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Electronic supplementary information

Organobase catalysis using 1-(2-pyrimidyl) piperazine in micellar medium: An approach for better performance and reusability of organobase

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Table S1. Control experiments: reaction of salicylaldehyde and diethyl malonate in absence of catalysts.

S. No.	1/ 2a molar ratio (2.5 mmol: 2.5 mmol)	Reaction temperature (°C)	Catalyst	Surfactant	Conversion of 2a (wt.%)	Selectivity of 3-substituted coumarin (3a)
1	1 : 1	Rt (30)	-	-	0	0
2	1 : 1	60°C	-	-	0	0
3	1 : 1	Rt (30)	-	CTAB	0	0
4	1 : 1	Rt (30)	-	SDS	0	0
5	1 : 1	Rt (30)	-	Tx-100	0	0
6	1 : 1	60°C	-	CTAB	0	0
7	1 : 1	60°C	-	SDS	0	0
8	1 : 1	60°C	-	Tx-100	0	0

Reaction time: 24 h.

Effect of reaction temperature on the reaction in 2-PP-SDS micellar solution

The reaction temperature of the Knoevenagel condensation reaction of (**1**) and (**2a**) in 2-PP-SDS micellar solution was varied from room temperature (30 to 60°C) to study the effect of temperature on the reaction. The reactions were carried out at three different temperatures, i.e., 30°C, 45°C and 60°C using 25 mM solution of SDS. It was observed that higher temperatures did not enhance the conversion and highest conversion of diethyl malonate was obtained at 30°C (Table S2). This shows that 30°C was optimum temperature for the reaction.

Table S2. Effect of reaction temperature on Knoevenagel condensation of salicylaldehyde and diethyl malonate with 2-PP-SDS micellar system.[a]

Entry	Temp. (°C)	Conversion (wt.%) of diethyl malonate	Selectivity % of	
			3a	4
1	30	94	99.9	0.1
2	45	89	99.4	0.6
3	60	86	99.0	1.0

[a] 2.5 mmol salicylaldehyde, 2.5 mmol diethyl malonate, 10 mol% 2-PP organobase, 5 ml SDS aqueous solution (25 mM) , 6 h.

Effect of catalyst amount on the reaction in 2-PP-SDS micellar solution

The optimum concentration of 2-PP organobase giving highest conversion of **2a** was found by performing the reaction using different concentrations of 2-PP i.e., 5, 10, 15 and 50 mol % in 25 mM of SDS aqueous micellar solution. The reaction using 10 mol% 2-PP gave substantial conversion (94%) of **2a** and conversion was decreased at 5 mol% (Table S3). It shows that 10 mol% of 2-PP was optimum concentration for the reaction.

Table S3. Conversion of diethyl malonate in Knoevenagel condensation with salicylaldehyde at different catalyst (2-PP) concentration in SDS micellar solution.[a]

Entry	Catalyst (mol%)	Conversion (wt.%) of diethyl malonate	Selectivity % of	
			3	**4**
1	5	61	100	00
2	10	94	99.9	0.1
3	15	98	99.5	0.5
4	50	99	97	03

[a] 2.5 mmol salicylaldehyde, 2.5 mmol diethyl malonate, 5 ml aqueous SDS surfactant solution (25mM), 30°C, 6 h.

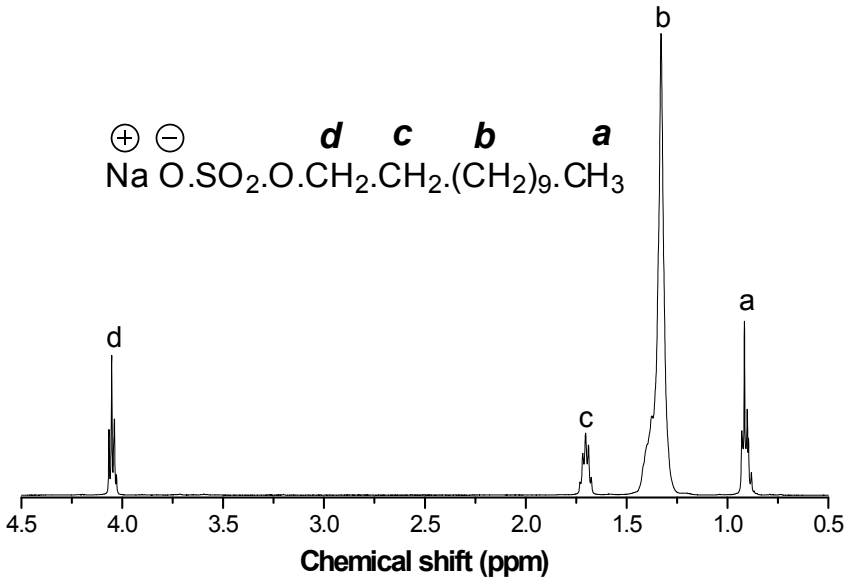


Figure S1. ^{1}H NMR spectrum of SDS in D_2O (25 mM; without reactants/ 2-PP).

