Palladium Catalyzed Asymmetric Hydrophosphination of α,β- and α,β,γ,δ-unsaturated Malonate Esters – Efficient Control of Reactivity, Stereo- and Regio-Selectivity

Xiang-Yuan Yang, [a] Jun Hao Gan, [a] Yongxin Li, [a] Sumod A. Pullarkat [a] and Pak-Hing Leung [a]

[a] Division of Chemistry & Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637616, Singapore Fax: (+65) 6791 1961; e-mail: sumod@ntu.edu.sg, pakhing@ntu.edu.sg.

Electronic Supporting Information

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**General Information**

All reactions were carried out under a positive pressure of nitrogen using standard Schlenk technique. NMR spectra were recorded on Bruker AV 300, AV 400 and AV 500 spectrometers. Chemical shifts were reported in ppm and referenced to an internal SiMe$_4$ standard (0 ppm) for $^1$H NMR, chloroform-d (77.23 ppm) for $^{13}$C NMR, and an external 85% H$_3$PO$_4$ for $^{31}$P{$^1$H} NMR. DCM, toluene, THF, acetone, acetonitrile and MTBE were purchased from their respective companies and used as supplied. Solvents were degassed prior to use when necessary. A Low Temp Pairstirrer PSL-1800 was used for controlling low temperature reactions. Column chromatography was carried out with Silica gel 60 (Merck). Melting points were measured using SRS Optimelt Automated Point System SRS MPA100. Optical rotation were measured with JASCO P-1030 Polarimeter in the specified solvent in a 0.1 dm cell at 22.0°C.

The palladacycle (S)-2$^{[1]}$ was prepared according to literature methods. All other reactants and reagents were used as supplied.

Caution! Perchlorate salts of metal complexes are potentially explosive compounds and should be handled with care.

**Preparation of PCP Pd Pincer (R,R)-4a**

To a solution of Ph$_2$PH (227 mg, 1.22 mmol, 2.1 equiv) in toluene (10 mL) was added catalyst (S)-2 (21.8 mg, 0.061 mmol, 5 mol %) and stirred for 10 minutes before cooling to -80°C. Aromatic dienone (196 mg, 0.578 mmol, 1.0 equiv) was added followed by the addition of NEt$_3$ (162 uL, 1.16 mmol, 2.0 equiv) in toluene (1 mL) dropwise. The solution was stirred at -80°C and the completion of the reaction was monitored by $^{31}$P{$^1$H} NMR. Upon completion, the solution was allowed to room temperature. Volatiles were removed under reduced pressure to afford crude (R,R)-3. PdCl$_2$(CH$_3$CN)$_2$ (151 mg, 0.578 mmol, 1.0 equiv) was added to a solution of diphosphine ligand (R,R)-3 in DCM (10 mL) and stirred overnight at room temperature. The solvent was removed and the crude (R,R)-4a was purified.
via silica gel column chromatography (eluted with DCM) to afford white solid of (R,R)-4a. (419 mg, 0.490 mmol, 85% yield) The data were consistent with the literature.[2]

Preparation of Catalyst (R,R)-4b-d

To a solution of (R,R)-4a (100 mg, 0.120 mmol, 1.0 equiv) in DCM (10 mL) was added AgOAc (29.4 mg, 0.177 mmol, 1.5 equiv) or AgTFA (38.9 mg, 0.177 mmol, 1.5 equiv) or KI (199.2 mg, 1.20 mmol, 10.0 equiv) and stirred vigorously overnight protected from light. The crude reaction mixture was passed through a short plug of silica gel and extracted into DCM (3 x 50 mL). The organic layers were combined and dried over MgSO4, filtered and evaporated to dryness to give white solid of (R,R)-4b, (R,R)-4c or (R,R)-4d.

(R,R)-4b (97.6 mg, 0.112 mmol, 95% yield). [α]D = +380 (c 0.1, DCM). Mp: 138-140°C. 31P{1H} NMR (CDCl3, 162 MHz): δ 44.5; 1H NMR (CDCl3, 400 MHz): δ 8.04-8.00 (m, 4H, Ar), 7.86-7.81 (m, 4H, Ar), 7.40-7.35 (m, 18H, Ar), 7.16-7.12 (m, 4H, Ar), 6.97 (d, 2H, 3J = 7.52 Hz, Ar), 6.69 (t, 1H, 3J = 7.48 Hz, Ar), 4.79-4.73 (m, 2H, PCHCH2), 3.58-3.49 (m, 2H, PCHCHH), 3.04 (ddd, 2H, 2J = 16.7 Hz, 3J = 10.2 Hz, 5.1 Hz, PCHCHH), 1.97 (s, 3H, OOCCH3); 13C NMR (CDCl3, 100 MHz): δ 198.0 (2C, COPh), 151.8 (1C, OOCCH3), 136.8-124.5 (42C, Ar), 47.8 (t, 2C, 1JPC = 14.9 Hz, PCH), 44.8 (t, 2C, 2JPC = 4.8 Hz, PCHCH2). HRMS (+ESI) m/z: (M + OAc)+ calcd for C48H39O2P2Pd, 815.1460; found, 815.1476. Anal. Calcd for C50H40O2P2Pd: C, 68.61; H, 4.84. Found: C, 68.78; H, 4.97%.

(R,R)-4c (102 mg, 0.108 mmol, 93% yield). [α]D = +382 (c 0.1, DCM). Mp: 189-190°C (dec). 31P{1H} NMR (CDCl3, 162 MHz): δ 45.6; 1H NMR (CDCl3, 400 MHz): δ 8.00-7.96 (m, 4H, Ar), 7.75-7.71 (m, 4H, Ar), 7.42-7.32 (m, 18H, Ar), 7.19-7.16 (m, 4H, Ar), 7.03 (d, 2H, 3J = 7.52 Hz, Ar), 6.77 (t, 1H, 3J = 7.44 Hz, Ar), 4.85-4.80 (m, 2H, PCHCH2), 3.53-3.44 (m, 2H, PCHCHH), 3.04 (ddd, 2H, 2J = 16.3 Hz, 3J = 11.1 Hz, 5.2 Hz, PCHCHH); 13C NMR (CDCl3, 100 MHz): δ 197.6 (2C, COPh), 151.9 (1C, OOCF3), 136.6-124.9 (43C, Ar and OOCOF3), 47.2 (t, 2C, 1JPC = 15.0 Hz, PCH), 44.8 (t, 2C, 2JPC = 4.6 Hz, PCHCH2). HRMS (+ESI) m/z: (M + TFA)+ calcd for C48H39O2P2Pd, 815.1460; found, 815.1474. Anal. Calcd for C50H40F2O2P2Pd: C, 65.76; H, 4.30. Found: C, 65.91; H, 4.51%.

(R,R)-4d (104 mg, 0.109 mmol, 90% yield). [α]D = -566 (c 0.1, DCM). Mp: 210-212°C (dec). 31P{1H} NMR (CDCl3, 162 MHz): δ 47.9; 1H NMR (CDCl3, 400 MHz): δ 8.07-8.02 (m, 4H, Ar), 7.89-7.84 (m, 4H, Ar), 7.48-7.45 (m, 6H, Ar), 7.42-7.40 (m, 2H, Ar), 7.38-7.38 (m, 4H, Ar), 7.34-7.32 (m, 6H, Ar), 7.27-7.25 (m, 4H, Ar), 7.18-7.06 (m, 2H, Ar), 6.84 (t, 1H, 3J = 7.60 Hz, Ar), 5.01-4.98 (m, 2H, PCHCH2), 3.27-3.21 (m, 2H, PCHCHH), 3.02 (m, 2H, PCHCHH); 13C NMR (CDCl3, 100 MHz): δ 197.6 (2C, COPh), 164.7-124.1 (42C, Ar),
49.1 (t, 2C, $^1J_{PC} = 14.9$ Hz, PCH), 44.9 (2C, PCHCH$_2$). HRMS (+ESI) m/z: (M - I)$^+$ calcld for C$_{48}$H$_{39}$O$_2$P$_2$Pd, 815.1460; found, 815.1487. Anal. Calcld for C$_{48}$H$_{39}$O$_2$P$_2$Pd: C, 61.13; H, 4.17. Found: C, 61.34; H, 4.30%.

