

*Supporting Information*

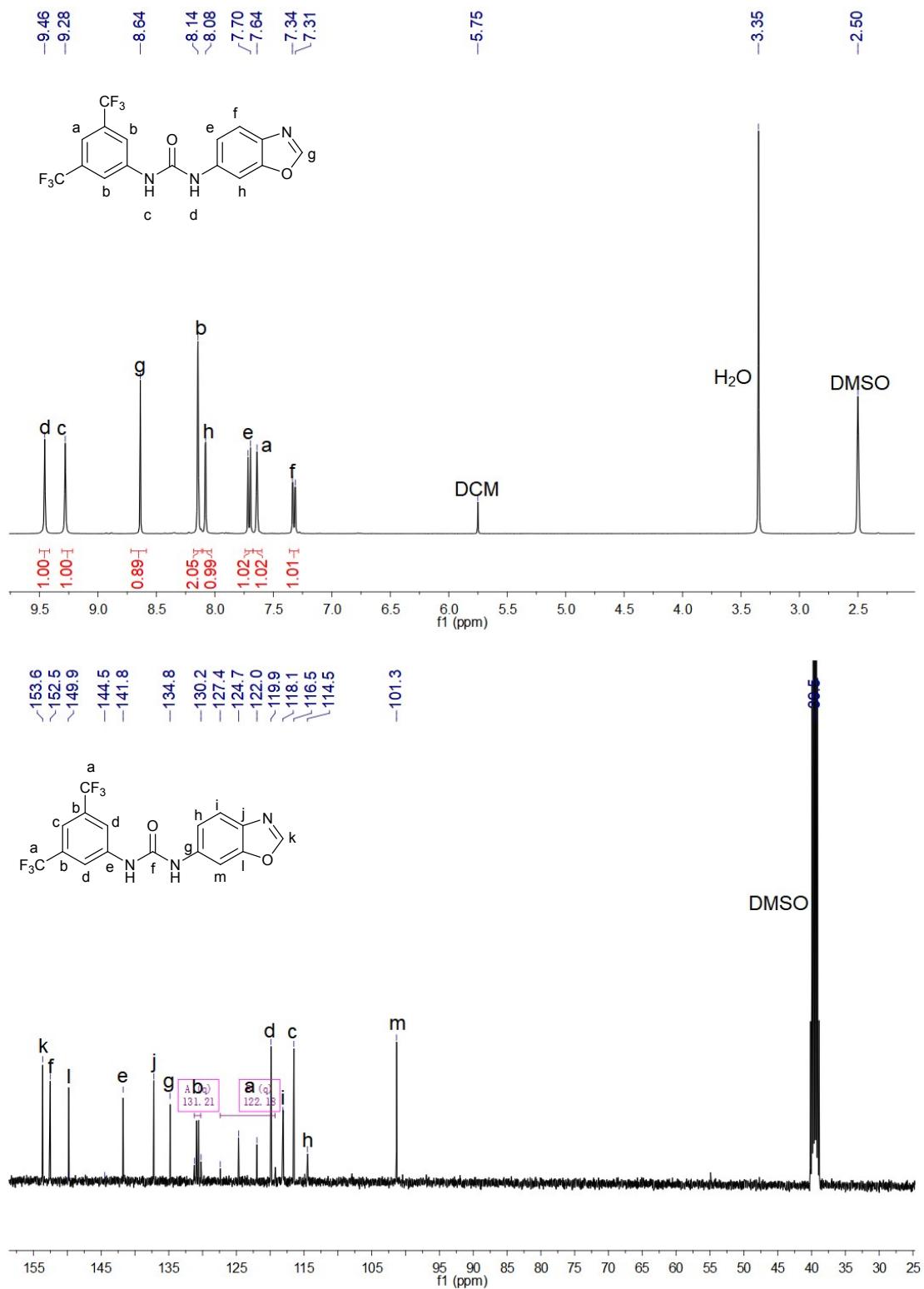
**Fast and Controlled Ring-Opening Polymerization of  $\delta$ -Valerolactone**

**Catalyzed by Benzoheterocyclic Ureas/MTBD**

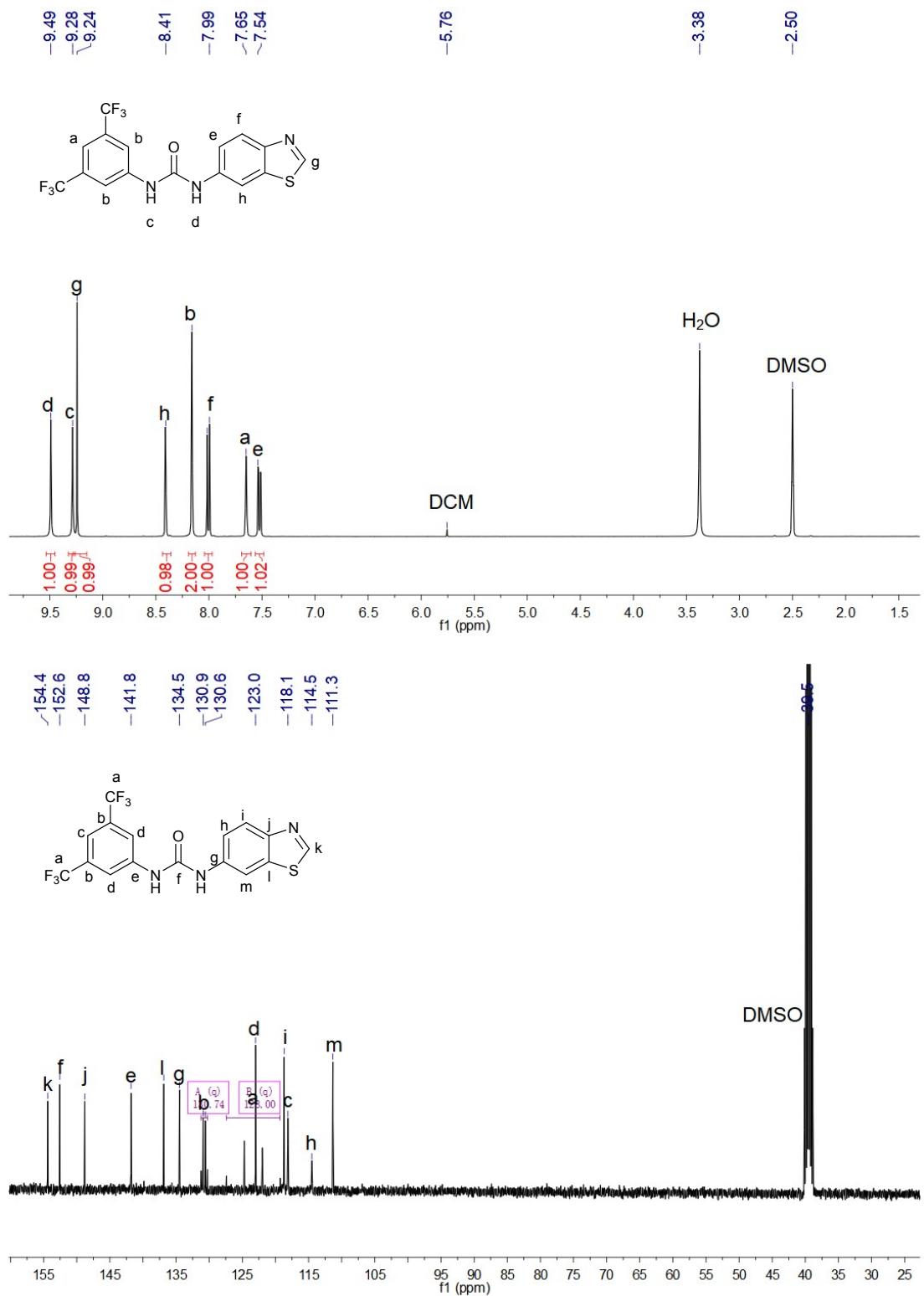
