Modular Synthesis of ChiraClick Ligands: A Library of P-Chirogenic Phosphines

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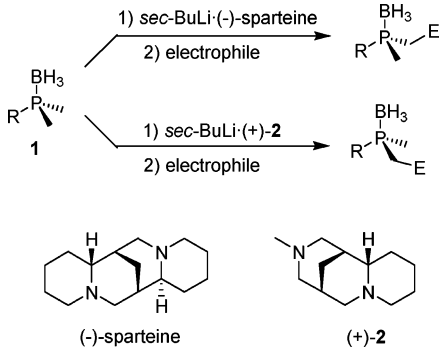
A library of novel and diverse P-chirogenic phosphine ligands containing a triazole moiety (ChiraClick ligands) were prepared in high yield in a modular fashion that allows for variation of both the phosphine and the triazole structure, as well as giving access to the two enantiomers of the ligand.

P-chirogenic phosphines are versatile ligands for asymmetric synthesis because the chiral center is positioned in close proximity to the reaction center upon coordination to a metal.[1] Methods for the preparation of P-chirogenic phosphines include a chiral auxiliary approach, employing ephedrine, reported by Jugé and Genêt,[2] Evans' desymmetrization of borane-protected prochiral phosphines using (−)-sparteine/*sec*-butyllithium complexes,[3] dynamic thermodynamic resolution of secondary phosphine boranes as reported by Livinghouse,[4] and enzymatic methods for desymmetrization.[5] The important contributions from the Imamoto group in this context also deserve mention.[6] Lately, methodologies employing transition metal catalysis have appeared, including the asymmetric palladium-catalyzed coupling of aryl halides with racemic secondary phosphines,[7] the asymmetric hydrophosphination reported by Glueck[8] and Gaumont,[9] and nucleophilic activation of phosphines via ruthenium or platinum coordination as described by Bergman and Toste,[10] as well as Glueck.[11] Of the listed methods, the Evans desymmetrization approach (Scheme 1) has rapidly become one of the most popular methods for the preparation of P-chirogenic phosphines, and the earlier limitation that only one phosphine enantiomer was accessible has been solved by the use of O'Brien's (+)-sparteine mimic (**2**).[12,13]

There have been several reports on the preparation of combinatorial libraries of chiral phosphine ligands.[14] Gilbertson was the first to investigate this area, focusing on the synthesis of phosphine ligands with a variable peptide backbone and their application in asymmetric hydrogenation and palladium-catalyzed desymmetrization.[15] Amino acid-based phosphine libraries have also been investigated in copper-catalyzed enantioselective conjugate addition by Hird and Hoveyda.[16] Feringa and de Vries have developed practical methods for the synthesis of their highly efficient phosphoramidite ligands in a 96-well format involving robotics,[17] while an elegant example of a bispidine-based phosphoramidite ligand library was reported by Waldmann and co-workers.[18] However, to our knowledge, there have been no reports on the preparation of ligand libraries based on P-chirogenic phosphine structures.

Scheme 1. Synthesis of P-Chirogenic Phosphines via Desymmetrization



The copper-catalyzed version of the Huisgen 1,3-dipolar cycloaddition reaction reported by Meldal[19] and Fokin and Sharpless,[20] is a versatile "click" reaction for ligating an azide and an alkyne[21] and could be a convenient way to diversify a phosphine scaffold. Zhang earlier reported the preparation of non-chiral ClickPhos ligands, where a triazole scaffold was prepared via a cycloaddition reaction of phenyl azide with different aryl acetylenes and subseqently derivatized with different phosphine moieties.[22] The solution and solid-phase preparation of ClickPhine ligands, also non-chiral, of a similar structure was recently disclosed by Reek, van Marseeveen, and co-workers.[23] Several bidentate phosphorus-containing triazole ligands have been prepared by Trofimenko and co-workers, and their coordination to iron, cobalt, nickel and copper has been described.[24] Also, Chen et al. have recently applied chiral amino-substituted triazole ligands in the silver(I)-promoted enantioselective allylation of aldehydes, indicating the potential of incorporating the triazole-moiety into ligand structures.[25] Chiral phosphine ligand libraries containing a pendent triazole moiety have not been reported, however, and we hereby disclose our results

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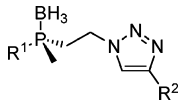


Figure 1. Modular ChiraClick Ligands.

concerning the derivatization of P-chirogenic ligand scaffolds with triazole functionalities.

In planning the ligand synthesis, we envisioned that a desymmetrization approach, starting from prochiral phosphine boranes, could be used to prepare azide-substituted P-chirogenic phosphines in a few steps. A copper-catalyzed 1,3-cycloaddition would then give access to diverse ChiraClick ligands containing both a P-chirogenic phosphine atom and a triazole moiety (Figure 1). This modular approach to ChiraClick ligands would allow for independent variation of the phosphine and triazole substitutents, at the same time giving access to both enantiomers of the ligands by using either (−)-sparteine or (+)-(**2**) in the desymmetrization.

The precursor azides **6** were prepared in four steps from borane-protected prochiral dimethyl phosphines **1** via an initial desymmetrization using either (−)-sparteine or (+)-**2** in conjunction with *sec*-BuLi, followed by reaction of the chiral anion with carbon dioxide.[26] Reduction of the α-carboxyphosphines **3** with borane dimethylsulfide complex afforded alcohols **4** (Scheme 2).

Treatment with *p*-toluenesulfonyl chloride in the presence of pyridine gave the corresponding tosylates **5a**−**d** and *ent*-**5a**, in general in crystalline form, enabling enhancement of the enantiomeric excess by recrystallization. The enantiomeric excess was determined by HPLC at this stage, having verified that no racemization took place in the ensuing reactions. Reaction with sodium azide in DMF at 80 °C for 1 h afforded the desired azides **6a**−**d** and *ent*-**6a** in high overall yields and enantioselectivities (Table 1).[27]

The preparation of azide **6e** was more troublesome, however. Although the corresponding alcohol **4e** could be prepared, attempted conversion to the tosylate resulted only in decomposition of the starting material, and no product could be isolated. An alternative route was thus employed (Scheme 3), converting alcohol **4e** to the corresponding bromide by treatment with carbon tetrabromide and triphenylphosphine in dichloromethane, affording **7** in a 65% yield. Subsequent reaction with sodium azide as described earlier gave the desired azido-derivatized phosphine borane **6e** in a 72% yield.

A diverse set of terminal alkynes with various steric and electronic properties were selected for the 1,3-dipolar cycloaddition reaction, incorporating aliphatic, as well as aromatic, moieties, substituents containing an additional potential chelating atom (nitrogen, sulfur, oxygen) in different positions, and a sterically hindered *tert*-butyl group in some cases. Azides **6a**−**e** and *ent*-**6a** were then reacted with the selected alkynes in the presence of $CuSO_4$ and ascorbic acid, affording 23 new borane-protected P-chirogenic phosphine ligands, that is, **8**−**26** and *ent*-**8**−**11** in good to excellent yields in most cases (Table 2). Although the crude products were purified by flash chromatography for characterization purposes, filtration through a short pad of silica gel was in general sufficient to afford pure crystalline products.

In one case, that is, the reaction of adamantyl-substituted phosphine borane azide **6b** with *t*-butyl acetylene, the yield was markedly lower (20%), probably because of steric interactions between the two bulky substituents used in this case. The mesityl substitution pattern again proved troublesome, causing decomposition of the precursor azide **6e** under the reaction conditions. No mesityl-substituted ChiraClick ligands could thus be isolated.

To complement the scope of the ligands prepared, two compounds with an additional chelating phosphorus atom at different spacer lengths and with different electronic properties were also synthesized (Scheme 4). The reaction of **6a** with borane-protected diphenylphosphine acetylene borane afforded the protected diphosphine ligand **27** in a 77% yield, while a mixed phosphine−phosphonite ligand (**28**) could be formed in an 87% yield using borane-protected diphenyl propargyl phosphonite as the alkyne component.

A preliminary screening of ligands **8**−**15**, as well as **27** and **28**, in the palladium-catalyzed asymmetric allylic alkylation of 1,3-diphenylprop-2-enyl acetate with dimethylmalonate in THF showed that many of these ligands were effective catalysts for this reaction, affording good to quantitative conversion in most cases, while the enantioselectivity was less promising, generally in the range of 8−12%. Further studies involving these ligands in organocatalytic transformations, as well as catalytic applications employing metals other than palladium, are in progress.

In summary, we have shown that ChiraClick ligands, containing both a P-chirogenic moiety and a pendent triazole unit can be easily prepared in a few high-yielding steps with independent variation of both the phosphine and triazole substitution patterns. The application of these ligands in different asymmetric transformations is under investigation.

