

# Asymmetric Rh-catalyzed hydrogenation using a furanoside phosphite-phosphoroamidite and diphosphoroamidite ligand library

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**Table SI.1.** Selected results for the asymmetric Rh-catalyzed hydrogenation of  $\alpha$ -dehydroamino-acid esters using phosphite-phosphoroamidite and diphosphoroamidite ligands **L1-L5a-f<sup>a</sup>**

Entry	Ligand	<b>S2</b>		<b>S3</b>	
		% Conv (h) <sup>b</sup>	%ee <sup>c</sup>	% Conv (h) <sup>b</sup>	%ee <sup>c</sup>
1	<b>L1a</b>	100 (6)	92 ( <i>S</i> )	100 (6)	94 ( <i>S</i> )
2	<b>L1b</b>	100 (6)	82 ( <i>S</i> )	100 (6)	85 ( <i>S</i> )
3	<b>L1c</b>	100 (6)	12 ( <i>R</i> )	100 (6)	18 ( <i>R</i> )
4	<b>L1d</b>	100 (6)	15 ( <i>S</i> )	100 (6)	13 ( <i>S</i> )
5	<b>L1e</b>	100 (6)	86 ( <i>R</i> )	100 (6)	83 ( <i>R</i> )
6	<b>L1f</b>	100 (6)	92 ( <i>S</i> )	100 (6)	93 ( <i>S</i> )
7	<b>L2a</b>	100 (6)	15 ( <i>S</i> )	100 (6)	18 ( <i>S</i> )
8	<b>L2b</b>	93 (6)	12 ( <i>S</i> )	95 (6)	17 ( <i>S</i> )
9	<b>L2c</b>	100 (6)	4 ( <i>S</i> )	100 (6)	8 ( <i>S</i> )
10	<b>L2e</b>	84 (6)	14 ( <i>R</i> )	89 (6)	17 ( <i>R</i> )
11	<b>L2f</b>	99 (6)	21 ( <i>S</i> )	99 (6)	22 ( <i>S</i> )
12	<b>L3a</b>	30 (6)	4 ( <i>R</i> )	48 (6)	6 ( <i>R</i> )
13	<b>L3b</b>	24 (6)	10 ( <i>R</i> )	36 (6)	11 ( <i>R</i> )
14	<b>L3c</b>	100 (6)	85 ( <i>S</i> )	100 (6)	78 ( <i>S</i> )
15	<b>L4a</b>	78 (6)	14 ( <i>S</i> )	69 (6)	13 ( <i>S</i> )
16	<b>L4b</b>	100 (6)	13 ( <i>S</i> )	100 (6)	16 ( <i>S</i> )
17	<b>L4c</b>	100 (6)	78 ( <i>S</i> )	100 (6)	71 ( <i>S</i> )
18	<b>L5a</b>	100 (6)	43 ( <i>S</i> )	100 (6)	44 ( <i>S</i> )
19 <sup>d</sup>	<b>L1a</b>	100 (12)	98 ( <i>S</i> )	100 (20)	98 ( <i>S</i> )
20 <sup>d,e</sup>	<b>L1a</b>	96 (20)	98 ( <i>S</i> )	65 (20)	98 ( <i>S</i> )

<sup>a</sup> [Rh(cod)<sub>2</sub>]BF<sub>4</sub> (1 mol%), ligand (1.1 mol%), substrate (1 mmol), CH<sub>2</sub>Cl<sub>2</sub> (6 mL), 5 bar of H<sub>2</sub>, room temperature. <sup>b</sup> % Conversion measured by GC. <sup>c</sup> Enantiomeric excess measured by GC. <sup>d</sup> Reaction carried out at 5 °C. <sup>e</sup> Reaction carried out using 0.1 mol% catalyst.

**Table SI.2.** Asymmetric Rh-catalyzed hydrogenation of *N*-(1-(4-methoxyphenyl)vinyl)-acetamide **S4** using phosphite-phosphoroamidite and diphosphoroamidite ligands **L1-L5a-f<sup>a</sup>**

Entry	Ligand	% Conv (h) <sup>b</sup>	%ee <sup>c</sup>	Entry	Ligand	% Conv (h) <sup>b</sup>	%ee <sup>c</sup>
1	<b>L1a</b>	100 (12)	73 ( <i>S</i> )	16	<b>L3d</b>	100 (12)	12 ( <i>R</i> )
2	<b>L1b</b>	100 (12)	65 ( <i>S</i> )	17	<b>L4a</b>	100 (12)	52 ( <i>S</i> )
3	<b>L1c</b>	99 (12)	14 ( <i>R</i> )	18	<b>L4b</b>	100 (12)	50 ( <i>S</i> )
4	<b>L1d</b>	100 (12)	16 ( <i>S</i> )	19	<b>L4c</b>	98 (12)	19 ( <i>S</i> )
5	<b>L1e</b>	100 (12)	46 ( <i>R</i> )	20	<b>L4d</b>	100 (12)	7 ( <i>R</i> )
6	<b>L1f</b>	100 (12)	70 ( <i>S</i> )	21	<b>L5a</b>	100 (12)	60 ( <i>S</i> )
7	<b>L2a</b>	100 (12)	18 ( <i>R</i> )	22	<b>L5b</b>	100 (12)	47 ( <i>S</i> )
8	<b>L2b</b>	100 (12)	13 ( <i>R</i> )	23	<b>L5c</b>	100 (12)	31 ( <i>S</i> )
9	<b>L2c</b>	97 (12)	14 ( <i>S</i> )	24	<b>L5e</b>	100 (12)	36 ( <i>S</i> )
10	<b>L2d</b>	100 (12)	7 ( <i>R</i> )	25	<b>L5f</b>	100 (12)	66 ( <i>S</i> )
11	<b>L2e</b>	94 (12)	17 ( <i>R</i> )	26 <sup>d</sup>	<b>L1a</b>	100 (12)	72 ( <i>S</i> )
12	<b>L2f</b>	99 (12)	33 ( <i>S</i> )	27 <sup>e</sup>	<b>L1a</b>	42 (24)	76 ( <i>S</i> )
13	<b>L3a</b>	100 (12)	54 ( <i>S</i> )	28 <sup>f</sup>	<b>L1a</b>	95 (18)	76 ( <i>S</i> )
14	<b>L3b</b>	100 (12)	49 ( <i>S</i> )	29 <sup>g</sup>	<b>L1a</b>	100 (24)	86 ( <i>S</i> )
15	<b>L3c</b>	98 (12)	6 ( <i>S</i> )	30 <sup>f,g</sup>	<b>L1a</b>	71 (36)	88 ( <i>S</i> )

<sup>a</sup> [Rh(cod)<sub>2</sub>]BF<sub>4</sub> (1 mol%), ligand (1.1 mol%), substrate (0.25 mmol), CH<sub>2</sub>Cl<sub>2</sub> (2 mL), room temperature, 30 bar of H<sub>2</sub>. <sup>b</sup> % Conversion measured by GC. <sup>c</sup> Enantiomeric excess measured by GC. <sup>d</sup> Reaction carried out at a ligand/Rh ratio of 2. <sup>e</sup> Reaction carried out using 2.5 bar of H<sub>2</sub>. <sup>f</sup> Reaction carried out using 5 bar of H<sub>2</sub>. <sup>g</sup> Reaction carried out at 5 °C.