Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

for

Molecular Interactions in the Ionic liquid Emim Acetate and Water Binary Mixtures Probed via NMR Spin Relaxation and Exchange Spectroscopy

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Table S1. Example iterative calculation of rotational correlation time

Iteration	Relaxation Time T_1	tc for goalseek	tc by formula	C/D*10^6 Unity *10^6	NOE max	NOE Factor	tc in ps
0	0.87	1.25E-09	1.25E-09	1000000	18.00	0.043	1251.30
1	20.00	7.91E-11	7.91E-11	1000000	20.02	0.039	79.08
2	22.25	7.11E-11	7.11E-11	1000000	20.05	0.039	71.12
3	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
4	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
5	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
6	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
7	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
8	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
9	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
10	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
11	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
12	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
13	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
14	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
15	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
16	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
17	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
18	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
19	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
20	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
21	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
22	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
23	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
24	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
25	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
26	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
27	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
28	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
29	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
30	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
31	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
32	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
33	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
34	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
35	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03
36	22.28	7.10E-11	7.10E-11	1000000	20.05	0.039	71.03

T_1 is highlighted as it is a measured value.

Table S2. Constants used for rotational correlation time calculations

parameter	value	Units	Alternative Units
uo=	1.2566E-06	Vs/Am	volt second/ampere meter
yC=	67262000	rad/sT	radians per second tesla
yH=	267513000	rad/sT	radians per second tesla
rij=	1.09E-10	meters	
h=	-1.055E-34	Joule seconds	
B	14.1 T	Tesla	
Dij	23320.1745	rad/s	
NH	3	Unitless	
NOE factor	0.45333333	Unitless	
wC	150941752	Hz	
wH	600322337 Hz	Hz	

NH and NOE factor are highlighted in yellow due to their being variable (NH is the number of attached protons) and measured (NOE factor) respectively. The assumptions are made in this calculation that T1 is entirely dipolar, and that the C-H bond length of 1.09 angstroms. h is the reduced planck constant, the dipolar coupling constant, Dij=(uo/4pi)yCyH(h/2pi)rij^-3; uo is the permeability of the vacuum; yC and yH are magnetogyric ratios of the 13C and 1H nuclei; and rij is the length of the internuclear vector between i and j.

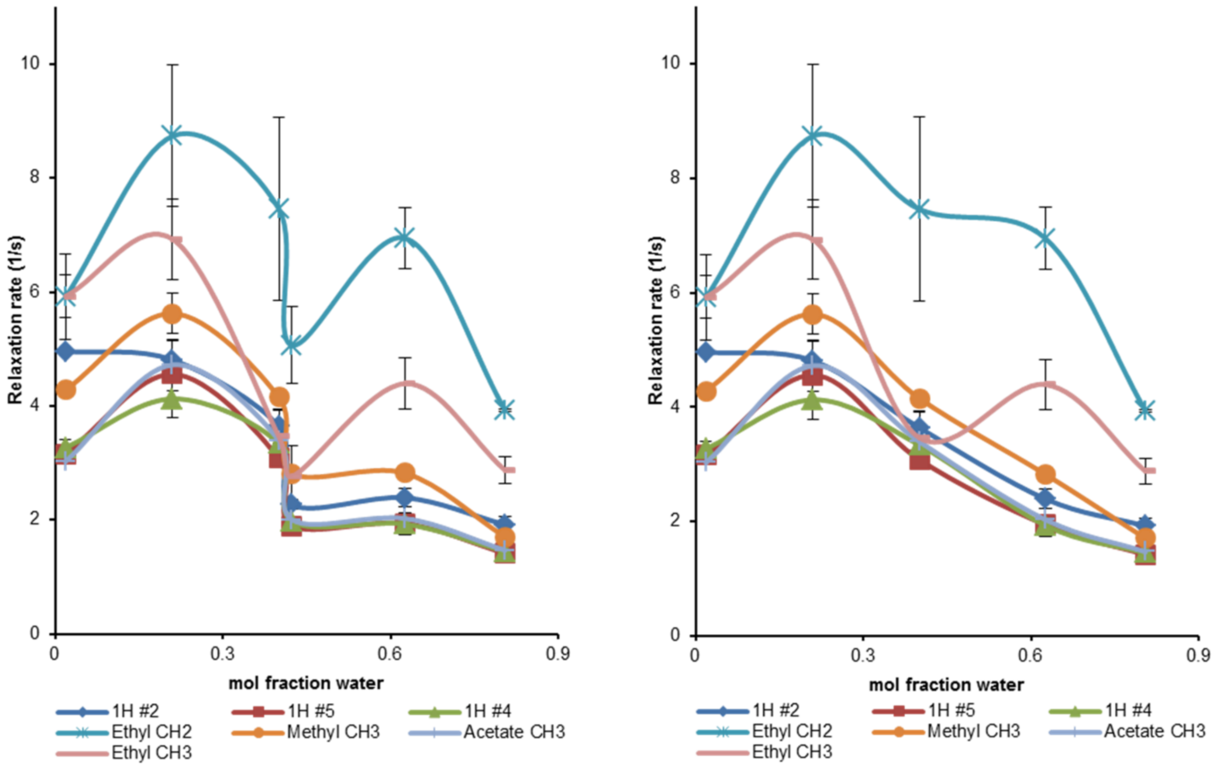


Figure S1. 1H R2 spin-spin relaxation rates as a function of emim acetate to water molar ratio show a peak in relaxation rates at ~20 mol% water (right). This is attributed to the competing effects of changes in viscosity and the propensity for water to cause dipolar relaxation with neighboring molecules. On the left, a dip in the graph is clearly seen with the 42 mol% water sample, showing the change in dynamics that occurs at this concentration. The ethyl CH_2 and CH_3 are seen to have faster than expected relaxation dynamics.

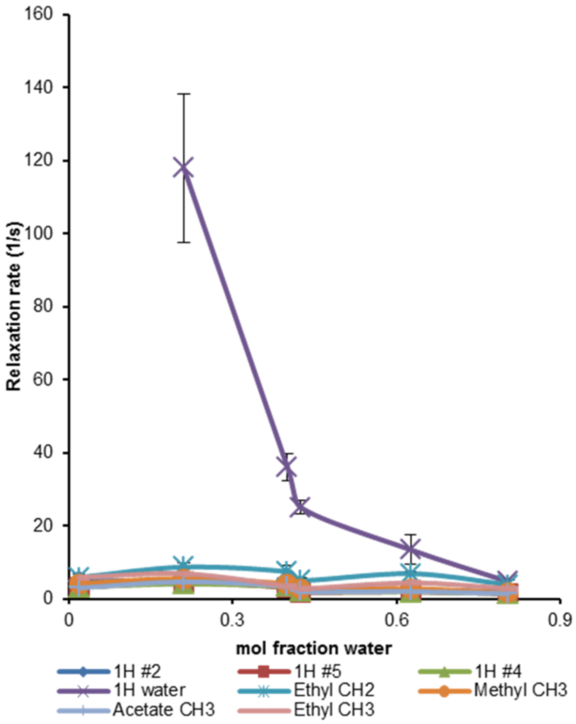
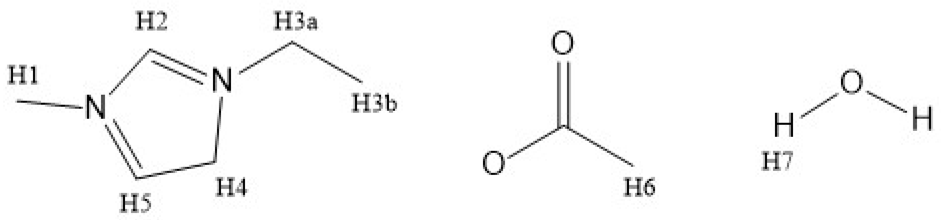


Figure S2. 1H R2 spin-spin relaxation rates as a function of emim acetate to water molar ratio show very fast relaxation of water.



Scheme S1. Numbering scheme used in labelling of ^{1}H NMR spectra.

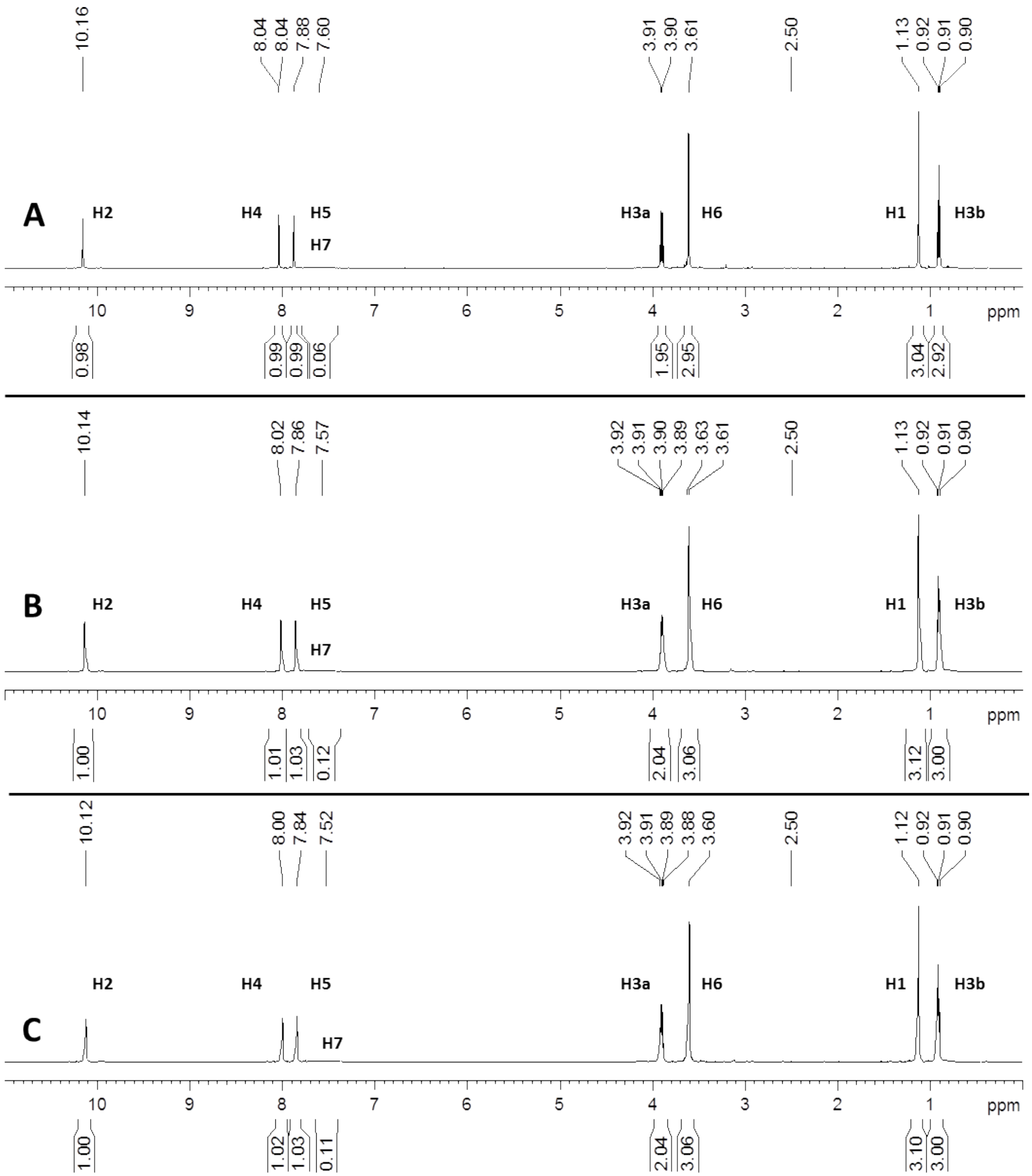


Figure S3. 1D ^{1}H NMR spectra of the 0.05 mole fraction water sample at (A) 60°C, (B) 70°C, and (C) 80°C. Peaks are labelled as in Scheme S1.

