Supplementary Information

Quaternary ammonium hydroxide as a metal-free and halogen-free catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide

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[A] Synthesis of cyclic carbonates from epoxides and CO_2.

General procedure. A 30-mL stainless autoclave was charged with epoxide **1** (10.0 mmol), catalyst (a catalytic amount), and then CO_2 (initial pressure 1 MPa at room temperature). The mixture was heated with stirring at a constant temperature for a reaction time. The reactor was cooled in an ice bath for 20 min, and excess CO_2 was released carefully. The crude product was dissolved in Et_2O. The NMR yield was determined by using 2-methoxynaphthalene as an internal standard. Purification by silica gel column chromatography (hexane/EtOAc (2:1 to 2:3)) afforded product **2**.

4-*n*-Butyl-1,3-dioxolan-2-one (2a).[1] 89% yield; pale yellow oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.94 (t, J = 6.9 Hz, 3H), 1.33–1.48 (m, 4H), 1.68–1.73 (m, 1H), 1.77–1.84 (m, 1H), 4.07 (dd, J = 7.2, 8.4 Hz, 1H), 4.52 (t, J = 8.1 Hz, 1H), 4.66–4.73 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 13.8, 22.2, 26.4, 33.5, 69.4, 77.2, 155.2; IR (neat) 2936, 2870, 1794, 1555, 1466, 1389, 1188, 1057, 775 cm^{-1}.

4-Methyl-1,3-dioxolan-2-one (2b).[1] 66% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.50 (d, J = 6.0 Hz, 3H), 4.03 (dd, J = 7.2, 8.4 Hz, 1H), 4.55 (dd, J = 7.8, 8.2 Hz, 1H), 4.81–4.88 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.1, 70.6, 73.6, 155.1; IR (neat) 2990, 2936, 1786, 1557, 1483, 1450, 1389, 1354, 1182, 1121, 1051, 957, 849, 777, 712 cm^{-1}.

4-Methoxymethyl-1,3-dioxolan-2-one (2c).[1] 90% yield; pale yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.43 (s, 3H), 3.58 (dd, J = 3.8, 11.0 Hz, 1H), 3.64 (dd, J = 4.2, 11.0 Hz, 1H), 4.39 (dd, J = 6.2, 8.2 Hz, 1H), 4.49 (t, J = 8.4 Hz, 1H), 4.77–4.83 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 59.1, 65.9, 71.2, 75.1, 155.0; IR (neat) 2992, 2934, 2897, 2822, 1790, 1479, 1456, 1398, 1362, 1339, 1173, 1132, 1103, 1049, 955, 849, 775, 714 cm^{-1}.

4-Phenyl-1,3-dioxolan-2-one (2d).[1] 88% yield; white solid; mp 55–56 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.35 (t, J = 7.8 Hz, 1H), 4.81 (t, J = 7.8 Hz, 1H), 5.68 (t, J = 8.0 Hz, 1H), 7.36–7.38 (m, 2H), 7.43–7.48 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 71.3, 78.1, 126.0, 129.4, 129.9, 135.9, 155.0; IR (KBr) 3069, 3038, 2980, 2926, 1780, 1487, 1458, 1358, 1327, 1169, 1055, 961, 907, 758, 698 cm^{-1}.

4-Chloromethyl-1,3-dioxolan-2-one (2e).[1] 74% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.71–3.79 (m, 2H), 4.42 (dd, J = 5.6, 7.2 Hz, 1H), 4.59 (t, J = 8.6 Hz, 1H), 4.92–4.98 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.1, 66.9, 74.5, 154.5; IR (neat) 2970, 2926, 1774, 1541, 1481, 1431, 1398, 1356, 1333, 1292, 1269, 1190, 1042, 851, 767, 716, 664, 523 cm^{-1}.

4,5-Tetramethylene-1,3-dioxolan-2-one (2f).[2] 65% yield; colorless viscous oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.39–1.49 (m, 2H), 1.58–1.70 (m, 2H), 1.88–1.94 (m, 4H), 4.65–4.72 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 18.9, 26.5, 75.7, 155.3; IR (CH_2Cl_2) 2951, 2870, 1801, 1354, 1207, 1169, 1142, 1034, 741 cm^{-1}.

4,5-Trimethylene-1,3-dioxolan-2-one (2g).[3] 42% yield; white solid; mp 38–39 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.62–1.86 (m, 4H), 2.13–2.20 (m, 2H), 5.10–5.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 33.0, 81.9, 155.5; IR (CH_2Cl_2) 2978, 1798, 1373, 1173, 1111, 1049, 748 cm^{-1}.

4-*t*-Butyl-1,3-dioxolan-2-one (2h).[4] 53% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 0.98 (s, 9H), 4.19–4.28 (m, 1H), 4.36–4.44 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 23.9, 33.2, 65.6, 83.6, 155.2; IR (neat) 2966, 2876, 1786, 1481, 1391, 1369, 1171, 1088, 1026, 773, 723 cm^{-1}.

