# Supporting Information

## Ternary ion-pair Complexation: A Protocol for Chiral Discrimination and the Assignment of Absolute Configuration of Hydroxy Acids

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S42: $^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DABCO at 298 K in the solvent $CDCl_3$

S43:$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and TEA at 298 K in the solvent $CDCl_3$

**Experimental Section:** Initially one equivalent of carboxylic acid and DMPA were mixed to ensure that acid gets dissolved properly in $CDCl_3$ (500 μL). To this solution one equivalent of R-BINOL was added. The $^1$H-NMR spectrum of the resulting solution was recorded using a 400 MHz NMR spectrometer. The peaks were referenced to TMS as an internal standard. In order to achieve better solution the spectra were recorded at low temperatures and the respective temperature is mentioned in the figure caption.

# S1

**Table 1**

Chemical shift difference $(\Delta\delta)^{R,S}$ (in Hz) of α-proton obtained for (*R/S*)-4-trifluoromethyl-mandelic acid in solvents of different polarities in the presence of one equivalent each of DMAP and *R*-BINOL

| Solvent | Chemical Shift Difference $[\Delta\delta^{R,S}$ (in Hz)] * |
|---|---|
| $CDCl_3$ | 11.0 |
| Benzene-$d_6$ | 6.0 |
| $CD_3$-CN | 3.2 |
| Acetone-$d_6$ | 2.0 |

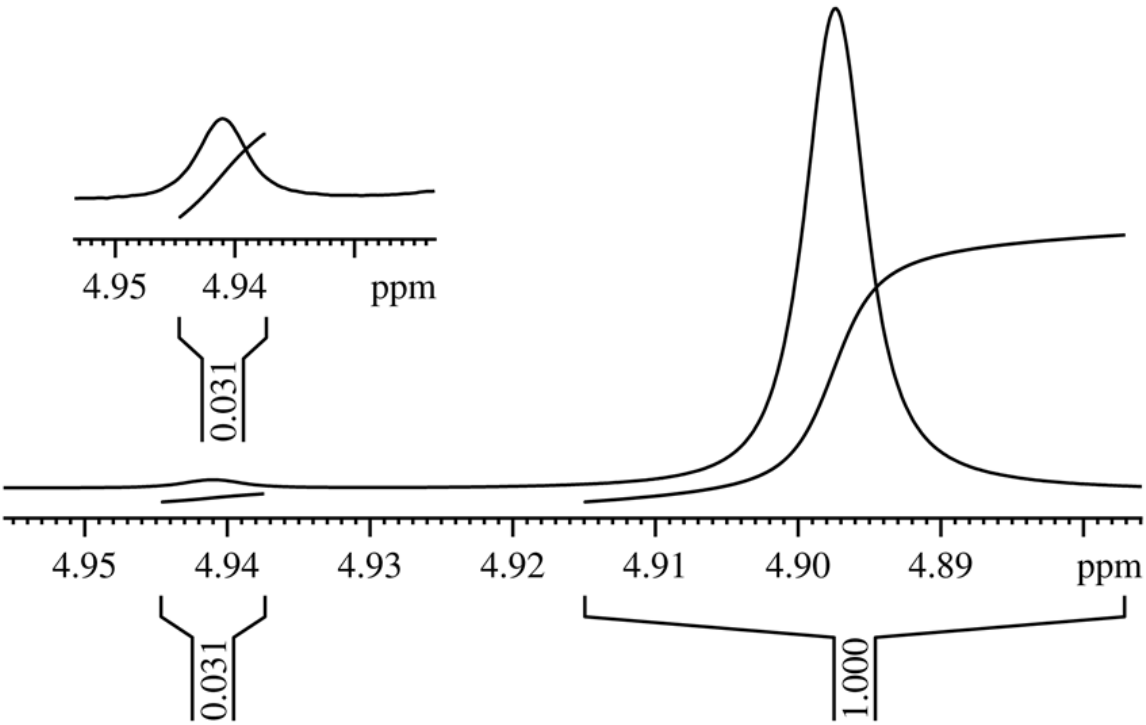
*This value is zero in the solvents DMSO-$d_6$, Pyridine-$d_5$ and Methanol-$d_4$.

**Table 2:** The enantiomeric excess measured from the proton $^{1}$H-NMR spectrum of Mandelic acid for the laboratory prepared samples of different scalemic ratios.

| Entry | $\delta_H$(ppm) *(R)* | $\delta_H$(ppm) *(S)* | Chemical shift difference $(\Delta\delta)^{R/S}$ (in Hz) | Integration *(R)*: *(S)* $I_{maj}$:$I_{min}$ | *ee* % $\frac{(I_{maj}-I_{min})}{(I_{maj}+I_{min})}$ *100 | Laboratory prepared scalemic ratio with excess of *R* enantiomer |
|---|---|---|---|---|---|---|
| Sample 1 | 5.01 | - | 0 | 1.0:0 | 100 | 100 |
| Sample 2 | 5.00 | 4.98 | 11 | 1.0 :0.5550 | 28 | 28 |
| Sample 3 | 5.00 | 4.97 | 15 | 1.0 : 0.2369 | 62 | 64 |
| Sample 4 | 5.0 | 4.97 | 14 | 1.0 :1.0 | 0 | 0 |
| Sample 5 | 4.94 | 4.89 | 32 | 1.0 : 0.031 | 94 | 96 |
| Sample 6 | 4.94 | 4.89 | 32 | 1.0 : 0.011 | 97.8 | 98 |
| Sample 7 | 4.92 | 4.86 | 32 | 1.0 : 0.006 | 98.8 | 99 |

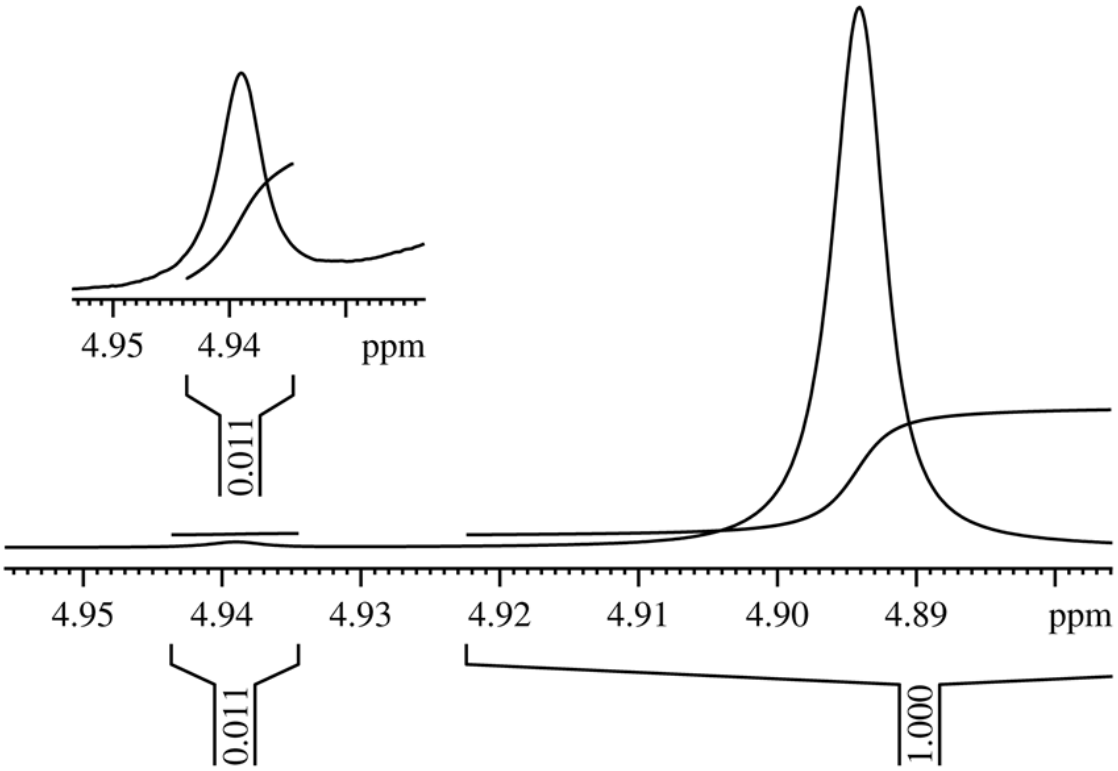
**Note:** $^{1}$H NMR spectra of samples 5, 6 and 7 were recorded on a 800 MHz spectrometer with 2.5 equivalent of *S*-BINOL, 1 equivalent of mandelic acid and 1 equivalent of DABCO at 298 K.

800 MHz $^{1}$H-NMR spectrum of mandelic acid with excess of *R* enantiomer in the presence of 3 equivalent of *R*-BINOL and one equivalent of DABCO in the solvent $CDCl_3$ recorded at 298K. (The prepared scalemic ratios are 96 % *R)*



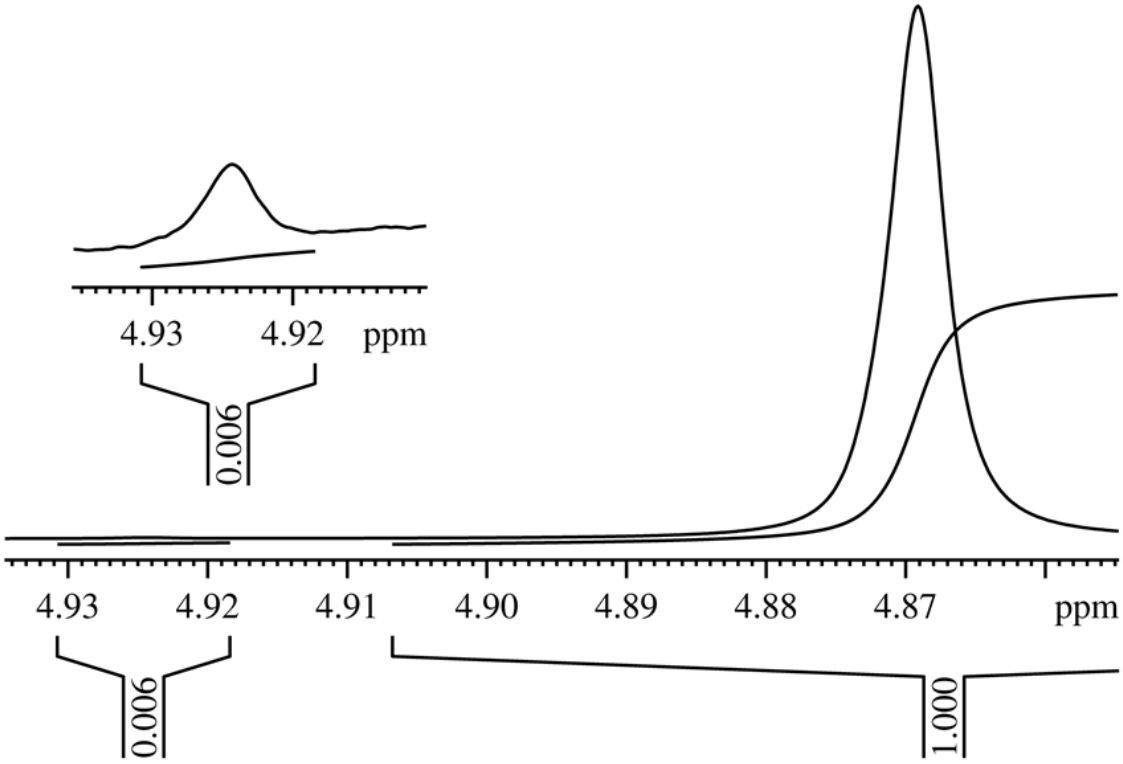

**S4**

800 MHz $^{1}$H-NMR spectrum of mandelic acid with excess of *R* enantiomer in the presence of 3 equivalent of *R*-BINOL and one equivalent of DABCO in the solvent $CDCl_3$ recorded at 298K. (The prepared scalemic ratios are 98 % *R)*



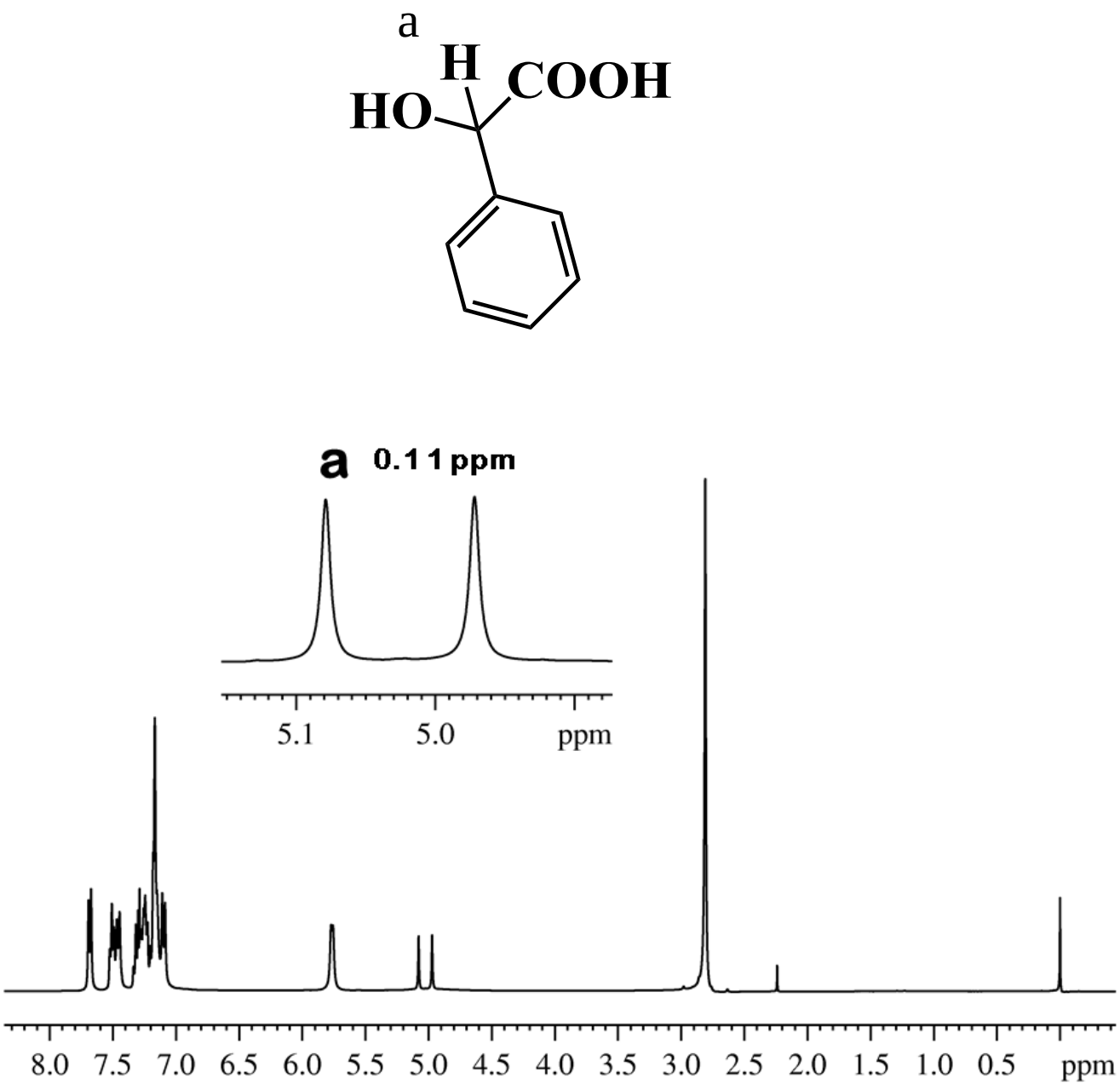

**S5**

800 MHz $^{1}$H-NMR spectrum of mandelic acid with excess of *R* enantiomer in the presence of 3 equivalent of *R*-BINOL and one equivalent of DABCO in the solvent $CDCl_3$ recorded at 298K. (The prepared scalemic ratios are 99 % *R)*

