

## Supporting Information

### Protic Pyrazolium Ionic Liquids for Efficient Chemical Fixation of CO<sub>2</sub>: Design, Synthesis, and Catalysis

Danning Zheng<sup>a,c</sup>, Tengfei Wang<sup>a,b,c</sup>, Xinrui Zhu<sup>a,c</sup>, Ci Chen<sup>a,c</sup>, Tiegang Ren<sup>\*a,b,c</sup>,

Li Wang<sup>\*a,c</sup>, Jinglai Zhang<sup>\*a,c</sup>

*<sup>a</sup>College of Chemistry and Chemical Engineering*

*<sup>b</sup>Engineering Laboratory for Flame Retardant and Functional Materials of Henan Province*

*<sup>c</sup>Henan University, Kaifeng, Henan 475004, P.R. China*

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| Route                                                                                                | Barrier height |
|------------------------------------------------------------------------------------------------------|----------------|
| *Corresponding author E-mail: <a href="mailto:rtg@henu.edu.cn">rtg@henu.edu.cn</a>                   |                |
| *Corresponding author E-mail: <a href="mailto:chemwangt@henu.edu.cn">chemwangt@henu.edu.cn</a>       |                |
| *Corresponding author E-mail: <a href="mailto:zhangjinglai@henu.edu.cn">zhangjinglai@henu.edu.cn</a> |                |

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|                                 |       |
|---------------------------------|-------|
| route 1 (HTMPzBr)               | 15.61 |
| route 2 (HMM <sub>3</sub> PzBr) | 14.46 |
| route 3 (HMM <sub>5</sub> PzBr) | 16.58 |

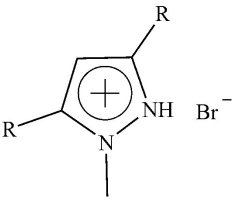
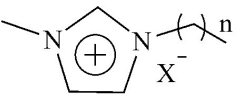
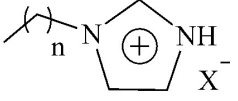
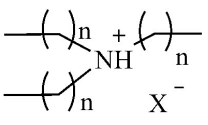
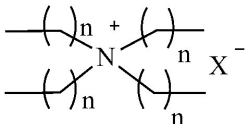
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**Table S1** The barrier heights ( $\Delta E$ , kcal/mol) of ring-opening step for routes 1-3.

**Table S2** The barrier heights ( $\Delta E$ , kcal/mol) of ring-opening step for routes 4-19.

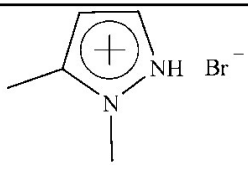
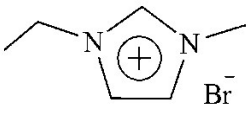
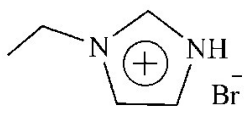
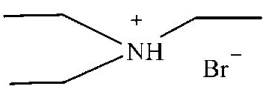
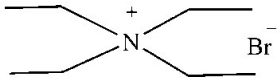
| Route                            | Barrier height |
|----------------------------------|----------------|
| route 4                          | 19.09          |
| route 5                          | 22.81          |
| route 6                          | 13.41          |
| route 7                          | 16.29          |
| route 8                          | 32.10          |
| route 9                          | 17.23          |
| route 10                         | 17.85          |
| route 11                         | 19.38          |
| route 12                         | 15.80          |
| route 13                         | 16.95          |
| route 14                         | 19.39          |
| route 15                         | 14.99          |
| route 16                         | 15.92          |
| route 17 (HTMPzBr)               | 8.47           |
| route 18 (HMM <sub>3</sub> PzBr) | 10.60          |
| route 19 (HMM <sub>5</sub> PzBr) | 7.84           |

**Table S3** The preparation conditions of other ILs.

| Entry          | ILs                                                                                 | Reaction conditions                                                                               |
|----------------|-------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------|
| 1              |    | 40°C, for 15 h.<br>remove water, washed with ethyl acetate.                                       |
| 2 <sup>a</sup> |    | 75°C, for 2 days, washed with anhydrous ether, dry<br>CH <sub>3</sub> CN, vacuum drying for 24 h. |
| 3 <sup>b</sup> |    | 60°C, for 4-5 h.<br>remove water.                                                                 |
| 4 <sup>b</sup> |  | 60°C, for 4-5 h.<br>remove water.                                                                 |
| 5 <sup>c</sup> |  | S: butyl acetate, reflux for 24 h;<br>crystallization from benzene.                               |

