Supporting Information for Asymmetric Hydrogenation Of Enol Phosphinates by Iridium Catalysts Having N, P Ligands

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Experimental.

All solvents were dried according to the reported procedures.¹ The chromatographic separations were performed on Kiesel gel 60 H silica gel (particle size: 0.063-0.100 mm). Thin layer chromatography (TLC) was performed on aluminium backed plates coated with Kieselgel 60 0.20mm (UV₂₅₄), and visualized under ultra-violet light (at 254 nm), or through staining with ethanolic phosphomolybdic acid followed by heating. ¹H NMR spectra were recorded at 500, 400, or 300 MHz in CDCl₃ using Chloroform (7.26ppm) peak as internal standard. ¹³C NMR spectra were recorded with at 100 and 75 MHz using the central peak of CDCl₃ (77.0ppm) as internal standard. ³¹P NMR was recorded at 121.47 MHz using 85% phosphoric acid as an external standard. Chemical shifts are reported in ppm (_ scale). IR spectra were recorded on Perkin-Elmer 100 FT/IR spectrometer. High Performance Liquid Chromatography (HPLC) was performed at 254 nm UV detector, using chiral columns (Chiralcel AD and S,S Whelk-O). Optical rotations were recorded on a thermo stated polarimeter using a 1.0 dm cell. Absolute configurations were determined for corresponding alcohols that were obtained upon hydrolysis² of the alkyl phopshinates. Trimethyl(1-phenylvinyl)oxy silane (**5a**) was purchased from Aldrich and used as received. 1-(1-methoxyvinyl) Benzene (**5b**), ³ 1-Phenylvinyl acetate (**5c**), ⁴ Diethyl 1-phenylvinyl phosphate (**5d**), ⁵ and 1-Phenylvinyl diphenylphosphinate (**5e**)² were been prepared according to the literature protocols, and their ¹H NMR spectra were compared to those in the literature.

General Procedure for synthesis of vinyl phosphinates:

Ketone (1 mmol) was dissolved in dry THF and cooled to -78 °C, and lithium bis(trimethylsilyl) amide (1 M solution in THF, 1.5mmol) was added. The mixture was left stirred for 30min. Diphenyl chlorophosphinate (1.2 mmol) was then added to the reaction, which was brought to room temperature and allowed to stir for 1h. The reaction mixture was quenched with saturated NH₄Cl (aq) and extracted with CH₂Cl₂ (20 x 2 ml). Combined organic phases were dried on MgSO₄, filtered, and evaporated *in vacuo*. Flash chromatography (70:30 Pentane / *iso*-propanol) of the residue afforded the corresponding enol phosphinate.

1) 1-*p*-Tolylvinyl diphenylphosphinate (**7a**):

Colorless gummy solid (72% yield)

¹H NMR (500 MHz, CDCl₃): 7.90-7.83 (4H, m), 7.51- 7.39 (8H, m), 7.14-7.10 (2H, m), 5.21 (1H, m), 5.14 (1H, m); ³¹P NMR: 31.62; ¹³C NMR (100 MHz, CDCl₃): 152.4 (d, *J*_{C,P} = 8.8 Hz), 138.6, 132.5 (d, *J*_{C,P} = 5.8 Hz), 132.0, 131.7, 131.6, 131.4, 128.9, 128.5, 128.4, 125, 96.8 (d, *J*_{C,P} = 5.2 Hz), 21.1. IR (CHCl₃)_v_{max}:

3061.41, 2997.41, 1633.21, 1592.93, 1577.29, 1493.97, 1270.27, 1216.94, 1130.37, 1107.46, 1074.80, 1028.76, 1003.57, 985.57, 865.86, 816.82, 728.33, 714.41, 693.66, 666.19. MS (EI) (*m/z*) (*rel.intensity*): 335.03 (MH⁺, 100%), 334.06 (M⁺, 25%), 319.16 (40%), 257.13 (25%), 243.17 (33%), 219.15 (73%), 201.12 (54%), 192.32 (90%), 179.32 (24%), 173.26 (19%), 119.25. (20%), 91.34 (16%), 77.33 (13%). HRMS (EI): Calcd for C₂₁H₁₉O₂P: 334.1123. Found: 334.1127.

2) 1-(4-*tert*-Butylphenyl) vinyl diphenylphosphinate (7b):

White solid (60.8% yield)

