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Supporting Information

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Parallel Synthesis and Screening of Polymer-supported P-stereogenic Aminophosphane-Phosphite and Phosphinite Ligands

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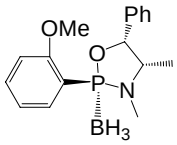
Supporting information

General experimental.

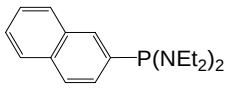
Unless stated otherwise, reactions were carried out under an atmosphere of argon using standard Schlenk techniques. Optical rotations were measured on a Perkin-Elmer 241 polarimeter. NMR spectra were recorded on a Varian Mercury 300, a Varian Inova 500 or a Bruker Avance DRX-300 spectrometer. Chemical shifts are reported in ppm and are given relative to tetramethylsilane (^{1}H, ^{13}C) and 85% H_3PO_4 (^{31}P). Gel-phase ^{31}P $\{^{1}H\}$ NMR experiments were recorded using standard NMR techniques in THF (using a D_2O inner tube). Alternatively, the gel-phase samples were recorded in C_6D_6 or CD_2Cl_2 as solvent on a Varian Inova 500 MHz 4 mm gH(X) indirect detection nano-probe, operating at 202.34 MHz and a magic angel spinning (MAS) rate of 2000 Hz. The nano-probe provides a sample cavity of 40 microliter. High Resolution Mass Spectra were recorded at the Department of Mass Spectrometry at the University of Amsterdam using Fast Atom Bombardment (FAB) ionization on a JOEL JMS SX/SX102A four-sector mass spectrometer, coupled to a JEOL MS-MP9021D/UPD system program. Samples were loaded in a matrix solution (3-nitrobenzyl alcohol) on to a stainless steel probe and bombarded with xenon atoms with an energy of 3KeV. Elemental analyses were carried out by Kolbe Mikroanalytisch Labor, Mülheim an der Ruhr (Germany).

Unless stated otherwise, all chemicals were obtained from commercial suppliers and used as received. THF and diethyl ether were distilled from sodium/benzophenone. Tertiary and secondary amines, CH_2Cl_2 and methanol were distilled from CaH_2 and toluene was distilled from sodium. Deuterated solvents were distilled from the appropriate drying agents. 4-Bromo polystyrene (**4**, 50-100 mesh, 1.9 mmole/g, 1% divinylbenzene/styrene copolymer) was purchased from Novabiochem. (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-[1,3,2]-oxazaphospholidine (**6**)[1], (2*R*,4*S*,5*R*)-3,4-dimethyl-2-ferrocenyl-5-phenyl-[1,3,2]-oxaza-phospholidine 2-borane (**1e**)[1], 2-methoxyphenyl-bis(*N*,*N*-diethylamino)-phosphane (**9b**)[2], (2*R*,4*S*,5*R*)-2,5-diphenyl-4-methyl-[1,3,2]-oxazaphospholidine 2-borane (**1a**)[3], 2,2'-biphenol phosphorochloridite (**11**)[4], bis(diethylamino)chlorophosphane[5] and bis(diethylamino)phenyl phosphane (**9a**)[6] were synthesized according to reported procedures.



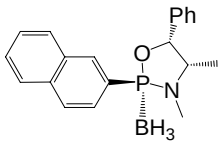
(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(2-methoxyphenyl)-5-phenyl-[1,3,2]-oxazaphospholidine 2-borane (1b)[7]

A solution of 2-methoxyphenyl-bis(*N*,*N*-diethylamino)phosphane (4.24 g, 15.0 mmol) and (1*R*,2*S*)-(-)-ephedrine (2.48 g, 15.0 mmol) in toluene (90 mL) was heated at 105 °C for 16 h. After cooling to room temperature, $BH_3 \cdot S(CH_3)_2$ (2.0 M in toluene, 7.5 mL, 15.0 mmol) was added. After 16 h, all volatiles were removed under reduced pressure. Compound **2b** was obtained by crystallization of the crude residue from methanol (1.17 g, 25 %) as a white solid. $[a]_D^{20} = -2.2°$ (c 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 7.72 (ddd, *J* = 11.5 Hz, *J* = 7.5 Hz, *J* = 1.5 Hz, 1H, H-arom), 7.52 (dt, *J* = 8.0 Hz, *J* = 1.5 Hz, 1H, H-arom), 7.42-7.34 (m, 5H, H-arom), 7.05 (t, *J* = 7.5 Hz, 1H, H-arom), 7.00 (dd, *J* = 8.0 Hz, *J* = 4.0 Hz, 1H, H-arom), 5.56 (dd, *J* = 7.0 Hz, *J* = 3.5 Hz, 1H, CH), 3.92 (s, 3H, OCH_3), 3.63 (m, 1H, CH), 2.71 (d, *J* = 11.5 Hz, 3H, NCH_3), 0.76 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (125 MHz, CD_2Cl_2): δ = 161.2 (d, *J* = 5.2 Hz, COMe), 137.7 (d, *J* = 5.0 Hz, C), 134.4 (CH), 133.7 (d, *J* = 10.6 Hz, CH), 128.7 (CH), 128.6 (CH), 127.5 (CH), 122.4 (d, *J* = 40.1 Hz, PC), 121.1 (d, *J* = 9.3 Hz, CH), 111.8 (d, *J* = 4.1 Hz, CH), 85.1 (d, *J* = 8.0 Hz, CHPh), 59.3 (CHMe), 56.1 (OCH_3), 30.1 (d, *J* = 8.0 Hz, NCH_3), 14.8 (d, *J* = 4.5 Hz, CCH_3); ^{31}P {^{1}H} NMR (121 MHz, CD_2Cl_2): δ = 131.83 (br); HRMS (FAB+): m/z calcd. for $C_{17}H_{22}BNO_2P$ (*M*+H^+): 314.1484; found: 314.1492; anal. calcd. for $C_{17}H_{23}BNO_2P$: C 64.79, H 7.36, N 4.44; found: C 64.69, H 7.42, N 4.47.



Bis(*N*,*N*-diethylamino)(2-naphthyl)phosphane (9c)

To a solution of 2-bromonaphthalene (1.34 g, 6.5 mmol) in diethyl ether (20 mL) was added *n*-BuLi (2.5 M in hexanes, 2.6 mL, 6.5 mmol) at -78 °C. After the addition was complete, the mixture was allowed to stir at room temperature for 1 h. Then, the reaction mixture was cooled to -78 °C and a solution of bis(diethylamino)chlorophosphane (1.4 mL, 6.5 mmol) in hexanes (5 mL) was added. The reaction was allowed to warm to room temperature overnight and then filtered. The solution was concentrated under reduced pressure to obtain bis(*N*,*N*-diethylamino)(2-naphthyl)phosphane (1.97 g, quant.) as a yellowish oil which was used without further purification. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.90 (m, 1H, H-arom), 7.80 (m, 3H, H-arom), 7.55 (m, 1H, H-arom), 7.36 (m, 2H, H-arom), 3.14 (m, 8H, CH_2), 1.16 (t, *J* = 7.1 Hz, 12H, CH_3); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ = 98.13.

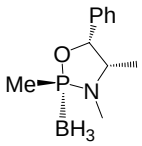


(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-(2-naphthyl)-5-phenyl-[1,3,2]-oxazaphospholidine 2-borane (1c)[7]

A solution of compound bis(*N*,*N*-diethylamino)(2-naphthyl)phosphane (1.97 g, 6.5 mmol) and (1*R*,2*S*)-(-)-ephedrine (1.07 g, 6.5 mmol) in toluene (25 mL) was heated at 105 °C for 16 h. After cooling to room temperature, $BH_3 \cdot S(CH_3)_2$ (2.0 M in toluene, 3.25 mL, 6.5 mmol) was added. After 16 h, all volatiles were removed under reduced pressure. Compound **2c** was obtained by crystallization of the crude residue from methanol (0.74 g, 34 %) as a white solid. $[a]_D^{20} = -8.4°$ (c 4.0, $CHCl_3$), ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (d, *J* = 12.0 Hz, 1H, H-arom), 7.92 (m, 3H, H-arom), 7.80 (dt, *J* = 8.3 Hz, *J* = 1.5 Hz, 1H, H-arom), 7.59 (m, 2H, H-arom), 7.43-7.25 (m, 5H, H-arom), 5.68 (dd, *J* = 6.3 Hz, *J* = 3.0 Hz, 1H, CH), 3.75 (m, 1H, CH), 2.71 (d, *J* = 11.1 Hz, 3H, NCH_3), 0.84 (d, *J* = 6.6 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (75 MHz, $CDCl_3$): δ = 136.6, 136.5, 135.3, 133.5, 133.3, 132.8, 132.6, 130.8, 130.2, 129.3, 128.8, 128.6, 128.6, 128.5, 128.1, 127.2, 126.9, 126.1, 125.9, 84.6 (d, *J* = 7.3 Hz, CHPh), 59.4 (CHMe), 29.8 (d, *J* = 7.3 Hz, NCH_3), 13.9 (d, *J* = 3.6 Hz, CCH_3), (due to the complex pattern in the aromatic region, no reliable multiplicity could de assigned, therefore all observed resonances are listed); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ = 133.14 (br); anal. calcd. for $C_{20}H_{23}BNOP$: C 71.67, H 6.92, N 4.18; found: C 71.57, H 6.88, N 4.09.

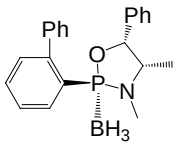
Bis(*N*,*N*-diethylamino)(methyl)phosphane (9d)

To a solution of bis(diethylamino)chlorophosphane (3.5 mL, 16.7 mmol) in THF (40 mL) was slowly added MeLi (1.6 M in Et_2O, 14.7 mL, 23.5 mmol) at -78 °C. After the addition was complete, the reaction was allowed to warm to room temperature. After stirring for 2 h, the solution was concentrated under reduced pressure. The residue was extracted with pentane (2 × 15 mL) and the combined extracts were concentrated *in vacuo* to obtain bis(*N*,*N*-diethylamino)(methyl)phosphane (2.28 g, 72 %) as a yellowish oil which was used without further purification. ^{1}H NMR (300 MHz, C_6D_6): δ = 2.88 (m, 8H, CH_2), 1.15 (d, *J* = 9.0 Hz, CH_3), 0.91 (t, *J* = 6.9 Hz, 12H, CH_3); ^{13}C {^{1}H} NMR (75 MHz, C_6D_6): δ = 42.9 (d, *J* = 15.9 Hz, CH_2), 15.7 (d, *J* = 3.6 Hz, CH_3), 14.8 (d, *J* = 7.3 Hz, CH_3); ^{31}P {^{1}H} NMR (121 MHz, C_6D_6): δ = 80.56.



(2*R*,4*S*,5*R*)-3,4-Dimethyl-2-methyl-5-phenyl-[1,3,2]-oxazaphospholidine 2-borane (1d)[7]

Oxazaphospholidine **2d** was synthesized following the procedure as described for compound **2b**. Starting from bis(*N*,*N*-diethylamino)(methyl)phosphane (2.28 g, 12.0 mmol) and (1*R*,2*S*)-(-)-ephedrine (1.98 g, 12.0 mmol), **2d** was obtained in 61 % yield (1.62 g) as a white solid. $[a]_D^{20} = -2.7°$ (c 2.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.38-7.32 (m, 5H, H-arom), 5.47 (dd, *J* = 6.0 Hz, *J* = 3.5 Hz, 1H, CH), 3.58 (m, 1H, CH), 2.66 (d, *J* = 11.5 Hz, 3H, NCH_3), 1.47 (d, *J* = 7.5 Hz, 3H, PCH_3), 0.76 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 136.5 (d, *J* = 5.0 Hz, C), 128.5 (CH), 126.8 (CH), 84.2 (d, *J* = 8.0 Hz, CHPh), 59.0 (CHMe), 29.3 (d, *J* = 7.5 Hz, NCH_3), 15.5 (d, *J* = 25.3 Hz, PCH_3), 13.6 (d, *J* = 4.3 Hz, CCH_3); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ = 147.46 (br q, J_{PB} = 77 Hz); HRMS (FAB+): m/z calcd. for $C_{11}H_{20}BNOP$ (M+H^+): 224.1378; found: 224.1379; anal. calcd. for $C_{11}H_{19}BNOP$: C 59.23, H 8.59, N 6.28; found: C 59.28, H 8.64, N 6.33.



(2*R*,4*S*,5*R*)-2-(2-Biphenyl)-3,4-dimethyl-5-phenyl-[1,3,2]-oxazaphospholidine 2-borane (1f)[7]

To a mixture of 2-bromobiphenyl (5.00 g, 21.4 mmol) in Et_2O (100 mL) was added *n*-butyllithium (2.5 M in hexanes, 9.4 mL, 23.5 mmol) at -78 °C. After stirring for 30 minutes at -78 °C the reaction mixture was allowed to warm to 0 °C. The slurry was transferred via a cannula to a second flask containing a solution of (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-[1,3,2]-oxazaphospholidine **4** (7.68 g, 33.4 mmol) in THF (100 mL) and previously cooled to -78 °C. After overnight stirring at room temperature, the mixture was cooled to 0 °C and $BH_3{\cdot}S(CH_3)_2$ (2.0 M in toluene, 16.7 mL, 33.4 mmol) was added. The reaction mixture was stirred for an additional 6 h at room temperature. Then, the mixture was washed with water (250 mL), extracted with ethyl acetate (250 mL), dried over $MgSO_4$ and concentrated under reduced pressure. Compound **2f** was obtained by crystallization of the crude residue from methanol (5.43 g, 70 %) as a white solid. $[a]_D^{20} = +15.5°$ (c 4.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.99 (dd, *J* = 12.5 Hz, *J* = 8.0 Hz, 1H, H-arom), 7.55 (t, *J* = 7.2 Hz, 1H, H-arom), 7.49 (t, *J* = 7.5 Hz, 1H, H-arom), 7.46-7.42 (m, 5H, H-arom), 7.36-7.29 (m, 4H, H-arom), 7.23 (m, 2H, H-arom), 4.70 (dd, *J* = 6.0 Hz, *J* = 1.5 Hz, 1H, CH), 3.42 (m, 1H, CH), 2.49 (d, *J* = 10.0 Hz, 3H, NCH_3), 0.69 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 146.1 (d, *J* = 8.8 Hz, C), 141.7 (d, *J* = 2.9 Hz, C), 136.9 (d, *J* = 6.4 Hz, C), 133.2 (d, *J* = 15.7

Hz, CH), 132.1 (d, *J* = 7.3 Hz, CH), 131.9 (d, *J* = 2.1 Hz, CH), 130.2 (CH), 128.7 (CH), 128.5 (CH), 128.2 (CH), 128.1 (CH), 127.4 (d, *J* = 10.6 Hz, CH), 126.7 (CH), 83.4 (d, *J* = 7.7 Hz, CHPh), 59.5 (d, *J* = 2.5 Hz, CHMe), 30.0 (d, *J* = 9.3 Hz, NCH_3), 13.7 (CCH_3); ^{31}P $\{^1H\}$ NMR (121 MHz, $CDCl_3$): δ = 134.43 (br); HRMS (FAB+): m/z calcd. for $C_{22}H_{24}BNOP$ (M-H^+): 360.1693; found: 360.1693; anal. calcd. for $C_{22}H_{25}BNOP$: C 73.15, H 6.98, N 3.88; found: C 72.59, H 7.06, N 3.80.

General procedure for the synthesis of resin bound aminophosphane boranes (2).

4-Bromopolystyrene (**4**, 0.5 g, 1.9 mmole/g) was swollen in toluene (20 mL) and *n*-BuLi (2.5 M in hexanes, 2.4 eq.) was added. The reaction mixture was gently stirred at 60 °C for 3 h. After cooling to room temperature, the liquid phase was removed. The lithiated resin (**5**) was washed twice with toluene (20 mL). A new portion of toluene (30 mL) was added followed by a solution of oxazaphospholidine borane **1** (1.5 eq.) in toluene (5 mL) and the reaction mixture was gently stirred for 16 h at room temperature. The liquid phase was removed and the resin was washed with 5 ml portions of subsequently THF, THF-water (1:1), THF, CH_2Cl_2, Et_2O, CH_2Cl_2 and Et_2O. Finally, the resin was dried with a gentle flow of argon and under reduced pressure.

2a: White resin; ^{31}P $\{^1H\}$ NMR (121 MHz, THF, D_2O inner tube): δ = 71.4 (br); elemental analysis (%): P, 1.10.

2b: White resin; ^{31}P $\{^1H\}$ NMR (121 MHz, THF, D_2O inner tube): δ = 70.0 (br); elemental analysis (%): P, 1.23.

2c: White resin; ^{31}P $\{^1H\}$ NMR (121 MHz, THF, D_2O inner tube): δ = 71.6 (br); elemental analysis (%): P, 1.68.

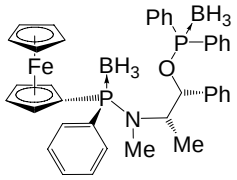
2d: White resin; ^{31}P $\{^1H\}$ NMR (121 MHz, THF, D_2O inner tube): δ = 67.1 (br); elemental analysis (%): P, 0.27.

2e: Orange resin; ^{31}P $\{^1H\}$ NMR (121 MHz, THF, D_2O inner tube): δ = 70.2 (br); elemental analysis (%): P, 1.30.

2f: White resin; ^{31}P $\{^1H\}$ NMR (121 MHz, THF, D_2O inner tube): δ = 71.1 (br); elemental analysis (%): P, 1.95.

General procedure for the synthesis of resin bound aminophosphane-phosphites and aminophosphane-phosphinites (12-21).

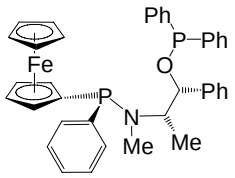
In a typical experiment, resin-bound aminophosphane borane **2** (50 mg) was washed with THF (5 mL) and allowed to swell in THF (5 mL) for 1 h. Subsequently, *N*-methyl morpholine (0.5 mL) and R_2PCl (1.3 eq.) were added. The reaction mixture was gently stirred for 16 h at room temperature. The liquid phase was removed and the resin was washed with THF, CH_2Cl_2, Et_2O, CH_2Cl_2 and Et_2O. In order to remove the borane, the resin was suspended in Et_2NH (2 mL) and heated to 50 °C. After 16 h, the solution phase was removed and the resin was washes with 1 ml portions of subsequently CH_2Cl_2, Et_2O, CH_2Cl_2 and Et_2O. Finally, the resin was dried with a gentle flow of argon and under reduced pressure.



(R_P)-*N*-Methyl-*N*-{(1*S*,2*R*)-[2-(diphenylphosphinito borane)-1-methyl-2-phenyl]ethyl}-amino-ferrocenylphenylphosphane borane (22·BH_3)

To a solution of oxazaphospholidine borane **1e** (0.44 g, 1.13 mmol) in THF (2 mL) was added phenyllithium (2.0 M in dibutylether, 1.13 mL, 2.26 mmol) at -78 °C. The reaction temperature was allowed to rise slowly to 0 °C and stirring was maintained for 3 h. Chlorodiphenylphosphane (0.41 mL, 2.26 mmol) was added and the mixture was stirred for 2 h at room temperature. Subsequently, borane-tetrahydrofuran complex (1.0 M in THF, 4.5 mL, 4.5 mmol) was added and the reaction was stirred for 20 h. All volatiles were removed under reduced pressure and the residue was hydrolyzed and then extracted with methylene chloride (2 × 30 mL). The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel chromatography (toluene/light pretroleum, 1:1) yielding diborane **22·BH_3** as a yellow oil. Finally, **22·BH_3** was obtained by crystallization from a CH_2Cl_2/hexane mixture as a yellow solid (0.68 g, 40 %). $[a]_D^{20} = -40.6°$ (c 1.0, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.73 (m, 2H, H-arom), 7.52-7.44 (m, 3H, H-arom), 7.33-7.25 (m, 6H, H-arom), 7.17-7.08 (m, 7H, H-arom), 6.94 (m, 2H, H-arom), 5.31 (t, *J* = 9.0 Hz, 1H, OCH), 4.58 (br, 1H, Cp), 4.51 (m, 1H, NCH), 4.49 (br, 1H, Cp), 4.42 (br, 1H, Cp), 4.27 (s, 5H, Cp), 4.05 (br, 1H, Cp), 2.08 (d, *J* = 8.0 Hz, 3H, NCH_3), 1.33 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 138.4 (Cq), 132.8 (Cq), 132.2 (d, *J* = 5.5 Hz, Cq), 132.1 (Cq), 131.8-131.4 (CH), 131.2 (d, *J* = 11.4 Hz, CH), 130.3 (d, *J* = 2.1 Hz, CH), 128.7 (CH), 128.7 (d, *J* = 10.6 Hz, CH), 128.4 (CH), 128.2 (CH), 128.0 (d, *J* = 10.6 Hz, CH), 127.9 (d, *J* = 10.2 Hz, CH), 83.6 (dd, *J* = 9.2 Hz, *J* = 2.5 Hz, O<u>C</u>H), 72.3 (d, *J* = 1.6 Hz, CH), 72.2 (d, *J* = 8.0 Hz, CH), 71.6 (Cq), 71.3 (d, *J* = 8.0 Hz, CH), 71.1 (CH), 71.0 (CH), 70.4 (CH), 57.1 (t, *J* = 19.5 Hz, N<u>C</u>H), 29.2 (d, *J* = 4.1 Hz, NCH_3), 16.0 (C<u>C</u>H_3); ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$):

δ = 107.73 (d, *J* = 71.4 Hz, PO), 71.65 (br, PN); HRMS (FAB+): m/z calcd. for $C_{38}H_{44}B_2FeNO_2P$ (*M*+H^+): 670.2441; found: 670.2447.



