Supporting information

Solid-Phase Synthesis of Recyclable Supported Diphosphine Ligands

Frank J. L. Heutz, Michiel C. Samuels and Paul C. J. Kamer*

School of Chemistry, University of St Andrews
St. Andrews, Fife, KY16 9ST, United Kingdom

Contents

General Experimental

All reactions and manipulations were carried out under inert conditions using standard Schlenk techniques or in an MBraun glovebox unless stated otherwise. All glassware was dried prior to use to remove traces of water. All chemicals were obtained from commercial suppliers and used as received unless otherwise stated. Toluene was distilled from sodium, diethyl ether and THF were distilled from sodium/benzophenone and triethylamine, dichloromethane and acetonitrile were distilled from calcium hydride. JandaJel-Cl™ (50-100 mesh, 0.96 mmol·g^{-1}, 2% cross-linked) was obtained from Sigma-Aldrich. Novabiochem™ Merrifield resin (100-200 mesh, 1.3 mmol·g^{-1}, 1% cross-linked) was obtained from EMD Millipore.

NMR spectra were recorded on a Bruker AVANCE 300, Bruker AVANCE II 400 or a Bruker AVANCE III 500. ^{1}H and ^{13}C NMR experiments were recorded using standard NMR techniques and chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Gel-phase ^{31}P{^{1}H} NMR spectra of all resins were recorded unlocked and without additional shimming using dry THF as solvent and chemical shifts are reported relative to 85% H_3PO_4 in water. IR spectra were recorded on a Nicolet Magna 860 IR spectrometer. Elemental analyses were measured by Mikroanalytisches Laboratorium Kolbe in Mülheim an der Ruhr, Germany. Trace metal analyses were performed by the microanalysis service at the University of Edinburgh on a Perkin Elmer Optima 5300 DV ICP-OES. GC measurements where performed on a Thermo Trace GC ultra, see further experimental details for columns and conditions.

General Procedure for the Preparation of Lithium Phosphides

Phosphine (~1.0 eq.) was introduced into a dry Schlenk vessel, dissolved in dry THF and cooled to −78 °C. 1.0 equivalent of *n*-BuLi (1.6 M in hexanes) was added dropwise, upon addition the solution colored bright yellow or orange. After 1 hour the cooling bath was removed and the reaction mixture was allowed to warm up to room temperature and was left for an additional amount of time until full conversion was confirmed by ^{31}P{^{1}H} NMR. The lithium phosphides were directly used in subsequent reactions.

Lithium Phenyl Phosphide

The lithium phosphide was obtained from phenylphosphine (0.35 g, 3.18 mmol, 1.05 eq.) and *n*-BuLi (1.9 mL, 1.6 M in hexanes, 1 eq.) in dry THF (15 mL) as a bright yellow solution (0.18 M). ^{31}P{^{1}H} NMR (162 MHz, THF): δ=−112.4 (s) ppm.

Lithium Cyclohexyl Phosphide

The lithium phosphide was obtained from cyclohexylphosphine (0.35 g, 3.01 mmol, 0.99 eq.) and *n*-BuLi (1.9 mL, 1.6 M in hexanes, 1.0 eq.) in dry THF (12 mL) as a light yellow solution (0.25 M). ^{31}P{^{1}H} NMR (202 MHz, THF): δ=−116.6 (s) ppm.

Lithium Diphenyl Phosphide

The lithium phosphide was obtained from diphenylphosphine (0.37 g, 2.01 mmol, 1.01 eq.) and *n*-BuLi (1.25 mL, 1.6 M in hexanes, 1.0 eq.) in dry THF (6 mL) as a bright orange solution (0.26 M). ^{31}P{^{1}H} NMR (162 MHz, THF): δ=−22.1 (s) ppm.

Lithium Di(o-tolyl) Phosphide

The lithium phosphide was obtained from di(o-tolyl)phosphine (0.22 g, 1.00 mmol, 0.99 eq.) and *n*-BuLi (0.63 mL, 1.6 M in hexanes, 1.0 eq.) in THF (4 mL) as a bright orange solution (0.22 M). ^{31}P{^{1}H} NMR (162 MHz, THF):δ=−41.1 (s) ppm.

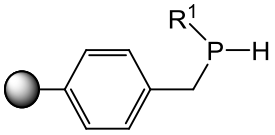
Lithium Dicyclohexyl Phosphide

The lithium phosphide was obtained from dicyclohexylphosphine (1.0 g, 5.01 mmol, 0.98 eq.) and *n*-BuLi (3.2 mL, 1.6 M in hexanes, 1.0 eq.) in dry THF (10 mL) as a bright yellow solution (0.35 M). ^{31}P{^{1}H} NMR (202 MHz, THF): δ=−14.8 (s) ppm.

General Procedure for the Synthesis of Resin-Bound Phosphine-Boranes

Step 1

JandaJel-Cl (**1a-b**, 2.0 g, 0.96 mmol·g^{-1}, 1.92 mmol, 1.0 eq.) or Merrifield resin (**1c**, 2.0 g, 1.3 mmol·g^{-1}, 2.6 mmol, 1.0 eq.) was swollen in THF (50 mL) and cooled to −78 °C. A freshly prepared primary lithium phosphide solution (1.2 eq.), also cooled to −78 °C was added under gentle stirring to avoid mechanical abrasion of the resin. The reaction mixture was allowed to warm up to room temperature and was left overnight without stirring. The supernatant solution was removed and the resin was washed subsequently with three 20 mL portions of THF followed by three 20 mL portions of Et_2O. The product was directly used in the next step without additional purification.

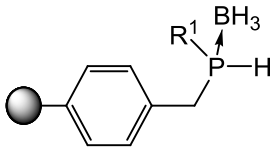


1a : JJ, R^1 = Ph
1b : JJ, R^1 = Cy
1c : MF, R^1 = Ph

1a: Light yellow resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=−41.7 (br m) ppm.
1b: Light yellow resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=−39.2 (s) ppm.
1c: Light yellow resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=−44.6 (br s) ppm.

Step 2

A resin-bound phosphine, synthesized in the previous step, was swollen in THF (50 mL). Next, $BH_3{\cdot}SMe_3$ (2.0 M in toluene, 10 eq.) was added under gentle stirring to avoid mechanical abrasion of the resin. Upon addition the resin colored white and the reaction was stopped when no gas evolution could be observed anymore. Next, the supernatant solution was removed and the resin was washed subsequently with three 20 ml portions of THF followed by three 20 ml portions of Et_2O. The product was dried *in vacuo* yielding a white resin-bound phosphine-borane.



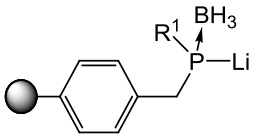
1a·BH$_3$: JJ, R^1 = Ph
1b·BH$_3$: JJ, R^1 = Cy
1c·BH$_3$: MF, R^1 = Ph

1a·BH$_3$: White resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=6.7 (br m) ppm; IR (KBr): $\tilde{\nu}$=2364 cm^{-1} (BH_3); elemental analysis (%): P, 2.37.
1b·BH$_3$: White resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=13.4 (s) ppm; IR (KBr): $\tilde{\nu}$=2383 cm^{-1} (BH_3); elemental analysis (%): P, 2.78.
1c·BH$_3$: White resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=5.6 (br m) ppm; IR (KBr): $\tilde{\nu}$=2389 cm^{-1} (BH_3); elemental analysis (%): P, 2.65.

General Procedure for the Synthesis of Resin-Bound Phosphine-Borane Sulfates

Step 1

A resin-bound phosphine-borane (500 mg) was swollen in THF (20 mL). Next, LDA (2.0 M in THF/heptane/ethylbenzene, 10 eq.) was added under gentle stirring to avoid mechanical abrasion of the resin. Upon addition the resin colored dark brown and was allowed to react for 3 hours. Next, the supernatant solution was removed and the resin was washed subsequently with three 10 mL portions of THF followed by three 10 mL portions of Et_2O. The product was used in the next step without additional purification.

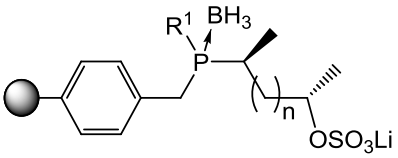


Li·1a·BH$_3$: JJ, R^1 = Ph
Li·1b·BH$_3$: JJ, R^1 = Cy
Li·1c·BH$_3$: MF, R^1 = Ph

Li·1a·BH$_3$: Brown resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=¯39.4 (br s) ppm.
Li·1b·BH$_3$: Brown resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=¯36.9 (br s) ppm.
Li·1c·BH$_3$: Brown resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=¯39.4 (br s) ppm.

Step 2

A lithiated resin-bound phosphine-borane (500 mg) synthesized in the previous step was swollen in THF (15 mL). A cyclic sulfate (1.2 eq.) was azeotropically dried with toluene (3 times), dissolved in THF (5 mL) and subsequently added to the resin under gentle stirring to avoid mechanical abrasion. Upon addition the resin turned from dark brown to yellow and was allowed to react overnight. Next, the supernatant solution was removed and the resin was washed subsequently with three 10 mL portions of THF followed by three 10 mL portions of Et_2O. The product was dried *in vacuo* yielding a light yellow resin.



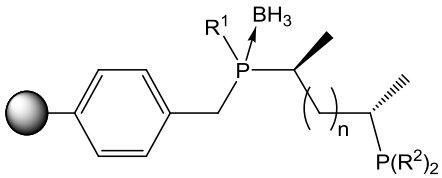
3a·BH$_3$: JJ, R_1 = Ph, n = 1, S_CS_C
3b·BH$_3$: JJ, R_1 = Cy, n = 1, S_CS_C
3c·BH$_3$: JJ, R_1 = Ph, n = 2, S_CS_C
3d·BH$_3$: JJ, R_1 = Ph, n = 2, R_CR_C
3e·BH$_3$: JJ, R_1 = Cy, n = 2, S_CS_C
3f·BH$_3$: MF, R_1 = Ph, n = 2, R_CR_C

3a·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=28.3 (br s) ppm; IR (KBr): $\tilde{\nu}$=2378 (BH_3),1257 (S=O) cm^{-1}; elemental analysis (%): P, 3.03, S, 2.40.
3b·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=30.7 (br s) ppm; IR (KBr): $\tilde{\nu}$=2381 (BH_3), 1249 (S=O) cm^{-1}; elemental analysis (%): P, 1.96, S, 2.84.
3c-d·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=28.0 (br s) ppm; IR (KBr): $\tilde{\nu}$=2374 (BH_3), 1249 (S=O) cm^{-1}; elemental analysis (%): P, 2.61, S, 2.20.
3e·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=30.5 (br s) ppm; IR (KBr): $\tilde{\nu}$=2372 (BH_3), 1247 (S=O) cm^{-1}; elemental analysis (%): P, 2.51, S, 2.14.
3f·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=28.3 (br s) ppm; IR (KBr): $\tilde{\nu}$=2372 (BH_3), 1254 (S=O) cm^{-1}; elemental analysis (%): P, 2.81, S, 2.88.

General Procedure for the Synthesis of Resin-Bound Diphosphines

Step 1

A resin-bound phosphine-borane sulfate (250 mg) was swollen in THF (10 mL) and cooled to −78 °C. A freshly prepared secondary lithium phosphide solution (10 eq.), also cooled to −78 °C was added under gentle stirring to avoid mechanical abrasion of the resin. The reaction mixture was allowed to warm up to room temperature and was left overnight without stirring. The supernatant solution was removed and the resin was washed subsequently with three 5 mL portions of THF followed by three 5 mL portions of Et_2O. The product was dried *in vacuo* yielding a light yellow/orange resin-bound diphosphine. The product was used directly in the next step without further purification.