^1H NMR (500 MHz, CDCl_3): 7.94-7.86 (4H m), 7.58-7.42 (8H, m), 7.41-7.36 (2H, m), 5.18 (1H, dd, $J = 3.0, 2.1$ Hz), 5.14 (1H, dd, $J = 3.0, 2.0$ Hz) 1.32 (9H, s); ^{31}P NMR: 30.3; ^{13}C NMR (100 MHz, CDCl_3): 152.3 (d, $J_{\text{C-P}} = 8.8$ Hz), 132.2, 132.0 (d, $J_{\text{C-P}} = 6.4$ Hz), 131.7, 131.5, 131.4, 130.3, 128.9, 128.5, 128.4, 124.9, 96.7 (d, $J_{\text{C-P}} = 5.5$ Hz), 21.1. IR (CHCl_3) ν_{max} : 3059.11, 2964.22, 2905.20, 2868.54, 1628.70, 1592.54, 1512.18, 1484.09, 1463.38, 1439.19, 1364.11, 1312.67, 1293.03, 1270.26, 1230.65, 1198.24, 1129.03, 1111.48, 1092.46, 1002.92, 982.94, 840.12, 814.68, 728.22, 692.73, 664.44. MS (EI) (m/z) (*rel.intensity*): 377.30 (MH^+ , 10%), 3764.28 (M^+ , 45%), 330.23 (65%), 319.25 (100%), 299.16(17%), 285.24 (32%), 244.16 (15%), 234.18 (31%), 219.22 (58%), 201.09 (31%), 179.10 (11%), 173.12 (20%), 161.23 (13%), 128.20 (13%), 105.10(10%), 77.11 (5%) HRMS: Calcd for $\text{C}_{24}\text{H}_{28}\text{O}_2\text{P}$: 376.1592. Found: 376.1575.

3) 1-(4-Methoxyphenyl) vinyl diphenylphosphinate (7c):

Pale yellow gummy solid (50.4% yield)

^1H NMR (500 MHz, CDCl_3): 7.91-7.85 (4H, m), 7.60-7.41 (2H, m), 7.47-7.42 (4H, m), 6.86 (2H, m), 5.10 (1H, dd, $J = 3.0, 2.0$ Hz), 5.03 (1H, dd, $J = 3.0, 2.0$ Hz), 3.8 (3H, s); ^{31}P NMR: 30.9; ^{13}C NMR (100 MHz, CDCl_3): 160.1, 152.4 (d, $J_{\text{C-P}} = 9.1$ Hz), 132.2, 131.8, 131.6, 131.5, 130.4, 128.5, 128.4, 127.4 (d, $J_{\text{C-P}} = 6.3$ Hz), 126.5, 113.7, 95.9 (d, $J_{\text{C-P}} = 5.7$ Hz), 52.2; HRMS: Calcd for $\text{C}_{21}\text{H}_{19}\text{O}_3\text{P}$: 350.1072. Found: 350.1064. MS (EI) (m/z) (*rel.intensity*): 350.0 (M^+ , 100%), 201.0 (70%), 152.2 (15%), 135.6 (75%), 132.2(25%), 77.1 (20%).

4) 1-(4-Bromophenyl) vinyl diphenylphosphinate (7d):

White solid (60% yield)

^1H NMR (500 MHz, CDCl_3): 7.86-7.80 (4H, m), 7.49-7.54 (2H, m), 7.46-7.38 (8H, m), 5.24 (1H, dd, $J = 3.1, 2.1$ Hz), 5.18 (1H, dd, $J = 3.1, 2.09$ Hz); ^{31}P NMR: 31.0; ^{13}C NMR (100 MHz, CDCl_3): 151.8 (d, $J_{\text{C-P}} = 8.5$ Hz), 134.2 (d, $J_{\text{C-P}} = 5.4$ Hz), 132.7, 131.9, 131.8, 130.6, 129, 128.7, 127, 123.4, 98.8 (d, $J_{\text{C-P}} = 5.4$ Hz). IR (CHCl_3) ν_{max} : 3060.31, 2997.61, 1632.75, 1590.72, 1487.61, 1439.52, 1286.60, 1265.90, 1230.46, 1217.20, 1130.50, 1111.02, 1097.20, 1004.33, 985.32, 832.75, 816.84, 729.68, 708.41, 693.79, 666.31. MS (EI) (m/z) (*rel.intensity*): 399.88 (MH^+ , 53%), 397.92 (M^+ , 50%), 397.02 (22%), 321.00 (20%), 320.02 (16%), 319.10 (24%), 307.00 (11%), 276.01 (18%), 274.01 (22%), 258.06 (73%), 256.11 (67%), 220.19 (13%), 219.16 (83%), 202.23 (36%), 201.20 (100%), 179.27 (22%), 173.23 (24%), 171.24 (20%), 153.33(7%), 152.25(9%), 129.21(9%), 77.22 (12%); HRMS (EI): Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{BrP}$: 398.0071. Found: 398.0062.

5) 1-(4-(Trifluoromethyl) phenyl) vinyl diphenylphosphinate (7e):

Pale yellow oil (77.7 % yield)