4-Isopropyloxymethyl-1,3-dioxolan-2-one (2i).[5] 68% yield; colorless oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 1.17 (d, J = 6.4 Hz, 6H), 3.59–3.67 (m, 3H), 4.37–4.41 (m, 1H), 4.48 (dt, J = 1.3, 8.3 Hz, 1H), 4.75–4.81 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.5, 21.7, 66.2, 66.9, 72.5, 75.3, 155.1; IR (neat) 2974, 2870, 1794,1371, 1171, 1132, 1101, 1055, 775 cm^{-1}.

4-Phenoxymethyl-1,3-dioxolan-2-one (2j).[5] 94% yield; white solid; mp 101–102 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.16 (dd, J = 3.6, 10.4 Hz, 1H), 4.24 (dd, J = 4.2, 10.6 Hz, 1H), 4.55 (dd, J = 6.2, 8.6 Hz, 1H), 4.62 (t, J = 8.4 Hz, 1H), 5.01–5.06 (m, 1H), 6.91 (d, J = 8.4 Hz, 2H), 7.02 (t, J = 7.2 Hz, 1H), 7.29–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 66.4, 67.0, 74.2, 114.7, 122.1, 129.8, 154.8, 157.9; IR (KBr) 3063, 2982, 2926, 2878, 1805, 1603, 1587, 1495, 1460, 1396, 1312, 1250, 1167, 1057, 1013, 760, 710 cm^{-1}.

References

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[B] Atomic coordinates of the optimized structures in path A.

(1) **R**

N	1.094930	0.496178	-0.003817
C	1.713066	-0.467791	0.990629
H	0.867783	-0.917083	1.518769
H	2.199682	-1.245944	0.403435
C	2.722359	0.123985	1.965925
H	2.265028	0.888452	2.601878
H	3.558688	0.596327	1.436530
C	3.274928	-0.988935	2.863973
H	3.749079	-1.757749	2.240622
H	2.443568	-1.477793	3.385914
C	4.282656	-0.458209	3.880887
H	3.822732	0.290421	4.535355
H	4.664480	-1.266135	4.512318
H	5.137550	0.011731	3.381469
C	0.270152	1.518085	0.769494
H	0.943015	1.983596	1.490678
H	-0.470455	0.926711	1.314687
C	-0.393488	2.602231	-0.073315
H	-0.876378	2.179431	-0.960705
H	0.355781	3.322653	-0.422442
C	-1.457540	3.335028	0.750850
H	-2.278231	2.646487	0.987066
H	-1.014230	3.684626	1.693194
C	-2.049946	4.513536	-0.015937
H	-2.556141	4.160756	-0.920607
H	-2.794071	5.035989	0.592566
H	-1.280600	5.238133	-0.309504
C	2.146746	1.229223	-0.798407
H	1.607195	1.876063	-1.491922
H	2.675902	1.875124	-0.093517
C	3.130886	0.364432	-1.570953
H	3.685472	-0.300100	-0.899012
H	2.598982	-0.266522	-2.290343
C	4.124519	1.249844	-2.329588
H	3.573039	1.922100	-2.998695
H	4.662024	1.888348	-1.617262
C	5.123878	0.426493	-3.138882

H	5.813156	1.075315	-3.687340
H	5.718577	-0.222952	-2.487119
H	4.608639	-0.209381	-3.867274
C	0.130285	-0.253402	-0.926349
H	-0.845063	-0.177888	-0.447099
H	0.095127	0.314749	-1.858302
C	0.393708	-1.725904	-1.214577
H	1.357820	-1.886793	-1.708534
H	0.391888	-2.301682	-0.285968
C	-0.735506	-2.262565	-2.102043
H	-0.762275	-1.710026	-3.050001
H	-1.695997	-2.082607	-1.602659
C	-0.576387	-3.756140	-2.375410
H	-1.389997	-4.129707	-3.004644
H	0.369921	-3.967005	-2.886363
H	-0.584783	-4.320224	-1.436489
O	-1.532063	-3.304303	1.123005
H	-2.227367	-3.781953	0.647839
C	-1.964575	-2.013322	1.248360
O	-1.223335	-1.223615	1.835741
O	-3.103793	-1.795370	0.710042
C	-3.684666	0.673304	-0.446819
H	-2.644127	0.843939	-0.801577
C	-3.732802	-0.061601	0.827460
H	-4.720263	-0.372498	1.142802
H	-3.041676	0.254188	1.596176
C	-4.493370	0.093521	-1.602394
H	-5.507339	-0.149277	-1.264345
H	-4.573746	0.836545	-2.404413
H	-4.028695	-0.813291	-2.009348
O	-4.251761	1.720888	0.222897

(2) **TS_1**

N	1.094930	0.496178	-0.003817
C	1.713066	-0.467791	0.990629
H	0.867783	-0.917083	1.518769
H	2.199682	-1.245944	0.403435
C	2.722359	0.123985	1.965925
H	2.265028	0.888452	2.601878
H	3.558688	0.596327	1.436530