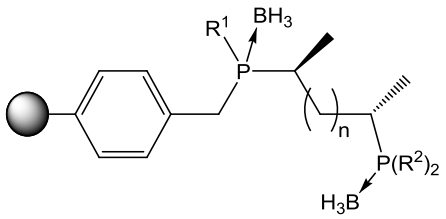


4a·BH$_3$: JJ, R^1 = Ph, n = 1, S_CS_C, R^2 = Ph
4b·BH$_3$: JJ, R^1 = Cy, n = 1, S_CS_C, R^2 = Ph
4c·BH$_3$: JJ, R^1 = Ph, n = 2, S_CS_C, R^2 = Ph
4d·BH$_3$: JJ, R^1 = Ph, n = 2, R_CR_C, R^2 = Ph
4e·BH$_3$: JJ, R^1 = Cy, n = 2, S_CS_C, R^2 = Ph
4f·BH$_3$: JJ, R^1 = Cy, n = 1, S_CS_C, R^2 = *o*-tol
4g·BH$_3$: JJ, R^1 = Ph, n = 2, S_CS_C, R^2 = *o*-tol
4h·BH$_3$: JJ, R^1 = Cy, n = 2, S_CS_C, R^2 = *o*-tol
4i·BH$_3$: JJ, R^1 = Ph, n = 2, S_CS_C, R^2 = Cy
4j·BH$_3$: JJ, R^1 = Cy, n = 2, S_CS_C, R^2 = Cy
4k·BH$_3$: MF, R^1 = Ph, n = 2, R_CR_C, R^2 = Ph

4a·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=−0.2 (s), 27.9 (br s) ppm.
4b·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=−0.6 (s), 31.5 (br s) ppm.
4c-d·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=−1.7 (s), 27.6 (br s) ppm.
4e·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (162 MHz, THF): δ=−2.2 (s), 30.9 (br s) ppm.
4f·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=−28.6 (s), 27.5 (br s) ppm.
4g·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=−27.2 (s), 31.5 (br s) ppm.
4h·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=−28.8 (s), 31.2 (br s) ppm.
4i·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=15.0 (br m), 22.4 (br m) ppm.
4j·BH$_3$: Light yellow resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=20.4 (br m), 26.3 (br m) ppm.
4k·BH$_3$: Light orange resin: $^{31}P\{^1H\}$ NMR (202 MHz, THF): δ=−1.7 (s), 27.8 (br s) ppm.

Step 2

A resin-bound diphosphine, synthesized in the previous step, was swollen in THF (10 mL). Next, $BH_3{\cdot}SMe_3$ (2.0 M in toluene, 10 eq.) was added under gentle stirring to avoid mechanical abrasion of the resin. Upon addition the resin colored white and the reaction was stopped when no gas evolution could be observed anymore. Next, the supernatant solution was removed and the resin was washed subsequently with three 5 mL portions of THF followed by three 5 mL portions of Et_2O. The product was dried *in vacuo* yielding a white resin−bound diphosphine-borane.



4a·(BH$_3$)$_2$: JJ, R^1 = Ph, n = 1, S_CS_C, R^2 = Ph
4b·(BH$_3$)$_2$: JJ, R^1 = Cy, n = 1, S_CS_C, R^2 = Ph
4c·(BH$_3$)$_2$: JJ, R^1 = Ph, n = 2, S_CS_C, R^2 = Ph
4d·(BH$_3$)$_2$: JJ, R^1 = Ph, n = 2, R_CR_C, R^2 = Ph
4e·(BH$_3$)$_2$: JJ, R^1 = Cy, n = 2, S_CS_C, R^2 = Ph
4f·(BH$_3$)$_2$: JJ, R^1 = Cy, n = 1, S_CS_C, R^2 = *o*-tol
4g·(BH$_3$)$_2$: JJ, R^1 = Ph, n = 2, S_CS_C, R^2 = *o*-tol
4h·(BH$_3$)$_2$: JJ, R^1 = Cy, n = 2, S_CS_C, R^2 = *o*-tol
4i·(BH$_3$)$_2$: JJ, R^1 = Ph, n = 2, S_CS_C, R^2 = Cy
4j·(BH$_3$)$_2$: JJ, R^1 = Cy, n = 2, S_CS_C, R^2 = Cy
4k·(BH$_3$)$_2$: MF, R^1 = Ph, n = 2, R_CR_C, R^2 = Ph

4a·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=25.4 (br s), 27.9 (br s) ppm; IR (KBr): $\tilde{\nu}$=2380 cm^{-1} (BH$_3$); elemental analysis (%): P, 3.29.
4b·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=25.2 (br s), 31.4 (br s) ppm; IR (KBr): $\tilde{\nu}$=2381 cm^{-1} (BH$_3$); elemental analysis (%): P, 3.70.
4c-d·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=22.2 (br s), 25.3 (br s) ppm; IR (KBr): $\tilde{\nu}$=2377 cm^{-1} (BH$_3$); elemental analysis (%): P, 3.51.
4e·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (162 MHz, THF): δ=24.2 (br s), 31.3 (br s) ppm; IR (KBr): $\tilde{\nu}$=2377 cm^{-1} (BH$_3$).; elemental analysis (%): P, 2.32.
4f·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (162 MHz, THF): δ=26.1 (br s), 31.7 (br s) ppm; IR (KBr): $\tilde{\nu}$=2384 cm^{-1} (BH$_3$); elemental analysis (%): P, 3.28.
4g·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=25.1 (br s), 27.4 (br s) ppm; IR (KBr): $\tilde{\nu}$=2377 cm^{-1} (BH$_3$); elemental analysis (%): P, 3.40.
4h·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=25.0 (br s), 30.7 (br s) ppm; IR (KBr): $\tilde{\nu}$=2372 cm^{-1} (BH$_3$); elemental analysis (%): P, 3.60.
4i·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=19.3 (m), 22.4 (m) ppm; IR (KBr): $\tilde{\nu}$=2381 cm^{-1} (BH$_3$); elemental analysis (%): P, 2.39.
4j·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=21.7 (m), 26.3 (m) ppm; IR (KBr): $\tilde{\nu}$=2370 cm^{-1} (BH$_3$); elemental analysis (%): P, 2.22.
4k·(BH$_3$)$_2$: White resin: ^{31}P{^{1}H} NMR (202 MHz, THF): δ=23.8 (br s), 26.9 (br s) ppm; IR (KBr): $\tilde{\nu}$=2372 cm^{-1} (BH$_3$); elemental analysis (%): P, 4.91.

General Procedure for the Synthesis of Cyclic Sulfates

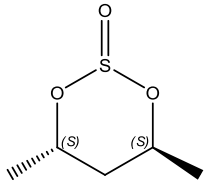
Step 1

To a solution of diol (1.0 eq.) and Et$_3$N (3.0 eq.) in CH$_2$Cl$_2$ at 0° C was slowly added SOCl$_2$ (1.1 eq.). The mixture was allowed to warm up to room temperature and was stirred for an additional 60 minutes. Next, the reaction was quenched by addition of 20 ml of ice water. The two layers were separated and the aqueous phase was extracted three times with 10 ml of Et$_2$O. The combined organic layers were washed with a 6% NaHCO$_3$ solution, brine and H$_2$O respectively. Next, the organic layer was dried with MgSO$_4$, filtered and the solvent was removed *in vacuo*. The obtained cyclic sulfite was used in the next reaction step without further purification.

Step 2

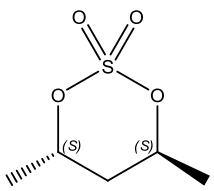
To a cooled solution (0 °C) of a previously prepared cyclic sulfite in a mixture of CH$_2$Cl$_2$ (10 ml) and MeCN (10 ml) was added RuCl$_3$·xH$_2$O (0.01 eq.) followed by the addition of a solution of NaIO$_4$ (1.5 eq.) in water (15 ml). The resulting two layer mixture was stirred at 0 °C for 15 minutes and allowed to warm to room temperature and was stirred for an additional 45 minutes during which the reaction mixture turned from dark brown to orange. Next, Et$_2$O (50 ml) was added and the two phases were separated followed by extraction of the aqueous layer with Et$_2$O. The organic layers were combined and washed subsequently with a saturated NaHCO$_3$ solution, brine and water. The organic layer was dried with MgSO$_4$, filtered and the solvent was removed *in vacuo*. The cyclic sulfates were obtained as white crystals after crystallization from Et$_2$O/pentanes.

*(4S,6S)-4,6-dimethyl-1,3,2-Dioxathiane, 2,2-dioxide (**2a**)*



Step 1

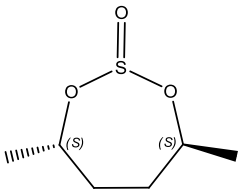
The cyclic sulfite was obtained from (2*S*,4*S*)-2,4-heptanediol (1.00 g, 9.6 mmol, 1 eq.), Et$_3$N (2.91 g, 28.8 mmol, 3 eq.) and SOCl$_2$ (1.26 g, 10.6 mmol, 1.1 eq.) in 50 ml of CH$_2$Cl$_2$ as a pale yellow oil and was directly used in the second step. Yield: 1.23 g (85.3%).



Step 2

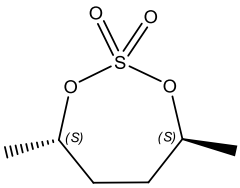
The cyclic sulfate was obtained from the corresponding cyclic sulfite (1.23 g, 8.2 mmol, 1 eq.), $RuCl_3 \cdot xH_2O$ (19.9 mg, 0.1 mmol, 0.01 eq.), $NaIO_4$ (3.08 g, 14.4 mmol, 1.8 eq.) in a mixture of CH_2Cl_2 (10 ml), MeCN (10 ml) and H_2O (15 ml) as white needles after crystallization from Et_2O/pentanes. Yield: 1.23 g (90.3%). NMR data matches literature values[1]: ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.62 (6H, d, *J* = 6.6 Hz, 2xCH_3), 2.06 (2H, t, *J* = 5.6 Hz, OCHCH_2) and 5.11 (2H, sext, *J* = 6.2 Hz, 2xOC*H*) ppm.

(4S,7S)-4,7-Dimethyl-1,3,2-dioxathiepane 2,2-dioxide (**2b**)



Step 1

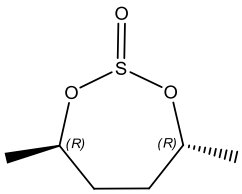
The cyclic sulfite was obtained from (2*S*,5*S*)-2,5-hexanediol (1.00 g, 8.5 mmol, 1 eq.), Et_3N (2.57 g, 25.4 mmol, 3 eq.) and $SOCl_2$ (1.11 g, 9.3 mmol, 1.1 eq.) in 50 ml of CH_2Cl_2 as a pale yellow oil and was directly used in the second step. Yield: 1.16 g (83.5%).



