General Synthesis of P-Stereogenic Compounds: The Menthyl Phosphinate Approach.

Olivier Berger and Jean-Luc Montchamp*

Department of Chemistry, Box 298860, Texas Christian University, Fort Worth, Texas 76129

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General Chemistry:

¹H NMR spectra were recorded on a 300 or 400-MHz spectrometer. Chemical shift for ¹H NMR spectra (in parts per million) relative to internal tetramethylsilane (Me₄Si, δ = 0.00 ppm) with CDCl₃. ¹³C NMR spectra were recorded at 75.5 or 101 MHz. Chemical shifts for ¹³C NMR spectra are reported (in parts per million) relative to CDCl₃ (δ = 77.0 ppm). ³¹P NMR spectra were recorded at 121.5 or 162 MHz, and chemical shifts reported (in parts per million) relative to external 85% phosphoric acid (δ = 0.0 ppm). TLC plates were visualized by UV or immersion in permanganate potassium (3 g KMnO4, 20 g K2CO3, 5 mL 5% NaOHaq and 300 mL of water) followed by heating.

Reagent and solvents:

All starting materials were purchased from commercial sources and used as received. The solvents were distilled under N_2 and dried according to standard procedures (THF from Na/ benzophenone ketyl; DMF from MgSO₄; CH₃CN, toluene and dichloromethane from CaH₂).

³¹P NMR Yield Measurements:

The NMR yields are determined by integration of all the resonances in the ^{31}P spectra, an approach which is valid if no phosphorus-containing gas (i.e. PH₃) evolves, or if the precipitate in a heterogeneous mixture does not contain phosphorus. The yields determined by NMR are generally accurate within ~10% of the value indicated, and are reproducible.

(R_p)-Menthyl (hydroxymethyl)-H-phosphinate 2:1



Paraformaldehyde (9.91 g, 330 mmol, 1.1 equiv) and hypophosphorous acid (39.6 g, 300 mmol, 1 equiv, 50% w.t. in water) were introduced in a round bottom flask and the reaction mixture was stirred for 24h at 75°C. The reaction mixture was cooled down to rt and the oil obtained was diluted in toluene (300 mL). L-menthol (46.9 g, 300 mmol, 1 equiv) was added and the reaction mixture was stirred for 24h at reflux under N₂ in a flask equipped with a Dean-Stark trap. The solvent was then removed under vacuum and the residue obtained was dissolved in a mixture of diethyl ether/hexane (50 mL: 200 mL) and the flask was placed in the fridge for 4h (2°C). The solid obtained was filtered and solubilized in diethyl ether (200 mL) and placed in the fridge (2°C) for 3h to afford the product as white needles (6.54 g, 10%, >99% de). Mp = 101-102°C; ³¹P NMR (162 MHz, CDCl₃): δ = 34.9 (dm, *J* = 542 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.16 (dm, *J* = 542 Hz, 1H), 4.04-4.23 (m, 2H), 3.82-4.00 (m, 2H), 2.14-2.24 (m, 1H), 1.98-2.11 (m, 1H), 2.04 (dquint., *J* = 2.4 and 7.0 Hz, 1H), 1.62-1.73 (m, 2H), 1.34-1.52 (m, 2H), 1.24 (q, *J* = 12.0 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 6H), 0.76-1.10 (m, 2H), 0.80 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 79.3 (d, *J*_{POC} = 8.3 Hz), 59.7 (d, *J*_{PC} = 111 Hz), 48.5 (d, *J*_{POCC} = 5.5 Hz), 43.3, 33.8, 31.5, 25.6, 22.9, 21.8, 20.8, 15.7; HRMS (ESI+) m/z calcd for C₁₁H₂₃O₃P ([M+Na]⁺) 257.1385, found 257.1423; [α]_{D²²} = -61.4° (chloroform).

(S_p)-Menthyl (hydroxymethyl)phenylphosphinate 3:1



To a solution of phenylphosphinic acid (42.6 g, 300 mmol, 1 equiv) in toluene (300 mL) was added L-menthol (46.9 g, 300 mmol, 1 equiv). The reaction mixture was stirred at reflux for 24 h under N_2 in a

flask equipped with a Dean-stark trap. After cooling down the reaction to rt, paraformaldehyde (9.01 g, 300 mmol, 1 equiv) was added and the reaction mixture was stirred at reflux for 24 h under N₂. The solvent was then removed under vacuum and the crude obtained was recrystallized at rt in diethyl ether (200 mL) to afford the product as colorless crystals (24.2 g, 26%, 97% de). Mp = 138-139°C; ³¹P NMR (162 MHz, CDCl₃): δ = 37.2 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.77-7.87 (m, 2H), 7.52-7.60 (m, 1H), 7.42-7.51 (m, 2H), 4.29-4.43 (m, 2H), 3.93-4.10 (m, 2H), 2.26 (dquint, *J* = 2.6 and 7.0 Hz, 1H), 1.80-1.91 (m, 1H), 1.57-1.73 (m, 2H), 1.26-1.47 (m, 2H), 0.96 (d, *J* = 7.1 Hz, 3H), 0.74-1.13 (m, 3H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.78 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 132.3 (d, *J*_{PCCCC} = 2.8 Hz), 131.7 (d, *J*_{PCCC} = 9.9 Hz, 2C), 130.6 (d, *J*_{PC} = 123 Hz), 128.3 (d, *J*_{PCC} = 12.1 Hz, 2C), 77.1 (d, *J*_{POCC} = 8.3 Hz), 60.2 (d, *J*_{PC} = 117 Hz), 48.7 (d, *J*_{POCC} = 6.1 Hz), 43.2, 34.0, 31.4, 25.5, 22.8, 21.9, 21.1, 15.7; HRMS (EI+) m/z calcd for C₁₆H₂₈O₃P ([M+H]⁺) 311.1776, found 311.1766; [α]_D²² = -46.7° (chloroform).

(R_p)-Menthyl cinnamyl(hydroxymethyl)phosphinate 4:¹



To a solution of cinnamylphosphinic acid (9.11 g, 50 mmol, 1 equiv) in toluene (100 mL) was added L-menthol (7.81 g, 50 mmol, 1 equiv). The reaction mixture was stirred at reflux for 24 h under N₂ in a flask equipped with a Dean-Stark trap. After cooling down the reaction to rt, paraformaldehyde (1.5 g, 50 mmol, 1 equiv) was added and the reaction mixture was stirred at reflux for 24 h under N₂. The solvent was then removed under vacuum and the crude obtained was recrystallized at rt in a mixture ethyl acetate/diethyl ether (30 mL : 150 mL) to afford the product as a white solid (5.6 g, 32%, > 99% de). Mp = 145-146°C; ³¹P NMR (162 MHz, CDCl₃): δ = 48.8 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.19-7.39 (m, 5H), 6.55 (dd, *J* = 4.7 and 15.8 Hz, 1H), 6.12-6.27 (m, 1H), 4.20-4.34 (m, 1H), 3.87 (s, 2H), 3.64 (s, 1H), 2.85 (dd, *J* = 7.6 and 17.6 Hz, 2H), 2.06-2.22 (m, 2H), 1.60-1.71 (m, 2H), 1.28-1.54 (m, 2H), 1.15 (q, *J* = 11.7 Hz, 1H), 0.74-1.07 (m, 2H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 136.8 (d, *J*_{PCCCC} = 3.3 Hz), 135.0 (d, *J*_{PCC} = 12.2 Hz), 128.5 (2C), 127.5, 126.2 (d, *J*_{PCCCC} = 1.7 Hz, 2C), 118.4 (d, *J*_{PCCCC} = 10.5 Hz), 76.7 (d, *J*_{POC} = 8.3 Hz), 59.5 (d, *J*_{PC} = 106 Hz), 48.6 (d, *J*_{POCCC} = 5.6 Hz, 2C), 43.5, 34.0, 31.6 (d, *J*_{PC} = 87.3 Hz), 31.5, 25.5, 22.7, 22.1, 21.0, 15.5; HRMS (EI+) m/z calcd for C₂₀H₃₁O₃P ([M]*) 350.2011, found 350.2012; [α]_D²⁴ = -51.6° (chloroform).

(R_p)-Menthyl (hydroxymethyl)phenylphosphinate 3:1



In a round bottom flask was introduced (R_p) -2 (117 mg, 0.5 mmol, 1 equiv), Pd(OAc)₂ (2.3 mg, 0.01 mmol, 2.0 mol %), xantphos (6.4 mg, 0.011 mmol, 2.2 mol %), a mixture of DMF and 1,2-dimethoxyethane (2.25 mL : 0.25 mL), DIPEA (0.11 mL, 0.65 mmol, 1.3 equiv) and bromobenzene (0.05 mL, 0.5 mmol, 1 equiv). The reaction mixture was stirred under a flow of N₂ for 10 minutes and then heated at 115°C for 24 hours before cooling down to rt. The solvent was then removed under vacuum and the resulting residue was dissolved in ethyl acetate and washed with a saturated aqueous solution of NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 5:5 to 3:7) to afford the product as a white solid (106 mg, 68%, de = 95%). Mp

= 103-105°C; ³¹P NMR (162 MHz, CDCl₃): δ = 37.4 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.91 (m, 2H), 7.45-7.62 (m, 3H), 4.09-4.21 (m, 1H), 4.02-4.08 (m, 2H), 2.77-2.87 (m, 1H), 2.29-2.39 (m, 1H), 1.90-2.05 (m, 1H), 1.58-1.69 (m, 3H), 1.22-1.50 (m, 2H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.76-1.02 (m, 2H), 0.47 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 132.3 (d, *J*_{PCCCC} = 2.7 Hz), 131.8 (d, *J*_{PCCC} = 9.9 Hz, 2C), 129.4 (d, *J*_{PC} = 124 Hz), 128.4 (d, *J*_{PCC} = 12.1 Hz, 2C), 77.4 (d, *J*_{POC} = 8.3 Hz), 60.4 (d, *J*_{PCC} = 115 Hz), 48.6 (d, *J*_{POCC} = 6.0 Hz), 43.6, 34.0, 31.5, 25.4, 22.6, 22.0, 21.0, 15.2; HRMS (EI+) m/z calcd for C₁₇H₂₇O₃P ([M+H]⁺) 311.1776, found 311.1773; [α]_D²² = -37.9° (chloroform).

(R_p)-Menthyl (hydroxymethyl)-1-naphtylphosphinate 5:1



In a round bottom flask was introduced (R_p) -2 (117 mg, 0.5 mmol, 1 equiv), Pd(OAc)₂ (2.3 mg, 0.01 mmol, 2.0 mol %), xantphos (6.4 mg, 0.011 mmol, 2.2 mol %), a mixture of DMF and 1,2dimethoxyethane (2.25 mL : 0.25 mL), DIPEA (0.11 mL, 0.65 mmol, 1.3 equiv) and 1bromonaphthalene (0.06 mL, 0.5 mmol, 1 equiv). The reaction mixture was stirred under a flow of N_2 for 10 minutes and then heated at 115°C for 24 hours before cooling down to rt. The solvent was then removed under vacuum and the resulting residue was dissolved in ethyl acetate and washed with a saturated aqueous solution of NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 5:5 to 0:10) to afford the product as a white solid (152 mg, 84%, 94% de). Mp = 102-103°C; ³¹P NMR (162 MHz, CDCl₃): δ = 38.6 (s); ¹H NMR (400 MHz, CDCl₃): δ = 8.54-8.60 (m, 1H), 8.20-8.30 (m, 1H), 8.03-8.10 (m, 1H), 7.88-7.96 (m, 1H), 7.52-7.64 (m, 3H), 4.29-4.43 (m, 1H), 4.08-4.27 (m, 2H), 2.35-2.44 (m, 1H), 1.88-2.00 (m, 1H), 1.59-1.74 (m, 3H), 1.35-1.54 (m, 3H), 0.96 (d, J = 6.2 Hz, 3H), 0.84-1.04 (m, 2H), 0.74 (d, J = 7.0 Hz, 3H), 0.44 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, $CDCl_3$): $\delta = 134.3$ (d, $I_{PCCC} = 7.7$ Hz), 133.6 (d, $I_{PCCC} = 9.4$ Hz), 133.5 (d, $I_{PCCC} = 2.7$ Hz), 133.0 (d, $I_{PCC} = 2.7$ Hz), 133.0 (d, 11.6 Hz), 129.0, 127.3, 126.2, 126.2 (d, J_{PCCC} = 3.3 Hz), 126.1 (d, J_{PC} = 121 Hz), 124.7 (d, J_{PCC} = 13.8 Hz), 78.0 (d, J_{POC} = 8.3 Hz), 61.8 (d, J_{PC} = 111 Hz), 48.7 (d, J_{POCC} = 5.0 Hz), 43.6, 34.0, 31.7, 25.4, 22.7, 22.1, 20.9, 15.2; HRMS (EI+) m/z calcd for $C_{21}H_{29}O_3P$ ([M]+) 360.1854, found 360.1860; $[\alpha]_D^{22} = -52.3^\circ$ (chloroform).

(R_p)-Menthyl (hydroxymethyl)p-anisylphosphinate 6:¹



In a round bottom flask was introduced (R_p) -2 (117 mg, 0.5 mmol, 1 equiv), Pd(OAc)₂ (2.3 mg, 0.01 mmol, 2.0 mol %), xantphos (6.4 mg, 0.011 mmol, 2.2 mol %), a mixture of DMF and 1,2-dimethoxyethane (2.25 mL : 0.25 mL), DIPEA (0.11 mL, 0.65 mmol, 1.3 equiv) and 4-bromoanisole (0.06 mL, 0.5 mmol, 1 equiv). The reaction mixture was stirred under a flow of N₂ for 10 minutes and then heated at 115°C for 24 hours before cooling down to rt. The solvent was then removed under vacuum and the resulting residue was dissolved in ethyl acetate and washed with a saturated aqueous solution of NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and

concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 5:5 to 0:10) to afford the product as a white solid (90 mg, 53%, 81% de). Mp = 110-112°C; ³¹P NMR (162 MHz, CDCl₃): δ = 37.8 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.74-7.84 (m, 2H), 6.96-7.03 (m, 2H), 4.05-4.18 (m, 1H), 3.96-4.05 (m, 2H), 3.87 (s, 3H), 2.60-2.71 (m, 1H), 2.29-2.39 (m, 1H), 2.01 (dquint, *J* = 2.6 and 7.3 Hz, 1H), 1.58-1.69 (m, 3H), 1.20-1.48 (m, 2H), 0.93 (d, *J* = 6.5 Hz, 3H), 0.87 (d, *J* = 6.7 Hz, 3H), 0.76-1.02 (m, 2H), 0.51 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 162.8 (d, *J*_{PCCCC} = 2.8 Hz), 133.7 (d, *J*_{PCCC} = 11.1 Hz, 2C), 120.5 (d, *J*_{PCC} = 131 Hz), 114.0 (d, *J*_{PCC} = 13.2 Hz, 2C), 77.2 (d, *J*_{POC} = 7.7 Hz), 60.5 (d, *J*_{PC} = 117 Hz), 55.3, 48.7 (d, *J*_{POCC} = 6.0 Hz), 43.6, 34.0, 31.5, 25.4, 22.7, 22.0, 21.0, 15.3; HRMS (EI+) m/z calcd for C₁₈H₂₉O₄P ([M]⁺) 340.1803, found 340.1801; [α]_D²⁴ = -68.3° (chloroform).

(R_p)-Menthyl cinnamyl(hydroxymethyl)phosphinate 4:¹



To a solution of (R_p)-2 (468 mg, 2 mmol, 1 equiv, > 99% de) in *tert*-amyl alcohol (10 mL) was added Pd₂dba₃ (18.3 mg, 0.02 mmol, 1 mol%), xantphos (23.2 mg, 0.04 mmol, 2 mol%) and cinnamyl alcohol (0.26 mL, 2 mmol, 1 equiv). The reaction mixture was stirred at reflux for 20 h under N₂ in a flask equipped with a Dean-Stark trap. After cooling down the reaction to rt, the solvent was removed under vacuum and the residue obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 90:10) to afford the product as a white solid (681 mg, 97%, > 99% de). Mp = 145-146°C; ³¹P NMR (162 MHz, CDCl₃): δ = 48.8 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.19-7.39 (m, 5H), 6.55 (dd, *J* = 4.7 and 15.8 Hz, 1H), 6.12-6.27 (m, 1H), 4.20-4.34 (m, 1H), 3.87 (s, 2H), 3.64 (s, 1H), 2.85 (dd, *J* = 7.6 and 17.6 Hz, 2H), 2.06-2.22 (m, 2H), 1.60-1.71 (m, 2H), 1.28-1.54 (m, 2H), 1.15 (q, *J* = 11.7 Hz, 1H), 0.74-1.07 (m, 2H), 0.91 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 6.8 Hz, 3H), 0.77 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 136.8 (d, *J*_{PCCC} = 3.3 Hz), 135.0 (d, *J*_{PCC} = 12.2 Hz), 128.5 (2C), 127.5, 126.2 (d, *J*_{PCCCC} = 1.7 Hz, 2C), 118.4 (d, *J*_{PCCC} = 10.5 Hz), 76.7 (d, *J*_{POC} = 8.3 Hz), 59.5 (d, *J*_{PC} = 106 Hz), 48.6 (d, *J*_{POCC} = 5.6 Hz, 2C), 43.5, 34.0, 31.6 (d, *J*_{PC} = 87.3 Hz), 31.5, 25.5, 22.7, 22.1, 21.0, 15.5; HRMS (EI+) m/z calcd for C₂₀H₃₁O₃P ([M]⁺) 350.2011, found 350.2012; [α]_D²⁴ = -51.6° (chloroform).

(R_p)-Menthyl (acetoxymethyl)phenylphosphinate 3a:²



To a solution of (R_p) -2 (703 mg, 3 mmol, 1 equiv, >99% de) in dichloromethane (15 mL) at 0°C under N₂ was added pyridine (0.30 mL, 3.75 mmol, 1.25 equiv) and acetic anhydride (0.34 mL, 3.6 mmol, 1.2 equiv). The ice-bath was removed and the reaction mixture was stirred for 16h at rt. The solvent was removed under vacuum and the residue obtained was solubilized in ethyl acetate. The organic layer was washed with NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a white solid (829 mg, 100%, 94% de). ³¹P NMR (162 MHz, CDCl₃): δ = 26.8 (dm, *J* = 567 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.14 (dt, *J* = 1.8 and 567 Hz, 1H), 4.09-4.21 (m, 2H), 3.94-4.05 (m, 1H), 2.01-2.08 (m, 1H), 1.95 (s, 3H), 1.83-1.92 (m, 1H), 1.47-1.55 (m, 2H), 1.20-1.36 (m, 2H), 1.10 (q, *J* = 11.1 Hz, 1H), 0.79-0.92 (m, 1H), 0.60-0.79 (m, 1H), 0.76 (d, *J* = 7.1 Hz, 3H), 0.75 (d, *J* = 6.4 Hz, 3H), 0.63 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 170.0 (d, *J*_{PCOC} = 6.5 Hz),

79.6 (d, J_{POC} = 7.8 Hz), 60.0 (d, J_{PC} = 113 Hz), 48.4 (d, J_{POCC} = 6.1 Hz), 43.2, 33.6, 31.4, 25.5, 22.8, 21.7, 20.7, 20.1, 15.6.

To a suspension of Mn(OAc)₂ (8.7 mg, 0.05 mmol, 5 mol%), MnO₂ (261 mg, 3 mmol, 3 equiv.), sodium acetate (246 mg, 3 mmol, 3 equiv.) and benzene (1.8 mL, 20 mmol, 20 equiv.) in acetic acid (2.5 mL) at 70°C under N₂ was added a solution of (R_p) -7 (276 mg, 1 mmol, 1 equiv, 94% de) in acetic acid (2.5 mL) over 2 hours via a syringe pump. The reaction mixture was then stirred for an additional 2h at 70°C under N₂. Ethyl acetate (~ 30 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~40 mL) were added. The biphasic suspension was stirred vigorously for 5 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of $Na_2S_2O_4$ 0.2M saturated with $NaHCO_3$ (~40 mL), a saturated aqueous solution of NaHCO₃ (\sim 40 mL) and brine (\sim 40 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 98:2 to 94:6) to afford the product as a yellow oil (183 mg, 52%, de = 94%). ³¹P NMR (162 MHz, CDCl₃): δ = 31.8 (s, 97%); ¹H NMR (400 MHz, CDCl₃): δ = 7.72-7.81 (m, 2H), 7.47-7.54 (m, 1H), 7.37-7.45 (m, 2H), 4.41 (dm, J = 43.8 Hz, 2H), 4.07-4.17 (m, 1H), 2.17-2.26 (m, 1H), 1.95 (s, 3H), 1.87-1.98 (m, 1H), 1.51-1.60 (m, 2H), 1.27-1.41 (m, 2H), 1.21 (q, J = 11.4 Hz, 1H), 0.69-0.92 (m, 2H), 0.84 (d, J = 6.4 Hz, 3H), 0.77 (d, J = 7.0 Hz, 3H), 0.44 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 169.8$ (d, $J_{PCOC} = 8.3$ Hz), 132.7 (d, JPCCCC = 2.5 Hz), 131.7 (d, JPCCC = 9.9 Hz, 2C), 129.2 (d, JPC = 131 Hz), 128.4 (d, JPCC = 13.0 Hz, 2C), 77.8 (d, JPOC = 7.5 Hz), 60.6 (d, JPC = 120 Hz), 48.6 (d, JPOCC = 6.3 Hz), 43.5, 33.9, 31.5, 25.4, 22.7, 21.9, 21.0, 20.4, 15.3; HRMS (CI+, methane) m/z calcd for C19H30O4P ([M+H]+) 353.1882, found 353.1873; $[\alpha]_D^{27} = -78.2^{\circ}$ (chloroform).

(R_p)-Menthyl (hydroxylmethyl)phenylphosphinate 3b:¹



To a solution of (R_p) -3a (150 mg, 0.43 mmol, 1 equiv) in methanol (2 mL) was added potassium carbonate (6 mg, 0.043 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and then the residue was solubilized in EtOAc (20 mL). Water (20 mL) and NaHSO₄ were added until the pH was around 1. The aqueous layer was saturated with NaCl and the 2 layers were separated. The organic layer was washed with saturated NaHCO₃ (20 mL) and brine (20 mL), dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a white solid (123 mg, 92%, 94% de). Mp = 103-105°C; ³¹P NMR (121.47 MHz, CDCl₃): δ = 37.4 (s); ¹H NMR (300 MHz, CDCl₃): δ = 7.80-7.91 (m, 2H), 7.45-7.62 (m, 3H), 4.09-4.21 (m, 1H), 4.02-4.08 (m, 2H), 2.77-2.87 (m, 1H), 2.29-2.39 (m, 1H), 1.90-2.05 (m, 1H), 1.58-1.69 (m, 3H), 1.22-1.50 (m, 2H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.76-1.02 (m, 2H), 0.47 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 132.4, 131.8 (d, *J*_{PCCC} = 9.7 Hz, 2C), 129.4 (d, *J*_{PCC} = 124 Hz), 128.4 (d, *J*_{PCC} = 12.4 Hz, 2C), 77.5 (d, *J*_{POC} = 7.3 Hz), 60.4 (d, *J*_{PCC} = 115 Hz), 48.7 (d, *J*_{POCC} = 5.7 Hz), 43.6, 34.0, 31.6, 25.4, 22.7, 22.0, 21.0, 15.3; [α]_D²⁷ = -69.0° (chloroform).

(R_p)-Menthyl (hydroxylmethyl)phenylphosphinate 3b:¹



To a suspension of $Mn(OAc)_2$ (313 mg, 1.81 mmol, 5 mol%), MnO_2 (9.45 g, 108.6 mmol, 3 equiv.), sodium acetate (8.91 g, 108.6 mmol, 3 equiv.) and benzene (32.4 mL, 362 mmol, 10 equiv.) in acetic acid (90 mL) at 70°C under N₂ was added a solution of $(S_p)/(R_p)$ -7 (10 g, 36.2 mmol, 1 equiv, ratio 54:46) in acetic acid (90 mL) over 2 hours *via* a syringe pump. The reaction mixture was then stirred for an additional 2 hours at 70°C under N₂. Ethyl acetate (~ 250 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 250 mL) were added. The suspension was stirred vigorously for 5 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 250 mL) and brine (~ 250 mL), dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a yellow oil (9.91 g, 78%). ³¹P NMR (162 MHz, CDCl₃): δ = 32.0 (s, 54%), 31.9 (s, 46%).

To a solution of $(S_p)/(R_p)$ -3a (8.42 g, 24 mmol, 1 equiv, ratio 54:46) in methanol (50 mL) was added potassium carbonate (330 mg, 2.4 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and then the residue was solubilized in EtOAc (100 mL). Water (100 mL) and NaHSO₄ were added until the pH was around 1. The aqueous layer was saturated with NaCl and the 2 layers were separated. The organic layer was washed with saturated NaHCO₃ (100 mL) and brine (100 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was precipitated in hexane to afford the product as a white solid (1.82 g, 24%, 95% de). Mp = 103-105°C; ³¹P NMR (121.47 MHz, CDCl₃): δ = 37.4 (s); ¹H NMR (300 MHz, CDCl₃): δ = 7.80-7.91 (m, 2H), 7.45-7.62 (m, 3H), 4.09-4.21 (m, 1H), 4.02-4.08 (m, 2H), 2.77-2.87 (m, 1H), 2.29-2.39 (m, 1H), 1.90-2.05 (m, 1H), 1.58-1.69 (m, 3H), 1.22-1.50 (m, 2H), 0.93 (d, *J* = 6.2 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H); 0.76-1.02 (m, 2H), 0.47 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 132.4, 131.8 (d, *J*_{PCCC} = 9.7 Hz, 2C), 129.4 (d, *J*_{PCC} = 124 Hz), 128.4 (d, *J*_{PCC} = 12.4 Hz, 2C), 77.5 (d, *J*_{PCC} = 7.3 Hz), 60.4 (d, *J*_{PC} = 115 Hz), 48.7 (d, *J*_{PCCC} = 5.7 Hz), 43.6, 34.0, 31.6, 25.4, 22.7, 22.0, 21.0, 15.3; [α]_D²⁷ = -69.0° (chloroform).

(R_p) -menthyl (acetoxymethyl) mesitylphosphinate 8a:²



To a solution of (R_p) -2 (703 mg, 3 mmol, 1 equiv, >99% de) in dichloromethane (15 mL) at 0°C under N₂ was added pyridine (0.30 mL, 3.75 mmol, 1.25 equiv) and acetic anhydride (0.34 mL, 3.6 mmol, 1.2 equiv). The ice-bath was removed and the reaction mixture was stirred for 16h at rt. The solvent was removed under vacuum and the residue obtained was solubilized in ethyl acetate. The organic layer was washed with NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a white solid (829 mg, 100%, 94% de). ³¹P NMR (162 MHz, CDCl₃): δ = 26.8 (dm, *J* = 567 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.14 (dt, *J* = 1.8 and 567 Hz, 1H), 4.09-4.21 (m, 2H), 3.94-4.05 (m, 1H), 2.01-2.08 (m, 1H), 1.95 (s, 3H), 1.83-1.92 (m, 1H), 1.47-1.55 (m, 2H), 1.20-1.36 (m, 2H), 1.10 (q, *J* = 11.1 Hz, 1H), 0.79-0.92 (m, 1H), 0.60-0.79 (m, 1H), 0.76 (d, *J* = 7.1 Hz, 3H), 0.75 (d, *J* = 6.4 Hz, 3H), 0.63 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 170.0 (d, *J*_{PCCC} = 6.5 Hz), 79.6 (d, *J*_{POCC} = 7.8 Hz), 60.0 (d, *J*_{PCC} = 113 Hz), 48.4 (d, *J*_{POCC} = 6.1 Hz), 43.2, 33.6, 31.4, 25.5, 22.8, 21.7, 20.7, 20.1, 15.6.

To a suspension of $Mn(OAc)_2$ (26 mg, 0.15 mmol, 5 mol%), MnO_2 (783 mg, 9 mmol, 3 equiv.), sodium acetate (738 mg, 9 mmol, 3 equiv.) and mesitylene (2.1 mL, 15 mmol, 5 equiv.) in acetic acid (7.5 mL) at 70°C under N₂ was added a solution of (R_p)-7 (828 mg, 3 mmol, 1 equiv, 94% de) in acetic acid (7.5 mL) over 2 h *via* a syringe pump. The reaction mixture was then stirred for an additional 2h at 70°C under N₂. Ethyl acetate (~ 50 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 50 mL) were added. The suspension was stirred vigorously for 10 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of

Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 50 mL), a saturated aqueous solution of NaHCO₃ (~ 50 mL) and brine (~ 50 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 95:5) to afford the product as a colorless oil (876 mg, 79%, 94% de). ³¹P NMR (162 MHz, CDCl₃): δ = 36.0 (s, 3%), 35.7 (s, 97%); ¹H NMR (400 MHz, CDCl₃): δ = 6.80 (d, *J* = 4.0 Hz, 2H), 4.31-4.47 (m, 1H), 4.35-4.40 (m, 2H), 2.54 (s, 6H), 2.18 (s, 3H), 2.06-2.13 (m, 1H), 1.91 (s, 3H), 1.82 (dquint, *J* = 1.8 and 6.8 Hz, 1H), 1.53-1.64 (m, 2H), 1.36-1.47 (m, 1H), 1.36-1.47 (m, 1H), 1.31 (t, *J* = 11.3 Hz, 1H), 1.20 (q, *J* = 11.6 Hz, 1H), 0.94 (dq, *J* = 2.6 and 12.6 Hz, 1H), 0.74-0.89 (m, 1H), 0.86 (d, *J* = 6.5 Hz, 3H), 0.73 (d, *J* = 7.0 Hz, 3H), 0.59 (d, *J* = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 169.8 (d, *J*_{PCCC} = 7.7 Hz), 143.3 (d, *J*_{PCCC} = 11.6 Hz, 2C), 141.9 (d, *J*_{PCCCC} = 2.8 Hz), 130.7 (d, *J*_{PCCC} = 13.5 Hz, 2C), 123.3 (d, *J*_{PCC} = 131 Hz), 76.8 (d, *J*_{POC} = 7.6 Hz), 62.4 (d, *J*_{PCC} = 110 Hz), 48.6 (d, *J*_{POCC} = 4.7 Hz), 43.6, 34.0, 31.6, 25.7, 23.3 (d, *J*_{PCCC} = 2.3 Hz, 2C), 22.8, 22.0, 20.9 (2C), 20.3, 15.4; HRMS (EI+) m/z calcd for C₂₂H₃₅O₄P ([M]+) 394.2273, found 394.2274.

