Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Supporting Information

Reducing the Reprocessing and Healing Temperature of Polyurea with Piperazine-Based Hindered Urea Bonds

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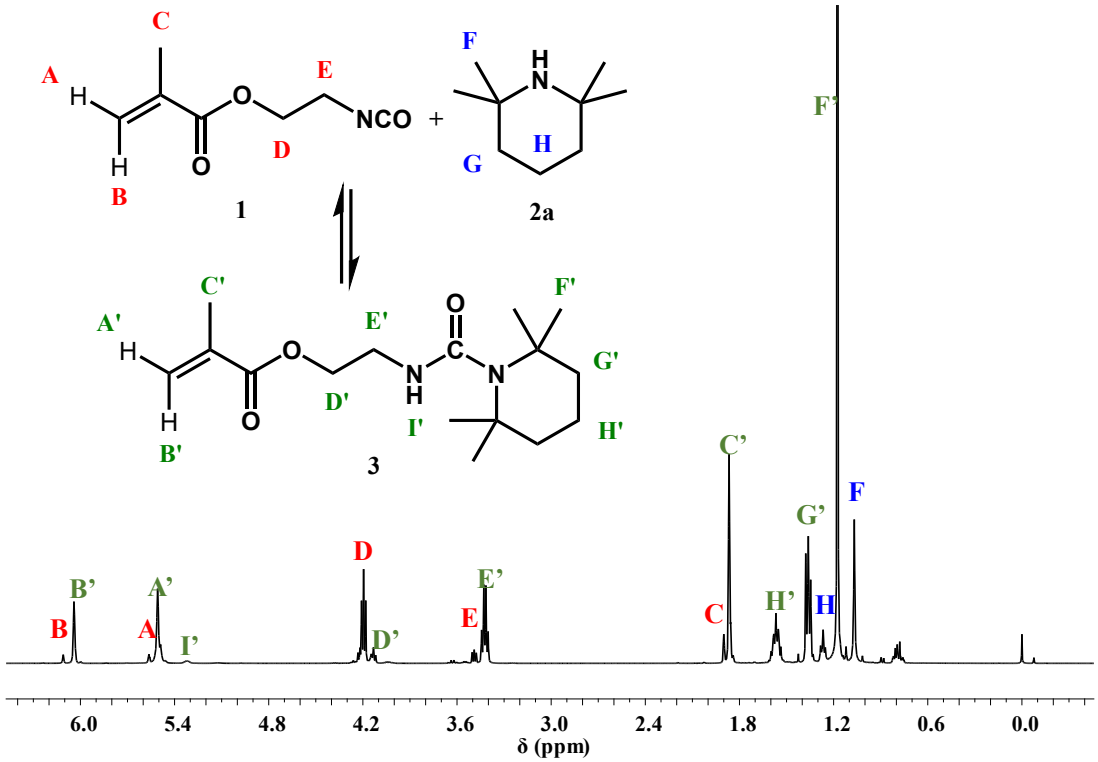

Figure S1. Thermodynamic equilibrium of the reaction between TMP and 2-Isocyanatoethylmethacrylate. $K_1 = [3]/([1][2a]) = 81.5\ mol^{-1}$.

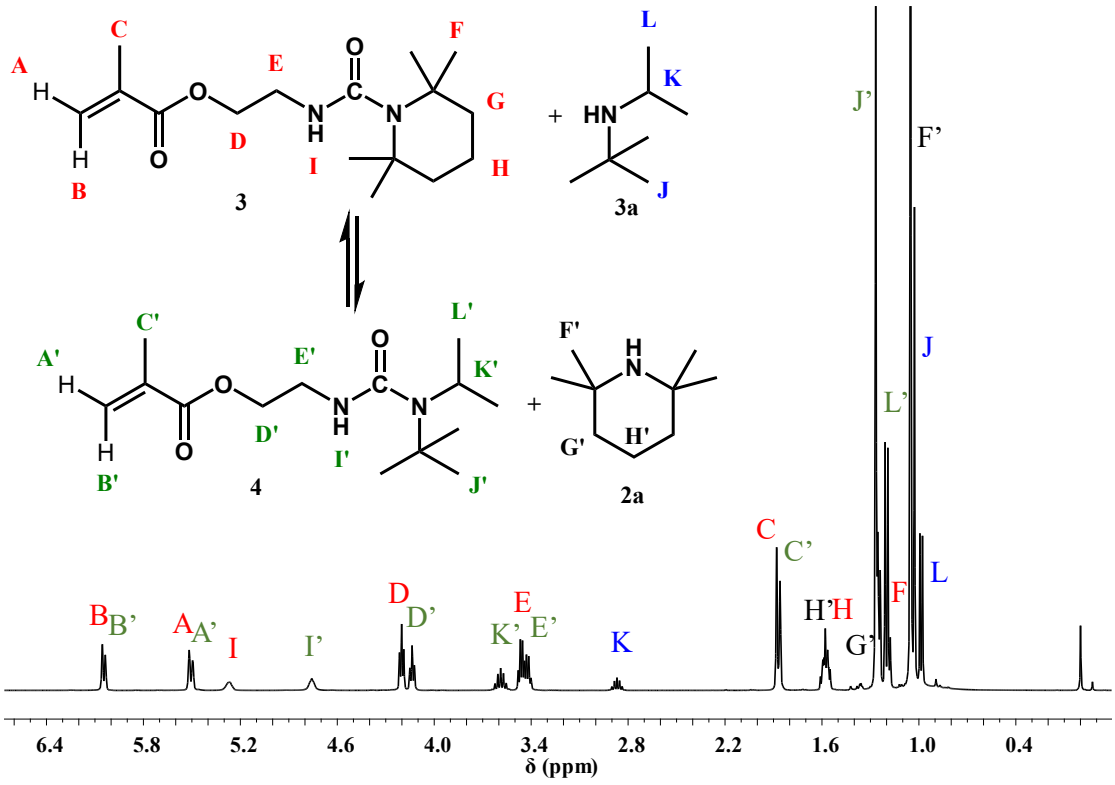

Figure S2. Thermodynamic equilibrium of the reaction between TMPCA and TBPA. $K_{eq} = ([4][2a])/([3][3a]) = 54.8$, $K_2 = K_1 \cdot K_{eq} = 4.47 \times 10^3\ mol^{-1}$.

