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Palladium-Catalyzed Asymmetric 1,6-Addition of Diarylphosphines to Allylidenemalonates for Chiral Phosphine Synthesis

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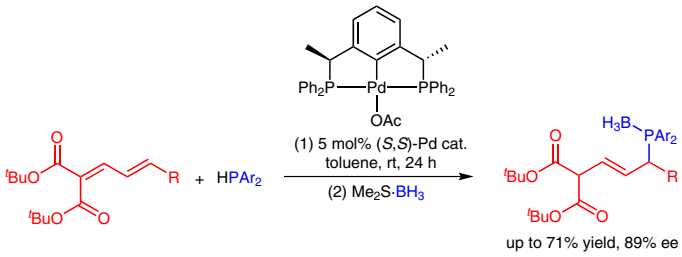

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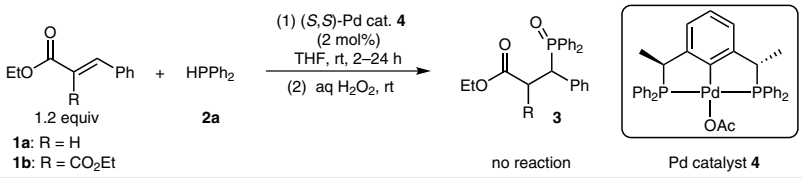
Abstract A pincer-palladium-catalyzed asymmetric 1,6-addition of diarylphosphines to allylidenemalonates has been developed for the synthesis of chiral allylic phosphines with up to 89% ee under mild conditions.

Key words asymmetric 1,6-addition, pincer palladium catalyst, chiral phosphines, allylidenemalonates

Chiral phosphines are widely used in catalysis as ligands coordinated to transition metals and as organocatalysts for controlling reactivity and stereoselectivity.[1] Therefore, discovering new methods for preparing optically active phosphorus compounds is essential and important. Asymmetric catalysis may provide more opportunities to offer efficient protocols compared to conventional methods which are usually based on the resolution of racemates with stoichiometric chiral reagents.[2] Asymmetric conjugate addition of phosphorus nucleophiles to electron-deficient alkenes is a direct method to construct chiral phosphines.[3,4] Most successful examples have been reported for 1,4-addition[5] rather than for 1,6-addition.[6] This may be due to the electronic difference at the β-position and the δ-position of the substrates. In general, 1,4-addition occurs more preferentially than 1,6-addition in numerous reported examples. By contrast, asymmetric 1,6-addition can be realized by carefully adjusting substrate structures or developing new catalysts. Recently, successful examples have been disclosed, including transition-metal-catalyzed addition of carbon nucleophiles to α,β,γ,δ-unsaturated systems and organocatalyzed 1,6-addition.[7–9] By contrast, phosphorus nucleophiles remain less explored in 1,6-addition reactions.[10]

We have previously studied asymmetric phosphorus addition to electron-deficient alkenes for chiral phosphine synthesis.[10a] During investigation of the diphenylphosphine reaction with α,β-unsaturated carboxylic esters, no reactivity was observed because of the low electrophilicity of substrate **1a** (Scheme 1).[10a] Subsequently, an electron-withdrawing group was introduced into the substrate to increase its reactivity; however, again no reaction occurred with **1b** (Scheme 1). It is worth mentioning that Leung and co-workers described a palladacycle-catalyzed enantioselective hydrophosphination of substituted methylidenemalonate ester **1b** with excellent enantioselectivity (96% ee).[11] They also reported the asymmetric addition of diphenylphosphine to α,β,γ,δ-unsaturated malonic ester **5a**, in which the 1,4-adduct was generated by the use of a palladacycle catalyst and the 1,6-adduct was produced with a pincer palladium catalyst.[10b,c] The regioselectivity (1,6-addition versus 1,4-addition) can be controlled by using different types of palladium catalysts. In the current study, we develop pincer-palladium-catalyzed[12] asymmetric addition of diarylphosphines to allylidenemalonates, which furnishes chiral allylic phosphine derivatives with good enantioselectivity in moderate yield.