(*R_p*)-Menthyl (hydroxymethyl)mesitylphosphinate 8b:



To a solution of (R_p) -8a (876 mg, 2.22 mmol, 1 equiv, 94% de) in methanol (10 mL) was added potassium carbonate (31 mg, 0.22 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and then the residue was solubilized in ethyl actate. Water and NaHSO₄ were added until the pH was around 1. The aqueous layer was saturated with NaCl and the 2 layers were separated. The organic layer was washed with saturated NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 90:10) to afford the product as a colorless oil (741 mg, 95%, 94% de). ³¹P NMR (162 MHz, CDCl₃): δ = 42.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 6.82 (s, 1H), 6.82 (s, 1H), 5.87 (s, 1H), 4.34-4.47 (m, 1H), 3.90-4.07 (m, 2H), 2.57 (s, 6H), 2.25-2.33 (m, 1H), 2.21 (s, 3H), 1.82-1.94 (m, 1H), 1.57-1.68 (m, 2H), 1.39-1.53 (m, 1H), 1.19-1.37 (m, 2H), 0.71-1.04 (m, 2H), 0.92 (d, *J* = 6.2 Hz, 3H), 0.77 (d, *J* = 6.9 Hz, 3H), 0.62 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 143.3 (d, *J*_{PCC} = 11.2 Hz, 2C), 141.6 (d, *J*_{PCCC} = 2.5 Hz), 130.6 (d, *J*_{PCCC} = 12.7 Hz, 2C), 123.5 (d, *J*_{PC} = 122 Hz), 76.7 (d, *J*_{POC} = 7.8 Hz), 62.4 (d, *J*_{PC} = 107 Hz), 48.8 (d, *J*_{POCC} = 4.4 Hz), 43.6, 34.2, 31.7, 25.7, 23.4 (d, *J*_{PCCC} = 1.8 Hz, 2C), 22.9, 22.2, 21.0, 21.0, 15.4; HRMS (EI+) m/z calcd for C₂₀H₃₃O₃P ([M]⁺) 352.2167, found 352.2164; [α]_D²⁵ = -21.1⁰ (chloroform).

$(R_p)/(S_p)$ Menthyl (hydroxylmethyl)mesitylphosphinate 8b:



To a suspension of $Mn(OAc)_2$ (467 mg, 2.7 mmol, 5 mol%), MnO_2 (13.92 g, 160 mmol, 3 equiv.), sodium acetate (13.12 g, 160 mmol, 3 equiv.) and mesitylene (37 mL, 266 mmol, 5 equiv.) in acetic acid (90 mL) at 70°C under N₂ was added a solution of $(S_p)/(R_p)$ -7 (14.7 g, 53.2 mmol, 1 equiv, ratio

54:46) in acetic acid (90 mL) over 2 hours *via* a syringe pump. The reaction mixture was then stirred for an additional 2h at 70°C under N₂. Ethyl acetate (~ 250 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 250 mL) were added. The suspension was stirred vigorously for 5 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 250 mL) acetate with NaHCO₃ (~ 250 mL), a saturated aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 250 mL) and brine (~ 250 mL), dried over MgSO₄, filtered and concentrated under vacuum.

The crude obtained was solubilized in methanol (100 mL) and potassium carbonate (733 mg, 5.3 mmol, 0.1 equiv.) was added and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and then the residue was solubilized in EtOAc (150 mL). Water (150 mL) and NaHSO₄ were added until the pH was around 1. The aqueous layer was saturated with NaCl and the 2 layers were separated. The organic layer was washed with saturated NaHCO₃ (150 mL) and brine (150 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was precipitated in hexane to afford the product as a white solid (11.3 g, 60% on 3 steps). ³¹P NMR (121.5 MHz, CDCl₃): δ = 41.5 (50%, s), 41.0 (50%, s); ¹H NMR (300 MHz, CDCl₃): δ = 6.92 (s, 2H), 4.32-4.49 (m, 1H), 3.77-4.12 (m, 3H), 2.64 (s, 3H), 2.61 (s, 3H), 2.21-2.34 (m, 4H), 1.84-1.95 (m, 1H), 1.61-1.73 (m, 2H), 1.22-1.54 (m, 3H), 0.76-1.13 (m, 9.5H), 0.64 (d, *J* = 6.7 Hz, 1.5H).

(*R_p*)/(*S_p*) Menthyl-[4-(acetamido)phenyl](hydroxylmethyl)phosphinate 9b:



To a suspension of Mn(OAc)₂ (385 mg, 2.23 mmol, 5 mol%), MnO₂ (11.62 g, 133.5 mmol, 3 equiv.), sodium acetate (10.95 g, 133.5 mmol, 3 equiv.) and acetanilide (30.1 g, 222.6 mmol, 5 equiv.) in acetic acid (90 mL) at 70°C under N₂ was added a solution of $(S_p)/(R_p)$ -7 (12.3 g, 44.5 mmol, 1 equiv) in acetic acid (90 mL) over 2 hours *via* a syringe pump. The reaction mixture was then stirred for an additional 2h at 70°C under N₂. Ethyl acetate (~ 200 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 200 mL) were added. The suspension was stirred vigorously for 5 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 200 mL) and brine (~ 200 mL), dried over MgSO₄, filtered and concentrated under vacuum.

The crude obtained was solubilized in methanol (100 mL) and potassium carbonate (622 mg, 4.5 mmol, 0.1 equiv.) was added and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and then the residue was solubilized in EtOAc (150 mL). Water (150 mL) and NaHSO₄ were added until the pH was around 1. The aqueous layer was saturated with NaCl and the 2 layers were separated. The organic layer was washed with saturated NaHCO₃ (150 mL) and brine (150 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was precipitated in hexane to afford the product as a white solid (6.0 g, 37% on 3 steps). ³¹P NMR (121.5 MHz, CDCl₃): δ = 37.8 (48%, s), 37.2 (52%, s); ¹H NMR (300 MHz, CDCl₃): δ = 9.44 (s, 1H), 7.31-7.48 (m, 2H), 7.13-7.26 (m, 2H), 4.16-4.33 (m, 1.5H), 3.95-4.12 (m, 1.5H), 2.11-2.24 (m, 1H), 2.15 (s, 3H), 1.93-2.05 (m, 1H), 1.75-1.83 (m, 1H), 1.58-1.72 (m, 2H), 1.22-1.44 (m, 2H), 0.95-1.08 (m, 1H), 0.98 (d, *J* = 7.0 Hz, 1.5H), 0.93 (d, *J* = 6.4 Hz, 1.5H), 0.86 (d, *J* = 6.8 Hz, 1.5H), 0.85 (d, *J* = 6.9 Hz, 1.5H), 0.80 (d, *J* = 6.5 Hz, 1.5H), 0.55 (d, *J* = 6.9 Hz, 1.5H).

(R_p)-Menthyl (hydroxymethyl)methylphosphinate 10:1



To a solution of (R_p) -2 (234 mg, 1 mmol, 1 equiv, 98% de) in dichloromethane (10 mL) at 0°C and under N₂ was added bis(trimethylsily)acetamide (0.49 mL, 2 mmol, 2 equiv) followed by iodomethane (0.062 mL, 1 mmol, 1 equiv). The ice-bath was removed and the reaction mixture was then stirred for 20 h at rt. Methanol was added (0.08 mL, 2 mmol, 2 equiv) and the reaction mixture was concentrated under vacuum. The residue obtained was dissolved in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 10:0 to 7:3) to afford the product as a white solid (188 mg, 76%, > 99% de). Mp = 82-83°C; ³¹P NMR (162 MHz, CDCl₃): δ = 51.9 (s); ¹H NMR (400 MHz, CDCl₃): δ = 4.15-4.28 (m, 1H), 3.73-3.90 (m, 2H), 3.07-3.16 (m, 1H), 2.08-2.18 (m, 1H), 2.06 (dquint, *J* = 2.3 and 7.0 Hz, 1H), 1.62-1.73 (m, 2H), 1.52 (d, *J* = 13.7 Hz, 3H), 1.40-1.58 (m, 1H), 1.24-1.38 (m, 1H), 1.15 (q, *J* = 11.1 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.78-1.08 (m, 2H), 0.82 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 76.2 (d, *J*_{POC} = 7.8 Hz), 60.6 (d, *J*_{PC} = 111 Hz), 48.4 (d, *J*_{POCC} = 5.5 Hz), 43.4, 33.9, 31.4, 25.6, 22.7, 21.9, 20.9, 15.6, 11.8 (d, *J*_{PC} = 91.2 Hz); HRMS (EI+) m/z calcd for C₁₂H₂₆O₃P ([M+H]⁺) 249.1620, found 249.1621; [α]_P²² = -60.6° (chloroform).

(R_p)-Menthyl allyl(hydroxymethyl)phosphinate 11:¹



To a solution of (R_p) -2 (117 mg, 0.5 mmol, 1 equiv, 98% de) in dichloromethane (5 mL) at 0°C and under N₂ was added bis(trimethylsily)acetamide (0.25 mL, 1 mmol, 2 equiv) followed by allyl bromide (0.09 mL, 1 mmol, 2 equiv). The ice-bath was removed and the reaction mixture was stirred for 36 h at rt. Methanol was added (0.04 mL, 1 mmol, 2 equiv) and the reaction mixture was then concentrated under vacuum. The residue obtained was dissolved in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 96:4) to afford the product as white solid (88 mg, 64%, 95% de). Mp = 69-71°C; ³¹P NMR (162 MHz, CDCl₃): δ = 48.4 (s); ¹H NMR (400 MHz, CDCl₃): δ = 5.74-5.93 (m, 1H), 5.19-5.32 (m, 2H), 4.18-4.32 (m, 1H), 3.81-3.89 (m, 2H), 3.53-3.64 (m, 1H), 2.64-2.77 (m, 2H), 2.06-2.18 (m, 2H), 1.61-1.72 (m, 2H), 1.40-1.54 (m, 1H), 1.24-1.39 (m, 1H), 1.15 (q, *J* = 11.5 Hz, 1H), 0.92 (d, *J* = 7.0 Hz, 6H), 0.78-1.08 (m, 2H), 0.81 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 127.2 (d, *J*_{PCCC} = 9.4 Hz), 120.3 (d, *J*_{PCC} = 12.7 Hz), 76.7 (d, *J*_{POCC} = 8.3 Hz), 59.1 (d, *J*_{PCC} = 107 Hz), 48.5 (d, *J*_{POCC} = 5.5 Hz), 43.4, 34.0, 32.4 (d, *J*_{PCC} = 86.8 Hz), 31.5, 25.5, 22.7, 22.0, 21.0, 15.6; HRMS (EI+) m/z calcd for C₁₄H₂₇O₃P ([M]⁺) 274.1698, found 274.1694; [α]_D²⁴ = -71.3° (chloroform).

(R_p)-Menthyl benzyl(hydroxymethyl)phosphinate 12:



To a solution of (R_p) -2 (1.17 g, 5 mmol, 1 equiv, 98% de) in dichloromethane (50 mL) was added at 0° C and under N₂ bis(trimethylsilyl)acetamide (2.45 mL, 10 mmol, 2 equiv) followed by benzylbromide (1.2 mL, 10 mmol, 2 equiv). The ice bath was removed and the reaction mixture was stirred for 12 h at rt. Methanol was then added (0.40 mL, 10 mmol, 2 equiv) and the mixture was concentrated under vacuum. The residue obtained was dissolved in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 98:2 to 90:10) to afford the product as a white solid (1.353 g, 84%, > 99% de). Mp = 133-134°C; ³¹P NMR (162 MHz, CDCl₃): δ = 47.1 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.22-7.36 (m, 5H), 4.35 (dt, J = 6.0 Hz, 1H), 4.16-4.26 (m, 1H), 3.71-3.86 (m, 2H), 3.17-3.32 (m, 2H), 2.02-2.09 (m, 1H), 1.85 (dquint., J = 2.5 and 7.0 Hz, 1H), 1.59-1.68 (m, 2H), 1.36-1.50 (m, 1H), 1.23-1.33 (m, 1H), 1.12 (q, J = 11.2 Hz, 1H), 0.97 (dq, J = 3.0 and 12.7 Hz, 1H), 0.76-0.93 (m, 1H), 0.90 (d, J = 6.6 Hz, 3H), 0.83 (d, J = 7.0 Hz, 3H), 0.67 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 131.3 (d, J_{PCC} = 7.9 Hz), 130.0 (d, JPCCC = 5.6 Hz, 2C), 128.5 (d, JPCCCC = 2.6 Hz, 2C), 126.7 (d, JPCCCC = 3.1 Hz), 76.6 (d, JPCC = 7.9 Hz), 59.2 (d, J_{PC} = 106 Hz), 48.6 (d, J_{POCC} = 5.3 Hz), 43.4, 34.1 (d, J_{PC} = 86.2 Hz), 34.0, 31.5, 25.3, 22.7, 22.1, 21.1, 15.4; HRMS (EI+) m/z calcd for C₁₈H₂₉O₃P ([M]⁺) 324.1854, found 324.1852; [α]_D²⁴ = -27.9° (chloroform).

(*R_p*)-Menthyl (hydroxymethyl)triphenylmethylphosphinate 13:



To a solution of (R_p) -2 (468 mg, 2 mmol, 1 equiv, 96% de) in dichloromethane (10 mL) was added at 0°C under N₂ bis(trimethylsily)acetamide (1.0 mL, 4 mmol, 2 equiv) followed by bromotriphenylmethane (1.29 g, 4 mmol, 2 equiv). The ice bath was removed and the reaction mixture was stirred for 12 h at rt. Methanol was then added (0.16 mL, 4 mmol, 2 equiv) and the mixture was concentrated under vacuum. The residue obtained was dissolved in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 95:5) to afford the product as a white solid (465 mg, 49%, 95% de). Mp = 157-158°C; ³¹P NMR (162 MHz, CDCl₃): δ = 47.7 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.43-7.55 (m, 6H), 7.22-7.35 (m, 9H), 4.27-4.47 (m, 2H), 3.75-3.88 (m, 1H), 3.44-3.55 (m, 1H), 2.18-2.27 (m, 1H), 1.48-1.67 (m, 3H), 1.34-1.45 (m, 1H), 1.03-1.19 (m, 2H), 0.76-1.01 (m, 2H), 0.90 (d, *J* = 6.3 Hz, 3H), 0.68 (d, *J* = 6.9 Hz, 3H), 0.64 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 141.3 (s, 3C), 130.9 (d, *J*_{PCCC} = 4.5 Hz, 6C), 128.0 (s, 6C), 127.0 (s, 3C), 78.4 (d, *J*_{PCCC} = 9.1 Hz), 63.3 (d, *J*_{PC} = 83.5 Hz), 60.6 (d, *J*_{PCC} = 92.9 Hz), 49.1 (d, *J*_{POCCC} = 5.3 Hz), 42.5, 34.0, 31.6, 24.5, 22.7, 22.2, 21.3, 15.8; HRMS (EI+) m/z calcd for C₃₀H₃₇O₃P ([M]⁺) 476.2480, found 476.2470; [α]_{P²⁵} = -9.9° (chloroform).

(R_p)-Menthyl (hydroxymethyl)methylphosphinate 10:¹



To a solution of (R_p) -2 (234 mg, 1 mmol, 1 equiv, 98% de) in tetrahydrofuran (5 mL) at -78°C and under N₂ was added a solution of LiHMDS 1.0M in tetrahydrofuran (2.0 mL, 2 mmol, 2 equiv). After 15 minutes of stirring, iodomethane (0.062 mL, 1 mmol, 1 equiv) was added at -78°C and then the reaction mixture was allowed to warm-up to room temperature over 1 hour. The mixture was then stirred for an additional 1 hour at rt. A saturated aqueous solution of NH₄Cl was added and the two layers were separated. The aqueous layer was extracted twice with dichloromethane. The combined organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 10:0 to 7:3) to afford the product as a white solid (202 mg, 81%, > 99% de). Mp = 82-83°C; ³¹P NMR (162 MHz, CDCl₃): δ = 51.9 (s); ¹H NMR (400 MHz, CDCl₃): δ = 4.15-4.28 (m, 1H), 3.73-3.90 (m, 2H), 3.07-3.16 (m, 1H), 2.08-2.18 (m, 1H), 2.06 (dquint., *J* = 2.3 and 7.0 Hz, 1H), 1.62-1.73 (m, 2H), 1.52 (d, *J* = 13.7 Hz, 3H), 1.40-1.58 (m, 1H), 1.24-1.38 (m, 1H), 1.15 (q, *J* = 11.1 Hz, 1H), 0.93 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.78-1.08 (m, 2H), 0.82 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 76.2 (d, *J*_{POC} = 7.8 Hz), 60.6 (d, *J*_{PC} = 111 Hz), 48.4 (d, *J*_{POCC} = 5.5 Hz), 43.4, 33.9, 31.4, 25.6, 22.7, 21.9, 20.9, 15.6, 11.8 (d, *J*_{PC} = 91.2 Hz); HRMS (EI+) m/z calcd for C₁₂H₂₆O₃P ([M+H]+) 249.1620, found 249.1621; [α]_D²² = -60.6° (chloroform).

(*R_p*)-Menthyl hydroxymethyl(*N*-methylphthalimide)phenylphosphinate 14:



To a solution of $(S_p)/(R_p)$ -2 (4.69 g, 20 mmol, 1.0 equiv, ratio 55:45) and N-(bromomethyl)phtalimide (4.8 g, 20 mmol, 1.0 equiv) in toluene was added at rt under N_2 hexamethyldisilazane (10.4 mL, 50 mmol, 2.5 equiv) and trimethylsilyl chloride (6.35 mL, 50 mmol, 2.5 equiv). The reaction mixture was stirred for 16 hours at reflux under N₂. Methanol (2.02 mL, 50 mmol, 2.5 equiv) was added and the mixture was concentrated under vacuum. The residue was dissolved in ethyl acetate and the organic layer was washed with NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The residue obtained was purified by crystallization in a mixture of dichloromethane/diethyl ether (20 mL:200 mL) to afford the product as a white solid (2.06 g, 26%, >99% de). Mp = 161-162°C; ³¹P NMR (162 MHz, CDCl₃): δ = 41.1 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.88-7.93 (m, 2H), 7.75-7.81 (m, 2H), 4.30-4.40 (m, 1H), 4.11-4.25 (m, 2H), 3.96 (d, J = 3.5 Hz, 2H), 3.43 (1H), 2.25-2.33 (m, 1H), 2.00 (dquint., J = 2.6 and 7.0 Hz, 1H), 1.62-1.71 (m, 2H), 1.42-1.56 (m, 1H), 1.31-1.39 (m, 1H), 1.28 (q, *J* = 11.1 Hz, 1H), 0.81-1.07 (m, 2H), 0.94 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 167.8$ (2C), 134.5 (2C), 131.8 (2C), 123.8 (2C), 78.5 (d, *J*_{POC} = 8.1 Hz), 59.2 (d, *J*_{PC} = 105 Hz), 48.5 (d, *J*_{POCC} = 6.0 Hz), 43.6, 34.8 (d, *J*_{PC} = 98.0 Hz), 33.9, 31.6, 25.6, 22.8, 21.9, 20.9, 15.5; HRMS (EI+) m/z calcd for C₂₁H₃₀O₅P ([M+H]⁺) 394.1783, found 394.1777; $[\alpha]_D^{25} = -24.5^{\circ}$ (chloroform).

(R_p)-Menthyl (acetoxymethyl)octylphosphinate 15:³



To a solution of (R_p) -2 (703 mg, 3 mmol, 1 equiv, >99% de) in dichloromethane (15 mL) at 0°C under N₂ was added pyridine (0.30 mL, 3.75 mmol, 1.25 equiv) and acetic anhydride (0.34 mL, 3.6 mmol, 1.2 equiv). The ice-bath was removed and the reaction mixture was stirred for 16h at rt. The solvent was removed under vacuum and the residue obtained was solubilized in ethyl acetate. The organic layer was washed with NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a white solid (829 mg, 100%, 95% de).^{7 31}P NMR (162 MHz, CDCl₃): δ = 26.8 (dm, *J* = 567 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.14 (dt, *J* = 1.8 and 567 Hz, 1H), 4.09-4.21 (m, 2H), 3.94-4.05 (m, 1H), 2.01-2.08 (m, 1H), 1.95 (s, 3H), 1.83-1.92 (m, 1H), 1.47-1.55 (m, 2H), 1.20-

1.36 (m, 2H), 1.10 (q, J = 11.1 Hz, 1H), 0.79-0.92 (m, 1H), 0.60-0.79 (m, 1H), 0.76 (d, J = 7.1 Hz, 3H), 0.75 (d, J = 6.4 Hz, 3H), 0.63 (d, J = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 170.0$ (d, $J_{PCC} = 6.5$ Hz), 79.6 (d, $J_{POC} = 7.8$ Hz), 60.0 (d, $J_{PC} = 113$ Hz), 48.4 (d, $J_{POCC} = 6.1$ Hz), 43.2, 33.6, 31.4, 25.5, 22.8, 21.7, 20.7, 20.1, 15.6.

To a solution of (R_p) -7 (553 mg, 2 mmol, 1 equiv) in DMSO (5 mL) was added 1-octene (0.31 mL, 2 mmol, 1 equiv) and Mn(OAc)₂ (17 mg, 0.1 mmol, 5 mol%). The reaction mixture was stirred for 16 h at 100°C under air. Ethyl acetate and an aqueous solution of Na₂S₂O₄ at 0.5M were added and the two layers were stirred for 10 minutes and then separated. The organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 8:2 to 7:3) to afford the product as a white solid (424 mg, 55%, 94% de). Mp = 57-59°C; ³¹P NMR (162 MHz, CDCl₃): δ = 46.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 3.97-4.12 (m, 2H), 1.88 (s, 3H), 1.49-1.59 (1H), 1.32-1.47 (m, 3H), 0.98-1.28 (m, 9H), 0.91 (q, *J* = 11.5 Hz, 1H), 0.71-0.84 (m, 1H), 0.54-0.72 (m, 1H), 0.68 (d, *J* = 7.0 Hz, 3H), 0.68 (d, *J* = 6.4 Hz, 3H), 0.64 (t, *J* = 6.8 Hz, 3H), 0.59 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (75.46 MHz, CDCl₃): δ = 169.5 (d, *J*_{PCCC} = 7.9 Hz), 76.2 (d, *J*_{PCC} = 7.7 Hz), 59.6 (d, *J*_{PCC} = 95.9 Hz), 25.4, 22.6, 22.4, 21.8, 20.9 (d, *J*_{PCCC} = 4.2 Hz), 20.8, 20.3, 15.4, 13.8; HRMS (EI+) m/z calcd for C₂₁H₄₁O₄P ([M+H]⁺) 389.2821, found 389.2812; [α]_D = -34.6°.

(R_p)-Menthyl phenyl-H-phosphinate 1:1



To a solution of *N*-chlorosuccinimide (4.0 g, 30 mmol, 3 equiv) in dichloromethane (150 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (2.2 mL, 30 mmol, 3 equiv) in dichloromethane (10 mL). After 30 minutes at -78°C, a solution of (S_p) -3 (3.1 g, 10 mmol, 1 equiv, >99% de) in dichloromethane (30 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (7 mL, 50 mmol, 5 equiv) was added over 15 minutes and the reaction was stirred for 30 minutes at -78°C. After warming up the reaction to rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 9:1 to 8:2) to afford the product as a colorless oil (2.58 g, 92%, >99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 24.7 (dm, *J* = 553 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.73-7.84 (m, 2H), 7.66 (d, *J* = 553 Hz, 1H), 7.46-7.64 (m, 3H), 4.22-4.36 (m, 1H), 2.14-2.27 (m, 2H), 1.62-1.75 (m, 2H), 1.38-1.54 (m, 2H), 1.24 (q, *J* = 11.2 Hz, 1H), 0.78-1.13 (m, 2H), 0.96 (d, *J* = 7.0 Hz, 3H); [α]_D²³ = -35.5° (chloroform, literature with 90% de: -21.0° in benzene).

(R_p)-Menthyl phenyl-H-phosphinate 1:1



To a solution of *N*-chlorosuccinimide (12.95 g, 97 mmol, 3 equiv) in dichloromethane (400 mL) at -78°C and under N₂ was added dropwise a solution of 1-(methylthio)dodecane (21 g, 97 mmol, 3 equiv) in dichloromethane (30 mL). After 30 minutes at -78°C, a solution of (S_p) -3 (10 g, 32 mmol, 1 equiv, >99% de) in dichloromethane (70 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (22.5 mL, 161 mmol, 5 equiv) was added over 15 minutes and the reaction was stirred for 30 minutes at -78°C. After warming up the reaction to rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic

layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 9:1 to 7:3) to afford the product as a colorless oil (5.8 g, 65%, >99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 24.7 (dm, *J* = 553 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.73-7.84 (m, 2H), 7.66 (d, *J* = 553 Hz, 1H), 7.46-7.64 (m, 3H), 4.22-4.36 (m, 1H), 2.14-2.27 (m, 2H), 1.62-1.75 (m, 2H), 1.38-1.54 (m, 2H), 1.24 (q, *J* = 11.2 Hz, 1H), 0.78-1.13 (m, 2H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H); $[\alpha]_{D^{23}}$ = -35.5° (chloroform, literature with 90% de: -21.0° in benzene).

(S_p)-Menthyl phenyl-H-phosphinate1:1



To a solution of *N*-chlorosuccinimide (110 mg, 0.82 mmol, 1.5 equiv) in dichloromethane (5 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.06 mL, 0.82 mmol, 1.5 equiv) in dichloromethane (1 mL). After 10 minutes at -78°C, a solution of (R_p)-Menthyl (hydroxymethyl)phenylphosphinate (170 mg, 0.55 mmol, 1 equiv, >99% de) in dichloromethane (2 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.38 mL, 2.74 mmol, 5 equiv) was added over 15 minutes and the reaction was allowed to warm up to rt. After 1h at rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 6:4) to afford the product as a colorless oil (125 mg, 81%, > 99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 22.4 (d, *J* = 557 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.67-7.82 (m, 2H), 7.68 (d, *J* = 557 Hz, 1H), 7.42-7.62 (m, 3H), 4.18-4.32 (m, 1H), 2.25-2.35 (m, 1H), 2.02-2.16 (m, 1H), 1.62-1.75 (m, 2H), 1.22-1.58 (m, 3H), 0.80-1.14 (m, 2H), 0.95 (d, *J* = 6.4 Hz, 3H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.67 (d, *J* = 7.0 Hz, 3H); [α]_D²³ = -77.4° (chloroform, literature with 70% de: -89.6° in benzene).

(S_p)-Menthyl methyl-H-phosphinate 16:¹



To a solution of *N*-chlorosuccinimide (470 mg, 3.5 mmol, 3 equiv) in dichloromethane (35 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.26 mL, 3.5 mmol, 3 equiv) in dichloromethane (3 mL). After 10 minutes at -78°C, a solution of (R_p)-10 (290 mg, 1.17 mmol, 1 equiv, >99% de) in dichloromethane (5 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.81 mL, 5.84 mmol, 5 equiv) was added over 15 minutes and the reaction was stirred for 30 minutes at -78°C. After warming up the reaction to rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 8:2 to 4:6) to afford the product as a colorless oil (134 mg, 61%, 96% de). ³¹P NMR (162 MHz, CDCl₃): δ = 28.5 (dm, J = 537 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.33 (d, *J* = 537 Hz, 1H), 4.15-4.29 (m, 1H), 2.06-2.20 (m, 2H), 1.62-1.73 (m, 2H), 1.52 (d, *J* = 15.2 Hz, 3H), 1.24-1.58 (m, 2H), 1.14 (q, *J* = 11.4 Hz, 1H), 0.93 (d, *J* = 6.2 Hz, 6H), 0.78-1.10 (m, 2H), 0.83 (d, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 76.8 (d, *J*_{PCC} = 7.2 Hz), 48.4 (d, *J*_{PCCC} = 6.1 Hz), 41.8, 34.0, 31.4, 29.6, 25.7, 23.1, 22.0, 20.8, 15.9, 15.3 (d, *J*_{PC} = 95.6 Hz); [α]_D²³ = -92.2° (chloroform, literature: -96.6° in benzene).



To a solution of *N*-chlorosuccinimide (100 mg, 0.75 mmol, 3 equiv) in dichloromethane (15 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.055 mL, 0.75 mmol, 3 equiv) in dichloromethane (2 mL). After 10 minutes at -78°C, a solution of (R_p) -5 (90 mg, 0.25 mmol, 1 equiv, 94% de) in dichloromethane (2 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.38 mL, 2.74 mmol, 5 equiv) was added over 15 minutes and the reaction was stirred for 30 minutes at -78°C. After warming up the reaction to rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 9:1 to 7:3) to afford the product as a colorless oil (72 mg, 87%, 94% de). ³¹P NMR (162 MHz, CDCl₃): δ = 23.3 (dm, J = 557 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 8.45-8.51 (m, 1H), 7.99-8.10 (m, 2H), 8.05 (d, J = 557 Hz, 1H), 7.90-7.96 (m, 1H), 7.54-7.67 (m, 3H), 4.31-4.44 (m, 1H), 2.34-2.44 (m, 1H), 2.05 (dquint., J = 2.6 and 7.0 Hz, 1H), 1.61-1.74 (m, 2H), 1.24-1.56 (m, 3H), 0.97 (d, J = 6.4 Hz, 3H), 0.75-1.10 (m, 2H), 0.80 (d, J = 7.0 Hz, 3H), 0.61 (d, J = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 133.6 (d, *J*_{PCCCC} = 2.8 Hz), 133.4 (d, *J*_{PCC} = 10.5 Hz), 132.5 (d, *J*_{PCCC} = 10.0 Hz), 131.7 (d, *J*_{PCCC} = 14.4 Hz), 128.9 (d, *J*_{PCCCC} = 1.7 Hz), 127.5, 126.7 (d, *J*_{PC} = 132 Hz), 126.7, 125.2 (d, J_{PCCC} = 7.2 Hz), 124.6 (d, J_{PCC} = 16.6 Hz), 77.8 (d, J_{POC} = 7.1 Hz), 48.5 (d, J_{POCC} = 6.7 Hz), 43.5, 42.2 (d, $J_{POCC} = 1.1 \text{ Hz}$, 34.0, 31.6, 25.3, 22.8, 22.0, 20.8, 15.4; $[\alpha]_D^{23} = -74.0^{\circ}$ (chloroform).