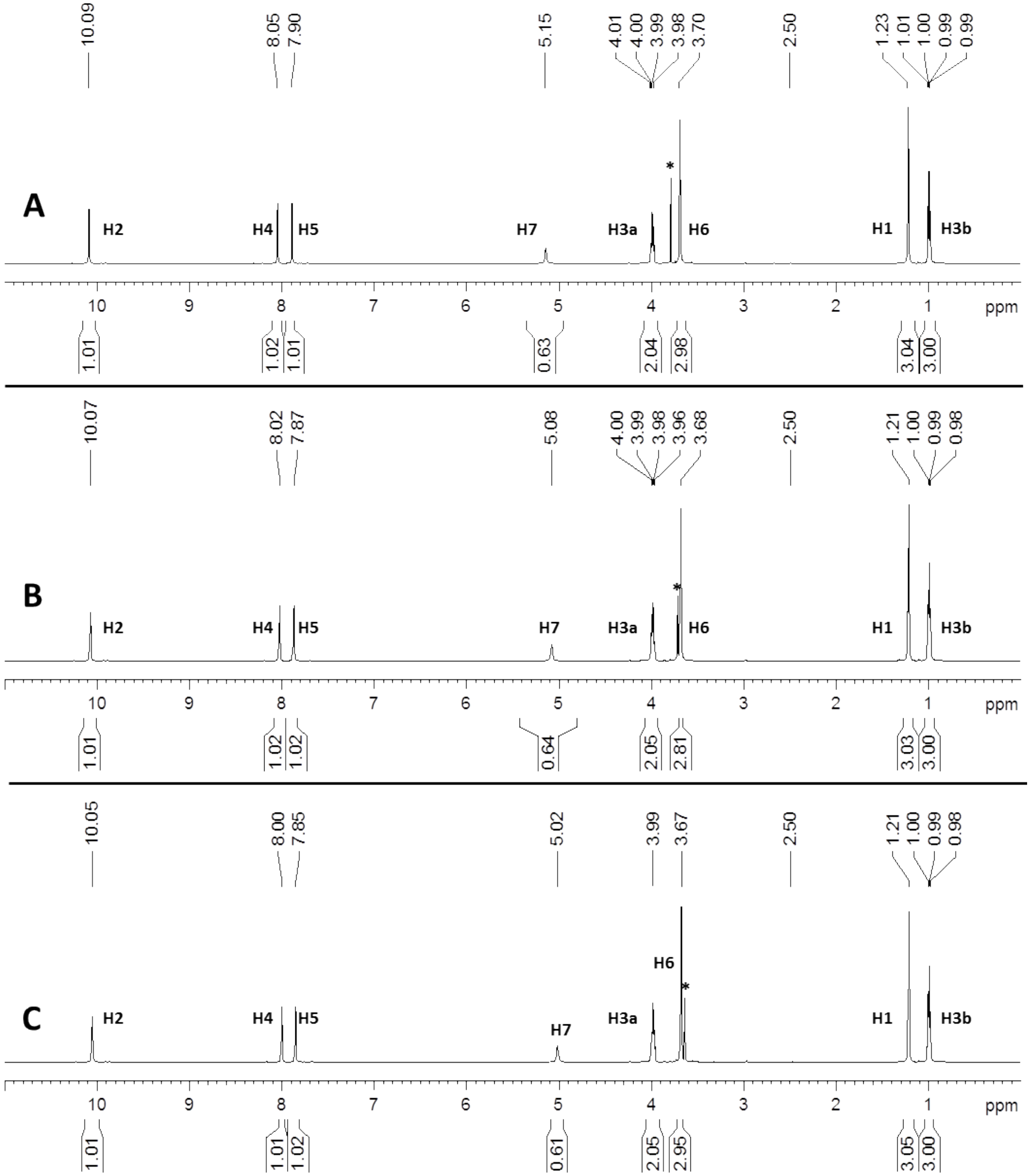


Figure S4. 1D ^{1}H NMR spectra of the 0.24 mole fraction water sample at (A) 60°C, (B) 70°C, and (C) 80°C. Peaks are labelled according to Scheme S1. The asterisk indicates an impurity in the sealed capillary containing DMSO-d_6, most likely water absorbed from the atmosphere. This impurity was confirmed to be present only in the sealed capillary by repeating the experiment with the capillary outside of the receiver region of the NMR probe (via inverting and then righting the NMR tube so that the capillary was "stuck" to the upper wall of the tube.)

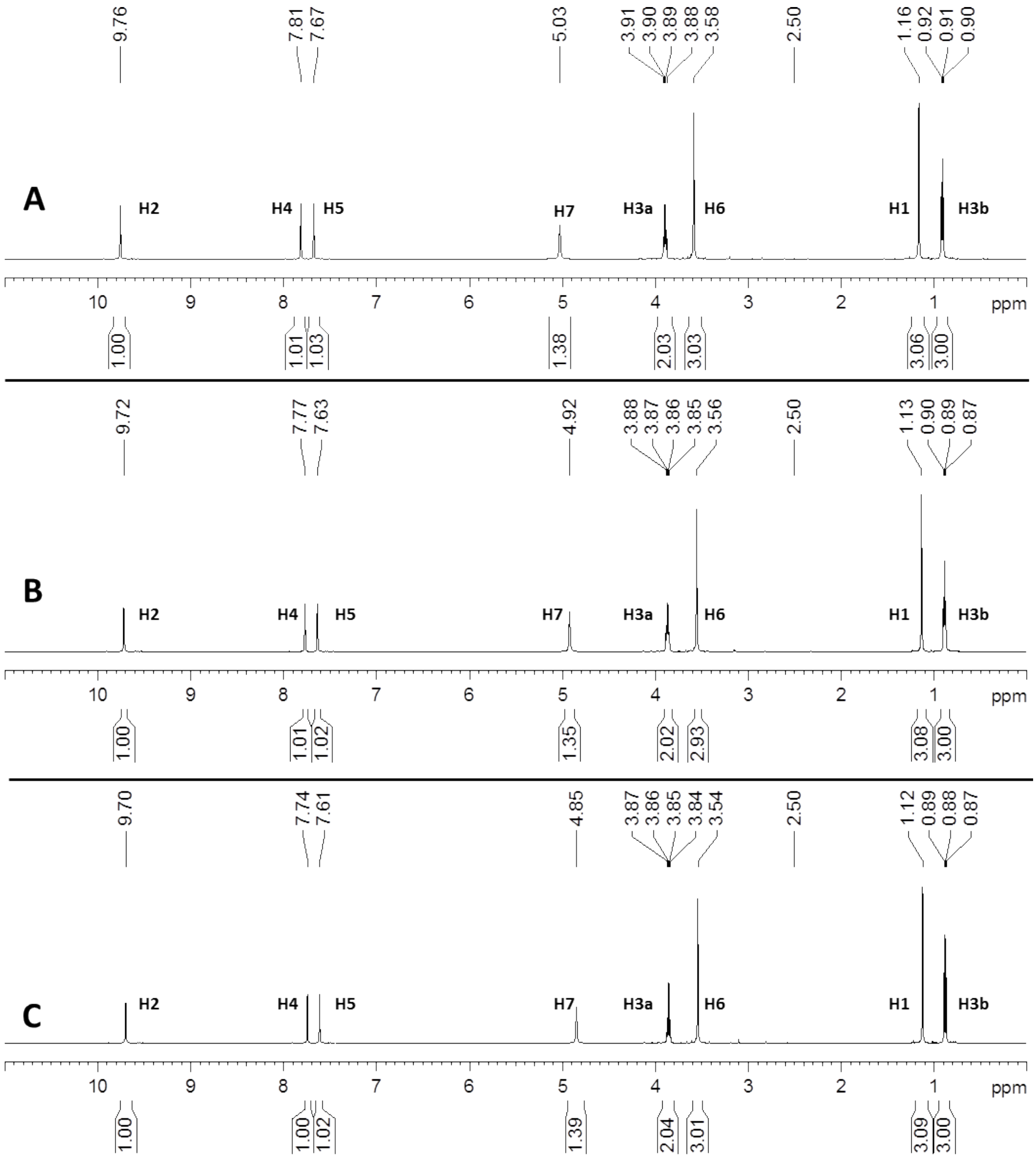


Figure S5. 1D ^{1}H NMR spectra of the 0.40 mole fraction water sample at (A) 60°C, (B) 70°C, and (C) 80°C. Peaks are labelled as in Scheme S1.

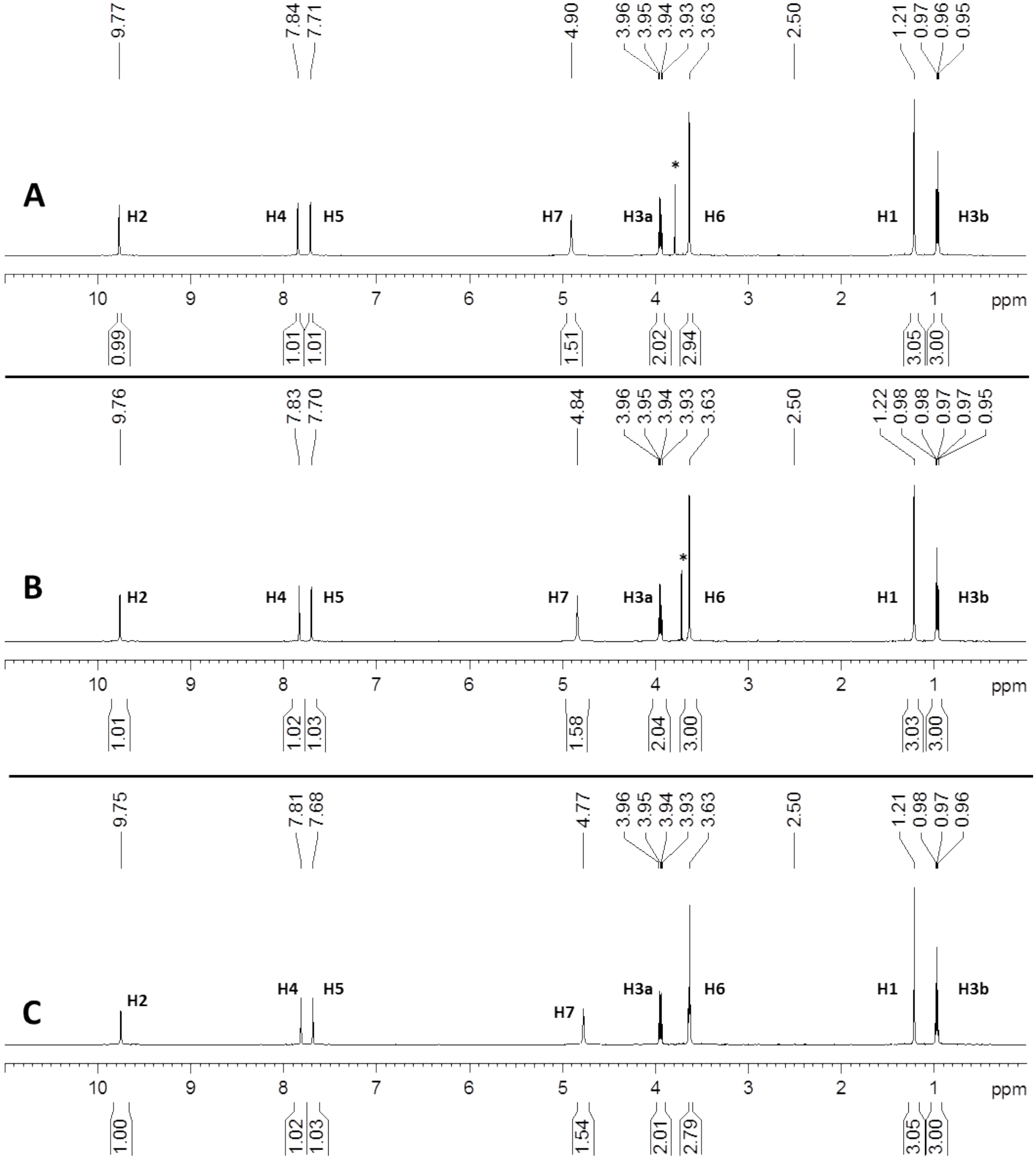


Figure S6. 1D ^{1}H NMR spectra of the 0.43 mole fraction water sample at (A) 60°C, (B) 70°C, and (C) 80°C. The asterisk indicates an impurity in the sealed capillary containing DMSO-d6, most likely water absorbed from the atmosphere. This impurity was confirmed to be present only in the sealed capillary by repeating the experiment with the capillary outside of the receiver region of the NMR probe (via inverting and then righting the NMR tube so that the capillary was “stuck” to the upper wall of the tube.)

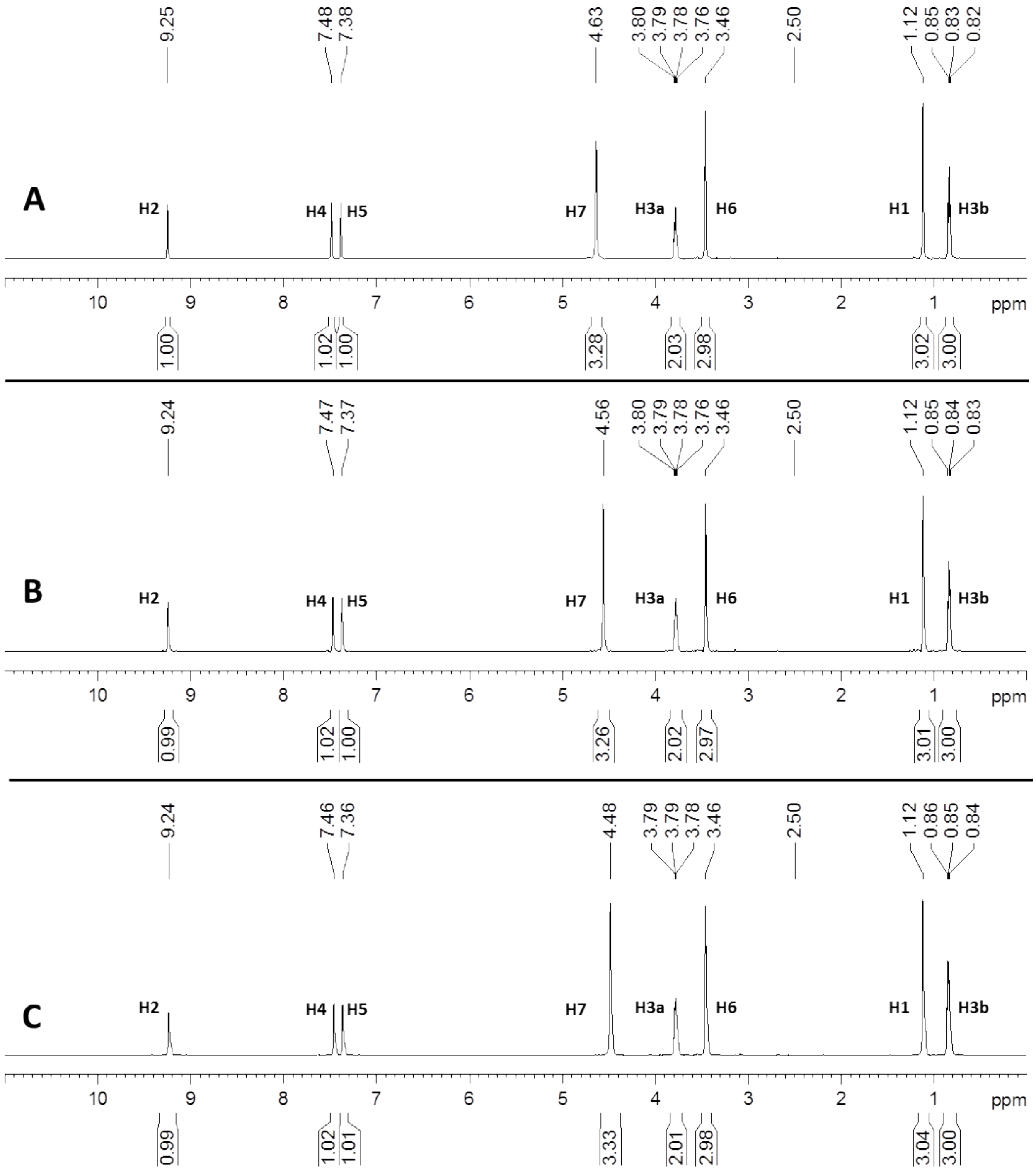


Figure S7. 1D ^{1}H NMR spectra of the 0.62 mole fraction water sample at (A) 60°C, (B) 70°C, and (C) 80°C. Peak labelling is as in Scheme S1.