C	3.274928	-0.988935	2.863973
H	3.749079	-1.757749	2.240622
H	2.443568	-1.477793	3.385914
C	4.282656	-0.458209	3.880887
H	3.822732	0.290421	4.535355
H	4.664480	-1.266135	4.512318
H	5.137550	0.011731	3.381469
C	0.270152	1.518085	0.769494
H	0.943015	1.983596	1.490678
H	-0.470455	0.926711	1.314687
C	-0.393488	2.602231	-0.073315
H	-0.876378	2.179431	-0.960705
H	0.355781	3.322653	-0.422442
C	-1.457540	3.335028	0.750850
H	-2.278231	2.646487	0.987066
H	-1.014230	3.684626	1.693194
C	-2.049946	4.513536	-0.015937
H	-2.556141	4.160756	-0.920607
H	-2.794071	5.035989	0.592566
H	-1.280600	5.238133	-0.309504
C	2.146746	1.229223	-0.798407
H	1.607195	1.876063	-1.491922
H	2.675902	1.875124	-0.093517
C	3.130886	0.364432	-1.570953
H	3.685472	-0.300100	-0.899012
H	2.598982	-0.266522	-2.290343
C	4.124519	1.249844	-2.329588
H	3.573039	1.922100	-2.998695
H	4.662024	1.888348	-1.617262
C	5.123878	0.426493	-3.138882
H	5.813156	1.075315	-3.687340
H	5.718577	-0.222952	-2.487119
H	4.608639	-0.209381	-3.867274
C	0.130285	-0.253402	-0.926349
H	-0.845063	-0.177888	-0.447099
H	0.095127	0.314749	-1.858302
C	0.393708	-1.725904	-1.214577
H	1.357820	-1.886793	-1.708534
H	0.391888	-2.301682	-0.285968

C	-0.735506	-2.262565	-2.102043
H	-0.762275	-1.710026	-3.050001
H	-1.695997	-2.082607	-1.602659
C	-0.576387	-3.756140	-2.375410
H	-1.389997	-4.129707	-3.004644
H	0.369921	-3.967005	-2.886363
H	-0.584783	-4.320224	-1.436489
O	-1.532063	-3.304303	1.123005
H	-2.227367	-3.781953	0.647839
C	-1.964575	-2.013322	1.248360
O	-1.223335	-1.223615	1.835741
O	-3.103793	-1.795370	0.710042
C	-3.684666	0.673304	-0.446819
H	-2.644127	0.843939	-0.801577
C	-3.732802	-0.061601	0.827460
H	-4.720263	-0.372498	1.142802
H	-3.041676	0.254188	1.596176
C	-4.493370	0.093521	-1.602394
H	-5.507339	-0.149277	-1.264345
H	-4.573746	0.836545	-2.404413
H	-4.028695	-0.813291	-2.009348
O	-4.251761	1.720888	0.222897

(3) **I_1**

N	1.117505	0.484055	-0.069308
C	1.584333	-0.415183	1.057705
H	0.674040	-0.817919	1.506812
H	2.122888	-1.240774	0.593014
C	2.473370	0.229762	2.112572
H	1.943748	1.021496	2.651652
H	3.363704	0.682063	1.659832
C	2.921598	-0.834297	3.120945
H	3.451454	-1.637215	2.592205
H	2.037347	-1.292853	3.579859
C	3.823976	-0.253639	4.207098
H	3.306363	0.531258	4.769598
H	4.131675	-1.027755	4.916396
H	4.729494	0.185551	3.773476
C	0.239445	1.579084	0.528095
H	0.857925	2.111389	1.252526

H	-0.554702	1.051732	1.063363
C	-0.354399	2.573902	-0.459398
H	-0.899577	2.059484	-1.257673
H	0.435459	3.174583	-0.926831
C	-1.335331	3.498433	0.270724
H	-2.165852	2.899953	0.672894
H	-0.812635	4.007843	1.092838
C	-1.955488	4.517893	-0.680299
H	-2.611316	3.996677	-1.385038
H	-2.574927	5.231667	-0.128022
H	-1.199511	5.084010	-1.239599
C	2.280287	1.132883	-0.781636
H	1.852913	1.700682	-1.609331
H	2.711761	1.853308	-0.082359
C	3.352868	0.191469	-1.308614
H	3.797696	-0.392746	-0.495361
H	2.922026	-0.517846	-2.023019
C	4.459791	0.988048	-2.007059
H	4.028571	1.558968	-2.838681
H	4.877407	1.721919	-1.306057
C	5.574574	0.083223	-2.526973
H	6.352043	0.667805	-3.027785
H	6.045402	-0.470297	-1.706944
H	5.186574	-0.646616	-3.246176
C	0.252565	-0.312667	-1.047550
H	-0.775796	-0.170335	-0.710995
H	0.354611	0.182470	-2.015505
C	0.499522	-1.809353	-1.188598
H	1.521695	-2.035144	-1.510385
H	0.330760	-2.314797	-0.234080
C	-0.492956	-2.374962	-2.210353
H	-0.337402	-1.895296	-3.184951
H	-1.514174	-2.120551	-1.898115
C	-0.366333	-3.889700	-2.349468
H	-1.083037	-4.277699	-3.079839
H	0.639161	-4.172940	-2.680642
H	-0.556960	-4.381272	-1.389453
O	-1.976933	-3.187074	0.810326
H	-2.754804	-3.588029	0.393798