(S_p)-Menthyl cinnamyl-H-phosphinate 18:1



To a solution of N-chlorosuccinimide (200 mg, 1.5 mmol, 3 equiv) in dichloromethane (20 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.11 mL, 1.5 mmol, 3 equiv) in dichloromethane (3 mL). After 10 minutes at -78°C, a solution of (R_p) -4 (175 mg, 0.5 mmol, 1 equiv, >99% de) in dichloromethane (3 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.35 mL, 2.5 mmol, 5 equiv) was added over 15 minutes and the reaction was stirred for 30 minutes at -78°C. After warming up to rt, water was added and the two layers were separated. The aqueous layer was then extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 9:1 to 7:3) to afford the product as a colorless oil (132 mg, 82%, > 99% de). ³¹P NMR (121.47 MHz, CDCl₃): δ = 30.9 (dm, J = 539 Hz); ¹H NMR (300 MHz, CDCl₃): δ = 7.20-7.41 (m, 5H), 7.17 (d, *I* = 539 Hz, 1H), 6.56 (dd, *I* = 5.9 and 15.8 Hz, 1H), 6.05-6.20 (m, 1H), 4.37-4.63 (m, 1H), 2.80 (dd, J = 7.6 and 18.5 Hz, 2H), 2.06-2.24 (m, 2H), 1.62-1.73 (m, 2H), 1.34-1.55 (m, 2H), 1.15 (q, J = 11.4 Hz, 1H), 0.75-1.12 (m, 2H), 0.92 (d, J = 6.5 Hz, 3H), 0.91 (d, J = 7.0 Hz, 3H), 0.82 (d, J = 7.0 Hz, 3H); ¹³C NMR (75.46 MHz, CDCl₃): $\delta = 136.8$ (d, $J_{PCCCC} = 3.3$ Hz), 135.8 (d, $J_{PCC} = 14.4$ Hz), 128.6 (d, J = 1.1 Hz, 2C), 127.8, 126.2 (d, J_{PCCCCC} = 2.3 Hz, 2C), 117.0 (d, J_{PCCC} = 10.0 Hz), 77.3 (d, J_{PCC} = 7.8 Hz), 48.4 (d, J_{POCC} = 6.1 Hz), 41.8, 34.3 (d, J_{PC} = 91.8 Hz), 34.0, 31.4, 25.7, 23.1, 21.9, 20.8, 15.8; HRMS (EI+) m/z calcd for C₁₉H₂₉O₂P ([M]⁺) 320.1905, found 320.1907; [a]_D²³ = -89.8° (chloroform).

(S_p)-Menthyl (3-phenylpropyl)-H-phosphinate 19:



To a solution of N-chlorosuccinimide (721 mg, 5.4 mmol, 3 equiv) in dichloromethane (30 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.4 mL, 5.4 mmol, 3 equiv) in dichloromethane (5 mL). After 10 minutes at -78°C, a solution of (R_p) -menthyl hydroxymethyl(3phenylpropyl)-H-phosphinate (630 mg, 1.8 mmol, 1 equiv, 98% de) in dichloromethane (5 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (1.25 mL, 9 mmol, 5 equiv) was added over 15 minutes and the reaction was allowed to warm up to rt. After 1h at rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 99:1 to 97:3) to afford the product as a colorless oil (554 mg, 96%, 96% de). ³¹P NMR (162 MHz, CDCl₃): δ = 33.3 (dsextuplet, / = 12.7 and 528 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.16-7.23 (m, 2H), 7.05-7.13 (m, 3H), 7.08 (d, J = 528 Hz, 1H), 4.07-4.19 (m, 1H), 2.62 (t, J = 7.4 Hz, 2H), 1.99-2.10 (m, 2H), 1.77-1.91 (m, 2H), 1.53-1.73 (m, 4H), 1.21-1.43 (m, 2H), 1.02 (q, J = 11.6 Hz, 1H), 0.94 (dquint., J = 3.0 and 12.4 Hz, 1H), 0.84 (d, I = 6.8 Hz, 6H), 0.69-0.85 (m, 1H), 0.74 (d, I = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): $\delta =$ 140.7, 128.4 (2C), 128.4 (2C), 126.1, 76.7 (d, J_{POC} = 7.4 Hz), 48.3 (d, J_{POCC} = 5.9 Hz), 41.6, 36.2 (d, J_{PCC} = 16.0 Hz), 33.9, 31.3, 28.1 (d, J_{PC} = 95.0 Hz), 25.6, 22.9, 22.4 (d, J_{PCCC} = 2.5 Hz), 21.9, 20.8, 15.7; $[\alpha]_D^{23}$ = -27.3^o (chloroform).

(S_p)-Menthyl cyclohexyl-H-phosphinate 20:



To a solution of N-chlorosuccinimide (400 mg, 3 mmol, 3 equiv) in dichloromethane (25 mL) at -78°C and under N_2 was added dropwise a solution of dimethyl sulfide (0.22 mL, 3 mmol, 3 equiv) in dichloromethane (3 mL). After 10 minutes at -78° C, a solution of (S_n) -methyl (hydroxymethyl)cyclohexylphosphinate (316 mg, 1 mmol, 1 equiv, > 99% de) in dichloromethane (5 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.70 mL, 5 mmol, 5 equiv) was added over 15 minutes and the reaction was allowed to warm up to rt. After 1h at rt, water was added and the two layers were separated. The aqueous layer was then extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated vacuum. The crude obtained was purified by column chromatography under (dichloromethane/acetone 100:0 to 90:10) to afford the product as a colorless oil (181 mg, 63%, > 99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 37.1 (s); ¹H NMR (400 MHz, CDCl₃): δ = 6.84 (d, *J* = 512 Hz, 1H), 4.08-4.17 (m, 1H), 2.01-2.14 (m, 2H), 1.71-1.90 (m, 4H), 1.53-1.69 (m, 4H), 1.10-1.47 (m, 7H), 1.04 (q, J = 11.2 Hz, 1H), 0.99 (dq, J = 2.4 and 12.6 Hz, 1H), 0.78-0.95 (m, 1H), 0.89 (d, J = 7.0 Hz, 3H), 0.88 (d, J = 6.5 Hz, 3H), 0.78 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 76.4$ (d, $J_{POC} = 7.8$ Hz), 48.4 (d, JPOCC = 5.8 Hz), 41.5 (d, JPOCC = 1.2 Hz), 37.1 (d, JPC = 97.7 Hz), 34.0, 31.3, 25.8 (2C), 25.6 (d, JPCC = 10.7 Hz), 25.6 (d, *J*_{PCC} = 9.5 Hz), 24.1 (2C), 22.9, 21.9, 20.8, 15.6.

(S_p)-Menthyl triphenylmethyl-H-phosphinate 21:



To a solution of N-chlorosuccinimide (100 mg, 0.75 mmol, 3 equiv) in dichloromethane (20 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.06 mL, 0.75 mmol, 3 equiv) in dichloromethane (2 mL). After 10 minutes at -78°C, a solution of (R_p) -13 (119 mg, 0.25 mmol, 1 equiv, 95% de) in dichloromethane (3 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.17 mL, 1.25 mmol, 5 equiv) was added over 15 minutes and the reaction was allowed to warm up to rt. After 1h at rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO4, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 97:3) to afford the product as a white solid (93 mg, 83%, 95% de). ³¹P NMR (162 MHz, CDCl₃): δ = 35.4 (dd, J = 4.4 and 550 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.66 (d, J = 549 Hz, 1H), 7.27-7.37 (m, 15H), 4.21-4.32 (m, 1H), 2.03-2.11 (m, 1H), 1.57-1.69 (m, 3H), 1.35-1.48 (m, 1H), 1.15-1.24 (m, 1H), 1.00 (q, J = 11.4 Hz, 1H), 0.98 (dq, J = 3.2 and 14.7 Hz, 1H), 0.89 (d, J = 6.6 Hz, 3H), 0.81 (dq, J = 3.4 and 12.1 Hz, 1H), 0.74 (d, J = 7.1 Hz, 3H), 0.70 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 140.5 (d, J_{PCC} = 3.2 Hz, 3C), 130.6 (d, J_{PCCC} = 6.9 Hz, 6C), 128.2 (s, 6C), 127.2 (d, J_{PCCCCC} = 1.8 Hz, 3C), 78.7 (d, J_{POC} = 8.7 Hz), 62.0 (d, J_{PC} = 90.7 Hz), 48.6 (d, J_{POCC} = 5.8 Hz), 41.1 (d, *J*_{POCC} = 1.9 Hz), 33.9, 31.5, 24.8, 22.6, 22.0, 20.9, 15.5; [a]_D²³ = -21.1^o (chloroform).

(S_p)-Menthyl mesityl-H-phosphinate 22:



To a solution of N-chlorosuccinimide (400 mg, 3 mmol, 3 equiv) in dichloromethane (40 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.22 mL, 3 mmol, 3 equiv) in dichloromethane (3 mL). After 10 minutes at -78°C, a solution of (R_p) -8b (352 mg, 1 mmol, 1 equiv, 94% de) in dichloromethane (5 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (0.7 mL, 5 mmol, 5 equiv) was added over 15 minutes and the reaction was allowed to warm up to rt. After 1h at rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 97:3) to afford the product as a colorless oil (275 mg, 85%, 94% de). ³¹P NMR (162 MHz, CDCl₃): δ = 18.7 (d, I = 548 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 8.09 (d, I = 548 Hz, 1H), 6.89 (s, 1H), 6.88 (s, 1H), 4.27-4.37 (m, 1H), 2.58 (s, 6H), 2.27-2.34 (m, 1H), 2.31 (s, 3H), 2.17 (dquint., J = 2.7 and 7.0 Hz, 1H), 1.65-1.74 (m, 2H), 1.45-1.57 (m, 1H), 1.34-1.43 (m, 1H), 1.22 (q, *J* = 11.3 Hz, 1H), 1.06 (dq, *J* = 3.2 and 12.5 Hz, 1H), 0.77-0.99 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 3H), 0.90 (d, *J* = 7.1 Hz, 3H), 0.80 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 142.2 (d, J_{PCCCC} = 1.9 Hz), 141.5 (d, JPCCC = 11.4 Hz, 2C), 130.0 (d, JPCC = 12.2 Hz, 2C), 123.7 (d, JPC = 136 Hz), 76.8 (d, JPOC = 7.0 Hz), 48.4 (d, $J_{POCC} = 6.3$ Hz), 41.6, 34.0, 31.4, 25.3, 22.8, 21.9, 21.1, 20.9, 20.8 (2C), 15.4; $[\alpha]_D^{22} = -28.8^{\circ}$ (chloroform).

(S_p)-Menthyl (benzoxymethyl)phenylphosphinate 23:



To a suspension of NaH (120 mg, 3 mmol, 1.5 equiv, 60% in mineral oil) in dichloromethane (15 mL) was added at 0°C under N₂ a solution of (S_p) -3 (621 mg, 2 mmol, 1 equiv, >99% de) in dichloromethane (5 mL). After 30 minutes at 0°C, benzylbromide (0.29 mL, 2.4 mmol, 1.2 equiv) was added. The reaction was stirred for 4 hours at rt. A saturated solution of NH₄Cl was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (3X). The combined organic layers was dried over MgSO4, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 9:1 to 7:3) to afford the product as colorless oil (801 mg, 100%, >99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 31.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.91 (m, 2H), 7.52-7.62 (m, 1H), 7.42-7.52 (m, 2H), 7.24-7.34 (m, 3H), 7.13-7.21 (m, 2H), 4.56 (s, 2H), 4.29-4.43 (m, 1H), 3.75-3.94 (m, 2H), 2.18-2.33 (m, 1H), 1.90-2.01 (m, 1H), 1.56-1.72 (m, 2H), 1.22-1.48 (m, 2H), 0.74-1.17 (m, 3H), 0.92 (d, J = 7.0 Hz, 3H), 0.82 (d, J = 6.7 Hz, 3H), 0.79 (d, J = 6.4 Hz, 3H); ¹³C NMR (100.62 MHz, CDCl₃): $\delta = 137.0$, 132.3 (d, $J_{PCCCC} = 2.7$ Hz), 131.8 (d, J_{PCCC} = 10.0 Hz, 2C), 131.2 (d, J_{PC} = 129 Hz), 128.3 (2C), 128.3 (d, J_{PCC} = 12.7 Hz, 2C), 127.8 (3C), 77.2 (d, J_{POC} = 7.2 Hz), 75.0 (d, J_{PCOC} = 12.2 Hz), 67.1 (d, J_{PC} = 119 Hz), 48.7 (d, J_{POCC} = 6.1 Hz), 43.4, 34.0, 31.5, 25.5, 22.8, 21.9, 21.1, 15.7; HRMS (EI+) m/z calcd for C₂₄H₃₄O₃P ([M+H]+) 401.2244, found 401.2246; $[\alpha]_{D^{25}} = -12.2^{\circ}$ (chloroform).

(S_p)-Menthyl (benzoxymethyl)phenylphosphinate 23:



To a solution of (S_p) -3 (3.1 g, 10 mmol, 1 equiv, >99% de) in acetonitrile (30 mL) was added benzylbromide (6 mL, 50 mmol, 5 equiv) followed by potassium fluoride on alumina (7.25 g, 50 mmol, 5 equiv, 40% w.t). The reaction was stirred for 3 days at rt under N₂. The suspension was filtered through celite. The solid was washed twice with acetonitrile and the filtrate was concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 95:5) to afford the product as colorless oil (3.97 g, 99%, >99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 31.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.91 (m, 2H), 7.52-7.62 (m, 1H), 7.42-7.52 (m, 2H), 7.24-7.34 (m, 3H), 7.13-7.21 (m, 2H), 4.56 (s, 2H), 4.29-4.43 (m, 1H), 3.75-3.94 (m, 2H), 2.18-2.33 (m, 1H), 1.90-2.01 (m, 1H), 1.56-1.72 (m, 2H), 1.22-1.48 (m, 2H), 0.74-1.17 (m, 3H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H), 0.79 (d, *J* = 6.4 Hz, 3H); ¹³C NMR (100.62 MHz, CDCl₃): δ = 137.0, 132.3 (d, *J*_{PCCCC} = 2.7 Hz), 131.8 (d, *J*_{PCCC} = 10.0 Hz, 2C), 131.2 (d, *J*_{PCC} = 129 Hz), 128.3 (2C), 128.3 (d, *J*_{PCCC} = 6.1 Hz), 43.4, 34.0, 31.5, 25.5, 22.8, 21.9, 21.1, 15.7; HRMS (EI+) m/z calcd for C₂₄H₃₄O₃P ([M+H]⁺) 401.2244, found 401.2246; [α]_{P²⁵} = -12.2° (chloroform).

(S_p)-Menthyl [(tert-butyldimethylsilyloxy)methyl]phenylphosphinate 24:



To a solution of (S_n) -3 (3.1 g, 10 mmol, 1 equiv, >99% de) in dichloromethane (20 mL) was added at 0°C under N₂ imidazole (1.5 mL, 27 mmol, 2.7 equiv) followed by tert-butyldimethylsilyl chloride (2.6 mL, 15 mmol, 1.5 equiv). The ice bath was removed and the reaction was stirred for 16 h under N_2 at rt. The solvent was then removed under vacuum and the crude obtained was dissolved in ethyl acetate. The organic layer was washed with NaHCO3 and brine, dried over MgSO4, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 95:5) to afford the product as colorless oil (4.23 g, 100%, > 99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 35.6 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.83-7.90 (m, 2H), 7.53-7.58 (m, 1H), 7.43-7.50 (m, 2H), 4.31-4.41 (m, 1H), 4.03 (dd, J = 9.3 and 13.8 Hz, 1H), 3.94 (dd, J = 4.6 and 13.8 Hz, 1H), 2.34 (dquint., J = 2.5 and 7.0 Hz, 1H), 1.98-2.05 (m, 1H), 1.61-1.73 (m, 2H), 1.32-1.48 (m, 2H), 1.12 (q, J = 11.1 Hz, 1H), 0.85-1.09 (m, 2H), 0.97 (d, J = 7.1 Hz, 3H), 0.89 (d, J = 6.9 Hz, 3H), 0.82 (d, J = 6.8 Hz, 3H), 0.81 (s, 9H), -0.06 (s, 3H), -0.10 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 132.1 (d, J_{PCCCC} = 2.8 Hz), 132.1 (d, J_{PCCC} = 9.7 Hz, 2C), 130.8 (d, J_{PC} = 128 Hz), 128.0 (d, J_{PCC} = 12.5 Hz, 2C), 76.9 (d, JPOC = 7.5 Hz), 61.0 (d, JPC = 123 Hz), 48.7 (d, JPOCC = 6.1 Hz), 43.5, 34.0, 31.5, 25.6 (3C), 25.4, 22.9, 21.9, 21.1, 18.2, 15.8, -5.9, -6.0; HRMS (EI+) m/z calcd for C₂₃H₄₂O₃PSi ([M+H]⁺) 425.2641, found 425.2629; $[\alpha]_D^{25} = -14.1^\circ$ (chloroform).

(S_p)-Menthyl (acetoxymethyl)phenylphosphinate 25:²



To a solution of (S_p) -3 (1.55 g, 5 mmol, 1 equiv, >99% de) in dichloromethane (10 mL) was slowly added at 0°C and under N₂ triethylamine (0.87 mL, 6.25 mmol, 1.25 equiv) followed by acetic anhydride (0.57 ml, 6 mmol, 1.2 equiv). The ice bath was removed and the reaction mixture was stirred at rt for 16 h. The solvent was removed under vacuum and the residue obtained was solubilized in ethyl acetate. The organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a colorless oil (1.73 g, 98%, >99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 30.3 (s).

(S_p)-Menthyl [(tosyloxy)methyl]phenylphosphinate 26:4



To a solution of (S_p) -3 (3.1 g, 10 mmol, 1 equiv, >99% de) in dichloromethane (20 ml) under N₂ was added *N*,*N*-diisopropylethylamine (4.4 mL, 25 mmol, 2.5 equiv). The mixture was cooled down to 0°C and a solution of tosyl chloride (2.89 g, 20 mmol, 2 equiv) in dichloromethane (15 ml) was added over 1h. The ice-bath was removed and the solution was stirred for 20h at rt. A saturated aqueous solution of NaHCO₃ was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (2X). The combined organic layers was dried over MgSO₄, filtered and concentrated under vacuum. The residue obtained was purified by column chromatography (hexanes/ethyl acetate 9:1 to 7:3) to afford the product as colorless crystals (4.6 g, 99%, > 99% de). Mp = 68-70°C; ³¹P NMR (162 MHz, CDCl₃): δ = 29.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.67-7.75 (m,

2H), 7.49-7.56 (m, 3H), 7.36-7.43 (m, 2H), 7.17-7.22 (m, 2H), 4.10-4.35 (m, 3H), 2.35 (s, 3H), 2.10 (dquint, J = 2.6 and 7.0 Hz, 1H), 1.86-1.93 (m, 1H), 1.53-1.66 (m, 2H), 1.22-1.42 (m, 2H), 1.06 (q, J = 11.1 Hz, 1H), 0.76-1.06 (m, 2H), 0.87 (d, J = 7.0 Hz, 3H), 0.75 (d, J = 6.8 Hz, 3H), 0.74 (d, J = 6.5 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 145.2$, 133.0 (d, $J_{PCCCC} = 2.8$ Hz), 131.8 (d, $J_{PCCC} = 10.0$ Hz, 2C), 131.4, 129.9 (2C), 129.3 (d, $J_{PC} = 137$ Hz), 128.5 (d, $J_{PCC} = 13.3$ Hz, 2C), 128.0 (2C), 78.5 (d, $J_{POC} = 7.4$ Hz), 64.3 (d, $J_{PC} = 115$ Hz), 48.5 (d, $J_{POCC} = 6.1$ Hz), 43.3, 33.9, 31.5, 25.5, 22.8, 21.8, 21.6, 21.0, 15.6; HRMS (EI+) m/z calcd for C₂₄H₃₄O₅PS ([M+H]⁺) 465.1865, found 465.1857; [α]_D²⁵ = -20.1° (chloroform).

(S_p)-Menthyl (benzoxymethyl)phenylphosphinate borane 27:



To a solution of (S_p)-23 (400 mg, 1 mmol, 1 equiv, >99% de) in benzene (5 mL) was added triethylamine (0.7 mL, 5 mmol, 5 equiv) followed by trichlorosilane (0.5 mL, 5 mmol, 5 equiv). After 2 hours at reflux under N₂, the reaction was cooled down to rt and then borane dimethylsulfide (2.5 mL, 5 mmol, 5 equiv, 2.0M solution in tetrahydrofuran) was added and the reaction was stirred for 12 hours at rt under N_2 . The solvent was removed under vacuum and the crude obtained was purified by column chromatography (hexane/ethyl acetate 100:0 to 90:10) to afford the product as colorless oil (302 mg, 76%, > 99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 104.7 (d, *J* = 85.8 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.80-7.87 (m, 2H), 7.53-7.59 (m, 1H), 7.46-7.52 (m, 2H), 7.27-7.36 (m, 3H), 7.19-7.24 (m, 2H), 4.54-4.62 (m, 2H), 4.18-4.28 (m, 1H), 3.87-3.98 (m, 2H), 2.23 (dquint., J = 2.6 and 7.0 Hz, 1H), 1.84-1.91 (m, 1H), 1.61-1.72 (m, 2H), 1.34-1.49 (m, 2H), 0.74-1.30 (m, 3H), 1.04 (dq, J = 3.6 and 12.5 Hz, 1H), 0.98 (q, / = 11.1 Hz, 1H), 0.95 (d, / = 7.0 Hz, 3H), 0.77-0.90 (m, 1H), 0.84 (d, / = 6.9 Hz, 3H), 0.82 (d, I = 6.6 Hz, 3H); ¹³C NMR (100.62 MHz, CDCl₃): $\delta = 137.1, 131.8$ (d, $I_{PCCCC} = 2.6$ Hz), 131.5 (d, J_{PC} = 57.2 Hz), 131.2 (d, J_{PCCC} = 10.5 Hz, 2C), 128.4 (d, J_{PCC} = 10.2 Hz, 2C),128.4 (2C), 127.8, 127.8 (2C), 80.3 (d, J_{POC} = 3.8 Hz), 75.2 (d, J_{PCOC} = 7.8 Hz), 69.9 (d, J_{PC} = 56.1 Hz), 48.9 (d, J_{POCC} = 6.5 Hz), 43.5, 34.1, 31.4, 25.4, 22.9, 22.0, 21.0, 15.9; HRMS (EI+) m/z calcd for C₂₄H₃₅BO₂P ([M-H]+) 397.2468, found 397.2461; $[\alpha]_{D^{24}} = -0.9^{\circ}$ (chloroform).

(*R_p*)-Menthyl [(tert-butyldimethylsilyloxy)methyl]phenylthiophosphinate 28a:



To a solution of (S_p) -24 (2.12 g, 5 mmol, 1 equiv, >99% de) in toluene (20 mL) was added Lawesson's reagent (1.21 g, 3 mmol, 0.6 equiv). The reaction mixture was stirred for 16 hours at reflux under N₂. After cooling down the reaction to rt, the solvent was concentrated under vacuum and the residue obtained was purified by column chromatography (Hexane/ethyl acetate 98:2 to 95:5) to afford the product as a yellow oil (2.05 g, 93%, > 99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 82.4 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.92-8.01 (m, 2H), 7.49-7.55 (m, 1H), 7.41-7.48 (m, 2H), 4.45-4.56 (m, 1H), 4.13 (dd, *J* = 8.1 and 13.2 Hz, 1H), 3.95 (d, *J* = 13.3 Hz, 1H), 2.29 (dquint, *J* = 2.5 and 7.0 Hz, 1H), 1.79-1.87 (m, 1H), 1.60-1.73 (m, 2H), 1.32-1.53 (m, 2H), 0.75-1.13 (m, 3H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.82 (s, 9H), 0.78 (d, *J* = 6.5 Hz, 3H), -0.05 (s, 3H), -0.12 (s, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 133.2 (d, *J*_{PCC} = 101 Hz), 132.0 (d, *J*_{PCCC} = 10.4 Hz, 2C), 131.9 (d, *J*_{PCCCC} = 3.0 Hz), 127.9 (d, *J*_{PCC} = 12.6 Hz, 2C), 77.2 (d, *J*_{PCC} = 7.9 Hz), 67.7 (d, *J*_{PCC} = 99.1 Hz), 48.5 (d, *J*_{PCCC} = 7.1 Hz), 43.4, 34.1, 31.4, 25.6 (3C), 25.3, 23.0, 22.0, 21.1, 18.2, 16.1, -5.8, -5.8; HRMS (EI+) m/z calcd for C₂₃H₄₂O₂PSSi ([M+H]⁺) 441.2412, found 441.2394; [α]_{D²⁵} = -16.8° (chloroform).

(*R_p*)-Menthyl (acetoxymethyl)phenylthiophosphinate 28b:



To a solution of (S_p) -25 (1.73 g, 5 mmol, 1 equiv, >99% de) in toluene (10 mL) was added Lawesson's reagent (1.21 g, 3 mmol, 0.6 equiv). The reaction mixture was stirred for 16 hours at reflux under N₂. After cooling down the reaction to rt, the solvent was concentrated under vacuum and the residue obtained was purified by column chromatography (Hexane/ethyl acetate 99:1 to 97:3) to afford the product as a colorless oil (1.85 g, 100%, > 99% de). ³¹P NMR (162 MHz, CDCl₃): δ = 78.9 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.92-7.99 (m, 2H), 7.55-7.61 (m, 1H), 7.47-7.53 (m, 2H), 4.48-4.61 (m, 3H), 2.19 (dquint, *J* = 2.7 and 7.0 Hz, 1H), 2.04 (s, 3H), 1.61-1.80 (m, 3H), 1.46-1.55 (m, 1H), 1.33-1.45 (m, 1H), 1.08 (dq, *J* = 3.4 and 13.3 Hz, 1H), 0.98 (q, *J* = 11.8 Hz, 1H), 0.98 (d, *J* = 7.0 Hz, 3H), 0.91 (d, *J* = 7.0 Hz, 3H), 0.85 (dq, *J* = 3.3 and 11.9 Hz, 1H), 0.78 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 169.8 (d, *J*_{PCCC} = 7.6 Hz), 132.9 (d, *J*_{PCC} = 7.5 Hz), 65.6 (d, *J*_{PCC} = 98.2 Hz), 48.4 (d, *J*_{POCC} = 7.3 Hz), 43.2, 34.1, 31.4, 25.6, 23.0, 21.9, 21.0, 20.5, 16.0.

(*R_p*)-Menthyl (hydroxymethyl)phenylthiophosphinate 29:



To a solution of (R_p) -28b (1.84 g, 5 mmol, 1 equiv, >99% de) in methanol (10 mL) was added potassium carbonate (69 mg, 0.5 mmol, 0.1 equiv.) and the mixture was stirred for 16 h at rt. The solvent was removed under vacuum and then the residue was solubilized in ethyl acetate. The organic layer was washed with saturated NaHCO₃ (150 mL) and brine (150 mL), dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a white solid (1.63 g, 100%, 96% de). Mp = 67-68 °C; ³¹P NMR (162 MHz, CDCl₃): δ = 83.6 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.87-7.97 (m, 2H), 7.51-7.58 (m, 1H), 7.43-7.50 (m, 2H), 4.47 (dd, *J* = 4.4 and 10.6 Hz, 1H), 3.84-4.03 (m, 2H), 2.75 (s, 1H), 2.17 (dquint, *J* = 2.6 and 7.0 Hz, 1H), 1.58-1.77 (m, 3H), 1.43-1.52 (m, 1H), 1.29-1.41 (m, 1H), 1.05 (dq, *J* = 3.0 and 12.9 Hz, 1H), 0.76-1.01 (m, 2H), 0.95 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.9 Hz, 3H), 0.75 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 133.0 (d, *J*_{PCC} = 98.4 Hz), 132.4 (d, *J*_{PCCCC} = 3.0 Hz), 131.4 (d, *J*_{PCCCC} = 7.1 Hz), 43.2, 34.1, 31.4, 25.6, 23.0, 22.0, 21.0, 16.0; HRMS (EI+) m/z calcd for C₁₇H₂₇O₂PS ([M]⁺) 326.1469, found 326.1466; [α]_P²⁵ = -24.9° (chloroform).

(S_p)-Menthyl (iodomethyl)phenylphosphinate 30:4



To a solution of (S_p) -26 (4.78 g, 12.5 mmol, 1 equiv, >99% de) in acetone (40 ml) was added sodium iodide (7.5 g, 50 mmol, 4 equiv). The reaction mixture was stirred for 24h at reflux. The solvent was removed under vacuum and the residue obtained was dissolved in dichloromethane. The organic layer was washed with brine, dried over MgSO₄, filtered and concentrated under vacuum. The solid obtained was purified by column chromatography (dichloromethane/ethyl acetate 10:0 to 9:1) to

afford the product as a yellow solid (4.06 g, 94%, 96% de). Mp = 66-68°C; ³¹P NMR (162 MHz, CDCl₃): δ = 31.9 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.59-7.68 (m, 2H), 7.30-7.36 (m, 1H), 7.20-7.28 (m, 2H), 4.11-4.23 (m, 1H), 3.01 (dd, *J* = 8.9 and 12.7 Hz, 1H), 2.88 (dd, *J* = 5.9 and 12.7 Hz, 1H), 2.12-2.24 (m, 1H), 1.58-1.67 (m, 1H), 1.35-1.51 (m, 2H), 1.18-1.28 (m, 1H), 1.03-1.17 (m, 1H), 0.54-0.86 (m, 3H), 0.75 (d, *J* = 7.0 Hz, 3H), 0.69 (d, *J* = 6.9 Hz, 3H), 0.52 (d, *J* = 6.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 132.5 (d, *J*_{PCCC} = 2.7 Hz), 131.8 (d, *J*_{PCCC} = 9.8 Hz, 2C), 130.2 (d, *J*_{PC} = 136 Hz), 128.3 (d, *J*_{PCC} = 13.1 Hz, 2C), 77.9 (d, *J*_{POC} = 7.2 Hz), 48.6 (d, *J*_{POCC} = 6.2 Hz), 42.9, 33.8, 31.3, 25.5, 22.7, 21.8, 21.0, 15.8, -6.5 (d, *J*_{PC} = 102 Hz); HRMS (EI+) m/z calcd for C₁₇H₂₇IO₂P ([M+H]+) 421.0793, found 421.0793; [α]_D = -29.5°.

(R_p, R_p)-Ethane-1,2-diylbis(menthyl phenylphosphinate 31:⁴



To a solution of (*S*_p)-30 (420.3 mg, 1 mmol, 1 equiv, 96% de) in THF (8 mL) at -78°C under N₂ was slowly added isopropylmagnesium chloride (0.55 mL, 1.1 mmol, 1.1 equiv, 2.0M in THF). After 1 h of stirring at -78°C, CuCl₂ (403 mg, 3 mmol, 3 equiv) was added. The dry ice-bath was removed and the reaction mixture was stirred for 2 h at rt. A saturated solution of NH₄Cl was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (3X). The combined organic layers was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 8:2 to 6:4) to afford the product as a white solid (237 mg, 81%, de = 89%). Mp = 78-79°C; ³¹P NMR (162 MHz, CDCl₃): δ = 39.7 (m); ¹H NMR (400 MHz, CDCl₃): δ = 7.77-7.87 (m, 4H), 7.44-7.59 (m, 6H), 4.23-4.36 (m, 2H), 2.21 (dquint., *J* = 2.3 and 7.0 Hz, 2H), 1.78-1.87 (m, 2H), 1.66 (d, *J* = 14.4 Hz, 4H), 1.56-1.72 (m, 4H), 1.25-1.44 (m, 4H), 0.74-1.11 (m, 6H), 0.97 (d, *J* = 7.1 Hz, 6H), 0.90 (d, *J* = 7.0 Hz, 6H), 0.78 (d, *J* = 6.4 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃): δ = 133.8 (d, *J*_{PCC} = 129 Hz, 2C), 131.8 (d, *J*_{PCCC} = 2.7 Hz, 2C), 130.7 (d, *J*_{PCCC} = 9.9 Hz, 4C), 128.3 (d, *J*_{PCC} = 12.7 Hz, 4C), 76.2 (d, *J*_{PCC} = 7.2 Hz, 2C), 48.6 (d, *J*_{PCCC} = 6.1 Hz, 4C), 43.1 (2C), 34.0 (2C), 31.3 (2C), 25.7 (2C), 21.9 (d, *J*_{PCC} = 138 Hz, 2C), 21.8 (2C), 17.1 (2C), 15.7 (2C); [α]_D²⁵ = -17.1° (chloroform).