Experimental Section

General. Dimethylphosphine boranes **1a**−**d** were prepared according to Imamoto et al.[28] Mesityl dimethylphosphine borane **1e** was prepared according to Mezzetti and coworkers.[29] (+)-Sparteine mimic **2** was prepared according to O'Brien and co-workers.[12] Carboxy-derivatives **3a**−**c** have been reported by Ohashi et al.,[30] as have alcohols **4a**−**c** and tosylates **5a**−**c**, while carboxy-derivative **3d** was reported by Danjo et al.[31]

General Procedure for the Synthesis of the P-Chirogenic α-Carboxyphosphine Boranes 3a−**e and *ent*-3a.** The chiral diamine ((−)-sparteine or (+)-**2**, 1.12 equiv) was solubilized in dry diethyl ether (2.5 mL $mmol^{-1}$) at room temperature under an inert atmosphere. This solution was cooled to −78 °C, and a 1.3 M solution (1.1 equiv) of *sec*-butyllithium in hexanes was added. The mixture was stirred for 30 min at −78 °C, before the slow addition of a diethyl ether solution (3 mL $mmol^{-1}$) of the prochiral phosphine borane. The mixture was stirred at the same temperature for 3 h before CO_2 was bubbled through the solution. The flask was slowly warmed up to room temperature over a period of 1 h; then the solution was acidified through the addition of 1 M HCl. The aqueous layer was extracted with ethyl acetate three times. The pH of the combined organic layers was adjusted to pH 12 by the addition of saturated sodium

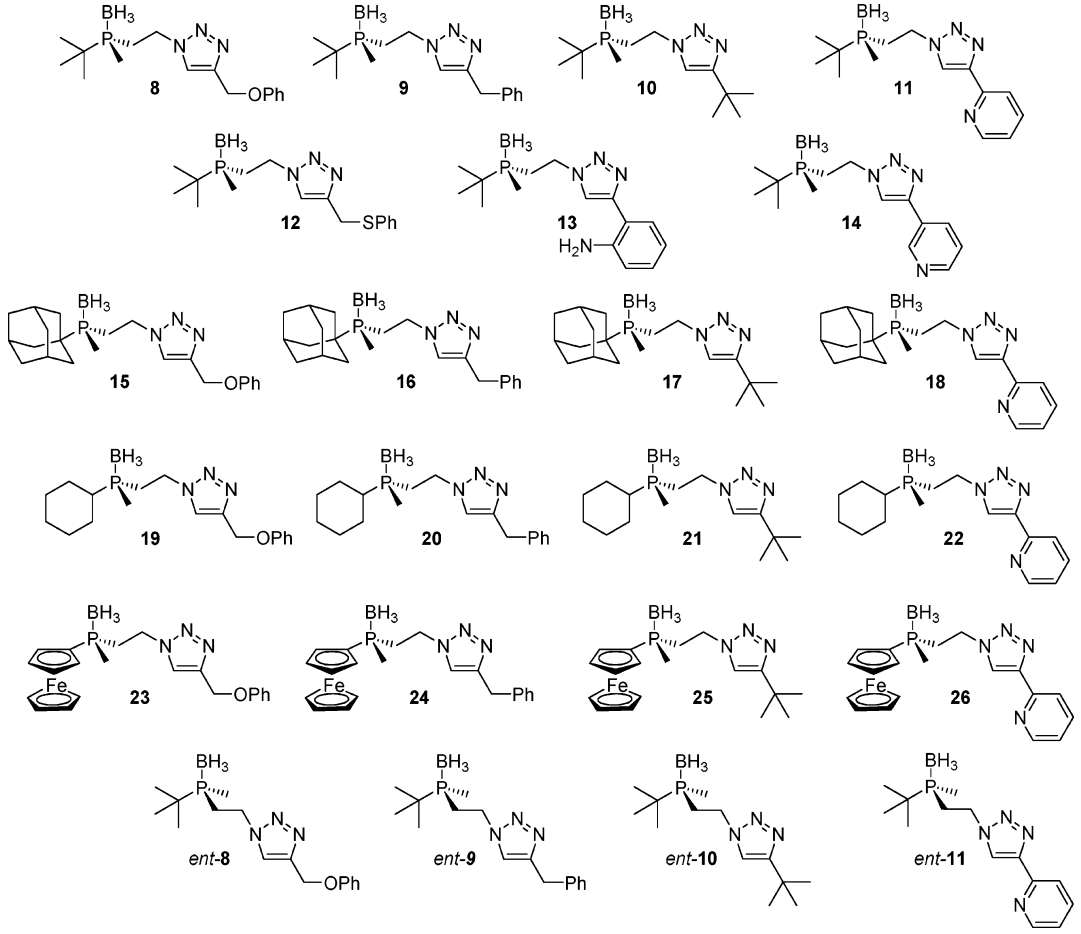
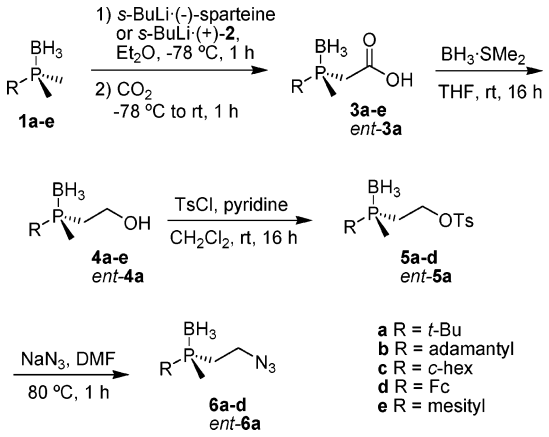


Figure 2. ChiraClick ligands Prepared from Azides **6a**−**d** and *ent*-**6a**.

Scheme 2. Preparation of Azides **6a**−**d** and *ent*-**6a**



carbonate. The phases were separated, and the aqueous layer was acidified by the addition of HCl and then extracted with ethyl acetate. The organic layer was washed with brine, dried over sodium sulfate, filtered, and concentrated to give the P-chirogenic α-carboxyphosphine boranes.

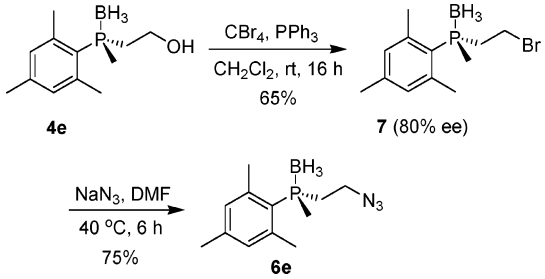
(*R*)-(−)-*tert*-Butyl(ethanoic acid)methylphosphine-borane (*ent*-3a). *ent*-**3a** was recrystallized from *n*-hexane/Et_2O and was obtained as a white solid (0.367 g, 86% yield). mp: 107−112 °C. IR (KBr): ν 2970, 2910, 2370, 1705, 1295, 925 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.42 (br q, J = 88.0, 3H), 1.19 (dd, J = 14.4 Hz, J = 4 Hz, 9H), 1.41 (dd, J = 10.0 Hz, J = 3.6 Hz, 3H), 2.72 (m, 2H), 9.93 (br s, 1H). ^{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). $[\alpha]^{21}_D$: −9.2 (*c* 1, $CHCl_3$, 90% ee). Anal. Calcd for $C_7H_{18}BO_2P$: C, 47.77; H, 10.31. Found: C, 47.86; H, 10.30.

Table 1. Yields and Enantioselectivities for Precursors **4**−**6**

	4 (−OH)[a] yield (%)	**5** (−OTs)[b] yield (ee) (%)	**6** (−N_3)[c] yield (%)
a	95	90 (97)	90
b	98	97 (97)	96
c	88	95 (95)	96
d	80	84 (94)	95
e	80		
ent-**a**	97	95 (94)	93

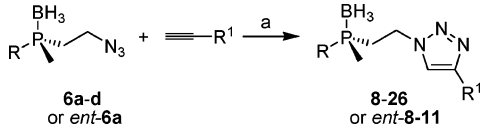
[a] BH_3·DMS, THF, room temp, 16 h. [b] TsCl, pyridine, CH_2Cl_2, room temp, 16 h. [c] NaN_3, DMF, 80 °C, 1 h.

