Supporting information

Modular solid-phase synthesis, catalytic application and efficient recycling of supported phosphine-phosphite ligand libraries

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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. Diethyl ether and THF were distilled from sodium/benzophenone and triethylamine, dichloromethane and acetonitrile were distilled from calcium hydride. Novabiochem™ Merrifield resin (100-200 mesh, 1.24 mmol⋅g⁻¹ or 1.47 mmol⋅g⁻¹, 1% cross-linked) was obtained from EMD Millipore. Cyclic sulfates are prepared according to literature: 2a and 2b,¹ 2c and 2d,² 2e³. Phosphorochloridites are also prepared according to literature⁴ from the corresponding diols: (S)- and (R)-1,1-bi-2-naphthol (BINOL, purchased from Sigma), (S)-3,3-bis(trimethylsilyl)-1,1-bi-naphthol⁵ and 3,3,5,5-tetra(tert-butyl)-2,2-biphenol.⁶

NMR spectra were recorded on a Bruker AVANCE II 400 or a Bruker AVANCE III 500. ¹H and ¹³C NMR experiments were recorded using standard NMR techniques and chemical shifts (δ) are reported in ppm relative to tetramethylsilane. Gel-phase ³¹P{¹H} 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% H₃PO₄ in water. IR spectra were recorded on Shimadzu IRAffinity-1 FTIR. 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

Primary 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. 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 ³¹P{¹H} 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, 1.00 eq.) in dry THF (15 mL) as a bright yellow solution (0.18 M). ³¹P{¹H} 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, 1.00 eq.) in dry THF (12 mL) as a light yellow solution (0.25 M). ³¹P{¹H} NMR (202 MHz, THF): δ=−116.6 (s) ppm.
General Procedure for the Synthesis of Resin-Bound Phosphine-Boranes

Step 1

Merrifield resin (1a, 2.0 g, 1.24 mmol·g⁻¹, 2.48 mmol, 1.0 eq.), (1b, 2.0 g, 1.48 mmol·g⁻¹, 2.96 mmol, 1.0 eq.) was swollen in THF (50 mL) and cooled to −78 °C. A freshly prepared primary lithium phosphide solution (20 mL, 0.15 M, 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 was removed and the resin was washed subsequently with three 20 mL portions of THF followed by three 20 mL portions of Et₂O. The product was directly used in the next step without additional purification.

1a: Light yellow resin: ³¹P{¹H} NMR (202 MHz, THF): δ=−41.7 (br m) ppm.
1b: Light yellow resin: ³¹P{¹H} NMR (202 MHz, THF): δ=−41.5 (s) ppm.

Step 2

A resin-bound phosphine, synthesized in the previous step, was swollen in THF (50 mL). Next, BH₃·SMe₂ (12.5 mL, 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 full conversion was observed by ³¹P NMR. Next, the supernatant was removed and the resin was washed subsequently with three 20 ml portions of THF followed by three 20 ml portions of Et₂O. The product was dried in vacuo yielding a white resin-bound phosphine-borane.

1a·BH₃: White resin: ³¹P{¹H} NMR (202 MHz, THF): δ=5.7 (br m) ppm; IR (KBr): ν=2387 cm⁻¹ (BH₃);
Elemental analysis calcld (%) for 1a·BH₃ (1.12 mmol·g⁻¹): P 3.47; found: P 3.41.

1b·BH₃: White resin: ³¹P{¹H} NMR (202 MHz, THF): δ=13.4 (s) ppm; IR (KBr): ν=2384 cm⁻¹ (BH₃);
Elemental analysis calcld (%) for 1b·BH₃ (1.29 mmol·g⁻¹): P 4.09; found: P 4.52.
General Procedure for the Synthesis of Resin-Bound Phosphine-Borane Sulfates

Step 1

A resin-bound phosphine-borane (1a-bBH₃, 500 mg, ~0.6 mmol) was swollen in THF (20 mL). Next, LDA (3 mL, 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 was removed and the resin was washed subsequently with three 10 mL portions of THF followed by three 10 mL portions of Et₂O. The product was used in the next step without additional purification.

Li-1aBH₃: Brown resin; ³¹P{¹H} NMR (202 MHz, THF): δ=-39.1 (br s) ppm.
Li-1bBH₃: Brown resin; ³¹P{¹H} NMR (162 MHz, THF): δ=-37.0 (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 (2a-e, 0.72 mmol, 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 was removed and the resin was washed subsequently with three 10 mL portions of THF followed by three 10 mL portions of Et₂O. The product was dried in vacuo yielding a light yellow resin. The product was used in the next step without additional purification.

