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Binaphthyl-Based Chiral Bifunctional Organocatalysts for Water Mediated Asymmetric List-Lerner-Barbas Aldol Reactions

Veeramanoharan Ashokkumar, Chinnadurai Chithirai kuma, Ayyanar Siva

Supramolecular and Organometallic Chemistry Lab, School of Chemistry, Madurai Kamaraj University,

Madurai 625 021, Tamil Nadu, India.

E-mail: drasiva@gmail.com

Supporting Information

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Figure S2: ¹³C NMR Spectrum of compound 14.













Figure S8: ¹³C NMR Spectrum of organocatalyst (17a).



Figure S10: ¹H NMR Spectrum of organocatalyst (17b).









Figure S14: ¹³C NMR Spectrum of aldol product 7a.



Figure S16: ¹³C NMR Spectrum of aldol product 7b.





Figure S18: ¹³C NMR Spectrum of aldol product 7c.







-2,12394 -2,12245 -2,0046 -2,0046 -2,0046 -2,0046 -2,2004



13





-7.5987 -7.5987 -7.5698 -7.64119 -6.5139 -6.53



Figure S28: ¹³C NMR Spectrum of aldol product 7h.





8,8201 8,1351 8,1551



17

7,7,946 7,7,946 7,7,946 7,946



Figure S34: ¹³C NMR Spectrum of aldol product 9c.





Figure S36: ¹³C NMR Spectrum of aldol product 10a.

4 1000 4 1000



Figure S38: ¹³C NMR Spectrum of aldol product 10b.





Figure S40: ¹³C NMR Spectrum of aldol product 10c.





Figure S42: ¹³C NMR Spectrum of aldol product 11a.





Figure S44: ¹³C NMR Spectrum of aldol product 11d.

7,73499 7,7359 7,7359 7,7359 4,430441,4304 4,43044,4304 4,4304 4,43044,4304 4,4304 4,43044,4304 4,4304 4,43044,4304 4,4304 4,43044,4304 4,43044,4304 4,43044,4304 4,4304



Figure S46: ¹³C NMR Spectrum of aldol product 11e.







PDA	A Ch1 2	54nm 4nm				
Pe	eak#	Ret. Time	Area	Height	Area %	Height %
	1	10.147	2317152	11569	50.713	52.819
	2	27.715	2151471	10896	49.287	47.181
	Total		4468624	22465	100.000	100.000

Figure S49: HPLC chromatogram of (7) Racemic mixture.



Figure S50: HPLC chromatogram of (7a) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA Ch1 2	54nm 4nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.452	331381981	389212	99.687	98.851
2	27.337	44433	4523	0.313	1.149
Total		331426414	393735	100.000	100.000

Figure S51: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S52: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and CH₃OH in 0 °C condition.



Figure S53: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and CH₃CH₂OH in 0 °C condition.



Figure S54: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and DMF in 0 °C condition.



Figure S55: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and 1,4-Dioxane in 0 °C condition.



Figure S56: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and CH₃OH + H₂O in 0 °C condition.



Figure S57: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and DMF + H₂O in 0 °C condition.



Figure S58: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and 1,4-Dioxane + H_2O in 0 °C condition.

Total

275328

100.000

100.000



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Figure S60: HPLC chromatogram of (7a) in the presence organocatalyst (17b), PhCOOH (2 mol%) and H₂O in 0 °C condition.



Figure S61: HPLC chromatogram of (7a) in the presence organocatalyst (17b), PhCOOH (10 mol%) and H_2O in 0 °C condition.



Figure S62: HPLC chromatogram of (7a) in the presence organocatalyst (17b), HCOOH (2 mol%) and H_2O in 0 °C condition.

100.000



Figure S63: HPLC chromatogram of (7a) in the presence organocatalyst (17b), HCOOH (10 mol%) and H_2O in 0 °C condition.



Figure S64: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S65: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (10 mol%) and H₂O in 0 °C condition.



Figure S66: HPLC chromatogram of (7a) in the presence organocatalyst (17b), Oxalic acid (2 mol%) and H₂O in 0 °C condition.



Figure S67: HPLC chromatogram of (7a) in the presence organocatalyst (17b), Oxalic acid (10 mol%) and H₂O in 0 °C condition.



Figure S68: HPLC chromatogram of (**7a**) in the presence organocatalyst (**17b**, 1 mol%), CH₃COOH (2 mol%) and H₂O in 30 °C condition.

