P-Chirogenic α-Carboxyphosphine Boranes as Effective Pre-Ligands in Palladium-Catalyzed Asymmetric Reactions

Franck Dolhem,[a] Magnus J. Johansson,[a] Thomas Antonsson,[b] Nina Kann*[a]

[a] Organic Chemistry, Department of Chemical and Biological Engineering, Chalmers University of Technology, 41296 Göteborg, Sweden
Fax +46(31)7723657; E-mail: kann@chalmers.se

[b] Medicinal Chemistry, AstraZeneca R&D Mölndal, 43183 Mölndal, Sweden

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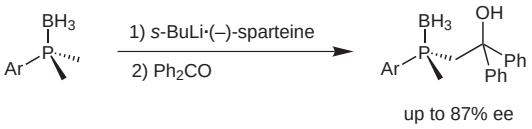
Abstract: P-Chirogenic α-carboxyphosphine boranes have been applied directly as pre-ligands in palladium-catalyzed asymmetric allylic alkylation and amination reactions, with in situ deprotection of the borane moiety. Using dimethylmalonate as the nucleophile afforded the alkylated product in up to 91% ee, while reaction with benzylamine gave amination in up to 94% ee. In both cases, the opposite enantiomer could be accessed in high ee by using the antipode of the ligand, easily accessible by exchanging (–)-sparteine for a (+)-sparteine mimic in the desymmetrization process used for preparing the ligands.

Key words: asymmetric catalysis, allylic alkylation, allylic amination, phosphine ligands, P-chiral

P-Chirogenic phosphine ligands in asymmetric catalysis are a useful alternative to phosphine ligands with chirality situated in the surrounding carbon skeleton.[1] Several routes are available for the formation of P-chirogenic phosphines. Jugé and Genêt used ephedrine as a chiral auxiliary in a practical method that affords highly enantiopure phosphine, but requires several steps for the transformation.[2] A one-pot method was reported by Evans in 1995, involving the asymmetric deprotonation of borane-protected prochiral dimethyl aryl phosphine using (–)-sparteine–alkyllithium complexes (Scheme 1).[3]



Scheme 1 Evans' method for the desymmetrization of prochiral phosphine boranes.

The latter method has been further extended by Livinghouse in the dynamic kinetic resolution of a racemic secondary phosphine borane.[4] However, both these methods suffer from the unavailability of (+)-sparteine, and there are in general few examples of methods where both enantiomers of a P-chirogenic phosphine ligand are prepared.[5] We have shown that O'Brien's (+)-sparteine mimic, (+)-**1** (Figure 1),[6] derived from easily accessible (–)-cytisine,[7] can be applied in the desymmetrization of phosphine boranes, affording the corresponding P-chirogenic ligand in up to 92% ee.[8]

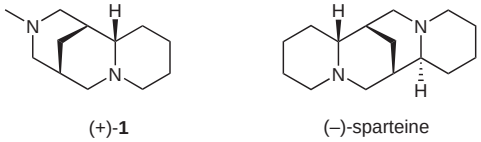


Figure 1

By using carbon dioxide as the electrophile in the Evans' desymmetrization, α-carboxyphosphines can be prepared, and Imamoto et al. have used such derivatives as intermediates in the preparation of P-chirogenic bisphosphine ligands.[9] Although a few examples of chiral α-carboxyphosphine ligands that are not P-chirogenic have been described,[10] there are to our knowledge only two reports of the use of the corresponding P-chiral α-carboxyphosphine ligands in catalytic asymmetric reactions. Hii and co-workers recently described two diarylic P-chirogenic α-carboxyphosphines and their application in palladium-catalyzed asymmetric allylic alkylation (AAA) with up to 81% ee.[11] Kobayashi and co-workers have also reported one example of a cyclic P-chirogenic phosphine carboxylic acid in AAA in 77% ee.[12] In the latter case, however, optical resolution with quinine was required to obtain enantiopure ligand. These two reports prompted us to disclose our recent results using P-chirogenic alkyl and aryl phosphine borane carboxylic acids directly as pre-ligands in asymmetric allylic alkylation and amination reactions catalyzed by palladium, with in situ deprotection of the phosphine borane.