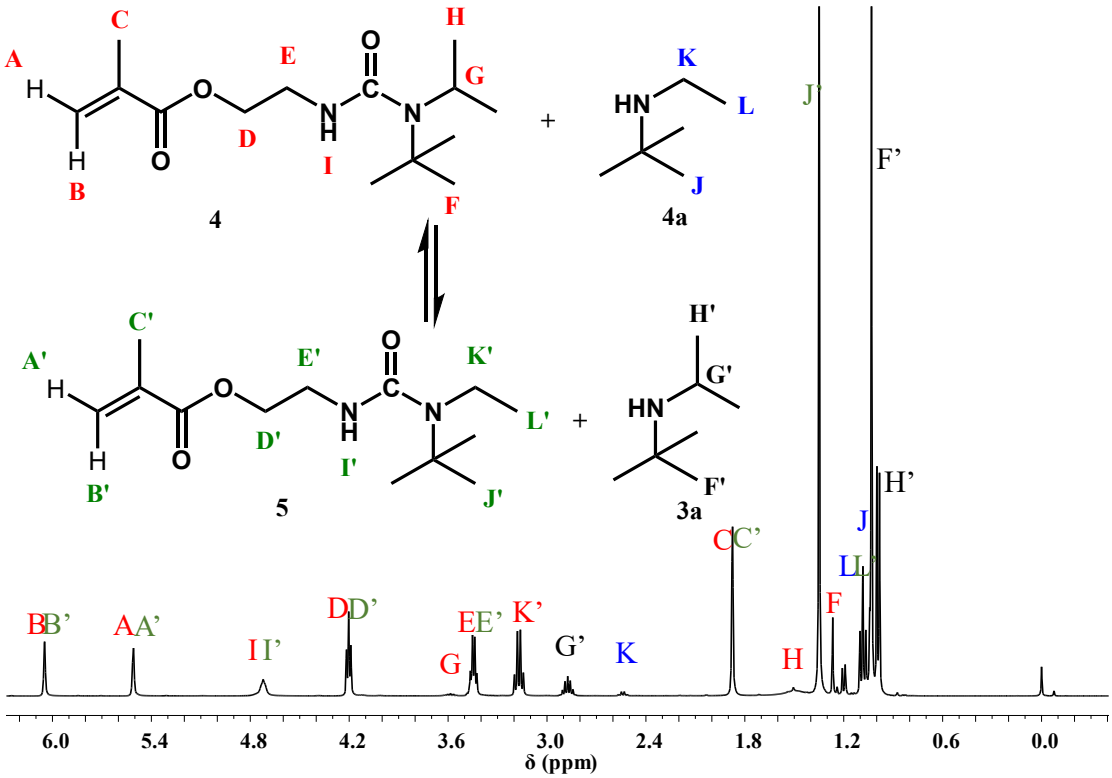

Figure S3. Thermodynamic equilibrium of the reaction between TBPU and TBEA. K_{eq} = ([5][3a])/([4][4a]) = 173.5, $K_3 = K_2 \cdot K_{eq} = 7.75 \times 10^5$ mol^{-1}.

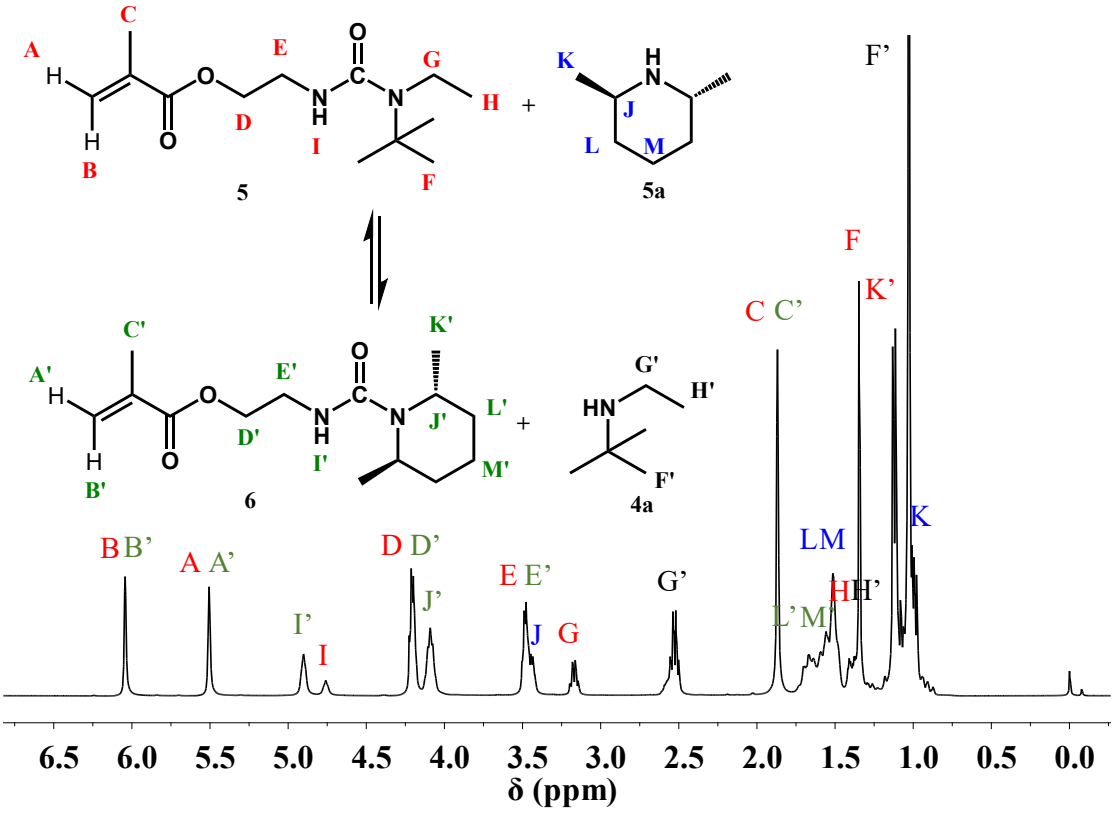

Figure S4. Thermodynamic equilibrium of the reaction between TBEU and *trans*-DMPip. K_{eq} = ([6][4a])/([5][5a]) = 27.0, $K_4 = K_3 \cdot K_{eq} = 2.09 \times 10^7$ mol^{-1}.

