Electronic supplementary information (ESI)

Fabrication of a hollow sphere N, S co-doped bifunctional carbon catalyst for sustainable fixation of CO_2 to cyclic carbonates

Anindya Ghosh,[a] G Naaresh Reddy,[b] Mohammed Siddhique P. K.,[b] Sauvik Chatterjee,[c] Sudip Bhattacharjee,[c] Rahul Maitra,[b] Sergey E. Lyubimov,[d] Ashot V. Arzumanyan,[d,e] Alexander Naumkin,[d] Asim Bhaumik,[c] and Biswajit Chowdhury [a] *

[a] *Department of Chemistry, Indian Institute of Technology (Indian School of Mines), Dhanbad, Jharkhand-826004, India.*

[b] *Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai-400076, India.*

[c] *School of Materials Sciences, Indian Association for the Cultivation of Science, Jadavpur, Kolkata-700032, India.*

[d] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, Moscow-119991, Russia.*

[e] *Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky Prospect, 119991 Moscow, Russian Federation.*

Corresponding author. Tel.: (+91)-326-2235663; Fax.: (+91)-326-2296563; E-mail: biswajit72@iitism.ac.in.

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Section S1: General reaction procedure

Procedure for the scaled-up of CO_2-epichlorohydrin cycloaddition reaction:

The optimized CO_2-epichlorohydrin cycloaddition reaction was under-taken treating 110 mmol of epichlorohydrin, 0.913 mmol of TBAI, and 110 mg NSC-773 catalyst in a 50 mL round-bottom flask. Stirring the reaction mixture under CO_2 atmosphere for 24 h at 343 K followed by addition of 11 mL methanol and removal of the catalyst by centrifugal separation. Finally, the reaction mixture was analyzed by gas chromatography (Agilent 7890B), showed ~93 % epichlorohydrin conversion, and 97 % cyclic carbonate (4-chloromethyl-1,3-dioxolan-2-one) selectivity with an isolated yield ~86 %.

Section S2: FTIR analysis

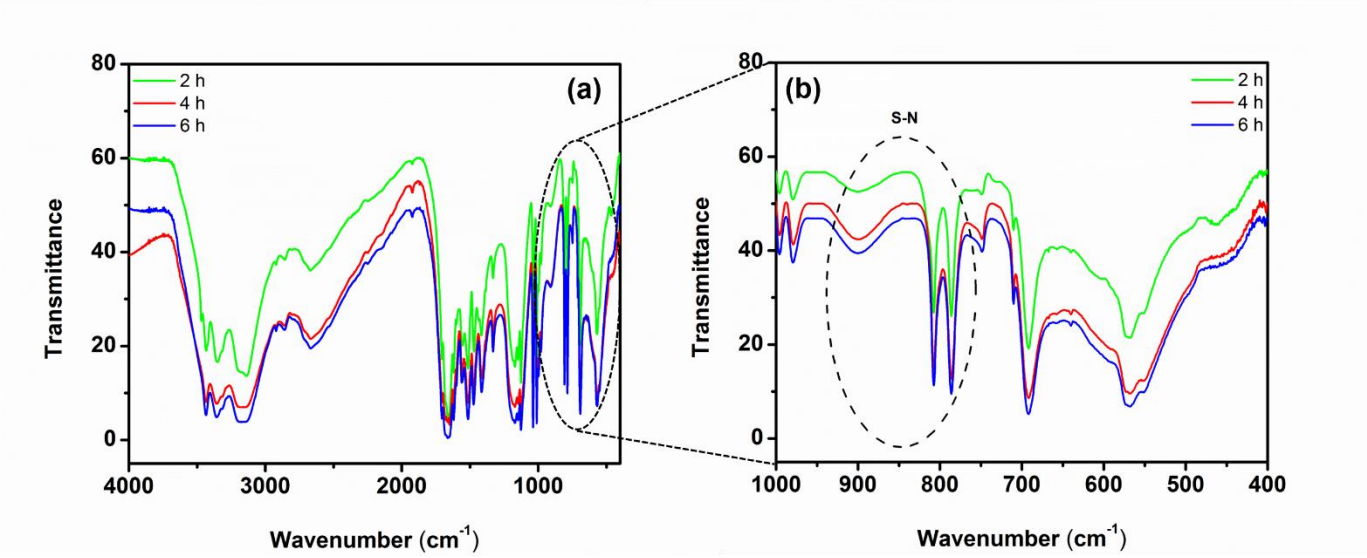


Fig. S1 FTIR spectra of NSC-773 before carbonization at different time interval (a) and enlarge view of the marked region (b).

Section S3: SEM analysis

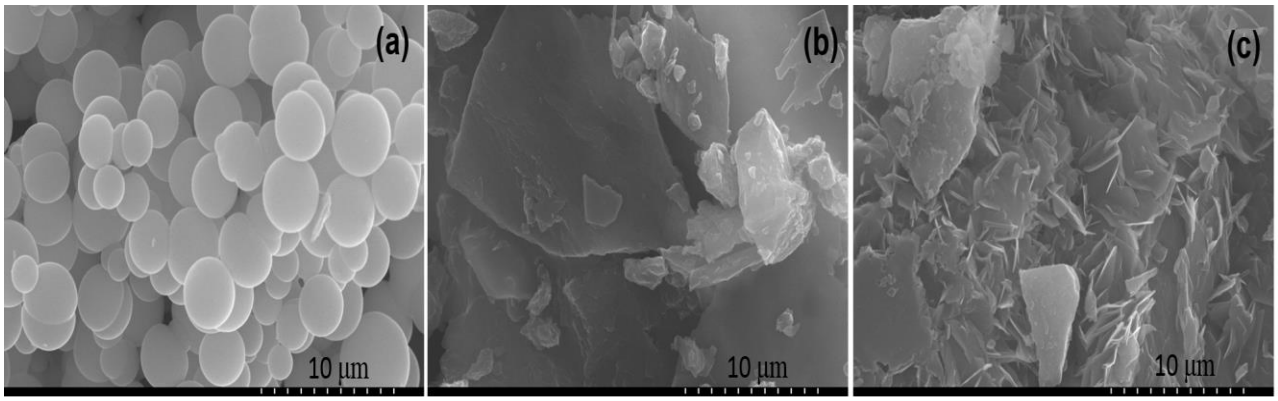


Fig. S2 SEM images of NSC-773 (a); NSC-873(b) and NSC-973 (c) catalysts.

Section S4: HRTEM analysis

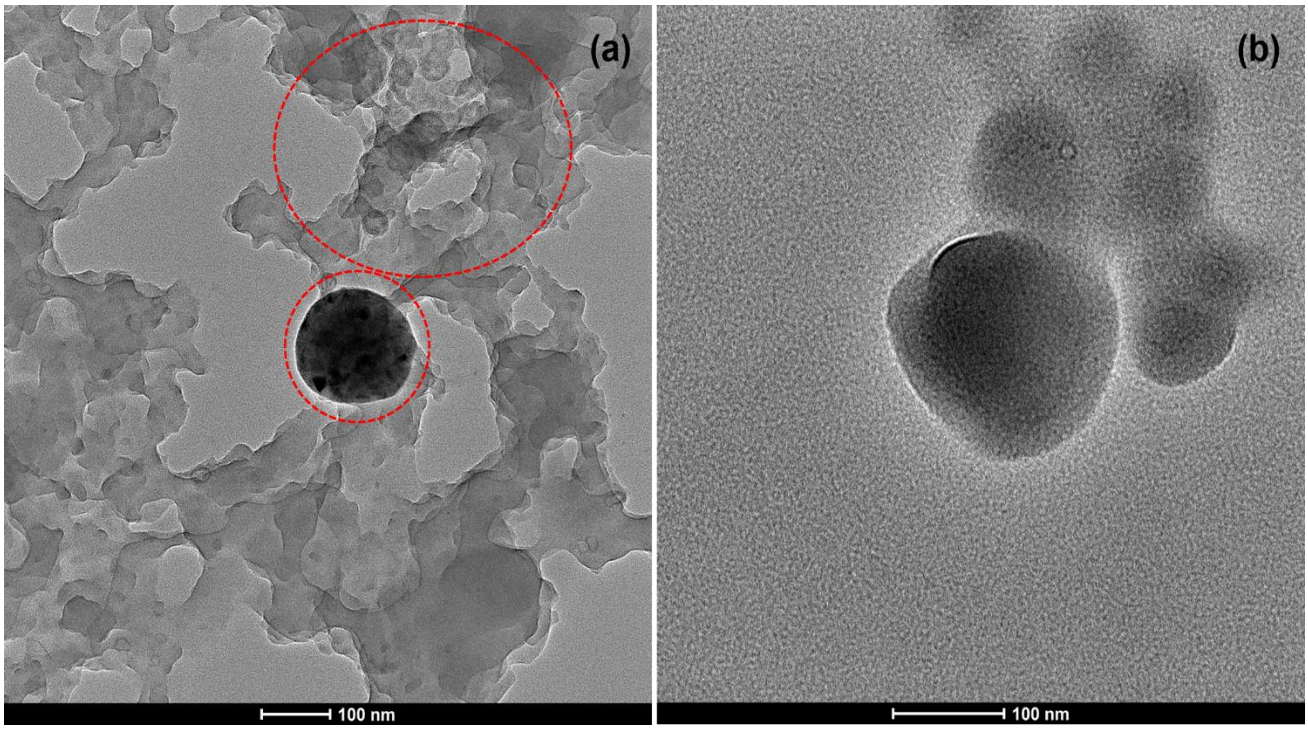


Fig. S3 Low magnification HRTEM images (a-b) of NSC-773 catalyst.

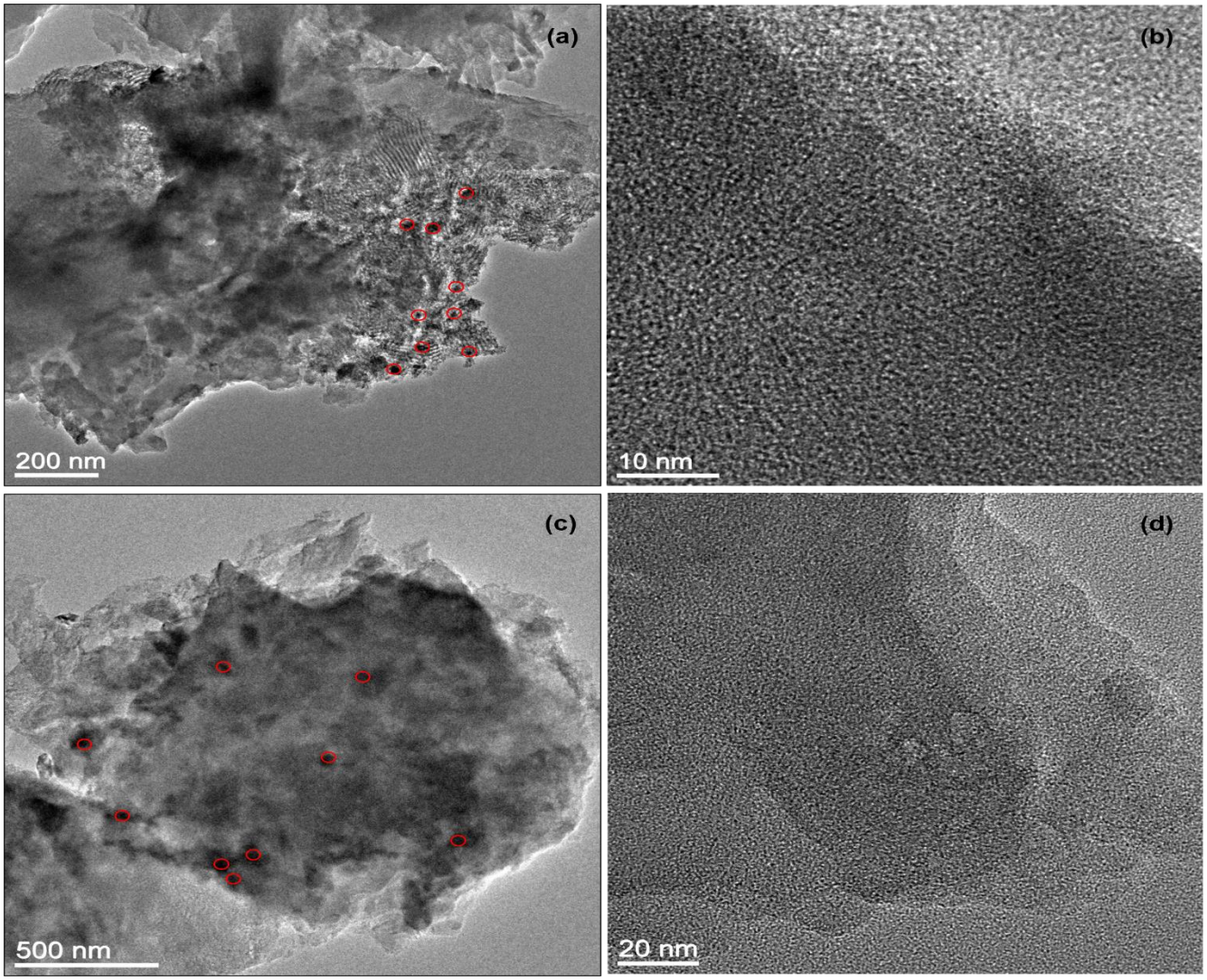


Fig. S4 HRTEM images of NSC-873 (a and b) and NSC-973 (c and d).

Section S5: XPS analysis

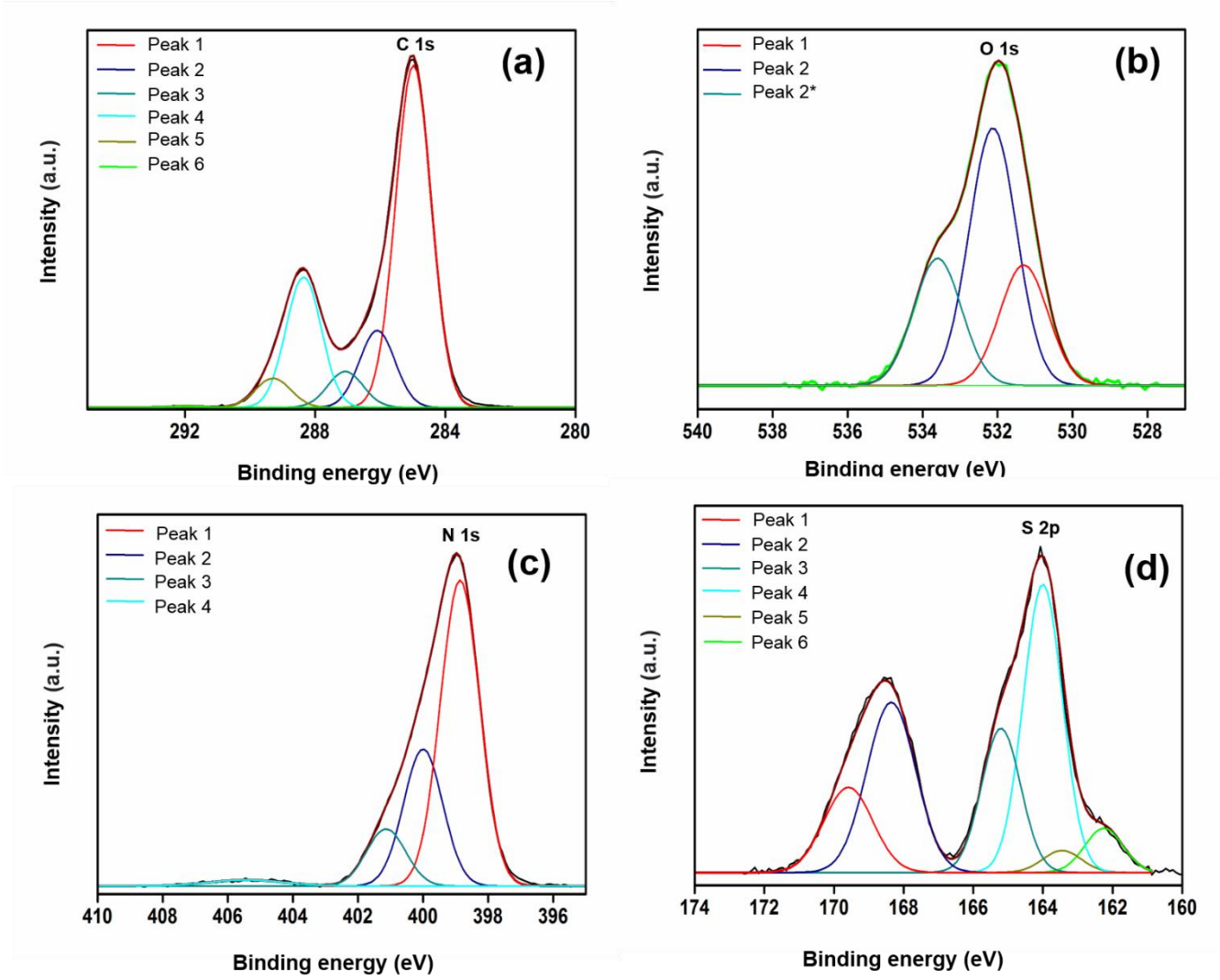


Fig. S5 XPS high resolution core-level spectra of C 1s (a); O 1s (b); N 1s (c); and S 2p (d) for NSC-873 catalyst.

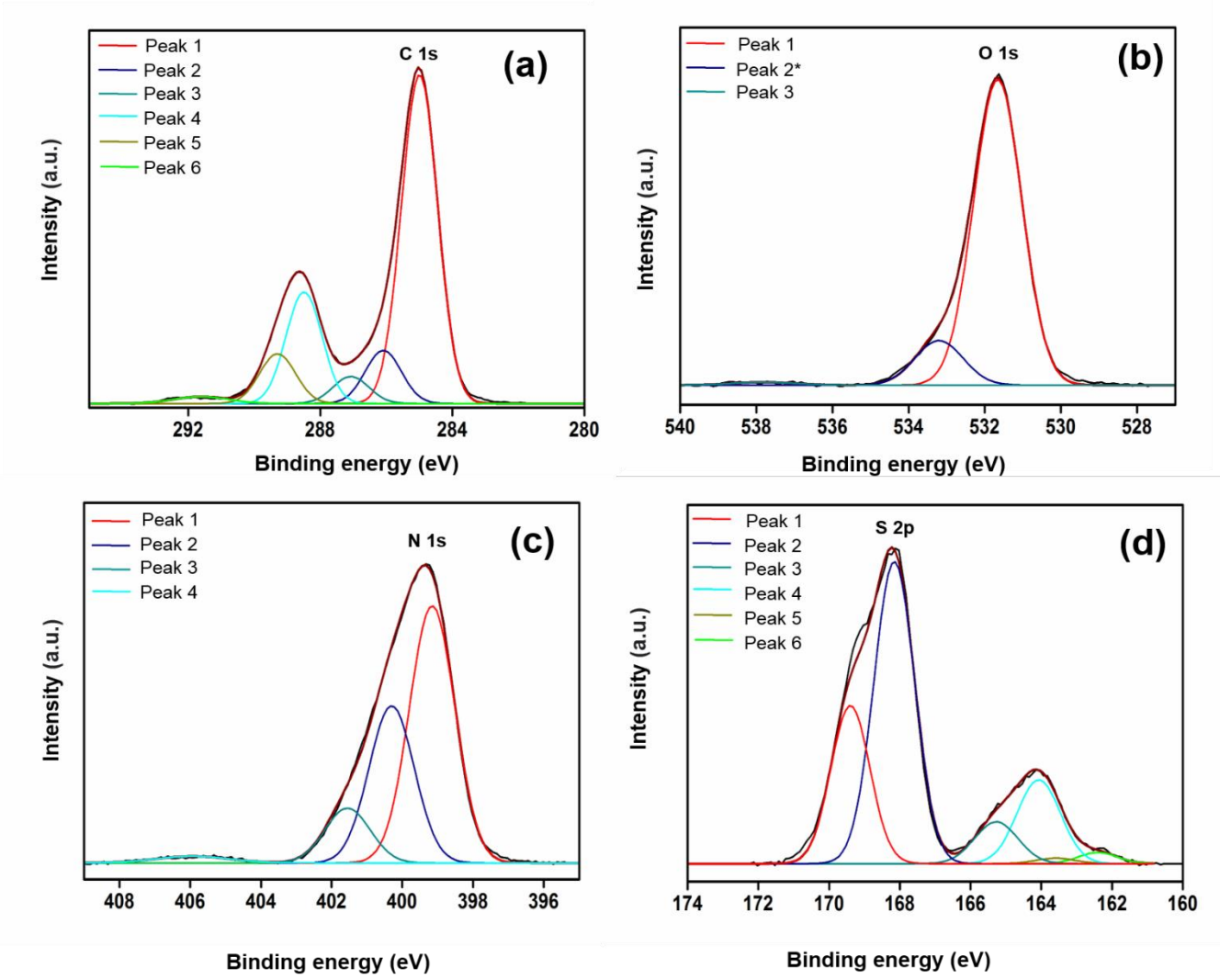


Fig. S6 XPS high resolution core-level spectra of C 1s (a); O 1s (b); N 1s (c); and S 2p (d) for NSC-973 catalyst.

Table S1 Binding energies (E_b), Gaussian widths (W), peak areas (P_a), and relative intensities (I_{rel}) for the C 1s spectra.

Catalyst		**Peak 1**	**Peak 2**	**Peak 3**	**Peak 4**	**Peak 5**	**Peak 6**
NSC-773	$E_{b,}$ eV	285.0	286.09	287.07	288.56	289.30	291.71
	W, eV	1.09	1.09	1.09	1.09	1.09	1.70
	P_a	23093	3072	1377	5466	3228	832
	I_{rel}	0.62	0.08	0.04	0.15	0.09	0.02

NSC-873	$E_{b,}$ eV	285.0	286.11	287.09	288.36	289.30	291.92
	W, eV	1.09	1.09	1.09	1.09	1.09	1.70
	P_a	26039	5857	2733	9917	2219	106
	I_{rel}	0.56	0.12	0.06	0.21	0.05	0.002
NSC-973	$E_{b,}$ eV	285.0	286.10	287.08	288.50	289.30	291.62
	W, eV	1.09	1.09	1.09	1.09	1.09	1.70
	P_a	21719	3505	1778	7353	3278	700
	I_{rel}	0.57	0.09	0.05	0.19	0.09	0.02

Table S2 Binding energies (E_b), Gaussian widths (W), peak areas (P_a), and relative intensities (I_{rel}) for the O 1s spectra.

Catalyst		**Peak 1**	**Peak 2**	**Peak 2***	**Peak 3**
NSC-773	$E_{b,}$ eV	531.71	-	533.32	537.85
	W, eV	1.28	-	1.28	1.63
	P_a	26436	-	3646	412
	I_{rel}	0.87	-	0.12	0.01
NSC-873	$E_{b,}$ eV	531.30	532.12	533.6	-
	W, eV	1.28	1.26	1.28	-
	P_a	9779	20618	10325	-
	I_{rel}	0.24	0.51	0.25	-
NSC-973	$E_{b,}$ eV	531.66	-	533.20	537.81
	W, eV	1.26	-	1.26	1.65
	P_a	21664	-	3154	271
	I_{rel}	0.86	-	0.13	0.01

Table S3 Binding energies (E_b), Gaussian widths (W), peak areas (P_a), and relative intensities (I_{rel}) for the N 1s spectra.

Catalyst		**Peak 1**	**Peak 2**	**Peak 3**	**Peak 4**
NSC-773	E_b, eV	399.28	400.42	401.67	406.00
	W, eV	1.32	1.30	1.30	1.81
	P_a	17606	10092	4110	571
	I_{rel}	0.54	0.31	0.13	0.02
NSC-873	E_b, eV	398.86	400.00	401.13	405.41
	W, eV	1.2	1.2	1.2	2.3
	P_a	22986	10250	4269	880
	I_{rel}	0.60	0.27	0.11	0.02
NSC-973	E_b, eV	399.16	400.30	401.55	405.94
	W, eV	1.28	1.28	1.28	2.10
	P_a	20049	12240	4266	845
	I_{rel}	0.54	0.33	0.11	0.02

Table S4 Binding energies (E_b), Gaussian widths (W), peak areas (P_a), and relative intensities I_{rel} for the S 2p spectra fitted with three spin-orbit doublets.

Catalyst		**Peak 6**	**Peak 5**	**Peak 4**	**Peak 3**	**Peak 2**	**Peak 1**
NSC-773	E_b, eV	161.9	163.1	164.04	165.29	168.19	169.43
	W, eV	1.1	1.1	1.22	1.22	1.14	1.1
	P_a	90	45	780	390	4150	2200
	I_{rel}	0.012	0.006	0.102	0.051	0.542	0.287
NSC-873	E_b, eV	162.25	163.45	164.00	165.20	168.36	169.59
	W, eV	1.1	1.1	1.12	1.12	1.40	1.40
	P_a	240	120	1600	800	1180	590

	I_{rel}	0.053	0.026	0.353	0.177	0.261	0.130
NSC-973	$E_{b,}$ eV	162.43	162.63	164.03	165.23	168.13	169.43
	W, eV	1.1	1.1	1.22	1.22	1.14	1.1
	P_a	1200	60	1000	500	3400	1700
	I_{rel}	0.143	0.007	0.119	0.060	0.405	0.202

Table S5 Relative atomic concentration (%) from the high-resolution core-level spectra.

Catalyst	N 1s (at. %)	O 1s (at. %)	S 2p (at. %)
NSC-773	26.3	15.2	4.4
NSC-873	26.7	8.3	2.7
NSC-973	29.5	12.4	3.9

Section S6: Micropore size distribution

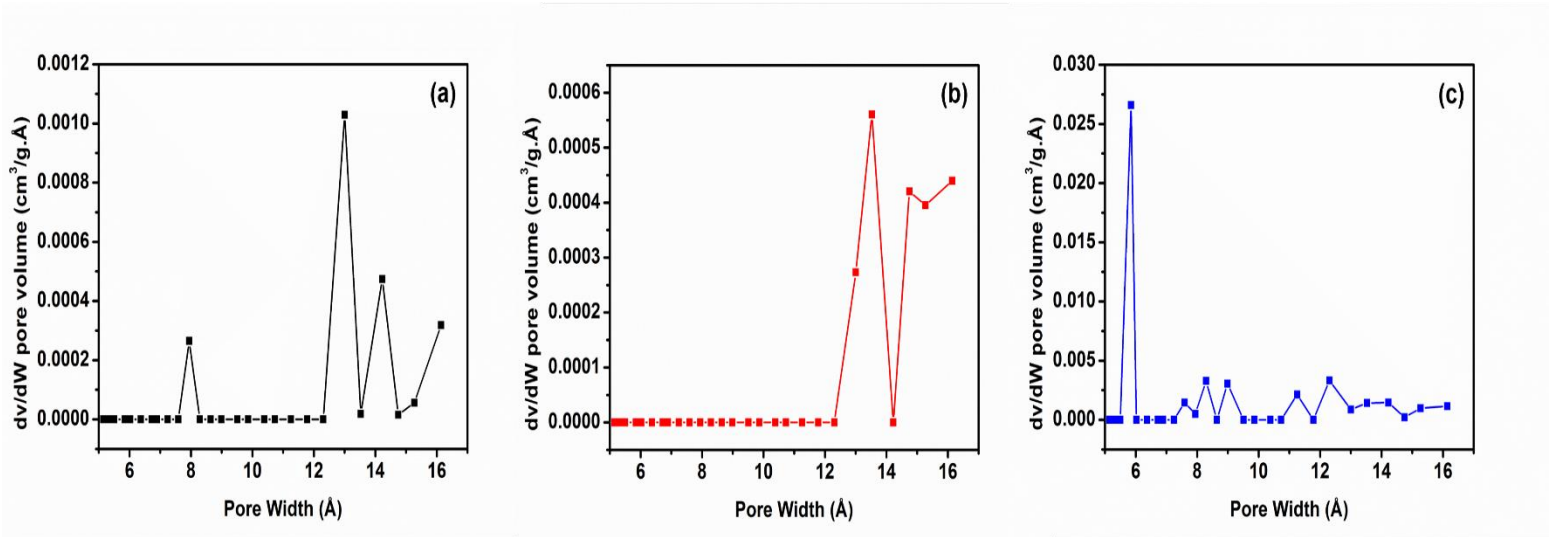


Fig. S7 NLDFT pore size distributions of NSC-773(a); NSC-873 (b) and NSC-973 (c) catalysts obtained from CO_2 adsorption.