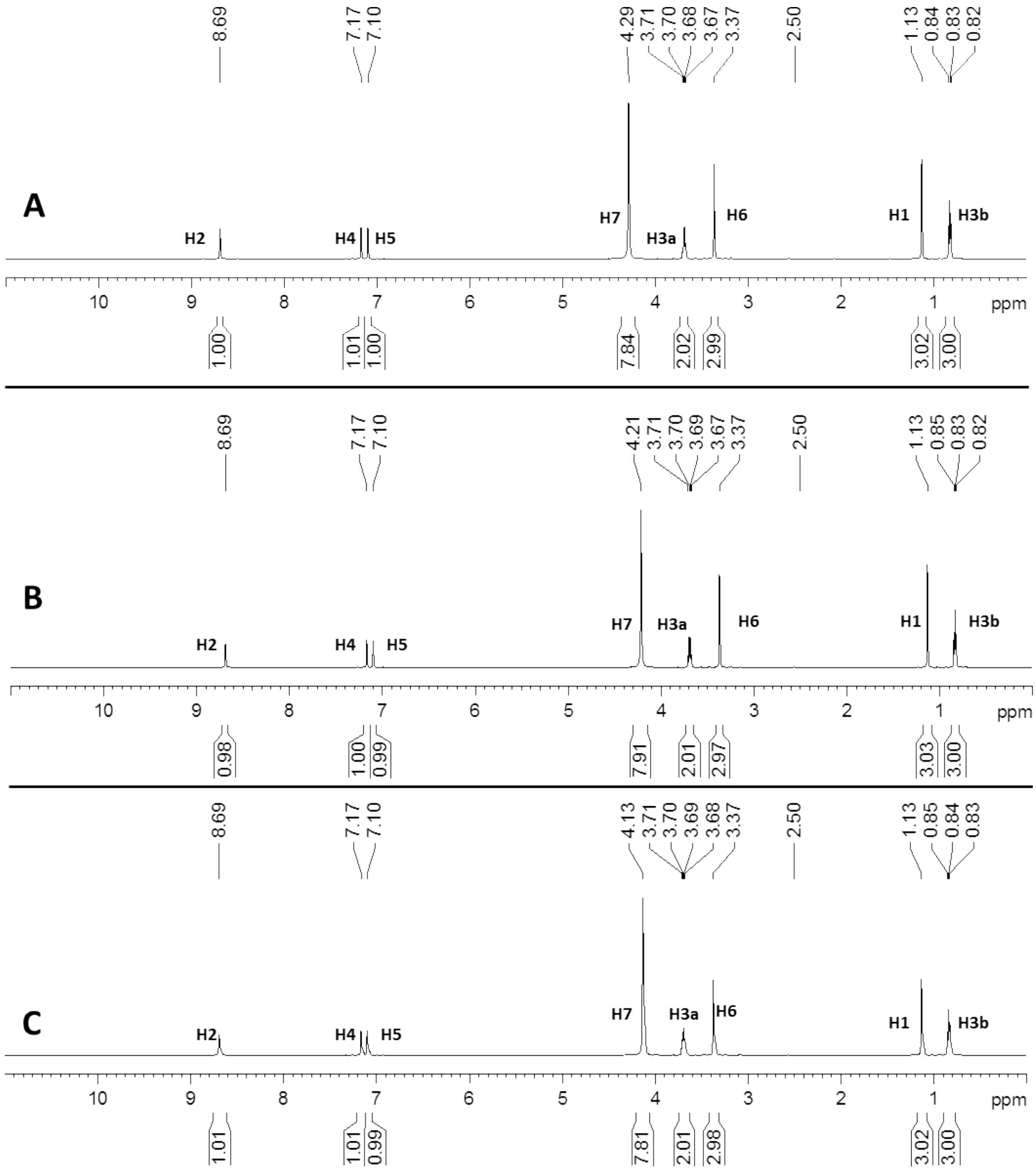


Figure S8. 1D ^{1}H NMR spectra of the 0.79 mole fraction water sample at (A) 60°C, (B) 70°C, and (C) 80°C. Peaks are labelled as in Scheme S1.

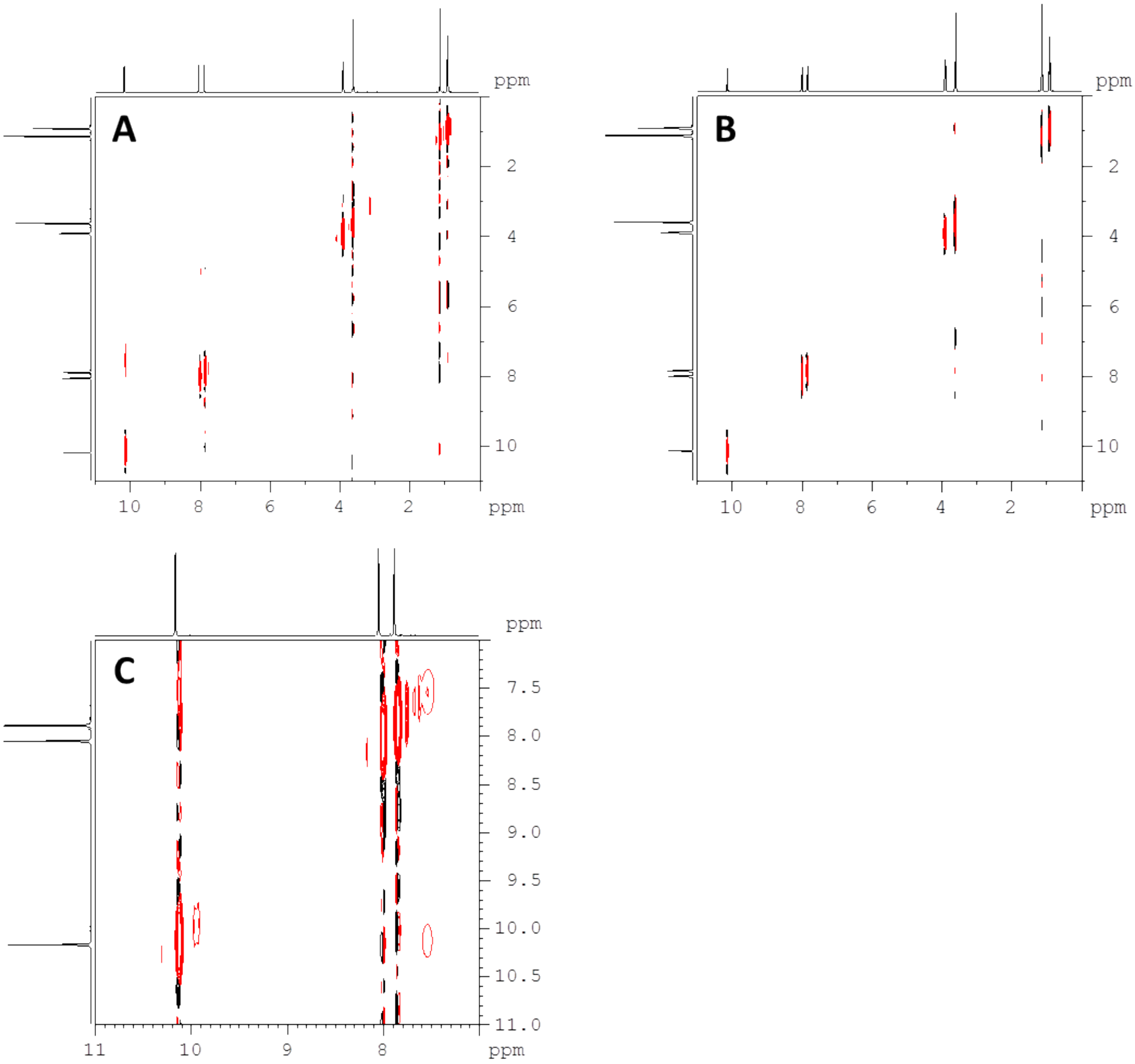


Figure S9. ^{1}H EXSY spectra of the 0.05 mole fraction water sample at 60°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

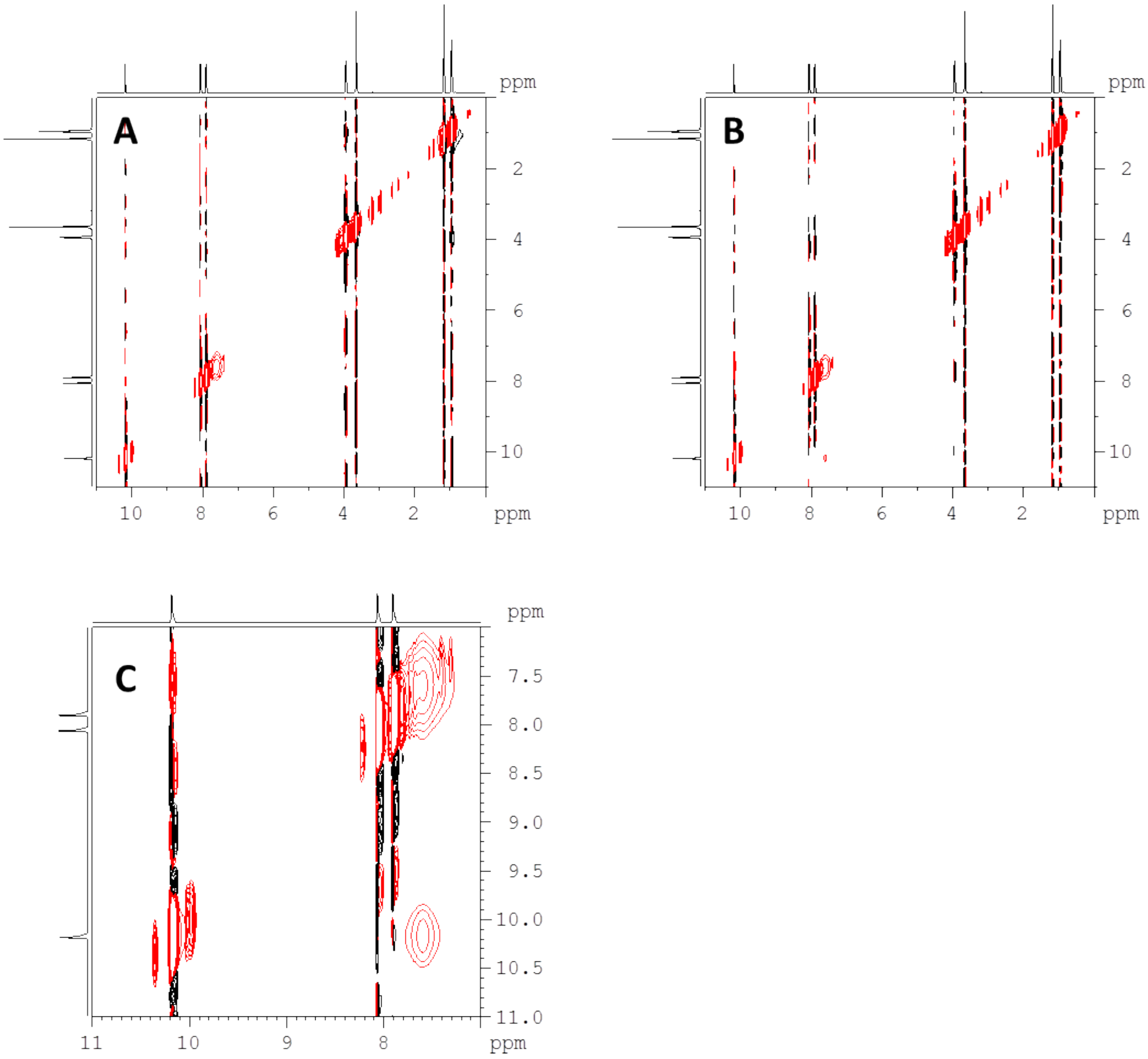


Figure S10. ^{1}H EXSY spectra of the 0.05 mole fraction water sample at 70°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