(R_P)-*N*-Methyl-*N*-{(1*S*,2*R*)-[2-(diphenylphosphinito)-1-methyl-2-phenyl]ethyl}-amino-ferrocenylphenylphosphane (22)

A mixture of diborane **22·BH$_3$** (0.20 g, 0.30 mmol) and Et_2NH (2 mL) in toluene (2 mL) was stirred at 50 °C for 12 h. The crude product was filtered over neural alumina using toluene/ethyl acetate (9:1) as eluent. After removal of the solvent, the free **22** was obtained as a orange solid (0.18 g, 95 %) and was used without further purification. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.49 (m, 2H, H-arom), 7.39-7.08 (m, 16H, H-arom), 6.84 (m, 2H, H-arom), 4.75 (t, *J* = 8.7 Hz, 1H, OCH), 4.36 (br, 1H, Cp), 4.30 (m, 2H, Cp), 4.23 (s, 5H, Cp), 4.04 (m, 1H, NCH), 3.89 (br, 1H, Cp), 2.10 (d, *J* = 3.0 Hz, 3H, NCH_3), 1.43 (d, *J* = 6.5 Hz, 3H, CH_3); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 142.3 (dd, *J* = 17.0 Hz, *J* = 14.8 Hz, Cq), 141.2 (d, *J* = 2.1 Hz, Cq), 140.4 (d, *J* = 9.7 Hz, Cq), 138.0 (Cq), 131.2 (d, *J* = 22.9 Hz, CH), 130.8 (d, *J* = 17.7 Hz, CH), 130.5 (d, *J* = 21.6 Hz, CH), 129.5 (CH), 128.9 (CH), 128.5-128.3 (CH), 128.0 (d, *J* = 5.0 Hz, CH), 127.9 (CH), 127.6 (d, *J* = 5.0 Hz, CH), 127.3 (CH), 86.7 (dd, *J* = 17.7 Hz, *J* = 10.6 Hz, O<u>C</u>H), 78.2 (d, *J* = 16.0 Hz, Cq), 72.8 (d, *J* = 23.6 Hz, CH), 70.4 (dd, *J* = 29.5 Hz, *J* = 5.0 Hz, CH), 69.7 (CH), 69.3 (CH), 65.2 (dd, *J* = 40.5 Hz, *J* = 7.5 Hz, CH), 57.1 (t, *J* = 19.5 Hz, N<u>C</u>H), 30.4 (d, *J* = 9.3 Hz, NCH_3), 16.8 (C<u>C</u>H_3); ^{31}P {^{1}H} NMR (121 MHz, $CDCl_3$): δ = 111.25 (PO), 62.33 (PN).

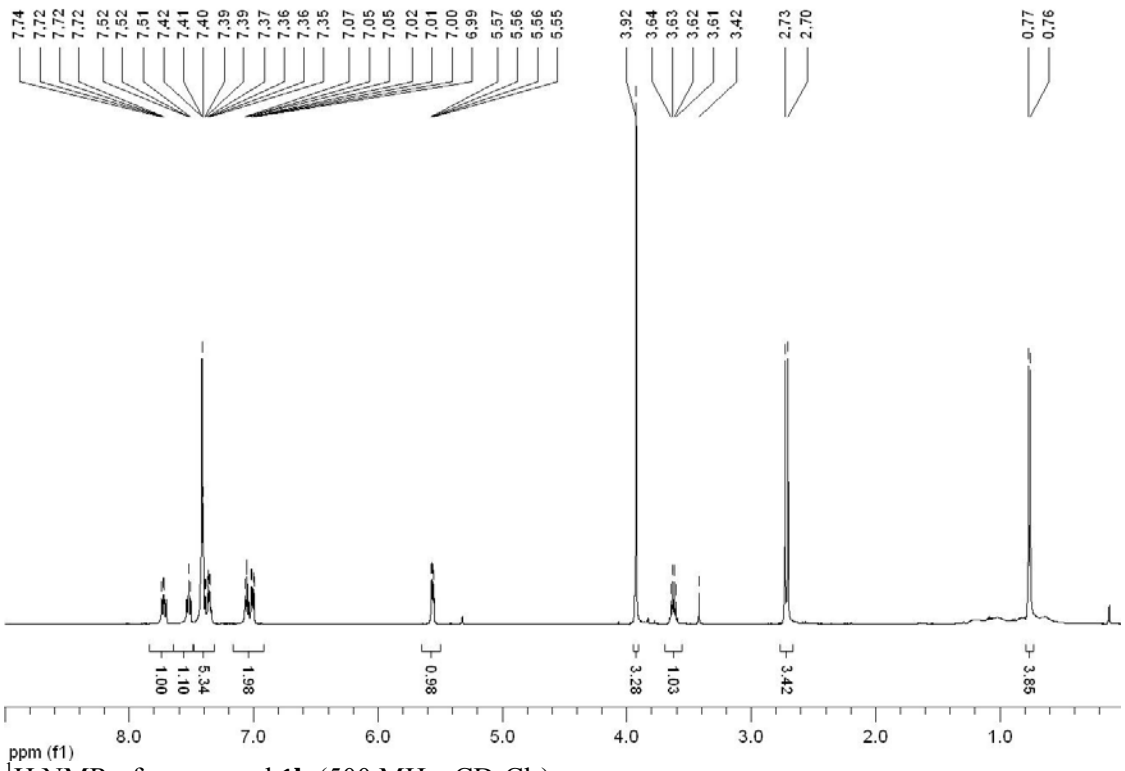
General procedure for asymmetric hydrogenation experiments

The hydrogenation experiments were carried out in a stainless steel autoclave (total volume is 150 mL) charged with an insert suitable for 14 reaction vessels including Teflon mini stirring bars for conducting parallel reactions. In a typical experiment, a reaction vessel was charged with polymer-supported ligand (1.25 μmol) and a solution of $[Rh(COD)_2]BF_4$ (0.5 mg, 1.25 μmol) in CH_2Cl_2 (0.5 mL) and the heterogeneous mixture was allowed to stir gently for 2 h. The solution phase was removed using a syringe and washed with CH_2Cl_2 (0.5 mL). Subsequently, to the reaction vessel was added a solution of substrate (37.5 μmol) in the appropriate solvent. Before starting the catalytic reactions, the charged autoclave was purged three times with 5 bar of H_2 and then pressurized to 15 bar H_2. The reaction mixtures were gently stirred at 25 °C for 20 h. Next, the autoclave was depressurized and the reaction mixtures were filtered over a plug of silica. The conversion was determined by GC measurement and the enantiomeric excess was measured by chiral GC using the following columns and conditions:

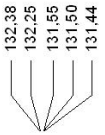
I: Chiralsil DEX-CB column (T_0 = 90 °C, then ΔT = 5 °C min^{-1}, t_R (*R*) = 15.3 min, t_R (*S*) = 15.4 min, t_R (**I**) = 19.2 min).

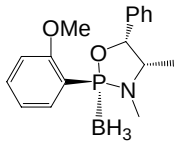
II: Chiralsil DEX-CB column (T = 70 °C for 1 min, then ΔT = 7 °C min^{-1}, t_R (**II**) = 6.4 min, t_R (*S*) = 7.2 min, t_R (*R*) = 7.4 min).

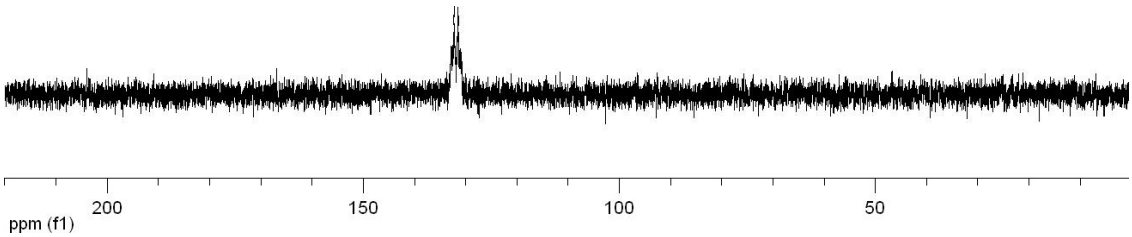
III: Supelco β-DEX 225 column (T = 70 °C for 50 min, then ΔT = 25 °C min^{-1}, t_R (*S*) = 51.7 min, t_R (*R*) = 52.3 min, t_R (**III**) = 53.5 min).



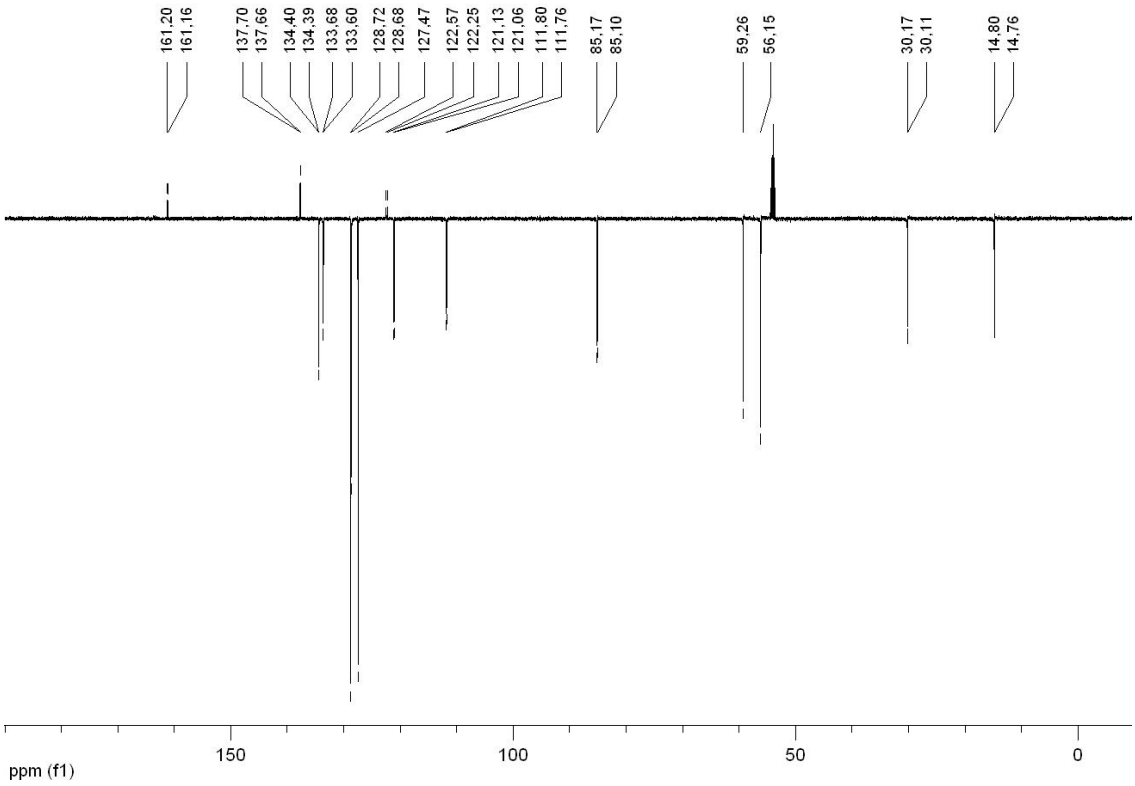
^{1}H NMR of compound **1b** (500 MHz, CD_2Cl_2).



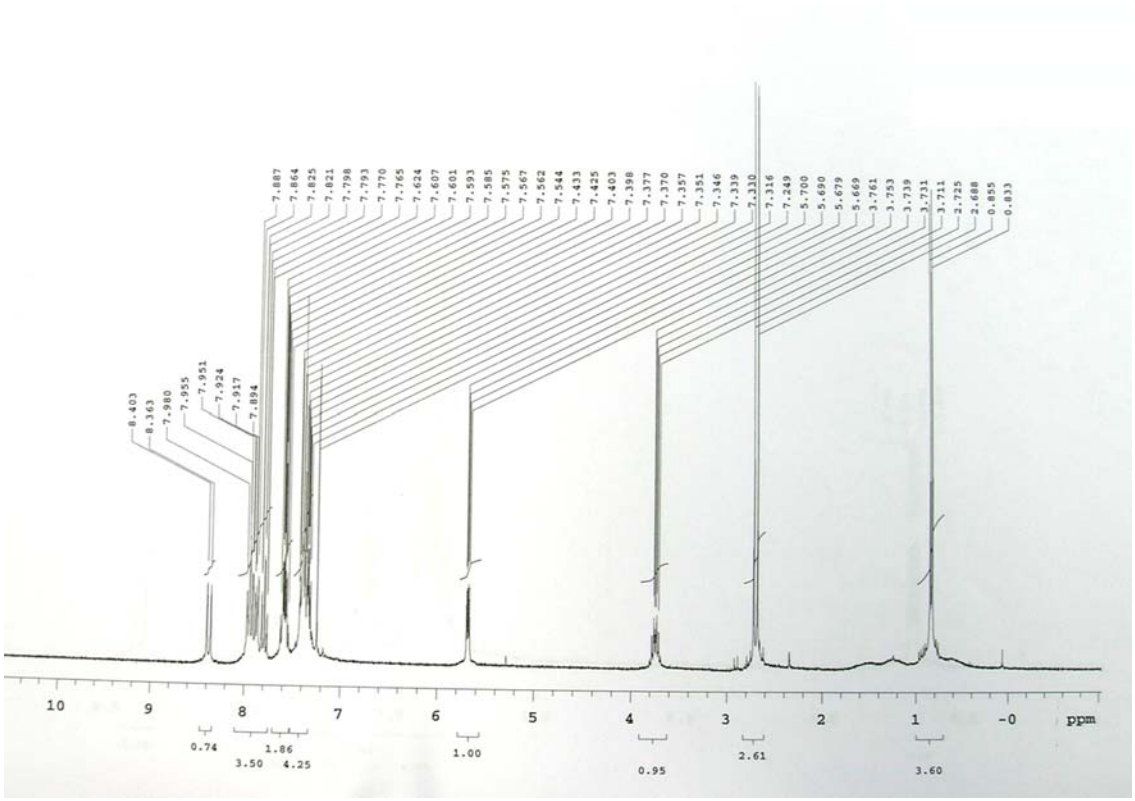




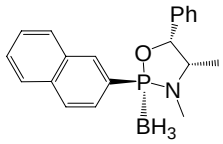
^{31}P {^{1}H} NMR of compound **1b** (121 MHz, CD_2Cl_2).

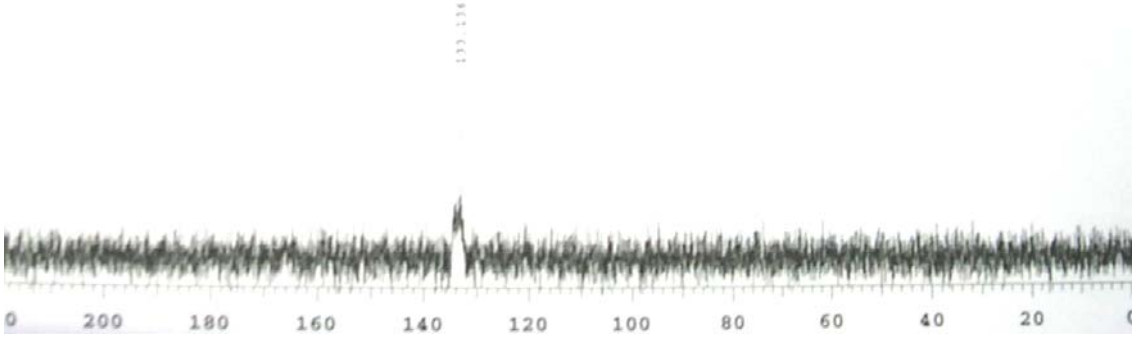


^{13}C {^{1}H} NMR of compound **1b** (125 MHz, CD_2Cl_2).

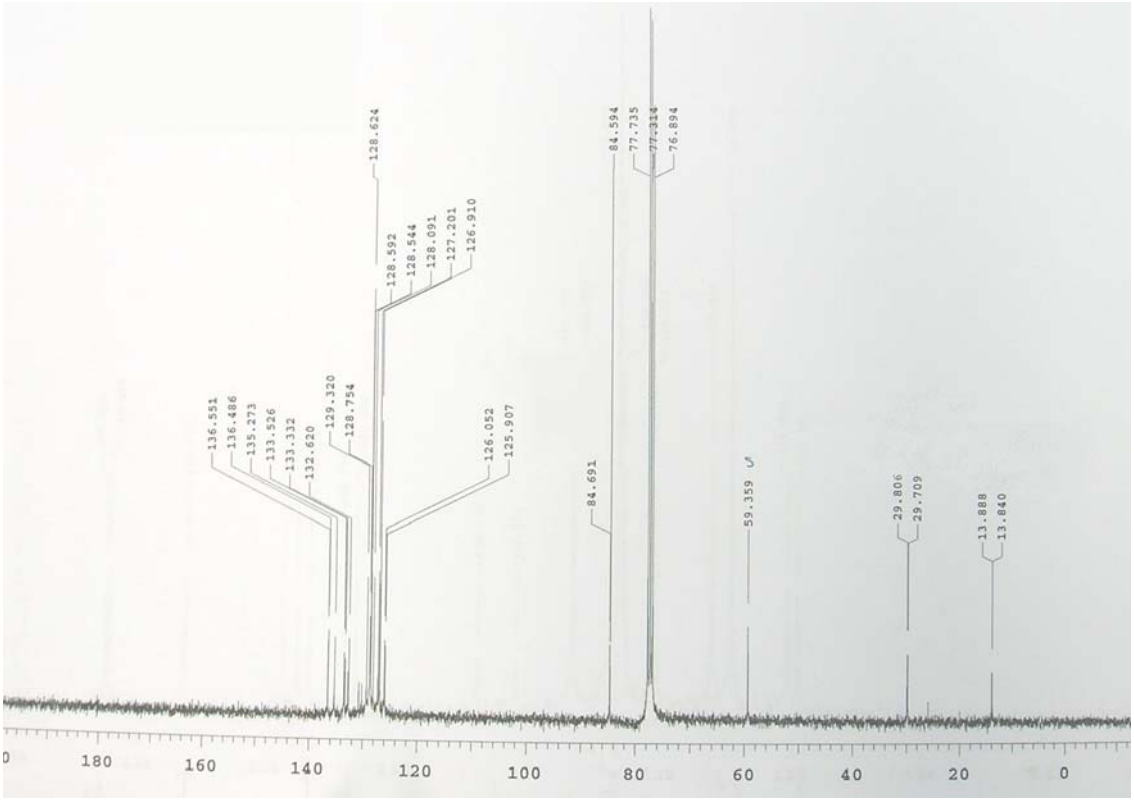


^{1}H NMR of compound **1c** (300 MHz, $CDCl_3$).

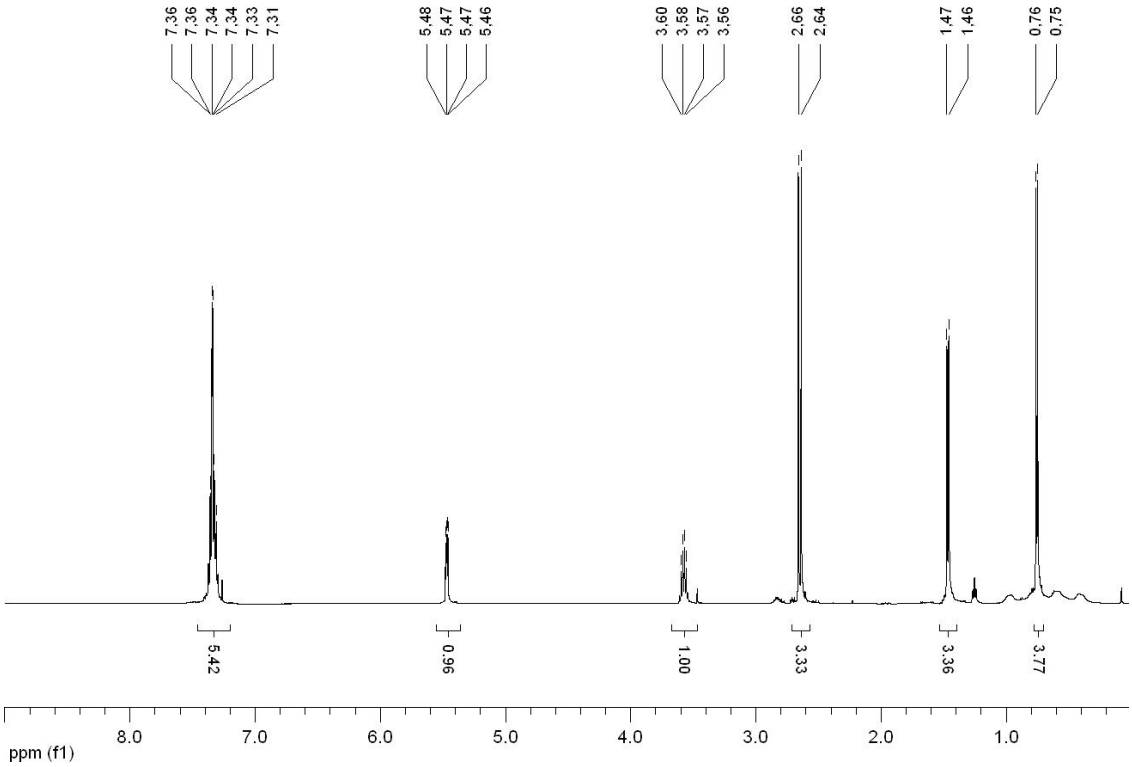




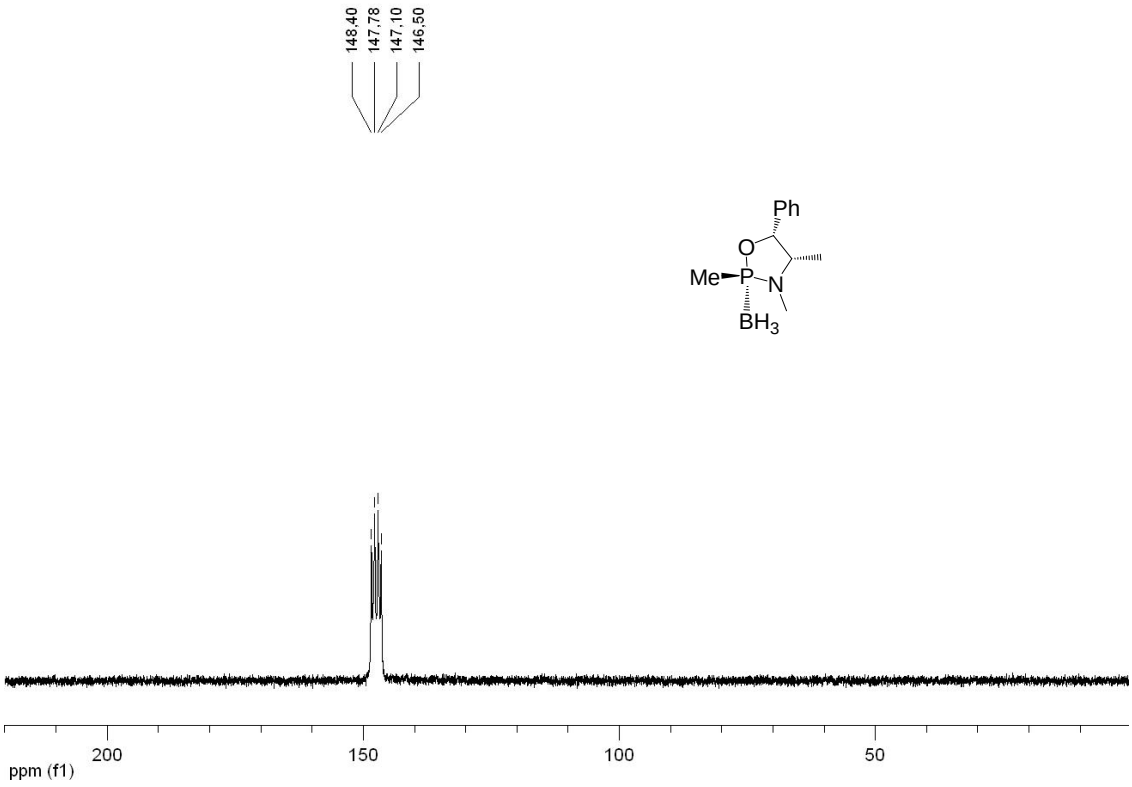
^{31}P {^{1}H} NMR of compound **1c** (121 MHz, $CDCl_3$).



