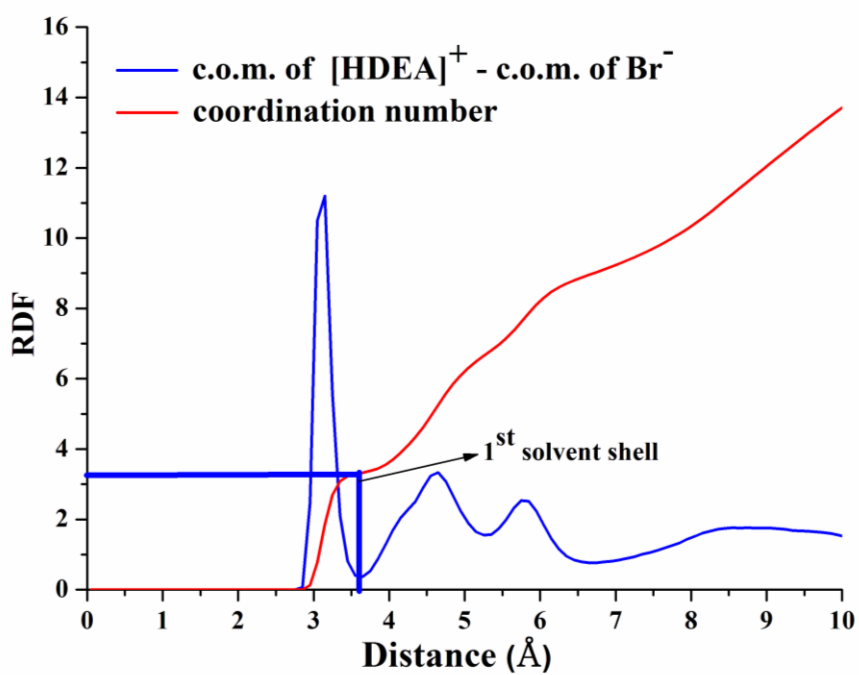
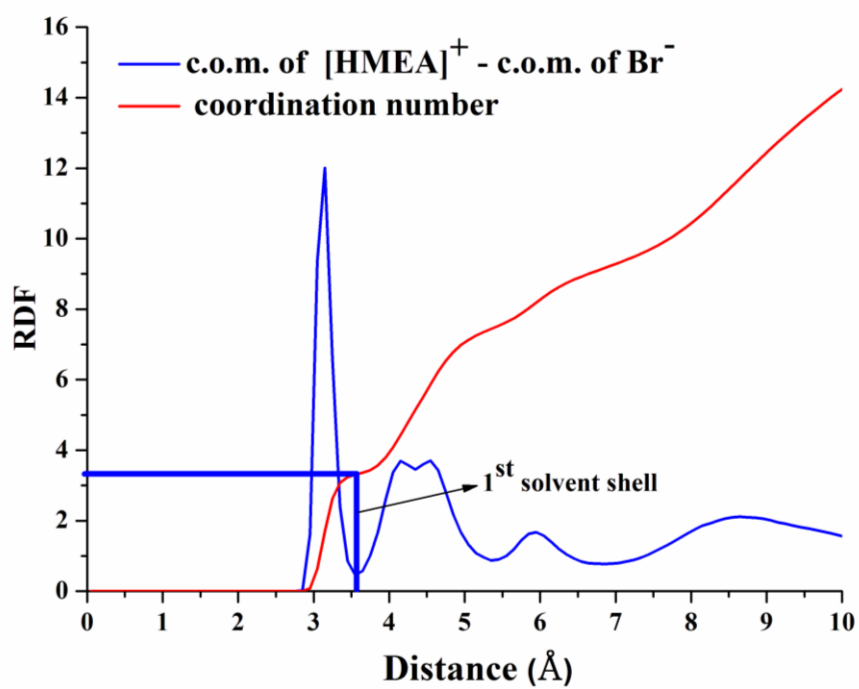


