol), Pd(OAc)₂ (210 mg, 0.94 mmol, 2.5 mol%), tri(*o*-tolyl)phosphine (525 mg, 1.87 mmol, 5 mol%) and potassium phosphate tribasic (11.1 g, 53 mmol, 1.2 eq.) were introduced in a round bottomed flask under argon. Degassed toluene (150 mL) and H₂O (1 mL) were added and the mixture was heated at 100 °C for 16 h. The reaction mixture was filtered on Celite and washed with toluene. Toluene was removed under reduced pressure. The residue was purified by column chromatography (eluent: heptane/EtOAc gradient from 95:5 to 80:20). The product was obtained as a white solid (6.46 g, 70% yield). *R*_f = 0.2 (heptane/EtOAc 9:1). **¹H NMR** (300.2 MHz, CDCl₃) : δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 7.3 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 7.3 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.0 Hz, 1H), 7.28 (t, *J* = 8.0 Hz, 1H), 7.02 (t, *J* = 8.0 Hz, 1H), 7.00 (d, *J* = 8.0 Hz, 1H), 5.24 (s, 1H). **¹³C NMR** (75.5 MHz, CDCl₃) : δ 152.7 (C), 140.9 (C), 140.7 (C), 136.2 (C), 130.5 (CH), 129.7 (CH), 129.4 (CH), 129.1 (CH), 128.1 (CH), 128.0 (C), 127.8 (CH), 127.3 (CH), 121.2 (CH), 116.1 (CH). **IR** : *v*_{max} = 3525, 3026, 1598, 1580, 1479, 1450, 1396, 1328, 1277, 1259, 1229, 1174, 1153, 1102, 1007, 828. **MS** (ESI) : *m/z* 245 [M-H].

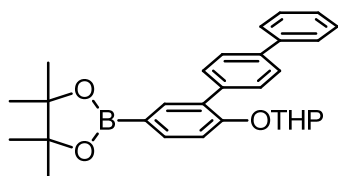


2-([1,1'-Biphenyl]-4-yl)-4-bromophenol. In a 500 mL three-necked flask equipped with a magnetic stir bar, a reflux condenser, an inlet thermometer and an addition funnel, 2-([1,1'-Biphenyl]-4-yl)phenol (6.40 g, 26.0 mmol) was dissolved in DCM (150 mL) and the solution was cooled to -10 °C. A solution of bromine (1.33 mL, 26.0 mmol) in DCM (22 mL) was added dropwise and the reaction mixture was allowed to warm up to room temperature overnight. The solution was washed with H₂O (30 mL) and aqueous Na₂S₂O₃ solution (2 x 30 mL), and dried over MgSO₄. The solvent was removed under reduced pressure to isolate the desired bromophenol. **¹H NMR** (300.2 MHz, CDCl₃) : δ 7.71 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 8.0 Hz, 2H), 7.50 (d, *J* = 8.0 Hz, 2H), 7.47 (t, *J* = 8.0 Hz, 2H), 7.41 (d, *J* = 2.3 Hz, 1H), 7.39-7.36 (m, 1H), 7.35 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.88 (d, *J* = 8.5 Hz, 1H), 5.21 (s, 1H). **¹³C NMR** (75.5 MHz, CDCl₃) : δ 151.9 (C), 141.5 (C), 140.5 (C), 134.8 (C), 132.9 (CH), 132.1 (CH), 129.9 (C), 129.6 (CH), 129.1 (CH), 128.3 (CH), 127.9 (CH), 127.3 (CH), 117.9 (CH), 113.1 (CH). **IR** : *v*_{max} = 3533, 3029, 1567, 1476, 1390, 1326, 1257, 1231, 1165, 1076, 1007, 842, 816. **MS** (ESI) *m/z* 325 [M-H].



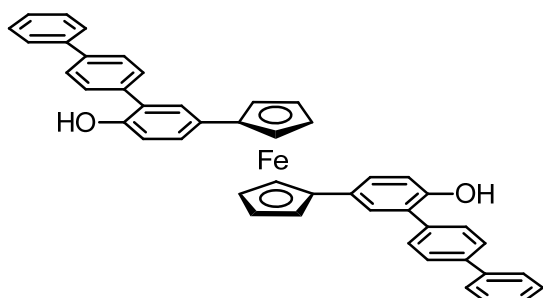
4-Bromo-([1,1'-Biphenyl]-4-yl)-1-(2'-tetrahydropyranyloxy)benzene. 2-(4-Biphenyl)-4-bromophenol (1.79 g, 5.50 mmol) was dissolved in 3,4-dihydro-2H-pyran (10 mL) and the solution was cooled to 0 °C. A catalytic amount of PTSA (105 mg, 0.55 mmol, 10 mol%) was introduced and the mixture was allowed to stir at room temperature for 2 h. After dilution with dichloromethane (30 mL) the organic phase was separated, washed with a 5% (w/w) aqueous solution of NaOH (ca. 15 mL), H₂O (ca. 15 mL) and dried over MgSO₄. The solvents were removed under reduced pressure. The residue was purified by column chromatography (eluent: heptane/MTBE 99:1). The product was obtained as a white solid (2.06 g, 92% yield). *R*_f = 0.5 (heptane/EtOAc 9:1). **¹H NMR** (300.2 MHz, CDCl₃) : δ 7.69-7.58 (m, 6H), 7.52 (d, *J* = 2.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.39-7.35 (m, 1H), 7.38 (dd, *J* = 8.8, 2.5 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.39 (t, *J* = 2.7 Hz, 1H), 3.79 (td, *J* = 10.9, 2.7 Hz, 1H), 3.58 (dq, *J* = 10.9, 2.7 Hz, 1H), 1.86-1.48 (m, 6H). **¹³C NMR** (75.5 MHz, CDCl₃) : δ 153.3 (C), 140.9 (C), 140.2 (C),

136.5 (C), 133.4 (CH), 131.4 (CH), 130.1 (CH), 129.0 (CH), 127.6 (CH), 127.3 (CH), 126.8 (CH), 117.8 (CH), 114.5 (C), 97.1 (CH), 62.1 (CH₂), 30.4 (CH₂), 25.3 (CH₂), 18.6 (CH₂). IR : ν_{\max} = 3029, 2943, 2872, 1599, 1478, 1385, 1356, 1254, 1225, 1200, 1182, 1109, 1021, 957, 908, 840. MS (ESI) m/z = 325 [M-THP-H]



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

4-Bromo-([1,1'-Biphenyl]-4-yl)-1-(2'-tetrahydropyranyloxy)benzene (3.67 g, 8.97 mmol), bis(pinacolato)diboron (2.73 g, 10.8 mmol,) and CH₃CO₂Na•3H₂O (3.66 g, 26.9 mmol) were dissolved in 1,4-dioxane (55mL) under argon. PdCl₂(dppf).CH₂Cl₂ (183 mg, 0,22 mmol, 2.5 mol%) was added and the mixture was refluxed for 24 h. The mixture was allowed to cool to room temperature and the solvents were removed under reduced pressure. The residue was purified by column chromatography (eluent: heptane/ EtOAc 97:3). The product was obtained as a white solid (3.40 g, 69% yield). R_f = 0.4 (heptane/EtOAc 95:5). ¹H NMR (300.2 MHz, CDCl₃) : 7.88 (d, J = 1.9 Hz, 1H), 7.77 (dd, J = 8.6, 1.9 Hz, 1H), 7.72-7.61 (m, 6H), 7.46 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.6 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 5.54 (s, 1H), 3.81 (td, J = 11.2, 2.7 Hz, 1H), 3.59 (bd, J = 11.2 Hz, 1H), 1.87-1.48 (m, 6H), 1.34 (s, 12H). ¹³C NMR (75.5 MHz, CDCl₃) : δ 156.7 (C), 141.2 (C), 139.6 (C), 137.8 (CH), 135.8 (CH), 130.6 (C), 130.3 (CH), 129.0 (CH), 127.4 (CH), 127.3 (CH), 126.6 (CH), 114.9 (CH), 96.4 (CH), 83.8 (C), 62.0 (CH₂), 30.4 (CH₂), 25.4 (CH₂), 25.1 (CH₃), 18.6 (CH₂). IR : ν_{\max} = 2977, 2941, 2867, 1599, 1485, 1389, 1351, 1318, 1293, 1226, 1200, 1140, 1108, 1041, 1023, 958, 919, 875. MS (ESI) m/z 457 [M+H]

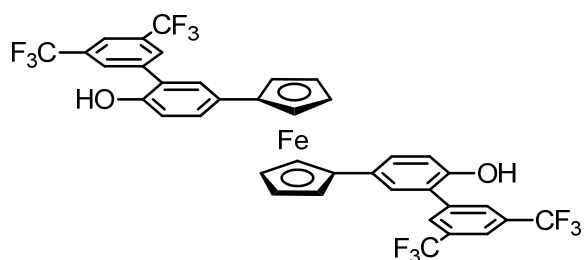


1,1'-Bis-[4-hydroxy-3-(4'-phenyl)-phenyl]ferrocene

(3c). 1,1'-Diiodoferrecene (87.0 mg, 0.20 mmol), the boronate above (200 mg, 0.44 mmol) and Ba(OH)₂•8H₂O (251 mg, 0.80 mmol) were dissolved in 1,4-dioxane (3 mL) under argon. PdCl₂(S-Phos)₂ (10.0 mg, 0,01 mmol, 5 mol%) was added and the mixture was heated at 100°C for 24 h. The mixture

was allowed to cool to room temperature, diluted with dichloromethane (ca 10 mL), washed with a 1M aqueous solution of HCl (10 mL) and the aqueous phase was extracted once with dichloromethane. The organic phase was dried over MgSO₄ and the solvents were removed under reduced pressure. The black residue was dissolved in MeOH (10 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 (eluent: heptane/EtOAc gradient from 95:5 to 80:20). Diol **3c** was obtained in quantitative yield, as an orange solid R_f = 0.3 (heptane/EtOAc 9:1); mp : 215-218 °C (decomposition). ¹H NMR (300.2 MHz, CDCl₃) : 7.69 (d, J = 8.0 Hz, 4H), 7.61 (d, J = 8.0 Hz, 4H), 7.50 (d, J = 8.0 Hz, 4H), 7.45 (t, J = 8.0 Hz, 4H), 7.37 (t, J = 8.0 Hz, 2H), 7.19 (d, J = 2.2 Hz, 2H), 7.14 (dd, J = 8.4, 2.2 Hz, 2H), 6.76 (d, J = 8.4 Hz, 2H), 5.15 (bs, 2H), 4.48 (s, 4H), 4.23 (s, 4H). ¹³C NMR (75.5 MHz, CDCl₃) : δ 151.1 (C), 140.9 (C), 140.7 (C), 136.3 (C), 130.4 (C), 129.7 (CH), 129.1 (CH), 128.1 (CH), 127.8 (CH), 127.6 (C), 127.3 (CH), 127.1 (CH), 116.0 (CH), 87.0 (C), 70.1 (CH), 67.4 (CH). IR : ν_{\max} = 3350, 3028, 2924, 1600, 1510, 1484, 1457, 1354, 1261, 1169, 1127, 1034, 1007, 962, 842, 816. HRMS (ESI) calcd. for C₄₆H₃₄FeO₂Cl [M+Cl]: 709.1597, found : 709.1594.

Synthesis of diol 3d.

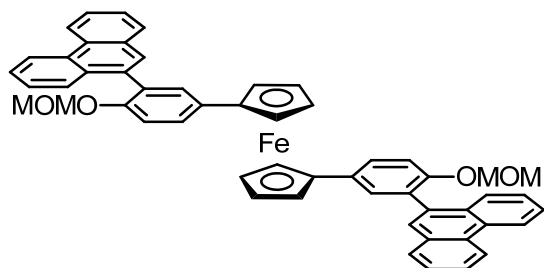


(a) The bis-pinacolborate **2** (PG = OMOM, 1.90 g, 2.68 mmol), 1-bromo-3,5-bis(trifluoromethyl)benzene (1.96 g, 6.69 mmol, 2.5 eq.), K_2CO_3 (1.85 g, 13.4 mmol, 5 eq.) and $Pd(PPh_3)_4$ (309 mg, 0.27 mmol, 10 mol%), were dissolved in a THF/water 1:1 mixture (40 mL) under argon. The mixture was heated at 70 °C for 18 h, then diluted with water

(10 mL) and extracted with EtOAc (3x30 mL). The organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by column chromatography (eluent: heptane/EtOAc gradient from 95:5 to 93:7). The MOM-protected diol was obtained as an orange solid (2.22 g, 94% yield).

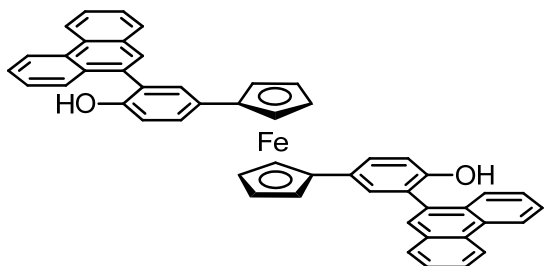
(b) To a solution of the MOM-protected diol (340 mg, 0.39 mmol) in THF/MeOH 1:1 (4 mL) was added PTSA (73.3 mg, 0.39 mmol, 1.0 eq.). The mixture was heated at 60 °C for 15 h, then diluted with water (4 mL) and extracted three times with EtOAc (3x10 mL). The organic phase was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The residue was purified by column chromatography (eluent: heptane/EtOAc 70:30). 1,1'-Bis-{4-hydroxy-3-[3',5'-bis(trifluoromethyl)phenyl]phenyl}ferrocene (**3d**) was obtained as an orange solid (295 mg, 96% yield). R_f = 0.3 (heptane/EtOAc 7:3). 1H NMR (300.2 MHz, $CDCl_3$): 7.85 (s, 4H), 7.81 (s, 2H), 6.92-6.90 (4H), 6.56 (d, J = 7.6 Hz, 2H), 4.82 (bs, 2H), 4.74 (s, 4H), 4.44 (s, 4H). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 151.2 (C), 139.9 (C), 131.8 (q, $J_{(F-C)}$ = 33.3 Hz, C), 130.5 (C), 129.4 (CH), 128.3 (CH), 128.2 (CH), 125.1 (C), 123.6 (q, $J_{(F-C)}$ = 272.3 Hz, CF_3), 121.2 (CH), 116.1 (CH), 86.4 (C), 70.9 (CH), 66.8 (CH). ^{19}F NMR (282.4 MHz, $CDCl_3$): -62.8. IR: ν_{max} = 3379, 3094, 2964, 1612, 1522, 1455, 1417, 1377, 1275, 1172, 1125, 1054, 922, 901, 890, 816. HRMS (ESI) calcd. for $C_{38}H_{22}F_{12}FeO_2$ [$M+H$] $^+$: 795.0856, found : 795.0857.

Synthesis of the phosphoric acid 7e



1,1'-Bis-[4-(methoxymethoxy)-3-(9-phenanthryl)-1-phenyl]-ferrocene. The bis-pinacolborate **2** (220 mg, 0.31 mmol), 9-bromophenanthrene (199 mg, 0.78 mmol, 2.5 eq.), $Ba(OH)_2 \cdot 8H_2O$ (391 mg, 1.24 mmol, 4 eq.) were dissolved in 1,4-dioxane (4 mL) and water (1 mL) under argon. $Pd(PPh_3)_4$ (35.8 mg, 0.03 mmol, 10 mol%) was added and the mixture was heated at 100 °C for 18 h. The mixture was

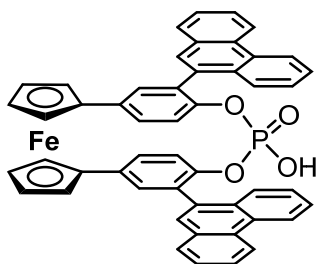
allowed to cool to room temperature, diluted with EtOAc (ca 10 mL) and washed with water (ca 10 mL). The organic layer was dried over $MgSO_4$ and the solvents were removed under reduced pressure. The product was purified by flash chromatography on silica gel (heptane/EtOAc gradient from 95:5 to 85:15) and obtained as an orange slurry (216 mg, 86% yield). R_f = 0.4 (heptane/EtOAc 8:2). 1H NMR (300.2 MHz, $CDCl_3$) : 8.85-8.70 (m, 4H), 7.98-7.83 (m, 2H), 7.81-7.31 (m, 16H), 7.08-6.97 (m, 2H), 5.02-4.86 (m, 4H), 4.47 (s, 4H), 4.22 (s, 4H), 3.17 (6H). ^{13}C NMR (75.5 MHz, $CDCl_3$) : δ 153.6 (C), 136.0 (C), 132.3 (C), 132.2 (C), 131.9 (C), 131.7 (C), 130.6 (C), 130.4 (C), 130.3 (C), 129.8 (CH), 128.8 (CH), 127.9 (CH), 127.4 (CH), 126.9 (CH), 126.7 (CH), 126.5 (CH), 122.9 (CH), 122.8 (CH), 116.2 (CH), 115.1 (CH), 94.7 (CH_2), 86.3 (C), 70.5 (CH), 68.4 (CH), 68.2 (CH), 67.9 (CH), 67.8 (CH), 56.2 (CH_3). HRMS (ESI) calcd. for $C_{54}H_{42}FeO_4$ [$M+H$] $^+$: 811.2511, found : 811.2622.



1,1'-Bis-[4-(hydroxy)-3-(9-phenanthryl)-1-phenyl]-ferrocene. To a solution of the MOM-protected diol **2d** (210 mg, 0.26 mmol) in THF/water (4:1, 5 mL), were added KI (430 mg, 2.6 mmol) and PTSA (148 mg, 0.78 mmol, 3 eq.) at room temperature. The mixture was heated at 105 °C for 2 h. The mixture was allowed to cool to room temperature and a saturated aqueous solution of NaHCO₃ was added,

the layers were separated and the aqueous layer was extracted with EtOAc (2x10 mL). The organic phase was dried over MgSO₄ and the solvents were removed under reduced pressure. The residue was purified by column chromatography (heptane/EtOAc gradient from 85:15 to 70:30). The product was obtained as an orange solid (150 mg, 80% yield). *R_f* = 0.2 (heptane/EtOAc 8:2). ¹H NMR (300.2 MHz, CDCl₃) : δ 8.79-8.68 (m, 4H), 7.90 (d, *J* = 7.7 Hz, 1H), 7.8-7.4 (m, 13H), 7.39-7.28 (m, 4H), 6.88 (bs, 2H), 4.83 (bs, 2H), 4.47 (s, 2H), 4.44 (s, 2H), 4.21 (s, 4H). ¹³C NMR (75.5 MHz, CDCl₃) : δ 151.8 (C), 132.6 (C), 131.4 (C), 130.9 (C), 130.4 (C), 129.1 (CH), 129.8 (CH), 127.3 (CH), 127.2 (CH), 127.1 (CH), 126.6 (CH), 126.5 (CH), 123.1 (CH), 122.7 (CH), 115.7 (CH), 86.8 (C), 70.3 (CH), 70.2 (CH), 67.8 (CH), 67.7 (CH), 67.5 (CH). HRMS (ESI) calcd. for C₅₀H₃₅FeO₂ [M+H]⁺ : 723.1986, found : 723.2017.

Phenanthryl-substituted phosphoric acid (**7e**).



(a) 1,1'-Bis-[4-(hydroxy)-3-(9-phenanthryl)-1-phenyl]-ferrocene (580 mg, 0.80 mmol) and 1*H*-tetrazole (236 mg, 3.37 mmol, 4.2 eq.) were dissolved in anhydrous dichloromethane (40 mL, 50 mL for 1 mmol of diol) under argon. 2-Cyanoethyl *N,N,N',N'*-tetra-isopropylphosphorodiamidite (290 mg, 0.96 mmol, 1.2 eq.) was added and the mixture was stirred at room temperature for 4 h and then quenched with a saturated aqueous solution of NaHCO₃. The layers were

separated, the organic phase was dried over MgSO₄ 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 as an orange solid (120 mg, 18% yield). *R_f* = 0.6 (heptane/EtOAc 7:3). Separation of enantiomers has been carried out by SFC : CHIRALPAK® IA column, with 45% EtOAc/Supercritical-CO₂, 4 mL/min. Retention times: 8 min ([α]_D = -871 (*c* = 1, CHCl₃)) and 14 min. ³¹P NMR (202.5 Hz, CDCl₃) : δ 129.5 ppm. HRMS (ESI) calcd. for C₅₃H₃₇FeNO₃P [M+H]⁺ : 822.1860, found : 822.1859.

(b) The phosphite above (10.5 mg, 12.8 μmol) was dissolved in DCM (2 mL). TBHP (5.5*M* in decane, 7 μL, 38.3 μmol, 3.0 eq.) was added to the solution at 0 °C and the reaction mixture was allowed to warm to room temperature and stirred for 45 minutes. The reaction was treated with saturated aqueous Na₂S₂O₃. The layers were separated, the organic layer was dried over MgSO₄ and concentrated *in vacuo*. The crude mixture was purified by chromatography on silica gel (eluent: heptane/EtOAc gradient from 7:3 to 6:4) the phosphate (6 mg, 57% yield). *R_f* = 0.15 (heptane/EtOAc 7:3). ³¹P NMR (202.5 MHz, CDCl₃) : δ -14.5 ppm. HRMS (ESI) calcd. for C₅₃H₃₇FeNO₄P [M+H]⁺ : 838.1810, found : 838.1883.

