Supporting Information

for

Stereospecific S_N2@P Reactions: Novel Access to Bulky P-Stereogenic Ligands

Contribution by

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EXPERIMENTAL SECTION

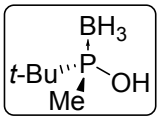
General Methods. All reactions were carried out under nitrogen atmosphere in dried solvents. THF, Et_2O and CH_2Cl_2 were dried in a PureSolv purification system from Innovative Technology, Inc. Other commercially available reagents and solvents were used with no further purification. Thin layer chromatography was carried out using TLC-aluminum sheets with silica gel (Merk 60 F_{254}). Silica gel chromatography was performed by using 35-70 mm silica or an automated chromatography system (Combiflash®, Teledyne Isco) with hexanes/ethyl acetate gradients as eluent unless noted otherwise. NMR spectra were recorded at 23°C on a Inova 300, Varian Mercury 400, Varian 500 or Bruker 600 apparatus. ^{1}H NMR and ^{13}C NMR spectra were referenced either to relative internal TMS or to residual solvent peaks. ^{31}P NMR spectra were referenced to phosphoric acid. Optical rotations were measured at room temperature (25°C) using a Jasco P-2000 iRM-800 polarimeter. Concentration is expressed in g/100 mL. The cell sized 10 cm long and had 1 mL of capacity, measuring λ was 589 nm, which corresponds to a sodium lamp. Melting points were determined using a Büchi melting point apparatus and were not corrected. IR spectra were recorded in a Thermo Nicolet Nexus FT-IR apparatus. HRMS were recorded in a LTQ-FT Ultra (Thermo Scientific) using Nanoelectrospray technique. HPLC chromatography was performed on an Agilent Technologies Series 1100 chromatograph with UV detector. Elemental analysis were done in a EA-1108 CE Instuments (Thermo Fisher). Synthesis of aminophosphine boranes **1a/b** and **5a/b** was performed as previously described by us.[1]

Acidic hydrolysis of aminophosphines 1a/b and 5a/b

GM1. The corresponding aminophosphine borane **1a/b** was dissolved in a mixture of methanol and water. Sulfuric acid (96 wt. % in H_2O) (4 eq) was slowly added drop wise and the solution was warmed up to 50 ºC and stirred for the specified period of time. Most of the methanol was removed *in vacuo* and CH_2Cl_2 and H_2O were added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried over $MgSO_4$. The crude was then purified by column chromatography on silica gel when purification was required.

GM2. The corresponding aminophosphine borane **5a/b** was dissolved in a mixture of methanol and water. Sulfuric acid (96 wt. % in H_2O) (8 eq) was slowly added drop wise and the solution was stirred 16 h at 80 ºC. Most of the methanol was removed *in vacuo* and CH_2Cl_2 and H_2O were added. The phases were separated and the aqueous phase was extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried over $MgSO_4$. The crude was then purified by column chromatography on silica gel when purification was required.

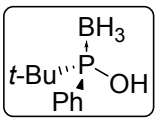
(–)-*(R)-tert*-butyl(methyl)phosphinous acid borane, (–)-3a



Following GM1, (*S*)-*tert*-butyl(methyl)aminophosphine borane, **(+)-1a** (1.00 g, 7.5 mmol), was dissolved in a mixture of methanol (40 mL) and water (2 mL). Sulfuric acid (96 wt. % in H_2O) (1.7 mL, 30.0 mmol) was slowly added. The solution was stirred 2 h at 50 ºC. Solvent removal under *vacuum* yielded 0.97 g (97 %) of **(-)-3a** as a semisolid which did not require further purification (*ee* of the methylated product > 99.9% (CG)). **Following GM2,** (1*S*,2*R*)-1-(*tert*-butyl(methyl)phosphinoamino)-2,3-dihydro-1H- inden-2-ol borane, **(-)-5a** (7.00 g, 26.4 mmol) was dissolved in a mixture of methanol (140 mL) and water (70 mL). Sulfuric acid (96 wt. % in H_2O) (11.2 mL, 211.2 mmol) was slowly added drop wise. The solution was stirred at 80 ºC overnight. Solvent removal under *vacuum* yielded 3.45 g (98 %) of **(-)-3a** as a semisolid which did not require further purification (*ee* of the methylated product > 99.9% (CG)).

$[\alpha]_D$: - 4.8 (c 1.50, $CHCl_3$). **IR (KBr) υ_{max}:** 3361, 2971, 2376, 1476, 921 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.53 (qd, J = 94, 15 Hz, 3H BH_3), 1.17 (d, J_P = 14 Hz, 9H), 1.45 (d, J_P = 9 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 11.1 (d, J_P = 38 Hz, CH_3), 24.0 (d, J_P = 4 Hz, 3xCH_3), 30.8 (d, J_P = 41 Hz, C) ppm. **^{31}P NMR (121 MHz, $CDCl_3$) δ;** 121.1 (q, J_B = 68 Hz, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_5H_{16}BOP - BH_3 + H]^+$: 121.0777, found 121.0777.

(–)-*(S)-tert*-butyl(phenyl)phosphinous acid borane, (–)-3b[2]



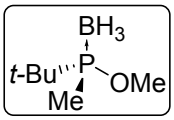
Following GM1, (*R*)-*tert*-butyl(phenyl)aminophosphine borane **(+)-1b,** (20 mg, 0.10 mmol), was dissolved in a mixture of methanol (0.66 mL) and water (0.33 mL) and sulfuric acid (96 wt. % in H_2O) (21 μL, 0.41 mmol) was slowly added. The solution was stirred 7 h at 50 ºC. After the aqueous work up and extractions with CH_2Cl_2, the crude was purified by column chromatography (SiO_2, CH_2Cl_2, 100%) to yield 12 mg (63 %) of **(-)-3b** as a white solid (*ee* of the methylated product > 99.9% (HPLC)). **Following GM2,** (1*S*,2*R*)-1-(*tert*-butyl(phenyl)phosphinoamino)-2,3-dihydro-1H-inden-2-ol borane, **(+)-5b** (200 mg, 0.61 mmol) was dissolved in a mixture of methanol (5.5 mL) and water (1.5 mL) and sulfuric acid (96 wt. % in H_2O) (0.26 mL, 4.89 mmol) was slowly added drop wise. The solution was stirred at 80 ºC overnight. After the aqueous work up and extractions with CH_2Cl_2, the crude was purified by column chromatography (SiO_2, CH_2Cl_2, 100 %) to yield 77 mg (66 %) of **(-)-3b** as a white solid (*ee* of the methylated product > 99.9% (HPLC)).

^{1}H NMR (400 MHz, $CDCl_3$) δ; 0.35-1.17 (br m, 3H-BH_3)1.12 (d, J_P = 15 Hz, 9H), 7.40-7.56 (m, 3H), 7.68-7.79 (m, 2H) ppm.

Determination of the optical purity of phosphinous acid boranes 3a and 3b

Phosphinous acid boranes were transformed to the corresponding methyl phosphinite boranes by reaction with trimethylsilyldiazomethane and analyzed by either chiral GC or HPLC.

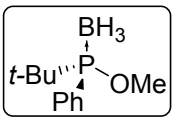
(–)-(*R*)-methyl *tert*-butyl(methyl)phosphinite borane.



Following **GM3**. Phosphinous acid borane **(–)-3a** (400 mg, 2.98 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (6:1, 12 mL) and the solution was cooled down to 0 ºC. Trimethylsilyl diazomethane (2 M in hexanes) (3 mL, 5.96 mmol) was added dropwise and the solution was stirred 1 h at rt. Filtration through a SiO_2 plug eluting with CH_2Cl_2 yielded the crude phosphinite as a yellow oil (69%). (*ee* > 99.9% (GC))

Mp: 88-89 ºC. **$[\alpha]_D$:** - 8.1 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 3340, 2962, 1655, 1559 cm^{-1}.**^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.47 (qd, J = 96, 16 Hz, 3H BH_3), 1.15 (d, J_P = 14 Hz, 9H), 1.37 (d, J_P = 8 Hz, 3H), 3.66 (d, J_P = 11 Hz, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 9.9 (d, J_P = 37 Hz, CH_3), 24.3 (d, J_P = 3 Hz, 3xCH_3), 31.5 (d, J_P = 42 Hz, C), 55.0 (d, J_P = 3 Hz, CH_3) ppm. **^{31}P NMR (121 MHz, $CDCl_3$) δ;** 133.6 (q, J_B = 68 Hz, P-BH_3) ppm. **HRMS (ESI):** calcd for $[C_6H_{18}BOP – BH_3+ H]^+$: 135.0933, found 135.0933. **GC**: *β*-DEX (30 m), 90 ºC, 1 mL/min t_R(+) = 17.9 min, t_R (-) = 18.5 min.

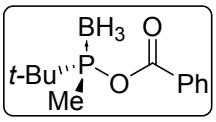
(–)-(*S*)-methyl *tert*-butyl(phenyl)phosphinite borane.[2]



Phosphinous acid borane **(–)-3b** (12 mg, 0.06 mmol) was dissolved in a mixture of CH_2Cl_2 and MeOH (6:1, 1 mL) and the solution was cooled down to 0 ºC. Trimethylsilyl diazomethane (0.6 M in hexanes) (0.2 mL, 0.12 mmol) was added dropwise and the solution was stirred for 1h at rt. Filtration through a SiO_2 plug eluting with CH_2Cl_2 yielded 10 mg (83%) of methyl phosphinite as a white solid (*ee* > 99.9% (HPLC)).

^{1}H NMR (400 MHz, $CDCl_3$) δ; 0.31-1.19 (br m, 3H-BH_3), 1.10 (d, J_P = 15 Hz, 9H), 3.69 (d, J_P = 11 Hz, 3H), 7.42-7.57 (m, 3H), 7.64-7.74 (m, 2H) ppm. **HPLC**: Chiralcel OJ, Heptane/EtOH - 0.2% DEA 70:30, 0.50 mL/min, λ= 210 nm, t_R (+) = 15.7 min, t_R (-) = 22.6 min.

Mixed anhydride between 3a and benzoic acid.



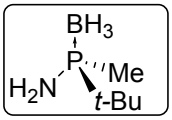
To a suspension of NaH (33 mg, 0.83 mmol, 60 % in mineral oil) in THF (6 mL) at 0 ºC was added a solution of phosphinous acid borane **(–)-3a** (100 mg, 0.75 mmol) in THF (2 ml). The resulting mixture was allowed to warm up to room temperature and stirred 1 h. The solution was then cooled down to 0 ºC and benzoyl chloride (0.10 mL, 0.89 mmol) was added drop wise. The resulting mixture was stirred 3 h at room temperature. Treatment with saturated aqueous solution of $NaHCO_3$ (3 mL) and extractions with EtOAc (2x10 mL) gave the crude which was concentrated. Purification by column chromatography (SiO_2, hexane:EtOAc; 9:1) afforded 120 mg (67 %) of the mixed anhydride as a white solid. Single crystals for X-ray analysis (*vide infra*) were obtained by slow evaporation of a CH_2Cl_2 solution.

Mp: 98-100 ºC. **$[\alpha]_D$:** - 4.3 (c 1.05, $CHCl_3$). **IR (KBr) υ_{max}:** 2981, 2412, 1731, 1251, 1053, 887 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.27-1.14 (m, 3H BH_3), 1.34 (d, J_P = 15 Hz, 9H), 1.85 (s, 9H), 1.71 (d, J = 8 Hz, 3H), 7.48 (t, J_P = 8 Hz, 2H), 7.60-7.66 (m, 1H), 7.98-8.04 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 10.2 (d, J_P = 28 Hz, CH_3), 24.5 (d, J_P = 3.1 Hz, 3xCH_3), 31.6 (d, J_P = 37 Hz, C), 128.9 (s, 2xCH), 129.3 (d, J_P = 3 Hz, C), 130.5 (s, 2xCH), 134.3(s, CH), 163.3 (d, J_P = 8 Hz, C=O) ppm. **^{31}P NMR (121 MHz, $CDCl_3$) δ;** 138.5 (q, J_B = 48 Hz, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{12}H_{20}BO_2P + NH_4]^+$: 256.1632, found 256.1631. **E.A:** calc for $C_{12}H_{20}BO_2P$: C, 60.54; H, 8.47. found C, 60.44; H, 8.77.

Synthesis of optically pure aminophosphanes, (–)-1a and (–)-1b

GM3. Phosphinous acid borane **(+)-3a** or **(+)-3b** (1 eq) and methanesulfonic anhydride (1.5 eq) were dissolved in anhydrous CH_2Cl_2. The reaction was cooled down to -20 ºC and anhydrous NEt_3 (2.5 eq) was slowly added drop wise. The reaction was stirred for 1 h at -20 ºC. NH_3 (g) was bubbled through the solution for 10 min at -20 ºC (formation of a white precipitate was observed) and the solution was stirred at -20 ºC for 30 min. The solution was allowed to warm up to room temperature and water was added. NH_3 was left to evaporate from the solution by stirring at room temperature in an open flask for 1 h. The phases were separated and the aqueous layer was extracted twice with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$ and concentrated to provide the desired products as white solids.

(–)-(*R*)-*tert*-butyl(methyl)phosphanamine borane, (–)-1a[1]

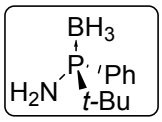


Following **GM3**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (50 mg, 0.37 mmol) and methansulfonic anhydride (98 mg, 0.56 mmol) in CH_2Cl_2 (4 mL). Then NEt_3 (0.13 mL, 0.93 mmol) was added. NH_3 (g) was bubbled through

the solution. Water (2 mL) was added. The phases were separated and the aqueous layer was extracted twice with CH_2Cl_2 (2x5 mL). The combined organic layers were dried over $MgSO_4$ and were concentrated to provide 50 mg (99 %) of **(–)-1a** as a white solid (*ee*= 96 % (CG)).

GC: *β*-DEX (30 m), 130 ºC, 1 mL/min t_R(+) = 15.2 min, t_R (–) = 15.6 min.

(–)-(*S*)-*tert*-butyl(phenyl)aminophosphine borane (–)-1b[1]



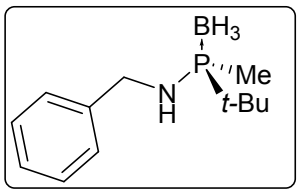
Following **GM3**, (*R*)-*tert*-butyl(phenyl)phosphinous acid borane **(+)-3b** (20 mg, 0.10 mmol) and methansulfonic anhydride (26 mg, 0.15 mmol) in CH_2Cl_2 (1.5 mL). Then NEt_3 (35 µL, 0.26 mmol) was added. NH_3 (g) was bubbled through the solution. Water (2 mL) was added. The phases were separated and the aqueous layer was extracted twice with CH_2Cl_2 (2x3 mL). The combined organic layers were dried over $MgSO_4$ and concentrated to provide 20 mg (99 %) of **(–)-1b** as a white solid (*ee*= 99.6 % (HPLC)).

HPLC: CHIRALCEL OD-H. Heptane/*i*-PrOH 70:30, 0.5 mL/min, λ = 254 nm. t_R (+)= 10.1 min, t_R (–)= 13.7.

Formation of optically pure aminophosphanes from phosphinous acid boranes 3a/b

GM4. A solution of phosphinous acid borane **(+)-3a** or **(+)-3b** (1 eq) and methansulfonic anhydride (1.5 eq) in CH_2Cl_2 was cooled to -20 ºC. To this solution, anhydrous NEt_3 (2.5 eq) was slowly added, and the mixture was stirred 1 h at -20 ºC. The corresponding amine or thiol (3-4 eq) was then added and the solution was stirred overnight at -20 ºC. Water was added and the mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous phase was extracted twice with CH_2Cl_2. The combined extracts were washed with brine and concentrated on a rotary evaporator under reduced pressure. Purification by column chromatography (SiO_2, hexane:EtOAc) yielded the corresponding compounds.