Step 2

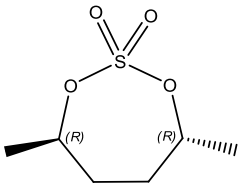
The cyclic sulfate was obtained from the corresponding cyclic sulfite (1.16 g, 7.1 mmol, 1 eq.), $RuCl_3 \cdot xH_2O$ (17.6 mg, 0.08 mmol, 0.01 eq.), $NaIO_4$ (2.72 g, 12.7 mmol, 1.8 eq.) in a mixture of CH_2Cl_2 (10 ml), MeCN (10 ml) and H_2O (15 ml) as white needles after crystallization from Et_2O/pentanes. Yield: 1.08 g (84.4%). NMR data matches literature values[2]. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.45 (6H, d, *J* = 6.4 Hz, 2xCH_3), 1.87-2.06 (4H, m, 2xOCHCH_2) and 4.80-4.88 (2H, m, 2xOC*H*) ppm.

(4R,7R)-4,7-Dimethyl-1,3,2-dioxathiepane 2,2-dioxide (**2c**)



Step 1

The cyclic sulfite was obtained from (2*R*,5*R*)-2,5-hexanediol (1.00 g, 8.5 mmol, 1 eq.), Et_3N (2.57 g, 25.4 mmol, 3 eq.) and $SOCl_2$ (1.11 g, 9.3 mmol, 1.1 eq.) in 50 ml of CH_2Cl_2 as a pale yellow oil and was directly used in the second step. Yield: 1.13 g (81.3%).



Step 2

The cyclic sulfate was obtained from the corresponding cyclic sulfite (1.16 g, 6.9 mmol, 1 eq.), $RuCl_3 \cdot xH_2O$ (15.2 mg, 0.07 mmol, 0.01 eq.), $NaIO_4$ (2.66 g, 12.4 mmol, 1.8 eq.) in a mixture of CH_2Cl_2 (10 ml), MeCN (10 ml) and H_2O (15 ml) as white needles after crystallization from Et_2O/pentanes. Yield: 1.03 g (80.6%). NMR data matches literature values[2]. ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.45 (6H, d, *J* = 6.4 Hz, 2xCH_3), 1.87-2.04 (4H, m, 2xOCHCH_2) and 4.80-4.86 (2H, m, 2xOC*H*) ppm.

General Procedure for Asymmetric Hydrogenation Experiments

Deprotection of Supported Diphosphine-Boranes

A resin-bound diphosphine-borane (100 mg, approximately 60 µmol) was suspended in THF (5 mL) and a solution of 1,4-Diazabicyclo[2.2.2]octane (DABCO, 10 eq.) in THF (5 mL) was added. The reaction was heated to 40 °C and left overnight without stirring. After complete deprotection was confirmed by ^{31}P NMR, the supernatant solution was removed and the resin was washed subsequently with three 5 mL portions of THF followed by three 5 mL portions of Et_2O. The product was dried *in vacuo* yielding a white deprotected resin−bound diphosphine. The product was used directly in the next step without further purification.

Asymmetric hydrogenation

The hydrogenation experiments were performed in a stainless steel autoclave charged with an insert suitable for 10 reaction vessels including Teflon mini stirring bars. In a typical experiment, a reaction vessel was charged with a deprotected resin-bound diphosphine (5 mg, approximately 3.0 µmol) and a solution of $[Rh(COD)_2]BF_4$ (3.0 µmol) in CH_2Cl_2 (1 mL) and the heterogeneous mixture was allowed to stir gently for 4 h. The supernatant solution was removed and the resulting orange resin was washed subsequently with three 1 mL portions of THF followed by three 1 mL portions of Et_2O. Next, a solution of substrate (0.5 mL, 0.18 M, 30 eq.) in THF was added to the reaction vessel. Subsequently, the autoclave was purged three times with 5 bar of H_2 and then pressurized to 1.2 bar. The reaction mixtures were gently stirred at 25 °C. After 16 h, the autoclave was depressurized and the reaction mixtures were filtered over a plug of silica. Prior to GC measurements substrate **II** and its products were derivatized using (trimethylsilyl)diazomethane (2 M in diethyl ether), in essence yielding substrate **III**. The conversion and the enantiomeric excess were determined by chiral GC using the following column and conditions:

I: Permabond-L-Chirasil-Val column: T_0 = 90 °C, ΔT = 8 °C min^{-1} to 170 °C, t_R (**I**) = 2.4 min. t_R (*R*) = 3.3 min, t_R (*S*) = 3.7 min.

III: Permabond-L-Chirasil-Val column: T_0 = 90 °C, ΔT = 8 °C min^{-1} to 150 °C, hold for 15 min, then ΔT = 8 °C min^{-1} to 180 °C, hold for 15 min, t_R (*R*) = 14.2 min. t_R (*S*) = 15.6 min, t_R (**III**) = 26.7 min.

General Procedure for Catalyst Recycling Experiments

The recycling experiments were performed in a glass Schlenk vessel including stirring bar. In a typical experiment, a reaction vessel was charged with a deprotected resin-bound diphosphine (15 mg, approximately 9.0 µmol) and a solution of $[Rh(COD)_2]BF_4$ (9.0 µmol) in CH_2Cl_2 (2 mL) and the heterogeneous mixture was allowed to stir gently for 4 h. The supernatant solution was removed and the resulting orange resin was washed subsequently with three 1 mL portions of THF followed by three 1 mL portions of Et_2O. Next, substrate stock solution (1.5 mL, 0.18 M, 30 eq.) in THF was added to the reaction vessel. The hydrogenation was performed under a flow of H_2 while gently being stirred at 25 °C. After 30 min, the supernatant was removed and submitted for analysis and the resin was washed 3 times with 1.5 mL of substrate stock solution while maintaining a H_2 atmosphere. Subsequently, a new reaction cycle was started by adding 1.5 mL of fresh substrate stock solution. The reaction mixtures were filtered over a plug of silica and submitted for chiral GC analysis, for columns and conditions see above.

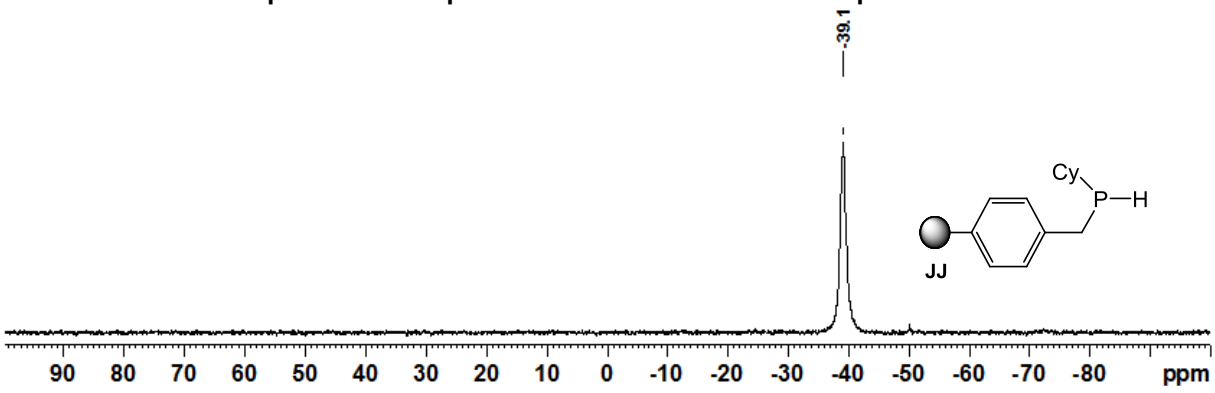
***In-Situ* Complexation Study**

50 mg of deprotected supported diphosphines was suspended in 2.5 mL of THF and 1.0 eq. of. $[Rh(COD)_2]BF_4$ in 2.5 mL of THF was added to the resin. The progress of the complexation was monitored using $^{31}P\{^1H\}$ NMR. The two peaks corresponding the non-complexated ligand disappeared in a 1:1 ratio indicating bidentate coordination and full complexation was observed within 3 hours. Moreover, a color change from white to bright orange was observed upon complexation.

ICP-OES Sample Preparation

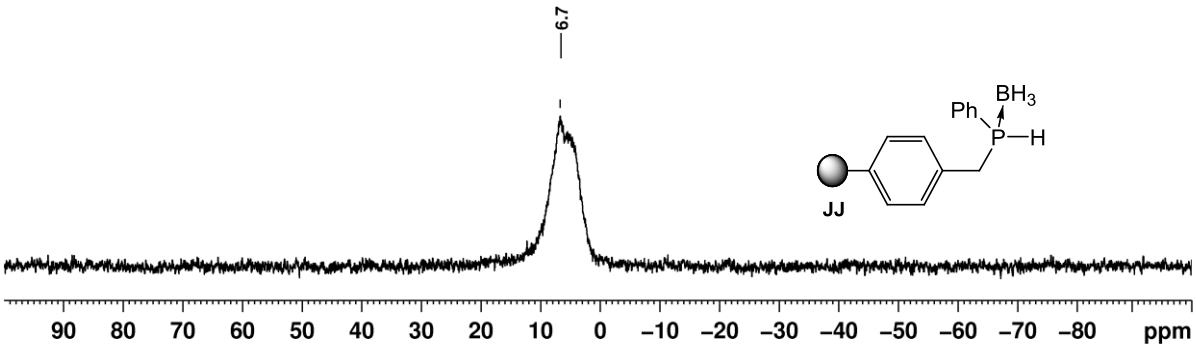
After each recycling experiment the supernatant was removed and the solvent was removed *in vacuo*. The residue was then dissolved in 1 mL of aqua regia and heated to 80 °C for 1h. Next the solution was filtered through glass wool, diluted with water to 10 mL and submitted for ICP-OES analysis

^{31}P Gel-Phase NMR Spectrum of Representative Resin−Bound Phosphine 1b

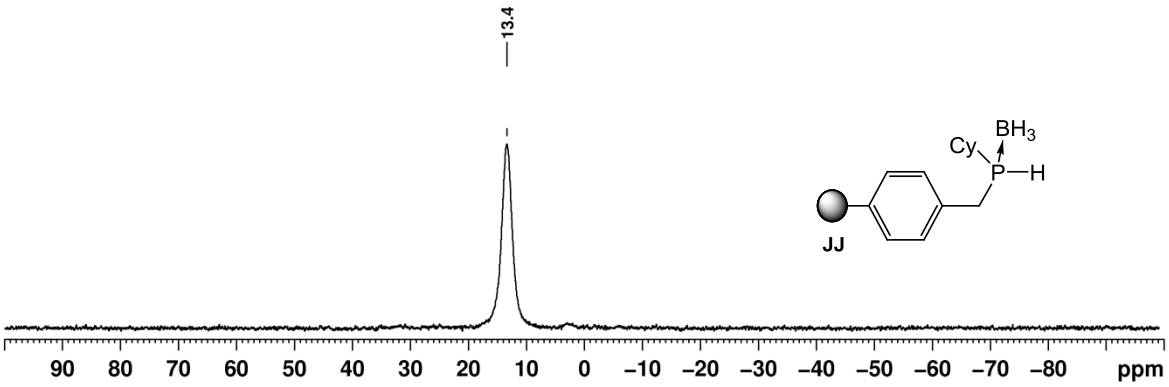


^{31}P{^{1}H} NMR of resin **1b·BH3** (202 MHz, THF).

