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

Supporting Information for

Enhanced Stability and Water Solubilizing Capacity of Water-in-Oil Microemulsions by Protic Ionic Liquids

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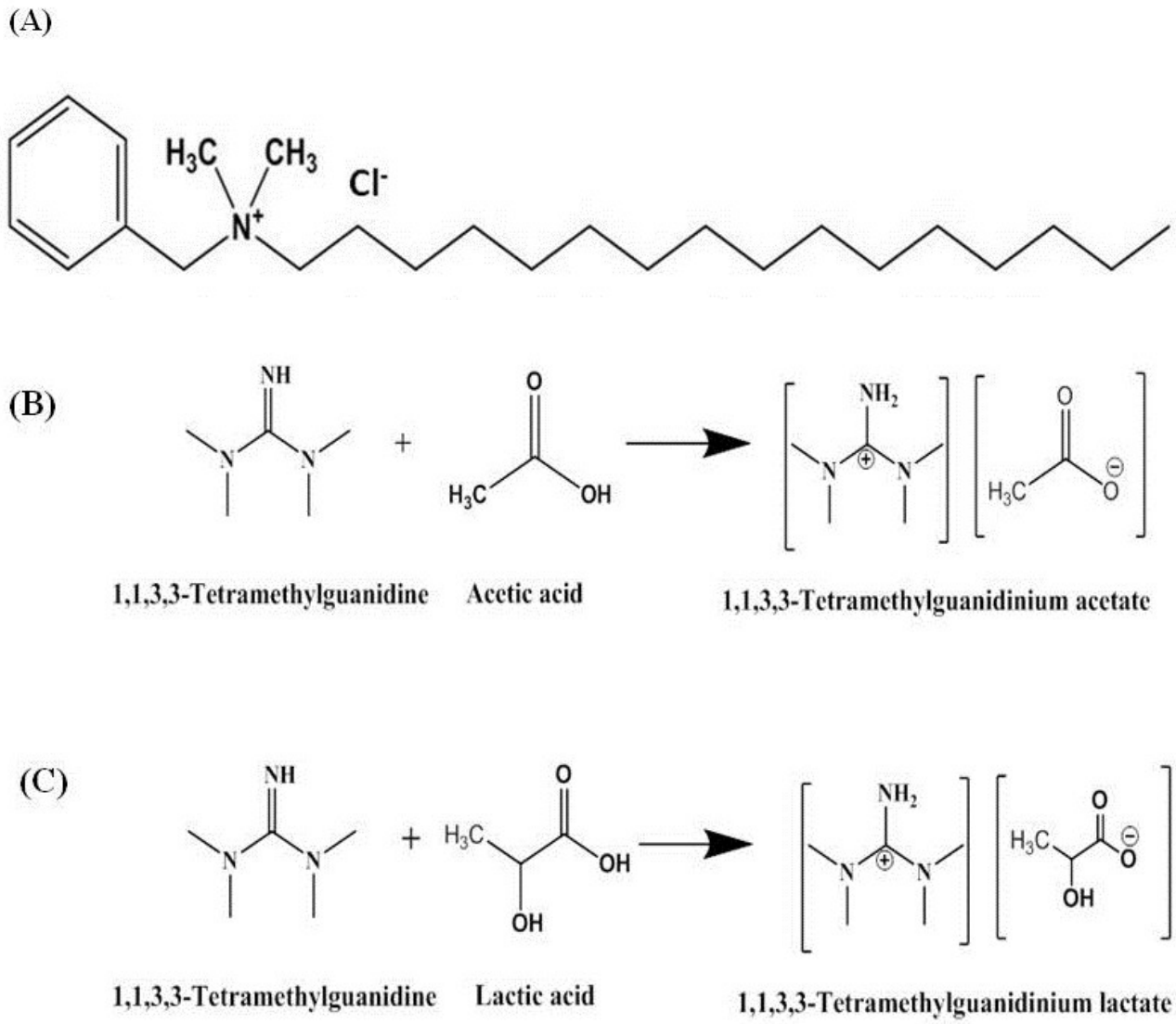


Figure S1. **(A)** Molecular structure of benzyl-n-hexadecyldimethylammonium chloride (BHDC). Scheme for synthesis of **(B)** 1,1,3,3-tetramethylguanidinium acetate ([TMG][Ace]) and **(C)** 1,1,3,3-tetramethylguanidinium lactate ([TMG][Lac]).

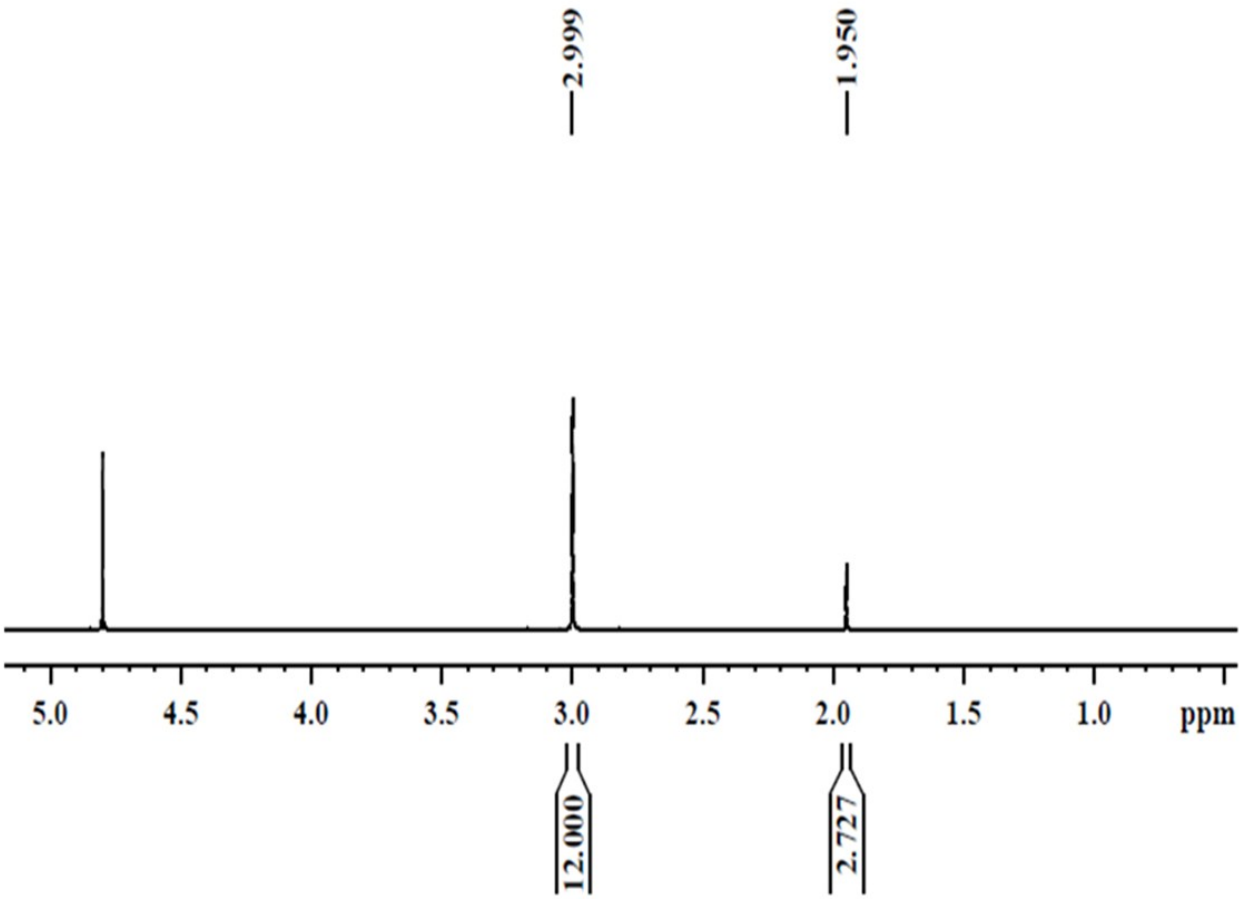


Figure S2. The ^{1}H NMR (500MHz, D_2O) spectra of [TMG][Ace].

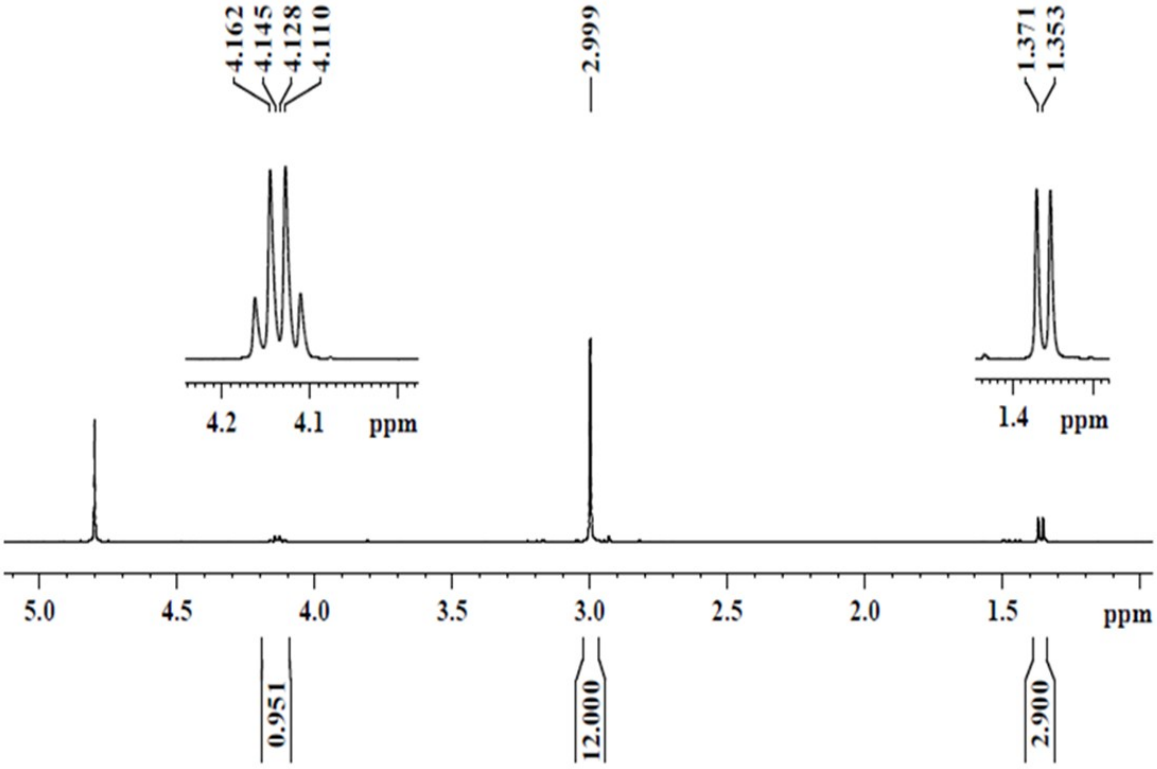
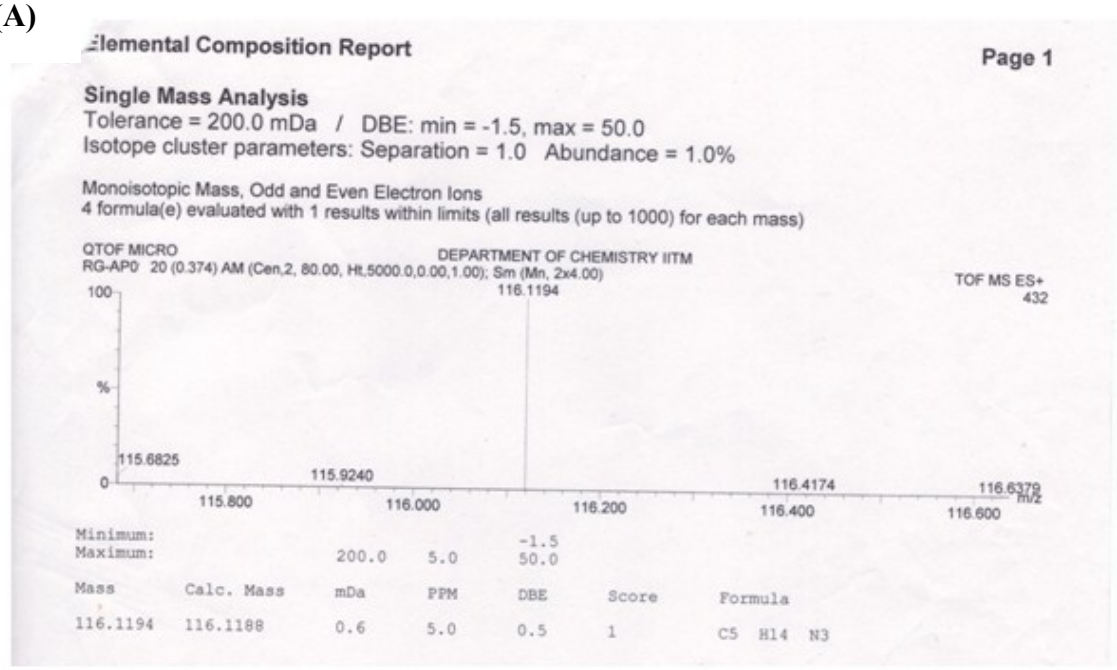


Figure S3. The ^{1}H NMR (500MHz, D_2O) spectra of [TMG][Lac].

(A)



(B)

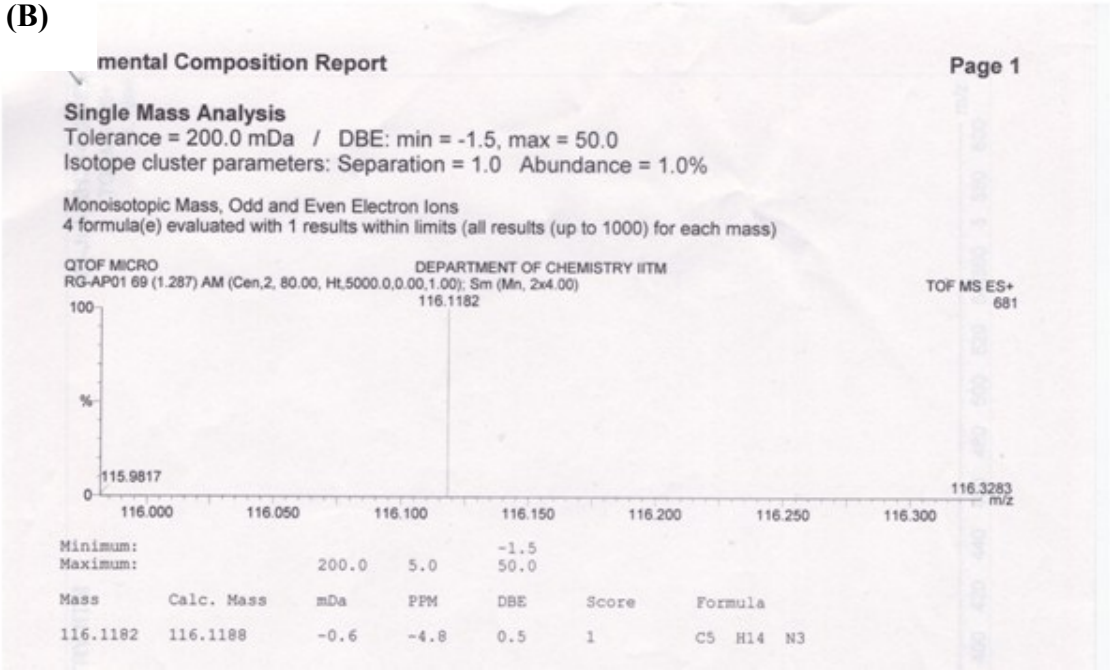
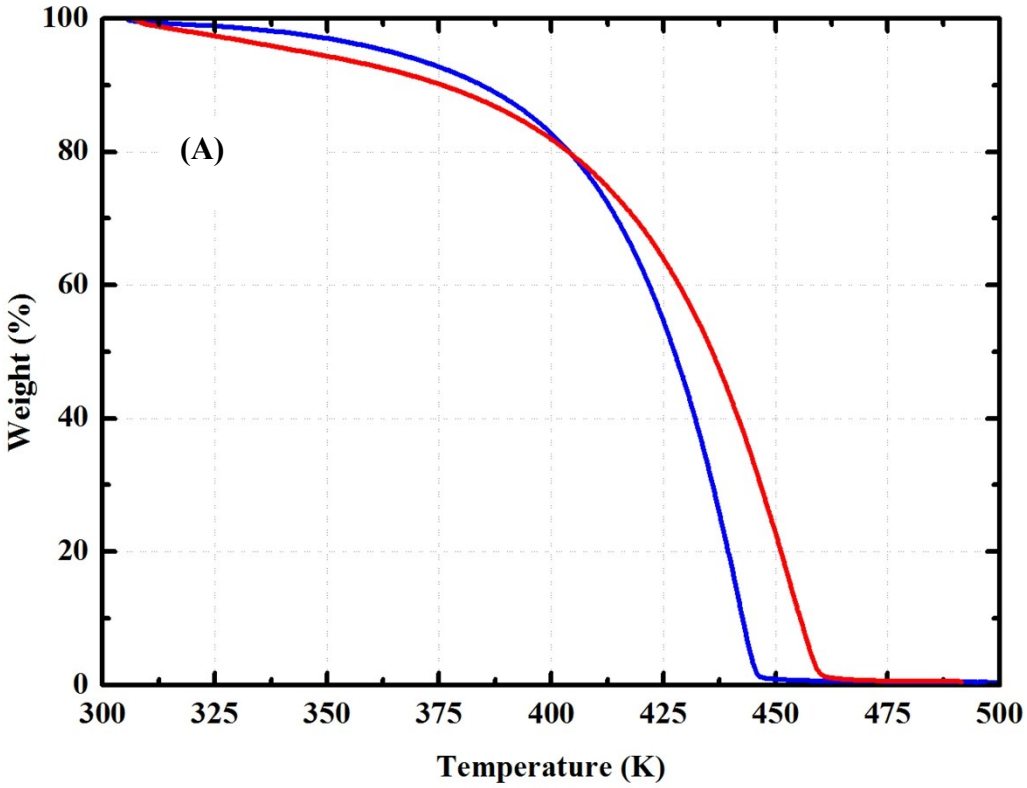
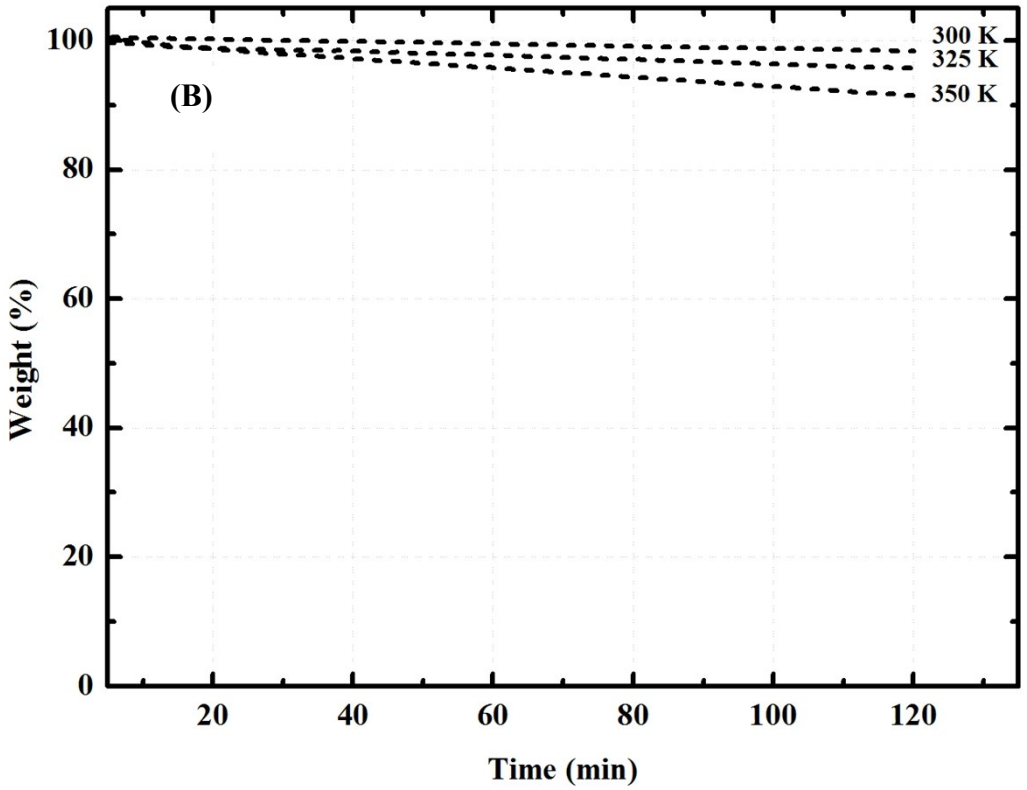