³¹P{¹H} NMR (202 MHz, THF): δ=27.8 (br s) ppm; IR (KBr): ν˜=2379 (BH₃), 1263 (S=O) cm⁻¹, 910 (S-OR) cm⁻¹. ³¹P{¹H} NMR (162 MHz, THF): δ=28.0 (br s) ppm; IR (KBr): ν˜=2384 (BH₃), 1260 (S=O) cm⁻¹, 910 (S-OR) cm⁻¹; (representative) elemental analysis calcd (%) for 3b-BH₃ (0.94 mmol·g⁻¹): P 2.92, S 3.02; found: P 2.99, S 3.06.

3a-BH₃: Light yellow resin; ³¹P{¹H} NMR (202 MHz, THF): δ=27.8 (br s) ppm; IR (KBr): ν˜=2380 (BH₃), 1263 (S=O) cm⁻¹, 910 (S-OR) cm⁻¹.
3b-BH₃: Light yellow resin; ³¹P{¹H} NMR (162 MHz, THF): δ=28.0 (br s) ppm; IR (KBr): ν˜=2384 (BH₃), 1260 (S=O) cm⁻¹, 910 (S-OR) cm⁻¹; (representative) elemental analysis calcd (%) for 3b-BH₃ (0.94 mmol·g⁻¹): P 2.92, S 3.02; found: P 2.99, S 3.06.
3c-BH₃: Light yellow resin; ³¹P{¹H} NMR (162 MHz, THF): δ=28.0 (br s) ppm; IR (KBr): ν˜=2384 (BH₃), 1260 (S=O) cm⁻¹, 937 (S-OR) cm⁻¹.
3d-BH₃: Light yellow resin; ³¹P{¹H} NMR (162 MHz, THF): δ=27.0 (br s) ppm; IR (KBr): ν˜=2384 (BH₃), 1260 (S=O) cm⁻¹, 937 (S-OR) cm⁻¹.
3e-BH₃: Light yellow resin; ³¹P{¹H} NMR (162 MHz, THF): δ=29.9 (br s) ppm; IR (KBr): ν˜=2379 (BH₃), 1257 (S=O) cm⁻¹, 913 (S-OR) cm⁻¹.
portions of THF and resuspended in THF. The progress of the hydrolysis of monitored using

H$_2$O. The resin was washed subsequently with five 10 mL portions of THF followed by three 10 mL portions of Et$_2$O. The product was dried in vacuo affording a white resin which was used in the next step without additional purification.

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

A resin-bound phosphine-borane sulfate (3a-hBH$_3$, 500 mg, ~0.5 mmol) was swollen, under gentle stirring, in a 1:1 mixture of THF and 0.1 M of degassed H$_2$SO$_4$ (20 mL). The resin was left overnight without stirring to avoid mechanical abrasion of the resin. Next the resin was washed with three 10 mL portions of THF and resuspended in THF. The progress of the hydrolysis of monitored using $^7$Li NMR. If no full consumption of Li was observed the resin was resuspended in a fresh mixture of THF and H$_2$SO$_4$ and left overnight. This procedure was repeated until no lithium signal could be observed anymore by $^7$Li NMR (on average 3 days). Next, the supernatant was removed and the resin was washed subsequently with five 10 mL portions of THF followed by three 10 mL portions of Et$_2$O. The product was dried in vacuo affording a white resin which was used in the next step without additional purification.

![Diagram](image-url)

4a BH$_3$: White resin: $^31P{(^1H)}$ NMR (202 MHz, THF): $\delta=27.6$ (s) ppm; IR (KBr): $\nu^\prime=2383$ (BH$_3$), 1113 (C-OH) cm$^{-1}$.

4b BH$_3$: White resin: $^31P{(^1H)}$ NMR (202 MHz, THF): $\delta=27.6$ (s) ppm; IR (KBr): $\nu^\prime=2387$ (BH$_3$), 1110 (C-OH) cm$^{-1}$; (representative) elemental analysis calcd (%) for 4b-BH$_3$ (1.02 mmol·g$^{-1}$): P 3.67, S 0.00; found: P 3.75, S 0.00.

4c BH$_3$: White resin: $^31P{(^1H)}$ NMR (202 MHz, THF): $\delta=27.6$ (s) ppm; IR (KBr): $\nu^\prime=2383$ (BH$_3$), 1111 (C-OH) cm$^{-1}$.