^1H NMR (300 MHz, CDCl_3): 7.90-7.81 (4H, m), 7.70-7.40 (10H, m), 7.33-7.29 (3H, m), 5.32 (1H, dd, $J = 3.2, 2.1$ Hz), 5.22 (1H, dd, $J = 3.2, 2.0$ Hz); ^{31}P NMR: 31.9; ^{13}C NMR (100 MHz, CDCl_3): 151.00 (d, $J_{\text{C-P}} = 8.6$ Hz), 138.25 (d, $J_{\text{C-P}} = 6.0$ Hz), 132.53, 131.6, 131.5, 131.3, 130.9, 130.5, 129.9, 128.7, 128.6, 126.4, 125.4 (m), 122.5, 99.9 (d, $J_{\text{C-P}} = 5.3$ Hz); IR (CHCl_3) ν_{max} : 3061.05, 2997.79, 1631.44, 1619.13, 1592.59, 1575.60, 1439.53, 1408.45, 1325.03, 1300.22, 1272.59, 1230.21, 1216.52, 1168.34, 1127.83, 1098.64, 1066.19, 1014.56, 1003.20, 983.38, 873.45, 847.55, 820.45, 734.91, 725.74, 710.54, 692.33, 666.13. MS (EI) (m/z) (*rel.intensity*): 388.89 (MH^+ , 23%), 387.94 (M^+ , 100%), 387.17 (45%), 311.08 (10%), 264.10 (20%), 246.20 (36%), 220.27 (12%), 219.17 (48%), 201.26 (65%), 174.47 (8%), 173.09, (25%), 171.24 (10%), 152.26 (6%), 129.24 (6%), 77.27 (7%); HRMS (EI): Calcd for $\text{C}_{21}\text{H}_{16}\text{O}_2\text{F}_3\text{P}$: 388.0840. Found: 388.0825.

6) 1-(4-Nitrophenyl) vinyl diphenylphosphinate (7f):

Yellow Solid (72% yield)

^1H NMR (500 MHz, CDCl_3): 8.20, (2H, m), 7.91-7.80 (4H, m), 7.72 (2H, m), 7.60-7.55 (2H, m), 7.52 – 7.46 (4H, m), 5.38 (1H, dd, $J = 3.4, 2.0$ Hz), 5.35 (1H, dd, $J = 3.4, 2.0$ Hz); ^{31}P NMR: 31.9; ^{13}C NMR (100 MHz, CDCl_3): 150.4 (d, $J_{\text{C-P}} = 8.3$ Hz), 140.9 (d, $J_{\text{C-P}} = 5.5$ Hz), 132.7, 131.6, 131.1, 131.1, 128.8, 128.7, 125.9, 123.7, 101.7 (d, $J_{\text{C-P}} = 5.2$ Hz); IR (CHCl_3) ν_{max} : 3060.87, 2998.77, 1630.86, 1596.24, 1519.77, 1493.12, 1439.45, 1346.27, 1318.75, 1300.28, 1272.41, 1216.27, 1130.24, 1110.86, 1096.36, 1002.93, 984.42, 857.87, 808.11, 729.19, 692.58, 666.20. MS (EI) (m/z)(*rel.intensity*): 366.01 (MH^+ , 10%), 365.03 (M^+ , 39%), 364.15 (23%), 334.08 (12%), 274.07 (10%), 241.11 (10%), 223.13 (17%), 219.15 (100%), 201.29 (67%), 192.35 (8%), 173.29 (11%), 171.26 (7%), 155.29 (4%), 87.26 (6%), 85.36 (33%), 83.39 (50%), 77.34 (7%) HRMS: Calcd for $\text{C}_{20}\text{H}_{16}\text{O}_4\text{NP}$: 365.0817 Found: 365.0833.

8) 1-(Naphthalen-2-yl) vinyl diphenylphosphinate (7g):

White solid (73.7% yield)

^1H NMR (500 MHz, CDCl_3): 8.50 (1H, m), 8.01-7.48 (16H, m), 5.36 (2H, m); ^{31}P NMR: 31.7; ^{13}C NMR (100 MHz, CDCl_3): 152.4 (d, $J_{\text{C-P}} = 9.2$ Hz), 133.4, 132.9, 132.4, 132.2, 132.1 (d, $J_{\text{C-P}} = 6.2$ Hz), 131.7, 131.6, 130.3, 128.7, 128.5, 128.1, 127.6, 126.6, 126.4, 124.4, 122.8, 98.4 (d, $J_{\text{C-P}} = 5.5$ Hz). IR (CHCl_3) ν_{max} : 3060.70, 2995.56, 1626.08, 1593.32, 1505.53, 1484.98, 1439.43, 1285.31, 1227.87, 1217.03, 1194.99, 1130.83, 1111.53, 1084.30, 1003.16, 987.87, 949.47, 883.73, 860.19, 818.64, 797.84, 731.45, 694.29, 666.09. MS (EI) (m/z)(*rel.intensity*): 387.96 (17%), 370.02 (M^+ , 55%), 333.95 (17%), 293.08 (13%), 279.08 (30%), 264.07 (6%), 246.13 (12%), 229.16 (22%), 219.12 (100%), 202.20 (55%), 201.20 (46%), 199.25 (8%), 173.20 (13%), 155.24, (28%), 152.22 (10%), 115.28 (7%), 104.28 (10%), 85.34 (26%), 83.36 (39%), 77.36 (11%) HRMS (EI): Calcd for $\text{C}_{24}\text{H}_{19}\text{O}_2\text{P}$: 370.1123. Found: 370.1117.

