# Supporting Information for: Quinine catalysed asymmetric Michael additions in a sustainable solvent

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#### Contents

#### Chiral HPLC traces for compounds 8a-c and 11a-l

5-(3-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11d

5-(2-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11e

4,4–Dicyano–5-(4-methoxyphenyl)-1,3–diphenylpentan–1–one 11g

4,4–Dicyano–5-(pentafluorophenyl)-1,3–diphenylpentan–1–one 11i

4,4–Dicvano–1,3–diphenyl-5-(4-trifluoromethylphenyl) pentan–1–one 11h

4,4–Dicyano–5-(4-nitrophenyl)-1,3–diphenylpentan–1–one 11f

4,4–Dicvano–1,3–diphenylpentan–1–one 11j

4,4–Dicyano–1,3–diphenylhept-6-en–1–one **11k** 

4,4–Dicyano–1,3–diphenylhept-6-yn–1–one 111

1	
The chromatogram of the racemate is given first followed by that of a non-racemic	sample.
2-Cyano-3,5-diphenyl-5-oxo-pentanonitrile 8a	2
3-(4-Chlorophenyl)-2-cyano-5-phenyl-5-oxo-pentanonitrile <b>8b</b>	4
3–(4–Methoxyphenyl)–2-cyano-5-phenyl-5-oxo-pentanonitrile 8c	6
4,4–Dicyano–1,3,5–triphenylpentan–1–one <b>11a</b>	8
5-(4-Bromophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one <b>11b</b>	10
5-(4-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one <b>11c</b>	12
5-(3-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11d	14
5-(2-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11e	16
4,4–Dicyano–5-(4-nitrophenyl)-1,3–diphenylpentan–1–one <b>11f</b>	18
4,4–Dicyano–5-(4-methoxyphenyl)-1,3–diphenylpentan–1–one <b>11g</b>	20
4,4–Dicyano–1,3–diphenyl-5-(4-trifluoromethylphenyl) pentan–1–one <b>11h</b>	22
4,4–Dicyano–5-(pentafluorophenyl)-1,3–diphenylpentan–1–one 11i	24
4,4–Dicyano–1,3–diphenylpentan–1–one <b>11j</b>	26
4,4–Dicyano–1,3–diphenylhept-6-en–1–one 11k	28
4,4–Dicyano–1,3–diphenylhept-6-yn–1–one 111	30
NMR spectra for compounds 8a–c and 11a–l	
2-Cyano-3,5-diphenyl-5-oxo-pentanonitrile 8a	32
3-(4-Chlorophenyl)-2-cyano-5-phenyl-5-oxo-pentanonitrile <b>8b</b>	34
3–(4–Methoxyphenyl)–2-cyano-5-phenyl-5-oxo-pentanonitrile 8c	36
4,4–Dicyano–1,3,5–triphenylpentan–1–one <b>11a</b>	38
5-(4-Bromophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one <b>11b</b>	40
5-(4-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one <b>11c</b>	42

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#### 2-Cyano-3,5-diphenyl-5-oxo-pentanonitrile 8a

#### **Racemic sample**





#### Sample prepared using the conditions of Table 1, entry 15 with 64% ee

#### 3-(4-Chlorophenyl)-2-cyano-5-phenyl-5-oxo-pentanonitrile 8b

#### **Racemic sample**





#### Sample prepared using the conditions of Table 2, entry 4 with 64% ee

#### 3-(4-Methoxyphenyl)-2-cyano-5-phenyl-5-oxo-pentanonitrile 8c

#### **Racemic sample**



Totals : 7.01838e4 4098.76453



#### Sample prepared using the conditions of Table 2, entry 8 with 65% ee

## 4,4-Dicyano-1,3,5-triphenylpentan-1-one 11a

### **Racemic sample**



Area Percent Report

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Sor	rted	Ву		:	Sigr	nal		
Mu]	ltip	lier		:	1.00	990		
Dil	lutio	on		:	1.00	990		
Do	not	use	Multiplier	&	Dilution	Factor	with	ISTDs

#### Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	9,926	BB	0.2486	5759.11621	356.19238	49.8929
2	19.481	BB	0.4613	5783.83643	194.31696	50.1071

Totals : 1.15430e4 550.50934



#### Sample prepared using the conditions of Table 3, entry 1 with 46% ee

## 5-(4-Bromophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11b

## **Racemic sample**



Area Percent Report

Sorted By	:	Sigi	nal	
Multiplier	:	1.00	000	
Dilution	:	1.00	000	
Use Multiplier	& Dilution	Fact or	with	I STDs

