## P-Chirogenic Monodentate Phosphine Ligands Bearing 2-Biphenyl Group

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This paper is dedicated to Professor Ryoji Noyori for his distinguished achievements in chemistry.

**Abstract:** Optically pure P-chirogenic monodentate phosphine ligands, [(S)-(2-biphenyl)(tert-butyl)methylphosphine <math>((S)-3a], (R)-(2-biphenyl)cyclohexylmethylphosphine <math>[(R)-3b], and (S)-(2-biphenyl)methylphosphine <math>[(S)-3c] were synthesized via phosphine–borane intermediates. Palladium-catalyzed asymmetric allylic alkylation using (S)-3a and (R)-3b as the chiral ligands afforded products with the same absolute configuration in high enantioselectivity.

**Key words:** P-chirogenic phosphines, monodentate phosphine ligands, asymmetric allylic alkylation, asymmetric synthesis

Catalytic asymmetric synthesis using transition metal complexes with chiral ligands is one of the most powerful and economically promising methods for the synthesis of enantiomerically enriched compounds.<sup>1</sup> In particular, chiral bidentate phosphine ligands have been most frequently used in asymmetric catalyses. On the other hand, chiral monodentate phosphine ligands also play a significant role in some asymmetric reactions.<sup>2,3</sup> Moreover, it has been reported that sterically congested phosphines remarkably increase the catalytic activities of the metal complexes.<sup>4</sup> These facts led us to develop new chiral monodentate phosphine ligands that are anticipated to exhibit high catalytic efficiency.

Previously, we reported that enantiomerically pure phosphines possessing asymmetric phosphorus atoms are synthesized by the use of phosphine-boranes as the intermediates.<sup>5</sup> Based on this methodology, we tried to prepare enantiomerically pure alkyl(2-biphenyl)methylphosphines (alkyl = *tert*-butyl, cyclohexyl, and phenyl), because monodentate phosphines possessing 2-biphenyl group have been employed as effective ligands in asymmetric catalyses such as Pd-catalyzed carbon-carbon bond forming reactions.4b-e tert-Butyldichlorophosphine, dichlorocyclohexylphosphine, and dichlorophenylphosphine were reacted successively with 2-lithiobiphenyl, lithium *l*-menthoxide, and borane-THF to give the corresponding diastereomer mixtures (ca. 1: 1) of key intermediates bearing 2-biphenyl and *l*-menthyloxy groups in 62-74% yields (Scheme 1). Each mixture was separated by preparative HPLC or recrystallization from hexane to give pure diastereomers.<sup>6</sup> The absolute configurations around the chirogenic phosphorus atom of compounds  $(R_{\rm p})$ -1b and  $(R_{\rm p})$ -1c were unequivocally determined by single crystal X-ray analyses.





Compound  $(S_P)$ -**1a** was reduced by 4,4'-di-*tert*-butylbiphenylide (LDBB) at -60 °C, followed by the treatment with iodomethane, to give (*S*)-**2a** with 75% ee in 72% yield.<sup>7,8</sup> Recrystallization of this product from hexane twice afforded enantiomerically pure compound, which in turn was dissolved in *N*-methylpyrrolidine to remove the boranato group. The deboranation reaction was monitored by silica gel TLC, and after disappearance of the phosphine–borane the solvent was evaporated. The residual oil was purified by passing through a short column of silica gel using degassed toluene to afford [(*S*)-(2-biphenyl)(*tert*-butyl)methylphosphine (*S*)-**3a**] in almost quantitative yield (Scheme 2).