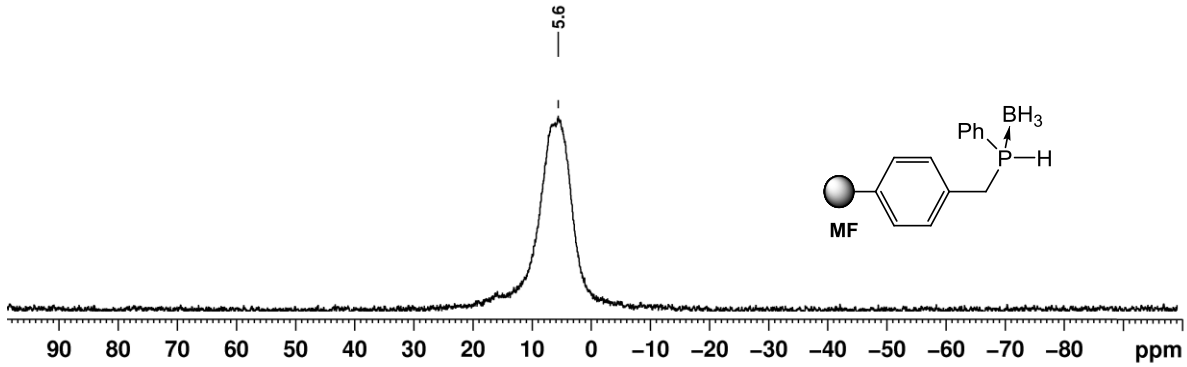
^{31}P Gel-Phase NMR Spectra of Resin−Bound Phosphine-Boranes 1a-c·BH$_3$



^{31}P{^{1}H} NMR of resin **1a·BH$_3$** (202 MHz, THF).

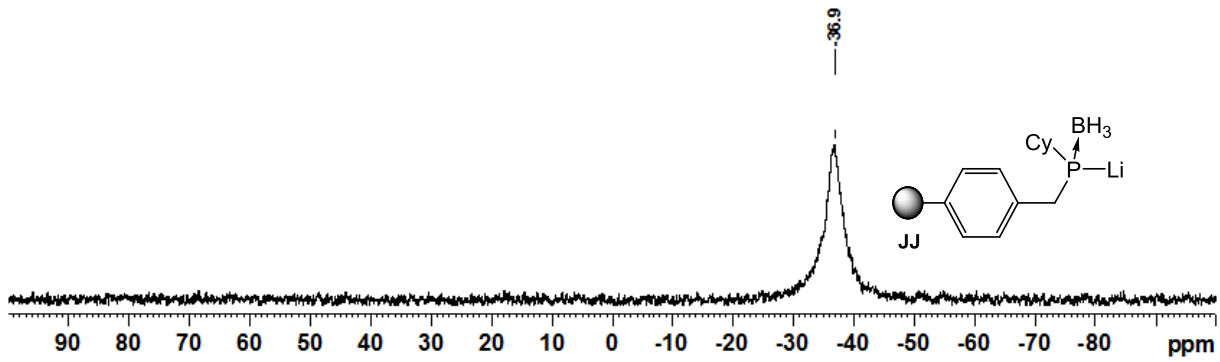


^{31}P{^{1}H} NMR of resin **1b·BH$_3$** (202 MHz, THF).



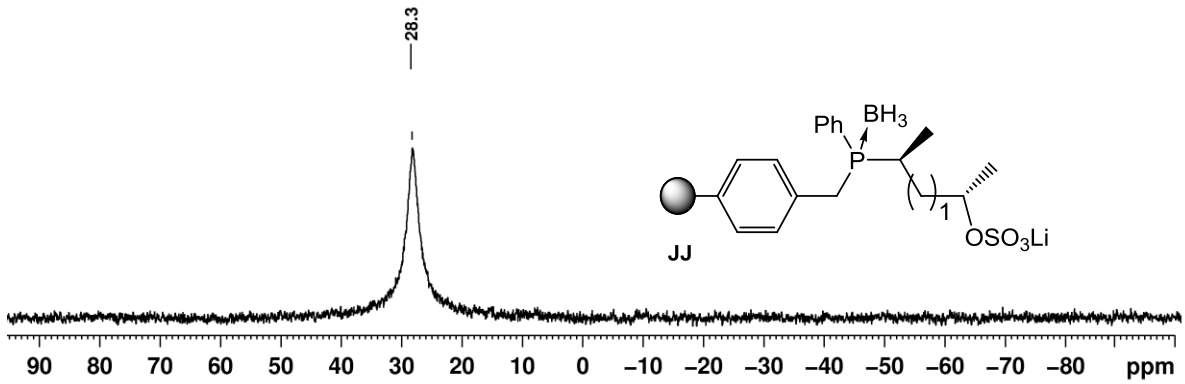
$^{31}P\{^{1}H\}$ NMR of resin **1c·BH$_3$** (162 MHz, THF).

^{31}P Gel-Phase NMR Spectrum of Representative Lithiated Resin−Bound Phosphine Li·1b·BH$_3$

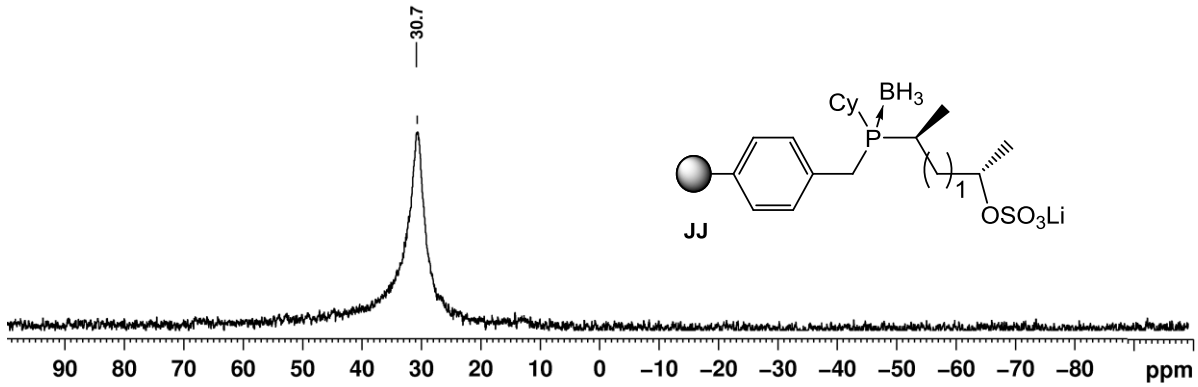


$^{31}P\{^{1}H\}$ NMR of resin **Li·1b·BH$_3$** (162 MHz, THF).

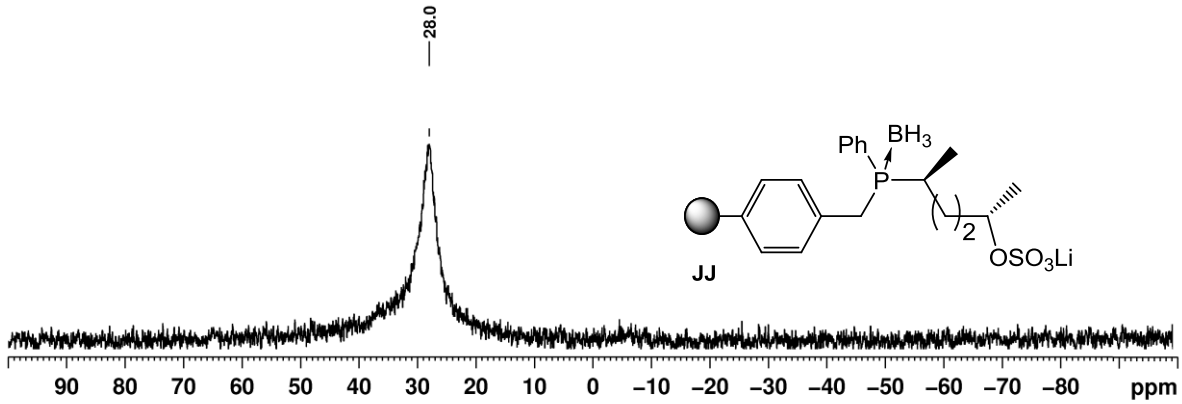
^{31}P Gel-Phase NMR Spectra of Resin−Bound Phosphine-Borane Sulfates 3a-f·BH$_3$



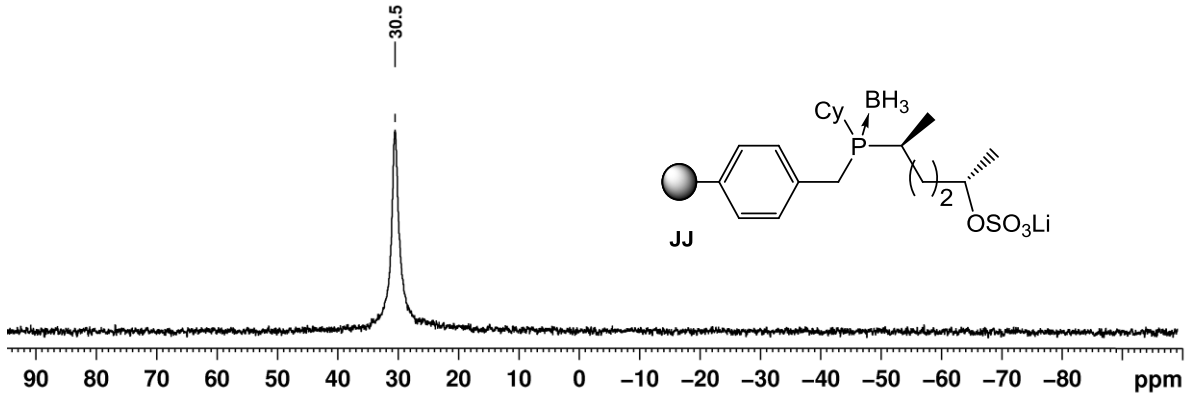
$^{31}P\{^{1}H\}$ NMR of resin **3a·BH$_3$** (202 MHz, THF).



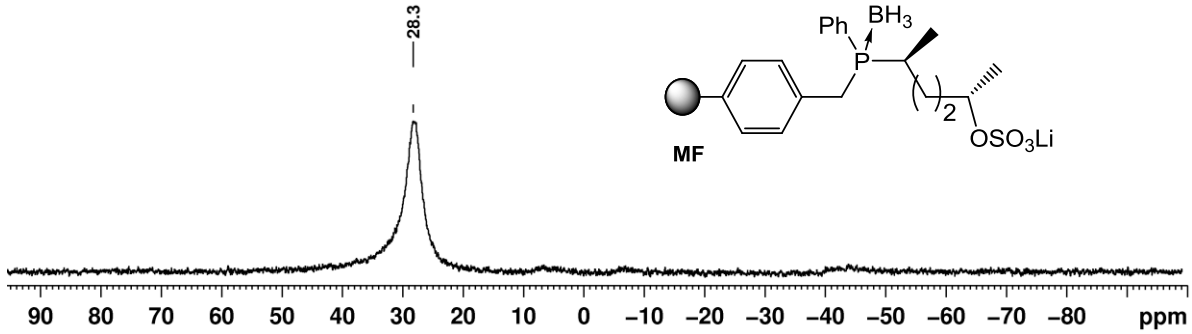
$^{31}P\{^{1}H\}$ NMR of resin **3b·BH$_3$** (162 MHz, THF).



$^{31}P\{^{1}H\}$ NMR of resin **3c-d·BH$_3$** (202 MHz, THF).