The α-carboxyphosphine boranes (Figure 2) were prepared in one step from the corresponding prochiral dimethyl phosphine boranes[13] via asymmetric deprotonation with *sec*-butyllithium and (–)-sparteine followed by quenching with carbon dioxide (Scheme 2),[14] affording enantioenriched pre-ligands **3a**–**i**.[15] Purification via recrystallization improved the initial enantioselectivity obtained to 90–96% ee in most cases with the exception of the more sterically hindered ligands **3e**,**h**,**i**, where lower enantioselectivities were obtained. For R = *tert*-butyl, the antipode of the ligand was also synthesized by exchanging (–)-sparteine for (+)-**1**, providing pre-ligand **4**.[16]

The phosphine boranes were subsequently applied directly in the palladium-catalyzed asymmetric allylic alkyla-

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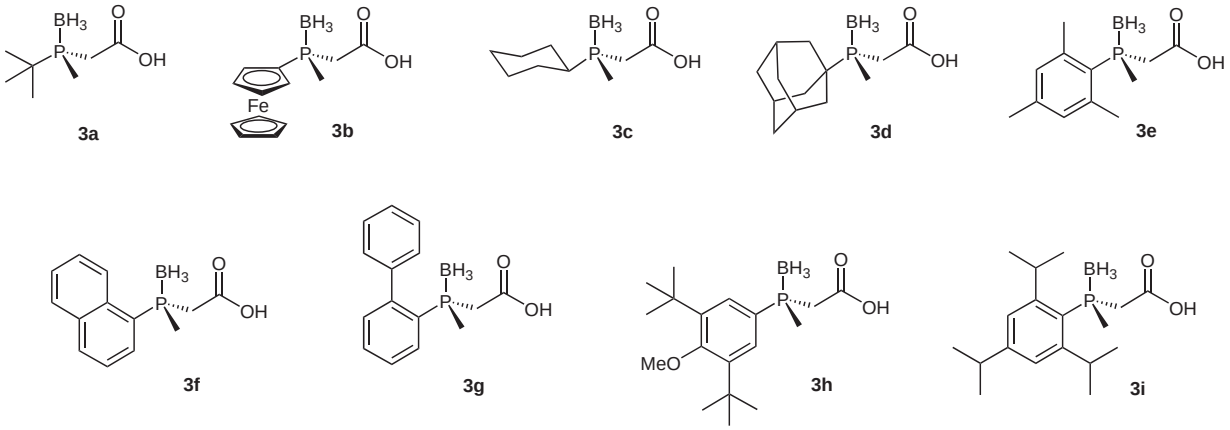
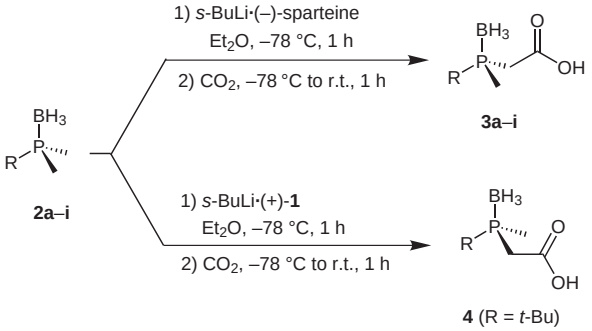


Figure 2 P-Chirogenic α-carboxyphosphine boranes **3a–i** used as pre-ligands in the asymmetric allylic alkylation and amination reactions.



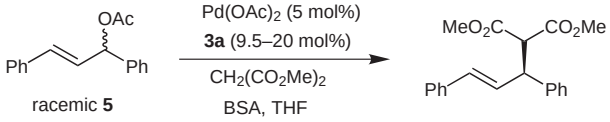
Scheme 2 Preparation of P-chirogenic α-carboxyphosphine boranes **3a–i** and **4**. See Figure 2 for structures of **3a–i**.

tion of 1,3-diphenylpropenyl acetate with dimethyl malonate.[17] To avoid an extra step, the in situ deboronation method of Jugé and co-workers was applied, where Pd(II) is reduced to Pd(0) by the phosphine–borane complex with concomitant deprotection of the phosphine.[18] This also evades handling of the air-sensitive free phosphine ligand. Some initial optimization studies were carried out with pre-ligand **3a** to determine the optimal conditions for the reaction (Table 1).