Figure S4. Mass Spectra of TMG cation of (A) [TMG][Lac] and (B) [TMG][Ace].


(A)
Weight (%)
Temperature (K)
100
80
60
40
20
0
300
325
350
375
400
425
450
475
500


(B)
300 K
325 K
350 K
Weight (%)
Time (min)
100
80
60
40
20
0
20
40
60
80
100
120

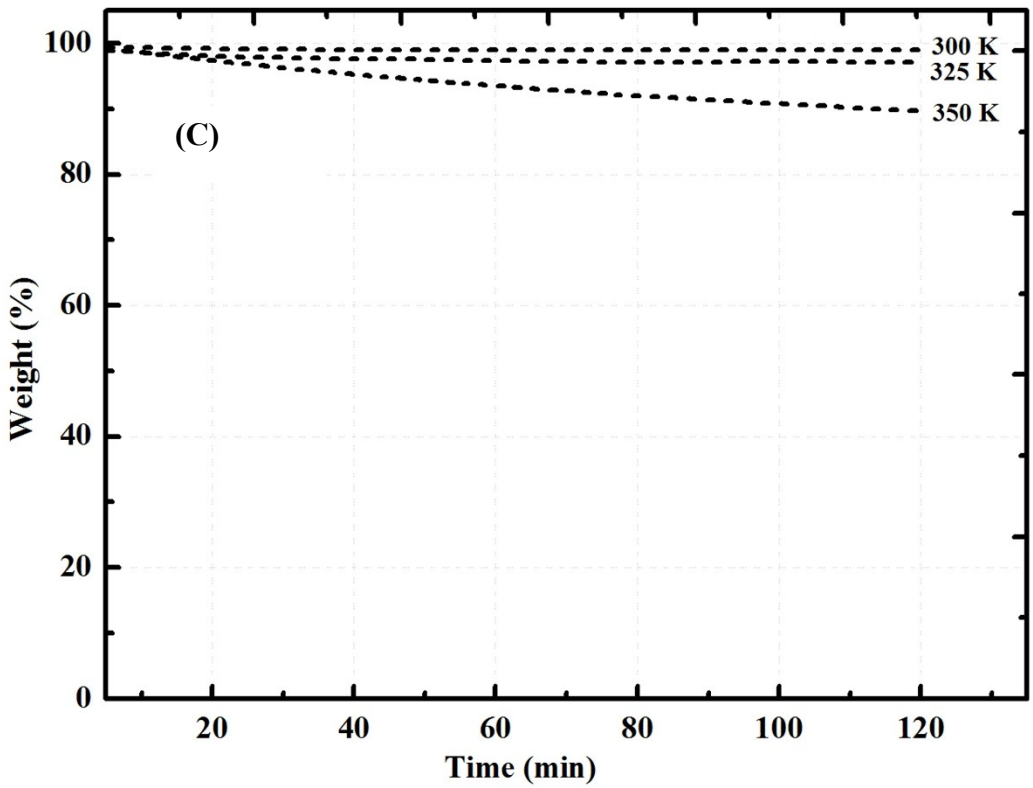
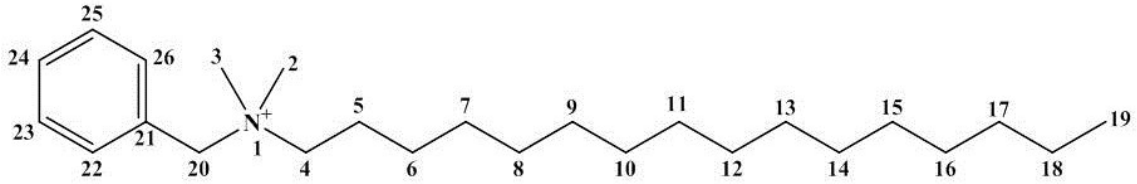


Figure S5. (A) Normal thermogravimetric analysis (TGA) of synthesized [TMG][Ace] (Blue) and [TMG][Lac] (Red). Static TGA for (B) [TMG][Ace] and (C) [TMG][Lac]. Both ILs exhibit good thermal stability up to 350 K (< 10% degradation).

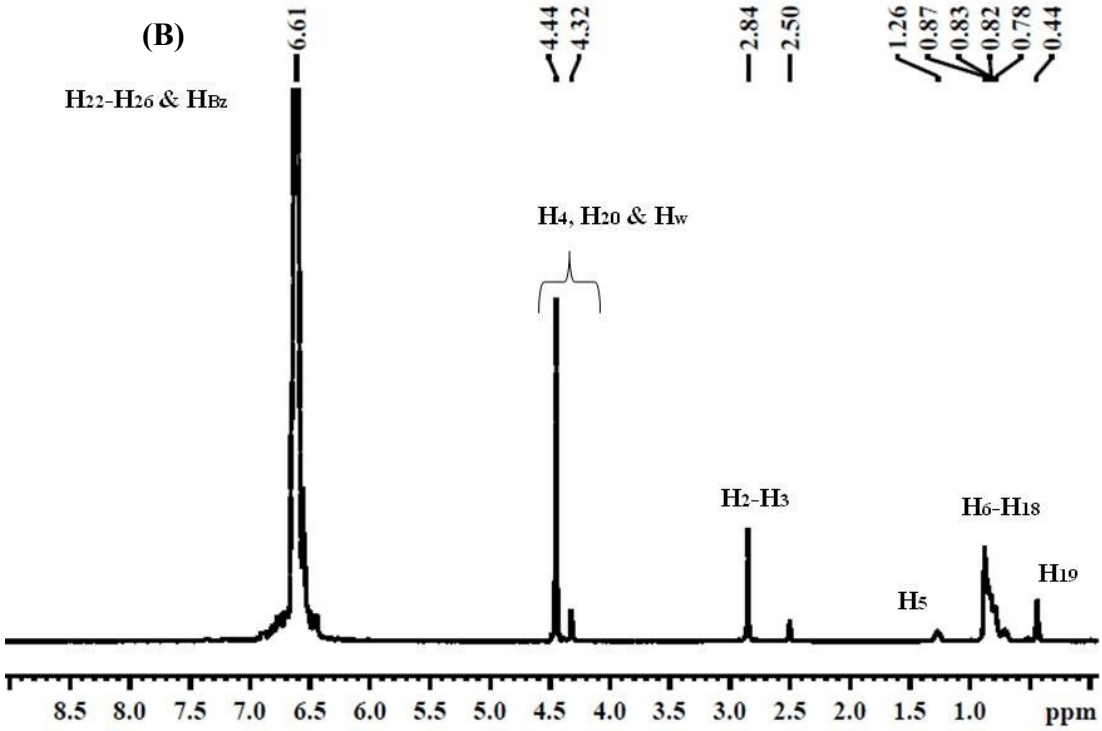
Table S1. Viscosity values of pure components and investigated mixtures of samples. Experimental error (in percent difference): ≤ 5%.

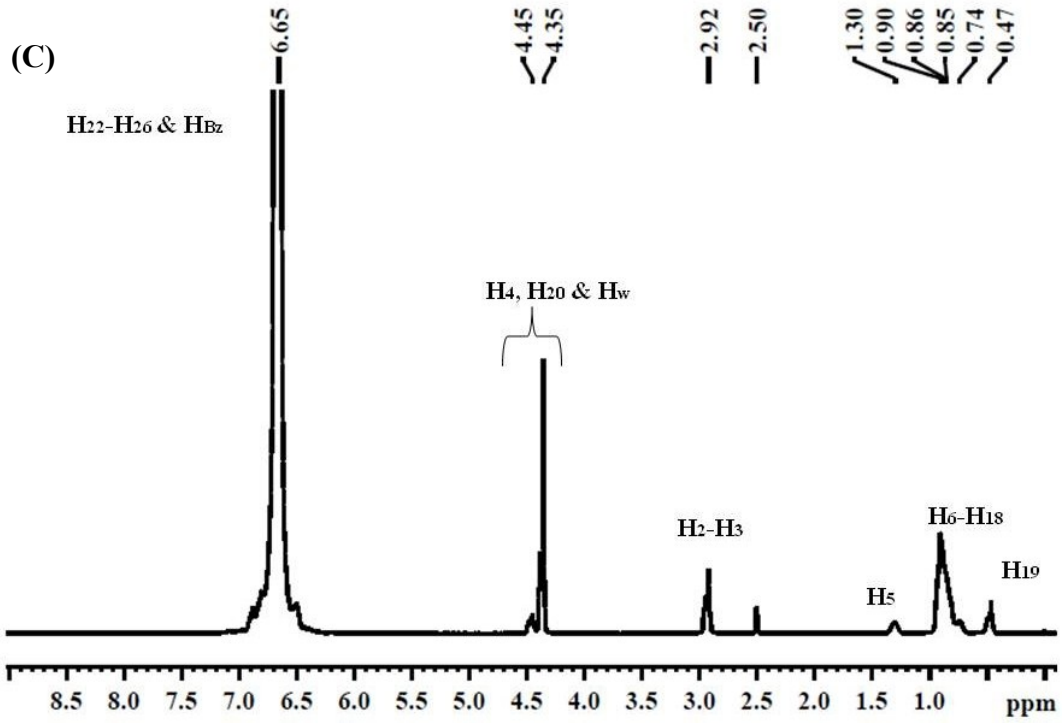
System and Composition	η/mPa·s
Bulk Benzene	0.601
Water, ω = 5	0.888
[TMG][Lac], ω = 5	0.805
[TMG][Ace], ω = 5	0.792
Water, ω = 10	1.100
[TMG][Lac], ω = 10	0.876
[TMG][Ace], ω = 10	0.807
Water, ω = 15	1.330
[TMG][Lac], ω = 15	0.920
[TMG][Ace], ω = 15	0.836
Water, ω = 28	1.400
[TMG][Lac], ω = 28	0.941
[TMG][Ace], ω = 28	0.857

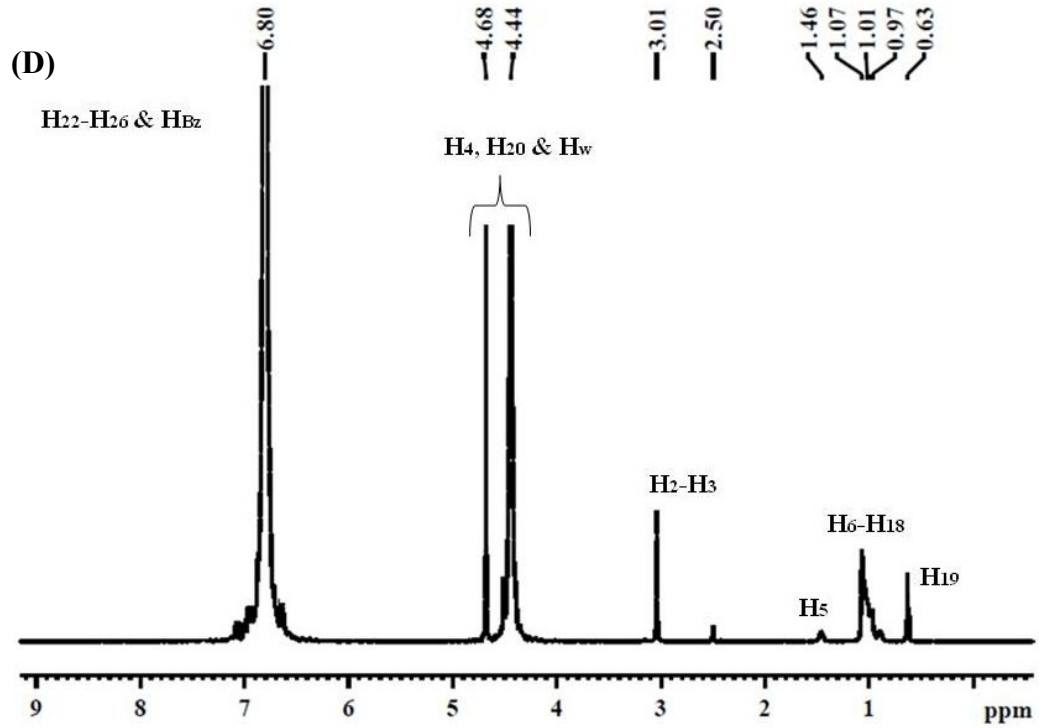
(A)


25
24
26
3
2
23
21
N+
1
5
7
9
11
13
15
17
19
22
20
4
6
8
10
12
14
16
18

(B)


6.61
4.44
4.32
2.84
2.50
1.26
0.87
0.83
0.82
0.78
0.44
H22-H26 & HBz
H4, H20 & Hw
H2-H3
H6-H18
H19
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


(C)
6.65
4.45
4.35
2.92
2.50
1.30
0.90
0.86
0.85
0.74
0.47
H22-H26 & HBz
H4, H20 & Hw
H2-H3
H6-H18
H19
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


(D)
6.80
4.68
4.44
3.01
2.50
1.46
1.07
1.01
0.97
0.63
H22-H26 & HBz
H4, H20 & Hw
H2-H3
H6-H18
H19
H5
9 8 7 6 5 4 3 2 1
ppm

