

Supporting Information

Enantioselective 1,4-addition of diarylphosphine oxides to α,β -unsaturated ketones catalyzed by oxazaborolidines

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1. General experimental information

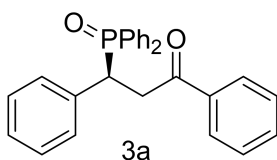
All reactions were carried out with anhydrous solvents (*vide infra*) under a nitrogen atmosphere using oven-dried glassware and standard Schlenk techniques. Reactions were monitored by ^1H NMR. Purification of the products was performed by column chromatography using Merck 60 Å 200-300 mesh silica gel. Components were visualized by UV and KMnO_4 staining (TLC). NMR data was collected on Bruker-Avance 400 MHz spectrometer (^1H at 400.0 MHz; ^{13}C at 100.58 MHz, ^{31}P at 162 MHz). Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak (CDCl_3 , ^1H : 7.26 ppm; ^{13}C : 77.16 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations. Enantiomeric excess (*ee*) were determined by chiral HPLC analysis using a Agilent HPLC (1260). High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer with ESI ionization.

Unless otherwise indicated, reagents and substrates (**1a**, **1b**, **1o**, **1q**, **1r**, **1v**, **1aa**, **1ac**, **1ad**, **1af**, **1ag**, **1ah**, **1ao**, **1ag**, **1ar**, **1au**, **1av**, **1aw**) were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use. Inert atmosphere experiments were performed with standard Schlenk techniques. All new compounds were fully characterized by ^1H and ^{13}C , ^{31}P NMR and HRMS techniques.

2. General procedures for asymmetric transformations

Asymmetric addition of aryl phosphate oxygen to α,β -unsaturated ketones catalyzed by chiral oxazaborane : In an argon-filled glove box, methylboronic acid (2.4 mg, 0.04 mmol) and (*S*)- α,α -Bis[3,5-bis(trifluoromethyl)phenyl]-2-pyrrolidinemethanol (25.2 mg, 0.048 mmol) were added to a dry Schlenk tube equipped with magnetic stirring bar, followed by addition of toluene (2 mL) and stirred under nitrogen atmosphere for 17 h at 120°C.^[1] Then (*2E*)-1,3-Diphenyl-2-propen-1-one (0.24 mmol, 1.2 equiv.) and diphenylphosphine oxide (0.2 mmol, 1 equiv) were added to the tube and stirred under nitrogen atmosphere for 3 h at room temperature (18-25°C). After that solvent was evaporated on rotary evaporator and the crude was purified by flash chromatography on silica gel.

General procedure for the preparation of racemic products: A sealed tube with a magnetic stir bar was charged with α,β -unsaturated ketones (0.24 mmol), diarylphosphine oxides (0.2 mmol) in Toluene (2 mL) and stirred at room temperature for 12 h. After that, the solvent was evaporated under reduced pressure and further purified by column chromatography on silica gel to afford racemic **3** (Yields: 85-99%).



(S)-3-(Diphenylphosphinyl)-1,3-diphenylpropan-1-one (3a)^[2]

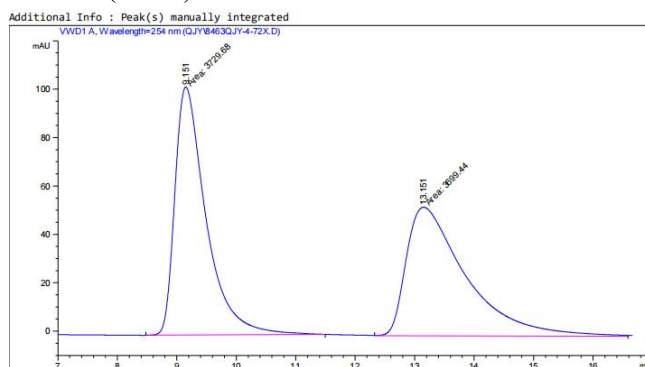
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 92% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 2H), 7.87 – 7.80 (m, 2H), 7.54 – 7.40 (m, 6H), 7.40 – 7.30 (m, 5H), 7.26 – 7.20 (m, 2H), 7.17 – 7.08 (m, 3H), 4.46 (ddd, *J* = 10.5, 6.8, 2.4 Hz, 1H), 4.03 (ddd, *J* = 18.2, 10.4, 4.3 Hz, 1H), 3.37 (ddd, *J* = 18.2, 11.2, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.68, 136.32, 135.88, 133.42, 132.09, 131.80, 131.46, 131.31, 131.05, 130.89, 129.85, 128.99, 128.59, 128.33, 128.15, 128.05, 127.09, 41.01, 38.99.

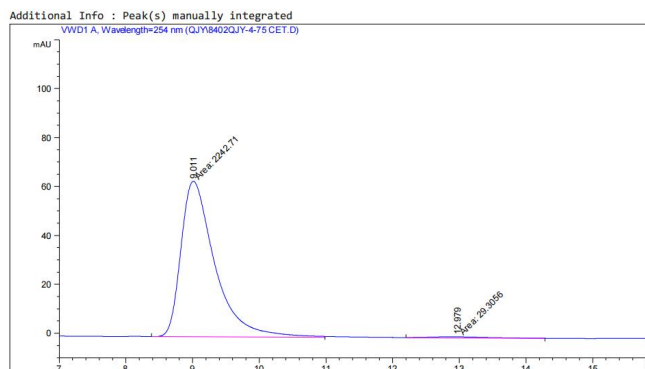
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.25.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₄O₂P [M+H]⁺: 411.1436, found: 411.1437.

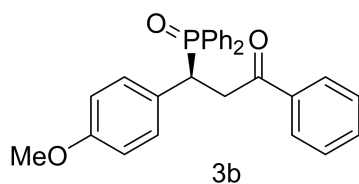
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.01 (major) and 12.98 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.151	MM	0.6065	3729.68457	102.48717	50.2036
2	13.151	MM	1.1594	3699.43774	53.17957	49.7964



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.011	MF	0.5881	2242.70898	63.55553	98.7102
2	12.979	MM	1.1005	29.30556	4.43817e-1	1.2898



(S)-3-(diphenylphosphoryl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (3b)^[2]

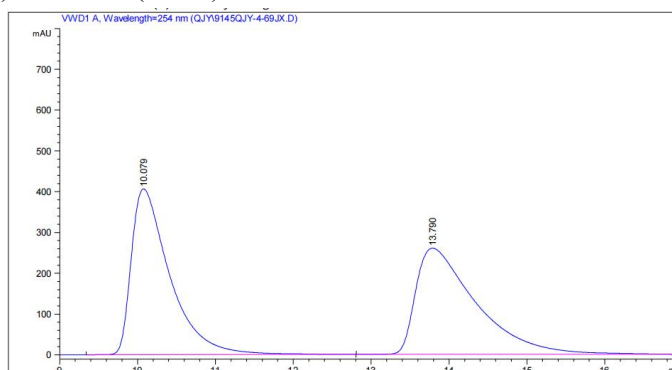
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 81% yield, 97% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.94 (m, 2H), 7.89 – 7.81 (m, 2H), 7.56 – 7.46 (m, 7H), 7.43 – 7.24 (m, 6H), 6.71 (d, *J* = 8.7 Hz, 2H), 4.46 (ddd, *J* = 10.6, 6.9, 2.4 Hz, 1H), 4.00 (ddd, *J* = 18.0, 10.5, 4.2 Hz, 1H), 3.70 (s, 3H), 3.36 (ddd, *J* = 18.0, 10.8, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.76, 158.48, 136.29, 133.34, 132.00, 131.42, 131.20, 130.92, 130.80, 128.92, 128.51, 128.15, 128.06, 127.58, 113.72, 55.03, 40.03, 38.98.

³¹P NMR (162 MHz, Chloroform-*d*) δ 34.20.

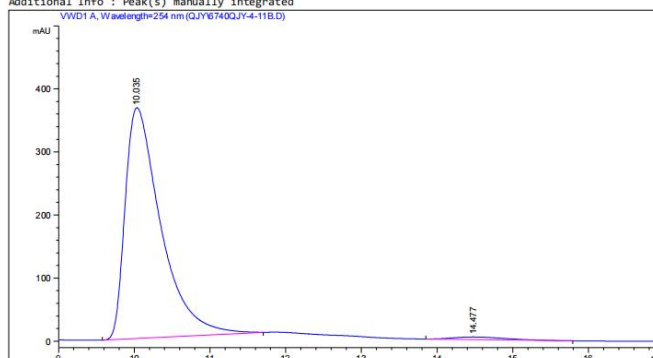
HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₆O₃P [M+H]⁺ : 441.1614, found 441.1620.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 10.03 (major) and 14.47 (minor).

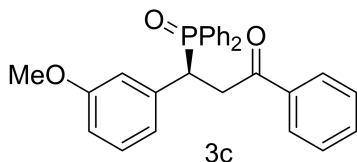


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.079	BB	0.5099	1.39972e4	406.34793	49.8162
2	13.790	BB	0.7938	1.41005e4	260.35846	50.1838

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.035	BB	0.4891	1.19824e4	365.84406	98.3428
2	14.477	BB	0.7296	201.92178	4.17207	1.6572



(S)-3-(diphenylphosphoryl)-3-(3-methoxyphenyl)-1-phenylpropan-1-one(3c)

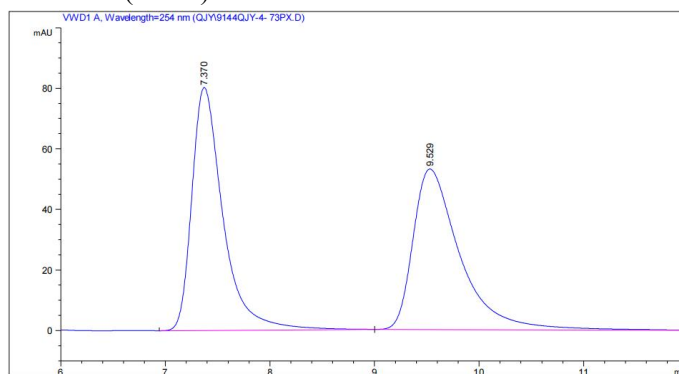
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 86% yield, 97% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.61 – 7.53 (m, 2H), 7.46 – 7.44 (m, 3H), 7.42 – 7.32 (m, 2H), 7.32 – 7.29 (m, 2H), 7.26 – 7.20 (m, 2H), 7.20 – 7.13 (m, 3H), 7.11 – 6.97 (m, 3H), 4.40 (m, 1H), 3.96 (ddd, *J* = 18.2, 10.5, 4.1 Hz, 1H), 3.28 (ddd, *J* = 18.1, 11.2, 2.3 Hz, 1H), 2.25(s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.69 (d, *J* = 13.4 Hz), 137.34, 135.26, 134.84 (d, *J* = 5.6 Hz), 133.08, 131.01 (d, *J* = 2.9 Hz), 130.38 (d, *J* = 2.8 Hz), 130.22 (d, *J* = 8.4 Hz), 129.88 (d, *J* = 8.9 Hz), 128.79 (d, *J* = 5.7 Hz), 127.96 (d, *J* = 4.0 Hz), 127.84 (d, *J* = 5.7 Hz), 127.69, 127.40, 127.25 (d, *J* = 1.9 Hz), 127.03 (d, *J* = 11.8 Hz), 126.00 (d, *J* = 2.5 Hz), 124.20, 39.89 (d, *J* = 69.3 Hz), 37.97, 20.18.

³¹P NMR (162 MHz, Chloroform-*d*) δ 34.51.

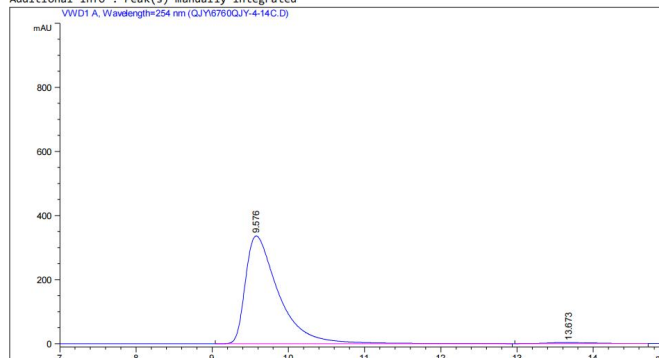
HRMS (ESI+, *m/z*): calcd for C₂₈H₂₆O₃P [M+H]⁺: 441.1614 , found 441.1613 .

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.57 (major) and 13.67 (minor).

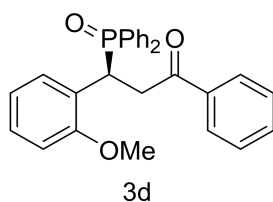


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.370	BB	0.3120	1663.73633	80.22320	50.0947
2	9.529	BB	0.4657	1657.44702	53.02517	49.9053

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.576	BB	0.4486	1.01539e4	336.00714	98.6069
2	13.673	BB	0.6366	143.45723	3.33655	1.3931



(S)-3-(diphenylphosphoryl)-3-(2-methoxyphenyl)-1-phenylpropan-1-one(3d)^[2]

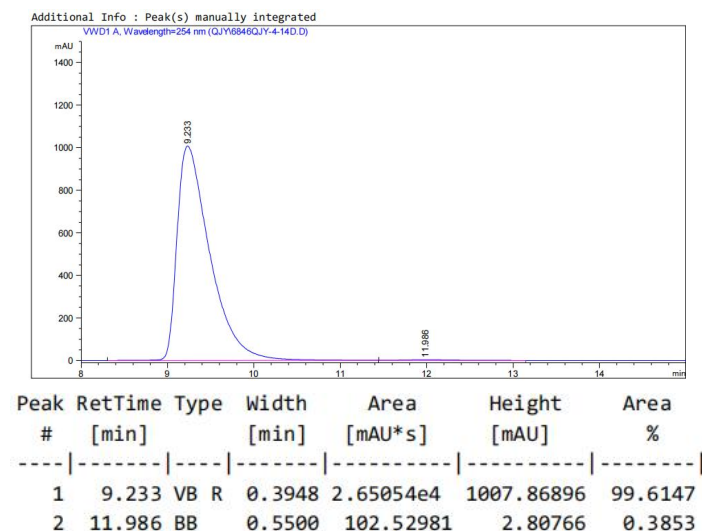
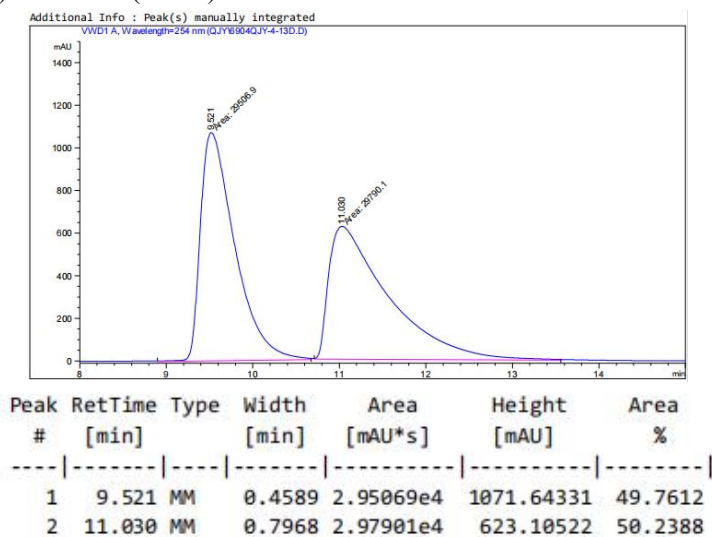
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 95% yield, 99% ee] **¹H NMR** (400 MHz, Chloroform-*d*) δ 8.08 – 7.99 (m, 2H), 7.88 – 7.82 (m, 2H), 7.63 (dt, *J* = 7.7, 2.1 Hz, 1H), 7.55 – 7.49 (m, 3H), 7.49 – 7.33 (m, 5H), 7.33 – 7.26 (m, 1H), 7.18 (td, *J* = 7.7, 3.1 Hz, 2H), 7.11 – 7.04 (m, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 6.54 (d, *J* = 8.2 Hz, 1H), 5.14 (ddd, *J* = 10.5, 7.2, 2.9 Hz, 1H), 4.06 (ddd, *J* = 18.1, 10.7, 5.4 Hz, 1H), 3.46 (s, 3H), 3.39 (ddd, *J* = 18.0, 10.1, 2.9 Hz, 1H).

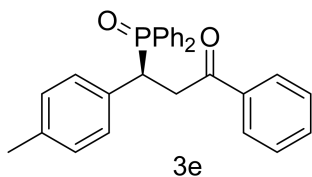
¹³C NMR (101 MHz, Chloroform-*d*) δ 196.80 (d, *J* = 13.6 Hz), 156.71 (d, *J* = 5.6 Hz), 136.44, 133.23, 132.02 (d, *J* = 2.7 Hz), 131.46 (d, *J* = 8.5 Hz), 131.17 (d, *J* = 2.8 Hz), 131.02, 130.94 (d, *J* = 3.1 Hz), 128.96 (d, *J* = 3.6 Hz), 128.83, 128.52, 128.16 (d, *J* = 3.6 Hz), 127.51 (d, *J* = 11.8 Hz), 124.18 (d, *J* = 5.9 Hz), 120.70 (d, *J* = 2.8 Hz), 110.24 (d, *J* = 2.3 Hz), 55.27, 38.10, 32.34 (d, *J* = 69.1 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 34.12.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₆O₃P [M+H]⁺ : 441.1614, found 441.1616.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.23 (major) and 11.98 (minor).





(S)-3-(diphenylphosphoryl)-1-phenyl-3-(p-tolyl)propan-1-one (3e)

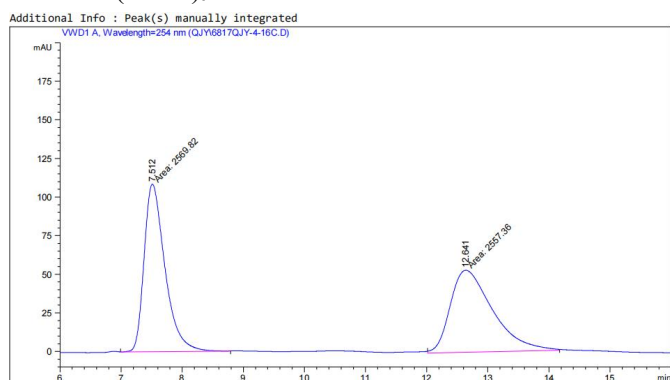
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 87% yield, 97% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 2H), 7.86 – 7.81 (m, 2H), 7.49 (m, 6H), 7.39 – 7.32 (m, 3H), 7.29 – 7.24 (m, 4H), 6.95 (d, *J* = 7.8 Hz, 2H), 4.46 (ddd, *J* = 9.8, 6.9, 2.4 Hz, 1H), 4.00 (ddd, *J* = 18.1, 10.4, 4.4 Hz, 1H), 3.36 (ddd, *J* = 18.1, 11.1, 2.4 Hz, 1H), 2.19 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.74 (d, *J* = 13.5 Hz), 136.66 (d, *J* = 2.5 Hz), 136.36, 133.37, 132.63 (d, *J* = 6.2 Hz), 132.08 (d, *J* = 8.5 Hz), 131.98 (d, *J* = 6.5 Hz), 131.45 (d, *J* = 2.7 Hz), 131.27 (d, *J* = 8.5 Hz), 131.07, 130.98, 130.75 (d, *J* = 11.6 Hz), 129.67 (d, *J* = 5.6 Hz), 129.07 (d, *J* = 2.0 Hz), 129.01, 128.90, 128.56, 128.16 (d, *J* = 3.6 Hz), 128.06, 40.50 (d, *J* = 69.5 Hz), 39.01, 21.06.

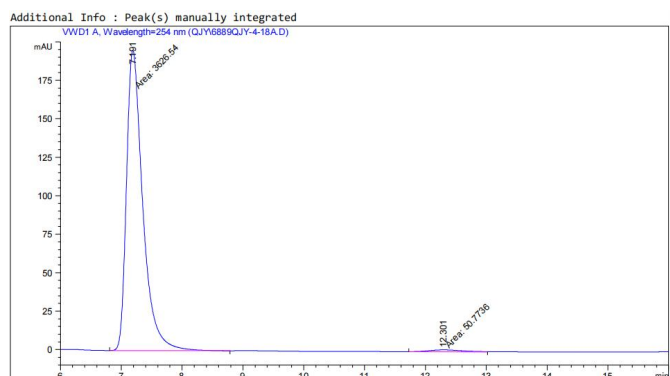
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.57.

HRMS (ESI+, *m/z*): calcd for C₂₈H₂₆O₂P [M+H]⁺: 425.1615, found: 425.1616.

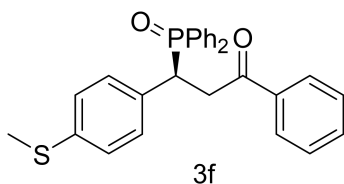
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.19 (major) and 12.30 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.512	MM	0.3949	2569.81934	108.45287	50.1215
2	12.641	MM	0.8032	2557.35864	53.06885	49.8785



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.191	MM	0.3097	3626.53564	195.16879	98.6193
2	12.301	MM	0.6518	50.77361	1.29835	1.3807



(S)-3-(diphenylphosphoryl)-3-(4-(methylthio)phenyl)-1-phenylpropan-1-one(3f)

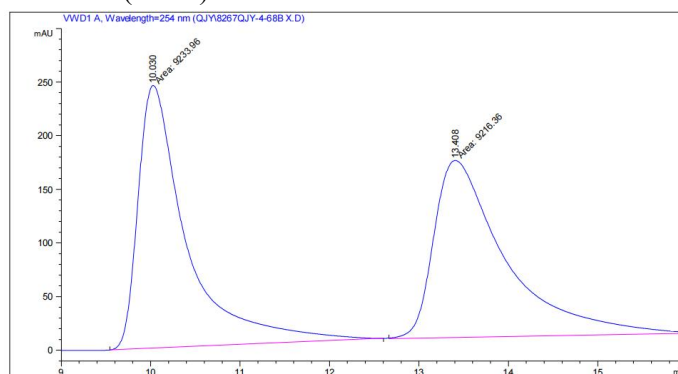
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 94% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.93 (m, 2H), 7.87 – 7.82 (m, 2H), 7.55 – 7.45 (m, 6H), 7.41 – 7.34 (m, 3H), 7.33 – 7.24 (m, 4H), 7.03 (d, *J* = 8.3 Hz, 2H), 4.44 (ddd, *J* = 10.5, 6.8, 2.4 Hz, 1H), 3.99 (ddd, *J* = 18.2, 10.6, 4.2 Hz, 1H), 3.34 (ddd, *J* = 18.2, 10.8, 2.3 Hz, 1H), 2.37 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.62 (d, *J* = 13.5 Hz), 137.11 (d, *J* = 2.8 Hz), 136.27, 133.48, 132.63 (d, *J* = 5.8 Hz), 132.09 (d, *J* = 2.8 Hz), 131.82, 131.56 (d, *J* = 2.9 Hz), 131.28, 131.20, 131.00, 130.91, 130.88, 130.26, 130.20, 129.06, 128.95, 128.61, 128.29, 128.17, 128.13, 126.32 (d, *J* = 1.9 Hz), 40.46 (d, *J* = 69.3 Hz), 38.97, 15.63.

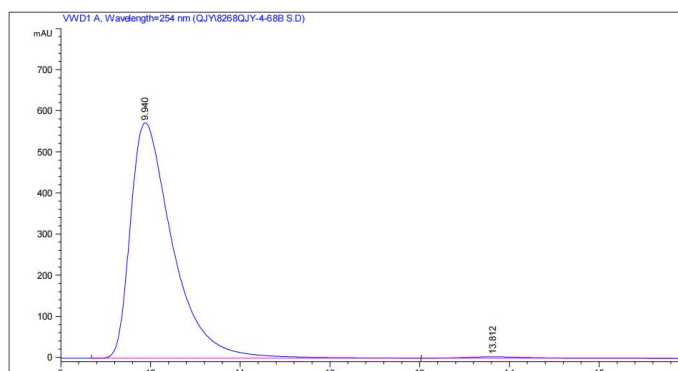
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.35.

HRMS (ESI+, *m/z*): calcd for C₂₈H₂₆O₂PS [M+H]⁺ : 457.1386, found: 457.1390.

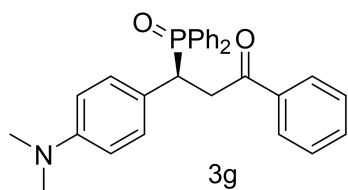
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.94 (major) and 13.81 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.030	MM	0.6288	9233.95801	244.73254	50.0477
2	13.408	MM	0.9304	9216.36230	165.09607	49.9523



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.940	BB	0.4911	1.87064e4	572.71179	99.0229
2	13.812	BB	0.7697	184.58835	3.40890	0.9771



(S)-3-(4-(dimethylamino)phenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3g)

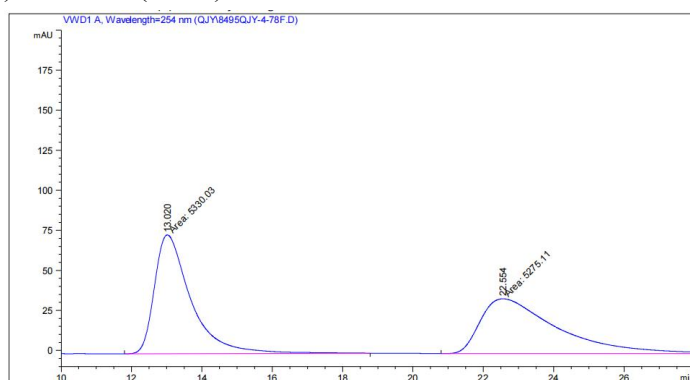
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 94% yield, 92% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.90 (m, 2H), 7.89 – 7.79 (m, 2H), 7.55 – 7.43 (m, 6H), 7.40 – 7.32 (m, 3H), 7.30 – 7.21 (m, 4H), 6.53 (d, *J* = 8.8 Hz, 2H), 4.40 (ddd, *J* = 9.9, 7.0, 2.4 Hz, 1H), 3.97 (ddd, *J* = 18.0, 10.4, 4.2 Hz, 1H), 3.33 (ddd, *J* = 18.0, 11.0, 2.4 Hz, 1H), 2.83 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.98 (d, *J* = 13.6 Hz), 149.51, 136.52, 133.25, 132.45 (d, *J* = 17.9 Hz), 131.85 (d, *J* = 2.8 Hz), 131.49 (d, *J* = 10.4 Hz), 131.36, 131.29 (d, *J* = 3.8 Hz), 131.17, 131.09, 130.74 (d, *J* = 11.4 Hz), 130.47 (d, *J* = 5.6 Hz), 128.90 (d, *J* = 3.1 Hz), 128.80, 128.51, 128.14 (d, *J* = 1.7 Hz), 128.01, 112.54, 40.52, 39.90 (d, *J* = 70.5 Hz), 39.12 (d, *J* = 1.7 Hz).

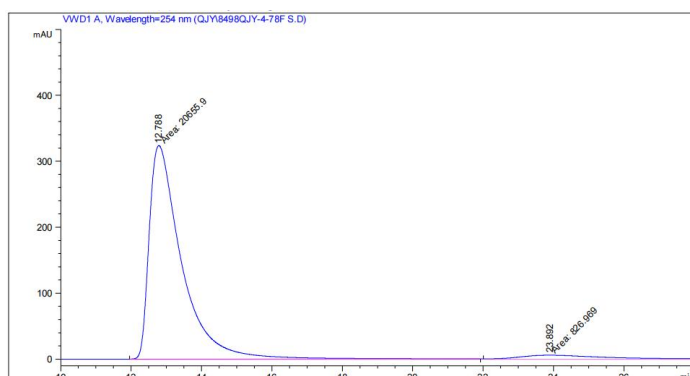
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.65.

HRMS (ESI+, *m/z*): calcd for C₂₉H₂₈O₂NP [M+H]⁺ : 454.1930, found: 454.1927.

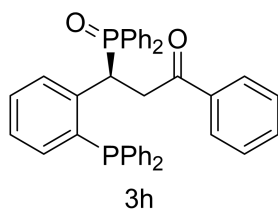
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 12.78 (major) and 23.89 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.020	MM	1.1984	5330.03271	74.12776	50.2589
2	22.554	MM	2.5697	5275.11182	34.21387	49.7411



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.788	MM	1.0634	2.06559e4	323.73654	96.1506
2	23.892	MM	2.4852	826.96881	5.54600	3.8494



(S)-3-(2-(diphenylphosphanyl)phenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one(3h)

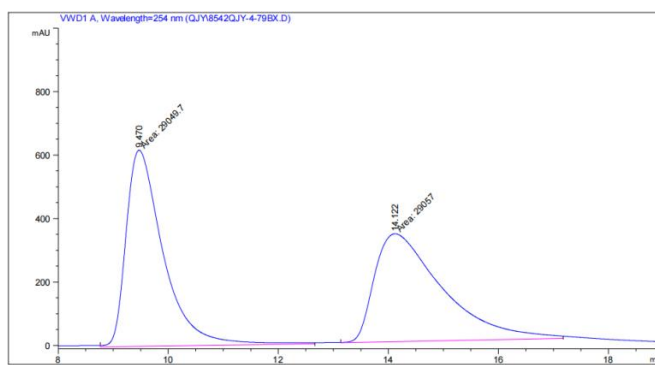
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid , 88% yield, 94% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.11 (m, 3H), 7.62 – 7.55 (m, 2H), 7.53 (m, 3H), 7.48 – 7.36 (m, 4H), 7.32 – 7.11 (m, 11H), 7.10 – 7.01 (m, 3H), 6.92 (dd, *J* = 7.8, 3.6 Hz, 1H), 6.74 – 6.67 (m, 2H), 6.09 – 5.97 (m, 1H), 3.84 (dddd, *J* = 17.3, 8.5, 6.6, 1.6 Hz, 1H), 3.51 (ddd, *J* = 17.4, 12.5, 3.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.00 (d, *J* = 11.9 Hz), 143.01 (d, *J* = 4.8 Hz), 142.73 (d, *J* = 4.9 Hz), 137.41 (d, *J* = 10.1 Hz), 136.84 (dd, *J* = 10.4, 7.2 Hz), 136.33, 135.78, 133.61, 133.42, 133.19, 133.00, 132.33, 132.06 (d, *J* = 2.8 Hz), 131.70, 131.62, 131.36 (d, *J* = 2.0 Hz), 131.32, 131.27 (d, *J* = 2.4 Hz), 130.76, 129.84, 129.59, 128.94, 128.83, 128.33, 128.26, 128.19 (d, *J* = 1.4 Hz), 128.11, 128.08, 127.96, 127.37 (d, *J* = 2.4 Hz), 40.16, 37.90 (dd, *J* = 67.4, 29.4 Hz).

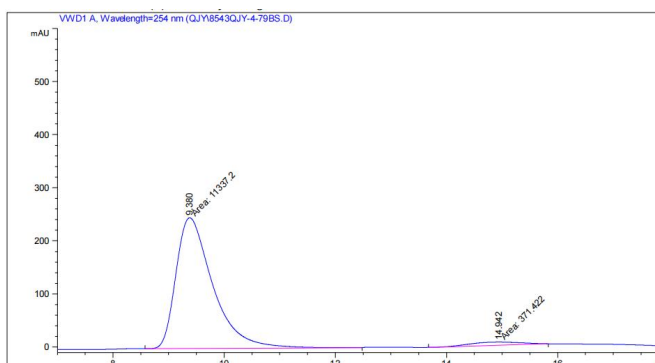
³¹P NMR (162 MHz, Chloroform-*d*) δ 35.28 (d, *J* = 3.7 Hz), -19.65.

HRMS (ESI+, *m/z*): calcd for C₃₉H₃₃O₂P₂ [M+H]⁺ : 595.1950, found: 595.1948.

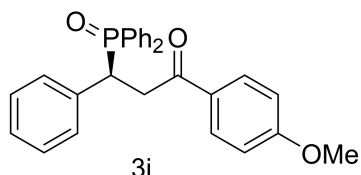
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.38 (major) and 14.94 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.470	MM	0.7834	2.90497e4	618.01691	49.9937
2	14.122	MM	1.4249	2.90570e4	339.87073	50.0063



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.380	MM	0.7682	1.13372e4	245.97728	96.8278
2	14.942	MM	1.0606	371.42184	5.83682	3.1722



(S)-3-(diphenylphosphoryl)-1-(4-methoxyphenyl)-3-phenylpropan-1-one(3i)

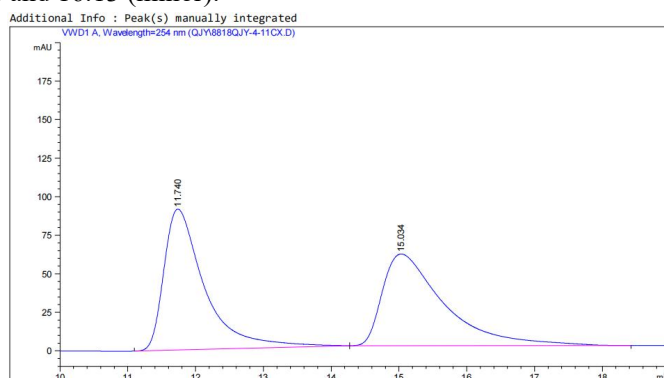
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 86% yield, 83% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 2H), 7.86 – 7.79 (m, 2H), 7.56 – 7.40 (m, 5H), 7.41 – 7.28 (m, 3H), 7.28 – 7.19 (m, 2H), 7.18 – 7.06 (m, 3H), 6.86 – 6.80 (m, 2H), 4.47 (ddd, *J* = 9.7, 6.7, 2.4 Hz, 1H), 3.98 (ddd, *J* = 17.9, 10.5, 4.1 Hz, 1H), 3.80 (s, 3H), 3.31 (ddd, *J* = 17.9, 11.2, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.06 (d, *J* = 13.3 Hz), 163.62, 135.87 (d, *J* = 5.8 Hz), 132.61 (d, *J* = 3.1 Hz), 132.02 (d, *J* = 2.8 Hz), 131.40 (d, *J* = 2.5 Hz), 131.30, 131.21, 130.94, 130.85, 130.69 (d, *J* = 11.5 Hz), 130.43, 129.81 (d, *J* = 5.7 Hz), 129.40, 128.99, 128.88, 128.25 (d, *J* = 1.9 Hz), 128.11, 127.99, 126.99 (d, *J* = 2.5 Hz), 113.63, 55.44, 41.01 (d, *J* = 69.1 Hz), 38.42.

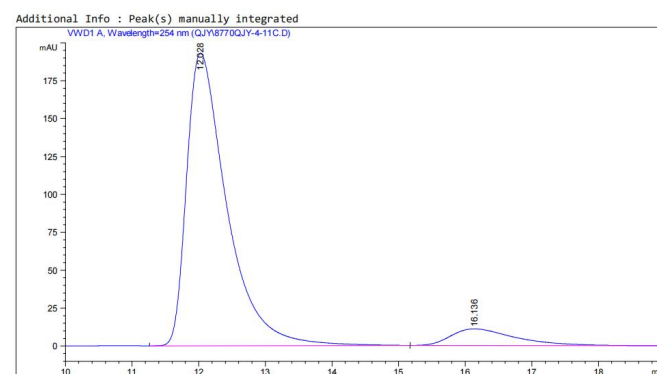
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.65.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₆O₃P [M+H]⁺: 441.1614, found: 441.1616.