**Preparation of PCP Pd Pincer (R,R)-6**

![Image of PCP Pd Pincer (R,R)-6]

The procedure is similar as the preparation of Pd Pincer (R,R)-4a. White solid. (85% yield). $[\alpha]_D = -559$ (c 0.1, DCM). Mp: 244-246°C (dec). $^{31}$P{$^1$H} NMR (CDCl$_3$, 162 MHz): $\delta$ 47.9; $^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ 7.98-7.94 (m, 4H, Ar), 7.84-7.80 (m, 4H, Ar), 7.45-7.37 (m, 12H, Ar), 7.07 (d, 2H, $^3J = 7.60$ Hz, Ar), 6.92 (t, 1H, $^3J = 7.50$ Hz, Ar), 4.82-4.78 (m, 2H, PC$_2$HCH); $^13$C NMR (CDCl$_3$, 100 MHz): $\delta$ 167.3 (d, 4C, $^3J_{PC} = 10.6$ Hz, CO$_2$Me), 147.0-125.6 (30C, Ar), 56.3 (2C, PCHCH), 52.4 (2C, CO$_2$Me), 51.7 (2C, CO$_2$Me), 51.1 (2C, PCHCH). HRMS (+ESI) m/z: (M - Cl)$^+$ calcld for C$_{42}$H$_{39}$O$_8$P$_2$Pd, 839.1155; found, 839.1174. Anal. Calcld for C$_{42}$H$_{39}$O$_8$P$_2$Pd: C, 57.61; H, 4.49. Found: C, 57.74; H, 4.61%.

**General Procedure for Catalytic Addition of Diphenylphosphine**

The catalyst (25 umol, 5 mol %) was added to a solution of diphenylphosphine (0.5 mmol, 1.0 equiv) in the stated solvent (1 mL) and brought to the desired temperature. The substrate (0.5 mmol, 1.0 equiv) was subsequently added and stirred at the stated temperature. Completion of the reaction was determined by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the $^{31}$P{$^1$H} NMR spectrum. Upon completion of the reaction, aq. H$_2$O$_2$ (0.1 mL, 31% v/v) was added to form the respective product. The volatiles were removed under reduced pressure and the crude product was directly loaded onto silica gel column (ethyl acetate:n-hexane = 2:1) to afford the pure product.

**General Procedure Not Involving Addition of External Base**

The catalyst (25 umol, 5 mol %) was added to a solution of diphenylphosphine (0.5 mmol, 1.0 equiv) in the stated solvent (1 mL) and brought to the desired temperature. The substrate (0.5 mmol, 1.0 equiv) was subsequently added and stirred at the stated temperature. Completion of the reaction was determined by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the $^{31}$P{$^1$H} NMR spectrum. Upon completion of the reaction, aq. H$_2$O$_2$ (0.1 mL, 31% v/v) was added to form the respective product. The volatiles were removed under reduced pressure and the crude product was directly loaded onto silica gel column (ethyl acetate:n-hexane = 2:1) to afford the pure product.
The catalyst (25 umol, 5 mol %) was added to a solution of diphenylphosphine (0.5 mmol, 1.0 equiv) in the stated solvent (0.5 mL) and brought to the desired temperature. The substrate (0.5 mmol, 1.0 equiv) and NEt₃ (0.5 mmol, 1.0 equiv) in the same solvent (0.5 mL) was consecutively added and stirred at the stated temperature. Completion of the reaction was determined by the disappearance of the phosphorous signal attributed to diphenylphosphine (-40 ppm) in the $^{31}$P{$^1$}H NMR spectrum. Upon completion of the reaction, aq. H₂O₂ (0.1 mL, 31% v/v) was added to form the respective product. The volatiles were removed under reduced pressure and the crude product was directly loaded onto silica gel column (ethyl acetate:n-hexane = 2:1) to afford the pure product.

**Product 5a**

White solid. The ee was determined on a Daicel Chiralpak AD column with n-hexane/2-propanol = 96.5/3.5, flow = 0.9 mL/min, wavelength = 220 nm. Retention times: 202.0 min (major product with catalyst (S)-2), 216.5 min (major product with catalyst (R,R)-4b). $[\alpha]_D^28$ = -32.1 (c 0.1, DCM). Mp: 108-110 °C. $^{31}$P{$^1$}H NMR (CDCl₃, 202 MHz): δ 34.2; $^1$H NMR (CDCl₃, 500 MHz): δ 7.87-7.78 (m, 4H, Ar), 7.53-7.42 (m, 6H, Ar), 4.15 (q, 2H, $^3$J = 6.95 Hz, CO₂CH₂), 3.96-3.89 (m, 1H, MeCHCH), 3.84-3.75 (m, 2H, CO₂CH₂), 3.37-3.30 (m, 1H, (CO₂)₂CH), 1.27-1.23 (m, 6H, CH₃CHCH and CO₂CH₂CH₃), 1.12 (t, 3H, $^3$J = 7.10 Hz, CO₂CH₂CH₃); $^{13}$C NMR (CDCl₃, 125 MHz): δ 168.1 (1C, CO₂CH₂CH₃), 167.7 (1C, CO₂CH₂CH₃), 131.9-128.5 (10C, Ar), 61.8 (1C, CO₂CH₂CH₃), 61.6 (1C, CO₂CH₂CH₃), 50.6 (1C, (CO₂)₂CH), 32.7 (d, 1C, $^1$JPC = 70.8 Hz, PCH), 14.0 (1C, CO₂CH₂CH₃), 13.8 (1C, CO₂CH₂CH₃), 11.0 (1C, CH₃CHP). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C₂₃H₂₅O₃P, 389.1519; found, 389.1522. Anal. Calcd for C₂₁H₂₅O₃P: C, 64.94; H, 6.49. Found: C, 65.09; H, 6.61%.

**Product 5b**

White solid. The ee was determined on a Daicel Chiralpak IC column with n-hexane/2-propanol = 87/13, flow = 1.0 mL/min, wavelength = 220 nm. Retention times: 93.5 min (major product with catalyst (R,R)-4b), 101.5 min (major product with catalyst (S)-2). $[\alpha]_D^28$ = +26.1 (c 0.1, DCM). Mp: 134-137 °C. $^{31}$P{$^1$}H NMR (CDCl₃, 121 MHz): δ 30.8; $^1$H NMR (CDCl₃, 400 MHz): δ 7.96-7.91 (m, 2H, Ar), 7.52-7.46 (m, 5H, Ar), 7.35-7.31 (m, 1H, Ar), 7.25-7.19 (m, 4H, Ar), 7.09-7.08 (m, 3H, Ar), 4.56-4.42 (m, 2H, CO₂CH₂CH₃), 3.83-3.70 (m, 3H, PhCH and CO₂CH₂CH₃), 3.60-3.52 (m, 1H, (CO₂)₂CH), 1.07 (t, 3H, $^3$J = 7.16 Hz, CO₂CH₂CH₃), 0.85 (t, 3H, $^3$J = 7.12 Hz, CO₂CH₂CH₃); $^{13}$C NMR (CDCl₃, 125 MHz): δ 167.6 (1C, CO₂CH₂CH₃), 167.1 (d, 1C, $^2$JPC = 15.1 Hz, CO₂CH₂CH₃), 133.9-127.6 (15C, Ar), 62.0 (1C, CO₂CH₂CH₃), 61.7 (1C, CO₂CH₂CH₃), 52.7 (1C, (CO₂)₂CH), 46.4 (d, 1C, $^1$JPC = 64.3 Hz, PCH), 13.9 (1C, CO₂CH₂CH₃), 13.7 (2C, CO₂CH₂CH₃). HRMS (+ESI) m/z: (M + H)$^+$ calcd for C₂₆H₂₆O₃P, 451.1675; found, 451.1676. Anal. Calcd for C₂₆H₂₆O₃P: C, 69.32; H, 6.04. Found: C, 69.57; H, 6.31%.