Section S7: Elemental analysis

Table S6 Elemental composition (mass %) of the catalysts

Catalyst	C (%) [a]	N (%) [a]	S (%) [a]	H (%) [a]
NSC-773	50.8	33.3	5.7	2.2
NSC-873	52.2	29.5	5.8	2.1
NSC-973	52.5	25.9	7.3	2.0
Raw material	37.8	26.7	9.3	5.1

[a] The contents of C, N, S are determined by CHNS.

Section S8: Catalytic activity study

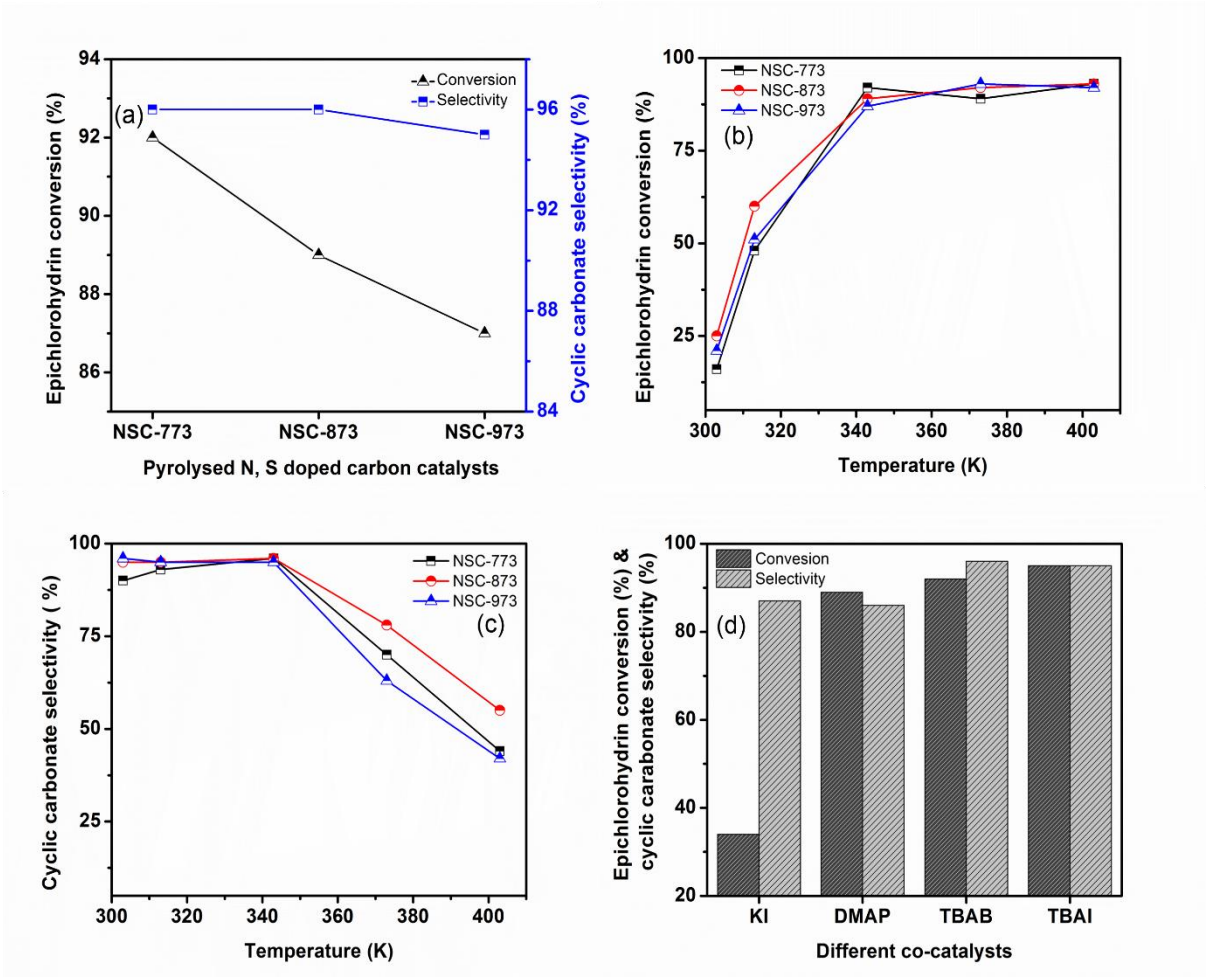


Fig. S8 Cycloaddition reaction of CO_2 with epichlorohydrin over different N, S doped carbon catalyst (a), reaction conditions: epichlorohydrin: 10 mmol, co-catalyst: TBAB (0.083 mmol),

CO_2 gas bladder, catalyst amount: 50 mg, reaction temperature: 343 K, TOS: 24 h; Effect of reaction temperature on epichlorohydrin conversion (b); and cyclic carbonate selectivity (c); reaction conditions: epichlorohydrin: 10 mmol, co-catalyst: TBAB (0.083 mmol), CO_2 gas bladder, catalyst: NSC-773 (50 mg), TOS: 24 h; Effect of different co-catalysts (d), reaction conditions: epichlorohydrin: 10 mmol, co-catalyst: 0.083 mmol, CO_2 gas bladder, catalyst: NSC-773 (50 mg), reaction temperature: 343 K, TOS: 24 h. (The solid lines shall guide the eye).

Table S7 Literature reports for the utilization of co-catalyst for CO_2-epoxide cycloaddition reaction.

Sr. No	**Catalyst**	**Co-catalyst**	**Temperature (K)**	**Pressure (bar)**	**Conversion of epoxide (%)**	**Selectivity of corresponding carbonate (%)**	**Ref.**
1	-	TBAI	353	20	9	50	47
	$CuCo_2O_4$	TBAI	353	20	94	94	
2	-	TBAB	RT	1 atm	1	-	49
	ZnMOF-2	TBAB	313	10	99	99	
3	-	TBAI	353	10	31	99	54
	ZrO_2-MCM-41	TBAI	353	10	97	99	
4	-	TBAI	343	1 atm	~1	69	Our work
	NSC-773	TBAI	343	1 atm	95	98	

Table S8 Comparison of CO_2 cycloaddition reaction with previously reported carbon-based catalysts

Entry	Catalyst	Epichlorohydrin (mmol)	Catalyst amount (mg)	Co-catalyst (mmol)	Solvent	Temperature (K)	Pressure (MPa)	TOS (h)	Conversion (%)	Selectivity (%)	Yield (%)	Ref.
1	$ZnBr_2$/g-C_3N_4	102	200	-	DMF	413	2	6	88	94	92	1
2	$BiCl_3$@Bi@g-C_3N_4	63	10	-	DMF	423	2	4	100	>99	>99	2
3	ZIF-8/C_3N_4	4.5	46	-	-	353	1.0	24	100	100	100	3
4	u-C_3N_4	255	120	-		393	2.0	5	98.3	98	96.3	4
5	MWCNTs-ammonium salt	214	770	-	-	383	2	6	86	94	81	5
6	ZnTPy-BIM4/CNT	6.63	-	-	-	393	1.5		98	-	-	6
7	GO-DMEDA-I	28.6	100	-	-	393	2	3	95.8	94.5	98.6	7

8	GO-H-Me	28.6	120	-	-	363	2	4	93.8	99.2	93	8
9	u-g-C_3N_4	21.5	100	-	-	403	2	24	99.6	96.4	96	9
10	GO-[SmIm]Br	191	600	-	-	413	2	4	94.7	99.5	94.2	10
11	CoPc/g-C_3N_4	40	200	-	-	403	3	24	-	-	97.6	11
12	C_{60}-fullerenol	100	100	KI (1)	-	393	2.0	8	-	-	99	12
13	AP-GO	10	30	TBAI (0.1)	-	373	0.1	27	-	-	75	13
14	NSC-773	10	10	TBAI (0.083)	-	343	0.1	24	95	98	93	Our catalyst

Section S9: GC chromatogram of different reaction mixtures

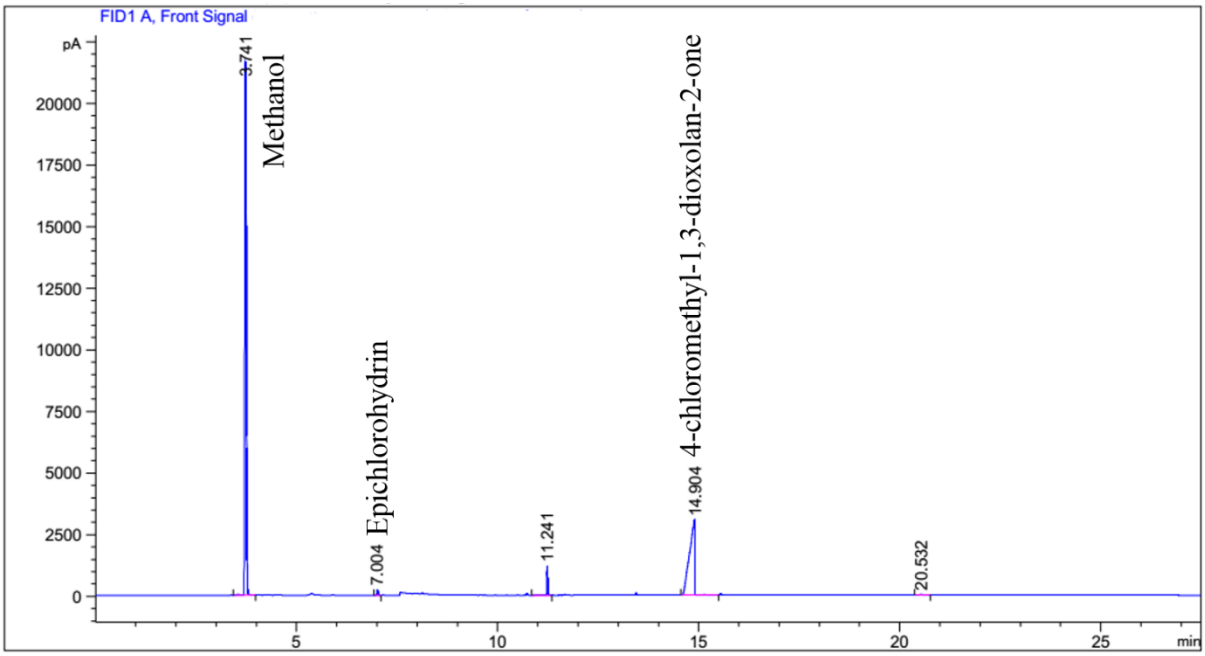


Fig. S9 GC chromatogram of CO_2-epichlorohydrin reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 13.5 min. FID temperature 280 ^{0}C, Split ratio: 50:1.

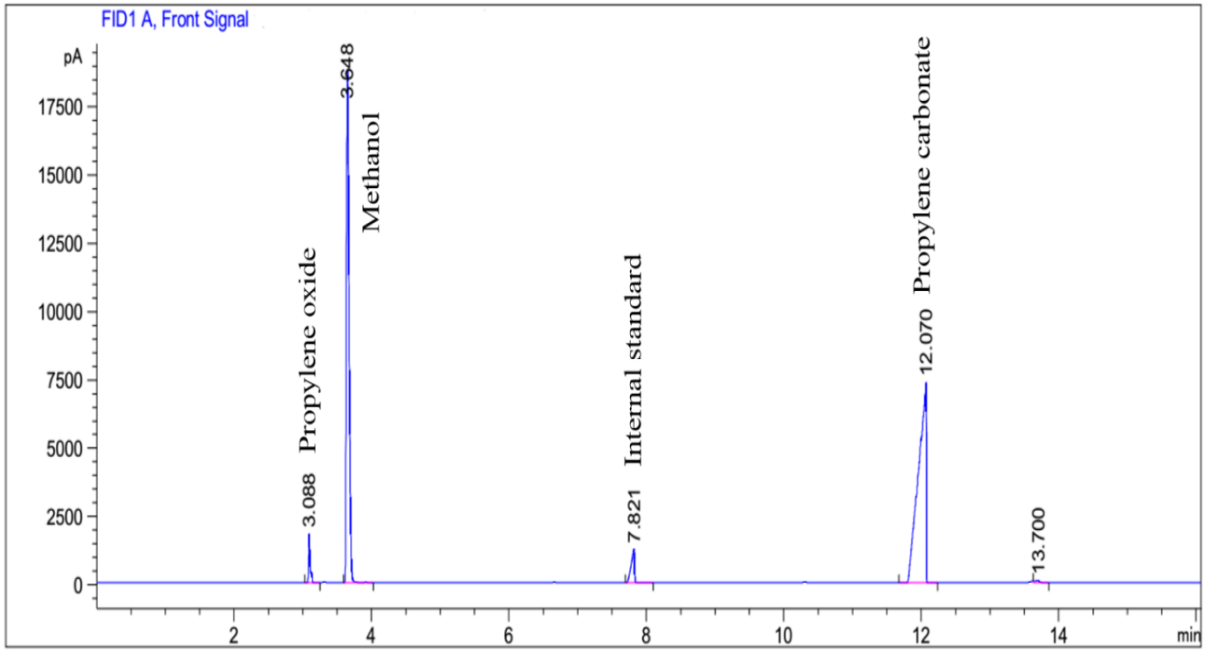


Fig. S10 GC chromatogram of CO_2-propylene oxide reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 3.5 min, FID temperature 280 ^{0}C, Split ratio: 50:1.

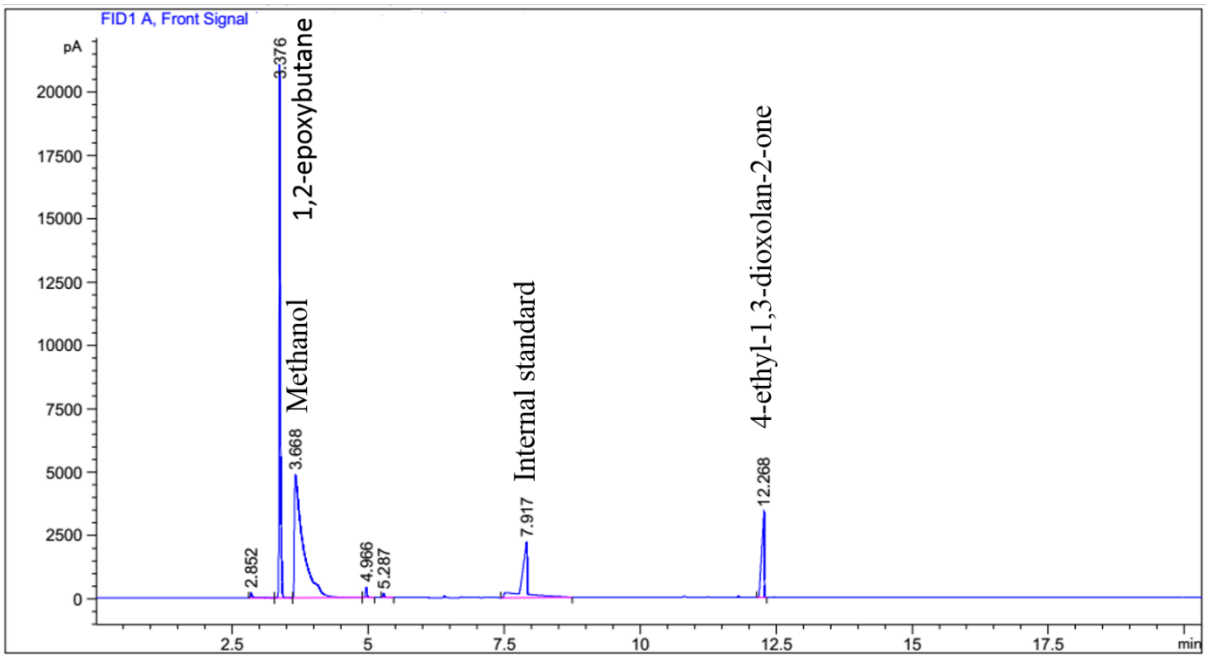


Fig. S11 GC chromatogram of CO_2-1, 2-epooxybutane reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 5.5 min, FID temperature 250 ^{0}C, Split ratio: 50:1.

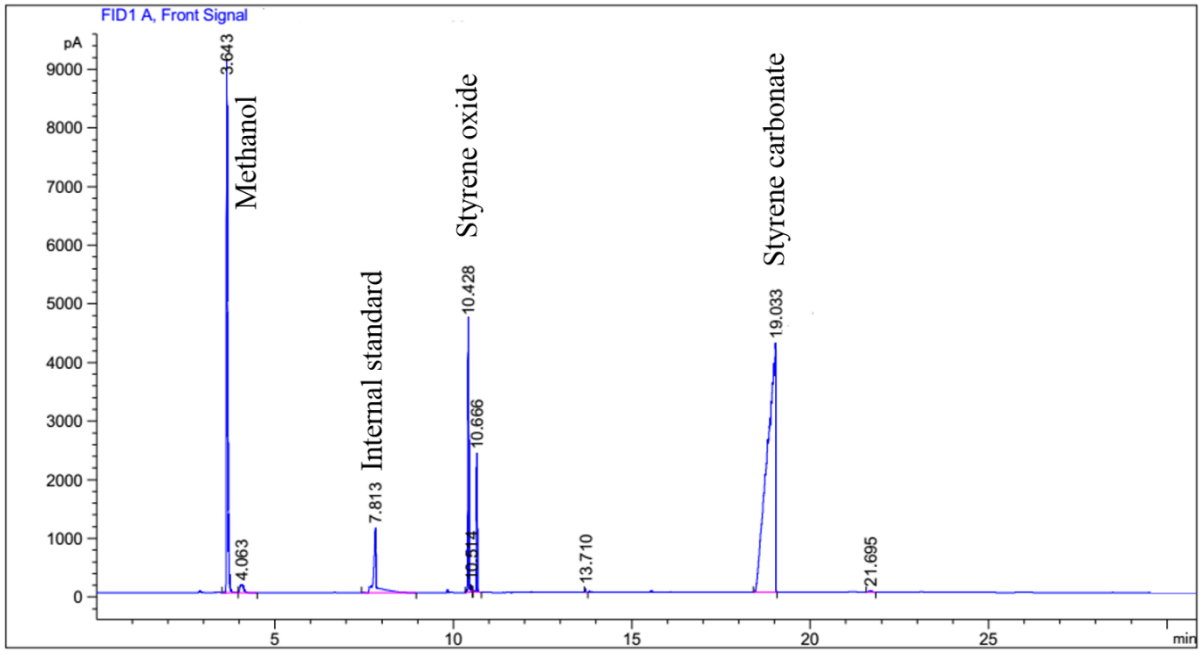


Fig. S12 GC chromatogram of CO_2-styrene oxide reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 17.5 min, FID temperature 280 ^{0}C, Split ratio: 80:1.

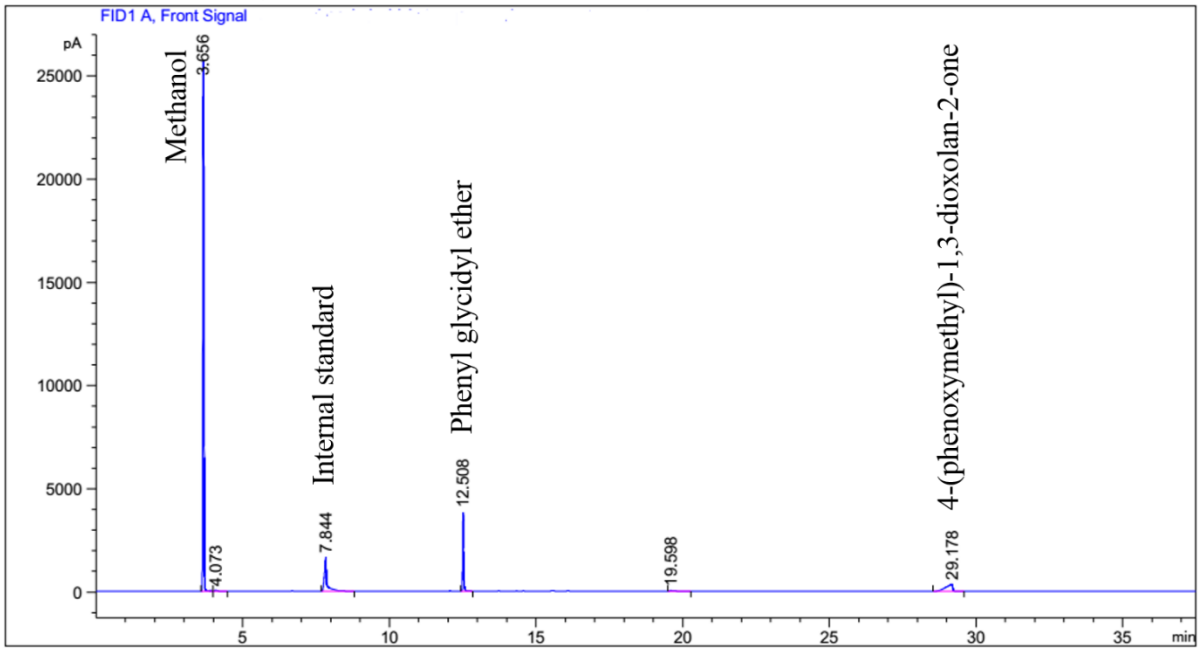


Fig. S13 GC chromatogram of CO_2-phenyl glycidyl ether reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 25 min, FID temperature 280 ^{0}C, Split ratio: 50:1.

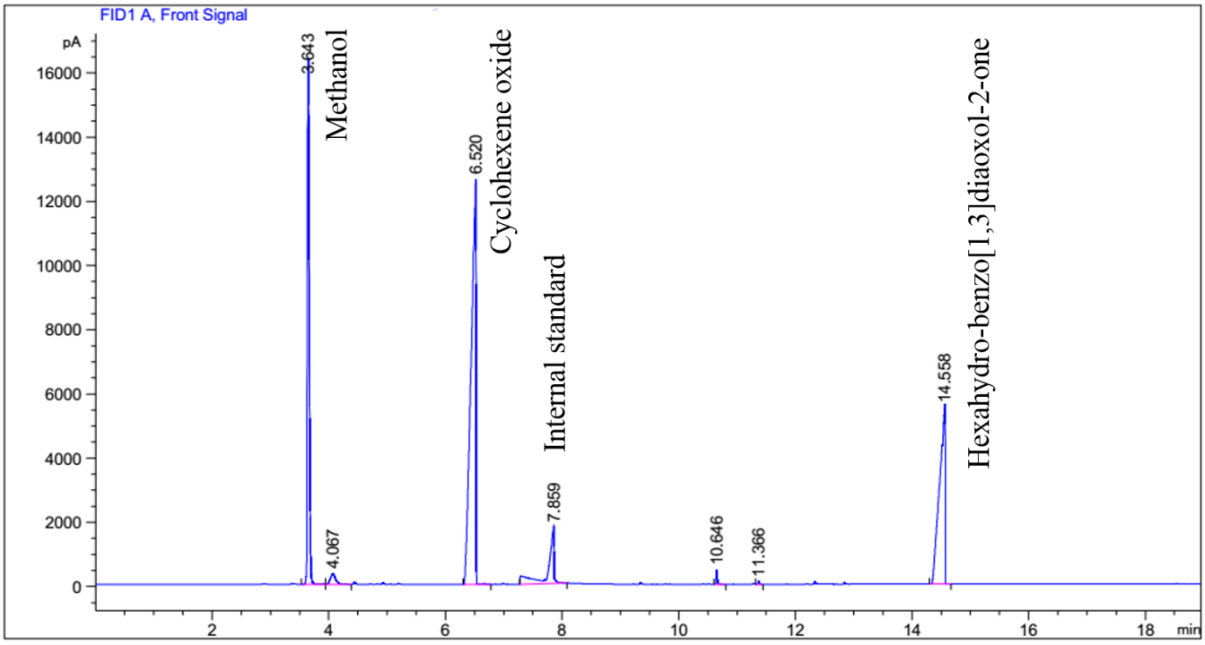


Fig. S14 GC chromatogram of CO_2-cyclohexene oxide reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 6 min, FID temperature 250 ^{0}C, Split ratio: 50:1.

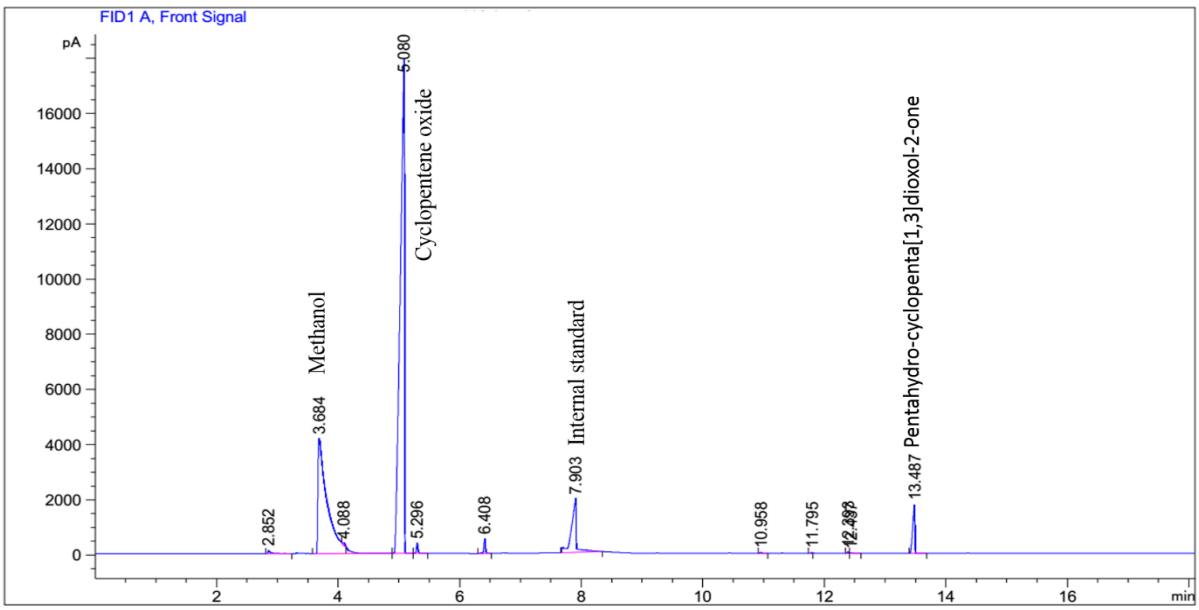


Fig. S15 GC chromatogram of CO_2-cyclopentene oxide reaction mixture. Injection amount :1 µL. GC program: Set point (Initial): 60 ^{0}C, Hold time (Initial): 4 min, Ramp: 20 ^{0}C/min, Set point (Final): 230 ^{0}C, Hold time (Final): 5.5 min, FID temperature 250 ^{0}C, Split ratio: 50:1.