9) 1-Cyclohexylvinyl diphenylphosphinate (7h):

White solid (54% yield)

^1H NMR (500 MHz, CDCl_3): 7.83-7.77 (4H, m), 7.52-7.39 (6H, m), 4.67 (1H, dd, $J = 2.5, 1.9$ Hz), 4.31 (1H, m), 2.13-2.05 (1H, m), 1.95-1.89 (2H, m), 1.83-1.65 (3H, m), 1.35-1.15 (5H, m); ^{31}P NMR: 29.0; ^{13}C NMR (100 MHz, CDCl_3): 159.7 (d, $J_{\text{C-P}} = 10.4$ Hz), 132.3, 132.1, 131.7, 131.6, 131.0, 95.1 (d, $J_{\text{C-P}} = 5.4$ Hz), 43.3 (d, $J_{\text{C-P}} = 4.4$ Hz), 30.6, 26.1, 26.0. IR (CHCl_3) ν_{max} : 3060.28, 2992.02, 2930.79, 2855.52, 1647.29, 1592.90, 1485.32, 1450.55, 1439.57, 1310.58, 1271.81, 1230.28, 1196.79, 1174.71, 1130.25, 1111.73, 1071.33, 1053.33, 1028.73, 1002.97, 984.28, 929.50, 843.31, 792.09, 729.16, 694.23, 665.23. MS (EI) (m/z)(*rel.intensity*): 327.01 (MH^+ , 4%), 220.09 (15%), 219.22 (100%), 202.29 (16%), 173.27 (5%), 159.10 (9%), 155.25 (2%), 77.41 (3%) HRMS (EI): Calcd for $\text{C}_{20}\text{H}_{23}\text{O}_2\text{P}$: 326.1436. Found: 326.1439.

10) 3, 3-dimethylbut-1-en-2-yl diphenylphosphinate(7j):

White solid (64.6% Yield)

^1H NMR (500 MHz, CDCl_3): 7.91-7.82 (4H, m), 7.46-7.58 (6H, m), 4.78 (1H, dd, $J = 2.9, 1.6$ Hz), 4.5 (1H, ddd, $J = 2.9, 1.6, 0.8$ Hz); ^{31}P NMR: 28.66; ^{13}C NMR (100 MHz, CDCl_3): 163.0, 132.9, 132.4, 131.9, 131.8, 131.0, 128.8, 128.6, 93.5, 36.7, 28.2. IR (CHCl_3) ν_{max} : 3060.98, 2973.23, 2872.29, 1642.08, 1592.89, 1481.85, 1481.85, 1460.76, 1439.57, 1387.36, 1361.96, 1279.96, 1231.77, 1154.74, 1129.33, 1111.47, 1071.03, 1031.06, 1002.50, 986.27, 936.72, 879.88, 857.65, 796.93, 731.25, 694.60, 665.07. MS (EI) (m/z)(*rel.intensity*): 301.07 (MH^+ , 46%), 299.28 (M^+ , 90%), 285.28 (11%), 257.20 (4%), 243.23 (9%), 220.54 (25%), 219.18 (100%), 201.22 (95%), 176.28 (26%), 160.53 (87%), 145.21 (51%), 142.88 (18%), 117.15 (10%), 77.51 (10%) HRMS (EI): Calcd for $\text{C}_{18}\text{H}_{21}\text{O}_2\text{P}$: 300.1279. Found: 300.1291.

General procedure for Ir catalyzed asymmetric hydrogenation of enol esters.

A vial was charged with substrate (0.5 mol) and Ir complex (0.5 mol %). Dry CH_2Cl_2 (2 mL) was added and the vial was placed in to a high-pressure hydrogenation apparatus fitted with a steel bomb. After repeated purging (three times) with hydrogen, the pressure of hydrogen gas was adjusted to 30 bar and allowed to stir for 1-3h at room temperature. After

releasing the pressure solvent was removed *in vacuo*. The crude product was chromatographed (70:30 Pentane / *iso*-propanol). Conversions were determined by ^1H NMR spectroscopy and *ee*'s were determined using the chiral HPLC.

11) 1-Phenylethyl diphenylphosphinate (6e):⁶

HPLC analysis: Chiralcel AD (95:5 n-hexane / *i*-PrOH), flow rate = 0.5 ml / min t_R = 32.3 min (major), t_s = 38.0 min (minor); $[\alpha]_D^{24.5}$ = +0.142 (*c* 1, CHCl_3)

12) 1-*p*-Tolyloethyl diphenylphosphinate (8a):⁷

HPLC analysis: Chiralcel AD (95:5 n-hexane / *i*-PrOH), flow rate = 0.5 ml / min t_R = 36.2 min (major), t_s = 41.9 min (minor); $[\alpha]_D^{24.5}$ = +0.152 (*c* 1, CHCl_3)

13) 1-(4-*tert*-Butylphenyl) ethyl diphenylphosphinate (8b):

HPLC analysis: Chiralcel AD (95:5 n-hexane / *i*-PrOH), flow rate = 0.5 ml / min t_R = 39.7 min (major), t_s = 46.5 min (minor); $[\alpha]_D^{23.9}$ = +0.241 (*c* 1, CHCl_3)

