

# A simple route to chiral phosphinous acid-boranes

## Electronic Supplementary Information

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### General remarks

#### Analyses:

- NMR spectra were recorded on Bruker Avance (200 or 300 MHz) spectrometers.  $^1\text{H}$  and  $^{13}\text{C}$  chemical shifts are reported in ppm relative to  $\text{CDCl}_3$  as internal standard ( $^1\text{H}$ : 7.26 ppm,  $^{13}\text{C}$ : 77.0 ppm).  $^{31}\text{P}$  NMR downfield chemical shifts are expressed with a positive sign, in ppm, relative to external 85%  $\text{H}_3\text{PO}_4$ .
- Specific optical rotations of chiral compounds were measured on a 341 Perkin Elmer spectrometer.
- High resolution MS analyses were performed on a QStar Elite (Applied Biosystems SCIEX) spectrometer by « Spectropole » at University of Aix-Marseille.

#### Reagents:

- Oxygen free solvents were used and all reactions were carried out under dry nitrogen atmosphere. Tetrahydrofuran was distilled over sodium before use.
- Methylolithium, butyllithium and *tert*-butyllithium were purchased from Aldrich. Aryllithium were synthesized in situ by adding two equivalent of *tert*-butyllithium to the corresponding arylbromide in THF at  $-78^\circ\text{C}$ .<sup>1</sup> 1-Furyllithium was synthesized by adding one equivalent of butyllithium to furane in THF at  $-78^\circ\text{C}$ .<sup>2</sup>
- (*Rp*)-(-)-menthyl hydrogenophenylphosphinate **1** was synthesized from menthol and dichlorophenylphosphine according to Mislow<sup>3a</sup> and Emmick<sup>3b</sup> (see below for experimental details). Enantiopure (*Rp*)-(-)- **1** was obtained after two successive recrystallizations in *n*-hexane. Mother liquors afforded nearly racemic **1**. This latter was used for the syntheses of nearly racemic samples of **3a-g**, which were used as standards for chiral HPLC analyses.

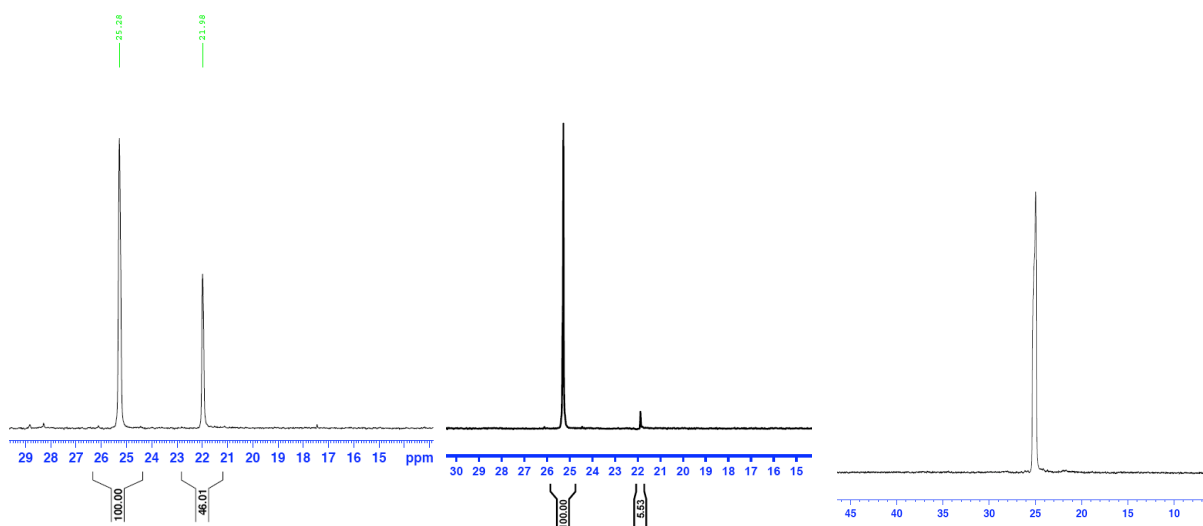
<sup>1</sup> J. Clayden, *Organolithiums: Selectivity for synthesis*, Elsevier, Oxford, 2002.

<sup>2</sup> L. Brandsma, S. F. Vasilevsky, H. D. Verkruijsse, In *Application of Transition Metal Catalysts in Organic Synthesis*, Springer-Verlag, Berlin, 1999, p. 15.

<sup>3</sup> (a) W. B. Farnham, R. K. Jr Murray, K. Mislow, *J. Am. Chem. Soc.* 1970, **92**, 5809–5810; (b) T. L. Emmick, R. L. Letsinger, *J. Am. Chem. Soc.* 1968, **90**, 3459–3465.

