Supporting Information

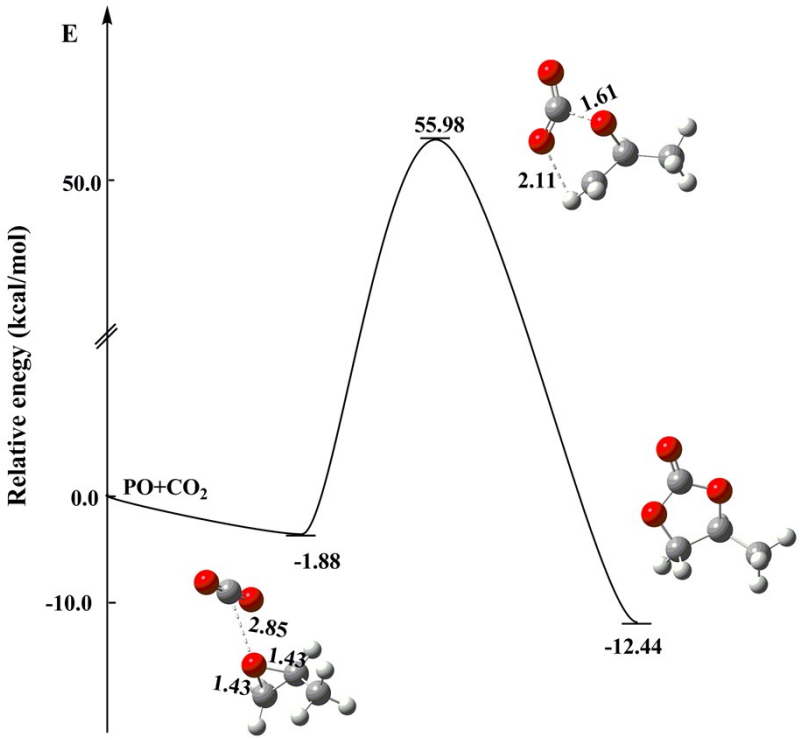


Fig. S1 The potential energy profile of uncatalyzed coupling reaction of CO_2 and PO calculated at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level along with the structures of intermediate and transition state. (Only the most favorable route is presented)