The highest enantioselectivity (entry 3, 91%), was attained using a ligand-to-Pd ratio of 2 at 0 °C. The rather low conversion at this temperature was not practical, however, and we opted instead for running the reaction at room temperature. A ligand to metal ratio of 1.9 equivalents (entry 4) gave a slightly better selectivity than running the reaction with 4 equivalents (entry 5), while the addition of potassium acetate (entries 1 and 2) was detrimental for the enantioselectivity. Therefore, these optimized conditions were used to scan through the different α-carboxyphosphine boranes (Table 2).[19]

Enantioselectivities were moderate (40–64% ee) with ligands **3b** and **3d–f** (entries 2, 3 and 5–7), while the biaryl ligand **3g** gave an ee of only 9% (entry 8). The more sterically hindered ligands **3h** and **3i** (entries 9 and 10) gave low conversion and racemic product. Best results were obtained with the *tert*-butyl-substituted ligand **3a** (entry 1) which afforded the chiral malonyl-substituted product in

Table 1 Optimization of Conditions for Palladium-Catalyzed AAA Using Ligand **3a** and Acetate **5**



Entry	Ratio **3a**:Pd	Additive	Time (h)	Temp (°C)	Conv. (%)[a]	ee (%)[b]
1	2	KOAc	36	20	33	47
2	4	KOAc	16	20	99	63
3	2	–	20	0	30	91
4	1.9	–	12	20	100	89
5	4	–	12	20	100	86

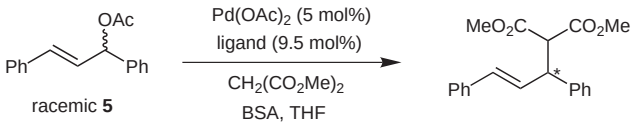
[a] Conversion measured by HPLC.
[b] Enantiomeric excess measured by chiral HPLC, see experimental part for details.

89% ee. The enantiomeric product could be prepared in 86% ee by employing ligand **4** (entry 11). Somewhat surprisingly, ligand **3c** with a cyclohexyl substituent, also afforded the opposite enantiomer and we have no good explanation for this observation.

Asymmetric alkylations with the corresponding carbonate **6** were also pursued (Table 3). A similar trend was seen in that ligands **3a** and **4** gave the best results, affording the two enantiomeric products in 91% and 88% ee, respectively (entries 1 and 10). In this case, not only ligands **3c** (entry 3) and **4** gave the opposite product enantiomer, but ligand **3i** (entry 9) also afforded the *S*-enantiomer. This is less surprising, however, as the corresponding reaction with the acetate **5** (Table 2, entry 10) gave racemic product.

Exchanging the malonate for an amine nucleophile like benzylamine gives access to a different product class and we therefore applied the two best pre-ligands, **3a** and **4**, in the palladium-catalyzed asymmetric allylic amination of substrates **5** and **6** (Table 4).[20,21] Due to the high intrinsic

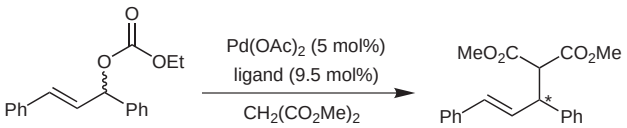
Table 2 Palladium-Catalyzed Asymmetric Allylic Alkylation with Acetate **5**



Entry	Ligand	Time (h)	Conv. (%)[a]	ee (%)[b]
1	**3a**	12	100	89 (*R*)
2	**3b**[c]	16	30	40 (*R*)
3	**3b**[d]	36	60	50 (*R*)
4	**3c**[d]	16	95	44 (*S*)
5	**3d**	16	85	60 (*R*)
6	**3e**	12	100	64 (*R*)
7	**3f**	12	100	47 (*R*)
8	**3g**	24	42	9 (*R*)
9	**3h**	12	33	0
10	**3i**	12	12	0
11	**4**	12	100	86 (*S*)

[a] Conversion measured by HPLC.
[b] Enantiomeric excess measured by chiral HPLC, see experimental part for details.
[c] Ligand to metal ratio 1.
[d] Ligand to metal ratio 2.

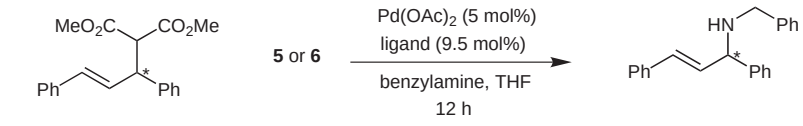
Table 3 Palladium-Catalyzed Asymmetric Allylic Alkylation of Carbonate **6**



Entry	Ligand	Time (h)	Conv. (%)[a]	ee (%)[b]
1	**3a**	12	100	91 (*R*)
2	**3b**	16	85	27 (*R*)
3	**3c**	16	90	26 (*S*)
4	**3d**	16	85	40 (*R*)
5	**3e**	12	100	64 (*R*)
6	**3f**	12	100	44 (*R*)
7	**3g**	12	100	30 (*R*)
8	**3h**	12	60	0
9	**3i**	12	10	6 (*S*)
10	**4**	12	100	88 (*S*)

[a] Conversion measured by HPLC.
[b] Enantiomeric excess measured by chiral HPLC, see experimental part for details.

