Supporting information

Efficient synthesis of cyclic carbonates from CO_2 under ambient condition over $Zn(betaine)_2Br_2$: experimental and theoretical study

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1. Materials

Zinc bromide (98%), n-butanol (99.5%) and styrene oxide (98%) were provided by Beijing InnoChem Science & Technology Co., Ltd. Cyclohexene oxide (98%), epibromohydrin (97%), epichlorohydrin (99%) were purchased from J&K Scientific Ltd. Betaine (98%), 1,2-epoxypropane (analytical pure) and Tetrabutylammonium bromide (TBAB, >98.0%) were obtained from China National Pharmaceutical Group Corporation. Absolute alcohol was analytical grade and purchased from Tianjin Concord Technology Co., Ltd. Glycidyl phenyl ether (99.0%) and 1,2-epoxy-5-hexene (96.0%) were obtained from TCI (Shanghai) Development Co., Ltd. Propylene carbonate (99.0%) and 1,2-epoxyhexane were provided by Alfalfa Aesar. All the chemicals were used without further purification. CO_2 was purchased from Beijing Analytical Instrument Factory with a purity of 99.99%. The ionic liquid (IL) 1-hexyl-3-methylimidazolium tetrafluoroborate (98%) was supplied by Lanzhou Institute of Chemical Physics; Chinese Academy of Sciences. The IL was used without further purification.

2. Preparation of catalyst $Zn(betaine)_2Br_2$

In the experiments, 10 mmol betaine and 100 mL absolute ethanol were added into a 250 ml round bottom flask in turn. After the betaine was completely dissolved by magnetic stirring, it was labeled as Solvent A. 10 mmol $ZnBr_2$ and 50 mL absolute ethanol were added into a 100 mL round bottom flask in turn. After the $ZnBr_2$ was completely dissolved, it was dropped into Solution A, and white precipitate was formed. After magnetic stirring for two hours at room temperature, the white precipitates were separated by filtration. Washing with 25 mL absolute ethanol for three times, and then vacuum dry at 60 ℃ for 12 hours to remove the residual absolute ethanol. Finally, a white precipitate with more than 99% purity was obtained as target product. Spectral characterizations and elemental analyses of the catalyst $Zn(betaine)_2Br_2$ were obtained as follows.

3. Reactions

Reactions were carried out in a 22 mL stainless-steel batch reactor equipped with a magnetic stirrer. In a typical experiment, $Zn(betaine)_2Br_2$ (0.1 mmol) and PO (20 mmol) were added into the reactor. After sealing and preheating in a constant-temperature oil bath (or water bath) at a desired temperature for 20 minutes, CO_2 was charged into the reactor until the desired pressure was reached. During the reaction, the reactor was continuously magnetically stirred. After the reaction, the reactor was placed into ice water for 10 min, and then the excess CO_2 was released slowly. After depressurization, n-butanol was added into the liquid phase as an internal standard for the quantitative analysis. The reactor was flushed by 2 mL absolute ethanol (or ethyl acetate). After centrifugation, the products were analyzed quantitatively by a gas chromatograph (Agilent 6820) equipped with a flame ionization detector and a capillary column (HP-INNOWAX).

For the experiments near the atmospheric pressure, the air in the reactor was replaced by atmospheric CO_2 for three times and the reactions were carried out in a 25 mL round bottom flask equipped with a magnetic stirrer.

Then the pressure of CO_2 was kept at near the atmospheric pressure (0.1 MPa) using a balloon with CO_2. For the experiment of adding solvent, such as PC or IL, the solvent and reactant can be added successively.

TON was calculated as (TON = mmol product/mmol catalyst; TOF = mmol product/mmol catalyst per h).

4. Structure characterization of catalyst and products

The structures and purity of the $Zn(betaine)_2Br_2$ were characterized by NMR and elemental analysis techniques. A Bruker AV400 (400 MHz) NMR spectrometer was utilized with DMSO-d_6 as the solvent. Chemical shifts (δ) were reported in parts per million (ppm) and referenced to the residual solvent peaks. Elemental analyses for C, H and N were carried out with a Flash EA 1112 elemental analyzer. The Zn in the complex was determined by induced coupled plasma optical emission spectrometer (ICP-OES). The Fourier transform infrared (FT-IR) spectra were collected at a resolution of 4 cm^{-1} on a Bruker Vector 27 spectrophotometer in the 400–4000cm^{-1} region. The IR spectra of the samples were measured by the conventional KBr pellet method (Figure S2).

Betaine: ^{13}C NMR (400 MHz, DMSO-d_6) δ = 164.29, 66.86, 52.86;
^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.13, 3.52.

$Zn(betaine)_2Br_2$: ^{13}C NMR (400 MHz, DMSO-d_6) δ = 166.42, 65.86, 52.49.
^{1}H NMR (400 MHz, DMSO-d_6) δ = 3.17, 3.87.

$Zn(betaine)_2Br_2$: Calcd Zn 14.23, C 26.14, H 4.83, N 6.09; Found Zn 13.34, C 26.41, H 4.91, N 6.09.

4-chloromethyl-[1,3]dioxolan-2-one: ^{1}H NMR (400 MHz, DMSO-d_6) δ = 5.13-5.09, 4.62-4.57, 4.30-4.25, 4.00-3.94. ^{13}C NMR (400 MHz, DMSO-d_6) δ = 154.97, 75.43, 67.36, 45.82.

5. Computational Methods

All calculations were performed with the Gaussian 09 package.[1] DFT calculations were employed with M062x.[2] Pople-style basis sets[3] 6-31+G(d), 6-311+G(d,p) and 6-311++G(d,p) were used for C, H, O, N, Zn atoms, and the LANL2DZ basis set[4] was used for the Br. The calculation of the catalyst-A-E in Figure S2 were carried out in the gas. To evaluate the solvent effects of PO and PC, self-consistent reaction field (SCRF) calculations based on the conductor polarized continuum model[5] (CPCM) were performed, and diethyl ether parameters were adopted to a lack of accurate date of PO. The value of the dielectric constant (ε=69) of PC were employ to simulate PC as solvent, and the radius (a_0=3.96) obtained by volume calculation. Intrinsic reaction coordinate (IRC) calculations at the 6-31+G(d) level (for C, H, O, N, Zn atoms) were performed to confirm that a given transition state (one imaginary frequency) connect a particular couple of consecutive minima (zero imaginary frequencies). Subsequently, geometry optimizations and frequency calculations were conducted at the 6-311+G(d,p) level (for C, H, O, N, Zn atoms) with 298.15 K and 1.00 atm to obtained the relative free energies (in kcal mol^{-1}). Natural population analysis (NPA) and bond-order calculations were also performed. The wiberg bond indices and natural charges were analyzed using the NBO with SCRF calculations method at the 6-311++G(d,p) level for C, H, O, N, Zn atoms and the LANL2DZ basis set for the Br.