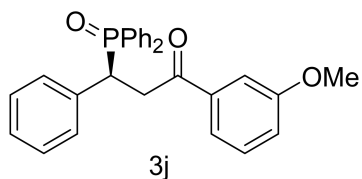
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 210nm. Retention time (min): 12.02 (major) and 16.13 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.740	BB	0.6168	3814.57788	91.42477	50.5179
2	15.034	BB	0.9258	3736.36792	59.48424	49.4821



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.028	BB	0.6252	8074.15332	192.96614	91.6315
2	16.136	BB	0.9827	737.39008	10.93597	8.3685



(S)-3-(diphenylphosphoryl)-1-(3-methoxyphenyl)-3-phenylpropan-1-one(3j)

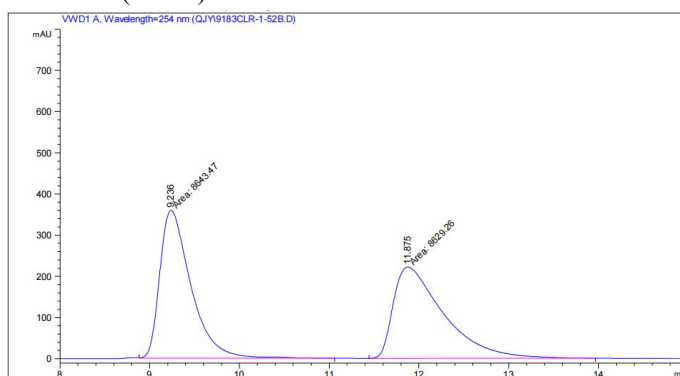
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 81% yield, 99% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.95 (m, 2H), 7.54 – 7.42 (m, 6H), 7.41 – 7.30 (m, 4H), 7.31 – 7.19 (m, 3H), 7.18 – 7.01 (m, 4H), 4.47 (ddd, $J = 9.9, 6.9, 2.4$ Hz, 1H), 4.02 (ddd, $J = 18.1, 10.4, 4.2$ Hz, 1H), 3.77 (s, 3H), 3.38 (ddd, $J = 18.2, 11.2, 2.4$ Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.12 (d, $J = 13.3$ Hz), 163.68, 135.93 (d, $J = 5.8$ Hz), 132.67 (d, $J = 3.1$ Hz), 132.08 (d, $J = 2.8$ Hz), 131.46 (d, $J = 2.5$ Hz), 131.32 (d, $J = 8.5$ Hz), 131.00, 130.91, 130.76 (d, $J = 11.5$ Hz), 130.49, 129.87 (d, $J = 5.7$ Hz), 129.47, 129.05, 128.94, 128.32 (d, $J = 1.9$ Hz), 128.17, 128.05, 127.05 (d, $J = 2.5$ Hz), 113.69, 55.51, 41.07 (d, $J = 69.1$ Hz), 38.48.

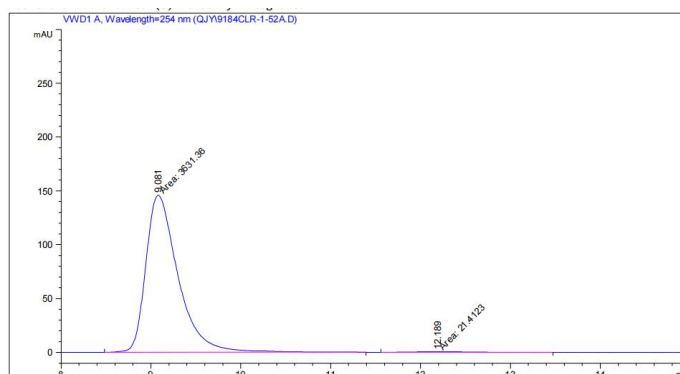
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.34.

HRMS (ESI⁺, m/z): calcd for C₂₈H₂₆O₃P [M+H]⁺: 441.1614, found: 441.1609.

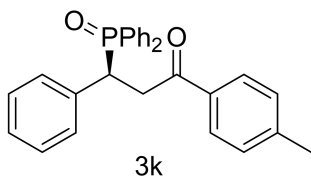
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.08 (major) and 12.18 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.236	MM	0.4013	8643.47168	358.98538	50.0411
2	11.875	MM	0.6497	8629.26465	221.37262	49.9589



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.081	MM	0.4150	3631.36133	145.84474	99.4138
2	12.189	MM	0.6468	21.41230	5.51766e-1	0.5862



(S)-3-(diphenylphosphoryl)-3-phenyl-1-(p-tolyl)propan-1-one (3k)

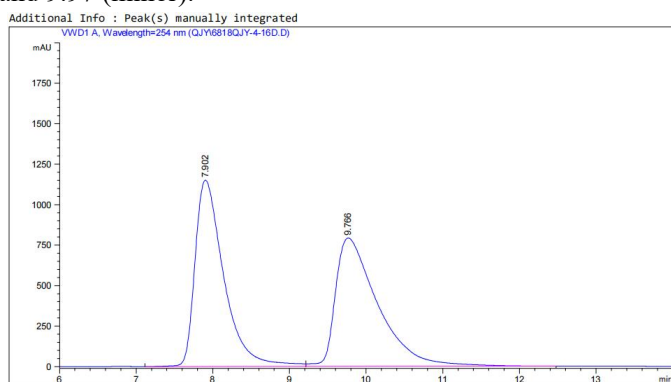
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 85% yield, 97% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.94 (m, 2H), 7.76 – 7.73 (m, 2H), 7.52 (m, 3H), 7.49 – 7.43 (m, 2H), 7.40 – 7.31 (m, 3H), 7.24 (m, 2H), 7.18 – 7.06 (m, 5H), 4.48 (ddd, *J* = 10.4, 6.8, 2.4 Hz, 1H), 4.01 (ddd, *J* = 18.1, 10.4, 4.2 Hz, 1H), 3.35 (ddd, *J* = 18.1, 11.2, 2.4 Hz, 1H), 2.34 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.26 (d, *J* = 13.3 Hz), 144.31, 135.88 (d, *J* = 5.6 Hz), 133.88, 132.08 (d, *J* = 2.8 Hz), 131.46 (d, *J* = 2.8 Hz), 131.30 (d, *J* = 8.5 Hz), 131.00, 130.91, 129.86 (d, *J* = 5.6 Hz), 129.25, 129.05, 128.93, 128.31 (d, *J* = 2.1 Hz), 128.27, 128.16, 128.05, 127.06 (d, *J* = 2.5 Hz), 41.01 (d, *J* = 69.1 Hz), 38.77, 21.65.

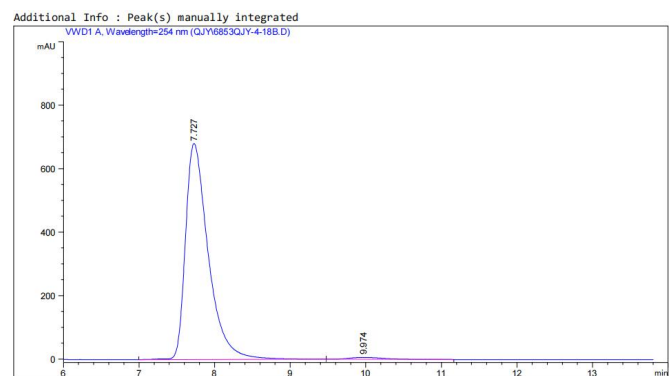
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.55.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₆O₂P [M+H]⁺ :425.1665, found: 425.1663.

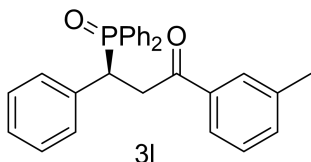
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.72 (major) and 9.97 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.902	BV	0.3935	3.00365e4	1150.74353	49.7198
2	9.766	VB	0.5672	3.03750e4	792.42438	50.2802



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.727	BB	0.3164	1.42403e4	679.74005	98.6284
2	9.974	BB	0.4808	198.04279	6.31665	1.3716



(S)-3-(diphenylphosphoryl)-3-phenyl-1-(m-tolyl)propan-1-one (3l)

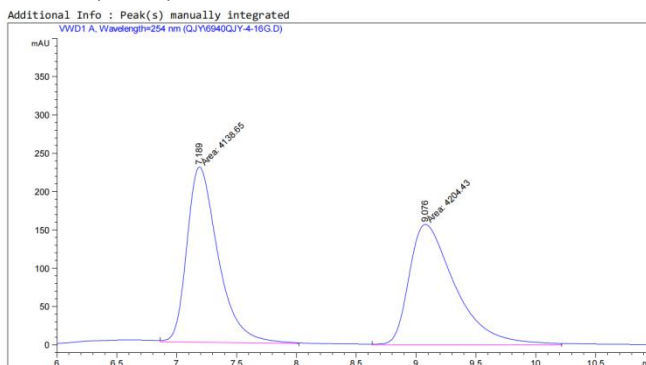
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 89% yield, 94% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.93 (m, 2H), 7.86 – 7.83 (m, 2H), 7.54 – 7.46 (m, 6H), 7.41 – 7.30 (m, 3H), 7.30 – 7.21 (m, 2H), 7.06 (t, *J* = 7.9 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.91 (d, *J* = 2.2 Hz, 1H), 6.65 (d, *J* = 8.2 Hz, 1H), 4.47 (ddd, *J* = 9.8, 7.0, 2.4 Hz, 1H), 4.03 (ddd, *J* = 18.2, 10.4, 4.3 Hz, 1H), 3.65 (s, 3H), 3.38 (ddd, *J* = 18.1, 11.3, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.56 (d, *J* = 13.2 Hz), 159.24 (d, *J* = 2.0 Hz), 137.30 (d, *J* = 5.5 Hz), 136.28, 133.35, 132.03 (d, *J* = 3.1 Hz), 131.44 (d, *J* = 2.8 Hz), 131.25 (d, *J* = 8.5 Hz), 131.01, 130.92, 130.77 (d, *J* = 8.6 Hz), 129.19 (d, *J* = 2.0 Hz), 128.98, 128.87, 128.52, 128.12, 128.08, 128.01, 122.17 (d, *J* = 5.7 Hz), 114.98 (d, *J* = 5.6 Hz), 113.15 (d, *J* = 2.5 Hz), 55.08, 41.06 (d, *J* = 69.0 Hz), 38.80.

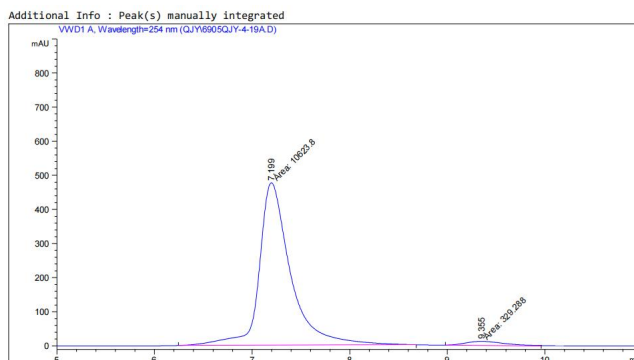
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.18.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₆O₂P [M+H]⁺: 425.1665, found: 425.1664.

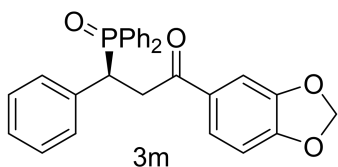
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.20 (major) and 9.35 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.189	MM	0.3016	4138.65234	228.68080	49.6058
2	9.076	MM	0.4462	4204.42725	157.04059	50.3942



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.199	MM	0.3720	1.06238e4	476.03223	96.9936
2	9.355	MM	0.4623	329.28754	11.87162	3.0064



(S)-1-(benzo[d][1,3]dioxol-5-yl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (3m)

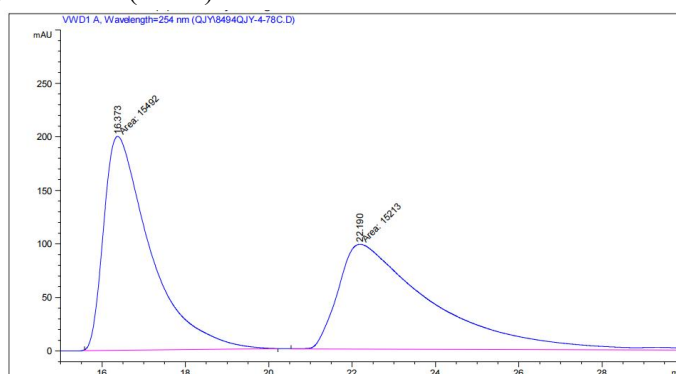
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid. 94% yield, 85% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.91 (m, 2H), 7.56 – 7.40 (m, 6H), 7.38 – 7.21 (m, 6H), 7.18 – 7.08 (m, 3H), 6.77 (d, *J* = 8.2 Hz, 1H), 6.01 – 5.95 (m, 2H), 4.46 (ddd, *J* = 10.5, 6.7, 2.5 Hz, 1H), 3.97 (ddd, *J* = 17.9, 10.5, 4.5 Hz, 1H), 3.27 (ddd, *J* = 17.9, 11.1, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 194.69 (d, *J* = 13.5 Hz), 151.95, 148.07, 135.82 (d, *J* = 5.7 Hz), 132.03 (d, *J* = 2.4 Hz), 131.41 (d, *J* = 2.7 Hz), 131.31, 131.23, 130.95, 130.87, 129.78 (d, *J* = 5.6 Hz), 128.94 (d, *J* = 11.2 Hz), 128.28 (d, *J* = 2.0 Hz), 128.06 (d, *J* = 11.8 Hz), 127.03 (d, *J* = 2.6 Hz), 124.58, 107.80, 101.84, 41.14 (d, *J* = 69.1 Hz), 38.56.

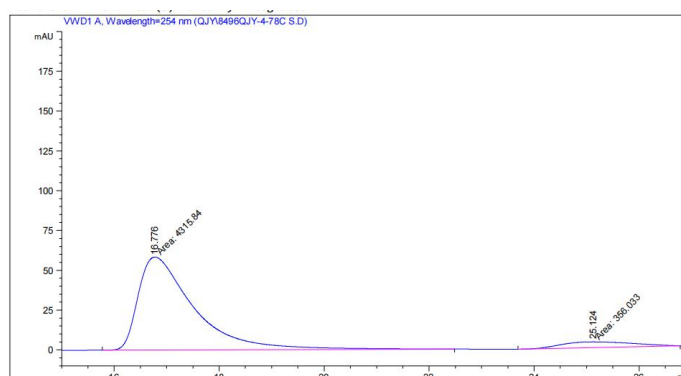
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.48.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₄O₄P [M+H]⁺: 455.1407, found: 455.1408.

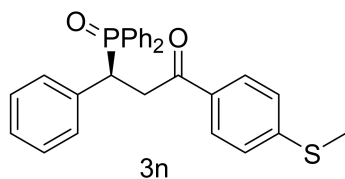
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 16.77(major) and 25.12 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.373	MM	1.2928	1.54920e4	199.72209	50.4543
2	22.190	MM	2.5916	1.52130e4	97.83443	49.5457



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.776	MM	1.2312	4315.83691	58.42198	92.3792
2	25.124	MM	1.1527	356.03320	3.68489	7.6208



(S)-3-(diphenylphosphoryl)-1-(4-(methylthio)phenyl)-3-phenylpropan-1-one (3n)

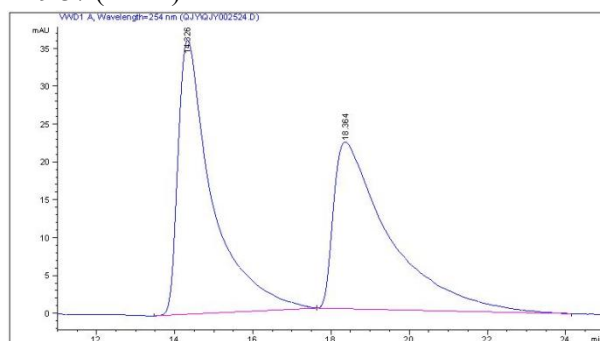
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 98% yield, 99% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.93 (m, 2H), 7.83 – 7.67 (m, 2H), 7.54 – 7.40 (m, 5H), 7.38 – 7.28 (m, 3H), 7.26 – 7.20 (m, 2H), 7.17 – 7.06 (m, 5H), 4.55 – 4.34 (m, 1H), 3.98 (ddd, *J* = 17.9, 10.4, 4.3 Hz, 1H), 3.32 (ddd, *J* = 18.0, 11.1, 2.4 Hz, 1H), 2.44 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.64 (d, *J* = 13.4 Hz), 146.44, 135.89 (d, *J* = 5.6 Hz), 132.58, 132.10, 132.09, 131.46 (d, *J* = 2.8 Hz), 131.34, 131.25, 130.99, 130.91, 129.83 (d, *J* = 5.7 Hz), 129.05, 128.94, 128.52, 128.33 (d, *J* = 2.0 Hz), 128.17, 128.05, 127.09 (d, *J* = 2.2 Hz), 124.77, 41.07 (d, *J* = 69.1 Hz), 38.64, 14.66.

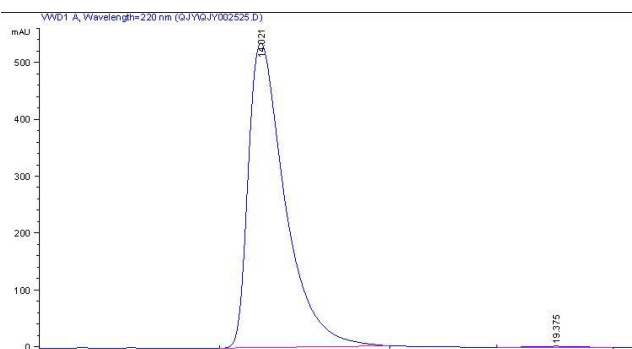
³¹P NMR (162 MHz, Chloroform-*d*) δ 31.14.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₆O₂PS [M+H]⁺: 457.1386, found: 457.1385.

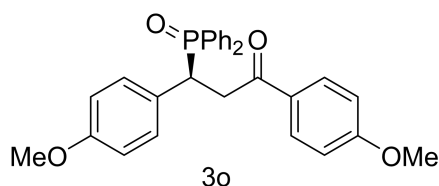
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 14.02 (major) and 19.37 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.326	BB	0.8546	2201.73291	36.19795	50.3514
2	18.364	BB	1.3114	2171.00439	21.99820	49.6486



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.021	BB	0.6855	2.46792e4	534.65369	99.4047
2	19.375	BB	0.7484	147.80658	2.35452	0.5953



(S)-3-(diphenylphosphoryl)-1,3-bis(4-methoxyphenyl)propan-1-one (3o)

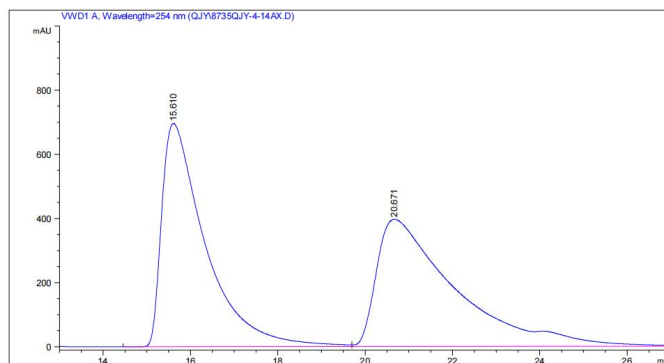
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 85% yield, 95% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 2H), 7.83 (d, *J* = 8.9 Hz, 2H), 7.53 – 7.43 (m, 6H), 7.34 – 7.24 (m, 4H), 6.83 (d, *J* = 8.9 Hz, 2H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.44 (ddd, *J* = 10.6, 6.8, 2.3 Hz, 1H), 3.94 (ddd, *J* = 17.8, 10.6, 4.2 Hz, 1H), 3.80 (s, 3H), 3.67 (s, 3H), 3.27 (ddd, *J* = 17.8, 10.9, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.21 (d, *J* = 13.6 Hz), 163.60, 158.44 (d, *J* = 2.3 Hz), 132.58 (d, *J* = 2.9 Hz), 132.27, 131.98, 131.93 (d, *J* = 2.9 Hz), 131.35 (d, *J* = 2.8 Hz), 131.25, 131.17, 130.96, 130.80 (dd, *J* = 10.1, 4.5 Hz), 130.62, 130.40, 129.48, 128.95 (d, *J* = 1.4 Hz), 128.83, 128.14, 128.02, 127.75 (d, *J* = 5.7 Hz), 113.62, 55.42, 55.04, 40.10 (d, *J* = 70.1 Hz), 38.52.

³¹P NMR (162 MHz, Chloroform-*d*) δ 34.94.

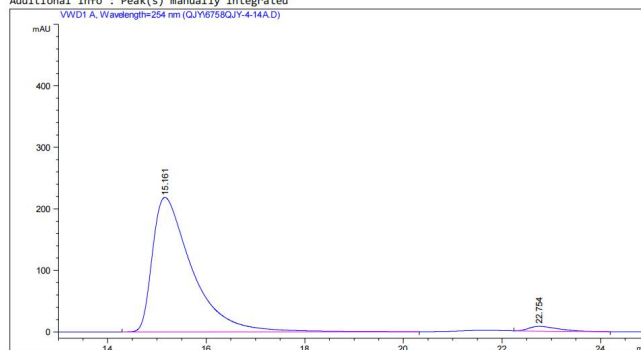
HRMS (ESI⁺, *m/z*): calcd for C₂₉H₂₈O₄P [M+H]⁺ : 471.1720, found: 471.1717.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 15.16 (major) and 22.754 (minor).

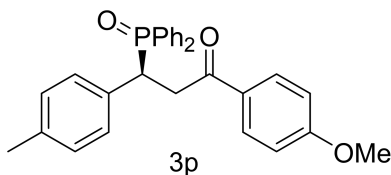


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.610	BV	1.0077	4.82205e4	695.66962	49.3610
2	20.671	VV R	1.7013	4.94689e4	396.32513	50.6390

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.161	BB	0.8292	1.21805e4	218.55498	97.5576
2	22.754	BBA	0.6126	304.94110	7.48022	2.4424



(S)-3-(diphenylphosphoryl)-1-(4-methoxyphenyl)-3-(p-tolyl)propan-1-one (3p)^[2]

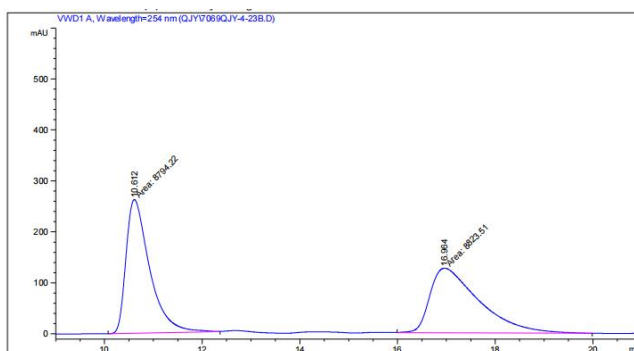
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid, 90% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.95 (m, 2H), 7.86 (d, *J* = 8.9 Hz, 1H), 7.57 – 7.48 (m, 6H), 7.42 – 7.33 (m, 1H), 7.32 – 7.24 (m, 4H), 6.98 (d, *J* = 7.9 Hz, 2H), 6.86 (d, *J* = 8.9 Hz, 2H), 4.54 – 4.44 (ddd, *J* = 10.6, 6.8, 2.3 Hz, 1H), 3.98 (ddd, *J* = 17.8, 10.5, 4.3 Hz, 1H), 3.83 (s, 3H), 3.32 (ddd, *J* = 17.9, 11.1, 2.4 Hz, 1H), 2.22 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.24 (d, *J* = 12.3 Hz), 163.63, 133.55, 133.01 (d, *J* = 5.4 Hz), 132.14 (d, *J* = 2.9 Hz), 131.86 (d, *J* = 6.9 Hz), 131.53 (d, *J* = 8.4 Hz), 131.23 (d, *J* = 2.8 Hz), 130.63 (d, *J* = 9.2 Hz), 130.47, 129.32, 129.03, 128.92, 128.58, 127.74, 127.62, 127.05 (d, *J* = 5.8 Hz), 125.99, 125.37 (d, *J* = 2.8 Hz), 125.26, 123.14, 113.63, 55.44, 39.74, 34.31 (d, *J* = 69.4 Hz).

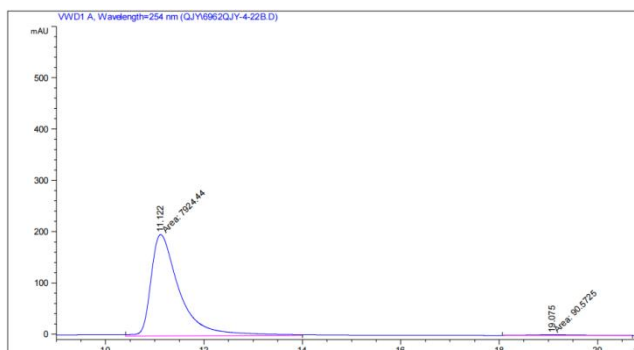
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.68.

HRMS (ESI+, *m/z*): calcd for C₂₉H₂₈O₃P [M+H]⁺ : 455.1776, found 455.1774.

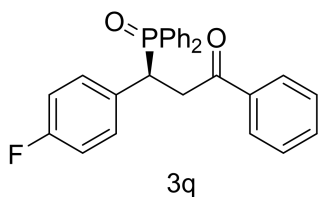
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 11.12 (major) and 19.077(minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.612	MM	0.5593	8794.21973	262.04874	49.9169
2	16.964	MM	1.1596	8823.51270	126.81302	50.0831



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.122	MM	0.6698	7924.43506	197.17471	98.8700
2	19.075	MM	1.2069	90.57246	1.25072	1.1300



(S)-3-(diphenylphosphoryl)-3-(4-fluorophenyl)-1-phenylpropan-1-one (3q)

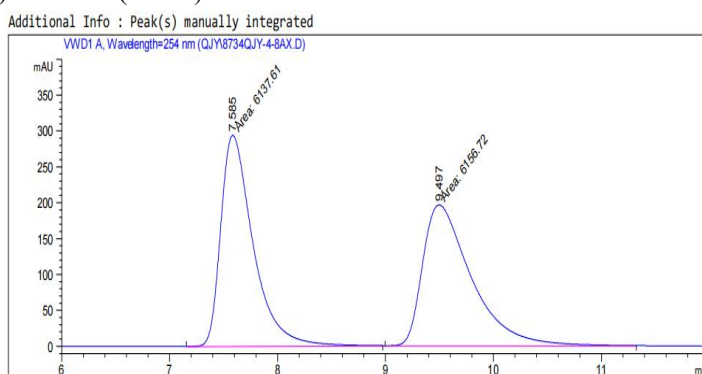
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 87% yield, 97% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (m, 2H), 7.90 – 7.84 (m, 2H), 7.56 – 7.41 (m, 5H), 7.41 – 7.30 (m, 3H), 7.24 (m, 2H), 7.20 – 7.06 (m, 3H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.45 (ddd, *J* = 9.9, 6.9, 2.5 Hz, 1H), 3.98 (ddd, *J* = 18.0, 10.3, 4.5 Hz, 1H), 3.36 (ddd, *J* = 18.0, 11.1, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.59 (d, *J* = 13.4 Hz), 161.88 (dd, *J* = 245.9, 2.7 Hz), 136.21, 133.54, 132.64 (d, *J* = 2.8 Hz), 132.20 (d, *J* = 2.8 Hz), 131.92, 131.62, 131.57 (d, *J* = 4.6 Hz), 131.42, 131.35 (d, *J* = 2.4 Hz), 131.27, 131.18, 130.91, 130.82, 130.64 (d, *J* = 7.9 Hz), 129.12, 129.01, 128.64, 128.30, 128.19, 128.12, 115.38 (d, *J* = 1.9 Hz), 115.17 (d, *J* = 1.9 Hz), 40.23 (d, *J* = 69.5 Hz), 39.04.

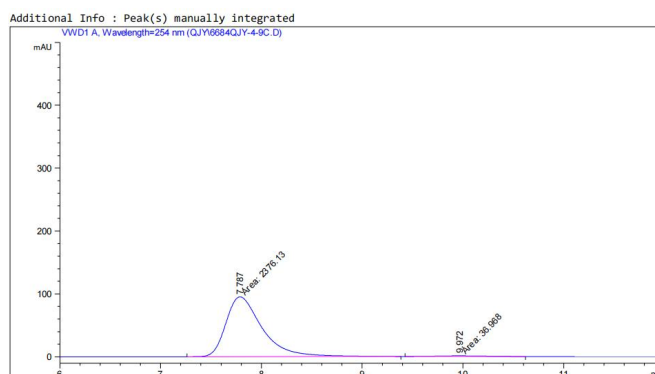
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.25.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₃FO₂P [M+H]⁺ :429.1414, found 429.1411.

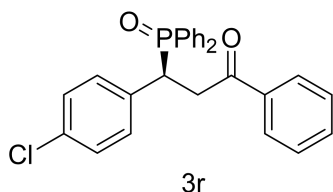
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.78 (major) and 9.97 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.585	MM	0.3478	6137.60742	294.15753	49.9223
2	9.497	MM	0.5230	6156.71777	196.18063	50.0777



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.787	MM	0.4163	2376.13086	95.13705	98.4680
2	9.972	MM	0.5994	36.96798	1.02799	1.5320



(S)-3-(4-chlorophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3r)

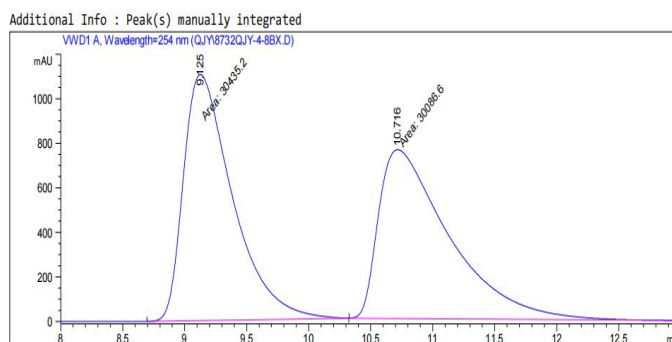
[Purification by flash column chromatography on silica gel (eluent, DCE: MeOH = 70:1). White solid, 93% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 (m, 2H), 7.87 – 7.81 (m, 2H), 7.57 – 7.48 (m, 6H), 7.38 (t, *J* = 7.7 Hz, 3H), 7.35 – 7.25 (m, 4H), 7.12 (d, *J* = 8.2 Hz, 2H), 4.46 (ddd, *J* = 9.7, 6.7, 2.4 Hz, 1H), 4.00 (ddd, *J* = 18.2, 10.6, 4.3 Hz, 1H), 3.34 (ddd, *J* = 18.2, 10.8, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.52 (d, *J* = 13.4 Hz), 136.09, 134.32 (d, *J* = 5.7 Hz), 133.60, 133.04 (d, *J* = 3.1 Hz), 132.74 (d, *J* = 2.9 Hz), 132.32 (d, *J* = 2.7 Hz), 131.79 (d, *J* = 2.9 Hz), 131.17, 131.09, 131.04, 130.86, 130.77, 130.65, 129.17, 129.05 (d, *J* = 1.5 Hz), 128.64, 128.49 (d, *J* = 1.9 Hz), 128.40, 128.28, 128.11, 49.54 (dt, *J* = 43.0, 21.5 Hz), 40.41 (d, *J* = 68.9 Hz), 38.72.

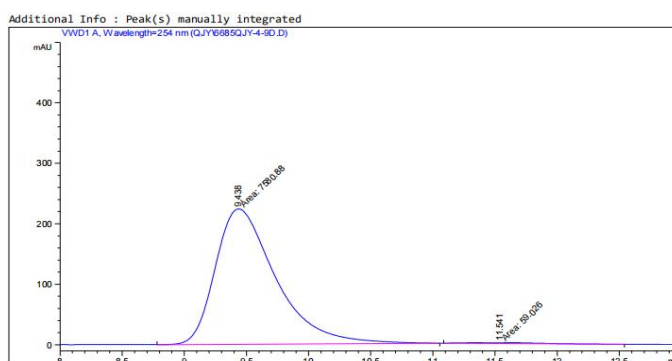
³¹P NMR (162 MHz, CDCl₃) δ 34.45.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₃O₂ClP [M+H]⁺ : 445.1119, found: 445.1114.

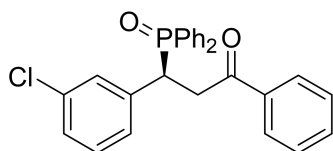
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.43 (major) and 11.54 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.125	MM	0.4595	3.04352e4	1103.92566	50.2880
2	10.716	MM	0.6613	3.00866e4	758.23993	49.7120



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.438	MM	0.5642	7580.88232	223.93806	99.2274
2	11.541	MM	0.5996	59.02604	1.64083	0.7726



3s

(S)-3-(3-chlorophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3s)

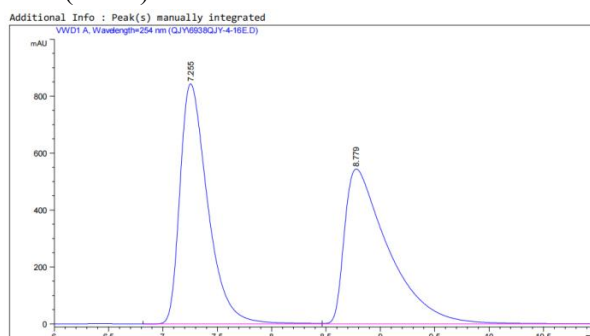
[Purification by flash column chromatography on silica gel (eluent, DCE: MeOH= 70:1). White solid, 90% yield, 96% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (m, 2H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.54 – 7.40 (m, 6H), 7.41 – 7.33 (m, 2H), 7.36 – 7.26 (m, 2H), 7.25 – 7.19 (m, 2H), 7.18 – 7.04 (m, 4H), 4.44 (ddd, *J* = 9.8, 6.9, 2.5 Hz, 1H), 3.98 (ddd, *J* = 18.2, 10.3, 4.6 Hz, 1H), 3.36 (ddd, *J* = 18.1, 11.0, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.59 (dd, *J* = 13.4, 2.0 Hz), 162.71 (d, *J* = 248.3 Hz), 138.37 (d, *J* = 6.1 Hz), 135.72 (d, *J* = 5.7 Hz), 132.15 (d, *J* = 2.7 Hz), 131.53 (d, *J* = 2.8 Hz), 131.34, 131.25, 131.01, 130.92, 130.29 (d, *J* = 7.6 Hz), 129.82, 129.77, 129.08, 128.97, 128.39 (d, *J* = 1.9 Hz), 128.19, 128.08, 127.20 (d, *J* = 2.5 Hz), 123.94 (d, *J* = 3.0 Hz), 120.56, 120.34, 114.93, 114.70, 41.08 (d, *J* = 69.0 Hz), 39.18.

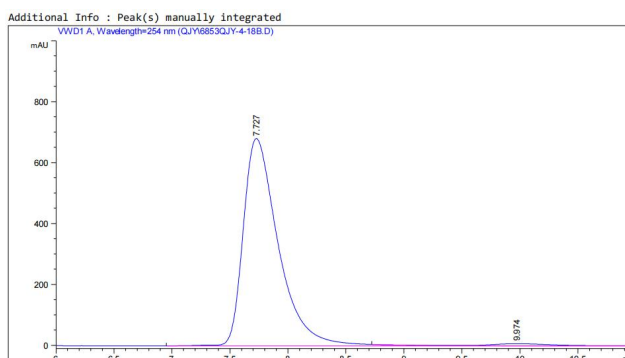
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.20.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₃O₂ClP [M+H]⁺ : 445.1119, found: 445.1114.

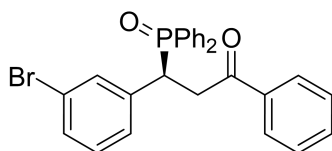
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.72 (major) and 9.97 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.255	BV	0.2711	1.49664e4	843.14417	49.2908
2	8.779	VV R	0.4061	1.53971e4	544.03400	50.7092



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.727	BV R	0.3176	1.43140e4	679.92059	98.0609
2	9.974	VB E	0.5848	283.05115	7.04404	1.9391



3t

(S)-3-(3-bromophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3t)^[2]

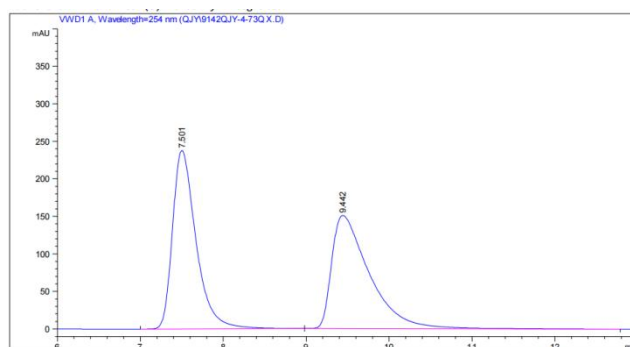
[Purification by flash column chromatography on silica gel (eluent, DCE: MeOH = 70:1). White solid, 85% yield, 94% ee]¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.03 – 7.93 (m, 2H), 7.88 – 7.81 (m, 2H), 7.59 – 7.44 (m, 6H), 7.42 – 7.33 (m, 4H), 7.34 – 7.24 (m, 3H), 7.08 (dd, $J = 4.3, 1.7$ Hz, 2H), 4.45 (ddd, $J = 10.5, 6.9, 2.4$ Hz, 1H), 4.00 (ddd, $J = 18.3, 10.5, 4.2$ Hz, 1H), 3.39 (ddd, $J = 18.3, 11.0, 2.4$ Hz, 1H).