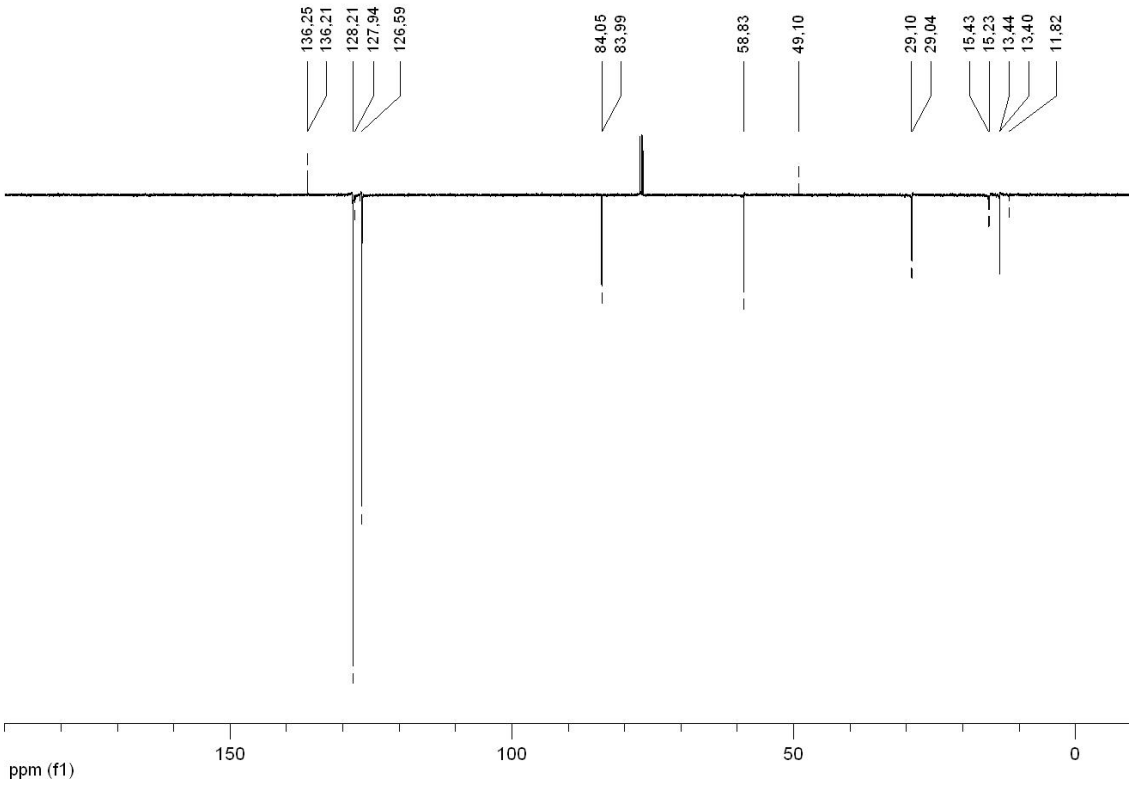
^{13}C {^{1}H} NMR of compound **1c** (75 MHz, $CDCl_3$).



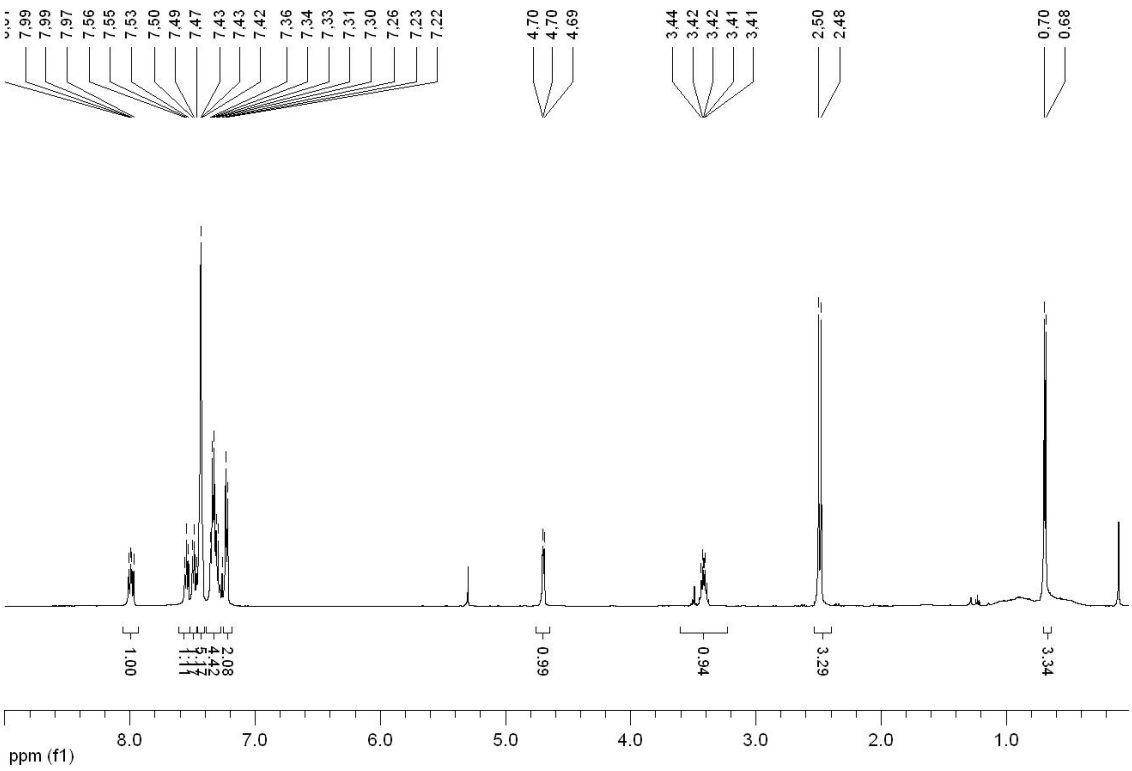
^{1}H NMR of compound **1d** (500 MHz, $CDCl_3$).



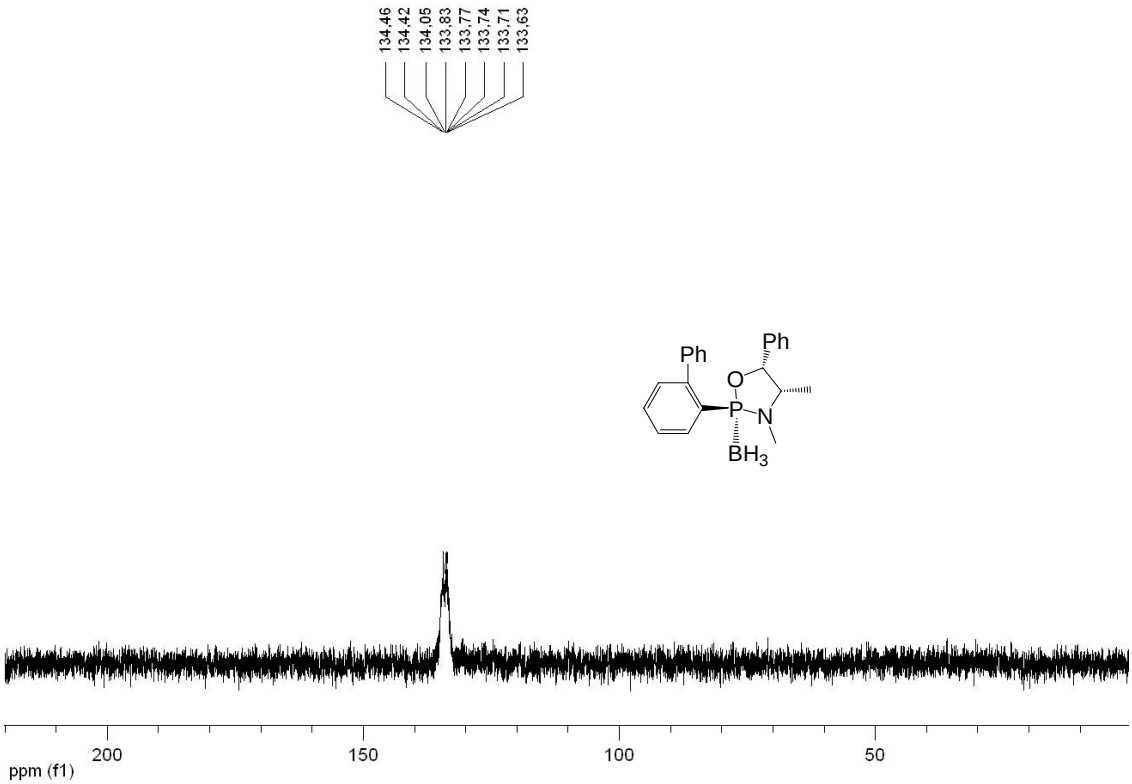
^{31}P {^{1}H} NMR of compound **1d** (121 MHz, $CDCl_3$).



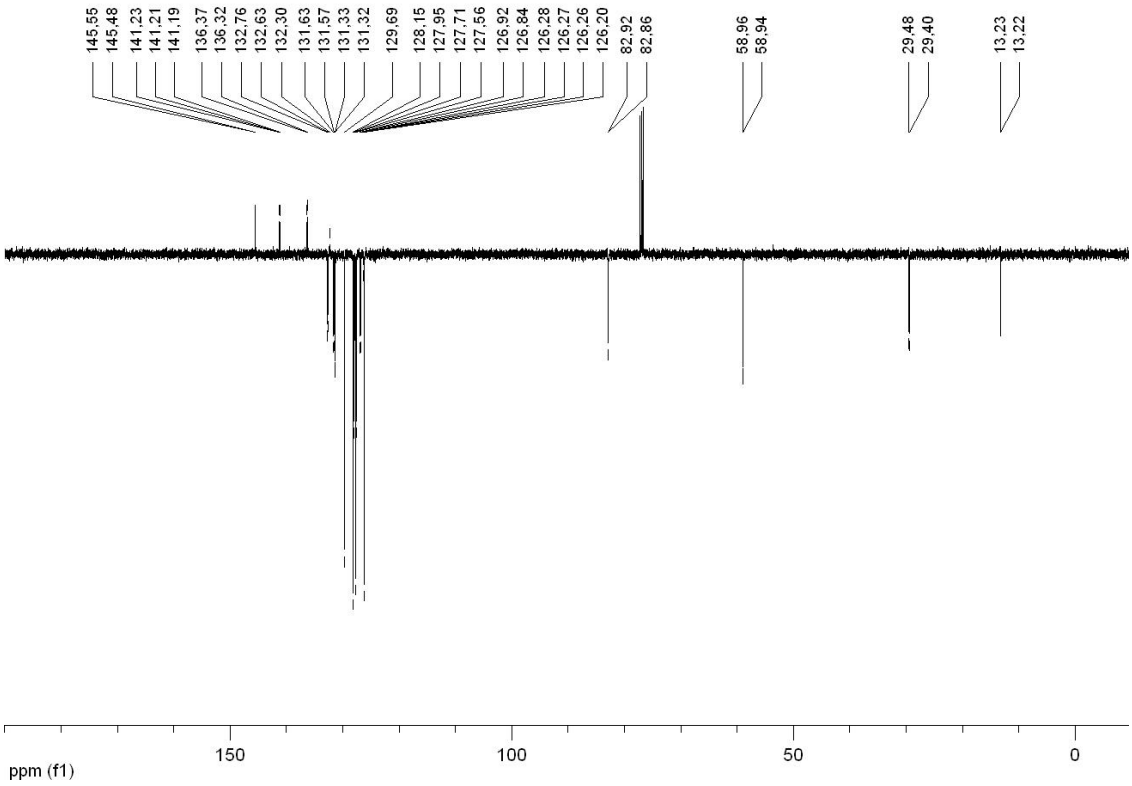
^{13}C {^{1}H} NMR of compound **1d** (125 MHz, $CDCl_3$).



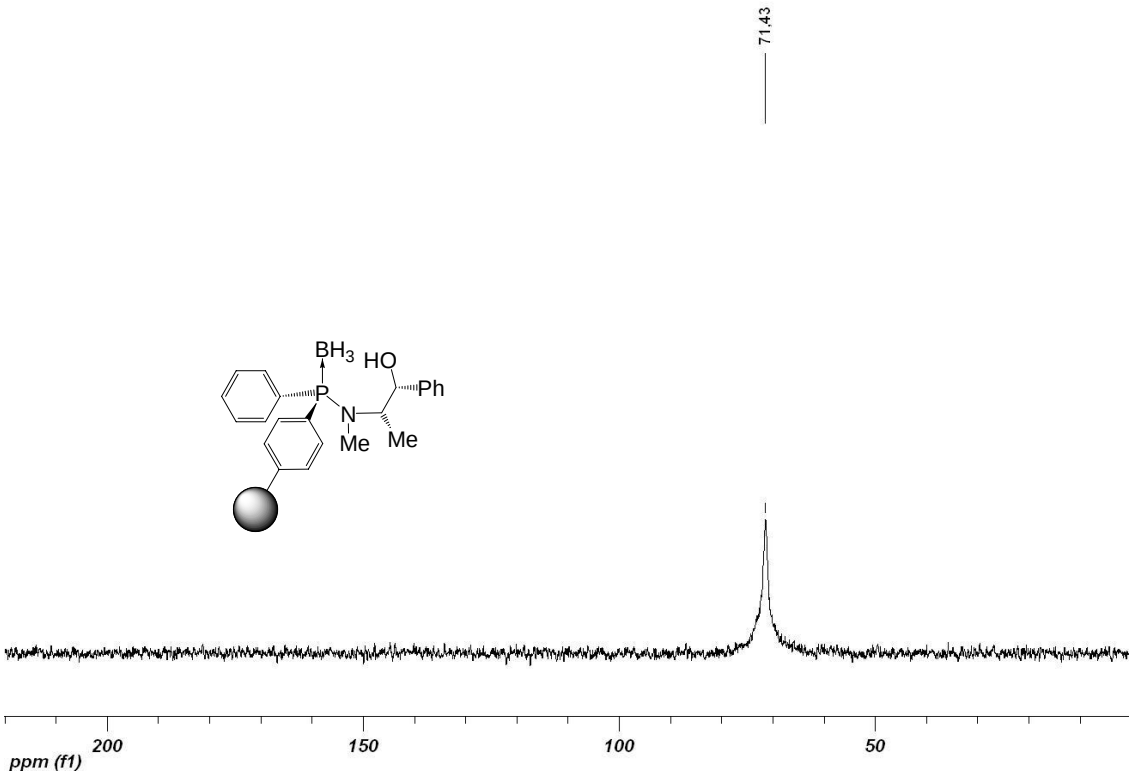
^{1}H NMR of compound **1f** (500 MHz, $CDCl_3$).



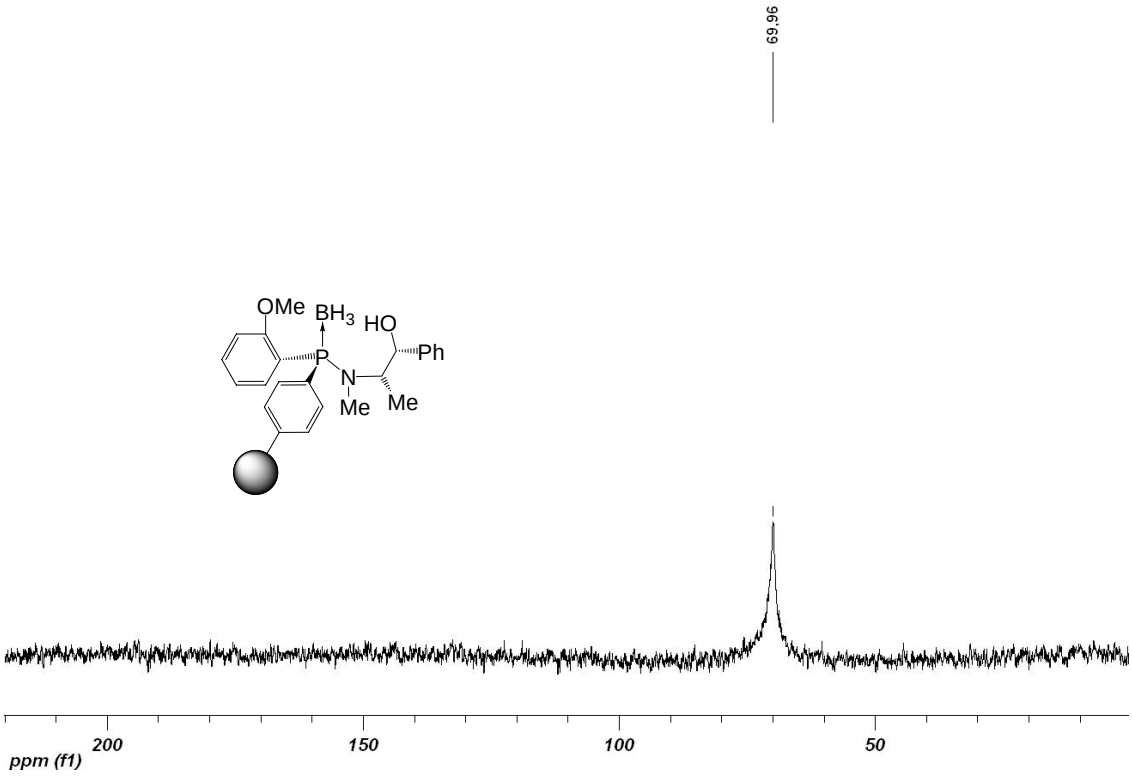
^{31}P {^{1}H} NMR of compound **1f** (121 MHz, $CDCl_3$).



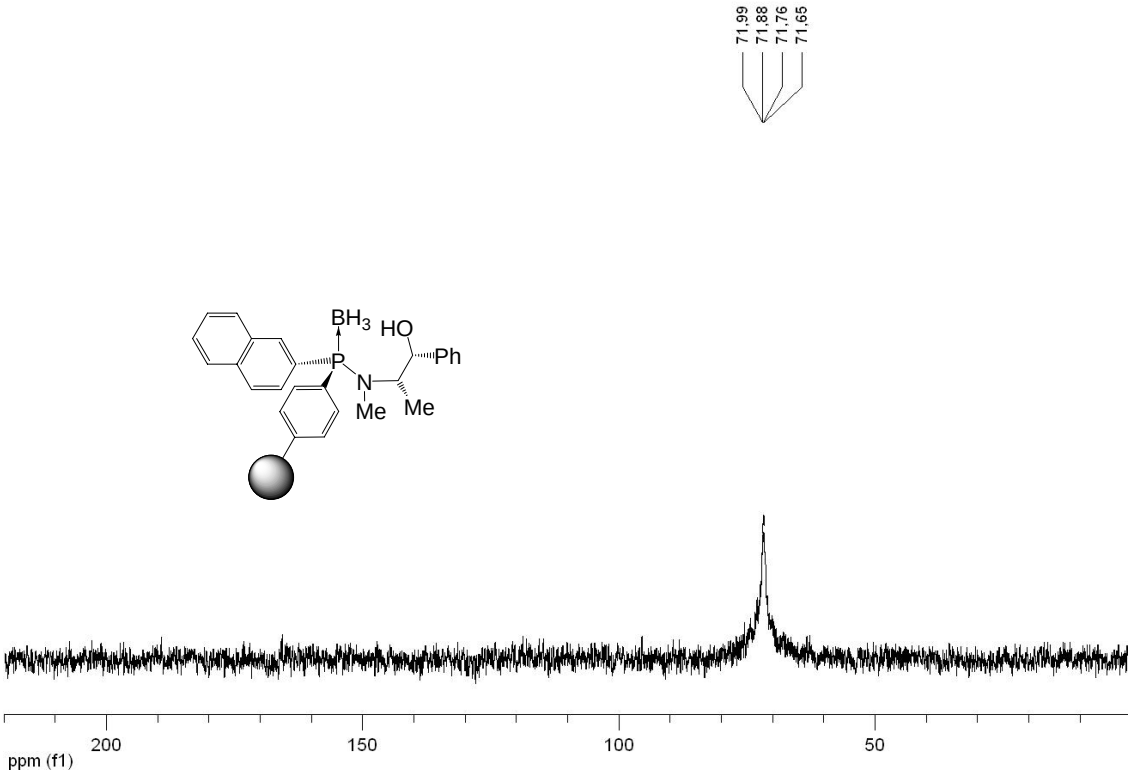
^{13}C {^{1}H} NMR of compound **1f** (125 MHz, $CDCl_3$).