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Figure S70: HPLC chromatogram of (**7a**) in the presence organocatalyst (**17b**, 1 mol%), CH₃COOH (2 mol%) and H₂O in 60 °C condition.



Figure S71: HPLC chromatogram of (7a) in the presence organocatalyst (17b, 1 mol%), CH₃COOH (2 mol%) and H₂O in -20 °C condition.



Figure S72: HPLC chromatogram of (**7a**) in the presence organocatalyst (**17b**, 5 mol%), CH₃COOH (2 mol%) and H₂O in 0 °C condition.

100.000

100.000

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Figure S74: HPLC chromatogram of (**7a**) in the presence organocatalyst (**17b**, 20 mol%), CH₃COOH (2 mol%) and H₂O in 0 °C condition.





Figure S76: HPLC chromatogram of (7a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S77: HPLC chromatogram of (8a) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



		PeakTable					
PDA Ch1 2	54nm 4nm						
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	7.759	1362622	9131	50.357	51.296		
2	20.847	1222762	8981	49.643	48.704		
Total		2585384	18112	100.000	100.000		

Figure S78: HPLC chromatogram of (7b) Racemic mixture.



Figure S79: HPLC chromatogram of (7b) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S80: HPLC chromatogram of (8b) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



1 PDA Multi 1/254nm 4nm

			PeakTable				
PDA Ch1 2:	54nm 4nm						
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	7.759	1362622	9131	50.357	51.296		
2	20.847	1222762	8981	49.643	48.704		
Total		2585384	18112	100.000	100.000		

Figure S81: HPLC chromatogram of (7c) Racemic mixture.



		PeakTable					
PDA Ch1 2:	54nm 4nm						
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	7.908	76821577	1226754	93.021	95.364		
2	20.933	5711609	146005	2.979	4.636		
Total		82533186	1372758	100.000	100.000		

Figure S82: HPLC chromatogram of (7c) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S83: HPLC chromatogram of (8c) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S84: HPLC chromatogram of (7d) Racemic mixture.



Figure S85: HPLC chromatogram of (7d) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S86: HPLC chromatogram of (8d) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Peak#	Ret. Time	Area	Height	Area %	Height %		
1	17.898	56742198	813778	97.469	97.488		
2	61.972	4621317	20965	2.531	2.512		
Total		61363515	834744	100.000	100.000		

Figure S87: HPLC chromatogram of (7e) in the presence organocatalyst (17b), CH₃COOH (2 mole%) and H₂O in 0 °C conditions.



Figure S88: HPLC chromatogram of (8e) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PeakTable PDA Ch1 254nm 4nm Height Height % Peak# Ret. Time Area Area % 13.974 113192421 374151 93.513 96.768 50.459 7852735 12497 6.487 3.232 2 386648 100.000 Total 121045156 100.000

Figure S89: HPLC chromatogram of (7f) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S90: HPLC chromatogram of (**8f**) in the presence organocatalyst (**18b**), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



1 PDA Multi 1/254nm 4nm

PDA Ch1 2	54nm 4nm		Ре	eakTable	
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.862	143622513	1483220	50.741	51.794
2	47.964	142638897	1365126	49.259	48.206
Total		286261409	2848346	100.000	100.000

Figure S91: HPLC chromatogram of (7g) Racemic mixture.



Figure S92: HPLC chromatogram of (7g) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S93: HPLC chromatogram of (8g) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S94: HPLC chromatogram of (7h) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S95: HPLC chromatogram of (8h) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S96: HPLC chromatogram of (9a) Racemic mixture.



Figure S97: HPLC chromatogram of (9a) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S98: HPLC chromatogram of (9a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA CITI 254IIII 4IIII								
Peak#	Ret. Time	Area	Height	Area %	Height %			
1	21.862	143622513	1483220	50.741	51.794			
2	46.964	142638897	1365126	49.259	48.206			
Total		286261409	2848346	100.000	100.000			

Figure S99: HPLC chromatogram of (9b) Racemic mixture.



PDA Ch1 2	54nm 4nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.015	20622334	254758	94.214	83.370
2	46.060	1741162	50817	10.786	16.630
Total		22363496	305575	100.000	100.000

Figure S100: HPLC chromatogram of (9b) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA Ch1 24	54nm 4nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	21.164	36665482	376897	93.816	85.381
2	46.267	2416824	64531	6.184	14.619
Total		39082306	441428	100.000	100.000

Figure S101: HPLC chromatogram of (**9b**) in the presence organocatalyst (**17b**), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S102: HPLC chromatogram of (9c) Racemic mixture.



