## **Supporting information**

## SUPRAphos-based palladium catalysts for the kinetic resolution of racemic cyclohexenyl acetate

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## **Catalysis: experimental procedure.**

In a 10 ml vial was placed L'n (0.015 mmol, 15.2 mg), 20 eq. dipea (diisopropyl ethyl amine) and Ln (0.012 mmol, 3.16 mg) in 2 ml CH<sub>2</sub>Cl<sub>2</sub>. The solution was stirred at RT, under N<sub>2</sub> for 20 min. Then a solution of  $[Pd(?^3-C_3H_5)Cl]_2$  (0.005 mmol, 1.83 mg) in 1 ml CH<sub>2</sub>Cl<sub>2</sub> was added and stirred for another 20 min. followed by the addition of *rac*-**1** (1 mmol, 0.25 mM), 3 mmol dimethyl malonate, 3 mmol BSA [*N*,*O*-bis (trimethylsilyl)acetamide], cat. KOAc in 1 ml CH<sub>2</sub>Cl<sub>2</sub>. (1 mol% Pd, Pd/L'1/Ln = 1/1.5/1.2 with respect to per Pd).

## Most important results are summarized in tables and figures below.

entry	Ln	t (h)	Conv. <sup>a</sup>	ee of ( <i>R</i> )-2	ee of ( <i>S</i> )-1	S
1	L3	0.6	75	37	99	8.6
2	L5	0.5	69	31	99	12
3	L6	0.5	81	17	99	6.4
4	L7	0.5	84	12	99	5.6
5	PPh <sub>3</sub>	24	34	45	26	3.9
6	- 6	1	41	11	22	2.4

Table 1 Important results using SUPRAphos ligands L'1/Ln and control experiments<sup>a</sup>

(a) Pd/L' 1/Ln = 1/1.5/1.2, for general conditions see above. (b) L'1 2.2 eq. with respect to Pd.

*Figure 1* Kinetic resolution in different solvents with Pd/L'1/L7; ee of (R)-2 are in the range of 2-12%. For general experimental condition see above.



Table 2 Kinetic resolution using different ratios of L'1/L5, general conditions see above

Entry	Pd/L'1/L5	t (min)	Conv.	ee of ( <i>R</i> )-2	ee of (S)- <b>1</b>	S
5		× /				
1	1/0.5/0.45	210	17	34	10	3
_	_,			•		-
2	1/1/1	105	73	33	73	3.4
_	1/1/1	100	10	55	15	5.1
3	1/1 5/1 2	30	69	31	99	12
5	1/1.5/1.2	50	07	51	,,	14
4	1/2/1	70	70	36	99	113
-	1/2/1	70	70	50	,,	11.5
5	1/2/2	80	81	16	99	64
5	1/ 2/ 2	00	01	10	,,	0.7
6	1/3/2 8	210	60	37	60	Δ
0	1/ 5/ 2.0	210	00	51	00	-
7	1/1/2 3	75	11	13	17	18
/	1/1/2.3	15		15	1/	1.0
	1			l	l	

Figure 2 Kinetic resolution using different palladium precursors Pd/L'1/L5 = 1/1.5/1.2



For general conditions see above, ee of (*R*)-2 are around 31%. Pd<sup>+</sup> was prepared from  $[Pd(?3-C_3H_5)Cl]_2$  and 2.2 eq. AgOTf in a mixture solvent of  $CH_2Cl_2$  and  $CH_3CN$  (4/1) followed the literature procedure<sup>1</sup> and was used immediately. dba = dibenzylidene acetone.

*Figure 3* Kinetic resolution using different nucleophiles  $[CH_2(COOR)_2]$  (R = Me, Et, i-Pr, *t*-Bu, Bn) and Pd/L'1/L5



**Different nucleophiles (R)** 

<sup>&</sup>lt;sup>1</sup> G. Carturan, M. Biasiolo, S. Daniele, G. A. Mazzocchin and P. Ugo, *Inorg. Chim. Acta*, **1986**, *119*, 19.