The above mentioned procedure was not applicable for the preparation of optically active (2-biphenyl)cyclohexylmethylphosphine, because the reduction of  $(R_p)$ -**1b** by LDBB and subsequent methylation resulted in disappointedly low enantiomeric excesses (ca. 20% ee) of the product, probably owing to rapid stereomutation of the generated tricoordinate phosphorus species. Therefore, we employed another promising method, although it required two more reaction steps. Thus, compound ( $R_p$ )-1b was subjected to deboranation by treatment with *N*-methylpyrrolidine at 50 °C and the generated phosphine was methylated with methyl triflate. The resulting phosphonium salt was stereospecifically reduced by LiAlH<sub>4</sub>.<sup>9</sup> Because of its air sensitivity, the product was converted to air stable borane adduct (R)-2b (97% ee) in 73% overall yield from ( $R_p$ )-1b. Enantiomerically pure (R)-2b, which was obtained by recrystallization from hexane, was transformed to desired monophosphine (R)-3b by the reaction with *N*-methylpyrrolidine (Scheme 3).





The third ligand (*S*)-**3c** was readily prepared from ( $R_P$ )-**1c** by nucleophilic substitution with methyllithium, followed by usual deboranation reaction (Scheme 4). It is noted that the substitution reaction proceeded in THF at 40 °C with inversion of configuration at phosphorus in 94% stereospecificity.<sup>10</sup>



## Scheme 4

With these ligands in hand, we evaluated their enantioselectivity in palladium-catalyzed asymmetric allylic alkylation, a typical catalytic carbon–carbon bond forming reaction.<sup>11,12</sup> The reactions were carried out using 1,3diphenyl-2-propenyl acetate (**4**) as a model substrate under various conditions. At first we tried the reaction of **4**  LETTER

with dimethyl malonate using (*S*)-**3***a* as the ligand in the presence of additives. The reactions proceed in  $CH_2Cl_2$  at room temperature to give the coupling product in almost quantitative yield. No distinct differences in the enantioselectivity were observed by changing the additive (Entries 1–5 in Table), and therefore potassium acetate was used as the additive in other reactions. The reaction in  $CH_2Cl_2$  gave the highest ee of the product among the solvents examined, and hence we used  $CH_2Cl_2$  in this series of reactions.

It is noted that ligand (R)-**3b** gave distinctly higher enantioselectivity than (S)-**3a** and in sharp contrast (S)-**3c** proved to be ineffective in this asymmetric reaction (Entries 10–12). Entries 13-19 show the results of the reactions with other active methylene compounds using (S)-**3a** and (R)-**3b** as the ligands. (R)-**3b** again afforded better enantioselectivity than (S)-**3a**. Another notable fact is that both (S)-**3a** and (R)-**3b** provided the coupling products with the same absolute configuration. These results can be interpreted by assuming that cyclohexyl group is sterically smaller than 2-biphenyl group and *tert*-butyl group is larger than 2-biphenyl group.

In summary, we have synthesized new enantiomerically pure P-chirogenic monodentate phosphine ligands possessing bulky groups, and demonstrated their utility in palladium-catalyzed asymmetric allylic alkylation.