4d BH$_3$: White resin: $^31P{(^1H)}$ NMR (202 MHz, THF): $\delta=27.5$ (s) ppm; IR (KBr): $\nu^\prime=2383$ (BH$_3$), 1111 (C-OH) cm$^{-1}$.

4e BH$_3$: White resin: $^31P{(^1H)}$ NMR (162 MHz, THF): $\delta=30.9$ (s) ppm; IR (KBr): $\nu^\prime=2383$ (BH$_3$), 1115 (C-OH) cm$^{-1}$.

4f BH$_3$: White resin: $^31P{(^1H)}$ NMR (162 MHz, THF): $\delta=31.1$ (s) ppm; IR (KBr): $\nu^\prime=2373$ (BH$_3$), 1117 (C-OH) cm$^{-1}$.

4g BH$_3$: White resin: $^31P{(^1H)}$ NMR (162 MHz, THF): $\delta=26.4$ (s) ppm; IR (KBr): $\nu^\prime=2383$ (BH$_3$), 1110 (C-OH) cm$^{-1}$.

4h BH$_3$: White resin: $^31P{(^1H)}$ NMR (162 MHz, THF): $\delta=31.6$ (s) ppm; IR (KBr): $\nu^\prime=2378$ (BH$_3$), 1115 (C-OH) cm$^{-1}$.
General Procedure for the Synthesis of Resin-Bound Phosphine-Phosphites

**Step 1**

A resin-bound hydroxyalkyl phosphine-borane (4a-hBH3, 250 mg, ~0.25 mmol) was suspended in THF (5 mL) and a solution of 1,4-Diazabicyclo[2.2.2]octane (5 mL, 0.5 M in THF, 10 eq.) was added. The reaction was heated to 40 °C and was left overnight without stirring. After complete deprotection was confirmed by 31P NMR, the supernatant was removed and the resin was washed subsequently with three 5 mL portions of THF followed by three 5 mL portions of Et2O. The product was dried in vacuo yielding a white deprotected resin-bound hydroxyalkyl phosphine. The product was used directly in the next step without further purification.

4a: White resin: 31P{1H} NMR (162 MHz, THF): δ=-2.5, -1.9 ppm.
4b: White resin: 31P{1H} NMR (162 MHz, THF): δ=-2.7, -1.9 ppm.
4c: White resin: 31P{1H} NMR (162 MHz, THF): δ=-4.5, -3.7 ppm.
4d: White resin: 31P{1H} NMR (162 MHz, THF): δ=-4.4, -3.5 ppm.
4e: White resin: 31P{1H} NMR (202 MHz, THF): δ=4.3 ppm.
4f: White resin: 31P{1H} NMR (202 MHz, THF): δ=1.8, 3.1 ppm.
4g: White resin: 31P{1H} NMR (202 MHz, THF): δ=-9.5 ppm.
4h: White resin: 31P{1H} NMR (202 MHz, THF): δ=-2.8 ppm.

**Step 2**

A deprotected resin-bound hydroxyalkyl phosphine, synthesized in the previous step, was swollen in THF (10 mL) and triethylamine (2.25 mmol, 9.0 eq.) was added. A chlorophosphite (0.75 mmol, 3.0 eq.) was dissolved in THF (5 mL) and was added to the resin at 0 °C under gentle stirring to avoid mechanical abrasion. Upon addition a precipitate was formed. The reaction was monitored using 31P NMR and full conversion was reached when a 1:1 ratio of phosphine to phosphite was observed (2-16 hours). Next, the supernatant was removed and the resin was washed subsequently with three 10 mL portions of DCM, three 10 mL portions of THF and three 10 mL portions of Et2O. The product was dried in vacuo yielding a white resin-bound phosphine-phosphite (L1, L2, L3 and L8 on 1.48 mmol·g⁻¹ Merrifield resin, L3, L4, L6, L7 and L9-L16 on 1.24 mmol·g⁻¹ Merrifield resin).
L₁: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -3.7, -2.2 (P), 152.6 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1202 (PO-Ar), 1154 (P-O-C), 943 (PO-C), 912 (PO-C), 823 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₁ (0.87 mmol·g⁻¹): P 5.75; found: P 5.81.

L₂: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -4.5, -2.5 (P), 147.8 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1202 (PO-Ar), 1156 (P-O-C), 942 (PO-C), 909 (PO-C), 824 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₂ (0.87 mmol·g⁻¹): P 5.75; found: P 5.41.