Scheme 3. Preparation of Azide **6e**



(*S*)-(−)-Mesityl(ethanoic acid)methylphosphine-borane (3e). 3e was obtained as a transparent oil (2.0 g, 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, 3H),

Table 2. Cycloadditions Using Azides **6a-d** or *ent*-**6a**

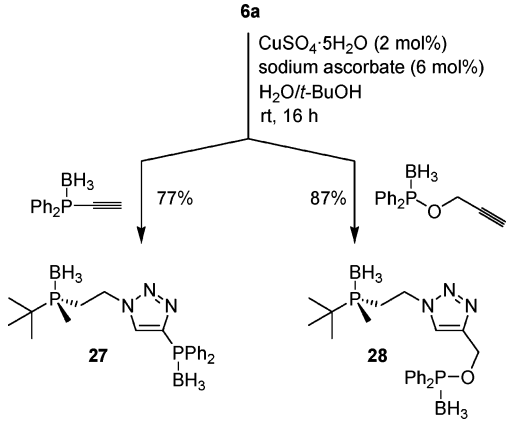


6a-d or *ent*-**6a** **8-26** or *ent*-**8-11**

entry	ligand	R	R^1	yield (%)
1	**8**	*t*-Bu	CH_2OPh	95
2	**9**	*t*-Bu	CH_2Ph	95
3	**10**	*t*-Bu	*t*-Bu	77
4	**11**	*t*-Bu	2-pyridyl	92
5	**12**	*t*-Bu	CH_2SPh	95
6	**13**	*t*-Bu	*o*-NH_2-C_6H_4	90
7	**14**	*t*-Bu	3-pyridyl	96
8	**15**	adamantyl	CH_2OPh	73
9	**16**	adamantyl	CH_2Ph	76
10	**17**	adamantyl	*t*-Bu	20
11	**18**	adamantyl	2-pyridyl	95
12	**19**	*c*-Hex	CH_2OPh	90
13	**20**	*c*-Hex	CH_2Ph	90
14	**21**	*c*-Hex	*t*-Bu	86
15	**22**	*c*-Hex	2-pyridyl	95
16	**23**	Fc	CH_2OPh	96
17	**24**	Fc	CH_2Ph	92
18	**25**	Fc	*t*-Bu	89
19	**26**	Fc	2-pyridyl	98
20	*ent*-**8**	*t*-Bu	CH_2OPh	96
21	*ent*-**9**	*t*-Bu	CH_2Ph	92
22	*ent*-**10**	*t*-Bu	*t*-Bu	86
23	*ent*-**11**	*t*-Bu	2-pyridyl	88

[a] $CuSO_4 \cdot 5H_2O$, sodium ascorbate, H_2O/*t*-BuOH, room temp, 16 h.

Scheme 4. ChiraClick Ligands with an Additional Phosphorus Atom



1.88 (d, $J = 9.2$ Hz, 3H), 2.24 (s, 3H), 2.55 (s, 6H), 2,98 (dd, $J = 14.0$ Hz, $J = 9.60$ Hz, 1H), 3.18 (dd, $J = 14.0$ Hz, $J = 9.6$ Hz, 1H), 6.85 (d, $J = 3.2$ Hz, 2H), 10.96 (br s, 1H). ^{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). $[\alpha]^{21}_D$: -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.

General Procedure for the Synthesis of the Alcohols 4a−e and *ent*-4a. The α-carboxyphosphine borane was solubilized in THF (2 mL mmol^{-1}) under a nitrogen atmosphere. A BH_3·DMS solution (2 M in THF, 4 equiv) was carefully added, and the mixture was stirred at room temperature overnight (16 h). The reaction was quenched by the addition of water at 0 °C. The mixture was washed with brine and extracted twice with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude was flashed over silica gel to afford the desired product.

(*R*)-(−)-2-[Boronato(*tert*-butyl)metylphosphino]-ethan-1-ol (*ent*-4a). After flash chromatography on silica gel (40% EtOAc in petroleum ether), the (*S*)-(−)-2-[boronato(*tert*-butyl)metylphosphino]-ethan-1-ol was obtained as a white solid (0.32 g, 97% yield). mp: 120.0−122.0 °C. IR (KBr): ν 3290, 2970, 2370, 1040 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.40 (bm, 3H), 1.11 (d, $J = 14.0$ Hz, 9H), 1.22 (d, $J = 10.0$ Hz, 3H), 1.81 (m, 1H), 1.87 (m, 1H), 2.67 (s, 1H), 3.87 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 6.05 (d, $J = 34.8$ Hz), 24.39 (d, $J = 31.5$ Hz), 24,69 (d, $J = 1.9$ Hz), 27.05 (d, $J = 35.3$ Hz), 57.59 (s). $[\alpha]_D^{22°}$: −9.8 (*c* 1, $CHCl_3$). Anal. Calcd for C_7H_{20}-BOP: C, 51.89; H, 12.44. Found, C, 51.85; H, 12.50.

(*S*)-(−)-2-[Boronato(ferrocenyl)methyl-phosphino]-ethanol (4d). Flash chromatography on silica gel (40% EtOAc in petroleum ether) afforded **4d** as a waxy orange solid (0.79 g, 79% yield). IR (KBr): ν 3105, 2980, 2385, 2345, 1715, 1700, 1425, 1295, 1065. ^{1}H NMR ($CDCl_3$): δ 0.80 (m, 3H), 1.59 (d, $J = 10.4$ Hz, 3H), 2.00 (m, 2H), 2.22 (bs, 1H), 3.73 (m, 2H), 4.30 (s, 5H), 4.47 (m, 1H), 4.48 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 12.00 (d, $J = 40.9$ Hz), 32.38 (d, $J = 36.5$ Hz), 57.99 (s), 69.80 (s), 69.97 (d, $J = 6.8$ Hz), 71.69 (d, $J = 5.30$ Hz), 71.78 (d, $J = 7.60$ Hz), 72.37 (d, $J = 13.7$ Hz). $[\alpha]_D^{24°}$: −8.0 (*c* 1,CH_2Cl_2). Anal. Calcd for $C_{13}H_{20}$BFeOP: C, 53.85; H, 6.95. Found, C, 54.02; H, 7.08.

(*S*)-(+)-2-[Boronato(mesityl)methyl-phosphino]-ethanol (4e). After purification by column chromatography on silica gel (25% EtOAc in petroleum ether), the (*S*)-(+)-2-[boronato(mesityl)methyl-phosphino]-ethanol was obtained as a white solid (0.18 g, 95% yield). mp: 45−50 °C. IR (KBr): ν 3250, 2900, 2400, 2300, 1604, 1449, 1296, 1153, 1035, 896, 765 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.1 (m, 3H), 1.78 (d, $J = 10.0$ Hz, 3H), 2.25 (s, 3H), 2.36 (m, 2H), 2.58 (s, 6H), 3.81 (m, 1H), 3.91 (m, 1H), 6.87 (br s, 2H). ^{13}C NMR ($CDCl_3$): δ 15.61 (d, $J = 41.0$ Hz), 20.94 (s), 24.29 (d, $J = 4.5$ Hz), 31.82 (d, $J = 35.7$ Hz), 58.26 (s), 122.19 (d, $J = 47.8$ Hz), 131.26 (d, $J = 8.4$ Hz), 141.32 (s), 143.47 (d, $J = 9.1$ Hz). $[\alpha]^{21}_D$: +12.1 (*c* 1, $CHCl_3$, 80% ee). Anal. Calcd for $C_{12}H_{22}$BOP: C, 64.32; H, 9.90. Found: C, 64.22; H, 9.96. The enantiomeric excess was determined by HPLC: Chiralcel OD-H, 90% *n*-hexane, 10% 2-propanol, 0.5 mL min^{-1}, 228 nm, $t_R(-) = 19.4$ min, $t_R(+) = 20.4$ min.

General Procedure for the Synthesis of the Tosylates 5a−d and *ent*-5a. The alcohol was solubilized in dichloromethane (4 mL mmol^{-1}) under a nitrogen atmosphere at room temperature. Then pyridine (5 equiv) was added, and the reaction mixture was immersed in a water bath, before the addition of tosyl chloride (2.5 equiv). The reaction mixture was stirred at room temperature overnight (16 h), washed with brine, and extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated. The crude was flashed over silica gel to

afford the desired product which was recrystallized either from diethyl ether/*n*-hexane or CH_2Cl_2/*n*-hexane.

(*R*)-(−)-1-Tosyl-2-[boronato(*tert*-butyl)methylphosphino]-ethan-1-ol (*ent*-5a). After flash chromatography on silica gel (15% EtOAc in petroleum ether), the desired compound was recrystallized from diethyl ether/*n*-hexane to afford white crystals (0.63 g, 90% yield). mp: 70.0−73.0 °C. IR (KBr): ν 2970, 2380, 1360, 1185, 940, 725 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.48 (bm, 3H), 1.11 (d, J = 14 Hz, 9H), 1.22 (d, J = 10.0 Hz, 3H), 1.99 (m, 2H), 2.43(s, 3H), 4.21 (m, 1H), 4.32 (m, 1H), 7.35 (d, J = 8.0 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 6.05 (d, J = 34.1 Hz), 21.65 (d, J = 30.2 Hz), 21,67 (s), 24.71 (d, J = 2.4 Hz), 27.35 (d, J = 33.9 Hz), 65.88 (d, J = 4.40 Hz), 127.86 (s), 129.99 (s), 132.48 (s), 145.17 (s). $[\alpha]_D^{22°}$: −5.2 (*c* 0.57, $CHCl_3$, 94% ee). Anal. Calcd for $C_{14}H_{26}BO_3PS$: C, 53.18; H, 8.29. Found, C, 53.35; H, 8.07. The enantiomeric excess was determined by HPLC: Chiralcel OD-H, 90% *n*-hexane, 10% 2-propanol, 1 mL min^{-1}, 254 nm, $t_R(-)$ = 15.3 min, $t_R(+)$ = 17.3 min.