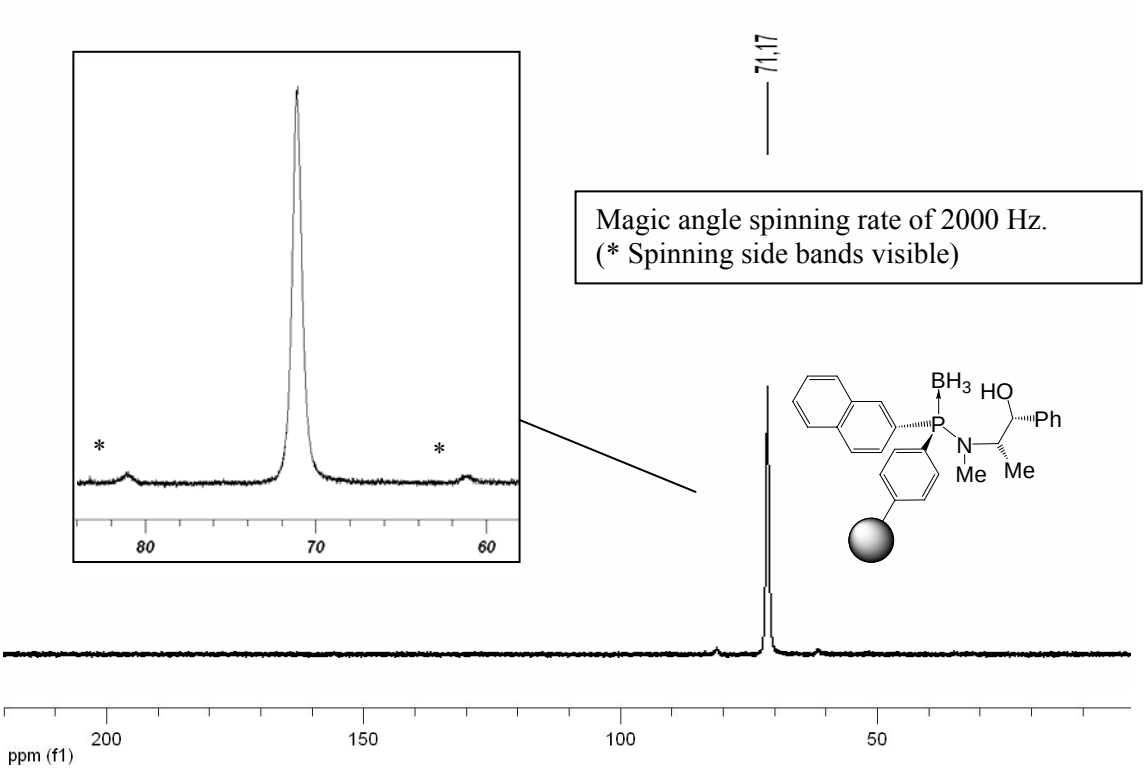
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2a** (121 MHz, THF, D_2O inner tube).



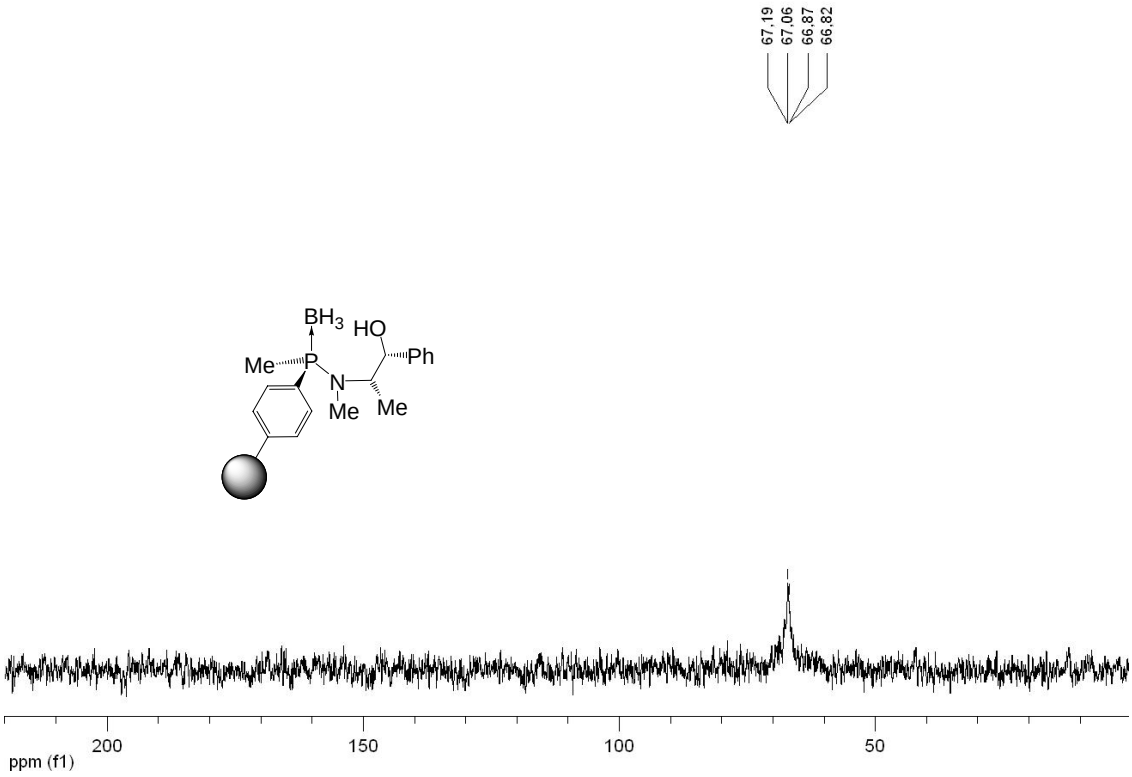
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2b** (121 MHz, THF, D_2O inner tube).



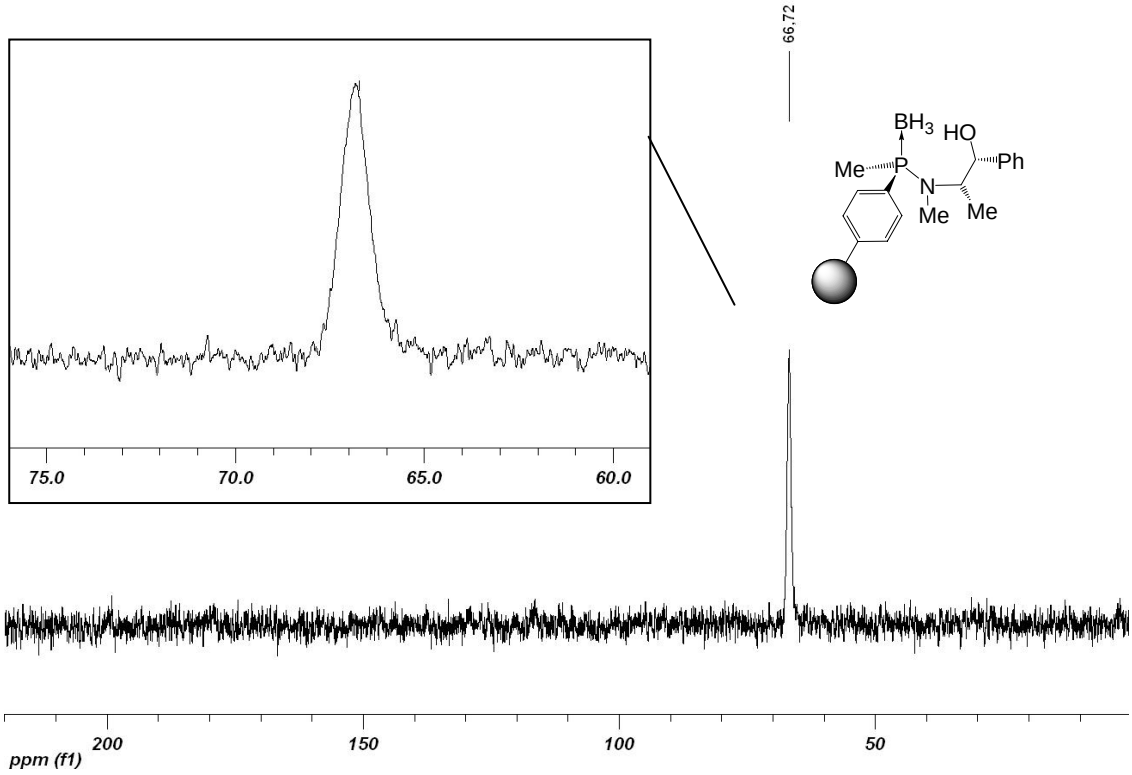
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2c** (121 MHz, THF, D_2O inner tube).



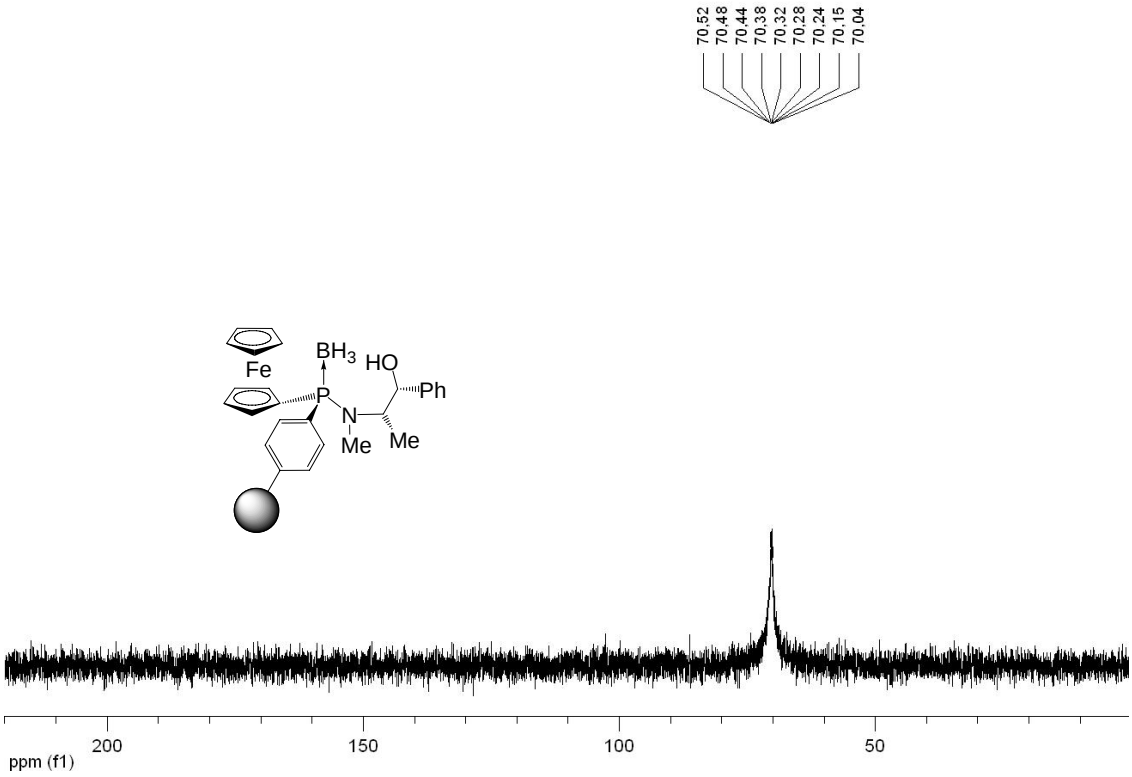
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2c** (202 MHz, CD_2Cl_2, nano-probe, 16 h)



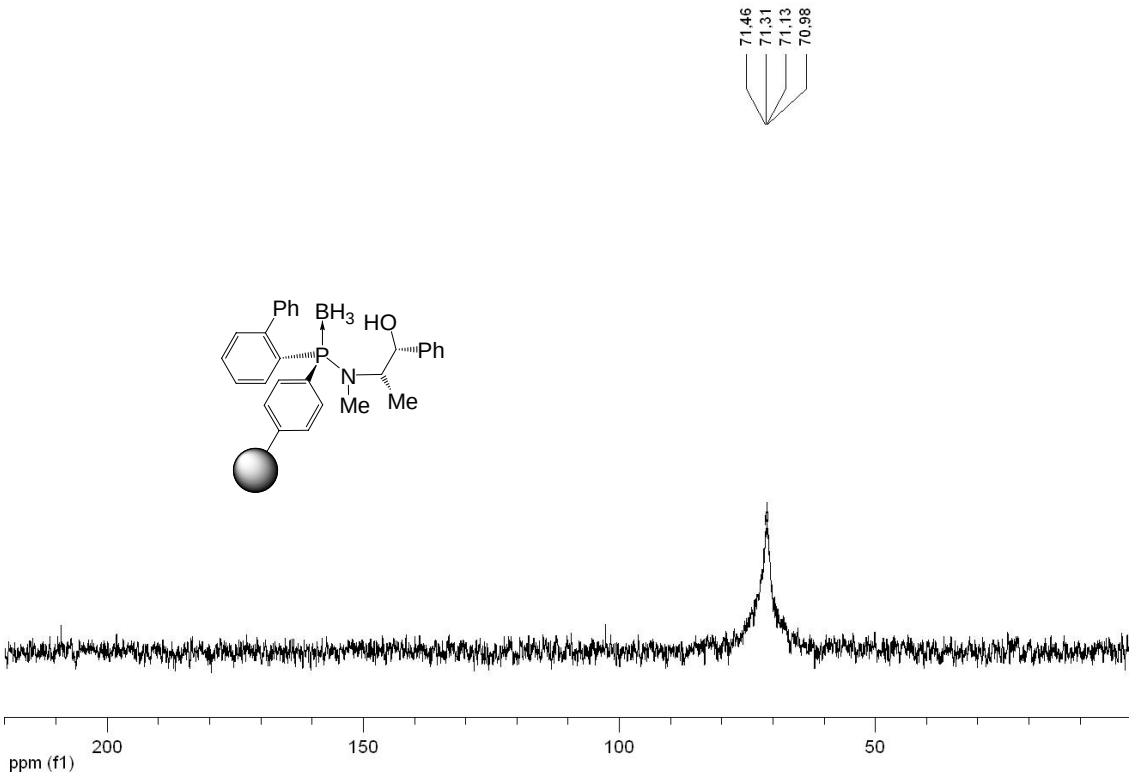
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2d** (121 MHz, THF, D_2O inner tube).



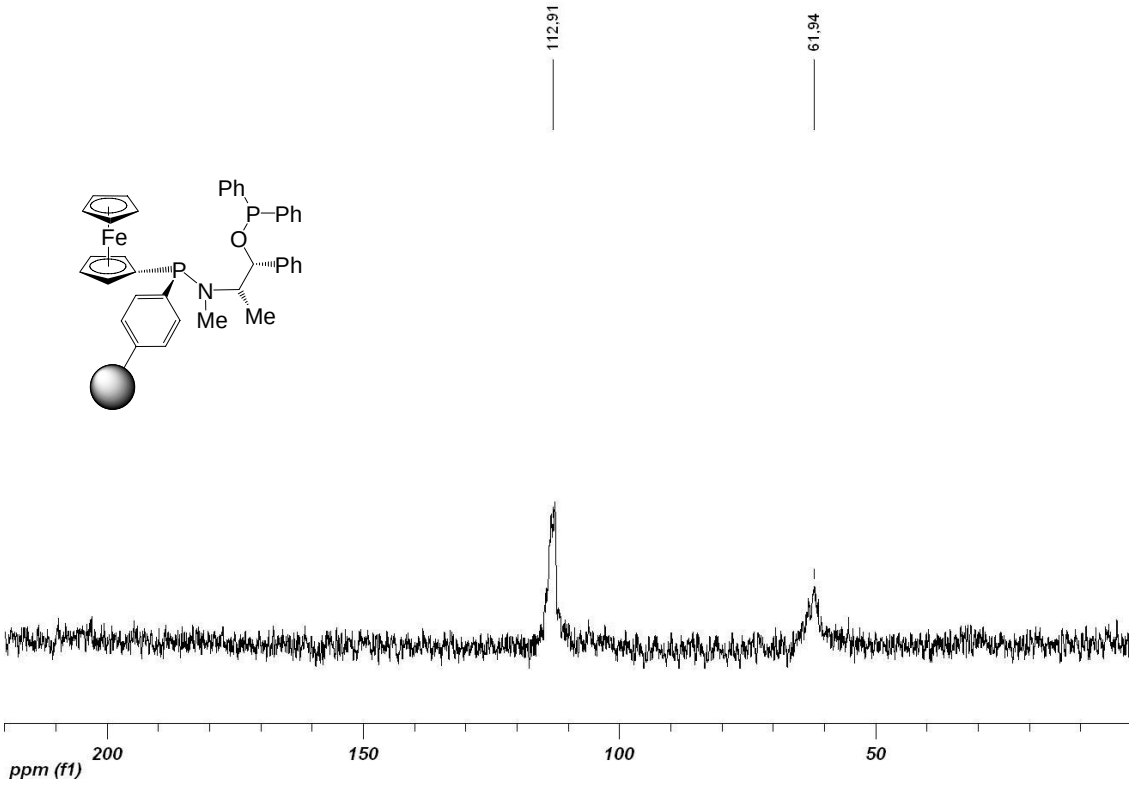
Gel-phase^{31}P $\{^{1}H\}$ NMR of compound **2d** (202 MHz, CD_2Cl_2, nano-probe, 3 h).



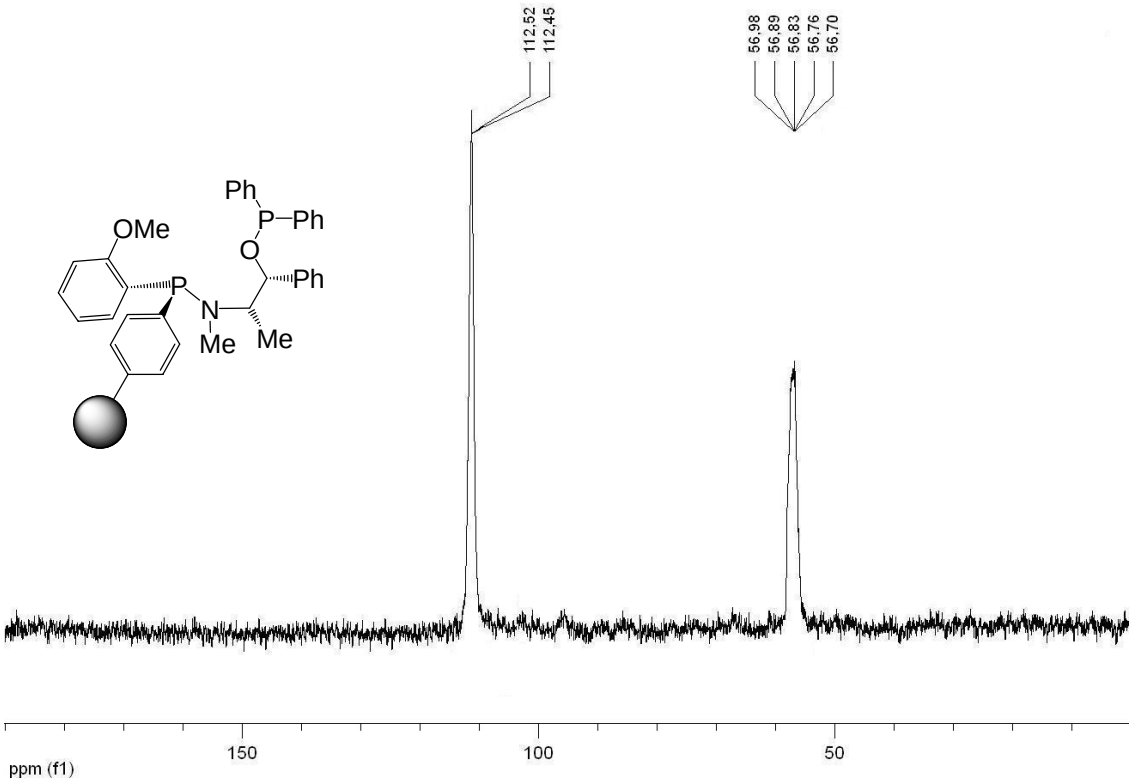
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2e** (121 MHz, THF, D_2O inner tube).



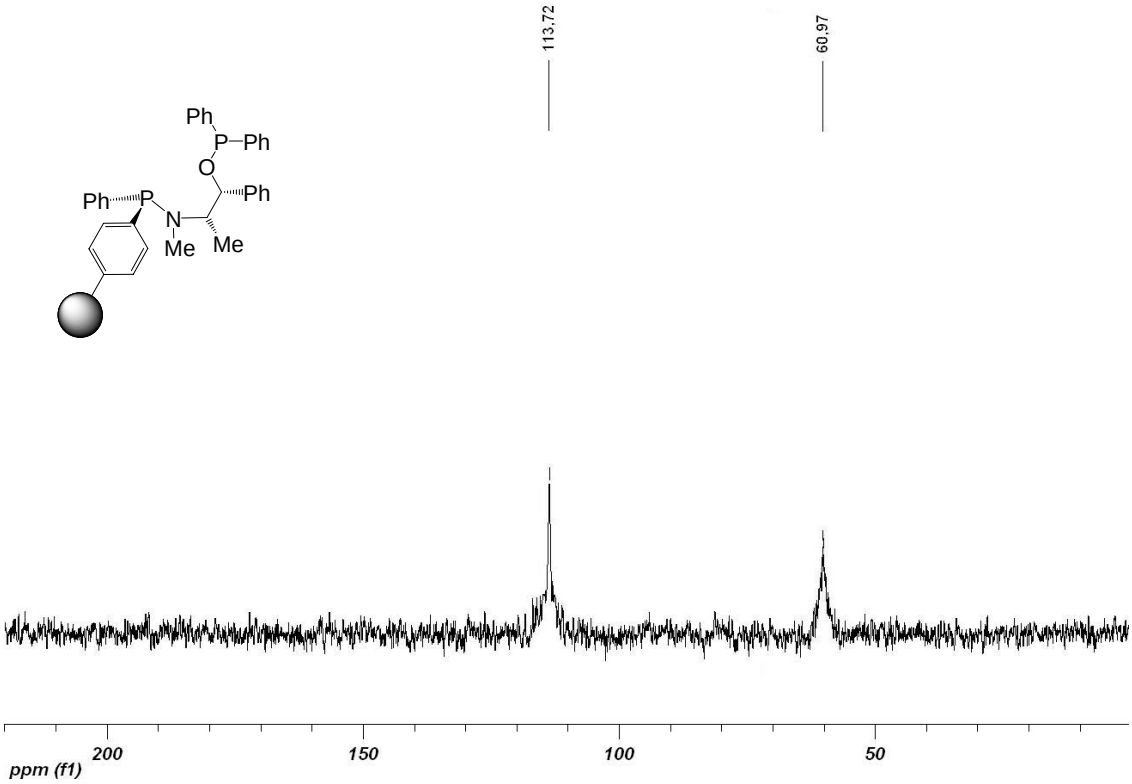
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **2f** (121 MHz, THF, D_2O inner tube).