**Product 7a**

White solid. The ee was determined on a Daicel Chiralpak AD column with n-hexane/2-propanol = 75/25, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 22.2 min, 28.2
min (major product with catalyst (S)-2). [α]D = +50.7 (c 0.1, DCM). Mp: 126-127 °C. 31P{1H} NMR (CDCl3, 202 MHz): δ 30.4; 1H NMR (CDCl3, 400 MHz): δ 7.90-7.79 (m, 4H, Ar), 7.52-7.45 (m, 6H, Ar), 7.26-7.15 (m, 5H, Ar), 6.41 (dd, 1H, 3J = 15.9 Hz, 3J = 3.20 Hz, PhCH=CH), 6.19-6.12 (m, 1H, PhCH=CH), 4.21-4.15 (m, 1H, (CO2)2CH), 4.13-3.99 (m, 4H, CO2CH2CH3), 3.98-3.88 (m, 1H, PCH), 1.15-1.10 (m, 6H, CO2CH2CH3); 13C NMR (CDCl3, 125 MHz): δ 167.6 (d, 1C, 3JPC = 10.8 Hz, CO2CH2CH3), 167.3 (d, 1C, 3JPC = 10.8 Hz, CO2CH2CH3), 136.4-121.5 (17C, Ar and C=C), 61.9 (1C, CO2CH2CH3), 61.7 (1C, CO2CH2CH3), 51.3 (1C, (CO2)2CH), 44.6 (d, 1C, 1JPC = 67.1 Hz, PCH), 14.0 (1C, CO2CH2CH3), 13.9 (1C, CO2CH2CH3). HRMS (+ESI) m/z: (M + H)+ calcd for C28H30O3P, 477.1832; found, 477.1830. Anal. Calcd for C28H29O2P: C, 70.58; H, 6.13. Found: C, 70.77; H, 6.34%.

**Product 7b**

White solid. The ee was determined on a Daicel Chiralpak AD column with n-hexane/2-propanol = 75/25, flow = 0.8 mL/min, wavelength = 230 nm. Retention times: 23.7 min, 41.3 min. [α]D = -8.4 (c 0.1, DCM). Mp: 139-141 °C. 31P{1H} NMR (CDCl3, 202 MHz): δ 33.6; 1H NMR (CDCl3, 400 MHz): δ 7.86-7.81 (m, 2H, Ar), 7.53-7.47 (m, 5H, Ar), 7.37-7.35 (m, 2H, Ar), 7.30-7.24 (m, 3H, Ar), 7.20-7.17 (m, 3H, Ar), 6.14 (ddd, 1H, 3J = 15.3 Hz, 9.28 Hz, 6.64 Hz, PhCHPC=CH), 5.72 (ddd, 1H, 3J = 15.4 Hz, 9.04 Hz, 3.80 Hz, PhCHPC=CH), 4.29-4.24 (m, 1H, PhCHP), 4.10 (q, 2H, 3J = 7.08 Hz, CO2CH2CH3), 4.03-3.99 (m, 2H, CO2CH2CH3), 3.93 (d, 1H, 3J = 9.08 Hz, (CO2)2CH), 1.19-1.14 (m, 6H, CO2CH2CH3); 13C NMR (CDCl3, 125 MHz): δ 167.7 (d, 1C, 3JPC = 3.14 Hz, CO2CH2CH3), 167.5 (d, 1C, 3JPC = 2.86 Hz, CO2CH2CH3), 135.3-126.7 (17C, Ar and C=C), 61.8 (1C, CO2CH2CH3), 61.8 (1C, CO2CH2CH3), 55.6 (1C, (CO2)2CH), 51.9 (d, 1C, 1JPC = 64.1 Hz, PCH), 14.1 (1C, CO2CH2CH3), 14.1 (1C, CO2CH2CH3). HRMS (+ESI) m/z: (M + H)+ calcd for C28H30O3P, 477.1832; found, 477.1835. Anal. Calcd for C28H29O2P: C, 70.58; H, 6.13. Found: C, 70.73; H, 6.37%.
catalyst (R,R)-4b
catalyst (R,R)-4b

Ph₂P-H

(R,R)-4b + PPh₂H + Ph⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻~-~-~

[ppm]
NMR Coordination Experiment with Chlorodiphenylphosphine

A solution of (R,R)-4b (4.00 mg, 0.00483 mmol, 1.0 equiv.) and ClPPh$_2$ (1.12 mg, 0.00507 mmol, 1.05 equiv.) in CDCl$_3$ (1 mL) was stirred at room temperature for 1 h before $^{31}$P{¹H} NMR was conducted. Similarly, all other experiments were carried out in CDCl$_3$ and stirred for 1 h at room temperature.

Chlorodiphenylphosphine was selected to replace the role of diphenylphosphine to prevent the hydrophosphination reaction from proceeding with the absence of a proton atom.

Based on the $^1$H NMR spectrum (page 7), the addition of diethyl 2-cinnamylidenemalonate to the catalyst (R,R)-4b in CDCl$_3$ does not result in coordination to the palladium metal center as no visible chemical shifts in the proton signals of both the catalyst and substrate were observed. Furthermore, the proton signal due to the -OAc group remained unchanged at 1.98 ppm. This indicates that the -OAc group coordinated to the palladium center has not been replaced.

From the results of the $^{31}$P{¹H} NMR spectrum (page 8), the addition of diethyl 2-cinnamylidenemalonate to the catalyst in CDCl$_3$ does not result in any coordination shift. This again suggests that the substrate is unable to coordinate to the metal center. However when 0.5 equivalent of chlorodiphenylphosphine was added to the catalyst, the $^{31}$P{¹H} signal of the phosphine shifted from 82.9 ppm to 21.9 ppm. The signal at 44.5 ppm is assigned to the PCP phosphines, and 21.9 ppm belongs to ClPPh$_2$. However, due to reasons such as the lability of ClPPh$_2$ or the possibly small P-P cis coupling, no coupling of the phosphines were observed. From this, it is evident that the phosphine has replaced the -OAc group on the metal center. The same observation was made when stochiometric amounts of catalyst, substrate and phosphine were added in the same solution.

NMR Coordination Experiment with Diphenylphosphine

The experimental procedure is similar to that for chlorodiphenylphosphine.

