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Supplementary data

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 μ m x 0.25 μ m). Phosphoramidites 1,¹ 2,² 3-5³ and 6² were prepared according to published procedures. (2)-**b**-(A cylamino) acrylates 7 and 8 were prepared according to literature procedures.

Procedure for the hydrogenation of (2)-**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 μ L) were added in an automated way by a robot. Then aliquots of the solutions of a single ligand (2 x 200 μ L) or a combination of 2 ligands (200 μ L each) were added in the corresponding glass tubes. A liquots of the solutions of substrates 7 or 8 (200 μ L) were then added. The resulting mixtures were stirred during 2 hours at 28 §C (DCM evaporation). The suitable solvent (\not PrOH, 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 \not P (9) and \not S(10), determined by comparing the sign of optical rotations with that of the reported ones. Racemic products 9 and 10 were prepared by hydrogenation of 7 and 8 using 10% Pd/C (10%) in M eOH under 1 atm of H₂ for 16 hours.

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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 7	EtOAc EtOAc	2 2	1	64 57	82.3
30				3	57	76.8
31 32	7 7	EtOAc EtOAc	2 2	4 5	62 43	83.5 77.1
33	7	EtOAc	2	6	43 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

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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

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Supplementary data

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