Catalytic Effect and Recyclability of Imidazolium-Tagged Bis(oxazoline) Based Catalysts in Asymmetric Henry Reactions

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Supplementary data

1. General procedure for the enantioselective Henry reaction

To an oven dried 10 mL two necked round-bottomed flask, a solution of ligand (0.05 mmol) and $Cu(OAc)_2 \cdot H_2O$. (9.80 mg, 0.049 mmol) in MeOH (1 mL) was stirred for 2 h at 25°C. Then the aldehyde (0.34 mmol) and nitromethane (17 mmol) were added and the resulting mixture was stirred at 0°C for the appropriate time. After completion as monitored by TLC, the solvent was removed and the resulting residue was purified by column chromatography on silica gel (Merck, 60–120 mesh, (ethyl acetate/hexane, 3:7) to afford the pure 2-nitroalcohol.

(*R*)-1-Phenyl-2-nitro ethanol **5a**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 11.2 min, *tr*(minor) = 13.2 min;

(*R*)-1-(2-Methoxylphenyl)-2-nitroethanol **5b**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, UV = 215 nm): *tr*(major) = 9.8 min, *tr*(minor) = 11.3 min ;

(*R*)-1-(3-Methoxyphenyl)-2-nitroethanol **5c**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 90:10 v/v, 0.8 mL/min, UV = 215 nm): *tr*(major) = 45.6 min, *tr*(minor) = 60.1 min ;

(*R*)-1-(4-Methoxyphenyl)-2-nitroethanol **5d**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 17.4min, *tr*(minor) = 22.1 min;

(*R*)-1-(4-Nitrophenyl)-2-nitroethanol **5e**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 18.7 min, *tr*(minor) = 23.6 min;

(*R*)-1-(2-Nitrophenyl)-2-nitroethanol **5f**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 90:10 v/v, 0.9 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 14.5 min, *tr*(minor) = 16.2 min;

(*R*)-1-(2-Chlorophenyl)-2-nitroethanol **5g**

HPLC (Chiralcel OJ-H, n-hexane/i-PrOH, 90:10 v/v, 1 mL/min, 23 °C, UV = 214 nm): *tr*(major) = 14.4 min, *tr*(minor)= 16.1 min;

(*R*)-1-(4-Chlorophenyl)-2-nitroethanol **5h**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15v/v 0.8 mL/min, 23 °C, UV = 215 nm):

tr(major) = 12.2 min, *tr*(minor) = 14.7 min;

(*R*)-1-(3-Bromophenyl)-2-nitroethanol **5i**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 90:10 v/v, 0.8 mL/min, 215 nm): *tr*(major) =10.1 min, *tr*(minor) =12.9 min;

(*R*)-1-(4-Bromophenyl)-2-nitroethanol **5j**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.9 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 11.1 min, *tr*(minor) = 14.2 min;

(*R*)-1-(2-Fluorophenyl)-2-nitroethanol **5k**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 90:10 v/v, 1.0 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 10.1 min, *tr*(minor) = 10.9 min;

(*R*)-1-(4-Fluorophenyl)-2-nitroethanol **5l**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 90:10 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 13.4 min, *tr*(minor) = 15.9 min;

(*R*)-1-(1-Naphthyl)-2-nitroethanol **5m**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 14.3 min, *tr*(minor) = 20.1 min;

(*R*)-1-(3,4-Dimethoxyphenyl)-2-nitroethanol **5n**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 22.9 min, *tr*(minor) = 30.1 min;

(*R*)-1-(2,4-Dichlorophenyl)-2-nitroethanol **5o**

HPLC (Chiralpak AD-H, n-hexane/i-PrOH, 90:10 v/v, 0.5 mL/min, 26 °C, UV = 215 nm): *tr*(major) = 15.9 min, *tr*(minor) = 18.9 min;

(*R*)-1-(3,5-Dimethoxyphenyl)-2-nitroethanol **5p**

HPLC (Chiralpak AD-H, n-hexane/i-PrOH, 90:10 v/v, 1.0 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 19.0 min, *tr*(minor) = 15.6 min;

(*R*) -1- (pyridin-4-yl) -2-nitroethanol **5q**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 75:25 v/v, 0.7 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 12.0 min, *tr*(minor) = 13.8 min;

(*R*)-1-Furfuryl-2-nitroethanol **5r**

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) = 57.7 min, *tr*(minor) = 62.3min;

(*R*)-2-nitro-1-(3,4,5-trimethoxyphenyl)ethanol 5s

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 85:15 v/v, 0.8 mL/min, 23 °C, UV = 215 nm): *tr*(major) =24.4 min, *tr*(minor) = 30.3 min