Section S10: ^{1}H NMR spectra of the synthesized carbonate

4-chloromethyl-1,3-dioxolan-2-one:

Appearance: pale yellow liquid, Isolated yield: 88 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.00-4.95 (m, 1H), 4.58 (t, *J*=8.5 Hz, 1H), 4.39 (q, *J*=5.7, 8.8 Hz, 1H), 3.78 (dd, *J*=5.3, 12.2 Hz, 1H), 3.71 (dd, *J*=3.6, 12.6 Hz, 1H). FTIR (ν_{max}/ cm^{-1}) 1809 (C=O) ,1074 (C-O), 2954 (C-H).

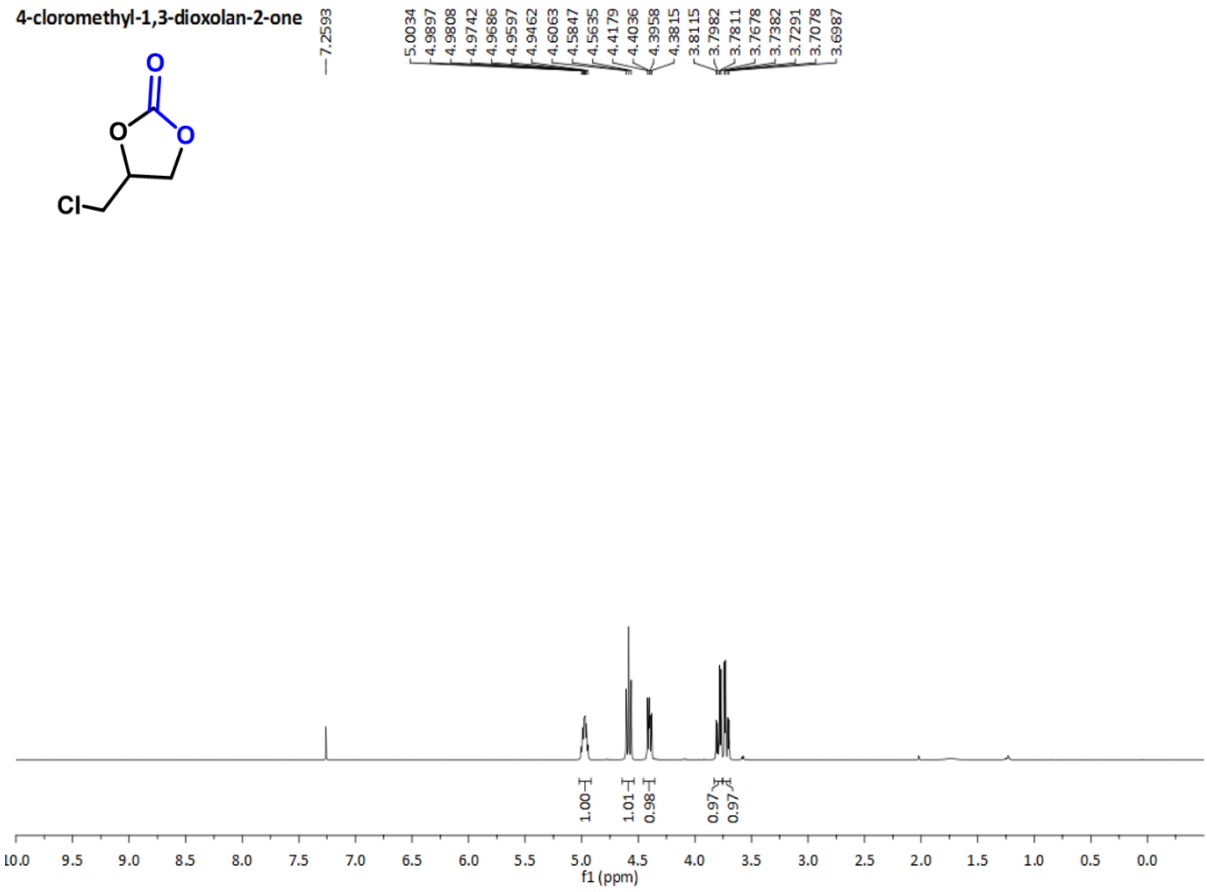


Fig. S16 ^{1}H NMR spectrum of 4-chloromethyl-1,3-dioxolan-2-one, synthesized from the CO_2-epichlorohydrin cycloaddition reaction using NSC-773 catalyst.

Propylene carbonate:

Appearance: colourless liquid, Isolated yield: 84 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.79-4.70 (m, 1H), 4.44 (q, *J*=7.7, 8.4 Hz, 1H), 3.90 (q, *J*= 7.2, 8.4 Hz, 1H), 1.34 (d, *J*= 6.2, 3H). FTIR (ν_{max}/ cm^{-1}) 1787 (C=O) ,1052 (C-O), 2928 (C-H).

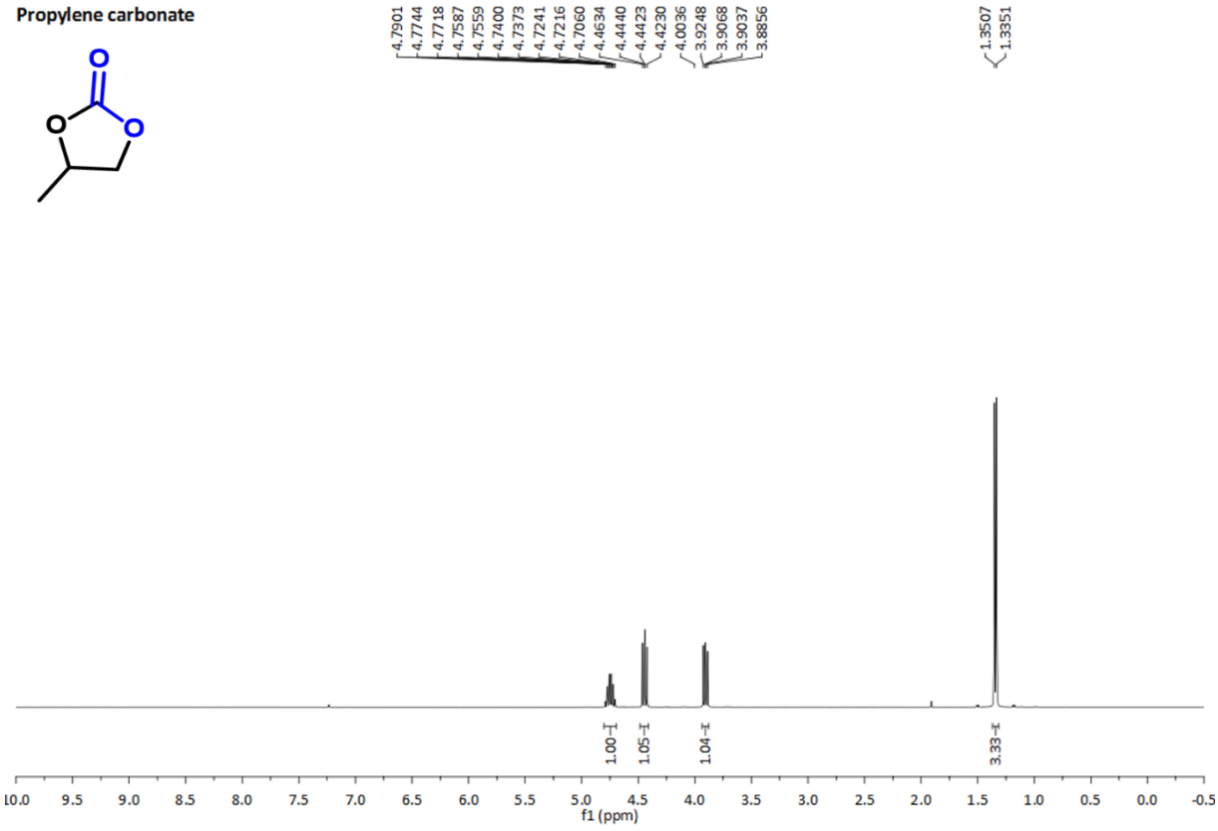


Fig. S17 ^{1}H NMR spectrum of Propylene carbonate, synthesized from the CO_2-propylene oxide cycloaddition reaction using NSC-773 catalyst.

4-ethyl-1,3-dioxolan-2-one:

Appearance: yellowish liquid**,** Isolated yield: 69 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.64-4.57(m, 1H), 4.47 (t, *J*=8.1 Hz, 1H), 4.01 (q, *J*=6.96, 8.44 Hz, 1H), 1.78-1.62 (m, 2H), 0.93 (t, *J*=7.4 Hz, 3H). FTIR (ν_{max}/ cm^{-1}) 1792 (C=O), 1056 (C-O), 2963 (C-H).

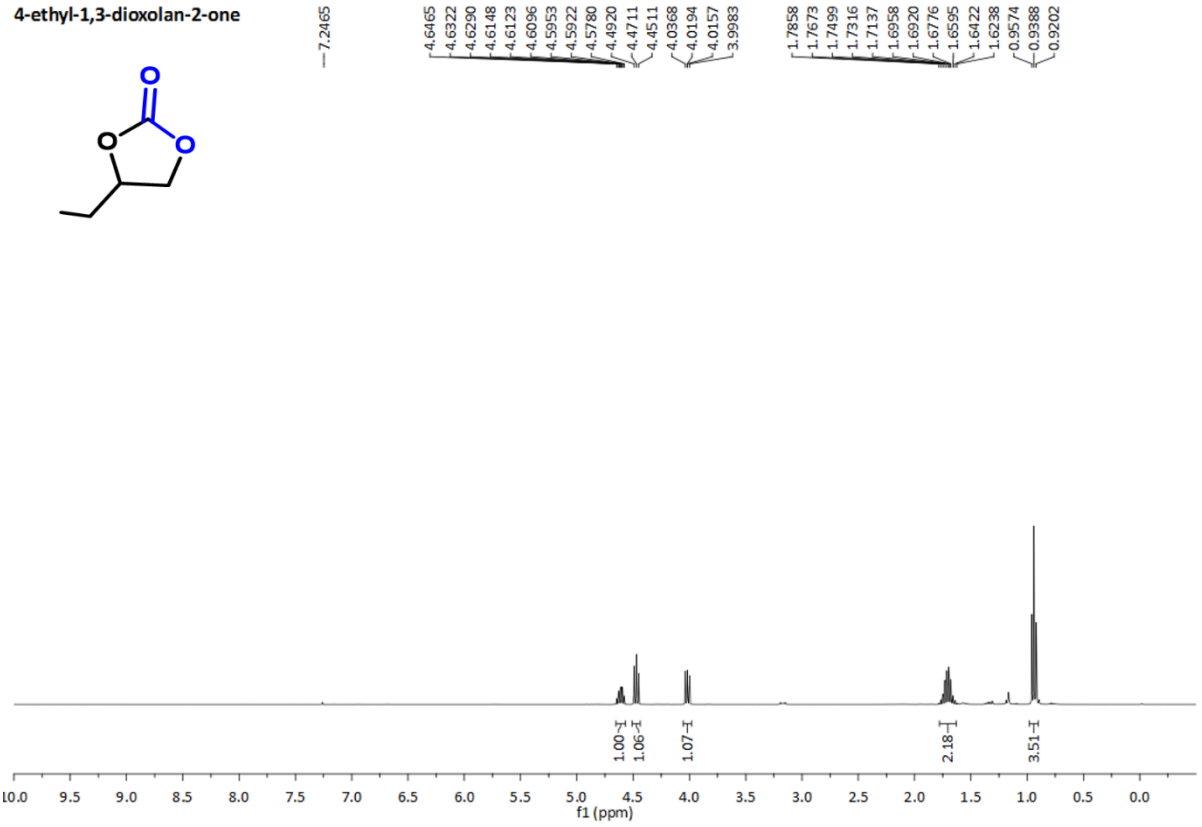


Fig. S18 ^{1}H NMR spectrum of 4-ethyl-1,3-dioxolan-2-one, synthesized from the CO_2-1,2-epoxybutane cycloaddition reaction using NSC-773 catalyst.

4-((allyloxy)methyl)-1,3-dioxolan-2-one:

Appearance: pale yellow liquid, Isolated yield: 91%

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.83-5.72 (m, 1H), 5.20-5.09 (m, 2H), 4.76-4.73 (m, 1H), 4.43-4.39 (m, 1H), 4.31-4.27 (m, 1H), 3.96-3.95 (m, 2H), 3.63-3.59 (m, 1H), 3.54-3.49 (m, 1H). FTIR (ν_{max}/ cm^{-1}) 1790 (C=O), 1044 (C-O), 2916 (C-H).

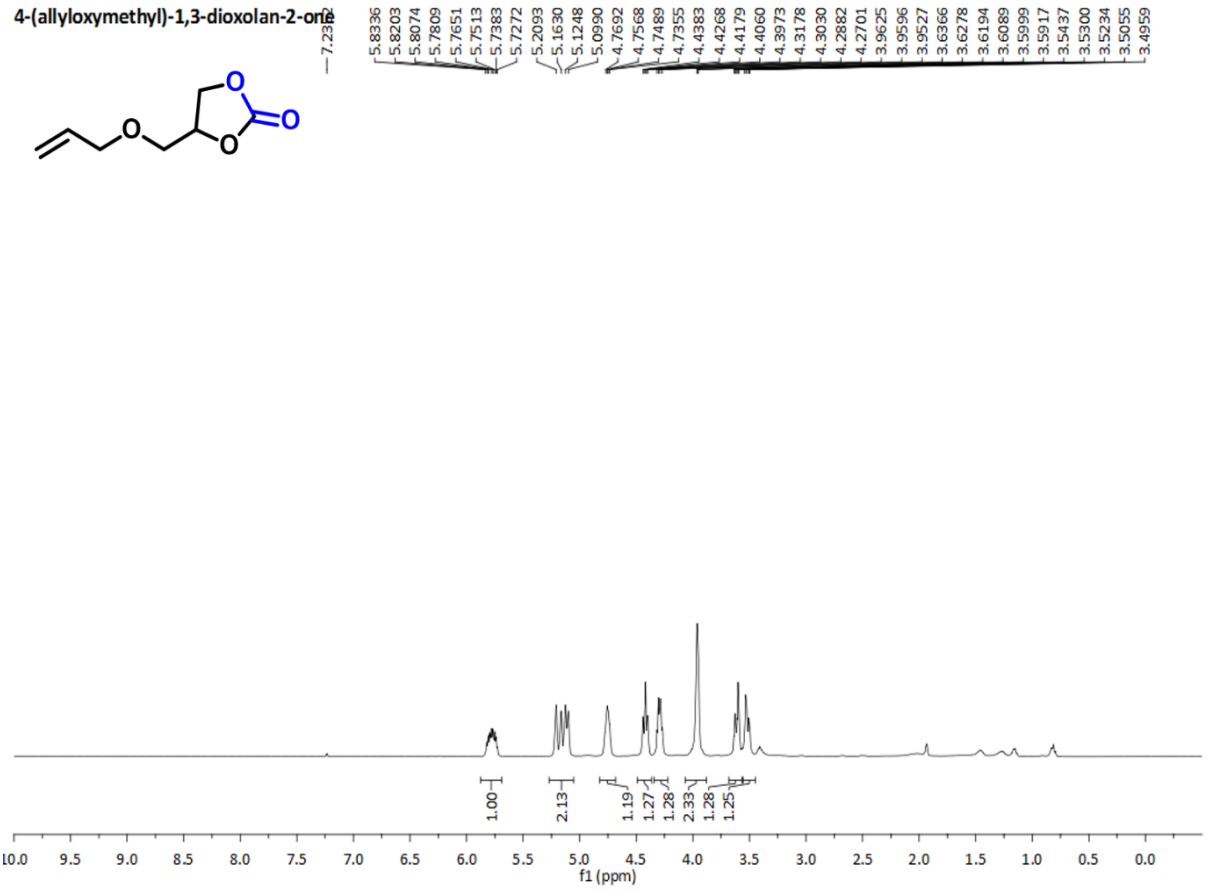


Fig. S19 ^{1}H NMR spectrum of 4-((allyloxy)methyl)-1,3-dioxolan-2-one, synthesized from the CO_2-allyl glycidyl ether cycloaddition reaction using NSC-773 catalyst.

4-(butoxymethyl)-1,3-dioxolan-2-one

Appearance: colourless liquid**,** Isolated yield: 89 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.79-4.73 (m, 1H), 4.44 (t, *J*=8.3 Hz, 1H), 4.32 (t, *J*=7.14 Hz, 1H), 3.63-3.60 (m, 1H), 3.55-3.52 (m, 1H), 3.45 (t, *J*=6.42 Hz, 2H), 1.53-1.46 (m, 2H), 1.36-1.26 (m, 2H), 0.85 (t, *J*=7.3 Hz, 3H). FTIR (ν_{max}/ cm^{-1}) 1795 (C=O), 1053 (C-O), 2924 (C-H).

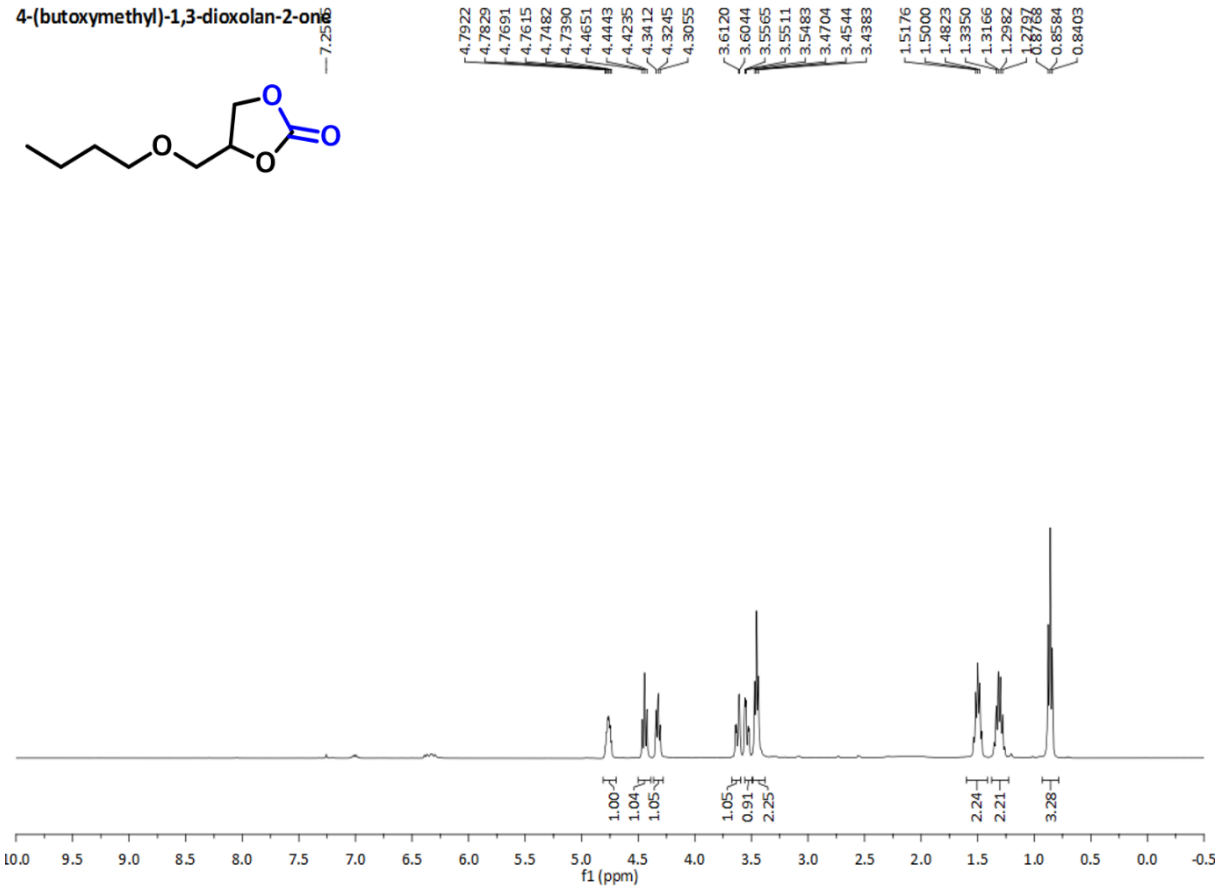


Fig. S20 ^{1}H NMR spectrum of 4-(butoxymethyl)-1,3-dioxolan-2-one, synthesized from the CO_2-n-butyl glycidyl ether cycloaddition reaction using NSC-773 catalyst.

4-hexyl-1,3-dioxolan-2-one

Appearance: pale yellow liquid**,** Isolated yield: 42 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.70-4.65 (m, 1H), 4.53-4.43 (m, 1H), 4.05 (t, *J*=7.7 Hz, 1H), 1.81-1.63 (m, 2H), 1.32-1.18 (m, 9H), 0.88-0.85 (m, 2H). FTIR (ν_{max}/ cm^{-1}) 1801 (C=O), 1062 (C-O), 2942 (C-H).

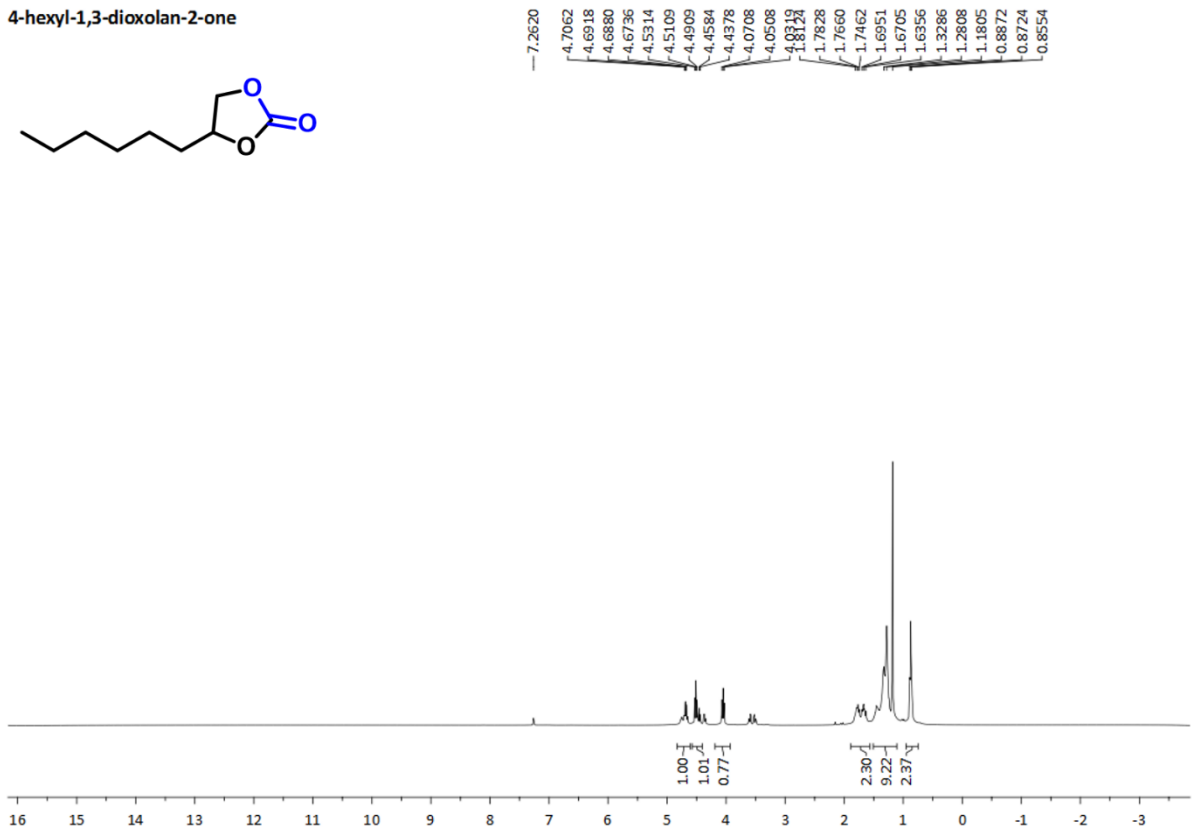


Fig. S21 ^{1}H NMR spectrum of 4-hexyl-1,3-dioxolan-2-one, synthesized from the CO_2-2-hexyloxirane cycloaddition reaction using NSC-773 catalyst.

4-(tert-butoxymethyl)-1,3-dioxolan-2-one

Appearance: brown liquid**,** Isolated yield: 63 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.78-4.72 (m, 1H), 4.46 (t, *J*=8.2 Hz, 1H), 4.38-4.35 (m, 1H), 3.60 (dd, *J*=4.5, 10.3 Hz, 1H), 3.52 (dd, *J*=6.4, 10.3 Hz, 1H), 1.18 (s, 9H). FTIR (ν_{max}/ cm^{-1}) 1794 (C=O), 1056 (C-O), 2975 (C-H).

