

# Efficient Asymmetric Syntheses of 1-Phenyl-phosphindane, Derivatives, and 2- or 3-Oxa Analogs: Mission Accomplished

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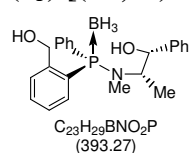
## 1. Preparation of Compounds

### Materials and methods

The following compounds were prepared according to literature procedures: (2*S*,4*R*,5*S*)-(–)-3,4-dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine-2-borane ((–)-oxazaPB; derived from (1*S*,2*R*)-(+)-ephedrine) and its enantiomer (2*R*,4*S*,5*R*)-(+)-oxazaPB (derived from (1*R*,2*S*)-(–)-ephedrine).<sup>1</sup> (*R*<sub>P</sub>)- and (*S*<sub>P</sub>)-(*o*-hydroxyphenyl)(methyl)(phenyl)phosphine-*P*-boranes (**10**) were prepared from (–)-oxazaPB and (+)-oxazaPB, respectively.<sup>2</sup>

Reactions were conducted under an inert atmosphere using anhydrous solvents when required. Analytical thin layer chromatography (TLC) was performed on Silica Gel 60F<sub>254</sub> plates. Chromatography over silica gel was carried out using Silica Gel 60 (40–63 μm). Melting points were determined on a Kofler apparatus and are uncorrected. Optical rotations were measured on a Perkin-Elmer 341 polarimeter. <sup>1</sup>H (300 MHz, internal Me<sub>4</sub>Si), <sup>13</sup>C (75 MHz, internal CDCl<sub>3</sub>), and <sup>31</sup>P NMR (120 MHz, external 85% H<sub>3</sub>PO<sub>4</sub>) were recorded for solutions in CDCl<sub>3</sub> if not stated otherwise. HRMS measurements were obtained on an Agilent 6224 Accurate Mass TOF LC/MS instrument coupled with an Agilent 1260 HPLC Infinity module and a dual ESI interface, and with a Waters Micromass Q-TOF Premier instrument equipped with orthogonal Z-spray ESI interface, respectively.

**(*S*<sub>P</sub>)-[(1*R*,2*S*)-*N*-Ephedrino](2-hydroxymethyl-phenyl)(phenyl)phosphine-*P*-borane ((*S*<sub>P</sub>)-**1**):** To a



cold (–70 °C) solution of 2-bromobenzyl alcohol (12.80 g, 68.4 mmol) in Et<sub>2</sub>O (500 mL) was added *s*-BuLi (1.25 M, 108 mL, 135 mmol). After stirring at –70 °C for 1 h, crystalline (+)-oxazaPB (15.00 g, 52.6 mmol) was added in one portion and the mixture allowed to warm up to rt with overnight stirring. Water (50 mL) and EtOAc (50 mL) were added, the organic layer separated, washed with brine, filtered through

a short path of silica gel/Na<sub>2</sub>SO<sub>4</sub>, and concentrated. Recrystallization (25.4 g) from hexane/CH<sub>2</sub>Cl<sub>2</sub>/toluene afforded a white crystalline powder (17.93 g, 86.8%): mp 118–119 °C; [ $\alpha$ ]<sub>D</sub><sup>25</sup> +49.4 (*c* 1.0, CHCl<sub>3</sub>) (>99.9% de by <sup>1</sup>H NMR); <sup>1</sup>H NMR:  $\delta$  7.68–7.58 (m, 1H), 7.58–7.18 (m, 13H), 4.92 (d, *J* = 3.7 Hz, 1H), 4.62 (q, *J* = 13.1 Hz, 2H), 4.42–4.14 (m, 1H), 2.64 (d, *J* = 7.7 Hz, 3H), 2.54–2.23 (br s, 1H), 1.92 (br s, 1H), 1.24 (d, *J* = 6.9 Hz, 3H), 1.77–0.52 (m, 3H); <sup>13</sup>C NMR:  $\delta$  144.8 (d, *J* = 13 Hz), 142.4, 132.7 (d, *J* = 7 Hz), 132.6, 131.7 (d, *J* = 8 Hz), 131.7, 131.1, 130.9, 128.6 (d, *J* = 10

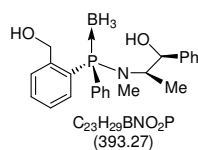
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(1) Jugé, S.; Stephan, M.; Laffitte, J. A.; Genêt, J. P. *Tetrahedron Lett.* **1990**, *31*, 6357–6360.

(2) Stephan, M.; Modéc, B.; Mohar, B. *Tetrahedron Lett.* **2011**, *52*, 1086–1089.

Hz), 128.4 (d,  $J = 61$  Hz), 128.3, 127.5, 127.4, 126.0, 78.9 (d,  $J = 3$  Hz), 62.6 (d,  $J = 5$  Hz), 58.1 (d,  $J = 10$  Hz), 31.6 (d,  $J = 3$  Hz), 11.7 (d,  $J = 4$  Hz);  $^{31}\text{P}$  NMR:  $\delta$  +68.9 (br m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{23}\text{H}_{30}\text{BNO}_2\text{P}$  [ $M^+ + \text{H}$ ] 394.2107, found 394.2113.

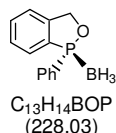
***(R\_P)*–[(1*S*,2*R*)-*N*-Ephedrinol](2-hydroxymethyl-phenyl)(phenyl)phosphine-*P*-borane ((*R\_P*)-1):**



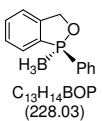
Following a similar procedure as for (*S\_P*)-1 starting from (–)-oxazaPB, a crystalline material (>99.9% de by  $^1\text{H}$  NMR) was obtained with identical characteristics as described above.

**Absolute configuration determination:** single X-ray crystal structure analysis revealed its (*R\_P*)-configuration.

***(R\_P)*-1-Phenyl-2-oxa-1-phosphindane-*P*-borane ((*R\_P*)-2):** To a solution of (*S\_P*)-1 (5.40 g, 13.05 mmol) in MeOH (100 mL) was added at rt under stirring a solution of 96%  $\text{H}_2\text{SO}_4$  (1.28 g, 13.05 mmol) in MeOH (20 mL). After stirring for 1.5 h, the reaction mixture was filtered through a bed of silica gel and concentrated. Purification on silica gel eluting with toluene afforded the title compound as a white powder (2.85 g, 96%): mp 44–46 °C; 97.5% ee by HPLC (see below). The ee was upgraded by single recrystallization from MeOH/ $\text{CH}_2\text{Cl}_2$  at 4 °C, and the enriched product was collected from the recrystallization filtrate. After concentration, the title compound was obtained as white crystals (2.2 g, 75% total yield):  $[\alpha]_{\text{D}}^{25} -50.5$  (c 1.0,  $\text{CHCl}_3$ ) (99.8% ee by HPLC, see below);  $^1\text{H}$  NMR:  $\delta$  7.69–7.54 (m, 4H), 7.54–7.36 (m, 5H), 5.80–5.28 (m, 2H), 1.82–0.39 (m, 3H);  $^{13}\text{C}$  NMR:  $\delta$  142.6 (d,  $J = 12$  Hz), 132.7 (d,  $J = 47$  Hz), 132.4 (d,  $J = 2$  Hz), 132.0 (d,  $J = 2$  Hz), 131.0 (d,  $J = 12$  Hz), 130.4 (d,  $J = 59$  Hz), 129.1 (d,  $J = 10$  Hz), 128.7 (d,  $J = 10$  Hz), 128.3 (d,  $J = 14$  Hz), 121.6 (d,  $J = 9$  Hz), 76.1 (d,  $J = 10$  Hz);  $^{31}\text{P}$  NMR:  $\delta$  +125.4 (br m); HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{13}\text{H}_{12}\text{OP}$  [ $M^+ + \text{H} - \text{BH}_3$ ] 215.062, found 215.0621.



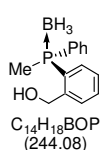
***(S\_P)*-1-Phenyl-2-oxa-1-phosphindane-*P*-borane ((*S\_P*)-2):** Following a similar procedure as for (*R\_P*)-2 starting from (*R\_P*)-1, a crystalline material (99.9% ee by HPLC, see below) was obtained with identical characteristics as described above.



**Absolute configuration determination:** single X-ray crystal structure analysis revealed its (*S\_P*)-configuration.

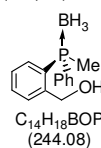
**HPLC determination of enantiomeric excess of 2:** a quasi-racemic mixture was prepared by mixing (*R\_P*)-2 and (*S\_P*)-2. HPLC analysis was carried out on a Daicel Chiralcel OD column (25 cm) conjugated with a Daicel Chiralcel OD-H column (15 cm): hexane/2-PrOH 98:2, 1.0 mL/min, UV detection ( $\lambda = 230$  nm),  $t_{\text{R}} = 21.4$  min (*S\_P*), 22.6 min (*R\_P*).

***(R\_P)*-(2-Hydroxymethyl-phenyl)(methyl)(phenyl)phosphine-*P*-borane ((*R\_P*)-3):** To a cold (–78 °C)



suspension of (*R\_P*)-2 (99.8% ee; 2.85 g, 12.5 mmol) in cumene (300 mL) was added MeLi·LiBr (1.5 M in  $\text{Et}_2\text{O}$ , 16.7 mL, 25 mmol) dropwise during 15 min. The mixture was stirred at –78 °C for 3 h then quenched with MeOH (2 mL). Water (100 mL) and  $\text{Et}_2\text{O}$  (150 mL) were added and the product extracted. The organic layer was washed with brine (40 mL), filtered through a bed of silica gel/ $\text{Na}_2\text{SO}_4$ , and concentrated affording a colourless oil (2.96 g, 97%).  $[\alpha]_{578}^{25} -23.97$  (c 1.0,  $\text{CHCl}_3$ ) (97.7% ee by HPLC, see below);  $^1\text{H}$  NMR:  $\delta$  7.71–7.51 (m, 5H), 7.51–7.33 (m, 4H), 4.67 (d,  $J = 13.4$  Hz, 1H), 4.35 (d,  $J = 13.4$  Hz, 1H), 2.46 (s, 1H), 1.86 (d,  $J = 9.9$  Hz, 3H), 1.75–0.47 (m, 3H);  $^{13}\text{C}$  NMR:  $\delta$  144.7 (d,  $J = 9$  Hz), 131.9 (d,  $J = 1$  Hz), 131.8 (d,  $J = 7$  Hz), 131.4 (d,  $J = 10$  Hz), 131.2 (d,  $J = 3$  Hz), 130.9 (d,  $J = 52$  Hz), 130.3 (d,  $J = 8$  Hz), 128.9 (d,  $J = 10$  Hz), 127.7 (d,  $J = 9$  Hz), 127.3 (d,  $J = 53$  Hz), 62.6 (d,  $J = 6$  Hz), 13.3 (d,  $J = 42$  Hz);  $^{31}\text{P}$  NMR:  $\delta$  +13.3 (br m); HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{16}\text{OP}$  [ $M^+ + \text{H} - \text{BH}_3$ ] 231.0933, found 231.0935.

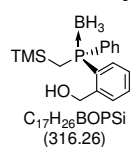
***(S\_P)*-(2-Hydroxymethyl-phenyl)(methyl)(phenyl)phosphine-*P*-borane ((*S\_P*)-3):** To a cold (–78 °C)



solution of (*R\_P*)-2 (99.8% ee; 2.85 g, 12.5 mmol) and (1*R*,2*R*)-*N,N,N',N'*-tetramethylcyclohexane-1,2-diamine (6.38 g, 37.5 mmol) in toluene (300 mL) was added dropwise MeLi (1.6 M in  $\text{Et}_2\text{O}$ , 11.7 mL, 18.75 mmol) during 15 min. The mixture was stirred at –78 °C for 3 h then quenched with MeOH (2 mL). Water (50 mL) was added and the product extracted with  $\text{Et}_2\text{O}$  (100 mL). The organic layer was washed with 1 M HCl (3×25 mL) then brine (40 mL), filtered through a bed of silica gel/ $\text{Na}_2\text{SO}_4$ , and concentrated affording a colourless oil (2.89 g, 94%) with identical characteristics as described above:  $[\alpha]_{578}^{25} +23.07$  (c 1.0,  $\text{CHCl}_3$ ) (95.3% ee by HPLC, see hereafter).

**HPLC determination of enantiomeric excess of 3:** a quasi-racemic mixture was prepared by mixing (*S<sub>P</sub>*)-**3** and (*R<sub>P</sub>*)-**3**. HPLC analysis was carried out on a Daicel Chiralcel OD column (25 cm) conjugated with a Chiralcel OD-H column (15 cm): hexane/2-PrOH 95:5, 1.0 mL/min, UV detection ( $\lambda = 230$  nm),  $t_R = 31.4$  min (*S<sub>P</sub>*), 33.8 min (*R<sub>P</sub>*).

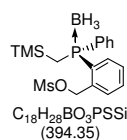
**(*R<sub>P</sub>*)-(2-Hydroxymethyl-phenyl)(phenyl)(trimethylsilylmethyl)phosphine-*P*-borane ((*R<sub>P</sub>*)-**4**),**



**Route A:** To a cold ( $-78$  °C) solution of (*R<sub>P</sub>*)-**2** (2.51 g, 11 mmol) in Et<sub>2</sub>O (100 mL) and (–)-sparteine (4.13 g, 17.6 mmol) was added dropwise TMSCH<sub>2</sub>Li (1.0 M in pentane, 16.5 mL, 16.5 mmol) during 10 min. The mixture was stirred at  $-78$  °C for 0.5 h then allowed to warm up to  $0$  °C over 6 h and quenched with MeOH (2 mL). Water (100 mL) was added and the product extracted with Et<sub>2</sub>O (150 mL). The organic layer was washed with brine (40 mL), filtered through a bed of silica gel/Na<sub>2</sub>SO<sub>4</sub>, and concentrated. The crude was purified by column chromatography eluting with petroleum ether 40-60/EtOAc (9:1). Colourless oil (2.8 g, 80%).  $[\alpha]_D^{25} = -14.5$  ( $c = 1.0$ , CHCl<sub>3</sub>) (90.2% ee by HPLC analysis of its Ms derivative **5**, see below); <sup>1</sup>H NMR:  $\delta$  7.89–7.68 (m, 1H), 7.65–7.51 (m, 4H), 7.47–7.35 (m, 4H), 4.62 (d,  $J = 13.2$  Hz, 1H), 4.37 (d,  $J = 13.2$  Hz, 1H), 1.76–1.63 (m, 1H), 1.61–1.47 (m, 1H), 1.57–0.41 (m, 3H),  $-0.02$  (s, 9H); <sup>13</sup>C NMR:  $\delta$  144.5 (d,  $J = 8$  Hz), 132.94 (d,  $J = 55$  Hz), 132.58 (d,  $J = 9$  Hz), 131.70 (d,  $J = 2$  Hz), 131.56 (d,  $J = 10$  Hz), 130.9 (d,  $J = 2$  Hz), 130.6 (d,  $J = 8$  Hz), 129.6 (d,  $J = 51$  Hz), 128.9 (d,  $J = 10$  Hz), 127.6 (d,  $J = 10$  Hz), 62.8 (d,  $J = 6$  Hz), 13.8 (d,  $J = 26$  Hz), 0.5 (d,  $J = 3$  Hz); <sup>31</sup>P NMR:  $\delta$  +13.1 (br m); HRMS (ESI):  $m/z$  calcd. for C<sub>17</sub>H<sub>24</sub>OPSi [ $M^+ + H - BH_3$ ] 303.1329, found 303.1326.

**Route B:** To a cold ( $-40$  °C) solution of (*R<sub>P</sub>*)-**3** (97.7% ee; 2.93 g, 12 mmol) in THF (100 mL) was added *s*-BuLi (1.3 M, 20.3 mL, 26.4 mmol). The resulting mixture was left to stir at  $-40$  °C for 1 h then TMSCl (4.57 mL, 36 mmol) was added and allowed to warm up to  $0$  °C during 1 h. The reaction mixture was quenched with satd. aq. NH<sub>4</sub>Cl (80 mL), stirred at rt for 3 h then extracted with Et<sub>2</sub>O (100 mL). The organic layer was washed with brine (40 mL), filtered through a bed of silica gel/Na<sub>2</sub>SO<sub>4</sub>, and concentrated affording a colourless oil (3.72 g, 98%) with identical characteristics as described above:  $[\alpha]_D^{25} = -15.9$  ( $c = 1.0$ , CHCl<sub>3</sub>) (97.7% ee by HPLC analysis of its Ms derivative **5**, see below).

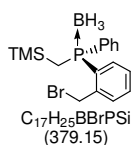
**(*R<sub>P</sub>*)-(2-Mesyloxymethyl-phenyl)(phenyl)(trimethylsilylmethyl)phosphine-*P*-borane ((*R<sub>P</sub>*)-**5**):** To a



cold ( $-20$  °C) solution of (*R<sub>P</sub>*)-**4** (97.7% ee; 3.76 g, 11.9 mmol) and Et<sub>3</sub>N (2.2 mL, 15.4 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (100 mL) was added dropwise mesyl chloride (1.1 mL, 14.3 mmol). After stirring for 1 h at  $-20$  °C, the reaction mixture was washed with H<sub>2</sub>O (80 mL) then brine (80 mL), and dried (Na<sub>2</sub>SO<sub>4</sub>). Purification by column chromatography on silica gel eluting with toluene/EtOAc 4:1 afforded a colourless oil (4.52 g, 96%): 97.7% ee by HPLC (see below). Recrystallization from MeOH at  $-15$  °C yielded the title compound as a white crystalline powder (3.6 g, 78%): mp  $92-94$  °C;  $[\alpha]_D^{25} = -15.0$  ( $c = 1.0$ , CHCl<sub>3</sub>) (>99.9% ee by HPLC, see below); <sup>1</sup>H NMR:  $\delta$  7.86 (m, 1H), 7.67–7.54 (m, 4H), 7.52–7.40 (m, 4H), 5.25 (d,  $J = 12.1$  Hz, 1H), 5.05 (d,  $J = 12.2$  Hz, 1H), 2.77 (s, 3H), 1.70 (m, 1H), 1.64–1.51 (m, 1H), 1.54–0.43 (m, 3H),  $-0.03$  (s, 9H); <sup>13</sup>C NMR:  $\delta$  137.1 (d,  $J = 7$  Hz), 133.0 (d,  $J = 10$  Hz), 132.2 (d,  $J = 54$  Hz), 131.688 (d,  $J = 2$  Hz), 131.685 (d,  $J = 10$  Hz), 131.2 (d,  $J = 2$  Hz), 131.0 (d,  $J = 7$  Hz), 130.96 (d,  $J = 7$  Hz), 130.94 (d,  $J = 48$  Hz), 128.9 (d,  $J = 10$  Hz), 68.5 (d,  $J = 5$  Hz), 37.4, 13.5 (d,  $J = 25$  Hz), 0.4 (d,  $J = 3$  Hz); <sup>31</sup>P NMR:  $\delta$  +14.7 (br m); HRMS (ESI):  $m/z$  calcd for C<sub>18</sub>H<sub>28</sub>BNaO<sub>3</sub>PSSi [ $M^+ + Na$ ] 417.1257, found 417.1249.

**HPLC determination of enantiomeric excess of 5:** a quasi-racemic mixture was prepared by mixing (*S<sub>P</sub>*)-**5** and (*R<sub>P</sub>*)-**5**. *S<sub>P</sub>*)-**5** was prepared via (*S<sub>P</sub>*)-**3** following Scheme 1 starting from (–)-oxazaPB. HPLC analysis was carried out on a Daicel Chiralcel AD-H column (25 cm): hexane/2-PrOH 95:5, 1.0 mL/min, UV detection ( $\lambda = 220$  nm),  $t_R = 15.1$  min (*S<sub>P</sub>*), 17.1 min (*R<sub>P</sub>*).