Peak#	Ret. Time	Area	Height	Area %	Height %
1	20.112	9427796	104252	80.483	73.552
2	40.068	2142474	37487	19.517	26.448
Total		11570271	141740	100.000	100.000

Figure S103: HPLC chromatogram of (9c) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S104: HPLC chromatogram of (9c) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA Ch1 254nm 4nm Peak# Ret. Time Height Area % Height % Area 61357098 746211 97.057 93.606 9.015 16.060 61860393 50970 2.943 6.394 Total 63217491 797180 100.000 100.000

Figure S105: HPLC chromatogram of (10a) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA Ch1 254nm 4nm						
Peak#	Ret. Time	Area	Height	Area %	Height %	
1	9.981	27835219	399135	98.489	94.977	
2	16.204	427069	21110	1.511	5.023	
Total		28262287	420246	100.000	100.000	

Figure S106: HPLC chromatogram of (10a) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PeakTable

PDA Ch1 254nm 4nm							
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	1 5.557	20622334	254758	92.214	83.370		
2	9.036	1741162	50817	7.786	16.630		
Tota	al	22363496	305575	100.000	100.000		





		Peak lable					
PDA Ch1 2:	54nm 4nm						
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	5.981	27802899	398992	94.885	93.769		
2	9.273	1498877	26514	5.115	6.231		
Total		29301776	425507	100.000	100.000		

Figure S108: HPLC chromatogram of (10b) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S109: HPLC chromatogram of (10c) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S110: HPLC chromatogram of (10c) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



		Peak Table							
P	DA Ch1 25	54nm 4nm							
Γ	Peak#	Ret. Time	Area	Height	Area %	Height %			
Γ	1	7.611	2753234	112968	95.961	98.933			
Γ	2	19.068	115892	1219	4.039	1.067			
Γ	Total		2869127	114187	100.000	100.000			

Figure S111: HPLC chromatogram of (11a) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



DACIN 254IIII 4IIII							
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	7.097	62830428	755323	99.182	94.164		
2	19.146	751420	46813	0.818	5.836		
Total		63581847	802136	100.000	100.000		

Figure S112: HPLC chromatogram of (11a) in the presence organocatalyst (17b),CH₃COOH (2 mol%) and H₂O in 0 °C condition.



	PeakTable						
PDA Ch1 25	54nm 4nm						
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	7.093	4838897	65126	3.259	4.206		
2	19.267	143622513	1483220	96.741	95.794		
Total		148461409	1548346	100.000	100.000		

Figure S113: HPLC chromatogram of (12a) in the presence organocatalyst (18a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA Ch1 25	54nm 4nm				
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.066	1896787	228145	0.457	9.206
2	19.048	412999376	2250170	99.543	90.794
Total		414896163	2478314	100.000	100.000

Figure S114: HPLC chromatogram of (**12a**) in the presence organocatalyst (**18b**), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S115: HPLC chromatogram of (11d) in the presence organocatalyst (18a), CH_3COOH (2 mol%) and H_2O in 0 °C condition.



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e S116: HPLC chromatogram of (11d) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S114: HPLC chromatogram of (11e) in the presence organocatalyst (18a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.

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29301776



Figure S118: HPLC chromatogram of (11e) in the presence organocatalyst (18b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



			PeakTable					
PDA Ch1 25	54nm 4nm							
Peak#	Ret. Time	Area	Height	Area %	Height %			
1	4.264	8473498	108659	83.721	74.717			
2	9.207	1647576	36770	16.279	25.283			
Total		10121074	145429	100.000	100.000			

Figure S119: HPLC chromatogram of (11f) in the presence organocatalyst (17a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S120: HPLC chromatogram of (11f) in the presence organocatalyst (17b), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



Figure S121: HPLC chromatogram of (12f) in the presence organocatalyst (18a), CH₃COOH (2 mol%) and H₂O in 0 °C condition.



PDA Ch1 254nm 4nm							
Peak#	Ret. Time	Area	Height	Area %	Height %		
1	4.093	11972419	110813	7.683	6.949		
2	9.267	143863194	1483918	92.317	93.051		
Total		155835613	1594731	100.000	100.000		

Figure S122: HPLC chromatogram of (**12f**) in the presence organocatalyst (**18b**), CH₃COOH (2 mol%) and H₂O in 0 °C condition.