C	-2.273085	-1.918976	1.137967
O	-1.450458	-1.201093	1.666707
O	-3.514209	-1.618990	0.819501
C	-3.589875	0.716090	-0.173036
H	-2.465964	0.607046	-0.286831
C	-3.944603	-0.225217	0.998179
H	-5.028487	-0.299346	1.106983
H	-3.499498	0.154013	1.919431
C	-4.168980	0.159521	-1.495731
H	-5.265909	0.161630	-1.445061
H	-3.871369	0.820047	-2.318809
H	-3.828820	-0.861213	-1.725598
O	-4.006425	1.943255	0.136741

(4) **TS_2**

N	1.553178	-0.146180	-0.301688
C	0.718491	-0.221724	0.959872
H	-0.197359	0.331757	0.694602
H	0.491313	-1.275627	1.127703
C	1.347744	0.395918	2.202001
H	1.352918	1.485840	2.108298
H	2.388928	0.075046	2.349651
C	0.522701	0.013107	3.434194
H	0.566989	-1.074032	3.580749
H	-0.530760	0.256251	3.247811
C	0.997937	0.728989	4.695371
H	0.906539	1.813802	4.585129
H	0.408735	0.426042	5.567142
H	2.050909	0.500859	4.904026
C	1.865344	1.325765	-0.533971
H	2.496635	1.637696	0.299660
H	0.892059	1.820457	-0.460041
C	2.555983	1.670758	-1.846443
H	1.889988	1.484486	-2.694594
H	3.463482	1.071564	-1.999429
C	2.932631	3.158122	-1.837941
H	2.039603	3.750483	-1.595785
H	3.658885	3.345111	-1.035149
C	3.510703	3.618197	-3.176184
H	2.786018	3.473529	-3.987846

H	3.770474	4.681896	-3.144339
H	4.419259	3.056889	-3.431360
C	2.844700	-0.926842	-0.205874
H	3.164033	-1.120679	-1.233711
H	3.580272	-0.255098	0.242584
C	2.822188	-2.229789	0.587118
H	2.614868	-2.032830	1.644141
H	2.041379	-2.905498	0.230512
C	4.180015	-2.930161	0.471599
H	4.388634	-3.150218	-0.583488
H	4.970918	-2.250594	0.812352
C	4.228223	-4.222785	1.283791
H	5.203650	-4.710936	1.187489
H	4.052263	-4.026277	2.347506
H	3.463359	-4.930014	0.942124
C	0.689023	-0.585798	-1.475262
H	-0.057242	0.213402	-1.551929
H	1.342580	-0.574324	-2.349028
C	-0.006822	-1.935688	-1.371459
H	0.709424	-2.751067	-1.218430
H	-0.719942	-1.943443	-0.541864
C	-0.776862	-2.209450	-2.668926
H	-0.074352	-2.260565	-3.511852
H	-1.450239	-1.368541	-2.871075
C	-1.586480	-3.501374	-2.586860
H	-2.129817	-3.685255	-3.519523
H	-0.935614	-4.364462	-2.403518
H	-2.314035	-3.449381	-1.768839
O	-4.985280	-2.401817	-0.045139
H	-5.723653	-1.798358	-0.219712
C	-3.914799	-1.675608	0.314718
O	-2.852310	-2.192250	0.573533
O	-4.214813	-0.381794	0.352210
C	-2.382528	0.928352	-0.713342
H	-2.188381	-0.051929	-1.222040
C	-3.115710	0.542065	0.584564
H	-3.582644	1.412830	1.049800
H	-2.415883	0.075755	1.282516
C	-3.321012	1.709847	-1.649010

H	-3.562283	2.679823	-1.197475
H	-2.812107	1.900007	-2.601373
H	-4.257586	1.174233	-1.856281
O	-1.243236	1.607473	-0.416199
C	-1.159259	3.543914	1.243416
O	0.010118	3.550329	1.245365
O	-2.307944	3.713027	1.370038

(5) **I_2**

N	1.454568	-0.273038	0.407401
C	1.408655	-0.514839	-1.091248
H	0.383317	-0.277671	-1.385645
H	2.088614	0.202955	-1.550119
C	1.754320	-1.923862	-1.547627
H	1.118267	-2.660177	-1.050021
H	2.802345	-2.163921	-1.327278
C	1.509627	-2.040157	-3.055325
H	2.041450	-1.237150	-3.583277
H	0.438701	-1.896002	-3.232636
C	1.950179	-3.395234	-3.603394
H	1.412635	-4.209904	-3.105886
H	1.749977	-3.469372	-4.676818
H	3.023751	-3.555693	-3.449039
C	0.480622	-1.253522	1.056164
H	0.987732	-2.219790	1.063110
H	-0.360314	-1.327455	0.360481
C	-0.002659	-0.931066	2.463396
H	-0.553900	0.014855	2.486147
H	0.828486	-0.839225	3.173666
C	-0.945683	-2.049249	2.924124
H	-1.766249	-2.143757	2.201861
H	-0.411317	-3.007235	2.914305
C	-1.507481	-1.790609	4.319794
H	-2.052886	-0.840202	4.356277
H	-2.199413	-2.584594	4.615757
H	-0.707169	-1.743380	5.067130
C	2.817876	-0.541453	0.997047
H	2.696617	-0.464520	2.080076
H	3.039105	-1.585833	0.767795
C	3.975106	0.339818	0.549946