(*S*)-(−)-1-Tosyl-2-[boronato(ferrocenyl)methyl-phosphino]-ethanol (5d). Flash chromatography on silica gel (15% EtOAc in petroleum ether), followed by recrystallization (CH_2Cl_2/*n*-hexane), afforded **5d** as orange crystals (0.98 g, 95% yield). mp: 101.5−105.°C. IR (KBr): ν 3000, 2398, 2335, 1593, 1357, 1173, 952, 814 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.61 (m, 3H), 1,57 (d, J = 10.4 Hz, 3H), 2.06 (m, 2H), 2.43 (s, 3H), 4.14 (m, 2H), 4.26 (m, 6H), 4.43 (m, 3H), 7.32 (d, J = 8.4 Hz, 2H), 7.72 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$): δ 11.19 (d, J = 40.3 Hz), 21.61 (s), 28.95 (d, J = 34.4 Hz), 65.41 (d, J = 2.3 Hz), 68.21 (d, J = 64.6 Hz), 69.65 (s), 69.68 (d, J = 5.5 Hz), 71.65 (d, J = 6.7 Hz), 71.73 (d, J = 8.4 Hz), 72.29 (d, J = 15.1 Hz), 127.77 (s), 129.87 (s), 132.35 (s), 145.03 (s). $[\alpha]_D^{24°}$: −11.6 (*c* 1.12, CH_2Cl_2, 94% ee). Anal. Calcd for $C_{20}H_{26}BFeO_3PS$: C, 54.09; H, 5.90. Found, C, 53.74; H, 5.81. The enantiomeric excess was determined by HPLC: Chiralpak AD-H, 80% *n*-hexane, 20% 2-propanol, 1 mL min^{-1}, 229 nm, $t_R(+)$ = 19.91 min, $t_R(-)$ = 27.12 min.

General Procedure for the Synthesis of the Azidophosphine Boranes 6a−d and *ent*-6a. The corresponding tosylate was solubilized in DMF (5 mL $mmol^{-1}$) under an inert atmosphere. Sodium azide (2 equiv) was added, and the reaction mixture was heated to 80 °C for 1 h (reaction monitored by TLC). After completion of the reaction, the mixture was diluted with ethyl acetate, washed with a solution of saturated aqueous NH_4Cl and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography (silica gel) to afford the desired pure azide product.

(*S*)-(+)-1-Azido-2-[boronato(*tert*-butyl)methylphosphino]-ethane (6a). Flash chromatography on silica gel (15% EtOAc in petroleum ether) yielded **6a** as a transparent oil (0.17 g, 90% yield). IR (KBr): ν 3450, 2965, 2371, 2260, 2099, 1635, 1466, 1260, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.40 (br m, 3H), 1.15 (d, J = 14 Hz, 9H), 1.26 (d, J = 9.6 Hz, 3H), 1.86 (m, 2H), 3.50 (m, 1H), 3.67 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 5.84 (d, J = 33.9 Hz), 21.00 (d, J = 30.2 Hz), 24.8 (s), 27.37 (d, J = 34.3 Hz), 46.48 (s). $[\alpha]_D^{23°}$: +9.4 (*c* 1, $CHCl_3$, 96% ee). Anal. Calcd for $C_7H_{19}BN_3P$: C, 44.95; H, 10.24. Found, C, 45.08; H, 10.19. The enantiomeric excess was determined from the corresponding tosylate by HPLC: Chiralcel OD-H, 90% *n*-hexane, 10% 2-propanol, 1 mL min^{-1}, 254 nm, $t_R(-)$ = 15.3 min, $t_R(+)$ = 17.3 min.

(*R*)-(−)-1-Azido-2-[boronato(*tert*-butyl)methylphosphino]-ethane (*ent*-6a). Flash chromatography (15% EtOAc in petroleum ether) afforded *ent*-**6a** as a transparent oil (0.09 g, 93% yield). IR (KBr): ν 3450, 2965, 2371, 2260, 2099, 1635, 1466, 1260, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.40 (br m, 3H), 1.15 (d, J = 14.0 Hz, 9H), 1.26 (d, J = 9.6 Hz, 3H), 1.86 (m, 2H), 3.50 (m, 1H), 3.67 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 5.84 (d, J = 33.9 Hz), 21.00 (d, J = 30.2 Hz), 24.83 (d, J = 2.3 Hz), 27.37 (d, J = 34.3 Hz), 46.48 (s). $[\alpha]_D^{23°}$: −9.0 (*c* 1, $CHCl_3$, 94% ee). Anal. Calcd for $C_7H_{19}BN_3P$: C, 44.95; H, 10.24. Found, C, 45.07; H, 10.20. The enantiomeric excess was determined from the corresponding tosylate (see **6a**).

(*S*)-(+)-1-Azido-2-[boronato(1-adamantyl)methylphosphino]-ethane (6b). Flash chromatography (10% EtOAc in petroleum ether) afforded **6b** as a white solid (0.60 g, 96% yield). mp: 60.0−64.0 °C. IR (KBr): ν 3450, 2965, 2371, 2260, 2099, 1635, 1466, 1260, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.32 (br m, 3H), 1.21 (d, J = 10.0 Hz, 3H), 1.74 (m, 13H), 1.90 (m, 1H), 2.04 (m, 3H), 3.47 (m, 1H), 3.65 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 4.38 (d, J = 34.6 Hz), 19.54 (d, J = 30.5 Hz), 27.48 (d, J = 8.8 Hz), 30.18 (d, J = 34.6 Hz), 35.55 (s), 36.34 (d, J = 1.4 Hz), 46.48 (d, J = 2.9 Hz). $[\alpha]_D^{24°}$: +3.6 (c 1, CH_2Cl_2, 97% ee). Anal. Calcd for $C_{13}H_{25}BN_3P$: C, 58.89; H, 9.50. Found, C, 58.86; H, 9.42. The enantiomeric excess was determined from the corresponding tosylate by HPLC: Chiralpak AD-H, 80% *n*-hexane, 20% 2-propanol, 1 mL min^{-1}, 254 nm, $t_R(-)$ = 14.9 min, $t_R(+)$ = 15.7 min.

(*S*)-(+)-1-Azido-2-[boronato(1-cyclohexyl)methylphosphino]-ethane (6c). Flash chromatography (10% EtOAc in petroleum ether) afforded **6c** as a transparent oil (0.50 g, 96% yield). IR (KBr): ν 3450, 2965, 2371, 2260, 2099, 1635, 1466, 1260, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.36 (br m, 3H), 1.25 (d, J = 10.0 Hz, 3H), 1.26 (m, 5H), 1.80 (m, 8H), 3.55 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 6.84 (d, J = 35.3 Hz), 21.48 (d, J = 32.1 Hz), 25.69 (d, J = 1.0 Hz), 25.93 (d, J = 2.1 Hz), 26.10 (bs), 26.34 (d, J = 0.7 Hz), 26.45 (d, J = 1.7 Hz), 33.72 (d, J = 35.0 Hz), 46.06 (d, J = 1.7 Hz). $[\alpha]_D^{23°}$: +2.6 (*c* 1.05, CH_2Cl_2, 95% ee). Anal. Calcd for $C_9H_{21}BN_3P$: C, 50.73; H, 9.93. Found, C, 50.75; H, 9.88. The enantiomeric excess was determined from the corresponding tosylate by HPLC: Chiralpak AD-H, 80% *n*-hexane, 20% 2-propanol, 1 mL min^{-1}, 225 nm, $t_R(-)$ = 12.5 min, $t_R(+)$ = 13.6 min.

(*S*)-(−)-1-Azido-2-[boronato(ferrocenyl)methyl-phosphino]-ethanol (6d). Flash chromatography (8% EtOAc in petroleum ether) afforded **6d** as an orange solid (0.46 g, 95% yield). mp: 40.5−42.5°C. IR (KBr): ν 3496, 3089, 2922, 2090, 1457, 1297, 1247, 1072, 997, 823 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.71 (m, 3H), 1.62 (d, J = 10.4 Hz, 3H), 1.96 (m, 2H), 3.35 (m, 1H), 3.49 (m, 1H), 4.28 (m, 6H), 4.48 (m, 3H). ^{13}C NMR ($CDCl_3$): δ 11.07 (d, J = 40.9 Hz), 28.64

(d, $J = 34.2$ Hz), 46.17 (d, $J = 1.5$ Hz), 68.58 (d, $J = 64.2$ Hz), 69.43 (d, $J = 5.0$ Hz), 69.60 (s), 71.63 (d, $J = 10.6$ Hz), 71.72 (d, $J = 8.6$ Hz), 72.6 (d, $J = 15.7$ Hz). $[\alpha]_D^{24°}$: −24.7 (*c* 1.3, CH_2Cl_2, 94% ee). Anal. Calcd for $C_{13}H_{19}BFeN_3P$: C, 49.58; H, 6.08. Found: C, 49.88; H, 6.09. The enantiomeric excess was determined from the corresponding tosylate.