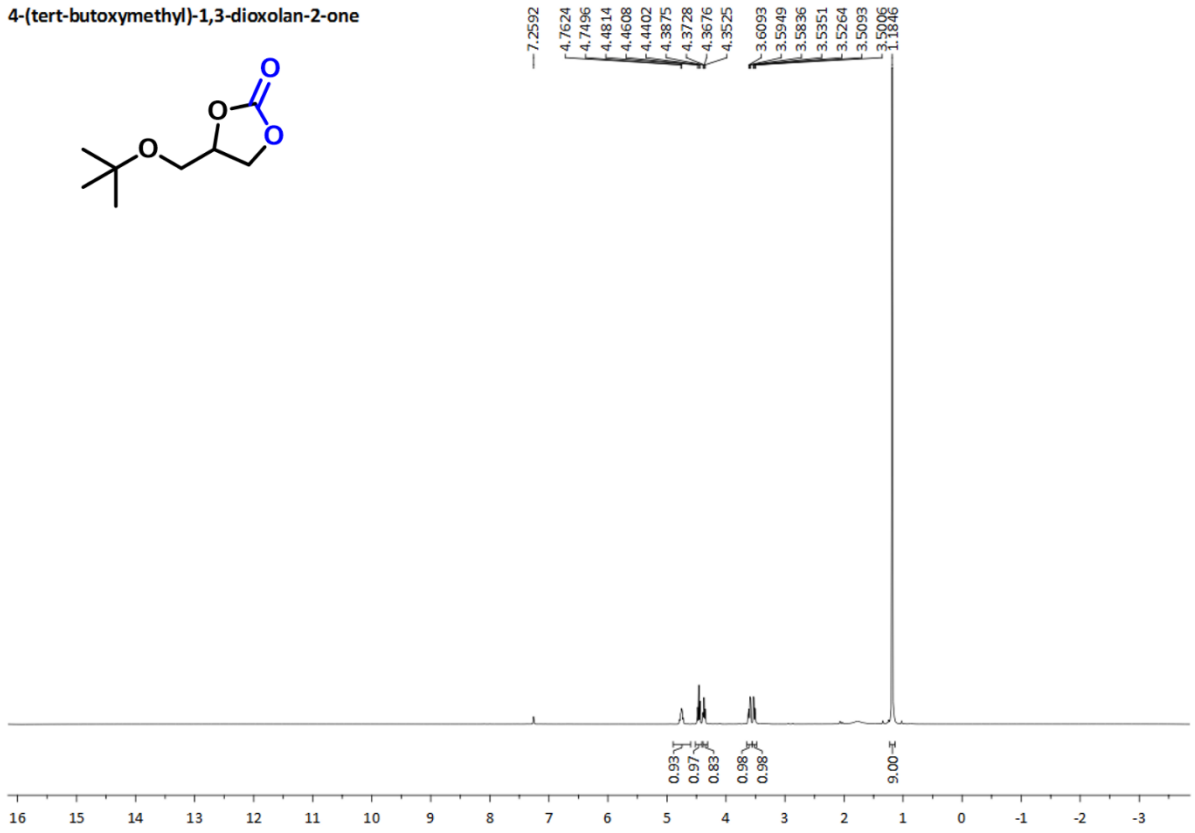


Fig. S22 ^{1}H NMR spectrum of 4-(tert-butoxymethyl)-1,3-dioxolan-2-one, synthesized from the CO_2-2-(tert-butoxymethyl) oxirane cycloaddition reaction using NSC-773 catalyst.

Styrene carbonate:

Appearance: white solid**,** Isolated yield: 61 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.42-7.32 (m, 5H), 5.65 (t, *J*=8 Hz, 1H), 4.78 (t, *J*=8.4 Hz, 1H), 4.32 (t, *J*=8.2 Hz, 1H). FTIR (ν_{max}/ cm^{-1}) 1797 (C=O) 1076 (C-O), 3043 (C-H).

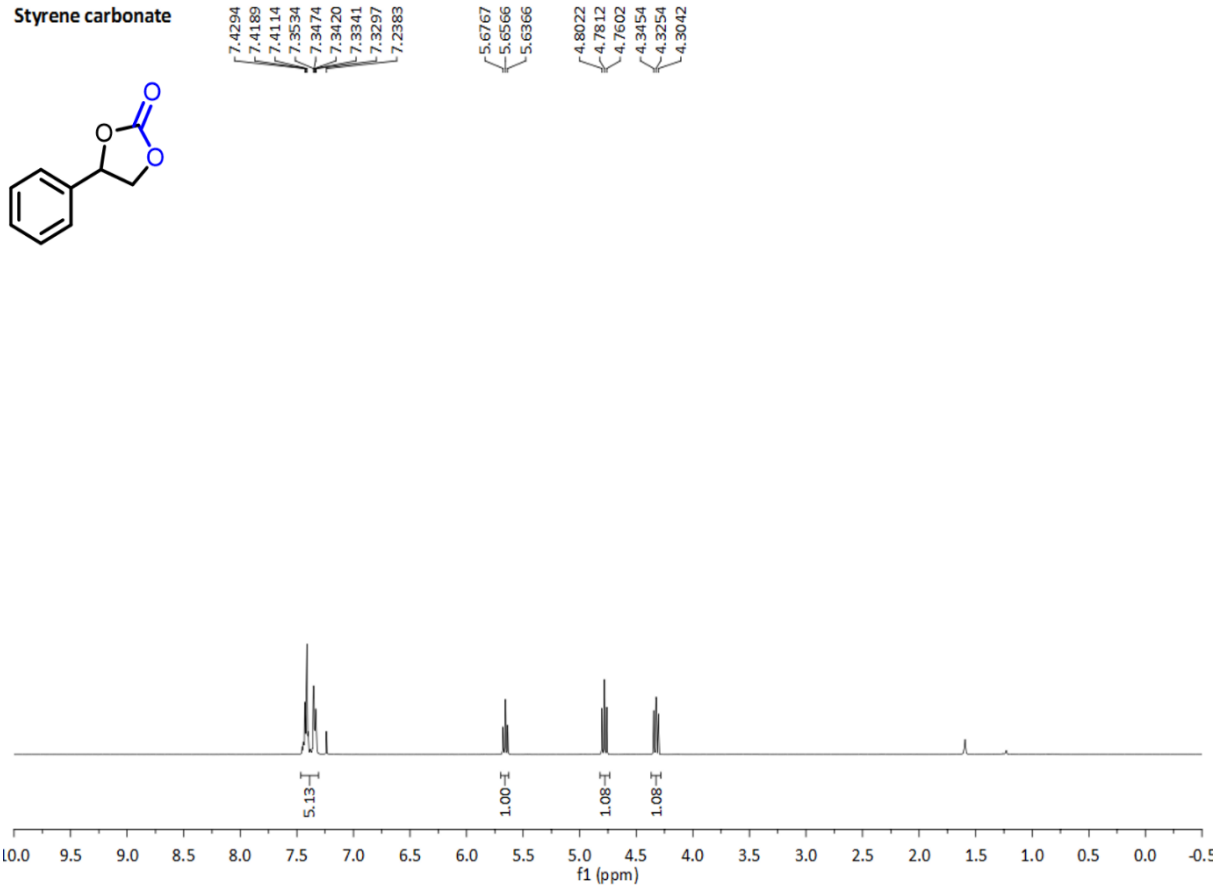


Fig. S23 ^{1}H NMR spectrum of styrene carbonate, synthesized from the CO_2-styrene oxide cycloaddition reaction using NSC-773 catalyst.

4-(phenoxymethyl)-1,3-dioxolan-2-one

Appearance: white solid**,** Isolated yield: 71 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 7.32-7.26 (m, 2H), 7.01 (t, *J*= 7.3 Hz, 1H), 6.92-6.89 (m, 2H), 5.05-4.99 (m, 1H), 4.60 (t, *J*= 8.4 Hz, 1H), 4.54-4.51 (m, 1H), 4.23 (dd, *J*= 4.0, 10.6, 1H), 4.13 (dd, *J*= 3.5, 10.6 Hz, 1H). FTIR (ν_{max}/ cm^{-1}) 1801 (C=O), 1091 (C-O), 2924 (C-H).

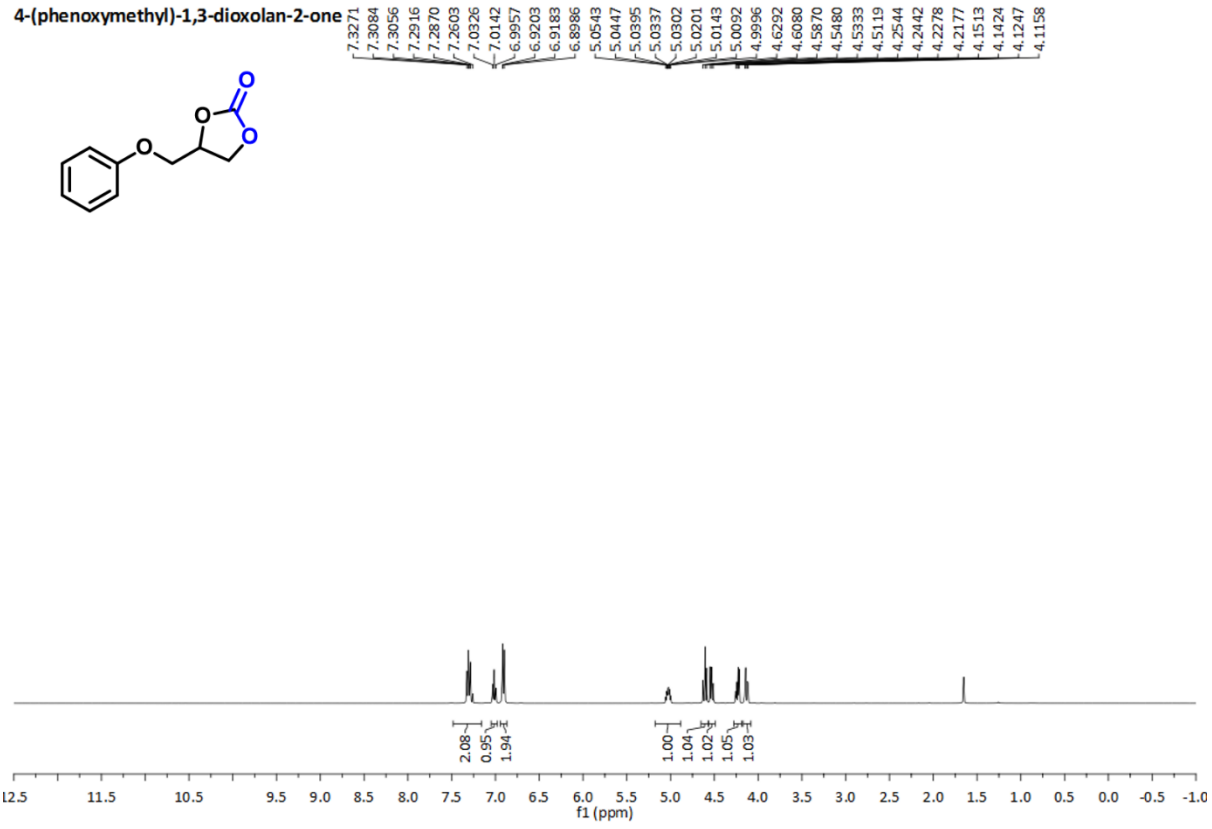


Fig. S24 ^{1}H NMR spectrum of 4-(phenoxymethyl)-1,3-dioxolan-2-one, synthesized from the CO_2-phenyl glycidyl ether cycloaddition reaction using NSC-773 catalyst.

Hexahydro-benzo [1,3] dioxol-2-one:

Appearance: Pale yellow liquid, Isolated yield: 47 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 4.69-4.07 (m, 2H), 1.87-1.85 (m, 4H), 1.64-4.54 (m, 2H), 1.44-1.35 (m, 2H). FTIR (ν_{max}/ cm^{-1}) 1801 (C=O), 1027, (C-O), 2936 (C-H).

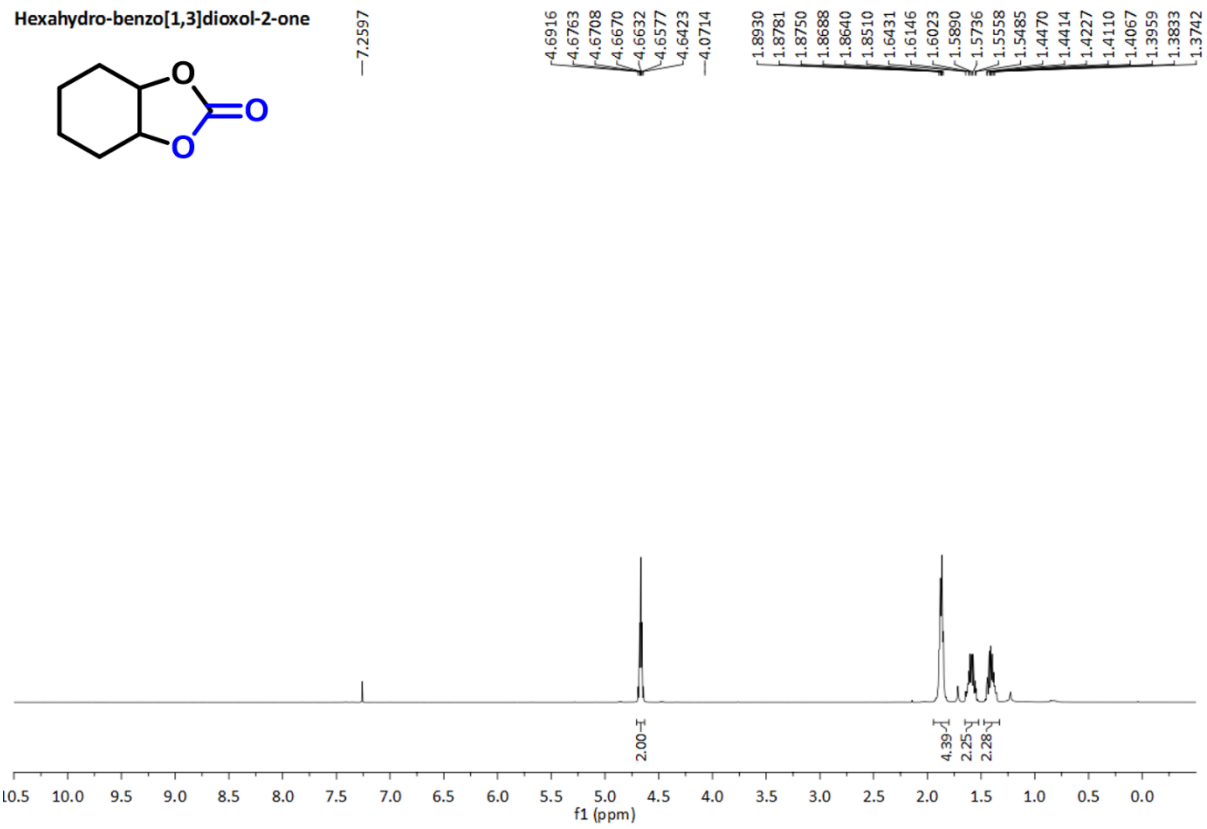


Fig. S25 ^{1}H NMR spectrum of hexahydro-benzo [1,3] dioxol-2-one, synthesized from the CO_2-cyclohexene oxide cycloaddition reaction using NSC-773 catalyst.

Pentahydro-cyclopenta [1,3] dioxal-2-one:

Appearance: white solid**,** Isolated yield: 26 %

^{1}H NMR ($CDCl_3$, 400 MHz) δ (ppm): 5.05-5.04 (m, 2H), 2.08-2.02 (m, 2H), 1.74-1.61 (m, 4H). FTIR (ν_{max}/ cm^{-1}) 1795 (C=O), 1041 (C-O), 2977 (C-H).

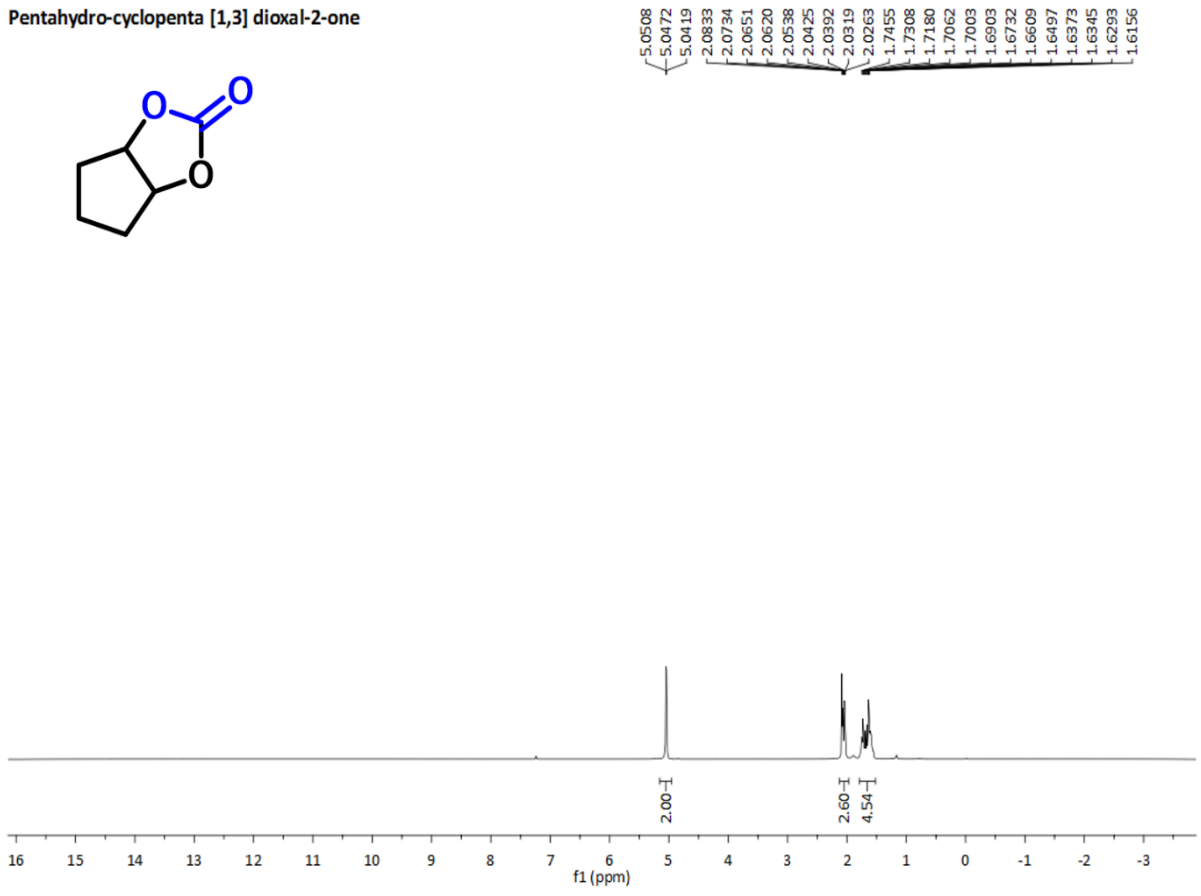


Fig. S26 ^{1}H NMR spectrum of pentahydro-cyclopenta [1,3] dioxal-2-one, synthesized from the CO_2-cyclopentene oxide cycloaddition reaction using NSC-773 catalyst.

Trans-1,2-limonene oxide:

Appearance: colourless reaction mixture turned into greenish

^{1}H NMR ($CDCl_3$, 400 MHz) of reaction mixture: δ (ppm)= 4.36-4.28 (m, 1H) is the characteristic signal of trans-1,2-limonene oxide. FTIR (ν_{max}/ cm^{-1}) 1798 (C=O), 1036 (C-O), 2961 (C-H).

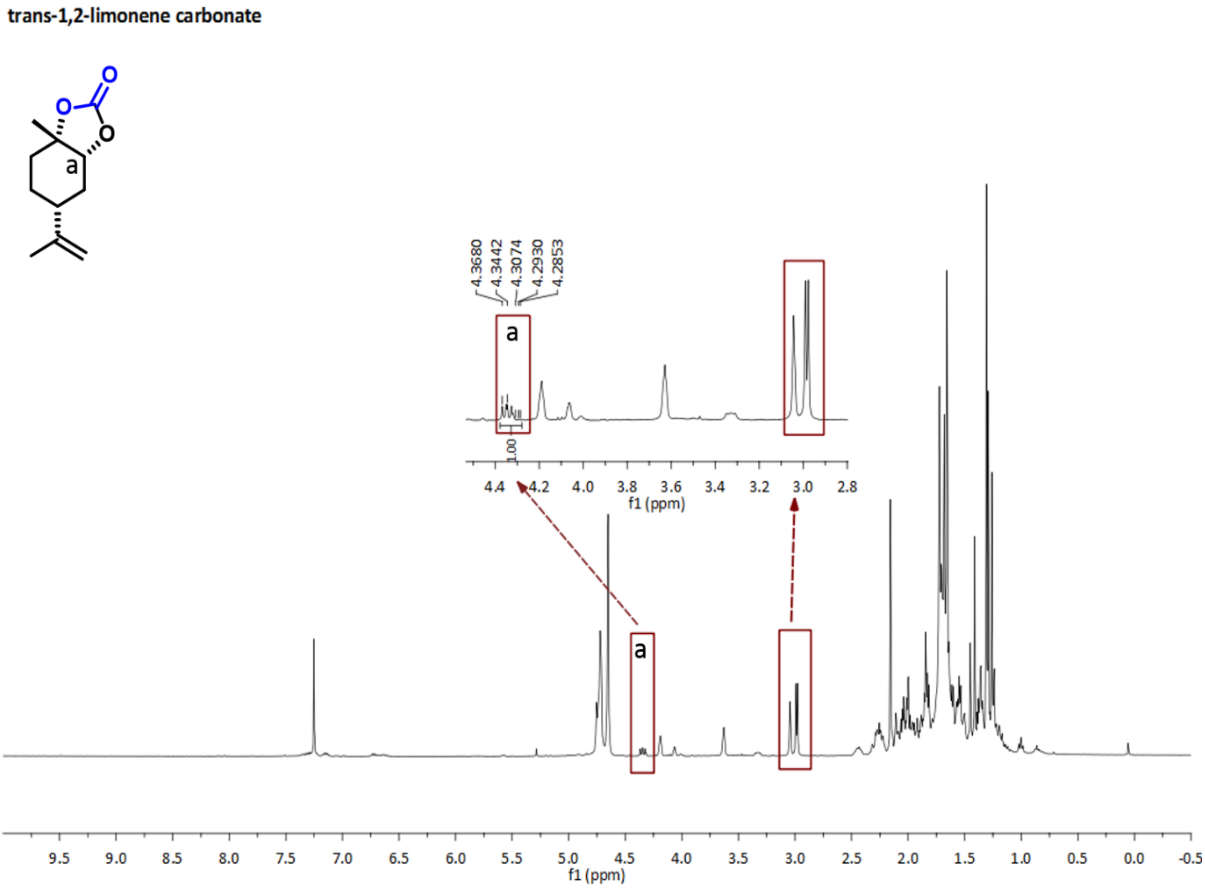


Fig. S27 ^{1}H NMR spectrum of trans-1,2-limonene oxide containing reaction mixture, obtained from the CO_2- cis/trans mixtures of 1,2-limomene oxide cycloaddition reaction using NSC-773 catalyst.

Section S11: Calculations

$$\textit{Conversion of}\ \text{epichlorohydrin}\ (\%) = \frac{\text{initial moles of epichlorohydrin} - \text{final moles of epichlorohydrin}}{\text{initial moles of epichlorohydrin}} \times 100$$

$$\textit{Selectivity of cyclic carbonate}\ (\%) = \frac{\text{moles of the cyclic carbonate formed}}{\text{moles of epichlorohydrin converted}} \times 100$$

The conversion of epichlorohydrin and selectivity of the corresponding carbonate were calculated by plotting the calibration curve through manually injecting standard epichlorohydrin and corresponding carbonate while for the other substrates, the internal standard was used for the calculation.

Section S12: FTIR analysis of various cyclic carbonates

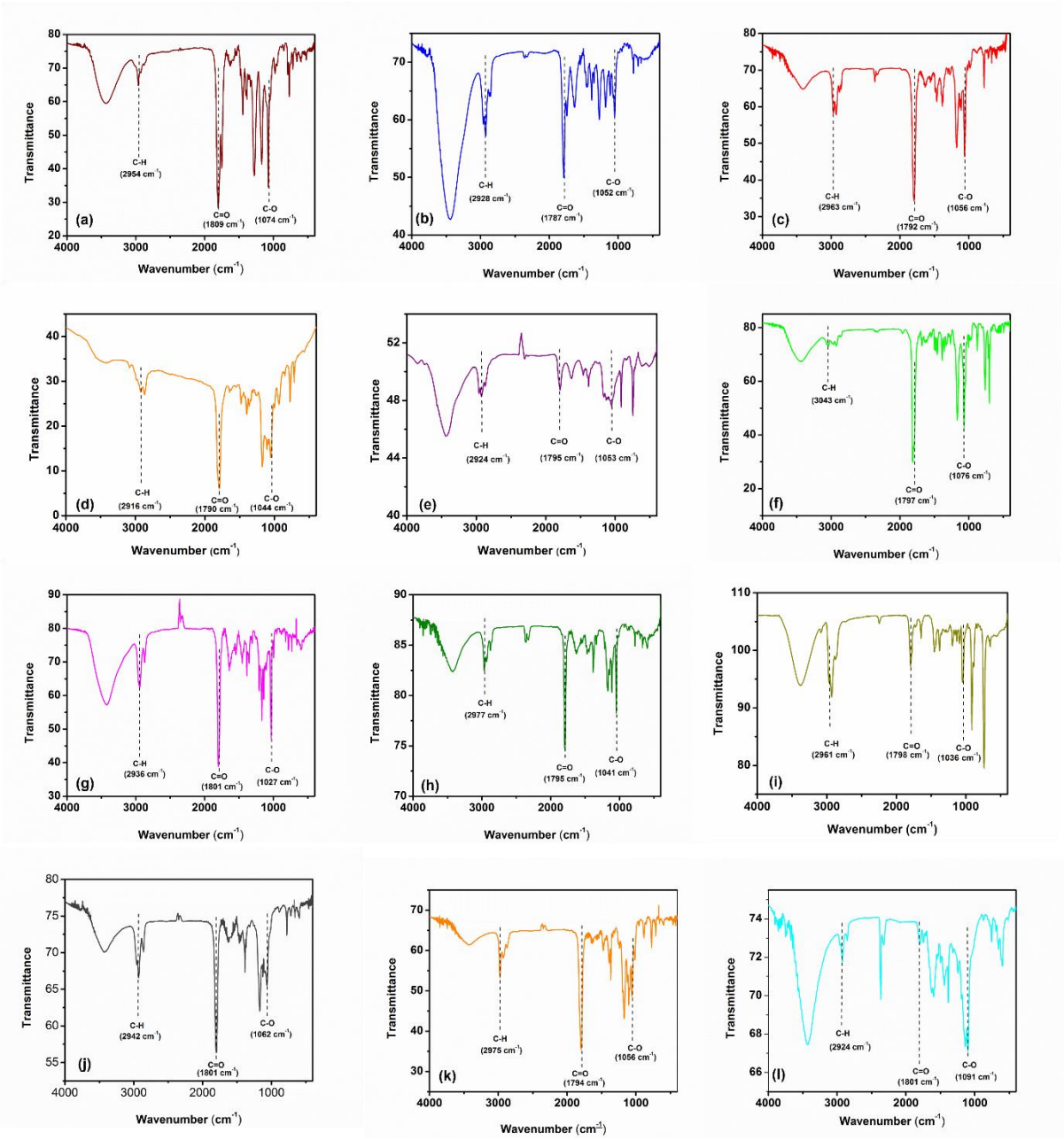
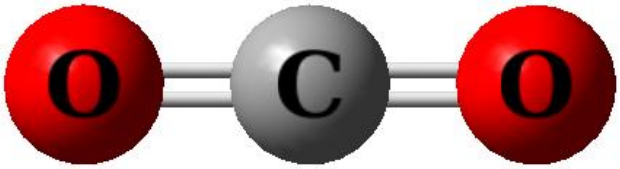


Fig. S28 FTIR analysis of respective cyclic carbonates of (a) epichlorohydrin; (b) propylene oxide; (c) 1,2-epoxybutane; (d) 4-((allyloxy)methyl)-1,3-dioxolan-2-one; (e) 4-(butoxymethyl)-1,3-dioxolan-2-one; (f) styrene oxide; (g) cyclohexene oxide; (h) cyclopentene oxide; (i) trans-1,2-limonene carbonate; (j) 4-hexyl-1,3-dioxolan-2-one; (k) 4-(tert-butoxymethyl)-1,3-dioxolan-2-one and (l) 4-(phenoxymethyl)-1,3-dioxolan-2-one.