H	4.022737	0.410455	-0.542329
H	3.855393	1.354740	0.942588
C	5.296227	-0.238758	1.067755
H	5.238813	-0.362819	2.156699
H	5.441889	-1.241000	0.645493
C	6.489249	0.646170	0.713920
H	7.422049	0.212652	1.086731
H	6.583099	0.765988	-0.371042
H	6.381850	1.643786	1.153976
C	0.975946	1.139966	0.686864
H	-0.113204	1.098187	0.621291
H	1.253903	1.353162	1.722528
C	1.436589	2.256971	-0.243966
H	2.520658	2.277656	-0.378067
H	0.976318	2.124874	-1.225251
C	0.969809	3.599642	0.326823
H	1.481533	3.793588	1.278752
H	-0.102937	3.543758	0.545398
C	1.218709	4.749036	-0.645936
H	0.893292	5.702402	-0.218227
H	2.282662	4.836387	-0.894477
H	0.663319	4.589245	-1.575956
O	-2.631350	3.858276	-0.760454
H	-3.542166	4.046121	-0.487480
C	-2.505255	2.548787	-0.995880
O	-1.466581	2.055871	-1.361495
O	-3.655146	1.914789	-0.770989
C	-3.111910	-0.242802	0.283351
H	-2.046173	-0.002398	0.364919
C	-3.661403	0.480809	-0.946483
H	-4.712419	0.227248	-1.094972
H	-3.072778	0.215623	-1.824625
C	-3.835323	0.148881	1.562333
H	-4.903061	-0.082110	1.486896
H	-3.424783	-0.406282	2.410809
H	-3.723266	1.219369	1.759959
O	-3.287001	-1.632256	0.102041
C	-2.414030	-2.314181	-0.802865
O	-2.689313	-3.507080	-0.917383

O	-1.509795	-1.620522	-1.323478

(6) **TS_3**

N	-1.558603	0.457511	-0.207779
C	-1.567319	-0.984401	-0.672100
H	-0.524390	-1.265578	-0.836258
H	-1.922536	-1.580200	0.167908
C	-2.399451	-1.301705	-1.906415
H	-1.991123	-0.807075	-2.793686
H	-3.437762	-0.967612	-1.792162
C	-2.388482	-2.817838	-2.137387
H	-2.855338	-3.315781	-1.278198
H	-1.351104	-3.170688	-2.171658
C	-3.120586	-3.209596	-3.418472
H	-2.650986	-2.750895	-4.295825
H	-3.108175	-4.294477	-3.560626
H	-4.167329	-2.885448	-3.390014
C	-1.041526	1.322247	-1.349479
H	-1.774553	1.240753	-2.154317
H	-0.108543	0.852829	-1.670511
C	-0.779876	2.786505	-1.023716
H	-0.089683	2.888169	-0.181958
H	-1.709537	3.310749	-0.773438
C	-0.127260	3.468026	-2.230726
H	0.779483	2.911209	-2.490460
H	-0.801547	3.427177	-3.096735
C	0.247389	4.914426	-1.916656
H	0.969459	4.937319	-1.094336
H	0.700494	5.401227	-2.786229
H	-0.631850	5.499927	-1.622403
C	-2.938739	0.941448	0.163564
H	-2.824399	1.989704	0.443636
H	-3.533214	0.911207	-0.752258
C	-3.648378	0.193401	1.281760
H	-3.728090	-0.876069	1.058113
H	-3.091940	0.293404	2.219356
C	-5.056707	0.765577	1.477134
H	-4.986973	1.840356	1.686575
H	-5.621588	0.664297	0.541913
C	-5.807359	0.069217	2.609916

H	-6.808257	0.493442	2.734154
H	-5.917762	-1.002187	2.409482
H	-5.275111	0.180303	3.561027
C	-0.588138	0.602537	0.962272
H	0.370015	0.840766	0.503245
H	-0.912275	1.482530	1.522514
C	-0.391502	-0.592412	1.889222
H	-1.333570	-0.941968	2.323881
H	0.047868	-1.429397	1.336971
C	0.568262	-0.188859	3.015004
H	0.099708	0.580725	3.641476
H	1.467106	0.268495	2.582697
C	0.967178	-1.387541	3.872695
H	1.647144	-1.086257	4.675401
H	0.089091	-1.856752	4.331058
H	1.474309	-2.146800	3.266775
O	2.558300	-4.349036	-0.288857
H	3.525378	-4.384920	-0.277031
C	2.218833	-3.032529	-0.373653
O	1.018877	-2.756114	-0.405034
O	3.223998	-2.237444	-0.409942
C	3.746017	0.044628	0.497075
H	3.755335	-0.699682	1.293608
C	2.750237	-0.400823	-0.563049
H	3.027202	-0.446732	-1.604203
H	1.734860	-0.650485	-0.298614
C	5.141268	0.234507	-0.075625
H	5.120975	0.982651	-0.874911
H	5.828693	0.572526	0.704178
H	5.506414	-0.711227	-0.485838
O	3.290070	1.252220	1.107966
C	2.525098	2.024880	0.263231
O	2.185176	3.134498	0.647938
O	2.232401	1.429343	-0.833996