Our studies began with the reaction of allylidenemalonate **5a** with diphenylphosphine in the presence of pincer palladium catalyst **4**.[10a] Due to the possible steric hindrance between the two bulky ester groups of **5a** and the phenyl groups of the phosphine nucleophile on the palladium catalyst, phosphorus nucleophiles would attack **5a** at the less hindered δ-position rather than the more electron-deficient β-position. Indeed, the reaction generated the 1,6-adduct **6** as the major product (Table 1, entry 1).[10a,13] Screening of the solvent provided no improvement in the ee and regioselectivity of the reaction (Table 1, entries 2–5). Malonates with other ester groups were subsequently tested. Experimental results revealed that **5b** bear-



Scheme 1 Our previous work

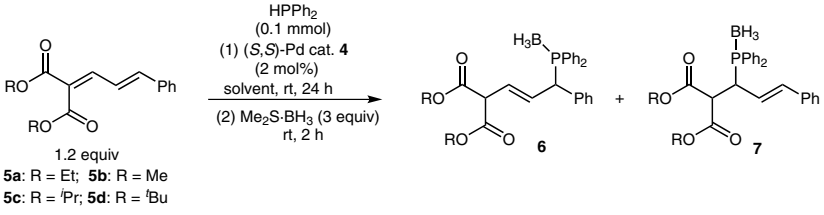
ing methyl ester groups provided a 1:1 mixture of the 1,4- and 1,6-adducts with moderate ee (Table 1, entry 6). By contrast, **5d** with bulky *tert*-butyl ester groups provided the 1,6-adduct **6** in highest ee and highest regioselectivity (Table 1, entry 8). To improve product yield, the catalyst loading and amount of **5d** were increased to 5 mol% and 4 equivalents, respectively, which furnished the 1,6-adduct in 70% yield with 89% ee (Table 1, entries 9 and 10).

The substrate scope was explored under the optimum conditions, and the results are shown in Table 2. Substrates that bear an alkyl, fluoro, chloro, bromo or methoxy moiety can be tolerated, and afford the corresponding products in moderate yield with good ee (Table 2, entries 1–9). For the nucleophilic component, the secondary phosphine with 4-methoxy groups was examined in the reaction with **5d**; the 1,6-adduct **6** was isolated in 53% yield with relatively low enantioselectivity (Table 2, entry 10).

A possible catalytic cycle is depicted in Scheme 2. First, the diarylphosphine **2** reacts with the pincer palladium catalyst **4** to produce a nucleophilic palladium–diarylphosphido intermediate.[4a] Then, this nucleophile attacks substrate **5d** at the δ-position to avoid the higher steric hindrance when such a nucleophile attacks at the β-position of the substrate. Finally, protonolysis of the resulting palladium–phosphine complex with acetic acid releases the 1,6-adduct and regenerates the palladium catalyst.

In summary, we have developed an asymmetric 1,6-addition of diarylphosphines to allylidenemalonates using a pincer palladium catalyst. The corresponding chiral allylic phosphine derivatives were produced with moderate to high enantioselectivity.

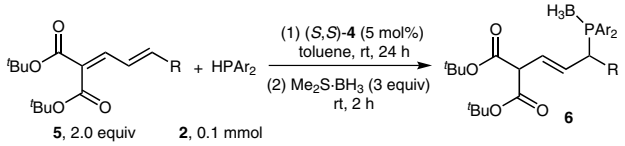
Table 1 Palladium-Catalyzed Addition of Diphenylphosphine to Allylidenemalonates **5**



Entry	Substrate	Solvent	Yield[a] (%) of **6**	Ratio of **6**/**7**	ee[b] (%) of **6**
1	**5a**	toluene	68	9:1	43
2	**5a**	THF	70	4:1	3
3	**5a**	CH_2Cl_2	63	3:1	15
4	**5a**	Et_2O	74	5:1	13
5	**5a**	MeCN	50	5:1	5
6	**5b**	toluene	34	1:1	38
7	**5c**	toluene	55	15:1	73
8	**5d**	toluene	32	15:1	88
9[c,d]	**5d**	toluene	70	15:1	89
10[c,e]	**5d**	toluene	70	15:1	89