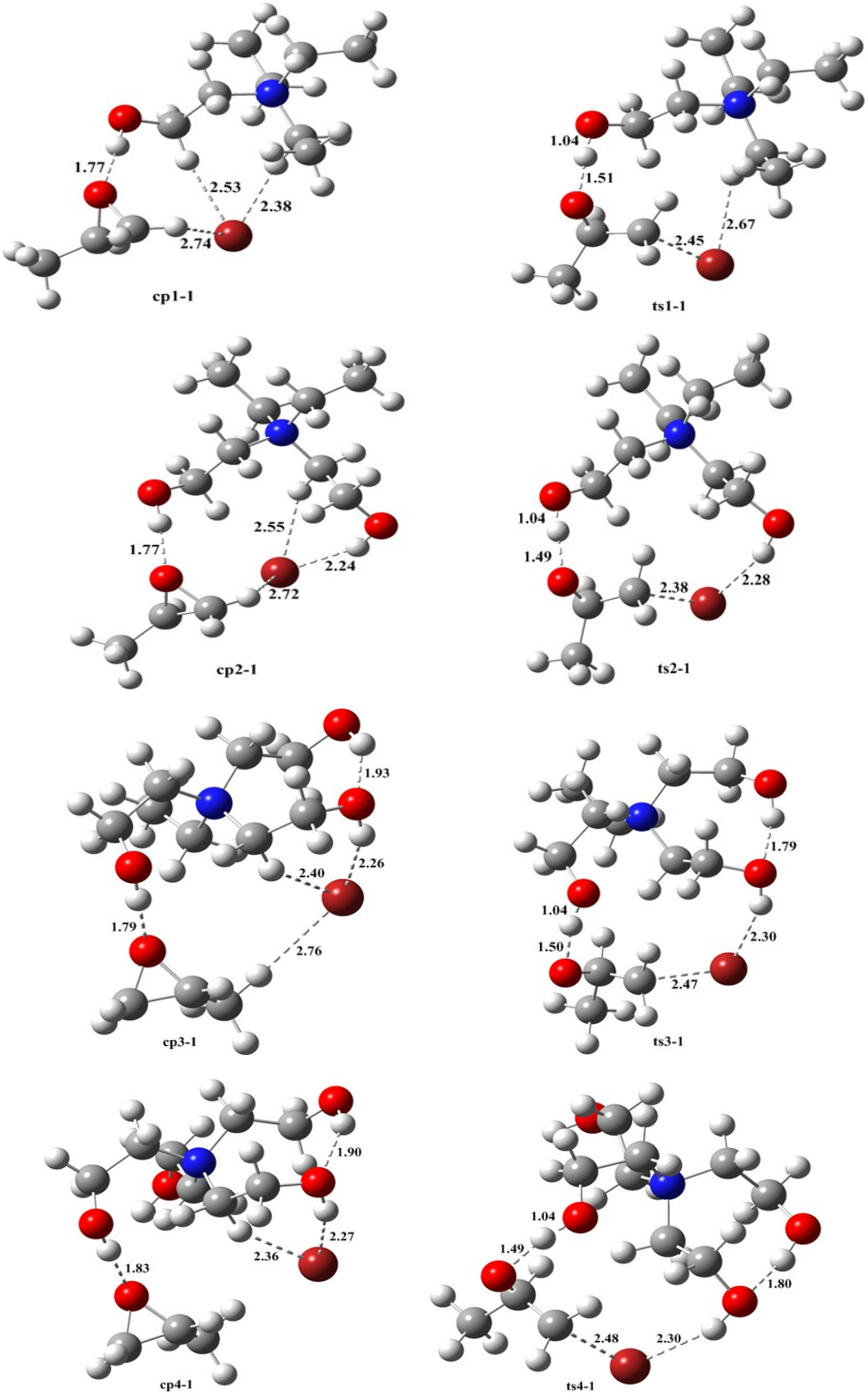


Fig. S2 The ball-and-stick structures of some key transition states and intermediates in routes 1-4. Bond lengths are in angstroms.