On page 9, the $^{31}$P{¹H} NMR spectrum shows 2 broad peaks appearing at 49.9 and -10.2 ppm corresponding to PCP phosphines and phosphido-palladium respectively when stochiometric amounts of catalyst and PPh$_2$H were reacted in CDCl$_3$ for 1 h. With the subsequent addition of the substrate into the mixture, the signals -10.2 ppm and 44.9 ppm disappeared with the formation of the phosphinated product at 4.8 ppm and the reappearance of the catalyst signal at 44.5 ppm. The results obtained were consistent with an analogous pincer catalyst reported by Duan. With the NMR data collected and detailed NMR studies reported previously, the mechanism was proposed. A trans-phosphination reaction generates a nucleophilic Pd-phosphido species and a subsequent external nucleophilic attack on the substrate at the δ-position due to steric hindrance with the bulky carboxylic ester moieties yields a π-allyl intermediate. The cationic Pd-phosphine complex was then protonolyzed with acetic acid to regenerate the active catalyst and formed the 1,6-adduct.
In the proposed catalytic pathway of palladacycle (S)-2, the substrate replaces the phosphine that is trans to the naphthalene carbon due to the lability of the Pd-P bond. The coordination of the phosphine to the Pd metal acidifies the P-H bond thus allowing for its deprotonation by a base. The nucleophilic phosphido species is then directed to attack the β-position of the substrate due to the formation of a favored 6-membered intermediate.
Variable Low Temperature $^{31}\text{P}\{^1\text{H}\}$ Studies of Pincer Catalyst (R,R)-4b.

When subjected to lower temperatures of up to -80°C, the broadening of the phosphorous signal of (R,R)-4b indicates the dynamic changes of the trans $\text{P} \rightarrow \text{Pd} \leftarrow \text{P}$ bonds. However the changes are so facile that the individual phosphorous signals (especially for the bidentate species 8) could not be trapped even at -80°C. To further ensure that the broadening of the peaks are not mainly due to other factors such as poor shimming, reduced solubility or increased viscosity, the analogous PCN-Pd pincer was subjected to the same low variable temperature conditions as the catalyst (R,R)-4b. The favourable trans $\text{N} \rightarrow \text{Pd} \leftarrow \text{P}$ system exhibited no significant peak broadening as shown below, hence we believe that the broadening in the trans $\text{P} \rightarrow \text{Pd} \leftarrow \text{P}$ system is due to the lability of the $\text{P} \rightarrow \text{Pd} \leftarrow \text{P}$ bonds.
**Determination of ee and de for Pincer (R,R)-6**

The determination of enantio- and diastereo-selectivity was conducted in the same manner as described extensively.\(^1\) Theoretically, 4 isomers (R,R), (S,R), (S,S) and (R,S) may be formed via the double hydrophosphination reaction, which may not be distinguished efficiently by \(^{31}\)P\(^{(1}H\) NMR spectroscopy. Upon addition of a chiral derivatizing agent such as (S)-8, 4 phosphorous peaks may be observed in the case of a racemic mixture of isomers, corresponding to (S, R, R), (S, S, R, S) + (S, R, S, S) and (S, S, S, S). Therefore, based on the integral ratio of the 4 signals, we are able to determine the values of ee and de respectively.
From the cross coordination experiment with (R)/(S)-8, since there is only one signal observed in the $^{31}$P/$^1$H NMR spectrum, we conclude that the $ee$ and $de$ of the asymmetric double hydrophosphination to be >99%. The $de$ was double confirmed upon metalation of the free diphosphine ligand to Pd metal, with the presence of only 1 peak at 47.9 ppm and the absence of the diastereomer peak at 50.2 ppm.

**Reference**


PCP Pd-I via CF(S)

$\text{Ph}_2\text{P} \xrightarrow{\text{Pd}} \text{PPh}_2$

$(R,R)-4d$
Pd Pincer (tetraester)
CP(S)

(R,R)-6
Pd Pincer (tetraester)

CP(S)

\[
\text{MeO}_2\text{C} \quad \text{CO}_2\text{Me} \\
\text{MeO}_2\text{C} \quad \text{Pd} \quad \text{PPh}_2 \\
\text{Ph}_2\text{P} \quad \text{Cl} \\
(R,R)-6
\]
diethyl ethylidenemalonate 1 eq + HPPh2 1 eq  
Pure product
diethyl ethylidenemalonate 1 eq + HPPh 2 eq + H2O2

Ph₂P=O
Me
CO₂Et

5a

[ppm]

200 100 0 -100 -200
diethyl ethyldienemalonate 1 eq + HPh2 1 eq + H2O2

Ph2PO
Me
\[\text{CO}_2\text{Et}\]
\[\text{CO}_2\text{Et}\]

5a
diethyl benzylidenemalonate 1 eq + HPPh2 2 eq

Ph₂P═O
Ph
\begin{align*}
\text{CO₂Et} & \\
\text{CO₂Et} & \\
\end{align*}

5b
diethyl benzylidene malonate 1 eq + HPPh2 1 eq + H2O2

5b
diethyl cinnamylidenemalonate + HPPh₂ + H₂O₂
1,4 product

Ph
\[
\begin{align*}
\text{Ph} & \quad \text{PhPO} \\
\text{C} & \quad \text{OEt} \\
\text{C} & \quad \text{OEt} \\
\end{align*}
\]

7a
diethyl cinnamylidenemalonate + HPPh₂ + H₂O₂
1,4 product

7a

[Chemical structure image]
diethyl cinnamylidenemalonate 1eq + HPh2 1eq + H2O2 [1,4 pdt]

\[
\begin{align*}
\text{Ph} & \quad \text{CO}_2\text{Et} \\
\text{Ph}_{2}\text{P} & \quad \text{O} \\
\end{align*}
\]

7a
diethyl cinnamylidenemalonate 1 eq + HFPPh2 1 eq + H2O2
Pure product
diethyl cinnamyliidenemalonate 1eq + HPh2 1eq + H2O2 [1,6 product]

7b
diethyl cinnamylidene malonate 1 eq + HPh2 1 eq + H2O2 [1,6-product]

\[
\text{Ph}_2\text{P} = \quad \text{CO}_2\text{Et}
\]

7b

150
100
50

[ppm]
Sample Info: diethyl ethyldeneacetaldehyde ethyl 3 \% CP racemic catalyst
DCM RT 2h
Column: AD-H
inj vol: 5\u3000L
25\degree C
0.6\%MeOH:3.8\%IPA
0.8\%/min

Additional Info: Peak(s) manually integrated

Area Percent Report

Sorted by: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISID

Signal 1: MWID F, Sig=220,16 Ref=360,100
Peak RetTime Type Width Area Height Area
# [min] [mm] [mm] [mAU] [mAU] [%]
1 282.8024 H 6.92004 4.61819e4 125.55495 49.9333
2 216.499 PM 6.87033 4.63532e4 112.33157 50.0667
Totals: 9.24870e4 237.88652
Table 1, Entry 1.

Sample Info: diethyl ethylidenemalonate leq + HEPPh2 leq
5% PCE Pd-CA
MeCN RT 0.5h
Column: AU-H
in) vol: 5uL
230
96.5Hex:3.5IPA
0.9mL/min

Additional Info: Peak(s) manually integrated

<table>
<thead>
<tr>
<th>Signal</th>
<th>Sort By</th>
<th>Multiplier:</th>
<th>Dilution:</th>
<th>Do not use Multiplier &amp; Dilution Factor with ISIDS</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW01 F</td>
<td>Signal</td>
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<td>1.0000</td>
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</tr>
</tbody>
</table>

Signal 1: MW01 F, Slg-220,16 Ref-160,160

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<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>200.380</td>
<td>MF</td>
<td>5.759</td>
<td>2.16255e4</td>
<td>62.58230</td>
<td>51.5947</td>
</tr>
<tr>
<td>2</td>
<td>214.336</td>
<td>FM</td>
<td>6.340</td>
<td>2.02387e4</td>
<td>53.33126</td>
<td>45.4053</td>
</tr>
</tbody>
</table>

Totals: 4.19142e4 115.91356
Table 1, Entry 2.

