Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

RES-TOCSY: A Simple approach to Resolve Overlapped ^{1}H NMR Spectra of Enantiomers

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Index

RES -TOCSY experiment: Acquisition and Processing parameters

- EBurp and ReBurp shaped pulses are used for 90^0 selective excitation and 180^0 selective refocusing. The pulse length and pulse power are calibrated for each sample separately.
  (The approximate range of pulse length used is 60 - 90 ms. and 40-55 dB range)
- Isotropic mixing is done by MLEV Block, the mixing time used is 0.06 sec.
- For measurement of *ee* relaxation delay (d1) of 5 sec was used.
- Z-gradients strengths of 10 % and -10 % are used for coherence selection.

	Time Domain points	**Zero Filling**	**Window Function**	**Line Broadening (Hz)**
F_1 dimension	**256**	**512**	**Sine**	**1**
F_2 dimension	**4k**	**8k**	**EM**	**0.3**

S1

RES-TOCSY pulse program

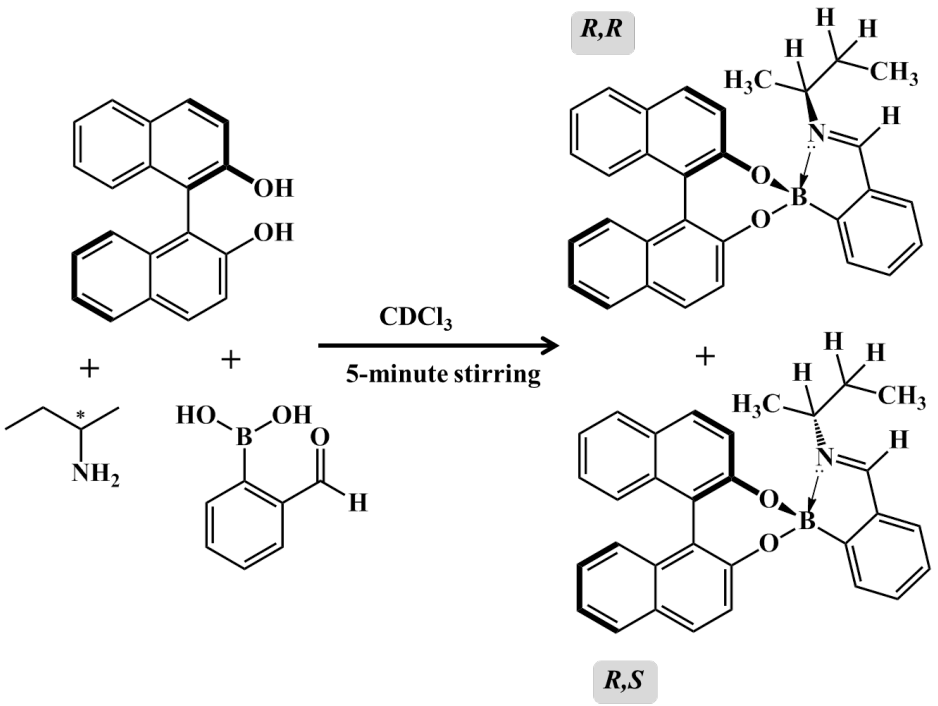
```
#include <Avance.incl>
#include <Grad.incl>
#include <Delay.incl>

"p5=p6*.667"
"p7=p6*2"
"d12=20u"

"SCALEF=p7*2/p5+0.5"
"FACTOR1=((d9-p17*2)/(p6*64+p5))/SCALEF+0.5"
"l1=FACTOR1*SCALEF"

"in0=inf1/2"

"d0=3u"


1 ze
2 d1
3 (p11:sp1 ph1):f1
  d0
  (p12:sp2 ph2):f1
  4u UNBLKGRAD
  p2:f1 ph2
  d0
  p16:gp1
  d16
  4u pl10:f1
  (p17 ph26)
                                        ;begin MLEV17
4 (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph22 p7 ph23 p6 ph22)
```

```
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph22 p7 ph23 p6 ph22)
  (p6 ph24 p7 ph25 p6 ph24)
  (p6 ph24 p7 ph25 p6 ph24)
  (p5 ph23)
  lo to 4 times l1
                                          ;end MLEV17
  (p17 ph26)
  p16:gp2
  d16 BLKGRAD
  go=2 ph31
  30m mc #0 to 2 F1QF(id0)
exit


ph1  = 0 0
ph2  = 0 2
ph22=3 1 3 1 0 2 0 2
ph23=0 2 0 2 1 3 1 3
ph24=1 3 1 3 2 0 2 0
ph25=2 0 2 0 3 1 3 1
ph26=0 2 0 2 1 3 1 3
ph31 = 0 0


;pl1 : f1 channel - power level for pulse (default)
;pl10: f1 channel - power level for TOCSY-spinlock
;p1 : f1 channel -  90 degree high power pulse
;p5 : f1 channel -  60 degree low power pulse
;p6 : f1 channel -  90 degree low power pulse
;p7 : f1 channel - 180 degree low power pulse
;p17: f1 channel - trim pulse                    [2.5 msec]
;d0 : incremented delay (2D)
;d1 : relaxation delay; 1-5 * T1
;d9 : TOCSY mixing time
;d12: delay for power switching                  [20 usec]
;d16: gradient recovery                          [150 us]
;l1: loop for MLEV cycle: (((p6*64) + p5) * l1) + (p17*2) = mixing time
;inf1: 1/SW = 2 * DW
;in0: 1/(1 * SW) = 2 * DW
;nd0: 2
;NS: 8 * n
```

