Supporting Information

Asymmetric Additive-Free Aryl Addition to Aldehydes Using Perhydrobenzoxazines as Ligands and Boroxins as Aryl Source

Rebeca Infante, Javier Nieto,* Celia Andrés*

Instituto CINQUIMA and Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Valladolid. 47011 Valladolid, Spain e-mail: javiernr@qo.uva.es; celian@qo.uva.es

Table of Contents

¹H, ¹³C, ¹⁹F-NMR spectra

HPLC data	S37
Diarylmethanols	S 8
Ligands	S 2





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is © The Royal Society of Chemistry 2011





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This¹H, ¹³C, ¹⁹F-NMR spectra mistry 2011















NMR Diarylmethanols Spectra











NMR Diarylmethanols Spectra























Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011

NMR Diarylmethanols Spectra













NMR Diarylmethanols Spectra









NMR Diarylmethanols Spectra

















Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011





Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011















S29

Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011









Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011



















Electronic Supplementary Material (ESI) for Organic and Biomolecular Chemistry This journal is @ The Royal Society of Chemistry 2011





(2-naphthyl)(phenyl)methanol (&ažYbH&U)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	18.093	15278.5	414.3	0.5614	49.905	0.709
2	22.014	15336.9	337.6	0.6805	50.095	0.697

From triphenylboroxin to 2-naphthaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	17.562	44011.2	1101.8	0.6658	97.308	0.530
2	21.372	1217.4	29.4	0.6902	2.692	0.724
				ee%	95	

From tri(2-naphthyl)boroxin to benzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	17.621	613.4	18.9	0.5414	2.945	0.756
2	20.897	20218.3	418.3	0.8056	97.055	0.518
				ee%	94	

(phenyl(o-tolyl)methanol (&VžYbH&V)

HPLC: Chiralpak AD-H column, ⁱPrOH/Hex 1/99, 1 ml/min, λ = 220 nm.



	TIme	Area	Height	Area%	Height%	Symmetry
1	27,192	10305572	322951	49,921	53,284	1,211
2	30,917	10338147	283138	50,079	46,716	1,256

From triphenylboroxin to o-tolualdehyde



	Time	Area	Height	Area%	Height%	Symmetry
1	25,150	11289060	384742	98,295	98,352	1,184
2	27,925	195786	6445	1,705	1,648	1,020
			ee%	97		

From tri(o-tolyl)boroxin to benzaldehyde



	Time	Area	Height	Area%	Height%	Symmetry
1	27,917	683765	21852	3,194	3,908	1,071
2	31,558	20724550	537299	96,806	96,092	1,442
			ee%	94		

(o-methoxyphenyl)(phenyl)methanol (&W)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 2/98, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	45.970	52232.6	549.3	1.5848	49.980	0.719
2	56.616	52274.7	400.8	2.1735	50.020	0.554

From triphenylboroxin to o-methoxybenzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	42.326	531.3	6.6	1.3389	3.599	0.612
2	53.476	14230.2	119.4	1.9863	96.401	0.615
				ee%	93	

(o-chlorophenyl)(phenyl)methanol (&X)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 2/98, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	26.704	57394.7	911.3	0.9428	49.915	0.697
2	35.100	57590.6	757.0	1.0219	50.085	0.790

From triphenylboroxin to o-chlorobenzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	26.552	813.1	13.2	1.0298	93.794	0.723
2	34.882	53.8	7.8E-1	1.1521	6.206	0.913
				ee%	88	

(o-bromophenyl)(phenyl)methanol (&Y)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 2/98, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	29.158	60506.6	906.2	0.9774	49.885	0.656
2	43.205	60785.4	678.5	1.1796	50.115	0.887

From triphenylboroxin to o-bromobenzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	28.976	10352.5	163.4	1.0556	94.955	0.777
2	42.335	550.0	7.1	1.2971	5.045	0.827
				ee%	90	

(*m*-chlorophenyl)(phenyl)methanol (&Z)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 2/98, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	40.980	234199.5	2021.2	1.9312	49.728	0.472
2	45.699	236760.5	1832.5	2.1533	50.272	0.477