Chenlin Ji,<sup>a</sup> Suyun Jie,<sup>\*a</sup> Pierre Braunstein<sup>b</sup> and Bo-Geng Li<sup>a</sup>

<sup>a</sup> State Key Laboratory of Chemical Engineering, College of Chemical and Biological Engineering, Zhejiang University, Hangzhou 310027, China

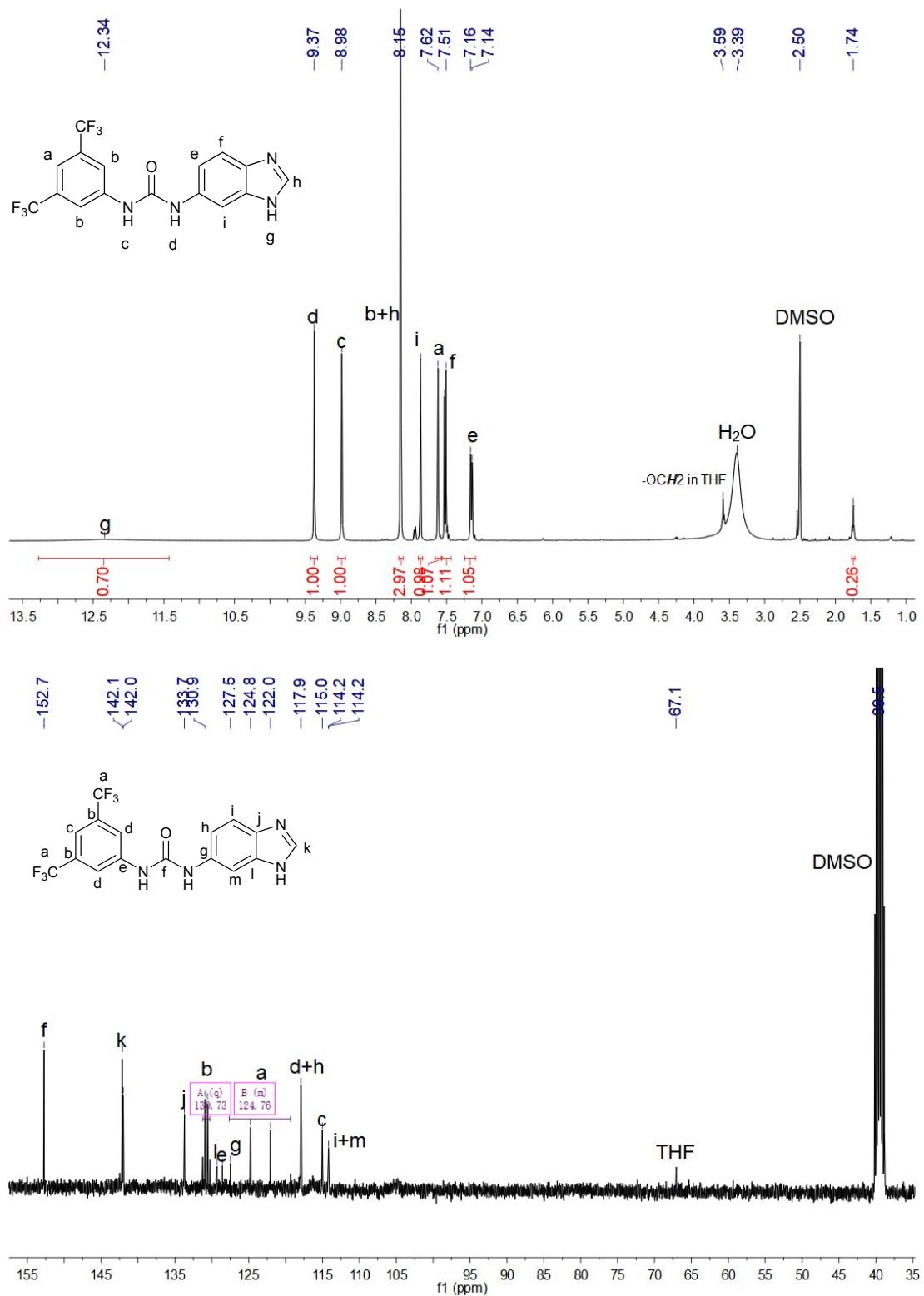
<sup>b</sup> Université de Strasbourg, CNRS, CHIMIE UMR 7177, Laboratoire de Chimie de Coordination, 4 rue Blaise Pascal, 