^1H NMR (500 MHz, CDCl_3): 7.89-7.81 (2H, m), 7.80-7.62 (2H, m), 7.54-7.38 (4H, m), 7.33-7.27 (4H, m), 7.22 (2H, m), 5.52 (1H, dq, J = 9.2, 6.5 Hz), 1.67 (3H, d, J = 6.5 Hz), 1.30 (3H, s); ^{31}P NMR: 31.3; ^{13}C NMR (100 MHz, CDCl_3): 150.7, 138.8 (d, J_{C-P} = 5.3 Hz), 133.2, 132.2, 131.93, 131.88, 131.78, 131.5, 131.4, 130.9, 128.4, 128.9, 128.2, 128.1, 125.7, 125.2, 74.4 (d, J_{C-P} = 5.7 Hz), 31.3, 24.7 (d, J_{C-P} = 3.14 Hz); IR (CHCl_3): ν_{max} : 2696.54, 1593.51, 1513.72, 1439.40, 1375.92, 1216.23, 1130.38, 1112.99, 1059.47, 1005.29, 959.86; MS (EI) (m/z) (*rel.intensity*): 378.91 (MH^+ , 5%), 377.92 (M^+ , 17%), 237.11 (4%), 219.05 (16%), 202.09 (100%), 201.32 (16%), 155.23 (11%), 145.23 (6%), 117.23 (4%), 91.53 (4%), 77.34 (3%) HRMS (EI): Calcd for $\text{C}_{24}\text{H}_{27}\text{O}_2\text{P}$: 378.1749. Found: 378.1762.

14) 1-(4-Methoxyphenyl) ethyl diphenylphosphinate (8c):

ee was determined on corresponding alcohol.
 $[\alpha]_D^{24.0}$ = +0.243 (*c* 1, CHCl_3)

15) 1-(4-Bromophenyl) ethyl diphenylphosphinate (8d):

HPLC analysis: Chiralcel AD (95:5 n-hexane / *i*-PrOH), flow rate = 0.5 ml / min t_R = 34.7 min (major), t_s = 46.3 min (minor); $[\alpha]_D^{23.5}$ = +0.345 (*c* 1, CHCl_3)

^1H NMR (500 MHz, CDCl_3): 7.90-7.61 (4H, m), 7.53-7.29 (7H, m), 7.22-7.09 (4H, m), 5.51 (1H, dq, J = 9.1, 6.5 Hz), 1.67 (3H, d, J = 6.5); ^{31}P NMR: 31.7; ^{13}C NMR (100 MHz, CDCl_3): 141.3, 132.5, 132.3, 132.1, 131.8, 131.7, 128.8, 128.6, 127.9, 122.1, 73.9 (d, J_{C-P} = 5.3 Hz), 25.1 (d, J_{C-P} = 3.7 Hz); IR (CHCl_3): ν_{max} : 3060.11, 2986.04, 1593.59, 1489.88, 1439.06, 1408.07, 1376.39, 1296.78, 1216.30, 1129.81, 1113.40, 1071.20, 1059.88, 1007.99, 956.62, 826.43, 729.03, 695.04, 665.84. IR (CHCl_3): 3060.98, 2973.23, 2872.29, 1642.08, 1592.89, 1481.85, 1481.85, 1460.76, 1439.57, 1387.36, 1361.96, 1279.96, 1231.77, 1154.74, 1129.33, 1111.47, 1071.03, 1031.06, 1002.50, 986.27, 936.72, 879.88, 857.65, 796.93, 731.25, 694.60, 665.07. MS (EI) (m/z) (*rel.intensity*): 399.99 (M^+ , 13%), 387.10 (23%), 386.11 (90%), 384.55 (60%), 383.87 (40%), 305.23 (17%), 220.81 (18%), 219.19 (52%), 202.83 (100%), 201.33 (63%), 184.07 (49%), 181.81 (24%), 156.65 (12%), 154.83 (42%), 152.97 (10%), 104.63 (29%), 103.11 (23%), 77.32 (9%); HRMS (EI): Calcd for $\text{C}_{20}\text{H}_{18}\text{O}_2\text{BrP}$: 400.0228. Found: 400.0224.

16) 1-(4-(Trifluoromethyl) phenyl) ethyl iphenylphosphinate (8e):