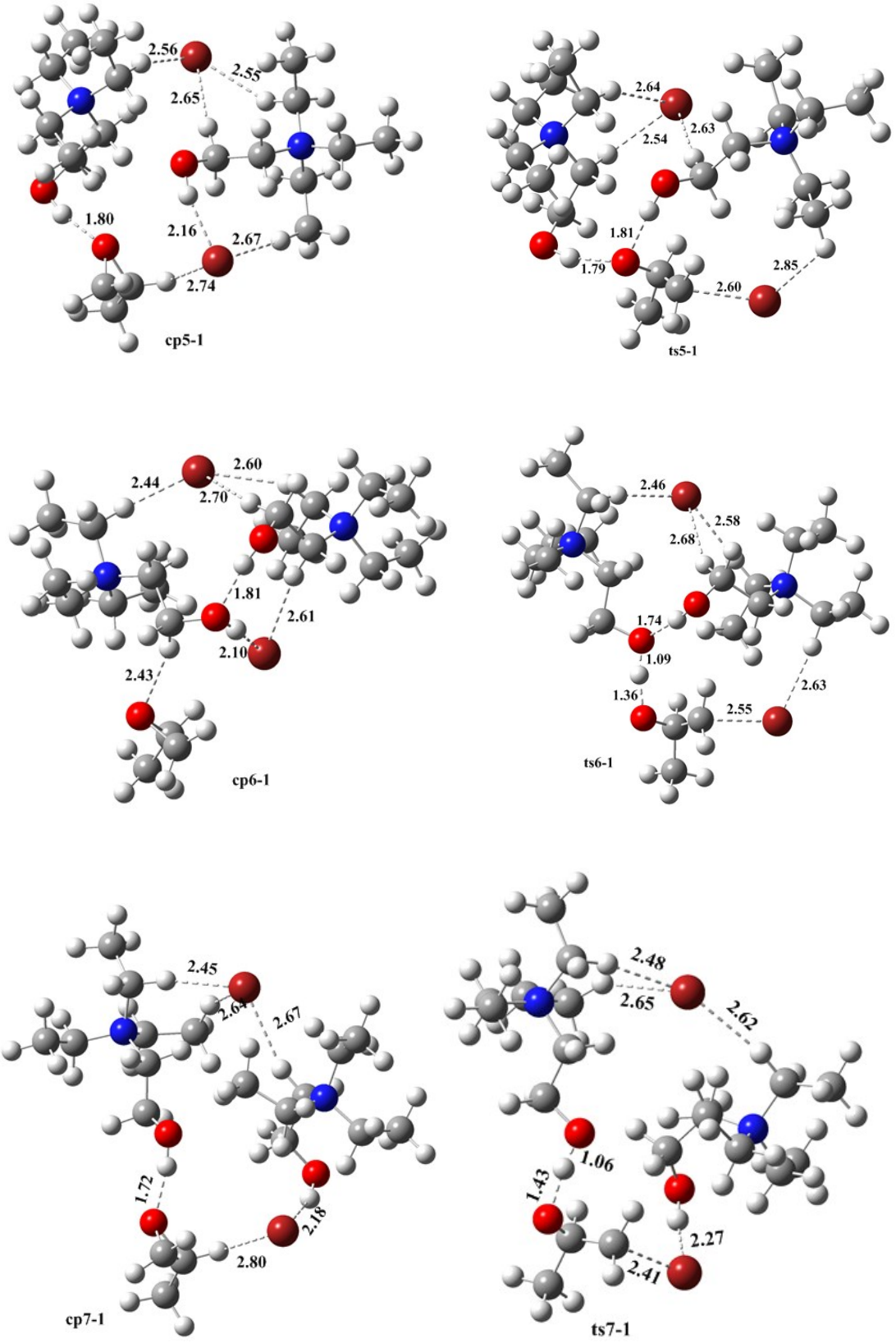