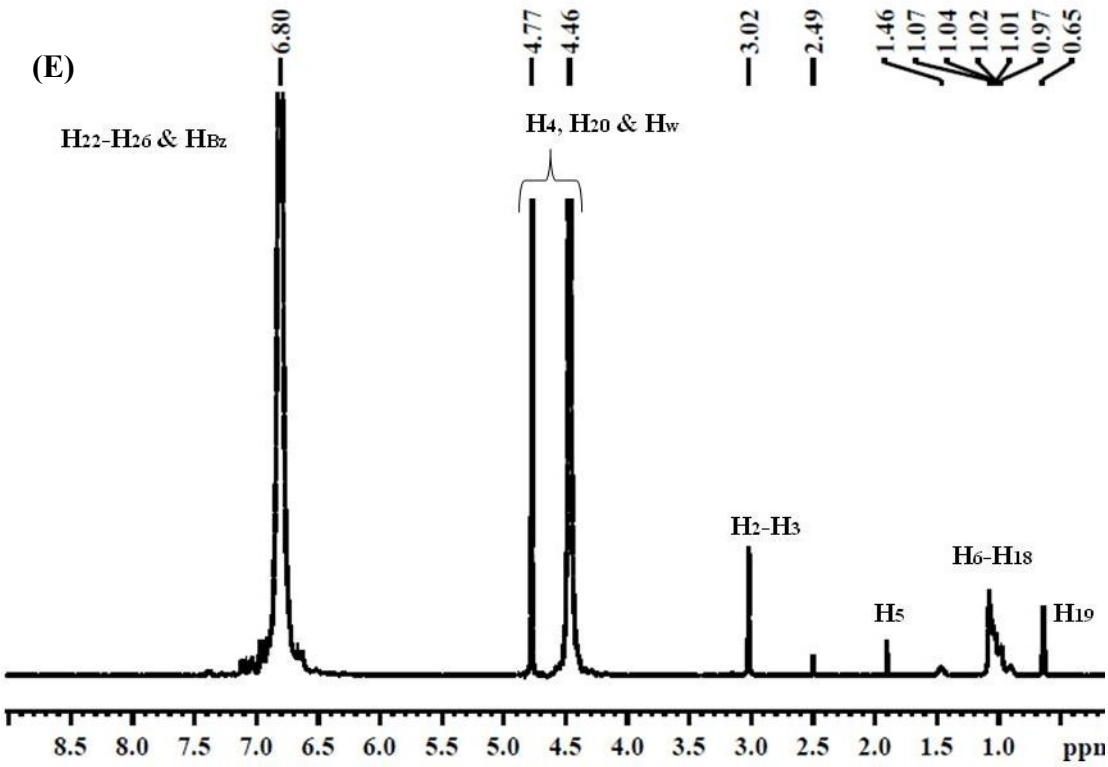
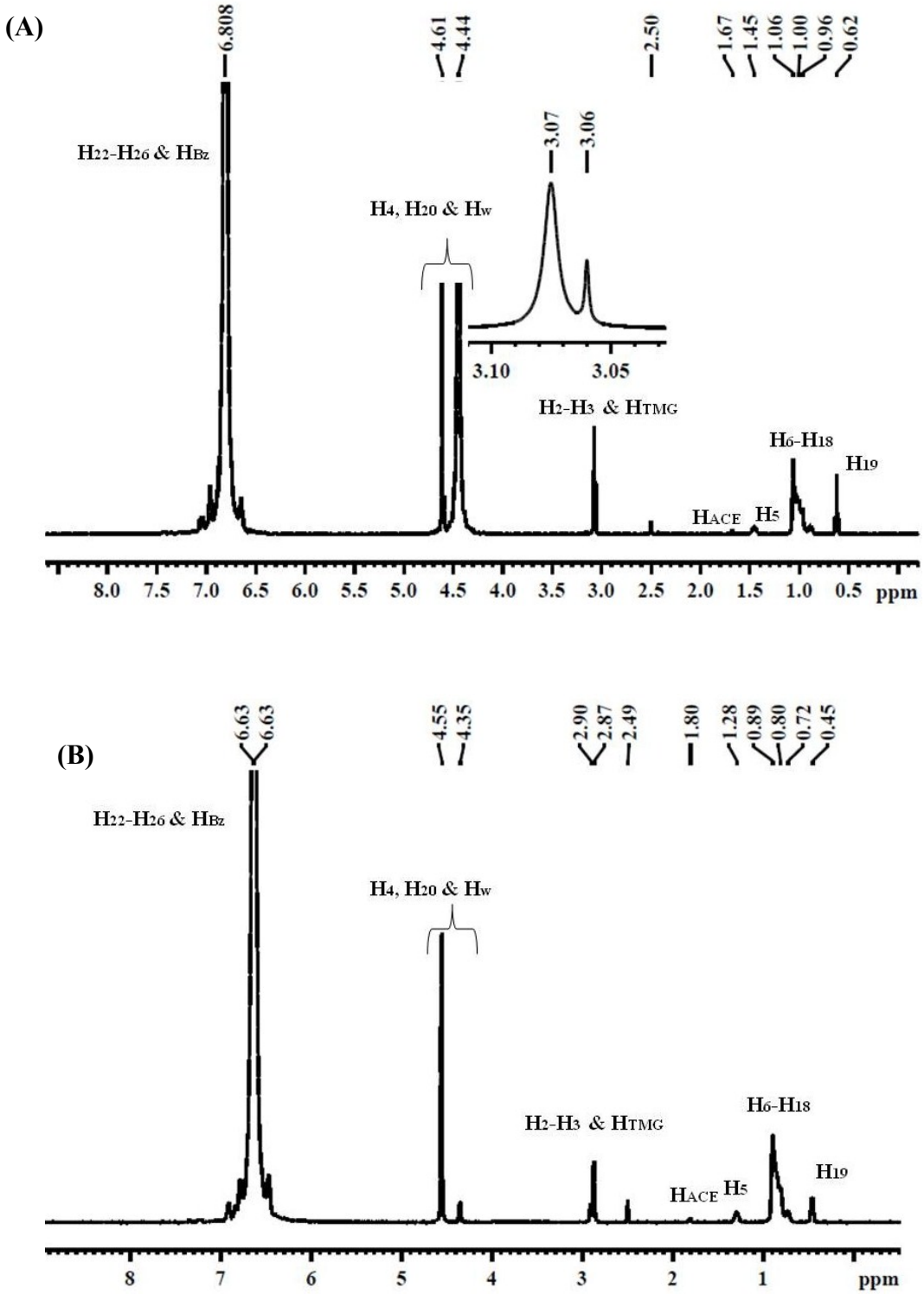


Figure S6. ^{1}H NMR spectra of BHDC in water/oil microemulsions at different water content. Proton notations are depicted according to the BHDC heavy atom numbering, as shown in (A). Different water content are shown as (B) ω = 5, (C) ω = 10, (D) ω = 15 and (E) ω_{max}.


(A)
6.808
4.61
4.44
2.50
1.67
1.45
1.06
1.00
0.96
0.62
3.07
3.06
H22-H26 & HBz
H4, H20 & Hw
3.10
3.05
H2-H3 & HTMG
H6-H18
H19
HACE
H5
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm
(B)
6.63
6.63
4.55
4.35
2.90
2.87
2.49
1.80
1.28
0.89
0.80
0.72
0.45
H22-H26 & HBz
H4, H20 & Hw
H2-H3 & HTMG
H6-H18
H19
HACE
H5
8 7 6 5 4 3 2 1 ppm

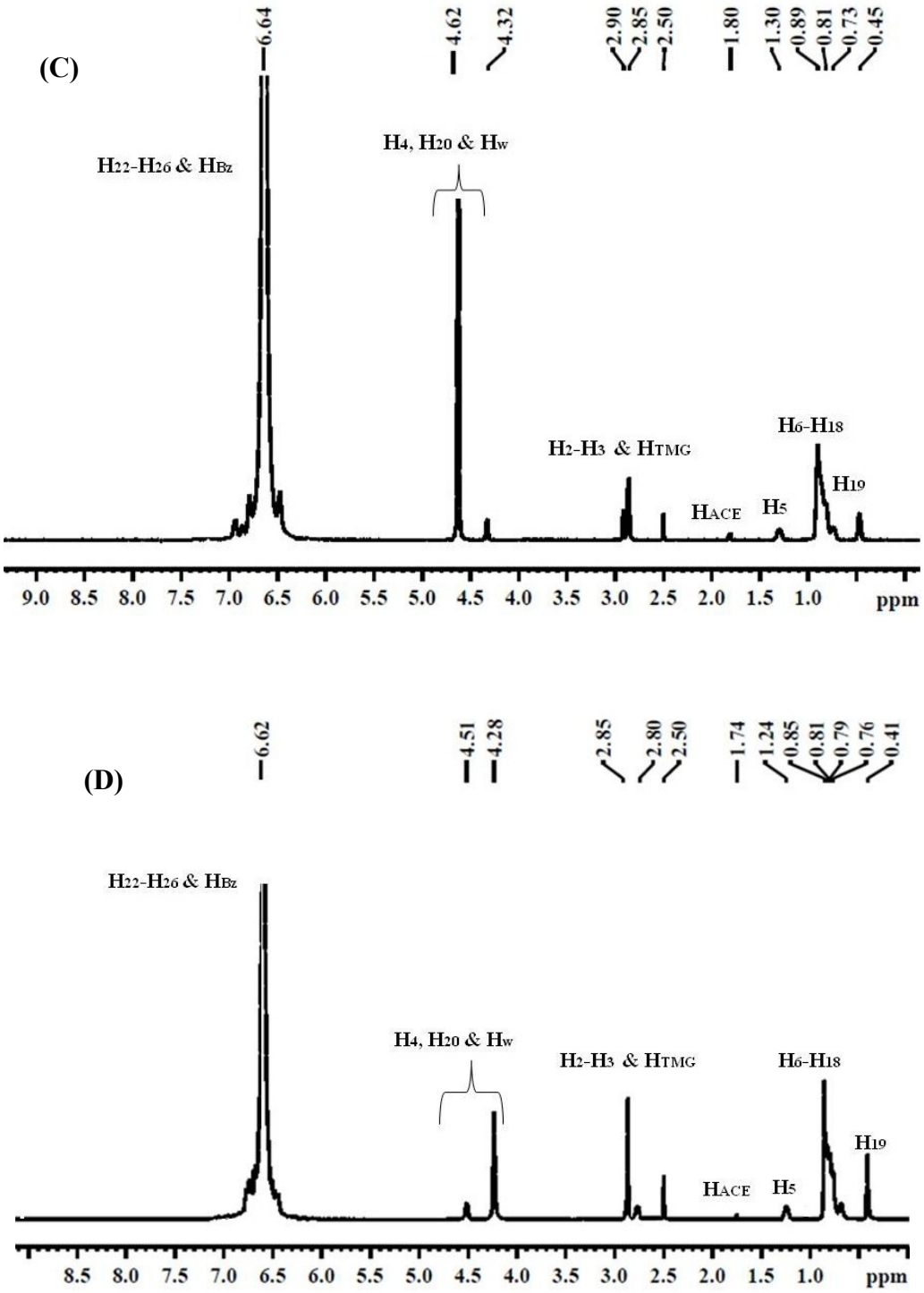
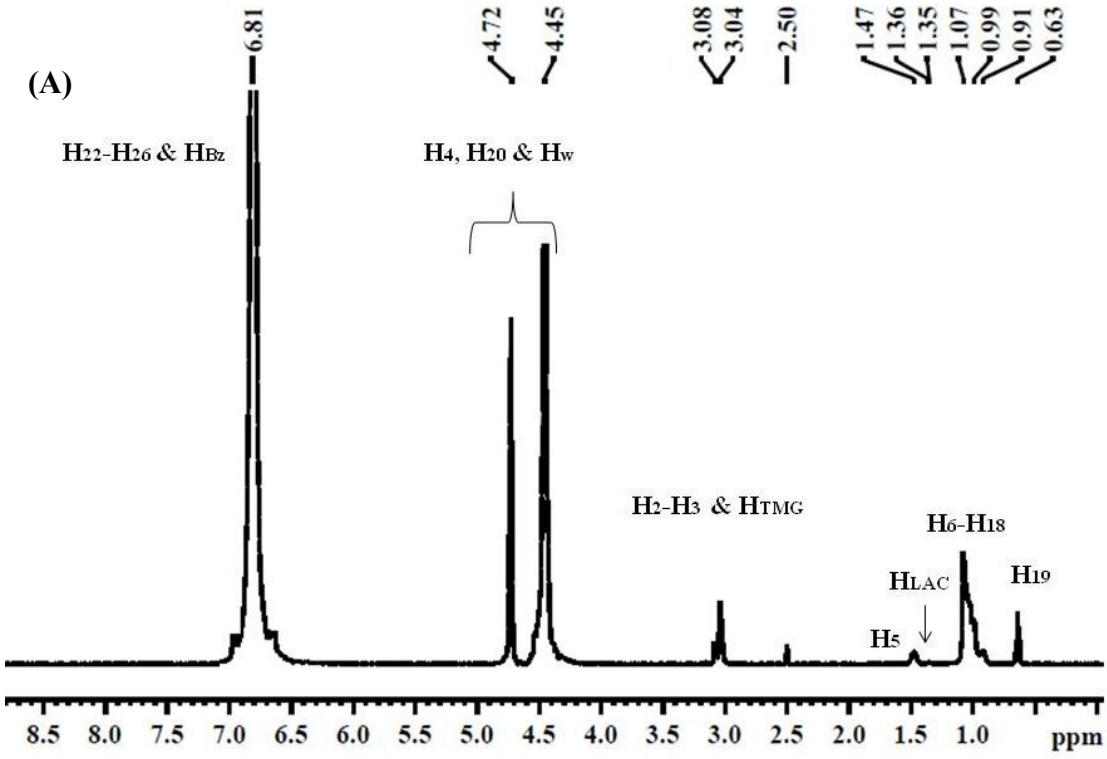
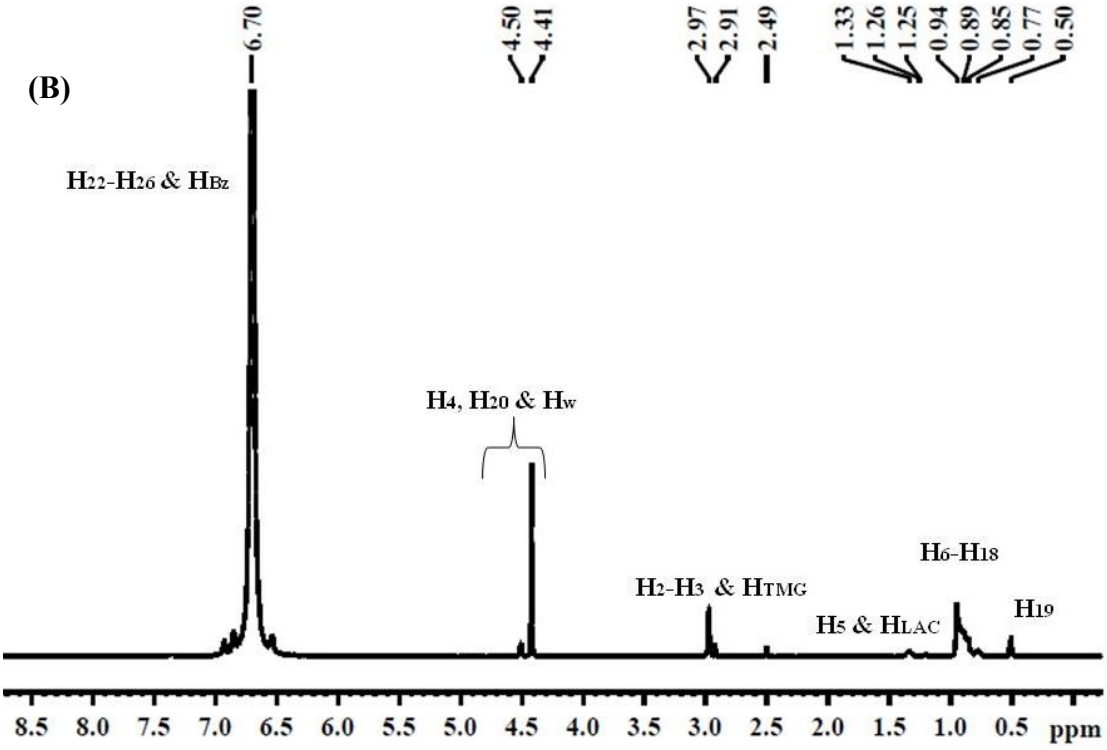


Figure S7. ^{1}H NMR spectra of BHDC in water/oil microemulsions in presence of [TMG][Ace] at different water content - (A) ω = 5, (B) ω = 10, (C) ω = 15 and (D) ω_{max}.