**(Rp)-(-)-menthyl hydrogenophenylphosphinate 1** (according to Mislow *et al.*).<sup>3</sup> A solution of (-)-menthol (100 g, 0.64 mol) and pyridine (51 mL, 0.64 mol) in hexane (300 mL) was added dropwise at 0°C to dichlorophenylphosphine (87 mL, 0.64 mol) in hexane (300 mL). After 12 hours, the resulting pyridine hydrochloride is removed by filtration and water (200 mL) was added slowly at 0°C. The two layers were separated, and the organic phase was washed with aqueous sodium bicarbonate solution (100 mL), dried over MgSO<sub>4</sub>, filtrated, and concentrated under reduced pressure to give 166 g of menthyl hydrogenophenylphosphinate with 37% diastereomeric excess. The crude product was then diluted in hexane (26 mL) and stored at refrigerator (-20°C) for 48h. The first crope was collected. After a second crystallisation in hexane, 41,5 g (25% yield) of diastereomerically pure menthyl hydrogenophenylphosphinate was obtained. **1**-(S<sub>p</sub>): <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81 MHz) δ = 25.2 (s); **1**-(R<sub>p</sub>): <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>, 81 MHz): δ = 21.9 (s); <sup>1</sup>H NMR (CDCl<sub>3</sub>, 200 MHz): δ = 0.81-1.32 (m, 12H), 1.36-1.53 (m, 2H), 1.56-1.7 (m, 2H), 2.10-2.29 (m, 2H), 4.30 (qd, <sup>1</sup>J<sub>H-H</sub> = 10.36Hz, <sup>3</sup>J<sub>P-H</sub> = 4.51Hz, 1H), 7.44-7.63 (m, 3H), 7.64 (d, <sup>1</sup>J<sub>P-H</sub> = 553.15 Hz, 1H), 7.71-7.84 (m, 2H); <sup>13</sup>C NMR {<sup>1</sup>H} (CDCl<sub>3</sub>, 50 MHz): δ = 15.80, 21.04, 22.98, 25.83, 31.69, 33.98, 43.56, 48.75 (d, <sup>1</sup>J<sub>P-C</sub> = 6.26 Hz), 79.00 (d, <sup>1</sup>J<sub>P-C</sub> = 7.15 Hz), 128.72 (d, <sup>2</sup>J<sub>P-C</sub> = 14.05 Hz, 2CH<sub>arom</sub>), 130.67 (d, <sup>3</sup>J<sub>P-C</sub> = 11.84 Hz, 2CH<sub>arom</sub>), 131.87 (d, <sup>1</sup>J<sub>P-C</sub> = 111.10 Hz, C<sub>qarom</sub>), 132.94 (d, <sup>4</sup>J<sub>P-C</sub> = 2.80 Hz, CH<sub>arom</sub>).

<sup>31</sup>P NMR spectra of the crude mixture (Left), after the first crystallisation (center), and after the second crystallisation (right).

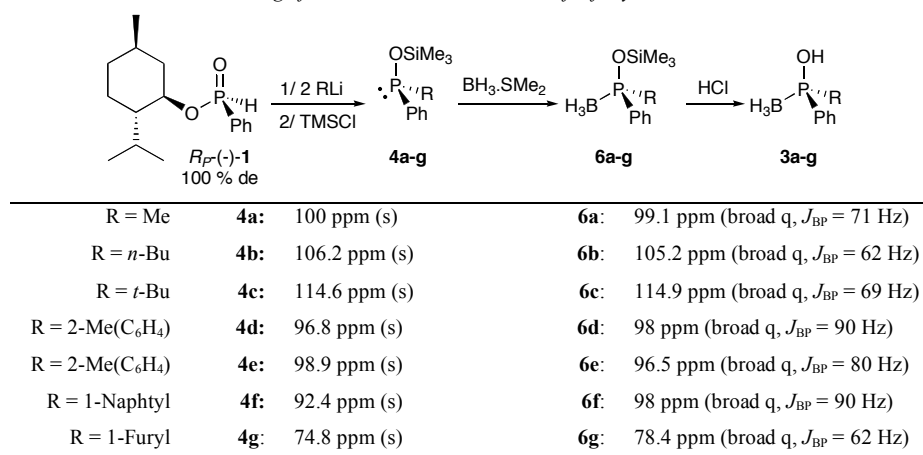


## One pot synthesis of phosphinous acid-boranes **3a-g**:

**Method A:** In a typical procedure, a dry schlenk is charged under nitrogen atmosphere with a solution of organolithium (3.9 mmol)<sup>4</sup> in THF (5 mL) and cooled down to -78 °C. A solution of (*Rp*)-(-)-menthyl hydrogenophenylphosphinate (500 mg, 1.78 mmol) in THF (3 mL) was added dropwise. After 3 hours at -78°C, the solution was slowly warmed up to room temperature and BH<sub>3</sub>.SMe<sub>2</sub> (393 μL, 3.9 mmol) was added. After 3 hours, aqueous HCl (5%) was added under vigorous stirring.

**Method B:** In a typical procedure, a dry schlenk is charged under nitrogen atmosphere with a solution of organolithium (3.9 mmol)<sup>4</sup> in THF (5 mL) and cooled down to -78 °C. A solution of (*Rp*)-(-)-menthyl hydrogenophenylphosphinate (500 mg, 1.78 mmol) in THF (3 mL) was added dropwise. After 3 hours at -78°C, the solution was slowly warmed up to room temperature and trimethylsilyl chloride (490 μL, 3.9 mmol) was added. The reaction was monitoring by <sup>31</sup>P NMR. Then, BH<sub>3</sub>.SMe<sub>2</sub> (393 μL, 3.9 mmol) was added at room temperature. After 3 hours, the completion of the reaction was confirmed by <sup>31</sup>P NMR. Aqueous HCl (5%) was added under vigorous stirring.

Monitoring of the reaction: <sup>31</sup>P chemical shift of key intermediates.