<sup>a</sup>from literature 32. <sup>b</sup>from literature 33. <sup>c</sup>from literature 34

**Table S4.** The catalytic performance of other imidazolium ILs

| Entry          | ILs                                                                                 | Name                  | Yield/% |
|----------------|-------------------------------------------------------------------------------------|-----------------------|---------|
| 1 <sup>a</sup> |    | HMM <sub>5</sub> PzBr | 86.2    |
| 2 <sup>b</sup> |    | EMImBr                | 52.7    |
| 3 <sup>c</sup> |    | HEImBr                | 85.8    |
| 4 <sup>d</sup> |   | HTEaBr                | 34.9    |
| 5 <sup>e</sup> |  | NEt <sub>4</sub> Br   | 63      |

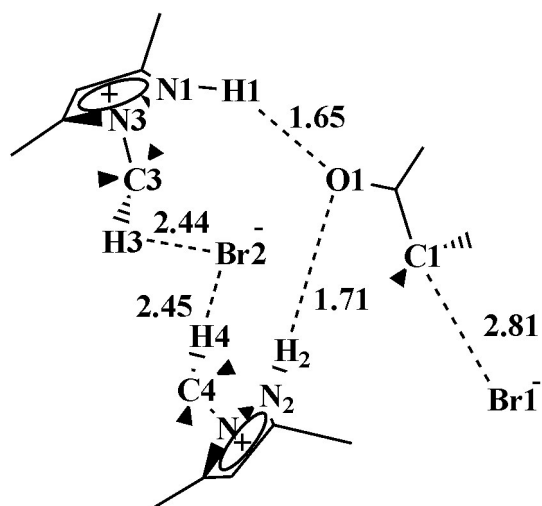
<sup>a</sup>Reaction conditions: PO: 100 mmol, catalyst: 1.0 mol%, CO<sub>2</sub>: 1.5 MPa, Temperature: 130 °C, time: 4.0 h.

<sup>b</sup>Reaction conditions: PO: 71.5 mmol, catalyst: 1.0 mol%, Temperature: 120 °C, CO<sub>2</sub>: 1.5 MPa, time: 1.5 h from literature 19.

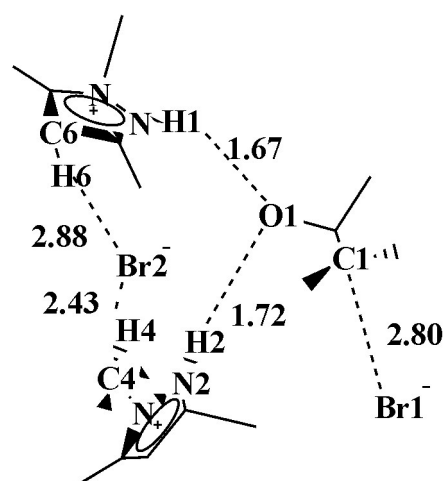
<sup>c</sup>Reaction conditions: PO: 70 mmol, catalyst 1.0 mol%, Temperature: 120 °C, CO<sub>2</sub>: 1.5 MPa, time: 2 h from literature 33.

<sup>d</sup>Reaction conditions: PO: 70 mmol, catalyst 1.0 mol%, Temperature: 120 °C, CO<sub>2</sub>: 1.5 MPa, time: 2 h from literature 33.

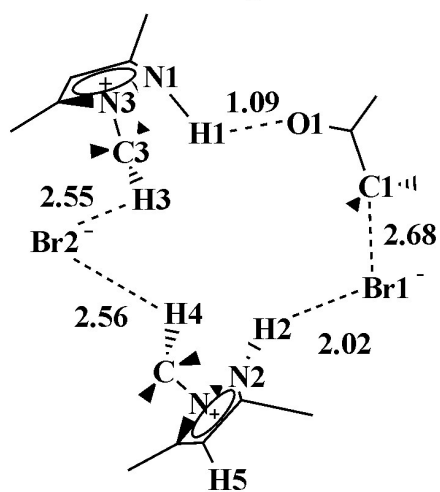
<sup>e</sup>Reaction conditions: PO: 14 mmol, catalyst: 1.0 mol %, Temperature: 120 °C, CO<sub>2</sub>: 1.5 MPa, time: 1 h from literature 35.