Signal 1: DAD1 A, Sig=250, 4 Ref=off

Peak #	Ret Time [min]	Туре	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13. 738	BB	0. 3405	645. 77692	28.91961	50.8791
2	28. 829	BB	0. 5831	623. 46155	12.82627	49.1209
Tot al	s :			1269. 23846	41.74587	



## Sample prepared using the conditions of Table 3, entry 2 with 94% ee

Area Percent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Hei ght	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	13.934	BB	0. 3285	166. 83731	6.93844	3.2634
2	29. 356	BB	0. 7842	4945. 56348	95.81300	96.7366

Tot al s : 5112. 40079 102. 75144

## 5-(4-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11c

## Racemic sample



Area Percent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
			.			
1	12. 539	BB	0. 2990	570. 37366	29.05391	50.7893
2	26. 749	BV	0. 5328	552. 64575	12.28516	49.2107

Tot al s :

1123.01941 41.33907



## Sample prepared using the conditions of Table 3, entry 3 with 89% ee

Area Percent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Height	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	12.788	BB	0. 4292	540. 39789	19.87690	5.4473
2	27.679	BB	0. 7850	9380. 08203	184. 54669	94.5527

Tot al s : 9920. 47992 204. 42359

## 5-(3-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11d

## **Racemic sample**



Area Percent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

#### Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Time	Туре	₩ dt h	Ar ea	Hei ght	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	11.255	BB	0. 2708	1582. 99780	91.04628	49.3087
2	19. 691	BB	0. 5279	1627. 38538	45.64938	50.6913
Tot al	s :			3210. 38318	136. 69566	



## Sample prepared using the conditions of Table 3, entry 13 with 50% ee

Ar ea Per cent Report

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Sorted By:SignalMultiplier:1.0000Dilution:1.0000Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Hei ght	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	11.119	BB	0.2467	1278. 54614	79.88173	24.8731
2	18.863	BB	0. 4283	3861. 72778	138.92717	75. 1269

Tot al s : 5140. 27393 218. 80890

## 5-(2-Chlorophenyl)-4,4-dicyano-1,3-diphenylpentan-1-one 11e

## **Racemic sample**



Ar ea Per cent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

#### Signal 1: DAD1 A, Sig=250, 4 Ref=off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Height	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	9. 520	BB	0.2170	1098. 13867	78.59915	50.1050
2	17.046	BB	0. 4231	1093. 53528	39.73511	49.8950
Tot al	s :			2191. 67395	118.33426	



## Sample prepared using the conditions of Table 3, entry 5 with 50% ee

Area Percent Report

Area Percent Report

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Sorted By	:	Sigr	nal	
Multiplier	ltiplier : 1.0000			
Dilution	:	1.00	000	
Use Multiplier &	Dilution	Factor	with	ISTDs

#### Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
				-		
1	9.512	BB	0.2100	241.11748	17.80276	24.9515
2	17.124	BB	0.4518	725.22601	24.32615	75.0485

Totals : 966.34349 42.12890

## 4,4–Dicyano–5-(4-nitrophenyl)-1,3–diphenylpentan–1–one 11f

## Racemic sample



Area Percent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

#### Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak #	Ret Time [min]	Туре	Width [min]	Area [mAll≭s]	Height [mAl]	Area %
1	27.002	BB	0. 6258	669. 88806	12.85789	49.6650
2	51. 529	MM	1. 3843	678. 92572	8.17438	50.3350
Tot al	s :			1348. 81378	21.03228	



## Sample prepared using the conditions of Table 3, entry 6 with 91% ee

Area Percent Report

Sorted By:SignalMultiplier:1.0000Dilution:1.0000Use Multiplier & Dilution Factor with ISTDs

#### Signal 1: DAD1 A, Sig=250, 4 Ref =off

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Peak	Ret Ti me	Туре	W/dth	Ar ea	Hei ght	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	27. 542	BB	0.6402	353. 27130	6.51935	4.6578
2	52. 767	BB	1. 1973	7231. 16943	78.45258	95.3422

Tot al s : 7584. 44073 84. 97194

## 4,4-Dicyano-5-(4-methoxyphenyl)-1,3-diphenylpentan-1-one 11g

## **Racemic sample**



Area Percent Report

Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

#### Signal 1: DAD1 A, Sig=250, 4 Ref=off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Hei ght	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	11.552	PM	0. 2992	765. 62335	42.64820	50.3343
2	24. 126	BB	0. 5348	755. 45447	17.74101	49.6657
Tot al	S :			1521, 07782	60.38920	