Supporting Information



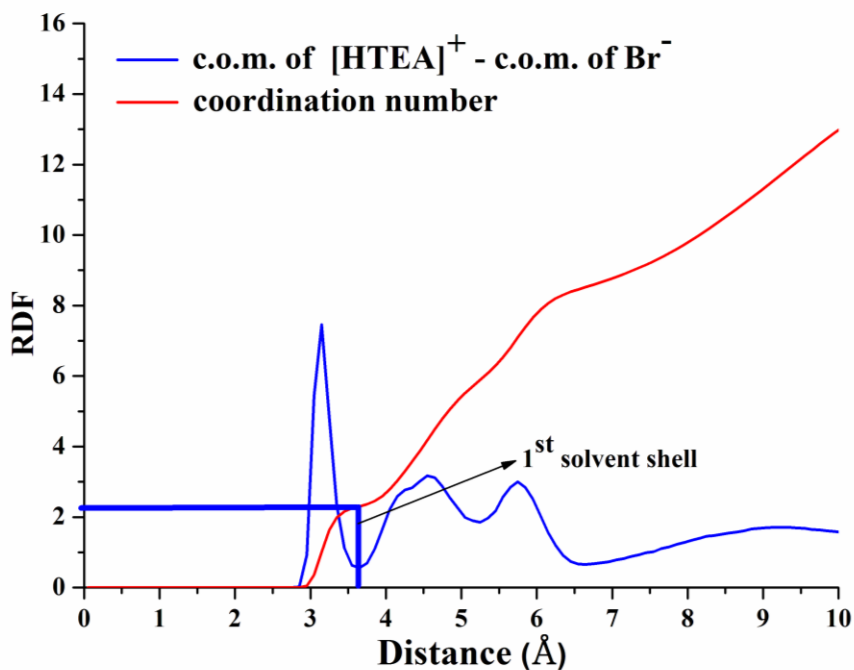


Figure S1. Radial distribution functions (blue line) and integrated coordination numbers (red line) with respect to the center of mass (c.o.m.) of [HMEA]⁺, [HDEA]⁺, and [HTEA]⁺ cation and the center of mass (c.o.m.) of Br⁻ anion. The first solvent shell is at a distance of around 3.6 Å, and all the coordination numbers are less than 4.