**(*R<sub>P</sub>*)-(2-Bromomethyl-phenyl)(phenyl)(trimethylsilylmethyl)phosphine-*P*-borane ((*R<sub>P</sub>*)-**6**):** To a



solution of (*R<sub>P</sub>*)-**5** (>99.9% ee; 3.40 g, 8.6 mmol) in THF (70 mL) was added a solution of LiBr (2.95 g, 34.4 mmol) in THF (40 mL) and the mixture heated at  $55$  °C for 2.5 h. after cooling to rt, H<sub>2</sub>O (20 mL) and Et<sub>2</sub>O (50 mL) were added and the organic layer separated and dried (Na<sub>2</sub>SO<sub>4</sub>). The concentrated residue was taken in toluene and filtered through a bed of silica gel affording a colourless oil (3.09 g, 95%):  $[\alpha]_D^{25} = -18.3$  ( $c = 1.0$ , CHCl<sub>3</sub>) (>99.9% ee by HPLC analysis of (*R<sub>P</sub>*)-**7** prepared from (*R<sub>P</sub>*)-**6**); <sup>1</sup>H NMR:  $\delta$  7.92–7.79 (m, 1H), 7.65–7.55 (m, 2H), 7.55–7.49 (m, 2H), 7.49–7.34 (m, 4H), 4.72–4.25 (m, 2H),

1.90–1.75 (m, 1H), 1.72–1.44 (m, 1H), 1.79–0.72 (m, 3H), –0.13 (s, 9H);  $^{13}\text{C}$  NMR:  $\delta$  141.4 (d,  $J$  = 5 Hz), 133.7 (d,  $J$  = 12 Hz), 133.2 (d,  $J$  = 7 Hz), 132.5 (d,  $J$  = 55 Hz), 131.9 (d,  $J$  = 2 Hz), 131.4 (d,  $J$  = 10 Hz), 130.9 (d,  $J$  = 2 Hz), 130.4 (d,  $J$  = 49 Hz), 128.9 (d,  $J$  = 10 Hz), 128.3 (d,  $J$  = 10 Hz), 31.4 (d,  $J$  = 5 Hz), 12.8 (d,  $J$  = 25 Hz), 0.5 (d,  $J$  = 3 Hz);  $^{31}\text{P}$  NMR:  $\delta$  +11.2 (br m); HRMS (ESI):  $m/z$  calcd for  $\text{C}_{17}\text{H}_{24}\text{BBrPSi}$  [ $M^+ - \text{H}$ ] 377.0661, found 377.0666.

**(*R<sub>P</sub>*)-1-Phenyl-phosphindane-*P*-borane ((*R<sub>P</sub>*)-7):** To a mixture of CsF (3.50 g, 23.5 mmol) and 4 Å molecular sieves<sup>3</sup> (2 g) in *N,N*-dimethylacetamide (100 mL) was added a solution of (*R<sub>P</sub>*)-6 (>99.9% ee; 3.09 g, 8.15 mmol) in the same solvent (50 mL) also containing 4 Å molecular sieves (2 g). After stirring at rt for 3 h, the mixture was cooled on an ice-bath and ice-water (100 mL) was added. Extraction with  $\text{Et}_2\text{O}$  (2×150 mL), filtration through a bed of silica gel/ $\text{Na}_2\text{SO}_4$  and concentration afforded the crude product which was purified by column chromatography eluting with hexane/EtOAc (99:1 to 98:2). Colourless oil (1.44 g, 78%);  $[\alpha]_{\text{D}}^{25}$  +17.36 ( $c$  1.0,  $\text{CHCl}_3$ ) (>99.9% ee by HPLC, see below);  $^1\text{H}$  NMR:  $\delta$  7.66–7.58 (m, 1H), 7.54–7.29 (m, 8H), 3.57–3.17 (m, 2H), 2.69–2.28 (m, 2H), 1.48–0.41 (m, 3H);  $^{13}\text{C}$  NMR:  $\delta$  148.4 (d,  $J$  = 15 Hz), 131.643 (d,  $J$  = 10 Hz), 131.643 (d,  $J$  = 2 Hz),<sup>4</sup> 131.2 (d,  $J$  = 3 Hz), 130.80 (d,  $J$  = 7 Hz), 130.17 (d,  $J$  = 12 Hz), 130.2 (d, 8 Hz), 128.7 (d,  $J$  = 10 Hz), 127.9 (d,  $J$  = 10 Hz), 125.6 (d,  $J$  = 8 Hz), 31.7 (d,  $J$  = 4 Hz), 25.9 (d,  $J$  = 38 Hz);  $^{31}\text{P}$  NMR:  $\delta$  +37.5 (br m); HRMS (ESI):  $m/z$  calcd. for  $\text{C}_{14}\text{H}_{14}\text{P}$  [ $M^+ + \text{H} - \text{BH}_3$ ] 213.0828, found 213.0828;  $^1\text{H}$  and  $^{31}\text{P}$  NMR data are in accordance with the literature.<sup>5</sup>

**HPLC determination of enantiomeric excess of 7:** a mixture with 38% ee was prepared by mixing (*S<sub>P</sub>*)-7 and (*R<sub>P</sub>*)-7 ((*R<sub>P</sub>*)-7 in excess). (*S<sub>P</sub>*)-7 was prepared from (*S<sub>P</sub>*)-6 via (*S<sub>P</sub>*)-3 following Scheme 1 starting from (–)-oxazaPB. HPLC analysis was carried out using a Daicel Chiralcel OJ-H column (25 cm): hexane/2-PrOH 95:5, 1.0 mL/min, UV detection ( $\lambda$  = 230 nm),  $t_{\text{R}}$  = 20.8 min (*S<sub>P</sub>*), 24.6 min (*R<sub>P</sub>*).

**(*R<sub>P</sub>*)-1-Phenyl-phosphindane ((*R<sub>P</sub>*)-8):** A solution of (*R<sub>P</sub>*)-7 (>99.9% ee; 300 mg, 1.33 mmol) in  $\text{Et}_2\text{NH}$  (5 mL) and toluene (10 mL) was stirred at rt for 16 h. After concentration, the residue was filtered through a  $\text{SiO}_2$  plug eluting with toluene. Colorless oil (276 mg, 98%). The product can be recrystallized from MeOH at –15 °C and filtering cold; white plates (mp <10 °C).  $[\alpha]_{\text{D}}^{25}$  +193.9 ( $c$  1.0,  $\text{CHCl}_3$ ) (>99.9% ee by HPLC analysis of (*R<sub>P</sub>*)-7 prepared from (*R<sub>P</sub>*)-8 by complexation with  $\text{Me}_2\text{S} \cdot \text{BH}_3$  in  $\text{CH}_2\text{Cl}_2$  at 0 °C);  $^1\text{H}$  NMR:  $\delta$  7.79–7.60 (m, 1H), 7.43–7.11 (m, 8H), 3.34–3.00 (m, 2H), 2.44–2.24 (m, 1H), 2.18–2.05 (m, 1H);  $^{13}\text{C}$  NMR:  $\delta$  149.4 (d,  $J$  = 2 Hz), 140.0 (d,  $J$  = 7 Hz), 139.6 (d,  $J$  = 23 Hz), 131.5 (d,  $J$  = 8 Hz), 131.2, 129.0, 128.2 (d,  $J$  = 6 Hz), 128.0, 126.7 (d,  $J$  = 8 Hz), 124.9 (d,  $J$  = 2 Hz), 34.3 (d,  $J$  = 6 Hz), 27.6 (d,  $J$  = 8 Hz);  $^{31}\text{P}$  NMR:  $\delta$  –3.5 (s).  $^1\text{H}$  and  $^{31}\text{P}$  NMR data are in accordance with the literature.<sup>5</sup>

**(*S<sub>P</sub>*)-1-Phenyl-phosphindane-*P*-oxide ((*S<sub>P</sub>*)-9):** To a cold (0 °C) solution of (*R<sub>P</sub>*)-8 (>99.9% ee; 95 mg, 0.45 mmol) in acetone was added 60% aq  $\text{H}_2\text{O}_2$  (100  $\mu\text{L}$ ) under stirring. After 10 min, the mixture was concentrated and the residual crude partitioned between EtOAc/ $\text{H}_2\text{O}$ . Filtration of the organic layer through a bed of  $\text{Na}_2\text{SO}_4/\text{MgSO}_4$  and concentration, afforded a colorless oil (97 mg, 95%);  $[\alpha]_{\text{D}}^{25}$  –36.5 ( $c$  1.0,  $\text{CHCl}_3$ ) (>99.9% ee by HPLC, see below);  $^1\text{H}$  NMR:  $\delta$  7.92–7.32 (m, 9H), 3.53–3.33 (m, 1H), 3.28–3.09 (m, 1H), 2.58–2.33 (m, 2H);  $^{13}\text{C}$  NMR:  $\delta$  147.6 (d,  $J$  = 31 Hz), 133.5 (d,  $J$  = 36 Hz), 132.8 (d,  $J$  = 2 Hz), 132.1 (d,  $J$  = 41 Hz), 131.8 (d,  $J$  = 3 Hz), 130.5 (d,  $J$  = 10 Hz), 129.0 (d,  $J$  = 10 Hz), 128.5 (d,  $J$  = 12 Hz), 127.8 (d,  $J$  = 10 Hz), 126.4 (d,  $J$  = 11 Hz), 28.2 (d,  $J$  = 4 Hz), 28.0 (d,  $J$  = 71 Hz);  $^{31}\text{P}$  NMR (243 MHz):  $\delta$  +56.5 (s). NMR data were consistent with those reported in the literature.<sup>6</sup>

**HPLC determination of enantiomeric excess of 9:** a mixture with 37% ee was prepared by mixing (*S<sub>P</sub>*)-9 and (*R<sub>P</sub>*)-9 ((*S<sub>P</sub>*)-9 in excess). (*R<sub>P</sub>*)-9 was prepared from (*S<sub>P</sub>*)-7 via (*S<sub>P</sub>*)-3 following Scheme 1 starting from (–)-oxazaPB. HPLC analysis was carried out on a Daicel Chiralcel AD-H column (25 cm): hexane/2-PrOH 95:5, 1.0 mL/min, UV detection ( $\lambda$  = 230 nm),  $t_{\text{R}}$  = 44.3 min (*R<sub>P</sub>*), 51.2 min (*S<sub>P</sub>*).

**Absolute configuration:** This was determined by comparison with the literature<sup>6</sup> of HPLC elution on Chiralpak IA column: heptane/EtOH 90:10, 1.0 mL/min, UV detection ( $\lambda$  = 230 nm):  $t_{\text{R}}$  = 20.5 min ((*R<sub>P</sub>*)-9), 22.2 min ((*S<sub>P</sub>*)-9).

(3) Activated powdered molecular sieves were used.

(4) Two separate doublets with different coupling constants but with identical chemical shifts.

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**(*R<sub>P</sub>*)-1-Phenyl-3-oxa-1-phosphindane-*P*-borane ((*R<sub>P</sub>*)-11):** To a cold (−20 °C) solution of (*R<sub>P</sub>*)-**10** ( $>99.9\%$  ee, 1.00 g, 4.34 mmol) in THF (50 ml) was added dropwise *s*-BuLi (6.67 ml, 8.46 mmol) in 5 min. The mixture was stirred at that temperature for 1 h. After cooling to −78 °C, a solution of iodine (1.10 g, 4.34 mmol) in THF (30ml) was added dropwise maintaining the temperature below −75 °C then allowed to reach rt over 3 h. Quenching with H<sub>2</sub>O (20 ml) followed by brine (40 ml), extraction with Et<sub>2</sub>O (2×70 mL), drying (Na<sub>2</sub>SO<sub>4</sub>), and concentration afforded the crude product. Purification by column chromatography eluting with hexane/toluene (9:1 to 7:3) yielded the title compound as a colorless syrup (0.81 g, 82%);  $[\alpha]_D^{25} -2.02$  (*c* 1.0, CHCl<sub>3</sub>) ( $>99.9\%$  ee by HPLC, see below); <sup>1</sup>H NMR: δ 7.65–7.33 (m, 7H), 7.20–6.96 (m, 2H), 4.87 (dd, *J* = 12.7, 5.2 Hz, 1H), 4.77 (dd, *J* = 12.7, 6.2 Hz, 1H), 1.89–0.34 (m, 3H); <sup>13</sup>C NMR: δ 164.2 (d, *J* = 8 Hz), 134.1 (d, *J* = 2 Hz), 132.1, 132.0 (d, *J* = 10 Hz), 130.2 (d, *J* = 11 Hz), 129.0 (d, *J* = 10 Hz), 129.0 (d, *J* = 45 Hz), 122.9 (d, *J* = 10 Hz), 114.6 (d, *J* = 61 Hz), 112.8 (d, *J* = 5 Hz), 71.6 (d, *J* = 29 Hz); <sup>31</sup>P NMR: δ 15.4 (br m); HRMS (ESI): *m/z* calcd. for C<sub>13</sub>H<sub>12</sub>OP [*M*<sup>+</sup>+H–BH<sub>3</sub>] 215.062, found 215.0619.

**HPLC determination of enantiomeric excess of 11:** a quasi-racemic mixture was prepared by mixing (*S<sub>P</sub>*)-**11** and (*R<sub>P</sub>*)-**11**. (*S<sub>P</sub>*)-**11** was prepared following Scheme 2 starting from (+)-oxazaPB. HPLC analysis was carried out on homoconjugated Daicel Chiralcel OD-H columns (25 cm + 15 cm): hexane/2-PrOH 99:1, 1.0 mL/min, UV detection ( $\lambda$  = 230 nm), *t<sub>R</sub>* = 12.1 min (*S<sub>P</sub>*), 13.3 min (*R<sub>P</sub>*).

## 2. Organolithiums reaction with (*R<sub>P</sub>*)-**2** under various explored conditions (Table S1)<sup>a</sup>

RLi <sup>b</sup>	Solvent	T °C	Additive <sup>c</sup> (equiv/RLi)	<b>3 or 4</b> % ee ( <i>Conf.</i> ) <sup>d</sup>
TMSCH <sub>2</sub> Li	THF	-78	-	13 ( <i>R<sub>P</sub></i> )
TMSCH <sub>2</sub> Li	Et <sub>2</sub> O	-40	-	77 ( <i>R<sub>P</sub></i> )
TMSCH <sub>2</sub> Li	Et <sub>2</sub> O	-78	TMEDA (1.1)	87 ( <i>R<sub>P</sub></i> )
TMSCH <sub>2</sub> Li	Et <sub>2</sub> O	-78	TMEDA (1.1)	Not Analyzed ( <b>4</b> in 60% yield + byproducts)
TMSCH <sub>2</sub> Li	Et <sub>2</sub> O	-78	(-)-Sparteine (1.1)	<b>90</b> ( <i>R<sub>P</sub></i> )
TMSCH <sub>2</sub> Li	Toluene	-60	-	20 ( <i>R<sub>P</sub></i> )
MeLi	THF	-30	-	43 ( <i>S<sub>P</sub></i> )
MeLi	THF	-78	-	35 ( <i>S<sub>P</sub></i> )
MeLi	Et <sub>2</sub> O	-78	-	68 ( <i>R<sub>P</sub></i> )
MeLi	Et <sub>2</sub> O	-78	TMEDA (1.1)	85 ( <i>S<sub>P</sub></i> )
MeLi	Et <sub>2</sub> O	-78	LiBr (2.2)	9 ( <i>R<sub>P</sub></i> )
MeLi	MTBE	-78	-	67 ( <i>R<sub>P</sub></i> )
MeLi	Bu <sub>2</sub> O	-78	-	86 ( <i>R<sub>P</sub></i> )
MeLi	Toluene	0	-	69 ( <i>R<sub>P</sub></i> )
MeLi	Toluene	-78	-	89 ( <i>R<sub>P</sub></i> )
MeLi	Toluene	-78	HMPA (1.1)	85 ( <i>R<sub>P</sub></i> )
MeLi	Toluene	-78	TMEDA (1.1)	67 ( <i>S<sub>P</sub></i> )
MeLi	Toluene	-78	TMEDA (2.2)	83 ( <i>S<sub>P</sub></i> )
MeLi	Toluene	-78	TMEDA (4.4)	83 ( <i>S<sub>P</sub></i> )
MeLi	Toluene	-78	TMEDA (2.2) <sup>e</sup>	<b>95</b> ( <i>S<sub>P</sub></i> )
MeLi	Toluene	-78	(-)-Sparteine (2.2)	46 ( <i>S<sub>P</sub></i> )
MeLi	Et-PhH	-78	-	90 ( <i>R<sub>P</sub></i> )
MeLi	Cumene	-78	-	91 ( <i>R<sub>P</sub></i> )
MeLi	Cumene	-78	TMEDA (2.2)	92 ( <i>S<sub>P</sub></i> )
MeLi·LiBr	Et <sub>2</sub> O	-78	-	12 ( <i>R<sub>P</sub></i> )
MeLi·LiBr	Hexane	-78	-	No reaction
MeLi·LiBr	Toluene	-78	-	94 ( <i>R<sub>P</sub></i> )
MeLi·LiBr	Toluene	-78	TMEDA (2.2)	90 ( <i>S<sub>P</sub></i> )
MeLi·LiBr	Cumene	-78	-	<b>97</b> ( <i>R<sub>P</sub></i> )
MeLi·LiBr	Cumene	-78	TMEDA (2.2)	94 ( <i>S<sub>P</sub></i> )
Me <sub>3</sub> MgLi·LiCl <sup>f</sup>	Et <sub>2</sub> O	-40	-	65 ( <i>R<sub>P</sub></i> )

<sup>a</sup> RLi (2 equiv to **2**) was added at the indicated temperature to (*R<sub>P</sub>*)-**2** (99.8% ee) premixed with the optional additive and the reaction was quenched with water after 2–3 h. This protocol was adopted due to convenience and to inconsistent results with preformed RLi-additive.

<sup>b</sup> TMSCH<sub>2</sub>Li (1 M in pentane); MeLi (1.6 M in Et<sub>2</sub>O); MeLi·LiBr (1.5 M in Et<sub>2</sub>O); Me<sub>3</sub>MgLi·LiCl prepared at 0 °C from 1 equiv MeMgCl (3 M in THF) and 2 equiv MeLi (1.6 M in Et<sub>2</sub>O).

<sup>c</sup> TMEDA: *N,N,N',N'*-Tetramethylethylenediamine; TMEDA: *trans-N,N,N',N'*-Tetramethyl-1,2-cyclohexane-diamine; HMPA: Hexamethylphosphoramide.

<sup>d</sup> Ee was determined by chiral HPLC (for details, see above).

<sup>e</sup> (*R,R*)- or (*S,S*)-TMEDA used.

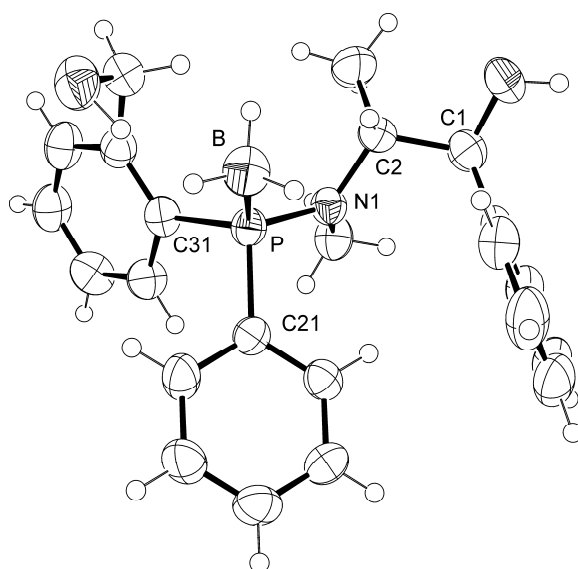
<sup>f</sup> Note that 60% ee was obtained with MeMgBr in THF at 60 °C while no reaction occurred at rt.

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#### 4. X-Ray Crystal Structures Determination

Data for (*R<sub>p</sub>*)-**1** and (*S<sub>p</sub>*)-**2** were collected on Agilent SuperNova diffractometer using monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) (crystal of (*R<sub>p</sub>*)-**1**) or Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å) (crystal of (*S<sub>p</sub>*)-**2**). The coordinates of some or all of the non-hydrogen atoms were found *via* direct methods using the structure solution SHELXS-97 program.<sup>7</sup> Positions of the remaining non-hydrogen atoms were located by using a combination of least-squares refinement and difference Fourier maps in the SHELXL-97 program.<sup>7</sup> Except hydrogen atoms, all atoms were refined anisotropically. The absolute configurations were determined by refinement of the completed models together with the Flack *x* parameters,<sup>8</sup> which refined to values of  $-0.12(12)$  and  $-0.02(2)$  for (*R<sub>p</sub>*)-**1** and (*S<sub>p</sub>*)-**2**, respectively, and thereby confirmed that the refined coordinates for each structure represent the true enantiomorph. Figures depicting the structures were prepared by Ortep3.<sup>9</sup> The supplementary crystallographic data (atomic coordinates, anisotropic displacement parameters, and extended lists of interatomic distances and angles) are contained in the cif files.