;DS: 16
;td1: number of experiments
;FnMODE: QF

S2

Scheme 1: The scheme for derivatization of secondary butyl amine (9 mg, 1 mmol) with 2-formylphenylboronic acid (20 mg, 1 mmol) and an enantiopure *R*-BINOL (22 mg, 1 mmol) in $CDCl_3$. The reaction mixture was stirred for 5 minutes at ambient temperature.



The derivatization protocol has already been reported [1]. The protocol for butyl amine is given above. The ^{1}H-NMR spectra of aliquot gave quantitative yield of diastereoisomers of iminoboronate esters (*R,S*) and (*S,S*).

Table: Experimentally measured *ee* for different concentrations of *R*-alphamethyl-benzylamine in *R*-BINOL Chiral solvating agent

Entry	Proton chosen	Integration I_R:I_S	*ee* % $\frac{(I_{maj}-I_{min})}{(I_{maj}+I_{min})}$ *100 (Experimental enatiomeric ratio)	Laboratory prepared enatiomeric ratio with excess of *R* enantiomer
Sample 1	CH_3	1.00:0.096	82.4	80
Sample 2	CH_3	1.00:0.2300	62	60
Sample 3	CH_3	1.00:0.6881	18.5	20
Sample 4	CH_3	1.00:1.00	0	0
Sample 5	CH_3	0.6196:1.00	-23	-22
Sample 6	CH_3	0.2375:1.00	-61	-60

