## **Electronic Supplementary Information**

# Thio-Michael addition of $\alpha,\beta$ -unsaturated amides catalyzed by Nmm-based ionic liquids

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#### **General experimental procedures**

The reaction is carried out at room temperature in water or solvent-free. NMR spectra were recorded on Bruker AVANCE III HD 400MHz; Proton and carbon magnetic resonance spectra (<sup>1</sup>H NMR and <sup>13</sup>C NMR) were recorded using tetramethylsilane (TMS) in the solvent of CDCl<sub>3</sub> as the internal standard (<sup>1</sup>H NMR: TMS at 0.00 ppm,CHCl<sub>3</sub> at 7.26 ppm; <sup>13</sup>C NMR: CDCl<sub>3</sub> at 77.16 ppm) or were recorded using tetramethylsilane (TMS) in the solvent of DMSO- $d_6$  as the internal standard (<sup>1</sup>H NMR: TMS at 0.00 ppm, DMSO at 2.50 ppm; <sup>13</sup>C NMR: DMSO at 39.51 ppm)

Compounds 2c, 2e-2i was synthesized by previous method.<sup>1</sup>

#### Recycling of the catalyst [Nmm-PDO][Gly]

**Table S1.** Recycling of the catalyst in thio-Michael addition of *N*,*N*-dimethylacrylamide with propanethiol

$SH + H = H_{CH_{3}} \xrightarrow{CH_{3}} H_{CH_{3}} \xrightarrow{(Nmm-PDO][Gly]} S \xrightarrow{CH_{3}} H_{2O, 25 \circ C} \xrightarrow{S} \xrightarrow{CH_{3}} H_{CH_{3}}$		
	1a 2b	3j
Run	Time/h	Yield (%) <sup>b</sup>
1	6	90
2°	15	84
3°	30	79

<sup>*a*</sup>Reaction conditions: propanethiol (0.5 mmol), *N*,*N*-dimethylacrylamide (0.5 mmol), catalyst [Nmm-PDO][Gly] (10 mol%), water (1 mL), room temperature. <sup>*b*</sup>Isolated yield. <sup>*c*</sup>Upon completion of the reaction, the solution was extracted with ethyl acetate. The residual IL-catalyst in aqueous phase was obtained just by concentration, and reused for next recycling.



<sup>13</sup>C NMR spectrum of *N*,*N*-dimethylacrylamide and *N*,*N*-dimethylacrylamide-[Nmm-PDO][Gly] mixture

Figure S1. <sup>13</sup>C NMR of *N*,*N*-dimethylacrylamide (2b)



Figure S2. <sup>13</sup>C NMR of *N*,*N*-dimethylacrylamide-[Nmm-PDO][Gly] mixture

### Reference

S. Chanthamath, S. Takaki, K. Shibatomi and S. Lwasa, *Angew. Chem., Int. Ed.*, 2013, **52**, 5818.



The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds [Nmm-PDO][X] and [Nbmm][OAc]







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The <sup>1</sup>H and <sup>13</sup>C NMR spectra of compounds 3a-3f'

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