¹³**C NMR** (101 MHz, Chloroform-*d*) δ 196.30 (d, $J = 13.2$ Hz), 138.13 (d, $J = 5.5$ Hz), 136.14, 134.01 (d, $J = 2.2$ Hz), 133.56, 132.24 (d, $J = 2.8$ Hz), 131.72 (d, $J = 2.6$ Hz), 131.25 (d, $J = 8.5$ Hz), 130.90 (d, $J = 8.9$ Hz), 130.60 (d, $J = 21.2$ Hz), 129.95 (d, $J = 5.6$ Hz), 129.51 (d, $J = 2.0$ Hz), 129.07 (d, $J = 11.3$ Hz), 128.64, 128.27 (d, $J = 12.0$ Hz), 128.13, 127.95 (d, $J = 5.6$ Hz), 127.34 (d, $J = 2.5$ Hz), 40.83 (d, $J = 68.5$ Hz), 38.85.

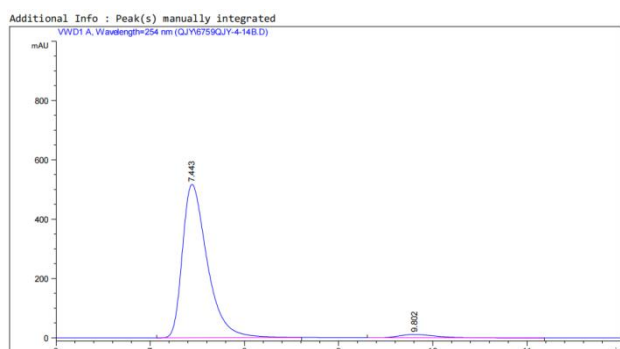
³¹**P NMR** (162 MHz, Chloroform-*d*) δ 34.48.

HRMS (ESI⁺, m/z): calcd for C₂₇H₂₃O₂BrP [M+H]⁺: 489.0614, found: 489.0615.

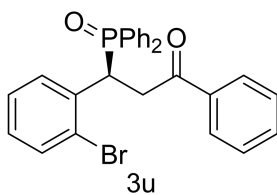
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.44 (major) and 9.80 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.501	BB	0.2993	4691.63623	237.68604	49.5677
2	9.442	BB	0.4675	4773.47070	150.69827	50.4323



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.443	BB	0.2782	9444.05273	516.84033	96.8966
2	9.802	BB	0.4109	302.47235	11.20563	3.1034



(S)-3-(2-bromophenyl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3v)

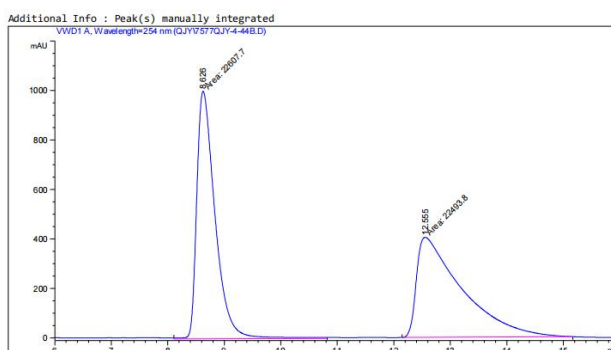
[Purification by flash column chromatography on silica gel (eluent, DCE: MeOH = 70:1). White solid, 90% yield, 99% ee] $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.12 – 8.02 (m, 2H), 7.89 – 7.81 (m, 2H), 7.58 (m, 3H), 7.53 – 7.44 (m, 1H), 7.43 – 7.24 (m, 6H), 7.19 (td, $J = 7.7, 3.0$ Hz, 2H), 6.98 (t, $J = 7.7$ Hz, 1H), 5.10 (ddd, $J = 10.0, 6.7, 2.8$ Hz, 1H), 4.06 (ddd, $J = 18.1, 10.5, 5.3$ Hz, 1H), 3.44 (ddd, $J = 18.2, 9.9, 2.8$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 196.27 (d, $J = 13.2$ Hz), 136.14, 135.76 (d, $J = 5.2$ Hz), 133.42, 132.74 (d, $J = 2.0$ Hz), 132.38 (d, $J = 2.8$ Hz), 131.71 (d, $J = 2.9$ Hz), 131.57, 131.48, 131.20, 131.10, 130.68 (d, $J = 42.5$ Hz), 129.95 (d, $J = 3.8$ Hz), 129.14, 129.03, 128.59, 128.19, 127.92, 127.80, 127.74 (d, $J = 2.5$ Hz), 126.63 (d, $J = 7.4$ Hz), 39.79 (d, $J = 67.6$ Hz), 39.27.

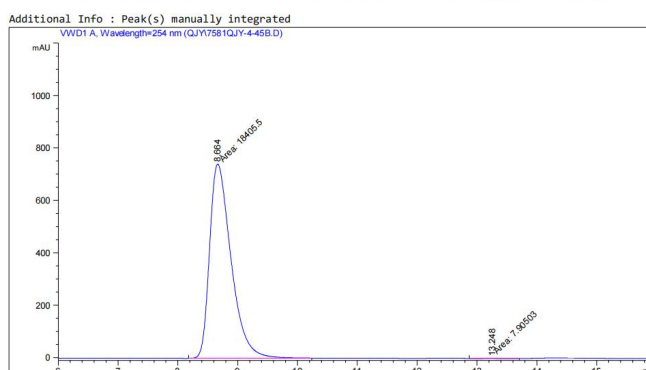
$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 34.69.

HRMS (ESI⁺, m/z): calcd for $\text{C}_{27}\text{H}_{23}\text{O}_2\text{BrP}$ $[\text{M}+\text{H}]^+$: 489.0614, found: 489.0617

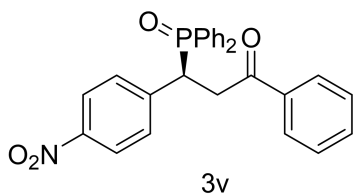
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254 nm. Retention time (min): 8.62 (major) and 13.24 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.626	MM	0.3768	2.26077e4	999.97961	50.1262
2	12.555	MM	0.9269	2.24938e4	404.44171	49.8738



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.664	MM	0.4145	1.84055e4	740.09576	99.9571
2	13.248	MM	0.3819	7.90503	3.45020e-1	0.0429



(S)-3-(diphenylphosphoryl)-3-(4-nitrophenyl)-1-phenylpropan-1-one (3v)^[2]

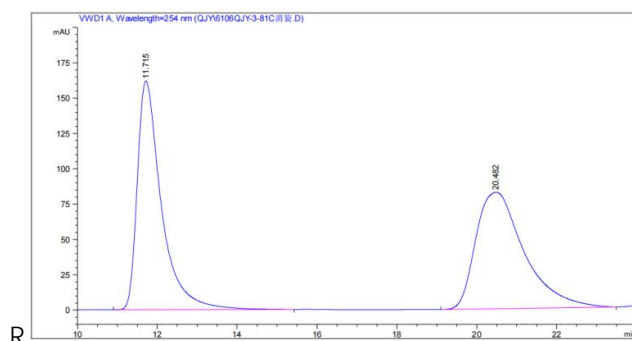
[Purification by flash column chromatography on silica gel (eluent, DCE: MeOH = 70:1). Yellow solid, 85% yield, 87% ee]¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.00 – 7.85 (m, 4H), 7.84 – 7.74 (m, 2H), 7.57 – 7.41 (m, 8H), 7.38 – 7.29 (m, 3H), 7.28 – 7.19 (m, 2H), 4.52 (ddd, *J* = 9.3, 6.6, 2.3 Hz, 1H), 3.99 (ddd, *J* = 18.4, 10.7, 3.9 Hz, 1H), 3.37 (ddd, *J* = 18.4, 10.4, 2.4 Hz, 1H).

¹³**C NMR** (101 MHz, Chloroform-*d*) δ 194.98 (d, *J* = 13.0 Hz), 145.76 (d, *J* = 2.6 Hz), 143.08 (d, *J* = 5.4 Hz), 134.79, 132.76, 131.45 (d, *J* = 2.8 Hz), 130.94 (d, *J* = 2.8 Hz), 130.12, 130.04, 129.67 (d, *J* = 5.7 Hz), 129.60 (d, *J* = 2.1 Hz), 128.23, 128.12, 127.68, 127.49, 127.37, 127.05, 122.35 (d, *J* = 1.9 Hz), 40.27 (d, *J* = 66.9 Hz), 37.81.

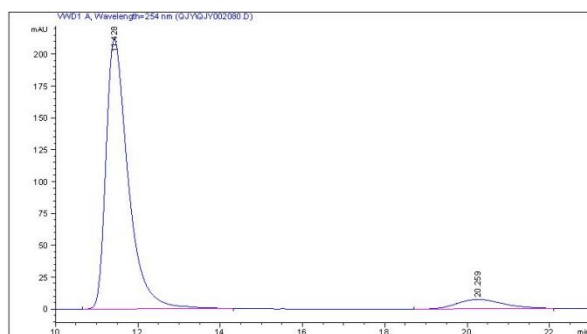
³¹**P NMR** (162 MHz, Chloroform-*d*) δ 33.28.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₂NO₄P [M+H]⁺: 455.1286, found: 455.1285.

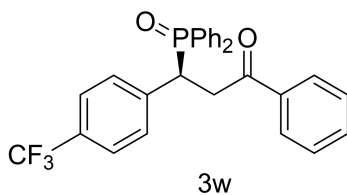
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 11.42 (major) and 20.25 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.715	BB	0.6228	6800.93604	161.98839	49.5664
2	20.482	BB	1.2632	6919.92188	82.44920	50.4336



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.428	BB	0.5659	7927.85059	211.68414	93.3443
2	20.259	BB	1.1355	565.27972	7.22721	6.6557



(S)-3-(diphenylphosphoryl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)propan-1-one (3w)

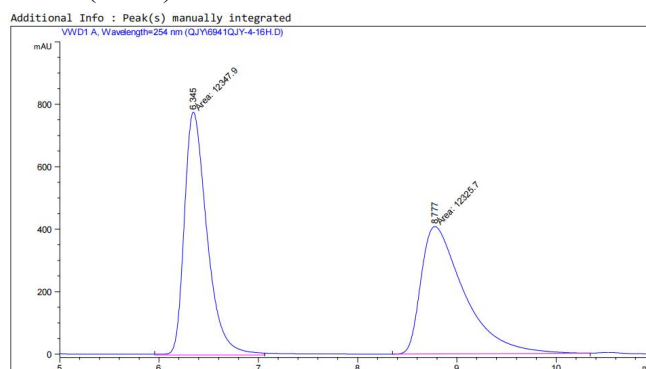
[Purification by flash column chromatography on silica gel (eluent, DCE: MeOH =70:1). White solid, 92% yield, 95% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.95 (m, 2H), 7.90 – 7.81 (m, 2H), 7.58 – 7.49 (m, 6H), 7.52 – 7.44 (m, 2H), 7.44 – 7.32 (m, 5H), 7.32 – 7.23 (m, 2H), 4.54 (ddd, *J* = 10.6, 6.8, 2.4 Hz, 1H), 4.04 (ddd, *J* = 18.3, 10.6, 4.2 Hz, 1H), 3.41 (ddd, *J* = 18.3, 10.9, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.27 (d, *J* = 13.2 Hz), 140.43 – 140.14 (m), 136.03, 133.66, 132.35 (d, *J* = 2.7 Hz), 131.81 (d, *J* = 2.9 Hz), 131.55, 131.26, 131.17, 130.84, 130.75, 130.55, 130.28, 130.14 (d, *J* = 5.5 Hz), 129.20, 129.09, 128.68, 128.39, 128.28, 128.12, 125.20, 41.03 (d, *J* = 67.9 Hz), 38.86.

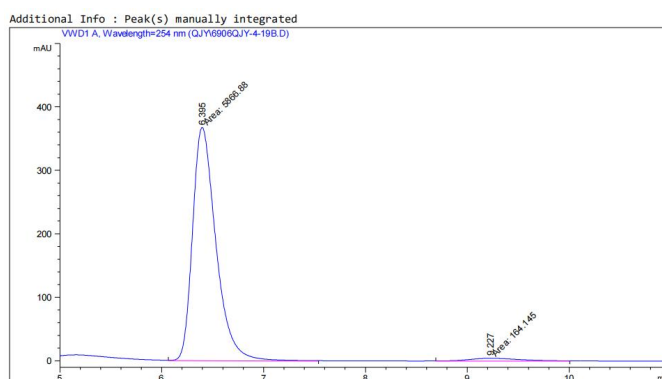
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.23.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₃O₂F₃P [M+H]⁺ : 479.1382, found: 479.1380.

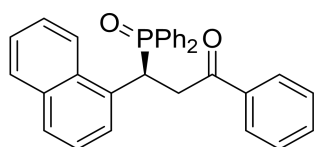
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 6.39 (major) and 9.22(minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.345	MM	0.2647	1.23479e4	777.58331	50.0450
2	8.777	MM	0.5040	1.23257e4	407.62524	49.9550



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.395	MM	0.2661	5866.88428	367.50113	97.2783
2	9.227	MM	0.6106	164.14453	4.48067	2.7217



3x

(S)-3-(diphenylphosphoryl)-3-(naphthalen-1-yl)-1-phenylpropan-1-one (3x)^[2]

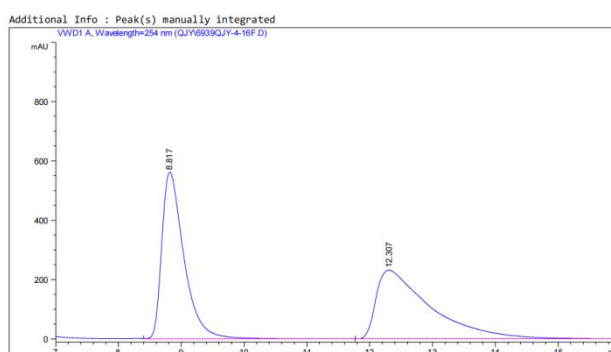
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 91% yield, 96% ee]¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.09 (d, J = 8.6 Hz, 1H), 7.94 (m, 3H), 7.72 – 7.65 (m, 2H), 7.58 – 7.45 (m, 2H), 7.41 (m, 3H), 7.38 – 7.23 (m, 3H), 7.25 – 7.10 (m, 5H), 6.94 (t, J = 7.5 Hz, 1H), 6.81 (td, J = 7.7, 2.9 Hz, 2H), 5.33 (ddd, J = 9.8, 7.3, 3.0 Hz, 1H), 4.00 (ddd, J = 18.2, 9.3, 5.5 Hz, 1H), 3.55 (ddd, J = 18.3, 11.6, 2.9 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.76 (d, J = 12.2 Hz), 136.12, 133.49, 133.32, 132.83 (d, J = 5.4 Hz), 132.11 (d, J = 2.8 Hz), 132.03 (d, J = 5.8 Hz), 131.72 (d, J = 3.9 Hz), 131.50, 131.42, 131.21 (d, J = 2.8 Hz), 130.74 (d, J = 2.8 Hz), 130.62, 130.53, 128.99, 128.88, 128.55, 128.47, 128.09, 127.77 (d, J = 2.5 Hz), 127.69, 127.58, 126.99 (d, J = 5.5 Hz), 125.95, 125.32 (d, J = 2.8 Hz), 125.22, 123.00, 40.14, 34.18 (d, J = 69.3 Hz).

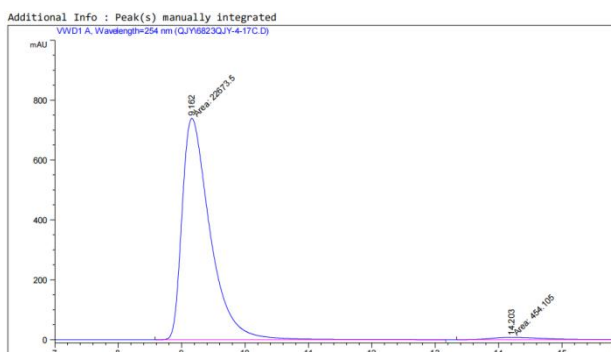
³¹P NMR (162 MHz, CDCl₃) δ 34.76.

HRMS (ESI⁺, *m/z*): calcd for C₃₁H₂₆O₂P [M+H]⁺ : 461.1592, found: 461.1596.

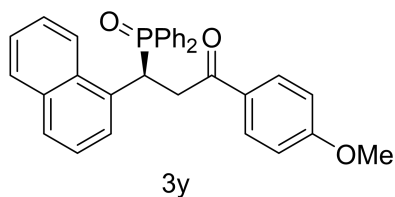
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.16 (major) and 14.20 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.817	VB	0.3702	1.37848e4	561.83118	49.7638
2	12.307	BBA	0.8339	1.39156e4	231.31133	50.2362



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.162	MM	0.5115	2.26735e4	738.75372	98.0365
2	14.203	MM	0.9727	454.10510	7.78059	1.9635



(S)-3-(diphenylphosphoryl)-1-(4-methoxyphenyl)-3-(naphthalen-1-yl)propan-1-one (3y)

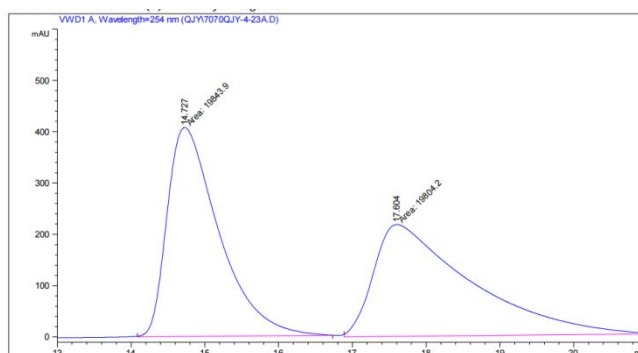
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). Yellow solid, 86% yield, 90% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.14 (d, J = 8.6 Hz, 1H), 8.03 – 7.94 (m, 3H), 7.72 (d, J = 8.9 Hz, 2H), 7.61 – 7.52 (m, 2H), 7.45 (m, 3H), 7.38 – 7.28 (m, 2H), 7.25 – 7.15 (m, 3H), 6.97 (td, J = 7.3, 1.5 Hz, 1H), 6.85 (td, J = 7.7, 2.9 Hz, 2H), 6.71 (d, J = 8.9 Hz, 2H), 5.38 (ddd, J = 9.8, 7.2, 2.9 Hz, 1H), 4.01 (ddd, J = 18.0, 9.3, 5.5 Hz, 1H), 3.69 (s, 3H), 3.53 (ddd, J = 18.1, 11.6, 2.9 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.24 (d, J = 12.3 Hz), 163.63, 133.55, 133.01 (d, J = 5.4 Hz), 132.14 (d, J = 3.1 Hz), 131.86 (d, J = 6.9 Hz), 131.57, 131.49, 131.23 (d, J = 2.8 Hz), 130.89, 130.68, 130.58, 130.47, 129.32, 129.03, 128.92, 128.58, 127.77 (d, J = 5.5 Hz), 127.62, 127.05 (d, J = 5.8 Hz), 125.99, 125.37 (d, J = 2.8 Hz), 125.26, 123.14, 113.63, 55.44, 39.74, 34.31 (d, J = 69.4 Hz).

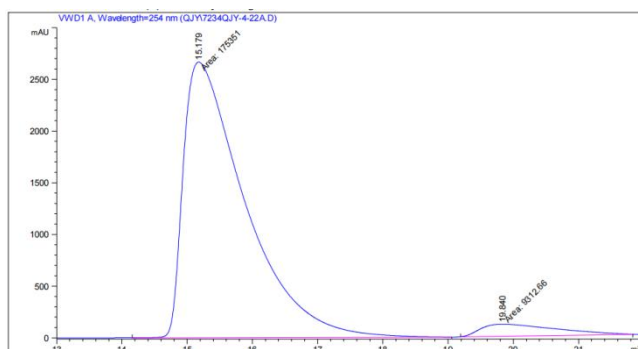
³¹P NMR (162 MHz, CDCl₃) δ 34.66.

HRMS (ESI⁺, *m/z*): calcd for C₃₂H₂₈O₃P [M+H]⁺ : 491.1771, found: 491.1776.

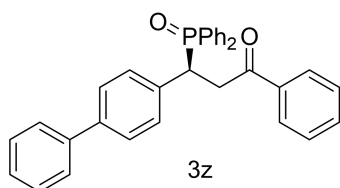
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 15.17 (major) and 19.84 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.727	MM	0.8123	1.98439e4	407.14825	50.0501
2	17.604	MM	1.5143	1.98042e4	217.97450	49.9499



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.179	MM	1.0964	1.75351e5	2665.57568	94.9570
2	19.840	MM	1.3338	9312.65820	116.37004	5.0430



(S)-3-([1,1'-biphenyl]-4-yl)-3-(diphenylphosphoryl)-1-phenylpropan-1-one (3z)

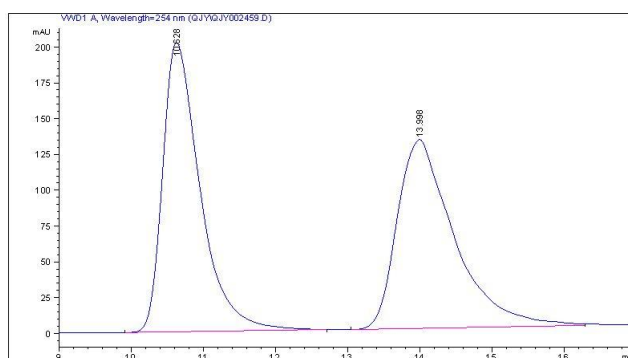
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 84% yield, 97% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (m, 2H), 7.90 (d, $J = 7.2$ Hz, 2H), 7.59 – 7.47 (m, 11H), 7.44 – 7.37 (m, 6H), 7.34 – 7.26 (m, 3H), 4.57 (ddd, $J = 9.8, 6.9, 2.4$ Hz, 1H), 4.11 (ddd, $J = 18.2, 10.5, 4.3$ Hz, 1H), 3.45 (ddd, $J = 18.2, 11.0, 2.4$ Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.69 (d, $J = 13.3$ Hz), 140.57, 139.71 (d, $J = 2.7$ Hz), 136.31, 134.97 (d, $J = 5.8$ Hz), 133.48, 132.65 (d, $J = 2.9$ Hz), 132.13 (d, $J = 2.8$ Hz), 131.56 (d, $J = 2.8$ Hz), 131.36, 131.27, 131.06, 130.97, 130.74 (d, $J = 11.5$ Hz), 130.25, 130.19, 129.09, 129.02, 128.97, 128.90, 128.72, 128.62, 128.25, 128.16, 128.14, 127.23, 126.99 (d, $J = 2.1$ Hz), 126.93, 40.74 (d, $J = 68.9$ Hz), 38.95.

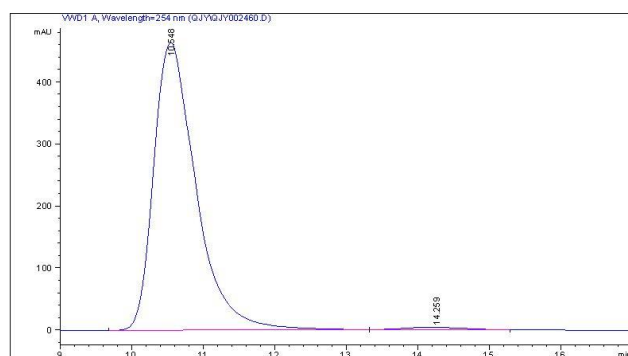
³¹P NMR (162 MHz, CDCl₃) δ 34.56.

HRMS (ESI⁺, *m/z*): calcd for C₃₃H₂₈O₂P [M+H]⁺ : 487,1821, found:487.1824.

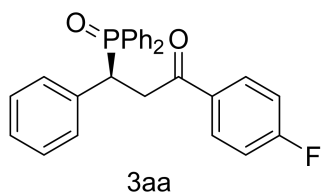
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min):10.54 (major) and 14.25 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.628	BB	0.5373	7268.51855	201.75163	50.0824
2	13.998	BV	0.7921	7244.61475	131.82991	49.9176



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.548	BB	0.6057	1.90353e4	463.90405	98.8576
2	14.259	BB	0.6798	219.96745	4.06184	1.1424



(S)-3-(diphenylphosphoryl)-1-(4-fluorophenyl)-3-phenylpropan-1-one (3aa)

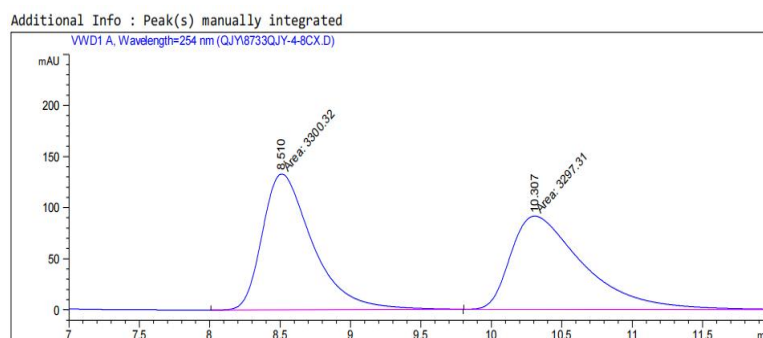
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 89% yield, 96% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 (m, 2H), 7.90 – 7.84 (m, 2H), 7.56 – 7.41 (m, 5H), 7.41 – 7.30 (m, 3H), 7.24 (m, 2H), 7.20 – 7.06 (m, 3H), 7.04 (t, *J* = 8.6 Hz, 2H), 4.45 (ddd, *J* = 9.9, 6.9, 2.5 Hz, 1H), 3.98 (ddd, *J* = 18.0, 10.3, 4.5 Hz, 1H), 3.36 (ddd, *J* = 18.0, 11.1, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.20 (d, *J* = 13.4 Hz), 167.13, 164.59, 135.80 (d, *J* = 5.6 Hz), 132.79, 132.13 (d, *J* = 2.8 Hz), 131.84 (d, *J* = 22.3 Hz), 131.51 (d, *J* = 2.8 Hz), 131.34, 131.25, 131.00, 130.91, 130.87, 130.78, 129.83, 129.77, 129.06, 128.95, 128.37 (d, *J* = 1.9 Hz), 128.18, 128.07, 127.16 (d, *J* = 2.5 Hz), 115.81, 115.59, 41.09 (d, *J* = 69.0 Hz), 38.86.

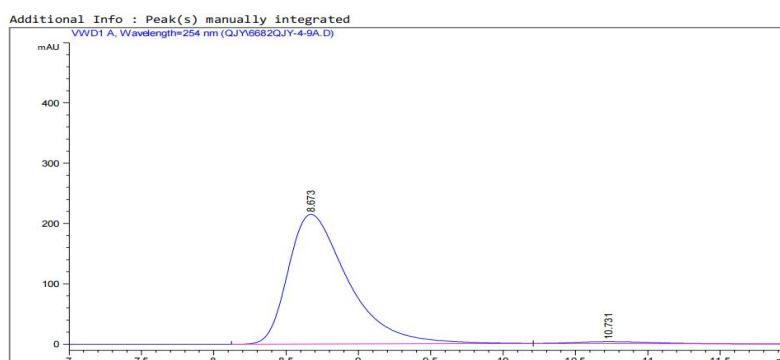
³¹P NMR (162 MHz, CDCl₃) δ 34.25.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₃O₂FP [M+H]⁺ : 429.1414, found: 429.1418.

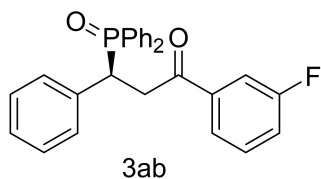
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 8.67 (major) and 10.73(minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.510	MM	0.4136	3300.32349	133.00629	50.0228
2	10.307	MM	0.6019	3297.31470	91.29690	49.9772



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.673	BB	0.4346	6185.82861	215.01453	98.0406
2	10.731	BB	0.5900	123.62520	3.14936	1.9594



(S)-3-(diphenylphosphoryl)-1-(3-fluorophenyl)-3-phenylpropan-1-one(3ab)

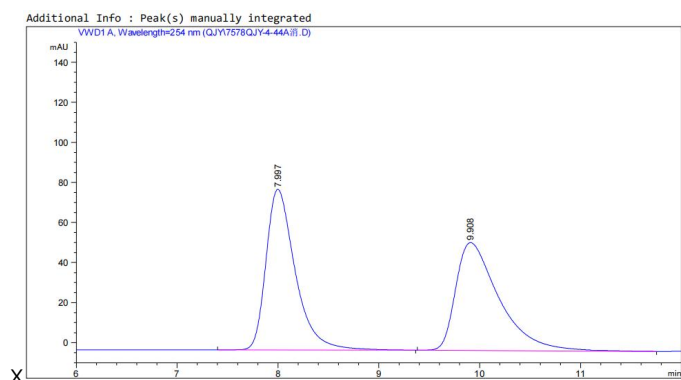
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH =70:1). White soild, 90% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.94 (m, 2H), 7.89 – 7.80 (m, 2H), 7.50 (m, 7H), 7.41 – 7.33 (m, 4H), 7.33 – 7.24 (m, 2H), 7.23 (m, 1H), 7.02 (t, *J* = 7.8 Hz, 1H), 4.44 (ddd, *J* = 9.8, 6.9, 2.4 Hz, 1H), 3.99 (ddd, *J* = 18.3, 10.4, 4.2 Hz, 1H), 3.39 (ddd, *J* = 18.3, 11.0, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.29 (d, *J* = 13.1 Hz), 138.39 (d, *J* = 5.4 Hz), 136.13, 133.57, 132.85 (d, *J* = 5.7 Hz), 132.26 (d, *J* = 2.8 Hz), 131.74 (d, *J* = 2.8 Hz), 131.53 (d, *J* = 27.5 Hz), 131.30, 131.21, 130.95, 130.86, 130.56 (d, *J* = 22.2 Hz), 130.26 (d, *J* = 2.5 Hz), 129.81 (d, *J* = 2.0 Hz), 129.13, 129.02, 128.65, 128.36 (d, *J* = 4.1 Hz), 128.22, 128.14, 122.23 (d, *J* = 2.2 Hz), 40.82 (d, *J* = 68.4 Hz), 38.82.

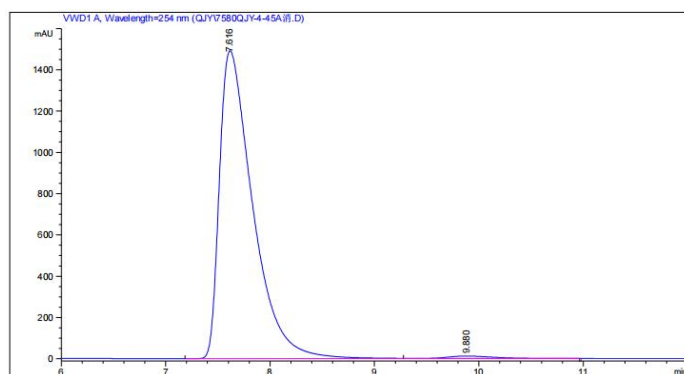
³¹P NMR (162 MHz, CDCl₃) δ 34.08.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₃O₂FP [M+H]⁺ : 429.1414, found: 429.1411.

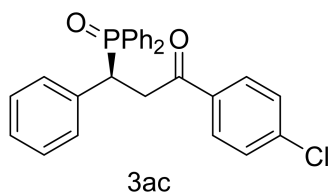
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.69 (major) and 9.98 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.997	BB	0.3045	1611.79956	80.18473	50.1043
2	9.908	BB	0.4459	1605.08850	53.82476	49.8957



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.616	BV R	0.3321	3.29937e4	1491.26257	98.8961
2	9.880	VB E	0.4630	368.28882	12.00197	1.1039



(S)-1-(4-chlorophenyl)-3-(diphenylphosphoryl)-3-phenylpropan-1-one (3ac)

[Purification by flash column chromatography on silica gel (eluent, DCM:MeOH = 70:1). White solid, 87% yield, 96% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.91 (m, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.51 (m, 3H), 7.46 – 7.39 (m, 2H), 7.35 – 7.27 (m, 5H), 7.23 (m, 2H), 7.17 – 7.07 (m, 3H), 4.43 (ddd, *J* = 9.8, 6.8, 2.6 Hz, 1H), 3.97 (ddd, *J* = 18.1, 10.4, 4.7 Hz, 1H), 3.32 (ddd, *J* = 18.1, 11.0, 2.6 Hz, 1H).

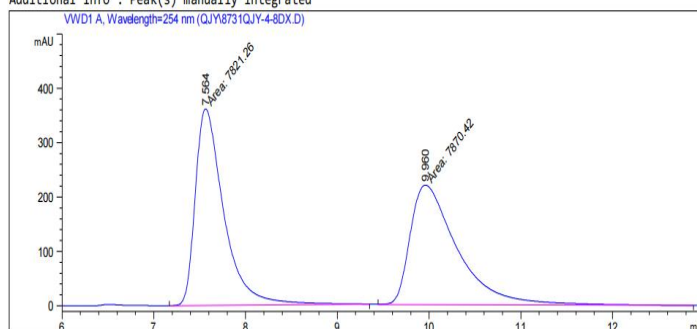
¹³C NMR (101 MHz, Chloroform-*d*) δ 195.67 (d, *J* = 13.4 Hz), 139.90, 135.55 (d, *J* = 5.8 Hz), 134.61, 132.72 (d, *J* = 2.9 Hz), 132.23 (d, *J* = 2.7 Hz), 131.62 (d, *J* = 2.4 Hz), 131.29, 131.20, 130.97, 130.88, 130.73 (d, *J* = 11.6 Hz), 129.78, 129.72, 129.57, 129.12, 129.01, 128.89, 128.39 (d, *J* = 2.1 Hz), 128.23, 128.11, 127.23 (d, *J* = 2.5 Hz), 41.07 (d, *J* = 69.0 Hz), 38.76.

³¹P NMR (162 MHz, CDCl₃) δ 34.12.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₃O₂ClP [M+H]⁺: 445.1119, found: 445.1114.

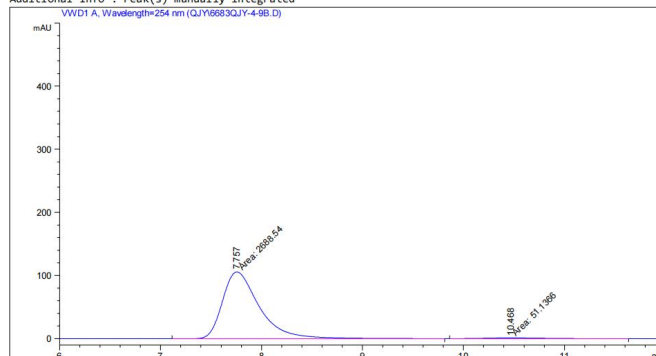
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.75 (major) and 10.46 (minor).