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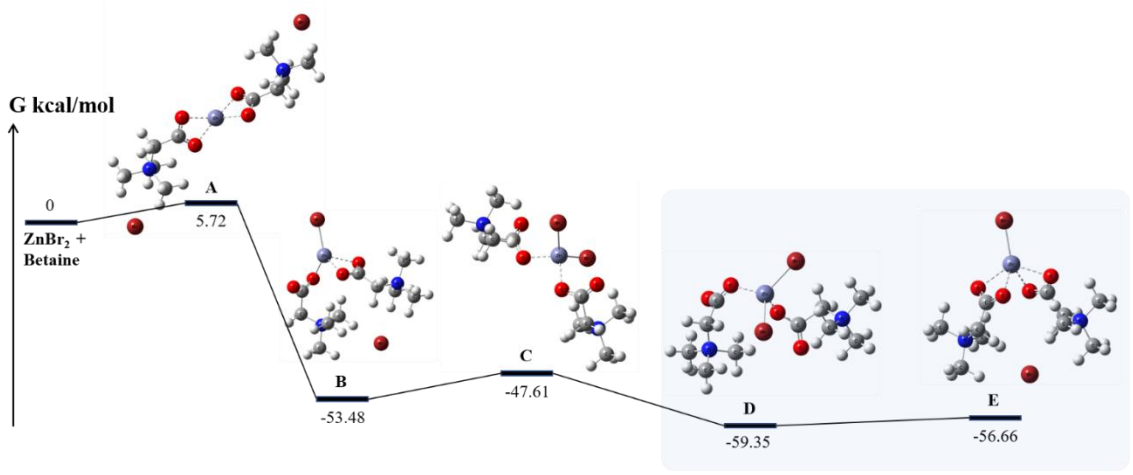

Figure S1. Relative free-energy profile of the $Zn(betaine)_2Br_2$ with various possible geometries in gas.

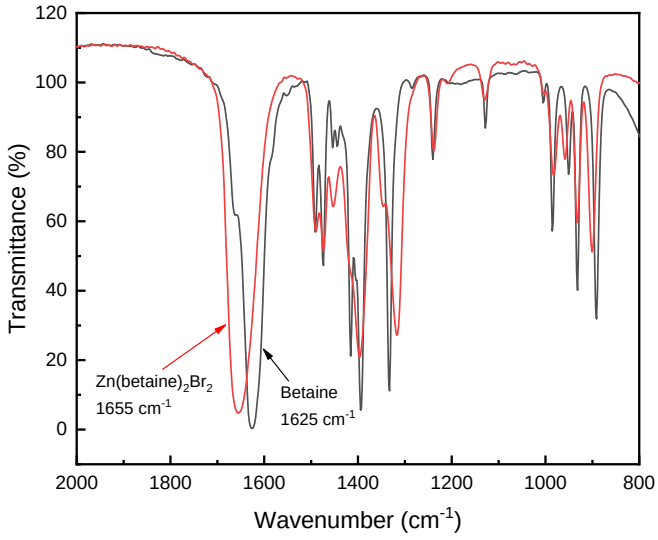

Figure S2. Fourier transform infrared (FT-IR) spectrums and the geometries of the catalyst and betaine.

Table S1. Comparison of catalytic activity of $Zn(betaine)_2Br_2$ with recently developed various catalysts for the of the cycloaddition of CO_2 with epoxides.

Entry	Catalyst, [mol%]	T [°C]	CO_2 Pressure	Epoxide mmol	Time hour	Con./Sel. [%]	Ref.
1[a]	ZnMOF-1/TBAB, 1.8 mol%	40	10 bar	10	3.5	99/99	[6]
2[b]	(I^-)Meim-Uio-66, 0.52 mol%	120	1atm	10	24	100/93	[7]
3[c]	Al(III)@cage, 0.33 mol%; TBAB, 10 mol%	r.t.	1 atm	1	48	58[d], 90[e]	[8]
4[f]	Zn/POF2, 2 wt%, TBAB, 2.5 mol%	90	2.5 bar	17.2	9	92/86[g] 99/95[h]	[9]
5[i]	HPIL-7, 1.5 mol%	120	1.5 MPa	14.3	3	99/99[j] 95/99[k]	[10]
6[l]	SH_4-Al(Cl) 0.25 mol%, $[C_1C_6Im][HCO_3]$ 0.25 mol%	25	1.0 MPa	20	24	99(94)[m] 97(92)[n]	[11]
7	$(L_1)AlMe_2$, 1.7 mol%; Bu_4NI 1.7 mol% L_1H, *(E)-N*-(2,6-diisopropylphenyl)-*N'*-(ferrocenyl)acetimidamide	25 80	1 bar	—	48 24	85[o] 98[p]	[12]
8[q]	cobalt complexes, 0.2 mol%; TBAB 3 mmol%	30	5 bar	10	24	98	[13]
9[r]	$H_3[Mn(T4CPP)]$, 0.02 mol%; TBAI, 1 mol%	90	1 atm	6.25	36	> 99%	[14]
10[s]	CPP-IL0.05, 30 mg	100	1 atm	12.8	24	99/100	[15]
11[t]	Zn(II)-based coordination network with a ladder motif ADES-3/TBAB=2.0/2.5 mol %	80	10 bar	17.4	8	99	[16]
12[u]	$[CoZn][(BDC)(DABCO)_{0.5}]$, 0.5 wt%	100	3 MPa	20.0 g	5	99/98	[17]
13	$Zn(betaine)_2Br_2$, 0.5 mol% $Zn(betaine)_2Br_2$, 2 mol% $Zn(betaine)_2Br_2$, 2 mol%	110 40 40	2 MPa 2 MPa 1 bar	20[v] 20[w] 20[x]	1 7 24	99/100 99/99 98/99	this work

[a] Reaction conditions: PO=10 mmol, $p_{CO_2} = 10\ bar$, 3.5 h, 40 °C, 600 rpm. Catalyst loading: ZnMOF-1=1.8 mol% (0.18 mmol, 0.082 g); TBAB=1.8 mol% (0.18 mmol, 0.058 g) reaction performed in a high-pressure reactor.

[b] Reaction conditions: epichlorohydrin (10 mmol), (I^-)Meim-Uio-66 (50 mg, 0.052 mmol), CO_2 (0.1 MPa), 393 K, t=24 h. Determined by GC-MS.

[c] Reaction conditions: 1 mmol epoxide, 0.33 mol% Al(III)@cage, 10 mol% TBAB, r.t., 1 atm CO_2, and 48 h.

[d] Epoxide: PO, isolated yields of PC.

[e] Epoxide: epichlorohydrin, isolated yields of 4-chloromethyl-[1,3]dioxolan-2-one.

[f] Epoxide (17.2 mmol), TBAB (cocatalyst, 2.5 mol%, 0.43 mmol), catalyst (POF or Zn/POF: 2 wt%, 20 mg), CO_2 (2.5 bar), 90 °C and 9 h.

[g] Epoxide: PO, the conversion/isolated yield of PC.

[h] Epoxide: epichlorohydrin, the conversion/isolated yield of 4-chloromethyl-[1,3]dioxolan-2-one.

[i] Reaction conditions: Epoxides (14.3 mmol), HPIL-7 (1.5 mol% of epoxides), 120 °C, 1.5 MPa, 3 h.

[j] Epoxide: PO, the conversion/isolated yield of PC.

[k] Epoxide: epichlorohydrin, the conversion/isolated yield of 4-chloromethyl-[1,3]dioxolan-2-one.

[l] Reaction conditions: SH_4-Al(Cl) 0.25 mol%, $[C_1C_6Im][HCO_3]$ 0.25 mol%, epoxide 20 mmol, CO_2 pressure 1.0 MPa, 25 °C, 24 h.

[m] Epoxide: PO, GC yield (isolated yield in parentheses) of cyclic carbonates.