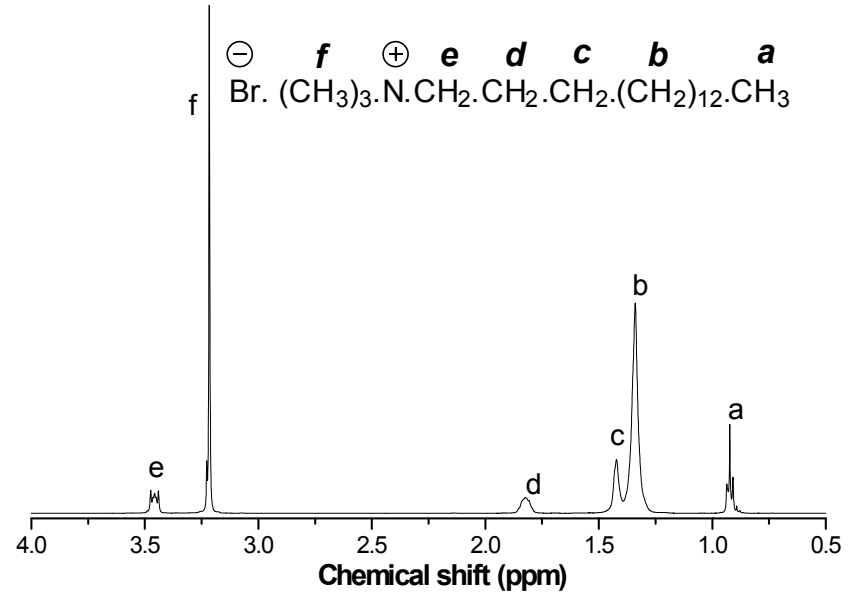
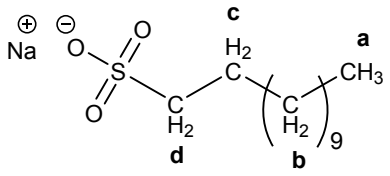


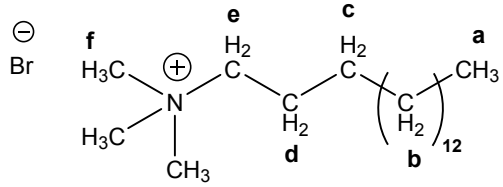
Figure S2. ^{1}H NMR spectrum of CTAB in D_2O (25 mM; without reactants/ 2-PP).

Table S4. Chemical shifts of SDS (25 mM) protons in presence of 2-PP.



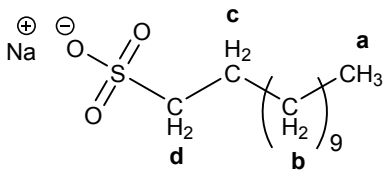
Surfactant solution	Chemical shifts (δ; ppm) of different protons			
	d	**c**	**b**	**a**
Pure SDS (25 mM)	4.05	1.70	1.33	0.92
2-PP-SDS (25 mM)	4.01	1.63	1.25	0.88
Δδ (ppm)	0.04	0.07	0.08	0.04

Table S5. Chemical shifts of CTAB (25 mM) protons in presence of 2-PP.



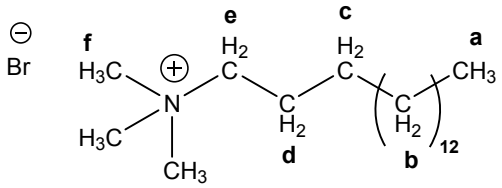
Surfactant solution	Chemical shifts (δ; ppm) of different protons					
	f	**e**	**d**	**c**	**b**	**a**
Pure CTAB (25 mM)	3.22	3.46	1.82	1.42	1.34	0.92
2-PP-CTAB (25 mM)	3.20	3.42	1.80	1.40	1.32	0.92
Δδ (ppm)	0.02	0.04	0.02	0.02	0.02	0.00

Table S6. Chemical shifts of SDS protons (25 mM) in presence of reactants (salicylaldehyde and DEM).



Surfactant solution	Chemical shifts (δ; ppm) of different protons			
	d	**c**	**b**	**a**
Pure SDS (25 mM)	4.05	1.70	1.33	0.92
Reactants-SDS (25 mM)	3.95	1.55	1.16	0.86
Δδ (ppm)	0.09	0.15	0.17	0.06

Table S7. Chemical shifts of CTAB protons (25 mM) in presence of reactants (salicylaldehyde and DEM).