2-nitro-1-phenylpropan-1-ol 9a

HPLC (Chiralpak AD-H, n-hexane/i-PrOH, 95:5 v/v, 0.5 mL/min, 23 °C, UV = 215 nm): *Anti*(major) = 30.2 min, *Anti*(minor) = 26.5 min, *Syn*(major) = 41.6 min, *Syn*(minor) = 36.8 min

2-nitro-1-(4-nitrophenyl)propan-1-ol 9e

HPLC (Chiralcel OD-H, n-hexane/i-PrOH, 90:10 v/v, 1.0 mL/min, 23 °C, UV = 215 nm): *Anti*(tr) = 19.5 min, *Syn*(major) = 29.5 min, *Syn*(minor) = 36.5 min; (Chiralpak AD-H, n-hexane/i-PrOH, 90:10 v/v, 1.0 mL/min, 23 °C, UV = 215 nm): *Anti*(major) = 19.7min, *Anti*(minor) = 26.2 min, *Syn* =24.5 min.[1]

2. Theoretical calculations results of 10b-Cu-15a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	29	0	-2.547523	3.472950	0.353470
2	7	0	-2.176275	2.398762	-1.290894
3	8	0	-3.397177	5.223514	-1.797747
4	8	0	-2.758552	3.888918	2.261416
5	8	0	-4.316463	4.087856	-0.082945
6	7	0	-0.586019	3.918333	0.453722
7	6	0	-4.345814	4.965512	-1.039278
8	8	0	-0.953934	1.541858	-2.960568
9	6	0	-4.065554	0.907083	-1.914202
10	6	0	-1.838960	8.909003	0.969569
11	1	0	-2.285050	9.897252	0.896055
12	8	0	1.618376	3.787038	0.078650
13	6	0	0.381514	3.296649	-0.113789
14	6	0	-0.020335	5.008222	1.288087
15	1	0	-0.100309	4.674913	2.328254
16	6	0	-6.097640	0.122346	-0.844365
17	1	0	-7.048366	0.345503	-0.366880
18	6	0	-5.296459	1.170930	-1.301483
19	1	0	-5.604958	2.199963	-1.146332
20	6	0	-3.182193	2.064418	-2.351244
21	1	0	-3.777230	2.959496	-2.521330
22	6	0	-1.274942	8.483692	2.174159
23	1	0	-1.280641	9.137432	3.042171
24	6	0	-0.705656	6.352517	1.162733
25	6	0	-1.269218	6.783961	-0.042674
26	1	0	-1.316611	6.121908	-0.900302
27	6	0	-1.022615	2.020151	-1.704545
28	6	0	-1.843206	8.053261	-0.132471
29	1	0	-2.304879	8.359804	-1.066539
30	8	0	-2.760500	1.672935	2.060719
31	6	0	-5.680161	5.686179	-1.186450
32	1	0	-5.671164	6.331515	-2.067263
33	1	0	-5.866624	6.291136	-0.292132
34	1	0	-6.500661	4.964461	-1.260382

35	6	0	-2.889290	2.711554	2.755180
36	6	0	-5.675392	-1.200955	-0.979421
37	1	0	-6.267528	-2.021948	-0.585919
38	6	0	-3.243898	2.618819	4.226966
39	1	0	-2.861507	1.689318	4.656440
40	1	0	-4.335962	2.617732	4.326210
41	1	0	-2.859397	3.480494	4.777925
42	6	0	-4.450854	-1.475544	-1.595244
43	1	0	-4.102866	-2.501144	-1.662016
44	6	0	2.827820	1.369351	-1.173515
45	6	0	3.919894	1.141651	-2.230452
46	1	0	3.154890	2.144820	-0.476048
47	1	0	2.715432	0.448115	-0.589478
48	6	0	5.232100	0.717050	-1.566523
49	1	0	3.593753	0.369255	-2.940528
50	1	0	4.075636	2.058006	-2.816195
51	1	0	5.610089	1.486748	-0.890248
52	1	0	5.130699	-0.186712	-0.958873
53	6	0	-0.037265	-0.561318	-0.317569
54	6	0	-0.347831	-1.583166	0.795326
55	1	0	-0.838982	-0.603370	-1.064048
56	1	0	0.879397	-0.876324	-0.829000
57	6	0	-1.774858	-1.422766	1.318683
58	1	0	-0.230331	-2.589881	0.378341
59	1	0	0.381765	-1.477143	1.610148
60	1	0	-1.946986	-0.423472	1.724702
61	1	0	-2.482222	-1.595875	0.502842
62	6	0	0.270701	1.987709	-0.885171
63	6	0	1.490682	1.753164	-1.827289
64	1	0	1.208883	0.958226	-2.522123
65	1	0	1.630453	2.651072	-2.441638
66	6	0	0.117699	0.871059	0.215256
67	1	0	-0.747587	1.140680	0.826942
68	1	0	0.998531	0.925623	0.866784
69	7	0	6.318225	0.462590	-2.529973
70	7	0	-2.123294	-2.397123	2.373055
71	7	0	7.734320	-0.575334	-3.807568
72	6	0	8.519687	-1.678191	-4.361794
73	1	0	7.911653	-2.272730	-5.046727
74	1	0	9.359285	-1.254585	-4.914392
75	1	0	8.880880	-2.285342	-3.527974
76	6	0	5.774090	-1.956706	-2.989364
77	1	0	5.734984	-2.242062	-1.929097
78	1	0	4.759081	-1.795404	-3.369537