(*S*)-(−)-1-Azido-2-[boronato(mesityl)methyl-phosphino]-ethane (6e). Bromide **7** was solubilized in DMF (5 mL $mmol^{-1}$) under an inert atmosphere. Sodium azide (1.1 equiv) was added in one portion at room temperature under a gentle stream of nitrogen. The reaction mixture was heated to 40 °C for 6 h (reaction monitored carefully by HPLC). After completion of the reaction, the mixture was diluted with EtOAc, washed with a solution of saturated aqueous NH_4Cl and brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography (silica gel) to afford azide **6e** as a clear oil (323 mg, 75%). ^{1}H NMR ($CDCl_3$): δ 0.40−1.50 (m, 3H), 1.79 (d, $J = 10.0$ Hz, 3H), 2.27 (s, 3H), 2.18−2.25 and 2.35−2.46 (m, 2H), 2.59 (s, 6H), 3.58−3.68 and 3.32−3.42 (m, 2H), 6.90 (s, 1H), 6.91 (s, 1H). ^{13}C NMR: δ 15.09 (d, $J = 54.5$ Hz), 20.75 (d, $J = 2.0$ Hz), 23.99 (d, $J = 6.1$ Hz), 28.03 (d, $J = 46.5$ Hz), 46.49 (d, $J = 4.0$ Hz), 121.2, 120.9 (d, 6.2 Hz), 131.14 (d, $J = 12.1$ Hz), 141.43 (s), 143.42 (d, $J = 12.1$ Hz). Anal. Calcd for $C_{12}H_{21}BN_3P$: C, 57.86; H, 8.50. Found: C, 57.98; H, 8.43.

(*S*)-(−)-1-Bromo-2-[boronato(mesityl)methyl-phosphino]-ethane (7). Alcohol **4e** was solubilized in dichloromethane (4 mL $mmol^{-1}$) under a nitrogen atmosphere, at room temperature. CBr_4 (1.8 equiv) and PPh_3 (2.0 equiv) were added in one portion under a gentle stream of nitrogen. The reaction mixture was stirred at room temperature overnight (16 h); then it as evaporated directly onto silica. The crude product was purified by flash chromatography using 2.5% EtOAc in petroleum ether, affording **7** as a clear oil (414 mg, 65%, 80% ee). ^{1}H NMR ($CDCl_3$): δ 0.60−1.50 (br m, 3H), 1.78 (d, $J = 9.6$ Hz, 3H), 2.27 (s, 3H), 2.58 (s, 6H), 2.50−2.80 (m, 2H), 3.29−3.40 and 3.56−3.67 (m, 2H), 6.90 (br s, 2H). ^{13}C NMR: δ 15.07 (d, $J = 53.6$ Hz), 20.8 (s), 24.05 (d, $J = 6.0$ Hz), 25.76 (d, $J = 5.1$ Hz), 32.81 (d, $J = 41.5$ Hz), 120.72 (d, $J = 60.8$ Hz), 131.24 (d, $J = 11.0$ Hz), 141.58 (d, $J = 2.9$ Hz), 143.56 (d, $J = 12.1$ Hz). Anal. Calcd for $C_{12}H_{21}BBrP$: C, 50.22; H, 7.38. Found: C, 50.18; H, 7.43.

General Procedure for the Synthesis of the 1,4-Triazoles. The azidophosphine borane was suspended in a 1/1 v/v mixture of water/*t*-BuOH (4 mL $mmol^{-1}$). Copper(II) sulfate pentahydrate (2 mol %) was added to this suspension, followed by sodium ascorbate (6 mol %, 1 M aq solution) and finally the alkyne (1.5 equiv of phenyl propargyl ether, 3-phenylprop-1-yne, 2-ethynyl pyridine, 3-ethynyl pyridine, phenyl propargyl sulfide, or 2-ethynylaniline; 5 equiv of 3,3-dimethylbut-1-yne). The heterogeneous mixture was stirred vigorously overnight (16 h) at room temperature. The mixture was then diluted with EtOAc and washed with brine. The organic layer was dried over Na_2SO_4, filtered, and concentrated. The crude product was filtered over a short pad of silica gel to afford the desired product.

Data for 8. Flash chromatography on silica gel (30% EtOAc in petroleum ether) afforded **8** as a white solid (0.081 g, 95% yield). mp: 104.0−108.0 °C. IR (KBr): ν 3450, 2450, 2371, 1630, 1460, 1360, 1070, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.13 (d, $J = 10.0$ Hz, 3H), 1.17 (d, $J = 14.0$ Hz, 9H), 2.24 (m, 1H), 2.35 (m, 1H), 4.55 (m, 1H), 4.66 (m, 1H), 5.21 (s, 2H), 6.98 (m, 3H), 7.29 (m, 2H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.46 (d, $J = 34.0$ Hz), 22.4 (d, $J = 29.9$ Hz), 24.80 (d, $J = 2.4$ Hz,), 27.49 (d, $J = 34.6$ Hz), 46.55 (d, $J = 3.3$ Hz), 61.75 (s), 114.68 (s), 121.24 (s), 123.34 (s), 129.50 (s), 144.26 (s), 158.01 (s). $[\alpha]_D^{24°}$: −5.5 (*c* 1, CH_2Cl_2, 97% ee). Anal. Calcd for $C_{16}H_{27}BN_3OP$: C, 60.21; H, 8.53. Found: C, 59.84; H, 8.53. The enantiomeric excess was verified by HPLC: Chiralpak AD-H, 90% *n*-hexane, 10% 2-propanol, 1 mL min^{-1}, 220 nm, $t_R(-) = 30.0$ min, $t_R(+) = 31.6$ min.

Data for *ent*-8. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded *ent*-**8** as a white solid (0.098 g, 96% yield). mp: 103.0−107.0 °C. IR (KBr): ν 3450, 2450, 2371, 1630, 1460, 1360, 1070, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.13 (d, $J = 10.0$ Hz, 3H), 1.17 (d, $J = 14.0$ Hz, 9H), 2.24 (m, 1H), 2.35 (m, 1H), 4.55 (m, 1H), 4.66 (m, 1H), 5.21 (s, 2H), 6.98 (m, 3H), 7.29 (m, 2H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.46 (d, $J = 34.0$ Hz), 22.4 (d, $J = 29.9$ Hz), 24.80 (d, $J = 2.4$ Hz,), 27.49 (d, $J = 34.6$ Hz), 46.55 (d, $J = 3.3$ Hz), 61.75 (s), 114.68 (s), 121.24 (s), 123.34 (s), 129.50 (s), 144.26 (s), 158.01 (s). $[\alpha]_D^{24°}$: +5.2 (*c* 1, CH_2Cl_2, 94% ee). Anal. Calcd for $C_{16}H_{27}BN_3OP$: C, 60.21; H, 8.53. Found: C, 59.86; H, 8.42. The enantiomeric excess was verified by HPLC: Chiralpak AD-H, 90% *n*-hexane, 10% 2-propanol, 1 mL min^{-1}, 220 nm, $t_R(-) = 30.0$ min, $t_R(+) = 31.6$ min.

Data for 9. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded **9** as a white amorphous solid (0.088 g, 95% yield). IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.11 (d, $J = 10.4$ Hz, 3H), 1.15 (d, $J = 14.0$ Hz, 9H), 2.17 (m, 1H), 2.30 (m, 1H), 4.06(s, 2H), 4.46 (m, 2H), 7.25 (m, 5H), 7.27 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.32 (d, $J = 34.1$ Hz), 22.23 (d, $J = 29.9$ Hz), 24.65 (s), 27.35 (d, $J = 34.4$ Hz), 32.08 (s), 45.19 (d, $J = 3.7$ Hz), 121.96 (s), 126.39 (s), 128.51 (s), 138.74 (s), 147.55 (s). $[\alpha]_D^{24°}$: +2.5 (*c* 1, $CHCl_3$). Anal. Calcd for $C_{16}H_{27}BN_3P$: C, 63.38; H, 8.98. Found: C, 63.33; H, 8.93.

Data for *ent*-9. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded *ent*-**9** as a white amorphous solid (0.060 g, 92% yield). IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.11 (d, $J = 10.4$ Hz, 3H), 1.15 (d, $J = 14.0$ Hz, 9H), 2.17 (m, 1H), 2.30 (m, 1H), 4.06 (s, 2H), 4.46 (m, 1H), 4.52 (m, 1H), 7.25 (m, 5H), 7.27 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.39 (d, $J = 34.5$ Hz), 22.32 (d, $J = 30.3$ Hz), 24.73 (d, $J = 2.3$ Hz), 27.42 (d, $J = 34.2$ Hz), 32.08 (s), 45.26 (d, $J = 3.1$ Hz), 121.96 (s), 126.48 (s), 128.58 (s), 138.80 (s), 147.68 (s). $[\alpha]_D^{23°}$: −1.5 (*c* 0.8, CH_2Cl_2). Anal. Calcd for $C_{16}H_{27}BN_3P$: C, 63.38; H, 8.98. Found: C, 63.34; H, 8.93.