(–)-(*R*)-*N*-benzyl-1-(*tert*-butyl)-1-methylphosphinamine borane, (–)-6

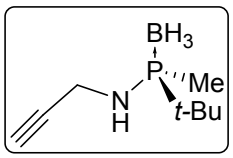


Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (50 mg, 0.37 mmol), methansulfonic anhydride (98 mg, 0.56 mmol), NEt_3 (0.13 mL, 0.93 mmol) and benzylamine (0.12 mL, 1.11 mmol) in CH_2Cl_2 (4 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 85:15) yielded 50 mg (60 %) of **(-)-6** as white solid (*ee* = 98.4 % (HPLC)).

Mp: 42-44 ºC. **IR(KBr):** υ_{max} = 3347, 2956, 2373, 1457, 1073, 880, 701 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.14 – 0.96 (m, 3H-BH_3), 1.16 (d, J_P = 15 Hz, 9H), 1.36 (d, J_P = 9 Hz, 3H), 1.76 (br s, 1H-NH), 3.94 – 4.17 (m, 1H), 4.17 – 4.30 (m, 1H), 7.22 – 7.39 (m, 5H) ppm. **^{13}C NMR**

(101 MHz, $CDCl_3$) δ; 9.2 (d, J_P = 39 Hz, CH_3), 24.8 (d, J_P = 3 Hz, 3xCH_3), 31.4 (d, J_P = 39 Hz, C), 47.5 (CH_2), 127.3 (CH), 127.4 (2xCH), 128.6 (2xCH), 140.6 (d, J_P = 6 Hz, C) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 70.2-71.3 (m) ppm. **HRMS** (ESI^+): Calc per $[C_{12}H_{23}BNP + NH_4]^+$ 214.1999, found 241.2000. **E.A:** Calc for $[C_{12}H_{23}BNP]$: C, 64.60; H, 10.39; N, 6.28 found C, 64.44; H, 10.80; N, 6.12. **HPLC**: CHIRALCEL OJ 250 x 4.6 mm, Heptane/EtOH-0.2%DEA 80:20, 0.50 mL/min, λ= 210 nm. t_R(-) = 12.3 min, t_R(+) = 13.8 min.

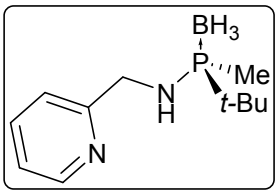
(–)-(*R*)-1-*tert*-butyl-1-methyl-*N*-(prop-2-yn-1-yl)phosphanamine borane, (–)-7



Following **GM4,** (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (100 mg, 0.75 mmol), methansulfonic anhydride (195 mg, 1.12 mmol), NEt_3 (0.26 mL, 1.88 mmol) and propargylamine (0.15 mL, 2.25 mmol) in CH_2Cl_2 (6 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 9:1) yielded 82 mg (64 %) of **(–)-7** as an oil.

$[\alpha]_D$: -11.1 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 3293, 2963, 2379, 1413, 1099, 893 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.47 (dq, J = 94, 15 Hz, 3H, BH_3), 1.14 (d, J_P = 14 Hz, 9H), 1.37 (d, J_P = 9 Hz, 3H), 1.74 (br s, 1H), 2.27 (t, J = 3 Hz 1H), 3.62-3.94 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 9.5 (d, J_P = 38 Hz, CH_3), 24.5 (d, J_P = 3 Hz, 3xCH_3), 30.9 (d, J_P = 40, Hz, C), 32.8 (CH_2), 71.6 (CH), 82.4 (d, J_P = 5 Hz, C) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 72.9-73.9 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_8H_{19}BNP+H]^+$: 172.1421, found 172.1421.

(–)-(*R*)-1-*tert*-butyl-1-methyl-*N*-(pyridin-2-ylmethyl)phosphinamine borane, (–)-8

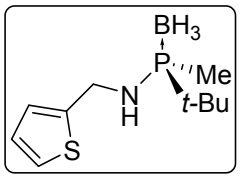


Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (100 mg, 0.75 mmol), methansulfonic anhydride (195 mg, 1.12 mmol), NEt_3 (0.26 mL, 1.88 mmol) and 2-picolylamine (0.31 mL, 3.00 mmol) in CH_2Cl_2 (6 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 7:3) yielded 146 mg (87 %) of **(–)-8** as white solid (*ee* = 99.3 % (HPLC)).

Mp: 75-76 ºC. **$[\alpha]_D$:** - 18.2 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 3244, 2967, 2380, 1589, 1129, 893 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.95 – 0.11 (m, 3H, BH_3), 1.13 (d, J_P = 14 Hz, 9H), 1.32 (d, J_P = 9 Hz, 3H), 2.79 (br s, 1H-NH), 4.18 – 4.43 (m, 2H), 7.14 – 7.19 (m, 1H), 7.24 – 7.29 (m, 1H), 7.64 (td, J = 8 and 2 Hz, 1H), 8.44 – 8.59 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 9.8 (d, J_P = 39 Hz, CH_3), 24.8 (d, J_P = 3 Hz, 3xCH_3), 31.4 (d, J_P = 39 Hz, C), 48.3 (d, J_P = 1 Hz, CH_2), 121.9 (CH) , 122.3 (CH) , 136.8 (CH), 149.1 (CH), 159.0 (d, J_P = 5 Hz, C) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 70.4-71.4 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{11}H_{22}BN_2P + H]^+$: 225.1686, found 225.1686. **E.A:** calc for $C_{11}H_{22}BN_2P$: C, 58.96; H, 9.90; N, 12.50. found C,

58.89; H, 10.32; N, 12.24. **HPLC:** CHIRALCEL OJ. Heptane:EtOH 90:10-0.2% DEA, 0.50 mL/min, λ= 210 nm. t_R(–) = 12.4 min, t_R (+) = 13.3 min.

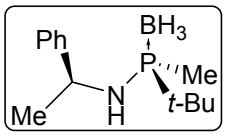
(–)-(*R*)-1-*tert*-butyl-1-methyl-*N*-(thiophen-2-ylmethyl)phosphinamine borane, (–)-9



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid **(+)-3a** (500 mg, 3.73 mmol), methansulfonic anhydride (974 mg, 5.59 mmol), NEt_3 (1.30 mL, 9.33 mmol) and 2-thiophenemethylamine (1.15 mL, 11.2 mmol) in CH_2Cl_2 (25 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 9:1) yielded 619 mg (73 %) of **(–)-9** as white solid (*ee* = 95.7 % (HPLC)).

Mp: 46-47 ºC. **[α]$_D$:** - 4.1 (c 1.00, $CHCl_3$). **IR (KBr) υ$_{max}$:** 3346, 2971, 2376, 1475, 1410, 1066, 893, 701 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.11 - 0.94 (m, 3H, BH_3), 1.15 (d, J_P = 14 Hz, 9H), 1.36 (d, J_P = 9 Hz, 3H), 1.87 (br s, 1H-NH), 4.26 - 4.48 (m, 2H), 6.91 - 6.96 (m, 2H), 7.19 - 7.23 (m, 1H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 9.6 (d, J_P = 38 Hz, CH_3), 24.8 (d, J_P = 3 Hz, 3xCH_3), 31.3 (d, J_P = 40 Hz, C), 42.6 (CH_2), 124.9 (CH), 124.9 (CH), 126.9 (CH), 144.8 (d, J_P = 6 Hz, C) ppm. **^{31}P NMR (243 MHz, $CDCl_3$) δ;** 71.0-71.9 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{10}H_{21}BNPS + NH_4]^+$: 247.1564, found 225.1565. **E.A:** calc for $C_{10}H_{21}BNPS$: C, 52.42; H, 9.24; N, 6.11; S, 13.52. found C, 52.66; H, 9.65; N, 5.86; S, 13.38. **HPLC:** CHIRALCEL OJ. Heptane:EtOH 80:20-0.2% DEA, 0.50 mL/min, λ= 210 nm. t_R(–) = 14.2 min, t_R (+) = 15.5 min.

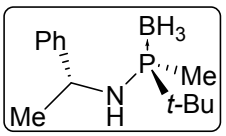
(–)-(*R*)-1-*tert*-butyl-1-methyl-*N*-((*S*)-1-phenylethyl)phosphanamine borane, (–)-10



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (100 mg, 0.75 mmol), methansulfonic anhydride (194 mg, 1.12 mmol), NEt_3 (0.26 mL, 1.88 mmol) and (*S*)-(1)-phenylethylamine (0.30 mL, 2.25 mmol) in CH_2Cl_2 (6 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 9:1) yielded 135 mg (76 %) of **(–)-10** as white solid (*de* = 98 % (NMR)).

Mp: 94-95 ºC. **[α]$_D$:** - 54.7 (c 1.00, $CHCl_3$). **IR (KBr) υ$_{max}$:** 3344, 2975, 2373, 1065, 899 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.12-0.96 (m, 3H, BH_3), 1.07 (d, J_P = 14 Hz, 9H), 1.24 (d, J_P = 9 Hz, 3H), 1.46 (d, J = 7 Hz, 3H), 1.81 (br d, J = 9 Hz, 1H, NH), 4.41-4.50 (m, 1H), 7.20 – 7.37 (m, 5H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 9.7 (d, J_P = 38 Hz, CH_3), 24.7 (d, J_P = 3 Hz, 3x CH_3), 26.8 (d, J_P = 4 Hz, C), 31.3 (d, J_P = 40 Hz, CH), 53.1 (CH), 125.7 (2xCH), 126.9 (CH), 128.6 (2xCH), 146.1 (d, J = 4 Hz, C) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 68.2-69.2 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{13}H_{25}BNP+H]^+$: 238.1890, found 238.1890. **E.A:** calc for $C_{13}H_{25}BNP$: C, 68.85; H, 10.63; N, 5.91. Found C, 65.72; H, 11.03; N, 5.80.

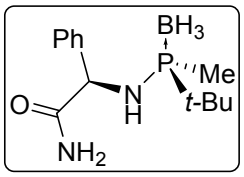
(+)-(*R*)-1-*tert*-butyl-1-methyl-*N*-((*R*)-1-phenylethyl)phosphanamine borane, (+)-11



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (100 mg, 0.75 mmol), methansulfonic anhydride (194 mg, 1.12 mmol), NEt_3 (0.26 mL, 1.88 mmol) and (*R*)-(1)-phenylethylamine (0.30 mL, 2.25 mmol) in CH_2Cl_2 (6 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 9:1) yielded 125 mg (71 %) of **(+)-11** as white solid (*de* = 95%(NMR)).

Mp: 102-103 ºC. **$[\alpha]_D$:** + 13.1 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 3335, 2943, 2354, 1450, 889 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.92-0.11 (m, 3H, BH_3), 1.11 (d, J_P = 14 Hz, 9H), 1.20 (d, J_P = 9 Hz, 3H), 1.44 (d, J = 7 Hz, 3H), 1.74 (br d, J = 10 Hz, 1H), 4.38 – 4.53 (m, 1H), 7.14-7.48 (m, 5H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 9.9 (d, J_P = 36 Hz, CH_3), 24.6 (d, J_P = 3 Hz, 3xCH_3), 26.6 (d, J_P = 5 Hz, CH_3), 30.5 (d, J_P = 42 Hz, C), 52.6 (CH), 125.8 (2xCH), 126.9 (CH), 128.5 (2xCH), 146.2 (d, J_P = 3 Hz, C) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 68.7-69.7 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{13}H_{25}BNP+H]^+$: 238.1890, found 238.1895. **E.A:** calc for $C_{13}H_{25}BNP$: C, 68.85; H, 10.63; N, 5.91. Found C, 65.45; H, 10.85; N, 5.70.

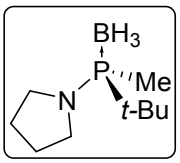
(–)-(2*R*)-2-[(*R*)-*tert*-butyl(methyl)phosphinoamino]-2-phenyl- acetamide borane, (–)-12



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (100 mg, 0.75 mmol), methansulfonic anhydride (194 mg, 1.12 mmol), NEt_3 (0.26 mL, 1.88 mmol) and (*R*)-2-phenylglycine amide (338 mg, 2.25 mmol) in CH_2Cl_2 (6 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 7:3) yielded 125 mg (63 %) of **(–)-12** as white solid (*de* = 97 % (NMR)).

Mp: 158-159 ºC. **$[\alpha]_D$:** - 112.2 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 3403, 2359, 1671, 1365, 931, 697cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.11– 0.87 (m, 3H, BH_3), 0.98 (d, J_P = 14 Hz, 9H), 1.39 (d, J_P = 9 Hz, 3H), 3.00 (br d, J = 9 Hz, NH), 4.99 (t, J = 9 Hz, 1H), 5.49 (br d, J = 32 Hz, NH_2), 7.28 – 7.34 (m, 2H), 7.34 – 7.38 (m, 3H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 10.4 (d, J_P = 37 Hz, CH_3), 24.2 (d, J_P = 3 Hz, 3xCH_3), 30.6 (d, J_P = 43 Hz, C), 60.0 (CH), 127.2, (2xCH), 129.0 (CH), 128.2 (2xCH), 140.3 (C), 174.0 (C=O) ppm. **^{31}P NMR (243 MHz, $CDCl_3$) δ;** 72.9-73.9 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{26}H_{48}B2N_4O_2P_2$ (2M) + H$]^+$: 533.3511, found 533.3518.

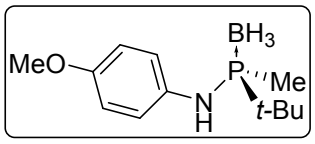
(–)-(*R*)-1-(*tert*-butyl(methyl)phosphanyl)pyrrolidine, (–)-13



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane, **(+)-3a** (200 mg, 1.49 mmol), methansulfonic anhydride (390 mg, 2.24 mmol), NEt_3 (0.52 mL, 3.73 mmol) and freshly distilled pyrrolidine (0.62 mL, 7.45 mmol) in CH_2Cl_2 (8 mL). Purification by column chromatography (SiO_2, isocratic CH_2Cl_2) yielded 180 mg (65 %) of **(–)-13** as oil (*ee* = 97.8 % (HPLC)).

$[\alpha]_D$: - 13.1 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 2971, 2377, 1475, 1363, 1291, 1068, 1012, 889, 781 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.51 (br q, J_B = 94 Hz, 3H, BH_3), 1.13 (d, J_P = 14 Hz, 9H), 1.36 (d, J_P = 9 Hz, 3H), 1.72-1.83 (m, 4H), 3.05-3.17 (m, 2H), 3.21-3.31 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 6.7 (d, J_P = 41 Hz, CH3), 25.7 (d, J_P = 3 Hz, 3xCH3), 26.4 (d, J_P = 6 Hz, 2xCH2), 34.0 (d, J_P = 37 Hz, C), 48.8 (d, J_P = 2 Hz, 2xCH2), ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 68.9 – 70.0 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_9H_{23}BNOP + H]^+$: 188.1734, found 188.1735. **HPLC:** Chiralcel OD-H. Heptane:*i*-PrOH = 99:1, 0.50 mL/min, λ= 210 nm. t_S(+) = 22.3 min, t_R(–) = 24.2 min.

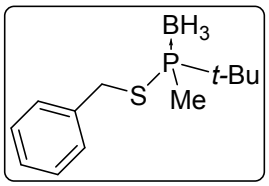
(+)-(*R*)-1-*tert*-butyl-*N*-(4-methoxyphenyl)-1-methylphosphanamine borane, (+)-14



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (200 mg, 1.49 mmol), methansulfonic anhydride (390 mg, 2.24 mmol), NEt_3 (0.52 mL, 3.73 mmol) and 4-methoxyaniline (550 mg, 4.47 mmol) in CH_2Cl_2 (6 mL). Purification by column chromatography (SiO_2, isocratic CH_2Cl_2) yielded 150 mg (42 %) of **(+)-14** as a yellow solid (*ee* = 91.0 % (HPLC)).