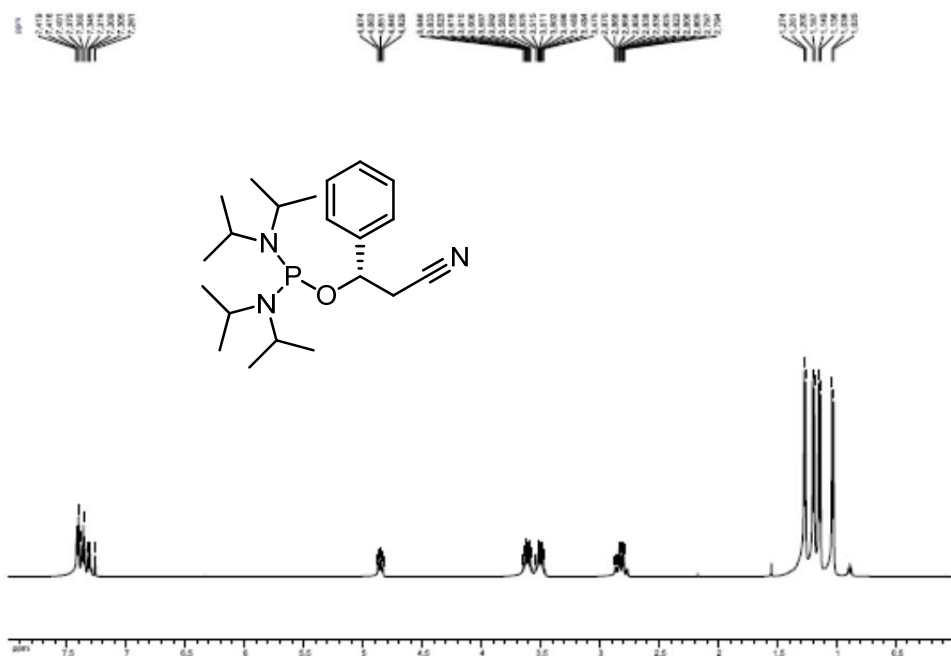
(c) The phosphate above (6 mg, 7.16 μmol) was dissolved in DCM (2 mL) and DBU (2 μL, 14.3 μmol, 2 eq.) was added to the solution at rt. After 30 min the reaction was diluted with DCM and hydrolyzed with saturated aqueous NaHCO₃. The layers were separated and the organic layer was washed twice with a 6*M* aqueous solution of HCl under vigorous stirring. The organic layer was dried over MgSO₄

and the solvent was removed under reduced pressure to afford the chiral phosphoric acid **7e** (5 mg, 83% yield). $R_f = 0.1$ (MeOH/DCM 1:9). ^{31}P NMR (121.5 MHz, CDCl_3) : δ -12.1 ppm. ^1H NMR (500.1 MHz, $\text{DMSO-}d_6$) : δ 8.89 (bd, $J = 8.7$ Hz, 4H), 8.34-8.28 (m, 2H), 8.08 (bs, 2H), 7.79-7.74 (m, 2H), 7.68-7.63 (m, 4H), 7.61-7.57 (m, 2H), 7.53 (t, $J = 7.4$ Hz, 2H), 7.24 (bs, 2H), 6.92 (bs, 4H), 4.90 (bs, 4H), 4.50 (bs, 2H), 4.44 (bs, 2H). ^{13}C NMR (125.8 MHz, $\text{DMSO-}d_6$) : δ 147.9 (d, $J_{\text{P-C}} = 6.8$ Hz, C), 135.2 (C), 131.5 (C), 130.1 (C), 130.0 (C), 129.7 (C), 129.6 (C), 129.1 (C), 128.5 (C), 128.0 (C), 126.9 (CH), 126.8 (CH), 126.6 (CH), 126.4 (CH), 126.2 (CH), 123.0 (CH), 122.7 (CH), 120.5 (CH), 85.9 (C), 69.2 (CH), 68.6 (CH), 66.6 (CH), 65.5 (CH). IR : $\nu_{\text{max}} = 3059, 2923, 2852, 1597, 1508, 1494, 1464, 1449, 1419, 1374, 1262, 1191, 1114, 1021, 946, 915, 883$. HRMS (ESI) calcd. for $\text{C}_{50}\text{H}_{34}\text{FeO}_4\text{P}$ $[\text{M}+\text{H}]^+$: 785.1544, found : 785.1548. $[\alpha]_D = -981$ ($c = 0.5$, CHCl_3).

NMR SPECTRA

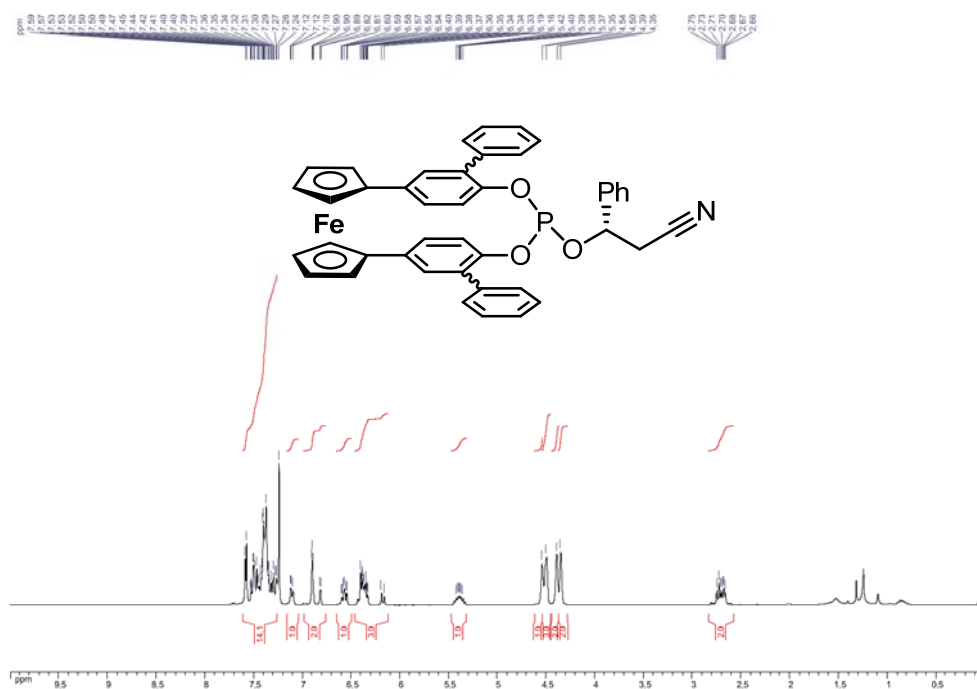
(1*S*)-(2-Cyano-1-phenylethyl)-*N,N,N',N'*-tetra-isopropylphosphorodiamidite (*S*)-8b.

^1H NMR (500.2 MHz, CDCl_3)



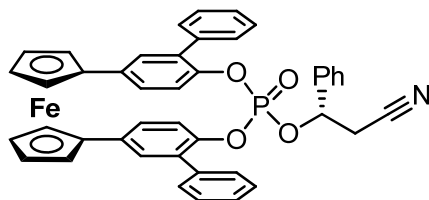
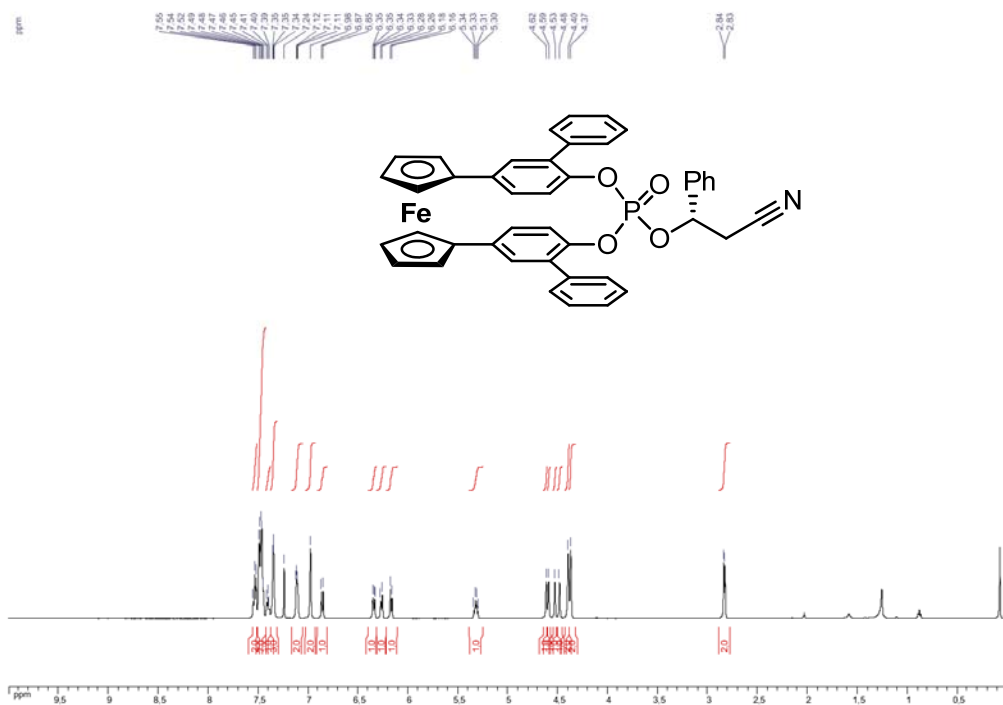
Phosphites 5a,a'

^1H NMR (300.2 MHz, CDCl_3)

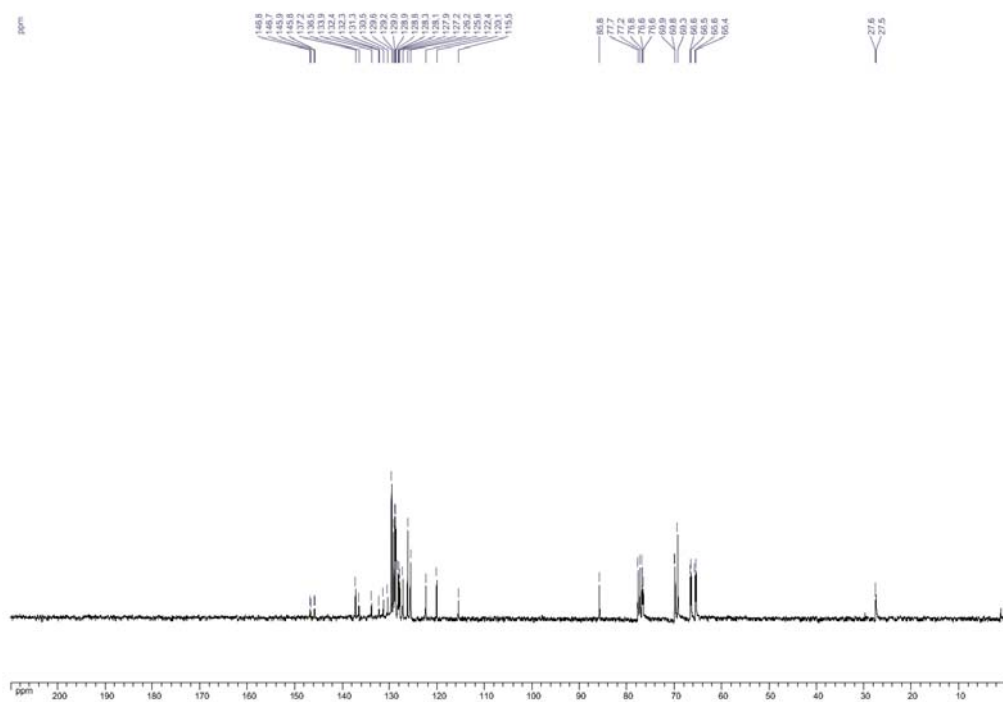


Phosphate 6a.

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

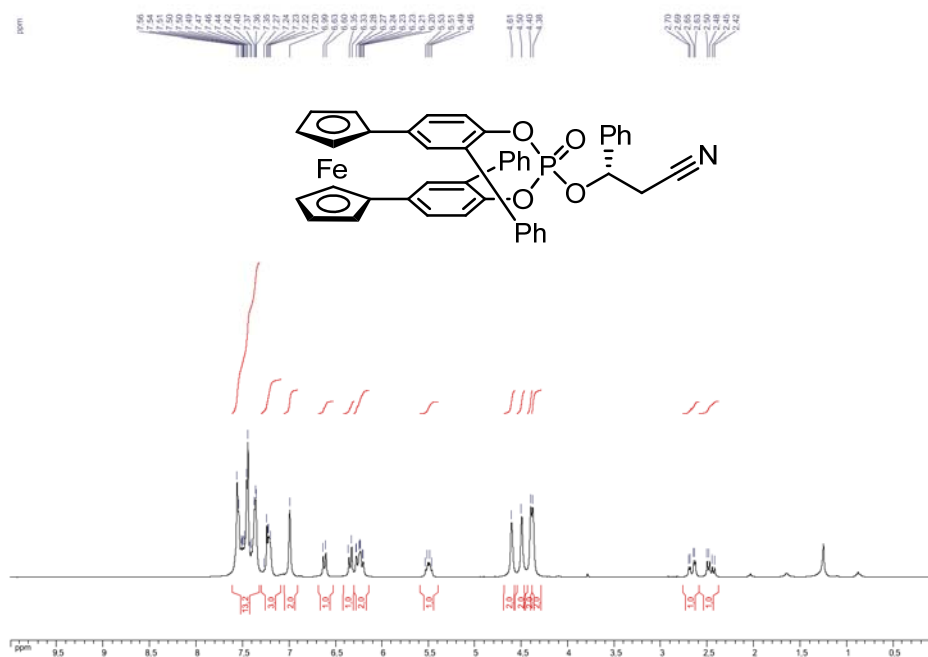


$^{13}\text{C NMR}$ (75.5 MHz, CDCl_3)

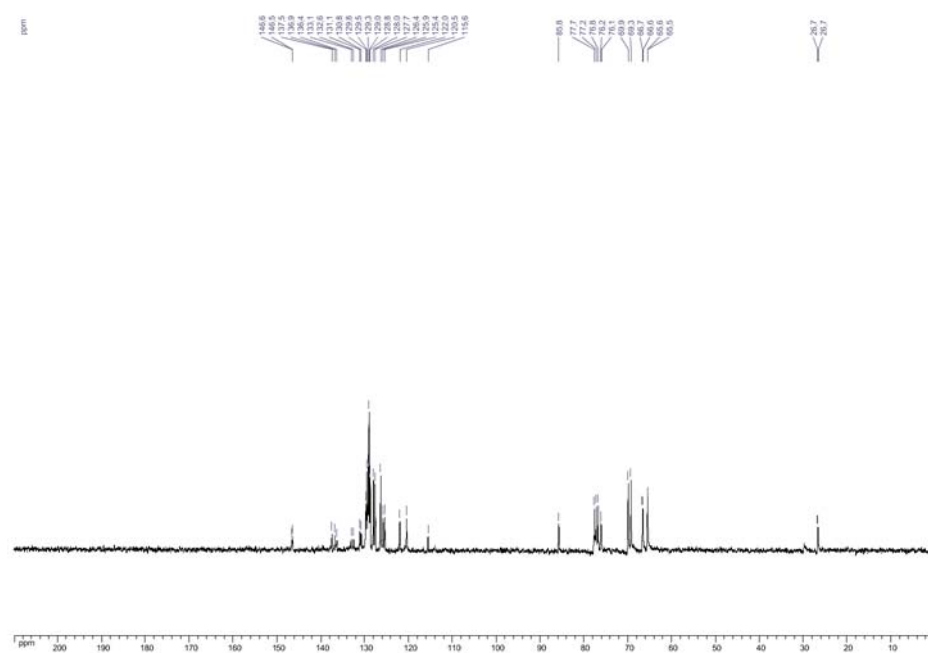


Phosphate 6a'.

^1H NMR (300.1 MHz, CDCl_3)

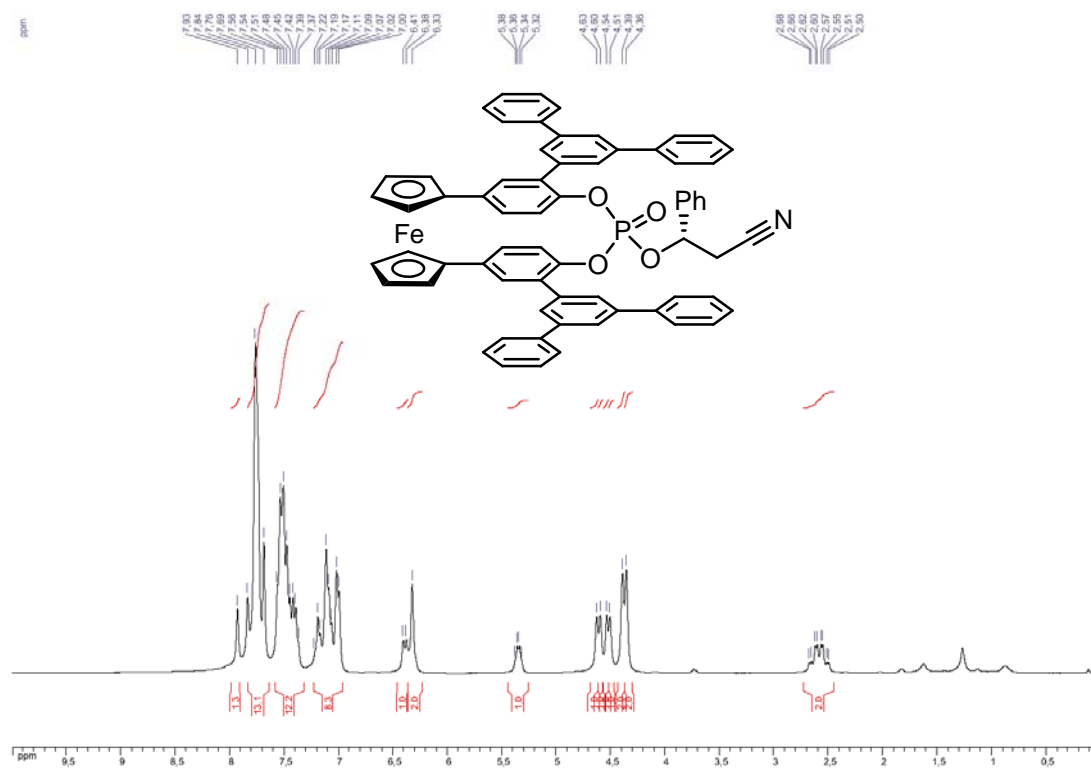


^{13}C NMR (75.5 MHz, CDCl_3)

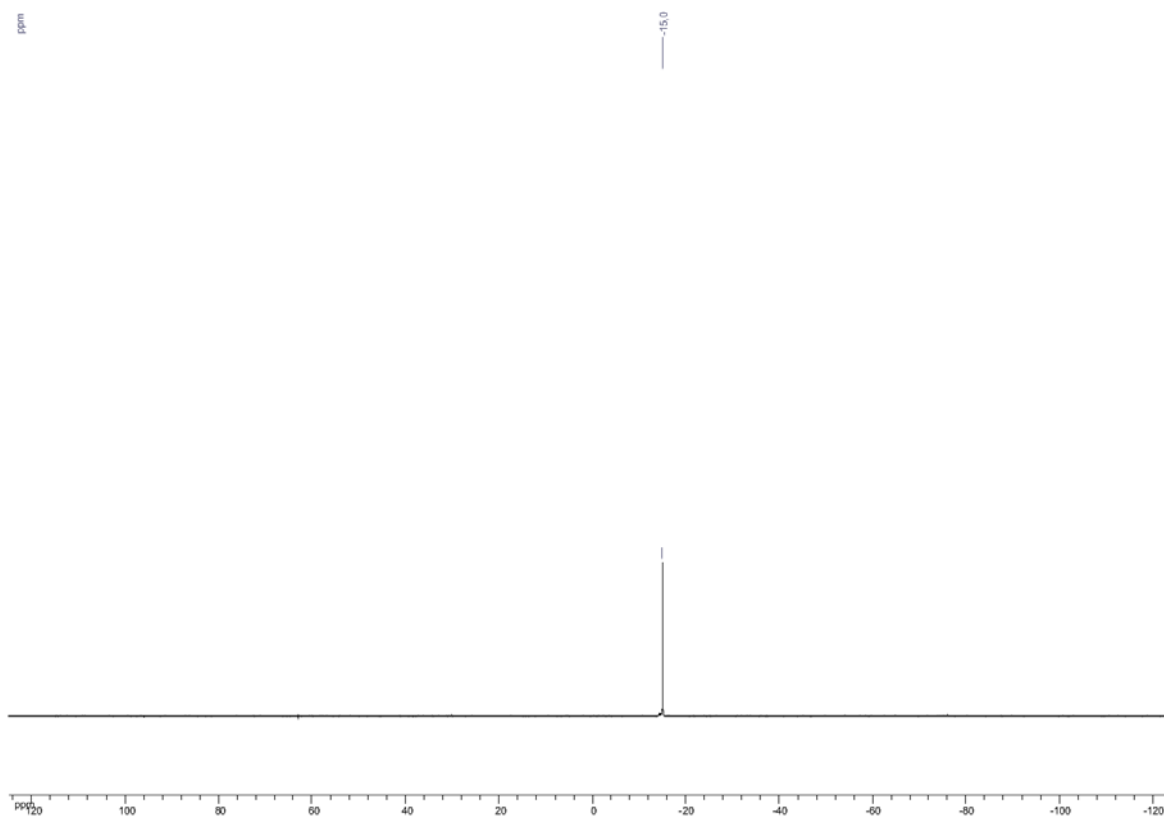


Phosphate 6b.