(A)
6.81
4.72
4.45
3.08
3.04
2.50
1.47
1.36
1.35
1.07
0.99
0.91
0.63
H22-H26 & HBz
H4, H20 & Hw
H2-H3 & HTMG
H6-H18
HLAC
H19
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
ppm


(B)
6.70
4.50
4.41
2.97
2.91
2.49
1.33
1.26
1.25
0.94
0.89
0.85
0.77
0.50
H22-H26 & HBz
H4, H20 & Hw
H6-H18
H2-H3 & HTMG
H19
H5 & HLAC
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
ppm

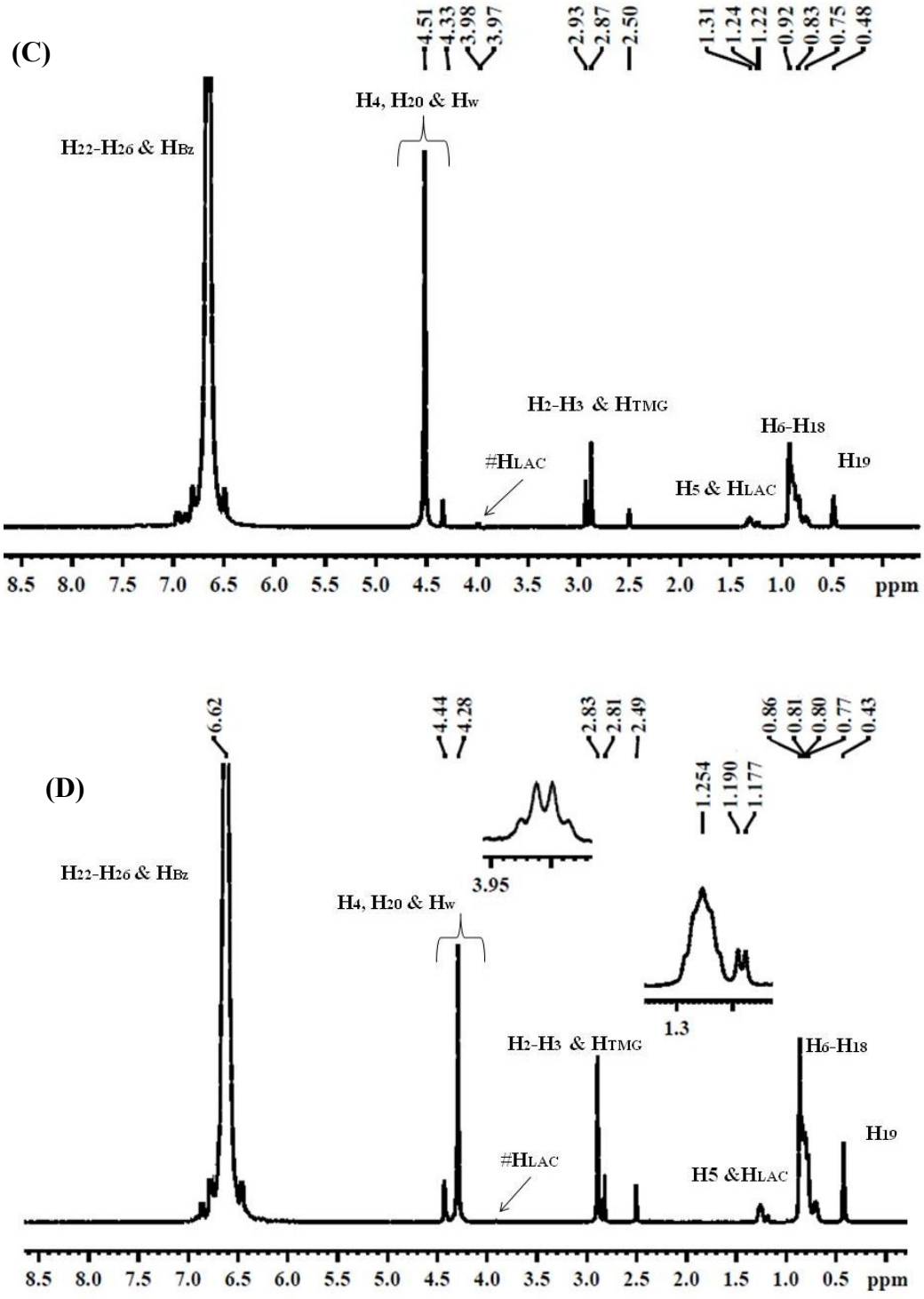
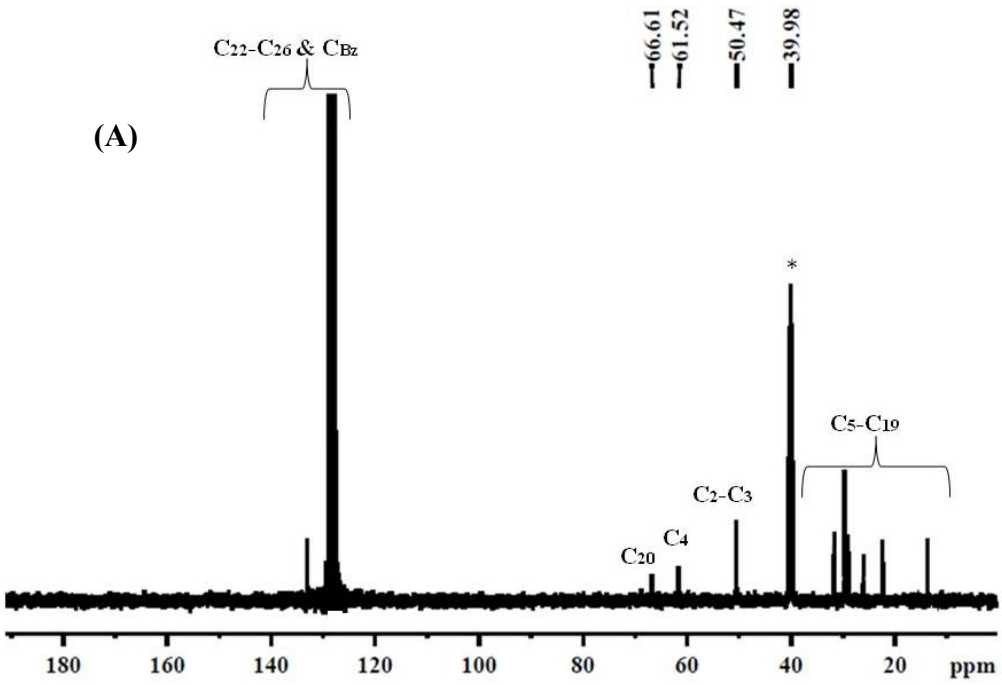
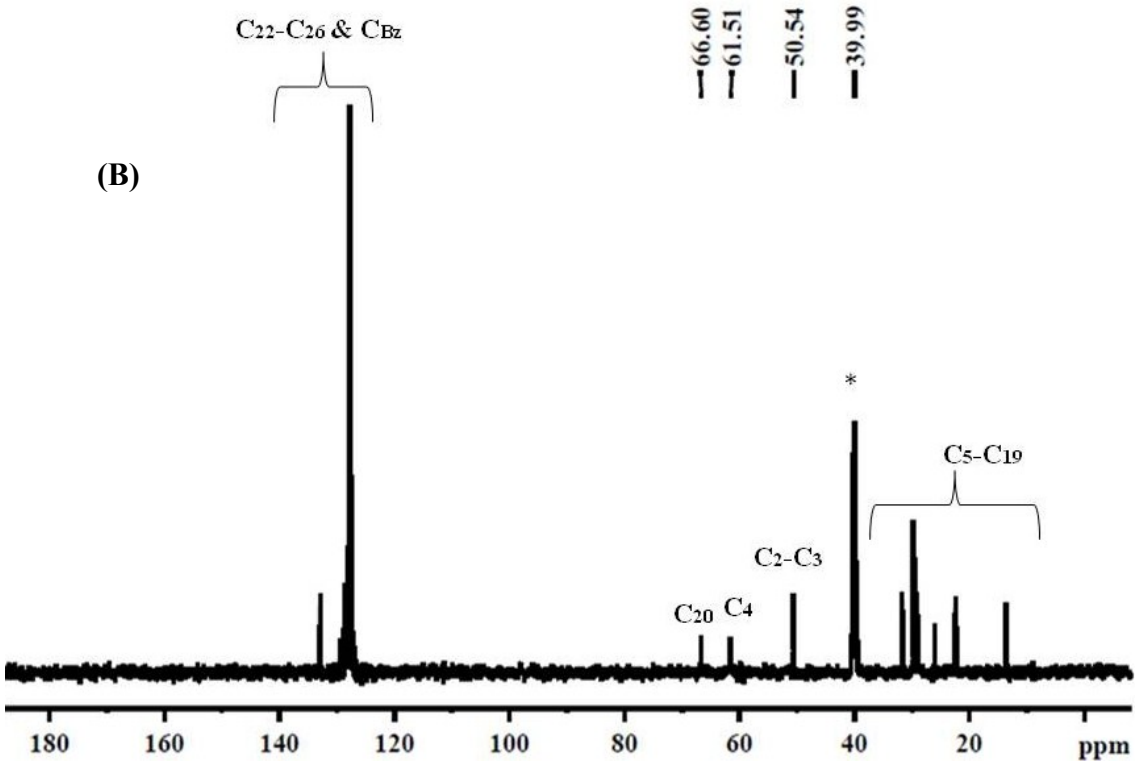


Figure S8. ^{1}H NMR spectra of BHDC in water/oil microemulsions in presence of [TMG][Lac] at different water content - (A) ω = 5, (B) ω = 10, (C) ω = 15 and (D) ω_{max}.


(A)
C22-C26 & CBz
66.61
61.52
50.47
39.98
*
C5-C19
C2-C3
C4
C20
180
160
140
120
100
80
60
40
20
ppm


(B)
C22-C26 & CBz
66.60
61.51
50.54
39.99
*
C5-C19
C2-C3
C20
C4
180
160
140
120
100
80
60
40
20
ppm

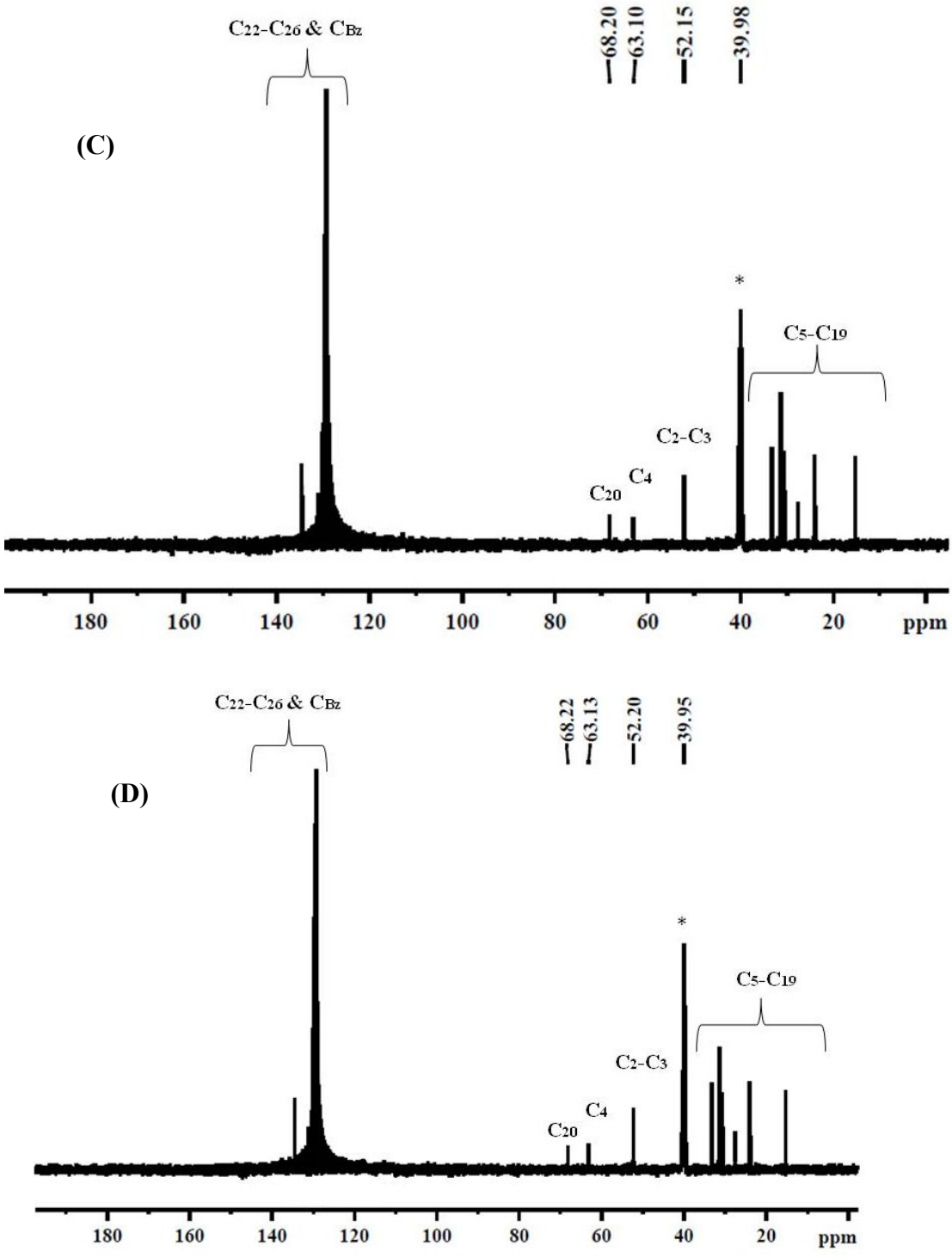
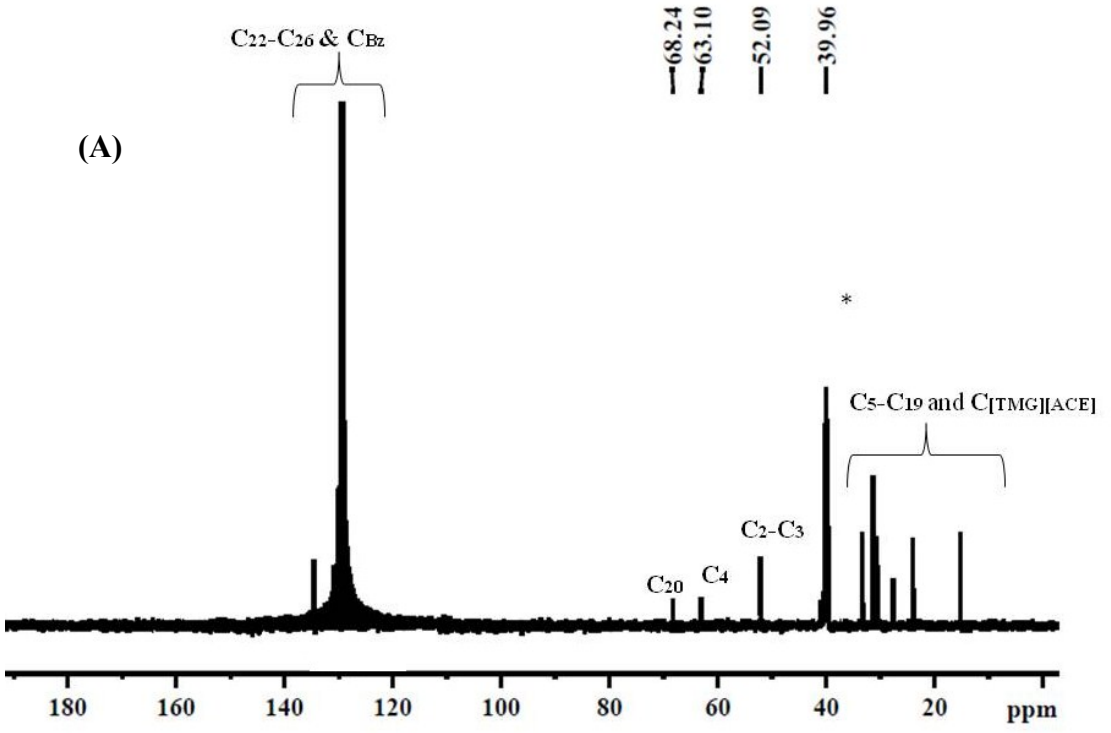
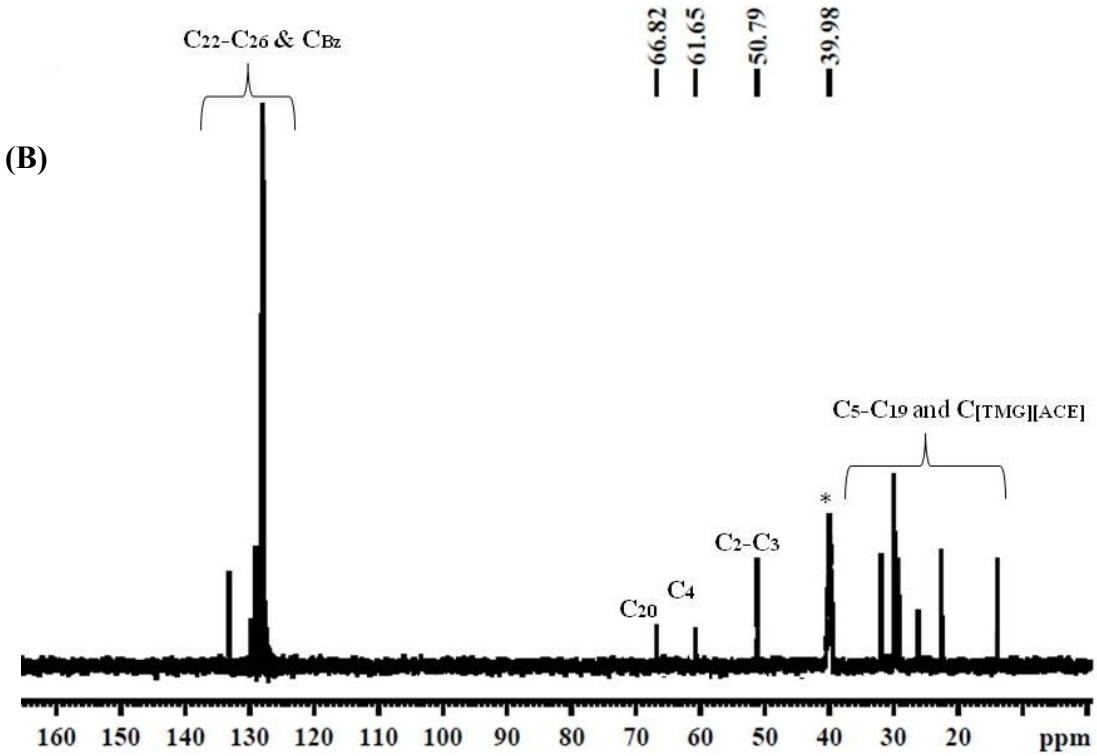


Figure S9. ^{13}C NMR spectra of BHDC in water/oil microemulsions at different water content - (A) $\omega = 5$, (B) $\omega = 10$, (C) $\omega = 15$ and (D) ω_{max}. Carbon atom notations are according to Fig. S6A.