Sample Info: diethyl herrylderenenate + KFPn2
% PEP D-0Ac
Acetone 0.5 hr RT
Column: AD-H
inj. vol: 5UL
IUC
96.5%Hex : 3.5%PA
0.9 ML/min

Additional Info: Peak(s) manually integrated

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area [MAU's]</th>
<th>Height [MAU]</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>105.966</td>
<td>MF</td>
<td>7.7995</td>
<td>4.2071e4</td>
<td>94.76733</td>
<td>47.1446</td>
</tr>
<tr>
<td>2</td>
<td>122.020</td>
<td>FM</td>
<td>9.5390</td>
<td>4.7170e3</td>
<td>82.41638</td>
<td>92.8552</td>
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</tbody>
</table>

Totals: 8.92443e4 177.18363
Table 1. Entry 3.

<table>
<thead>
<tr>
<th>Sample info</th>
<th>diethyl ethylenediamine 1eq + EPPh2 1eq</th>
</tr>
</thead>
<tbody>
<tr>
<td>5% PCF Pd-Cac</td>
<td></td>
</tr>
<tr>
<td>DCM RT 1h</td>
<td></td>
</tr>
<tr>
<td>Column: AS-H</td>
<td></td>
</tr>
<tr>
<td>Inj vol: 5uL</td>
<td></td>
</tr>
<tr>
<td>25C</td>
<td></td>
</tr>
<tr>
<td>96%MeOH:3.0IPA</td>
<td></td>
</tr>
<tr>
<td>0.9mL/min</td>
<td></td>
</tr>
</tbody>
</table>

Additional Info: Peak(s) manually integrated

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**Area Percent Report**

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

<table>
<thead>
<tr>
<th>Signal 1: MWD1 F, Sig=220,16 Ref=350,100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak</td>
</tr>
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<td>-----</td>
</tr>
<tr>
<td>1</td>
</tr>
<tr>
<td>2</td>
</tr>
<tr>
<td>Totals</td>
</tr>
</tbody>
</table>

---

42
Table 1. Entry 4.

Sample Info: diethyl benzylidemalonate + KPH2
5% PCP Pd-OAc
DCM 1.5hr -80
Column: AD-H
Inj. vol: 5μL
23°C
96.5% EtOAc : 3.5%IPA
0.9 mL/min

Additional Info: Peak(s) manually integrated

---

Area Percent Report

---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISIDs

Signal 1: MWD1 f, Sig=220,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>209.066</td>
<td>0.005</td>
<td>5824.54441</td>
<td>13.3843</td>
<td>45.3427</td>
</tr>
<tr>
<td>2</td>
<td>228.225</td>
<td>0.005</td>
<td>7021.06555</td>
<td>13.6216</td>
<td>54.6573</td>
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<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1.28456e4</td>
<td>27.19805</td>
<td></td>
</tr>
</tbody>
</table>
Table 1, Entry 5.

**Sample Info**: diethyl beryllidenederacolate + EPPH2
- % CP(S) catalyst
- DCM 1.5 hr -80
- Column: AD-H
- Inf. vol: 5 µL
- 25°C
- 98% Ex.: 1.3 mPA
- 0.9 mL/min

**Additional Info**: Peak(s) manually integrated

---

**Area Percent Report**

**Sorted By**: Signal

**Multiplier**: 1.0000

**Dilution**: 1.0000

Use Multiplier & Dilution Factor with Intensities

**Signal**: MW01 F, Sig-220.16 Ref-360.100

<table>
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<th>#</th>
<th>Retention Type</th>
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<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
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</thead>
<tbody>
<tr>
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<td>105.762 MF</td>
<td>0.1915</td>
<td>6.67270e4</td>
<td>139.63464</td>
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<tr>
<td>2</td>
<td>227.115 PM</td>
<td>0.3253</td>
<td>1.33911e4</td>
<td>24.29075</td>
<td>15.5104</td>
<td></td>
</tr>
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</table>

**Totals**: 8.23181e4 164.12539
Table 1, Entry 6.

Sample Info: diethyl ethylenediamine 1eq + HFPH2 1eq
5% PCE Pd-OAc
Toluene RT 1h
column: AD-H
inj vol: 5μL
25°C
96.8Heq: 3.516A
0.9ml/min

Additional Info: Peak(s) manually integrated

<table>
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<tr>
<th>Peak Ret Time Type</th>
<th>Width</th>
<th>Area [mAU]</th>
<th>Weight [mAU]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1 199.675 HR</td>
<td>6.1297</td>
<td>4.4388e4</td>
<td>120.69040</td>
<td>56.0824</td>
</tr>
<tr>
<td>2 214.162 FH</td>
<td>6.5380</td>
<td>3.2034e4</td>
<td>91.66218</td>
<td>41.9176</td>
</tr>
</tbody>
</table>

Totals: 7.6422e6 232.34258
Table 1, Entry 7.

Sample Info: diethyl benzylidenemalonate + HFFH2
5% PCE Pd-OAc
Toluene -80 3h
Column: AD-H
Inj. vol: 5uL
25°C
96.5%ex: 3.5%IPA
0.9 mL/min

Additional Info: Peak(s) manually integrated

Area Percent Report

<table>
<thead>
<tr>
<th>Sorted By</th>
<th>Signal</th>
<th>Multiplier:</th>
<th>Dilution:</th>
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<td>1.0000</td>
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</table>

Use Multiplier & Dilution Factor with ISIDs

Signal 1: MWD1 F. Sig=220.16 Ref=360.100

<table>
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<th>Width</th>
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<th>Weight</th>
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<tr>
<td>1 207.105 MH</td>
<td>6.9203</td>
<td>2.9959e4</td>
<td>70.9408</td>
<td>20.2366</td>
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<tr>
<td>2 220.790 FM</td>
<td>9.7986</td>
<td>7.4870e4</td>
<td>127.3477</td>
<td>71.7634</td>
</tr>
</tbody>
</table>

Totals: 1.04329e5 190.29591

46
Table 1, Entry 8.

Sample Info: diethyl ethylidenemalonate 1 eq + HPh2 1 eq + H2O2
5% CP(S) catalyst
Toluene ~80 hr
Injection Vol.: % uL
Flow Rate: 8.9 mL / min
n-Heptane : I.P.A = 96.5 : 3.5
Temp: 23
Column: AD-N

Additional Info: Peak(s) manually integrated

---

Area Percent Report
---

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Sample Amount: : 1000.000 [ng/ul] (not used in calc.)
Do not use Multiplier & Dilution factor with zeros

Signal 1: MWG1 F, Sig=210,16 Rel=160,100

Peak RetTime Type Width Area Height Area
<p>| | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 202.482 MF 6.5713 6.9127e4 175.32637 53.7944</td>
<td></td>
<td></td>
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<td></td>
</tr>
<tr>
<td>2 216.567 FM 7.4310 5.93753e4 133.17049 46.2056</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Totals: 1.28502e5 308.49686

---
Table 1, Entry 11.

Sample Info:
- Dihydrate ethylidenemalonate 1eq + HPPA2 1eq + MRT3 1eq
- 5% PPE P4-C1
- Toluene RT 24h
- Column: AD-H
- Flow rate: 0.9 mL/min
- Eluent: 96.5% Hex : 3.5% IPA
- 23C

Additional Info: Peak(s) manually integrated

---

Area Percent Report

---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 [mg/mL] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISIDs

Signal 1: MWD1 F, Sig=230.16 Ref=160,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
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<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
</tr>
<tr>
<td>1</td>
<td>203.955 MF</td>
<td>6.4188</td>
<td>4.81150e4</td>
<td>124.93208</td>
</tr>
<tr>
<td>2</td>
<td>218.199 PM</td>
<td>7.2111</td>
<td>4.87594e4</td>
<td>112.69516</td>
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<tr>
<td>Totals</td>
<td></td>
<td></td>
<td></td>
<td>9.68743e4</td>
</tr>
</tbody>
</table>

---
Table 1. Entry 12.