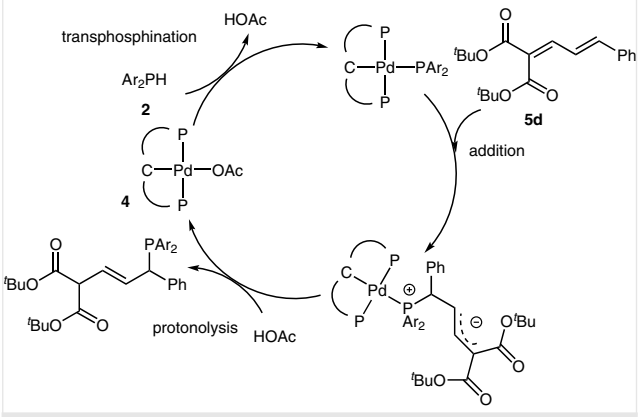
[a] Isolated yield.
[b] Determined by chiral HPLC (hexane/2-propanol).
[c] Catalyst **4** (5 mol%) used.
[d] **5d** (2 equiv) used.
[e] **5d** (4 equiv) used.

Table 2 Palladium-Catalyzed Addition of Diarylphosphines to Di-*tert*-butyl Allylidenemalonates



Entry	R	Ar	Yield[a] (%)	ee[b] (%)
1	Ph	Ph	70	89
2	4-MeC_6H_4	Ph	51	80
3	4-$MeOC_6H_4$	Ph	53	66
4	3-MeC_6H_4	Ph	58	83
5	3-$MeOC_6H_4$	Ph	63	89
6	4-BrC_6H_4	Ph	56	86
7	3-FC_6H_4	Ph	61	88
8	3-ClC_6H_4	Ph	71	87
9	2-naphthyl	Ph	50	78
10	Ph	4-$MeOC_6H_4$	53	62

[a] Isolated yield.
[b] Determined by chiral HPLC (hexane/2-propanol).



Scheme 2 Proposed catalytic cycle

Commercially available reagents were used without further purification. Solvents were treated prior to use according to standard methods. ^1H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded at room temperature in $CDCl_3$ on a Varian instrument (400 MHz, 100 MHz and 162 MHz, respectively) with TMS as internal standard. HRMS analyses were conducted on a Bruker Daltonics APEXIII™ ESI-FTICRMS mass spectrometer. Preparative TLC was performed on silica gel (300–400 mesh).

Asymmetric Phosphorus Addition Catalyzed by Pincer Palladium 4 (Table 2); Typical Procedure

Diarylphosphine (0.10 mmol) was added to a solution of (*S*,*S*)-palladium catalyst **4** (3.4 mg, 5 μmol Pd) and an α,β,γ,δ-unsaturated dicarboxylic ester **5** (0.20 mmol) in toluene (2.0 mL) at room temperature, and the resulting solution was stirred for 24 h. Then, $Me_2S{\cdot}BH_3$ (2 M in THF; 0.15 mL, 0.30 mmol) was added, and the resulting solution was stirred for 2 h. The excess borane was quenched with H_2O and the mixture was extracted with EtOAc. The organic phase was washed with saturated aq NaCl solution, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by silica gel preparative TLC (hexane/EtOAc, 10:1) to afford the 1,6-adduct as a white solid.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-phenyl-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 1)

White solid; yield: 37 mg (0.070 mmol, 70%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 80:20; flow = 1.0 mL/min); t_R = 4.8 (major enantiomer), 5.6 min (minor enantiomer); 89% ee.

$[\alpha]_D^{20}$ –31.0 (*c* 1.00, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.90–7.80 (m, 2 H), 7.55–7.16 (m, 9 H), 7.14 (d, J_{HH} = 6.8 Hz, 2 H), 7.06 (d, J_{HH} = 6.4 Hz, 2 H), 6.11 (ddd, *J* = 14.8, 9.2, 6.8 Hz, 1 H), 5.73 (ddd, *J* = 14.8, 8.0, 2.8 Hz, 1 H), 4.44 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.77 (d, *J* = 8.4 Hz, 1 H), 1.37 (s, 9 H), 1.36 (s, 9 H), 0.88 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.8 Hz), 166.9 (d, J_{CP} = 2.2 Hz), 135.8 (d, J_{CP} = 1.5 Hz), 133.7 (d, J_{CP} = 8.5 Hz), 133.0 (d, J_{CP} = 8.6 Hz), 131.6 (d, J_{CP} = 2.6 Hz), 131.1 (d, J_{CP} = 2.6 Hz), 130.6, 129.6 (d, J_{CP} = 4.8 Hz), 128.8 (d, J_{CP} = 9.7 Hz), 128.4 (d, J_{CP} = 9.7 Hz), 128.3 (d, J_{CP} = 52.7 Hz), 128.2 (d, J_{CP} = 2.2 Hz), 127.4 (d, J_{CP} = 2.6 Hz), 127.3 (d, J_{CP} = 52.7 Hz), 127.1 (d, J_{CP} = 10.8 Hz), 82.04, 81.98, 57.3 (d, J_{CP} = 1.1 Hz), 47.9 (d, J_{CP} = 30.0 Hz), 27.95, 27.93.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 23.9 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{32}H_{44}BNO_4P$: 547.3132; found: 547.3121.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-(4-methylphenyl)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 2)