From triphenylboroxin to *m*-chlorobenzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	41.530	284.2	3.5	1.3475	4.588	0.860
2	45.908	5910.1	62.0	1.5883	95.412	0.776
				ee%	91	

(phenyl)(p-tolyl)methanol (&[z̈Ybh&[)

HPLC: Chiralpak AS-H column, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	8.346	10049.8	511.9	0.3272	51.097	0.478
2	9.166	9618.2	416.6	0.3848	48.903	0.495

From triphenylboroxin to *p*-tolualdehyde



	Time	Area	Height	Width	Area%	Symmetry
1	8.893	34032.5	1950.7	0.2908	97.461	0.754
2	9.747	886.7	47.9	0.3082	2.539	0.879
				ee%	95	

From tri(p-tolyl)boroxin to benzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	8.766	629.7	36.4	0.2887	1.385	1.064
2	9.506	44827.5	2277.5	0.3281	98.615	0.768
				ee%	97	

(p-methoxyphenyl)(phenyl)methanol (& žYbH&)

HPLC: Chiralpak AD-H column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	13.261	13233.4	746.5	0.2955	49.543	0.888
2	14.435	13477.7	698.1	0.3218	50.457	0.902

From triphenylboroxin to *p*-methoxybenzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	14.23	14849.5	731.5	0.3136	98.046	0.735
2	15.313	295.9	13.3	0.3271	1.954	0.742
				ee%	96	

From tri(p-methoxyphenyl)boroxin to benzaldehyde



	Time	Area	Height	Area%	Height%	Symmetry
1	13,667	318277	20863	3,170	3,878	1,040
2	14,892	9721581	517162	96,830	96,122	1,039
			ee%	94		

(p-chlorophenyl)(phenyl)methanol (&]zYbH&])

HPLC: Chiralpak AD-H column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 220 nm.



	Time	Area	Height	Area%	Height%
1	8,642	5394947	527194	49,900	52,619
2	9,333	5416666	474717	50,100	47,381

From triphenylboroxin to *p*-chlorobenzaldehyde



	Time	Area	Height	Area%	Height%
1	8,200	7075645	750227	96,622	96,775
2	8,792	247354	24999	3,378	3,225
			%ee	93	





	Time	Area	Height	Area%	Height%
1	8,717	500093	51521	5,785	6,621
2	9,533	8144767	726583	94,215	93,379
			%ee	88	

(phenyl)(p-(trifluoromethyl)phenyl)methanol (&化

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	11.246	720.6	29.0	0.4139	49.829	0.703
2	12.400	725.6	25.8	0.4691	50.171	0.656

From triphenylboroxin to *p*-(trifluoromethyl)benzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	11.142	2263	93.3	0.3695	95.679	0.627
2	12.303	102.2	4.1	0.4127	4.321	0.726
				ee%	91	

(2-furyl)(phenyl)methanol (&_Ł

HPLC: Chiralcel OD column, ⁱPrOH/Hex 2/98, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	32.940	78931.5	1063.4	1.0292	50.039	0.545
2	41.491	78807.8	841.9	1.2648	49.961	0.530

From triphenylboroxin to 2-furfural



	Time	Area	Height	Width	Area%	Symmetry
1	34.609	2571.5	36	1.1917	7.498	0.765
2	43.491	31723.2	340	1.5549	92.502	0.691
				ee%	85	

(phenyl)(2-thienyl)methanol (&)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 2/98, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	37.775	7095.5	87.5	1.3519	49.913	0.716
2	42.120	7120.2	79.7	1.4893	50.087	0.739

From triphenylboroxin to 2-thiophenecarboxaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	37.024	949.7	13.5	1.1758	4.634	0.789
2	40.921	19544.6	230.0	1.4163	95.366	0.677
				ee%	91	

1,3-diphenylprop-2-en-1-ol (&a)

HPLC: Chiralpak AS-H column, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	11.035	31013.6	1930.8	0.2677	49.890	0.788
2	12.653	31150	1671.3	0.3106	50.110	0.794