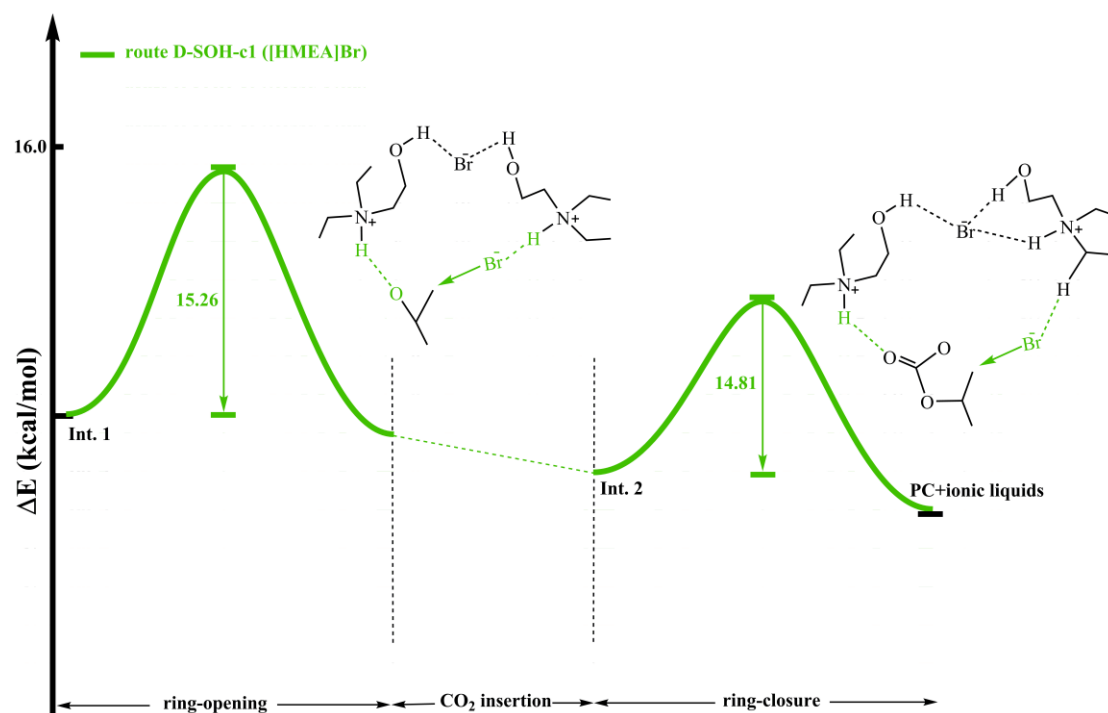


Figure S2. Potential energy profile and sketch structures of transition states for the ring-opening step and ring-closure step along route D-SOH-c1 calculated at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level. Int. 1 and Int. 2 represent the corresponding intermediates.

Table S1. The corresponding schematic structures of transition states and barrier heights catalyzed by [HMEA]Br at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level.

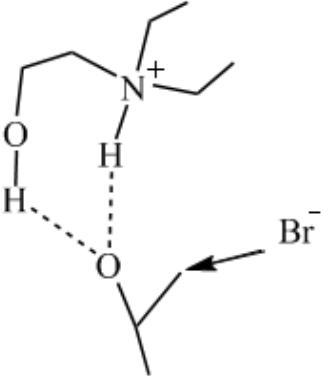
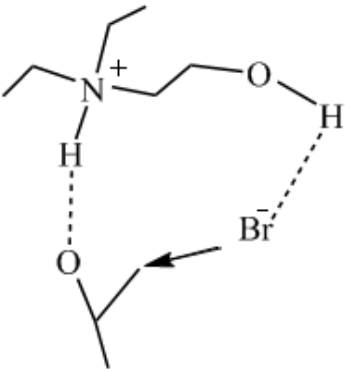
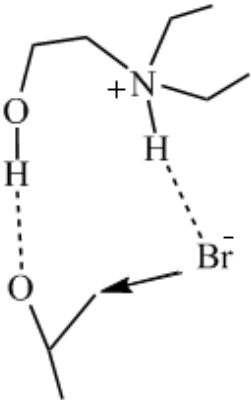
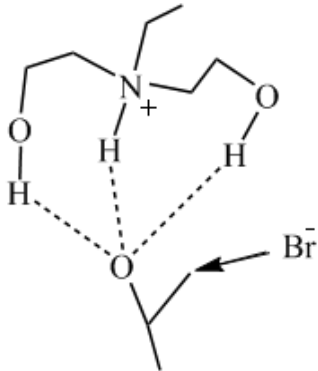
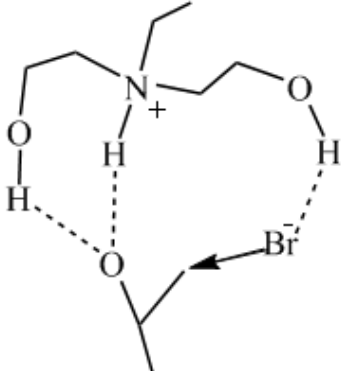
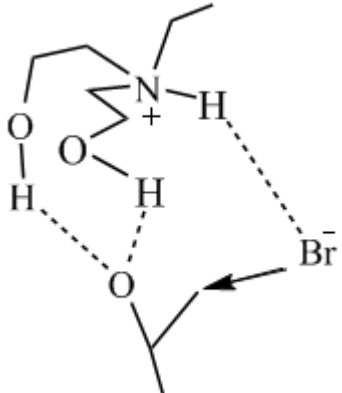
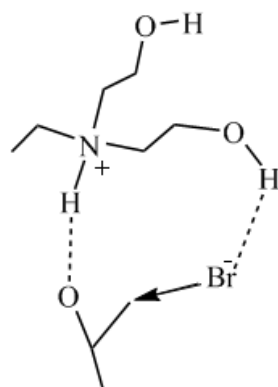
routes	schematic structures of transition states	barrier heights (kcal/mol)
route S-SOH-1		30.36
route S-SOH-2		21.53
route S-SOH-3		25.41

Table S2. The corresponding schematic structures of transition states and barrier heights catalyzed by [HDEA]Br at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level.