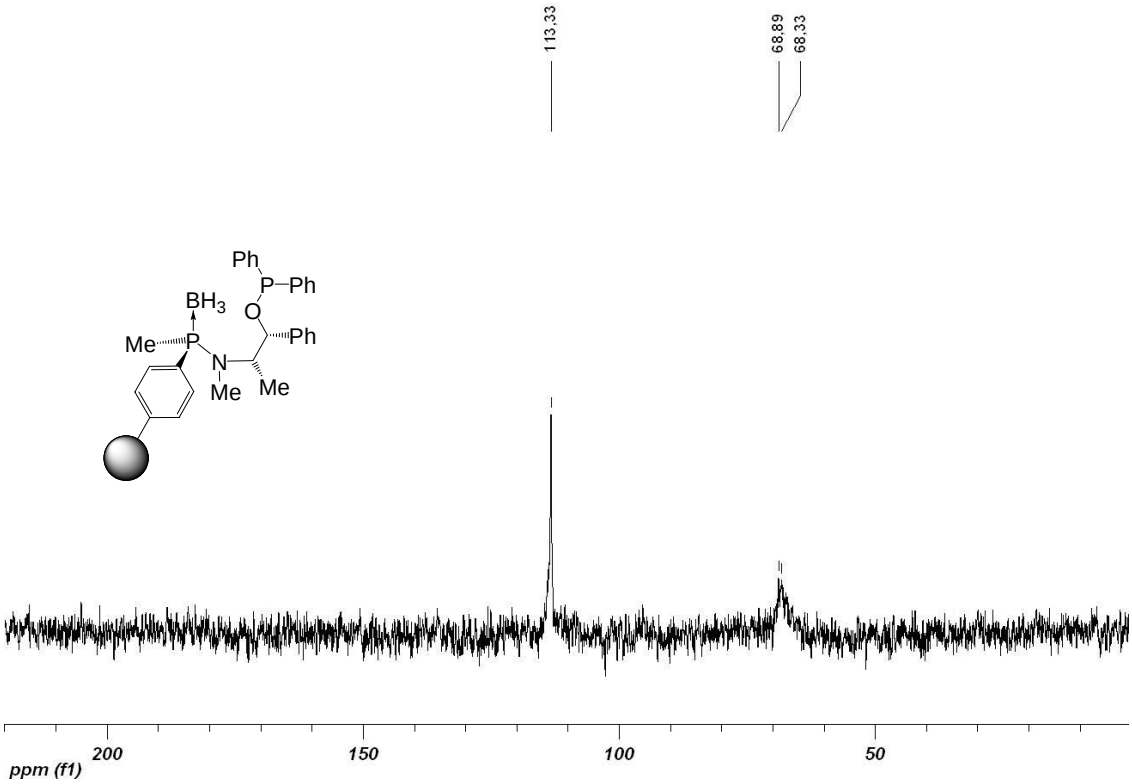
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **12** (121 MHz, C_6D_6, nano-probe).



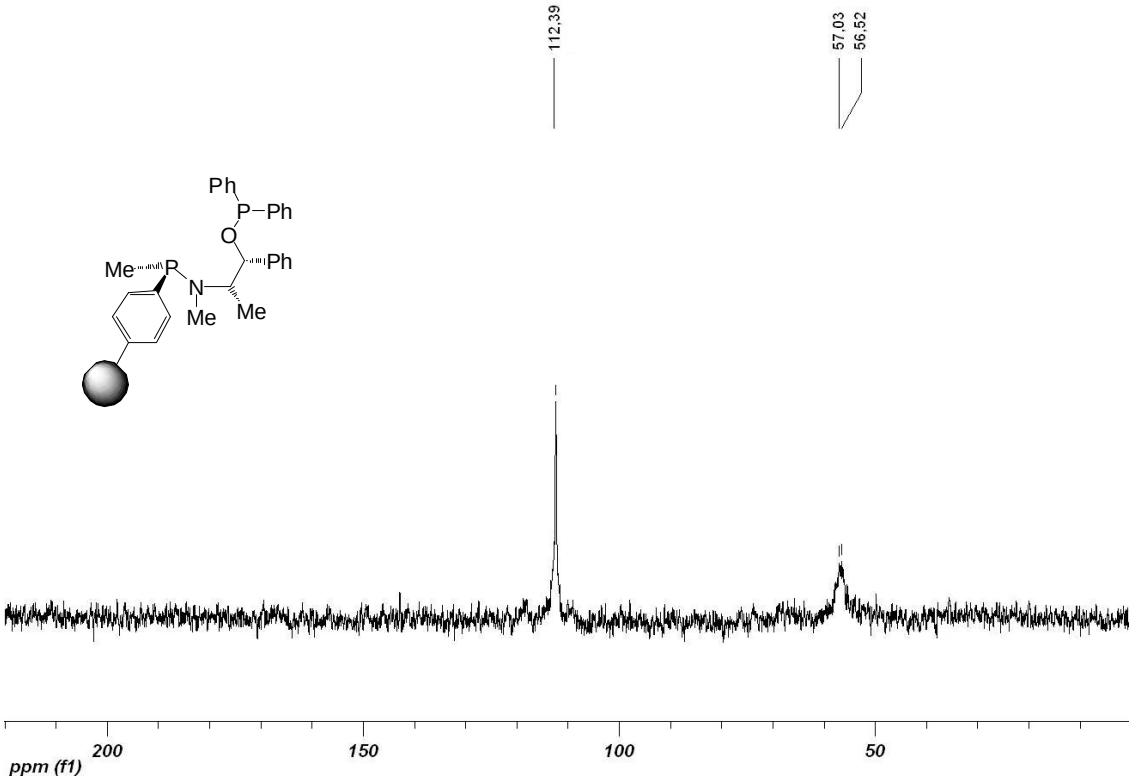
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **13** (202 MHz, C_6D_6, nano-probe).



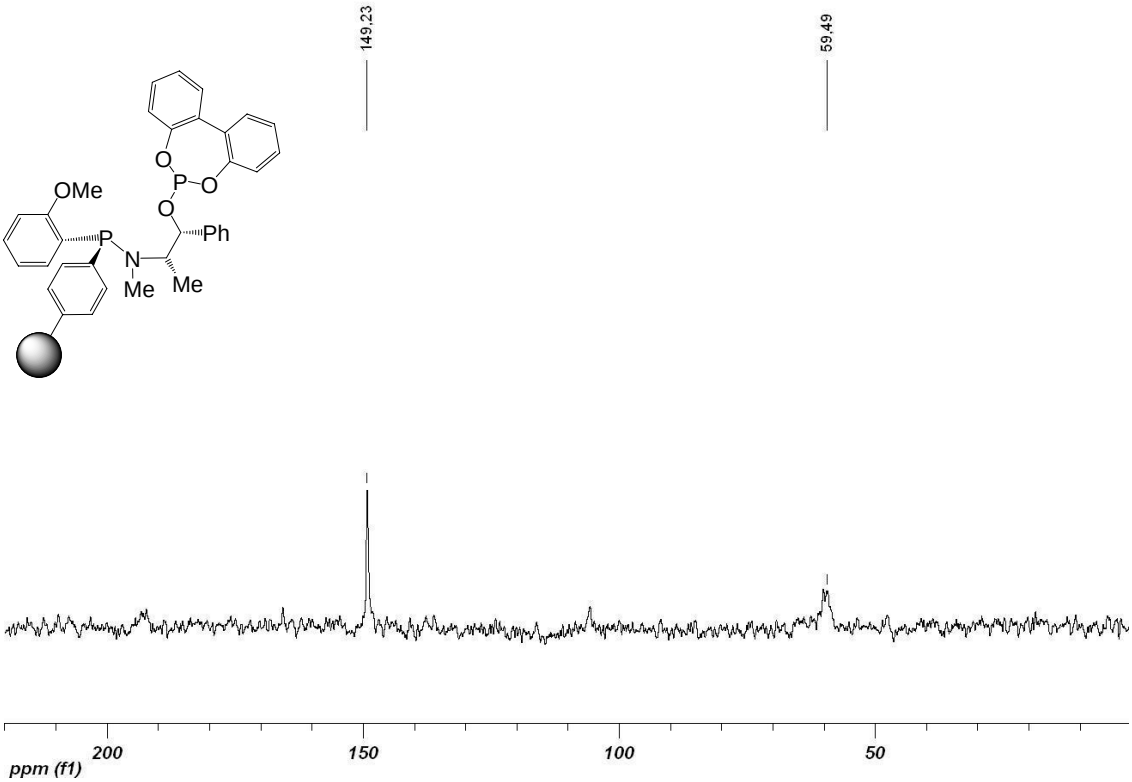
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **14** (121 MHz, THF, D_2O inner tube).



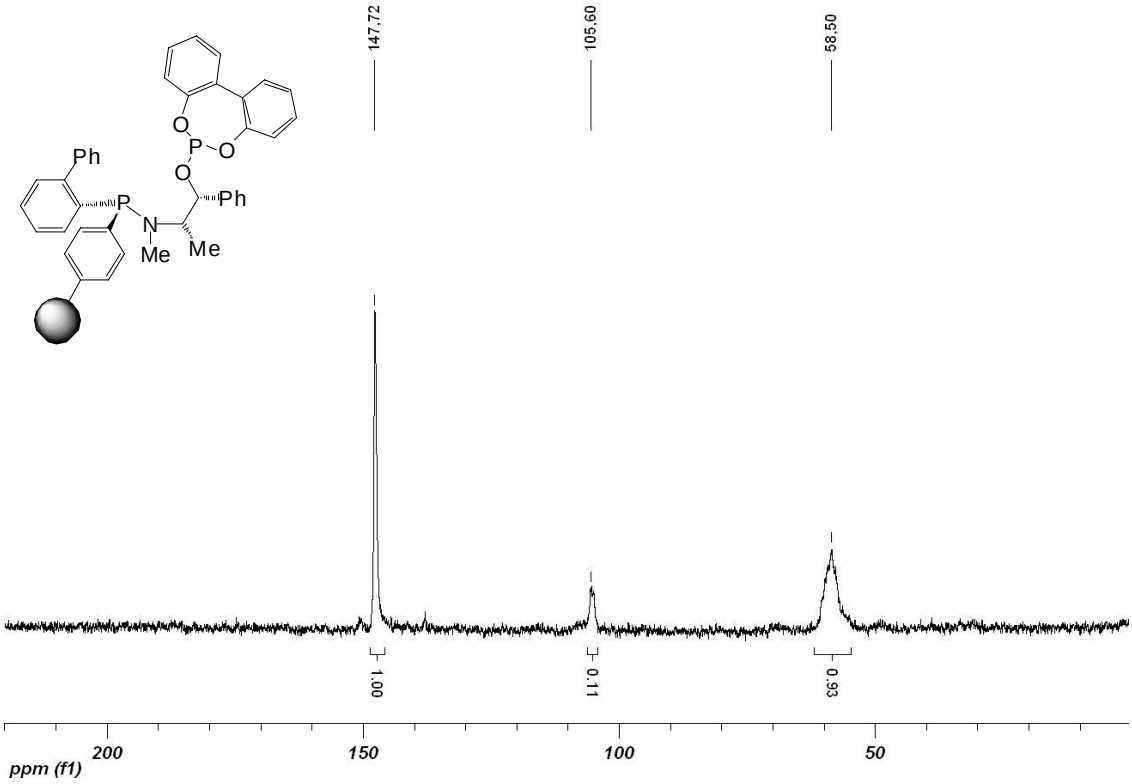
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **15·BH_3** (121 MHz, THF, D_2O inner tube).



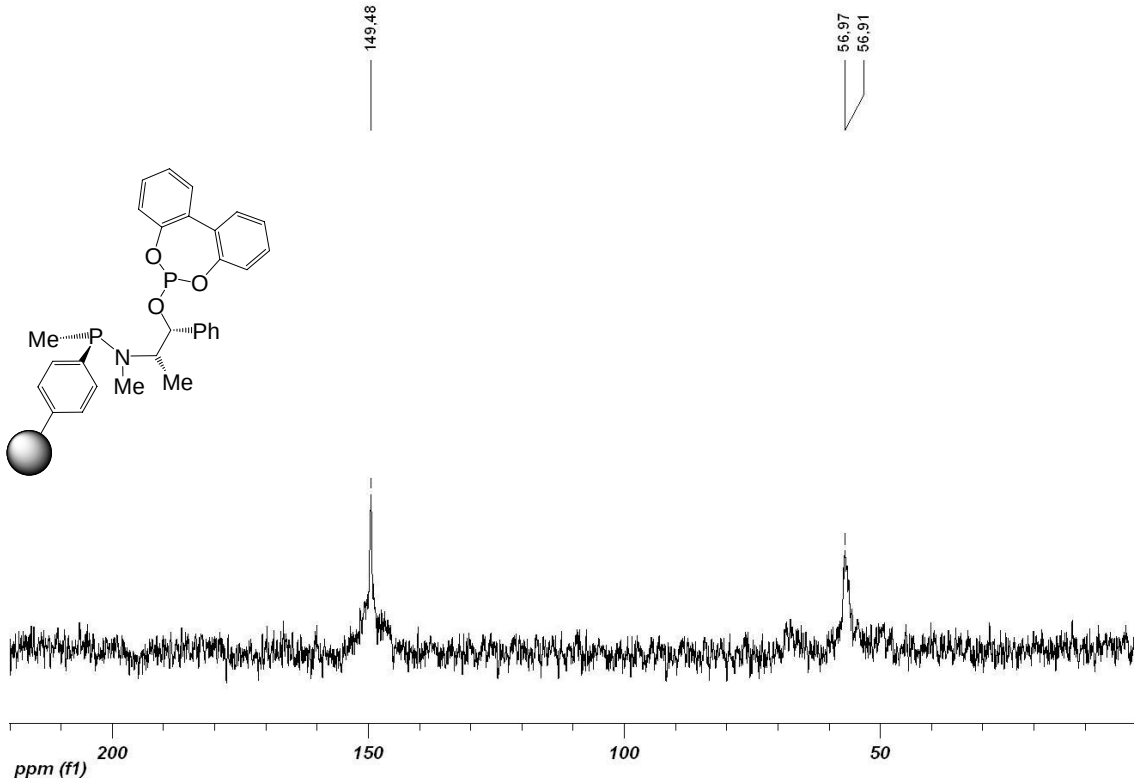
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **15** (121 MHz, THF, D_2O inner tube).



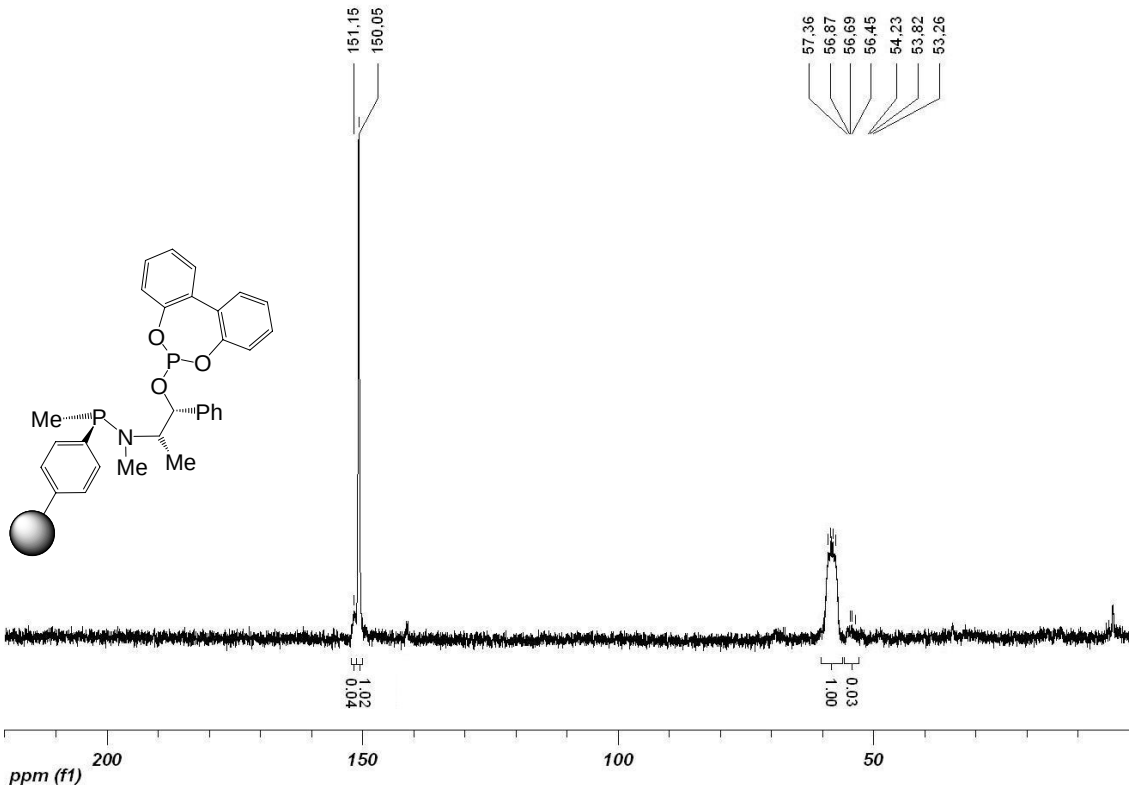
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **17** (121 MHz, THF, D_2O inner tube).



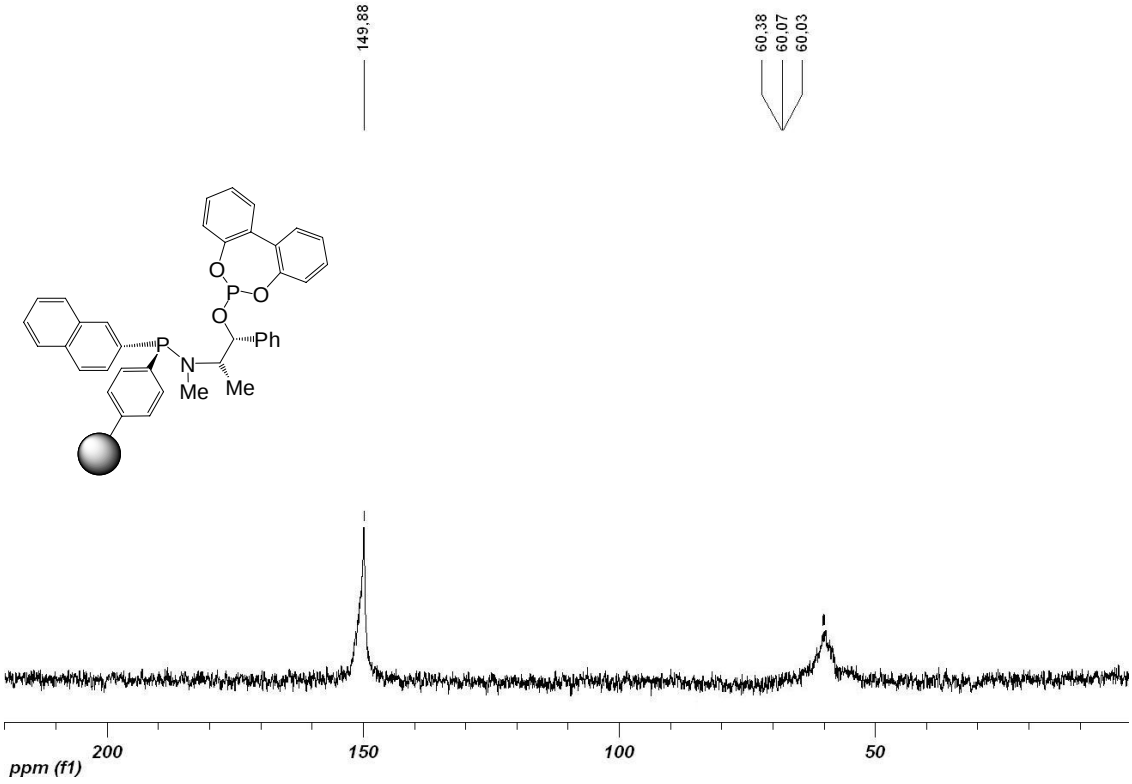
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **18** (202 MHz, C_6D_6, nano-probe).