Additional Info : Peak(s) manually integrated

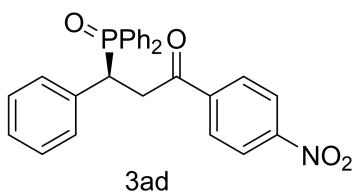


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.564	MM	0.3611	7821.26221	361.01724	49.8434
2	9.960	MM	0.5975	7870.42090	219.52318	50.1566

Additional Info : Peak(s) manually integrated



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.757	MM	0.4235	2688.53760	105.81068	98.1335
2	10.468	MM	0.6948	51.13657	1.22672	1.8665



(S)-3-(diphenylphosphoryl)-1-(4-nitrophenyl)-3-phenylpropan-1-one (3ad)^[2]

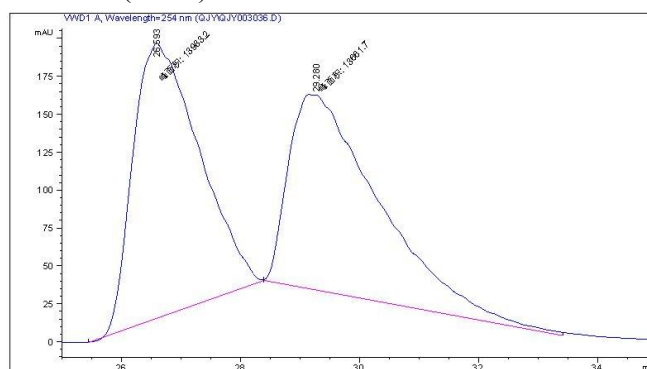
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). Yellow solid, 86% yield, 98% ee]¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.25 – 8.17 (m, 2H), 8.03 – 7.91 (m, 4H), 7.60 – 7.48 (m, 3H), 7.51 – 7.41 (m, 2H), 7.36 (m, 3H), 7.30 – 7.22 (m, 2H), 7.21 – 7.08 (m, 3H), 4.43 (ddd, $J = 10.0, 7.0, 2.8$ Hz, 1H), 4.02 (ddd, $J = 18.1, 10.2, 5.1$ Hz, 1H), 3.45 (ddd, $J = 18.1, 10.7, 2.8$ Hz, 1H).

¹³**C NMR** (101 MHz, Chloroform-*d*) δ 195.61 (d, $J = 13.3$ Hz), 150.34, 140.68, 135.48 (d, $J = 5.6$ Hz), 132.27 (d, $J = 2.7$ Hz), 131.66 (d, $J = 2.8$ Hz), 131.54 (d, $J = 3.4$ Hz), 131.33, 131.25, 131.02, 130.93, 130.57 (d, $J = 3.0$ Hz), 129.74, 129.69, 129.18, 129.13, 129.02, 128.48 (d, $J = 2.0$ Hz), 128.25, 128.13, 127.36 (d, $J = 2.5$ Hz), 123.80, 41.23 (d, $J = 68.6$ Hz), 39.56.

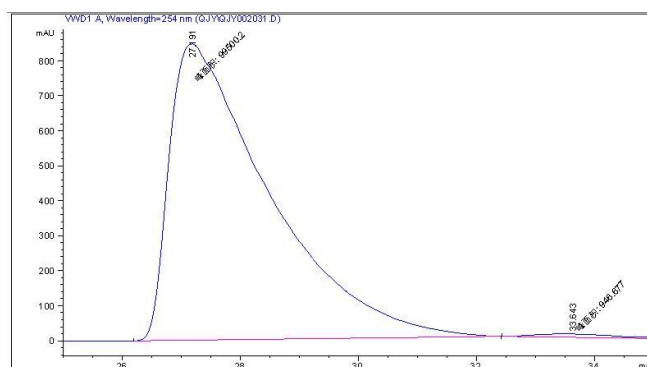
³¹**P NMR** (162 MHz, CDCl₃) δ 34.08.

HRMS (ESI⁺, m/z): calcd for C₂₇H₂₂O₄NP [M+H]⁺ : 456.1286, found: 456.1247.

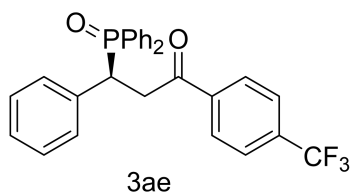
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 27.19 (major) and 33.64 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	26.593	MM	1.2849	1.39832e4	181.38112	50.5815
2	29.280	MM	1.7683	1.36617e4	128.76357	49.4185



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.191	MM	1.9597	9.95002e4	846.23236	99.0575
2	33.643	MM	1.6812	946.67712	9.38499	0.9425



(S)-3-(diphenylphosphoryl)-3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (3ae)

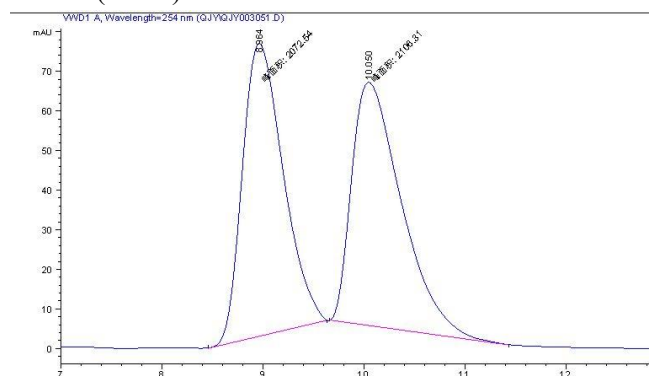
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH =70:1). White solid, 95% yield, 96% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 7.96 (m, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.55 – 7.44 (m, 5H), 7.41 – 7.31 (m, 3H), 7.25 (m, 2H), 7.19 – 7.09 (m, 3H), 4.46 (ddd, *J* = 9.9, 6.9, 2.6 Hz, 1H), 4.03 (ddd, *J* = 18.2, 10.3, 4.8 Hz, 1H), 3.43 (ddd, *J* = 18.2, 10.9, 2.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.99 (d, *J* = 13.3 Hz), 138.92, 135.62 (d, *J* = 5.6 Hz), 134.57 (d, *J* = 32.7 Hz), 132.20 (d, *J* = 2.7 Hz), 131.76, 131.59 (d, *J* = 3.0 Hz), 131.33, 131.25, 131.01, 130.93, 130.78 (d, *J* = 3.3 Hz), 130.68, 129.79, 129.73, 129.10, 128.99, 128.48, 128.43 (d, *J* = 1.9 Hz), 128.22, 128.10, 127.26 (d, *J* = 2.3 Hz), 125.64 (q, *J* = 3.8 Hz), 41.12 (d, *J* = 68.8 Hz), 39.31.

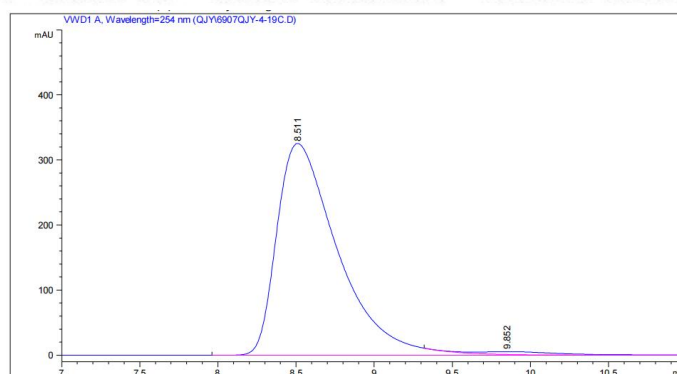
³¹P NMR (162 MHz, CDCl₃) δ 34.25.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₃O₂F₃P [M+H]⁺ : 479.1382, found: 479.1380.

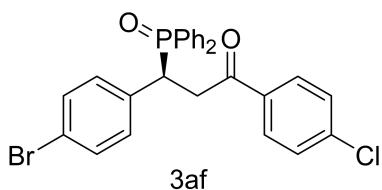
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 8.51 (major) and 9.85 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.964	MM	0.4676	2072.53955	73.86913	49.5959
2	10.050	MM	0.5720	2106.31079	61.37356	50.4041



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.511	BV R	0.4096	8855.49121	325.26755	97.9521
2	9.852	VB E	0.5925	185.14598	4.37681	2.0479



(S)-3-(4-bromophenyl)-1-(4-chlorophenyl)-3-(diphenylphosphoryl)propan-1-one(3af)

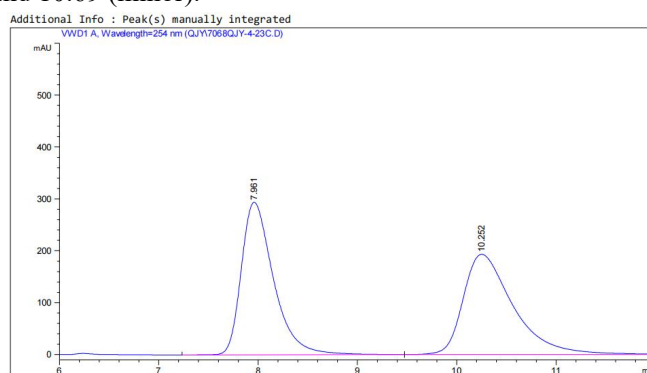
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH =70:1). White solid, 97% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 7.91 (m, 2H), 7.89 – 7.81 (m, 2H), 7.60 – 7.42 (m, 5H), 7.40 – 7.33 (m, 1H), 7.29-7.20 (m, 6H), 7.03 (t, *J* = 8.6 Hz, 2H), 4.68 – 4.31 (m, 1H), 3.93 (ddd, *J* = 18.1, 10.5, 4.4 Hz, 1H), 3.34 (ddd, *J* = 18.2, 10.7, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 194.99 (d, *J* = 13.5 Hz), 167.23, 164.69, 134.74 (d, *J* = 5.6 Hz), 132.56 (d, *J* = 2.9 Hz), 132.40 (d, *J* = 2.7 Hz), 131.89 (d, *J* = 2.9 Hz), 131.48 (d, *J* = 2.0 Hz), 131.40, 131.35, 131.17, 131.08, 130.92, 130.84 (d, *J* = 3.3 Hz), 130.77, 130.11 (d, *J* = 13.1 Hz), 129.21, 129.10, 128.45, 128.33, 121.33 (d, *J* = 3.1 Hz), 115.90, 115.68, 49.54 (dt, *J* = 43.0, 21.5 Hz), 40.52 (d, *J* = 68.8 Hz), 38.53.

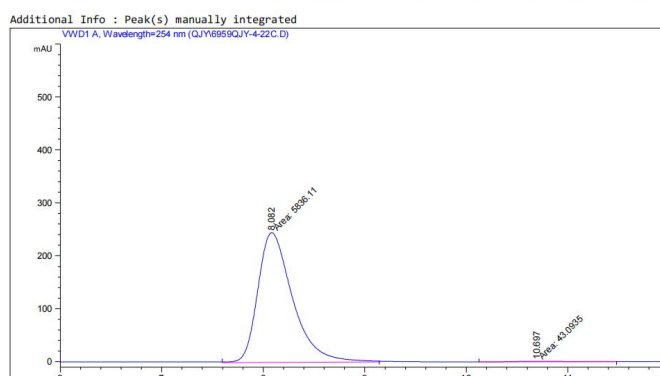
³¹P NMR (162 MHz, CDCl₃) δ 34.24.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₂O₂BrClP [M+H]⁺ : 523.0151, found: 523.0152.

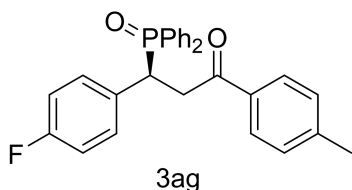
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 8.08 (major) and 10.69 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.961	BB	0.3430	6625.76563	293.94424	49.3381
2	10.252	BB	0.5277	6803.53223	193.27744	50.6619



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.082	MM	0.3970	5836.11230	245.01759	99.2670
2	10.697	MM	0.5951	43.09346	1.20698	0.7330



(S)-3-(diphenylphosphoryl)-3-(4-fluorophenyl)-1-(p-tolyl)propan-1-one (3ag)

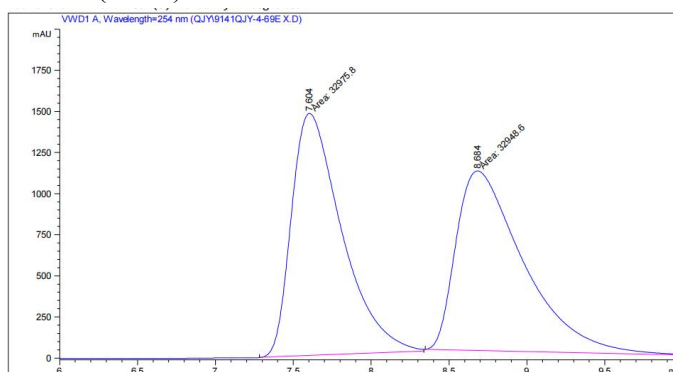
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 94% yield, 95% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.02 – 7.93 (m, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.54 – 7.45 (m, 5H), 7.41 – 7.31 (m, 3H), 7.30 – 7.24 (m, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 6.83 (t, *J* = 8.7 Hz, 2H), 4.46 (ddd, *J* = 10.6, 6.7, 2.3 Hz, 1H), 3.96 (ddd, *J* = 18.1, 10.6, 4.1 Hz, 1H), 3.32 (ddd, *J* = 18.0, 10.8, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.18 (d, *J* = 13.5 Hz), 163.08 (d, *J* = 2.6 Hz), 160.63 (d, *J* = 2.6 Hz), 144.46, 133.79, 132.16 (d, *J* = 2.8 Hz), 131.70 (dd, *J* = 5.6, 3.2 Hz), 131.59, 131.56, 131.42, 131.36 (d, *J* = 2.4 Hz), 131.27, 131.19, 130.91, 130.82, 129.30, 129.10, 128.99, 128.29, 128.24, 128.17, 115.35 (d, *J* = 1.9 Hz), 115.14 (d, *J* = 2.0 Hz), 40.25 (d, *J* = 69.5 Hz), 38.85, 21.65.

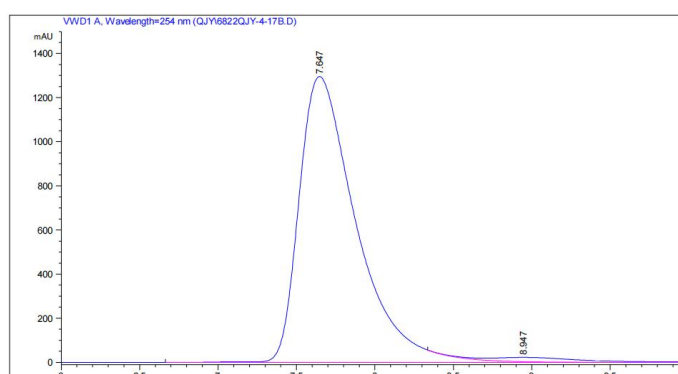
³¹P NMR (162 MHz, CDCl₃) δ 34.44.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₅FO₂P [M+H]⁺ : 443.1571, found 443.1574.

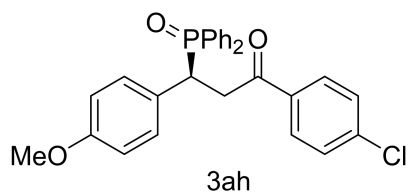
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.64(major) and 8.94 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.501	BB	0.2993	4691.63623	237.68604	49.5677
2	9.442	BB	0.4675	4773.47070	150.69827	50.4323



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.647	WV R	0.3794	3.27503e4	1296.07996	97.2331
2	8.947	VB E	0.6559	931.95990	19.80801	2.7669



(S)-1-(4-chlorophenyl)-3-(diphenylphosphoryl)-3-(4-methoxyphenyl)propan-1-one (3ah)

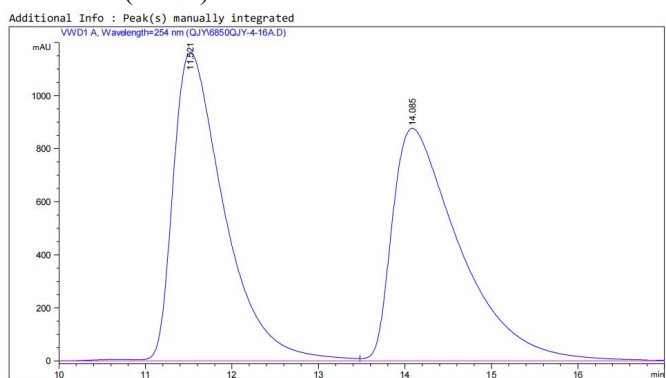
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 93% yield, 97% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 – 7.92 (m, 2H), 7.76 (d, *J* = 8.6 Hz, 2H), 7.54 – 7.45 (m, 5H), 7.40 – 7.22 (m, 7H), 6.69 (d, *J* = 8.7 Hz, 2H), 4.40 (ddd, *J* = 9.9, 6.9, 2.5 Hz, 1H), 3.92 (ddd, *J* = 17.9, 10.5, 4.5 Hz, 1H), 3.68 (s, 3H), 3.31 (ddd, *J* = 18.0, 10.6, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.73 (d, *J* = 13.6 Hz), 158.53 (d, *J* = 2.3 Hz), 139.79, 134.65, 132.02 (d, *J* = 2.3 Hz), 131.84, 131.44 (d, *J* = 2.7 Hz), 131.25, 131.16, 130.98, 130.89, 130.77, 130.71, 129.49, 128.99, 128.88, 128.82, 128.18, 128.06, 127.50 (d, *J* = 5.7 Hz), 113.76 (d, *J* = 1.8 Hz), 55.06, 40.13 (d, *J* = 69.9 Hz), 38.98.

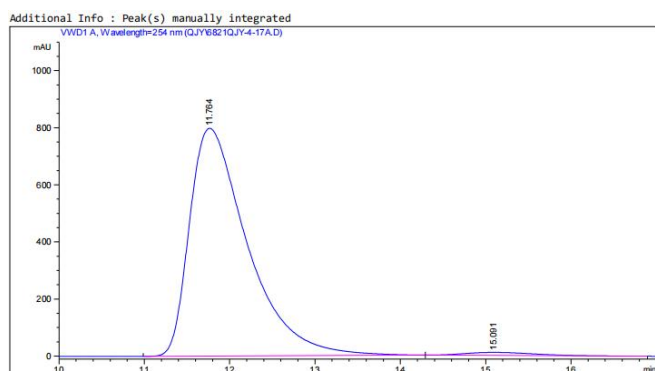
³¹P NMR (162 MHz, CDCl₃) δ 34.24.

HRMS (ESI⁺, *m/z*): calcd for C₂₈H₂₅O₃ClP [M+H]⁺ : 475.1224, found: 475.1221.

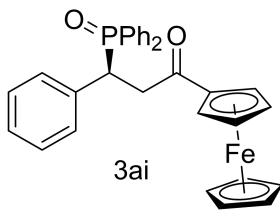
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 11.76 (major) and 15.09 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.521	VV R	0.6151	4.77359e4	1162.39478	50.0109
2	14.085	VBA	0.8073	4.77151e4	876.19025	49.9891



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.764	BB	0.7118	3.75904e4	797.64685	98.3911
2	15.091	BBA	0.8711	614.67249	10.83122	1.6089



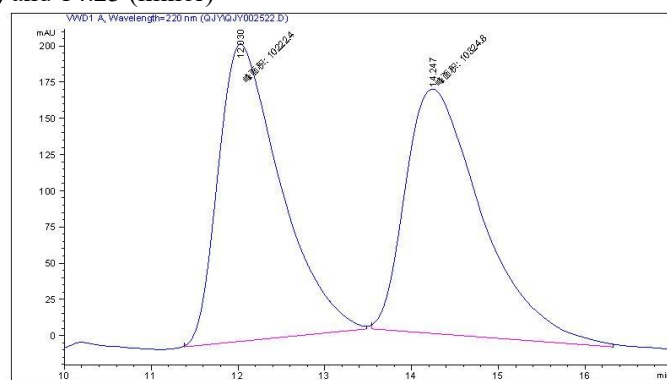
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). Red solid, 92% yield, 88% ee]. $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.10 – 7.94 (m, 2H), 7.56 – 7.42 (m, 7H), 7.35 – 7.29 (m, 1H), 7.28 – 7.16 (m, 4H), 7.16 – 7.09 (m, 1H), 4.72 (dt, $J = 2.6, 1.3$ Hz, 1H), 4.66 (dt, $J = 2.6, 1.3$ Hz, 1H), 4.48 (ddd, $J = 10.9, 6.3, 1.7$ Hz, 1H), 4.42 (ddq, $J = 5.1, 2.6, 1.2$ Hz, 2H), 3.74 (s, 5H), 3.71 – 3.64 (m, 1H), 3.05 (ddd, $J = 18.1, 11.7, 1.7$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 200.27 (d, $J = 14.3$ Hz), 136.41 (d, $J = 5.4$ Hz), 132.08 (d, $J = 2.7$ Hz), 131.40 (d, $J = 2.6$ Hz), 131.32, 131.24, 130.93, 130.84, 130.12 (d, $J = 5.9$ Hz), 129.08, 128.97, 128.47 (d, $J = 1.7$ Hz), 128.19, 128.07, 127.34 (d, $J = 2.4$ Hz), 78.26, 72.51, 69.59, 69.47, 68.86, 40.65, 40.56, 39.95.

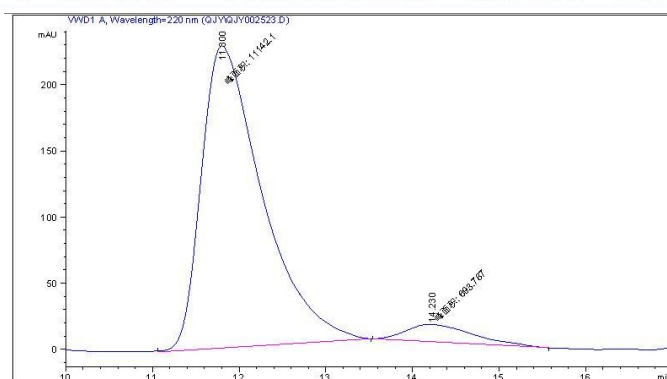
$^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 34.67.

HRMS (ESI⁺, m/z): calcd for $\text{C}_{31}\text{H}_{28}\text{O}_2\text{FeP}$ $[\text{M}+\text{H}]^+$: 519.1171, found: 519.1171.

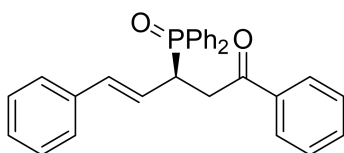
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 11.80 (major) and 14.23 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.030	MM	0.8300	1.02224e4	205.27940	49.7509
2	14.247	MM	1.0201	1.03248e4	168.69176	50.2491



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.800	MM	0.8134	1.11421e4	228.29538	94.1383
2	14.230	MM	0.8912	693.78741	12.97483	5.8617



3aj

(*S, E*)-3-(diphenylphosphoryl)-1,5-diphenylpent-4-en-1-one (3aj)

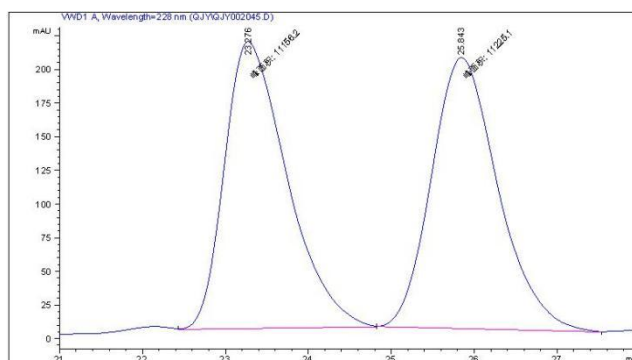
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). Yellow soild, 84% yield, 99% ee]. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.87 (m, 3H), 7.84 – 7.77 (m, 2H), 7.71 (dd, *J* = 13.7, 6.9 Hz, 1H), 7.55 – 7.38 (m, 9H), 7.23 – 7.11 (m, 5H), 6.41 (dd, *J* = 15.8, 4.0 Hz, 1H), 6.12 (ddd, *J* = 15.6, 9.1, 6.2 Hz, 1H), 4.17 (q, *J* = 9.3 Hz, 1H), 3.67 (ddd, *J* = 17.8, 10.2, 4.2 Hz, 1H), 3.29 (ddd, *J* = 17.6, 11.4, 2.4 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 135.53, 135.42, 134.36 (d, *J* = 11.6 Hz), 132.40, 131.59, 131.04, 130.82, 130.37, 130.28, 130.18, 130.10, 129.70 (d, *J* = 11.3 Hz), 127.95, 127.83, 127.60, 127.51, 127.39, 127.34, 127.13, 126.55, 125.27, 122.22 (d, *J* = 7.4 Hz), 37.85 (d, *J* = 71.5 Hz), 36.01.

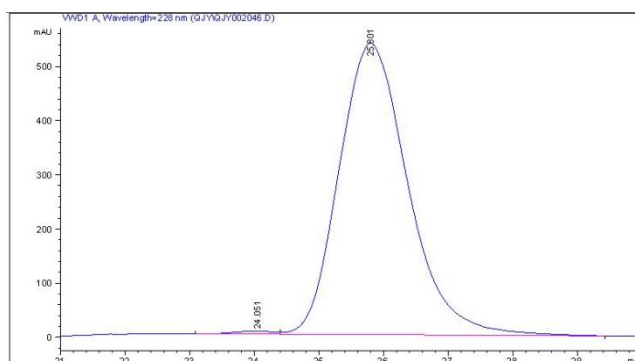
³¹P NMR (162 MHz, CDCl₃) δ 34.38.

HRMS (ESI⁺, *m/z*): calcd for C₂₉H₂₆O₂P [M+H]⁺ : 437.1665, found: 437.1668.

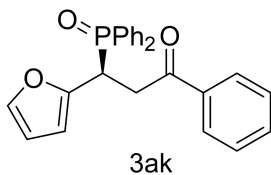
HPLC analysis: Chiracel-ADH, n-heptane/*i*-PrOH= 70:30, 1 mL/min, 22°C, detection at 228nm. Retention time (min): 24.05 (minor) and 25.80 (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.276	MM	0.8725	1.11562e4	213.10361	49.8460
2	25.843	MM	0.9290	1.12251e4	201.37524	50.1540



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	24.051	BV	0.5651	212.00438	5.00553	0.5302
2	25.801	VB	1.1518	3.97706e4	538.42078	99.4698



(S)-3-(diphenylphosphoryl)-3-(furan-2-yl)-1-phenylpropan-1-one (3ak)^[2]

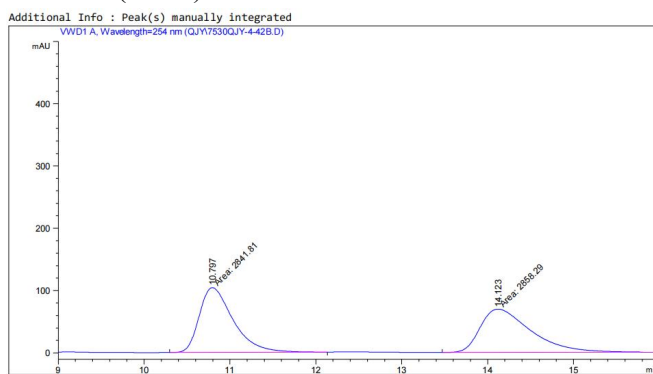
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 93% yield, 98% ee]. ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.86 (m, 4H), 7.62 – 7.44 (m, 7H), 7.44 – 7.35 (m, 4H), 7.17 (d, *J* = 2.1 Hz, 1H), 6.19 – 6.15 (m, 1H), 6.06 (t, *J* = 3.3 Hz, 1H), 4.73 (td, *J* = 10.4, 2.7 Hz, 1H), 3.95 (ddd, *J* = 18.0, 10.7, 4.5 Hz, 1H), 3.42 (ddd, *J* = 18.0, 10.0, 2.7 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.40 (d, *J* = 12.5 Hz), 148.96 (d, *J* = 6.7 Hz), 141.87 (d, *J* = 2.9 Hz), 136.18, 133.48, 132.63 (d, *J* = 2.9 Hz), 132.22 (d, *J* = 2.8 Hz), 131.90 (d, *J* = 2.9 Hz), 131.35 (d, *J* = 3.8 Hz), 131.26 (d, *J* = 4.0 Hz), 130.73 (d, *J* = 11.5 Hz), 128.98 (d, *J* = 5.5 Hz), 128.86 (d, *J* = 4.1 Hz), 128.62, 128.35, 128.21 (d, *J* = 4.9 Hz), 110.75 (d, *J* = 2.8 Hz), 108.84 (d, *J* = 6.2 Hz), 36.43, 35.90 (d, *J* = 70.6 Hz).

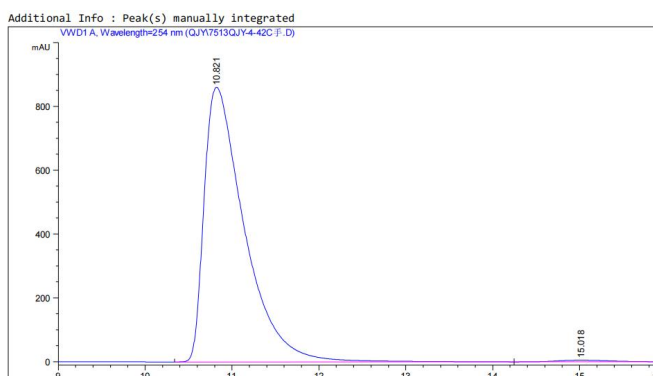
³¹P NMR (162 MHz, Chloroform-*d*) δ 32.80.

HRMS (ESI⁺, *m/z*): calcd for C₂₅H₂₂O₃P [M+H]⁺ : 401.1301, found 401.1299.

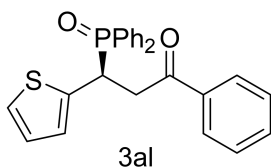
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 10.82(major) and 15.01 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.797	MM	0.4560	2841.81323	103.86420	49.8555
2	14.123	MM	0.6850	2858.28906	69.54278	50.1445



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.821	BB	0.4802	2.76686e4	860.33020	99.0533
2	15.018	BB	0.7109	264.45032	5.49071	0.9467



(S)-3-(diphenylphosphoryl)-1-phenyl-3-(thiophen-2-yl)propan-1-one (3aI)^[2]

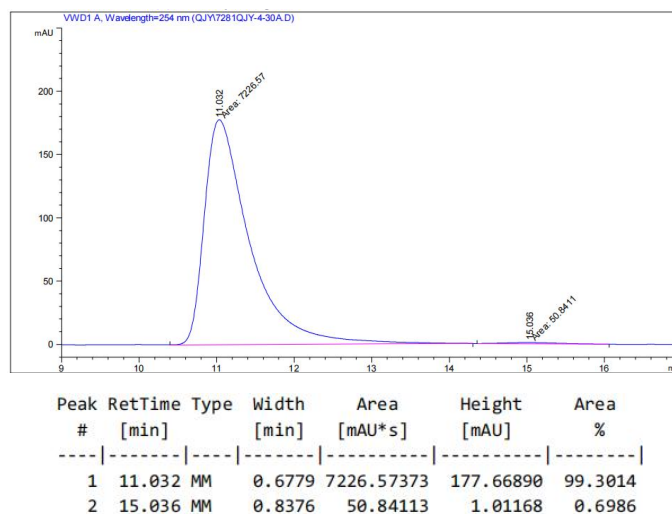
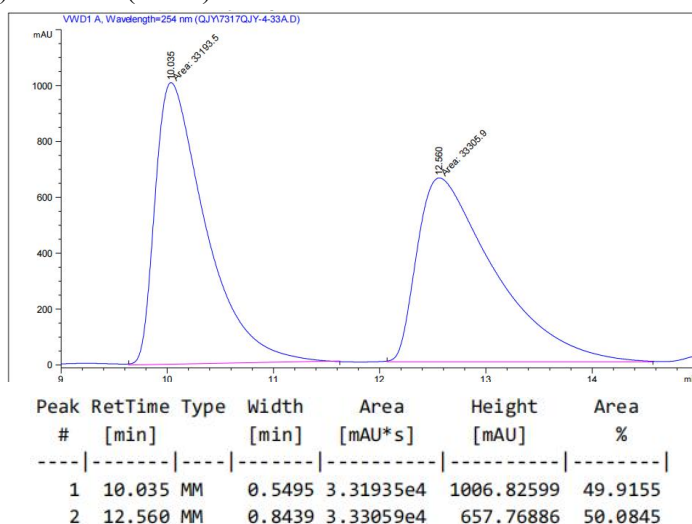
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 93% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.85 (m, 2H), 7.78 (d, *J* = 7.7 Hz, 2H), 7.54 – 7.48 (m, 2H), 7.46 – 7.40 (m, 4H), 7.37 – 7.26 (m, 3H), 7.28 – 7.19 (m, 2H), 6.97 – 6.91 (m, 2H), 6.71 (t, *J* = 4.2 Hz, 1H), 4.76 (ddd, *J* = 10.2, 7.8, 2.5 Hz, 1H), 3.89 (ddd, *J* = 17.7, 10.3, 4.0 Hz, 1H), 3.27 (ddd, *J* = 17.9, 10.4, 2.6 Hz, 1H).

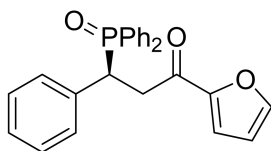
¹³C NMR (101 MHz, Chloroform-*d*) δ 195.24 (d, *J* = 12.8 Hz), 136.45 (d, *J* = 6.5 Hz), 132.44, 131.56 (d, *J* = 2.9 Hz), 131.15 (d, *J* = 2.9 Hz), 130.67 (d, *J* = 2.9 Hz), 130.23, 130.14, 130.02, 129.93, 129.70, 129.58, 128.01, 127.91 (d, *J* = 3.8 Hz), 127.80, 127.53, 127.24, 127.12, 127.10, 126.34 (d, *J* = 6.4 Hz), 125.69 (d, *J* = 2.5 Hz), 123.87 (d, *J* = 2.9 Hz), 38.80 (d, *J* = 1.6 Hz), 35.42 (d, *J* = 70.9 Hz).

³¹P NMR (162 MHz, Chloroform-*d*) δ 33.30.

HRMS (ESI⁺, *m/z*): calcd for C₂₅H₂₂O₂PS [M+H]⁺ : 417.1073, found 417.1077.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 10.03(major) and 15.03(minor)





3am

(S)-3-(diphenylphosphoryl)-1-(furan-2-yl)-3-phenylpropan-1-one (3am)

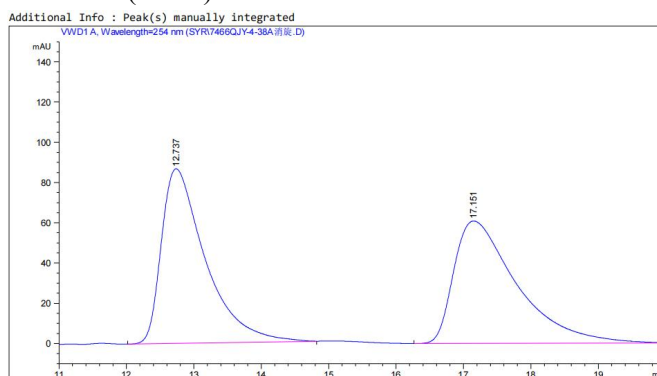
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 90% yield, 99% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.88 (m, 2H), 7.51 (m, 3H), 7.47 – 7.40 (m, 3H), 7.36 – 7.27 (m, 3H), 7.22 (td, *J* = 7.5, 3.1 Hz, 2H), 7.16 – 7.04 (m, 4H), 6.40 (dd, *J* = 3.6, 1.7 Hz, 1H), 4.39 (ddd, *J* = 10.2, 6.9, 2.8 Hz, 1H), 3.85 (ddd, *J* = 17.5, 10.7, 5.1 Hz, 1H), 3.17 (ddd, *J* = 17.6, 10.7, 2.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 185.68 (d, *J* = 14.1 Hz), 152.06 (d, *J* = 1.6 Hz), 146.85, 135.33 (d, *J* = 5.6 Hz), 132.15 (d, *J* = 2.7 Hz), 131.55 (d, *J* = 2.8 Hz), 131.35, 131.26, 130.98, 130.89, 130.78 (d, *J* = 1.5 Hz), 130.60 (d, *J* = 13.2 Hz), 129.83 (d, *J* = 5.6 Hz), 129.05, 128.93, 128.33 (d, *J* = 1.9 Hz), 128.20, 128.08, 127.19 (d, *J* = 2.5 Hz), 118.13, 112.32, 40.82 (d, *J* = 69.2 Hz), 38.49.

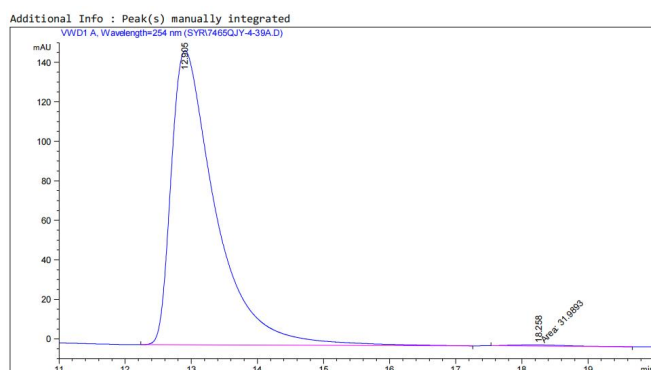
³¹P NMR (162 MHz, CDCl₃) δ 34.46.