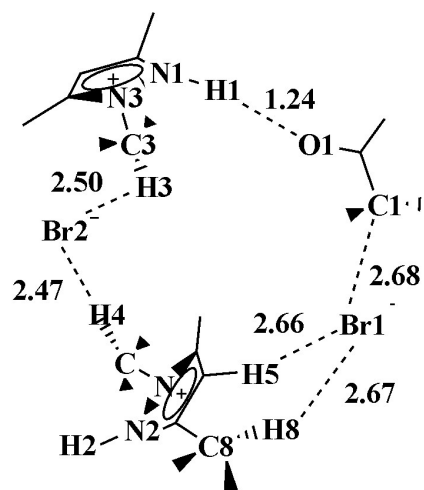
TS4



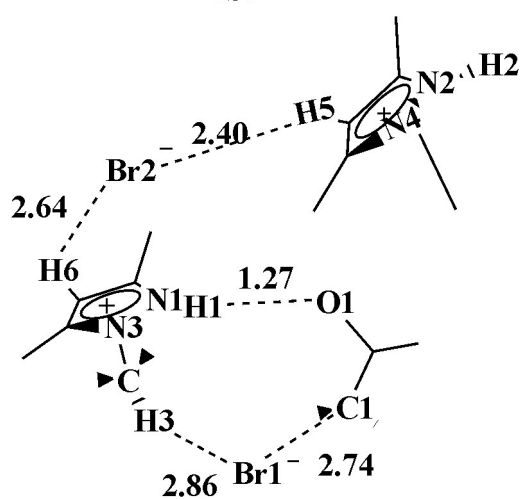
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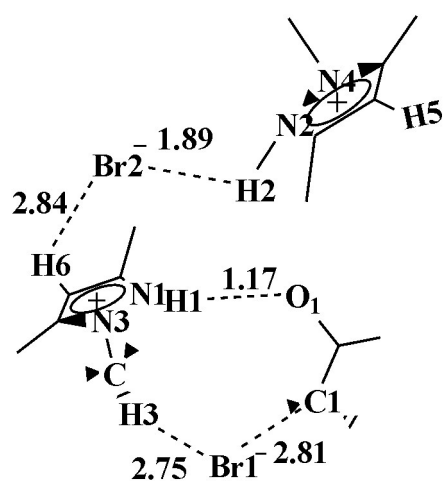
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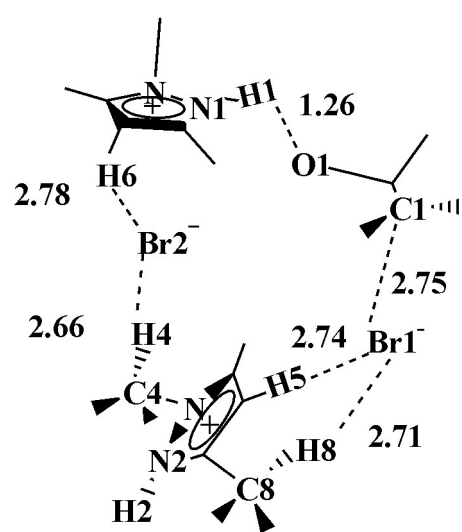
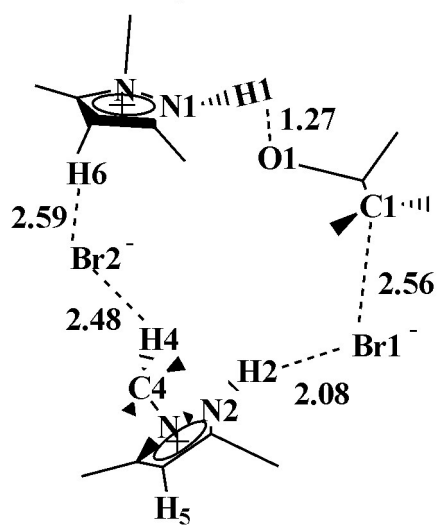
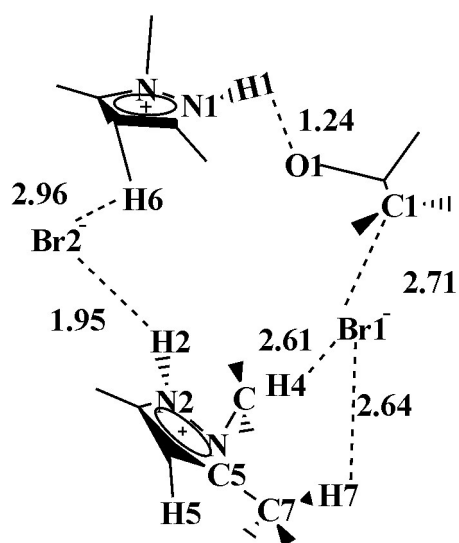
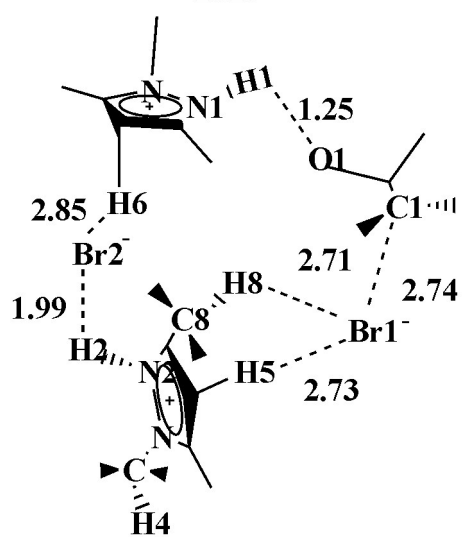