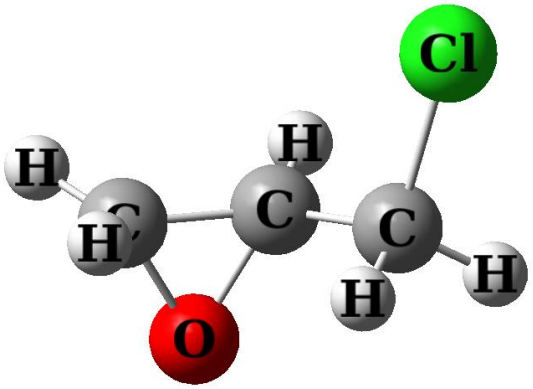
Section S13: Computational details



E = -188.5088194385 au

C	-3.51167	2.43022	0.00000
O	-2.34921	2.41428	0.00000
O	-4.67415	2.44613	0.00000

Fig. S29 Optimized geometry, energy, and Cartesian coordinates of CO_2 molecule at M06-2X level of theory with 6-31G(d, p) basis set.

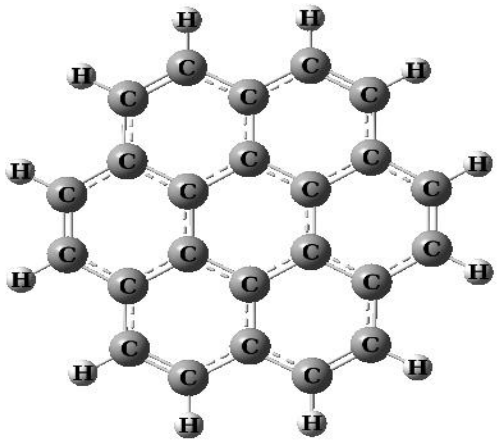


E = -652.5889146489 au

C	-9.61716	3.27833	0.07373
C	-8.16635	3.12150	0.21127
C	-7.41787	2.19548	-0.70650
Cl	-7.29134	0.56397	0.02952
H	-6.40214	2.54665	-0.88960

H	-7.94556	2.09968	-1.65605
O	-8.71652	4.25695	-0.42862
H	-10.20688	3.58537	0.93343
H	-10.14109	2.69450	-0.68080
H	-7.70421	3.30633	1.18002

Fig. S30 Optimized geometry, energy, and Cartesian coordinates of epichlorohydrin molecule at M06-2X level of theory with 6-31G(d, p) basis set.

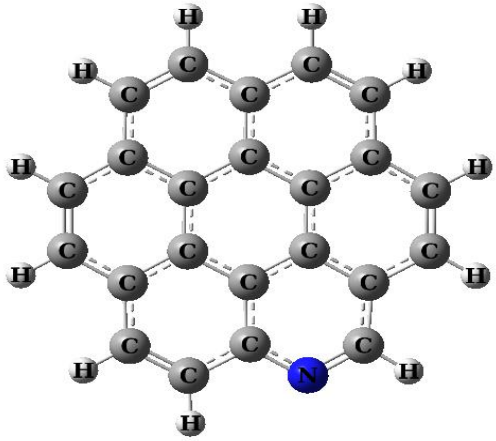


E = -921.5441224954 au

C	-5.64333	1.65394	-0.79494
C	-5.60603	0.33038	-0.45757
C	-4.44671	2.41621	-0.91610
C	-4.36931	-0.33245	-0.21538
C	-3.20752	1.78245	-0.68116
C	-3.16869	0.40091	-0.32893
C	-1.99449	2.52337	-0.79588
C	-0.74255	1.88305	-0.55846
C	-0.70372	0.50151	-0.20623
C	-1.91676	-0.23941	-0.09150
C	0.45807	2.61641	-0.67201
C	0.53545	-0.13226	0.02870
C	-1.87832	-1.60680	0.25711
C	-2.03293	3.89077	-1.14449
C	-4.30313	-1.71038	0.13765
C	-4.45802	3.79646	-1.26638
C	-3.10367	-2.32396	0.36513
C	-0.61547	-2.22241	0.48895
C	0.54677	-1.51250	0.37898
H	1.50340	-1.99496	0.55873
C	1.73208	0.63001	-0.09246
C	-3.29578	4.50637	-1.37633
C	-0.80758	4.60792	-1.25251
C	0.39188	3.99433	-1.02503
C	1.69478	1.95357	-0.42983

H	-0.84336	5.65994	-1.52123
H	1.31919	4.55373	-1.11106
H	-6.52679	-0.23928	-0.36860
H	-6.59403	2.14713	-0.97698
H	2.61554	2.52323	-0.51880
H	2.68278	0.13681	0.08956
H	-5.41465	4.27891	-1.44612
H	-5.23045	-2.26976	0.22368
H	-3.06788	-3.37597	0.63385
H	-0.59223	-3.27493	0.75705
H	-3.31903	5.55889	-1.64444

Fig. S31 Optimized geometry, total energy, and Cartesian coordinates of coronene at M06-2X level of theory with 6-31G(d, p) basis set.

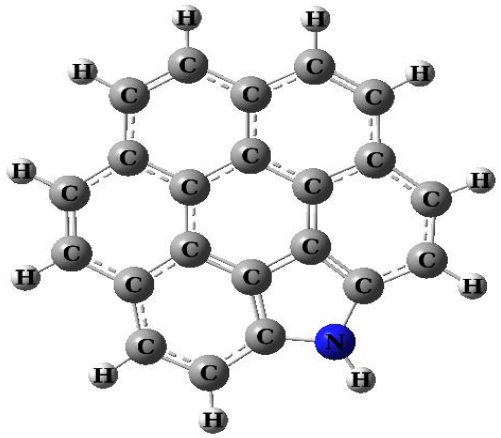


E = -937.5785019451 au

C	-5.63181	1.67547	-0.79954
C	-5.60601	0.34923	-0.46222
C	-4.42214	2.41551	-0.91427
C	-4.37603	-0.33166	-0.21587
C	-3.20190	1.76419	-0.67586
C	-3.16860	0.38702	-0.32513
C	-1.99917	2.50580	-0.79150
C	-0.74593	1.87781	-0.55708
C	-0.70465	0.49727	-0.20499
C	-1.91578	-0.24788	-0.08914
C	0.44301	2.62484	-0.67490
C	0.53590	-0.13075	0.02844
C	-1.87862	-1.61369	0.25870
C	-2.07090	3.86695	-1.14089
C	-4.31107	-1.71057	0.13706
C	-4.36348	3.79979	-1.26175
C	-3.10962	-2.32417	0.36453
C	-0.61308	-2.22591	0.48968

C	0.54802	-1.51217	0.37882
H	1.50500	-1.99397	0.55827
C	1.72726	0.64210	-0.09572
N	-3.26397	4.49869	-1.37290
C	-0.85797	4.60461	-1.25500
C	0.35055	4.00318	-1.02985
C	1.68347	1.96675	-0.43371
H	-0.93169	5.65247	-1.52517
H	1.26898	4.57652	-1.12008
H	-6.53290	-0.21061	-0.37624
H	-6.57688	2.17848	-0.98387
H	2.60272	2.53865	-0.52344
H	2.68179	0.15582	0.08468
H	-5.29833	4.32802	-1.45202
H	-5.23698	-2.27190	0.22352
H	-3.07815	-3.37653	0.63283
H	-0.58525	-3.27826	0.75778

Fig. S32 Optimized geometry, total energy, and Cartesian coordinates of pyridine functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.

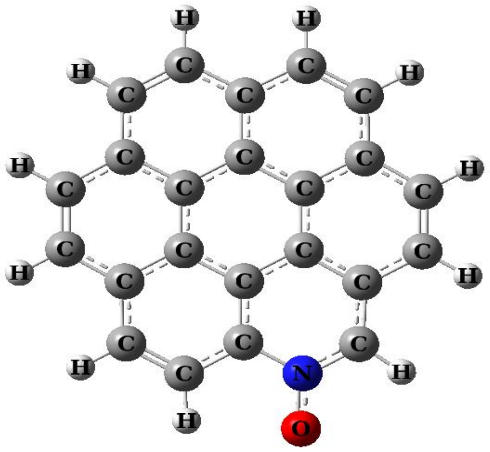


E = -899.4503842825 au

C	-5.51361	1.77343	-0.82242
C	-5.55638	0.41740	-0.47983
C	-4.25148	2.41157	-0.90812
C	-4.40421	-0.38634	-0.20541
C	-3.16392	1.60122	-0.63560
C	-3.16546	0.26259	-0.29505
C	-1.99904	2.34041	-0.75294
C	-0.74730	1.79725	-0.53855
C	-0.69415	0.41894	-0.18462
C	-1.89889	-0.34575	-0.06351
C	0.36320	2.63919	-0.68536
C	0.56036	-0.16447	0.03993
C	-1.86415	-1.70334	0.28344

C	-2.31394	3.64108	-1.10334
C	-4.33471	-1.77600	0.15189
N	-3.71845	3.68228	-1.19929
C	-3.12688	-2.39005	0.38110
C	-0.58025	-2.28265	0.50866
C	0.57937	-1.54664	0.39230
H	1.53665	-2.02829	0.57292
C	1.71597	0.68363	-0.10546
C	-1.20406	4.50830	-1.25668
C	0.08083	3.99487	-1.04775
C	1.63358	2.01180	-0.44842
H	-1.31631	5.55238	-1.52939
H	0.91806	4.67649	-1.17039
H	-6.53406	-0.05284	-0.41970
H	-6.44383	2.29839	-1.01268
H	2.54566	2.59508	-0.54143
H	2.69468	0.24340	0.06592
H	-4.25925	4.49637	-1.43953
H	-5.25090	-2.35312	0.24291
H	-3.11354	-3.44306	0.64946
H	-0.51962	-3.33341	0.77932

Fig. S33 Optimized geometry, total energy, and Cartesian coordinates of pyrrole functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.

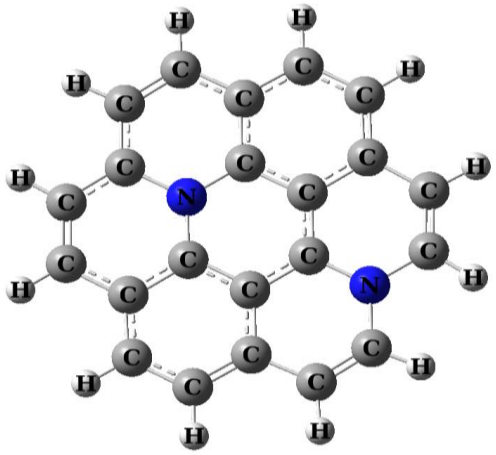


E = -1012.7104847862 au

C	-5.64168	1.67357	-0.80457
C	-5.60869	0.34840	-0.46495
C	-4.43370	2.42072	-0.92191
C	-4.37972	-0.33064	-0.21755
C	-3.21298	1.76752	-0.68142
C	-3.17560	0.39424	-0.32923
C	-2.01150	2.51322	-0.79876
C	-0.75424	1.88976	-0.56364

C	-0.71241	0.50910	-0.20933
C	-1.92130	-0.23841	-0.09216
C	0.43546	2.63745	-0.68211
C	0.52940	-0.11611	0.02501
C	-1.88130	-1.60370	0.25788
C	-2.04528	3.86735	-1.14625
C	-4.31165	-1.70830	0.13745
C	-4.41535	3.79008	-1.27024
C	-3.10964	-2.31955	0.36581
C	-0.61457	-2.21212	0.48947
C	0.54518	-1.49603	0.37735
H	1.50329	-1.97520	0.55739
C	1.72071	0.65749	-0.09993
N	-3.28293	4.49611	-1.38194
C	-0.85753	4.62180	-1.26662
C	0.34865	4.01327	-1.03820
C	1.67752	1.98044	-0.43948
H	-0.94768	5.66547	-1.53830
H	1.26731	4.58539	-1.12847
H	-6.53559	-0.21141	-0.37845
H	-6.58901	2.17077	-0.98873
H	2.59554	2.55369	-0.53002
H	2.67515	0.17148	0.08161
H	-5.30898	4.36611	-1.47152
H	-5.23676	-2.27090	0.22478
H	-3.07449	-3.37111	0.63580
H	-0.58424	-3.26391	0.75922
O	-3.29740	5.72515	-1.69679

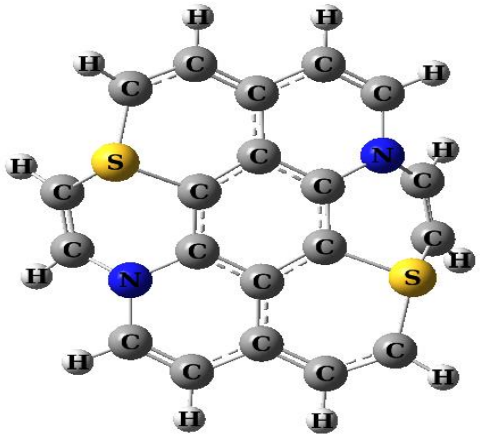
Fig. S34 Optimized geometry, total energy, and Cartesian coordinates of pyridinium oxide functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.



E = -954.7032003489 au

C	-5.61539	1.65380	-0.79320
C	-5.61961	0.33948	-0.46054
C	-4.43532	2.41048	-0.91399
C	-4.36781	-0.32844	-0.21622
N	-3.18878	1.77282	-0.67758
C	-3.15776	0.42657	-0.33474
C	-2.01034	2.50019	-0.79098
C	-0.75650	1.86942	-0.55592
C	-0.72252	0.51105	-0.20982
C	-1.91304	-0.22061	-0.09605
C	0.45843	2.62622	-0.67457
N	0.50463	-0.11676	0.02295
C	-1.88688	-1.61239	0.25801
C	-2.03533	3.88709	-1.14374
C	-4.29476	-1.67391	0.12888
C	-4.44211	3.77438	-1.25994
C	-3.06616	-2.30826	0.36333
C	-0.57315	-2.20223	0.48648
C	0.53938	-1.47163	0.36832
C	1.69253	0.61257	-0.09042
C	-3.31092	4.51207	-1.37879
C	-0.83418	4.58065	-1.24713
C	0.39951	3.95551	-1.01473
C	1.70118	1.90804	-0.41798
H	-0.87145	5.63075	-1.51542
H	1.32090	4.52366	-1.10331
H	-6.54033	-0.22452	-0.37296
H	-6.54349	2.18381	-0.98327
H	2.64474	2.43505	-0.49470
H	2.59112	0.04144	0.10830
H	-5.41780	4.21840	-1.43104
H	-5.22120	-2.23111	0.21441
H	-3.04107	-3.36043	0.63143
H	-0.50079	-3.24912	0.75614
H	-3.33878	5.56142	-1.64639
H	1.53407	-1.86907	0.52885

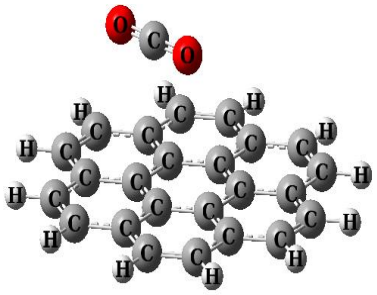
Fig. S35 Optimized geometry, total energy, and Cartesian coordinates of quaternary-N functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.



E = -1674.5896061273 au

C	-5.69795	1.84700	-0.43695
C	-5.87625	0.57616	0.10721
C	-4.50434	2.51232	-0.63361
S	-4.56733	-0.44074	0.54647
C	-3.25172	1.88789	-0.27509
C	-3.14047	0.56708	0.19634
C	-2.03567	2.58291	-0.41512
C	-0.84125	1.98235	-0.02004
C	-0.71504	0.59833	0.19840
C	-1.92667	-0.11500	0.26536
S	0.56551	3.07598	-0.02858
C	0.55194	-0.08578	0.31734
N	-1.91199	-1.53059	0.26780
N	-2.01073	3.83311	-1.07899
C	-4.13689	-1.75430	-0.61665
C	-4.42110	3.87470	-1.10414
C	-2.88526	-2.21142	-0.45644
C	-0.67282	-2.18694	0.51607
C	1.73425	0.62711	0.31062
C	-3.25092	4.49439	-1.30806
C	-0.94462	4.12021	-1.92530
C	0.30364	3.67577	-1.71207
C	1.88627	2.00902	0.21060
H	-1.20939	4.70609	-2.80239
H	1.14267	3.79976	-2.38206
H	-6.83224	0.20987	0.44888
H	-6.61456	2.39523	-0.65058
H	2.80805	2.51936	0.44446
H	2.65326	0.06852	0.48321
H	-5.33964	4.42770	-1.27524
H	-2.54104	-3.13300	-0.91997
H	-3.15921	5.52463	-1.62549
C	0.48405	-1.51142	0.53500
H	-0.75727	-3.24779	0.71118
H	-4.89951	-2.20188	-1.23818
H	1.40017	-2.05401	0.74740

Fig. S36 Optimized geometry, total energy, and Cartesian coordinates of N, S co-doped coronene at M06-2X level of theory with 6-31G(d, p) basis set.

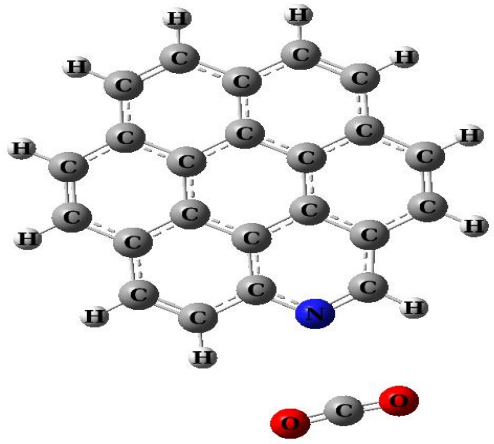


E = -1110.0592831720 au

C	-5.63534	1.62403	-0.92824
C	-5.60083	0.31034	-0.55556
C	-4.43876	2.38566	-1.05183
C	-4.36701	-0.34391	-0.27848
C	-3.20097	1.76043	-0.78599
C	-3.16488	0.38709	-0.39721
C	-1.98793	2.50368	-0.88962
C	-0.73973	1.87406	-0.60901
C	-0.70362	0.50220	-0.22210
C	-1.91566	-0.24111	-0.11516
C	0.45987	2.60992	-0.71225
C	0.53184	-0.12006	0.05689
C	-1.88083	-1.59753	0.27405
C	-2.02461	3.86371	-1.26593
C	-4.30378	-1.71049	0.11699
C	-4.44756	3.75874	-1.42935
C	-3.10671	-2.31403	0.38146
C	-0.62119	-2.20204	0.54888
C	0.54040	-1.49067	0.44357
H	1.49478	-1.96380	0.65691
C	1.72812	0.64373	-0.05700
C	-3.28523	4.46968	-1.53308
C	-0.79989	4.58363	-1.36316
C	0.39629	3.97947	-1.09745
C	1.69342	1.95842	-0.42726
H	-0.83411	5.62969	-1.65431
H	1.32342	4.54036	-1.17526
H	-6.52199	-0.25725	-0.45946
H	-6.58422	2.11208	-1.13152
H	2.61354	2.53014	-0.50914
H	2.67610	0.15902	0.15882
H	-5.40248	4.23482	-1.63308
H	-5.23157	-2.26840	0.20636
H	-3.07329	-3.35730	0.68267

H	-0.60051	-3.24652	0.84689
H	-3.30675	5.51697	-1.82110
C	-3.41262	1.88892	2.27765
O	-2.25190	1.92017	2.34737
O	-4.57456	1.86316	2.22650

Fig. S37 Optimized geometry, total energy, and Cartesian coordinates of Fig. 12(a) at M06-2X level of theory with 6-31G(d, p) basis set.

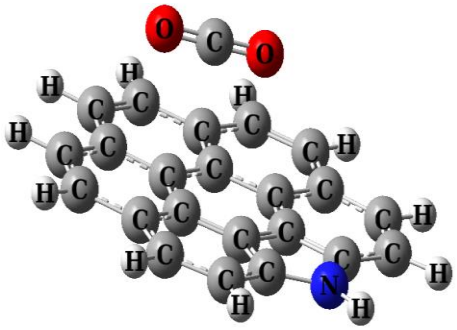


E = -1126.0981407474 au

C	-5.64088	1.63853	-0.80807
C	-5.60766	0.31484	-0.46243
C	-4.43482	2.38421	-0.92589
C	-4.37390	-0.35733	-0.21055
C	-3.21042	1.74207	-0.68117
C	-3.17012	0.36728	-0.32198
C	-2.01090	2.48892	-0.79927
C	-0.75489	1.86918	-0.55870
C	-0.70699	0.49111	-0.19867
C	-1.91428	-0.25968	-0.08070
C	0.42998	2.62215	-0.67908
C	0.53648	-0.12904	0.03984
C	-1.87036	-1.62340	0.27419
C	-2.08601	3.84704	-1.15825
C	-4.30215	-1.73390	0.14980
C	-4.38555	3.76467	-1.28420
C	-3.09772	-2.33981	0.38200
C	-0.60198	-2.22788	0.51001
C	0.55547	-1.50860	0.39725
H	1.51484	-1.98416	0.58043
C	1.72388	0.64961	-0.08661
N	-3.28577	4.46434	-1.39709
C	-0.87896	4.59354	-1.27576
C	0.33111	3.99755	-1.04320
C	1.67359	1.97208	-0.43197

H	-0.95789	5.63902	-1.55421
H	1.24707	4.57452	-1.13518
H	-6.53117	-0.25006	-0.37386
H	-6.58797	2.13578	-0.99682
H	2.58968	2.54869	-0.52341
H	2.68060	0.16928	0.09802
H	-5.31668	4.29556	-1.48365
H	-5.22529	-2.29943	0.23796
H	-3.06082	-3.39057	0.65579
H	-0.56931	-3.27871	0.78340
C	-3.82638	6.99562	-2.16722
O	-2.71586	7.34126	-2.19797
O	-4.95993	6.73127	-2.16209

Fig. S38 Optimized geometry, total energy, and Cartesian coordinates of Fig. 12(b) at M06-2X level of theory with 6-31G(d, p) basis set.

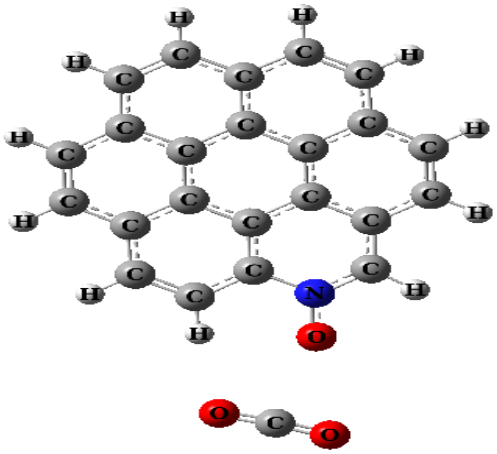


E = -1087.9632137127 au

C	-5.71362	1.68238	-1.43463
C	-5.73555	0.38536	-0.91092
C	-4.47830	2.37430	-1.47883
C	-4.58887	-0.30077	-0.39833
C	-3.38958	1.66656	-1.00251
C	-3.37537	0.39682	-0.45918
C	-2.26078	2.46644	-1.06235
C	-1.03048	2.05605	-0.58565
C	-0.95979	0.74766	-0.02425
C	-2.12902	-0.07796	0.03994
C	0.02967	2.97225	-0.63642
C	0.26445	0.31476	0.50504
C	-2.08564	-1.34930	0.62851
C	-2.60256	3.70536	-1.57507
C	-4.50837	-1.60592	0.19607
N	-3.98235	3.64026	-1.84553
C	-3.31766	-2.09457	0.67710
C	-0.82852	-1.78341	1.14450
C	0.29532	-0.98742	1.08629
H	1.23054	-1.35354	1.50115

C	1.37429	1.23002	0.43303
C	-1.54221	4.64246	-1.64354
C	-0.27694	4.25786	-1.18603
C	1.27286	2.49118	-0.10188
H	-1.68023	5.64744	-2.02838
H	0.52102	4.99306	-1.24218
H	-6.69344	-0.12662	-0.88150
H	-6.64031	2.12606	-1.78309
H	2.14577	3.13799	-0.10997
H	2.32855	0.90432	0.83797
H	-4.53469	4.39134	-2.22452
H	-5.40443	-2.21559	0.27418
H	-3.29620	-3.08410	1.12581
H	-0.76231	-2.76587	1.60428
C	-1.72797	2.54746	2.37085
O	-0.60667	2.70720	2.63606
O	-2.85534	2.39605	2.12662

Fig. S39 Optimized geometry, total energy, and Cartesian coordinates of Fig. 12(c) at M06-2X level of theory with 6-31G(d, p) basis set.

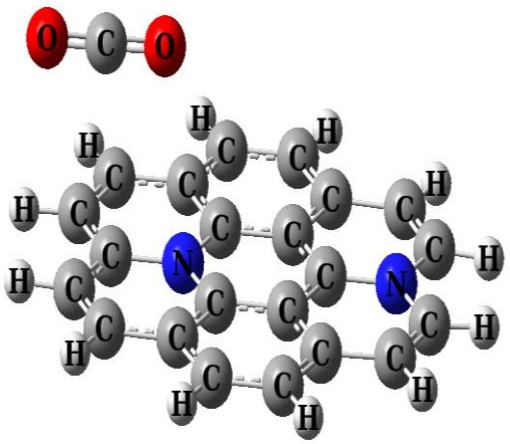


E = -1201.2274240666 au

C	-5.71526	1.52858	-0.78852
C	-5.62929	0.20993	-0.43386
C	-4.53687	2.31810	-0.92509
C	-4.37310	-0.41882	-0.18975
C	-3.28950	1.71580	-0.68881
C	-3.19770	0.34909	-0.32085
C	-2.11815	2.50500	-0.82572
C	-0.83684	1.93114	-0.59444
C	-0.74008	0.55781	-0.22418
C	-1.91875	-0.23313	-0.08725
C	0.32293	2.72127	-0.73234
C	0.52630	-0.01761	0.00691
C	-1.82458	-1.59131	0.27916

C	-2.20534	3.85384	-1.18823
C	-4.25045	-1.78827	0.18130
C	-4.57177	3.68309	-1.28851
C	-3.02432	-2.35094	0.40657
C	-0.53411	-2.14904	0.50719
C	0.59683	-1.39131	0.37597
H	1.57381	-1.83176	0.55333
C	1.68662	0.79833	-0.13798
N	-3.46840	4.42698	-1.41775
C	-1.04750	4.65168	-1.32818
C	0.18120	4.08823	-1.10328
C	1.59076	2.11438	-0.49313
H	-1.16854	5.69025	-1.60882
H	1.07680	4.69347	-1.20788
H	-6.53340	-0.38351	-0.33221
H	-6.68196	1.98810	-0.96975
H	2.48562	2.72069	-0.59873
H	2.66015	0.35073	0.04085
H	-5.48732	4.22443	-1.48824
H	-5.15303	-2.38386	0.28368
H	-2.94764	-3.39701	0.68907
H	-0.46200	-3.19545	0.78955
O	-3.54435	5.65501	-1.74866
C	-2.80853	8.14107	-2.13060
O	-3.92585	8.41817	-2.27844
O	-1.67061	7.92914	-1.99351

Fig. S40 Optimized geometry, total energy, and Cartesian coordinates of Fig. 12(d) at M06-2X level of theory with 6-31G(d, p) basis set.