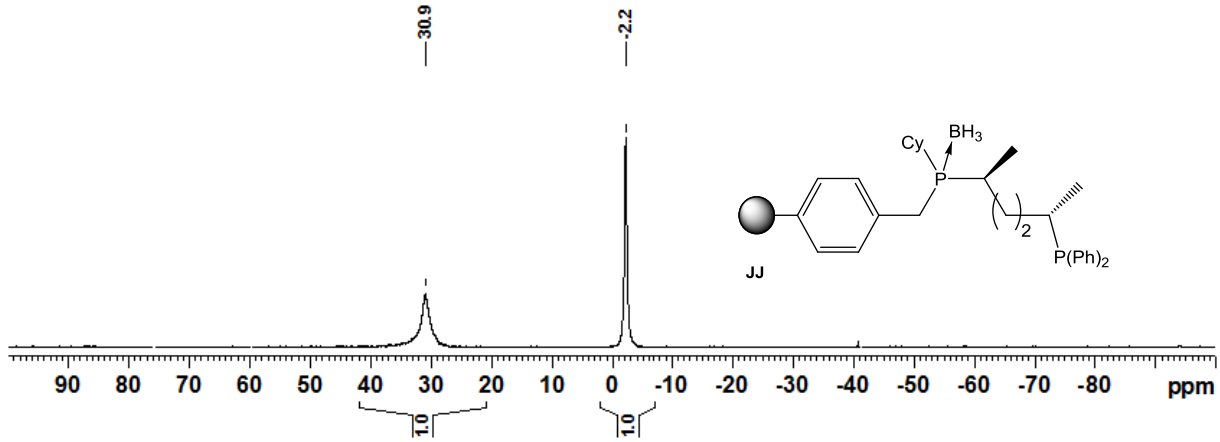


$^{31}P\{^{1}H\}$ NMR of resin **3e·BH$_3$** (202 MHz, THF).



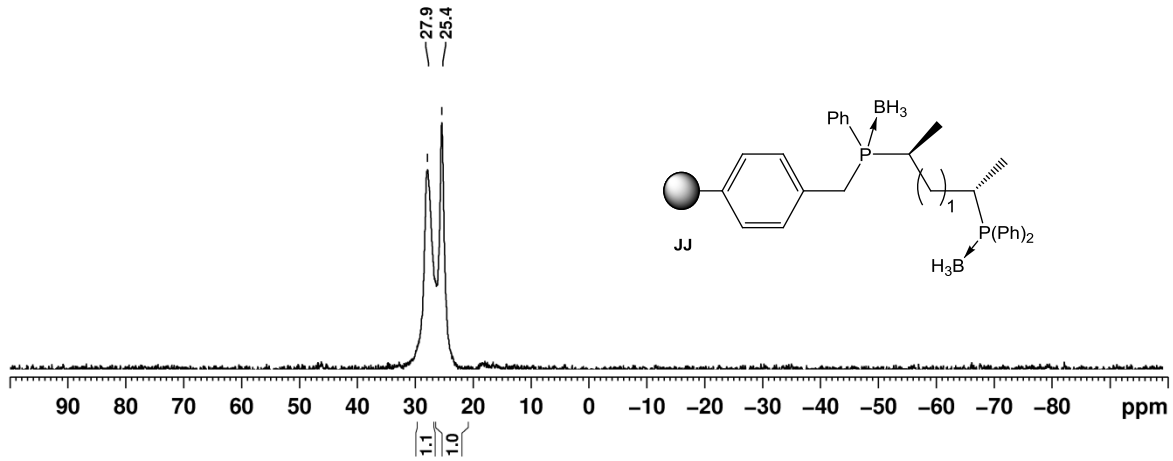
$^{31}P\{^1H\}$ NMR of resin **3f·BH$_3$** (202 MHz, THF).

^{31}P Gel-Phase NMR Spectrum of Representative Resin−Bound Diphosphine-Borane 4e·BH$_3$

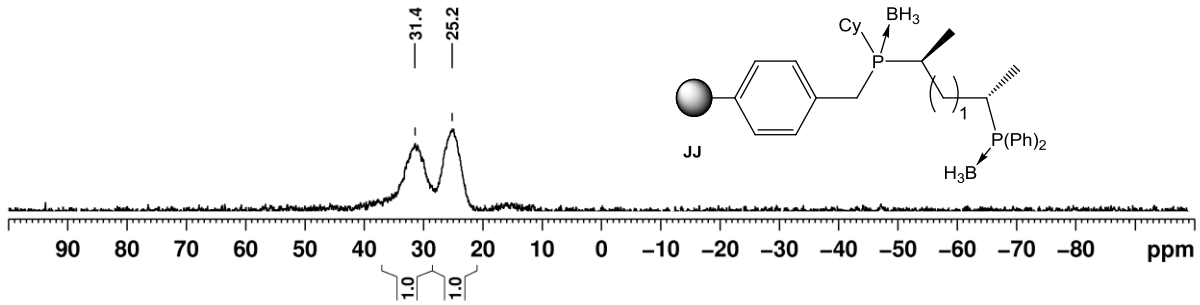


$^{31}P\{^1H\}$ NMR of resin **4e·(BH$_3$)** (162 MHz, THF).

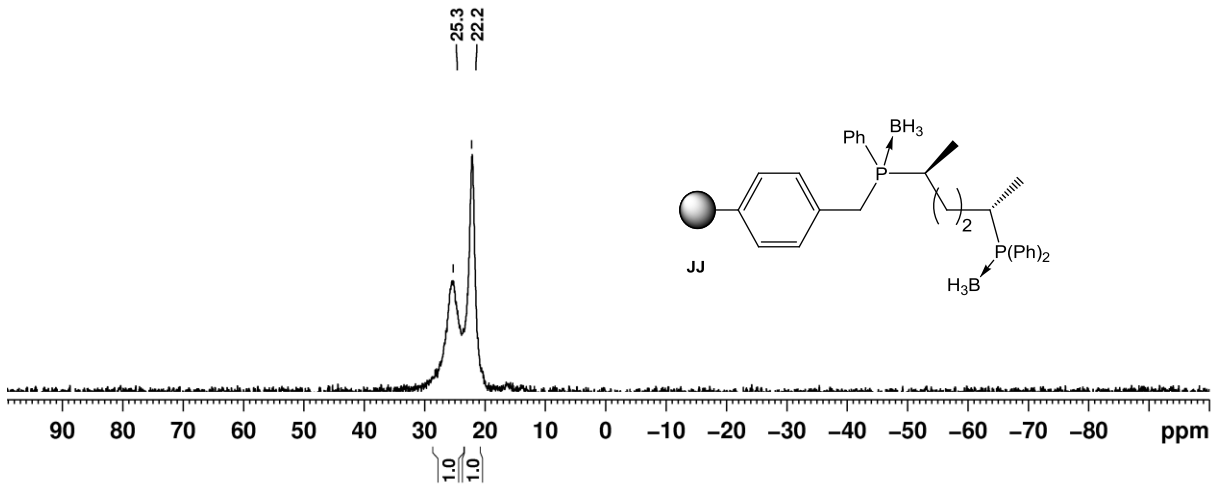
^{31}P Gel-Phase NMR Spectra of Resin−Bound Diphosphine-Diboranes 4a-k·(BH$_3$)$_2$



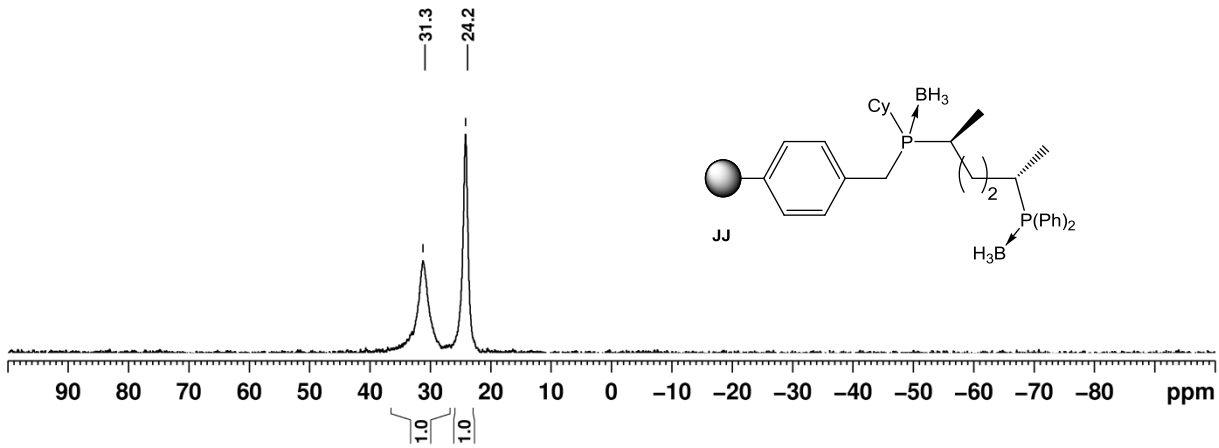
$^{31}P\{^1H\}$ NMR of resin **4a·(BH$_3$)$_2$** (202 MHz, THF).



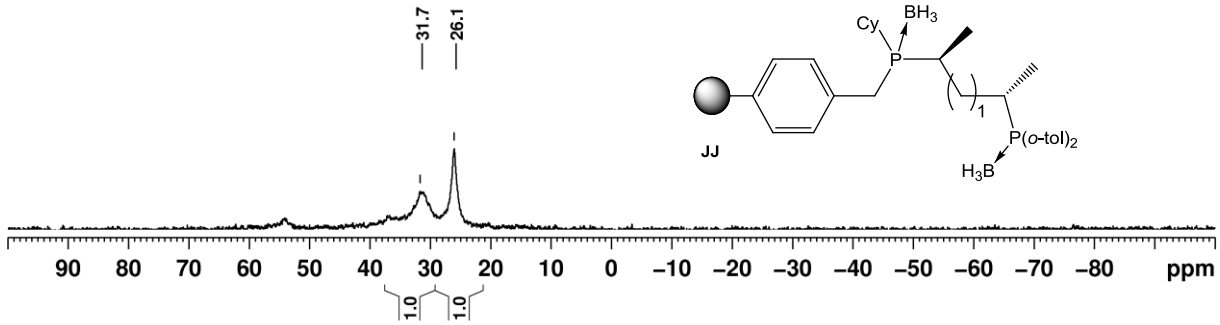
$^{31}P\{^{1}H\}$ NMR of resin **4b·(BH$_3$)$_2$** (202 MHz, THF).



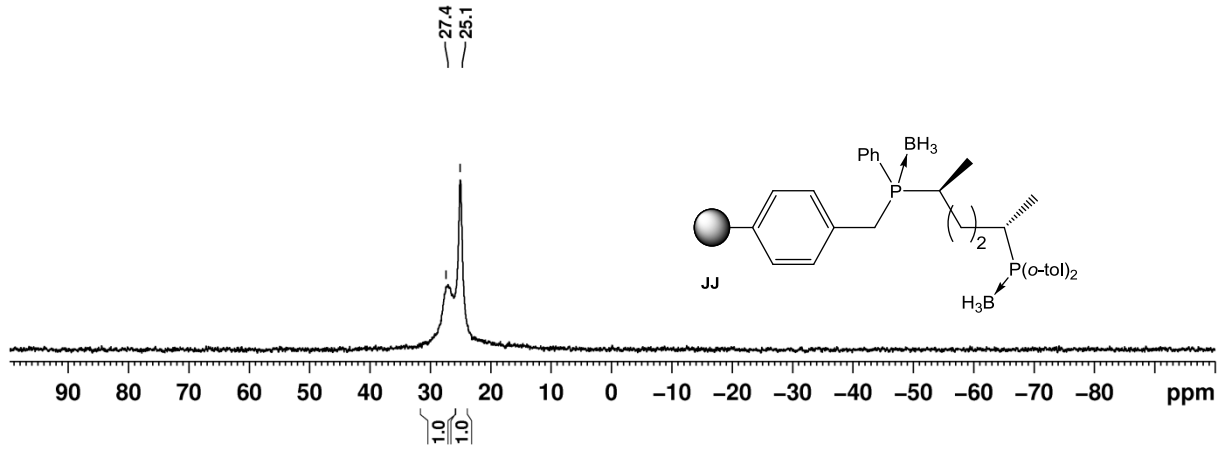
$^{31}P\{^{1}H\}$ NMR of resin **4c-d·(BH$_3$)$_2$** (162 MHz, THF).