## Purification (all methods):

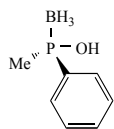
The aqueous layer was washed with dichloromethane (3 times). The organic layers were combined and volatiles were removed under vacuum. The residue was dissolved in diethylether. Aqueous NaOH (10 %) was added under vigorous stirring until pH>10. The organic layer was extracted with water and the combine aqueous layers were washed with diethylether (2 times). Aqueous HCl (5 %) was added dropwise until pH<1. The product was extracted with diethylether (3 times). The organic layers were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub> and volatiles were removed under vacuum. When necessary, the product could be purified by flash chromatography. (silica, eluent: petroleum ether/diethylether 9:1). Phosphinous acid-boranes **3a-g** proved to be stable to air and moisture. However neat compound proved to lose their BH<sub>3</sub> moieties to afford the corresponding secondary phosphine oxide. This undesirable transformation also occurred upon prolonged exposition to high vacuum. Thus **3a-g** were preferentially stored in solution and “neat” samples usually featured trace amounts of solvents.

## Synthesis of enantiopure *tert*-butylphenylphosphinous acid-borane **3c**:

A solution of enantiopure *tert*-butylphenylphosphine oxyde<sup>5</sup> (91.1 mg, 0.5 mmol) was cooled down to -78°C. Then a 1.7 M solution of *tert*-butyllithium in hexane (412 μL, 0.7 mmol) was added. After warming up to room temperature, trimethylsilyl chloride (89 μL, 0.7 mmol) was added. The reaction was monitoring by <sup>31</sup>P NMR: **4c** featured a singlet at 115 ppm. Then, BH<sub>3</sub>.SMe<sub>2</sub> (70 μL, 0.7 mmol) was added at room temperature. After 3 hours, the completion of the reaction was confirmed by <sup>31</sup>P NMR (**5c** appeared as a broad quadruplet at 115 ppm,  $J_{PB}$  = 69 Hz). Aqueous HCl (5 %) was added under vigorous stirring. The product was purified as described above. The product is isolated as a white powder. 85 % yield (84 mg). Spectroscopic and analytic data: see below.

<sup>4</sup> With MeLi: 5.34 mmol were introduced.

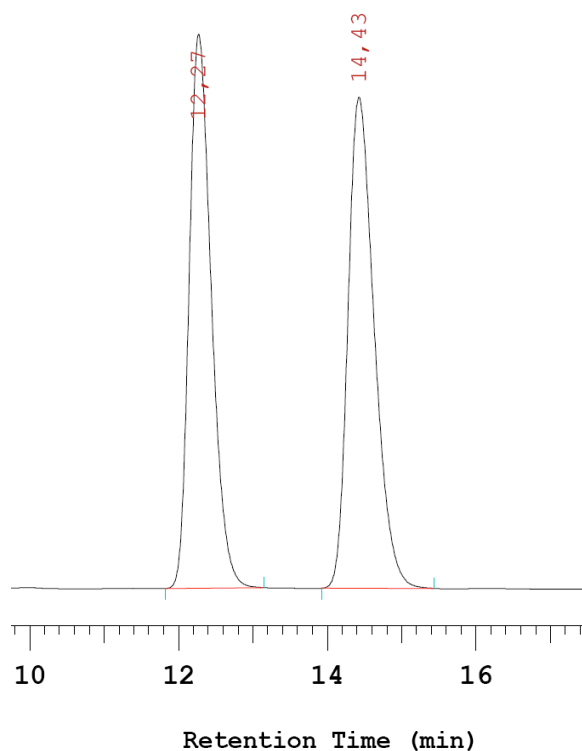
<sup>5</sup> (a) A. Leyris, D. Nuel, L. Giordano, M. Achard, G. Buono, *Tetrahedron Lett.* 2005, **46**, 8677–8680; (b) A. Leyris, J. Bigeault, D. Nuel, L. Giordano, G. Buono, *Tetrahedron Lett.* 2007, **48**, 5247–5250.



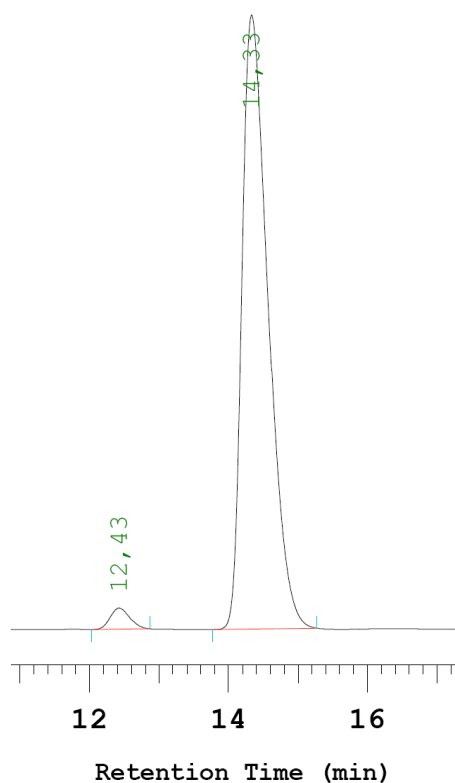
**3a**: milky liquid. 78% yield (239 mg).  $[\alpha]_D^{20}$  -11.4 ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 102.6$  (broad q,  $J_{\text{PB}} = 65.3$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.5$ -1.5 (broad, 3H,  $\text{BH}_3$ ), 1.73 (d,  $J_{\text{PH}} = 9.5$  Hz, 3H), 7.47-7.54 (m, 3H), 7.74-7.85 (m, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 17.4$  (d,  $J_{\text{PC}} = 44.6$  Hz,  $\text{CH}_3$ ), 128.5 (d,  $J_{\text{PC}} = 10.5$  Hz, CH), 129.7 (d,  $J_{\text{PC}} = 11.5$  Hz, CH), 131.5 (d,  $J_{\text{PC}} = 2.2$  Hz, CH), 133.7 (d,  $J_{\text{PC}} = 61.6$  Hz, C). IR:  $\nu = 3232, 3056, 2916, 2369, 2259, 2034, 1973, 1894, 1815, 1767, 1669, 1590, 1481, 1432, 1402, 1292, 1140, 1055, 922, 897, 745, 690$   $\text{cm}^{-1}$ . MS (ESI-MS)  $[\text{M}+\text{Na}]^+$ : 177,  $[\text{M}+\text{NH}_4]^+$ : 172,  $[\text{M}-\text{H}]^-$ : 153.