HRMS (ESI⁺, *m/z*): calcd for C₂₅H₂₂O₃P[M+H]⁺ : 401.1301, found: 401.1299.

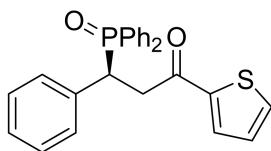
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 12.90 (major) and 18.25 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.737	BB	0.6698	3925.57568	86.77723	49.8494
2	17.151	BB	0.9642	3949.30225	60.85100	50.1506



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.905	BB	0.6859	6915.37988	148.87871	99.5395
2	18.258	MM	0.9252	31.98934	5.76284e-1	0.4605



3an

(S)-3-(diphenylphosphoryl)-3-phenyl-1-(thiophen-2-yl)propan-1-one (3an)

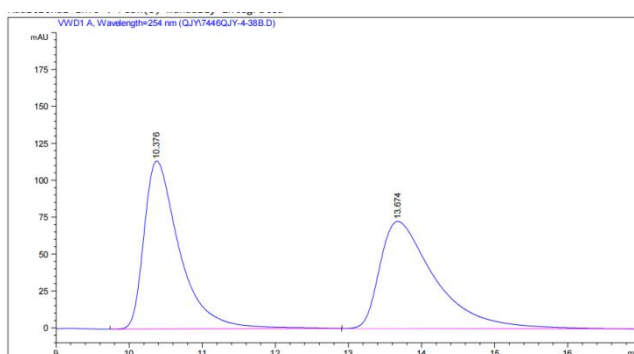
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 89% yield, 96% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (m, 2H), 7.64 (d, *J* = 3.8 Hz, 1H), 7.57 – 7.49 (m, 4H), 7.47 – 7.41 (m, 2H), 7.40 – 7.30 (m, 3H), 7.23 (td, *J* = 7.7, 2.9 Hz, 2H), 7.17 – 7.06 (m, 3H), 7.06 – 6.99 (m, 1H), 4.42 (ddd, *J* = 9.9, 6.8, 2.6 Hz, 1H), 3.93 (ddd, *J* = 17.6, 10.6, 4.5 Hz, 1H), 3.31 (ddd, *J* = 17.6, 10.8, 2.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.73 (d, *J* = 13.9 Hz), 143.58 (d, *J* = 1.6 Hz), 135.28 (d, *J* = 5.6 Hz), 134.34, 132.73, 132.23 (d, *J* = 2.7 Hz), 131.61 (d, *J* = 3.0 Hz), 131.30, 131.21, 130.94, 130.85, 130.72 (d, *J* = 11.5 Hz), 129.78 (d, *J* = 5.6 Hz), 129.09 (d, *J* = 6.2 Hz), 128.97 (d, *J* = 7.7 Hz), 128.36 (d, *J* = 1.9 Hz), 128.23, 128.11, 127.23 (d, *J* = 2.5 Hz), 49.58 (dt, *J* = 42.9, 21.4 Hz), 41.19 (d, *J* = 69.1 Hz), 39.22.

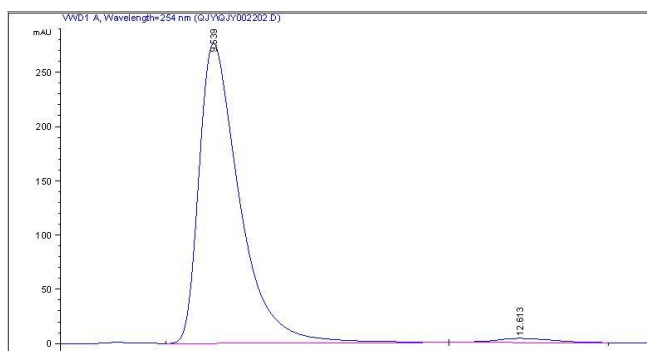
³¹P NMR (162 MHz, CDCl₃) δ 34.25.

HRMS (ESI⁺, *m/z*): calcd for C₂₅H₂₂O₂PS [M+H]⁺ : 417.1073, found: 417.1068.

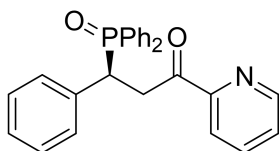
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.54(major) and 12.61 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.376	BB	0.5048	3840.66528	113.76929	50.1667
2	13.674	BB	0.7797	3815.14063	72.53152	49.8333



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.539	BB	0.4236	7788.19971	276.48401	98.0783
2	12.613	BB	0.5545	152.59601	3.88254	1.9217



3ao

(S)-3-(diphenylphosphoryl)-3-phenyl-1-(pyridin-2-yl)propan-1-one (3ao)^[2]

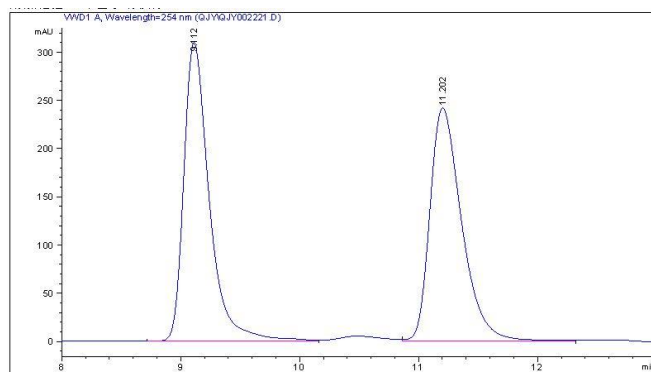
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1), White solid, 94% yield, 99% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.86 (m, 2H), 7.74 (d, *J* = 8.8 Hz, 2H), 7.59 – 7.48 (m, 3H), 7.45 – 7.33 (m, 3H), 7.33 – 7.21 (m, 4H), 7.18 – 7.05 (m, 3H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.50 (ddd, *J* = 10.4, 6.6, 2.5 Hz, 1H), 3.98 (ddd, *J* = 17.8, 10.4, 4.7 Hz, 1H), 3.26 (ddd, *J* = 17.8, 11.2, 2.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 195.20 (d, *J* = 13.4 Hz), 135.80 (d, *J* = 5.6 Hz), 132.79, 132.13 (d, *J* = 2.8 Hz), 131.96, 131.73, 131.51 (d, *J* = 2.8 Hz), 131.34, 131.26, 130.98 (d, *J* = 4.6 Hz), 130.91, 130.87, 130.78, 129.80 (d, *J* = 5.7 Hz), 129.06, 128.95, 128.37 (d, *J* = 1.9 Hz), 128.18, 128.07, 127.16 (d, *J* = 2.5 Hz), 115.81, 115.59, 41.09 (d, *J* = 69.0 Hz), 38.86.

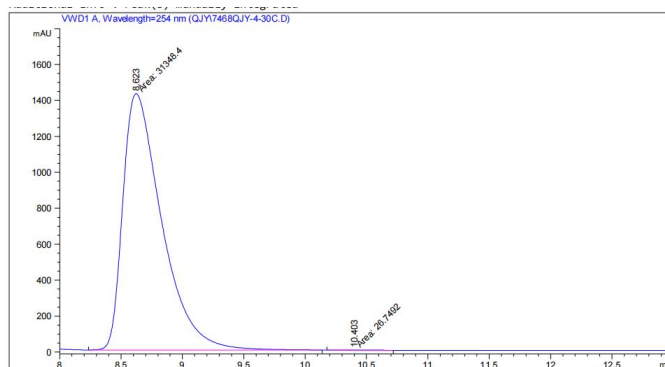
³¹P NMR (162 MHz, CDCl₃) δ 33.70.

HRMS (ESI⁺, *m/z*): calcd for C₂₆H₂₃NO₂P [M+H]⁺ : 412.1461, found: 412.1469.

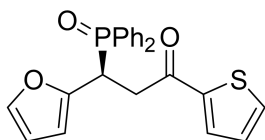
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 8.62 (major) and 10.40 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.112	BV	0.2249	4615.63574	309.64758	50.9032
2	11.202	VB	0.2821	4451.83301	241.49976	49.0968



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.623	MM	0.3664	3.13484e4	1425.93701	99.9147
2	10.403	MM	0.3043	26.74918	1.46518	0.0853



3ap

(S)-3-(diphenylphosphoryl)-3-(furan-2-yl)-1-(thiophen-2-yl)propan-1-one (3ap)

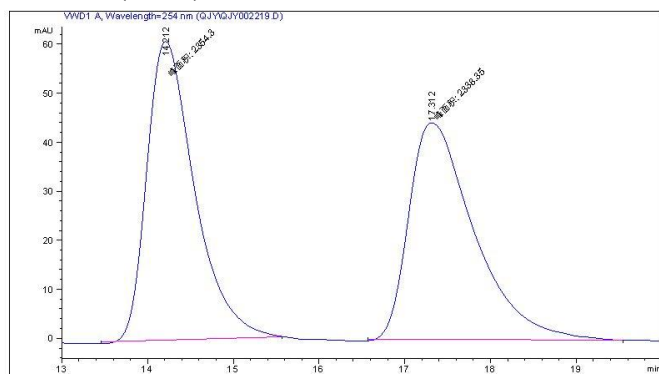
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 90% yield, 98% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.86 (m, 2H), 7.71 (dd, J = 3.8, 1.2 Hz, 1H), 7.62 – 7.44 (m, 7H), 7.41 – 7.34 (m, 2H), 7.18 (m, 1H), 7.09 (dd, J = 5.0, 3.8 Hz, 1H), 6.20 – 6.14 (m, 1H), 6.09 (t, J = 3.2 Hz, 1H), 4.73 – 4.63 (m, 1H), 3.87 (ddd, J = 17.5, 10.8, 4.7 Hz, 1H), 3.33 (ddd, J = 17.5, 9.8, 2.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.32 (d, J = 13.0 Hz), 141.97 (d, J = 2.9 Hz), 134.32, 132.62 (d, J = 3.5 Hz), 132.25 (d, J = 2.7 Hz), 131.91 (d, J = 2.8 Hz), 131.35, 131.25 (d, J = 1.7 Hz), 131.15, 130.75, 130.64, 128.98 (d, J = 2.4 Hz), 128.86, 128.29 (d, J = 11.7 Hz), 110.73 (d, J = 2.6 Hz), 108.98 (d, J = 5.9 Hz), 36.96, 36.00 (d, J = 70.3 Hz).

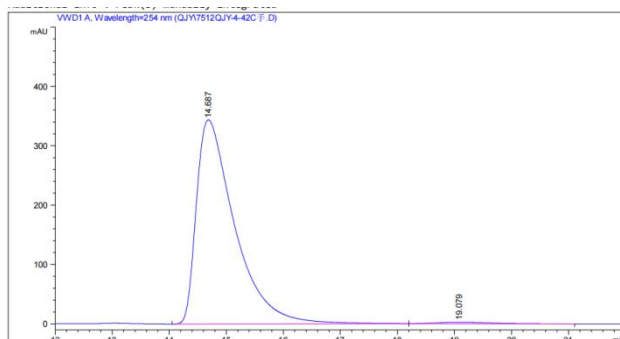
³¹P NMR (162 MHz, Chloroform-*d*) δ 32.46.

HRMS (ESI⁺, m/z): calcd for C₂₃H₂₀O₃PS [M+H]⁺: 407.0865, found: 407.0868.

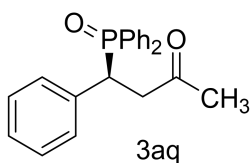
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 14.68 (major) and 19.07(minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.212	MM	0.6444	2354.29712	60.88744	50.1699
2	17.312	MM	0.8822	2338.34839	44.17653	49.8301



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.687	BB	0.6928	1.60280e4	343.89383	99.0574
2	19.079	BB	0.8606	152.52225	2.38031	0.9426



(S)-4-(diphenylphosphoryl)-4-phenylbutan-2-one (3aq)^[2]

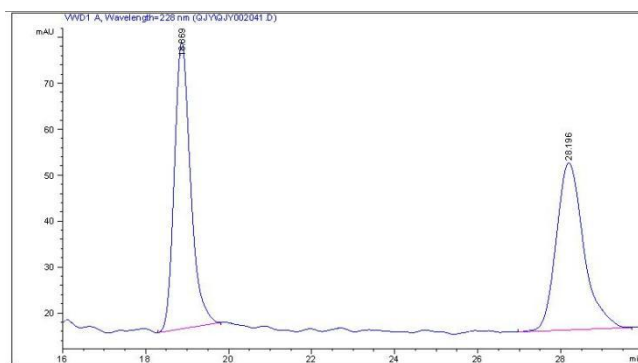
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 7:1). White solid, 84% yield, 93% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 7.89 (m, 2H), 7.54 (m, 3H), 7.43 (dd, *J* = 11.3, 7.7 Hz, 2H), 7.38 – 7.19 (m, 5H), 7.16 (m, 3H), 4.22 (ddd, *J* = 10.1, 7.0, 2.8 Hz, 1H), 3.34 (ddd, *J* = 18.0, 10.2, 5.3 Hz, 1H), 2.94 (ddd, *J* = 18.1, 11.1, 2.9 Hz, 1H), 1.96 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 205.40 (d, *J* = 12.8 Hz), 135.66 (d, *J* = 5.6 Hz), 132.06 (d, *J* = 2.7 Hz), 131.67 (d, *J* = 11.1 Hz), 131.46 (d, *J* = 2.8 Hz), 131.29, 131.21, 130.94, 130.86, 130.74 (d, *J* = 1.6 Hz), 129.67 (d, *J* = 5.7 Hz), 128.95, 128.84, 128.32 (d, *J* = 2.0 Hz), 128.12, 128.00, 127.12 (d, *J* = 2.5 Hz), 43.43, 40.97 (d, *J* = 68.7 Hz), 30.62.

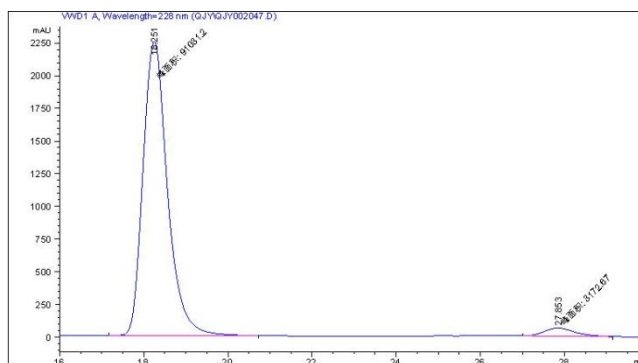
³¹P NMR (162 MHz, Chloroform-*d*) δ 33.84.

HRMS (ESI⁺, *m/z*): calcd for C₂₂H₂₂O₂P [M+H]⁺: 349.1352, found: 349.1352.

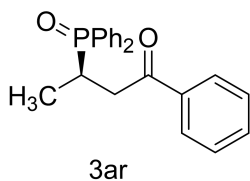
HPLC analysis: Chiralcel-ADH, n-heptane/*i*-PrOH = 70:30, 0.5 mL/min, 22°C, detection at 228nm. Retention time (min): 18.25 (minor) and 27.85 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.869	BB	0.4157	1703.32458	62.35729	50.5669
2	28.196	BB	0.6921	1665.13440	36.36980	49.4331



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.251	MM	0.6733	9.10312e4	2253.44946	96.6321
2	27.853	MM	0.8425	3172.66870	62.76096	3.3679



(S)-3-(diphenylphosphoryl)-1-phenylbutan-1-one (3ar)

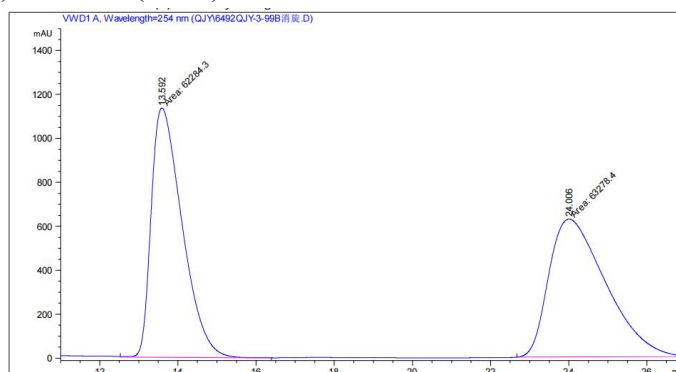
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). colorless oi, 78% yield, 85% ee] $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.95 – 7.88 (m, 2H), 7.86 (m, 4H), 7.57 – 7.47 (m, 4H), 7.51 – 7.39 (m, 5H), 3.45 – 3.27 (m, 2H), 3.16 – 3.03 (m, 1H), 1.21 (dd, $J = 16.5, 6.6$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 197.58 (d, $J = 14.1$ Hz), 136.50, 133.46, 132.03 (d, $J = 6.8$ Hz), 131.88 (d, $J = 2.6$ Hz), 131.78 (d, $J = 2.7$ Hz), 131.01, 130.92, 130.82, 128.93, 128.80 (d, $J = 3.5$ Hz), 128.67, 128.63, 128.12, 38.02, 27.53 (d, $J = 74.1$ Hz), 13.03 (d, $J = 2.8$ Hz).

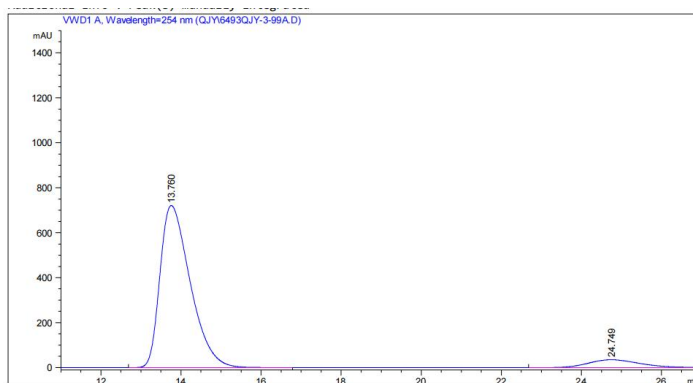
$^{31}\text{P NMR}$ (162 MHz, Chloroform-*d*) δ 37.46.

HRMS (ESI⁺, *m/z*): calcd for C₂₂H₂₂O₂P [M+H]⁺ : 349.1352, found: 349.1352.

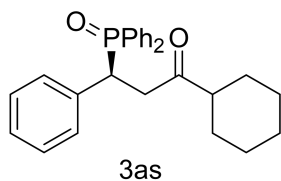
HPLC analysis: Chiracel-ASH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 13.76 (major) and 24.74 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.592	MM	0.9153	6.22843e4	1134.12805	49.6041
2	24.006	MM	1.6815	6.32784e4	627.21631	50.3959



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.760	BB	0.8070	3.77680e4	721.18488	92.2721
2	24.749	BB	1.3766	3163.10474	35.02539	7.7279



(S)-1-cyclohexyl-3-(diphenylphosphoryl)-3-phenylpropan-1-one (3as)^[3]

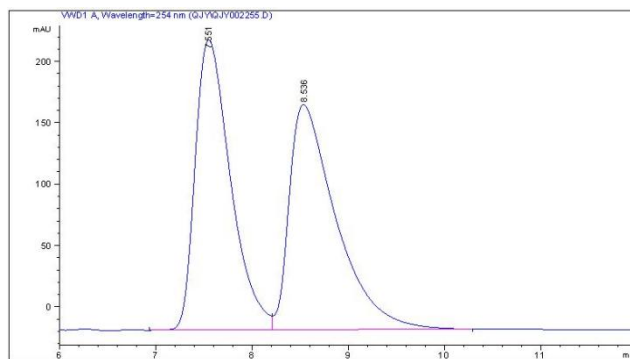
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid 91% yield, 92% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.03 – 7.87 (m, 2H), 7.56 – 7.49 (m, 3H), 7.47 – 7.40 (m, 2H), 7.33 – 7.26 (m, 3H), 7.22 (td, *J* = 7.7, 2.6 Hz, 2H), 7.20 – 7.09 (m, 3H), 4.26 (ddd, *J* = 10.0, 6.7, 2.9 Hz, 1H), 3.37 (ddd, *J* = 17.9, 10.0, 5.2 Hz, 1H), 2.89 (ddd, *J* = 17.9, 11.3, 3.0 Hz, 1H), 2.10 (ddd, *J* = 11.1, 7.7, 3.4 Hz, 1H), 1.70 – 1.47 (m, 5H), 1.17 – 0.92 (m, 5H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 210.68 (d, *J* = 12.0 Hz), 136.03 (d, *J* = 5.3 Hz), 132.23 – 131.79 (m), 131.40 (d, *J* = 3.2 Hz), 131.29, 131.14, 130.96, 130.88, 129.76 (d, *J* = 5.5 Hz), 128.93, 128.82, 128.28 (d, *J* = 1.6 Hz), 128.13, 128.02, 127.03 (d, *J* = 2.2 Hz), 51.11, 41.50 – 40.31 (m), 27.78 (d, *J* = 3.8 Hz), 25.66, 25.38 (d, *J* = 10.0 Hz).

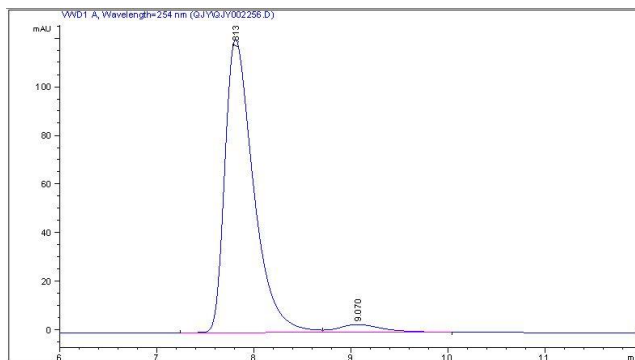
³¹P NMR (162 MHz, CDCl₃) δ 34.55.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₃₀O₂P [M+H]⁺: 417.1978, found: 417.1975.

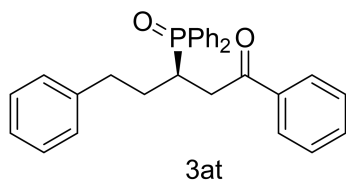
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.81 (major) and 9.07 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.551	BV	0.3937	6031.98975	236.41457	49.3736
2	8.536	VB	0.5006	6185.04639	183.34062	50.6264



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.813	BV	0.3108	2466.03271	120.47008	95.9194
2	9.070	VB	0.4622	104.91032	3.30607	4.0806



(S)-3-(diphenylphosphoryl)-1,5-diphenylpentan-1-one (3at)

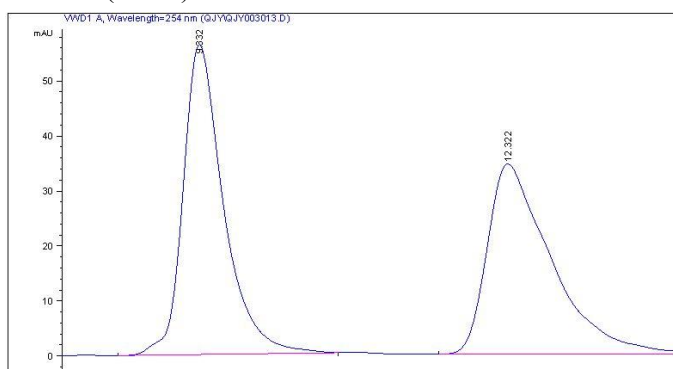
[Purification by flash column chromatography on silica gel(eluent, DCM: MeOH = 70:1). colorless oil, 87% yield, 99% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 (d, J = 7.3 Hz, 2H), 7.85 – 7.73 (m, 4H), 7.57 – 7.33 (m, 9H), 7.26 – 7.06 (m, 3H), 6.98 (d, J = 6.9 Hz, 2H), 3.54 – 3.44 (m, 1H), 3.43 – 3.22 (m, 2H), 2.67 (ddd, J = 14.9, 10.2, 5.1 Hz, 1H), 2.44 (ddd, J = 13.7, 10.1, 6.7 Hz, 1H), 2.12 – 1.85 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 197.55 (d, J = 10.5 Hz), 141.16, 136.29, 133.47, 132.46 (d, J = 3.2 Hz), 131.77 (d, J = 2.8 Hz), 131.51 (d, J = 2.3 Hz), 130.99 (d, J = 1.9 Hz), 130.91 (d, J = 1.9 Hz), 128.82 (d, J = 2.7 Hz), 128.70 (d, J = 2.6 Hz), 128.65, 128.46, 128.35, 128.11, 126.00, 37.02, 33.86 (d, J = 10.3 Hz), 31.79, 31.07, 30.64 (d, J = 1.5 Hz).

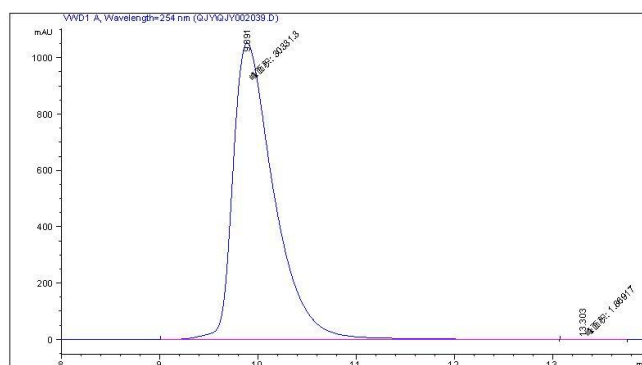
³¹P NMR (162 MHz, CDCl₃) δ 34.55.

HRMS (ESI⁺, m/z): calcd for C₂₉H₂₈O₂P [M+H]⁺ : 439.1821, found: 439.1824.

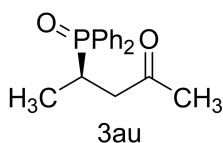
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 9.89(minor) and 13.30(minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.332	BB	0.4084	1537.26294	56.32273	50.7832
2	12.322	BB	0.6030	1489.84802	34.55276	49.2168



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.891	MM	0.4807	3.03313e4	1051.64954	99.9938
2	13.303	MM	0.3407	1.86917	9.14463e-2	6.162e-3



(S)-4-(diphenylphosphoryl)pentan-2-one(3au)

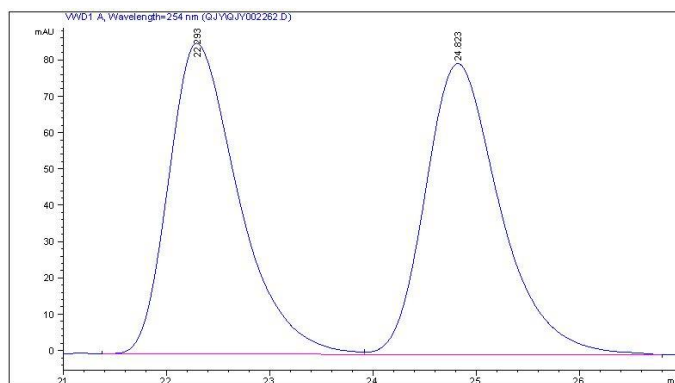
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). colorless oil., 72% yield, 91% ee] $^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.83 – 7.72 (m, 4H), 7.55 – 7.40 (m, 6H), 3.13 – 3.02 (m, 1H), 2.76 – 2.56 (m, 2H), 2.06 (s, 3H), 1.10 (dd, $J = 16.4, 7.0$ Hz, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 206.20 (d, $J = 13.4$ Hz), 131.86 (d, $J = 2.9$ Hz), 131.77 (d, $J = 2.7$ Hz), 131.00, 130.91, 130.83, 128.88, 128.76 (d, $J = 2.2$ Hz), 128.63, 42.83, 30.60, 27.23 (d, $J = 73.9$ Hz), 12.97 (d, $J = 2.9$ Hz).

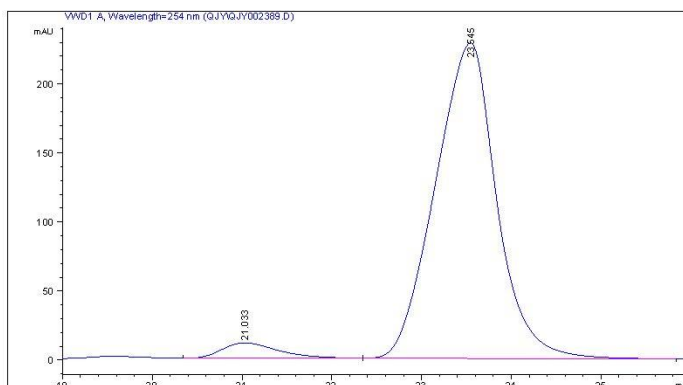
$^{31}\text{P NMR}$ (162 MHz, CDCl_3) δ 34.65.

HRMS (ESI⁺, m/Z): calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2\text{P}$ $[\text{M}+\text{H}]^+$: 287.1195, found: 287.1195.

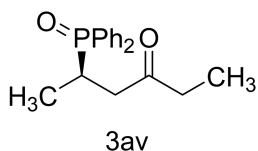
HPLC analysis: Chiralcel-ADH, n-heptane/*i*-PrOH=90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 21.03(minor) and 23.54(major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	22.293	BV	0.7062	4013.60522	85.57813	49.9916
2	24.823	VB	0.7584	4014.95630	80.01646	50.0084



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.033	BB	0.6507	485.96890	11.23368	4.2998
2	23.545	BB	0.7215	1.08161e4	228.38295	95.7002



(S)-5-(diphenylphosphoryl)hexan-3-one(3av)

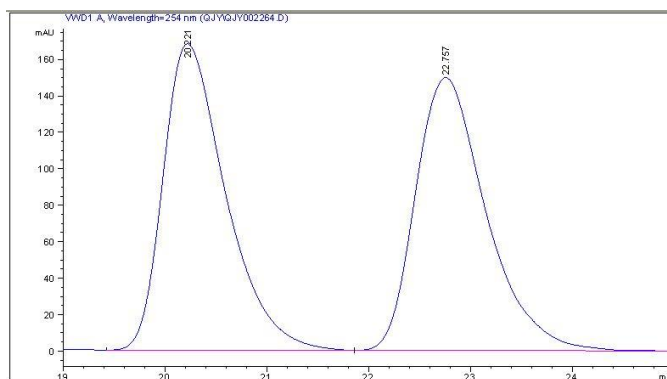
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). colorless oil, 85% yield, 92% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.82 – 7.71 (m, 4H), 7.50 – 7.39 (m, 6H), 3.11-3.08 (m, 1H), 2.67 – 2.54 (m, 2H), 2.29 (q, *J* = 7.3 Hz, 2H), 1.08 (dd, *J* = 16.4, 7.0 Hz, 3H), 0.93 (t, *J* = 7.3 Hz, 3H)..

¹³C NMR (101 MHz, Chloroform-*d*) δ 207.99 (d, *J* = 12.9 Hz), 130.79 (d, *J* = 2.8 Hz), 130.71 (d, *J* = 2.7 Hz), 129.89 (dd, *J* = 8.8, 4.7 Hz), 127.82, 127.71, 127.60, 40.48, 35.69, 26.24 (d, *J* = 73.9 Hz), 11.95 (d, *J* = 2.9 Hz), 6.62.

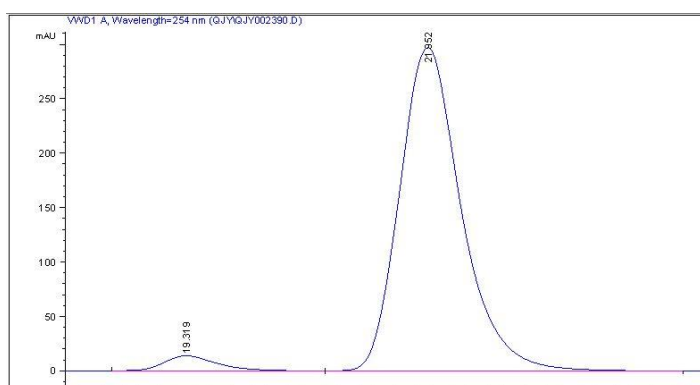
³¹P NMR (162 MHz, CDCl₃) δ 34.94.

HRMS (ESI⁺, *m/z*): calcd for C₁₈H₂₂O₂P [M+H]⁺ : 301.1352, found: 301.1353.

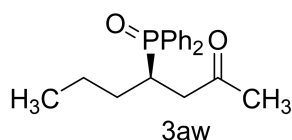
HPLC analysis: Chiracel-ADH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 19.31 (minor) and 21.95 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.221	BB	0.6474	7181.36377	168.10245	49.9157
2	22.757	BB	0.7433	7205.61719	149.77527	50.0843



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.319	BB	0.5867	525.87927	13.58196	3.6665
2	21.952	BB	0.7102	1.38171e4	296.76974	96.3335



(S)-4-(diphenylphosphoryl)heptan-2-one (3aw)

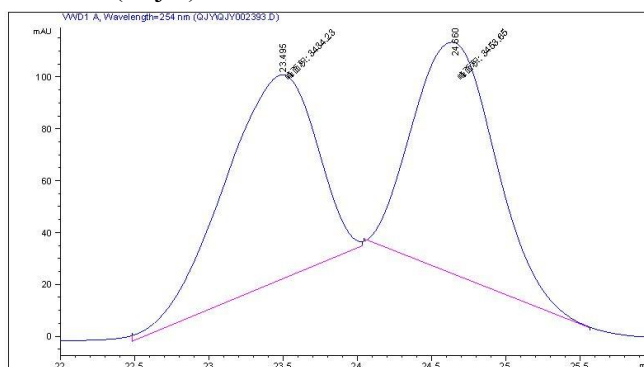
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). colorless oil., 84% yield, 99% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.87 – 7.72 (m, 4H), 7.54 – 7.38 (m, 6H), 3.18 (ddd, *J* = 10.4, 7.6, 3.9 Hz, 1H), 2.76 (ddd, *J* = 19.6, 16.0, 3.8 Hz, 1H), 2.63 (ddd, *J* = 18.8, 7.5 Hz, 1H), 1.98 (s, 3H), 1.69 – 1.39 (m, 2H), 1.27 (m, 1H), 1.12 (m, 1H), 0.78 (t, *J* = 7.3 Hz, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 206.10 (d, *J* = 9.7 Hz), 132.50, 131.74 (dd, *J* = 4.7, 2.8 Hz), 131.54, 130.99, 130.91 (d, *J* = 1.9 Hz), 130.84, 128.77, 128.65 (d, *J* = 1.3 Hz), 41.74, 31.50, 30.77, 30.67 (d, *J* = 1.9 Hz), 30.08, 20.89 (d, *J* = 11.5 Hz), 13.98.

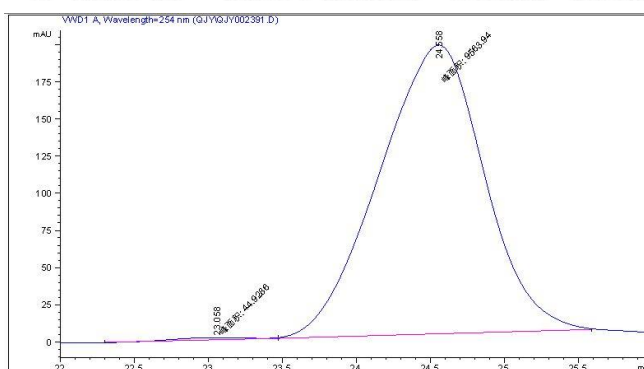
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.53.

HRMS (ESI⁺, *m/z*): calcd for C₁₉H₂₄O₂P [M+H]⁺ : 315.1508, found: 315.1508.