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	Ph Ph Ph		1.5 mol% [PdCl(C <sub>3</sub> H <sub>7</sub> )] <sub>2</sub> , 6 mol% ligand 2eq. Nu-H, 2eq. BSA 10 mol% additive		Ph Ph		<	
							`Ph	
entry	ligand	Nu	addtive	solvent	temp	time (h)	yield (%) <sup>a</sup>	ee (%) <sup>b</sup>
1	(S)- <b>3a</b>	CH(COOMe) <sub>2</sub>	KOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	15	>99	80
2	(S)- <b>3a</b>	CH(COOMe) <sub>2</sub>	LiOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	17	>99	65
3	(S) <b>-3a</b>	CH(COOMe) <sub>2</sub>	NaOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	15	>99	78
4	(S) <b>-3a</b>	CH(COOMe) <sub>2</sub>	RbOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	15	>99	81
5	(S)- <b>3a</b>	CH(COOMe) <sub>2</sub>	CsOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	15	>99	76
6	(S)- <b>3a</b>	CH(COOMe) <sub>2</sub>	KOAc	THF	rt	15	>99	55
7	(S) <b>-3a</b>	CH(COOMe) <sub>2</sub>	KOAc	toluene	rt	15	52	61
8	(S)- <b>3a</b>	CH(COOMe) <sub>2</sub>	KOAc	$(CICH_2)_2$	rt	15	>99	75
9	(S)- <b>3a</b>	CH(COOMe) <sub>2</sub>	KOAc	$CH_2CI_2$	0 °C	96	>99	61
10	( <i>R</i> )- <b>3b</b>	CH(COOMe) <sub>2</sub>	KOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	17	>99	91
11	( <i>R</i> )- <b>3b</b>	CH(COOMe) <sub>2</sub>	KOAc	$CH_2CI_2$	0 °C	105	>99	96
12	(S)- <b>3c</b>	CH(COOMe) <sub>2</sub>	KOAc	$CH_2CI_2$	rt	17	>99	rac
13	(S) <b>-3a</b>	CH(COO <sup>t</sup> Bu) <sub>2</sub>	KOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	40	97	83
14	( <i>R</i> )- <b>3b</b>	CH(COO <sup>t</sup> Bu) <sub>2</sub>	KOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	40	98	93
15	( <i>R</i> )- <b>3b</b>	CH(COO <sup>t</sup> Bu) <sub>2</sub>	KOAc	$CH_2CI_2$	0 °C	163	97	96
16	(S)- <b>3a</b>	C(NHAc)(COOMe)	2 KOAc	$CH_2CI_2$	rt	39	92	81
17	( <i>R</i> )- <b>3b</b>	C(NHAc)(COOMe)	2 KOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	39	99	79
18	(S)- <b>3a</b>	CH(COMe) <sub>2</sub>	KOAc	$CH_2Cl_2$	rt	41	21	65
19	( <i>R</i> )- <b>3b</b>	CH(COMe) <sub>2</sub>	KOAc	CH <sub>2</sub> Cl <sub>2</sub>	rt	39	95	89

Table Asymmetric Allylic Alkylation Catalyzed by Palladium Complexes Coordinated with Monodentate Phosphine Ligands.

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<sup>a</sup>Yield of isolated product. <sup>b</sup>Determined by HPLC analysis employing Daicel CHIRALCEL OD-H or CHIRALPAK AD.

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(6) The mixtures of  $(R_p)$ -1a and  $(S_p)$ -1a,  $(R_p)$ -1b and  $(S_p)$ -1b, and  $(R_{\rm P})$ -1c and  $(S_{\rm P})$ -1c were separated by preparative HPLC using ODS-column. Diasteromerically pure  $(R_p)$ -1b,  $(S_p)$ -1b,  $(R_{\rm P})$ -1c, and  $(S_{\rm P})$ -1c were obtained also by fractional recrystallization.  $(R_{\rm P})$ -1a: Colorless syrup;  $[\alpha]_{\rm D}^{25}$  –46.0° (*c* 0.97, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.08–1.37 (m, 8H), 0.77 (d, J = 4.6 Hz, 3H), 0.79 (d, J = 4.8 Hz, 3H), 0.92 (d, J = 7.0 Hz, 3H), 0.98 (d, J = 14.3 Hz, 9H), 1.60–1.64 (m, 2H), 1.96–1.99 (m, 1H), 2.21-2.24 (m, 1H), 4.16-4.23 (m, 1H), 7.20-7.48 (m, 8H), 7.95 (ddd, J = 9.2, 7.7, 1.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.5, 21.1, 22.2, 22.6, 25.1, 25.3, 31.4, 33.9, 34.3, 34.4, 43.3, 49.1, 49.2, 79.3, 125.7, 125.8, 126.8, 127.4, 129.8, 130.2, 130.4, 130.9, 132.2, 132.3, 133.4, 141.1, 146.9, 147.0; <sup>11</sup>B (CDCl<sub>3</sub>) δ

