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SUPPLEMENTARY INFORMATION

Improving conversion and enantioselectivity in hydrogenation by combining different monodentate phosphoramidites; a new combinatorial approach in asymmetric catalysis

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General Procedures.

Reagent grade dried solvents were purchased from Fluka and used as received. Enantiomeric excesses were determined by capillary GC analysis with a CP-Chirasil-Dex-CB column (25.0 m x 250 µm x 0.25 µm). Phosphoramidites **1**,¹ **2**,² **3**-³ and **6**² were prepared according to published procedures. (Z)-b-(Acylamino)acrylates **7** and **8** were prepared according to literature procedures.²

Procedure for the hydrogenation of (Z)-b-(acylamino)acrylates **7** and **8**.

In a glove box, stock solutions of Rh(COD)₂BF₄ (5 mM), ligands **1**-**6** (5 mM) and substrates **7** and **8** (0.5 M) were prepared in DCM. In 88 glass tubes equipped with stirring bars, aliquots of the Rh(COD)₂BF₄ solution (200 µL) were added in an automated way by a robot. Then aliquots of the solutions of a single ligand (2 x 200 µL) or a combination of 2 ligands (200 µL each) were added in the corresponding glass tubes. Aliquots of the solutions of substrates **7** or **8** (200 µL) were then added. The resulting mixtures were stirred during 2 hours at 28 °C (DCM evaporation). The suitable solvent (iPrOH, DCM, AcOEt or THF) was added (2 mL each) in an automated way. These glass tubes were closed and placed in a 96-vessels autoclave that was purged 5 times with nitrogen and 3 times with hydrogen. Then, the autoclave was pressurized with H₂ to 10 bar and the reactions were stirred at room temperature during 16 hours. The resulting mixtures were subjected to conversion and ee determination (capillary GC). The configuration of products were *R* (**9**) and *S* (**10**), determined by comparing the sign of optical rotations with that of the reported ones.² Racemic products **9** and **10** were prepared by hydrogenation of **7** and **8** using 10% Pd/C (10%) in MeOH under 1 atm of H₂ for 16 hours.

Supplementary data

entry	substrate	solvent	L1	L2	conv (%)	ee (%)
1	7	i-PrOH	1	1	60	39.4
2	7	i-PrOH	3	3	42	41.7
3	7	i-PrOH	4	4	92	4.3
4	7	i-PrOH	5	5	16	29.2
5	7	i-PrOH	6	6	66	20.6
6	7	i-PrOH	2	2	97	84
7	7	i-PrOH	2	1	88	84.8
8	7	i-PrOH	2	3	85	81.7
9	7	i-PrOH	2	4	99	81
10	7	i-PrOH	2	5	74	84.6
11	7	i-PrOH	2	6	99	87.4
12	7	DCM	1	1	46	68.4
13	7	DCM	3	3	42	60.7
14	7	DCM	4	4	26	54.1
15	7	DCM	5	5	100	79.6
16	7	DCM	6	6	21	60.5
17	7	DCM	2	2	100	79.6
18	7	DCM	2	1	99	86.5
19	7	DCM	2	3	95	85.6
20	7	DCM	2	4	96	91.2
21	7	DCM	2	5	88	85.2
22	7	DCM	2	6	96	82
23	7	EtOAc	1	1	16	17
24	7	EtOAc	3	3	26	25.4
25	7	EtOAc	4	4	4	30.7
26	7	EtOAc	5	5	13	23.8
27	7	EtOAc	6	6	22	28.8
28	7	EtOAc	2	2	79	85.1
29	7	EtOAc	2	1	64	82.3
30	7	EtOAc	2	3	57	76.8
31	7	EtOAc	2	4	62	83.5
32	7	EtOAc	2	5	43	77.1
33	7	EtOAc	2	6	61	85.1
34	7	THF	1	1	23	27.8
35	7	THF	3	3	22	25.1
36	7	THF	4	4	7	19
37	7	THF	5	5	11	20
38	7	THF	6	6	13	49.7
39	7	THF	2	2	68	83.9
40	7	THF	2	1	42	68.7
41	7	THF	2	3	53	67.6
42	7	THF	2	4	57	78.7
43	7	THF	2	5	41	62.3
44	7	THF	2	6	54	83.2
45	8	i-PrOH	1	1	99	52.7
46	8	i-PrOH	3	3	99	63.5
47	8	i-PrOH	4	4	99	24.8
48	8	i-PrOH	5	5	42	52.9

Supplementary data

49	8	i-PrOH	6	6	66	57.9
50	8	i-PrOH	2	2	100	88.6
51	8	i-PrOH	2	1	98	80.1
52	8	i-PrOH	2	3	94	78.7
53	8	i-PrOH	2	4	100	84.5
54	8	i-PrOH	2	5	74	75
55	8	i-PrOH	2	6	99	84.1
56	8	DCM	1	1	83	68.5
57	8	DCM	3	3	75	65.7
58	8	DCM	4	4	43	16.3
59	8	DCM	5	5	49	77.3
60	8	DCM	6	6	35	73
61	8	DCM	2	2	100	69.9
62	8	DCM	2	1	100	82.8
63	8	DCM	2	3	100	83.3
64	8	DCM	2	4	100	90.8
65	8	DCM	2	5	100	82
66	8	DCM	2	6	100	79.3
67	8	EtOAc	1	1	62	31.8
68	8	EtOAc	3	3	49	38.8
69	8	EtOAc	4	4	20	13.1
70	8	EtOAc	5	5	32	45.7
71	8	EtOAc	6	6	25	48.9
72	8	EtOAc	2	2	91	72.8
73	8	EtOAc	2	1	74	62.4
74	8	EtOAc	2	3	67	68.8
75	8	EtOAc	2	4	75	73.2
76	8	EtOAc	2	5	53	66.9
77	8	EtOAc	2	6	67	67.6
78	8	THF	1	1	44	36.8
79	8	THF	3	3	52	45.4
80	8	THF	4	4	12	33.6
81	8	THF	5	5	20	44.5
82	8	THF	6	6	29	67
83	8	THF	2	2	97	85.3
84	8	THF	2	1	86	71.8
85	8	THF	2	3	81	76.4
86	8	THF	2	4	92	84.9
87	8	THF	2	5	67	78
88	8	THF	2	6	83	81.6

Supplementary data

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