Supporting Information

Inclusion of Picolines by a Substituted Binaphthyl Diol Host: Selectivity and Structure

Luigi R Nassimbeni,*^a Samipillai Marivel^a, Hong Su^a, and Edwin Weber^b

^aDepartment of Chemistry, University of Cape Town, Private Bag, Rondebosch 7701, South Africa Email: Luigi.Nassimbeni@uct.ac.za

^bInstitut für Organische Chemie, Technische Universität, Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/ Sachsen, Germany. E-mail: Edwin.Weber@chemie.tu-freiberg.de

List of Contents

- Table 1S.X-Ray data and refinement parameters for the compounds V-IX
- Table 2S.¹H-NMR values for H.2PIC/3PIC, H.2PIC/4PIC, H.3PIC/4PIC

Table 3S.¹H-NMR values of three-guest competition experiment, H.2PIC/3PIC/4PIC

Sl. No	Content	Page	Sl. No.	Content	Page
		No.			No.
1	¹ H-NMR of Host - H	6	2d	¹ H-NMR of H.2PIC/4PIC (0.7 : 0.3)	22
2	¹ H-NMR of H.2PIC - I	7	2e	¹ H-NMR of H.2PIC/4PIC (0.8 : 0.2)	23
3	¹ H-NMR of H.3PIC - II	8	2f	¹ H-NMR of H.2PIC/4PIC (0.85 : 0.15)	24
4	¹ H-NMR of H.4PIC - III	9	2g	¹ H-NMR of H.2PIC/4PIC (0.9 : 0.1)	25
	H.2PIC/3PIC			H.3PIC/4PIC	
1a	¹ H-NMR of H.2PIC/3PIC (0.1 : 0.9)	10	3a	¹ H-NMR of H.3PIC/4PIC (0.9 : 0.1)	26
1b	¹ H-NMR of H.2PIC/3PIC (0.2 : 0.8)	11	3b	¹ H-NMR of H.3PIC/4PIC (0.8 : 0.2)	27
1c	¹ H-NMR of H.2PIC/3PIC (0.3 : 0.7)	12	3c	¹ H-NMR of H.3PIC/4PIC (0.7 : 0.3)	28
1d	¹ H-NMR of H.2PIC/3PIC (0.4 : 0.6)	13	3d	¹ H-NMR of H.3PIC/4PIC (0.6 : 0.4) - VI and VII	29
1e	¹ H-NMR of H.2PIC/3PIC (0.5 : 0.5)	14	3e	¹ H-NMR of H.3PIC/4PIC (0.5 : 0.5)	30
1f	¹ H-NMR of H.2PIC/3PIC (0.6 : 0.4) - V	15	3f	¹ H-NMR of H.3PIC/4PIC (0.4 : 0.6)	31
1g	¹ H-NMR of H.2PIC/3PIC (0.7 : 0.3) - IV	16		H.2PIC/3PIC/4PIC	
1h	¹ H-NMR of H.2PIC/3PIC (0.8 : 0.2)	17	4a	¹ H-NMR of H.2PIC/3PIC/4PIC (0.6 : 0.2 : 0.2)	32
1i	¹ H-NMR of H.2PIC/3PIC (0.9 : 0.1)	18	4b	¹ H-NMR of H.2PIC/3PIC/4PIC (0.4 : 0.4 : 0.2) - IX	33
	H.2PIC/4PIC		4c	¹ H-NMR of H.2PIC/3PIC/4PIC (0.4 : 0.2 : 0.4)	34
2a	¹ H-NMR of H.2PIC/4PIC (0.4 : 0.6)	19	4d	¹ H-NMR of H.2PIC/3PIC/4PIC (0.2 : 0.6 : 0.2) - VIII	35
2b	¹ H-NMR of H.2PIC/4PIC (0.5 : 0.5)	20	4e	¹ H-NMR of H.2PIC/3PIC/4PIC (0.2 : 0.4 : 0.4)	36
2c	¹ H-NMR of H.2PIC/4PIC (0.6 : 0.4)	21	4f	¹ H-NMR of H.2PIC/3PIC/4PIC (0.2 : 0.2 : 0.6)	37
			4g	¹ H-NMR of H.2PIC/3PIC/4PIC (0.33 : 0.33 : 0.33)	38