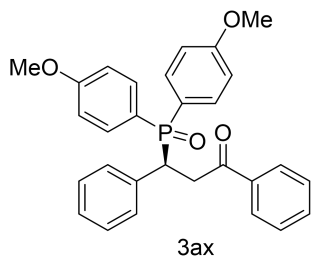
HPLC analysis: Chiracel-ADH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 23.05(minor) and 24.55 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.495	MM	0.7267	3434.22656	78.76094	49.8590
2	24.660	MM	0.6440	3453.64600	89.37630	50.1410



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	23.058	MM	0.5386	44.92859	1.39030	0.4676
2	24.558	MM	0.8213	9563.94043	194.07855	99.5324



(S)-3-(bis(4-methoxyphenyl)phosphoryl)-1,3-diphenylpropan-1-one(3ax)^[2]

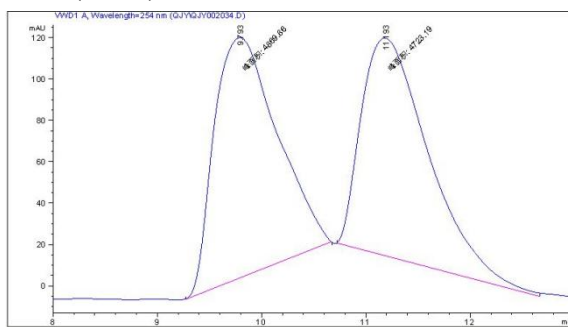
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 85% yield, 97% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.91 – 7.80 (m, 4H), 7.50 – 7.45 (m, 1H), 7.39 – 7.25 (m, 6H), 7.19 – 7.08 (m, 3H), 7.02 – 6.96 (m, 2H), 6.76 – 6.69 (m, 2H), 4.36 (ddd, *J* = 10.0, 7.2, 2.5 Hz, 1H), 3.97 (ddd, *J* = 18.1, 10.3, 4.4 Hz, 1H), 3.80 (s, 3H), 3.71 (s, 3H), 3.39 (ddd, *J* = 18.1, 11.2, 2.4 Hz, 1H)..

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.89 (d, *J* = 13.3 Hz), 136.47 – 136.20 (m), 133.35, 133.16, 133.06, 132.88, 132.76 (d, *J* = 3.3 Hz), 132.62, 129.85 (d, *J* = 5.5 Hz), 128.55, 128.30 (d, *J* = 1.9 Hz), 128.12, 126.98 (d, *J* = 2.5 Hz), 114.53 (d, *J* = 2.3 Hz), 114.40 (d, *J* = 4.0 Hz), 113.66, 113.53, 55.38 (d, *J* = 5.8 Hz), 55.20, 41.53 (d, *J* = 69.7 Hz), 39.07.

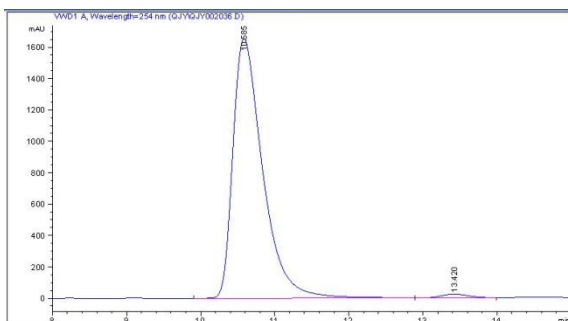
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.56.

HRMS (ESI⁺, *m/z*): calcd for C₂₉H₂₈O₄P [M+H]⁺ : 471.1647, found: 470.1643.

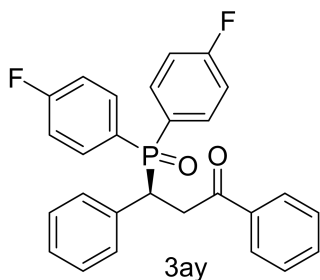
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 70:30, 0.6 mL/min, 22°C, detection at 254nm. Retention time (min): 10.58(major) and 13.42 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.793	MM	0.6991	4869.85693	116.09930	50.7644
2	11.193	MM	0.7477	4723.19336	105.28025	49.2356



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.585	BB	0.4236	4.62206e4	1656.04065	98.5990
2	13.420	BV	0.4068	656.75177	24.97425	1.4010



(S)-3-(bis(4-fluorophenyl)phosphoryl)-1,3-diphenylpropan-1-one (3ay)

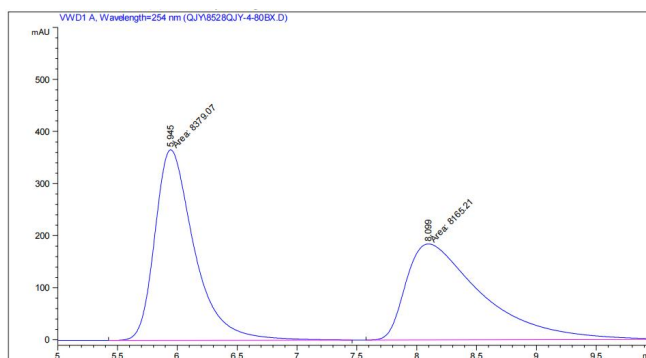
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH =70:1). White solid, 82% yield, 99% ee]¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (m, 2H), 7.86 – 7.82 (m, 2H), 7.53 – 7.47 (m, 1H), 7.44 – 7.33 (m, 6H), 7.24 – 7.09 (m, 5H), 6.94 (td, J = 8.8, 2.2 Hz, 2H), 4.43 (ddd, J = 9.7, 6.8, 2.6 Hz, 1H), 3.99 (ddd, J = 18.2, 10.0, 4.8 Hz, 1H), 3.38 (ddd, J = 18.2, 11.8, 2.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.44 (d, J = 12.9 Hz), 136.17, 135.61 (d, J = 5.6 Hz), 133.89, 133.80, 133.70, 133.56, 133.48, 133.39 (d, J = 1.6 Hz), 133.29, 129.78 (d, J = 5.8 Hz), 128.64, 128.51 (d, J = 2.0 Hz), 128.12, 127.34 (d, J = 2.5 Hz), 116.51 (dd, J = 21.4, 12.3 Hz), 115.60 (dd, J = 21.4, 13.0 Hz), 41.18 (d, J = 70.3 Hz), 38.89.

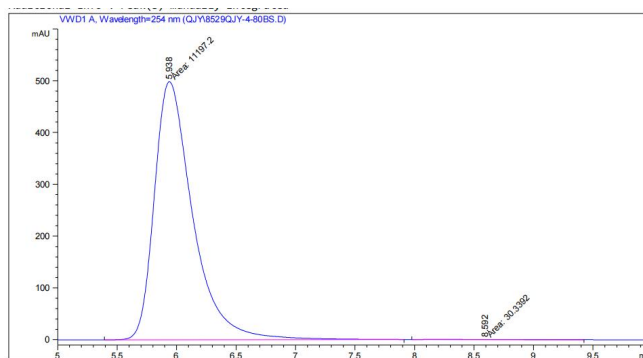
³¹P NMR (162 MHz, Chloroform-*d*) δ 34.57.

HRMS (ESI⁺, *m/z*): calcd for C₂₇H₂₂O₂F₂P [M+H]⁺ :447.1320, found: 447.1316.

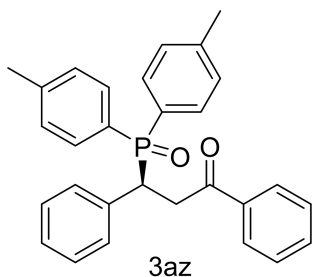
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 5.93 (major) and 8.59 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.945	MM	0.3818	8379.07227	365.81290	50.6463
2	8.099	MM	0.7380	8165.20703	184.38971	49.3537



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.938	MM	0.3746	1.11972e4	498.23904	99.7298
2	8.592	MM	0.8302	30.33924	6.09104e-1	0.2702



(S)-3-(di-p-tolylphosphoryl)-1,3-diphenylpropan-1-one (3az)^[2]

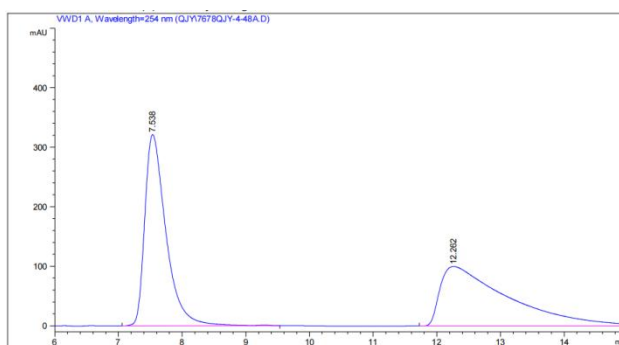
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 85% yield, 98% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.81 (m, 4H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.26 (m, 8H), 7.18 – 7.07 (m, 3H), 7.03 (dd, *J* = 8.2, 2.8 Hz, 2H), 4.42 (ddd, *J* = 9.8, 7.0, 2.4 Hz, 1H), 4.01 (ddd, *J* = 18.1, 10.5, 4.2 Hz, 1H), 3.36 (ddd, *J* = 18.1, 11.1, 2.4 Hz, 1H), 2.36 (s, 3H), 2.25 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 196.81 (d, *J* = 13.5 Hz), 142.45 (d, *J* = 2.8 Hz), 141.75 (d, *J* = 2.7 Hz), 136.38, 136.20 (d, *J* = 5.6 Hz), 133.35, 131.31, 131.22, 131.02, 130.93, 129.92, 129.86, 129.76, 129.64, 128.92, 128.79, 128.54, 128.30 (d, *J* = 2.0 Hz), 128.13, 126.99 (d, *J* = 2.4 Hz), 41.15 (d, *J* = 69.2 Hz), 39.13, 31.62, 22.70, 21.60, 21.52, 14.20.

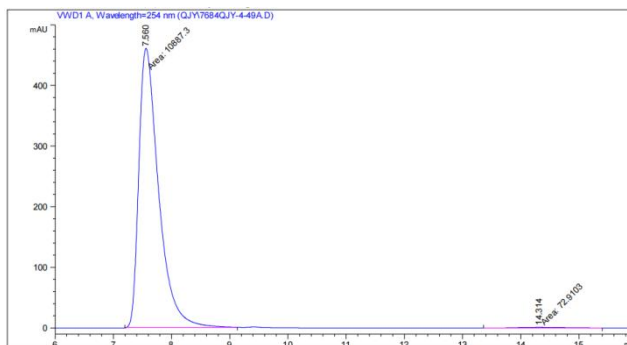
³¹P NMR (162 MHz, Chloroform-*d*) δ 33.99.

HRMS (ESI⁺, *m/z*): calcd for C₂₉H₂₈O₂P [M+H]⁺: 439.1827, found 439.1829.

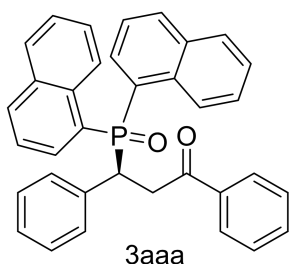
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 7.56 (major) and 14.31 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.538	BV R	0.3487	7427.11426	321.33218	49.6754
2	12.262	BB	1.0276	7524.16504	99.90671	50.3246



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.560	MM	0.3941	1.08873e4	460.41727	99.3348
2	14.314	MM	1.0149	72.91031	1.19734	0.6652



(S)-3-(di(naphthalen-1-yl)phosphoryl)-1,3-diphenylpropan-1-one (3aaa)^[3]

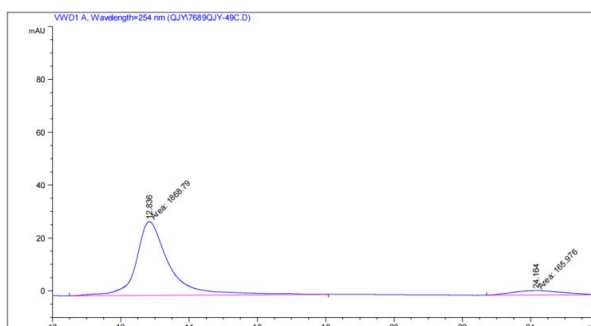
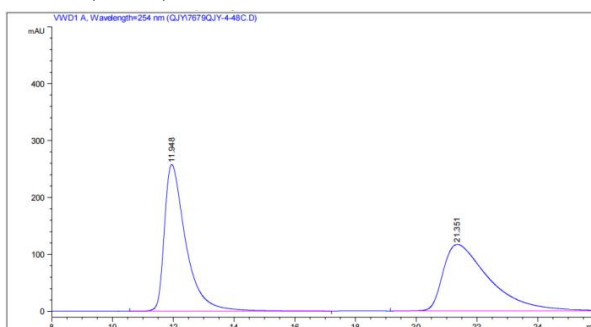
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH= 70:1). White solid, 80% yield, 84% ee] ¹H NMR (400 MHz, Chloroform-*d*) δ 8.87 – 8.80 (m, 1H), 8.67 – 8.57 (m, 1H), 8.20 (ddd, *J* = 13.3, 7.2, 1.1 Hz, 1H), 7.97 (d, *J* = 8.1 Hz, 1H), 7.87 (m, 3H), 7.81 – 7.72 (m, 2H), 7.68 – 7.60 (m, 1H), 7.59 – 7.21 (m, 11H), 7.00 – 6.82 (m, 3H), 4.97 (ddd, *J* = 9.8, 7.0, 2.1 Hz, 1H), 4.32 (ddd, *J* = 18.5, 10.4, 3.7 Hz, 1H), 3.88 (ddd, *J* = 18.5, 10.7, 2.1 Hz, 1H).

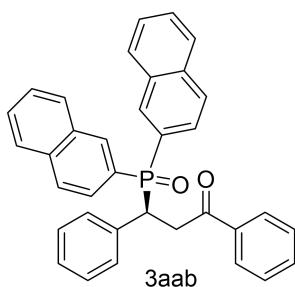
¹³C NMR (101 MHz, Chloroform-*d*) δ 196.98 (d, *J* = 13.3 Hz), 136.42, 136.25 (d, *J* = 5.0 Hz), 134.27 (d, *J* = 8.6 Hz), 134.07 (d, *J* = 7.1 Hz), 133.72 (d, *J* = 3.1 Hz), 133.50, 133.39 (d, *J* = 2.8 Hz), 133.26 (d, *J* = 9.4 Hz), 132.80 (d, *J* = 2.9 Hz), 132.52 (d, *J* = 9.9 Hz), 130.84 (d, *J* = 9.6 Hz), 129.73 (d, *J* = 5.8 Hz), 128.99, 128.65, 128.57, 128.22, 128.12 (d, *J* = 2.3 Hz), 127.50, 126.99, 126.95 (d, *J* = 2.9 Hz), 126.87, 126.59, 126.10 (d, *J* = 4.3 Hz), 125.95, 124.57, 124.44, 124.25, 124.12, 41.22 (d, *J* = 70.5 Hz), 40.02.

³¹P NMR (162 MHz, Chloroform-*d*) δ 34.29.

HRMS (ESI⁺, *m/z*): calcd for C₃₅H₂₈O₂P [M+H]⁺ : 511.1748, found: 511.1749.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH =90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 12.83 (major) and 24.16(minor).





(S)-3-(di(naphthalen-2-yl)phosphoryl)-1,3-diphenylpropan-1-one (3aab)^[3]

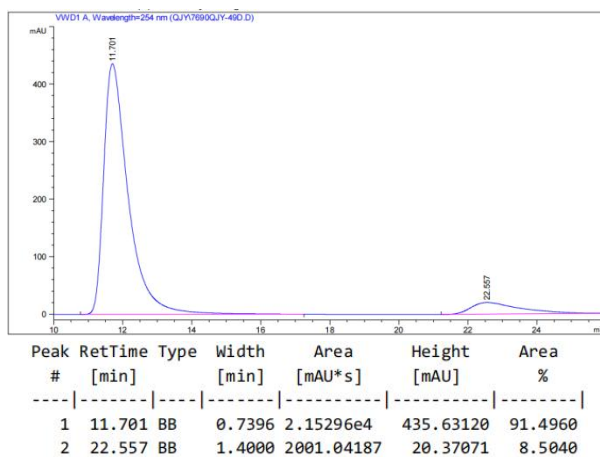
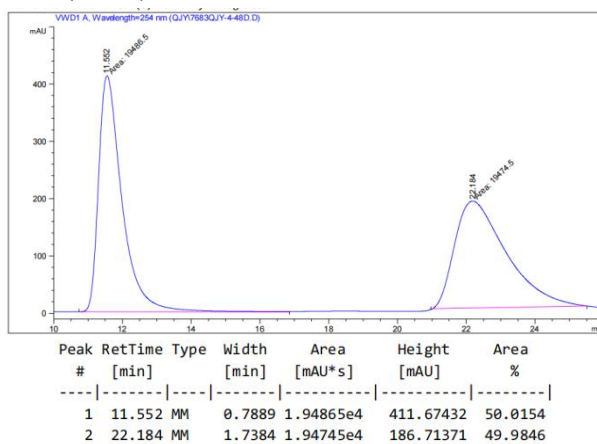
[Purification by flash column chromatography on silica gel (eluent, DCM: MeOH = 70:1). White solid, 96% yield, 83% ee]¹**H NMR** (400 MHz, Chloroform-*d*) δ 8.73 – 8.64 (m, 1H), 8.13 (dd, J = 13.3, 1.4 Hz, 1H), 8.03 – 7.91 (m, 3H), 7.89 – 7.77 (m, 3H), 7.72 (dd, J = 8.7, 2.8 Hz, 3H), 7.62 – 7.37 (m, 8H), 7.29 (t, J = 7.8 Hz, 2H), 7.14 (dd, J = 8.3, 6.7 Hz, 2H), 7.11 – 7.03 (m, 1H), 4.75 (ddd, J = 10.4, 6.7, 2.5 Hz, 1H), 4.17 – 4.04 (m, 1H), 3.47 (ddd, J = 18.1, 11.2, 2.4 Hz, 1H).

¹³**C NMR** (101 MHz, Chloroform-*d*) δ 196.68 (d, J = 13.3 Hz), 136.28, 136.00 (d, J = 5.6 Hz), 134.74 (d, J = 2.3 Hz), 134.37 (d, J = 2.4 Hz), 133.78 (d, J = 7.4 Hz), 133.39, 133.36, 133.28, 132.73 (d, J = 12.3 Hz), 132.29 (d, J = 12.8 Hz), 129.96 (d, J = 5.8 Hz), 129.10, 129.01, 128.88 (d, J = 3.7 Hz), 128.54, 128.48 (d, J = 2.0 Hz), 128.38, 128.11, 128.02, 127.89 (d, J = 3.2 Hz), 127.69, 127.23 (d, J = 2.5 Hz), 127.15, 126.72, 125.79 (d, J = 3.7 Hz), 125.70 (d, J = 3.6 Hz), 40.98 (d, J = 69.3 Hz), 39.15.

³¹**P NMR** (162 MHz, Chloroform-*d*) δ 34.42.

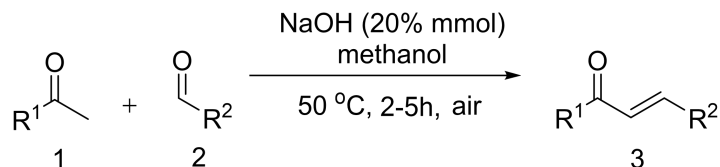
HRMS (ESI⁺, m/Z): calcd for C₃₅H₂₈O₂P [M+H]⁺ : 511.1748, found: 511.1749.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 8.07 (major) and 8.90 (minor).



3. General procedure for synthesis of α,β -Unsaturated ketone

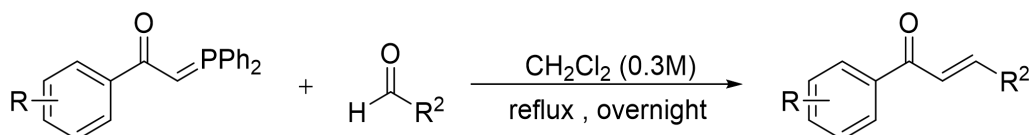
Method 1: (1c-1h ,1j-1n ,1p ,1s-1u ,1w-1z ,1ab ,1ae ,1ai ,1ak-1an ,1ap ,1as)



Scheme S1 Synthesis of α,β -unsaturated ketones.

Ketone 1 (10 mmol), Aldehydes 2 (10 mmol), NaOH (20 mol %), and methanol (20 mL) were introduced in a flask (50 mL). Then, it was stirred at 50 °C under atmosphere for 2~5 hours. After cooling down to room temperature, the reaction mixture was concentrated by removing the solvent under vacuum, and the residue was purified by column chromatography.^[4]

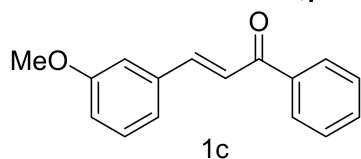
Method 2: (1aj ,1at)



Scheme S2 Synthesis of α,β -unsaturated ketones.

To a solution of the aldehyde (10 mmol, 1 equiv.) in CH_2Cl_2 (33 mL) phosphonium ylide (13 mmol, 1.3 equiv.) was added in one portion. The mixture was refluxed for 16h. Then, the solvent was evaporated and hexane was added. Triphenylphosphine oxide precipitated and was then filtered off. the filtrate was concentrated under reduced pressure. The residue was purified by flash chromatography.^[5]

Characterisation of α,β -unsaturated ketone substrates

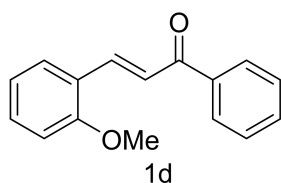


(*E*)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.04 – 7.99 (m, 2H), 7.77 (d, $J = 15.7$ Hz, 1H), 7.62 – 7.46 (m, 4H), 7.32 (t, $J = 7.9$ Hz, 1H), 7.23 (dt, $J = 7.6, 1.3$ Hz, 1H), 7.17 – 7.10 (m, 1H), 6.95 (ddd, $J = 8.1, 2.6, 1.0$ Hz, 1H), 3.83 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.57, 159.94, 144.82, 138.15, 136.24, 132.89, 130.01, 128.69, 128.56, 122.33, 121.15, 116.34, 113.45, 55.37.

White solid (2.14 g, 90% yield).

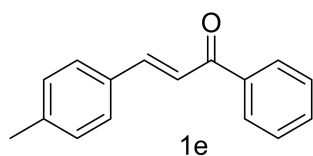


(*E*)-3-(2-methoxyphenyl)-1-phenylprop-2-en-1-one

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.13 (d, $J = 15.9$ Hz, 1H), 8.04 – 8.00 (m, 2H), 7.65 (d, $J = 2.0$ Hz, 1H), 7.63 – 7.60 (m, 1H), 7.60 – 7.54 (m, 1H), 7.52 – 7.46 (m, 2H), 7.39 – 7.35 (m, 1H), 7.00 (t, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 9.3$ Hz, 1H), 3.90 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, CDCl_3) δ 191.20, 158.82, 140.48, 138.51, 132.62, 131.85, 129.28, 128.59, 128.57, 123.87, 122.82, 120.76, 111.23, 55.57.

Yellow solid (2.18 g, 92% yield).

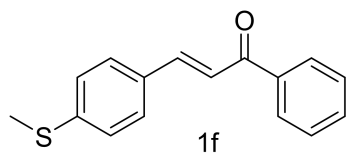


(*E*)-1-phenyl-3-(p-tolyl)prop-2-en-1-one

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 7.94 – 7.88 (m, 2H), 7.69 (d, $J = 15.7$ Hz, 1H), 7.50 – 7.34 (m, 6H), 7.11 (d, $J = 7.9$ Hz, 2H), 2.27 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.67, 144.99, 141.14, 138.37, 132.72, 132.16, 129.75, 128.63, 128.54, 128.51, 121.08, 21.58.

Yellow solid (1.82 g, 82% yield).

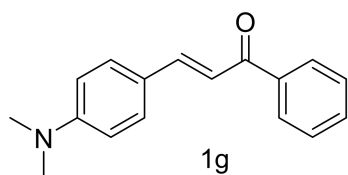


(*E*)-3-(4-(methylthio)phenyl)-1-phenylprop-2-en-1-one

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.04 – 7.98 (m, 2H), 7.77 (d, $J = 15.7$ Hz, 1H), 7.62 – 7.46 (m, 6H), 7.27 – 7.22 (m, 2H), 2.51 (s, 3H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 190.50, 144.39, 142.46, 138.29, 132.79, 131.29, 128.88, 128.66, 128.50, 125.88, 120.89, 15.10.

Yellow solid (1.96 g, 78% yield).

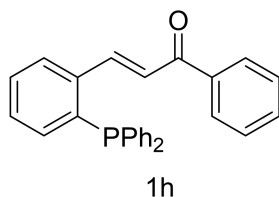


(E)-3-(4-(dimethylamino)phenyl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.06 – 7.99 (m, 2H), 7.81 (d, *J* = 15.4 Hz, 1H), 7.58 – 7.53 (m, 3H), 7.49 (dd, *J* = 8.2, 6.5 Hz, 2H), 7.34 (d, *J* = 15.5 Hz, 1H), 6.68 (d, *J* = 8.9 Hz, 2H), 3.03 (s, 6H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.57, 151.94, 145.86, 138.95, 132.13, 130.40, 128.41, 128.25, 122.40, 116.62, 111.70, 40.04.

Yellow solid (2.31 g, 92% yield).

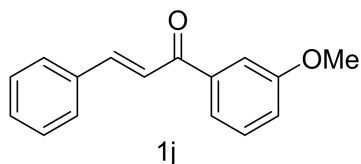


(E)-3-(2-(diphenylphosphanyl)phenyl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.36 (dd, *J* = 15.8, 4.5 Hz, 1H), 7.78 – 7.69 (m, 3H), 7.43 – 7.37 (m, 4H), 7.36 – 7.31 (m, 6H), 7.30 – 7.24 (m, 5H), 7.18 (d, *J* = 15.8 Hz, 1H), 6.98 – 6.87 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 191.97, 143.69, 143.45, 139.67 (d, *J* = 21.9 Hz), 138.43 (d, *J* = 16.4 Hz), 137.93, 135.84 (d, *J* = 9.9 Hz), 134.21, 134.01, 133.74, 132.50, 131.99 (d, *J* = 9.8 Hz), 130.02, 129.18, 129.04, 128.74, 128.71, 128.67, 128.51, 126.98 (d, *J* = 4.0 Hz), 125.60 (d, *J* = 3.2 Hz).

Yellow solid (2.66 g, 68% yield).

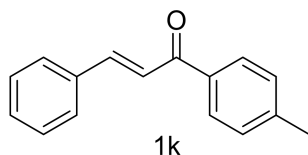


(E)-1-(3-methoxyphenyl)-3-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.77 (d, *J* = 15.7 Hz, 1H), 7.59 – 7.45 (m, 5H), 7.32 (p, *J* = 4.6 Hz, 4H), 7.05 (dd, *J* = 8.1, 2.7 Hz, 1H), 3.75 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.84, 159.89, 144.65, 139.53, 134.85, 130.56, 129.61, 128.95, 128.52, 121.94, 121.06, 119.19, 112.98, 55.31.

Yellow solid (2.02 g, 85% yield).

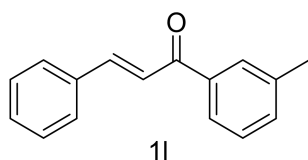


(E)-3-phenyl-1-(p-tolyl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.81 (d, *J* = 15.7 Hz, 1H), 7.67 – 7.61 (m, 2H), 7.54 (d, *J* = 15.7 Hz, 1H), 7.41 (dd, *J* = 5.0, 2.0 Hz, 3H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.02, 144.44, 143.72, 135.62, 134.99, 130.50, 129.39, 128.98, 128.71, 128.47, 122.03, 21.74.

Yellow solid (1.38 g, 62% yield).

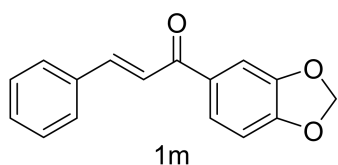


(E)-3-phenyl-1-(m-tolyl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 – 7.74 (m, 3H), 7.68 – 7.59 (m, 2H), 7.52 (d, *J* = 15.7 Hz, 1H), 7.41–7.31 (m, 5H), 2.42 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.75, 144.71, 138.51, 138.24, 134.93, 133.67, 130.57, 129.09, 129.00, 128.54, 128.51, 125.76, 122.20, 21.47.

Yellow solid (1.55 g, 70% yield).

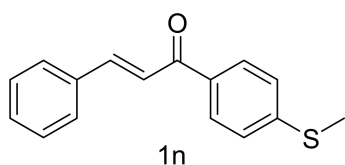


(E)-1-(benzo[d][1,3]dioxol-5-yl)-3-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.79 (d, *J* = 15.6 Hz, 1H), 7.68 – 7.61 (m, 3H), 7.53 (d, *J* = 1.7 Hz, 1H), 7.49 (d, *J* = 15.6 Hz, 1H), 7.43 – 7.39 (m, 3H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.05 (s, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 188.27, 151.75, 148.32, 144.29, 134.96, 132.93, 130.47, 128.97, 128.43, 124.74, 121.63, 108.45, 107.95, 101.93.

White solid (1.36 g, 54% yield).

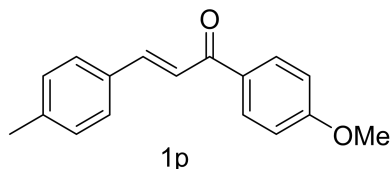


(E)-3-(3-methoxyphenyl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 15.6 Hz, 1H), 7.68 – 7.61 (m, 2H), 7.53 (d, *J* = 15.6 Hz, 1H), 7.45 – 7.39 (m, 3H), 7.30 (d, *J* = 8.5 Hz, 2H), 2.53 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.20, 145.75, 144.54, 134.93, 134.36, 130.55, 129.00, 128.48, 125.04, 121.67, 14.80.

Yellow solid (1.32 g, 52% yield).

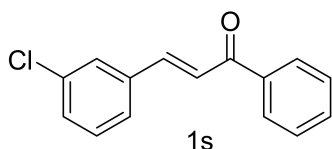


(E)-1-(4-methoxyphenyl)-3-(p-tolyl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.9 Hz, 2H), 7.79 (d, *J* = 15.6 Hz, 1H), 7.60 – 7.45 (m, 3H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.98 (d, *J* = 8.9 Hz, 2H), 3.88 (s, 3H), 2.39 (s, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 188.82, 163.36, 144.09, 140.88, 132.32, 131.20, 130.81, 129.71, 128.44, 120.79, 113.83, 55.51, 21.57.

Yellow solid (1.73g, 69% yield).

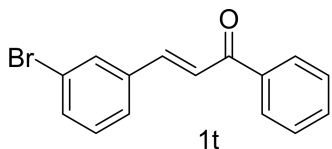


(E)-3-(3-chlorophenyl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 8.00 (m, 2H), 7.72 (d, *J* = 15.7 Hz, 1H), 7.65 – 7.55 (m, 2H), 7.57 – 7.45 (m, 4H), 7.37 – 7.32 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.10, 143.09, 137.87, 136.70, 134.97, 133.10, 130.39, 130.26, 128.75, 128.58, 127.93, 126.87, 123.15.

Yellow solid (1.59 g, 66% yield).

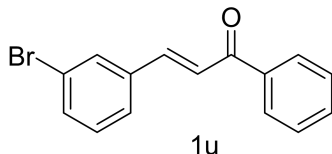


(E)-3-(3-bromophenyl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 – 7.99 (m, 2H), 7.80 (t, *J* = 1.8 Hz, 1H), 7.73 (d, *J* = 15.7 Hz, 1H), 7.65 – 7.58 (m, 1H), 7.58 – 7.48 (m, 5H), 7.30 (t, *J* = 7.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.08, 142.98, 137.82, 133.25, 133.06, 130.80, 130.48, 128.93, 128.71, 128.63, 128.53, 127.28, 123.14.

Yellow solid (2.05g, 72% yield).

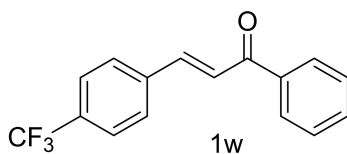


(E)-3-(2-bromophenyl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.17 (d, *J* = 15.7 Hz, 1H), 8.11 – 8.02 (m, 2H), 7.77 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.71 – 7.60 (m, 2H), 7.55 (dd, *J* = 8.2, 6.7 Hz, 2H), 7.47 (d, *J* = 15.8 Hz, 1H), 7.39 (td, *J* = 7.6, 1.3 Hz, 1H), 7.29 (dd, *J* = 7.7, 1.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.40, 143.20, 137.87, 135.03, 133.57, 133.01, 131.40, 128.71, 128.68, 127.91, 127.77, 125.93, 125.00.

Yellow solid (2.11g, 74% yield).

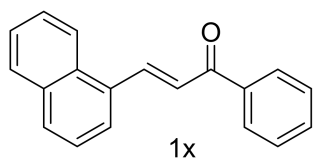


(E)-1-phenyl-3-(4-(trifluoromethyl)phenyl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.05 – 8.01 (m, 2H), 7.81 (d, *J* = 15.8 Hz, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.67 (d, *J* = 8.2 Hz, 2H), 7.65 – 7.57 (m, 2H), 7.52 (dd, *J* = 8.3, 6.8 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 188.99, 141.70, 137.18, 136.69, 132.14, 130.96, 130.64, 127.72, 127.53, 127.48, 124.86 (CF₃, q, *J* = 3.8 Hz), 123.09.

Yellow solid (1.68 g, 61% yield).

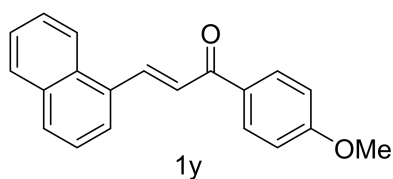


(E)-3-(naphthalen-1-yl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.70 (d, $J = 15.4$ Hz, 1H), 8.30 – 8.23 (m, 1H), 8.14 – 8.06 (m, 2H), 7.97 – 7.86 (m, 3H), 7.69 – 7.49 (m, 7H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.41, 141.82, 138.16, 133.76, 133.00, 132.34, 131.79, 130.92, 128.83, 128.76, 128.66, 127.06, 126.37, 125.51, 125.16, 124.60, 123.52.

Yellow solid (1.59 g, 62% yield).

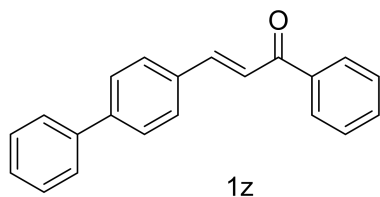


(E)-1-(4-methoxyphenyl)-3-(naphthalen-1-yl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, $J = 15.3$ Hz, 1H), 8.29 – 8.23 (m, 1H), 8.12 – 8.05 (m, 2H), 7.96 – 7.84 (m, 3H), 7.67 – 7.46 (m, 4H), 7.05 – 6.95 (m, 2H), 3.88 (s, 3H)

¹³C NMR (101 MHz, CDCl₃) δ 190.41, 141.82, 138.16, 133.76, 133.00, 132.34, 131.79, 130.92, 128.83, 128.76, 128.66, 127.06, 126.37, 125.51, 125.16, 124.60, 123.52.

Yellow solid (1.93 g, 67% yield).

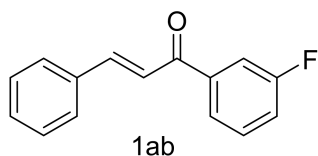


(E)-3-([1,1'-biphenyl]-4-yl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.09 – 8.03 (m, 2H), 7.88 (d, $J = 15.7$ Hz, 1H), 7.73 (d, $J = 8.4$ Hz, 2H), 7.69 – 7.45 (m, 10H), 7.42 – 7.37 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.49, 144.46, 143.32, 140.11, 138.27, 133.85, 132.90, 129.09, 129.01, 128.73, 128.59, 128.00, 127.64, 127.12, 121.83.

Yellow solid (2.07g, 73% yield).

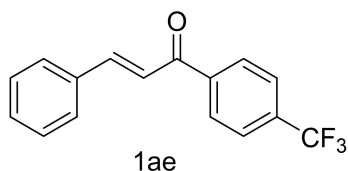


(E)-1-(3-fluorophenyl)-3-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 – 7.77 (m, 2H), 7.70 (dt, $J = 9.5, 2.1$ Hz, 1H), 7.67 – 7.62 (m, 2H), 7.52 – 7.45 (m, 2H), 7.44 – 7.41 (m, 3H), 7.31 – 7.25 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.15 (d, $J = 2.2$ Hz), 162.89 (d, $J = 247.9$ Hz), 145.61, 140.32 (d, $J = 6.2$ Hz), 134.64, 130.85, 130.32 (d, $J = 7.6$ Hz), 129.04, 128.58, 124.20 (d, $J = 3.0$ Hz), 121.49, 119.82 (d, $J = 21.3$ Hz), 115.32 (d, $J = 22.3$ Hz).