Sample Info: diethyl ethylidenemalonate leq + HPh2 leq + NEt3
5% PCP Pd-TFA
Toluene RT 3h
Column: AD-R
Flow rate: 0.9 min/mL
Eluent: 36.2% MeOH : 3.8% IPA
23C

Additional Info: Peak(s) manually integrated

![Graph Image]

---

Area Percent Report

---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 [ng/ul] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: MW01 F, Sig=229,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1  208.102 M4</td>
<td>6.0004</td>
<td>2.303908e4</td>
<td>63.92656</td>
<td>52.5980</td>
<td></td>
</tr>
<tr>
<td>2  223.229 M4</td>
<td>6.9041</td>
<td>2.07647e4</td>
<td>93.20967</td>
<td>47.1040</td>
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</tbody>
</table>

Totals: 4.30037e4 117.20264
Table 1, Entry 13.

Sample Info: diethyl ethyldienemalonate 1eq = HPPh2 1.1eq = H2O2
5% PDP 44:
Toluene RT 24h
Flow rate: 0.9 mL/min
Eluant: 96.5%:3.5%IPA
Column: AD-H 23C

Additional Info: Peak(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: MSD F Sig-220,16 Ref-360,100

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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>101.590</td>
<td>MF</td>
<td>7.4204</td>
<td>3.12008e4</td>
<td>69.92673</td>
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<td>2</td>
<td>116.646</td>
<td>MF</td>
<td>8.9682</td>
<td>3.42392e4</td>
<td>63.62173</td>
<td>42.3116</td>
</tr>
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</table>

Totals: 6.54428e4 133.54848
Sample Info: diethyl benzylidenemalonate leq + BPPh2 leq
5% racemic CP catalyst
DCM RT
Column: IC
Flow rate: 1 min/mL
Eluent: 87% MeOH/13% IPA
23°C

Additional Info: Peaks(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: MWDI F, Sig-220,16 Ref-360,100

<table>
<thead>
<tr>
<th>Peak Ret Time Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
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<tr>
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<td>[min]</td>
<td>[min]</td>
<td>[mAU's]</td>
<td>[mAU]</td>
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<tr>
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<td>93.405</td>
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<td>181.533</td>
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<td>2.04135e4</td>
<td>100.37639</td>
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</table>

Totals: 4.08397e4 | 212.87141
Table 1, Entry 14.

Sample Info: diethyl benzylidenemalonate leq + HEPH2 leq
5% PFC Pd-OAc
Toluene RT 5h
Column: IC
Flow rate: 1 min/mL
Eluent: 87% Hex : 13% IPA
23°C

Additional Info: Peak(s) manually integrated

<table>
<thead>
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<th>Area Percent Report</th>
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<tbody>
<tr>
<td>Sorted By: Signal</td>
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<tr>
<td>Multiplier: 1.0000</td>
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<tr>
<td>Dilution: 1.0000</td>
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<tr>
<td>Do not use Multiplier &amp; Dilution Factor with ISTDs</td>
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Signal 1: MWDF F, Sig=220,16 Ref=360,100

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<th>Height</th>
<th>Area %</th>
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<tbody>
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<td>4628.7759</td>
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<td>49.6966</td>
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<tr>
<td>2 104.333 NM</td>
<td></td>
<td>3.6193</td>
<td>4685.29736</td>
<td>21.52908</td>
<td>50.3034</td>
</tr>
</tbody>
</table>

Totals: 9314.07275 45.38203
Table 1, Entry 15.

Sample Info: diethyl benzylidenemalonate leq + HPh2 leq + H2O2
  % CP(s) catalyst
  Toluene =80 24h
  Injection volume: 5uL
  Eluent: 9/HeAme:18IPA
  Column: IC
  23C

Additional Info: Peak(s) manually integrated

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<table>
<thead>
<tr>
<th>mAU</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
</tr>
<tr>
<td>50</td>
</tr>
<tr>
<td>100</td>
</tr>
<tr>
<td>150</td>
</tr>
<tr>
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<tr>
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<td>450</td>
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<tr>
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</tr>
<tr>
<td>900</td>
</tr>
<tr>
<td>950</td>
</tr>
<tr>
<td>1000</td>
</tr>
</tbody>
</table>
------------------------------------------------------------------------

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: MWDF F, Sig=220.16 Ref=360.100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time Type Width Area</th>
<th>Height Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94.494 MP 5.0914 6047.90239 32.60362 65.65384</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>102.510 FM 3.4676 3493.40361 16.59847 36.33466</td>
<td></td>
</tr>
</tbody>
</table>

Totals: 9501.30420 49.20409
Table 1, Entry 16.

Sample Info : diethyl benzylideneacetone leq + EPFh2 leq
5% Pd Pd-OAc
DCM RT 5h
Column: IC
Flow rate: 1 min/mL
Eluent: 87% Hex : 13% IPA
23C

Additional Info : Peak(s) manually integrated

Area Percent Report

Sorted By : Signal
Multiplier: : 1.0000
Dilution: : 1.0000
Do not use Multiplier & Dilution Factor with ISIDs

Signal 1: MW01 F, Sig=220,16 Ref=360,103 (XYD/DEF_IC:2014-02-17 21:47:52:00 14/17/029000003, 3)

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.503</td>
<td>MM</td>
<td>3.1327</td>
<td>2.2626e4</td>
<td>117.40113</td>
<td>51.4133</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>104.077</td>
<td>MM</td>
<td>3.5303</td>
<td>2.08537e4</td>
<td>98.44944</td>
<td>48.5867</td>
<td></td>
</tr>
</tbody>
</table>

Totals : 4.29205e4 215.85057
Table 1, Entry 17.

Sample Info: diethyl benzylidenemalonate leq + RPPH2 leq + H2O2
5% PFC PD-OAc
DCM 0 24h
Injection Volume: 5μL
Eluant: 80%Hexane:20IPA
Column: IC
23C

Additional Info: Peak(s) manually integrated

![Graph showing peaks and area percent report]

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.000000 [μg/μL] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: MW01 F, Sig=220.16 Ref=360.100

| Peak | RetTime | Type | Width | Area [mAU] | Height [mAU] | Area [%]
<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>93.956</td>
<td>MF</td>
<td>1.991</td>
<td>1.01596e4</td>
<td>103.07168</td>
<td>58.7576</td>
</tr>
<tr>
<td>2</td>
<td>102.013</td>
<td>FM</td>
<td>1.4909</td>
<td>1.34493e4</td>
<td>64.20625</td>
<td>41.2424</td>
</tr>
</tbody>
</table>

Totals: 3.26079e4 167.27792
Table 1. Entry 18.

Sample Info: diethyl benzylidenenemalonate leq + HFFh2 leq + H2O2
5% Cu(s) catalyst
DCM -80 4h
Injection Volume: 5uL
Eluant: 67Hexane:33IPA
Column: XC
23C

Additional Info: Peak(s) manually integrated

<table>
<thead>
<tr>
<th>Signal</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>94.987 Min</td>
<td>3.2728</td>
<td>463.73572</td>
<td>2.35160</td>
</tr>
<tr>
<td>2</td>
<td>102.335 Min</td>
<td>3.4278</td>
<td>1.676838e4</td>
<td>81.53196</td>
</tr>
</tbody>
</table>

Totals: 1.7232e4 83.89356
Table 2, Entry 1.