(S_p)-Menthyl [(diphenylphosphino)methyl]phenylphosphinate 32:



To a solution of (S_p) -30 (676 mg, 2 mmol, 1 equiv, 96% de) in tetrahydrofuran (10 mL) was added at -78°C and under N₂ isopropylmagnesium chloride (1.1 mL, 2.2 mmol, 1.1 equiv, 2.0M solution). After 2 hours at -78°C, chlorodiphenylphosphine (0.37 mL, 2 mmol, 1 equiv) was added. The dry-ice bath was removed and the reaction was allowed to warm up to rt and was stirred for 4 hours at rt. A saturated solution of NH₄Cl was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (3X). The combined organic layers was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 98:2) to afford the product as a white solid (371 g, 39%, 96% de). Mp = 54-55°C; ³¹P NMR (162 MHz, CDCl₃): δ = 32.2 (d, *J* = 9.7 Hz, 46%), 11.9 (s, 54%); ¹H NMR (400 MHz, CDCl₃): δ = 7.84-7.92 (m, 2H), 7.50-7.59 (m, 4H), 7.39-7.49 (m, 4H), 7.32-7.38 (m, 1H), 7.21-7.31 (m, 4H), 4.09-4.20 (m, 1H), 3.03 (dd, *J* = 2.1 and 11.1 Hz, 1H), 2.99 (d, *J* = 11.1 Hz, 1H), 2.07 (dquint, *J* = 2.1 and 7.0 Hz, 1H), 1.51-1.65 (m, 3H), 1.12-1.29 (m, 2H), 0.69-1.50 (m, 3H), 0.94 (q, *J* = 11.0 Hz, 1H), 0.69-0.97 (m, 2H), 0.87 (d, *J* = 7.0 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.70 (d, *J* = 6.5 Hz, 3H);

¹³C NMR (101 MHz, CDCl₃): δ = 132.8 (d, *J*_{PCCC} = 9.9 Hz, 2C), 132.7 (d, *J*_{PCCC} = 9.6 Hz, 2C), 132.2 (d, *J*_{PC} = 134 Hz), 132.1 (d, *J*_{PCCCC} = 2.8 Hz), 131.5 (d, *J*_{PCCC} = 10.5 Hz, 2C), 131.4 (d, *J*_{PCCCC} = 2.3 Hz), 131.2 (d, *J*_{PCCCC} = 2.4 Hz), 128.7 (d, *J*_{PCC} = 10.7 Hz, 2C), 128.5 (d, *J*_{PC} = 134 Hz), 128.5 (d, *J*_{PC} = 135 Hz), 128.4 (d, *J*_{PCC} = 10.3 Hz, 2C), 128.2 (d, *J*_{PCC} = 13.3 Hz, 2C), 77.7 (d, *J*_{POC} = 7.4 Hz), 48.5 (d, *J*_{POCC} = 5.3 Hz), 42.9, 33.9, 31.4, 28.8 (dd, *J*_{PC} = 92.6 Hz), 25.5, 22.7, 21.9, 21.2, 15.6; HRMS (EI+) m/z calcd for C₂₉H₃₆O₂P₂ ([M]⁺) 478.2191, found 478.2190; [α]_P²⁴ = -0.9° (chloroform).

(*R_p*)-Menthyl (hydroxymethyl) (3-phenylpropyl)phosphinate 33:



To a suspension of Pd/C (191 mg, 0.18 mmol, 10 mol%) in ethanol (2 mL) flushed with N₂ was added a solution of (R_p)-4 (630 g, 1.8 mmol, 1 equiv, >99% de) in ethanol (8 mL). The tube was placed in a hydrogenator and stirred for 20 hours at 50 psi of H₂. The suspension was then filtered through celite and the solid was washed with ethanol three times. The filtrate was concentrated under vacuum to afford the product as a white solid (633 g, 100%, 98% de). ³¹P NMR (162 MHz, CDCl₃): δ = 52.5 (septuplet, J = 6.5 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.24-7.31 (m, 2H), 7.13-7.21 (m, 3H), 4.12-4.22 (m, 1H), 3.83 (dd, J = 6.1 and 14.5 Hz, 1H), 3.75 (dd, J = 1.9 and 14.5 Hz, 1H), 2.69 (t, J = 7.4 Hz, 2H), 2.01-2.12 (m, 2H), 1.88-1.99 (m, 2H), 1.74-1.84 (m, 2H), 1.61-1.69 (m, 2H), 1.37-1.51 (m, 1H), 1.25-1.34 (m, 1H), 1.16 (q, J = 11.3 Hz, 1H), 0.98 (dquint, J = 2.5 and 12.8 Hz, 1H), 0.90 (d, J = 6.4 Hz, 3H), 0.90 (d, J = 7.2 Hz, 3H), 0.69-0.90 (m, 1H), 0.77 (d, J = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 141.0, 128.5 (2C), 128.4 (2C), 126.1, 76.3 (d, J_{PCC} = 7.7 Hz), 59.8 (d, J_{PCC} = 105 Hz), 48.6 (d, J_{POCC} = 5.6 Hz), 43.6, 36.8 (d, J_{PCC} = 15.7 Hz), 34.0, 31.5, 25.9 (d, J_{PC} = 90.2 Hz), 25.6, 23.3 (d, J_{PCCC} = 3.5 Hz), 22.7, 22.0, 21.0, 15.6.

(S_p)-Menthyl (3-phenylpropyl)-H-phosphinate 19:



To a solution of N-chlorosuccinimide (721 mg, 5.4 mmol, 3 equiv) in dichloromethane (30 mL) at -78°C and under N₂ was added dropwise a solution of dimethyl sulfide (0.4 mL, 5.4 mmol, 3 equiv) in dichloromethane (5 mL). After 10 minutes at -78°C, a solution of (R_p) -33 (630 mg, 1.8 mmol, 1 equiv, 98% de) in dichloromethane (5 mL) was added over 20 minutes. After 1h at -78°C, triethylamine (1.25 mL, 9 mmol, 5 equiv) was added over 15 minutes and the reaction was allowed to warm up to rt. After 1h at rt, water was added and the two layers were separated. The aqueous layer was extracted with dichloromethane (X2). The combined organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 99:1 to 97:3) to afford the product as a colorless oil (554 mg, 96%, 96% de). ³¹P NMR (162 MHz, CDCl₃): δ = 33.3 (dsextuplet, *J* = 12.7 and 528 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.16-7.23 (m, 2H), 7.05-7.13 (m, 3H), 7.08 (d, / = 528 Hz, 1H), 4.07-4.19 (m, 1H), 2.62 (t, / = 7.4 Hz, 2H), 1.99-2.10 (m, 2H), 1.77-1.91 (m, 2H), 1.53-1.73 (m, 4H), 1.21-1.43 (m, 2H), 1.02 (q, J = 11.6 Hz, 1H), 0.94 (dquint., J = 3.0 and 12.4 Hz, 1H), 0.84 (d, J = 6.8 Hz, 6H), 0.69-0.85 (m, 1H), 0.74 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 140.7, 128.4 (2C), 128.4 (2C), 126.1, 76.7 (d, *J*_{POC} = 7.4 Hz), 48.3 (d, JPOCC = 5.9 Hz), 41.6, 36.2 (d, JPCC = 16.0 Hz), 33.9, 31.3, 28.1 (d, JPC = 95.0 Hz), 25.6, 22.9, 22.4 (d, J_{PCCC} = 2.5 Hz), 21.9, 20.8, 15.7; [α]_D²³ = -27.3^o (chloroform).

(*R_p*)-1-Menthyloxy-1,2,3,4-tetrahydro-1-phosphinoline-1-oxide 34:



To a suspension of $Mn(OAc)_2$ (8.7 mg, 0.05 mmol, 5 mol%), MnO_2 (261 mg, 3 mmol, 3 equiv.) and sodium acetate (246 mg, 3 mmol, 3 equiv.) in acetic acid (2.5 mL) at 70°C under N2 was added a solution of (S_p) -19 (322 mg, 1 mmol, 1 equiv, 96% de) in acetic acid (2.5 mL) over 2 h via a syringe pump. The reaction mixture was then stirred for an additional 2h at 70°C under N₂. Ethyl acetate (\sim 30 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~40 mL) were added. The suspension was stirred vigorously for 5 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of $Na_2S_2O_4$ 0.2M saturated with NaHCO₃ (~40 mL), a saturated aqueous solution of NaHCO₃ (~ 40 mL) and brine (~ 40 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 95:5) to afford the product as a colorless oil (300 mg, 94%, 96% de). ³¹P NMR (162 MHz, CDCl₃): $\delta = 36.3$ (s); ¹H NMR (400 MHz, CDCl₃): $\delta = 7.71$ -7.79 (m, 1H), 7.28-7.34 (m, 1H), 7.20-7.27 (m, 1H), 7.05-7.12 (m, 1H), 4.17-4.28 (m, 1H), 2.33-2.47 (m, 2H), 1.54-1.79 (m, 6H), 1.53-1.62 (m, 2H), 1.29-1.42 (m, 1H), 1.18-1.28 (m, 1H), 1.02 (q, J = 10.9 Hz, 1H), 0.94 (dquint., J = 2.6 and 12.5 Hz, 1H), 0.83 (d, J = 7.0 Hz, 3H), 0.79 (d, J = 6.9 Hz, 3H), 0.79 (d, J = 6.6 Hz, 3H), 0.75 (dquint, J = 3.2 and 12.8 Hz, 1H); ¹³C NMR (101 MHz, CDCl₃): $\delta = 143.7$ (d, $J_{PCC} =$ 9.9 Hz), 131.6 (d, JPCCCC = 2.4 Hz), 129.8 (d, JPCCC = 5.1 Hz), 129.8 (d, JPC = 123 Hz), 128.9 (d, JPCC = 11.5 Hz), 126.5 (d, JPCCC = 11.5 Hz), 76.4 (d, JPOC = 7.2 Hz), 48.6 (d, JPOCC = 5.9 Hz), 43.6, 34.0, 31.5, 31.3 (d, /PCC = 8.5 Hz), 26.5 (d, /PC = 92.8 Hz), 25.6, 22.7, 22.0, 21.2 (d, /PCCC = 5.1 Hz), 21.1, 15.6; HRMS (EI+) m/z calcd for C₁₉H₂₉O₂P ([M]⁺) 320.1905, found 320.1907; $[\alpha]_D^{22} = -8.6^{\circ}$ (chloroform).

(S_p)-1-menthyl-2,3-diphenyl-1-phosphindole 35:5



To a suspension of Mn(OAc)₂ (8.7 mg, 0.05 mmol, 5 mol%), MnO₂ (261 mg, 3 mmol, 3 equiv.), sodium acetate (246 mg, 3 mmol, 3 equiv.) and diphenylacetylene (178 mg, 1 mmol, 1 equiv.) in acetic acid (2.5 mL) at 70°C under N₂ was added a solution of (R_p)-1 (280 mg, 1 mmol, 1 equiv, >99% de) in acetic acid (2.5 mL) over 2 h *via* a syringe pump. The reaction mixture was then stirred for an additional 2h at 70°C under N₂. Ethyl acetate (~ 30 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~40 mL) were added. The suspension was stirred vigorously for 5 minutes, filtered through celite and the two layers were separated. The organic layer was washed with an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~ 40 mL) and brine (~ 40 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 98:2) to afford the product as a white solid (130 mg, 29%, > 99% de). Mp = 159-160°C; ³¹P NMR (162 MHz, CDCl₃): δ = 44.8 (s); ¹H NMR (400 MHz, CDCl₃): δ = 7.69-7.79 (m, 1H), 7.05-7.56 (m, 13H), 4.29-4.42 (m, 1H), 2.25-2.38 (s, 1H), 1.53-1.76 (m, 3H), 1.38-1.51 (m, 1H), 1.16-1.36 (m, 2H), 0.75-1.10 (m, 2H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.66 (d, *J* = 7.0 Hz, 3H), 0.43 (d, *J* = 6.8 Hz, 3H); HRMS (EI+) m/z calcd for C₃₀H₃₃O₂P ([M]⁺) 456.2218, found 456.2212; [α]_D²⁵ = -52.9° (chloroform).

(*R_p*)-Menthyl (acetoxymethyl)cyclohexylphosphinate 36:



To a solution of (R_p) -7 (2.76 g, 10 mmol, 1 equiv, 96% de) in acetonitrile (40 mL) in a sealed tube was added cyclohexene (2.03 mL, 20 mmol, 2 equiv) and AIBN (82 mg, 0.5 mmol, 5 mol%) and the reaction was stirred at reflux under N₂ for 2 hours. After cooling down the reaction to rt, AIBN (82 mg, 0.5 mmol, 5 mol%) was added and the reaction was stirred at reflux under N₂ for 2 hours. 2 additional addition of AIBN was made every 2 hours. 2 hours after the last addition, the reaction was cooled down to rt (81% NMR).

(S_p)-Menthyl (acetoxymethyl)(1-hydroxycyclohexyl)phosphinate 37:



To a solution of (Sp)/(Rp)-7 (13.8 g, 50 mmol, 1 equiv, dr 54:46) in toluene (75 mL) was added at rt and under N₂ pyridine (0.4 mL, 5 mmol, 0.1 equiv) and cyclohexanone (10.3 mL, 100 mmol, 2 equiv). The reaction mixture was stirred for 3 days at reflux. After cooling down to rt, the solvent was removed under vacuum and the residue obtained was purified by column chromatography (dichloromethane/acetone 98:2 to 90:10) to afford the (R_p)/(S_p) mixture product as a white solid (15 g, 80%, 54:46 dr). This solid was recrystallized at -18°C in diethyl ether to afford the product as a white solid (5.1 g, 27%, 92% de). Mp = 125-126°C; ³¹P NMR (162 MHz, CDCl₃): δ = 42.6 (s); ¹H NMR (400 MHz, CDCl₃): δ = 4.46-4.55 (m, 2H), 4.25-4.35 (m, 1H), 3.22 (s, 1H), 2.19 (dquint, *J* = 2.7 and 7.0 Hz, 1H), 2.10-2.16 (m, 1H), 2.12 (s, 3H), 1.91-1.98 (m, 1H), 1.77-1.85 (m, 1H), 1.64-1.74 (m, 7H), 1.54-1.63 (m, 3H), 1.41-1.52 (m, 1H), 1.31-1.40 (m, 1H), 1.16-1.29 (m, 1H), 1.14 (q, *J* = 11.2 Hz, 1H), 1.01 (dquint, *J* = 3.5 and 12.4 Hz, 1H), 0.92 (d, *J* = 7.0 Hz, 3H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.78-0.92 (m, 1H), 0.81 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 170.2 (d, *J*_{PCCC} = 7.5 Hz), 77.5 (d, *J*_{PCCC} = 8.9 Hz), 72.3 (d, *J*_{PCC} = 116 Hz), 57.2 (d, *J*_{PCC} = 97.9 Hz), 48.8 (d, *J*_{PCCC} = 5.3 Hz), 43.2, 34.0, 31.6, 30.8 (d, *J*_{PCCC} = 3.5 Hz), 30.2 (d, *J*_{PCCC} = 3.7 Hz), 25.4, 22.6, 22.0, 21.2, 20.7, 20.0 (d, *J*_{PCC} = 9.9 Hz), 19.9 (d, *J*_{PCC} = 10.1 Hz), 15.4; [α]_{D²⁴} = -22.4° (chloroform).

(R_p)-Menthyl (acetoxymethyl)(cyclohex-1-ene)phosphinate 38:



To a solution of (S_p) -37 (374 mg, 1 mmol, 1 equiv, 92% de) in benzene (5 mL) was added at rt under N₂ thionyl chloride (0.087 mL, 1.2 mmol, 1.2 equiv.) followed by triethylamine (0.17 mL, 1.2 mmol, 1.2 equiv.). The mixture was then stirred for 16 h at reflux under N₂. After cooling down the reaction to rt, the solvent was removed under vacuum. The residue obtained was solubilized in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column

chromatography (dichloromethane/acetone 99:1 to 95:5) to afford the product as a colorless oil (307 mg, 86%, 92% de). ³¹P NMR (162 MHz, CDCl₃): δ = 32.8 (s); ¹H NMR (400 MHz, CDCl₃): δ = 6.71 (d, *J* = 20.4 Hz, 1H), 4.03-4.31 (m, 3H), 1.98-2.16 (m, 5H), 1.99 (s, 3H), 1.92 (dquint, *J* = 2.5 and 7.0 Hz, 1H), 1.46-1.61 (m, 6H), 1.27-1.40 (m, 1H), 1.17-1.26 (m, 1H), 1.06 (q, *J* = 11.4 Hz, 1H), 0.88 (dq, *J* = 2.4 and 10.6 Hz, 1H), 0.79 (d, *J* = 6.4 Hz, 3H), 0.79 (d, *J* = 7.0 Hz, 3H), 0.67-0.79 (m, 1H), 0.64 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 170.0 (d, *J*_{PCOC} = 8.1 Hz), 144.3 (d, *J*_{PCC} = 7.9 Hz), 129.0 (d, *J*_{PCC} = 127 Hz), 76.7 (d, *J*_{POC} = 7.3 Hz), 59.4 (d, *J*_{PC} = 115 Hz), 48.5 (d, *J*_{POCC} = 5.8 Hz), 43.5, 33.9, 31.5, 26.0 (d, *J*_{PCC} = 15.4 Hz), 25.5, 24.1 (d, *J*_{PCCC} = 9.8 Hz), 22.7, 21.9 (d, *J*_{PCCC} = 8.9 Hz), 21.9, 21.2, 21.0, 20.4, 15.6; HRMS (EI+) m/z calcd for C₁₉H₃₃O₄P ([M]⁺) 356.2116, found 356.2114; [α]_{D²³} = -28.7⁰ (chloroform).

(*R_p*)-Menthyl (hydroxymethyl)cyclohexylphosphinate 39:



To a solution of (R_p)-38 (356 mg, 1 mmol, 1 equiv, 92% de) in methanol (5 mL) was added potassium carbonate (14 mg, 0.1 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and the crude obtained was purified by column chromatography (dichloromethane/acetone 95:5 to 85:15) to afford the product as a white solid (135 mg, 43%, 80% de). Mp = 80-81°C; ³¹P NMR (162 MHz, CDCl₃): δ = 38.7 (s); ¹H NMR (400 MHz, CDCl₃): δ = 6.74 (d, *J* = 20.4 Hz, 1H), 5.16 (s, 1H), 4.03-4.13 (m, 1H), 3.76-3.89 (m, 2H), 2.07-2.22 (m, 5H), 1.99 (dquint, *J* = 2.5 and 7.0 Hz, 1H), 1.52-1.71 (m, 6H), 1.32-1.46 (m, 1H), 1.19-1.30 (m, 1H), 1.10 (q, *J* = 11.2 Hz, 1H), 0.92 (dq, *J* = 2.5 and 12.8 Hz, 1H), 0.86 (d, *J* = 6.1 Hz, 3H), 0.84 (d, *J* = 6.6 Hz, 3H), 0.73-0.90 (m, 1H), 0.69 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 143.6 (d, *J*_{PCC} = 7.4 Hz), 129.0 (d, *J*_{PCC} = 119 Hz), 76.4 (d, *J*_{PCC} = 7.7 Hz), 58.8 (d, *J*_{PC} = 112 Hz), 48.6 (d, *J*_{PCC} = 10.4 Hz), 21.1, 21.0, 15.7; HRMS (EI+) m/z calcd for C₁₇H₃₁O₃P ([M]+) 314.2011, found 314.2007; [α]_D²⁴ = -29.9° (chloroform).

To a suspension of Pd/C (34 mg, 0.032 mmol, 10 mol%) in ethanol (1 mL) flushed with N₂ was added a solution of (R_p)-menthyl (hydroxymethyl)(cyclohex-1-ene)phosphinate (100 mg, 0.32 mmol, 1 equiv, 80% de) in ethanol (4 mL). The tube was placed in a hydrogenator and stirred for 20 hours at 50 psi of H₂. The suspension was then filtered through celite and the solid was washed with ethanol three times. The filtrate was concentrated under vacuum to afford the product as a white solid (102 mg, 100%, 80% de). Mp = 134-135°C; ³¹P NMR (162 MHz, CDCl₃): δ = 51.8 (s, 90%); ¹H NMR (400 MHz, CDCl₃): δ = 50.6 (s, 1H), 4.10-4.23 (m, 1H), 3.76-3.89 (m, 2H), 2.04-2.22 (m, 2H), 1.74-2.03 (m, 5H), 1.69-1.71 (m, 3H), 1.16-1.48 (m, 7H), 1.07 (q, *J* = 11.4 Hz, 1H), 0.97 (dq, *J* = 2.5 and 12.8 Hz, 1H), 0.89 (d, *J* = 7.0 Hz, 3H), 0.88 (d, *J* = 6.4 Hz, 3H), 0.74-0.87 (m, 1H), 0.79 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 76.0 (d, *J*_{PCC} = 8.0 Hz), 58.2 (d, *J*_{PCC} = 13.9 Hz), 25.9, 25.4, 25.3 (d, *J*_{PCCC} = 3.3 Hz), 24.8 (d, *J*_{PCCC} = 2.9 Hz), 22.6, 22.1, 21.1, 15.5; HRMS (EI+) m/z calcd for C₁₇H₃₃O₃P ([M]⁺) 316.2167, found 316.2162; [α]_D²³ = -32.1° (chloroform).

(*R_p*)-Menthyl (hydroxymethyl)cyclohexylphosphinate 39:



To a solution of $(S_p)/(R_p)$ -7 (13.8 g, 50 mmol, 1 equiv, 54:46 dr) in toluene (75 mL) was added at rt and under N₂ pyridine (0.4 mL, 5 mmol, 0.1 equiv) and cyclohexanone (10.3 mL, 100 mmol, 2 equiv). The reaction mixture was stirred for 3 days at reflux. After cooling down to rt, the solvent was removed under vacuum and the residue obtained was purified by column chromatography (dichloromethane/acetone 98:2 to 90:10) to afford the (R_p)/(S_p) mixture as a white solid (15 g, 80%). ³¹P NMR (162 MHz, CDCl₃): δ = 43.9 (s, 46%), 42.8 (s, 54%).

To a solution of $(S_p)/(R_p)$ -37 (10.5 g, 28 mmol, 1 equiv, 54:46 dr) in benzene (80 mL) was added at rt under N₂ thionyl chloride (2.3 mL, 31 mmol, 1.1 equiv.) followed by triethylamine (4.3 mL, 31 mmol, 1.1 equiv.). The mixture was then stirred for 16 h at reflux under N₂. After cooling down the reaction, the solvent was removed under vacuum. The residue obtained was solubilized in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 99:1 to 95:5) to afford the product as a colorless oil (8.57 g, 86%). ³¹P NMR (162 MHz, CDCl₃): δ = 37.9 (s, 42%), 37.2 (s, 58%).

To a solution of the crude obtained (8.5 g, 24 mmol, 1 equiv, 52:48 dr) in methanol (50 mL) was added potassium carbonate (331 mg, 2.4 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum and the crude obtained was purified by column chromatography (dichloromethane/acetone 80:20) to afford the product as a white solid (6.58 g, 87%). ³¹P NMR (162 MHz, CDCl₃): δ = 39.2 (s, 44%), 38.5 (s, 56%).

To a suspension of Pd/C (2.2 g, 2.07 mmol, 10 mol%) in ethanol (25 mL) flushed with N₂ was added a solution of the crude obtained (6.5 g, 20.7 mmol, 1 equiv) in ethanol (50 mL). The flask was placed in a hydrogenator and stirred for 4 days at 50 psi of H₂. The suspension was then filtered through celite and the solid was washed with ethanol three times. The filtrate was concentrated under vacuum to afford the product as a white solid (6.54 g, 100%). This solid was crystallized in ethyl acetate (200 mL) at rt to afford the product as a white solid (1.55 g, 24%, > 99% de, 14% overall yield). ³¹P NMR (162 MHz, CDCl₃): δ = 47.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 4.76-4.83 (m, 1H), 4.11-4.22 (m, 1H), 3.78-3.90 (m, 2H), 2.18-2.25 (m, 1H), 1.89-2.06 (m, 3H), 1.76-1.88 (m, 3H), 1.60-1.73 (m, 3H), 1.18-1.51 (m, 7H), 1.11 (q, *J* = 11.0 Hz, 1H), 0.98 (dq, *J* = 2.5 and 12.9 Hz, 1H), 0.90 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.77-0.90 (m, 1H), 0.79 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 76.5 (d, *J*_{PCC} = 8.0 Hz), 57.5 (d, *J*_{PCC} = 14.7 Hz), 25.9, 25.5, 25.3 (d, *J*_{PCC} = 3.2 Hz), 24.7 (d, *J*_{PCCC} = 3.1 Hz), 22.7, 22.0, 21.2, 15.6; HRMS (EI+) m/z calcd for C₁₇H₃₃O₃P ([M]⁺) 316.2167, found 316.2162; [α]_{D²³} = -32.1° (chloroform).

(*R_p*)-Menthyl (hydroxymethyl)cyclohexylphosphinate 39:



To a solution of $(R_p)/(S_p)$ -7 (8.28 g, 30 mmol, 1 equiv, 54:46 dr) in DMSO (150 mL) was added Mn(OAc)₂ (368 mg, 1.5 mmol, 5 mol%) and cyclohexene (15.2 mL, 150 mmol, 5 equiv.) and the reaction was stirred at 100°C under N₂ for 16 hours. After cooling down the reaction to rt, ethyl acetate (~ 150 mL) and an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~150 mL) were added and the suspension was stirred vigorously for 5 minutes. The 2 layers were separated and the organic layer was washed with an aqueous solution of Na₂S₂O₄ 0.2M saturated with NaHCO₃ (~150 mL), a saturated aqueous solution of NaHCO₃ (~ 150 mL) and brine (~ 150 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 100:0 to 94:6) to afford the product as a colorless oil (5.37 g, 50%).

To a solution of the crude obtained (5.37 g, 15 mmol, 1 equiv, 54:46 dr) in methanol (50 mL) was added potassium carbonate (207 mg, 1.5 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt.

The solvent was removed under vacuum and the crude obtained was purified by column chromatography (dichloromethane/acetone 95:5 to 60:40) to afford the product as a white solid (4.31 g, 91%). This solid was crystallized in acetonitrile at rt to afford the product as a white solid (1.47g, 31%, > 99% de). Mp = 143-144 °C; ³¹P NMR (162 MHz, CDCl₃): δ = 52.3 (s); ¹H NMR (400 MHz, CDCl₃): δ = 4.35-4.42 (m, 1H), 4.13-4.24 (m, 1H), 3.80-3.91 (m, 2H), 2.19-2.27 (m, 1H), 1.90-2.07 (m, 3H), 1.78-1.88 (m, 3H), 1.62-1.74 (m, 3H), 1.20-1.51 (m, 7H), 1.13 (q, *J* = 11.0 Hz, 1H), 0.99 (dq, *J* = 2.8 and 12.7 Hz, 1H), 0.78-0.95 (m, 1H), 0.92 (d, *J* = 7.1 Hz, 3H), 0.91(d, *J* = 6.4 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 76.6 (d, *J*_{POC} = 8.0 Hz), 57.6 (d, *J*_{PC} = 99.3 Hz), 48.7 (d, *J*_{POCC} = 5.9 Hz), 44.0, 36.4 (d, *J*_{PCC} = 91.5 Hz), 34.1, 31.5, 26.3 (d, *J*_{PCC} = 13.7 Hz, 2C), 25.9, 25.5, 25.3 (d, *J*_{PCCC} = 3.3 Hz), 24.8 (d, *J*_{PCCC} = 3.0 Hz), 22.8, 22.0, 21.2, 15.6; HRMS (EI+) m/z calcd for C₁₇H₃₃O₃P ([M]⁺) 316.2167, found 316.2162; [α]_P²³ = -32.1° (chloroform).

$(R_p)/(S_p)$ Menthyl acetoxymethyl(1,1-diethoxyethyl)phosphinate 40:



 $(R_p)/(S_p)$ -7 (4.95 g, 17.9 mmol, 1 equiv, 51:49 dr), triethyl orthoformate (19.7 mL, 107.5 mmol, 6 equiv) and boron trifluoride diethyl etherate (0.45 mL, 3.6 mmol, 0.2 equiv.) were introduced in a flask and the reaction mixture was stirred at rt under N₂ for 24 hours. Ethyl acetate (~ 150 mL) and an aqueous solution of NaHCO₃ (~150 mL) were added and the 2 layers were separated. The organic layer was washed with brine (~ 150 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (hexane/ethyl acetate 90:10 to 70:30) to afford the product as a colorless oil (5.17 g, 74%). ³¹P NMR (162 MHz, CDCl₃): δ = 35.9 (s, 52%) and 35.1 (s, 48%).

$(R_p)/(S_p)$ Menthyl hydroxymethyl(1,1-diethoxyethyl)phosphinate 41:



To a solution of 40 (6.6 g, 17 mmol, 1 equiv) in methanol (30 mL) was added potassium carbonate (235 mg, 1.7 mmol, 0.1 equiv.) and the mixture was stirred for 20 h at rt. The solvent was removed under vacuum to afford the product as a colorless oil (5.95 g, 100%). ³¹P NMR (162 MHz, CDCl₃): δ = 42.0 (s, 53%) and 41.7 (s, 47%).

(R_p)/(S_p) Menthyl (1,1-diethoxyethyl)-H-phosphinate 43:



To a solution of concentrated H_3PO_2 (3.3 g, 50 mmol, 1 equiv) was added slowly, at room temperature under nitrogen, trifluoroacetic acid (1.14 mL, 10 mmol, 0.2 equiv) followed by triethyl orthoformate (20 mL, 110 mmol, 2.2 equiv.). After 4 hours of stirring at room temperature, chloroform was added (100 mL) as well as a saturated aqueous solution of NaHCO₃ (~100 mL). The 2

layers were separated and the organic layer was washed with brine (~ 100 mL), dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a yellow oil (9.87 g, 84% purity). ³¹P NMR (162 MHz, CDCl₃): δ = 31.0 (d, *J* = 543 Hz, 84%), 17.4 (s, 3%) and 7.3 (d, 13%). ¹H NMR (400 MHz, CDCl₃): δ = 6.96 (d, *J* = 543 Hz, 1H), 4.09-4.32 (m, 2H), 3.63-3.82 (m, 4H), 1.50 (d, *J* = 12.6 Hz, 3H), 1.40 (t, *J* = 7.0 Hz, 3H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.24 (t, *J* = 7.0 Hz, 3H).