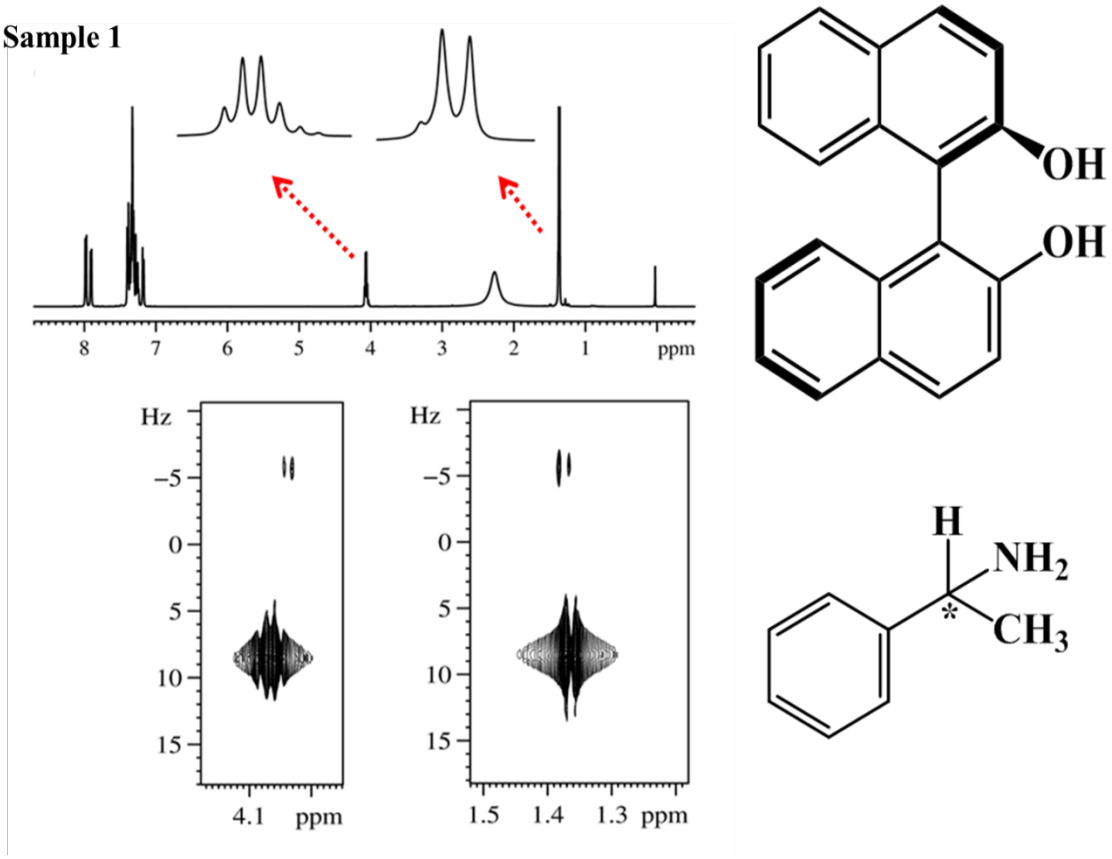


Fig 1: 1D ^{1}H-NMR (upper trace) and 2D RES-TOCSY (Bottom trace) spectra of alpha-methylbenzylamine with binol as chiral solvating agent in $CDCl_3$. (excess of *R*-alpha-methylbenzylamine, 80 %)