**Sample Info**: diethyl cinnamylidenemalonate leq + KPFh2 leq
5% PTF Pd-OAc
RT DCM 2h
Injection Vol.: % uL
Flow Rate: 6.8 mL / min
n-Heptane : I.P.A = 75 : 25
Temp: 23
Column: AD-R

Additional Info: Peak(s) manually integrated

---

**Area Percent Report**

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 [ng/uL] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

**Signal**: MWDI D, Sig=230.16 Ref=306.100

<table>
<thead>
<tr>
<th>Peak RetTime Type Width Area Height Area</th>
<th>[min]</th>
<th>[min]</th>
<th>[mAU's]</th>
<th>[mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 23.676 NM 0.7040 7804.65449 194.76332 30.9329</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 41.270 NM 1.3377 1.74267e4 217.11789 69.0671</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Totals:                              2.52310e4 491.03121</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---
Table 2, Entry 2.

Sample Info: diethyl pinaamylidenemalonate leq + RPh2 leq
5% KCl Pd-OAc
80% DCM 24h
Injection Vol.: 5 μL
Flow Rate: 0.8 mL / min
n-Heane : I.P.A - 75 : 25
Temp: 23
Column: AD-H

Additional Info: Peak(s) manually integrated

---

Area Percent Report
---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 (ng/μL) (not used in calc.)
Do not use Multiplier & Dilution Factor with ISIDS

Signal 1: MW01 D, Sig=230,16 Ref=260,100

<table>
<thead>
<tr>
<th>Peak Ret Time Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>fr</td>
<td>[min]</td>
<td>[μL]</td>
<td>[μL]</td>
<td>[μL]</td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
<td>------</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>1</td>
<td>23.67 ±</td>
<td>0.7007</td>
<td>1549.99912</td>
<td>36.41917</td>
</tr>
<tr>
<td>2</td>
<td>41.39 ±</td>
<td>1.2513</td>
<td>6264.51660</td>
<td>83.44115</td>
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<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>7809.61972</td>
</tr>
</tbody>
</table>
Table 2, Entry 3.

Sample Info: diethyl cinnamyldenedeoalactone leq + 5HF2 leq
5% PCF Pd-OAc
RT MBE 1h
Injection Vol.: 3 uL
Flow Rate: 0.8 mL/min
n-Hexane: T.F.A = 75 : 25
Temp: 23
Column: AD-R

Additional Info: Peak(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 [ng/ul] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISIDs

Signal 1: MW31 D, Sig-230,16 Ref-160,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MM</td>
<td>0.719</td>
<td>1.966e6</td>
<td>435.5759</td>
</tr>
<tr>
<td>2</td>
<td>MM</td>
<td>1.281</td>
<td>1.2408e6</td>
<td>161.4278</td>
</tr>
<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>3.2069e4</td>
<td>617.00372</td>
</tr>
</tbody>
</table>

59
Table 2, Entry 4.

Sample Info: diethyl cinnamyliidenemalonate leq + HPh2 leq
5% PCP Pd-OAc
Toluene RT 3h
Column: AD-H
Flow rate: 0.8 min/mL
Eluent: 75% Hex : 25% IPA
23C

Additional Info: Peak(s) manually integrated

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.404</td>
<td>ISD</td>
<td>0.7562</td>
<td>4.29363e4</td>
<td>947.54669</td>
<td>63.7250</td>
</tr>
<tr>
<td>2</td>
<td>41.173</td>
<td>ISD</td>
<td>1.3634</td>
<td>2.44411e4</td>
<td>295.42606</td>
<td>16.8750</td>
</tr>
</tbody>
</table>

Totals: 6.73774e4 1246.97275
Table 2, Entry 5.

Sample Info: diethyl cinnamylidenemalate leq + HPh2 leq
5% PCP P4-OAc
-80°C Toluene 24h
Injection Vol.: 5 μL
Flow Rate: 0.5 mL/min
t-Hexane : I.P.A = 75 : 25
Temp: 23
Column: AD-H

Additional Info: Peak(s) manually integrated

<table>
<thead>
<tr>
<th>MW1 D, Sig=230,16 Ref=360,100 (YXYYX-140/264/30)</th>
</tr>
</thead>
</table>

---|------------------|------------------|------------------|------------------|------------------|
|     |      |      |      |      |      |
| MW1 D, Sig=230,16 Ref=360,100 |      |      |      |      |      |

Area Percent Report

| Sorted By  | : Signal |
| Multiplier | : 1.0000 |
| Dilution   | : 1.0000 |
| Sample Amount | : 1.0000 [ng/μL] (not used in calc.) |
Do not use Multiplier & Dilution Factor with ISHDs

Signal 1: MW1 D, Sig=230,16 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area [nAU*s]</th>
<th>Height [nAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td>[min]</td>
<td></td>
<td></td>
</tr>
<tr>
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<td>23.604</td>
<td>0.7022</td>
<td>7007.83350</td>
<td>166.32829</td>
</tr>
<tr>
<td>2</td>
<td>41.442</td>
<td>1.2862</td>
<td>1246.27100</td>
<td>17.22065</td>
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<tr>
<td>Totals</td>
<td></td>
<td></td>
<td>854.10449</td>
<td>183.54894</td>
</tr>
</tbody>
</table>
Table 2, Entry 6.

Sample Info: diethyl cinnamylideneacetaldehyde leq + HPPH2 leq
5% CP(S) catalyst
DCM RT 2h
Column: AD-H
Flow rate: 0.8 min/mL
Eluent: 75% Hex : 25% IPA
25°C

Additional Info: Peak(s) manually integrated

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 [mg/mL] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: MW01. Sig-230.16 Ref-360.100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Weight Area [mAU]</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.153</td>
<td>0.7099</td>
<td>4006.14063</td>
<td>94.05885</td>
<td>22.3540</td>
</tr>
<tr>
<td>2</td>
<td>20.215</td>
<td>0.8741</td>
<td>1.391464e6</td>
<td>265.30789</td>
<td>77.6452</td>
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<td>Totals</td>
<td></td>
<td></td>
<td>1.79207e4</td>
<td>359.35874</td>
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</tr>
</tbody>
</table>
Table 2, Entry 7.

Sample Info: diethyl cinnamylidenemalonate leq + HPh2 leq
5% CP(S) catalyst
DCM –80 3h
Column: A0-8
Flow rate: 0.3 min/mL
Eluent: 75% Hex : 25% IPA
23C

Additional Info: Peak(s) manually integrated

---

Area Percent Report

---

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.0000 [ng/µL] (not used in calc.)
Do not use Multiplier & Dilution Factor with ISIDs

Signal 1: MWCL D, Sig=231,16 Ref=363,100

<table>
<thead>
<tr>
<th>#</th>
<th>Ret Time (min)</th>
<th>Width (min)</th>
<th>Area (mAU's)</th>
<th>Height (mAU)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>22.181</td>
<td>0.4924</td>
<td>100.17543</td>
<td>6.43705</td>
<td>0.3797</td>
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<tr>
<td>2</td>
<td>28.130</td>
<td>0.8879</td>
<td>964.890344</td>
<td>936.662411</td>
<td>99.6233</td>
</tr>
</tbody>
</table>

Totals: 5.94895e+04 943.00444
Table 2. Entry 8.

Sample Info:
- diethyl cinnamylidenemalonate "eq + HPN2 "eq + H2O
- 5% CP(S) catalyst
- DCM 50C 0.5hr
- Injection Vol.: 5 µL
- Flow Rate: 0.3 mL / min
- n-Hexane : I.P.A - 75 : 25
- Temp: 23
- Column: AD-H

Additional Info: Peak(s) manually integrated

---

Area Percent Report

Sorted By: Signal
Multiplier: 1.0000
Dilution: 1.0000
Sample Amount: 1.00000 [mg/µL] (not used in calc.)