^1H NMR (300.2 MHz, CDCl_3)

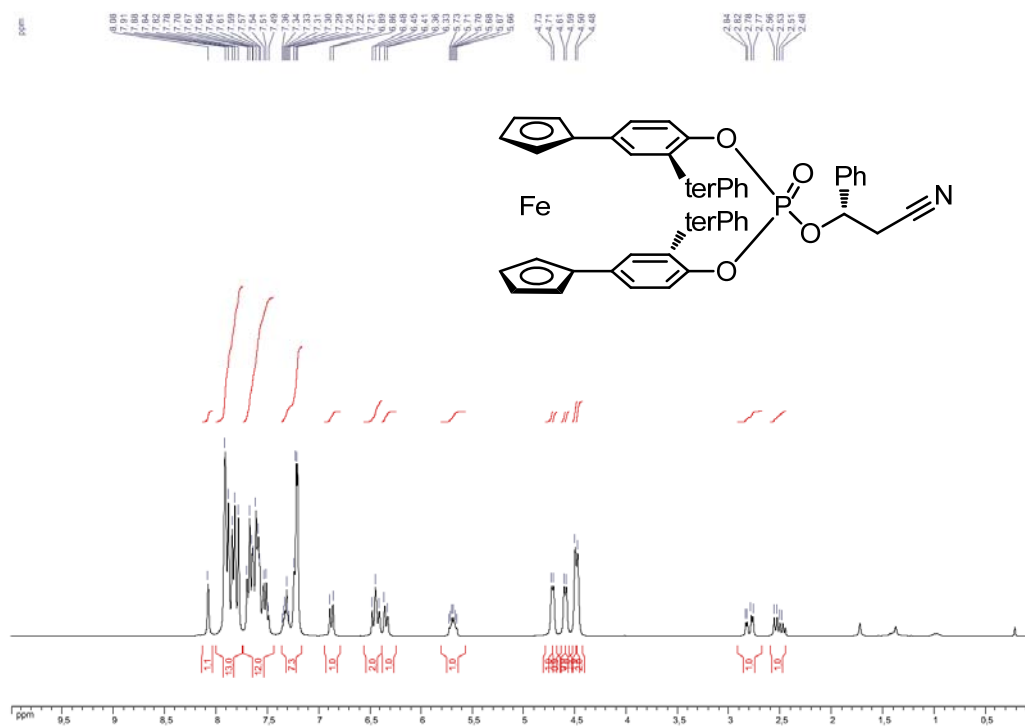


³¹P NMR (202.5 MHz, CDCl₃)

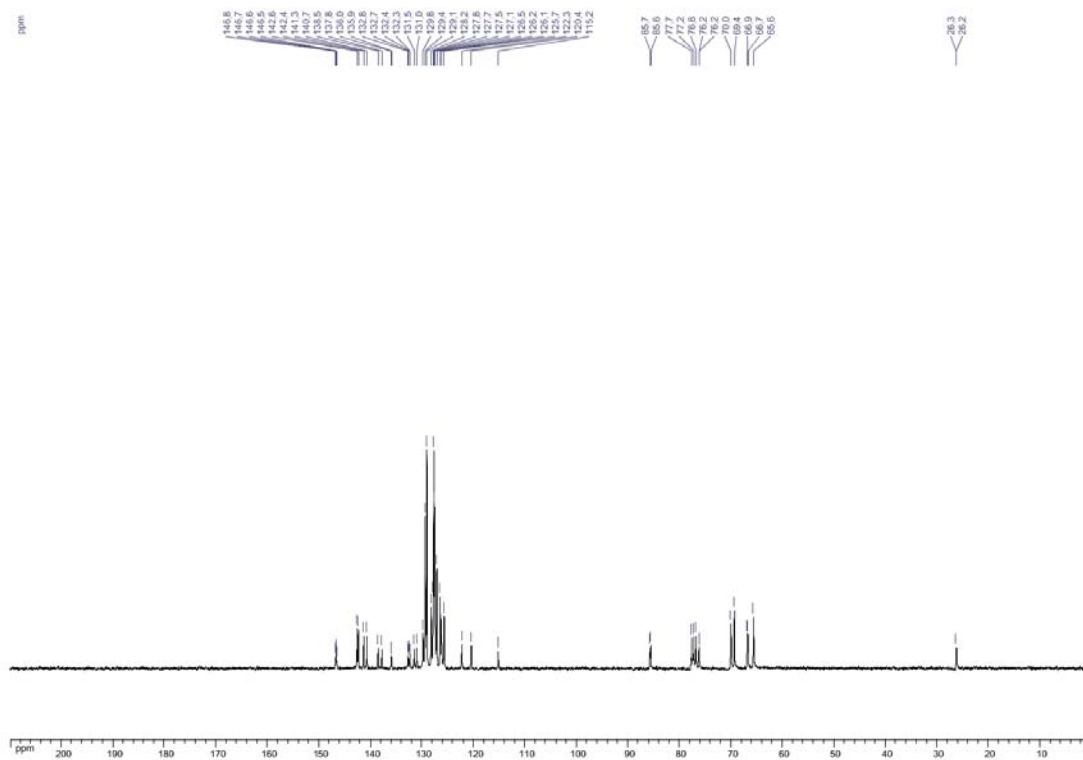


Phosphate 6b'

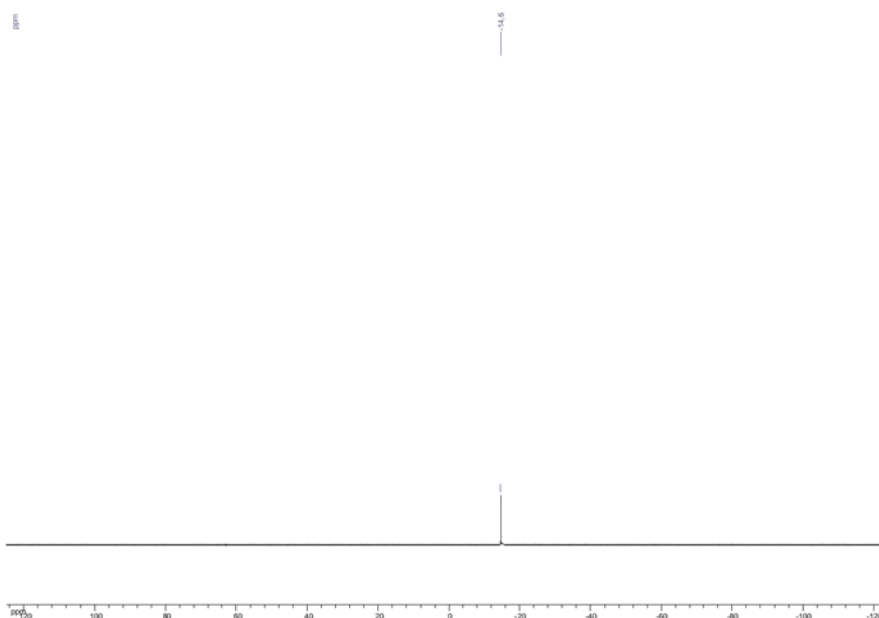
¹H NMR (300.2 MHz, CDCl₃)



¹³C NMR (75.5 MHz, CDCl₃)

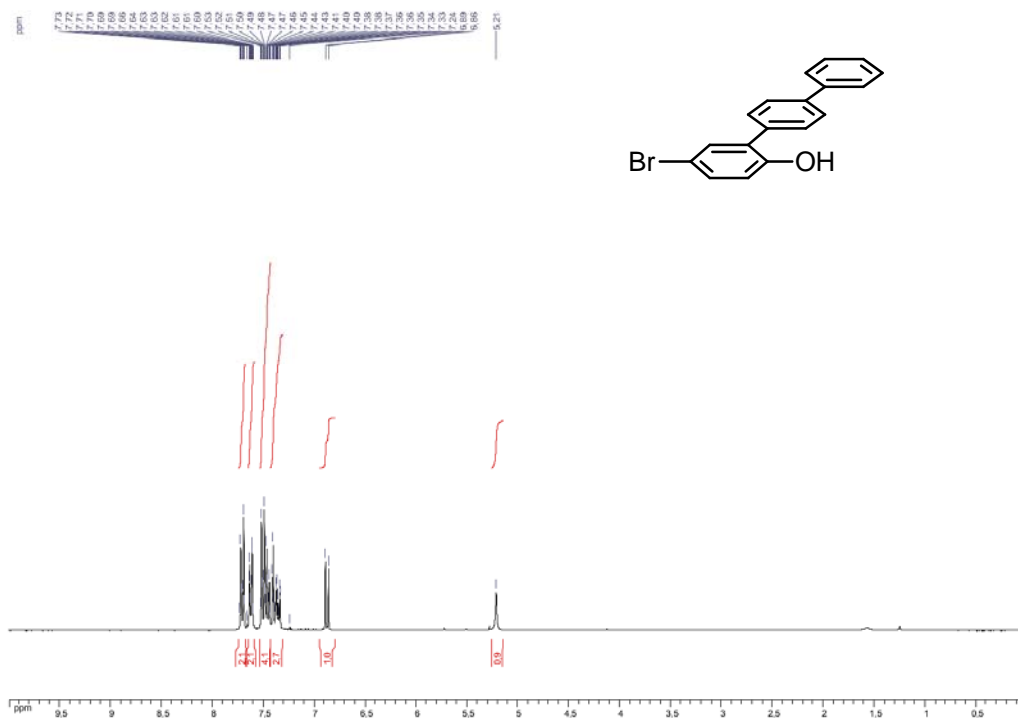


³¹P NMR (202.5 MHz, CDCl₃)

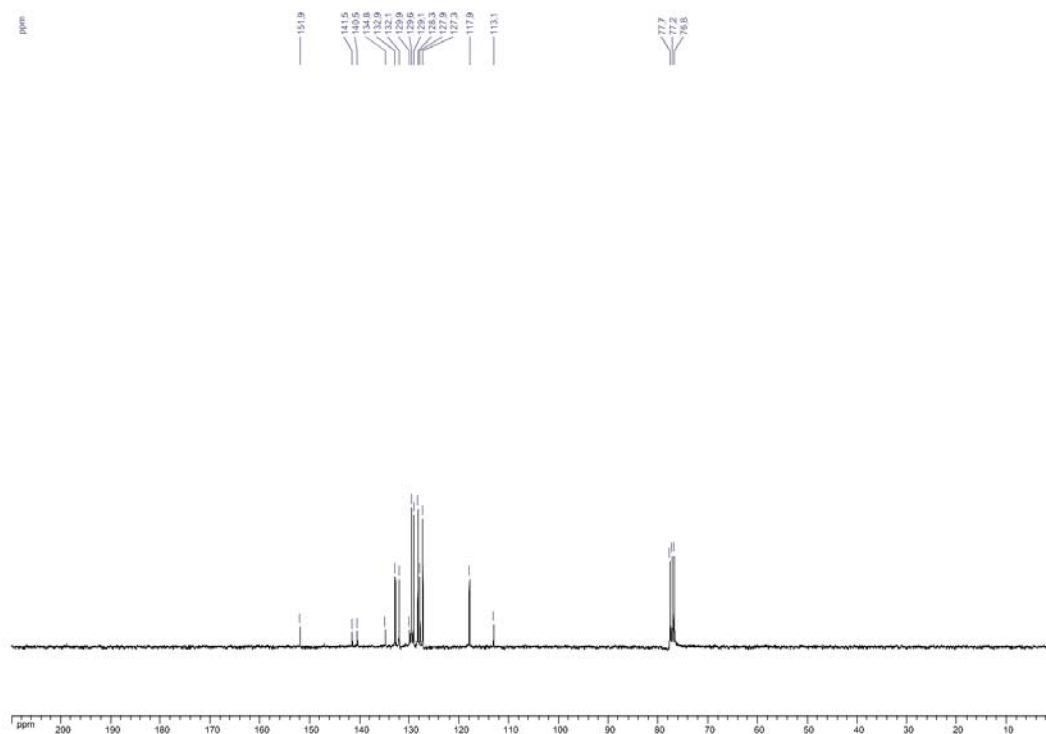


4-bromo-2-([1,1'-biphenyl]-4-yl)phenol

¹H NMR (300.2 MHz, CDCl₃)

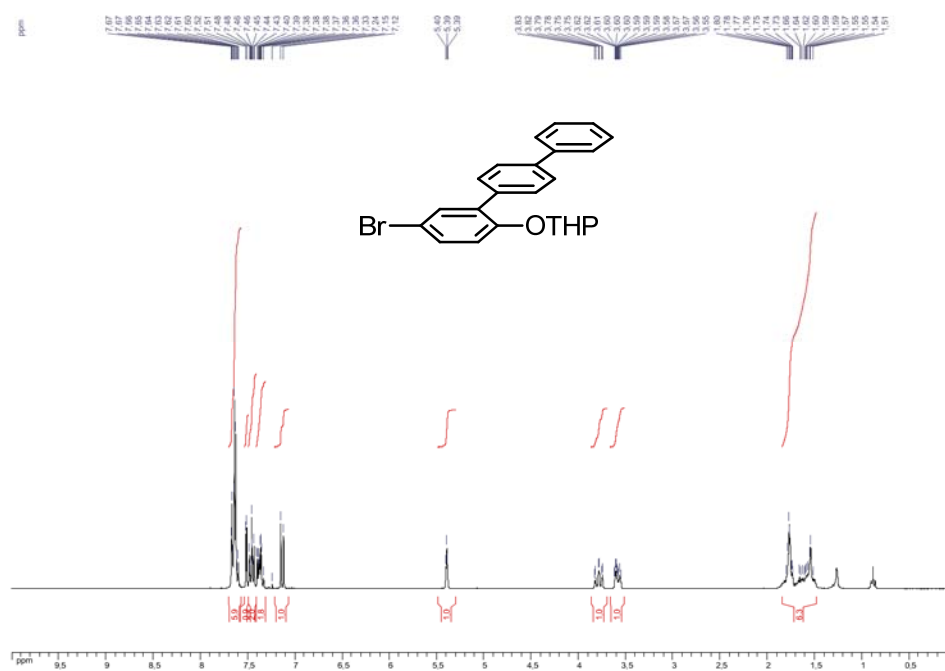


¹³C NMR (75.5 MHz, CDCl₃)

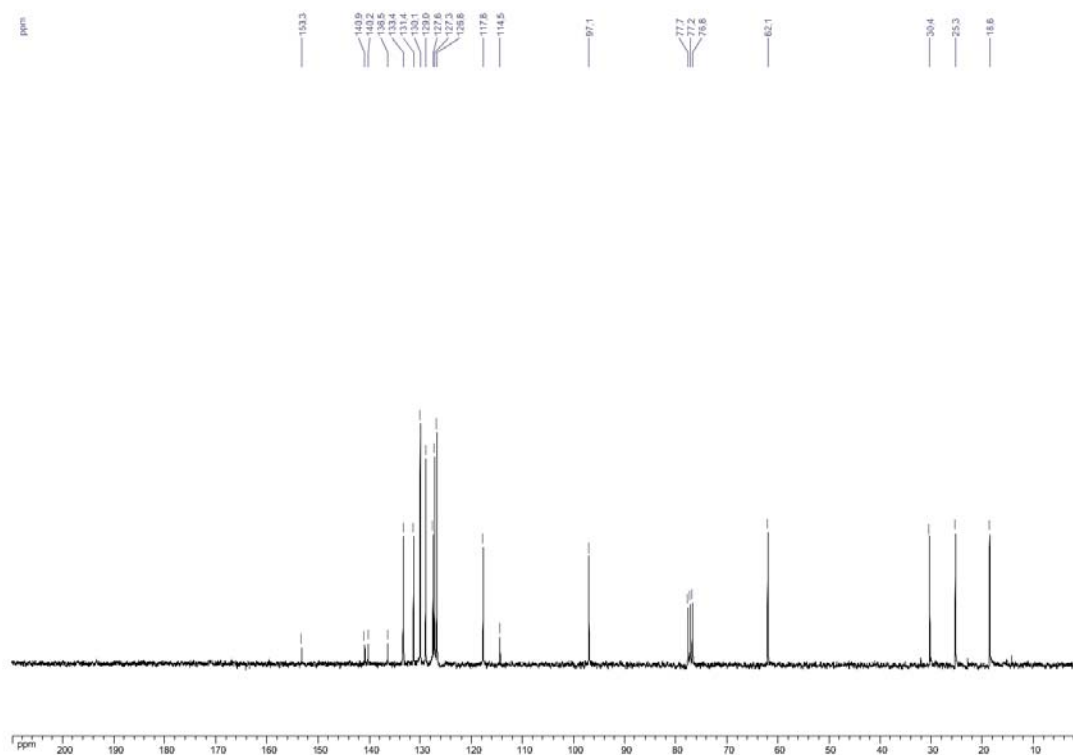


4-Bromo-([1,1'-biphenyl]-4-yl)-1-(2'-tetrahydropyranyloxy)benzene

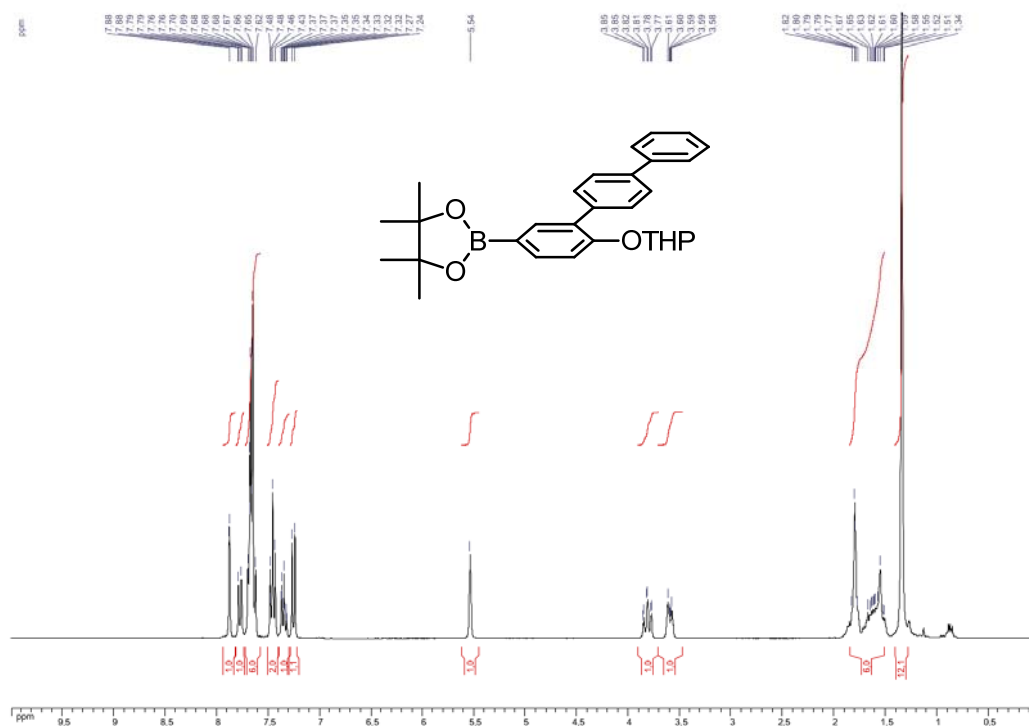
^1H NMR (300.2 MHz, CDCl_3)



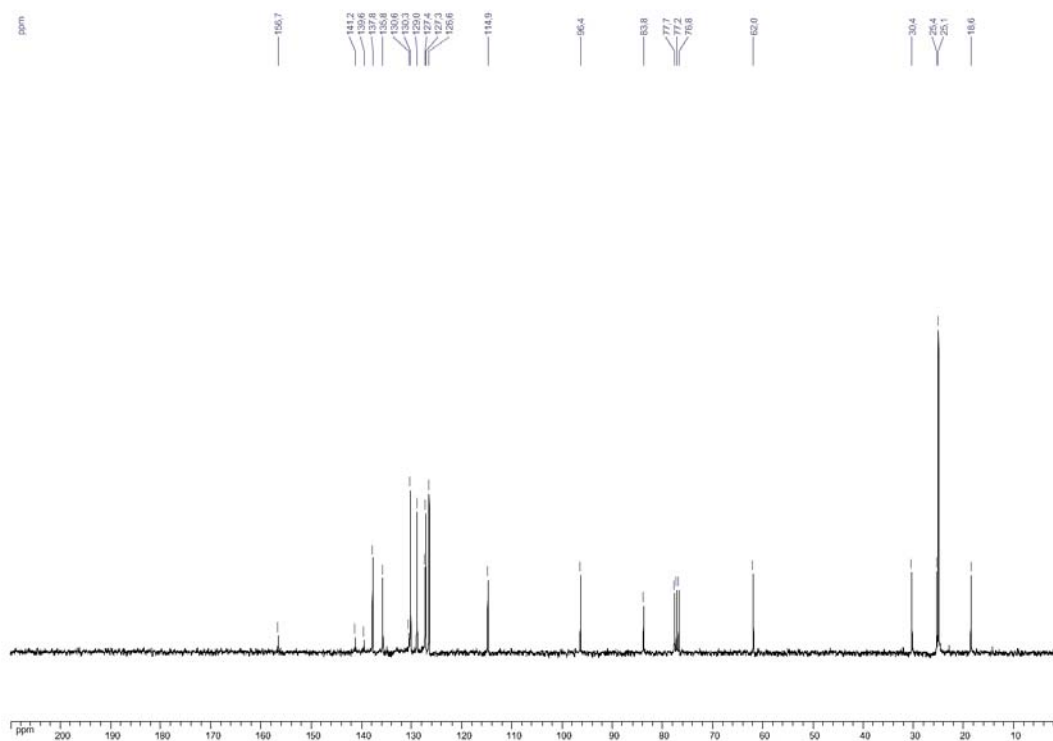
^{13}C NMR (75.5 MHz, CDCl_3)