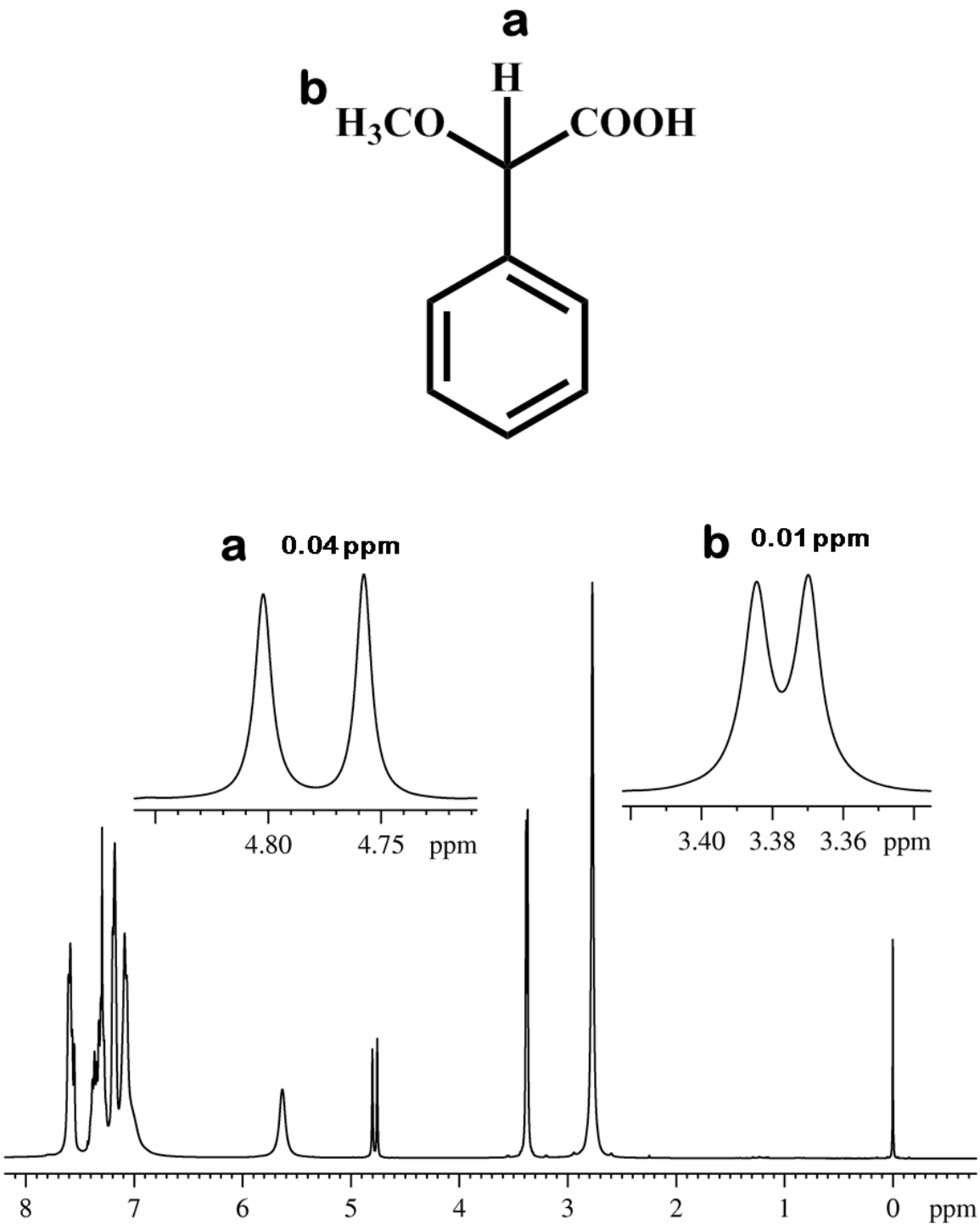



**S6**

$^{1}$H-NMR spectrum of the racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K

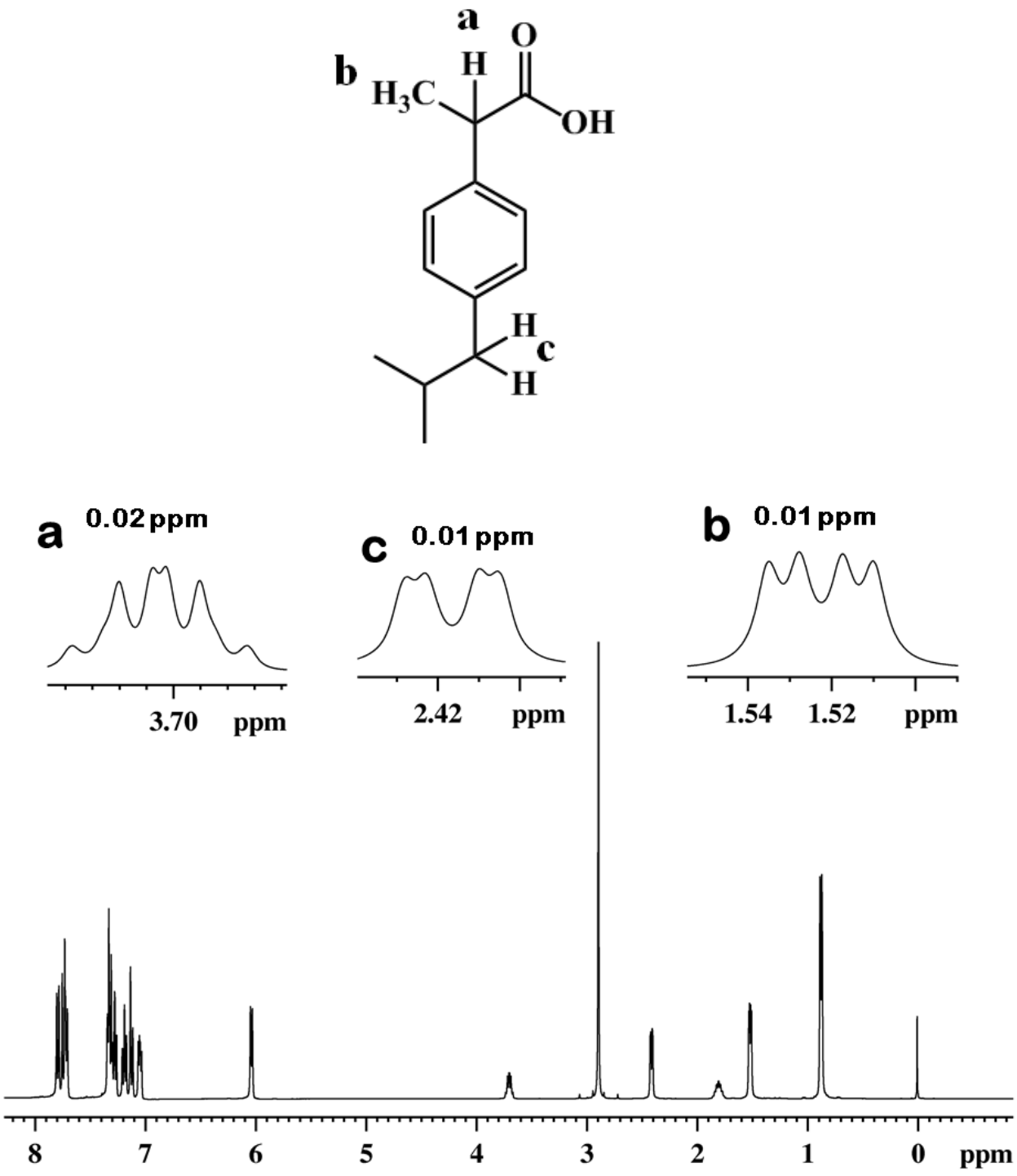


$^{1}$H-NMR spectrum of racemic mixture of alpha-methoxyphenylacetic acid with one equivalent of *R*-BINOL and DMAP at 298 K

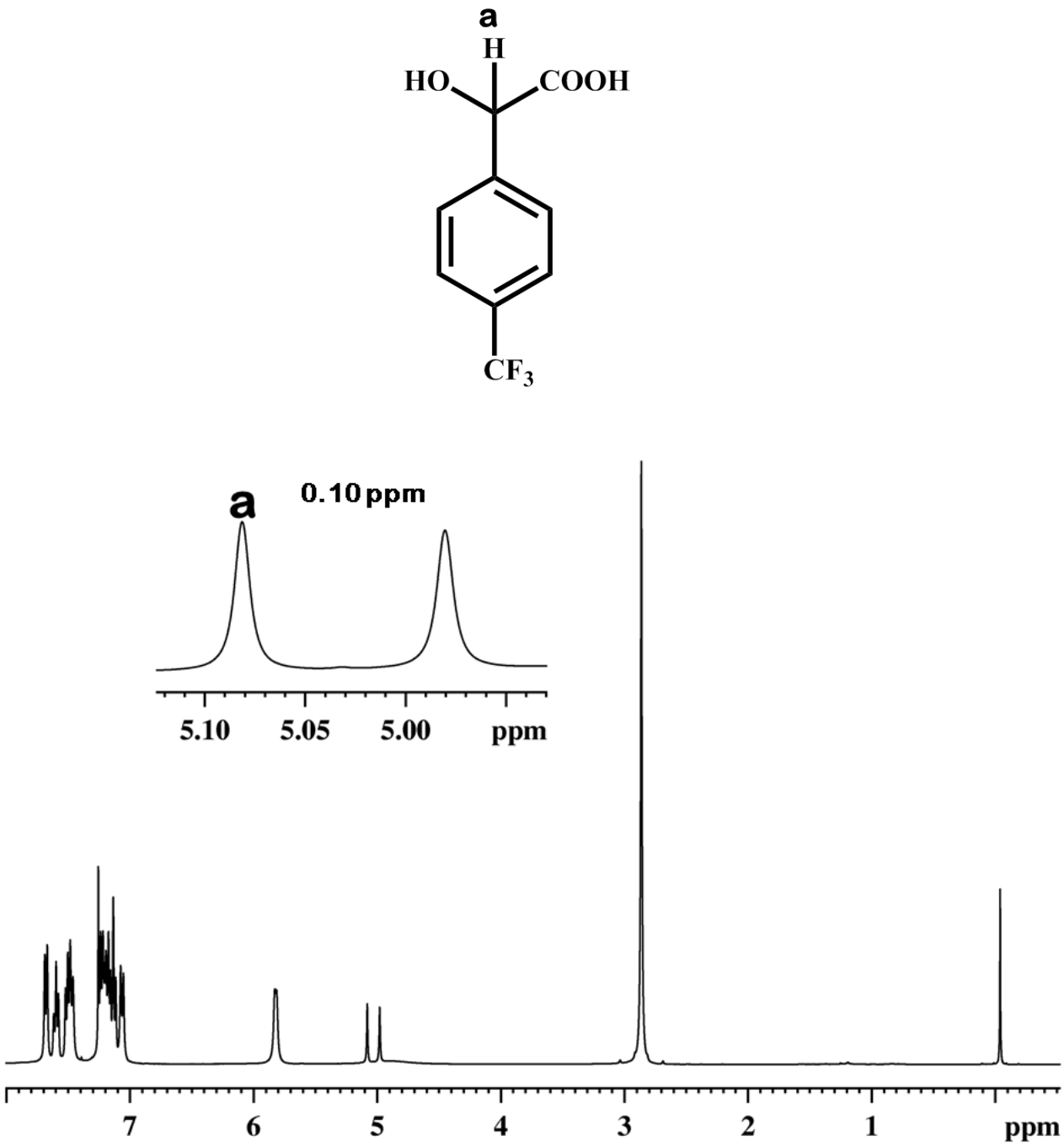



**S8**

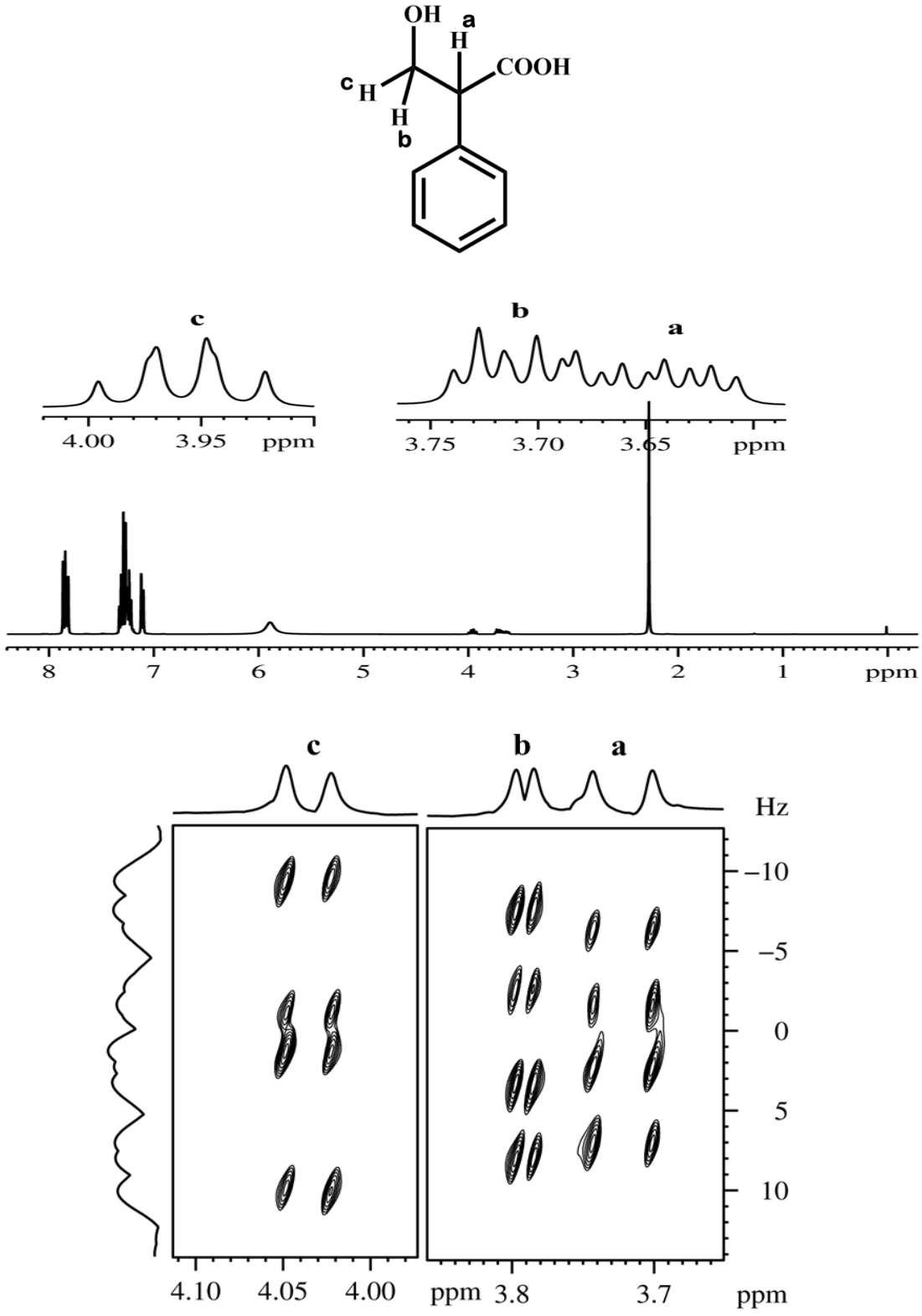
$^{1}$H-NMR spectrum of racemic mixture of Ibuprofen with one equivalent of *R*-BINOL and DMAP at 240 K



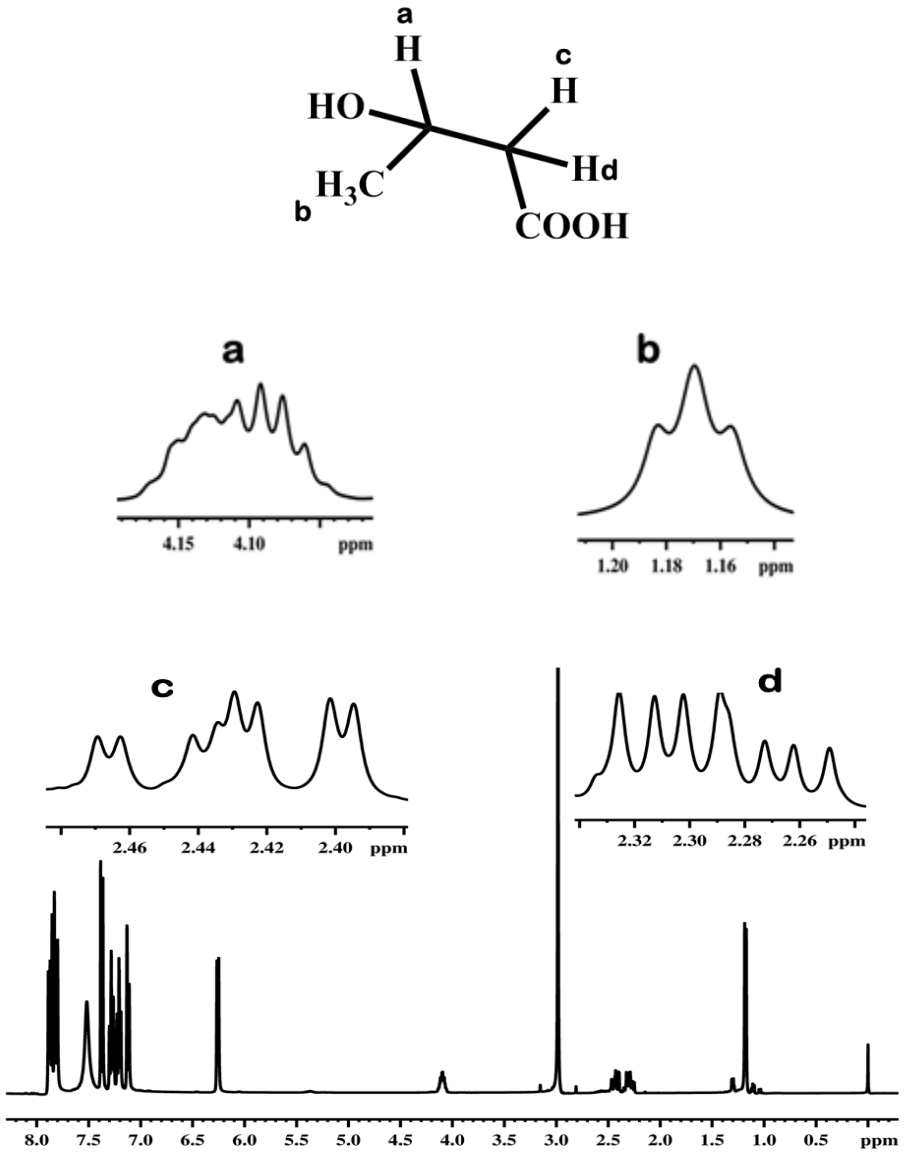
$^{1}$H-NMR spectrum of racemic mixture of 4-(trifluoromethyl)mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K.