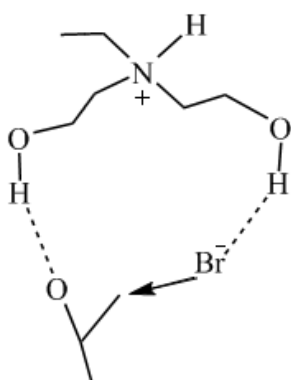
routes	schematic structures of transition states	barrier heights (kcal/mol)
route S-DOH-1		29.32
route S-DOH-2		20.58
route S-DOH-3		—

route S-DOH-4



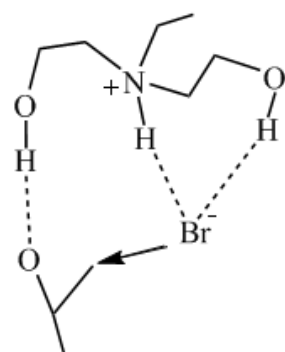
22.19

route S-DOH-5



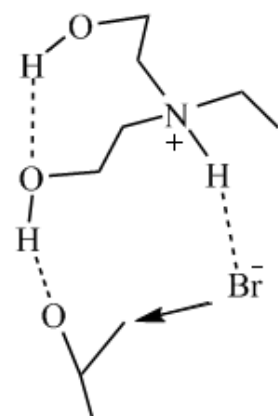
21.85

route S-DOH-6



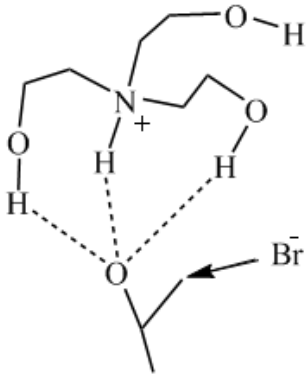
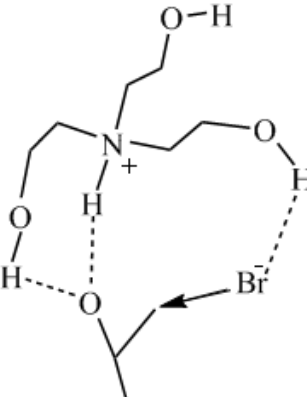
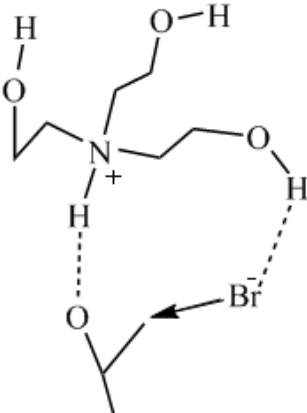
27.00

route S-DOH-7

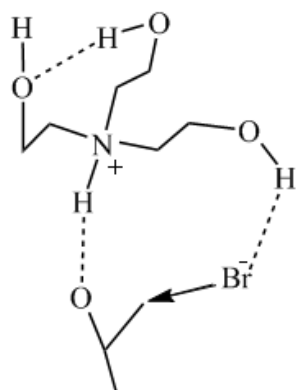


28.56

Table S3. The corresponding schematic structures of transition states and barrier heights catalyzed by [HTEA]Br at the M06/6-311+G(2d,2p) (PCM)/B3PW91/6-31G(d,p) level.

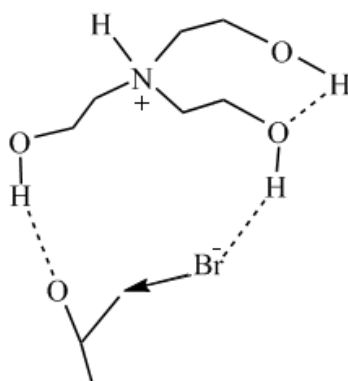
routes	schematic structures of transition states	barrier heights (kcal/mol)
route S-TOH-1		30.50
route S-TOH-2		24.21
route S-TOH-3		21.73