Do not use Multiplier & Dilution Factor with ISTDs

Signal 1: H6D11, Sig-230,16 Ref-360,100

<table>
<thead>
<tr>
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<th>RetTime</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
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<td>9430.19141</td>
<td>244.09305</td>
<td>26.1613</td>
</tr>
<tr>
<td>2</td>
<td>23.7973</td>
<td>0.6072</td>
<td>3622.57790</td>
<td>87.66178</td>
<td>10.0001</td>
</tr>
<tr>
<td>3</td>
<td>20.0633</td>
<td>0.6626</td>
<td>1.5435m54</td>
<td>296.29289</td>
<td>42.3251</td>
</tr>
<tr>
<td>4</td>
<td>41.6193</td>
<td>1.2939</td>
<td>7035.50049</td>
<td>100.26747</td>
<td>20.9600</td>
</tr>
</tbody>
</table>

Totals: 3.60464e4 730.51740
Crystallographic Data

Chemical formula  \( \text{C}_{43}\text{H}_{41}\text{Cl}_{3}\text{O}_{8}\text{P}_{2}\text{Pd} \)
Formula weight  960.45
Temperature  173(2) K
Wavelength  0.71073 Å
Crystal size  0.320 x 0.400 x 0.400 mm
Crystal habit  colorless block
Crystal system  orthorhombic
Space group  \( \text{P } 2_1 \text{ } 2_1 \text{ } 2_1 \)
Unit cell dimensions  
\[ a = 10.4536(4) \text{ Å}, \quad \alpha = 90° \]
\[ b = 17.2754(6) \text{ Å}, \quad \beta = 90° \]
\[ c = 24.4730(9) \text{ Å}, \quad \gamma = 90° \]
Volume  4419.6(3) Å\(^3\)
\( Z \)  4
Density (calculated)  1.443 g/cm\(^3\)
Absorption coefficient  0.724 mm\(^{-1}\)
\( F(000) \)  1960
Theta range for data collection  1.44 to 37.57°
Index ranges  
\(-17 \leq h \leq 11, -24 \leq k \leq 29, -41 \leq l \leq 41 \)
Reflections collected  63361
Independent reflections  23124 [\( R(\text{int}) = 0.0479 \)]
Coverage of independent reflections  99.8%
Absorption correction  multi-scan
Max. and min. transmission  0.8015 and 0.7607
Structure solution technique  direct methods
Structure solution program  SHELXS-97 (Sheldrick, 2008)
Refinement method  Full-matrix least-squares on \( F^2 \)
Refinement program  SHELXL-97 (Sheldrick, 2008)
Function minimized  \( \sum w(F_o^2 - F_c^2)^2 \)
Data / restraints / parameters  23124 / 85 / 547
Goodness-of-fit on \( F^2 \)  1.013
\( \Delta/\sigma_{\text{max}} \)  0.003
Final R indices  
18774 data; \( I>2\sigma(I) \) \( R_1 = 0.0415, \quad wR_2 = 0.0776 \)
all data \( R_1 = 0.0605, \quad wR_2 = 0.0880 \)
Weighting scheme  \( w=1/[\sigma^2(F_o^2)+(0.0373P)^2+0.0000P] \)
where \( P=(F_o^2+2F_c^2)/3 \)
Absolute structure parameter  -0.0(0)
Largest diff. peak and hole  0.617 and -0.634 eÅ\(^{-3}\)
R.M.S. deviation from mean  0.101 eÅ\(^{-3}\)
Chemical formula: $C_{28}H_{29}O_5P$
Formula weight: 476.48
Temperature: 103(2) K
Wavelength: 0.71073 Å
Crystal size: 0.080 x 0.100 x 0.420 mm
Crystal habit: colorless needle
Crystal system: monoclinic
Space group: P 1 21 1
Unit cell dimensions:
\[
\begin{align*}
\text{a} &= 10.751(2) \text{ Å} & \alpha &= 90^\circ \\
\text{b} &= 5.8887(8) \text{ Å} & \beta &= 103.361(9)^\circ \\
\text{c} &= 19.552(3) \text{ Å} & \gamma &= 90^\circ \\
\end{align*}
\]
Volume: 1204.3(3) Å$^3$
Z: 2
Density (calculated): 1.314 g/cm$^3$
Absorption coefficient: 0.152 mm$^{-1}$
F(000): 504
Theta range for data collection: 3.21 to 31.22°
Index ranges:
\[-15 \leq h \leq 15, -8 \leq k \leq 8, -28 \leq l \leq 26\]
Reflections collected: 20068
Independent reflections: 7734 [R(int) = 0.0856]
Coverage of independent reflections: 99.2%
Absorption correction: multi-scan
Max. and min. transmission: 0.9880 and 0.9390
Refinement method: Full-matrix least-squares on F$^2$
Refinement program: SHELXL-2013 (Sheldrick, 2013)
Function minimized: \[\Sigma w(F_o^2 - F_c^2)^2\]
Data / restraints / parameters: 7734 / 1 / 309
Goodness-of-fit on F$^2$: 0.990
Final R indices:
\[\text{l} > 2\sigma(\text{l})\]
\[R1 = 0.0648, wR2 = 0.1045\]
[all data]
\[R1 = 0.1106, wR2 = 0.1236\]
Weighting scheme:
\[w = \left(\frac{\sigma(F_o^2)}{2} + 0.0327P\right)^2\]
where \[P = (F_o^2 + 2F_c^2)/3\]
Absolute structure parameter: 0.1(1)
Largest diff. peak and hole: 0.480 and -0.477 eÅ$^{-3}$
R.M.S. deviation from mean: 0.076 eÅ$^{-3}$
<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C$<em>{28}$H$</em>{29}$O$_5$P</td>
</tr>
<tr>
<td>Formula weight</td>
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</tr>
<tr>
<td>Temperature</td>
<td>103(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.200 x 0.400 x 0.420 mm</td>
</tr>
<tr>
<td>Crystal habit</td>
<td>colorless block</td>
</tr>
<tr>
<td>Crystal system</td>
<td>triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P -1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 5.6363(4) Å, α = 103.051(6)°</td>
</tr>
<tr>
<td></td>
<td>b = 12.4972(11) Å, β = 96.273(5)°</td>
</tr>
<tr>
<td></td>
<td>c = 18.9559(17) Å, γ = 102.019(5)°</td>
</tr>
<tr>
<td>Volume</td>
<td>1254.98(18) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.261 g/cm$^3$</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.145 mm$^{-1}$</td>
</tr>
<tr>
<td>F(000)</td>
<td>504</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>3.15 to 31.21°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-8&lt;=h&lt;=8, -18&lt;=k&lt;=18, -27&lt;=l&lt;=27</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>38041</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8090 [R(int) = 0.0705]</td>
</tr>
<tr>
<td>Coverage of independent reflections</td>
<td>99.2%</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>multi-scan</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9710 and 0.9410</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F$^2$</td>
</tr>
<tr>
<td>Refinement program</td>
<td>SHELXL-2013 (Sheldrick, 2013)</td>
</tr>
<tr>
<td>Function minimized</td>
<td>$\Sigma w(F_o^2 - F_c^2)^2$</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8090 / 925 / 489</td>
</tr>
<tr>
<td>Goodness-of-fit on F$^2$</td>
<td>1.043</td>
</tr>
<tr>
<td>Final R indices</td>
<td>R1 = 0.0502, wR2 = 0.1138</td>
</tr>
<tr>
<td></td>
<td>all data R1 = 0.0775, wR2 = 0.1272</td>
</tr>
<tr>
<td>Weighting scheme</td>
<td>w=1/[σ$^2$(F$_o$)+0.0580P$^2$+0.1067P]</td>
</tr>
<tr>
<td></td>
<td>where P=(F$_o^2+2F_c^2$)/3</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.375 and -0.364 eÅ$^{-3}$</td>
</tr>
<tr>
<td>R.M.S. deviation from mean</td>
<td>0.062 eÅ$^{-3}$</td>
</tr>
</tbody>
</table>