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## **Supporting information**

## Organocatalytic Asymmetric Michael Addition of 1-Acetylcyclohexene and 1- Acetylcyclopentene to Nitroolefins

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2. Determination of relative structure of <b>4b</b>	<b>S</b> 18
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4. Determination of relative structure of <b>6</b>	S27
5. HPLC data of the products	S28-S48







200 180 160 140 120 100 80 - 60 40 20 ppm















230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 fi (ppm)





























60 50 40

70

230 220 210 200 190 180 170 160 150 140 130 120 110 100

13

-10

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30 20 10















## Determination of the relative structure of 4a and 4b:



The structure major diastereomer **4a** is confirmed by X-ray crystallographic data. The <sup>1</sup>H NMR spectra of inseparable diastereomeric mixture showed that the peaks corresponding to C<u>H</u>NO<sub>2</sub> of major and minor diastereomer have same larger coupling constant and different smaller coupling constant indicating phenyl and nitro groups of the two diastereoisomers are in similar orientation (structure **4e**, **4f**, **4g** and **4h** can be ruled out) and **H-9** and **H-1** of the two diastereoisomers are in opposite orientation (for major diastereomer **H-9** and **H-1** are *trans* so for minor diastereomer **H-9** and **H-1** should be *cis*) leaving only structure **4b** and **4d** in count. G. Pitacco et al.<sup>7</sup> have reported syntheses of isomers **4b**, **4d**, **4f** and **4h** by reacting preformed enamine of 1-acetylcyclohexene and *trans*- $\beta$ -nitrostyrene followed by hydrolysis and interconversion between isomers using different reagents. Structure **4d** can be ruled out by comparing the characterization data and our NMR data leaving **4b** to be the minor diastereomer and it was confirmed by characterization data for **4b** (in C<sub>6</sub>D<sub>6</sub>) provided by G. Pitacco et al.<sup>7</sup>

1. G. Pitaco, A. Risaliti, M. L. Trevisan, E. Valentin, Tetrahedron, 1977, 33, 3145.

## **CRYSTAL DATA OF COMPOUND 4a**



Compound No.	4a
Formulae	$C_{16}H_{19}O_3N_1$
Mol. wt.	273.32
Space group	P2 <sub>1</sub> /c
a /Å	13.9327(12)
b /Å	5.8545(5)
c /Å	18.9127(15)
α/°	90.00
β/°	109.456(5)
γ/°	90.00

V/ Å <sup>3</sup>	1454.6(2)
Density/g.cm <sup>-3</sup>	1.248
Abs. Coeff. /mm <sup>-1</sup>	0.086
F(000)	584
Total no. of reflections	2549
Reflections, $I > 2\sigma(I)$	1946
Max. θ/°	24.99
Ranges (h, k, l)	$-16 \le h \le 16$
	$-6 \le k \le 0$ $-22 \le 1 \le 22$
Complete to $2\theta$ (%)	100.00
Data/	2549/ 0/ 181
Restraints/Parameters	
Goof $(F^2)$	1.235
R indices $[I > 2\sigma(I)]$	0.0901
$wR_2 \left[ I > 2\sigma \left( I \right) \right]$	0.1455
R indices (all data)	0.1735
wR <sub>2</sub> (all data)	0 1667













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From NOESY NMR spectra of compound **6** it is evident that neither the pair of hydrogen Hf and Hc showing any NOE, nor the pair  $H_c$  and  $H_h$ .  $H_h$  and  $H_f$  is showing weak NOE. We can conclude that phenyl and hydroxyl group are opposite to each other and  $H_c$  and  $H_h$  are also in opposite orientation. So the structure of major diastereomer is **6**.



No.	Ret.Time	Peak Name	Height	Area	Rel.Area	Amount	Туре
	min		mAU	mAU*min	%		
1	13.28	n.a.	33.724	19.193	49.37	n.a.	BMb
2	15.63	n.a.	34.084	19.683	50.63	n.a.	bMB
Total:			67.808	38.876	100.00	0.000	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ic	Height	Amount
		min	mAU*min	%	mAU	
	а	13.29166667	14.49537	87.68883	22.92594	
	b	15.67166667	2.035093	12.31117	4.05918	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(io	Height	Amount
		min	mAU*min	%	mAU	
	а	16.63833333	35.52918	50.52981	77.60755	
	b	20.24333333	34.78407	49.47012	63.12092	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(id	Height	Amount
		min	mAU*min	%	mAU	
	a	16.68666667	29.4997	76.86299	63.94995	
	b	20.34	8.879889	23.13701	19.19585	