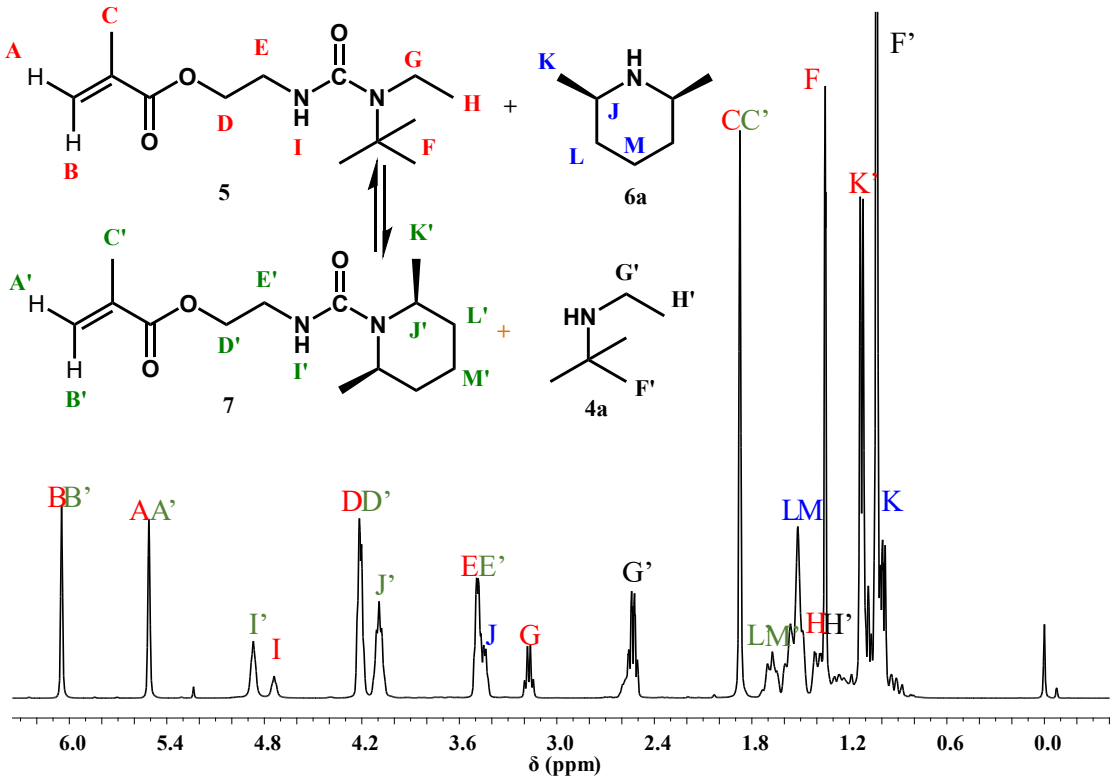

Figure S5. Thermodynamic equilibrium of the reaction between TBEU and *cis*-DMPip. K_{eq} = ([7][4a])/([5][6a]) = 30.1, $K_5 = K_3 \cdot K_{eq} = 2.33 \times 10^7$ mol^{-1}.

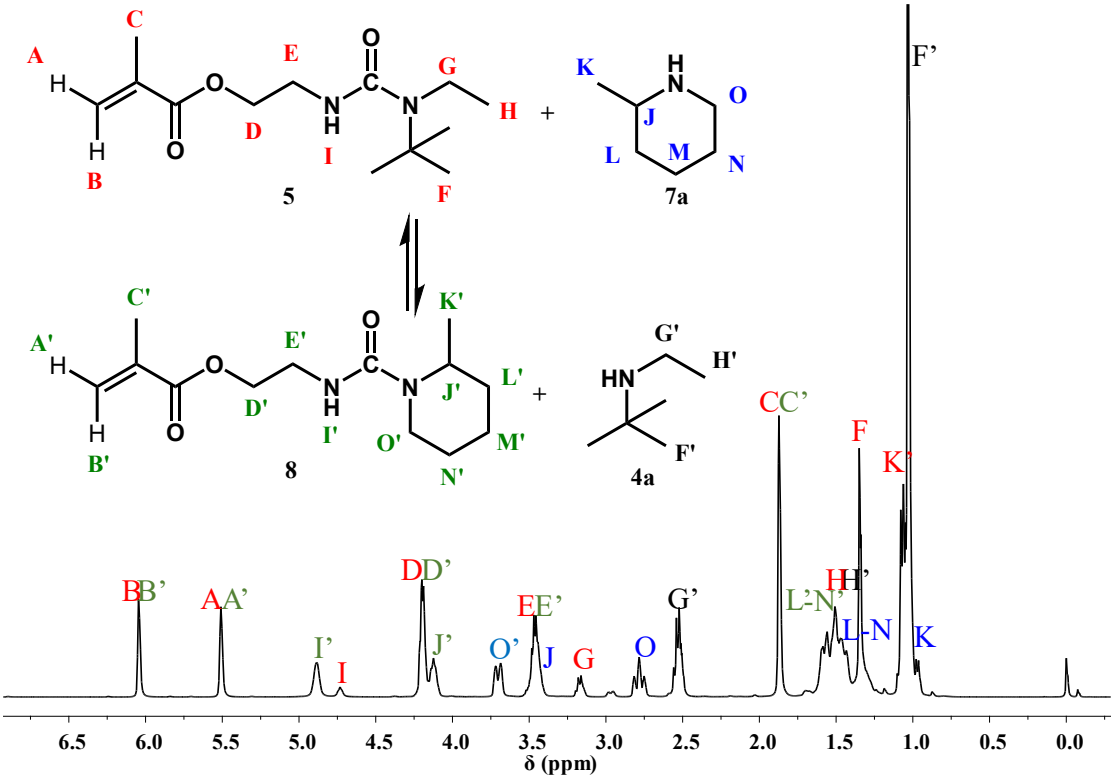

Figure S6. Thermodynamic equilibrium of the reaction between TBEU and MPip. K_{eq} = ([8][4a])/([5][7a]) = 30.6, $K_6 = K_3 \cdot K_{eq} = 2.37 \times 10^7$ mol^{-1}.