[n] Epoxide: epichlorohydrin, GC yield (isolated yield in parentheses) of 4-chloromethyl-[1,3]dioxolan-2-one.

[o] (L1)$AlMe_2$ (1.7 mol%), Bu_4NI (1.7 mol%), 25 °C, CO_2 (1 bar, balloon), 48 h, isolated yield from purified PC.

[p] (L1)$AlMe_2$ (1.7 mol%), Bu_4NI (1.7 mol%), 80 °C, CO_2 (1 bar, balloon), 24 hour, isolated yield from purified 4-chloromethyl-[1,3]dioxolan-2-one.

[q] PO (10.0 mmol), catalyst (0.02 mol, 0.2 mol %), TBAB (0.3 mmol, 3 mol %), no solvent, 30 °C, $p_{CO_2} = 5\ bar$, 24 h, yields were determined by GC using biphenyl as an internal standard.

[r] Conditions: 0.02 mol% of H_3[Mn(T4CPP)], (0.00125 mmol), 1 mol% of TBAI (0.0625 mmol), 6.25 mmol of epichlorohydrin, 90 °C, 1 atm of CO_2, 36 h.

[s] Reaction conditions: 2-(chloromethyl)oxirane (12.8 mmol), CPP-IL0.05 (30 mg), CO_2 (1.0 atm), 100 °C, 24 h.

[t] Reaction conditions: epichlorohydrin=17.4 mmol, catalyst: ADES-3/TBAB=2.0/2.5 mol %; $p_{CO_2} = 10\ bar$, 8 h, and 80 °C; Yield determined by GC analysis.

[u] Reaction conditions: catalyst ([CoZn][(BDC)$(DABCO)_{0.5}$]) 0.5 wt% of epichlorohydrin, epichlorohydrin 20.0 g, CO_2 3 MPa, 100 °C, 5 h.

[V] Reaction condition: PO (20 mmol), Zn(betaine)$_2Br_2$ (0.1 mmol, 0.5 mol%), without solvent;

[w] PO, [HMIm][BF_4] (as solvent, 0.5 g).

[x] Epichlorohydrin, [HMIm][BF_4] (as solvent, 0.5 g).

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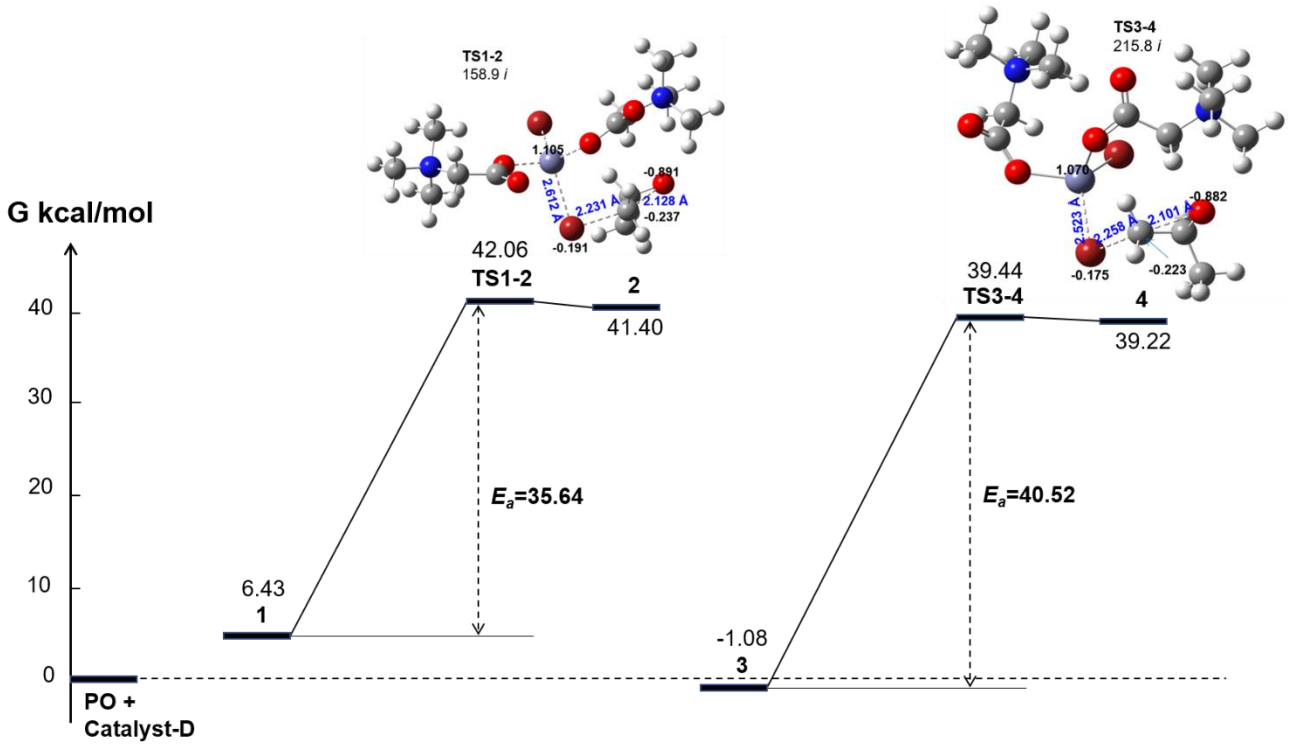


Figure S3. Relative free-energy profile of the Catalyst-D promoted ring opening step, via transition state TS1-2 and TS3-4 in gas. The atomic charges, the bond distances (in blue) and the imaginary vibrational frequencies (cm^{-1}) are labeled in the corresponding positions.