White solid; yield: 28 mg (0.051 mmol, 51%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 90:10; flow = 1.0 mL/min); t_R = 5.1 (major enantiomer), 6.8 min (minor enantiomer); 80% ee.

$[\alpha]_D^{20}$ –31.6 (*c* 1.00, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.82 (t, J_{HH} = 8.0 Hz, 2 H), 7.52–7.41 (m, 5 H), 7.37 (t, J_{HH} = 7.2 Hz, 1 H), 7.27 (td, *J* = 8.0, 2.0 Hz, 2 H), 6.95 (s, 4 H), 6.07 (ddd, *J* = 15.6, 8.8, 7.2 Hz, 1 H), 5.70 (ddd, *J* = 15.6, 8.4, 3.2 Hz, 1 H), 4.41 (dd, *J* = 15.6, 8.8 Hz, 1 H), 3.76 (d, J_{HH} = 8.8 Hz, 1 H), 2.25 (s, 3 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.88 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.8 Hz), 166.9 (d, J_{CP} = 2.6 Hz), 137.0 (d, J_{CP} = 2.6 Hz), 133.7 (d, J_{CP} = 8.2 Hz), 133.0 (d, J_{CP} = 8.2 Hz), 132.6 (d, J_{CP} = 1.7 Hz), 131.5 (d, J_{CP} = 2.6 Hz), 131.0 (d, J_{CP} = 2.2 Hz), 130.8, 129.5 (d, J_{CP} = 4.8 Hz), 128.9 (d, J_{CP} = 2.3 Hz), 128.8 (d, J_{CP} = 9.3 Hz), 128.5 (d, J_{CP} = 50.1 Hz), 128.4 (d, J_{CP} = 9.7 Hz), 127.5 (d, J_{CP} = 52.4 Hz), 126.9 (d, J_{CP} = 10.8 Hz), 82.0, 81.9, 57.3 (d, J_{CP} = 1.5 Hz), 47.5 (d, J_{CP} = 29.9 Hz), 27.96, 27.94, 21.2 (d, J_{CP} = 0.7 Hz).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 23.5 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{33}H_{46}BNO_4P$: 561.3288; found: 561.3291.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-(4-methoxyphenyl)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 3)

White solid; yield: 30 mg (0.053 mmol, 53%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 90:10; flow = 1.0 mL/min); t_R = 7.0 (major enantiomer), 11.6 min (minor enantiomer); 66% ee.

$[\alpha]_D^{20}$ –40.9 (*c* 1.00, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.82 (t, J_{HH} = 8.8 Hz, 2 H), 7.60–7.25 (m, 8 H), 6.97 (dd, *J* = 8.4, 1.6 Hz, 2 H), 6.68 (d, J_{HH} = 8.1 Hz, 2 H), 6.06 (ddd, *J* = 15.6, 8.4, 6.0 Hz, 1 H), 5.70 (ddd, *J* = 15.6, 8.4, 3.2 Hz, 1 H), 4.41 (dd, *J* = 15.6, 8.8 Hz, 1 H), 3.76 (d, J_{HH} = 8.4 Hz, 1 H), 3.73 (s, 3 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.93 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.3 Hz), 166.9 (d, J_{CP} = 2.2 Hz), 158.8 (d, J_{CP} = 2.6 Hz), 133.7 (d, J_{CP} = 8.2 Hz), 133.0 (d, J_{CP} = 8.2 Hz), 131.5 (d, J_{CP} = 2.6 Hz), 131.1 (d, J_{CP} = 2.2 Hz), 130.8, 130.7 (d, J_{CP} = 2.4 Hz), 128.8 (d, J_{CP} = 9.7 Hz), 128.45 (d, J_{CP} = 53.0 Hz), 128.44 (d, J_{CP} = 9.7 Hz), 127.6 (d, J_{CP} = 1.4 Hz), 127.4 (d, J_{CP} = 52.3 Hz), 126.9 (d, J_{CP} = 10.7 Hz), 113.6 (d, J_{CP} = 1.9 Hz), 82.01, 81.96, 57.3 (d, J_{CP} = 1.5 Hz), 55.3, 47.0 (d, J_{CP} = 30.7 Hz), 27.94, 27.91.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 18.9 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{33}H_{46}BNO_5P$: 577.3237; found: 577.3243.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-(3-methylphenyl)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 4)