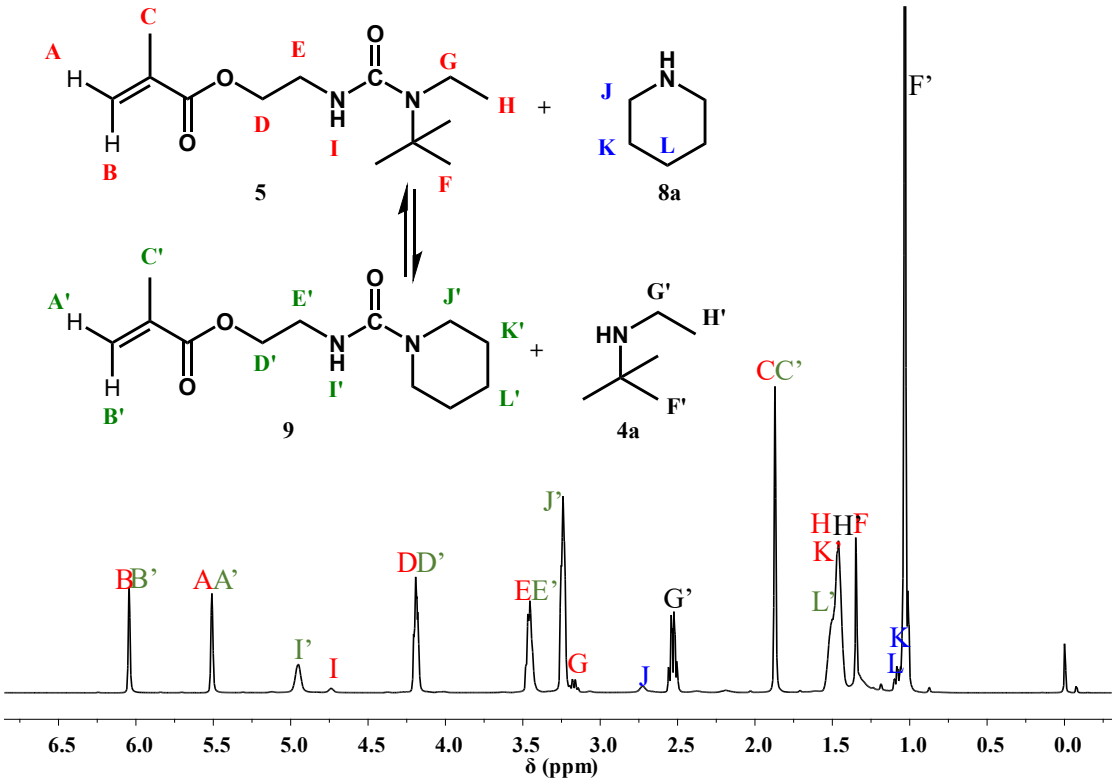

Figure S7. Thermodynamic equilibrium of the reaction between TBEU and piperidine. K_{eq} = ([9][4a])/([5][8a]) =127.7, $K_7 = K_3 \cdot K_{eq} = 9.90 \times 10^7$ mol^{-1}.

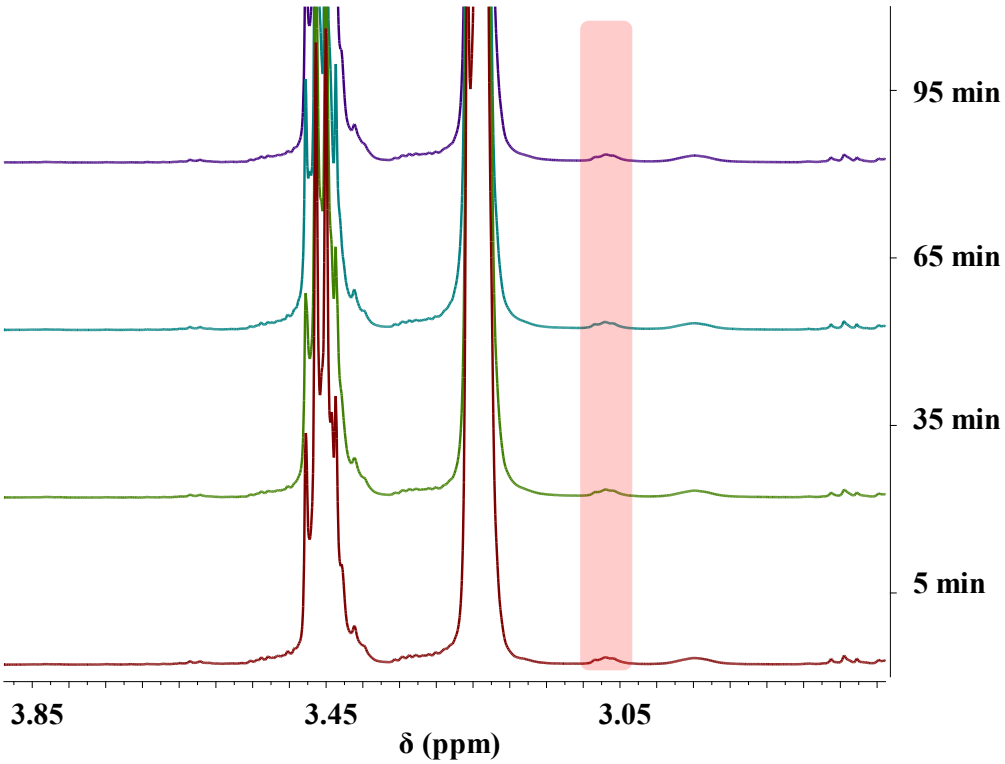

Figure S8. Time resolved ^{1}H NMR spectra showing exchange reaction between n-PA and PipU at room temperature.

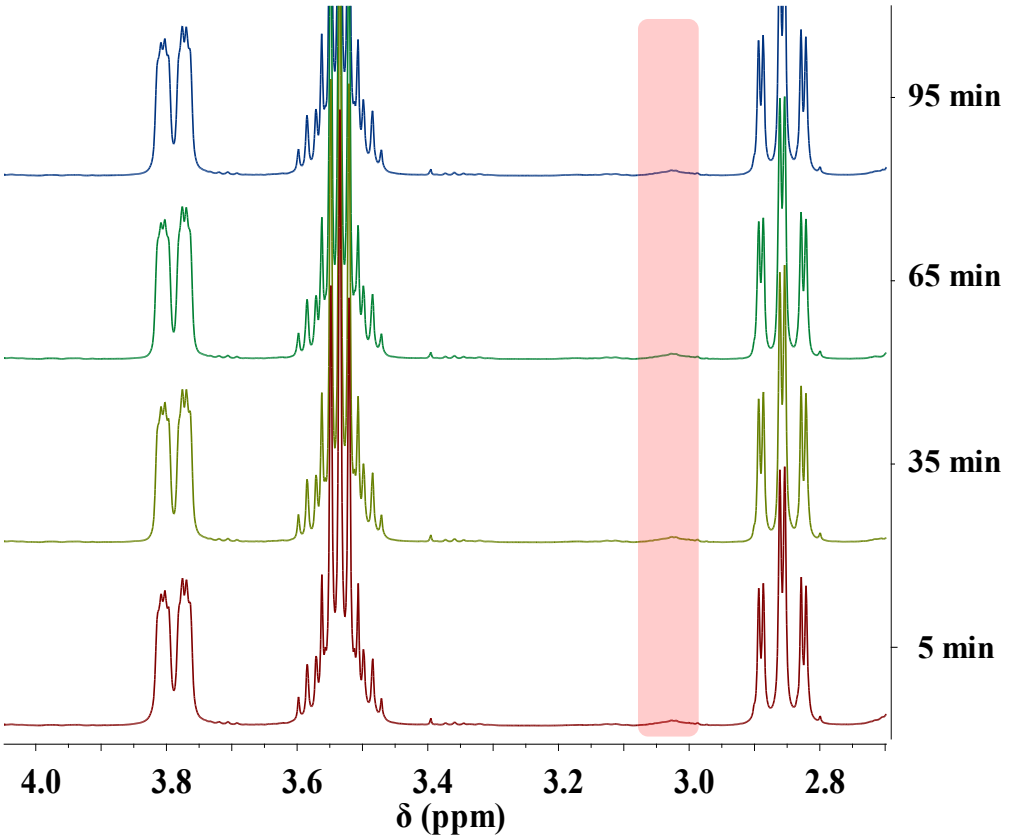

Figure S9. Time resolved ^{1}H NMR spectra showing exchange reaction between n-PA and MPipU at room temperature.

