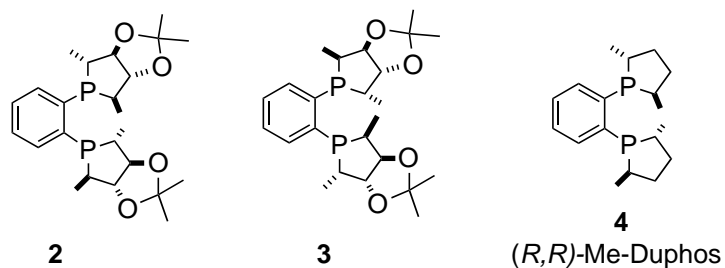


**Ligand Tuning in Asymmetric Catalysis: Mono- and Bis-Phospholanes for a Prototypical Pd-Catalyzed Asymmetric Allylation Reaction**

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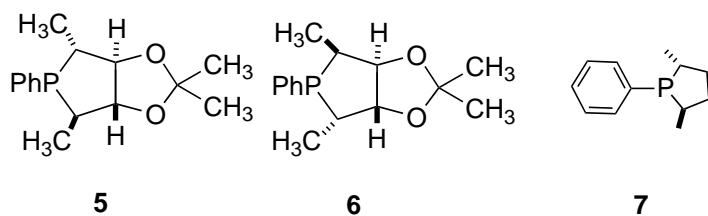
**Supporting Information**

**Table 1. Pd-catalyzed allylations with bisphospholanes<sup>a,b</sup>**

No.	Ligand	Solvent	Base	Malonate	L*/[Pd]	Yield.%	ee%(conf.) <sup>c</sup>
1	<b>2</b>	THF	BSA	di-Me	1.6/1	99.0	94.8 (S) <sup>d</sup>
2	<b>2</b>	THF	BSA	di-Me	1.6/1	97.0	91.2 (S) <sup>e</sup>
3	<b>2</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.6/1	98.0	93.0 (S)
4	<b>2</b>	THF	BSA	di-Me	1.6/1	98.0	94.0 (S)
5	<b>2</b>	toluene	BSA	di-Me	1.6/1	99.0	84.6 (S)
6	<b>2</b>	THF	BSA	di-Et	1.6/1	98.0	93.2 (S)
7	<b>3</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.6/1	98.1	>99.0 (R)
8	<b>3</b>	THF	BSA	di-Me	1.6/1	98.7	>99.0 (R)
9	<b>4</b>	THF	BSA	di-Me	2/1	99.0	96.7 (S)

Conditions: a) Reaction with BSA: [Pd(allyl)Cl]<sub>2</sub>, 1 mmol%; ligand, 2 mmol%; 1,3-diphenylpropenyl acetate, 1 mmol; malonate, 3 mmol; base, 3 mmol, at room temperature for 2 h. b) reaction with NaH: [Pd(allyl)Cl]<sub>2</sub>, 1 mmol%; ligand, 2 mmol%; allylic acetate, 1 mmol; malonate, 1.5 mmol; base, 1.5 mmol, at room temperature for 2 h. c) **dimethyl adduct**, ee measured on a Daicel Chiralcel OD-H column a  $\lambda=254$  nm; flow rate 0.5 mL/min.; eluent: hexane/PrOH 98/2. **diethyl adduct**, ee measured on a OJ column a  $\lambda=254$  nm; flow rate 0.5 mL/min.; eluent: hexane/PrOH 95/5. d) reaction at -10 °C for 18 h. e) reaction at -15 °C for 18 h.

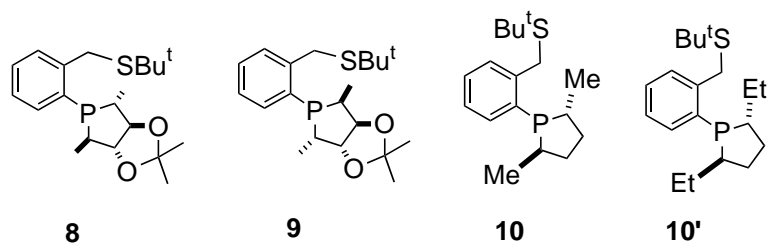
**Table 2. Pd-catalyzed allylations with monophospholanes<sup>a,b</sup>**