Data for 10. Flash chromatography on silica gel (25% EtOAc in petroleum ether) afforded **10** as a white amorphous

solid (0.067 g, 77% yield). IR (KBr): ν 3460, 2960, 2470, 1639, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.10 (d, $J = 9.6$ Hz, 3H), 1.13 (d, $J = 14.0$ Hz, 9H), 1.31 (s, 9H), 2.17 (m, 1H), 2.32 (m, 1H), 4.48 (m, 1H), 4.59 (m, 1H), 7.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.27 (d, $J = 34.0$ Hz), 22.35 (d, $J = 30.1$ Hz), 24.75 (d, $J = 2.3$ Hz), 27.38 (d, $J = 34.8$ Hz), 30.24 (s), 30.65 (s), 45.02 (d, $J = 3.5$ Hz), 119.31 (s), 157.65 (s). $[\alpha]_D^{25°}$: +1.0 (*c* 1, $CHCl_3$). Anal. Calcd for $C_{13}H_{29}BN_3P$: C, 58.01; H, 10.86. Found: C, 57.87; H, 10.81.

Data for *ent*-10. Flash chromatography on silica gel (25% EtOAc in petroleum ether) afforded *ent*-**10** as a white amorphous solid (0.053 g, 86% yield). IR (KBr): ν 3460, 2960, 2470, 1639, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.10 (d, $J = 9.6$ Hz, 3H), 1.13 (d, $J = 14.0$ Hz, 9H), 1.31 (s, 9H), 2.17 (m, 1H), 2.32 (m, 1H), 4.48 (m, 1H), 4.59 (m, 1H), 7.34 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.31 (d, $J = 34.0$ Hz), 22.41 (d, $J = 29.6$ Hz), 24.74 (d, $J = 2.4$ Hz), 27.43 (d, $J = 34.7$ Hz), 30.28 (s), 30.70 (s), 45.07 (d, $J = 3.6$ Hz), 119.26 (d, $J = 2.6$ Hz), 157.65 (s). $[\alpha]_D^{24°}$: −3.0 (*c* 0.99, CH_2Cl_2). Anal. Calcd for $C_{13}H_{29}BN_3P$: C, 58.01; H, 10.86. Found: C, 57.87; H, 10.93.

Data for 11. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded **11** as a white solid (0.036 g, 92% yield). mp: 130.0−134.0 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.43 (br m, 3H), 1.16 (d, $J = 13.6$ Hz, 9H), 1.19 (d, $J = 9.2$ Hz, 3H), 2.35 (m, 2H), 4.61 (m, 1H), 4.71 (m, 1H), 7.21 (t, $J = 6.0$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 8.12 (d, $J = 7.6$ Hz, 1H), 8.20 (s, 1H), 8.56 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 5.53 (d, $J = 34.1$ Hz), 22.51 (d, $J = 29.6$ Hz), 24.78 (d, $J = 2.3$ Hz), 27.50 (d, $J = 34.9$ Hz), 45.62 (s), 120.16 (s), 122.38 (s), 122.95 (s), 136.86 (s), 148.51 (s), 149.45 (s), 149.92 (s). $[\alpha]_D^{24°}$: + 6.0 (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{14}H_{24}BN_4P$: C, 57.95; H, 8.34. Found: C, 58.26; H, 8.28.

Data for *ent*-11. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded *ent*-**11** as a white solid (0.053 g, 88% yield). mp: 130.0−134.0 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.43 (br m, 3H), 1.16 (d, $J = 13.6$ Hz, 9H), 1.19 (d, $J = 9.2$ Hz, 3H), 2.35 (m, 2H), 4.61 (m, 1H), 4.71 (m, 1H), 7.21 (t, $J = 6.0$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 8.12 (d, $J = 7.6$ Hz, 1H), 8.20 (s, 1H), 8.56 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 5.49 (d, $J = 33.4$ Hz), 22.46 (d, $J = 29.6$ Hz), 24.74 (d, $J = 3.1$ Hz), 27.46 (d, $J = 34.2$ Hz), 45.58 (s), 120.11 (s), 122.34 (s), 122.91 (s), 136.82 (s), 148.47 (s), 149.41 (s), 149.88 (s). $[\alpha]_D^{24°}$: −4,7 (*c* 0.61, CH_2Cl_2). Anal. Calcd for $C_{14}H_{24}BN_4P$: C, 57.95; H, 8.34. Found: C, 58.50; H, 8.40.

Data for 12. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded **12** as an amorphous solid (0.094 g, 95% yield). IR (KBr): ν 3450, 2450, 2371, 1630, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.42 (br m, 3H), 1.04 (d, $J = 10.0$ Hz, 3H), 1.14 (d, $J = 14.0$ Hz, 9H), 2.14 (m, 1H), 2.29 (m, 1H), 4.21 (s, 2H), 4.48 (m, 1H), 4.57 (m, 1H), 7.16 (dt, $J = 6.4$ Hz, $J = 1.6$ Hz, 1H), 7.25 (m, 2H), 7.31 (m, 2H), 7.44 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.35 (d, $J = 33.9$ Hz), 22.22 (d, $J = 29.9$ Hz), 24.73 (d, $J = 2.4$ Hz,), 27.44 (d, $J = 34.6$ Hz), 28.62 (s), 45.41 (d, $J = 3.7$ Hz), 122.74 (s), 126.43 (s), 128.96 (s), 129.34 (s), 135.28 (s), 145.00 (s). $[\alpha]_D^{24°}$: −4.4 (*c* 0.63, CH_2Cl_2). Anal. Calcd for $C_{16}H_{27}BN_3PS$: C, 57.32; H, 8.12. Found: C, 57.18; H, 8.06.

Data for 13. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded **13** as a brownish solid (0.070 g, 90% yield). mp: 114.0−115.6 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.48 (br m, 3H), 1.15 (d, $J = 10.0$ Hz, 3H), 1.17 (d, $J = 14.0$ Hz, 9H), 2.25 (m, 1H), 2.36 (m, 1H), 4.59 (m, 1H), 4.69 (m, 1H), 5.47 (bs, 2H), 6.70 (dt, $J = 7.6$ Hz, $J = 0.8$ Hz, 1H), 6.76 (dd, $J = 8.0$ Hz, $J = 0.8$ Hz, 1H), 7.11 (dd, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 7.33 (dd, 7.6 Hz, $J = 1.6$ Hz, 1H), 7.84 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.48 (d, $J = 33.4$ Hz), 22.35 (d, $J = 29.6$ Hz), 24.76 (d, $J = 3.0$ Hz), 27.49 (d, $J = 34.7$ Hz), 45.50 (d, $J = 3.8$ Hz), 113.27 (s), 116.68 (s), 117.32 (s), 120.53 (s), 127.75 (s), 129.09 (s), 145.00 (s), 148.35 (s). $[\alpha]_D^{24°}$: +2.8 (*c* 0.56, CH_2Cl_2). Anal. Calcd for $C_{15}H_{26}BN_4P$: C, 59.23; H, 8.62. Found: C, 59.21; H, 8.70.

Data for 14. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded **14** as a white solid (0.036 g, 92% yield). mp: 130.0−134.0 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.43 (br m, 3H), 1.16 (d, $J = 13.6$ Hz, 9H), 1.19 (d, $J = 9.2$ Hz, 3H), 2.35 (m, 2H), 4.61 (m, 1H), 4.71 (m, 1H), 7.21 (t, $J = 6.0$ Hz, 1H), 7.75 (t, $J = 7.6$ Hz, 1H), 8.12 (d, $J = 7.6$ Hz, 1H), 8.20 (s, 1H), 8.56 (d, $J = 6.0$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 5.53 (d, $J = 34.1$ Hz), 22.51 (d, $J = 29.6$ Hz), 24.78 (d, $J = 2.3$ Hz), 27.50 (d, $J = 34.9$ Hz), 45.62 (s), 120.16 (s), 122.38 (s), 122.95 (s), 136.86 (s), 148.51 (s), 149.45 (s), 149.92 (s). $[\alpha]_D^{24°}$: + 6.0 (*c* 0.5, CH_2Cl_2). Anal. Calcd for $C_{14}H_{24}BN_4P$: C, 57.95; H, 8.34. Found: C, 58.26; H, 8.28.

Data for 15. Flash chromatography on silica gel (30% EtOAc in petroleum ether) afforded **15** as a white solid (0.044 g, 88% yield). mp: 148.5−150.0 °C. IR (KBr): ν 3450, 2450, 2371, 1630, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.40 (br m, 3H), 1.11 (d, $J = 10.0$ Hz, 3H), 1.76 (m, 12H), 2.05 (m, 3H), 2.26 (m, 2H), 4.55 (m, 1H), 4.65 (m, 1H), 5.21 (s, 2H), 6.98 (m, 3H), 7.29 (m, 2H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 4.01 (d, $J = 34.6$ Hz), 20.99 (d, $J = 30.4$ Hz), 27.41 (d, $J = 8.9$ Hz,), 30.24 (d, $J = 34.8$ Hz), 35.46 (s), 36.26 (s), 45.54 (d, $J = 4.2$ Hz), 61.74 (s), 114.66 (s), 121.20 (s), 123.23 (d, $J = 2.1$ Hz), 129.48 (s), 144.24 (s), 158.00 (s). $[\alpha]_D^{24°}$: −7.2 (*c* 1.4, CH_2Cl_2). Anal. Calcd for $C_{22}H_{33}BN_3OP$: C, 66.51; H, 8.37. Found: C, 66.38; H, 8.31.