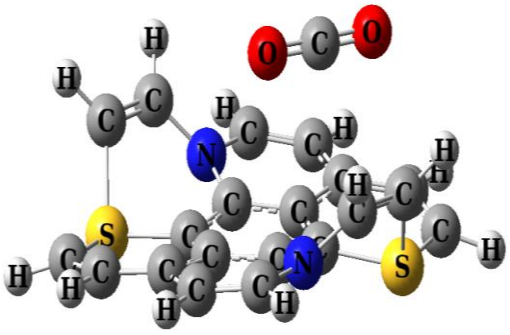


E = -1143.2200291133 au

C	-5.46028	1.68598	-0.36374
C	-5.49410	0.35189	-0.12412
C	-4.26279	2.39868	-0.56379
C	-4.25752	-0.38556	-0.07573
N	-3.02877	1.69280	-0.50335

C	-3.02999	0.32600	-0.26377
C	-1.83423	2.38167	-0.66005
C	-0.59558	1.68492	-0.60376
C	-0.59359	0.30057	-0.37857
C	-1.80191	-0.38958	-0.20484
C	0.63832	2.40017	-0.77426
N	0.61625	-0.39260	-0.32412
C	-1.80803	-1.80604	0.03341
C	-1.82515	3.79556	-0.88091
C	-4.21576	-1.75636	0.15346
C	-4.23677	3.78863	-0.78665
C	-3.00344	-2.45979	0.20578
C	-0.50948	-2.46532	0.07708
C	0.62025	-1.77257	-0.09504
C	1.82275	0.29468	-0.49472
C	-3.08579	4.49158	-0.93214
C	-0.60743	4.44753	-1.03795
C	0.61217	3.75670	-0.98631
C	1.86267	1.61322	-0.70824
H	-0.61929	5.51914	-1.20464
H	1.54691	4.29454	-1.11419
H	-6.42651	-0.17725	0.03057
H	-6.37442	2.27034	-0.40215
H	2.81884	2.10691	-0.83463
H	2.70684	-0.32826	-0.43824
H	-5.20210	4.28447	-0.81732
H	-5.15516	-2.27967	0.29465
H	-3.00417	-3.53072	0.38594
H	-0.46168	-3.53349	0.25227
H	-3.08753	5.56196	-1.09866
H	1.60557	-2.22133	-0.06999
C	-4.15724	3.36914	2.23684
O	-5.21929	3.84396	2.25894
O	-3.09227	2.90072	2.24771

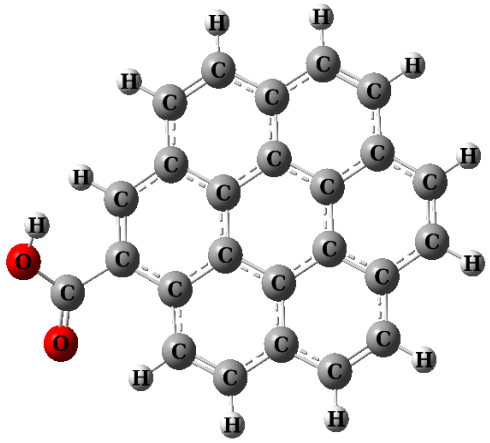
Fig. S41 Optimized geometry, total energy, and Cartesian coordinates of Fig. 12(e) at M06-2X level of theory with 6-31G(d, p) basis set.



E = -1863.1079686032 au

C	-5.81453	1.90862	-0.14145
C	-5.97888	0.63976	0.40882
C	-4.62395	2.55481	-0.41249
S	-4.66146	-0.40396	0.75009
C	-3.36299	1.91287	-0.12785
C	-3.24310	0.59172	0.34092
C	-2.14735	2.58647	-0.34837
C	-0.93852	1.96982	-0.02623
C	-0.82169	0.58252	0.19014
C	-2.03952	-0.10993	0.32932
S	0.48548	3.02848	-0.17810
C	0.43656	-0.12711	0.22010
N	-2.05107	-1.52503	0.30917
N	-2.14638	3.82207	-1.03915
C	-4.32028	-1.69504	-0.46610
C	-4.54984	3.91411	-0.89285
C	-3.06908	-2.17213	-0.38740
C	-0.81249	-2.20706	0.48149
C	1.62935	0.56235	0.12371
C	-3.38553	4.50983	-1.18284
C	-1.14990	4.05734	-1.98016
C	0.10096	3.58251	-1.85792
C	1.79579	1.94029	0.00364
H	-1.47242	4.63180	-2.84569
H	0.88619	3.66400	-2.59650
H	-6.91857	0.28354	0.80227
H	-6.73345	2.47249	-0.29652
H	2.74364	2.43581	0.14762
H	2.54800	-0.01243	0.23201
H	-5.46778	4.48393	-1.00024
H	-2.76048	-3.08104	-0.89858
H	-3.29534	5.53702	-1.51046
C	0.35585	-1.55241	0.43620
H	-0.90539	-3.26724	0.67648
H	-5.11998	-2.10525	-1.06639
H	1.27328	-2.11208	0.59048
C	-0.77668	0.69643	-2.88961
O	0.38479	0.69052	-2.95386
O	-1.94005	0.69330	-2.84965

Fig. S42 Optimized geometry, total energy, and Cartesian coordinates of Fig. 12(f) at M06-2X level of theory with 6-31G(d, p) basis set.

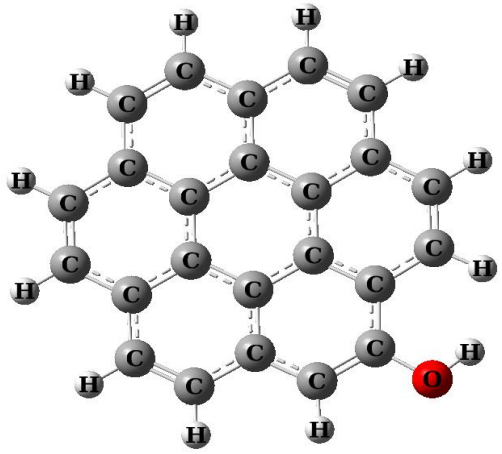


E = -1110.0449274228 au

C	-5.61078	1.60321	-0.80842
C	-5.58020	0.26725	-0.49100
C	-4.42653	2.37461	-0.92560
C	-4.33095	-0.40317	-0.26824
C	-3.18624	1.74600	-0.68962
C	-3.14040	0.35748	-0.35753
C	-1.98269	2.50488	-0.78880
C	-0.72459	1.88044	-0.54867
C	-0.67257	0.49682	-0.21215
C	-1.87655	-0.26288	-0.11832
C	0.46649	2.63165	-0.64453
C	0.57439	-0.12109	0.02538
C	-1.81474	-1.63270	0.21264
C	-2.03701	3.87550	-1.12495
C	-4.23909	-1.78571	0.06887
C	-4.45743	3.75603	-1.26881
C	-3.02607	-2.37034	0.29968
C	-0.54534	-2.23330	0.44863
C	0.60615	-1.50505	0.35875
H	1.56907	-1.97386	0.54032
C	1.76158	0.65826	-0.07662
C	-3.30385	4.47997	-1.36397
C	-0.82164	4.61108	-1.21615
C	0.38394	4.01170	-0.98415
C	1.71044	1.98474	-0.39938
H	-0.87049	5.66466	-1.47573
H	1.30413	4.58440	-1.05721
C	-6.88083	-0.48307	-0.43989
H	-6.55989	2.09115	-1.02092
H	2.62375	2.56791	-0.47463
H	2.71662	0.17465	0.10775
H	-5.41930	4.22561	-1.45382
H	-5.14601	-2.37313	0.12334
H	-2.97419	-3.42529	0.55353
H	-0.51086	-3.28879	0.70262

H	-3.33606	5.53383	-1.62485
O	-7.03855	-1.60747	-0.83317
O	-7.92591	0.21016	0.06551
H	-7.60807	1.02215	0.47955

Fig. S43 Optimized geometry, total energy, and Cartesian coordinates of -COOH functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.

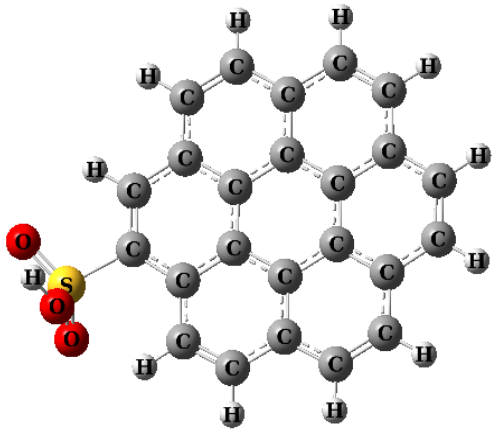


E = -996.7388837878 au

C	-5.64952	1.64839	-0.84748
C	-5.61060	0.33030	-0.48874
C	-4.45398	2.41351	-0.95575
C	-4.37623	-0.32139	-0.21151
C	-3.21625	1.78984	-0.68589
C	-3.17636	0.41513	-0.31165
C	-2.00421	2.53328	-0.78700
C	-0.75305	1.90288	-0.51413
C	-0.71263	0.52525	-0.13885
C	-1.92713	-0.21398	-0.03916
C	0.44197	2.64699	-0.61688
C	0.53035	-0.09358	0.13053
C	-1.88662	-1.57559	0.33170
C	-2.04279	3.89539	-1.15768
C	-4.30869	-1.69331	0.16427
C	-4.46404	3.78801	-1.32743
C	-3.11219	-2.29744	0.42568
C	-0.63617	-2.18521	0.59949
C	0.53261	-1.47711	0.50474
O	1.68551	-2.14122	0.77988
C	1.71902	0.68246	0.01848
C	-3.30310	4.50142	-1.42460
C	-0.82133	4.62002	-1.25304
C	0.37680	4.01867	-0.99253
C	1.67697	1.99979	-0.34076
H	-0.85965	5.66740	-1.53891
H	1.30301	4.58113	-1.06841

H	-6.52948	-0.24394	-0.40925
H	-6.59844	2.13397	-1.05644
H	2.59566	2.57357	-0.42033
H	2.69326	0.24300	0.21715
H	-5.41898	4.26300	-1.53406
H	-5.23450	-2.25683	0.24032
H	-3.07625	-3.34465	0.71140
H	-0.58709	-3.23054	0.88611
H	-3.32471	5.54958	-1.70930
H	2.44277	-1.55611	0.68453

Fig. S44 Optimized geometry, total energy, and Cartesian coordinates of -OH functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.

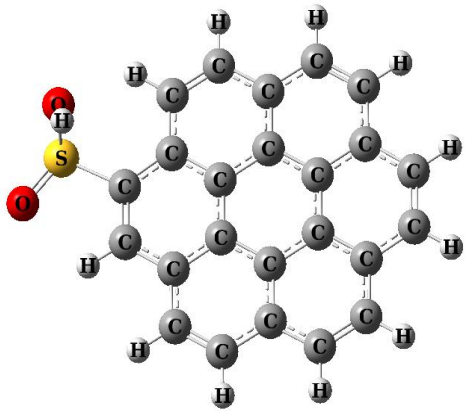


E = -1545.2282277791 au

C	-5.66039	1.65712	-0.87604
C	-5.62394	0.33671	-0.52453
C	-4.46000	2.40664	-0.98398
C	-4.40359	-0.36055	-0.25216
C	-3.23203	1.76659	-0.71344
C	-3.20477	0.38529	-0.34632
C	-2.01811	2.50916	-0.80697
C	-0.77116	1.87594	-0.53266
C	-0.73949	0.49957	-0.16555
C	-1.95307	-0.24432	-0.07326
C	0.42976	2.61153	-0.62378
C	0.49597	-0.12689	0.10660
C	-1.91314	-1.60662	0.29071
C	-2.05115	3.87377	-1.17074
C	-4.33683	-1.73598	0.11415
C	-4.47012	3.78191	-1.35041
C	-3.13368	-2.32852	0.37494
C	-0.65472	-2.21643	0.56002
C	0.50622	-1.50342	0.47152
H	1.46060	-1.97882	0.67897
C	1.69337	0.63677	0.00783

C	-3.30595	4.48957	-1.44054
C	-0.82568	4.59355	-1.25630
C	0.36868	3.98536	-0.99270
C	1.66204	1.95653	-0.34406
H	-0.85830	5.64223	-1.53713
H	1.29651	4.54610	-1.06172
S	-7.18947	-0.49562	-0.43111
H	-6.61621	2.13334	-1.07112
H	2.58284	2.52818	-0.41619
H	2.63969	0.14706	0.21881
H	-5.42396	4.25785	-1.55738
H	-5.24632	-2.32119	0.17424
H	-3.09843	-3.37833	0.65114
H	-0.63645	-3.26612	0.83835
H	-3.32065	5.53874	-1.72088
O	-7.14985	-1.70874	-1.21169
O	-8.24758	0.48318	-0.59697
O	-7.22849	-0.96965	1.11811
H	-7.75286	-0.32022	1.61258

Fig. S45 Optimized geometry, total energy, and Cartesian coordinates of -SO_3H functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.

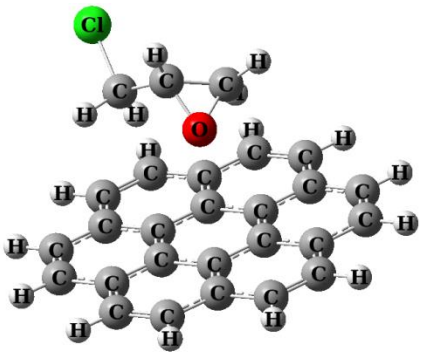


E = -1470.0402530163 au

C	-5.63185	1.74839	-0.56879
C	-5.59845	0.41514	-0.27766
C	-4.42647	2.48257	-0.73724
C	-4.37307	-0.30158	-0.10765
C	-3.19370	1.81447	-0.57463
C	-3.16718	0.42169	-0.25650
C	-1.97386	2.53713	-0.72561
C	-0.72426	1.87198	-0.55681
C	-0.69520	0.48329	-0.23738
C	-1.91483	-0.24122	-0.08857
C	0.48266	2.58829	-0.70432
C	0.54225	-0.17452	-0.06816

C	-1.88054	-1.61634	0.22653
C	-2.00334	3.91342	-1.04145
C	-4.31142	-1.69178	0.19880
C	-4.43145	3.87016	-1.05446
C	-3.10845	-2.31892	0.36420
C	-0.61958	-2.25730	0.39246
C	0.54746	-1.56259	0.25091
H	1.50333	-2.06225	0.37976
C	1.74561	0.57053	-0.22168
C	-3.26158	4.55956	-1.20262
C	-0.77148	4.61289	-1.18676
C	0.42531	3.97472	-1.02403
C	1.71710	1.90173	-0.52843
H	-0.80109	5.67100	-1.43032
H	1.35771	4.52056	-1.13698
S	-7.19000	-0.40364	-0.01321
H	-6.59642	2.24066	-0.66520
H	2.64256	2.45881	-0.64316
H	2.69407	0.05772	-0.08981
H	-5.38718	4.37119	-1.17595
H	-5.22920	-2.26232	0.28704
H	-3.07702	-3.37873	0.60013
H	-3.27475	5.61820	-1.44523
O	-8.20032	0.63076	-0.33574
O	-7.07488	-1.47062	-1.27193
H	-0.60364	-3.31595	0.63500
H	-6.92376	-0.97703	-2.09585

Fig. S46 Optimized geometry, total energy, and Cartesian coordinates of -SO_2H functionalized coronene at M06-2X level of theory with 6-31G(d, p) basis set.

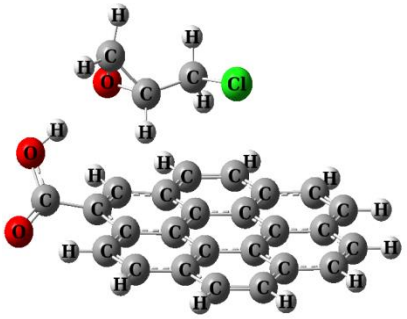


E = -1574.1449956670 au

C	-5.59341	1.75455	-0.65388
C	-5.54689	0.49323	-0.13079
C	-4.40168	2.49544	-0.89617
C	-4.30333	-0.12461	0.18517
C	-3.15725	1.90554	-0.58991
C	-3.10764	0.58686	-0.05198

C	-1.95067	2.63135	-0.81098
C	-0.69389	2.03930	-0.49319
C	-0.64230	0.71814	0.03980
C	-1.85010	-0.00719	0.26387
C	0.50033	2.76093	-0.70479
C	0.60259	0.13114	0.35483
C	-1.80058	-1.30791	0.81195
C	-2.00059	3.93758	-1.34120
C	-4.22708	-1.43344	0.74359
C	-4.42528	3.81410	-1.43342
C	-3.02243	-2.00346	1.04685
C	-0.53158	-1.87866	1.12014
C	0.62603	-1.18589	0.89727
H	1.58659	-1.63087	1.14100
C	1.79317	0.88217	0.13681
C	-3.26866	4.50830	-1.64852
C	-0.78150	4.64362	-1.54896
C	0.42330	4.07767	-1.24124
C	1.74301	2.14873	-0.37352
H	-0.82701	5.64930	-1.95735
H	1.34607	4.62786	-1.40242
H	-6.46368	-0.06006	0.05255
H	-6.54834	2.21507	-0.89130
H	2.65827	2.71102	-0.53620
H	2.74770	0.42643	0.38452
H	-5.38662	4.26186	-1.66912
H	-5.15128	-1.97467	0.92613
H	-2.97820	-3.00203	1.47232
H	-0.49996	-2.87912	1.54208
H	-3.30000	5.51436	-2.05726
O	-2.31182	2.29264	2.36066
C	-3.07701	1.40734	3.16846
C	-1.77353	1.91272	3.61314
H	-3.14510	0.38368	2.79928
H	-3.98925	1.83040	3.58150
H	-1.73418	2.70190	4.36321
C	-0.55687	1.03505	3.51653
H	-0.72252	0.22809	2.80309
Cl	-0.20796	0.28778	5.11305
H	0.32655	1.60390	3.22183

Fig. S47 Optimized geometry, total energy, and Cartesian coordinates of Fig. 13(a) at M06-2X level of theory with 6-31G(d, p) basis set.

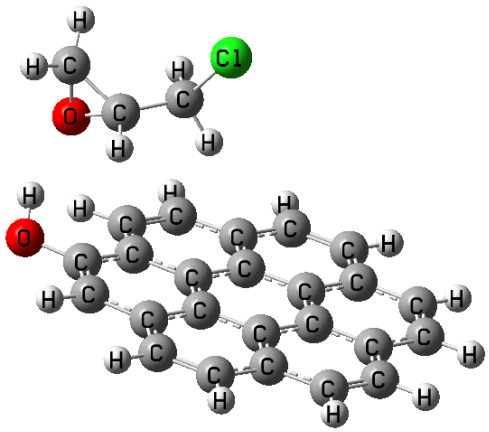


E = -1762.6546277582 au

C	-5.55582	1.63094	-0.51228
C	-5.51438	0.27941	-0.28188
C	-4.37367	2.40251	-0.64492
C	-4.26214	-0.41610	-0.21214
C	-3.12644	1.76025	-0.48518
C	-3.07143	0.34766	-0.28092
C	-1.92652	2.53121	-0.51518
C	-0.66467	1.89129	-0.34489
C	-0.60408	0.48063	-0.15430
C	-1.80384	-0.28997	-0.12361
C	0.52175	2.65499	-0.36539
C	0.64673	-0.15291	0.00993
C	-1.73682	-1.68510	0.07345
C	-1.98930	3.92906	-0.70643
C	-4.16581	-1.82559	-0.01453
C	-4.41244	3.81125	-0.85547
C	-2.94736	-2.42996	0.11562
C	-0.46296	-2.30179	0.22933
C	0.68563	-1.56348	0.19915
H	1.65176	-2.04460	0.32190
C	1.82963	0.63921	-0.01661
C	-3.26146	4.54711	-0.88155
C	-0.77835	4.67723	-0.72087
C	0.43072	4.06282	-0.55604
C	1.77019	1.99213	-0.19618
H	-0.83343	5.75204	-0.86759
H	1.34774	4.64499	-0.56946
C	-6.81003	-0.43816	-0.01682
H	-6.51510	2.14056	-0.56096
H	2.68019	2.58498	-0.21266
H	2.78805	0.14410	0.11101
H	-5.37846	4.29138	-0.98174
H	-5.07693	-2.41022	0.01140
H	-2.88932	-3.50525	0.25897
H	-0.42211	-3.37720	0.37631
H	-3.29997	5.62178	-1.03519
O	-7.11017	-1.50112	-0.49611
O	-7.63737	0.20611	0.82157
H	-7.18086	0.95211	1.25768

O	-6.18835	2.08685	2.40643
C	-5.81073	1.46983	3.64219
C	-4.81003	1.79510	2.62135
C	-3.93098	3.00984	2.74036
H	-4.40794	0.98850	2.01109
H	-6.14083	0.44073	3.75609
H	-5.91176	2.10812	4.51648
H	-4.33860	3.72037	3.46085
H	-3.80653	3.49774	1.77219
Cl	-2.30414	2.50913	3.29689

Fig. S48 Optimized geometry, total energy, and Cartesian coordinates of Fig. 13(b) at M06-2X level of theory with 6-31G(d, p) basis set.

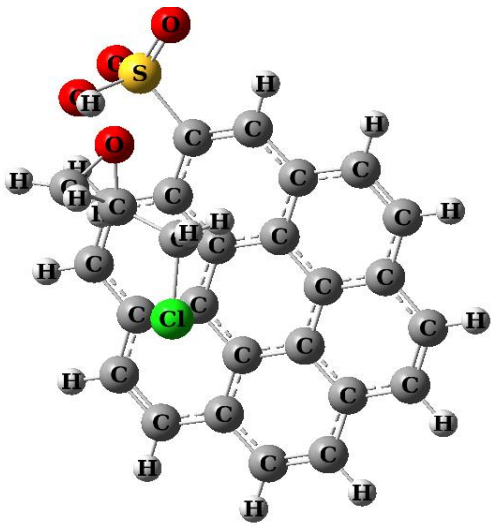


E = -1649.3470642911 au

C	-5.22773	1.69906	-1.51537
C	-5.32531	0.40412	-1.09061
C	-3.98474	2.39299	-1.47456
C	-4.18898	-0.29630	-0.59570
C	-2.84302	1.72093	-0.98702
C	-2.94485	0.36870	-0.54705
C	-1.58812	2.39558	-0.92902
C	-0.43475	1.71808	-0.43107
C	-0.53437	0.35931	-0.00293
C	-1.79167	-0.31148	-0.06004
C	0.80293	2.39553	-0.35714
C	0.61324	-0.30913	0.47832
C	-1.88805	-1.65074	0.37508
C	-1.48779	3.73620	-1.35902
C	-4.26217	-1.64554	-0.14751
C	-3.85485	3.74340	-1.90654
C	-3.15624	-2.29810	0.31942
C	-0.71779	-2.32321	0.81724
C	0.49663	-1.68962	0.85287
O	1.58968	-2.38885	1.26071
C	1.84116	0.40470	0.57679

C	-2.65256	4.39032	-1.85102
C	-0.22580	4.39195	-1.28301
C	0.87691	3.74786	-0.79879
C	1.93181	1.70689	0.16894
H	-0.15628	5.42363	-1.61626
H	1.83226	4.26150	-0.73946
H	-6.27955	-0.11415	-1.12516
H	-6.10254	2.22176	-1.89144
H	2.87450	2.24037	0.25167
H	2.71140	-0.09607	0.98606
H	-4.73622	4.25493	-2.28294
H	-5.22209	-2.15309	-0.18468
H	-3.22785	-3.32837	0.65570
H	-0.76625	-3.36587	1.11455
H	-2.56779	5.42134	-2.18256
H	2.33107	-2.18284	0.66523
O	3.09803	-1.74297	-1.01720
C	2.09227	-1.71413	-2.02794
C	3.28236	-2.55754	-2.17599
C	1.98286	-0.40716	-2.76243
H	1.15116	-2.18764	-1.75086
H	3.20288	-3.62732	-2.00635
H	4.08380	-2.23078	-2.83433
H	2.96226	0.06902	-2.82520
H	1.27501	0.26812	-2.27956
Cl	1.39304	-0.70259	-4.43120

Fig. S49 Optimized geometry, total energy, and Cartesian coordinates of Fig. 13(c) at M06-2X level of theory with 6-31G(d, p) basis set.

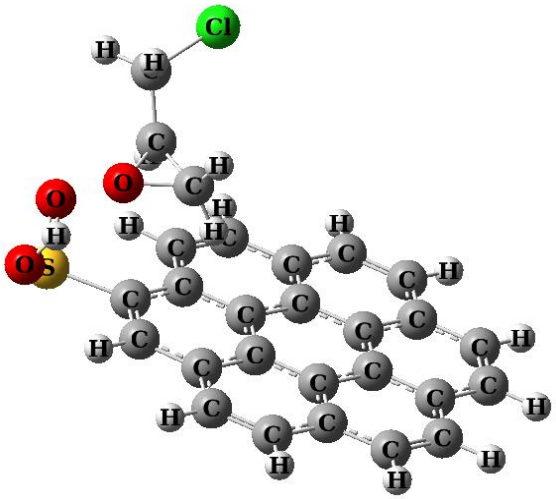


E = -2197.8398806244 au

C	-5.90198	1.54678	-0.85386

C	-5.74405	0.22748	-0.53163
C	-4.78250	2.42086	-0.89826
C	-4.46384	-0.34383	-0.23686
C	-3.50678	1.90994	-0.57265
C	-3.34932	0.52884	-0.23778
C	-2.38080	2.78494	-0.56023
C	-1.09231	2.28422	-0.21383
C	-0.93097	0.90892	0.11996
C	-2.05540	0.03208	0.10452
C	0.02060	3.15152	-0.19825
C	0.34430	0.41578	0.47018
C	-1.88876	-1.32649	0.44315
C	-2.54370	4.14913	-0.88818
C	-4.26638	-1.71855	0.09003
C	-4.92304	3.79901	-1.22575
C	-3.02354	-2.18170	0.42060
C	-0.59242	-1.80100	0.79255
C	0.48393	-0.96109	0.80547
H	1.46855	-1.33332	1.07346
C	1.45168	1.31048	0.47832
C	-3.84044	4.63163	-1.22373
C	-1.40418	5.00266	-0.86862
C	-0.16972	4.52155	-0.53613
C	1.29641	2.62886	0.15553
H	-1.53564	6.05020	-1.12351
H	0.69150	5.18350	-0.52388
S	-7.22492	-0.76533	-0.48307
H	-6.89697	1.92657	-1.06476
H	2.14940	3.30127	0.16546
H	2.42982	0.92288	0.74822
H	-5.91020	4.17516	-1.47693
H	-5.10805	-2.40004	0.06364
H	-2.88774	-3.23087	0.66698
H	-0.47570	-2.84981	1.04947
H	-3.95518	5.68191	-1.47546
O	-7.05737	-1.93659	-1.31294
O	-8.35634	0.12350	-0.65539
O	-7.21170	-1.30695	1.02351
H	-7.36705	-0.55782	1.65238
O	-6.90247	0.68191	2.77089
C	-5.48453	0.54414	2.89484
C	-6.36441	0.27210	4.03448
C	-4.74740	1.84581	2.75892
H	-5.06156	-0.30188	2.35379
H	-6.57540	-0.75722	4.30994
H	-6.46486	1.01432	4.82188
H	-5.18124	2.60807	3.40734
H	-4.77109	2.19027	1.72402
Cl	-3.03104	1.62538	3.21188

Fig. S50 Optimized geometry, total energy, and Cartesian coordinates of 13(d) at M06-2X level of theory with 6-31G(d, p) basis set.