White solid; yield: 32 mg (0.058 mmol, 58%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 90:10; flow = 1.0 mL/min); t_R = 4.9 (major enantiomer), 6.2 min (minor enantiomer); 83% ee.

$[\alpha]_D^{20}$ –31.1 (*c* 1.00, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (t, J_{HH} = 8.0 Hz, 2 H), 7.52–7.41 (m, 4 H), 7.36–7.23 (m, 4 H), 7.10 (t, J_{HH} = 7.2 Hz, 1 H), 6.95 (d, J_{HH} = 7.2 Hz, 1 H), 6.86–6.81 (m, 2 H), 6.10 (ddd, *J* = 15.2, 9.2, 6.4 Hz, 1 H), 5.72 (ddd, *J* = 15.2, 8.4, 3.6 Hz, 1 H), 4.40 (dd, *J* = 15.2, 9.6 Hz, 1 H), 3.78 (d, J_{HH} = 8.4 Hz, 1 H), 2.18 (s, 3 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.88 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.9 Hz), 166.9 (d, J_{CP} = 2.7 Hz), 137.7 (d, J_{CP} = 2.3 Hz), 135.5 (d, J_{CP} = 1.5 Hz), 133.7 (d, J_{CP} = 8.0 Hz), 133.0 (d, J_{CP} = 8.3 Hz), 131.5 (d, J_{CP} = 2.3 Hz), 131.4 (d, J_{CP} = 8.7 Hz), 131.0 (d, J_{CP} = 2.3 Hz), 130.7, 130.4 (d, J_{CP} = 5.0 Hz), 128.8 (d, J_{CP} = 9.5 Hz), 128.4 (d, J_{CP} = 53.0 Hz), 128.3 (d, J_{CP} = 9.9 Hz), 128.0 (d, J_{CP} = 2.2 Hz), 127.4 (d, J_{CP} = 52.7 Hz), 127.0 (d, J_{CP} = 11.0 Hz), 126.6 (d, J_{CP} = 5.0 Hz), 82.00, 81.97, 57.3 (d, J_{CP} = 1.5 Hz), 47.8 (d, J_{CP} = 29.8 Hz), 27.93, 27.91, 21.4.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 23.5 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{33}H_{46}BNO_4P$: 561.3288; found: 561.3292.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-(3-methoxyphenyl)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 5)

White solid; yield: 35 mg (0.063 mmol, 63%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 90:10; flow = 1.0 mL/min); t_R = 6.4 (major enantiomer), 7.8 min (minor enantiomer); 89% ee.

$[\alpha]_D^{20}$ –19.2 (*c* 1.00, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (t, J_{HH} = 8.0 Hz, 2 H), 7.60–7.26 (m, 8 H), 7.05 (t, J_{HH} = 8.0 Hz, 1 H), 6.72–6.64 (m, 3 H), 6.06 (ddd, *J* = 15.2, 9.2, 6.0 Hz, 1 H), 5.72 (ddd, *J* = 15.2, 8.4, 3.2 Hz, 1 H), 4.41 (dd, *J* = 14.8, 8.8 Hz, 1 H), 3.78 (d, J_{HH} = 8.4 Hz, 1 H), 3.65 (s, 3 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.90 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.9 Hz), 166.9 (d, J_{CP} = 2.6 Hz), 159.3 (d, J_{CP} = 1.8 Hz), 133.7 (d, J_{CP} = 8.2 Hz), 133.0 (d, J_{CP} = 8.2 Hz), 132.7 (d, J_{CP} = 8.5 Hz), 131.6 (d, J_{CP} = 2.3 Hz), 131.1 (d, J_{CP} = 2.3 Hz), 130.5, 129.2 (d, J_{CP} = 1.9 Hz), 128.8 (d, J_{CP} = 9.7 Hz), 128.6 (d, J_{CP} = 9.7 Hz), 128.3 (d, J_{CP} = 52.7 Hz), 127.5 (d, J_{CP} = 52.7 Hz), 127.2 (d, J_{CP} = 10.8 Hz), 122.1 (d, J_{CP} = 5.2 Hz), 114.5 (d, J_{CP} = 4.5 Hz), 113.8 (d, J_{CP} = 2.2 Hz), 82.04, 81.99, 57.3 (d, J_{CP} = 1.5 Hz), 55.2, 48.0 (d, J_{CP} = 30.0 Hz), 27.95, 27.94.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 24.6 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{33}H_{46}BNO_5P$: 577.3237; found: 577.3242.