(A)
C22-C26 & CBz
68.24
63.10
52.09
39.96
*
C5-C19 and C[TMG][ACE]
C2-C3
C20
C4
180
160
140
120
100
80
60
40
20
ppm


(B)
C22-C26 & CBz
66.82
61.65
50.79
39.98
C5-C19 and C[TMG][ACE]
*
C2-C3
C4
C20
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

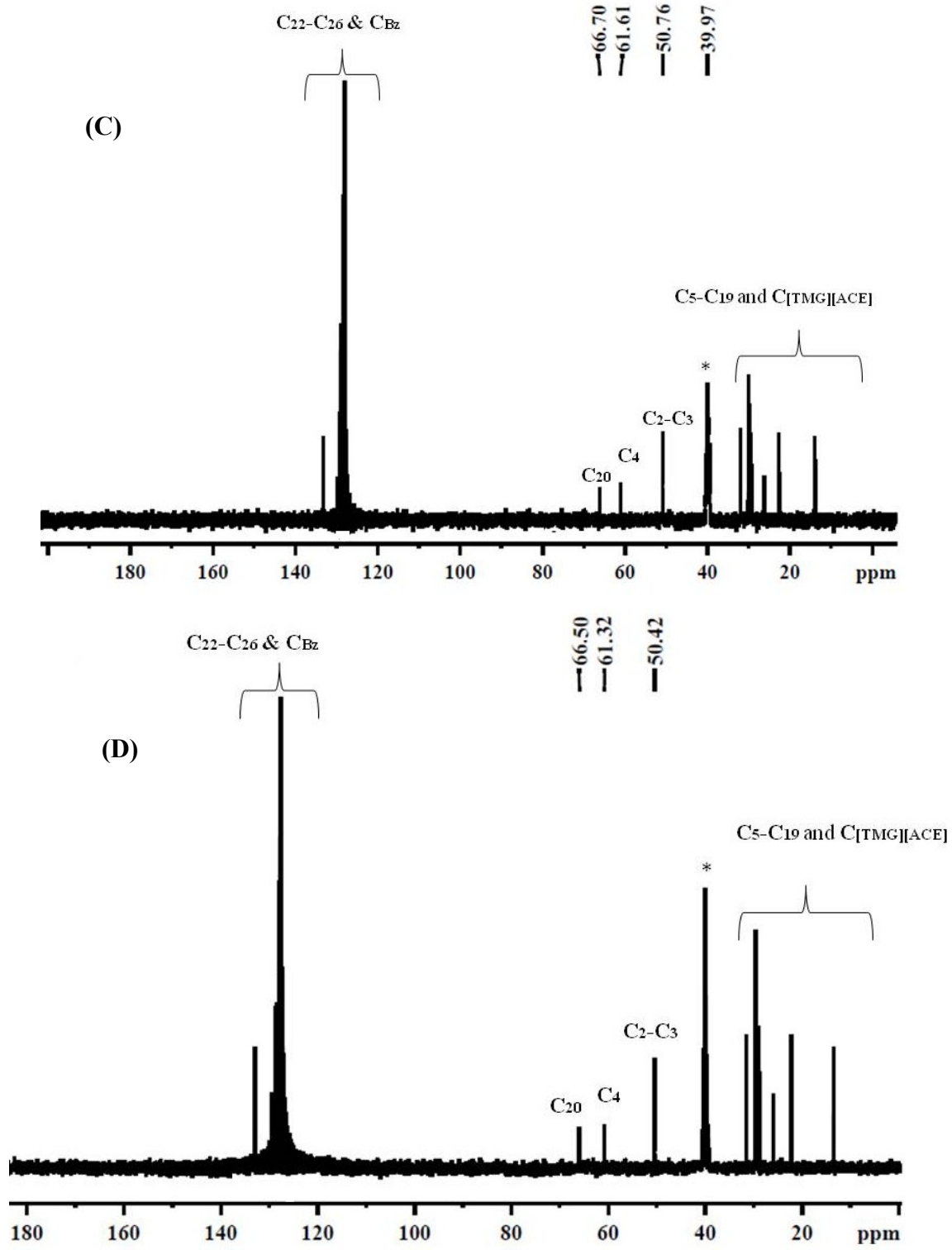
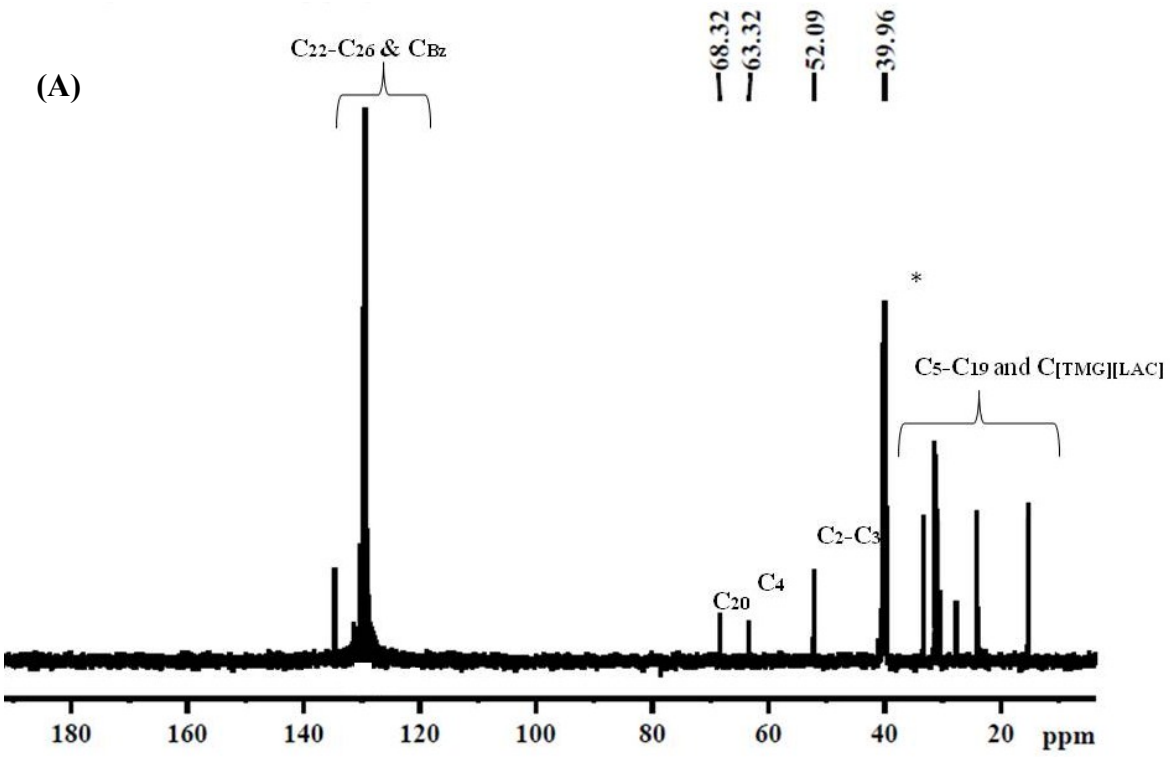
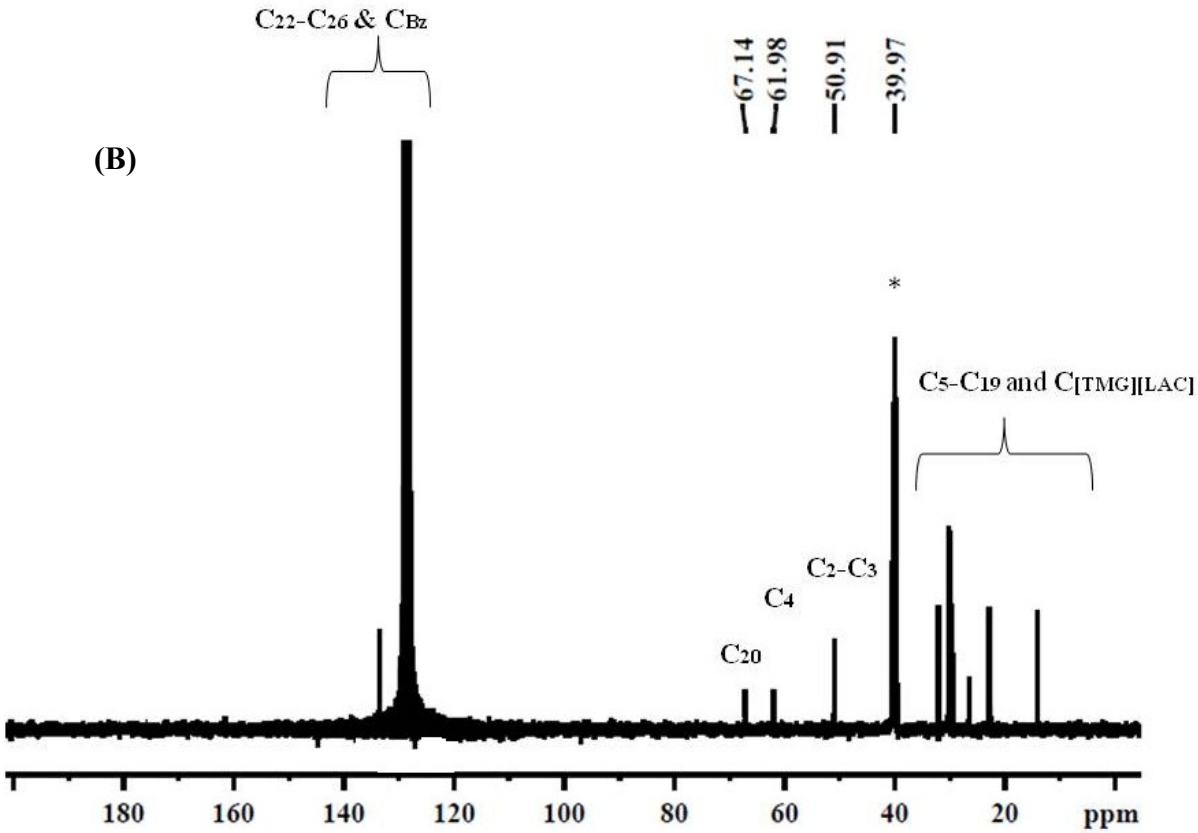


Figure S10. ^{13}C NMR spectra of BHDC in water/oil microemulsions in presence of [TMG][Ace] at different water content - (A) ω = 5, (B) ω = 10, (C) ω = 15 and (D) ω_{max}.


(A)
C22-C26 & CBz
68.32
63.32
52.09
39.96
*
C5-C19 and C[TMG][LAC]
C2-C3
C4
C20
180
160
140
120
100
80
60
40
20
ppm


(B)
C22-C26 & CBz
67.14
61.98
50.91
39.97
*
C5-C19 and C[TMG][LAC]
C2-C3
C4
C20
180
160
140
120
100
80
60
40
20
ppm

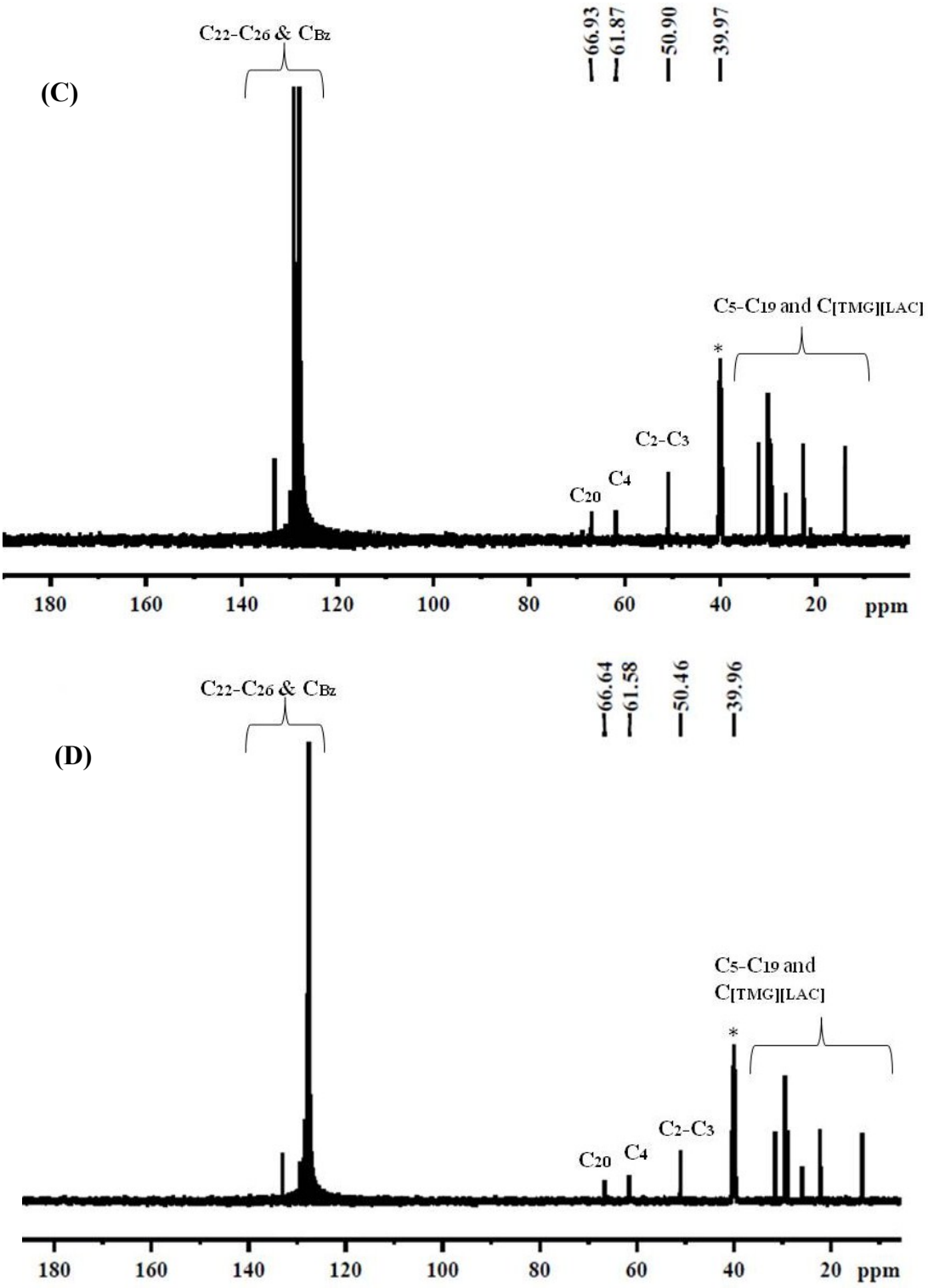


Figure S11. ^{13}C NMR spectra of BHDC in water/oil microemulsions in presence of [TMG][Lac] at different water content - (A) ω = 5, (B) ω = 10, (C) ω = 15 and (D) ω_{max}.

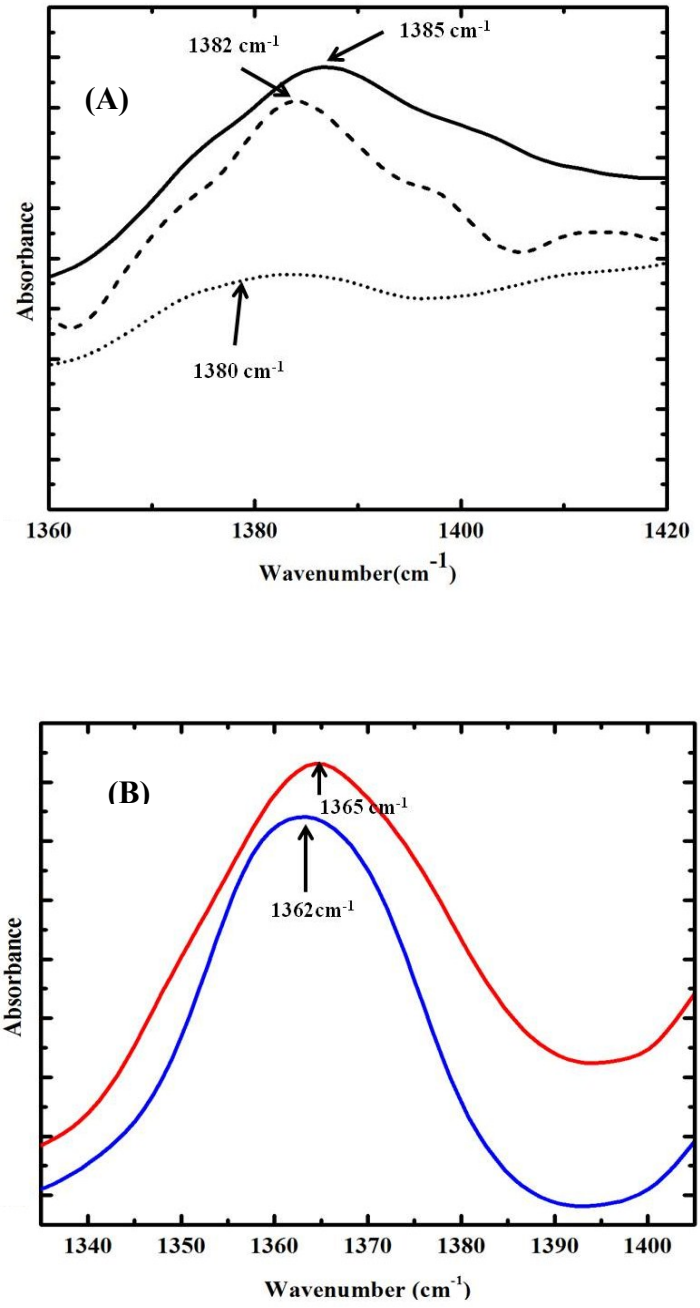
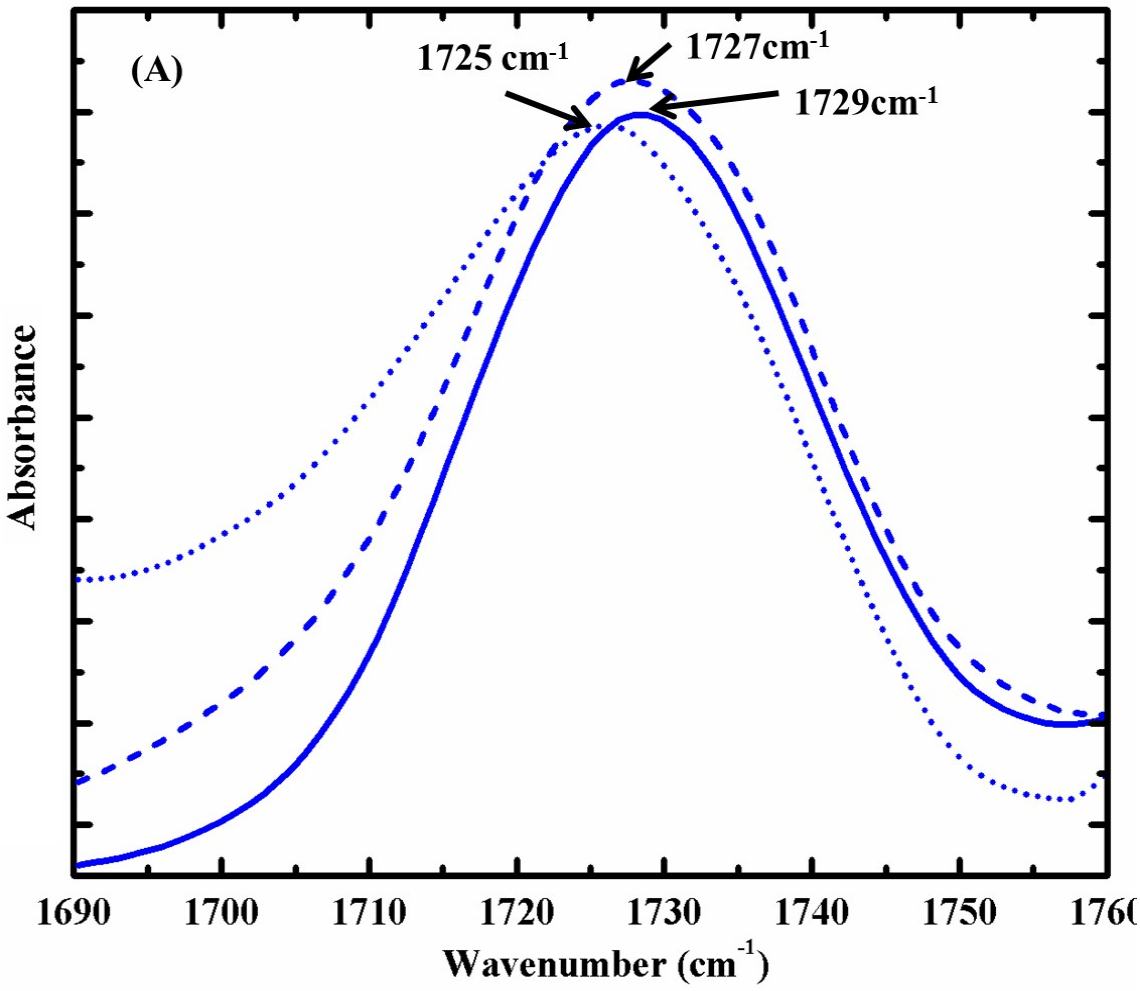