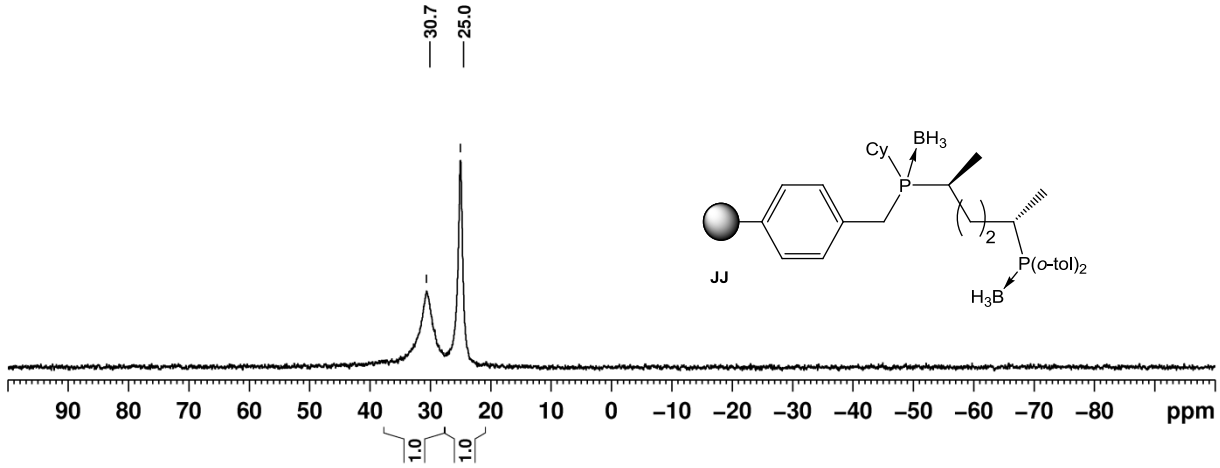
$^{31}P\{^{1}H\}$ NMR of resin **4e·(BH$_3$)$_2$** (162 MHz, THF).



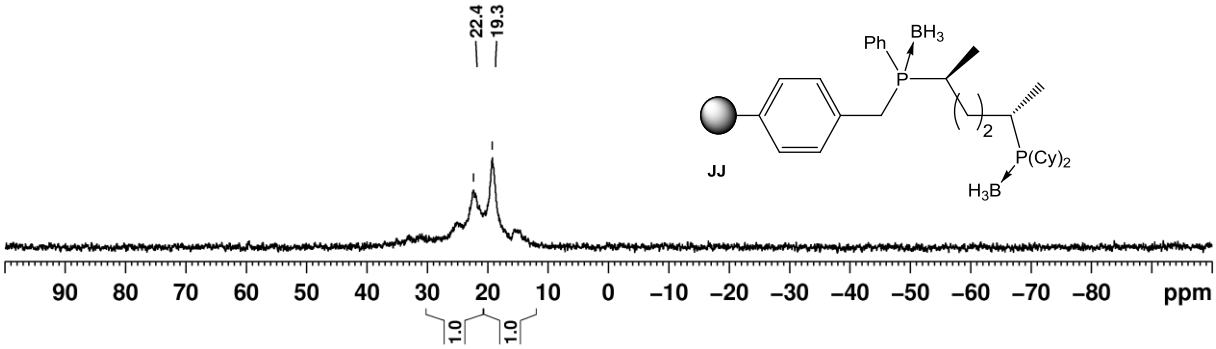
$^{31}P\{^{1}H\}$ NMR of resin **4f·(BH$_3$)$_2$** (202 MHz, THF).



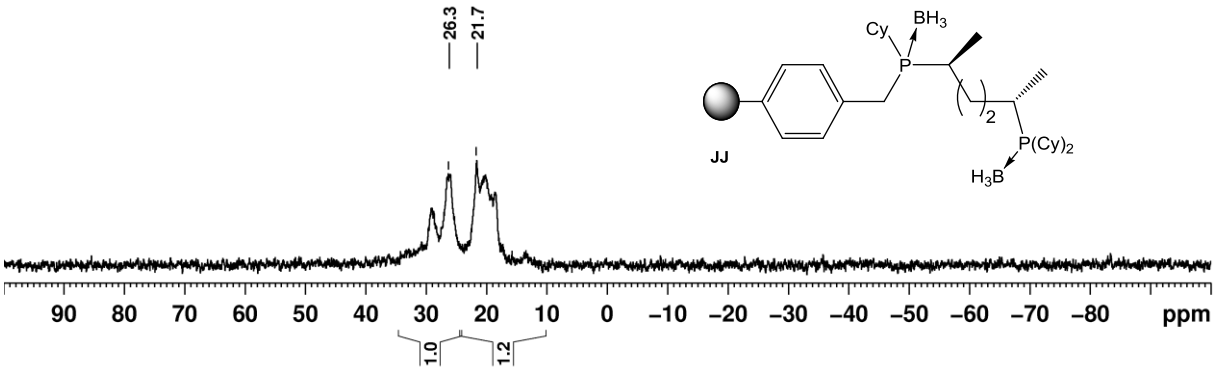
$^{31}P\{^{1}H\}$ NMR of resin **4g·(BH$_3$)$_2$** (202 MHz, THF).



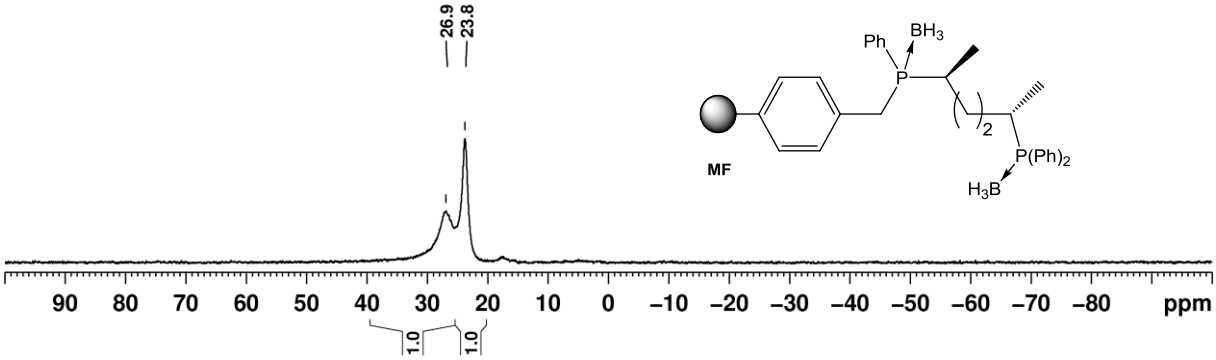
$^{31}P\{^{1}H\}$ NMR of resin **4h·(BH$_3$)$_2$** (202 MHz, THF).



$^{31}P\{^{1}H\}$ NMR of resin **4i·(BH$_3$)$_2$** (202 MHz, THF).

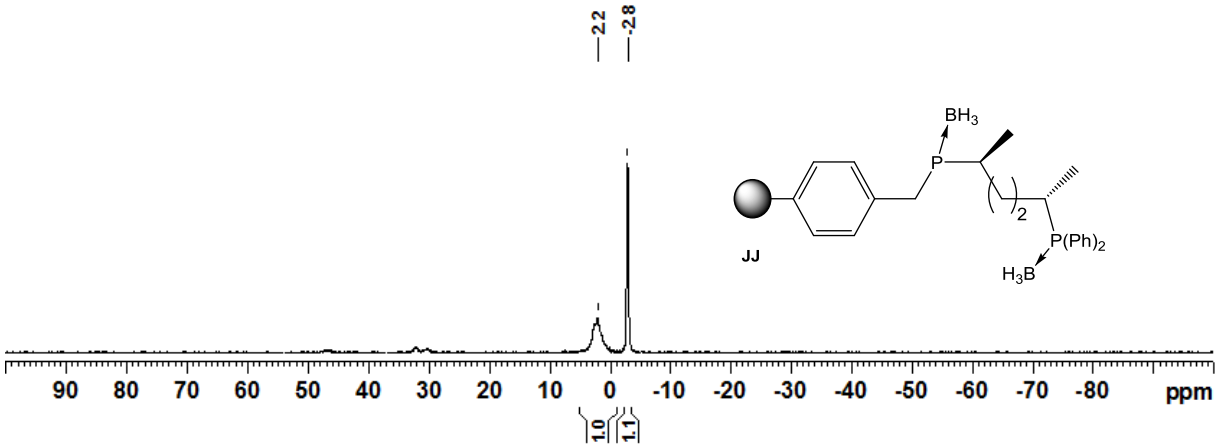


$^{31}P\{^{1}H\}$ NMR of resin **4j·(BH$_3$)$_2$** (202 MHz, THF).



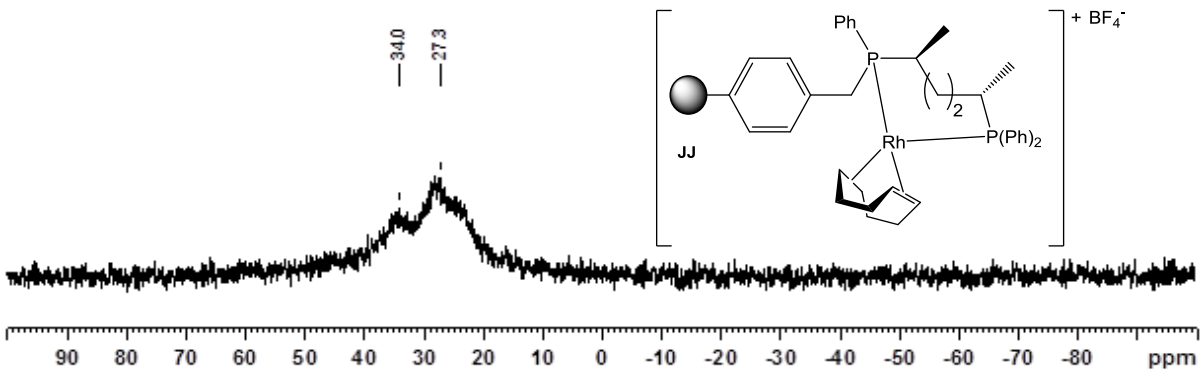
$^{31}P\{^{1}H\}$ NMR of resin **4k·(BH$_3$)$_2$** (202 MHz, THF).