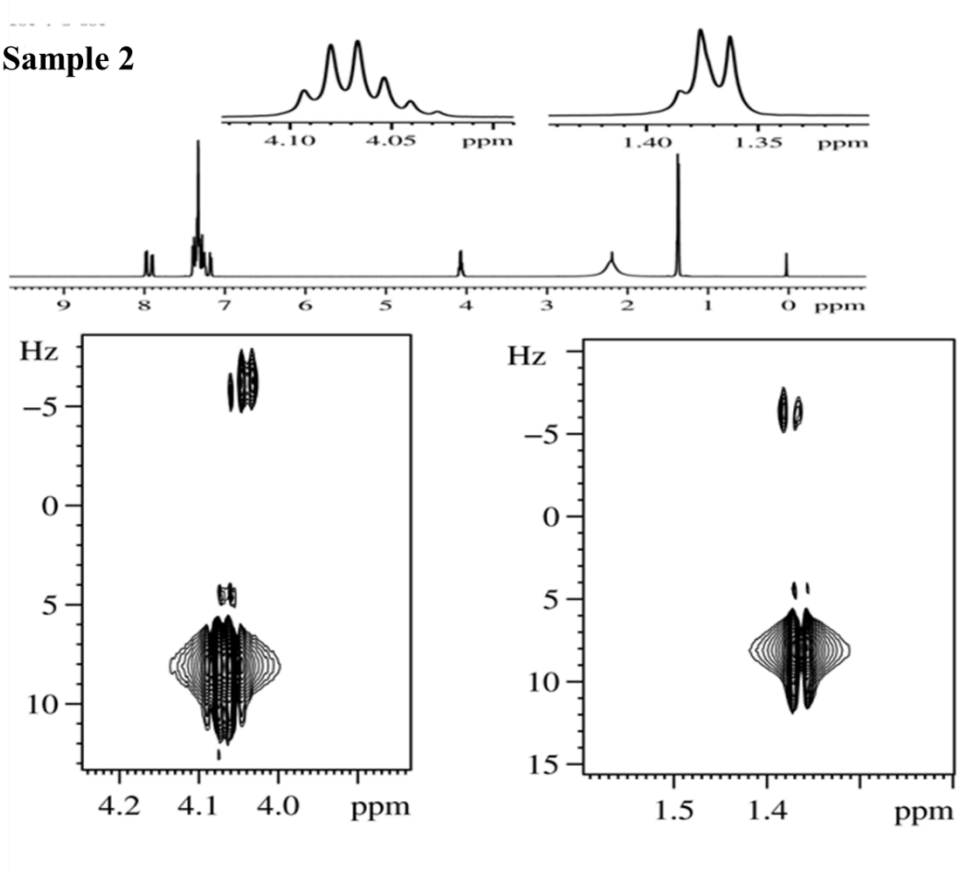


Fig 2: 1D ^{1}H-NMR (upper trace) and 2D RES-TOCSY (Bottom trace) spectra of alpha-methylbenzylamine with binol as chiral solvating agent in $CDCl_3$. (excess of *R*-alpha-methylbenzylamine, 60 %)