Surfactant solution	Chemical shifts (δ; ppm) of different protons					
	f	**e**	**d**	**c**	**b**	**a**
Pure CTAB (25 mM)	3.22	3.46	1.82	1.42	1.34	0.92
Reactants-CTAB (25 mM)	3.11	3.25	1.62	1.31	1.31	0.92
Δδ (ppm)	0.11	0.21	0.20	0.11	0.03	0.00

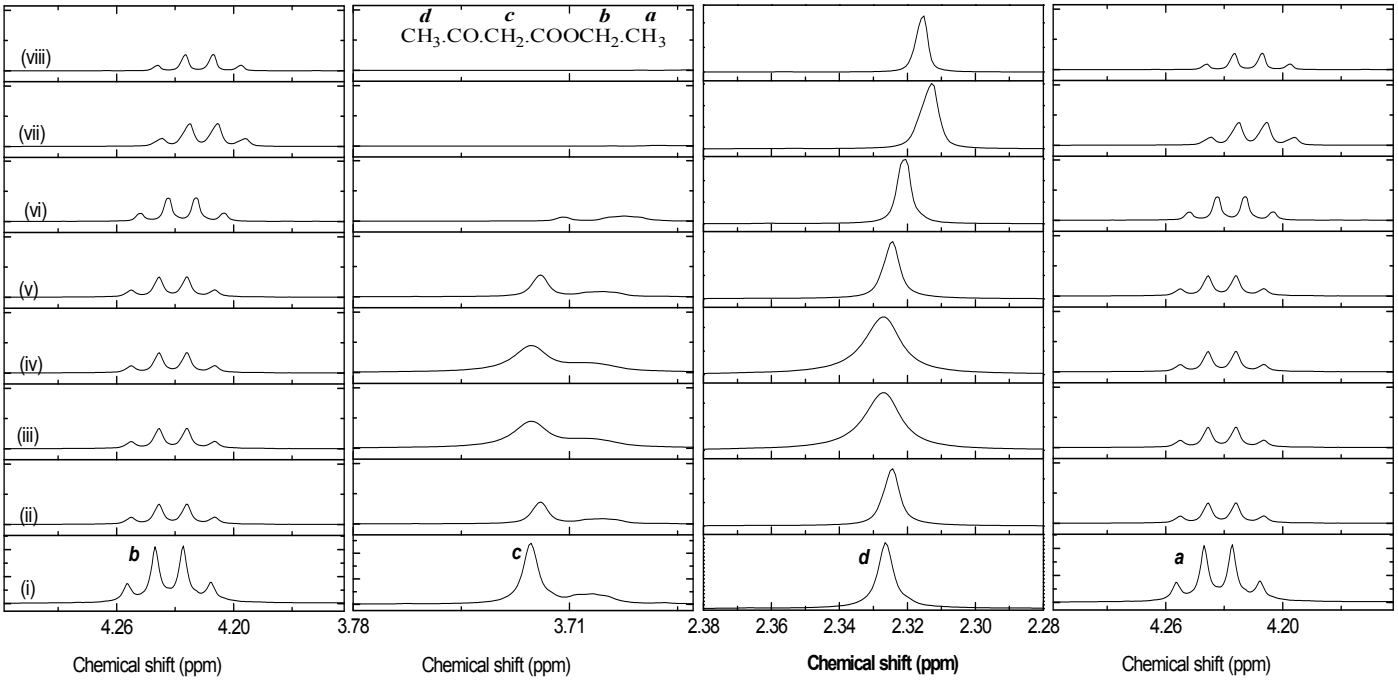


Figure S3. ^{1}H NMR chemical shifts for different protons of EAA in D_2O and in SDS solutions of different concentrations [(i) D_2O, (ii) 1 mM SDS, (iii) 5 mM SDS, (iv) 10 mM SDS, (v) 15 mM SDS, (vi) 25 mM SDS, (vii) 50 mM SDS, (viii) 100 mM SDS].

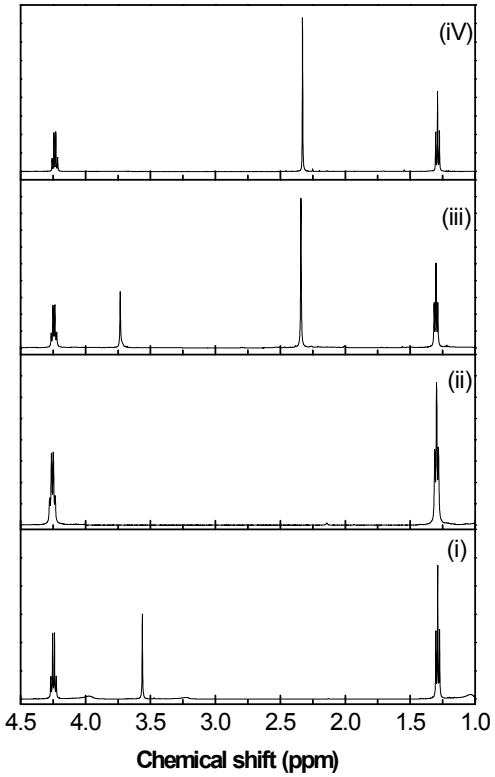


Figure S4. ^{1}H NMR spectra of DEM in D_2O (i) and in 25 mM Na_2SO_4 aqueous solution (ii), and EAA in D_2O (iii) and in 25 mM Na_2SO_4 aqueous solution (iv).