### Sample prepared using the conditions of Table 3, entry 7 with 77% ee

Area Percent Report

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Sorted By	:	Si gr	nal	
Multiplier	:	1.00	000	
Dilution	:	1.00	000	
Use Multiplier	& Dilution	Fact or	with	I STDs

Signal 1: DAD1 A, Sig=250, 4 Ref=off

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Peak	Ret Ti me	Туре	W/dth	Ar ea	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	12.451	BB	0.3130	309. 65198	15.37255	11.7629
2	28. 378	BB	0. 7825	2322. 79224	43.67145	88.2371
Tot al	S :			2632. 44421	59.04400	

## 4,4–Dicyano–1,3–diphenyl-5-(4-trifluoromethylphenyl) pentan–1–one 11h

## **Racemic sample**



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Area Percent Report

Sor	rted	Ву		:	Sigr	nal		
Mu]	ltip	lier		:	1.00	900		
Dil	lutio	on		:	1.00	900		
Do	not	use	Multiplier	&	Dilution	Factor	with	ISTDs

Signal 1: DAD1 A, Sig=250,4 Ref=off

Peak	RetTime	Туре	Width	Area	Height	Area
#	[min]		[min]	[mAU*s]	[mAU]	%
1	13.907	BB	0.3690	9881.61328	416.19177	49.9816
2	29.587	BB	0.7462	9888.89355	201.64113	50.0184



#### Sample prepared using the conditions of Table 3, entry 8 with 80% ee

## 4,4-Dicyano-5-(pentafluorophenyl)-1,3-diphenylpentan-1-one 11i

## Racemic sample



Sorted By	:	Si gnal	
Multiplier	:	1.0000	
Dilution	:	1.0000	
Use Multiplier	& Dilution	Factor with	I STDs

#### Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Hei ght	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	13. 718	BB	0.3128	716. 70416	35.61340	49.5514
2	17. 628	MM	0. 4822	729. 68170	25. 21881	50.4486
Tot al	s :			1446. 38586	60.83221	



## Sample prepared using the conditions of Table 3, entry 17 with 21% ee

Area Percent Report

Sorted By:SignalMultiplier:1.0000Dilution:1.0000Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=250, 4 Ref =off

Peak	Ret Ti me	Туре	W/dth	Ar ea	Height	Area
#	[min]		[ mi n]	[mAU*s]	[mAU]	%
1	14. 544	BB	0. 3389	6084. 52881	280.69244	39.7215
2	18.006	BB	0. 4229	9233. 45313	337. 74756	60.2785

Tot al s : 1.53180e4 618.44000

### 4,4-Dicyano-1,3-diphenylpentan-1-one 11j

### **Racemic sample**





### Sample prepared using the conditions of Table 3, entry 19 with 48% ee

#### 4,4-Dicyano-1,3-diphenylhept-6-en-1-one 11k

#### **Racemic sample**





### Sample prepared using the conditions of Table 3, entry 21 with 50% ee

#### 4,4-Dicyano-1,3-diphenylhept-6-en-1-one 111

#### **Racemic sample**





### Sample prepared using the conditions of Table 3, entry 22 with 38% ee





## <sup>13</sup>C NMR spectrum of 2-Cyano-3,5-diphenyl-5-oxo-pentanonitrile 8a



<sup>1</sup>H NMR spectrum of 3–(4–Chlorophenyl)–2-cyano-5-phenyl-5-oxo-pentanonitrile 8b



<sup>13</sup>C NMR spectrum of 3–(4–Chlorophenyl)–2-cyano-5-phenyl-5-oxo-pentanonitrile 8b



#### <sup>1</sup>H NMR spectrum of 3–(4–Methoxyphenyl)–2-cyano-5-phenyl-5-oxo-pentanonitrile 8c



<sup>13</sup>C NMR spectrum of 3–(4–Methoxyphenyl)–2-cyano-5-phenyl-5-oxo-pentanonitrile 8c













































## <sup>13</sup>C NMR spectrum of 4,4–Dicyano–1,3–diphenylpentan–1–one 11j



<sup>1</sup>H NMR spectrum of 4,4–Dicyano–1,3–diphenylhept-6-en–1–one 11k



<sup>13</sup>C NMR spectrum of 4,4–Dicyano–1,3–diphenylhept-6-en–1–one 11k





## <sup>13</sup>C NMR spectrum of 4,4–Dicyano–1,3–diphenylhept-6-yn–1–one 111