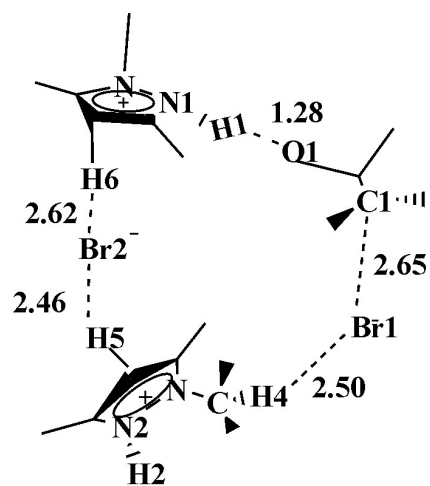
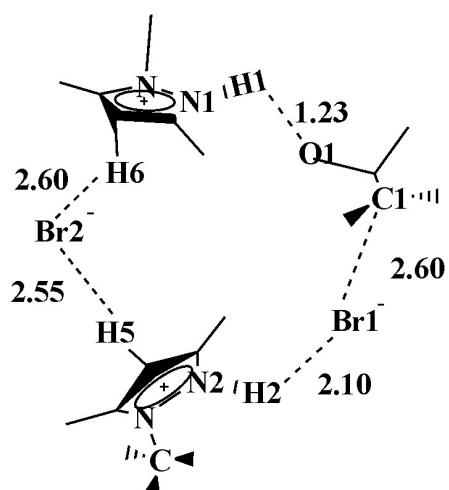
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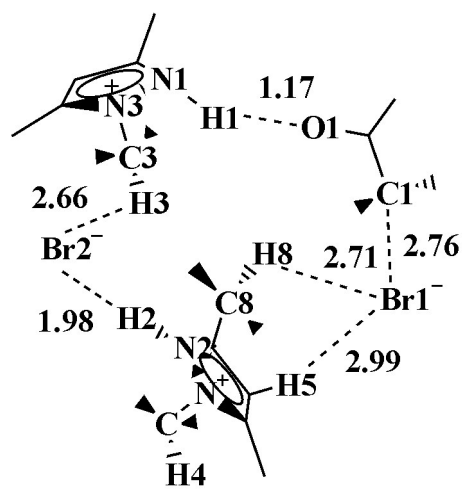


TS8

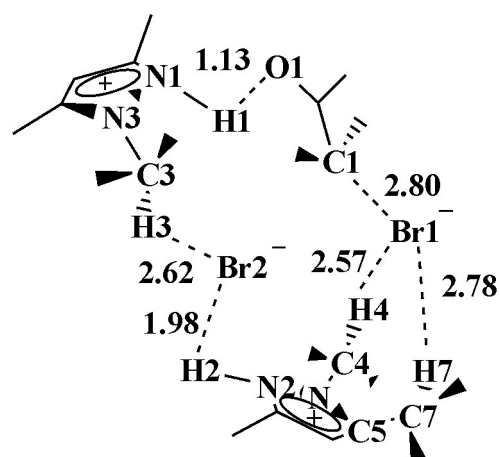


TS9





TS16



TS17

**Fig. S1.** The schematic structures of transition states for the ring-opening step of routes 4-17. Bond lengths are in angstroms.