To a solution of *ethyl* (1,1-*diethoxyethyl*)-*H*-*phosphinate* (6 g, 28.6 mmol, 1 equiv, 84% purity) in toluene (40 mL) was added L-menthol (17.85 g, 114 mmol, 4 equiv) followed by Ti(OiPr)₄ (0.85 mL, 2.86 mmol, 10 mol%). The reaction mixture was stirred for 24 hours under N₂ at a slow reflux with a Dean-Stark trap to remove the etanol generated during the reaction. After cooling down the reaction to rt, the solvent was removed under vacuum and the residue was purified by column chromatography (dichloromethane/acetone 100:0 to 95:5) to afford the product a colorless oil (5.44 g, 72%). ³¹P NMR (162 MHz, CDCl₃): δ = 29.8 (s, 51%), 25.3 (s, 49%).

$(R_p)/(S_p)$ Menthyl hydroxymethyl(1,1-diethoxyethyl)phosphinate 41:



To a solution of *menthyl* (1,1-*diethoxyethyl*)-*H*-*phosphinate* (5.12 g, 16 mmol, 1 equiv, 51:49 dr) in toluene (30 mL) was added paraformaldehyde (0.53 g, 17.6 mmol, 1.1 equiv). The reaction mixture was stirred in a sealed tube at reflux for 20 hours under N₂. After cooling down the reaction to rt, the solvent was removed under vacuum and the residue was purified by column chromatography (dichloromethane/acetone 100:0 to 90:10) to afford the product a colorless oil (2.58 g, 46%). ³¹P NMR (162 MHz, CDCl₃): δ = 42.0 (s, 54%) and 41.7 (s, 46%).

$(R_p)/(S_p)$ Menthyl benzoxymethyl (hydroxymethyl)phosphinate 44:



To a solution of $(R_p)/(S_p)$ -2 (4.68 g, 20 mmol, 1 equiv, 54:46 dr) in dichloromethane (30 mL) at 0°C and under N₂ was added bis(trimethylsilyl)acetamide (10 mL, 40 mmol, 2 equiv) followed by benzyl chloromethyl ether (5.6 mL, 40 mmol, 2 equiv). The ice-bath was removed and the reaction mixture was then stirred for 20 h at rt. Methanol was added (1.62 mL, 40 mmol, 2 equiv) and the reaction mixture was concentrated under vacuum. The residue obtained was dissolved in ethyl acetate and the organic layer was washed with a saturated aqueous solution of NaHCO₃ and brine. The organic layer was dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was purified by column chromatography (dichloromethane/acetone 10:0 to 9:1) to afford the product as white solid (5.27 g, 74%). ³¹P NMR (162 MHz, CDCl₃): δ = 41.8 (s, 40%), 41.7 (s, 60%).

$(R_p)/(S_p)$ Menthyl acetoxymethyl(hydroxymethyl)phosphinate 45:



Paraformaldehyde (4.95 g, 165 mmol, 1.1 equiv) and hypophosphorous acid (9.9 g, 150 mmol, 1 equiv, 50% in water) were introduced in a round bottom flask and the reaction mixture was stirred for 24h at 75°C. The reaction was cooled down to rt and the crude was diluted in toluene (150 mL). L-

menthol (23.44 g, 150 mmol, 1 equiv) was added and the reaction mixture was stirred for 24h at reflux under N₂ in a flask equipped with a Dean-Stark trap. The solvent was then removed under vacuum and the residue obtained was dissolved in dichloromethane (300 mL). triethylamine (26 mL, 187.5 mmol, 1.25 equiv) and acetic anhydride (17.1 mL, 180 mmol, 1.2 equiv) was then added at 0°C under N₂. The ice-bath was removed and the reaction mixture was stirred for 16h at rt. The solvent was removed under vacuum and the residue obtained was solubilized in ethyl acetate. The organic layer was washed with NaHCO₃ and brine, dried over MgSO₄, filtered and concentrated under vacuum to afford the product as a white solid (38.7 g, 93%, 46:54 dr). ³¹P NMR (162 MHz, CDCl₃): δ = 25.9 (dm, *J* = 567 Hz, 46%), 21.9 (dm, *J* = 567 Hz, 54%).

To a solution of *menthyl (acetoxymethyl)-H-phosphinate* (38.7 g, 140 mmol, 1 equiv, 46:54 dr) in toluene (250 mL) was added paraformaldehyde (5.11 g, 170 mmol, 1.2 equiv) and the reaction was stirred at reflux under N₂ for 16 hours. The solvent was removed under vacuum to afford the product as a white solid (42.7 g, 100%, 52:48 dr). ³¹P NMR (162 MHz, CDCl₃): δ = 43.8 (s, 52%), 43.3 (s, 48%).

Menthyl [(3,5-dinitrobenzoyloxy)methyl](acetoxymethyl)phenylphosphinate 46:



To a solution of $(R_p)/(S_p)$ -45 (9.18 g, 30 mmol, 1 equiv, 54:46 dr) in dichloromethane (60 mL) was added at 0°C under N₂ triethylamine (4.81 mL, 34.5 mmol, 1.15 equiv) followed by 3,5-dinitrobenzoyl chloride (7.61 g, 33 mmol, 1.1 equiv) in dichloromethane (20 mL). The reaction mixture was then stirred for 20 hours at rt. The reaction mixture was concentrated under vacuum. The residue was dissolved in ethyl acetate (~ 100 mL) and the organic layer was washed with an aqueous solution of NaHCO₃ (~ 100 mL) and brine (~ 100 mL), dried over MgSO₄, filtered and concentrated under vacuum. The crude obtained was crystallized in toluene (80 mL) to obtain the product as yellow needles (4.35 g, 29%, >99% de). Mp = 139-140°C; ³¹P NMR (121.47 MHz, CDCl₃): δ = 34.9 (s); ¹H NMR (400 MHz, CDCl₃): δ = 9.27 (s, 1H), 9.17 (s, 2H), 4.71-4.84 (m, 2H), 4.48-4.57 (m, 2H), 4.36-4.47 (m, 1H), 2.13-2.22 (m, 1H), 2.15 (s, 3H), 2.02-2.11 (m, 1H), 1.65-1.74 (m, 2H), 1.36-1.57 (m, 2H), 1.25 (d, *J* = 11.8 Hz, 1H), 1.04 (d, *J* = 13.2 Hz, 1H), 0.85-0.97 (m, 1H), 0.94 (d, *J* = 6.2 Hz, 3H), 0.90 (d, *J* = 6.3 Hz, 3H), 0.82 (d, *J* = 6.7 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃): δ = 169.9 (d, *J*_{PCC} = 7.2 Hz), 162.0 (d, *J*_{PCC} = 7.1 Hz), 148.8 (2C), 132.6, 129.6 (2C), 123.0, 79.1 (d, *J*_{POC} = 7.8 Hz), 60.0 (d, *J*_{PC} = 112 Hz), 59.0 (d, *J*_{PCC} = 114 Hz), 48.4 (d, *J*_{POCC} = 5.9 Hz), 43.4, 33.8, 31.6, 25.9, 22.8, 21.9, 20.8, 20.5, 15.6; HRMS (EI+) m/z calcd for C₂₁H₃₀N₂O₁₀P ([M+H]+) 501.1638, found 501.1621; [α]_D²⁵ = -18.2° (chloroform).

(R_p)-Menthyl phenyl-H-phosphinate 1:1



To a solution of $(R_p)/(S_p)$ -1 (8.4 g, 30 mmol, 1 equiv, 50:50 dr) in diethylether (200 mL) was slowly added at rt under N₂ phosphorus trichloride (3.14 mL, 36 mmol, 1.2 equiv) followed by pyridine (2.91 mL, 36 mmol, 1.2 equiv). After 2 hours at rt, the reaction was cooled down to -78°C and then a mixture of diethylether – water (50 mL) was added over 20 minutes. After 4 hours at -78°C, the reaction was allowed to warm up to rt. Brine was added and the 2 layers were separated. The organic layer was dried over magnesium sulfate, filtered and concentrated. The crude obtained was purified by column chromatography (hexane/ethyl acetate 7:3) to afford the product as a colorless oil (7.3 g, 65%, 63% de). The oil obtained was crystallized in petroleum ether (7.5 mL) at -30°C to afford the product as a colorless oil (2.5 g, 22%, 96% de). ³¹P NMR (162 MHz, CDCl₃): δ = 24.7 (dm, *J* = 553 Hz); ¹H NMR (400 MHz, CDCl₃): δ = 7.73-7.84 (m, 2H), 7.66 (d, *J* = 553 Hz, 1H), 7.46-7.64 (m, 3H), 4.22-4.36 (m, 1H), 2.14-2.27 (m, 2H), 1.62-1.75 (m, 2H), 1.38-1.54 (m, 2H), 1.24 (q, *J* = 11.2 Hz, 1H), 0.78-1.13 (m, 2H), 0.96 (d, *J* = 7.0 Hz, 3H), 0.90 (d, *J* = 6.4 Hz, 3H), 0.86 (d, *J* = 7.0 Hz, 3H); [α]_D²³ = -35.5° (chloroform, literature with 90% de: -21.0° in benzene).

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exp1 Phosphorus

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bs	64	1b	1.00
d1	1.000	fn	not used
nt	16		DISPLAY
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exp1 Carbon

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sw	18115.9	in	n
at	1.301	dp	У
np	47120	hs	nn
fb	10000		PROCESSING
bs	64	1b	0.50
d1	2.000	fn	not used
nt	750		DISPLAY
ct	750	sp	-1135.5
TRANSMI	TTER	wp	18115.4
tn	C13	rf1	1136.1
sfrq	75.454	rfp	0
tof	766.0	rp	9.2
tpwr	58	lp	-182.4
pw	9.250		PLOT
DECOUP	LER	WC	250
dn	H1	SC	0
dof	0	۷S	332
cim	УУУ	th	6
dmm	W	ai	cdc ph
dpwr	35		
dmf	6700		



220 200 180 160 140 120 100 80 60 40 20 0 ppm

0B 876 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMPL	E		SPEC1	AL
date Dec	18 2012	tem)	not used
solvent	cdc13	gaii	า	25
file /home/	TCUuser~	spii	1	20
/vnmrsys/da	ta/auto~	hst		0.008
_2012.12.14	/s_2012~	pw9()	18.300
1218_04/dat	a/cdc13~	alfa	1 I	10.000
	01.fid		FLAG	S
ACQUISIT	ION	i 1		- n
sw	15797.8	in		n
at	1.600	db		v
np	50552	hs		ท่ง
fb	8800		PROCES	SING
bs	64	1b		1.00
d1	1.000	fn		not used
nt	16		DISPL	AY
ct	16	sp		-3647.3
TRANSMIT	TER	wp		15797.3
tn	P31	rf1		3647.8
sfrq	121.465	rfp		0
tof	7421.1	rp		68.9
tpwr	55	lp		-113.7
pw	9.150		PLO	Т
DECOUPL	ER	WC		250
dn	H1	SC		0
dof	0	VS		12
dm	УУУ	th		2
dmm	W	ai	cdc p	h
dpwr	35			
dmf	6700			



and send of the local data and so the send of the send

exp1 Phosphorus

	SAMPL	E		SPE	CIAL	
date	Dec	18 2012	temp)	no	t used
solvei	nt	cdc13	gair	ו		25
file,	/home/	TCUuser≁	spir	ı		20
/vnmrs	sys/da	ta/auto~	hst			0.008
_2012	.12.14	/s_2012~	pw9()		18.300
1218_0)4/data	a/cdc13~	alfe	1		10.000
		_02.fid		FL	AGS	
ACC	UISIT	ION	í 1			n
sw		15797.8	in			n
at		1.600	dp			V
np		50552	hs			ny
fb		8800		PROC	ESSI	IG
bs		64	1b			1.00
d1		1.000	fn		not	used:
nt		16		DIS	PLAY	
ct		16	sp			3647.3
TRA	ANSMIT	FER	wp		15	5797.3
tn		P31	rf1		3	3647.8
sfrq		121.465	rfp			0
tof		7421.1	rp			50.4
tpwr		55	lp		-	113.7
pw		9.150		P	LOT	
DE	COUPLI	ER	WC			250
dn		H1	SC			0
dof		0	VS			58
dm		ynn	th			4
dmm		w	ai	cdc	ph	
dpwr		35			•	
dmf		6700				



Compound (Bp)-3 ³¹P/¹H NMR coupled

etterenter and and a street and a	ng manang kang sa kang kanang kang kang kang kang kang k	na jyran yw anglaniai y para) dan inayya.	na tana matana kata mana mana kata kata kata kata kata kata kata k	of the second of the second	i antimur production and extension	runnun haupa	the second and the second s	ereiten tekster antisisteritter		*****	ja seden ser sere sere si se sere si se	njulijstainstitus ^t onstitutjen	det de state de tates de states
1 1 1	90	80 80	70	60 60	50	40	30	20	10	0	-10	-20	ppm



exp1 Carbon

SAMPLI	E		SPECIAL
date Dec	18 2012	temp	not used
solvent	cdc13	gain	20
file /home/	ſCUuser≁	spin	20
/vnmrsys/da	ta/auto~	hst	0.008
2012.12.14	/s 2012~	pw90	18.500
1218_04/data	a/cdc13~	alfa	10.000
	_03.fid		FLAGS
ACQUISIT	ION	i1	n
sw .	18115.9	in	n
at	1.301	dp	У
np	47120	hs	nn
fb	10000		PROCESSING
bs	64	1b	0.50
d1	2.000	fn	not used
nt	800		DISPLAY
ct	800	sp	-1135.5
TRANSMIT	TER	wp	18115.4
tn	C13	rf1	1136.1
sfrq	75.454	rfp	0
tof	766.0	rp	43.1
tpwr	58	lp	-199.8
pw	9.250		PLOT
DECOUPL	ER	WC	250
dn	H1	SC	0
dof	0	VS	483
dm	УУУ	th	7
dmm	W	ai	cdc ph
dpwr	35		
dmf	6700		





OB 882 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMPLE			SPECI	AL
date Dec 1	8 2012	tem	b	not used
solvent	cdc13	gai	'n	20
file /home/T	CUuser≁	iqa	n	20
/vnmrsys/dat	a/auto~	hst		0.008
_2012.12.14/	s_2012~	pw9	D	18.300
1218_31/data	/cdc13~	alf	a	10.000
	02.fid		FLAG	s
ACQUISITĪ	ON	i1		n
sw 1	5797.8	in		n
at	1.600	dp		v
np	50552	hs		nv
fb	8800		PROCES	SING
bs	64	1b		1.00
d1	1.000	fn		not used
nt	16		DISPL	ΑY
ct	16	sp		-3647.3
TRANSMITT	ER	wp		15797.3
tn	P31	rfl		3647.8
sfrq 1	21.465	rfp		0
tof	7421.1	гр		29.2
tpwr	55	lp		-113.7
pw	9.150		PL0	Г
DECOUPLE	R	WC		250
dn	H1	S C		0
dof	0	VS		7
dm	УУУ	th		2
dmm	W	ai	cdc pl	1
dpwr	35			
dmf	6700			



Compound (R_p)-5 ³¹P/^IH NMR decoupled

			9999 - Mar Balancel ang anto rang ngangangangan ang nganggang				da da namena mana mata any amin'	aller men en gelage støder fører och kalter i på stød kalt hat den er mit systemed en some		a the second	
90	80	70	60	50	40	30	2.0	10	 -10	-20	ppm

exp1 Phosphorus

	SAMPLE			SPECIAL
date	Dec 18	2012	temp	not used
solver	nt	cdc13	gain	20
file /	home/TC	Uuser~	spin	20
/vnmrs	ys/data	/auto~	hst	0.008
_2012.	12.14/s	2012~	pw90	18.300
1218_3	1/data/	cdc13~	alfa	10.000
	_0	4.fid		FLAGS
ACQ	UISITIO	N	i1	n
sw	15	797.8	in	n
at		1.600	dp	v
np		50552	hs	ny
fb		8800		PROCESSING
bs		64	16	1.00
d1		1.000	fn	not used
nt		16		DISPLAY
ct		16	sp	-3647.3
TRA	NSMITTE	R	wp	15797.3
tn		P31	rf1	3647.8
sfrq	12	1.465	rfp	0
tof	7	421.1	rp	31.8
tpwr		55	lp	-113.7
pw		9.150		PLOT
DE	COUPLER		wc	250
dn		H1	sc	0
dof		0	VS	26
dm		ynn	th	2
dmm		W	ai	cdc ph
dpwr		35		•
dmf		6700		



Compound (Bp)-5 ³¹P/¹H NMR coupled





exp1 Proton

SAMPLE date Dec 18 2012 solvent cdc13 file /home/TCUuser~ /vmmrsys/data/aucor~ _2012.12.14/s_2012~ 1218_28/data/cdc13~	DEC. & VT dfrq 75.454 dn Cl3 dpwr 43 dof 0 dm nnn dmm c fn 13100 PROCESSING wtfile proc ft fn not used werr xmreact wexp abortoff flus~ h procplot aborton wbs wnt		HOJJJ Compound (Fp.)-5 ¹ H NMR
14 13	12 11	10 9 8 7	
		$\begin{array}{r} 1.11 \ 1.04 \ 3.00 \\ 1.01.03 \end{array}$	2.22



 Lynch
 <thLynch</th>
 <thL

exp1 Carbon

SAMPL	E		SPECIAL
date Dec	18 2012	temp	not used
solvent	cdc13	gair	ע 20
file /home/	TCUuser∼	spir	n 20
/vnmrsys/da	ta/auto~	hst	0.008
_2012.12.14	/s_2012~	pw90	18.500
1218_31/dat	a/cdc13~	alfa	u 10.000
	_05.fid		FLAGS
ACQUISIT	ION	i 1	n
sw	18115.9	in	n
at	1.301	dp	У
np	47120	hs	nn
fb	10000		PROCESSING
bs	64	1b	0.50
d1	2.000	fn	not used
nt	1000		DISPLAY
ct	1000	sp	-1135.5
TRANSMIT	TER	wp	18115.4
tn	C13	rf1	1136.1
sfrq	75.454	rfp	0
tof	766.0	rp	-7.6
tpwr	58	lp	-201.1
pw	9.250		PLOT
DECOUPL	ER	WC	250
dn	H1	SC	0
dof	0	٧s	272
dm	УУУ	th	6
dmm	W	ai	cdc ph
dpwr	35		
dmf	6700		



Compound (B_p)-5 ¹³C NMR



OB 883 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

	SAMPLE			SPE	CIAL			
date	Dec 1	9 2012	tem)	no	bt	used	
solver	nt	cdc13	aair	1			25	
file	/home/T	CUuser~	spir	ו			2.0	
/vnmr	svs/dat	a/auto~	hst			0	. 008	
2012	.12.14/	s 2012~	nw9()		18	.300	
1219	02/data	/cdc13~	alfa	á		10		
	,	01.fid		È FI	AGS	x 0		
ACI	DUISITĪ	ON	11		1100		n	
SW	1	5797.8	in				'n	
at		1.600	db				v	
np		50552	hs				nv	
fb		8800		PROC	ESST	NG		
bs		64	16				1 00	
d1		1.000	fn		no	t.	used	
nt		16		DTS	PI AY			
ct		16	sn	0.0		36	47 3	
TRA	ANSMITT	FR	wn		1	57	97 3	
tn		P31	rf1		-	36	47 8	
sfra	1	21.465	rfn			00	ŏ	
tof		7421.1	rn				52 2	
towr		55	10			- 1	13 7	
wa		9.150	. 10	р	I OT	*	2011	
DI	COUPLE	R	wc	•			250	
dn		Η1	sc				0	
dof		0	vs				10	
dm		XXX	th				5	
dmm		Ŵ	ai	cdc	ph			
dpwr		35						
dmf		6700						



Compound (R_p)-6 ³¹P/¹H NMR decoupled

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ttttttttt-	0 N	80	70	C 0		1	20	<u> </u>	10				
	30	00	70	00	50	40	30	20	10	U	-10	-20	ppm

08 883

exp1 Phosphorus

SAMPL	E		SPECIAL
date Dec	19 2012	temp	not used
solvent	cdc13	gair	า 25
file /home/	TCUuser~	spir	n 20
/vnmrsys/da	ta/auto~	hst	0.008
_2012.12.14	/5 2012~	pw9(18.300
1219_02/dat	a/cdc13~	alfe	10.000
	02.fid		FLAGS
ACQUISIT	ĪON	i1	n
sw	15797.8	in	n
at	1.600	dp	v
np	50552	hs	nv
fb	8800		PROCESSING
bs	64	lb	1.00
d1	1.000	fn	not used
nt	16		DISPLAY
ct	16	sp	-3647.3
TRANSMIT	TER	wp	15797.3
tn	P31	rf1	3647.8
sfrq	121.465	rfp	0
tof	7421.1	rp	70.0
tpwr	55	lp	-113.7
pw	9.150		PLOT
DECOUPL	ER	WC	250
dn	H1	SC	0
dof	0	VS	59
dm	ynn	th	4
dmm	Ŵ	ai	cdc ph
dpwr	35		-
dmf	6700		



Compound (R_p)-6 ³¹P/¹H NMR coupled

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r	90	80	70	60	5 0	40	30	20	1.0	0	-10	-20	ppm

-37.382

-37.798



0B 883

exp1 Carbon

SAMPLE			SPECIAL
date Dec 19 2	012	temp	not used
solvent cd	c13	gain	20
file /home/TCUu	ser~	spin	20
/vnmrsys/data/a	uto~	hst	0.008
2012.12.14/5 2	012~	pw90	18.500
1219_02/data/cd	c13~	alfa	10.000
03.	fid		FLAGS
ACQUISITION		i 1	n
sw 1811	5.9	in	n
at 1.	301	dp	У
np 47	120	hs	nn
fb 10	000		PROCESSING
bs	64	1b	0.50
d1 2.	000	fn	not used
nt	800		DISPLAY
ct	800	sp	-1135.5
TRANSMITTER		wp	18115.4
tn	C13	rf1	1136.1
sfrg 75.	454	rfp	0
tof 76	6.0	rp	5.2
tpwr	58	lp	-204.1
pw 9.	250		PLOT
DECOUPLER		WC	250
dn	Η1	SC	0
dof	0	vs	510
dm	ууу	th	7
dmm	W	ai	cdc ph
dpwr	35		
dmf 6	700		





				но.) Bio		>				BRUKER
				С этру	ompound ¹ H NMR d	i (R _p)-4 lecoupled					Current Data Parameters NAME OB 2157 after column EXPNO 1 PROCNO 1
											$\begin{array}{cccc} F2 & - & Acquisition Parameters \\ Date 20150828 \\ Time 18.10 \\ INSTRUM spect \\ PROBHD 5 mm PABBO BB/ \\ PULPROG zgpg30 \\ TD 65536 \\ SOLVENT CDC13 \\ NS 16 \\ DS 4 \\ SWH 64102.563 Hz \\ FIDRES 0.978127 Hz \\ AQ 0.5111808 sec \\ RG 203.57 \\ DW 7.800 usec \\ DE 6.50 usec \\ TE 295.4 K \\ D1 2.0000000 sec \\ D11 0.0300000 sec \\ TD0 1 \\ \end{array}$
											SFO1 CHANNEL f1 science NUC1 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
											CHANNEL f2 SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.0000000 W PLW12 0.31604999 W PLW13 0.25600001 W
											F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40
100	90	 80	70	60		••••• 40	 30	20	 10	•••••• <u>•</u> •••••	nom

			но))- \	\rangle						BR	UKER	Ł
			Со этр,	/ ¹ H NMB	d (R _p)4 (coupled							Current NAME EXPNO PROCNO	Data Parameter OB 2157 after	s column 2 1
												F2 - Acq Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG RG DW DE TE D1 TD0	uisition Param 2015082: 18.1 spec: 5 mm PABBO BB, 2g3 6553 CDC1: 32 64102.565 0.97812 0.5111806 203.5 7.800 6.50 294.5 2.00000000	eters } 1 //) 3 4 3 Hz 7 Hz 3 8 7 1 0 0 0 0 0 0 0 0 0 0 0 0 0
												SFO1 NUC1 P1 PLW1	CHANNEL f1 === 161.9674942 31E 14.25	MHz) usec
												F2 - Prod SI SF WDW SSB LB GB PC	cessing paramet 32768 161.9755930 0 0 1.00 0	ers MHz Hz
+1+5+5+5+5+1+5+5+5+5+5+5+5+5+5+5+5+5+5+				~~~~~~				1995		«	n inanalkanawakan	₩.		
100	90 80	70	60	50	40	30	20	10	0	-10	ppn	ì		



					لر	D					
				ŕ	$\sim \sim $, I					
				3	Compour 'P/'H NMB	nd (R _p)-7 decoupled				Current Data NAME EXPNO PROCNO	Parameters OB 1904 1 1
										F2 - Acquisi Date Time INSTRUM PROBHD 5 m PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0	tion Parameters 20150121 11.14 spect m PABBO BB/ zgpg30 65536 Acetone 16 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 297.4 K 2.00000000 sec 0.03000000 sec 1
										SFO1 NUC1 P1 PLW1 SFO2 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12	NNEL f1 161.9674942 MHz 31P 14.25 usec 15.00000000 W NNEL f2 400.1316005 MHz 1H waltz16 90.00 usec 10.00000000 W 0.31604999 W
							<u> </u>			PLW13 F2 - Process SI SF WDW SSB 0 LB GB 0	0.25600001 W ing parameters 32768 161.9755930 MHz EM 1.00 Hz 1 40
80	70	60	50	40	30	20	10	0	-10	ppm	

			Comp ³¹ P/ ¹ H	oound (I NMR co	Bp)-7 upled			C N E P	urrent AME XPNO ROCNO	Data	Paramet OB 1	ers 904 2 1
								F D T I P P T S N D S S F A R D D T T D T	2 - Acc ate_ ime NSTRUM ROBHD ULPROG D OLVENT S S WH IDRES Q G G W E E 1 D D 0	puisit 5 mm	ion Par; 20150. 11 sp PABBO 1 23 65 Acet 64102. 0.978 0.5111 203 7. 6 29 2.00000	amete 121 21 3B/ 330 536 32 4 563 H 127 H 308 s .57 4 300 u .50 u .50 u .50 u .50 u .50 u
								= S N P P	F01 UC1 1 LW1	CHAN 1	INEL fl 61.9674 14 .5.00000	942 M 31P .25 u 200 W
								F S S S C O P	2 - Prc I F DW SB B B C	ocessi 1 0 0	ng para 32 .61.9755 1 1	neter 768 930 M EM .00 H .40





FRCEND FRCEND			AcO Comp	cound (R	p)-8a			Current Data Pa NAME OB 1 EXPNO	rameters 379 pure 5
					Japrea			FROCNO F2 - Acquisitio Date Time INSTRUM PROBHD 5 mm P PULPROG TD SOLVENT NS DS SWH 6 FIDRES AQ 0 RG DW DE TE D1 2. D11 0. TD0	1 Parame 20140320 18.02 spect ABBO BB/ 20065536 CDC13 16 4 4102.563 0.978127 .5111808 203.57 7.800 6.50 296.5 00000000 03000000
F2 - Processing para SI 32 SF 161.9755 WDW SSB 0 LB 1 GB 0 PC 1								SFO1 CHANNE SFO1 161 NUC1 P1 PLW1 15. SFO2 400 NUC2 CPDPRG {2 CPDPRG {2 PCPD2 PLW2 10. PLW12 0.	.9674942 31P 14.25)0000000 ; f2 .1316005 1H waltz16 90.00 00000000 31604999 25600001
		 						 F2 - Processing SI SF 161 WDW SSB 0 LB GB 0 PC	paramete 32768 9755930 EM 1.00 1.40

				Ac O	ound (R	,)-3a upled				Current D NAME EXPNO PROCNO F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TDO SFO1 NUC1 P1 PLW1 F2 - Proc SI SF SB LB GB PC	ata Parameters OB 1379 pure 2 1 isition Parameters 20140320 18.06 spect 5 mm PABBO BB/ 2g30 65536 CDC13 32 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 295.7 K 2.00000000 sec 1 CHANNEL f1 161.9674942 MHz 31P 14.25 usec 15.0000000 W essing parameters 32768 161.9755930 MHz EM 0 1.00 Hz 0 1.40
 80	70	60	50	40	30	20	 0	-10	ppm	GB (PC	0 1.40







			3		d (R _p)3 coupled					Current Data Parameters NAME OB 1438 pure EXPNO 2 PROCNO 1 F2 - Acquisition Parameters Date_ 20140424 Time 17.05 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG 2q30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 Hz
										FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 295.2 K D1 2.00000000 sec TD0 1 SFO1 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W F2 Processing parameters SI 32768 SF 161.9755930 MHz WDW EM
										WDW EAA SSB 0 LB 1.00 Hz GB 0 PC 1.40
90	 70	60	50	40	30	20	10	0	ppm	

7 1







Compound (B.)-8a	NAME OB 1843 after EXPNO 2 PROCNO 1
³¹ P/ ¹ H NMR coupled	F2 - Acquisition Parame Date20141121 Time 9.24 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zg30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.50 TE 296.1
	D1 2.0000000 TD0 1 =====CHANNEL fl === SF01 161.9674942 NUC1 31P P1 14.25 PLW1 15.0000000 F2 - Processing paramet
	SF 161.9755930 WDW EM SSB 0 LB 1.00 GB 0 PC 1.40
	Compound (Rp)-8a ^э ነթ/iH NMR coupled






TDO 	Compound (R _p)-8b ³¹ P/ ¹ H NMR coupled	NAME OB 1857 after EXPNO 2 PROCNO 1 F2 Acquisition Parame Date_ 20141203 Time 17.08 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG PULPROG 2330 TD 65536 SOLVENT CDC13 NS 32 DS 46 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.550 TE 297.7 D1 2.00000000
GB U		TD0 1











	Curre NAME EXPNO PROCN	nt Data Parameters OB 1419 pure 1 0 1
Сот ^э тр/тн Ni	pound 8b F2 MR decoupled Time INSTR PROBH PULPR TD SOLVE NS DS SWH FIDRE AQ RG DW DE TE D1 D11 TD0 TD0	Acquisition Parameter 20140411 10.39 UM spect D 5 mm PABBO BB/ OG 2gpg30 65536 NT CDC13 16 4 64102.563 H: S 0.978127 H: 0.5111808 sc 203.57 7.800 u: 6.50 u: 296.1 K 2.00000000 sc 0.03000000 sc
	SF01 NUC1 P1 PLW1	CHANNEL f1 161.9674942 M 31P 14.25 u 15.00000000 W
	SFO2 NUC2 CEDPR PCPD2 PLW2 PLW12 PLW13	=== CHANNEL f2 ===== 400.1316005 M 1H G[2 waltz16 90.00 u 10.00000000 W 0.31604999 W 0.25600001 W
	F2 - SI SF WDW SSB LB GB PC	Processing parameter 32768 161.9755930 M 6 0 1.00 H 0 1.40

*

 90	 80	 70	60	<u>50</u>	40	30	20	10	Ó	ppm			
											F2 - Pr SI SF WDW SSB LB GB PC	rocessing par 161.97 0 0	ameters 2768 55930 MHz EM 1.00 Hz 1.40
											SFO1 NUC1 P1 PLW1		4942 MHz 31P 4.25 usec
											INSTRUM PROBHD PULPROBHD TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	s 5 mm PABBO 64102 0.97 0.511 20 7 2.0000	pect BB/ zg30 5536 DCl3 32 4 .563 Hz 8127 Hz 1808 sec 3.57 .800 usec 6.50 usec 95.7 K 0000 sec 1
				HC	Сотроц	nd 8b coupled					Current NAME EXPNO PROCNO F2 - Acc Date_ Time	Data Parame OB quisition Pa 2014 1	ters 1415 2 1 rameters 0407 6.59