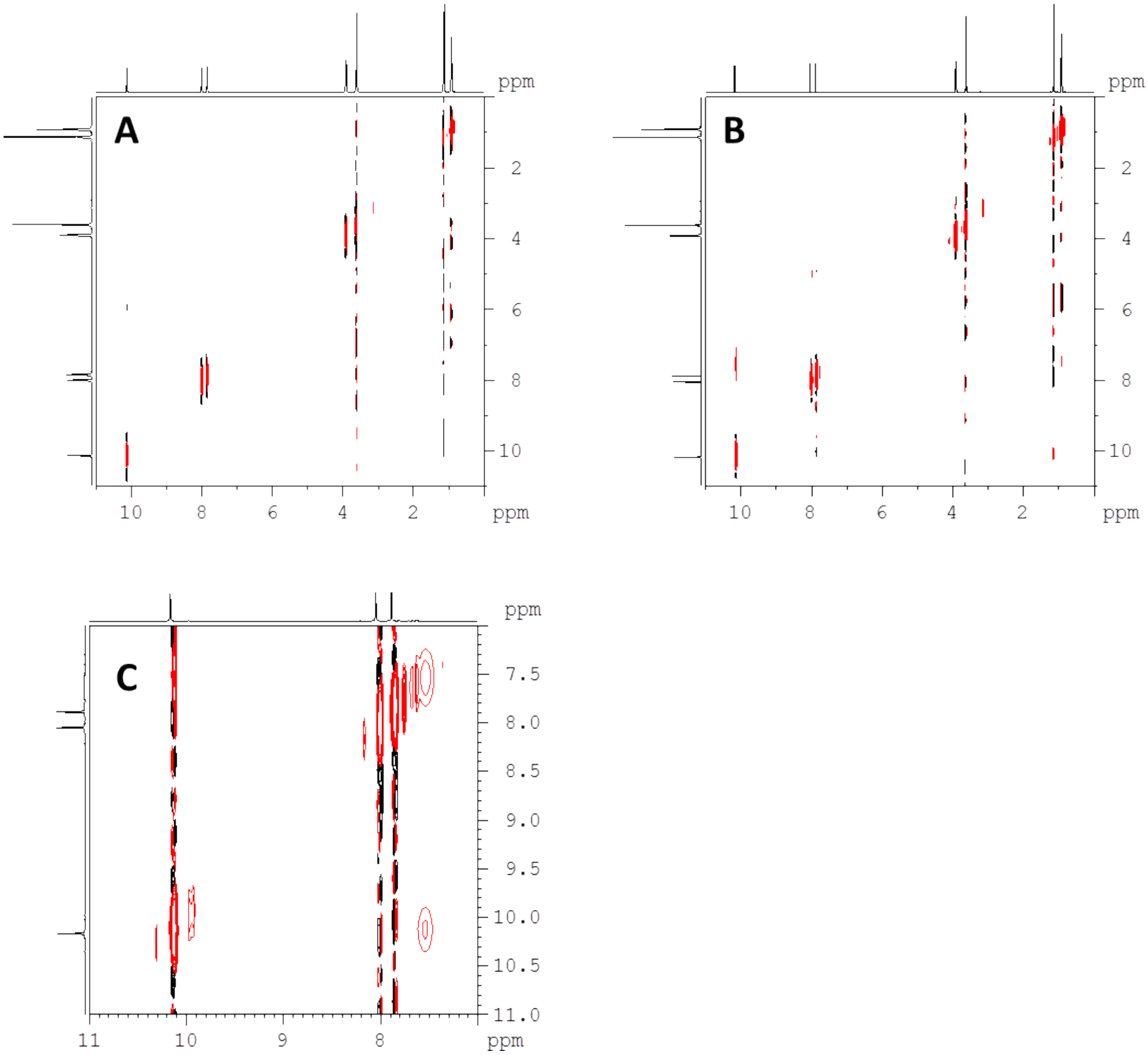


Figure S11. ^{1}H EXSY spectra of the 0.05 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

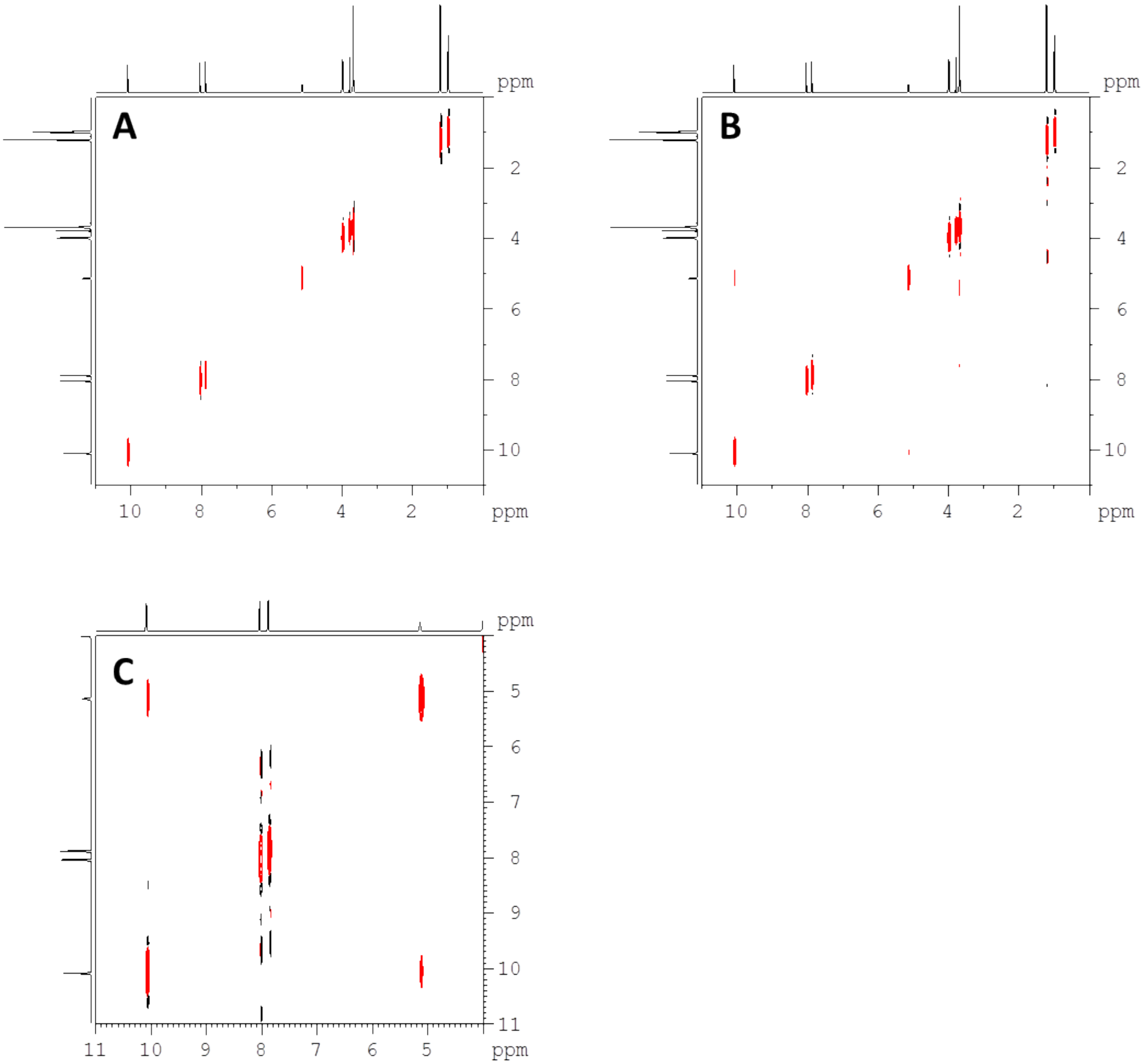


Figure S12. ^{1}H EXSY spectra of the 0.24 mole fraction water sample at 60°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

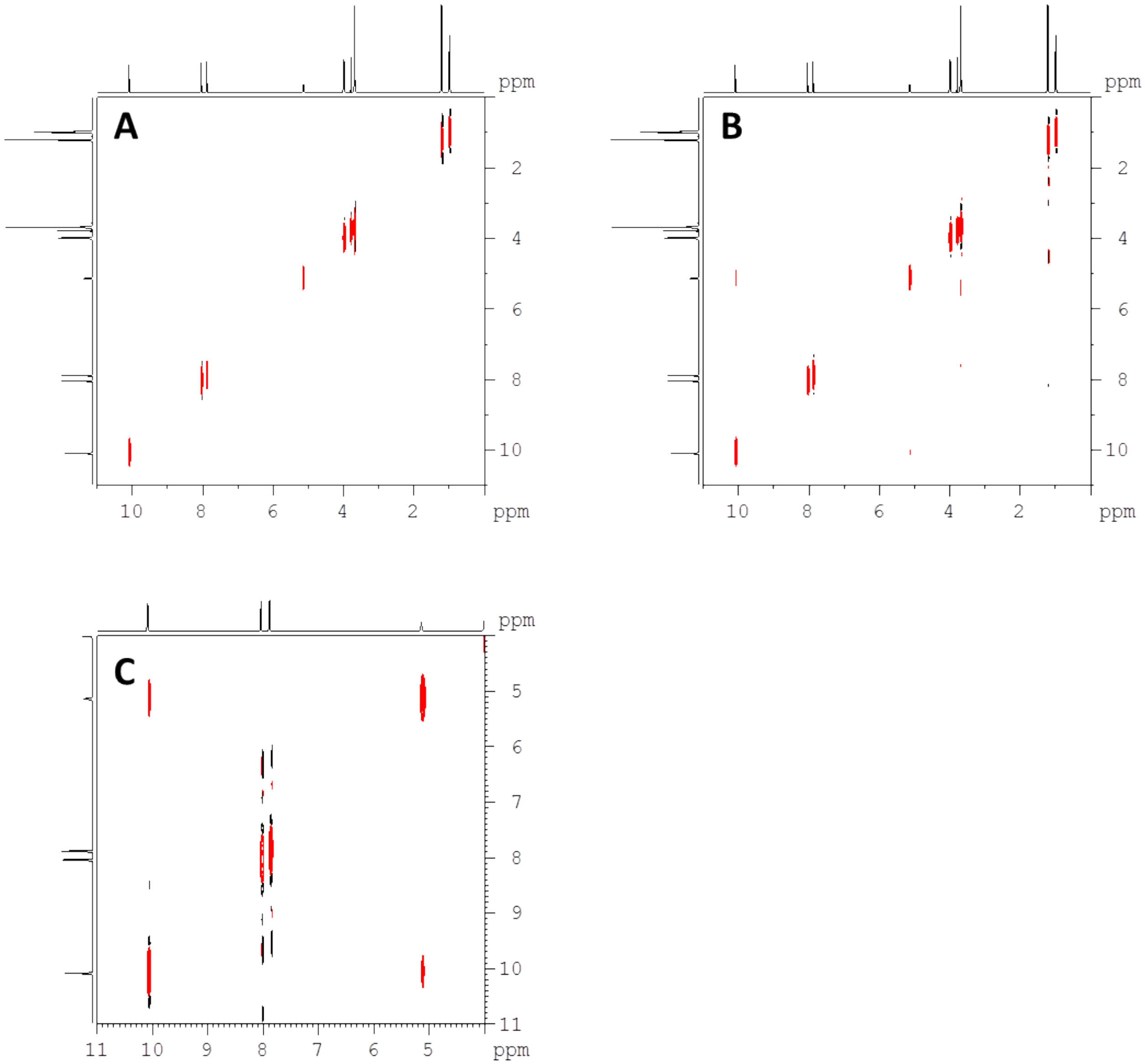


Figure S13. ^{1}H EXSY spectra of the 0.24 mole fraction water sample at 70°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

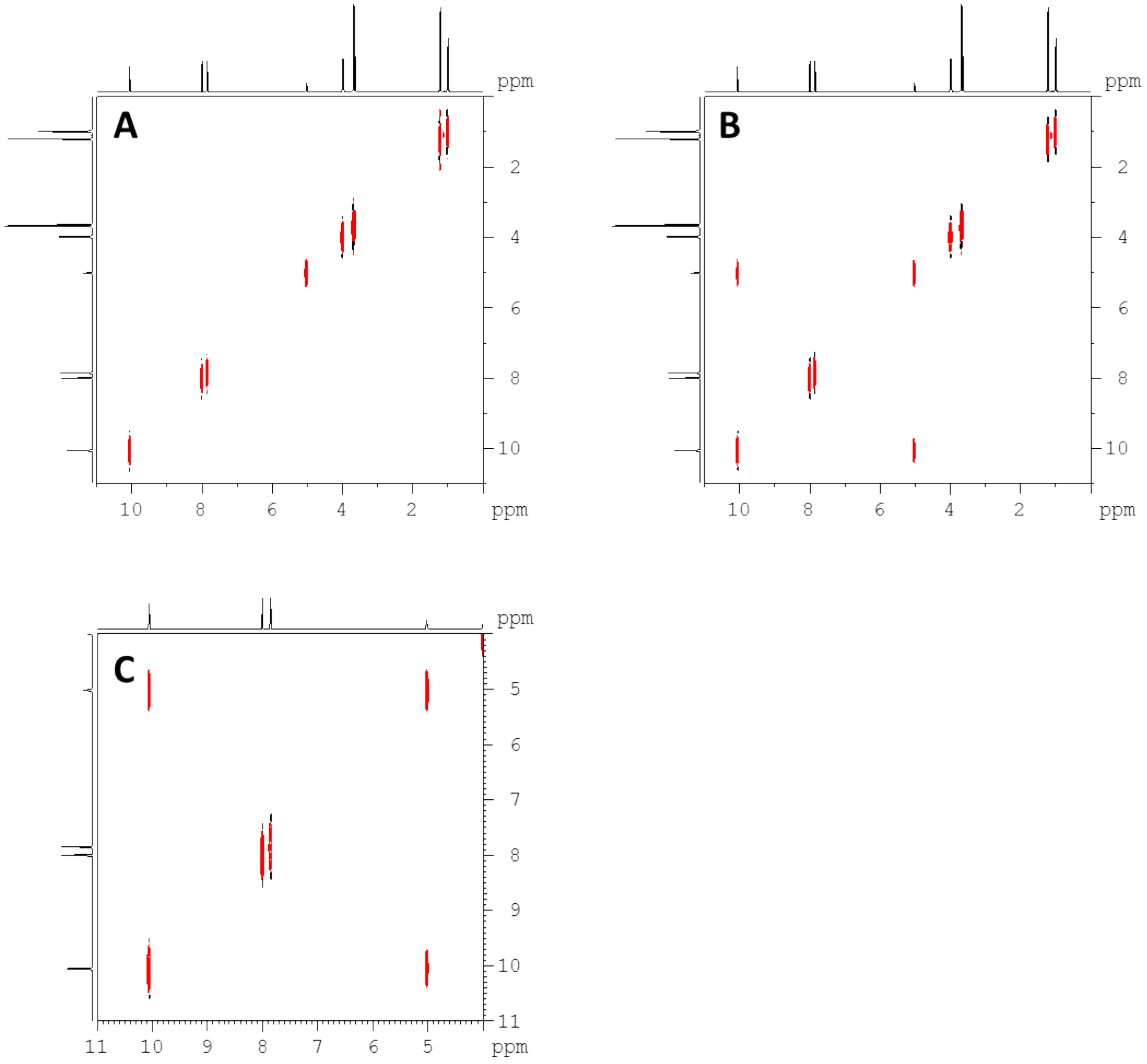


Figure S14. ^{1}H EXSY spectra of the 0.24 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification

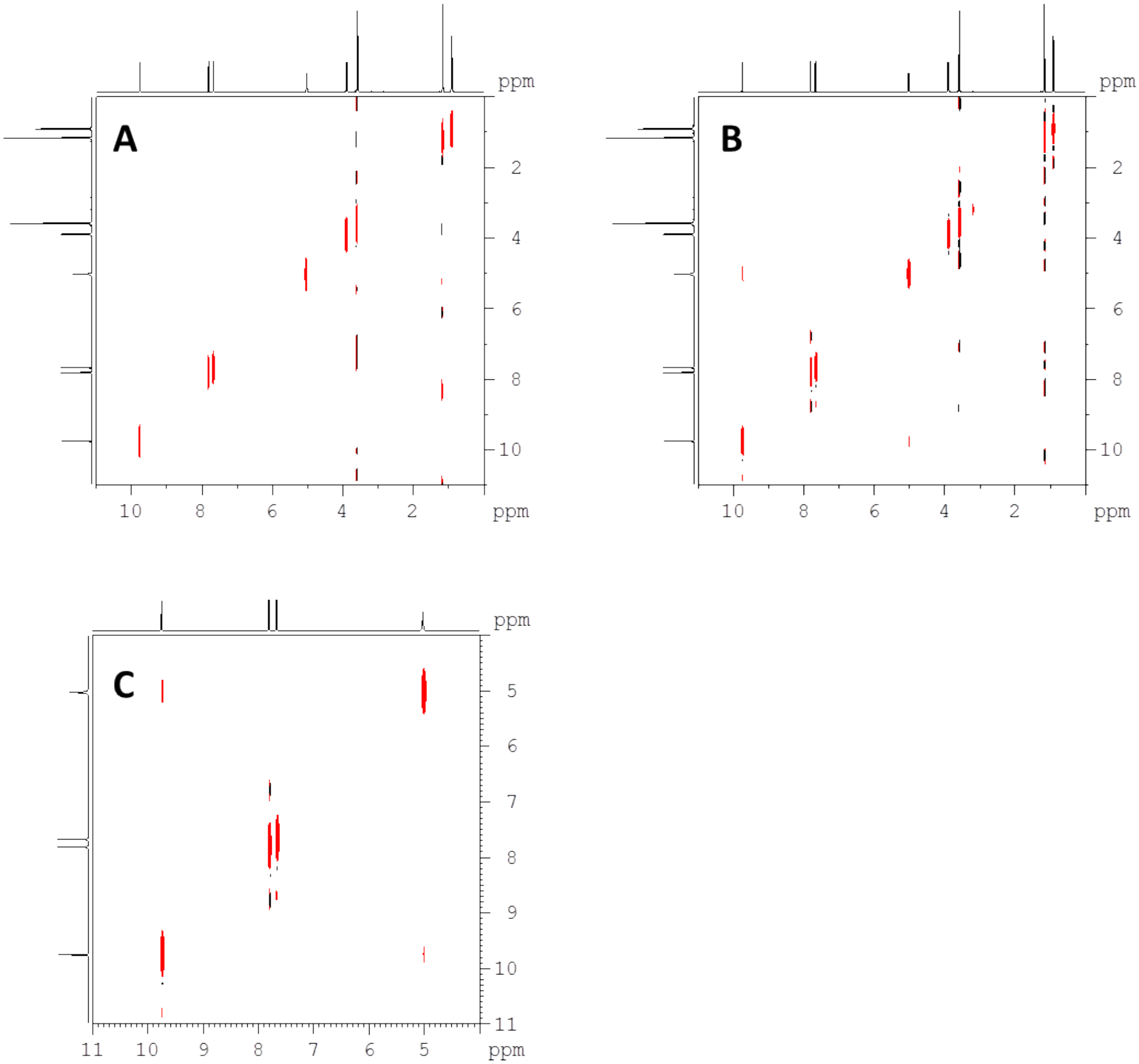


Figure S15. ^{1}H EXSY spectra of the 0.40 mole fraction water sample at 60°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

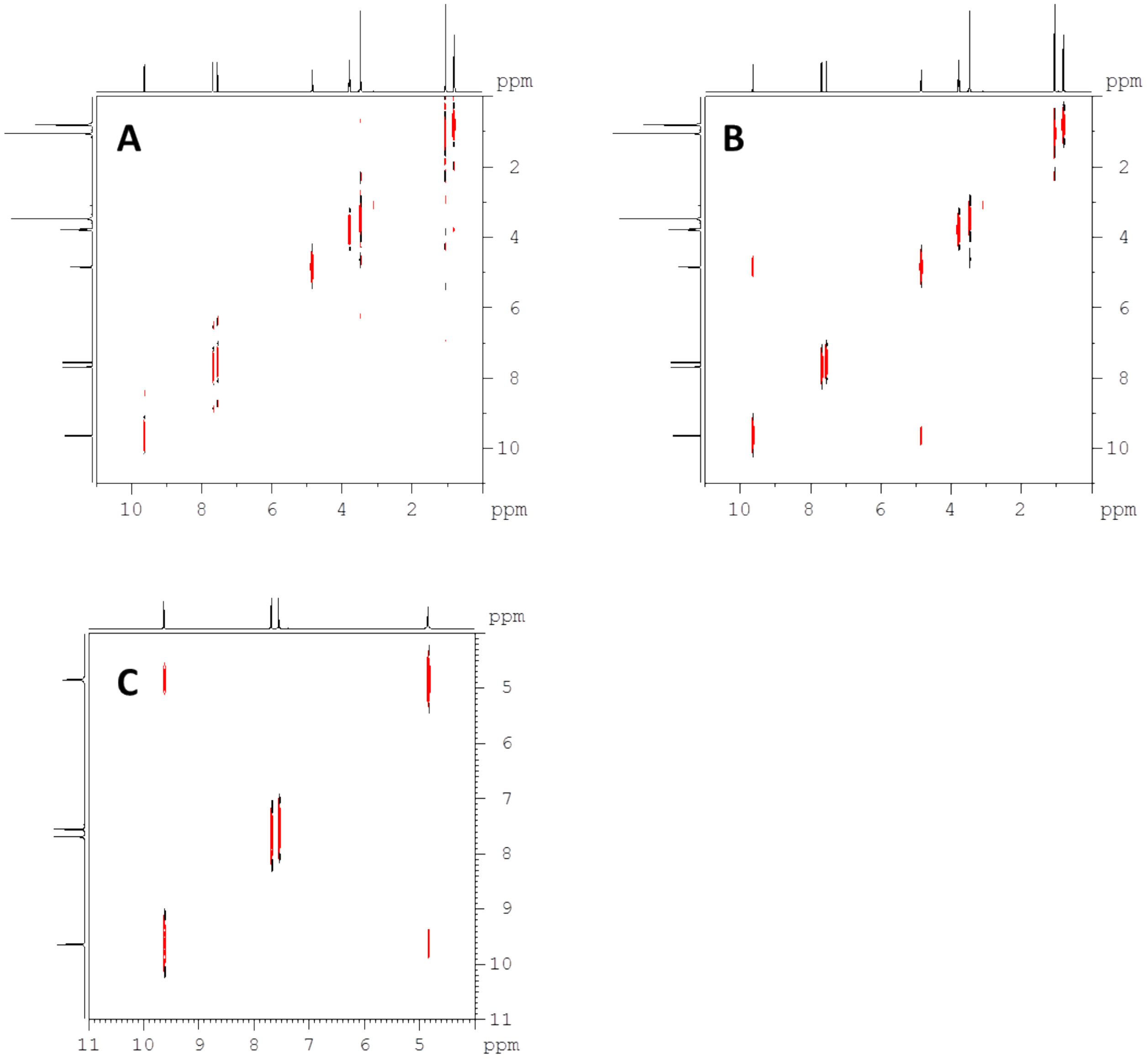


Figure S16. ^{1}H EXSY spectra of the 0.40 mole fraction water sample at 70°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

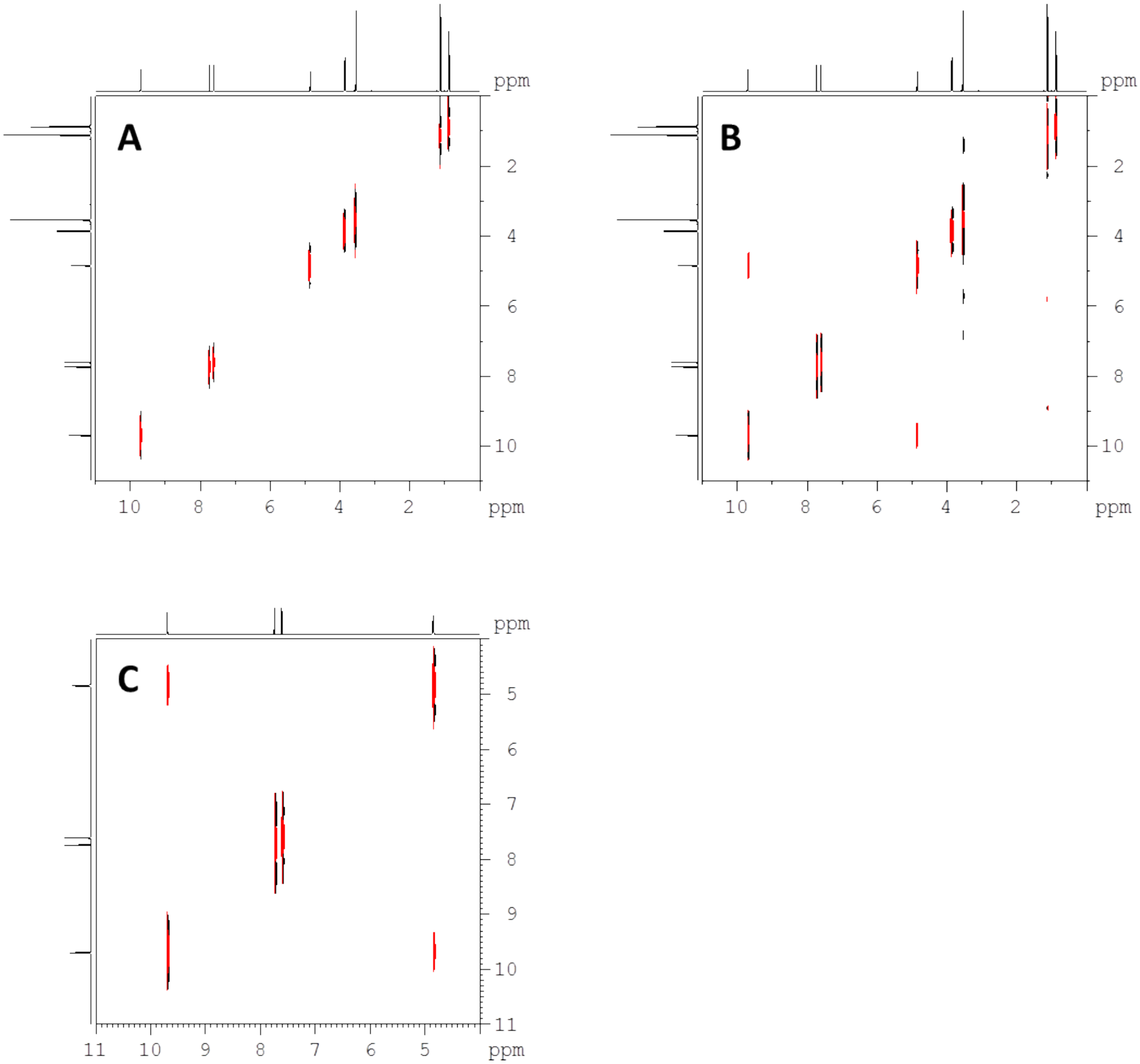


Figure S17. ^{1}H EXSY spectra of the 0.40 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

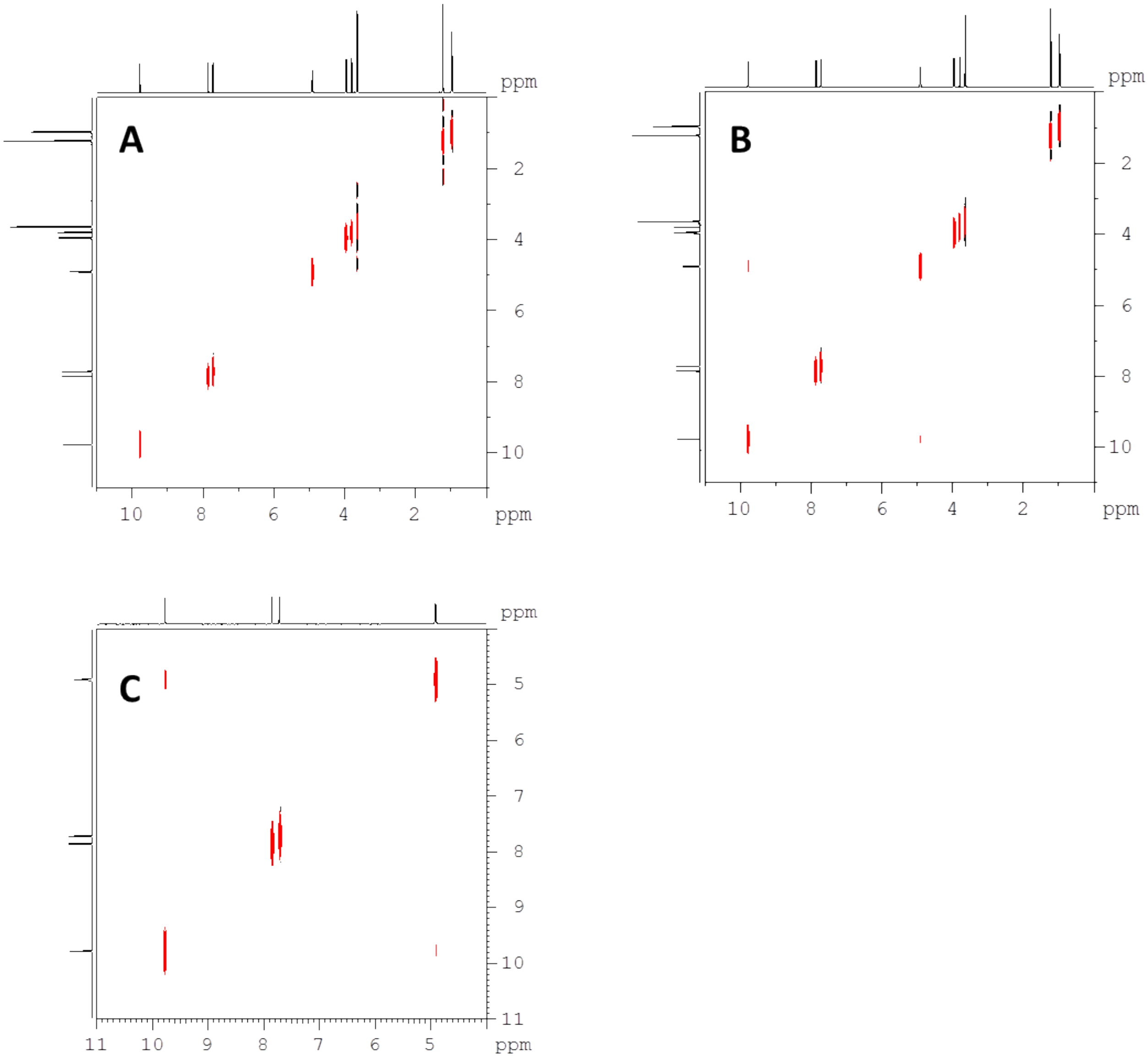


Figure S18. ^{1}H EXSY spectra of the 0.43 mole fraction water sample at 60°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