The enantiomeric excess was determined by HPLC analysis on a chiralpak AS-H column with a UV detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent : hexane/i-PrOH 99:1; (+)-**3a**:  $t_r = 12.4$  min, (-)-**3a**:  $t_r = 14.3$  min.

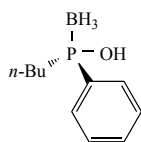
Left: nearly racemic sample. Right: enantioenriched **3a**.



RT	Area	Conc 1
12,27	1022685	48,762
14,43	1074599	51,238
	2097284	100,000



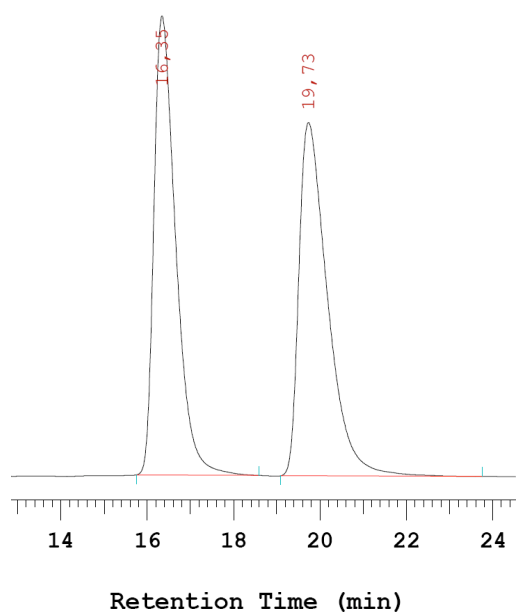
RT	Area	Conc 1
12,43	77368	2,502
14,33	3014595	97,498
	3091963	100,000



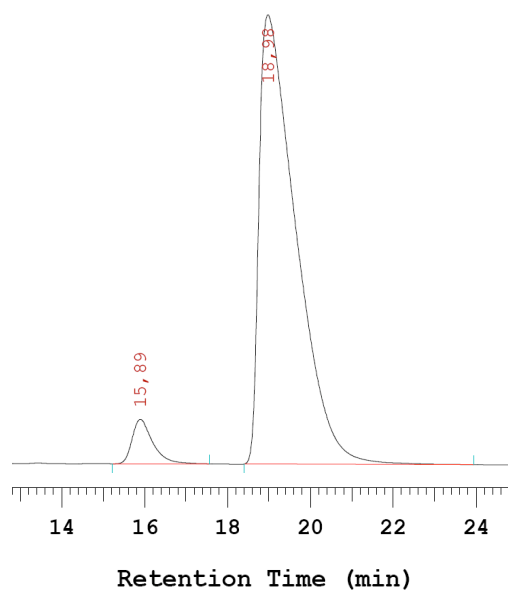
**3b**: milky liquid. 70 % yield (328 mg).  $[\alpha]_D^{20}$  -12.6 ( $c = 1.0$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 105.3$  (broad q,  $J_{\text{PB}} = 62.3$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.5$ -1.5 (broad, 3H,  $\text{BH}_3$ ), 0.87 (t,  $J_{\text{HH}} = 7$  Hz, 3H), 1.26-1.58 (m, 4H), 1.79-2.01 (m, 2H), 7.47-7.50 (m, 3H), 7.7-7.81 (m, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 13.4$  (s,  $\text{CH}_3$ ), 23.7 (d,  $J_{\text{PC}} = 13.9$  Hz,  $\text{CH}_2$ ), 23.8 (s,  $\text{CH}_2$ ), 31.0 (d,  $J_{\text{PC}} = 43.0$  Hz,  $\text{CH}_2$ ), 128.6 (d,  $J_{\text{PC}} = 10.4$  Hz, CH), 130.0 (d,  $J_{\text{PC}} = 11.1$  Hz, CH), 131.3 (d,  $J_{\text{PC}} = 2.3$  Hz, CH), 132.8 (d,  $J_{\text{PC}} = 59.7$  Hz, C). IR:  $\nu = 3361$ , 3059, 2959, 2873, 2372, 2246, 1964, 1805, 1818, 1653, 1465, 1437, 1119, 1097, 910, 880, 793, 732  $\text{cm}^{-1}$ . HRMS (ESI-MS)  $[\text{M}+\text{Na}]^+$ : found 219.1084; calculated for  $\text{C}_{10}\text{H}_{18}\text{OBPNa}$ : 219.1082.

The enantiomeric excess was determined by HPLC analysis on a chiralpak AS-H column with a UV detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent : hexane/i-PrOH 98:2; (+)-**3b**:  $t_r = 15.9$  min, (-)-**3b**:  $t_r = 19.0$  min.