L₃: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -4.4, -2.3 (P), 148.0 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1233 (PO-Ar), 1201 (PO-Ar), 1155 (P-O-C), 943 (PO-C), 911 (PO-C), 823 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₃ (0.78 mmol·g⁻¹): P 4.85; found: P 4.71.

L₄: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -3.2, -2.0 (P), 152.9 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1201 (PO-Ar), 1155 (P-O-C), 943 (PO-C), 912 (PO-C), 823 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₄ (0.78 mmol·g⁻¹): P 4.85; found: P 4.67.

L₅: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -4.2 (P), 144.2, 146.3 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1202 (PO-Ar), 1156 (P-O-C), 982 (PO-C), 940 (PO-C), 824 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₅ (0.85 mmol·g⁻¹): P 5.69; found: P 5.40.

L₆: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -4.4 (P), 146.6 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1202 (PO-Ar), 1155 (P-O-C), 982 (PO-C), 941 (PO-C), 824 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₆ (0.77 mmol·g⁻¹): P 4.80; found: P 4.98.

L₇: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -3.3 (P), 146.7 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1203 (PO-Ar), 1156 (P-O-C), 983 (PO-C), 941 (PO-C), 824 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₇ (0.77 mmol·g⁻¹): P 4.98; found: P 4.89.

L₈: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta$ = -4.6 (P), 144.2, 146.4 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1202 (PO-Ar), 1155 (P-O-C), 981 (PO-C), 941 (PO-C), 823 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₈ (0.85 mmol·g⁻¹): P 5.69; found: P 5.37.

L₉: White resin: $^{31}$P($^1$H) NMR (202 MHz, THF): $\delta$ = -9.8 (P), 149.5 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1233 (PO-Ar), 1203 (PO-Ar), 1156 (P-O-C), 984 (PO-C), 938 (PO-C), 824 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₉ (0.76 mmol·g⁻¹): 4.70; found: P 4.97.

L₁₀: White resin: $^{31}$P($^1$H) NMR (202 MHz, THF): $\delta$ = 4.0 (P), 152.6 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1232 (PO-Ar), 1202 (PO-Ar), 1156 (P-O-C), 943 (PO-C), 913 (PO-C), 823 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₁₀ (0.78 mmol·g⁻¹): 4.83; found: P 4.95.

L₁₁: White resin: $^{31}$P($^1$H) NMR (202 MHz, THF): $\delta$ = 2.9, 1.3 (P), 146.5 (-OP) ppm; IR (KBr): $\tilde{\nu}$ = 1233 (PO-Ar), 1202 (PO-Ar), 1155 (P-O-C), 982 (PO-C), 941 (PO-C), 823 (P-OAr) cm⁻¹; Elemental analysis calcd (%) for L₁₁ (0.77 mmol·g⁻¹): 4.78; found: P 4.25.
L_{12}: White resin: $^{31}$P($^1$H) NMR (202 MHz, THF): $\delta = -3.5$ (P), 149.0 (-OP) ppm; IR (KBr): $\tilde{\nu} = 1232$ (PO-Ar), 1202 (PO-Ar), 1155 (PO-C), 982 (PO-C), 940 (PO-C), 823 (P-OAr) cm$^{-1}$; Elemental analysis calcd (%) for L_{12} (0.75 mmol g$^{-1}$): 4.68; found: P 4.83.

L_{13}: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta = -4.1, -2.1$ (P), 147.8 (-OP) ppm; IR (KBr): $\tilde{\nu} = 1249$ (Si-Me$_3$), 1233 (PO-Ar), 1208 (PO-Ar), 1161 (P-O-C), 989 (PO-C), 944 (PO-C), 896 (Si-Me$_3$), 840 (P-OAr) cm$^{-1}$; Elemental analysis calcd (%) for L_{13} (0.70 mmol g$^{-1}$): 4.37; found: P 4.42.

L_{14}: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta = -4.4$ (P), 146.6 (-OP) ppm; IR (KBr): $\tilde{\nu} = 1249$ (Si-Me$_3$), 1233 (PO-Ar), 1208 (PO-Ar), 1162 (P-O-C), 989 (PO-C), 943 (PO-C), 896 (Si-Me$_3$), 840 (P-OAr) cm$^{-1}$; Elemental analysis calcd (%) for L_{14} (0.70 mmol g$^{-1}$): 4.33; found: P 4.39.