No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ic	Height	Amount
		min	mAU*min	%	mAU	
	A	10.14	12.03725	77.14042	29.28104	
	В	11.75	3.567085	22.85958	10.24287	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(id	Height	Amount
		min	mAU*min	%	mAU	
	Α	11.075	14.71204	50.86724	61.51782	
	В	12.00333333	14.21038	49.13276	52.23421	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(id	Height	Amount
		min	mAU*min	%	mAU	
	A	11.01166667	253.3018	79.07758	719.0155	n.a.
	В	11.94833333	67.01882	20.92242	222.1025	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(id	Height	Amount
		min	mAU*min	%	mAU	
	а	21.12333333	134.9431	50.06105	89.57273	
	b	32.045	134.6139	49.93891	64.5809	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mau~min	%	MAU	
	44 a	20.97	11.84492	80.10067676	6.02558	n.a.
	92 b	31.75	2.943	19.89932324	1.870	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	а	24.515	808.2006	50.55	89.86148	
	b	44.64333333	790.5441	49.45	137.0227	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
1	а	21.91	70.88501	79.38084379	11.20089	n.a.
2	b	42.67	18.412	20.61915621	3.187	n.a.







No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ic	Height	Amount
		min	mAU*min	%	mAU	
	а	20.03833333	8.552458	81.3533	5.89463	
	b	31.68333333	1.960265	18.64657	1.02288	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	а	34.54333333	12.31673	51.01	12.90599	
	b	37.255	11.83045	48.99	11.52697	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ic	Height	Amount
		min	mAU*min	%	mAU	
	а	34.465	1.196359	92.9199	0.93567	
	b	37.975	0.091135	7.07838	0.08057	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
1	8 a	20.64	48.56639	51.33115313	31.53503	n.a.
2	0 b	26.52	46.047	48.66864816	15.729	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	14 a	20.63	1.992465	86.49691513	1.71597	n.a.
	19 b	26.23	0.311	13.50262615	0.462	n.a.







No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(id	Height	Amount
		min	mAU*min	%	mAU	
	а	7.181666667	1.094235	85.73204	2.67337	
	b	13.005	0.182065	14.26455	0.31003	





Peak Results								
	Name	RT	Area	Height	% Area			
1		15.435	4535657	164027	76.88			
2		19.925	1364039	41618	23.12			



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	а	12.27333333	0.553053	50.84	1.15614	
	b	14.427	0.53485	49.16	0.88993	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	а	12.32833333	1.290351	88.35	2.24291	
	b	14.49333333	0.170121	11.65	0.30912	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ic	Height	Amount
		min	mAU*min	%	mAU	
	а	17.24333333	342.4752	50.61273	429.6465	
	b	26.29333333	334.183	49.38727	206.3195	



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	3 a	17.26	144.1871	84.85743746	141.1033	n.a.
	9 b	26.35	25.730	15.14256254	17.788	n.a.

ua-cp-2-me-chiral



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
99	A	18.77	11.06917	50.48663813	12.37154	n.a.
100	В	27.71	10.856	49.51332523	8.256	n.a.



No.		Peak Name	Ret.Time (detected	()	Area	Rel	l.Area(ident.)	Height	Amount
			min		mAU*min	%		mAU	
	223	A.	19.	.71	0.762717		85.02907519	0.34392	n.a.
	261	В	27.	.50	0.137		14.97092481	0.143	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
39	a	9.88	372.2558	50.55535782	562.3682	n.a.
40	b	11.27	364.077	49.44463501	517.872	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
Ę	59 a	10.13	3.493381	21.12609615	2.94854	n.a.
6	51 b	12.40	13.042	78.87255249	12.295	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
54	l c	30.345	31.38767	48.67968264	28.98986	n.a.
80	) d	43.78	33.090	51.32	21.268	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	54 c	31.40666667	63.14059	96.74638753	24.38137	n.a.
	55 d	45.27	2.123	3.25	1.677	n.a.

ua-cp-d-rac



ua-cp-d-chiral



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	4 a	13.75	37.55983	21.79277328	28.27168	n.a.
	5 b	18.10	134.862	78.20722672	69.739	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	51 a	31.46	115.8814	50.08853161	67.24239	n.a.
	52 b	36.18	115.472	49.91146072	72.734	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	50 a	30.72	110.5389	76.66288312	60.74909	n.a.
	51 b	35.27	33.649	23.33706486	26.109	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
1	а	22.33	1386.027	47.61786269	1062.432	n.a.
2	b	30.98	1524.702	52.38213731	852.076	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	23 a	22.71	489.2636	22.18699242	416.716	n.a.
	25 b	30.96	1715.919	77.81300444	906.572	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
11	a	24.52	364,1878	49.17570769	264.4276	n.a.
12	b	34.34	376.397	50.82429231	253.501	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	111 a	24.80	185.4415	15.03403138	97.92028	n.a.
	123 b	33.35	1048.036	84.9659673	436.372	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	102 a	18.57	313.1467	50.68435508	92.37086	n.a.
	103 b	27.61	304.690	49.31564357	70.515	n.a.



No.	Peak Name	Ret.Time (detected)	Area	Rel.Area(ident.)	Height	Amount
		min	mAU*min	%	mAU	
	36 a	18.25	100.0082	84.48040325	32.47279	n.a.
	40 b	27.59	18.372	15.51957412	4.478	n.a.