Figure S12. The change in C-N stretching band of BHDC ($\upsilon_{C\text{-}N}$) - **(A)** In absence of IL. Solid, dash, and dotted lines represent the spectra in RMs with ω = 5, 10 and 15, respectively. **(B)** In presence of ILs in the representative RM with ω = 5. Color scheme: red for [TMG][Lac]-water and blue for [TMG][Ace]-water containing microemulsion systems.


(A)
1725 cm-1
1727cm-1
1729cm-1
Absorbance
1690
1700
1710
1720
1730
1740
1750
1760
Wavenumber (cm-1)

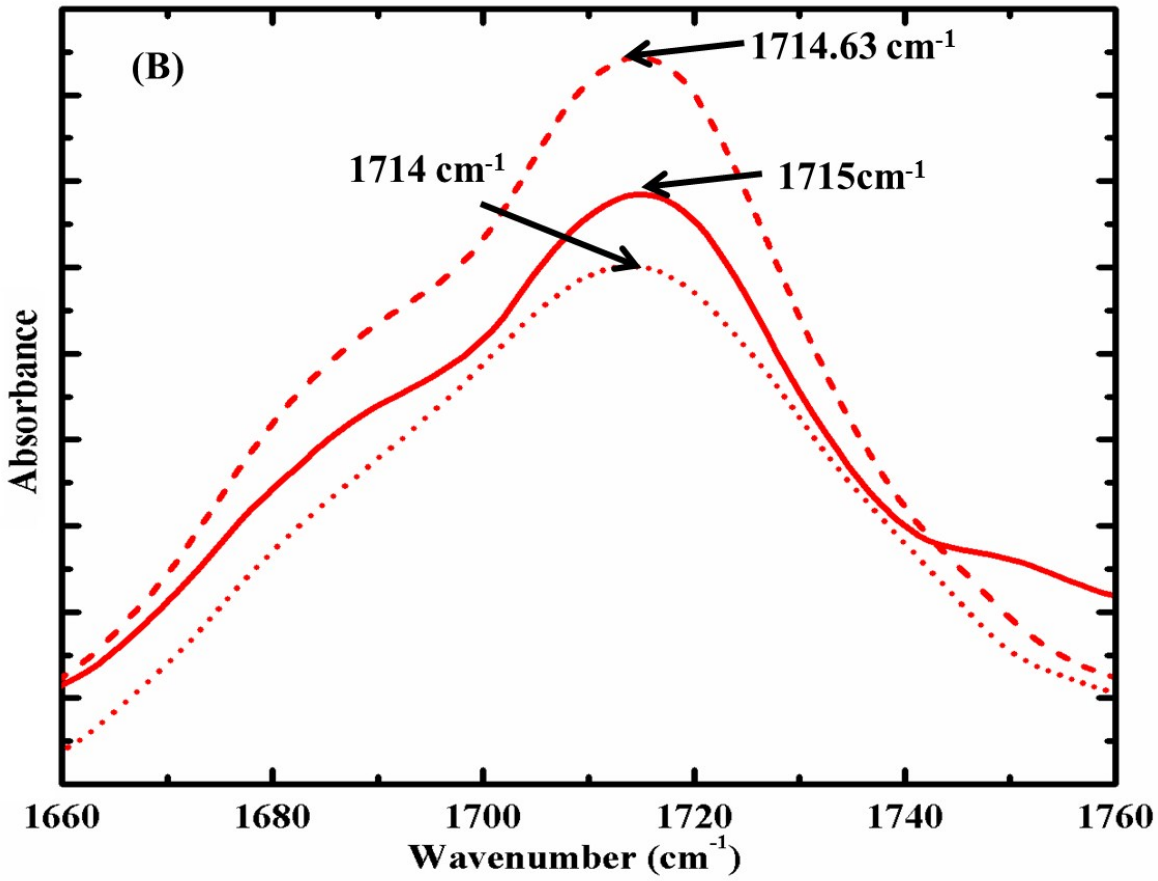


Figure S13. The carbonyl stretching mode of **(A)** $[Ace]^-$ and **(B)** $[Lac]^-$ anions of the ILs. The solid, dash, and dotted lines represent the spectra in bulk aqueous phase, RM systems of $\omega = 5$ and $\omega = 10$, respectively.

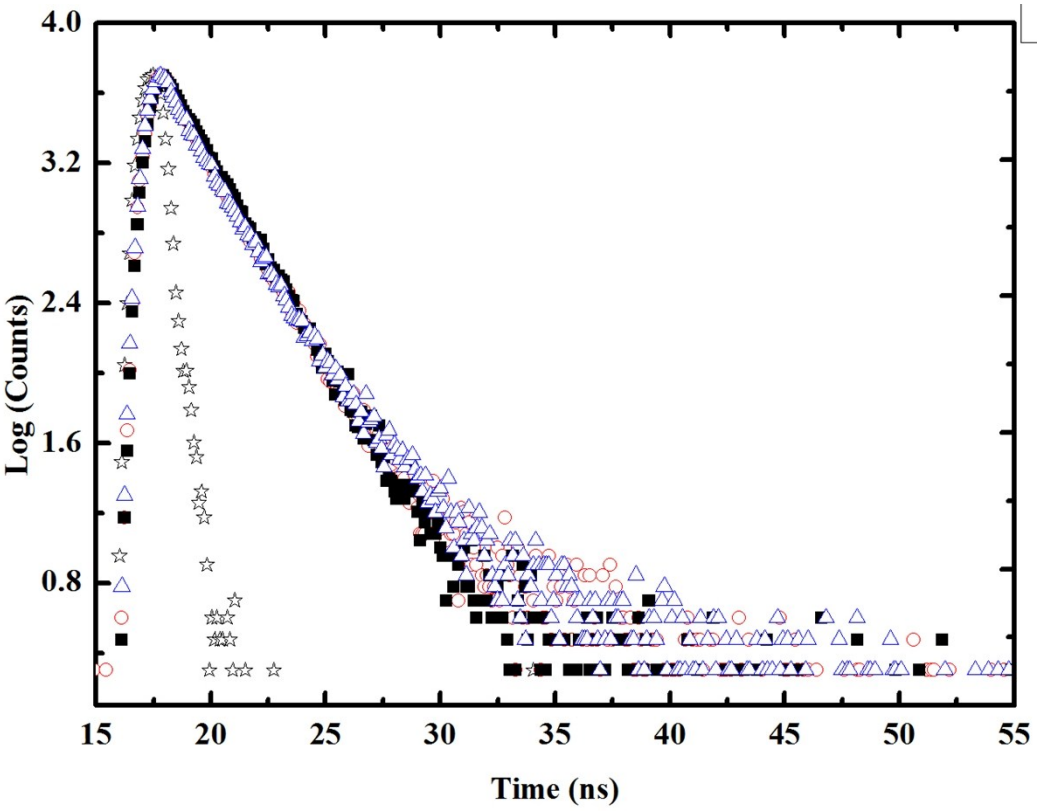


Figure S14. Lifetime decay of EtBr in absence and presence of the ILs at ω = 28. Color scheme: black for neat water, red for [TMG][Lac]-water and blue for [TMG][Ace]-water containing microemulsion systems

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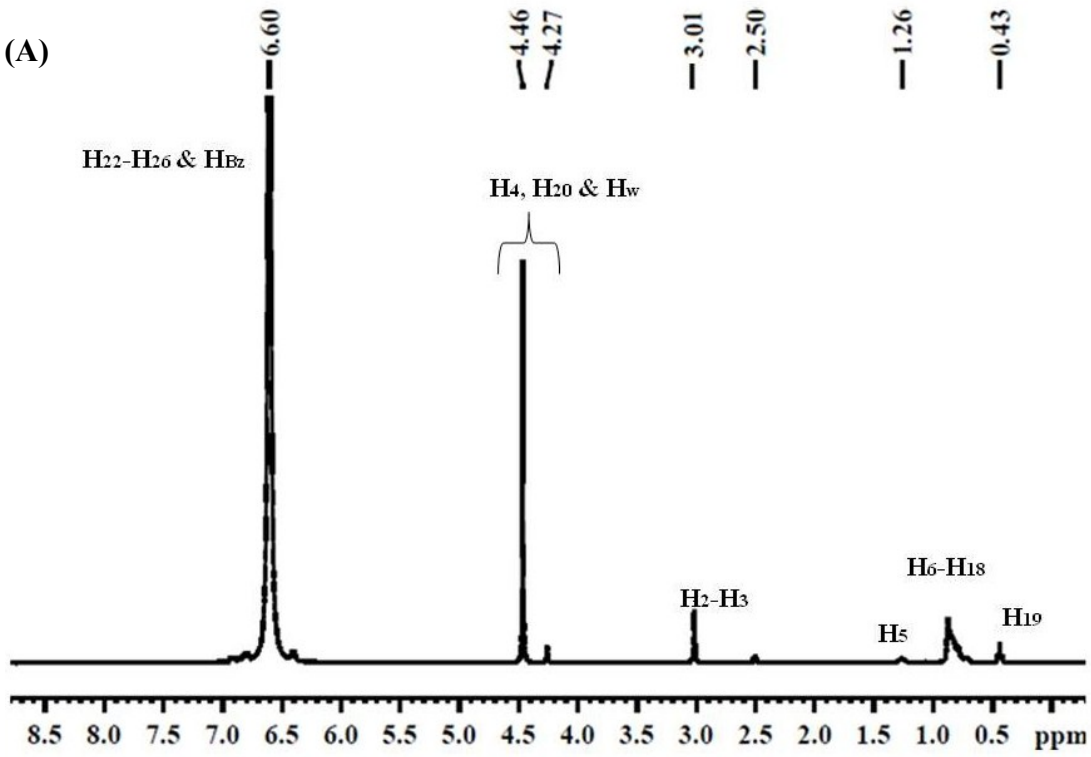
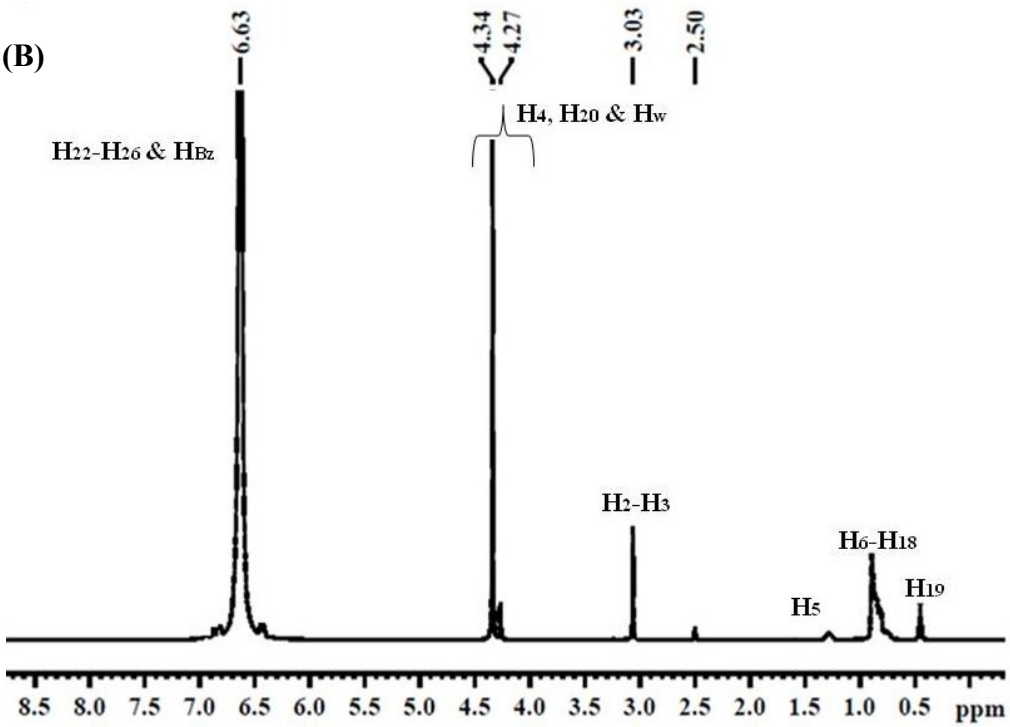

(A)
6.60
4.46
4.27
3.01
2.50
1.26
0.43
H22-H26 & HBz
H4, H20 & Hw
H2-H3
H6-H18
H19
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


(B)
6.63
4.34
4.27
3.03
2.50
H4, H20 & Hw
H22-H26 & HBz
H2-H3
H6-H18
H19
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