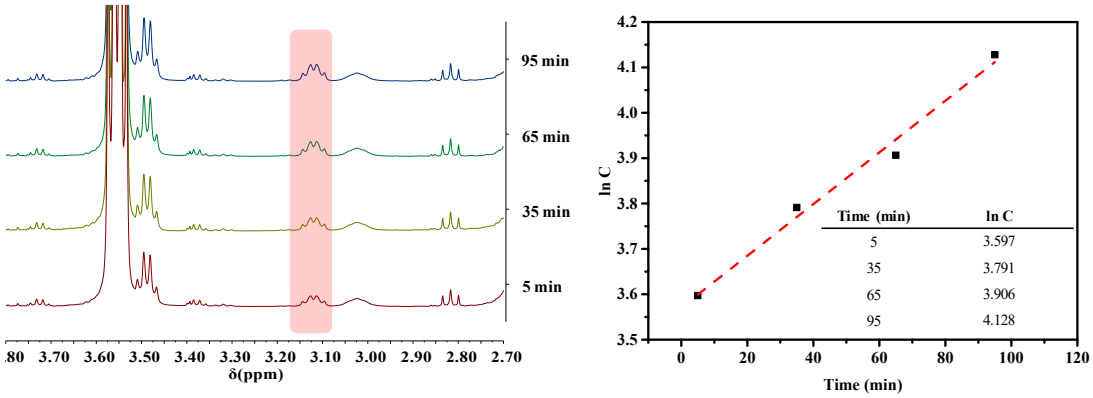

Figure S10. Time resolved ^{1}H NMR spectra showing exchange reaction between n-PA and *cis*-DMPipU at room temperature.

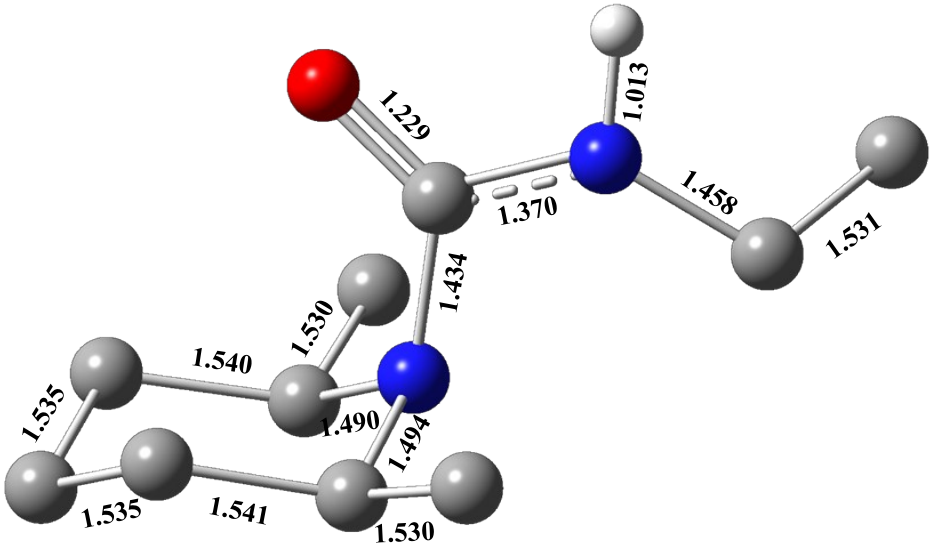

Figure S11. Structure and bond lengths of *cis*-DMPipU in ground state.

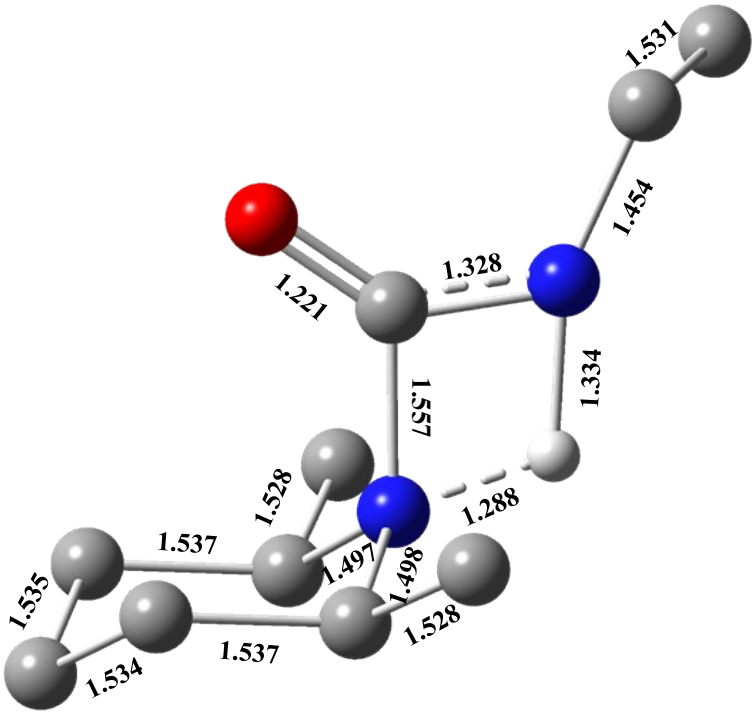

Figure S12. Structure and bond lengths of *cis*-DMPipU in TS1 state.

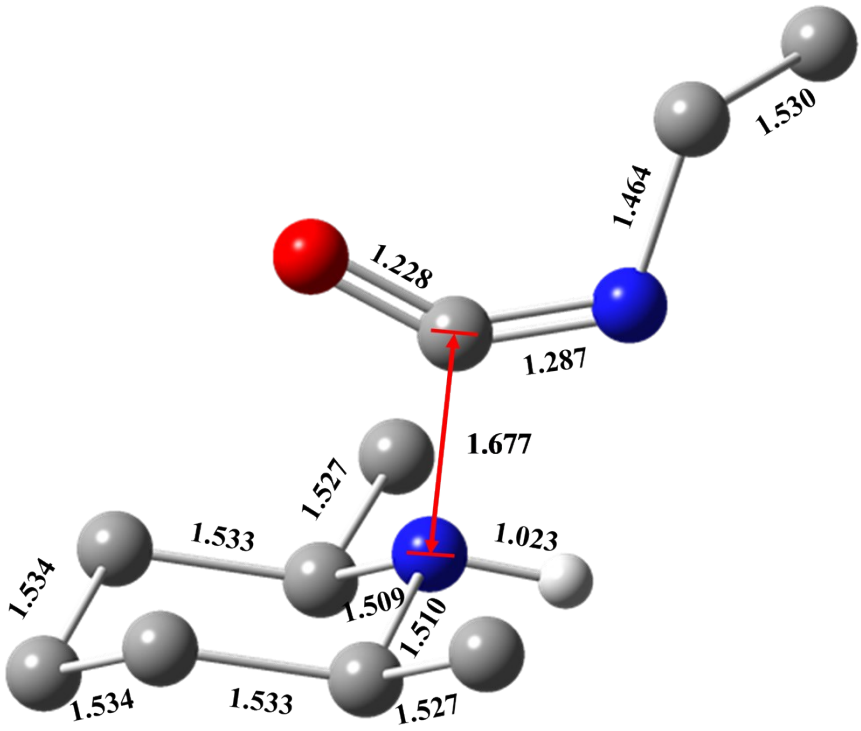

Figure S13. Structure and bond lengths of *cis*-DMPipU in P1 state.