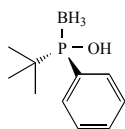
Left: nearly racemic sample. Right: enantioenriched **3b**.



RT	Area	Conc 1
16,35	864727	49,653
19,73	876798	50,347
	1741525	100,000



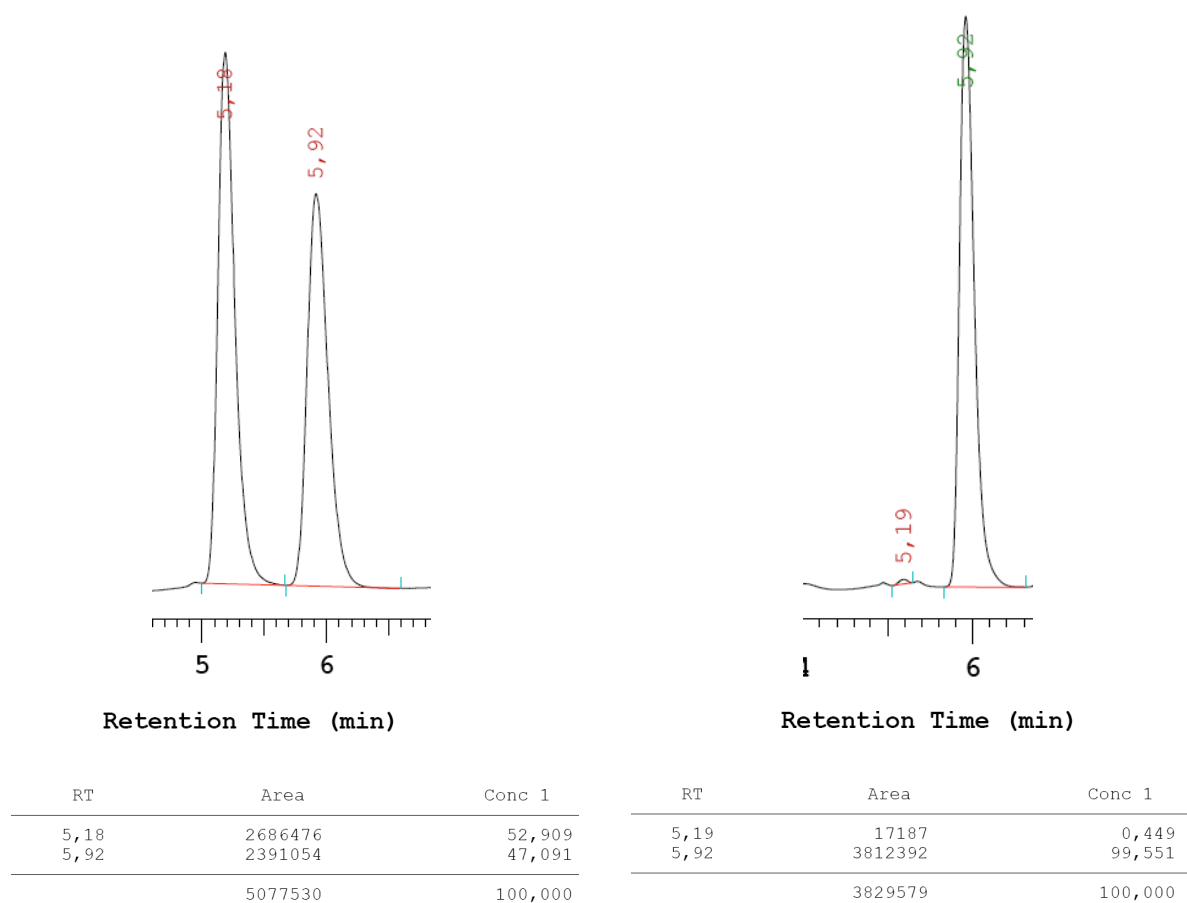
RT	Area	Conc 1
15,89	155453	5,293
18,98	2781524	94,707
	2936977	100,000

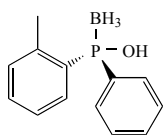


**3c**: glassy solid. 71 % yield (280 mg).  $[\alpha]_D^{20}$  -42.4 ( $c = 1.15$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 113.7$  (broad q,  $J_{\text{PB}} = 63.6$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.0$ -1.7 (broad m, 3H), 1.1 (d,  $J_{\text{PH}} = 14.66$  Hz, 9H), 3.7 (broad s, 1H), 7.4-7.6 (m, 3H), 7.7-7.9 (m, 2H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 23.9$  (d,  $J_{\text{CP}} = 3.44$  Hz), 31.7 (d,  $J_{\text{CP}} = 41.1$  Hz), 127.9 (d,  $J_{\text{CP}} = 10.1$  Hz), 131.2; 131.4 (d,  $J_{\text{CP}} = 10.4$  Hz); a quaternary carbon was not observed.

The enantiomeric excess was determined by HPLC analysis on a chiralpak AS-H column with a UV detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent : hexane/i-PrOH 99:1; (+)-**3c**:  $t_r = 5.2$  min, (-)-**3c**:  $t_r = 5.9$  min.

Left: nearly racemic sample. Right: enantioenriched **3c**.