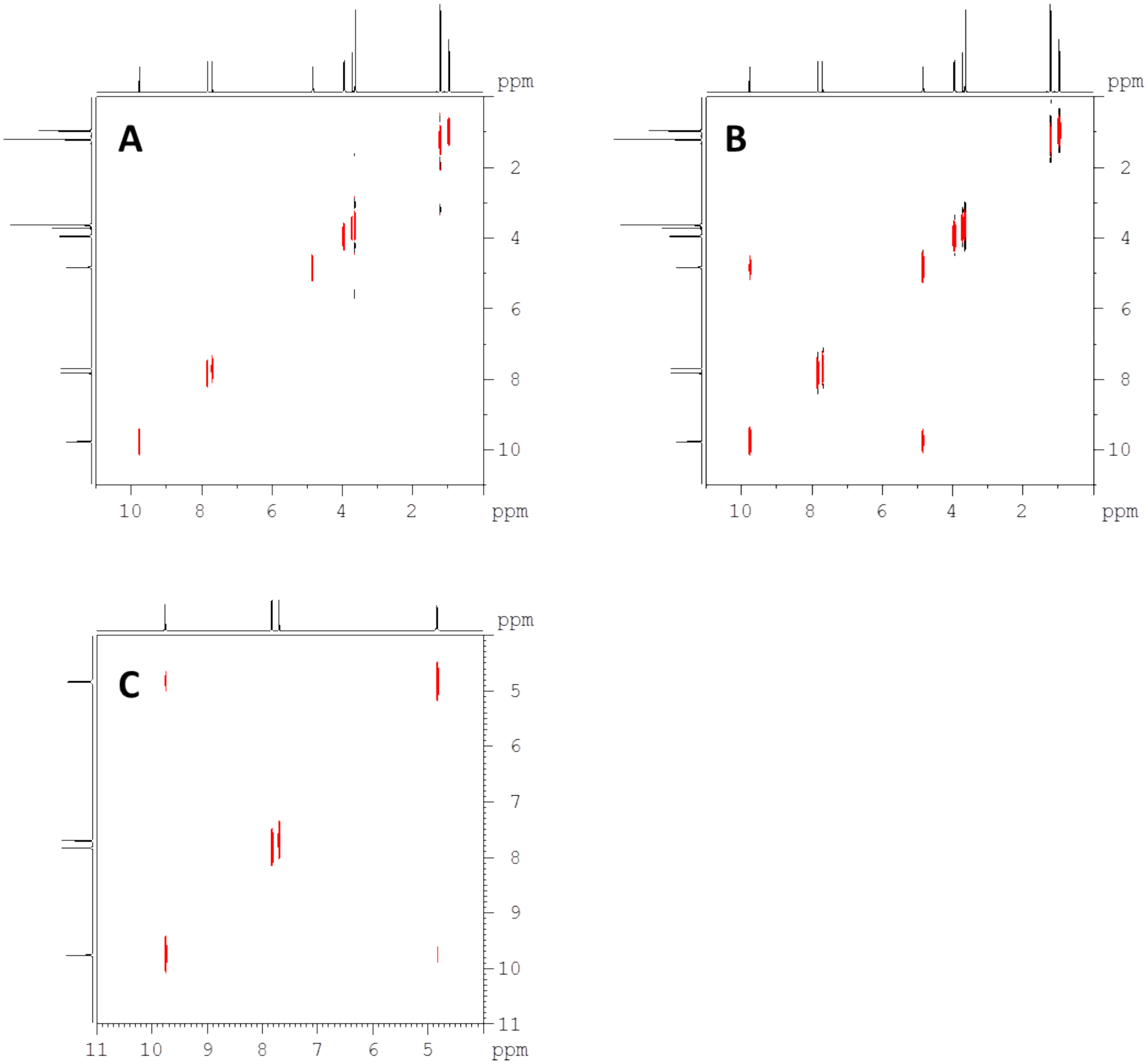


Figure S19. ^{1}H EXSY spectra of the 0.43 mole fraction water sample at 70°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

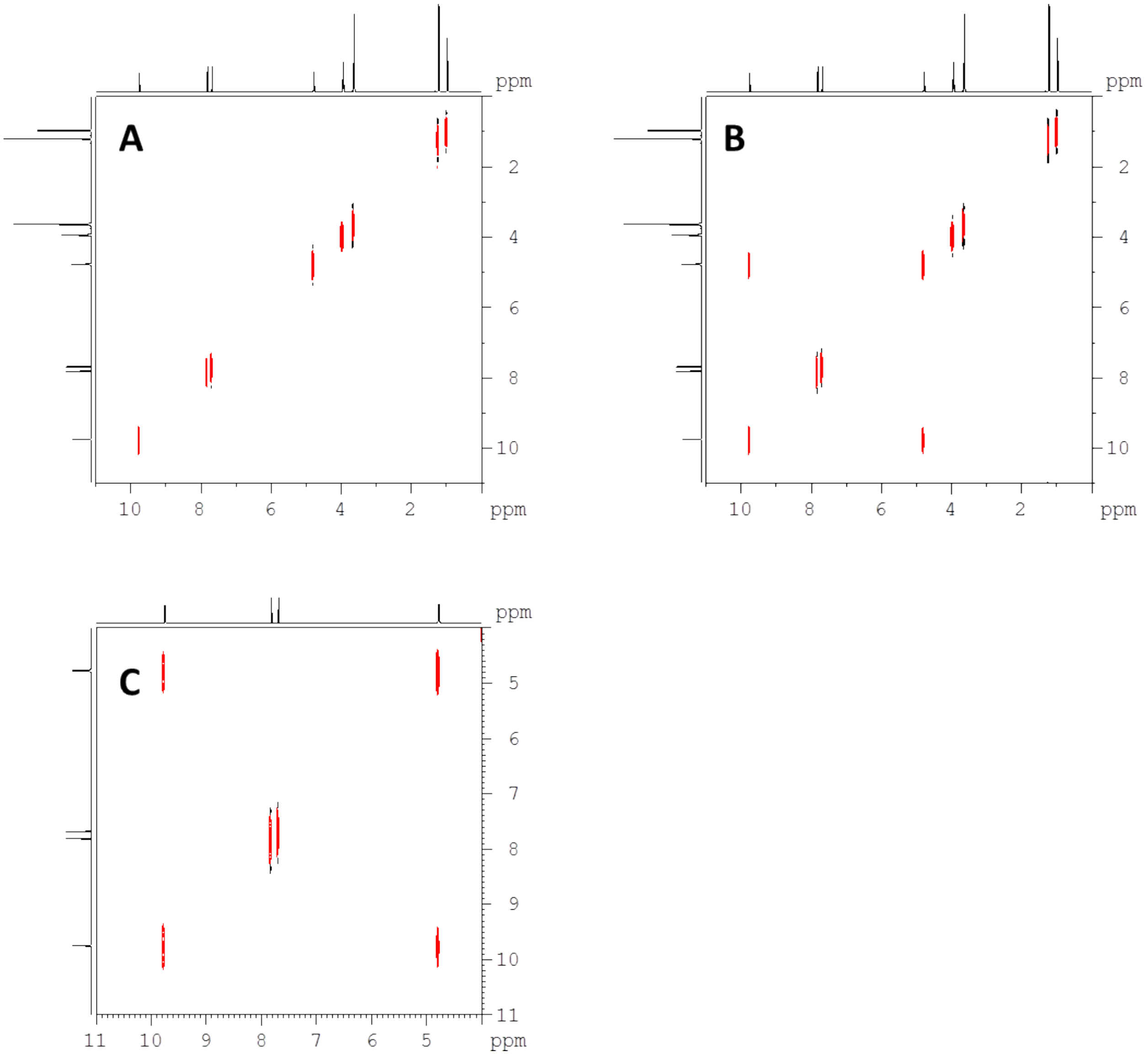


Figure S20. ^{1}H EXSY spectra of the 0.43 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

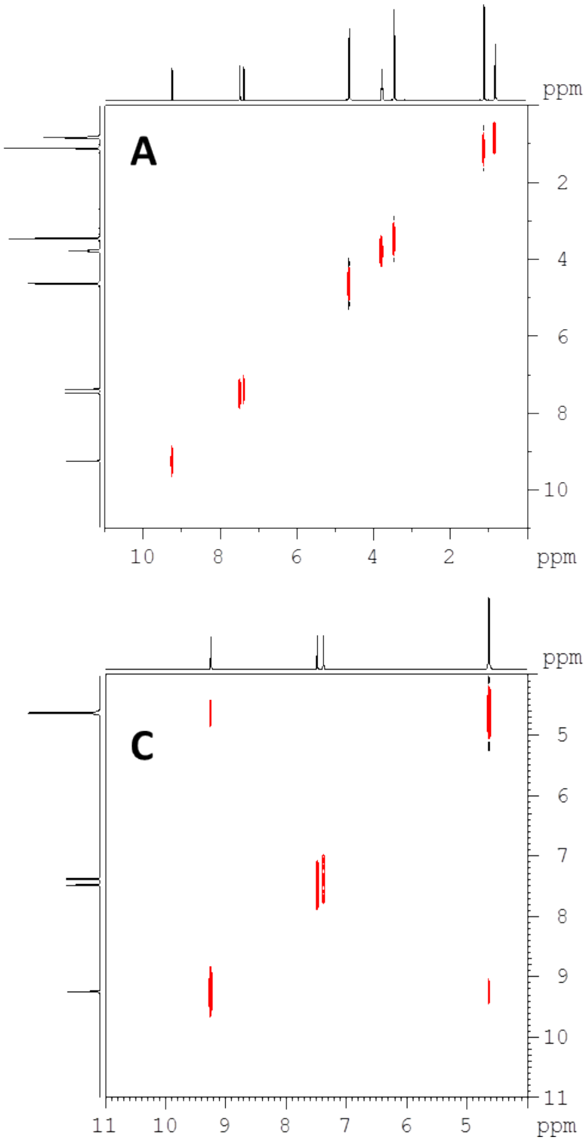


Figure S21. ^{1}H EXSY spectra of the 0.62 mole fraction water sample at 60°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

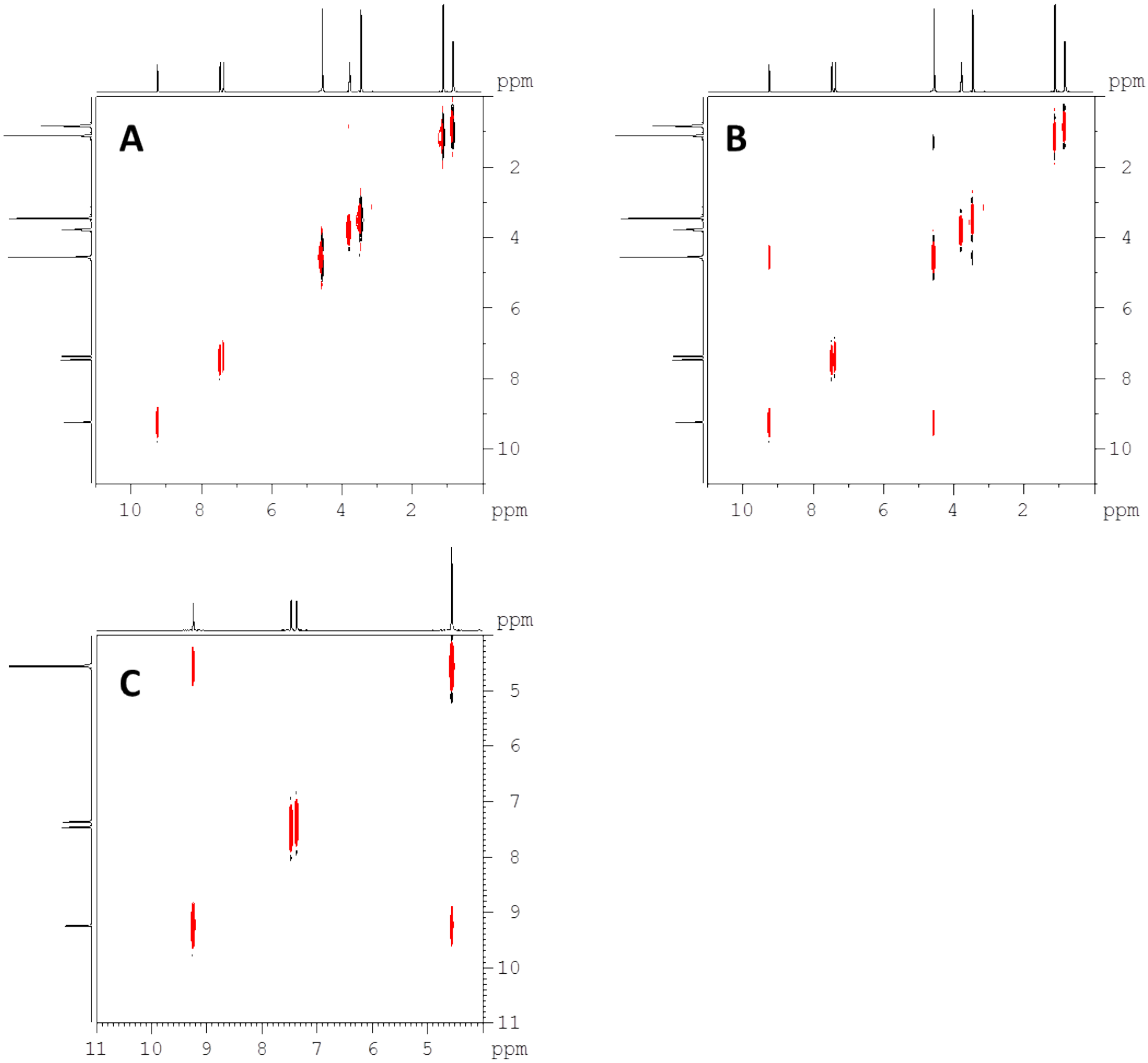


Figure S22. ^{1}H EXSY spectra of the 0.62 mole fraction water sample at 70°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