67081 Strasbourg Cedex, France



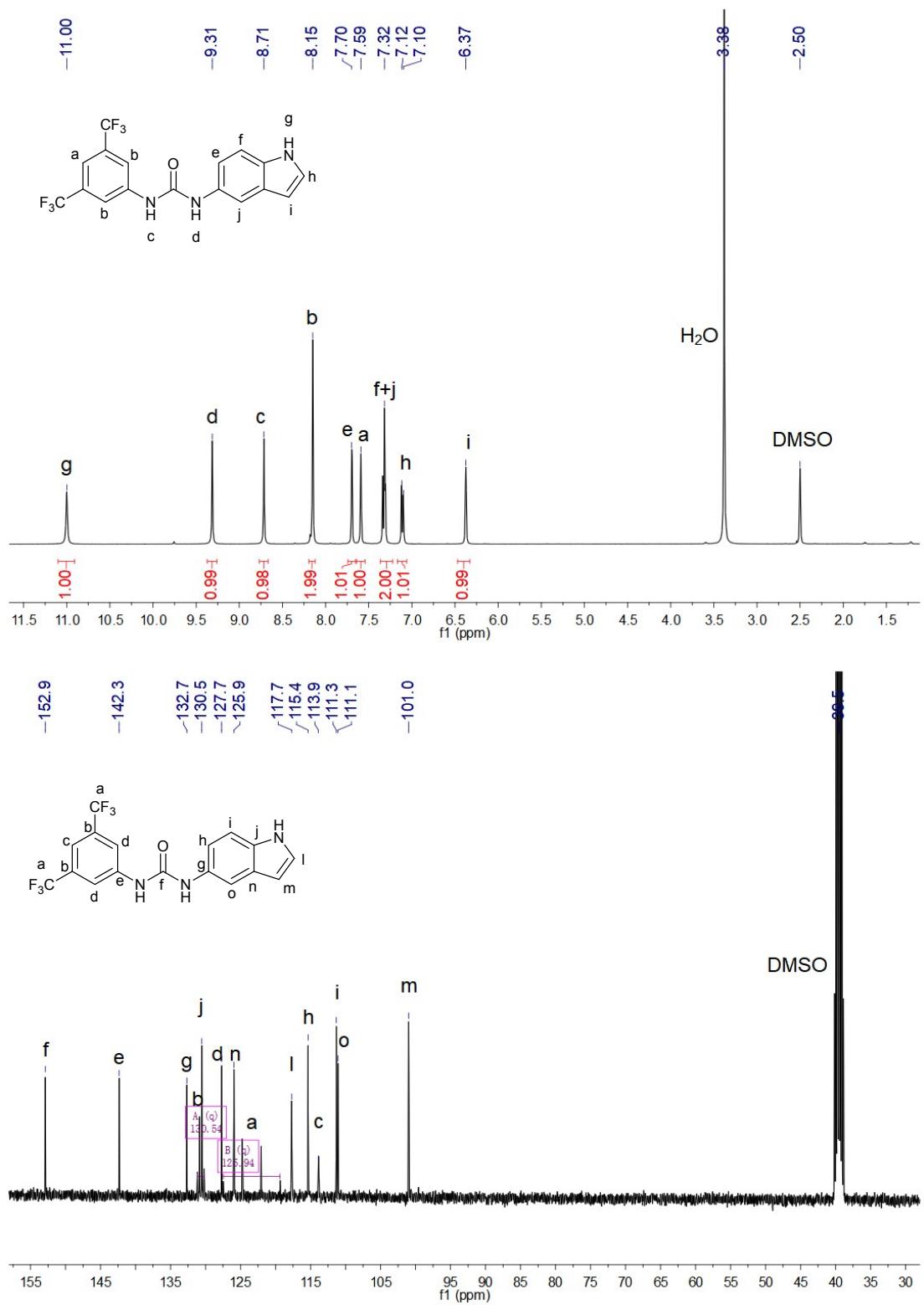
**Figure S1.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **NO** in  $\text{DMSO}-d_6$



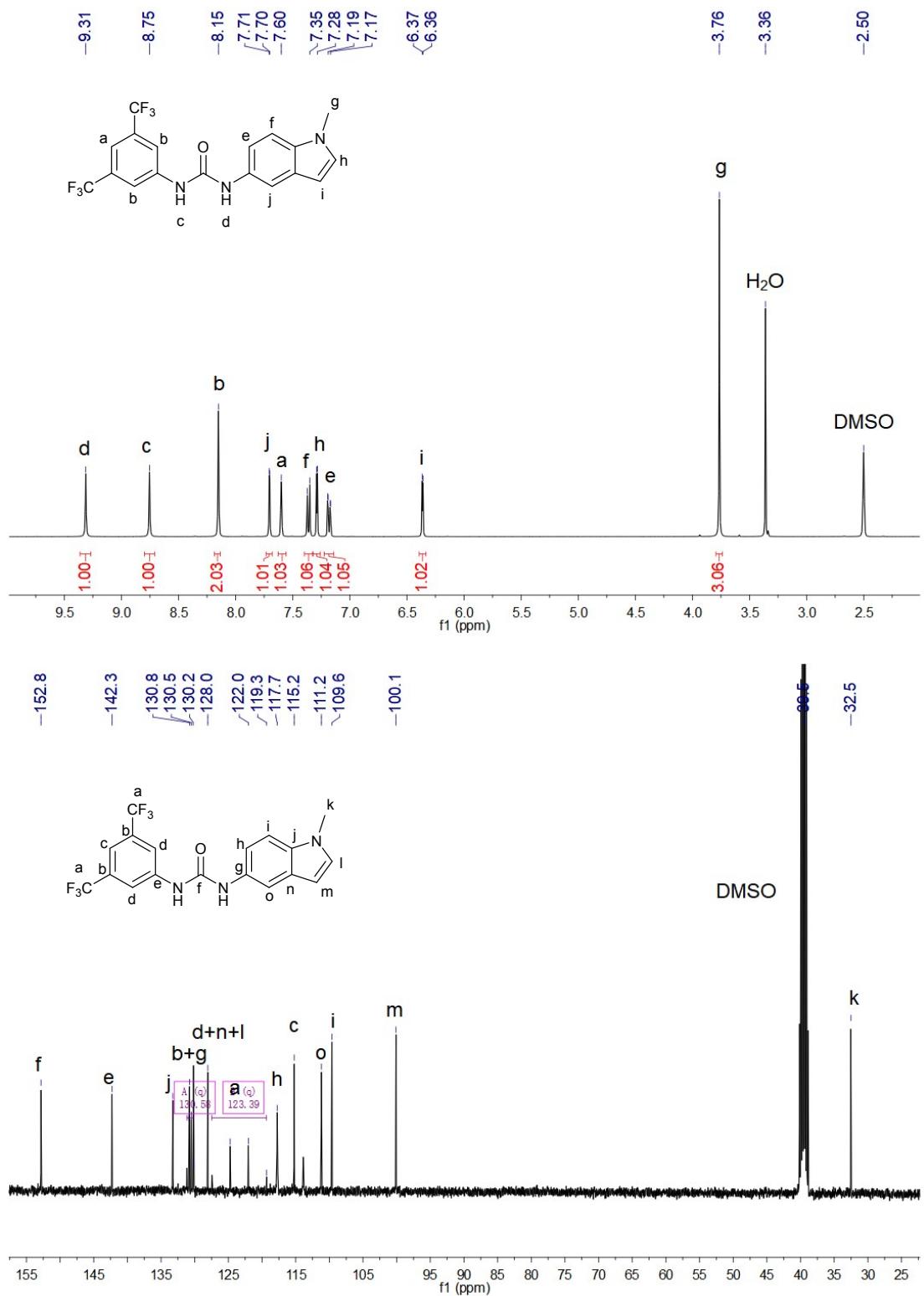