Table 4 Palladium-Catalyzed Asymmetric Allylic Aminations of Acetate **5** and Carbonate **6**



Entry	Ligand	Substrate	Temp. (°C)	Conv. (%)[a]	ee (%)[b]
1	**3a**[c]	**5**	20	100	76 (*S*)
2	**3a**	**5**	5	100	94 (*S*)
3	**3a**	**6**	20	99	60 (*S*)
4	**4**[d]	**5**	20	95	66 (*R*)
5	**4**	**5**	5	95	87 (*R*)

[a] Conversion measured by HPLC.
[b] Enantiomeric excess measured by chiral HPLC, see experimental part.
[c] Ligand to metal ratio 2.2.
[d] Ligand to metal ratio 2.

reactivity of the nucleophile in this case, the reaction could be carried out at 5 °C and still give complete conversion, affording the amine-substituted product in up to 94% ee (entry 1). The other enantiomer was prepared in a somewhat lower, but still respectable, 87% ee (entry 5).

To investigate if the ligands were acting in a bidentate chelating fashion or as monodentate ligands, NMR studies were carried out. ^{13}C NMR on a complex formed using a 2:1 ligand-to-metal ratio in CD_2Cl_2 showed six signals in the region of δ = 120–150 ppm which could correspond to the four aromatic and two different allylic carbons of a symmetrically substituted π-allyl diphosphine complex. The singlet arising from the carboxyl group remained at δ = 174 ppm, corresponding to that of the free ligand. These observations, together with the fact that the use of one equivalent of ligand was detrimental to the reaction, lead us to believe that the phosphine is in fact coordinating to palladium in a monodentate fashion, with two ligands attached to each metal atom. Further studies are underway to clarify this issue.

In conclusion, we have shown that enantioenriched P-chirogenic dialkyl and alkyl aryl α-carboxyphosphine boranes, easily prepared in one step from non-chiral starting materials, are efficient pre-ligands in the palladium-catalyzed asymmetric allylic alkylation and amination of racemic 1,3-diphenylpropenyl acetate and carbonate with stereoselectivities of up to 94% ee. The opposite enantiomer of the product can be easily accessed by use of the phosphine ligand antipode.

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(13) Compounds **2a**,**c**,**d**,[22] **2b**,[23] **2e**[24] and **2f**[3] were prepared as described in the literature. Compounds **2g** and **2h** were prepared via the corresponding phosphine sulfides using the same procedure as for **2f**.[3] Compound **2i** was prepared from PCl_3 and 2,4,6-tri(isopropyl)-1-phenylmagnesium bromide, following a literature procedure.[25]

***P*,*P*-Dimethyl(2-biphenyl)phosphine Sulfide (Precursor to 2g)**

Waxy solid; 89% yield; mp 99–101 °C. IR (KBr): ν = 2986, 2873, 1770, 1458, 1383, 1140 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.58 (d, *J* = 13.2 Hz, 6 H), 7.18–7.47 (m, 8 H), 8.20–8.27 (m, 1 H). ^{13}C NMR ($CDCl_3$): δ = 23.56 (d, *J* = 56.9 Hz), 127.39 (d, *J* = 12.2 Hz), 127.87, 128.05, 129.54, 130.80 (d, *J* = 3.1 Hz), 131.23 (d, *J* = 9.1 Hz), 131.96 (d, *J* = 75.8 Hz), 132.23 (d, *J* = 12.1 Hz), 140.88 (d, *J* = 3.1 Hz), 144.07 (d, *J* = 8.3 Hz). Anal. Calcd for $C_{14}H_{15}PS$: C, 68.27; H, 6.14. Found: C, 68.21; H, 6.10.