HPLC analysis: Chiralcel AD (95:5 n-hexane / *i*-PrOH), flow rate = 0.5 ml / min t_R = 23.7 min (major), t_s = 34.5 min (minor); $[\alpha]_D^{24.5} = +0.123$ (c 1, CHCl₃)
¹H NMR (300 MHz, CDCl₃): 7.92-7.86 (2H, m), 7.80-7.72 (1H, m), 7.72-7.64 (2H, m), 7.62-7.54 (3H, m), 7.54- 7.44 (6H, m), 7.42-7.34 (2H, m), 5.61 (1H, dq, $J = 9.2, 6.5$ Hz), 1.69 (3H, d, $J = 6.5$ Hz); ³¹P NMR: 31.2; ¹³C NMR (100 MHz, CDCl₃): 146.0 (d, $J_{C-P} = 5.0$ Hz), 132.2, 132.1, 131.7, 131.6, 131.5, 131.4, 128.6, 128.4, 128.2, 126.2, 125.4 (m), 73.6 (d, $J_{C-P} = 5.6$ Hz), 24.9 (d, $J_{C-P} = 3.4$ Hz); IR (CHCl₃) ν_{max} : 3061.24, 2987.47, 1622.21, 1593.33, 1485.54, 1439.65, 1420.86, 1377.49, 1326.30, 1217.60, 1167.65, 1129.44, 1095.83, 1069.38, 1009.45, 960.23, 842.55, 729.64, 696.88, 665.18. IR (CHCl₃) ν_{max} : 3060.98, 2973.23, 2872.29, 1642.08, 1592.89, 1481.85, 1481.85, 1460.76, 1439.57, 1387.36, 1361.96, 1279.96, 1231.77, 1154.74, 1129.33, 1111.47, 1071.03, 1031.06, 1002.50, 986.27, 936.72, 879.88, 857.65, 796.93, 731.25, 694.60, 665.07. MS (EI) (m/z)(*rel.intensity*): 390.85 (MH⁺, 5%), 389.91 (M⁺, 8%), 249.08 (4%), 203.12 (13%), 202.13 (100%), 201.35 (16%), 199.38 (6%), 155.20 (13%), 133.22 (8%), 77.35 (4%) HRMS (EI): Calcd for C₂₁H₁₈O₂F₃P: 390.0997. Found: 390.1007.

17) 1-(4-Nitrophenyl) ethyl diphenylphosphinate (8f):

HPLC analysis: (S, S) Whelk-O (99:1 n-hexane / *i*-PrOH), flow rate = 0.8 ml / min t_R = 41.9 min (major), t_s = 45.5 min (minor); $[\alpha]_D^{23.0} = +0.305$ (c 1, CHCl₃)
¹H NMR (500 MHz, CDCl₃): 8.18 (2H, m), 7.88-7.82(2H, m), 7.68-7.64 (2H, m), 7.58-7.52(1H, m), 7.51-7.41 (5H, m), 7.37-7.31 (2H, m), 5.60 (1H, dq, $J = 9.2, 6.5$ Hz), 1.65 (3H, d, $J = 6.5$ Hz); ³¹P NMR: 32.19; ¹³C NMR (100 MHz, CDCl₃): 149.2 (d, $J_{C-P} = 4.6$ Hz), 147.3, 132.3, 132.2, 131.7, 131.6, 131.5, 131.4, 131.3, 130.8, 130.4, 128.6, 128.4, 128.3, 126.6, 123.7, 72.9 (d, $J_{C-P} = 5.3$ Hz), 24.8 (d, $J_{C-P} = 3.6$ Hz); IR (CHCl₃) ν_{max} : 3060.87, 2998.77, 1630.86, 1596.24, 1519.77, 1493.12, 1439.45, 1346.27, 1318.75, 1300.28, 1272.41, 1216.27, 1130.24, 1110.86, 1096.36, 1002.93, 984.42, 857.87, 808.11, 729.19, 692.58, 666.20. MS (EI) (m/z)(*rel.intensity*): 367.91 (MH⁺, 3%), 366.87 (M⁺, 7%), 321.05 (3%), 273.98 (4%), 229.09 (5%), 219.05 (14%), 217.04 (18%), 202.08 (100%), 201.26 (17%), 199.28 (8%), 156.25 (5%), 149.14, (15%), 91.26 (3%), 87.23 (8%), 85.30 (48%), 83.37 (72%), 77.33 (4%) HRMS (EI): Calcd for C₂₀H₁₈O₄NP: 367.0973. Found: 367.0974.

18) 1-(Naphthalen-2-yl) ethyl diphenylphosphinate (8g):

HPLC analysis: Chiralcel AD (95:5 n-hexane / *i*-PrOH), flow rate = 0.5 ml / min t_R = 44.1 min (major), t_s = 69.0 min (minor); $[\alpha]_D^{24.0} = +0.184$ (c 1, CHCl₃)
¹H NMR (500 MHz, CDCl₃): 7.93-7.76 (5H, m), 7.72-7.68 (3H, m), 7.60-7.38 (7H, m), 7.32-6.66 (2H, m), 5.72 (1H, dq, $J = 9.2, 6.3$ Hz); ³¹P NMR: 32.5; ¹³C NMR (100 MHz, CDCl₃): 139.4 (d, $J_{C-P} = 5.3$ Hz), 133.0 (d, $J_{C-P} = 2.3$ Hz), 132.0, 131.9, 131.8, 131.7, 131.5, 131.4, 130.9, 128.5, 128.4, 128.3, 128.2, 128.1, 128.0, 127.6, 126.1, 126.0, 124.9, 123.8, 74.7 (d, $J_{C-P} = 5.5$ Hz), 24.9 (d, $J_{C-P} = 2.9$ Hz). IR (CHCl₃) ν_{max} : 3060.08, 2986.55, 1593.23, 1439.25, 1378.45, 1309.85, 1215.58, 1130.11, 1113.58, 1059.21, 1007.30, 992.98, 965.39, 944.06, 894.95, 878.75, 858.25, 819.94, 731.36, 695.87, 666.95; MS (EI) (m/z)(*rel.intensity*): 372.93 (MH⁺, 5%), 371.93 (M⁺, 13%), 335.96 (4%), 274.02 (4%), 229.11 (5%), 219.08 (30%), 202.12 (100%), 201.32 (22%), 156.32 (6%), 155.26 (18%), 154.27 (14%), 153.27 (7%), 152.26 (3%), 83.46 (7%), 77.34 (3%) HRMS (EI): Calcd for C₂₄H₂₁O₂P: 372.1279. Found: 372.1282.