**Figure S2.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of NS in DMSO-*d*<sub>6</sub>



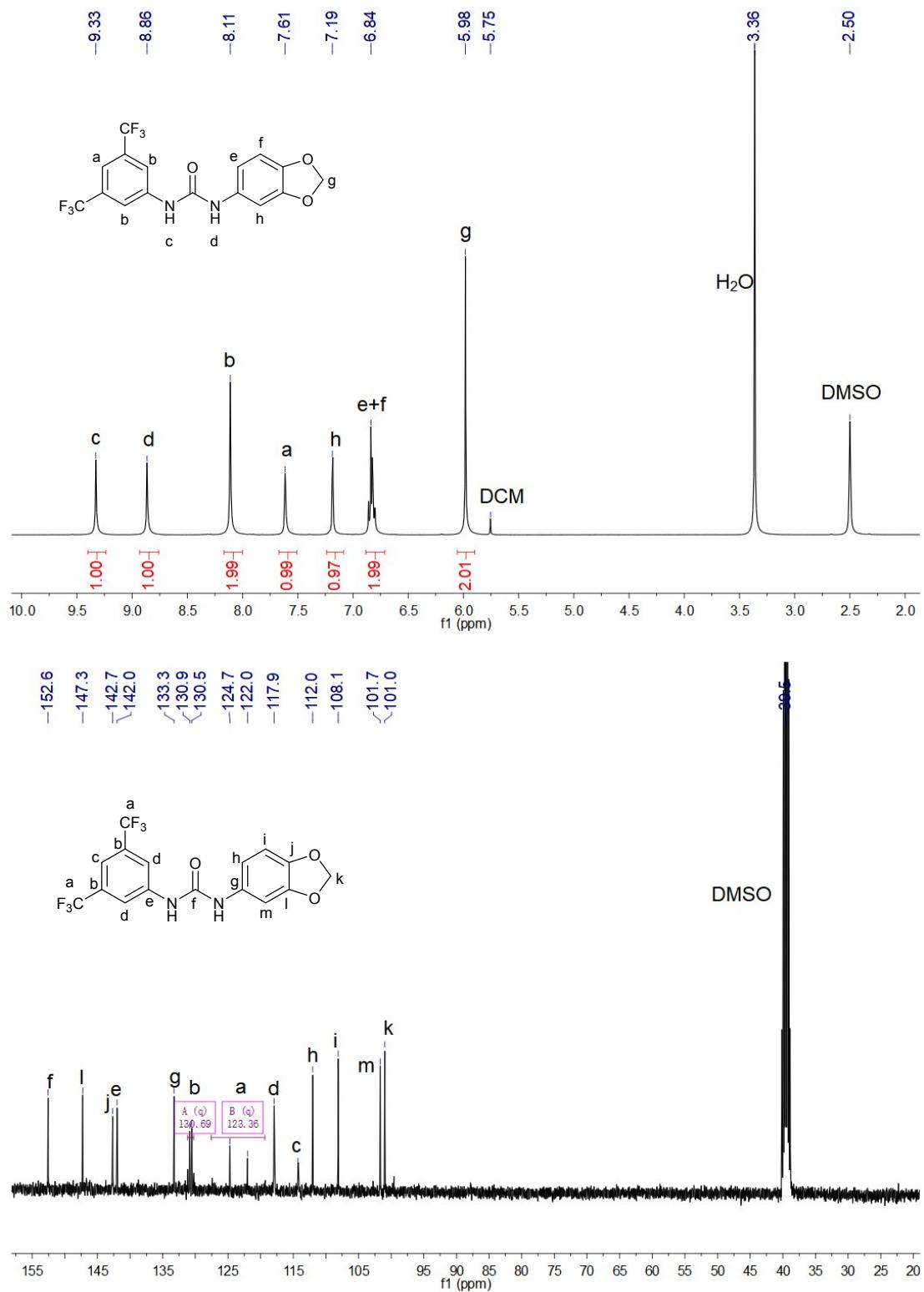
**Figure S3.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of NNH in  $\text{DMSO}-d_6$