Data for 16. Flash chromatography on silica gel (30% EtOAc in petroleum ether) afforded **16** as a white solid (0.057 g, 76% yield). mp: 111.8−113.0 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.39 (br m, 3H), 1.09 (d, $J = 9.6$ Hz, 3H), 1.76 (m, 12H), 2.03 (m, 3H), 2.20 (m, 2H), 4.07 (s, 2H), 4.56 (m, 2H), 7.26 (s, 1H), 7.28 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 3.99 (d, $J = 34.6$ Hz), 20.95 (d, $J = 30.5$ Hz), 27.42 (d, $J = 8.8$ Hz), 30.22 (d, $J = 34.8$ Hz), 32.19 (s), 35.46 (s), 36.26 (d, $J = 1.5$ Hz), 45.29 (d, $J = 4.1$ Hz),

121.98 (d, $J = 2.8$ Hz), 126.48 (s), 128.59 (s), 128.62 (s), 138.84 (s), 147.67 (s). $[\alpha]_D^{24°}$: −10.6 (*c* 1, $CHCl_3$). Anal. Calcd for $C_{22}H_{33}BN_3P$: C, 69.30; H, 8.72. Found, C, 65.15; H, 8.66.

Data for 17. Flash chromatography on silica gel (30% EtOAc) afforded **17** as a white solid (0.018 g, 20% yield). mp: 144.5−147.0 °C. IR (KBr): ν 3460, 2960, 2470, 1639, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.40 (br m, 3H), 1.10 (d, $J = 9.6$ Hz, 3H), 1.35 (s, 9H), 1.72 (m, 12H), 2.04 (m, 3H), 2.27 (m, 2H), 4.50 (m, 1H), 4.61 (m, 1H), 7.33 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 3.93 (d, $J = 34.7$ Hz), 21.06 (d, $J = 31.0$ Hz), 27.44 (d, $J = 8.8$ Hz), 30.23 (d, $J = 35.1$ Hz), 30.31 (s), 30.73 (s), 35.47 (s), 36.28 (d, $J = 1.4$ Hz), 45.08 (d, $J = 4.0$ Hz), 119.19 (d, $J = 1.7$ Hz), 157.65 (s). $[\alpha]_D^{25°} = -7.8$ (*c* 0.38, CH_2Cl_2). Anal. Calcd for $C_{19}H_{35}BN_3P$: C, 65.71; H, 10.16. Found: C, 65.71; H, 10.08.

Data for 18. Flash chromatography on silica gel (50% EtOAc in petroleum ether) afforded **18** as a white solid (0.066 g, 95% yield). mp: 156.5−158.5 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.41 (br m, 3H), 1.16 (d, $J = 9.6$ Hz, 3H), 1.75 (m, 12H), 2.04 (m, 3H), 2.28 (m, 2H) 4.59 (m, 1H), 4.71 (m, 1H), 7.23 (ddd, $J = 7.6$ Hz, $J = 4.8$ Hz, $J = 1.2$ Hz, 1H), 7.76 (dt, $J = 8.0$ Hz, $J = 2$ Hz, 1H), 8.13 (dt, $J = 8.0$ Hz, $J = 0.8$ Hz, 1H), 8.20 (s, 1H), 8.57 (ddd, $J = 4.8$ Hz, $J = 1.2$ Hz, $J = 0.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 4.10 (d, $J = 34.6$ Hz), 21.11 (d, $J = 30.3$ Hz), 27.43 (d, $J = 8.9$ Hz), 30.27 (d, $J = 34.7$ Hz), 35.50 (s), 36.28 (s), 45.64 (d, $J = 4.4$ Hz), 120.14 (s), 122.28 (s), 122.91 (s), 136.91 (s), 148.49 (s), 149.42 (s), 149.94 (s). $[\alpha]_D^{24°}$: −12.5 (*c* 0.02, CH_2Cl_2). Anal. Calcd for $C_{20}H_{30}BN_4P$: C, 65.23; H, 8.21. Found, C, 65.18; H, 8.06.

Data for 19. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded **19** as a white solid (0.074 g, 90% yield). mp: 85.6−88.0 °C. IR (KBr): ν 3450, 2450, 2371, 1630, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.43 (br m, 3H), 1.14 (d, $J = 10.0$ Hz, 3H), 1.21 (m, 5H), 1.67 (m, 6H), 2.28 (m, 2H), 4.59 (m, 2H), 5.20 (s, 2H), 6.97 (m, 3H), 7.28 (m, 2H), 7.71 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 6.40 (d, $J = 35.5$ Hz), 23.76 (d, $J = 31.8$ Hz), 25.61 (d, $J = 1.4$ Hz,), 25.86 (d, $J = 2.3$ Hz), 26.02 (d, $J = 0.9$ Hz), 26.24 (d, $J = 4.6$ Hz), 26.36 (d, $J = 5.5$ Hz), 33.68 (d, $J = 35.3$ Hz), 45.12 (d, $J = 3.7$ Hz), 61.64 (s), 114.60 (s), 121.16 (s), 123.28 (s), 129.44 (s), 144.20 (s), 157.95 (s). $[\alpha]_D^{24°}$: −4.0 (*c* 1.0, CH_2Cl_2). Anal. Calcd for $C_{18}H_{29}BN_3OP$: C, 62.62; H, 8.47. Found, C, 62.45; H, 8.47.

Data for 20. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded **20** as a white solid (0.069 g, 90% yield). mp: 64.0−67.0 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.40 (br m, 3H), 1.13 (d, $J = 10.0$ Hz, 3H), 1.19 (m, 5H), 1.68 (m, 6H), 2.25 (m, 2H), 4.06 (s, 2H), 4.51 (m, 2H), 7.25 (m, 6H). ^{13}C NMR ($CDCl_3$): δ 6.37 (d, $J = 35.6$ Hz), 23.74 (d, $J = 31.2$ Hz), 25.60 (d, $J = 1.4$ Hz), 25.84 (d, $J = 2.3$ Hz), 26.00 (d, $J = 0.9$ Hz), 26.23 (d, $J = 4.7$ Hz), 26.34 (d, $J = 5.5$ Hz), 32.13 (s), 33.62 (d, $J = 35.3$ Hz), 44.87(d, $J = 3.4$ Hz), 121.94 (s), 126.44 (s), 128.54 (s), 128.55 (s), 138.77 (s), 147.66 (s). $[\alpha]_D^{24°}$: −8.5 (*c* 0.77, CH_2Cl_2). Anal. Calcd for $C_{18}H_{29}BN_3P$: C, 65.67; H, 8.88. Found: C, 65.95; H, 8.78.

Data for 21. Flash chromatography on silica gel (25% EtOAc in petroleum ether) afforded **21** as a white solid (0.062 g, 86% yield). mp: 102.0−106.0 °C. IR (KBr): ν 3460, 2960, 2470, 1639, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.43 (br m, 3H), 1.12 (d, $J = 10.0$ Hz, 3H), 1.18 (m, 5H), 1.31 (s, 9H), 1.69 (m, 6H), 2.25 (m, 2H), 4.53 (m, 2H), 7.33 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 6.32 (d, $J = 35.5$ Hz), 23.84 (d, $J = 31.9$ Hz), 25.63 (d, $J = 1.4$ Hz), 25.86 (d, $J = 2.4$ Hz), 26.02 (d, $J = 0.6$ Hz), 26.27 (d, $J = 7.0$ Hz), 26.39 (d, $J = 8.0$ Hz), 30.27 (s), 30.68 (s), 33.58 (d, $J = 35.2$ Hz), 44.69 (d, $J = 2.9$ Hz), 119.21 (d, $J = 2.1$ Hz), 157.62 (s). $[\alpha]_D^{24°}$: −4.0 (*c* 1.35 in CH_2Cl_2). Anal. Calcd for $C_{15}H_{31}BN_3P$: C, 61.03; H, 10.58. Found, C, 61.22; H, 10.47.

Data for 22. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded **22** as a white solid (0.080 g, 95% yield). mp: 127.5−131.5 °C. IR (KBr): ν 3450, 2460, 2030, 1638, 1460, 1360, 1070, 900 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.43 (br m, 3H), 1.18 (d, $J = 10.0$ Hz, 3H), 1.19 (m, 5H), 1.69 (m, 6H), 2.30 (m, 2H), 4.65 (m, 2H), 7.21 (ddd, $J = 7.6$ Hz, $J = 4.8$ Hz, $J = 1.2$ Hz, 1H), 7.75 (dt, $J = 7.6$ Hz, $J = 1.6$ Hz, 1H), 8.11 (dt, $J = 8.0$ Hz, $J = 0.8$ Hz, 1H), 8.19 (s, 1H), 8.57 (ddd, $J = 4.8$ Hz, $J = 1.6$ Hz, $J = 0.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 6.51 (d, $J = 35.4$ Hz), 23.88 (d, $J = 31.6$ Hz), 25.61 (d, $J = 1.5$ Hz), 25.89 (d, $J = 2.3$ Hz), 26.04 (d, $J = 1.0$ Hz), 26.25 (d, $J = 2.7$ Hz), 26.37 (d, $J = 3.4$ Hz), 33.72 (d, $J = 35.3$ Hz), 45.21 (d, $J = 3.6$ Hz), 120.11 (s), 122.36 (s), 122.94 (s), 136.84 (s), 148.50 (s), 149.43 (s), 149.88 (s). $[\alpha]_D^{24°}$: −6.0 (*c* 0.91, CH_2Cl_2). Anal. Calcd for $C_{16}H_{26}BN_4P$: C, 60.78; H, 8.29. Found: C, 60.67; H, 8.21.