**Figure S1.** ORTEP drawing at the 50% probability level of (*R<sub>p</sub>*)-**1** derived from (+)-ephedrine. Selected bond lengths (Å) and angles (°): P–B 1.930(4); P–N1 1.657(2); P–C21 1.810(3); P–C31 1.840(3); B–P–N1 113.7(2); N1–P–C21 107.1(2), C21–P–C31 103.5(1); C31–P–B 118.4(2).

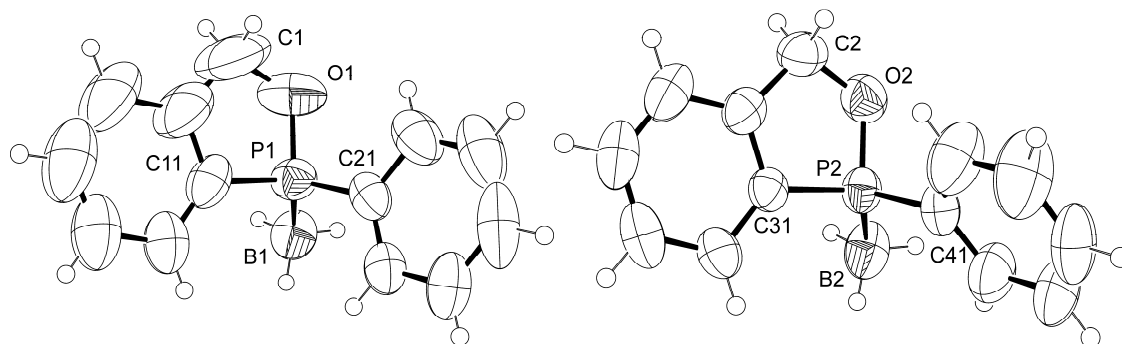
$C_{23}H_{29}BNO_2P$ ,  $M_r = 393.25$ , monoclinic, space group  $P 2_1$  (No. 4),  $a = 9.1640(16)$ ,  $b = 14.0102(17)$ ,  $c = 9.5202(18)$  Å,  $\alpha = 90$ ,  $\beta = 117.23(2)$ ,  $\gamma = 90^\circ$ ,  $V = 1086.8(3)$  Å<sup>3</sup>,  $Z = 2$ ,  $T = 293(2)$  K,  $d_{\text{calcd}} = 1.202$  g cm<sup>-3</sup>,  $\mu = 0.144$  mm<sup>-1</sup>, 10885 measured reflections, 4980 unique reflections ( $R_{\text{int}} = 0.0555$ ), 272 refined parameters,  $R_1 [I > 2\sigma(I)] = 0.0582$ ,  $wR2$  [all data] = 0.1584.

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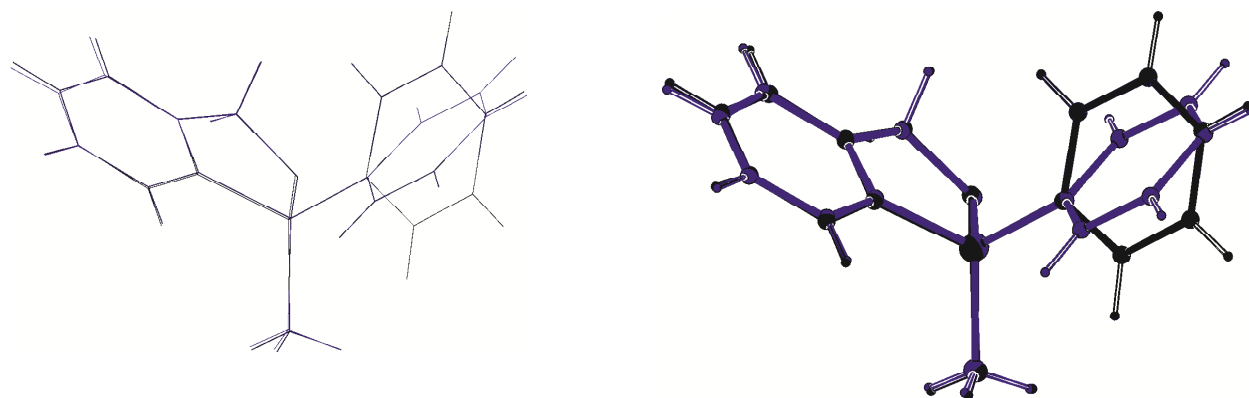
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**Figure S2.** ORTEP drawings at the 50% probability level of both molecules found in the asymmetric unit of (*S<sub>P</sub>*)-**2**. Selected bond lengths (Å) and angles (°) for the left molecule: P1–O1 1.599(2); P1–B1 1.880(4); P1–C11 1.804(3); P1–C21 1.813(3); C1–O1 1.492(7); O1–P1–C21 106.6(2); C21–P1–B1 114.8(2); B1–P1–C11 114.9(2); C11–P1–O1 95.2(2). Selected bond lengths (Å) and angles (°) for the right molecule: P2–O2 1.613(2); P2–B2 1.891(4); P2–C31 1.788(2); P2–C41 1.800(2); C2–O2 1.445(4); O2–P2–C41 104.6(1); C41–P2–B2 113.9(2); B2–P2–C31 116.5(1); C31–P2–O2 94.7(1).

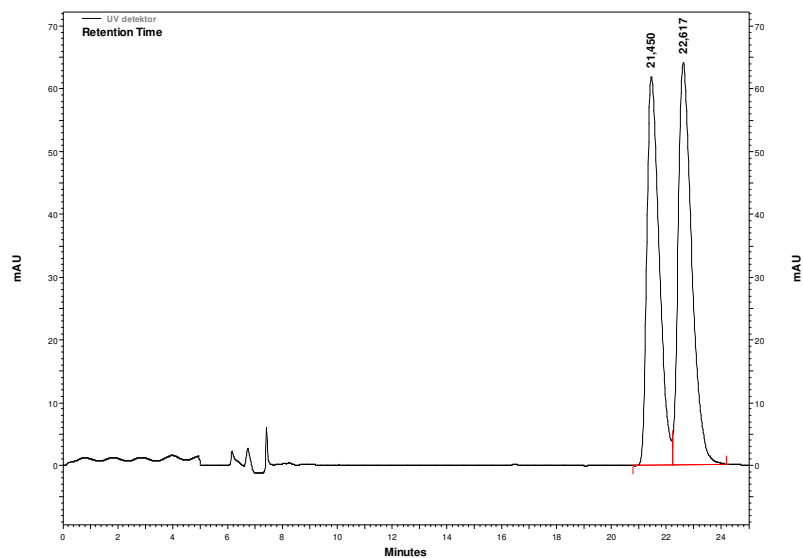
$C_{13}H_{14}BOP$ ,  $M_r = 228.02$ , monoclinic, space group  $P 2_1$  (No. 4),  $a = 11.8787(2)$ ,  $b = 8.9358(2)$ ,  $c = 12.7533(3)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 108.685(2)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 1282.36(5)$  Å<sup>3</sup>,  $Z = 4$ ,  $T = 293(2)$  K,  $d_{\text{calcd}} = 1.181$  g cm<sup>-3</sup>,  $\mu = 1.685$  mm<sup>-1</sup>, 14321 measured reflections, 5239 unique reflections ( $R_{\text{int}} = 0.0347$ ), 289 refined parameters,  $R_1 [I > 2\sigma(I)] = 0.0459$ ,  $wR2 [\text{all data}] = 0.1376$ .



**Figure S3.** An overlay of the two molecules belonging to the asymmetric unit in (*S<sub>P</sub>*)-**2**. The pair does not differ significantly in geometric parameters. The main difference is in the relative orientation of phenyl ring.

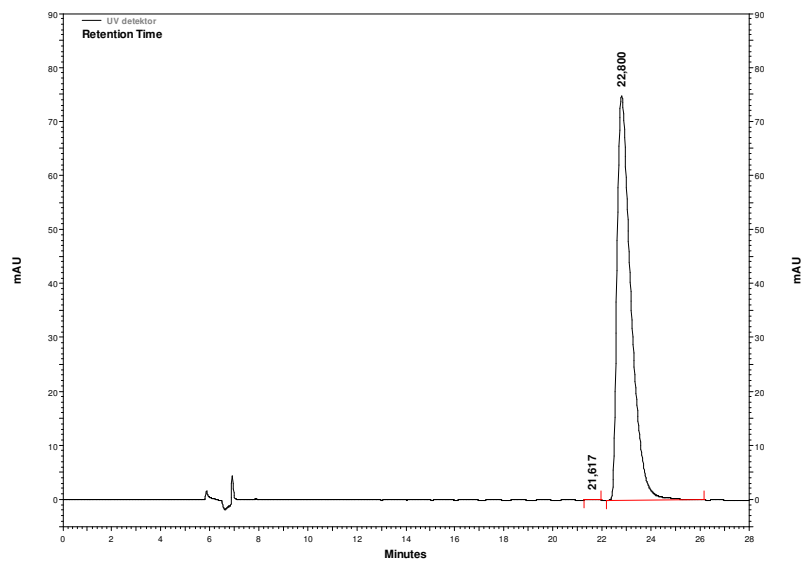
## 5. HPLC Chromatograms

### Quasi-*rac*-1-Phenyl-2-oxa-1-phosphindane-*P*-borane (*rac*-**2**)



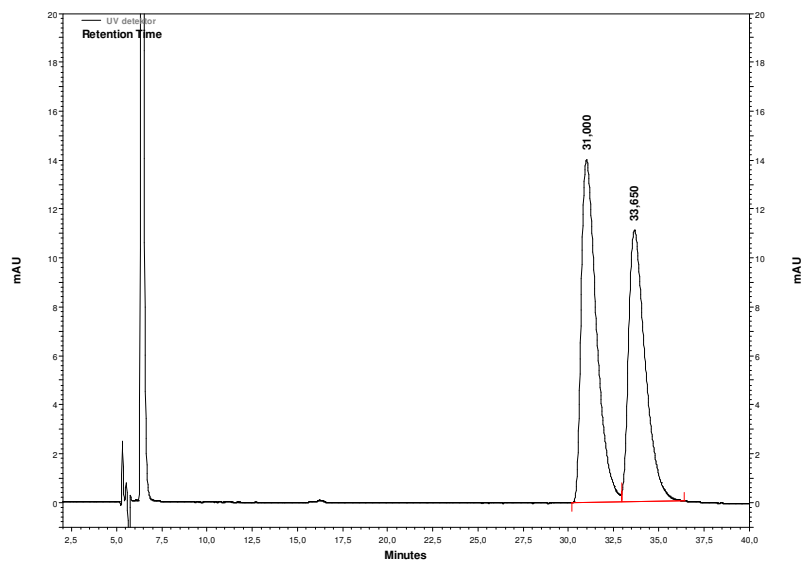
	Ret. Time	Area	Area %	Height	Height %
1	21,45	1941625	46,746	61828	49,106
2	22,617	2211960	53,254	64079	50,894

### (*R<sub>P</sub>*)-1-Phenyl-2-oxa-1-phosphindane-*P*-borane ((*R<sub>P</sub>*)-**2**), 99.8% ee; prepared from (–)-ephedrine



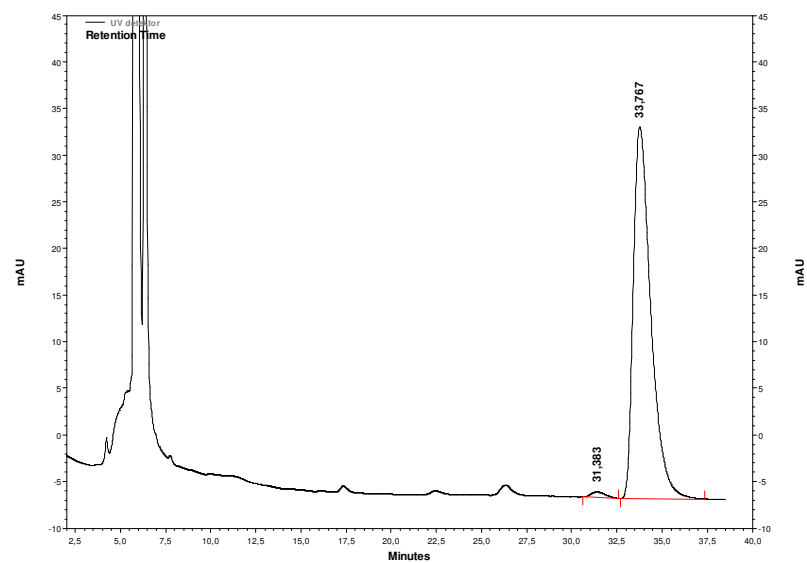
	Ret. Time	Area	Area %	Height	Height %
1	21,617	2124	0,072	87	0,116
2	22,8	2954815	99,928	74787	99,884

Quasi-*rac*-(2-Hydroxymethyl-phenyl)(methyl)(phenyl)phosphine-*P*-borane (*rac*-**3**)



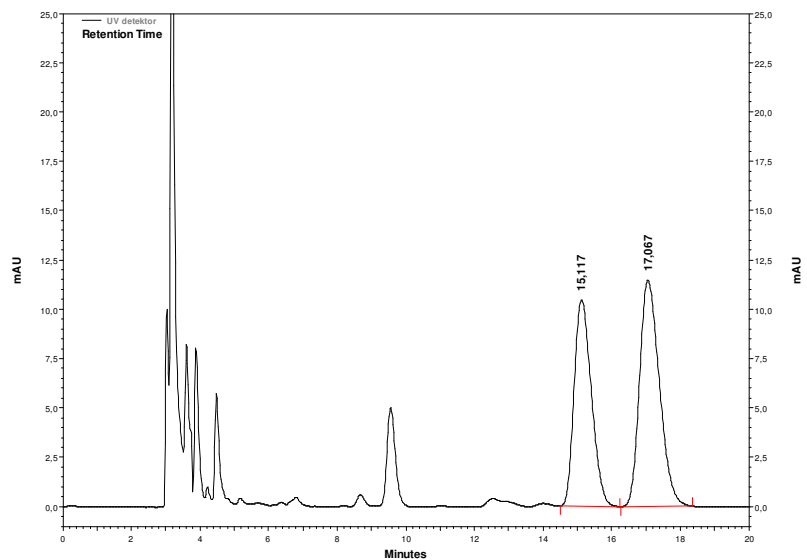
	Ret. Time	Area	Area %	Height	Height %
1	31	826168	53,64	14021	55,783
2	33,65	714027	46,36	11114	44,217

(*R<sub>P</sub>*)-(2-Hydroxymethyl-phenyl)(methyl)(phenyl)phosphine-*P*-borane ((*R<sub>P</sub>*)-**3**), 97.7% ee



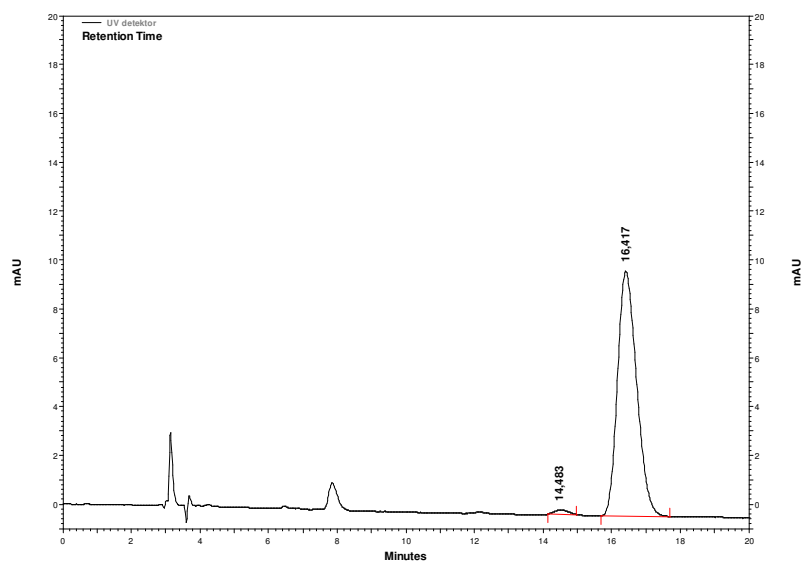
	Ret. Time	Area	Area %	Height	Height %
1	31,383	31656	1,169	592	1,464
2	33,767	2675673	98,831	39844	98,536

Quasi-*rac*-(2-Mesyloxymethyl-phenyl)(phenyl)(trimethylsilylmethyl)phosphine-*P*-borane (*rac*-**5**)



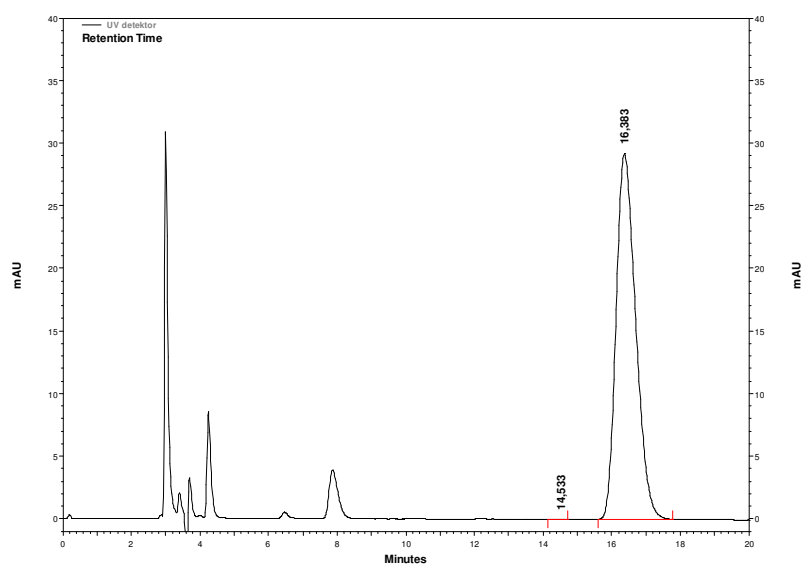
	Ret. Time	Area	Area %	Height	Height %
1	15,117	367444	44,253	10475	47,755
2	17,067	462873	55,747	11460	52,245

(*R<sub>p</sub>*)-(2-Mesyloxymethyl-phenyl)(phenyl)(trimethylsilylmethyl)phosphine-*P*-borane ((*R<sub>p</sub>*)-**5**), 97.5% ee



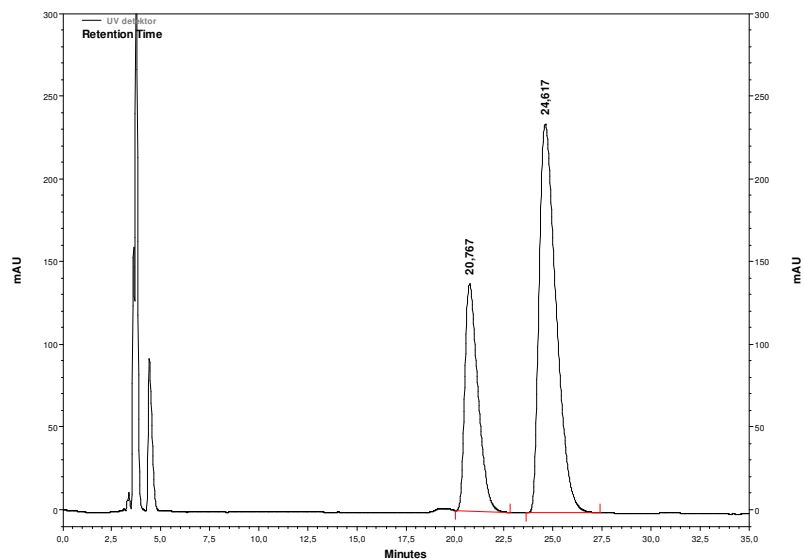
	Ret. Time	Area	Area %	Height	Height %
1	14,483	4795	1,218	166	1,629
2	16,417	388884	98,782	10022	98,371

(*R*<sub>P</sub>)-(2-Mesyloxymethyl-phenyl)(phenyl)(trimethylsilylmethyl)phosphine-*P*-borane ((*R*<sub>P</sub>)-**5**), >99.9% ee