4,4,5,5-tetramethyl-2-[6-(tetrahydro-2H-pyran-2-yloxy)biphenyl-3-yl]-1,3,2-dioxaborolane
¹H NMR (300.2 MHz, CDCl₃)

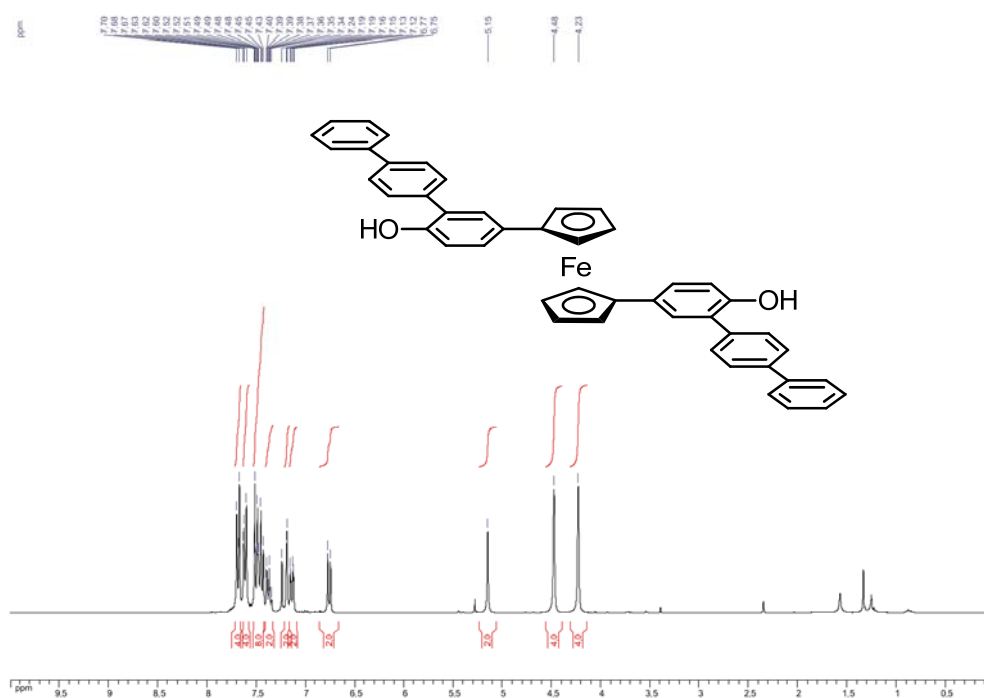


¹³C NMR (75.5 MHz, CDCl₃)

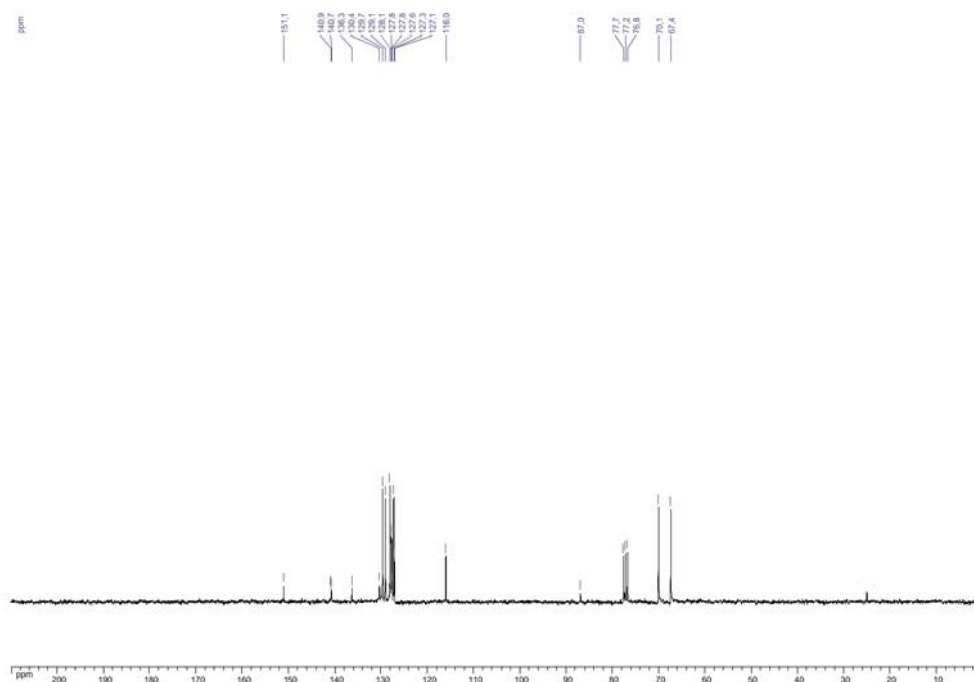


1,1'-Bis-[4-hydroxy-3-(4'-phenyl)phenyl]ferrocene (3c).

¹H NMR (300.2 MHz, CDCl₃)

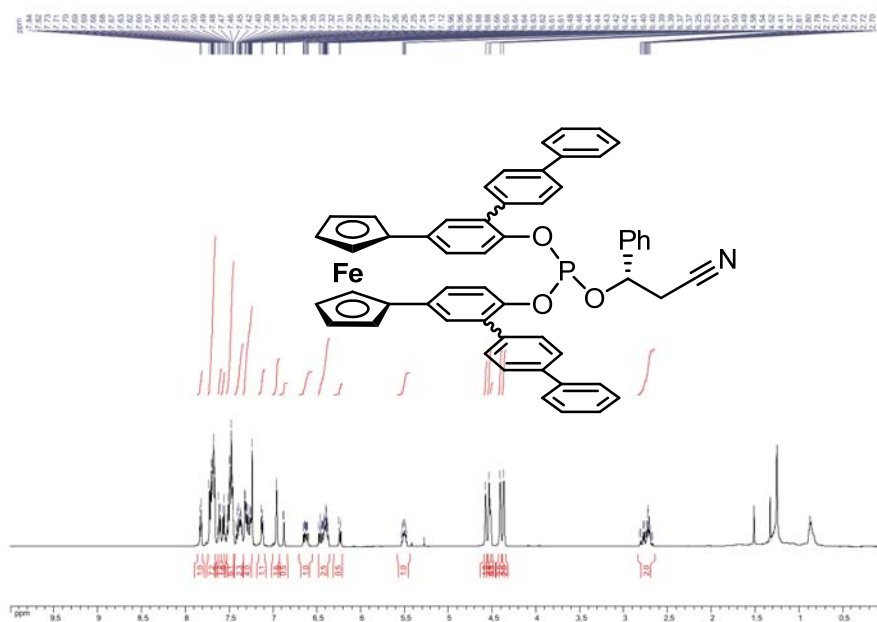


¹³C NMR (75.5 MHz, CDCl₃)

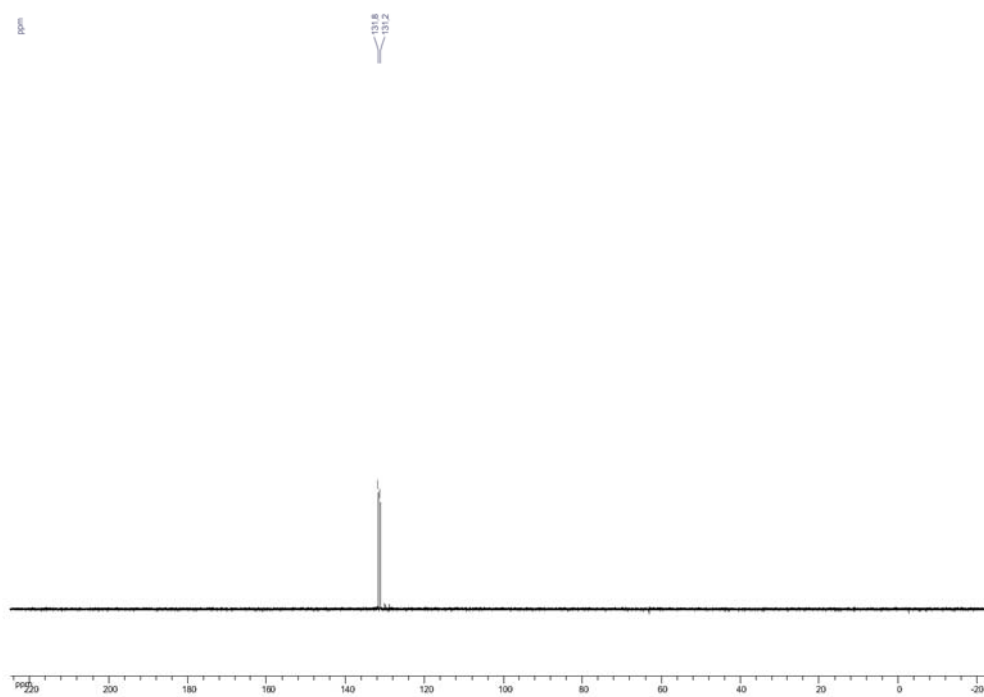


Phosphonites 5c,c'

^1H NMR (500.2 MHz, CDCl_3)

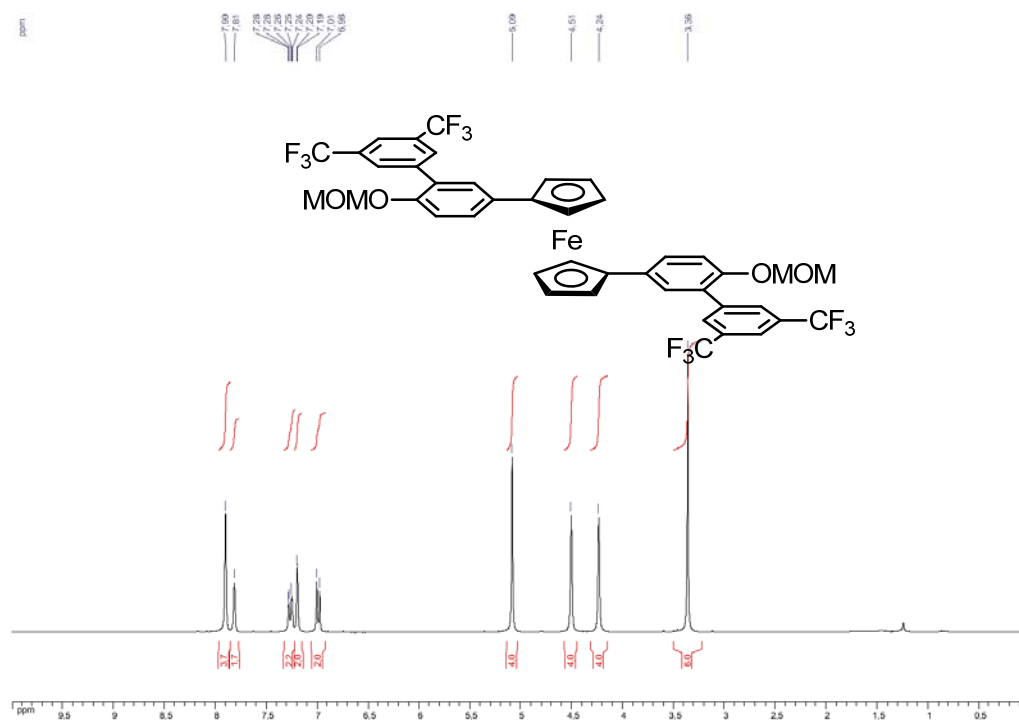


^{31}P NMR (202.5 MHz, CDCl_3)

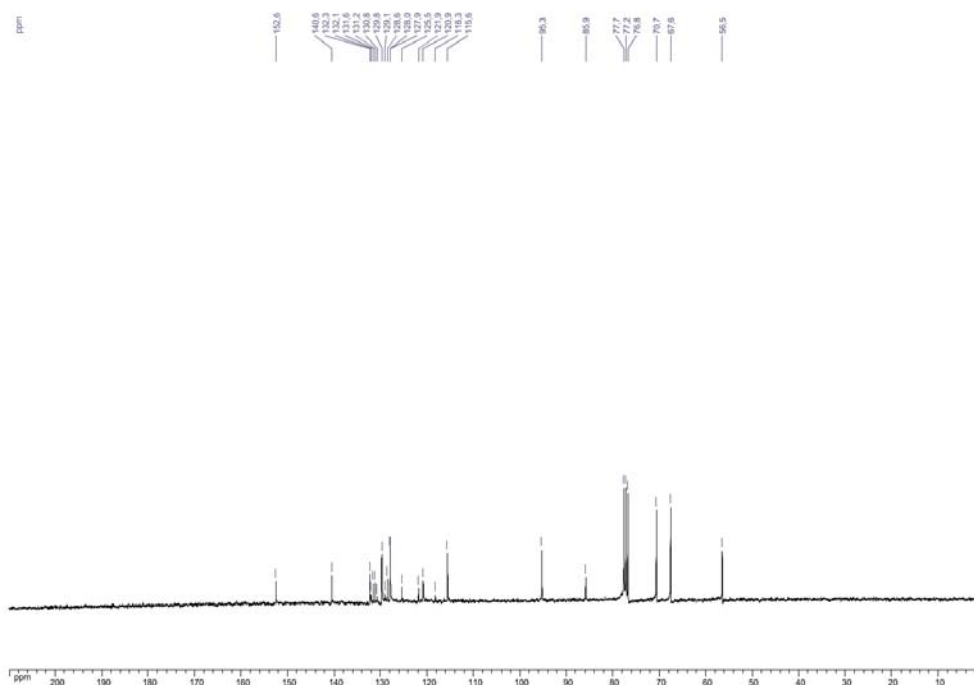


1,1'-Bis-{4-[methoxymethoxy]-3-[3',5'-bis(trifluoromethyl)phenyl]phenyl}ferrocene

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

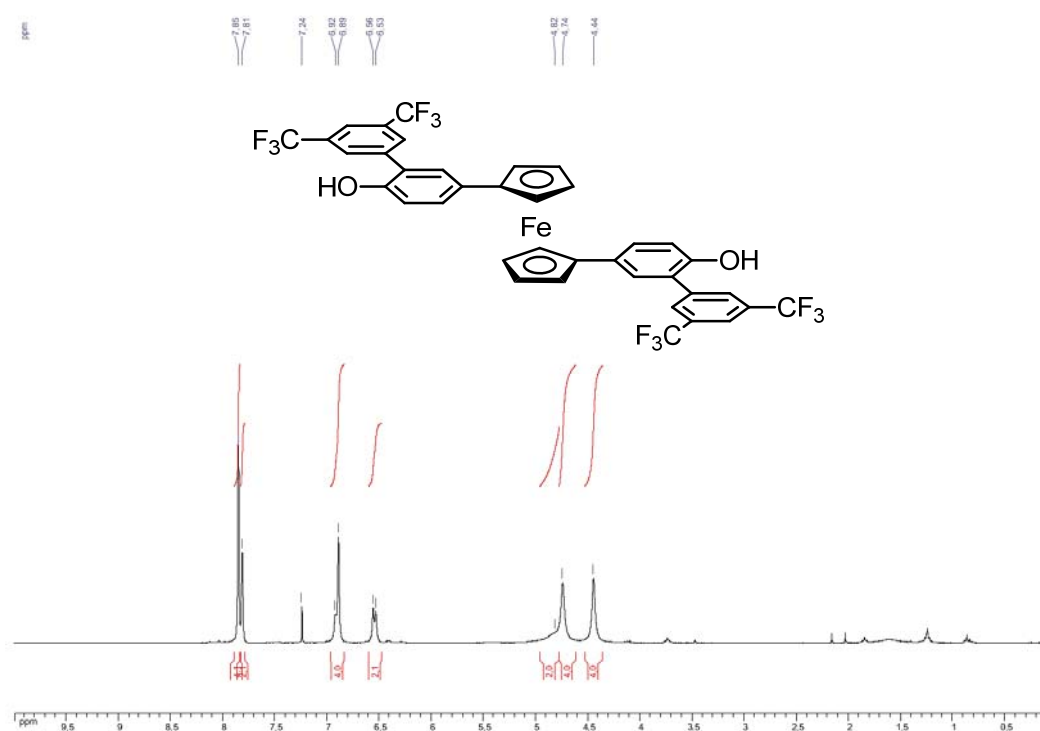


$^{13}\text{C NMR}$ (75.5 MHz, CDCl_3)

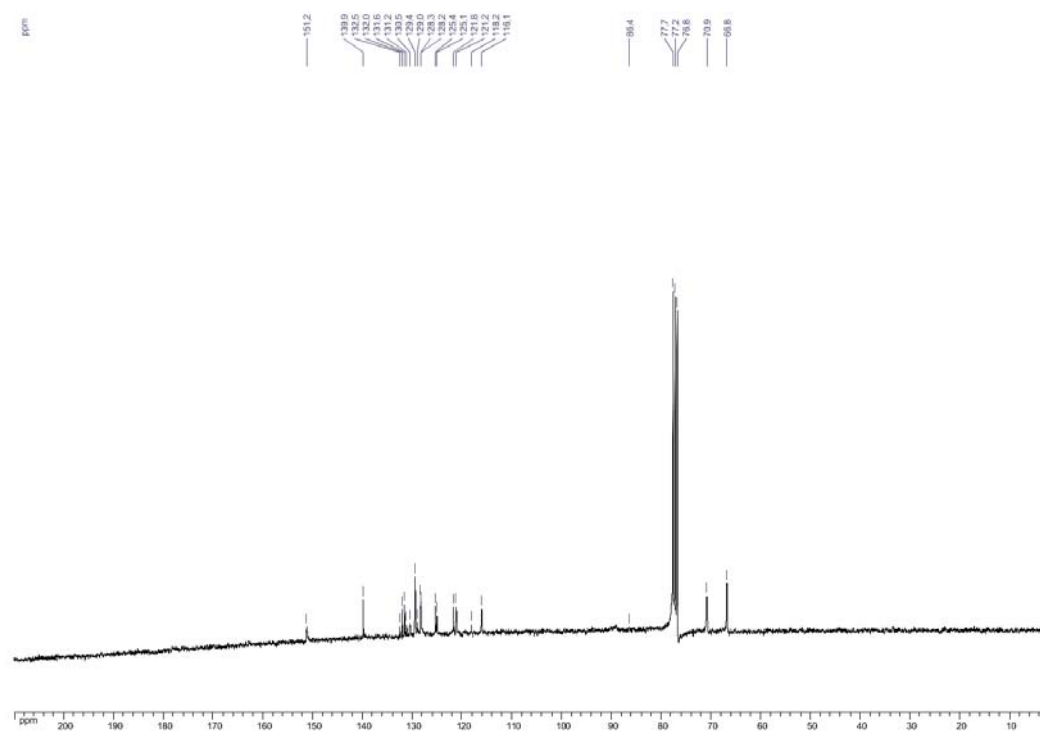


1,1'-Bis-{4-hydroxy-3-[3',5'-bis(trifluoromethyl)phenyl]phenyl}ferrocene (3d).