***P*,*P*-Dimethyl(2-biphenyl)phosphineborane (2g)**

White powder; 90% yield; mp 91–93 °C. IR (KBr): ν = 2918, 2383, 1466, 1433, 1300, 1064, 952, 921 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.22 (d, *J* = 10.0 Hz, 6 H), 7.24–7.52 (m, 8 H), 7.97 (dd, *J* = 13.6, 8.8 Hz, 1 H). ^{13}C NMR ($CDCl_3$): δ = 13.76 (d, *J* = 39.4 Hz), 127.48 (d, *J* = 11.4 Hz), 127.97 (s), 128.10 (s), 128.79 (d, *J* = 50.0 Hz), 129.53 (s), 130.56 (d, *J* = 2.2 Hz), 131.24 (d, *J* = 6.1 Hz), 133.61 (d, *J* = 15.9 Hz), 141.09 (d, *J* = 2.3 Hz), 146.29 (d, *J* = 2.3 Hz). Anal. Calcd for $C_{14}H_{18}BP$: C, 73.72; H, 7.95. Found: C, 73.64; H, 8.06.

***P*,*P*-Dimethyl[3,5-di(*tert*-butyl)-6-methoxyphenyl]phosphine Sulfide (Precursor to 2h)**

White powder; 25% yield; mp 150–155 °C. IR (KBr): ν = 2970, 2840, 1590, 1576, 1475, 1270, 1240, 1000, 920 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.33 (s, 18 H), 1.86 (d, *J* = 13.2 Hz, 6 H), 3.60 (s, 3 H), 7.63 (d, *J* = 14.0 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 23.21 (d, *J* = 56.9 Hz), 32.00 (s), 36.20 (s), 64.54 (s), 126.90 (d, *J* = 83.5 Hz), 128.58 (d, *J* = 12.9 Hz), 144.36 (d, *J* = 12.1 Hz), 162.55 (d, *J* = 3.8 Hz). Anal. Calcd for $C_{17}H_{29}OPS$: C, 65.35; H, 9.36. Found: C, 65.12; H, 9.27.

***P*,*P*-Dimethyl[3,5-di(*tert*-butyl)-6-methoxyphenyl]phosphineborane (2h)**

White powder; 79% yield; mp 120–126 °C. IR (KBr): ν = 2960, 2367, 1500, 1400, 1230, 1150, 1067, 1006, 930 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.45 (s, 18 H), 1.55 (d, *J* = 10.0 Hz, 6 H), 3.72 (s, 3 H), 7.59 (d, *J* = 11.6 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 13.14 (d, *J* = 38.7 Hz), 31.68 (s), 35.83 (s), 64.15 (s), 123.66 (d, *J* = 58.5 Hz), 129.14 (d, *J* = 11.4 Hz), 144.22 (d, *J* = 9.9 Hz), 162.0 (br s). Anal. Calcd for $C_{17}H_{32}BOP$: C, 69.40; H, 10.96. Found: C, 69.26; H, 11.07.

***P*,*P*-Dimethyl[2,4,6-tri(isopropyl)phenyl]phosphineborane (2i).**

White powder; 60% yield; mp 158–162 °C. IR (KBr): ν = 2961, 2370, 1601, 1555, 1458, 1150, 1074, 939 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.10 (br m, 3 H), 1.26 (d, *J* = 7.2 Hz, 6 H), 1.27 (d, *J* = 6.8 Hz, 12 H), 1.75 (d, *J* = 9.6 Hz, 6 H), 2.89 (q, *J* = 6.8 Hz, 1 H), 3.88 (q, *J* = 6.8 Hz, 2 H), 7.09 (d, *J* = 3.2 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ = 16.94 (d, *J* = 41.0 Hz), 23.58 (s), 25.07 (s), 30.56 (d, *J* = 6.1 Hz), 34.03 (s), 121.0 (d, *J* = 49.8 Hz), 123.12 (d, *J* = 8.3 Hz), 151.75 (d, *J* = 2.3 Hz), 154.33 (d, *J* = 9.1 Hz). Anal. Calcd for $C_{17}H_{32}BP$: C, 73.39; H, 11.59. Found: C, 73.31; H, 11.68.

(14) Compounds **3a**–**d** were prepared according the literature,[22,23] affording ligands of the following enantiopurity as determined by reduction to the corresponding alcohol: **3a** (96%), **3b** (85%), **3c** (90%), **3d** (92%).