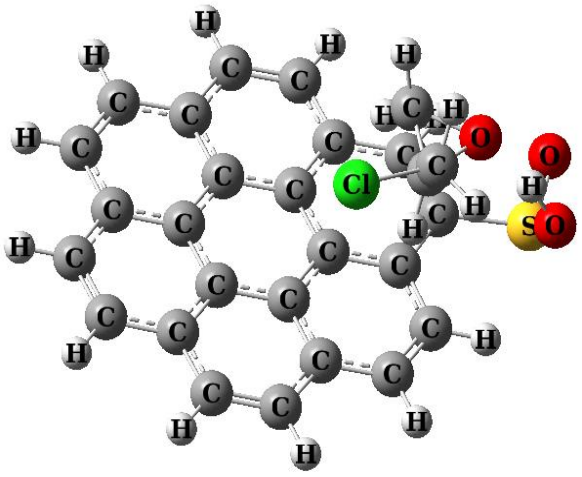


E = -2122.6485962234 au

C	-5.52491	1.54013	-0.42134
C	-5.42622	0.22082	-0.06586
C	-4.37356	2.35753	-0.56188
C	-4.15749	-0.37949	0.23417
C	-3.10477	1.79336	-0.31375
C	-2.99767	0.42742	0.09056
C	-1.93627	2.59821	-0.46633
C	-0.64980	2.04182	-0.21239
C	-0.53516	0.68343	0.20127
C	-1.70447	-0.12034	0.35595
C	0.50673	2.83672	-0.36616
C	0.74013	0.13471	0.45911
C	-1.57715	-1.46096	0.77452
C	-2.05429	3.94688	-0.86811
C	-3.99399	-1.73172	0.66742
C	-4.46946	3.72064	-0.96305
C	-2.75369	-2.24134	0.92771
C	-0.28106	-1.99131	1.03099
C	0.83669	-1.22251	0.87725
H	1.82129	-1.63703	1.07380
C	1.89166	0.95575	0.29432
C	-3.34946	4.48675	-1.11142
C	-0.87310	4.72717	-1.01731
C	0.36057	4.19177	-0.77641
C	1.78023	2.25766	-0.10376
H	-0.97138	5.76343	-1.32757
H	1.25432	4.79800	-0.89349
S	-6.98633	-0.70886	0.12522

H	-6.49908	1.97304	-0.62559
H	2.66672	2.87355	-0.22487
H	2.86840	0.52417	0.49341
H	-5.45423	4.13877	-1.14962
H	-4.86484	-2.36399	0.77418
H	-2.65411	-3.27182	1.25647
H	-3.43022	5.52547	-1.41851
O	-6.72075	-2.07813	-0.39687
O	-7.85290	0.11766	-0.97891
H	-0.19887	-3.02568	1.35180
H	-7.38618	0.03466	-1.84584
O	-6.22450	-0.34991	-3.15890
C	-5.34377	-1.47402	-3.10645
C	-4.82973	-0.13198	-3.39155
C	-5.56661	-2.45567	-4.22192
H	-5.21067	-1.89474	-2.11194
H	-4.30894	0.41421	-2.60901
H	-4.58540	0.13697	-4.41661
H	-5.81316	-1.93234	-5.14659
H	-6.36202	-3.15764	-3.97197
Cl	-4.07583	-3.41132	-4.50314

Fig. S51 Optimized geometry, total energy, and Cartesian coordinates of 13(e) at M06-2X level of theory with 6-31G(d, p) basis set..

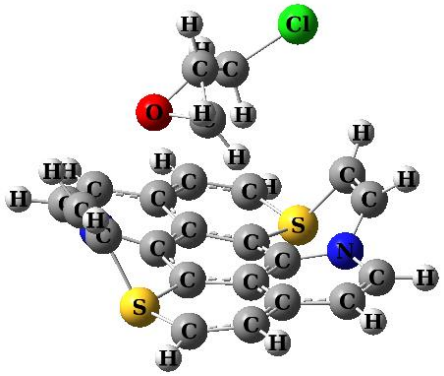


E = -2122.6487884959 au

C	-5.74764	1.78293	-0.53579
C	-5.75471	0.44065	-0.28510
C	-4.52453	2.48243	-0.73034
C	-4.54675	-0.31730	-0.17428
C	-3.31117	1.76283	-0.66936
C	-3.32288	0.36008	-0.39336
C	-2.07599	2.43931	-0.89321
C	-0.84835	1.71624	-0.85117

C	-0.85635	0.31672	-0.58267
C	-2.09070	-0.35974	-0.34984
C	0.37329	2.38556	-1.07718
C	0.35913	-0.39965	-0.54521
C	-2.09063	-1.74427	-0.07515
C	-2.06969	3.82556	-1.16320
C	-4.51702	-1.71339	0.12003
C	-4.49314	3.87911	-1.00488
C	-3.33200	-2.39406	0.16789
C	-0.85123	-2.44526	-0.04524
C	0.32870	-1.79728	-0.27304
H	1.26818	-2.34184	-0.24805
C	1.57797	0.29797	-0.77832
C	-3.30799	4.52656	-1.21067
C	-0.82336	4.47808	-1.38410
C	0.35274	3.78444	-1.34269
C	1.58513	1.64019	-1.03371
H	-0.82524	5.54474	-1.58897
H	1.29655	4.29418	-1.51404
S	-7.38537	-0.32006	-0.02598
H	-6.69845	2.30600	-0.60114
H	2.52217	2.16092	-1.20882
H	2.50929	-0.26018	-0.74819
H	-5.43371	4.42002	-1.04749
H	-5.44757	-2.24373	0.28347
H	-3.32666	-3.45722	0.39088
H	-3.29368	5.59253	-1.41875
O	-8.33946	0.73375	-0.44525
O	-7.24836	-1.47825	-1.17226
H	-0.86271	-3.51086	0.16439
H	-6.85291	-1.12981	-2.00338
O	-5.77497	-0.85974	-3.42993
C	-4.41061	-1.26925	-3.44985
C	-4.77466	0.13354	-3.66923
C	-4.05973	-2.15630	-4.61105
H	-3.99944	-1.56007	-2.48469
H	-4.63798	0.85327	-2.86754
H	-4.76982	0.52703	-4.68300
H	-4.53243	-1.79563	-5.52529
H	-4.36105	-3.18787	-4.42781
Cl	-2.28449	-2.15139	-4.85376

Fig. S52 Optimized geometry, total energy, and Cartesian coordinates of 13(f) at M06-2X level of theory with 6-31G(d, p) basis set.

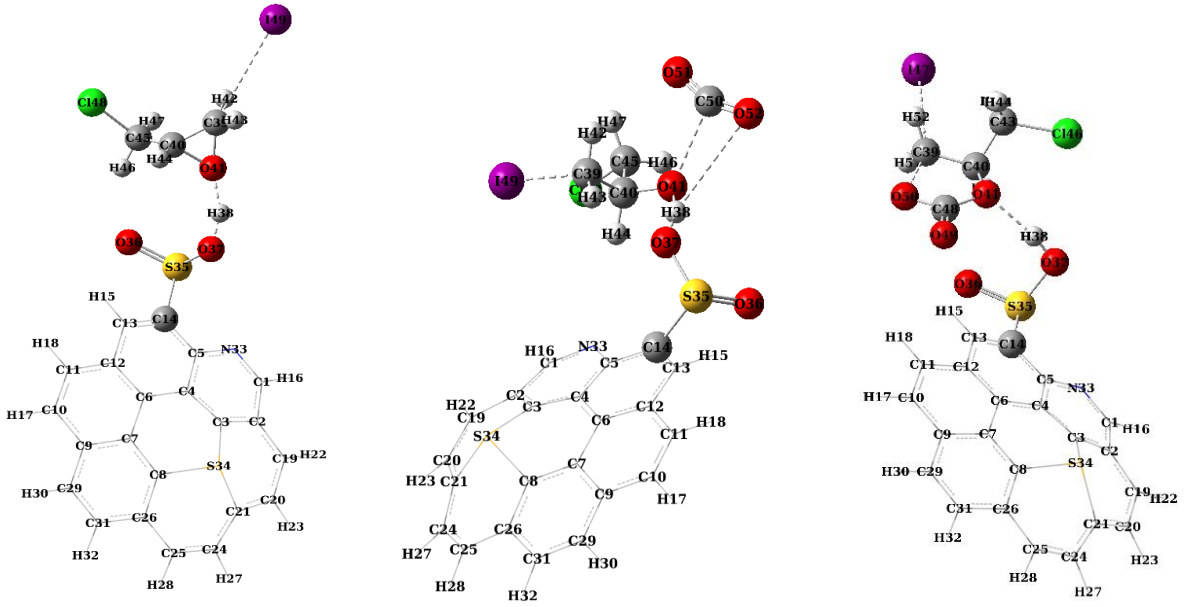


E = -2327.1972985682 au

C	-5.56139	2.31844	-0.96177
C	-5.93475	1.00546	-0.67361
C	-4.29668	2.86621	-0.88518
S	-4.80757	-0.20493	-0.21300
C	-3.17552	2.05748	-0.46580
C	-3.25787	0.67906	-0.19270
C	-1.88813	2.61832	-0.35469
C	-0.82172	1.83392	0.07964
C	-0.86184	0.42627	0.10560
C	-2.13596	-0.14341	-0.07453
S	0.68589	2.74701	0.34146
C	0.30638	-0.40987	0.25423
N	-2.25628	-1.53793	-0.29726
N	-1.64601	3.93041	-0.82214
C	-4.32243	-1.36271	-1.51040
C	-4.01454	4.26110	-1.13244
C	-3.15675	-1.98094	-1.25977
C	-1.13533	-2.36296	0.00975
C	1.54856	0.15588	0.47023
C	-2.77167	4.75641	-1.10069
C	-0.48100	4.15756	-1.55158
C	0.68059	3.54497	-1.27608
C	1.85468	1.51011	0.57090
H	-0.59941	4.83211	-2.39536
H	1.59255	3.61724	-1.85172
H	-6.96116	0.70240	-0.53420
H	-6.38188	2.99044	-1.21019
H	2.79184	1.87704	0.96051
H	2.37765	-0.52445	0.66074
H	-4.84134	4.93690	-1.32883
H	-2.82803	-2.84946	-1.82580
H	-2.53357	5.80051	-1.25509
C	0.06966	-1.83415	0.26158
H	-1.35208	-3.42231	0.04552
H	-5.01113	-1.60583	-2.30837
H	0.89056	-2.50149	0.50601
O	-2.11673	2.70218	-3.40746

C	-2.60743	1.72667	-4.30788
C	-1.46512	1.43661	-3.43350
H	-2.43130	1.93638	-5.36245
C	-3.97257	1.19825	-3.96389
H	-1.62522	0.81168	-2.55500
H	-0.45591	1.44437	-3.83746
H	-4.02646	0.92382	-2.90965
Cl	-4.31269	-0.27542	-4.93653
H	-4.75555	1.92334	-4.18740

Fig. S53 Optimized geometry, total energy, and Cartesian coordinates of 13(g) at M06-2X level of theory with 6-31G(d, p) basis set.



O37-H38: 1.73 H38-O41: 1.49
C40-O41: 1.51 C39-O41: 1.53
12.41*i* cm^{-1}

TS_1

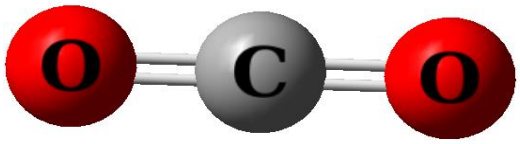
O41-C50: 2.50 H38-O52: 3.13
H38-O41: 1.06 C40-O41: 1.45
3.51*i* cm^{-1}

TS_2

O41-C50: 2.50 H38-O52: 3.13
H38-O41: 1.06 C40-O41: 1.45
8.07*i* cm^{-1}

TS_3

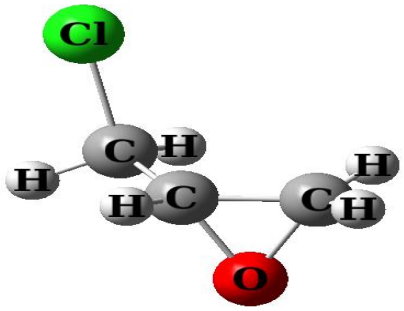
Fig. S54 Optimized ground state energy structures of the transition states TS_1, TS_2, and TS_3 in the CO_2 cycloaddition with the epichlorohydrin and NSC-773 catalyst including the most relevant calculated distances (in Å) and values of the negative imaginary vibrational frequencies.



E = -188.540119 au

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.000000	0.000000	0.000000
2	8	0	0.000000	0.000000	1.193247
3	8	0	0.000000	0.000000	-1.193247

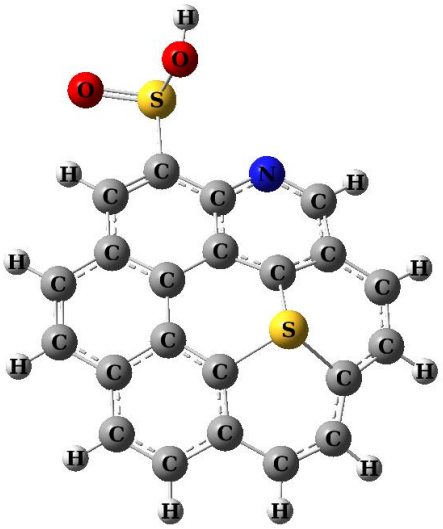
Fig. S55 The optimized geometry, energy, and Cartesian coordinates of CO_2 molecule at B3LYP level of theory using lanl2dz basis set.



E = -207.412805 au

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.778159	-0.109640	0.477579
2	6	0	1.651918	0.895198	-0.190322
3	8	0	2.138322	-0.519528	-0.022025
4	1	0	0.694175	-0.089638	1.562039
5	1	0	2.177191	1.630533	0.413795
6	1	0	1.443397	1.182664	-1.218818
7	6	0	-0.358777	-0.764175	-0.260828
8	1	0	-0.574895	-1.767099	0.108435
9	1	0	-0.197211	-0.773831	-1.339092
10	17	0	-1.945708	0.226194	0.028898

Fig. S56 The optimized geometry, energy, and Cartesian coordinates of epichlorohydrin molecule at B3LYP level of theory using lanl2dz basis set.



NSC-773 catalyst

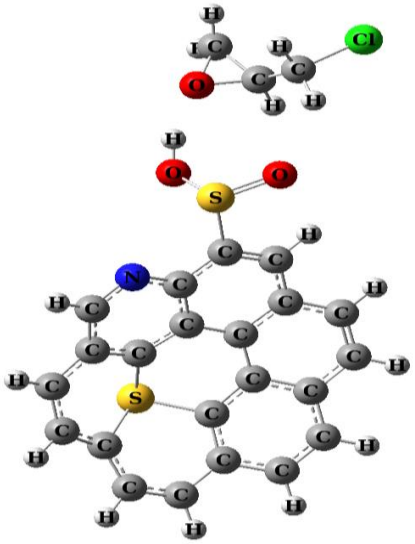
E= -1070.017239 au

Zero-point correction = 0.268604 (Hartree/Particle)
Thermal correction to Energy = 0.288132
Thermal correction to Enthalpy = 0.289076
Thermal correction to Gibbs Free Energy = 0.222038

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	1.157377	-3.013370	-0.429473
2	6	0	-0.222416	-2.723858	-0.115874
3	6	0	-0.434860	-1.393333	0.288772
4	6	0	0.506770	-0.354286	0.170615
5	6	0	1.841144	-0.791906	-0.128277
6	6	0	0.195920	1.058384	0.244727
7	6	0	-1.178352	1.524706	0.214014
8	6	0	-2.305622	0.679416	0.327946
9	6	0	-1.451413	2.912058	-0.044074
10	6	0	-0.356653	3.837129	-0.093492
11	6	0	0.951232	3.402086	0.005552
12	6	0	1.254586	2.001420	0.108648
13	6	0	2.606243	1.542344	-0.032985
14	6	0	2.866505	0.198417	-0.162754
15	1	0	3.432575	2.247110	-0.100947
16	1	0	1.433008	-4.027405	-0.712726
17	1	0	-0.574183	4.892854	-0.237280
18	1	0	1.774389	4.108917	-0.056957
19	6	0	-1.295734	-3.668316	-0.314882
20	6	0	-2.643382	-3.285151	-0.410502

21	6	0	-3.193224	-2.033283	-0.062834
22	1	0	-1.026235	-4.684955	-0.584716
23	1	0	-3.342982	-4.003378	-0.840109
24	6	0	-4.403989	-1.367377	-0.364017
25	6	0	-4.659008	0.002351	-0.224164
26	6	0	-3.627406	1.004297	-0.029012
27	1	0	-5.194637	-1.989549	-0.784925
28	1	0	-5.656479	0.362769	-0.457708
29	6	0	-2.808880	3.316064	-0.262464
30	1	0	-3.011760	4.369257	-0.443213
31	6	0	-3.849665	2.399283	-0.302538
32	1	0	-4.857185	2.724534	-0.550460
33	7	0	2.139855	-2.113303	-0.393840
34	16	0	-2.067591	-1.007680	1.045449
35	16	0	4.630814	-0.342856	-0.433622
36	8	0	5.415822	1.084137	-0.613984
37	8	0	4.792952	-0.812263	1.358264
38	1	0	5.667704	-1.255910	1.484849

Fig. S57 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of modelled NSC-773 catalyst at B3LYP level of theory using lanl2dz basis set.



NSC-773 catalyst + ECH

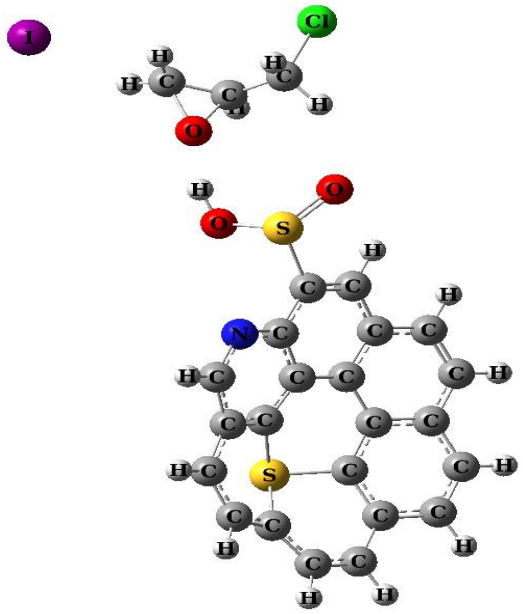
E = -1277.450469 au

Zero-point correction = 0.347787 (Hartree/Particle)
Thermal correction to Energy = 0.374040
Thermal correction to Enthalpy = 0.374984
Thermal correction to Gibbs Free Energy = 0.288906

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.008004	-3.179392	-0.664964
2	6	0	-2.303276	-2.709209	-0.231223
3	6	0	-2.292422	-1.373897	0.210723
4	6	0	-1.225769	-0.473527	0.031621
5	6	0	0.005338	-1.084768	-0.384505
6	6	0	-1.327316	0.965967	0.153273
7	6	0	-2.620264	1.620130	0.243179
8	6	0	-3.842658	0.937441	0.437832
9	6	0	-2.714636	3.038209	0.028885
10	6	0	-1.507711	3.802330	-0.098581
11	6	0	-0.270624	3.186595	-0.114544
12	6	0	-0.160242	1.755139	-0.055746
13	6	0	1.097853	1.114936	-0.313369
14	6	0	1.155417	-0.247901	-0.483956
15	1	0	2.006959	1.698660	-0.442321
16	1	0	-0.901992	-4.213452	-0.987307
17	1	0	-1.584877	4.881387	-0.209530
18	1	0	0.636131	3.773250	-0.236364
19	6	0	-3.511774	-3.489220	-0.354273
20	6	0	-4.795227	-2.920068	-0.330268
21	6	0	-5.133600	-1.613737	0.081844
22	1	0	-3.410839	-4.525638	-0.661924
23	1	0	-5.621435	-3.522130	-0.710789
24	6	0	-6.258205	-0.777478	-0.106783
25	6	0	-6.305011	0.610362	0.074505
26	6	0	-5.129909	1.452982	0.197383
27	1	0	-7.160208	-1.271708	-0.469510
28	1	0	-7.257126	1.112534	-0.069460
29	6	0	-4.014577	3.633197	-0.069675
30	1	0	-4.080619	4.708761	-0.217693
31	6	0	-5.174261	2.872007	-0.035966
32	1	0	-6.142426	3.341069	-0.194103
33	7	0	0.091098	-2.426717	-0.696736
34	16	0	-3.787825	-0.784676	1.107033
35	16	0	2.802851	-1.027382	-0.902733
36	8	0	3.764036	0.302879	-1.114111
37	8	0	3.084116	-1.564762	0.811185
38	1	0	4.067771	-1.766374	0.912341
39	6	0	6.828543	-1.076567	1.737670
40	6	0	6.189110	-0.155957	0.757249
41	8	0	5.774160	-1.614287	0.800866
42	1	0	7.823912	-1.467013	1.540595
43	1	0	6.525966	-1.040713	2.780976
44	1	0	5.408354	0.516235	1.100432
45	6	0	6.860046	0.240409	-0.528812
46	1	0	6.122578	0.539194	-1.272290

47	1	0	7.534774	-0.530195	-0.903032
48	17	0	7.937150	1.763974	-0.201424

Fig. S58 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of NSC-773 catalyst with epichlorohydrin (ECH) at B3LYP level of theory using lanl2dz basis set.



NSC-773 catalyst + ECH + I^- (Int_0)

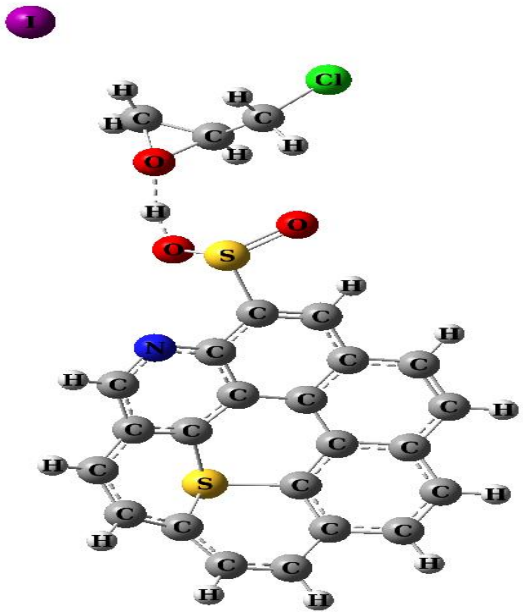
E = -1288.938566 au

Zero-point correction = 0.347258 (Hartree/Particle)
Thermal correction to Energy = 0.376105
Thermal correction to Enthalpy = 0.377049
Thermal correction to Gibbs Free Energy = 0.279842

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.247418	-2.299496	2.117665
2	6	0	3.476178	-2.430405	1.373036
3	6	0	3.639851	-1.439058	0.389758
4	6	0	2.847828	-0.282322	0.267913
5	6	0	1.641406	-0.300221	1.050791
6	6	0	3.212417	0.892363	-0.495899
7	6	0	4.557318	1.062787	-1.015755
8	6	0	5.539767	0.045990	-1.024039
9	6	0	4.983800	2.356856	-1.474982
10	6	0	4.016099	3.411893	-1.568958

11	6	0	2.716343	3.229397	-1.137347
12	6	0	2.306510	1.991484	-0.531785
13	6	0	1.036096	1.891216	0.124412
14	6	0	0.738024	0.791545	0.895271
15	1	0	0.311627	2.702355	0.079271
16	1	0	2.008516	-3.040620	2.878329
17	1	0	4.332609	4.373534	-1.966939
18	1	0	1.996107	4.041565	-1.192202
19	6	0	4.498269	-3.404513	1.688262
20	6	0	5.828818	-3.285608	1.263058
21	6	0	6.326639	-2.401596	0.276883
22	1	0	4.256663	-4.159145	2.431127
23	1	0	6.577463	-3.901071	1.764114
24	6	0	7.609419	-1.914301	-0.055642
25	6	0	7.899230	-0.790222	-0.843524
26	6	0	6.925914	0.227132	-1.192128
27	1	0	8.449221	-2.451791	0.387256
28	1	0	8.941926	-0.564267	-1.047987
29	6	0	6.364940	2.546985	-1.804741
30	1	0	6.678942	3.524543	-2.165011
31	6	0	7.308672	1.544518	-1.627801
32	1	0	8.362069	1.743711	-1.811287
33	7	0	1.360387	-1.320362	1.938376
34	16	0	4.982119	-1.706761	-0.842081
35	16	0	-0.914292	0.758606	1.779514
36	8	0	-1.452776	2.301500	1.516901
37	8	0	-1.651906	-0.280835	0.500614
38	1	0	-2.651261	-0.341322	0.688856
39	6	0	-5.618177	0.104919	0.856794
40	6	0	-4.760891	1.300450	0.629925
41	8	0	-4.135802	0.060218	1.231968
42	1	0	-6.266595	0.075091	1.729255
43	1	0	-5.921401	-0.534647	0.027454
44	1	0	-4.424825	1.504949	-0.383776
45	6	0	-4.706544	2.464631	1.584533
46	1	0	-3.700119	2.881929	1.638191
47	1	0	-5.087721	2.204129	2.572715
48	17	0	-5.825531	3.859993	0.951469
49	53	0	-8.025006	-1.845272	-1.412113

Fig. S59 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of NSC-773 catalyst + ECH+ I^- (Int_0) at B3LYP level of theory using lanl2dz basis set.