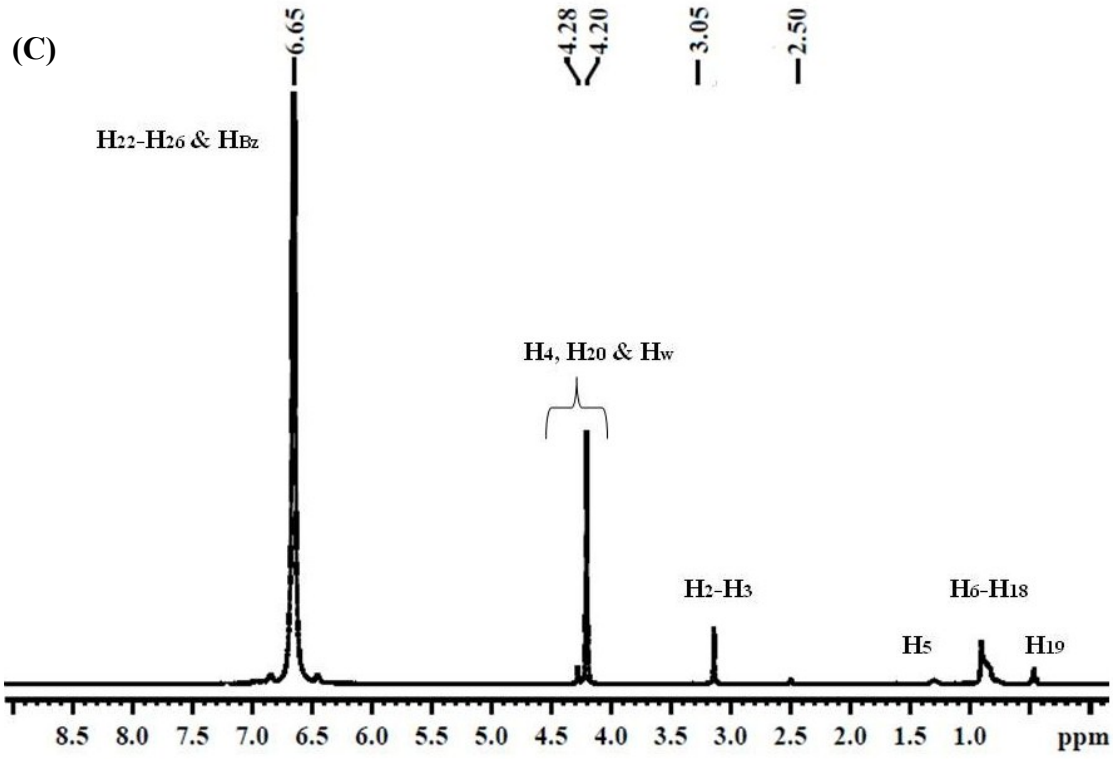
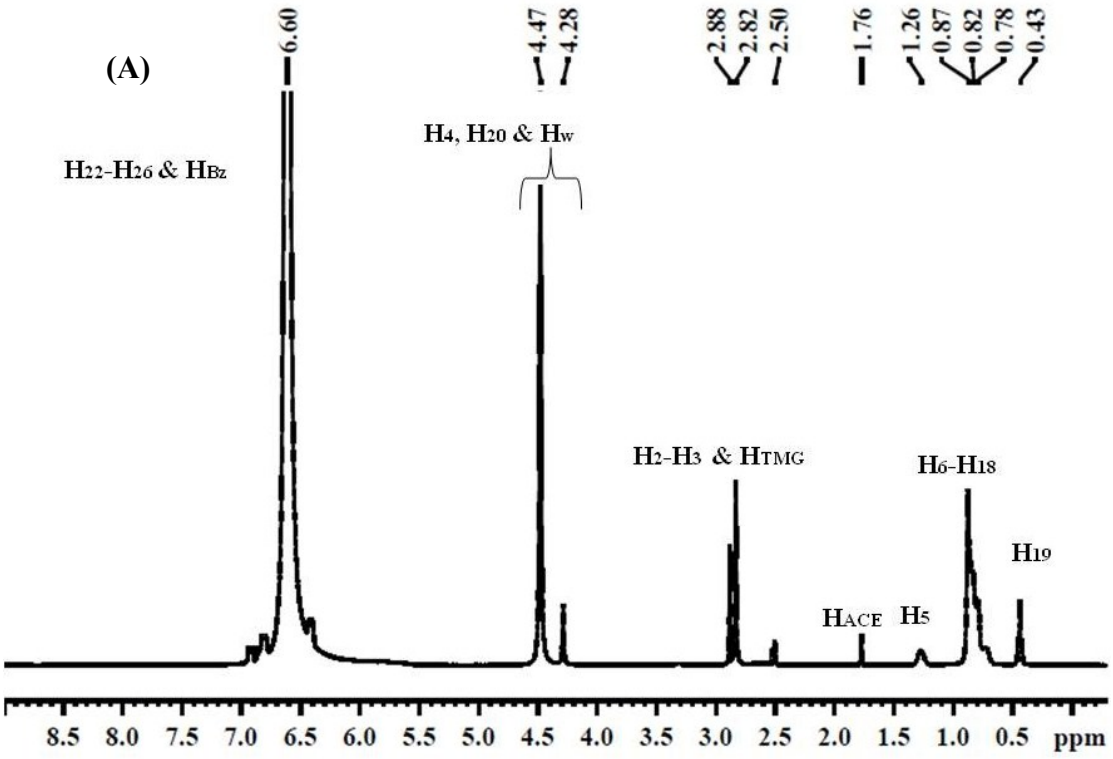
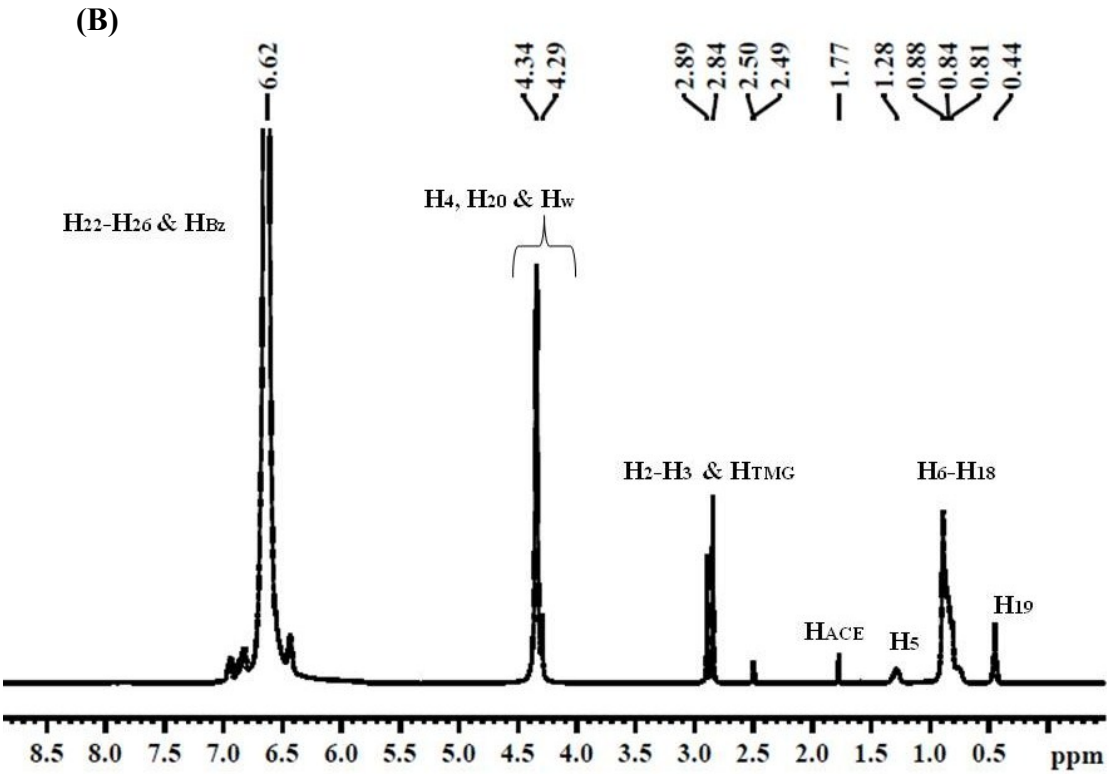


Figure S15. ^{1}H NMR spectra of BHDC in water/oil microemulsions at fixed water content (ω_{max}) and at different temperatures - (A) T = 303, (B) T = 313, and (C) T = 318. Atom notations are according to Fig. S6A


(A)
6.60
4.47
4.28
2.88
2.82
2.50
1.76
1.26
0.87
0.82
0.78
0.43
H22-H26 & HBz
H4, H20 & Hw
H2-H3 & HTMG
H6-H18
H19
HACE
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


(B)
6.62
4.34
4.29
2.89
2.84
2.50
2.49
1.77
1.28
0.88
0.84
0.81
0.44
H22-H26 & HBz
H4, H20 & Hw
H2-H3 & HTMG
H6-H18
H19
HACE
H5
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

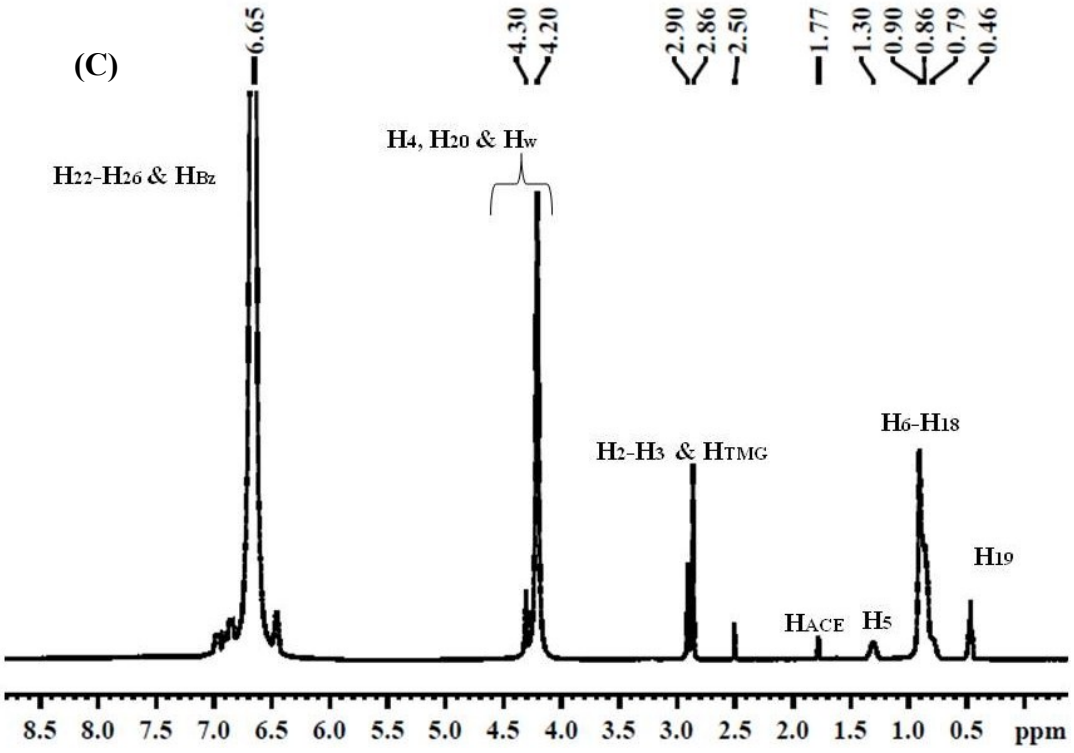
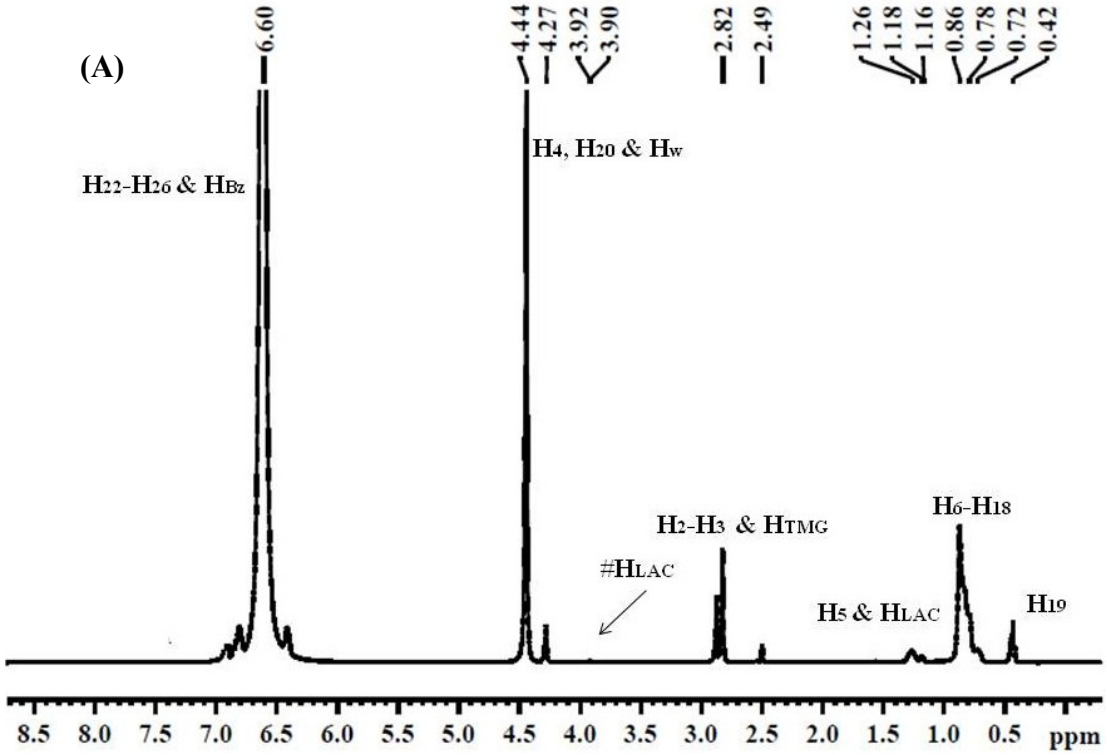
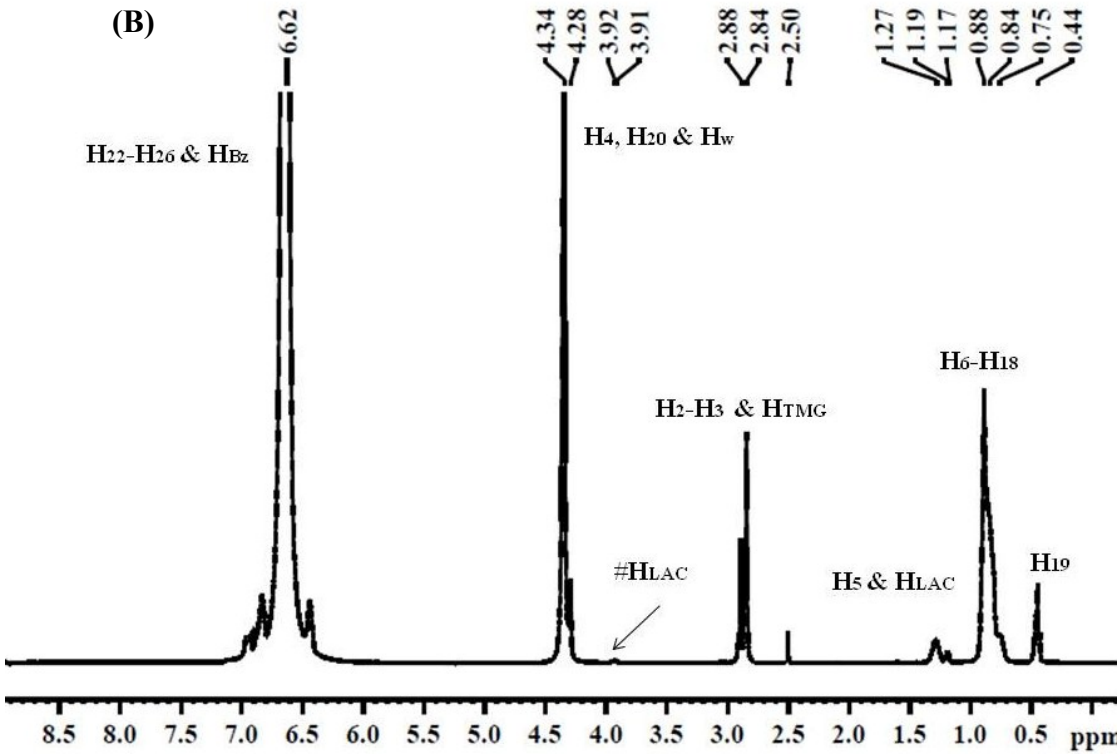


Figure S16. ^{1}H NMR spectra of BHDC in water/oil microemulsions in presence of [TMG][Ace] at fixed water content (ω_{max}) with different temperatures: (A) T = 303, (B) T = 313, and (C) T = 318.


(A)
6.60
4.44
4.27
3.92
3.90
2.82
2.49
1.26
1.18
1.16
0.86
0.78
0.72
0.42
H22-H26 & HBz
H4, H20 & Hw
H2-H3 & HTMG
#HLAC
H6-H18
H5 & HLAC
H19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm


(B)
6.62
4.34
4.28
3.92
3.91
2.88
2.84
2.50
1.27
1.19
1.17
0.88
0.84
0.75
0.44
H22-H26 & HBz
H4, H20 & Hw
H2-H3 & HTMG
#HLAC
H6-H18
H5 & HLAC
H19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 ppm