From triphenylboroxin to (E)-cinnamaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	10.872	20873	1292.2	0.2692	90.918	0.802
2	12.463	2085.2	118.4	0.2936	9.082	0.931
				ee%	82	

3-(*p*-methoxyphenyl)-1-phenylprop-2-en-1-ol (&b)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	18.618	6847.2	165.4	0.611	47.049	0.644
2	21.092	7706	162.5	0.7006	52.951	0.683

From triphenylboroxin to (*E*)-*p*-methoxycinnaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	18.237	4631.2	116	0.6653	9.424	0.668
2	20.548	44511.8	956.1	0.776	90.576	0.682
				ee%	81	

3-(2-furyl)-1-phenylprop-2-en-1-ol (&cŁ

HPLC: Chiralpak AS-H, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	12.855	59056.1	2320.0	0.4026	49.799	0.733
2	16.131	59533.3	1772.4	0.5167	50.201	0.591

From triphenylboroxin to (E)-3-(2-furanyl)acrylaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	12.859	65746.3	2863.9	0.3826	93.738	0.692
2	16.251	4392.1	159.0	0.4603	6.262	0.817
				ee%	87	

(p-chlorophenyl)(o-tolyl)methanol (&džYbH&d)

HPLC: Chiralpak AD-H, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 254 nm.



	Time	Area	Height	Area%	Height%	Symmetry
1	11,842	563756	38994	50,022	51,883	1,062
2	12,558	563267	36164	49,978	48,117	1,109

From tri(o-tolyl)boroxin to p-chlorobenzaldehyde



	Time	Area	Height	Area%	Height%	Symmetry
1	12,333	81554	5514	94,382	94,926	1,059
2	13,325	4854	295	5,618	5,074	0,936
			ee	89%		

From tri(p-chlorophenyl)boroxin to o-tolualdehyde



	Time	Area	Height	Area%	Height%	Symmetry
1	12,042	3574	285	2,767	3,532	0,961
2	13,000	125565	7783	97,233	96,468	14863
			ee	94%		

(p-chlorophenyl)(p-tolyl)methanol (&ezYbH&e)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 220 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	14.562	58692.2	1768.5	0.5056	49.831	0.601
2	15.977	59090.4	1543.1	0.5748	50.169	0.578

From tri(p-tolyl)boroxin to p-chlorobenzaldehyde



	Time	Area	Height	Width	Area%	Symmetry
1	14.373	34535.8	1081.3	0.5323	98.389	0.631
2	15.736	565.5	21.0	0.4496	1.611	0.617
			%ee	97		

From tri(*p*-chlorophenyl)boroxin to *p*-tolualdehyde



	Time	Area	Height	Width	Area%	Symmetry
1	14.431	45.9	1.6	0.4884	8.167	0.685
2	15.75	516.6	14.8	0.5818	91.833	0.646
			%ee	84		

(2-naphthyl)(p-tolyl)methanol (&fžYbH&f)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 254 nm.



Racemic



	Time	Area	Height	Width	Area%	Symmetry
1	29.117	5846	82.6	1.1802	49.993	0.607
2	32.987	5847.7	73.3	1.3299	50.007	0.579

From tri(2-naphtyl)boroxin to *p*-tolualdehyde

	Time	Area	Height	Width	Area%	Symmetry
1	27.178	4611.7	75.1	1.0228	99.041	0.621
2	30.679	44.7	8.6E-1	0.8649	0.959	0.696
				ee%	98	

From tri(p-tolyl)boroxin to 2-naphthaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	27.222	96.8	1.8	0.8848	2.383	0.662
2	30.425	3966.7	59.5	1.1115	97.617	0.565
				ee%	95	

(p-methoxyphenyl)(2-naphthyl)methanol (&gzYbH&g)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 254 nm.