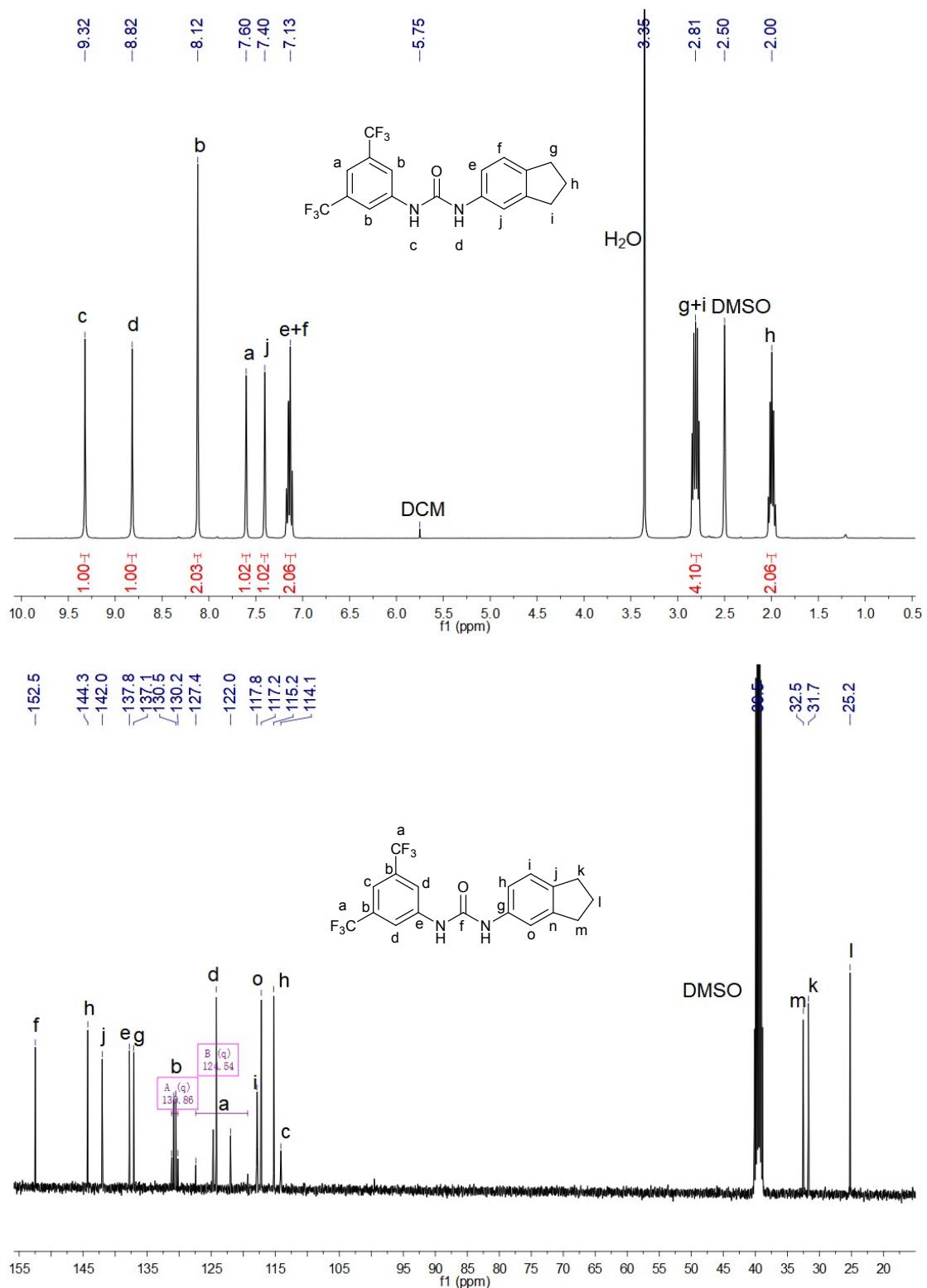
**Figure S4.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **NHC** in  $\text{DMSO}-d_6$



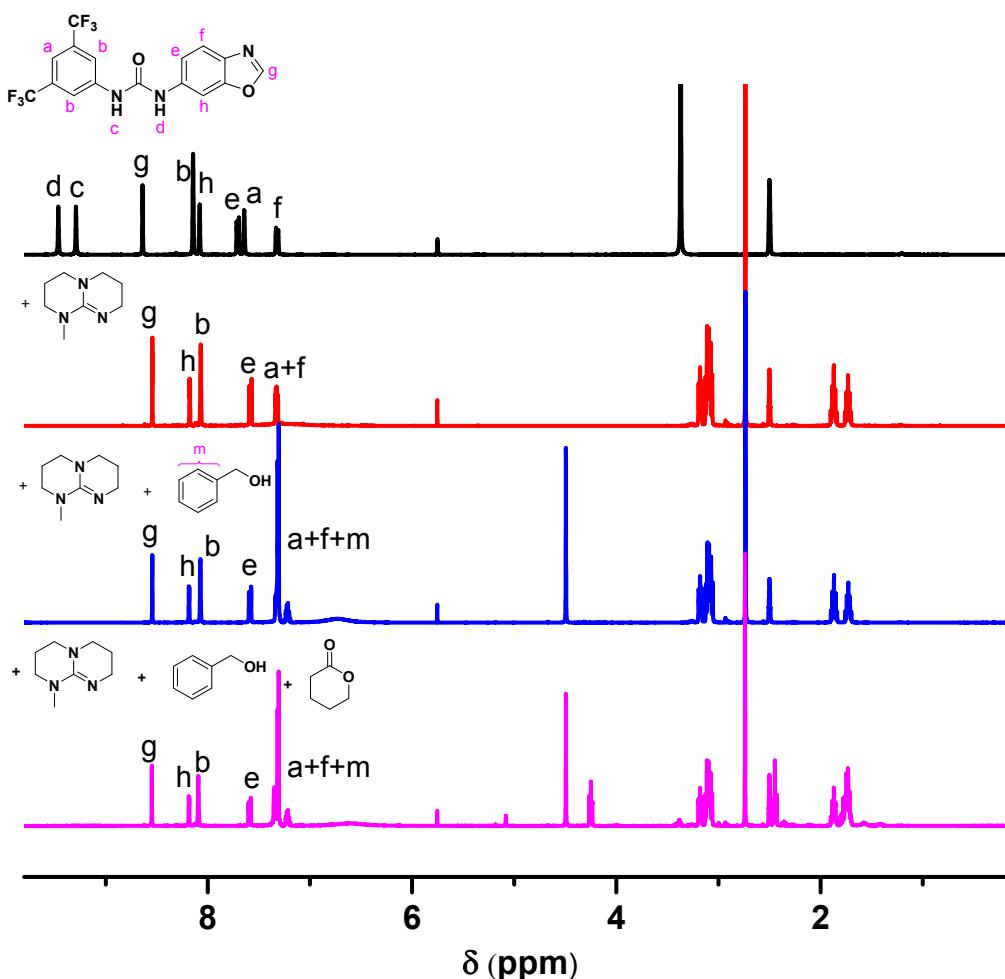
**Figure S5.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of NCC in  $\text{DMSO}-d_6$



**Figure S6.** <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of **OO** in DMSO-*d*<sub>6</sub>



**Figure S7.**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of **CC** in  $\text{DMSO}-d_6$



**Figure S8.** Comparison of  $^1\text{H}$  NMR spectra between pure **NO**, **NO**/MTBD, **NO**/MTBD/BnOH, and **NO**/MTBD/BnOH/ $\delta$ -VL in  $\text{DMSO}-d_6$