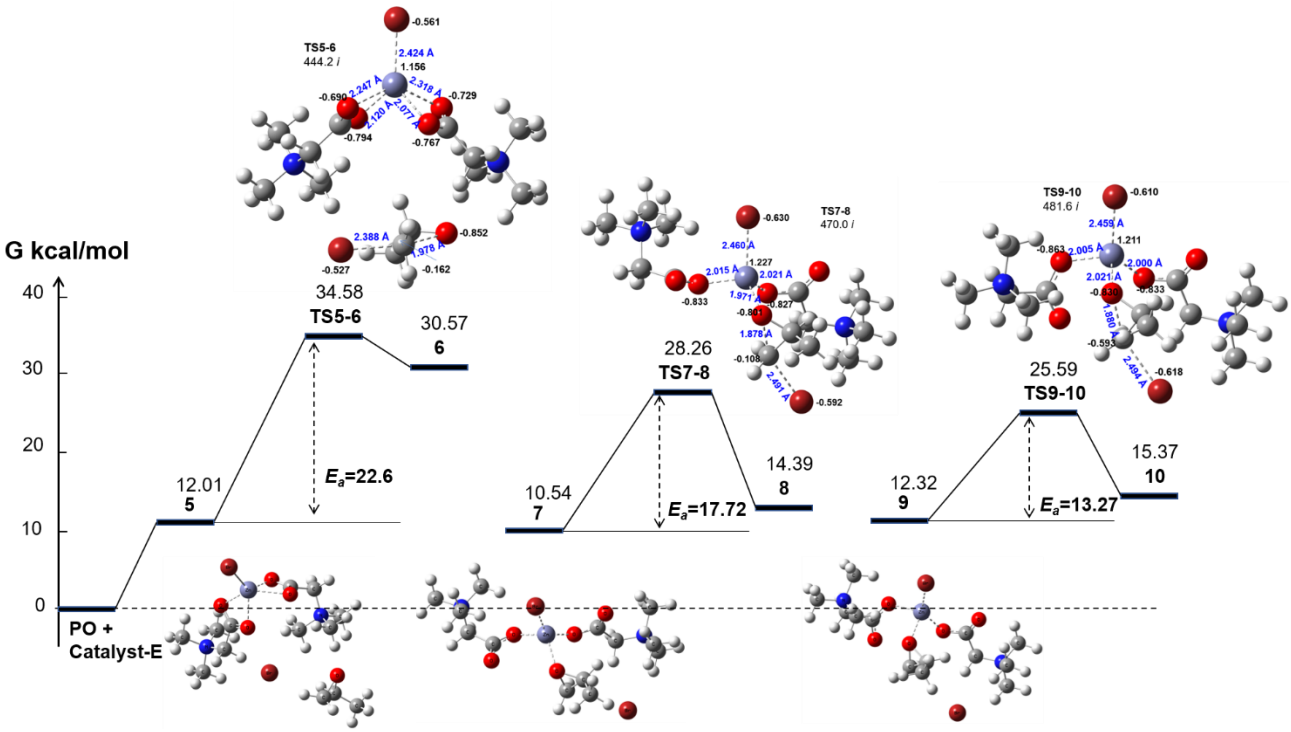


Figure S4. Relative free-energy profile of the Catalyst-E promoted ring opening steps, via transition state TS5-6, TS7-8 and 9-10 in gas. The atomic charges, the bond distances (in blue) and the imaginary vibrational frequencies (cm^{-1}) are labeled in the corresponding positions.

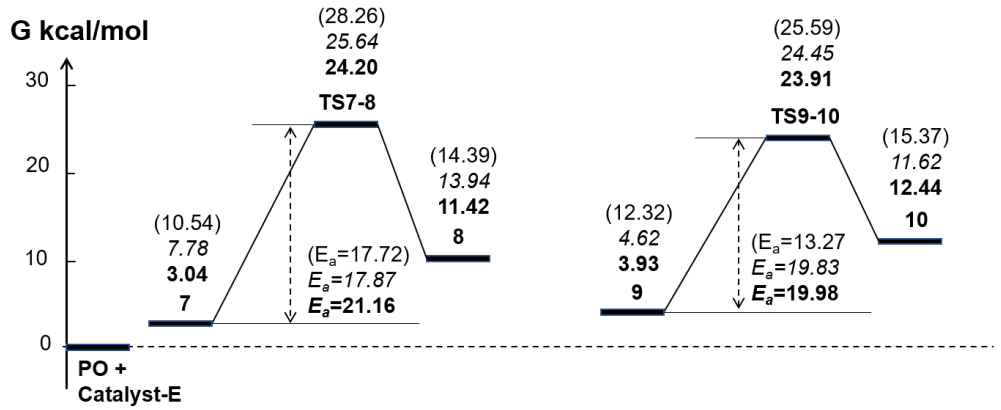
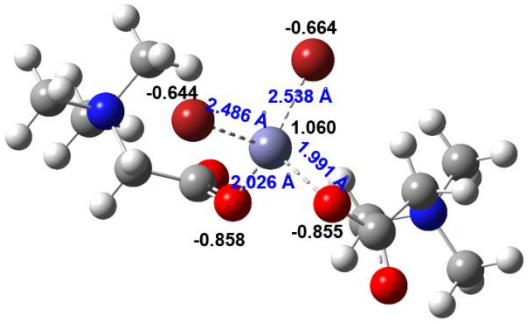


Figure S5. Relative free-energy profile of the Catalyst-E promoted ring opening steps, via transition state TS7-8 and 9-10 in gas (the numbers in brackets) with the solvent effects of PO (the numbers in italics) and PC (the bold numbers). The atomic charges (bold), the bond distances (in blue) and the imaginary vibrational frequencies (cm^{-1}) are labeled in the corresponding positions.

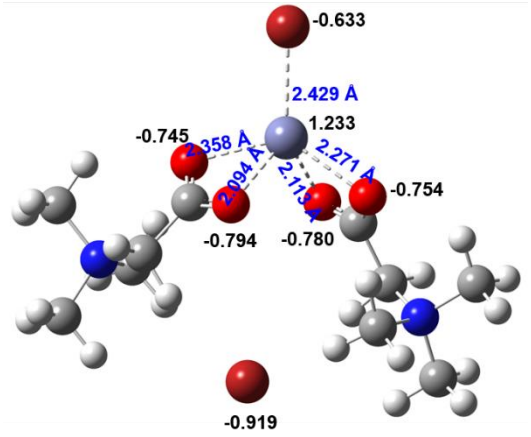
6. Cartesian coordinates of the geometric structures

Catalyst-D			
N	-0.14537445	0.81497796	0.00000000
C	0.33772255	0.60264596	-1.40959200
H	0.53059355	-0.46390504	-1.51655700
H	-0.47540545	0.88842396	-2.08009600
C	-0.72619945	2.18199296	0.19611300
H	-1.55917945	2.29989096	-0.49472600
H	-1.07694645	2.25024496	1.22417400
H	0.04567555	2.91682896	-0.00657700
C	0.98443055	0.60079396	0.95899600
H	1.41867855	-0.38085404	0.76599100
H	1.72964655	1.37702196	0.80285100
H	0.58724255	0.64991496	1.97126200
C	-1.20931545	-0.20296004	0.27127200
H	-0.76985845	-1.19504504	0.18297300
H	-1.58968145	-0.04357204	1.27825300
H	-2.00551545	-0.07439104	-0.45927700
C	1.60633055	1.39216996	-1.79580000
O	2.42683755	0.71444196	-2.50205700
O	1.72430055	2.56515696	-1.46558100
N	6.51919355	2.08760896	-3.09305100
C	6.61707655	0.59237296	-2.92985300
H	7.64666155	0.30951296	-3.15466000
H	6.39931355	0.37844496	-1.88579900
C	5.08773155	2.52307096	-3.01344400
H	4.67280955	2.19592796	-2.06043700
H	5.05909355	3.60883096	-3.08815600
H	4.53600855	2.07309796	-3.83626900
C	7.11451655	2.54126796	-4.39063700
H	8.15945255	2.23652096	-4.41230500
H	6.56855455	2.07431596	-5.20419200
H	7.03657855	3.62593596	-4.43386000
C	7.27514355	2.71597896	-1.96337800
H	8.30565855	2.36750096	-1.99760500
H	7.23685555	3.79670496	-2.08399700
H	6.80224255	2.41891896	-1.02833100
C	5.66403555	-0.19758104	-3.85143200
O	5.75602555	-0.04887404	-5.06351800
O	4.87081155	-1.00202904	-3.25638100
Zn	3.61960355	-0.73030104	-1.73210400
Br	2.29293055	-2.78705804	-1.29901600
Br	4.64129655	0.35518096	0.32217700