(7) **P**

N	1.225596	-0.253801	0.463257
C	0.984414	-0.543728	-1.007692
H	0.188553	0.142933	-1.317008
H	1.890752	-0.256808	-1.539358

C	0.642550	-1.987156	-1.354359
H	-0.212898	-2.353928	-0.781602
H	1.489071	-2.653339	-1.145210
C	0.294329	-2.082579	-2.842932
H	1.166900	-1.798372	-3.445613
H	-0.497133	-1.359916	-3.070807
C	-0.171780	-3.485187	-3.224413
H	-1.078018	-3.750580	-2.668916
H	-0.397132	-3.550336	-4.293544
H	0.595411	-4.234120	-2.996122
C	-0.102932	-0.436229	1.179197
H	-0.415964	-1.465285	1.004703
H	-0.788440	0.252286	0.675189
C	-0.116398	-0.153491	2.675070
H	0.330220	0.820100	2.902754
H	0.446725	-0.914048	3.228425
C	-1.571744	-0.152599	3.157839
H	-2.108327	0.654220	2.644849
H	-2.056545	-1.090646	2.860681
C	-1.679508	0.030425	4.669398
H	-1.213943	0.970859	4.985507
H	-2.726320	0.049991	4.988105
H	-1.180974	-0.787547	5.202245
C	2.232706	-1.203007	1.058243
H	2.326490	-0.933760	2.112011
H	1.782499	-2.197530	1.013310
C	3.608818	-1.208181	0.409302
H	3.533855	-1.391169	-0.668133
H	4.094253	-0.235033	0.541258
C	4.487427	-2.294410	1.036762
H	4.564025	-2.124356	2.118063
H	4.003882	-3.270863	0.906564
C	5.884858	-2.327958	0.421771
H	6.496696	-3.111167	0.879240
H	5.834247	-2.524820	-0.654881
H	6.399609	-1.371236	0.564047
C	1.659076	1.200256	0.658508
H	0.739210	1.759733	0.838011
H	2.255506	1.215908	1.574195

C	2.413187	1.877139	-0.480847
H	3.306655	1.317152	-0.778223
H	1.759645	1.958069	-1.354554
C	2.820555	3.288590	-0.046266
H	3.489408	3.231529	0.822480
H	1.923551	3.833560	0.268669
C	3.506229	4.051972	-1.177169
H	3.793216	5.058107	-0.856046
H	4.410958	3.534285	-1.515996
H	2.835556	4.152695	-2.037970
O	-0.453002	3.978242	-0.851605
H	-0.124995	4.105995	-1.752249
C	-0.928426	2.673632	-0.824753
O	-1.390759	2.315236	0.277459
O	-0.804493	2.027426	-1.892563
C	-3.850822	0.317071	-0.195974
H	-3.215755	1.044705	0.316699
C	-3.211153	-0.069825	-1.531932
H	-3.951104	-0.323331	-2.297957
H	-2.496842	0.675591	-1.887637
C	-5.286929	0.777276	-0.277047
H	-5.910139	0.026736	-0.773583
H	-5.688979	0.968569	0.721223
H	-5.336153	1.709347	-0.848754
O	-3.770994	-0.924523	0.552984
C	-2.892908	-1.744529	-0.028386
O	-2.497313	-2.777812	0.450587
O	-2.479152	-1.265127	-1.208459

[C] Complete list of ref. 21 in the main text.

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09*, revision D.01, Gaussian, Inc., Wallingford, CT, 2009.

[D] Comparison between α and β attack.