Yellow solid (1.60g, 71% yield).

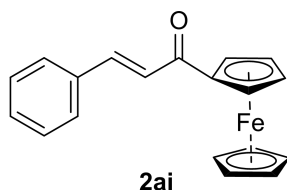


(E)-3-phenyl-1-(4-(trifluoromethyl)phenyl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 15.8 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.67 – 7.63 (m, 2H), 7.50 (d, *J* = 15.7 Hz, 1H), 7.46 – 7.40 (m, 3H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.67, 146.16, 141.03, 134.49, 134.17, 133.85, 131.03, 129.09, 128.81, 128.65, 125.69 (q, *J* = 3.8 Hz), 121.51.

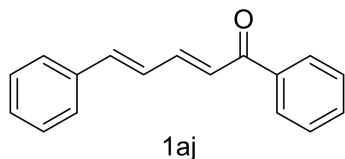
Yellow solid (2.26 g, 82% yield).



¹H NMR (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 15.6 Hz, 1H), 7.63 – 7.55 (m, 2H), 7.45 – 7.28 (m, 3H), 7.06 (d, *J* = 15.7 Hz, 1H), 4.84 (t, *J* = 2.0 Hz, 2H), 4.52 (t, *J* = 1.9 Hz, 2H), 4.14 (s, 5H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 193.04, 140.90, 135.16, 130.18, 128.99, 128.32, 122.92, 80.60, 72.89, 70.16, 69.78.

Red solid (2.11 g, 67% yield).

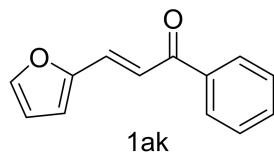


(2E,4E)-1,5-diphenylpenta-2,4-dien-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.01 – 7.94 (m, 2H), 7.65 – 7.51 (m, 2H), 7.52 – 7.43 (m, 4H), 7.40 – 7.30 (m, 3H), 7.08 (d, *J* = 14.9 Hz, 1H), 7.00 (d, *J* = 8.4 Hz, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.50, 144.89, 141.97, 138.24, 136.13, 132.71, 129.27, 128.90, 128.63, 128.43, 127.34, 126.97, 125.44.

Yellow solid (1.61g, 69% yield).

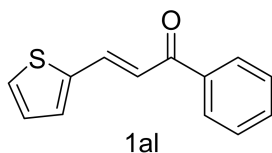


(E)-3-(furan-2-yl)-1-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.10 – 8.00 (m, 2H), 7.67 – 7.39 (m, 6H), 6.71 (d, *J* = 3.4 Hz, 1H), 6.50 (dd, *J* = 3.4, 1.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.80, 151.65, 144.98, 138.12, 132.81, 130.69, 128.64, 128.44, 119.26, 116.33, 112.73.

Yellow solid (1.36g, 69% yield).

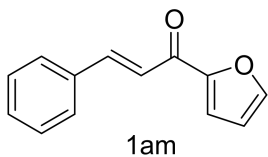


(E)-1-phenyl-3-(thiophen-2-yl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.97 (m, 2H), 7.94 (d, *J* = 15.3 Hz, 1H), 7.60 – 7.53 (m, 1H), 7.52 – 7.44 (m, 2H), 7.39 (dt, *J* = 5.1, 1.0 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.06 (dd, *J* = 5.1, 3.6 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 189.87, 140.38, 138.09, 137.27, 132.85, 132.23, 128.94, 128.68, 128.45, 120.71.

Yellow solid (1.82 g, 85% yield).

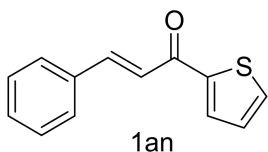


(E)-1-(furan-2-yl)-3-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 15.8 Hz, 1H), 7.66 – 7.62 (m, 3H), 7.48 – 7.38 (m, 4H), 7.34 (d, *J* = 3.5 Hz, 1H), 6.59 (dd, *J* = 3.6, 1.7 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 178.01, 153.68, 146.61, 143.99, 134.70, 130.65, 128.97, 128.56, 121.14, 117.62, 112.60.

Yellow solid (1.42 g, 72% yield).

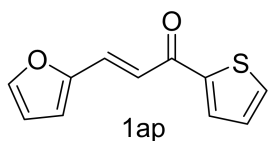


(E)-3-phenyl-1-(thiophen-2-yl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.89 – 7.83 (m, 2H), 7.68 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.66 – 7.62 (m, 2H), 7.46 – 7.40 (m, 4H), 7.18 (dd, *J* = 4.9, 3.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 182.08, 145.55, 144.10, 134.70, 133.99, 131.90, 130.65, 129.01, 128.53, 128.32, 121.60.

Yellow solid (1.19 g, 56% yield).

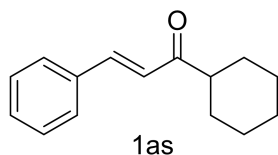


(E)-3-(furan-2-yl)-1-(thiophen-2-yl)prop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, *J* = 3.8, 1.2 Hz, 1H), 7.66 (dd, *J* = 5.0, 1.1 Hz, 1H), 7.60 (d, *J* = 15.2 Hz, 1H), 7.53 (d, *J* = 1.8 Hz, 1H), 7.33 (d, *J* = 15.2 Hz, 1H), 7.17 (dd, *J* = 4.9, 3.8 Hz, 1H), 6.72 (d, *J* = 3.4 Hz, 1H), 6.51 (dd, *J* = 3.4, 1.8 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 181.74, 151.47, 145.67, 145.03, 133.89, 131.76, 129.96, 128.30, 119.08, 116.47, 112.76.

Yellow solid (1.08 g, 53% yield).

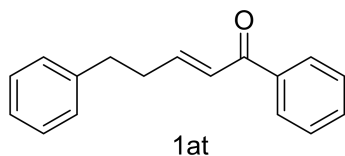


(E)-1-cyclohexyl-3-phenylprop-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.62 – 7.50 (m, 3H), 7.35 (dd, *J* = 4.8, 1.9 Hz, 3H), 6.80 (d, *J* = 16.0 Hz, 1H), 2.64 (tt, *J* = 11.3, 3.4 Hz, 1H), 1.94 – 1.85 (m, 2H), 1.81 (ddd, *J* = 10.6, 5.4, 2.3 Hz, 2H), 1.73 – 1.65 (m, 1H), 1.48 – 1.18 (m, 5H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 203.05, 142.19, 134.75, 130.29, 128.89, 128.27, 124.72, 49.38, 28.73, 25.93, 25.78.

Yellow solid (1.49 g, 70% yield).



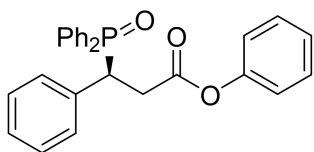
(E)-1,5-diphenylpent-2-en-1-one

¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 – 7.69 (m, 2H), 7.46 – 7.37 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.23 – 7.14 (m, 2H), 7.09 (dd, *J* = 7.3, 5.4 Hz, 3H), 7.02 – 6.90 (m, 1H), 6.74 (dt, *J* = 15.4, 1.6 Hz, 1H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.57 – 2.45 (m, 2H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 190.85, 148.54, 140.89, 137.90, 132.77, 128.63, 128.60, 128.56, 128.50, 126.56, 126.28.

Yellow oil (1.82 g, 85% yield).

4. Conversion of Chiral phosphine compound



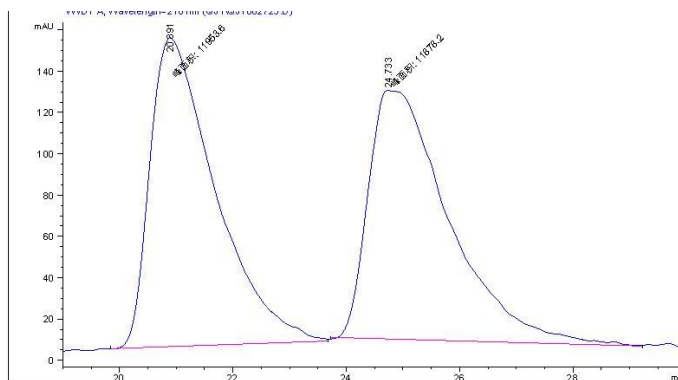
phenyl (S)-3-(diphenylphosphoryl)-3-phenylpropanoate^[6]

A 10-mL Schlenk tube was charged with (S)-3-(Diphenylphosphinyl)-1,3-diphenylpropan-1-one (98% ee, 123.mg, 0.30mmol), mCPBA (273 mg, 1.2 mmol, about 70% purity, Aldrich), trifluoroacetic acid (48 μ L, 0.60 mmol) and in CH_2Cl_2 (2.4 mL). The solution was stirred with refluxing for 48 h. The organic phase was washed with saturated aqueous NaHCO_3 (3x20 mL), extracted with CH_2Cl_2 , dried over Na_2SO_4 and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (DCM/MeOH= 70:1) to afford the product as White solid (71mg, 54% yield,96% ee).

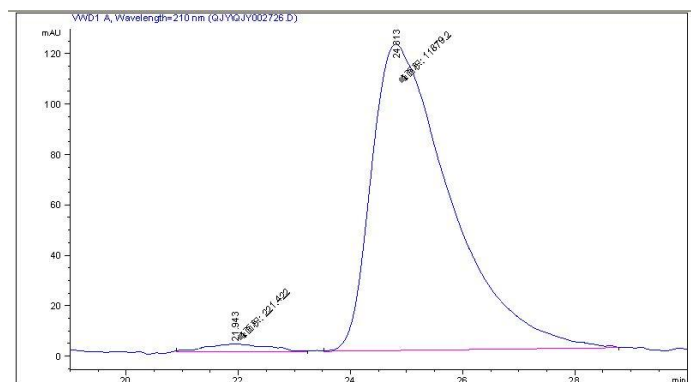
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.08 – 7.92 (m, 2H), 7.63 – 7.54 (m, 3H), 7.54 – 7.43 (m, 2H), 7.38 – 7.30 (m, 3H), 7.29 – 7.19 (m, 7H), 7.17 – 7.11 (m, 1H), 6.68 (dd, $J = 7.8, 1.6$ Hz, 2H), 4.16 (ddd, $J = 10.7, 7.6, 3.2$ Hz, 1H), 3.38 (ddd, $J = 16.2, 11.5, 6.6$ Hz, 1H), 3.13 (ddd, $J = 16.2, 8.2, 3.6$ Hz, 1H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 170.10 (d, $J = 18.0$ Hz), 150.36, 134.52, 132.30 (d, $J = 2.4$ Hz), 131.74, 131.46 (d, $J = 8.6$ Hz), 131.19, 131.10, 130.29, 129.85 (d, $J = 5.3$ Hz), 129.32, 129.12, 129.00, 128.48 (d, $J = 1.7$ Hz), 128.28, 128.16, 127.59 (d, $J = 2.2$ Hz), 125.90, 121.32, 43.22 (d, $J = 67.9$ Hz), 35.02.

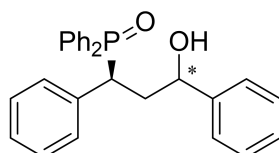
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 210nm. Retention time (min): 20.89 (minor) and 8.90 (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.891	MM	1.3327	1.19536e4	149.49181	50.1582
2	24.733	MM	1.6454	1.18782e4	120.31526	49.8418



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.943	MM	1.2348	221.42233	2.98867	1.8298
2	24.813	MM	1.6292	1.18792e4	121.52374	98.1702



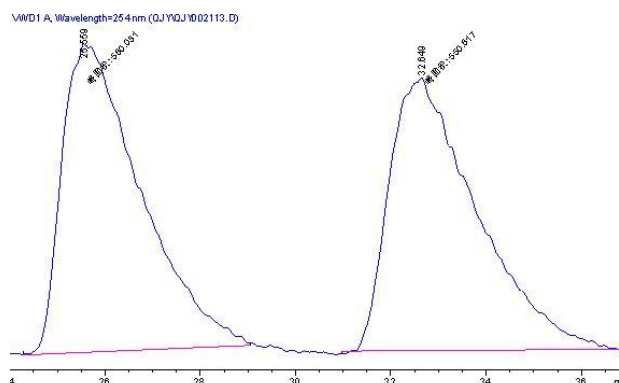
((1S,3S)-3-hydroxy-1,3-diphenylpropyl)diphenylphosphine oxide⁶¹

A 10-mL Schlenk tube was charged with (S)-3-(Diphenylphosphinyl)-1,3-diphenylpropan-1-one (98% ee, 123 mg, 0.30 mmol), NaBH₄ (13.5 mg, 0.36 mmol) in MeOH (2.4 mL). The solution was stirred with refluxing for 48 h. The organic phase was washed with saturated aqueous NaHCO₃ (3x20 mL), extracted with CH₂Cl₂, dried over Na₂SO₄ and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography (DCM/MeOH=70:1) to afford the product as White solid (106 mg, 86% yield, 96% ee).

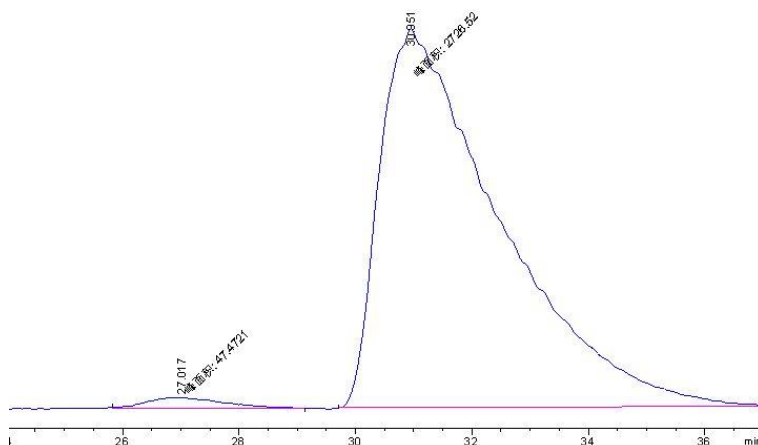
¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.50 (m, 3H), 7.44 (td, *J* = 7.6, 3.0 Hz, 2H), 7.38 – 7.11 (m, 15H), 4.48 (dd, *J* = 8.9, 5.2 Hz, 1H), 3.18 (ddd, *J* = 10.6, 9.4, 3.4 Hz, 1H), 2.72 (dddd, *J* = 13.9, 10.6, 6.7, 5.2 Hz, 1H), 2.31 (dddd, *J* = 13.9, 12.2, 8.9, 3.5 Hz, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.99, 135.22 (d, *J* = 5.7 Hz), 131.86 (d, *J* = 2.9 Hz), 131.46, 131.38, 131.34 (d, *J* = 2.7 Hz), 131.06, 130.98, 129.90 (d, *J* = 5.6 Hz), 128.74, 128.62, 128.55, 128.47 (d, *J* = 1.9 Hz), 128.04, 127.92, 127.22 (d, *J* = 2.5 Hz), 126.76, 72.34 (d, *J* = 13.3 Hz), 43.56 (d, *J* = 67.5 Hz), 38.68.

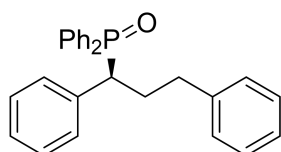
HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254 nm. Retention time (min): 27.01 (minor) and 30.95 (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	25.559	MM	1.9087	560.03064	4.89027	50.4238
2	32.649	MM	2.1240	550.61694	4.32054	49.5762



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	27.017	MM	1.4928	47.47207	5.29996e-1	1.7113
2	30.951	MM	2.3897	2726.52441	19.01552	98.2887

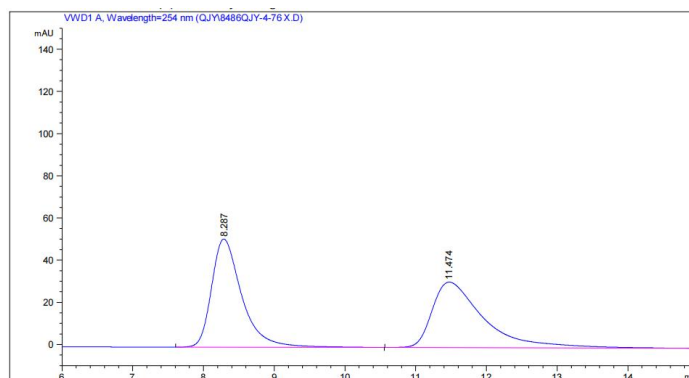


(S)-(1,3-diphenylpropyl)diphenylphosphine oxide^[6]

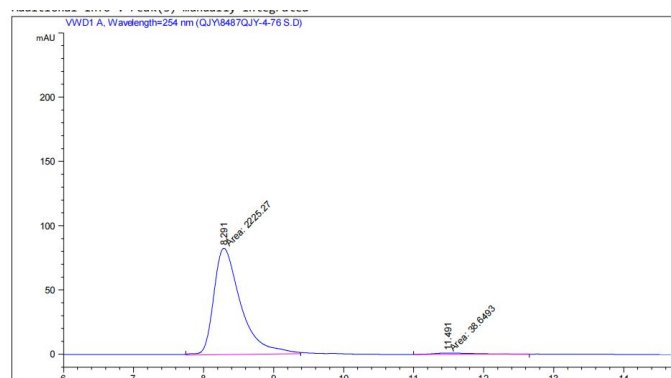
In an argon-filled glove box, an 8-mL vial was charged with (S)-3-(Diphenylphosphinyl)-1,3-diphenylpropan-1-one (98% ee, 123.mg, 0.30mmol), analytical-grade ethyl acetate (2 mL) and 5% Pd/C (32 mg, 0.015 mmol). The vial was placed in a 125-mL Parr bomb and pressurized with 30 psi of H₂ gas. The mixture was stirred at 25 °C for 48hours until completion as monitored by TLC. The mixture was passed through a pad of Celite with ethyl acetate washing (5 mL). After concentration of the filtrate, the residue was purified by flash chromatography (DCM/MeOH=70:1) to afford the titled compound as White solid (98 mg, 83% yield, 96% ee). ¹H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.51 (m, 3H), 7.45 m, 2H), 7.39 – 7.30 (m, 3H), 7.28 (m, 4H), 7.22 – 7.11 (m, 8H), 4.48 (dd, *J* = 8.8, 5.4 Hz, 1H), 3.19 (td, *J* = 10.0, 3.5 Hz, 1H), 2.83 (s, 1H), 2.68 (m, 1H), 2.31 (m, 1H).

¹³C NMR (101 MHz, Chloroform-*d*) δ 142.94, 135.30, 131.88, 131.48, 131.39, 131.36, 131.08, 131.00, 130.54, 129.90 (d, *J* = 5.8 Hz), 128.73, 128.59 (d, *J* = 4.3 Hz), 128.48 (d, *J* = 2.0 Hz), 128.06 (d, *J* = 3.5 Hz), 127.93, 127.26, 126.71, 72.37 (d, *J* = 13.0 Hz), 43.61 (d, *J* = 67.5 Hz), 38.71.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH= 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 8.28 (major) and 11.49 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.287	BB	0.4473	1522.36841	51.28486	49.1367
2	11.474	BB	0.7529	1575.86353	31.06284	50.8633

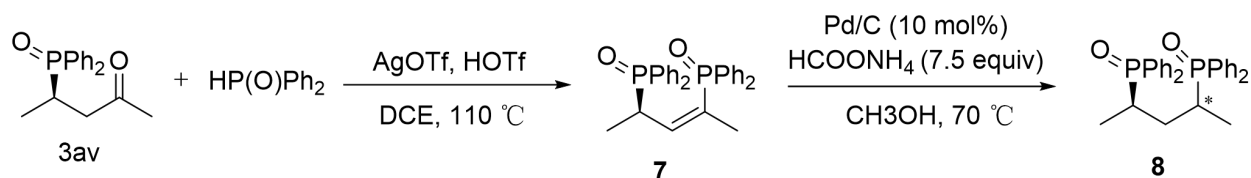


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.291	MM	0.4484	2225.26709	82.71955	98.2928
2	11.491	MM	0.6568	38.64930	9.80792e-1	1.7072

((2S,4S)-pentane-2,4-diy)bis(diphenylphosphine oxide)^[7]

An oven-dried 10 mL screw-capped vial containing **3av** (0.3 mmol, 1.0 equiv), AgOTf (0.03 mmol, 0.1 equiv), and DCE (2 mL) was added via syringe, dimethyl phosphate[HP(O)(OCH₃)₂] (0.75 mmol, 2.5 equiv), HOTf (0.3 mmol, 1.0 equiv), and then heated to 110 °C in an oil bath until the starting material has disappeared for 15 h (monitored by TLC). And then the solvent was removed in vacuo and residue was purified by column chromatography on a short silica gel column using DCM/MeOH as eluent to afford the desired product **7** (68% yield).

A mixture of **7** (188 mg, 0.4 mmol), ammonium formate (189.0 mg, 3.0 mmol) and palladium on carbon (10%, 38.3 mg) in MeOH (1.0 mL) was heated to reflux for 15 h under nitrogen atmosphere. After being cooled to room temperature, the mixture was diluted with EtOAc (15.0 mL). The catalyst was filtered off using a short pad of silica gel. The reaction mixture was evaporated to dryness in vacuo. The residue was diluted with H₂O (5.0 mL) and extracted with EtOAc for three times. The combined organic layers were washed with saturated brine, dried (MgSO₄), filtered and evaporated. The pale yellow oil obtained was purified by column chromatography (silica gel, DCM/MeOH=70:1) to give **8** in 76% yield as a colorless oil.

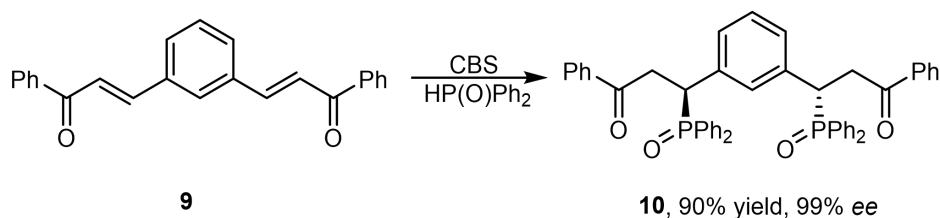


Scheme S3 Synthesis of **8**

$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.26 – 7.65 (m, 8H), 7.58 – 7.25 (m, 12H), 2.68 (dd, $J = 8.8, 5.6$ Hz, 4H), 1.13 (dd, $J = 16.4, 7.0$ Hz, 6H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 132.36, 131.75 (d, $J = 2.4$ Hz), 131.66 (d, $J = 2.3$ Hz), 131.40, 131.05, 130.98 (d, $J = 3.6$ Hz), 130.91, 130.72, 128.73 (d, $J = 4.3$ Hz), 128.61 (d, $J = 4.4$ Hz), 29.82 (d, $J = 12.1$ Hz), 29.11 (d, $J = 12.2$ Hz), 28.56, 11.70 (d, $J = 2.4$ Hz).

(3*S*,3'*S*)-3,3'-(1,3-phenylene)bis(3-(diphenylphosphoryl)-1-phenylpropan-1-one)^[8]

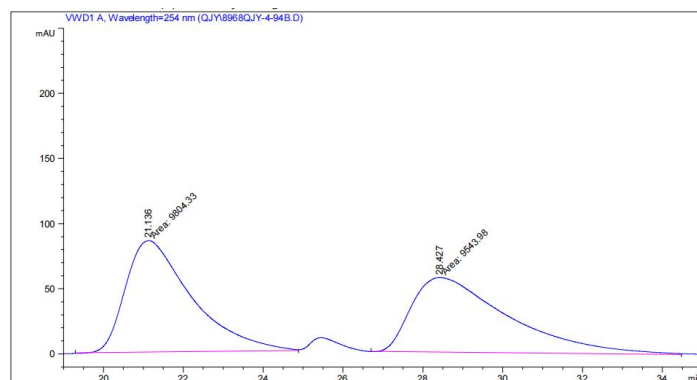


Scheme S4 Synthesis of **10**

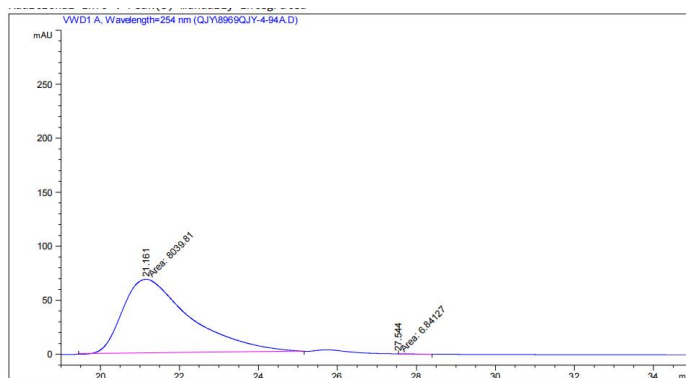
$^1\text{H NMR}$ (400 MHz, Chloroform-*d*) δ 8.01 – 7.88 (m, 5H), 7.83 – 7.75 (m, 4H), 7.64 – 7.51 (m, 4H), 7.50 – 7.36 (m, 10H), 7.35 – 7.29 (m, 5H), 7.23 – 7.12 (m, 6H), 4.40 (dddd, $J = 31.3, 9.8, 6.9, 2.5$ Hz, 2H), 3.91 (dddd, $J = 55.9, 17.8, 10.1, 4.1$ Hz, 2H), 3.33 (dddd, $J = 20.5, 18.0, 11.2, 2.4$ Hz, 2H).

$^{13}\text{C NMR}$ (101 MHz, Chloroform-*d*) δ 196.47 (d, $J = 13.0$ Hz), 190.51, 144.56, 138.13, 136.89 (d, $J = 5.5$ Hz), 136.23, 134.86, 133.53, 132.80, 132.25, 131.96 (d, $J = 5.5$ Hz), 131.71 (d, $J = 2.6$ Hz), 131.30 (d, $J = 8.8$ Hz), 131.00, 130.91, 129.72 (d, $J = 5.7$ Hz), 129.13, 129.02, 128.63 (d, $J = 1.8$ Hz), 128.57, 128.29, 128.15, 127.53, 122.22, 41.08 (d, $J = 68.6$ Hz), 38.80.

HPLC analysis: Chiracel-ODH, n-heptane/*i*-PrOH = 90:10, 1 mL/min, 22°C, detection at 254nm. Retention time (min): 21.16(minor) and 27.54(minor).



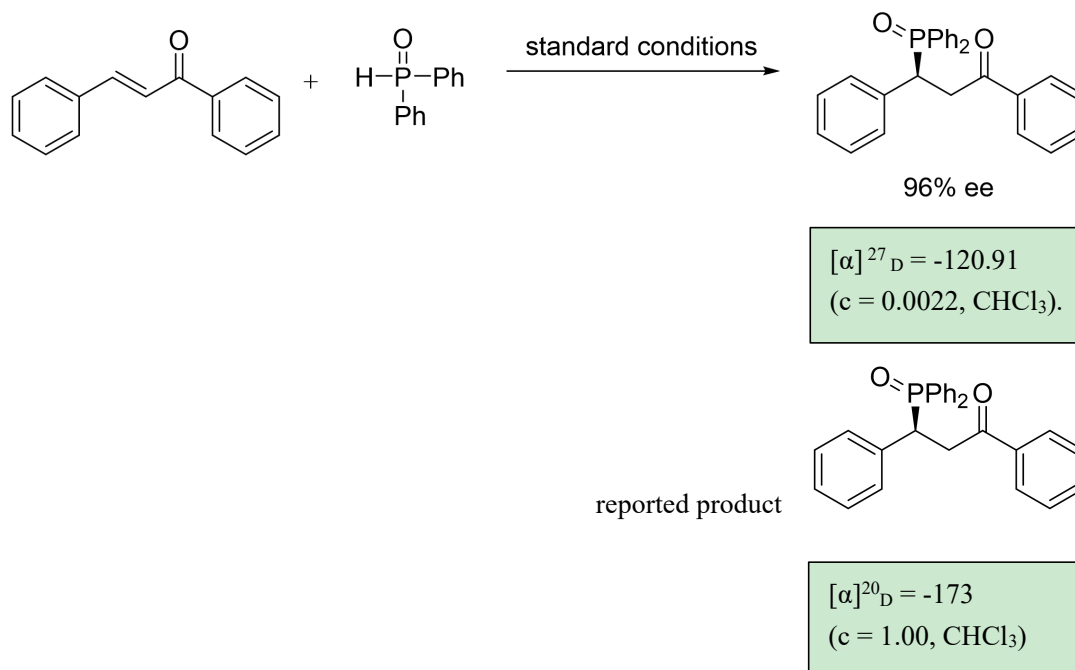
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.136	MM	1.9115	9804.33203	85.48429	50.6728
2	28.427	MM	2.7814	9543.97852	57.18884	49.3272



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	21.161	MM	1.9652	8039.81006	68.18500	99.9150
2	27.544	MM	0.5229	6.84127	1.53532e-1	0.0850

5. Determination of absolute configuration

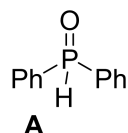
The absolute configuration was determined through the known compound as follow^[8]. $[\alpha]^{27}_D = -120.91$ ($c = 0.0022$, CHCl_3). By comparison to the reported optical rotations $[\alpha]^{20}_D = -173$ ($c = 1.00$, CHCl_3 for optically pure product); the absolute configuration was determined to be (*S*).



6. Calculation Detail and Atom Coordination

DFT Methods

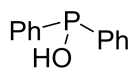
All computations were performed in ORCA 5.0.4.^[9] Molecular geometries force constant and vibration frequency was calculated under Grimme's r²SCAN-3c composite method^[10] in vacuum condition. Solvation effects were included in the single point energy calculation using the SMD^[11] solvation model. Frequency calculations were carried out to confirm the stationary points as either minimum (no imaginary frequencies) or saddle points (one imaginary frequency) on the potential energy surface, and to obtain thermal corrections to the Gibbs free energies and enthalpy at 298 K by Shermo 2.3.5.^[12] Intrinsic reaction coordinate (IRC) calculations were performed to ensure that the saddle points found were true transition states connecting the reactants and the products. Single-point energies were calculated with the M06-2X functional combined with the D3 dispersion correction with RIJCOSX approximations and using the def2-TZVP basis set^[13]. Molecular structures were visualized using CYLview^[14], conformational searches were performed with the ABCluster3.0^[15] with xTB^[16] method to ensure that the lowest energy conformations of intermediates are presented.



The Cartesian coordinates (Å) and energies at 298.15 K for the optimized structures

P	-0.02891100	1.20584200	-0.76510200
C	1.46667600	0.30367700	-0.25407500
C	2.01605300	-0.73409900	-1.01917200
C	2.06878700	0.67762000	0.95551700
C	3.14894600	-1.41294900	-0.56368800
H	1.56919300	-1.00742800	-1.97954400
C	3.20193900	-0.00165300	1.40667500
H	1.64627200	1.51029500	1.52289200
C	3.73887100	-1.04891900	0.65070900
H	3.57781400	-2.22109500	-1.16092700
H	3.67250200	0.28985500	2.34869100

H	4.62703100	-1.57788500	1.00470500
C	-1.45212500	0.17751100	-0.26568900
C	-1.54031500	-1.19516500	-0.53788000
C	-2.48674200	0.82400500	0.42317700
C	-2.66314800	-1.91534500	-0.12721400
H	-0.72995600	-1.70874200	-1.06133100
C	-3.60832400	0.09875200	0.83424400
H	-2.39092100	1.89264200	0.62883200
C	-3.69741900	-1.26827500	0.55853800
H	-2.73129400	-2.98528100	-0.33797400
H	-4.41487100	0.60260100	1.37237200
H	-4.57458100	-1.83471700	0.88078700
O	-0.12307500	2.60938500	-0.24049400
H	0.00789400	1.04608600	-2.18487100



B

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -880.468939 Hartree

Enthalpy (calculated by Shermo 2.3.5): -880.2517755 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -880.3300876 Hartree

P	-0.00964700	1.08727700	-1.25665300
C	-1.41075600	0.03231500	-0.67028700
C	-1.12085400	-1.28145800	-0.29167700
C	-2.71919200	0.50916400	-0.52254200
C	-2.11680000	-2.10501700	0.22648000
H	-0.10694700	-1.65803000	-0.40520300
C	-3.71200400	-0.31097700	0.00052300
H	-2.96567200	1.52091800	-0.83739700
C	-3.41186000	-1.61960800	0.37446200

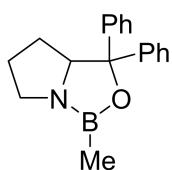
H	-1.88117400	-3.12580300	0.51346900
H	-4.72448300	0.06744400	0.11071100
H	-4.19042800	-2.26104200	0.77778500
C	-0.92183700	2.17027600	-2.43658800
C	-1.65198800	1.59902200	-3.48634200
C	-0.81062200	3.56168300	-2.36829100
C	-2.27357200	2.40379800	-4.43276200
H	-1.74705400	0.51723800	-3.55538700
C	-1.43787400	4.36620400	-3.31706000
H	-0.22513000	4.01607100	-1.57351000
C	-2.17119600	3.79125600	-4.34924300
H	-2.84384500	1.94769800	-5.23715900
H	-1.34890200	5.44691200	-3.24890000
H	-2.65907100	4.41953800	-5.08883200
O	0.21040100	2.11602200	0.04389700
H	-0.62705200	2.45066500	0.39813700

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -880.461912 Hartree

Enthalpy (calculated by Shermo 2.3.5): -880.2434323 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -880.3220981 Hartree



C	0.83258600	3.26767300	-0.04835100
C	2.12480500	3.55388000	-0.87468700
C	2.93963000	2.24823800	-0.81133900
C	1.84633900	1.18874700	-0.62436000
C	2.20710100	-0.13485100	0.11967200

H	0.77119100	3.87754000	0.85995000
H	-0.06180900	3.47641700	-0.65110900
H	1.86219300	3.78807600	-1.91194800
H	3.55742500	2.08614400	-1.69955100
H	3.60136900	2.23725900	0.06355500
H	2.68371900	4.40681800	-0.47965400
H	1.36665700	0.97920700	-1.58989400
N	0.91825900	1.84977300	0.30042500
B	1.12210200	1.29249900	1.59024600
O	1.90419900	0.15005500	1.50462900
C	3.68348800	-0.49086400	-0.01005400
C	4.53830900	-0.41964100	1.08844900
C	4.20520600	-0.86773700	-1.24987200
C	5.89190100	-0.71697000	0.94688600
H	4.13622300	-0.13260000	2.05342000
C	5.55693200	-1.15553700	-1.39132600
H	3.54964400	-0.94672300	-2.11252400
C	6.40746700	-1.08210600	-0.29108100
H	6.54494600	-0.66172700	1.81350100
H	5.94631300	-1.44551000	-2.36315500
H	7.46325800	-1.31309400	-0.39911800
C	1.34744300	-1.32605100	-0.31189600
C	0.93962700	-1.52791600	-1.63149200
C	1.01460300	-2.29153300	0.64255300
C	0.20725700	-2.65778300	-1.98685800
H	1.18460300	-0.80710100	-2.40551600
C	0.28230600	-3.41773600	0.28849500
H	1.32977900	-2.14768900	1.67025900
C	-0.12661500	-3.60681200	-1.02858100
H	-0.10494900	-2.79044500	-3.01888700

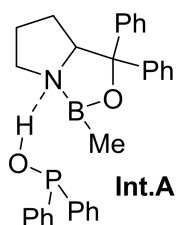
H	0.02953200	-4.15349800	1.04687200
H	-0.70060800	-4.48641000	-1.30522600
C	0.62638000	1.84674200	2.96950700
H	0.38840200	1.03583100	3.66638700
H	1.41307000	2.44625800	3.44781200
H	-0.25602100	2.48761100	2.87547600

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -852.835012 Hartree

Enthalpy (calculated by Shermo 2.3.5): -852.4593543 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -852.5591904 Hartree



C	-4.50155500	8.89806000	1.42807400
C	-3.34722700	9.93659200	1.44180200
C	-3.95342100	11.19283600	2.08546900
C	-4.95205800	10.59192400	3.07770400
C	-6.19117600	11.44347100	3.48221500
H	-4.90942800	8.74214800	0.42318000
H	-4.16222400	7.92506800	1.80456800
H	-2.51940800	9.56453500	2.05558600
H	-3.20755100	11.83707100	2.55932200
H	-4.49565600	11.79439200	1.34485700
H	-2.95311900	10.12712300	0.43972000
H	-4.41846900	10.22005400	3.96152400
N	-5.54316200	9.47498700	2.30725300
B	-6.81977900	9.94439700	1.82942700
O	-7.17796200	11.10686900	2.47239200