79	1	0	6.229187	-2.774329	-3.548945
80	6	0	6.590608	-0.720542	-3.111836
81	6	0	7.323032	1.359775	-2.837057
82	1	0	7.330117	2.359528	-2.435352
83	6	0	8.209842	0.712350	-3.632920
84	1	0	9.141153	1.036930	-4.067846
85	6	0	-4.442744	-1.464671	2.749610
86	1	0	-5.052254	-1.401191	3.655824
87	1	0	-4.054281	-0.469676	2.516359
88	1	0	-5.083052	-1.820297	1.932882
89	6	0	-3.342331	-2.443953	2.941056
90	6	0	-4.623692	-4.079984	4.311953
91	1	0	-4.405597	-5.071728	4.705783
92	1	0	-4.930237	-3.417262	5.126588
93	1	0	-5.400214	-4.163409	3.547819
94	7	0	-3.407249	-3.569419	3.675969
95	6	0	-2.214678	-4.253844	3.560147
96	1	0	-2.065692	-5.214557	4.023322
97	6	0	-1.410507	-3.522207	2.747694
98	1	0	-0.415397	-3.721293	2.390820
99	8	0	8.436573	-1.904834	-1.225821
100	16	0	7.749239	-1.343192	-0.019752
101	8	0	6.326688	-1.813254	0.083251
102	8	0	7.894233	0.133183	0.108610
103	6	0	8.586976	-2.053162	1.408507
104	6	0	8.201418	-3.304262	1.892329
105	6	0	9.645257	-1.368248	2.005745
106	6	0	8.883731	-3.868826	2.968485
107	1	0	7.358705	-3.814337	1.437184
108	6	0	10.320567	-1.943369	3.081875
109	1	0	9.916115	-0.384642	1.636226
110	6	0	9.957026	-3.202765	3.576753
111	1	0	8.574500	-4.840716	3.348072
112	1	0	11.140356	-1.402200	3.550174
113	6	0	10.712201	-3.834957	4.723216
114	1	0	11.153534	-3.077538	5.380020
115	1	0	10.060216	-4.471588	5.331389
116	1	0	11.533675	-4.467193	4.359285
117	8	0	-3.389746	-4.093464	0.115384
118	16	0	-4.523733	-4.868544	0.710454
119	8	0	-5.642090	-3.991645	1.195324
120	8	0	-4.096195	-5.870150	1.724682
121	6	0	-5.224766	-5.805586	-0.664265
122	6	0	-6.595787	-6.057474	-0.713372

123	6	0	-4.385001	-6.326536	-1.650839
124	6	0	-7.121754	-6.830575	-1.748604
125	1	0	-7.238417	-5.637947	0.053646
126	6	0	-4.921056	-7.098235	-2.679994
127	1	0	-3.321179	-6.115480	-1.609110
128	6	0	-6.296495	-7.362506	-2.747557
129	1	0	-8.192317	-7.023316	-1.782069
130	1	0	-4.261745	-7.502708	-3.445839
131	6	0	-6.874650	-8.173441	-3.884509
132	1	0	-6.186706	-8.964117	-4.204573
133	1	0	-7.821471	-8.644761	-3.599848
134	1	0	-7.075530	-7.545101	-4.763156
135	6	0	-2.265169	1.791242	-3.557806
136	1	0	-2.158873	2.665343	-4.206217
137	1	0	-2.533940	0.915549	-4.147207
138	6	0	1.457746	5.030724	0.823676
139	1	0	2.186471	5.028842	1.635345
140	1	0	1.664379	5.855529	0.136052
141	6	0	-0.718554	7.208910	2.270745
142	1	0	-0.301805	6.872188	3.217693
143	6	0	-3.658721	-0.427330	-2.064235
144	1	0	-2.710109	-0.661049	-2.543272

References

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