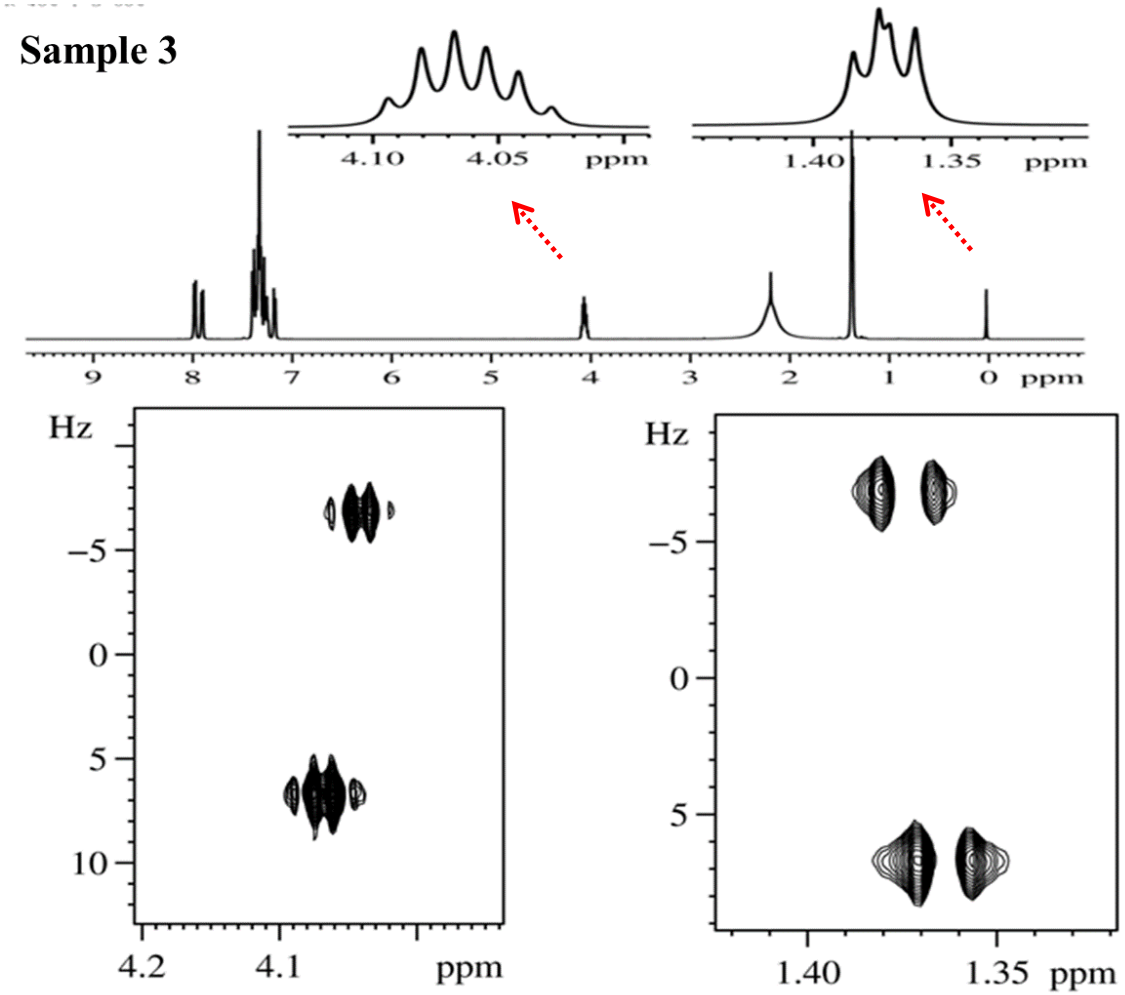


Fig 3: 1D ^{1}H-NMR (upper trace) and 2D RES-TOCSY (Bottom trace) spectra of alpha-methylbenzylamine with binol as chiral solvating agent in $CDCl_3$. (excess of *R*-alpha-methylbenzylamine, 20 %)