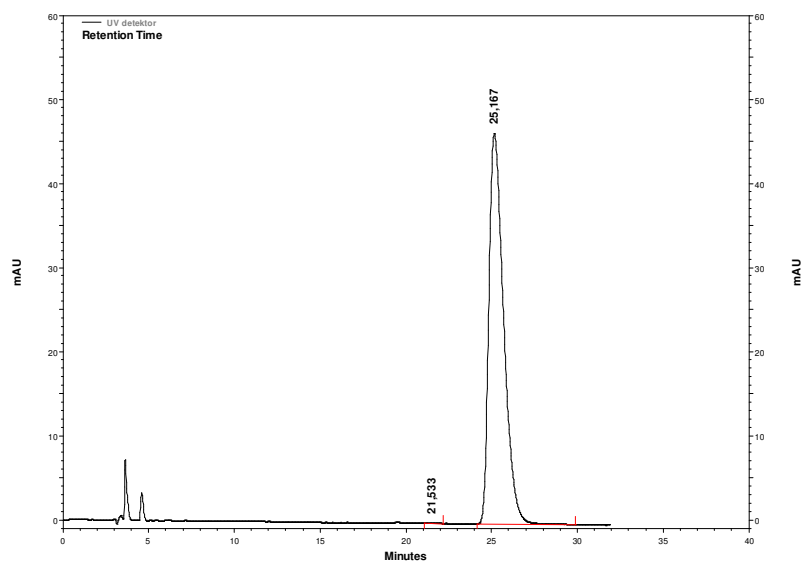
	Ret. Time	Area	Area %	Height	Height %
1	14,533	404	0,035	18	0,062
2	16,383	1157535	99,965	29206	99,938

1-Phenyl-phosphindane-*P*-borane ((*R<sub>P</sub>*)-**7**), 38% ee



	Ret. Time	Area	Area %	Height	Height %
1	20,767	6418976	31,082	137416	36,906
2	24,617	14232848	68,918	234927	63,094

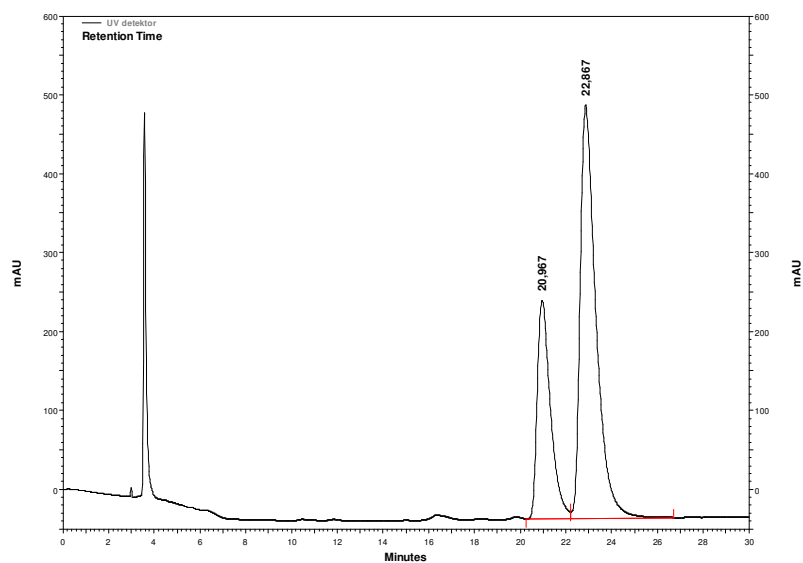
(*R<sub>P</sub>*)-1-Phenyl-phosphindane-*P*-borane ((*R<sub>P</sub>*)-**7**), >99.9% ee



	Ret. Time	Area	Area %	Height	Height %
1	21,533	1186	0,043	37	0,08
2	25,167	2757201	99,957	46447	99,92

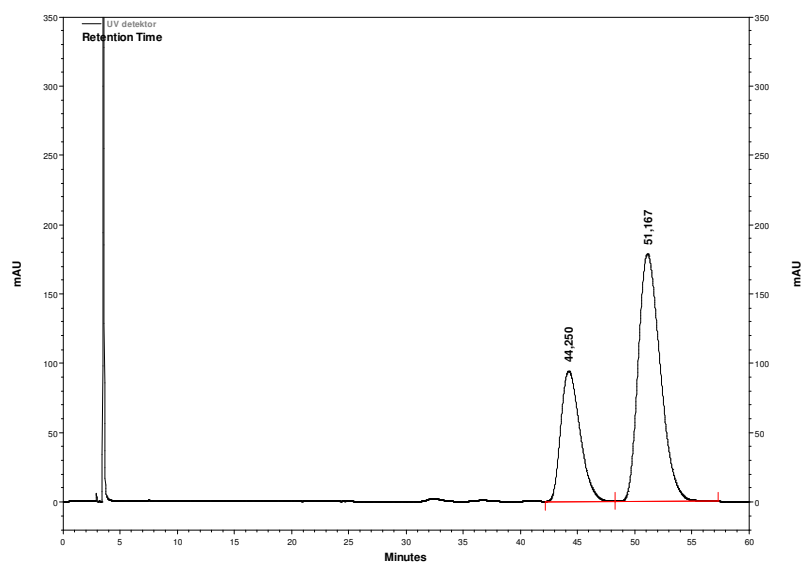
1-Phenyl-phosphindane-*P*-oxide ((*S*<sub>P</sub>)-**9**), 37% ee

Chiralpak IA column



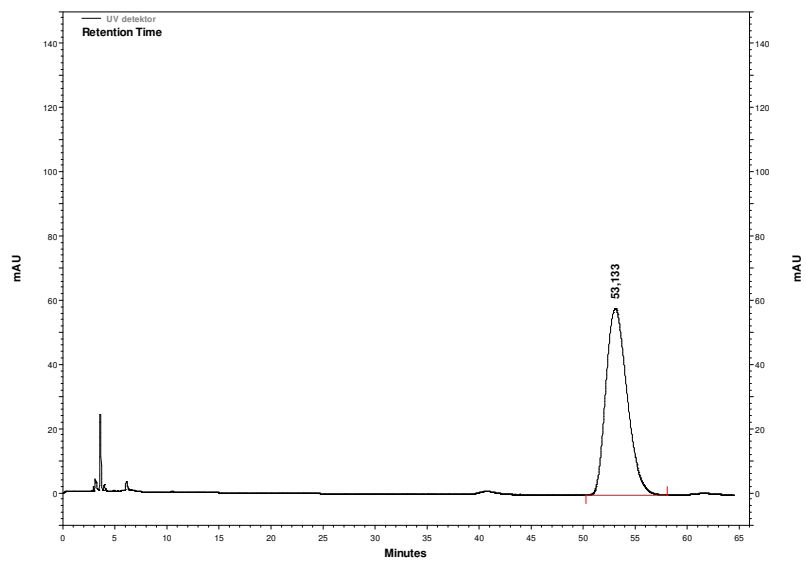
	Ret. Time	Area	Area %	Height	Height %
1	20,967	11157612	30,823	276538	34,561
2	22,867	25040957	69,177	523598	65,439

Chiralcel AD-H column



	Ret. Time	Area	Area %	Height	Height %
1	44,25	10943186	31,377	93883	34,357
2	51,167	23916767	68,576	178295	65,249

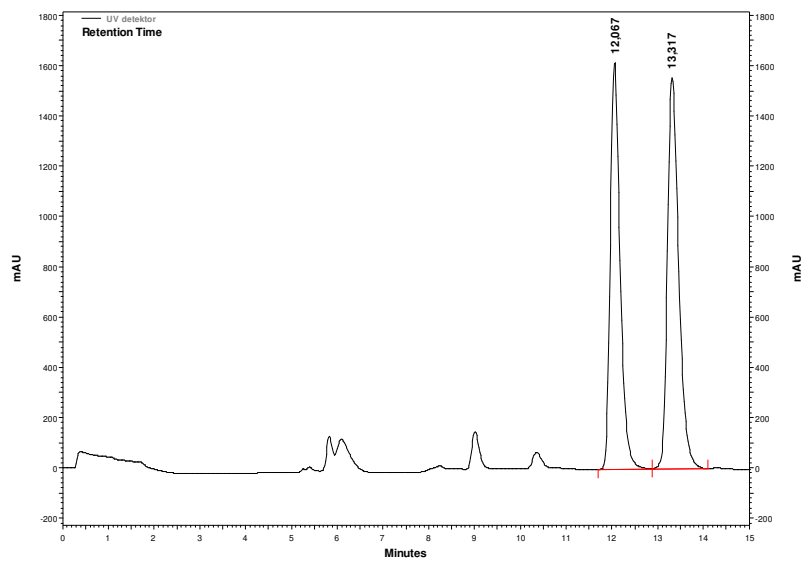
(*S<sub>P</sub>*)-1-Phenyl-phosphindane-*P*-oxide ((*S<sub>P</sub>*)-**9**), >99.9% ee



	Ret. Time	Area	Area %	Height	Height %
1	53,133	8235642	100	58114	100

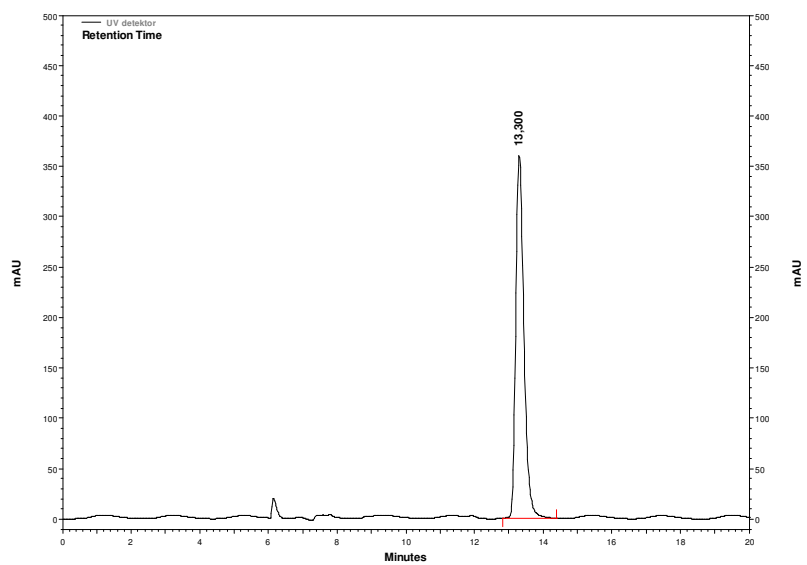


Quasi-*rac*-1-Phenyl-3-oxa-1-phosphindane-*P*-borane (*rac*-**11**)



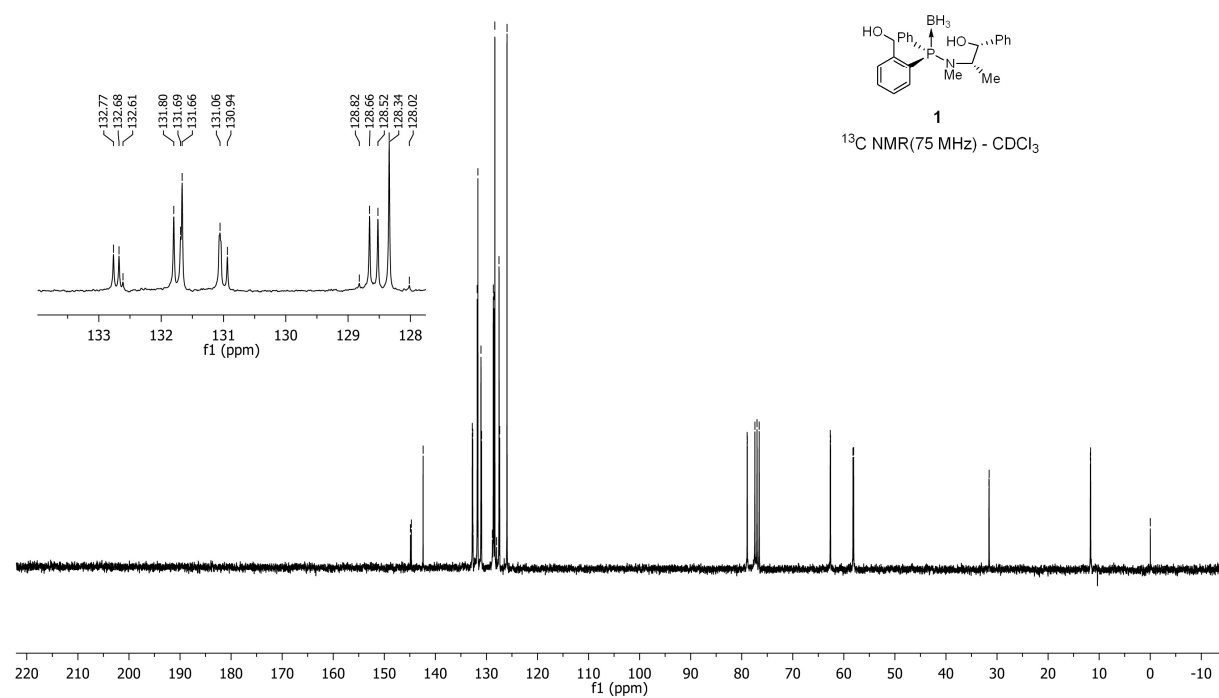
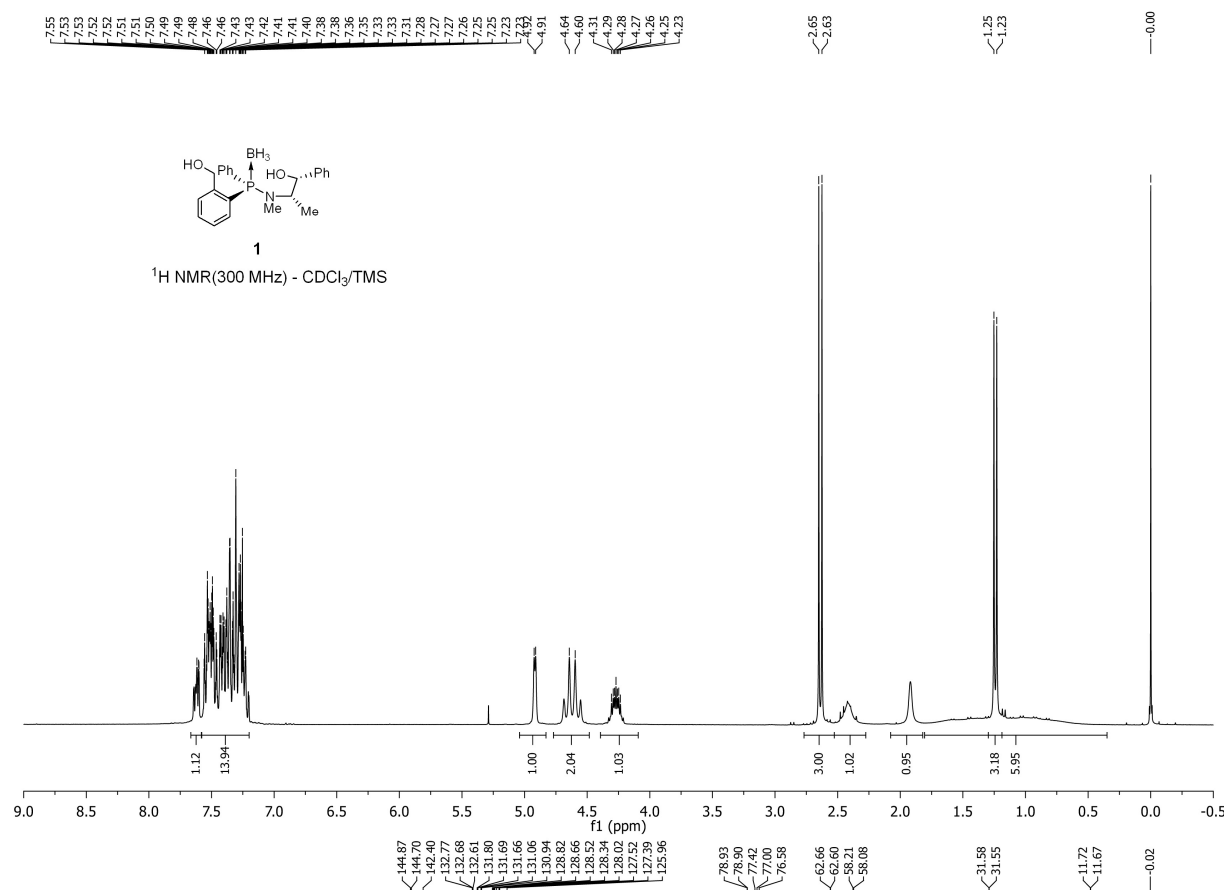
	Ret. Time	Area	Area %	Height	Height %
1	12,067	24250769	47,576	1617280	50,953
2	13,317	26722007	52,424	1556804	49,047

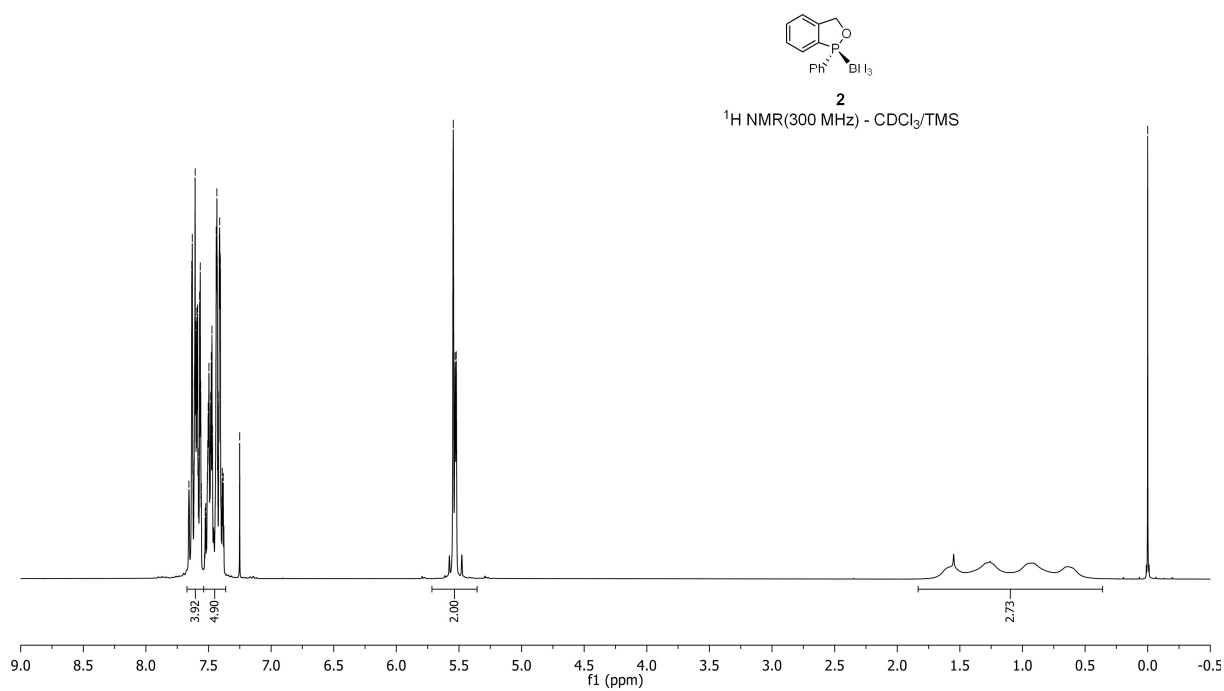
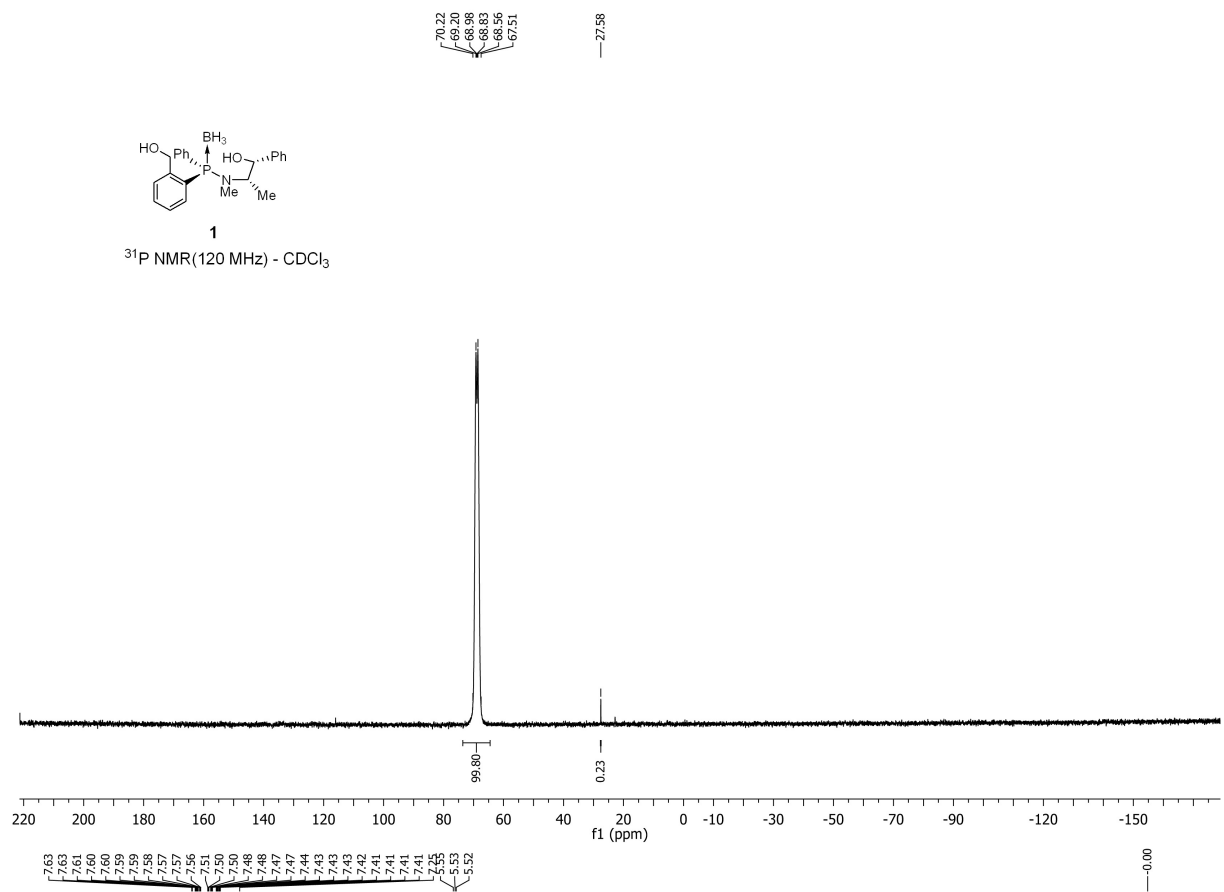
(*R<sub>P</sub>*)-1-Phenyl-3-oxa-1-phosphindane-*P*-borane ((*R<sub>P</sub>*)-**11**), >99.9% ee

