Supporting Information

Fine Tuning of Chiral Bis(*N*-Heterocyclic Carbene) Palladium Catalysts for Asymmetric Suzuki-Miyaura Cross-Coupling Reactions: Exploring the Ligand Modification

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Figure S1. The top view (above, H atoms omitted for clarity) and side view (below) of molecular structure of (*S*)-**6**.



Figure S2. Selected 13 C NMR region of the two isomeric complexes (S)-7 and (S)-7'





Figure S4. The 13 C NMR spectrum of (S)-9 in CDCl₃ at 20 $^{\circ}$ C



Figure S5. The 1 H NMR spectrum of H₂[(*S*)-2]Cl₂ in CDCl₃ at 20 ${}^{\circ}$ C



Figure S6. The ^{13}C NMR spectrum of (S)- $H_2[(S)\mbox{-}2]Cl_2$ in CDCl_3 at 20 $^{\circ}C$



Figure S7. The 1 H NMR spectrum of (S)-5 in CDCl₃ at 20 ${}^{\circ}$ C



Figure S8. The 13 C NMR spectrum of (S)-5 in CDCl₃ at 20 $^{\circ}$ C



Figure S10. The 13 C NMR spectrum of (S)- 6 in CDCl₃ at 20 $^{\circ}$ C



Figure S11. The 1 H NMR spectrum of (S)-11b in CDCl₃ at 20 ${}^{\circ}$ C



Figure S12. The ^{13}C NMR spectrum of (S)-11b in CDCl3 at 20 $^{\circ}\text{C}$



Figure S13. The 1 H NMR spectrum of (S)-11c in CDCl₃ at 20 ${}^{\circ}$ C



Figure S14. The 13 C NMR spectrum of (S)-11c in CDCl₃ at 20 $^{\circ}$ C



Figure S15. The ¹H NMR spectrum of (S)-111d in CDCl₃ at 20 $^{\circ}$ C



Figure S16. The 13 C NMR spectrum of (S)-11d in CDCl₃ at 20 $^{\circ}$ C



Figure S17. The 1 H NMR spectrum of (S)-11e in CDCl₃ at 20 $^{\circ}$ C



Figure S18. The ¹³C NMR spectrum of (S)-11e in CDCl₃ at 20 °C



Figure S19. The ^1H NMR spectrum of (S)-11f in CDCl₃ at 20 $^{\circ}\text{C}$



Figure S20. The ^{13}C NMR spectrum of (S)-11f in CDCl3 at 20 $^{\circ}\text{C}$



Figure S21. The ^1H NMR spectrum of (S)-11g in CDCl3 at 20 $^{\circ}\text{C}$



Figure S22. The ^{13}C NMR spectrum of (S)-11g in CDCl3 at 20 $^{\circ}\text{C}$



Figure S23. The 1 H NMR spectrum of (S)-13b in CDCl₃ at 20 ${}^{\circ}$ C



Figure S24. The ^{13}C NMR spectrum of (S)-13b in CDCl3 at 20 $^{\circ}\text{C}$



Figure S25. The ¹H NMR spectrum of (S)-**13c** in $CDCl_3$ at 20 ^oC



Figure S26. The 13 C NMR spectrum of (S)-13c in CDCl₃ at 20 $^{\circ}$ C





Figure S28. The ^{13}C NMR spectrum of (S)-13d in CDCl3 at 20 $^{\circ}\text{C}$



Figure S29. The 1 H NMR spectrum of (S)-13e in CDCl₃ at 20 ${}^{\circ}$ C



Figure S30. The ^{13}C NMR spectrum of (S)-13e in CDCl₃ at 20 $^{\circ}\text{C}$



Figure S31. The 1 H NMR spectrum of (S)-13f in CDCl₃ at 20 ${}^{\circ}$ C



Figure S32. The 13 C NMR spectrum of (S)-13f in CDCl₃ at 20 $^{\circ}$ C



Figure S33. The 1 H NMR spectrum of (S)-13g in CDCl₃ at 20 ${}^{\circ}$ C



Figure S34. The ^{13}C NMR spectrum of (S)-13g in CDCl3 at 20 $^{\circ}\text{C}$



Figure S36. The ¹³C NMR spectrum of (S)-7b in CDCl₃ at 20 °C



Figure S37. The ¹H NMR spectrum of (S)-7c in CDCl₃ at 20 °C



Figure S38. The ¹³C NMR spectrum of (S)-7c in CDCl₃ at 20 °C





Figure S40. The 13 C NMR spectrum of (S)-7d in CDCl₃ at 20 $^{\circ}$ C



Figure S41. The ¹H NMR spectrum of (S)-7e in CDCl₃ at 20 °C



Figure S42. The ¹³C NMR spectrum of (S)-7e in CDCl₃ at 20 °C



Figure S43. The 1 H NMR spectrum of (S)-7f in CDCl₃ at 20 ${}^{\circ}$ C



Figure S44. The 13 C NMR spectrum of (S)-7f in CDCl₃ at 20 $^{\circ}$ C



Figure S46. The ^{13}C NMR spectrum of (S)-7g in CDCl₃ at 20 $^{\circ}\text{C}$



Figure S47. The GC curve and analysis data (Table 3, entry 2)