route S-TOH-4



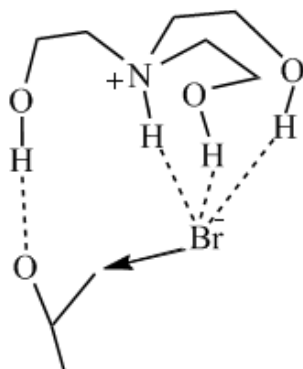
22.49

route S-TOH-5



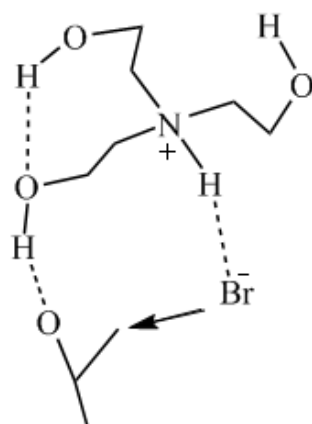
20.74

route S-TOH-6



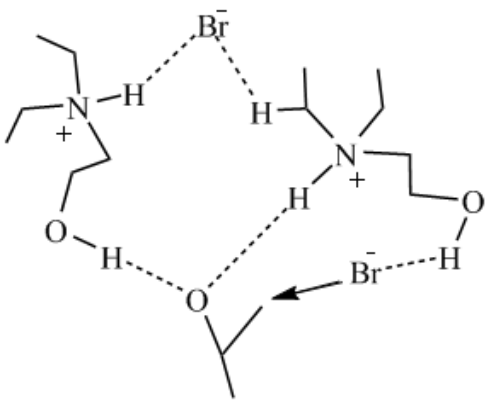
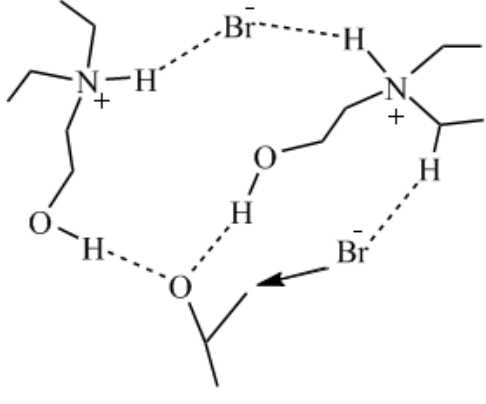
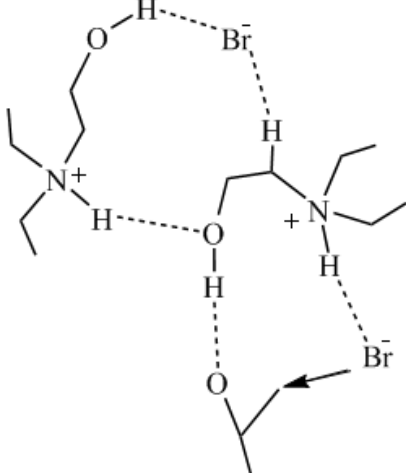
28.56

route S-TOH-7

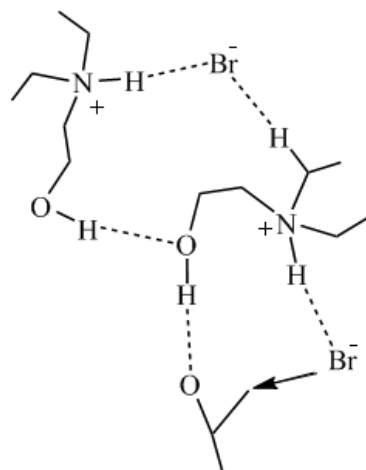


28.91

Table S4. The corresponding schematic structures of transition states and barrier heights catalyzed by two [HMEA]Br at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level.

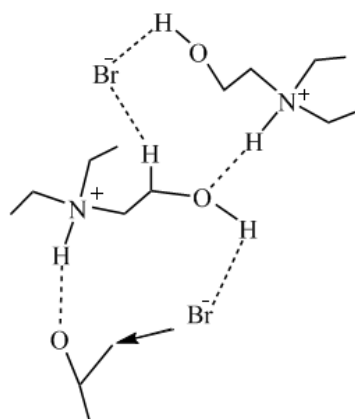
routes	schematic structures of transition states	barrier heights (kcal/mol)
route D-SOH-a1		21.80
route D-SOH-a2		17.98
route D-SOH-b1		29.19