No.	Ligand	Solvent	Base	Malonate	L/[Pd]	Yield%	ee% (conf.) <sup>c</sup>
1	<b>5</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	2/1	95.2	76.6 (R)
2	<b>5</b>	THF	BSA	di-Me	2/1	99.0	79.6 (R)
3	<b>5</b>	CH <sub>3</sub> CN	BSA	di-Me	2/1	94.0	79.3 (R)
4	<b>5</b>	toluene	BSA	di-Me	2/1	98.8	84.1 (R)
5	<b>5</b>	THF	NaH	di-Me	2/1	94.0	71.7 (R)
6	<b>5</b>	THF	BSA	di-Me	1/1	96.0	29.3 (R)
7	<b>5</b>	THF	BSA	di-Me	3/1	98.0	78.4 (R)
8	<b>5</b>	THF	BSA	di-Me	4/1	98.0	78.9 (R)
9	<b>5</b>	THF	BSA	di-Me	2/1	98.0	88.8 (R) <sup>d</sup>
10	<b>5</b>	toluene	BSA	di-Me	2/1	97.0	92.0 (R) <sup>d</sup>
11	<b>5</b>	toluene	BSA	di-Me	2/1	99.0	93.8 (R) <sup>e</sup>
12	<b>5</b>	toluene	BSA	di-Et	2/1	99.0	82.5 (R)
13	<b>5</b>	THF	BSA	di-Et	2/1	97.0	78.3 (R)
14	<b>6</b>	toluene	BSA	di-Me	2/1	95.9	81.6 (S)
15	<b>6</b>	THF	BSA	di-Me	2/1	99.2	76.2 (S)
16	<b>6</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	2/1	98.9	74.6 (S)
17	<b>6</b>	CH <sub>3</sub> CN	BSA	di-Me	2/1	96.8	70.8 (S)
18	<b>6</b>	toluene	BSA	di-Me	2/1	97.3	91.1 (S) <sup>d</sup>
19	<b>6</b>	toluene	BSA	di-Me	2/1	98.0	93.2 (S) <sup>e</sup>
20	<b>7</b>	toluene	BSA	di-Me	2/1	96.2	37.3 (R)

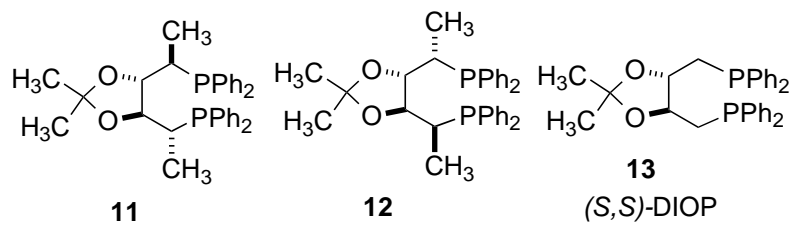
Footnotes: see, Table 1.

**Table 3. Pd-catalyzed allylations with Monophospholanes with Pendant SBU<sup>t</sup>-group<sup>a,b</sup>**



No.	Ligand	Solvent	Base	Malonate	L/[Pd]	Yield%	ee%(conf.) <sup>c</sup>
1	<b>8</b>	toluene	BSA	di-Me	2/1	99.0	51.7 (S)
2	<b>8</b>	toluene	BSA	di-Me	1.1/1	84.8	38.6 (S)
3	<b>8</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.1/1	97.0	12.7 (S) <sup>d</sup>
4	<b>8</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.1/1	99.0	43.8 (S)
5	<b>8</b>	THF	BSA	di-Me	1.1/1	96.2	42.0 (S)
6	<b>8</b>	CH <sub>3</sub> CN	BSA	di-Me	1.1/1	97.1	43.4 (S)
7	<b>8</b>	C <sub>6</sub> H <sub>6</sub>	BSA	di-Me	1.1/1	96.5	31.9 (S)
8	<b>9</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.1/1	98.0	60.0 (R)
9	<b>10</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.1/1	97.0	30.6 (S)
10	<b>10'</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	1.1/1	95.6	46.5 (R)

See footnotes, Table 1.

**Table 4. Pd-catalyzed allylations with DIOP derivatives<sup>a,b</sup>**

No.	Ligand	Solvent	Base	Malonate	L/[Pd]	Yield%	ee%(conf.)
1.	<b>11</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	2/1	98.0	1.1 (R)
2.	<b>11</b>	toluene	BSA	di-Me	2/1	98.0	9.7 (R)
3.	<b>12</b>	toluene	BSA	di-Me	2/1	96.0	56.0 (S)
4.	<b>12</b>	THF	BSA	di-Me	2/1	95.0	55.0 (S)
5.	<b>12</b>	CH <sub>2</sub> Cl <sub>2</sub>	BSA	di-Me	2/1	92.0	63.0 (S)

See footnotes, Table 1.