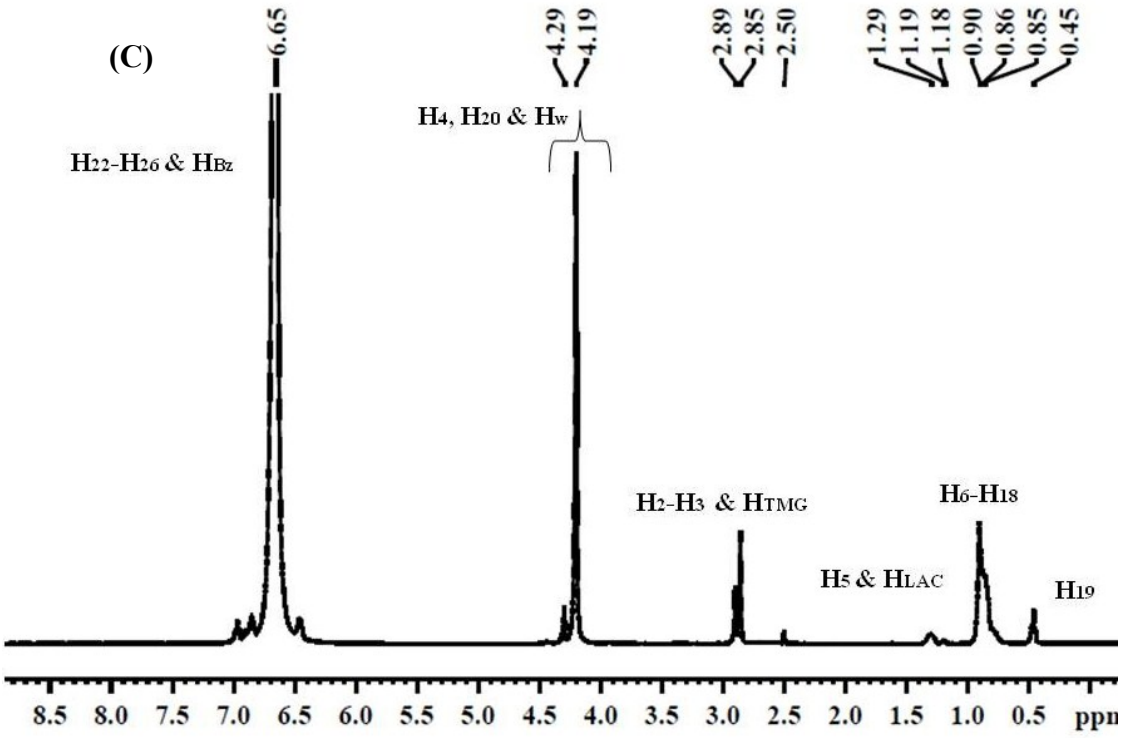
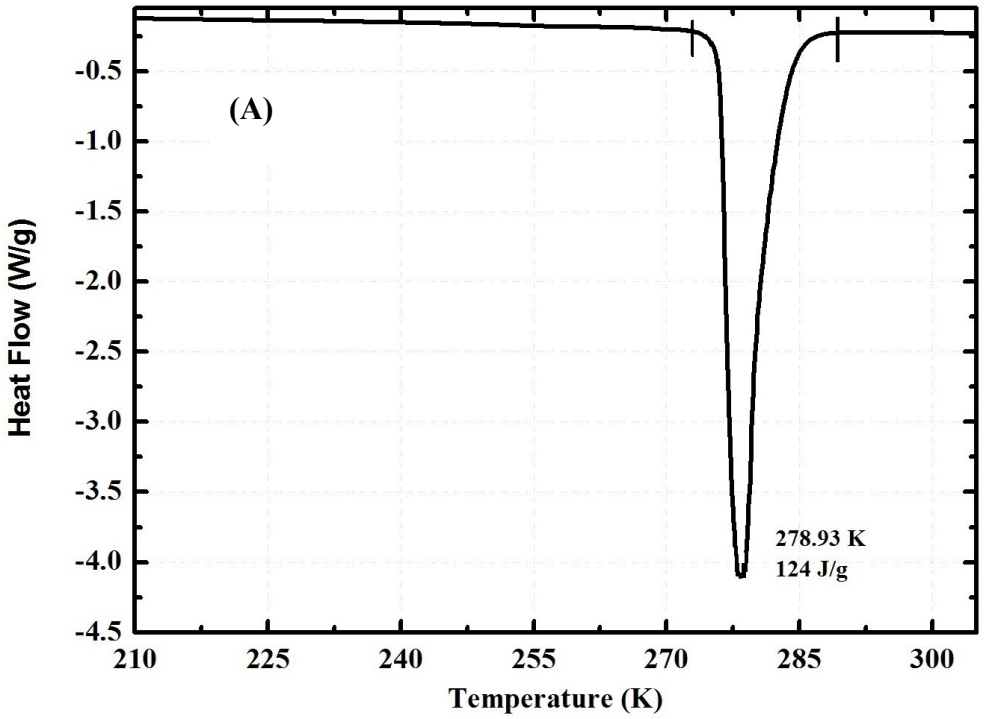
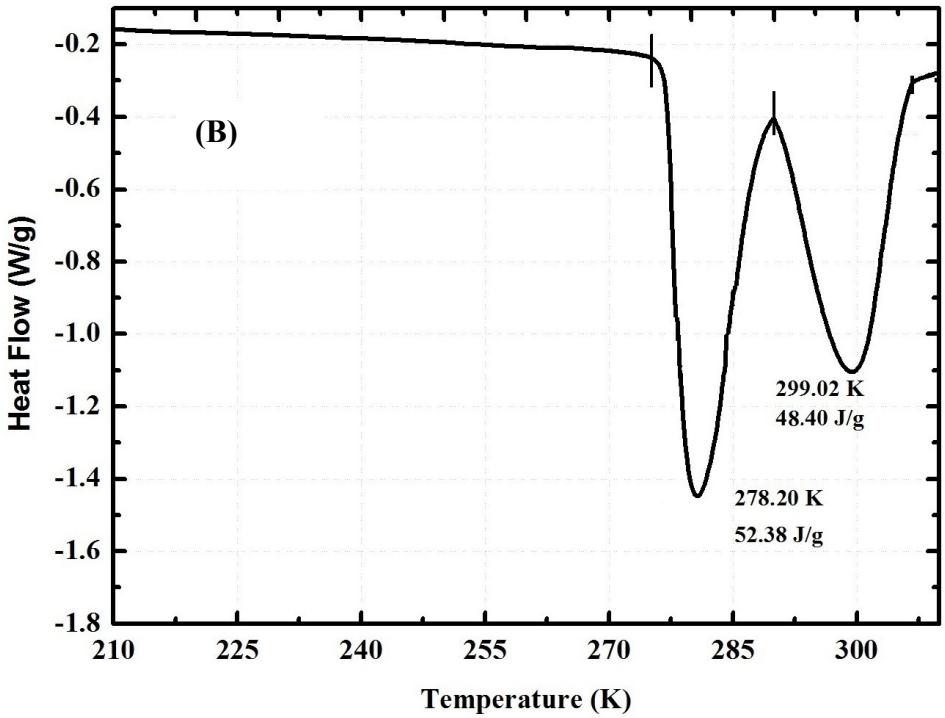
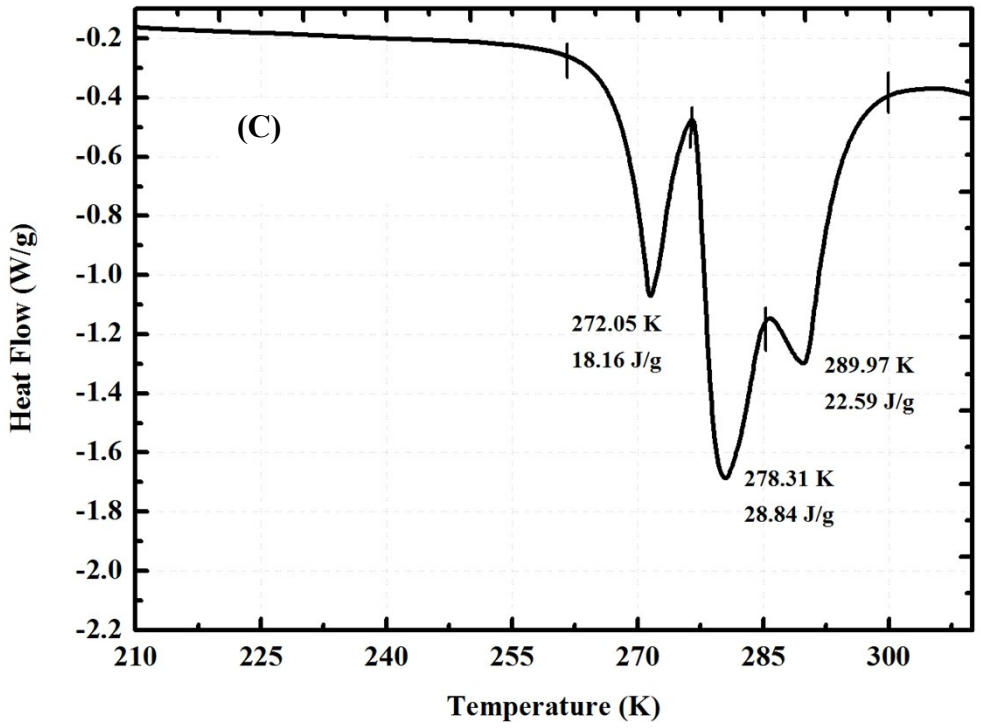
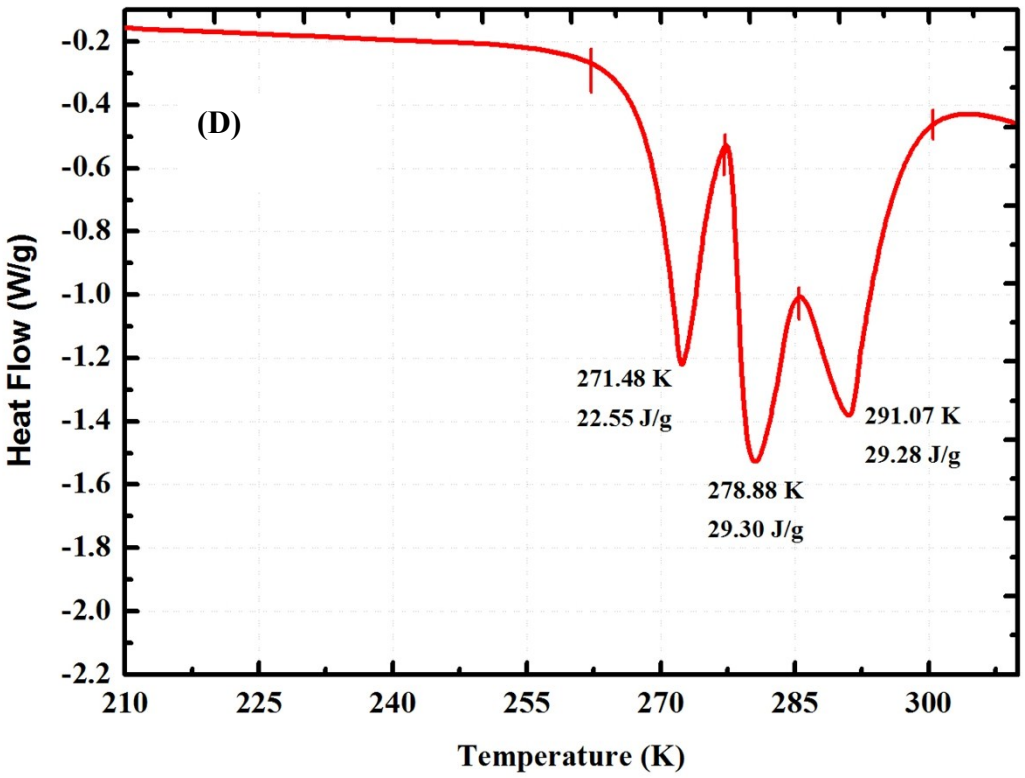


Figure S17. ^{1}H NMR spectra of BHDC in water/oil microemulsions in presence of [TMG][Lac] at fixed water content (ω_{max}) and at different temperatures - (A) T = 303, (B) T = 313, and (C) T = 318.


(A)
Heat Flow (W/g)
-0.5
-1.0
-1.5
-2.0
-2.5
-3.0
-3.5
-4.0
-4.5
210
225
240
255
270
285
300
Temperature (K)
278.93 K
124 J/g


(B)
Heat Flow (W/g)
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
210
225
240
255
270
285
300
Temperature (K)
299.02 K
48.40 J/g
278.20 K
52.38 J/g


(C)
Heat Flow (W/g)
Temperature (K)
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
210
225
240
255
270
285
300
272.05 K
18.16 J/g
278.31 K
28.84 J/g
289.97 K
22.59 J/g


(D)
Heat Flow (W/g)
Temperature (K)
-0.2
-0.4
-0.6
-0.8
-1.0
-1.2
-1.4
-1.6
-1.8
-2.0
-2.2
210
225
240
255
270
285
300
271.48 K
22.55 J/g
278.88 K
29.30 J/g
291.07 K
29.28 J/g

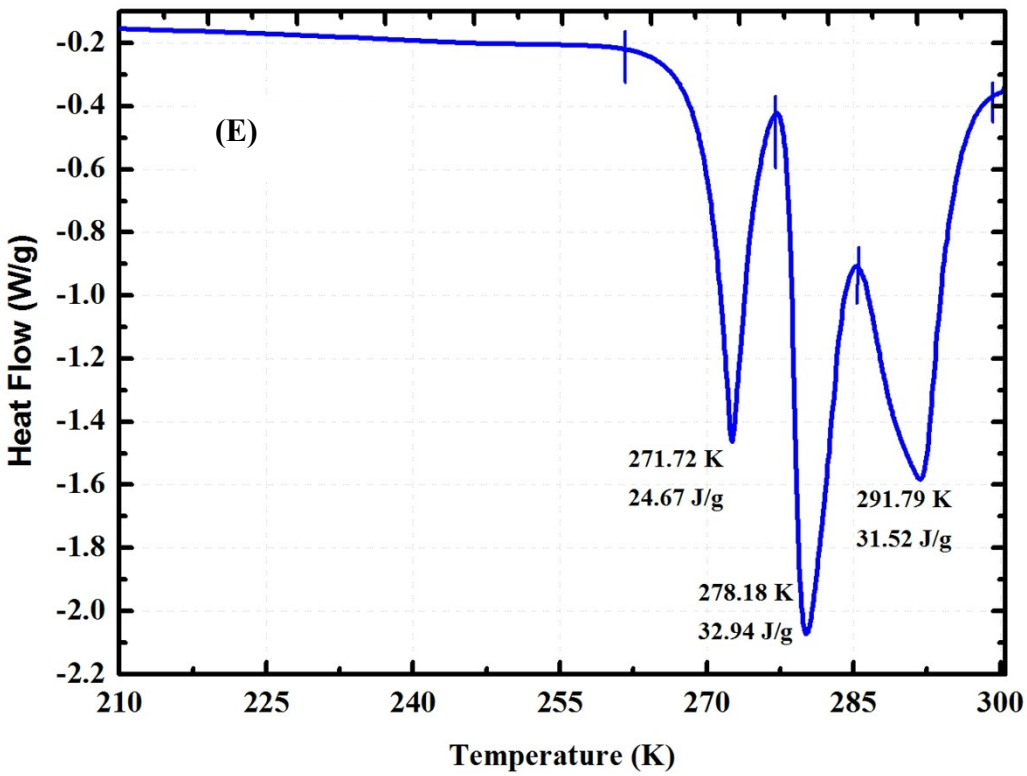


Figure S18. DSC thermograms of (A) benzene, (B) BHDC/benzene, (C) BHDC/benzene/water, (D) BHDC/benzene/water/[TMG][Lac], and (E) BHDC/benzene/water/[TMG][Ace]. Vertical bar on curve represent onset and endset temperatures.

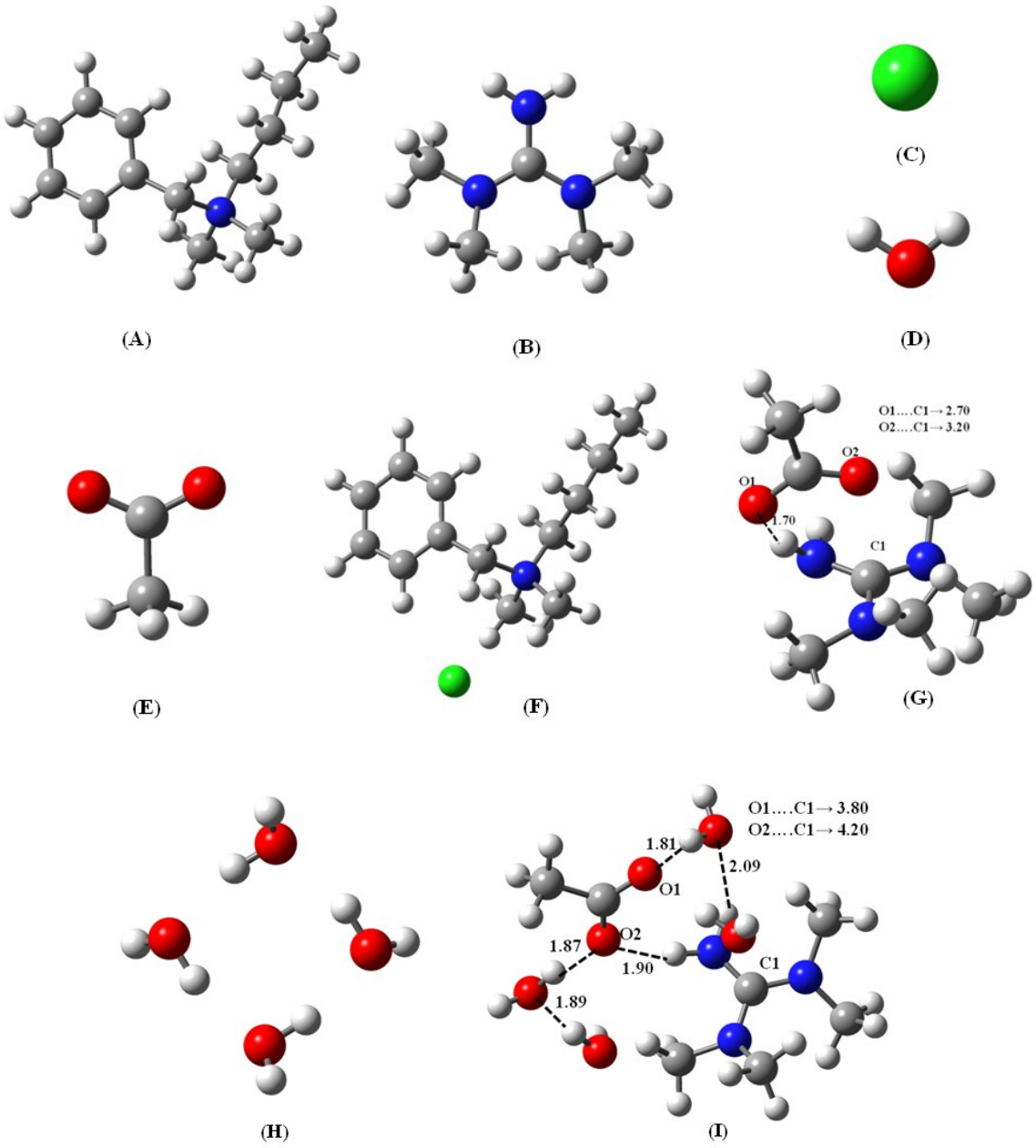


Figure S19. Minimum energy structures of (A) $[BHD]^+$, (B) $[TMG]^+$, (C) Cl^-, (D) water, (E) $[Ace]^-$, (F) BHDC, (G) [TMG][Ace] ion pair, (H) four water molecules and (I) [TMG][Ace] + 4 water. The dotted lines represent the H-bonding interactions and the corresponding distance values are included. The distance between carboxylate oxygens (O1 and O2), and [TMG] cation central carbon (C1) are also shown. All distance are in Å and energies in kcal/mol. Atom notations: C – grey, H –white, O – red, N – blue, Cl - green.