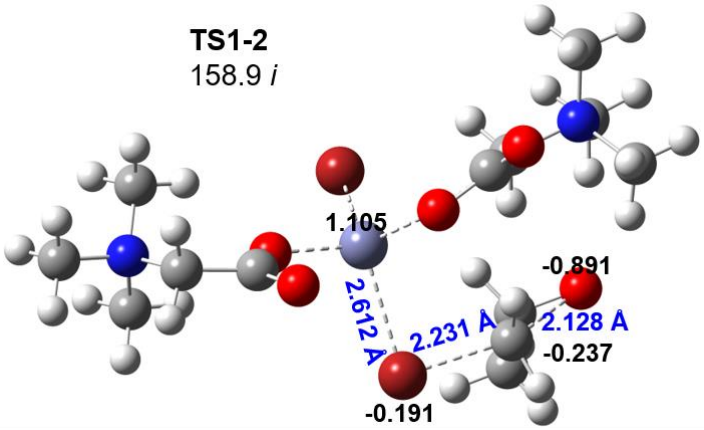
With the solvent effects of PC

Catalyst-E			
N	-0.26872246	0.81497796	0.00000000
C	0.70853254	-0.23206304	0.44875900
H	0.57254554	-0.37332804	1.52227300
H	0.44923154	-1.15757304	-0.06956200
C	-0.13072346	1.09358196	-1.46903500
H	-0.18720746	0.14142696	-1.99620500
H	-0.95289846	1.74470096	-1.75982600
H	0.82523554	1.57747596	-1.64071200
C	-0.09902746	2.08093496	0.77989600
H	-0.24852046	1.85783396	1.83491500
H	0.90312354	2.46044696	0.60308600
H	-0.84756446	2.79259196	0.43630200
C	-1.64048446	0.26283796	0.24231000
H	-1.74102846	0.02375296	1.29934200
H	-2.36987846	1.01731396	-0.04532500
H	-1.75685946	-0.63343604	-0.36587400
C	2.17803154	0.04320796	0.17289700
O	2.93850654	-0.93867204	0.40866100
O	2.59877054	1.12742796	-0.26598400
N	3.96984154	-4.22891604	-3.01449600
C	3.78547754	-2.77012304	-3.31658200
H	4.26133254	-2.56709404	-4.27773200
H	2.71154454	-2.59420804	-3.40475800
C	3.39624254	-4.58008604	-1.67143100
H	2.37382454	-4.20365304	-1.63590900
H	3.41081354	-5.66447504	-1.57904100
H	4.00818254	-4.11924304	-0.90266200
C	5.41414454	-4.61724404	-3.07201800
H	5.79125854	-4.39481004	-4.06878400
H	5.95189954	-4.04910804	-2.31850400
H	5.48387254	-5.68512504	-2.87356200
C	3.20941854	-4.98817104	-4.05940800
H	3.57493454	-4.69448704	-5.04157000
H	3.37321154	-6.05140604	-3.89720000
H	2.15330854	-4.74206904	-3.95468400
C	4.32013354	-1.79088704	-2.28476800
O	5.07090554	-2.13327004	-1.34793300
O	3.92126954	-0.60457804	-2.42968100
Zn	4.61282854	-0.07480404	-0.50480600
Br	0.16314254	-2.65561704	-2.33419900
Br	6.34128254	1.44083396	0.27816600



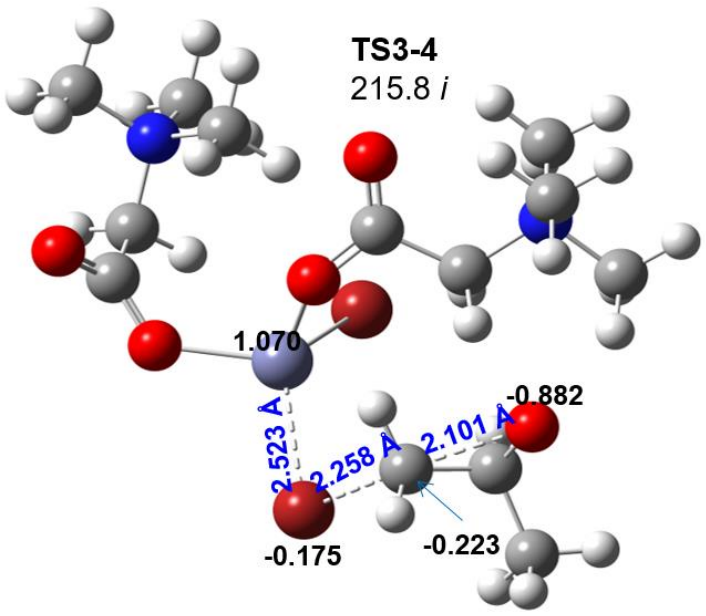
With the solvent effects of PC

TS1-2			
N	-0.80321284	1.32530120	0.00000000
C	0.09304016	0.62528020	-0.98640800
H	1.06900816	0.49311920	-0.51238300
H	-0.35637584	-0.35541780	-1.12630200
C	-2.16797584	1.55078420	-0.58985300
H	-2.53634284	0.57337720	-0.91402700
H	-2.79877284	1.95981620	0.19982100
H	-2.07114484	2.25601920	-1.41017800
C	-0.20899684	2.61649220	0.44918300
H	0.76291116	2.40967120	0.89745600
H	-0.10313684	3.26590120	-0.41561500
H	-0.87490284	3.05522520	1.19192200
C	-0.95734084	0.40013820	1.17077100
H	0.03439716	0.17618520	1.56416300
H	-1.55640184	0.90914220	1.92610400
H	-1.46031584	-0.50138480	0.80124000
C	0.28312716	1.32298620	-2.34445100
O	0.82445216	0.56678920	-3.22647000
O	-0.06027584	2.47885520	-2.50651300
N	4.73689416	-3.90859980	-4.66952600
C	4.37876316	-3.07127580	-5.87934000
H	5.27253916	-2.50551580	-6.15093900
H	4.12599416	-3.76261480	-6.68232800
C	3.50154316	-4.51955080	-4.07366100
H	2.90981816	-4.95790680	-4.87741500
H	3.81159416	-5.28371280	-3.36178000
H	2.93791316	-3.74839980	-3.55558000
C	5.45240016	-3.10219880	-3.62396200
H	6.38816716	-2.74772080	-4.05613300
H	4.81586916	-2.27360680	-3.32757600
H	5.64700916	-3.75503280	-2.77349400
C	5.64032016	-5.00352680	-5.12751700
H	6.49547116	-4.56350880	-5.63896200
H	5.97361916	-5.56890080	-4.25826200
H	5.09100516	-5.65241980	-5.80814300
C	3.18577516	-2.10348280	-5.68024200
O	2.41910616	-1.98993180	-6.60737800
O	3.18527316	-1.52354580	-4.53908800
Zn	1.69006316	-1.15567680	-3.31065300
Br	-0.08154884	-2.87768380	-4.15958600
Br	2.72984116	-1.94457380	-1.20492600
O	-2.26723284	-1.49367180	-0.82969600
C	-1.44846284	-2.44181180	-1.37178400
C	-1.59254584	-1.97011580	-2.79137900
H	-0.38656284	-2.37776380	-1.05343300
H	-2.51587384	-2.26734480	-3.28121500
H	-1.31898584	-0.93758280	-2.97592900
C	-1.91510684	-3.87901880	-1.17345700
H	-1.89378684	-4.11801980	-0.10859800
H	-2.94668684	-3.97525280	-1.52283200
H	-1.27958584	-4.58990280	-1.70934000