19) 1-Cyclohexylethyl diphenylphosphinate (8h):

HPLC analysis: (S, S) Whelk-O (99:1 n-hexane / *i*-PrOH), flow rate = 0.8 ml / min t_R = 32.6 min (major), t_s = 37.3 min (minor); $[\alpha]_D^{22.7} = +0.066$ (c 1, CHCl₃)
¹H NMR (500 MHz, CDCl₃): 7.90-7.74 (4H, m), 7.59-7.39 (6H, m), 4.46-4.32 (1H, m); 1.83-1.49 (7H, m), 1.26. (3H, d, $J = 6.7$ Hz), 0.94 (4H, m) ³¹P NMR: 30.4; ¹³C NMR (100 MHz, CDCl₃): 134.0, 133.6, 132.2, 132.1, 132.07, 132.03, 131.9, 131.8, 44.4 (d, $J_{C-P} = 5.0$ Hz), 28.7, 28.2, 26.7, 26.3, 19.0 (d, $J_{C-P} = 2.4$ Hz). IR (CHCl₃) ν_{max} :

3060.65, 2983.62, 2928.93, 2854.81, 2232.17, 1593.18, 1484.99, 1450.06, 1439.00, 1380.68, 1216.11, 1129.39, 1112.75, 1044.74, 1028.89, 1003.46, 990.12, 963.57, 906.07, 842.73, 792.01, 753.19, 694.10, 666.10. MS (EI) (*m/z*)(*rel.intensity*): 329.03 (MH⁺, 16%), 220.20 (13%), 219.29 (100%), 201.16 (16%), 159.07 (8%), 155.22 (3%), 79.90 (5%); HRMS (EI): Calcd for C₂₀H₂₅O₂P: 328.1592. Found: 328.1591.

20) 3, 3-Dimethylbutan-2-yl diphenylphosphinate (8i):

HPLC analysis: (S, S) Whelk-O (99:1 n-hexane / *i*-PrOH), flow rate = 0.8 ml / min t_R = 44.0 min (major), t_s = 48.9 min (minor); $[\alpha]_D^{24.6}$ = +0.142 (*c* 1, CHCl₃)
¹H NMR (500 MHz, CDCl₃): 7.90-7.79 (4H, m), 7.43-7.57 (6H, m), 4.33 (1H, dq, *J* = 7.9, 6.5 Hz), 1.24 (3H, d, *J* = 6.5 Hz), 0.96 (9H, s); ³¹P NMR: 30.19; ¹³C NMR (100 MHz, CDCl₃): 134.0, 133.3, 132.2, 131.8, 131.76, 131.67, 131.6, 131.5, 131.4, 128.4, 128.2, 80.8 (d, *J*_{C-P} = 7.3 Hz), 35.2 (d, *J*_{C-P} = 6.1 Hz), 25.8, 17.1. IR (CHCl₃) ν_{max} : 3061.00, 2975.96, 2910.30, 2873.25, 1593.57, 1480.13, 1465.82, 1439.07, 1397.25, 1380.21, 1366.03, 1215.86, 1129.60, 1112.02, 1075.04, 1047.86, 1028.78, 1007.68, 992.01, 933.14, 798.10, 726.42, 695.51, 665.70. MS (EI) (*m/z*)(*rel.intensity*): 303.05 (MH⁺, 14%), 246.17 (4%), 245.17 (12%), 219.25 (100%), 201.28 (39%), 173.11 (5%), 158.97 (8%), 152.06 (3%), 77.47 (4%)
 HRMS (EI): Calcd for C₁₈H₂₃O₂P: 302.1436. Found: 302.1425.

References:

- 1) Perrin, D.D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*. **1985**, Pergamon Press, Oxford.
- 2) Tamio, H.; Koichi, K.; Makoto, K. *Tetrahedron Lett.* **1981**, 22, 4417- 4420.
- 3) Shou_Ri S.; Hai_Rong L.; Wu_Kang S.; Xiao_Ling L.; Qin X.; Qiu_Ying W. *Synth. Commun.* **2005**, 35, 2839-2845.
- 4) Wiles, C.; Watts, P.; Haswell, S.; Pombo-V.E. *Tetrahedron Lett.* **2002**, 43, 2945- 2948.
- 5) Kamei, K., Maeda, N., Tatsuoka, T. *Tetrahedron Letters*. **2005**, 46, 229-232.
- 6) Bergens, U. *Eur. Pat. Appl.* **2005**, 17pp. coden: EPXXDW EP1582527 A1 20051005
- 7) Noyce, D. S., Virgilio, J. A. *J. Org. Chem.* **1972**, 37, 2643-2647.