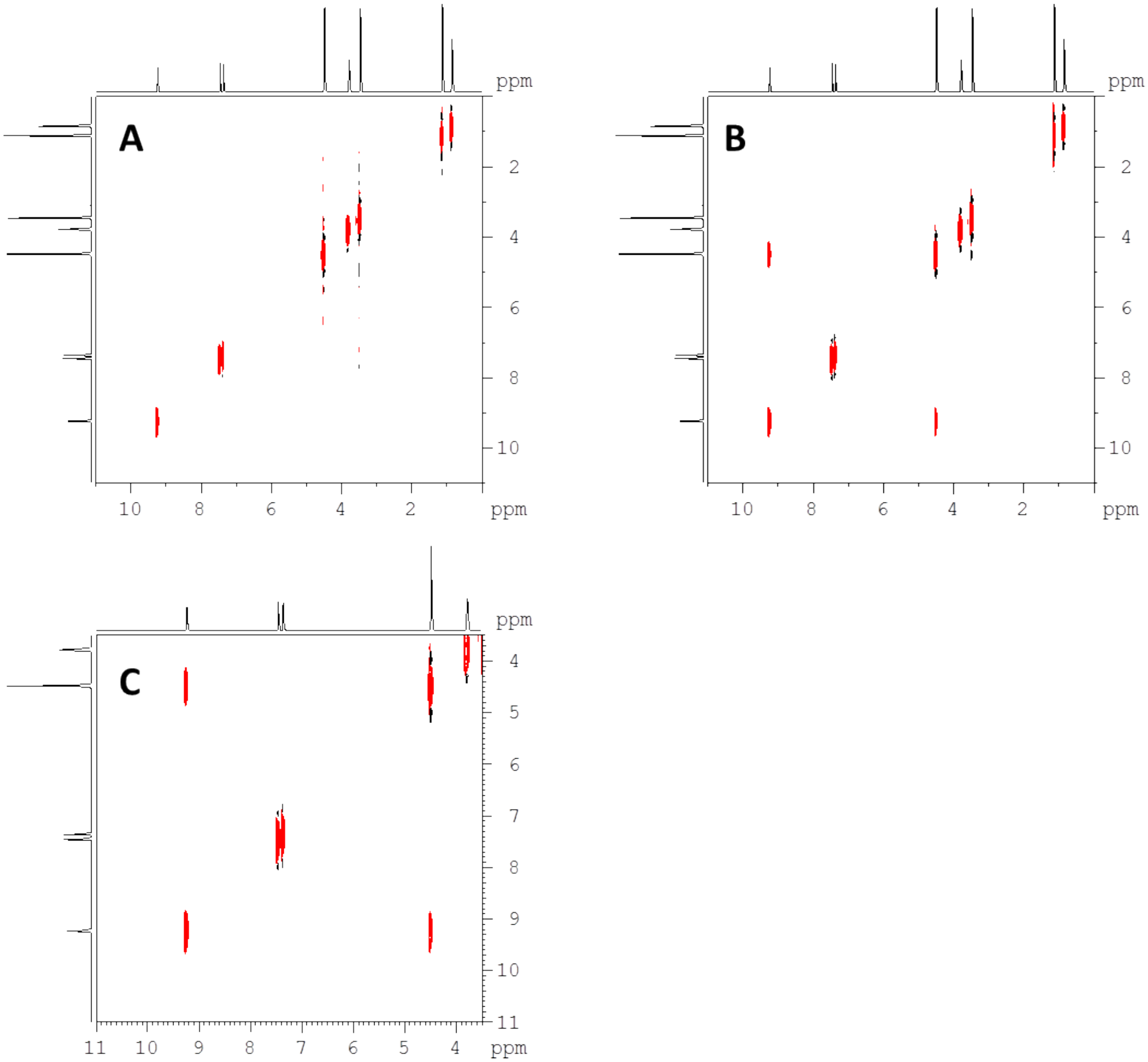


Figure S23. ^{1}H EXSY spectra of the 0.62 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

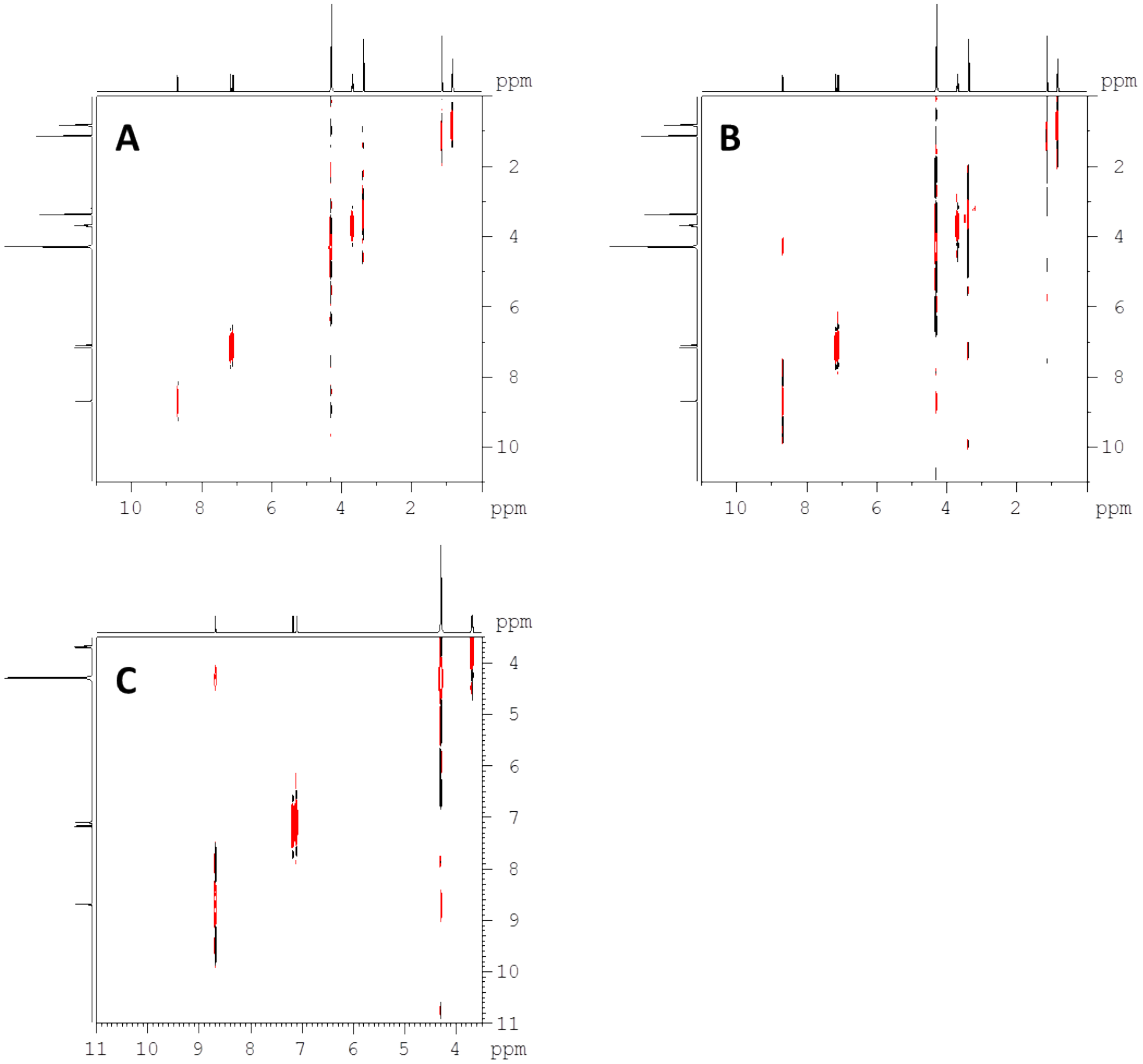


Figure S24. ^{1}H EXSY spectra of the 0.79 mole fraction water sample at 60°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

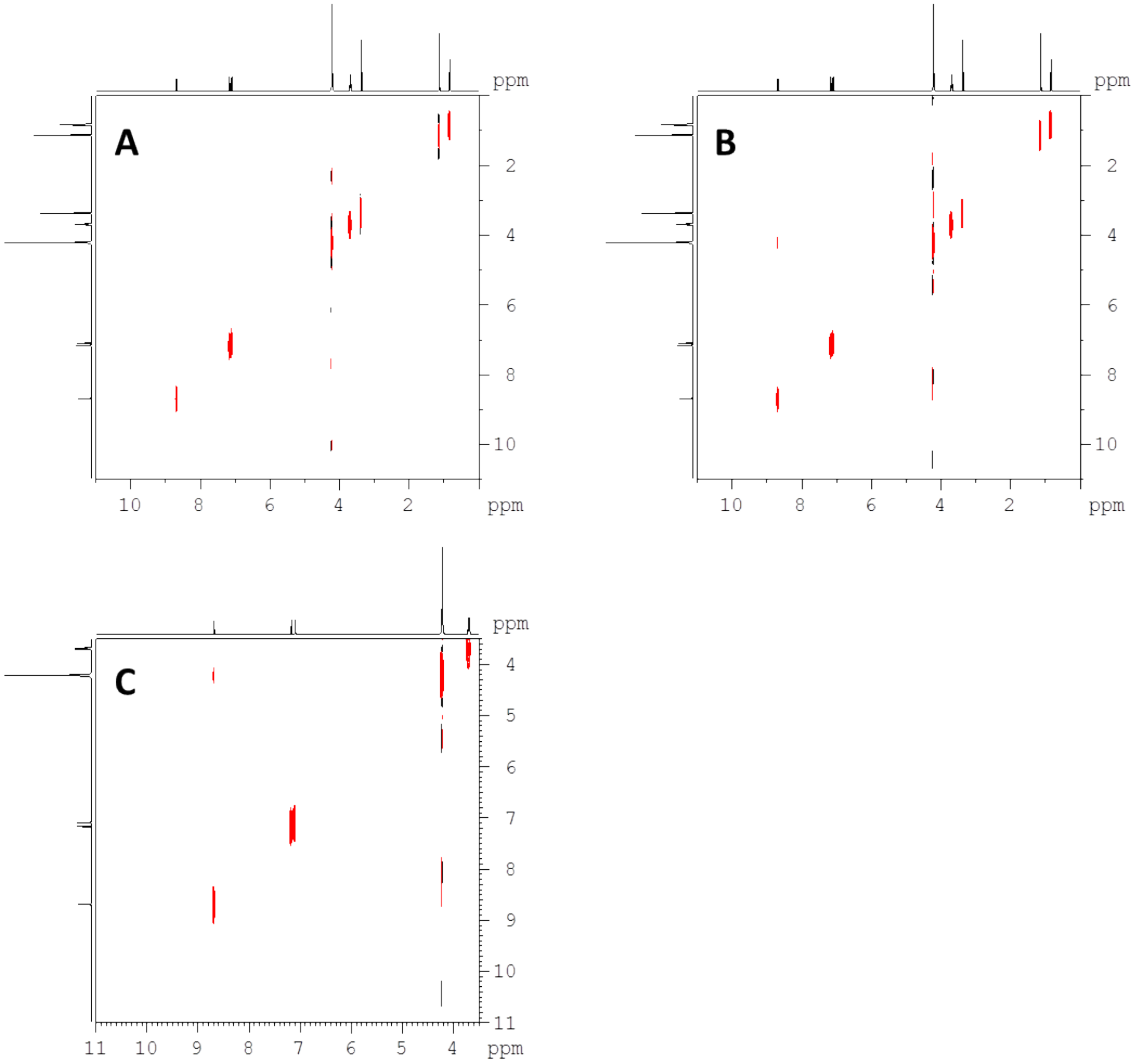


Figure S25. ^{1}H EXSY spectra of the 0.79 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