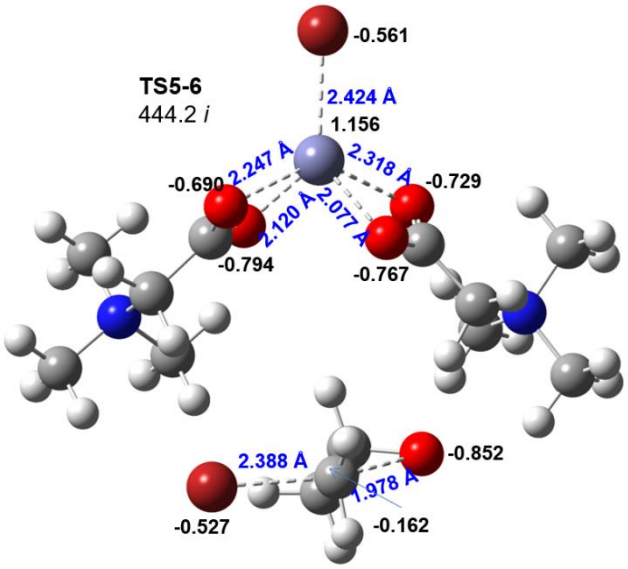
In gas

TS3-4			
N	0.33132530	1.36546184	0.00000000
C	1.53175630	0.70032584	-0.62337900
H	2.31578230	0.63494584	0.13579200
H	1.19191830	-0.29856516	-0.87866100
C	-0.74226970	1.51048584	-1.03798000
H	-0.94472470	0.50805484	-1.42610800
H	-1.62502870	1.92539184	-0.55153600
H	-0.37995370	2.18930784	-1.80791700
C	0.66258630	2.69010784	0.60044700
H	1.44007430	2.54015684	1.34956100
H	1.01894730	3.35095784	-0.18375000
H	-0.23899570	3.07788784	1.07424400
C	-0.17516270	0.44593884	1.07312500
H	0.62108630	0.30537684	1.80407800
H	-1.03473770	0.92285984	1.54450100
H	-0.45438870	-0.49720316	0.58658500
C	2.10582030	1.40755984	-1.86509100
O	2.56802130	0.61765684	-2.75096400
O	2.11866930	2.63239584	-1.92086400
N	6.48575330	2.31580384	-2.84974300
C	6.70980930	0.90564984	-3.34898300
H	7.74464030	0.85115984	-3.69167500
H	6.56061630	0.24560784	-2.49614900
C	5.02547330	2.53825984	-2.57559900
H	4.71640230	1.81749384	-1.82091900
H	4.89190530	3.55350384	-2.20549100
H	4.45181730	2.39288184	-3.48923100
C	6.97425130	3.32830184	-3.83586500
H	8.03954130	3.16385984	-3.99592600
H	6.43595530	3.18875784	-4.76962900
H	6.80354030	4.31813884	-3.41351600
C	7.23642230	2.46660384	-1.56891100
H	8.29189030	2.27259184	-1.75683800
H	7.10053830	3.48334484	-1.20145700
H	6.84150430	1.74556584	-0.85276100
C	5.75825930	0.53808584	-4.51776000
O	5.81888930	1.21876184	-5.52595300
O	5.01888630	-0.47515216	-4.30217400
Zn	3.81224830	-0.93282616	-2.82844000
Br	2.52148830	-2.96056516	-3.59597200
Br	4.87000830	-0.85204816	-0.58770700
O	-0.57673170	-1.59185316	-1.08691900
C	0.44035830	-2.48124316	-1.29897300
C	0.61194230	-2.11350416	-2.73893600
H	1.37534630	-2.26855916	-0.73465100
H	-0.11738970	-2.54616316	-3.41780300
H	0.84837930	-1.07535716	-2.93722400
C	0.07430130	-3.94208116	-1.07735000
H	-0.16216570	-4.09704316	-0.02300900
H	-0.81525970	-4.18584216	-1.66396400
H	0.89234730	-4.61125516	-1.35752000



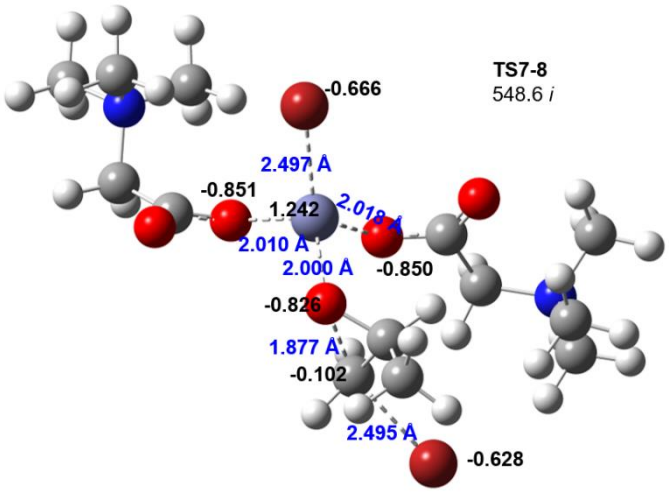
In gas

TS5-6			
N	0.41164658	1.36546184	0.00000000
C	-0.97469742	0.83132084	-0.24993600
H	-0.94025642	-0.23531316	-0.00835600
H	-1.65096542	1.34106984	0.43873200
C	0.44986058	2.84395984	-0.19294400
H	-0.27068242	3.29998184	0.48589000
H	1.45483558	3.19381784	0.04142200
H	0.19485558	3.06157284	-1.22771200
C	1.42441358	0.70363784	-0.89500400
H	1.31947358	-0.37268916	-0.73896700
H	1.21439058	0.99489684	-1.91956500
H	2.40800858	1.05330284	-0.58043400
C	0.75767158	1.02238084	1.41616200
H	0.73911158	-0.06660716	1.50411700
H	1.74906358	1.42092584	1.63008300
H	0.02094158	1.48271284	2.07406700
C	-1.50276142	0.99320884	-1.66635800
O	-2.66209142	0.52309584	-1.83201600
O	-0.83630942	1.51070784	-2.57572700
N	-1.14630842	-3.81738216	-4.83451900
C	-2.44389942	-3.26007416	-4.30470200
H	-3.24309442	-3.63223816	-4.94632300
H	-2.58647542	-3.67085016	-3.29994400
C	0.00610358	-3.51211816	-3.91812000
H	-0.20245942	-3.97725116	-2.95429200
H	0.89992558	-3.95045816	-4.36186100
H	0.09809858	-2.43277316	-3.83464100
C	-0.86590842	-3.27171016	-6.19728800
H	-1.72648742	-3.47534516	-6.83424200
H	-0.69771542	-2.20080616	-6.11232400
H	0.01685358	-3.77399616	-6.59123000
C	-1.29948342	-5.30489416	-4.91386200
H	-2.10653142	-5.53449216	-5.60857400
H	-0.36189642	-5.72671316	-5.27420900
H	-1.52836542	-5.67825616	-3.91489700
C	-2.54297742	-1.74083016	-4.24399100
O	-1.50272842	-1.02624616	-4.30755200
O	-3.67915842	-1.27422816	-4.09239600
Zn	-2.68230942	0.70702884	-3.86921100
Br	-1.84440842	-5.19154616	-1.17581000
Br	-3.33975042	2.34193184	-5.43556100
O	0.27556258	-1.81797916	0.34200000
C	0.37904258	-3.16233316	0.02511600
C	-1.03596542	-3.06221516	-0.36308800
H	1.04396458	-3.37037416	-0.82967200
H	-1.75883242	-3.01655816	0.43949800
H	-1.27545542	-2.52009016	-1.26927700
C	0.69597458	-4.08470116	1.18373100
H	0.60702458	-5.13123116	0.88470800
H	1.71195258	-3.89469916	1.53731000
H	0.00165658	-3.88933116	2.00448600