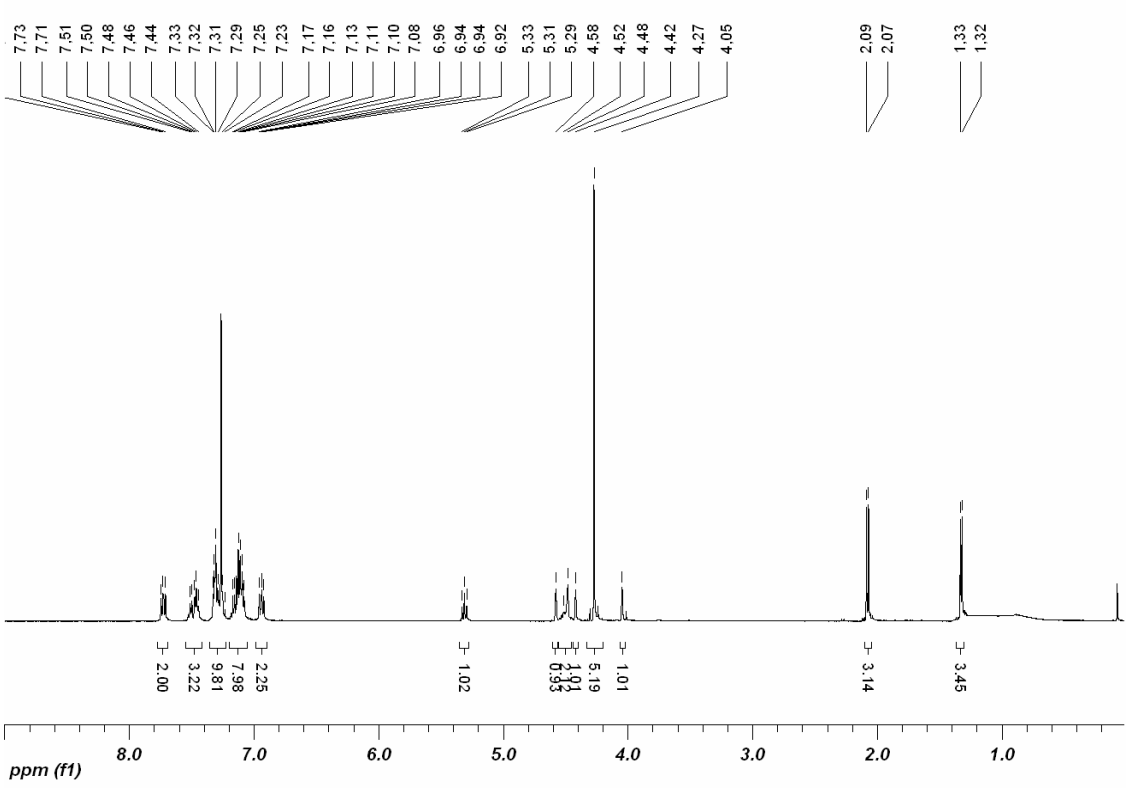
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **19** (121 MHz, THF, D_2O inner tube).



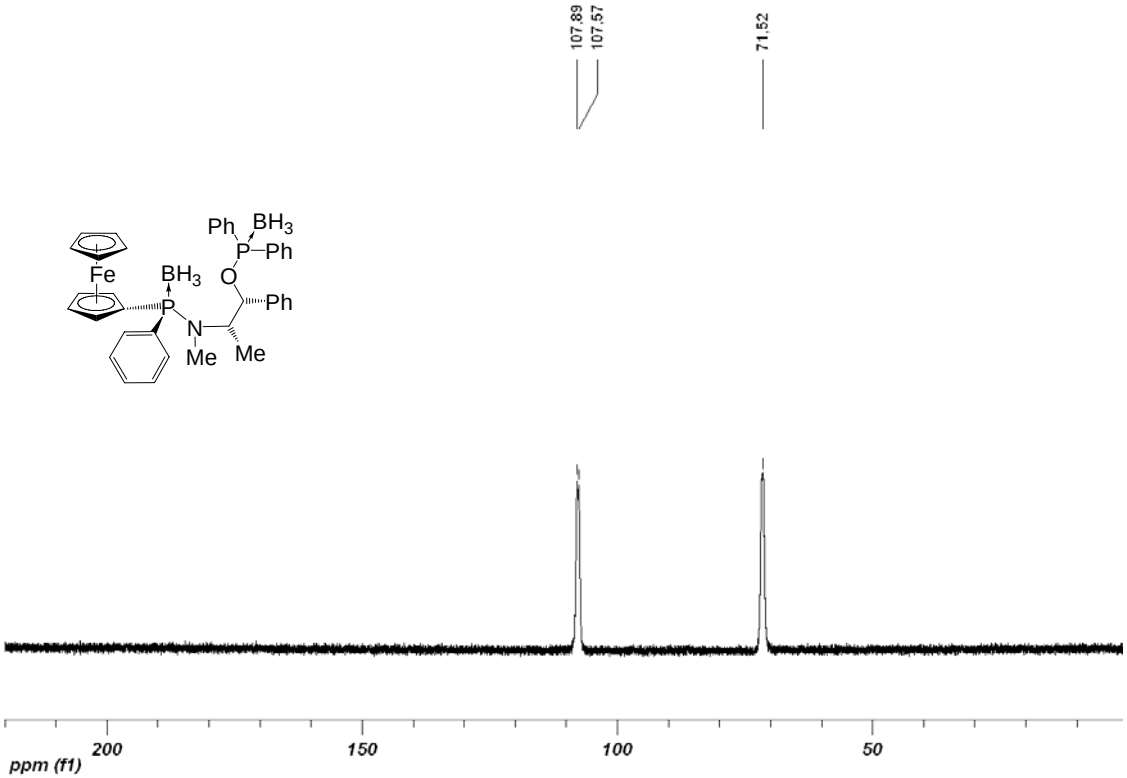
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **19** (202 MHz, CD_2Cl_2, nano-probe, 16 h).



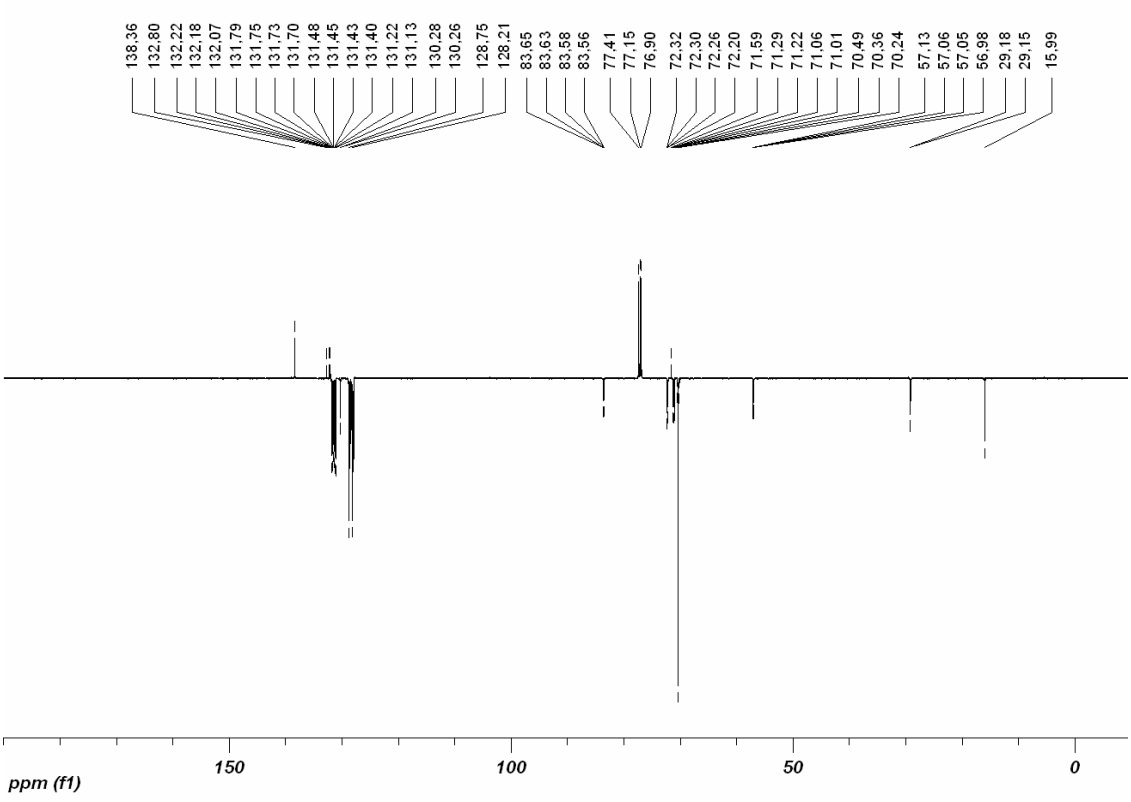
Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **20** (121 MHz, THF, D_2O inner tube).



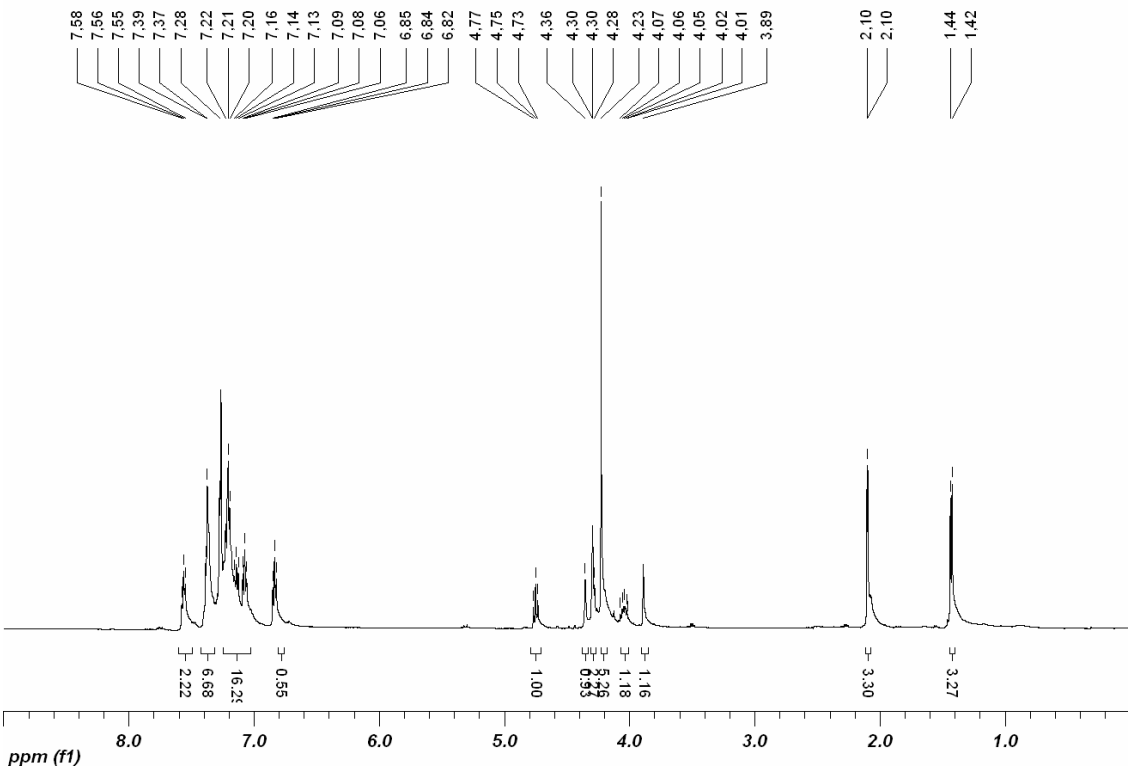
^{1}H NMR of compound **22·BH$_3$** (500 MHz, $CDCl_3$).



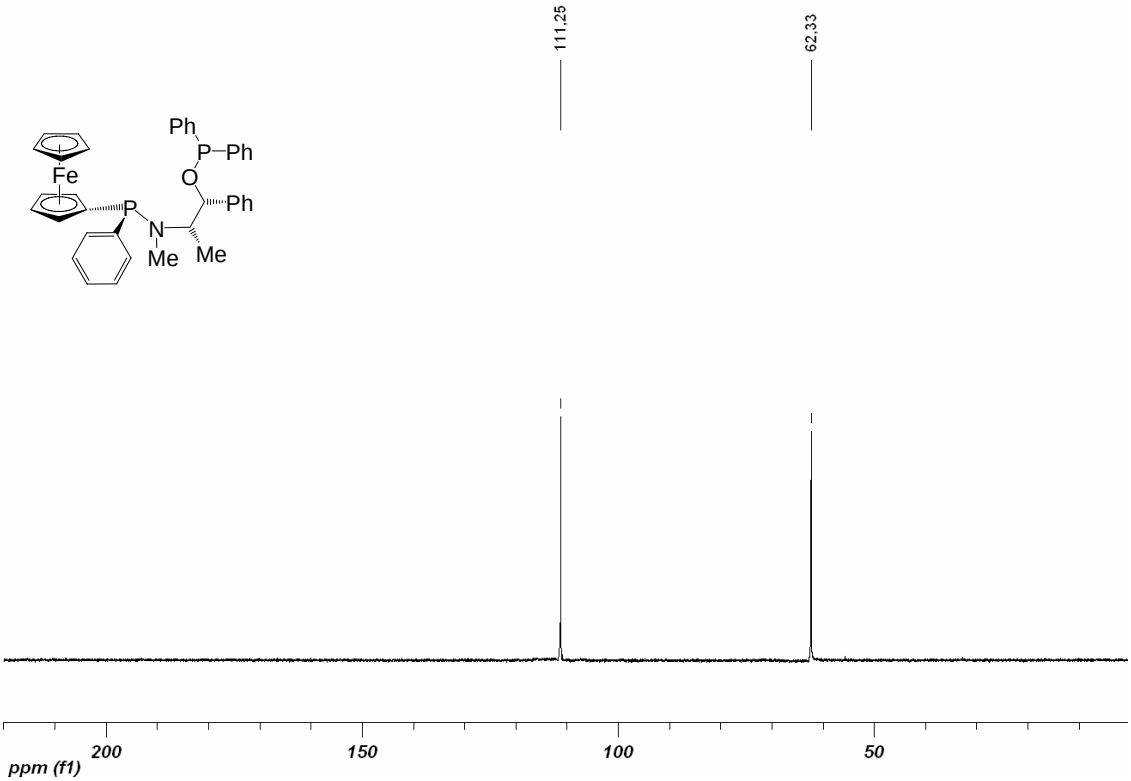
^{31}P {^{1}H} NMR of compound **22·BH$_3$** (202 MHz, $CDCl_3$).



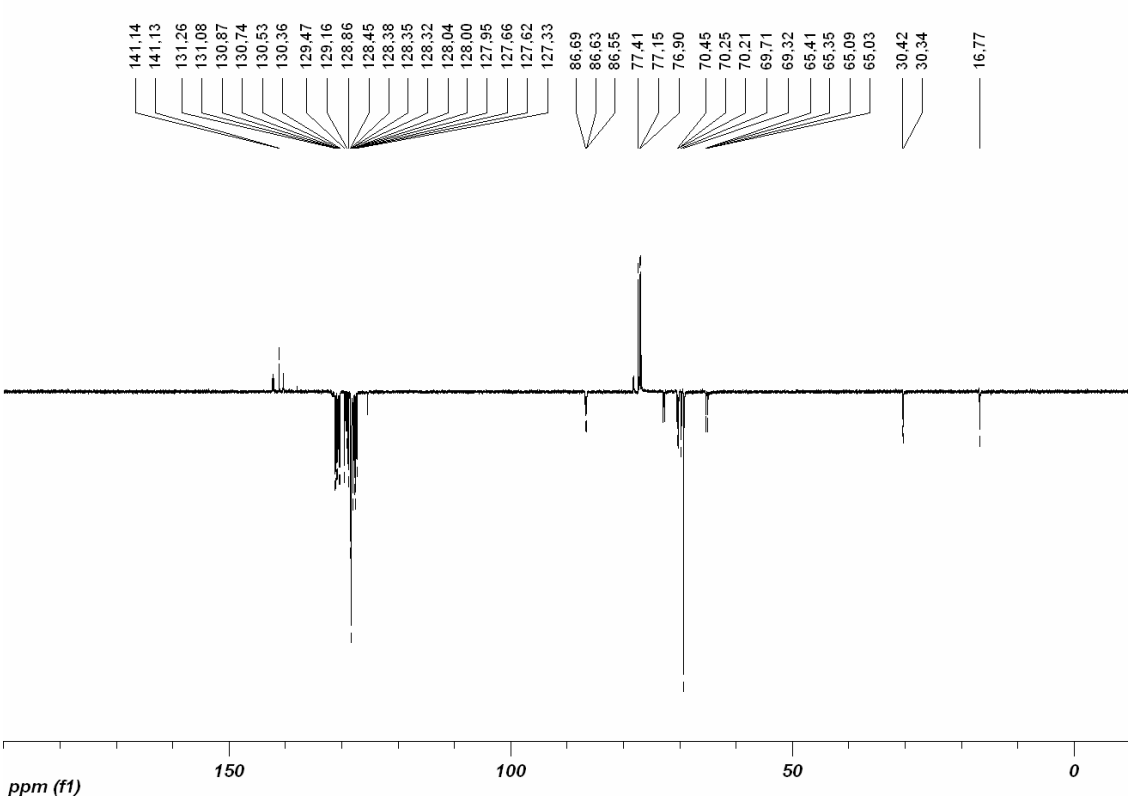
^{13}C {^{1}H} NMR of compound **22·BH$_3$** (125 MHz, $CDCl_3$).



^{1}H NMR of compound **22** (500 MHz, $CDCl_3$).



^{31}P $\{^{1}H\}$ NMR of compound **22** (202 MHz, $CDCl_3$).



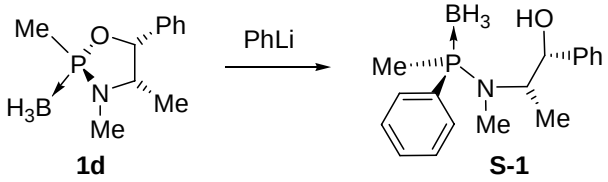
^{13}C {^{1}H} NMR of compound **22** (125 MHz, $CDCl_3$).

Determination of the diastereoselectivity of the ring-opening of oxazaphospholidine borane 1d.

Comparison of NMR data of solution and resin based ring opening.

The ring-opening of (2*R*,4*S*,5*R*)-2,5-diphenyl-4-methyl-[1,3,2]-oxazaphospholidine 2-borane (**1a**) by reaction with alkyl and aryl lithium compounds, gives the corresponding aminophosphane boranes with a diastereomeric ratio better than 92:8 as stated by Jugé and Genet.[3] The ring-opening reaction of oxazaphospholidine boranes with substituents at the P-atom other than phenyl has been studied to a lesser extent.[8,9] Since no alkyl-oxazaphospholidine borane derivitives have been reported, we discuss the diastereoselective ring-opening of **1d** in more detail.

Treatment of oxazaphospholidine borane **1d** with phenyllithium results in the cleavage of the P-O bond to give the hydroxy compound **S-1**. Only one diastereoisomer was detected with ^{1}H NMR spectroscopy and **S-1** was obtained in 89 % after flash column chromatography. For comparison, we synthesized diastereoisomer **S-2** by the reaction of oxazaphospholidine borane **1a** with methyllithium.[3] By altering the configuration of the phosphorus atom, the chemical shift in ^{31}P {^{1}H} NMR shows a difference of 0.8 ppm. A mixture of **S-1** and **S-2** (1:2) displays a broad signal in ^{31}P NMR spectroscopy (~4 ppm). The ^{31}P {^{1}H} NMR of immobilized compound **2d** (202 MHz, CD_2Cl_2, nano-probe, 3 h) showed no presence of the other diasteromer (see page S-20) within the detection limit estimated at <10%.

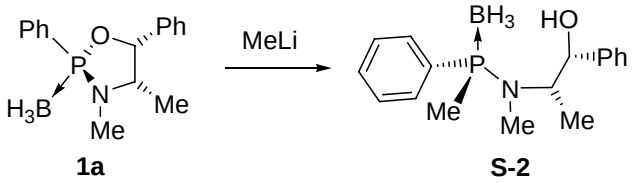


1d **S-1**

(*S*$_P$,1*S*,2*R*)-2-*N*-Methyl-*N*-(methylphenylphosphano borane)2-amino-1-phenylpropane-1-ol (S-1)

To a solution of oxazaphospholidine borane **1d** (13 mg, 0.045 mmol) in THF (1 mL) was added phenyllithium (2.0 M in dibutylether, 45 µL, 0.09 mmol) at -78 °C. The reaction temperature was allowed to rise slowly to 0 °C and stirring was maintained for 3 h. Water (1 mL) was added and the aqueous phase was extracted with diethyl ether (2 × 2 mL). The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (toluene/ethyl acetate, 95:5) yielding aminophosphane borane **S-1** as a colorless oil (12 mg, 89 %). Only one diastereoisomer was

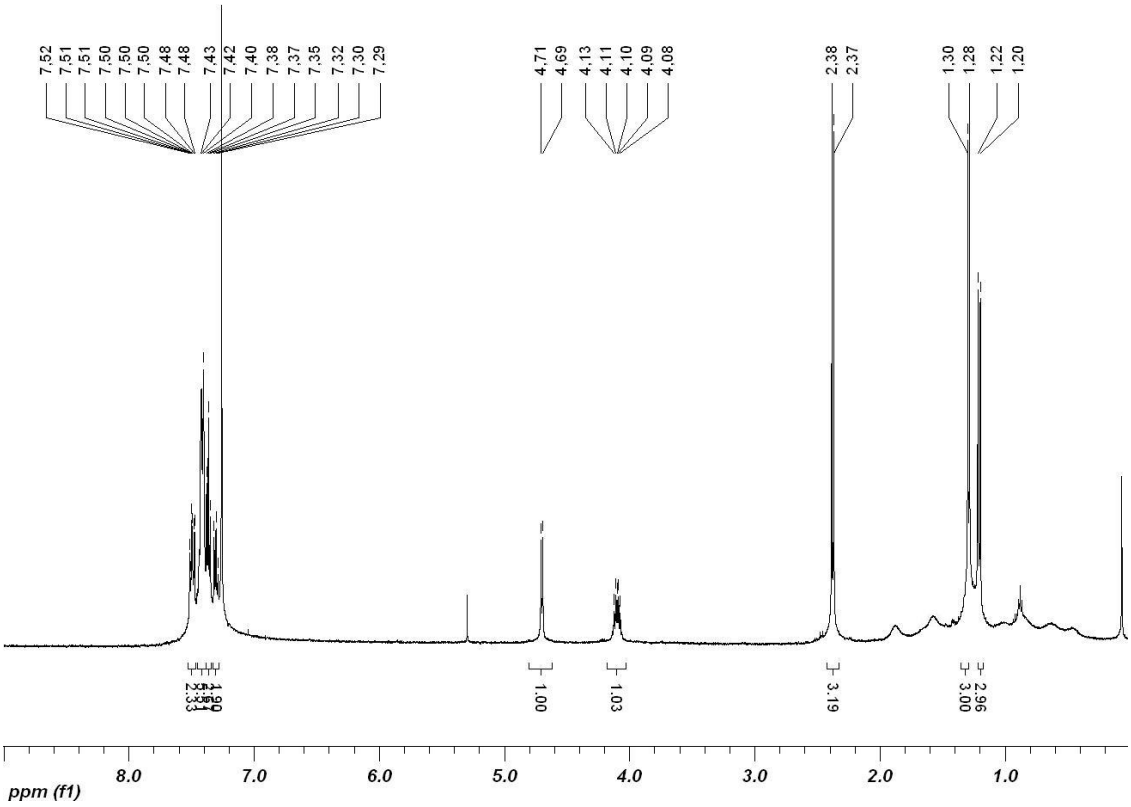
detected by ^{1}H NMR integration. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.50 (m, 2H, H-arom), 7.48-7.35 (m, 6H, H-arom), 7.30 (m, 2H, H-arom), 4.70 (d, *J* = 6.5 Hz, 1H, OCH), 4.10 (m, 1H, NCH), 2.38 (d, *J* = 8.0 Hz, 3H, NCH_3), 1.29 (d, *J* = 6.5 Hz, 3H, CCH_3), 1.21 (d, *J* = 9.0 Hz, 3H, PCH_3); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 142.8 (Cq), 133.2 (d, *J* = 62.5 Hz, Cq), 130.9 (CH), 130.5 (d, *J* = 10.1 Hz, CH), 128.8 (d, *J* = 10.1 Hz, CH), 128.6 (CH), 128.2 (CH), 127.0 (CH), 78.6 (CH), 58.6 (d, *J* = 9.3 Hz, N<u>C</u>H), 29.1 (NCH_3), 14.3 ($C\underline{C}H_3$), 10.8 (d, *J* = 44.4 Hz, PCH_3); ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$): δ = 67.61 (br).