Mp: 124-125 ºC. **$[\alpha]_D$:** + 5.7 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 3308, 2403, 1511, 1246, 1037, 934, 826 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 1.01 – 0.22 (m, 3H, BH_3), 1.17 (d, J_P = 14 Hz, 9H), 1.50 (d, J_P = 9 Hz, 3H), 3.74 (br s, 1H, NH), 3.76 (s, 3H), 6.78 (d, J = 9 Hz, 2H), 7.00 (d, J = 8 Hz, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 69.5 (d, J_P = 40 Hz, CH_3), 25.1 (d, J_P = 3 Hz, 3xCH_3), 32.1 (d, J_P = 35 Hz, C), 55.5 (CH_3), 114.4 (2xCH), 123.2 (d, J_P = 3 Hz, 2xCH), 134.7 (d, J_P = 4 Hz, C), 155.6 (C) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ;** 69.5 – 70.3 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{12}H_{23}BNOP - BH_3 + H]^+$: 226.1355, found 226.1351. **E.A:** calc for $C_{12}H_{23}BNOP$: C, 60.28; H, 9.82; N, 5.80; found C, 60.11; H, 9.70; N, 5.86. **HPLC:** Chiralpak IA. Heptane:*i*-PrOH = 90:10, 0.50 mL/min, λ= 210 nm. t_R(+) = 14.7 min, t_R(–) = 18.5 min.

(–)-(benzylthio)(*tert*-butyl)(methyl)phosphine borane, (–)-17

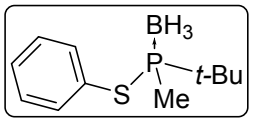


Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (100 mg, 0.75 mmol), methansulfonic anhydride (195 mg, 1.12 mmol),

NEt_3 (0.26 mL, 1.86 mmol) and benzylthiol (0.26 mL, 2.25 mmol) in CH_2Cl_2 (6 mL). The solution was stirred 16 h at -20 ºC. Purification by preparative HPLC (SiO_2, hexane:Et_2O; 96:4) yielded 64 mg (22 %) of **(–)-17** as yellow oil.

$[\alpha]_D$: - 23.5 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 2962, 2392, 1454, 1059, 699 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.39-1.21 (m, 3H BH_3), 1.21 (d, J_P= 15 Hz, 9H), 1.47 (d, J_P= 9 Hz, 3H), 4.05 (dd, J = 13, 8 Hz, 1H), 4.17 (dd, J = 13, 8 Hz, 1H), 7.39 – 7.20 (m, 5H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 11.3 (d, J_P = 30 Hz, CH_3), 25.1 (d, J_P = 3 Hz, 3xCH_3), 31.9 (d, J_P = 27 Hz, C), 34.9 (CH_2), 127.7 (CH), 128.8 (2xCH), 129.2 (2xCH), 138.0 (C) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 70.4-71.3 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{12}H_{22}BPS\text{-}BH_3+O+H]^+$: 243.0972, found 243.0988.

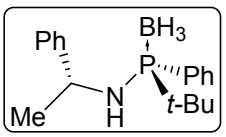
(–)-*tert*-butyl(methyl)(phenylthio)phosphine borane, (–)-18



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane **(+)-3a** (50 mg, 0.37 mmol), methansulfonic anhydride (98 mg, 0.56 mmol), NEt_3 (0.13 mL, 0.93 mmol) and phenylthiol (0.12 mL, 1.11 mmol) in CH_2Cl_2 (4 mL). The solution was stirred 16 h at -10 ºC. Purification by column chromatography (SiO_2, hexane:CH_2Cl_2; 6:4) yielded 32 mg (36 %) of **(–)-18** as a yellow oil.

$[\alpha]_D$: - 2.1 (c 1.49, $CHCl_3$). **IR(KBr):** υ_{max} = 2962, 2384, 1473, 1057, 747 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.12-0.94 (m, 3H BH_3), 1.27 (d, J_P = 15 Hz, 9H), 1.50 (d, J_P = 8 Hz, 3H), 7.30-7.41 (m, 3H), 7.54-7.60 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 10.8 (d, J_P = 26 Hz, CH_3), 25.6 (d, J_P = 3 Hz, 3xCH_3), 32.2 (d, J_P= 24 Hz, C), 126.8 (d, J_P = 4 Hz, C), 129.1 (d, J_P = 2 Hz, 2xCH), 129.6 (d, J_P = 2 Hz, CH), 137.0 (d, J_P = 3 Hz, 2xCH) ppm. **^{31}P NMR (202 MHz, $CDCl_3$) δ;** 75.1-75.7 (m, P-BH_3) ppm. **HRMS** (ESI^+): Calc per $[C_{11}H_{20}BPS–BH_3+O+H]^+$ 229.0811, found 229.0809.

(–)-(*S*)-1-*tert*-butyl-1-phenyl-N-((*R*)-1-phenylethyl)phosphanamine borane, (–)-19[3]

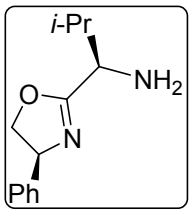


Following **GM4**, (*R*)-*tert*-butyl(phenyl)phosphinous acid **(+)-3b** (100 mg, 0.51 mmol), methansulfonic anhydride (134 mg, 0.77 mmol), NEt_3 (0.18 mL, 1.28 mmol) and (*R*)-(1)-phenylethylamine (0.33 mL, 2.55 mmol) in CH_2Cl_2 (4 mL). Purification by column chromatography (SiO_2, hexane:EtOAc; 95:5) yielded 110 mg (72 %) of **(–)-19** as white solid (*de* = 96 % (NMR)).

$[\alpha]_D$: - 7.6 (c 1.00, $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.41-1.24 (m, 3H, BH_3), 1.09 (d, J_P = 14 Hz, 9H), 1.58 (d, J = 7 Hz, 3H), 2.09 (br d, J = 10 Hz, 1H), 4.47 – 4.65 (m, 1H), 7.14-7.24 (m, 4H), 7.22-7.31 (m, 3H), 7.40-7.47 (m, 2H) ppm.

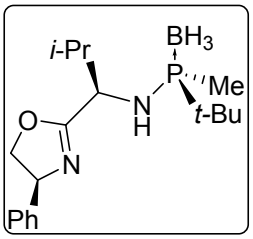
(*R*)-2-Methyl-1-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)propan-1-amine, 20

Compound **20** was obtained following procedures described in the literature.[4]



^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.01 (d, *J* = 7 Hz, 3H), 1.05 (d, *J* = 7 Hz, 3H), 1.58 (br s, 2H), 2.00-2.14 (m, 1H), 3.45 (dd, *J* = 5, 1 Hz, 1H), 4.12 (t, *J* = 9 Hz, 1H), 4.67 (dd, *J* = 10, 9 Hz, 1H), 5.21 (t, *J* = 9 Hz, 1H), 7.22-7.33 (m, 3H), 7.31-7.40 (m, 2H) ppm.

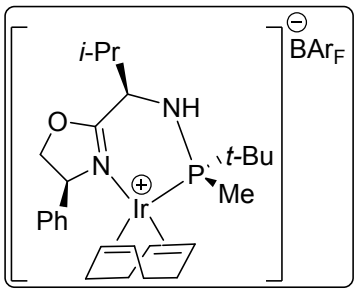
(*R*)-(+)-1-*tert*-butyl-1-methyl-*N*-((*R*)-2-methyl-1-((*S*)-4-phenyl-4,5-dihydrooxazol-2-yl)propyl)phosphanamine borane, (+)-21



Following **GM4**, (*S*)-*tert*-butyl(methyl)phosphinous acid borane, **(+)-3a** (250 mg, 1.86 mmol), methansulfonic anhydride (390 mg, 2.24 mmol), NEt_3 (0.65 mL, 4.65 mmol) and amine **20** (756 mg, 3.47 mmol) in CH_2Cl_2 (15 mL). Water (10 mL) was added and the mixture was allowed to warm to room temperature. The organic layer was separated and the aqueous phase was extracted twice with CH_2Cl_2 (2x15mL). The combined organic layers were washed twice with $NaOH_{aq}$ (1 M) (2x10 mL). The organic layer was dried over $MgSO_4$ and concentrated on a rotary evaporator under reduced pressure. Purification by column chromatography (SiO_2, hexane:EtOAc; 85:15) yielded 269 mg (43 %) of **(+)-21** as a white solid (*de* = 98.5 % (NMR)).

Mp: 66-67 ºC. **[α]$_D$:** + 14.8 (c 1.00, $CHCl_3$). **IR (KBr) υ_{max}:** 2964, 2380, 1660, 1466, 1137, 916 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 0.88-0.09 (m, 3H), 1.00 (d, *J* = 7 Hz, 3H), 1.05 (d, *J* = 7 Hz, 3H), 1.15 (d, J_P = 14 Hz, 9H), 1.36 (d, J_P = 9 Hz, 3H), 2.02-2.14 (m, 1H), 2.14-2.23 (m, 1H), 3.91-4.02 (m, 1H), 4.11 (t, *J* = 9 Hz, 1H), 5.17-5.24 (m, 1H), 7.22-7.31 (m, 3H), 7.33-7.39 (m, 2H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 10.4 (d, J_P = 33 Hz, CH_3), 18.0 (CH_3), 19.5 (CH_3), 24.7 (d, J_P = 3 Hz, 3xCH_3), 30.8 (d, J_P = 45 Hz, C), 33.3 (d, J_P = 6 Hz, CH), 56.7 (CH), 69.5 (CH), 75.5 (CH), 126.9 (2xCH), 127.9 (CH), 129.0 (2xCH), 142.0 (C), 171.0 (C) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ;** 71.8-73.0 (m, P-BH_3) ppm. **HRMS (ESI):** calc for $[C_{18}H_{32}BN_2OP+H]^+$: 335.2416, found 335.2416.

[Ir(26)(COD)]BAr_F, (+)-22



Borane protected phosphine-oxazoline **(+)-21** (200 mg, 0.60 mmol) was dissolved in freshly distilled pyrrolidine (10 mL) and

the solution was stirred 16 h at 90 ºC. After this period of time, pyrrolidine was removed *in vacuo*. When all the pyrrolidine was removed, the crude was left under *vacuum* at 50 ºC for 30 min, keeping always the crude under N_2. A solution of $[Ir(COD)(Cl)]_2$ (200 mg, 0.30 mmol) in CH_2Cl_2 (8 mL) was added to the free ligand via cannula or syringe. The resulting mixture was left to stir 40 min at room temperature. $NaBAr_F$ (531 mg, 0.60 mmol) was then added and the solution was stirred 1 h at room temperature. The formation of an apolar product was observed by TLC; Rf = 0.9 (100% CH_2Cl_2).The crude was then filtered through a small plug of silica gel (washed first with Et_2O) under N_2 eluting with hexane:CH_2Cl_2 (50-100%) mixtures. The orange fraction was collected and concentrated *in vacuo* to yield 800 mg (89 %) of [Ir**(25)**(COD)]BAr_F, **(+)-22** as an orange solid.

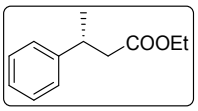
Mp: 190-191 ºC. **$[\alpha]_D$:** + 57.9 (c 0.50, $CHCl_3$). **IR (KBr) υ_{max}:** 2925, 1612, 1354, 1276, 1134, 886, 701 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$) δ;** 1.06 (d, J = 7 Hz, 3H), 1.11 (d, J_P = 15 Hz, 9H), 1.15 (d, J = 7 Hz, 3H), 1.30 (d, J_P = 8 Hz, 3H), 1.46-1.62 (m, 2H), 1.84-2.04 (m, 4H), 2.05-2.15 (m, 1H), 2.15-2.26 (m, 1H), 2.38 (br d, J = 7 Hz, 1H), 2.85-3.05 (m, 1H), 3.38-3.54 (m, 3H), 4.13-4.19 (m, 1H), 4.43 (dd, J = 9, 5 Hz, 1H), 4.63-4.82 (m, 2H), 5.03 (dd, J = 10, 5 Hz, 1H), 7.21-7.28 (m, 2H), 7.35-7.46 (m, 3H), 7.53 (br s, 4H), 7.71 (br s, 8H) ppm. **^{13}C NMR (101 MHz, $CDCl_3$) δ;** 7.9 (d, J_P = 35 Hz, CH_3), 18.6 (CH_3), 19.2 (CH_3), 25.6 (d, J_P = 5 Hz, 3xCH_3), 28.3 (d, J_P = 1 Hz, CH_2), 30.4 (d, J_P = 3 Hz, CH_2), 30.5 (d, J_P = 3 Hz, CH_2), 33.4 (d, J_P = 3 Hz, CH_2), 36.6 (d, J_P = 38 Hz, C), 36.9 (d, J_P = 5 Hz, CH), 58.3 (CH), 60.8 (d, J = 5 Hz, CH), 63.6 (CH), 71.3 (CH), 78.4 (CH_2), 89.3 (d, J_P = 13 Hz, CH), 94.5 (d, J_P = 10 Hz, CH), 117.5 (hept, J_F = 4 Hz, 4xCH), 124.5 (q, J_F = 273 Hz, 8xCF_3), 126.6 (2xCH), 128.9 (qq, ^2J_F= 31, ^4J_F= 3 Hz, 8xC), 129.8 (2xCH), 130.4 (CH), 134.8 (8xCH), 138.5 (C), 161.7 (q, J_B = 50 Hz, 4xC), 177.8 (d, J_P = 5 Hz, C) ppm. **^{31}P NMR (162 MHz, $CDCl_3$) δ;** 57.4 ppm. **^{19}F NMR (376 MHz, $CDCl_3$) δ;** -62.38 ppm. **HRMS (ESI):** calc for $[C_{26}H_{41}IrN_2OP]^+$: 621.2580, found 621.2573. Calc for $[C_{32}H_{12}BF_{24}]^-$: 863.0654, found 863.0627.

Typical procedure for olefin hydrogenation

The alkene (0.5 mmol) and Ir complex **(+)-22** (1 mol%) were dissolved in CH_2Cl_2 (1 mL) in a high-pressure autoclave. The autoclave was purged four times with hydrogen. Then, it was

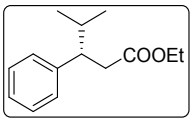
pressurized at the desired pressure. After the desired reaction time, the autoclave was depressurized and the solvent evaporated off. The residue was dissolved in Et_2O (1 ml) and filtered through a short plug of celite. The conversions were determined by ^1H NMR or GC and enantiomeric excess was determined by chiral GC or chiral HPLC. All conversions were 100%.