Di-*tert*-butyl 2-[(1*E*)-3-(4-Bromophenyl)-3-(diphenylphosphino)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 6)

White solid; yield: 34 mg (0.056 mmol, 56%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 90:10; flow = 1.0 mL/min); t_R = 6.4 (major enantiomer), 10.0 min (minor enantiomer); 86% ee.

$[\alpha]_D^{20}$ –26.3 (*c* 1.00, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.85–7.82 (m, 2 H), 7.55–7.38 (m, 10 H), 6.93 (d, J_{HH} = 6.8 Hz, 2 H), 6.10–6.00 (m, 1 H), 5.72 (ddd, *J* = 15.2, 8.0, 6.8 Hz, 1 H), 4.41 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.77 (d, J_{HH} = 8.8 Hz, 1 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.90 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (d, J_{CP} = 1.5 Hz), 166.8 (d, J_{CP} = 2.3 Hz), 134.9 (d, J_{CP} = 1.1 Hz), 133.6 (d, J_{CP} = 8.6 Hz), 133.2 (d, J_{CP} = 8.2 Hz), 133.0 (d, J_{CP} = 8.1 Hz), 131.7 (d, J_{CP} = 2.6 Hz), 131.4, 131.3 (d, J_{CP} = 1.3 Hz), 131.2 (d, J_{CP} = 4.8 Hz), 130.0, 128.9 (d, J_{CP} = 10.0 Hz), 128.6 (d, J_{CP} = 10.0 Hz), 127.9 (d, J_{CP} = 52.5 Hz), 127.7 (d, J_{CP} = 10.4 Hz), 127.2 (d, J_{CP} = 52.8 Hz), 82.2, 82.1, 57.3 (d, J_{CP} = 1.1 Hz), 47.3 (d, J_{CP} = 30.1 Hz), 28.0, 27.9.

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 24.4 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{32}H_{43}BBrNO_4P$: 625.2237; found: 625.2238.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-(3-fluorophenyl)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 7)

White solid; yield: 33 mg (0.061 mmol, 61%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 80:20; flow = 1.0 mL/min); t_R = 5.4 (major enantiomer), 6.4 min (minor enantiomer); 88% ee.

$[\alpha]_D^{20}$ –29.9 (*c* 1.00, CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.86–7.80 (m, 2 H), 7.55–7.38 (m, 6 H), 7.29 (td, *J* = 8.0, 2.4 Hz, 2 H), 7.12–7.07 (m, 1 H), 6.84 (d, J_{HH} = 8.0 Hz, 2 H), 6.77 (dd, *J* = 10.0, 2.0 Hz, 1 H), 6.06 (ddd, *J* = 15.6, 9.2, 6.4 Hz, 1 H), 5.74 (ddd, *J* = 15.6, 8.8, 3.2 Hz, 1 H), 4.44 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.78 (d, J_{HH} = 8.8 Hz, 1 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.90 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (d, J_{CP} = 1.4 Hz), 166.8 (d, J_{CP} = 2.2 Hz), 133.6 (d, J_{CP} = 8.2 Hz), 132.9 (d, J_{CP} = 8.5 Hz), 131.7 (d, J_{CP} = 2.6 Hz), 131.3 (d, J_{CP} = 2.6 Hz), 130.0, 129.6 (dd, *J* = 8.2, 2.0 Hz), 128.9 (d, J_{CP} = 9.7 Hz), 128.6 (d, J_{CP} = 9.6 Hz), 127.9 (d, J_{CP} = 52.4 Hz), 127.7 (d, J_{CP} = 10.8 Hz), 127.0 (d, J_{CP} = 52.4 Hz), 125.4 (d, J_{CP} = 3.4 Hz), 125.3 (d, J_{CP} = 2.2 Hz), 116.5 (dd, J_{CF} = 22.6 Hz, J_{CP} = 4.8 Hz), 114.3 (dd, J_{CF} = 20.8