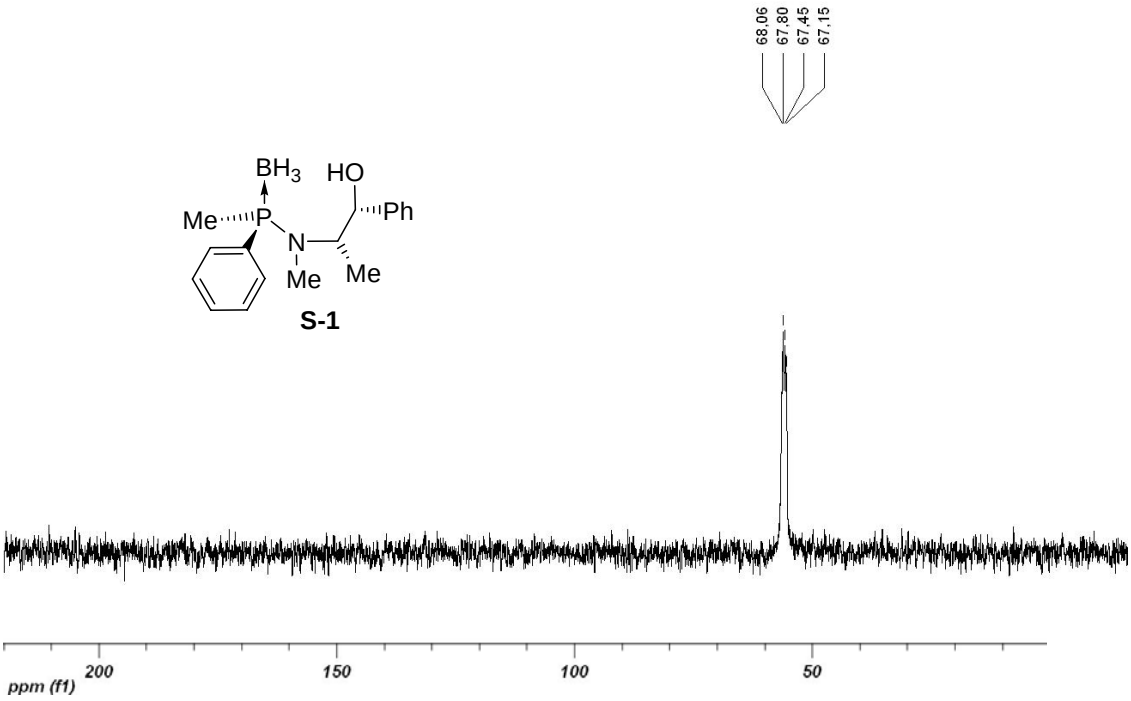
1a **S-2**

(R_P,1*S*,2*R*)-2-*N*-Methyl-*N*-(methylphenylphosphano borane)2-amino-1-phenylpropane-1-ol (S-2)

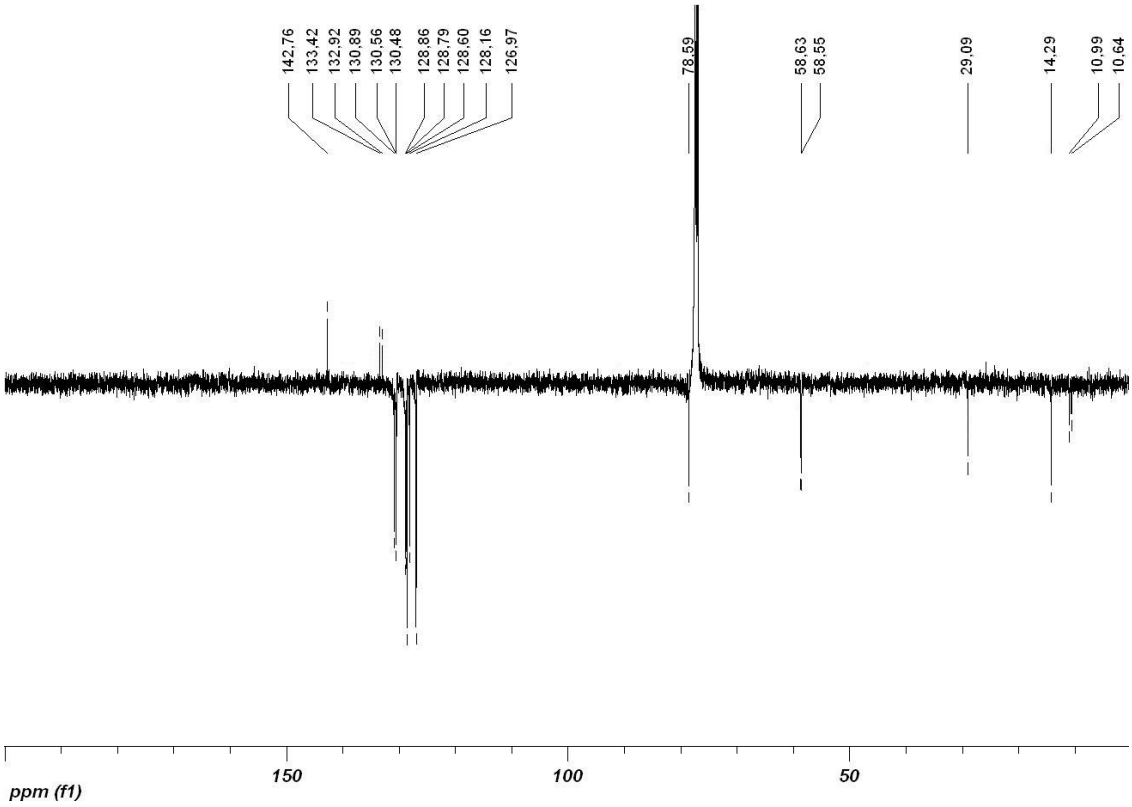
This compound was prepared according to a literature procedure.[3] To a solution of oxazaphospholidine borane **1a** (0.95 g, 3.33 mmol) in THF (5 mL) was added methyllithium (2.0 M in dibutylether, 1.67 mL, 3.33 mmol) at -78 °C. The reaction temperature was allowed to rise slowly to 0 °C and stirring was maintained for 0.5 h. Water (1 mL) was added and the aqueous phase was extracted with diethyl ether (2 × 5 mL). The organic extracts were dried over $MgSO_4$ and concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography (toluene/ethyl acetate, 95:5) yielding aminophosphane borane **S-2** as a colorless oil (0.93 g, 93 %). The diastereomeric ratio of the isolated material was determined to be 12:1 by ^{1}H NMR integration.[10] ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.42 (m, 2H, H-arom), 7.37-7.31 (m, 4H, H-arom), 7.25 (m, 2H, H-arom), 7.05 (m, 2H, H-arom), 4.67 (d, *J* = 7.5 Hz, 1H, OCH), 4.00 (m, 1H, NCH), 2.44 (d, *J* = 8.5 Hz, 3H, NCH_3), 1.50 (d, *J* = 9.0 Hz, 3H, PCH_3), 1.23 (d, *J* = 6.5 Hz, 3H, CCH_3); ^{13}C {^{1}H} NMR (125 MHz, $CDCl_3$): δ = 142.8 (Cq), 132.8 (d, *J* = 66.2Hz, Cq), 130.5 (CH), 130.2 (d, *J* = 10.2 Hz, CH), 128.4 (d, *J* = 10.1 Hz, CH), 128.4 (CH), 127.8 (CH), 126.9 (CH), 77.1 (CH), 58.0 (d, *J* = 7.7 Hz, N<u>C</u>H), 28.8 (NCH_3), 14.3 ($C\underline{C}H_3$), 11.2 (d, *J* = 41.3 Hz, PCH_3); ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$): δ = 66.80 (br).



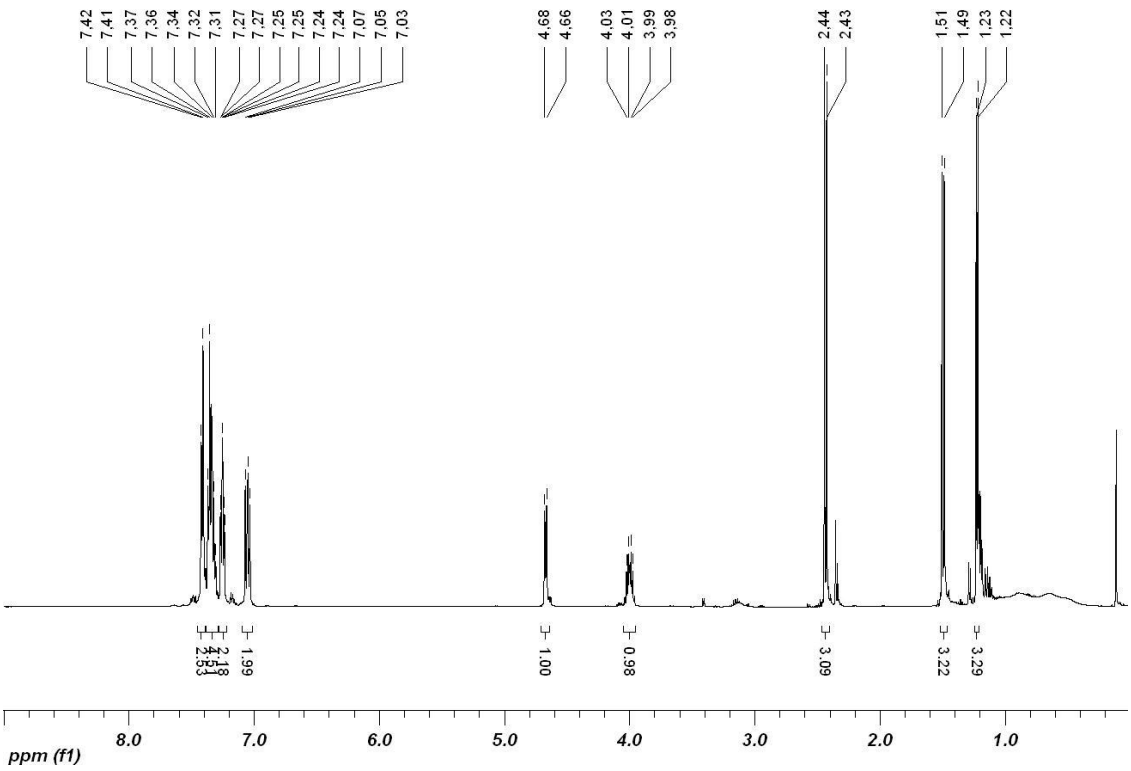
^{1}H NMR of compound **S-1** (500 MHz, $CDCl_3$).



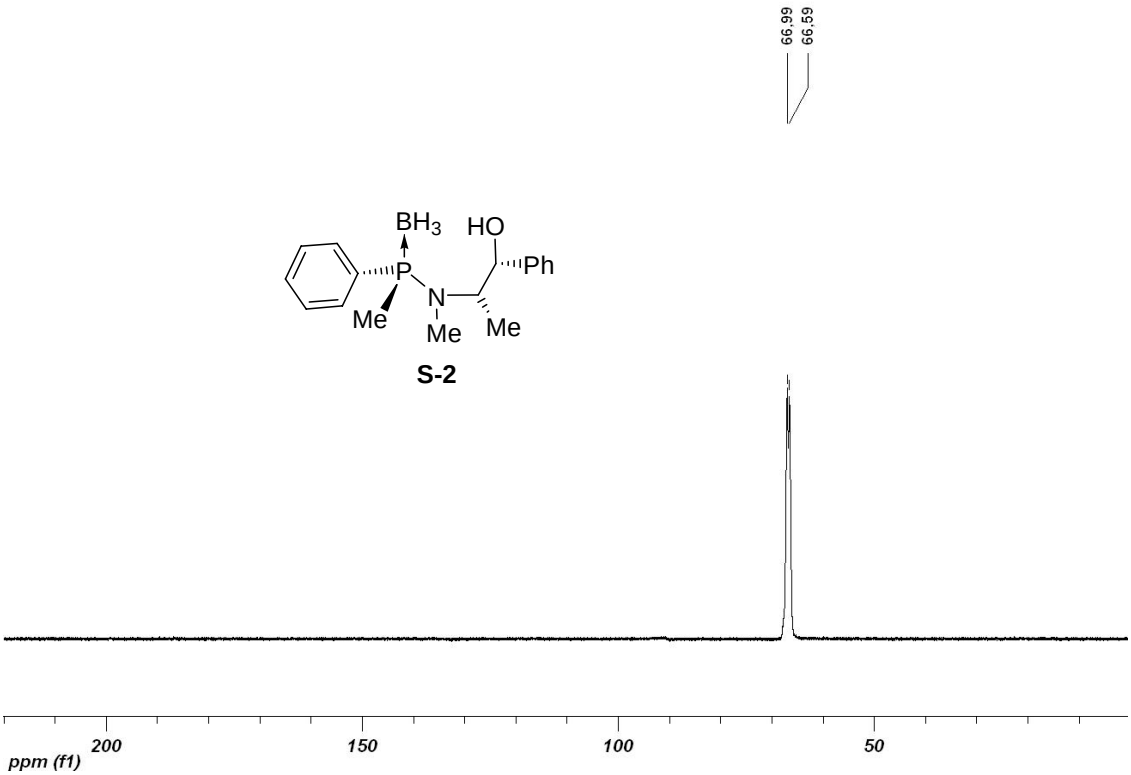
^{31}P {^{1}H} NMR of compound **S-1** (202 MHz, $CDCl_3$).



^{13}C {^{1}H} NMR of compound **S-1** (125 MHz, $CDCl_3$).

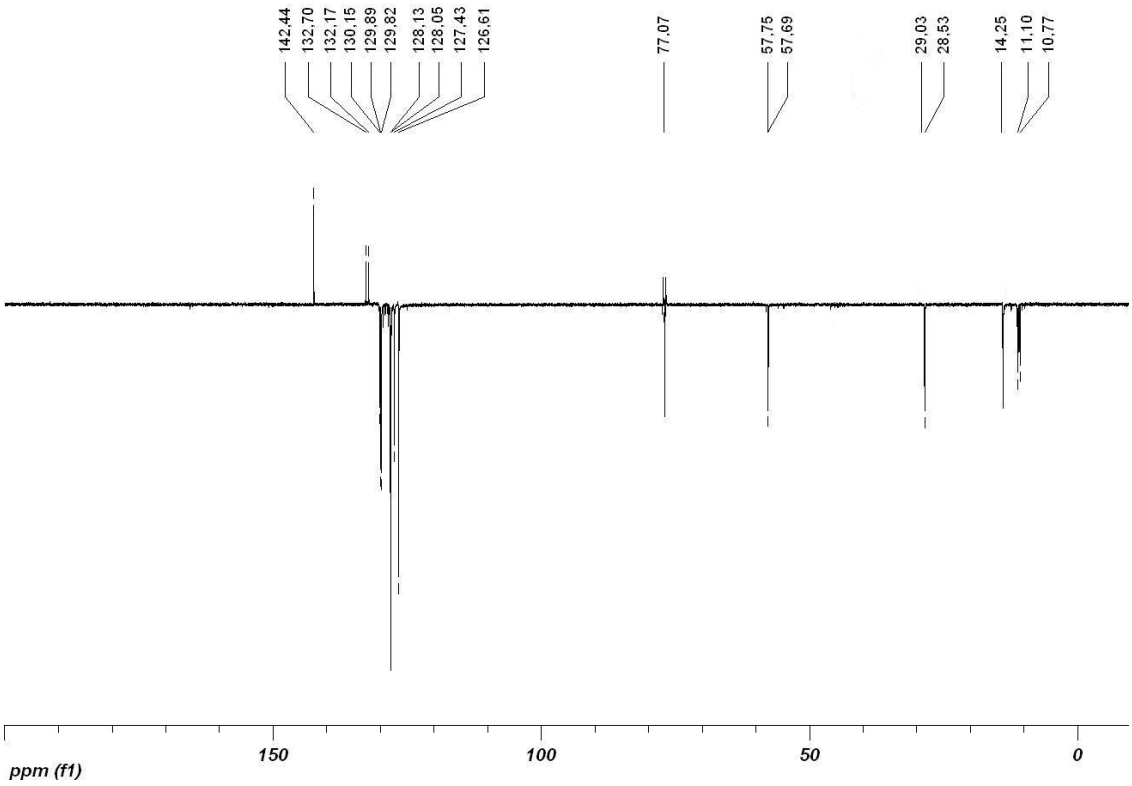


^{1}H NMR of compound **S-2** (500 MHz, $CDCl_3$).

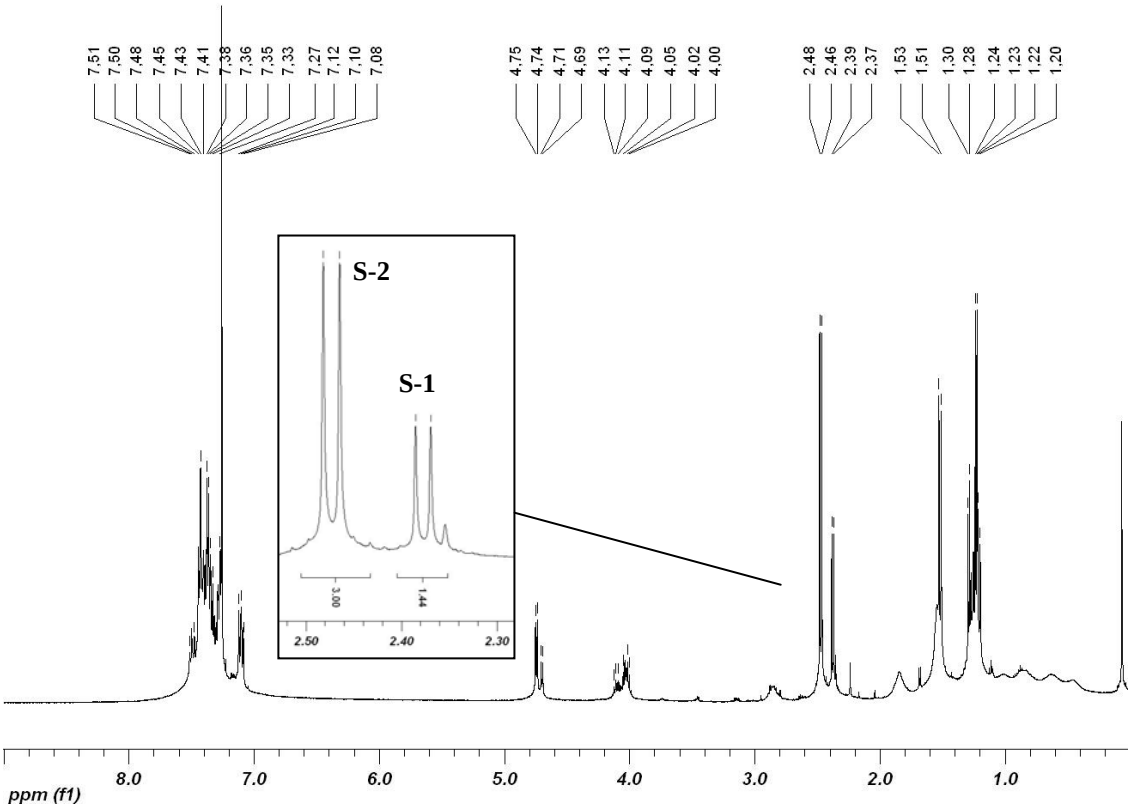


S-2

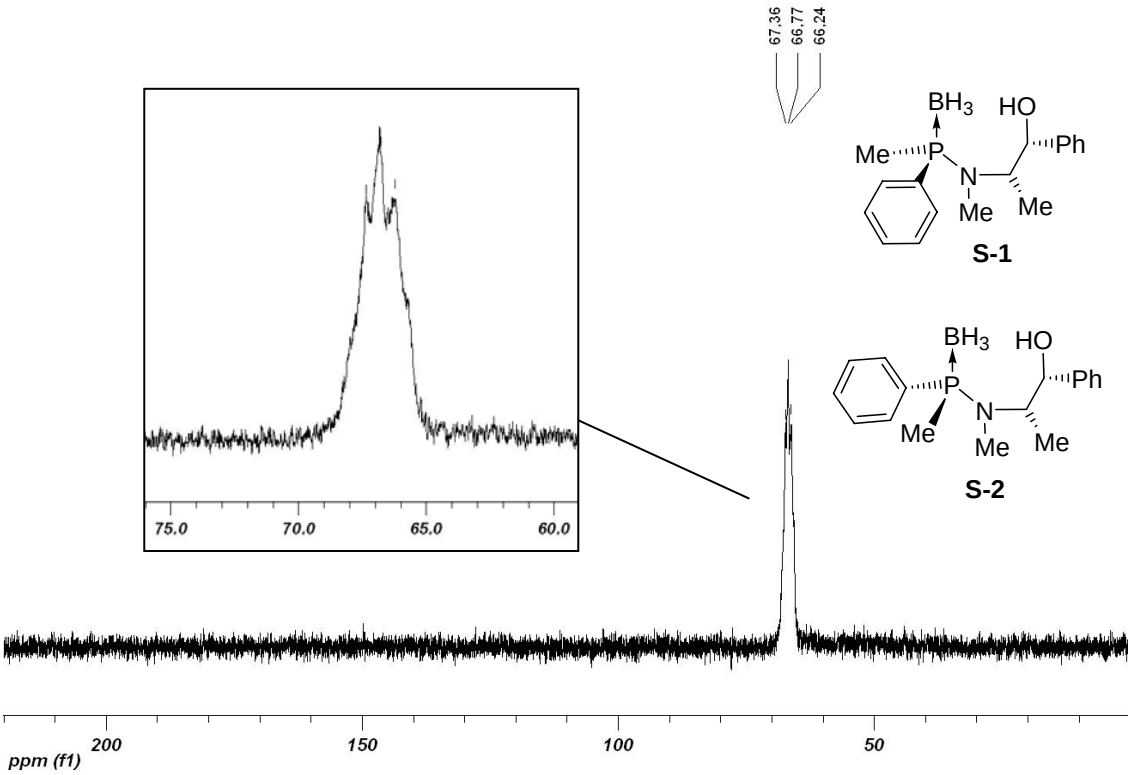
^{31}P {^{1}H} NMR of compound **S-2** (202 MHz, $CDCl_3$).