¹H-NMR Spectra

Compound	H.2PIC:3PIC(0.21:0.79)	H.3PIC	H.4PIC	H.3PIC	H.4PIC
Structure	V	VI	VII	VIII	IX
Comment	Similar to IV	Same as II	Same as III	Same as II	Same as III
Empirical formula	$C_{52}H_{37}NO_2$	$C_{58}H_{44}N_2O_2$	$C_{52}H_{37}NO_2$	$C_{58}H_{44}N_2O_2$	C ₅₂ H ₃₇ NO ₂
Formula weight	707.83	800.95	707.83	800.95	707.83
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_{1}/c$	$P2_1/n$	$P2_{1}/c$	$P2_1/n$
<i>a</i> [Å]	9.873(2)	16.709(4)	9.9384(6)	16.6896(3)	9.9367(6)
<i>b</i> [Å]	20.894(6)	11.588(2)	20.7758(12)	11.5679(2)	20.7808(13)
<i>c</i> [Å]	18.825(6)	22.298(9)	18.8529(11)	22.3133(5)	18.8561(12)
α [°]	90	90	90	90	90
β[°]	99.15(3)	95.08(1)	100.60(1)	95.14(3)	100.66(1)
γ [°]	90	90	90	90	90
V[Å ³]	3833.85(18)	4300.7(2)	3826.2(4)	4290.56(18)	3826.4(4)
Ζ	4	4	4	4	4
Temperature(K)	173	173	173	173	173
$D_{calc}(g/cm^{-3})$	1.226	1.237	1.229	1.240	1.229
μ (Mo-K α)(mm ⁻¹)	0.074	0.074	0.074	0.074	0.074
<i>F</i> (000)	1488	1688	1488	1688	1488.0
Crystal size/mm	0.09x0.18x0.29	0.09x0.16x0.24	0.09x0.12x0.24	0.08x0.16x0.21	0.1x0.12x0.28
Reflections collected	8782	18447	44983	8756	27993
Independent reflections	8782	9465	9631	8756	8755
Observed reflections $[I \ge 2s(I)]$	6668	7131	6536	5673	5861
Parameters	498	569	505	569	505
Goodness-of-fit F^2	1.032	1.035	1.018	1.016	1.019
$R_1[I \ge 2s(I)]^a$	0.0467	0.0475	0.0476	0.0496	0.0458
$wR_2(all data)^b$	0.1213	0.1370	0.1224	0.1380	0.1212

Table 1S. X-Ray data and refinement parameters for V-IX

H.2PIC/3PIC	X _{3PIC} Z _{3PIC}	0.10 0.15	-	0.20 0.47	0.30 0.58	0.40 0.67	-	0.50 0.76	0.60 0.85	0.70 0.87	0.80 0.93	0.90 0.99	1.0 1.0
H.2PIC/4PIC	X _{4PIC} Z _{4PIC}	0.10 0.02	0.15 0.74	0.20 0.91	0.30 0.92	0.40 0.97	-	0.50 0.98	0.60 0.98	0.70	0.80	0.90	1.0 1.0
H.3PIC/4PIC	X _{4PIC} Z _{4PIC}	0.10 0.04	-	0.20 0.09	0.30 0.18	0.40 0.27	0.45 0.90	0.50 0.93	0.60	0.70	0.80	0.90	1.0 1.0

Table 2S. ¹H-NMR values for H.2PIC/3PIC, H.2PIC/4PIC, H.3PIC/4PIC

Name of the experiment	*Mole fraction	2PIC	3PIC	4PIC	Structure	Comment	
	Z_{Sol}	0.60	0.20	0.20		Same as III	
Α	X_{NMR}	0.12	0.09	0.78	IX	(H.4PIC)	
-	Z_{Sol}	0.40	0.40	0.20			
В	X_{NMR}	0.03	0.20	0.77			
~	Z_{Sol}	0.40	0.20	0.40			
С	X_{NMR}	0.03	0.08	0.89			
_	Z_{Sol}	0.20	0.60	0.20		Same as II	
D	X_{NMR}	0.01	0.82	0.17	VIII	(H.3PIC)	
_	Z_{Sol}	0.20	0.40	0.40			
E	X_{NMR}	0.01	0.11	0.88			
_	Z_{Sol}	0.20	0.20	0.60			
F	X_{NMR}	0.01	0.07	0.92			
~	Z_{Sol}	0.33	0.33	0.33			
G	X_{NMR}	0.02	0.11	0.86			

Table 3S. ¹H-NMR values of three-guest competition experiment, **H.2PIC/3PIC/4PIC**

 $*Z_{Sol}$ = Mole fraction in solution mixture, X_{NMR} = Mole fraction in crystals, obtained by ¹H-NMR



¹H-NMR (400 MHz) spectrum of **Host** (**H**) in CDCl₃ at 25°C

6

1. HOST (H)





¹H-NMR (400 MHz) spectrum of **H.2PIC** (I) in CDCl₃ at 25°C



¹H-NMR (400 MHz) spectrum of **H.3PIC (II)** in CDCl₃ at 25° C

8

3. H.3PIC



4. H.4PIC

1a. H.2PIC/3PIC (0.1:0.9)







¹H-NMR (400 MHz) spectrum of **H.2PIC/3PIC (0.2:0.8)** in CDCl₃ at 25°C



1d. H.2PIC/3PIC (0.4:0.6)









1f. H.2PIC/3PIC (0.6:0.4) - V

¹H-NMR (400 MHz) spectrum of **H.2PIC/3PIC (0.6:0.4)** in CDCl₃ at 25°C

11. Marivel 2244 1 /opt/APR Pete [le] Web 43 2PIC-3PIC (70:30) in CDC13 1H Spectrum Marivel 13 2.7015 2,3860 9 SPIC 3PIC = 1.3505 8 2prc = 1.0000 $\overline{2.3505}$ ω -2PIC $\frac{1.2000}{2.3505} = 0.425$ (0x) 42%Z2pic = 4 \mathbf{N} 0 0000 3505 3.0 2.2 2.8 2.6 2.4 2.0 1.8 [ppm]