General Procedure for 3e–i

To a solution of (–)-sparteine or (+)-**1** (1.12 equiv) in anhyd Et_2O (2.5 mL/mmol) under argon at –78 °C was added a 1.3 M solution (1.1 equiv) of *sec*-BuLi in hexane. The mixture was stirred for 30 min at –78 °C before the slow addition of a Et_2O solution (3 mL/mmol) of the prochiral phosphine borane. The mixture was stirred at –78 °C for 3 h before CO_2 was bubbled through the solution. The flask was slowly warmed up to r.t. over a period of 1 h and then acidified with 1 M HCl. The aqueous layer was extracted with EtOAc (3 ×). The pH of the combined organic layers was adjusted to pH 12 using sat. Na_2CO_3. After phase separation, the aqueous layer was acidified with HCl and extracted with EtOAc. The organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the P-chirogenic α-carboxyphosphine boranes. To measure the enantiomeric excess, the ligands were first reduced to their corresponding alcohol using BH_3·DMS, and then subjected to analysis by HPLC on a Chiralcel OD-H column, eluting with *n*-hexane–*i*-PrOH.

(15) **(*S*)-(–)-Mesityl(ethanoic acid)methylphosphine-borane (3e)**

Transparent gel; 90% yield. IR (KBr): ν = 3100, 2960, 2720, 2520, 2170, 1705, 1640, 1340, 1180, 995 cm^{-1}. ^1H NMR

($CDCl_3$): δ = 1.1 (m, 3 H), 1.88 (d, *J* = 9.2 Hz, 3 H), 2.24 (s, 3 H), 2.55 (s, 6 H), 2.98 (dd, *J* = 14.0, 9.6 Hz, 1 H), 3.18 (dd, *J* = 14.0, 9.6 Hz, 1 H), 6.85 (d, *J* = 3.2 Hz, 2 H), 10.96 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 15.9 (d, *J* = 39.5 Hz), 21.04 (s), 24.10 (d, *J* = 4.6 Hz), 35.61 (d, *J* = 27.3 Hz), 121.14 (d, *J* = 47.0 Hz), 131.38 (d, *J* = 9.1 Hz), 141.16 (d, *J* = 3.1 Hz), 143.26 (d, *J* = 9.9 Hz), 173.69 (d, *J* = 4.5 Hz). $[\alpha]_D^{21}$ –15.0 (*c* 1, $CHCl_3$, 80% ee). Anal. Calcd for $C_{12}H_{20}BO_2P$: C, 60.54; H, 8.47. Found: C, 60.28; H, 8.43. Retention times for alcohol (90% *n*-hexane, 10% *i*-PrOH): 0.5 mL/min, 228 nm, t_R (–) = 19.4 min, t_R (+) = 20.4 min.

(*S*)-(+)-1-Naphtyl(ethanoic acid)methylphosphine-borane (3f)

Recrystallized from *n*-hexane–Et_2O; white solid, 86% yield; mp 92–98 °C. IR (KBr): ν = 3000, 2414, 1834, 1713, 1500, 1424, 1260, 1130, 920, 840, 800, 770 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.1 (br m, 3 H), 1.95 (d, *J* = 9.6 Hz, 3 H), 3.09 (dd, *J* = 13.6, 9.2 Hz, 1 H), 3.31 (dd, *J* = 13.6, 10.8 Hz, 1 H), 7.49 (dt, *J* = 8.8, 1.6 Hz, 1 H), 7.55 (dt, *J* = 8.8, 0.8 Hz, 1 H), 7.63 (dt, *J* = 8.8, 1.2 Hz, 1 H), 7.87 (dd, *J* = 7.2, 0.8 Hz, 1 H), 7.91 (d, *J* = 7.6 Hz, 1 H), 7.99 (d, *J* = 8.4 Hz, 1 H), 8.40 (d, *J* = 8.4 Hz, 1 H), 10.00 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 11.14 (d, *J* = 39.5 Hz), 33.86 (d, *J* = 25.8 Hz), 123.79 (d, *J* = 50.1 Hz), 124.8 (d, *J* = 12.2 Hz), 125.18 (d, *J* = 6.8 Hz), 126.46 (s), 127.36 (s), 129.64 (s), 132.75 (d, *J* = 10.6 Hz), 132.85 (d, *J* = 9.1 Hz), 133.20 (d, *J* = 2.3 Hz), 133.71 (d, *J* = 6.9 Hz), 173.01 (d, *J* = 5.3 Hz). $[\alpha]_D^{21}$ +24.0 (*c* 1, $CHCl_3$, 94% ee). Anal. Calcd for $C_{13}H_{16}BO_2P$: C, 63.46; H, 6.55. Found: C, 63.34; H, 6.43. Retention times for alcohol (90% *n*-hexane, 10% *i*-PrOH): 1 mL/min, 224 nm, t_R (+) = 16.99 min, t_R (–) = 20.38 min.