Hz, J_{CP} = 3.0 Hz), 82.2, 82.1, 57.3 (d, J_{CP} = 1.5 Hz), 47.6 (dd, J_{CP} = 30.2 Hz, J_{CF} = 2.3 Hz,), 27.94, 27.93.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25.0 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{32}H_{43}BFNO_4P$: 565.3038; found: 565.3045.

Di-*tert*-butyl 2-[(1*E*)-3-(3-Chlorophenyl)-3-(diphenylphosphino)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 8)

White solid; yield: 40 mg (0.071 mmol, 71%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 80:20; flow = 1.0 mL/min); t_R = 4.0 (major enantiomer), 4.5 min (minor enantiomer); 87% ee.

$[\alpha]_D^{20}$ –42.1 (*c* 1.00, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.4 Hz, 2 H), 7.55–7.36 (m, 6 H), 7.30 (t, *J* = 7.2 Hz, 2 H), 7.12 (t, J_{HH} = 7.2 Hz, 1 H), 7.08 (t, J_{HH} = 8.0 Hz, 1 H), 6.97 (d, J_{HH} = 8.0 Hz, 1 H), 6.96 (s, 1 H), 6.06 (ddd, *J* = 15.6, 8.8, 7.6 Hz, 1 H), 5.75 (ddd, *J* = 15.6, 8.4, 2.8 Hz, 1 H), 4.41 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.78 (d, J_{HH} = 8.4 Hz, 1 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.92 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (d, J_{CP} = 1.9 Hz), 166.7 (d, J_{CP} = 2.7 Hz), 137.8 (d, J_{CP} = 1.2 Hz), 133.9 (d, J_{CP} = 2.6 Hz), 133.6 (d, J_{CP} = 8.4 Hz), 132.9 (d, J_{CP} = 8.7 Hz), 131.7 (d, J_{CP} = 2.6 Hz), 131.4 (d, J_{CP} = 2.3 Hz), 129.8, 129.6 (d, J_{CP} = 4.5 Hz), 129.4 (d, J_{CP} = 2.2 Hz), 128.9 (d, J_{CP} = 9.8 Hz), 128.84 (d, J_{CP} = 52.7 Hz), 128.83 (d, J_{CP} = 6.0 Hz), 128.6 (d, J_{CP} = 9.9 Hz), 127.7, 127.5 (d, J_{CP} = 2.7 Hz), 126.8 (d, J_{CP} = 52.7 Hz), 82.2, 82.1, 57.3 (d, J_{CP} = 1.1 Hz), 47.5 (d, J_{CP} = 29.2 Hz), 27.92, 27.90.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 24.3 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{32}H_{43}BClNO_4P$: 581.2742; found: 581.2749.

Di-*tert*-butyl 2-[(1*E*)-3-(Diphenylphosphino)-3-(2-naphthyl)-1-propen-1-yl]propanedioate–Borane Complex (Table 2, Entry 9)

White solid; yield: 29 mg (0.050 mmol, 50%).

The ee was determined on a Daicel Chiralpak AD column (hexane/2-propanol, 80:20; flow = 1.0 mL/min); t_R = 4.5 (major enantiomer), 6.2 min (minor enantiomer); 78% ee.