(*R*)-Ethyl 3-phenylbutanoate[5]



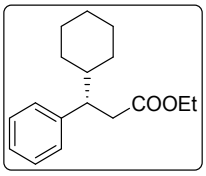
^{1}H NMR (400 MHz, $CDCl_3$) δ; 1.16 (t, 3H, *J*= 7.2 Hz), 1.30 (d, 3H, *J*= 6.8 Hz), 2.54 (m, 2H), 3.28 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.2-7.4 (m, 5H). **HPLC**: Chiracel IB column (hexane/2-propanol=99.5/0.5, 1 mL/min, 254 nm). t_R (*R*) = 12.4 min; t_R (*S*) = 26.3 min. (*ee* = 94.7% (*R*) (HPLC))

(*R*)-Ethyl 4-methyl-3-phenylpentanoate.[6]



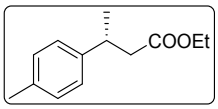
^{1}H NMR (400 MHz, $CDCl_3$) δ; 0.77 (d, 3H, *J* = 6.0 Hz), 0.97 (d, 3H, *J* = 6.0 Hz), 1.06 (t, 3H, *J*= 6.8 Hz), 1.86 (m, 1H), 2.60 (m, 1H), 2.80 (m, 1H), 2.88 (m, 1H), 3.96 (q, 2H, *J*= 6.8 Hz), 7.1-7.3 (m, 5H). **HPLC**: Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R (*R*) = 11.0 min; t_R (*S*) = 18.8 min. (*ee* = 97.1% (*R*) (HPLC))

(*R*)-Ethyl 3-cyclohexyl-3-phenylpropanoate[7]



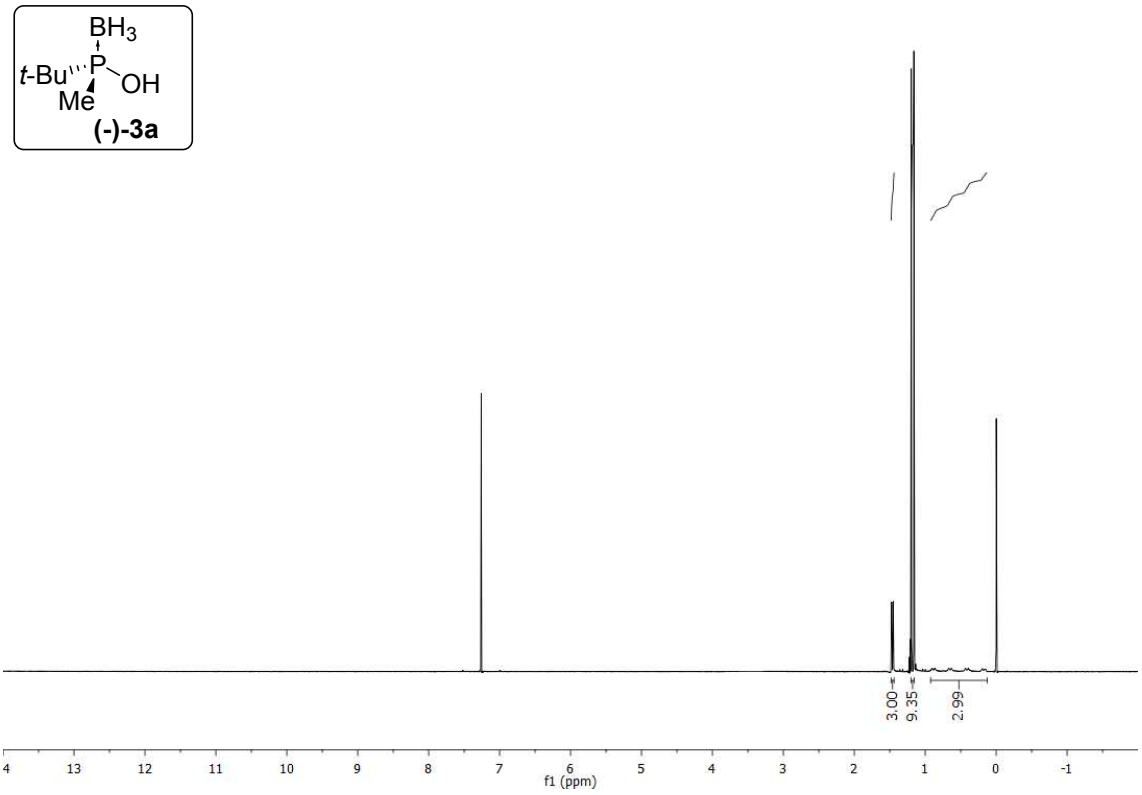
^{1}H NMR ($CDCl_3$) δ: 0.90 (m, 1H), 0.93 (m, 1H), 1.06 (t, 3H, *J*= 7.2 Hz), 1.12 (m, 1H), 1.24 (m, 2H), 1.42 (m, 2H), 1.60 (m, 2H), 1.72 (m, 1H), 1.80 (m, 1H), 2.54 (m, 1H), 2.78 (m, 1H), 2.89 (m, 1H), 3.92 (q, 2H, *J*= 7.2 Hz), 7.1-7.3 (m, 5H). **HPLC**: Chiracel OD-H column (hexane/2-propanol=99/1, 0.5 mL/min, 254 nm). t_R (*R*) = 10.3 min; t_R (*S*) = 17.0 min. (*ee* = 97.1% (*R*) (HPLC)).

(*R*)-Ethyl 3-(*p*-tolyl)butanoate.[5]

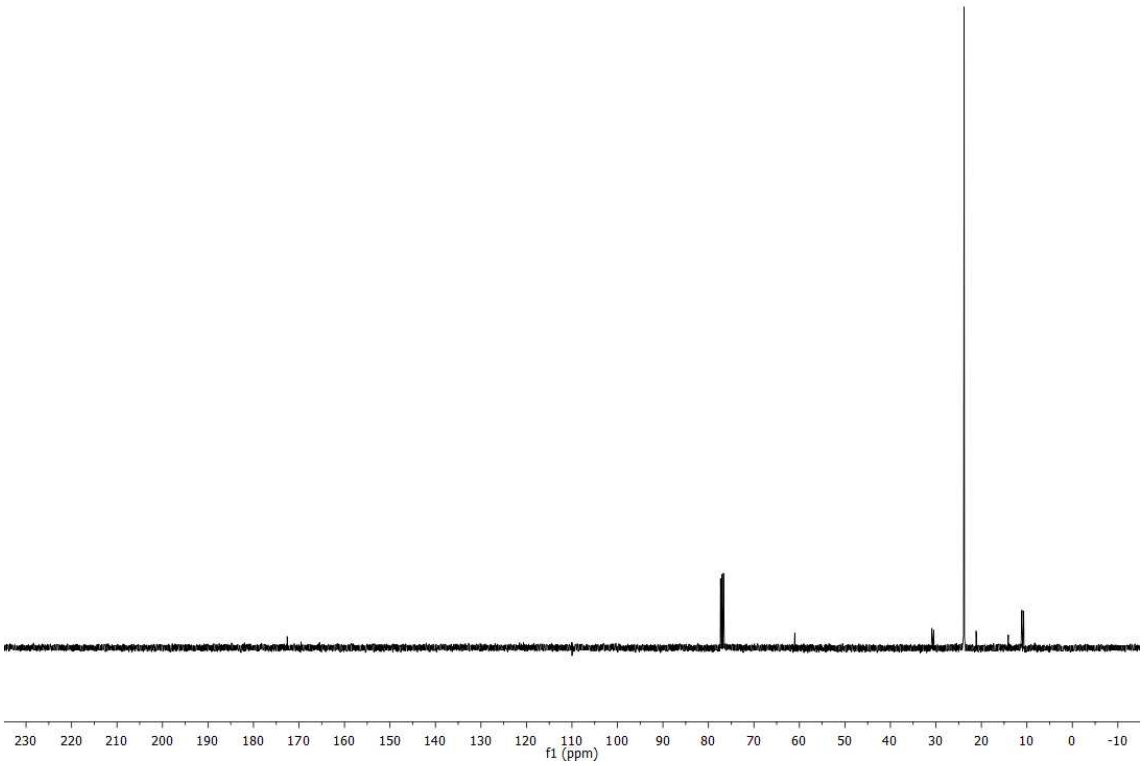


^{1}H NMR ($CDCl_3$) δ: 1.18 (t, 3H, *J*= 7.2 Hz), 1.28 (d, 3H, *J*= 6.0 Hz), 2.31 (s, 3H), 2.56 (m, 2H), 3.25 (m, 1H), 4.08 (q, 2H, *J*= 7.2 Hz), 7.12 (m, 4H) ppm. **HPLC**: Chiracel IB column (hexane/2-propanol=99.5/0.5, 0.5 mL/min, 254 nm). t_R (*R*) = 10.9 min; t_R (*S*) = 12.0 min. (*ee* = 99.9% (*R*) (HPLC)).

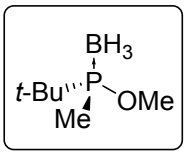
^{1}H NMR (400 MHz, $CDCl_3$)



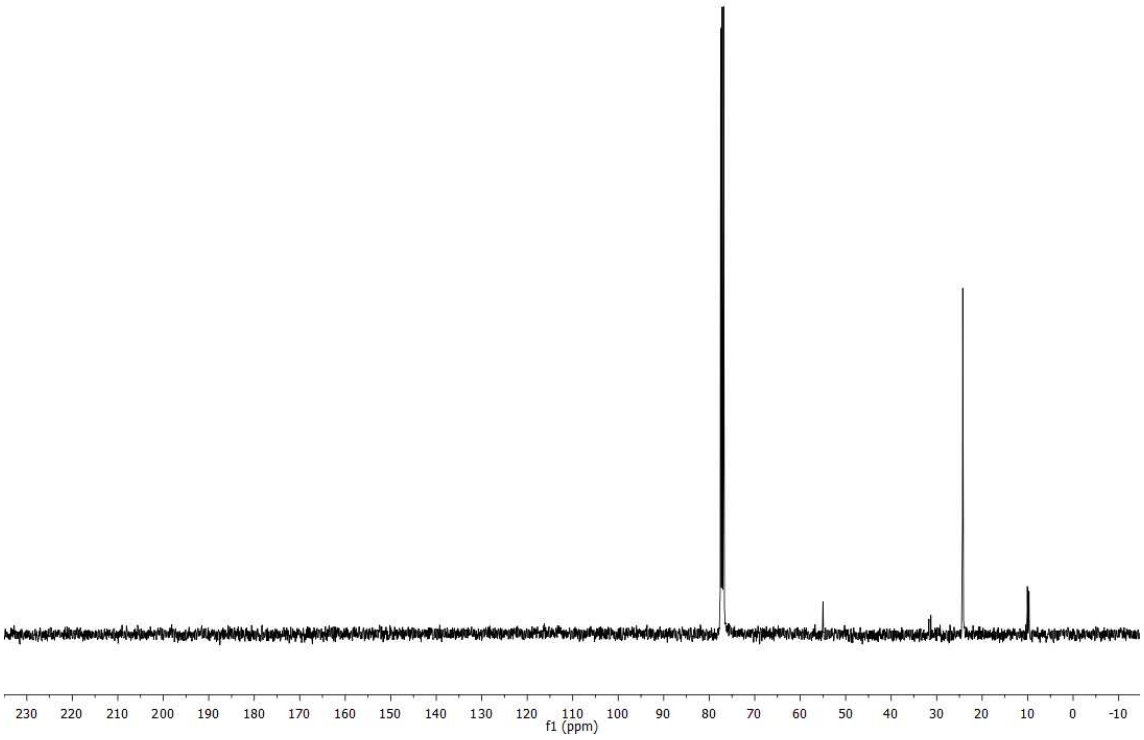
^{13}C NMR (101 MHz, $CDCl_3$)



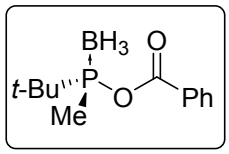
^{1}H NMR (400 MHz, $CDCl_3$)



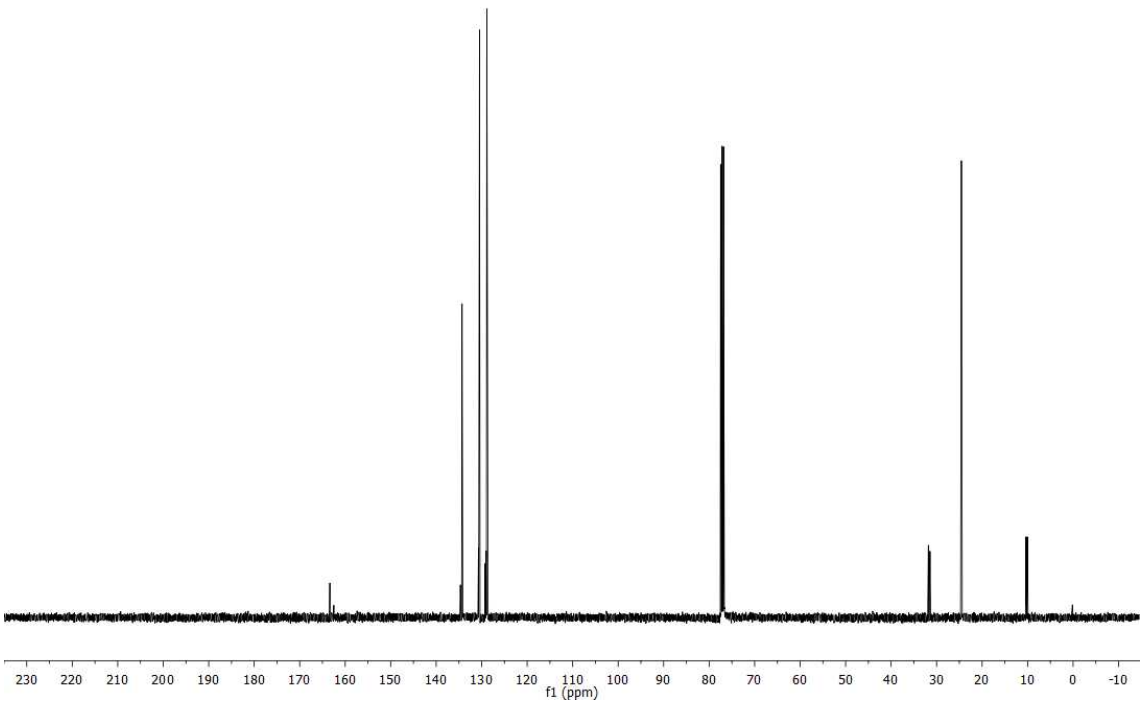
^{13}C NMR (101 MHz, $CDCl_3$)



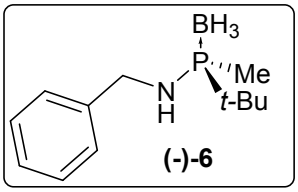
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

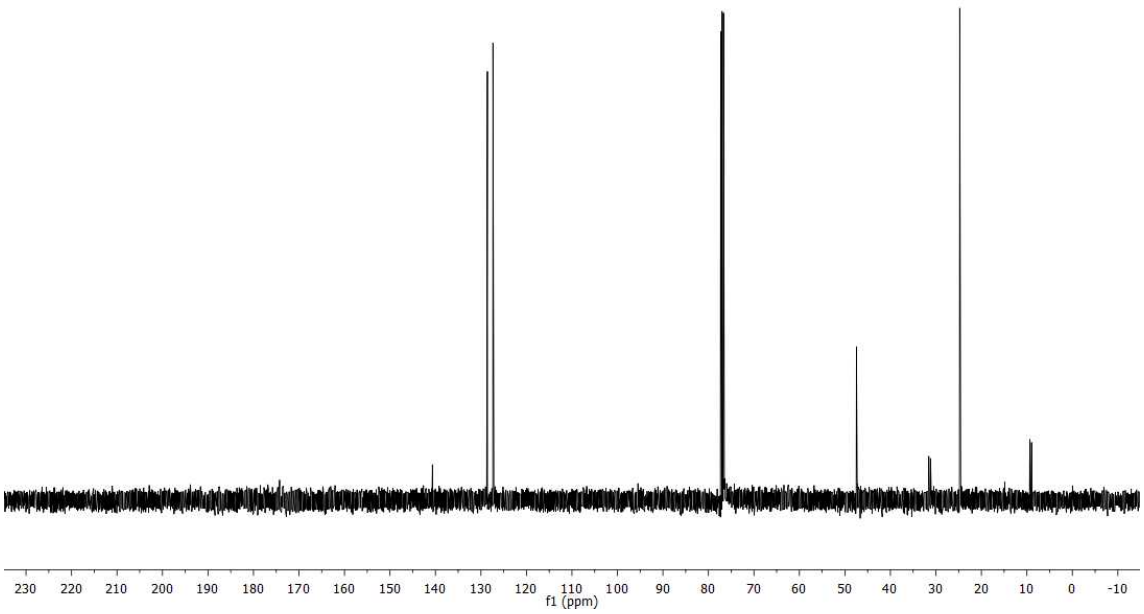


^{1}H NMR (400 MHz, $CDCl_3$)

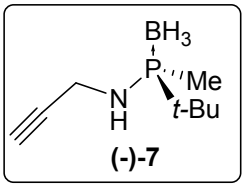


(-)-6

^{13}C NMR (101 MHz, $CDCl_3$)