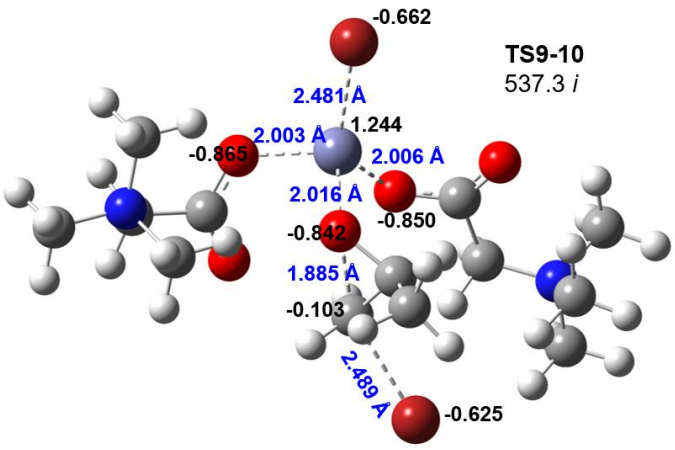
In gas

TS7-8			
N	0.63876651	1.02643170	0.00000000
C	0.59500251	-0.09840830	1.00541700
H	0.64633151	0.36139970	1.99057400
H	-0.35847549	-0.60743530	0.87114900
C	0.47114851	0.51883970	-1.40083600
H	-0.44414249	-0.06783530	-1.44848800
H	0.40564751	1.38229270	-2.06024500
H	1.32902151	-0.09593430	-1.65974500
C	1.93812851	1.76482870	0.10273700
H	2.06564051	2.10082970	1.13014400
H	2.74753951	1.09586970	-0.18431800
H	1.89630051	2.61637670	-0.57376900
C	-0.48512449	1.96587270	0.31046800
H	-0.34941049	2.35134570	1.31865400
H	-0.46101949	2.78033270	-0.41061600
H	-1.42440649	1.42187170	0.23425400
C	1.76737151	-1.07970530	0.82279800
O	2.74984851	-0.95872930	1.54566300
O	1.59041851	-1.93869630	-0.10292200
N	2.38015751	-7.03228130	-4.28635000
C	1.79644051	-6.00012830	-3.36382900
H	0.79357451	-5.76541330	-3.72484500
H	1.70952851	-6.47147530	-2.38270500
C	3.77298251	-7.40197330	-3.86895200
H	3.74265951	-7.69384330	-2.81887100
H	4.09242451	-8.24136930	-4.48406300
H	4.42033851	-6.54434630	-4.02164700
C	2.37914151	-6.55334830	-5.70406900
H	1.35156851	-6.33600030	-5.99028100
H	2.99502251	-5.66127730	-5.76297300
H	2.78312551	-7.34759730	-6.32903200
C	1.52119251	-8.25555130	-4.18029800
H	0.50082251	-7.99007130	-4.45056200
H	1.90941651	-9.00666530	-4.86531900
H	1.56489051	-8.61445230	-3.15242500
C	2.58412951	-4.69269430	-3.19858200
O	3.55192951	-4.41826930	-3.89875200
O	2.09702751	-3.99700730	-2.24834300
Zn	3.15514051	-2.73639830	-1.08065500
Br	2.59074451	-8.08330430	-0.19876000
Br	4.36965651	-0.72769230	-1.93275900
O	4.10649551	-4.08590030	0.04921900
C	4.39653151	-5.37491830	-0.45546000
C	3.12644251	-5.67971430	0.20299800
H	4.36964851	-5.43344030	-1.54728900
H	3.13928851	-5.80965330	1.27569200
H	2.20630351	-5.38008630	-0.27615300
C	5.65157451	-5.98793330	0.11125600
H	5.73067051	-7.03281330	-0.19537200
H	6.52631051	-5.44605030	-0.25296200
H	5.63294951	-5.93660530	1.20216500



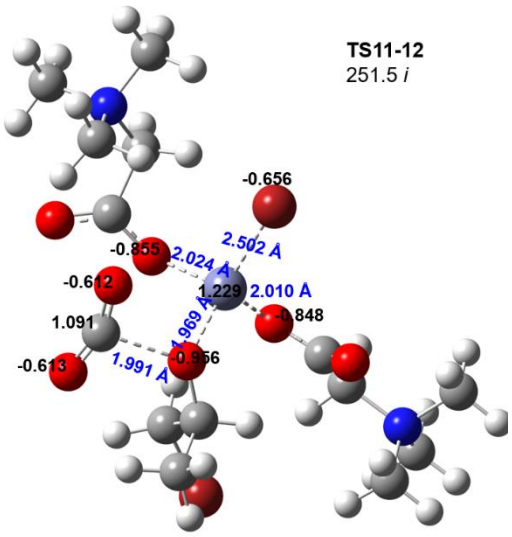
With the solvent effects of PC

TS9-10			
N	-0.69277107	0.80321285	0.00000000
C	-1.89004607	-0.06143015	-0.31194300
H	-2.21487907	-0.49819715	0.63012000
H	-2.66800607	0.59334985	-0.70627900
C	-0.32689807	1.70333185	-1.14280400
H	-1.19447807	2.31360685	-1.38762400
H	0.49665893	2.33432885	-0.81396500
H	-0.03972507	1.09564485	-1.99450400
C	0.47824493	-0.06295715	0.34935800
H	0.18506193	-0.71831615	1.16863900
H	0.76881493	-0.64777415	-0.52491100
H	1.29693293	0.58313485	0.66099500
C	-1.04312007	1.65908685	1.17774600
H	-1.25970307	1.01467685	2.02692300
H	-0.19505907	2.30368085	1.39974400
H	-1.91582207	2.25725085	0.92218200
C	-1.57959907	-1.18892215	-1.31210200
O	-1.76270707	-2.34494115	-0.95477700
O	-1.16101807	-0.78463515	-2.44837000
N	0.92669493	-7.04382515	-4.47294400
C	0.03183593	-5.93687615	-3.99310300
H	-0.99192407	-6.19823515	-4.26552300
H	0.10656093	-5.92321315	-2.90376100
C	2.36020093	-6.76142515	-4.13223800
H	2.42158893	-6.58159615	-3.05836800
H	2.94671093	-7.63758615	-4.40318800
H	2.68397593	-5.89240515	-4.69611000
C	0.77946193	-7.25485115	-5.94730600
H	-0.26431207	-7.48347015	-6.15685100
H	1.08695993	-6.34625015	-6.45592000
H	1.41093693	-8.09378215	-6.23314600
C	0.51272493	-8.29181115	-3.75386700
H	-0.53172207	-8.49649915	-3.98141900
H	1.14133793	-9.11075515	-4.09795300
H	0.64832093	-8.12960115	-2.68505100
C	0.33622193	-4.52386715	-4.50975700
O	1.18043293	-4.30746815	-5.37073900
O	-0.38668007	-3.66760615	-3.90111000
Zn	0.18733193	-1.77901315	-3.54530200
Br	1.36969593	-6.07299515	-0.36740900
Br	1.11971993	-0.11648015	-5.13320300
O	1.49632093	-2.14137815	-2.05513200
C	2.19955393	-3.36431215	-1.97695400
C	1.08194293	-3.71202215	-1.09944900
H	2.22290693	-3.91515215	-2.92236900
H	0.11759493	-3.92959715	-1.53255600
H	1.11091793	-3.33353815	-0.08653400
C	3.57194093	-3.24693915	-1.36328400
H	4.00238093	-4.23814015	-1.20730300
H	4.22657893	-2.67881815	-2.02699900
H	3.50848293	-2.72991515	-0.40277400