Data for 23. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded **23** as a waxy orange solid (0.054 g, 96% yield). IR (KBr): ν 3490, 2918, 2480, 1171, 1069, 1051, 1030, 980 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.61 (br m, 3H), 1.52 (d, $J = 10.4$ Hz, 3H), 2.37 (m, 2H), 4.20 (m, 1H), 4.29 (s, 5H), 4.48 (m, 5H), 5.17 (s, 2H), 6.97 (m, 3H), 7.29 (m, 2H), 7.58 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 10.76 (d, $J = 40.9$ Hz), 30.06 (d, $J = 34.3$ Hz), 45.25 (d, $J = 3.3$ Hz,), 61.74 (s), 67.94 (d, $J = 64.3$ Hz), 69.39 (d, $J = 4.9$ Hz), 69.65 (s), 71.86 (d, $J = 5.4$ Hz), 71.94 (d, $J = 3.4$ Hz), 72.67 (d, $J = 15.9$ Hz), 114.64 (s), 121.19 (s), 122.95 (d, $J = 2.0$ Hz), 129.47 (s), 144.24 (s), 157.98 (s). $[\alpha]_D^{24°}$: −11.2 (*c* 0.74, CH_2Cl_2). Anal. Calcd for $C_{22}H_{27}BFeN_3OP$: C, 59.10; H, 6.09. Found: C, 58.90; H, 6.02.

Data for 24. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded **24** as an orange solid (0.053 g, 92% yield). mp: 119.0−123.5 °C. IR (KBr): ν 3494, 2920, 3160, 2493, 1174, 1069, 1047, 1028, 970, 819 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.73 (br m, 3H), 1.51 (d, $J = 10.4$ Hz, 3H), 2.32 (m, 2H), 4.03 (s, 2H), 4.25 (m, 1H), 4.28 (s, 5H), 4.38 (s, 5H), 6.978 (m, 3H), 7.13 (s, 1H), 7.26 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 10.87 (d, $J = 40.9$ Hz), 30.02 (d, $J = 34.3$ Hz), 32.17 (s), 45.00 (d, $J = 3.0$ Hz), 67.99 (d, $J = 64.2$ Hz), 69.41 (d, $J = 4.9$ Hz), 69.62 (s), 71.80 (d, $J = 4.9$ Hz), 71.88 (d, $J = 2.7$ Hz), 72.64 (d, $J = 16.2$ Hz), 121.65 (d, $J = 2.4$ Hz), 126.46 (s), 128.57 (s), 128.60 (s),

138.79 (s), 147.72 (s). $[\alpha]_D^{24°}$: −17.7 (*c* 0.85, CH_2Cl_2). Anal. Calcd for $C_{22}H_{27}BFeN_3P$: C, 61.29; H, 6.31. Found, C, 61.19; H, 6.24.

Data for 25. Flash chromatography on silica gel (35% EtOAc in petroleum ether) afforded **25** as an orange solid (0.045 g, 89% yield). mp: 121.5−123.9 °C. IR (KBr): ν 3441, 3094, 2960, 2880, 1457, 1365, 1232, 1075, 969, 822 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.66 (br m, 3H), 1.30 (s, 9H), 1.51 (d, $J = 10.4$ Hz, 3H), 2.36 (m, 2H), 4.27 (m, 1H), 4.28 (s, 5H), 4.42 (m, 2H), 6.978 (m, 3H), 7.22 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 10.66 (d, $J = 40.8$ Hz), 30.06 (d, $J = 34.7$ Hz), 30.27 (s), 30.66 (s), 44.82 (d, $J = 3.0$ Hz), 68.15 (d, $J = 64.3$ Hz), 69.48 (d, $J = 5.0$ Hz), 69.62 (s), 71.78 (d, $J = 3.7$ Hz), 71.85 (d, $J = 1.8$ Hz), 72.59 (d, $J = 15.4$ Hz), 118.83 (d, $J = 2.2$ Hz), 157.65 (s). $[\alpha]_D^{24°}$: −19.7 (*c* 0.47, CH_2Cl_2). Anal. Calcd for $C_{19}H_{29}BFeN_3P$: C, 57.47; H, 7.36. Found: C, 57.27; H, 7.28.

Data for 26. Flash chromatography on silica gel (60% EtOAc in petroleum ether) afforded **26** as an orange solid (0.051 g, 97% yield). mp: 37.5−42.0 °C. IR (KBr): ν 3462, 3085, 2915, 1595, 1471, 1419, 1175, 1065, 1028, 784 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.73 (br m, 3H), 1.56 (d, $J = 10.4$ Hz, 3H), 2.40 (m, 2H), 4.27 (m, 1H), 4.29 (s, 5H), 4.50 (m, 5H), 7.21 (ddd, $J = 7.6$ Hz, $J = 4.8$ Hz, $J = 1.2$ Hz, 1H), 7.75 (dt, $J = 8.0$ Hz, $J = 2.0$ Hz, 1H), 8.09 (s, 1H), 8.11 (m, 1H), 8.55 (ddd, $J = 4.8$ Hz, $J = 1.6$ Hz, $J = 0.8$ Hz, 1H). ^{13}C NMR ($CDCl_3$): δ 10.79 (d, $J = 39.8$ Hz), 30.11 (d, $J = 34.3$ Hz), 45.31 (d, $J = 2.5$ Hz), 61.74 (s), 67.90 (d, $J = 64.1$ Hz), 69.39 (d, $J = 4.9$ Hz), 69.62 (s), 71.86 (d, $J = 4.4$ Hz), 71.93 (d, $J = 2.1$ Hz), 72.76 (d, $J = 16.1$ Hz), 120.07 (s), 122.17 (s), 122.84 (s), 136.80 (s), 148.36 (s), 149.34 (s), 149,87 (s). $[\alpha]_D^{24°}$: (*c* , CH_2Cl_2). Anal. Calcd for $C_{20}H_{24}BFeN_4P$: C, 57.46; H, 5.79. Found: C, 57.28; H, 5.70.

Data for 27. Flash chromatography (15% EtOAc in petroleum ether) afforded **27** as a white solid (84 mg, 77% yield). mp: 50.5−53.5 °C. IR (KBr): ν 3125, 3055, 2958, 2880, 2256, 1436, 1107, 1066, 902, 738, 690 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.15 (bm, 6H), 1.76 (d, $J = 14.0$ Hz, 9H), 1.22 (d, $J = 10.0$ Hz, 3H), 2.29 (m, 2H), 4.59 (m, 1H), 4.75 (m, 1H), 7.46 (m, 6H), 7.84 (m, 4H), 8.23 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 5.62 (d, $J = 34.0$ Hz), 22.47 (d, $J = 29.6$ Hz), 24.75 (d, $J = 2.5$ Hz,), 27.51 (d, $J = 34.1$ Hz), 45.80 (d, $J = 4.9$ Hz), 127.90 (d, $J = 6.7$ Hz), 128.52 (d, $J = 6.9$ Hz), 128.67 (d, $J = 10.8$ Hz), 131.40 (bs), 131.84 (d, $J = 30.2$ Hz), 132.80 (d, $J = 5.5$ Hz), 132.91 (d, $J = 5.5$ Hz), 137.61 (s), 138.41 (s). $[\alpha]_D^{24°}$: −4.5 ($c = 0.44$ in CH_2CL_2).

Data for 28. Flash chromatography (20% EtOAc in petroleum ether) afforded **28** as a white amorphous solid (83 mg, 87% yield). IR (KBr): ν 3434, 2962, 1436, 1274, 1144, 1066, 991, 750 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.95 (bm, 6H), 1.14 (d, $J = 9.6$ Hz, 3H), 1.16 (d, $J = 14.0$ Hz, 9H), 2.22 (m, 2H), 4.49 (m, 1H), 4.59 (m, 1H), 5.15 (d, $J = 8.8$ Hz), 7.45 (m, 6H), 7.64 (s, 1H), 7.72 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 5.46 (d, $J = 34.0$ Hz), 22.31 (d, $J = 29.8$ Hz), 24.72 (d, $J = 2.4$ Hz,), 27.43 (d, $J = 34.7$ Hz), 45.45 (d, $J = 4.6$ Hz), 60.16 (s), 123.97 (d, $J = 1.3$ Hz), 128.52 (d, $J = 1.4$ Hz), 128.63 (d, $J = 1.3$ Hz), 131.10 (s), 131.21 (s), 131.74 (d, $J = 1.3$ Hz), 131.92 (d, $J = 2.5$ Hz), 143.59 (d, $J = 7.7$ Hz). $[\alpha]_D^{24°}$: −2.3 ($c = 1.33$ in CH_2Cl_2).

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