$[\alpha]_D^{20}$ –29.8 (*c* 1.00, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.86 (dd, J_{HH} = 8.8, 7.2 Hz, 2 H), 7.76–7.71 (m, 1 H), 7.62 (d, J_{HH} = 8.8 Hz, 2 H), 7.55–7.36 (m, 8 H), 7.32 (t, J_{HH} = 7.2 Hz, 1 H), 7.25–7.20 (m, 3 H), 6.21 (ddd, *J* = 15.2, 9.2, 7.2 Hz, 1 H), 5.77 (ddd, *J* = 15.6, 8.4, 3.2 Hz, 1 H), 4.62 (dd, *J* = 15.2, 8.8 Hz, 1 H), 3.80 (d, J_{HH} = 8.4 Hz, 1 H), 1.36 (s, 9 H), 1.35 (s, 9 H), 0.92 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.9 Hz), 166.9 (d, J_{CP} = 2.3 Hz), 133.7 (d, J_{CP} = 8.3 Hz), 133.3 (d, J_{CP} = 1.5 Hz), 133.1 (d, J_{CP} = 2.2 Hz), 133.0 (d, J_{CP} = 8.3 Hz), 132.5 (d, J_{CP} = 1.9 Hz), 131.6 (d, J_{CP} = 2.3 Hz), 131.2 (d, J_{CP} = 2.7 Hz), 130.6, 128.8 (d, J_{CP} = 9.5 Hz), 128.6 (d, J_{CP} = 25.4 Hz), 128.5 (d, J_{CP} = 9.9 Hz), 127.9 (d, J_{CP} = 0.7 Hz), 127.8 (d, J_{CP} = 1.9 Hz), 127.6 (d, J_{CP} = 1.1 Hz), 127.5 (d, J_{CP} = 3.9 Hz), 127.33, 127.28 (d, J_{CP} = 31.9 Hz), 126.1 (d, J_{CP} = 0.7 Hz), 126.0 (d, J_{CP} = 1.1 Hz), 82.06, 82.03, 57.3 (d, J_{CP} = 1.2 Hz), 48.0 (d, J_{CP} = 29.6 Hz), 27.9.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 24.8 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{36}H_{46}BNO_4P$: 597.3288; found: 597.3288.

Di-*tert*-butyl 2-{(1*E*)-3-[Bis(4-methoxyphenyl)phosphino]-3-phenyl-1-propen-1-yl}propanedioate–Borane Complex (Table 2, Entry 10)

White solid; yield: 31 mg (0.053 mmol, 53%).

The ee was determined on a Daicel Chiralpak IC column (hexane/2-propanol, 98:2; flow = 0.5 mL/min); t_R = 88.9 (major enantiomer), 101.0 min (minor enantiomer); 62% ee.

$[\alpha]_D^{20}$ –39.1 (*c* 1.00, CH_2Cl_2).

^1H NMR (400 MHz, $CDCl_3$): δ = 7.74 (t, J_{HH} = 9.2 Hz, 2 H), 7.35–7.22 (m, 3 H), 7.22–7.15 (m, 2 H), 7.10–7.02 (m, 2 H), 7.00 (dd, *J* = 8.4, 1.2 Hz, 2 H), 6.78 (dd, *J* = 8.4, 1.2 Hz, 2 H), 6.08 (ddd, *J* = 14.8, 8.8, 6.8 Hz, 1 H), 5.69 (ddd, *J* = 14.8, 8.4, 3.2 Hz, 1 H), 4.34 (dd, *J* = 15.2, 9.2 Hz, 1 H), 3.83 (s, 3 H), 3.77 (d, J_{HH} = 8.4 Hz, 1 H), 3.76 (s, 3 H), 1.38 (s, 9 H), 1.36 (s, 9 H), 0.90 (br, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.1 (d, J_{CP} = 1.9 Hz), 166.9 (d, J_{CP} = 2.6 Hz), 162.1 (d, J_{CP} = 2.3 Hz), 161.7 (d, J_{CP} = 2.2 Hz), 135.4 (d, J_{CP} = 9.3 Hz), 134.6 (d, J_{CP} = 9.3 Hz), 130.9, 129.6 (d, J_{CP} = 4.8 Hz), 128.8 (d, J_{CP} = 9.7 Hz), 128.1 (d, J_{CP} = 2.2 Hz), 127.2 (d, J_{CP} = 2.6 Hz), 126.8 (d, J_{CP} = 10.8 Hz), 119.4 (d, J_{CP} = 57.7 Hz), 118.2 (d, J_{CP} = 57.6 Hz), 114.4 (d, J_{CP} = 10.7 Hz), 114.0 (d, J_{CP} = 10.0 Hz), 82.0, 81.9, 57.4 (d, J_{CP} = 1.1 Hz), 55.4, 55.3, 48.5 (d, J_{CP} = 30.9 Hz), 27.94, 27.90.

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 21.2 (m).

HRMS (ESI): *m*/*z* $[M + NH_4]^+$ calcd for $C_{34}H_{48}BNO_6P$: 607.3343; found: 607.3338.

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Supporting Information

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