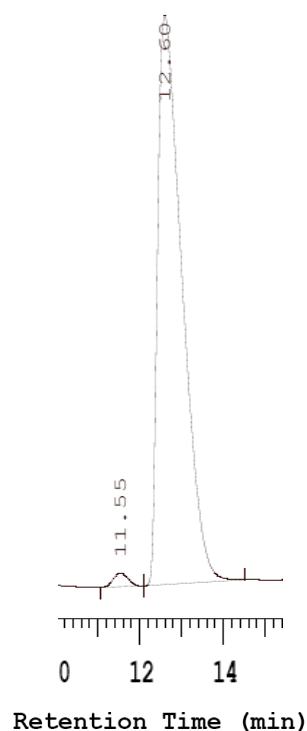
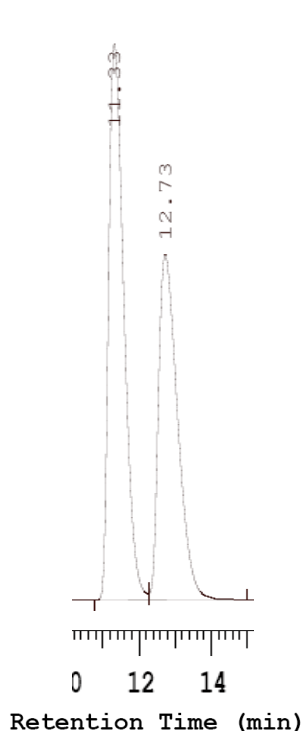


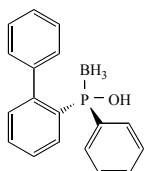


**3d**: white solid. 70 % yield (340 mg).  $[\alpha]_D^{20} +3.1$  ( $c = 0.98$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 98.0$  (broad q,  $J_{\text{PB}} = 59.4$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.2$ -2.0 (broad m, 3H), 2.17 (s, 3H), 4.2 (broad s, 1H), 7.1-7.2 (m, 1H), 7.2-7.5 (m, 5H), 7.5-7.7 (m, 2H), 7.89 (ddd, 1H,  $J_{\text{HP}} = 13$  Hz,  $J_{\text{HH}} = 7.4$  Hz and 1.4 Hz);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 21.4$  (d,  $J_{\text{CP}} = 5$  Hz,  $\text{CH}_3$ ), 125.9 (d,  $J_{\text{CP}} = 12$  Hz, CH), 128.7 (d,  $J_{\text{CP}} = 11$  Hz, 2CH), 129.8 (d,  $J_{\text{CP}} = 63$  Hz, C), 130.9 (d,  $J_{\text{CP}} = 12$  Hz, 2CH), 131.6 (d,  $J_{\text{CP}} = 9$  Hz, CH), 131.8 (d,  $J_{\text{CP}} = 2$  Hz, CH), 132.3 (d,  $J_{\text{CP}} = 2$  Hz, CH), 132.9 (d,  $J_{\text{CP}} = 15$  Hz, CH), 132.9 (d,  $J_{\text{CP}} = 64$ , C), 141.6 (d,  $J_{\text{CP}} = 9$  Hz, C). IR:  $\nu = 3364$  (broad band), 2961, 2382, 1590, 1473, 1453, 1437, 1285, 1139, 1115, 1079, 1045, 884, 807, 761, 744, 689,  $626\text{ cm}^{-1}$ . HRMS (ESI-MS)  $[\text{M}+\text{Na}]^+$ : found 253.0925; calculated for  $\text{C}_{13}\text{H}_{18}\text{NaOPB}$ : 253.0927.

The enantiomeric excess was determined by HPLC analysis on a chiralpak AS-H column with a UV detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent : hexane/i-PrOH 95:5; (-)-**3d**:  $t_r = 11.33$  min, (+)-**3d**:  $t_r = 12.73$  min.

Left: nearly racemic sample. Right: enantioenriched **3d**.