90	80	70	60	50	40	30	20	 10	0	-10	ppm	
use which is the manager of the	Manta jany kanta ketan keta	Mmdrth/Selicendesinglicates	andre with adressing and some	anaamintaanii yaasaa gaashiya ay	Hereford and the second and the second	hansyndystarsanjadjoran (dissidayara	an ingles and a start for a start of the start	٢٠ ٩ ٠٩٩٩ مەرمەم بەرمەر يەرمەر يەرم	hiteory and the first figure and a start figure	nthalfar ^{an} ananga Mayoonoo isigi yaha	ant-thailtean an Antonia	
												1.40
												F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 C 1 co
												Image: Characteria Constraint TE 293.5 K D1 2.00000000 sec TD0 1 ************************************
												PROBHD 5 INR PABBO BB/ PULPROG 2330 70
								Compo ³¹ P/ ¹ H NM	NHAc und 9b R coupled			Current Data Parameters NAME OB 1425 2nd crystallization in CH3CN EXPRO 2 PROCNO 1 F2 - Acquisition Parameters Date 20151111 Time 11.51 INSTRUM spect
					37.78				\rightarrow			BRUKER
								,ل				



OB 320

pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMPI	. E	SPECIAL
date Apr	12 2012	temp not used
solvent	cdc13	pain 14
file /home	/TCUuser~	snîn 20
THE THOME,		- bet 0.000
/vnarsys/da	ata/auto~	nst 0.008
_2012.04.10	J/S_2012~	pw90 18.300
0412_30/dat	ta/cdc13~	alfa 10.000
· · · · ·	03.fid	FLAGS
ACOUISI	FION	il n
sw	15797 8	in n
at	1 600	dn v
u	E 1 6 6 6 9	hr y
np	20222	нь ну
ат	8800	PRUCESSING
bs	64	1b 1.00
d 1	1.000	fn not used
nt	16	DISPLAY
ct	16	sn -3647-3
TDANCHT	10	un 15707.9
TRANSPIT.	11LK 004	wp 10/07.0
ιn.	P31	ITI 3047.8
strq	121.465	rtp 0
tof	7421.1	rp 63.9
tpwr	55	lp -113.7
Wa	9.150	PLOT
DECOUPI	FR	wc 250
dn	ц1	rc 0
un de C	11	SU U
001	U	vs 37
dm	ууу	th 13
dmm	W	aicdc ph
dpwr	35	
dmf	6700	

80

70

60

50

40

30

20

10

-10

0

-20

ppm

90



Compound (R_p)-10 ³¹P/H NMR decoupled **0**B 320

exp1 Phosphorus

	SAMPLE		SPECIAL
date	Apr 12 2012	temp	not used
solver	nt cdcl3	gair	n 14
file /	/home/TCUuser≁	spir	1 20
/vnmrs	ys/data/auto~	hst	0.008
_2012.	04.10/s_2012~	pw90	18.300
0412_3	30/data/cdc13~	alfa	10.000
	_06.fid		FLAGS
ACC	UISITION	i 1	n
sw	15797.8	in	n
at	1.600	dp	У
np	50552	hs	ny
fb	8800		PROCESSING
bs	64	1b	1.00
d1	1.000	fn	not used
nt	16		DISPLAY
ct	16	sp	-3647.3
TRA	NSMITTER	wp	15797.3
tn	P31	rf1	3647.8
sfrq	121.465	rfp	0
tof	7421.1	гр	67.1
tpwr	55	1p	-113.7
pw	9.150		PLOT
DE	COUPLER	wc	250
dn	H1	S C	0
dof	0	vs	116
dm	ynn	th	22
dmm	W	ai	cdc ph
dpwr	35		
dmf	6700		



Compound (R_p)-10 ³¹ P/¹H NMR coupled

*********		`desarchister ¹ febreichen en sy bei het	in the state of the		and Junior	\		and party and the first of the		ndin the tradition of the	********	an in the state of	and the second
ł	90	80	70	60	50	40	30	2.0	10	0 0	-10	-20	ppm



OB 320

OB 320

exp1 Carbon

SAMPLE	SPECIAL
date Apr 12 2012	temp not used
solvent cdc13	gain 20
file /home/TCUuser	všpin 20
/vnmrsys/data/auto-	v hst 0.008
2012.04.10/s 2012-	v pw90 18.500
0412_30/data/cdc13-	~ alfa 10.000
07.fid	FLAGS
ACQUISITION	il a
sw 18115.9	in n
at 1.301	dp y
np 47120	hs nn
fb 10000	PROCESSING
bs 64	1b 0.50
d1 2.000	fn notused
nt 512	DISPLAY
ct 512	sp -1135.5
TRANSMITTER	wp 18115.4
tn C13	rfl 1136.1
sfrg 75.454	rfp 0
tof 766.0	гр -3.0
tpwr 58	1p -195.3
pw 9.250	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 297
dm yyy	th 4
dmm w	ai cdc ph
dpwr 35	
dmf 6700	

0.0**~** HQ Me

Compound (R_p)-10 ¹³C NMR

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220	200	<u>180</u>	160	140	120	100	80		4 (1. 1	2.0	 0 ppm

0B 877f2 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMPLE	SPECIAL
date Dec 19 2012	temp not used
solvent cdc13	gain 20
file /home/TCUuser~	spin 20
/vnmrsys/data/auto~	hst 0.008
2012.12.14/s 2012~	pw90 18.300
1219_28/data/cdc13~	alfa 10.000
02.fid	FLAGS
ACQUISITION	il n
sw 15797.8	in n
at 1.600	dp y
np 50552	hs ny
fb 8800	PROCESSING
bs 64	1b 1.00
d1 1.000	fn notused
nt 16	DISPLAY
ct 16	sp -3647.3
TRANSMITTER	wp 15797.3
tn P31	rfl 3647.8
sfrq 121.465	rfp 0
tof 7421.1	rp 18.5
tpwr 55	1p -113.7
pw 9.150	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 19
dm yyy	th 3
dmm W	ai coic ph
dpwr 35	
dmf 6700	



Compound (B_p)-11 ⁹¹P/^IH NMR decoupled

		****		M								tel philosophispanan maningan tervitrate
90	80	7 0	60	50	40	30	2 0	10	0	1 0	-20	bbw

OB 877f2

exp1 Phosphorus

SAMPLE	SPECIAL
date Dec 19 2012	temp not used
solvent cdc13	gain 20
file /home/TCUuser	~ špin 20
/vnmrsys/data/auto	~ hst 0.008
_2012.12.14/s_2012	~ pw90 18.300
1219_28/data/cdc13	~ alfa 10.000
_04.fid	FLAGS
ACQUISITION	il n
sw 15797.8	in n
at 1.600	dp y
np 50552	hs ny
fb 8800	PROCESSING
bs 64	1b 1.00
d1 1.000	fn notused
nt 16	DISPLAY
ct 16	sp -3647.3
TRANSMITTER	wp 15797.3
tn P31	rfl 3647.8
sfrq 121.465	rfp 0
tof 7421.1	rp 26.9
tpwr 55	lp -113.7
pw 9.150	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 115
dm ynn	th 4
dmm w	ai cdc ph
dpwr 35	-
dmf 6700	

48.428



Compound (B_p)-11 ³¹P/¹H NMR coupled

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90	<u> </u>	80	70	60 50	40	30	20	10	0	- 1 0	-20	ppm



OB 877f2

exp1 Carbon

SAMP	LE		SPECIAL
date Dec	19 2012	temp) not used
solvent	cdc13	gair	n 20
file /home	/TCUuser~	spir	n 20
/vnmrsys/de	ata/auto~	hst	0.008
2012.12.1	4/s 2012~	pw90	18.500
1219_28/da	ta/cdc13~	alfa	ı 10.000
	_05.fid		FLAGS
ACQUISI	TION	i 1	n
SW	18115.9	in	n
at	1.301	dp	У
np	47120	hs	nn
fb	10000		PROCESSING
bs	64	lb	0.50
d1	2.000	fn	not used
nt	1800		DISPLAY
ct	1800	sp	-1135.5
TRANSMI	TTER	wp	18115.4
tn	C13	rf1	1136.1
sfrq	75.454	rfp	0
tof	766.0	rp	-2.0
tpwr	58	lp	-210.4
pw	9.250		PLOT
DECOUP	LER	WC	250
dn	H1	SC	0
dof	0	٧s	513
dm	УУУ	th	8
dmm	W	ai	cdc ph
dpwr	35		
dmf	6700		

HOL

Compound (R_p)-11 ¹³C NMR

		n d ang a she shara a		 nendrungsa ina M Yomaanaa		

				H C ³¹ P	O O C O M D O M P O M P O M P O M P O O C O C O C O C O C O C O C O C O C	-Ph nd (Rp)-1 3 decoup	2 lied					Current 1 NAME EXPNO PROCNO	Data Parameters OB 1614 after column 1 1
												F2 - Acq Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0	lisition Parameters 20140805 9.06 spect 5 mm PABBO BB/ zgpg30 65536 CDC13 16 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 295.4 K 2.00000000 sec 0.03000000 sec
												SF01 NUC1 P1 PLW1 SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13 F2 - Proc SI SF WDW SSB LB GB PC	CHANNEL f1 ===================================
110 10	0 90	80	70	60	50	40	30	20	10	0	-10	ppm	

		3Jb JH M	na (rµp ∥Rcoupl	ed			Current NAME EXPNO PROCNO F2 - AC Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ BG	Data Parameters OB 1614 after co 2 1 quisition Parameter 20140805 9.08 spect 5 mm PABBO BB/ 2230 65536 CDC13 32 4 64102.563 H 0.978127 H 0.5111808 s 203 57
							NG DE TE D1 TD0 SF01 NUC1 P1 PLW1	203.57 7.800 c 6.50 u 295.0 K 2.00000000 s 1 = CHANNEL fl ====== 161.9674942 N 31P 14.25 u 15.00000000 W
							F2 - Pr SI SF WDW SSB LB GB PC	DCESSING parameter 32768 161.9755930 M EM 0 1.00 H 0 1.40







								HO)-13			BR Current NAME	Data P		s 2
								31P/1H 1	NM H COU	ipied			EXPNO PROCNO F2 - Acc Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES	quisiti 5 mm	on Param 2014112 17.5 spec PABBO BB 2g3 6553 CDC1 3 64102.56 0 97812	2 1 eters 0 0 t / 0 6 3 2 4 3 Hz 7 Hz
													AQ RG DW DE TE D1 TD0 SF01 NUC1 P1 PLW1	2 = CHANN! 16 15	0.511180 203.5 7.80 6.5 295. .00000000 EL fl === 1.967494 311 14.2 .00000000	<pre>% 12 % 28 % 28 % 28 % 28 % 28 % 28 % 28 % 2</pre>
													F2 - Pro SI SF WDW SSB LB GB PC	ocessing 163 0 0	g paramet 32768 1.975593(EN 1.0(1.4(ters 3 1 1 1 1 1 1 1 1 1 1
 100	90	80	70	60	50	40	30	20	10	0	-10	ppm				





					J J J H C	ompound AH NMR o	(P _p)-14 lecouple	d		Current D NAME EXPNO PROCNO F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0 SF01 NUC1 P1 PLW1 SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13 F2 - Proc	<pre>vata Parameters</pre>
										SI SF WDW	32768 161.9755930 MHz EM
 independences and a construction of a standard		 ſĸŎŗġĸġĊŀĿĨĊŦŎĊĊĿŎĸĊĬŔĊĸĸĸŎŎŎ	anna haoranna	the support and an and a support			\\\#\$\$\$\\$\\$\\$\\$\\$\\$\\$\\$\\$	yur ay hab sowed to shu yy tel) oprine) op ye i ne og d	ามสำหรักของสารายๆให้สารารุปประกาศประกาศประสาทธิการทุบประกาศ	SSB LB	0 1.00 Hz
								*****		GB	0 1 40

Current I NAME EXPNO PROCNO	Jata	Para ()B 1	ers .052 2 1	
F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS	isit 5 mm	ion 20 PAE	Par 10 10 3BO 22 69 CE	ramet)510).08 pect BB/ :g30 ;536)C13 32	ers
SWH FIDRES AQ RG DW DE TE D1 TD0		641 0.5 2.00	.02. 978 5111 203 7. 6 29	563 3127 .808 3.57 800 5.50 96.3 0000 1	Hz Hz usec usec K sec
SFO1 NUC1 P1 PLW1	CHAN 1 1	NEL 61.9 5.00	f1 674 14	942 31P .25	MHz USEC W
F2 - Proc SI SF WDW SSB LB	cessi 1 0	ng p 61.9	ara 32 755	mete 768 930 EM	ers MHz Hz
GB PC	0		1	.40	

normal second and the second and the

					****						****		
100	90	80	70	60	50	40	30	20	10	0	-10	-20	ppm





Aco Compound (Rp)-15 ³¹ P/H NMR decoupled		Current Data Parameters NAME OB 1172 EXPNO 1 PROCNO 1
		F2 - Acquisition Parameters Date 20130717 Time 20.05 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 294.6 K D1 2.0000000 sec D11 0.03000000 sec TD0 1
		SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
		SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltzl6 PCPD2 90.00 usec PLW2 10.0000000 W PLW12 0.31604999 W PLW13 0.25600001 W
Id	*****	F2 - Processing parameters SI 32768 SF 161.9755930 MHz

		Compo ³¹ P/H (ound (R _p)-15 MMR coupled	Current D NAME EXPNO BROCNO	ata Parameters OB 1172 2
				F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0 ======= SF01 NUC1	isition Parameters 20130717 20.11 spect 5 mm PABBO BB/ 2g30 65536 CDC13 32 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 293.9 K 2.00000000 sec 1 CHANNEL f1 ======= 161.9674942 MHz 31P
				PLW1 F2 - Proc SI SF WDW SSB LB GB BC	15.00000000 W essing parameters 32768 161.9755930 MHz EM 0 1.00 Hz 0
				 FC.	1.40




	BRUKER
Compound (R _p)-1 ³¹ P/H NMR decoupled	Current Data Parameters NAME OB 2018 EXPNO 1 PROCNO 1
	F2 - Acquisition Paramet Date_ 20150429 Time 17.03 INSTRUM spect PROBHD 5 mm PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.50 TE 295.7 D1 2.00000000 D11 0.03000000 TD0 1
	SF01 CHANNEL fl ==== SF01 161.9674942 NUC1 31P P1 14.25 PLW1 15.00000000
	SF02 CHANNEL f2 SF02 400.1316005 NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 PLW2 10.00000000 PLW12 0.31604999 PLW13 0.25600001
	F2 - Processing paramete SI 32768 SF 161.9755930 WDW EM SSB 0 LB 1.00 CP 0

Compound (Bp)-1 ³¹ P/ ¹ H NMR coupled	Current Data Parameters NAME OB 2018 EXPNO 2 PROCNO 1
	F2 - Acquisition Paramete Date_ 20150429 Time 17.05 INSTRUM spect PROBHD 5 mm PULPROG zg30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 H FIDRES 0.978127 H AQ 0.5111808 s RG 203.57 DW 7.800 u DE 6.50 u TE 295.4 K D1 2.00000000 s TD0 1
	SF01 CHANNEL f1 ===== NUC1 31P P1 14.25 u PLW1 15.00000000 W
	F2 - Processing parameter: SI 32768 SF 161.9755930 MI WDW EM SSB 0 LB 1.00 H GB 0 PC 1.40

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SAMPLE			SPECIAL
date Oct 24 :	2011	ì∈mp	not used
solvent Cl	DC13	gain	not used
file	exp	spin	2.0
ACQUISITION		hst	0.008
sw 2673	38.0	pw90	18.300
at 1	.598	alfa	20.000
np 85	5476		FLAGS
fb 1.	1800	1 I	n
bs	16	in	в
55	-4	áp	У
d1 1	0.00	hs	nn
nt	64	1	PROCESSING
ct	32	i tr	1.06
TRANSMITTER		fn	not used
tn	P31		OISPLAY
sfrq 121	.471	SID	-0.2
tof 105	38.8	Wp	10010.0
tpwr	55	111	2437.5
pw 7	.117	r f p	0
DECOUPLER		гр	-140.4
dn	H1	1 1	-288.8
dof	0		PLOT
dm	YVY -	WG	250
diata	Ŵ	εc	1)
dpwr	35	VS	5
dm f (5700	th	4

th ai no ph





ppm

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exp1-s2put-

SAMF	PLE		SPECIAL
date Oct	24 2011	tem	p not used
solvent	CDC13	gai	n not used
file	exp	spi	n 20
ACQUISI	TION	hst	0.008
sw	26738.0	pw91	0 18.300
at	1.598	alfa	a 20.000
np	85476		FLAGS
fb	14800	i 1	n
bs	16	in	n
55	4	ab	V
d1	1.000	hs	ກກ
nt	64		PROCESSING
ct	32	1b	1.00
TRANSMI	TTER	fn	not used
tn	P31		DISPLAY
sfrq	121.471	50	-0.2
tof	10598.6	wb	10010.0
tpwr	55	cf1	2437.5
p. Wq	7.117	rfp	0
DECOUP	LER	rp	-135.0
din	H1	15	-326.4
dof	0	· J-	PLOT
dm	Vnn	WC	250
dmm	W	SC	200
dpwr	35	VS	71
dmif	6700	th	12
	21.00	ai	no nh

0 ∎.0⊷ H−P.

Compound (Sp)-1 ³¹P/¹H NMR coupled

19 Y	· · · · · · · · · · · · · · · · · · ·	Illeader as A tabut of Link.	्या संदर्भवे के क्यांग्राम् का मान्या का गयती गांध कि कि दिन र ग	in heide halls is ta beite da uh heide in	al al collar de la subrita d'un en la seconda de la seconda de la collar de la collar de la collar de la collar	a Barada	A	ta da ca cata de la
en an Allein, Íslan, ha	n al schullen. Bairea fur ministernik (Eller flererins) autorister in die bistorie statistiker in der schulter in die schulter in	java uta plananaja, de indevid 1. di trincia de cambo andere	la kiri dalah mataka sa kita ana ing disaka sa sa kiri a	ing a fill a chaine an star an		Hitsenson Hitlensonsona	والمتحديقة والمراجع فيأتوا ورواز أوحمه والأو	Manim
	מי ווט אוו					24.7		

0B 085

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exp1 s2pul

12

SAMPLE			SPEC	IAL	
date Oct 24 20	11	temp		not	used
solvent CDC	1.3	gain		not	used
file e	хp	spin			20
ACQUISITION		hst			800.0
sw 4803	. 1	pw90		1	7.200
at 1.9	94	alfa		2	0.000
np 191	58		FLA	GS	
fb not us	ed	11			n
bs	16	in			n
ss	4	dp			У
d1 1.0	00	hs			nn
nt	16		PROCE	SSIN	G
ct	16	fn		not	used
TRANSMITTER			DISP	LAY	
tn	H1	sp		-	598.0
sfrq 300.0	147	wp		4	802.8
tof 277	.8	rf1			598.3
tpwr	55	rfp			0
pw 8.6	600	гp		-	117.1
DECOUPLER		1p			-79.0
dn (:13		PL.	0T	
dof	0	wc			250
dm t	nn	S C			0
dmm	С	vs			179
dpwr	45	th			4
dmf 131	00	ai	cdc	ph	



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OB 953 pad≠10 run with findz0 before acquisitio n

exp10 Phosphorus

SAMPLE	SPECIAL
date Feb 14 2013	temp not used
solvent cdc13	gain 25
file /home/TCUuser~	špin 20
/vnmrsys/data/auto~	hst 0.008
_2013.02.14/s_2013~	pw90 18.300
0214_12/data/cdc13~	alfa 10.000
_01.fid	FLAGS
ACQUISITION	il n
sw 15797.8	in n
at 1.600	dp y
np 50552	hs ny
fb 8800	PROCESSING
bs 64	1b 1.00
d1 1.000	fn notused
nt 64	DISPLAY
ct 64	sp -3647.3
TRANSMITTER	wp 15797.3
tn P31	rfl 3647.8
sfrq 121.465	rfp 0
tof 7421.1	rp 105.2
tpwr 55	lp -113.7
pw 9.150	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 163
dm yyy	th 21
dmm w	ai cdc ph
dpwr 35	
dmf 6700	



Compound (S_p)-16 ³¹P/H NMR decoupled

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90	80	70	60	50	40	30	20	10	0	-1.0	20	ppm

08 953

exp10 Phosphorus

SAMPLE	SPECIAL
date Feb 14 201	3 temp not used
solvent cdcl:	3 gain 25
file /home/TCUuse	r≁spin 20
/vnmrsys/data/auto	o~hst 0.008
_2013.02.14/s_201	3~ pw90 18.300
0214_12/data/cdc1:	3~ alfa 10.000
_02.fi	d FLAGS
ACQUISITION	il n
sw 15797.1	8 in n
at 1.60	0 dp V
np 5055:	2 hs ny
fb 880	0 PROCESSING
bs 6	4 lb 1.00
d1 1.00	0 fn notused
nt 6-	4 DISPLAY
ct 6-	4 sp -3647.3
TRANSMITTER	wp 15797.3
tn P3	1 rfl 3647.8
sfrq 121.46	5 rfp 0
tof 7421.	1 rp 113.7
tpwr 5	5 lp -113.7
pw 9.15	0 PLOT
DECOUPLER	wc 250
dn H.	1 sc 0
dof	0 vs 357
dm yni	nth 12
dmm v	waicdc ph
dpwr 31	5
dmf 670	0

H Me

Compound (Sp)-16 ³¹P/¹H NMR coupled





exp10 Proton

SAMPLE		DEC.	& VT	
date Feb 20 201	13	dfra	75.454	1
solvent cdc	13	dn	C1.9	3
file /home/TCUuse	er≁	dowr	43	2
/vnmrsvs/data/aut	to~	dof	í.	ĥ
2013.02.14/s 201	13~	dm	nnr	'n
0220 27/data/cdc1	13~	dmm		-
01.fi	h	dmf	13100	ñ
ACOUISITION		PROC	ESSING	·
sfra 300.04	17	wtfile		
tn H	11	proc	ft	
at 1.99	18	fn	not user	í
np 1918	34			•
sw 4800.	8	werr	xmreact	
fb 260	0	wexn abo	rtoff flus	~
bs 1	6	h nrocnl	nt abortor	1
towr	55	whs	00 4601 001	•
pw 7.	9	wnt		
d1 1.00	n n			
tof 277.	g			
nt	32			
ct S	22			
alock	V.			
gain not use	2 d			
FLAGS	/ M			
11	n			
in	n			
do	v			
DISPLAY	3			
sp -596.	6			
wp 4800.	5			
vs 25	1			
sc	ō			
WC 24	i ñ			
hzmm 20.0	iñ.			
is 419.6	9			
rfl 596.	9			
rfp	0			
th	2			
ins 1.00	0			
ai cdc ph				





exp10 Carbon

SAMPLE	SPECIAL
date Feb 20 2013	temp not used
solvent cdcl3	gain 20
file /home/TCUuser~	spin 20
/vnmrsys/data/auto~	hst 0.008
_2013.02.14/s_2013~	pw90 18.500
0220_28/data/cdc13~	alfa 10.000
06.fid	FLAGS
ACQUISITION	il n
sw 18115.9	in n
at 1.301	dp y
np 47120	hs nn
fb 10000	PROCESSING
bs 64	lb 0.50
d1 2.000	fn notused
nt 800	DISPLAY
ct 800	sp -1135.5
TRANSMITTER	wp 18115.4
tn C13	rfl 1136.1
sfrq 75.454	rfp 0
tof 766.0	rp 55.8
tpwr 58	lp -160.4
pw 9.250	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 256
dm yyy	th 4
dmm w	ai cdc ph
dpwr 35	
dmf 6700	

ы,o-H-I Me

Compound (S_p)-16 ¹³C NMR

		W-1 M-1 M-1 M-1 M-1 M-1 M-1 M-1 M-1 M-1 M								
220 200	180	<u>160</u>	140	120	1.00	80	60	40	20	 maa 0

0B 949 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMP	LE		SPECIA	L
date Feb	9 2013	temp) n	ot used
solvent	cdc13	gair	1	20
file /home,	/TCUuser~	spir	1	20
/vnmrsys/da	ata/auto~	hst		0.008
_2013.02.0	9/s_2013~	pw90)	18.300
0209_05/da	ta/cdc13≁	alfa	L	10.000
	_02.fid		FLAGS	
ACQUISI	FION	i1		n
sw	15797.8	in		n
at	1.600	dp		v
np	50552	hs		ny
fb	8800		PROCESS	ING
bs	64	lb		1.00
d1	1.000	fn	n	ot used
nt	16		DISPLA	Ý
ct	16	sp		-3647.3
TRANSMI	FTER	wp		15797.3
tn	P31	rf1		3647.8
sfrq	121.465	гfр		0
tof	7421.1	rp		136.0
tpwr	55	lp		-124.4
pw	9.150		PLOT	
DECOUPI	.ER	WC		250
dn	H1	SC		0
dof	0	vs		7
dm	УУУ	th		12
dmm	W	ai	cdc ph	
dpwr	35			
dmf	6700			



Compound (S_p)-17 ³¹P/^IH NMR decoupled



exp1 Phosphorus

SAMPLE			SPECIAL
date Feb 9	2013	temp	not used
solvent d	dc13	gair) 20
file /home/TCL	Juser≁	spir	1 20
/vnmrsys/data/	∕auto~	hst	0.008
_2013.02.09/s	2013~	pw90	18.300
0209_05/data/0	dc13~	alfa	10.000
04	l.fid		FLAGS
ACQUISITION	1	11	n
sw 157	97.8	in	n
at 1	.600	dp	V
np 5	0552	hs	ný
fb	8800		PROCESSING
bs	64	1b	1.00
d1 1	1.000	fn	not used
nt	16		DISPLAY
ct	16	sp	-3647.3
TRANSMITTER	ł.	wp	15797.3
tn	P31	rf1	3647.8
sfrq 121		rfp	0
tof 74	121.1	гр	130.0
tpwr	55	lp	-114.3
pw 9	1.150		PLOT
DECOUPLER		WC	250
dn	H1	SC	0
dof	0	VS	111
dm	ynn	th	6
dmm	W	ai	cdc ph
dpwr	35		
dmf	6700		



Compound (Sp)-17 ³¹P/¹H NMR coupled

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<u> </u>	<u> </u>	80	70	60	50	40	30	20	10	0	-1.0	-20	ppm



exp1 Carbon

	SAMPL	E			SPE	CIAL		
date	Feb	9	2013	tem	3	nc)t :	used
solve	nt	C	dc13	gaii	1 I			20
file	/home/	TCU	iser≁	spir	n			20
/vnmr	sys/da	ta/a	auto≁	hst			0	.008
_2013	.02.09	/s_1	2013~	pw91)		18	.500
0209_	05/dat	a/c	dc13~	alfa	a		10	.000
		_05	.fid		FL	AGS		
AC	QUISIT	ĪON		i 1				n
sw		181	15.9	1n				n
at		1	.301	dp				V
np		- 41	7120	hs				nň
fb		1	0000		PROC	ESSI	NG	
bs			64	1b				0.50
d1		2	.000	fn		no	it i	used
nt			1600		DIS	PLAY	,	
ct			1600	sp			11:	35.5
TR	ANSMIT	TER		wp		1	81	15.4
tn			C13	rf1			113	36.1
sfrq		75	454	rfp				0
tof		- 76	56.0	rp			1	61.2
tpwr			58	1p			-1	97.6
pw		9	.250		P	LOT		
D	ECOUPLI	ER		wc				250
dn			H1	sc				0
dof			0	٧s				396
dm			ууу	th				6
dmm			W	ai	cdc	ph		
dpwr			35					
dmf		6	5700					



Compound (Sp)-17 ¹³C NMR



OB 948 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMPLE	SPECIAL
date Feb 11 2013	3 temp not used
solvent cdcl3	gain 25
file /home/TCUuser	`∼ špin 20
/vnmrsys/data/auto	• hst 0.008
_2013.02.09/s 2013	3∼ pw90 18,300
0211_20/data/cdc13	3∼ alfa 10.000
01.fic	FLAGS
ACQUISITION	il n
sw 15797.8	in n
at 1.600	dp v
np 50552	hs nv
fb 8800	PROCESSING
bs 64	1b 1.00
d1 1.000	fn not used
nt 16	DISPLAY
ct 16	sp -3647.3
TRANSMITTER	wp 15797.3
tn P31	rfl 3647.8
sfrq 121.465	rfp 0
tof 7421.1	rp 113.6
tpwr 55	lp -113.7
pw 9.150	PLOT
DECOUPLER	WC 250
dn H1	sc 0
dof 0	vs 14
dm yyy	th 11
dmm w	ai cdc ph
dpwr 35	,
dmf 6700	



Compound (Sp)-18 ³¹P/¹H NMR decoupled

helen have been and the second and the s

90 80 70 60 50 40 30 20 10 0 -10 -20

ppm

1000

exp1 Phosphorus

SAMPLE			SPECIAL
date Feb 11	2013	temp	not used
solvent	cdc13	gain	n 25
file /home/TC	Uuser~	spin	n 20
/vnmrsys/data	/auto~	hst	0.008
_2013.02.09/s	_2013~	pw90	18.300
0211_20/data/	cdc13≁	alfa	ı 10.000
0	2.fid		FLAGS
ACQUISITĪO	N	i 1	n
sw 15	797.8	in	n
at	1.600	dp	У
np	50552	hs	ny
fb	8800		PROCESSING
bs	64	16	1.00
d1	1.000	fn	not used
nt	16		DISPLAY
ct	16	sp	-3647.3
TRANSMITTE	R	wp	15797.3
tn	P31	rfl	3647.8
sfrq 12	1.465	rfp	0
tof 7	421.1	rp	-142.4
tpwr	55	۱p	-336.5
pW	9.150		PLOT
DECOUPLER		WC	250
dn	H1	sc	0
dof	0	vs	178
dm	ynn	th	12
dmm	w	ai	cdc ph
dpwr	35		
dmf	6700		



Compound (S_p)-18 ³¹P/H NMR coupled

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ranismistration											antar fan	
90	80	70	60	50	40	30	20	10	0	-10	-20	ppm



exp1 Carbon

	SAMPLE		SPECIAL
date	Feb 11 2013	temp	not used
solve	nt cdc13	gair	1 20
file	/home/TCUuser~	spir	20
/vnmr	sys/data/auto~	hst	0.008
2013	.02.09/5 2013~	pw90	18,500
0211	20/data/cdc13~	alfa	10.000
	03.fid		FLAGS
AC	QUISITION	11	n
SW	18115.9	in	n
at	1.301	dp	v
np	47120	hs	กก้
fb	10000		PROCESSING
bs	64	16	0.50
d 1	2.000	fn	not used
nt	650		DISPLAY
ct	650	sp	-1135.5
TR	ANSMITTER	Wp	18115.4
tn	C13	rf1	1136.1
sfrq	75.454	rfp	0
tof	766.0	rp	55.8
tpwr	58	1p	-193.3
pw	9.250		PLOT
D	ECOUPLER	wc	250
dn	H1	SC	0
dof	0	VS	1156
dm	ууу	th	10
dam	W	ai	cdc ph
dpwr	35		
dmf	6700		