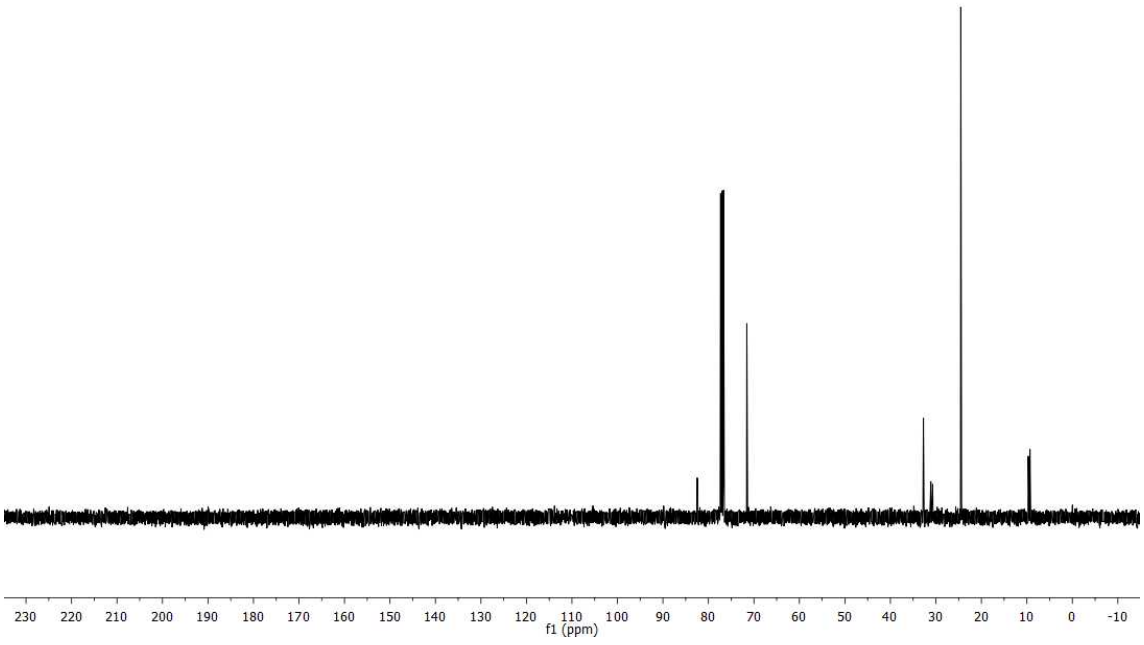


^{1}H NMR (400 MHz, $CDCl_3$)

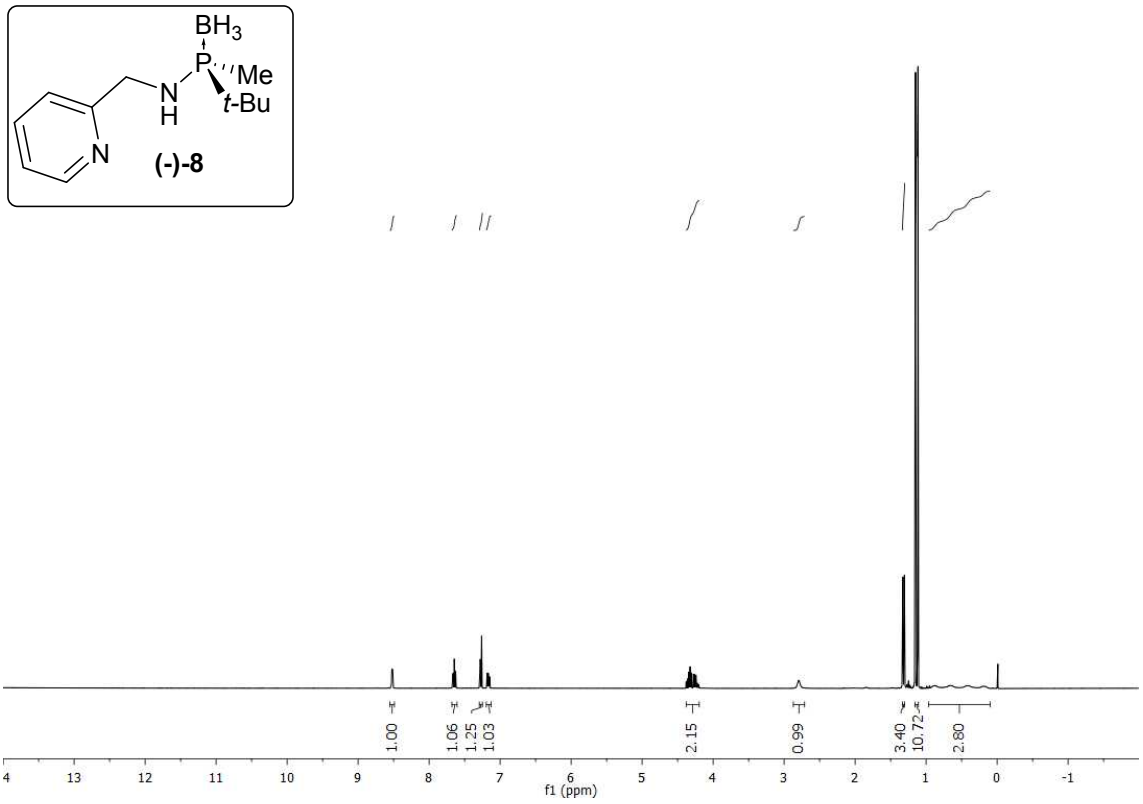


(-)-7

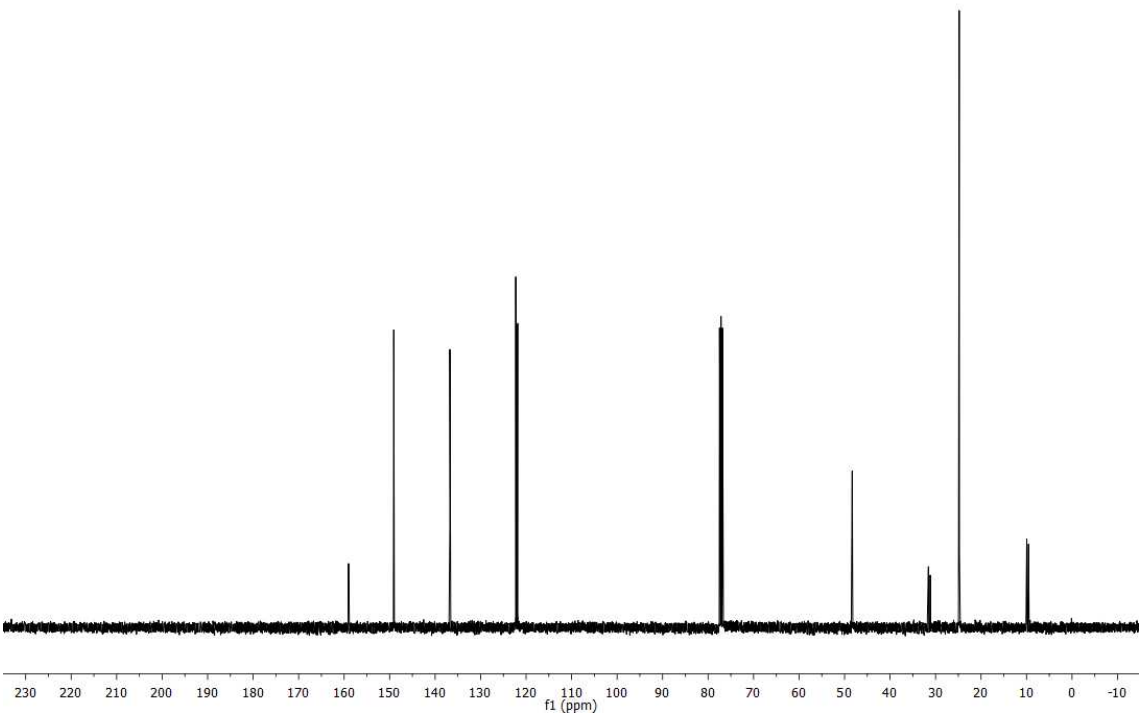
^{13}C NMR (101 MHz, $CDCl_3$)



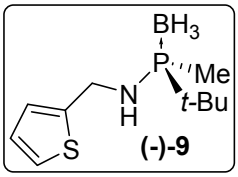
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

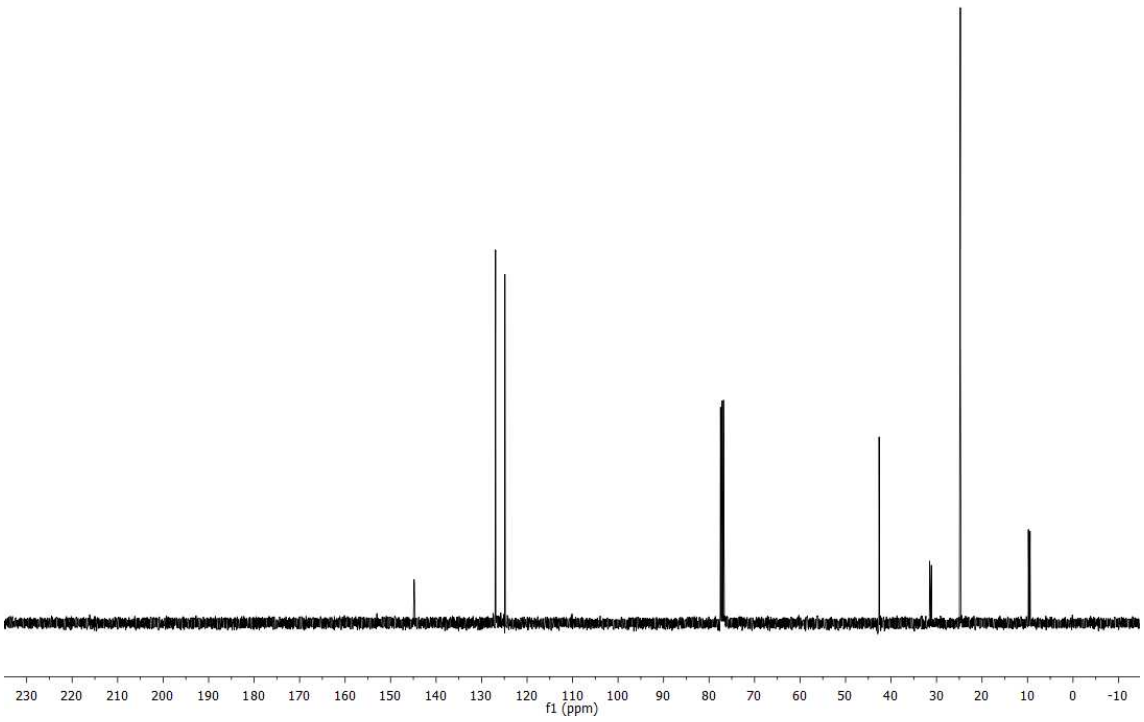


^{1}H NMR (400 MHz, $CDCl_3$)

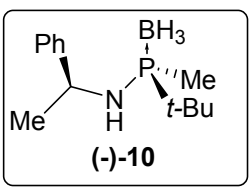


(-)-9

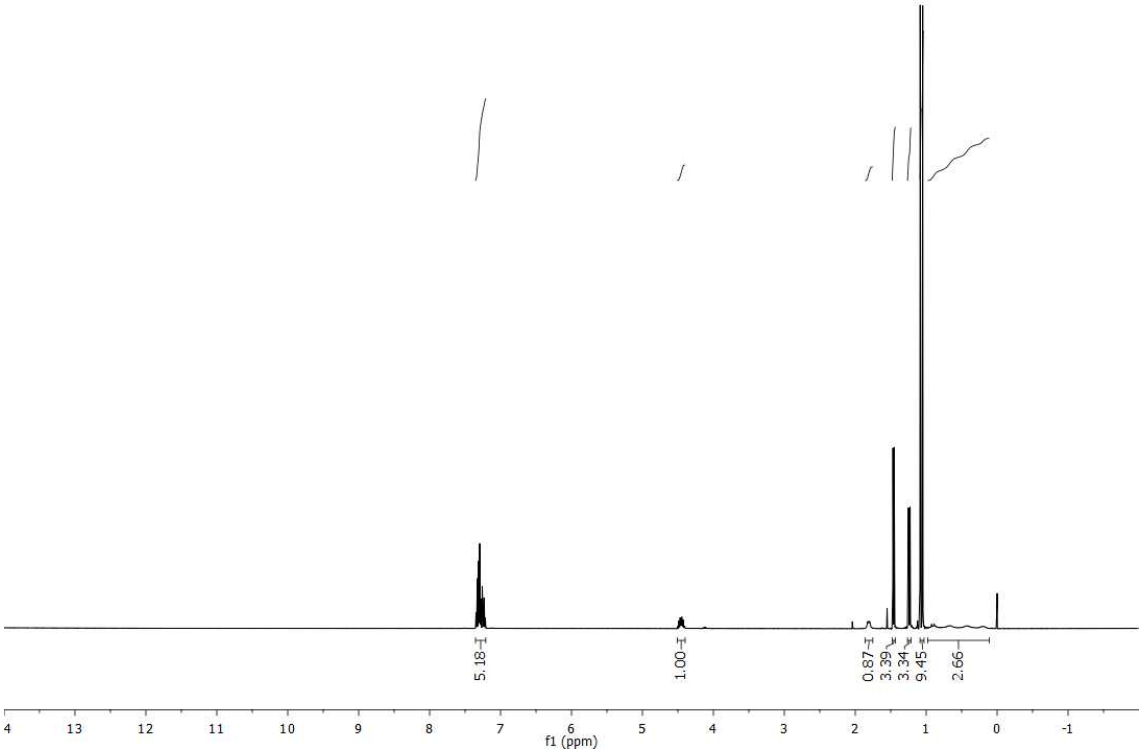
^{13}C NMR (101 MHz, $CDCl_3$)



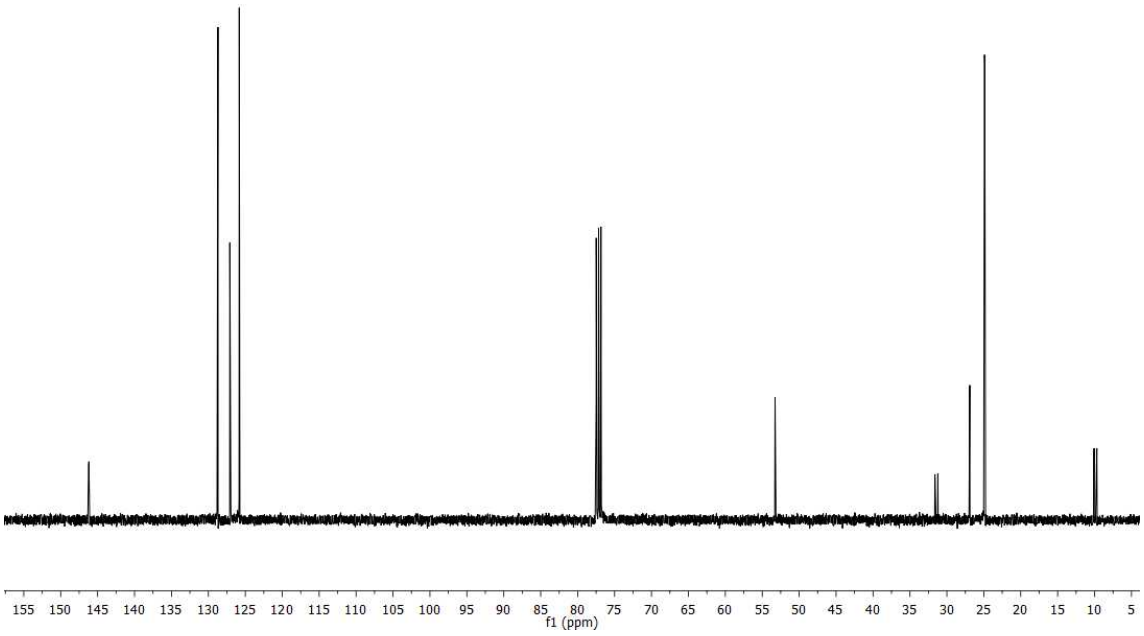
^{1}H NMR (400 MHz, $CDCl_3$)