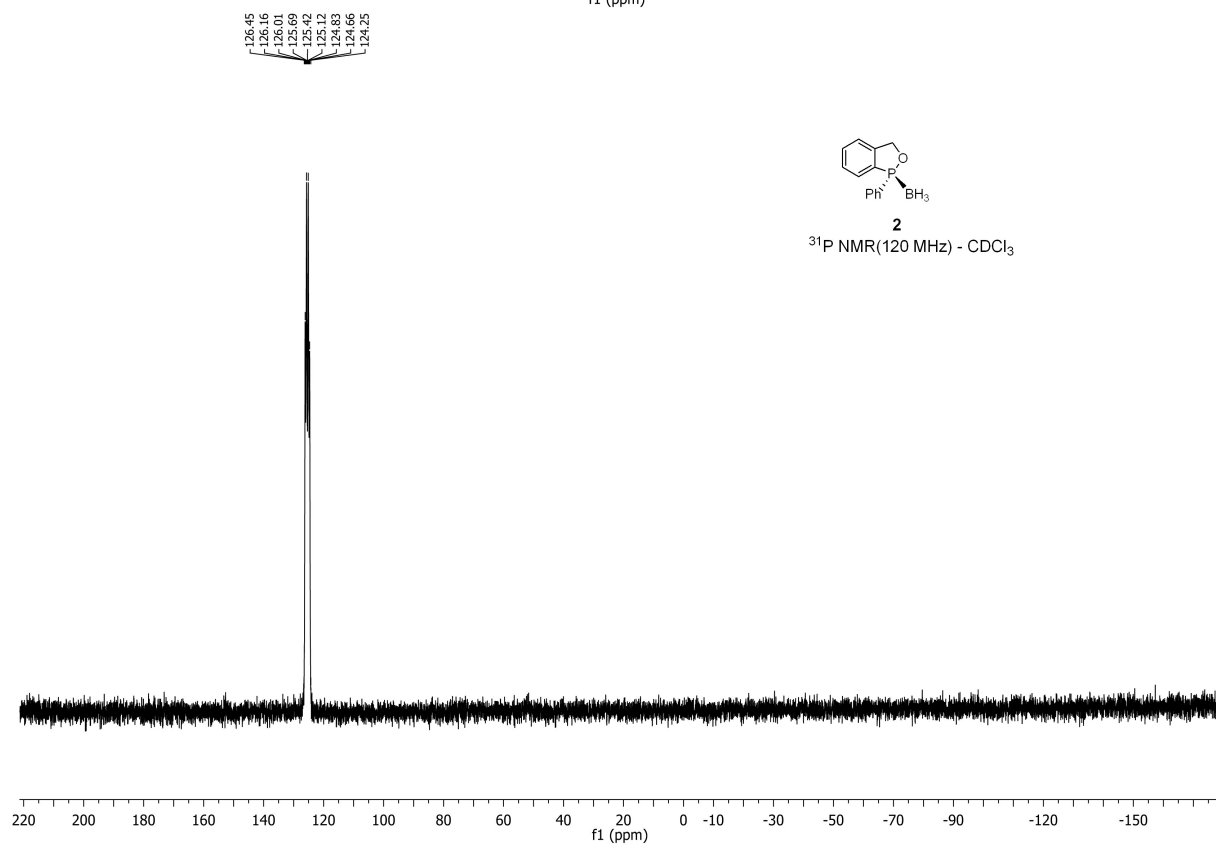
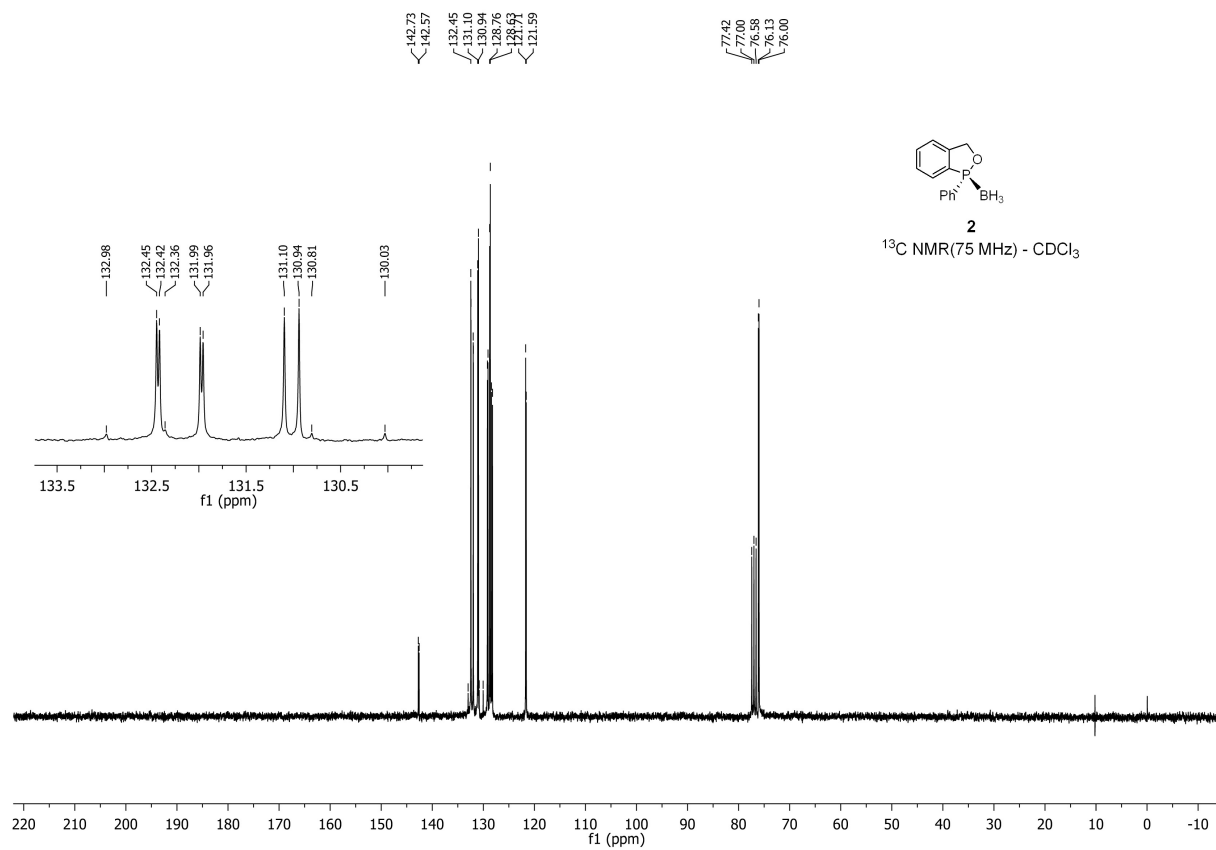


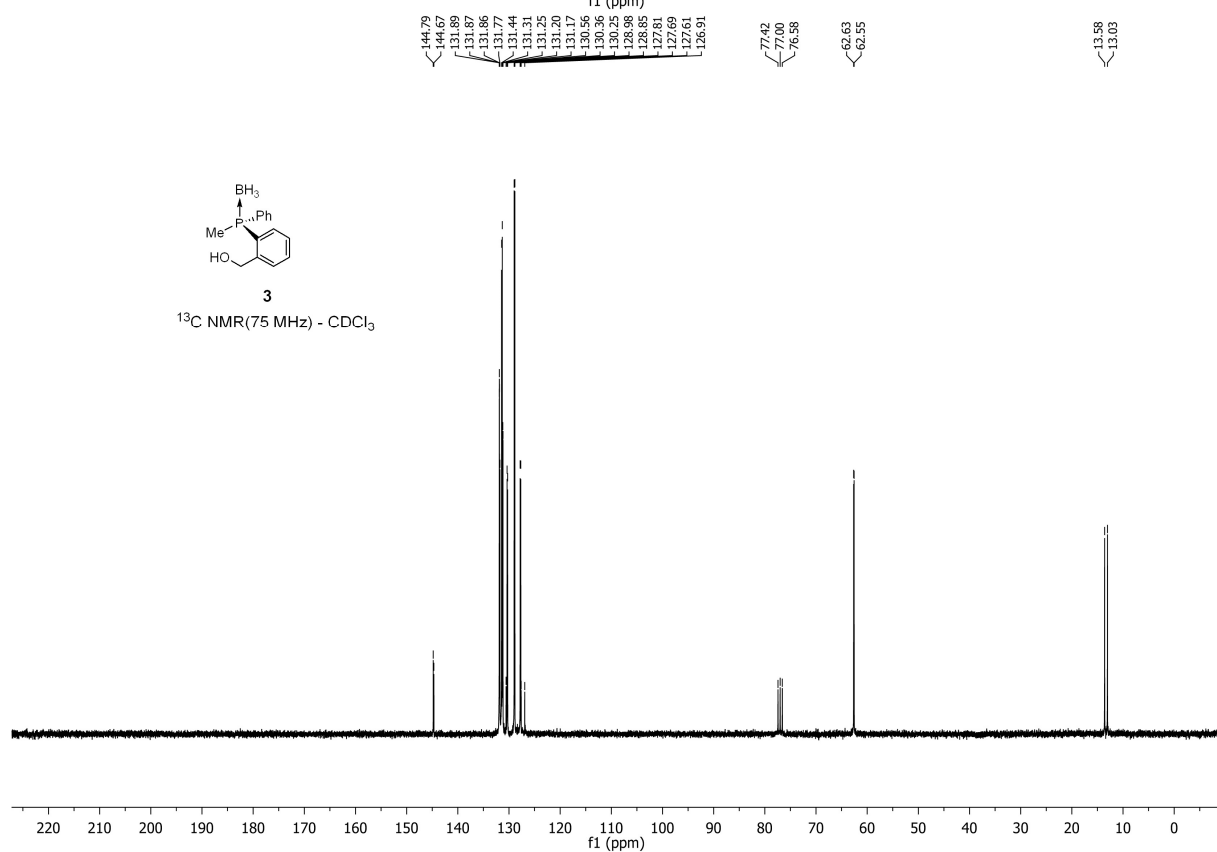
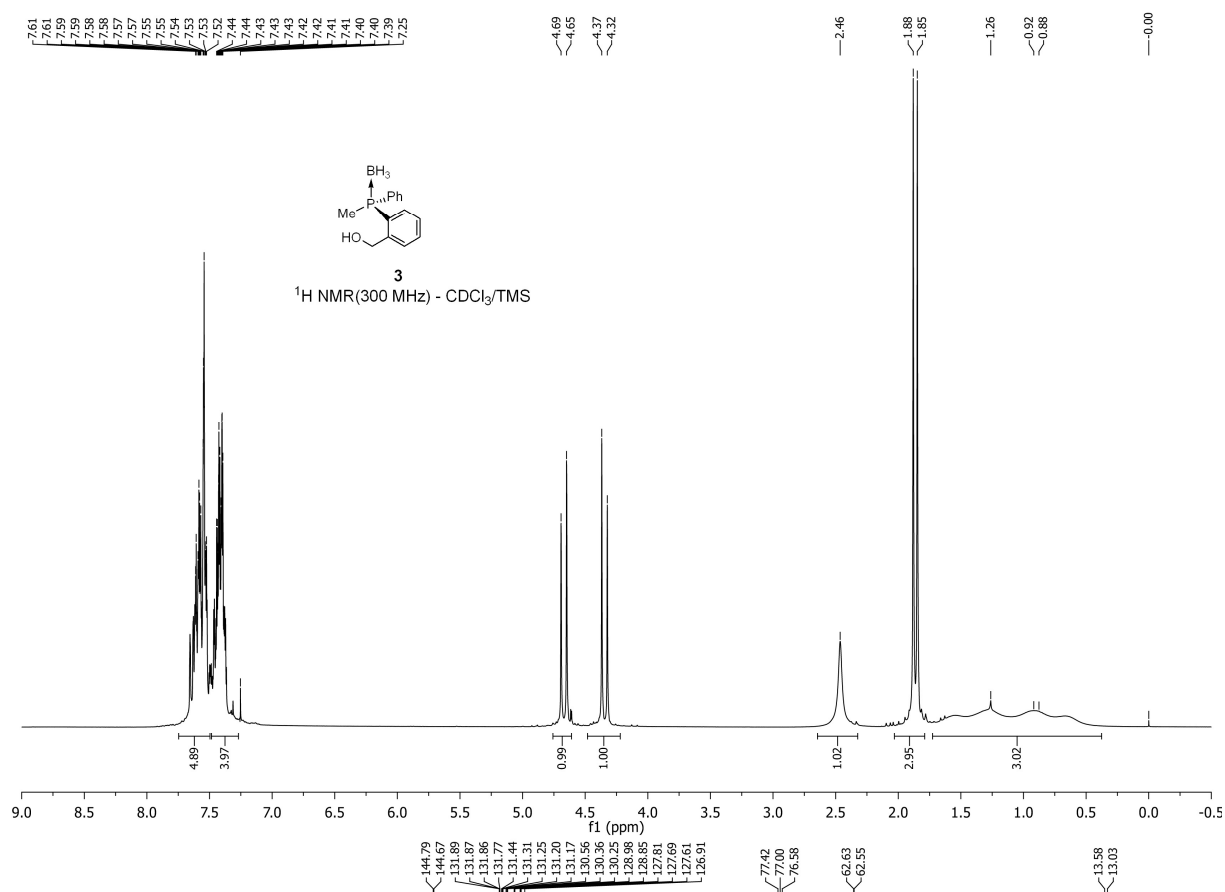
	Ret. Time	Area	Area %	Height	Height %
1	13,3	5822522	100	359397	100

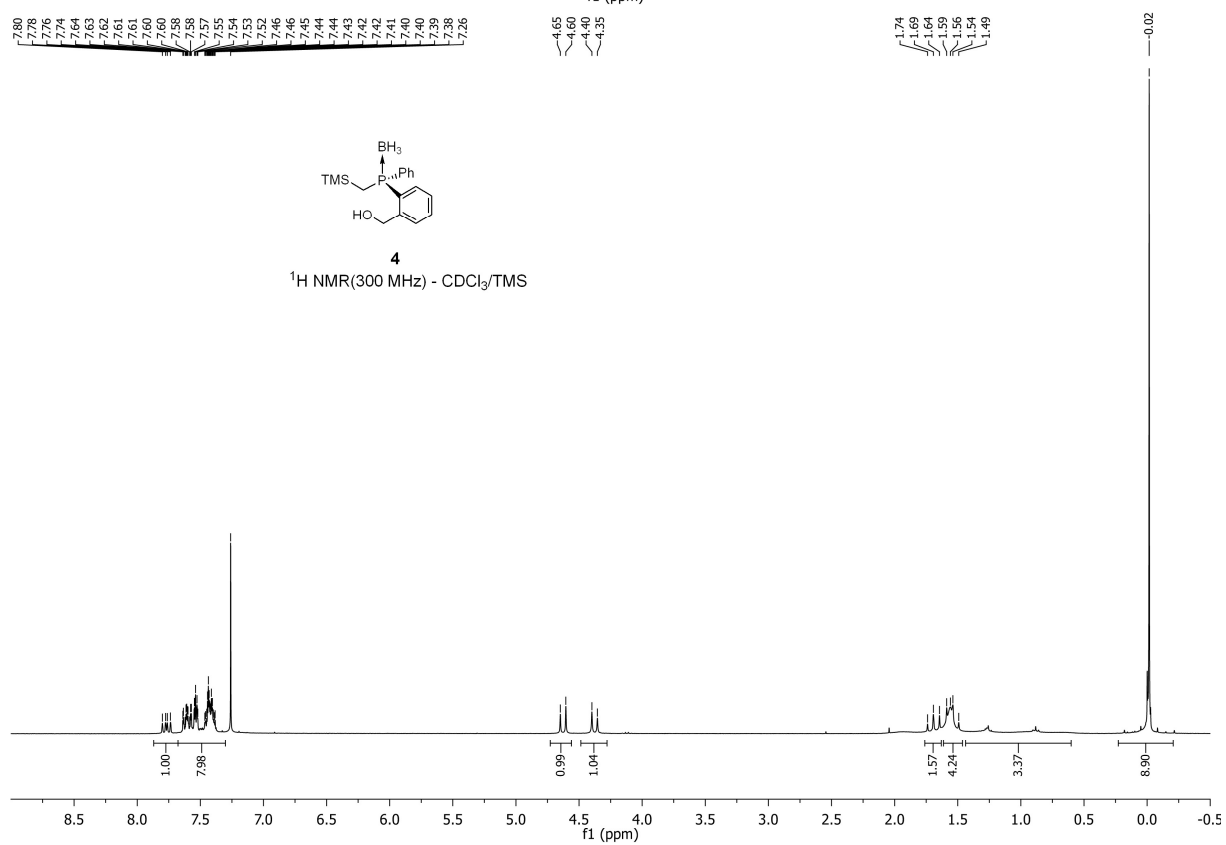
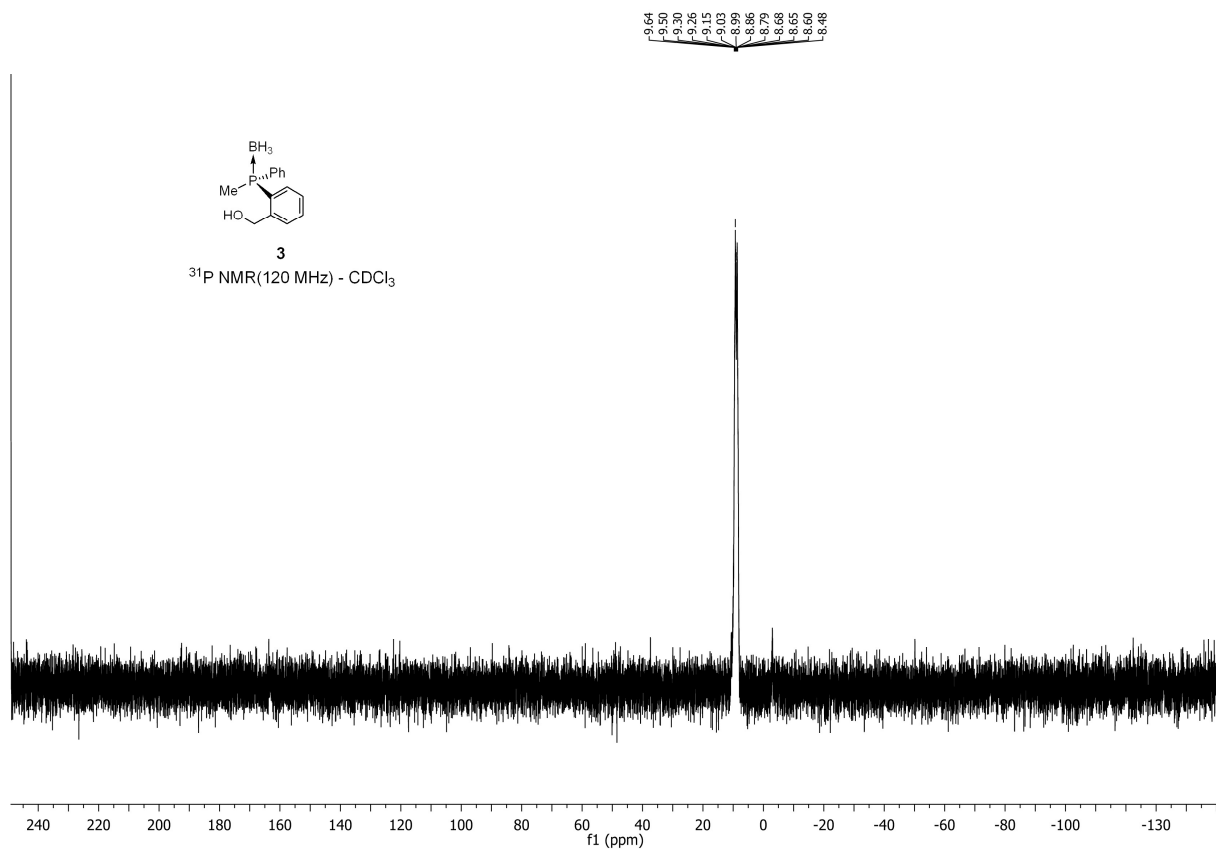
## 6. $^1\text{H}$ NMR and $^{13}\text{C}$ NMR spectra