S7

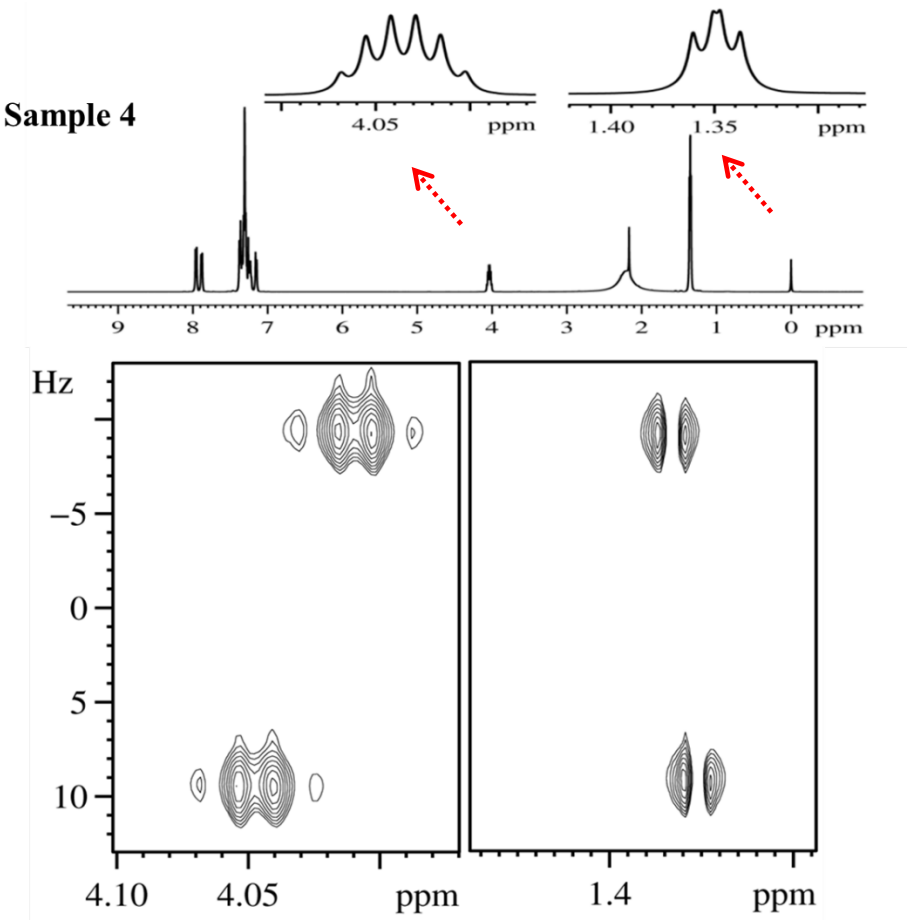


Fig 4: 1D ^{1}H-NMR (upper trace) and 2D RES-TOCSY (Bottom trace) spectra of alpha-methylbenzylamine with binol as chiral solvating agent in $CDCl_3$. (racemic mixture)

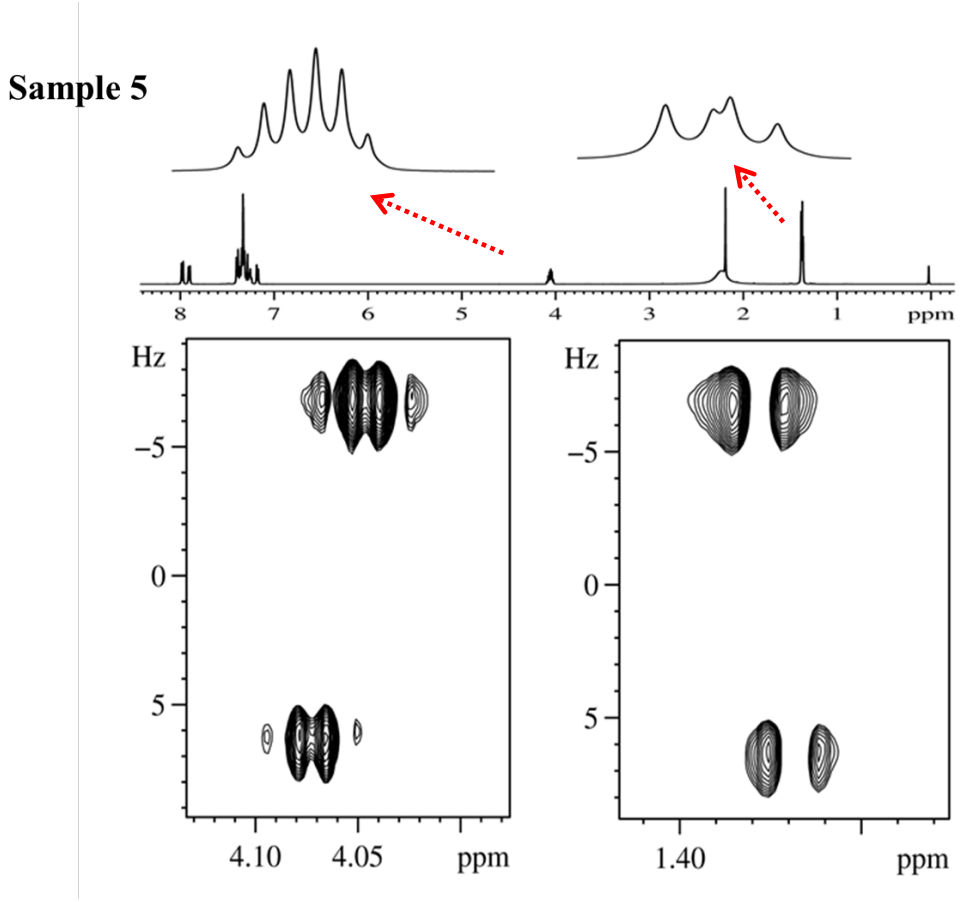


Fig 5: 1D ^{1}H-NMR (upper trace) and 2D RES-TOCSY (Bottom trace) spectra of alpha-methylbenzylamine with binol as chiral solvating agent in $CDCl_3$. (excess of *R*-alpha-methylbenzylamine, - 22%)