Compound (S_p)-18 ¹³C NMR

<u>ى با </u>	<u>╸╷┑╶┌╶╶┎╺┎┍┎┍┲┍</u> ┎┍┍╺╶╸ ╔╔╶╢╴┰┎╺┠╴╗╗┇╝╝╝╝╸╸┇╸╎╸┥╸	ر میں ایک میں کے بار کی		
220 200 180 16	0 140 120	0 100 80	60 40	20 O ppm



Current Data Param NAME OB 2095 a Compound (Sp)-19 EXPNO PROCNO	eters fter co 2 1
F2 - Acquisition P Date_ 201 Time INSTRUM PROBHD 5 mm PABE PULPROG TD SOLVENT NS DS SWH 6410 FIDRES 0.9 AQ 0.51 RG 2 DW DE TE D1 2.000 TD0 TD0 TD0 TD0 TD0	aramete 50630 9.40 spect 0 BB/ zg30 65536 CDC13 32 4 (2.563 H (2.563 H (2.563 H 1808 s 03.57 7.800 u 6.50 u 294.0 K 00000 s 1 1 1
PLW1 15.000 F2 - Processing pa SI SF 161.97 WDW SSB 0 LB GB 0 PC	00000 V rameter 32768 55930 N EM 1.00 F 1.40





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H C	BRUKER
Compound (S _p)-20 ³¹ P/H NMR decoupled	Current Data Parameters NAME OB 1826 after column EXPNO 1 PROCNO 1
	F2 - Acquisition Parameters Date20141112 Time 9.44 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16
	DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 298.6 K D1 2.0000000 sec D11 0.03000000 sec
	TD0 1 ===== CHANNEL f1 ===== SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
	====== CHANNEL f2 SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.00000000 W PLW12 0.31604999 W PLW13 0.25600001 W
	F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz
	PC 1.40

$G_{\text{compound}}(S_{\mu})-20$	Current Data Parameters NAME OB 1826 after colu
• P/H NWIR coupled	PROCNO 1 F2 - Acquisition Parameters Date_ 20141112 Time 11.08 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zg30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 use DE 6.50 use TE 297.8 K D1 2.0000000 sec
	TD0 1 SF01 161.9674942 MHz NUC1 31P P1 14.25 use PLW1 15.0000000 W F2 - Processing parameters 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40







			Ph Compo ³¹ P/1H M	und (S _p)-2 IMR couple	ti əd		Current NAME EXPNO PROCNO	Data Parameter OB 1843 after
							F2 - Acq Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	uisition Param 2014112 17.4 spec 5 mm PABBO BB 2g3 6553 CDC1 3 64102.56 0.97812 0.511180 203.5 7.80 6.5 295. 2.0000000
							SFO1 NUC1 P1 PLW1	CHANNEL fl == 161.967494 31 14.2 15.0000000
							F2 - Pro SI SF WDW SSB LB GB FC	cessing parame 3276 161.975593 E 0 1.0 0 1.4
		a						







Compound (Sp)-22 ³¹ P/ ¹ H NMR coupled	Current Data Parameters NAME OB 1866 after c EXPNO 2 PROCNO 1
	F2 - Acquisition Paramet Date20141210 Time 8.59 INSTRUM spect PROBHD 5 mm PULPROG zg30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.50 TE 298.6 D1 2.0000000 TD0 1
	SF01 161.9674942 NUC1 31P P1 14.25 PLW1 15.0000000
	F2 - Processing paramete SI 32768 SF 161.9755930 WDW EM SSB 0 LB 1.00 GB 0 PC 1.40




OB 396

exp1 Phosphorus

SAMPLE	SPECIAL
date Apr 25 2012	temp not used
solvent D20	gain 20
file /home/TCUuser^	spin 20
/vnmrsys/data/auto~	hst 0.008
_2012.04.23/s_2012^	pw90 18.300
0425_05/data/D20_0^	alfa 10.000
2.fid	FLAGS
ACQUISITION	il n
sw 15797.8	in n
at 1.600	dp y
np 50552	hs ny
fb 8800	PROCESSING
bs 64	1b 1.00
d1 1.000	fn notused
nt 16	DISPLAY
ct 16	sp -3647.3
TRANSMITTER	wp 15797.3
tn P31	rfl 3647.8
sfrq 121.465	rfp 0
tof 7421.1	rp 56.4
tpwr 55	lp -113.7
pw 9.150	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 16
dm yyy	th 10
dmm w	ai cdic ph
dpwr 35	
dmf 6700	

0 ₩.**0**= Ph'

Compound (Sp)-23 ³¹P/¹H NMR decoupled



08 396

-⊊-13°

exp1 Phosphorus

SAMPL	E		SPECIAL
date Apr	25 2012	temp	not used
solvent	D20	gain	20
file /home/	TCUuser~	spin	20
/vnmrsys/da	ta/auto~	hsi	0.008
2012.04.23	/s 2012~	pw90	18.300
0425_05/dat	a/D20_0~	alfa	10.000
	4.fid		FLAGS
ACQUISIT	ION	i1	n
SW	15797.8	în	n
at	1.600	dp	У
np	50552	hs	ny
fb	8800		PROCESSING
bs	64	1b	1.00
d1	1.000	fn	not used
nt	16		DISPLAY
ct	16	sp	-3647.3
TRANSMIT	TER	wp	15797.3
tn	P31	rfl.	3647.8
sfrq	121.465	rfp	0
tof	7421.1	rp	111.5
tpwr	55	1p	-113.7
pw	9.150		PLOT
DECOUPL	ER	WC	250
dn	H1	SC	0
dof	0	vs	75
dm	ynn	th	17
dmm	Ŵ	ai	cdc ph
dpwr	35		
dmf	6700		



	<u>ىرىمۇمۇمۇمۇمىرىكى ئۆركىيەر بۇرىمۇمۇمۇمۇرىيەر ئېرمۇرۇ</u>	يوعد المحرد الذا الاجر (الأوديو) بدائية الإرتباع المحاصية المحاصية المحاصية المحاصية المحاصية المحاصية المحاصي	and the second		ومواد المارين المواد والمارك و	الم	and the second		والمعامر والمراجع والمراجع المراجع المراجع المراجع والمراجع والمراجع والمراجع والمراجع والمراجع والمراجع والم		naada saaraanaana	ira,qaldadadadadadadada	and the second secon
e de la milio													······
	90	80	70	60	50	40	30	2 0	10	0	-10	-20	ppm

OB 396 pad=10 run with findz0 before acquisitio n

exp1 Proton

			0.5.4		11T	
	SAMPLE	~ ~ ~ ~ ~ ~	DEU	5. X	VI	~ .
date	Apr 2	5 2012	dtrq		75.4	54
solver	ıt	cdc13	dn		C	13
file /	/home/T	CUuser≁	dpwr			43
/vnmrs	ys/dat	a/auto~	dof			0
2012.	04.23/	s 2012~	dm		n	inn
0425 0	2/data	/cdc13~	dmm			с
0,50,00		01_fid	dmf		131	0.0
ACC	UTSTT	NN	PRI	DOESS	TNG	
efra	2	00 047	wtfile			
3114	0	H1	nroc			ft
5 H		1 0 9 8	fn		not us	bo
at		10104	1.11	,	ior as	-cu
np		13104				c+
sw		4800.8	werr		xmrea	Ct
1.0		2600	wexp a	porte	DTT TI	us~
bs		16	h proc	plot	abort	on
tpwr		55	wbs			
pW		7.9	wnt			
d1		1.000				
tof		277.9				
nt		32				
ct		32				
alock		v				
dain	no	t used				
guin	FLAGS					
i 1		n				
in		n				
dn						
up 1	NTSPI AV	, J				
۱ د ۲	JISTLAI	~500 8				
sp		1000 5				
wp		4000.0				
VS		192				
sc		0 10				
we		240				
hZmm		20.00				
15		458.77				
rf1		600.1				
rfp		0				
th		3				
ins		2.000				
ai ce	dic ph					





OB 396

pad≃10 run with findz0 before acquisitio n

exp1 Carbon

SAMPLE	SPECIAL
date Apr 25 2012	temp not used
solvent cdc13	gain 20
file /home/TCUuser~	špin 20
/vnmrsys/data/auto~	hst 0.008
2012.04.23/s 2012~	pw90 18.500
0425 06/data/cdc13~	alfa 10.000
01.fid	FLAGS
ACQUISITION	il n
sw 18115.9	ín n
at 1.301	dp y
np 47120	hs nn
fb 10000	PROCESSING
bs 64	1b 0.50
d1 2.000	fn not used
nt 512	DISPLAY
ct 512	sp -1135.5
TRANSMITTER	wp 18115.4
tn C13	rfl 1136.1
sfrg 75.454	rfp 0
tof 766.0	rp 3.1
tpwr 58	1p -206.2
pw 9.250	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 219
dm yyy	th 4
dmm ₩	ai cdc ph
dpwr 35	
dmf 6700	



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220 200	180	160	140	120	100	80	60	4	0 0	20	0	ກດຕ

$\begin{array}{c} & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ &$	Current Data Parameters NAME OB 1816 after colum EXPNO 1 PROCNO 1
	F2 - Acquisition Parameters Date20141107 Time 17.36 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 use DE 6.50 use TE 295.8 K D1 2.0000000 sec D11 0.0300000 sec TD0 1
	PLW13 0.25600001 W F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 2.00 Hz GB 0 PC 1.40

Compound (Sp)-23	Current Data Parameters NAME OB 1816 after columr EXPNO 2 PROCNO 1
	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
	D1 2.00000000 sec TD0 1 SF01 161.9674942 MHz NUC1 31P P1 14.25 usec
	PLW1 15.00000000 W F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40





					<			► MS					BR	V	KER	
					aıt (Compou P/H NMI	nd (S _p)-24 Ridecoupl	4 led					Current NAME EXPNO PROCNO	Data Ol	Parameters B 158 4 pure 1 1	
													F2 - Acc Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0 SFO1 NUC1	guisi 5 mr = CHAN	<pre>tion Paramet 20140716 10.20 spect n PABBO BB/ zgpg30 65536 CDCl3 16 4 64102.563 0.978127 0.5111808 203.57 7.800 6.50 294.8 2.00000000 1 NNEL f1 ==== 161.9674942 31P</pre>	ers Hz Hz sec usec K sec sec mHz
													P1 PLW1		14.25 1 15.00000000 '	usec W
													SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13	- CHAI	NNEL 12 ===== 400.1316005 1 1H waltz16 90.00 10.00000000 0.31604999 0.25600001	MHz usec W W W
													F2 - Pro SI SF WDW	cess	ing paramete 32768 161.9755930 EM	rs MHz
800	ng, αγχανή χαιος αναι άλη μα ^{το} πογιομέ - αλλή αλιομογιούα	a, med-a space in the figure from the damage of the dama	nga mpin Panga - Pangan Jawa Jawa Jawa Kata Pangga na j	*****		ana an ann an		**************************************	angin ka Kanga na	ŊIJġĸĊĸĬĸŦĬĬĸġĸĸġŔġĸġŔŔġŔĊŊĸĸĸĸŊŔĸţĸĸċ	anah aya a yana ka waka ma ka a ba ka	kang antridge-gent nga maja miti n miti nang miti nang miti nang miti n	-SSB LB GB	0	1.00	Hz
100	••••• 90	••••• 80	•••••• 70	 60	 50	 40	····· 30	 20	<u>1</u> 0	•••••	-10	ppn	-PC n		1.40	

-40

90	0 80	70	60	50	40	30	20	10	0	-10	ppm				
Name and the second	niteria alexandra alexandra da car	haddanatistikan katalan katala			inningan kalanga na kalan	here she was to be	aatteyddinyd dirollwyda yn di			ani, antipipolika filaanik iyon the	dalahan dalam d				
											P F S S W S L G G P	LW1 2 - Prc I F DW SB B B C	15. ocessing 161 0 0	00000000 paramet 32768 .9755930 EM 1.00 1.40	W ers MHz Hz
											= S N P	F01 UC1 1	CHANNE	L f1 === .9674942 31P 14.25	MHz usec
											R D T T	G W E I D0	2.	203.57 7.800 6.50 294.5 00000000 1	usec usec K sec
											S N D S F A	OLVENT S S WH IDRES	6	CDCL3 32 4 4102.563 0.978127 5111808	Hz Hz
											T I F T T	ime NSTRUM ROBHD ULPROG D	5 mm P	10.22 spect ABBO BB/ zg30 65536	:

မို့စ -OTBDMS

-3

Compound (Sp)-24 ³¹P/¹H NMR coupled



Date_

Current Data Parameter NAME OB 158 pure EXPNO 2 PROCNO 1

F2 - Acquisition Parameters

20140716

Current Data Parameters





BRU	JKER
Current Da NAME EXPNO PROCNO	ta Parameters OB 1591 1 1
F2 - Acqui Date Time INSTRUM PROBHD 5 PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE	sition Paramet 20140722 9.29 spect 5 mm PABBO BB/ 2gpg30 65536 Acetone 16 4 64102.563 0.978127 0.5111808 203.57 7.800 6.50 295.6
D1 D11 TD0 SF01 NUC1	2.00000000 0.03000000 1 CHANNEL f1 ==== 161.9674942 31P
P1 PLW1	14.25 15.00000000
SFO2 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13	CHANNEL F2 ==== 400.1316005 1H waltz16 90.00 10.00000000 0.31604999 0.25600001
F2 - Proce SI SF WDW SSB (LB GB (essing paramete 32768 161.9755930 EM 0 1.00
b	SFO2 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13 F2 - Proce SI SF WDW SSB LB GB GB TPC

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	ر ۳	Compound (S	Ac Ac			C N E F	Current NAME EXPNO PROCNO	Data Parameters OB 1591 2 1	
						F I I F F F S N I I S S F I I S S I I S S I I S S I I S S I I S S I I S S I I I S S I I I S S I I I I I I S S I I I I S S I I I I I S S I I I I I I I I I S S I I I I I I S S I	F2 - Acq Date_ Time ENSTRUM PROBHD PULPROG TD SOLVENT NS OS SWH FIDRES AQ RG DW DE FE	uisition Parame 20140722 9.31 spect 5 mm PABBO BB/ 2g30 65536 Acetone 22 4 64102.563 0.978127 0.5111808 203.57 7.800 6.50 295.2	Hz Hz Sec usec usec K
						1 7 5 1 1 1 1 1	D1 FD0 SFO1 NUC1 P1 PLW1	2.00000000 1 CHANNEL fl === 161.9674942 31P 14.25 15.00000000	sec MHz usec W
							F2 - Pro SI SF WDW SSB LB GB FC	cessing paramet 32768 161.9755930 EM 0 1.00 0 1.40	ers MHz 1) Hz)

eo g

	Compound (Sp)-25 ³¹ P/ ¹ H NMR coupled		Current Data Parameters NAME OB 1591 EXPNO 2 PROCNO 1 F2 - Acquisition Parameter Date 20140722 Time 9.31 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG 2g30 TD 65536 SOLVENT Acetone NS 22 DS 4
			SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 se RG 203.57 DW 7.800 us DE 6.50 us TE 295.2 K D1 2.0000000 se TD0 1 ====== CHANNEL f1 SF01 161.9674942 MI
			NUC1 31P P1 14.25 u PLW1 15.00000000 W F2 - Processing parameter SI 32768 SF 161.9755930 M WDW EM SSB 0 LB 1.00 H GB 0 PC 1.40

BRUKER
Current Data Parameters NAME OB 648 2nd EXPNO 1 PROCNO 1
F2 - Acquisition Parameters Date_ 20151119 Time 9.45 INSTRUM spect PROBHD 5 mm PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.50 DE 6.50 DI 2.0000000 D1 2.0000000 D1 0.03000000 TD0 1
CHANNEL f1SF01161.9674942NUC131PP114.25USCUSCPLW115.00000000
====== CHANNEL f2 SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 use PLW2 10.0000000 W PLW12 0.31604999 W PLW13 0.25600001 W
F2 - Processing parameters SI 32768 SF 161.9755930 MH2 WDW FM

Compound (Sp)-26 ³¹ P/ ¹ H NMR coupled	Current Data Parameters NAME OB 648 2nd EXPNO 2 PROCNO 1
	$\begin{array}{ccccc} F2 & - \ Acquisition \ Parameters \\ Date 20151119 \\ Time 9.48 \\ INSTRUM spect \\ PROBHD 5 \ mm \ PABBO \ BB/ \\ PULPROG 2 g30 \\ TD 65536 \\ SOLVENT CDC13 \\ NS 32 \\ DS 4 \\ SWH 64102.563 \ Hz \\ FIDRES 0.978127 \ Hz \\ AQ 0.5111808 \ sec \\ RG 203.57 \\ DW 7.800 \ usec \\ DE 6.50 \ usec \\ TE 295.2 \ K \\ D1 2.0000000 \ sec \\ TD0 1 \\ \end{array}$
	SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.0000000 W F2 Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz
	GB 0 PC 1.40





						BRU	KER
	Compo ³¹ P/ ¹ H NM	`−−Ph und (S _p)-27 IR decoupled				Current Data NAME OB EXPNO PROCNO	Parameters 1707 after col 1 1
						F2 - Acquisi Date Time INSTRUM PROBHD 5 r PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0 ===== CH2 SF01 NUC1 P1 PLW1 ===== CH2	.tion Parameter 20140911 17.17 spect am PABBO BB/ zgpg30 65536 CDC13 16 4 64102.563 H: 0.978127 H: 0.5111808 se 203.57 7.800 us 6.50 us 294.8 K 2.00000000 se 0.03000000 se 1 4NNEL f1 161.9674942 MI 31P 14.25 u: 15.0000000 W ANNEL f2
						NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13	1H waltz16 90.00 w 10.00000000 W 0.31604999 W 0.25600001 W
Januar aniny nakang mungupa kuka kun nu takang kunga unga nga kuka kun ngana man	An jung sang mang mang mang mang mang mang mang m	gard Change and a start and	484 (Sama)-Sama Sama Sama Sama Sama Sama Sama Sama	vaanaan disalaan sala araa sala araa sala ahaa ahaa ahaa ahaa ahaa ahaa ah	างสารครามสาวประวงความรู้รางสาวประกอบสาวประก	F2 - Proces. SI SF WDW SSB 0 LB MMMANGB 0 PC	sing parameter 32768 161.9755930 M EM 1.00 H

			BRU	IKER
Compound (S _p)-27 ³¹ P/ ¹ H NMR coupled			Current Da NAME O EXPNO PROCNO	ta Parameters B 1707 after co 2 1
			F2 - Acqui Date Time INSTRUM PROBHD 5 PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	sition Paramete 20140911 17.20 spect mm PABBO BB/ 2g30 65536 CDC13 32 4 64102.563 H 0.978127 H 0.51118008 203.57 7.800 U 6.50 U 294.5 F 2.00000000 s 1
			SFO1 NUC1 P1 PLW1	HANNEL fl ===== 161.9674942 N 31P 14.25 U 15.00000000 V
			F2 - Proce SI WDW SSB C LB GB C PC	essing parameter 32768 161.9755930 M EM 1.00 M 1.40





							÷	S S Compour P/H NM		MS Xa led		Current Data Parameters NAME OB 1588 pure2 EXPNO 1 PROCNO 1
												F2 - Acquisition Parameters Date20151124 Time 11.00 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG 2gpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 292.2 K D1 2.0000000 sec D11 0.0300000 sec TD0 1
												SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
												SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.00000000 W PLW12 0.31604999 W PLW13 0.25600001 W
				united and a second stand	19 1 International Contract Contract	t		l				F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM
140	130	120	110	100	90	80	70	60	50	40	30	ppm 1.40

				aib'iH MM	Rcouple	d		NAME EXPNO PROCNO F2 - Acq Date Time INSTRUM PROBHD	uisitior 2 5 mm Pi	2 1 Parameter 20151124 11.02 spect ABBO BB/	`S
								PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	64 (0. 2.(zg30 65536 CDC13 32 4 4102.563 H2 0.978127 H2 5111808 se 203.57 7.800 us 6.50 us 291.7 K 30000000 se 1	; ;; ;ec ;ec
								SFO1 NUC1 P1 PLW1	CHANNEI 161	5 f1 ===== .9674942 MH 31P 14.25 us 20000000 W	lz sec
								F2 - Pro SI SF WDW SSB LB GB PC	cessing 161 0 0	parameters 32768 .9755930 MH EM 1.00 H2 1.40	[z





Compound (R _p)-28b ³¹ P/H NMR decoupled	Current Data Parameters NAME OB 1595 pure EXPNO 1 PROCNO 1
	F2 - Acquisition Parameters Date_ 20140723 Time 19.43 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 295.3 K D1 2.0000000 sec D11 0.0300000 sec TD0 1
	SF01 CHANNEL f1 ====== NUC1 31P P1 14.25 usec PLW1 15.00000000 W
- -	SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.0000000 W PLW12 0.31604999 W PLW13 0.25600001 W
	F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz

								<>-	S.o.	L						
								Compo Jip/iH	Յթ) Գ ⊷ОАс ound (Rթ) NMR cou	;)-28b ipled				Current E NAME EXPNO PROCNO	ata Paramete OB 1595 pu	rs re 2 1
														F2 - Acqu Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	aisition Para 201407 19. 5 mm PABBO E 20 655 CDC 64102.5 0.9781 0.51118 203. 7.8 6. 294 2.000000	meters 23 46 ct 30 36 13 32 4 63 Hz 27 Hz 608 sec 57 600 usec 50 usec 50 usec 1
														SF01 NUC1 P1 PLW1	CHANNEL f1 = 161.96749 14 15.000000	42 MHz 1P 25 usec
														F2 - Proc SI SF WDW SSB LB GB PC	cessing param 32 161.97559 0 1 0 1	eters 68 930 MHz EM 00 Hz
nyitayogo deserinyingan	1	len skotski kojestaj ogo	ter som det state att bester	in the second second	nya nya katang katan	everyoned weapon	in the state of the	Handina an Andrea	ny bara daga daga kata kata daga ka	New York and an investigation of the	se for an a state of the state	maninghilisense	1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.	A N		
140	130	120	110	100	90	80	70	60	50	40	30	20	ppn	n		





Compo 3 ¹ P/H NM	$B_{g,0}$ COH und (B_{g})-29 IR decoupled			Current Da NAME EXPNO PROCNO	TA Parameters OB 1601
				F2 - Acqui Date Time INSTRUM PROBHD 5 PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D1 D11 TD0	sition Parameters 20140724 9.50 spect mm PABBO BB/ zgpg30 65536 Acetone 16 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 295.5 K 2.00000000 sec 0.03000000 sec 1
				C: SF01 NUC1 P1 PLW1 SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13 F2 - Proce: SI	HANNEL f1 ====== 161.9674942 MHz 31P 14.25 usec 15.00000000 W HANNEL f2 ====== 400.1316005 MHz 1H waltz16 90.00 usec 10.00000000 W 0.31604999 W 0.25600001 W ssing parameters 32768
130 120 110 100 90	80 70	60 50	40 30	ppm _{SSB} 0 LB GB 0 PC	161.9755930 MHz EM 1.00 Hz 1.40

F2 - Acq	quisition Parameters 20140724 9.52
Date INSTRUM PROBHD PULPROG TD SOLVENT NS SWH FIDRES AQ RG DW DE TE TE TE DI TDO TDO F2 - Pro SI SF MWI F2 - Pro SI SF MWI F2 - Pro SI SF MWI F2 - Pro SI SF	spect 5 mm PABBO BB/ zg30 65536 Acetone 32 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 295.2 K 2.00000000 sec 1 = CHANNEL f1 ======= 161.9674942 MHz 31P 14.25 usec 15.00000000 W ocessing parameters 32768 161.9755930 MHz EM 0 1.00 Hz 0 1.40

1.






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<u>_</u>	_e od	2

						Cor 31p/	mpound ¹¹ H NMR o	(S _p)-30 xoupled				Current NAME EXPNO PROCNO	Data Parameters OB 1662 after v 2 1	work-up
												F2 - Acc Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE	guisition Parame 20140815 17.53 spect 5 mm PABBO BB/ 2g30 65536 CDC13 16 4 64102.563 0.978127 0.5111808 203.57 7.800 6.50	Hz Hz sec usec usec
											- - - - - - - - - - - - - - - - - - -	TE D1 TD0 SF01 NUC1 P1 PLW1 F2 - Pr: SI	294.9 2.00000000 1 = CHANNEL f1 ==== 161.9674942 31p 14.25 15.00000000 pcessing paramet 32768	K sec MHz usec W ers
												NDW SSB LB GB PC	0 0 1.00 0 1.40	ΗI
90	80	70	60	50	40	 20	10	0	-10	-20	ppm			





0B 927 pad=10 run with findz0 before acquisitio n

exp1 Phosphorus

SAMPLE	SPECTAL
date Jan 31 2013	temp not used
solvent rdr13	nain 14
file /home/TCHuser~	snin 20
/vomrsvs/data/auto~	hst 0.008
2019 01 20/c 2013~	not 0.000
0191 14/data/cdc12w	alfa 10.000
0151_14/data/cdc154	ELACS
ACOUTSTITION	il n
sw 15797.8	in n
at 1.600	dn v
nn 50552	hs nv
fb 8800	PROCESSING
hs 64	16 1 00
dt 1 000	fp pot used
ui 1.000	
10 10 10	UISPLAT
	sp = 3647.3
TRANSMITTER	wp 15/9/.3
in P31	171 3547.8
STEQ 121.465	rtp U
tot 7421.1	rp -137.9
tpwr 55	lp -350.5
pw 9.150	PLOT
DECOUPLER	wc 250
dn H1	sc 0
dof 0	vs 21
dan yyy	th 5
dmm w	ai cdc ph
dpwr 35	
dmf 6700	

80

90

70

60

50



Compound (R_p, R_p) -81 ³¹ P/¹H NMR decoupled

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ppm

-20

-10

0

40	
44 5 52	
9/ /8	

30

20

10

OB 927

exp1 Phosphorus

SPECIAL
temp not used
gain 14
spin 20
hst 0.008
pw90 18.300
alfa 10.000
FLAGS
il n
in n
dp V
hs ny
PROCESSING
1b 1.00
fn not used
DISPLAY
sp -3647.3
wp 15797.3
rfl 3647.8
rfp 0
rp 108.7
1p -113.7
PLOT
wc 250
sc 0
vs 170
th 4
ai cdc ph



Compound (Rp,Rp)-31 ³¹P/¹H NMR coupled

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1 8 8 8	90	80	70	60 5	i 0 4	10	30	20	10	0	-10	-20	bbw

OB 927 pad=10 run with findz0 before acquisitio n

exp1 Proton

	SAMPLE	DEC	& VT
date	Jan 31 2013	dfra	75 454
coluer	t cdc19	do	C19
	/home/TCllusers	dmar	49
///////////////////////////////////////	We (data /autow	dof	43
/ VH8H 3	01 20/m 2012	do	0
2013	01.20/5_2013~	um Jaco	mm
0131_1	13/data/cdc13~	amin	10100
A.C.(U1.110	amt	13100
AUC	200 047	PROG	COSTNO
STIQ	300.047	wittie	C 4
th	1 0 0 0	proc	JT t
at	1.998	tn	not used
np	19184		
SW	4800.8	werr	xmreact
fb	2600	wexp abo	rtoff flus≁
bs	16	h procpl	ot aborton
tpwr	55	wbs	
pW	7.9	wnt	
d1	1.000		
tof	277.9		
nt	16		
ct	16		
alock	V		
gain	not used		
3	FLAGS		
i1	n		
in	n		
dp	У		
· I	DISPLAY		
sp	-593.4		
wp	4800.5		
VS	344		
SC	0		
WC	240		
hzmm	20.00		
is	419.49		
rfl -	593.6		
rfp	0		
th	2		
ins	1.000		
ai cr	tc ph		

О C **∖**₂0 'n Compound (Rp,Rp)-81 ¹H NMR



OB 927

exp1 Carbon

SAMPLE			SPECIAL
date Jan 3	1 2013	temp	not used
solvent	cdc13	gain	20
file /home/T	CUuser≁	spin	20
/vnmrsys/date	a/auto~	hst	0.008
2013.01.20/	s 2013~	pw90	18.500
0131 14/data	/cdc13~	alfa	10.000
	07.fid		FLAGS
ACQUISITĪ	ON	i 1	n
sw 1	8115.9	in	n
at	1.301	dp	У
np	47120	hs	nn
fb	10000		PROCESSING
bs	64	1b	0.50
d1	2.000	fn	not used
nt	800		DISPLAY
ct	800	sp	-1135.5
TRANSMITT	ER	wp	18115.4
tn	C13	rf1	1136.1
sfrq	75.454	rfp	0
tof	766.0	rp	23.6
tpwr	58	1p	-181.3
wq	9.250		PLOT
DECOUPLE	R	wc	250
dn	H1	SC	0
dof	0	VS	228
dm	УУУ	th	6
dmm	Ŵ	ai	cdc ph
dpwr	35		
dmf	6700		



Compound (R_p,R_p)-81 ¹³C NMR





DE 6.50 usec TE 295.2 K D1 2.00000000 sec TD0 1
DE 6.50 usec TE 295.2 K D1 2.0000000 sec TD0 1 ====== SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.0000000 W F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40
DE 6.50 usec TE 295.2 K D1 2.00000000 sec TD0 1 ==================================
DE 6.50 usec TE 295.2 K D1 2.0000000 sec TD0 1
INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zg30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7 800 usec
NAME OB 1719f2 pure EXPNO 2 PROCNO 1 F2 - Acquisition Parameters Date_ 20140919 Time 18.04





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								Сотро Этриц м	ound (R _p			Current Data Parameters NAME OB 2092 after column EXPNO 1 PROCNO 1
												F2 - Acquisition Parameters Date_ 20150626 Time 17.17 INSTRUM spect PROBHD 5 mm PROBHD 5 mm PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.50 DE 6.50 TE 294.5 D1 2.00000000 Sec D1 D1 0.03000000
												SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
												SFO2 CHANNEL f2 f2 NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.00000000 W PLW12 0.31604999 W PLW13 0.25600001 W
											,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40
 110	100	90	80	70	60	50	40		20	10	0	ppm

	Current Data Parameters NAME OB 2092 after colu: EXPNO 2 PROCNO 1
	$\begin{array}{cccc} F2 & - \ Acquisition \ Parameters \\ Date_ & 20150626 \\ Time & 17.19 \\ INSTRUM & spect \\ PROBHD & 5 \ mm \ PABBO \ BB/ \\ PULPROG & 2g30 \\ TD & 65536 \\ SOLVENT & CDC13 \\ NS & 32 \\ DS & 4 \\ SWH & 64102.563 \ Hz \\ FIDRES & 0.978127 \ Hz \\ AQ & 0.5111808 \ sec \\ RG & 203.57 \\ DW & 7.800 \ use \\ DE & 6.50 \ use \\ TE & 294.1 \ K \\ D1 & 2.00000000 \ sec \\ TD0 & 1 \\ \end{array}$
	SFO1 161.9674942 MHz NUC1 31P P1 14.25 use PLW1 15.00000000 W
	F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40