1g. H.2PIC/3PIC (0.7:0.3) - IV

¹H-NMR (400 MHz) spectrum of **H.2PIC/3PIC (0.7:0.3)** in CDCl₃ at 25°C

1h. H.2PIC/3PIC (0.8:0.2)



1i. H.2PIC/3PIC (0.9:0.1)



18

, Marivel 1242 1 /opt/APR Pete [rel] Web 43 2PIC-4PIC (40:60) in CDC13 r., 1H Spectrum Marivel X4piz= 0-60 **9** 4 tolal 1237 123 mm 4 puz 125 2 Pic XAPOZ **N** -23 0-98 Zapiz -125.5 1 1 = 2.5 = 0-02 chi, 125.5 يىن 0 0.0207 0000 3.0 2.8 - 2.6 2.6 2.4 2.5 2.4 2.4 2.2 2.0 1.8 [ppm]

¹H-NMR (400 MHz) spectrum of **H.2PIC/4PIC (0.4:0.6)** in CDCl₃ at 25°C



2b. H.2PIC/4PIC (0.5:0.5)



2c. H.2PIC/4PIC (0.6:0.4)



¹H-NMR (400 MHz) spectrum of **H.2PIC/4PIC (0.6:0.4)** in CDCl₃ at 25°C

2d. H.2PIC/4PIC (0.7:0.3)



2e. H.2PIC/4PIC (0.8:0.2)



¹H-NMR (400 MHz) spectrum of **H.2PIC/4PIC (0.8:0.2)** in CDCl₃ at 25°C

2f. H.2PIC/4PIC (0.85:0.15)



(7. Eric/4Fic (- - - -Marivel 1241 1 /opt/APR Pete A.C. [rel] Web 43 2PIC-4PIC (90:10) in CDC13 1H Spectrum Marivel 2.5 2.0 (24 984 -126 126 Zapic = 124 mm 'n, ÷. = 0.016 2 pv2 50.0 1.0 0.5 PIZ 0.0 0000 0.0203 2.6 2.8 2.4 2.2 [ppm]

¹H-NMR (400 MHz) spectrum of **H.2PIC/4PIC (0.9:0.1)** in CDCl₃ at 25°C

2g. H.2PIC/4PIC (0.9:0.1)

3a. H.3PIC/4PIC (0.9:0.1)



¹H-NMR (400 MHz) spectrum of **H.3PIC/4PIC (0.9:0.1)** in CDCl₃ at 25°C

3b. H.3PIC/4PIC (0.8:0.2)



T Same 1.5 The second second Marivel 1543 1 /opt/APR Pete [rel] Web 43 3 PIC/4Pic (70:30) in CDC13 \sim 1H Spectrum Marivel - 12 <u>e</u>. $Z_{3Pic} = \frac{4.4921}{5.4921} \times 100$ $\frac{1.5000}{4.4921}$ $\frac{4.921}{5.4921}$ $Z_{3Pic} = 0.82 (0v) 82'$ <u>ا</u>م ο 0000 4921 2.4 2.5 2.3 [ppm]

3c. H.3PIC/4PIC (0.7:0.3)

¹H-NMR (400 MHz) spectrum of **H.3PIC/4PIC (0.7:0.3)** in CDCl₃ at 25°C



3d. H.3PIC/4PIC (0.6:0.4) contains mixture of H.3PIC (VI) and H.4PIC (VII)

3e. H.3PIC/4PIC (0.55:0.45)





3f. H.3PIC/4PIC (0.5:0.4)

4a. H.2PIC/3PIC/4PIC (0.6:0.2:0.2) - 'A'



4b. H.2PIC/3PIC/4PIC (0.4:0.4:0.2) – 'B' - IX



[rel]

1H Spectrum Marivel

4c. H.2PIC/3PIC/4PIC (0.4:0.2:0.4) - 'C' I MANY STRUTTE Marivel 853 1 /opt/MAY Pete Web 43 2PIC/3PIC/4PIC (40:20:40) in CDC13 4pre = 40.3174 3pre = 3.4460



¹H-NMR (400 MHz) spectrum of **H.2PIC/3PIC/4PIC (0.4:0.2:0.4)** in CDCl₃ at 25°C

2.2

2.0

1.8

[ppm]

2.4

2.6

2.8

4d. H.2PIC/3PIC/4PIC (0.2:0.6:0.2) – 'D' - VIII



4e. H.2PIC/3PIC/4PIC (0.2:0.4:0.4) - 'E'



¹H-NMR (400 MHz) spectrum of **H.2PIC/3PIC/4PIC (0.2:0.4:0.4)** in CDCl₃ at 25°C

4f. H.2PIC/3PIC/4PIC (0.2:0.2:0.6) - 'F'



4g. H.2PIC/3PIC/4PIC (0.33:0.33:0.33) - 'G'