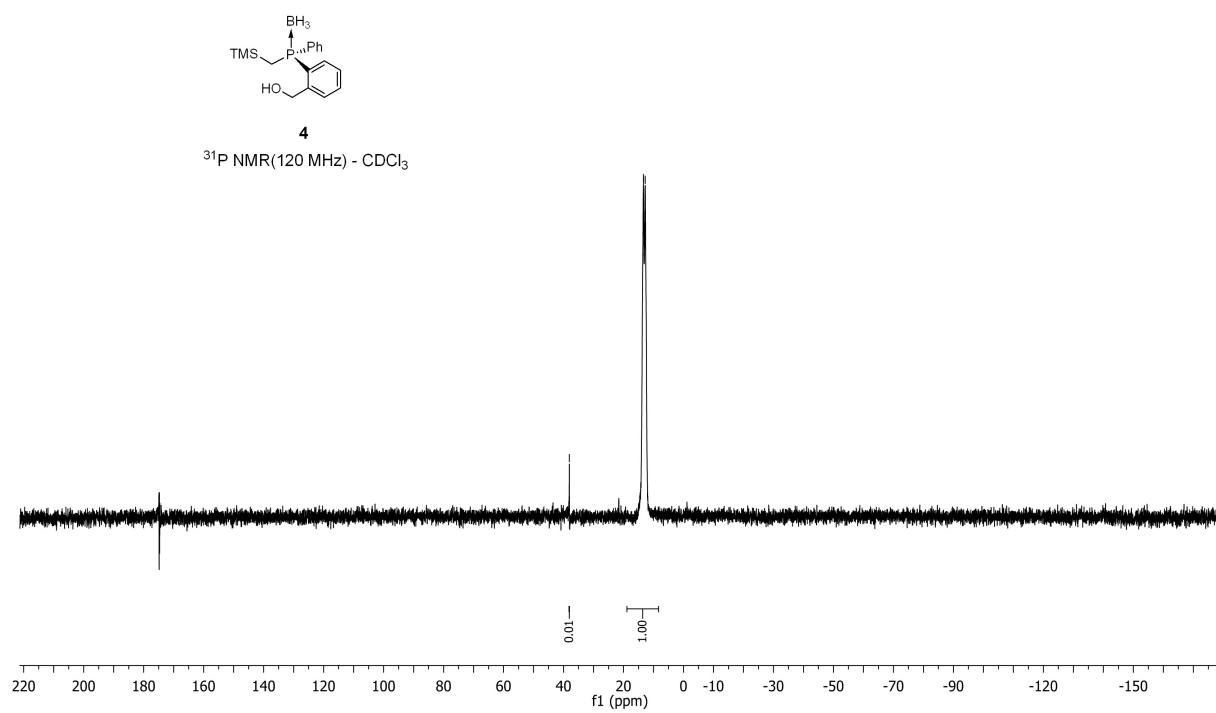
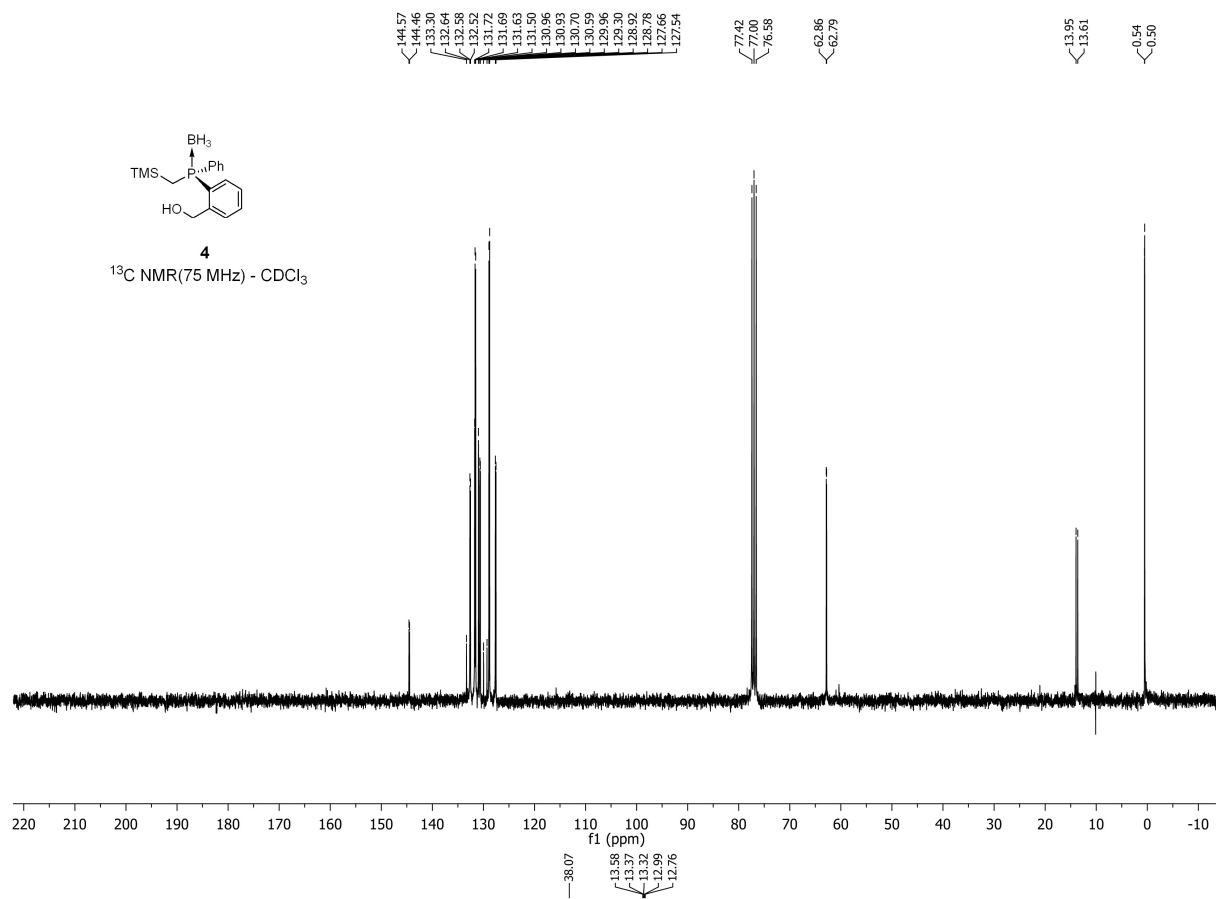


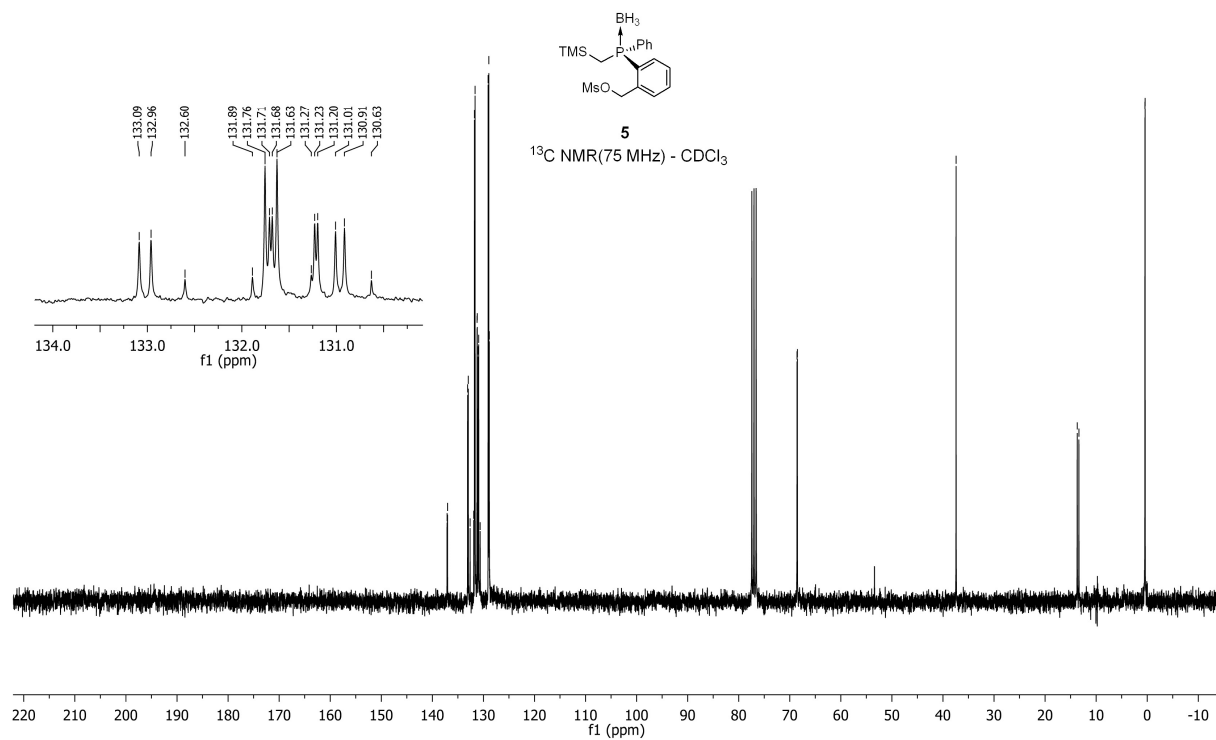
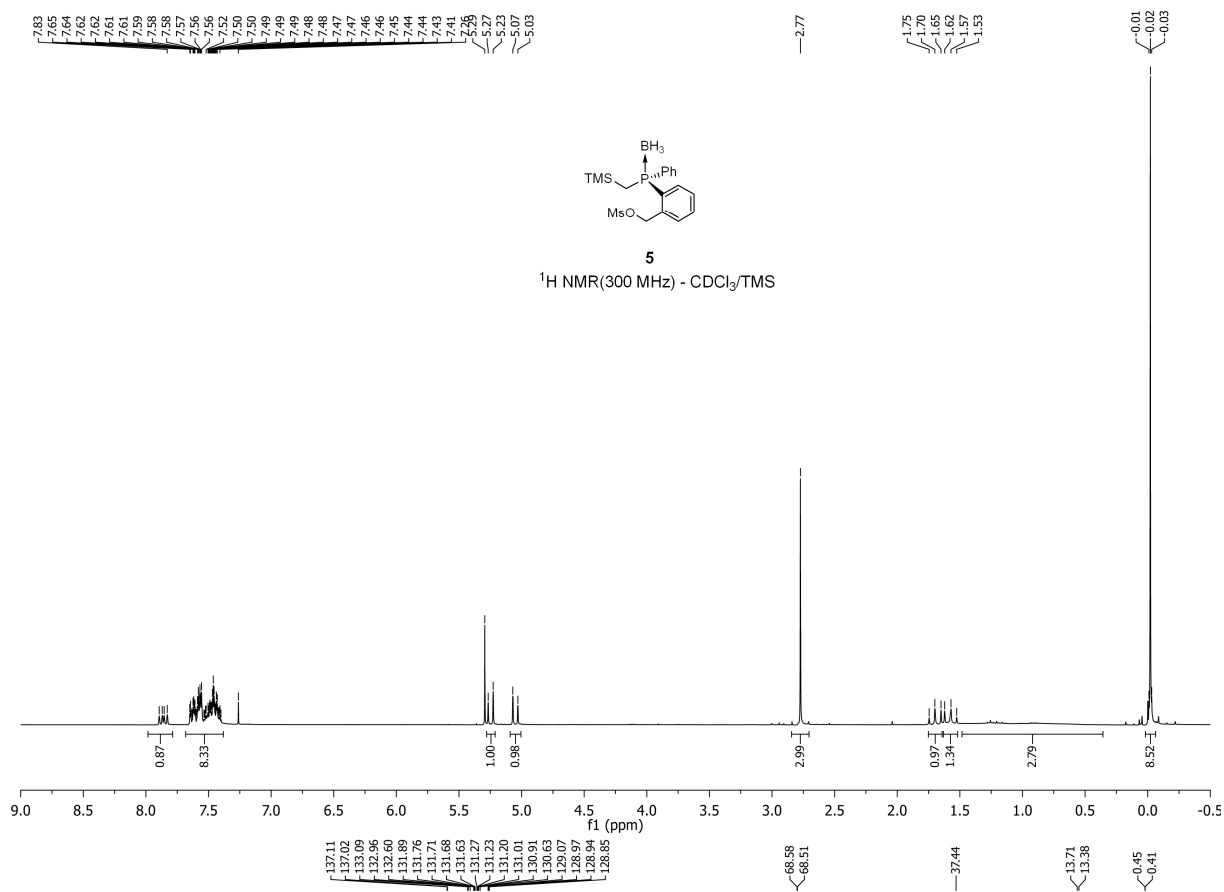




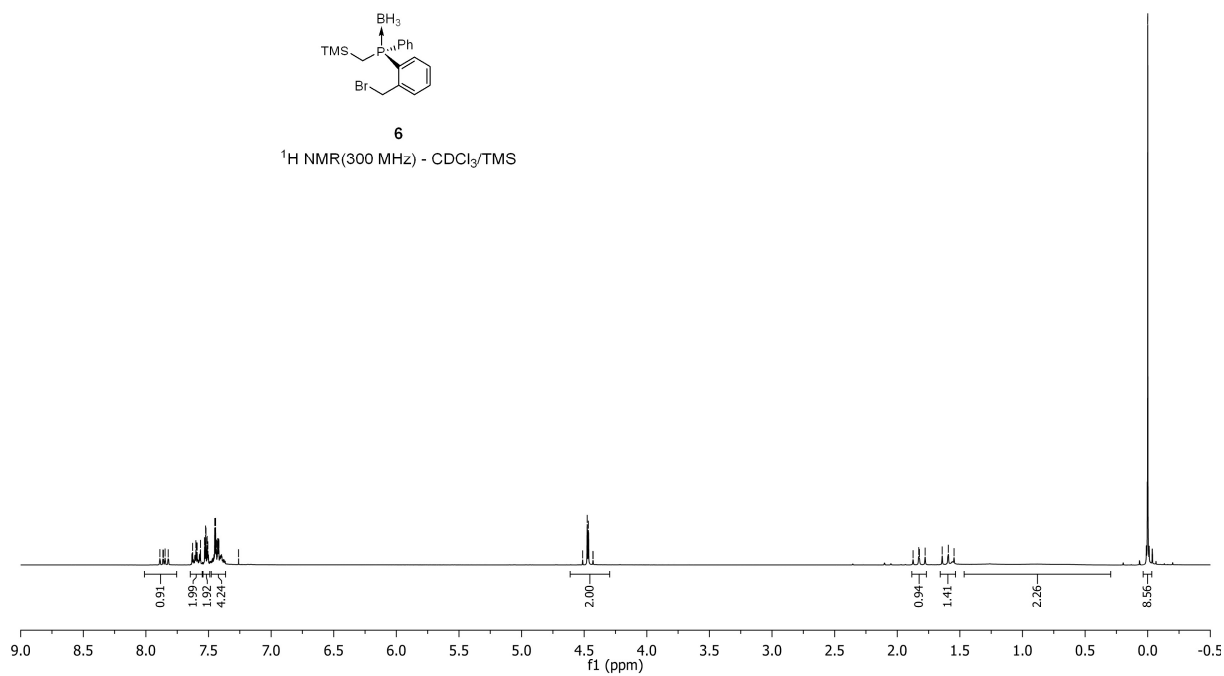
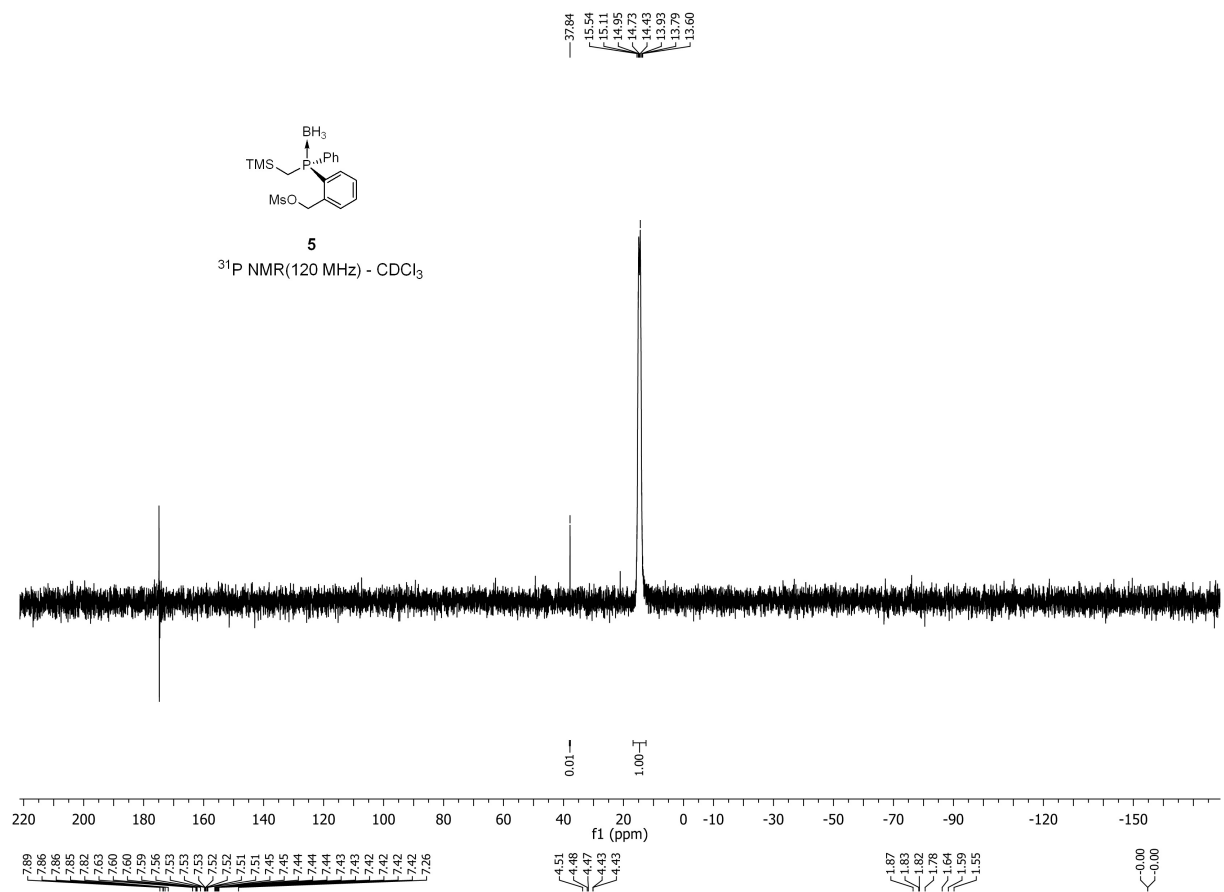