#	RT	Scan	Height	Area	Area%
0	DMASS\WAQ.PF	zhangda o-1	1	0	
	6.58	911	2109162112	50152228	21.806
	9.281	1452	777067840	17297180	7.521
	11.762	1945	3228367872	71030688	30.884
	15.604	2713	2320576768	46530800	20.231
	16.359	2864	2126499968	44983892	19.559



Figure S48. The GC curve and analysis data (Table 4, entry 1)



Figure S49. The GC curve and analysis data (Table 4, entry 2)



Figure S50. The GC curve and analysis data (Table 4, entry 3)

#	RT	Scan	Height	Area	Area%
0	DMASS\WAQ.PF	zhangdao-3	1	0	
	8.936	1380	945697216	18181866	12.904
1	9.276	1440	136681872	5149945.5	3.655
	11.752	1944	3788995584	84903328	60.257
	13.548	2300	1157565568	21671152	15.380
1	16.799	2944	29476336	1110558.25	0.788
	18.295	3248	299124064	9885809	7.016



Figure S51. The GC curve and analysis data (Table 4, entry 4)

#	RT	Scan	Height	Area	Area%
0	DMASS\WAQ.PF	zhangdao-4	1	0	
	8.596	1314	2426171904	52794764	29.766
	11.757	1944	5162245632	119427472	67.335
1	15.744	2743	130847096	2611861.75	1.473
1	16.189	2823	121528320	2529134.75	1.426



Figure S52. The GC curve and analysis data (Table 4, entry 5)

#	RT	Scan	Height	Area	Area%
0	DMASS\WAQ.PF	zhangda o-2	1	0	
	6.54	903	2888442624	71060904	10.724
	7.791	1152	2326769920	47085764	7.106
	10.562	1702	8409667072	213464192	32.215
	15.604	2712	5181645824	111185696	16.780
	15.669	2725	9087902720	219827184	33.175



Figure S53. The chiral HPLC and analysis data (Table 3, entry 2)

DAD1 A, Sig=254,8 Ref=360,100 Signal:

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
4.913	0.193	173.110	14.354	51.3847	2.769
5.596	0.222	163.781	11.824	48.6153	

Signal: DAD1 B, Sig=214,8 Ref=360,100

RT [min]	Width [min]	Area <mark>[</mark> mAU*S]	Height [mAU]	Area%	ee value%
4.913	0.194	2810.979	230.703	51.4571	2.914
5.597	0.225	2651.787	190.058	48.5429	



Signal: DAD1 A, Sig=254,16 Ref=450,100

RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
4.691	0.181	130.753	9.974	13.0184	73.963
5.353	0.214	873.616	56.185	86.9816	

Signal:	: DAD1 B, Sig=214,16 Ref=450,100						
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%		
4.690	0.184	1504.839	113.009	12.9978	74.004		
5.353	0.218	10072.787	640.188	87.0022			



Figure S54. The chiral HPLC and analysis data (Table 4, entry 1)



Signal:	DAD1 A, Sig=254,16 Ref=450,100	
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RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
9.317	0.495	204.505	5.804	23.3288	53.3
10.917	0.540	672.116	17.598	76.6712	

Signal:	: DAD1 B, Sig=214,16 Ref=450,100						
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%		
9.316	0.545	2285.833	61.004	23.7185	52.5		
10.918	0.570	7351.488	185.749	76.2815			





Signal:	DAD1 A, Sig=254,16 Ref=450,100						
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%		
5.621	0.232	502.132	30.815	48.8382	RAC		
7.025	0.315	526.022	23.888	51.1618			

Signal:	DAD1 B, S	Sig=214,16	Ref=450,100
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RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee ∨alue%
5.621	0.230	4150.419	257.551	48.4037	
7.024	0.309	4424.166	199.789	51.5963	



Signal: DAD1 A, S	Sig=254,16 Ref=450,100
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RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
5.638	0.218	25.938	1.662	15.4636	69.0
7.045	0.298	141.799	6.732	84.5364	

Signal: DAD1 B, Sig=214,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee ∨alue%
5.637	0.228	221.785	13.911	15.7298	68.5
7.045	0.300	1188.183	56.240	84.2702	

Figure S56. The chiral HPLC and analysis data (Table 4, entry 2)





Signal: DAD1 A, Sig=254,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
5.200	0.109	3895.893	541.866	49.8803	0.239
6.791	0.158	3914.589	379.228	50.1197	

Signal:	L: DAD1 B, Sig=214,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%	
5.200	0.109	4259.155	595.644	49.6028	0.794	
6.791	0.158	4327.360	417.362	50.3972		



Signal:	DAD1 A, Sig=254,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%	
5.165	0.106	3582.957	512.300	80.5553	61.111	
6.707	0.157	864.866	84.164	19.4447		

Signal: DAD1 B, Sig=214,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%
5.165	0.107	4008.495	564.878	80.0350	60.070
6.707	0.164	999.930	92.529	19.9650	



Figure S57. The chiral HPLC and analysis data (Table 4, entry 6)

Signal:	ignal: DAD1 A, Sig=254,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%	
10.940	0.212	1761.310	128.721	39.81 <mark>5</mark> 5	20.369	
11.774	0.234	2662.365	176.780	60. <mark>1</mark> 845		

Signal:	DAD1 B, Sig=214,16 Ref=450,100					
RT [min]	Width [min]	Area [mAU*S]	Height [mAU]	Area%	ee value%	
10.940	0.207	2963.889	223.144	39.4031	21.194	
11.774	0.231	4558.078	306.127	60.5969		