¹H NMR (300.2 MHz, CDCl₃)

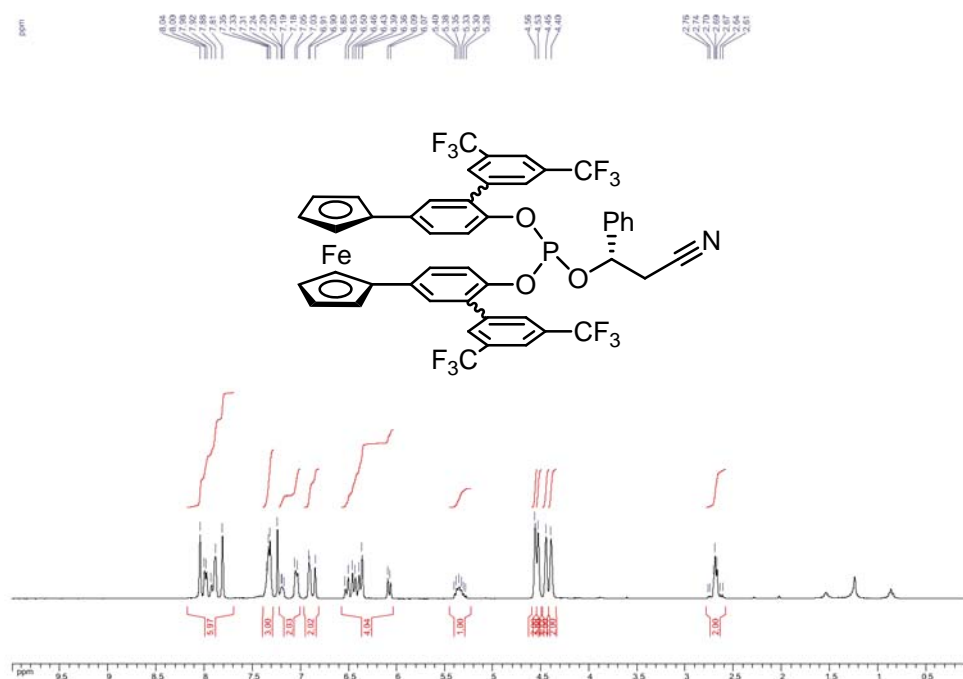


¹³C NMR (75.5 MHz, CDCl₃)

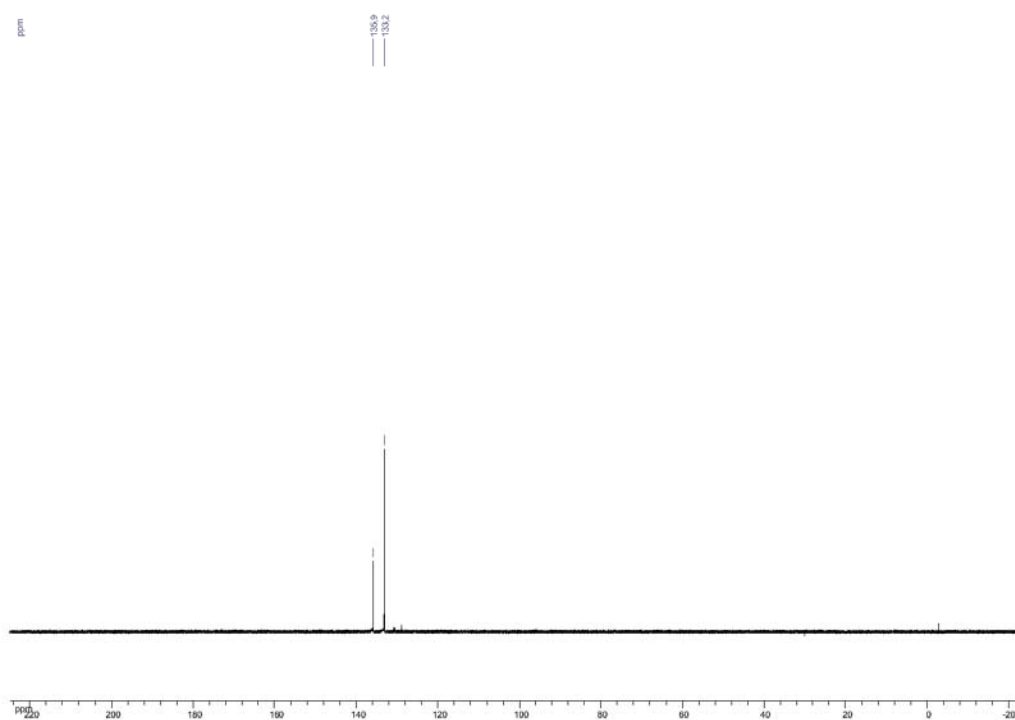


Phosphites 5d,d'

^1H NMR (300.2 MHz, CDCl_3)

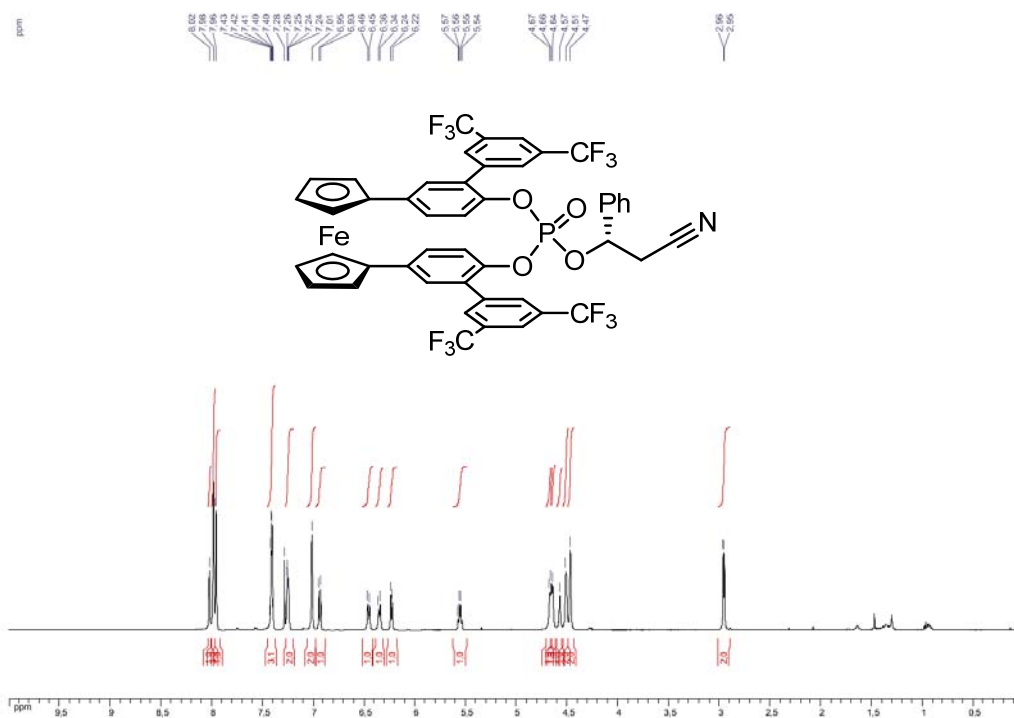


^{31}P NMR (202.5 MHz, CDCl_3)

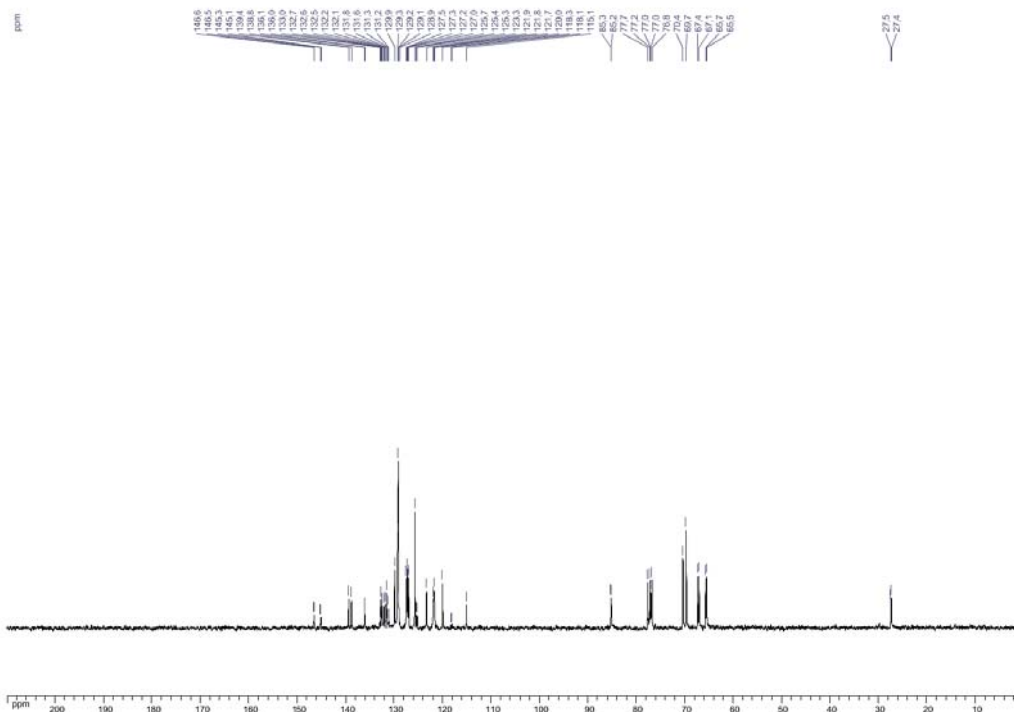


Phosphate 6d

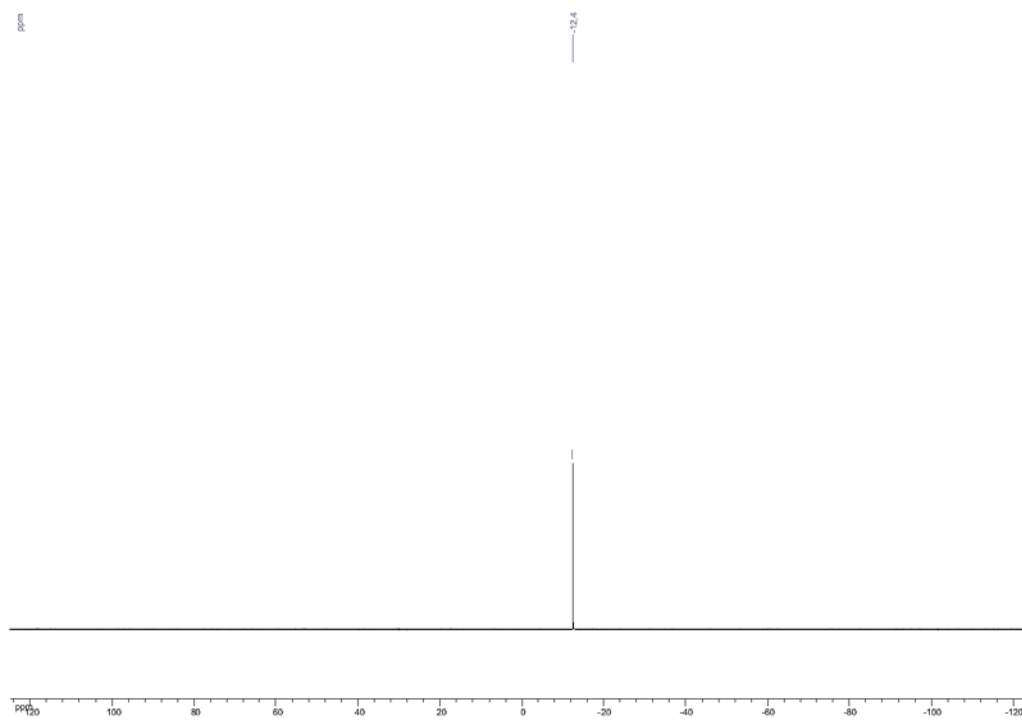
^1H NMR (500.2 MHz, CDCl_3)



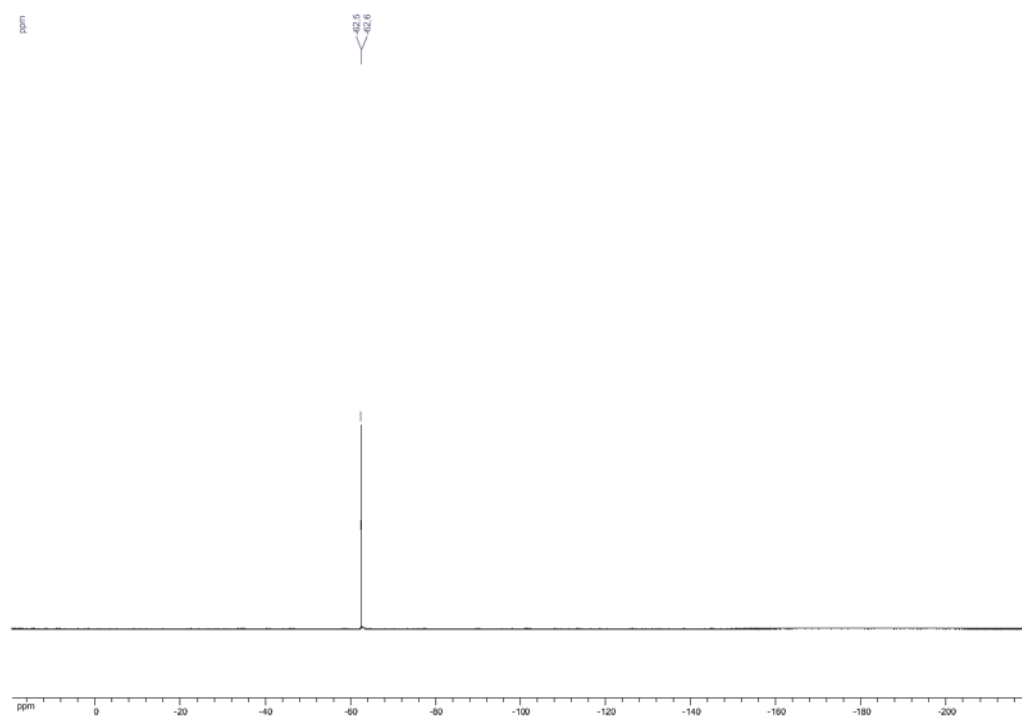
^{13}C NMR (75.5 MHz, CDCl_3)



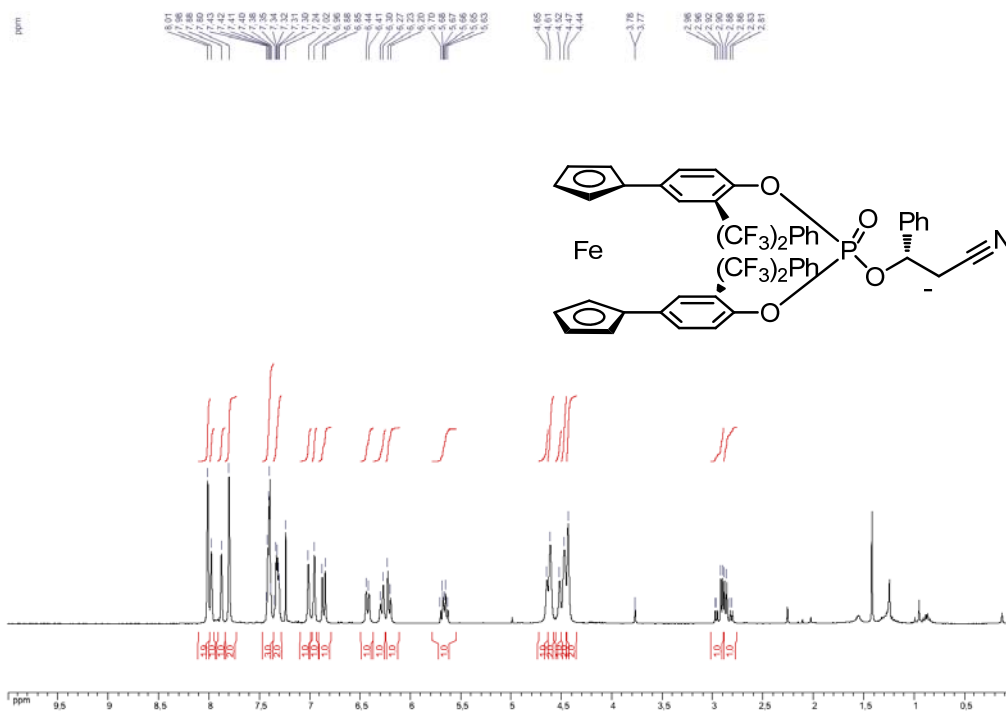
^{31}P NMR (202.5 Hz, CDCl_3) :



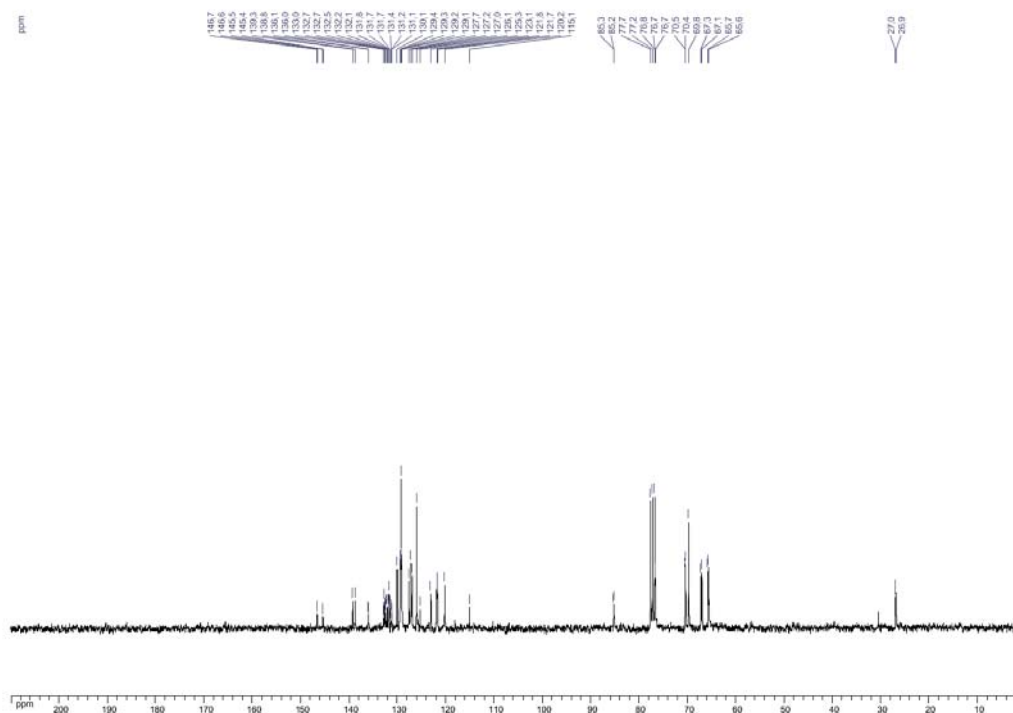
^{19}F NMR (282.4 MHz, CDCl_3) :



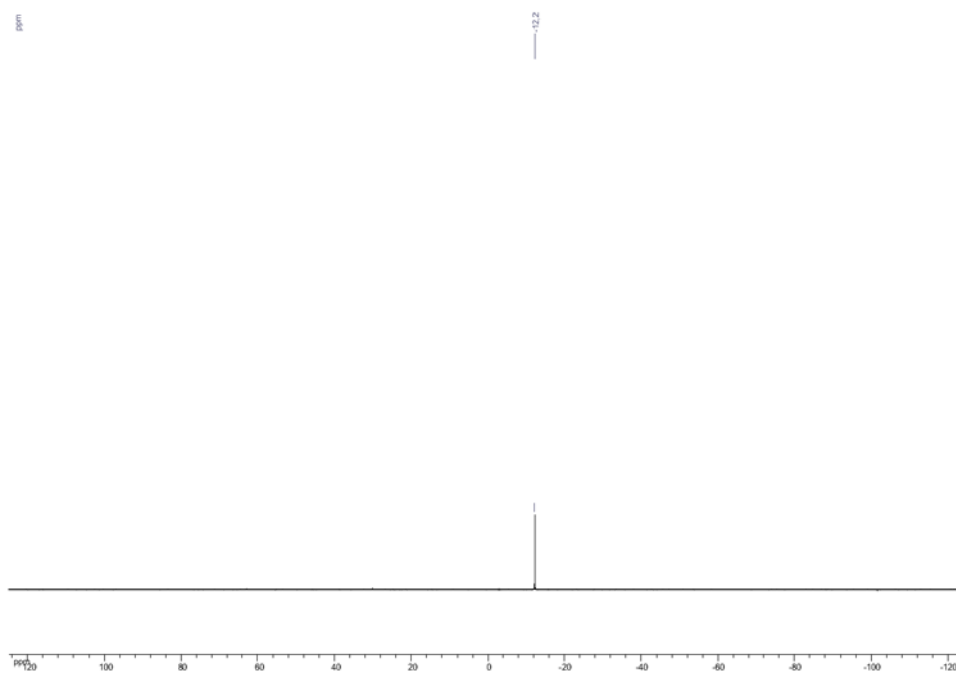
Phosphate 6d'



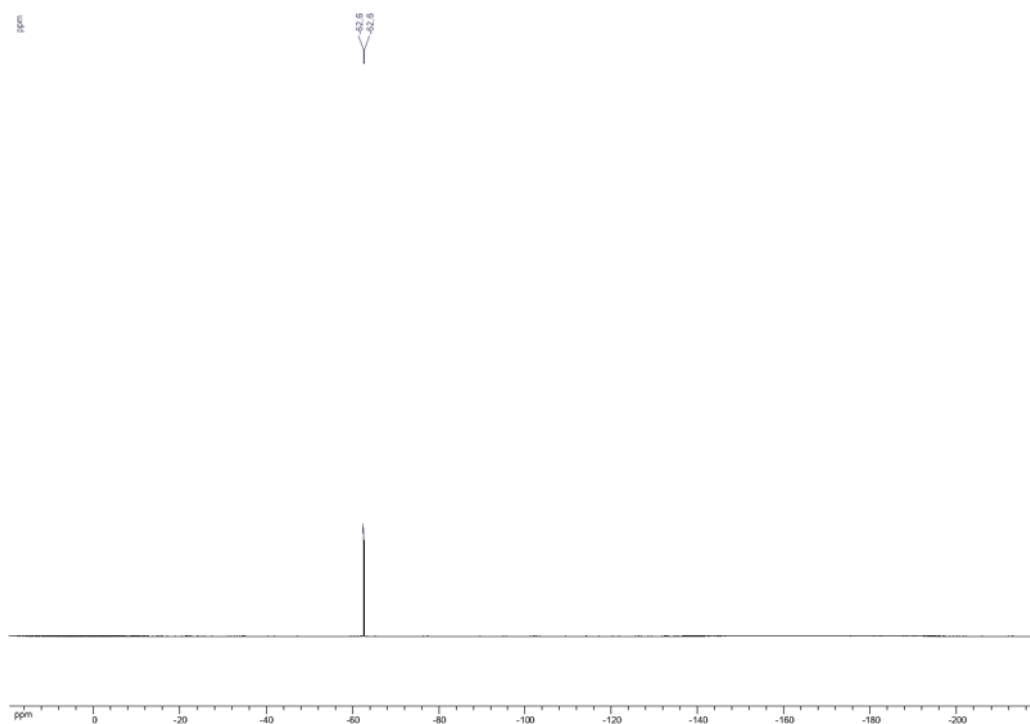
¹³C NMR (75.5 MHz, CDCl₃)