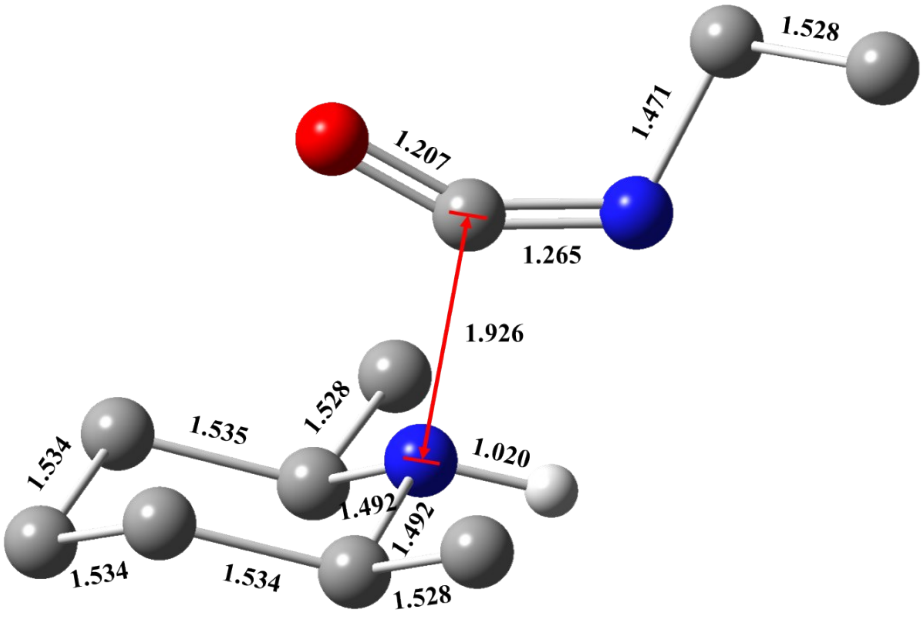

Figure S14. Structure and bond lengths of *cis*-DMPipU in TS2 state.

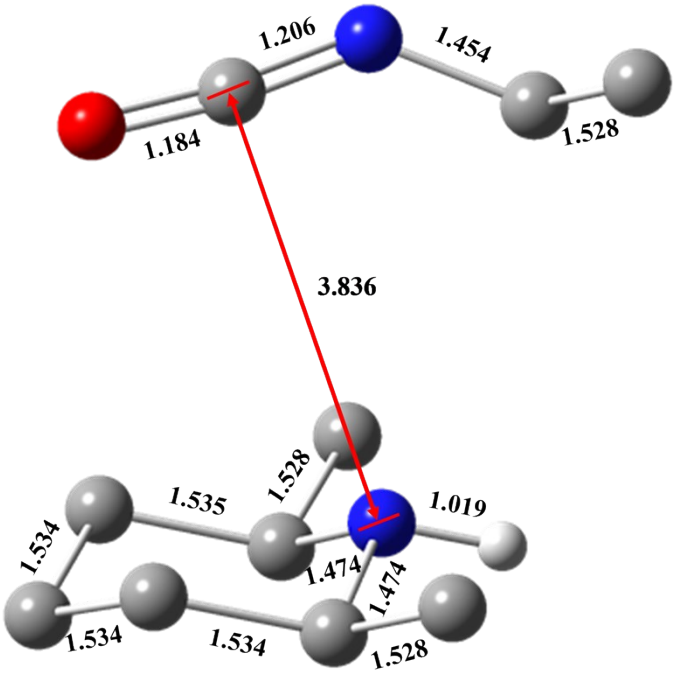

Figure S15. Structure and bond lengths of *cis*-DMPipU in P2 state.

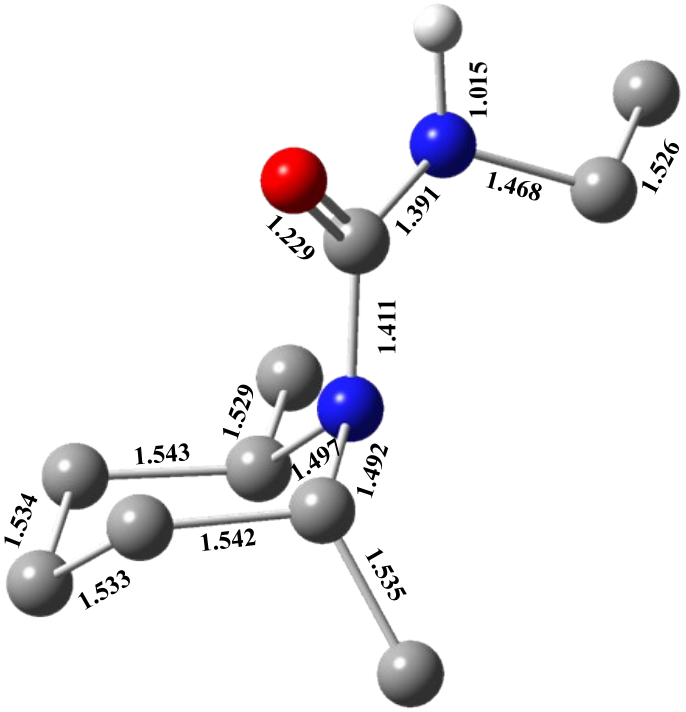

Figure S16. Structure and bond lengths of *trans*-DMPipU in ground state.

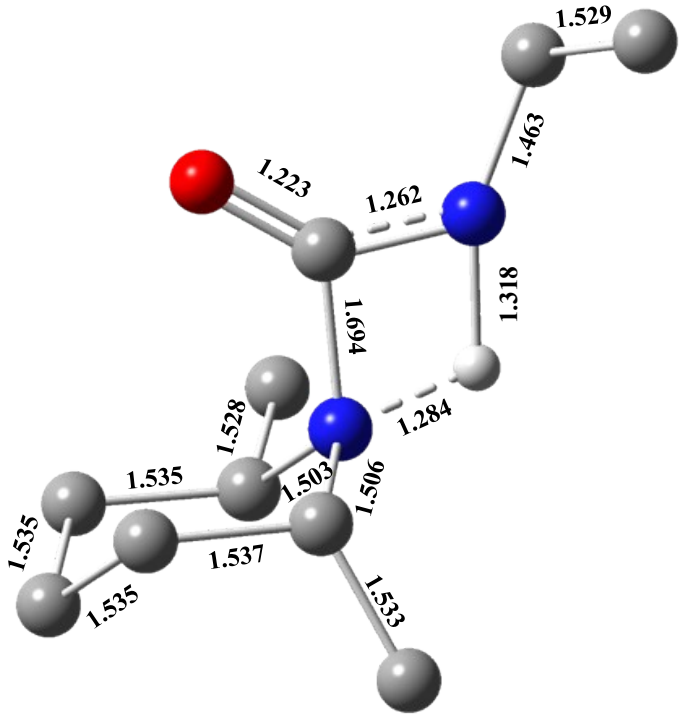

Figure S17. Structure and bond lengths of *trans*-DMPipU in TS1 state.