$^{1}$H-NMR 1D and 2D NMR spectra of racemic mixture of Tropic acid with one equivalent of *R*-BINOL and DMAP at 298 K

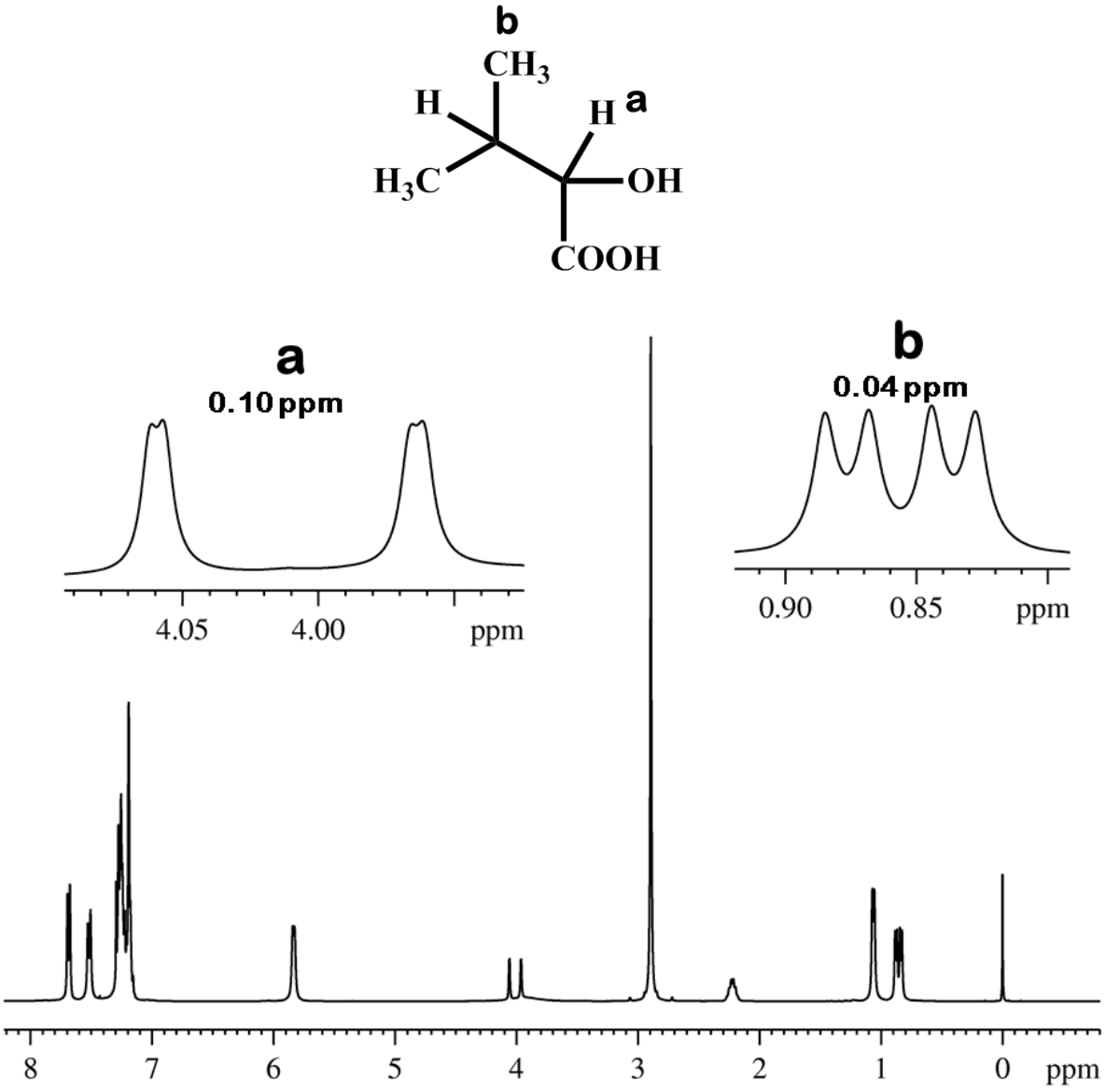


$^{1}$H-NMR spectrum of racemic mixture of 3-hydroxybutyric acid with one equivalent of *R*-BINOL and DMAP at 298 K

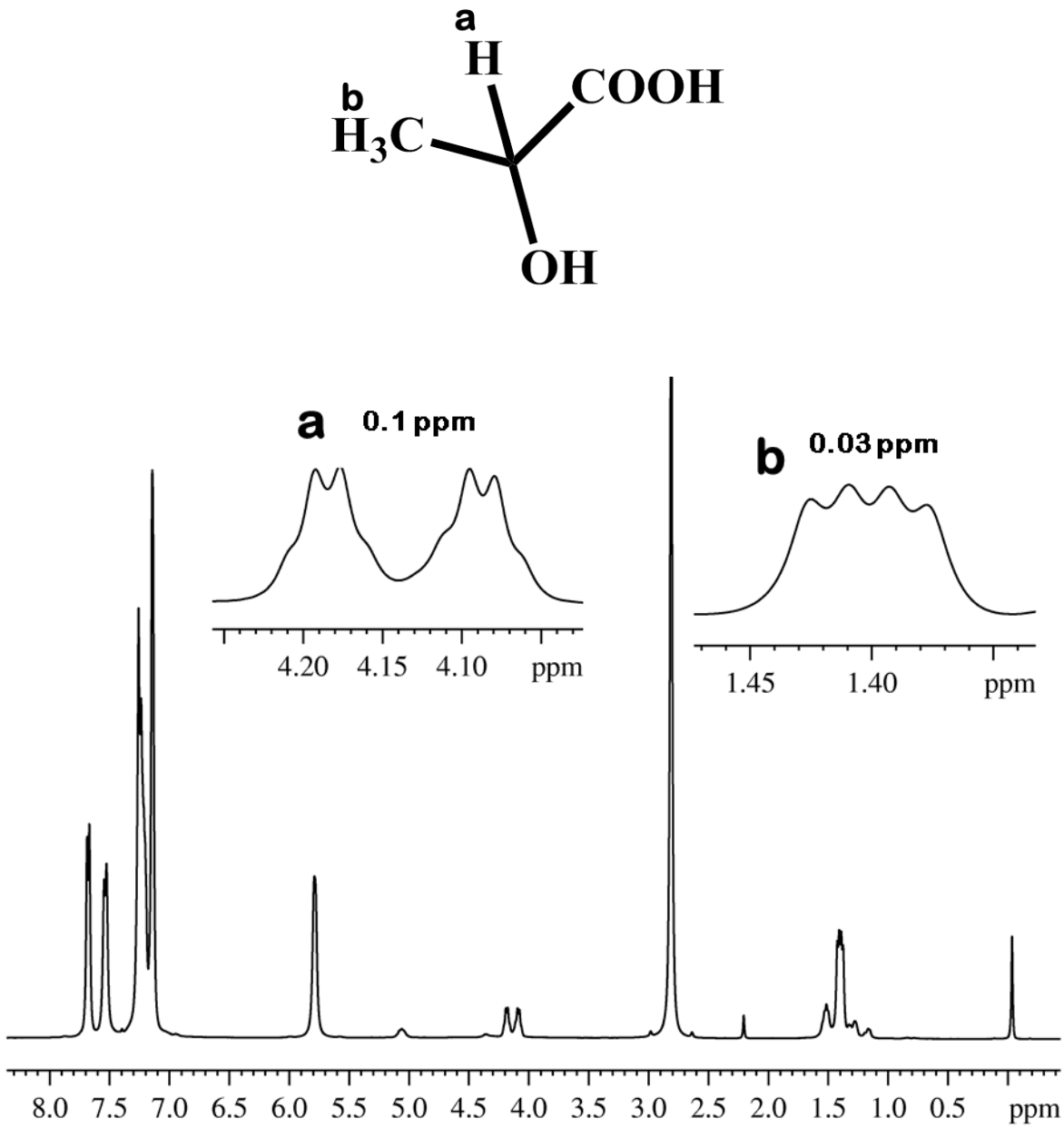



# S12

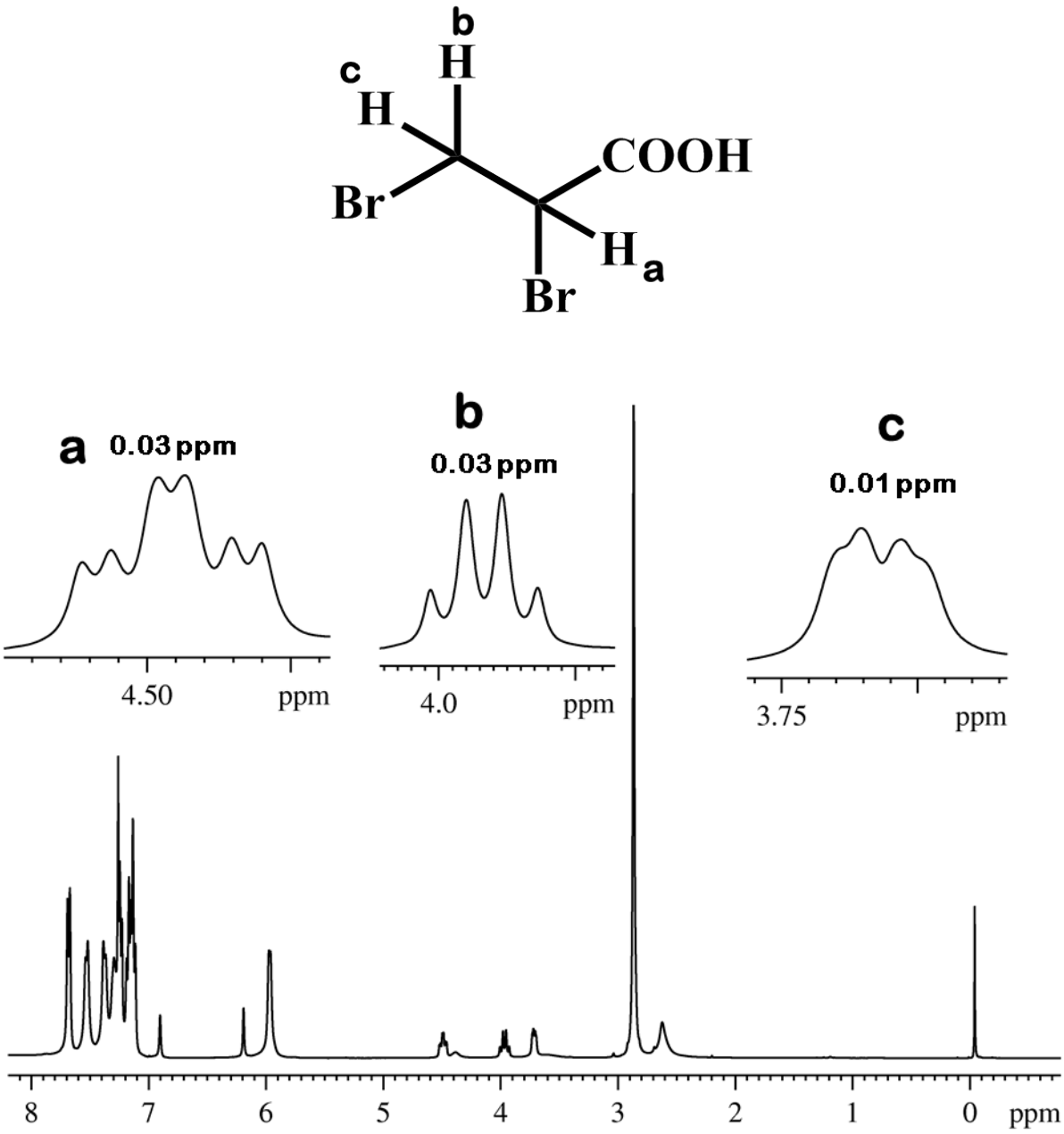
$^{1}$H-NMR spectrum of racemic mixture of 2-Hydroxy-3-methylbutyric acid with one equivalent of *R*-BINOL and DMAP at 298 K



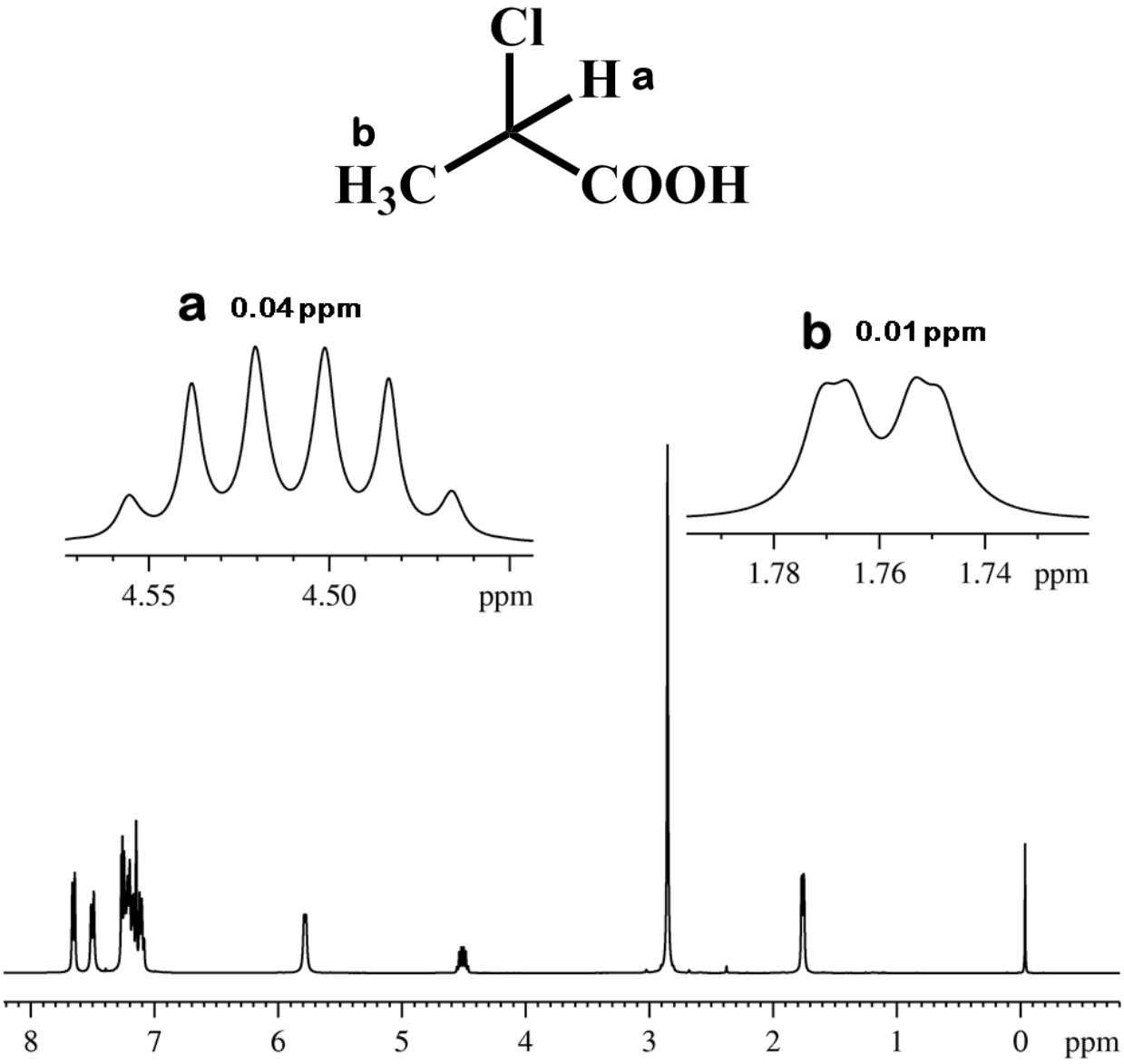
$^{1}$H-NMR spectrum of from racemic mixture of lactic acid with one equivalent of *R*-BINOL and DMAP at 298 K



$^{1}$H-NMR spectrum of from racemic mixture of 2,3-dibromopropanoic acid with one equivalent of *R*-BINOL and DMAP at 298 K