^{31}P NMR (202.5 Hz, CDCl_3) :

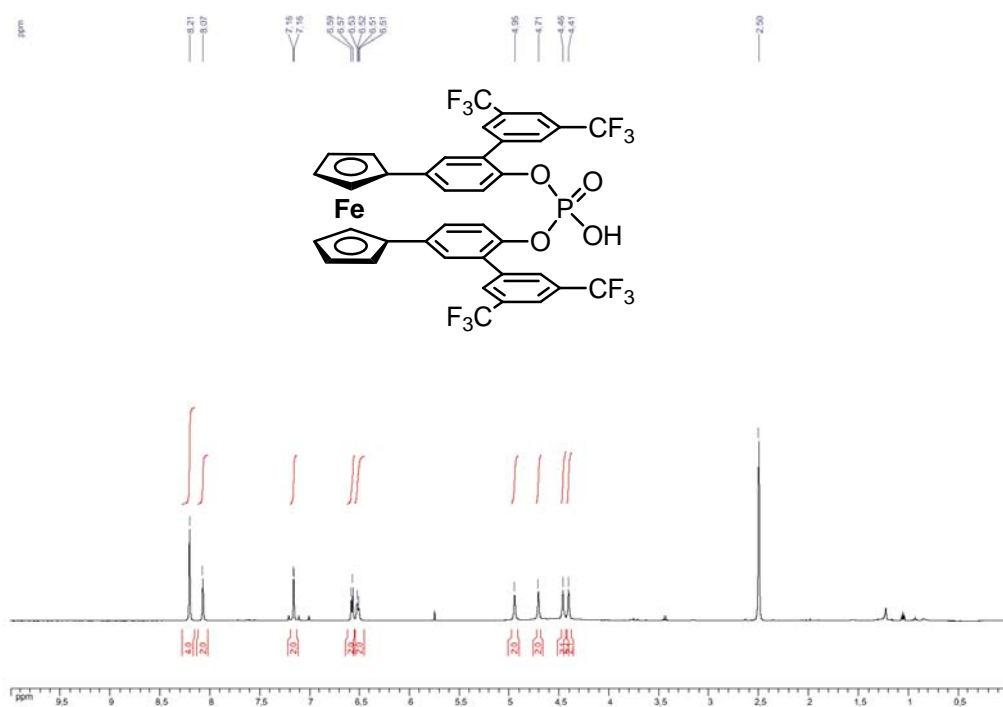


^{19}F NMR (282.4 MHz, CDCl_3) :

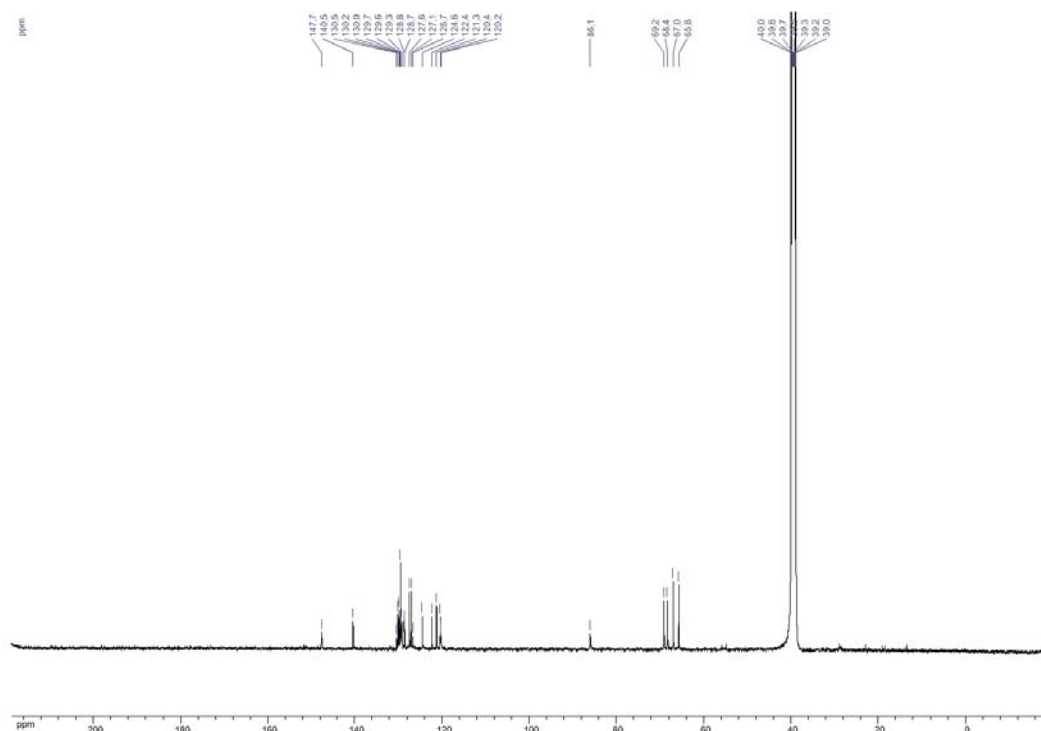


Phosphoric acid 7d

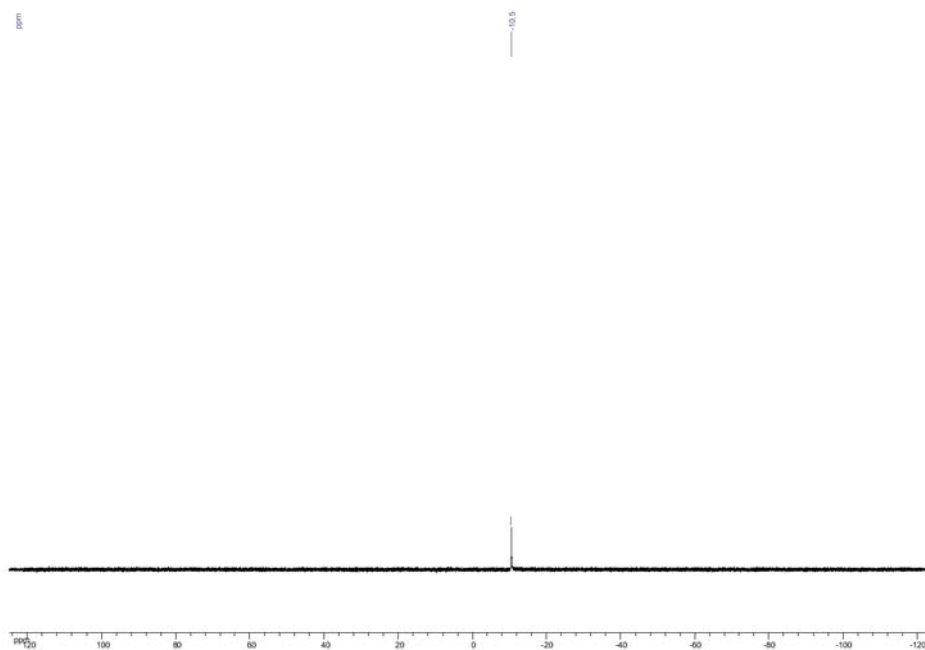
^1H NMR (500.1 MHz DMSO- d_6)



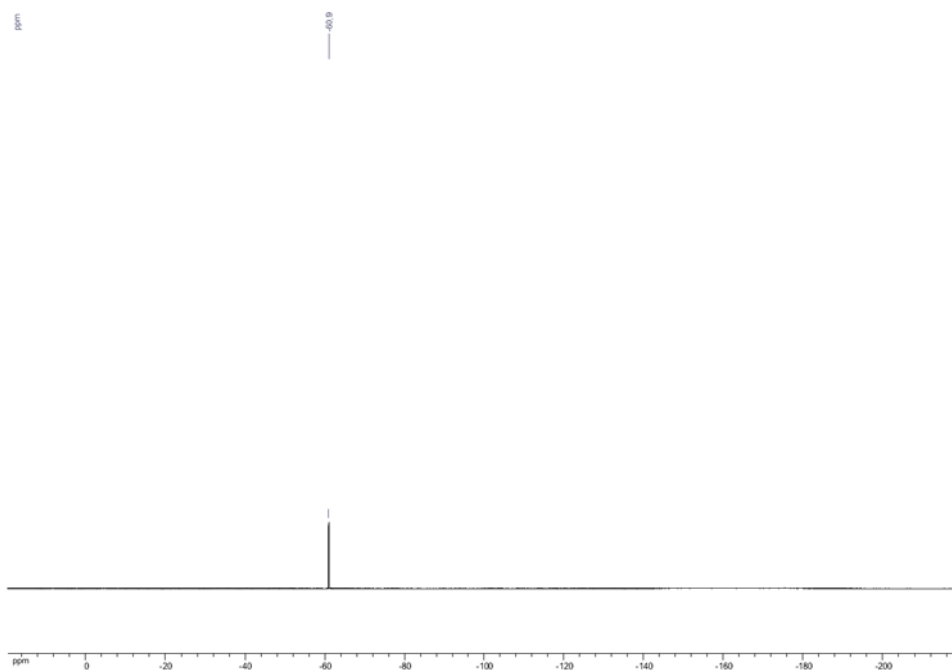
^{13}C NMR (125.8 MHz DMSO- d_6)



³¹P NMR (202.5 MHz DMSO-*d*₆) :

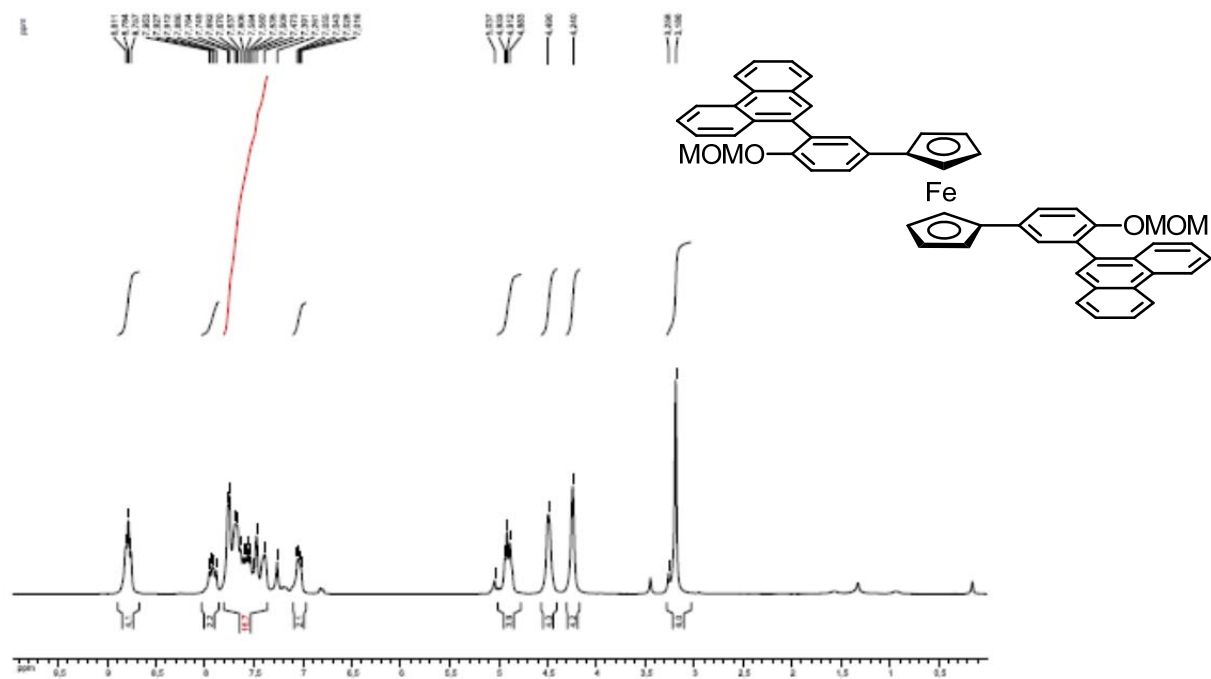


¹⁹F NMR (282.4 MHz DMSO-*d*₆) :

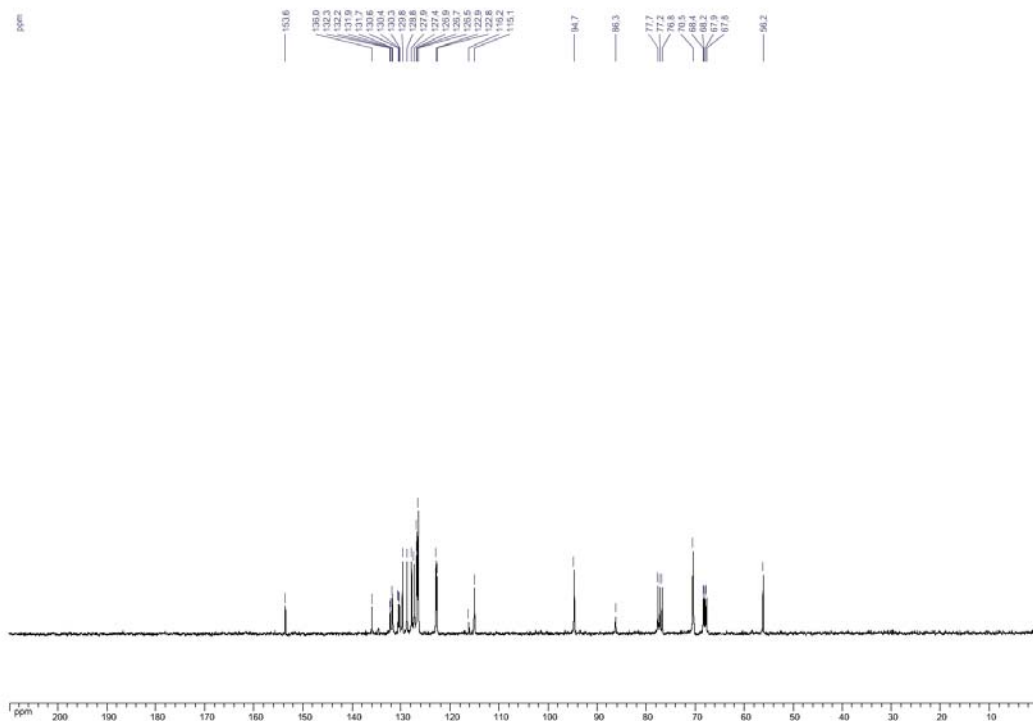


1,1'-Bis-[4-(methoxymethoxy)-3-(9-phenanthryl)-1-phenyl]-ferrocene

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

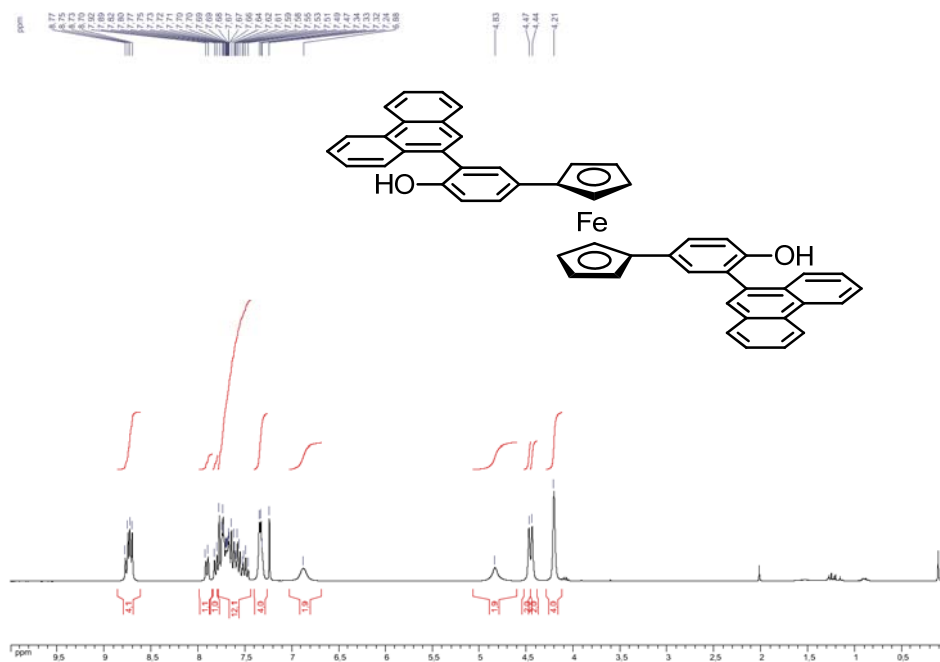


$^{13}\text{C NMR}$ (75.5 MHz, CDCl_3)

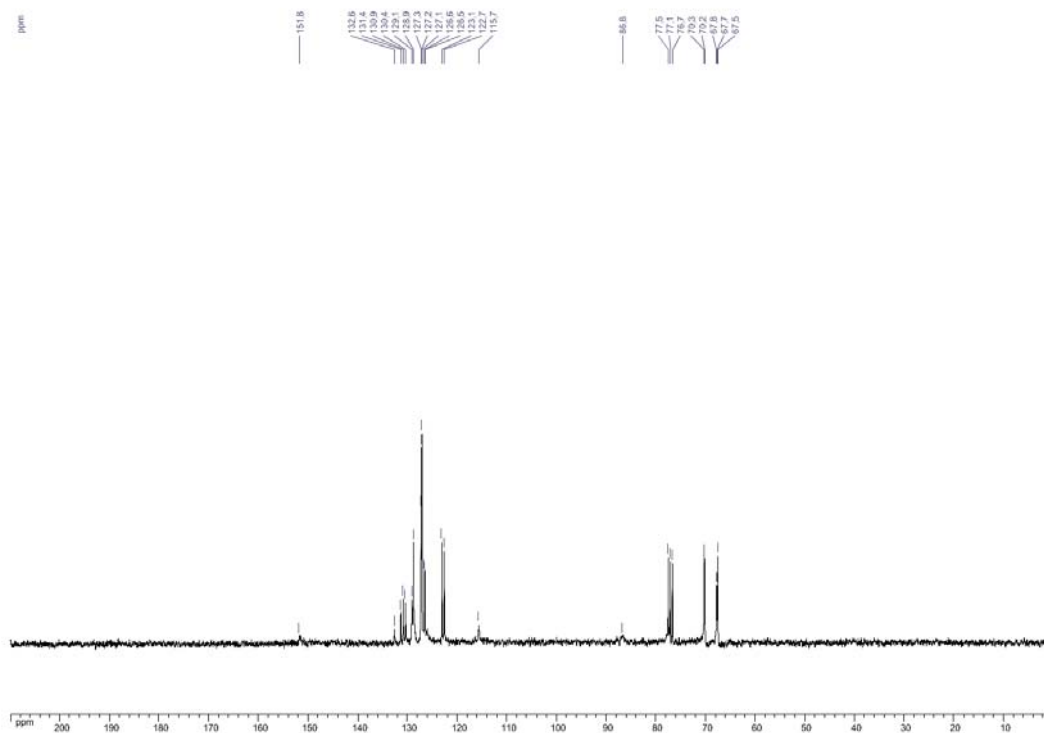


1,1'-Bis-[4-(hydroxy)-3-(9-phenanthryl)-1-phenyl]-ferrocene

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

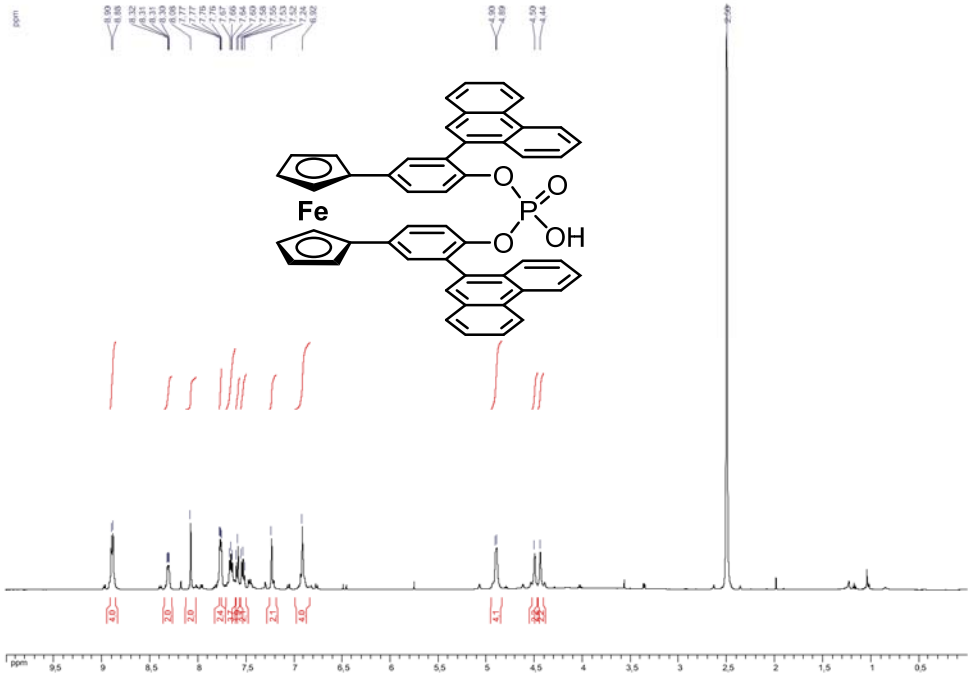


$^{13}\text{C NMR}$ (75.5 MHz, CDCl_3)