TS_1

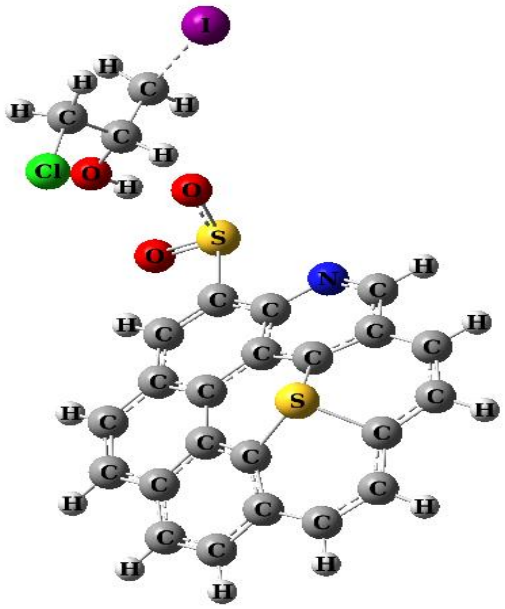
E = -1288.938918 au

Zero-point correction = 0.347117 (Hartree/Particle)
Thermal correction to Energy = 0.375140
Thermal correction to Enthalpy = 0.376084
Thermal correction to Gibbs Free Energy = 0.281706

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.357330	2.762305	-1.455030
2	6	0	3.638278	2.710790	-0.793415
3	6	0	3.840793	1.526353	-0.063294
4	6	0	3.025998	0.381435	-0.137167
5	6	0	1.768915	0.586116	-0.805881
6	6	0	3.408680	-0.936723	0.323768
7	6	0	4.781033	-1.234538	0.692639
8	6	0	5.791014	-0.257358	0.848655
9	6	0	5.200807	-2.603324	0.826268
10	6	0	4.211828	-3.640645	0.759566
11	6	0	2.891112	-3.351146	0.475409
12	6	0	2.475957	-2.005249	0.186218
13	6	0	1.166801	-1.747273	-0.336850
14	6	0	0.847416	-0.501323	-0.825510
15	1	0	0.424740	-2.539609	-0.417728
16	1	0	2.087908	3.654621	-2.017309
17	1	0	4.527413	-4.670251	0.913339
18	1	0	2.153571	-4.146341	0.404098
19	6	0	4.664087	3.716277	-0.965285

20	6	0	6.017084	3.489682	-0.676402
21	6	0	6.556631	2.405233	0.054839
22	1	0	4.393628	4.617634	-1.507610
23	1	0	6.746545	4.189501	-1.086829
24	6	0	7.844508	1.839646	0.176887
25	6	0	8.155553	0.566757	0.678310
26	6	0	7.179683	-0.489172	0.869377
27	1	0	8.666722	2.449318	-0.200710
28	1	0	9.202917	0.287534	0.749928
29	6	0	6.595403	-2.879238	1.003086
30	1	0	6.905166	-3.916055	1.117393
31	6	0	7.553380	-1.874931	0.978593
32	1	0	8.610754	-2.123386	1.035127
33	7	0	1.456555	1.779621	-1.426890
34	16	0	5.273644	1.500190	1.093084
35	16	0	-0.859743	-0.256487	-1.560652
36	8	0	-1.424008	-1.811943	-1.593284
37	8	0	-1.484832	0.491764	-0.040085
38	1	0	-2.500103	0.562258	-0.124189
39	6	0	-5.427289	0.092017	0.079226
40	6	0	-4.559656	-1.097039	-0.144027
41	8	0	-4.032982	0.266895	-0.532835
42	1	0	-6.244115	0.329836	-0.594849
43	1	0	-5.538435	0.511287	1.073740
44	1	0	-4.038595	-1.529471	0.707406
45	6	0	-4.700181	-2.005922	-1.337381
46	1	0	-3.719697	-2.311289	-1.706326
47	1	0	-5.319444	-1.570717	-2.121865
48	17	0	-5.575496	-3.602624	-0.809665
49	53	0	-8.840948	1.335906	0.940831

Fig. S60 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of TS_1 at B3LYP level of theory using lanl2dz basis set.



Int_1

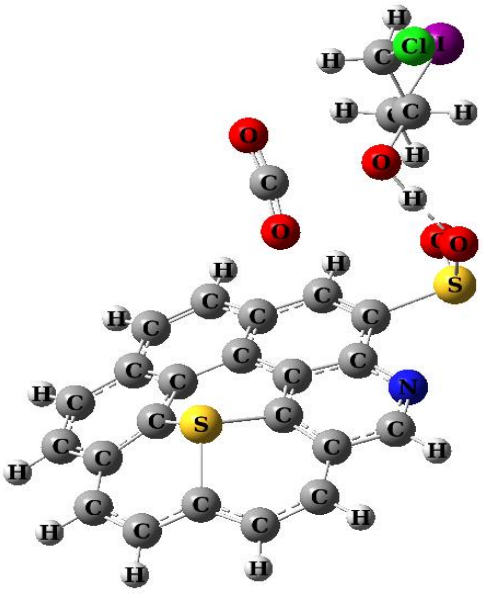
E = -1288.963486 au

Zero-point correction = 0.347524 (Hartree/Particle)
Thermal correction to Energy = 0.375643
Thermal correction to Enthalpy = 0.376587
Thermal correction to Gibbs Free Energy = 0.282090

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-0.896352	-2.005169	-2.329146
2	6	0	-1.961362	-2.365457	-1.423670
3	6	0	-2.339211	-1.318477	-0.572143
4	6	0	-1.928465	0.022306	-0.700587
5	6	0	-0.832144	0.232939	-1.614982
6	6	0	-2.580326	1.143653	-0.059619
7	6	0	-3.872545	0.999863	0.588806
8	6	0	-4.494453	-0.241688	0.856004
9	6	0	-4.639443	2.171010	0.917327
10	6	0	-4.036853	3.462015	0.749203
11	6	0	-2.778741	3.594226	0.193214
12	6	0	-2.052973	2.447661	-0.281912
13	6	0	-0.862674	2.613276	-1.063667
14	6	0	-0.286059	1.548907	-1.717093
15	1	0	-0.409478	3.593254	-1.223452
16	1	0	-0.508356	-2.759607	-3.012198
17	1	0	-4.602283	4.342392	1.048171
18	1	0	-2.336294	4.576631	0.049248
19	6	0	-2.656683	-3.637051	-1.474290

20	6	0	-3.919323	-3.844011	-0.905935
21	6	0	-4.585762	-2.992348	0.008986
22	1	0	-2.253142	-4.398518	-2.135864
23	1	0	-4.479486	-4.726172	-1.220602
24	6	0	-5.926998	-2.854181	0.428217
25	6	0	-6.488725	-1.749317	1.085742
26	6	0	-5.851909	-0.447739	1.168631
27	1	0	-6.590613	-3.681393	0.170577
28	1	0	-7.531715	-1.806937	1.385045
29	6	0	-5.983351	2.002406	1.384085
30	1	0	-6.553507	2.892864	1.642609
31	6	0	-6.585833	0.753928	1.463329
32	1	0	-7.633095	0.665820	1.744635
33	7	0	-0.334911	-0.798732	-2.390733
34	16	0	-3.438918	-1.758344	0.843328
35	16	0	1.308492	1.919279	-2.725875
36	8	0	1.238775	3.589689	-2.697163
37	8	0	2.450575	1.367537	-1.588305
38	1	0	2.724234	1.830663	-0.188930
39	6	0	4.903551	0.522695	-0.002478
40	6	0	3.802699	0.664438	1.075349
41	8	0	3.131582	1.900177	0.768612
42	1	0	5.660000	1.307299	0.071716
43	1	0	4.435595	0.511714	-0.989877
44	1	0	3.128442	-0.202831	1.013224
45	6	0	4.391703	0.775880	2.477645
46	1	0	4.798700	1.775402	2.639303
47	1	0	5.120104	-0.006844	2.691345
48	17	0	3.065694	0.561842	3.817388
49	53	0	6.067004	-1.402013	0.092530

Fig. S61 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of Int_1 at B3LYP level of theory using lanl2dz basis set.



Int_2

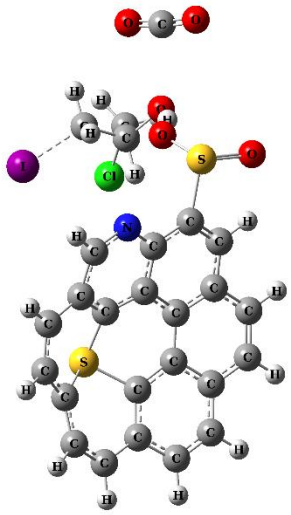
E = -1477.520563 au

Zero-point correction = 0.359364 (Hartree/Particle)
Thermal correction to Energy = 0.391343
Thermal correction to Enthalpy = 0.392288
Thermal correction to Gibbs Free Energy = 0.289749

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.688514	3.162184	1.464802
2	6	0	-3.760772	2.607395	0.674131
3	6	0	-3.480584	1.323875	0.186601
4	6	0	-2.390377	0.525524	0.580182
5	6	0	-1.373497	1.221558	1.327106
6	6	0	-2.299602	-0.901848	0.362627
7	6	0	-3.445365	-1.675273	-0.082564
8	6	0	-4.651509	-1.108436	-0.555695
9	6	0	-3.423950	-3.108908	0.027370
10	6	0	-2.205479	-3.754385	0.422010
11	6	0	-1.092765	-3.017213	0.781348
12	6	0	-1.135588	-1.581020	0.819288
13	6	0	-0.056764	-0.835109	1.400869
14	6	0	-0.176317	0.511400	1.649783
15	1	0	0.873202	-1.316932	1.704517
16	1	0	-2.798910	4.166202	1.872069
17	1	0	-2.180088	-4.841699	0.455899
18	1	0	-0.179090	-3.512999	1.099492
19	6	0	-5.048915	3.254013	0.510849
20	6	0	-6.205300	2.571127	0.116553
21	6	0	-6.272246	1.267185	-0.433750

22	1	0	-5.146738	4.269101	0.885513
23	1	0	-7.166091	3.061763	0.281261
24	6	0	-7.303103	0.314705	-0.584633
25	6	0	-7.145063	-1.055981	-0.841072
26	6	0	-5.889186	-1.766668	-0.688962
27	1	0	-8.318206	0.689545	-0.442876
28	1	0	-8.039126	-1.658859	-0.974715
29	6	0	-4.628222	-3.835933	-0.245435
30	1	0	-4.601470	-4.921607	-0.172199
31	6	0	-5.823699	-3.196827	-0.544652
32	1	0	-6.738679	-3.772362	-0.667968
33	7	0	-1.547939	2.529770	1.736154
34	16	0	-4.623305	0.657483	-1.099363
35	16	0	1.340242	1.414040	2.399653
36	8	0	2.342473	0.080219	2.617308
37	8	0	1.855515	2.272253	1.019083
38	1	0	2.244923	1.528120	-0.146697
39	6	0	4.160528	-0.506219	0.087356
40	6	0	4.044637	0.752297	-0.804202
41	8	0	2.627376	0.973074	-0.967944
42	1	0	3.779144	-1.397808	-0.416893
43	1	0	3.665226	-0.343382	1.053334
44	1	0	4.512982	1.603905	-0.291765
45	6	0	4.687024	0.542776	-2.173376
46	1	0	4.074241	-0.107743	-2.797238
47	1	0	5.715744	0.190443	-2.098527
48	17	0	4.815660	2.172196	-3.140814
49	53	0	6.276344	-1.049785	0.641023
50	6	0	0.963410	-0.089030	-2.458738
51	8	0	0.052572	0.521896	-1.989139
52	8	0	1.747357	-0.785478	-3.037814

Fig. S62 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of Int_2 at B3LYP level of theory using lanl2dz basis set.



TS_2

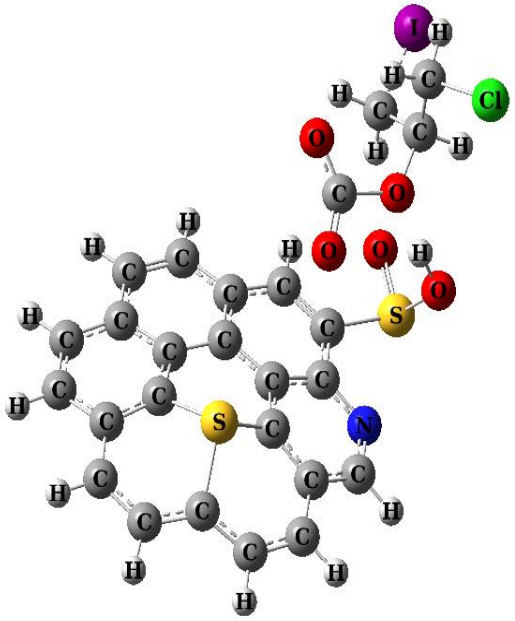
E = -1477.510231 au

Zero-point correction = 0.358643 (Hartree/Particle)
Thermal correction to Energy = 0.390175
Thermal correction to Enthalpy = 0.391119
Thermal correction to Gibbs Free Energy = 0.288420

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.491904	-0.605232	-3.288170
2	6	0	-2.518335	-1.186235	-2.455910
3	6	0	-2.578172	-0.618725	-1.175783
4	6	0	-1.902083	0.548823	-0.772741
5	6	0	-0.879819	0.999908	-1.685346
6	6	0	-2.231838	1.321094	0.405674
7	6	0	-3.456142	1.081023	1.150378
8	6	0	-4.301897	-0.034549	0.951314
9	6	0	-3.917514	2.059653	2.097374
10	6	0	-3.070734	3.175188	2.407925
11	6	0	-1.873346	3.367247	1.745509
12	6	0	-1.460478	2.484310	0.688610
13	6	0	-0.343368	2.820710	-0.145326
14	6	0	-0.076054	2.114357	-1.295105
15	1	0	0.290128	3.685134	0.061373
16	1	0	-1.342313	-1.000125	-4.292086
17	1	0	-3.402238	3.884901	3.163218
18	1	0	-1.246926	4.226744	1.970202

19	6	0	-3.473097	-2.166761	-2.934121
20	6	0	-4.690154	-2.427763	-2.293106
21	6	0	-5.065614	-2.017637	-0.990539
22	1	0	-3.308487	-2.579320	-3.925560
23	1	0	-5.455336	-2.965448	-2.855542
24	6	0	-6.298819	-1.897541	-0.313456
25	6	0	-6.543016	-1.161793	0.855897
26	6	0	-5.635388	-0.161058	1.385815
27	1	0	-7.146787	-2.399543	-0.782400
28	1	0	-7.539950	-1.199536	1.286425
29	6	0	-5.214780	1.891053	2.681483
30	1	0	-5.552026	2.628840	3.407194
31	6	0	-6.061301	0.854830	2.311064
32	1	0	-7.070754	0.799428	2.712973
33	7	0	-0.692064	0.391791	-2.913311
34	16	0	-3.604452	-1.504886	0.075778
35	16	0	1.448904	2.681067	-2.320471
36	8	0	1.751725	4.125570	-1.539027
37	8	0	2.551970	1.489788	-1.784410
38	1	0	3.457527	1.545514	-0.678522
39	6	0	3.692783	-1.020726	-0.253366
40	6	0	3.594912	0.106273	0.790219
41	8	0	4.118001	1.285187	0.114956
42	1	0	4.731527	-1.220786	-0.521698
43	1	0	3.102044	-0.748154	-1.129945
44	1	0	2.547259	0.264162	1.079974
45	6	0	4.468869	-0.051530	2.043990
46	1	0	4.777519	0.937869	2.378814
47	1	0	5.326772	-0.707127	1.895113
48	17	0	3.528718	-0.778465	3.528195
49	53	0	2.877659	-3.011141	0.355699
50	6	0	6.538050	1.542392	-0.536156
51	8	0	6.870631	0.478378	-0.093120
52	8	0	6.382246	2.621896	-1.017070

Fig. S63 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of TS_2 at B3LYP level of theory using lanl2dz basis set.



Int_3

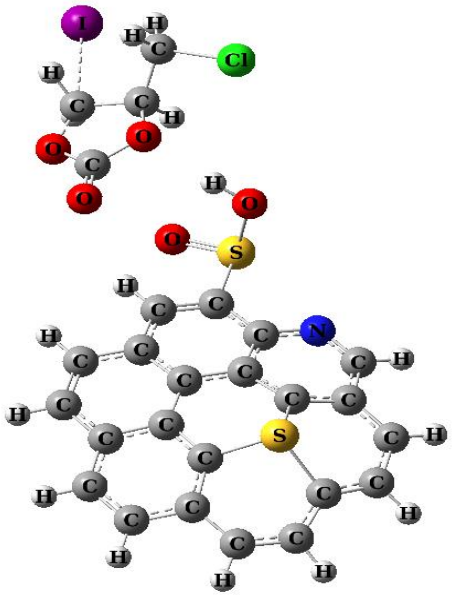
E = -1477.522949 au

Zero-point correction = 0.361128 (Hartree/Particle)
Thermal correction to Energy = 0.391946
Thermal correction to Enthalpy = 0.392891
Thermal correction to Gibbs Free Energy = 0.295255

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.606380	-3.144661	-1.442082
2	6	0	-3.632513	-2.584536	-0.598503
3	6	0	-3.336323	-1.289804	-0.148369
4	6	0	-2.277261	-0.492671	-0.614586
5	6	0	-1.305811	-1.195752	-1.404053
6	6	0	-2.178852	0.937351	-0.425333
7	6	0	-3.297997	1.710295	0.077447
8	6	0	-4.470081	1.142228	0.628716
9	6	0	-3.288561	3.141997	-0.048762
10	6	0	-2.096589	3.787420	-0.516369
11	6	0	-1.001941	3.049774	-0.925832
12	6	0	-1.044572	1.614579	-0.945351
13	6	0	0.009842	0.864285	-1.565765
14	6	0	-0.127203	-0.484225	-1.781317
15	1	0	0.924623	1.351693	-1.897895
16	1	0	-2.732336	-4.154795	-1.828447
17	1	0	-2.075225	4.874415	-0.557793
18	1	0	-0.103899	3.545324	-1.285641

19	6	0	-4.904260	-3.235518	-0.349576
20	6	0	-6.038650	-2.550253	0.101804
21	6	0	-6.077832	-1.238469	0.634579
22	1	0	-5.018154	-4.257644	-0.699641
23	1	0	-7.005272	-3.047052	0.002350
24	6	0	-7.105420	-0.291060	0.836213
25	6	0	-6.940920	1.083189	1.065011
26	6	0	-5.699517	1.797196	0.828210
27	1	0	-8.124620	-0.674280	0.762522
28	1	0	-7.828155	1.683484	1.247046
29	6	0	-4.478261	3.867407	0.286012
30	1	0	-4.460811	4.952397	0.201607
31	6	0	-5.650134	3.225868	0.662360
32	1	0	-6.559025	3.798556	0.834621
33	7	0	-1.487410	-2.507088	-1.787303
34	16	0	-4.396831	-0.614350	1.197758
35	16	0	1.303989	-1.407908	-2.601657
36	8	0	2.396576	-0.164874	-2.767025
37	8	0	1.809743	-2.422732	-1.250590
38	1	0	1.944106	-1.882067	-0.357036
39	6	0	3.935560	0.626631	0.097634
40	6	0	3.769164	-0.719108	0.836691
41	8	0	2.342685	-1.048915	0.807173
42	1	0	3.528467	1.459617	0.669352
43	1	0	3.502678	0.549546	-0.903915
44	1	0	4.250220	-1.509557	0.248929
45	6	0	4.343132	-0.714156	2.254860
46	1	0	3.694443	-0.180130	2.945024
47	1	0	5.365186	-0.335411	2.269841
48	17	0	4.488402	-2.482218	2.933919
49	53	0	6.070078	1.167650	-0.289558
50	6	0	1.280130	-0.190836	1.622179
51	8	0	0.140363	-0.657735	1.422806
52	8	0	1.798839	0.761866	2.262339

Fig. S64 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of Int_3 at B3LYP level of theory using lanl2dz basis set.



TS_3

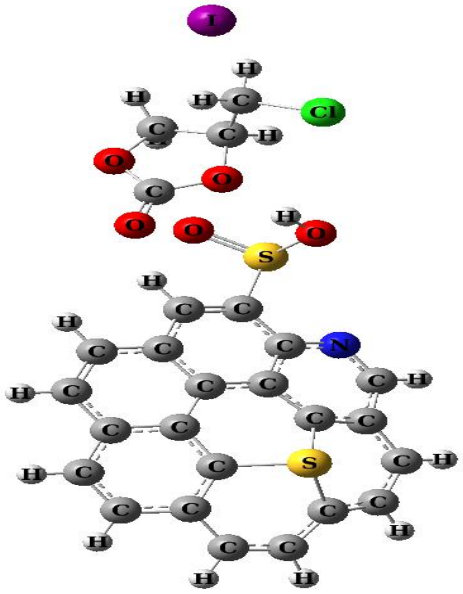
E = -1477.518657 au

Zero-point correction = 0.363353 (Hartree/Particle)
Thermal correction to Energy = 0.393531
Thermal correction to Enthalpy = 0.394475
Thermal correction to Gibbs Free Energy = 0.296392

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.455552	-2.972191	-1.732239
2	6	0	-3.461110	-2.576101	-0.778170
3	6	0	-3.254927	-1.292199	-0.252826
4	6	0	-2.311834	-0.366024	-0.727459
5	6	0	-1.336005	-0.917398	-1.623636
6	6	0	-2.334685	1.051379	-0.442802
7	6	0	-3.480880	1.673680	0.188537
8	6	0	-4.546934	0.955706	0.779250
9	6	0	-3.616745	3.104141	0.165497
10	6	0	-2.530657	3.894512	-0.336236
11	6	0	-1.401842	3.298111	-0.865757
12	6	0	-1.306049	1.869929	-0.978681
13	6	0	-0.222427	1.266588	-1.701391
14	6	0	-0.248815	-0.072830	-2.005999
15	1	0	0.629324	1.856233	-2.037564
16	1	0	-2.518766	-3.958270	-2.189353
17	1	0	-2.617989	4.978526	-0.305261
18	1	0	-0.585379	3.904266	-1.250144
19	6	0	-4.642626	-3.365529	-0.490454
20	6	0	-5.796766	-2.828337	0.092280

21	6	0	-5.916038	-1.565918	0.723221
22	1	0	-4.686883	-4.367857	-0.907016
23	1	0	-6.717392	-3.410678	0.026369
24	6	0	-7.010225	-0.742696	1.068425
25	6	0	-6.959112	0.622648	1.386400
26	6	0	-5.813156	1.470550	1.112985
27	1	0	-7.991100	-1.220244	1.039229
28	1	0	-7.881811	1.118011	1.675998
29	6	0	-4.840557	3.683781	0.634783
30	1	0	-4.933107	4.768204	0.627732
31	6	0	-5.912731	2.904851	1.047023
32	1	0	-6.855634	3.371151	1.324913
33	7	0	-1.426697	-2.207346	-2.099481
34	16	0	-4.262765	-0.818335	1.213070
35	16	0	1.212662	-0.780049	-2.975884
36	8	0	2.205661	0.545559	-3.011302
37	8	0	1.871913	-1.935502	-1.798638
38	1	0	1.937611	-1.565322	-0.847034
39	6	0	4.006148	0.837887	0.658154
40	6	0	3.710535	-0.645345	0.923957
41	8	0	2.291256	-0.921712	0.663071
42	1	0	4.240275	-1.257080	0.189801
43	6	0	4.110155	-1.040929	2.344680
44	1	0	3.399284	-0.667457	3.081724
45	1	0	5.129144	-0.721341	2.566175
46	17	0	4.136272	-2.917712	2.561220
47	53	0	6.420809	0.915554	0.043273
48	6	0	1.324059	0.023164	1.268320
49	8	0	0.196142	-0.496322	1.403697
50	8	0	1.829369	1.171332	1.514750
51	1	0	3.754826	1.224339	-0.318472
52	1	0	4.204552	1.514428	1.470311

Fig. S65 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of TS_3 at B3LYP level of theory using lanl2dz basis set.



NSC-773 catalyst + ECH carbonate + I^- (FC)

E = -1477.529585 au

Zero-point correction = 0.363714 (Hartree/Particle)
Thermal correction to Energy = 0.394589
Thermal correction to Enthalpy = 0.395533
Thermal correction to Gibbs Free Energy = 0.294726

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.029693	-3.395518	-0.537567
2	6	0	-4.302097	-2.857396	-0.118009
3	6	0	-4.243695	-1.495342	0.219744
4	6	0	-3.157540	-0.640503	-0.046206
5	6	0	-1.950718	-1.313662	-0.444366
6	6	0	-3.219704	0.805017	-0.020077
7	6	0	-4.489393	1.504202	0.056150
8	6	0	-5.727257	0.874277	0.319876
9	6	0	-4.545018	2.908755	-0.243831
10	6	0	-3.317373	3.626499	-0.436204
11	6	0	-2.100376	2.971892	-0.440592
12	6	0	-2.037474	1.542445	-0.307207
13	6	0	-0.806024	0.854068	-0.565439
14	6	0	-0.781343	-0.518867	-0.645579
15	1	0	0.100834	1.422603	-0.749586
16	1	0	-2.956760	-4.454684	-0.777941
17	1	0	-3.363109	4.700415	-0.602229
18	1	0	-1.172268	3.514149	-0.597194
19	6	0	-5.537816	-3.608539	-0.157312
20	6	0	-6.802761	-3.002180	-0.149738

21	6	0	-7.095045	-1.657397	0.171798
22	1	0	-5.471684	-4.667760	-0.388025
23	1	0	-7.655048	-3.606468	-0.464176
24	6	0	-8.198915	-0.803382	-0.054164
25	6	0	-8.204821	0.595218	0.031915
26	6	0	-7.004210	1.410879	0.073803
27	1	0	-9.121646	-1.295683	-0.364626
28	1	0	-9.145849	1.113688	-0.128572
29	6	0	-5.829632	3.534173	-0.354683
30	1	0	-5.866786	4.600114	-0.569390
31	6	0	-7.011036	2.812599	-0.250615
32	1	0	-7.968218	3.300273	-0.420975
33	7	0	-1.911486	-2.678961	-0.649126
34	16	0	-5.702619	-0.799459	1.102858
35	16	0	0.849235	-1.377358	-1.046445
36	8	0	1.733924	-0.124985	-1.663281
37	8	0	1.414701	-1.599480	0.658840
38	1	0	1.914531	-0.775313	0.949336
39	6	0	4.760113	1.116813	-0.616556
40	6	0	4.479430	0.227952	0.622881
41	8	0	3.070441	0.621039	0.974423
42	1	0	5.764872	1.534092	-0.641329
43	1	0	4.527859	0.603760	-1.549600
44	1	0	4.463539	-0.832111	0.373036
45	6	0	5.419976	0.508566	1.783460
46	1	0	5.410579	1.556375	2.090911
47	1	0	6.426854	0.172808	1.513617
48	17	0	4.910716	-0.475194	3.314058
49	53	0	8.114731	-0.394345	-0.761911
50	6	0	2.746289	1.838424	0.355667
51	8	0	1.698176	2.447210	0.555403
52	8	0	3.770347	2.236240	-0.459459

Fig. S66 The optimized geometry, energy, thermal corrections, and Cartesian coordinates of NSC-773 catalyst + ECH carbonate + I^- (FC) at B3LYP level of theory using lanl2dz basis set.

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