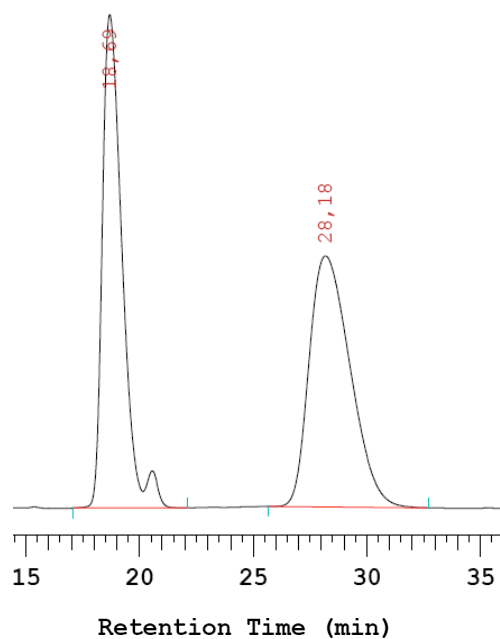




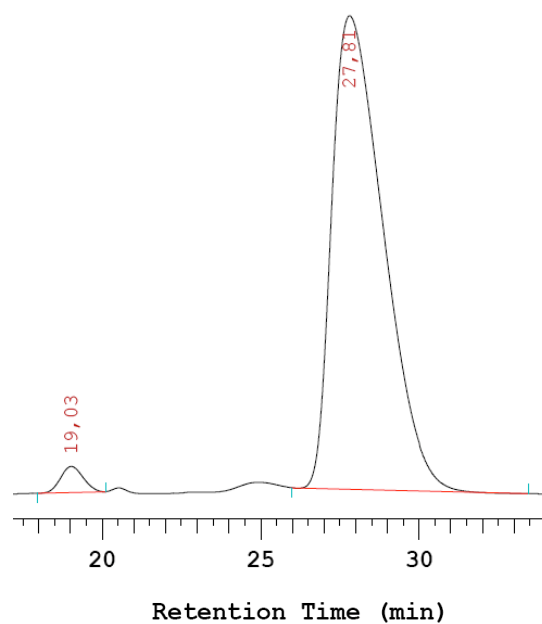
**3e**: white solid. 84% (245 mg).  $[\alpha]_D^{20}$  -6.6 ( $c = 0.9$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 97.4$  (broad q,  $J_{\text{PB}} = 79.8$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.1$ -1.9 (broad m, 3H), 3.8 (broad s, 1H), 6.92 (m, 2H), 7.06-7.40 (m, 9H), 7.42-7.60 (m, 2H), 8.06-8.22 (m, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 127.2$  (d,  $J_{\text{CP}} = 11$  Hz, 1CH), 127.5 (s, 1CH), 127.6 (s, 2CH), 128.1 (d,  $J_{\text{CP}} = 11$  Hz, 2CH), 129.7 (s, 2CH), 130.5 (d,  $J_{\text{CP}} = 12$  Hz, 2CH), 130.9 (d,  $J_{\text{CP}} = 2$  Hz, CH), 131.4 (d,  $J_{\text{CP}} = 60$  Hz, C), 131.5 (d,  $J_{\text{CP}} = 6$  Hz, CH), 131.6 (broad s, CH), 133.2 (d,  $J_{\text{CP}} = 15$  Hz, CH), 133.9 (d,  $J_{\text{CP}} = 65$  Hz, C), 140.3 (d,  $J_{\text{CP}} = 3$  Hz, C), 146.3 (d,  $J_{\text{CP}} = 7$  Hz, C). IR:  $\nu = 3200$  (broad band), 3058, 2953, 2343, 2260, 1952, 1891, 1813, 1763, 1588, 1561, 1467, 1438, 1115, 1062, 906, 883, 623, 614  $\text{cm}^{-1}$ . HRMS (ESI-MS)  $[\text{M}+\text{Na}]^+$ : found 315.1075; calculated for  $\text{C}_{18}\text{H}_{18}\text{NaOPB}$ : 315.1084.

The enantiomeric excess was determined by HPLC analysis on a chiralpak AS-H column with a UV detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent : hexane/i-PrOH 95:5; (+)-**3e**:  $t_r = 19.0$  min, (-)-**3e**:  $t_r = 27.8$  min.

Left: nearly racemic sample. Right: enantioenriched **3e**.

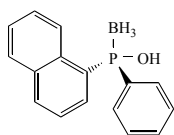


RT	Area	Conc 1
18,69	16608345	48,931
28,18	17333961	51,069
	33942306	100,000



RT	Area	Conc 1
19,03	698233	2,362
27,81	28859161	97,638
	29557394	100,000





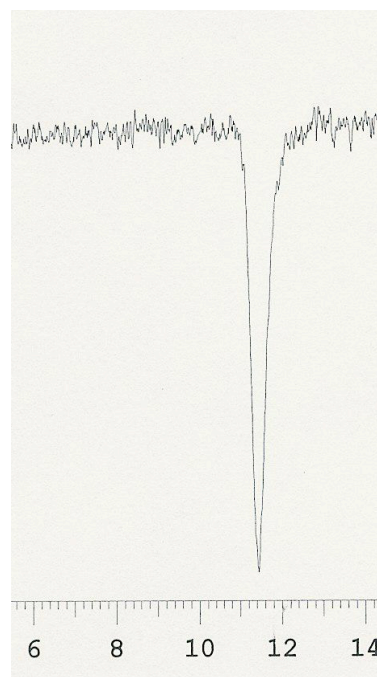
**3f**: white sticky solid. 75 % yield (350 mg).  $[\alpha]_D^{20}$  -33.1 ( $c = 1.5$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 96.4$  (broad q,  $J_{\text{PB}} = 88$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.5$ -2.5 (broad, 3H,  $\text{BH}_3$ ), 7.3-7.8 (m, 8H), 7.88 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 8.04 (d,  $J_{\text{HH}} = 8$  Hz, 1H), 8.15 (d,  $J_{\text{HH}} = 9$  Hz, 1H), 8.33 (dd,  $J_{\text{HH}} = 7$  and 15 Hz, 1H);  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 124.6$  (d,  $J_{\text{PC}} = 14$  Hz, CH), 126.1 (s, CH), 126.6 (s, CH), 126.7 (s, CH), 128.4 (d,  $J_{\text{PC}} = 10$  Hz, CH), 128.8 (s, CH), 129.5 (s, C), 130.5 (d,  $J_{\text{PC}} = 12$  Hz, CH), 131.1 (d,  $J_{\text{PC}} = 2$  Hz, CH), 132.4 (d,  $J_{\text{PC}} = 7$  Hz, C), 133.0 (d,  $J_{\text{PC}} = 2$  Hz, CH), 133.4 (d,  $J_{\text{PC}} = 16$  Hz, CH), 133.6 (d,  $J_{\text{PC}} = 11$  Hz, C), 134.1 (d,  $J_{\text{PC}} = 59$  Hz, C). IR:  $\nu = 3500$  (broad band), 2922, 2382, 1591, 1437, 1113, 918, 801, 774, 662  $\text{cm}^{-1}$ . HRMS (ESI-MS)  $[\text{M}+\text{Na}]^+$ : found 289.0927; calculated for  $\text{C}_{16}\text{H}_{16}\text{OBPNa}$ : 289.0927.