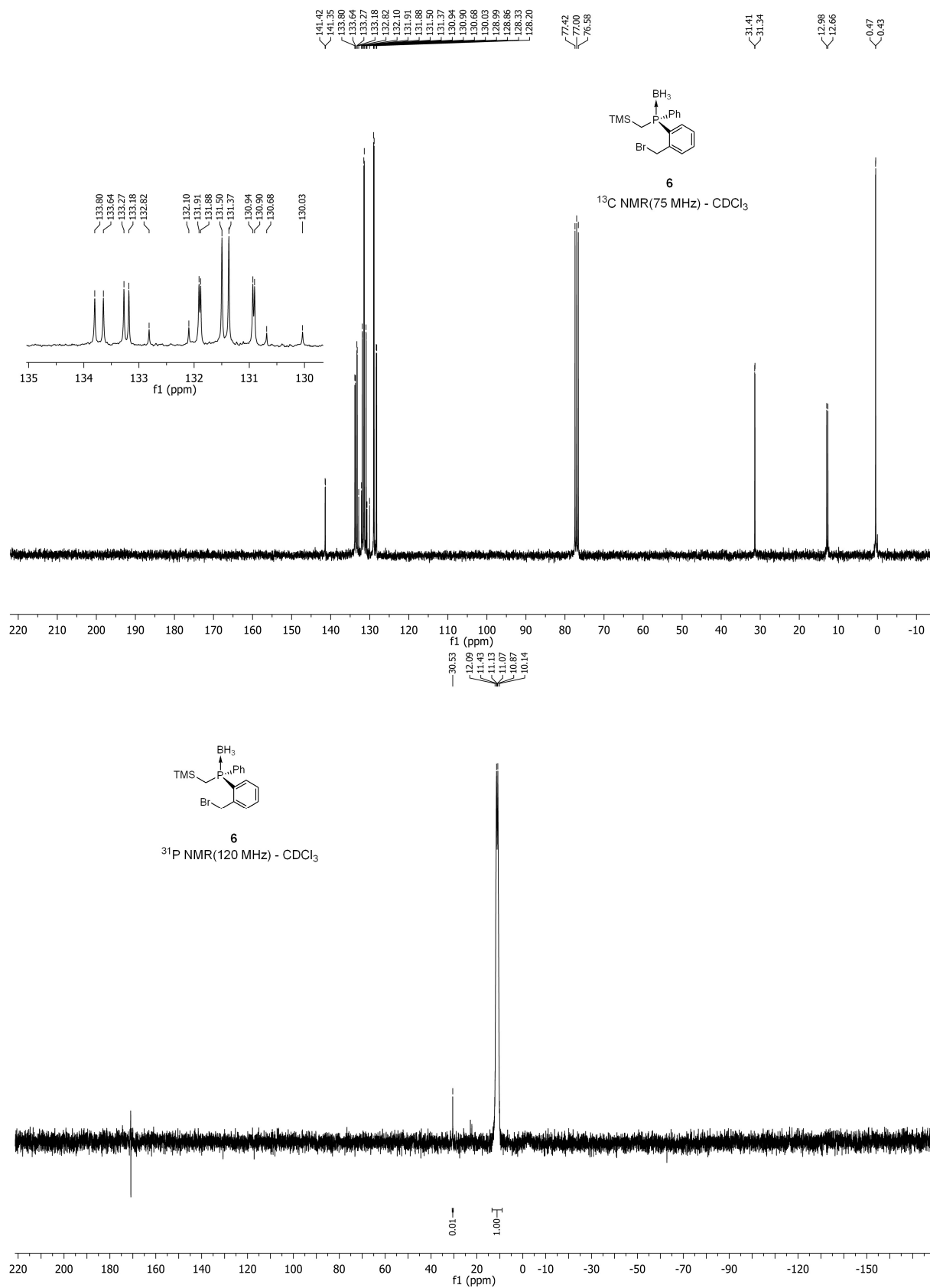


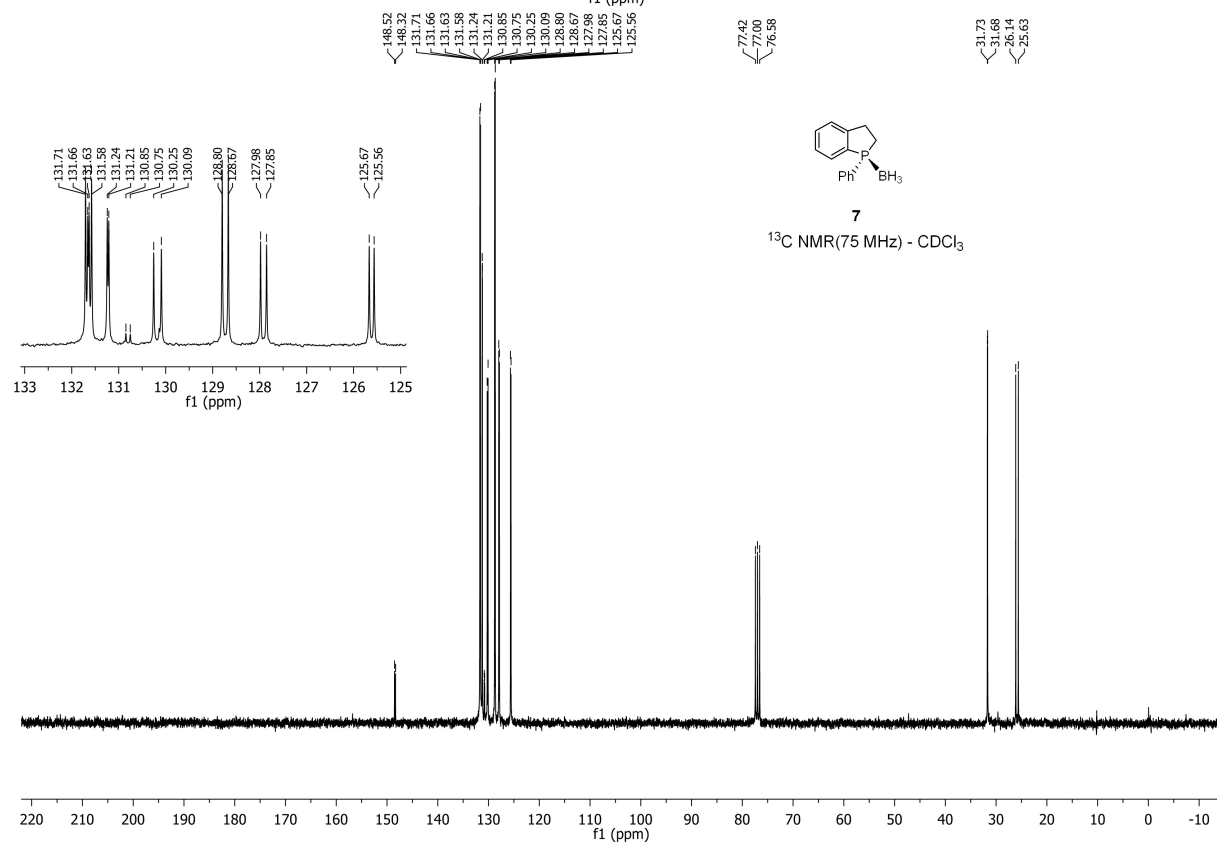
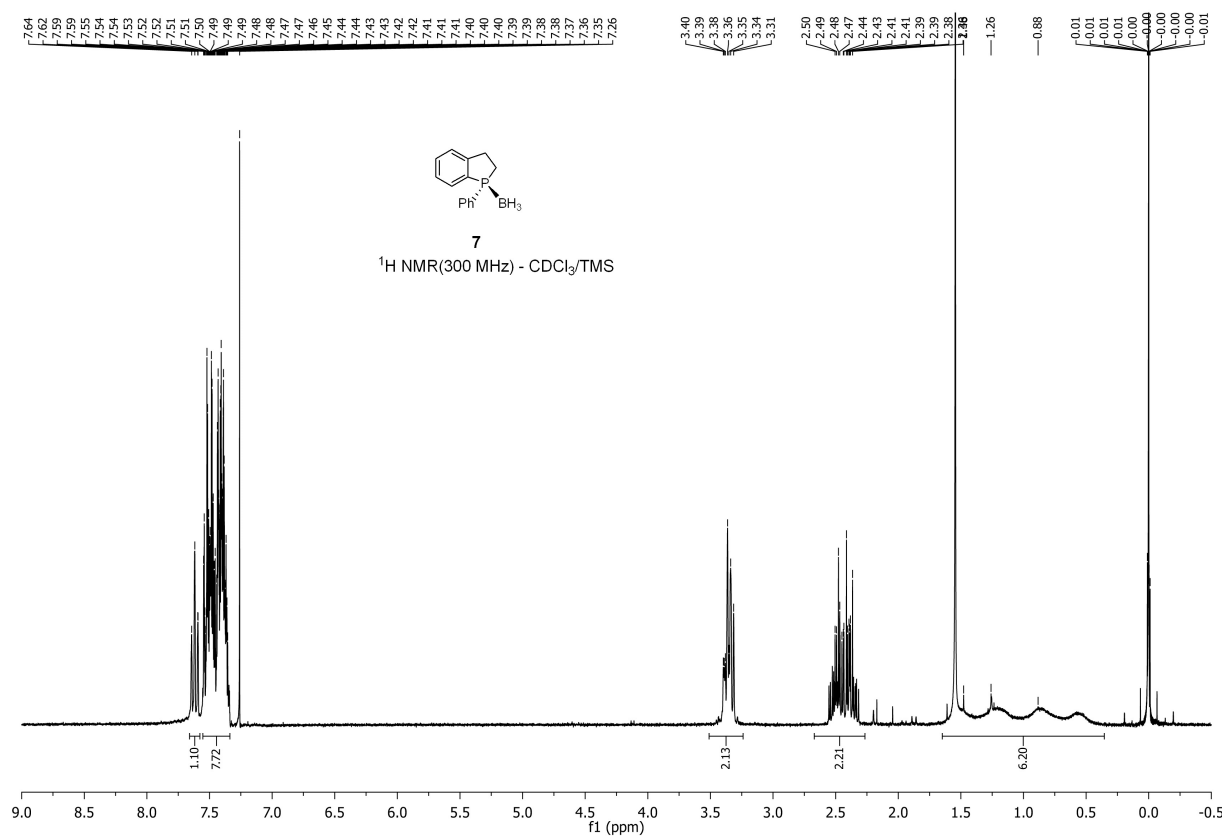


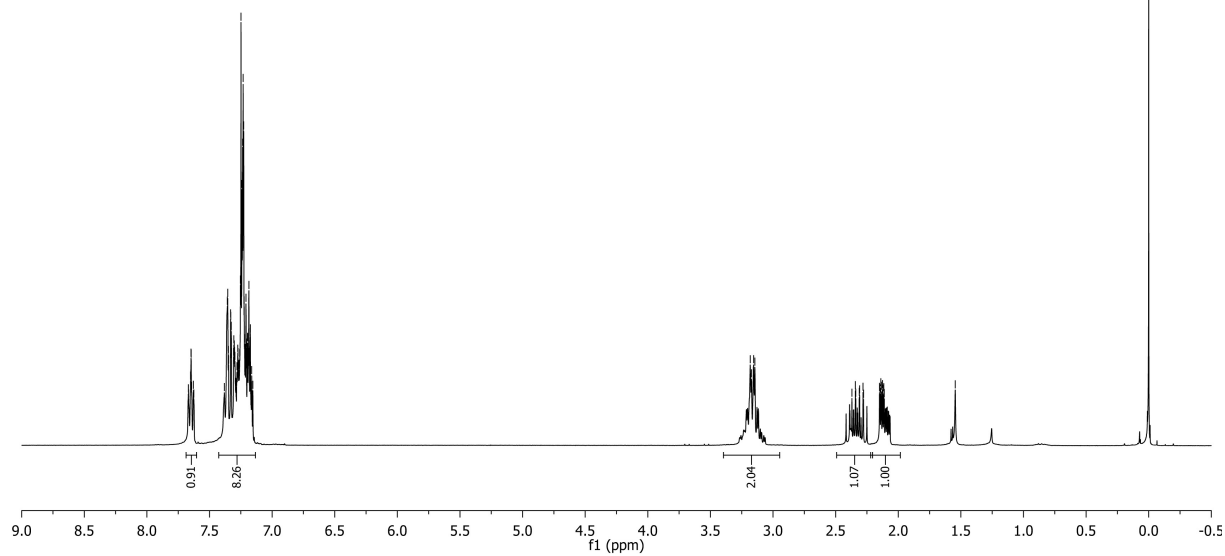
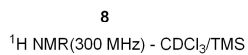
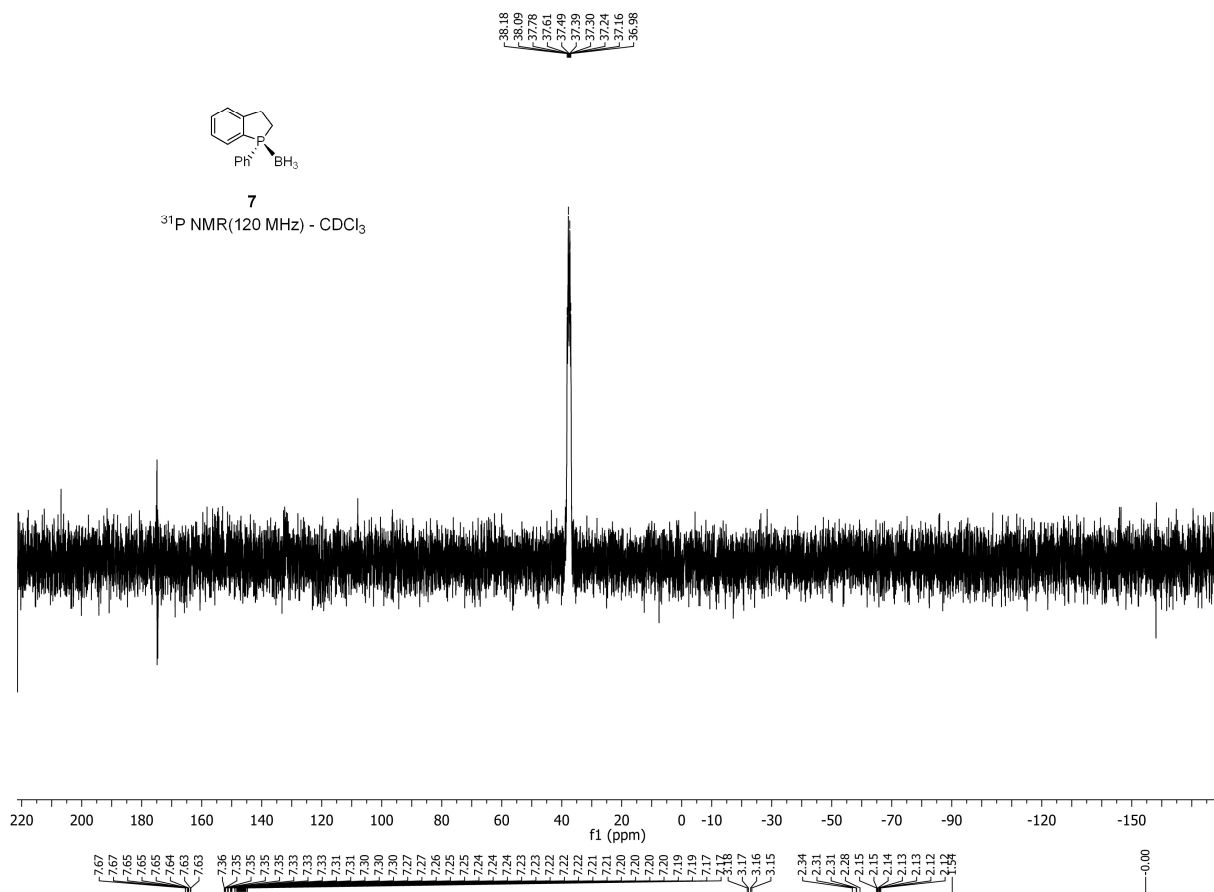
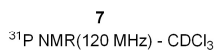