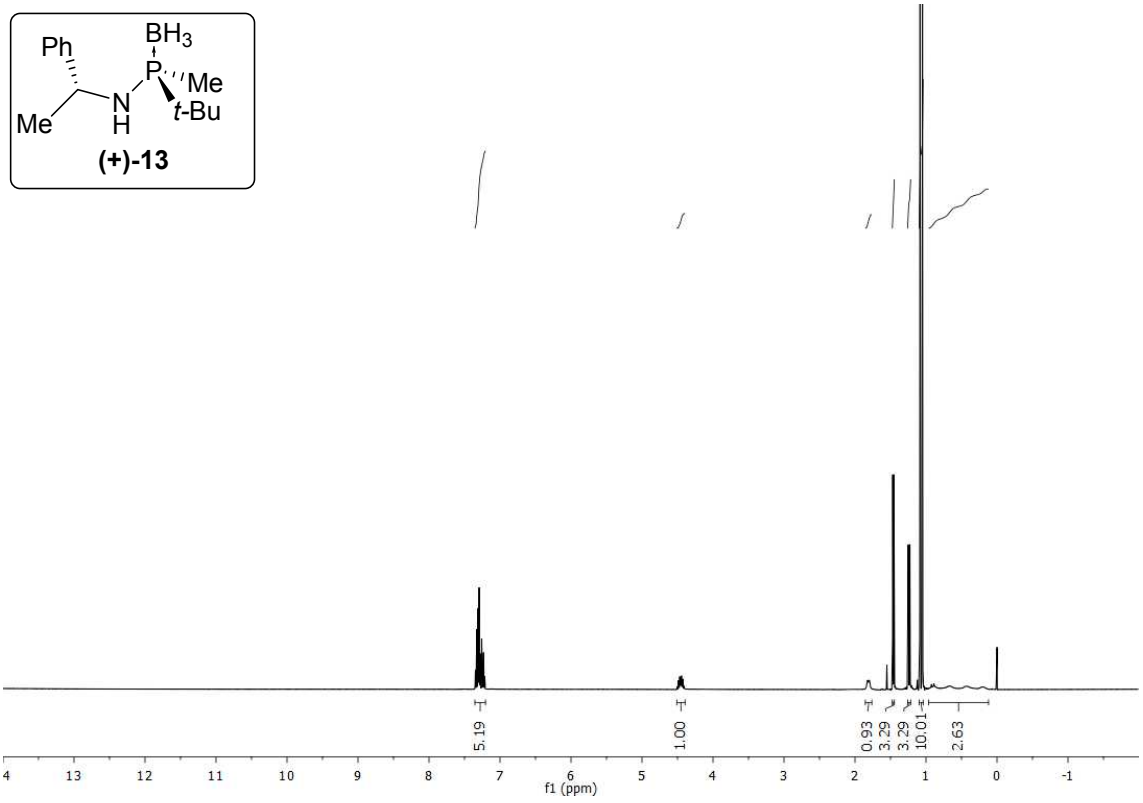
(-)-10



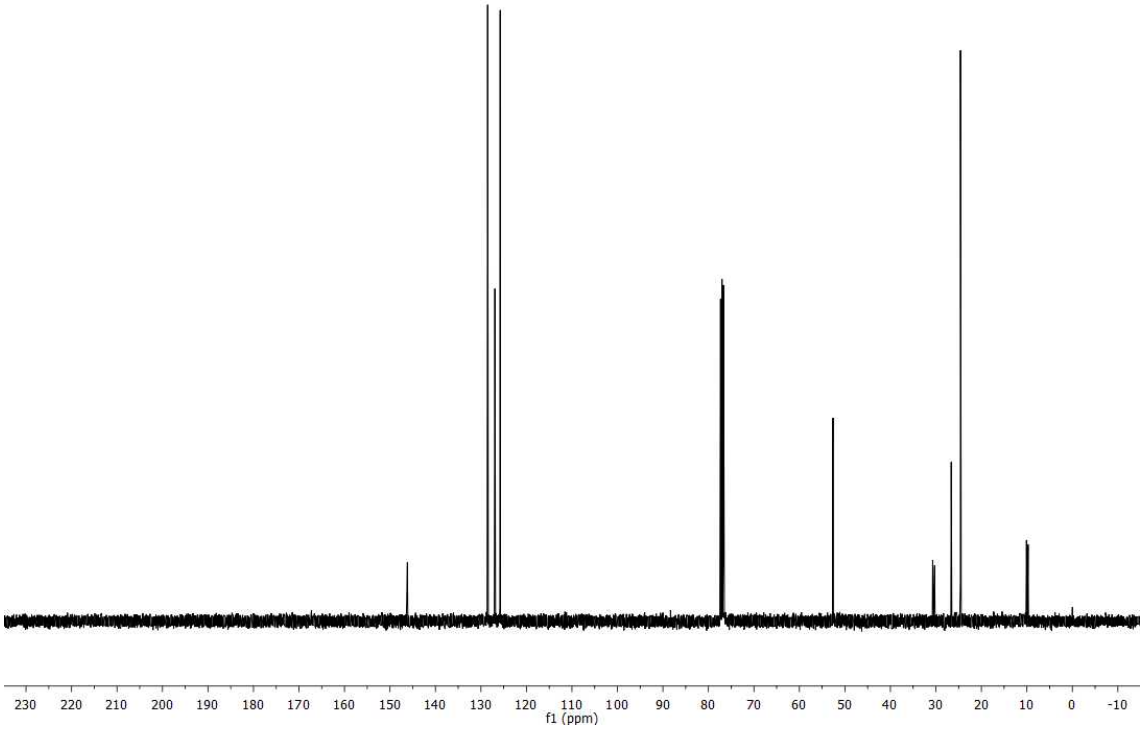
^{13}C NMR (101 MHz, $CDCl_3$)



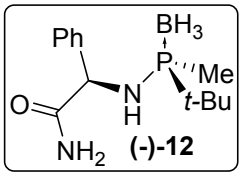
^{1}H NMR (400 MHz, $CDCl_3$)



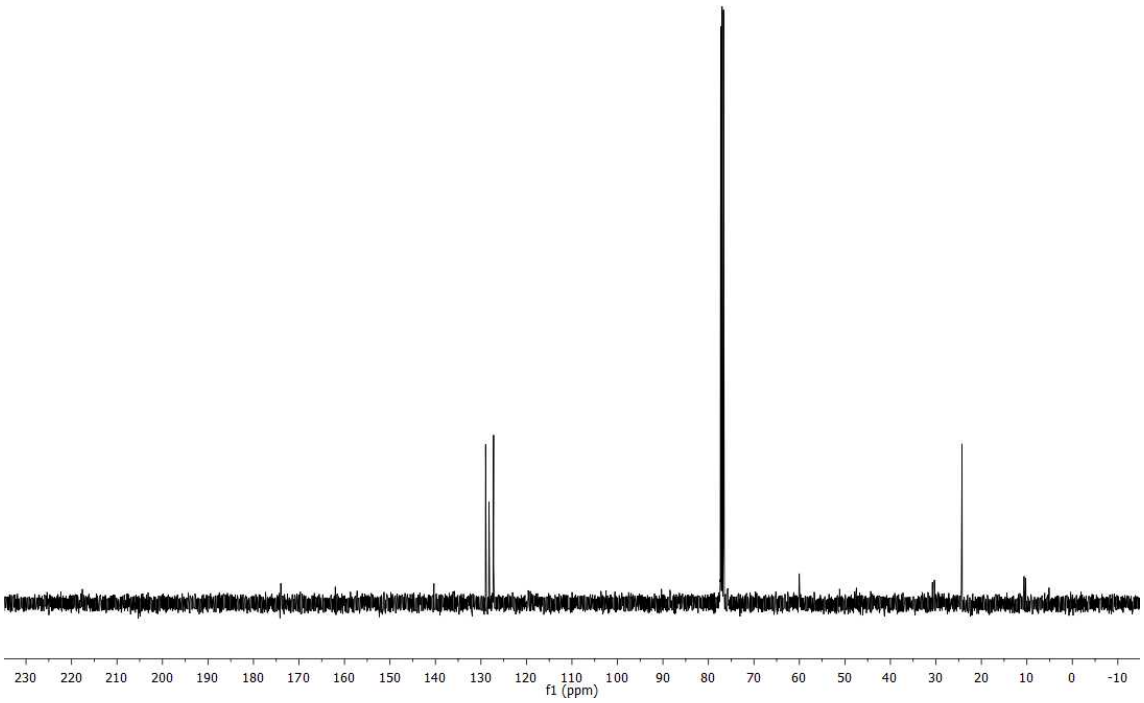
^{13}C NMR (101 MHz, $CDCl_3$)



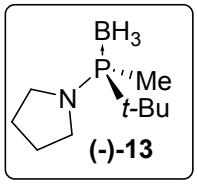
^{1}H NMR (400 MHz, $CDCl_3$)



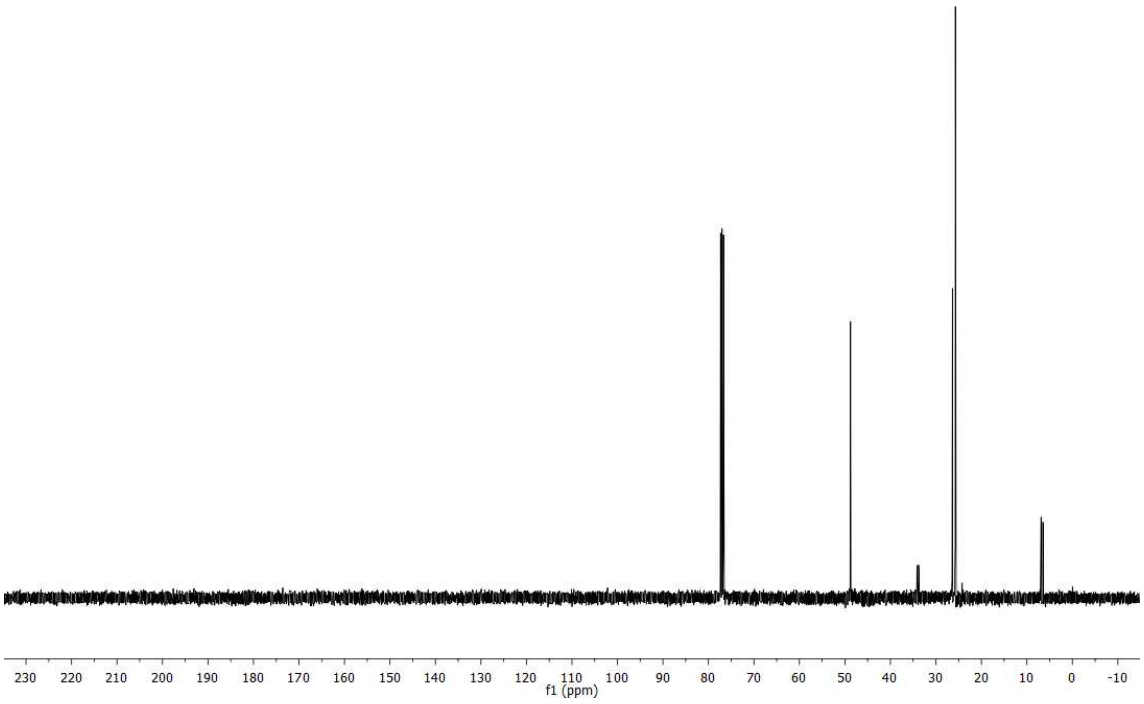
^{13}C NMR (101 MHz, $CDCl_3$)



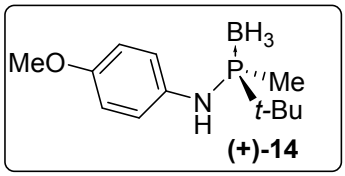
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)

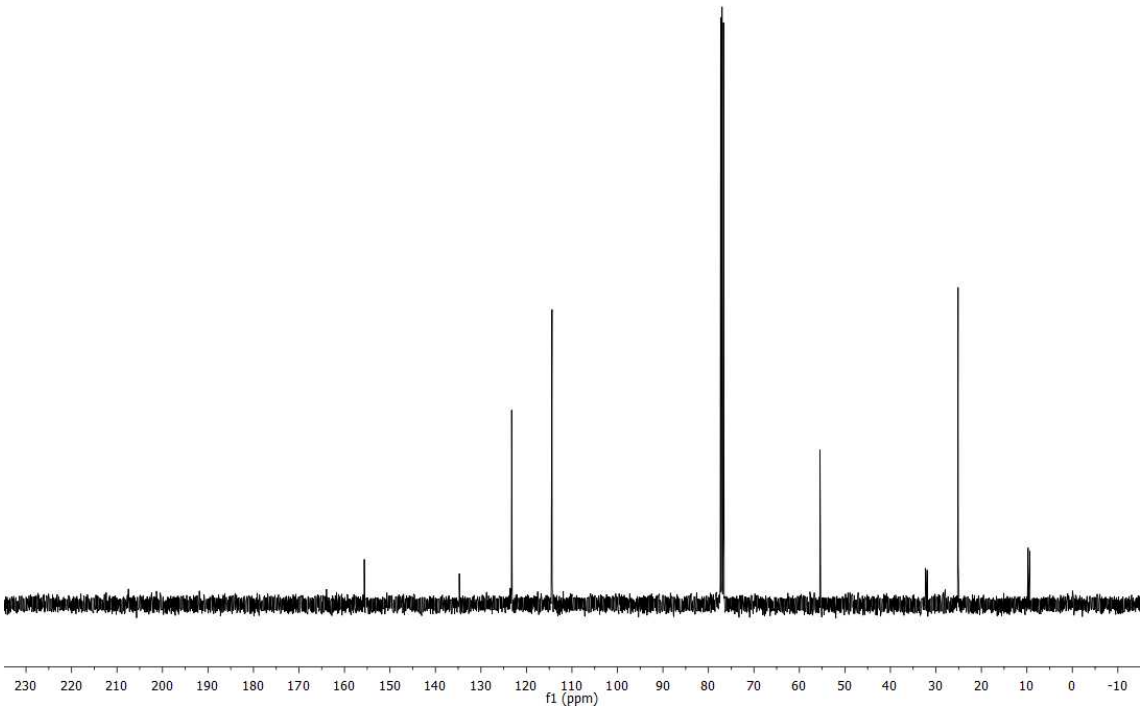


^{1}H NMR (400 MHz, $CDCl_3$)

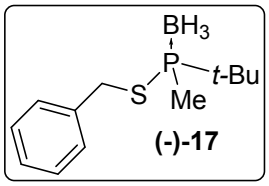


(+)-14

^{13}C NMR (101 MHz, $CDCl_3$)

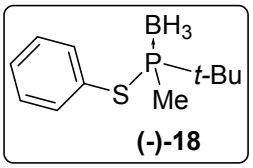


^{1}H NMR (400 MHz, $CDCl_3$)