-59.3 (brs); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 114.3 (m); IR (Neat) 3055, 2950, 2390, 1575, 1465, 1365, 1070, 985, 755, 700 cm<sup>-1</sup>; HRMS calced for  $C_{26}H_{40}BKOP$  449.2547 found 449.2514.  $(S_{\rm P})$ -**1a**: Colorless syrup;  $[\alpha]_{\rm D}^{25}$  –59.3° (*c* 0.91, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.07–1.43 (m, 8H), 0.61 (d, J = 6.8 Hz, 3H), 0.73 (d, J = 7.0 Hz, 3H), 0.73 (d, J = 6.5 Hz, 3H), 1.00 (d, J = 14.5 Hz, 9H), 1.57–1.64 (m, 2H), 1.71–1.78 (m, 1H), 2.07-2.10 (m, 1H), 4.18-4.23 (m, 1H), 7.18-7.48 (m, 8H), 7.94 (ddd, J = 9.2, 7.7, 1.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  15.7, 21.0, 22.2, 22.7, 25.3, 25.6, 31.5, 33.9, 34.0, 34.3, 43.9, 48.9, 80.0, 125.5, 125.6, 126.8, 127.3, 128.9, 129.4, 130.3, 130.7, 132.0, 132.1, 133.5, 141.2, 147.1, 147.2; <sup>11</sup>B NMR (CDCl<sub>3</sub>) δ -59.7 (brs); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 120.4 (m); IR (Neat) 3055, 2955, 2395, 1585, 1455, 1065, 950, 755, cm<sup>-1</sup>; HRMS calced for C<sub>26</sub>H<sub>40</sub>BKOP 449.2547 found 449.2557.  $(R_{\rm P})$ -1b: Colorless crystals; mp 186.5–187.5 °C;  $[\alpha]_{\rm D}^{26}$ -13.8° (c 1.2, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.58-1.64 (m, 21H), 0.75 (d, J = 4.1 Hz, 3H), 0.76 (d, J = 4.1 Hz, 3H), 0.90 (d, J = 7.2 Hz, 3H), 1.98–2.06 (m, 2H), 4.06–4.14 (m, 1H), 7.26-7.54 (m, 8H), 8.18 (ddd, J = 12.8, 7.7, 1.2 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.6, 21.0, 22.0, 22.9, 25.2, 25.3, 25.3, 25.7, 25.7, 26.0, 26.2, 26.5, 26.6, 31.3, 34.3, 36.1, 36.6, 42.8, 43.3, 49.4, 49.5, 79.3, 79.4, 127.0, 127.2, 127.2, 127.7, 130.2, 130.4, 130.9, 131.2, 131.3, 131.4, 135.2, 135.4, 141.0, 141.0, 146.0; <sup>11</sup>B NMR (CDCl<sub>3</sub>)  $\delta$  -61.8 (d, J = 64.5 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 122.7 (m); IR (KBr) 3050, 2935, 2395, 1590, 1560, 985, 775, 705, cm<sup>-1</sup>; FAB MS m/z 433 (M<sup>+</sup>-3H); Anal. Calcd for C<sub>28</sub>H<sub>42</sub>BOP: C, 77.06; H, 9.70. Found: C, 77.14 H, 9.79.  $(S_{\rm P})$ -1b: Colorless crystals; mp 148.0–149.0 °C;  $[\alpha]_{\rm D}^{25}$  – 93.7° (c 1.04, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.32-1.67 (m, 22H), 0.49 (d, J = 6.8 Hz, 3H), 0.70 (d, J = 7.0 Hz, 3H), 0.91 (d, J = 6.5 Hz, 3H), 2.03–2.06 (m, 1H), 4.12–4.21 (m, 1H), 7.26-7.54 (m, 8H), 8.22 (dd, J = 14.3, 7.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.5, 21.0, 22.1, 22.5, 25.5, 25.6, 25.7, 25.9, 26.1, 26.5, 26.7, 31.4, 34.0, 35.3, 35.8, 43.6, 48.8, 48.8, 79.5, 79.6, 126.9, 127.0, 127.6, 127.7, 129.0, 129.5, 129.8, 131.4, 131.4, 135.7, 135.9, 141.4, 141.5, 145.5; <sup>11</sup>B (CDCl<sub>3</sub>) δ -62.1 (d, J = 66.8 Hz; <sup>31</sup>P NMR (CDCl<sub>3</sub>)  $\delta$  117.2 (m); IR (KBr) 3055, 2930, 2385, 1560, 1445, 980, 755, 695  $\rm cm^{-1};$  FAB MS  $\rm m/z$ 433 (M<sup>+</sup>-3H); Anal. Calcd for C<sub>28</sub>H<sub>42</sub>BOP: C, 77.06; H, 9.70. Found: C, 77.27; H, 9.72.