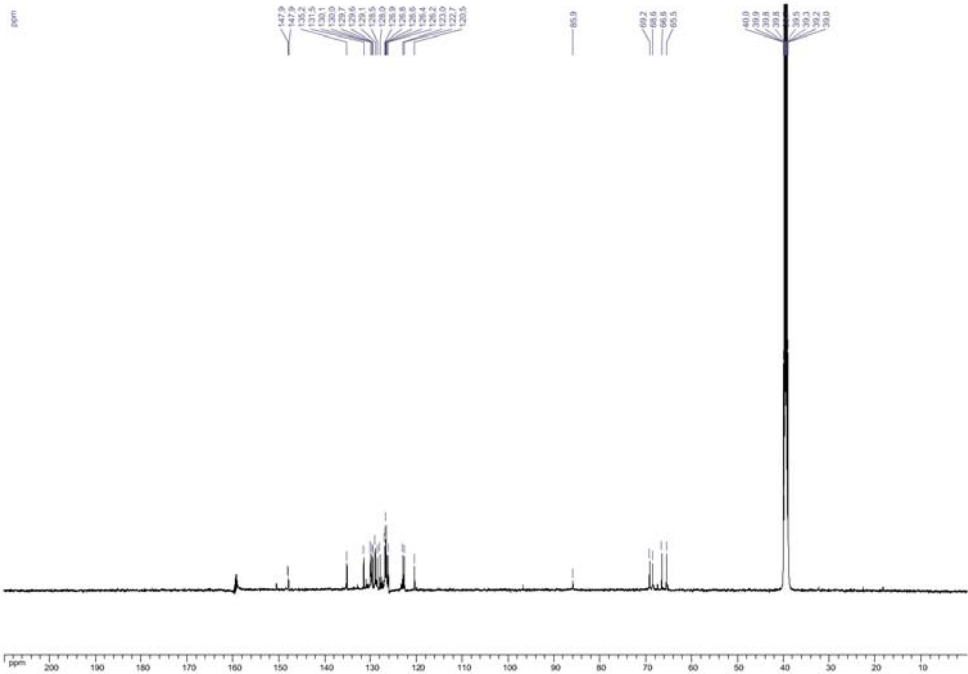


Phosphoric acid 7e

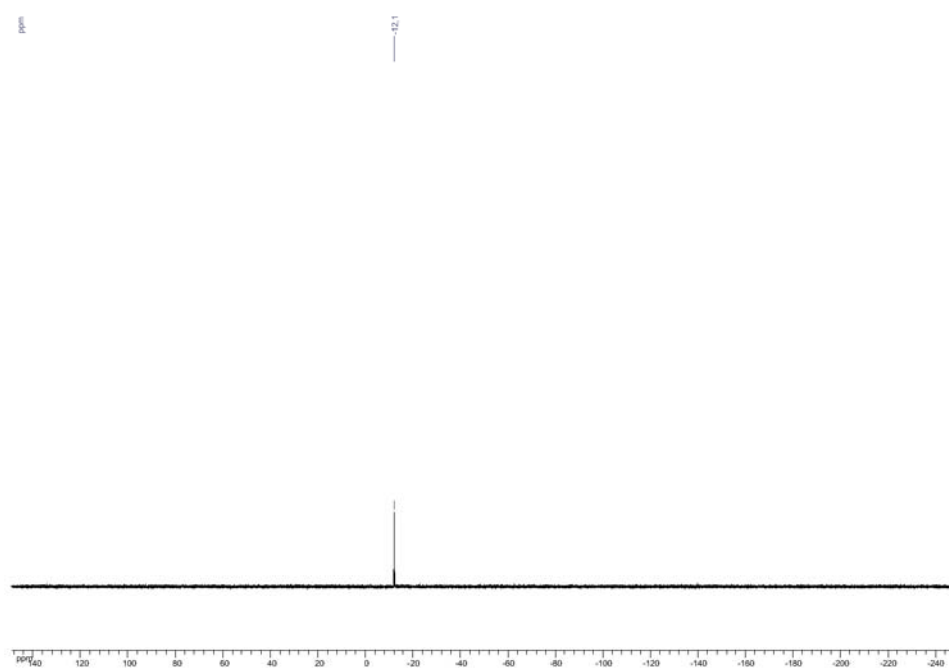
¹H NMR (500.1 MHz, DMSO-d₆)



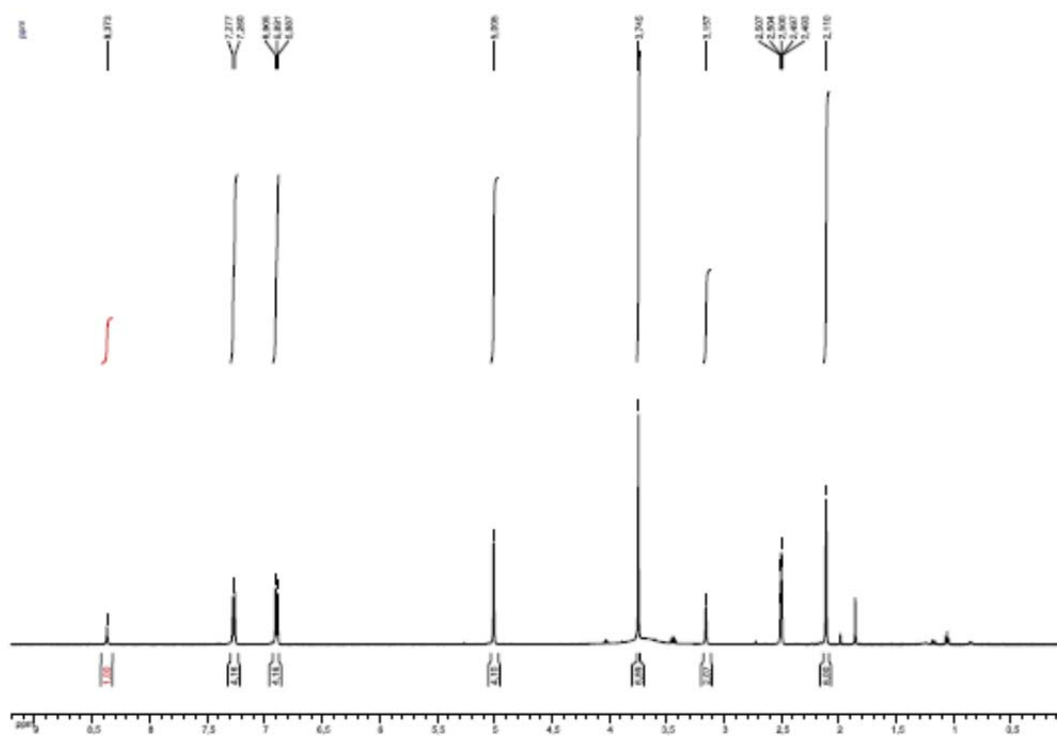
¹³C NMR (125.8 MHz, DMSO-d₆)



³¹P NMR (202.5 MHz, DMSO-d₆)

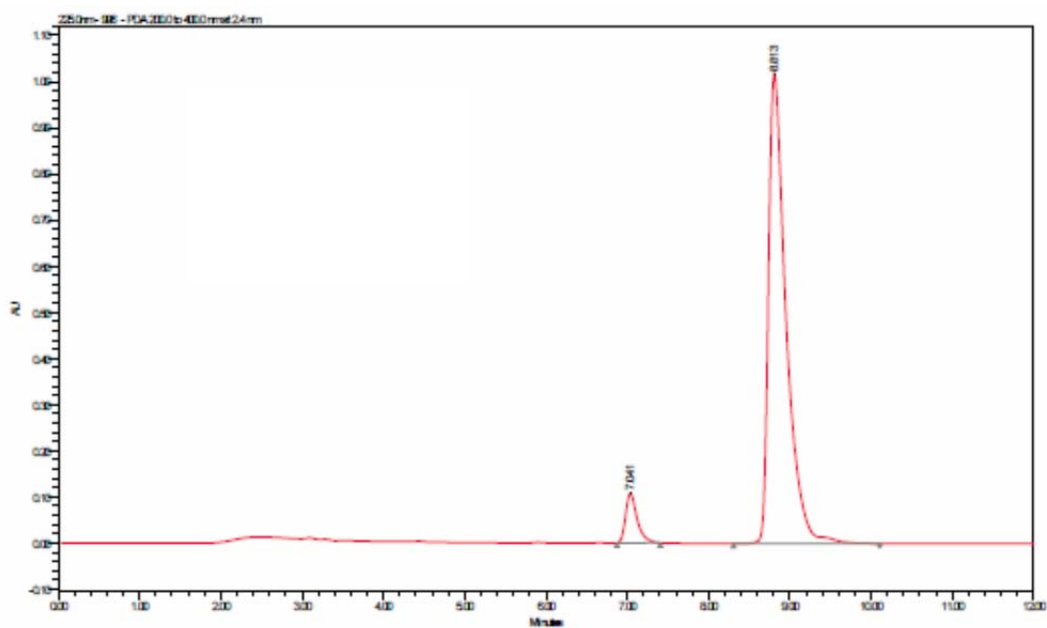


Bis-(4-methoxybenzyl) 2,6-dimethyl-1,4-dihydropyridine-3,5-dicarboxylate, 9e

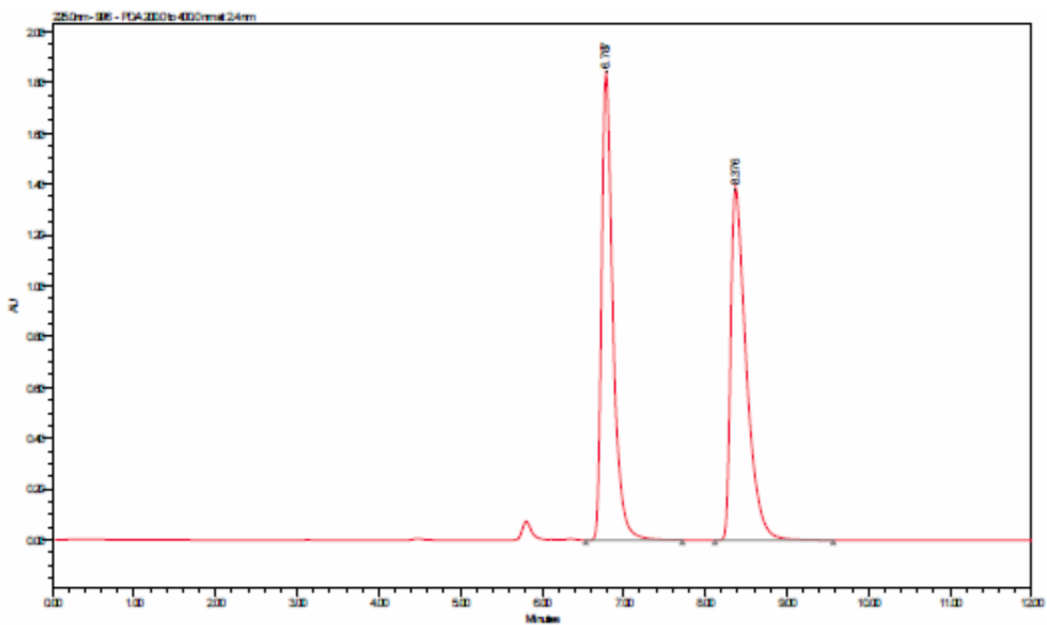


HPLC

2-Phenyl-1,2,3,4-tetrahydroquinoline 11a (entry 10, Table 1)

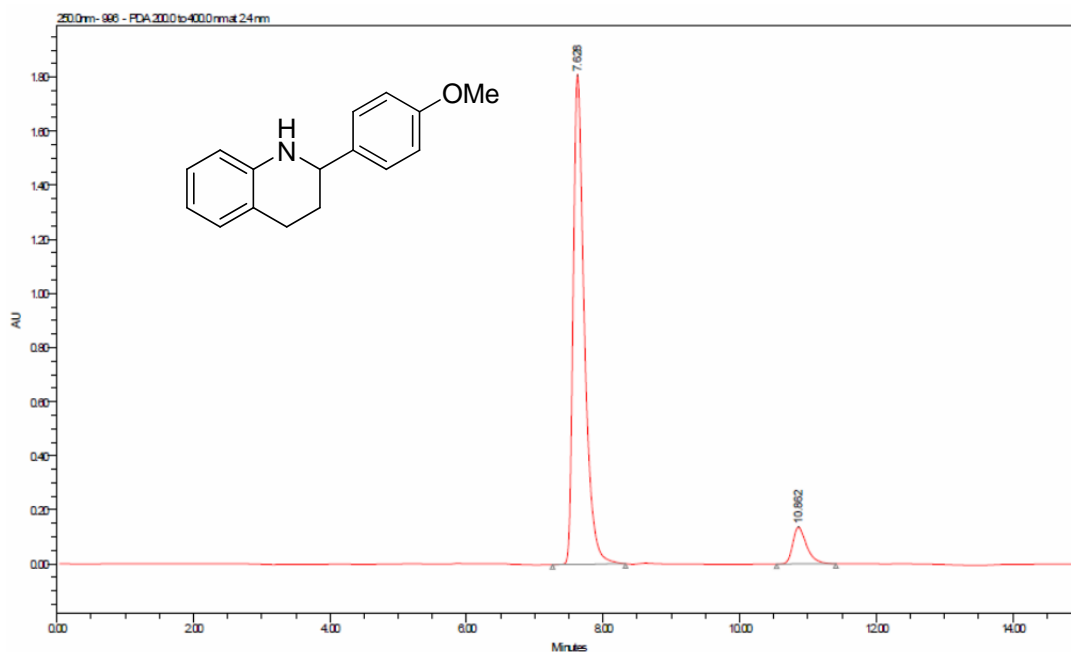


	RT	Area	%Area
1	7.041	1059022	6.50
2	8.613	15224231	93.50

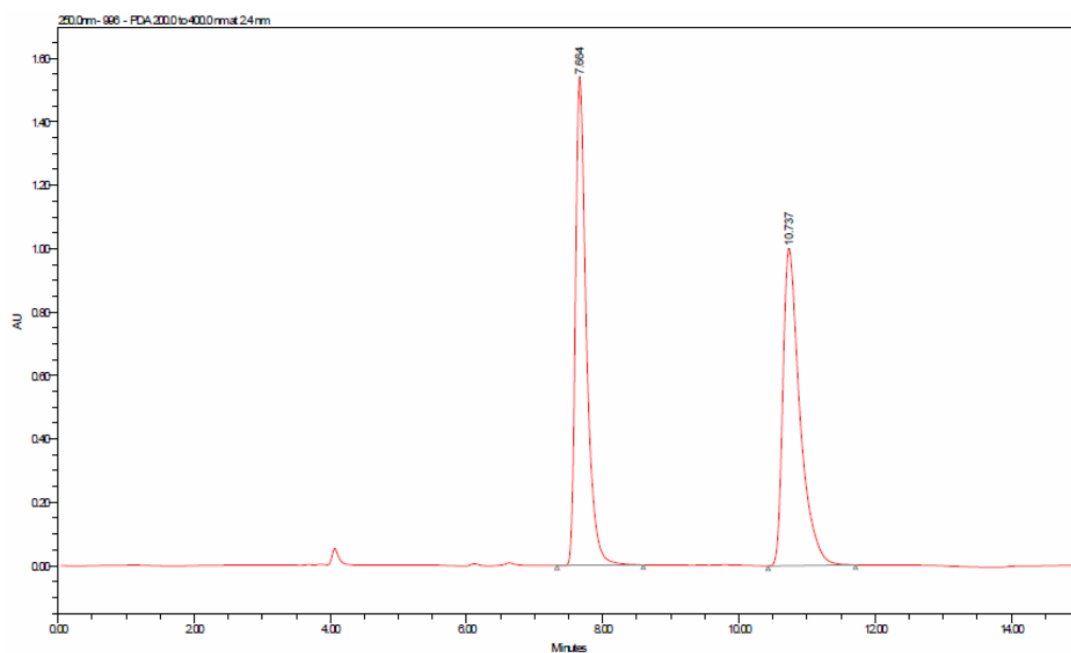


	RT	Area	%Area
1	6.787	17781266	49.10
2	8.376	18434080	50.90

2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline 11b (entry 2 in Table 2)

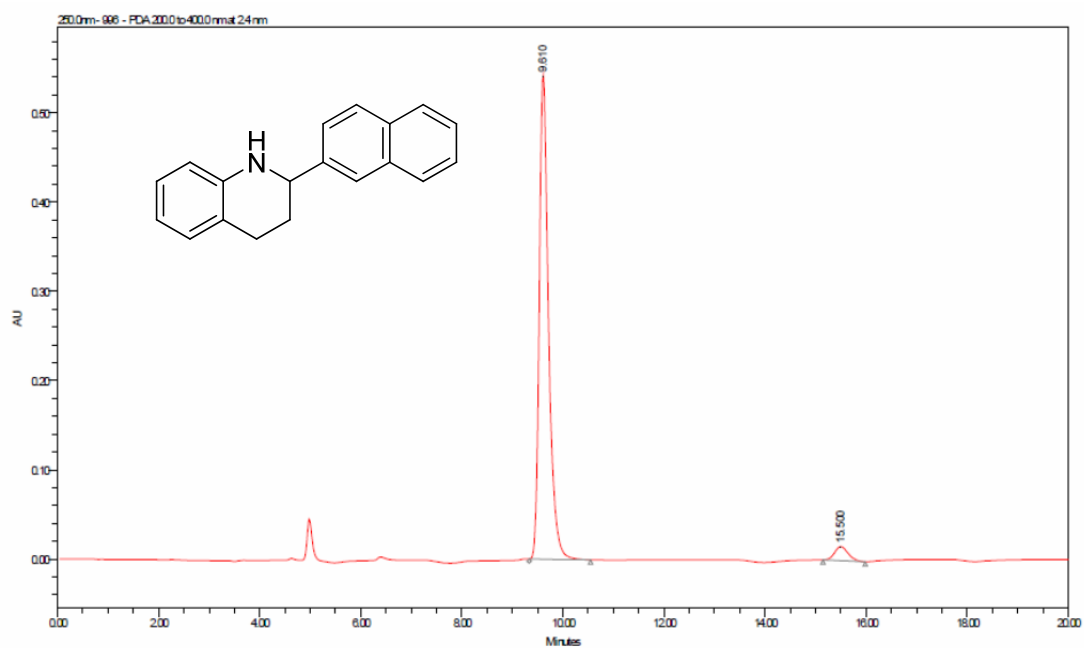


	RT	Area	%Area
1	7.628	20575825	91.50
2	10.862	1912405	8.50

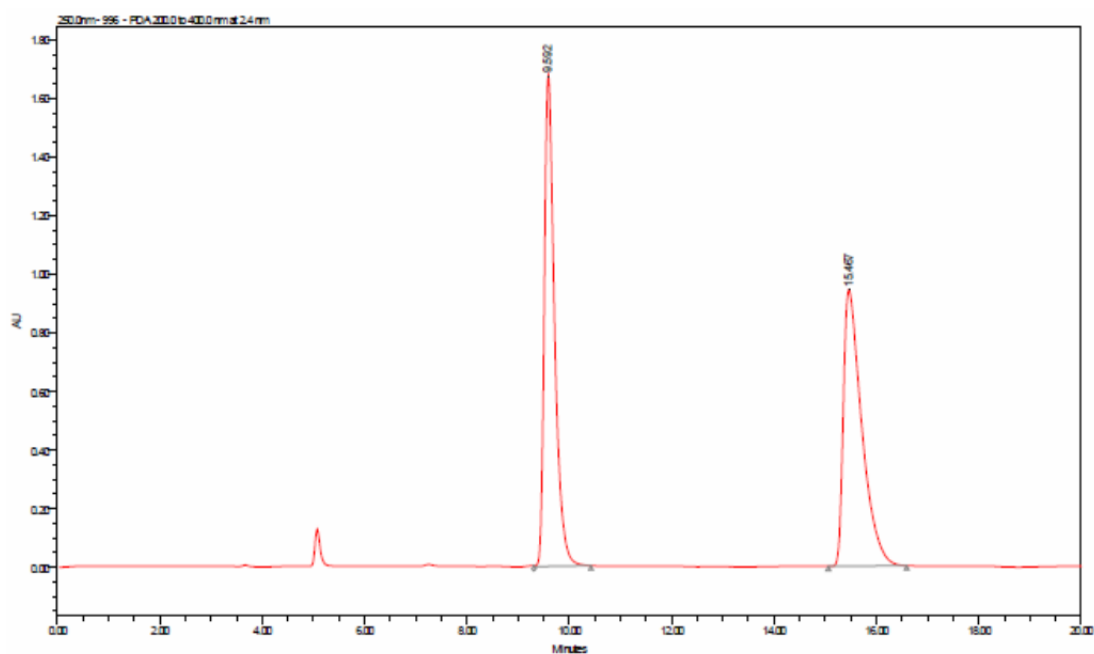


	RT	Area	%Area
1	7.664	17169272	49.80
2	10.737	17306052	50.20

2-(2-naphthyl)-1,2,3,4-tetrahydroquinoline 11c (entry 3 in Table 2)