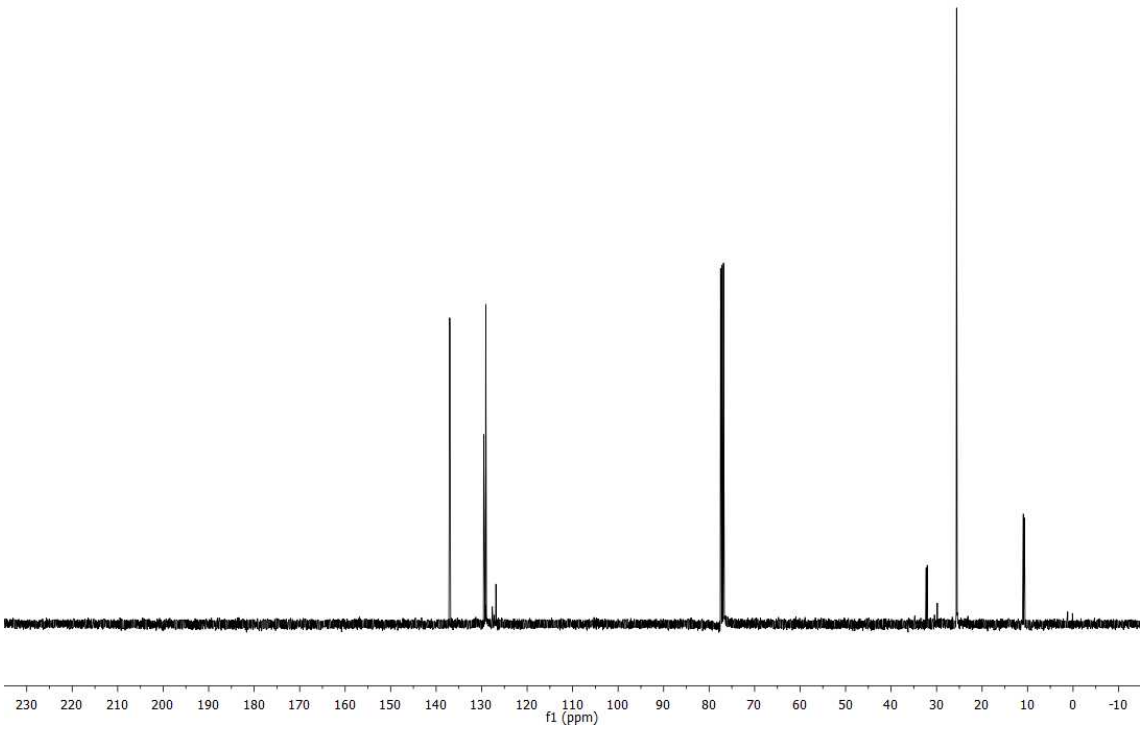
^{13}C NMR (101 MHz, $CDCl_3$)

^{1}H NMR (400 MHz, $CDCl_3$)

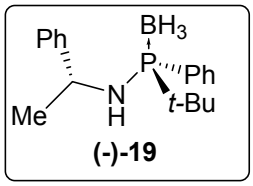


(-)-18

^{13}C NMR (101 MHz, $CDCl_3$)

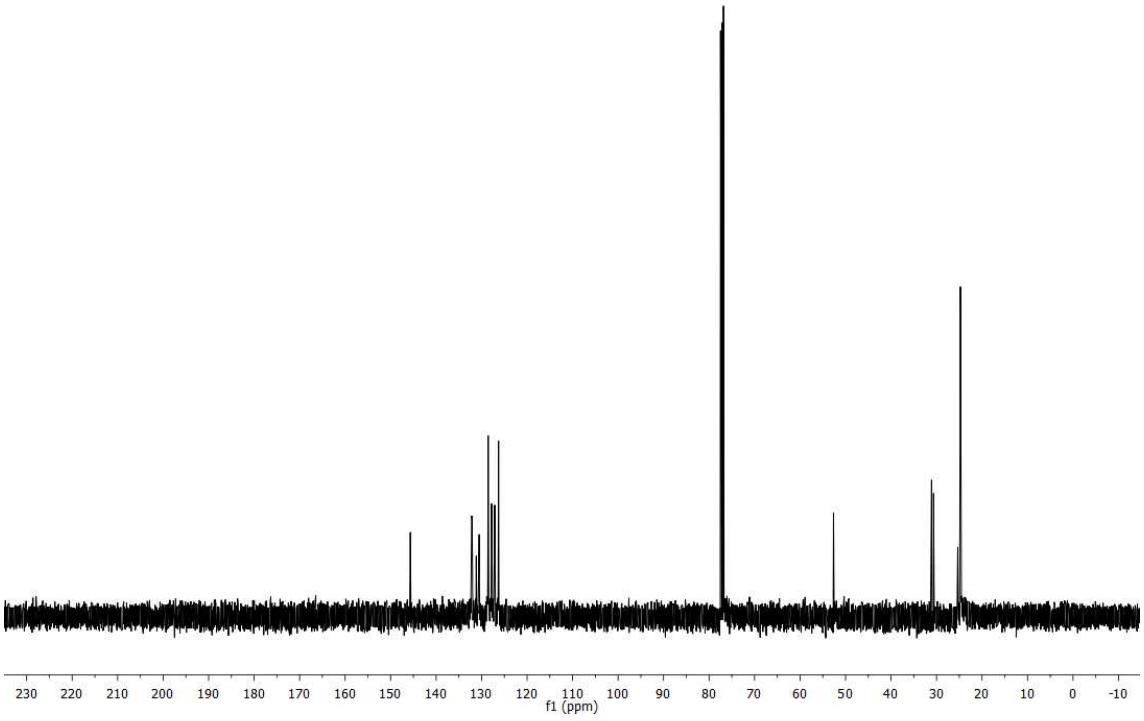


^{1}H NMR (400 MHz, $CDCl_3$)

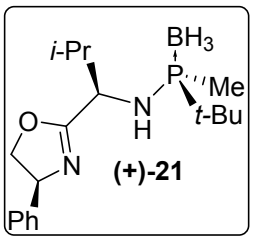


(-)-19

^{13}C NMR (101 MHz, $CDCl_3$)

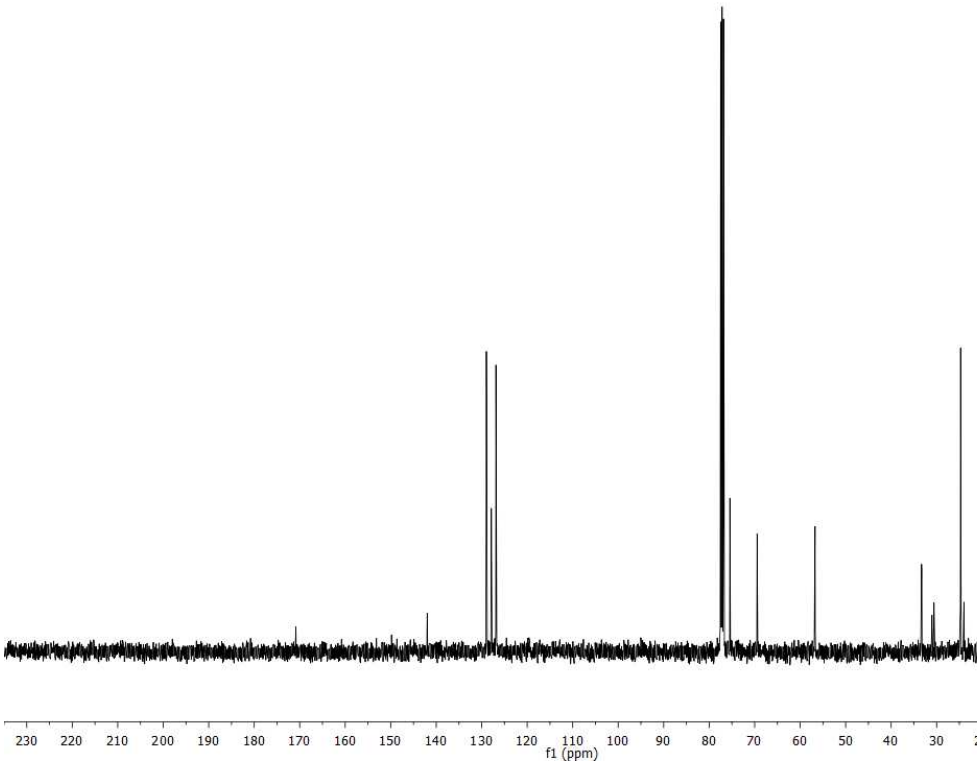


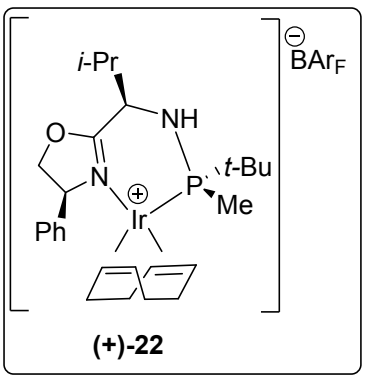
^{1}H NMR (400 MHz, $CDCl_3$)



(+)-21

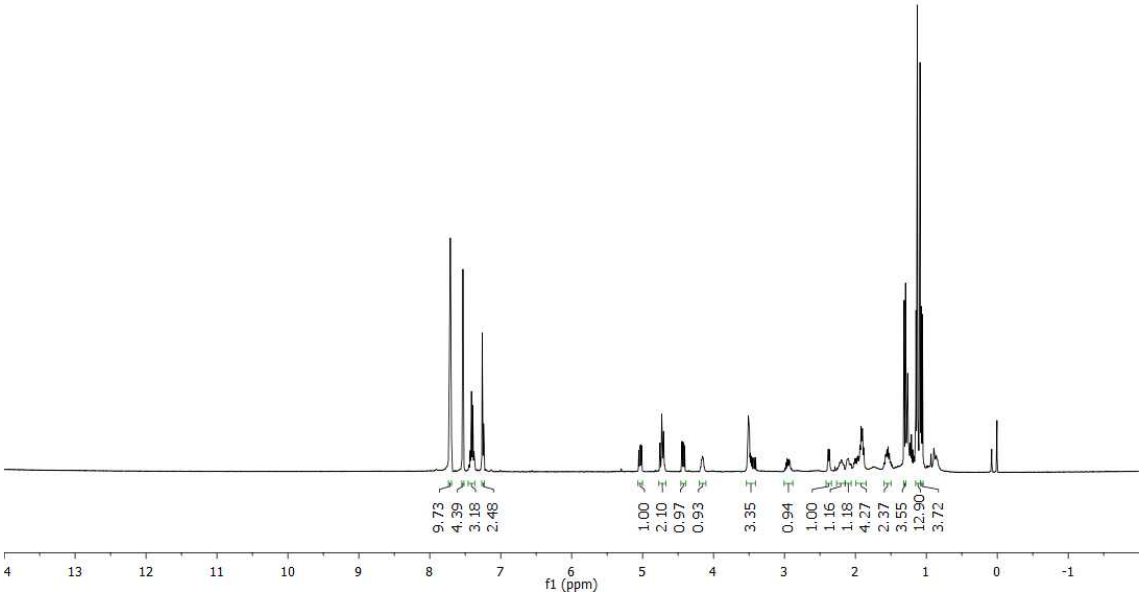
^{13}C NMR (101 MHz, $CDCl_3$)



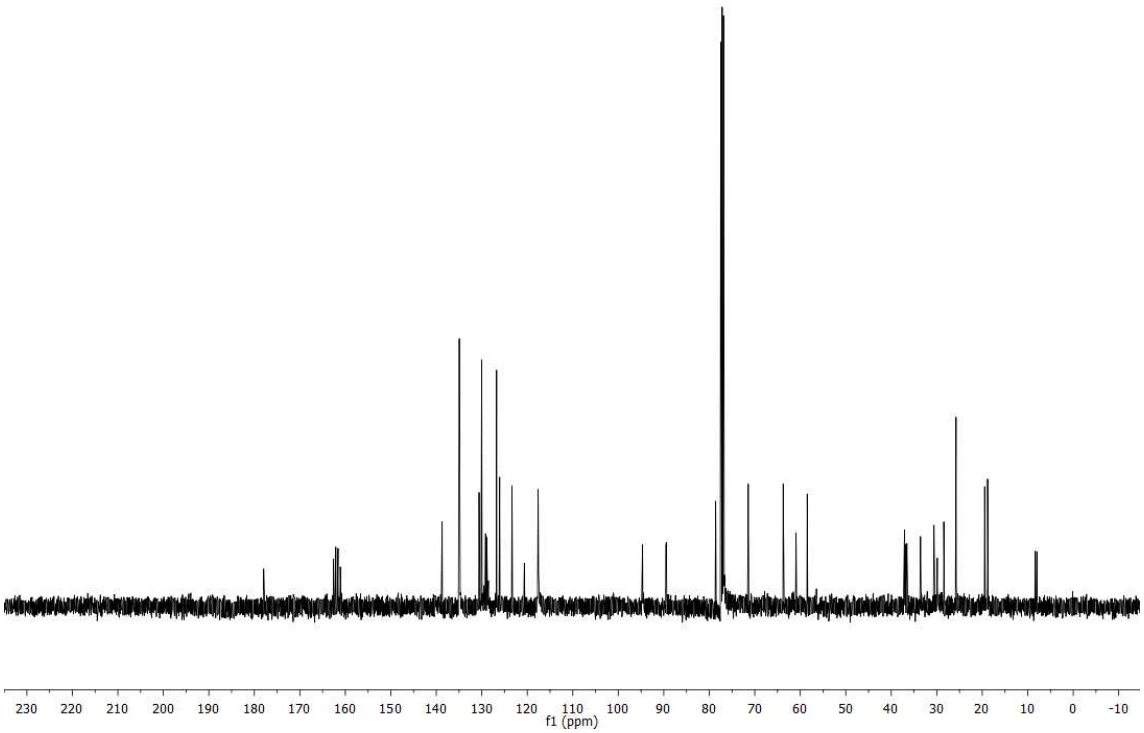


(+)-22

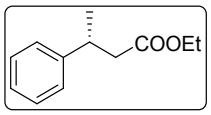
^{1}H NMR (400 MHz, $CDCl_3$)



^{13}C NMR (101 MHz, $CDCl_3$)



^{1}H NMR (400 MHz, $CDCl_3$)



HPLC, Racemic sample

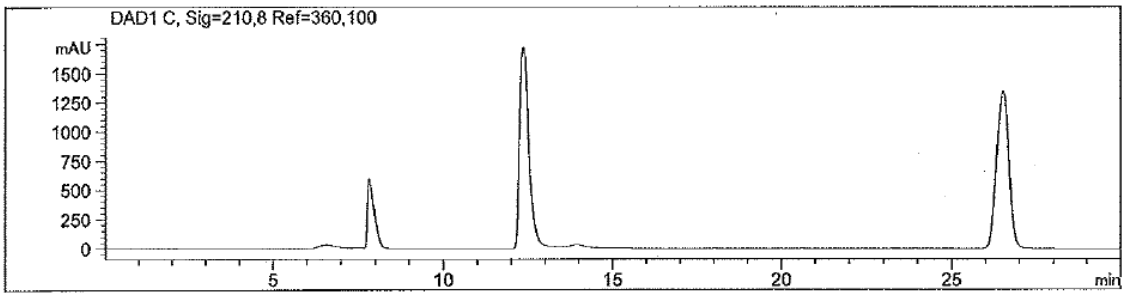
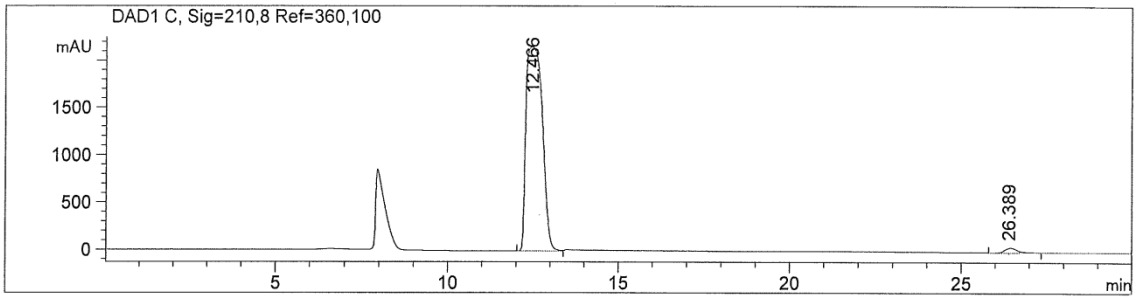
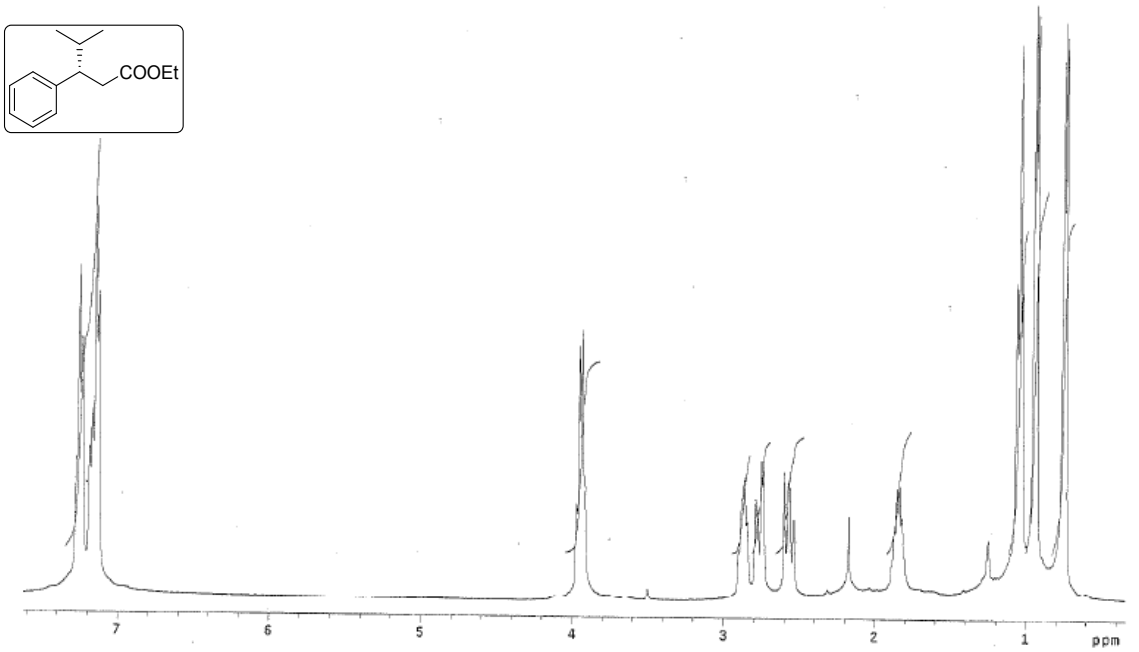