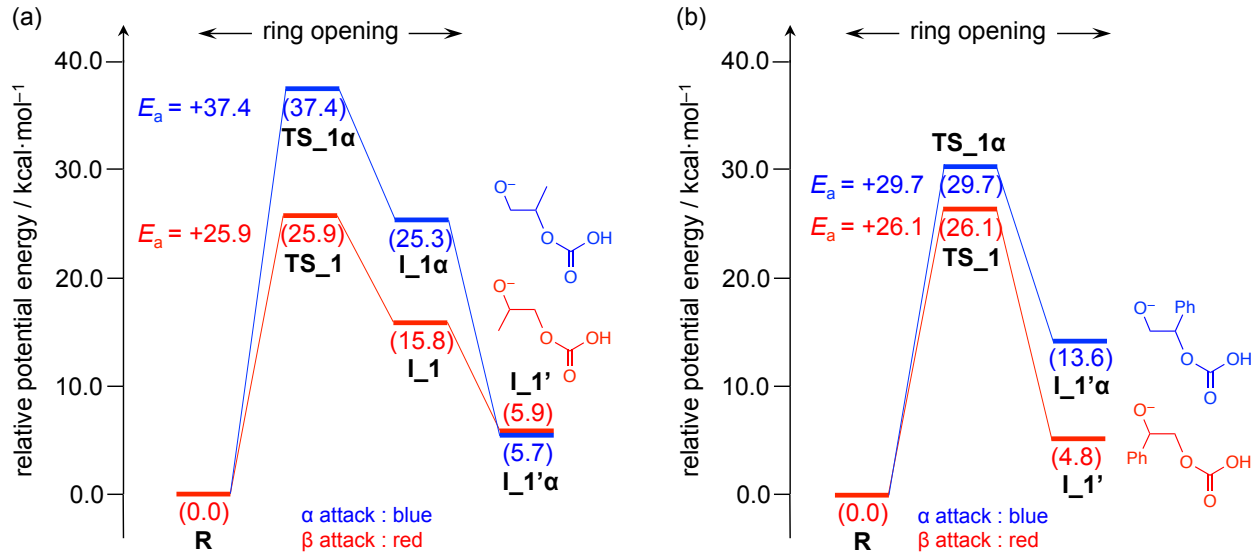

Fig. S1. The regioselectivity in the initial ring-opening reaction of (a) propylene oxide (**1b**) and (b) styrene oxide (**1d**) with TBABC. The α and β attacks are shown in blue and red, respectively. Computations were performed at the ωB97XD/6-31G* level with the self-consistent reaction field (SCRF) method (Et_2O). The relative potential energies based on reactant **R** are shown in parenthesis in kcal/mol. The TBA cation is omitted from the structures. In the case of styrene oxide, intermediates **I_1** and **I_1α** could not be located probably because of the interactions around the phenyl group.

[E] Intermediate and transition-state structures in path B.

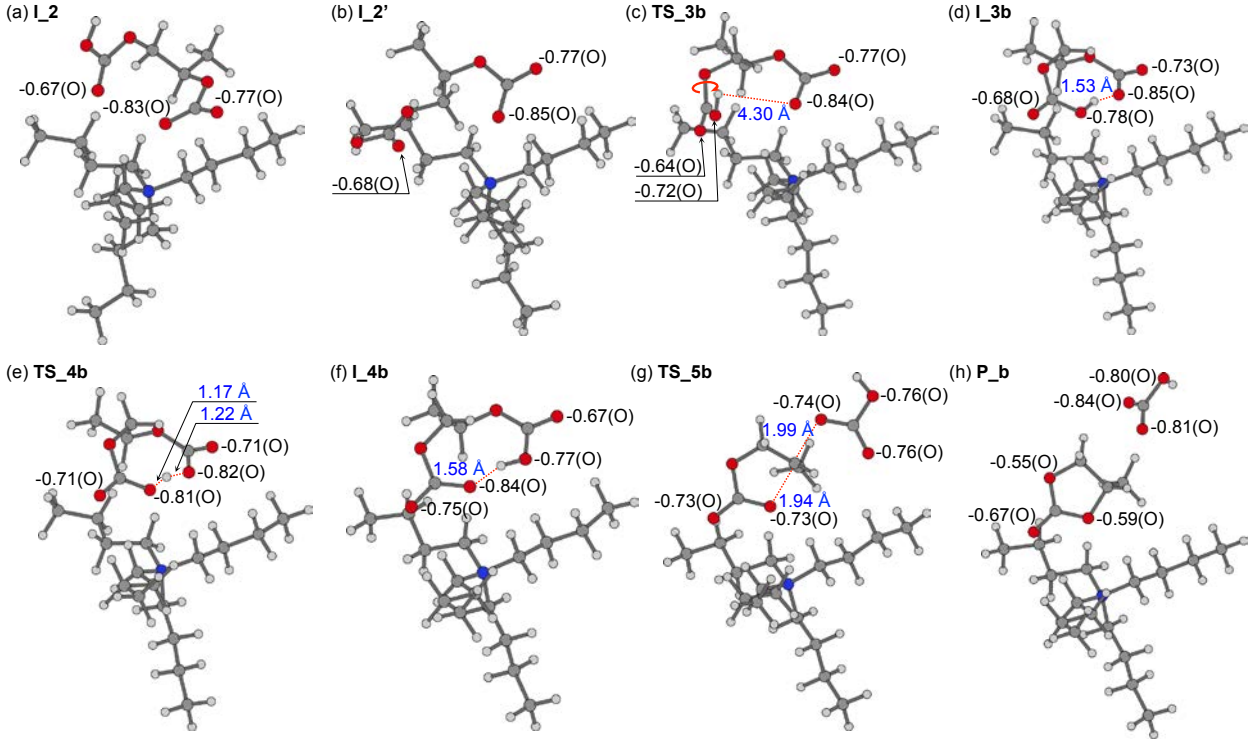

Fig. S2. Optimized structures in path B.

[F] Positions of the leaving bicarbonate ion in paths A and B.