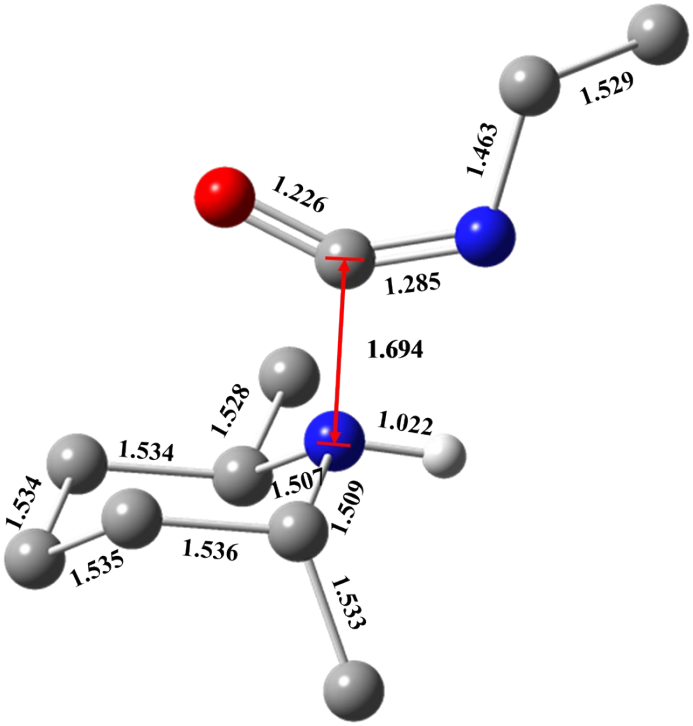

Figure S18. Structure and bond lengths of *trans*-DMPipU in P1 state.

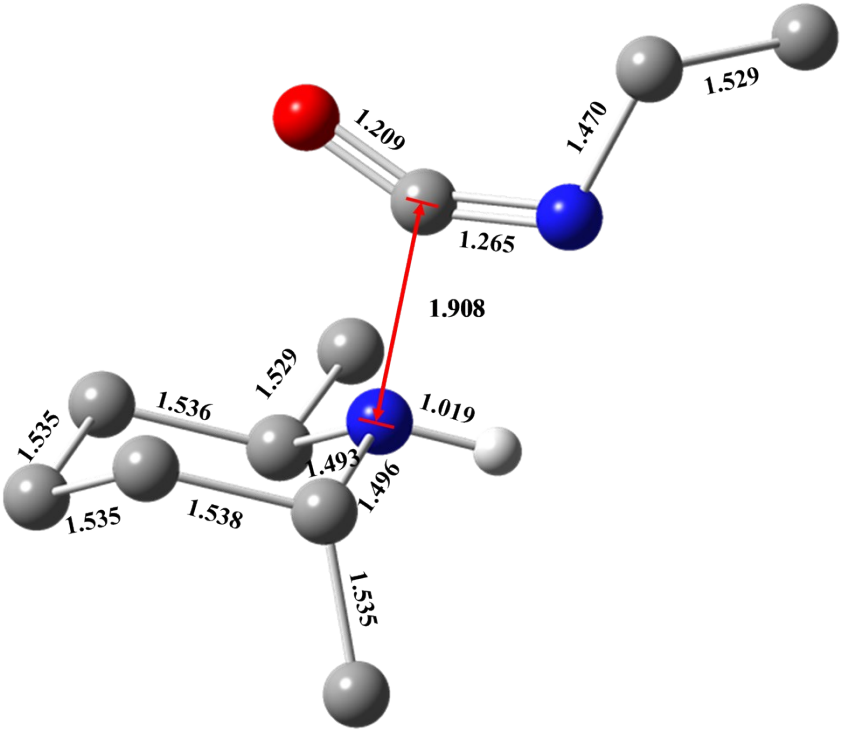

Figure S19. Structure and bond lengths of *trans*-DMPipU in TS2 state.

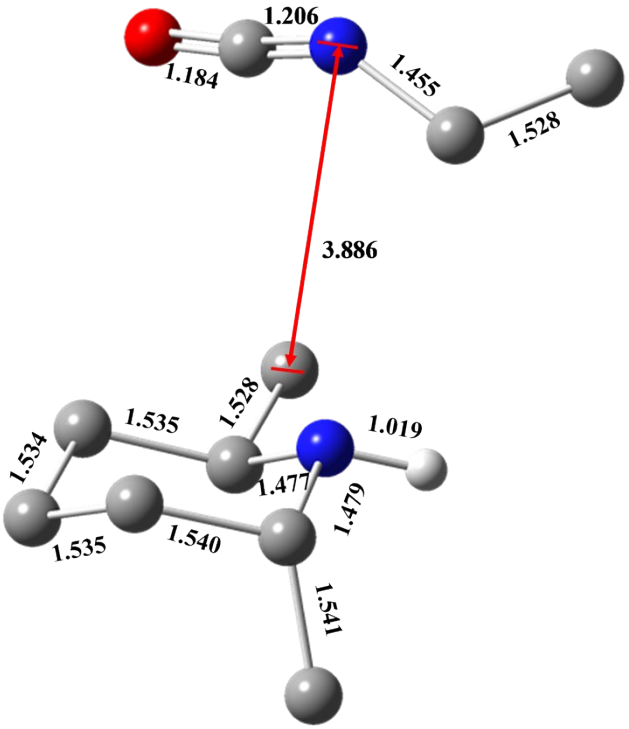

Figure S20. Structure and bond lengths of *trans*-DMPipU in P2 state.