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								Co 31p/1	mpound H NMR de	(R _p)-84 accupted	I	Current Data Parameters NAME OB 2097 after column EXPNO 1 PROCNO 1
												$\begin{array}{cccc} F2 & - \ Acquisition \ Parameters\\ Date_ 20151201\\ Time 11.29\\ INSTRUM spect\\ PROBHD 5 \ mm \ PABBO \ BB/\\ PULPROG 2gpg30\\ TD 65536\\ SOLVENT CDC13\\ NS 16\\ DS 4\\ SWH 64102.563 \ Hz\\ FIDRES 0.978127 \ Hz\\ AQ 0.5111808 \ sec\\ RG 203.57\\ DW 7.800 \ usec\\ DE 6.50 \ usec\\ TE 291.9 \ K\\ D1 2.0000000 \ sec\\ D11 0.03000000 \ sec\\ TD0 1\\ \end{array}$
												SF01 CHANNEL f1 f1 NUC1 31P P1 14.25 usec PLW1 15.00000000 W
												SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.00000000 W PLW12 0.31604999 W PLW13 0.25600001 W
												F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40
1	90	80	70	60	50	40	····· 30	20	10	••••••••••••••••••••••••••••••••••••••	-10	ppm

			Compound ³¹ P/H NMF	l (R _p)-34 Coupled	Current Da NAME C EXPNO PROCNO	ita Parameter)B 2097 after
					F2 - Acqui Date Time INSTRUM PROBHD S PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	.sition Param 2015120 11.3 spec 5 mm PABBO BB 2g3 6553 CDC1 3 64102.56 0.97812 0.511180 203.5 7.80 6.5 291. 2.0000000
					SFO1 NUC1 P1 PLW1	CHANNEL f1 161.967494 31 - 14.2 15.0000000
					F2 - Proc SI WDW SSB LB GB PC	≥ssing parame 3276 161.975593 E 0 2.0 0 1.4





	Compound (Sp)-35 ³¹ P/H NMR decoupled	Current Data Parameters NAME OB 1481 pure EXPNO 1 PROCNO 1
		F2 - Acquisition Parameters Date_ 20140514 Time 9.36 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 297.1 K D1 2.00000000 sec D11 0.03000000 sec TD0 1
		SF01 CHANNEL f1 ====== SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
		SF02 CHANNEL f2 SF02 400.1316005 NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.00000000 W PLW12 0.31604999 W PLW13 0.25600001 W
90 80 70 60 50	40 30 20 10 0	F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM -10 ppmssb 0 LB 1.00 Hz GB 0 PC 1.40

	Compound (S _p)-35 ³¹ P/ ¹ H NMR coupled	Current Data Parameters NAME OB 1481 pure EXPNO 2 PROCNO 1
		F2 - Acquisition Paramete Date
		SF01 CHANNEL f1 ===== SF01 161.9674942 NUC1 31P P1 14.25 NUC1 15.0000000 N
		F2 - Processing parameter SI 32768 SF 161.9755930 M WDW EM SSB 0 LB 1.00 H GB 0 PC 1.40







		Compou ³¹ P/ ¹ H NM	ınd (S _p)-37 vîRcoupled	Current Data Parameters NAME OB 2105 1st crysta EXPNO 2 PROCNO 1 F2 - Acquisition Parameters Date_ Date_ 20150716 Time 15.38 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG 2g30 TD 65536 SOLVENT CDC13 NS 32 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 295.2 K D1 2.0000000 sec TD0 1
				NUC1 31P P1 14.25 used PLW1 15.0000000 W F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40





	ACO BUD	
	Compound (R _p)-88 ³¹ P/H NMR decoupled	Current Data Parameters NAME OB 2096 after co EXPNO 1 PROCNO 1
		F2 - Acquisition Parameta Date 20150701 Time 10.05 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 FIDRES 0.978127 AQ 0.5111808 RG 203.57 DW 7.800 DE 6.50 TE 294.8 D1 2.00000000 D11 0.03000000 TD0 1
		SF01 CHANNEL f1 ===== CHANNEL f1 =====
		NUC1 31P P1 14.25
		PLW1 15.0000000 '
		SF02 400.1316005 NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 FLW2 10.00000000 PLW12 0.31604999 PLW13 0.25600001
		F2 - Processing paramete
		SF 161.9755930
90 80 70 60 50 40 3	20 10 0 -10 -20	DDM ^{LB} 1.00
"		PC 1.40

						Ac O P Compound (Pp)-38 ³¹ P/ ¹ H NMR coupled							Current Data Parameters NAME OB 2096 after colu EXPNO 2 PROCNO 1					
														F2 - Acc Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TD0	1 quisition Parameters 20150701 10.07 spect 5 mm PABBO BB/ 2g30 65536 CDC13 32 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 294.4 K 2.00000000 sec 1			
														SF01 NUC1 P1 PLW1 F2 - Prc SI SF WDW SSB LB GB PC	CHANNEL f1 ======= 161.9674942 MHz 31P 14.25 usec 15.00000000 W DCessing parameters 32768 161.9755930 MHz EM 0 1.00 Hz 0 1.40	2		
 90	80	70	60	50	40	30	20	10	0	-10	-20	-30	ppr	 n				





HO		
эльН	NMR decoupled	Current Data Parameters NAME OB 2114 after column EXPNO 5 PROCNO 1
		F2 - Acquisition Parameters Date20150715 Time 16.05 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 295.4 K D1 2.00000000 sec D11 0.03000000 sec TD0 1
		SF01 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W
		SFO2 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 UW2 10.00000000 W PLW12 0.31604999 W PLW13 0.25600001 W
		F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM
100 90 80 70 60 50	40 30 20 10 0 -10 -20 -30 pr	M SSB 0 M LB 1.00 Hz GB 0 PC 1.40

	 	 	and the second						
		ł		~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~			GB PC	0	1.40
							SFO1 NUC1 P1 PLW1 F2 - SI SF WDW SSB LB	=== CHANNEI 161 15.(Processing 161 0	1 f1 9674942 MHz 31P 14.25 use 0000000 W parameters 32768 .9755930 MHz EM 1.00 Hz
						ţ	F2 - 7 Date_ Time INSTRI PROBHI PULPRO TD SOLVE NS DS SWH FIDRE AQ RG DW DE TE D1 TD0	JM D 5 mm PA DG NT S 64 S 0. 2.0	11111111111111111111111111111111111111
				но	bled		Curren NAME EXPNO PROCNO F2 - 1	nt Data Par OB 2114 D Acquisition	ameters after colum 2 1 Parameters




		ł	(پېلې ده		~				
		ал ^н (Compoun 9/1H NMB	d (R _p)-8: decoupl	ed			Curren NAME EXPNO PROCNO	t Data Parameters OB 2115 dry 1 1
								F2 - A Date_ Time INSTRU PROBHD PULPRO TD SOLVEN NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0	cquisition Parameters 20150716 17.30 M spect 5 mm PABBO BB/ G zgpg30 65536 M CDC13 16 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 use 6.50 use 295.5 K 2.00000000 sec 1 = CHANNEL f1 ===== 161.9674942 MHz
								P1 PLW1	31P 14.25 use 15.00000000 W
								SFO2 NUC2 CPDPRG PCPD2 PLW2 PLW12 PLW13	CHANNEL f2 ====== 400.1316005 MHz 1H 2 waltz16 90.00 use 10.00000000 W 0.31604999 W 0.25600001 W
	*******			,,,,,,,,,,,,	****			F2 - Pı SI TTTTTSF	ocessing parameters 32768 161.9755930 MHz
110 100 90 80 70 60	0 50	40	30	20	10	0	-10	ppm ^{WDW} SSB LB	EM 0 1.00 Hz
	10.16 89.84							GB PC	1.40

				HO	ر چ ^{ار} ر	\rightarrow		B	RUKEF	8
				Cor Jip/	npound (¹ H NMR o	R _p)-39 oupled		Curr NAME EXPN PROC	ent Data Paramete OB 2115 c O	ers lry 2
								F2 Date Time INST PROB PULP TD SOLVI NS DS SWH FIDRI AQ RG DW DE TE D1	Acquisition Para 201507 RUM spe HD 5 mm PABBO F ROG 20 ENT CDC 64102.5 ES 0.9781 0.51118 203. 7.8 6. 295 2.000000	meters 16 33 ct B/ 30 36 13 32 4 63 Hz 27 Hz 08 sec 57 00 use 50 use .1 K 00 sec
								SFOI NUC1 P1 P1W1	==== CHANNEL f1 = 161.96749 14. 15.000000	42 MHz 1P 25 use
								FLWI F2 SI SF WDW SSB LB GB GB PC	Processing param 327 161.97559 0 1. 0 1.	eters 68 30 MHz EM 00 Hz 40
analysyc-day water as wysterrad as other	ann a tha a faith a su a s	146 1500 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100 - 100		Yan Yangi manaka na Bagatan yan ma	anno-kaspagaannanja-aanjo-kasu-spoj	مەرە بەھەرە بەرە ئەرە بەرە بەرە بەرە بەرە بەرە ب	1.000.000	norde general habitation of		





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$\begin{aligned} & $												
$H_{0} \downarrow_{0} \downarrow_{0} \downarrow_{0}$ Compound (P,) 39 3 ¹ P/H NMR decoupled $P_{1} = P_{1} + P_{1} + P_{1} + P_{2} + P$												1. 1. 1.
$H_{0} = \int_{0}^{1} \int_{0}^{1} \int_{0}^{1} \frac{1}{1000} \int_{0}^{1} \frac{1}{1000} \int_{0}^{1} \frac{1}{10000} \int_{0}^{1} \frac{1}{100000} \int_{0}^{1} \frac{1}{10000000} \int_{0}^{1} \frac{1}{10000000000000000000000000000000000$												F2 - Processing parameters SI 22768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40
Hough to the second sec												CHANNEL f2 f2 second SF02 400.1316005 MHz H NUC2 1H CPDFRG[2 waltz16 PCPD2 90.00 usec Usec PLW12 0.31604999 W PLW13 0.25600001 W Second V V
$\begin{aligned} \begin{array}{c} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} \mathbf{h} h$												Image CHANNEL fl Image Image
HOJGG Compound (R.)-39 3 ⁿ P/ ¹ H NMR decoupled P2 - Acquisition Parameters 102 102 102 102 102 102 102 102 102 102												PRUBRUG 5 WMM PARBO BB/ PULPROG 25036 SOLVENT CCC13 NS 16 DS 4 SWM 64102.563 H2 FIDRES 0.979H27 H2 AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 256.4 D1 2.0000000 sec UND 0.000000 sec
HO HO BRUKI					Com aibliH	pound (R _p NMR deco)-89 upled					Current Data Parameters NAME OB 1930 2nd crystal EXPNO 1 PROCNO 1 F2 - Acquisition Parameters Date 20150210 Time 10.27 INSTRUM spect
					но	j. Ko						BRUKE



Data Parameters OB 1930 2nd crystallization in CH3CN

12817.8	20150210
Time	10.27
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zapa30
TD	65536
SOLVENT	chc13
NS	16
DS	4
SWH	64102.563 Hz
FIDRES	0 978127 Hz
AO	0 5111808 800
RG	203.57
0W	7 800 неес
DE	6 50 usec
TE	296 4 K
D1	2 00000000 000
D11	0.03000000 sec
700	1
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	CHANNEL FI
SFOL	161.9674942 MH2
NUCT	310
P1	14 25 11000
PLW1	15 0000000 8
	+0:00000000
	CHANNEL f2 == = = maxim
SFO2	400.1316005 MHz
NUC2	7日
CPDPRG/2	waltzli
PCPD2	90 00 usec
PLW2	10.0000000 W
PLW12	0.31604999 W
PLW13	0.25600001 W
	0120000000
F2 - Proc	cessing parameters
SI	32768
SF	161.9755930 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40
	A . 10



Compound (R_p)-89 ³¹P/¹H NMR coupled



Current Data Parameters NAME OB 1930 2nd crystallization in CH3CN EXPNO 2 PROCNO 1

F2 - Acqu	isition Parameters
Date	20150210
Time	10.29
INSTRUM	spect
PROBHD	5 mm PABRO 88/
PULPROG	2030
17 D	65536
SOLVENT	CDC13
NS	32
ns	12
Sidu	6/300 660 0
TTNDTC	04102,000 82
200000	0.5111000 000
- NV - NV	0.JIII000 Sec
2553	7 800 04-1
DN DN	7.000 usec
DE.	5.DU USEC
15	296.1 A
U1 mp.0	2.00000000 sec
1.D0	1
220222000 (MANNEL EI novemmente
SFOI	161.9674942 MHz
NUCL	318
P1	14.25 usec
PLW1	15.0000000 W
F2 - Proce	essing parameters
SI	32766
SF	161.9755930 MHz
WOW	EM
SSB ()
1.8	1.00 Hz
-68 ()
D.C.	1 4.0

1.40







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		HO Comi ³¹ P/1F	pound (R _p	,)-39 ipled		Current Data Pa NAME OB 214 EXPNO PROCNO F2 - Acquisitio Date_ Time INSTRUM PROBHD 5 mm P PULPROG TD SOLVENT NS DS SWH 6 FIDRES AQ 0 RG DW DE TE D1 2. TD0	rameters 8 4th crystallization 2 1 n Parameters 20150902 17.37 spect ABB0 BB/ zg30 65536 Acetone 32 4 4102.563 Hz 0.978127 Hz .5111808 sec 203.57 7.800 usec 6.50 usec 294.7 K 00000000 sec 1 1 =================================
 	 				 *****	SF01 161 NUC1 PLW1 15. F2 - Processing SI SF 161 WDW SSB 0 LB GB 0 PC	.9674942 MHz 31P 14.25 usec 00000000 W parameters 32768 .9755930 MHz EM 1.00 Hz 1.40





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exp1 Phosphorus

$\begin{array}{cccccccccccccccccccccccccccccccccccc$	SAMP	LE		SPECIAL
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	date Apr	9 2013	temp	not used
file /home/TCUuser~ $\sin n$ 20 /vnmrsys/data/auto~ hst 0.008 _2013.04.06/s_2013~ pw90 18.300 0409_41/data/cdc13~ alfa 10.000 _04.fid FLAGS ACQUISITION i1 n sw 15797.8 in n at 1.600 dp y np 50552 hs ny fb 8800 PROCESSING bs 64 lb 1.00 d1 1.000 fn not used nt 32 DISPLAY ct 32 cp -3647.3 TRANSMITTER wp 15797.3 tn P31 rf1 3647.8 sfrq 121.465 rfp 0 tof 7421.1 rp -96.9 tpwr 55 lp -495.4 pw 9.150 PLOT DECOUPLER wc 250 dn H1 sc 0 dof 0 vs 33 dm yyy th 111 dmm w ai cdc ph dpwr 35 dmf 6700	solvent	cdcl3	gain	8
$\begin{tabular}{lllllllllllllllllllllllllllllllllll$	file /home	/TCUuser~	spin	20
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	/vnmrsys/d	lata/auto≁	hst	0.008
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	_2013.04.0	6/s_2013~	pw90	18.300
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0409_41/da	ta/cdc13~	alfa	10.000
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		_04.fid		FLAGS
	ACQUISI	TION	i 1	n
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	sw	15797.8	în –	n
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	at	1.600	dp	У
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	np	50552	hs	ný
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	fb	8800		PROCESSING
$ \begin{array}{cccccccccccccccccccccccccccccccccccc$	bs	64	1b	1.00
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	d1	1.000	fn	not used
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	nt	32		DISPLAY
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	ct	32	sp	-3647.3
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	TRANSMI	TTER	wp	15797.3
sfrq 121.465 rfp 0 tof 7421.1 rp -96.9 tpwr 55 1p -495.4 pw 9.150 PLOT DECOUPLER wc 250 dn H1 sc 0 dof 0 vs 33 dm yyy th 11 dmm w ai cdc ph dpwr 35 dmf 6700	tn	P31	rf1	3647.8
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	sfrq	121.465	rfp	0
tpwr 55 1p -495.4 pw 9.150 PLOT DECOUPLER wc 250 dof 41 sc 0 dof 0 vs 33 dm yyy th 11 dmm w ai cdc ph dpwr 35 dm 6700	tof	7421.1	rp	-96.9
pw 9.150 PLOT DECOUPLER wc 250 dn H1 sc 0 dof 0 vs 33 dm yyy th 11 dmm w ai cdc ph dpwr 35 dmf 6700	tpwr	55	1p	-495.4
DECOUPLER wc 250 dn H1 sc 0 dof 0 vs 33 dm yyy th 11 dmm w ai cdc ph dpwr 35 dmf 6700	pw	9.150		PLOT
dn H1 sc 0 dof 0 vs 33 dm yyy th 11 dmm w ai cdc ph dpwr 35 dmf 6700 5	DECOUP	LER	WC	250
dof 0 vs 33 dm yyy th 11 dmm w ai cdc ph dpwr dpwr 35 dmf	dn	H1	sc	0
dm yyy th 11 dmm w ai cdc ph dpwr 35 dmf 6700	dof	0	VS	33
dmm waicdcph dpwr 35 dmf 6700	dm	УУУ	th	11
dpwr 35 dmf 6700	dmm	Ŵ	ai	cdc ph
dmf 6700	dpwr	35		-
	dmf	6700		



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exp1 Phosphorus

:	SAMPLE		SPECIAL				
date	Apr	9 2013	temp	not used			
solven	t	cdc13	gain	25			
file /	home/T	CUuser≁	spin) 20			
/vnmrs	ys/dat	a/auto~	hst	0.008			
2013.	04.06/	s_2013~	pw90	18.300			
0409_2	2/data	/cdc13~	alfa	10.000			
-		02.fid		FLAGS			
ACQ	UISITĪ	ON	11	n			
sw	1	5797.8	in	n			
at		1.600	dp	Y			
np		50552	hs	ný			
fb		8800		PROCESSING			
bs		64	lb	1.00			
d1		1.000	fn	not used			
nt		64		DISPLAY			
ct		64	sp	-3647.3			
TRA	NSMITT	ER	wp	15797.3			
tn		P31	rf1	3647.8			
sfrq	1	21.465	rfp	0			
tof		7421.1	rp	27.0			
tpwr		55	lp	-113.7			
pw		9.150		PLOT			
. DE	COUPLE	R	wc	250			
dn		H1	SC	0			
dof		0	vs	344			
dm		ynn	th	7			
dmm		Ŵ	ai	cdc ph			
dpwr		35		·			
dmf		6700					





*	HO Eto	BRUKER
	Compound 41 ³¹ P/ ¹ H NMR decoupled	Current Data Parameters NAME OB 1592 EXPNO 1 PROCNO 1
		F2 - Acquisition Parameters Date_ 20140722 Time 9.33 INSTRUM spect PROBHD 5 mm PULPROG zgpg30 TD 65536 SOLVENT Acetone NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 295.5 K D1 2.00000000 sec D11 0.03000000 sec TD0 1
		SFO1 CHANNEL f1 f1 <thf1< th=""> <thf1< th=""> <thf1< th=""></thf1<></thf1<></thf1<>
		CHANNEL f2 ====== SF02 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.0000000 W PLW12 0.31604999 W PLW13 0.25600001 W
90 85 80 75 70 65 60	55 50 45 40 35 30 25 20 15 10 5	SI 32768 SF 161.9755930 MHz 0 ppm SSB 0 LB 1.00 Hz GB 0 PC 1.40

		с но но		~			BR	UKER
		Com 31P/1H M	o pound 41 IMRcoupl	led			Current NAME EXPNO PROCNO	Data Parameter OB 159
							F2 - Acc Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG CW DE TE D1 TD0	quisition Parar 2014072 9.3 5 mm PABBO BI 2g3 6553 Aceton 64102.56 0.97812 0.511180 203.2 7.88 6.5 295 2.0000000
							SFO1 NUC1 P1 PLW1	= CHANNEL fl == 161.967494 33 14.2 15.0000000
							F2 - Pro SI SF WDW SSB LB GB PC	ocessing param 327 161.975593 0 0 1.0 0 1.0
				1				

		EtO EtO H Compound 42 ³¹ P/H NMR decoupled		Current Data Parameters NAME OB 1725 after work-up EXPNO 5 PROCNO 1
				F2 - Acquisition Parameters Date_ 20140917 Time 12.01 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT CDC13 NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 296.0 K D1 2.00000000 sec D1 2.00000000 sec D1 2.00000000 sec D1 0.03000000 sec D1 161.9836917 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W CHANNEL f2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 0.31604999 W PLW13 0.25600001 W
				F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0
110 100 90 8	80 70 60 50 40	0 01 02 08 3.08 3.08 3.08 3.08 3.08 3.08 3.08 3.	-10 -20 -30 ppn	GB 0 nPC 1.40

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						isa Ng Ng	EtO EtO Compo V ¹ H NM	POF →-P H ound 42 IR coup	∃t 2 bled							Current NAME EXPNO BROCKO		Paramete 1725 afte	rs r work-up 1
																FROCNO F2 - Ac Date_ Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 TDO SFO1 NUC1 PL PLW1	quisit 5 mr	tion Para 201409 12. spe m PABBO E 20 655 CDC 64102.5 0.978: 0.51116 203 7.6 6 299 2.000000 NNEL f1 161.9674 14 15.00000	meters 17 02 cct 18 17 02 17 02 17 17 02 17 17 17 17 17 17 17 17 17 17
																F2 - Pr SI SF WDW SSB LB GB PC	ocess 0 0	ing para 32 161.9755 1 1	meters 768 930 MHz EM .00 Hz .40
ייייז 9 (0 80	70	60	50	40	30	20	10	0	-10	-20	-30	-40	-50	ppi	m			



					Et EtC 31p/1		n 43 decoupled	-				Current I NAME EXPNO PROCNO	Data Parameters OB 1701f2
												F2 - Acqu Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS DS SWH FIDRES AQ RG DW DE TE D1 D11 TD0	nisition Parameters 20140910 9.04 spect 5 mm PABBO BB/ 2gpg30 65536 DMSO 16 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 usec 6.50 usec 295.6 K 2.0000000 sec 0.0300000 sec 1
												SFO1 NUC1 P1 PLW1	CHANNEL f1 161.9674942 MHz 31P 14.25 usec 15.0000000 W
												SFO2 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13	CHANNEL f2 ====== 400.1316005 MHz 1H waltz16 90.00 usec 10.00000000 W 0.31604999 W 0.25600001 W
			****		1. 1. 1. 1. 1. 1. 1. 1. 1. 	***** ⁽ henree	* * * * * * * * * * * * *		****	••••••••••••••••••••••••••••••••••••••		F2 - Proc SI SF	cessing parameters 32768 161.9755930 MHz
90	0 80	70	60	50	40	51.26 0C	48.74	10	0	-10	-20	WDW PPM _{SSB} LB GB PC	EM 0 1.00 Hz 0 1.40

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					EtO EtO Co ³¹ P/1⊢		d 43 coupled	•						Current NAME EXPNO PROCNO	Data H	Parameters OB 1701f2 1	
														F2 - Ac Date Time INSTRUM PROBHD PULPROG TD SOLVENT NS SWH FIDRES AQ RG DW DE TE D1 TD0 SF01 NUC1 P1 PLW1 F2 - Pr SI	quisit: 5 mm = CHANN 10 11 ocessin	ion Parameters 20140910 9.06 spect PABBO BB/ 2g30 65536 DMSO 32 4 64102.563 Hz 0.978127 Hz 0.5111808 sec 203.57 7.800 use 6.50 use 295.3 K 2.00000000 sec 1 NEL f1 ======= 61.9674942 MHz 31P 14.25 use 5.00000000 W mg parameters 32768 61.975520 WU	
period de la constantina de la constant	using mits, a margine in weak	endigo independenti den p	in the interior of the interior	ikadan Makada Makada Panana Pa	ang dang dari dag kan dara kan dari dari		the forther that the second	Mit grap i handra vitetist	na la den de la den d	Sacial Line and Internet	1	najust yan dan sun kain yin shaday	ung en gebeken ung den under	SF WDW SSB LB GB PC	0	61.9755930 MHZ EM 1.00 Hz 1.40	
 90	80	70	 60	50	40	30	20	<u>10</u>	0	-10	-20	-30	pp	m			

OB 1037

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exp1 Phosphorus

SAMPL	E		SPECIA	L	
date Mar	26 2013	temp) ne	ot used	
solvent	cdc13	gair	ı	25	
file /home/	TCUuser~	spir	1	20	
/vnmrsys/da	ta/auto~	hst		0.008	
_2013.03.09	/s_2013~	pw9()	18.300	
0326_36/dat	a/cdc13≁	alfe	1	10.000	
	_01.fid		FLAGS		
ACQUISIT	ION	i 1		n	
SW	15797.8	in		n	
at	1.600	dp		Y	
np	50552	hs		ný	
fb	8800		PROCESS:	ING	
bs	64	1b		1.00	
d1	1.000	fn	ne	ot used	
nt	64		DISPLA	Y	
ct	64	sp		-3647.3	
TRANSMIT	TER	wp	-	15797.3	
tn	P31	rf1		3647.8	
sfrq	121.465	rfp		0	
tof	7421.1	rp		-168.2	
tpwr	55	lp		-341.1	
pw	9.150		PLOT		
DECOUPL	ER	wc		250	
dn	H1	SC		0	
dof	0	Vs		62	
dm	УУУ	th		7	
dmm	W	ai	cdc ph		
dpwr	35				
dmf	6700				



Compound 41 ³¹P/¹H NMR decoupled



- 43.828 - 43.272 **OB** 1037

-69

exp1 Phosphorus

SAM	IPLE	SPECIAL					
date Ma	r 26 2013	temp	n	ot used			
solvent	cdc13	gain	I	25			
file /hom	ie/TCUuser≁	spin	l i	20			
/vnmrsys/	data/auto~	hst		0.008			
_2013.03.	09/s_2013~	pw90		18.300			
0326_36/d	ata/cdc13~	alfa		10.000			
	_02.fid		FLAGS				
ACQUIS	ITION	il.		n			
sw	15797.8	in		n			
at	1.600	dp		У			
np	50552	hs		ný			
fb	8800		PROCESS.	ING			
bs	64	1b		1.00			
d1	1.000	fn	n	ot used			
nt	64		DISPLA	Ý			
ct	64	sp		3185.7			
TRANSM	ITTER	wp		4513.5			
tn	P31	rf1		3647.8			
sfrq	121.465	rfp		0			
tof	7421.1	rp		2.6			
tpwr	55	lp		-113.7			
pw	9.150		PLOT				
DECOU	PLER	wc		250			
dn	H1	sc		0			
dof	0	VS		235			
dm	ynn	th		15			
dmm	W	ai	cdc ph				
dpwr	35						
dmf	6700						



60

55

	HO HO Compound 44 ³¹ P/ ¹ H NMR decoupled	Current Data Parameters NAME OB 2110 EXPNO 1 PROCNO 1
		F2 - Acquisition Parameters Date_ 20150709 Time 9.23 INSTRUM spect PROBHD 5 mm PABBO BB/ PULPROG zgpg30 TD 65536 SOLVENT Acetone NS 16 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 294.3 K D1 2.00000000 sec D11 0.03000000 sec D11 0.03000000 sec TD0 1 FFO1 161.9674942 MHz NUC1 31P P1 14.25 usec PLW1 15.00000000 W SFO2 400.1316005 MHz NUC2 1H CPDPRG[2 waltz16 PCPD2 90.00 usec PLW2 10.00000000 W PLW12 0.31604999 W
51 50 49 48 47 46 45	44 43 42 41 40 39 38 37	F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40

0 'O HO_N -⊃Bn

Compound 44 ³¹P/¹H NMR coupled

Current Dat.	a Parameters
NAME	OB 2110
EXPNO	2
PROCNO	1
F2 - Acquis	ition Parameters
Date_	20150709
Time	9.25
INSTRUM	spect
PROBHD 5	mm PABBO BB/
PULPROG	2g30
TD	65536
SOLVENT	Acetone
NS	32
DS	4
SWH	64102.563 Hz
FIDRES	0.978127 Hz
AQ	0.5111808 sec
RG	203.57
DW	7.800 usec
DE	6.50 usec
TE	293.9 K
D1	2.00000000 sec
TD0	1
SF01 NUC1 P1 PLW1	HANNEL fl ======= 161.9674942 MHz 31P 14.25 usec 15.00000000 W
F2 - Proce	essing parameters
SI	32768
SF	161.9755930 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

را جان دیدر زیدی مرجع از در بردی	y system to a set the set	a an an an ann an an an an an an an an a	an sana sana sana kati	an the carry track	A. Press of the	a martin and	e Santa ang panta ang santa	or ^{art} de correct	in a start warden betalt	ar water a we and a star of and formed	Reference and the second second
 48	47	46	45	44	43	42	41	40	39	38	ppm

							Q₂N			OAc	-				
						ł		Com ³¹ P/ ¹ H N	pound 4 MR deco	6 upled			Current D NAME EXPNO PROCNO	ata Parameters DB 1474 recrys 1 1	t toluene
													F2 - Acqu Date_ Time INSTRUM PROBHD TD SOLVENT NS SSWH FIDRES AQ RG DW DE TE D1 D11 TD0	isition Parame 20140708 18.51 spect 5 mm BBI 1H/D- 2gpg30 65536 CDC13 16 4 64102.563 0.978127 0.5111808 203.57 7.800 6.50 294.0 2.00000000 0.03000000	Hz Hz sec usec usec K sec sec
													SFO1 NUC1 P1 PLW1	CHANNEL f1 === 161.9674942 31P 14.44 50.00000000	MHz usec W
													SF02 NUC2 CPDPRG[2 PCPD2 PLW2 PLW12 PLW13	CHANNEL f2 === 400.1316005 1H waltz16 90.00 20.00000000 0.07200000 0.05832000	MHz usec W W W
													F2 - Proc SI SF WDW SSB LB GB PC	essing paramet 32768 161.9755930 EM 0 1.00 0 1.40	ers MHz Hz
	80	70	60	50	40	30	20	10	0	-10	-20	ppn]		

Current Data Parameters NAME OB 1474 recryst toluene EXPNO 2 PROCNO 1
F2 - Acquisition Parameters Date20140708 Time 18.52 INSTRUM spect PROBHD 5 mm BBI 1H/D- PULPROG zg30 TD 65536 SOLVENT CDC13 NS 8 DS 4 SWH 64102.563 Hz FIDRES 0.978127 Hz AQ 0.5111808 sec RG 203.57 DW 7.800 usec DE 6.50 usec TE 294.0 K D1 2.0000000 sec TD0 1
PLW1 50.0000000 W F2 - Processing parameters SI 32768 SF 161.9755930 MHz WDW EM SSB 0 LB 1.00 Hz GB 0 PC 1.40

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90	80	70	60	50	40	30	20	10	0	-10	ppm