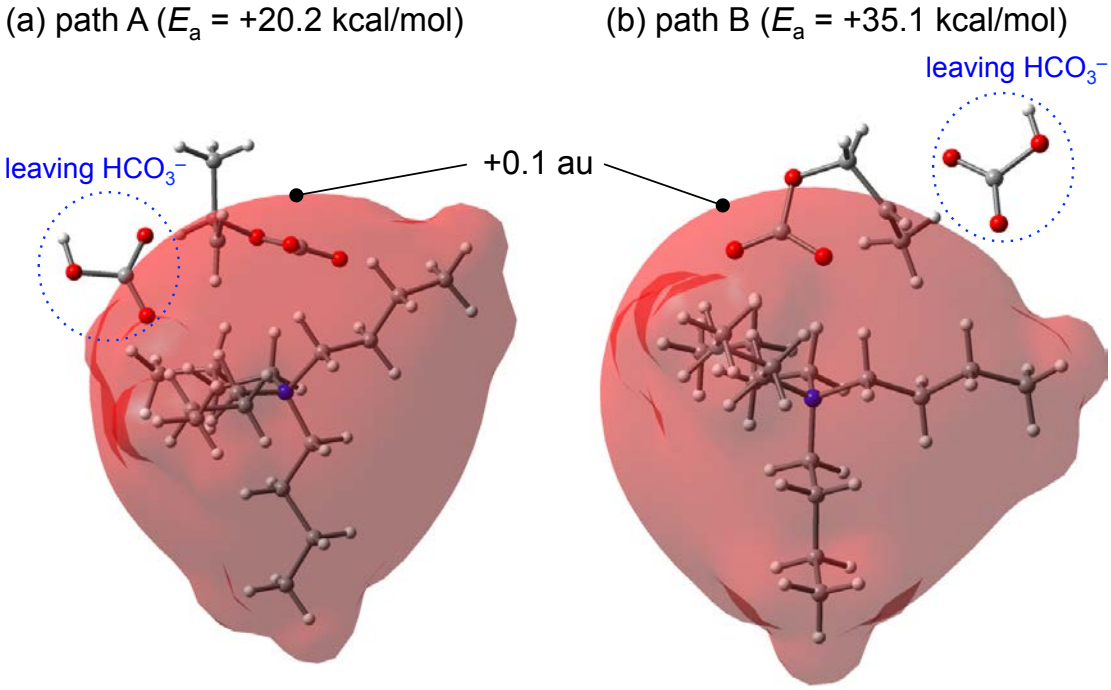

Fig. S3. The isoelectrostatic potential surface (+0.1 au) of the TBA cation in the ring-closing transition state in (a) path A and (b) path B. At the +0.10 au, a –1 charge gains a coulombic stabilization of 63 kcal/mol.

[G] Intermediate and transition-state structures in paths C and C'.

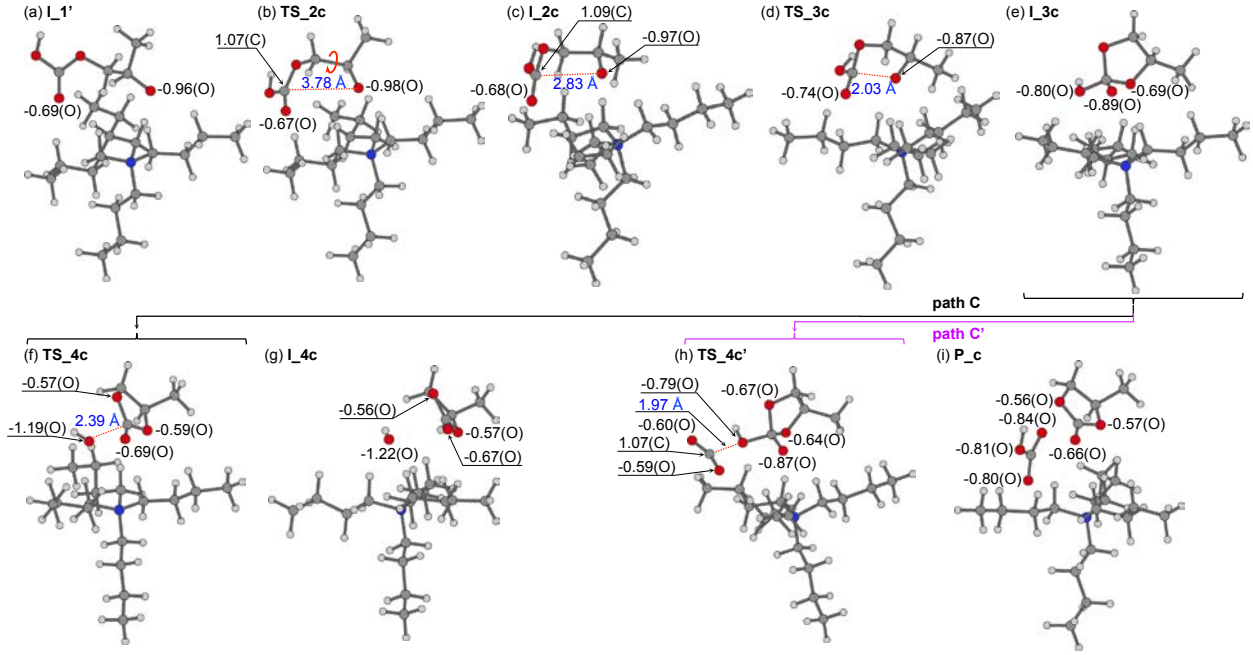

Fig. S4. Optimized structures in paths C and C'.