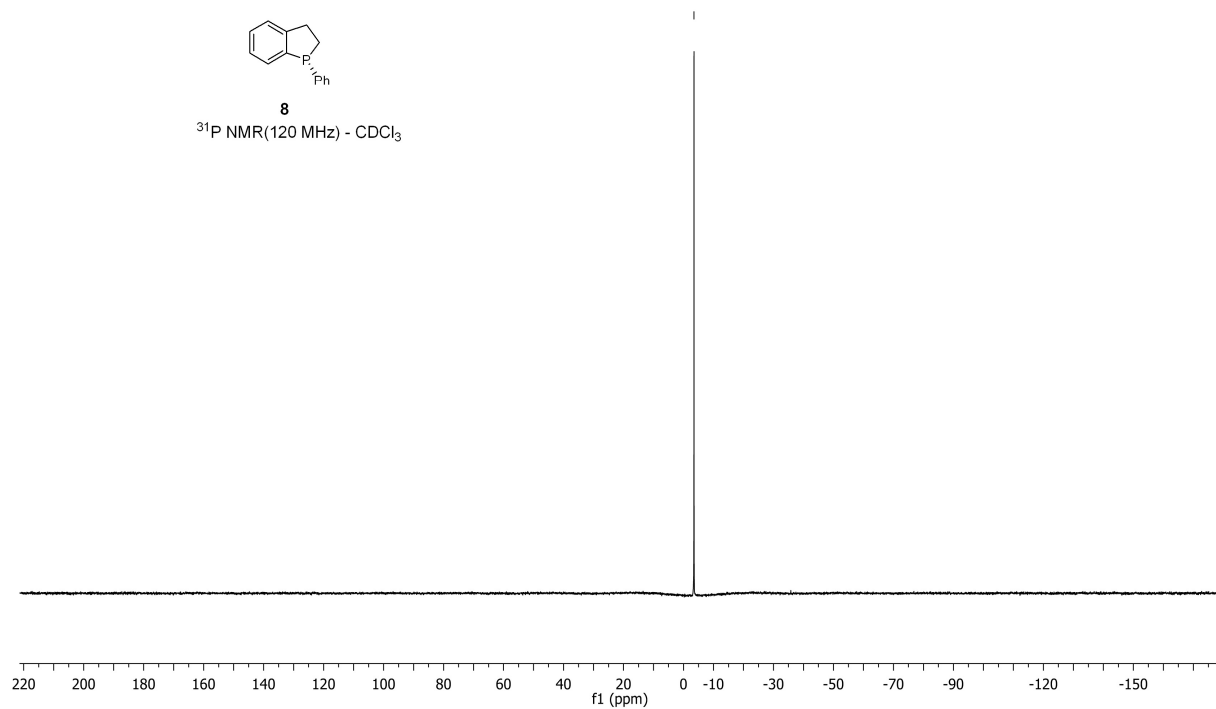
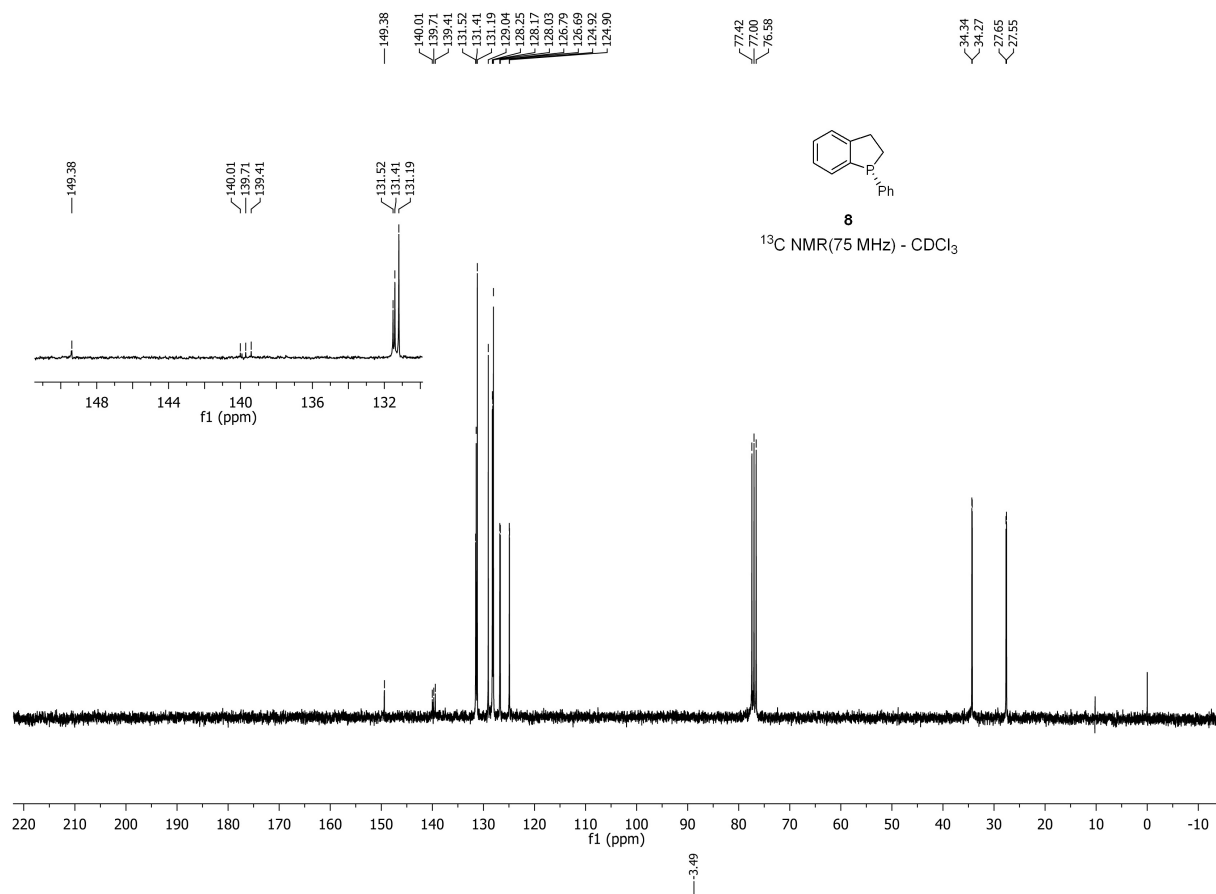


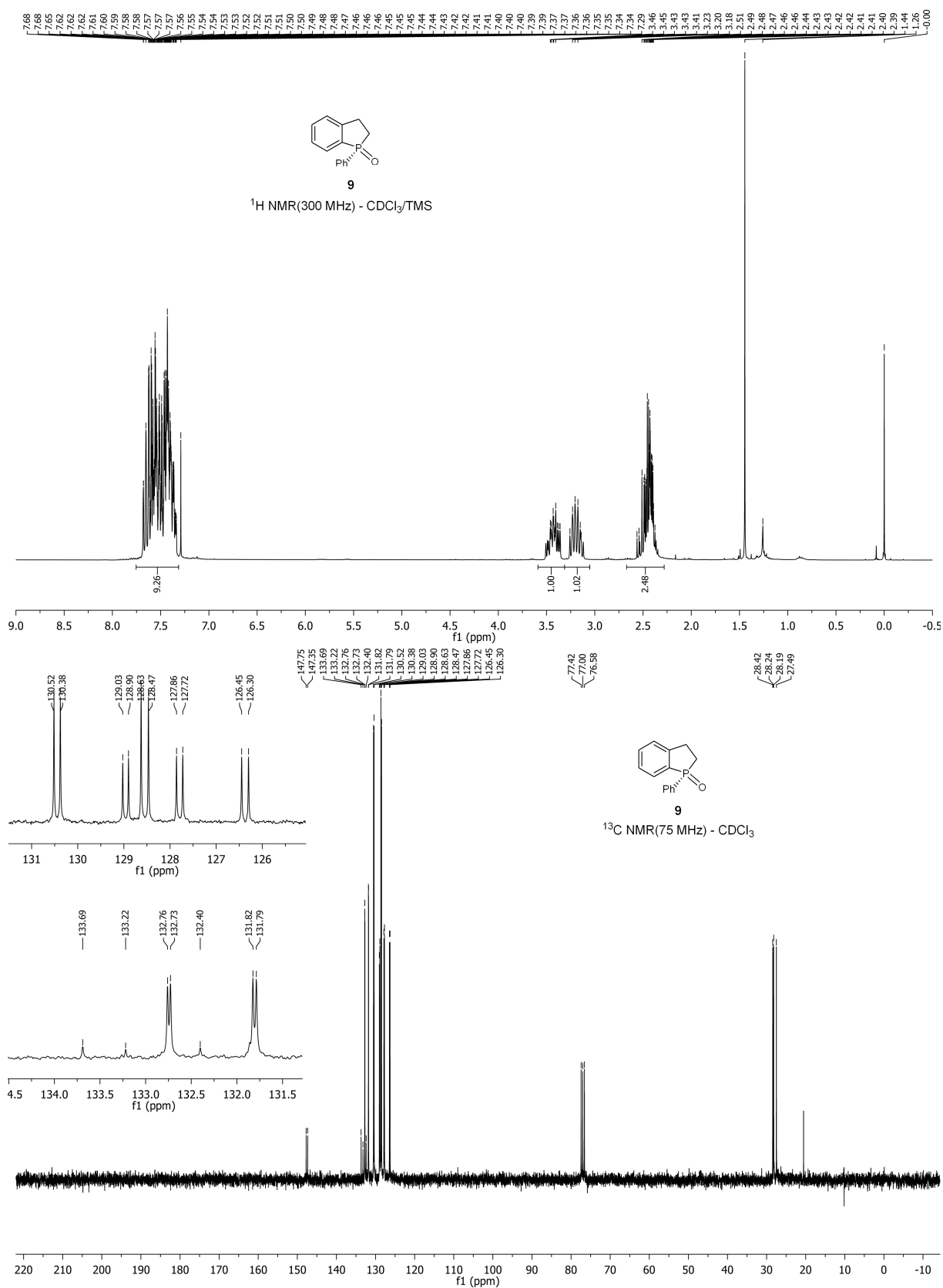


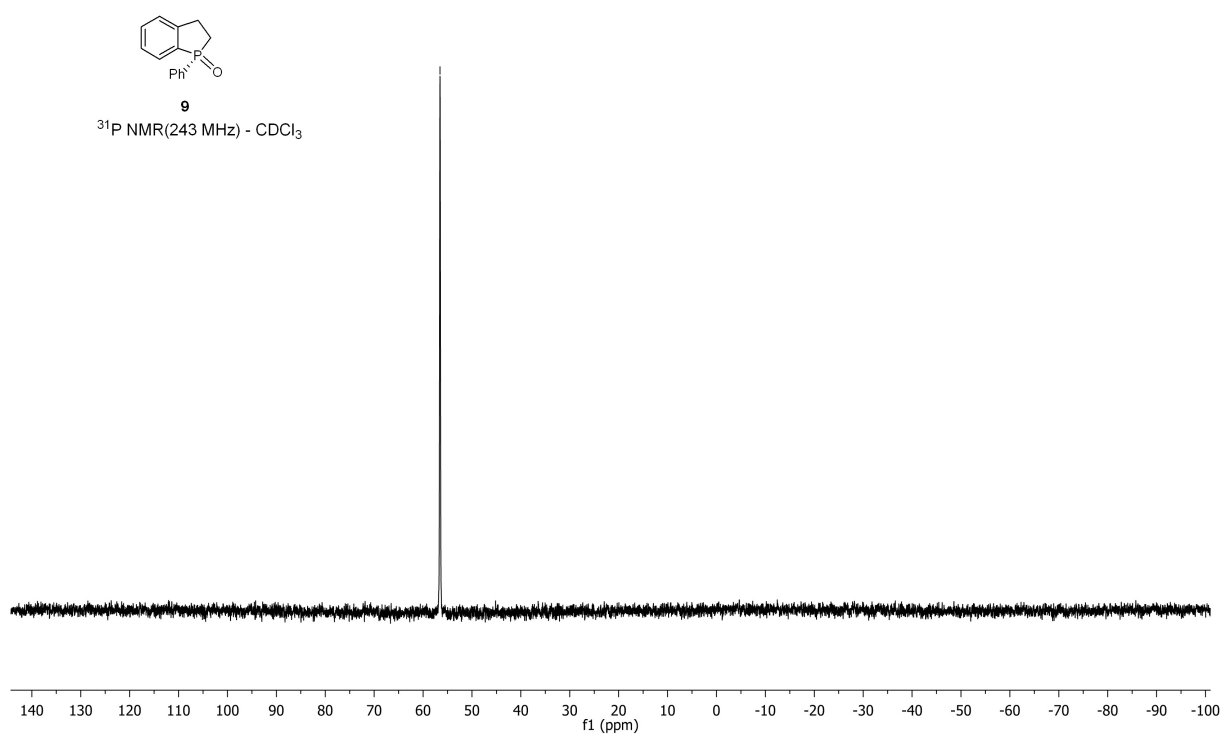
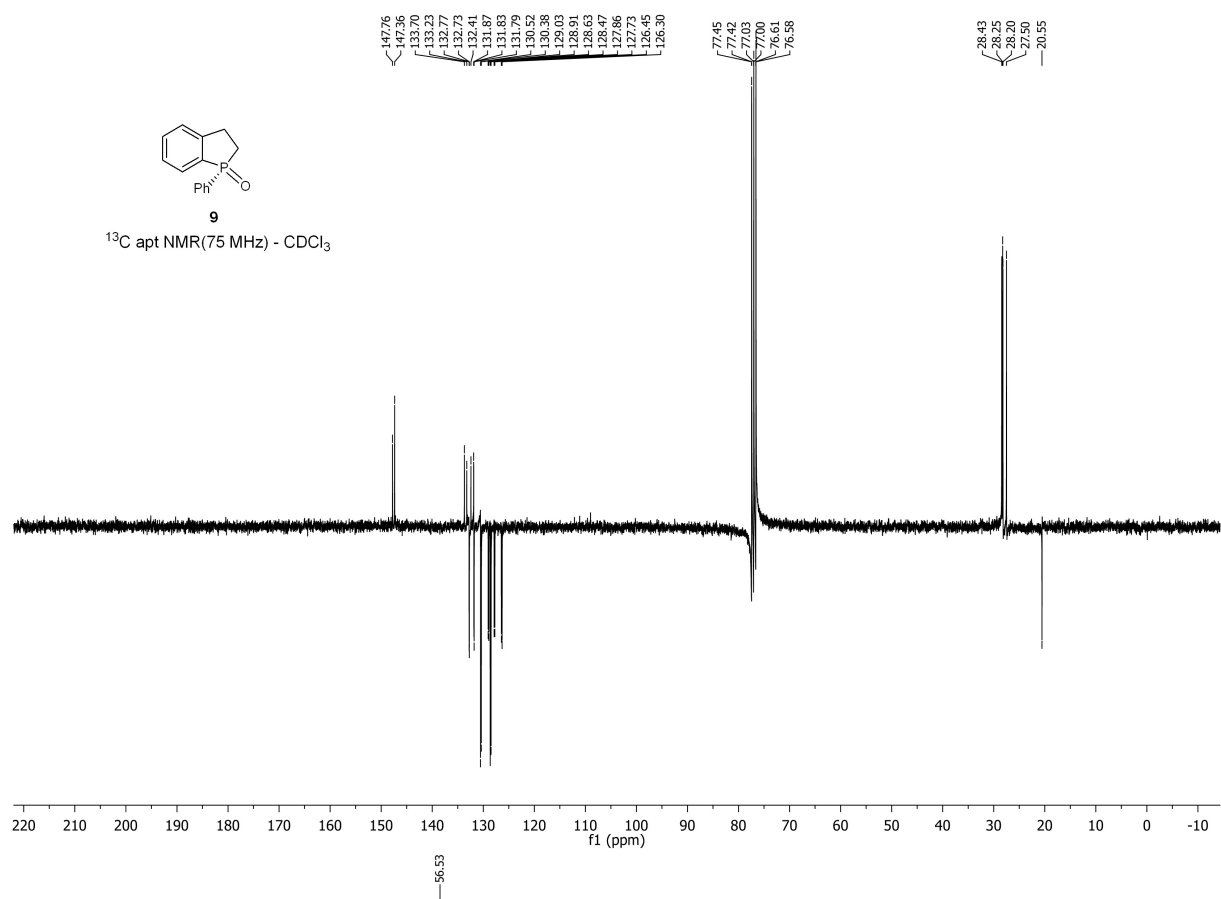


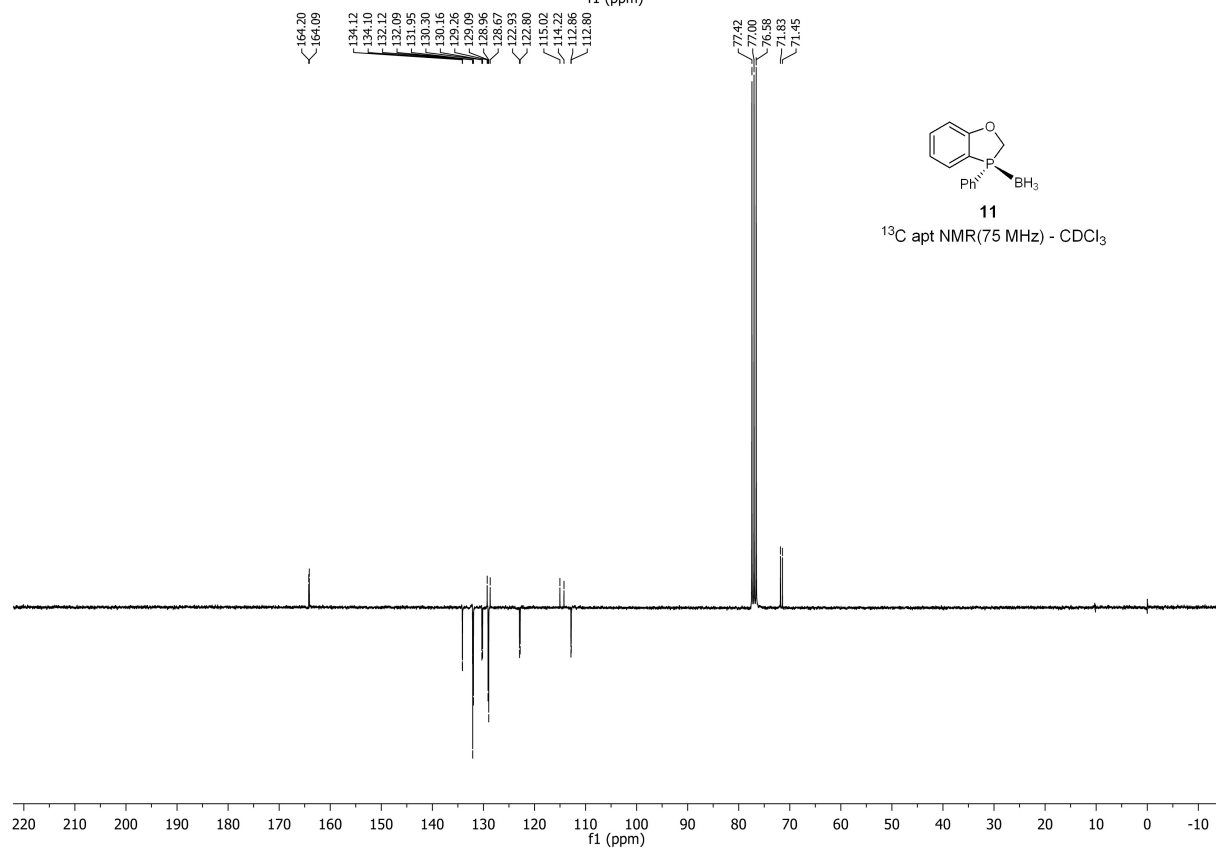
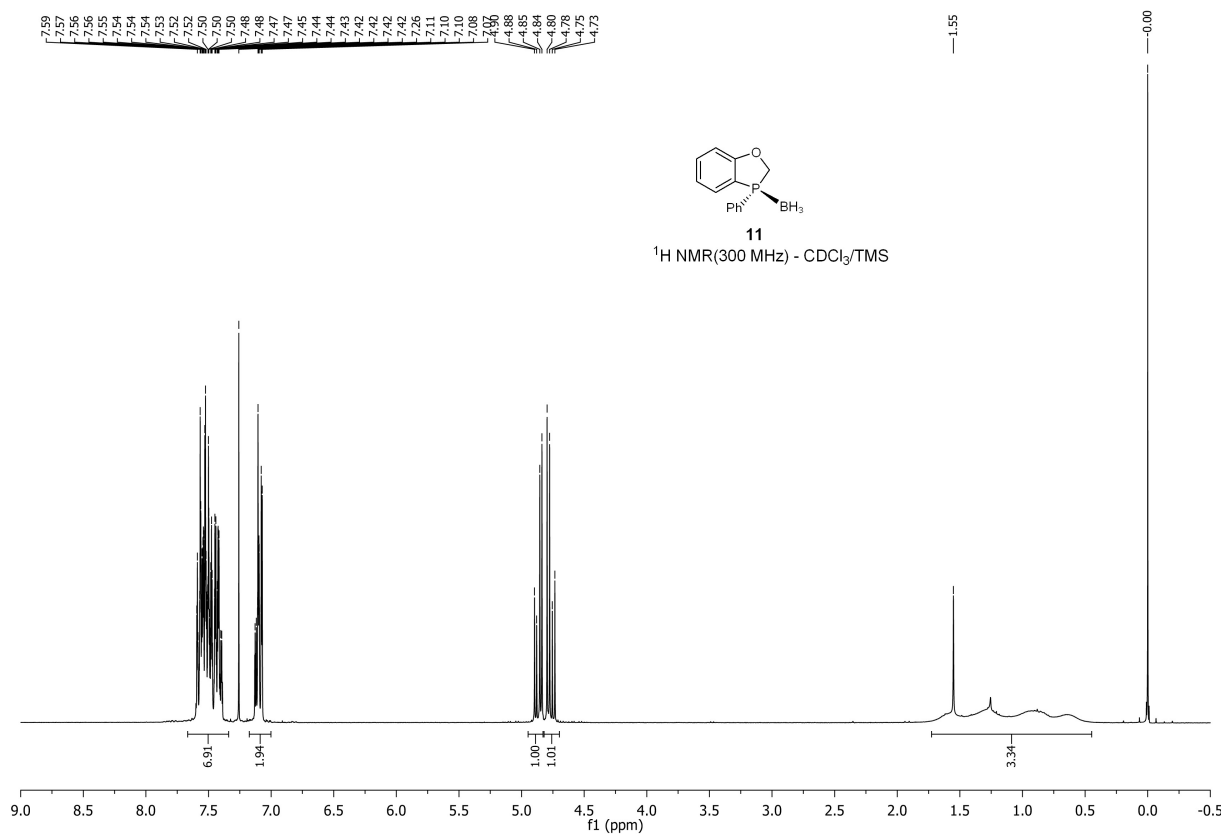




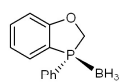












**11**

$^{31}\text{P}$  NMR(243 MHz) -  $\text{CDCl}_3$