^{13}C {^{1}H} NMR of compound **S-2** (125 MHz, $CDCl_3$).



^{1}H NMR of a mixture of **S-1** and **S-2** (500 MHz, $CDCl_3$).



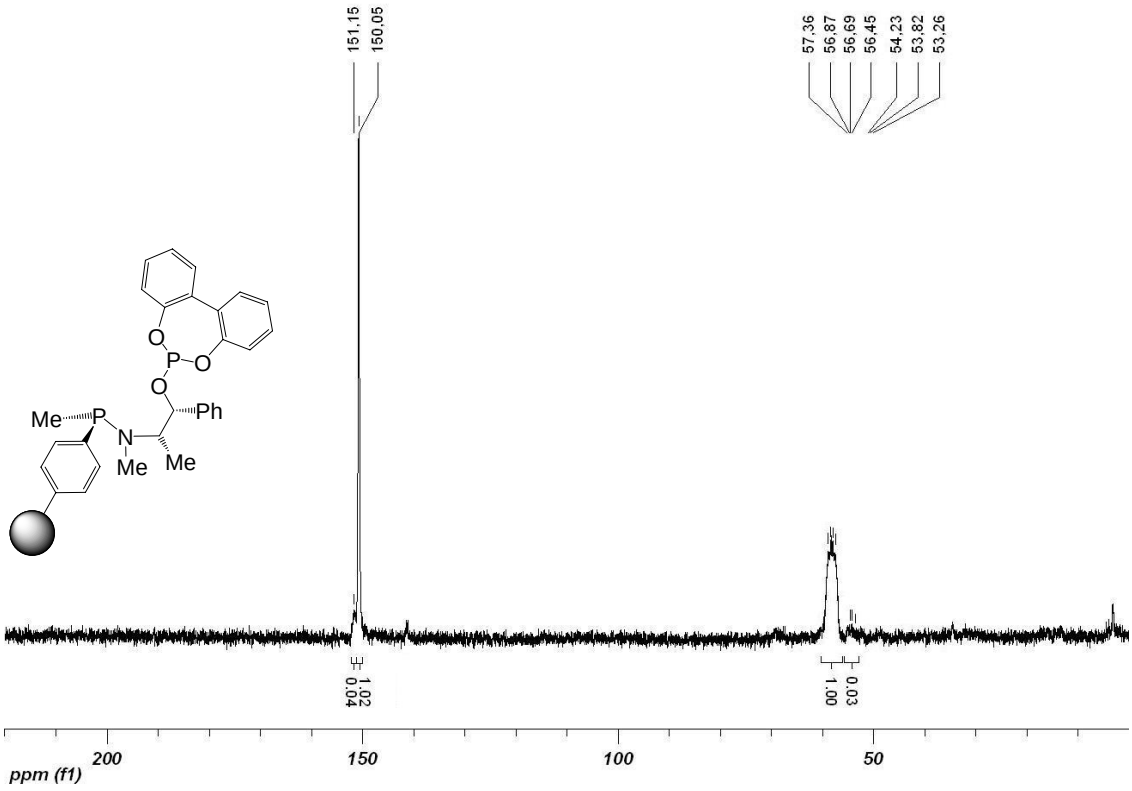
S-1

S-2

^{31}P {^{1}H} NMR of a mixture of **S-1** and **S-2** (202 MHz, $CDCl_3$).

Improved line width in gel phase ^{31}P MAS NMR spectroscopy of 19 derived from 2d

The line width of the gel phase NMR MAS spectra could be improved by changing the solvent to CD_2Cl_2. For resin **19**, the line width for the phosphite signal became less than 0.5 ppm and for the aminophosphane less than 2 ppm. The solution synthesis of the diastereoisomer of this ligand has been reported.[11,12] The NMR data of that ligand shows chemical shifts for the two diastereoisomers of 50.7 and 56.0 ppm for the aminophosphane signal and 148.8 and 145.1 ppm for the phosphite signal respectively.[12] The reported spectrum is consistent with the gel phase spectrum of resin based ligand **19** which allows an integration of the diastereomers, confirming a diastereomeric ratio > 96 : 4.

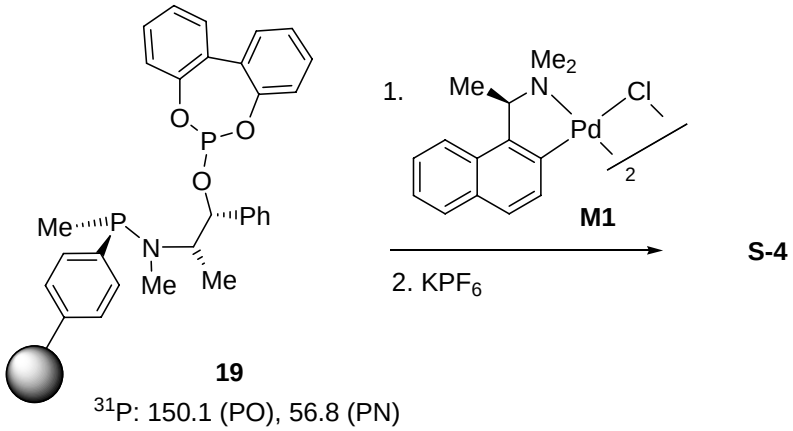


Gel-phase ^{31}P $\{^1H\}$ NMR of compound **19** (202 MHz, CD_2Cl_2, nano-probe, 16 h).

Complexation of 19 to a chiral Pd-precursor

The complexation of P-stereogenic phosphanes to optically pure Pd-precursors has been widely used to gain insight in the enantiopurity of the phosphane and for the separation of the enantiomers.[14] Although this approach has been studied to a lesser extent for P-stereogenic aminophosphanes, complexation of the resin-bound aminophosphanes to chiral Pd-complexes can give additional information on the diastereoselectivity of the ring-opening reaction in the formation of **2a-f**. Unfortunately, we were unable to remove the BH_3-group of resin-bound aminophosphane boranes **2a-f** at room temperature. At elevated temperature the aminophosphanes rearranges to phosphonites as is addressed in more detail on page S-42.

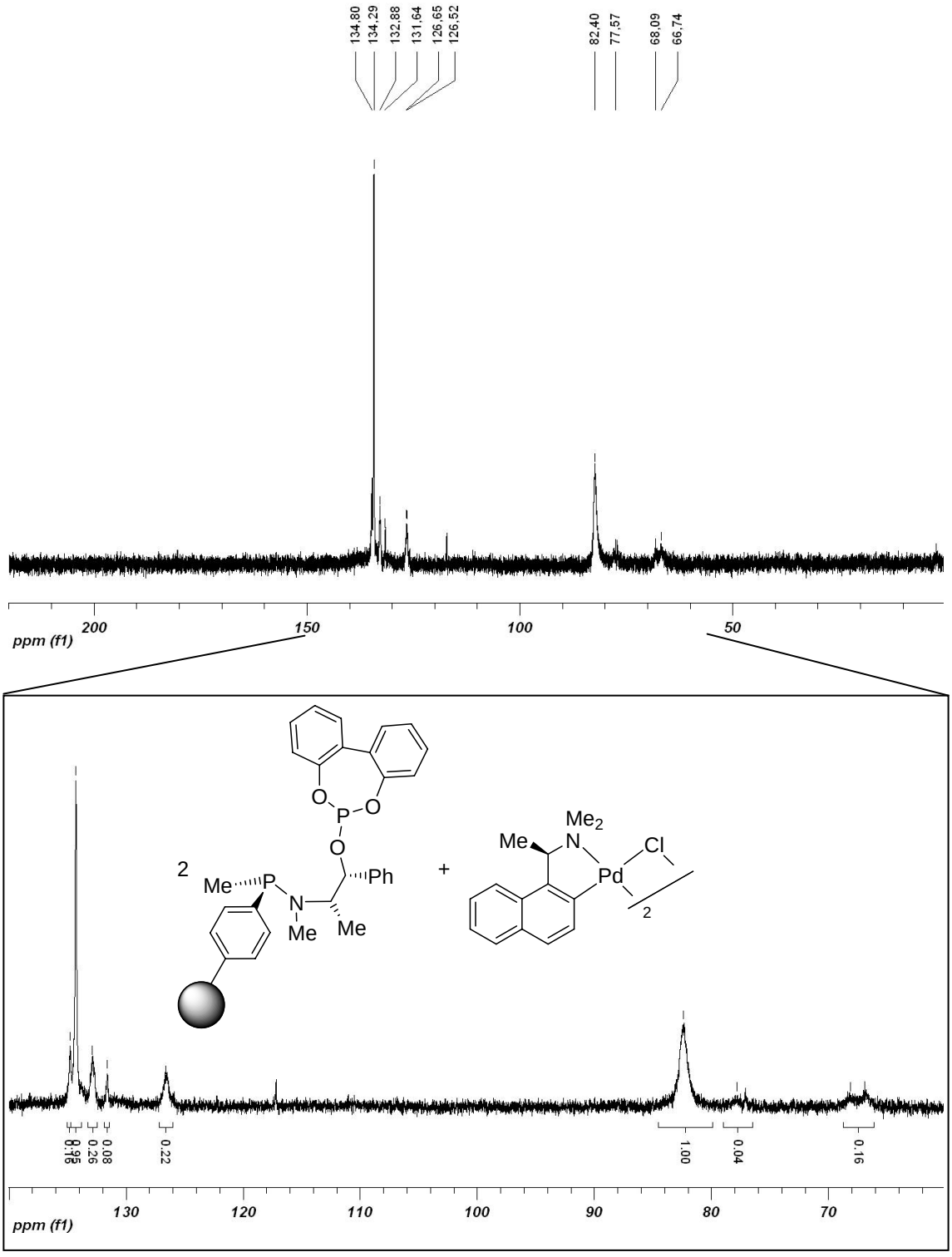
The resin-bound bidentate ligands **12-21** can be complexed to chiral Pd-precursors, although it has been shown that certain aminophosphane phosphinite ligands form complexes with optically pure Pd-precursors that are able to isomerize and decompose in time.[15] The treatment of 2 equivalents of **19** with the palladium dimer **M1** in the presence of KPF_6 to ensure coordination in a bidentate fashion[16], gave resin **S-4**.



19

^{31}P: 150.1 (PO), 56.8 (PN)

The gel phase ^{31}P $\{^1H\}$ NMR spectrum of **S-4** shows clear separation of the aminophosphane signal (82 and 78 ppm), confirming the integration of the free ligand (see page S-38). The phosphite region is more complicated because the free ligand already shows more phosphite NMR signals owing to the atropisomeric behaviour of the bisphenol moiety, as has been described for the non-supported diastereoisomer.[12]



Gel-phase ^{31}P $\{^{1}H\}$ NMR of compound **S-4** (202 MHz, CD_2Cl_2, nano-probe, 24 h)

Lineshape analysis of gel phase ^{31}P {^{1}H} NMR of diarylaminophosphane 2c

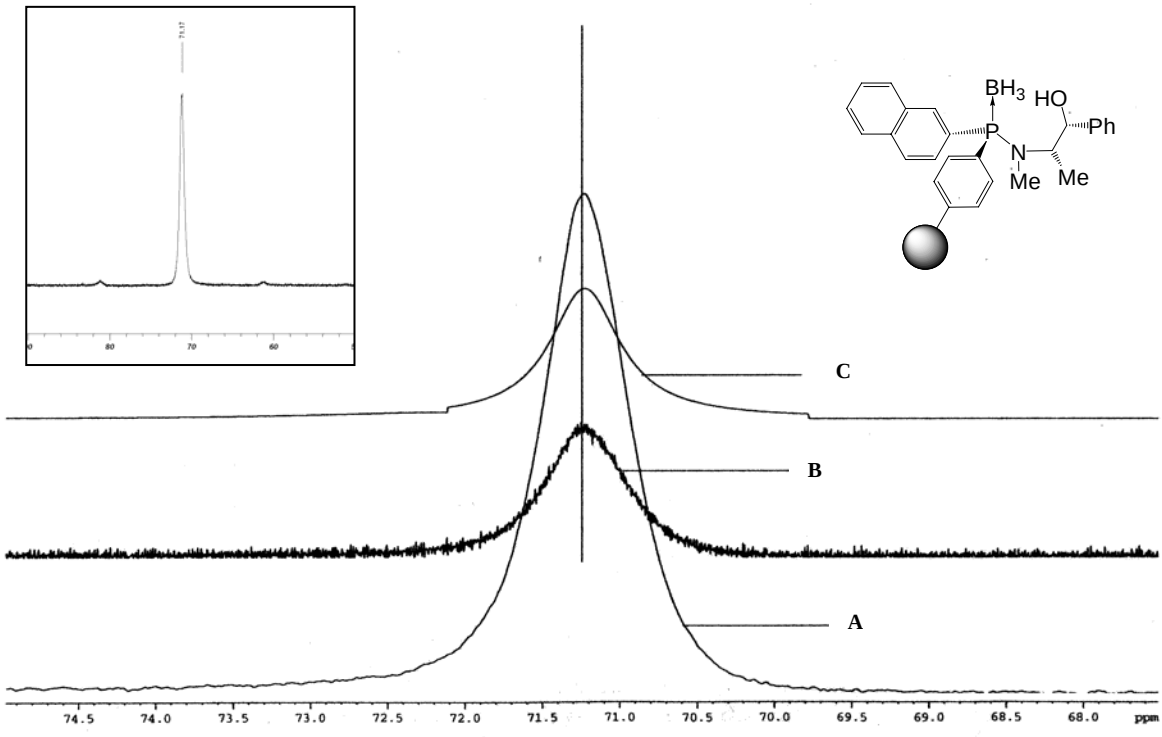
To determine the presence of overlapped signals (*i.e.* the presence of diastereoisomers) in the gel-phase ^{31}P {^{1}H} MAS NMR of compound **2c**, the data was subjected to deconvolution using the deconvolution routine of the Bruker TopSpin NMR software.

A) Data with Fourier transformation and phase correction.

B) Data with Gaussian multification (gb = 0.7) and phase correction

C) Deconvolution of data **B**.

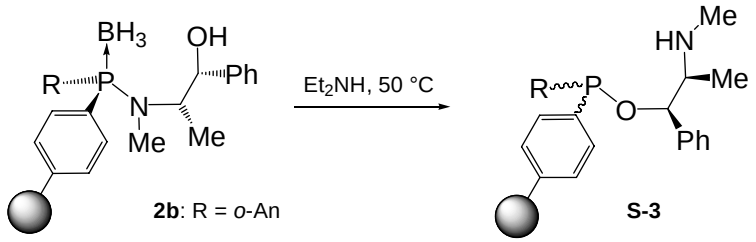
Using these calculations, no additional signal could be observed which is in line with the report of Jugé and Genet.[3]

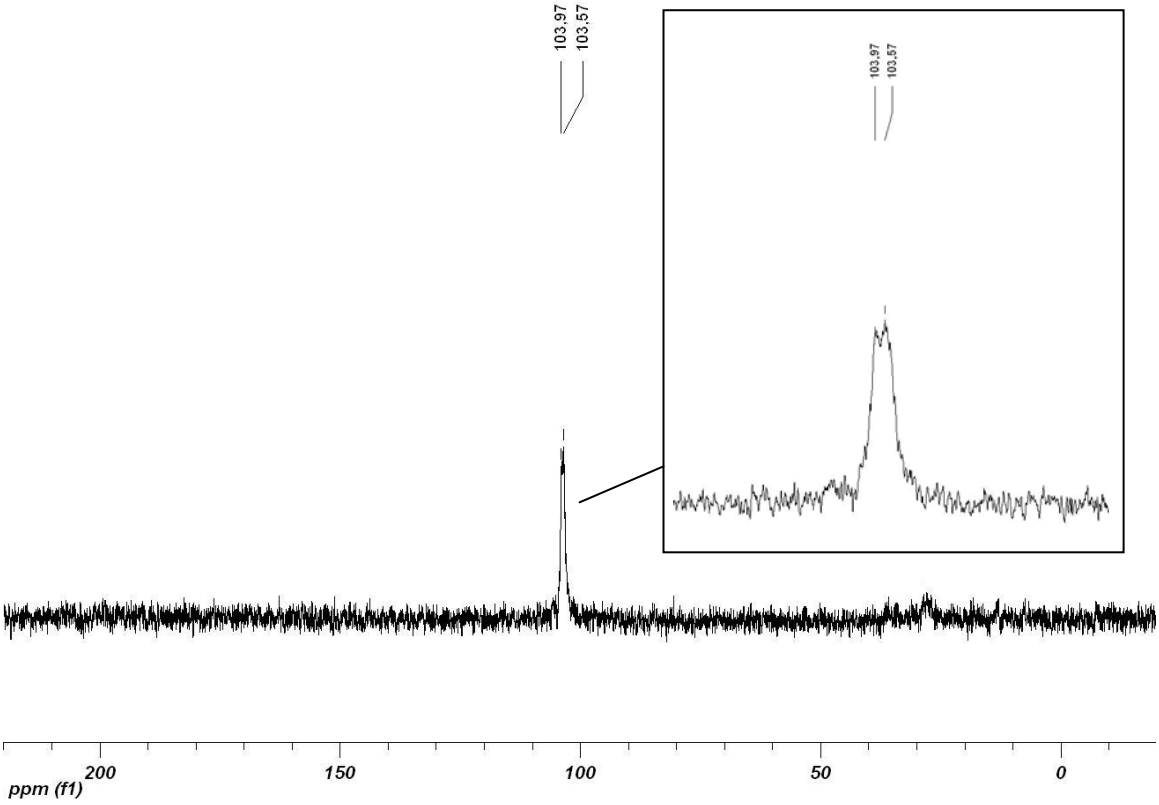


Deconvolution of gel-phase ^{31}P {^{1}H} NMR spectrum of compound **2c**.

Intramolecular rearrangement of resin-bound aminophosphane

In the synthesis of resin-bound aminophosphane phosphite and phosphinite ligands (**12**-**20**), the complete conversion of the hydroxyl group of the aminophosphane boranes (**2**) to the phosphite or phosphinite is of importance. During the removal of the borane group with diethylamine at 50 °C, the non-reacted aminophosphane alcohol will rearrange to resin-bound phosphonite derivatives. For homogeneous analogues, this rearrangement is known to readily proceed at elevated temperature.[13] Treatment of resin **2b** with Et_2NH at 50 °C for 16 h, resulted in a resin that displayed a signal at 104 ppm in gel-phase ^{31}P $\{^1H\}$ NMR and which we assume to be **S-3**.

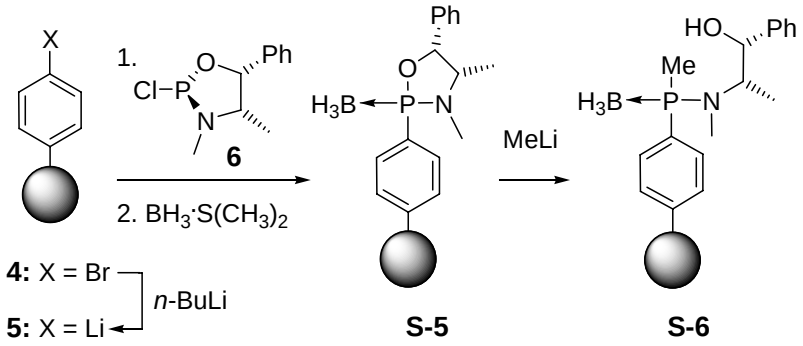




Gel-phase ^{31}P $\{^1H\}$ NMR of compound **S-3** (202 MHz, CD_2Cl_2, nano-probe, 2 h)

Alternative route towards resin-bound P-stereogenic aminophosphane-phosphite and phosphinite ligands

Commercially available 4-bromo functionalized polystyrene **4** was converted to the corresponding lithio derivative (**5**) and subsequently reacted with an excess (2*R*,4*S*,5*R*)-2-chloro-3,4-dimethyl-5-phenyl-1,3,2-oxazaphospholidine **6**, followed by reaction with an excess $BH_3{\cdot}S(CH_3)_2$. The resonance at 125 ppm observed with ^{31}P gel phase NMR, indicates the formation of oxazaphospholidine borane **S-5**, although the extremely broad nature of the resonance prevented exact identification.[17] The broad resonance at 145 ppm observed for the resin prior to reaction with BH_3 is a further evidence for the successful formation of the resin-bound oxazaphospholidine, as the chemical shift corresponds closely to the chemical shift observed for the non-supported analogue (142 ppm).[18] Subsequent reaction of resin **S-5** with 2.1 equivalents of methyllithium yielded a mixture of unidentified resin-bound compounds, but the formation of **S-6** (approximately 40%) was confirmed by a resonance at 66 ppm, which is in accordance with the chemical shift observed for the non-supported analogue (67 ppm).[3] Since a mixture of resin-bound compounds cannot be purified, the route towards resin-bound P-stereogenic aminophosphane-phosphite and phosphinite ligands as described in the main text was explored.



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