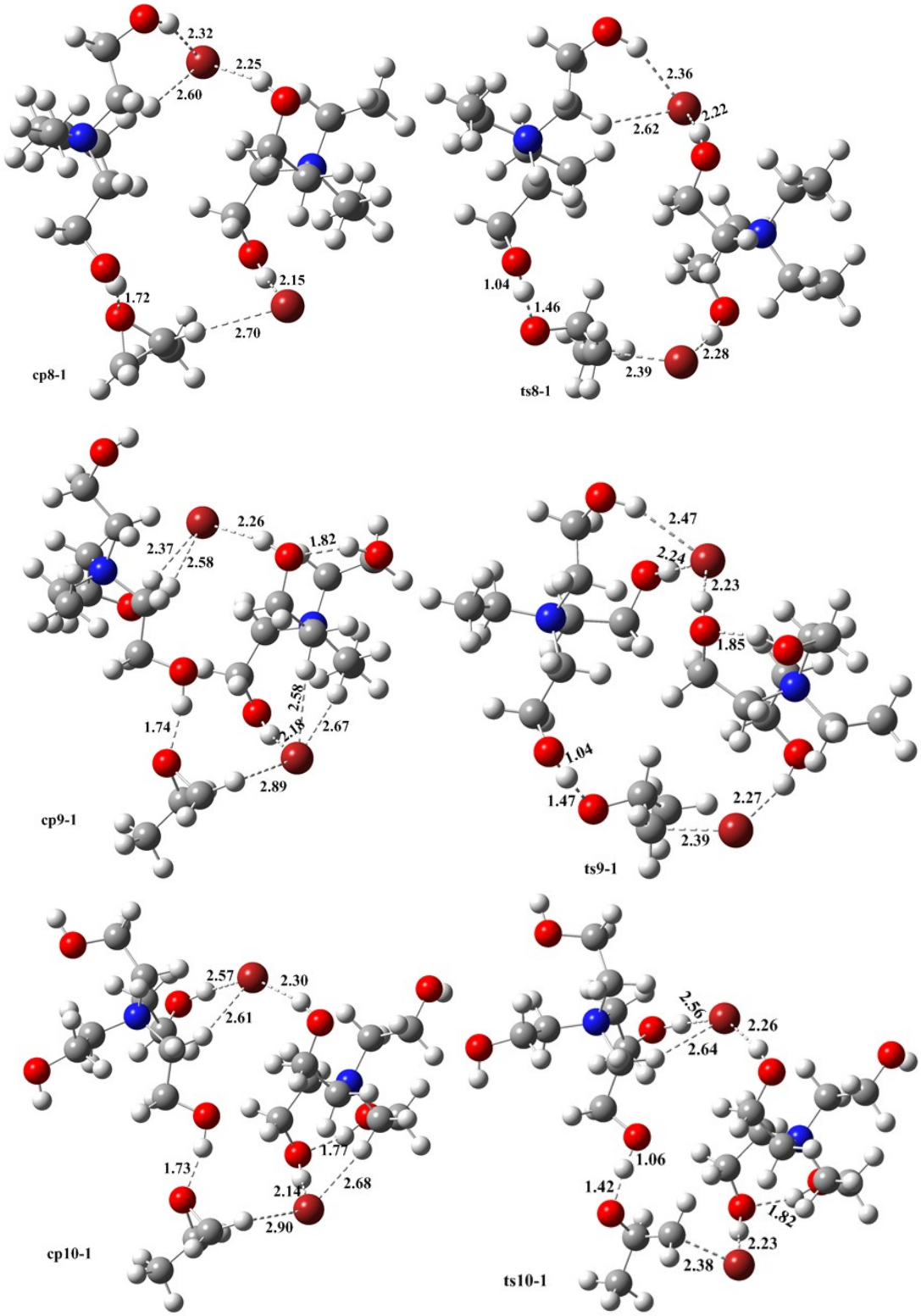