route D-SOH-b2



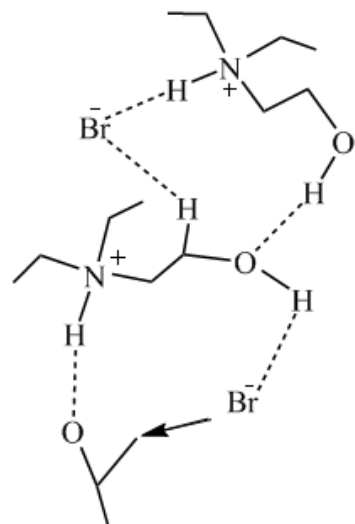
24.43

route D-SOH-b3



19.98

route D-SOH-b4



24.22

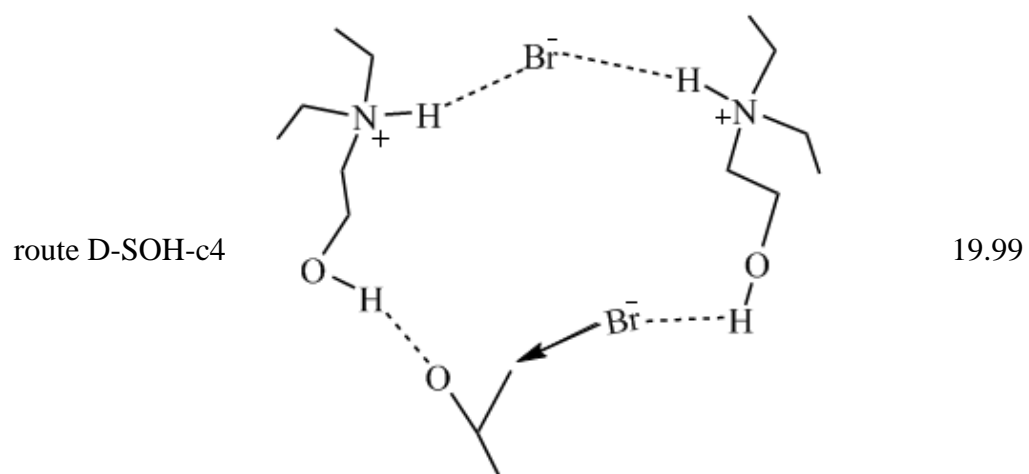
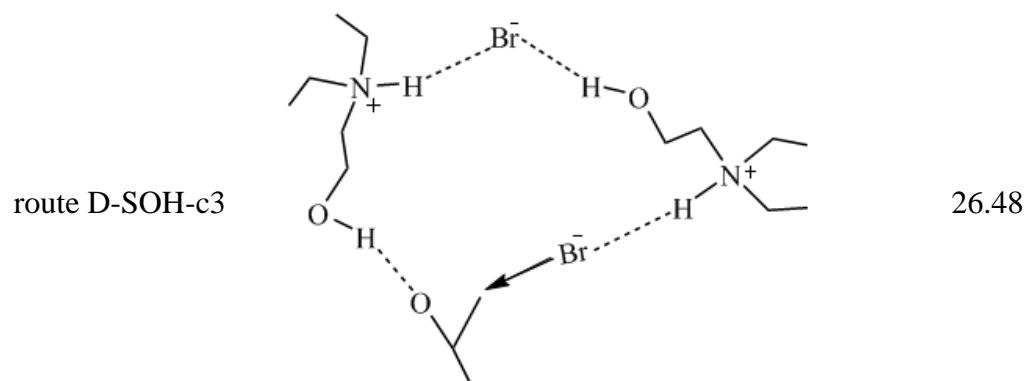
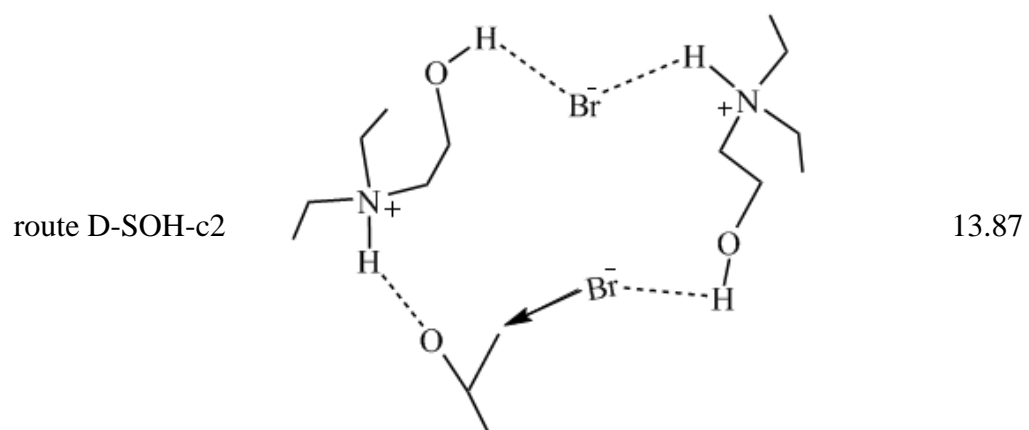
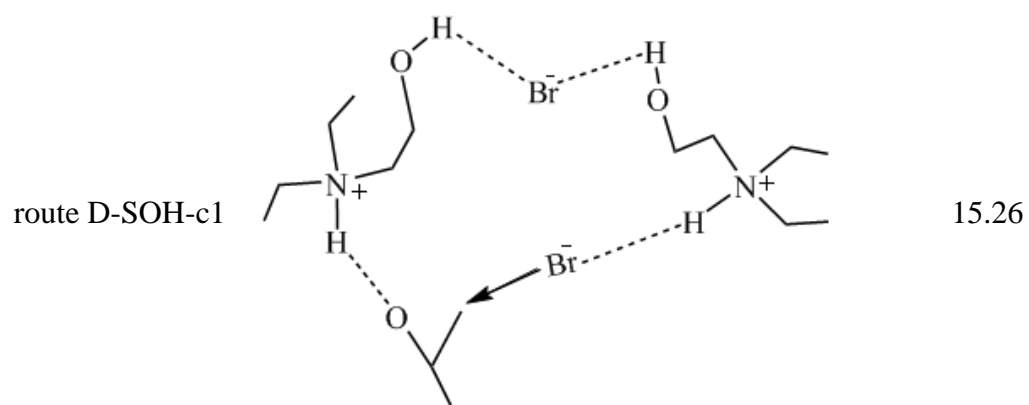
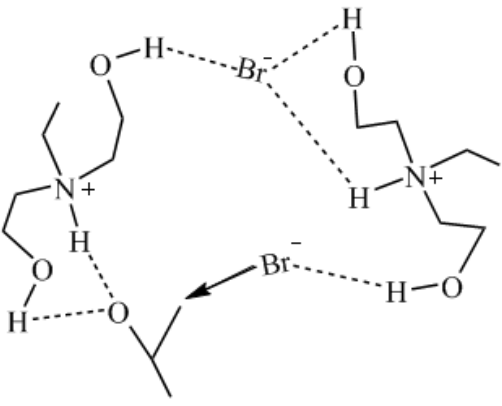
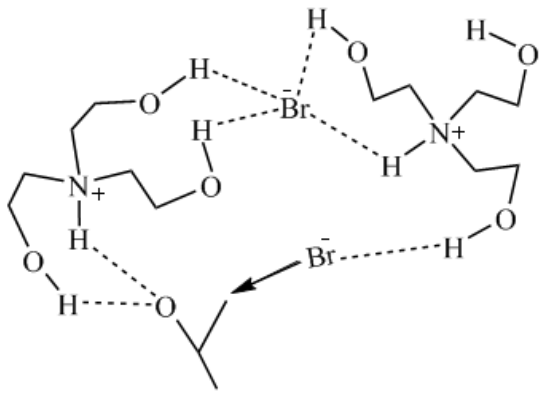


Table S5. The corresponding schematic structures of transition states and barrier heights catalyzed by two [HDEA]Br (two [HTEA]Br) following the similar mechanism of route D-SOH-c2 at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level.

routes	schematic structures of transition states	barrier heights (kcal/mol)
route D-DOH-c2		12.51
route D-TOH-c2		20.41