L_{15}: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta = -4.5, -2.4$ (P), 147.4 (-OP) ppm; IR (KBr): $\tilde{\nu} = 1229$ (PO-Ar), 1202 (PO-Ar), 1121 (P-O-C), 960 (PO-C), 942 (PO-C), 823 (P-OAr) cm$^{-1}$; Elemental analysis calcd (%) for L_{15} (0.71 mmol g$^{-1}$): 4.43; found: P 4.34.

L_{16}: White resin: $^{31}$P($^1$H) NMR (162 MHz, THF): $\delta = -4.4, -2.1$ (P), 146.0 (-OP) ppm; IR (KBr): $\tilde{\nu} = 1230$ (PO-Ar), 1201 (PO-Ar), 1124 (P-O-C), 961 (PO-C), 941 (PO-C), 878 (P-OAr) cm$^{-1}$; Elemental analysis calcd (%) for L_{16} (0.71 mmol g$^{-1}$): 4.54; found: P 4.39.

**General Procedure for Asymmetric Hydrogenation Experiments**

**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 resin-bound phosphine-phosphite (5 mg, approximately 4.0 $\mu$mol) and a solution of $[\text{Rh(COD)}_2]X$ (0.9 eq.) in CH$_2$Cl$_2$ (1 mL) was added and the heterogeneous mixture was allowed to stir gently for 4 h. The supernatant 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$_2$O. Next, a solution of substrate (0.5 mL, 0.24 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, $\Delta T = 8$ °C min$^{-1}$ to 170 °C, $t_R$ (I) = 2.3 min. $t_R$ (R) = 3.2 min, $t_R$ (S) = 3.5 min.

**III**: Permabond-L-Chirasil-Val column: $T_0 = 90$ °C, $\Delta T = 8$ °C min$^{-1}$ to 150 °C, hold for 15 min, then $\Delta T = 8$ °C min$^{-1}$ to 180 °C, hold for 15 min, $t_R$ (R) = 13.2 min. $t_R$ (S) = 14.4 min, $t_R$ (III) = 26.3 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 resin-bound phosphine-phosphite (5 mg, approximately 4.0 μmol) and a solution of [Rh(COD)2]X (0.9 eq.) in CH2Cl2 (1 mL) was added and the heterogeneous mixture was allowed to stir gently for 4 h. The supernatant was removed and the resulting orange resin was washed subsequently with three 1 mL portions of THF followed by three 1 mL portions of Et2O. Next, substrate stock solution (1.5 mL, 0.08 M, 30 eq.) in THF was added to the reaction vessel. The hydrogenation was performed under a flow of H2 while gently being stirred at 25 °C. After 20 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 H2 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 supported phosphine-phosphite was suspended in 2.5 mL of THF and 1.0 eq. of [Rh(COD)2]BF4 in 2.5 mL of THF was added to the resin. The progress of the complexation was monitored using 31P{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 yellow/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.
Results Catalyst Recycling

Table S-I. Full results of catalyst recycling of L₉ in the Rh-catalyzed asymmetric hydrogenation of substrate III.ᵃ

<table>
<thead>
<tr>
<th>Run</th>
<th>Conversionᵇ (%)</th>
<th>eeᶜ (%)</th>
<th>TOFᵈ (h⁻¹)</th>
<th>Rh Leachingᵉ (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>46.3</td>
<td>97.1 (R)</td>
<td>41.7</td>
<td>1.6</td>
</tr>
<tr>
<td>2</td>
<td>48.5</td>
<td>97.0 (R)</td>
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ᵃ Reaction conditions: In a Schlenk vessel under an H₂ atmosphere, Rh/substrate = 1:30, p(H₂) = 1.2 bar, T = 25 °C, t = 20 min, 1.5 mL of THF, all runs were performed in duplicate.ᵇ Percentage conversion determined by GC.ᶜ Enantiomeric excess of product determined by chiral GC (absolute configuration drawn in parenthesis).ᵈ Time averaged turnover frequency.ᵉ Rh-leaching determined by ICP-OES of the reaction solution after each run.
$^{31}$P Gel-Phase NMR Spectra of Resin-Bound Phosphine-Boranes 1a-b·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 Gel-Phase NMR Spectra of Resin-Bound Phosphine-Borane Sulfates 3a-h·BH$_3$

$^{31}$P{$^1$H} NMR of resin 3a·BH$_3$ (202 MHz, THF).
$^{31}$P($^1$H) NMR of resin $3b\mathrm{BH}_3$ (162 MHz, THF).

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

$^{31}$P($^1$H) NMR of resin $3d\mathrm{BH}_3$ (162 MHz, THF).
$^{31}\text{P} \{^1\text{H}\}$ NMR of resin 3e $\text{BH}_3$ (162 MHz, THF).