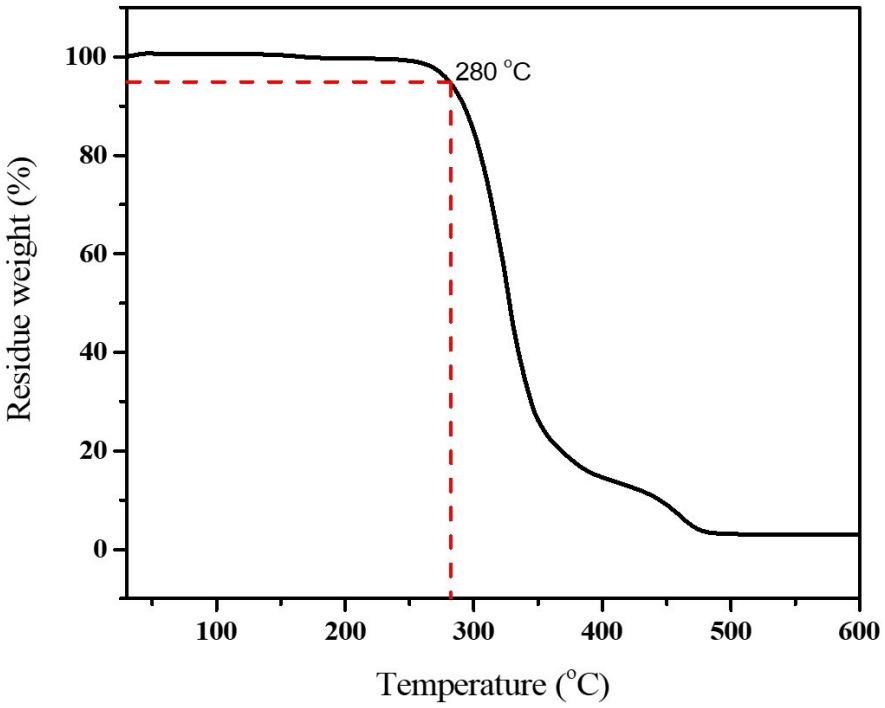

Figure S21. TGA curve of *trans*-DMPzU-PU from 30 °C to 600 °C.

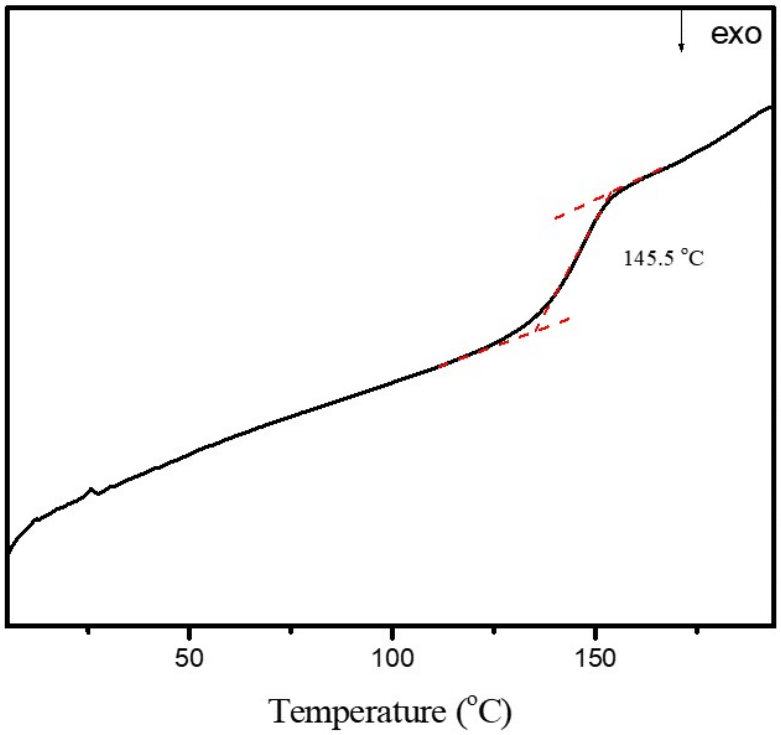

Figure S22. DSC curve of *trans*-DMPzU-PU from 0 °C to 200 °C.

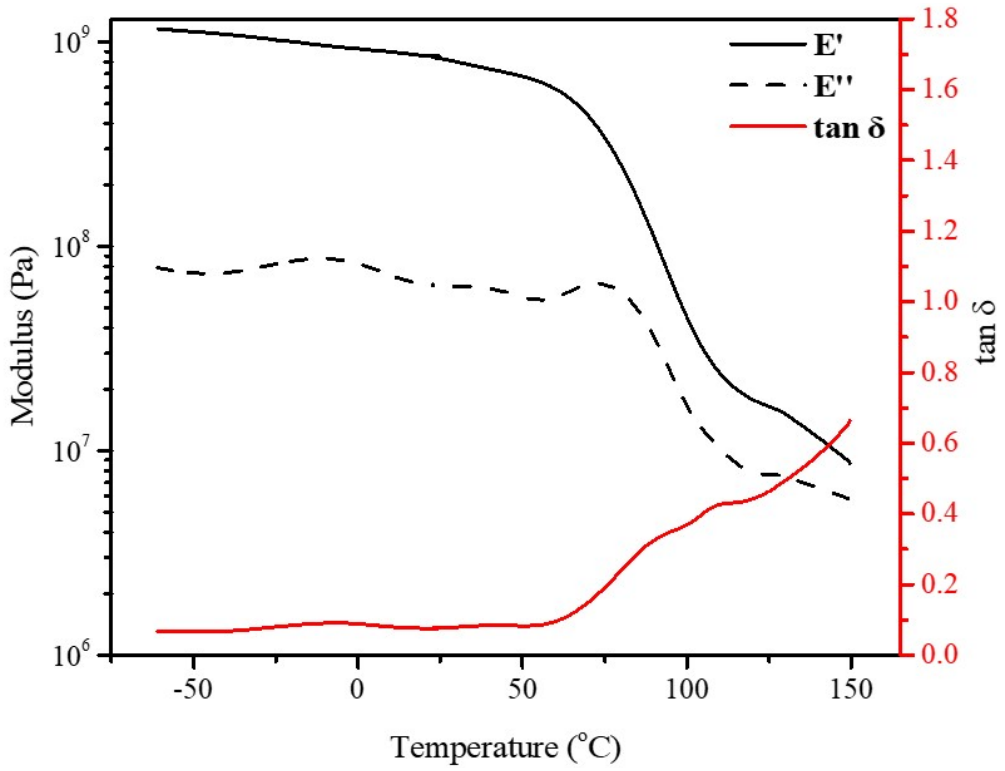

Figure S23. DMA curve of *trans*-DMPzU-PU from -60 °C to 150 °C.

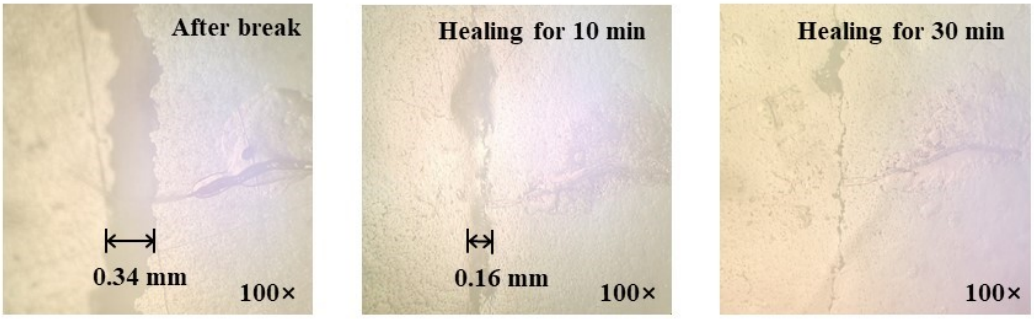

Figure S24. Photographs of *trans*-DMPzU-PU after break and healing at 70 °C for 10 min and 30 min with a small force (less than 5 N) to make the pieces touch tight.