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(R<sub>p</sub>)-1c: Colorless crystals; mp 130.5–131.0 °C; [a]_{D}^{26}
-23.5° (c 0.82, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.34–1.64 (m,
10H), 0.51 (d, J = 6.8 Hz, 3H), 0.81 (d, J = 7.0 Hz, 3H), 0.85
(d, J = 6.5 Hz, 3H), 1.81–1.89 (m, 1H), 2.16–2.19 (m, 1H),
4.19–4.27 (m, 1H), 6.82–6.84 (m, 2H), 7.00–7.04 (m, 2H),
7.13–7.30 (m, 7H), 7.48–7.55 (m, 2H), 8.23–8.28 (m, 1H);
<sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.2, 21.0, 21.0, 22.1, 22.6, 25.3, 25.4,
31.4, 34.2, 43.3, 49.0, 49.0, 79.9, 126.8, 126.9, 127.0, 127.7,
127.8, 129.9, 130.3, 130.4, 131.3, 131.6, 131.7, 132.1, 132.7,
133.5, 133.6, 133.7, 133.7, 134.3, 140.4, 140.4, 146.5, 146.5;
<sup>11</sup>B NMR (CDCl<sub>3</sub>) δ –57.5 (d, J = 55.7 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>)
δ 101.3 (m); IR (KBr) 3055, 2945, 2420, 1590, 1440, 1060,
975, 775, 755, 700 cm<sup>-1</sup>; FAB MS m/z 427 (M<sup>+</sup>–3H); Anal.
Calcd for C<sub>28</sub>H<sub>36</sub>BOP: C, 78.14; H, 8.43. Found: C, 78.13 H,
8.49.
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(*S*<sub>p</sub>)-**1c**: Colorless crystals; mp 105.5–106.5 °C;  $[α]_D^{25}$ –84.7° (*c* 0.84, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.50–1.69 (m, 10H), 0.73 (d, *J* = 6.8 Hz, 3H), 0.82 (d, *J* = 6.5 Hz, 3H), 0.85 (d, *J* = 7.0 Hz, 3H), 1.84–1.92 (m, 2H), 4.34–4.42 (m, 1H), 6.74–6.76 (m, 2H), 6.97–7.24 (m, 9H), 7.48–7.55 (m, 2H), 8.32–8.38 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 15.6, 21.2, 22.1, 22.7, 25.8, 31.4, 34.1, 43.7, 48.9, 49.0, 80.8, 80.8, 126.8, 126.9, 126.9, 127.6, 127.7, 129.8, 129.8, 130.0, 130.0, 131.0, 131.3, 131.6, 131.6, 131.7, 132.0, 133.9, 134.1, 134.2, 134.6, 134.9, 140.4, 140.5, 146.5, 146.5; <sup>11</sup>B (CDCl<sub>3</sub>) δ –60.7 (d, *J* = 63.4 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) δ 104.2 (m); IR (KBr) 3065, 2955, 2375, 1435, 1130, 1060, 1010, 755, 695 cm<sup>-1</sup>; FAB MS m/z 427 (M<sup>+</sup>–3H); Anal. Calcd for C<sub>28</sub>H<sub>42</sub>BOP: C, 78.14; H, 8.43. Found: C, 78.26; H, 8.48.