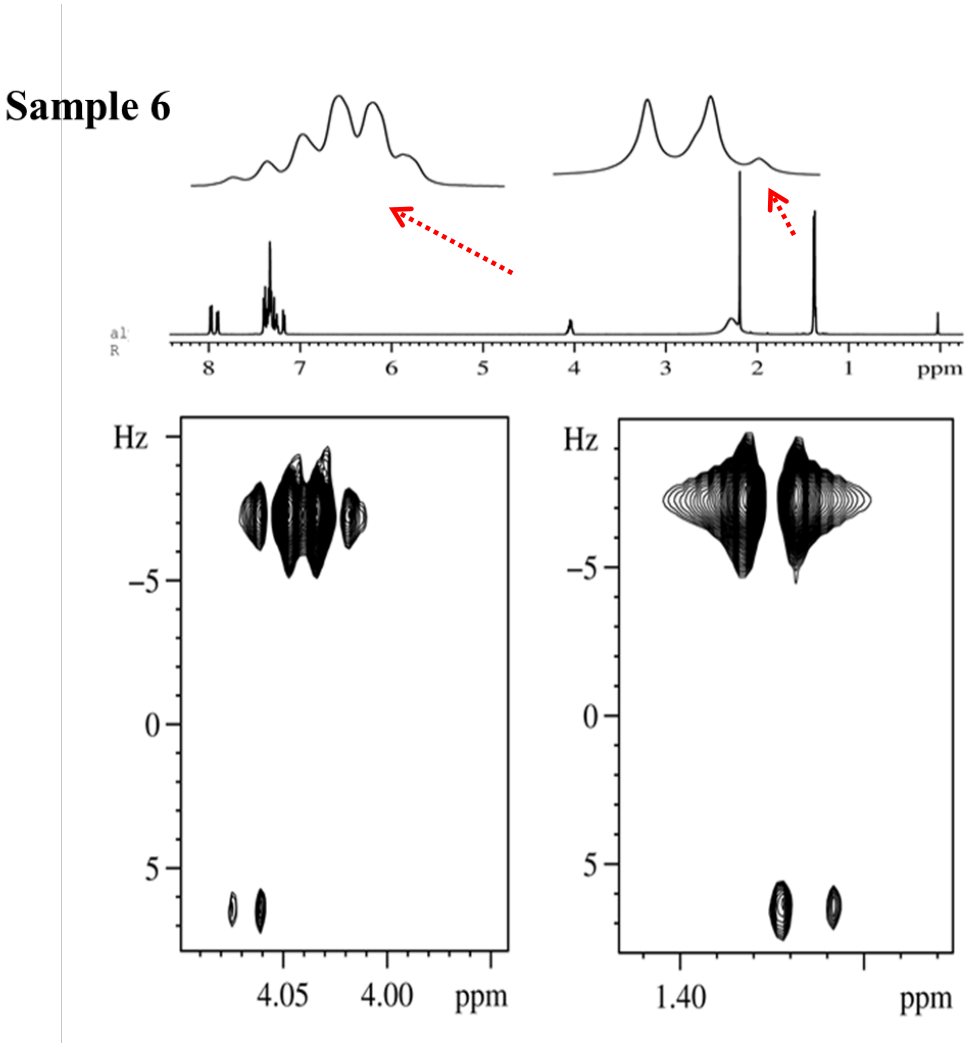


Fig 6: 1D ^{1}H-NMR (upper trace) and 2D RES-TOCSY (Bottom trace) spectra of alpha-methylbenzylamine with binol as chiral solvating agent in $CDCl_3$. (excess of *R*-alpha-methylbenzylamine, -60 %).

References:

1] (a) K. Tanaka, M. Ootani and F. Toda, *Tetrahedron:Asymmetry*, 1992, **3**,709-721; (b) F. Toda, K. Mori and A. Sato, *Bull. Chem. Soc. Jpn.,* 1988, **61**, 4167-4169.

S11