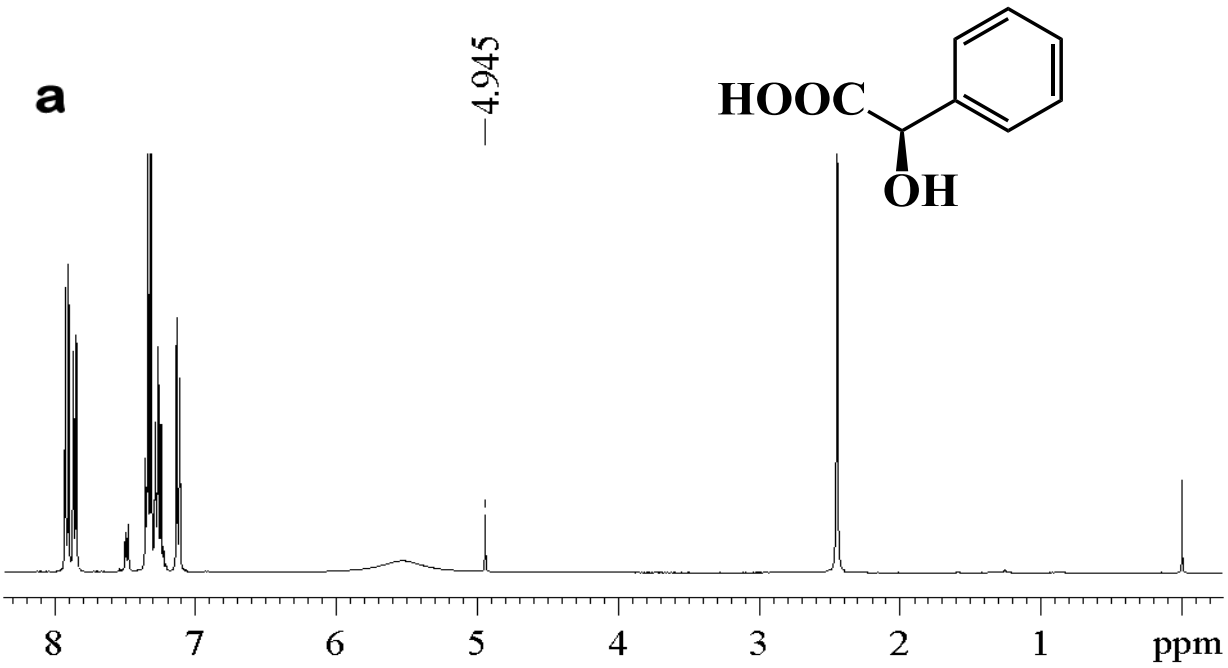


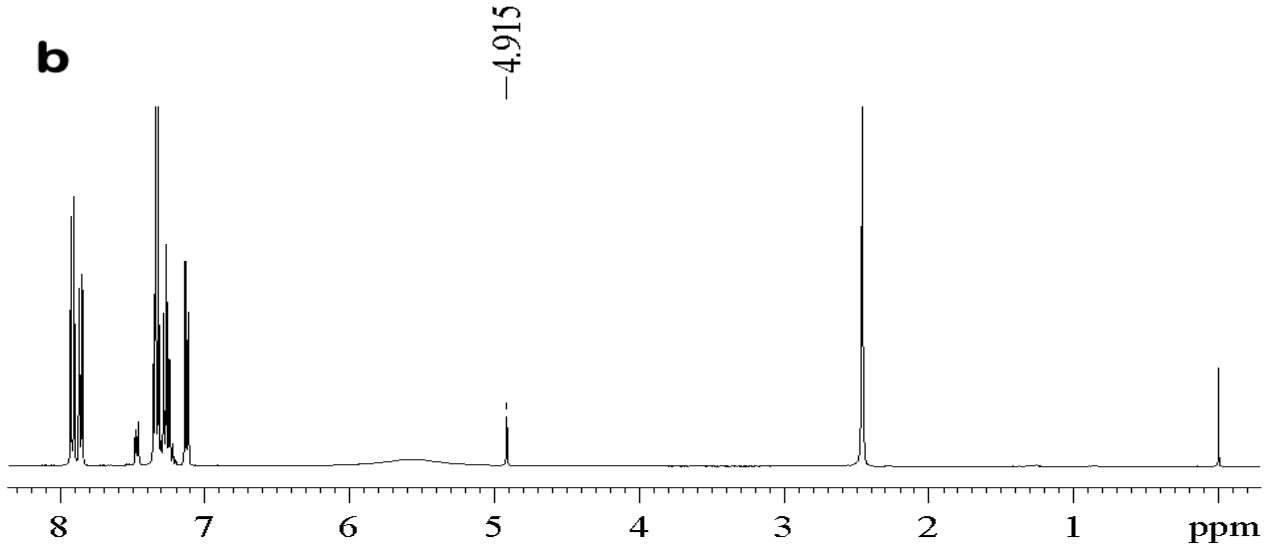
$^{1}$H-NMR spectrum of from racemic mixture of 2-chloropropanoic acid with one equivalent of *R*-BINOL and DMAP at 298 K



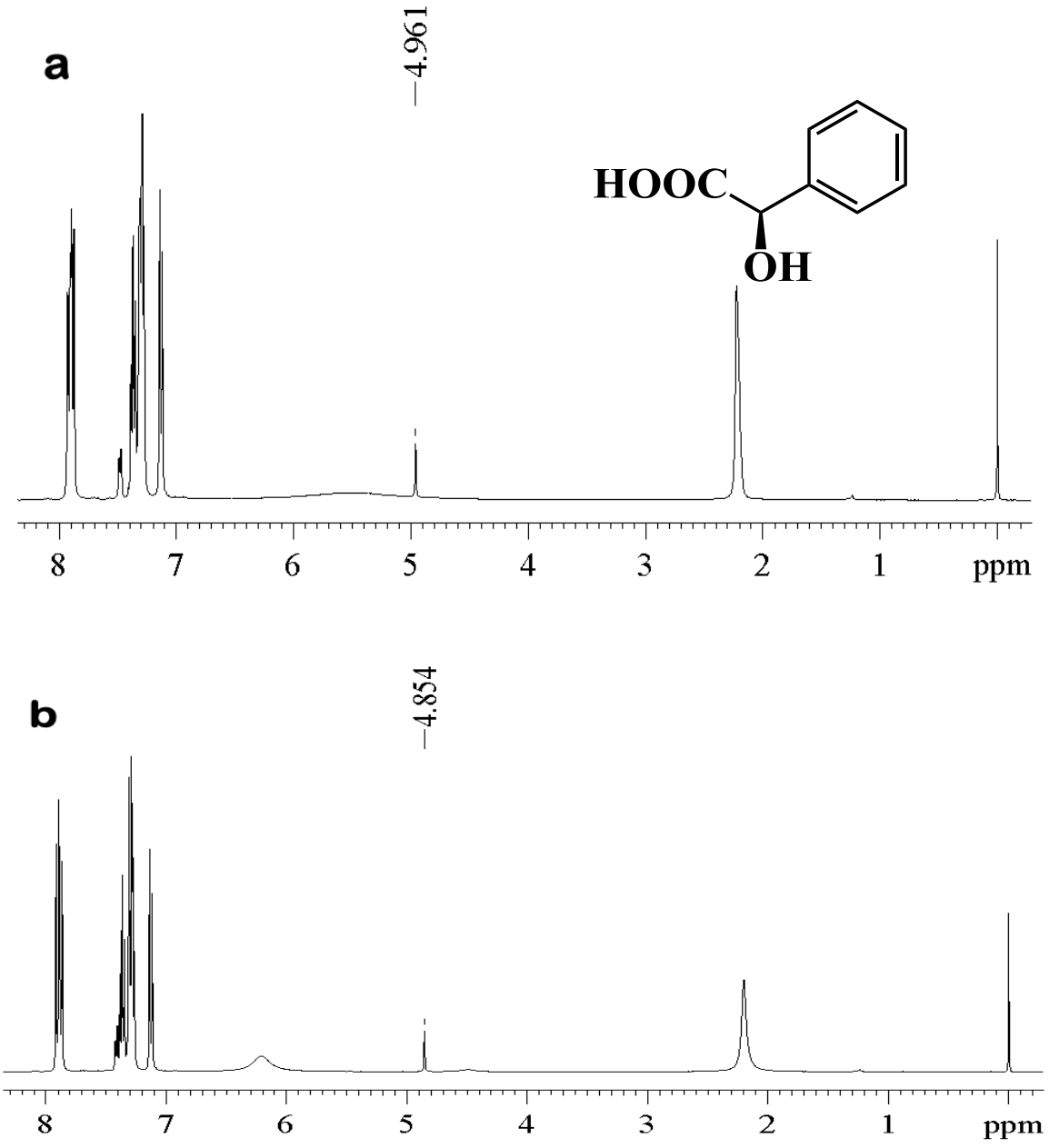

# S16

$^{1}$H NMR spectra of *R*-mandelic acid and DABCO at 298K in a) *R*-BINOL and b) *S*-BINOL



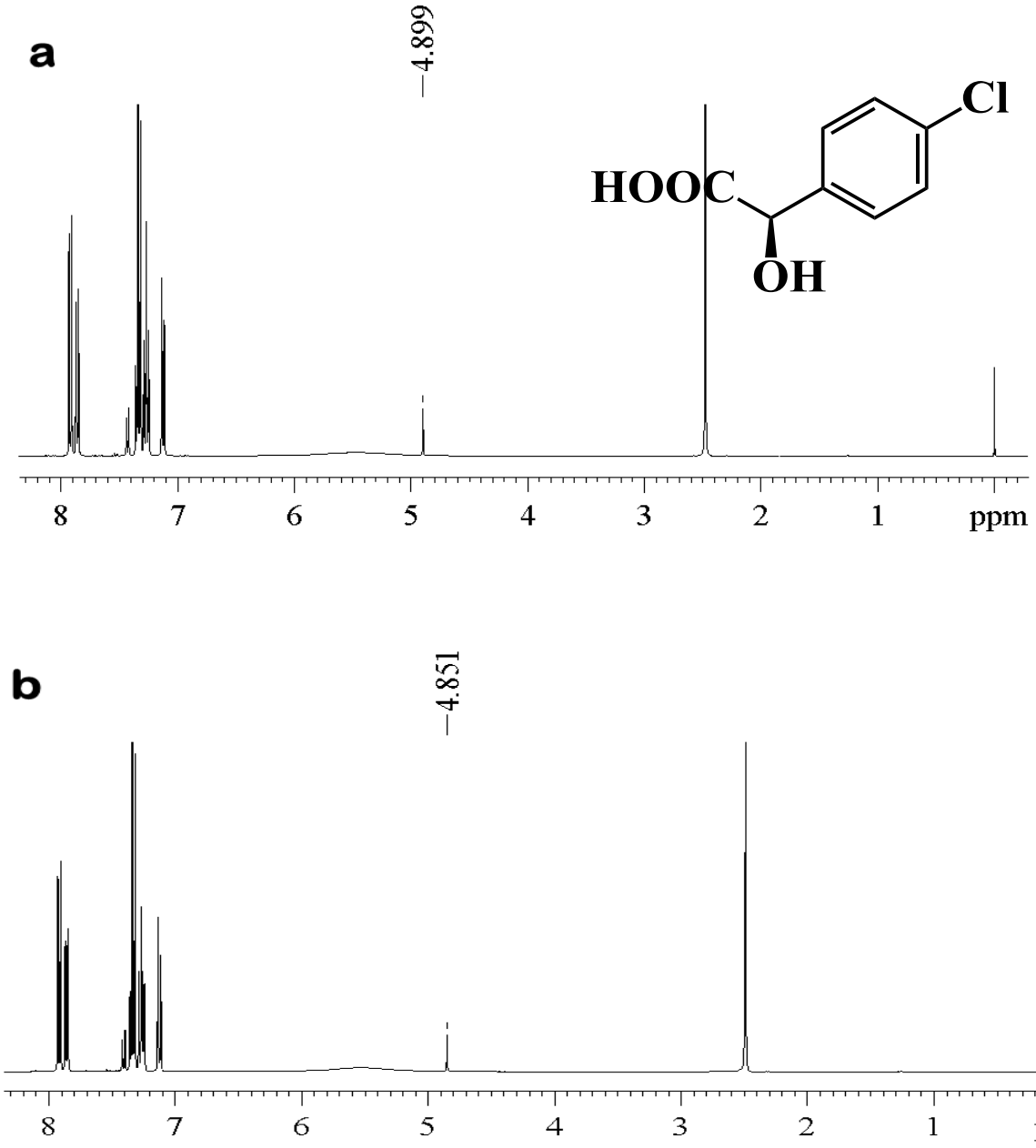



$^{1}$H NMR spectra of *R*-mandelic acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL

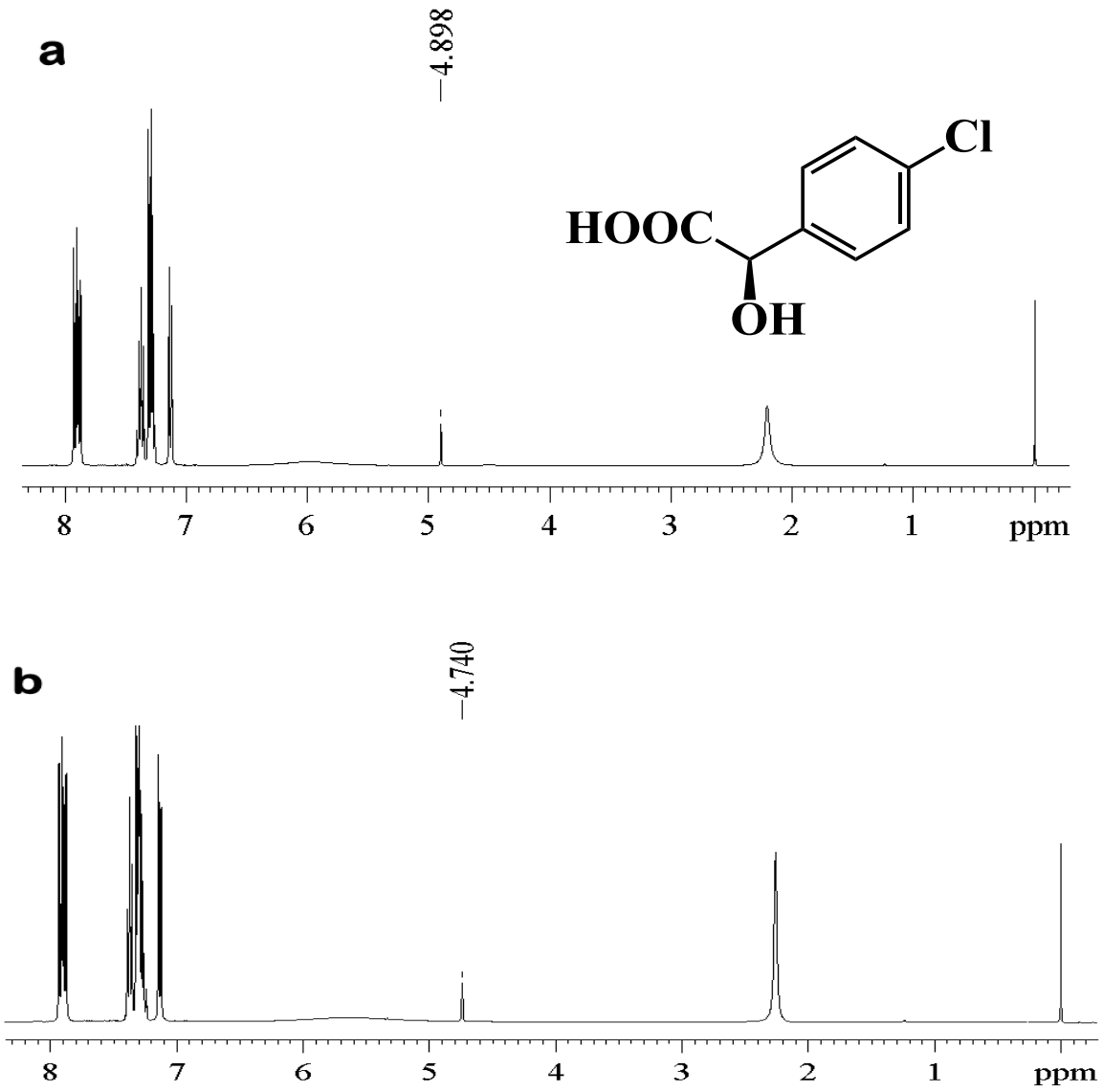



**S18**

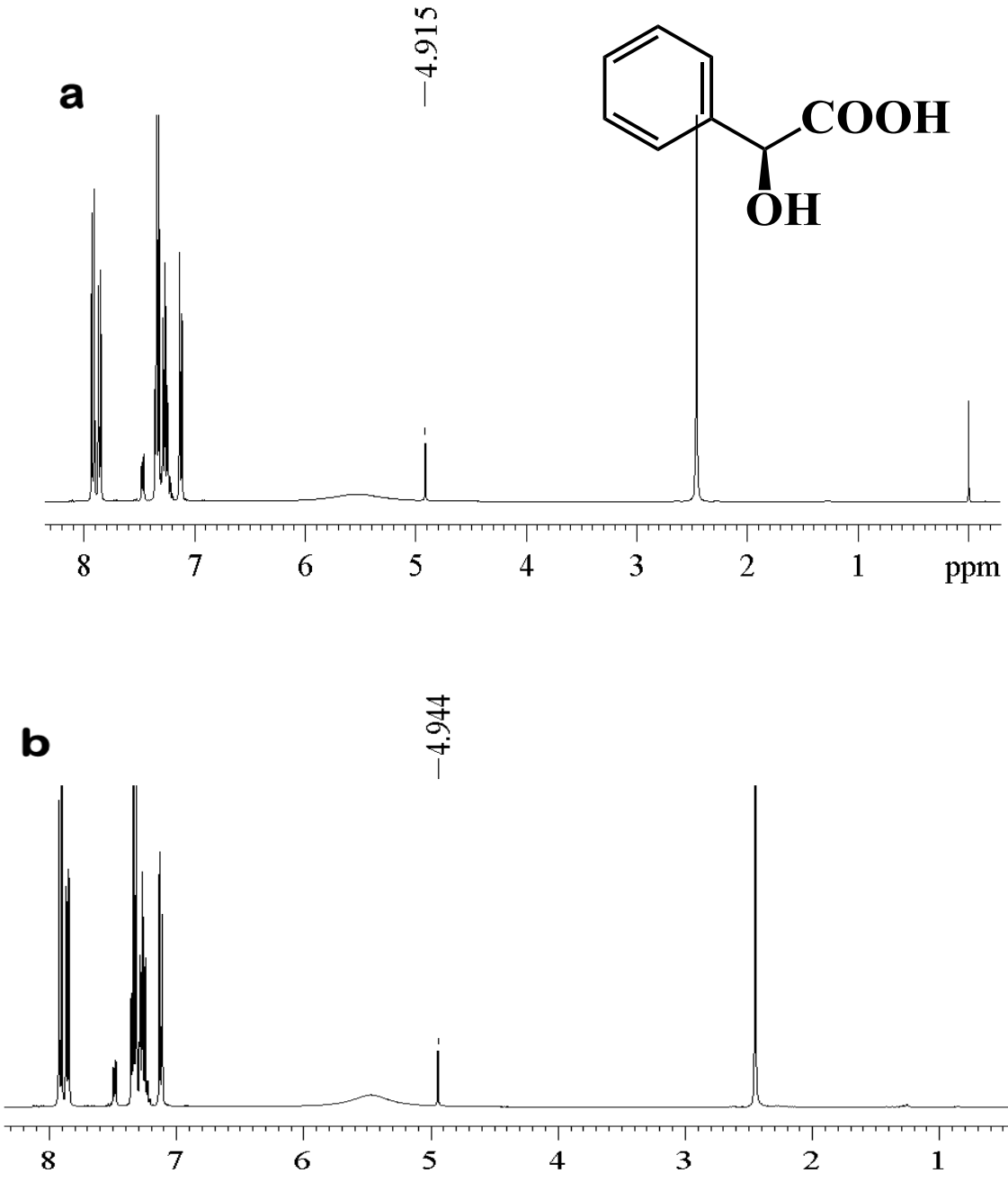
$^{1}$H NMR spectra of *R*-4-chloromandelic acid and DABCO at 298K in a) *R*-BINOL and b) *S*-BINOL



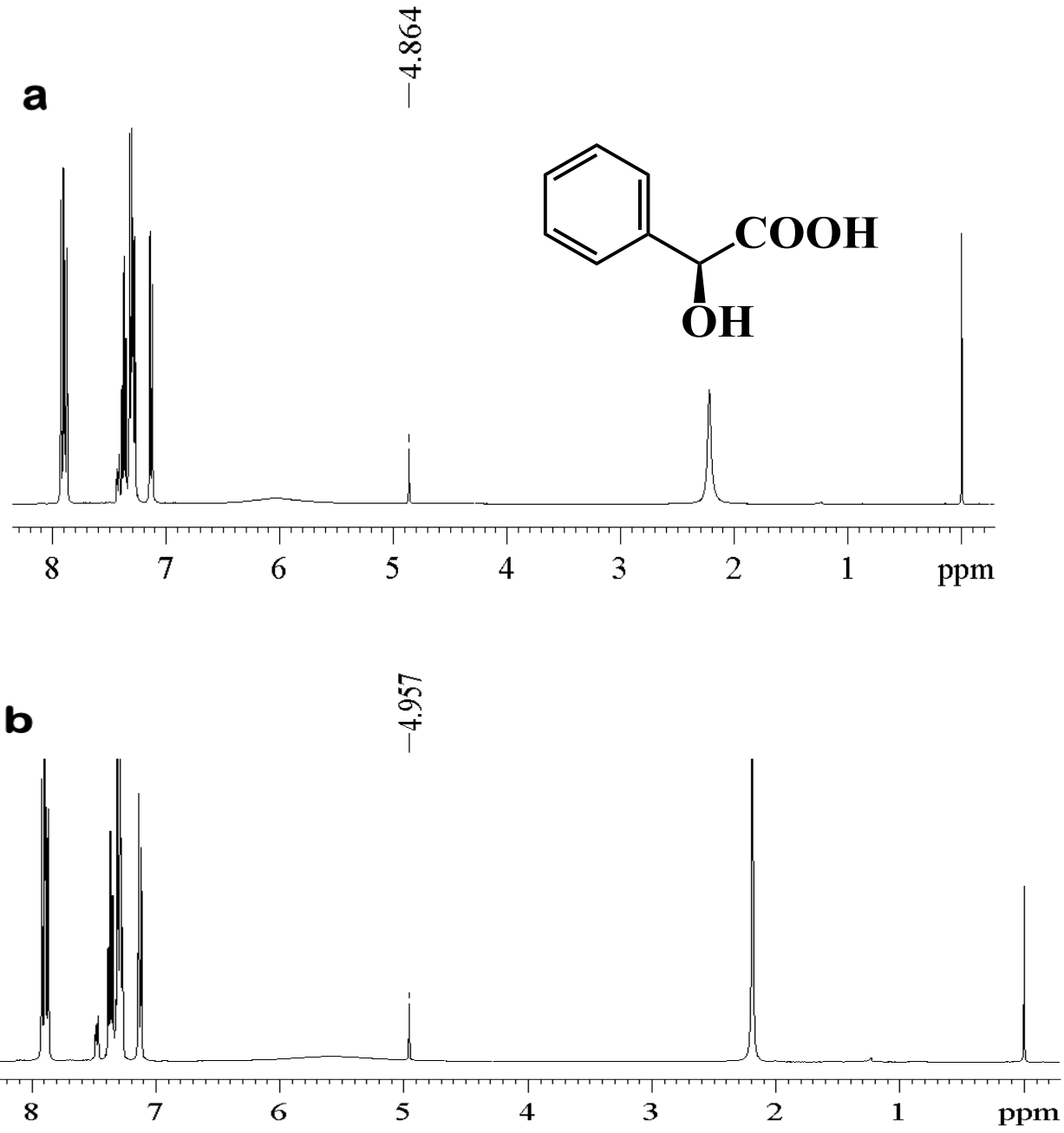
$^{1}$H NMR spectra of *R*-4-chloro-mandelic acid and DABCO at 240K in a) *R*-BINOL and b) *S*-BINOL



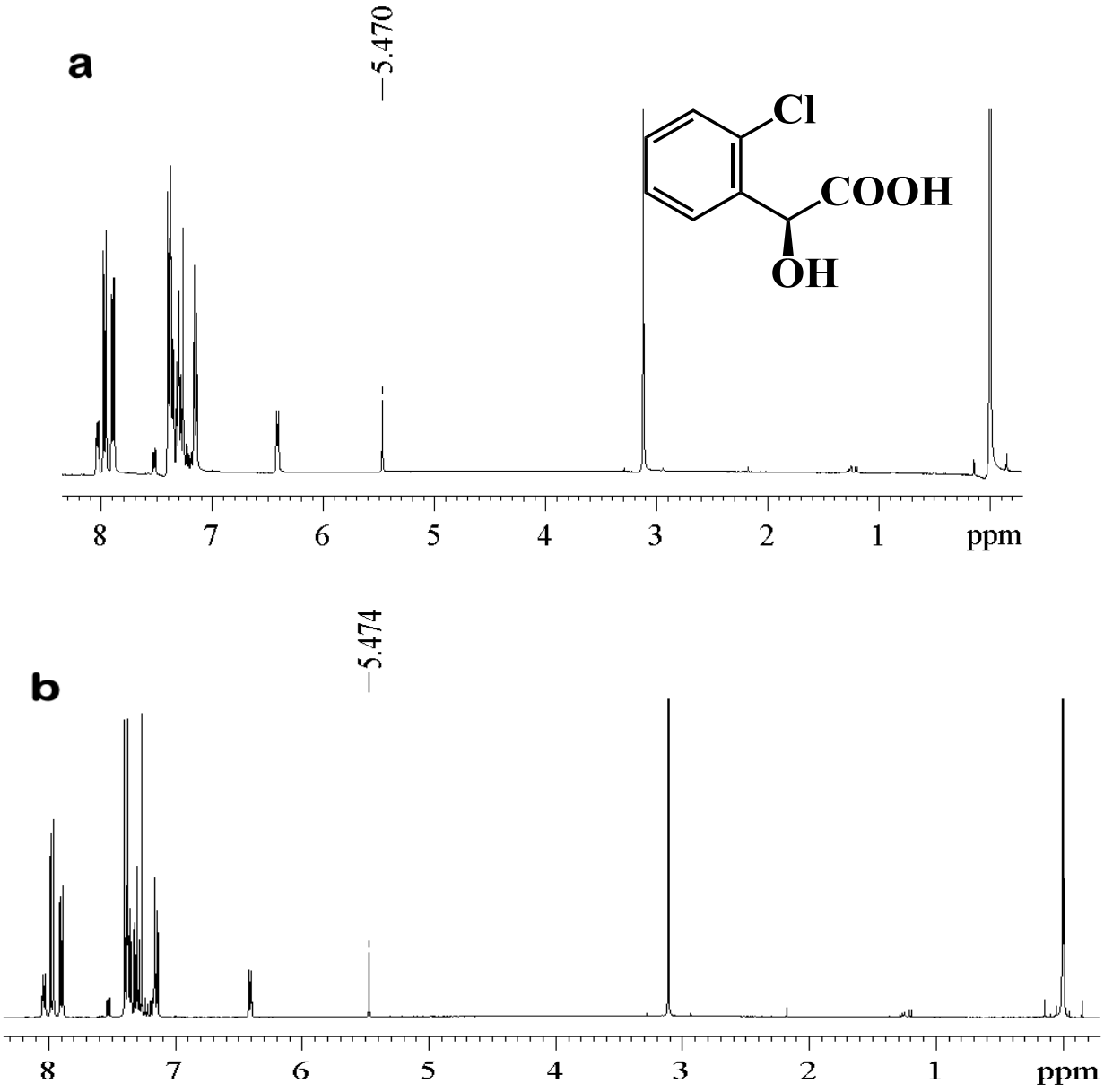
$^{1}$H NMR spectra of *S*-mandelic acid and DABCO at 298K in a) *R*-BINOL and b) *S*-BINOL



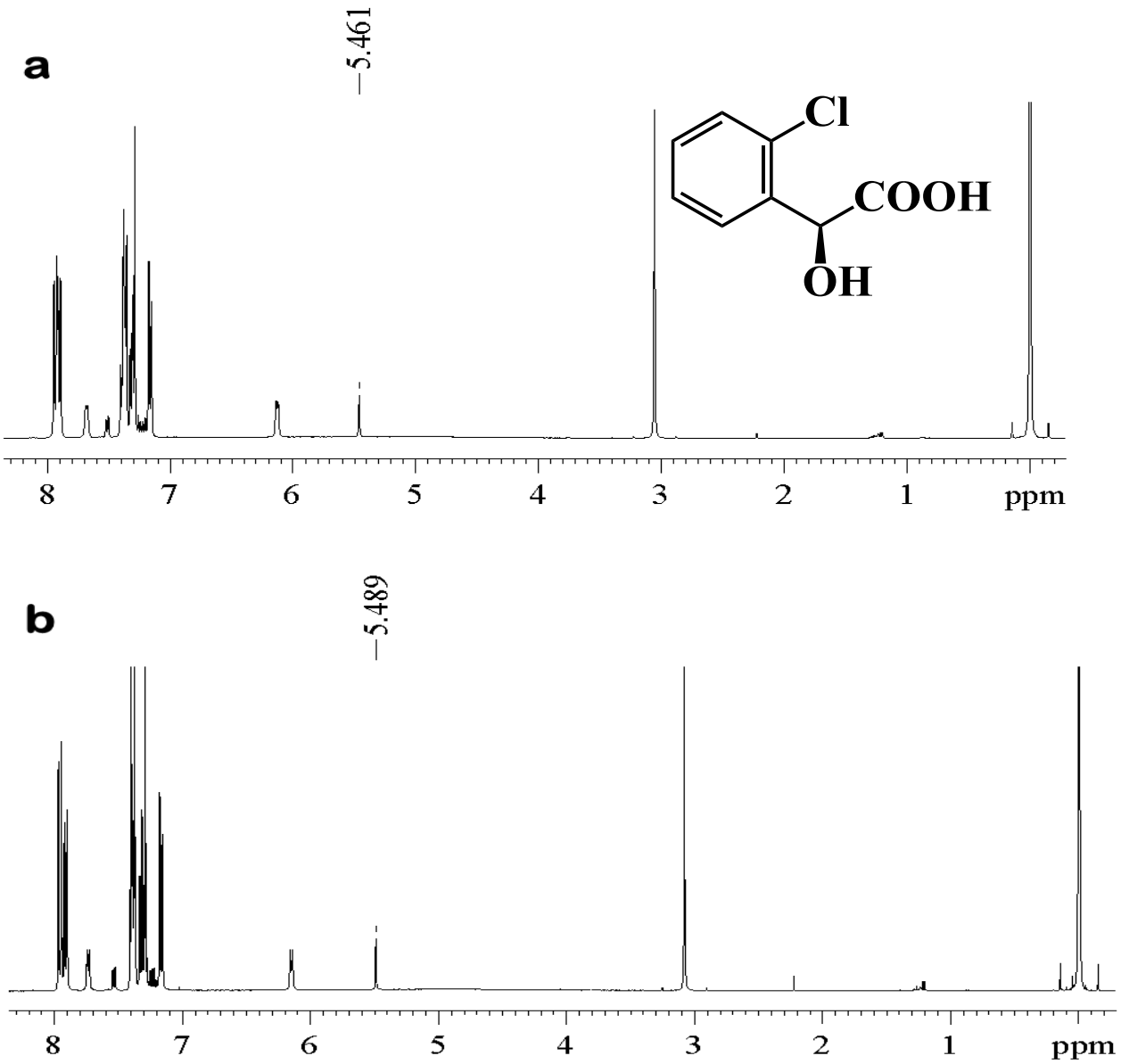
$^{1}$H NMR spectra of *S*-mandelic acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL



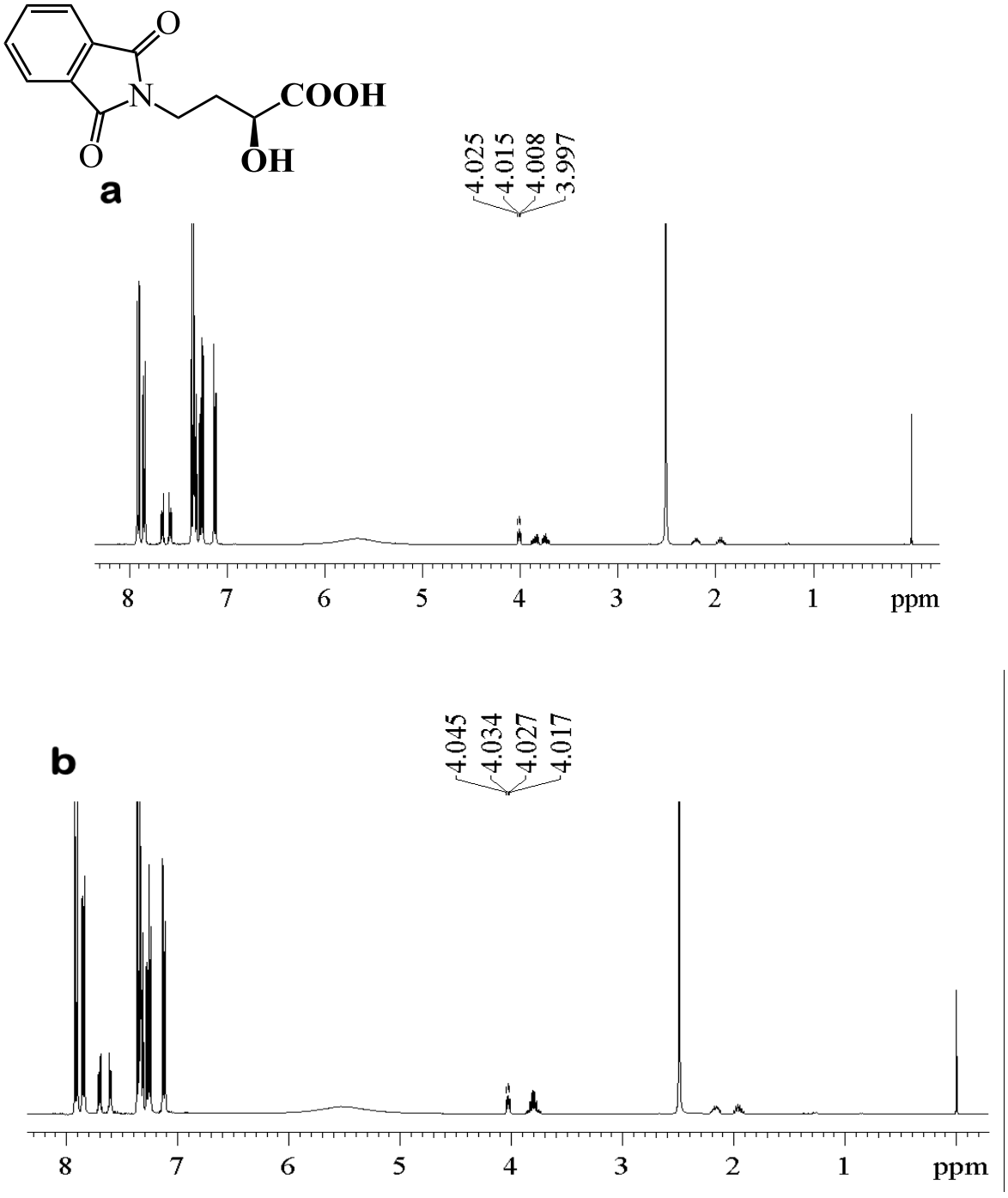
$^{1}$H NMR spectra of *S*-2-chloromandelic acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL



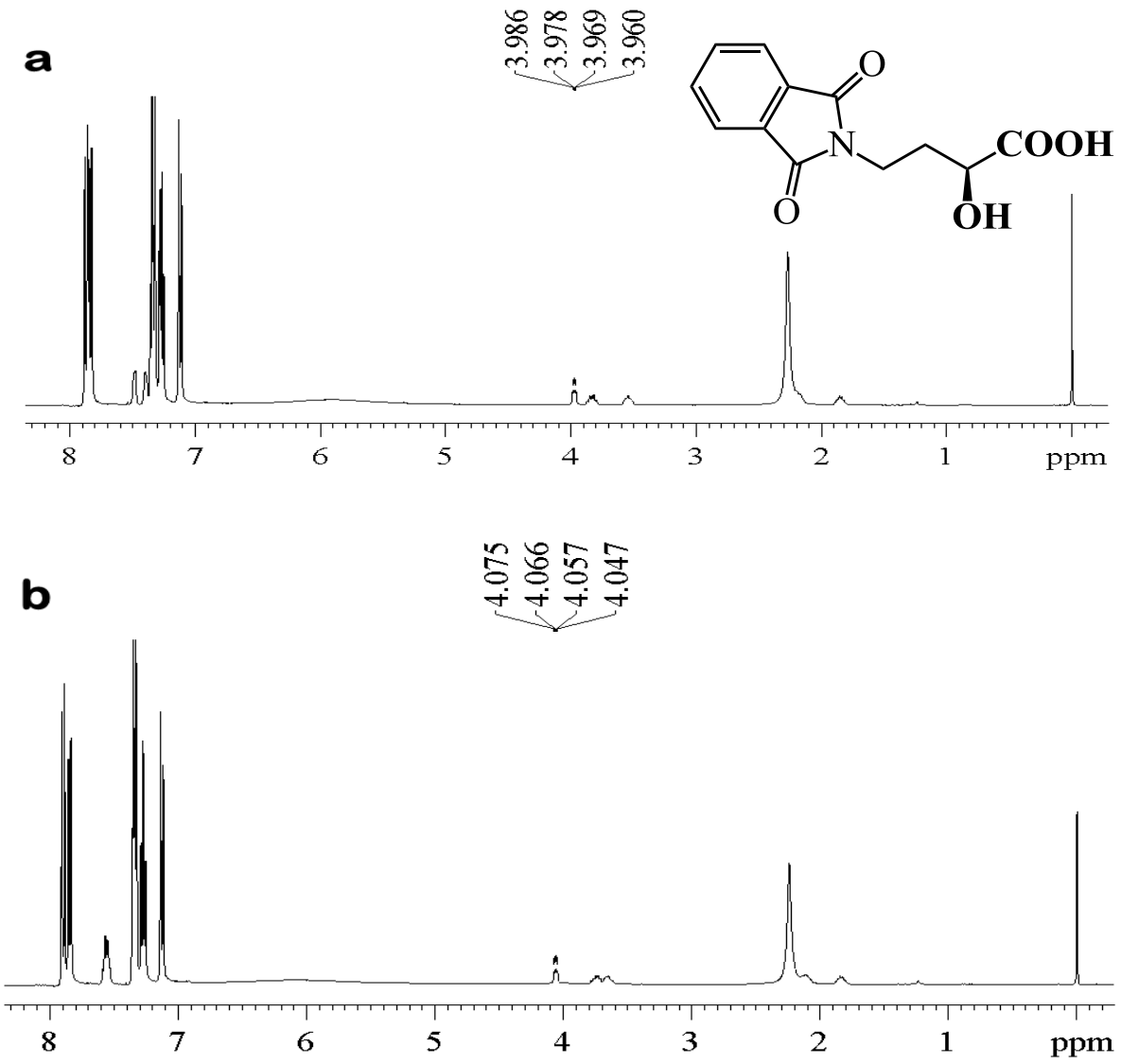
$^{1}$H NMR spectra of *S*-2-chloromandelic acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL



$^{1}$H NMR spectra of *S*-alpha-hydroxy-1,3-dioxo-2-isoindolinebutyric acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL

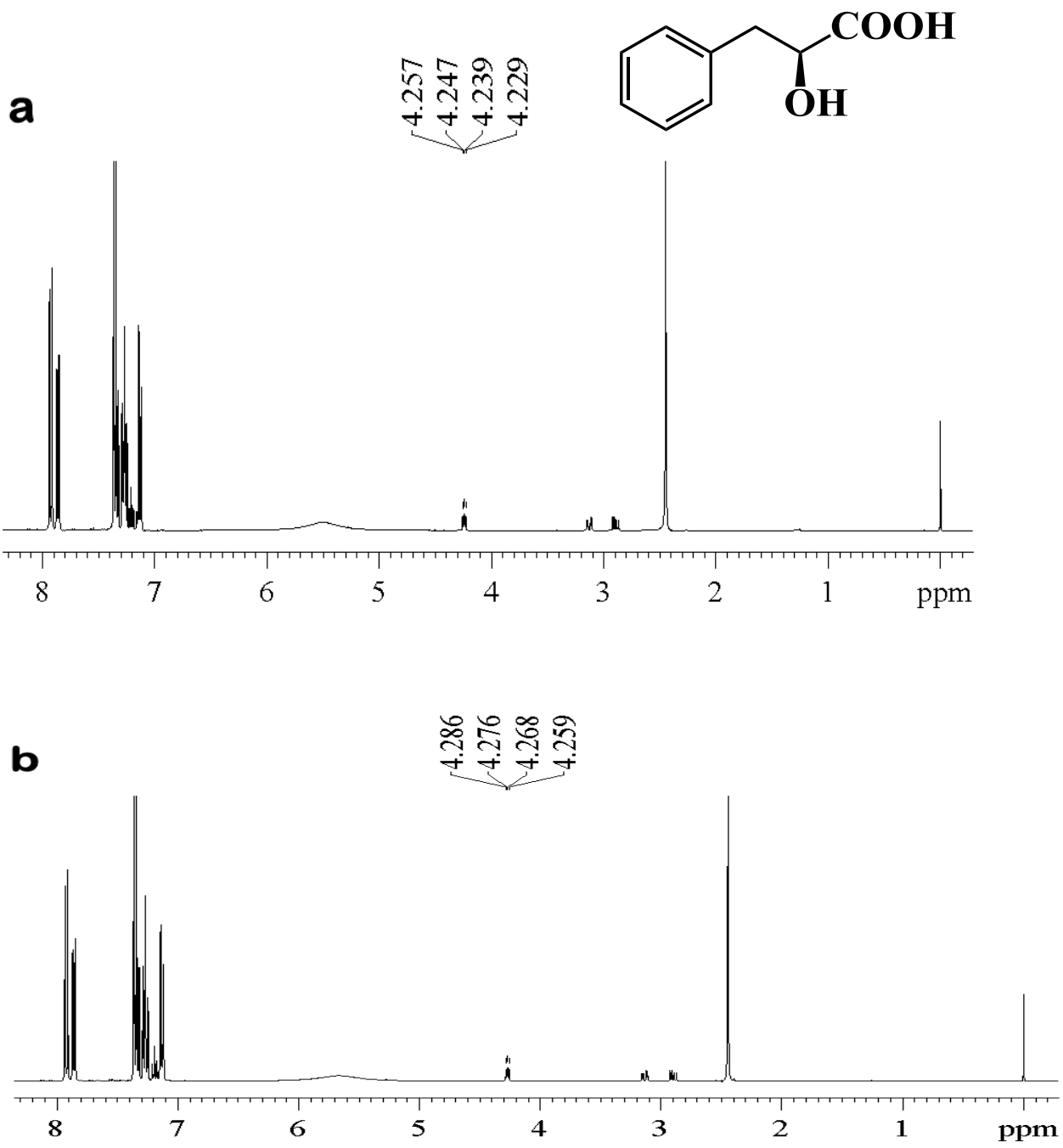


$^{1}$H NMR spectra of *S*-alpha-hydroxy-1,3-dioxo-2-isoindolinebutyric acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL

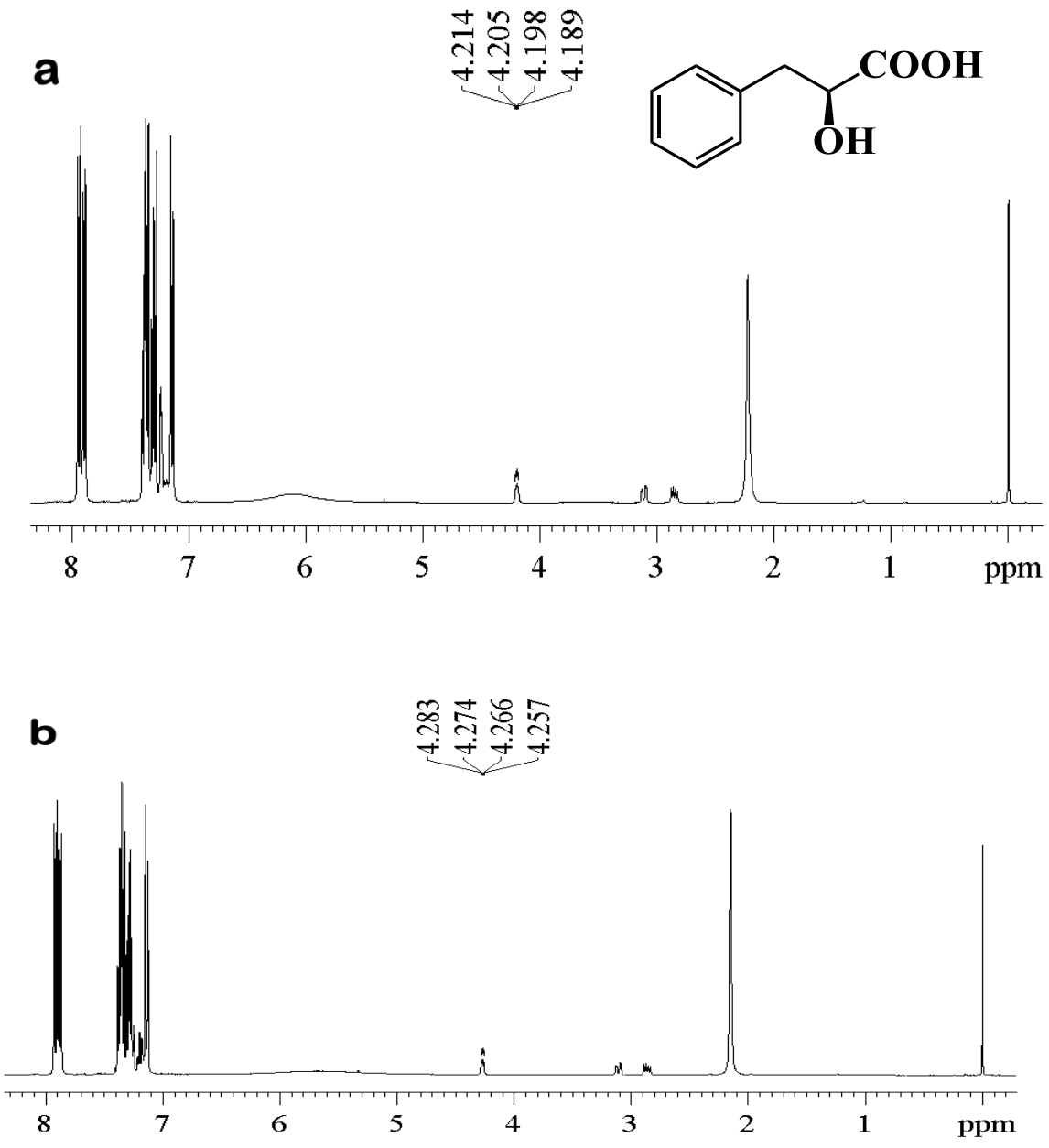



**S26**

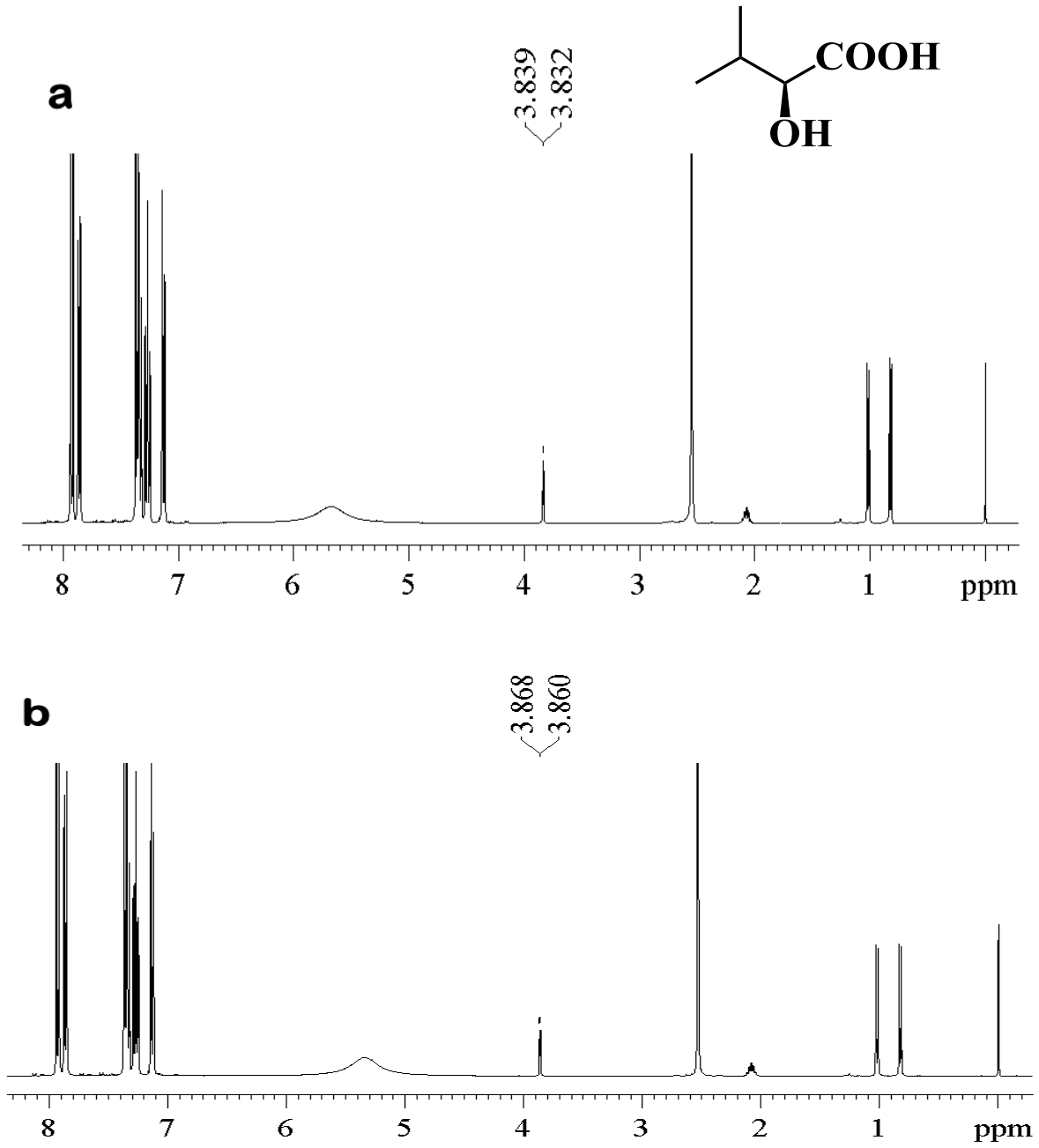
$^1$H NMR spectra of *L*-phenyllactic acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL



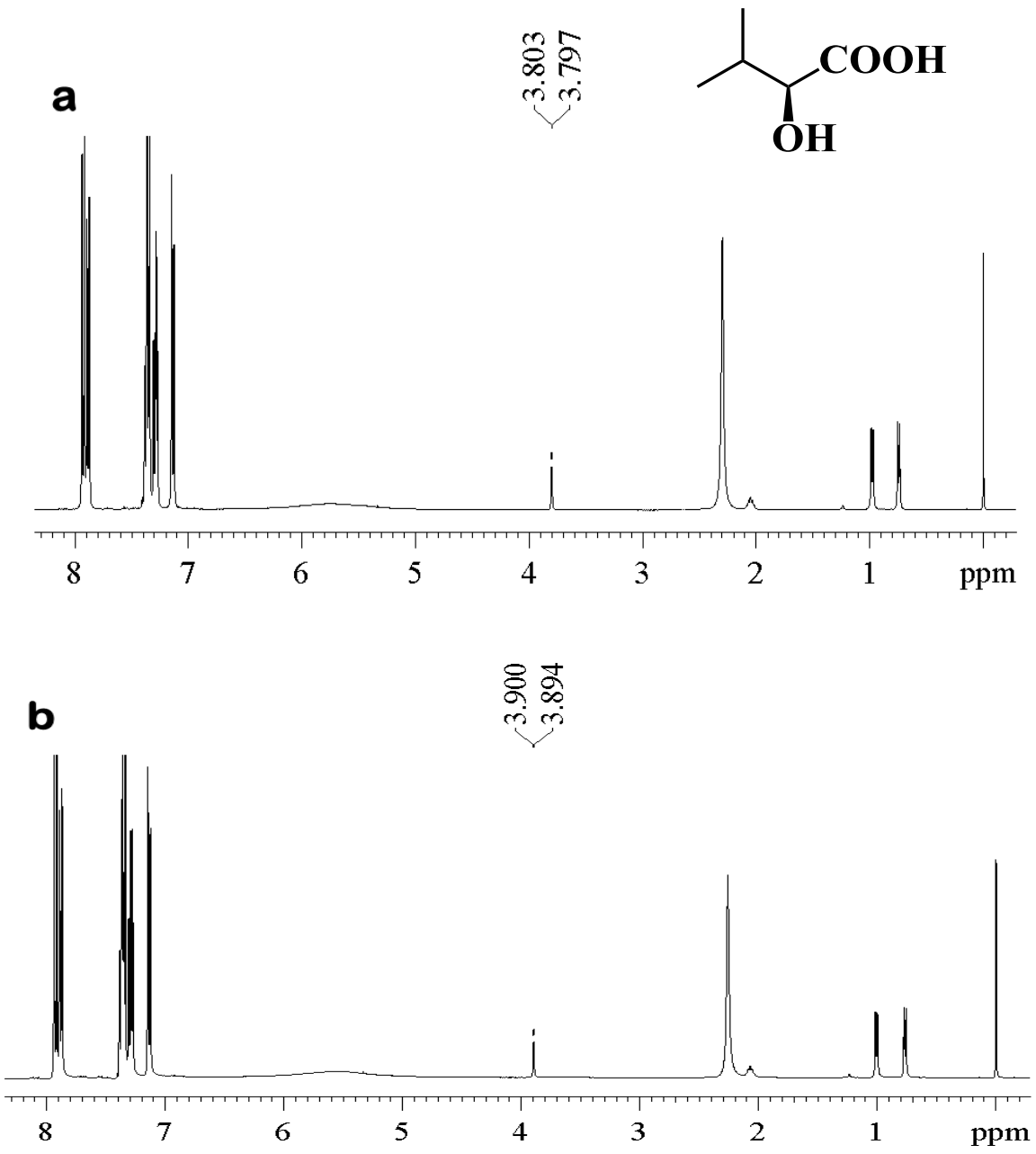
$^1$H NMR spectra of *L*-phenyllactic acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL



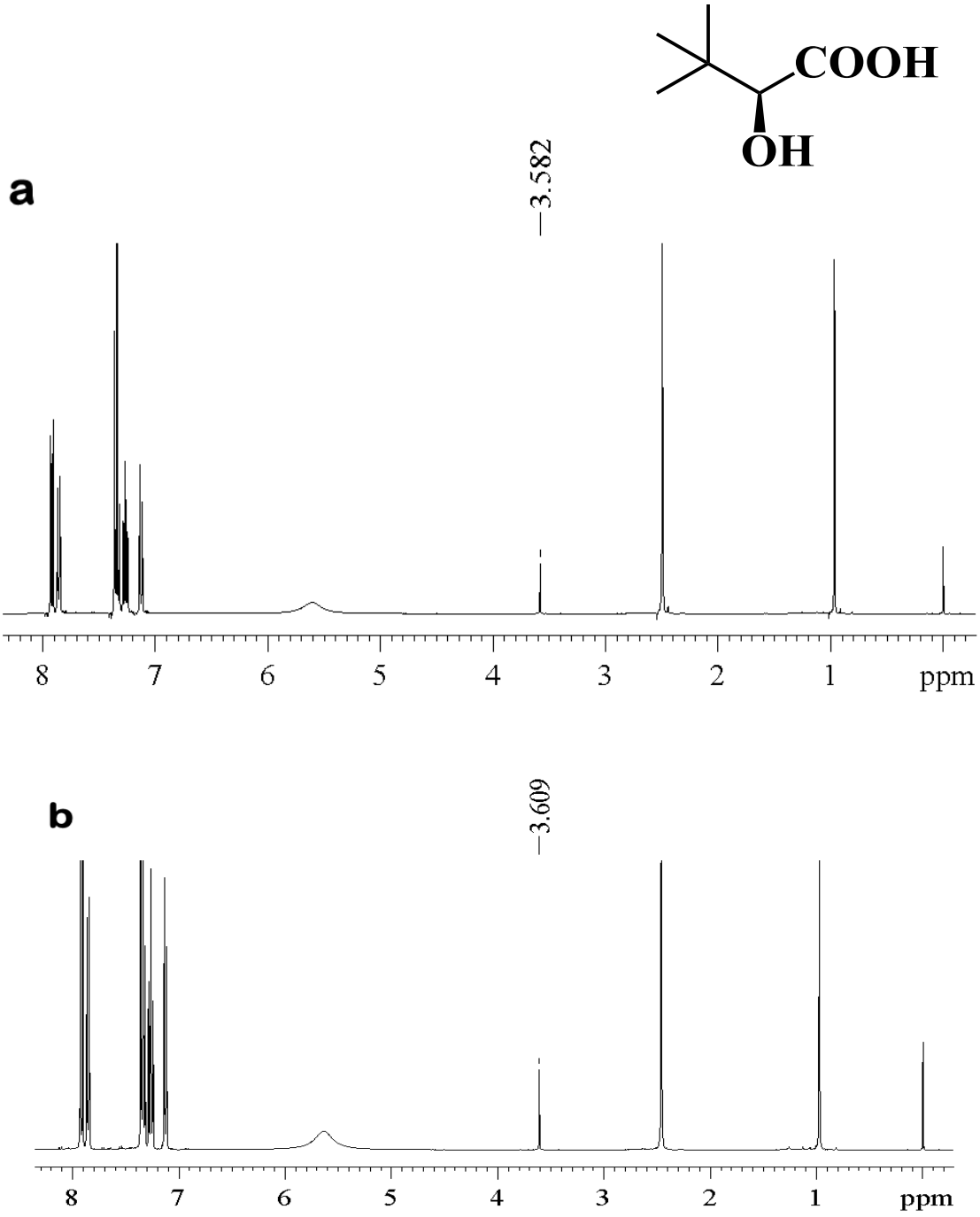
$^{1}$H NMR spectra of *S*-2-hydroxy-3-methylbutyric acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL



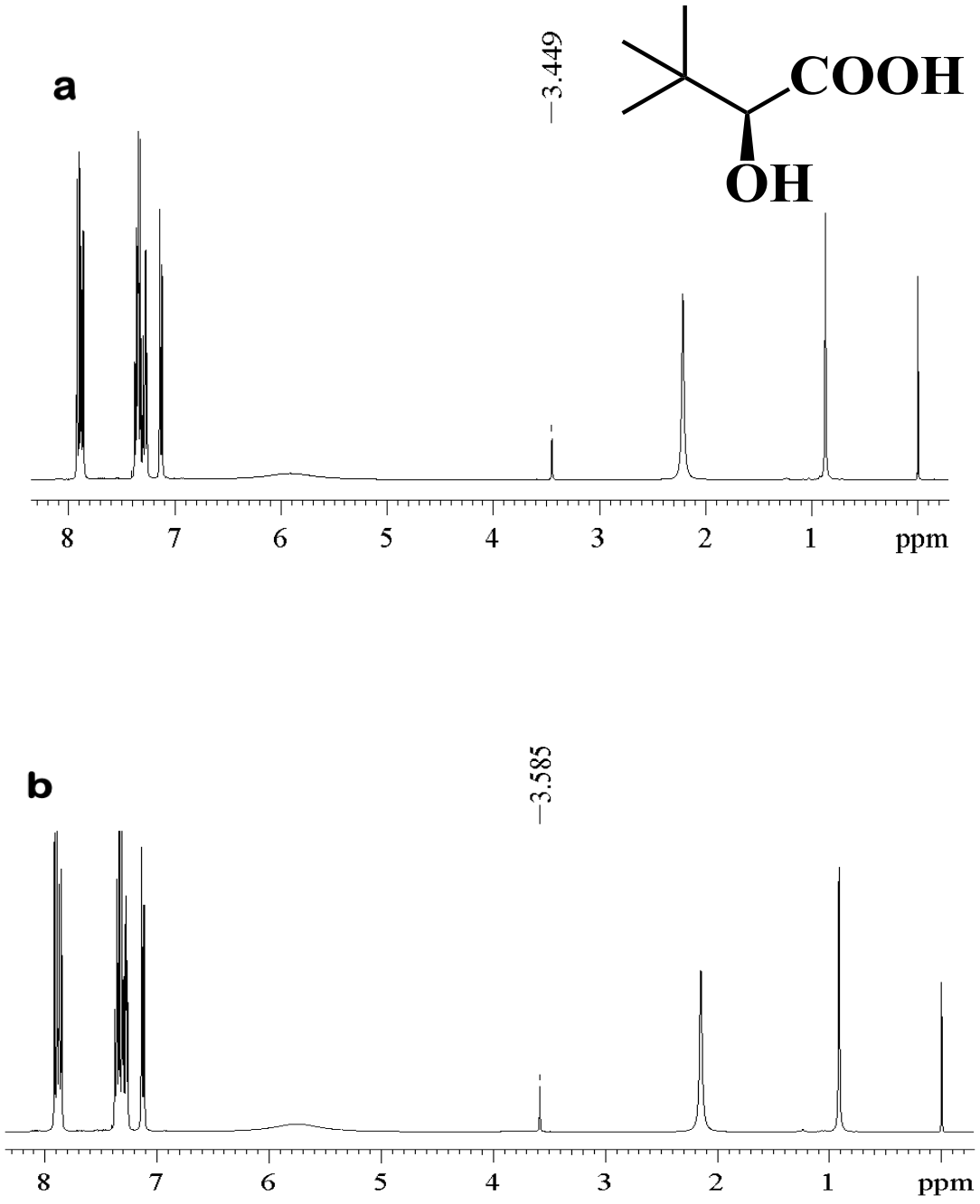
$^{1}$H NMR spectra of *S*-2-hydroxy-3-methylbutyric acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL



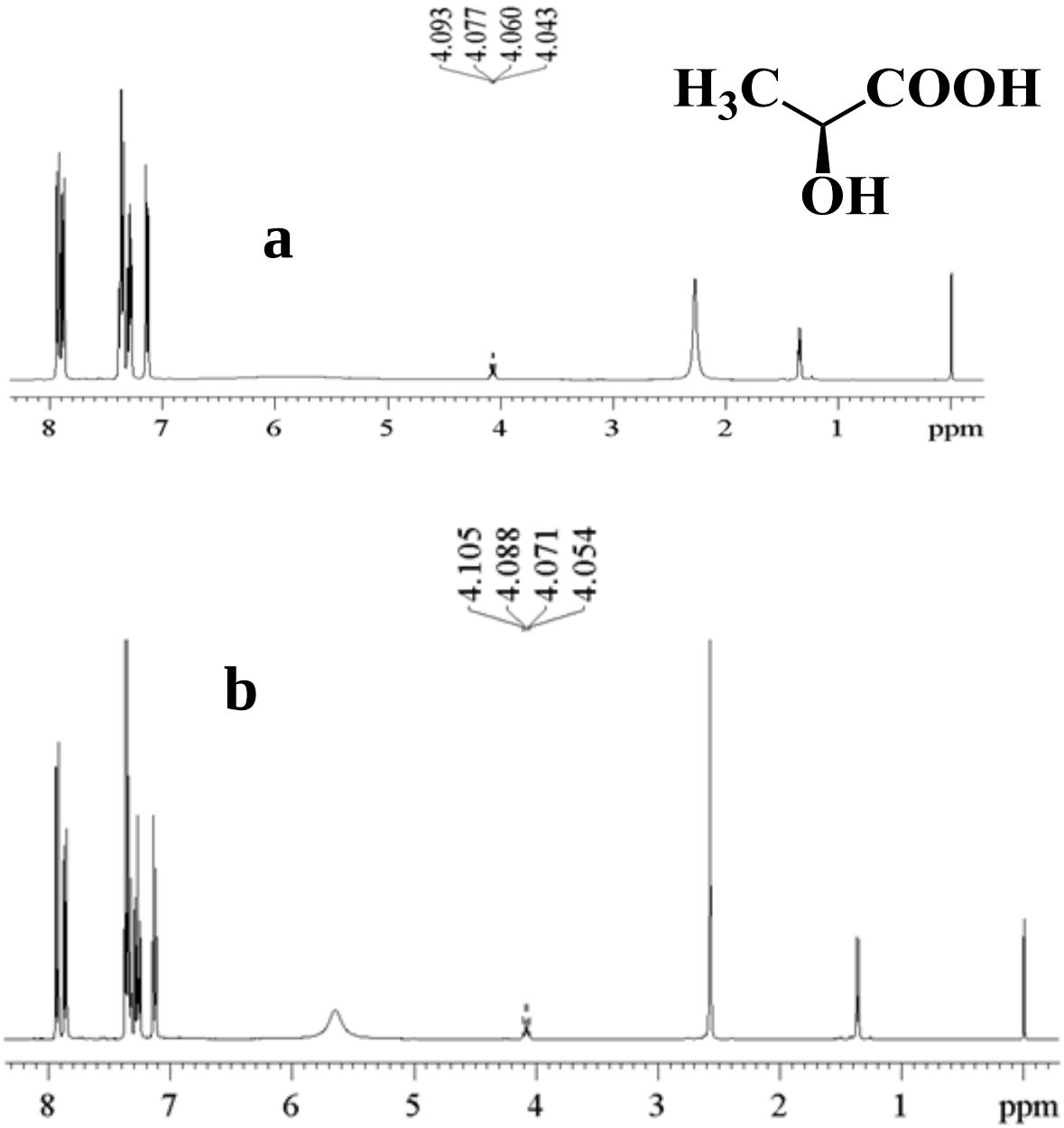
$^1$H NMR spectra of *S*-2-hydroxy-3,3-dimethylbutyric acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL



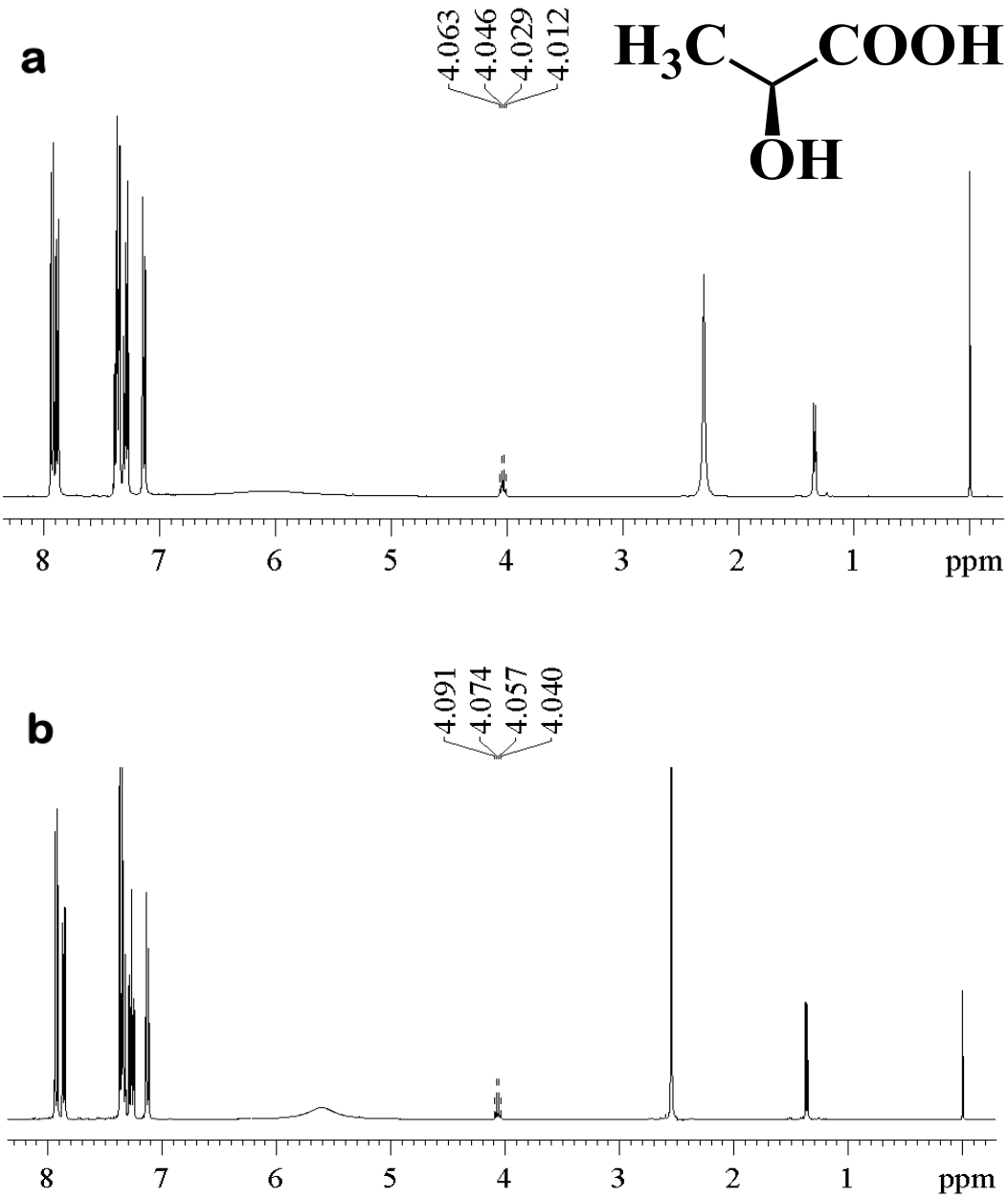
$^{1}$H NMR spectra of *S*-2-hydroxy-3,3-dimethylbutyric acid and DABCO at 240 K in a) *R*-BINOL and b) *S*-BINOL



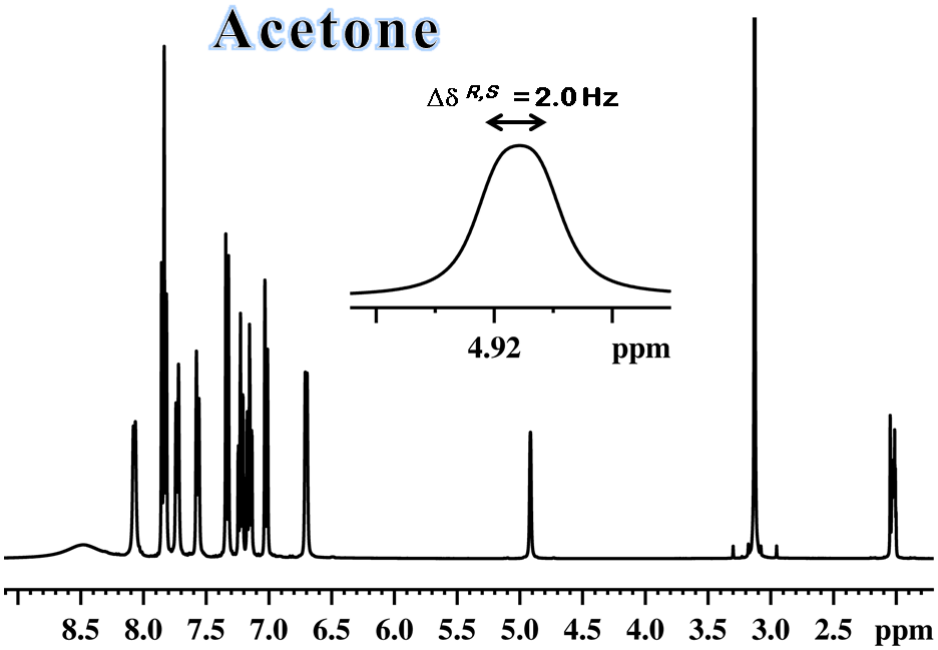
$^{1}$H NMR spectra of *L*-lactic acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL



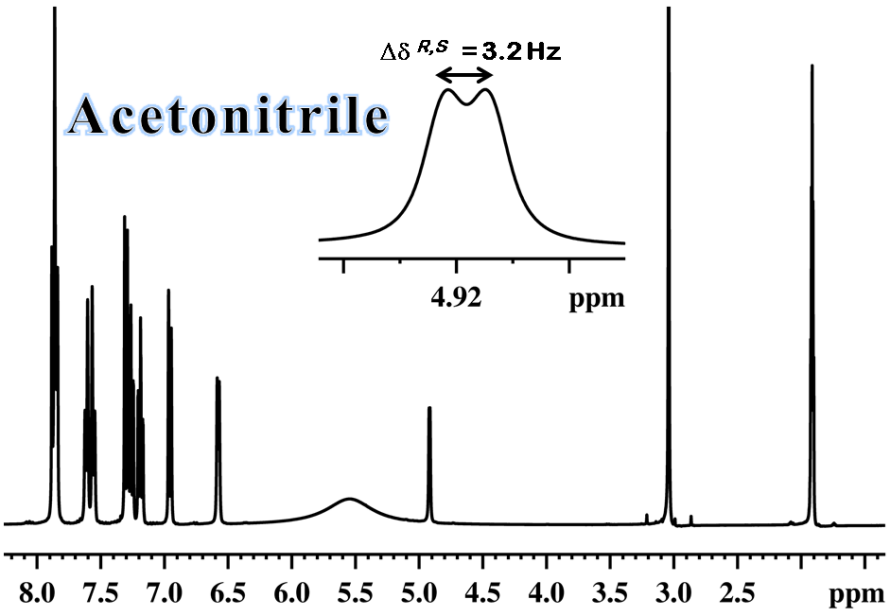
$^{1}$H NMR spectra of *L*-lactic acid and DABCO at 298 K in a) *R*-BINOL and b) *S*-BINOL



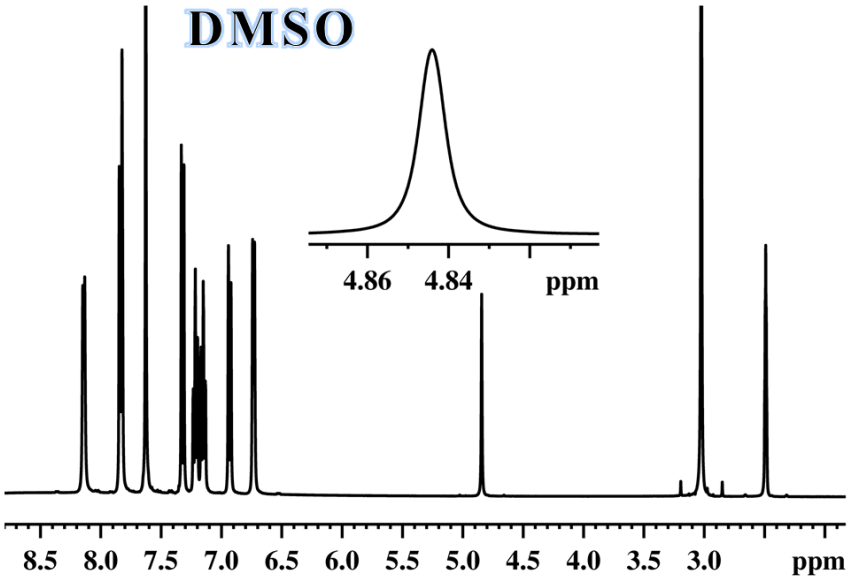
$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent Acetone-$D_6$



$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent Acetonitrile-$D_3$

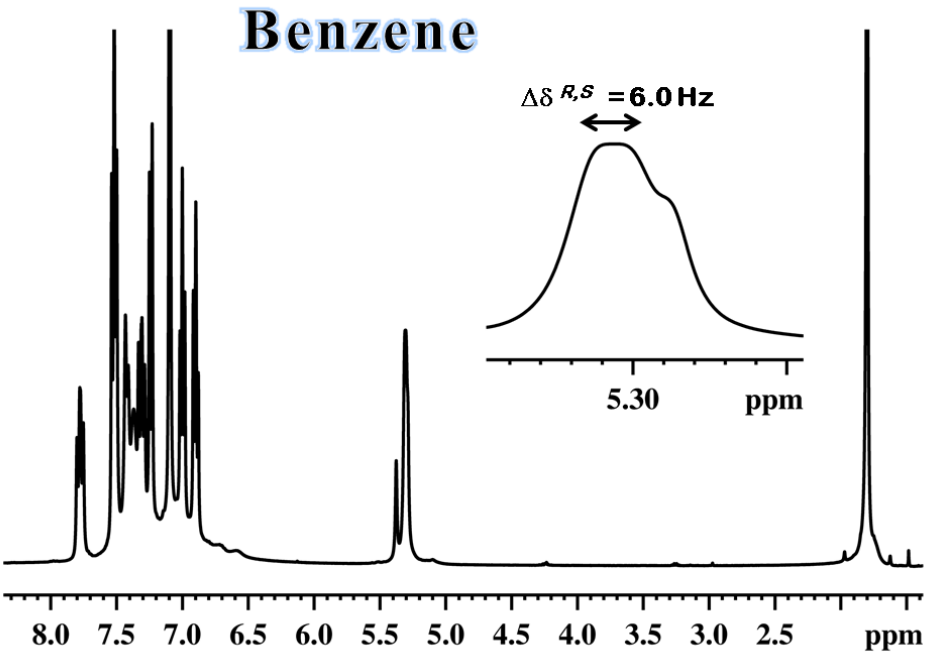


$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent DMSO-$D_6$

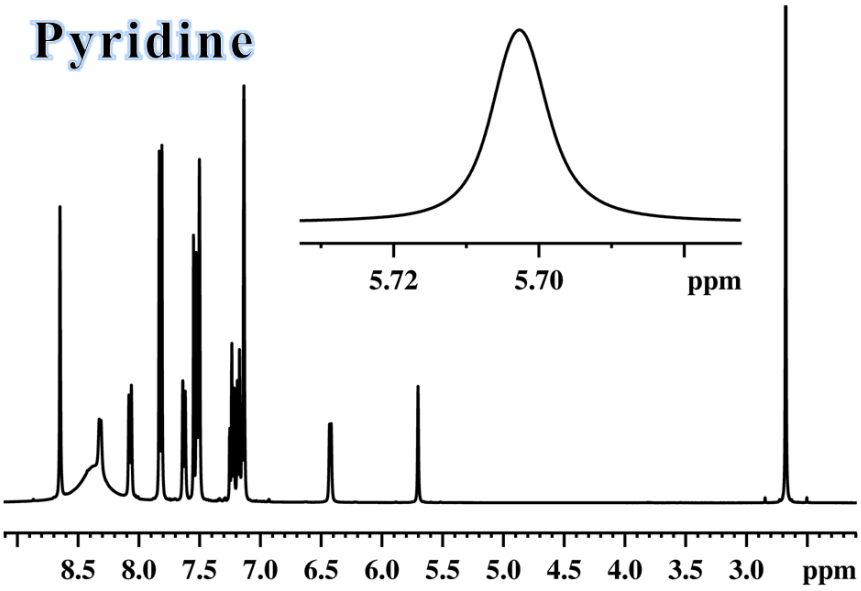



# S37

$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent benzene-$D_6$

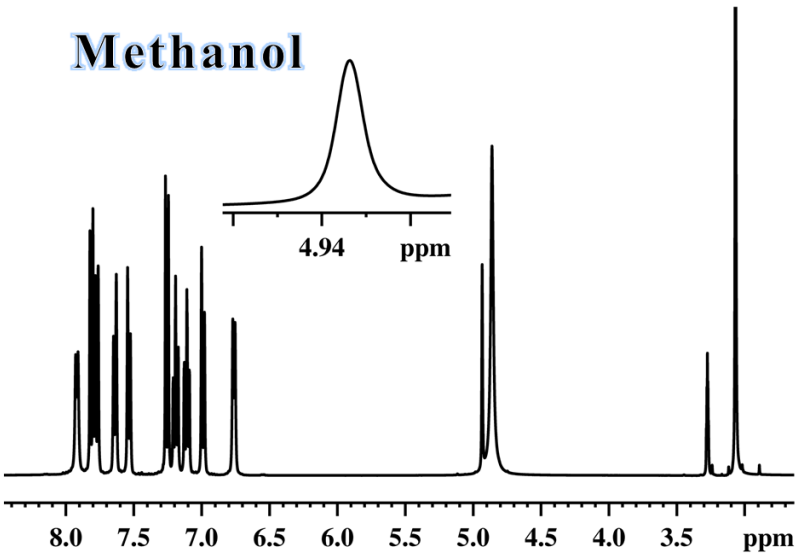


$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent Pyridine-$D_5$



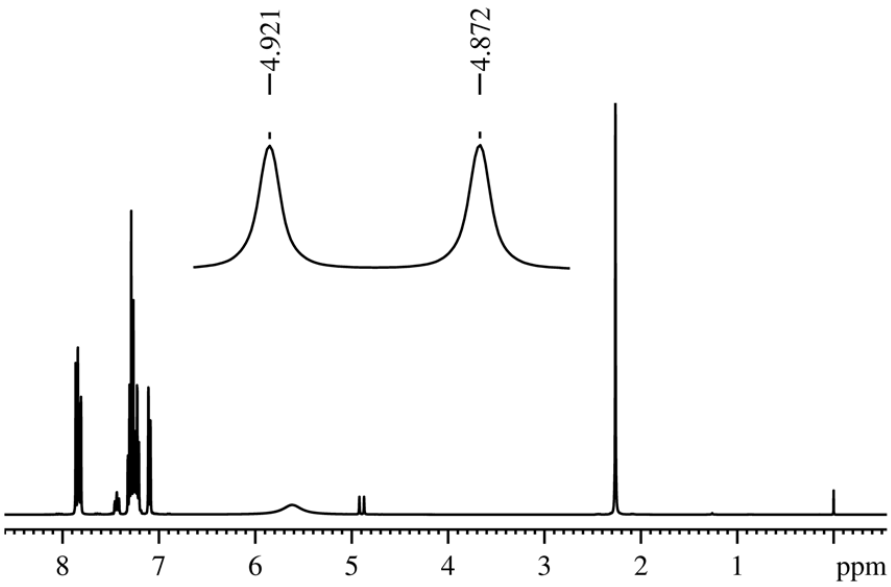

**S39**

$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent Methanol-$D_4$



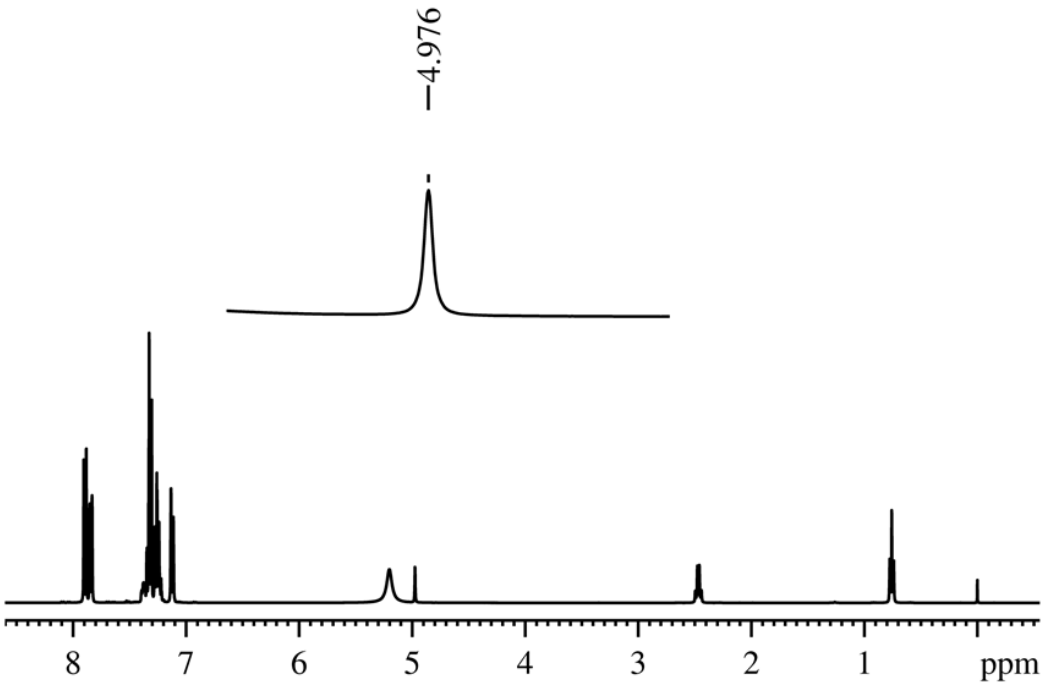

# S40

$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DABCO at 298 K in the solvent $CDCl_3$




**S41**

$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and TEA at 298 K in the solvent $CDCl_3$




**S42**

$^{1}$H-NMR spectrum of racemic mixture of mandelic acid with one equivalent of *R*-BINOL and DMAP at 298 K in the solvent $CDCl_3$