With the solvent effects of PC

TS11-12			
N	0.11044177	1.06425703	0.00000000
C	1.36668777	1.73192703	-0.49040000
H	1.06877877	2.51632803	-1.18982900
H	1.83344477	2.19164603	0.37778400
C	0.45652977	-0.14923697	0.80840800
H	1.16818977	0.14977603	1.57791600
H	-0.45969223	-0.53004097	1.25588500
H	0.90501177	-0.88792597	0.15085600
C	-0.79352423	0.68594003	-1.13212600
H	-1.06015823	1.59219803	-1.67339000
H	-0.25901923	-0.00346997	-1.77775900
H	-1.68508123	0.22368903	-0.71236200
C	-0.59881723	2.04037103	0.88637800
H	-0.80863423	2.94292103	0.31552300
H	-1.52641423	1.58540903	1.22830200
H	0.04755677	2.26835203	1.73275600
C	2.38299077	0.81245603	-1.19237700
O	3.59173477	1.17626403	-1.02451100
O	1.99573477	-0.12340397	-1.88327000
N	9.32169977	4.27820503	0.39948800
C	8.03180377	3.86945403	-0.25268900
H	7.52277177	4.77975303	-0.57230700
H	8.28815777	3.28823403	-1.13984300
C	10.11425577	3.07533603	0.81600400
H	10.24733477	2.43672003	-0.05603300
H	11.07844477	3.41988603	1.18505800
H	9.56604177	2.55297303	1.59353300
C	9.07410077	5.16427403	1.58263600
H	8.49062377	6.02123403	1.25073600
H	8.53408977	4.59569503	2.33244900
H	10.03874277	5.49403703	1.96332800
C	10.11488877	5.04527603	-0.61378900
H	9.53834277	5.91572103	-0.92052300
H	11.05078877	5.35579403	-0.15371200
H	10.30991377	4.39927103	-1.46755300
C	7.06387777	3.03680103	0.59863400
O	7.29538877	2.76246003	1.77130800
O	6.04639477	2.69162403	-0.08356800
Zn	4.71130577	1.37957903	0.64909200
Br	8.79583177	0.36103203	-1.94358700
Br	3.36865977	2.04322003	2.65384800
O	5.64328577	-0.35454497	0.68235700
C	6.97079677	-0.39440897	0.21662100
C	6.96378177	-0.15193597	-1.29416300
H	7.53220377	0.42863103	0.68039200
H	6.69723177	-1.03467597	-1.86793500
H	6.34162577	0.69778903	-1.56033700
C	7.64331277	-1.70886997	0.59167700
H	8.68675777	-1.72058997	0.26895800
H	7.61592777	-1.83617297	1.67520400
H	7.12142477	-2.54680697	0.12565400
C	4.26705077	-1.64678097	0.04983300
O	4.79300477	-2.25261697	-0.80786100
O	3.38851477	-1.34637697	0.77156100



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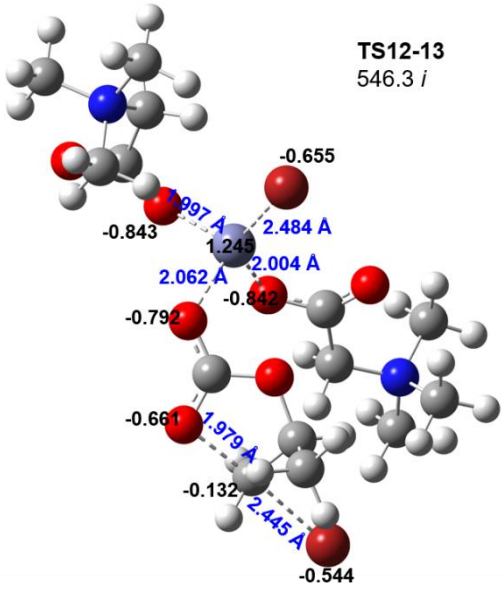
TS12-13			
N	0.45180722	2.34939758	0.00000000
C	1.33235822	3.56693058	-0.13657800
H	0.67605822	4.41900058	-0.31686800
H	1.84121322	3.69077458	0.81692100
C	1.28250622	1.10399858	-0.02986500
H	2.03735722	1.17523458	0.75282200
H	0.62815322	0.25398558	0.15359900
H	1.74422922	1.01496958	-1.01153700
C	-0.57759778	2.29399258	-1.08747600
H	-1.19642878	3.18680058	-1.01680200
H	-0.06708278	2.26231158	-2.04508900
H	-1.18177078	1.40233758	-0.93203600
C	-0.24167578	2.43402558	1.32499000
H	-0.79913578	3.36790058	1.36453900
H	-0.91739078	1.58558058	1.41441400
H	0.51392622	2.40639658	2.10909500
C	2.34639722	3.44929458	-1.29361700
O	3.57602922	3.51422658	-0.96925900
O	1.91415722	3.33341258	-2.43544500
N	9.63379022	5.29377058	0.97382800
C	8.59805222	4.51996958	0.20718200
H	8.44624922	5.03186558	-0.74263500
H	9.03480022	3.53945658	-0.00066500
C	10.06098122	4.55783158	2.20877000
H	10.49171722	3.60576658	1.89867400
H	10.81565822	5.16001258	2.71164500
H	9.19218422	4.41472458	2.84334000
C	9.12221722	6.65327858	1.33690400
H	8.77247422	7.14062158	0.42816000
H	8.31271022	6.53813758	2.05053400
H	9.94442222	7.21749158	1.77255900
C	10.82960922	5.44590258	0.08234100
H	10.54151322	6.02412658	-0.79356800
H	11.60644622	5.96632858	0.63923900
H	11.17055822	4.45227758	-0.20662800
C	7.23344922	4.32199658	0.88831800
O	7.06949922	4.56489758	2.07739800
O	6.37369722	3.87412058	0.06254300
Zn	4.66846322	2.97616258	0.61289900
Br	11.31263422	1.41402758	0.08316300
Br	3.58761422	2.74044058	2.83689300
O	7.16026922	1.27983958	1.16651700
C	8.53354922	0.85481558	1.19975500
C	9.00287022	0.67819358	-0.23766400
H	9.05843522	1.68060158	1.67299300
H	9.38241822	-0.26940742	-0.58178500
H	8.88555522	1.47063758	-0.95987900
C	8.68398822	-0.41616942	2.01109700
H	9.74038422	-0.68161742	2.07692100
H	8.29359122	-0.26337942	3.01702700
H	8.14114422	-1.23500042	1.53444400
C	6.49219422	0.79701358	0.09497800
O	7.16738322	0.09693258	-0.69455600
O	5.28939822	1.11030958	-0.00673000



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