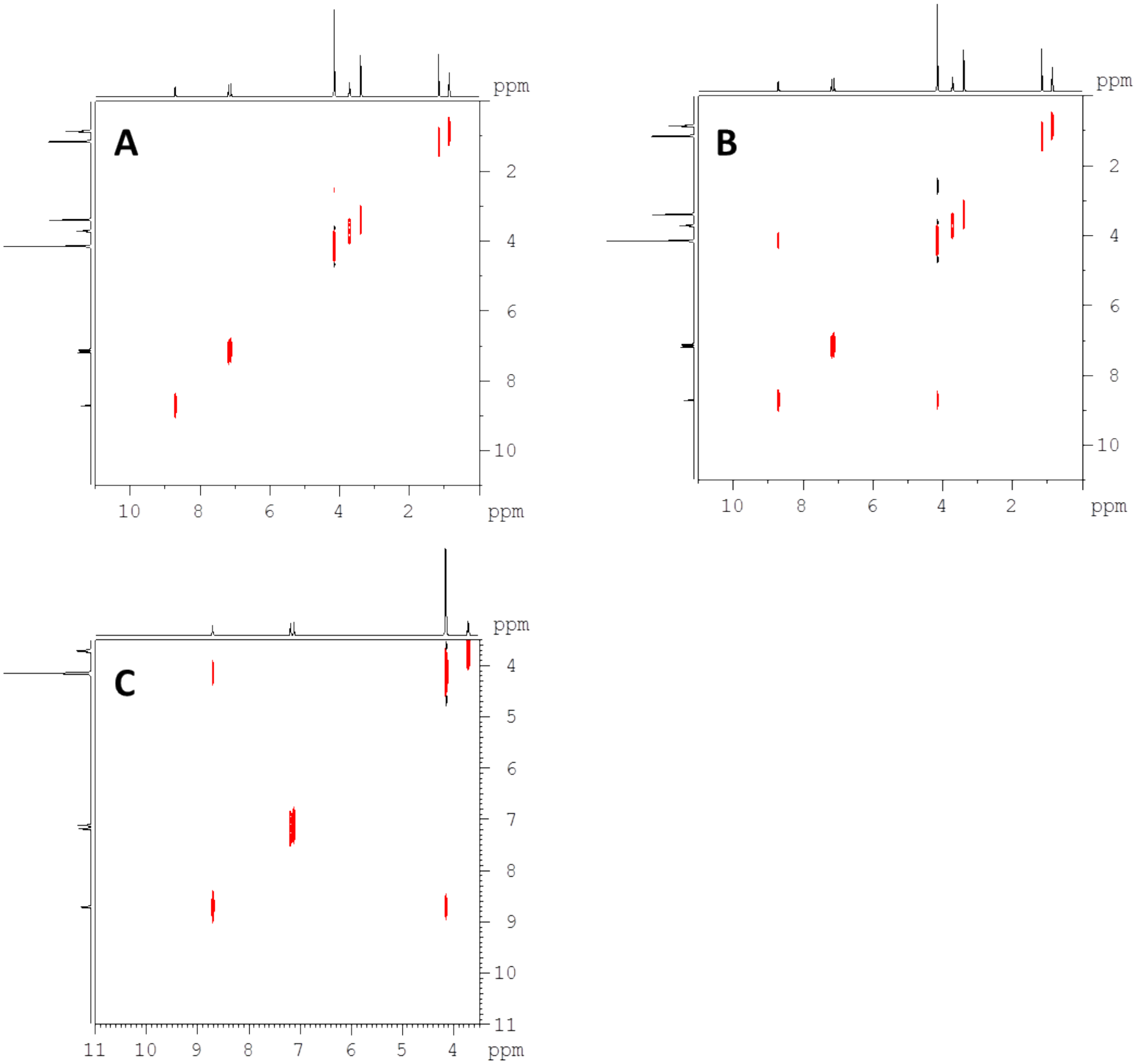


Figure S26. ^{1}H EXSY spectra of the 0.79 mole fraction water sample at 80°C with mixing times of (A) 0ms (B) 100ms, and (C) 100ms (expansion of exchanging peaks). Projections displayed are 1D spectra above to facilitate peak identification.

Note regarding chemical shift referencing

The study of binary mixtures requires the use of external referencing. These spectra were acquired using a sealed capillary of DMSO-d_6 as the chemical shift reference. However, external chemical shift referencing using a simple capillaries (i.e. without controlling for capillary geometry) can be quite poor in accuracy of chemical shifts, with variation of up to 0.5 ppm between samples due to the differences in the geometries and magnetic susceptibilities of the external reference capillary and the sample.[1] Additionally, the capillaries were not sealed under and inert atmosphere; atmospheric water absorbed by the DMSO may also affect its chemical shift.[2]

Table S3. EXSY diagonal and crosspeak volumes of the 5% mole fraction water sample

Temperature (C)	0ms mixing time diagonal peak volume (arbitrary units x 10^{-4})		100ms mixing time crosspeak volume (arbitrary units x 10^{-4})			
	A	B	AA	AB	BA	BB
60	-1604800	-172480				
60			-1480200	-11908	-31174	-119400
60			-1447100	-9369	-16762	-105670
60			-1508700	-10258	-67479	-112720
70	-1467400	-157630				
70			-1325300	-28197	-25099	-118490
70			-1350300	-28746	-29217	-110470
70			-1359800	-29167	-29016	-124070
80	-1508700	-112720				
80			-1311000	-59624	-77160	-133800
80			-1335700	-61077	-64339	-140040
80			-1321000	-44374	-59949	-71797

Table S4. EXSY diagonal and crosspeak volumes of the 24% mole fraction water sample

Temperature (C)	0ms mixing time diagonal peak volume (arbitrary units x 10^{-4})		100ms mixing time crosspeak volume (arbitrary units x 10^{-4})			
	A	B	AA	AB	BA	BB
60	-1667900	-1003800				
60			-1440000	-82654	-81911	-664570
60			-1432000	-79811	-82088	-653110
60			-1419600	-81346	-78509	-650420
70	-1603500	-972680				
70			-1306000	-173080	-170190	-586730
70			-1296300	-173250	-174250	-583050
70			-1229100	-160590	-162940	-552430
80	-1458800	-894050				
80			-1059600	-287450	-287650	-448000
80			-1058500	-289460	-290840	-448070
80			-977320	-266300	-265160	-412060

Table S5. EXSY diagonal and crosspeak volumes of the 40% mole fraction water sample

Temperature (C)	0ms mixing time diagonal peak volume (arbitrary units x 10^{-4})		100ms mixing time crosspeak volume (arbitrary units x 10^{-4})			
	A	B	AA	AB	BA	BB
60	-1775700	-2252000				
60			-1481000	-81053	-85584	-1587300
60			-1459000	-87909	-81972	-1581000
60			-1300600	-72414	-70863	-1468200
70	-1519900	-2043100				
70			-1202600	-185460	-180000	-1415200
70			-1300000	-188380	-189880	-1522400
70			-1285400	-185890	-192550	-1515900
80	-1595500	-2125300				
80			-1077000	-370190	-372690	-1389300
80			-1054000	-355740	-359860	-1362100
80			-1023800	-355340	-351130	-1338900

Table S6. EXSY diagonal and crosspeak volumes of the 43% mole fraction water sample

Temperature (C)	0ms mixing time crosspeak volume (arbitrary units x 10^{-4})		100ms mixing time crosspeak volume (arbitrary units x 10^{-4})			
	A	B	AA	AB	BA	BB
60	-1552300	-2350900				
60			-1291500	-144060	-141130	-1674700
60			-1322800	-137970	-138780	-1687600
60			-1309100	-136310	-141690	-1669600
70	-1465000	-2293400				
70			-1081400	-291790	-290840	-1556000
70			-1072800	-295710	-288430	-1545800
70			-1062000	-274660	-274540	-1509300
80	-1360500	-2169000				
80			-791430	-492400	-481820	-1339500
80			-788610	-488700	-479610	-1330500
80			-787830	-461250	-459960	-1349100

Table S7. EXSY diagonal and crosspeak volumes of the 62% mole fraction water sample

Temperature (C)	0ms mixing time crosspeak volume (arbitrary units x 10^{-4})		100ms mixing time crosspeak volume (arbitrary units x 10^{-4})			
	A	B	AA	AB	BA	BB
60	-1503500	-4858100				
60			-1206100	-94037	-88013	-3524600
60			-1343400	-102580	-99259	-3981700
60			-1287100	-95568	-90998	-3802500
70	-1328800	-4463900				
70			-963470	-210070	-200720	-3243300
70			-1105700	-222000	-211140	-3566200
70			-1064500	-220340	-217050	-3566000
80	-1247300	-4212200				
80			-749570	-416580	-407330	-3190000
80			-751100	-416950	-408520	-3216300
80			-749300	-415610	-407380	-3199100

Table S8. EXSY diagonal and crosspeak volumes of the 79% mole fraction water sample

Temperature (K)	0ms mixing time crosspeak volume (arbitrary units x 10^{-4})		100ms mixing time crosspeak volume (arbitrary units x 10^{-4})			
	A	B	AA	AB	BA	BB
60	-1216300	-9531800				
60			-1109500	-69269	-58149	-7332100
60			-1078800	-76996	-57484	-6737200
60			-1075800	-72856	-53601	-6697900
70	-1126100	-8889200				
70			-901640	-175870	-140640	-7166100
70			-879290	-144550	-141560	-6679400
70			-877960	-178130	-144640	-6721000
80	-980760	-7810700				
80			-615730	-323950	-306490	-6465600
80			-622330	-332440	-315730	-6349700
80			-614780	-321930	-316370	-6347200

Modified power-gated pulse sequence for measuring 13C NOE factors

```
;zgpg
;avance-version (07/04/03)
;1D sequence with power-gated decoupling
;
;$CLASS=HighRes
;$DIM=1D
;$TYPE=
;$SUBTYPE=
;$COMMENT=
#include <Avance.incl>
#include <Delay.incl>
"d11=30m"
"DELTA=d1-100m"
"acqt0=-p1*2/3.1416"
1 ze
 d11
2 30m do:f2
 10u pl12:f2
 d1 cpd2:f2
 p1 ph1
 go=2 ph31
 30m do:f2 mc #0 to 2 F0(zd)
exit
ph1=0 2 2 0 1 3 3 1
ph31=0 2 2 0 1 3 3 1
;pl1 : f1 channel - power level for pulse (default)
;pl12: f2 channel - power level for CPD/BB decoupling
;pl13: f2 channel - power level for second CPD/BB decoupling
;p1 : f1 channel - high power pulse
;d1 : relaxation delay; 1-5 * T1
;d11: delay for disk I/O [30 msec]
;NS: 1 * n, total number of scans: NS * TD0
;cpd2: decoupling according to sequence defined by cpdprg2
;pcpd2: f2 channel - 90 degree pulse for decoupling sequence S7
```

A modified t1irpg pulse sequence for measuring 13C T2 relaxation under decoupling conditions is given below:

```
;t1irpg.j
;avance-version (07/07/03)
;T1 measurement using inversion recovery
;with power gated decoupling
;
;$CLASS=HighRes
;$DIM=2D
```

```
;$TYPE=
;$SUBTYPE=
;$COMMENT=
#include <Avance.incl>
"p2=p1*2"
"d11=30m"
"d12=20u"
"acqt0=-p1*2/3.1416"
1 ze
2 d11 do:f2
 d12 pl12:f2
 d1
 p2 ph1 cpd2:f2
 vd
 p1 ph2
 go=2 ph31
 d11 wr #0 if #0 ivd
 lo to 1 times td1
 d11 do:f2
exit
ph1=0 2
ph2=0 0 2 2 1 1 3 3
ph31=0 0 2 2 1 1 3 3
;pl1 : f1 channel - power level for pulse (default)
;pl12: f2 channel - power level for CPD/BB decoupling
;pl13: f2 channel - power level for second CPD/BB decoupling
;p1 : f1 channel - 90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;d1 : relaxation delay; 1-5 * T1
;d11: delay for disk I/O [30 msec]
;d12: delay for power switching [20 usec]
;vd : variable delay, taken from vd-list
;NS: 8 * n
;DS: 4
;td1: number of experiments = number of delays in vd-list
;FnMODE: undefined
;cpd2: decoupling according to sequence defined by cpdprg2
;pcpd2: f2 channel - 90 degree pulse for decoupling sequence
;define VDLIST S8
;this pulse program produces a ser-file (PARMOD = 2D)
```

Modified CPMG pulse sequence for measuring 13C T2 relaxation

```
;cpmg
;avance-version (00/02/07)
;T2 measurement using Carr-Purcell-Meiboom-Gill sequence with inverse gated decoupling
;
;$CLASS=HighRes
;$DIM=2D
;$TYPE=
;$SUBTYPE=
;$COMMENT=
#include <Avance.incl>
"p2=p1*2"
"d11=30m"
"d21=d20-100u"
1 ze
2 d11 do:f2 pl12:f2
 d1
 p1 ph1
3 d20
 p2 ph2
 d20
 lo to 3 times c
 d20
 p2 ph2
 d21
 100u cpd2:f2
 go=2 ph31
 d11 do:f2 wr #0 if #0 ivc
 lo to 1 times td1
 d11
exit
ph1=0 0 2 2 1 1 3 3
ph2=1 3 1 3 0 2 0 2
ph31=0 0 2 2 1 1 3 3
;pl1 : f1 channel - power level for pulse (default)
;pl12: f2 channel - power level for CPD/BB decoupling
;p1 : f1 channel - 90 degree high power pulse
;p2 : f1 channel - 180 degree high power pulse
;d1 : relaxation delay; 1-5 * T1
;d11: delay for disk I/O [30 msec]
;d20: fixed echo time to allow elimination of diffusion
; and J-mod. effects
;vc : variable loop counter, taken from vc-list
;NS: 8 * n
;DS: 16
;cpd2: decoupling according to sequence defined by cpdprg2
;pcpd2: f2 channel - 90 degree pulse for decoupling sequence
```

```
;td1: number of experiments = number of values in vc-list S9
;define VCLIST
;this pulse program produces a ser-file (PARMOD = 2D)
;d20: d20 should be << 1/J ,but > (50 * P2)
;vc : vc should contain even numbers to provide
; for cancellation of 180 degree p
```

References

1. K. Momoki and Y. Fukazawa, *Anal. Sci.*, 1994, **10**, 53-58.
2. J. Catalán, C. Díaz and F. García-Blanco, *The Journal of Organic Chemistry*, 2001, **66**, 5846-5852.