(*S*)-(+)-[(2-Phenyl)phenyl](ethanoic acid)methylphosphine-borane (3g)

Recrystallized from *n*-hexane–Et_2O; white solid; 93% yield; mp 98–106 °C. IR (KBr): ν = 3000, 2360, 1695, 1440, 1300, 1130, 1064, 920, 840, 800, 770 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.90 (br m, 3 H), 1.35 (d, *J* = 10.0 Hz, 3 H), 2.68 (dd, *J* = 10.0, *J* = 2.0 Hz, 2 H), 7.28 (ddd, *J* = 7.6, *J* = 3.2, *J* = 1.2 Hz, 1 H), 7.36 (m, 2 H), 7.48 (m, 5 H), 7.94 (dd, *J* = 13.6, *J* = 7.6 Hz, 1 H), 10.00 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 11.97 (d, *J* = 38.7 Hz), 34.28 (d, *J* = 28.1 Hz), 125.56 (d, *J* = 50.1 Hz), 127.46 (d, *J* = 12.2 Hz), 127.96 (s), 128.25 (s), 129.36 (s), 131.01 (s), 131.32 (d, *J* = 6.8 Hz), 133.68 (d, *J* = 16.7 Hz), 140.39 (s), 146.36 (s), 172.6 (d, *J* = 5.3 Hz). $[\alpha]_D^{21}$ +13.0 (*c* 1, $CHCl_3$, 95% ee). Anal. Calcd for $C_{15}H_{18}BO_2P$: C, 66.21; H, 6.67. Found: C, 66.03; H, 6.58. Retention times for alcohol (95% *n*-hexane, 5% *i*-PrOH): 0.4 mL/min, 220 nm, t_R (–) = 59.80 min, t_R (+) = 62.30 min.

(*S*)-(–)-[3,5-Di(*tert*-butyl)-6-methoxyphenyl](ethanoic acid)methylphosphine-borane (3h)

Precipitated in *n*-hexane; white solid; 89% yield; mp 118–121 °C. IR (KBr): ν = 2960, 2360, 1725, 1410, 1225, 1130, 1064, 1000, 920, 840, 800, 770 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.88 (br m, 3 H), 1.42 (s, 18 H), 1.77 (d, *J* = 10.0 Hz, 3 H), 2.94 (dd, *J* = 10.4, 6.4 Hz, 2 H), 3.71 (s, 3 H), 7.63 (d, *J* = 12.0 Hz, 2 H), 9.05 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 10.41 (d, *J* = 37.9 Hz), 31.78 (s), 35.13 (d, *J* = 26.5 Hz), 36.04 (s), 64.39 (s), 120.0 (d, *J* = 50.0 Hz), 130.03 (d, *J* = 11.4 Hz), 144.65 (d, *J* = 11.4 Hz), 162.8 (s)173.7 (d, *J* = 5.3 Hz). $[\alpha]_D^{21}$ –21.5 (*c* 1, $CHCl_3$, 81% ee). Anal. Calcd for $C_{18}H_{32}BO_3P$: C, 63.92; H, 9.57. Found, C: 64.04; H, 9.49. Retention times for alcohol (99% *n*-hexane, 1% *i*-PrOH): 0.75 mL/min, 224 nm, t_R (–) = 30.7 min, t_R (+) = 32.9 min.

(*S*)-(–)-[2,3,6-Tri(isopropyl)phenyl](ethanoic acid)methylphosphine-borane (3i)