Archive directory: /home/vnmr1/varsys/data
 Sample directory:
 Pulse Sequence: szpul
 Solvent: cdcl3
 Temp: 25.0 C / 298.1 K
 File: VP-parac73-1H
 Mercury-1000B "mercury"
 User: pradeep
 Date: Aug 17 2006
 Pulse 43.2 degrees
 Acq. time 3.700 sec
 Width 4800.0 Hz
 16 repetitions
 OBSERVE H1 300.0262751 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 1 min, 8 sec

STANDARD 1H OBSERVE

Pulse Sequence: s2pul
 Solvent: cdcl3 298.1 K
 Temp: 25.0 C
 File: vph-paramitro-1h
 UNIT: 400 "unity400"
 User: bradsp
 Date: Oct 13 2006
 PULSE SEQUENCE: s2pul
 Pulse: 37.1 degrees
 Acq. time: 3.744 sec
 Width: 6000.6 Hz
 Wdth: 6000.6 Hz
 OBSERVE: H1oms 399.98 MHz
 DATA PROCESSING
 Line broadening 0.2 Hz
 FT size 65536
 Total time 1 minute

STANDARD PROTON PARAMETERS
Pulse Sequence: s2pul
Solvent: cdcl3
Temp: 25.0 C / 298.1 K
INOVA-500 "unity500"
User: pradeep
Date: Feb 13 2007
PULSE SEQUENCE: s2pul
Pulse: 79.5 degrees
Acq. time: 3.000 sec
Width: 8000.0 Hz
12 repetitions
OBSERVE: H1, 499.94 MHz
DATA PROCESSING
Line broadening: 0.2 Hz
FT size: 131072
Total time: 1 minutes

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 File:
 UNITY-400 "unity400"
 User: pradeep
 Date: Oct 2 2008
 PULS SEQUENCE: s2pul
 Relax delay: 1.000 sec
 Pulse: 64.5 degrees
 Acq. time: 1.198 sec
 Width: 21000.0 Hz
 1140 repetitions
 OBSERVE: C13: 100.58 MHz
 DECOUPLE: H1: 299.98 MHz
 Power: 48 dB
 Continuously on
 WALTZ-16 simulated
 Single precision data
 DATA PROCESSING
 Line broadening: 1.0 Hz
 FT size: 65528
 Total time: 47 minutes

Pulse Sequence: #2pul
 Solvent: cdcl3
 Temp: 25.0 C / 298.1 K
 File: VPS-12-16
 INOVA-500 'unity500'
 User: pradep
 Date: Aug 24 2006
 PULSE SEQUENCE: #2pul
 Pulse: 73.5 degree
 Acq. time: 3.000 sec
 Width: 8000.0 Hz
 16 repeats
 OBSERVE: H1, 499.94 MHz
 DATA PROCESSING
 Line broadening: 0.2 Hz
 FT size: 65536
 Total time: 1 minute

Pulse Sequence: zgpg30
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 File:
 UNITY-400 "unity400"
 User: pradeep
 Date: Aug 24 2008
 PULS1 SEQUENCE: zgpg30
 Relax delay: 1.000 sec
 Pulse 64.5 degrees
 Acq. time: 1.198 sec
 Width: 21000.0 Hz
 714 repetitions
 OBSERVE: C13, 100.58 MHz
 DECOUPLE: H1, 299.98 MHz
 Power: 0.0 dB
 Continuously on
 WALTZ-16 simulated
 Single precision data
 DATA PROCESSING
 Line broadening: 1.0 Hz
 FT size: 65536
 Total time: 28 minutes

Pulse Sequence: s2pul
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 File:
 UNITY-400 "unity400"
 User: pradeep
 Date: Sep 7 2006
 PULSE SEQUENCE: s2pul
 Relax delay: 1.000 sec
 Pulse: 64.5 degrees
 Acq. time: 1.159 sec
 Width: 21000.0 Hz
 1168 repetitions
 OBSERVE: C13, 100.58 MHz
 DECOUPLE: H1, 399.98 MHz
 Power: 48 dB
 Continuously on
 WALTZ-16 modulated
 Single precision data
 DATA PROCESSING
 Line broadening: 1.0 Hz
 FT size: 65536
 Total time: 12 minutes

Pulse Sequence: a2pul
 Solvent: CDCl3
 Temp: 25.0 C / 298.1 K
 File:
 UNITY-400 "unity400"
 User: pradeep
 Date: Nov 9 2008
 PULS SEQUENCE: a2pul
 Relax delay: 1.000 sec
 Pulse: 64.5 degrees
 Acq. time: 1.198 sec
 Width: 23000.0 Hz
 2500 repetitions
 OBSERVE: C13: 100.58 MHz
 DECOUPLE: H1: 299.98 MHz
 Power: 48 dB
 Continuously on
 WALTZ-16 simulated
 Single precision data
 DATA PROCESSING
 FT a198 65536
 Total time 73 minutes