^{31}P Gel-Phase NMR Spectrum of Representative Resin−Bound Diphosphine 4e

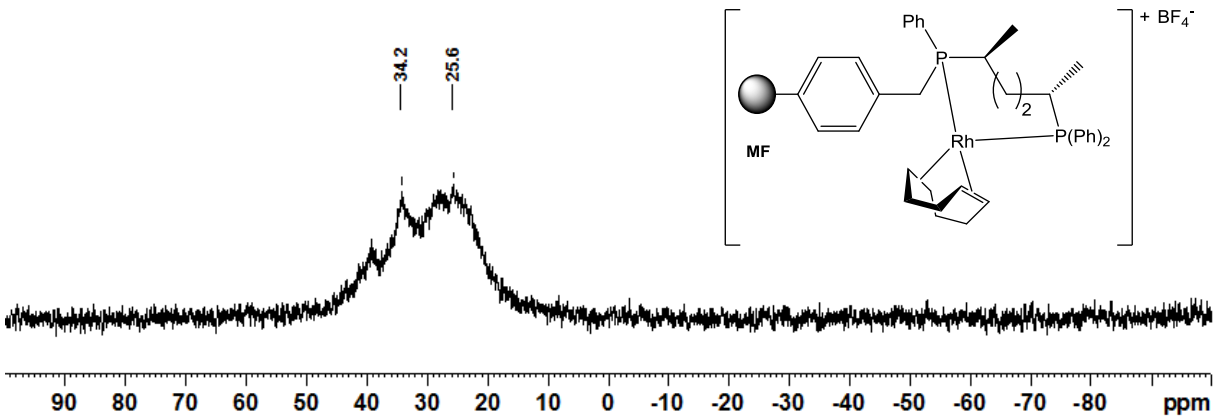


^{31}P{^{1}H} NMR of resin **4e** (202 MHz, THF).

^{31}P Gel-Phase NMR Spectra of Representative Rh Complexes of Resin−Bound Diphosphines

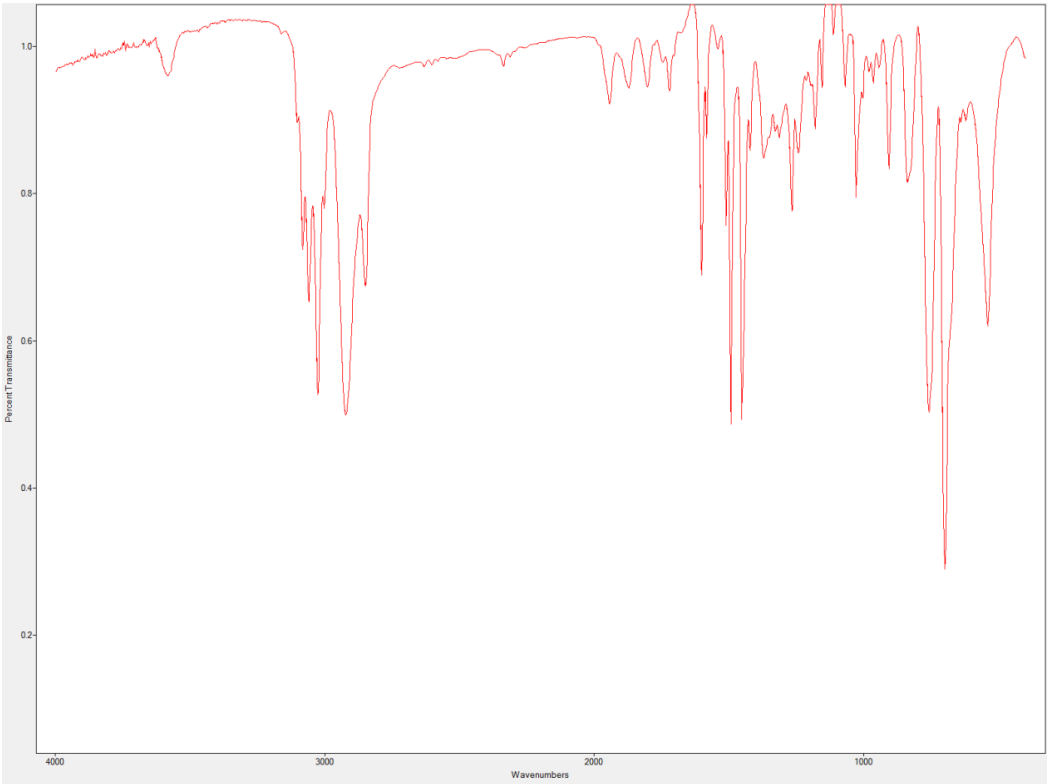


^{31}P{^{1}H} NMR of Rh-complexated resin **4c** (202 MHz, THF).

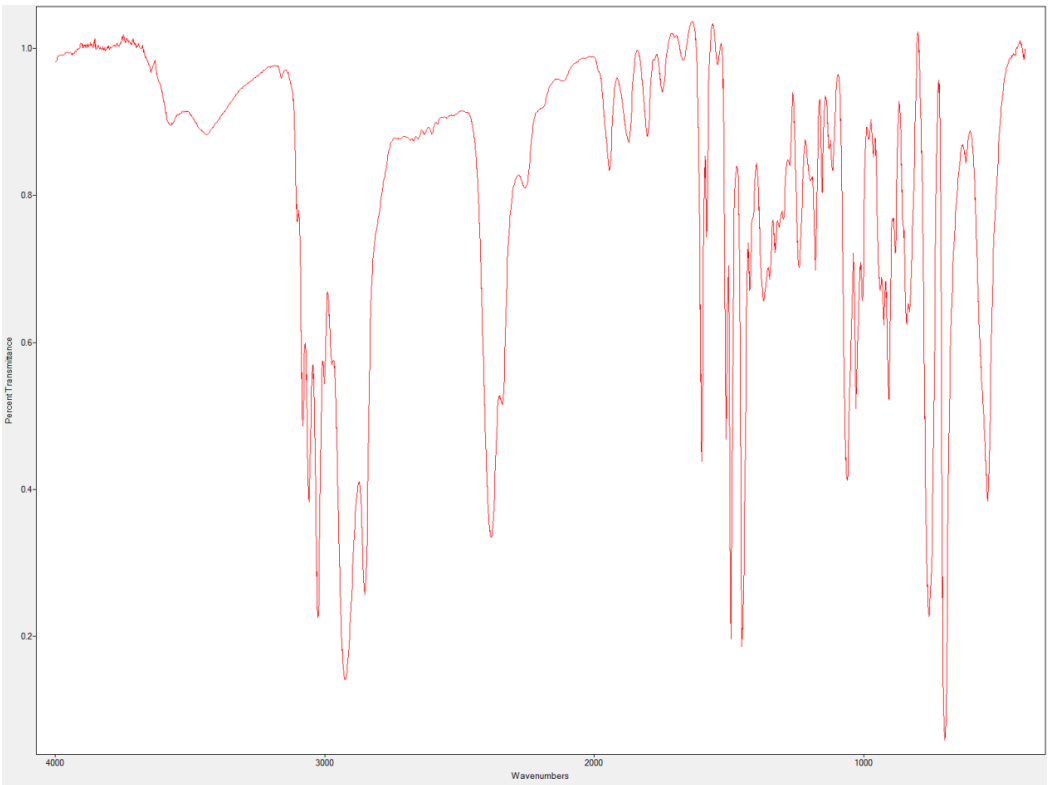


^{31}P{^{1}H} NMR of Rh-complexated resin **4k** (202 MHz, THF).

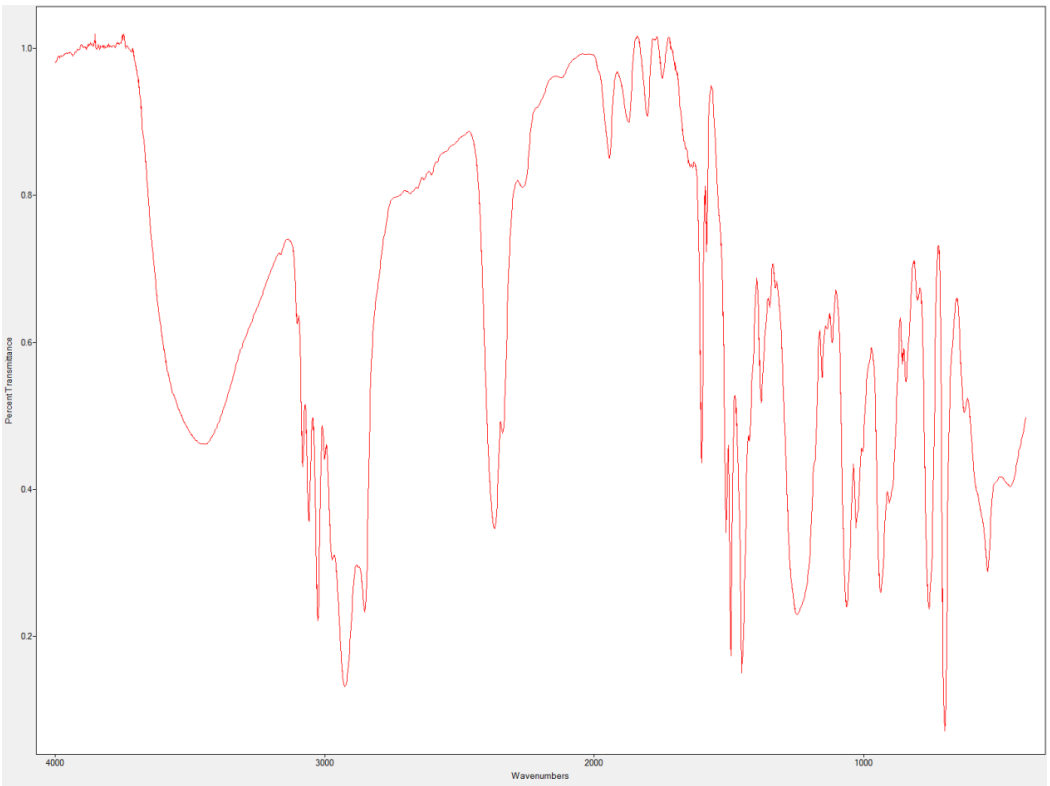
Representative FT-IR Spectra of Resins



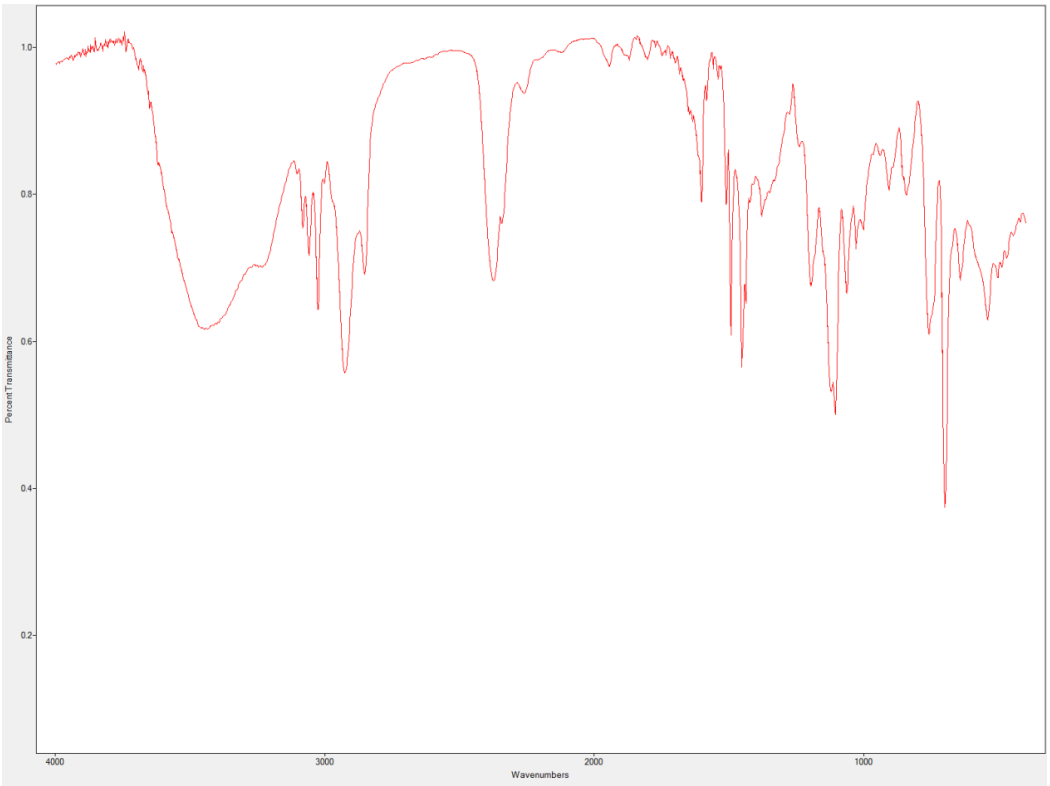
FT-IR (KBr) spectrum of JandaJel-Cl (**JJ-Cl**)