C	-5.90306400	12.93725100	3.42786100
C	-5.07058300	13.51712900	4.38805900
C	-6.42728600	13.73718400	2.41414000
C	-4.75659100	14.86902100	4.32694600
H	-4.67676800	12.91135800	5.19957700
C	-6.11922200	15.09461500	2.36055900
H	-7.08154000	13.29437500	1.67143000
C	-5.28105100	15.66477800	3.31151800
H	-4.10780800	15.30493500	5.08130900
H	-6.54037200	15.70795900	1.56881500
H	-5.04236600	16.72343500	3.26771600
C	-6.77892900	11.07183300	4.84447600
C	-8.15596600	11.22249300	5.03411000
C	-5.99866100	10.65330700	5.92288300
C	-8.73591100	10.94198000	6.26372300
H	-8.77249400	11.54958400	4.20394100
C	-6.58063400	10.37700100	7.15775200
H	-4.92581700	10.52116100	5.82131100
C	-7.95073000	10.51598800	7.33143600
H	-9.80942200	11.05384200	6.38752900
H	-5.95892000	10.02176700	7.97465900
H	-8.40418300	10.28466800	8.29089200
P	-7.01138700	7.22409500	5.08134400
C	-7.40625000	5.43180700	4.87597000
C	-8.72060800	5.01054900	5.08647800
C	-6.43390300	4.49167200	4.52409700
C	-9.05631500	3.66340400	4.97384200
H	-9.48852300	5.74243100	5.32947400
C	-6.77363900	3.14998400	4.39677400
H	-5.41264600	4.81862800	4.34954200

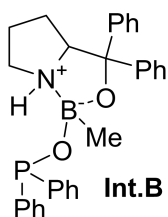
C	-8.08349900	2.73184400	4.62693500
H	-10.08122100	3.34439600	5.14198900
H	-6.01316800	2.42391100	4.12194100
H	-8.34476900	1.68184300	4.52930600
C	-6.21458100	7.11333200	6.74195300
C	-7.02052000	6.90286500	7.86482400
C	-4.84711100	7.32734800	6.91794500
C	-6.46935900	6.90531000	9.14011800
H	-8.09058000	6.74496500	7.74214200
C	-4.29599400	7.33193000	8.19759900
H	-4.21918000	7.49603000	6.04820600
C	-5.10345600	7.12549700	9.31173200
H	-7.10679600	6.73996600	10.00442700
H	-3.22917300	7.49780200	8.32373500
H	-4.67285800	7.13338600	10.30901400
O	-5.65328100	7.35005600	4.13281500
H	-5.75817400	8.10519700	3.50272500
C	-7.69672300	9.29448500	0.71008100
H	-7.37620400	9.64182600	-0.28200600
H	-7.61745900	8.20200000	0.70314700
H	-8.75208200	9.56424200	0.81484000

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -1733.318825 Hartree

Enthalpy (calculated by Sherma 2.3.5): -1732.7222116 Hartree

Gibbs Free Energy (calculated by Sherma 2.3.5): - 1732.8707964 Hartree



C	-4.45915500	8.85960100	1.36212400
C	-3.52801400	10.04914800	0.99416200
C	-4.13015800	11.26365800	1.72225800
C	-4.73994300	10.62024800	2.97212000
C	-5.95806800	11.31036600	3.65692800
H	-5.08037700	8.53244400	0.51528500
H	-3.87509600	7.98539600	1.69380800
H	-2.50882500	9.85546900	1.36365700
H	-3.39302600	12.04546600	1.95102200
H	-4.93019300	11.72824300	1.12430300
H	-3.45553800	10.20117300	-0.09238500
H	-3.94475800	10.41247600	3.70342800
N	-5.31328200	9.36897300	2.44539800
B	-6.73693000	9.58115700	2.33156600
O	-7.09286600	10.73422300	2.98583900
C	-5.95982000	12.82236500	3.44912900
C	-4.97515900	13.61764400	4.05280800
C	-6.92093400	13.43384500	2.63725700
C	-4.94552200	14.99596400	3.83907300
H	-4.22932500	13.15945900	4.70483300
C	-6.89594100	14.81676200	2.42928400
H	-7.69095300	12.81716600	2.17454300
C	-5.90794800	15.60226100	3.02526300
H	-4.17064700	15.60098800	4.31611700
H	-7.65648700	15.28078800	1.79631200
H	-5.88862700	16.68237500	2.86182300
C	-6.07559400	10.98728500	5.15239200
C	-7.35576700	10.89232400	5.71726700
C	-4.96312600	10.84835100	5.99144800
C	-7.51658400	10.66895300	7.08434600

H	-8.22604200	10.98369800	5.06794900
C	-5.12471500	10.62561100	7.36201600
H	-3.95084300	10.90780000	5.58859900
C	-6.40136100	10.53781300	7.91469800
H	-8.52130000	10.58170000	7.50346900
H	-4.24368100	10.50296400	7.99583900
H	-6.52804200	10.33653700	8.97982400
P	-6.89883000	7.40973400	4.88200400
C	-7.23129100	5.63038800	4.49852400
C	-8.54694300	5.14811700	4.57337000
C	-6.20618700	4.76227200	4.09766900
C	-8.83012000	3.81255600	4.27947500
H	-9.35896900	5.82294800	4.86087100
C	-6.49198200	3.42849700	3.79417300
H	-5.18656900	5.14684900	4.02958100
C	-7.80197300	2.94905200	3.88814000
H	-9.85770400	3.44601700	4.34653000
H	-5.68619500	2.75721400	3.48511500
H	-8.02320500	1.90543000	3.65110000
C	-6.76701500	7.28845700	6.71650200
C	-7.93686300	7.30883800	7.48937600
C	-5.52302300	7.22773100	7.35670200
C	-7.86622400	7.25031200	8.88240400
H	-8.91219100	7.38334100	6.99962500
C	-5.45269700	7.17445300	8.75083100
H	-4.61663200	7.23626200	6.74958600
C	-6.62162500	7.18474500	9.51730000
H	-8.78414200	7.26543900	9.47562800
H	-4.47770000	7.12751900	9.24329500
H	-6.56410000	7.14504000	10.60795200

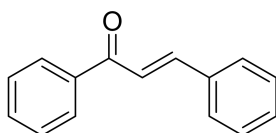
O	-5.28597300	7.51094800	4.48865200
H	-5.21162200	8.18180800	3.76361200
C	-7.74584600	8.71242500	1.51045500
H	-7.74126300	9.02543000	0.45020300
H	-7.48576000	7.64304600	1.53652700
H	-8.77267800	8.83042900	1.88572100

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -1733.337197 Hartree

Enthalpy (calculated by Shermo 2.3.5): -1732.7396962 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -1732.8824688 Hartree



C	-3.86509600	-2.77650800	-0.07873700
C	-2.85214000	-1.83143700	-0.13907900
C	-2.05567100	-1.57211100	0.98258000
C	-2.28265800	-2.29394200	2.15978800
C	-3.28638500	-3.25505700	2.21253800
C	-4.08452100	-3.49180700	1.09774100
H	-4.48585800	-2.96176300	-0.95056800
H	-2.65429400	-1.27410500	-1.04928700
H	-1.65716400	-2.13559500	3.03272800
H	-3.44494900	-3.82122800	3.12570000
H	-4.87438100	-4.23623400	1.14304100
C	-0.96625500	-0.55529000	0.84948100
O	-0.56886900	-0.22467900	-0.26325800
C	-0.41110500	0.04355200	2.08176000
C	0.65255000	0.86471100	2.01557800
H	-0.89616300	-0.17490100	3.02757000

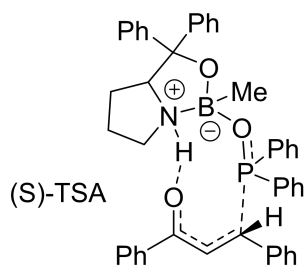
H	1.07242000	1.02961800	1.02285200
C	1.30907200	1.55591000	3.11346300
C	2.44361300	2.33367700	2.83188700
C	0.86432800	1.48708500	4.44507800
C	3.11319900	3.01497100	3.83968500
H	2.79726200	2.39728600	1.80596900
C	1.53274800	2.16811900	5.44929700
H	-0.01350500	0.89917100	4.69492500
C	2.66038000	2.93444600	5.15252600
H	3.98931600	3.61032900	3.60041500
H	1.17492500	2.10555200	6.47291200
H	3.18047900	3.46642700	5.94364900

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -653.995232 Hartree

Enthalpy (calculated by Shermo 2.3.5): -653.7477348 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -653.8305834 Hartree



C	-0.78298100	-2.90273800	-2.50532800
C	-2.17745500	-3.53548600	-2.36356700
C	-2.77227600	-2.84471700	-1.13458400
C	-2.25659900	-1.41636900	-1.28024500
C	-2.13682100	-0.61193400	0.03282300
H	-0.00128300	-3.53994600	-2.08862600
H	-0.53362000	-2.66791000	-3.54476200
H	-2.78428700	-3.31599100	-3.24944000

H	-3.86344500	-2.88597900	-1.09548100
H	-2.37990200	-3.27994000	-0.20790700
H	-2.12389600	-4.62265500	-2.25682000
H	-2.82371000	-0.89386600	-2.05843500
N	-0.83469200	-1.61332600	-1.72630700
B	0.05311200	-1.45431500	-0.33174700
O	-0.97951800	-1.16122100	0.64256800
C	-3.35794200	-0.86398100	0.90988900
C	-3.27188000	-1.65815400	2.05056200
C	-4.59317600	-0.32249600	0.54624300
C	-4.40907800	-1.91225200	2.81426800
H	-2.30808800	-2.06938600	2.33116400
C	-5.72849500	-0.58627200	1.30250900
H	-4.66097800	0.32326900	-0.32642700
C	-5.64000000	-1.38336500	2.44172800
H	-4.32986500	-2.52812500	3.70603600
H	-6.68364900	-0.16022300	1.00849300
H	-6.52548400	-1.58367500	3.03817800
C	-1.97866900	0.90253700	-0.16354800
C	-2.17328500	1.56958900	-1.37190900
C	-1.65709500	1.65341700	0.97253800
C	-2.07250600	2.96123400	-1.43973800
H	-2.37821700	1.02979400	-2.29061500
C	-1.55588600	3.03484600	0.90703400
H	-1.49063000	1.13451900	1.91241900
C	-1.77676200	3.69743800	-0.30063800
H	-2.21815400	3.45874800	-2.39521400
H	-1.30887900	3.60040700	1.80122100
H	-1.71100700	4.78096200	-0.35049000
C	0.91279900	-2.75101400	0.05683500

H	1.37817400	-2.60600200	1.03828800
H	0.28178500	-3.64517600	0.14087000
H	1.73024100	-2.98577600	-0.64024400
H	-0.58825300	-0.85820100	-2.40716500
O	0.87703800	-0.20042900	-0.53644200
P	2.34507900	-0.04175300	-1.12965100
C	3.53612700	-0.67459200	0.11739200
C	4.76854800	-1.19513600	-0.28224600
C	3.20856300	-0.61543100	1.47591000
C	5.67400300	-1.64513000	0.67588000
H	5.02321900	-1.25284200	-1.33738100
C	4.11353800	-1.07360400	2.42441800
H	2.24482200	-0.21453500	1.77994100
C	5.34694900	-1.58801600	2.02630700
H	6.63278100	-2.04778800	0.36187700
H	3.85830800	-1.02705100	3.47942900
H	6.05137000	-1.94557900	2.77198300
C	2.61902600	1.74584600	-1.05953100
C	3.91870500	2.26476000	-1.02518800
C	1.52651400	2.61082700	-1.16306400
C	4.12013600	3.63806200	-1.09068800
H	4.77104400	1.59639700	-0.93092900
C	1.73714500	3.98541700	-1.21669000
H	0.51700000	2.21263400	-1.17927700
C	3.02893300	4.50059900	-1.18831000
H	5.12970800	4.03708600	-1.05211900
H	0.88002000	4.64877500	-1.28869500
H	3.18852800	5.57446300	-1.23207800
C	2.27182200	-0.32377100	-3.46611100
C	1.66475000	0.84815700	-3.94163400

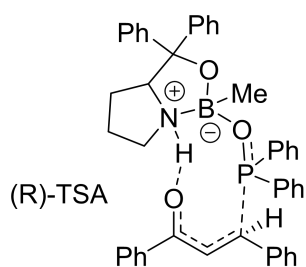
H	1.62196900	-1.19886300	-3.42905300
C	0.26222100	0.95269400	-4.08515000
O	-0.53714700	-0.00006400	-3.84972400
C	-0.33635400	2.23984600	-4.56074300
C	-0.31808700	4.64852700	-4.82676300
C	-1.63910200	2.21691800	-5.07329700
C	0.31754700	3.47206600	-4.44620700
H	2.28195200	1.70083400	-4.19487800
C	-2.26834700	3.39048500	-5.46691600
H	-2.14306000	1.25867400	-5.15069800
C	-1.61186200	4.61317600	-5.34004100
H	1.31226300	3.52391700	-4.01649400
H	4.38916600	1.39953200	-3.79167900
H	-3.27680100	3.35503700	-5.86984500
C	3.69399400	-0.64189600	-3.71591300
C	6.00593000	0.01194500	-4.03225900
C	4.67065900	0.35272800	-3.85080400
C	4.09255000	-1.98268600	-3.79030600
H	-2.10697300	5.53327600	-5.63765000
C	5.42540600	-2.32260600	-3.98433800
H	3.34332400	-2.76431900	-3.68535700
C	6.39087100	-1.32507700	-4.09790200
H	6.75165000	0.79650600	-4.12568100
H	0.19757500	5.59851200	-4.71560300
H	5.71276400	-3.36858300	-4.04258800
H	7.43457900	-1.58735500	-4.24363400

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -2387.352682 Hartree

Enthalpy (calculated by Shermo 2.3.5): -2386.5065199 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -2386.6925394 Hartree



B	-0.24084500	-1.30026900	0.23081400
N	-1.02541500	-1.82718900	-1.09275800
O	-0.43880600	0.14359300	0.11289100
C	-0.74144400	-2.01108900	1.58412600
O	1.21971200	-1.60925700	0.07560600
C	-1.97722500	-2.98281000	-1.02189400
C	-1.77372600	-0.65184900	-1.68192500
H	-0.32840600	-2.11325400	-1.82402400
C	-1.51245200	0.55464400	-0.70245600
H	-0.22709100	-1.57516300	2.45001100
H	-1.81644800	-1.89425700	1.76761600
H	-0.51411600	-3.08502400	1.59504400
P	2.29386700	-0.66132500	-0.64350200
C	-2.98383700	-2.68021600	-2.12489100
H	-1.41902200	-3.91240600	-1.16131800
H	-2.46159200	-2.99356200	-0.04147500
C	-3.19138900	-1.17344900	-1.94139000
H	-1.28532400	-0.42503800	-2.63646200
C	-2.72575000	0.94839300	0.15754800
C	-1.08005300	1.81520100	-1.45513400
C	2.62699000	0.76211000	0.45665700
C	3.79238700	-1.67565100	-0.57568100
H	-2.54266700	-2.90194600	-3.10360400
H	-3.90935300	-3.25371600	-2.01636600

H	-3.65597700	-0.69006400	-2.80619400
H	-3.83099500	-0.99116900	-1.07161200
C	-2.66089500	0.85613200	1.54589200
C	-3.88586300	1.46956300	-0.42415200
C	-1.56807500	2.13411000	-2.72331300
C	-0.22045200	2.71385100	-0.81838800
C	2.14590100	0.76389500	1.76911300
C	3.29721600	1.88654600	-0.03660200
C	3.67374100	-3.05594200	-0.78429600
C	5.06403100	-1.09876900	-0.49250800
C	-3.74330300	1.24227400	2.33401600
H	-1.74989200	0.49252200	2.00587900
C	-4.96706400	1.85069900	0.35957300
H	-3.94516100	1.59121700	-1.50217100
C	-1.21200200	3.33107400	-3.34192700
H	-2.23517300	1.45343600	-3.24697500
C	0.13759300	3.90506700	-1.43703300
H	0.17192500	2.46522600	0.16242300
C	2.33823900	1.87688200	2.57808500
H	1.61505800	-0.10350200	2.14777100
C	3.49378400	2.99411000	0.78263500
H	3.65328200	1.91042400	-1.06231800
C	4.81467500	-3.84496800	-0.89072000
H	2.68942300	-3.51038900	-0.83945600
C	6.19949100	-1.89306500	-0.60438900
H	5.16795800	-0.03023700	-0.32528100
C	-4.90224000	1.73376700	1.74624800
H	-3.67282500	1.16236400	3.41534300
H	-5.85998600	2.25006700	-0.11310300
C	-0.36135500	4.22293400	-2.69813400

H	-1.59867700	3.56128700	-4.33065900
H	0.81641500	4.58547500	-0.93020900
C	3.01063000	2.99477900	2.08746600
H	1.96090800	1.87246000	3.59685800
H	4.01640300	3.86247300	0.39113600
C	6.07740300	-3.26615700	-0.80743100
H	4.71185200	-4.91558200	-1.04437900
H	7.18308600	-1.43919200	-0.52337400
H	-5.74512000	2.03599900	2.36106200
H	-0.08517800	5.15745400	-3.17856500
H	3.15461800	3.86465900	2.72204800
H	6.96670000	-3.88459200	-0.89104600
O	0.28456600	-2.81512400	-3.19361900
C	1.49459000	-2.92245700	-3.55327300
C	2.42317800	-1.86193900	-3.48159600
C	1.92837100	-4.24256400	-4.10898800
C	2.06025800	-0.58767600	-3.02688800
H	3.44356900	-2.03641700	-3.79670800
C	3.26969400	-4.63951500	-4.17944400
C	0.94199700	-5.13509800	-4.54541800
C	2.89778800	0.59868700	-3.29469900
H	0.99234900	-0.37778400	-2.98321500
C	3.61218000	-5.88968700	-4.68160100
H	4.05417600	-3.98528300	-3.81326000
C	1.28592900	-6.37810700	-5.05938400
H	-0.09595800	-4.82648100	-4.47424600
C	4.29172800	0.51624800	-3.41756800
C	2.28796100	1.85413400	-3.40822500
C	2.62326500	-6.76140400	-5.12929800
H	4.65678900	-6.18598300	-4.72060200

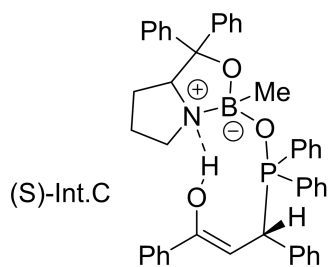
H	0.50884700	-7.05409900	-5.40543600
C	5.04994100	1.66074900	-3.63359400
H	4.79076100	-0.44308900	-3.32254200
C	3.04686700	2.99486900	-3.63592400
H	1.20942800	1.93565300	-3.30228900
H	2.89324400	-7.73612600	-5.52580200
C	4.43241700	2.90513800	-3.74309800
H	6.13019700	1.58060200	-3.71787300
H	2.55083800	3.95749300	-3.71945800
H	5.02790700	3.79715500	-3.91493800

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -2387.3503 Hartree

Enthalpy (calculated by Shermo 2.3.5): -2386.5039399 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -2386.6925394 Hartree



C	-0.46812600	-1.76575400	-2.95758600
C	-1.91824500	-2.16287500	-3.27554900
C	-2.62263900	-2.07331000	-1.92061300
C	-1.98119400	-0.83105800	-1.30692800
C	-1.98900500	-0.74744000	0.23813800
H	0.16532700	-2.64342400	-2.80976300
H	-0.01604200	-1.13905300	-3.73366000
H	-2.36238400	-1.44820100	-3.97812200
H	-3.70909000	-1.98451400	-1.99634400
H	-2.39556300	-2.94764700	-1.29857600

H	-1.98099000	-3.15729600	-3.72636400
H	-2.39764900	0.06551700	-1.78038600
N	-0.53406800	-0.98154300	-1.67295100
B	0.16915400	-1.57195400	-0.32685000
O	-0.91332700	-1.59025200	0.62422400
C	-3.30257900	-1.30274100	0.77813500
C	-3.35981700	-2.55315800	1.38790400
C	-4.47747400	-0.56283000	0.62532000
C	-4.57878400	-3.05922000	1.83425400
H	-2.44245000	-3.11884800	1.51227600
C	-5.69397900	-1.07373300	1.06038500
H	-4.43394200	0.42747100	0.17715400
C	-5.74872000	-2.32620100	1.66825800
H	-4.61162600	-4.03289100	2.31557700
H	-6.60079600	-0.48876900	0.93494900
H	-6.69793400	-2.72309600	2.01667900
C	-1.78474300	0.66072300	0.80962800
C	-1.73774000	1.82702200	0.05089100
C	-1.68125200	0.76079500	2.20194300
C	-1.62637700	3.07147900	0.67071700
H	-1.75385900	1.79425100	-1.03241400
C	-1.56970400	1.99766600	2.82009000
H	-1.70375800	-0.14861300	2.79613200
C	-1.55883300	3.16323300	2.05391500
H	-1.57853900	3.96790400	0.05916200
H	-1.50368300	2.05582500	3.90309400
H	-1.48834300	4.13459500	2.53592200
C	0.84742000	-3.02235200	-0.44127500
H	1.10941600	-3.37448400	0.56400100
H	0.13952900	-3.76056400	-0.83976700

H	1.75870700	-3.08471400	-1.04886000
H	-0.09079900	-0.01534000	-1.86703600
O	1.18377200	-0.48456800	0.10318400
P	2.47236000	0.17157800	-0.47752200
C	3.81920700	-0.43473800	0.59177900
C	5.07383600	0.18388900	0.57788600
C	3.60966700	-1.54896100	1.40517100
C	6.11205100	-0.32996100	1.34180700
H	5.24287500	1.06726300	-0.03028000
C	4.65225200	-2.05574600	2.17555600
H	2.62835100	-2.00777600	1.44345200
C	5.90574800	-1.45569300	2.13649500
H	7.08525900	0.15123200	1.31826900
H	4.48011900	-2.92086000	2.80934500
H	6.72018000	-1.85573600	2.73378100
C	2.49039700	1.95244700	-0.20451000
C	3.31722000	2.79092500	-0.95585500
C	1.73017800	2.46525700	0.84781700
C	3.37021100	4.14836400	-0.65896100
H	3.88311200	2.39605900	-1.79214500
C	1.80290300	3.82051400	1.14286200
H	1.07272000	1.81424200	1.41737300
C	2.61929700	4.66291000	0.39291200
H	3.99762600	4.80382500	-1.25562100
H	1.20782900	4.21850300	1.95886000
H	2.66709600	5.72274800	0.62649900
C	2.89905900	-0.36259500	-2.25560400
C	2.51324000	0.63278100	-3.30521200
H	3.14584600	0.67492200	-4.18241000
C	1.38210400	1.39092100	-3.19577500

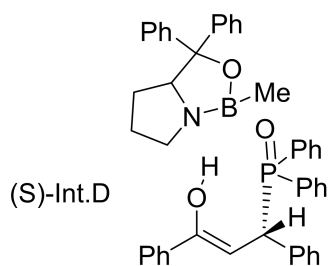
O	0.59213100	1.29066100	-2.16296100
C	1.00911200	2.39655900	-4.23392800
C	1.88490000	2.82189100	-5.24183400
C	-0.27195600	2.95757300	-4.19158900
C	1.48417700	3.75900200	-6.18512500
H	2.89682500	2.43079500	-5.28242000
C	-0.67420900	3.89579900	-5.13557000
H	-0.94006900	2.64556600	-3.39547200
C	0.20027000	4.29953000	-6.13949000
H	2.18027400	4.07751400	-6.95636200
H	-1.67475700	4.31711000	-5.08528900
H	-0.11040900	5.03476100	-6.87634900
C	4.34386000	-0.81560600	-2.34908100
C	5.35211400	0.04884600	-2.77997500
C	4.70055800	-2.11030000	-1.96459100
C	6.68026100	-0.36400300	-2.80950700
H	5.09618800	1.05562500	-3.09723200
C	6.02622200	-2.52499400	-1.98887000
H	3.93196800	-2.79853500	-1.62239600
C	7.02436700	-1.65042000	-2.40813100
H	7.44908400	0.32475900	-3.14841400
H	6.27940200	-3.53435900	-1.67801200
H	8.06154700	-1.97196400	-2.42801400
H	2.27529000	-1.27362900	-2.30558900

Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -2387.361988 Hartree

Enthalpy (calculated by Shermo 2.3.5): -2386.5168414 Hartree

Gibbs Free Energy (calculated by Shermo 2.3.5): -2386.7008379 Hartree



C	-2.44772900	-2.02060900	-3.17387500
C	-3.37284900	-0.77917200	-3.12488100
C	-3.57073100	-0.50783200	-1.62259400
C	-2.18127400	-0.84226600	-1.08256300
C	-1.94460400	-1.32012000	0.39300000
H	-3.02846000	-2.94332500	-3.31304700
H	-1.72375700	-1.94678100	-3.99684800
H	-2.86795400	0.07714500	-3.58843700
H	-3.88960000	0.51896100	-1.41408900
H	-4.31547700	-1.19245600	-1.20152100
H	-4.31483600	-0.93871300	-3.65797700
H	-1.48878700	-0.00939700	-1.28901600
N	-1.79790000	-2.01299900	-1.86831500
B	-1.07224200	-2.91116600	-1.07116800
O	-1.07603300	-2.47568900	0.25602300
C	-3.24902900	-1.76936400	1.05200200
C	-3.64843100	-3.10531900	1.00342400
C	-4.10133800	-0.83716000	1.64968400
C	-4.87493900	-3.49786200	1.53431500
H	-2.98940500	-3.84427000	0.56127100
C	-5.32595000	-1.22856500	2.17744400
H	-3.80059500	0.20484000	1.70993100
C	-5.71986400	-2.56281400	2.12091800
H	-5.16707400	-4.54358300	1.49077600
H	-5.97169600	-0.48881900	2.64246500

H	-6.67436500	-2.87084100	2.53809100
C	-1.24198200	-0.28570700	1.25392400
C	-1.41585700	1.08335900	1.05101400
C	-0.44128400	-0.70977600	2.31548700
C	-0.79884600	2.01002500	1.88671000
H	-2.03283800	1.44084900	0.23071800
C	0.18927000	0.21387400	3.14059500
H	-0.30968400	-1.77342300	2.48359200
C	0.01144500	1.57865800	2.93038100
H	-0.93602500	3.07232700	1.70586300
H	0.82301000	-0.13511800	3.95144700
H	0.50509100	2.30204200	3.57324100
C	-0.33908400	-4.22887800	-1.49891600
H	-0.36584500	-4.99569000	-0.71677300
H	-0.74728200	-4.65704000	-2.42095700
H	0.71948100	-4.00971500	-1.69562500
H	0.79741300	-0.90905900	-2.92130300
O	0.92439300	-0.71022900	-1.29313500
P	2.23640000	-0.04270700	-0.92929000
C	3.09365900	-0.94543100	0.39051700
C	4.37971500	-0.63184400	0.84921400
C	2.40419300	-2.03268300	0.93722700
C	4.96170300	-1.39943100	1.85154900
H	4.93476900	0.19767100	0.42168200
C	2.99554200	-2.79367700	1.94020700
H	1.40355200	-2.26332500	0.58110200
C	4.27119500	-2.47877200	2.39794200
H	5.96003600	-1.15497600	2.20258400
H	2.45404100	-3.63487900	2.36346200
H	4.73129500	-3.07622400	3.18018700

C	2.01395700	1.68755900	-0.42832900
C	2.66225300	2.26487800	0.66432900
C	1.13843500	2.46047200	-1.20238900
C	2.46264600	3.60888100	0.96248300
H	3.30859500	1.66491100	1.29648400
C	0.94665400	3.80348000	-0.90190300
H	0.60601000	2.00408100	-2.03142800
C	1.61385200	4.38082800	0.17592000
H	2.96659400	4.05049800	1.81731700
H	0.27004600	4.39896600	-1.50797900
H	1.46147200	5.43098100	0.40960500
C	3.29477600	-0.06084600	-2.47754800
C	2.61156200	0.69084100	-3.58726500
H	3.07335300	1.62220200	-3.89302300
C	1.51358100	0.27789400	-4.26205300
O	0.75981900	-0.78962300	-3.91192500
C	1.01183100	0.97723200	-5.46268900
C	1.85275900	1.74649900	-6.27818600
C	-0.34087100	0.86888400	-5.80909400
C	1.34654400	2.41539200	-7.38422400
H	2.91552400	1.79584100	-6.06118200
C	-0.84356900	1.53554500	-6.91998800
H	-0.98983700	0.25553400	-5.19376900
C	-0.00483900	2.31650000	-7.70903100
H	2.01379800	3.00289600	-8.00850700
H	-1.89649100	1.44268800	-7.17140400
H	-0.39675300	2.83422900	-8.57975300
C	4.70965600	0.39032200	-2.22934700
C	5.00630200	1.73635500	-1.99195000
C	5.74647300	-0.54407600	-2.18374400

C	6.30686000	2.13195100	-1.69843200
H	4.21167700	2.47739500	-2.01908400
C	7.04827700	-0.14844000	-1.89498900
H	5.52693400	-1.59353300	-2.36369100
C	7.33204100	1.19079300	-1.64522300
H	6.51944500	3.18037300	-1.50956200
H	7.84193000	-0.88935400	-1.86372100
H	8.34746400	1.50141100	-1.41717100
H	3.29448900	-1.13793700	-2.71318100

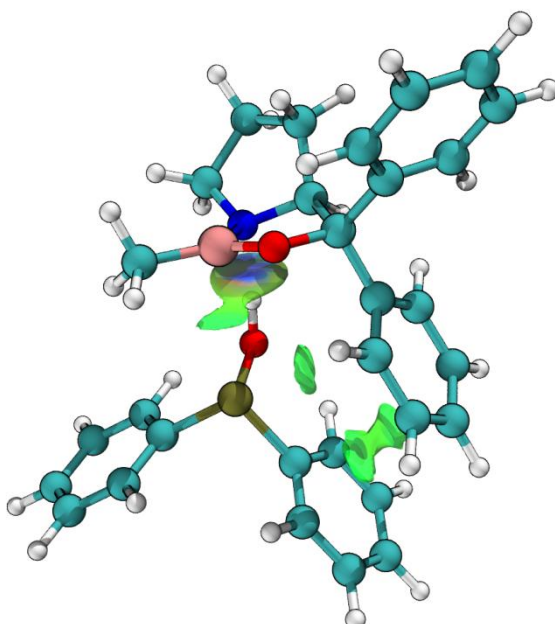
Charge: 0 Multiplicity: 1

Single Point Energy (M06-2X/def2-TZVP, SMD: in toluene): -2387.369886 Hartree

Enthalpy (calculated by Sermo 2.3.5): -2386.5223241 Hartree

Gibbs Free Energy (calculated by Sermo 2.3.5): -2386.7146314 Hartree

The π - π interactions between CBS and diphenylphosphine oxide¹⁷



Scheme S5. The π - π interactions between CBS and diphenylphosphine oxide

7. References

1. S. Jones, D. Valette, Enantioselective synthesis of allylic alcohols via an oxazaborolidinium ion catalyzed Diels-Alder/Retro-Diels-Alder sequence. *Org. Lett.* **2009**, *11*, 5358-5361.
2. X. Hao, J. Huang, T. Wang, J. Lv, J. Gong & M. Song, PCN pincer palladium (II) complex catalyzed enantioselective hydrophosphination of enones: synthesis of pyridine-functionalized chiral phosphine oxides as NCsp³O pincer preligands. *J. Org. Chem.* **2014**, *79*, 9512-9530.
3. A. Russo, A. Lattanzi, Asymmetric organocatalytic conjugate addition of diarylphosphane oxides to chalcones. 2010, Wiley Online Library.
4. Y. Liu, C. Wang, Y. Tong, Y. Ling, C. Zhou, B. Xiong, Cascade reaction of α,β -unsaturated ketones and 2-aminoaryl alcohols for the synthesis of 3-acylquinolines by a copper nanocatalyst. *Adv. Synth. Catal.* **2021**, *363*, 4422-4429.
5. J. Humbrías-Martín, M. C. Pérez-Aguilar, R. Mas-Ballesté, A. D. Litta, A. Lattanzi, G. D. Sala, J. A. Fernández-Salas, J. Alemán, Enantioselective conjugate azidation of α,β -unsaturated ketones under bifunctional organocatalysis by direct activation of TMSN₃. *Adv. Synth. Catal.* **2019**, *361*, 4790-4796.
6. C. Wu, G. Yue, C. D. Nielsen, K. Xu, H. Hirao, J. Zhou, Asymmetric conjugate addition of organoboron reagents to common enones using copper catalysts. *J. Am. Chem. Soc.* **2016**, *138*, 742-745.
7. X. Wei, C. Bai, L. Zhao, P. Zhang, Z. Li, Y. Wang, Q. Su, Lewis acid enables ketone phosphorylation: synthesis of alkenyl phosphonates. *Chin. J. Chem.* **2021**, *39*, 1855-1860.
8. J. Feng, X. Chen, M. Shi, W. Duan, Palladium-catalyzed asymmetric addition of diarylphosphines to enones toward the synthesis of chiral phosphines. *J. Am. Chem. Soc.* **2010**, *132*, 5562-5563.
9. a) F. Neese, "Software update: the ORCA program system, version 4.0" *WIREs Comput. Mol. Sci.* **2017**, *8*, 1327.
b) F. Neese, "The ORCA program system" *WIREs Comput. Mol. Sci.* **2012**, *2*, 73-78.
10. S. Grimme, A. Hansen, S. Ehlert, J. M. Mewes, *J. Chem. Phys.* **2021**, *154*, 064103.
11. A. V. Marenich, C. J. Cramer, D. G. Truhlar, Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Phys. Chem. B* **2009**, *113*, 6378-6396.
12. T. Lu, Q. Chen, Shermo: A general code for calculating molecular thermochemistry properties, *Comput. Theor. Chem.* **2021**, *1200*, 113249.

13. a) Y. Zhao, D. G. Truhlar, The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215-241 b) F. Weigend, R. Ahlrichs, Balanced basis sets of split valence, triple zeta valence and quadruple zeta valence quality for H to Rn: Design and assessment of accuracy. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297-3305. c) F. Neese, F. Wennmohs, A. Hansen, U. Becker, Efficient, approximate and parallel Hartree-Fock and hybrid DFT calculations. A 'chain-of-spheres' algorithm for the Hartree-Fock exchange. *Chem. Phys.* **2009**, *356*, 98-109. d) S. Ehlert, U. Huniar, J. Ning, J. W. Furness, J. Sun, A. D. Kaplan, J. P. Perdew, J. G. Brandenburg, *J. Chem. Phys.* **2021**, *154*, 061101. e) S. Grimme, S. Ehrlich, L. Goerigk, Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456-1465. f) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.*, **2010**, *132*, 154104.
14. CYLview20, C. Y. Legault, Université de Sherbrooke, 2020 (<http://www.cylview.org>)
15. a) J. Zhang, M. Dolg, ABCluster: The Artificial Bee Colony Algorithm for Cluster Global Optimization. *Phys. Chem. Chem. Phys.* **2015**, *17*, 24173-24181. b) J. Zhang, M. Dolg, Global Optimization of Rigid Molecular Clusters by the Artificial Bee Colony Algorithm. *Phys. Chem. Chem. Phys.*, **2016**, *18*, 3003-3010.
16. C. Bannwarth, S. Ehlert, S. Grimme, GFN2-xTB-An Accurate and Broadly Parametrized Self-Consistent Tight-Binding Quantum Chemical Method with Multipole Electrostatics and Density-Dependent Dispersion Contributions. *J. Chem. Theory Comput.* **2019**, *15*, 1652-1671.
17. T. Lu, Q. Chen, Independent gradient model based on Hirshfeld partition: A new method for visual study of interactions in chemical systems. *J. Comput. Chem.* **2022**, *43*, 539-555.