Recrystallized from *n*-hexane–Et_2O; white solid; 72% yield; mp 116–123 °C. IR (KBr): ν = 3000, 2414, 1834, 1713, 1500, 1424, 1260, 1130, 920, 840, 800, 770 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 1.20 (br m, 3 H), 1.26 (d, *J* = 6.8 Hz, 6 H), 1.26 (dd, *J* = 6.4, 4.8 Hz, 12 H), 1.90 (d, *J* = 8.8 Hz, 3 H), 2.89 (q, *J* = 6.8 Hz, 1 H), 3.13 (d, *J* = 9.6 Hz, 2 H), 3.85 (dq, *J* = 6.8, 2.0 Hz, 2 H), 7.10 (d, *J* = 3.2 Hz, 2 H), 8.90 (br s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 16.15 (d, *J* = 40.2 Hz), 23.79 (s), 25.26 (d, *J* = 11.4 Hz), 30.84 (d, *J* = 6.0 Hz), 34.30 (s), 36.53 (d, *J* = 28.1 Hz), 120.14 (d, *J* = 47.8 Hz), 123.76 (d, *J* = 9.1 Hz), 152.76 (s), 155.04 (d, *J* = 9.9 Hz), 173.4 (d, *J* = 3.0 Hz). $[\alpha]_D^{21}$ –3.6 (*c* 1, $CHCl_3$, 71% ee). Anal. Calcd for $C_{18}H_{32}BO_2P$: C, 67.09; H, 10.01. Found: C, 66.87; H, 9.89. Retention times for alcohol (99% *n*-hexane, 1% *i*-PrOH): 0.75 mL/min, 227 nm, t_R (–) = 24.25 min, t_R (+) = 25.91 min.

(16) **(*S*)-(–)-*tert*-Butyl(ethanoic acid)methylphosphine-borane (4)**

Recrystallized from *n*-hexane–Et_2O; white solid; 86% yield; mp 107–112 °C. IR (KBr): ν = 2970, 2910, 2370, 1705, 1295, 925 cm^{-1}. ^1H NMR ($CDCl_3$): δ = 0.42 (br q, *J* = 88.0 Hz, 3 H), 1.19 (dd, *J* = 14.4, 4.0 Hz, 9 H), 1.41 (dd, *J* = 10.0, 3.6 Hz, 3 H), 2.72 (m, 2 H), 9.93 (br s, 1 H). ^{13}C NMR ($CDCl_3$): δ = 5.67 (d, *J* = 32.4 Hz), 24.96 (s), 28.15 (d, *J* = 31.9 Hz), 29.26 (d, *J* = 21.3 Hz), 174.17 (d, *J* = 4.5 Hz). $[\alpha]_D^{21}$ –9.2 (*c* 1, $CHCl_3$, 90% ee). Anal. Calcd for $C_7H_{18}BO_2P$: C, 47.77; H, 6.14. Found: C, 47.86; H, 10.30.

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(19) **General Procedure for the Palladium-Catalyzed Allylic Asymmetric Alkylation Reactions.**

To the phosphine-borane (0.019 mmol, 9.5% mol) under an argon atmosphere was added an anhyd degassed solution of $Pd(AcO)_2$ (2.3 mg, 5 mol%) in 0.8 mL THF. This mixture was stirred at r.t. for 15 min whereupon 1,3-diphenylpropenyl acetate (**5**, 50 μL, 1 equiv) or 1,3-diphenylpropenyl ethylcarbonate (**6**, 56 μL, 1 equiv) was added. After 15 min at r.t., dimethylmalonate (70 μL, 3 equiv) and BSA (150 μL, 3 equiv) were successively added. The mixture was stirred at r.t. and the reaction was monitored by HPLC and TLC. The mixture was purified by flash chromatography on silica gel, eluting with PE–EtOAc 95:5. The enantiomeric excess was determined by chiral HPLC, Chiralpak AD-H, *n*-hexane–*i*-PrOH (9:1) 1 mL/min, 254 nm, retention time: t_R (*R*) = 9.60 min, t_R (*S*) = 13.22 min.

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(21) **General Procedure for the Palladium-Catalyzed Asymmetric Allylic Amination Reactions.**
To the phosphine-borane (0.019 mmol, 9.5 mol%), evacuated and flushed with argon, was added an anhyd, degassed THF solution (0.8 mL) of $Pd(OAc)_2$ (2.3 mg, 5 mol%). This mixture was stirred at r.t for 15 min, followed by the addition of 1,3-diphenylpropenyl acetate (**5**, 50 μL, 1 equiv) or 1,3-diphenylpropenyl ethylcarbonate (**6**, 56 μL, 1 equiv). After 15 min the reaction was cooled to 5 °C and benzylamine (66 μL) was added. The mixture was stirred at 5 °C and monitored by HPLC and TLC. The mixture was purified by flash chromatography on silica gel, eluting with PE–EtOAc 95:5. The enantiomeric excess was determined by chiral HPLC, Chiralpak AD-H, *n*-hexane–*i*-PrOH (9:1) 0.35 mL/min, 254 nm, retention time : t_R (*S*) = 28.64 min, t_R (*R*) = 33.92 min.

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