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

$^{31}\text{P} \{^1\text{H}\}$ NMR of resin 3g $\text{BH}_3$ (202 MHz, THF).
$^{31}$P{¹H} NMR of resin 3h·BH$_3$ (162 MHz, THF).

$^{31}$P Gel-Phase NMR Spectra of Resin-Bound Hydroxyalkyl Phosphine-Boranes 4a-h·BH$_3$

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

$^{31}$P{¹H} NMR of resin 4b·BH$_3$ (202 MHz, THF).
$^{31}$P{¹H} NMR of resin 4c BH₃ (202 MHz, THF).

$^{31}$P{¹H} NMR of resin 4d BH₃ (202 MHz, THF).

$^{31}$P{¹H} NMR of resin 4e BH₃ (162 MHz, THF).
$^{31}$P($^1$H) NMR of resin 4f BH$_3$ (162 MHz, THF).

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

$^{31}$P($^1$H) NMR of resin 4h BH$_3$ (162 MHz, THF).
$^{31}$P Gel-Phase NMR Spectra of Resin-Bound Phosphine-Phosphites $\text{L}_1$-$\text{L}_{16}$

$^{31}$P($^1$H) NMR of resin $\text{L}_1$ (162 MHz, THF).

$^{31}$P($^1$H) NMR of resin $\text{L}_2$ (162 MHz, THF).

$^{31}$P($^1$H) NMR of resin $\text{L}_3$ (162 MHz, THF).
$^{31}$P{$^1$H} NMR of resin $L_4$ (162 MHz, THF).

$^{31}$P{$^1$H} NMR of resin $L_5$ (162 MHz, THF).

$^{31}$P{$^1$H} NMR of resin $L_6$ (162 MHz, THF).
$^{31}\text{P} \{^1\text{H}\}$ NMR of resin \( L_7 \) (162 MHz, THF).

$^{31}\text{P} \{^1\text{H}\}$ NMR of resin \( L_8 \) (162 MHz, THF).

$^{31}\text{P} \{^1\text{H}\}$ NMR of resin \( L_9 \) (202 MHz, THF).
$^{31}P\{(^{1}H)\}$ NMR of resin $L_{10}$ (202 MHz, THF).

$^{31}P\{(^{1}H)\}$ NMR of resin $L_{11}$ (202 MHz, THF).

$^{31}P\{(^{1}H)\}$ NMR of resin $L_{12}$ (162 MHz, THF).
$^{31}$P{$^1$H} NMR of resin $L_{13}$ (162 MHz, THF).

$^{31}$P{$^1$H} NMR of resin $L_{14}$ (162 MHz, THF).

$^{31}$P{$^1$H} NMR of resin $L_{15}$ (162 MHz, THF).
$^{31}$P($^1$H) NMR of resin $L_{16}$ (162 MHz, THF).
Representative $^1$H Gel-Phase NMR Spectrum of Resin-Bound Phosphine-Phosphite $L_5$

$^1$H NMR of resin $L_{15}$ (400 MHz, $C_6D_6$).

Representative $^{13}$C Gel-Phase NMR Spectrum of Resin-Bound Phosphine-Phosphite $L_5$

$^{13}$C($^1$H) NMR of resin $L_{15}$ (101 MHz, $C_6D_6$).
Representative FT-IR Spectra of Resins

FT-IR (KBr) spectrum of Merrifield Resin (MF-Cl)

FT-IR (KBr) spectrum of resin-bound phosphine-borane 1aBH₃
FT-IR (KBr) spectrum of resin-bound phosphine-borane sulfate 3a\textcdot BH_3

FT-IR (KBr) spectrum of resin-bound hydroxyalkyl phosphine-borane 4a\textcdot BH_3
FT-IR (KBr) spectrum of resin-bound phosphine-phosphite $L_3$
Representative GC Traces of Asymmetric Hydrogenation Experiments

Asymmetric hydrogenation of substrate I

<table>
<thead>
<tr>
<th>Peak No.</th>
<th>Retention Time (min)</th>
<th>Area (mV·min)</th>
<th>Height (mV)</th>
<th>Area (%)</th>
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<tbody>
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<td>2.9397</td>
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Racemic product asymmetric hydrogenation of substrate I

<table>
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<th>Area (%)</th>
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Asymmetric hydrogenation of substrate III

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Racemic product asymmetric hydrogenation of substrate II/III

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References