(7) (*S*)-**2a**: Colorless thin plate; mp 112.5–113.5 °C;  $[a]_D^{25}$ -11.4° (*c* 0.68, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.38–1.26 (m, 3H), 0.89 (d, *J* = 10.1 Hz, 3H), 1.05 (d, *J* = 13.8 Hz, 9H), 7.15–7.65 (m, 8H), 8.01–8.09 (m, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 7.5, 7.5, 7.8, 7.8, 25.8, 25.8, 25.9, 29.7, 30.0, 125.0, 125.4, LETTER

- 136.1, 136.2, 136.2, 141.6, 141.6, 146.4; <sup>11</sup>B NMR (CDCl<sub>3</sub>) δ  $-56.8 \text{ (d, } J = 60.9 \text{ Hz}\text{)}; {}^{31}\text{P} \text{ NMR} (\text{CDCl}_3) \delta 31.9 \text{ (m)}; \text{ IR}$ (KBr) 3050, 2970, 2380, 1555, 1465, 1075, 1070, 765, 710 cm<sup>-1</sup>; FAB MS m/z 267 (M<sup>+</sup>–3H); Anal. Calcd for  $C_{17}H_{24}BP$ : C, 75.58; H, 8.95. Found: C, 75.60; H, 8.94. (*R*)-**2b**: Colorless prism; mp 131.0–132.0 °C;  $[\alpha]_{D}^{26}$ –68.6° (*c* 0.84, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.34–1.73 (m, 14H), 1.13 (d, J = 11.3 Hz, 3H), 7.20-7.30 (m, 3H), 7.35-7.64 (m, 5H), 8.04 (ddd, J = 11.8, 7.5, 1.5 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  9.6, 9.6, 10.0, 10.0, 25.6, 26.4, 26.5, 26.6, 34.3, 34.7, 126.5, 127.0, 127.3, 127.4, 127.8, 128.0, 129.4, 130.4, 130.4, 131.2, 131.3, 135.6, 135.8, 141.3, 141.4, 146.3; <sup>11</sup>B NMR (CDCl<sub>3</sub>) δ -58.1  $(d, J = 57.2 \text{ Hz}); {}^{31}\text{P} \text{ NMR} (\text{CDCl}_3) \delta 19.8 \text{ (m)}; \text{ IR} (\text{KBr}) 3055,$ 2935, 2360, 1465, 1445, 1065, 910, 765, 710 cm<sup>-1</sup>; FAB MS m/z 293 (M<sup>+</sup>-3H); Anal. Calcd for C<sub>19</sub>H<sub>26</sub>BP: C, 77.05; H, 8.85. Found: C, 77.07; H, 8.82. (S)-2c: Colorless prism; mp 124.0–124.5 °C;  $[\alpha]_D^{25}$  54.8° (c 0.82, CHCl<sub>3</sub>); <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  0.64–1.47 (m, 3H), 1.43 (d, J = 10.1 Hz, 3H), 6.89–6.91 (m, 2H), 7.11–7.70 (m, 11H), 7.99 (ddd, J = 13.5, 7.7, 1.7 Hz, 1H); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$ 11.0, 11.6, 11.7, 12.0, 127.2, 127.4, 127.5, 128.2, 128.3, 128.4, 128.7, 129.4, 130.4, 130.9, 130.1, 131.2, 131.5, 131.5, 132.0, 132.6, 134.2, 134.2, 134.3, 134.4, 140.5, 140.5, 146.8, 146.9; <sup>11</sup>B NMR (CDCl<sub>3</sub>)  $\delta$  -54.4 (d, *J* = 54.3 Hz); <sup>31</sup>P NMR (CDCl<sub>3</sub>) & 12.7 (m); IR (KBr) 3055, 2935, 2360, 1465, 1445, 1065, 910, 765, 710 cm<sup>-1</sup>; FAB MS m/z 287 (M<sup>+</sup>-3H); Anal. Calcd for C<sub>19</sub>H<sub>20</sub>BP: C, 78.65; H, 6.95. Found: C, 78.62; H, 6.88
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