Racemic

	Time	Area	Height	Width	Area%	Symmetry
1	21.636	18806.8	358.5	0.8041	49.909	0.596
2	25.838	18875.6	283.2	1.0047	50.091	0.543

From tri(2-naphtyl)boroxin to *p*-methoxybenzaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	20.992	5417.8	112.4	0.8035	96.145	0.636
2	25.184	217.2	4.1	0.8845	3.855	0.706
				ee%	92	

From tri(p-methoxyphenyl)boroxin to 2-naphthaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	21.330	777.9	17.6	0.6211	3.024	0.699
2	25.101	24943.8	420.5	0.9886	96.976	0.510
				ee%	94	

(p-chlorophenyl)(2-naphthyl)methanol (&hžYbH&h)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 254 nm.

Racemic

	Time	Area	Height	Width	Area%	Symmetry
1	19.301	9094.5	202	0.6821	49.991	0.605
2	21.632	9097.8	167.8	0.8276	50.009	0.553

From tri(2-naphtyl)boroxin to p-chlorobenzaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	19.749	5561.8	122.4	0.7576	96.491	0.64
2	22.377	202.2	4.3	0.7749	3.509	0.732
				ee%	93	

From tri(p-chloropheyl)boroxin to 2-naphthaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	18.037	472.9	12.2	0.6486	6.047	0.716
2	20.391	7347.1	150.5	0.8135	93.953	0.589
				ee%	88	

(2-naphthyl)(p-(trifluoromethyl)phenyl)methanol (&)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 220 nm.

Racemic

	Time	Area	Height	Width	Area%	Symmetry
1	20.112	11037.5	250.1	0.6652	50.050	0.705
2	22.884	11015.6	218.2	0.7427	49.950	0.692

From tri(2-naphtyl)boroxin to p-(trifluoromethyl)benzaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	19.755	8604	189.4	0.7572	95.008	0.632
2	22.543	452.1	9.5	0.7962	4.992	0.667
				ee%	90	

(o-tolyl)(p-(trifluoromethyl)phenyl)methanol (&j)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 220 nm.

Racemic

	Time	Area	Height	Width	Area%	Symmetry
1	10.930	46896.9	1759.5	0.4442	49.672	0.595
2	12.455	47515.9	1673.6	0.4732	50.328	0.897

From tri(o-tolyl)boroxin to p-(trifluoromethyl)benzaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	10.905	1163.6	48.0	0.4039	5.644	0.684
2	12.222	19452.9	710.2	0.4565	94.356	0.778
				ee%	89	

(p-tolyl)(p-(trifluoromethyl)phenyl)methanol (&k žYbH&k)

HPLC: Chiralcel OD column, ⁱPrOH/Hex 10/90, 1 ml/min, λ = 220 nm.

Racemic

	Time	Area	Height	Width	Area%	Symmetry
1	9.137	14301.6	669.7	0.3259	50.183	0.65
2	10.824	14197.3	570.1	0.415	49.817	0.669

From *p*-tolylboroxin to *p*-(trifluoromethyl)benzaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	9.087	32980.3	1622	0.3389	94.375	0.618
2	10.731	1965.7	91.5	0.3581	5.625	0.698
				ee%	89	

From tri(*p*-(trifluoromethyl)phenyl)boroxin to *p*-tolualdehyde (and 10% mol of DiMPEG)

	Time	Area	Height	Width	Area%	Symmetry
1	9.274	542.1	26.4	0.3419	2.674	0.670
2	11.009	19728.5	830.8	0.3958	97.326	0.634
				ee%	95	

(p-chlorophenyl)(p-(trifluoromethyl)phenyl)methanol (& 논

HPLC: Chiralcel OD column, ⁱPrOH/Hex 5/95, 1 ml/min, λ = 220 nm.

Racemic

	Time	Area	Height	Width	Area%	Symmetry
1	15.217	16111.8	459.5	0.5371	49.845	0.7
2	16.665	16211.8	417.6	0.597	50.155	0.684

From tri(*p*-chloropheyl)boroxin to *p*-(trifluoromethyl)benzaldehyde

	Time	Area	Height	Width	Area%	Symmetry
1	15.180	51350.8	1449.2	0.5906	98.102	0.650
2	16.718	993.4	30.8	0.538	1.898	0.669
				ee%	96	