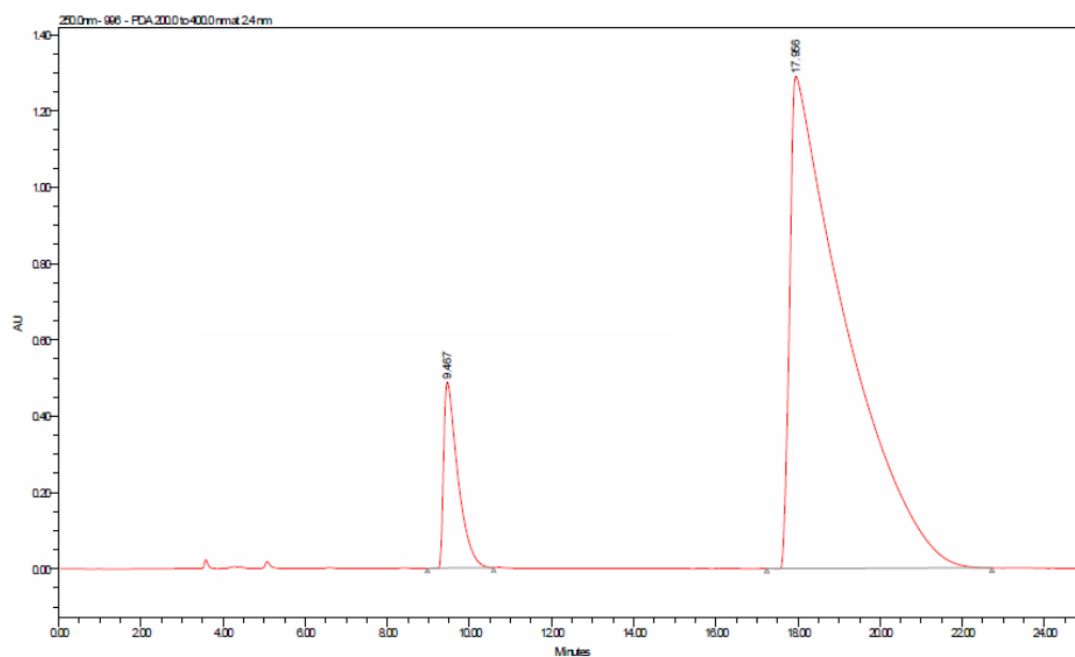


RT	Area	%Area
9.610	6912858	95.90
15.500	296657	4.10

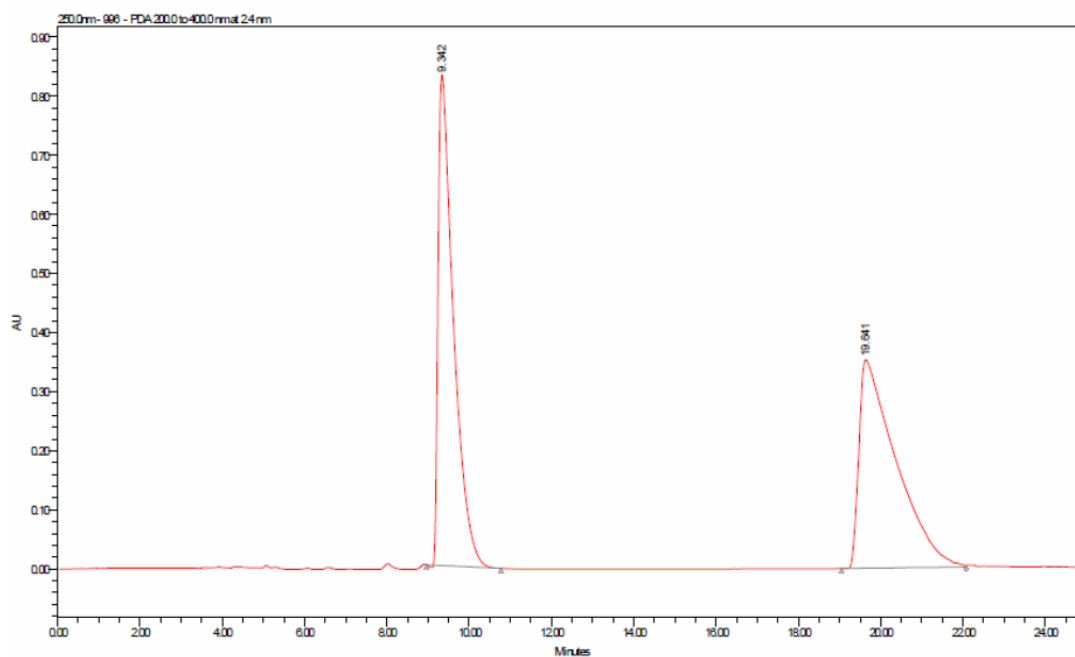


RT	Area	%Area
9.582	23304776	49.79
15.487	23489335	50.21

2-(*p*-biphenyl)-1,2,3,4-tetrahydroquinoline **11d** (entry 4 in Table 2)

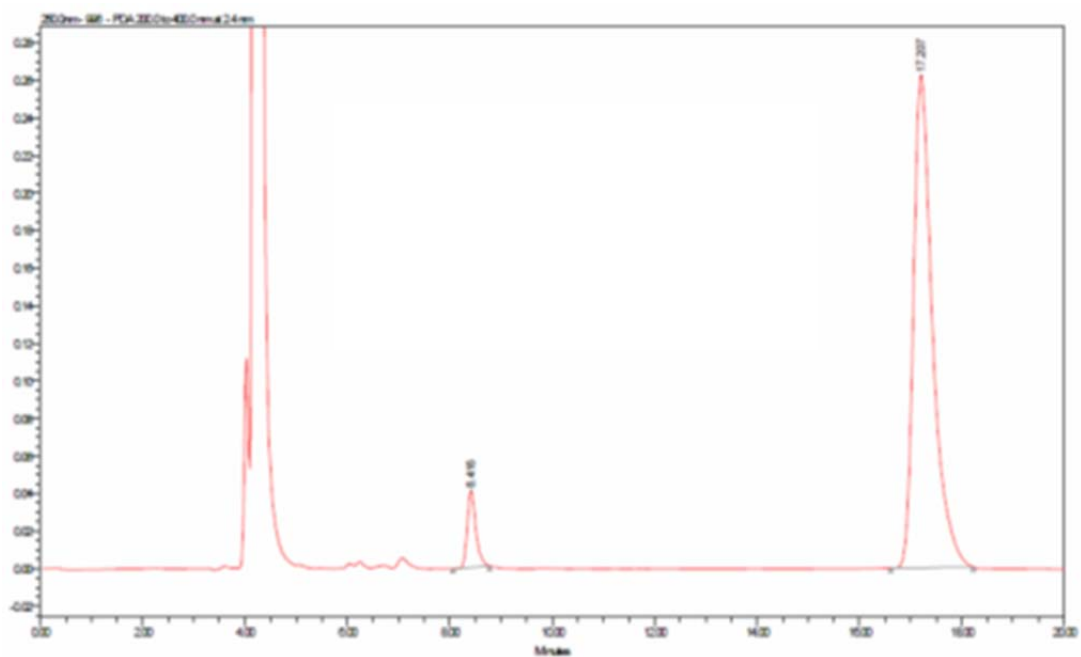


	RT	Area	%Area
1	9.467	11718102	8.79
2	17.966	121531154	91.21

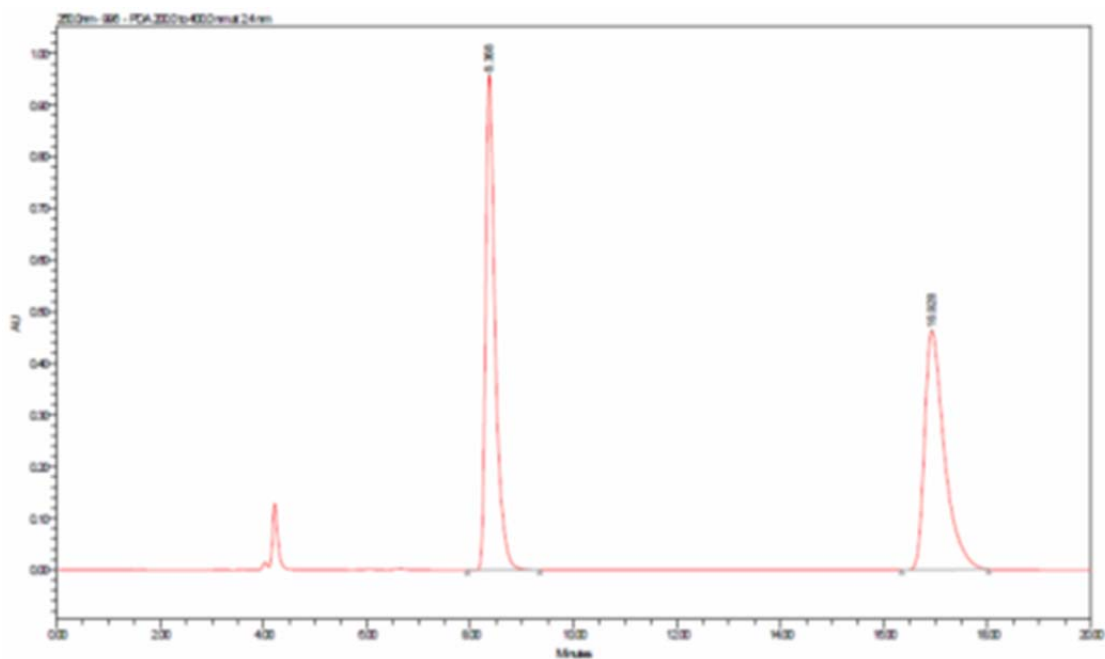


	RT	Area	%Area
1	9.342	21527174	49.37
2	19.641	22076490	50.63

2-(3,5-bis(trifluoromethyl)phenyl)-1,2,3,4-tetrahydro-quinoline 11e (entry 5 in Table 2)

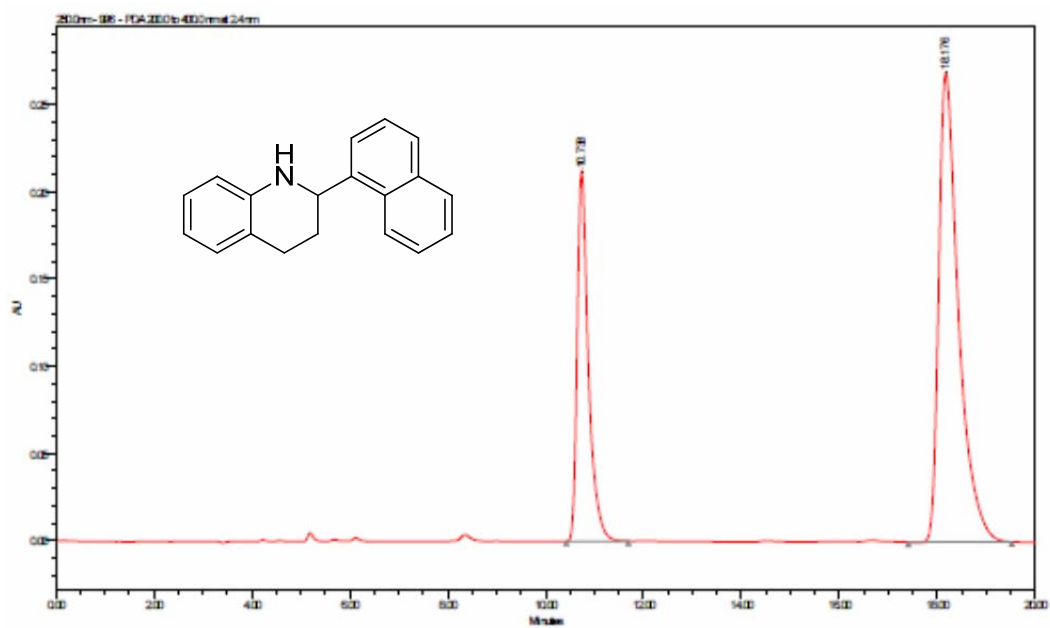


	RT	Area	%Area
1	8.416	476972	6.57
2	17.207	6788096	93.43

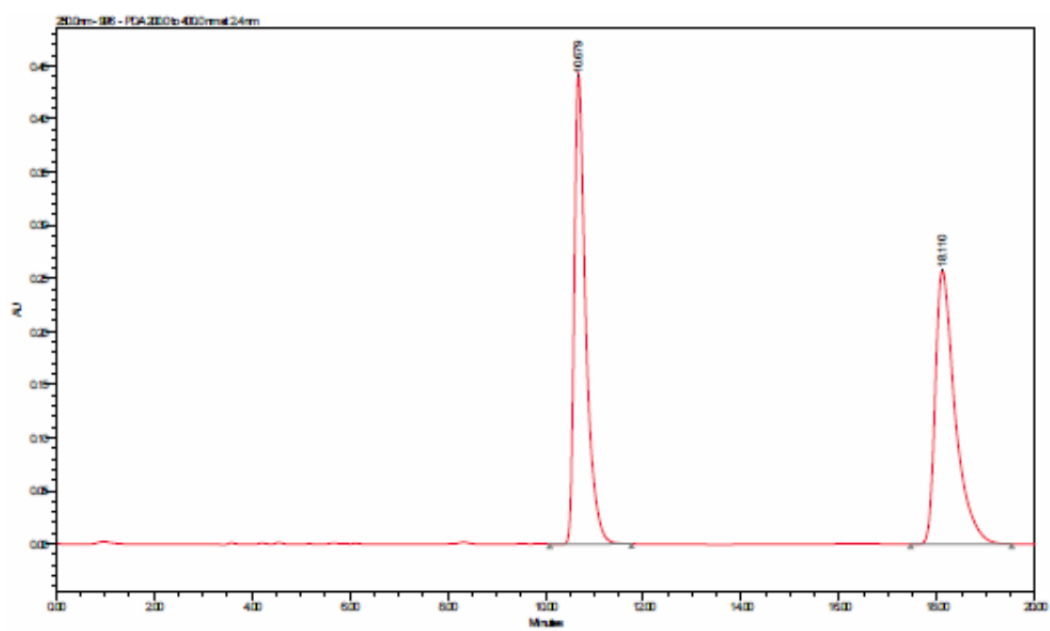


	RT	Area	%Area
1	8.368	1232286	49.93
2	16.928	1236626	50.07

2-(1-naphthyl)-1,2,3,4-tetrahydroquinoline 11f (entry 6 in Table 2)

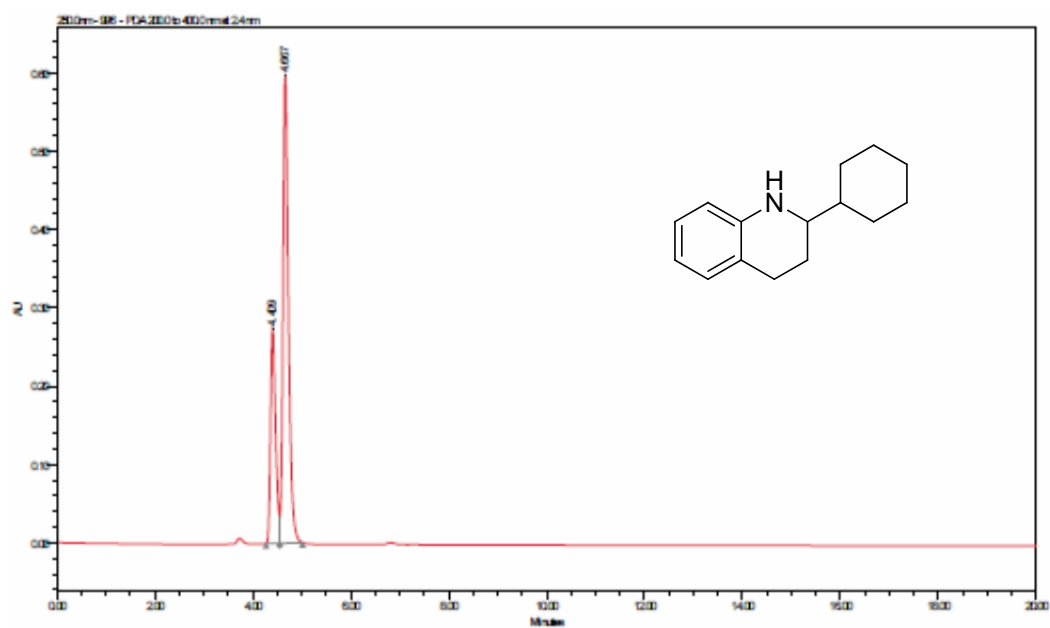


RT	Area	%Area
10.738	3367270	30.95
18.176	7558233	69.05

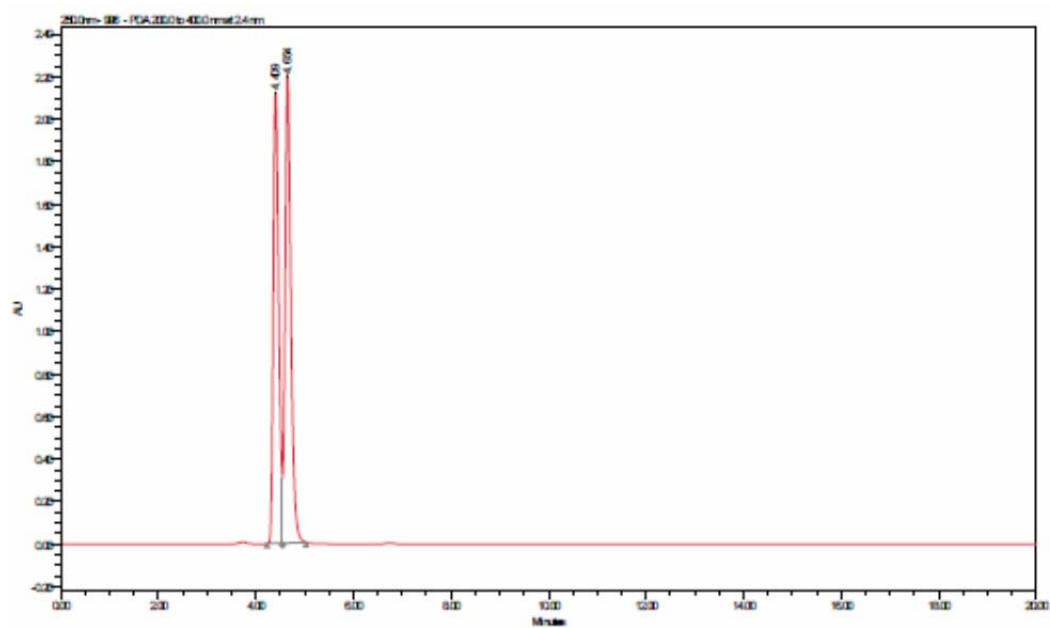


RT	Area	%Area
10.679	7216517	49.95
18.110	7229771	50.05

2-(1-cyclohexyl)-1,2,3,4-tetrahydroquinoline 11g (entry 7 in Table 2)



	RT	Area	%Area
1	4.409	1994731	29.93
2	4.667	4569491	70.07



	RT	Area	%Area
1	4.409	1626389	47.16
2	4.654	18223647	52.84

X-RAY DATA

X-ray crystal data for (S_P,S)-6c':

C₅₅H₄₀FeNO₄P; Mr = 865.70 gmol⁻¹;
space group: P 2₁ 2₁ 2₁; a = 7.7258 (1), b = 14.3900(3), c = 39.324(3) Å;
V = 4371.8(4) Å³; Z = 4;
D_{calcd} = 1.315 gmL⁻³;
T = 193(2) K;
λ = 1.5418 Å;
μ = 3.499 mm⁻¹;
total reflections: 15884; unique reflections: 3256; observed: 1843 [I > 2 σ(I)];
parameters refined: 536;
R1 = 0.1219,
wR2 = 0.1477 for all data;
GOF = 1.007;

X-ray data were recorded with a Rigaku MM007 HF copper rotating-anode generator with Osmic confocal optics and a rapid II Curved Image Plate at low temperature, 193(2)K and treated with the CrystalClear suite.¹ The structure was solved by direct methods (SHELXS-97)² and refined on F² by means of full-matrix least-squares methods (SHELXL-97).² All non-hydrogen atoms were allowed anisotropic thermal motion. Aromatic C – H hydrogen atoms were included at calculated positions, with C – H = 0.95 Å respectively and were refined with a riding model and with U_{iso} set to 1.2 times that of the attached C atom. To counterbalance the poor diffraction and the resulting poor data / parameter ratio rigid group refinement for phenyl rings (AFIX 66 instructions) was performed and soft 'rigid bond' and similar anisotropic U_{ij} restraints (DELU and SIMU instructions with standard deviation values) were applied along the entire connectivity set. 1307 Friedel opposites (93% of coverage) were kept unmerged and the absolute configuration of the compound (P (S), C47 (S)) was determined unambiguously from convergent criteria as the value of the Flack parameter,³ x = 0.013(10) derived from SHELXL and those issued from Bayesian statistics⁴ implemented within PLATON.⁵

CCDC 951975 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

¹ CrystalClear-SM Expert 2.0 r4 (Rigaku, 2009)

² Sheldrick, G. M. (2008) *Acta Crystallogr., Sect. A*, **64**, 112-122; Welter, R. (2006). The Crystalbuilder Project, *Acta Cryst.* A62, s252.

³ Flack, H. D. (1983), *Acta Cryst.* A39, 876-881.

⁴ Hoof, R.W.W., Straver, L.H., Spek, A.L. (2008). *J. Appl. Cryst.*, **41**, 96-103.

⁵ Spek, A. L. (2003) *J. Appl. Cryst.* 36, 7-13.

ORTEP view of (*S_p*,*S*)-6c'