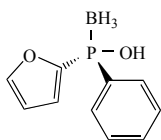
The enantiomeric excess was determined by HPLC analysis on a CHIRACEL OD-H column with a CD detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent Hexane/EtOH, 8:2; (+)-**3f**:  $t_r = 8.5$  min, (-)-**3f**:  $t_r = 11.3$  min.

Left: nearly racemic sample. Right: enantioenriched **3f**.



RT	Area	Conc 1
8.47	703322	50.282
11.30	695424	49.718
	1398746	100.000

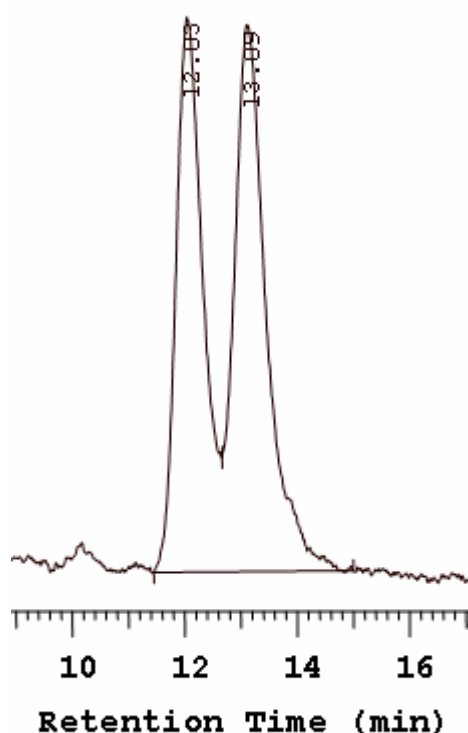




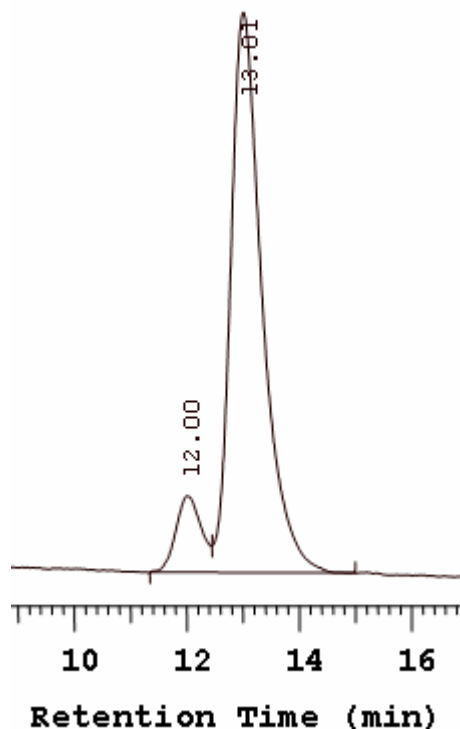
**3g**: oil. 92 % yield (189 mg).  $[\alpha]_D^{20} +5.8$  ( $c = 0.92$ ,  $\text{CHCl}_3$ ).  $^{31}\text{P}$  NMR (81 MHz,  $\text{CDCl}_3$ ):  $\delta = 78.3$  (broad q,  $J_{\text{PB}} = 62$  Hz);  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ ):  $\delta = 0.1$ -1.9 (broad m, 3H), 5.4 (broad s, 1H), 6.45 (m, 1H), 7.09 (broad d,  $J = 3$  Hz, 1H), 7.4-7.5 (m, 3H), 7.65 (broad s, 1H), 7.7-7.9 (m, 2H), 7.89 ;  $^{13}\text{C}$  NMR (50 MHz,  $\text{CDCl}_3$ ):  $\delta = 110.8$  (d,  $J_{\text{CP}} = 8$  Hz, CH), 122.8 (d,  $J_{\text{CP}} = 22$  Hz, CH), 128.6 (d,  $J_{\text{CP}} = 11$  Hz, 2CH), 131.0 (d,  $J_{\text{CP}} = 12.2$  Hz, 2CH), 131.8 (d,  $J_{\text{CP}} = 2$  Hz, CH), 148.5 (d,  $J_{\text{CP}} = 6$  Hz, CH), quaternary carbons were not observed. IR  $\nu = 3312$  (broad band), 2386, 2260, 1731, 1553, 1440, 1369, 1195, 1069, 1010, 884, 748, 641  $\text{cm}^{-1}$ . HRMS (ESI-MS)  $[\text{M}-\text{H}]^-$ : found 205.0594; calculated for  $\text{C}_{10}\text{H}_{11}\text{O}_2\text{PB}$ : 205.0597.

The enantiomeric excess was determined by HPLC analysis on a chiralpak OD-H column with a UV detector at  $\lambda = 254$  nm; flow rate 1 mL/min; eluent : hexane/i-PrOH 90:10; (-)-**3g**:  $t_r = 12$  min, (+)-**3g**:  $t_r = 13$  min.

Left: nearly racemic sample. Right: enantioenriched **3g**.



RT	Area	Conc 1
12.03	154156	45.674
13.09	183354	54.326
	337510	100.000



RT	Area	Conc 1
12.00	166023	9.887
13.01	1513172	90.113
	1679195	100.000