Fig. S3 The ball-and-stick structures of some key transition states and intermediates in routes 5-7. Bond lengths are in angstroms.


2.32
2.25
2.60
2.15
1.72
2.70
cp8-1
2.36
2.22
2.62
1.04
1.46
2.28
2.39
ts8-1
2.26
2.37
2.58
1.82
2.58
1.74
2.67
2.89
cp9-1
2.47
2.24
2.23
1.85
1.04
1.47
2.27
2.39
ts9-1
2.57
2.30
2.61
1.73
1.77
2.14
2.68
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2.26
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1.06
1.42
1.82
2.23
2.38
ts10-1

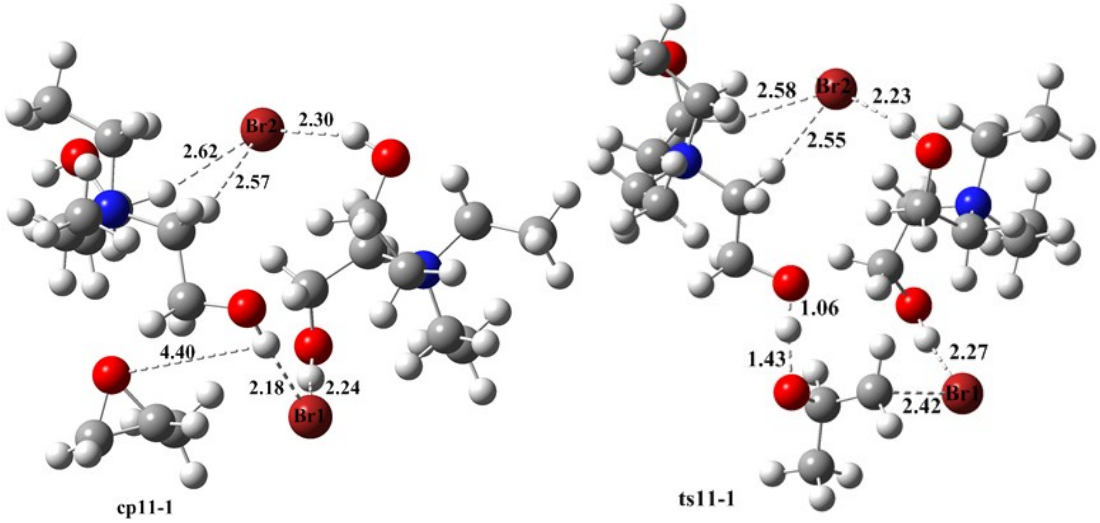

Fig. S4 The ball-and-stick structures of some key transition states and intermediates in routes 8-10 along with the ts11-1 and cp11-1. Bond lengths are in angstroms.