FT-IR (KBr) spectrum of resin−bound phosphine-borane **1b·BH$_3$**



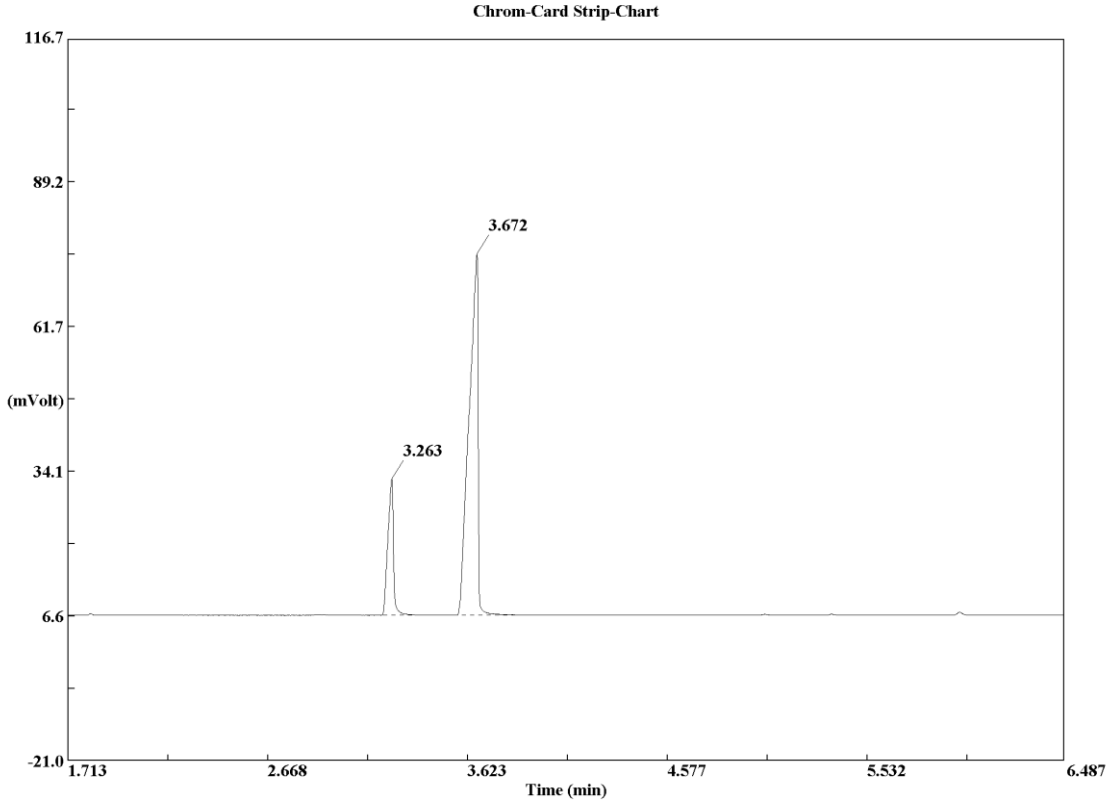
FT-IR (KBr) spectrum of resin−bound phosphine-borane sulfate **3e·BH$_3$**



FT-IR (KBr) spectrum of resin−bound diphosphine-diborane **4e·(BH$_3$)$_2$**

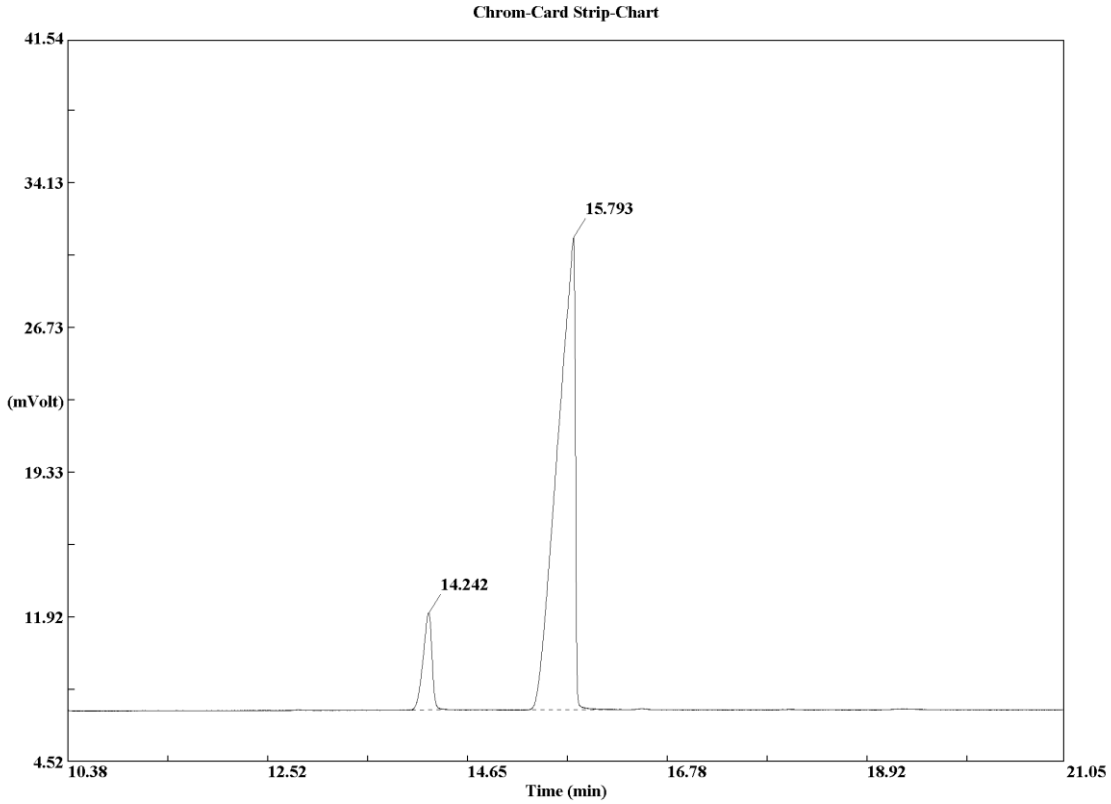
Representative GC Traces of Asymmetric Hydrogenation Experiments

Asymmetric hydrogenation of substrate **I** by supported ligand **4g**



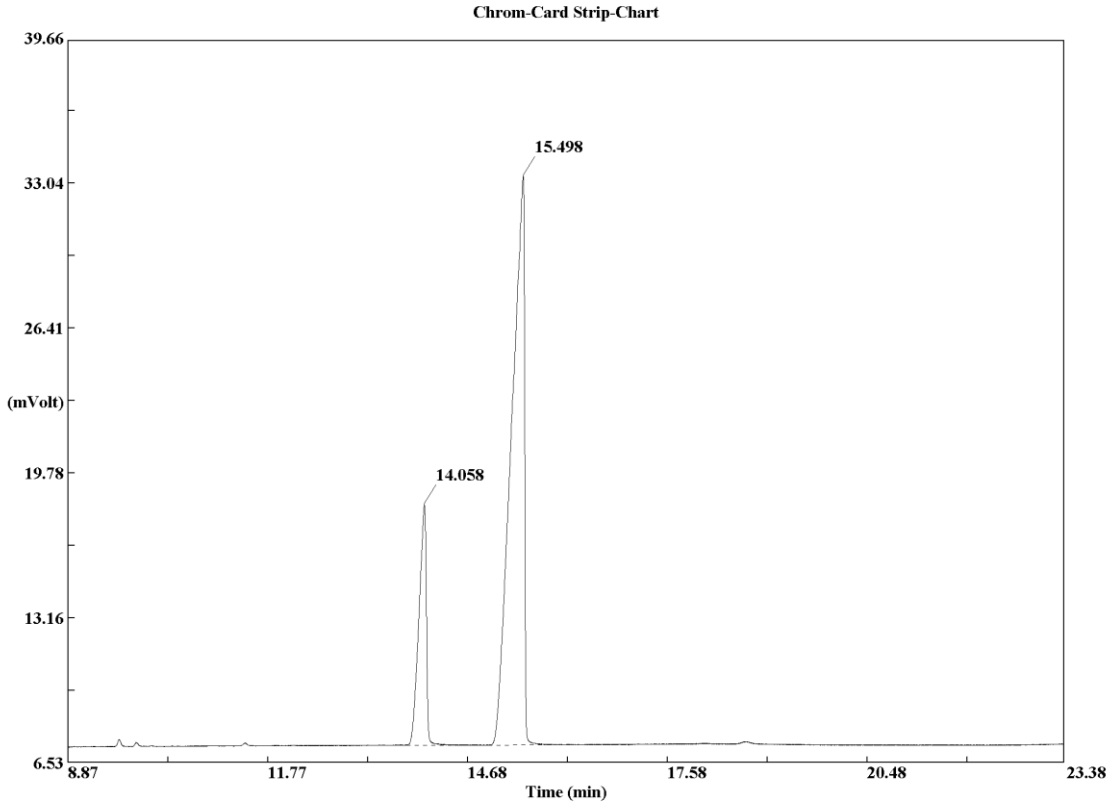
Peak No.	Retention Time (min)	Area (μV·s)	Height (μV)	Area (%)
1	3.263	485838	26018	18.831
2	3.672	2094204	68950	81.169
Total		2580042	94968	

Asymmetric hydrogenation of substrate **II** by supported ligand **4c**



Peak No.	Retention Time (min)	Area (μV·s)	Height (μV)	Area (%)
1	14.242	328476	4980	9.353
2	15.793	3183471	24265	90.647
Total		3511947	29245	

Asymmetric hydrogenation of substrate **III** by supported ligand **4g**



Peak No.	Retention Time (min)	Area (μV·s)	Height (μV)	Area (%)
1	14.058	833855	11079	19.467
2	15.498	3449676	26129	80.533
Total		4283531	37208	

References

[1] G. Fries, J. Wolf, K. Ilg, B. Walfort, D. Stalke, H. Werner, *Dalton Trans.* 2004, 1873-1881.

[2] I. Bonnaventure, A. B. Charette, *J. Org. Chem.* 2008, **73**, 6330-6340.