Table 3, entry 1



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.466	BV	0.5523	7.23319e4	2162.12012	97.3750
2	26.389	BB	0.3914	1958.07683	58.28409	2.6250

^{1}H NMR (400 MHz, $CDCl_3$)



HPLC, Racemic sample

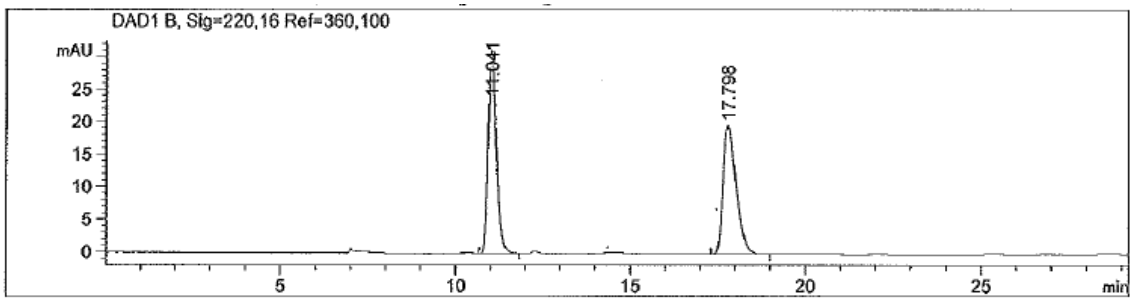
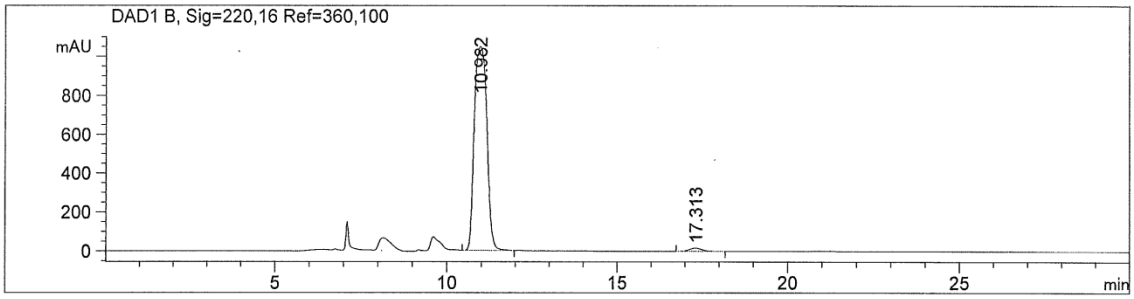
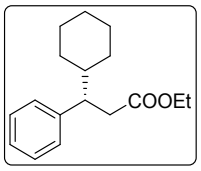


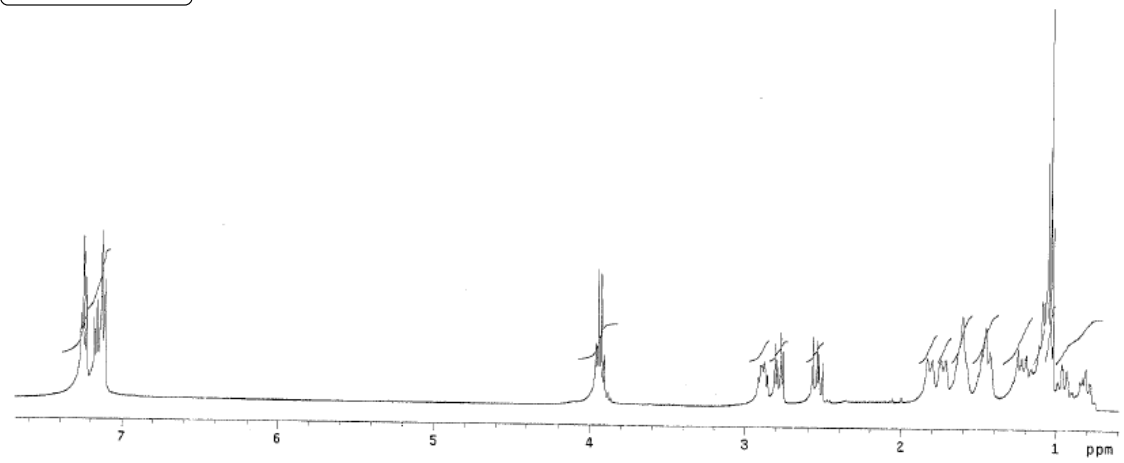
Table 3, entry 2



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.982	BB	0.4178	2.67081e4	1046.33557	98.5447
2	17.313	BB	0.3836	394.42252	16.10957	1.4553

^{1}H NMR (400 MHz, $CDCl_3$)





HPLC, Racemic sample

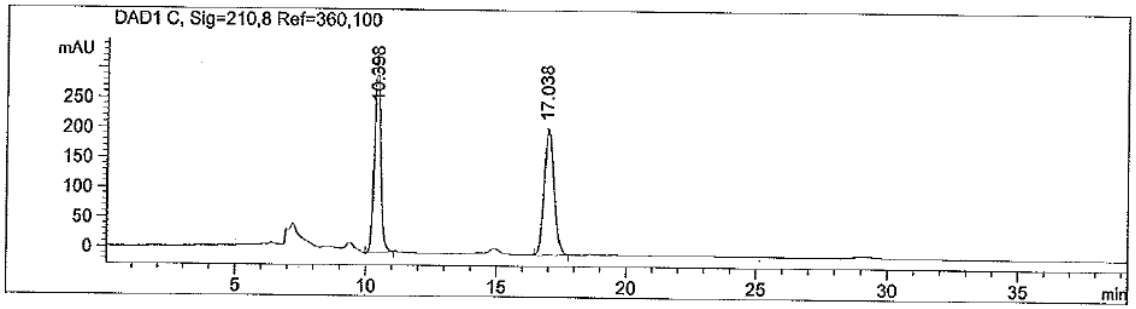
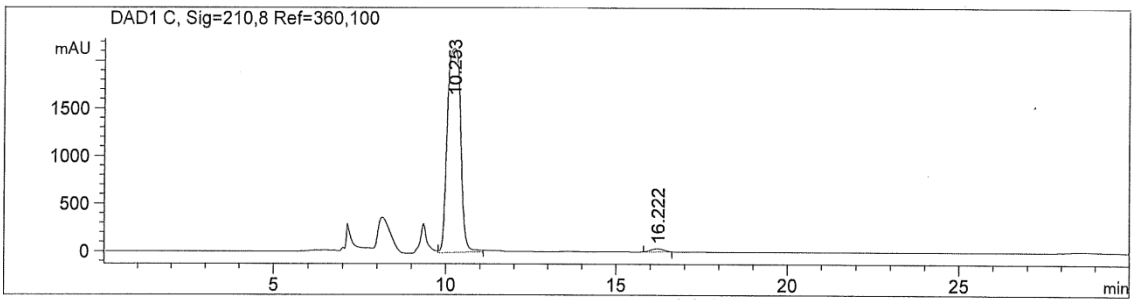
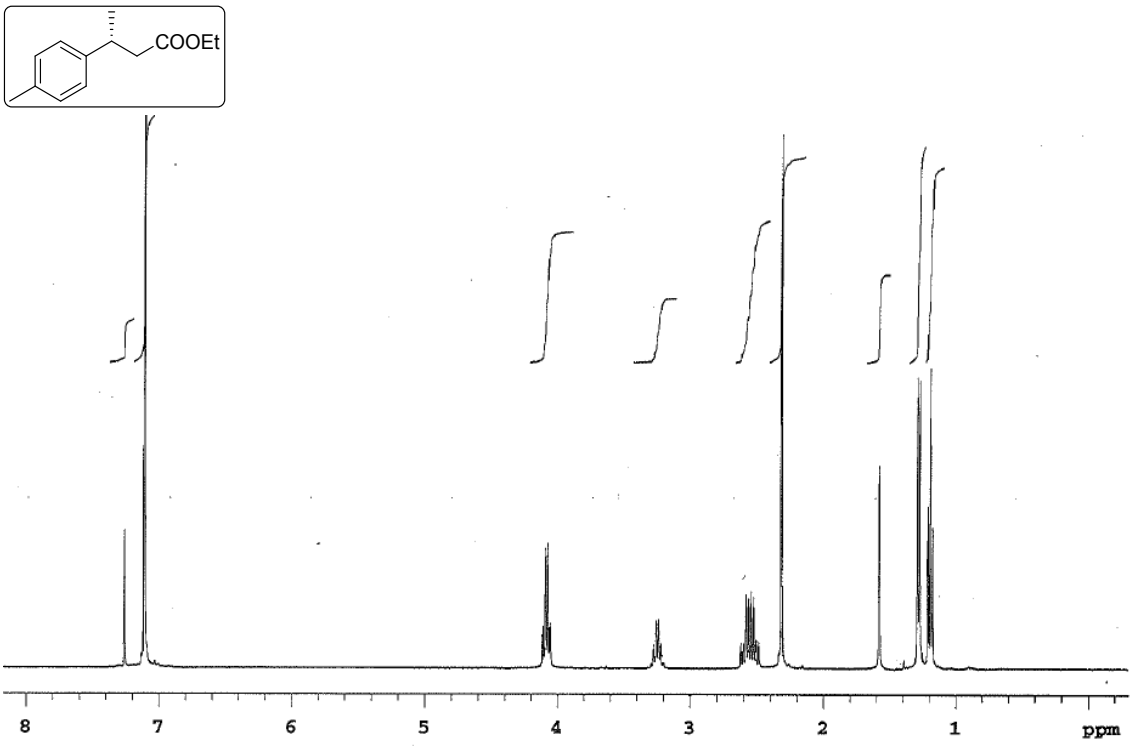


Table 3, entry 3



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.253	VV	0.4410	5.80911e4	2138.13599	98.5588
2	16.222	MM	0.4398	849.43115	32.18805	1.4412

^{1}H NMR (400 MHz, $CDCl_3$)



HPLC, Racemic sample

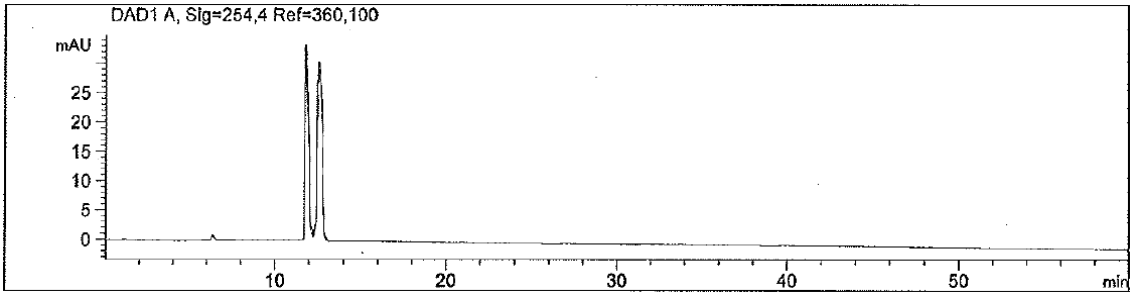
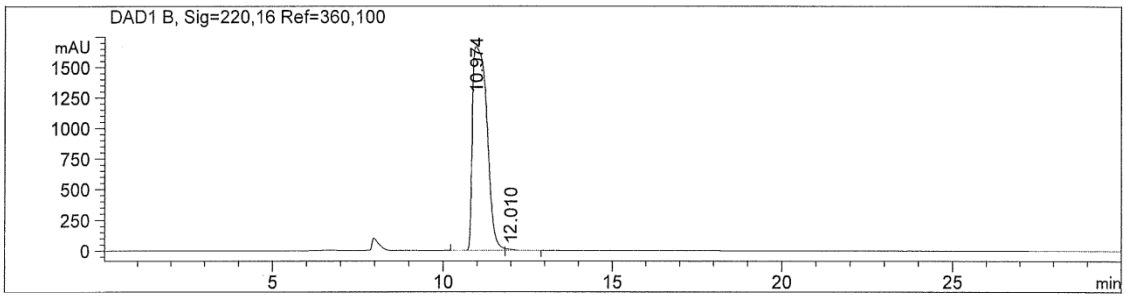
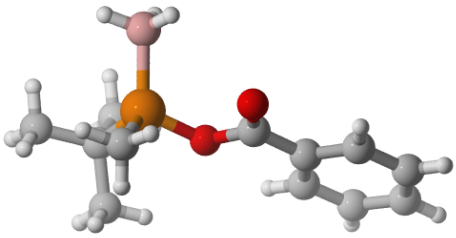


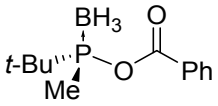
Table 3, entry 4



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.974	BB	0.4895	4.99645e4	1668.06482	99.9718
2	12.010	MM	0.0717	14.11242	3.27870	0.0282

Crystal data and structure refinement for mixed anhydride between 3a and benzoic acid





Empirical formula	C12 H20 B O2 P	
Formula weight	238.06	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	P2(1)2(1)2(1)	
Unit cell dimensions	a = 10.5960(9) Å	α= 90.00 °.
	b = 11.0390(9) Å	β = 90.00 °.
	c = 11.6053(9) Å	γ = 90.00 °.
Volume	1357.46(19) Å^3	
Z	4	
Density (calculated)	1.165 Mg/m^3	
Absorption coefficient	0.186 mm^{-1}	
F(000)	512	
Crystal size	0.15 x 0.02 x 0.02 mm^3	
Theta range for data collection	2.55 to 33.10 °.	
Index ranges	-13 <=h<=15 ,-15 <=k<=16 ,-16 <=l<=15	
Reflections collected	9755	
Independent reflections	4313 [R(int) = 0.0142]	
Completeness to theta =33.10 °	86.7%	
Absorption correction	Empirical	
Max. and min. transmission	0.9963 and 0.9726	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4313 / 0 / 150	
Goodness-of-fit on F^2	1.264	
Final R indices [I>2sigma(I)]	R1 = 0.0271 , wR2 = 0.0795	
R indices (all data)	R1 = 0.0316 , wR2 = 0.0955	
Flack parameter	x =-0.03(6)	
Largest diff. peak and hole	0.492 and -0.604 e.Å^{-3}	

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