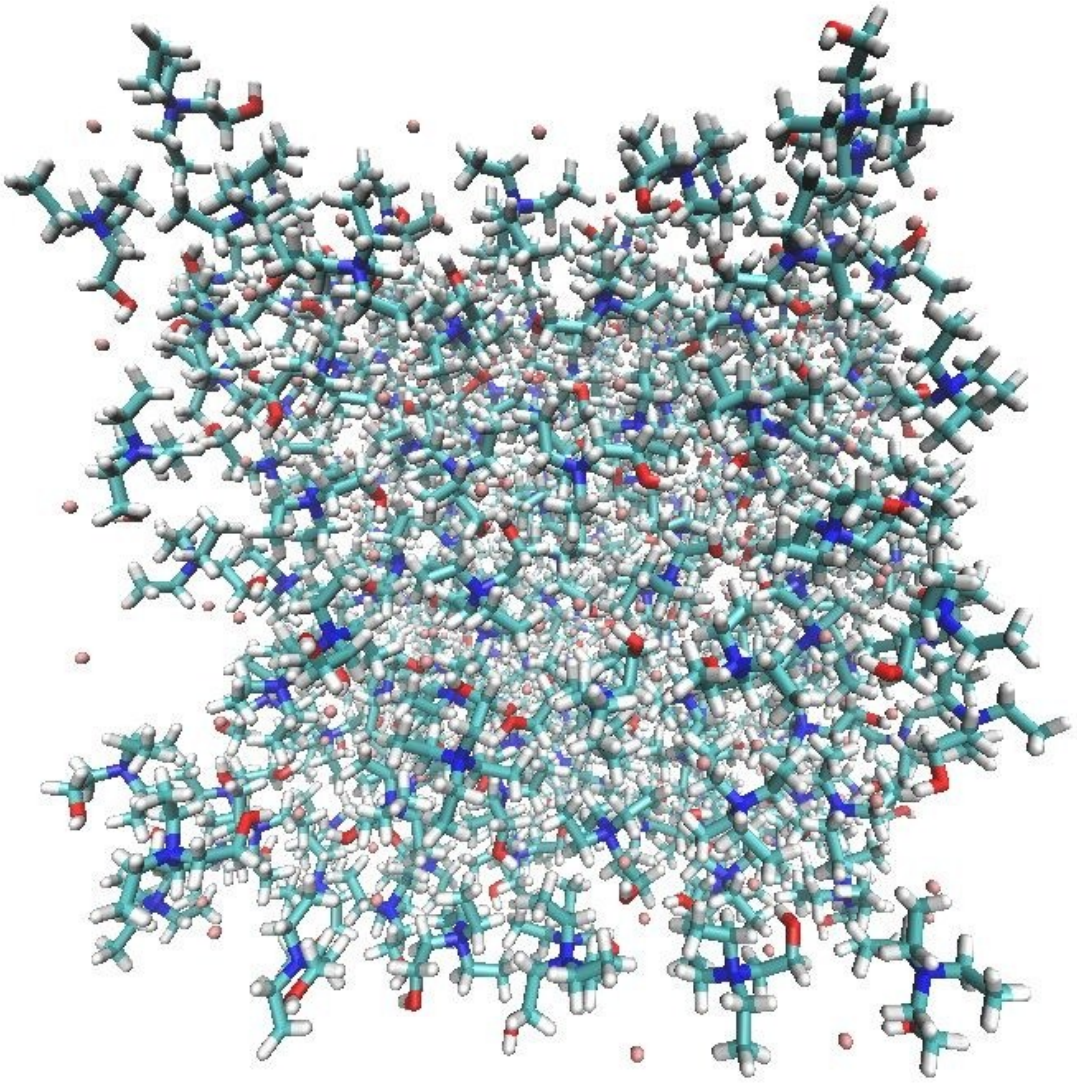

Fig. S5 Snapshots of the NEt_3(HE)Br ILs system after 5ns simulation. The N atoms are shown blue, O atoms are shown red, C atoms are shown green, Br atoms are shown pink, and H atoms are shown white.

Table S1 Atom types and their definitions in GAFF.

number	atom	type	description
1	N1	n4	sp^3 N with four connected atoms
2	C1	c3	sp^3 C
3	H1	hx	H bonded to C next to positively charged group
4	H2	hx	H bonded to C next to positively charged group
5	C2	c3	sp^3 C
6	H3	hc	H bonded to aliphatic carbon without electrwd. group
7	H4	hc	H bonded to aliphatic carbon without electrwd. group
8	H5	hc	H bonded to aliphatic carbon without electrwd. group
9	C3	c3	sp^3 C
10	H6	hx	H bonded to C next to positively charged group
11	C4	c3	sp^3 C
12	H7	hx	H bonded to C next to positively charged group
13	H8	hx	H bonded to C next to positively charged group
14	C5	c3	sp^3 C
15	H9	hc	H bonded to aliphatic carbon without electrwd. group
16	H10	hc	H bonded to aliphatic carbon without electrwd. group
17	H11	hc	H bonded to aliphatic carbon without electrwd. group
18	C6	c3	sp^3 C
19	H12	hx	H bonded to C next to positively charged group
20	H13	hx	H bonded to C next to positively charged group
21	C7	c3	sp^3 C
22	H14	h1	H bonded to aliphatic carbon with 1 electrwd. Group
23	H15	h1	H bonded to aliphatic carbon with 1 electrwd. Group
24	O1	oh	Oxygen in hydroxyl group
25	H16	ho	Hydroxyl group
26	C8	c3	sp^3 C
27	H17	hc	H bonded to aliphatic carbon without electrwd. group
28	H18	hc	H bonded to aliphatic carbon without electrwd. group
29	H19	hc	H bonded to aliphatic carbon without electrwd. group
30	H20	hx	H bonded to C next to positively charged group
31	Br1	br	any bromine

Table S2 All relative energies (kcal/mol) of routes 1-10 calculated at the M06/6-311+G(2d,2p) (PCM)//B3PW91/6-31G(d,p) level. Letter n indicates route number.

route	1	2	3	4	5	6	7	8	9	10
cpn-1	-3.36	-3.30	-3.70	-3.23	-21.31	-20.88	-16.88	-14.54	-18.97	-18.60
tsn-1	17.75	19.56	16.06	16.64	0.97	0.44	1.45	1.48	-5.37	0.62
cpn-2	4.65	8.84	5.66	5.24	-19.63	-17.25	-9.02	-5.08	-13.89	-11.44
cpn-3	-11.28	-6.49	-14.84	-16.58	-28.09	-23.35	-19.40	-16.39	-19.75	-24.55
tsn-3	3.25	8.29	1.89	0.26	-8.15	-6.30	-10.12	-9.65	-12.83	-15.55
cpn-4	-22.17	-21.58	-25.67	-13.12	-30.35	-29.47	-34.57	-33.32	-36.50	-39.92